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Synthesis of aromatic compounds possessing the fluorene unit

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Syntéza aromatických sloučenin s fluorenovou jednotkou

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Prohlášení

Prohlašuji, že jsem tuto práci vypracovala samostatně pod vedením školitele prof. RNDr. Martina Kotory, CSc. a řádně ocitovala všechny použité prameny. Dále prohlašuji, že jsem tuto práci ani její část nepředložila k získání stejného nebo jiného akademického titulu.

V Praze dne

Ilaria Caivano

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ABSTRACT

Thermal cyclotrimerization was first discovered in 1866 by Bertholet, then, in 1948, Reppe and Schweckendiek reported the first transition metal catalyzed [2+2+2] cyclotrimerization of alkynes using Ni complexes. In the following 70 years of research, transition metal catalyzed [2+2+2] cyclotrimerization have become a powerful method for the synthesis of variously decorated aromatic rings and new catalytic systems as well as reaction conditions have been successfully applied.

Herein, I would like to show the use of this reaction for the synthesis of the important class of fluorene-based compounds.

In particular, a regioselective cyclotrimerization of 2,4-disubstituted fluorenols was achieved by Ru-catalyzed partially intermolecular [2+2+2] cyclotrimerization of diynes with terminal alkynes.

Rh-based complex proved to be a straightforward transition metal catalyst for the construction of selectively fluorinated [5] and [6]helical dispiroindenofluorenes using intramolecular [2+2+2] cycloaddition of triynediols as the key synthetic step.

Moreover, Ni complexes demonstrated to be a valid choice for the selective synthesis of unsymmetrical [7]helical indenofluorenones, while other catalytic systems based on Rh, Ru, Pd and Co gave mixture of the desired cyclotrimerization compound together with the dehydro-Diels-Alder side-products.

Enantioselective cyclotrimerization for the synthesis of enantioenriched [7]helical indenofluorenones were also attempted.

ABSTRAKT

Termální cyklotrimerizaci poprvé objevil v roce 1866 Bertholet, poté v roce 1949 Reppe zveřejnil první katalytickou [2+2+2]-cyklotrimerizaci alkynů pomocí komplexních sloučenin Ni. V následujících 70 letech [2+2+2] cyklotrimerizace katalyzovaná komplexními sloučeninami přechodných kovů stala hojně využívanou metodou metodou pro syntézu různě substituovaných aromatických kruhů a také byly úspěšně vyvinuty nové katalytické systémy a reakční podmínky.

V této práci bych ráda ukázala využití této reakce pro syntézu důležité třídy aromatických sloučenin na bázi fluorenu.

Konkrétně jsem se, na příklad, zabývala regioselektivní cyklotrimerizací 2,4-disubstituovaných fluorenolů pomocí částečně intermolekulární [2+2+2] cyklotrimerizace diynů s koncovými alkyny za katalýzy komplexními sloučeninami Ru.

Komplexy na bázi Rh se ukázaly být vhodnými katalyzátory pro intramolekulární [2+2+2]cykloadici triyndiolů jako klíčového syntetického kroku během přípravy selektivně fluorovaných [5] a [6]helikálních dispiroindenofluorenů.

Dále se ukázalo, že komplexy Ni jsou vhodnou volbou pro selektivní syntézu nesymetrických [7]helikálních indenofluorenonů, zatímco jiné katalytické systémy založené na Rh, Ru, Pd a Co poskytly směsi požadovaného produktu cyklotrimerizace spolu s produktem dehydro-Diels-Alderovy reakce.

Byly také zkoušeny enantioselektivní katalytické cyklotrimerizace pro syntézu enantiomerně obohacených [7]helikálních indenofluorenonů.

AUTHOR'S PUBLICATIONS

1. Kaiser, R. P.; Caivano, I.; Kotora, M. Transition-Metal-Catalyzed Methods for Synthesis of Fluorenes. *Tetrahedron* **2019**, *75*, 2981–2992.

2. Caivano, I.; Kaiser, R. P.; Schnurrer, F.; Mosinger, J.; Císařová, I.; Nečas, D.; Kotora, M. Synthesis of Tri- and Disubstituted Fluorenols and Derivatives Thereof Using Catalytic [2+2+2] Cyclotrimerization. *Catalysts* **2019**, *9*, 942.

3. Caivano, I.; Tošner, Z.; Císařová, I.; Nečas, D.; Kotora, M. A General Synthetic Approach and Photophysical Properties of Regioselectively Fluorinated [5]- and [6]-Helical Bispiroindenofluorenes. *ChemPlusChem* **2020**, *85*, 2010–2016.

4. D'Orsi, R.; Caivano, I.; Funicello, M.; Lupattelli, P.; Chiummiento, L. Structural Insights into the TES/TFA Reduction of Differently Substituted Benzofurans: Dihydrobenzofurans or Bibenzyls? *Synlett* **2021**, *32*, 63-68.

5. Caivano, I.; Bingel, S.; Císařová, I.; Nečas, D.; Kotora, M.; Catalytic Approach to Unsymmetrical [7]-Helical Indenofluorenes: Cyclotrimerization vs. Dehydro-Diels-Alder Reaction Pathways. *Catalysis Today* **2021**, Accepted manuscript.

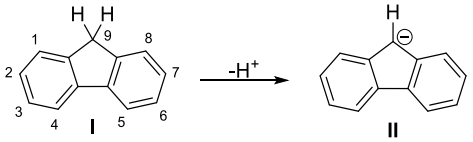
Table of Contents

1 STATE OF THE ART

1.1 Synthesis and application of the fluorene moiety

1.1.1 The importance of fluorene-based compounds

The fluorene scaffold **I** comprises the cyclopentadiene moiety which is embedded between two benzene rings. The particular structure of the fluorene scaffold is responsible for its unique properties which stems between the aromaticity of benzene rings and non-aromaticity and acidity of cyclopentadiene. As a consequence, the central C(9)(sp^3)–H subunit disrupts the annulene network of the π bonds along the molecular structure. Moreover, the C(9)–H of fluorene moiety shows acidity (Scheme I) with pK_a = 22.6 in DMSO, which is weaker if compared with cyclopentadiene (pK_a = 18.0 in DMSO).[1] The acidity of fluorene is due to the stability of the fluorenyl anion **II**, which belongs to Huckel (4n+2)π aromatic systems with 14 π-electrons. Interestingly, the fluorene scaffold if opportunely modified (Figure I) can behave as a superacid.[2]



Scheme I. Deprotonation of 9*H*-fluorene

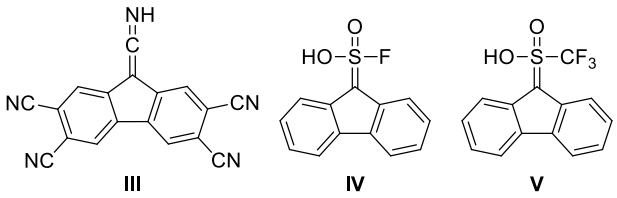


Figure I. Possible superacid fluorene scaffolds

The fluorene framework has been found in natural products,[3] for instance dendroflorin **VI** was isolated from *Dendrobium densiflorum*[4] and nobilone **VII** from *Dendrobium nobile*[5]. Both possess the fluorenone moiety and proved to have high antioxidant activity (Figure II). Another class of important natural compounds, involving a diazotetrahydrobenzo[*b*]fluorene

scaffold, are kinamycins **VIII** and lomaiviticins which are a series of bacterial metabolites with potent anticancer and antimicrobial activity.[6]

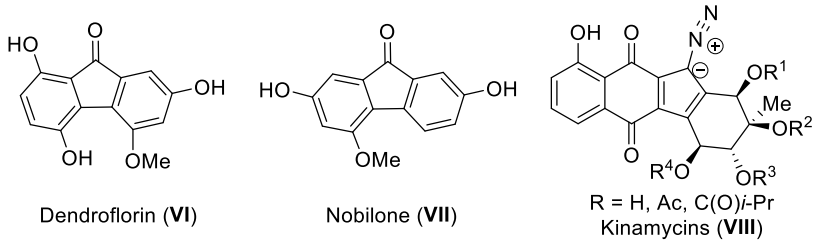


Figure II. Fluorene scaffold in natural compounds

Due to the peculiar properties of the fluorene scaffold, these compounds have been carefully studied by academic community as well as by industry researchers.

In particular, the fluorenyl anion with high-lying HOMO orbitals, proved to form strong interactions with accepting orbitals of metal atoms. This led to a huge development of fluorenyl-based ligand complexes. The metal can bind the fluorenyl scaffold through the bridgehead C(9)-atom or, to lesser extent, through the two C atoms of benzene scaffolds. Thus, these bonding confer the most important feature of fluorenyl ligands: the facile slippage of the central metal from $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ coordination (Figure III). Although this behavior resulted in some difficulties in isolating fluorenyl complexes, it was responsible for their high activity in catalysis. The most important family of fluorenyl based complexes are the *ansa*-cyclopentadienyl fluorenyl ones, which were firstly designed by Razavi and Ewen.[7] Those catalysts showed outstanding results in stereoselective olefin polymerization in the form of Zr or Hf complexes (Figure IV).[8]

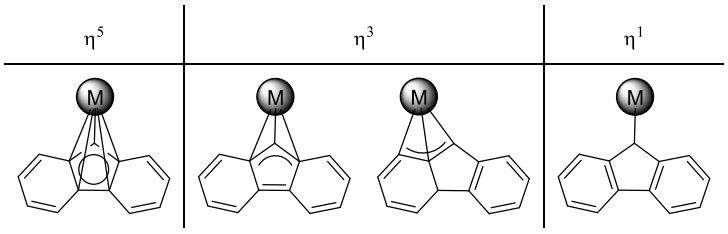


Figure III. Coordination mode of fluorenyl ligands observed for various metals

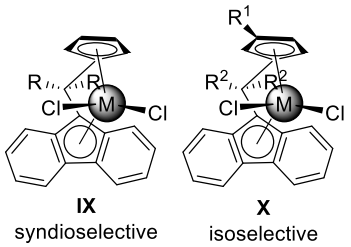


Figure IV. Main examples of {Cp/Flu} metallocene catalysts

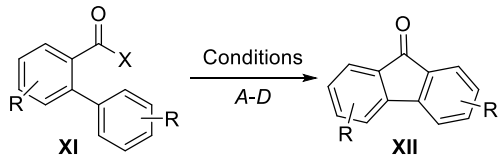
Thanks to the high thermal and chemical stability as well as the high emission quantum yields, fluorene derivatives have been extensively explored also in the field of organic semiconductors for applications in optoelectronics and molecular electronics.[9] For example, fluorene-based compounds were studied as novel hole transport materials (HTMs) for organic light emitting diodes (OLEDs)[10], as luminous molecular liquids (LMLs) for organic liquid laser[11], as *n*-type polymer acceptors or small molecules and polymer donors for active layers in organic photovoltaic cells (OPVs).[12]

Furthermore, due to versatile functionalization at 9-position, fluorene proved to be a basic building block to design organic wide-bandgap semiconductor polymers (OWBSPs) that are one of the components for lasing, RGB display, radar, white lighting source and radio frequency devices.[13]

Finally polyfluorene-based nanoparticles and nanowires have been also fabricated and synthesized. The nano approach extends the fluorene-based materials into biomedicine, nanoelectronics, nanophotonics and in thin-film electronics.[14]

1.1.2 Traditional methods for the synthesis of the fluorene scaffold

Several strategies have been developed for synthesis of fluorene. The traditional methods include: i) Friedel-Crafts type reactions; ii) radical reactions; iii) dehydro-Diels-Alder cyclization. Selected examples of Friedel-Crafts methods are depicted in Scheme II where biarylcarboxylic acids (conditions *A*),[15] esters (conditions *B*),[16] secondary amides (conditions *C*)[17] and even aldehydes (conditions *D*)[18] were turned into corresponding fluorenones **XII** by intramolecular electrophilic aromatic cyclization.

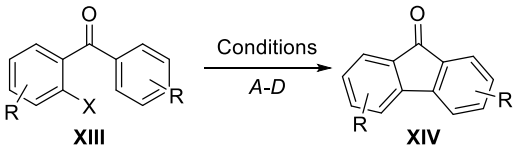


R = hydrogen, alkyl, aryl

A: X = OH $SOCl_2$, 75 °C, 3 h, up to 93%.
B: X = OEt MsOH, 130 °C, 30 min., up to 43%.
C: X = NHR $(CF_3CO)_2O$, 100 °C, 2 h, then HCl, 100 °C, 2 h, up to 89%.
D: X = H IPy_2BF_4/HBF_4, CH_2Cl_2, -60 °C, 15 h, 27%.

Scheme II: Friedel-Crafts formation of fluorenones

Radical reactions for the synthesis of fluorenones can be divided in two categories: radical cyclization of *ortho*-substituted benzophenones and radical cyclization through acyl radical formation.

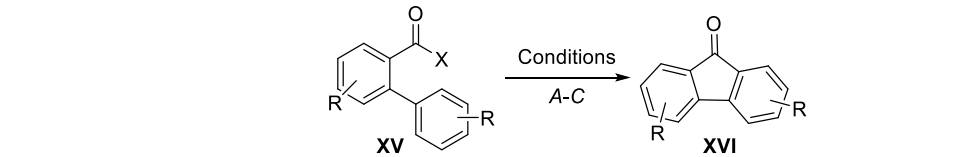


R = H, F, OMe, Me, CF_3

A: X = NH_2 $NaNO_2$, H_2SO_4, then hv, 0 to 25 °C, 2 h, up to 55%.
B: X = Br hv, CH_3CN, r.t., 14-72 h, up to 98%.
C: X = BF_3K $AgNO_3$, $K_2S_2O_8$, $PhCF_3$-H_2O, 60 °C, 1 h, up to 77%.
D: X = COOH AgOAc, $K_2S_2O_8$, d_3-CH_3CN,130 °C, MW, 1 h, up to 84%.

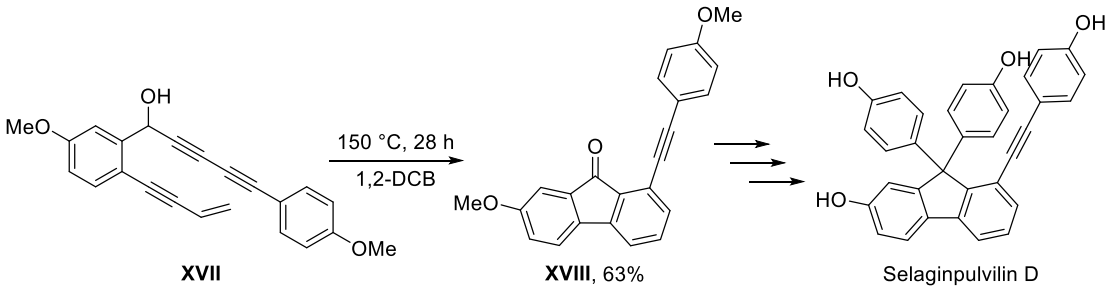
Scheme III. Radical cyclization of *ortho*-substituted benzophenones

The first class of radical reactions are based on Pschorr-type cyclization (Scheme III) which involves formation of aryl radicals by C–X homolysis of arenediazonium salt (conditions *A*),[19] 2-bromobenzophenones (conditions *B*),[20] aryltrifluoroborates (conditions *C*)[21] and arylbenzoic acids (conditions *D*).[22] The second class of radical reactions (Scheme IV) employs biarylaldehydes which undergo intramolecular dehydrogenative arylation using *t*-BuOOH (conditions *A*)[23] or $K_2S_2O_8$ (conditions *B*)[24] as oxidants. Interestingly in 2017, Zhu's group developed a deoxygenative radical acylation of biarylcarboxylic acid via photoredox catalysis (conditions *C*).[25]



Scheme IV. Radical cyclization through acyl radical formation

Finally, dehydro-Diels-Alder reactions were also reported for the synthesis of compounds with the fluorene scaffold; an interesting example is the synthesis of natural product selaginpulvilin D (Scheme V) where the tricyclic fluorene framework was constructed upon heating the enyne-diyne **XVII** at 150 °C in 1,2-dichlorobenzene (1,2-DCB) for 28 h. The chemoselective enyne-alkyne dehydro-Diels-Alder reaction, followed by air oxidation of the alcohol to ketone, afforded the desired fluorene **XVIII** in 63% yield.[26]



Scheme V. Dehydro-Diels-Alder reaction for the synthesis of selaginpulvilin D

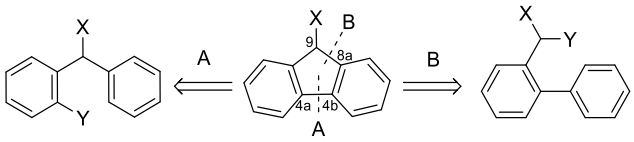
However, the above-mentioned methods often require high temperatures and the use of strong acids which are incompatible with many functional groups. Due to these drawbacks and deficiencies, new strategies based on transition metal-catalyzed functionalization have been developed as alternatives for the syntheses of these exclusive compounds. The most important outcomes will be discussed briefly in the following section.

1.1.3 Synthesis of the fluorene scaffold by transition metal-catalyzed methods

Transition metal-catalyzed reaction for fluorene synthesis have been reviewed by Ye in 2015 [27] and by me, Kaiser R. and Kotora M. in 2019.[28]

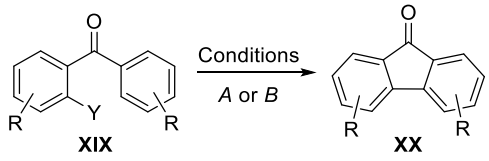
To organize the numerous literature examples about this subject, we decided to classify the synthetic approaches into two categories derived from two possible retro-synthetic

disconnections (Scheme VI): approach A, derived from the C(4a)–C(4b) bond disconnection, is based on diarylmethanes or benzophenones as starting materials; approach B which is derived from the C(9)–C(8a) bond disconnection, relies on biaryls as starting materials.



Scheme VI. General disconnection approaches A and B for transition metal-catalyzed fluorene synthesis

The first example (resembling approach A) was developed by Blum *et al*. in 1969, when conversion of benzoic anhydride into fluorenones was achieved by catalysis with $RhCl(PPh_3)_3$.[29] This pioneering work opened the doors to more effective strategies that appeared 30 years later. For instance Pd- and Cu-catalyzed cyclizations of benzophenones were reported. Representative examples are shown in Scheme VII where conditions *A* referred to Pd-catalyzed oxidative dehydrogenative dual C–H functionalization of benzophenone **XIX**,[30] whereas conditions B^1 and B^2 involve halogenated benzophenones in the direct intramolecular arylation using Pd-[31] or Cu-[32] catalysis.



R = alkyl, aryl, alkoxy, halide

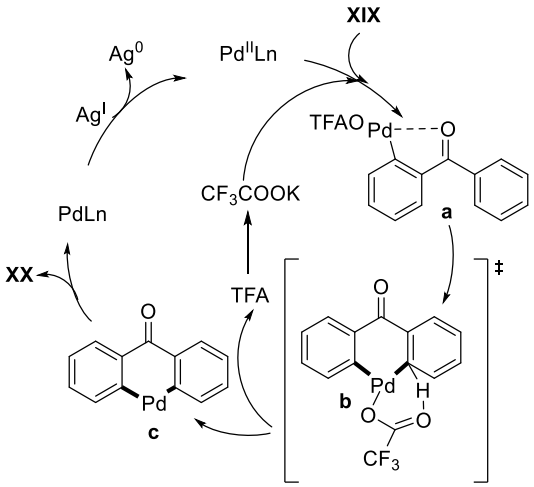
A: Y = H $Pd(OAc)_2$ (5 mol%), Ag_2O, K_2CO_3, TFA, 140 °C, 24 h, up to 94%.

B^1: Y = Br, I $Pd(PPh_3)_4$ (6 mol%), DavePhos, KOAc, K_2CO_3, DMA, 110 °C, 22 h, up to 96%.

B^2: Y = I Cu(I) (15 mol%), K_3PO_4, DMF, 160 °C, MW, up to 90%.

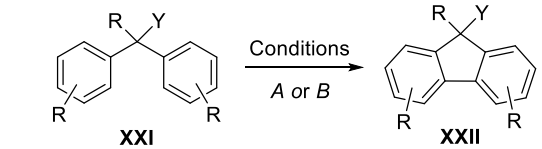
Scheme VII. Benzophenones and halogenated benzophenones as starting materials for fluorenone synthesis

The proposed mechanism for the double C–H bond activation of benzophenone relative to conditions *A*, is illustrated in Scheme VIII. $Pd(OTFA)_2$ is formed from $Pd(OAc)_2$ and TFA, then the *ortho* C–H activation takes place to form a five-membered palladacycle intermediate **a** which undergoes the second C–H bond activation generating a six-membered palladacycle complex **c** by concerted metalation-deprotonation of intermediate **b**. Reductive eliminations afford product **XX** and Pd^0 is oxidized to Pd^{II} by Ag_2O to restart the catalytic cycle.



Scheme VIII. Proposed mechanism for Pd-catalyzed oxidative dehydrogenative cyclization of benzophenone

Similar double C–H bond activations were also developed employing Rh- or Ir- as catalysts and diarylmethanes as starting materials. Model methods are outlined below (Scheme IX) where triarylmethylamines were converted into fluorene derivatives by Rh-catalyzed cyclization (conditions *A*)[33] and triarylmethanols were cyclized by Ir-catalyzed transformation (conditions *B*).[34]



R = alkyl, aryl, alkoxy, halide

A: Y = NH_2 $[RhCl(cod)]_2$ (2 mol% Rh), $Cu(OAc)_2$ (2 eq), xylene, up to 98%.
B: Y = OH $[Cp^*IrCl_2]_2$, (2 mol% Ir), $Cu(OAc)_2$ (2 eq), dodecane, up to 82%.

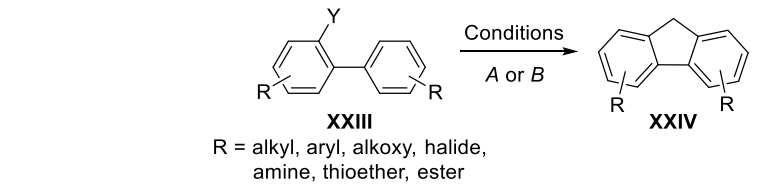
Scheme IX. [Rh] and [Ir] catalyzed double C–H bond activation of diarylmethanes

Regarding the second approach for the synthesis of the fluorene scaffold, namely the approach B (Scheme VI) based on 1,1'-biphenyls as precursors, it was reported for the first time in 1980s by Allison *et al.* They described reaction of 2,2'-dilithiobiphenyl with a stoichiometric amount of $PPh_3(CO)_4ReBr$ or $(CO)_5ReBr$ as the CO source and gained 89% isolated yield of fluorenone.[35] After this example, biphenyls became the substrate of choice for the construction of fluorene moiety because of their widespread availability.

Two main synthetic strategies with biphenyls as precursors were developed: i) the use of biphenyl with the preinstalled C(9) carbon, i.e. the preinstalled methylene group in the case

of fluorene synthesis or the preinstalled carbonyl group in the case of fluorenones; ii) the use of biphenyl and an external source of the C(9) carbon.

Selected examples of the first strategy involve 2-trifluoromethylbiphenyl which undergoes Nb-catalyzed unusual double C–F/C–H activation (Scheme X, conditions *A*)[36] and 2-arylbenzyl chlorides which affords polyarylfluorenes through Pd-catalyzed cyclization (conditions *B*).[37]



XXIII **XXIV**

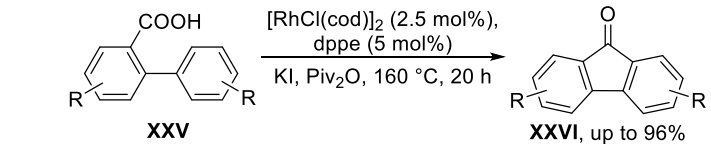
R = alkyl, aryl, alkoxy, halide, amine, thioether, ester

A: Y = CF_3 $NbCl_5$ (30 mol%), $LiAlH_4$, 1,4-dioxane, reflux, 4 h, up to 92%.

B: Y = CH_2Cl $Pd(OAc)_2$ (2 mol%), *rac*-BINAP (2,2 mol%), Cs_2CO_3, DME, 100 °C, 12 h, up to 99%.

Scheme X. Synthetic pathways to fluorenes from biphenyls with the preinstalled C(9) carbon

Analogously, syntheses of fluorenones by using the biphenyl scaffold with the preinstalled C(9) carbon, have been developed employing biphenylcarboxylic acids. For instance, Scheme XI shows Rh-catalyzed intramolecular acylation of biphenylcarboxylic acids **XXV** which afforded **XXVI** in good to excellent yields. [38]

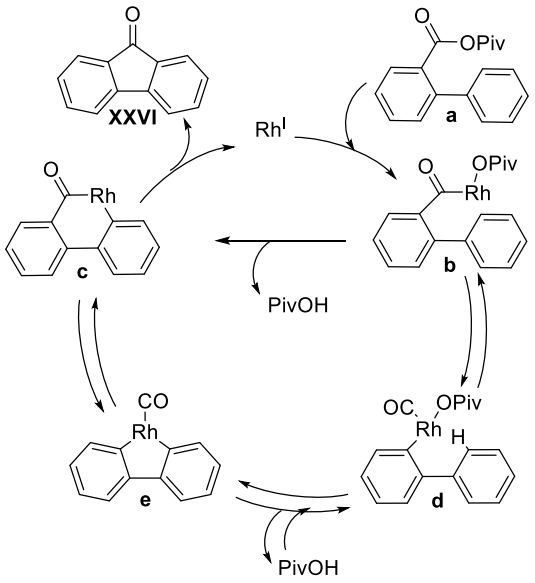


XXV **XXVI**, up to 96%

R = alkyl, aryl, alkoxy, halide, ester

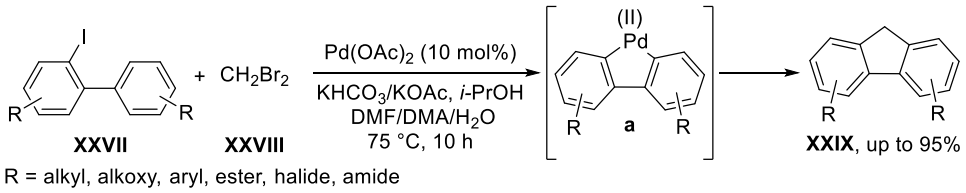
Scheme XI. Synthesis of fluorenones from biphenyls with the preinstalled C(9) carbonyl source

The proposed mechanism is illustrated in Scheme XII. After formation of anhydride **a**, rhodium(I) catalyst undergoes oxidative addition of the acyl–O bond to give acylrhodium species **b**, which then undergo an intramolecular C−H acylation to afford the rhodacycle **c**. Reductive elimination affords fluorenone **XXVI** and regenerates the key rhodium(I) species. Other Rh-carbonyl complexes, such as **d** and **e**, can be formed in equilibrium with **b** and **c**.



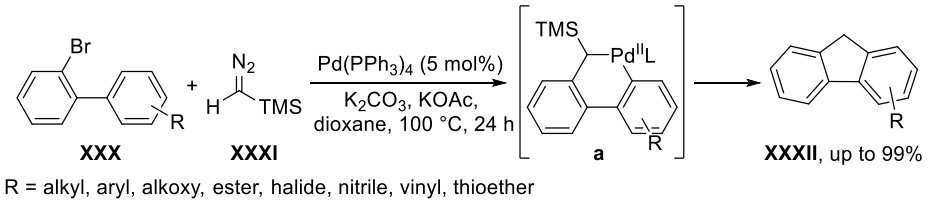
Scheme XII. Proposed reaction mechanism for Rh-catalyzed intramolecular acylation of biphenylcarboxylic acids

The majority of other publications about fluorene syntheses have been focused on the use of biphenyls and an external source of carbon C(9). The first example was reported by Zhang *et al.* in 2016 when they developed synthesis of variously substituted fluorenes using iodobiphenyls and dibromomethane as the source of the methylene group (Scheme XIII).[39] The reaction, catalyzed by $Pd(OAc)_2$, proceeds via C–H activation and the formation of dibenzopalladacyclopentadiene intermediate (**a**, Scheme XIII) which provides the desired products via tandem C–C bond sequence formation.



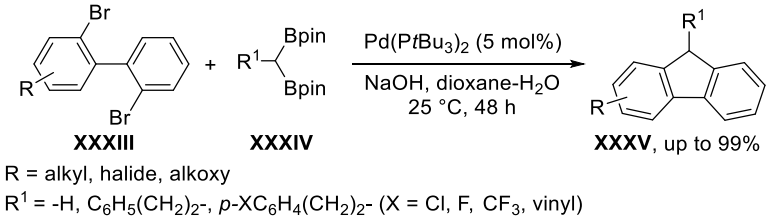
Scheme XIII. Synthesis of fluorene **XXIX** from 2-iodobiphenyls and dibromomethane

A similar approach was followed also by Wang's group in 2017. His group developed Pd-catalyzed [4+1] annulation between 2-bromobiphenyl and (trimethylsilyl)diazomethane, the C(9) source, for the access to monosubstituted fluorenes with various functional groups (Scheme XIV).[40] The proposed reaction mechanism concerns a metal carbene migratory insertion process and C–H bond activation to afford the palladacycle intermediate **a** (see Scheme XIV), then the reductive elimination and desilylation afford the desired products **XXXII**.



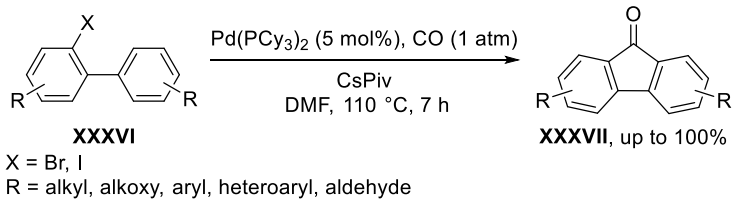
Scheme XIV. Pd-catalyzed synthesis of fluorene from 2-bromobiphenyls and (trimethylsilyl)diazomethane

In 2015 the same group reported the use of 1,1-diboronates as the methylene source and 2,2'-dibromobiphenyls for the synthesis of fluorene derivatives through Pd(0)-catalyzed tandem coupling reaction (Scheme XV).[41] This method exploits the higher reactivity of 1,1-diboron compounds and the ease of intramolecular process in order to overcome the low reactivity of alkylboron compounds, which are generally not employed in Suzuki-Miyaura cross coupling reactions. Moreover, the reaction was found to not be affected by the electronic nature of the substituents, indeed a broad range of fluorene compounds were prepared in 63-99% yields.



Scheme XV. Pd-catalyzed cross-coupling of 1,1-diboronates with 2,2'-dibromobiphenyls

The approach based on external source of the C(9) carbon for biphenyl building blocks, have been also explored for the synthesis of fluorenones. In this context the most straightforward method remains the use of carbon monoxide gas. The procedure was developed by Larock and Campo in 2000s and regards a Pd-catalyzed cyclocarbonylation of *ortho*-halobiaryls (Scheme XVI).[42] The results showed almost quantitative yields, an excellent tolerance of both electron-withdrawing and electron-donating groups and a good regioselectivity in the case of 3-substituted halobiaryls.

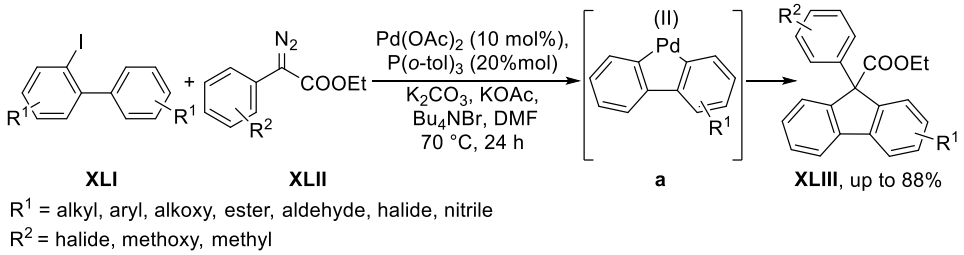


Scheme XVI. Pd-catalyzed cyclocarbonylation of *ortho* halobiaryls

In order to avoid the use of hazardous CO gas, alternative strategies have been reported. For instance, in 2018 Manabe *et al.* reported Pd-catalyzed CO-free carbonylation with phenyl formate, the CO surrogate, which can generate CO under weakly basic conditions (Scheme XVII).[43] This method was applied in the reaction of 2-bromobiphenyl and 2-iodobiphenyl affording several monosubstituted fluorenones in good to excellent yields.

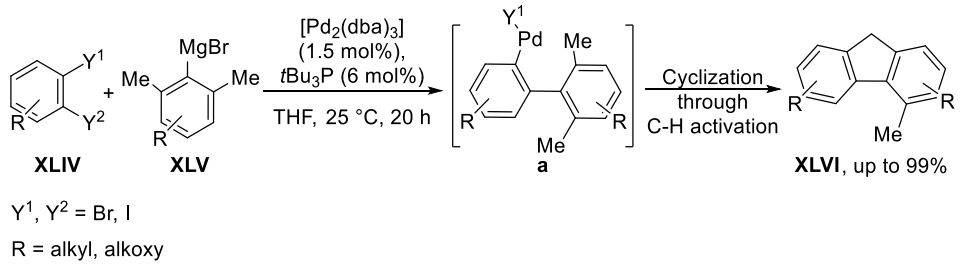
Scheme XVII. Pd-catalyzed external carbon monoxide-free carbonylation

Biphenyls have been also selected as starting materials for the preparation of 9-aryl fluorenes through cascade intermolecular arylation/annulation strategies. In this context, Zhang *et al.* reported the reaction between 2-iodobiphenyl **XLI** and α-aryl diazoesters **XLII** with $Pd(OAc)_2$ as catalyst, to afford the desired fluorenes **XLIII** in 24-88% yield and with a broad range scope (Scheme XVIII).[44] Mechanistic study revealed the formation of the key palladacycle intermediate **a**, shown in Scheme XVIII, via C(sp^2) –H activation, followed by insertion of aryl-diazoesters and reductive elimination. The presence of ester group in 9' position of the fluorene scaffold gives the possibility for further transformation, extending the synthetic application of this strategy.



Scheme XVIII. Synthesis of 9,9-disubstituted fluorenes from 2-iodobiphenyls and α-diazoesters

Syntheses of fluorenes and fluorenones were also accomplished by tandem reactions, which are considered as a powerful and elegant tool in the modern organic chemistry. Hu and Dong developed tandem approaches for the synthesis of fluorenes by Pd-catalyzed reactions. For instance in 2006, they reported tandem annulation based on Pd-catalyzed cross-coupling and C(sp^3)–H bond-activation of 1,2-dihalobenzenes **XLIV** and hindered Grignard reagents **XLV** (Scheme XIX).[45] Bulky Grignard reagents were employed in order to reach the cyclization pathway and to avoid the formation of an undesired second cross coupled product, which can be generated if the Pd-biphenyl complex **a**, shown in Scheme XIX, undergoes a second cross coupling with another equivalent of organometallic reagent.

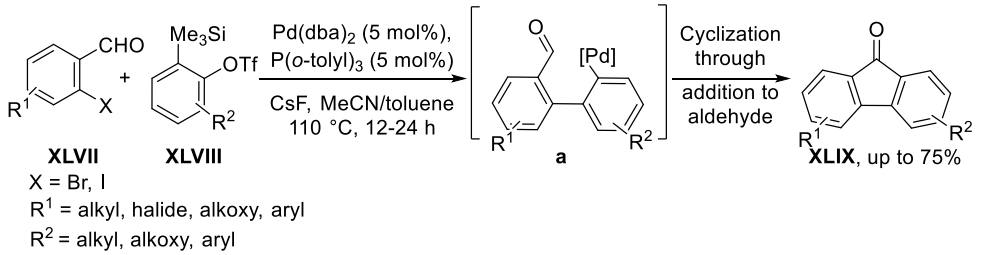


Scheme XIX. Synthesis of fluorenes by Pd-catalyzed tandem reaction

Regarding syntheses of fluorenones, more reports involving tandem reactions are available when compared with those for fluorenes. These strategies can be classified in three main groups: i) tandem reactions involving an aryne intermediate; ii) tandem reactions based on Suzuki-Miyaura cross coupling reaction in the first step; iii) tandem reaction based on C–H bond activations.

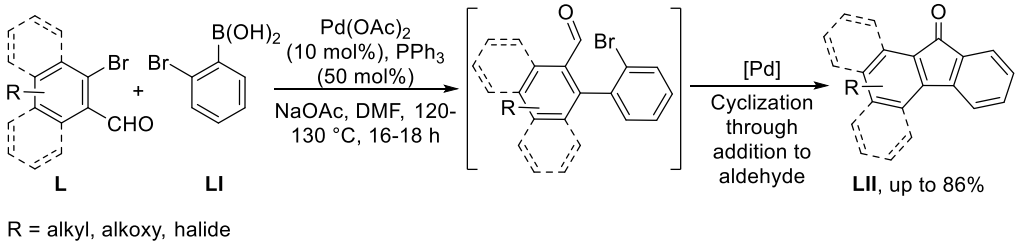
The first strategy was developed by Larock *et al.* who reported the synthesis of fluorenones by Pd-catalyzed annulation of *o*-halobenzaldehydes **XLVII** and arynes, *in situ* generated by silylaryltriflates **XLVIII** (Scheme XX).[46] One of the proposed mechanisms concerns the coordination of Pd(0) to the triple bond of aryne followed by oxidative addition

of arylhalide and reductive elimination to afford arylpalladium intermediate **a** illustrated in Scheme XX. The target molecule was obtained after cyclization through addition to aldehyde. A number of substituted fluorenones were prepared in moderate to good yields.



Scheme XX. Synthesis of fluorenones by annulation of aryne and 2-halobenzaldehydes

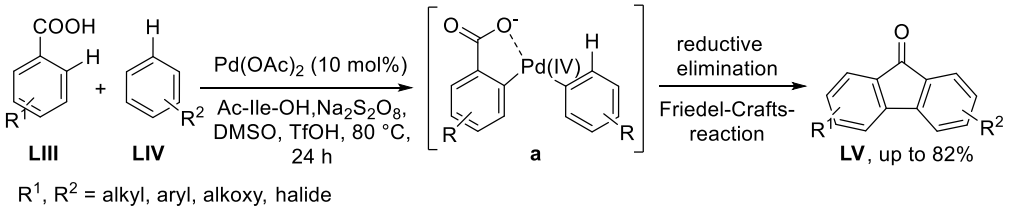
Regarding the second strategy for the synthesis of fluorenones, it consists of domino reactions based on Suzuki cross coupling; a representative example is illustrated in Scheme XXI.[47] The method was developed by Paul *et al.* who employed 2-bromophenyl boronic acids **LI** with 2-bromocarboxaldehydes **L** to synthetize fluorenones and condensed fluorenones in 51-86% yields. The reaction involves a tandem Pd-catalyzed Suzuki cross coupling followed by arylpalladium addition to aldehyde.



Scheme XXI. Synthesis of fluorenones via domino reaction based on Suzuki-Miyaura cross-coupling

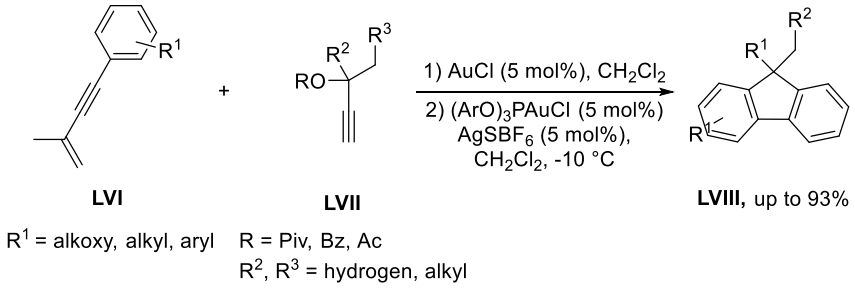
The third and last category of tandem reactions involves C–H activations. A model strategy was disclosed by You and co-workers who successfully conducted a direct oxidative *ortho*-C–H bond activation of aromatic carboxylic acids through double C–H activation followed by intramolecular Friedel-Crafts acylation (Scheme XXII).[48] The reaction afforded fluorenones in 53-82% yields with a broad range scope; however, carboxylic acids with strongly electron-withdrawing groups were unreactive. The proposed mechanism first involves *ortho*-C–H bond activation of **LIII** with the resulting formation of a five-membered palladacycle which upon oxidation with $Na_2S_2O_8$ generates Pd(IV) intermediate; the reaction of this complex

with **LIV** forms the critical aryl-palladacycle **a**, shown in Scheme XXII, which after reductive elimination provides 2-biphenylcarboxylic acid. Finally, Friedel-Craft acylation gives the desired fluorenones.



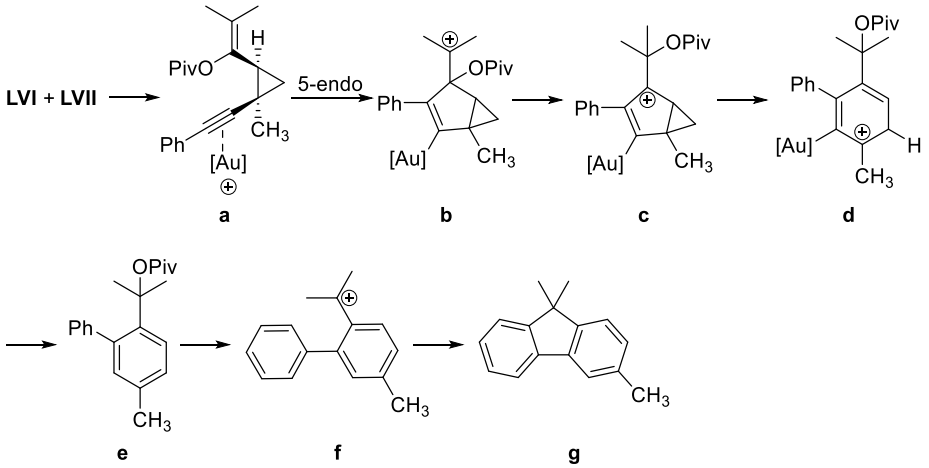
Scheme XXII. Fluorenone synthesis by tandem C–H activations

Besides the above-mentioned approaches based on diarylmethanes or biphenyls, other strategies were also developed, for instance employing alkenes and alkynes as starting materials. In this context, Toste and co-workers disclosed transformation of 1,3-enynes **LVI** and propargyl esters **LVII** into fluorenes via Au(I)-catalyzed annulation (Scheme XXIII).[49]



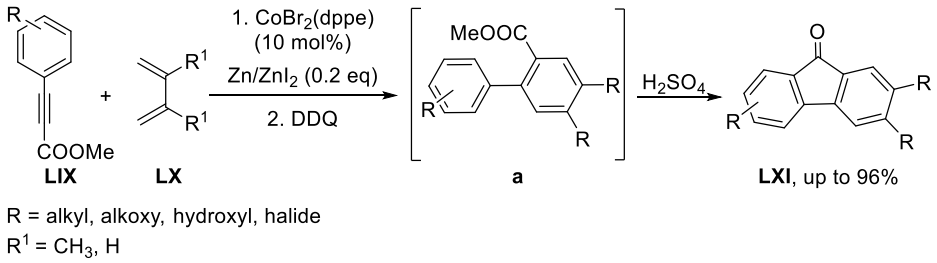
Scheme XXIII. Au(I)-catalyzed annulation of 1,3-enynes and propargyl esters

The proposed mechanism (Scheme XXIV) involves intermolecular cyclopropanation reaction between enyne **LVI** and propargyl ester **LVII**, which is the carbene precursor. After formation of **a**, the gold catalyst coordinates to the triple bond and 5-endo-dig cyclization occurs to afford tertiary carbocation **b**. Migration of the pivaloyloxy group gives an allylic carbocation **c**, which undergoes the cyclopropyl ring opening to provide intermediate **d**. After aromatization, an intramolecular S_N1 reaction forms the fluorene scaffold.



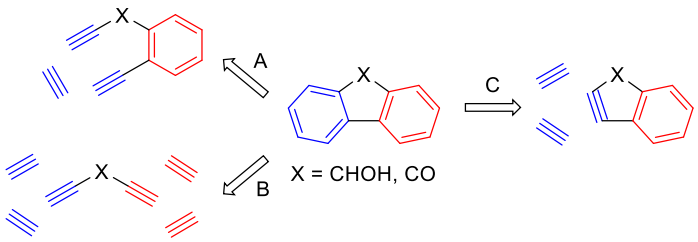
Scheme XXIV. Proposed mechanism for Au-catalyzed annulation of enynes and alkynes

Transition metal catalyzed Diels-Alder reaction for the synthesis of fluorenes have been also reported. An interesting contribution to this field was given by Hilt *et al.* in 2013; they synthesized variously substituted fluorenones by Co-catalyzed Diels-Alder reaction of aryl-substituted propiolate **LIX** and 1,3-diene **LX** followed by aromatization with DDQ to afford diaryl ester intermediate **a** (Scheme XXV). The subsequent Friedel-Craft reaction with sulfuric acid gave fluorenones **LXI** in up 96% yield.[50]



Scheme XXV. Co-catalyzed Diels-Alder reaction for synthesis of fluorenones

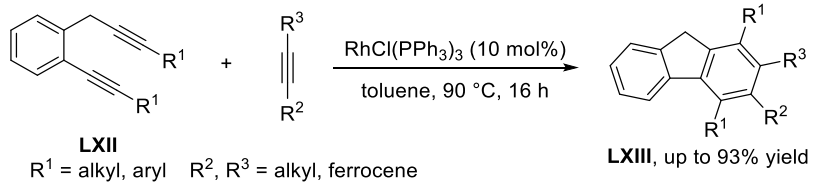
The last but worthwhile approach for the synthesis of fluorene moiety is [2+2+2] cyclotrimerization. It is a powerful reaction for construction of variously substituted aromatic rings[51] and in this context for the construction of 1,2,3,4-tetrasubstituted fluorenes and fluorenones. The reaction offers the advantages to be atom-economical step and to allow to use a wide range of substrates. There are three strategies for the preparation of the fluorene-like moiety using transition metal catalyzed [2+2+2] cycloaddition, as depicted in Scheme XXVI.



Scheme XXVI. Retrosynthetic approach for fluorene scaffold using [2+2+2] cycloaddition

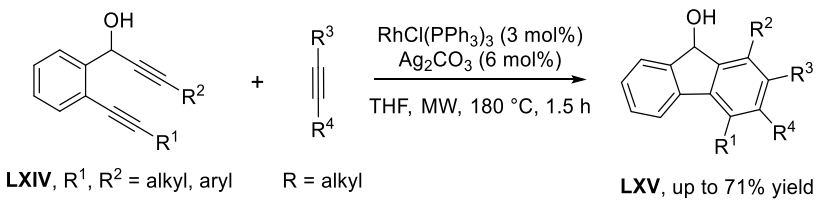
The approach A is a partially intramolecular [2+2+2] cyclotrimerization of diynes with alkynes. The approach B is cycloaddition of a tethered diyne with four alkynes to build two aromatic rings in a simultaneous fashion. Finally the strategy C is a fully intermolecular transformation of two alkynes with a bicyclic alkyne surrogate.

The first development of approach A was reported by our group in 2015. As outlined in Scheme XXVII, the synthesis of 1,2,3,4-tetrasubstituted fluorenes **LXIII** was obtained by Rh-catalyzed [2+2+2] cyclotrimerization of symmetrically substituted diynes **LXII** with internal alkynes.[52] The reaction provided various alkyl and aryl substituted fluorenes in up to 93% isolated yields.



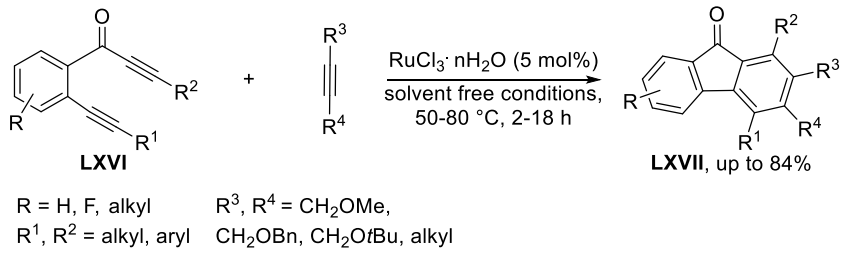
Scheme XXVII. [2+2+2] Rh-catalyzed cyclotrimerization of dynes with alkynes

In a subsequent work, developed by our group, variously decorated fluorenols **LXV** were prepared starting from diynols **LXIV** and internal alkynes by $RhCl(PPh_3)_3/Ag_2CO_3$ catalytic system (Scheme XXVIII).[53] The Rh-catalyzed [2+2+2] cyclotrimerization reaction showed a high functional group tolerance and good yields up to 71%.



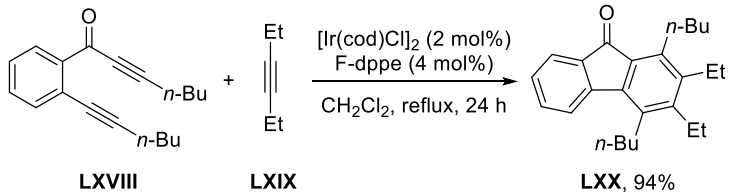
Scheme XXVIII. [2+2+2] Rh-catalyzed cyclotrimerization of dynols with alkynes

A similar approach was also described by Ratovelomanana-Vidal and co-workers in 2016. They developed a Ru-catalyzed [2+2+2] cyclotrimerization of diynones **LXVI** and alkynes to afford fluorenones **LXVII** in up to 84% yield (Scheme XXIX).[54] The reaction was carried out under solvent-free conditions and without additional additives or ligands. This eco-friendly approach allowed the synthesis of not only variously substituted fluorenones, but also of azafluorenones, benzo[*b*]furanones and indeno-thiophenones.



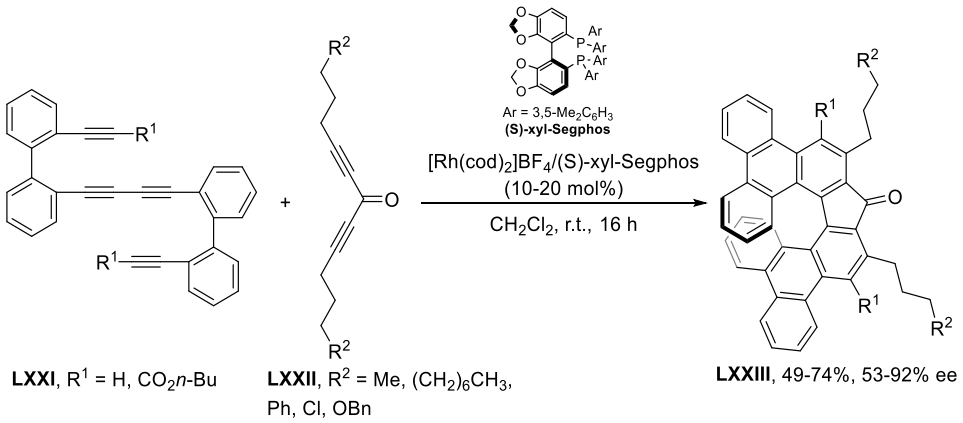
Scheme XXIX. Ru-catalyzed [2+2+2] cyclotrimerization for the synthesis of fluorenones

Recently Takeuchi's group showed one example of [Ir]-catalyzed cycloaddition of internal alkyne **LXIX** with the benzene-linked ketodiyne **LXVIII** in the presence of 1,2-bis[bis(pentafluorophenyl)phosphino]ethane (F-dppe) as ligand (Scheme XXX).[55] The reaction yielded fluorenone **LXX** in 94% yield.



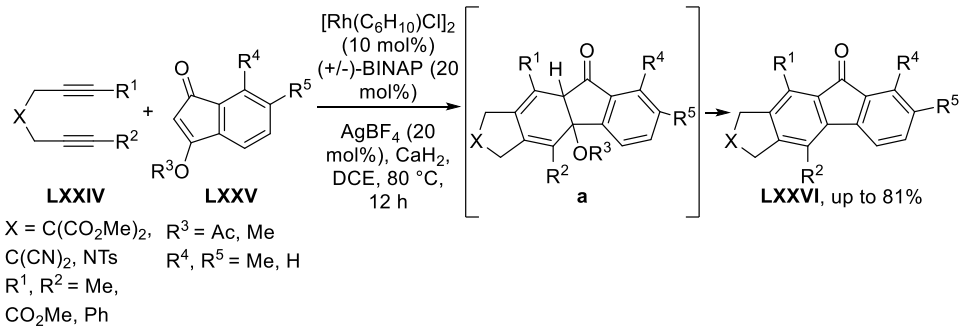
Scheme XXX. [Ir]-catalyzed cyclotrimerization of ketodyne with internal alkyne

Regarding the approach B (see Scheme XXVI), it was designed by Tanaka *et al.* for the construction of fluorenones-[9]helicenes.[56, 57] For example, they reported in 2012 a [2+2+2] Rh-catalyzed enantioselective cyclotrimerization of biaryl-linked tetrayne **LXXI** with dialkynyl ketone **LXXII** for the synthesis of helically chiral 1,1'-bitriphenylene **LXXIII** (Scheme XXXI).[57] Using (*S*)-xyl-Segphos and $[Rh(cod)_2]BF_4$ as catalytic system, the reaction afforded the desired helicenes in up to 74% yield and 92% ee.



Scheme XXXI. Rh-catalyzed enantioselective cyclotrimerization of biaryl-linked tetraynes with dialkynyl ketones

The last approach (C, Scheme XXVI) for the construction of the fluorene scaffold was recently designed by Commeiras and co-workers in 2020.[58] The group proposed a novel Rh-catalyzed [2+2+2] cycloaddition of diynes **LXXIV** with 3-acetoxy or 3-alkoxyindenones **LXXV** as an alkyne surrogate for a highly reactive benzocyclopentynone (Scheme XXXII). The reaction proceeds through [2+2+2] cycloaddition between diynes and indenone, which behaves as a regular 2π partner, leading to the cycloadduct **a**. Afterwards, this intermediate undergoes aromatization by β-hydride elimination to afford the desired fluorenone. With this procedure several substituted fluorenones were obtained with up to 81% yield.



Scheme XXXII. Synthesis of fluorenones by using a benzocyclopentynone surrogate for [2+2+2] cycloaddition reaction

1.2 Synthesis and application of spirobifluorenes

1.2.1 The importance of spirobifluorene based compounds

The molecular structure of spirobifluorene (**LXXVIII**, Figure V) comprises two fluorene moieties which are bound together through a sp^3-carbon atom. This linkage creates a cross-shape molecule where the two π-systems of the fluorene scaffold have a perpendicular arrangement. A 3D prospective view of spirobifluorene is shown in Figure V: the ball and stick molecular structure was obtained by me after optimization of geometry with DFT calculation (B3LYP/6-311G+(d,p) level of theory).

Moreover, spirobifluorenes and, even more, fluorenes resemble biphenyl compounds, **LXXVII**, which can be considered their conceptual progenitors. However, the presence of the additional central carbon atom forces the two benzene rings of biphenyl core to be planar, thus losing one rotational degree of freedom.

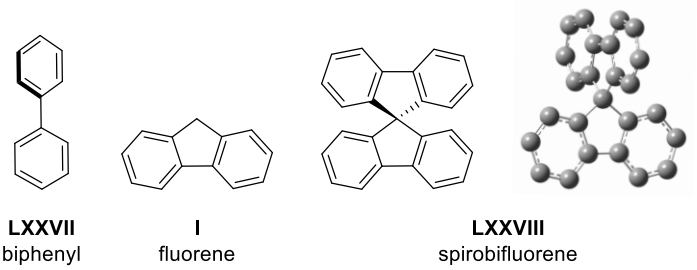


Figure V. Molecular structure of biphenyl, fluorene and spirobifluorene

The particular molecular structure of spirobifluorenes is responsible of the interesting properties related to them. Indeed, the orthogonal core suppresses the intermolecular π-π interactions, giving to spirobifluorenes a better solubility. In addition, the cross-shape and the rigidity of the structure hinders recrystallization and thus increases the glass transition temperature (T_g) and consequently the morphological stability. The sterically hindered structure can also suppresses the excimer formation, which is important characteristic to build efficient fluorescent material for organic electronics. Regarding the electronic properties, spirobifluorene resembles the fluorene moiety because the central sp^3-carbon atom and the perpendicular arrangement of π-systems disrupt the electron conjugation and thus make the two halves electronically independent.[59] Due to their particular structure and properties, spirobifluorenes have attracted attention of academic community as well as industry.

One of their applications is in asymmetric catalysis as chiral ligands, because the impossibility of rotation between the two halves of the molecule gives rise to axial chirality. Moreover, since the two rings are connected at the quaternary center through σ-bond, racemization of chiral spiro compounds are virtually impossible. Although several spiro, mono and bidentate ligands have been successfully applied in transition metal catalyzed asymmetric reactions,[60] only one example of spirobifluorene based ligands have been reported for homogenous catalysis. Indeed, Zhou and co-workers developed a new spirobifluorene-based diphosphane ligands with a large dihedral angle (**LXXIX**, Figure VI).[61] Their ruthenium complexes proved to be highly efficient catalysts for asymmetric hydrogenation of α,β-unsaturated carboxylic acids.[62] Regarding heterogeneous catalysis, Poriel's group showed some examples of [Mn], [Fe] and [Ru] spirobifluorenylporphyrin polymers, which were tested in cyclopropanation and epoxidation of olefins.[63]

To date the most important application of spirobifluorene based compounds is in hole transport material (HTM) for organic solar cells. In 1998 Grätzel reported the first employment of 2,2',7,7'-tetrakis[*N*,*N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD, **LXXX**, Figure VI) as HTM for solid state solar cell with high photon to electron conversion efficiencies.[64] After that, many alternative HTMs have been developed for perovskite and dye-sensitized solar cells, but spiro-OMeTAD remains superior and still the best promising material.[65, 66, 67] Recently fluorinated spiro-OMeTAD derivatives have also been synthesized and applied in perovskite solar cells (**LXXXI**, Figure VI).[68] The employment of these new materials has brought organic solar cells to the record of 25% of power conversion efficiency (PCE) which is comparable to that of Si-based solar cells (26.6% PCE).[69]

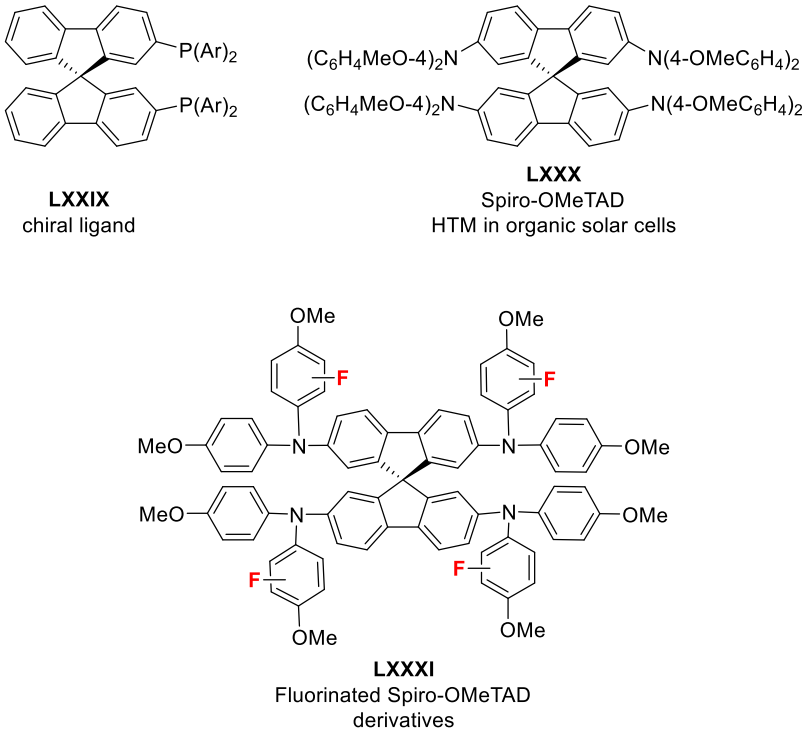


Figure VI. Spirobifluorene applications in catalysis and in organic solar cells

Spirobifluorenes can also find further applications as organic semiconductors in organic field-effect transistors (OFETs), phototransistors, solid state lasers,[70] organic light emitting diodes (OLEDs), etc.[59] In the context of spirobifluorenes based OLEDs, Poriel's group have devoted much effort to this topic in the last decade.[71] As result, they have developed an interesting spirobifluorene based compound (**LXXXII**, Figure VII) as universal host for red, green and blue (RGB) phosphorescent OLEDs (PhOLEDs).[72, 73] Outstanding results have also been achieved for blue thermally activated delayed fluorescence (TADF) materials using spiroacridine (an heteroatom substituted spirobifluorene) framework as the emitting layer.[74, 75] For instance, Kaji and co-workers reported an efficient deep-blue TADF emitters based on spiroacredine-adamantyl framework, **LXXXIII** (Figure VII). The device reached high external quantum efficiency (EQE = 11%) in the deep blue region.[76]

In the less explored field of organic light-emitting transistors (OLETs),[77] spirobifluorene oligomers have been also studied as active layers (**LXXXIV**) in the pioneering work of Adachi *et al.*[78]

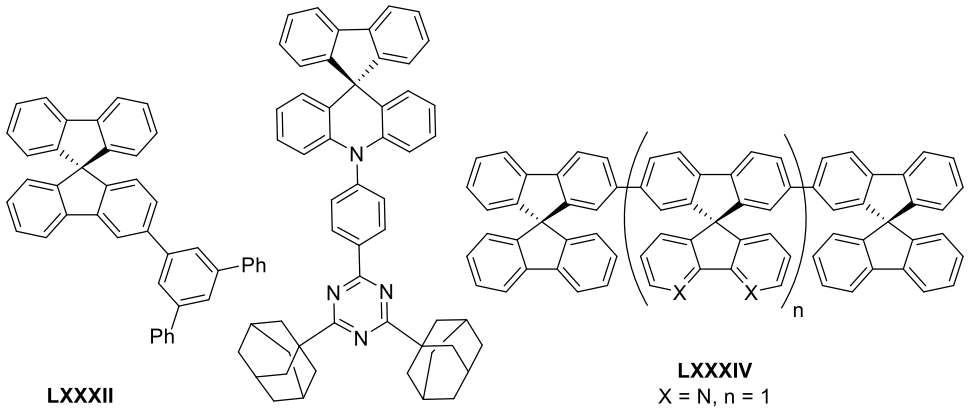
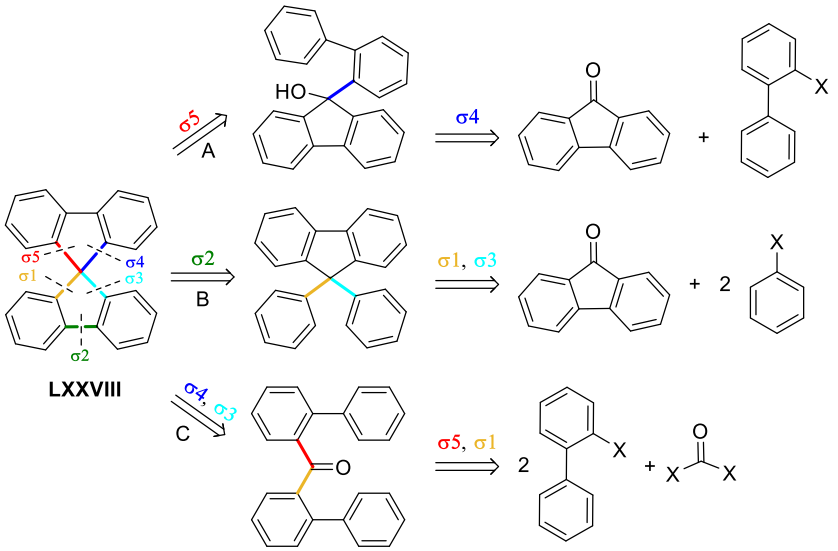


Figure VII. Spirobifluorenes derivatives for PhOLEDs, TADFs, OLETs

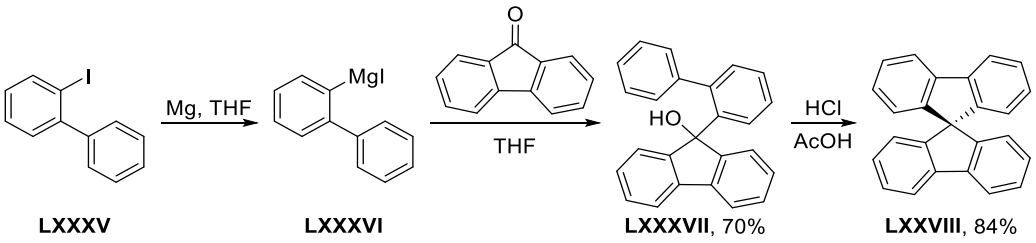
1.2.2 Synthesis of spirobifluorenes

For the synthesis of spirobifluorene there are three major synthetic routes which have been classified by Huang *et al*. They are classified as *o*-halobiaryl method, diarylfluorene method and dibiarylketone method, according to starting material and sequences of bond breakages.[79] Scheme XXXIII illustrates the retrosynthetic analysis of spirobifluorene based on different positions of bond breakages. The *o*-halobiaryl method (route A, Scheme XXXIII) relies on breakage of the σ–bond σ5 which gives a carbinol intermediate, followed by the σ4 bond which leads to fluorenone and *o*-halobiphenyl as starting materials. Method B consists of formation of the C–C bond σ2 at the final step after formation of the σ1 and σ3 bonds. This route passes through a diarylfluorene synthetic intermediate and avoids the use of expensive *o*-halobiaryls. The di(biaryl)ketone method (route C) considers the one-step formation of the C–C bond σ4 and σ3 starting from a methanone *ortho*-connected with two biphenyl groups. This di(biaryl)ketone can be formed from biphenyls and a carbonyl source.



Scheme XXXIII. Retrosynthetic analysis of spirobifluorene

The first synthesis of 9,9'-spirobifluorene is an example of the above-mentioned *o*-halobiaryl method (route A) and was reported by Clarkson and Gomberg in 1930 (Scheme XXXIV).[80] They started form 2-iodobiphenyl, **LXXXV**, which was treated with magnesium in THF to afford the Grignard reagent **LXXXVI**. Afterwards the Grignard reagent was added to 9-fluorenone to obtain 9-(biphenyl-2-yl)-9-fluorenol, **LXXXVII**, in 70% yield. In the final step to a boiling solution of carbinol in acetic acid, catalytic amount of HCl was added and the ring-closure reaction afforded the desired spirobifluorene **LXXVIII** in 84 % yield.

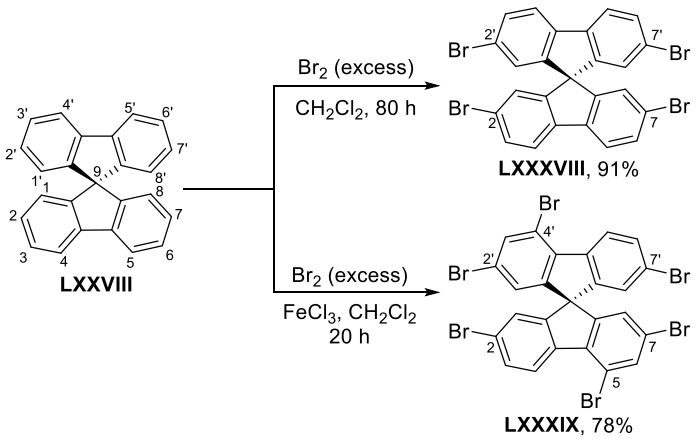


Scheme XXXIV. First synthesis of unsubstituted spirobifluorene

After this preliminary result, other syntheses were developed employing 2-bromobiphenyl instead of the iodo analogue and *n*-BuLi or *t*-BuLi instead of magnesium.[59]

The spirobifluorene **LXXVIII** can be use as starting material for preparation of compounds which are identically substituted in *para* positions (2,2',7,7' positions). Indeed electrophilic aromatic substitution of spirobifluorene leads to the preferentially formation of products with substituents on 2 and 7 positions. A catalyst free bromination in CH_2Cl_2 was developed by Salbeck's group affording 2,2',7,7'-tetrabromo-9,9'-spirobifluorene **LXXXVIII**

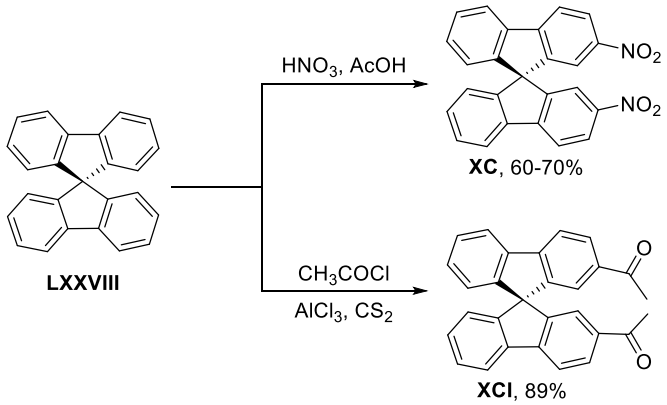
in 91% yield.[59] Interestingly, the use of a catalytic amount of $FeCl_3$ and an excess of bromine gave 2,2',5,4',7,7'-hexabromo-9,9'-spirobifluorene, **LXXXIX**, in good yields (78%).



Scheme XXXV. Bromination of spirobifluorene

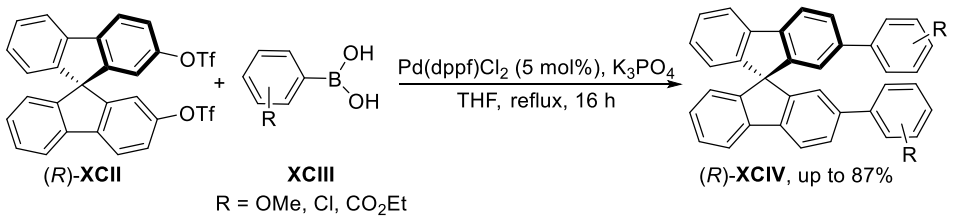
2,7-Dihalogenated spirobifluorene and the 2-monohalogenated one can be prepared by direct halogenation of fluorenone,[81] which can lead to spiro scaffold after reaction with 2-lithium-biphenyl (or the Grignard analogue) and cyclization of the resulting carbinol in acidic media (see Scheme XXXIV). The halogenated spirobifluorenes can be easily employed in cross-coupling or amination reactions for further substitution.

Regarding the preparation of 2,2'-disubstituted spirobifluorene, nitration and acylation reaction proved to be effective, whereas halogenation gave inseparable mixture of 2,2'-dihalo-, 2-mono- and 2,7-dihalospirobifluorenes. In particular, the treatment of **LXXVIII** with concentrated nitric acid in refluxing acetic acid gave the 2,2'-dinitro-9,9'-spirobifluorene, **XC**, in up 70% yield (Scheme XXXVI).[82] Formation of side-products such as 2-nitro-9,9'-spirobifluorene was also observed. However, unlike the case of bromination, the products could be separated. Friedel-Crafts acylation was achieved with acetyl chloride and aluminum chloride in carbon disulfide and the bisacetylated product **XCI** was formed in 89% yield (Scheme XXXVI).[83] Also in this case the occurring byproducts (monoacetylated, 2,2',7-triacetyl-9,9'-spirobifluorene, and 2,2',7,7'-tetraacetyl-9,9'-spirobifluorene) could be easily separated from the main product by chromatography.



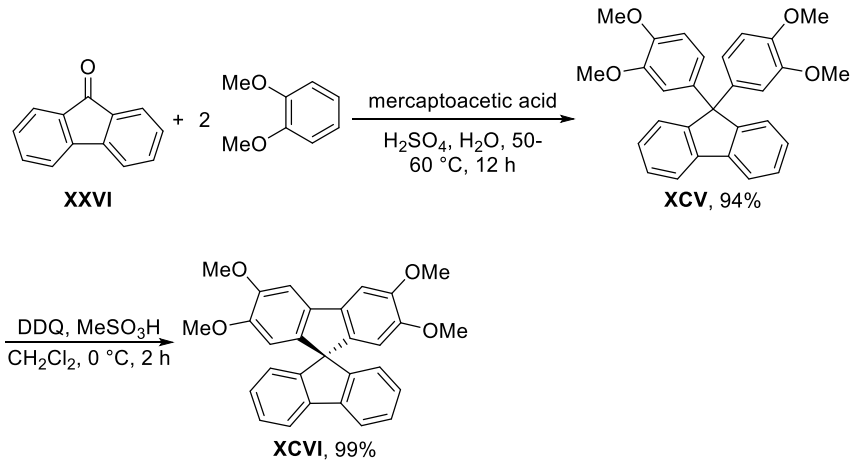
Scheme XXXVI. Nitration and acylation of spirobifluorene

Both the nitro and acetyl groups can be converted into halides and triflates respectively, by using classic chemistry transformations. These two functional groups can be easily employed in cross coupling reactions to further functionalize the spirobifluorene scaffold. For example bistriflate **XCII** (Scheme XXXVII) was employed in Suzuki-Miyaura cross coupling reaction with several aryl boronic acids to obtain 2,2'-diphenyl-9,9'-spirobifluorene **XCIV** in up to 87 % yield.[82b]



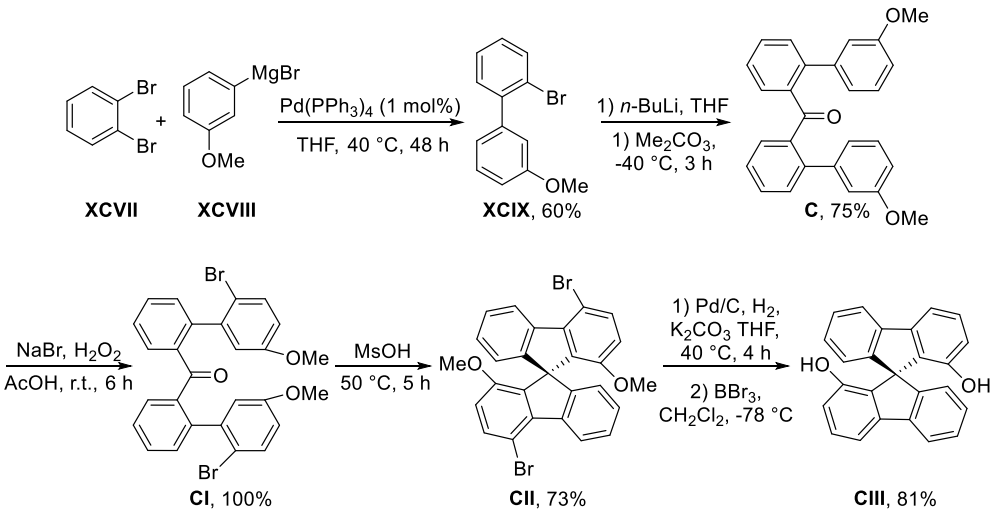
Scheme XXXVII. Suzuki-Miyaura reaction to obtain 2,2'-diphenyl-9,9'-spirobifluorenes

For substitution in other positions of the spirobifluorene core, variously substituted fluorenones can be engaged as starting materials in the *o*-halobiaryl method (route A, Scheme XXXIII). The synthesis of substituted fluorenones have been covered in section 1.1.2 and 1.1.3 of this thesis. The other two methods, route B and C in Scheme XXXIII, also offer another way for synthesis of modified spirobifluorene scaffolds. For instance, method B was successfully used by Rathore *et al.* for the synthesis of 2,3,6,7-tetramethoxy-9,9'-spirobifluorene **XCVI** (Scheme XXXVIII).[84] They prepared the key intermediate 9,9-bis(3,4-dimethoxyphenyl)fluorene **XCV** in 94% yield by acid-catalyzed condensation of 1,2-dimethoxybenzene with fluorenone. Using DDQ as oxidant, the Scholl-type oxidative C–C bond formation allowed to obtain **XCVI** in excellent 99% yield.



Scheme XXXVIII. Spirobifluorene synthesis with diarylfluorene method

The last method (route C, Scheme XXXIII) was used for the synthesis of 1,1'-disubstituted spirobifluorene. In this context, Zhou *et al.* reported the synthesis of 1,1'-dihydroxy-9,9'-spirobifluorene.[85] They performed Kumada coupling of 1,2-dibromobenzene **XCVII** with 3-methoxyphenylmagnesium bromide **XCVIII** to afford 2-bromo-3'-methoxybiphenyl **XCIX** which was treated with *n*-BuLi and then with dimethylcarbonate to produce the key di(biaryl)ketone intermediate **C** in 75% yield (Scheme XXXIX). The obtained compound was brominated with NaBr in the presence of H_2O_2 to form dibromoketone **CI** in the quantitative yield. With the brominated di(biaryl)ketone, they performed ring-closing reaction using methanesulfonic acid. The 4,4'-dibromo-1,1'-dimethoxy-9,9'-spirobifluorene **CII** was obtained with 73% yield. Reductive debromination by Pd/C catalyzed hydrogenation followed by demethylation afforded the target 1,1'-dihydroxy-9,9'-spirobifluorene **CIII** in 81% yield for the last two steps.



Scheme XXXIX. Synthesis of spirobifluorene with di(biaryl)ketone method

To briefly summarize this section, the synthesis of the spirobifluorene scaffold can be achieved by three main methods which are classified according to their key synthetic intermediate: i) *o*-halobiaryl method; ii) diarylfluorene method; iii) dibiarylketone method. Position 2,2' and 7-7' of the spirobifluorene moiety are active to electrophilic aromatic substitution, therefore, tetrasubstitution and disubstitution can be accomplished by classic halogenation, nitration or acylation of the aromatic rings. For substitution in other positions, the selection of right method can offer versatility.

1.3 Synthesis and application of dihydroindenofluorene

1.3.1 The importance of dihydroindenofluorene based compounds

Dihydroindenofluorenes belong to the family of bridged terphenyls and their core can be viewed as the fusion of the fluorene unit with the indene fragment. Just as terphenyls possesses three possible regioisomers depending on phenyl linkages (*para*/*meta*/*ortho*) (see Figure VIII), dihydroindenofluorenes form three main regioisomers: *para* (**CIV** and **CV**), *meta* (**CVI** and **CVII**) and *ortho* (**CVIII**) based on benzene ring connections. However, two additional positional isomers come from the *anti* or *syn* orientation of the two methylene groups.

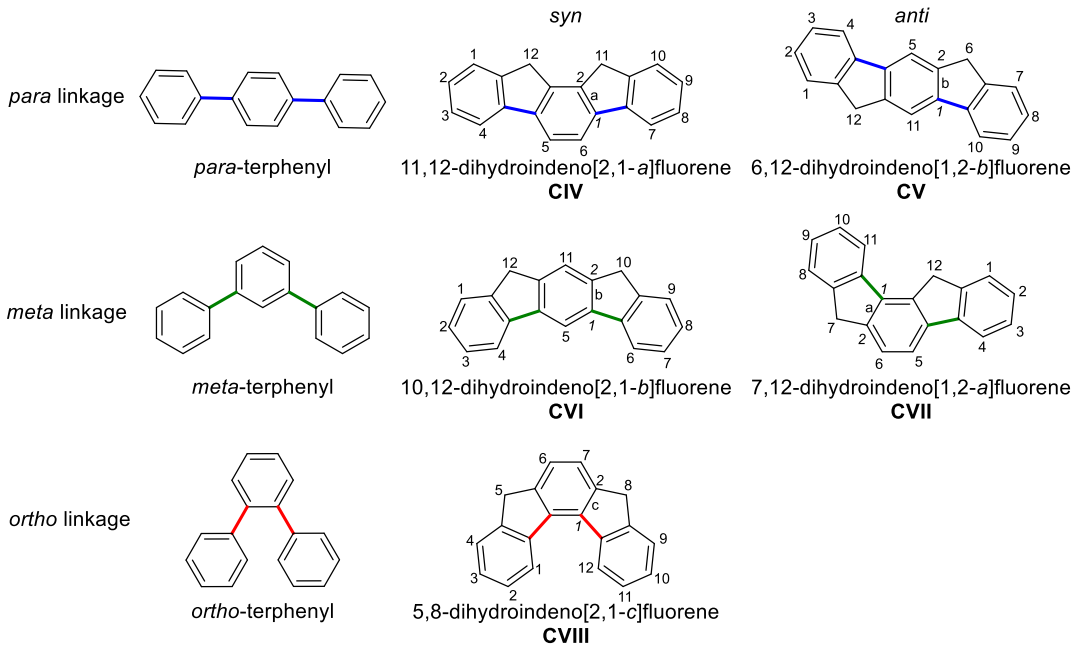


Figure VIII. Dihydroindenofluorene and terphenyl regioisomers

In the dihydroindenofluorene nomenclature, the letters *a*, *b* and *c* refer to the edge of the indene/fluorene ring fusion, whereas the number in the square brackets corresponds to the orientation of the two methylene groups. If the methylenes have *anti* relationship the isomers are named 1,2, if their relationship is *syn*, the name is 2,1.

In comparison with the fluorene scaffold, this new class of phenylene oligomers possesses a more extended coplanar fused structure which leads to enhanced π-conjugation, more π-π intermolecular interactions and improved charge carrier mobility. Besides those interesting properties dihydroindenofluorene have been rarely reported in literature due to difficulties in their syntheses.

However, among the five isomers, the 6,12-dihydroindeno[1,2-*b*]fluorene is the most studied one. Preliminary articles showed its possible application in organic electronics. For instance, Seok and coworkers used a polymer containing dihydroindeno[1,2-*b*]fluorene and triarylamine (**CIX**, Figure IX) as hole transport material for organic perovskite solar cells.[86] The fabricated device resulted in high photovoltage of 1.40 V, power conversion efficiency (PCE) up to 6.7% and good hole mobility. Another interesting application of this isomer was demonstrated by Laquai *et al.* in 2011 in the field of blue organic lasing.[87] They reported a novel indenofluorene-phenanthrene copolymer (**CX**, Figure IX) with high gain coefficients, improved photoluminescence quantum efficiency and excellent hole mobility.

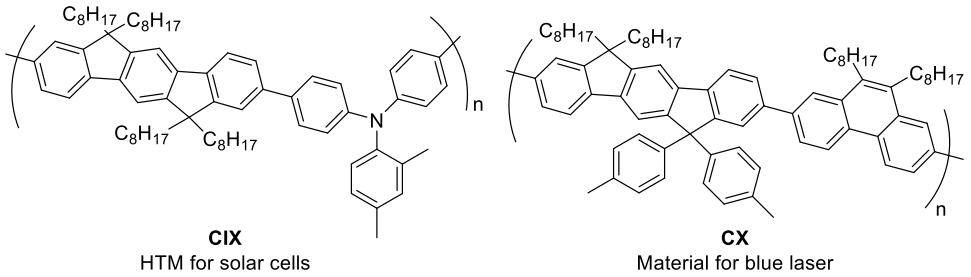


Figure IX. Selected applications of dihydroindeno[1,2-*b*]fluorene

When appropriately functionalized, indeno[1,2-*b*]fluorene-based ladder-type building blocks demonstrated their applicability in high performance and ambient-stable *n*-channel (electron-transporting) semiconductors for organic field-effect transistors (OFETs).[88]

Additional application of this compound can be found in blue OLEDs as the emitter material. Indeed, after the pioneered work of Muller in 2001, who developed a single-layer polyindenofluorene-*co*-anthracene device,[89] more studies have been undertaken in this field.[90] It's worthy to mention also the use of indeno[1,2-*b*]fluorene scaffold as photocatalyst; in this context Chen's group reported a poly(indenofluorene) based photocatalyst for water splitting with a high hydrogen evolution rate (HER).[91]

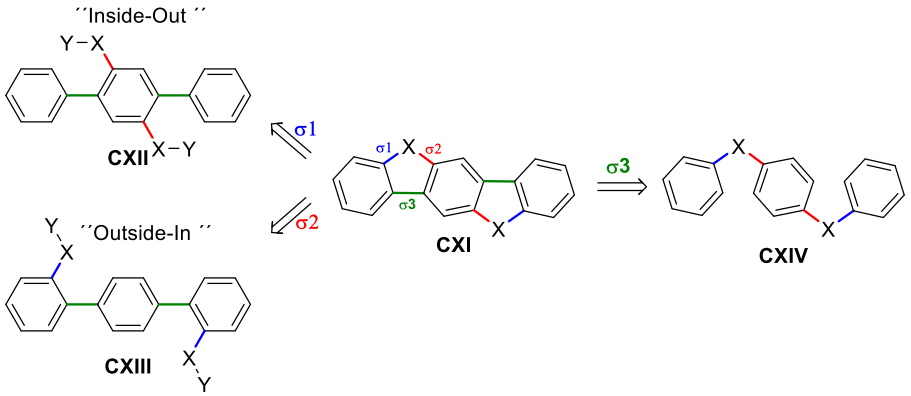
As far as the other four positional isomers are concerned, few reports have been published. The major contribution in this field have been done by Poriel and coworkers, who developed strategies for the synthesis of all the isomers and studied their photophysical properties for possible application in phosphorescent OLEDs.[92]

5,8-Dihydroindeno[2,1-*c*]fluorenes are the least studied class of compounds in the series but they are the most interesting ones because they have a unique structure: their *ortho*-linkage confers a helicoidal turn to the dihydroindenofluorene core. The chemistry of helicene compounds has recently grown and become an important field of research, due to the interesting properties of these compounds such as the strong chiroptical activity, good conductivity, biological activity, catalytic reactivity, self-assembly.[93] For those reasons together with the synthetic challenge, in our group we focused on the synthesis and structure-property relationship study of 5,8-dihydroindeno[2,1-*c*]fluorenes.

In the following section the main synthetic pathways for the synthesis of dihydroindenofluorenes have been covered and also our strategy for construction of the 5,8-dihydroindeno[2,1-*c*]fluorene has been described.

1.3.2 Synthetic strategies of dihydroindenofluorene based compounds

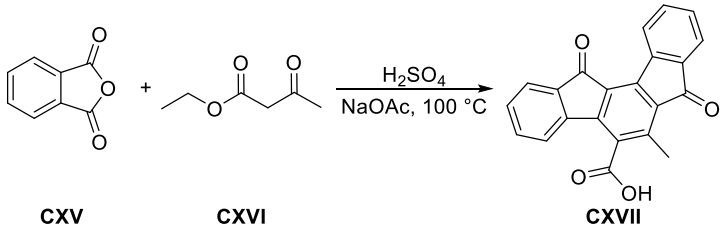
Most syntheses of dihydroindenofluorenes follow the below-mentioned retrosynthetic pathway. The dihydroindeno[1,2-*b*]fluorene, illustrated in Scheme XL, has been used as a model substrate, however the same retrosynthesis can be applied for the other isomers.



Scheme XL. Retrosynthetic pathway for dihydroindenofluorenes

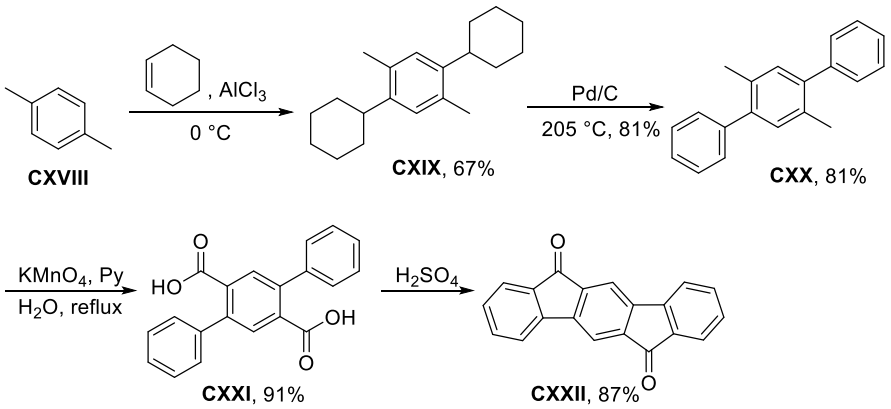
The retrosynthetic approach compromises two main routes: one based on terphenyls **CXII** and **CXIII** as the key intermediate and the second one on the diphenylmethane scaffold, **CXIV**. The general pathway involving terphenyl as the key intermediate can be split in two additional strategies named ''inside-out'' and ''outside-in'' by Haley.[94] The ''inside-out'' method is related to two σ1 single bond breakages and employs terphenyl **CXII** with X-Y substituents attached to the central benzene ring. In the ''outside-in'' route, the substituents X-Y are present on the outer rings of terphenyl **CXIII** and cyclize onto the central benzene after formation of the two σ2 single bonds to afford **CXI**. The third approach is related to disconnection of two σ3 single bonds and indeed to the use of **CXIV** type intermediate.

Probably the first synthesis of a compound with the dihydroindenofluorene scaffold was done in 1884 by Gabriel. He condensed two equivalents of phthalic anhydride **CXV** and ethyl acetoacetonate **CXVI** to afford carboxylic acids **CXVII** (Scheme XLI).[95]



Scheme XLI. First synthesis of dihydroindenofluorene

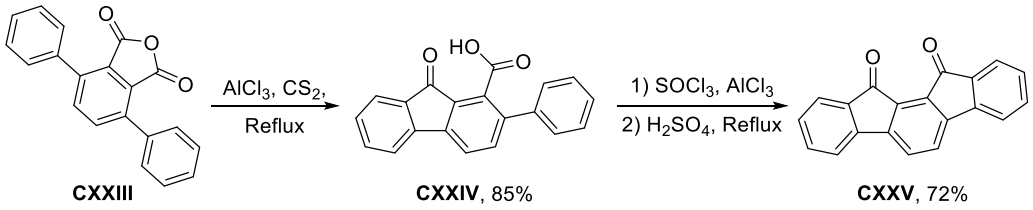
However, at that time it was not possible to confirm its structure due to unavailability of the modern NMR techniques; therefore, the structure **CXVII** cannot be completely verified. Early studies about synthesis of indenofluorene were reviewed in 1951 by Deuschel.[96] These pioneering approaches were based mainly on Fiedel-Craft reactions for the construction of the internal fused rings. As an example, in 1939 Bodroux reported the synthesis of indenofluorenone **CXXII** starting from *p*-xylene **CXVIII** and two equivalents of cyclohexene (Scheme XLII).[97] After Friedel-Craft alkylation, tricyclic compound **CXIX** was formed and converted to terphenyl **CXX** by aromatization with Pd/C. The following oxidation of methyl groups with $KMnO_4$ gave the dicarboxylic acid **CXXI** which was subjected to cyclization with concentrated sulfuric acid to yield indenofluorenone **CXXII** in 87%.



Scheme XLII. Synthesis of [1,2-*b*]indenofluorenone

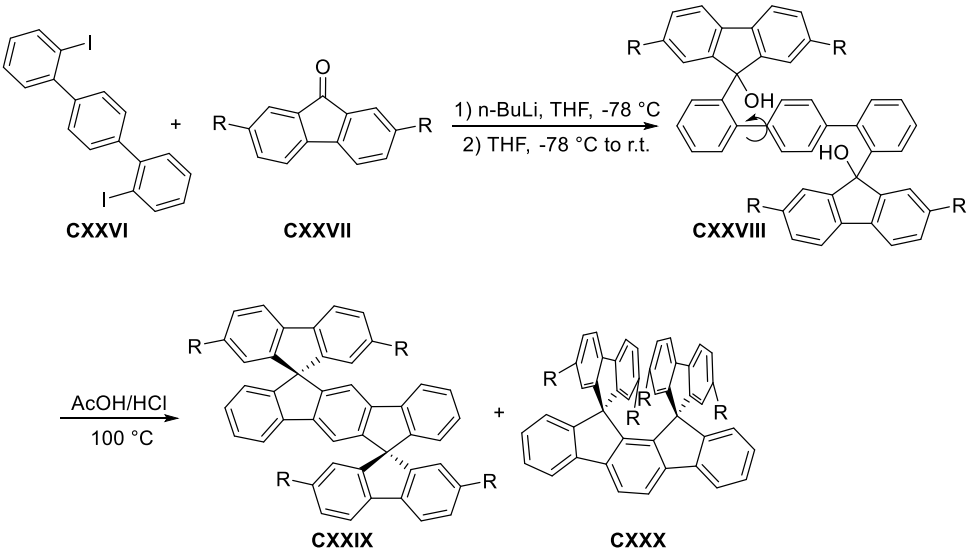
Several synthetic approaches are currently available for preparation of compounds with the dihydroindenofluorene scaffold and all the five isomers have been synthetized. In the next part of this section the main approaches for the construction of all regioisomers will be briefly covered with more focus on preparation of the *ortho*-isomer (5,8-dihydroindeno[2,1-*c*]fluorene).

The 11,12-dihydroindeno[2,1-*a*]fluorene, the *para-syn* isomer, was prepared for the first time as indeno[2,1-*a*]fluorenedione derivative in 1939 by Weizmann.[98] The approach was relied on intramolecular Friedel-Craft acylation of 3,6-diphenylphthalic anhydride in the presence of $AlCl_3$. The cyclization afforded the fluorenone intermediate **CXXIV** which underwent further intramolecular acylation in sulfuric acid to provide the target compound **CXXV**.



Scheme XLIII. Preparation of indeno[2,1-*a*]fluorenone with Weizmann's method

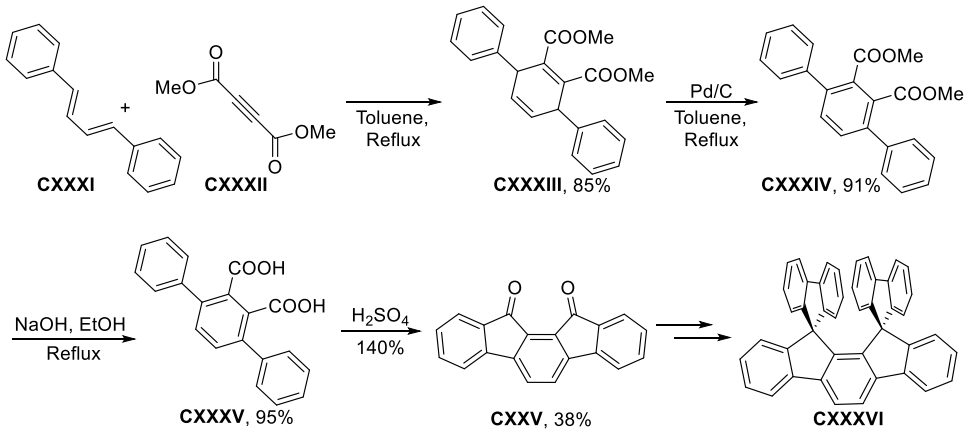
Synthesis of dispirofluorene-indeno[2,1-*a*]fluorene was developed by Poriel *et al.* in 2008 and was based on the non-regioselective pathway (Scheme XLIV). Later, in 2010, the synthesis was improved by using the regioselective route (Scheme XLV). The first synthesis employed 2,2''-diiodo-1,1':4',1''-terphenyl compound **CXXVI** and fluorenone **CXXVII** as the starting materials (Scheme XLIV). [99]



Scheme XLIV. Poriel's synthesis of *para* isomers **CXXIX** and **CXXX**

After treatment of diiodide **CXXVI** with *n*-BuLi, the 2,2''-dilithium-1,1':4',1''-terphenyl was formed and it was added to fluorenone **CXXVII** to generate diol **CXXVIII**. This key-intermediate possesses rotational degree of freedom around the single C–C bonds of the terphenyl core. As a result the following cyclization step can occur in two different directions leading to a mixture of *anti* and *syn* isomers, **CXXIX** and **CXXX** respectively. Interestingly Poriel discovered that the *anti*/*syn* ratio are a function of three parameters: solvent, temperature and substituents. With low polar solvents like CH_2Cl_2, low temperature and small substituents, the isomer *anti* is favored up to 99/1, *anti*/*syn* ratio. On the other hand, by using polar solvent such as CH_3CN, higher temperature and bulky substituents the *syn* isomer prevails, up to 0/100.

Besides this already interesting results, Poriel's group developed also a regioselective synthesis of dispirofluorene-indeno[2,1-*a*]fluorene. [100] The synthesis is based on the use of terphenyl as key intermediate using the ''inside-out'' approach, previously described in Scheme XL.

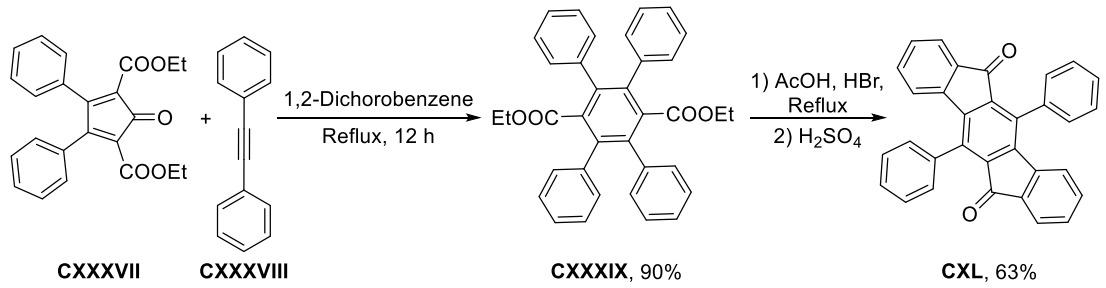


Scheme XLV. Poriel's regioselective synthesis of 11,12-dihydroindeno[2,1-*a*]fluorene

In order to build the terphenyl unit, Diels-Alder reaction between (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene (**CXXXI**) and dimethyl but-2-ynedioate (**CXXXII**) was carried out to obtain cyclohexadiene (**CXXXIII**). It was then converted into terphenyl **CXXXIV** upon oxidation with Pd/C, Scheme XLV. After saponification of the ester moieties to the dicarboxylic acid **CXXXV**, the intramolecular Friedel-Craft acylation afforded indeno[2,1-*a*]fluorenone (**CXXV**) in 38% yield. The dione was then converted into the dispirofluorene analogue **CXXXVI** according to the known two steps procedure.

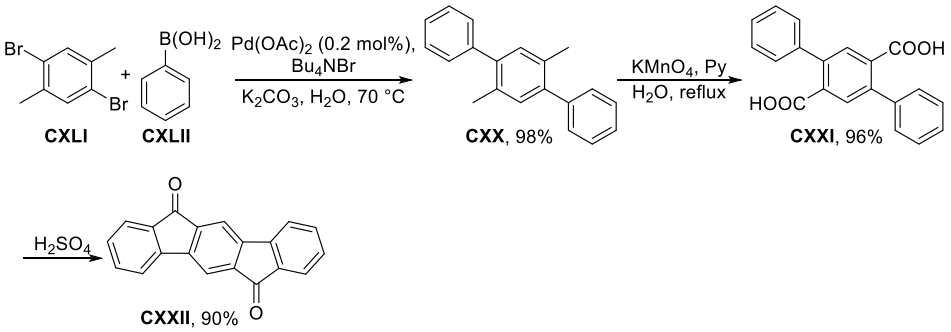
As far as the *para-anti* isomer, 6,12-dihydroindeno[1,2-*b*]fluorene, is concerned, it is the most studied class of indenofluorenes. Hence, a number of synthetic strategies have been developed using terphenyls or diphenylmethane-type compounds as the key synthetic intermediates.

In this context, Wang and coworkers prepared the terphenyl core by Diels-Alder reaction (Scheme XLVI).[101] They performed [4+2] cycloaddition of cyclopentadienone **CXXXVII** and diphenylacetylene, **CXXXVIII**. The reaction occurred with the concomitant aromatization by cheletropic elimination of CO, which led to diester terphenyl **CXXXIX**. Ester hydrolysis under acidic conditions and intramolecular Friedel-Craft acylation generated the target 5,11-diphenylindeno[1,2-*b*]fluorene-6,12-dione **CXL** in up 63% yield for the last two steps.



Scheme XLVI. Wang's synthesis of 5,11-diphenyl-[1,2-*b*]-indenofluorenone **CXL**

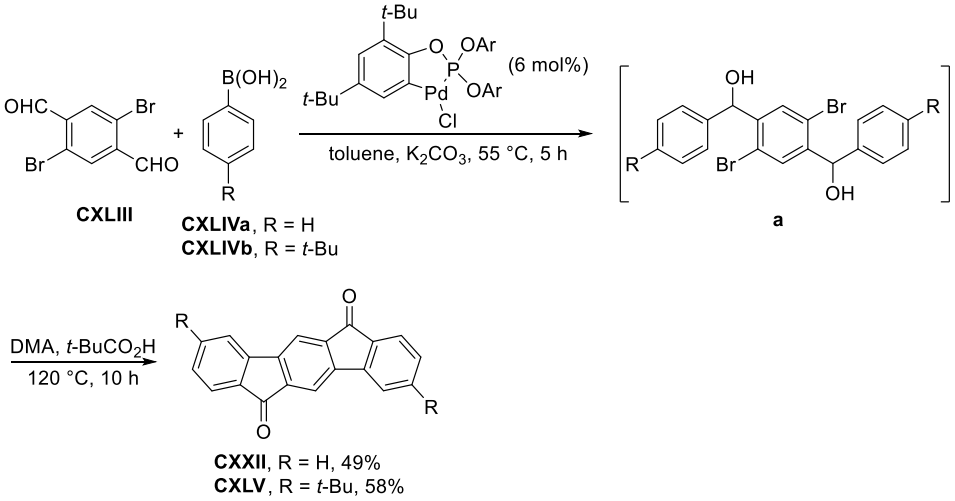
In the same paper, Wang demonstrated that the unsubstituted 6,12-dihydroindeno[1,2-*b*]fluorenone can be prepared via terphenyl intermediate built by Suzuki-Miyaura cross-coupling reaction (Scheme XLVII). 1,4-Dibromo-2,5-dimethylbenzene (**CXLI**) was coupled with phenylboronic acid (**CXLII**) to give terphenyl **CXX** in 98% yield. Afterwards, they followed the same two steps procedure of Bodroux (Scheme XLII) to go from dimethyl substituted terphenyl to *para-anti* indenofluorenone **CXXII**, which was obtained in 88% yield over two steps.



Scheme XLVII. Wang's synthesis of 6,12-dihydroindeno[1,2-*b*]fluorenone, **CXXII**

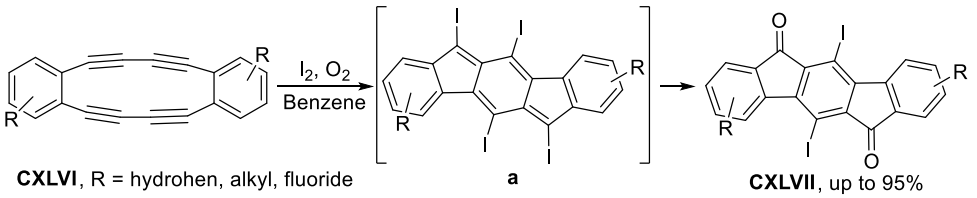
The alternative route based on the diphenylmethane scaffold intermediate (see **CXIV**, Scheme XL), was employed by Hu *et al.* in 2011.[102] During their work about air-stable palladacycle (II) complexes for addition of arylboronic acids to carbonyl compounds, the group discovered a one-pot synthesis of *para-anti* indenofluorenones, starting from 2,5-dibromoterephthaldehyde **CXLIII** and phenylboronic acids (Scheme XLVIII). The reaction afforded 6,12-dihydroindeno[1,2-*b*]fluorenone **CXXII** in 49% yield and **CXLV** in 58%. The transformation did not proceed via Suzuki-Miyaura cross-coupling reaction, but by addition of the arylboronic acids to the dialdehyde giving intermediate **a**. After increasing the temperature

and adding DMA and *t*-$BuCO_2H$, **a** underwent cyclization to indenofluorenols followed by oxidation to indenofluorenones.



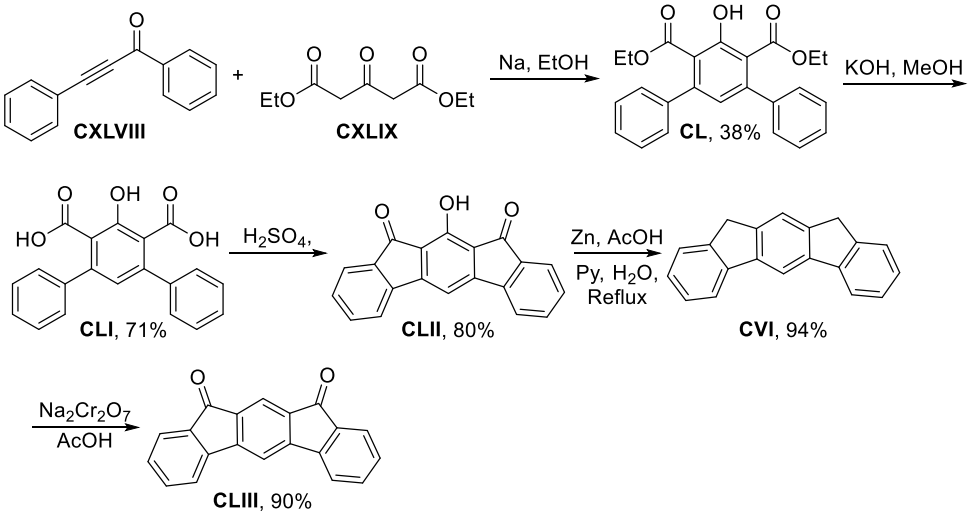
Scheme XLVIII. Hu's synthesis of *para-anti* indenofluorenones

Another worthwhile method for the synthesis of *para-anti* isomer was developed by Swager in 1994[103] and Komatsu in 2007.[104] Both groups reacted dehydro[12]annulene **CXLVI** with iodine to achieve intramolecular cyclization and formation of a 20 π-electron tetraiodide fused ring intermediate, **a** (Scheme XLIX). This intermediate undergoes reaction with oxygen to produce compound **CXLVII** in which two of the vinyl iodides have been converted to ketones.



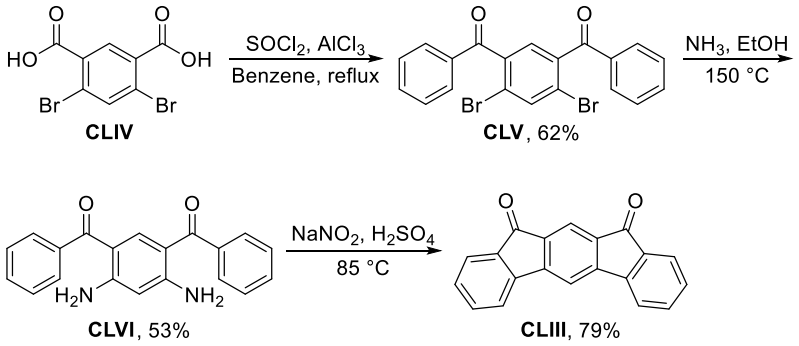
Scheme XLIX. Iodine induced transannular cyclization

Regarding the synthesis of *meta-syn* isomer, namely 10,12-dihydroindeno[2,1-*b*]fluorene **CVI (**Figure VIII), the first synthesis dates 1951, when Deuschel reported condensation of 1,3-diphenylprop-2-yn-1-one **CXLVIII** and ketodiester **CXLIX** to yield *m*-terphenyl intermediate **CL** (Scheme L).[105] Upon saponification of ester moieties and intramolecular Friedel-Craft acylation, 11-hydroxy[2,1-*b*]indenofluorenone **CLII** was obtained in 80% yield. Reduction with Zn provided the target molecule **CVI** which was further oxidized to dione **CLIII** using sodium dichromate.



Scheme L. Deuschel's synthesis of 10,12-dihydroindeno[2,1-*b*]fluorene **CVI**

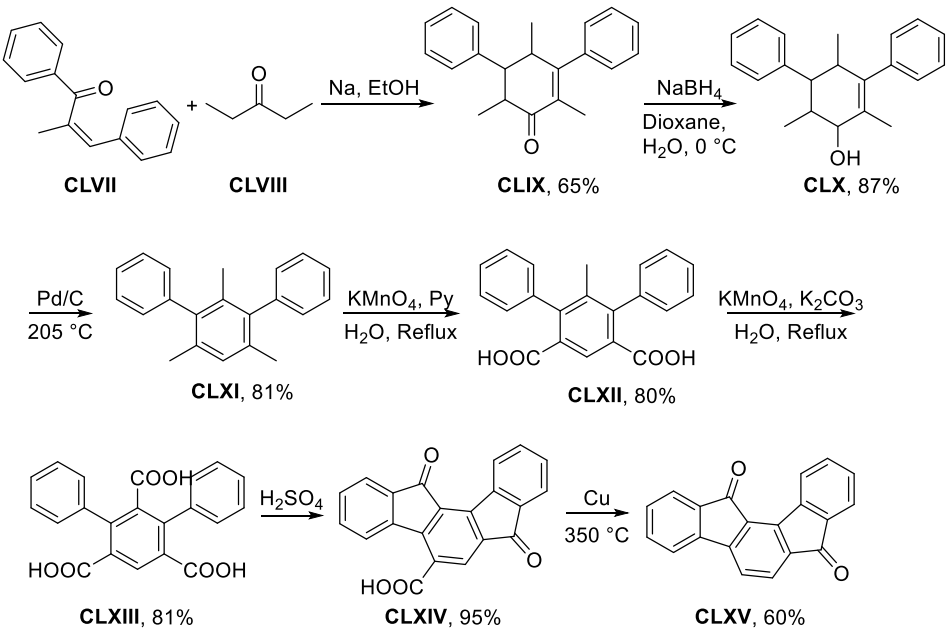
In 1955 a different approach for the synthesis of *meta-syn* isomer was developed by Chardonnens, who proposed conversion of 4,6-dibromoisophthalic acid **CLIV** to the acid chloride with subsequent Friedel-Craft acylation of benzene to afford **CLV** in 62% yield (Scheme LI).[106] Amination with NH_3 and cyclization through Sandmeyer reaction yielded the desired indeno[2,1-*b*]fluorene-10,12-dione **CLIII**.



Scheme LI. Chardonnens' synthesis of indeno[2,1-*b*]fluorene-10,12-dione, **CLIII**.

The synthesis of *meta-anti* isomer (7,12-dihydroindeno[1,2-*a*]fluorene, **CVII**, Figure VIII) was developed from terphenyldicarboxylic acids precursors; however, a mixture of [1,2-*a*] and [2,1-*b*] was generally obtained during the Friedel-Craft cyclization. One example, in which the *meta-anti* isomer was the exclusive compound obtained, was shown again by Chardonnens' group.[107] They performed condensation reaction between α-methylchalcone **CLVII** and pentan-3-one **CLVIII** in the presence of sodium in ethanol, to afford cyclohexenone

CLIX in 65% yield (Scheme LII). Reduction with $NaBH_4$ gave cyclohexenol **CLX**, which was subjected to aromatization with Pd/C and to two-steps oxidation with $KMnO_4$ in order to obtain the terphenyl triacid **CLXIII**. The usual Friedel-Craft cyclization in acidic media led to the *meta-anti* indenofluorene core **CLXIV** and the subsequent decarboxylation with Cu at high temperature afforded the target molecule **CLXV** in 60% yield.



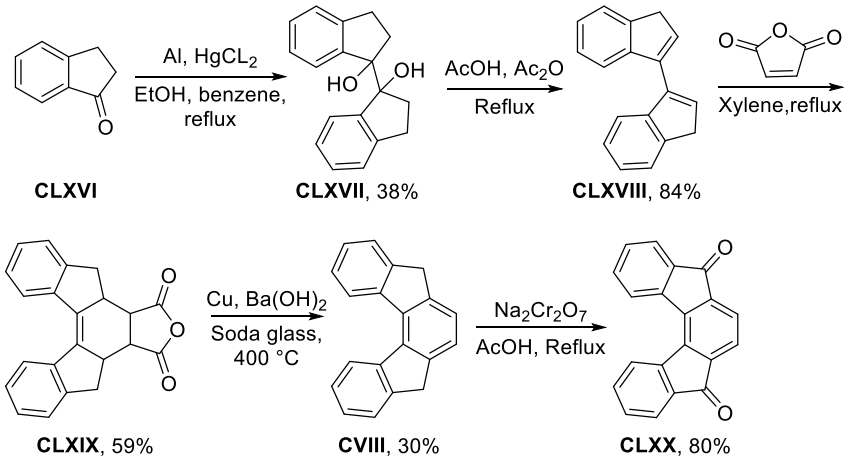
CLVII **CLVIII** **CLIX**, 65% **CLX**, 87%

CLXI, 81% **CLXII**, 80%

CLXIII, 81% **CLXIV**, 95% **CLXV**, 60%

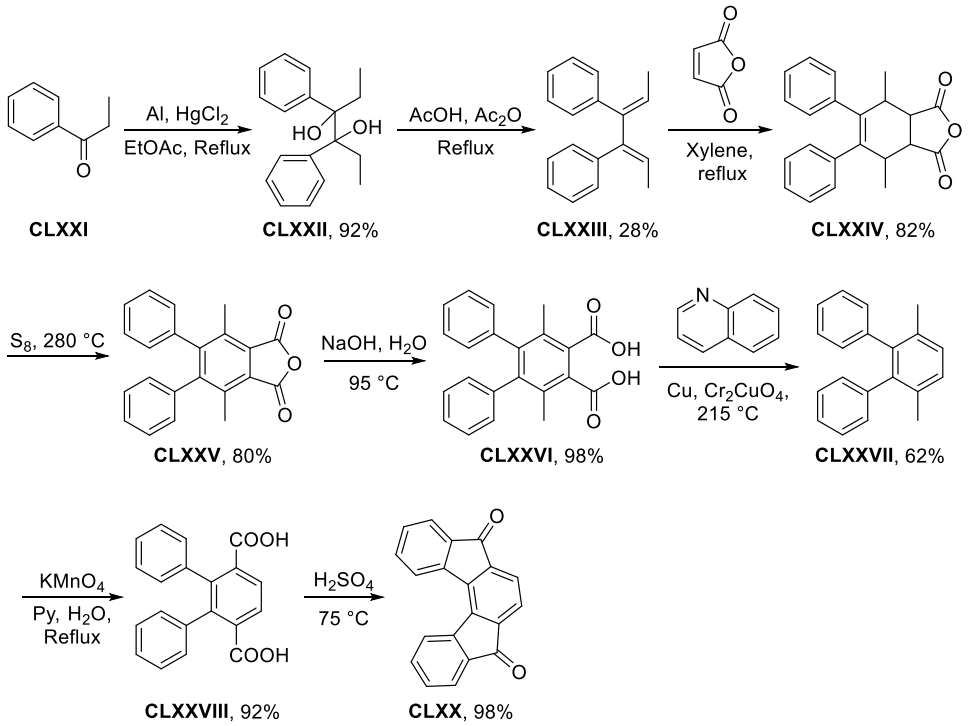
Scheme LII. Synthesis of indeno[1,2-*a*]fluorene-7,12-dione via tricarboxylic acid precursor

Dihydroindeno[2,1-*c*]fluorene is the unique isomer possessing the helicene-like structure, however is the least studied one, due to difficult synthetic approaches. The first account of this isomer dates to 1961 when Ginsburg and Altman elaborated a strategy for its synthesis (Scheme LIII).[108] They reacted indanone **CLXVI** with Al amalgam to produce the 1,1'-bi-indanyl-1,l'-diol (**CLXVII**) in 38% yield. After two-fold dehydration of the diol in a mixture of acetic acid and acetic anhydride, the resulting 3*H*,3'*H*-1,1'-biindene (**CLXVIII**) was subjected to [4+2] cycloaddition with maleic anhydride to afford anhydride **CLXIX**. Decarboxylation in the presence of Cu, gave dihydroindeno[2,1-*c*]fluorenes **CVIII** in 30% yield. The target compound was also oxidized to the dione derivative **CLXX** with sodium dichromate.



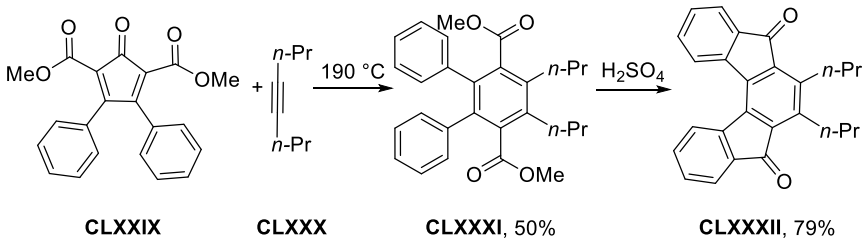
Scheme LIII. First synthesis of dihydroindeno[2,1-*c*]fluorenes, **CVIII**

Five years later in 1966, Chardonnens' group developed an alternative pathway based on a terphenyl intermediate.[109] In particular, they started with propiophenone which was reduced with Al amalgam to produce 3,4-diphenylhexane-3,4-diol (**CLXXII**) in 92% yield (Scheme LIV). Afterwards, two-fold dehydration of the diol in a mixture of acetic acid and acetic anhydride afforded ((2*E*,4*E*)-hexa-2,4-diene-3,4-diyl)dibenzene (**CLXXIII**) which underwent Diels-Alder cyclization with maleic anhydride to generate cyclohexene **CLXXIV** in 82% yield. Aromatization of the central ring with sulfur gave the terphenyl intermediate **CLXXV** which was hydrolyzed with NaOH at 95 °C. After decarboxylation, 3',6'-dimethyl-1,1':2',1''-terphenyl **CLXXVII** was formed in 62% yield and oxidized with potassium permanganate yielding diacid **CLXXVIII** in 92%. In the last step Friedel-Craft cyclization with concentrated sulfuric acid gave the target compound **CLXX**.



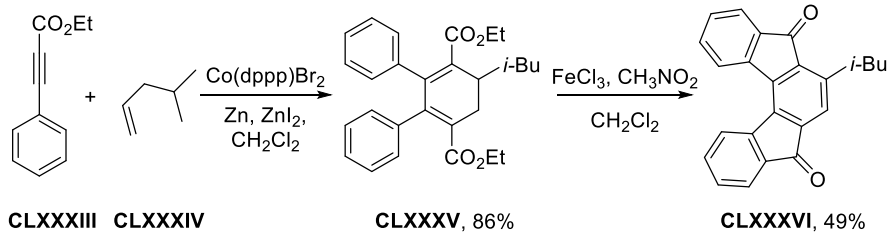
Scheme LIV. Chardonnens' synthesis of indeno[2,1-*c*]fluorene-5,8-dione

Wang's group synthetized indeno[2,1-*c*]fluorene-5,8-dione with substitution at 6- and 7- positions.[110] They used cyclopentadienone **CLXXIX** in a Diels-Alder reaction with 4-octyne to form the terphenyl diester intermediate **CLXXXI** (Scheme LV). Cyclization with concentrated sulfuric acid gave 6,7-disubstituted indeno[2,1-*c*]fluorene-5,8-dione in 79% yield.



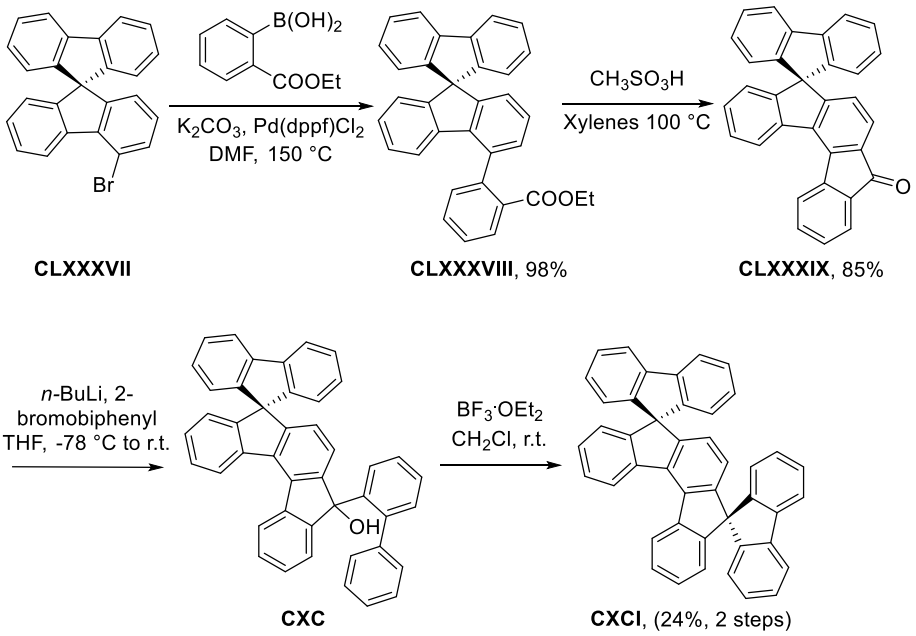
Scheme LV. Synthesis of 6,7-disubstituted indeno[2,1-*c*]fluorene-5,8-dione

Hilt and co-workers showed one example of monosubstituted indeno[2,1-*c*]fluorene-5,8-dione by [2+2+2] cyclotrimerization of 2 equivalents of ethyl 3-phenylpropiolate **CLXXXIII** and 4-methylpent-1-ene **CLXXXIV** to afford 1,3-cyclohexadiene derivative **CLXXXV** in 86% yield (Scheme LVI).[111] In the presence of an excess of $FeCl_3$, the oxidation of the dihydroaromatic ring took place alongside the two Friedel-Crafts-type cyclizations of the ester moieties to yield compound **CLXXXVI** in an acceptable yield of 49%.



Scheme LVI. Synthesis of 6-isobutylindeno[2,1-*c*]fluorene-5,8-dione

In 2015 Poriel's group developed a synthesis of dispirofluorene-indeno[2,1-*c*]fluorene starting from bromo substituted spirobifluorene **CLXXXVII** and a Suzuki-Miyaura reaction afforded **CLXXXVIII** in 98% yield (Scheme LVII).[112] Intramolecular cyclization gave a compound with the dihydroindeno[2,1-*c*]fluorene scaffold **CLXXXIX** in 85% yield. Finally, dispirofluorene **CXCI** was obtained by attaching the biphenyl unit to the fluorenone skeleton followed by cyclization in acidic media.

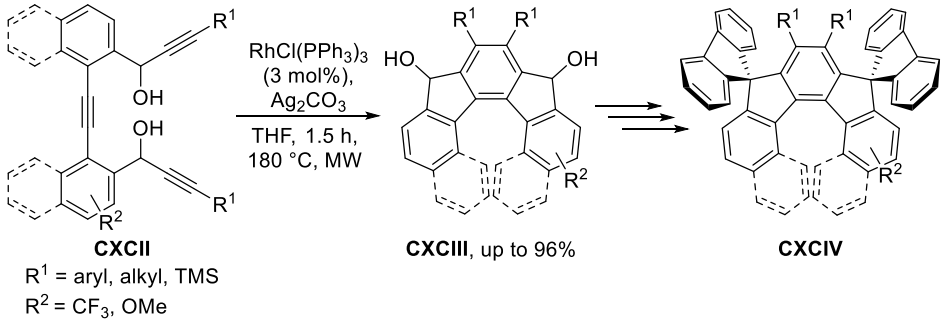


Scheme LVII. Poriel's synthesis of dispiro[fluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene]

The methods for the synthesis of the indeno[2,1-*c*]fluorene scaffold mentioned so far, suffer from harsh reaction conditions (e.g. high temperature and acidic environment), numerous synthetic steps and very low substrate scope (only substitution in position 6 and 7 was reported).

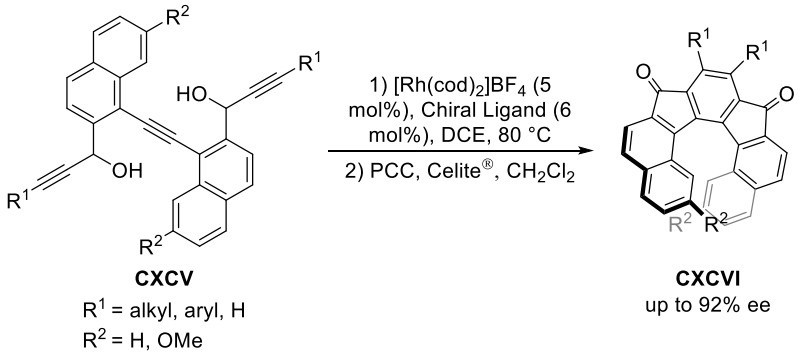
Therefore, in our group we envisaged that [2+2+2] cyclotrimerization could be a straightforward method for the construction of substituted indeno[2,1-*c*]fluorene and to overcome the above-cited limitations.

In this context, in 2019 Kotora's group developed [Rh]-catalyzed [2+2+2] cyclotrimerization of triynediols **CXCII** to afford indeno[2,1-*c*]fluorene-5,8-diols **CXCIII** in up 96% yield (Scheme LVIII).[113] The strategy allowed to obtain both [5] and [7]helical indenofluorenes, which were also converted into their dispirofluorene analogues **CXCIV**.



Scheme LVIII. Kotora's synthesis of [5] and [7]helical indenofluorenes

As extension of the method, in 2021 our group developed also the enantioselective version of the previous synthesis.[114] Indeed, [Rh]-catalyzed enantioselective cyclotrimerization of triynediols **CXCV** followed by oxidation of diols with PCC gave corresponding [7]helical indenofluorenone **CXCVI** in up 92% ee (Scheme LIX).



Scheme LIX. Kotora's synthesis of enantioenriched [7]helical indenofluorenes

2 AIM OF THE WORK

My Ph.D. project focuses on synthesis of fluorene-based compounds using Ru, Rh, Ni and Co catalyzed [2+2+2] cyclotrimerizations.

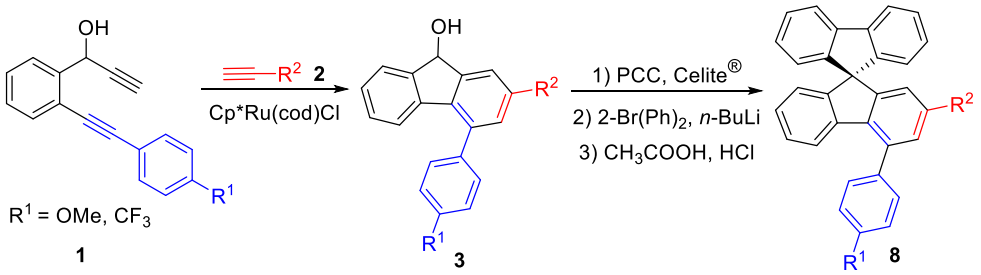
As demonstrated in Section 1.1.1 the fluorene scaffold have been gaining much attention in academia and industry due to the biological activities of fluorene-based natural compounds and drugs, the interesting properties as organic semiconductor with possible applications in organic electronics, and the strong interaction of the fluorenyl anion with metal atoms which has led to development of fluorenyl ligands based complexes. Numerous syntheses of the fluorene core have been reported involving Friedel-Crafts type reactions, radical reactions, dehydro-Diels-Alder cyclizations and transition metal-catalyzed transformations (Section 1.1.2 and 1.1.3). However, most of these methods suffer from harsh reaction conditions and poor versatility.

In this context, [2+2+2] cyclotrimerization represents a powerful tool for developing new and highly substituted fluorene frameworks with possible extension to the enantioselective version.

In this work, I would like to describe my results about the synthesis of three new types of fluorene-based compounds. Moreover, due to importance of spirobifluorene core in increasing stability and solubility of fluorenes (see Section 1.2.1), I decided to convert all the designed fluorenes into corresponding spirobifluorene analogues.

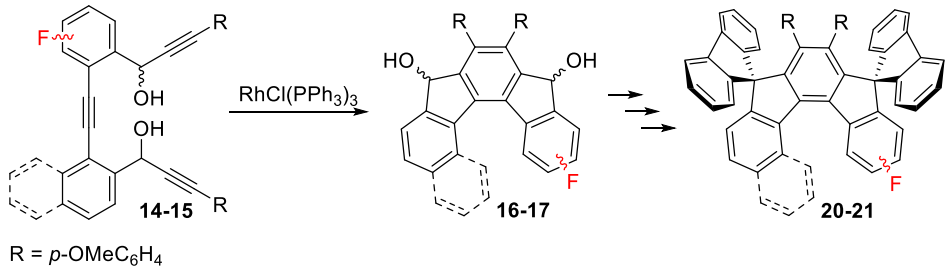
In particular, during my Ph.D. study in Kotora's group I planned:

1) Ru-catalyzed regioselective [2+2+2] cyclotrimerization of unsymmetrically substituted diynols **1** and terminal alkynes **2** for the synthesis of 2,4-disubstituted fluorenols **3** (Scheme 1). The prepared fluorenols **3** should be converted into corresponding spirobifluorenes **8**, whose structure-properties relationship study should be performed (Section 3.1).



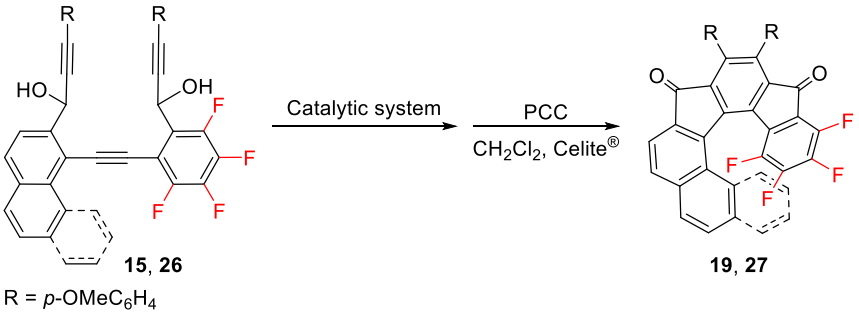
Scheme 1. Regioselective cyclotrimerization for the synthesis of 2,4-disubstituted spirobifluorenes **8**

2) Intramolecular Rh-catalyzed [2+2+2] cyclotrimerization as a suitable method for the synthesis of a new class of fluoro substituted [5] and [6]helical dispiroindeno[2,1-*c*]fluorenes. After preparation of various fluoro-substituted triynols **14-15**, the $RhCl(PPh_3)_3$ catalyzed cyclotrimerization should afford the desired fluoro 5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol **16** and 5,8-dihydrobenzo[*c*]indeno[1,2-*g*]fluorene-5,8-diol **17** (Scheme 2). Fluorinated indenofluorenols should be converted into the corresponding fluorinated dispiroindeno[2,1-*c*]fluorenes **20** and dispirobenzo[*c*]indeno[1,2-*g*]fluorene **21**, whose structural and photophysical properties should be also studied in order to determine the impact of the fluorine substitutions on the indenofluorene core (Section 3.2).



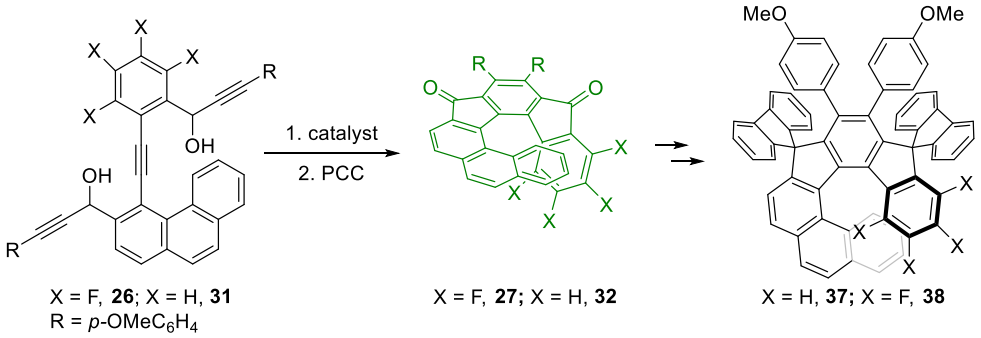
Scheme 2. Intramolecular Rh-catalyzed [2+2+2] cyclotrimerization for the synthesis of fluorinated [5] and [6]helical dispiroindeno[2,1-*c*]fluorenes

3) Enantioselective cyclotrimerization for the synthesis of enantiomerically enriched unsymmetrical [6] and [7]helical indeno[2,1-*c*]fluorendione **19** and **27** (Scheme 3). For this purpose, Ni- and Rh- catalysts in combination with several chiral ligands should be screened in [2+2+2] cycloaddition of triynediols **15** and **26** followed by direct oxidation with PCC of the crude reaction mixture (Section 3.3).



Scheme 3. Enantioselective cyclotrimerization for the synthesis of [6] and [7]helical indeno[2,1-*c*]fluorene dione

4) Study of the racemic transition metal catalyzed [2+2+2] cyclotrimerization of fluorinated and non-fluorinated triynediols **26** and **31** which possess a phenanthrene moiety (Scheme 4). In this context, various transition metal catalysts should be screened, such as Co, Rh, Ru, Pd and Ni, in order to selectively formed the desired [7]helical benzoindaceno[2,1-*c*]phenanthrenediones, **27** and **32**. Also in this case, the dispirofluorene analogues should be prepared and their photophysical and structural properties evaluated (Section 3.4).

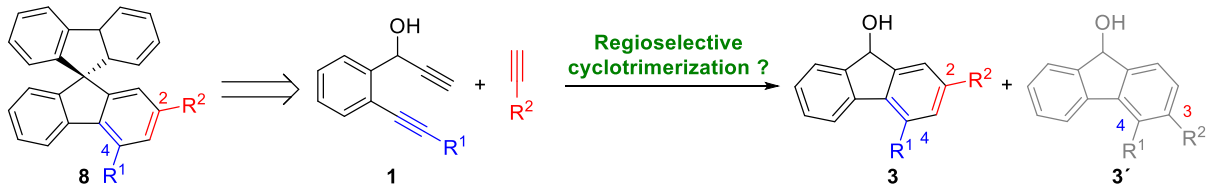


Scheme 4. [2+2+2] cyclotrimerization for the synthesis of unsymmetrical [7]helical dispiroindeno[2,1-*c*]fluorenes

3 RESULTS AND DISCUSSION

3.1 Synthesis of 2,4-disubstituted-9,9'-spirobifluorenes

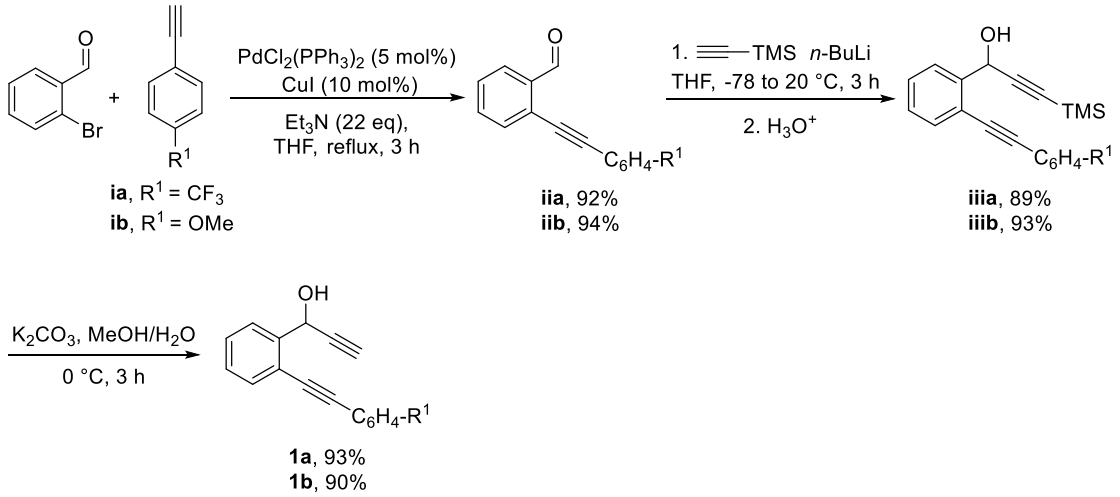
The first part of my Ph.D. project was focused on the synthesis of a new class of 9,9'-spirobifluorenes (SBFs) with 2 substituents concurrently present in position 2 and 4 of the fluorene scaffold (structure **8**, Scheme 5). As summarized in section 1.2.2, the prevailing method for synthesis of variously substituted spirocompounds employs common cross-coupling reactions on halogenated SBFs scaffold or on halogenofluorenones.[59] Despite the simplicity, this approach restricts the position, number and variety of substituents. Therefore, syntheses of more advanced SBFs were highly necessary due to paramount importance of spiro compounds as organic semiconductors. With this intention, in our group a new synthetic approach towards the synthesis of SBFs was developed involving partially intermolecular [2+2+2] cyclotrimerization as the key step. This approach provided the synthesis of variously 1,2,3,4-substituted SBFs.[52, 53] As a further step we wanted to selectively synthesize the 2,4-disubstituted-9,9'-spirobifluorenes in order to: i) develop a regioselective [2+2+2] cyclotrimerization for the synthesis of 2,4-substituted fluorenes **3** to the detriment of the 3,4 isomer **3'**; ii) explore the structural and photophysical properties of the new class of SBFs. Therefore in this Section 3.1 , the development of regioselective cyclotrimerization of diynols **1** and terminal alkynes will be discussed (Sections 3.1.1 and 3.1.2) as well as the conversion of the obtained fluorenols in spirobifluorenes (Section 3.1.3) and their structure-property relationship study (Sections 3.1.4 and 3.1.5). The major findings of this study were published as my first author paper in Kotora's group.[115]



Scheme 5. Regioselective [2+2+2] cyclotrimerization as key step for the synthesis of 2,4-SBFs

3.1.1 Preparation of starting material: unsymmetrically substituted diynols

Starting materials for cyclotrimerization reactions were prepared in three synthetic steps (Scheme 6). Firstly, Sonogashira cross coupling reaction between 2-bromobenzaldehyde and 1-ethynyl-4-(trifluoromethyl)benzene, **ia**, or 1-ethynyl-4-methoxybenzene, **ib**, afforded 2-((4-(trifluoromethyl)phenyl)ethynyl)benzaldehyde **iia** and the methoxyphenyl analogue **iib** in 92 and 94% yield respectively. Secondly, alkynylation of **ii** with trimethylsilylacetylene furnished protected diynes **iiia** and **iiib** in 89 and 93% yield. Lastly, deprotection of the trimethylsilyl group with potassium carbonate generated diynols **1a** and **1b** in 93 and 90% yield respectively. The calculated overall yield is 76% for **1a** and 79% for **1b**.



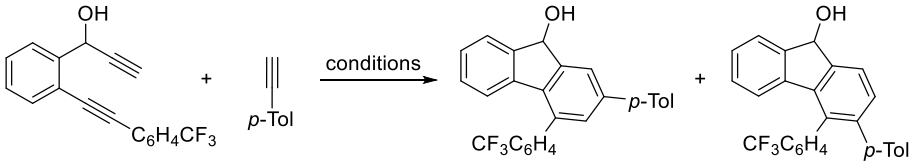
Scheme 6. Synthesis of diynols **1a** and **1b**

3.1.2 [2+2+2] Cyclotrimerization of unsymmetrical diynols and terminal alkynes

In order to prove the feasibility of regioselective cyclotrimerization for the synthesis of 2,4-disubstituted fluorenols, **1a** and *p*-tolylacetylene **2h** were used as model substrates. The results listed in Table 1 were performed in our laboratory by a visiting student (Florian Schnurrer) from Friedrich-Schiller-Universität. As it is evident from Entry 1, catalysis by Wilkinson's catalyst produced a mixture of regioisomers **3h** and **3h'** in 1:2 ratio in 62% combined isolated yield. The sterically more hindered product **3h'**– 3,4-disubstituted fluorenol (*ortho* type isomer) – was formed preferentially. The use of $[Rh(cod)_2]BF_4$ and dppp (Entry 2) afforded a mixture of both regioisomers in a lower combined yield (40%). The catalysis of the reaction by $Cp^*Ru(cod)Cl$ also provided a mixture of **3h** and **3h'** in a moderate yield of 46%

(Entry 3). Gratifyingly, the desired 2,4-disubstituted fluorenol **3h** was formed in high molar ratio of 10:1 with respect to **3h'**.

Table 1. Catalytic cyclotrimerization of **1a** with **2h** with different catalytic systems



1a **2h** **3h** **3h´**

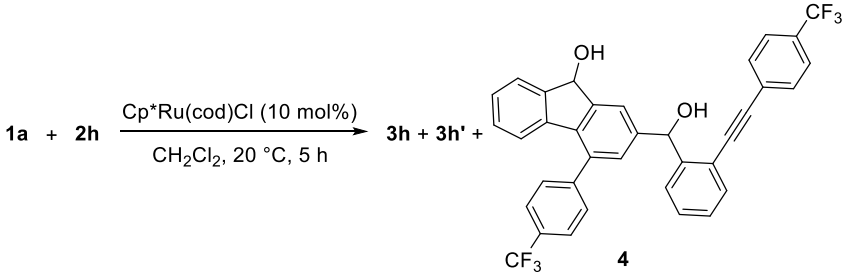
Entry	Catalytic System	Conditions	**3h**/**3h'** [a]	Yield (%) [b]
1	$[RhCl(PPh_3)_3]$ (3 mol%), Ag_2CO_3 (6 mol%)	MW, THF,180 °C, 1 h	1:2	62
2	$[Rh(cod)_2]BF_4$ (10 mol%), dppp	THF, 60 °C, 16 h	1:1.25	40
3	Cp*Ru(cod)Cl (10 mol%)	CH_2Cl_2, 20 °C, 5 h	10:1	46

[a] Determined by ^1H NMR of the crude mixture. [b] Combined isolated yields.

Those results are in agreement with similar literature publications, which showed as Rh-catalysts favors formation of 1,2-isomers (*ortho*-isomer) instead of 1,3-isomers (*meta*-isomers)[116] whereas Ru-catalysts are known to be more regioselective for the *meta* ones.[117, 118]

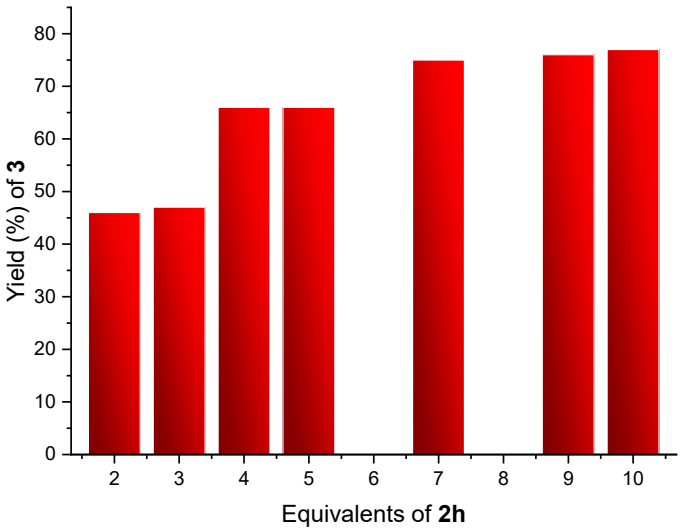
With the right catalytic system in hand, I repeated cyclotrimerization between **1a** and alkyne **2h**. The yield of this reaction was very similar to the previous result showing reproducibility of the method, however during the experiment it was possible to isolate and fully characterized the undesired product **4** (40% yield), which is the result of homo-cyclotrimerization of **1a**. Therefore, it was clear that the formation of the desired product **3** is hampered by this unwanted homo-cyclotrimerization involving two molecules of **1a**. In order to increase the yield of **3** various equivalents of alkyne **2h** were screened (Table 2).

Table 2. Catalytic cyclotrimerization of **1a** with various amounts of **2h**



Entry	**2h** (eq)	**3h/3h'**, Yield(%) [a]	**4**, Yield(%) [a]
1	2	46	40
2	3	47	40
3	4	66	19
4	5	66	18
5	7	75	14
6	9	76	14
7	10	77	15 [b]

[a] Isolated yields. [b] Determined by ^{1}H NMR using 1,2,3,4-tetramethylbenzene as internal standard.



Scheme 7. Yield of **3h/3h'** versus equivalents of **2h**

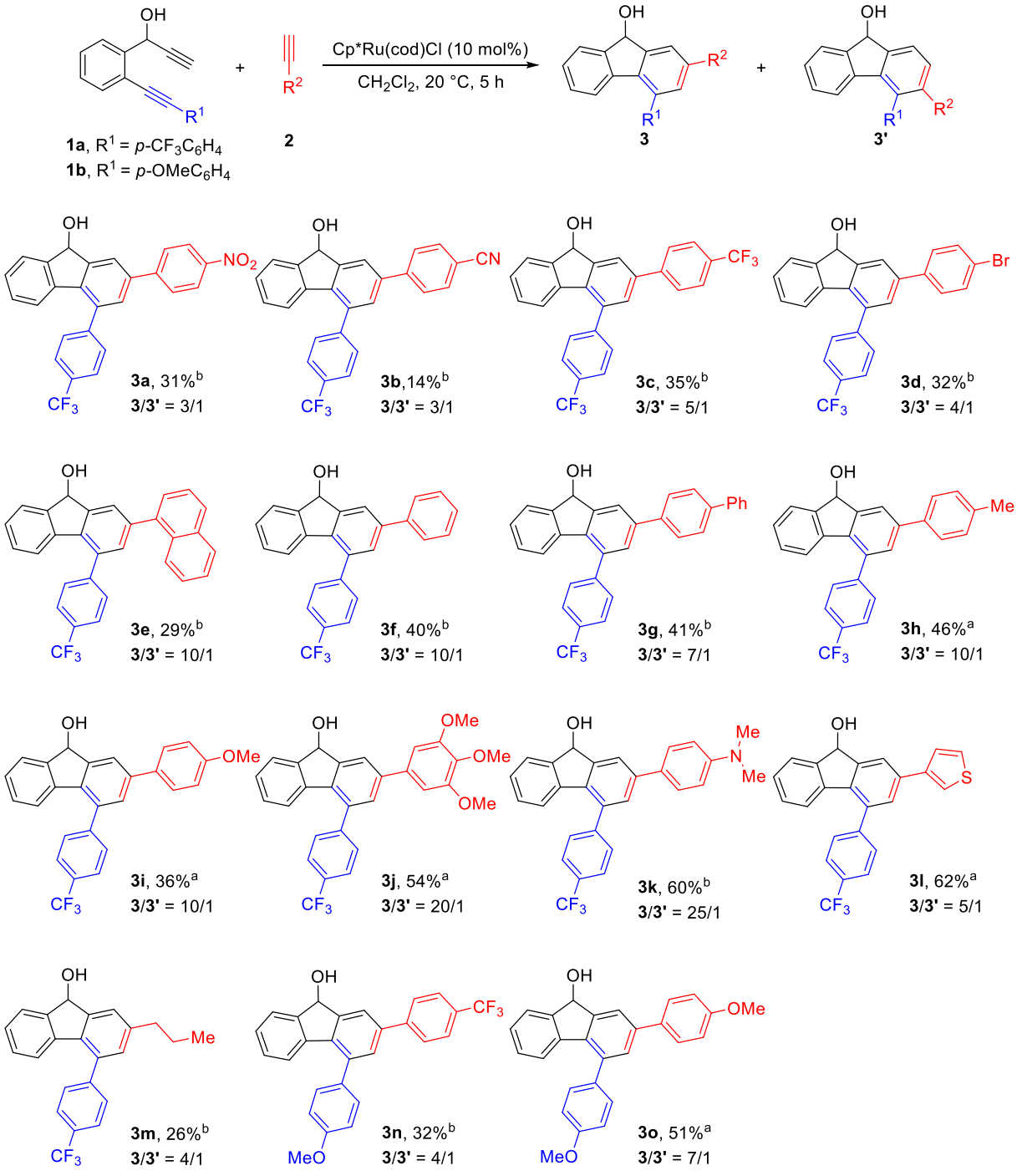
It is evident (see also Scheme 7) that changing the amount of alkyne **2h** from 2 to 3 equivalents does not affect the yield of fluorenol **3**, whereas doubling the amount (from 2 to 4 eq.) raises the yield by 20% and a further doubling (from 4 to 7-9 eq) leads to 10% growth. The yield of homo-cyclotrimerized compound **4** follows the reverse trend, going from 40% to 14%. Therefore, an excess of seven-fold or higher of alkyne **2** is required for a high level yield of fluorenol **3**.

Consequently, I proceeded to assess the scope of cyclotrimerization of **1a** and **1b** with various terminal alkynes **2**. All the reactions were carried out with $Cp^*Ru(cod)Cl$ (10 mol%) in dichloromethane at 20 °C for 5 h. The amount of alkyne used was kept to 2 eq. for a better evaluation of functional group effect on yield and for avoiding wastefulness of alkynes.

Thirteen cyclotrimerizations were performed with diynol **1a** bearing *p*-(trifluoromethyl)phenyl group and two with **1b** bearing *p*-methoxyphenyl. As it is shown in Scheme 8, the best yields were obtained with arylethynes possessing strongly electron-donating groups: 3,4,5-trimethoxyphenylethyne (**3j**, 54% yield), 4-(*N,N'*-dimethylamino)phenylethyne (**3k**, 60% yield) or 3-thienylethyne (**3l**, 62% yield). On the other hand, arylalkynes bearing electron-withdrawing groups (**3a**-**3d**, **3n**) gave modest yields in the range 14-35%. In a similar manner, the reaction with 1-pentyne (**3m**) proceeded with a low yield (26%). Moderate yields were obtained also for phenylethyne (**3f**) and biphenylethyne (**3g**) that were isolated in 40% and 41% yields, respectively. Regarding the regioselectivity of reaction, 2,4-disubstituted fluorenols were always formed as major compounds: the highest '*meta*/*ortho*' ratios (10:1-25:1) were reached by phenylethynes bearing electro-donating group (**3h**-**3k**), lower ratios (3:1-5:1) were found for electro-withdrawing groups (**3a**-**3d**).

In the majority of cases the isolation of '*meta*' regioisomer was successfully achieved by column chromatography technique (**3a**-**3g**, **3k**, **3m**, **3n**); only in five cases the regioisomeric mixtures were inseparable (**3h**-**3j**, **3l** and **3o**), therefore for these five fluorenols, the yields were reported as combined yield of *meta* and *ortho* isomers.

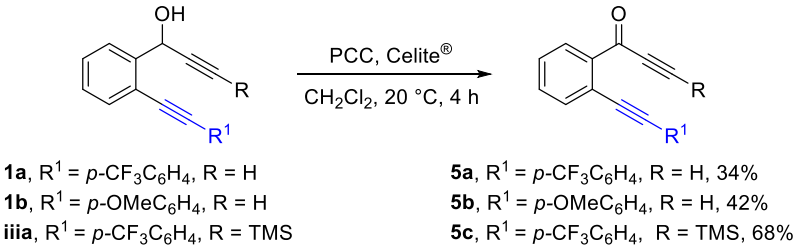
^{1}H NMR analysis allowed distinguishing unquestionably between the two regioisomers. 2,4-Disubstituted fluorenols were identified by the characteristic doublets in the range of 7.89-8.01 ppm with J_{meta}= 1.6 Hz, while the 3,4-disubstituted ones showed peculiar doublets in the range of 6.22-6.45 ppm with J_{ortho}= 7.6 Hz. The *ortho*-isomer was isolated and fully characterized in the case of **3n'**.



[a] Isolated yields of mixture of both regioisomers (**3** and **3'**).
[b] Isolated yields of the only *meta* regioisomer (**3**).

Scheme 8. Scope of cyclotrimerization of **1** with **2**

Moreover, in order to test the effect of the carbonyl group in benzylic position on the course of the reaction and compare the results with those obtained for the diynols **1**, diynones **5a-c** were synthetized by oxidation of diynols **1a-b** and **iiia** with PCC (Scheme 9). The oxidation afforded the desired products **5** in yields within the 34-68% range.

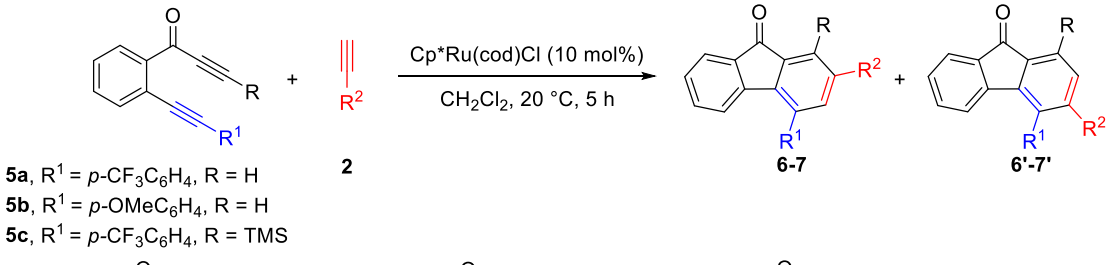


1a, R^1 = *p*-$CF_3C_6H_4$, R = H
1b, R^1 = *p*-$OMeC_6H_4$, R = H
iiia, R^1 = *p*-$CF_3C_6H_4$, R = TMS

5a, R^1 = *p*-$CF_3C_6H_4$, R = H, 34%
5b, R^1 = *p*-$OMeC_6H_4$, R = H, 42%
5c, R^1 = *p*-$CF_3C_6H_4$, R = TMS, 68%

Scheme 9. PCC oxidation of diynols **1a-1b** and **iiia**

The subsequent cyclotrimerizations of **5a-c** were performed under the same reaction conditions as those in Scheme 8. The results, illustrated in Scheme 10, show that *meta*-isomer is the major product. In particular, **7h** and **7h'** were obtained with lower regioselectivity when compared with **3h** and **3h'** (3:1 vs. 10:1) albeit in an improved yield (67% vs. 46%). The cyclotrimerization of diynone **5b** gave a similar yield of **7n** and **7n'** respect to that of fluorenols **3n** and **3n'** (40% vs. 32%) and same regioselectivity (4:1). The presence of the trimethylsilyl group in **5c** had a substantial effect on *meta*/*ortho* ratio of **6** and **6'** (1:1) providing an increased amount of *ortho* isomer. However, the yield was considerably lower (only 16%) due to poor reactivity of **5c** which was recovered after reaction in 60% yield. In the case of cyclotrimerization of **5a**, the homocyclotrimerization side-product **4a** (see its structure in Scheme 11) was detected in ^{1}H NMR spectrum of the crude mixture in low amount (1:10, **4a**/**7h** ratio). In order to undoubtedly identify the structure of **4a**, the diol analogue **4**, isolated during cyclotrimerizations of **1a** (Table 2 and Scheme 8), was oxidized with 2 equivalent of PCC, Scheme 11, to afford the corresponding diketone in 86% yield. The ^{1}H and ^{19}F spectra of the obtained diketone were compared with those of **4a** side-product and confirmed its structure.

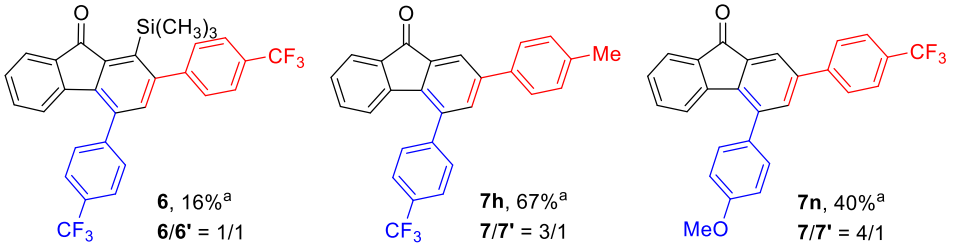


5a, R^1 = *p*-$CF_3C_6H_4$, R = H
5b, R^1 = *p*-$OMeC_6H_4$, R = H
5c, R^1 = *p*-$CF_3C_6H_4$, R = TMS

2

6-7

6'-7'



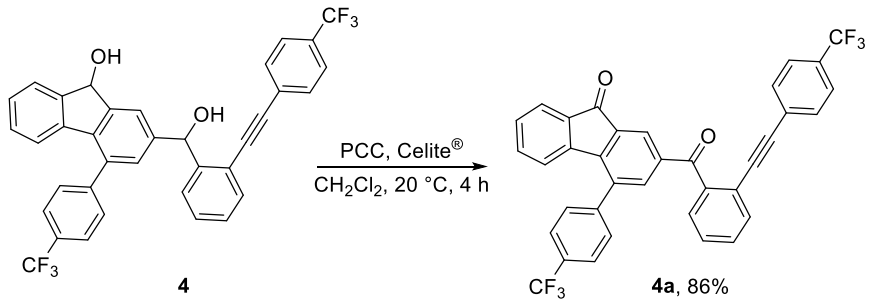
6, 16%[a]
6/6' = 1/1

7h, 67%[a]
7/7' = 3/1

7n, 40%[a]
7/7' = 4/1

[a] Isolated yields of mixture of both regioisomers (**6-6'** and **7-7'**).

Scheme 10. Cyclotrimerization of **5a-5c**

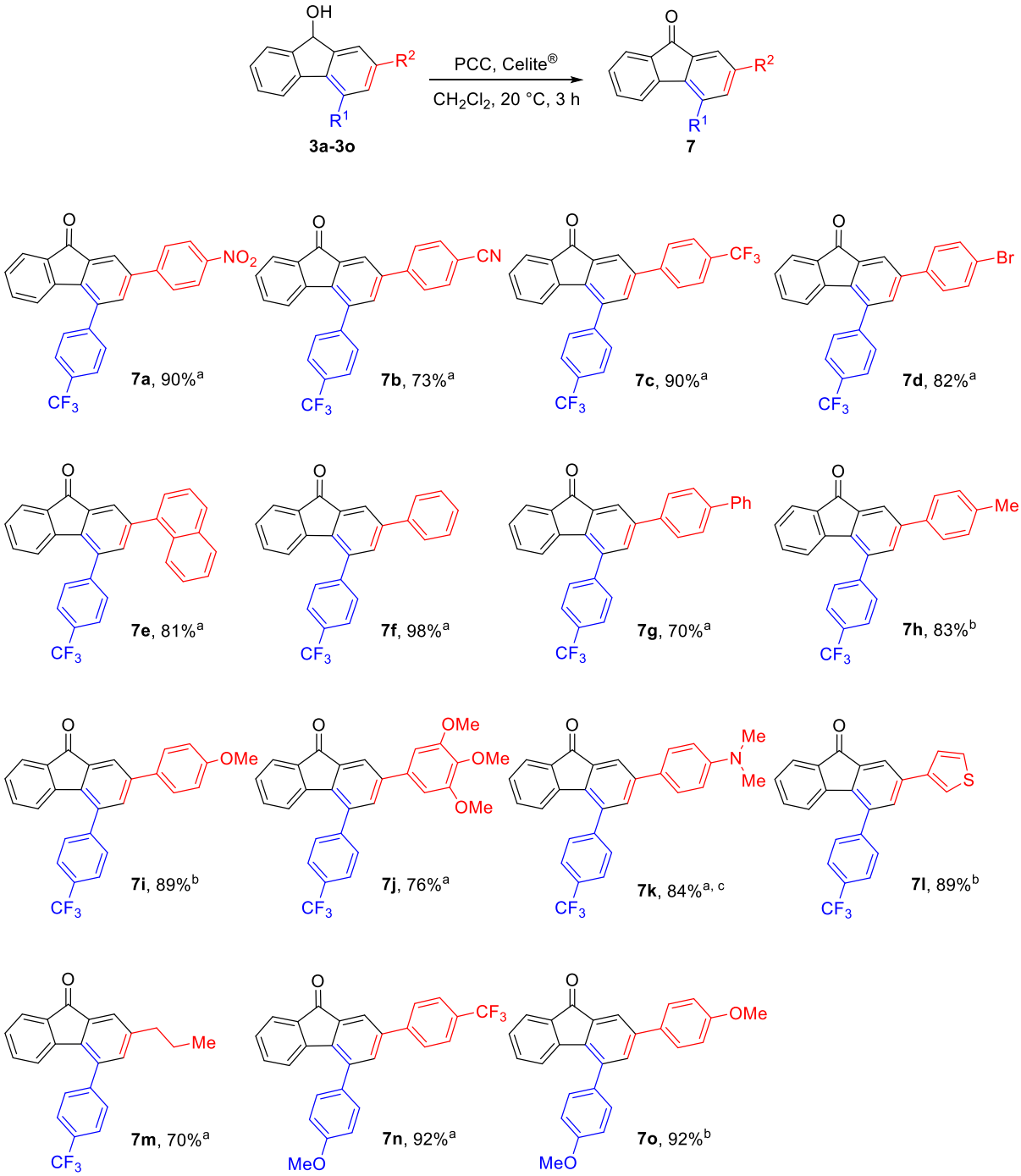


Scheme 11. Oxidation of **4** with PCC

In summary, cyclotrimerizations, if directly performed with diynones **5**, did not proceed with improved regioselectivity for *meta* isomer and an inseparable mixture of both regioisomers was always obtained. For those two reasons cyclotrimerization of diynols **1** proved to be superior.

3.1.3 Synthesis of 9,9'-spirobifluorenes

In order to synthesize the final spirobifluorene compounds, oxidation of fluorenols **3a-3o** was performed with PCC (Scheme 12); high yields were obtained in the range of 70-98%. In the case of **3k**, bearing *N*,*N*'-dimethylaniline moiety in position 2, oxidation with PCC gave a complex reaction mixture, therefore a more selective oxidation was performed using an excess of activated MnO_2 at room temperature for 20 h. As outcome, MnO_2, which is known for selective oxidation of benzylic and allylic alcohol,[119] afforded fluorenone **7k** in 84% yield. All the oxidized compounds were isolated by column chromatography as bright yellow solids. The structure of **7h** was unambiguously confirmed by single crystal X-ray analysis (Figure 1).



[a] Isolated yields of **7.**

[b] Isolated yields of mixture of both regioisomers.

[c] Oxidation performed with MnO_2, CH_2Cl_2, 20 °C, 20 h.

Scheme 12. Oxidation with PCC or MnO_2 of **3a-3o**

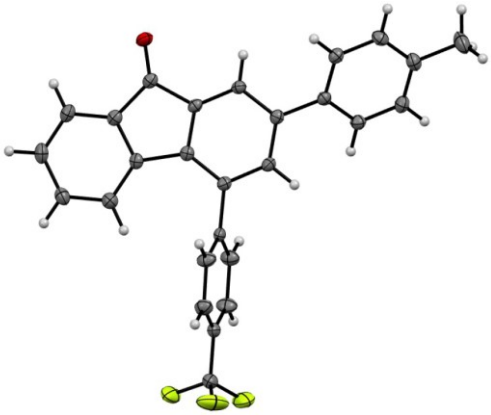
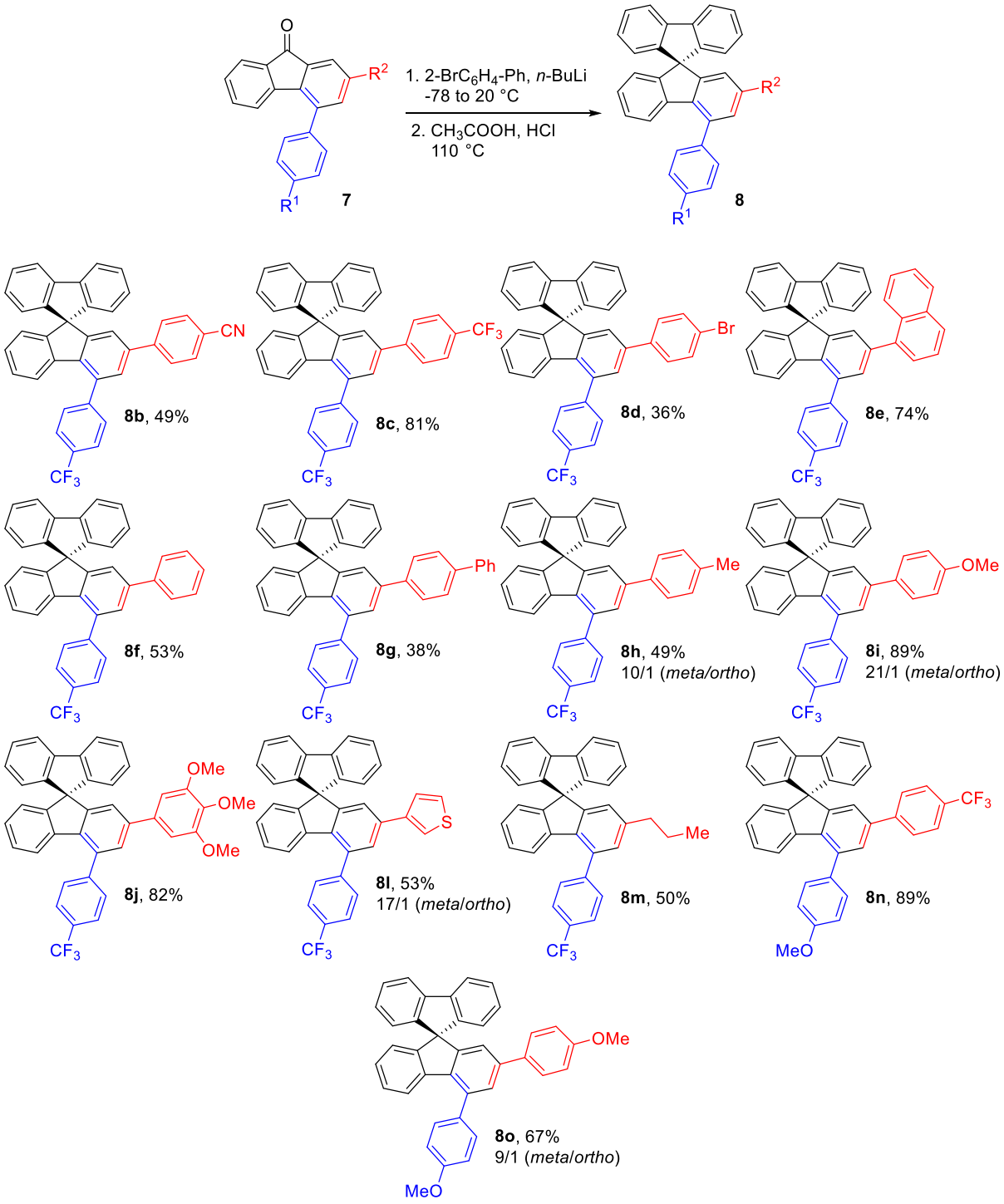


Figure 1. ORTEP drawing of 2-(*p*-tolyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one, **7h**, (grey C, white H, green F, red O)

The desired fluorenones were then converted into the corresponding spirobifluorenes by known two steps procedure[79] involving nucleophilic addition of preformed 2-biphenyllithium to carbonyl group of **7**, followed by Friedel-Crafts ring-closure[80] of the resulting alcohols by treatment with AcOH/HCl under reflux. The corresponding 2,4-disubstituted-9,9'-spirobifluorenes **8b-8o** were obtained in 36-89% overall yields for two steps (Scheme 13). Since the first reaction is rather sensitive to operational conditions, in some cases low yields were obtained (e.g. **8d**, **8g**) and the starting fluorenones were recovered unreacted. The majority of spirobifluorenes were isolated and characterized as pure *meta* regioisomer, because of successful separation of *meta* isomers from the *ortho* ones after the cyclotrimerization step (Scheme 8). Compound **8j** was separated from the *ortho* regioisomer during the oxidation step (Scheme 12). In four cases spirobifluorenes were obtained as mixture of both regioisomers (**8h**, **8i**, **8l**, **8o**), however the ratio *meta*/*ortho* was always very high (9:1-21:1), indeed the amount of *ortho* isomers was negligible.



Yield of the last two steps.

Scheme 13. Formation of spirobifluorenes **8**

The formation of spirobifluorene moiety was not successful for nitrogen-containing fluorenones (**7a**, **7k**). ^{1}H NMR spectra of crude reaction mixtures didn't reveal any presence of the desired spirobifluorenes **8a** and **8k**. A particularly complex mixture was observed in case of **7k**, whereas **7a** gave an undesired product, which was isolated in very low yield (8%). The

structural formula of the above-mentioned side-product was not clearly understood. The mass spectrometric analysis of the unknown compound reported a peak with exact mass of 704.25385 m/z which could indicate a second arylation involving the nitro group. A possible structure is depicted in Figure 2 that reports also the exact mass for $[M+H]^+$ cation. The formation of this side-product can be rationalized by addition of aryl lithium to the nitro group to give a *N*-hydroxy-*N*,*O*-diarylhydroxylamine intermediate **a**, which decomposes to 2-biphenol and nitroso derivative **b** (Scheme 14). The nitroso compound can react with 2 eq. of aryl lithium affording 2-bipnenol and litium diarylylamide **d**, which affords **8a** during the work-up.[120,121] The formation of 2-biphenol was verified by its isolation during column chromatography.

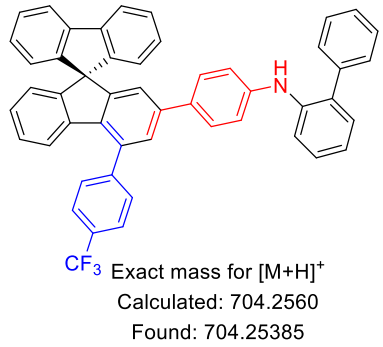
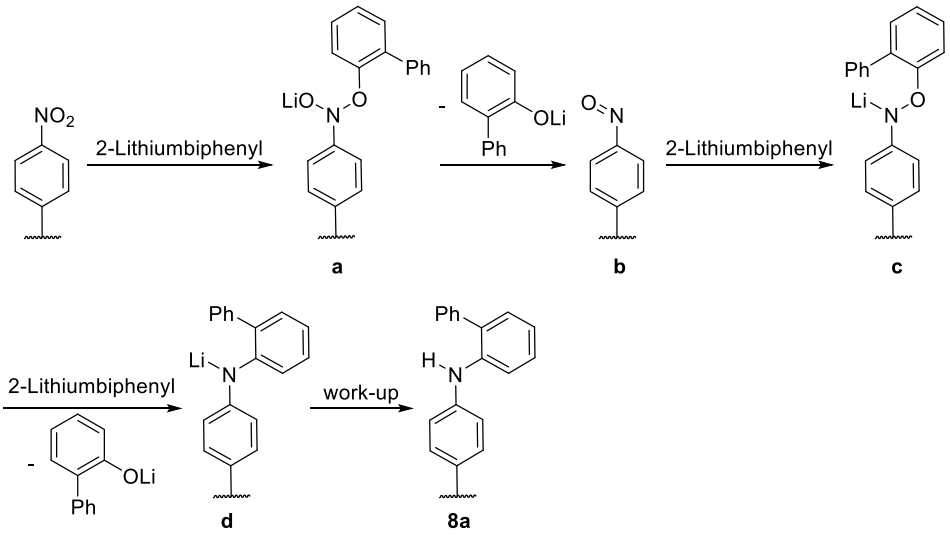


Figure 2. Possible structure of **8a**



Scheme 14. Possible mechanism for formation of **8a**

All the synthesized spirobifluorenes proved to be highly bench stable white solids. Good stability was also found even if they were left in solution for several days. Moreover, the compounds were impressively soluble in the majority of solvents ranging from non-polar (e.g.

hexane, cyclohexane, pentane) to polar solvent (such as acetonitrile, acetone). They were less soluble in methanol. As stated in Section 1.2.1, the high solubility and stability of spirobifluorenes stems from the peculiar perpendicular arrangement of the π-systems created by the spiro-linkage. Indeed, the cross-shape structure suppresses the intermolecular π-π interactions, giving to spirobifluorenes a better solubility.

3.1.4 Structural properties of SBFs

The structure of spirobifluorenes **8c**, **8g**, **8h**, **8h'**, **8i** and **8n** was confirmed by single crystal X-ray analyses (Figure 3). In general, the structure determination of spirobifluorenes was troublesome due to several reasons: the disorder of one -CF_3 group for **8c**; the presence of two symmetrically independent molecules in the unit cell of **8g**, **8h** and **8i**; the presence of two isomers in the case of **8h**; the presence of six symmetrically independent molecules in the unit cell of **8n**.

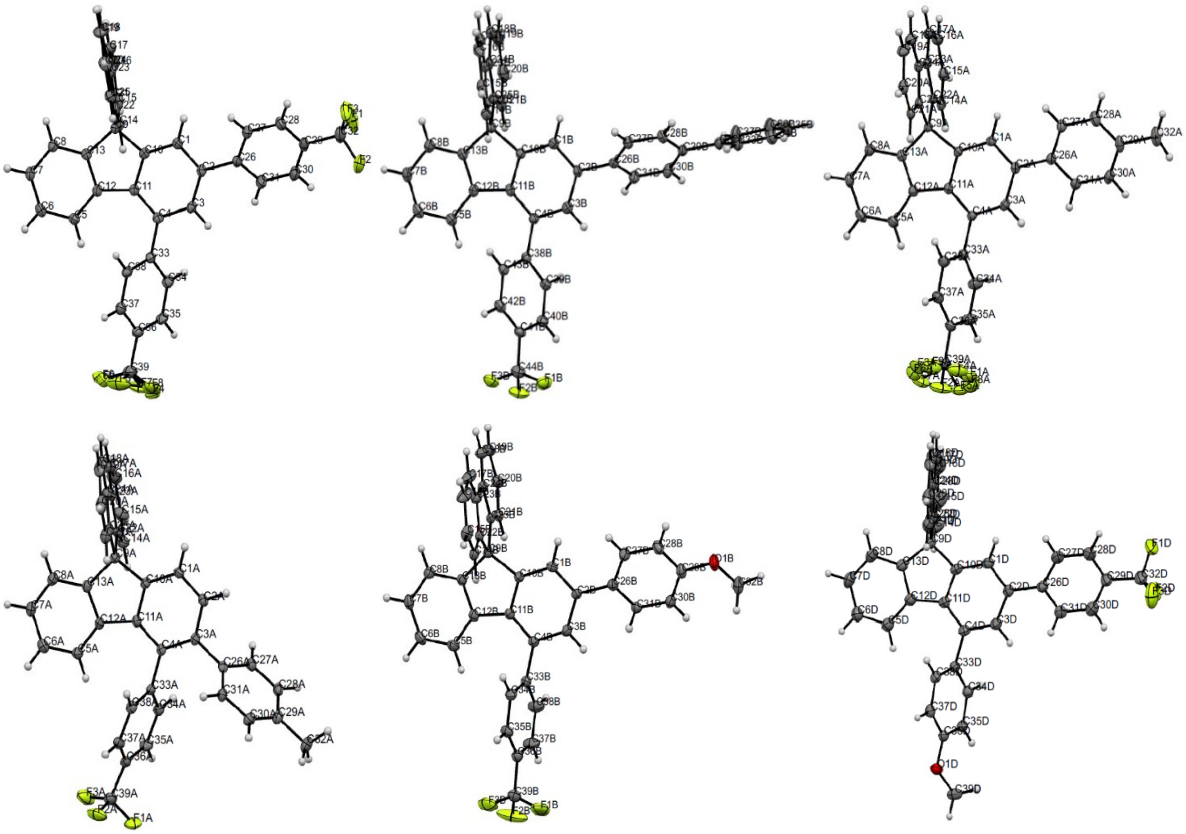


Figure 3. ORTEP drawing of **8c**, **8g**, **8h**, **8h'** (*ortho* isomer), **8i**, **8n** respectively from left to right (grey C, white H, green F, red O)

However, taking into account the dihedral angles formed by the three C–C bonds C5–C12–C11–C4, it is possible to note that the fluorenyl scaffold is only slightly deformed. The values of those angles are 1.8° (**8c**), 7.9 and 4.0° (**8g**), 2.8 and 4.1° (**8h**), 2.1° (**8h'**), 1.3 and 2.2° (**8i**), 2.4-7.4° (**8n**).

The angles between the plane of the substituted fluorene scaffold and the plane of the pendant phenyl rings have been calculated as well. As example see Figure 4 which illustrates the plane formed by the substituted fluorene scaffold (green color) and the plane of *p*-$CH_3C_6H_4$ in position C(3) (blue color) of **8h'**.

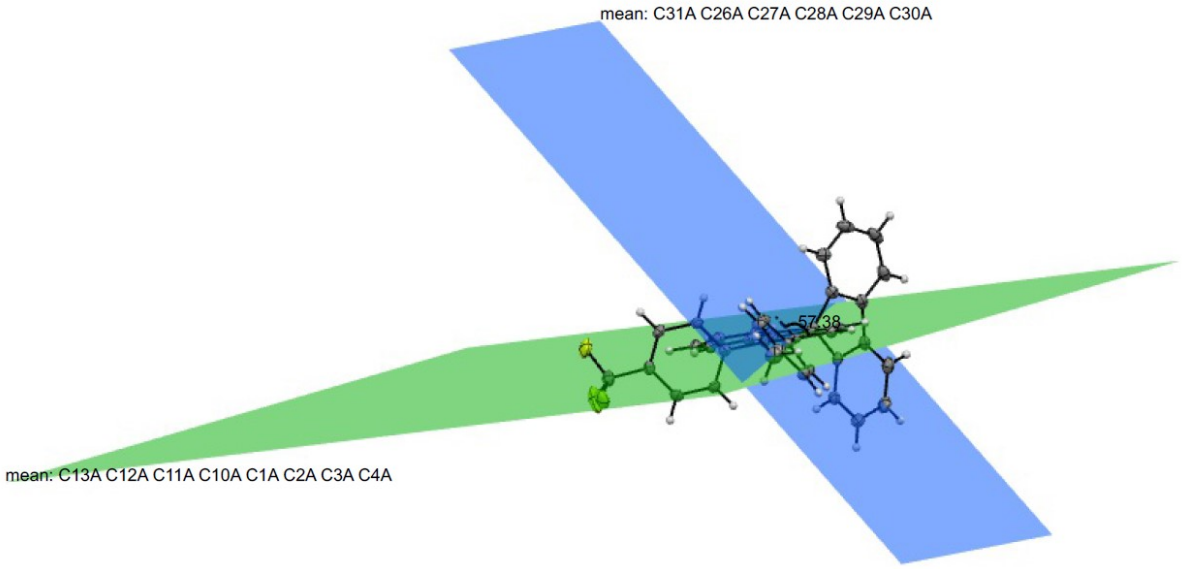


Figure 4. 8h' used as model substrate to show calculation of angle between the plane of fluorene scaffold (green) and the plane of *p*-$CH_3C_6H_4$ ring (blue) in C(3) position.

The calculated angles are listed in Table 3. The general trend is that the angle between the plane of fluorene scaffold and the plane of phenyl substituents in position C(2) is lower than that one formed with phenyl substituents on position C(4). This results is in accordance with literature reported angles for 2-monosubstituted spirobifluorenes and 4-monosubstituted spirobifluorenes. [122] For instance the 2-phenyl-9,9'-spirobifluorene showed a fluorene/phenyl dihedral angle of 37.4 which is lower in comparison of that one of 4-phenyl-9,9'-spirobifluorene which showed angle of 51.2° and 56.6° respectively for the two independent molecules found in the unit cell. The lower angles of 2-monosubstituted *vs.* 4-monosubstituted spirobifluorenes have been assigned by Poriel *et al*. to the *para*-linkage of the terphenyl unit (*para* linkage between bonds C(12)–C(11) and C(2)–C(26)) which increase the conjugation among the phenyl rings involved. Moreover, the bigger dihedral angles of 4-monosubstituted have been attributed to the steric interaction between the hydrogen atoms in the *ortho* position

of the pendant phenyl ring and those of fluorenyl core and it was accounted for the π-conjugation breaking generally observed in 4-substituted spirobifluorenes.[71a]

In our case, for **8h**, **8i** and **8n** the angles involving the substituents on position C(2) are in the range 22.9-34.6° which is even lower than that of 2-phenyl-9,9'-spirobifluorene, suggesting better conjugation between the fluorene and the C(2) *p*-$CH_3C_6H_4$, *p*-$OMeC_6H_4$ and *p*-$CF_3C_6H_4$ substituents. Interestingly, **8c** with *p*-$CF_3C_6H_4$ on C(2) and C(4) possesses larger dihedral angle between the fluorene and its substituent in C(2) (40.4°) and also the smallest angle between the fluorene and its substituent in C(4) (49.1°). An exceptional case is represented by compound **8g** bearing a biphenyl on position C(2). This compound has the highest value (59.5°) of angle between the fluorene and the attached biphenyl in position 2, whereas the angle with *p*-$CF_3C_6H_4$ substituent in position 4 is lower and equal to 50.6°. These findings break the general rule of having lower angles with C(2) substituents and larger with C(4) ones and suggests that steric hindrance of the pendant biphenyl is responsible of π-conjugation breaking on C(2) position. Regarding the angles of fluorene and the substituents on C(4) for the other compounds, those angle are generally very large with the maximum value of 79.7° reached by **8i** and they are even higher than that of 4-phenyl-9,9'-spirobifluorene (~54°). These results confirms the disruption of conjugation between the fluorene and C(4) pendant substituents. Lastly, the *ortho* isomer **8h'** possesses angle between the fluorene and the *p*-$CH_3C_6H_4$ on C(3) which is 57.4°, much higher than that of monosubstituted analogue 3-phenyl-9,9'-spirobifluorene (34.2°).[123] The substituent on C(4) in **8h'** forms an angle of 72.4° with the fluorene scaffold. These high values for the *ortho* disubstituted isomer can come from the proximity of the two substituents in position 3 and 4 which increases the distortion in the molecule.

Interestingly comparing spirobifluorene **8h** with the fluorenone analogue **7h** (Figure 1), the angles involving the *p*-$CH_3C_6H_4$ substituent on C(2) are similar (33.0 and 22.9° for **8h** and 33.0 and 28.6° for **7h**), showing that the additional spirofluorene moiety is not influencing the orientation of C(2) pendant ring. Slightly higher distortion of the C(4) phenyl substituent was observed in the case of **7h** (68.9 and 58.6° for **8h** vs. 73.1 and 63.0° for **7h**).

Table 3. Angles between the plane of the substituted fluorene scaffold and the plane of the pendant phenyl rings attached on C(2) (or C(3) in the case of *ortho* isomer, **8h'**) and C(4) carbon atoms

8-7	C(2) or C(3)	C(4)
8c	40.4°	49.1°
8g	59.5°	50.6°
8h	33.0°[a] 22.9°	68.9°[a] 58.6°
8h'	57.4°	72.4°
8i	30.2°[a] 34.6°	79.7°[a] 74.1°
8n	27.6°[b]	62.8°[b]
7h	28.6°[a] 33.0°	63.0°[a] 73.1°

[a] Two angles are reported because two independent molecules were found in the unit cell; [b] The reported angle is the average of the angles of six independent molecules present in the unit cell.

To conclude, the simultaneous presence of substituents in position C(4) and C(2) increases the angles between the plane of fluorene and the plane of the pendant substituents at C(4) (up to 79.7°) with values much higher than that of monosubstituted analogue 4-phenyl-9,9'-spirobifluorene (~54°). Generally the substituents on C(2) shows low value of dihedral angles (22.9-40.4°) and as consequence they are more π-conjugated with the fluorene scaffold. Furthermore, the nature of substituent can also have a great impact on the angles as demonstrated by **8g** with a biphenyl in C(2) position which break the usual π-conjugation with the fluorene framework (angle of 59.5°).

3.1.5 Photophysical properties of SBFs

I also proceeded to study the relationship between photophysical properties and structure by recording the UV-Vis absorption, fluorescence emission spectra and the fluorescence absolute quantum yields of the synthesized spirobifluorenes.

All the samples showed to be highly fluorescent as it is demonstrated in Figure 5 where some micromolar solutions of compounds **8** were exposed to 365 nm long-wave ultraviolet light.

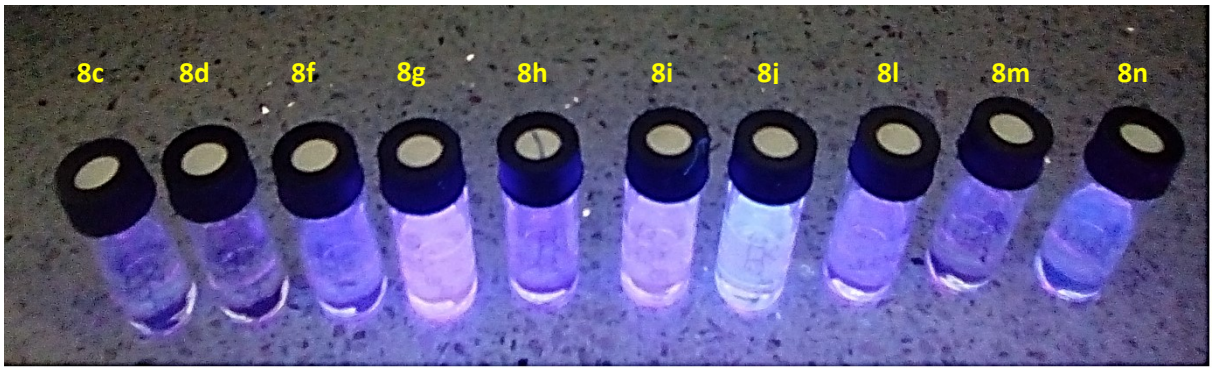


Figure 5. 3 mL vials containing sample solutions in cyclohexane under 365 nm UV light

Absorption spectra of **8b**-**8o** were recorded in cyclohexane solution at 10^{-5} M and are reported in Figure 6. The spectra appear very similar with two narrow bands at ~297 and ~309 nm, which are typical of all known unsubstituted and substituted spirobifluorenes.[122, 124] In particular, the band at 308 nm is attributed to π-π* transition of the fluorene unit. In addition, a more or less intensive large band is present at higher wavelengths in the range of 323-331 nm. This band is due to elongation of π-electron conjugation from fluorene core to phenyl ring of the substituents. Therefore, larger and slightly red-shifted terminal bands were obtained in case of spirobifluorenes with aromatic substituent at position C2, as a sign of more effective conjugation. On the other hand, compound **8m** with *n*-propyl substituted in C2 position exhibited a lower intensity tail as matter of limited degree of conjugation.

The fluorescence spectra were recorded using 10^{-6} M solution of spirobifluorenes in cyclohexane (Figure 7) and absolute quantum yields (Φ_s) were determined with the same solutions using $\lambda = 280$ nm as excitation wavelength. The most important data are summarized in Table 4. The emission spectra present mainly an unresolved band (**8b**, **8c**, **8i**, **8j**, **8n** and **8o**) or partially resolved structure (**8d**-**8h**, **8l**, and **8m**), as it is typical for all the known 4-aryl substituted spirobifluorenes described in literature. [52, 53, 71a, 122, 124]

The emission maxima are listed in Table 4 and range from 365 nm to 391 nm. In the case of spirobifluorenes bearing *p*-CF_3-phenyl group in C4 position (**8b**-**8m**), the emission is influenced by electron density on C2 aryl substituents. Indeed electron-withdrawing groups such as *p*-CN-C_6H_4 or *p*-CF_3-C_6H_4 in **8b** and **8c** lead to slightly blue shift emission maxima (367, 368 nm respectively), whereas the electron-donating groups in C2, for instance $(OMe)_3$-C_6H_2 in **8j**, exhibit more red-shifted emission (391 nm for **8j**).

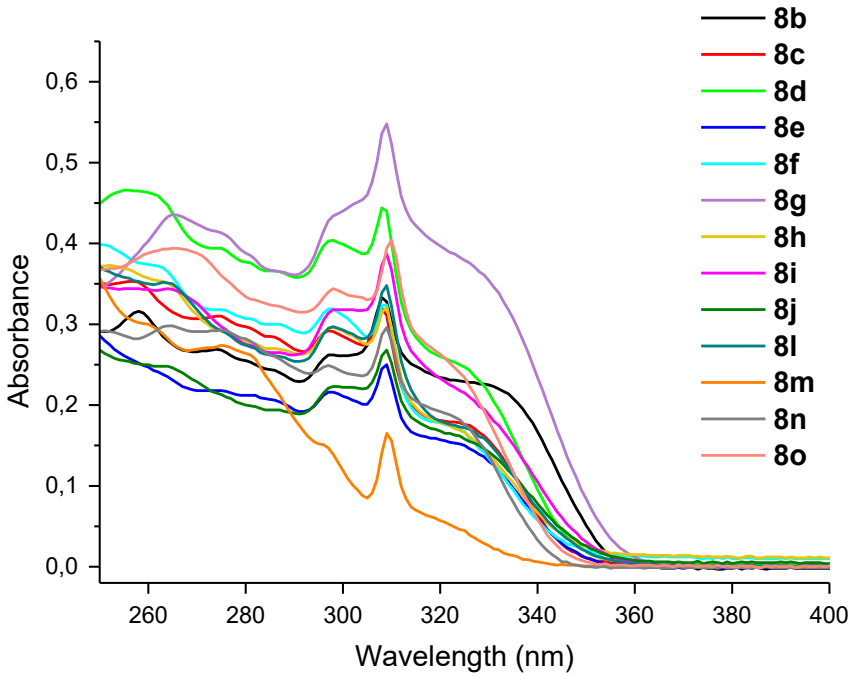


Figure 6. Absorption spectra of **8** (10^{-5} M) in cyclohexane

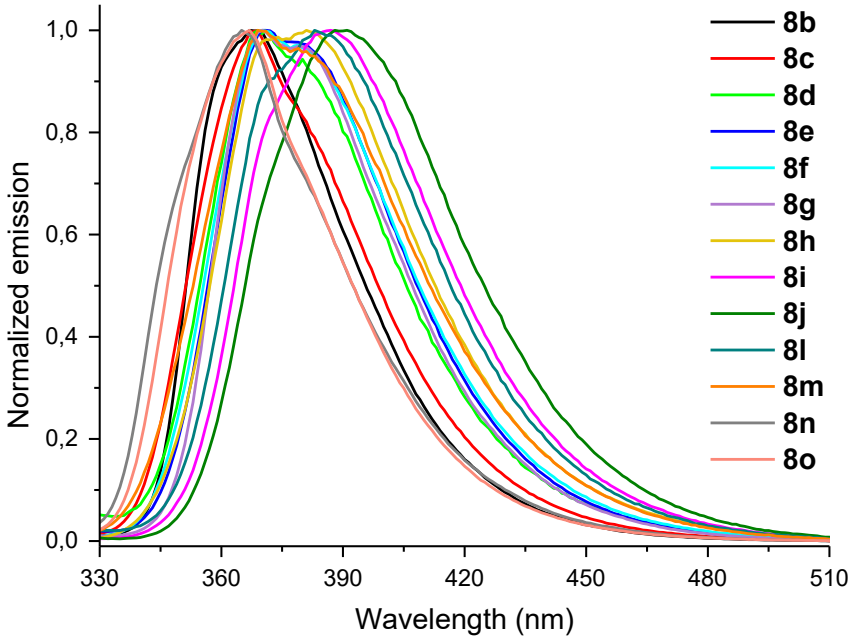


Figure 7. Normalized emission spectra of **8** (10^{-6} M) in cyclohexane

However, spirobifluorenes with *p*-OMe-C_6H_4 moiety in C4 position, **8n** and **8o**, show unchanged spectra upon alteration of C2-substituent with respectively 365 and 367 nm as emission maxima.

Table 4. Absorption and emission data for **8**

8	λ_{abs}/nm (ε/10^4 $mol^{-1}\cdot dm^3\cdot cm^{-1}$)	λ_{em}/nm	Φ_s [a]
8b	258 (3.1), 274 (sh), 297 (2.6), 308 (3.3), 331 (sh)	367	0.92
8c	256 (3.5), 274 (sh), 297 (2.9), 308 (3.2), 326 (sh)	368, 378	0.88
8d	258 (4.6), 275 (sh), 298 (4.0), 308 (4.4), 326 (sh)	369, 380	0.14
8e	255 (sh), 275 (sh), 297 (2.1), 309 (2.4), 323 (sh)	371, 379	0.77
8f	250 (sh), 262 (sh), 297 (3.1), 309 (3.1), 323 (sh)	370, 379	0.86
8g	265(4.4), 275 (sh), 298 (sh), 309 (5.5), 326 (sh)	370, 380	1.00
8h	252 (sh), 263 (sh), 298 (2.9), 309 (3.1), 325 (sh)	373, 380	0.69
8i	264 (sh), 299 (3.2), 309 (3.9), 323 (sh)	386	0.78
8j	264 (sh), 298 (2.2), 309 (2.7), 324 (sh)	391	0.37
8l	264 (3.5), 298 (3.0), 309 (3.5), 326 (sh)	372, 385	0.44
8m	260 (sh), 278 (2.5), 297 (sh), 309 (1.6)	370, 380	0.64
8n	264 (3.0), 275 (sh), 297 (2.5), 309 (3.0), 323 (sh)	365	0.86
8o	265 (3.9), 298 (3.4), 310 (4.0), 323 (sh)	367	0.91

[a] Absolute quantum yields were calculated at λ_{exc} = 280 nm.

The Stokes shifts are up to 66 nm (~5200 cm^{-1}) and indicate, together with the structureless emission spectra character, a strong reorganization between geometries of S_0 (ground state) and S_1 (first singlet excited state), as it was found for the majority of C4-aryl substituted spirobifluorenes.[124, 125]

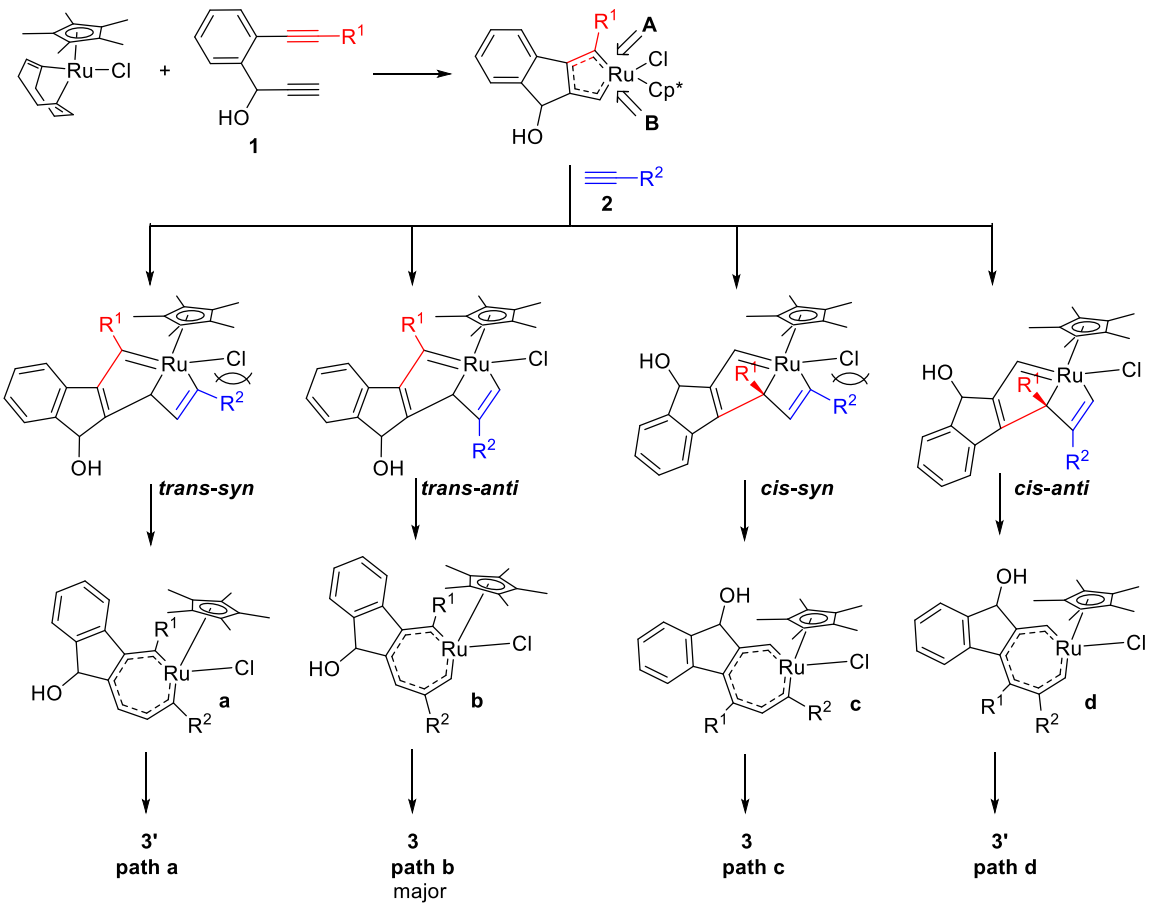
Regarding the absolute quantum yields, the recorded values range from 0.14 (**8d**) to the highest level of 1.00, reached by spirobifluorenes bearing biphenyl on C2 (**8g**).

3.1.6 Mechanistic considerations for regioselectivity of cyclotrimerization

To conclude the section about the synthesis of 2,4-disubstituted SBFs, I would like to propose a hypothesis rationalizing the observed regioselectivity during [2+2+2] cyclotrimerization of diynes and terminal alkynes catalyzed by Cp*RuCl(cod). Partially intramolecular cyclotrimerizations catalyzed by this catalyst were extensively studied by Itoh's group.[118, 126] Important information on the probable course of the reaction were obtained by isolation of key reaction intermediates and by DFT calculations. It is generally accepted that the Ru-catalyzed cyclotrimerization of diynes with alkyne is known to proceed via oxidative cyclization producing a ruthenacycle intermediate. Its formation is the rate-determining step. The subsequent steps involve alkyne insertion/reductive elimination route rather that the direct [4+2] cycloaddition of the ruthenacyclopentadiene with an alkyne. The alkyne insertion takes

place via [2+2] cycloaddition of the ruthenacyclopentadiene with an alkyne leading to a ruthenabicycloheptatriene. The final step is the ring closure with formation of benzene moiety.

The regioselectivity is determined in the [2+2] cycloaddition step. Indeed, four possible regio-isomers can be formed during this step (Scheme 15): ***trans-syn***, ***trans-anti***, ***cis-syn***, ***cis-anti***, where *trans* or *cis* refers to the position of R^2 and R^1 groups on the bicyclic ruthenacycle complex and *syn* or *anti* to the orientation of R^2 group toward the Cp* ligand. By single point energy calculations found in literature for similar ruthenacycle isomers,[118] it is clear that *syn*-isomers are less thermodynamic stable if compared with *anti*-ones, because of steric repulsion with both Cp* ligand and chlorine atom. Comparing the ***cis-anti*** with ***trans-anti***, the former proved to be less favorable because of repulsion between R^1 and Cp* ligand during C–C bond formation with the terminal alkyne. As result, the pathway leading to *meta*-product via the lowest energy *trans-anti* transition state is considered the most favorable.

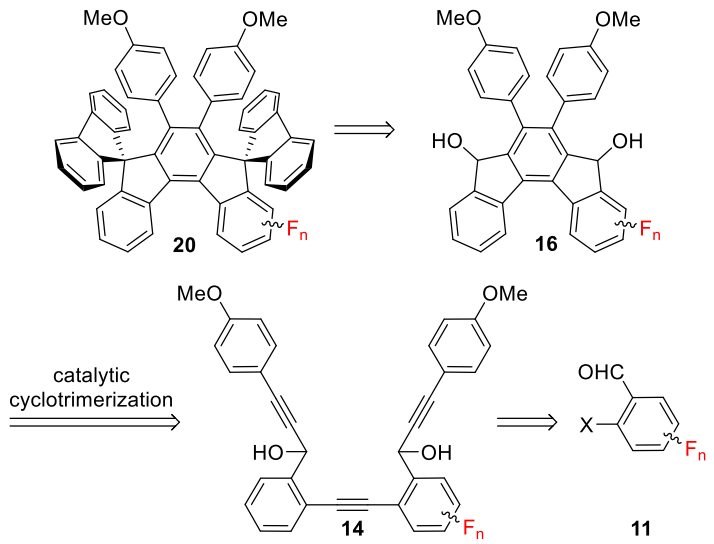


Scheme 15. Proposed regioselection mechanism for [2+2+2] of **1** with **2**

3.2 Synthetic approach and photophysical properties of regioselectively fluorinated [5] and [6]helical dispiroindenofluorenes

In the second part of my project I explored a general synthetic approach towards regioselectively fluorinated [5] and [6]helical bispiroindenofluorenes using intramolecular Rh-catalyzed [2+2+2] cyclotrimerization with accessible fluorinated building blocks (Sections 3.2.1-3.2.4). The impact of the fluorine substitution on chemical properties and photophysical characterization of the synthesized compounds were studied as well (Sections 3.2.5 and 3.2.6).

The retro-synthetic approach is outlined in Scheme 16 and is based on the previous Kotora group's approaches.[113, 114] The spirobifluorene moiety is created by arylation and cyclization on bis(4-methoxyphenyl)indeno[2,1-*c*]fluorene-5,8-dione which is prepared by oxidation of bis(4-methoxyphenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol, **16**. The dihydroindenofluorene scaffold is built by intramolecular transition metal catalyzed [2+2+2] cyclotrimerization that represents the key step of the whole synthetic pathway. Finally, the preparation of starting triynediols **14** is performed using variously fluorinated 2-halobenzaldehyde **11**. The major findings of this study were published as my second first-authored paper in Kotora's group.[127]



Scheme 16. Retrosynthetic analysis of fluorinated indenofluorenes

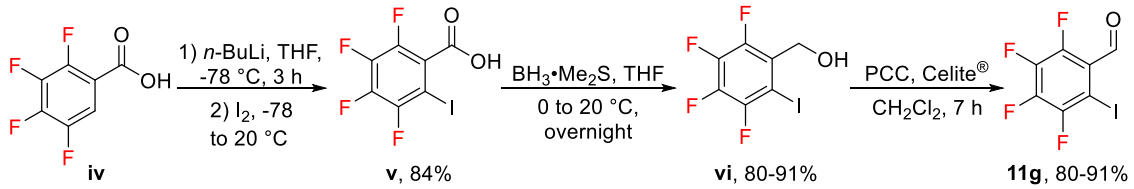
3.2.1 Synthesis of fluorinated triynediols

The first synthetic step regards the preparation of dialdehydes **12a-12g** and **13**, which was achieved by Sonogashira coupling reaction between 2-ethynylbenzaldehyde **9** or 1-

ethynyl-2-naphthaldehyde **10** and variously fluorinated 2-halobenzaldehydes **11a-11g** (Scheme 18).

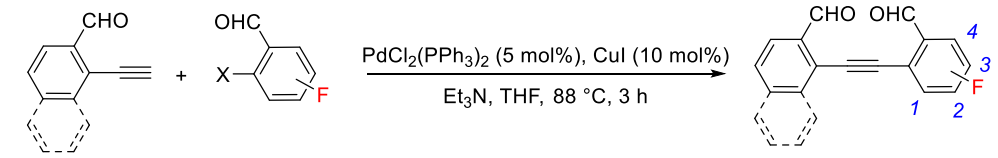
Compounds **9** and **11a-11f** were commercially available, whereas **10** was prepared by Sonogashira reaction between 1-bromo-2-naphthaldehyde and ethynyltrimethylsilane followed by desilylation of the crude mixture with K_2CO_3 in MeOH/H_2O (74% overall yield).

The starting material, 2,3,4,5-tetrafluoro-6-iodobenzaldehyde (**11g**), which is not supplied by chemical vendors, was prepared from 2,3,4,5-tetrafluorobenzoic acid (**iv**), by three step synthesis: i) iodination with *n*-BuLi and I_2 to obtain **v** in 84% yield; ii) reduction of carboxyl group with borane-dimethyl sulfide complex solution to alcohol **vi**; iii) oxidation of the obtained alcohol **vi** to aldehyde **11g** with PCC (Scheme 17). The overall yield for this synthesis was up to 70%.



Scheme 17. Synthesis of 2,3,4,5-tetrafluoro-6-iodobenzaldehyde (**11g**)

With all the starting materials available, the Sonogashira cross-coupling reaction was performed and afforded the desired dialdehydes **12a-12g** in good isolated yields in the range of 64-99% (Scheme 18).



9, benzaldehyde
10, naphthaldehyde

11a, 1-F, X = Br
11b, 2-F, X = Br
11c, 3-F, X = Br
11d, 4-F, X = Br
11e, 2,3-F, X = Br
11f, 3,4-F, X = Br
11g, 1,2,3,4-F, X = I

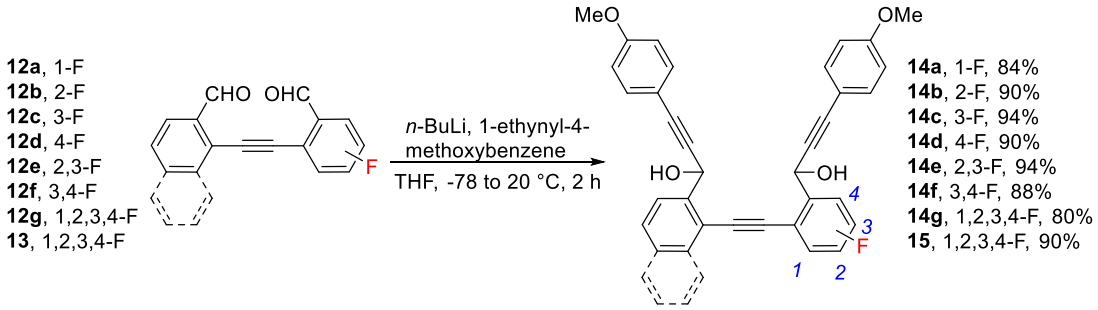
12a, 1-F, 84%
12b, 2-F, 99%
12c, 3-F, 76%
12d, 4-F, 79%
12e, 2,3-F, 86%
12f, 3,4-F, 74%
12g, 1,2,3,4-F, 64%
13, 1,2,3,4-F, 40%

Scheme 18. Synthesis of starting dialdehydes **12a-12g** and **13**

The Sonogashira cross-coupling of **10** with **11g** furnished the target dialdehyde **13** in lower yield (40%). This result was the consequence of homocoupling of **10** that led to formation of a Hay coupling product[128] whose separation from the compound **13** was not achieved by

column chromatography; indeed, both compounds showed the same R_f in all the tested eluent mixtures. Under those circumstances, the isolation of product **13** was accomplished upon recrystallization from CH_2Cl_2.

After the preparation of the desired set of fluorinated dialdehydes, triynediols **14a-g** and **15** were obtained by bisalkynylation of **12a-g** and **13** with lithium acetylide, prepared *in situ* by metalation of 1-ethynyl-4-methoxybenzene with *n*-BuLi. The target compounds were isolated with very good yields in the range of 80-94% (Scheme 19).

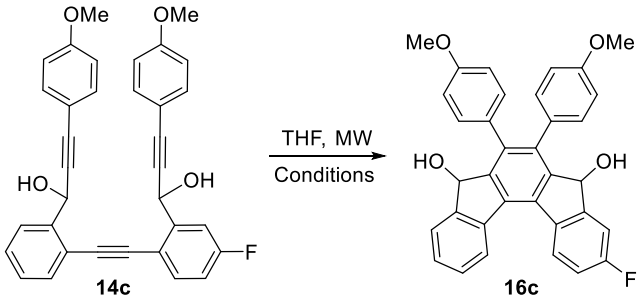


Scheme 19. Synthesis of starting triynediols **14a-g** and **15**

3.2.2 Intramolecular cyclotrimerization of fluorinated triynediols and scope of reaction

With triynediols **14a-g** and **15** in hands, the catalytic [2+2+2] cyclotrimerization forming the indenofluorene scaffold was carried out. Foremost, I followed the previous strategy developed in our group, involving the use of Wilkinson's catalyst and Ag_2CO_3 as an additive under microwave irradiation at 170 °C.[53] The cyclotrimerization of a model substrate, **14c**, afforded dihydroindeno[2,1-*c*]fluorene-5,8-diol **16c** in 50% isolated yield (Table 5, Entry 1). ^{19}F NMR analysis of the crude reaction mixture revealed the formation of other intractable side-products along with the target compound (major signal at -113.5 ppm in Figure 8). Lowering the reaction temperature to 150 °C increased the yield to 76% (Entry 2, Table 5) and reduced the formation of side-products (again confirmed by ^{19}F NMR analysis of the crude mixture, see the second spectrum in Figure 8). In addition, performing the reaction without Ag_2CO_3, furnished **14c** in 71% isolated yield, demonstrating that this additive is not strictly required for the successful course of cyclotrimerization (Entry 3, Table 5). Therefore, the last conditions ($RhCl(PPh_3)_3$ (3 mol%), 150 °C, microwave irradiation, 1.5 h) were selected as the most convenient ones and the scope of the reaction with triynediols **14a-14g** and **15** was performed (Scheme 20).

Table 5. [2+2+2] cyclotrimerization of **14c** to **16c** under different conditions



Entry	Catalyst	Additive	T (°C)	t (h)	**16c**, Yield (%)
1	$RhCl(PPh_3)_3$ (3 mol%)	Ag_2CO_3 (6 mol%)	170	1.5	50%
2	$RhCl(PPh_3)_3$ (3 mol%)	Ag_2CO_3 (6 mol%)	150	1.5	76%
3	$RhCl(PPh_3)_3$ (3 mol%)	/	150	1.5	71%

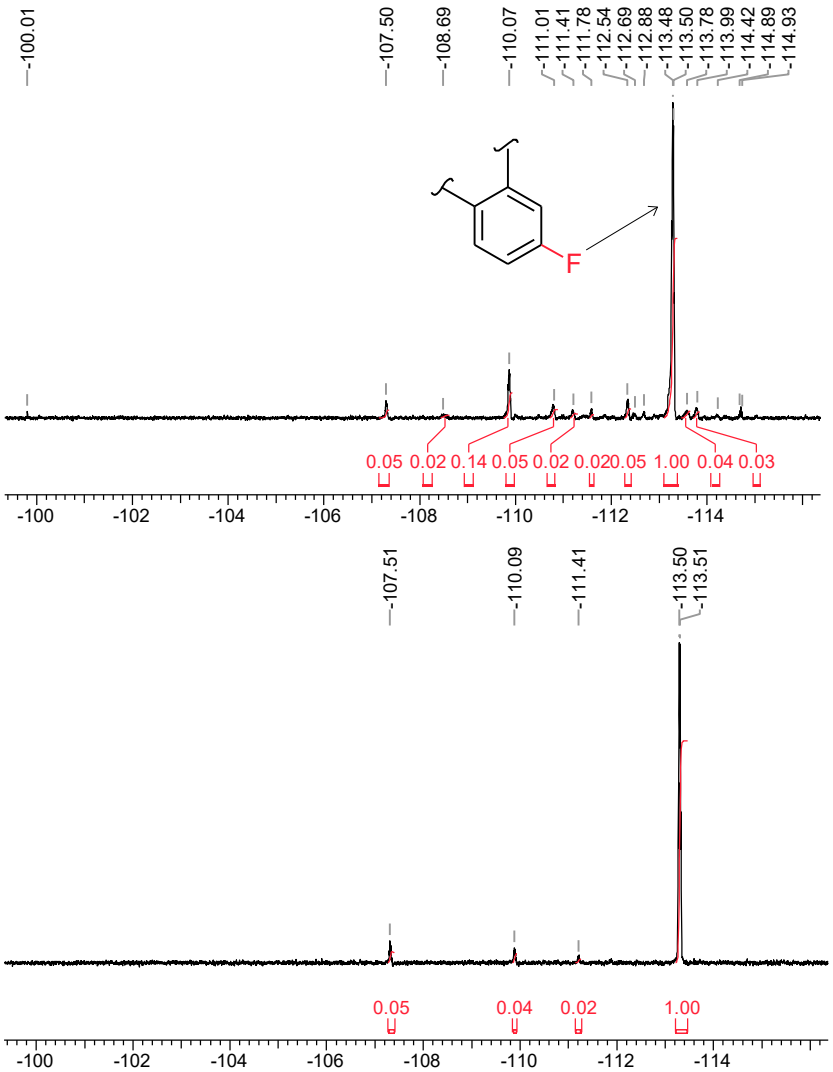
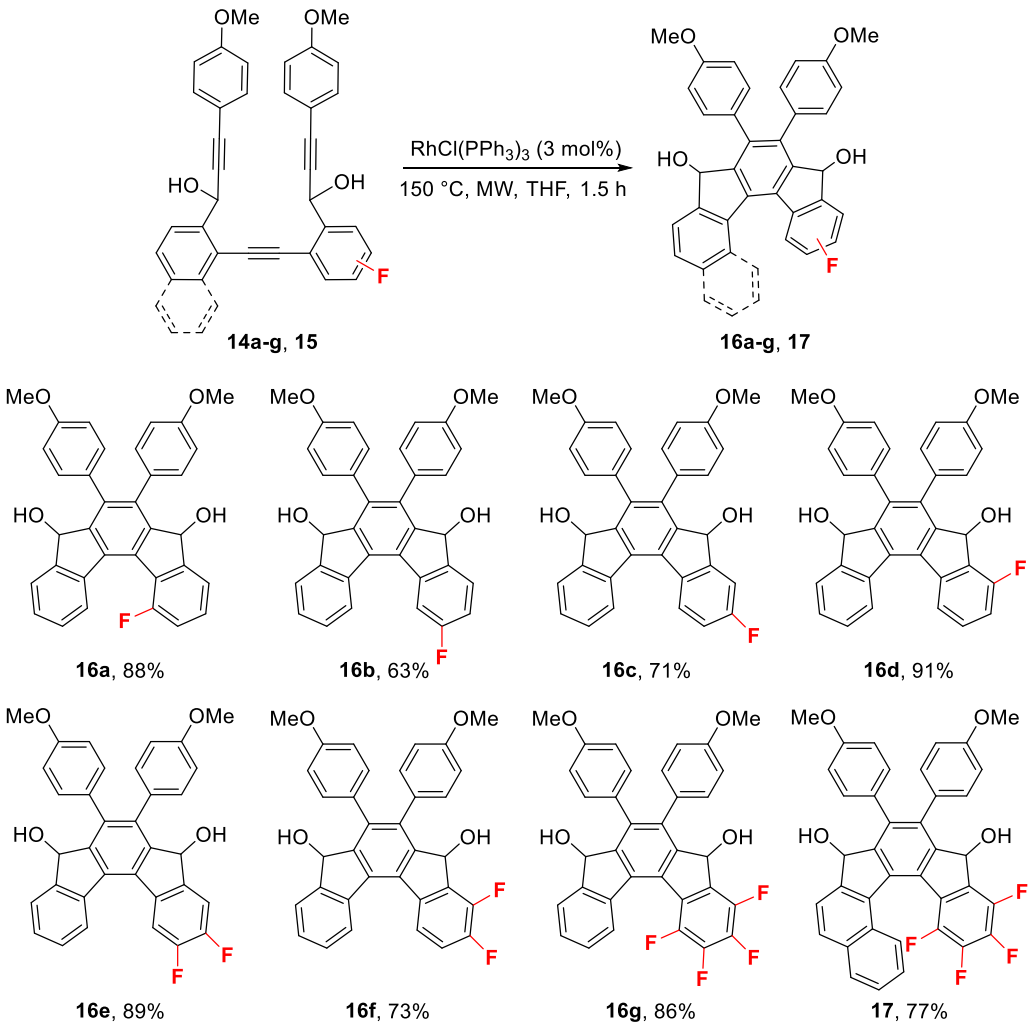


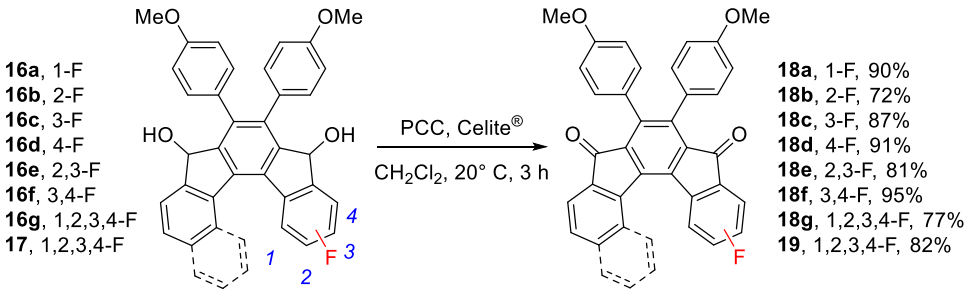
Figure 8. ^{19}F NMR spectra of the crude reaction mixtures. First spectrum refers to conditions described in Entry 1, Table 5, whereas second spectrum refers to Entry 2

The desired fluorinated [5]helical dihydroindeno[2,1-*c*]fluorenediols **16a-16g** and [6]helical tetrafluoro dihydroindeno[1,2-*g*]fluorenediol **17** were obtained in high isolated yields ranging from 63 to 91% (Scheme 20). The products were formed in all cases as separable mixtures of two diastereoisomers (*anti* and *syn* alcohols) that were separated and isolated by column chromatography on silica gel and fully characterized. However, dihydroindenofluorenediol **17** gave a mixture of four diasteroisomers (*syn* and *anti*) that were separated into two fractions. The increased number of diasteroisomers for **17** can be ascribed to the presence of element of helical chirality derived from the [6]helical framework with one more fused benzene ring.

The dihydroindenofluorenediols **16a-g** and **17** were subsequently oxidized to corresponding diketones **18a-g** and **19** with PCC in dichloromethane. The oxidation proceeded uneventfully with good yields in the range of 72-95% (Scheme 21).



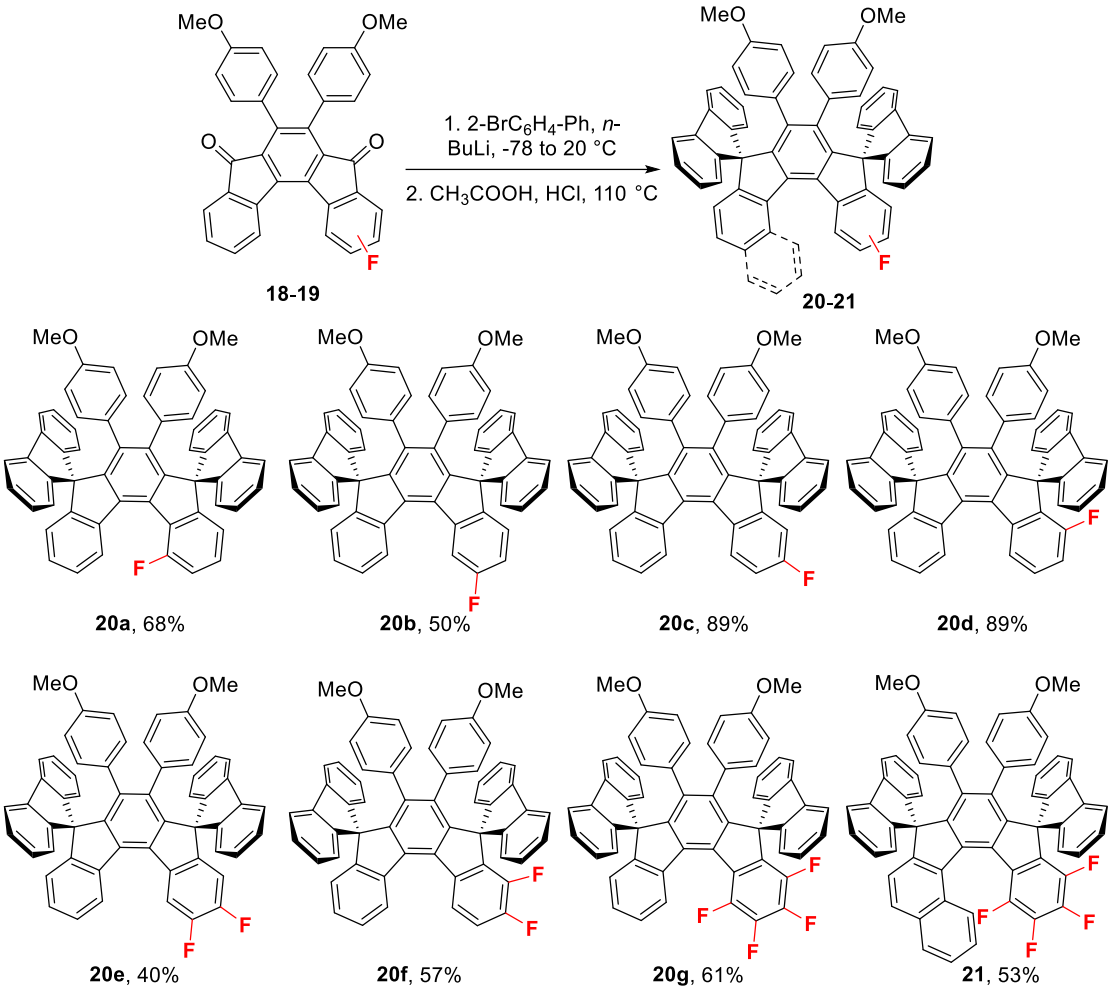
Scheme 20. Scope of Rh-catalysed [2+2+2] cyclotrimerization of **14a-g** and **15**



Scheme 21. Oxidation of **16a-g** and **17** diketones **18a-g** and **19**

3.2.3 Synthesis of final fluorinated DSF-IFs and DSF-BIF

In order to obtain the final dispiroindeno[2,1-*c*]fluorenes, diketones **18** and **19** were subjected to the known two-steps procedure for the construction of the spiro bridge. Particularly, 2-bromobiphenyl was turned into 2-lithiumbiphenyl by metal–halogen exchange reaction with *n*-BuLi. Diketones **18a-g** and **19** were added to the preformed 2-lithiumbiphenyl and the resulting diols underwent an intramolecular spirocyclization under acidic conditions. The last transformations afforded dispiroindeno[2,1-*c*]fluorenes **20a-g** and dispirobenzo[*c*]indeno[1,2-*g*]fluorene **21** in 50-89% overall yields (after two steps, Scheme 22). Surprisingly, the synthesis of **20e** was challenged by undesired formation of **20b** as the inseparable impurity (5%) when 5 eq. of *n*-BuLi and 2-bromobiphenyl were employed. To avoid defluorination of the C(3)–F bond, the amount of *n*-BuLi and 2-bromobiphenyl were decreased to 3.5 eq. As result, **20e** was cleanly obtained, albeit in a lower yield of 40%. Other attempts like the addition of HMPA during the first step or the use of 2.5 eq. of *n*-BuLi were not met with success and the starting material **18e** was recovered.



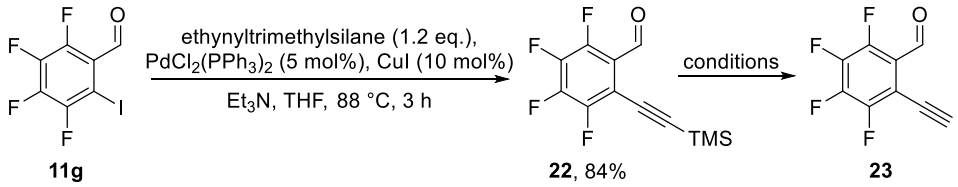
Scheme 22. Synthesis of **20a-g** and **21**

3.2.4 Synthesis of octa-fluorinated DSF-IF

As last compound to complete the set of dispiroindenofluorenes, I wanted to synthetize octafluorinated dispirodihydroindeno[2,1-*c*]fluorene **20h**. However, since its synthesis was challenging and many reaction steps needed to be changed, the preparation of this compound is discussed separately.

Firstly, the preparation of compound 2,3,4,5-tetrafluoro-6-((trimethylsilyl)ethynyl)benzaldehyde **22** was attained by Sonogashira cross coupling reaction between 2,3,4,5-tetrafluoro-6-iodobenzaldehyde **11g** and ethynyltrimethylsilane in 84% isolated yield. The subsequent deprotection of the trimethylsilyl group proved to be tricky; indeed the use of K_2CO_3 or KOH gave a complex reaction mixture (Entry 1 and 2, Table 6), $Bu_4NF \cdot 3H_2O$ furnished only traces of the product **23** (Entry 4), but finally KF in MeOH afforded the target molecule **23** in 86% yield (Entry 3).

Table 6. Synthesis of starting compounds **22** and **23**

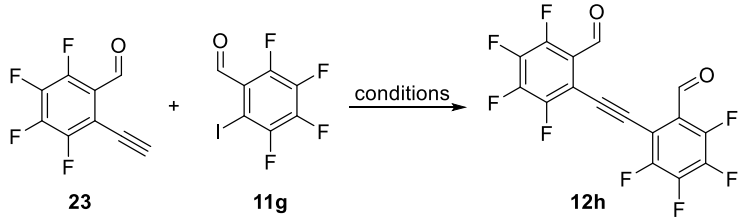


11g **22**, 84% **23**

Entry	Conditions	**23**, Yield (%)
1	MeOH, KOH, 20 °C	complex mixture
2	MeOH, H_2O, K_2CO_3, 0 °C	complex mixture
3	KF, MeOH, 20 °C	86%
4	$Bu_4NF{\cdot}3H_2O$, THF, 20 °C	Traces

In order to obtain the corresponding octafluorinated dialdehyde **12h**, the coupling between **11g** and **23** was studied (Table 7). Unfortunately, the standard conditions for Sonogashira cross-coupling generated a complex reaction mixture (Entry 1, Table 7). Furthermore, the non-Sonogashira-type palladium-catalyzed coupling reaction assisted by Ag_2O[129] was also unsuitable and the starting materials were recovered (Entry 2). With the hypothesis of instability of **23** in presence of the typical amines used for the classical Pd/Cu-catalyzed Sonogashira reaction, I then investigated a new version of this coupling employing $PdCl_2(PhCN)_2$/CuI/P(2-furyl)$_3$/KF system, which was designed by Rossi *et al*. for amine-sensitive compounds.[130] Under these conditions the desired product **12h** was obtained albeit in low yield and as an inseparable mixture with the homocoupling side-product (Entries 3-4).

Table 7. Coupling between **23** and **11g** using different experimental conditions



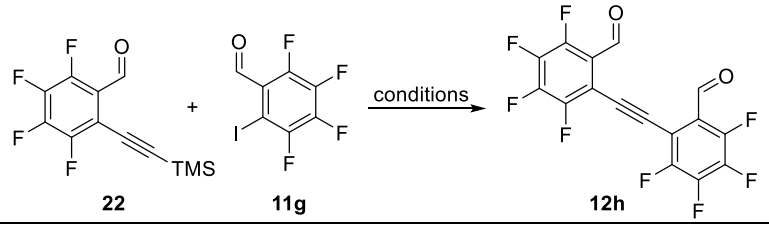
23 **11g** **12h**

Entry	Catalyst system	Base	Solvent	T (°C)	t (h)	**12h**, Yield %
1	$Pd(PPh_3)_2Cl_2$, CuI	Et_3N	THF	88	4	_[b]
2	$Pd(PPh_3)_2Cl_2$, Ag_2O	/	THF	60	16	_[c]
3	$Pd(PhCN)_2Cl_2$, CuI, P(2-furyl)$_3$	KF	Toluene	60	16	26[d]
4[a]	$Pd(PhCN)_2Cl_2$, CuI, P(2-furyl)$_3$	KF	Toluene/water	60	70	30[d]

[a] The reaction was performed in the presence of Bu_4NI. [b] Formation of a complex mixture was observed. [c] No reaction. [d] ^1H NMR yield of **12h** isolated as an inseparable mixture with the homocoupling product of **23**.

Therefore, I decided to examine the direct coupling between the protected alkyne **22** and **11g** (Hiyama-type coupling)[131] with the intention of further improving the yield (Table 8). Using amines as solvent or base[132] (Entry 1 and 2) complex reaction mixtures were obtained. In contrast to the previous findings (Entries 3 and 4, Table 7), the systems composed of $PdCl_2(PhCN)_2$/CuI/KF and $P(2\text{-furyl})_3$ or $P(Cy)_3$ as ligands did not catalyzed the coupling (Entry 3-4, Table 8); however, employing CsF instead of KF as base and under phase transfer conditions, the cross-coupling product, **12h**, was successfully obtained in 79% yield (entry 5). These last conditions with $P(Cy)_3$ ligand promoted the coupling as well, but in a lower yield (40%, entry 6). Indeed, the best conditions, presented in entry 5, were applied to prepare compound **12h**.

Table 8. Coupling between **22** and **11g** using different experimental conditions



22 **11g** **12h**

Entry	Catalyst system	Base	Solvent	T (°C)	t (h)	Yield (%)[d]
1	$Pd(Ph_3)_4$, CuI	*i*-Pr_2NH	DMF	80	15	_[b]
2	$Pd(PPh_3)_2Cl_2$, PPh_3, CuI	CsF	DMF	80	18	_[b]
3	$Pd(PhCN)_2Cl_2$, CuI, $P(2\text{-furyl})_3$	KF	Toluene	60	16	_[c]
4	$Pd(PhCN)_2Cl_2$, CuI, $P(Cy)_3$	KF	Toluene	60	16	_[c]
5[a]	$Pd(PhCN)_2Cl_2$, CuI, $P(2\text{-furyl})_3$	CsF	Toluene/H_2O	60	16	75-79
6[a]	$Pd(PhCN)_2Cl_2$, CuI, $P(Cy)_3$	CsF	Toluene/ H_2O	60	48	40

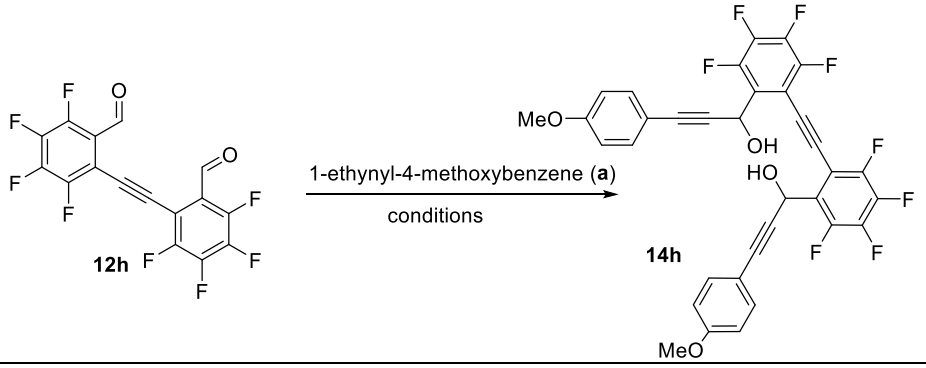
[a] The reaction was performed in the presence of Bu_4NI. [b] Formation of a complex mixture was observed. [c] No reaction. [d] Isolated yield of **12h**.

The next synthetic step, the bisalkynylation reaction of **12h**, was performed with the same conditions described in Scheme 19. In other words, **12h** was added to 3 eq. of lithium acetylide, prepared by metalation of 1-ethynyl-4-methoxybenzene with *n*-BuLi. Those conditions were unsuitable for the synthesis of octafluorinated triynediol **14h** (Entry 1, Table 9). Lowering the amount of *n*-BuLi to 2.2 eq. or employing EtMgBr were again not successful strategies (Entries 2 and 3). Finally, I found that Et_2Zn was an effective reagent for the bisalkynylation and the best results were obtained with 5.0 eq., instead of 2.5 eq. (Entries 4 and 5). Therefore, **14h** was isolated with 91% yield.

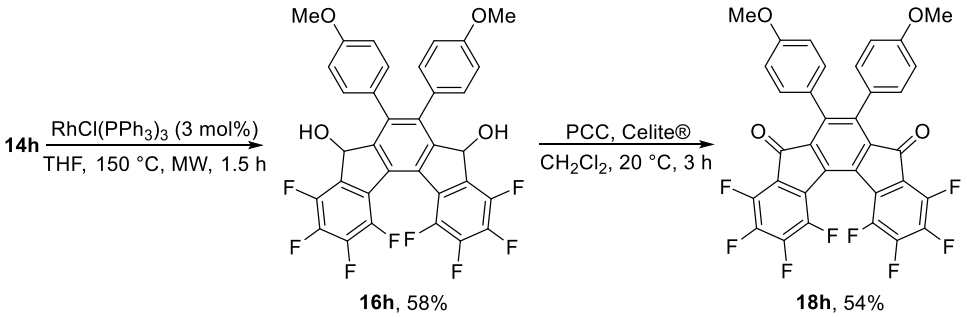
With triynediol **14h** in hand I performed the [2+2+2] cyclotrimerization by using my previous method ($RhCl(PPh_3)_3$ (3 mol%), 150 °C, 1.5 h under microwave irradiation). The

desired dihydroindenofluorenediol **16h** was isolated in 58% yield (Scheme 23). The next synthetic step, the oxidation of **16h** to diketone **18h**, proceeded with moderate yields (48-54%) using PCC in CH_2Cl_2 (Scheme 23).

Table 9. Bisalkynylation of **12h** for the synthesis of octa-fluorinated triynediol **14h**



Entry	Reagents	Solvent	T (°C)	t (h)	**14h**, Yield (%)
1	**a** (3.0 eq.), *n*-BuLi (3.0 eq.)	THF	-78 to 20	4	Complex mixture
2	**a** (2.2 eq.), *n*-BuLi (2.2 eq.)	THF	-78 to 20	4	Complex mixture
3	**a** (3.3 eq.), EtMgBr (3.0 eq.)	THF	0 to 20	3	Complex mixture
4	**a** (3.0 eq.), Et_2Zn (2.5 eq.)	HMPA, CH_2Cl_2	40 to 20	24	25
5	**a** (6.0 eq.), Et_2Zn (5.0 eq.)	HMPA, CH_2Cl_2	40 to 20	24	91

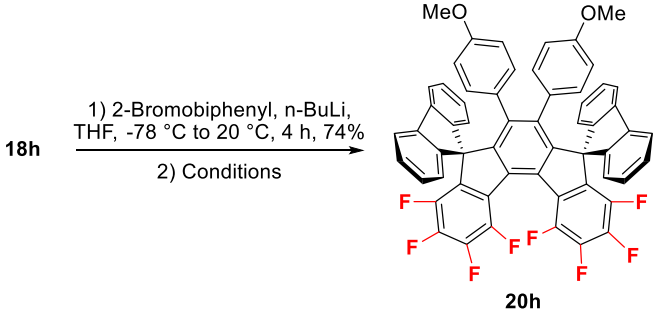


Scheme 23. Synthesis of **16h** by [2+2+2] cyclotrimerization, followed by oxidation to **18h**

Finally, to obtain the desired octafluorinated dispiroindeno[2,1-*c*]fluorene, the usual metal-halogen exchange reaction between 2-bromobiphenyl and *n*-BuLi followed by the addition of diketone **18h** provided the desired bis-arylated intermediate in 74% yield. Disappointingly, the intramolecular spirocyclization was ineffective under our classic conditions: CH_3COOH, HCl and work-up with K_2CO_3 (Entry 1, Table 10); however, changing the work-up using the saturated solution of $NaHCO_3$ instead of K_2CO_3 was sufficient to reach the target compound **20h** (Entry 2). An effort to induce cyclization with trifluoroacetic

anhydride (TFAA) in dichloromethane turned out to be unproductive (Entry 3). Satisfyingly, the use of $BF_3 \cdot Et_2O$ also proved to be suitable giving **20h** in 79% yield (Entry 4).

Table 10. Synthesis of **20h** with optimization of the last step



20h

Entry	Conditions	Work-up	Solvent	T (°C)	t (h)	**20h**, Yield (%)[a]
1	CH_3COOH, HCl (cat.)	K_2CO_3 (sat. sol.)	/	110	3	_[b]
2	CH_3COOH, HCl (cat.)	$NaHCO_3$ (sat. sol.)	/	110	3	60
3	TFAA		CH_2Cl_2	0 to 50	24	_[c]
4	$BF_3 \cdot Et_2O$		CH_2Cl_2	40	2	79

[a] Isolated yield. [b] A complex reaction mixture was formed. [c] No reaction. The starting material was recovered.

3.2.5 Structural properties of DSF-IFs and DSF-BIF

To unequivocally confirm the structure of the synthesized dispiroindenofluorenes **20** and **21**, single crystal X-ray diffraction analyses of **20c**, **20h** and **21** were performed (Figure 9). In the case of **20c**, the fluorine atom was found to be disordered in two positions with almost equal occupancy. Interestingly, the distance between H(1) and H(16) atoms proved to be very close and equal to 1.88(3) Å, which is significantly lower than the sum of atom radii 2.40 Å.

The degree of molecular twist can be evaluated by the sum of torsional angles involved in the helical turn; in the case of **20c**, the three dihedral angles derive from C(16), C(17), C(18), C(19), C(20) and C(1) carbon atoms and the sum of these angles was calculated to be 18.5°, which indicates almost planar conformation of the terminal benzenes rings.

Concerning compound **21**, the degree of molecular twist was the sum of four dihedral angles derived from six C−C bonds (C(1), C(24), C(23), C(22), C(21), C(20), C(19)), and it was found to be 56.9°. This angle is bigger if compared to 18.5° of [5]helical dispiroindenofluorene **20c**, but smaller if compared to 68.7° of 7*H*-benzo[*c*]indeno[1,2-*g*]phenanthrene[133] or 87.5° of 1,2,3,4-tetrafluoro[6]helicene,[134] which are structurally related to dispiroindenofluorenes. The lower degree of molecular twist of **21** may derive by the two cyclopentadiene rings that promote a more opened helical shell and consequently reduce the

steric repulsion between the terminal benzene rings. The more widely opened helical shell of **21** could be also one of the factors strongly contributing to its configurational instability (see Section 3.3.1). The C(1)−C(19) and C(2)−C(18) distances were calculated as 3.127(2) and 4.512(2) Å, respectively. The C(19) −F(1) and F(1)−H(19) distances showed to be 2.717(2) and 2.651 Å respectively. With those values, there is no clear indication of intramolecular strong π···π, CH···π or CH···F interactions.

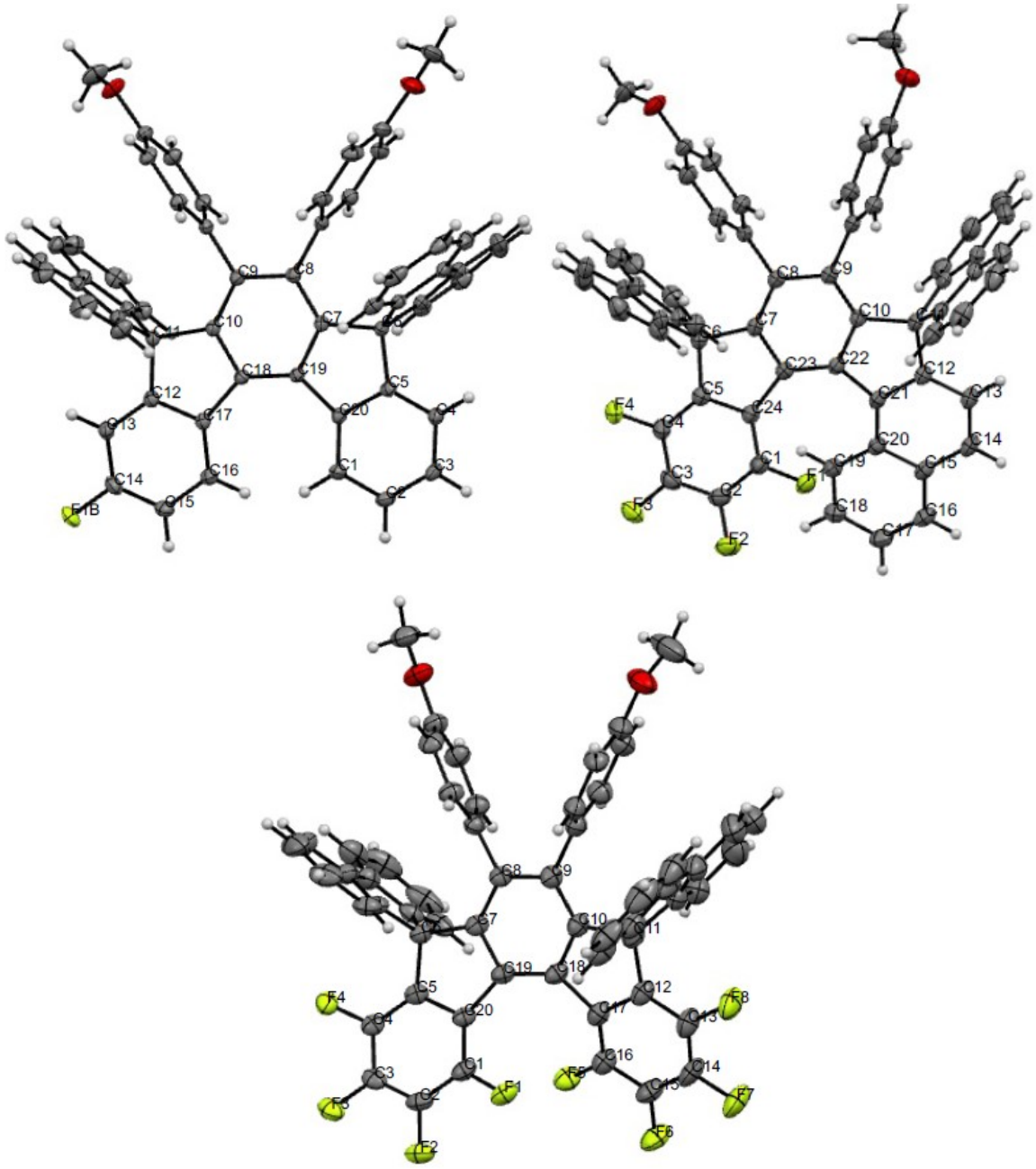


Figure 9. ORTEP drawing of **20c**, **21** and **20h** respectively from left to right (grey C, white H, green F, red O)

Regarding compound **20h**, bearing eight fluorine atoms on the indenofluorene scaffold, the degree of molecular twist was equal to 50.3° which is much higher if compared with that of the monofluorinated analogue **20c** (18.5°) and almost similar to the torsion of [6]helical indenofluorene **21** (56.9°). This result indicates that 8 fluorine atoms increase the molecular twist of indenofluorene core, probably due to bulkier fluorine atoms and to C−F···F−C interactions. As proof, the F(1)−F(5) distance is 2.509 Å, which is closer than the sum of the van der Waals radii (2.94 Å), and the angles between C(1)−F(1)−F(5) and F(1)−F(5)−C(16) are 91.95° and 89.60° respectively, indicating possible type III F···F interactions, as depicted in Figure 10.[135]

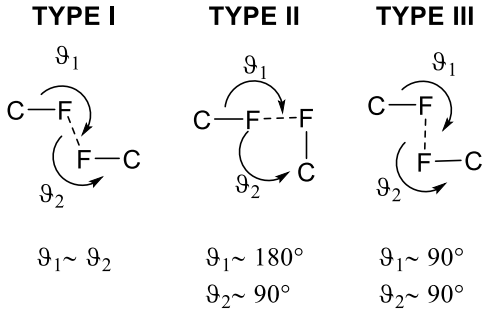


Figure 10. Graphical representation and classification of C−F···F−C interactions in accordance with the literature (Types I, II and III)

3.2.6 Photophysical properties of fluoro DSF-IFs and DSF-BIF

In our group, it was previously found that substitution in positions C(6) and C(7) of the dihydroindenofluorene scaffold does not affect the absorption properties of the dispiroindenofluorenes,[113] which showed also absorption spectra similar to the maternal unsubstituted analogue.[92, 112] Therefore we were interested to analyze the effect of fluorine atoms directly attached to the helical π-system of the dihydroindenofluorene moiety in the prepared fluorinated [5]helical dispiroindeno[2,1-*c*]fluorenes **20a-h** and [6]helical dispirobenzo[*c*]indeno[1,2-*g*]fluorene **21**.

With this purpose, I proceeded to the photo-physical characterization of all the synthesized compounds. Hence, the UV-Vis absorption and fluorescence spectra, as well as absolute quantum yields were measured. The obtained spectra are reported in Figure 11 and Figure 13 and the most relevant values are summarized in Table 11.

The absorption spectra were recorded using 10^{-5} M solution of samples in CH_2Cl_2. The results in Figure 11 clearly outline that compounds **20a-g** (mono- to tetrafluorinated

dispiroindenofluorenes) possess very similar absorption spectra and molar attenuation coefficients. They all present the characteristic strong absorption band at 308-312 nm and the moderate intensity band at 319-329 nm typical for all of known [5]helical dispiroindeno[2,1-*c*]fluorenes. [92, 112, 113] However, some minor differences can be noted in the absorption spectra: i) an additional band at higher wavelengths (342 nm) for the tetrafluorinated dispiroindeno[2,1-*c*]fluorene (**20g**); ii) a slightly red-shifted lower energy absorption of **20b** and **20e** (329, 327 nm respectively) both of which possess at least one fluorine in position C(2). Regardless those variations, we can claim that fluorination on one terminal benzene ring of the dispiroindenofluorene helical core does not have a significant effect on the absorption properties. Indeed, neither the number nor the position of fluorine atoms showed any influences on Uv-Vis spectra. The absorption spectrum of octafluorinated **20h**, which possesses four fluorine atoms on both terminal rings of the helical core, evinces much lower molar absorption. The lowest energy absorption bands of **20h**, at 345 nm, and of **20g** resemble each other and can be attributed to the increasing intramolecular charge transfer character of the HOMO→LUMO transition (Figure 12).

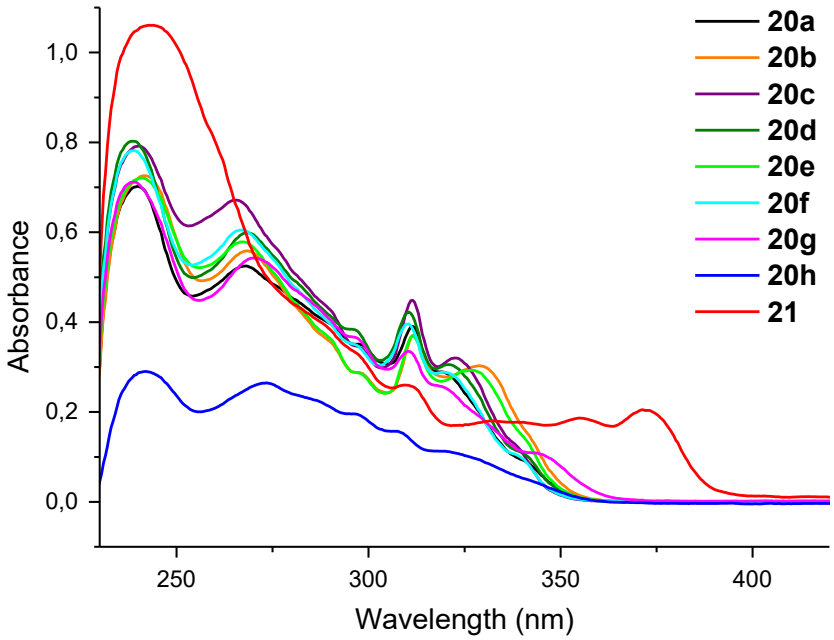


Figure 11. Absorption spectra of **20a-20h** and **21** (10^{-5} M) in CH_2Cl

Regarding the [6]helical dispirobenzo[*c*]indeno[1,2-*g*]fluorene **21** with an additional fused benzene ring on the helical core, its absorption spectrum shows the characteristic

absorption band at 310 nm followed by less resolved medium intensity bands (355, 371 nm) of lower energy absorptions. The observed red shift is a direct consequence of the extended π-electron delocalization, which is derived from elongation of helical structure. Moreover, TD-DFT calculations of **20a**, **20g** and **20h** were performed by Dr. David Nečas using B3LYP functional and extended 6-311++G(d,p) basis set with a continuum solvent model for CH_2Cl_2 on the optimized geometry of S_0 (B3LYP/6-311+G(d,p)). The calculated data for the optimized structures in the ground state S_0 suggest that the lowest-energy absorption band of **20a**, **20g** and **20h** corresponds to HOMO→LUMO transition with oscillator strengths 0.293, 0.185 and 0.093 respectively. Figure 12 illustrates HOMO and LUMO orbitals of **20a**, **20g** and **20h**. The LUMOs are distributed entirely over the dihydroindenofluorene core for all the three structures, whereas spatial location of HOMOs depends significantly on the number of fluorine atoms. While HOMO of monofluorinated **20a** extends over the helical core and over both methoxyphenyls groups, HOMO of octafluorinated **20h** is located just over the 4-methoxyphenyl substituents.

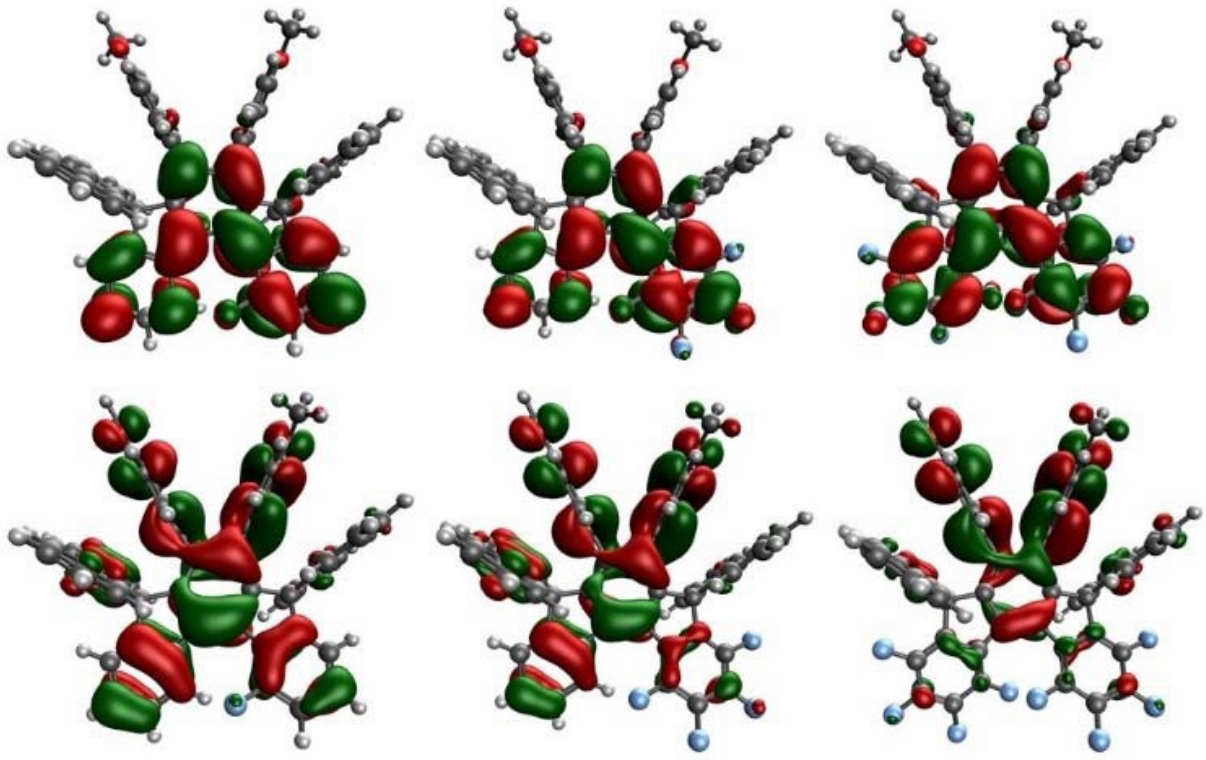


Figure 12. DFT calculated HOMOs (bottom) and LUMOs (up) of **20a**, **20g** and **20h**

Emission spectra and absolute quantum yields were measured using micromolar solutions of the samples in dichloromethane with λ = 290-300 nm as excitation wavelength. All

the spectra, reported in Figure 13, consist of an unresolved broad band with maxima ranging from 386 to 395 nm for **20a**-**20g**, 413 nm for **20h** and 412 nm for **21** (see also Table 11 and Figure 14).

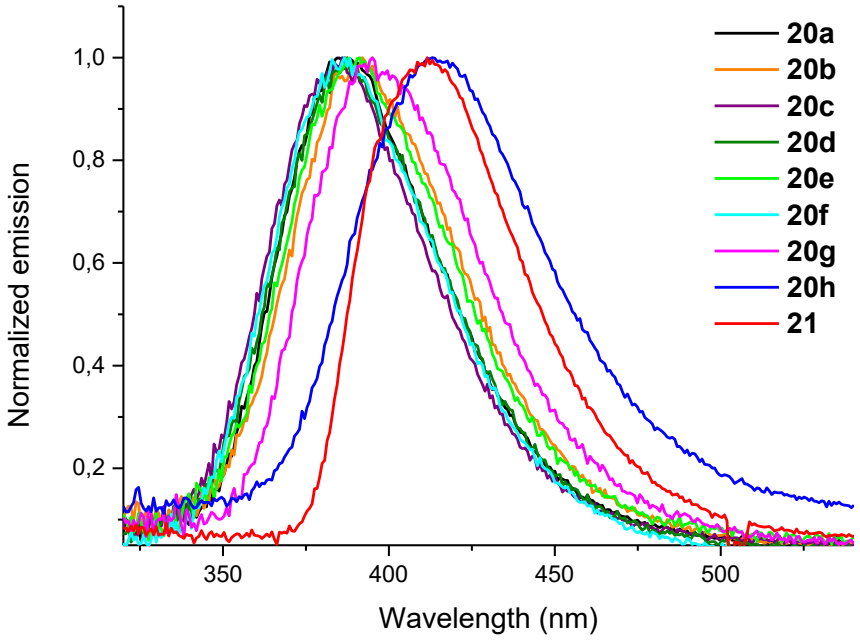


Figure 13. Normalized emission spectra of **20a**-**20h** and **21** in CH_2Cl_2

Table 11. Photophysical properties of **20a**-**20h** and **21** in dichloromethane

20 or **21**	λ_{abs}/nm ($\varepsilon/10^4$ mol^{-1}·dm^3·cm^{-1})	λ_{em}/nm	Φ_s [a]
20a	298 (3.50), 312 (3.85), 319 (2.88)	387	0.48
20b	298 (2.85), 312 (3.71), 329 (3.03)	392	0.52
20c	298 (3.45), 312 (4.45), 323 (3.20)	386	0.47
20d	296 (3.84), 310 (4.22), 321 (3.05)	387	0.49
20e	298 (2.85), 312 (3.70), 327 (2.93)	391	0.42
20f	296 (3.51), 310 (3.96), 320 (2.89)	387	0.44
20g	296 (3.67), 310 (3.34), 342 (1.09)	395	0.45
20h	297 (1.96), 308 (1.56), 319 (1.13)	413	0.89
21	309 (2.60), 355 (1.86), 371 (2.05)	412	0.92[b]

[a] Absolute quantum yield, λ_{exc} = 290 nm.
[b] λ_{exc} = 300 nm.

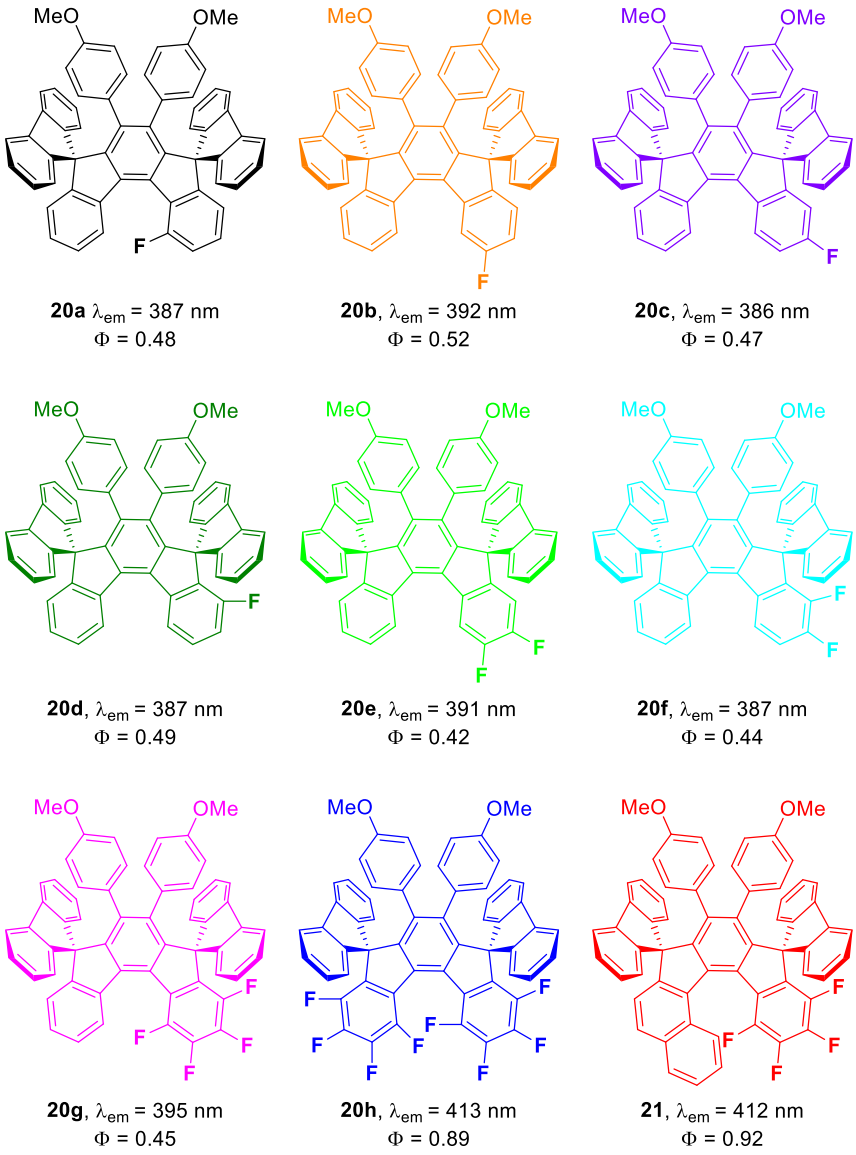


Figure 14. Structures and selected photo-physical properties of compounds **20a**-**20h** and **21**

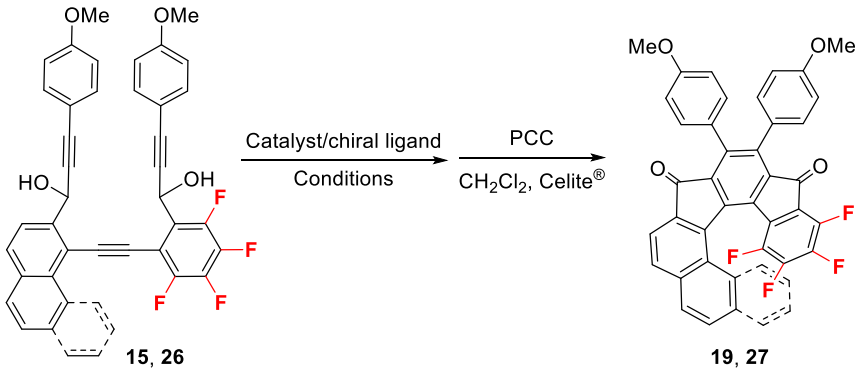
Although, the comparison of photophysical properties of fluorinated dispiroindenofluorenes with non-fluorinated ones is intricate,[113] emission maxima of mono- and tetrafluorinated **20a**-**g** appear slightly red-shifted up to ~15 nm reached by the tetrafluorinated **20g**. The octafluorinated dispiroindenofluorene **20h** hit the highest bathochromic shift (~33 nm) among the series. This compound also showed higher absolute quantum yield: 0.89 instead of ~0.50, which is the average value of **20a**-**20g**. This is also the highest measured quantum yield for all the [5]helical dispiroindenofluorenes so far synthesized. [92, 113] Surprisingly **20h** showed also high Stokes shift of 7135 cm^{-1} that is more than 2000 cm^{-1} higher than those of **20a**-**20g**. With regard to [6]helical tetrafluorinated dispirobenzo[*c*]indeno[1,2-*g*]fluorene **21**, its emission

maximum (412 nm) was red shifted as well and its absolute quantum yield was 0.92, the highest value of the dispiroindenofluorenes synthesized in this work.

In conclusion, these findings prove that the extension of π-system from [5]helical dispiroindenofluorenes to [6]helical dispirobenzo[*c*]indeno[1,2-*g*]fluorene or the intramolecular charge transfer promoted by polyfluorination of terminal benzene rings in dispiroindenofluorenes are responsible for the bathochromic shifts of emission showed by **20h** and **21**. The high fluorescence quantum yields of **20-21** in general and those of **20h** and **21** in particular are by an order of magnitude higher if compared with those of structurally related fluorinated [6]helicenes[136] that showed quantum yields of 0.033 and 0.046 for tetrafluorinated and octafluorinated, respectively.

3.3 Synthesis of unsymmetrical fluorinated [6] and [7]helical dihydroindenofluorenes: enantioselective cyclotrimerization

In the previous Section 3.2, I demonstrated that [2+2+2] cyclotrimerization proved to be a straightforward method for the construction of variously fluorinated indeno[2,1-*c*]fluorenes. Since such compounds possess the helicene-like structure, which have been attracted attention in scientific community for their potential application to optical or electronic functional materials, I wanted to evaluate a possibility of enantioselective cyclotrimerization as a method for the synthesis of enantiopure [6] and [7]dispiroindeno[2,1-*c*]fluorene. To achieve the new proposal, enantioselective cyclotrimerizations of triynediols **15** and **26** were tested with different transition metal complexes and chiral ligands under various conditions (Scheme 24). The results are reported in Sections 3.3.1 and 3.3.2.

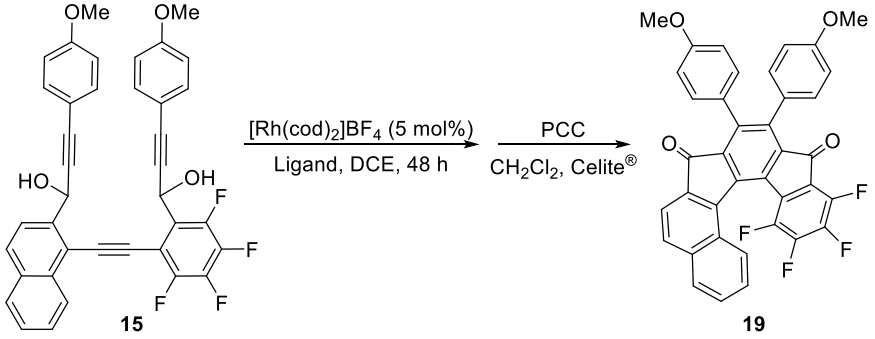


Scheme 24. Synthesis of **19** and **27** by enantioselective [2+2+2] cyclotrimerization, followed by oxidation

3.3.1 Configurational stability of [6]helical dihydroindenofluorenone

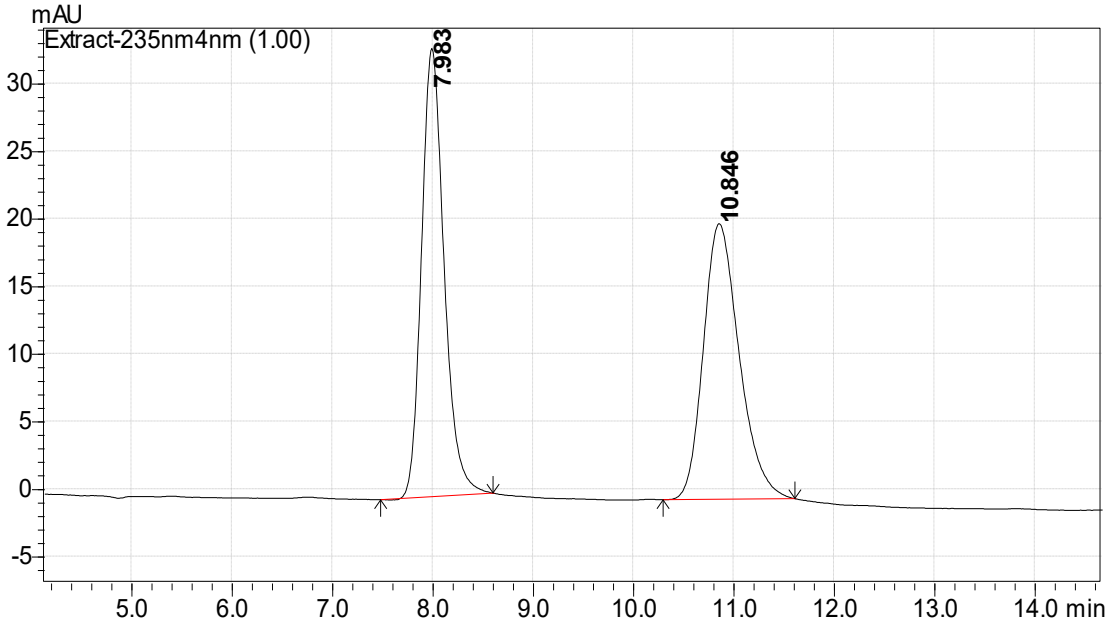
Initially, triynediols **15** was subjected to cyclotrimerization with $[Rh(cod)_2]BF_4$ and (*S*)-SEGPHOS as chiral ligand for 48 h in DCE.[114] The obtained crude product was immediately oxidized with PCC (Table 12). The cyclotrimerization at 80 °C gave the desired [6]helical dihydroindenofluorene, **19**, in 48% yield without asymmetric induction (Entry 1). When the experiment was repeated at a lower temperature of 30 °C (Entry 2), the yield decreased drastically, due to the low conversion of starting material, and the enantiomeric excess was again 0%. For an example, see the chromatogram of **19** (Figure 15), when the cyclotrimerization was carried out under the conditions described in Entry1.

Table 12. Enantioselective cyclotrimerization of **15**



Entry	Ligand (6 mol%)	T (°C)	ee (%)[a]	**19**, Yield (%)[b]
1	(*S*)-SEGPHOS	80	0	48
2	(*S*)-SEGPHOS	30	0	6

[a] ee determined by HPLC with a chiral stationary phase.
[b] Isolated yield of last two steps.



Peak Table

Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		7.983	50.63794	518797	33160	7.477	8.597	50.6379
2		10.846	49.36206	505725	20393	10.293	11.605	49.3621

Figure 15. Selected chromatogram of compound **19** obtained using HPLC with Chiralpak IA column and 80/20 Heptane/*i*-PrOH as eluent

The absence of asymmetric induction in **19** can be rationalized assuming a low racemization barrier. In order to have more insights, we performed ^{1}H-NMR spectra of **19** at different temperatures. Interestingly the ^{1}H-NMR spectrum of **19** revealed that proton Ha **(**the hydrogen atom in position 14 of the indenofluorenone scaffold, see Figure 16) is coupled through-space with fluorine in position 1. Indeed, Ha appears as a doublet of doublets with the

coupling constants of 4 and 8 Hz (blue line in Figure 16). Additional ^{1}H spectra measured with ^{19}F decoupling showed that the same proton Ha became a simple doublet with *J* constant of 8 Hz (red line in Figure 16). The disappearance of 4 Hz *J* constant in the decoupled spectrum clearly indicates that this coupling comes from the interaction with the nearest fluorine atom. Particularly it comes from the close contact of these two atoms leading to an overlap of their electron clouds.

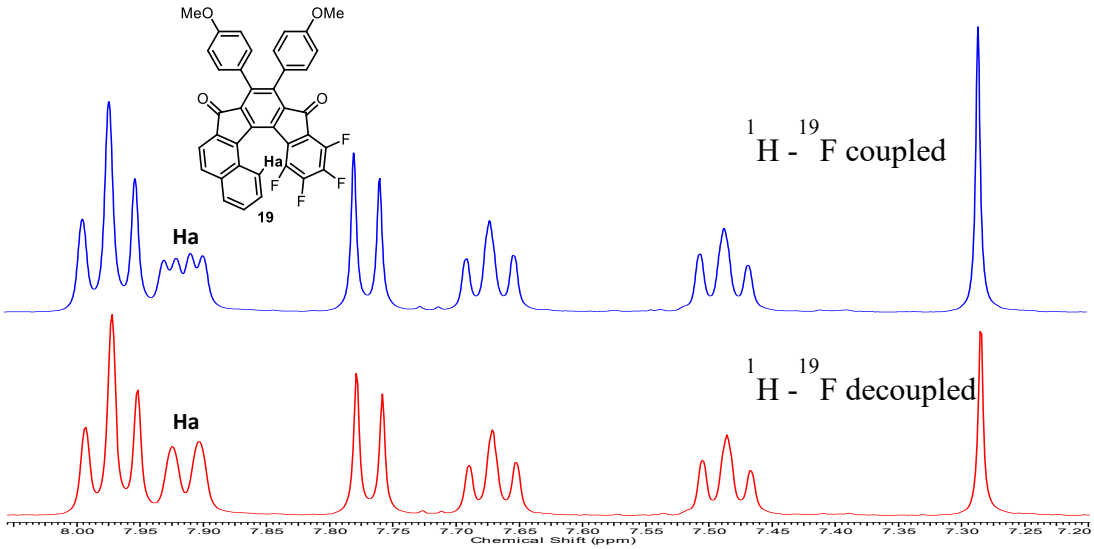


Figure 16. Enlarged region from 8.0 to 7.0 ppm of **19** ^{1}H NMR spectrum. The blue line shows the coupled spectrum with fluorine, while the red line is the decoupled ^{1}H-^{19}F spectrum.

To have more insights, I performed ^{1}H NMR study of **19** at different temperatures ranging -40 to 55°C (Figure 17). As it can be noted in the following pictures, at the lowest temperature of -40 °C the signal of Ha is shielded at 7.87 ppm and its coupling constant with fluorine is 3.6 Hz. However, by increasing the temperature up to 55 °C, Ha appears more deshielded (going from 7.87 to 7.91 ppm) and having a larger coupling constant of 4.1 Hz. A similar temperature dependence leading to a higher chemical shift at a higher temperature was also found for unsubstituted [6]helicene and tetrafluoro[6]helicene.[134] Interestingly there are not any significant differences between the spectrum measured at room temperature and the one at 55 °C. Those findings can be rationalized assuming that at lower temperature the molecule is conformational more rigid and the conformer with the helicene-type structure is more populated. This can explain the upfield shift of Ha, which is placed above the plane of aromatic system. When temperature raises the molecule interconverts faster from one configuration to the opposite one with the effect of spending more time in the flat conformation.

The increased average time in the planar position reflects the greater-coupling constant between Ha(14) and F(1) as well as the downfield shift of Ha. Moreover, since the spectrum at room temperature shows the same $J_{H\text{-}F}$ of spectrum at 55 °C and similar chemical shift, the interconversion of *P* and *M* configuration of helicene can be assumed to happen already at room temperature.

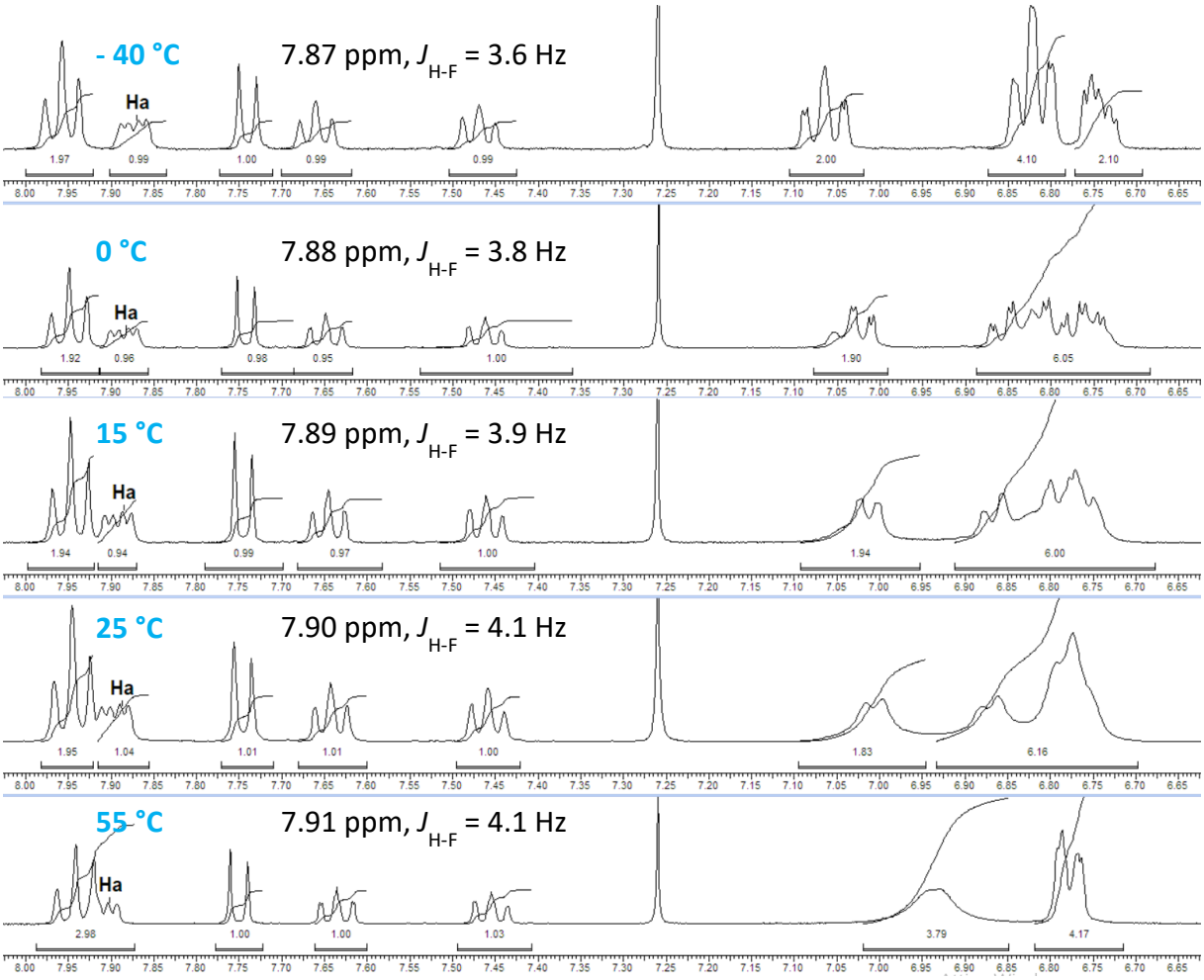


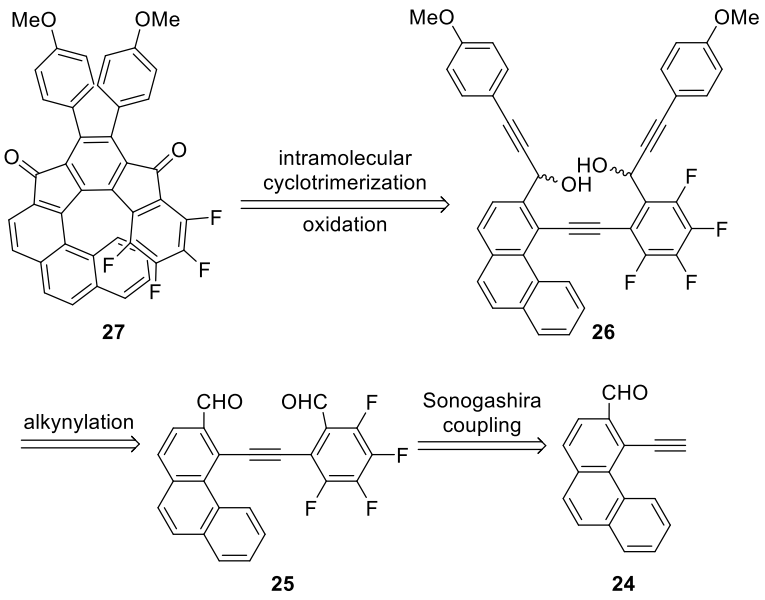
Figure 17. Enlarged region from 8.0 to 6.6 ppm of **19** ^{1}H NMR spectrum measured at different temperatures

This conclusion is also supported by literature data about racemization barrier calculated for similar molecules. The racemization barrier of 7*H*-benzo[*c*]indeno[1,2-*g*]phenanthrene was calculated to be ~29 kcal·mol^{-1},[133] whereas for 1,2,3,4-tetrafluoro[6]helicene was 38.9 kcal·mol^{-1}.[136] The closest structurally similar compound is benzo[*d*]naphtha-[1,2-*d*']-benzo-[1,2-*b*:4,3-*b*']-dithiophene which showed racemization barrier of 23.7 kcal·mol^{-1}. Indeed, this compound proved to be configurationally unstable at 22 °C and underwent fast racemization in

$CHCl_3$.[137] Therefore, from the all data collected, the configurational instability of [6]helical dihydroindenofluorenone is highly likely.

3.3.2 Enantioselective cyclotrimerization of [7]helical benzoindaceno[2,1-*c*]phenanthrenedione

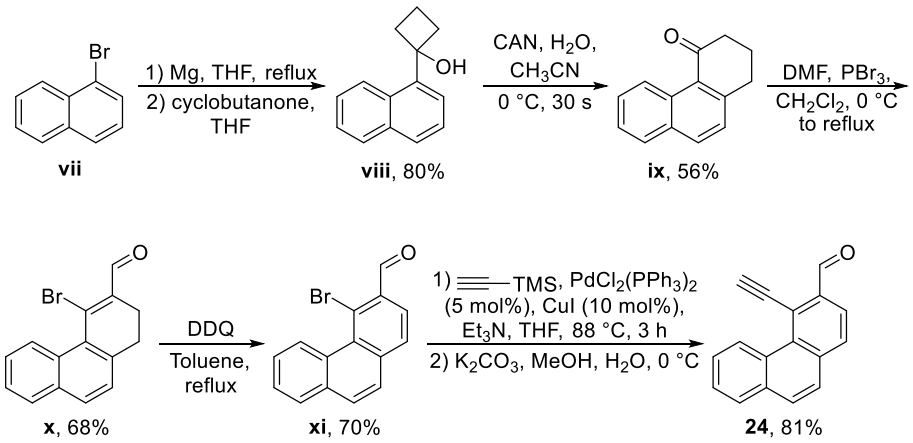
For the synthesis of [7]helical benzoindaceno[2,1-*c*]phenanthrenedione **27**, the usual synthetic pathway was applied (Scheme 25): i) intramolecular [2+2+2] cyclotrimerization of triynediols **26** followed by oxidation of the crude mixture with PCC; ii) the triynediols were prepared by alkynylation reaction of dialdehydes **25**; iii) **25** was obtained by Sonogashira cross coupling reaction between 2,3,4,5-tetrafluoro-6-iodobenzaldehyde (**11g**) and 4-ethynylphenanthrene-3-carbaldehyde **24**.



Scheme 25. Retrosynthetic analysis of [7]benzoindaceno[2,1-*c*]phenanthrenedione

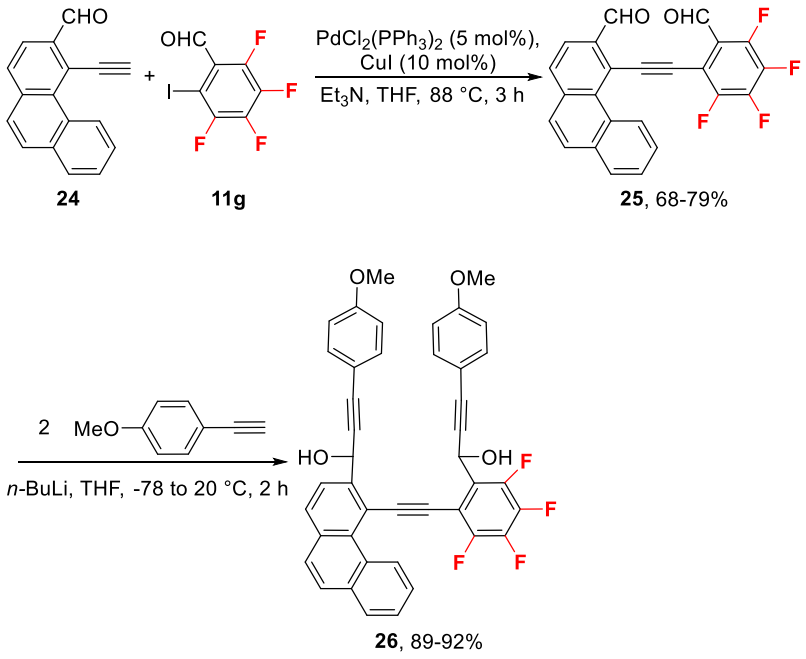
Synthesis of the starting material 4-ethynylphenanthrene-3-carbaldehyde (**24**) was achieved by 5 steps procedure (Scheme 26): i) a reaction between cyclobutanone and naphthalen-1-ylmagnesium bromide which was prepared *in situ* by reaction of 1-bromonaphthalene **vii** and magnesium providing 1-(naphthalen-1-yl)cyclobutan-1-ol **viii** in 80% isolated yield; ii) oxidative ring-opening/cyclization reaction of **viii** with CAN to afford 2,3-dihydrophenanthren-4(1*H*)-one **ix** in 56% yield;[138] iii) combined enolization and Vilsmeier–Haack reaction for the synthesis of 4-bromo-1,2-dihydrophenanthrene-3-

carbaldehyde **x** in 68% yield; iv) oxidation with DDQ to gain the fully aromatized phenanthrene ring **xi** (70% yield); vi) Sonogashira cross coupling and deprotection to obtain the target compound **24** in 81% overall yield for the last two steps.



Scheme 26. Synthetic pathway for the formation of starting material **24**

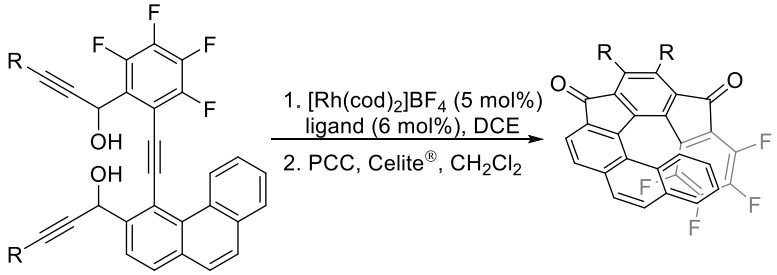
Compound **24** was subjected to Sonogashira cross coupling reaction with **11g**, whose synthesis was described in Section 3.2.1 (Scheme 17). The cross-coupling reaction afforded dialdehyde **25** in 68-79% yield. The following alkynylation with 1-ethynyl-4-methoxybenzene gave triynediols **26** in the range 89-92% yield (Scheme 27).



Scheme 27. Synthetic pathway for the formation of triynediols **26**

For enantioselective cyclotrimerization of **26** the well-known catalytic system based on $[Rh(cod)_2]BF_4$/phosphine chiral ligand[139, 114] was tried as the first attempt (Table 13). It is important to note that the catalytic system was previously prepared by bubbling H_2 gas through the mixture of $[Rh(cod)_2]BF_4$/ligand and DCE for 45 min. This treatment is required for a better displacement of the cyclooctadiene ligand upon reduction, allowing the new ligand to coordinate the metal.[140] The substrate **26** was added after changing the hydrogen atmosphere to the argon one. The reaction was carried out at 60 °C for 48 h. The obtained reaction mixture was immediately subjected to oxidation step without purification. Therefore, the yields reported in Table 13 refer to overall yields after two steps.

Table 13. Enantioselective cyclotrimerization of **26** with Rh-catalyst



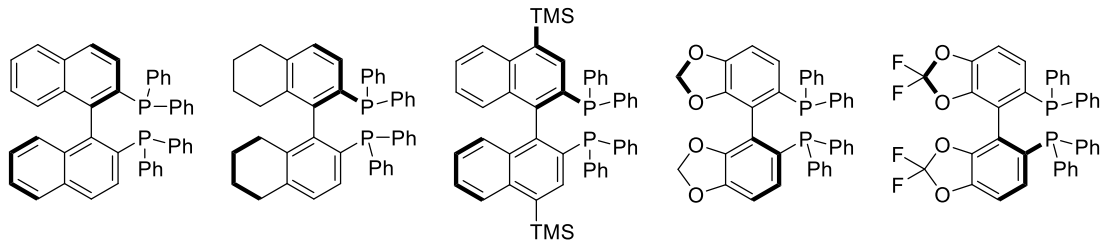
26, R = *p*-$MeOC_6H_4$ **27**

Entry[a]	Ligand	Solvent	(M)	T (°C)	**27**, Yield (%)[b]	ee (%)[c]
1	(*S*)-SEGPHOS	DCE	0.1	60	8	48
2	(*R*)-BINAP	DCE	0.1	60	7	35
3	(*S*)-DIFLUORPHOS	DCE	0.1	60	9	51
4	(*R*)-TMS-BINAP	DCE	0.1	60	15	44
5	(*R*)-H_8-BINAP	DCE	0.1	60	5	40
6	(*S*)-SEGPHOS	DCE	0.01	60	4	27

[a] Reactions were carried out on 0.1 mmol scale. [b] Isolated yield after oxidation reaction.
[c] Determined by HPLC with a chiral stationary phase

Several phosphine ligands (see Scheme 28 for molecular structures) were screened but unfortunately poor isolated yields of the desired diketone **27** were obtained (4-15%). The poor yields are due to side-products formation, which will be discussed in the next Section (3.4). Because [7]helical benzoindaceno[2,1-*c*]phenanthrenedione skeleton in **27** is more configurationally stable in comparison with the [6]helical homologue **19** higher asymmetric induction was achieved. The best enantiomeric excess (51% ee) was achieved with (*S*)-DIFLUORPHOS, but the yield was mere 9% (Entry 3). The use of other phosphines e.g. (*R*)-BINAP like-ligands and (*S*)-SEGPHOS, didn't give better results (Entries 1, 2, 4 and 5): ee were in the range 35-48%. Interestingly, the last experiment showed that the ee is highly

dependent on concentration, since a more diluted solution (0.01 M vs. 0.1 M) afforded lower enantiomeric excess (only 27% ee) together with a lower yield (4%, entry 6).



(*R*)-BINAP (*R*)-H_8-BINAP (*R*)-TMS-BINAP (*S*)-SEGPHOS (*S*)-DIFLUORPHOS

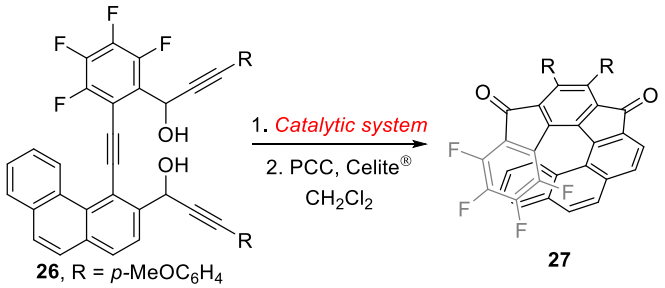
Scheme 28. List of chiral ligands used for cyclotrimerization of **26** with $[Rh(COD)_2]BF_4$

In order to improve yields of **26** as well as asymmetric induction, other catalytic systems were screened (Table 14). Particularly, I focused on [Ni] complexes due to the recent interesting results reported by Starý's group for Ni-catalyzed enantioselective cyclotrimerizations.[141] Firstly, conditions for racemic cyclotrimerization were screened in order to increase the yield by suppressing the formation of side-products, which occur during the reaction (see next Section 3.4).

Furthermore, in order to avoid the use of a glove-box technique which is required for manipulation of highly sensitive $Ni(cod)_2$, the *in situ* reduction of Ni(II) salts to Ni(0) was selected as a more convenient method. The optimization of conditions were done by screening several kind of Ni sources, solvents, temperatures, reductants and amounts of ligands. During the optimization, $Ni(acac)_2$ was found to be the best source of Ni, whereas $NiCl_2$ did not catalyze the reaction. The best reducing agent was *i*-PrMgCl, while *n*-BuLi and Zn were unsuitable. Screening the ratio between $Ni(acac)_2$ and Grignard reagent (Entries 1-3, Table 14) demonstrated that 1/1 ratio is sufficient (Entry 2) with up to 30% NMR yield. This result was important in order to avoid excess of Grignard reagent that can deprotonate the OH groups of **26**. Increasing the temperature to 60 °C was detrimental for the reaction (Entry 4). The use of IMes as ligand gave the starting material at room temperature and after heating (Entry 5). The amount of ligand (PPh_3) proved to be pivotal for the outcome of the experiment: indeed with 1/1 ratio $Ni(acac)_2/PPh_3$ the reaction didn't take place (Entry 7) even with an increased catalytic load (40% instead of 20%), while 4/1 ratio resulted in the formation of the desired compound but without any improvement in the yield which was steady at 25% (Entry 6). The best result with $Ni(acac)_2$/*i*-PrMgCl system was found by changing the solvent to toluene instead of THF (Entry 8) which afforded **27** in isolated 66% yield. However the use of BINAP as ligand in toluene didn't catalyze the reaction (Entry 9) and starting material was recovered. Lowering the

catalyst's load to 20% instead of 40% was not successful (Entries 10-12) and only traces of the product were detected by ^{1}H and ^{19}F NMR of the crude mixture; 30 mol% of the catalyst furnished **27** in mere 20% yield (Entry 13). Attempts to decrease the amount of ligand, showed that the minimal amount required is 2/1 ratio PPh_3/$Ni(acac)_2$ (Entry 14), which resulted in a high 66% yield. A lower ratio like 1/1 provided only traces of product (Entry 15). Shortly, the best result (Entry 14) involved 40% of $Ni(acac)_2$, 1/1 ratio between [Ni] and *i*-PrMgCl, 2/1 ratio [Ni]/ligand, toluene as the solvent and 20 °C temperature. It is also important to note that the increased dilution, when going from THF to toluene, is due to the low solubility of **26** in this solvent.

Table 14. Ni-catalyzed racemic cyclotrimerization of **26** under different reaction conditions (Ni^{II}-salts)



26, R = *p*-$MeOC_6H_4$ **27**

Entry[a]	$Ni(acac)_2$ (mol%)	*i*-PrMgCl (mol%)	Ligand (mol%)	Solvent	(M)	T (°C)	t (h)	**27**, Yield (%)[b]
1	20	90	PPh_3, 40	THF	0.025	20	2	21 (29)
2	20	20	PPh_3, 40	THF	0.033	20	15	27 (30)
3	20	200	PPh_3, 40	THF	0.033	20	15	(21)
4	20	20	PPh_3, 40	THF	0.025	60	15	9
5	20	40	IMes, 40	THF	0.025	20-60	15	-[c]
6	40	40	PPh_3,160	THF	0.025	20	15	25
7	40	40	PPh_3, 40	THF	0.025	20	15	traces[c]
8	40	40	PPh_3, 160	toluene	0.01	20	15	66
9	40	40	BINAP, 80	toluene	0.01	20	15	-[c]
10	20	20	PPh_3, 60	toluene	0.01	20	15	traces[c]
11	20	20	PPh_3, 80	toluene	0.01	20	20	(13)
12	20	20	PPh_3, 40	toluene	0.01	20	20	traces[c]
13	30	30	PPh_3, 60	toluene	0.01	20	20	(20)
14	40	40	PPh_3, 80	toluene	0.01	20	20	63 (66)
15	40	40	PPh_3, 40	toluene	0.01	20	20	traces[c]

[a] Cyclotrimerization reaction was followed by direct oxidation of the crude mixture. [b] Isolated yield after oxidation (^{19}F NMR yields are given in parenthesis; α,α,α-Trifluorotoluene was used as internal standard). [c] Starting material was recovered.

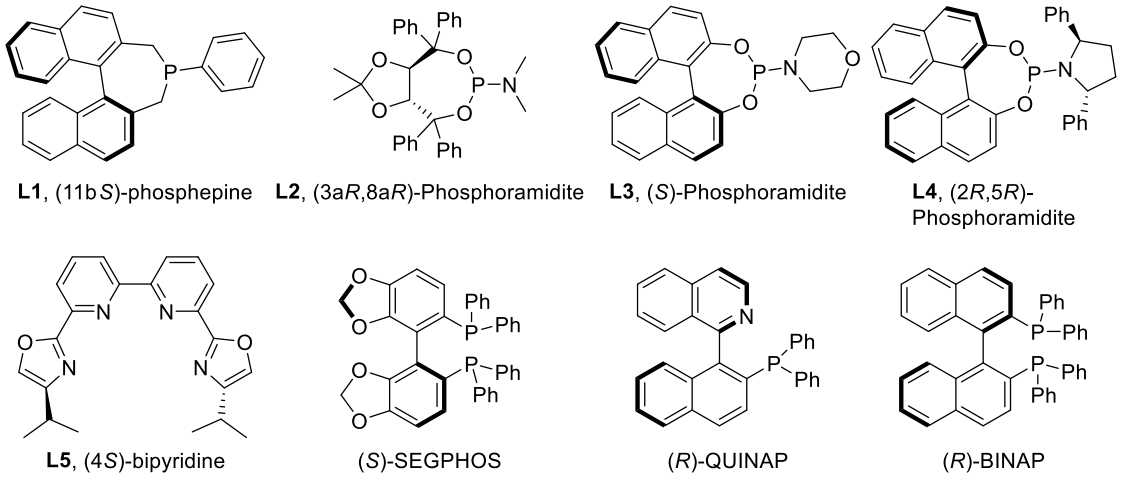
I also decided to test cyclotrimerization of **26** with the new commercially available Ni(cod)(DQ), which is a bench stable source of Ni (0).[142] As far as I know, this is the first example in which this catalyst has been employed for [2+2+2] cyclotrimerization. Therefore, it was necessary to find the conditions for such a transformation (Table 15). PPh_3 was selected as ligand due to the previous successful results with $Ni(acac)_2$. During the screening of conditions, it was soon clear that high temperature was required in order to promote the catalytic cycle; indeed formation of product **27** was observed in 37% NMR yield after increasing the temperature from 20 to 100°C (Entry 1), whereas the reaction didn't occur if conducted at room temperature in toluene (Entry 2). Premixing Ni(cod)(DQ) with PPh_3 ligand at 100 °C and adding the starting material after 15 min at room temperature, didn't promote the reaction even after increasing again the temperature to 80 °C (Entry 3). As in the previous case with $Ni(acac)_2$, THF proved to be not a suitable solvent for this cyclotrimerization (Entries 4-6). It was demonstrated that toluene was again the best option and **27** was obtained in 55% yield (^{19}F NMR yield) by refluxing **26** in toluene for 24 h (Entry 7). At lower temperature, 80 °C, a drop in yield was observed (22%, Entry 8). Irradiation using 200 W light bulb did not promote the reaction in DCE (Entry 9); however, the reaction proceeded under these conditions successfully in toluene, albeit in slightly lower yield of 36% (Entry 10).

Table 15. Ni-catalyzed cyclotrimerization of **26** under different reaction conditions (Ni(cod)(DQ) (10 mol%), PPh_3 (20 mol%))

Entry[a]	Solvent	(M)	T (°C)	t (h)	**27**, Yield (%)[b]
1	toluene	0.01	20 to 100	20	35 (37)
2	toluene	0.01	20	72	-[c]
3	toluene	0.01	100 to 80	20	traces
4	THF	0.025	70	20	(20)
5	THF	0.0125	60 (MW)[d]	2	traces
6	THF	0.025	80 (MW)[d]	2	(18)
7	toluene	0.025	100	24	53 (55)
8	toluene	0.025	80	20	(22)
9[e]	DCE	0.01	20	12	(7)
10[e]	toluene	0.01	20	12	(36)

[a] Cyclotrimerization reaction was followed by direct oxidation of the crude product. [b] Isolated yield after oxidation (^{19}F NMR yields are given in parenthesis; α,α,α-Trifluorotoluene was used as internal standard). [c] Starting material was recovered. [d] Reaction was carried out in a microwave reactor. [e] Reaction was performed under irradiation with visible light (200 W).

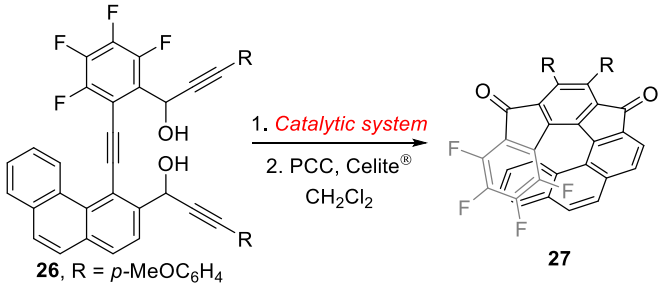
With the best conditions found for racemic cyclotrimerization with $Ni(acac)_2$ and Ni(cod)(DQ), the enantioselective version was tried. Results are depicted in Table 16 and a list of the employed ligands is illustrated in Scheme 29. When $Ni(acac)_2$ was tested, low yield together with low ee were obtained (Entries 1-4, Table 16). Particularly (*R*)-BINAP and (4*S*)-bipyridine **L5** did not catalyze the reaction and the starting material was recovered (Entry 1 and 4). Monodentate ligands **L1** and phosporamidite **L4** gave low yields 5% and 2%, respectively, and poor ee 7% and 5% respectively (Entries 2 and 3). Ni(cod)(DQ) gave better results in terms of yield with phosporamidite ligands **L2** and **L4** which afforded the product in 24% isolated yields but poor ee, 3% and 4%, respectively (Entries 5 and 7). (*S*)-SEGPHOS, which gave 48% ee when employed with Rh-catalyst (see previous Table 13), with Ni(cod)(DQ) afforded **27** in 11% yield without asymmetric induction (Entry 9). Bipyridine **L5** resulted in 9% ee and poor yield of 7% (Entry 10). The best ee with this catalyst was obtained using (*R*)-QUINAP as ligand: up to 16% ee and 14% isolated yield. (Entry 11). Performing the reaction under irradiation with visible light and (*R*)-QUINAP or (*R*)-BINAP as ligands improved neither the asymmetric induction, 12-6% ee, nor the yields, 4%, (Entries 12 and 13).



Scheme 29. List of chiral ligands used with Nickel catalyst

In conclusion, the use of Ni catalysts didn't improve the asymmetric induction of **27**, indeed the best result was obtained by Rh-catalyzed enantioselective cyclotrimerization, which gave the product in up to 51% ee (Table 13). As proof of the results regarding enantioselective cyclotrimerizations for the synthesis of [7]helical benzoindaceno[2,1-*c*]phenanthrenedione **27**, the chromatogram of the $[Rh(COD)_2]BF_4$/DIFLUORPHOS catalyzed reaction is reported below (Figure 18 and Figure 19).

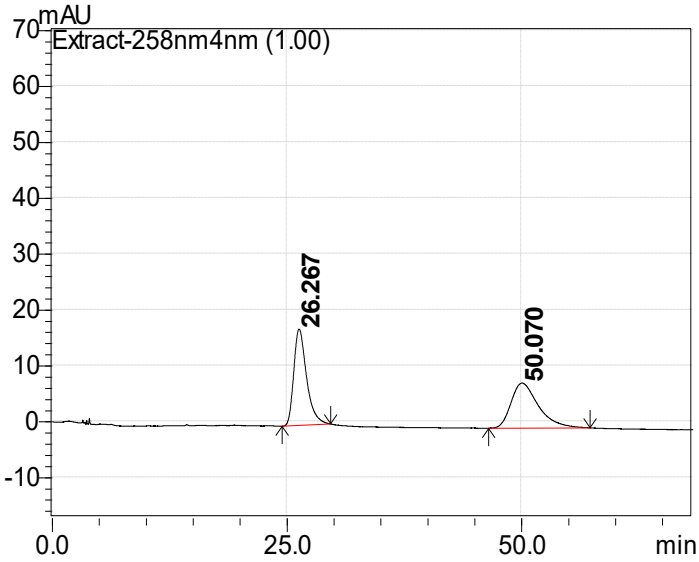
Table 16. Ni-catalyzed enantioselective cyclotrimerization of **26** under different reaction conditions



26, R = *p*-$MeOC_6H_4$ **27**

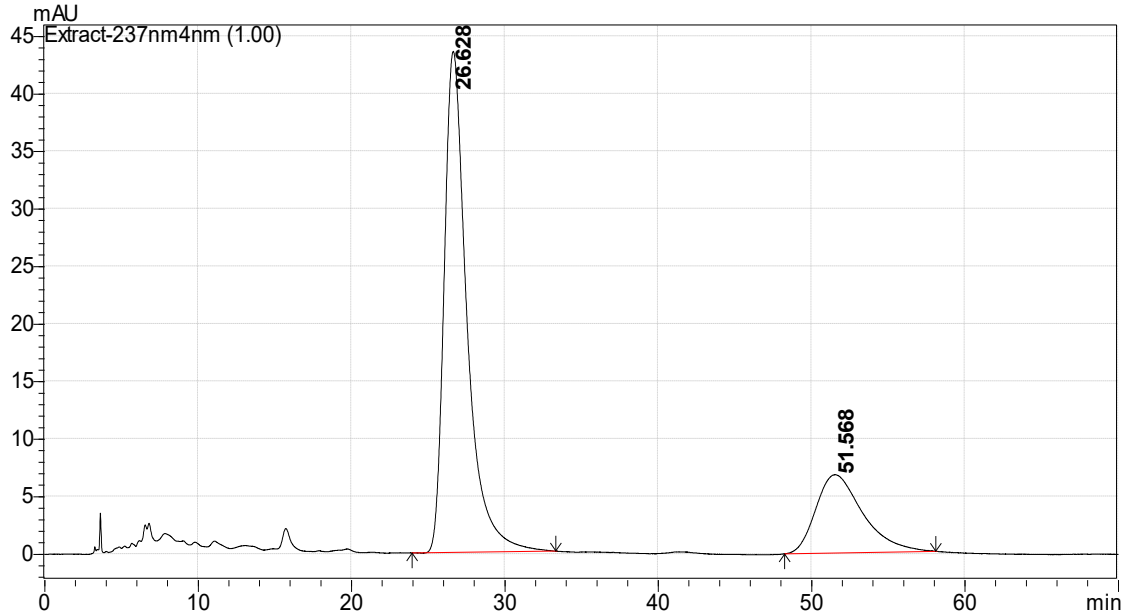
Entry[a]	Catalytic system (mol%)	Ligand (mol%)	Solvent	(M)	T (°C)	t (h)	**27**, Yield (%)[b]	ee (%)[c]
1	$Ni(acac)_2$ (40), *i*-PrMgCl (40)	(*R*)-BINAP, 80	toluene	0.01	20		-[e]	nd
2		L1, 80	toluene	0.01	20		5	7
3		L4, 40	toluene	0.01	20		2	5
4		L5, 40	toluene	0.01	20		-[e]	nd
5	Ni(cod)(DQ) (10)	L2, 20		0.025	100		24	3
6		L3, 20		0.025	100		4	5
7		L4, 20		0.025	100		24 (28)	4
8[f]		L4, 20		0.025	100		traces	nd
9		(*S*)-SEGPHOS, 20		0.025	100		11	0
10		L5, 20		0.025	100		(7)	9
11		(*R*)-QUINAP, 20		0.025	80		14	16
12		(*R*)-QUINAP, 20		0.01	hv[d]		4	12
13		(*R*)-BINAP, 20		0.01	hv[d]		4	6

[a] Cyclotrimerization reaction was followed by direct oxidation of the crude product. [b] Isolated yields after oxidation (^{1}F NMR yields are given in parenthesis; α,α,α-Trifluorotoluene was used as internal standard). [c] ee determined by HPLC. [d] Reaction was performed under irradiation with visible light (200 W). [e] Starting material was recovered. [f] The ligand was mixed with the catalyst and stirred for 30 min, before the addition of **26**.



Peak#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1	26.267	49.93245	1636574	17258	24.469	29.632	49.9325
2	50.070	50.06755	1641002	8063	46.475	57.259	50.0675

Figure 18. HPLC of (rac)-**27**. Column Daicel Chiralpak® IC-3/IC, *n*-heptane/IPA 80/20, flow rate 1 mL/min, UV 258 nm, t_S = 26.3 min, t_R = 50.1 min

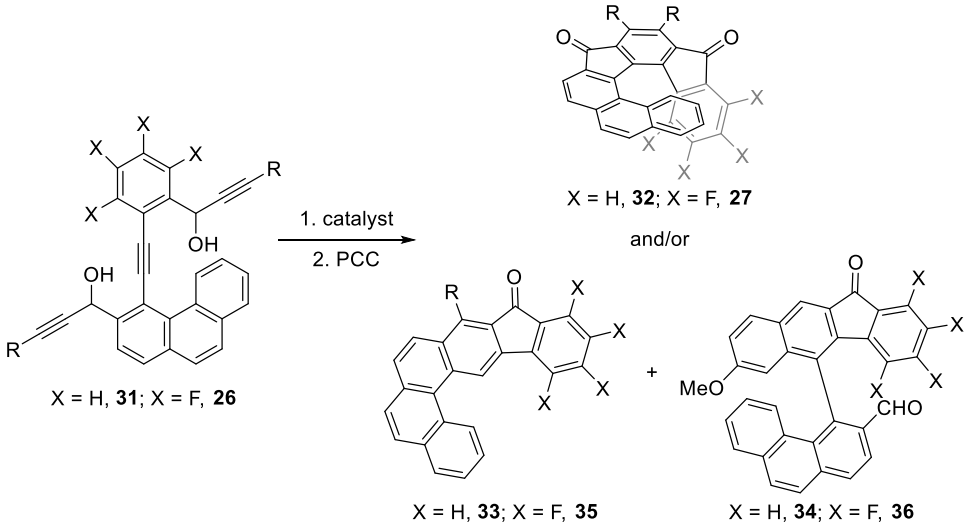


Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1			26.628	75.66449	4487238	43544	23.957	33.323	75.6645
2			51.568	24.33551	1443203	6804	48.245	58.091	24.3355

Figure 19. HPLC of the best ee obtained with $[Rh(COD)_2]BF_4$ (Entry 3, Table 13). Column Daicel Chiralpak® IC-3/IC, *n*-heptane/IPA 80/20, flow rate 1 mL/min, UV 237 nm, t_S = 26.6 min, t_R = 51.6 min

3.4 Synthesis of unsymmetrical fluorinated [7]helical indenofluorenones: cyclotrimerization vs. dehydro-Diels-Alder reaction pathways

During the study of enantioselective cyclotrimerization for the synthesis of enantioenriched [7]helical benzoindaceno[2,1-*c*]phenanthrenediones **27**, I noticed that the yield of this reaction was hampered by side-products formation. Therefore, I decided to look into the nature of those side-reactions in order to find the best conditions to control the selectivity of the cyclotrimerization (Scheme 30). Herein I would like to report the study of [2+2+2] cyclotrimerization for the synthesis of non-fluorinated [7]helical benzoindaceno[2,1-*c*]phenanthrenedione **27** and its fluorinated analogue **32**, by employing several catalytic systems based on Rh, Ru, Co, Ni complexes (Sections 3.4.1 and 3.4.2). The diketones were also transformed into their dispiroindenofluorenes counterpart (Section 3.4.3) whose structural and photophysical properties were also evaluated (Sections 3.4.4 and 3.4.5).

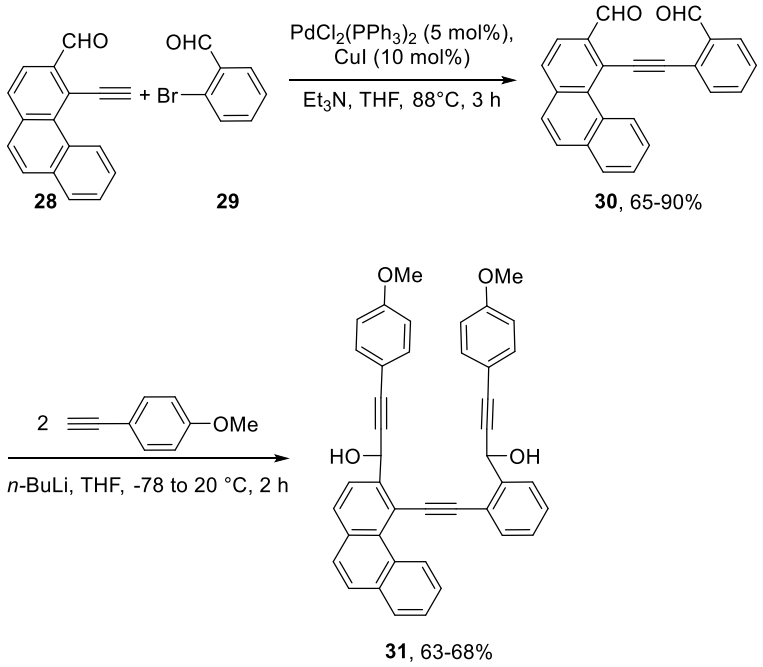


Scheme 30. Study of cyclotrimerization of [7]helical benzoindaceno[2,1-*c*]phenanthrenedione

3.4.1 Cyclotrimerization study of fluorinated and non-fluorinated [7]helical indenofluorenone

The synthesis of 1-(2-((3-(1-hydroxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)phenanthren-4-yl)ethynyl)phenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (**31**) as well as its cyclotrimerization reactions were accomplished by the visiting student Selina Bingel from IMC - University of Applied Sciences in Krems, Austria.

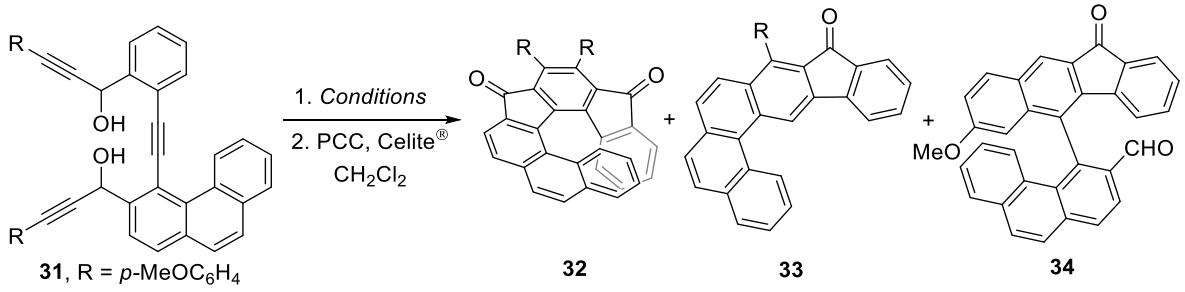
The usual pathway was applied for the synthesis of triynediols **31** (Scheme 31): i) Sonogashira cross coupling of 4-ethynylphenanthrene-3-carbaldehyde (**28**) and 2-bromobenzaldehyde (**29**) afforded dialdehyde **30** in 65-90% yield; ii) alkynylation of **30** with 1-ethynyl-4-methoxybenzene gave triynediols **31** in 63-68% yield.



Scheme 31. Synthetic pathway for the formation of triynediols **31**

With the compound **31** in hand, cyclotrimerization reactions were carried out with different catalysts as reported in Table 17. The intermolecular cyclotrimerization for the synthesis of [7]helical benzoindaceno[2,1-*c*]phenanthrenedione **32**, proved to be in competition with dehydro-Diels-Alder reaction (DDAR) which leads to the formation of side-product **33** with the 10*H*-benz[*g*]indeno[2,1-*b*]phenanthrene scaffold and **34** with the 5-phenanthryl-11*H*-benzo[*b*]fluorene scaffold.

Table 17. Cyclotrimerization of **31** under different reaction conditions



31, R = *p*-$MeOC_6H_4$ **32** **33** **34**

Entry[a]	Catalytic system	Solvent	T (°C)	**32** (%)[b]	**33** (%)[b]	**34** (%)[b]
1	$RhCl(PPh_3)_3$ (3 mol%), Ag_2CO_3 (6 mol%)	THF	170[c]	29 (29)	6 (6)	(5)
2	$RhCl(PPh_3)_3$ (3 mol%)	THF	170[c]	33 (30)	3 (4)	(2)
3	$CpCo[P(OEt)_3](dmfu)$ (5 mol%)	Toluene	110	traces	(13)	(11)
4	$CpCo(CO)_2$ (5 mol%), PPh_3 (10 mol%)	THF	180[c]	(15)	4 (4)	(3)
5	Ni(cod)(DQ) (10 mol%), PPh_3 (10 mol%)	Toluene	100	48 (50)	traces	0
6[d]	-	THF	170[c]	0	(11)	(8)
7	Ag_2CO_3 (6 mol%)	THF	170[c]	0	20	15

[a] Reactions were carried out on 0.1 mmol scale. [b] Isolated yield after oxidation reaction; ^{1}H-NMR yields are given in parentheses (1,3,5-trimethylbenzene was used as the internal standard). [c] Reaction was performed on a Microwave reactor. [d] The reaction was carried out on 0.5 mmol scale.

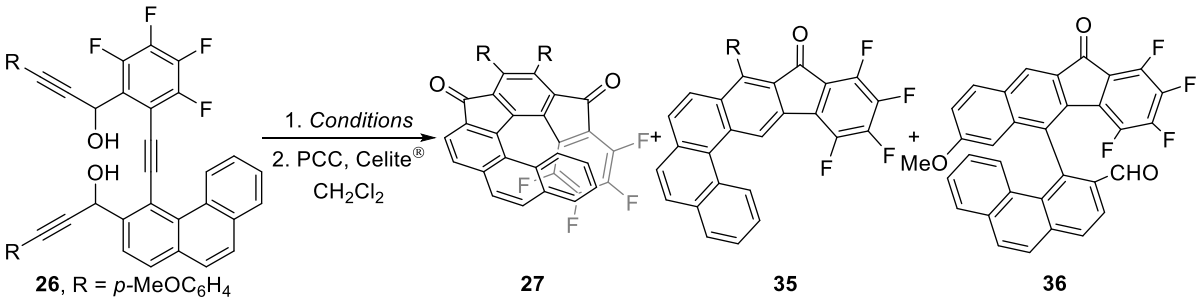
As the first attempt (entry 1), Selina and I tested our standard catalytic system comprising $RhCl(PPh_3)_3$ (3 mol%) and Ag_2CO_3 (6 mol%)[53] which resulted in the formation of a mixture of compounds with the predominant formation of the helical product **32** in 29% isolated yield along with DDAR-products **33** (the 10*H*-benz[*g*]indeno[2,1-*b*]phenanthrene scaffold) and **34** (the 5-phenanthryl-11*H*-benzo[*b*]fluorene scaffold). Products **33** and **34** were obtained in 6 and 5% ^{1}H NMR yields, respectively. Similar selectivity was observed with $RhCl(PPh_3)_3$ which yielded **32** in 30% ^{1}H NMR yield and **33** and **34** in 4 and 2% respectively (Entry 2). Surprisingly, the catalysis by air-stable and highly active $CpCo[P(OEt)_3](dmfu)$ (5 mol%),[143] furnished the cyclotrimerization product **32** in trace amounts (~2%) and only side-products **33** and **34** were detected from the reaction mixture in 13 and 11% ^{1}H NMR yield respectively (Entry 3). Likewise, the use of Vollhardt's catalyst ($CpCo(CO)_2$, 5 mol%) provided only 15% yield of **32** and a lower amount of side-products (Entry 4). The use of Ni(0) catalyst, (Ni(cod)(DQ), 10 mol%), selectively generated the helical compound **32** in a good ^{1}H NMR yield of 50% (Entry 5) and only traces of **33** were detected. As expected the use of thermal conditions without any metal compound (Entry 6) or in the presence of Ag_2CO_3 (Entry 7) led to the exclusive formation of **33** and **34**. The use of Ag_2CO_3 gave slightly higher yield of **33** and **34**, 20% and 15% respectively, if compared with thermal reaction without the additive. The

structures of compounds **32** and **34** were unequivocally confirmed by single crystal X-ray analyses (Figure 20 and Figure 22).

As further evidence of the competition between [2+2+2] intramolecular cyclotrimerization and intramolecular DDAR of triynediols with the phenanthrene moiety, I also studied cyclotrimerization of tetrafluorinated triynediols **26** under different reaction conditions (Table 18).

At the outset, I performed cyclotrimerization of **26** under our standard conditions for intramolecular reaction ($Rh(PPh_3)_3Cl$ with $AgCO_3$ as the additive, Entry 1). The reaction yielded **27** in only 10% isolated yield together with **35** and **36** in 17% and 5% yields respectively. The use of $Rh(PPh_3)_3Cl$ at 150°C without an additive gave slightly better yield of benzoindaceno[2,1-*c*]phenanthrenedione (24% ^{1}H NMR yield) and of the DDAR-product **35** (21% ^{1}H NMR yield) (Entry 2). The use of Co catalysts (Entries 3 and 4) provided better selectivity for **27** when compared with the previous results obtained for non-fluorinated analogue **32**. Particularly, $CpCo[P(OEt)_3](dmfu)$ and $CpCo(CO)_2/2PPh_3$ gave preferentially the [7]helical compound **27** in 54 and 50% ^{1}H NMR yields, respectively. Minor amounts of compound **35** (7 and 6%) and **36** (5 and 4%) were formed as well. When Cp*Ru(cod)Cl was employed, its catalytic efficacy was rather low: **27** was isolated in only 23% yield (Entry 5). On the other hand, the Ni-catalyzed cyclotrimerization was the most selective one. Indeed, the $Ni(acac)_2$/*i*-PrMgCl/$2PPh_3$ system, whose optimization have been described in Section 3.3.2, afforded fluorinated benzoindaceno[2,1-*c*]phenanthrenedione as the exclusive product in 63% isolated yield (Entry 6). Comparably $Ni(cod)(DQ)/2PPh_3$ catalyzed the reaction at 100 °C furnishing almost selectively **27** in 53% isolated yield (Entry 7). In accordance with the previous observations, reactions carried out with **26** under only thermal conditions (Entry 8) afforded DDAR-products in 26% and 14% ^{1}H NMR yields. The same reaction carried out in the presence of Ag_2CO_3 (Entry 9) gave rise to **35** in 25% yield, while **36** was detected in 13% ^{1}H NMR yield. Carrying out the reaction on a larger scale (Entry 10) enabled to increase the amount of **35** to use for next transformations. The structures of compounds **27** and **35** were unequivocally confirmed by single crystal X-ray analyses (Figure 20 and Figure 21). Other catalytic systems based on $(Pd_2(dba)_3)\cdot CHCl_3$ and $[Ir(COD)_2]BF_4$/dppe) were tested as well. However, the former provided **27** in only 10% yield, whereas the latter did not catalyze reaction at all. It is important to outline that during the cyclotrimerization as well as thermal reactions other unidentified aromatic compounds were detected by NMR analyses of the respective crude mixtures. However, their structures could not be elucidated, because they could not be isolated as individual substances.

Table 18. Cyclotrimerization of **26** under different reaction conditions



Entry[a]	Catalytic system	Solvent	T (°C)	**27** (%)[b]	**35** (%)[b]	**36** (%)[b]
1	$RhCl(PPh_3)_3$ (3 mol%), Ag_2CO_3 (6 mol%)	THF	170[c]	10	17	5
2	$RhCl(PPh_3)_3$ (3 mol%)	THF	150[c]	22 (24)	10 (21)	(12)
3	CpCo[$P(OEt)_3$](dmfu) (5 mol%)	Toluene	110	41 (54)	4 (7)	(5)
4	$CpCo(CO)_2$ (5 mol%), PPh_3 (10 mol%)	THF	180[c]	49 (50)	(6)	(4)
5	Cp*Ru(cod)Cl (5 mol%)	DCE	80	23 (27)	2 (4)	(3)
6	$Ni(acac)_2$ (40 mol%), *i*-PrMgCl (40 mol%) PPh_3 (80 mol%)	Toluene	20	63 (66)	0	0
7	Ni(cod)(DQ) (10 mol%), PPh_3 (20 mol%)	Toluene	100	53 (55)	traces[d]	0
8	-	THF	170[c]	0	21 (26)	(14)
9	Ag_2CO_3 (6 mol%)	THF	170[c]	0	25	(13)
10	Ag_2CO_3 (6 mol%) (0.2 mmol scale)	THF	170[c]	0	21 (25)	(18)

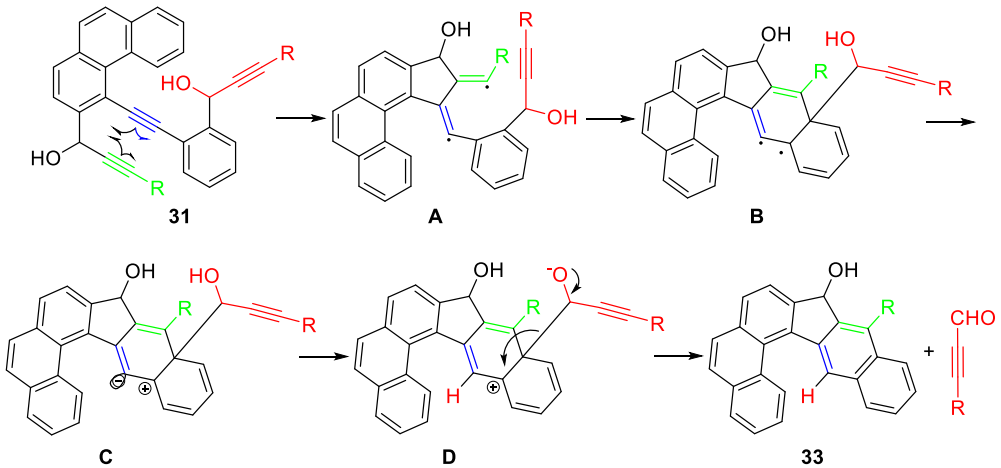
[a] Reactions were carried out on 0.1 mmol scale. [b] Isolated yields after oxidation reaction. ^{1}H NMR yields are given in parentheses (1,2,4,5-Tetramethylbenzene was used as internal standard). [c] Reaction was performed in a Microwave reactor.

To summarized the cyclotrimerization study of **26** and **31**, the use of [Rh], [Ru] catalysts resulted in complex reaction mixtures in which the [7]helical compounds **27** and **32** were obtained as major compounds in the most of cases. The DDAR-products were also observed, with the 10*H*-benz[*g*]indeno[2,1-*b*]phenanthrene scaffold **33** and **35**, being the major side-products formed. On the other end, the side-products with the 5-phenanthryl-11*H*-benzo[*b*]fluorene scaffold, such as **34** and **36**, were observed in minor amounts. [Co] catalysts didn't catalyzed cyclotrimerization of **31** in good yields, whereas better results were obtained for triynediol **26**, which underwent cyclotrimerization reaction with a high selectivity. The best results in term of selectivity and yields were gained by [Ni] catalysts for both triynediols. Particularly $Ni(acac)_2$ *in situ* reduced to Ni(0) gave the highest yield observed for cyclotrimerization of triynediol **26** (66% yield of **27**) and the bench stable Ni(cod)(DQ) afforded the [7]helical products **27** and **32** with up to 55% ^{1}H NMR yield even though a high temperature was required. The thermal reactions carried out with or without additive proved to promote the DDAR with the formation of side-products **33**, **34** and **35**, **36**.

3.4.2 Mechanistic considerations regarding synthesis of dehydro-Diels-Alder reaction products

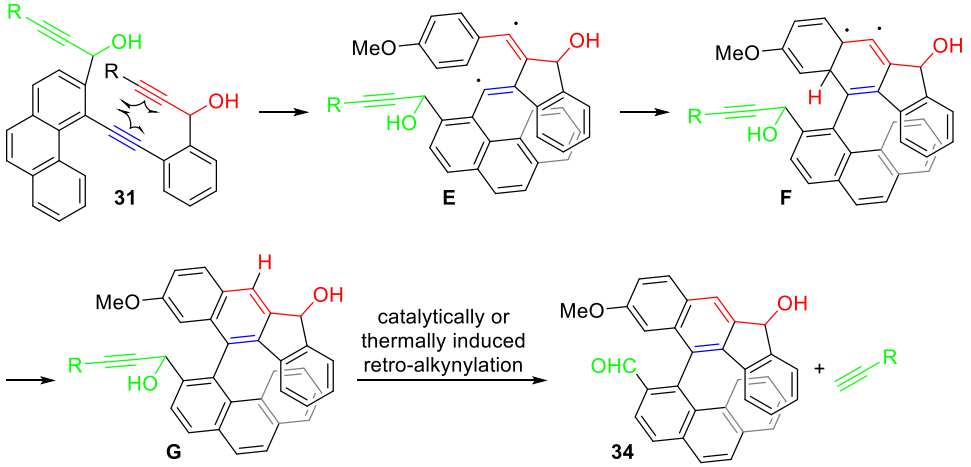
In order to explain the formation of undesired products **33-36** during [2+2+2] cyclotrimerization of **26** and **31**, both with the phenanthrene moiety, I supposed that the dehydro-Diels Alder (DDA) pathway competes with the cyclotrimerization.

In literature, some examples of DDA reactions involving diynes under thermal conditions have been reported, whereas in other cases DDA reactions were suggested to occur with a possible catalytic cycle.[144] However, in none of these cases a loss of a part of the starting molecules was observed. In this respect, I proposed the following DDA reaction pathway for the formation of compound **33** (Scheme 32): i) a thermal radical annulation of two alkyne moieties to form the dienyl diradical **A**; ii) the radical **A** is transformed to a new diradical **B** by addition of one radical to the aromatic ring; iii) ensuing electron transfer gives rise to the zwitter ion **C**; iv) a proton transfer in **C** takes place affording the zwitter ion **D**; v) **D** undergoes fragmentation to propargyl aldehyde and compound **33**. Similar pathway can be written for formation of fluorinated analogue **35**.



Scheme 32. The proposed radical reaction mechanism for the formation of **33**

On the other hand, the formation of compound **34** can be explained by a different course of the reaction (Scheme 33): i) a thermally induced radical annulation of two alkyne moieties forms the dienyl diradical **E**; ii) the radical **E** turns into a new diradical **F** by addition of one radical to the anisyl moiety; iii) an intramolecular [1,5] hydrogen shift provides the neutral molecule **G**. iv) thermally or catalytically induced retro-alkynylation furnishes compound **34**. Likewise, the formation of the fluorinated analogue **36** can be explained.

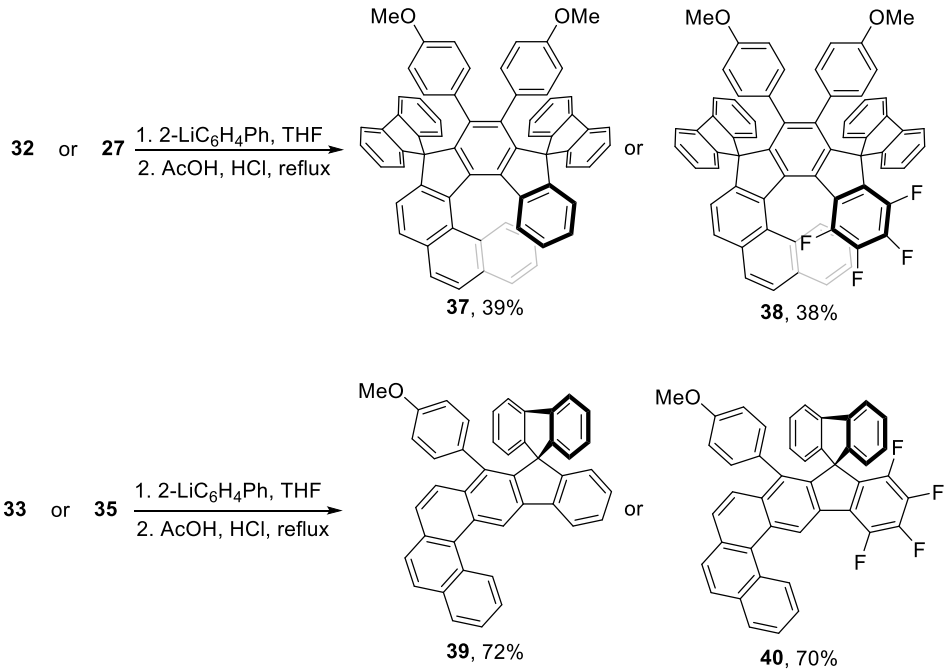


Scheme 33. The proposed radical reaction mechanism for the formation of **34**

The main difference between formation of **33** and **34** relies on the different propargyl alcohol involved in the first radical annulation: the propargyl alcohol on the phenanthryl unit (green color) is involved in the formation of **33**, whereas **34** is formed by interaction of propargyl alcohol on the phenyl unit (red color) with the internal alkyne (blue color).

3.4.3 Synthesis of spirocompounds

[7]Helical benzoindaceno[2,1-*c*]phenanthrenediones **27** and **32**, and 10*H*-benzo[*g*]indeno[2,1-*b*]phenanthren-10-ones **33** and **35**, were converted into the corresponding spirocompounds by using already mentioned two-step reaction sequence: i) the addition of 2-lithiobiphenyl to the carbonyl compound; ii) acidic treatment of the tertiary alcohol intermediates (Scheme 34). As result, **32** and **27** were converted to the corresponding dispirocompounds **37** and **38** in 39 and 38% isolated yields, respectively. In addition, the monoketones **33** and **35** afforded the corresponding spirocompounds **39** and **40** in 72 and 70% isolated yields, respectively.



Scheme 34. Conversion of diketones and monoketones to the corresponding spirobifluorenes

3.4.4 Structural properties of [7]helical indenofluorenes and related side-products

Single-crystal X-ray diffraction analyses of [7]helical indenofluorenones **32**, **27**, and of DDAR-products **34**, **35**, and **39** were performed to unambiguously determine their molecular structures. The crystals were obtained by hexane diffusion into their CH_2Cl_2 solutions or by slow evaporation from CH_2Cl_2/MeOH solutions.

As far as the X-ray structures of [7]helical indenofluorenones **32** and **27** are concerned (Figure 20), the degree of molecular twist was calculated by the sums of the five dihedral angles formed by C(22), C(23), C(24), C(25), C(26), C(27), C(28) and C(1) carbon atoms. The helical twist was found to be 74.6 and 77.1° for **32** and **27** respectively. The bigger lead in **27** with respect to **32** can be attributed to the steric strain imposed by the fluorine atoms. Moreover, because of the additional benzene ring, the twist values of **32** and **27** are bigger when compared with [6]helical dispiroindenofluorene **21**, whose twist is only 56.9°. Apart from comparison with compound **21**, these values are also higher by 3.3 and 6.8° respectively than the one for the related symmetrical [7]helical indenofluorene (71.3°).[113] On the other hand, the degree of molecular twist is smaller than those of the structurally related [7]helical fluorenes. For example, compound **LXXIII**, described in Section 1.1.3 (Scheme XXXI), showed a molecular twist equal to 97.8°[57] and other related compounds possessed a range of 80.9-90.8°.[145]

Interestingly, the C(1)−C(22) and C(2)−C(21) distances were found equal to 3.085 and 4.061 Å for **32** and 3.081 and 3.854 Å for **27** respectively. The C(22)−H(1) distance is 2.988 Å

in **32** and the H(22)−F(1) one is 3.478 Å in **27**; both distances are bigger than the sum of van der Waals radii of the corresponding elements. Therefore, those values does not suggest presence of strong intramolecular π···π, CH···π or CH···F interactions.

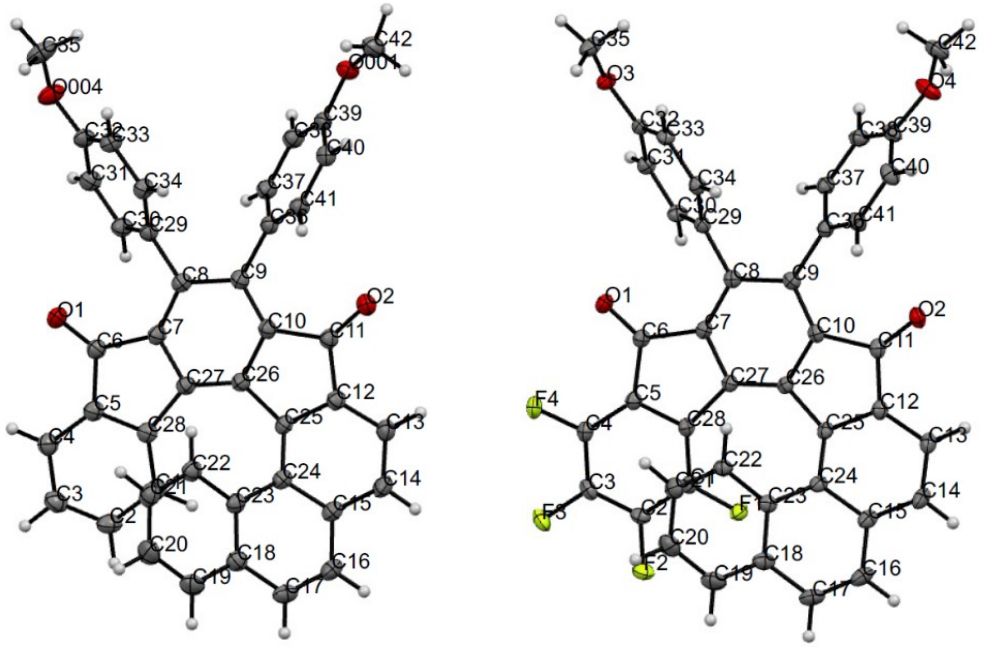


Figure 20. ORTEP drawing of **32** and **27** respectively from left to right (grey C, white H, green F, red O)

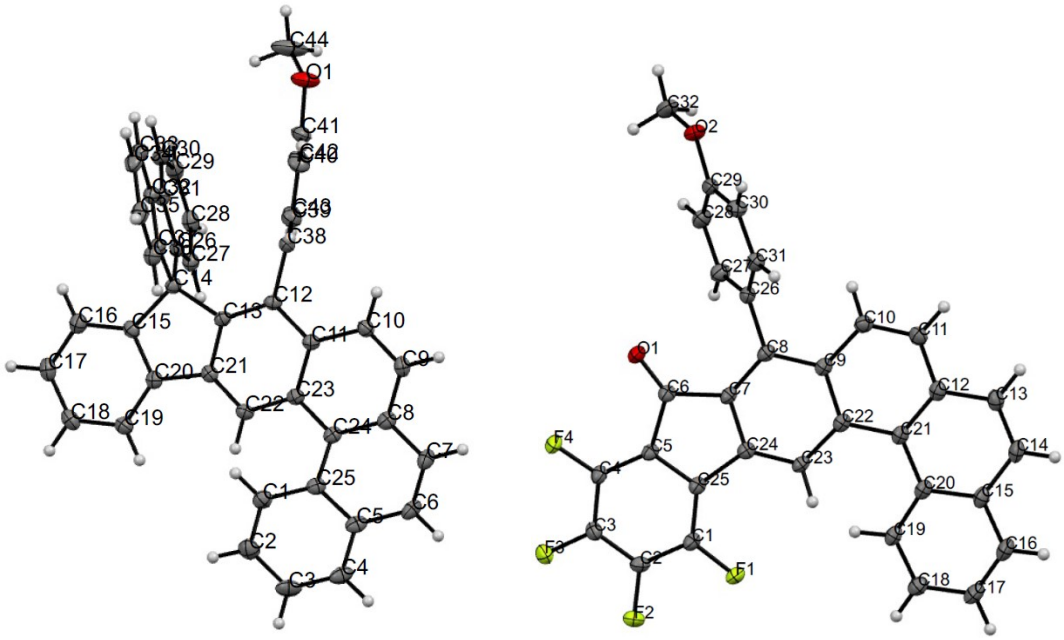


Figure 21. ORTEP drawing of **39** and **35** respectively from left to right (grey C, white H, green F, red O)

X-ray analyses of DDAR side-products with the 10*H*-benz[*g*]indeno[2,1-*b*]phenanthrene scaffold **39** and **35** are illustrated in Figure 21. In order to estimate the helical twist of **39**, the sum of the two dihedral angles (∠ C(22)−C(23)−C(24)−C(25) and ∠ C(23)−C(24)−C(25)−C(1)) was calculated and found to be 38.4°. Similar calculations for **35** gave a torsion degree of 30.0°, which is slightly lower than that of **39**. Probably the presence of the spirobifluorene core in **39** increases the molecular strain and, indeed, accounts for the higher degree of molecular twist.

Lastly, Figure 22 illustrates the structure of compund **34** with the 5-phenanthryl-11*H*-benzo[*b*]fluorene scaffold.

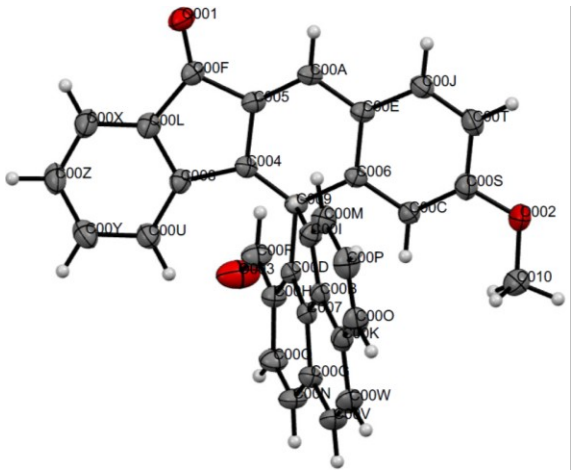


Figure 22. ORTEP drawing of **34** (grey C, white H, red O)

3.4.5 Photophysical properties of spirocompounds

The photophysical properties of spirobifluorene **37**-**40** were studied by measuring UV-Vis absorption and fluorescence spectra in dichloromethane together with absolute quantum yields. The most significant spectral data are summarized in Table 19. The [7]helical dispiroindenofluorenes **37**-**38** show very similar UV-Vis absorption spectra (black and red lines in Figure 23): an absorption band at 312, 311 nm, a partially resolved medium intensity band at 341 nm, a low intensity band at 355 nm and two lower intensity band at 372, 375 nm and 392, 393 nm, respectively. The first band at ~311 nm is typical of all known spirobifluorenes and dispiroindenofluorenes (see Sections 3.1.5 and 3.2.6), the subsequent two bands are red-shifted if compared with [5]helical dispiroindenofluorenes previously synthesized in our group[113] or described in Section 3.2.6. The second to last adsorption at ~372 nm is similar to the last absorption band of [6]helical dispirobenzo[*c*]indeno[1,2-*g*]fluorene **21**. The last band at lower energy (392 and 393 nm) is new if compared with **21** and it is due to the elongation of

helical structure that extend π- electron conjugation**.** This finding is corroborated by UV-Vis absorption spectra of symmetrical [7]helical dispiroindenofluorenes which also presented two lower energy absorption bands at ~370 and ~390 nm.[113] The UV-Vis spectra of monospirocompounds **39** and **40** (green and blue lines in Figure 23) are similar to each other and show higher intensity band at 308 nm, followed by medium intensity band at 324, 323 nm. The last three band with progressively lower molar attenuation coefficients can be attributed to the benzo[*c*]phenanthrene moiety, since similar absorptions are found in the reported UV-Vis spectra of this compound.[146]

Table 19. Photophysical properties of **37**-**40** in dichloromethane

37-40	λ_{abs}/nm ($\varepsilon/10^4$ mol^{-1}·dm^3·cm^{-1})	λ_{em}/nm	Φ_s [a]
37	282 (6.12), 312 (2.73), 341 (1.68), 355 (1.83), 372 (1.18), 392 (1.15)	409, 422	0.53
38	280 (5.77), 311 (2.47), 341 (1.42), 355 (1.27), 375 (0.92), 393 (1.05)	411, 424	0.59
39	299 (6.48), 308 (7.18), 323 (4.09), 336 (2.43), 351 (2.08), 372 (0.38), 393 (0.30)	394, 416, 441	0.25
40	298 (6.11), 308 (7.39), 324 (2.91), 334 (2.02), 349 (1.64), 371 (0.13), 390 (0.05)	395, 417, 442	0.14[b]

[a] Absolute quantum yield, λ_{exc} = 300 nm.
[b] λ_{exc} = 330 nm.

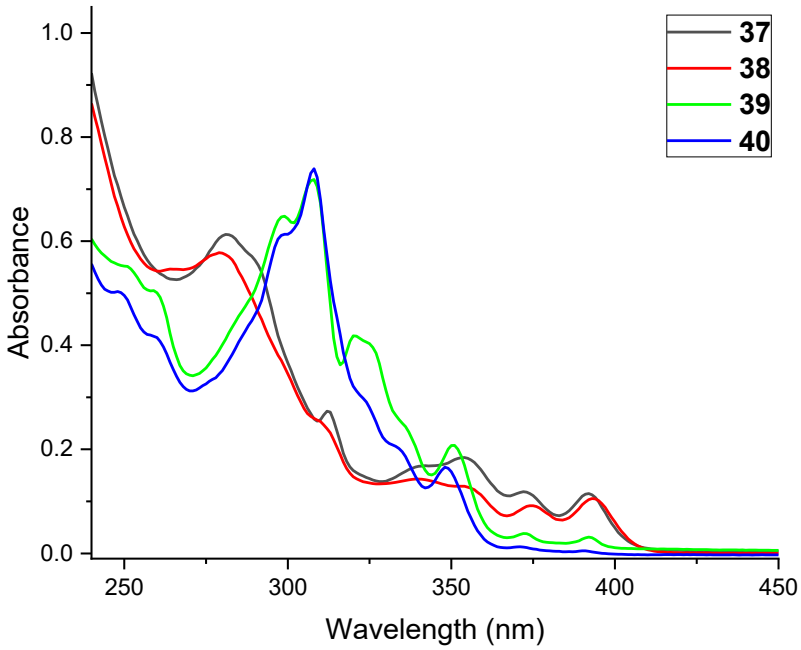
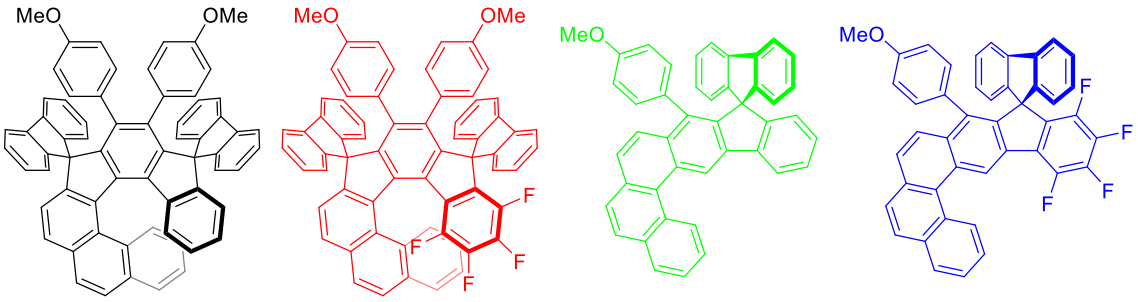


Figure 23. Absorption spectra of **37**-**40** (10^{-5} M) in CH_2Cl_2

All compounds behave as violet-blue light fluorescent emitters. The emission spectra of [7]helical compounds are partially resolved with maxima at 409 and 422 nm for **37** and at 411, 424 nm for **38** (Figure 24-Figure 25). These values are slightly blue-shifted in comparison with symmetrical [7]helical bispiroindenofluorene (λ_{em} = 418 and 428 nm)[113] and red-shifted of ~10 nm if compared with unsymmetrical [6]helical dispirobenzo[*c*]indeno[1,2-*g*]fluorene **21** (λ_{em}= 412 nm). The observed bathochromic shift is a result of extension of the π-system from 6-rings to 7. The emission spectra of **39** and **40** have three maxima for each at λ_{em} = 394, 416, 441 and 395, 417, 442 nm, respectively. The measured quantum yields, Φ_s, of [7]helical compounds **37** and **38** (Φ_s= 0.53 for **37** and 0.59 for **38**) are significantly lower if compared with the [6]helical analogue **21** (Φ_s= 0.92) and with symmetrical [7]helical bispiroindenofluorenes (Φ_s= 0.75-0.88).[113] The monospiro compounds proved to be less efficient emitters with Φ_s= 0.25 (**39**), and 0.14 (**40**).



37, λ_{em} = 409, 422 nm
Φ = 53%

38, λ_{em} = 411, 424 nm
Φ = 59%

39, λ_{em} = 394, 416 nm
Φ = 25%

40, λ_{em} = 395, 417 nm
Φ = 14%

Figure 24. Structures and selected photo-physical properties of compounds **37-40**

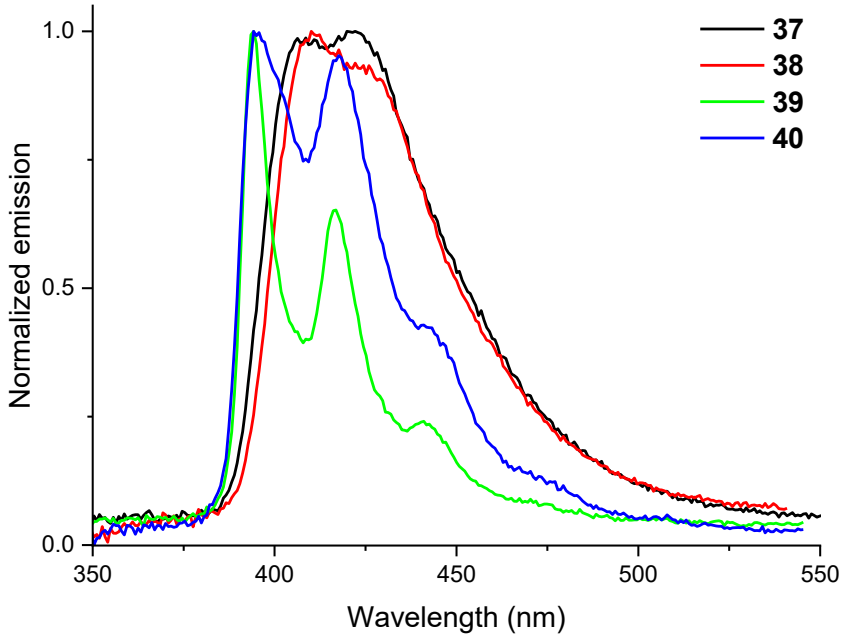
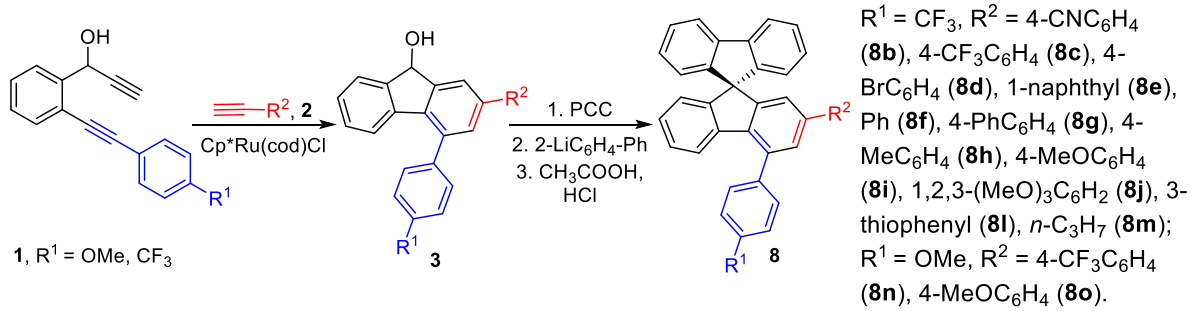


Figure 25. Normalized emission spectra of **37-40** in CH_2Cl_2

4 CONCLUSION

During the first part of my Ph.D. project, I developed new regioselective [2+2+2] cyclotrimerization as key step for the synthesis of 2,4-disubstituted fluorenols **3** and the respective spirobifluorenes **8**.[115] The partially intramolecular cyclotrimerization of diynes **1** and terminal alkynes **2** catalyzed by Rh gave preferentially the 3,4-disubstituted isomer (*ortho* isomer, **3'**) or ~1/1 mixture of *ortho*/*meta*. Interestingly Cp*Ru(cod)Cl proved to be regioselective for the *meta* regioisomer and gave 2,4-disubstituted fluorenols (**3**) in 14-62% yields and 3/1-25/1 ratios of **3**/**3'** (Scheme 35). The yields of reactions were diminished by formation of side-product upon homo-cyclotrimerization of **1**. However, I demonstrated that the yield of the cyclotrimerization of diynes **1** with terminal alkynes can be increased by adding more equivalents of **2** (7-9 eq.).

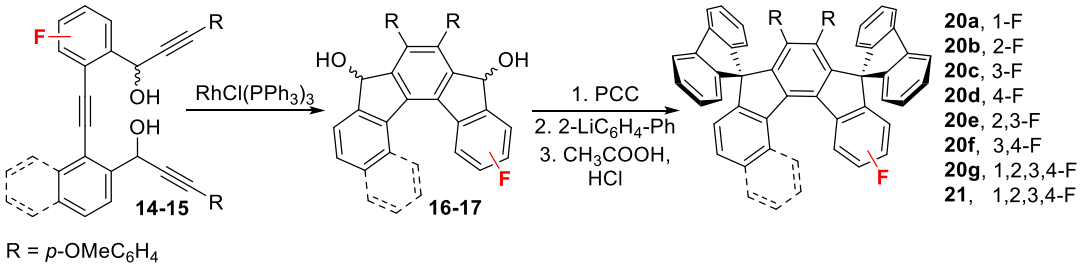


Scheme 35. Ru-catalyzed regioselective [2+2+2] cyclotrimerization of **1** with **2**

After oxidation with PCC to obtain corresponding fluorenones **7** in the range 70-98% yield, fluorenones were transformed in 2,4-disubstituted spirobifluorenes by known two-steps procedures. Single crystal X-ray diffraction analyses of **8** unambiguously confirmed their structures. By measuring the angles between the plane of substituted fluorene and the plane of pendants phenyl rings, the general trend showed lower dihedral angles for the C(2)-substituents and bigger for substituents in position 4. As result, the substituents on C(2) proved to be more conjugated with the fluorene core, whereas the pendant phenyl rings on C(4) led to disruption of π-conjugation. The photophysical properties of 2,4-disubstituted spirobifluorenes were studied by recording absorption and emission spectra as well as the absolute quantum yields. All the compounds **8b**-**8o** behaves as blue light emitters, with absorption in the range of 250-326 nm and emission in the narrow region of 365-391 nm. In the case of spirobifluorenes with

p-CF_3-C_6H_4 group in position 4 (**8b**-**8m**), electron withdrawing groups on C2 led to slight blue shift emission maxima (e.g. 367, 368 nm for **8b** and **8c** respectively), whereas electron donating groups on C2 resulted in more red-shifted emission (e.g. 391 nm for **8j**). The highest quantum yield was equal to 1.00 possessed by **8g** which bears the biphenyl framework on C(2). The other compounds showed absolute quantum yields in the range of 0.14-0.92.

In the second part of my Ph.D. study, I developed Rh-catalyzed fully intramolecular [2+2+2] cyclotrimerization for the synthesis of variously fluorinated [5] and [6]helical dispiroindenofluorenes (**20** and **21**).[127] After screening of conditions, the cyclotrimerizations of triynediols **14a**-**14g** and **15** were carried out under microwave irradiation at 150 °C for 1.5 h and afforded desired [5]helical dihydroindeno[2,1-*c*]fluorenediols, **16a**-**16g**, and [6]helical tetrafluoro dihydroindeno[1,2-*g*]fluorenediol, **17**, in the range 63-91% yield (Scheme 36).



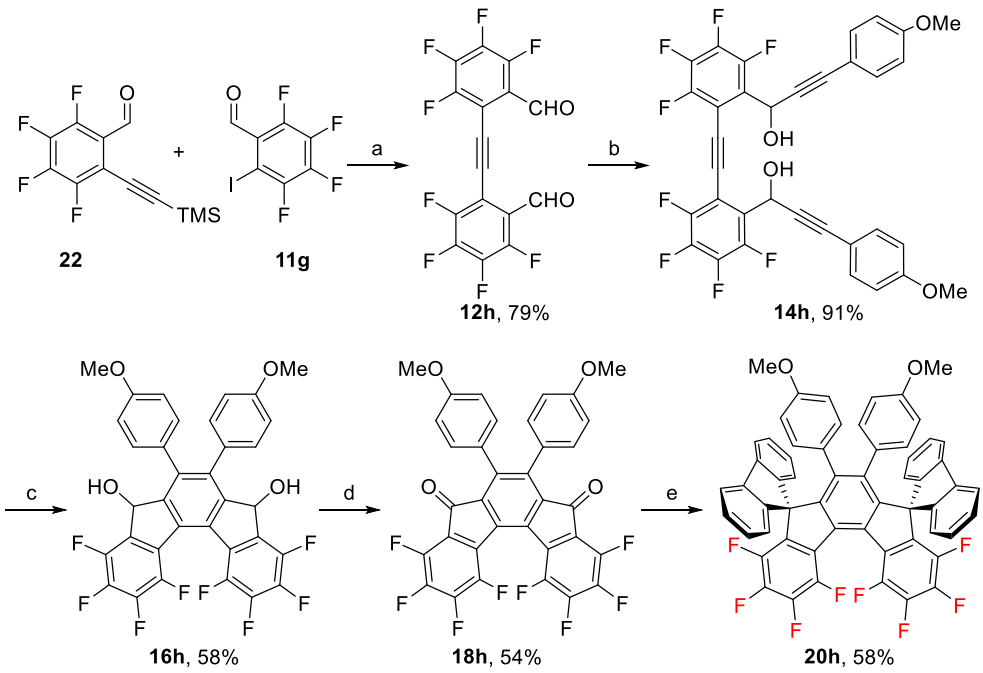
Scheme 36. Rh-catalyzed [2+2+2] intramolecular cyclotrimerization for the synthesis of fluorinated [5] and [6]helical dispiroindenofluorenes

The prepared fluorinated dihydroindenofluorenediols were oxidized with PCC to afford diketones in 72-95% yields. With diketones in hand, the two spirofluorenes framework were introduced using usual two step procedure: i) addition of 2-bromo biphenyl and *n*-BuLi to ketones; ii) cyclization of resulting diols in acidic media. Indeed, dispiroindeno[2,1-*c*]fluorenes **20a**-**g** and dispirobenzo[*c*]indeno[1,2-*g*]fluorene **21** were synthetized in 40-89% overall yields of two steps.

Unexpectedly, the synthesis of octafluorinated dispiroindeno[2,1-*c*]fluorenes **20h** was troublesome and the majority of reaction conditions needed to be re-optimized.

Scheme **37** summarizes all the synthetic steps for the preparation of **20h**. Firstly, the Hiyama-type cross coupling reaction of 2,3,4,5-tetrafluoro-6-((trimethylsilyl)ethynyl)benzaldehyde **22** with 2,3,4,5-tetrafluoro-6-iodobenzaldehyde (**11g**) was performed with $PdCl_2(PhCN)_2$ as catalyst and P(2-furyl)$_3$ as ligand under phase transfer conditions. The reaction gave the dialdehyde **12h** in 79% yield. Alkynylation of **12h** was accomplished with Et_2Zn and HMPA to afford octafluorinated triynediols **14h** in 91% yield.

Cyclotrimerization of triynediols **14h** and oxidation of the resulting indenofluorenols **18h** were carried out with the same conditions previously described for **14a**-**14g** and **15**; however, lower yields were obtained in this case (58 and 54%). After usual addition on 2-lithium biphenyl to diketone **18h**, the cyclization step was performed with the Lewis acid $BF_3{\cdot}Et_2O$ in dichloromethane instead of AcOH/HCl system. The final octafluorinated dispiroindeno[2,1-*c*]fluorene **20h** was obtained in 58% overall yield of the last two steps.



Conditions: a) $PdCl_2(PhCN)_2$, P(2-furyl)$_3$, CuI, CsF, Bu_4NI, toluene/water, 60 °C; b) 1-ethynyl-4-methoxybenzene, Et_2Zn, HMPA, CH_2Cl_2, 40 to 20 °C; c) $RhCl(PPh_3)_3$, THF, 150 °C, MW; d) PCC, Celite, CH_2Cl_2, 20 °C; e) 1. 2-Bromobiphenyl, *n*-BuLi, THF, -78 °C; 2. $BF_3.Et_2O$, CH_2Cl_2, 40 °C.

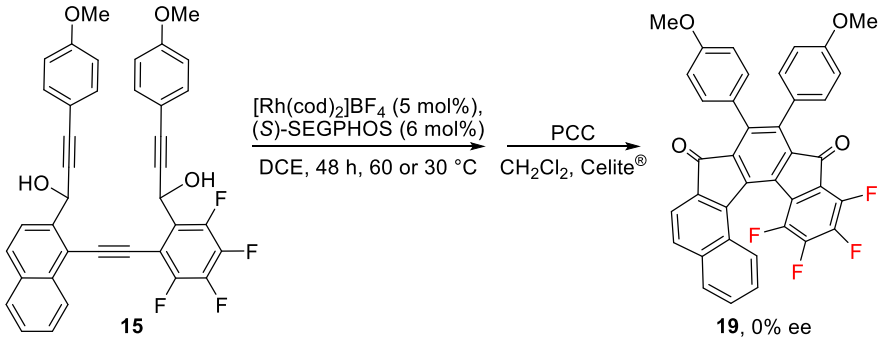
Scheme 37. Synthesis of octafluorinated dispiroindeno[2,1-*c*]fluorenes **20h**

The structures of the prepared fluorinated dispiroindenofluorenes were confirmed by single crystal X-ray diffraction analyses. Interestingly the degree of indenofluorene twist was evaluated to be 18.5° for monofluorinated **20c**, 50.3° for octafluorinated **20h** and 56.9° for the tetrafluorinated [6]helical dispiroindenofluorene **21**. The higher molecular twist of **20h** with respect to [5]helical analogue **20c** can be attributed to increased bulkiness of the eight fluorine atoms and to a possible C−F(1)···F(5)−C trough space interactions.

As far as the photophysical properties of **20a**-**20h** and **21** are concerned, the [5]helical mono- to tetrafluorinated **20a**-**20g** showed very similar absorption spectra and molar attenuation coefficients. The absorption spectrum of **21** bearing an additional fused benzene ring on indenofluorene core, displayed red-shifted medium intensity bands at 355 and 371 nm

as consequence of the extended π-electron delocalization. Regarding emission spectra, the mono- to tetrafluorinated [5]helical dispiroindenofluorenes **20a**-**20g** exhibited slightly red shift of 7-15 nm in their emission maxima (λem = 386-395 nm) if compared with their non-fluorinated counterpart (λem = 370, 380 nm).[113] Interestingly, the octafluorinated [5]helical dispiroindenofluorene **20h** and the tetrafluorinated [6]helical dispirobenzo[*c*]indeno[1,2-*g*]fluorene **21** showed much more red shifted emission maxima at 413 nm and 412 nm, respectively. The absolute quantum yields of the [5]helical dispirodihydroindenofluorenes **20a**-**20g** were in the range 0.42-0.52 which are higher than those of their non-fluorinated congeners.[113] The [5]helical octafluorinated dispiroindenofluorene **20h** and [6]helical tetrafluorinated dispirobenzo[*c*]indeno[1,2-*g*]fluorene **21** displayed absolute quantum yields as high as 0.89 and 0.92, respectively. Indeed, these results assessed that mono to tetra fluorine atoms on the indenofluorene core have a slight impact on the photophysical properties; on the other hand, polyfluorination on the [5]helical scaffold or the extended conjugation of [6]helical indenofluorene cause a bathochromic shift of emission spectra and increases the fluorescence quantum yields.

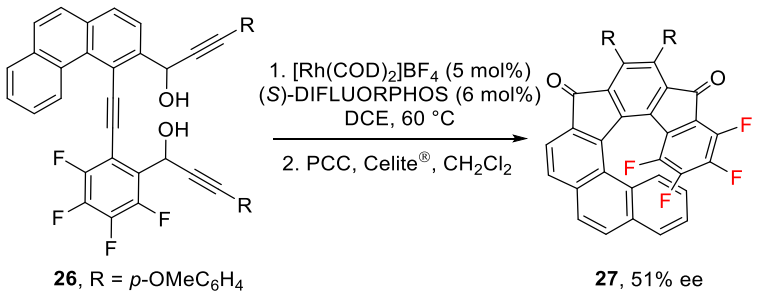
The third part of my project focused on enantioselective cyclotrimerization for the synthesis of enatiopure [6] and [7]helical dispiroindeno[2,1-*c*]fluorene. In order to achieve this goal, I performed cyclotrimerization of triynediols **15** with $[Rh(cod)_2]BF_4$ and (*S*)-SEGPHOS as chiral ligand (Scheme 38). However, no asymmetric induction was observed. Moreover, the recorded ^1H NMR experiments at different temperatures, together with the low racemization barrier calculated for similar molecules in literature,[137] suggested that [6]helical dihydroindenofluorenone is configurational unstable.



Scheme 38. Enantioselective cyclotrimerization of **15**

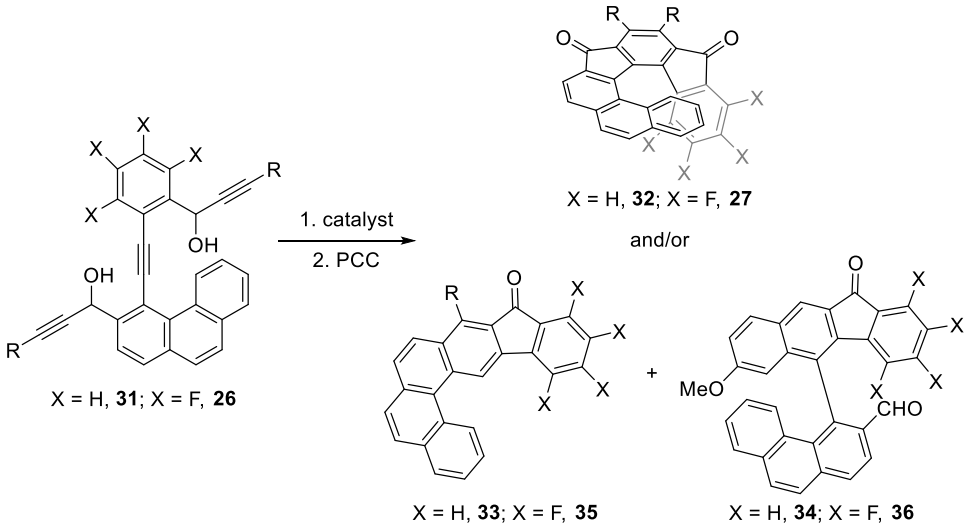
Regarding the enantioselective cyclotrimerizations for the synthesis of enantioenriched [7]helical benzoindaceno[2,1-*c*]phenanthrenedione **27**, the best ee was 51% obtained with

[Rh(COD)$_2$]BF$_4$/DIFLUORPHOS catalytic system (Scheme 39). Whereas the screened Ni-catalytic systems didn't exceed 16% ee.



Scheme 39. Enantioselective cyclotrimerization of **26**

Since during cyclotrimerization of **26** side-products formation was observed, in the last part of my project, I studied the course of this reaction (Scheme 40). In particular, Ni-catalyzed [2+2+2] cyclotrimerization of fluorinated and non-fluorinated triynediols, **26** and **31**, proved to be selective for the formation of the desired unsymmetrical [7]helical benzoindaceno[2,1-*c*]phenanthrenediones **32** and **27** with up 66% yields. Other transition metal catalysts based on Rh, Ru, Co, Ir, Pd were unselective and gave **32** and **27** in lower yields with the competitive formation of undesired products **33-36** which derived from dehydro-Diels Alder type reactions (DDAR). Carrying out the reaction under thermal conditions promoted the only formation of DDAR-products in higher yields.

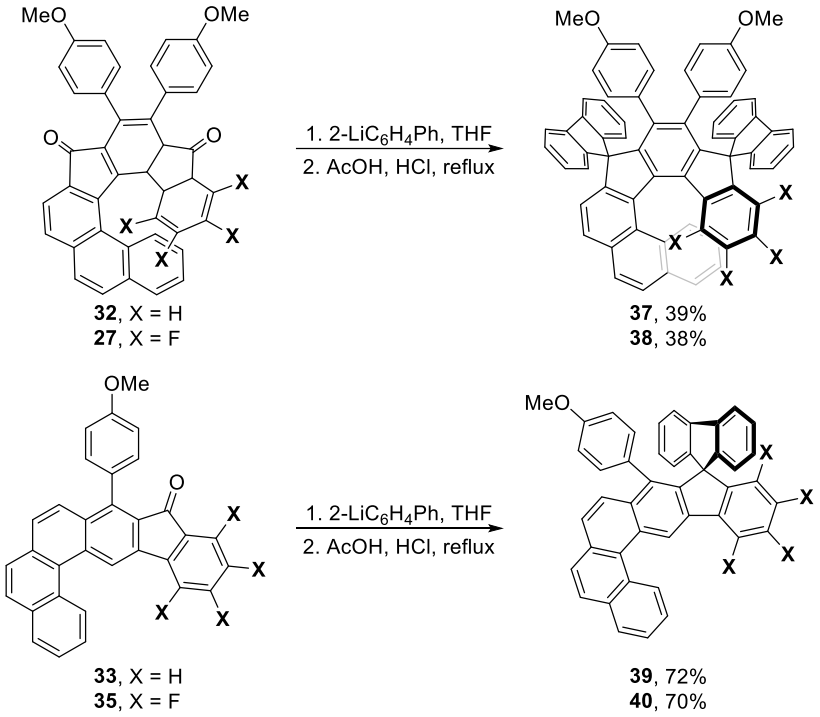


Scheme 40. Cyclotrimerization vs. dehydro-Diels Alder reaction pathways

The structures of the above-mentioned compounds were confirmed by single crystal X-ray diffraction analyses. The helical twist of **32** and **27** was found to be 74.6 and 77.1°

respectively. Those values are bigger if compared with [6]helical analogue **21**, whose twist is only 56.9° and are also higher by 3.3 and 5.8° respectively than the one of the related symmetrical [7]helical indenofluorene (71.3°).[113]

The [7]helical benzoindaceno[2,1-*c*]phenanthrenediones **27** and **32**, and the 10*H*-benzo[*g*]indeno[2,1-*b*]phenanthren-10-ones, **33** and **35**, were converted into the corresponding spirocompounds (Scheme 41) and their photophysical properties were evaluated.



Scheme 41. Synthesis of unsymmetrical [7]helical dispiroindenofluorenes **37** and **38** and monospiro-compounds **39** and **40**.

The absorption spectra of **37**-**38** and **39**-**40** are similar, proving that four fluorine atoms are not enough to change the photophysical properties, as demonstrated also in Section 3.2. The absorption spectra of unsymmetrical [7]helical **37** and **38** possessed additional bands at lower energy (392 and 393 nm) if compared with [6]helical analogue **21**, showing extended π-conjugation due to the elongation of helical structure. Moreover, the emission spectra of **3**7 and **38** are red-shifted of ~10 nm (λ_{em} = 409, 422 nm for **37** and 411, 424 nm for **38**) if compared with unsymmetrical [6]helical analogue **21** (λ_{em}= 412 nm). The red-shift can be attributed to the elongation of the π-conjugation from 6 to 7-rings. However, their emission was slightly blue-shifted in comparison with the symmetrical [7]helical dispiroindenofluorenes,[113] probably due to a bigger molecular twist of the helical core in the unsymmetrical compounds, which partially disrupts the conjugation. The measured quantum yields, were up to 59% for the

dispirobifluorenes compounds, whereas the monospiro compounds, **39** and **40**, proved to be less efficient emitters with quantum yields up to 25%.

To conclude during my Ph.D. study, I demonstrated that [2+2+2] cyclotrimerization with Rh, Ru, and Ni catalysts was a powerful and versatile method to construct various fluorene based compounds.

5 EXPERIMENTAL PART

5.1 General

Reactions were performed in heat-gun dried glassware under argon atmosphere using standard Schlenk Line techniques unless otherwise noted. All chemicals were purchased from Acros Organics, Sigma-Aldrich, Strem Chemicals, Lach-ner, Fluorochem and PENTA companies. Solvents for reactions were purified and dried by distillation: dichloromethane and 1,2-dichloroethane (DCE) from calcium hydride, tetrahydrofuran (THF) and toluene from sodium benzophenone ketyl. Solvents for column chromatography were distilled prior to use. Hexamethylphosphoramide (HMPA) and *N*,*N*-Dimethylacetamide (DMA) were purified by distillation over CaH and under reduced pressure. 1-bromonaphthalene was filtrated through aluminum oxide and distilled under reduced pressure. Other solvents and chemicals were used without further purification. Where indicated, the solvents were degassed by bubbling argon through the solvent for 30 min. Microwave reactions were performed in a Biotage Initiator device. Column chromatography was performed on Merck Silica gel 60 (0.040-0.063 mm) or on Aluminum Oxide 90 active neutral (0.063-0.200 mm), thin layer chromatography (TLC) on Merck silica gel 60 F_{254} coated aluminum sheets. Preparative TLC were done on Aluminum Oxide 60 neutral F_{254} with glass support or on Merck silica gel 60 F_{254} coated aluminum sheets. Spots on TLC plates were visualized by UV lamp (λ = 254, 366 nm) or by commonly employed stains: e.g. *p*-anisaldehyde, potassium permanganate. The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker AVANCE III Spectrometer (^{1}H at 400 or 600 MHz, ^{13}C at 101 or 151 MHz, ^{19}F at 376 MHz) or on Varian VNMRS 300 (^{1}H at 300 MHz, ^{19}F at 282 MHz) as solutions in $CDCl_3$ CD_2Cl_2, acetone-d_6 or $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in δ-scale and referenced internally to the residual solvent resonances: ^{1}H NMR spectra to $CDCl_3$ at δ 7.26, to CD_2Cl_2 at δ 5.32, or to acetone-d_6 at δ 2.05; ^{13}C NMR spectra to $CDCl_3$ at δ 77.0, to CD_2Cl_2 at δ 53.5, or to acetone-d_6 at δ 29.8. ^{19}F NMR spectra were referenced at δ -63.72 using trifluorotoluene 0.05% in $CDCl_3$ as external standard. Coupling constants (*J*) are given in Hertz (Hz) and splitting patterns are designed as s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), sxt (sextet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet), dm (doublet of multiplet), ddd (doublet of doublet of doublet),

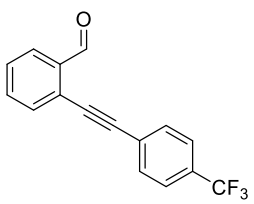
td (triplet of doublet). ^{1}H-NMR yields were determined by using 1,3,5-trimethylbenzene or 1,2,4,5-tetramethylbenzene as internal standard. ^{19}F-NMR yields were determined by using α,α,α-trifluorotoluene as internal standard. The IR spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer in KBr powder and are reported in wavenumbers (cm^{-1}). The MS spectra were recorded on an Agilent 5975 Inert MSD, GC×GCTOFMS LECO Pegasus IVD or Agilent 6530 Q-TOF device. The UV-Vis absorption spectra were recorded using Unicam 340 spectrometer. Corrected steady-state emission spectra were recorded on an Aminco Bowman (AB2) spectrometer. The absolute quantum yields were recorded on Quantaurus-QY Plus UV-NIR absolute PL quantum yield spectrometer (Hamamatsu). All melting points are uncorrected and were determined on a Kofler apparatus. Chiral HPLC analyses were performed on Shimadzu chromatograph with Daicel Chiralpak® IC-3 or IA-3 column. Crystallographic data were collected on Bruker D8 VENTURE Kappa Duo PHOTON100 by IμS micro-focus sealed tube at 150 K.

5.2 Procedures for synthesis of SBFs

5.2.1 Synthesis of unsymmetrically substituted diynes (1a-1b)

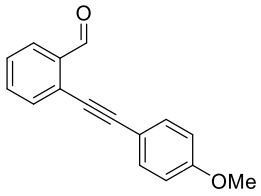
General procedure for Sonogashira reaction. Preparation of iia-iib and trimethyl((3,4,5-trimethoxyphenyl)ethynyl)silane. In a dried two-neck flask under argon, 2-bromobenzaldehyde or 5-bromo-1,2,3-trimethoxybenzene (0.700 mL, 6.0 mmol), $Pd(PPh_3)_2Cl_2$ (210 mg, 0.3 mmol) and CuI (114 mg, 0.6 mmol) were added and dissolved in triethylamine (18 mL) and THF (20 mL). Then a terminal alkyne (7.2 mmol) was added and the resulting mixture was stirred for 3 h at 80 °C. After being cooled down to room temperature, the reaction mixture was filtered through a pad of Celite®/silica gel, washed with diethyl ether, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes/EtOAc) furnished the products.

2-((4-(Trifluoromethyl)phenyl)ethynyl)benzaldehyde (iia). With 2-bromobenzaldehyde (817 μL, 7.0 mmol) and 1-ethynyl-4-(trifluoromethyl)benzene **ia** (1.37 mL, 8.4 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 1.76 g (92%) of the title compound as a yellowish oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.97 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.58–7.71 (m, 6H), 7.50 (t, *J* = 7.6 Hz, 1H); **^{13}C**

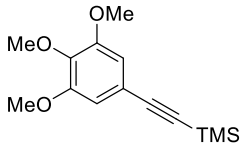


NMR (101 MHz, $CDCl_3$) δ 191.2, 136.0, 133.8, 133.4, 131.9, 130.7 (q, $^2J_{C-F}$ = 32.8 Hz), 129.2, 127.6, 126.1, 125.8, 125.5 (q, $^3J_{C-F}$ = 3.8 Hz), 123.8 (q, $^1J_{C-F}$ = 272.3 Hz), 94.5, 87.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.90. The spectral data were in agreement with the previously published results.[147]

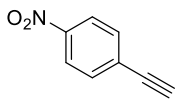
2-((4-Methoxyphenyl)ethynyl)benzaldehyde (iib). With 2-bromobenzaldehyde (715 µL, 6.0 mmol) and 1-ethynyl-4-methoxybenzene **ib** (963 µL, 7.2 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 1.34 g (94%) of the title compound as a pale yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.65 (d, *J* = 0.7 Hz, 1H), 7.94 (ddd, *J* = 7.6, 1.2, 0.5 Hz, 1H), 7.59–7.63 (m, 1H), 7.57 (dt, *J* = 7.6, 1.7 Hz, 1H), 7.51 (dt, *J* = 9.0, 2.7 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 6.91 (dt, *J* = 9.0, 2.7 Hz, 2H), 3.84 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.8, 160.2, 135.6, 134.0, 133.7, 133.2, 133.0, 128.2, 127.3, 127.2, 114.2, 96.6, 83.8, 55.3. The spectral data were in agreement with the previously published results. [147]



Trimethyl((3,4,5-trimethoxyphenyl)ethynyl)silane. With 5-bromo-1,2,3-trimethoxybenzene (1.02 g, 4.1 mmol) and ethynyltrimethylsilane (699 µL, 4.9 mmol) following the general procedure. Column chromatography on silica gel (7/1 hexanes/EtOAc) gave 498 mg (46%) of the title compound as a pale brown solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.64 (s, 2H), 3.76 (s, 9H), 0.18 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.7, 138.8, 117.8, 108.9, 104.9, 92.7, 60.6, 55.8, -0.3; The spectral data were in agreement with the previously published results.[148]



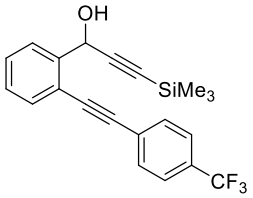
1-Ethynyl-4-nitrobenzene.[149] In a dried two-neck flask under argon, 1-iodio-4-nitrobenzene (5.0 mmol, 1.24 g) was added together with triethylamine (14 mL) and stirred for 10 min. under argon. Afterwards CuI (53 mg, 0.28 mmol), $Pd_2(dba)_3$ (128 mg, 0.14 mmol) and PPh_3 (73 mg, 0.28 mmol) were added. After addition of trimethylsilylacetylene (1.10 mL, 7.5 mmol), the reaction was carried out at 20 °C for 4 h. The resulting mixture was concentrated under reduced pressure and directly used for the next step. To a solution of the crude in MeOH (10 mL), MeOH/KOH (10 mL, 1 M) was added dropwise and the resulting mixture was stirred for 15 min. After evaporation of methanol under reduced pressure, the crude was extracted with diethyl ether (3 × 30 mL), the combined organic layers were washed with H_2O, dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography of the residue on silica gel (10/1 hexanes/EtOAc) gave 576 mg (78%) of the



title compound as a pale brown solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 3.36 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5, 132.9, 128.8, 123.5, 82.3, 81.5; The spectral data were in agreement with the previously published results.[150]

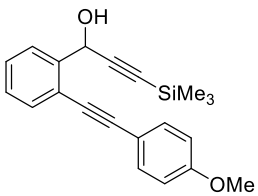
General procedure for alkynylation reaction. Preparation of iiia and iiib. In a dried Schlenk flask under argon, trimethylsilylacetylene (1.12 mL, 7.9 mmol) and anhydrous THF (19 mL), were added. The resulting solution was cooled to -78 °C and *n*-BuLi (1.6 M in hexane, 5.00 mL, 7.9 mmol) was added dropwise. After stirring for 30 min at -78 °C, aldehyde **iia** or **iib** (5.7 mmol) in THF (6 mL) was added under argon. The reaction was carried out for 5 min at -78 °C and then gradually warmed to 20 °C. Once the reaction was complete (TLC monitoring, typically 3 h), the work-up was performed with saturated aqueous NH_4Cl solution. The aqueous layer was extracted with diethyl ether (3 × 30 mL), the combined organic layers were washed with saturated solution of $NaHCO_3$ (1 × 30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography of the residue on silica gel provided products.

1-(2-((4-(Trifluoromethyl)phenyl)ethynyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (iiia).



With **iia** (949 mg, 3.5 mmol) and trimethylsilylacetylene (680 µL, 4.8 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 1.15 g (89%) of the title compound as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.64 (m, 4H), 7.57 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.43 (td, *J* = 7.6, 1.5 Hz, 1H), 7.35 (td, *J* = 7.6, 1.2 Hz, 1H), 5.92 (d, *J* = 5.9 Hz, 1H), 2.56 (br s, 1H), 0.18 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.2, 132.5, 131.7, 130.1 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.3, 128.2, 126.6, 123.8 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 125.2 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 120.8, 104.4, 93.3, 91.5, 88.9, 63.4, -0.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.77; **IR** (KBr) ν_{max} 3058, 3028, 2956, 2926, 2881, 2854, 2217, 1598, 1488, 1473, 1461, 1443, 1251, 1186, 1111, 1075, 842, 776, 752 692 cm^{-1}; **HRMS** (EI) *m/z* for $C_{21}H_{19}O_3Si$ $[M]^+$ calcd: 372.1157, found: 372.1155; ***R*$_f$** (5/1 hexanes/EtOAc) = 0.56.

1-(2-((4-Methoxyphenyl)ethynyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (iiib). With **iib**

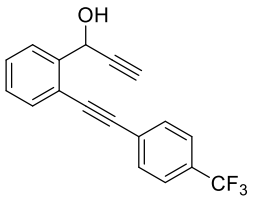


(1.3 g, 5.7 mmol) and trimethylsilylacetylene (1.1 mL, 7.9 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 1.76 g (93%) of the title compound as a pale yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.45 - 7.57 (m, 3H), 7.37 (td, *J* = 7.7, 1.6 Hz, 1H), 7.31 (td, *J* = 7.6, 1.5 Hz, 1H), 6.89 (d, *J* =

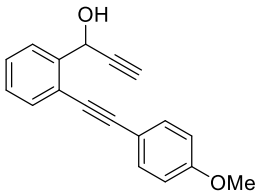
9.0 Hz, 2H), 5.94 (d, J = 4.4 Hz, 1H), 3.82 (s, 3H), 2.82 (br s, 1H), 0.19 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 141.7, 133.0, 132.1, 128.4, 128.2, 126.7, 121.9, 114.8, 114.0, 104.4, 95.1, 91.3, 85.3, 63.7, 55.3, -0.2. The spectral data were in agreement with the previously published results. [151]

General procedure for desilylation reaction. Preparation of 1a-1b. In one-neck round bottom flask, the trimethylsilated alkyne **iiia** or **iiib** (5.25 mmol) was dissolved in MeOH (23 mL) with catalytic amount of H_2O (4 drops) under atmospheric conditions. Afterwards the resulting mixture was cooled down to 0 °C and K_2CO_3 (1.45 g, 10.5 mmol) was added. The mixture was stirred for 3 h at the same low temperature. The reaction was quenched with HCl (2 M) till pH = 7, then mixture was extracted with diethyl ether (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using hexanes/EtOAc as eluent.

1-(2-((4-(Trifluoromethyl)phenyl)ethynyl)phenyl)prop-2-yn-1-ol (1a). With **iiia** (2.34 g, 5.9 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 1.65 g (93%) of the title compound as an orange oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.6 Hz, 1H), 7.59 (m, 5H), 7.40 (t, J = 7.3 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 5.97 (br s, 1H), 3.28 (br s, 1H), 2.67 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 132.5, 131.7, 130.1 (q, $^2J_{C\text{-}F}$ = 32.4 Hz), 129.4, 128.3, 126.5, 125.2 (q, $^3J_{C\text{-}F}$ = 3.3 Hz),123.8 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 120.6, 93.4, 88.7, 82.9, 74.7, 62.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.79; **IR** (KBr) ν_{max} 3295, 3061, 3024, 2955, 2924, 2855, 1593, 1489, 1471, 1446, 1391, 1250, 1102, 1069, 1000, 848, 755 cm^{-1}; **HRMS** (CI) *m/z* for $C_{18}H_{12}OF_3$ $[M+H]^+$ calcd: 301.0840, found: 301.0839; ***R$_f$*** (5/1 hexanes/EtOAc) = 0.35.

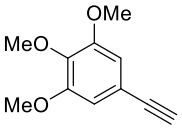


1-(2-((4-Methoxyphenyl)ethynyl)phenyl)prop-2-yn-1-ol (1b). With **iiib** (1.80 g, 5.2 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 1.20 g (90%) of the title compound as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 7.7, 1.3 Hz, 1H), 7.54 (dd, J = 7.5, 1.6 Hz, 1H), 7.50 (d, J = 8.8 Hz, 2H), 7.35 (td, J = 7.6, 1.5 Hz, 1H), 7.30 (td, J = 7.3, 1.5 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 5.99 (br s, 1H), 3.77 (s, 3H), 3.40 (br s, 1H), 2.67 (d, J = 2.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 141.3, 132.8, 131.9, 128.4, 128.1, 126.3, 121.4, 114.6, 113.9, 94.9, 85.1, 83.1, 74.4, 62.6, 55.1; **IR**



(KBr) ν_{max} 3476, 3446, 3387, 3366, 3297, 3288, 3067, 3013, 2932, 2836, 2214, 1607, 1565, 1509, 1461, 1446, 1290, 1248, 1180, 1153, 1111, 1093, 1030, 952, 839, 812, 761, 671, 641 cm^{-1}; **HRMS** (CI) *m/z* for $C_{18}H_{15}O_2$ $[M+H]^+$ calcd: 263.1072, found: 263.1071; R_f (5/1 hexanes/EtOAc) = 0.26.

5-Ethynyl-1,2,3-trimethoxybenzene. With trimethyl((3,4,5-trimethoxyphenyl)ethynyl)silane

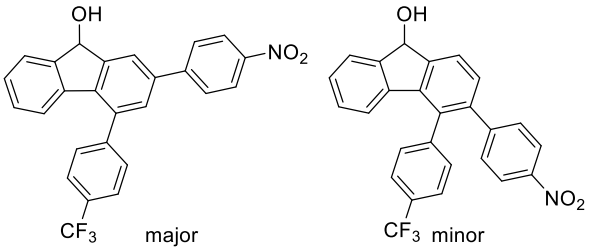


(477 mg, 1.8 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 319 mg (88%) of the title compound as a pale yellow solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.72 (s, 2H), 3.84 (s, 3H), 3.84 (s, 6H), 3.02 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.0, 139.2, 117.0, 109.3, 83.6, 76.2, 60.9, 56.1. The spectral data were in agreement with the previously published results.[152]

5.2.2 Synthesis and characterization of fluorenols (3a-3o).

General procedure for cyclotrimerization with Cp*Ru(Cod)Cl. Preparation of 3a-3o. In a two-neck flask starting material **1a** or **1b** (0.5 mmol) and CH_2Cl_2 (6 mL) were added under argon atmosphere. Afterwards the terminal alkyne **2** (1.0 mmol) was added followed by Cp*Ru(cod)Cl (19 mg, 0.05 mmol) and the reaction mixture was stirred for 4 h at 25 °C. After removal of volatiles under reduced pressure, the crude product was purified by column chromatography on silica gel using hexanes/EtOAc as eluent.

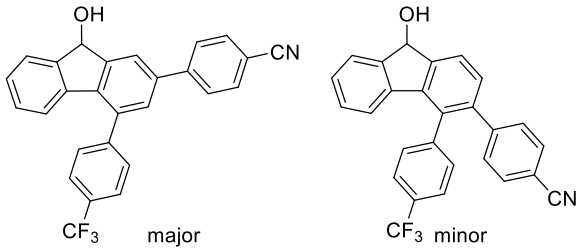
2-(4-Nitrophenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (3a). With **1a** (30.0 mg,



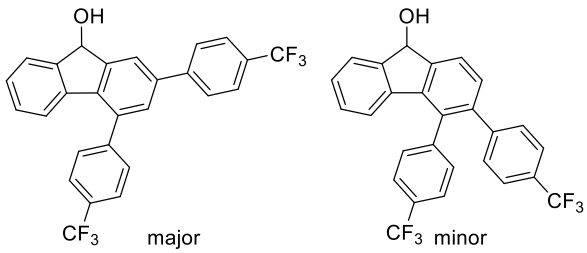
0.10 mmol) and 1-ethynyl-4-nitrobenzene (29.4 mg, 0.20 mmol) following the general procedure. According to the ^{1}H NMR analysis of the reaction mixture regioisomers **3a** and **3a'** were formed in 3:1 ratio. Column chromatography on silica gel (2/1 hexanes/EtOAc) gave 13.7 mg (31%) of **3a** as a yellow solid. The minor regioisomer **3a'** was not isolated. **mp** (decomp) 210-212; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.8 Hz, 2H), 7.99 (d, J = 0.7 Hz, 1H), 7.76 - 7.89 (m, 4H), 7.60 - 7.73 (m, 3H), 7.49 (d, J = 1.5 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 5.71 (s, 1H), 1.79 (br s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 147.2, 146.6, 146.5, 143.7, 138.7, 138.0, 137.6, 136.9, 130.3 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 130.0, 129.4 (br), 129.1, 128.4, 127.7, 125.8 (br), 125.5 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 125.2, 124.2, 123.5, 122.9, 74.7; **^{19}F NMR**

(376 MHz, $CDCl_3$) δ -62.41; IR (KBr) ν_{max} 3500, 3089, 3084, 1598, 1518, 1455, 1344, 1326, 1174, 1117, 1105, 1072, 1027, 845, 833, 752, 743 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{26}H_{15}O_3NF_3$ $[M-H]^-$ calcd: 446.10095, found: 446.10025; ***R_f*** (2/1 hexanes/EtOAc) = 0.30.

4-(9-Hydroxy-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-2-yl)benzonitrile (3b). With **1a** (150 mg, 0.50 mmol) and 4-ethynylbenzonitrile (127 mg, 1.00 mmol) following the general procedure. According to the ^1H NMR analysis of the reaction mixture regioisomers **3b** and **3b'** were formed in 3:1 ratio. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 30 mg (14%) of **3b** as a pale brown solid. The minor regioisomer **3b'** was not isolated. **mp** (decomp) 246-253 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.95 (s, 1H), 7.73 - 7.83 (m, 6H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 1.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 5.70 (br s, 1H), 1.97 (br s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.0, 146.4, 144.7, 143.8, 138.7, 138.4, 137.3, 136.8, 132.7, 130.4 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 129.8, 129.1, 128.3, 127.6, 127.4, 125.8 (br), 125.2, 124.2 (q, $^1J_{C\text{-}F}$ = 270.2 Hz), 123.4, 122.9, 118.8, 111.3, 74.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.41; **ATR** ν_{max} 3428, 3076, 2929, 2851, 2226, 1604, 1512, 1455, 1404, 1332, 1278, 1168, 1120, 1072, 1024, 899, 839, 752 cm^{-1}; **HRMS** (EI) *m/z* for $C_{27}H_{14}NOF_3$ $[M-2H]^+$ calcd: 425.1027, found: 425.1029; ***R_f*** (5/1 hexanes/EtOAc) = 0.18.

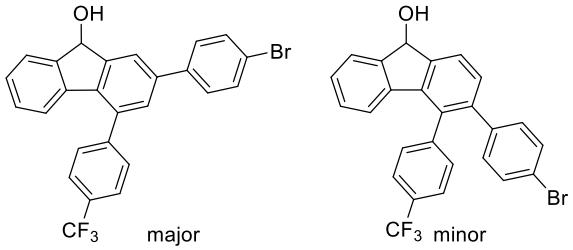


2,4-Bis(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (3c). With **1a** (150 mg, 0.54 mmol) and 4-ethynyl-α,α,α-trifluorotoluene (175 µL, 1.07 mmol) following the general procedure. According to the ^1H NMR analysis of the reaction mixture regioisomers **3c** and **3c'** were formed in 5:1 ratio. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 89 mg (35%) of **3c** as a brown solid. The minor regioisomer **3c'** was not isolated. **mp** (decomp) 184-187 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.96 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.76 - 7.82 (m, 4H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 6.8 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 1.6 Hz, 1H), 7.31 (td, *J* = 7.6, 1.2 Hz, 1H), 7.15 (t, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.70 (d, *J* = 9.8 Hz, 1H), 1.98 (d, *J* = 10 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 146.4, 144.9, 143.9, 143.7, 139.1, 138.9, 136.8, 136.7, 130.4, 129.5, 129.4 (br), 129.9, 129.0, 128.2, 127.3, 125.9 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.7 (br),

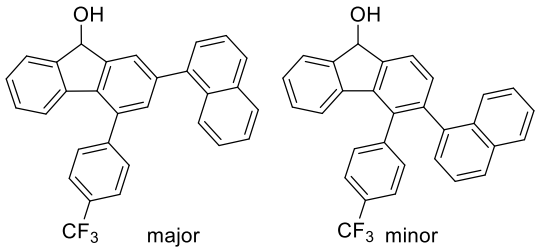


125.2, 123.4, 122.8, 74.8; **<u>^{19}F NMR</u>** (376 MHz, $CDCl_3$) δ -62.37, -62.42; **<u>ATR</u>** ν_{max} 3411, 3392, 1616, 1511, 1454, 1407, 1394, 1328, 1290, 1166, 1103, 1068, 1017, 897, 834, 793, 745 cm^{-1}; **<u>HRMS</u>** (APCI) *m/z* for $C_{27}H_{16}OF_6$ $(M)^+$ calcd: 470.10999, found: 470.10978; R_f (5/1 hexanes/EtOAc) = 0.23.

2-(4-Bromophenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (3d). With **1a** (162 mg, 0.54 mmol) and 1-bromo-4-ethynylbenzene (196 mg, 1.08 mmol) following the general procedure. According to the ^{1}H NMR analysis of the reaction mixture regioisomers **3d** and **3d'** were formed in 4:1 ratio. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 83 mg (32%) of **3d** as light brown solid. The minor regioisomer **3d'** was not isolated. **<u>mp</u>** (decomp) 229-235 °C; **<u>^{1}H NMR</u>** (400 MHz, $CDCl_3$) (major) δ 7.91 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.62-7.55 (m, 4H), 7.41 (d, *J* = 2 Hz, 1H), 7.29 (td, *J* = 7.6, 1.2 Hz, 1H), 7.14 (td, *J* = 7.6, 0.8 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 5.68 (br d, *J* = 10 Hz, 1H), 1.99 (br d, *J* = 10.0 Hz, 1H); **<u>^{13}C NMR</u>** (101 MHz, $CDCl_3$) δ 147.8, 146.3, 144.08, 144.07, 139.4, 139.1, 139.0, 136.6, 136.3, 132.0, 130.0, 129.5 (br), 129.0, 128.6, 128.0, 125.7 (br), 125.5, 125.1, 123.1, 122.6, 122.0, 74.8; **<u>^{19}F NMR</u>** (376 MHz, $CDCl_3$) δ -62.38; **<u>IR</u>** (KBr) ν_{max} 3434, 3387, 3043, 2926, 2860, 1494, 1455, 1401, 1323, 1290, 1180, 1126, 1072, 1033, 1009, 893, 851, 824, 752 cm^{-1}; **<u>HRMS</u>** (ESI) *m/z* for $C_{26}H_{15}OBrF_3$ $[M-H]^-$ calcd: 479.02639, found: 479.02618; ***<u>R_f</u>*** (3/1 hexanes/EtOAc) = 0.35.

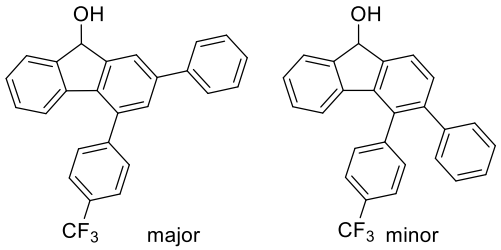


2-(Naphth-1-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (3e). With **1a** (150 mg, 0.54 mmol) and 1-ethynylnaphthalene (154 μL, 1.08 mmol) following the general procedure. According to the ^{1}H NMR analysis of the reaction mixture regioisomers **3e** and **3e'** were formed in 10:1 ratio. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 72 mg (29%) of **3e** as a brown solid. The minor regioisomer **3e'** was not isolated. **<u>mp</u>** (decomp) 189-192 °C; **<u>^{1}H NMR</u>** (400 MHz, $CDCl_3$) (major) δ 8.02 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.86 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 6.8 Hz, 3H), 7.59-7.44 (m, 4H), 7.38 (d, *J* = 1.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 5.72 (br s, 1H), 1.99 (s, 1H); **<u>^{13}C NMR</u>** (101

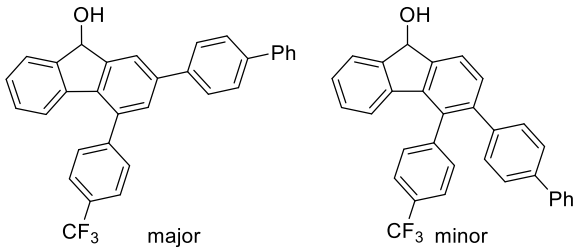


MHz, $CDCl_3$) δ 147.1, 146.4, 144.1, 140.3, 139.2, 139.2, 136.1, 135.8, 133.8, 132.6, 131.4, 130.1 (q, $^2J_{C\text{-}F}$ = 32.1 Hz), 129.5 (br), 128.9, 128.4, 128.0, 127.9, 127.1, 126.3, 126.3, 125.9, 125.7, 125.6 (br), 125.4, 125.1, 122.6, 74.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.32; **IR** (KBr) ν_{max} 3338, 3050, 2920, 2860, 1926, 1619, 1575, 1508, 1464, 1448, 1391, 1318, 1160, 1119, 1106, 1068, 1040, 1014, 894, 843, 802, 780, 736 cm^{-1}; **HRMS** (MALDI) *m/z* for $C_{30}H_{19}F_3O$ $[M]^+$ calcd: 452.1388, found: 452.1383; ***R$_f$*** (5/1 hexanes/EtOAc) = 0.28.

2-Phenyl-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (3f). With **1a** (151 mg, 0.50 mmol) and phenylacetylene (110 μL, 1.01 mmol) following the general procedure. According to the ^{1}H NMR analysis of the reaction mixture regioisomers **3f** and **3f'** were formed in 10:1 ratio. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 81 mg (40%) of **3f** as a pale brown solid. The minor regioisomer **3f'** was not isolated. **mp** (decomp) 189-195 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.95 (d, *J* = 1.6 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.68-7.63 (m, 5H), 7.46 (m, 3H), 7.38 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.28 (td, *J* = 7.4, 0.8 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 5.68 (br s, 1H), 2.00 (br s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.6, 146.4, 144.3, 140.6, 140.1, 139.1, 136.5, 135.8, 130.2, 129.9, 129.7 (br), 128.9, 128.8, 127.8, 127.7, 127.0, 125.6 (br), 125.1, 123.3, 122.9, 122.5, 74.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.34; **ATR** ν_{max} 3419, 3055, 3031, 2923, 1619, 1458, 1413, 1395, 1329, 1290, 1162, 1123, 1105, 1066, 1024, 893, 848, 764, 749, 698 cm^{-1}; **HRMS (ESI)** *m/z* for $C_{26}H_{16}OF_3$ $[M\text{-}H]^-$ calcd: 401.11587, found: 401.11554; ***R$_f$*** (3/1 hexanes/EtOAc) = 0.35.

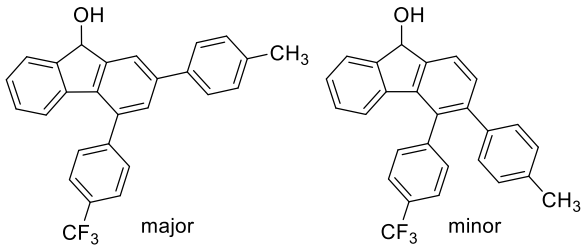


2-([1,1'-Biphenyl]-4-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (3g). With **1a** (151 mg, 0.50 mmol) and 4-ethynylbiphenyl (183 mg, 1.01 mmol) following the general procedure. According to the ^{1}H NMR analysis of the reaction mixture regioisomers **3g** and **3g'** were formed in 7:1 ratio. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 98 mg (41%) of **3g** as light brown solid. The minor regioisomer **3g'** was not isolated. **mp** (decomp) 220-227 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 8.01 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.78 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.71 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.68-7.66 (m, 5H), 7.52 (d, *J* = 1.6 Hz, 1H),

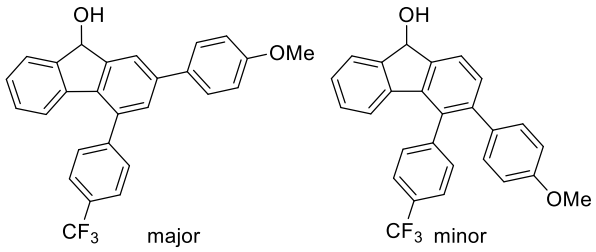


7.48 (tt, *J* = 7.6, 2.0 Hz, 2H), 7.38 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.30 (td, *J* = 7.6, 0.8 Hz, 1H), 7.15 (td, J = 7.6, 0.4 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 5.72 (br d, *J* = 9.6 Hz, 1H), 1.98 (br d, *J* = 9.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.7, 146.4, 144.3, 140.6, 140.5, 140.1, 139.1, 139.0, 136.9, 136.6, 135.9, 130.2, 129.6, 129.4 (br), 128.9, 128.8, 127.9, 127.6, 127.5, 127.4, 127.0, 125.6 (br), 125.1, 123.1, 122.6, 74.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.34; **IR** (KBr) ν_{max} 3423, 3043, 2917, 1606, 1455, 1404, 1332, 1272, 1174, 1126, 1108, 1066, 1027, 1003, 973, 923, 896, 836, 770, 740, 695 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{32}H_{20}OF_3$ $[M-H]^-$ calcd: 477.14717, found: 477.14647; ***R*$_f$** (3/1 hexanes/EtOAc) = 0.34.

2-(*p*-Tolyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (3h). With **1a** (74 mg, 0.24 mmol) and 4-ethynyltoluene (64 μL, 0.49 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 47 mg (46%) of an inseparable mixture of title regioisomers (**3h**:**3h'** / 10:1) as a pale brown solid: **mp** (decomp) 181-186 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.94 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.65 (m, 3H), 7.58 (dt, *J* = 8.0, 2.0 Hz 2H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.25-7.29 (m, 3H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.68 (d, *J* = 10 Hz, 1H), 2.41 (s, 3H), 1.94 (d, *J* = 10 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.6, 146.3, 144.4, 140.6, 139.2, 137.6, 137.2, 136.5, 135.6, 130.1, 129.9, 129.6, 129.5, 129.3 (br), 128.9, 127.7, 126.9, 125.6 (br), 125.1, 123.1, 122.5, 74.9, 21.1; **IR** (KBr) ν_{max} 3482, 3048, 3052, 3028, 2972, 2850, 1604, 1457, 1324, 1251, 1220, 1160, 1122, 1104, 1066, 1014, 954, 846, 818, 741 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{27}H_{19}OF_3Na$ $[M+Na]^+$ calcd: 439.12802, found: 439.12787; ***R*$_f$** (5/1 hexanes/EtOAc) = 0.60.

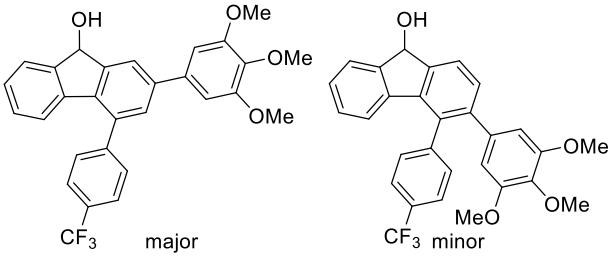


2-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (3i). With **1a** (150 mg, 0.50 mmol) and 4-ethynylanisole (130 μL, 1.00 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 77 mg (36%) of an inseparable mixture of title regioisomers (**3i**:**3i'** / 10:1) as a pale brown solid: **mp** (decomp) 201-206 °C*;* **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.90 (d, *J* = 1.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.66-7.60 (m, 5H), 7.41 (d, *J* = 1.6 Hz, 1H), 7.26 (td, *J* = 7.6, 0.8, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.82 (d,

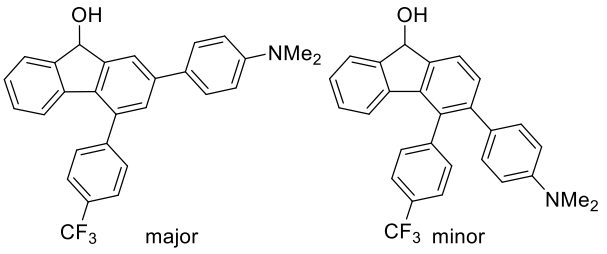


J = 7.6 Hz, 1H), 5.65 (br s, 1H), 3.86 (s, 3H), 2.02 (br s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.5, 147.6, 146.3, 144.4, 140.3, 139.3, 136.5, 135.2, 132.6, 130.1 (q, $^2J_{C\text{-}F}$ = 32.1 Hz), 129.2, 128.9, 128.1, 127.7, 125.6 (br), 125.1, 125.0, 122.8, 122.5, 114.4, 113.2, 74.9, 55.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.34; **IR** (KBr) ν_{max} 3419, 3058, 2944, 2836, 1604, 1518, 1458, 1443, 1410, 1320, 1290, 1251, 1180, 1117, 1063, 1027, 890, 851, 830, 749 cm^{-1}; **HRMS** (EI) *m/z* for $C_{27}H_{17}O_2F_3$ $[M\text{-}2H]^+$ calcd: 430.1181, found: 430.1182; ***R*$_f$** (5/1 hexanes/EtOAc) = 0.25.

4-(4-(Trifluoromethyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-9*H*-fluoren-9-ol (3j). With **1a** (250 mg, 0.83 mmol) and 5-ethynyl-1,2,3-trimethoxybenzene (320 mg, 1.66 mmol) following the general procedure. According to the ^{1}H NMR analysis of the reaction mixture regioisomers **3j** and **3j'**were formed in 20:1 ratio. Column chromatography on silica gel (5/1/1 DCM/hexanes/EtOAc) gave 222 mg (54%) of **3j** as a brown solid. The minor regioisomer **3j'** was not isolated. **mp** (decomp) 101-103 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.91 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.65 (t, *J* = 7.3 Hz, 3H), 7.40 (d, *J* = 1.5 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.78 - 6.89 (m, 3H), 5.68 (br s, 1H), 3.94 (s, 6H), 3.90 (s, 3H), 2.13 (br s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.6, 147.6, 146.3, 144.2, 140.7, 139.1, 138.0, 136.4, 136.1, 135.9, 130.1 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.6 (br), 129.5, 128.9, 127.8, 125.6 (br), 125.1, 123.2, 122.5, 104.3, 74.8, 61.0, 56.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.33; IR (KBr) ν_{max} 3452, 2998, 2935, 2836, 1622, 1583, 1512, 1461, 1413, 1359, 1323, 1281, 1240, 1168, 1120, 1108, 1069, 1018, 1009, 964, 848, 830, 746 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{29}H_{23}O_4F_3Na$ $[M+Na]^+$ calcd: 515.14406, found: 515.14364; ***R*$_f$** (5/1/1 DCM/hexanes/EtOAc) = 0.34.

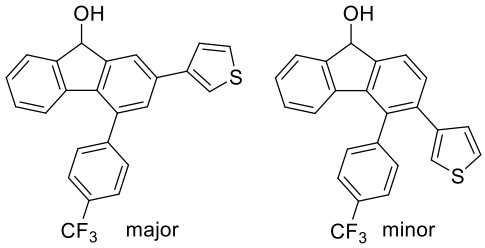


2-(4-(*N,N*-Dimethylamino)phenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (3k). With **1a** (98 mg, 0.32 mmol) and 4-ethynyl-*N,N*-dimethylaniline (97 mg, 0.65 mmol) following the general procedure. According to the ^{1}H NMR analysis of the reaction mixture were regioisomers **3k** and **3k'** were formed in 25:1 ratio. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 87 mg (60%) of **3k** as a dark brown solid. The minor regioisomer **3k'** was not isolated. **mp** (decomp) 104-106 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.63 (m, *J* =

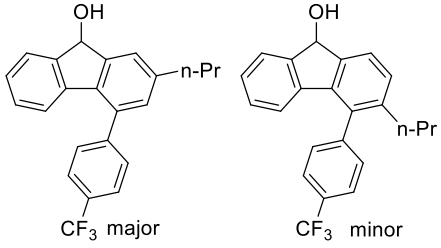


7.1 Hz, 3H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 1.7 Hz, 1H), 7.25 (td, *J* = 7.3, 0.7 Hz, 1H), 7.11 (t, *J* = 8.2 Hz, 1H), 6.78 - 6.88 (m, 3H), 5.63 (s, 1H), 3.00 (s, 6H), 2.17 (br s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.0 (br), 147.6, 146.3, 144.6, 140.6, 139.4, 136.4, 134.5, 129.5 (br), 129.5 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 128.7, 128.6, 127.6, 127.4, 125.5 (br), 125.0, 124.2 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 122.3, 122.2, 113.0 (br), 74.8, 40.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.28; **IR** (KBr) ν_{max} 3351, 3046, 2929, 2884, 2851, 2806, 1613, 1607, 1530, 1479, 1458, 1446, 1410, 1362, 1329, 1275, 1228, 1201, 1168, 1123, 1108, 1069, 1018, 955, 893, 851, 818, 740, 644, 606, 534, 510 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{28}H_{23}ONF_3$ $[M+H]^+$ calcd: 446.17263, found: 446.17226; ***R*$_f$** (3/1 hexanes/EtOAc) = 0.30.

2-(Thien-3-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (3l). With **1a** (130 mg, 0.43 mmol) and 3-ethynylthiophene (87 µL, 0.85 mmol) following the general procedure. Column chromatography on silica gel (3/1 hexanes/ EtOAc) gave 107 mg (62%) of an inseparable mixture of title regioisomers (**3l**:**3l'** / 5:1) as a brown solid. **mp** (decomp) 177-183 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.94 (d, *J* = 1.6 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.66-7.62 (m, 3H), 7.55 (dd, *J* = 2.8, 1.6 Hz, 1H), 7.47-7.45 (m, 2H), 7.42 (dd, *J* = 4.8, 2.8 Hz, 1H), 7.27 (td, *J* = 7.6, 0.8 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.66 (br s, 1H), 1.99 (br s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.6, 146.3, 144.2, 141.4, 139.2, 136.5, 135.6, 135.3, 130.1 (q, $^2J_{C\text{-}F}$ = 33.0 Hz), 129.6, 129.4 (br), 128.9, 127.8, 126.6, 126.2, 125.6 (br), 125.1, 124.7, 122.6, 122.5, 120.8, 74.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.35; **IR** (KBr) ν_{max} 3510, 3100, 2923, 2854, 1458, 1404, 1326, 1171, 1123, 1105, 1069, 1036, 848, 785, 755 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{24}H_{14}OF_3S$ $[M-H]^-$ calcd: 407.07229, found: 407.07196; ***R*$_f$** (3/1 hexanes/EtOAc) = 0.30.

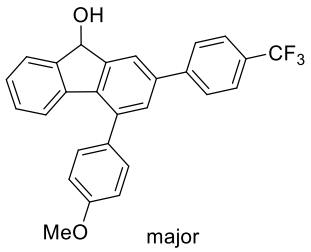


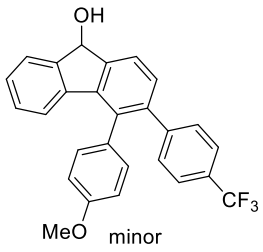
2-Propyl-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (3m). With **1a** (192 mg, 0.64 mmol) and pent-1-yne (320 µL, 3.21 mmol) following the general procedure. According to the ^{1}H NMR analysis of the reaction mixture regioisomers **3m** and **3m'** were formed in 4:1 ratio. Column chromatography on silica gel (7/1 hexanes/EtOAc) gave 62 mg (26%) of **3m**. The minor regioisomer **3m'** was not isolated. **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.56 - 7.65 (m, 3H), 7.53 (d, *J* = 0.7 Hz, 1H), 7.23 (td, *J* = 7.5, 1.0 Hz, 1H), 7.10 (td, *J* =



7.6, 0.7 Hz, 1H), 7.03 (d, *J* = 1.2 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 5.58 (d, *J* = 9.3 Hz, 1H), 2.68 (t, *J* = 7.3 Hz, 2H), 1.91 (d, *J* = 9.8 Hz, 1H), 1.72 (sxt, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0, 146.1, 144.5, 142.6, 139.5, 135.9, 134.3, 131.0, 129.9, 129.6, 129.3, 128.7, 127.4, 125.5 (br), 125.0, 124.8, 122.2, 74.8, 37.9, 24.5, 13.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.37; **IR** (KBr) ν_{max} 3461, 3303, 3049, 3028, 2962, 2932, 2869, 1619, 1458, 1401, 1380, 1329, 1248, 1222, 1168, 1129, 1105, 1069, 1024, 967, 952, 899, 881, 848, 797, 749, 632, 612 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{23}H_{19}F_3NaO$ $[M+Na]^+$ calcd: 391.128137, found: 391.128021; ***R*$_f$** (7/1 hexanes/EtOAc) = 0.60.

4-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (3n) and 4-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (3n'). With **1b** (262 mg, 1.0 mmol) and 4-ethynyl-α,α,α-trifluorotoluene (336 μL, 2.00 mmol) following the general procedure. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 138 mg (32%) of **3n** and 37 mg (8%) of **3n'** as brown solids. **3n** (major): 138 mg (32%); **mp** (decomp) 118-121 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 1.6 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.28 (td, *J* = 7.6, 0.8 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.64 (br s, 1H), 3.93 (s, 3H), 2.31 (br s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 147.6, 146.3, 144.0, 139.4, 138.7, 138.0, 137.1, 132.5, 130.2, 129.9 (br), 129.4 (q, $^2J_{C\text{-}F}$ = 32.1 Hz), 128.8, 127.7, 127.2, 125.7 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.9, 124.2 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 123.0, 122.5, 114.0, 74.8, 55.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.34; **IR** (KBr) ν_{max} 3366, 3064, 2998, 2962, 2926, 2899, 2839, 1613, 1512, 1455, 1416, 1326, 1290, 1251, 1177, 1123, 1069, 1030, 1018, 955, 926, 896, 839, 749, 704, 662, 582 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{27}H_{19}O_2F_3Na$ $[M+Na]^+$ calcd: 455.12294, found: 455.12259; ***R*$_f$** (3/1 hexanes/EtOAc) = 0.47.

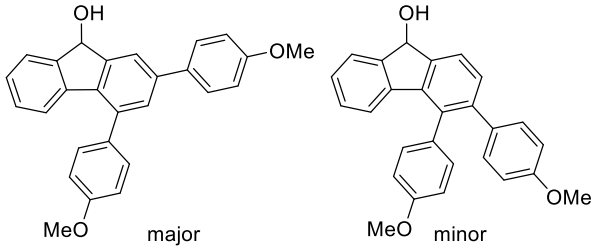




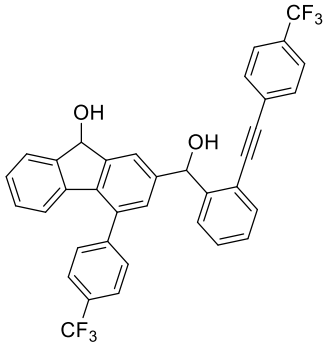
3n' (minor): 37 mg (8%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.6, 0.7 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.20 - 7.25 (m, 3H), 7.14 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.06 (t, *J* = 7.3 Hz, 1H), 7.00 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.89 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.84 (dd, *J* = 8.6, 2.9 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 5.65 (d, *J* = 9.5 Hz, 1H), 3.85 (s, 3H), 1.89 (d, *J* = 9.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 146.3, 146.1, 144.9, 144.9, 141.6, 140.0, 138.6, 135.7, 131.3, 130.9, 130.5, 130.1, 129.3, 128.8, 128.4 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 127.6, 124.8, 124.2 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 124.1, 124.5 (q, $^3J_{C\text{-}}$

$_F$ = 3.8 Hz), 123.2, 114.0, 113.9, 74.6, 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.37; ***R*$_f$** (3/1 hexanes/EtOAc) = 0.37.

2,4-Bis(4-methoxyphenyl)-9*H*-fluoren-9-ol (3o). With **1b** (145 mg, 0.55 mmol) and 4-ethynylanisole (148 μL, 1.10 mmol) following the general procedure. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 110 mg (51%) of an inseparable mixture of title regioisomers (**3o**:**3o'** / 7:1) as a brown solid: **mp** (decomp) 96-98 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.85 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.65-7.60 (m, 3H), 7.45 - 7.39 (m, 3H), 7.24 (td, *J* = 7.6, 1.2 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.64 (br s, 1H), 3.92 (s, 3H), 3.86 (s, 3H), 1.96 (br s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.25, 159.19, 147.4, 146.3, 140.0, 139.8, 137.8, 135.6, 133.0, 132.9, 130.8, 130.1, 129.5, 128.6, 128.0, 127.2, 124.8, 122.7, 121.9, 114.2, 113.9, 113.0, 74.9, 55.3; **IR** (KBr) ν_{max} 3411, 3384, 3070, 3046, 3028, 2995, 2953, 2932, 2902, 2836, 1610, 1512, 1455, 1437, 1329, 1290, 1245, 1183, 1117, 1030, 964, 943, 926, 896, 833, 788, 776, 749, 698, 650, 582, 534 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{27}H_{22}O_3Na$ $[M+Na]^+$ calcd: 417.14612, found: 417.14633; ***R*$_f$** (3/1 hexanes/EtOAc) = 0.34.



2-(Hydroxy(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)methyl)-4-(4-(trifluoromethyl) phenyl)-9*H*-fluoren-9-ol (4). With **1a** (74 mg, 0.24 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 30 mg (40%) of the title compound as a clear brown solid: **mp** (decomp) 221-223 °C; **^{1}H NMR** (400 MHz, acetone-d_6) δ 7.96 (d, *J* = 7.8 Hz, 1H), 7.75 - 7.86 (m, 3H), 7.63 - 7.73 (m, 4H), 7.50 - 7.63 (m, 4H), 7.45 (d, *J* = 1.5 Hz, 1H), 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 7.22 (td, *J* = 7.3, 1.0 Hz, 1H), 7.06 (t, *J* = 8.1 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.45 (d, *J* = 4.2 Hz, 1H), 5.57 (d, *J* = 7.6 Hz, 1H), 5.17 - 5.19 (m, 1H), 4.88 (d, *J* = 7.6 Hz, 1H), 2.88 (br s, 1H); **^{13}C NMR** (101 MHz, acetone-d_6) δ 149.5, 148.8, 148.1, 145.9, 144.9, 139.9, 136.5, 136.3, 133.2, 132.9, 130.6 (br), 130.49 (q, $^3J_{C\text{-}F}$ = 10.8 Hz), 130.48, 130.3, 128.9, 128.3, 128.2, 128.1, 127.12, 127.09, 126.4-126.3 (m), 126.0, 124.2, 124.1, 123.0, 121.1, 121.0, 93.8, 91.2, 74.9, 74.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.48, -62.93; **IR** (KBr) ν_{max} 3336, 3067, 2920, 2851, 2220, 1927, 1616, 1571, 1518, 1476,

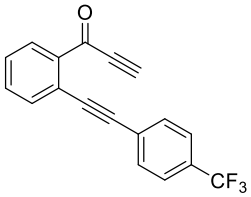


1458, 1407, 1326, 1174, 1129, 1105, 1069, 1033, 1027, 955, 845, 758, 740, 710, 603 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{36}H_{21}O_2F_6$ $[M-H]^+$ calcd: 599.14403, found: 599.14372; ***R*$_f$** (5/2 hexanes/EtOAc) = 0.27.

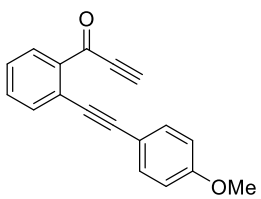
5.2.3 Synthesis and characterization of ethynylphenylpropynones (5a-5c) and fluorenones (7a-7o)

General procedure for oxidation reaction with PCC. Preparation of 5 and 7. In a one-neck flask under atmospheric conditions, PCC (102 mg, 0.47 mmol), Celite® (same mass of PCC) and anhydrous CH_2Cl_2 (15 mL) were added. Then, the starting material **3**, **1a-1b** or **iiia** (0.31 mmol) was added and the resulting mixture was stirred for 3 h at room temperature. The residue was filtered through a Celite®/silica gel plug and purified by column chromatography on silica gel to afford the corresponding fluorenone derivatives.

1-(2-((4-(Trifluoromethyl)phenyl)ethynyl)phenyl)prop-2-yn-1-one (5a). With 1-(2-((4-(Trifluoromethyl)phenyl)ethynyl)phenyl)prop-2-yn-1-ol **1a** (151 mg, 0.50 mmol) following the general procedure. Column chromatography on silica gel (8/1 hexanes/EtOAc) gave 51.5 mg (34%) of the title compound as an orange oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.67 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.57 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.49 (td, *J* = 7.6, 1.3 Hz, 1H), 3.46 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.3, 137.1, 134.5, 133.0, 132.5, 132.1, 130.2 (q, $^2J_{C-F}$ = 33 Hz), 128.5, 126.9 (q, $^4J_{C-F}$ = 1.5 Hz), 125.2 (q, $^3J_{C-F}$ = 3.8 Hz), 122.5, 122.3, 93.5, 90.3, 80.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.80; **IR** (KBr) ν_{max} 3291, 3255, 3073, 2932, 2101, 1721, 1655, 1610, 1592, 1559, 1482, 1407, 1326, 1296, 1269, 1234, 1168, 1126, 1102, 1063, 1015, 1000, 961, 842, 755, 695 cm^{-1}; **HRMS** (EI) *m/z* for $C_{18}H_9OF_3$ $[M]^+$ calcd: 298.0605, found: 298.0602; ***R*$_f$** (8/1 hexanes/EtOAc) = 0.25.

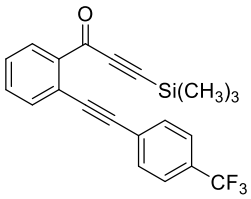


1-(2-((4-Methoxyphenyl)ethynyl)phenyl)prop-2-yn-1-one (5b). With 1-(2-((4-methoxyphenyl)ethynyl)phenyl)prop-2-yn-1-ol **1b** (39 mg, 0.15 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 17 mg (42%) of the title compound as a pale yellow solid. **mp** (decomp) 80-83 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.51 - 7.59 (m, 3H), 7.42 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.43 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.6,



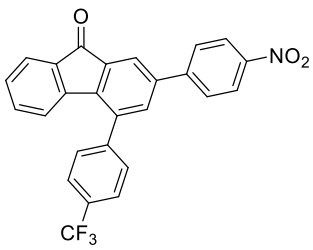
160.0, 136.8, 134.1, 133.5, 132.9, 132.3, 127.5, 123.6, 115.2, 114.0, 95.9, 87.1, 81.2, 80.6, 55.3; **IR** (KBr) ν_{max} 3100, 2998, 2208, 2088, 1717, 1651, 1594, 1508, 1458, 1439, 1283, 1249, 1226, 1169, 1147, 1106, 1027, 986, 964, 831, 751 cm^{-1}; **HRMS** (EI) *m/z* for $C_{18}H_{12}O_2$ $[M]^+$ calcd: 260.0837, found: 260.0839; ***R_f*** (5/1 hexanes/EtOAc) = 0.22.

1-(2-((4-(Trifluoromethyl)phenyl)ethynyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-one (5c).

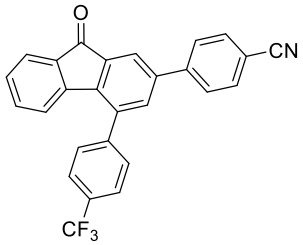


With 1-(2-((4-methoxyphenyl)ethynyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol **iiia** (47 mg, 0.13 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 32 mg (68%) of the title compound as a yellow solid. **mp** (decomp) 42-44 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.66 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.56 (td, *J* = 7.5, 1.3 Hz, 1H), 7.49 (td, *J* = 7.6, 1.2 Hz, 1H), 0.27 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.8, 137.8, 134.3, 132.6, 132.4, 132.1, 130.2 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 128.4, 127.1 (q, $^4J_{C\text{-}F}$ = 1.5 Hz), 125.2 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.2 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 122.6, 122.1, 101.4, 100.7, 93.3, 90.5, -0.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.79; **IR** (KBr) ν_{max} 3061, 2965, 2905, 2152, 1652, 1619, 1592, 1559, 1476, 1407, 1326, 1296, 1240, 1165, 1117, 1069, 1021, 863, 842, 791, 755, 701, 686, 629, 600 cm^{-1}; **HRMS** (EI) *m/z* for $C_{21}H_{17}OF_3Si$ $[M]^+$ calcd: 370.1001, found: 370.1000; ***R_f*** (5/1 hexanes/EtOAc) = 0.53.

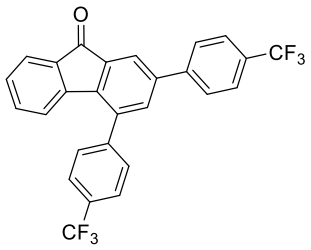
2-(4-Nitrophenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (7a). With **3a** (125 mg, 0.28 mmol) following the general procedure Column chromatography on silica gel (7/1 hexanes/EtOAc) gave 112 mg (90%) of the title compound as a bright orange solid: **mp** (decomp) 234-269 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 1.7 Hz, 1H), 7.77 - 7.87 (m, 4H), 7.70 - 7.75 (m, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 1.7 Hz, 1H), 7.23 - 7.33 (m, 2H), 6.73 - 6.81 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.7, 147.6, 145.4, 143.4, 142.6, 141.2, 139.5, 137.2, 135.9, 135.0, 134.9, 134.6, 131.0 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.5, 129.3, 127.6, 126.0 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.7, 124.3, 124.0 (q, $^1J_{C\text{-}F}$ = 271.1 Hz), 123.1, 122.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.50; **IR** (KBr) ν_{max} 3084, 3072, 1718, 1595, 1521, 1461, 1398, 1338, 1329, 1293, 1225, 1171, 1117, 1102, 1066, 1015, 958, 842, 812, 743, 689, 665 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{26}H_{14}O_3NF_3$ $[M]^+$ calcd: 445.09203, found: 445.09165; ***R_f*** (7/1 hexanes/EtOAc) = 0.39.



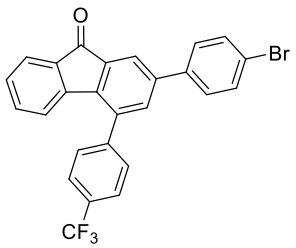
4-(9-Oxo-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-2-yl)benzonitrile (7b). With **3b** (30 mg, 0.07 mmol) following the general procedure. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 22 mg (73%) of the title compound as a bright yellow solid: **mp** (decomp) 254-260 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.78-7.74 (m, 4H), 7.72-7.70 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 1.6 Hz, 1H), 7.29-7.27 (m, 2H), 6.77-6.75 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.9, 143.5, 143.4, 142.6, 141.0, 139.8, 137.1, 135.8, 134.9, 134.6, 132.8, 130.6 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.4, 129.3, 127.4, 125.9 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.7, 124.0 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 123.1, 122.6, 122.3, 118.6, 111.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.44; **IR** (KBr) ν_{max} 3058, 2956, 2923, 2854, 2232, 1715, 1601, 1577, 1467, 1404, 1323, 1296, 1213, 1171, 1129, 1108, 1078, 1063, 1021, 937, 854, 839, 818, 758, 701 cm^{-1}; **HRMS** (EI) *m/z* for $C_{27}H_{14}NOF_3$ $[M]^+$ calcd: 425.1027, found: 425.1025; ***R*$_f$** (3/1 hexanes/EtOAc) = 0.71.



2,4-Bis(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (7c). With **3c** (85 mg, 0.18 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 76 mg (90%) of the title compound as a bright yellow solid: **mp** (decomp) 179-182°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 1.96 Hz, 1H), 7.82 (d, *J* = 8.07 Hz, 2H), 7.70 - 7.78 (m, 5H), 7.67 (d, *J* = 8.07 Hz, 2H), 7.56 (d, *J* = 1.71 Hz, 1H), 7.23 - 7.31 (m, 2H), 6.72 - 6.79 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.0, 143.6, 142.9, 142.6, 140.6, 140.5, 137.1, 135.8, 134.9, 134.8, 134.7, 130.9 - 130.1 (m), 129.4, 129.3, 127.1, 126.1 - 125.8 (m), 125.4 – 122.7 (m), 124.6, 123.0, 122.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.48, -62.53; **IR** (KBr) ν_{max} 3061, 2938, 1730, 1619, 1580, 1464, 1410, 1392, 1326, 1290, 1266, 1222, 1168, 1105, 1072, 1015, 958, 905, 839, 737, 707, 686 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{27}H_{15}F_6O$ $[M+H]^+$ calcd: 469.10216, found: 469.10205; ***R*$_f$** (5/1 hexanes/EtOAc) = 0.67.

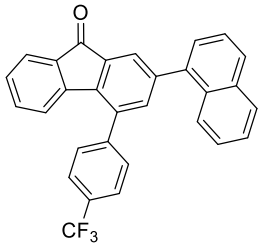


2-(4-Bromophenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (7d). With **3d** (83 mg, 0.17 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 68 mg (82%) of the title compound as a bright yellow solid: **mp** (decomp) 206-211 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 0.8 Hz, 1H), 7.81 (d, *J* = 5.2 Hz, 2H), 7.70-7.69 (m, 1H), 7.65 (d, *J* = 5.2 Hz, 2H), 7.58 (d, *J* = 6.0 Hz, 2H), 7.51-7.50 (m, 3H), 7.25-7.24 (m, 2H), 6.74-6.73 (m, 1H); **^{13}C NMR** (101 MHz,

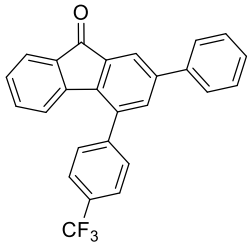


$CDCl_3$) δ 193.2, 143.7, 142.9, 140.8, 140.0, 138.0, 137.0, 135.7, 134.6, 134.4, 132.1, 130.6 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.3, 129.1, 128.3, 125.8 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.5, 124.0 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 122.9, 122.6, 122.5, 122.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.40; **IR** (KBr) ν_{max} 3073, 3058, 2962, 2923, 2851, 1978, 1942, 1909, 1715, 1607, 1577, 1497, 1461, 1404, 1329, 1296, 1231, 1165, 1120, 1102, 1075, 1012, 937, 854, 830, 806, 764, 737, 704 cm^{-1}; **HRMS** (EI) *m/z* for $C_{26}H_{14}OF_3Br$ $[M]^+$ calcd: 478.0180, found: 478.0181; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.36.

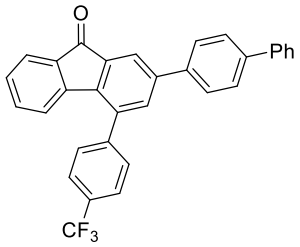
2-(Naphth-1-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (7e). With **3e** (66 mg, 0.14 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 53 mg (81%) of the title compound as a bright yellow solid: **mp** (decomp) 172-175 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.87 (m, 4H), 7.80 (d, *J* = 8.00 Hz, 2H), 7.75-7.67 (m, 3H), 7.44-7.57 (m, 5H), 7.28-7.27 (m, 2H), 6.86-6.79 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.3, 143.9, 143.1, 141.9, 139.9, 138.2, 137.7, 136.5, 135.2, 134.7, 134.6, 133.9, 131.2, 130.5 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.4, 129.1, 128.5, 128.5, 126.9, 126.5, 126.1, 125.8 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.5, 125.4, 125.3, 124.5, 124.1 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 122.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.46; **IR** (KBr) ν_{max} 3094, 3061, 3037, 2917, 2851, 2364, 2328, 1924, 1826, 1715, 1610, 1509, 1467, 1455, 1416, 1398, 1323, 1287, 1231, 1168, 1123, 1108,1066, 1024, 973, 949, 902, 851, 800, 782, 743, 686, 662 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{30}H_{18}F_3O$ $[M+H]^+$ calcd: 451.13043, found: 451.13026; ***R*$_f$** (5/1 hexanes/EtOAc) = 0.62.



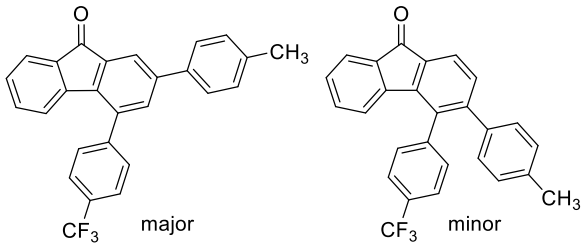
2-Phenyl-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (7f). With **3f** (61 mg, 0.15 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 59 mg (98%) of the title compound as a bright yellow solid: **mp** (decomp) 174-178 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 2.0, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.71-7.69 (m, 1H), 7.68-7.64 (m, 4H), 7.55 (d, *J* = 1.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.25-7.23 (m, 2H), 6.76-6.73 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.3, 143.9, 143.2, 142.1, 139.7, 139.1, 136.9, 135.7, 134.7, 134.6, 130.5 (q, $^2J_{C\text{-}F}$ = 33.0 Hz), 129.4, 129.02, 128.96, 128.2, 126.8, 125.8 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 124.7 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 124.5, 122.8, 122.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.45; **IR** (KBr) ν_{max} 3061, 2917, 2851, 1712, 1604, 1577, 1467, 1452, 1407, 1326, 1296, 1263, 1222, 1168, 1123, 1105, 1078, 1063, 1021, 955, 937, 893, 860, 842, 809, 755, 740, 698 cm^{-1}; **HRMS** (EI) *m/z* for $C_{26}H_{15}OF_3$ $[M]^+$ calcd: 400.1075, found: 400.1073; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.62.



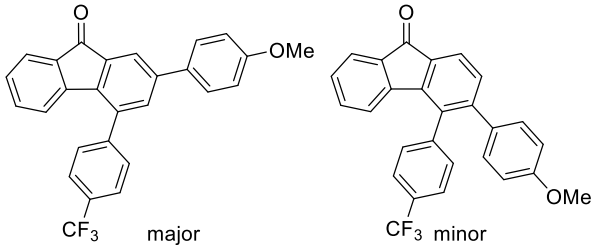
2-([1,1'-Biphenyl]-4-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (7g). With **3g** (94 mg, 0.20 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 65 mg (70%) of the title compound as a bright yellow solid: **mp** (decomp) 132-138 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.75-7.63 (m, 9H), 7.60 (d, *J* = 1.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.38 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.26-7.24 (m, 2H), 6.76-6.74 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.3, 143.9, 143.2, 141.6, 141.1, 140.3, 139.7, 137.9, 136.9, 135.7, 134.7, 134.7, 134.5, 134.5, 130.6 (q, $^{2}J_{C\text{-}F}$ = 32.9 Hz), 129.4, 129.0, 128.9, 127.7, 127.6, 127.1, 127.0, 125.8 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.5, 124.1 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 122.8, 122.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.44; **IR** (KBr) ν_{max} 3061, 3031, 2926, 2854, 1718, 1604, 1574, 1488, 1464, 1443, 1404, 1326, 1293, 1231, 1162, 1132, 1108, 1066, 1024, 1006, 958, 934, 905, 857, 839, 812, 767, 734, 692 cm^{-1}; **HRMS** (EI) *m/z* for $C_{32}H_{19}OF_3$ $[M]^+$ calcd: 476.1388, found: 476.1374; R_f(10/1 hexanes/EtOAc) = 0.32.



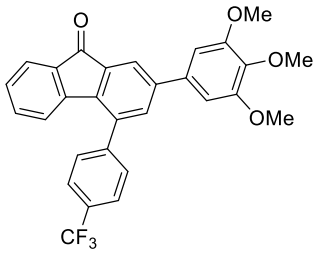
2-(*p*-Tolyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (7h). With **3h** (215 mg, 0.52 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 180 mg (83%) of the two inseparable title regioisomer compounds in the ratio of 10:1 as a bright yellow solid. **mp** (decomp) 182-186 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.97 (d, *J* = 1.7 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.68 - 7.71 (m, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.55 (dt, *J* = 8.3, 2.0 Hz, 2H), 7.53 (d, *J* = 1.7 Hz, 1H), 7.22 - 7.29 (m, 4H), 6.71 - 6.76 (m, 1H), 2.41 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.4, 143.9, 143.3, 142.0, 139.4, 138.2, 136.8, 136.2, 135.7, 134.7, 134.6, 134.4, 130.5 (q, $^{2}J_{C\text{-}F}$ = 33.1 Hz), 129.7, 129.4, 128.9, 126.8 (q, $^{1}J_{C\text{-}F}$ = 270.1 Hz), 126.6, 125.8 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 124.4, 122.7, 122.2, 21.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.44; **IR** (KBr) ν_{max} 3058, 3031, 2917, 2863, 1963, 1906, 1712, 1607, 1577, 1518, 1461, 1410, 1395, 1329, 1293, 1225, 1159, 1123, 1102, 1066, 1021, 958, 902, 848, 821, 776, 746, 689, 656, 621, 600, 516, 474 cm^{-1}; **HRMS** (EI) *m/z* for $C_{27}H_{17}OF_3$ $[M]^+$ calcd: 414.1232, found: 414.1229; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.46.



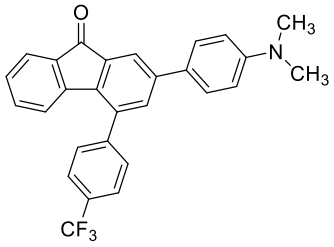
2-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (7i). With **3i** (66 mg, 0.15 mmol) following the general procedure. Column chromatography on silica gel (5/2 hexanes/EtOAc) gave 59 mg (89%) of the two inseparable title regioisomer compounds in the ratio of 10:1 as a bright yellow solid: **mp** (decomp) 163-167 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.94 (d, *J* = 1.6, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.70-7.68 (m, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.24-7.22 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.72-6.71 (m, 1H), 3.86 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.5, 159.9, 144.0, 141.7, 139.8, 139.0, 136.8, 135.7,134.7, 134.6, 134.1, 131.6, 130.6, 129.4, 128.8, 127.9, 125.8 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.5, 122.7, 121.9, 114.4, 105.2, 55.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.44; **IR** (KBr) ν_{max} 3061, 3013, 2965, 2920, 2854, 1712, 1607, 1574, 1518, 1461, 1413, 1389, 1329, 1290, 1251, 1183, 1168, 1120, 1105, 1069, 1033, 1018, 955, 824, 737 cm^{-1}; **HRMS** (EI) *m/z* for $C_{27}H_{17}O_2F_3$ $[M]^+$ calcd: 430.1181, found: 430.1179; R_f(5/2 hexanes/EtOAc) = 0.52.



4-(4-(Trifluoromethyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-9*H*-fluoren-9-one(7j). With **3j** (172 mg, 0.35 mmol) following the general procedure. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 130 mg (76%) of the title compound as a bright yellow solid: **mp** (decomp) 214-215 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.62 - 7.71 (m, 3H), 7.49 (d, *J* = 1.7 Hz, 1H), 7.16 - 7.29 (m, 2H), 6.78 - 6.88 (m, 2H), 6.72 (m, *J* = 5.1 Hz, 1H), 3.93 (s, 6H), 3.90 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.3, 153.6, 143.8, 143.1, 142.1, 139.6, 138.4, 136.8, 135.6, 134.9, 134.7, 134.6, 134.4, 130.6 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.3, 128.9, 125.8 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.5, 124.0 (q, $^{1}J_{C\text{-}F}$ = 270.4 Hz), 122.8, 122.2, 104.0, 60.9, 56.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.43; **IR** (KBr) ν_{max} 3004, 2938, 2836, 1718, 1607, 1589, 1518, 1464, 1434, 1410, 1359, 1326, 1234, 1165, 1126, 1072, 1009, 905, 851, 830, 743, 698, 665 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{29}H_{22}O_4F_3$ $[M+H]^+$ calcd: 491.14647, found: 491.14628; ***R*$_f$** (3/1 hexanes/EtOAc) = 0.31.

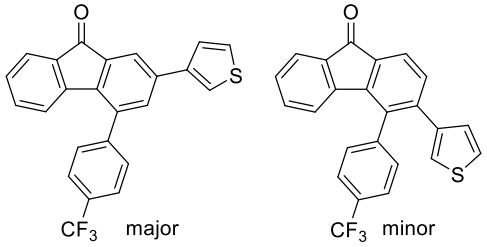


2-(4-(*N,N-D*imethylamino)phenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (7k).

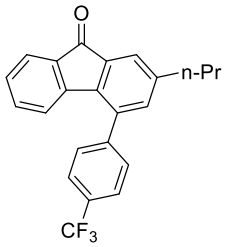


To a solution of the fluorenol **3k** (0.21 mmol, 92 mg) in dry CH_2Cl_2 (10 mL) the commercially available 85% active MnO_2 (2.8 mmol, 212 mg) was added. The suspension was vigorously stirred at room temperature for 20 h. The reaction mixture was filtered through a Celite® pad and purified by column chromatography on silica gel (5/1 hexanes/EtOAc) which gave 77 mg (84%) of the title compound as a bright orange solid: **mp** (decomp) 186-190 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.7 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.62 - 7.69 (m, 3H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 1.7 Hz, 1H), 7.19 - 7.22 (m, 2H), 6.82 (d, *J* = 6.1 Hz, 2H), 6.69 - 6.73 (m, 1H), 3.02 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.7, 144.2, 143.6, 142.0, 138.2, 136.8, 135.7, 134.7, 134.5, 133.3, 130.7, 130.4 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.4, 128.9, 128.5, 127.4, 125.7 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.4, 124.1(q, $^1J_{C\text{-}F}$ = 270.4 Hz), 122.5, 121.4, 112.8, 43.6, 40.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.41; **IR** (KBr) ν_{max} 3052, 2965, 2920, 2890, 2854, 2800, 1954, 1924, 1718, 1601, 1533, 1461, 1413, 1368, 1326, 1287, 1234, 1195, 1168, 1120, 1108, 1066, 1021, 958, 884, 848, 815, 800, 740 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{28}H_{21}ONF_3$ $[M+H]^+$ calcd: 444.15698, found: 444.15659; ***R*$_f$** (5/1 hexanes/EtOAc) = 0.26.

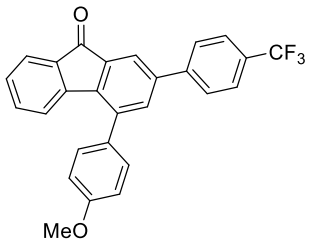
2-(Thien-3-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (7l). With **3l** (65 mg, 0.16 mmol) following the general procedure. Column chromatography on silica gel (5/2 hexanes/EtOAc) gave 58 mg (89%) of the two title regioisomer compounds in the ratio of 16:1 as a bright yellow solid: **mp** (decomp) 163-171 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.91 (d, *J* = 1.6 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.67-7.62 (m, 3H), 7.54 (t, *J* = 2.4 Hz, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.41 (d, *J* = 2.4 Hz, 2H), 7.23-7.20 (m, 2H), 6.73-6.69 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.3, 143.8, 143.06, 143.04, 140.2, 139.2, 136.8, 136.5, 135.5, 134.6, 134.5, 133.6, 130.4 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.3, 128.8, 126.8, 125.8 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.4, 124.0 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 122.6, 121.5, 121.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.34; **IR** (KBr) ν_{max} 3108, 3076, 2932, 2851, 1930, 1712, 1604, 1574, 1533, 1464, 1413, 1326, 1165, 1111, 1078, 1063, 1018, 976, 934, 905, 848, 800, 782, 740, 710, 689, 668 cm^{-1}; **HRMS** (EI) *m/z* for $C_{24}H_{13}OSF_3$ $[M]^+$ calcd: 406.0639, found: 406.0642; ***R*$_f$** (5/2 hexanes/EtOAc) = 0.59.



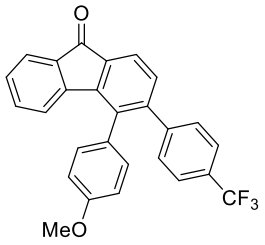
2-Propyl-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (7m). With **3m** (62 mg, 0.17 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 41 mg (70%) of the title compound as a bright yellow solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.6 Hz, 2H), 7.67 - 7.64 (m, 1H), 7.60 (d, J = 7.8 Hz, 2H), 7.55 (d, J = 1.6 Hz, 1H), 7.17 - 7.23 (m, 2H), 7.11 (d, J = 1.6 Hz, 1H), 6.66 - 6.72 (m, 1H), 2.64 (t, J = 7.4 Hz, 2H), 1.69 (sxt, J = 7.4 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.8, 144.2, 144.2, 143.4, 138.6, 136.3, 135.1, 134.5, 134.5, 130.0 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.3, 128.6, 128.2, 127.7, 125.7 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.3, 124.0, 122.5, 37.5, 24.2, 13.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.41; **IR** (KBr) ν_{max} 3315, 3070, 2965, 2932, 2875, 2854, 1718, 1607, 1467, 1329, 1287, 1242, 1189, 1174, 1111, 1069, 1015, 985, 923, 908, 857, 836, 743, 695, 659 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{23}H_{17}F_3NaO$ $[M+Na]^+$ calcd: 389.112337, found: 389.112371; ***R*$_f$** (7/1 hexanes/EtOAc) = 0.64.



4-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (7n). With **3n** (133 mg, 0.31 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 123 mg (92%) of the title compound as a bright yellow solid: **mp** (decomp) 165-166 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, J = 1.6 Hz, 1H), 7.75 - 7.67 (m, 4H), 7.65 (m, J = 0.5 Hz, 1H), 7.56 (d, J = 2.0 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.25 - 7.18 (m, 2H), 7.06 (d, J = 8.8 Hz, 2H), 6.92 - 6.86 (m, 1H), 3.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.4, 159.7, 144.2, 142.9, 140.8, 140.0, 138.4, 135.6, 135.4, 134.6, 134.5, 131.2, 130.0 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.9, 128.8, 127.0, 125.8 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.0 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 124.2, 123.2, 121.5, 114.2, 55.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.43; **IR** (KBr) ν_{max} 3393, 3073, 3058, 3034, 3007, 2965, 2941, 2911, 2839, 2543, 2528, 2098, 1909, 1870, 1832, 1709, 1604, 1577, 1521, 1464, 1416, 1404, 1323, 1290, 1251, 1204, 1168, 1123, 1114, 1084, 1069, 1036, 1015, 961, 937, 887, 860, 845, 812, 779, 758, 728, 704, 674, 626, 603 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{27}H_{18}F_3O_2$ $[M+H]^+$ calcd: 431.12534, found: 431.12492; ***R*$_f$** (5/1 hexanes/EtOAc) = 0.40.

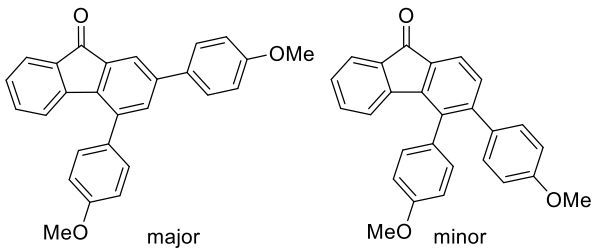


4-(4-Methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (7n'). With **3n'**



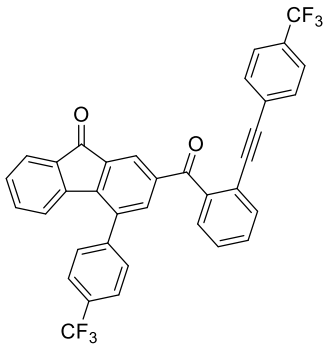
(36.9 mg, 0.085 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 26.7 mg (73%) of the title compound as a bright yellow solid: **mp** (decomp) 209-211 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.3 Hz, 1H), 7.66 (dd, *J* = 7.1, 0.7 Hz, 1H), 7.45 (dd, *J* = 8.6, 0.7 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.18 - 7.24 (m, 3H), 7.15 (td, *J* = 7.6, 1.7 Hz, 1H), 7.07 (dt, *J* = 8.8, 2.7 Hz, 2H), 6.88 (dt, *J* = 8.8, 2.7 Hz, 2H), 6.35 (dt, *J* = 7.6, 0.9 Hz, 1H), 3.85 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.5, 159.2, 147.2, 144.5, 144.0 (q, $^{4}J_{C\text{-}F}$ = 1.5 Hz), 142.8, 136.3, 134.8, 134.5, 134.1, 131.0, 130.6, 129.8, 129.3, 129.1 (q, $^{2}J_{C\text{-}F}$ = 32.1 Hz), 128.7, 124.7 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.1, 124.1 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 123.4, 123.2, 114.1, 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.50; IR (KBr) ν_{max} 3392, 3092, 3051, 3012, 2968, 2917, 2841, 1708, 1603, 1575, 1515, 1464, 1404, 1321, 1283, 1245, 1166, 1109, 1062, 1033, 1014, 932, 834, 755, 694 cm^{-1}; **HRMS** (EI) *m/z* for $C_{27}H_{17}O_2F_3$ $[M]^+$ calcd: 430.1181, found: 430.1179; ***R*$_f$** (5/2 hexanes/EtOAc) = 0.46.

2,4-Bis(4-methoxyphenyl)-9*H*-fluoren-9-one (7o). With **3o** (106 mg, 0.27 mmol) following



the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 97 mg (92%) of the two title regioisomer compounds in the ratio of 10:1 as a bright yellow solid: **mp** (decomp) 86-90 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.87 (d, *J* = 2.0 Hz, 1H), 7.67 - 7.63 (m, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.22 - 7.17 (m, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.88 - 6.84 (m, 1H), 3.92 (s, 3H), 3.85 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.9, 159.6, 159.5, 144.6, 141.3, 139.3, 138.2, 135.5, 134.70, 134.68, 134.4, 131.9, 131.8, 130.0, 128.3, 127.8, 124.1, 122.9, 121.1, 114.3, 114.1, 55.35, 55.33; **ATR** ν_{max} 3067, 3049, 3028, 3013, 2995, 2956, 2926, 2899, 2836, 1715, 1613, 1574, 1458, 1446, 1419, 1329, 1284, 1251, 1183, 1111, 1102, 1066, 1036, 955, 899, 839, 809, 773, 743, 689 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{27}H_{20}O_3Na$ $[M+Na]^+$ calcd: 415.13047, found: 415.13081; ***R*$_f$** (5/1 hexanes/EtOAc) = 0.36.

4-(4-(Trifluoromethyl)phenyl)-2-(2-((4-(trifluoromethyl)phenyl)ethynyl)benzoyl)-*9H*-

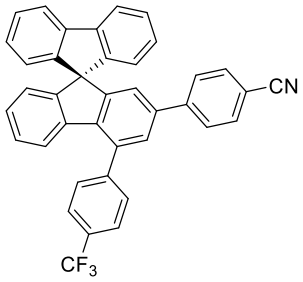


fluoren-9-one (4a). With **4** (64 mg, 0.10 mmol) following the general procedure. Column chromatography on silica gel (5/2 hexanes/EtOAc) gave 54 mg (86%) of the title compound as a bright yellow solid: **mp** (decomp) 86-90 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 1.6 Hz, 1H), 7.91 (d, *J* = 1.6 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.72 (dt, *J* = 7.2, 0.7 Hz, 1H), 7.66 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.61 (td, *J* = 7.0, 1.2 Hz, 1H), 7.56 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.50 - 7.55 (m, 3H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.32 (td, *J* = 7.6, 1.0 Hz, 1H), 7.24 - 7.29 (m, 3H), 6.75 (d, *J* = 7.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.0, 192.1, 144.9, 142.8, 142.1, 140.7, 138.2, 137.8, 136.6, 135.0, 135.0, 134.9, 133.6, 133.0, 131.5, 131.1, 130.8, 130.2, 129.2, 129.1, 128.9, 126.3, 126.0 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.1 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.7, 123.6, 122.3, 121.2, 93.9, 89.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.56, -62.93; **IR** (KBr) δ_{max} 3067, 2926, 1718, 1667, 1604, 1565, 1473, 1440, 1407, 1362, 1326, 1284, 1231, 1171, 1135, 1105, 1063, 1018, 1000, 955, 929, 842, 803, 755, 740, 710, 689, 662, 597, 516 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{36}H_{19}O_2F_6$ $[M+H]^+$ calcd: 597.12838, found: 597.12793; ***R*$_f$** (5/2 hexanes/EtOAc) = 0.79.

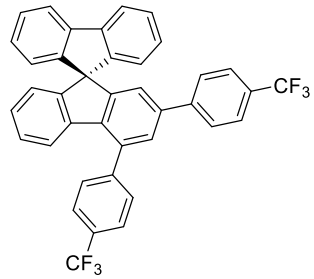
5.2.4 Synthesis and characterization of 2,4-disubstituted-9,9'-spirobifluorene (8b-8o).

General procedure for synthesis of 2,4-disubstituted-9,9'-spirobifluorene 8.[153] A dried Schlenk flask was filled up with 2-bromobiphenyl (95 μL, 0.55 mmol) and anhydrous THF (7.0 mL) under argon atmosphere. After cooling down to -78 °C, *n*-BuLi (1.6 M in hexanes, 340 μL, 0.55 mmol) was added dropwise. The resulting solution was stirred for 30 min at -78 °C, then fluorenone **7** (0.36 mmol) in THF (12 mL) was added dropwise. The reaction mixture was stirred for 15 min at -78 °C and then warmed up gradually to 25 °C. After 4 hours, the reaction was quenched with saturated aqueous $NaHCO_3$ solution and extracted with diethyl ether (3 x 20 mL). The combined organic fractions were dried over Na_2SO_4 and concentrated with rotary evaporator. The crude was purified by silica gel column chromatography (10/1 hexanes/EtOAc). The resulting pure alcohol was subjected immediately to the next step. The compound was dissolved in acetic acid (18 mL) and catalytic amount of concentrated HCl (5-6 drops). The resulting mixture was refluxed for 3 hours and then neutralized with saturated aqueous K_2CO_3 solution. Extraction with diethyl ether (3 × 20 mL), drying over Na_2SO_4, filtration and evaporation under reduced pressure afforded the crude which was purified by column chromatography on silica gel.

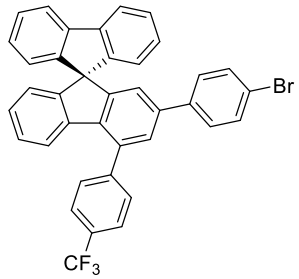
4-(4-(4-(Trifluoromethyl)phenyl)-9,9'-spirobifluoren-2-yl)benzonitrile (8b). With **7b** (77 mg, 0.18 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 50 mg (49%) of the title compound as a white solid: **mp** (decomp) 122-123 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (t, *J* = 8.1 Hz, 4H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.40 - 7.45 (m, 3H), 7.17 (td, *J* = 7.5, 1.0 Hz, 2H), 7.06 - 7.14 (m, 3H), 6.98 (d, *J* = 1.7 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.73 (dd, *J* = 6.4, 1.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.0, 149.6, 148.3, 144.6, 144.1, 141.8, 140.2, 139.1, 138.3, 136.7, 132.4, 130.3 (q, $^{2}J_{C\text{-}F}$ = 31.9 Hz), 129.7, 128.7, 128.3, 128.02, 128.00, 127.59, 127.55, 125.7 (q, ^{3}J = 3.8 Hz), 125.6, 124.2, 124.0, 122.8, 122.1, 120.2, 118.8, 110.9, 65.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.27; **IR** (KBr) ν_{max} 3061, 3040, 3019, 2929, 2229, 1604, 1512, 1446, 1410, 1389, 1329, 1261, 1251, 1222, 1171, 1132, 1108, 1066, 1018, 839, 752, 740, 677, 650 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{39}H_{22}NF_3$ $[M]^+$ calcd: 561.16989, found: 561.16931; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.40.



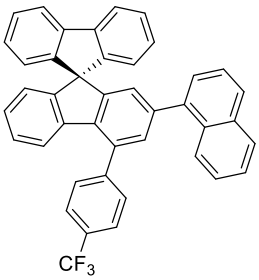
2,4-Bis(4-(trifluoromethyl)phenyl)-9,9'-spirobifluorene (8c). With **7c** (55 mg, 0.12 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 58 mg (81%) of the title compound as a white solid: **mp** (decomp) 184-187 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 - 7.91 (m, 4H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.50 - 7.58 (m, 4H), 7.38 - 7.44 (m, 3H), 7.16 (td, *J* = 7.5, 1.1 Hz, 2H), 7.06 - 7.13 (m, 2H), 7.03 (td, *J* = 7.6, 1.6 Hz, 1H), 6.97 (d, *J* = 1.6 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.73 (dd, *J* = 7.3, 0.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.9, 149.6, 148.5, 144.32, 144.30, 143.7, 141.8, 140.4, 139.0, 138.6, 136.6, 130.2 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.7, 129.4 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 128.8, 128.2, 128.0, 127.5, 127.3, 125.7 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 125.5 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 124.2, 124.1, 122.8, 122.3, 120.2, 65.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.30, -62.50; **IR** (KBr) ν_{max} 3064, 3043, 3013, 2929, 2851, 2361, 2325, 1954, 1921, 1616, 1571, 1479, 1449, 1410, 1392, 1326, 1278, 1245, 1171, 1123, 1066, 1018, 887, 842, 758, 743, 689, 653, 618 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{39}H_{22}F_6$ $[M]^+$ calcd: 604.16202, found: 604.16138; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.64.



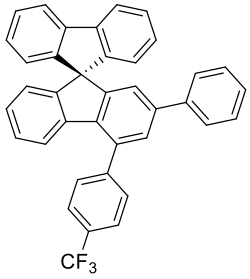
2-(4-Bromophenyl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobifluorene (8d). With **7d** (68 mg, 0.14 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 33 mg (36%) of the title compound as a white solid: **mp** (decomp) 211-214 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 - 7.94 (m, 6H), 7.36 - 7.47 (m, 5H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), 7.10 (td, *J* = 7.2, 1.2 Hz, 1H), 7.00 - 7.08 (m, 2H), 6.93 (d, *J* = 1.6 Hz, 1H), 6.85 (d, *J* = 7.2 Hz, 2H), 6.72 (d, *J* = 6.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.7, 149.5, 148.6, 144.4, 141.8, 140.5, 139.2, 139.1, 138.1, 136.5, 131.7, 130.1 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.7, 128.6, 128.4, 128.01, 127.96, 127.9, 127.5, 125.6 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.1, 122.9, 122.6, 121.9, 121.7, 120.1, 65.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.26; **IR** (KBr) ν_{max} 3067, 3040, 3016, 2923, 2851, 1619, 1598, 1583, 1494, 1479, 1449, 1404, 1383, 1326, 1278, 1248, 1165, 1123, 1105, 1069, 1021, 1009, 973, 961, 943, 926, 884, 851, 824, 782, 761, 743, 689, 656, 623 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{38}H_{22}BrF_3$ $[M]^+$ calcd: 614.08515, found: 614.08531; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.64.



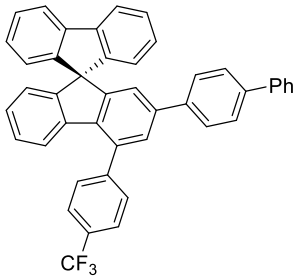
2-(Naphth-1-yl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobifluorene (8e). With **7e** (53 mg, 0.12 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 51 mg (74%) of the title compound as a white solid: **mp** (decomp) 142-144 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.80 (m, 7H), 7.77 (dd, *J* = 8.0, 5.3 Hz, 2H), 7.44-7.39 (m, 2H), 7.37 (dd, *J* = 7.6, 1.6 Hz, 3H), 7.34-7.28 (m, 2H), 7.18 (td, *J* = 7.5, 0.9 Hz, 2H), 7.15-7.05 (m, 3H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 1.6 Hz, 1H), 6.77 (d, *J* = 7.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.2, 149.5, 148.6, 144.5, 141.8, 140.9, 139.9, 139.2, 137.5, 135.9, 133.7, 131.4, 131.3, 130.1, 129.8, 128.3, 127.88, 127.86, 127.83, 127.79, 127.4, 126.9, 126.0, 125.7, 125.6, 125.6 (q, $^1J_{C\text{-}F}$ = 3.8 Hz), 125.4, 125.2, 124.2, 124.0, 122.6, 120.1, 65.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.25; **IR** (KBr) ν_{max} 3058, 3040, 3019, 3010, 2950, 2923, 2851, 1619, 1509, 1476, 1449, 1392, 1326, 1281, 1242, 1168, 1129, 1108, 1084, 1066, 1021, 893, 845, 800, 779, 758, 740, 659 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{42}H_{25}F_3$ $[M]^+$ calcd: 586.19029, found: 586.18954; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.47.



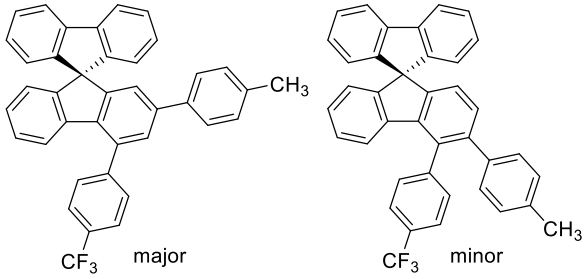
2-Phenyl-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobifluorene (8f). With **7f** (59 mg, 0.15 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 42 mg (53%) of the title compound as a white solid: **mp** (decomp) 147-150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 - 7.90 (m, 6H), 7.37 - 7.45 (m, 5H), 7.31 (tt, *J* = 7.2, 1.6 Hz, 2H), 7.25 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.15 (td, *J* = 7.5, 1.1 Hz, 2H), 7.00 - 7.12 (m, 3H), 6.96 (d, *J* = 1.6 Hz, 1H), 6.86 (dt, *J* = 7.5, 0.9 Hz, 2H), 6.72 (d, *J* = 7.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5, 149.5, 148.7, 144.6, 141.8, 140.7, 140.5, 140.1, 137.6, 136.4, 130.0 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.7, 128.6, 127.9, 127.8, 127.43, 127.39, 127.0, 125.6 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.12, 124.09, 124.3 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 122.5, 122.2, 120.1, 65.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.18; **IR** (KBr) ν_{max} 3061, 1619, 1595, 1452, 1413, 1395, 1326, 1168, 1126, 1111, 1084, 1072, 1018, 887, 851, 755, 740, 695, 653, 626 cm^{-1}; **HRMS** (EI) *m/z* for $C_{38}H_{23}F_3$ $[M]^+$ calcd: 536.1752, found: 536.1749; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.44.



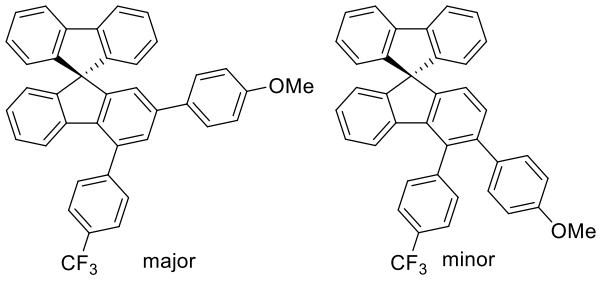
2-([1,1'-Biphenyl]-4-yl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobifluorene (8g). With **7g** (65 mg, 0.14 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 32 mg (38%) of the title compound as a white solid: **mp** (decomp) 214-216 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 - 7.94 (m, 6H), 7.49 - 7.58 (m, 6H), 7.48 (d, *J* = 1.2 Hz, 1H), 7.37 - 7.45 (m, 4H), 7.33 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.16 (td, *J* = 7.6, 0.8 Hz, 2H), 7.11 (td, *J* = 7.6, 1.6 Hz, 1H), 7.02 - 7.08 (m, 2H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 2H), 6.73 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.6, 149.5, 148.7, 144.6, 141.8, 140.6, 140.5, 140.3, 139.9, 139.0, 137.7, 136.4, 130.0 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.7, 128.7, 128.5, 127.94, 127.86, 127.4, 127.3, 127.0, 126.9, 125.6 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.13, 124.09, 124.3 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 122.6, 122.1, 120.1, 65.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.18; **IR** (KBr) ν_{max} 3058, 3028, 2926, 1613, 1598, 1488, 1473, 1446, 1413, 1392, 1309, 1284, 1168, 1120, 1111, 1066, 1021, 851, 836, 761, 743, 698, 674, 647, 623 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{44}H_{27}F_3$ $[M]^+$ calcd: 612.20594, found: 612.20599; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.42.



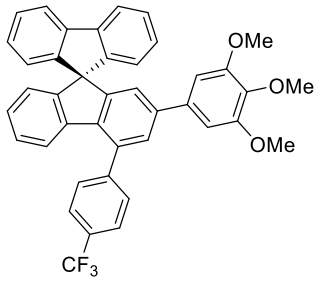
2-(*p*-Tolyl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobifluorene (8h). With **7h** (151 mg, 0.36 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 98 mg (49%) of the two title regioisomer compounds in the ratio of 10:1 as a white solid: **mp** (decomp) 132-138 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.84 - 7.94 (m, 5H), 7.39 - 7.46 (m, 3H), 7.35 (d, J = 7.6 Hz, 2H), 7.26 (s, 1H), 7.09 - 7.20 (m, 5H), 7.06 (t, J = 6.4 Hz, 2H), 6.98 (d, J = 0.7 Hz, 1H), 6.88 (d, J = 7.2 Hz, 2H), 6.74 (d, J = 7.6 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5, 149.5, 148.7, 144.7, 141.8, 140.7, 140.4, 137.35, 137.29, 137.2, 136.3, 131.0, 130.1, 129.7, 129.3, 128.4, 127.9, 127.8, 127.7, 127.4, 126.8, 125.6 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.13, 124.06, 122.5, 122.0, 120.1, 65.7, 21.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.16; **IR** (KBr) ν_{max} 3047, 2923, 2870, 1913, 1616, 1515, 1448, 1407, 1321, 1280, 1252, 1163, 1125, 1103, 1065, 1017, 846, 812, 732 cm^{-1}; **HRMS** (EI) *m/z* for $C_{39}H_{25}F_3$ $[M]^+$ calcd: 550.1908, found: 550.1907; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.41.



2-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobifluorene (8i). With **7i** (55 mg, 0.13 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/ EtOAc) gave 65 mg (89%) of the two title regioisomer compounds in the ratio of 21:1 as a white solid: **mp** (decomp) 131-134 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.81 - 7.91 (m, 6H), 7.35 - 7.43 (m, 5H), 7.16 (td, J = 7.5, 1.1 Hz, 2H), 7.10 (td, J = 7.6, 1.2 Hz, 1H), 7.04 (td, J = 8.3, 1.6 Hz, 2H), 6.94 (d, J = 2.0 Hz, 1H), 6.83 - 6.89 (m, 4H), 6.70 - 6.75 (m, 1H), 3.78 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 150.5, 149.4, 148.8, 144.7, 141.8, 140.8, 140.1, 137.0, 136.3, 132.6, 129.9 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.7, 128.1, 128.0, 127.9, 127.8, 127.7, 127.4, 125.6 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.1, 124.3 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 124.0, 122.4, 121.7, 120.1, 114.0, 65.7, 55.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.18; **IR** (KBr) ν_{max} 3050, 2961, 2936, 1606, 1578, 1515, 1445, 1318, 1287, 1245, 1166, 1122, 1106, 1065, 1033, 1017, 881, 850, 831, 751, 736 cm^{-1}; **HRMS** (EI) *m/z* for $C_{39}H_{25}F_3O$ $[M]^+$ calcd: 566.1858, found: 566.1856; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.32.

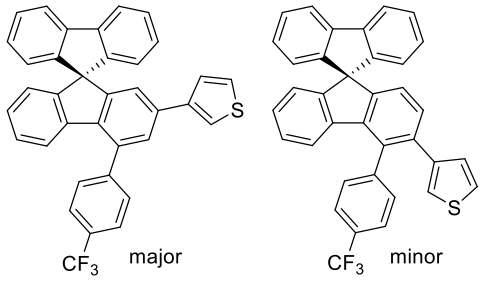


4-(4-(Trifluoromethyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-9,9'-spirobifluorene (8j). With

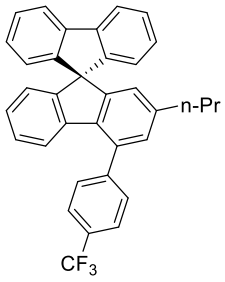


7j (130 mg, 0.27 mmol) following the general procedure. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 136 mg (82%) of the title compound as a white solid: **mp** (decomp) 156-160 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 - 7.92 (m, 6H), 7.41 (td, *J* = 7.5, 1.1 Hz, 2H), 7.37 (d, *J* = 1.7 Hz, 1H), 7.16 (td, *J* = 7.5, 1.1 Hz, 2H), 7.10 (td, *J* = 7.3, 1.5 Hz, 1H), 7.04 (td, *J* = 7.6, 1.5 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 1.7 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 2H), 6.70 (dd, *J* = 6.8, 1.0 Hz, 1H), 6.59 - 6.62 (m, 2H), 3.82 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.4, 150.4, 149.6, 148.6, 144.58, 144.56, 141.8, 140.7, 140.5, 138.0, 137.8, 136.34, 136.32, 130.1 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.8, 128.6, 127.92, 127.85, 127.4, 125.6 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.3 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 124.1, 124.0, 122.5, 122.2, 120.1, 104.7, 65.8, 60.9, 56.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.24; **IR** (KBr) ν_{max} 3073, 3040, 3013, 2962, 2941, 2842, 2827, 1616, 1583, 1509, 1443, 1404, 1362, 1329, 1275, 1242, 1165, 1132, 1117, 1105, 1063, 1006, 929, 908, 851, 836, 734, 668, 647, 615, 513, 489 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{41}H_{29}O_3F_3Na$ $[M+Na]^+$ calcd: 649.19610, found: 649.19577; ***R*$_f$** (3/1 hexanes/EtOAc) = 0.34.

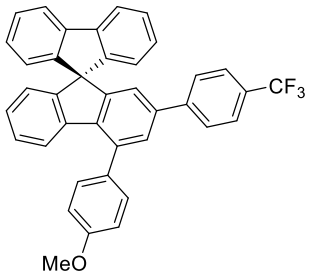
3-(4-(4-(Trifluoromethyl)phenyl)-9,9'-spirobifluoren-2-yl)thiophene (8l). With **7l** (58 mg, 0.14 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 42 mg (53%) of the two title regioisomer compounds in the ratio of 17:1 as a white solid: **mp** (decomp) 140-142 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.78 - 7.91 (m, 6H), 7.36 - 7.45 (m, 3H), 7.30 (dd, *J* = 3.2, 1.5 Hz, 1H), 7.25 - 7.28 (m, 1H), 7.22 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.15 (td, *J* = 7.2, 0.8 Hz, 2H), 7.09 (td, *J* = 7.6, 1.5 Hz, 1H), 6.98 - 7.06 (m, 2H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.85 (dt, *J* = 7.6, 0.9 Hz, 2H), 6.69 - 6.72 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5, 149.5, 148.7, 144.6, 141.8, 141.4, 140.7, 137.5, 136.4, 135.1, 130.7, 130.0 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.7, 127.94, 127.90, 127.86, 127.8, 127.4, 126.21, 126.18, 125.6 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.12, 124.05, 122.5, 121.5, 120.7, 120.1, 65.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.24; **IR** (KBr) ν_{max} 3100, 3067, 3046, 3016, 2926, 2857, 1622, 1601, 1583, 1446, 1404, 1326, 1281, 1248, 1171, 1120, 1108, 1084, 1066, 1018, 982, 934, 908, 884, 866, 851, 782, 755, 740, 647 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{36}H_{21}F_3S$ $[M]^+$ calcd: 542.13106, found: 542.13073; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.63.



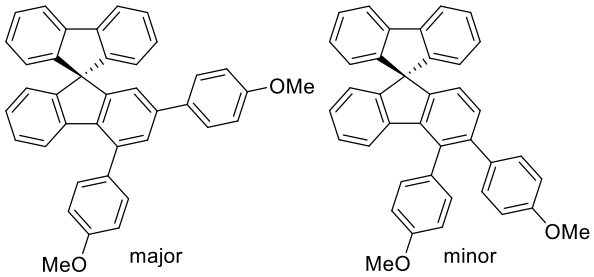
2-Propyl-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobifluorene (8m). With **7m** (27 mg, 0.07 mmol) following the general procedure. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 18 mg (50%) of the title compound as a white solid: **mp** (decomp) 81-83 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.39 (td, *J* = 7.6, 1.0 Hz, 2H), 7.15 (td, *J* = 7.5, 1.1 Hz, 2H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 6.96 - 7.02 (m, 3H), 6.81 (d, *J* = 7.6 Hz, 2H), 6.65 - 6.70 (m, 1H), 6.56 (d, *J* = 1.5 Hz, 1H), 2.45 (t, *J* = 8.1 Hz, 2H), 1.50 (sxt, *J* = 8.0 Hz, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.9, 149.2, 149.1, 144.9, 142.5, 141.8, 141.1, 136.1, 135.8, 129.9, 129.8, 129.7, 127.8, 127.7, 127.3, 127.2, 125.4 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.1, 124.4 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 124.0, 123.7, 122.2, 120.0, 65.6, 37.8, 24.4, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.24; **IR** (KBr) ν_{max} 3060, 2958, 2923, 2866, 1948, 1923, 1616, 1587, 1515, 1448, 1416, 1397, 1318, 1277, 1245, 1163, 1119, 1106, 1065, 1017, 935, 894, 846, 799, 761, 739, 682 cm^{-1}; **HRMS** (CI) *m/z* for $C_{35}H_{26}F_3$ $[M+H]^+$ calcd: 503.1987, found: 503.1985; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.70.



4-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-9,9'-spirobifluorene (8n). With **7n** (123 mg, 0.28 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 144 mg (89%) of the title compound as a white solid: **mp** (decomp) 133-135 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.53 (s, 4H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.40 (td, *J* = 7.5, 0.8 Hz, 2H), 7.07 - 7.18 (m, 6H), 7.04 (td, *J* = 7.2, 1.2 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.70 (d, *J* = 7.2 Hz, 1H), 3.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 150.5, 149.5, 148.8, 144.1, 141.8, 141.0, 139.0, 138.7, 138.0, 132.9, 130.3, 129.1, 129.0, 127.9, 127.84, 127.77, 127.34, 127.30, 125.54, 125.46 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.1, 123.9, 123.1, 121.4, 120.1, 114.1, 65.8, 55.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.45; **IR** (KBr) ν_{max} 3058, 3037, 3013, 2956, 2932, 2905, 2836, 1613, 1574, 1515, 1446, 1395, 1329, 1293, 1245, 1165, 1129, 1075, 1060, 1033, 1015, 1003, 964, 952, 923, 887, 839, 758, 740, 674, 659, 621, 579 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{39}H_{25}OF_3$ $[M]^+$ calcd: 566.18520, found: 566.18524; ***R*$_f$** (10/1 hexanes/EtOAc) = 0.22.



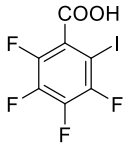
2,4-Bis(4-methoxyphenyl)-9,9'-spirobifluorene (8o). With **7o** (92 mg, 0.24 mmol) following the general procedure. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 83 mg (67%) of the two title regioisomer compounds in the ratio of 9:1 as a white solid: **mp** (decomp) 141-142 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major) δ 7.87 (dt, *J* = 7.6, 0.9 Hz, 2H), 7.60 (dt, *J* = 8.6, 2.0 Hz, 2H), 7.35 - 7.41 (m, 5H), 7.10 - 7.19 (m, 5H), 7.07 (td, *J* = 7.5, 1.3 Hz, 1H), 7.01 (td, *J* = 7.3, 1.2 Hz, 1H), 6.81 - 6.88 (m, 5H), 6.69 (d, *J* = 7.2 Hz, 1H), 3.96 (s, 3H), 3.77 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 159.1, 150.1, 149.3, 149.1, 141.8, 141.4, 139.8, 137.7, 137.5, 133.4, 133.1, 131.5, 131.0, 130.4, 128.5, 128.0, 127.9, 127.7, 127.3, 127.2, 124.2, 123.8, 122.7, 120.8, 120.0, 114.0, 113.9, 65.8, 55.4, 55.3; **IR** (KBr) ν_{max} 3064, 3040, 3013, 2947, 2932, 2905, 2839, 1607, 1577, 1515, 1449, 1437, 1392, 1287, 1245, 1180, 1156, 1108, 1066, 1030, 1003, 970, 949, 926, 884, 839, 806, 779, 758, 740, 689, 671, 653, 623, 576 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{39}H_{29}O_2$ $[M+H]^+$ calcd: 529.21621, found: 529.21654; ***R*$_f$** (5/1 hexanes/EtOAc) = 0.47.



5.3 Procedures for synthesis of fluorinated DSF-IFs and DSF-BIF

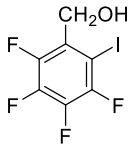
5.3.1 Preparation of starting materials: fluorinated triynediols

2,3,4,5-Tetrafluoro-6-iodobenzoic acid (v).[154] In a dried two-neck flask 2,3,4,5-tetrafluorobenzoic acid **iv** (2.5 g, 13.0 mmol) and anhydrous THF (42 mL) were added under argon atmosphere. After cooling down to -78 °C, *n*-BuLi (17.7 mL, 1.6 M in hexanes, 28.0 mmol) was added dropwise. The resulting solution was stirred for 3 h at the same low temperature. Then iodine (3.82 g, 15 mmol) in THF (8 mL) was added slowly until the colour of the reaction mixture turned permanently into brown. The reaction was gradually warmed up to room temperature; during the warming process, the brown colour faded so a further quantity of iodine solution was added until the colour was persistent. Afterwards a saturated aqueous solution of $NaHSO_3$ was added dropwise until the brown colour slightly faded (if an excessive amount of $NaHSO_3$ is added, a lower yield could be obtained). After removal of solvent by rotary evaporator, the residue in AcOEt was treated with H_2SO_4 (2 M) which was added slowly at 0 °C until pH = 1. The resulting mixture was extracted with AcOEt (3 × 100 mL), the combined organic layers were washed with saturated solution of



$NaHSO_3$ (300 mL), H_2O (300 mL) and brine (300 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting crude solid was sonicated in hexane for 10 min and, after decantation for 5 h, the pure compound was obtained upon filtration and washing with hexane. The filtrate was concentrated under reduced pressure and the purification procedure was repeated again to obtain more product. The procedure yielded 3.49 g (84%) of the title compound as a white solid: **mp** (decomp) 118-121 °C; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3 (br s), 148.1 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 235.5, 11.5, 4.0, 2.0 Hz), 145.6 (dd, $^{1,2}J_{C\text{-}F}$ = 250, 12.0 Hz), 141.3 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 261, 18.5, 12.0, 4.0 Hz), 140.8 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 256, 16.5. 13.0, 3.0 Hz), 122.37 (dd, $^{2,3}J_{C\text{-}F}$ = 15.0, 3.0 Hz), 74.98 (dd, $^{2,3}J_{C\text{-}F}$ = 27.0, 4.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.66-(-112.25) (m, 1F), -136.19-(-135.87) (m, 1F), -149.18-(-148.78) (m, 1F), -152.8-(-152.54) (m, 1F); **HRMS** (ESI) *m/z* for $C_7O_2F_4I$ $[M\text{-}H]^-$ calcd: 318.88846, found: 318.88858. The spectral data were in accordance with the previously published results.[154]

(2,3,4,5-Tetrafluoro-6-iodophenyl)methanol (vi).[155] A dried Schlenk flask was filled up with



2,3,4,5-tetrafluoro-6-iodobenzoic acid (**v**) (7.99 g, 25.0 mmol) in THF (31 mL) under argon. $BH_3{\cdot}Me_2S$ (2 M solution in THF) (37.5 mL, 74.9 mmol) was added slowly at 0 °C. After cooling to room temperature, the resulting mixture was refluxed at 70 °C for 7 h. The reaction was quenched by addition of THF/H_2O (60 mL) and extracted with EtOAc (3×100 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Column chromatography of the residue on silica gel (5/1 to 4/1 hexanes/AcOEt) yielded 6.41 g (84%) of the title compound as a colourless solid: **mp** (decomp) 52-53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 (s, 2H), 2.25 (br s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.5 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 252, 11.3, 4.4, 3.0 Hz), 145.7 (ddd, $^{1,2,3,4}J_{C\text{-}F}$ = 258, 12.0, 3.0 Hz), 140.5 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 254, 23.3, 13.5, 4.50 Hz), 139.7 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 258.0, 20.3, 12.0, 4.5 Hz), 126.4 (dd, $^{2,3}J_{C\text{-}F}$ = 14.9, 4.5 Hz), 81.01 (app dt, $^{2,3}J_{C\text{-}F}$ = 24.0, 3.0 Hz), 61.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.42 (ddd, $J_{F\text{-}F}$ = 22.6, 11.3, 3.8 Hz, 1F), -140.25-(-140.06) (m, 1F), -153.43 (ddd, $J_{F\text{-}F}$ = 22.56, 18.80, 3.76 Hz, 1F), -154.64 (ddd, $J_{F\text{-}F}$ = 22.60, 19.76, 3.80 Hz, 1F); **IR** (KBr) ν_{max} 3282, 3201, 2956, 2926, 2899, 2857, 1628, 1503, 1464, 1359, 1287, 1263, 1219, 1069, 1120, 1021, 946, 791, 746, 674 cm^{-1}; **HRMS** (EI) *m/z* for $C_7H_3OF_4I$ $[M]^+$ calcd: 305.9165, found: 305.9163; ***R$_f$*** (3/1 CH_2Cl_2/hexanes) = 0.51.

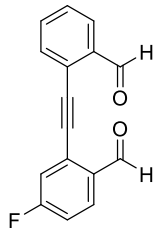
2,3,4,5-Tetrafluoro-6-iodobenzaldehyde (11g). In a dried two-neck flask, pyridinium chlorochromate (PCC, 9.03 g, 0.42 mmol), Celite® (9.03 g) and CH_2Cl_2 (200 mL) were added. After stirring for 10 min, the starting compound **vi** (6.41 g, 0.21 mmol) was added and the mixture was stirred for 3 h at 25 °C and under argon. Afterwards the residue was filtered through a Celite®/silica gel plug. Column chromatography of the crude on silica gel (2/1 hexanes/CH_2Cl_2) afforded 5.80 g (91%) of the title compound as pale yellow liquid: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.01 (s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 187.9, 149.0 (app ddt, $^{1,2,3}J_{C\text{-}F}$ = 267, 11.1, 3.3 Hz), 147.7 (ddd, $^{1,2,3}J_{C\text{-}F}$ = 246, 10.0, 3.3 Hz), 142.74 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 267, 19.9, 12.2, 4.4 Hz), 140.7 (dtd, $^{1,2,3,4}J_{C\text{-}F}$ = 259, 15.5, 15.5, 3.3 Hz), 119.28-119.92 (m), 78.3 (dd, J = 26.5, 4.4 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.15 (ddd, $J_{F\text{-}F}$ = 22.6, 11.3, 3.8 Hz, 1F), -143.77 (dt, $J_{F\text{-}F}$ = 18.8, 11.3 Hz, 1F), -144.84-(-144.63) (m, 1F), -153.29 (app td, $J_{F\text{-}F}$ = 18.8, 3.8 Hz, 1F); **IR** (KBr) ν_{max} 2863, 1712, 1619, 1500, 1458, 1416, 1395, 1344, 1278, 1138, 1075, 1057, 961, 940, 821, 800, 776, 758, 621 cm^{-1}; **HRMS** (EI) *m/z* for C_7HOF_4I $[M]^+$ calcd: 303.9008, found: 303.9005; R_f(2/1 hexanes/CH_2Cl_2) = 0.45.

General procedure for Sonogashira reaction .Preparation of 12a-12g and 13. A dried two-neck flask was filled up with commercially available fluorinated 2-bromobenzaldehyde, **11a-11f**, or with previously synthesized, **11g**, (6.0 mmol). Then $Pd(PPh_3)_2Cl_2$ (210 mg, 0.3 mmol) and CuI (114 mg, 0.6 mmol) were added under argon, followed by triethylamine (21 mL) and THF (21 mL). To the resulting mixture, the terminal alkyne (**9** or **10**) (7.2 mmol) was added. The reaction was carried out for 3 h under reflux. After being cooled down, the mixture was filtered off over a pad of Celite®/silica gel, washed with CH_2Cl_2 and the combined organic layers were concentrated by rotary evaporator. Column chromatography of the residue on silica gel (toluene/CH_2Cl_2) and recrystallization provided the corresponding products.

3-Fluoro-2-((2-formylphenyl)ethynyl)benzaldehyde (12a). With 2-ethynylbenzaldehyde (**9**) (625 mg, 4.8 mmol) and 2-bromo-3-fluorobenzaldehyde (**11a**) (812 mg, 4.0 mmol) according to the general procedure. Column chromatography (3/1 to 1/1 toluene/CH_2Cl_2) and recrystallization from acetone yielded 844 mg (84%) of the title compound as a pale yellow solid: **mp** (decomp) 148-152 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 10.56 (s, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.65 (app td, J = 7.5, 1.1 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.48-7.54 (m, 1H), 7.41 (app t, J = 8.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.1, 189.8 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 163.2 (d, $^1J_{C\text{-}F}$ = 258 Hz), 137.5, 136.2, 133.8, 133.6, 130.4 (d, $^3J_{C\text{-}F}$

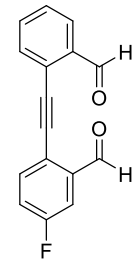
= 8.1 Hz), 129.7, 128.0, 125.1, 123.9 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 120.8 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 113.8 (d, $^{2}J_{C\text{-}F}$ = 17.0 Hz), 96.9 (d, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 85.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.12 (dd, $J_{F\text{-}H}$ = 8.5, 5.1 Hz, 1F); **IR** (KBr) ν_{max} 3363, 3076, 3046, 2857, 2839, 2756, 1694, 1604, 1586, 1565, 1488, 1470, 1395, 1299, 1260, 1251, 1192, 1159, 1141, 1090, 1060, 1003, 985, 958, 923, 857, 800, 788, 770, 728, 635 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{16}H_9O_2FNa$ $[M+Na]^+$ calcd: 275.04788, found: 275.04745; ***R*$_f$** (3/1 toluene/CH_2Cl_2) = 0.23.

4-Fluoro-2-((2-formylphenyl)ethynyl)benzaldehyde (12b). With 2-ethynylbenzaldehyde (**9**)



(781 mg, 6.0 mmol) and 2-bromo-4-fluorobenzaldehyde (**11b**) (1.02 g, 5.0 mmol) according to the general procedure. Column chromatography (3/1 toluene/CH_2Cl_2) yielded 1.25 g (99%) of the title compound as a pale yellow solid: **mp** (decomp) 140-144 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.56 (s, 1H), 10.54 (s, 1H), 7.95-8.03 (m, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.64 (app t, *J* = 7.3 Hz, 1H), 7.55 (app t, *J* = 7.3 Hz, 1H), 7.37 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.21 (app td, *J* = 8.3, 2.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.7, 189.4, 165.6 (d, $^{1}J_{C\text{-}F}$ = 267 Hz), 136.2, 133.9, 133.8, 132.9 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 130.8 (d, $^{3}J_{C\text{-}F}$ = 10.2 Hz), 129.8, 128.5, 128.0 (d, $^{3}J_{C\text{-}F}$ = 10.7 Hz), 124.6, 120.2 (d, $^{2}J_{C\text{-}F}$ = 23.7 Hz), 117.2 (d, $^{2}J_{C\text{-}F}$ = 22.1 Hz), 92.9, 90.2 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.81 (app td, $J_{F\text{-}H}$ = 8.3, 5.8 Hz, 1F); **IR** (KBr) ν_{max} 3094, 3070, 3037, 2959, 2923, 2887, 2869, 2771, 2675, 2534, 2211, 1975, 1942, 1906, 1796, 1763, 1688, 1655, 1607, 1571, 1485, 1446, 1398, 1323, 1290, 1266, 1251, 1222, 1198, 1162, 1132, 1087, 1075, 952, 899, 821, 767, 725, 692, 650, 641, 612, 570, 507 cm^{-1}; **HRMS** (CI) *m/z* for $C_{16}H_{10}O_2F$ $[M+H]^+$ calcd: 253.0665, found: 253.0664; ***R*$_f$** (3/1 hexanes/EtOAc) = 0.59.

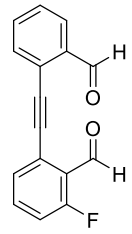
5-Fluoro-2-((2-formylphenyl)ethynyl)benzaldehyde (12c). With 2-ethynylbenzaldehyde (**9**)



(786 mg, 6.0 mmol) and 2-bromo-5-fluorobenzaldehyde (**11c**) (1.02 g, 5.0 mmol) according to the general procedure. Column chromatography (3/1 toluene/CH_2Cl_2) and recrystallization from acetone yielded 959 mg (76%) of the title compound as a colourless solid: **mp** (decomp) 135-138 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.58 (d, *J* = 2.9 Hz, 1H), 10.55 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.66-7.73 (m, 2H), 7.59-7.65 (m, 2H), 7.52 (app t, *J* = 7.3 Hz, 1H), 7.33 (app td, *J* = 8.1, 2.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.8, 189.8 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 162.8 (d, $^{1}J_{C\text{-}F}$ = 264 Hz), 138.2 (d, $^{3}J_{C\text{-}F}$ = 6.9 Hz), 136.1, 135.7 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 133.9, 133.6, 129.5, 128.5, 125.0, 121.7 (d, $^{4}J_{C\text{-}F}$ = 1.8 Hz), 121.5 (d, $^{2}J_{C\text{-}F}$ = 22.3 Hz), 114.4 (d, $^{2}J_{C\text{-}F}$ = 22.7 Hz), 91.6 (d, $^{5}J_{C\text{-}F}$ = 2.3 Hz), 90.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.56-(-108.47) (m). **IR** (KBr) ν_{max} 3354, 3106,

3097, 3055, 2881, 2765, 2492, 1688, 1634, 1604, 1589, 1580, 1497, 1422, 1398, 1290, 1269, 1216, 1198, 1150, 1090, 1078, 967, 893, 875, 833, 818, 758, 638 cm^{-1}; **HRMS** (CI) *m/z* for $C_{16}H_{10}O_2F$ $[M+H]^+$ calcd: 253.0665, found: 253.0662; R_f(3/1 toluene/CH_2Cl_2) = 0.38.

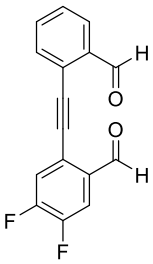
2-Fluoro-6-((2-formylphenyl)ethynyl)benzaldehyde (12d). With 2-ethynylbenzaldehyde (**9**)



(787 mg, 6.0 mmol) and 2-bromo-6-fluorobenzaldehyde (**11d**) (1.02 g, 5.0 mmol) according to the general procedure. Column chromatography (1/1 toluene/ CH_2Cl_2) and recrystallization from acetone yielded 997 mg (79%) of the title compound as colourless needle crystals: **mp** (decomp) 142-146 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.66 (s, 1H), 10.56 (s, 1H), 7.94 (d, J = 7.7 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.60 (app td, J = 7.5, 1.1 Hz, 1H), 7.54-7.58 (m, 1H), 7.46 - 7.52 (m, 2H), 7.15-7.20 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.53,* 191.50,* 187.1 (d, $^3J_{C\text{-}F}$ = 4.8 Hz),* 187.0 (d, $^3J_{C\text{-}F}$ = 4.8 Hz),* 163.7 (d, $^1J_{C\text{-}F}$ = 262.3 Hz), 136.3, 135.0 (d, $^2J_{C\text{-}F}$ = 10.7 Hz), 133.7 (d, $^4J_{C\text{-}F}$ = 4.8 Hz), 130.04, 130.02, 129.4, 127.7, 125.4, 124.8 (d, $^4J_{C\text{-}F}$ = 3.6 Hz), 124.3 (d, $^3J_{C\text{-}F}$ = 7.2 Hz), 117.3 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 92.1 (d, $^4J_{C\text{-}F}$ = 3.6 Hz), 91.7; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -118.50 (dd, $J_{F\text{-}H}$ = 10.4, 5.2 Hz, 1F); **IR** (KBr) ν_{max} 3387, 3129, 3070, 3025, 2998, 2848, 2762, 2681, 2594, 2208, 2092, 1993, 1963, 1829, 1697, 1682, 1598, 1565, 1413, 1326, 1269, 1242, 1195, 1093, 1003, 985, 848, 806, 770, 716, 698, 638, 606, 519 cm^{-1}; **HRMS** (*m/z*) for $C_{16}H_{10}O_2F$ $[M+H]^+$ calcd: 253.0665, found: 253.0666; ***R_f*** (1/1 toluene/CH_2Cl_2) = 0.38.

* It is presumed that the presence of hydrogen bonding between the proton of one aldehyde moiety with the oxygen atom of the second carbonyl moiety (C=O)H--O=C(H)) and *vice versa* is responsible for observation of 4 carbonyl signals instead of two.

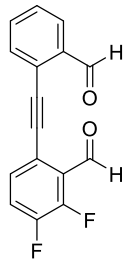
4,5-Difluoro-2-((2-formylphenyl)ethynyl)benzaldehyde (12e). With 2-ethynylbenzaldehyde



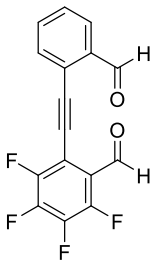
(**9**) (468 mg, 3.6 mmol) and 2-bromo-4,5-difluorobenzaldehyde (**11e**) (663 mg, 3.0 mmol) according to the general procedure. Recrystallization from acetonitrile yielded 701 mg (86%) of the title compound as a colorless solid: **mp** (decomp) 188-191 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.53 (d, J = 3.2 Hz, 1H), 10.52 (s, 1H), 7.98 (dd, J = 7.7, 0.9 Hz, 1H), 7.75-7.83 (m, 1H), 7.70 (dd, J = 7.6, 0.7 Hz, 1H), 7.65 (app td, J = 7.5, 1.2 Hz, 1H), 7.57 (app t, J = 7.8 Hz, 1H), 7.48 - 7.54 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.6, 188.7, 153.8 (dd, $^{1,2}J_{C\text{-}F}$ = 260, 13.5 Hz), 151.2 (dd, $^{1,2}J_{C\text{-}F}$ = 257, 13.1 Hz), 136.2, 133.9, 133.8, 129.8, 129.0, 124.2, 123.0 (dd, $^{3,4}J_{C\text{-}F}$ = 8.9, 3.9 Hz), 122.2 (d, $^2J_{C\text{-}F}$ = 19.2 Hz), 116.8 (dd, $^{2,3}J_{C\text{-}F}$ = 18.5, 2.3 Hz), 92.7 (m), 89.1 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -127.59 (app dt, J = 21.1, 8.9 Hz, 1F), -132.84 (dddd, J = 20.4, 10.2, 6.8, 2.7 Hz, 1F);

IR (KBr) ν_{max} 3354, 3123, 3100, 3079, 3064, 2884, 2869, 2774, 2211, 2017, 1981, 1948, 1778, 1691, 1649, 1616, 1589, 1506, 1452, 1422, 1401, 1341, 1302, 1275, 1248, 1189, 1144, 1099, 1069, 1039, 1012, 964, 899, 887, 830, 788, 761, 719, 668, 632, 579, 552, 516 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{16}H_8O_2F_2Na$ $[M+Na]^+$ calcd: 293.03846, found: 293.03834; R_f (3/1 toluene/CH_2Cl_2) = 0.33.

2,3-Difluoro-6-((2-formylphenyl)ethynyl)benzaldehyde (12f). With 2-ethynylbenzaldehyde (**9**) (468 mg, 3.6 mmol) and 6-bromo-2,3-difluorobenzaldehyde (**11f**) (663 mg, 3.0 mmol) according to the general procedure. Column chromatography (3/1 toluene/CH_2Cl_2) and recrystallization from acetonitrile yielded 598 mg (74%) of the title compound as a colorless solid: **mp** (decomp) 153-155 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 10.58 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.3 Hz, 1H), 7.63 (app td, *J* = 7.5, 1.2 Hz, 1H), 7.53 (app t, *J* = 7.6 Hz, 1 H), 7.45-7.50 (m, 1H), 7.38-7.44 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.3, 186.4 (dd, $^{3,4}J_{C\text{-}F}$ = 5.0, 3.0 Hz), 151.4 (dd, $^{1,2}J_{C\text{-}F}$ = 265, 13.5 Hz), 150.6 (dd, $^{1,2}J_{C\text{-}F}$ = 256, 12.5 Hz), 136.3, 133.8, 133.7, 130.1 (dd, $^{2,3}J_{C\text{-}F}$ = 6.0, 4.5 Hz), 129.6, 128.1, 126.2 (app d, $^{3}J_{C\text{-}F}$ = 5.2 Hz), 125.1, 122.3 (dd, $^{2,3}J_{C\text{-}F}$ = 20.3, 2.0 Hz), 120.3 (dd, $^{3,4}J_{C\text{-}F}$ = 4.3, 2.3 Hz), 91.6 (d, $^{5}J_{C\text{-}F}$ = 2.3 Hz), 91.0 (dd, $^{4,5}J_{C\text{-}F}$ = 3.9, 2.3 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -133.88 (ddd, *J* = 20.4, 8.9, 4.1 Hz, 1F), -143.23 (dd, *J* = 21.8, 7.5 Hz, 1F); **IR** (KBr) ν_{max} 3366, 3100, 3067, 3040, 2887, 2771, 1703, 1691, 1661, 1610, 1589, 1494, 1434, 1407, 1329, 1281, 1222, 1198, 1159, 1144, 1093, 1036, 1009, 982, 833, 761, 689, 638, 612, 582, 561 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{16}H_9O_2F_2$ $[M+H]^+$ calcd: 271.05651, found: 271.05613; R_f (2/1 toluene/CH_2Cl_2) = 0.32.

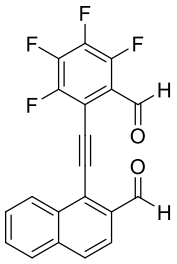


2,3,4,5-Tetrafluoro-6-((2-formylphenyl)ethynyl)benzaldehyde (12g). With 2-ethynylbenzaldehyde (**9**) (781 mg, 6.0 mmol) and 2,3,4,5-tetrafluoro-6-iodobenzaldehyde (**11g**) (1.52 g, 5.0 mmol) according to the general procedure. Column chromatography (1/1 to 1/2 hexanes/CH_2Cl_2) and recrystallization from acetonitrile yielded 976 mg (64%) of the title compound as a pale yellow solid: **mp** (decomp) 128-130 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 10.47 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.64 (app td, *J* = 7.6, 1.2 Hz, 1H), 7.57 (app t, *J* = 7.6 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.1, 184.2 (br s), 149.2 (ddd, $^{1,2,3}J_{C\text{-}F}$ = 262, 11.0, 3.4 Hz), 148.9 (ddd, $^{1,2,3}J_{C\text{-}F}$ = 256, 11.3, 3.0 Hz), 142.6 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 263, 16.1, 12.8, 4.7 Hz), 140.9 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 262, 18.8, 12.4, 2.8 Hz), 136.5, 134.0, 133.8, 130.3, 128.5, 124.2, 120.4 (dd, $^{2,3}J_{C\text{-}F}$ = 5.9, 3.0 Hz), 109.0 (d, $^{2}J_{C\text{-}F}$ = 14.3 Hz), 98.6 (dd, $^{4,5}J_{C\text{-}}$



$_F$ = 5.1, 2.7 Hz), 83.0 (dd, $^{3,4}J_{C\text{-}F}$ = 6.4, 4.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -133.77 (ddd, *J* = 20.4, 11.6, 4.1 Hz, 1F), -145.23-(-145.03) (m, 1F), -146.25 (app td, *J* = 20.4, 8.9 Hz, 1F), -152.48 (td, *J* = 20.4, 4.1 Hz, 1F); **IR** (KBr) ν_{max} 3064, 2860, 2759, 2594, 2211, 1700, 1619, 1592, 1565, 1509, 1488, 1473, 1416, 1386, 1326, 1287, 1272, 1240, 1195, 1150, 1111, 1084, 994, 979, 946, 931, 824, 806, 776, 635 cm^{-1}; **HRMS** (CI) *m/z* for $C_{16}H_7O_2F_4$ $[M+H]^+$ calcd: 307.0382, found: 307.0383; ***R_f*** (1/1 hexanes/CH_2Cl_2) = 0.38.

1-((2,3,4,5-Tetrafluoro-6-formylphenyl)ethynyl)-2-naphthaldehyde (13). With 1-ethynyl-2-naphthaldehyde (**10**) (1.00 g, 5.5 mmol) and 2,3,4,5-tetrafluoro-6-iodobenzaldehyde (**11g**) (1.40 g, 4.6 mmol) according to the general procedure. Recrystallization from CH_2Cl_2 yielded 658 mg (40%) of the title compound as a pale yellow solid: **mp** (decomp) 208-210 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.94 (s, 1H), 10.52 (s, 1H), 8.77 (d, *J* = 8.2 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.76 (app t, *J* = 7.0 Hz, 1H), 7.72 (app t, *J* = 7.3 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.9 (d, $^3J_{C\text{-}F}$ = 4.8 Hz), 183.5, 150.0 (ddt, $^{1,2,3}J_{C\text{-}F}$ = 261, 10.7, 3.6 Hz), 149.4 (ddd, $^{1,2,3}J_{C\text{-}F}$ = 254, 10.7, 3.6 Hz), 144.3 (app dm, $^1J_{C\text{-}F}$ = 263.4 Hz), 140.8 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 262.3, 16.7, 13.1, 3.6 Hz), 135.6, 135.6, 133.3, 130.7, 129.6, 128.54, 128.47, 127.2, 124.9, 122.2, 120.2 (dd, $^{2,3}J_{C\text{-}F}$ = 7.2, 3.6 Hz), 108.2 (d, $^2J_{C\text{-}F}$ = 15.5 Hz), 96.6 (dd, $^{3,4}J_{C\text{-}F}$ = 6.0, 2.4 Hz), 89.2 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -132.96-(-132.62) (m, 1F), -145.71 (app td, *J* = 20.4, 8.9 Hz, 1F), -146.18-(-145.96) (m, 1F), -152.16 (app td, *J* = 20.4, 4.8 Hz, 1F); **IR** (KBr) ν_{max} 3061, 2872, 2848, 2783, 2211, 1703, 1685, 1667, 1616, 1589, 1556, 1512, 1476, 1461, 1437, 1410, 1359, 1329, 1311, 1287, 1278, 1237, 1132, 1120, 1057, 1030, 991, 937, 905, 878, 836, 806, 788, 770, 761, 659, 629, 588, 576 cm^{-1}; **HRMS** (CI) *m/z* for $C_{20}H_9O_2F_4$ $[M+H]^+$ calcd: 357.05332, found: 357.05318; ***R_f*** (1/1 hexanes/CH_2Cl_2) = 0.14.

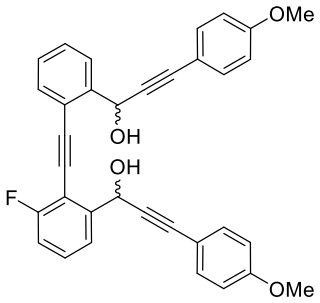


General procedure for alkynylation reaction. Preparation of 14a-14g and 15. A dried Schlenk flask was filled up with 1-ethynyl-4-methoxybenzene (175 μL, 1.35 mmol) and anhydrous THF (10 mL). The resulting solution was stirred at -78 °C for 10 min., then *n*-BuLi 1.6 M in hexanes (840 μL, 1.35 mmol) was added dropwise. After 30 min of stirring at the same low temperature, dialdehyde **12a-12g** or **13** (0.45 mmol) in THF (5 mL) was added and the resulting mixture was stirred for 5 min at -78 °C. Afterwards the reaction mixture was warmed up to room temperature and stirred for 3h. The reaction was quenched with NH_4Cl_{aq} and extracted with diethyl ether (3×15 mL), the combined organic phases were washed with a

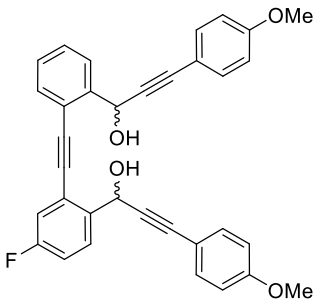
saturated solution of $NaHCO_3$, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes/EtOAc) afforded products.

Note: In all cases the triynediols were obtained as mixtures of two diastereoisomers (*anti* and *syn* alcohols). In case of compounds **14f** and **14g** the two diasteroisomers were separable and full assignment of NMR signals was possible. In all other cases the two diasteroisomers were obtained as inseparable mixture and therefore NMR spectra showed the signals of both isomers which often are covered by each other. In those cases the peaks and integration in ^{1}H NMR spectra are listed as observed.

1-(3-Fluoro-2-((2-(1-hydroxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)phenyl)ethynyl)phenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (14a). With 3-fluoro-2-((2-formylphenyl)ethynyl)benzaldehyde (**12a**) (680 mg, 2.70 mmol) according to the general procedure. Column chromatography (2/1 hexanes/EtOAc) yielded 1.17 g (84%) of an inseparable mixture of two diastereoisomers (1:1) as a pale yellow solid: **mp** (decomp) 52-54 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (mixture) δ 7.89-7.74 (m, 1H), 7.71-7.51 (m, 2H), 7.47-7.28 (m, 7H), 7.11 (app t, J = 8.6 Hz, 1H), 6.80 (m, 4H), 6.20 (s, 1H), 6.14 (s, 1H), 3.83-3.70 (m, 6H), 3.55-3.17 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) (mixture) δ 163.1 (d, $^1J_{C\text{-}F}$ = 252 Hz), 161.7 (d, $^1J_{C\text{-}F}$ = 252 Hz), 159.9, 159.80, 159.76, 159.7, 144.6, 144.4, 142.3, 142.2, 133.3, 133.0, 132.9, 130.0 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 129.9 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 129.33, 129.28, 128.44, 128.41, 127.3, 127.1, 122.70 (d, $^2J_{C\text{-}F}$ = 23.9 Hz), 122.67 (d, $^2J_{C\text{-}F}$ = 23.9 Hz), 121.6, 121.5, 115.43 (d, $^2J_{C\text{-}F}$ = 20.8 Hz), 115.36 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 114.4 (d, $^3J_{C\text{-}F}$ = 15.4 Hz), 113.9, 110.7 (d, $^3J_{C\text{-}F}$ = 16.2 Hz), 110.6 (d, $^3J_{C\text{-}F}$ = 17.0 Hz), 97.6, 97.5, 87.2 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 87.2 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 86.6, 86.38, 86.35, 85.6, 64.0, 63.9, 63.6 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 63.5 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 55.3; **^{19}F NMR** (282 MHz, $CDCl_3$) (mixture) δ -109.80 (dd, J = 8.7, 5.2 Hz, 1F), -109.89 (dd, J = 8.7, 5.2 Hz, 1F); **IR** (KBr) ν_{max} 3360, 3005, 2987, 2836, 2540, 1607, 1571, 1509, 1464, 1440, 1290, 1248, 1174, 1105, 1033, 961, 920, 839, 800, 764 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{25}O_4FNa$ $[M+Na]^+$ calcd: 539.16291, found: 539.16279; ***R$_f$*** (2/1 hexanes/EtOAc) = 0.42.

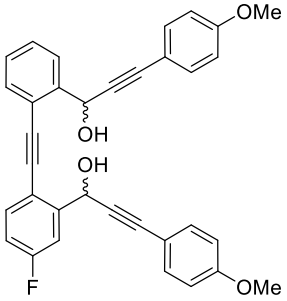


1-(4-Fluoro-2-((2-(1-hydroxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)phenyl)ethynyl)phenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (14b). With 4-fluoro-2-((2-



formylphenyl)ethynyl)benzaldehyde (**12b**) (252 mg, 1 mmol) according to the general procedure. Column chromatography (3/1 hexanes/EtOAc) yielded 0.462 g (90%) of an inseparable mixture of two diastereoisomers (1:1) as a pale yellow solid: **mp** (decomp) 56-59 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (mixture) δ 7.88-7.77 (m, 1H), 7.77-7.69 (m, 1H), 7.60 (d, J = 7.3 Hz, 1H), 7.45-7.31 (m, 6H), 7.28 (dd, J = 9.2, 2.6 Hz, 1H), 7.11-7.01 (m, 1H), 6.79 (dd, J = 8.8, 2.4 Hz, 4H), 6.10 (s, 1H), 6.21 (s, 1H), 3.93 (br s, 1H), 3.80-3.72 (s, 6H), 3.64 (br s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) (major) δ 162.0 (d, $^{1}J_{C\text{-}F}$ = 248 Hz), 159.73, 159.71, 142.4, 138.4 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 133.2, 132.9, 129.24, 129.19, 129.0 (d, $^{3}J_{C\text{-}F}$ = 10.0 Hz), 128.3, 127.3, 123.7 (d, $^{3}J_{C\text{-}F}$ = 9.2 Hz), 121.3, 119.2 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz), 115.8 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 114.4, 114.3, 113.8, 93.0, 91.1 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 87.0, 86.65, 86.62, 63.8, 63.1, 55.2 (2C); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.64-(-114.49) (m, 1F); **IR** (KBr) ν_{max} 3414, 3073, 3004, 2953, 2935, 2905, 2836, 2537, 2232, 1604, 1580, 1509, 1464, 1446, 1416, 1374, 1290, 1248, 1210, 1174, 1108, 1078, 1033, 964, 872, 833, 806, 758, 701, 626, 609, 561, 531 cm^{-1}; **HRMS** (*m/z*) for $C_{34}H_{25}O_4FNa$ $[M+Na]^+$ calcd: 539.16291, found: 539.16199; ***R$_f$*** (3/1 hexanes/EtOAc) = 0.25.

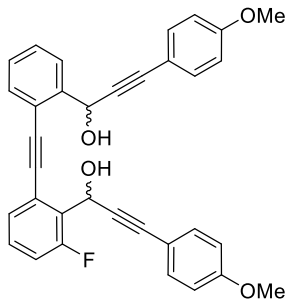
1-(5-Fluoro-2-((2-(1-hydroxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)phenyl)ethynyl)phenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (14c). With 5-fluoro-2-((2-



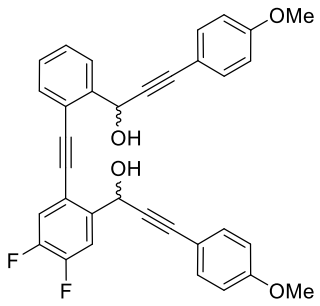
formylphenyl)ethynyl)benzaldehyde (**12c**) (893 mg, 3.5 mmol) according to the general procedure. Column chromatography (2/1 hexanes/EtOAc) yielded 1.72 g (94%) of an inseparable mixture of two diastereoisomers (1:0.3) as a pale yellow solid: **mp** (decomp) 138-140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (major isomer) δ 7.77 (d, J = 7.6 Hz, 1H), 7.65-7.55 (m, 2H), 7.52 (dd, J = 9.5, 2.4 Hz, 1H), 7.45-7.31 (m, 6H), 7.04 (app td, J = 8.3, 2.6 Hz, 1H), 6.83-6.75 (m, 4H), 6.17 (d, J = 7.1 Hz, 2H), 3.78 (s, 6H), 3.64 (br s, 1H), 3.36 (br s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) (major) δ 162.6 (d, $^{1}J_{C\text{-}F}$ = 251 Hz), 159.9, 159.8, 145.1 (d, $^{3}J_{C\text{-}F}$ = 6.9 Hz), 142.1, 134.6, 134.5, 133.33, 133.28, 132.8, 129.0, 128.4, 127.2, 121.7, 117.8 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 115.5 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 114.7 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz), 114.3 (d, $^{3}J_{C\text{-}F}$ = 18.5 Hz), 113.91, 113.89, 91.8, 91.3, 87.2, 87.1, 86.6, 86.1, 64.0, 63.4, 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) (minor) δ -110.03 (app td, $J_{F\text{-}H}$ = 8.7, 5.8 Hz, 1F), (major) -110.14 (app td, $J_{F\text{-}H}$ = 8.7, 5.8 Hz, 1F); **IR** (KBr) ν_{max} 3309, 2965, 2932, 2911, 2836, 2223, 1610, 1565, 1515, 1494, 1446, 1416, 1293, 1248, 1210, 1180, 1153, 1102, 1033, 988,

967, 931, 899, 833, 809, 758 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{25}O_4FNa$ $[M+Na]^+$ calcd: 539.16291, found: 539.16269; R_f (3/1 hexanes/EtOAc) = 0.20.

1-(2-((3-Fluoro-2-(1-hydroxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)phenyl)ethynyl)phenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (14d). With 2-fluoro-6-((2-formylphenyl)ethynyl)benzaldehyde (**12d**) (882 mg, 3.5 mmol) according to the general procedure. Column chromatography (3/1 to 1/1 hexanes/EtOAc) yielded 1.62 g (90%) of an inseparable mixture of two diastereoisomers (1:1) as a pale brown solid: **mp** (decomp) 58-62 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (mixture) δ 7.91-7.80 (m, 2H), 7.61 (app t, *J* = 8.8 Hz, 2H), 7.46-7.42 (m, 2H), 7.42-7.36 (m, 6H), 7.36-7.24 (m, 8H), 7.15-7.03 (m, 2H), 6.85-6.77 (m, 4H), 6.76-6.69 (m, 4H), 6.36 (s, 1H), 6.29-6.18 (m, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 2.93 (br s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) (mixture) δ 159.8, 159.71, 159.69, 160.0 (d, $^1J_{C\text{-}F}$ = 248 Hz), 159.6 (d, $^1J_{C\text{-}F}$ = 247 Hz), 142.4, 142.0, 133.4 (d, $^3J_{C\text{-}F}$ = 10.8 Hz), 133.3, 133.2, 132.7 (d, $^3J_{C\text{-}F}$ = 13.9 Hz), 130.3, 130.1, 130.0, 129.63, 129.60, 129.45, 129.36, 129.28 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 129.24, 129.20, 129.17, 128.4 (d, $^2J_{C\text{-}F}$ = 16.2 Hz), 127.2, 126.8, 123.09, 123.07, 123.0, 121.9, 121.2, 116.6 (d, $^2J_{C\text{-}F}$ = 23.1 Hz), 116.4 (d, $^2J_{C\text{-}F}$ = 23.1 Hz), 114.5, 114.40, 114.39, 114.3, 113.9, 113.82, 113.81, 113.78, 93.6, 93.3, 91.4 (d, $^4J_{C\text{-}F}$ = 4.6 Hz), 91.3 (d, $^4J_{C\text{-}F}$ = 4.6 Hz), 87.4, 87.1, 86.7, 86.6, 86.5 (d, $^4J_{C\text{-}F}$ = 1.5 Hz), 86.3, 85.90 (d, $^4J_{C\text{-}F}$ = 1.5 Hz), 63.6, 63.3, 58.5 (d, $^3J_{C\text{-}F}$ = 6.2 Hz), 57.7 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 55.3, 55.22, 55.19, 55.1; **^{19}F NMR** (376 MHz, $CDCl_3$) (mixture) δ -118.20 (dd, $J_{F\text{-}H}$ = 10.2, 5.4 Hz, 1F), -118.95 (dd, $J_{F\text{-}H}$ = 10.2, 5.4 Hz, 1F). **IR** (KBr) ν_{max} 3351, 3073, 3040, 3001, 2959, 2932, 2836, 2549, 2492, 2229, 1604, 1568, 1509, 1488, 1470, 1449, 1413, 1383, 1287, 1251, 1174, 1108, 1036, 982, 967, 833, 803, 758, 743, 549, 534 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{25}O_4FNa$ $[M+Na]^+$ calcd: 539.16291, found: 539.16269; R_f(3/1 hexanes/EtOAc) = 0.18.

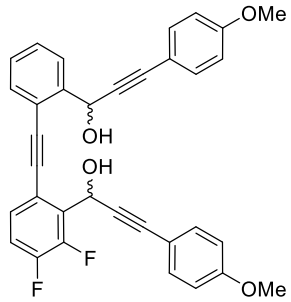


1-(4,5-Difluoro-2-((2-(1-hydroxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)phenyl)ethynyl)phenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (14e). With 4,5-difluoro-2-((2-formylphenyl)ethynyl)benzaldehyde (**12e**) (701 mg, 2.59 mmol) according to the general procedure. Column chromatography (3/1 to 1/1 hexanes/EtOAc) yielded 1.30 g (94%) of an inseparable mixture of two diastereoisomers (2:1) as a pale yellow solid: **mp** (decomp)

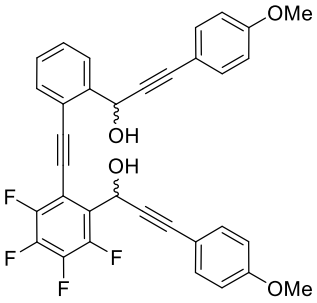


135-138 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (mixture) δ 7.86-7.70 (m, 1H), 7.68-7.53 (m, 2H), 7.46-7.31 (m, 7H), 6.80 (dd, J = 8.8, 2.4 Hz, 4H), 6.29-5.94 (m, 2H), 4.59-3.96 (m, 2H), 3.82-3.74 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) (mixture) δ 159.7, 159.6, 150.1 (dd, $^{1,2}J_{C\text{-}F}$ = 253, 12.3 Hz), 149.3 (dd, $^{1,2}J_{C\text{-}F}$ = 251, 13.9 Hz), 142.2, 142.0, 140.1-139.9 (m), 133.3-133.0 (m), 132.8, 132.5, 129.2, 128.3-128.1 (m), 127.2, 127.0, 121.1, 120.9, 120.7, 118.3 (dd, $^{3,4}J_{C\text{-}F}$ = 8.1, 3.5 Hz), 118.1 (dd, $^{3,4}J_{C\text{-}F}$ = 7.7, 3.9 Hz), 116.6 (d, $^{2}J_{C\text{-}F}$ = 18.5 Hz), 116.3 (d, $^{2}J_{C\text{-}F}$ = 19.3 Hz), 114.2, 114.0, 113.8, 92.6, 90.1, 87.05, 87.02, 86.96, 86.90, 86.6, 86.2, 86.1, 63.7, 63.5, 62.5, 62.4, 55.1; **^{19}F NMR** (376 MHz, $CDCl_3$) (mixture) δ -135.01-(-134.86) (m, 1F), -135.19-(-135.02) (m, 1F), -138.89-(-138.55) (m, 2F); **IR** (KBr) ν_{max} 3324, 3055, 3013, 2962, 2926, 2905, 2836, 2229, 1607, 1568, 1506, 1470, 1440, 1413, 1404, 1341, 1296, 1248, 1183, 1147, 1108, 1075, 1039, 961, 902, 890, 860, 836, 803, 758 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{24}O_4F_2Na$ $[M+Na]^+$ calcd: 557.15349, found: 557.15291; ***R$_f$*** (3/1 hexanes/EtOAc) = 0.25.

1-(2-((3,4-Difluoro-2-(1-hydroxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)phenyl)ethynyl)phenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol) (14f). With 2,3-difluoro-6-((2-formylphenyl)ethynyl)benzaldehyde (**12f**) (547 mg, 2.14 mmol) according to the general procedure. Column chromatography (40/1 to 10/1 CH_2Cl_2/EtOAc) yielded 1.01 g (88%) a separable mixture of two diastereoisomers (1:1) as a colourless solid: **mp** (decomp) 56-58 °C, 60-61 °C; <u>One diastereoisomer</u>: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.3 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.44-7.28 (m, 7H), 7.11 (app q, J = 8.8 Hz, 1H), 6.81 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 6.33 (d, J = 6.1 Hz, 1H), 6.23 (d, J = 8.1 Hz, 1H), 4.48 (br s, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.36 (br s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.79, 159.78, 150.6 (dd, $^{1,2}J_{C\text{-}F}$ = 253, 13.1 Hz), 147.8 (dd, $^{1,2}J_{C\text{-}F}$ = 251, 13.9 Hz), 141.8, 133.5, 133.2, 132.7, 132.6 (d, $^{3}J_{C\text{-}F}$ = 10.8 Hz), 129.7 (dd, $^{2,3}J_{C\text{-}F}$ = 6.5, 4.2 Hz), 129.1, 128.5, 127.2, 121.9, 118.2 (m), 116.6 (d, $^{2}J_{C\text{-}F}$ = 17.7 Hz), 114.4, 114.1, 113.8, 93.1 (d, $^{4}J_{C\text{-}F}$ = 1.5 Hz), 90.7 (br s), 87.5, 86.2, 86.1, 86.0, 63.3, 57.5 (dd, $^{3,4}J_{C\text{-}F}$ = 7.7, 2.3 Hz), 55.2, 55.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -135.06 (ddd, J = 21.1, 9.5, 4.8 Hz, 1F), -142.97 (dd, J = 21.1, 7.5 Hz, 1F); **IR** (KBr) ν_{max} 3327, 3300, 3061, 2998, 2953, 2926, 2836, 2537, 2226, 1604, 1568, 1509, 1437, 1416, 1380, 1323, 1296, 1278, 1245, 1216, 1174, 1105, 1036, 979, 964, 893, 830, 761, 698, 555, 540 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{24}O_4F_2Na$ $[M+Na]^+$ calcd: 557.15349, found: 557.15317; ***R$_f$*** (3/1 hexanes/EtOAc) = 0.22.

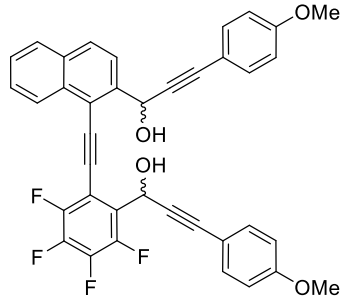


3-(4-Methoxyphenyl)-1-(2,3,4,5-tetrafluoro-6-((2-(1-hydroxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)phenyl)ethynyl)phenyl)prop-2-yn-1-ol (14g). With 2,3,4,5-tetrafluoro-6-((2-formylphenyl)ethynyl)benzaldehyde (**12g**) (144 mg, 0.47 mmol) according to the general procedure. Column chromatography (3/1 hexanes/EtOAc) yielded 0.215 g (80%) of a separable mixture of two diastereoisomers (1:1) as a pale yellow solid.



One diastereoisomer: **mp** (decomp) 61-63 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.3 Hz, 1H), 7.64 (d, J = 7.3 Hz, 1H), 7.44-7.35 (m, 4H), 7.31 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 6.72 (d, J = 8.8 Hz, 2H), 6.30 (s, 1H), 6.15 (s, 1H), 5.04 (br s, 1H), 3.86 (br s, 1H), 3.80 (s, 3H), 3.70 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.95, 159.86, 148.7 (dd, $^{1}J_{C\text{-}F}$ = 252, $^{2}J_{C\text{-}F}$ = 10.8 Hz), 144.6 (dd, $^{1}J_{C\text{-}F}$ = 247, $^{2}J_{C\text{-}F}$ = 10.8 Hz), 142.0, 140.6 (d, $^{1}J_{C\text{-}F}$ = 257 Hz), 140.2 (d, $^{1}J_{C\text{-}F}$ = 255 Hz), 133.5, 133.2, 133.0, 129.6, 128.6, 127.3, 127.0 (dd, $^{2,3}J_{C\text{-}F}$ =12.3, 3.1 Hz), 121.5, 114.3, 113.92, 113.88, 113.8, 107.2 (d, $^{2}J_{C\text{-}F}$ =15.4 Hz), 100.1, 87.8, 86.6, 85.8, 85.4, 82.8 (q, $^{3}J_{C\text{-}F}$ = 3.1 Hz), 63.2, 56.9 (d, $^{3}J_{C\text{-}F}$ = 6.9 Hz), 55.3, 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -135.07 (ddd, $J_{F\text{-}F}$ = 21.1, 10.9, 2.0 Hz, 1F), -144.76 (ddd, $J_{F\text{-}F}$ = 20.4, 11.6, 2.7 Hz, 1F), -154.17 (app td, $J_{F\text{-}F}$ = 19.8, 2.7 Hz, 1F), -156.71 (app td, $J_{F\text{-}F}$ = 19.8, 2.7 Hz, 1F); **IR** (KBr) ν_{max} 3504, 2941, 2911, 2839, 2226, 1610, 1568, 1509, 1494, 1476, 1401, 1290, 1248, 1177, 1135, 1114, 1084, 1039, 1000, 976, 911, 830, 809, 785, 758 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{22}O_4F_4Na$ $[M+Na]^+$ calcd: 593.13464, found: 593.13361; R_f (CH_2Cl_2) = 0.16.

3-(4-Methoxyphenyl)-1-(2,3,4,5-tetrafluoro-6-((2-(1-hydroxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)naphthalen-1-yl)ethynyl)phenyl)prop-2-yn-1-ol (15). With 1-((2,3,4,5-tetrafluoro-6-formylphenyl)ethynyl)-2-naphthaldehyde (**13**) (618 mg, 1.74 mmol) according to the general procedure. Column chromatography (2/1 to 1/1 cyclohexane/Et_2O) yielded 0.964 g (90%) an inseparable mixture of two diastereoisomers (1:1) as a pale brown solid: **mp** (decomp) 97-101 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) (mixture) δ 8.56 (d, J = 8.5 Hz, 1H), 8.51 (d, J = 8.2 Hz, 1H), 8.02-7.95 (m, 3H), 7.93 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 7.9 Hz, 2H), 7.64 (app t, J = 7.9 Hz, 1H), 7.60-7.53 (m, 3H), 7.43-7.36 (m, 4H), 7.32 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 6.61 (s, 1H), 6.50 (s, 1H), 6.23 (br s, 2H), 4.64 (br s, 1H), 3.87 (br s, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.73 (s, 3H), 3.69 (s, 3H), 3.21 (br s, 1H), 2.80 (br s, 1H); **^{13}C NMR** (151



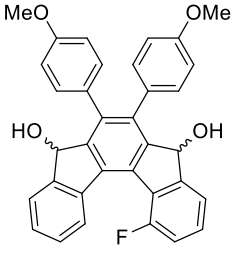
MHz, $CDCl_3$) (mixture) δ 160.0, 159.9, 149.0 (dd, $^{1,2}J_{C\text{-}F}$ = 253, 11.9 Hz), 148.7 (dd, $^{1,2}J_{C\text{-}F}$ = 250, 8.3 Hz), 145.2 (dd, $^{1,2}J_{C\text{-}F}$ = 248, 8.3 Hz), 144.7 (dd, $^{1,2}J_{C\text{-}F}$ = 249, 9.5 Hz), 141.8, 140.9, 133.5, 133.42, 133.39, 133.3, 133.2 (d, $^{2}J_{C\text{-}F}$ = 16.7 Hz), 132.9 (d, $^{2}J_{C\text{-}F}$ = 17.9 Hz), 130.4, 130.1, 128.3, 128.2, 127.9, 127.8, 127.1, 127.0, 126.7 (dd, $^{2,3}J_{C\text{-}F}$ = 13.1, 3.6 Hz), 126.3, 126.2, 124.3, 123.9, 119.0, 117.5, 114.2, 114.1, 113.92, 113.89, 113.90, 113.87, 113.7, 113.6, 107.4-107.2 (m), 107.2-107.1 (m), 98.5 (dd, $^{3,4}J_{C\text{-}F}$ = 4.8, 2.4 Hz), 98.1 (dd, $^{3,4}J_{C\text{-}F}$ = 4.8, 2.4 Hz), 88.4-88.3 (m), 88.1, 88.1-88.0 (m), 87.6, 87.0, 86.8, 86.7, 85.9, 85.3, 85.1, 63.9, 63.7, 58.0 (d, $^{3,4}J_{C\text{-}F}$ = 4.8 Hz), 57.0 (d, $^{3,4}J_{C\text{-}F}$ = 8.3 Hz), 55.30, 55.25, 55.20, 55.15; **^{19}F NMR** (282 MHz, $CDCl_3$) (mixture) δ -134.63-(-134.09) (m, 2F), -144.99 (dd, $J_{F\text{-}F}$ = 21.7, 11.3 Hz, 1F), -144.87 (dd, $J_{F\text{-}F}$ = 21.7, 11.3 Hz, 1F), -153.57 (app td, $J_{F\text{-}F}$ = 20.8, 2.6 Hz, 1F), -153.87 (app t, $J_{F\text{-}F}$ = 20.8 Hz, 1F), -156.22 (app t, $J_{F\text{-}F}$ = 19.9 Hz, 1F), -156.47 (app t, $J_{F\text{-}F}$ = 20.8 Hz, 1F); **IR** (KBr) ν_{max} 3414, 3339, 3058, 3001, 2959, 2938, 2908, 2839, 2543, 2229, 1607, 1571, 1509, 1482, 1461, 1440, 1410, 1371, 1332, 1287, 1248, 1171, 1111, 1066, 1039, 988, 955, 905, 887, 869, 827, 800, 791, 767, 659, 647, 567, 537 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{38}H_{24}O_4F_4Na$ $[M+Na]^+$ calcd: 643.15029, found: 643.14972; ***R*$_f$** (2/1 cyclohexane/Et_2O) = 0.15.

5.3.2 Preparation of dihydroindeno[2,1-*c*]fluorenediols

General procedure for cyclotrimerization with Wilkinson's catalyst $RhCl(PPh_3)_3$. Preparation of 16a-16c and 17. A dried microwave vial was charged with starting materials **14a-14g** or **15** (0.1 mmol) and THF (6 mL) under argon atmosphere. Afterwards Wilkinson's catalyst (0.003 mmol, 2.8 mg) was added and the vial was sealed with a cap. The reaction was carried out in a microwave reactor at 150 °C for 1.5 h. After cooling down to room temperature, the solvent was evaporated under reduced pressure. Column chromatography of the residue on silica gel (CH_2Cl_2/EtOAc) yielded products.

Note: In all cases the products were obtained as a separable mixture of two diastereoisomers (*anti* and *syn* alcohols) which were both characterized.

1-Fluoro-6,7-bis(4-methoxyphenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (16a). With



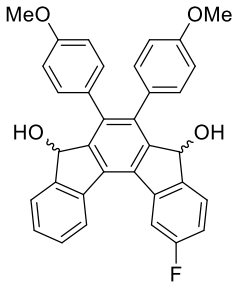
14a (258 mg, 0.50 mmol) according to the general procedure. Column chromatography (6/0.1 to 1/0.1 CH_2Cl_2/EtOAc) yielded 229 mg (88%) of a mixture of separable diastereoisomers (1.2:1) as a pale yellow solid.

Diasteroisomer 1: **mp** (decomp) 256-257 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (app t, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.32 - 7.51 (m, 6H),

7.20 (app t, J = 10.5 Hz, 1H), 7.07-6.60 (m, 6H), 5.94 (d, J = 3.7 Hz, 2H), 3.82 (s, 6H), 1.86 (d, J = 4.4 Hz, 1H), 1.82 (d, J = 4.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 156.8 (d, $^{1}J_{C\text{-}F}$ = 253 Hz), 148.5 (d, $^{4}J_{C\text{-}F}$ = 4.6 Hz), 147.9, 146.7, 145.7, 139.9, 137.4, 136.6, 135.3, 131.6 (br s), 129.72, 129.70, 129.64, 129.62, 129.6 (br s), 128.42, 128.41, 127.7, 127.1 (d, $^{3}J_{C\text{-}F}$ =15.4 Hz), 125.1 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 124.4, 121.1 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 116.8 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz), 114.1 (br s), 114.0, 74.5, 74.4 (d, $^{4}J_{C\text{-}F}$ =1.5 Hz), 55.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.12-(-102.95) (m, 1F); **IR** (KBr) ν_{max} 3360, 3076, 3010, 2932, 2878, 2833, 1613, 1521, 1509, 1455, 1422, 1365, 1329, 1290, 1242, 1183, 1159, 1105, 1081, 1054, 1033, 976, 836, 800, 779, 755 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{25}O_4FNa$ $[M+Na]^+$ calcd: 539.16291, found: 539.16248; ***R$_f$*** (6/0.1 CH_2Cl_2/EtOAc) = 0.38.

Diasteroisomer 2: **mp** (decomp) 210-216 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (app t, J = 7.6 Hz, 1H), 7.58 (d, J = 7.3 Hz, 1H), 7.53-7.31 (m, 4H), 7.26-7.01 (m, 5H), 6.83 (d, J = 7.6 Hz, 4H), 5.68-5.55 (m, 2H), 3.80 (s, 6H), 2.00 (d, J = 5.4 Hz, 1H), 1.95 (d, J = 5.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 158.5, 156.9 (d, $^{1}J_{C\text{-}F}$ = 254 Hz), 148.6 (d, $^{4}J_{C\text{-}F}$ = 3.9 Hz), 147.1, 145.9, 145.6, 139.9, 138.9, 138.0, 135.0, 129.8, 129.69, 129.68, 129.6, 129.4, 128.54, 128.52, 127.7, 127.0 (d, $^{3}J_{C\text{-}F}$ = 14.6 Hz), 125.2 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 124.6, 121.2 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 117.0 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz), 113.6 (br s), 74.24, 74.15 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 55.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.73 (ddd, $J_{F\text{-}H}$ = 10.7, 6.6, 4.4 Hz, 1F); **IR** (KBr) ν_{max} 3384, 2956, 2935, 2908, 2833, 1610, 1580, 1518, 1464, 1425, 1377, 1290, 1245, 1183, 1102, 1078, 1039, 970, 937, 899, 845, 821, 800, 779, 737, 552 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{25}O_4FNa$ $[M+Na]^+$ calcd: 539.16291, found: 539.16204; ***R$_f$*** (6/0.1 CH_2Cl_2/EtOAc) = 0.09.

2-Fluoro-6,7-bis(4-methoxyphenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (16b). With



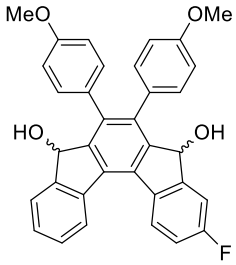
14b (258 mg, 0.5 mmol) according to the general procedure. Column chromatography (6/0.1 to 2/0.1 CH_2Cl_2/EtOAc) yielded 163 mg (63%) of a mixture of separable diasteroisomers (1.3:1) as a pale yellow solid.

Diasteroisomer 1: **mp** (decomp) >300 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, diasteroisomer 1) δ 8.28 (d, J = 7.8 Hz, 1H), 8.05 (dd, J = 9.9, 2.3 Hz, 1H), 7.62 (d, J = 7.3 Hz, 1H), 7.58-7.49 (m, 2H), 7.49-7.32 (m, 3H), 7.06 (app td, J = 8.5, 2.3 Hz, 1H), 7.01-6.60 (m, 6H), 5.87 (d, J = 3.9 Hz, 1H), 5.83 (d, J = 3.4 Hz, 1H), 3.80 (s, 6H), 1.78 (br s, 1H), 1.77 (br s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.5 (d, $^{1}J_{C\text{-}F}$ = 243 Hz), 158.7, 147.8, 147.2, 145.8, 141.9 (d, $^{3}J_{C\text{-}F}$ = 8.8 Hz), 141.3 (d, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 139.6, 137.9, 137.3, 135.2, 134.0, 133.9, 131.5 (br s), 129.8 (br s), 129.7, 129.6, 129.1, 128.1, 126.5 (d, $^{3}J_{C\text{-}F}$ = 10.0 Hz), 125.5, 123.4, 114.4 (d, $^{2}J_{C\text{-}F}$ = 23.2 Hz), 114.1 (br s), 110.8 (d, $^{2}J_{C\text{-}F}$ = 24.3

Hz), 74.3, 73.7, 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.72-(-113.57) (m, 1F); **IR** (KBr) ν_{max} 3569, 3049, 3010, 2953, 2935, 2839, 1610, 1518, 1464, 1434, 1332, 1287, 1245, 1180, 1105, 1069, 1033, 961, 923, 836, 815, 791, 764, 740, 549 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{25}O_4FNa$ $[M+Na]^+$ calcd: 539.16291, found: 539.16268; ***R*$_f$** (2/0.1 CH_2Cl_2/EtOAc) = 0.58.

Diasteroisomer 2: **mp** (decomp) > 290; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.6 Hz, 1H), 8.06 (dd, *J* = 10.0, 2.0 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.57-7.48 (m, 2H), 7.38 (app t, *J* = 7.1 Hz, 1H), 7.21-6.99 (m, 5H), 6.81 (d, *J* = 8.8 Hz, 4H), 5.58 (s, 1H), 5.55 (s, 1H), 3.79 (s, 6H), 1.90 (br s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.5 (d, $^1J_{C\text{-}F}$ = 242 Hz), 158.6, 147.3, 146.6, 145.8, 141.8 (d, $^3J_{C\text{-}F}$ = 8.8 Hz), 141.3 (d, $^4J_{C\text{-}F}$ = 2.2 Hz), 139.5, 139.2, 138.6, 135.0, 133.73, 133.72, 129.8 (br s), 129.71, 129.66, 129.1, 128.1, 126.5 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 125.6, 123.4, 114.4 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 113.7 (br s), 110.8 (d, $^2J_{C\text{-}F}$ = 25.4 Hz), 74.1, 73.5, 55.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.56 (app td, $J_{F\text{-}H}$ = 9.0, 5.8 Hz, 1F); **IR** (KBr) ν_{max} 3548, 3076, 3043, 3028, 3013, 2962, 2932, 2839, 2531, 1610, 1589, 1515, 1461, 1431, 1329, 1287, 1242, 1183, 1111, 1096, 1027, 955, 929, 839, 800, 764, 737, 549 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{25}O_4FNa$ $[M+Na]^+$ calcd: 539.16291, found: 539.16269; ***R*$_f$** (2/0.1 CH_2Cl_2/EtOAc) = 0.22.

3-Fluoro-6,7-bis(4-methoxyphenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (16c). With

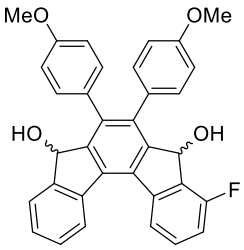


14c (52.5 mg, 0.1 mmol) according to the general procedure. Column chromatography (4/0.1 to 2/0.1 CH_2Cl_2/EtOAc) yielded 37.4 mg (71%) of a mixture of separable diastereoisomers (1.5:1) as a pale yellow solid.

Diasteroisomer 1: **mp** (decomp) >280 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 8.5, 4.7 Hz, 1H), 8.31 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.51 (app t, *J* = 7.6 Hz, 1H), 7.47-7.42 (m, 1H), 7.40 (app t, *J* = 7.3 Hz, 1H), 7.32 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.26 (overlapped to $CHCl_3$ signal, 1H), 7.20 (app td, *J* = 8.7, 2.1 Hz, 1H), 7.09-6.66 (m, 6H), 5.90 (br s, 1H), 5.87 (br s, 1H), 3.82 (s, 6H), 1.83 (br s, 1H), 1.80 (br s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.6 (d, ^1J = 248 Hz), 158.63, 158.61, 148.3 (d, ^3J = 8.3 Hz), 147.2, 147.0 (d, ^4J = 2.4 Hz), 145.8, 139.7, 137.3, 137.1, 135.9, 135.9, 134.6, 134.1, 131.5 (br s), 129.74, 129.68, 128.9, 128.0, 125.5, 124.6 (d, ^3J = 8.3 Hz), 123.2, 115.6 (d, ^2J = 22.7 Hz), 114.1 (br s), 112.9 (d, ^2J = 22.6 Hz), 74.3, 74.1 (d, ^4J = 2.4 Hz), 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.48 (app td, $J_{F\text{-}H}$ = 8.3, 5.1 Hz, 1F); **IR** (KBr) ν_{max} 3560, 3070, 3043, 3010, 2962, 2932, 2836, 1610, 1521, 1482, 1470, 1434, 1290, 1245, 1183, 1138, 1105, 1033, 952, 842, 803, 761, 740, 552 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{25}O_4FNa$ $[M+Na]^+$ calcd: 539.16291, found: 539.16254; ***R*$_f$** (4/0.1 CH_2Cl_2/EtOAc) = 0.58.

Diasteroisomer 2: **mp** (decomp) > 280 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.5, 4.7 Hz, 1H), 8.30 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.49 (app t, *J* = 7.5 Hz, 1H), 7.37 (app t, *J* = 7.3 Hz, 1H), 7.29 (dd, *J* = 7.9, 2.1 Hz, 1H), 7.26 (overlapped to $CHCl_3$ signal, 1H), 7.21-7.09 (m, 4H), 6.82 (d, *J* = 7.3 Hz, 4H), 5.58 (br s, 2H), 3.79 (s, 6H), 1.90 (br s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.4 (d, $^1J_{C\text{-}F}$ = 248 Hz), 158.6, 158.5, 148.3 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 146.6, 146.5 (d, $^4J_{C\text{-}F}$ = 2.4 Hz), 145.7, 139.7, 138.6, 138.4, 135.83, 135.81, 134.4, 133.8, 129.75, 129.73, 128.0, 127.9, 125.6, 124.6 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 123.2, 115.7 (d, $^2J_{C\text{-}F}$ = 22.7 Hz), 113.6 (br s), 112.93 (d, $^2J_{C\text{-}F}$ = 22.7 Hz), 74.08, 73.93 (d, $^4J_{C\text{-}F}$ = 2.4 Hz), 55.13; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.47 (app td, $J_{F\text{-}H}$ = 8.3, 5.1 Hz, 1F); **IR** (KBr) ν_{max} 3566, 3073, 3010, 2962, 2932, 2836, 1613, 1518, 1506, 1464, 1431, 1290, 1251, 1180, 1135, 1114, 1096, 1036, 955, 931, 842, 797, 770, 737 cm-1; **HRMS** (ESI) *m/z* for $C_{34}H_{25}O_4FNa$ $[M+Na]^+$ calcd: 539.16291, found: 539.16255; ***R$_f$*** (4/0.1 CH_2Cl_2/EtOAc) = 0.18.

4-Fluoro-6,7-bis(4-methoxyphenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (16d). With



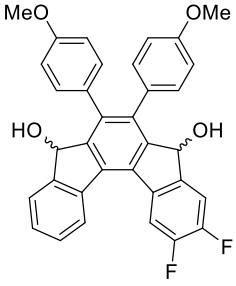
14d (259 mg, 0.50 mmol) according to the general procedure. Column chromatography (6/0.1 to 2/0.1 CH_2Cl_2/EtOAc) yielded 235 mg (91%) of a mixture of separable diastereoisomers (1:1) as a yellowish solid.

Diastereoisomer 1: **mp** (decomp) 292.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.55-7.47 (m, 2H), 7.44-7.36 (m, 3H), 7.06 (app t, *J* = 8.6 Hz, 1H), 7.02-6.61 (m, 6H), 6.09 (d, *J* = 3.9 Hz, 1H), 5.87 (d, *J* = 4.2 Hz, 1H), 3.82 (s, 6H), 1.91 (d, *J* = 4.2 Hz, 1H), 1.81 (d, *J* = 4.4 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.4 (d, $^1J_{C\text{-}F}$ = 252 Hz), 158.7, 147.2, 146.5, 145.8, 143.3 (d, $^4J_{C\text{-}F}$ = 4.8 Hz), 139.7, 138.2, 137.8, 135.2, 134.2, 131.5 (br s), 131.1 (d, $^3J_{C\text{-}F}$ = 7.2 Hz), 130.9 (d, $^2J_{C\text{-}F}$ = 16.7 Hz), 129.9 (br s), 129.7, 129.6, 128.9, 128.1, 125.5, 123.5, 119.55, 119.53, 115.1 (d, $^2J_{C\text{-}F}$ = 20.3 Hz), 114.1 (br s), 74.2, 72.1, 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.69 (dd, $J_{F\text{-}H}$ = 8.9, 5.4 Hz, 1F); **IR** (KBr) ν_{max} 3572, 3557, 2959, 2932, 2836, 1622, 1610, 1518, 1434, 1290, 1248, 1180, 1105, 1084, 1030, 982, 845, 785, 767, 728 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{25}O_4FNa$ $[M+Na]^+$ calcd: 539.16291, found: 539.16244; ***R$_f$*** (4/0.1 CH_2Cl_2/EtOAc) = 0.68.

Diastereoisomer 2: **mp** (decomp) 278.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.8 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.55-7.46 (m, 2H), 7.40 (app t, *J* = 7.8 Hz, 1H), 7.26-7.09 (m, 4H), 7.05 (app t, *J* = 8.6 Hz, 1H), 6.89-6.79 (m, 4H), 5.81 (d, *J* = 4.6 Hz, 1H), 5.65 (d, *J* = 5.1 Hz, 1H), 3.81 (s, 6H), 2.06 (d, *J* = 4.9 Hz, 1H), 1.90 (d, *J* = 5.1 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.3 (d, $^1J_{C\text{-}F}$ = 250 Hz), 158.6, 146.9, 145.93, 145.91,

143.2 (d, $^{4}J_{C\text{-}F}$ = 4.8 Hz), 139.5, 139.2, 138.9, 135.0, 134.0 (d, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 131.9 (br s), 131.2 (d, $^{3}J_{C\text{-}F}$ = 7.2 Hz), 130.9 (d, $^{2}J_{C\text{-}F}$ = 15.5 Hz), 130.2 (br s), 129.8, 129.6, 128.9, 128.1, 125.5, 123.5, 119.4 (d, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 115.1 (d, $^{2}J_{C\text{-}F}$ = 20.3 Hz), 113.7 (br s), 74.2, 71.8, 55.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.82 (dd, $J_{F\text{-}H}$ = 8.9, 5.4 Hz, 1F); **IR** (KBr) ν_{max} 3554, 2962, 2932, 2836, 1613, 1518, 1434, 1290, 1245, 1180, 1111, 1027, 979, 926, 839, 782, 767, 734 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{25}O_4FNa$ $[M+Na]^+$ calcd: 539.16291, found: 539.16268; ***R*$_f$** (4/0.1 CH_2Cl_2/EtOAc) = 0.20.

2,3-Difluoro-6,7-bis(4-methoxyphenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (16e).



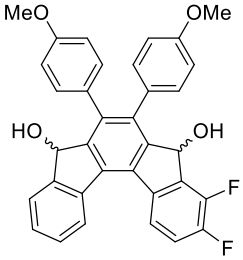
With **14e** (714 mg, 1.33 mmol) according to the general procedure. Column chromatography (6/0.1 to 2/0.1 CH_2Cl_2/EtOAc) yielded 632 mg (89%) of a mixture of separable diastereoisomers (1.2:1) as a pale yellow solid.

Diastereoisomer 1: **mp** (decomp) > 320 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.6 Hz, 1H), 8.18-8.12 (m, 1H), 7.62 (d, *J* = 7.3 Hz, 1H), 7.51 (app t, *J* = 7.6 Hz, 1H), 7.47-7.33 (m, 4H), 7.05-6.63 (m, 5H), 5.87 (d, *J* = 4.1 Hz, 1H), 5.81 (d, *J* = 3.8 Hz, 1H), 3.80 (s, 6H), 1.78 (dd, *J* = 12.8, 4.3 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.73, 158.69, 150.8 (dd, $^{1,2}J_{C\text{-}F}$ = 247, 11.9 Hz), 150.0 (dd, $^{1,2}J_{C\text{-}F}$ = 250, 13.1 Hz), 147.38, 147.37, 145.8, 142.3-142.2 (m), 139.5, 137.7, 137.3, 136.3 (dd, $^{3,4}J_{C\text{-}F}$ = 7.2, 3.6 Hz), 134.8, 133.3, 131.7-131.4 (m), 129.6, 129.5, 129.1, 128.2, 125.6, 123.1, 114.5 (d, $^{2}J_{C\text{-}F}$ = 17.9 Hz), 114.2 (br s), 112.4 (d, $^{2}J_{C\text{-}F}$ =19.1 Hz), 74.3, 73.9, 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -137.48 (ddd, *J* = 16.9, 11.3, 8.3 Hz, 1F), -138.43 (ddd, *J* = 18.8, 11.3, 7.1 Hz, 1F); **IR** (KBr) ν_{max} 3564, 3537, 3442, 3010, 2964, 2935, 2839, 1608, 1589, 1518, 1487, 1464, 1458, 1446, 1435, 1412, 1387, 1363, 1333, 1308, 1286, 1248, 1209, 1200, 1178, 1159, 1126, 1115, 1090, 1065, 1034, 1011, 893, 872, 841, 820, 793, 777, 769, 760, 739, 586, 544 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{24}O_4F_2Na$ $[M+Na]^+$ calcd: 557.15349, found: 557.15290; ***R*$_f$** (6/0.1 CH_2Cl_2/EtOAc) = 0.42.

Diastereoisomer 2: **mp** (decomp) > 320 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.9 Hz, 1H), 8.19 (dd, *J* = 11.0, 7.2 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.54 (app t, *J* = 7.6 Hz, 1H), 7.45-7.36 (m, 2H), 7.14 (br s, 4H), 6.84 (d, *J* = 7.6 Hz, 4H), 5.59 (d, *J* = 5.3 Hz, 1H), 5.56 (d, *J* = 5.0 Hz, 1H), 3.81 (s, 6H), 1.94 (d, *J* = 5.3 Hz, 1H), 1.92 (d, *J* = 5.3 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.7, 158.6, 150.8 (dd, $^{1,2}J_{C\text{-}F}$ = 247, 13.1 Hz), 150.0 (dd, $^{1,2}J_{C\text{-}F}$ = 250, 13.1 Hz), 146.88, 146.86, 146.7, 145.8, 142.2 (dd, $^{3,4}J_{C\text{-}F}$ = 6.0, 3.6 Hz), 139.4, 139.0, 138.6, 136.2 (dd, $^{3,4}J_{C\text{-}F}$ = 7.2, 3.6 Hz), 134.6, 133.1, 129.6, 129.5, 129.2, 128.2, 125.7, 123.1, 114.6 (d, $^{2}J_{C\text{-}F}$ =

17.9 Hz), 114.0-113.5 (m), 112.4 (d, $^{2}J_{C\text{-}F}$ = 20.3 Hz), 74.1, 73.7, 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -137.40 (m, 1F), -138.39 (m, 1F); **IR** (KBr) ν_{max} 3577, 3560, 3039, 3005, 2958, 2933, 2837, 1610, 1518, 1510, 1485, 1462, 1433, 1410, 1286, 1246, 1180, 1155, 1130, 1109, 1090, 1061, 1030, 1012, 939, 895, 879, 868, 839, 789, 775, 766, 735 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{24}O_4F_2Na$ $[M+Na]^+$ calcd: 557.15349, found: 557.15303; ***R*$_f$** (6/0.1 CH_2Cl_2/EtOAc) = 0.10.

3,4-Difluoro-6,7-bis(4-methoxyphenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (16f).



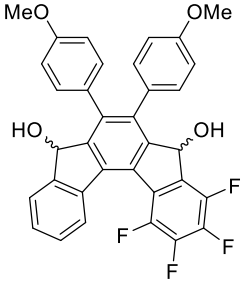
With **14f** (670 mg, 1.25 mmol) according to the general procedure. Column chromatography (6/0.1 to 2/0.1 CH_2Cl_2/EtOAc) and sonication of the obtained solid with CH_3CN, followed by decantation and filtration, yielded 488 mg (73%) of a mixture of separable diastereoisomers (1:1) as a pale yellow solid.

Diastereoisomer 1: mp (decomp) >300 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.6 Hz, 1H), 8.08 (dd, *J* = 8.4, 3.3 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.50 (app t, *J* = 7.3 Hz, 1H), 7.40 (app t, *J* = 7.3 Hz, 2H), 7.34-7.24 (overlapped to $CHCl_3$ signal, 2H), 7.08-6.64 (m, 6H), 6.09 (d, *J* = 3.9 Hz, 1H), 5.87 (d, *J* = 4.2 Hz, 1H), 3.82 (s, 6H), 1.93 (d, *J* = 4.2 Hz, 1H), 1.81 (d, *J* = 4.4 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.70, 158.66, 150.1 (dd, $^{1,2}J_{C\text{-}F}$ = 250, 11.9 Hz), 148.3 (dd, $^{1,2}J_{C\text{-}F}$ = 253, 13.1 Hz), 147.3, 146.5, 145.8, 139.5, 138.0 (m), 137.9, 137.8, 135.0, 133.5, 133.4, 131.5 (br s), 129.7 (br s), 129.5, 129.3, 128.9, 128.1, 125.6, 123.2, 119.2 (dd, $^{2,3}J_{C\text{-}F}$ = 6.0, 3.6 Hz), 117.9 (d, $^{2}J_{C\text{-}F}$ = 17.9 Hz), 114.2 (br s), 74.2, 72.2 (d, $^{3}J_{C\text{-}F}$ = 2.4 Hz), 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -140.02 (ddd, *J* = 21.8, 10.9, 3.4 Hz, 1F), -143.50 (dd, *J* = 21.8, 7.5 Hz, 1F); **IR** (KBr) ν_{max} 3560, 3010, 2958, 2933, 2839, 1608, 1510, 1464, 1431, 1327, 1281, 1246, 1215, 1178, 1105, 1084, 1032, 993, 970, 841, 823, 796, 762, 741cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{24}O_4F_2Na$ $[M+Na]^+$ calcd: 557.15349, found: 557.15318; ***R*$_f$** (6/0.1 CH_2Cl_2/EtOAc = 0.17.

Diastereoisomer 2: **mp** (decomp) >290 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.8 Hz, 1H), 8.07 (dd, *J* = 8.4, 3.5 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.48 (app t, *J* = 6.4 Hz, 1H), 7.38 (app t, *J* = 7.1 Hz, 1H), 7.33-7.27 (m, 1H), 7.23-6.97 (m, 4H), 6.82 (d, *J* = 8.8 Hz, 4H), 5.79 (d, *J* = 5.1 Hz, 1H), 5.61 (d, *J* = 5.4 Hz, 1H), 3.79 (s, 6H), 2.07 (d, *J* = 4.9 Hz, 1H), 1.89 (d, *J* = 5.4 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.7, 158.6, 150.1 (dd, $^{1,2}J_{C\text{-}F}$ = 250, 11.9 Hz), 148.3 (dd, $^{1,2}J_{C\text{-}F}$ = 252, 14.3 Hz), 147.1, 146.0, 145.9, 139.4, 139.0 (d, $^{3}J_{C\text{-}F}$ = 9.5 Hz), 138.0, 134.8, 133.5 (d, $^{2}J_{C\text{-}F}$ = 13.1 Hz), 133.3, 131.8 (br s), 130.2 (br s), 129.6, 129.4, 129.0, 128.2, 125.6, 123.2, 119.2 (dd, $^{3,4}J_{C\text{-}F}$ = 6.0, 3.6 Hz), 118.0 (d, $^{2}J_{C\text{-}F}$ = 17.9 Hz), 113.7 (br s), 74.1, 71.9 (d, $^{3}J_{C\text{-}F}$ = 2.4 Hz), 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -140.03 (ddd, *J* = 21.8, 10.2, 2.7 Hz, 1F),

-143.62 (dd, J = 21.8, 7.5 Hz, 1F); **IR** (KBr) ν_{max} 3554, 3547, 3406, 3394, 3063, 3003, 2956, 2933, 2910, 2837, 1608, 1518, 1508, 1466, 1429, 1410, 1327, 1282, 1275, 1244, 1215, 1178, 1107, 1030, 991, 843, 835, 814, 795, 777, 768, 739, 731 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{24}O_4F_2Na$ $[M+Na]^+$ calcd: 557.15349, found: 557.15329; ***R*$_f$** (6/0.1 CH_2Cl_2/EtOAc) = 0.10.

1,2,3,4-Tetrafluoro-6,7-bis(4-methoxyphenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol



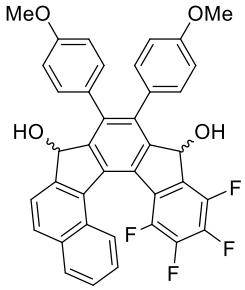
(16g). With **14g** (215 mg, 0.38 mmol) according to the general procedure. Column chromatography (CH_2Cl_2 to 4/0.1 - 2/0.1 CH_2Cl_2/EtOAc) yielded 186 mg (86%) of a mixture of separable diastereoisomers (1:1.2) as a pale yellow solid.

Diastereoisomer 1: **mp** (decomp) 136-138 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (app t, J = 7.9 Hz, 1H), 7.57 (d, J = 7.3 Hz, 1H), 7.45 (app t, J = 7.5 Hz, 1H), 7.36 (app t, J = 7.3 Hz, 2H), 7.34-7.28 (m, 1H), 6.83 (br m, 6H), 6.08 (d, J = 3.8 Hz, 1H), 5.88 (d, J = 3.8 Hz, 1H), 3.87-3.70 (m, 6H), 1.96 (d, J = 4.1 Hz, 1H), 1.80 (d, J = 4.4 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.81, 158.77, 148.3, 146.0, 145.7, 144.89 (dd, $^{1,2}J_{C\text{-}F}$ = 250.3, 11.9 Hz), 142.16 (app dt, $^{1,2}J_{C\text{-}F}$ = 252.7, 16.7 Hz), 141.98 (dm, $^{1}J_{C\text{-}F}$ = 256.3 Hz), 140.20 (dm, $^{1}J_{C\text{-}F}$ = 256.3 Hz), 139.2, 138.7, 137.2, 135.7, 131.5 (br s), 129.6 (br s), 129.2, 128.9, 128.7, 128.2, 127.5 (br s), 126.9 (d, $^{2}J_{C\text{-}F}$ = 15.5 Hz), 124.73, 124.72 (d, $^{2}J_{C\text{-}F}$ = 21.5 Hz), 124.1 (d, $^{3}J_{C\text{-}F}$ = 13.1 Hz), 114.3 (br s), 114.2 (br s), 74.4, 72.6, 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -130.26-(-129.95) (m, 1F), -144.02 (dd, $J_{F\text{-}F}$ = 21.1, 15.7 Hz, 1F), -154.93 (app t, $J_{F\text{-}F}$ = 19.4 Hz, 1F), -156.67 (ddd, $J_{F\text{-}F}$ = 21.1, 18.4, 2.7 Hz, 1F); **IR** (KBr) ν_{max} 3554, 2956, 2932, 2836, 1610, 1509, 1491, 1458, 1434, 1287, 1245, 1177, 1114, 1090, 1036, 970, 952, 917, 842, 791, 770 cm^{-1}; HRMS (ESI) *m/z* for $C_{34}H_{22}O_4F_4Na$ $[M+Na]^+$ calcd: 593.13464, found: 593.13385; R_f(CH_2Cl_2) = 0.35.

Diastereoisomer 2: **mp** (decomp) 135-136 °C; **^{1}H NMR** (400 MHz, $CDCl_3$,) δ 7.77 (app t, J = 8.1 Hz, 1H), 7.56 (d, J = 7.3 Hz, 1H), 7.46 (app t, J = 7.5 Hz, 1H), 7.36 (app t, J = 6.8 Hz, 1H), 7.12 (d, J = 8.6 Hz, 4H), 6.82 (d, J = 8.6 Hz, 4H), 5.77 (d, J = 4.6 Hz, 1H), 5.66 (d, J = 4.6 Hz, 1H), 3.79 (s, 6H), 2.12 (d, J = 5.1 Hz, 1H), 1.89 (d, J = 5.1 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.74, 158.69, 148.0, 145.7, 145.2, 145.0 (dd, $^{1,2}J_{C\text{-}F}$ = 252, 11.9 Hz), 142.3 (dd, $^{1,2}J_{C\text{-}F}$ = 254, 15.5 Hz), 142.1 (dd, $^{1,2}J_{C\text{-}F}$ = 254, 13.1 Hz), 139.8, 140.1 (dt, $^{1,2}J_{C\text{-}F}$ = 256, 14.3 Hz), 139.1, 138.3, 135.4, 132.3-131.5 (m), 131.3-130.4 (m), 130.3-129.7 (m), 129.3, 128.9, 128.7, 128.2, 127.3 (br s), 126.8 (d, $^{2}J_{C\text{-}F}$ = 14.3 Hz), 124.9, 124.7, 123.9 (d, $^{2}J_{C\text{-}F}$ = 13.1 Hz), 114.4-113.2 (m), 74.2, 72.0, 55.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -129.12-(-128.84) (m, 1F), -144.03 (ddd, $J_{F\text{-}F}$ = 21.1, 15.7, 2.7 Hz, 1F), -154.78 (app t, $J_{F\text{-}F}$ = 19.8 Hz, 1F), -156.77 (ddd, $J_{F\text{-}}$

$_F$ = 21.1, 17.7, 2.7 Hz, 1F); **IR** (KBr) ν_{max} 3554, 2932, 2842, 1613, 1509, 1491, 1467, 1425, 1290, 1248, 1183, 1135, 1114, 1093, 1033, 973, 958, 917, 842, 788, 764 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{22}O_4F_4Na$ $[M+Na]^+$ calcd: 593.13464, found: 593.13440; ***R_f*** (CH_2Cl_2) = 0.06.

1,2,3,4-Tetrafluoro-6,7-bis(4-methoxyphenyl)-5,8-dihydrobenzo[*c*]indeno[1,2-*g*]fluorene-5,8-diol (17). With **15** (124 mg, 0.20 mmol) according to the general procedure. Column chromatography (6/0.1 to 2/0.1 CH_2Cl_2/EtOAc) yielded 96 mg (77%) of the title compound as mixture of four diasteroisomers (*syn* and *anti*) that were separated into two fractions.



Fraction 1 (1:0.6 mixture of two diastereoisomers): **mp** (decomp) 170.8 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01-7.86 (m, 6H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.48-7.36 (m, 8H), 6.84 (br s, 12H), 6.38 (d, *J* = 3.8 Hz, 1H), 6.11 (d, *J* = 4.4 Hz, 1H), 5.98 (d, *J* = 4.4 Hz, 1H), 5.71 (d, *J* = 5.3 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 2.10 (d, *J* = 5.0 Hz, 1H), 2.00 (d, *J* = 4.1 Hz, 1H), 1.93 (d, *J* = 6.2 Hz, 1H), 1.77 (d, *J* = 4.4 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.9, 158.78, 158.75, 158.7, 149.7, 147.1, 146.2, 144.4, 145.3 (dd, $^{1,2}J_{C\text{-}F}$ = 238, 11.9 Hz), 144.2, 144.0, 144.6 (dd, $^{1,2}J_{C\text{-}F}$ = 250, 10.7 Hz), 142.2 (dt, $^{1,2}J_{C\text{-}F}$ = 253, 13.1 Hz), 142.6-140.7 (m), 141.4 (dd, $^{1,2}J_{C\text{-}F}$ = 256, 10.7 Hz), 139.2, 138.1, 137.0, 136.8, 136.5, 136.2, 136.1, 135.6, 134.5, 134.2, 131.5 (br s), 130.9 (br s), 130.1, 129.7, 129.6 (d, $^3J_{C\text{-}F}$ = 6.0 Hz), 129.5 (d, $^4J_{C\text{-}F}$ = 4.8 Hz), 129.3 (br s.), 129.3, 129.0, 128.97 (br s), 128.9, 128.7, 128.5, 128.2 (br s), 126.5 (d, $^2J_{C\text{-}F}$ = 14.3 Hz), 126.0, 125.9, 125.6 (d, $^3J_{C\text{-}F}$ = 6.0 Hz), 125.1, 125.0 (d, $^3J_{C\text{-}F}$ = 6.0 Hz), 122.2, 121.9, 114.3 (d, $^2J_{C\text{-}F}$ = 17.9 Hz), 114.0 (d, $^2J_{C\text{-}F}$ = 13.1 Hz), 75.2, 74.4, 74.2, 71.6, 55.21, 55.16, 55.1; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -125.51 (dd, $J_{F\text{-}F}$ = 20.8, 16.5 Hz, 1F), -128.11 (app t, $J_{F\text{-}F}$ = 18.6 Hz, 1F), -143.92 (app t, $J_{F\text{-}F}$ = 19.1 Hz, 1F), -144.61 (app t, $J_{F\text{-}F}$ = 18.2 Hz, 1F), -154.71 (app t, $J_{F\text{-}F}$ = 20.8 Hz, 1F), -155.56 (app t, $J_{F\text{-}F}$ = 19.9 Hz, 1F), -156.47 (app t, $J_{F\text{-}F}$ = 19.1 Hz, 1F), -156.71 (app t, $J_{F\text{-}F}$ = 18.6 Hz, 1F); **IR** (KBr) ν_{max} 3554, 3452, 2933, 2837, 2360, 1708, 1609, 1509, 1247, 1033, 841, 546, 423 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{38}H_{24}O_4F_4$ $[M]^+$ calcd: 620.16052, found: 620.16029; ***R_f*** (2/0.1 CH_2Cl_2/EtOAc) = 0.64.

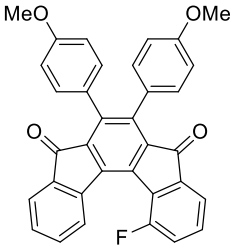
Fraction 2 (1:0.5 mixture of two diastereoisomers): **mp** (decomp) 162.3 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.6, 5.3 Hz, 1H), 7.99-7.84 (m, 4H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.56-7.47 (m, 2H), 7.44-7.32 (m, 4H), 7.25-6.63 (m, 14H), 6.28 (br s, 1H), 6.01 (br s, 1H), 5.65 (br s, 1H), 5.38 (br s, 1H), 3.85-3.77 (m, 12H), 2.41-2.23 (m, 1H), 2.16-2.09 (m, 1H), 2.06 (br s, 1H), 1.81 (br s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.80, 158.78, 158.73, 158.72, 149.7, 147.0, 145.8, 144.4, 144.1, 145.1 (dd, $^{1,2}J_{C\text{-}F}$ = 253, 11.9 Hz), 143.9,

144.6 (dd, $^{1,2}J_{C\text{-}F}$ = 252, 13.1 Hz), 142.2 (app dt, $^{1,2}J_{C\text{-}F}$ = 254, 14.3 Hz), 141.9 (dd, $^{1,2}J_{C\text{-}F}$ = 256, 14.3 Hz), 142.6-140.5 (m), 139.2, 138.5, 137.9, 137.5, 136.7, 136.3, 135.5, 134.5, 134.2, 130.2, 129.7, 129.6 (br s), 129.6, 129.5, 129.3, 128.9 (br s), 128.8, 128.62, 128.58, 128.55, 128.0 (br s), 126.9 (d, $^{3}J_{C\text{-}F}$ = 14.3 Hz), 126.0, 125.6 (d, $^{2}J_{C\text{-}F}$ = 16.7 Hz), 125.33, 125.28, 125.2 (d, $^{2}J_{C\text{-}F}$ = 16.7 Hz), 122.2, 121.9, 114.04, 113.96, 75.2, 74.3, 74.1, 71.6, 55.2; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -126.98 (dd, $J_{F\text{-}F}$ = 19.9, 16.5 Hz, 1F), -127.18 (dd, $J_{F\text{-}F}$ = 19.1, 17.3 Hz, 1F), -144.07 (dd, $J_{F\text{-}F}$ = 19.9, 18.2 Hz, 1F), -144.78 (dd, $J_{F\text{-}F}$ = 19.9, 15.6 Hz, 1F), -154.90 (app t, $J_{F\text{-}F}$ = 19.9 Hz, 1F), -155.52 (app t, $J_{F\text{-}F}$ = 19.9 Hz, 1F), -156.34 (app t, $J_{F\text{-}F}$ = 18.2 Hz, 1F), -156.86 (app t, $J_{F\text{-}F}$ = 18.2 Hz, 1F); **IR** (KBr) ν_{max} 3555, 3452, 2957, 2837, 2367, 1609, 1509, 1247, 1033, 842, 553 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{38}H_{24}O_4F_4Na$ $[M+Na]^+$ calcd: 643.15029, found: 643.14982; ***R_f*** (2/0.1 CH_2Cl_2/EtOAc) = 0.20.

5.3.3 Synthesis of dispirofluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorenes and dispirofluorene-9,5'-benzo[*c*]indeno[1,2-*g*]fluorene-8',9''-fluorene

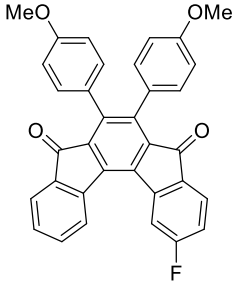
General procedure for oxidation reaction with PCC. Preparation of 18a-18g and 19. In a one-neck flask, pyridinium chlorochromate (PCC, 130 mg, 0.60 mmol), Celite® (130 mg) and CH_2Cl_2 (20 mL) were added. Afterwards, the starting compound **16a-16g** or **17** (0.2 mmol) was added and the mixture was stirred for 3 h at 25 °C and under atmospheric conditions. Afterwards the residue was filtered through a Celite®/silica gel plug. Column chromatography of the residue on silica gel (CH_2Cl_2/hexanes) yielded products.

1-Fluoro-6,7-bis(4-methoxyphenyl)indeno[2,1-*c*]fluorene-5,8-dione (18a). With **16a** (608 mg, 1.18 mmol) according to the general procedure. Column chromatography (4/1 to 7/1 CH_2Cl_2/hexanes) yielded 546 mg (90%) of the title compound as an orange solid: **mp** (decomp) 295-297 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (app t, *J* = 7.3 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.61 (app t, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.48-7.31 (m, 3H), 6.91 (dd, *J* = 8.8 Hz, 4H), 6.76 (d, *J* = 8.8 Hz, 4H), 3.79 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.7, 190.2 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 158.8 (2C), 156.7 (d, $^{1}J_{C\text{-}F}$ = 257 Hz), 143.4, 143.2, 143.0, 138.6 (d, $^{4}J_{C\text{-}F}$ = 1.3 Hz), 138.1 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 136.9, 136.2, 135.3, 134.5 (d, $^{5}J_{C\text{-}F}$ = 1.4 Hz), 133.4, 131.6 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 131.0, 130.9, 129.4, 129.0 (d, $^{3}J_{C\text{-}F}$ = 14.7 Hz), 126.9, 125.6, 125.4, 124.1, 123.2 (d, $^{2}J_{C\text{-}F}$ = 23.5 Hz), 120.8 (d, $^{4}J_{C\text{-}F}$ = 2.7 Hz), 113.1, 113.0, 55.0 (2C); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.66-(-101.55) (m, 1F); **IR** (KBr) ν_{max} 3410, 3078,



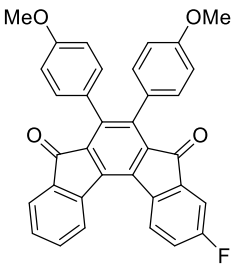
3070, 2956, 2926, 2835, 1711, 1610, 1589, 1518, 1475, 1466, 1458, 1437, 1423, 1377, 1300, 1288, 1248, 1203, 1180, 1155, 1149, 1134, 1113, 1101, 1086, 1076, 1034, 1012, 997, 982, 953, 931, 912, 835, 820, 798, 789, 754, 735, 714, 555, 536, 417, 407 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{34}H_{22}O_4F$ $[M+H]^+$ calcd: 513.14966, found: 513.14961; R_f (3/1 CH_2Cl_2/hexanes) = 0.31.

2-Fluoro-6,7-bis(4-methoxyphenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (18b). With



16b (145 mg, 0.28 mmol) according to the general procedure. Column chromatography (3/1 CH_2Cl_2/hexanes) yielded 104 mg (72%) of the title compound as a red solid: **mp** (decomp) >330 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 1H), 7.89 (dd, *J* = 9.3, 2.0 Hz, 1H), 7.76-7.62 (m, 3H), 7.43 (app t, *J* = 7.3 Hz, 1H), 7.08 (app td, *J* = 8.3, 2.0 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 4H), 6.76 (d, *J* = 8.6 Hz, 4H), 3.79 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.6, 190.1, 167.08 (d, $^1J_{C\text{-}F}$ = 255 Hz), 158.88, 158.83, 145.4 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 144.0, 143.4, 142.4, 138.3, 136.43, 136.40 (d, $^4J_{C\text{-}F}$ = 2.5 Hz), 136.2, 135.5, 135.0, 131.6 (d, $^4J_{C\text{-}F}$ = 2.2 Hz), 130.93, 130.90, 129.9, 127.0, 126.9, 126.8 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 125.0, 123.7, 116.2 (d, $^2J_{C\text{-}F}$ = 23.1 Hz), 113.0 (2C), 111.8 (d, $^2J_{C\text{-}F}$ = 25.6 Hz), 55.1 (2C); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.58 (td, $J_{F\text{-}H}$ = 8.9, 5.4 Hz, 1F); **IR** (KBr) ν_{max} 3043, 3007, 2964, 2924, 2906, 2852, 1718, 1610, 1518, 1458, 1379, 1354, 1259, 1178, 1095, 1086, 1049, 1018, 957, 908, 866, 858, 802, 796; **HRMS** (APCI) *m/z* for $C_{34}H_{21}O_4FNa$ $[M+Na]^+$ calcd: 535.13161, found: 535.13119; R_f (3/1 CH_2Cl_2/hexanes) = 0.23.

3-Fluoro-6,7-bis(4-methoxyphenyl)indeno[2,1-*c*]fluorene-5,8-dione (18c). With **16c** (210



mg, 0.41 mmol) according to the general procedure. Column chromatography (3/1 to 4/1 CH_2Cl_2/hexanes) yielded 182 mg (87%) of the title compound as an orange solid: **mp** (decomp) > 320 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.3, 4.2 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.66 (app t, *J* = 7.6 Hz, 1H), 7.43 (app t, *J* = 7.5 Hz, 1H), 7.39-7.30 (m, 2H), 6.92 (d, *J* = 8.8 Hz, 4H), 6.78 (d, *J* = 8.6 Hz, 4H), 3.81 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.6, 190.5 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 163.4 (d, $^1J_{C\text{-}F}$ = 253 Hz), 158.84, 158.79, 143.7, 143.1, 142.6, 138.5 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 137.8 (d, $^3J_{C\text{-}F}$ = 7.3 Hz), 137.6 (m), 137.2, 136.4, 136.3 (d, $^5J_{C\text{-}F}$ = 2.3 Hz), 135.5, 134.9, 130.93, 130.88, 129.7, 127.0, 126.9, 125.2 (d, $^3J_{C\text{-}F}$ = 7.9 Hz), 124.9, 123.5, 121.1 (d, $^2J_{C\text{-}F}$ = 23.1 Hz), 113.03, 113.00, 112.1 (d, $^2J_{C\text{-}F}$ = 23.3 Hz), 55.0 (2C); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -111.14 -(-110.92) (m); **IR** (KBr) ν_{max} 3419, 3070, 3039, 3001, 2978, 2962, 2939, 2839, 1716, 1610, 1518, 1479, 1466, 1423, 1379,

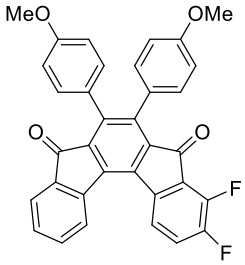
1363, 1300, 1284, 1246, 1221, 1200, 1178, 1153, 1120, 1105, 1076, 1030, 1014, 958, 887, 833, 800, 779, 766, 756 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{21}O_4FNa$ $[M+Na]^+$ calcd: 535.13161, found: 535.13119; ***R_f*** (4/1 CH_2Cl_2/hexanes) = 0.31.

4-Fluoro-6,7-bis(4-methoxyphenyl)indeno[2,1-*c*]fluorene-5,8-dione (18d). With **16d** (798 mg, 1.54 mmol) according to general procedure. Column chromatography (4/1 to 7/1 CH_2Cl_2/hexanes) yielded 718 mg (91%) of the title compound as an orange solid: **mp** (decomp) 329-330 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.3 Hz, 1H), 7.66-7.57 (m, 2H), 7.41 (app t, *J* = 7.3 Hz, 1H), 7.06 (app t, *J* = 8.4 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.0 Hz, 4H), 6.80-6.69 (m, 4H), 3.79 (s, 3H), 3.78 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.6, 188.2, 159.8 (d, $^1J_{C\text{-}F}$ = 266 Hz), 158.81, 158.80, 144.8 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 143.7 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 142.5, 138.4, 136.9 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 136.1, 135.9, 135.5, 134.8, 130.93, 130.88, 129.8, 126.8, 126.7, 124.9, 123.7, 121.5 (d, $^3J_{C\text{-}F}$ = 12.0 Hz), 119.7 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 118.0 (d, $^2J_{C\text{-}F}$ = 20.1 Hz), 113.1, 113.09, 55.0 (2C); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.42 (dd, $J_{F\text{-}H}$ = 8.5, 5.1 Hz, 1F); **IR** (KBr) ν_{max} 3408, 3070, 3005, 2968, 2951, 2926, 2901, 2839, 2831, 1711, 1610, 1581, 1518, 1479, 1468, 1421, 1379, 1313, 1290, 1252, 1201, 1180, 1149, 1113, 1101, 1090, 1072, 1059, 1036, 1016, 997, 943, 926, 835, 808, 798, 768, 719 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{21}O_4FNa$ $[M+Na]^+$ calcd: 535.1316, found: 535.1319; ***R_f*** (2/1 hexanes/EtOAc) = 0.35.

2,3-Difluoro-6,7-bis(4-methoxyphenyl)indeno[2,1-*c*]fluorene-5,8-dione (18e). With **16e** (632 mg, 1.18 mmol) according to procedure. Column chromatography (4/1 CH_2Cl_2/hexanes) yielded 509 mg (81%) of the title compound as a red solid: **mp** (decomp) >320 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.6 Hz, 1H), 8.06 (dd, *J* = 10.3, 6.6 Hz, 1H), 7.65-7.81 (m, 2H), 7.57-7.42 (m, 2H), 6.98-6.65 (m, 4H), 6.78 (d, *J* = 8.6 Hz, 4H), 3.81 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.4, 189.4, 159.91, 158.90, 154.4 (dd, $^{1,2}J_{C\text{-}F}$ = 259, 15.8 Hz), 151.0 (dd, $^{1,2}J_{C\text{-}F}$ = 255, 14.1 Hz), 143.7, 143.6, 142.2, 139.6 (dd, $^{3,4}J_{C\text{-}F}$ = 8.3, 3.6 Hz), 138.0, 136.4, 136.1, 135.9, 135.5, 135.1, 132.2 (m), 130.9 (2C), 130.0, 126.8, 126.7, 125.1, 123.4, 114.1 (d, $^2J_{C\text{-}F}$ = 18.5 Hz), 113.4 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 113.1, 113.0, 55.1 (2C); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -126.73-(-126.32) (m, 1F), -134.87-(-134.96) (m, 1F); **IR** (KBr) ν_{max} 3049, 3003, 2970, 2939, 2908, 2899, 2839, 1718, 1608, 1589, 1518, 1485, 1466, 1427, 1387, 1362, 1298, 1288, 1246, 1219, 1178, 1144, 1107, 1070, 1030, 912, 891, 879, 833,

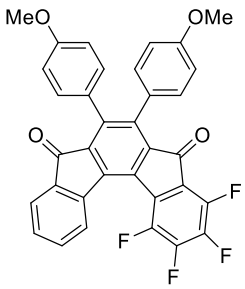
796, 791, 777, 756, 719, 557; **HRMS** (ESI) *m/z* for $C_{34}H_{21}O_4F_2$ $[M+H]^+$ calcd: 531.14024, found: 531.14046; R_f (4/1 CH_2Cl_2/hexanes) = 0.41.

3,4-Difluoro-6,7-bis(4-methoxyphenyl)indeno[2,1-*c*]fluorene-5,8-dione (18f). With **16f**



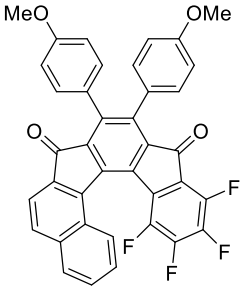
(435 mg, 0.81 mmol) according to the general procedure. Column chromatography (4/1 CH_2Cl_2/hexanes) yielded 411 mg (95%) of the title compound as a red solid: **mp** (decomp) 300-302 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.6 Hz, 1H), 7.95 (dd, *J* = 7.9, 2.6 Hz, 1H), 7.70 (d, *J* = 7.3 Hz, 1H), 7.64 (app t, *J* = 7.5 Hz, 1H), 7.49-7.36 (m, 2H), 6.89 (d, *J* = 7.8 Hz, 4H), 6.75 (d, *J* = 8.1 Hz, 4H), 3.78 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.5, 187.3 (m), 158.94, 158.91, 150.8 (dd, $^{1,2}J_{C\text{-}F}$ = 255, 12.3 Hz), 147.8 (dd, $^{1,2}J_{C\text{-}F}$ = 268, 14.6 Hz), 144.0, 143.5, 142.3, 139.3 (m), 138.2, 136.40 (m), 136.37, 136.2 (m), 135.4, 134.9, 130.9, 130.8, 129.9, 126.8, 126.6, 125.0, 123.7 (d, $^3J_{C\text{-}F}$ = 18.7 Hz), 123.5, 122.7 (d, $^2J_{C\text{-}F}$ = 18.8 Hz), 119.7 (dd, $^{3,4}J_{C\text{-}F}$ = 6.0, 3.7 Hz), 113.1, 113.0, 55.1 (2C); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -135.97 (dd, *J* = 18.4, 7.5 Hz, 1F), -139.31 (dd, *J* = 21.1, 6.8 Hz, 1F); **IR** (KBr) ν_{max} 3073, 3040, 2998, 2953, 2926, 2905, 2833, 1715, 1610, 1577, 1521, 1509, 1500, 1467, 1422, 1371, 1293, 1272, 1245, 1204, 1174, 1102, 1075, 1036, 997, 890, 836, 803, 764, 725, 686, 665, 644, 555 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{21}O_4F_2$ $[M+H]^+$ calcd: 531.14024, found: 531.13986; R_f (4/1 CH_2Cl_2/hexanes) = 0.27.

1,2,3,4-Tetrafluoro-6,7-bis(4-methoxyphenyl)indeno[2,1-*c*]fluorene-5,8-dione (18g). With



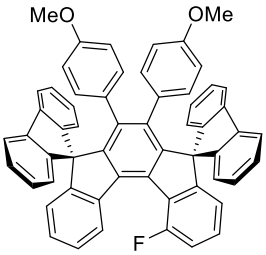
16g (478 mg, 0.84 mmol) according to the general procedure. Column chromatography (3/1 CH_2Cl_2/hexanes) yielded 366 mg (77%) of the title compound as a red solid: **mp** (decomp) 267-270 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.3 Hz, 1H), 7.60-7.67 (m, 2H), 7.43 (app t, *J* = 7.6 Hz, 1H), 6.93-6.85 (m, 4H), 6.76 (d, *J* = 8.8 Hz, 4H), 3.79 (s, 3H), 3.78 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.2, 185.1, 159.1, 159.0, 145.6 (app dt, $^{1,2}J_{C\text{-}F}$ = 266, 13.0 Hz), 145.3 (app dd, $^{1,2}J_{C\text{-}F}$ = 267.0, 12.6 Hz), 144.2, 144.0, 142.3, 142.2 (app dd, $^{1,2}J_{C\text{-}F}$ = 266, 13.0 Hz), 141.3 (app dt, $^{1,2}J_{C\text{-}F}$ = 262, 15.7 Hz), 139.4, 137.1, 135.9, 135.2, 134.7, 130.9, 130.8, 130.6, 129.9, 126.4, 126.1, 125.2 (d, $^2J_{C\text{-}F}$ = 20.3 Hz), 125.15 (m), 124.4, 117.5 (d, $^3J_{C\text{-}F}$ = 10.1 Hz), 113.1, 113.0, 55.1 (2C); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -126.12-(-125.81) (m, 1F), -139.67-(-138.87) (m, 1F), -144.66 (ddd, $J_{F\text{-}F}$ = 21.1, 15.7, 8.9 Hz, 1F), -152.44 (ddd, $J_{F\text{-}F}$ = 21.8, 17.0, 4.1 Hz, 1F); **IR** (KBr) ν_{max} 3005, 2968, 2937, 2914, 2839, 1716, 1608, 1518, 1500, 1489, 1466, 1456, 1431, 1419, 1396, 1333, 1300, 1290, 1246, 1198,

1176, 1142, 1111, 1063, 1038, 960, 839, 769 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{34}H_{19}O_4F_4$ $[M+H]^+$ calcd: 567.12140, found: 567.12030; ***R*$_f$** (3/1 CH_2Cl_2/hexanes) = 0.28.

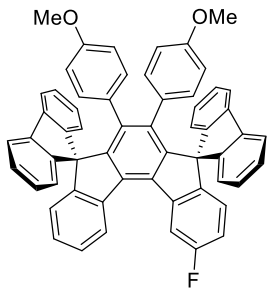
1,2,3,4-Tetrafluoro-6,7-bis(4-methoxyphenyl)benzo[*c*]indeno[1,2-*g*]fluorene-5,8-dione (19).  With **17** (74 mg, 0.12 mmol) according to the general procedure. Column chromatography (3/1 CH_2Cl_2/hexanes) yielded 61 mg (82%) of the title compound as a red solid: **mp** (decomp) 278-279 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.89 (dd, *J* = 8.4, 3.4 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.64 (app t, *J* = 7.5 Hz, 1H), 7.46 (app t, *J* = 7.6 Hz, 1H), 7.09-6.94 (m, 2H), 6.92-6.83 (m, 2H), 6.82-6.72 (m, 4H), 3.79 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.6, 185.0, 159.2, 159.1, 145.5 (dt, $^{1,2}J_{C\text{-}F}$ = 262, 14.3 Hz), 144.3, 145.0 (dd, $^{1,2}J_{C\text{-}F}$ = 267, 11.9 Hz), 144.0, 143.0, 141.9 (dd, $^{1,2}J_{C\text{-}F}$ = 261, 13.1 Hz), 140.9, 141.3 (dt, $^{1,2}J_{C\text{-}F}$ = 260, 14.3 Hz), 138.4, 137.5, 136.1, 134.1, 131.5, 131.4, 131.2 (br s), 130.7 (br s), 129.3, 129.1, 129.0 (d, $^{4}J_{C\text{-}F}$ = 4.8 Hz), 126.7 (d, $^{2}J_{C\text{-}F}$ = 11.9 Hz), 126.6, 126.2, 125.9, 124.5 (d, $^{4}J_{C\text{-}F}$ = 4.8 Hz), 119.7, 117.2 (d, $^{3}J_{C\text{-}F}$ = 10.7 Hz), 113.2, 113.1 (d, $^{2}J_{C\text{-}F}$ = 13.1 Hz), 55.1 (2C); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -124.14 (app t, $J_{F\text{-}F}$ = 16.5 Hz, 1F), -139.56-(-139.23) (m, 1F), -145.32 (ddd, $J_{F\text{-}F}$ = 21.7, 17.3, 9.5 Hz, 1F), -152.24 (ddd, $J_{F\text{-}F}$ = 20.8, 17.3, 3.5 Hz, 1F); **IR** (KBr) ν_{max} 3051, 3005, 2956, 2931, 2837, 1713, 1632, 1608, 1579, 1518, 1500, 1491, 1456, 1431, 1389, 1329, 1306, 1292, 1250, 1178, 1140, 1111, 1028, 951, 845, 837, 798, 787, 764, 752 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{38}H_{21}O_4F_4$ $[M+H]^+$ calcd: 617.13705, found: 617.13660; ***R*$_f$** (4/1 CH_2Cl_2/hexanes) = 0.25.

General procedure for creation of 9,9'-spirobifluorene. Preparation of 20a-20g and 21.[153] In a dried Schlenk flask, 2-bromobiphenyl (78 μL, 0.45 mmol) and anhydrous THF (3 mL) were added under argon atmosphere. The resulting solution was cooled down to -78 °C and *n*-BuLi 1.6 M (280 μL, 0.45 mmol) was added dropwise. After stirring for 30 min, **18a-18g** or **19** (0.15 mmol) in THF (3 mL) was added dropwise and the reaction was carried out at -78 °C for 15 min. Then it was warmed up gradually to 25 °C and stirred for 4 h. The reaction was quenched with the saturated aqueous $NaHCO_3$ solution and extracted with diethyl ether (3×10 mL). The combined organic layers were dried over Na_2SO_4, and the solvent was removed by rotary evaporator. Column chromatography on silica gel (hexanes/EtOAc) afforded the corresponding alcohols, which were subjected immediately to the next step. The diol was dissolved in acetic acid (10 mL) with few drops of HCl (12 mol/L) and the resulting mixture

was stirred under reflux for 2 h. The reaction was quenched adding saturated aqueous K_2CO_3 solution till pH = 7 and extracted with diethyl ether (3×15 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel, followed by sonication of the obtained solid with CH_3CN, decantation and filtration.

1'-Fluoro-6',7'-bis(4-methoxyphenyl)dispiro[fluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene] (20a). 

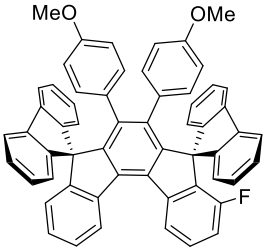
With **18a** (546 mg, 1.06 mmol) according to the general procedure. Column chromatography of the residue on silica gel (5/1 to 7/1 hexanes/EtOAc for the first reaction and 1/1 CH_2Cl_2/hexanes for the second reaction) followed by sonication of the obtained solid with CH_3CN, decantation and filtration, provided 570 mg (68%) of the title compound as a colourless solid: **mp** (decomp) 396-397 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 (app t, *J* = 8.2 Hz, 1H), 7.46 (app t, *J* = 7.6 Hz, 1H), 7.36-7.32 (m, 4H), 7.23-7.11 (m, 7H), 7.1-7.06 (m, 4H), 6.95 (app t, *J* = 8.5 Hz, 4H), 6.59 (d, *J* = 7.3 Hz, 1H), 6.42 (d, *J* = 7.3 Hz, 1H), 5.77 (dd, *J* = 8.5, 2.3 Hz, 4H), 5.62-5.55 (m, 4H), 3.50 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.9 (d, $^1J_{C\text{-}F}$ = 253 Hz), 156.4, 156.3, 153.4 (d, $^4J_{C\text{-}F}$ = 3.8 Hz), 150.1, 148.9 (2C), 148.5 (2C), 147.4, 146.5, 142.04 (2C), 141.98 (2C), 141.5, 139.9, 138.9, 136.7, 131.0, 130.5 (2C), 130.4 (2C), 129.1 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 128.6, 128.5, 128.4, 127.2 (4C), 127.1 (2C), 127.0 (2C), 125.2, 125.0, 123.9 (2C), 123.8 (2C), 119.8 (2C), 119.7 (m), 119.6 (2C), 115.2 (d, ^2J = 26.5 Hz), 111.1 (4C), 66.4, 66.2, 54.9 (2C); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.48-(-101.38); **IR** (KBr) ν_{max} 3093, 3072, 2951, 2931, 2906, 2827, 1612, 1518, 1508, 1473, 1446, 1417, 1284, 1248, 1242, 1174, 1036, 829, 754 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{58}H_{38}O_2F$ $[M+H]^+$ calcd: 785.28504, found: 785.28461; ***R*$_f$** (5/1 hexanes/EtOAc) = 0.47.

2'-Fluoro-6',7'-bis(4-methoxyphenyl)dispiro[fluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene] (20b). 

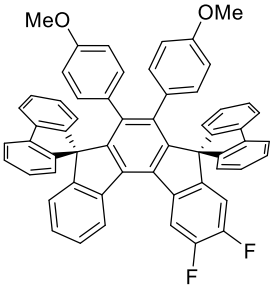
With **18b** (145 mg, 0.28 mmol) according to the general procedure. Column chromatography of the residue on silica gel (2/1 to 4/1 CH_2Cl_2/hexanes) followed by sonication of the obtained solid with CH_3CN, decantation and filtration, provided 111 mg (50%) of the title compound as a colourless solid: **mp** (decomp) 383-384 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 7.8 Hz, 1H), 8.45 (dd, *J* = 10.3, 2.3 Hz, 1H), 7.50 (app td, *J* = 7.7, 1.0 Hz, 1H), 7.31 (dd, *J* = 7.4, 2.8 Hz, 4H), 7.20-7.11 (m, 5H), 7.10-7.03 (m, 4H), 6.94-6.88 (m, 4H), 6.83 (app td, *J* = 8.5, 2.3 Hz, 1H), 6.61 (d, *J* = 7.6

Hz, 1H), 6.54 (dd, J = 8.4, 5.4 Hz, 1H), 5.79-5.69 (m, 4H), 5.60-5.51 (m, 4H), 3.48 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.5 (d, ^{1}J = 242 Hz), 156.4 (2C), 150.6, 148.7 (2C), 148.2 (2C), 148.0, 147.4, 148.8, 143.1 (d, ^{3}J = 8.5 Hz), 142.1 (2C), 142.0 (2C), 141.1, 140.3, 139.7, 136.7, 135.5 (d, ^{4}J = 2.5 Hz), 130.5 (2C), 130.4 (2C), 128.6, 128.5, 127.8, 127.4, 127.2 (2C), 127.1 (4C), 127.0 (2C), 124.2, 123.7 (2C), 123.6 (2C), 123.3, 119.8 (2C), 119.7 (2C), 125.0 (d, ^{3}J = 9.0 Hz), 114.3 (d, ^{2}J = 24.1 Hz), 111.1 (4C), 110.5 (d, ^{2}J = 25.6 Hz), 66.23, 65.61, 54.9 (2C); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.17-(-116.07) (m); **IR** (KBr) ν_{max} 3037, 2951, 2933, 2910, 2906, 2827, 1610, 1518, 1508, 1473, 1460, 1446, 1416, 1284, 1259, 1246, 1174, 1034, 835, 827, 810, 779, 766, 754, 741cm^{-1}; **HRMS** (ESI) *m/z* for $C_{58}H_{37}O_2FNa$ $[M+Na]^+$ calcd: 807.26698, found: 807.26712; ***R$_f$*** (2/1 CH_2Cl_2/hexanes) = 0.58.

3'-Fluoro-6',7'-bis(4-methoxyphenyl)dispiro[fluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene] (20c) With **18c** (672 mg, 1.31 mmol) according to the general procedure. Column chromatography of the residue on silica gel (5/1 hexanes/EtOAc for the first reaction and 1/1 CH_2Cl_2/hexanes for the second reaction) followed by sonication of the obtained solid with CH_3CN, decantation and filtration, provided 890 mg (89%) of the title compound as a colourless solid: **mp** (decomp) 369 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.83-8.61 (m, 2H), 7.49 (app t, J = 7.3 Hz, 1H), 7.33 (d, J = 7.6 Hz, 4H), 7.22-7.04 (m, 10H), 6.93 (app t, J = 7.0 Hz, 4H), 6.62 (d, J = 7.6 Hz, 1H), 6.30 (dd, J = 8.6, 2.4 Hz, 1H), 5.75 (d, J = 8.3 Hz, 4H), 5.58 (d, J = 8.8 Hz, 4H), 3.48 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2 (d, ^{1}J = 247 Hz), 156.3 (2C), 156.2 (2C), 153.0 (d, ^{3}J = 7.9 Hz), 150.5, 148.8 (2C), 148.2 (2C), 147.3, 147.11, 147.08, 142.1, 141.9 (2C), 141.2, 139.6, 139.4, 137.4 (d, ^{5}J = 2.4 Hz), 136.0, 135.5, 130.49 (2C), 130.47 (2C), 128.6 (d, ^{4}J = 5.0 Hz), 127.6, 127.2 (2C), 127.16 (2C), 127.1 (2C), 127.0 (2C), 124.5 (d, ^{3}J = 7.8 Hz), 124.1, 123.7 (4C), 123.1, 119.8 (2C), 119.7 (2C), 114.2 (d, ^{2}J = 22.8 Hz), 111.2 (d, ^{2}J = 25 Hz), 111.1 (4C), 66.2 (2C), 54.9 (2C); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.81 (app td, J_{F-H} = 8.2, 5.4 Hz, 1F); **IR** (KBr) ν_{max} 3064, 3041, 3003, 2960, 2929, 2833, 1608, 1591, 1518, 1475, 1466, 1448, 1419, 1363, 1281, 1263, 1244, 1176, 1030, 984, 829, 752, 741, 731 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{58}H_{38}O_2F$ $[M+H]^+$ calcd: 785.28504, found: 785.28498; ***R$_f$*** (1/1 hexanes/CH_2Cl_2) = 0.36.

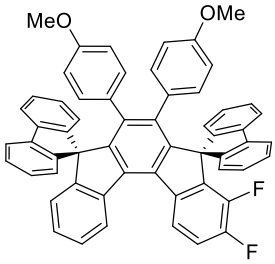
4'-Fluoro-6',7'-bis(4-methoxyphenyl)dispiro[fluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene] (20d). 

With **18d** (718 mg, 1.40 mmol) according to the general procedure. Column chromatography of the residue on silica gel (4/1 hexanes/EtOAc for the first reaction and 1/1 CH_2Cl_2/hexanes for the second reaction), followed by sonication of the obtained solid with CH_3CN, decantation and filtration, provided 983 mg (89%) of the title compound as a colourless solid: **mp** (decomp) > 350 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 7.8 Hz, 1H), 8.59 (d, *J* = 7.8 Hz, 1H), 7.56-7.43 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 4H), 7.22-7.032 (m, 9H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 6.82 (app t, *J* = 8.8 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 5.81-5.69 (m, 4H), 5.61-5.43 (m, 4H), 3.49 (s, 3H), 3.48 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.5 (d, ^1J = 241 Hz), 156.2 (2C), 150.6, 148.7 (2C), 147.4, 147.3, 146.4 (2C), 144.5 (d, ^3J = 5.4 Hz), 142.4 (2C), 142.0 (2C), 141.1, 140.4, 139.6, 136.6, 135.9 (d, ^2J = 13.8 Hz), 135.5 (d, ^4J = 2.2 Hz), 130.41 (2C), 130.48 (2C), 129.2 (d, ^3J = 9.5 Hz), 128.5, 128.3, 127.7, 127.2, 127.1 (2C), 127.07 (2C), 127.0 (2C), 126.9 (2C), 124.1, 123.7 (2C), 123.4, 123.2 (2C), 119.8 (2C), 119.7 (2C), 119.2 (d, ^4J = 3.3 Hz), 114.8 (d, ^2J = 20.0 Hz), 111.2 (2C), 111.1 (2C), 66.2, 64.3, 54.9, 54.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.19 (dd, J_{F-H} = 9.5, 5.5 Hz, 1F); IR (KBr) ν_{max} 3064, 3014, 2958, 2935, 2835, 1612, 1585, 1518, 1475, 1464, 1446, 1417, 1365, 1304, 1284, 1244, 1217, 1173, 1107, 1036, 1007, 837, 827, 818, 781, 754, 742, 731 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{58}H_{38}O_2F$ $[M+H]^+$ calcd: 785.28504, found: 785.28555; ***R*$_f$** (2/1 CH_2Cl_2/ hexanes) = 0.42.

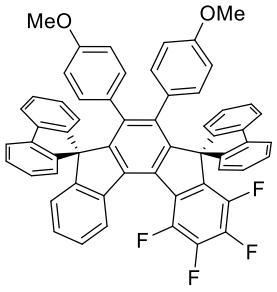
2',3'-Difluoro-6',7'-bis(4-methoxyphenyl)dispiro[fluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene] (20e). 

With **18e** (226 mg, 0.43 mmol) according to the general procedure. Column chromatography of the residue on silica gel (5/1 hexanes/EtOAc for the first reaction and 1/1 CH_2Cl_2/hexanes for the second reaction) followed by sonication of the obtained solid with CH_3CN, decantation and filtration, provided 137 mg (40%) of the title compound as a colourless solid: **mp** (decomp) 371-372 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 7.7 Hz, 1H), 8.58 (dd, *J* = 11.4, 7.1 Hz, 1H), 7.53 (app t, *J* = 7.6, 1H), 7.34 (app d, *J* = 7.6, 4H), 7.23-7.15 (m, 5H), 7.15-7.04 (m, 4H), 6.93 (dd, *J* = 11.1, 8.6 Hz, 4H), 6.56 (d, *J* = 7.8 Hz, 1H), 6.40 (dd, *J* = 9.6, 7.6 Hz, 1H), 5.79-5.74 (m, 4H), 5.61-5.55 (m, 4H), 3.50 (s, 3H); 3.49 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.4, 156.3, 148.9 (dd, $^{1,2}J$ = 258, 13.4 Hz), 148.8 (dd, $^{1,2}J$ = 247, 14.3 Hz), 150.5, 148.6 (2C), 147.9 (2C), 147.51 (m), 147.49, 146.8 (dd, $^{3,4}J$ = 5.2, 2.3 Hz), 142.1 (2C), 141.9 (2C), 140.9, 140.0, 139.7, 137.5

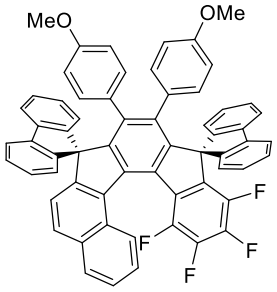
(dd, $^{3,4}J$ = 6.9, 2.9 Hz), 136.3, 134.8, 130.42 (2C), 130.39 (2C), 128.5, 128.4, 127.9, 127.4, 127.3 (2C), 127.2 (2C), 127.11 (2C), 127.07 (2C), 124.3, 123.7 (2C), 123.6 (2C), 123.0, 119.9 (2C), 119.7 (2C), 112.8 (d, ^{2}J = 18.3 Hz), 112.1 (d, ^{2}J = 20.3 Hz), 111.1 (4C), 66.2, 65.9, 54.9 (2C); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -138.89-(-138.44) (m, 1F), -140.05-(-139.40) (m, 1F); **IR** (KBr) ν_{max} 3091, 3080, 2951, 2933, 2906, 2827, 1610, 1516, 1508, 1485, 1448, 1417, 1362, 1286, 1244, 1174, 1038, 837, 752, 741 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{58}H_{37}O_2F_2$ $[M+H]^+$ calcd: 803.27561, found: 803.27520; ***R*$_f$** (3/1 pentane/$CHCl_3$) = 0.45.

3',4'-Difluoro-6',7'-bis(4-methoxyphenyl)dispiro[fluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene] (20f). 

With **18f** (562 mg, 1.06 mmol) according to the general procedure. Column chromatography (5/1 hexanes/EtOAc for the first reaction and 1/3 pentane/$CHCl_3$ for the second reaction) followed by sonication of the obtained solid with CH_3CN, decantation and filtration, provided 489 mg (57%) of the title compound as a colourless solid: **mp** (decomp) 370 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 7.6 Hz, 1H), 8.51 (dd, *J* = 8.5, 3.5 Hz, 1H), 7.50 (app t, *J* = 7.5, 1H), 7.39-7.30 (m, 5H), 7.25-7.05 (m, 9H), 7.05-6.97 (m, 2H), 6.96-6.87 (m, 2H), 6.64 (d, *J* = 7.5 Hz, 1H), 5.82-5.72 (m, 4H), 5.61-5.51 (m, 4H), 3.51 (s, 3H); 3.50 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.33, 156.31, 150.6, 149.9 (dd, $^{1,2}J$ = 250, 11.7 Hz), 148.6 (2C), 147.6, 147.3, 146.9 (dd, $^{1,2}J$ = 245, 14.1 Hz), 145.9 (2C), 142.4 (2C), 142.1 (2C), 141.0, 140.2, 139.7, 139.3 (m), 138.6 (d, ^{3}J = 10.6 Hz), 136.4, 134.8, 130.4 (4C), 128.4, 128.1, 127.9, 127.4 (2C), 127.2, 127.1 (2C), 127.0 (4C), 124.3, 123.7 (2C), 123.3 (2C), 123.1, 119.9 (2C), 119.7 (2C), 118.8 (m), 116.4 (d, ^{2}J = 18.3 Hz), 111.2 (2C), 111.1 (2C), 66.2, 64.6, 54.93, 54.91; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.45-(-139.75) (m), -143.55-(-143.85) (m); **IR** (KBr) ν_{max} 3040, 3001, 2959, 2932, 2908, 2827, 1610, 1571, 1506, 1467, 1449, 1416, 1371, 1281, 1245, 1174, 1114, 1039, 1006, 863, 836, 803, 755, 743, 728, 561 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{58}H_{37}O_2F_2$ $[M+H]^+$ calcd: 803.27561, found: 803.27504; ***R*$_f$** (1/3 pentane/$CHCl_3$) = 0.36.

1',2',3',4'-Tetrafluoro-6',7'-bis(4-methoxyphenyl)dispiro[fluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene] (20g). 

With **18g** (460 mg, 0.81 mmol) according to the general procedure. Column chromatography of the residue on silica gel (7/1 to 5/1 hexanes/EtOAc for the first reaction and 1/3 pentane/CH_3Cl for the second reaction) followed by sonication of the obtained solid with CH_3CN, decantation and filtration, provided 415 mg (61%) of the title compound as a colourless solid: **mp** (decomp) 380-381 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.16-8.03 (m, 1H), 7.55-7.43 (m, 1H), 7.31-7.40 (m, 4H), 7.26-7.11 (m, 7H), 7.11-7.05 (m, 2H), 7.04-6.97 (m, 2H), 6.96-6.89 (m, 2H), 6.65-6.55 (m, 1H), 5.81-5.73 (m, 4H), 5.61-5.48 (m, 4H), 3.51 (s, 3H); 3.50 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.5, 156.4, 150.3, 148.3 (2C), 148.2, 146.6, 145.2 (2C), 143.0 (app dm, J = ~260 Hz), 142.3 (2C), 142.1 (2C), 141.6 (app dm, J = ~260 Hz), 141.1, 140.8, 140.0 (app dm, J = ~260 Hz), 139.7 (app dm, J = ~260 Hz), 139.0, 137.0, 132.0 (d, ^3J = 12.4 Hz), 130.4 (2C), 130.3 (2C), 128.8, 128.1, 127.9, 127.7 (2C), 127.6, 127.2 (2C), 127.1 (4C), 126.9, 125.2 (d, ^2J = 12.9 Hz), 124.7 (d, ^2J = 20.3), 123.7 (2C), 123.4, 123.2 (2C), 121.1 (2C), 119.8 (2C), 111.3 (2C), 111.2 (2C), 66.2, 64.9, 54.92 (2C). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -128.50-(-128.80) (m), -145.40-(-145.70) (m), -157.35-(-157.70) (m, 2F); **IR** (KBr) ν_{max} 3061, 3037, 2980, 2953, 2931, 2910, 2895, 2829, 1610, 1516, 1508, 1489, 1448, 1421, 1362, 1284, 1248, 1238, 1174, 1107, 1093, 1072, 1038, 1003, 995, 958, 935, 912, 847, 831, 818, 795, 771, 754, 741, 727, 613, 555 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{58}H_{35}O_2F_4$ $[M+H]^+$ calcd: 839.25677, found: 839.25578; ***R*$_f$** (1/3 pentane/$CHCl_3$) = 0.36.

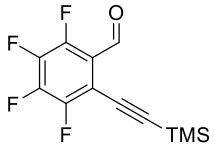
1',2',3',4'-Tetrafluoro-6',7'-bis(4-methoxyphenyl)dispiro[fluorene-9,5'-benzo[*c*]indeno[1,2-*g*]fluorene-8',9''-fluorene] (21) 

With **19** (79.9 mg, 0.13 mmol) following the general procedure. Column chromatography of the residue on silica gel (1/4 hexanes/EtOAc for the first reaction and 1/1 to 1/2 hexanes/CH_2Cl_2 for the second reaction) followed by sonication of the obtained solid with CH_3CN, decantation and filtration, provided 62 mg (53%) of the title compound as a colourless solid: **mp** (decomp) 325-326 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.41-8.28 (m, 1H), 7.99-7.89 (m, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.61-7.54 (m, 2H), 7.47 (app t, J = 7.0 Hz, 2H), 7.36 (app t, J = 6.7 Hz, 2H), 7.32 (app t, J = 7.6 Hz, 1H), 7.28 (d, J = 7.6 Hz, 3H), 7.20 (app t, J = 7.3 Hz, 1H), 7.17-7.10 (m, 2H), 7.05 (app t, J = 7.5 Hz, 2H), 6.92-6.83 (m, 2H), 6.69 (d, J = 8.2 Hz, 1H), 6.60 (d, J = 7.6 Hz, 1H), 5.91-5.983 (m, 2H), 5.77-5.70 (m, 2H), 5.64-5.58 (m,

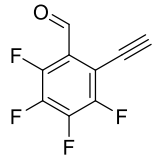
3H), 5.56 (dd, J = 8.4, 1.6 Hz, 1H), 3.51 (s, 3H), 3.50 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.6, 156.5, 148.8, 148.1, 147.3, 146.9, 146.6, 145.4, 145.1, 142.8, 142.5, 142.9 (dd, $^{1,2}J_{C\text{-}F}$ = 252, 10.7 Hz), 141.95, 141.91, 141.3 (dd, $^{1,2}J_{C\text{-}F}$ = 256, 10.7 Hz), 141.0 (app dt, $^{1,2}J_{C\text{-}F}$ = 250, 14.3 Hz), 140.0, 139.8 (app dt, $^{1,2}J_{C\text{-}F}$ = 253, 13.1 Hz), 138.2, 137.6, 137.4, 133.5, 131.2, 131.0 (d, $^{3}J_{C\text{-}F}$ = 13.1 Hz), 130.9, 130.0 (d, $^{4}J_{C\text{-}F}$ = 6.0 Hz), 129.8, 129.62, 129.59, 128.7, 128.0, 127.62, 127.60, 127.5, 127.2, 127.1, 126.9, 125.4, 125.21, 125.18, 123.8, 123.5, 123.0, 121.3, 120.4, 120.2, 119.8, 119.5, 111.6 (d, $^{2}J_{C\text{-}F}$ = 20.3 Hz), 111.1 (d, $^{2}J_{C\text{-}F}$ = 17.9 Hz), 66.8, 65.2, 54.9 (2C); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -127.77 (app t, $J_{F\text{-}F}$ = 19.1 Hz, 1F), -145.87 (dd, $J_{F\text{-}F}$ = 20.4, 15.7 Hz, 1F), -157.42 (app t, $J_{F\text{-}F}$ = 19.8 Hz, 1F), -157.87 (app t, J = 19.8 Hz, 1F); **IR** (KBr) ν_{max} 3060, 2959, 2920, 2837, 2332, 1875, 1610, 1509, 1489, 1417, 1279, 1245, 1173, 1076, 1036, 995, 915, 844, 821, 754, 737, 617, 553, 424 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{62}H_{37}O_2F_4$ $[M+H]^+$ calcd: 889.27242, found: 889.27266; ***R*$_f$** (1/1 hexanes/CH_2Cl_2) = 0.24.

5.3.4 Synthesis of octafluorinated indenofluorene 20h

2,3,4,5-Tetrafluoro-6-((trimethylsilyl)ethynyl)benzaldehyde (22). With 2,3,4,5-tetrafluoro-6-iodobenzaldehyde **11g** (3.0 g, 9.87 mmol) following the general Sonogashira cross coupling procedure (see Section 5.3.1). Column chromatography of the residue on silica gel (5/1 to 4/1 hexanes/CH_2Cl_2) yielded 2.29 g (84%) of the title compound as a yellow liquid: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.38 (s, 1H), 0.29 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.7 (br s), 148.8 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 255, 10.8, 4.0, 1.2 Hz), 147.5 (app ddt, $^{1,2,3}J_{C\text{-}F}$ = 266, 10.8, 3.3 Hz), 144.0 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 263, 16.8, 12.9, 4.4 Hz), 140.9 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 261, 15.8, 12.7, 2.8 Hz), 120.6 (dd, $^{2,3}J_{C\text{-}F}$ = 6.1, 3.8 Hz), 111.6 (dd, $^{3,4}J_{C\text{-}F}$ = 4.8, 2.8 Hz), 111.1 (app dm, $^{2}J_{C\text{-}F}$ = 16.0 Hz), 90.1 (app q, $^{4}J_{C\text{-}F}$ = 3.4 Hz), -0.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -134.58 (ddd, $J_{F\text{-}F}$ = 21.1, 12.9, 4.8 Hz, 1F), -143.38-(-143.16) (m, 1F), -146.90 (ddd, $J_{F\text{-}F}$ = 21.8, 20.4, 9.5 Hz, 1F), -153.23 (t, $J_{F\text{-}F}$ = 19.8 Hz, 1F); **IR** (KBr) ν_{max} 2965, 2902, 2854, 2753, 2161, 1712, 1628, 1509, 1479, 1398, 1371, 1308, 1251, 1150, 1120, 994, 943, 931, 851, 761, 701, 677, 629; **HRMS** (EI) *m/z* for $C_{12}H_{10}OF_4Si$ $[M]^+$ calcd: 274.0437, found: 274.0436. ***R*$_f$** (5/1 hexanes/CH_2Cl_2) = 0.11.

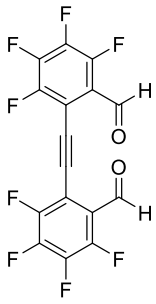


2-Ethynyl-3,4,5,6-tetrafluorobenzaldehyde (23). A one-neck flask was filled up with 2,3,4,5-tetrafluoro-6-((trimethylsilyl)ethynyl)benzaldehyde **22** (0.30 g, 1.07 mmol), MeOH (5.5 mL) and KF (0.22 g, 3.87 mmol). The reaction mixture was stirred for 4 h at 20 °C under atmospheric conditions, then it was extracted with CH_2Cl_2



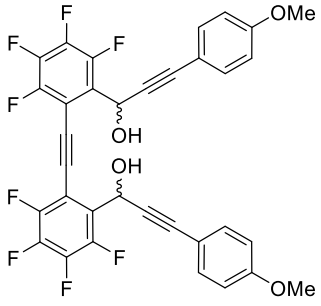
(3×20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography of the residue on silica gel (5/1 to 4/1 hexanes/CH_2Cl_2) yielded 0.19 g (86%) of the title compound as a pale yellow solid: **mp** (decomp) 74-76 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 3.78 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.0-184.8 (m), 149.5 (dddd, $^{1,2,3}J_{C\text{-}F}$ = 257, 11.2, 4.1, 1.2 Hz), 148.2 (app ddt, $^{1,2,3}J_{C\text{-}F}$ = 269, 11.0, 3.5 Hz), 144.1 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 280, 17.1, 13.2, 2.5 Hz), 141.2 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 261, 15.7, 12.1, 2.9 Hz), 120.7 (dd, $^{2,3}J_{C\text{-}F}$ = 6.7, 3.8 Hz), 109.2 (dm, $^{2}J_{C\text{-}F}$ = 14.4 Hz), 91.6 (dd, $^{3}J_{C\text{-}F}$ = 5.9, 3.0 Hz), 70.4 (app q, $^{4}J_{C\text{-}F}$ = 3.6 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -134.11 (m, 1F), -143.58 (ddd, $J_{F\text{-}F}$ = 21.1, 12.3, 9.5 Hz, 1F), -146.21 (app td, $J_{F\text{-}F}$ = 20.4, 9.5 Hz, 1F), -152.09 (app td, $J_{F\text{-}F}$ = 19.9, 3.7 Hz, 1F); **IR** (KBr) ν_{max} 3267, 2959, 2929, 2893, 2848, 2122, 1703, 1628, 1586, 1562, 1518, 1476, 1404, 1374, 1311, 1278, 1260, 1147, 1114, 994, 970, 943, 806, 695, 671, 632, 561, 492, 438; **HRMS** (EI) *m/z* for $C_9H_2OF_4$ $[M]^+$ calcd: 202.0042, found: 202.0043; ***R_f*** (5/1 hexanes/CH_2Cl_2) = 0.16

6,6'-(Ethyne-1,2-diyl)bis(2,3,4,5-tetrafluorobenzaldehyde) (12h). In three-neck flask under

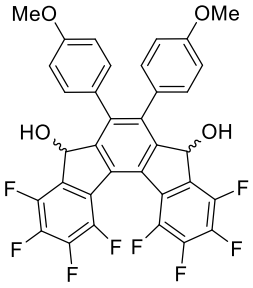


argon 2,3,4,5-tetrafluoro-6-((trimethylsilyl)ethynyl)benzaldehyde (**22**) (1.08 g, 3.9 mmol) and 2,3,4,5-tetrafluoro-6-iodobenzaldehyde (**11g**) (1.00 g, 3.3 mmol) were dissolved in a degassed mixture of 1/1 toluene/water (60 ml); $PdCl_2(PhCN)_2$ (63 mg, 0.165 mmol), CuI (63 mg, 0.33 mmol), P(2-furyl)$_3$ (76 mg, 0.33 mmol), CsF (2.01 g, 13.2 mmol), Bu_4NI (1.22 g, 3.3 mmol) were added and the reaction was carried out at 60 °C for 16 h. After cooling down to room temperature, the work-up was performed by addition of saturated aqueous NH_4Cl solution. The resulting mixture was extracted with AcOEt (3x100 mL), the combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (1/1 hexanes/CH_2Cl_2) provided 1.01 g (79%) of the title compound as a colourless solid: **mp** (decomp) 103-106 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.51 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.01-184.73 (m), 149.2 (ddd, $^{1,2,3}J_{C\text{-}F}$ = 257, 7.6, 3.4 Hz), 149.0 (app ddt, $^{1,2,3}J_{C\text{-}F}$ = 263, 10.9, 3.7 Hz), 144.3 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 255, 17.0, 13.0, 4.5 Hz), 141.6 (dddd, $^{1,2,3,4}J_{C\text{-}F}$ = 253, 17.9, 13.3, 3.1 Hz), 120.9-120.4 (m), 108.3 (app dm, $^{2}J_{C\text{-}F}$ =13.1 Hz), 89.5-89.1 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -132.95-(-132.63) (m, 2F), -144.18-(-144.29) (m, 2F), -146.06 (app td, $J_{F\text{-}F}$ = 19.9, 9.2 Hz, 2F), -150.70 (app t, $J_{F\text{-}F}$ = 20.4 Hz, 2F); **IR** (KBr) ν_{max} 2965, 2896, 2872, 2786, 2220, 1709, 1619, 1586, 1556, 1512, 1476, 1410, 1359, 1350, 1320, 1302, 1281, 1263, 1177, 1141, 1093, 1018, 973, 940, 878, 803, 635,

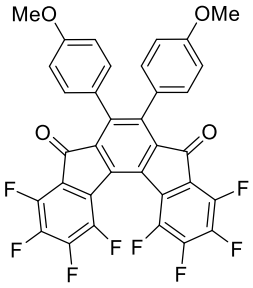
600; **HRMS** (EI) *m/z* for $C_{16}H_2O_2F_8$ $[M]^+$ calcd: 377.9927, found: 377.9925; ***R_f*** (1/1 hexanes/CH_2Cl_2) = 0.21

1,1'-(Ethyne-1,2-diylbis(3,4,5,6-tetrafluoro-2,1-phenylene))bis(3-(4-methoxyphenyl)-prop-2-yn-1-ol) (14h). 

A dried vial was filled up with anhydrous CH_2Cl_2 (6.5 mL), 1-ethynyl-4-methoxybenzene (0.67 mL, 5.15 mmol), HMPA (0.60 mL, 3.43 mmol) and Et_2Zn (3.9 mL, 4.29 mmol) under argon. The vial was sealed with a cap and heated overnight at 40°C. Afterwards 6,6'-(ethyne-1,2-diyl)bis(2,3,4,5-tetrafluorobenzaldehyde) (**12h**) (0.311 g, 0.822 mmol) in CH_2Cl_2 (6.5 mL) was added under argon and the reaction mixture was stirred at 20°C. After completion of reaction, a saturated aqueous NH_4Cl solution was poured, the resulting mixture was extracted with CH_2Cl_2 (3×30 mL) and the combined organic layers were dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the crude was purified with column chromatography on silica gel (4/1 hexanes/AcOEt), yielding 482 mg (91%) of an inseparable mixture of two diastereoisomers as a pale yellow solid: **mp** (decomp) 67-68 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (mixture) δ 7.36-7.15 (m, 4H), 6.73 (d, J = 8.6 Hz, 4H), 6.18 (s, 2H), 4.22 (br s, 1H), 3.91-3.57 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) (mixture) δ 160.0, 148.7 (dd, $^{1,2}J_{C\text{-}F}$ = 254, 11.6 Hz), 145.1 (dd, $^{1,2}J_{C\text{-}F}$ = 251, 10.8 Hz), 141.4 (dt, $^{1,2}J_{C\text{-}F}$ = 261, 15.4 Hz), 140.3 (d, $^{1,2}J_{C\text{-}F}$ = 255, 17.2 Hz), 133.3, 126.9 (dd, $^{2,3}J_{C\text{-}F}$ = 11.9, 3.5 Hz), 113.8, 113.6, 106.3 (d, $^{2,3}J_{C\text{-}F}$ = 14.6 Hz), 90.0 (br s), 87.2, 84.5, 77.2, 58.5 (br s), 57.6 (d, $^{3}J_{C\text{-}F}$ = 4.6 Hz), 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) (mixture) δ -133.78 (ddd, $J_{F\text{-}F}$ = 21.1, 10.9, 3.4 Hz, 2F), -143.14 (ddd, $J_{F\text{-}F}$ = 21.1, 10.9, 2.7 Hz, 2F), -151.92 (td, $J_{F\text{-}F}$ = 21.1, 4.1 Hz, 2F), -155.66 (td, $J_{F\text{-}F}$ = 20.4, 3.4 Hz, 2F); **IR** (KBr) ν_{max} 3330, 3010, 2962, 2935, 2911, 2899, 2839, 2226, 1631, 1607, 1568, 1512, 1476, 1425, 1368, 1335, 1290, 1251, 1174, 1126, 1087, 1033, 1006, 931, 911, 872, 833, 809, 785; **HRMS** (ESI) *m/z* for $C_{34}H_{18}O_4F_8Na$ $[M+Na]^+$ calcd: 665.09696, found: 665.09687; ***R_f*** (4/1 hexanes/AcOEt) = 0.15.

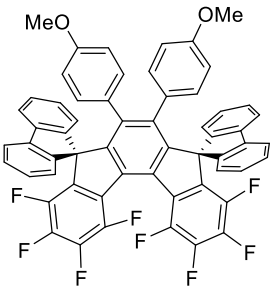
1,2,3,4,9,10,11,12-Octafluoro-6,7-bis(4-methoxyphenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (16h). 

With 1,1'-(ethyne-1,2-diylbis(3,4,5,6-tetrafluoro-2,1-phenylene))bis(3-(4-methoxyphenyl)prop-2-yn-1-ol) (**14h**) (161 mg, 0.25 mmol) according to the general cyclotrimerization procedure described in Section 5.3.2. Column chromatography on silica gel (60/1 to 20/1 CH_2Cl_2/AcOEt) yielded 94.4 mg (58%) of an inseparable mixture of two diastereoisomers as pale yellow solid: **mp** (decomp) 168-169 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (mixture) δ 7.80-6.40 (br m, 8H), 7.40-5.70 (br m, 2H), 3.79 (s, 6H), 1.88-2.25 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) (mixture) δ 158.9, 146.2 (d, $^1J_{C\text{-}F}$ = 249 Hz), 145.2 (d, $^1J_{C\text{-}F}$ = 242 Hz), 144.3 (d, $^1J_{C\text{-}F}$ = 256 Hz), 141.8 (dd, $^{2,3}J_{C\text{-}F}$ = 17.7, 11.6 Hz), 140.5 (br s), 139.9, 139.3 (d, $^2J_{C\text{-}F}$ = 15.4 Hz), 140.3 (d, $^1J_{C\text{-}F}$ = 235 Hz), 137.9 (br s), 131.4 (br s), 130.7 (br s), 129.6 (br s), 129.1 (br s), 128.2 (br s), 126.6 (br s), 126.0 (br s), 124.0 (br s), 114.2, 73.9, 71.8, 55.1; **^{19}F NMR** (376 MHz, $CDCl_3$) (major) δ -135.89 (br s, 2F), -144.52 (br s, 2F), -155.32 (br s, 2F), -155.68 (br s, 2F); (minor) -134.52 (br s, 2F), -143.72 (br s, 2F), -153.40 (br s, 2F), -154.93 (br s, 2F); **IR** (KBr) ν_{max} 3461, 3031, 2998, 2956, 2932, 2905, 2839, 1721, 1610, 1574, 1515, 1485, 1464, 1431, 1404, 1362, 1323, 1308, 1293, 1245, 1180, 1135, 1120, 1051, 1033, 970, 949, 842, 797, 782, 767, 623, 579, 537; **HRMS** (ESI) *m/z* for $C_{34}H_{18}O_4F_8Na$ $[M+Na]^+$ calcd: 665.09696, found: 665.09706; ***R*$_f$** (CH_2Cl_2) = 0.14.

1,2,3,4,9,10,11,12-Octafluoro-6,7-bis(4-methoxyphenyl)indeno[2,1-*c*]fluorene-5,8-dione (18h). 

With 1,2,3,4,9,10,11,12-octafluoro-6,7-bis(4-methoxyphenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (**16h**) (263 mg, 0.41 mmol) according to the oxidation procedure described in Section 5.3.3. Column chromatography on silica gel (3/1 hexanes/CH_2Cl_2) yielded 140 mg (54%) of the title compound as a violet solid: **mp** (decomp) 126,8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14-6.41 (m, 8H), 3.79 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 184.3, 159.4, 145.6 (app dm, $^1J_{C\text{-}F}$ = 261 Hz), 145.1 (dd, $^{1,2}J_{C\text{-}F}$ = 267, 10.7 Hz), 144.7, 143.1 (app dt, $^{1,2}J_{C\text{-}F}$ = 272, 15.0 Hz), 141.8 (app dt, $^{1,2}J_{C\text{-}F}$ = 261, 14.8 Hz), 136.5, 133.6, 131.2, 130.7, 125.2, 117.0 (d, $^2J_{C\text{-}F}$ = 10.7 Hz), 113.3, 55.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -132.56 (br s, 2F), -139.59-(-138.14) (m, 2F), -144.78-(-144.02) (m, 2F), -151.23 (app t, $J_{F\text{-}F}$ = 18.7 Hz, 2F); **IR** (KBr) ν_{max} 3070, 3031, 2980, 2932, 2908, 2836, 2549, 1730, 1631, 1607, 1580, 1503, 1491, 1467, 1422, 1389, 1338, 1320, 1290, 1254, 1180, 1141, 1120, 1033, 967, 863, 821, 791, 734, 701, 683, 606, 564, 534; **HRMS** (ESI) *m/z* for $C_{34}H_{14}O_4F_8Na$ $[M+Na]^+$ calcd: 661.06566, found: 661.06524; ***R*$_f$** (3/1 hexanes/CH_2Cl_2) = 0.52.

1',2',3',4',9',10',11',12'-Octafluoro-6',7'-bis(4-methoxyphenyl)dispiro[fluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene] (20h).



With 1,2,3,4,9,10,11,12-octafluoro-6,7-bis(4-methoxyphenyl)indeno[2,1-*c*]fluorene-5,8-dione (**18h**) (76 mg, 0.12 mmol), arylation was carried out according to procedure described in Section 5.3.3. However, the intramolecular spirocyclization was performed as described below. In one neck flask diols intermediate (83.4 mg, 0.088 mmol) and CH_2Cl_2 (38 mL) were added, followed by $BF_3{\cdot}Et_2O$ (0.26 mmol, 33 μL). The resulting mixture was stirred for 2 h under reflux. After evaporation under reduced pressure, column chromatography of the residue on silica gel (5/1 hexanes/EtOAc for the first reaction and 1/1.5 CH_2Cl_2/hexanes for the second reaction) yielded 64 mg (58%) of the title compound as a colourless solid: **mp** (decomp) 200-202 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.6 Hz, 2H), 7.32 (app td, J = 7.3, 1.0 Hz, 2H), 7.27-7.25 (m, 3H), 7.21 (app t, J = 8.3 Hz, 3H), 7.12 (app t, J = 7.1 Hz, 2H), 7.04 (app t, J = 7.6 Hz, 2H), 6.78 (d, J = 7.6 Hz, 2H), 5.88-5.81 (m, 2H), 5.77-5.68 (m, 2H), 5.50-5.45 (m, 4H), 3.49 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.7, 147.3, 144.6, 144.4, 142.9 (app dd, $^{1,2}J_{C\text{-}F}$ = 252, 11.7 Hz), 142.6 (dm, $^1J_{C\text{-}F}$ = ~260 Hz), 142.5, 141.9, 140.4, 141.1 (dm, $^1J_{C\text{-}F}$ = ~260 Hz), 140.4 (app dt, $^{1,2}J_{C\text{-}F}$ = 256, 15.1 Hz), 131.2 (d, $^3J_{C\text{-}F}$ = 12.2 Hz), 130.9, 130.8, 129.4, 128.1, 127.7, 127.3, 127.2, 126.9, 125.4 (br s), 123.5, 122.9, 120.4, 119.9, 111.7, 111.2, 65.4, 54.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -135.47 (br s, 2F), -146.09-(-144.69) (m, 2F), -156.54 (app t, $J_{F\text{-}F}$ = 19.8 Hz, 2F), -157.48-(-157.58) (m, 2F); **IR** (KBr) ν_{max} 3061, 3040, 2959, 2923, 2851, 1610, 1574, 1518, 1485, 1443, 1425, 1395, 1353, 1317, 1287, 1263, 1245, 1180, 1099, 1021, 976, 863, 848, 800, 737, 677, 546; **HRMS** (ESI) *m/z* for $C_{58}H_{30}O_2F_8Na$ $[M+Na]^+$ calcd: 933.20103, found: 933.20093; R_f (1/1 hexanes/CH_2Cl_2) = 0.54.

5.4 Synthesis of unsymmetrical fluorinated [6] and [7]helical dihydroindenofluorenes.

5.4.1 Preparation of starting materials: triynediols

1-(Naphthalen-1-yl)cyclobutan-1-ol (viii). A dried three-neck flask was charged with Mg turnings (0.46 g, 18.9 mmol) under argon. Few drops of pure 1-bromonaphthalene were used to initiate the reaction. When reaction started, 1-bromonaphtalene (3.91 g, 18.9 mmol) in THF (15 mL) was added dropwise. Afterwards, the mixture was refluxed for 30 min. Then it was cooled down to 0 °C and cyclobutanone (1.20 g, 17.0 mmol) in THF (37 mL) was added by cannulation at the same low temperature. The reaction mixture was warmed up to room temperature and stirred overnight. The quench was made with saturated aqueous NH_4Cl solution and the resulting mixture was extracted with AcOEt (4 × 100 mL); the combined organic phases were dried over $MgSO_4$. The solvent was removed by rotary evaporator and the resulting crude was purified by column chromatography on silica gel (8/1 hexanes/AcOEt). The procedure yielded 2.68 g (80%) of the title compound as a white solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 - 8.32 (m, 1H), 7.86 - 7.92 (m, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.48 - 7.55 (m, 3H), 7.44 (dd, *J* = 8.1, 7.1 Hz, 1H), 2.80 - 2.92 (m, 2H), 2.63 (m, 2H), 2.23 (br s, 1H), 2.10 - 2.20 (m, 1H), 1.62 - 1.78 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.3, 134.7, 130.8, 128.9, 128.7, 126.2, 125.7, 125.6, 124.8, 122.9, 78.5, 36.6, 14.5. The spectral data were in accordance with the previously published results.[156]

2,3-Dihydrophenanthren-4(1*H*)-one (ix). In a one-neck flask, 1-(naphthalen-1-yl)cyclobutan-1-ol (**viii**) (2.68 g, 13.5 mmol) and H_2O/CH_3CN (80 mL:80 mL) were added. The mixture was cooled down to 0 °C and stirred for 10 min. Afterwards, CAN (18.5 g, 33.7 mmol) was added and the reaction was stirred at the same low temperature for 60 s. Then saturated aqueous $Na_2S_2O_3$ solution (80 mL) was poured in the flask and the resulting mixture was extracted by AcOEt (3×100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Column chromatography of the residue on silica gel (8/1 hexanes/AcOEt) yielded 1.50 g (56%) of the title compound as a pale yellow solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.42 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.63 (app t, *J* = 8.6 Hz, 1H), 7.49 (app t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 3.12 (t, *J* = 6.1 Hz, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 2.09 - 2.25 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.4, 146.7, 134.2, 132.8, 131.4, 128.8, 128.2,

127.3, 126.9, 126.7, 125.8, 41.1, 31.6, 23.0. The spectral data were in accordance with the previously published results.[138]

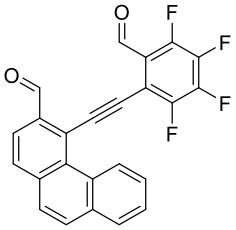
4-Bromo-1,2-dihydrophenanthrene-3-carbaldehyde (x). In a dried two-neck flask with a solution of anhydrous DMF (1.35 mL, 17.4 mmol) and CH_2Cl_2 (20 mL), PBr_3 (1.42 mL, 14.9 mmol) was added dropwise at 0 °C under argon. After 1 hour stirring 2,3-dihydrophenanthren-4(1*H*)-one (**ix**) (0.975 g, 5.0 mmol) in CH_2Cl_2 was added at the same low temperature and the resulting mixture was refluxed for 4 h. Afterwards, the reaction was cooled down to 0 °C and $NaHCO_3$ (saturated solution) was added until the end of gas generation. The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic fractions were washed with distilled H_2O (100 mL) and dried over Na_2SO_4. After filtration and removal of the solvent, column chromatography of the residue on silica gel (11/1 hexanes/AcOEt) yielding 0.97 g (68%) of the title compound as a pale yellow viscous liquid: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.34 (s, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.59 (dd, *J* = 8.6, 6.9 Hz, 1H), 7.52 (dd, *J* = 7.9, 6.9 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 2.79 - 2.93 (m, 2H), 2.55 - 2.66 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.8, 140.9, 137.8, 135.6, 133.7, 131.8, 130.3, 130.1, 128.7, 126.3, 125.8, 125.7, 125.3, 29.7, 22.6. The spectral data were in accordance with the previously published results.[157]

4-Bromophenanthrene-3-carbaldehyde (xi). In a two-neck flask, 4-bromo-1,2-dihydrophenanthrene-3-carbaldehyde (**x**) (0.975 g, 3.39 mmol) was dissolved in dry toluene (10 mL) under argon. DDQ (2.31 g, 10.2 mmol) was added and the reaction was refluxed for 16 h. Afterwards hexanes was added and the resulting mixture was filtered and concentrated under reduced pressure. Column chromatography of the residue on silica gel (2/1 Hexanes/CH_2Cl_2) gave 0.673 g (70 % yield) of the title compound as yellow solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.68 (s, 1H), 9.66 - 9.74 (m, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.79 - 7.87 (m, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.59 - 7.65 (m, 2H), 7.49 (d, *J* = 8.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.1, 138.2, 133.8, 133.5, 131.0, 129.8, 129.1, 128.6, 128.4, 127.43, 127.36, 126.2, 125.9, 125.8, 125.4. The spectral data were in accordance with the previously published results.[158]

4-Ethynylphenanthrene-3-carbaldehyde (24). A two-neck flask was filled up with 4-bromophenanthrene-3-carbaldehyde (**xi**) (0.673 g, 2.36 mmol), CuI (15.7 mg, 3.5 mol%) and $PdCl_2(PPh_3)_2$ (49.7 mg, 3.0 mol%) under argon. Then triethylamine (1.6 mL, 11.8 mmol) and THF (9.4 mL) were added. Upon addition of trimethylsilylacetylene (0.400 mL, 2.83 mmol), the reaction was stirred for 3 h at reflux. The mixture was filtered through a pad of celite/silica gel, washed with CH_2Cl_2 and concentrated under reduced pressure. The crude product was used for the next step without purification. In one-neck flask, the crude was dissolved in MeOH (30 mL) and water (2.0 mL). After cooling down to 0°C, K_2CO_3 (0.652g, 4.7 mmol) was added and the resulting mixture was stirred for 1 h. After quenching by addition of HCl (2M), the reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL), the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography of the residue on silica gel (2/1 hexanes/CH_2Cl_2) provided product in 0.439 g (81% yield): **mp** (decomp) 135-145 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 10.28 - 10.41 (m, 1H), 8.14 (d, J = 8.3 Hz, 1H), 7.92 - 8.01 (m, 2H), 7.89 (d, J = 8.8 Hz, 1H), 7.65 - 7.78 (m, 3H), 4.15 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.0, 137.0, 136.5, 133.3, 131.1, 130.7, 130.5, 130.2, 128.8, 127.7, 126.9, 126.6, 126.5, 123.8, 92.2, 81.0; **IR** (KBr) ν_{max} 3228, 3066, 3055, 3043, 3020, 2960, 2925, 2875, 2785, 2765, 2085, 1942, 1923, 1828, 1774, 1678, 1608, 1587, 1556, 1520, 1452, 1427, 1381, 1321, 1304, 1259, 1219, 1203, 1171, 1151, 1099, 1066, 1041, 1018, 868, 847, 818, 806, 768, 741, 696, 677, 521 cm^{-1}; **HRMS** (EI) *m/z* for $C_{17}H_{10}O$ $[M]^+$ calcd: 230.0732, found: 230.0733; **R_f** (1/1 hexanes/EtOAc) = 0.43.

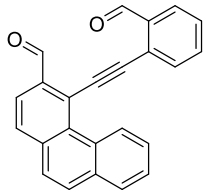
General procedure for Sonogashira reaction. Preparation of 26 and 31. In a two-neck round-bottom flask with reflux condenser, 2-bromobenzaldehyde or 2,3,4,5-tetrafluoro-6-iodobenzaldehyde **11g** (10.0 mmol), $PdCl_2(PPh_3)_2$ (210 mg, 0.3 mmol) and CuI (67 mg, 0.35 mmol) were added. Triethylamine (7.0 mL) and THF (40 mL) were also inserted in the same flask. After stirring for 2 min, 4-ethynylphenanthrene-3-carbaldehyde, **24**, (11.0-15.0 mmol) was added and the mixture was refluxed for 3 h. Upon completion of the reaction, the mixture was cooled down to room temperature, filtered off with celite/silica (3/1) and washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel.

4-((2,3,4,5-Tetrafluoro-6-formylphenyl)ethynyl)phenanthrene-3-carbaldehyde (25). With



4-ethynylphenanthrene-3-carbaldehyde (**24**) (506 mg, 2.2 mmol) and 2,3,4,5-tetrafluoro-6-iodobenzaldehyde (**11g**) (669 mg, 2.2 mmol) according to the general procedure. Column chromatography on silica gel (hexanes/CH_2Cl_2 1/1) yielded 706 mg (79%) of the title compound as a pale yellow solid: **mp** (decomp) 228.0 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 11.14 (s, 1H), 10.51 (br s, 1H), 10.23 (br s, 1H), 8.24 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 7.3 Hz, 1H), 7.90 - 8.02 (m, 2H), 7.77 (m, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.0 (d, $^3J_{C\text{-}F}$ = 3.6 Hz), 183.8 (br s), 149.8 (dm,$^1J_{C\text{-}F}$ = 257.5 Hz), 149.5 (dm, $^1J_{C\text{-}F}$ = 257.5 Hz), 144.4 (dm, $^1J_{C\text{-}F}$ = 264.6 Hz), 140.9 (dm, $^1J_{C\text{-}F}$ = 268.2 Hz), 137.2, 136.5, 133.4, 131.3, 131.1, 130.7, 130.3, 128.8, 128.0, 126.8, 126.7, 124.1, 121.6, 120.6 (d, $^2J_{C\text{-}F}$ = 3.6 Hz), 99.9 - 100.1 (m), 90.3 - 90.5 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -133.07 - (-132.71) (m, 1F), -145.23 (m, 1F), -145.59 (app td, $J_{F\text{-}F}$ = 20.4, 8.9 Hz, 1F), -151.80 (ddd, $J_{F\text{-}F}$ = 20.4, 19.1, 4.8 Hz, 1F); **IR** (KBr) ν_{max} 3055, 2959, 2917, 2872, 2175, 1703, 1682, 1616, 1589, 1509, 1473, 1422, 1392, 1362, 1317, 1284, 1251, 1228, 1204, 1180, 1132, 1105, 1042, 1009, 902, 866, 854, 803, 764, 743, 632 cm^{-1}; **HRMS** (EI) *m/z* for $C_{24}H_{10}O_2F_4$ $[M]^+$ calcd: 406.0617, found: 406.0625; ***R$_f$*** (1/1 hexanes/CH_2Cl_2) = 0.20.

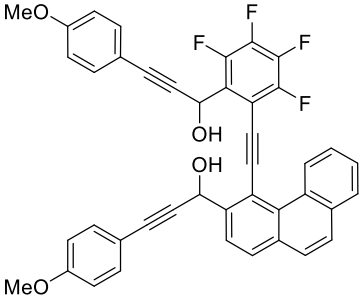
4-((2-Formylphenyl)ethynyl)phenanthrene-3-carbaldehyde (30). With 4-



ethynylphenanthrene-3-carbaldehyde (**24**) (1.57 g, 6.82 mmol) and 2-bromobenzaldehyde **29** (0.724 mL, 6.20 mmol) according to the general procedure. Column chromatography of the residue on silica gel (2/1 to 4/1 CH_2Cl_2/hexane), followed by second column chromatography on silica gel (5/1 to 3/2 hexanes/EtOAc) provided 1.78 g (86% yield) of the title compound as a pale yellow solid: **mp** (decomp) 125.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.85 (d, J = 1.0 Hz, 1H), 10.43 (d, J = 0.7 Hz, 1H), 9.90 - 10.01 (m, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.93 (dd, J = 7.9, 1.1 Hz, 1H), 7.78 - 7.82 (m, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.66 (dd, J = 1.0 Hz, 1H), 7.61 (dd, J = 1.0 Hz, 1H), 7.58 (dd, J = 2.2, 1.5 Hz, 1H), 7.53 - 7.57 (m, 2H), 7.48 - 7.53 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.0, 190.5, 136.2, 136.1, 136.0, 133.8, 133.3, 133.1, 130.8, 130.3, 130.0, 129.3, 128.70, 128.66, 127.6, 126.6, 126.4, 126.0, 124.8, 123.7, 122.5, 98.9, 93.3; **IR** (KBr) ν_{max} 3057, 2960, 2922, 2862, 2750, 2731, 2187, 1948, 1923, 1834, 1772, 1682, 1589, 1518, 1477, 255, 1194, 845, 761, 742, 664, 521 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{24}H_{15}O_2$ $[M+H]^+$ calcd: 335.10666, found: 335.10661; **R$_f$** (5/1 hexanes/EtOAc) = 0.31.

General procedure for alkynylation reaction. Preparation of 26 and 31. A Schlenk flask was filled up with 1-ethynyl-4-methoxybenzene (1.24 mL, 9.54 mmol) and anhydrous THF (20 mL). The solution was cooled down to -78 °C and stirred for 5 min. Afterwards *n*-BuLi 1.6 M in hexanes (6.0 mL, 9.54 mmol) was added dropwise. The resulting solution was stirred for 30 min at the same low temperature. Then dialdehyde **25** or **30** (2.73 mmol) in THF (50 mL) was added and the resulting mixture was stirred for 5 min at -78 °C and then at room temperature for 3 h. The reaction was quenched by saturated solution of NH_4Cl and extracted with diethyl ether (3×50 mL). The combined organic phases were washed with a saturated solution of $NaHCO_3$, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel afforded products.

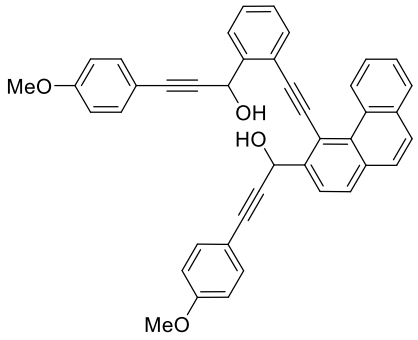
3-(4-Methoxyphenyl)-1-(2,3,4,5-tetrafluoro-6-((3-(1-hydroxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)phenanthren-4-yl)ethynyl)phenyl)prop-2-yn-1-ol (26).



With 4-((2,3,4,5-tetrafluoro-6-formylphenyl)ethynyl)phenanthrene-3-carbaldehyde (**25**) (489 mg, 1.20 mmol) according to the general procedure. Column chromatography on silica gel (5/1 to 1/1 hexanes/AcOEt) yielded 805 mg (92%) of an inseparable mixture of two diastereoisomers (1:1.5) as a pale yellow solid: **mp** (decomp) 148-150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) (mixture) δ 10.34 (d, *J* = 8.1 Hz, 1H), 10.26 (d, *J* = 7.8 Hz, 1H), 8.20 (d, *J* = 8.3 Hz, 2H), 7.95 - 8.01 (m, 2H), 7.89 - 7.95 (m, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.59 - 7.76 (m, 6H), 7.35 - 7.45 (m, 4H), 7.24 - 7.29 (m, 3H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.88 (s, 1H), 6.81 (d, *J* = 8.8 Hz, 4H), 6.64 - 6.71 (m, 2H), 6.46 (d, *J* = 9.0 Hz, 2H), 6.28 (br s, 1H), 6.23 (d, *J* = 5.6 Hz, 1H), 4.84 (br s, 1H), 4.19 (br s, 1H), 3.75 - 3.84 (m, 6H), 3.68 (s, 6H), 3.30 (br s, 1H), 3.04 (br s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) (mixture) δ 160.0, 159.94, 159.90, 159.8, 149.6 (dd, $^{1,2}J_{C\text{-}F}$ = 257.5, 11.9 Hz), 149.0 (dd, $^{1,2}J_{C\text{-}F}$ = 252.7, 13.1 Hz), 145.5 (dd, $^{1,2}J_{C\text{-}F}$ = 248.0, 10.7 Hz), 144.9 (dd, $^{1,2}J_{C\text{-}F}$ = 239.6, 9.5 Hz), 143.7, 143.2, 141.0 (dm, $^{1,2}J_{C\text{-}F}$ = 256.3 Hz), 140.4 (dm, $^{1,2}J_{C\text{-}F}$ = 258.7 Hz), 133.7, 133.4 (br s), 133.35, 133.30, 133.27, 133.24, 133.22, 133.1, 131.0, 130.9, 130.8, 130.6, 130.31, 130.27, 128.8, 128.6, 128.5, 128.4, 127.53, 127.46, 127.2 (dd, $^{2,3}J_{C\text{-}F}$ = 13.1, 3.6 Hz), 126.93, 126.92, 126.87, 126.8, 126.6, 126.32, 126.28, 125.2, 125.0, 117.2, 116.6, 114.29, 114.27, 114.0, 113.9, 113.8, 113.7, 113.64, 113.56, 107.4 (dd, $^{2,3}J_{C\text{-}F}$ = 26.2, 14.3 Hz), 101.6 (br s), 101.2 (br s), 89.4 (br s), 89.2 (br s), 88.0, 87.7, 87.1, 87.0, 86.8, 86.6, 85.3, 85.1, 64.1, 63.8, 57.9 (d, $^{3}J_{C\text{-}F}$ = 4.8 Hz), 57.30 (d, $^{3}J_{C\text{-}F}$ = 7.2 Hz), 55.32, 55.29, 55.2; **^{19}F NMR** (282 MHz, $CDCl_3$) (mixture) δ -133.94 (dd, $J_{F\text{-}F}$ = 18.2, 11.3 Hz, 1F), -135.00 (ddd, $J_{F\text{-}F}$ = 18.2, 11.3, 3.5

Hz, 1F), -143.64 (ddd, J_{F-F} = 20.8, 11.3, 3.5 Hz, 1F), -144.22 (dd, J_{F-F} = 18.6, 10.8 Hz, 1F), -153.24 (app td, J_{F-F} = 20.8, 3.5 Hz, 1F), -153.44 (app td, J_{F-F} = 20.8, 3.5 Hz, 1F), -156.03 (ddd, J_{F-F} = 19.9, 17.3, 3.5 Hz, 1F), -156.40 (app td, J_{F-F} = 20.8, 3.5 Hz, 1F); **IR** (KBr) ν_{max} 3336, 3046, 3001, 2959, 2935, 2905, 2836, 2226, 1601, 1565, 1506, 1485, 1467, 1440, 1290, 1245, 1171, 1129, 1108, 1033, 958, 911, 890, 845, 827, 785, 762, 647, 612, 567, 637 cm^{-1}; **HRMS** (ESI) *m/z* for $C_{42}H_{26}O_4F_4Na$ $[M+Na]^+$ calcd: 693.16594, found: 693.16584; ***R*$_f$** (4/1 hexanes/AcOEt) = 0.26.

1-(2-((3-(1-Hydroxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)phenanthren-4-yl)ethynyl)phenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (31). With 4-((2-formylphenyl)ethynyl)phenanthrene-3-carbaldehyde (**30**) (1.60 g, 4.78 mmol) according to the general procedure. Column chromatography of the residue on silica gel (3/2 hexanes/EtOAc) afforded 1.94 g (68%) of an inseparable mixture of two diastereoisomers (1:0.5) as a light brown solid: **mp** (decomp) 76-80°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.36 (d, *J* = 8.6 Hz, 1H), 8.16 (t, *J* = 1.0 Hz, 1H), 7.90 (d, *J* = 1.0 Hz, 2H), 7.84 (dd, *J* = 1.0 Hz, 1H), 7.77 - 7.81 (m, 1H), 7.76 (d, *J* = 1.0 Hz, 1H), 7.69 (d, *J* = 1.0 Hz, 2H), 7.64 (t, *J* = 1.0 Hz, 1H), 7.32 - 7.48 (m, 6H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.66 - 6.76 (m, 3H), 6.30 (d, *J* = 1.0 Hz, 1H), 3.83 (br s, 1H), 3.75 (t, *J* = 1.0 Hz, 6H), 3.45 - 3.67 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.70, 159.68, 143.4, 142.3, 133.4, 133.3, 133.2, 133.0, 132.7, 130.7, 130.4, 129.9, 129.2, 128.6, 128.5, 128.3, 127.5, 127.1, 127.0, 126.6, 126.0, 125.1, 124.9, 122.1, 117.7, 114.6, 114.4, 113.82, 113.78, 98.8, 94.3, 87.4, 87.13, 87.06, 86.8, 64.12, 64.10, 55.20, 55.16; **IR** (KBr) ν_{max} 3321, 3040, 3003, 2960, 2933, 2908, 2808, 2542, 2225, 2050, 1917, 1894, 1699, 1604, 1508, 1290, 1250, 1173, 1032, 831, 800, 750, 536 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{42}H_{31}O_4$ $[M+H]^+$ calcd: 599.22169, found: 599.22156; **R$_f$** (3/2 hexanes/EtOAc) = 0.29.



5.4.2 Cyclotrimerization reactions

A$_1$: General procedure for cyclotrimerization with Wilkinson's catalyst ($RhCl(PPh_3)_3$) and Ag_2CO_3. A dried microwave vial was filled up with starting material **26** or **31** (0.1 mmol) and dissolved in THF (6 mL) under argon atmosphere. After addition of $RhCl(PPh_3)_3$ (2.8 mg, 3 mol%) and the additive Ag_2CO_3 (1.6 mg, 6 mol%), the reaction mixture was sealed with a cap and heated up to 170 °C for 1.5 h in a microwave reactor. The reaction mixture was cooled

down to room temperature and the solvent was evaporated under reduced pressure. The obtained crude was subjected directly to oxidation step (see procedure C).

A_2: General procedure for cyclotrimerization with Wilkinson's catalyst ($RhCl(PPh_3)_3$). A dried microwave vial was charged with starting material **26** or **31** (0.1 mmol) and THF (6 mL). After addition of Wilkinson's catalyst (2.8 mg, 3 mol%), the vial was sealed with a cap and heated up to 170 °C for 1.5 h in a microwave reactor. The reaction mixture was cooled down to room temperature and the solvent was evaporated under reduced pressure. The crude diols were directly oxidized to the corresponding diketones without any further purification (see procedure C).

A_3: General procedure for cyclotrimerization with $CpCo[P(OEt)_3](dmfu)$.[143] A dry vial was charged with starting material **26** or **31** (0.1 mmol), $CpCo[P(OEt)_3](dmfu)$ (2.0 mg, 4.8 mol %) and toluene (2.5 mL). The vial was sealed with a cap and the reaction mixture was refluxed for 24 h. The solvent was evaporated under reduced pressure and the crude was immediately subjected to oxidation step (see procedure C).

A_4: General procedure for cyclotrimerization with Vollhardt's catalyst ($CpCo(CO)_2$). A dry microwave vial was filled up with PPh_3 (10 mg, 40 mol%). Starting material **26** or **31** (0.1 mmol) in THF (3.3 mL) was added under argon atmosphere. After addition of $CpCo(CO)_2$ catalyst (3.6 mg, 20 mol%) the reaction vessel was sealed and heated up to 180 °C for 30 min in a microwave reactor. The reaction mixture was cooled down to room temperature and the solvent was evaporated under reduced pressure. The resulting crude was immediately subjected to oxidation step (see procedure C).

A_5: General procedure for cyclotrimerization with $Ni(acac)_2$.[141(b)] $Ni(acac)_2$ was loaded into a vial and heated to 150°C for 4 h under high vacuum. Then the vial was cooled down to room temperature and filled back up with argon atmosphere. The dried catalyst thus obtained was employed for several reactions over one month. The commercially available *i*-PrMgCl solution (1 mL, 2 M) was diluted with anhydrous THF (4 mL) to obtain a concentration of 0.4 M. Titration with menthol/phenanthroline system was carried out for correction of concentration before each experiments.

In a dry vial, the previously dried $Ni(acac)_2$ (10.3 mg, 40 mol%) and PPh_3 (21.0 mg, 80 mol%) were added. The mixture of two solids was heated up to 80°C for 1 h under vacuum. After

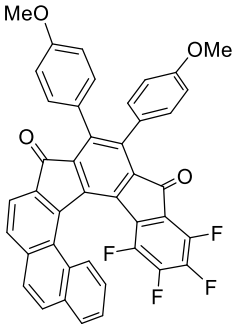
cooling down to room temperature, toluene (1 mL) was added. Upon addition of the previously prepared 0.4 M solution of *i*-PrMgCl (110 μL, 0.04 mmol), the reaction mixture turned black. The starting material **26** (67.1 mg, 0.1 mmol) in toluene (7 mL) was added and the reaction was stirred for 20 h at room temperature. The solvent was removed under reduced pressure and the crude was directly oxidized (see procedure C).

A_6: General procedure for cyclotrimerization with Ni(COD)(DQ). A dried vial was loaded with Ni(COD)(DQ) (3.3 mg, 10 mol%) and PPh_3 (7.8 mg, 20 mol%) and subjected to two cycles of vacuum/argon. Freshly distilled toluene (4 mL) was added and the resulting mixture was stirred for 10 min at room temperature. After addition of starting material **26** or **31** (0.1 mmol), the vial was sealed and heated up to 100 °C for 20 h. The solvent was eliminated under reduced pressure and the crude was directly oxidized (see procedure C).

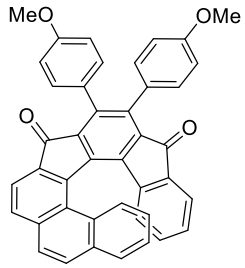
B_1: General procedure for thermal reaction. In a dried microwave vial, the starting material **26** or **31** (0.1 mmol) was dissolved in THF (4 mL). The vial was sealed and heated up to 170 °C for 1.5 h in a microwave reactor. The reaction mixture was cooled down to room temperature and the solvent was eliminated by rotary evaporator. The crude was directly used for the oxidation step (see procedure C).

B_2: General procedure for thermal reaction with Ag_2CO_3. In a dried microwave vial, Ag_2CO_3 (8.6 mg, 6.0 mol%) and the starting material **26** or **31** (0.52 mmol) were dissolved in THF (20 mL). The vial was sealed and placed in a microwave reactor. The reaction was carried out at 170 °C for 1.5 h. After cooling down to room temperature, the solvent was evaporated under reduced pressure. The crude was directly used for the oxidation step (see procedure C).

C: General procedure for oxidation reaction. A two-neck flask was charged with pyridinium chlorochromate (PCC, 65 mg, 0.3 mmol) and Celite® (65 mg); the crude (approximately 0.1 mmol) in CH_2Cl_2 (5 mL) was added and the reaction mixture was stirred for 3 h at 25 °C and under argon atmosphere. Afterwards the residue was filtered through a Celite®/silica gel plug (1:4). Column chromatography yielded the desired products **27**, **32** as a bright orange solid and/or **33**-**35**.

9,10,11,12-Tetrafluoro-6,7-bis(4-methoxyphenyl)benzo[7,8]-*as*-indaceno[2,1-*c*]phenanthrene-5,8-dione (27). 

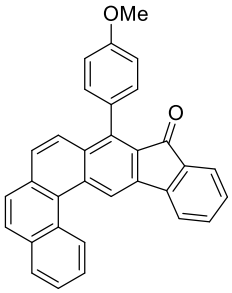
With **26** (67 mg, 0.10 mmol) according to the general procedure A_3 and then C. Column chromatography of the residue on aluminum oxide 90 active basic (3/1 to 1/1 cyclohexane/CH_2Cl_2) yielded 27 mg (41%) of the desired product as a bright orange solid: **mp** (decomp) 329.4 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.2 Hz, 1H), 7.82 - 7.90 (m, 4H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.44 (app t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.18 (br s, 1H), 7.00 (app t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.79 - 6.88 (m, 2H), 6.66 - 6.78 (m, 3H), 3.81 (s, 3H), 3.80 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 189.9, 185.2, 159.21, 159.18, 143.6, 144.5 (dm, $^1J_{C\text{-}F}$ = 265.8 Hz), 143.4, 141.92, 141.90 (dd, $^{1,2}J_{C\text{-}F}$ = 261.1, 13.1 Hz), 141.0 (dt, $^{1,2}J_{C\text{-}F}$ = 262.3, 15.5 Hz), 137.9, 137.6, 136.0, 135.3, 132.6, 132.2 (br s), 131.7 (br s), 130.9, 130.5 (br s), 130.4 (br s), 130.1, 129.8 (d, $^4J_{C\text{-}F}$ = 6.0 Hz), 129.0 (d, $^3J_{C\text{-}F}$ = 7.2 Hz), 128.3, 127.5, 127.2 (d, $^2J_{C\text{-}F}$ = 11.9 Hz), 126.9, 126.7, 126.1, 125.4, 124.7, 120.7, 116.3 (d, $^2J_{C\text{-}F}$ = 9.5 Hz), 113.3 (br s), 113.1 (br s), 112.9 (br s), 55.10, 55.08; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -123.33 (ddd, *J* = 21.1, 15.7, 6.1 Hz, 1F), -139.17 (ddd, *J* = 29.3, 15.7, 8.2 Hz, 1F), -146.23 (ddd, *J* = 20.4, 17.7, 8.9 Hz, 1F), -152.00 (tdd, *J* = 17.7, 17.7, 5.5, 4.1 Hz, 1F); **IR** (KBr) ν_{max} 3047, 3001, 2956, 2925, 2852, 1709, 1631, 1608, 1583, 1568, 1504, 1491, 1464, 1423, 1392, 1358, 1329, 1308, 1277, 1252, 1178, 1138, 1111, 1090, 1061, 1034, 998, 982, 945, 920, 862, 850, 827, 796, 785, 756, 725, 702, 660, 644, 611, 563 cm^{-1}; **HRMS** (CI) *m/z* for $C_{42}H_{23}O_4F_4$ $[M+H]^+$ calcd: 667.15270, found: 667.15291; ***R*$_f$** (3/1 CH_2Cl_2/hexanes) = 0.24 (silica gel plate), bright orange spot.

6,7-Bis(4-methoxyphenyl)benzo[7,8]-*as*-indaceno[2,1-*c*]phenanthrene-5,8-dione (32). 

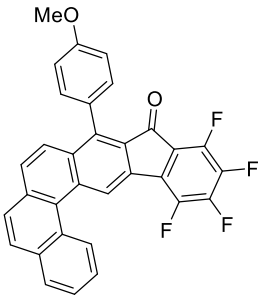
With **31** (251 mg, 0.42 mmol) according to procedure A_6 and then C. Column chromatography on silica gel (3/1 hexanes/AcOEt) yielded 105 mg (42%) of the title compound as a bright red solid: **mp** (decomp) 298.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.3 Hz, 1H), 7.83 - 7.90 (m, 4H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.37 (app t, *J* = 1.0 Hz, 1H), 7.30 (br s, 1H), 7.06 (app t, *J* = 7.5 Hz, 2H), 6.91 (app t, *J* = 1.0 Hz, 2H), 6.80 (br s, 4H), 6.73 (br s, 1H), 6.63 (td, *J* = 7.6, 0.98 Hz, 1H), 6.01 (d, *J* = 7.8 Hz, 1H), 3.82 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.1, 190.5, 158.9, 158.8, 143.0, 142.8, 142.5, 141.8, 141.4, 138.2, 137.4, 136.9, 136.8, 135.9, 134.5, 132.5, 132.3, 131.2, 130.3, 130.2, 130.0, 128.6, 128.0, 127.9, 127.5, 127.4, 127.1, 126.9, 126.5, 125.6, 125.2, 123.4, 121.0, 113.0, 55.1; **IR** (KBr) ν 3045, 3001, 2952, 2927, 2852, 2835, 1714, 1608, 1516, 1466, 1425, 1302, 1252, 1176, 1034,

833, 802, 746, 559 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{42}H_{27}O_4$ $[M+H]^+$ calcd: 595.19039, found: 595.18995; **R_f** (5/2 hexanes/EtOAc) = 0.31, bright orange spot.

9-(4-Methoxyphenyl)-10*H*-benzo[*g*]indeno[2,1-*b*]phenanthren-10-one (33). With **31** (718 mg, 1.20 mmol) according to the general procedure B_2 and then C. Column chromatography of the residue on silica gel (5/2 hexanes/AcOEt) followed by a second column on silica gel (2/1 CH_2Cl_2/toluene) yielded 70 mg (13%) of the desired product as a bright yellow solid: **mp** (decomp) 245.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 9.07 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.73 - 7.81 (m, 4H), 7.67 - 7.72 (m, 2H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.56 (td, *J* = 7.5, 1.2 Hz, 1H), 7.36 - 7.41 (m, 2H), 7.33 (td, *J* = 7.4, 0.9 Hz, 1H), 7.08 - 7.15 (m, 2H), 3.95 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.4, 159.5, 144.3, 141.0, 139.3, 136.3, 134.6, 134.4, 133.9, 133.7, 132.5, 131.2, 130.4, 129.1, 128.9, 128.8, 128.3, 128.0, 127.92, 127.89, 127.2, 127.0, 126.5, 126.4, 126.3, 124.2, 120.5, 118.6, 113.6, 55.3; **IR** (KBr) ν_{max} 3055, 3033, 3006, 2960, 2922, 2852, 2837, 1705, 1614, 1601, 1510, 1245, 1176, 1032, 1024, 841, 748, 729 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{32}H_{21}O_2$ $[M+H]^+$ calcd: 437.15361, found: 437.15322; **R_f** (5/2 hexanes/EtOAc) = 0.42.

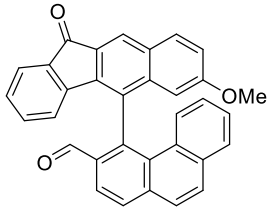


11,12,13,14-Tetrafluoro-9-(4-methoxyphenyl)-10*H*-benzo[*g*]indeno[2,1-*b*]phenanthren-10-one (35). With **26** (549 mg, 0.82 mmol) according to the general procedure B_2 and then C. Column chromatography of the residue on aluminum oxide 90 active basic (hexanes/CH_2Cl_2 3/1 to 1/1) followed by recrystallization in CH_2Cl_2/CH_3CN yielded 48 mg (12%) of the desired product as a bright yellow solid: **mp** (decomp) 265.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 9.05 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.75 - 7.84 (m, 4H), 7.71 (t, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 3.94 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 186.1, 159.8, 145.2 (d, $^1J_{C\text{-}F}$ = 261.1 Hz), 144.8 (dd, $^{1,2}J_{C\text{-}F}$ = 263.5, 10.7 Hz), 142.3, 143.0 (dd, $^{1,2}J_{C\text{-}F}$ = 259.9, 13.1 Hz), 140.9 (dm, $^1J_{C\text{-}F}$ = 261.1 Hz), 134.4, 133.92, 133.87 (br s), 133.8, 132.8, 131.1, 130.2, 129.6, 128.9, 128.4, 128.0, 127.7, 127.1, 126.9, 126.9, 126.8, 126.7, 126.4, 126.1 (d, $^2J_{C\text{-}F}$ = 11.9 Hz), 123.6 (d, $^3J_{C\text{-}F}$ = 7.2 Hz), 118.2 (d, $^2J_{C\text{-}F}$ = 10.7 Hz), 113.8, 55.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -140.67 (ddt, *J* = 17.7, 11.6, 8.9, 8.9 Hz, 1F), -144.52 (dd, *J* = 19.8, 17.7 Hz, 1F), -146.41 (td, *J* = 18.4, 8.2 Hz, 1F), -154.59 (dd, *J* = 19.8, 18.4 Hz, 1F); **IR** (KBr) ν_{max} 3049, 2960, 2924, 2850, 1722, 1635, 1606, 1572, 1508, 1489, 1464, 1444, 1402, 1385, 1358, 1321,



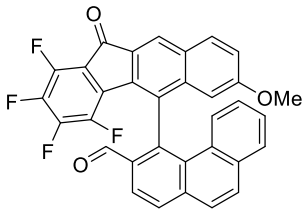
1304, 1290, 1259, 1221, 1203, 1178, 1140, 1119, 1099, 1074, 1026, 968, 920, 889, 870, 843, 800, 758, 728, 690, 598, 580, 523 cm^{-1}; **HRMS** (CI) *m/z* for $C_{32}H_{17}O_2F_4$ $[M+H]^+$ calcd: 509.11592, found: 509.11550; R_f (1/1 CH_2Cl_2/hexanes) = 0.31 (silica gel plate).

4-(7-methoxy-11-oxo-11*H*-benzo[*b*]fluoren-5-yl)phenanthrene-3-carbaldehyde (34). With



31 (718 mg, 1.20 mmol) according to the general procedure B_2 and then C. Column chromatography of the residue on silica gel (hexanes/AcOEt 5/2) followed by a second column on silica gel (2/1 CH_2Cl_2/toluene) yielded 62 mg (11%) of the desired product as an orange solid: **mp** (decomp) 227.4 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.40 (d, *J* = 1.0 Hz, 2H), 8.26 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 9.1 Hz, 1H), 7.94 (s, 2H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.9 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 2.0 Hz, 1H), 5.70 (d, *J* = 7.6 Hz, 1H), 3.48 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.6, 191.9, 161.1, 143.7, 139.8, 138.7, 138.1, 137.7, 136.6, 134.8, 133.6, 133.5, 132.8, 131.6, 131.0, 130.70, 130.67, 129.7, 129.2, 129.14, 129.09, 128.4, 127.3, 127.2, 126.9, 126.3, 126.2, 124.9, 124.2, 122.9, 118.8, 107.0, 55.2; **IR** (KBr) ν_{max} 3066, 3049, 3005, 2952, 2931, 2860, 1709, 1687, 1612, 1591, 1510, 1466, 1367, 1300, 1282, 1236, 1185, 1144, 1111, 1036, 908, 850, 760, 727, 530 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{33}H_{21}O_3$ $[M+H]^+$ calcd: 465.14852, found: 465.14843; **R_f** (5/2 hexanes/EtOAc) = 0.17.

4-(1,2,3,4-tetrafluoro-7-methoxy-11-oxo-11*H*-benzo[*b*]fluoren-5-yl)phenanthrene-3-carbaldehyde (36). With **26** (67.1 mg, 0.10 mmol) according to the general procedure A_1 and then C. Column chromatography of the residue on aluminum oxide 90 active basic (hexanes/CH_2Cl_2 3/1 to 1/1) followed by purification with preparative TLC on silica gel (hexanes/AcOEt 5/1 to 4/1) yielded 3.0 mg (5%) of the desired product as a yellow solid: **mp** (decomp) 233-236 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.66 (s, 1H), 8.49 (s, 1H), 8.32 (d, *J* = 7.7 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.93 (s, 2H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 7.1 Hz, 1H), 7.20 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.48 (s, 1H), 3.40 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.8, 186.4, 161.6, 145.4 (ddd, $^{1,2,3}J_{C\text{-}F}$ = 258.7, 16.7, 14.3 Hz), 144.7 (dd, $^{1,2}J_{C\text{-}F}$ = 264.6, 9.5 Hz), 142.5 (dd, $^{1,2}J_{C\text{-}F}$ = 261.1, 15.5 Hz), 140.4 (d, $^{4}J_{C\text{-}F}$ = 4.8 Hz), 141.0 (ddd, $^{1,2,3}J_{C\text{-}F}$ = 261.1, 16.7, 14.3 Hz), 139.0, 137.3, 134.4 (br s), 134.0 (d, $^{4}J_{C\text{-}F}$ = 4.8 Hz), 133.7, 133.1, 132.8, 131.3, 130.7,



130.5, 129.8, 129.6 (d, $^{3}J_{C\text{-}F}$ = 4.8 Hz), 129.5, 128.2, 127.6, 127.5, 127.0, 126.8, 125.8, 124.7 (d, $^{2}J_{C\text{-}F}$ = 13.1 Hz), 124.3, 120.1, 119.0 (d, $^{2}J_{C\text{-}F}$ = 10.7 Hz), 108.1, 55.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -132.75 (ddd, *J* = 21.1, 16.4, 5.5 Hz, 1F), -140.53 - (-140.25) (m, 1F), -144.37 - (-144.18) (m, 1F), -152.80 - (-152.59) (m, 1F); **IR** (KBr) ν_{max} 3084, 3062, 2958, 2918, 2848, 1782, 1722, 1682, 1628, 1606, 1558, 1516, 1504, 1487, 1468, 1442, 1423, 1391, 1365, 1315, 1298, 1281, 1255, 1240, 1221, 1171, 1149, 1122, 1084, 1041, 1028, 1003, 970, 941, 868, 854, 833, 750, 706, 540 cm^{-1}; **HRMS** (APCI) *m/z* for $C_{33}H_{17}F_4O_3$ $[M+H]^+$ calcd: 537.1108, found: 537.10453; **R_f** (1/1 hexanes/CH_2Cl_2) = 0.17 (aluminum oxide 60 neutral plate).

5.4.3 Enantioselective cyclotrimerization reactions

General procedure for enantioselective cyclotrimerization using rhodium catalyst and chiral ligand. A dried 5 mL microwave vial was loaded with $[Rh(cod)_2]BF_4$ (2.4 mg, 0.006 mmol), chiral ligand (0.008 mmol) and DCE (2 mL) under argon atmosphere. In order to activate the catalyst, H_2 gas was bubbled through the reaction mixture for 45 min. Afterwards three vacuum/argon cycle were performed to restore the argon atmosphere in the reaction vessel. Then starting material **26** (67 mg, 0.1 mmol) was added, the vial was sealed with a cap and the reaction was carried out at 60°C for 48 h. The resulting mixture was cooled down to 25 °C and the solvent was removed under reduced pressure. The crude diol was subjected to oxidation step following the general procedure C. Column chromatography of the residue on aluminum oxide 90 active basic (3/1 to 1/1 cyclohexane /CH_2Cl_2) yielded product **27**.

General procedure for enantioselective cyclotrimerization with Ni(acac)$_2$. $Ni(acac)_2$ was added in a vial and heated under vacuum at 150 °C for 4 h. Afterwards the vial was cooled down to room temperature and filled with argon atmosphere. The dried catalyst was employed for several reactions over one month. The commercially available *i*-PrMgCl solution (1 mL, 2 M) was diluted with anhydrous THF (4 mL) to obtain a concentration of 0.4 M. Titration with menthol/phenanthroline system was carried out for correction of concentration before each experiments. The previously dried $Ni(acac)_2$ (5.1 mg, 40 mol%) and chiral ligand (40-80 mol%) were added in a dried vial. The mixture of two solids was heated up to 50°C for 1 h under vacuum. After cooling down to room temperature, toluene (1 mL) was added. Upon addition of the previously prepared 0.4 M solution of *i*-PrMgCl (55 µL), the reaction mixture turned black. The starting material **26** (34 mg, 0.05 mmol) in toluene (4 mL) was added and the reaction was stirred for 20 h at room temperature. The solvent was removed under reduced

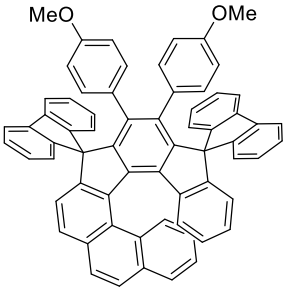
pressure and the crude was directly oxidized following the general procedure C. Column chromatography of the residue on aluminum oxide 90 active basic (cyclohexane /CH_2Cl_2 3/1 to 1/1) yielded product **27**.

General procedure for cyclotrimerization with Ni(COD)(DQ). A dried vial was loaded with Ni(COD)(DQ) (1.7 mg, 10 mol%) and chiral ligand (20 mol%) and subjected to two cycles of vacuum/argon. Freshly distilled toluene (2 mL) was added and the resulting mixture was stirred for 10 min. After addition of starting material **26** (34 mg, 0.05 mmol), the vial was sealed and heated up to 100 °C for 20 h. The solvent was eliminated by rotary evaporator and the crude was directly oxidized according to the general procedure C. Column chromatography of the residue on aluminum oxide 90 active basic (cyclohexane/CH_2Cl_2 3/1 to 1/1) yielded product **27**.

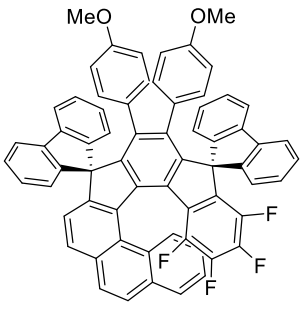
5.4.4 Synthesis of spirobifluorenes

General procedure for creation of 9,9'-dispiroindenobifluorene. Preparation of 37-38 and 39-40. A dried Schlenk flask was charged with 2-bromobiphenyl (0.14 mL, 0.83 mmol in the case of **27**, **32** and 83 µL, 0.48 mmol for **35**, **33**) and anhydrous THF (3.3 mL) under argon atmosphere. The resulting solution was cooled down to -78 °C and *n*-Butyllithium, 1.6 M solution in hexanes, (0.52 ml, 0.83 mmol in the case of **27**, **32** and 0.30 mL, 0.48 mmol for **35**, **33**) was added dropwise. After stirring for 30 minutes, starting material **27**, **32** (0.17 mmol, 1.0 eq) or **35**, **33** (0.16 mmol, 1.0 eq) in THF (3.3 mL) was added dropwise and the reaction mixture was stirred for 15 minutes at -78 °C. Then it was allowed to warm up to room temperature and stirred for 4 hours. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with diethyl ether (3×20 mL). The combined organic fractions were dried over Na_2SO_4 and concentrated by rotary evaporator. Column chromatography of the residue on silica gel (hexanes/EtOAc) afforded the corresponding diol, which was subjected to the next step. The alcohol was dissolved in acetic acid (11 mL) with a catalytic amount of HCl (12 mol/L) and the resulting solution was stirred under reflux for 2 hours. The reaction mixture was neutralized with saturated aqueous K_2CO_3 solution and extracted with diethyl ether (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (CH_2Cl_2/hexanes), followed by sonication of the obtained solid with CH_3CN, decantation and filtration, provided products.

6',7'-Bis(4-methoxyphenyl)dispiro[fluorene-9,5'-benzo[7,8]-*as*-indaceno[2,1-*c*]phenanthrene-8',9''-fluorene] (37). With **32** (105 mg, 0.18 mmol) according to the general procedure. Column chromatography of the residue on silica gel (5/1 to 3/1 hexanes/AcOEt for the first reaction and 2/1 CH_2Cl_2/hexanes for the second one) followed by sonication of the obtained solid with CH_3CN, decantation and filtration, provided 60 mg (39%) of the title compound as a colourless solid: **mp** (decomp) > 365 C°; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.10 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.83 (q, *J* = 10.5 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.41 - 7.46 (m, 2H), 7.33 - 7.41 (m, 3H), 7.27 - 7.33 (m, 4H), 7.16 (td, *J* = 7.5, 1.0 Hz, 1H), 7.07 - 7.13 (m, 3H), 6.97 - 7.03 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.78 (td, *J* = 7.5, 1.2 Hz, 1H), 6.71 (d, *J* = 7.3 Hz, 1H), 6.53 - 6.57 (m, 1H), 6.43 - 6.49 (m, 2H), 5.84 - 5.90 (m, 2H), 5.77 - 5.83 (m, 2H), 5.71 - 5.77 (m, 3H), 5.64 - 5.69 (m, 1H), 3.52 (d, *J* = 2.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.4, 156.3, 150.7, 149.05, 149.01, 148.97, 148.7, 147.6, 146.4, 146.3, 142.8, 142.2, 141.9, 141.4, 139.1, 138.4, 137.5, 136.5, 136.2, 132.8, 132.0, 131.4, 131.1, 130.8, 130.5, 129.6, 128.83, 128.80, 128.7, 127.5, 127.3, 127.2, 127.10, 127.08, 127.03, 127.01, 126.97, 126.84, 126.79, 126.77, 126.6, 125.1, 125.0, 124.4, 123.9, 123.81, 123.77, 123.5, 122.4, 121.5, 120.1, 119.9, 119.7, 119.4, 111.3, 111.2, 111.1, 111.0, 66.5, 66.2, 54.9; **IR** (KBr) ν_{max} 3062, 3041, 3014, 2951, 2933, 2904, 2831, 1946, 1907, 1880, 1805, 1745, 1610, 1577, 1516, 1446, 1284, 1174, 1038, 910, 833, 796, 754, 739, 609, 555, 546 cm^{-1}; **HRMS** (CI) *m/z* for $C_{66}H_{43}O_2$ $[M+H]^+$ calcd: 867.32576, found: 867.32584; **R_f** (2/1 CH_2Cl_2/hexanes) = 0.35.

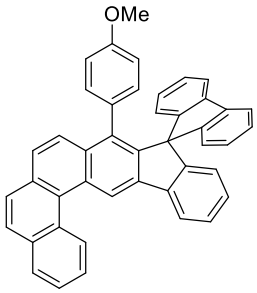


9',10',11',12'-tetrafluoro-6',7'-bis(4-methoxyphenyl)dispiro[fluorene-9,5'-benzo[7,8]-*as*-indaceno[2,1-*c*]phenanthrene-8',9''-fluorene] (38). With **27** (112 mg, 0.17 mmol) according to the general procedure. Column chromatography of the residue on silica gel (4/1 hexanes/EtOAc for the first reaction and 2/1 hexanes/CH_2Cl_2 for the second one) followed by sonication of the obtained solid with CH_3CN, decantation and filtration, provided 59 mg (38%) of the title compound as a colourless solid: **mp** (decomp) 210.7 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.93 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.77 - 7.88 (m, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.37 - 7.55 (m, 6H), 7.25 - 7.36 (m, 3H), 7.11 - 7.23 (m, 4H), 6.92 - 7.10 (m, 4H), 6.85 (d, *J* = 7.0 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 5.54 - 6.03 (m, 8H), 3.54 (br s, 6H); **^{13}C NMR** (151 MHz,

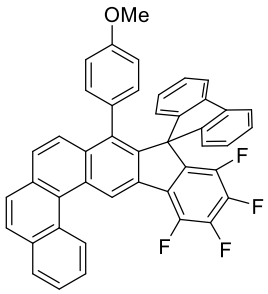


$CDCl_3$) δ 156.53, 156.49, 150.0, 148.1, 147.3, 147.2, 145.6, 145.5, 142.7, 142.6, 141.9, 142.4 (dd, $^{1,2}J_{C\text{-}F}$ = 252.7, 11.9 Hz), 141.5 (dd, $^{1,2}J_{C\text{-}F}$ = 255.1, 13.1 Hz), 140.13, 140.08 (dt, $^{1,2}J_{C\text{-}F}$ = 250.3, 15.5 Hz), 139.8 (dt, $^{1,2}J_{C\text{-}F}$ = 257.5, 14.3 Hz), 138.73, 138.69, 136.3, 132.4, 132.3, 131.1, 131.0 (br s), 130.7, 130.4 (d, $^{2}J_{C\text{-}F}$ = 7.2 Hz), 129.93, 129.87 (br s), 129.6, 129.4, 129.0 (d, $^{2}J_{C\text{-}F}$ = 7.2 Hz), 128.0, 127.9, 127.7, 127.6, 127.42, 127.39 (br s), 127.3, 127.24, 127.15, 127.1, 127.0, 126.6, 126.3, 125.7, 123.9, 123.8, 123.5, 123.1, 123.0, 121.0, 120.4, 120.0, 119.8, 119.7, 111.5, 111.34, 111.25, 111.2, 66.4, 64.9, 54.9; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -127.93 (app t, *J* = 18.6 Hz, 1F), -146.77 (dd, *J* = 19.1, 16.5 Hz, 1F), -157.83 (dd, *J* = 19.9, 18.2 Hz, 1F), -159.81 (app t, *J* = 19.9 Hz, 1F); **IR** (KBr) ν_{max} 3047, 3014, 2954, 2931, 2835, 1739, 1610, 1576, 1516, 1489, 1448, 1419, 1408, 1356, 1317, 1284, 1246, 1174, 1126, 1107, 1086, 1076, 1066, 1038, 1005, 991, 904, 835, 814, 796, 768, 754, 737, 660, 615, 548, 534 cm^{-1}; **HRMS** (CI) *m/z* for $C_{66}H_{39}O_2F_4$ $[M+H]^+$ calcd: 939.28807, found: 939.28824; R_f (2/1 hexanes/CH_2Cl_2) = 0.26.

9-(4-Methoxyphenyl)spiro[benzo[*g*]indeno[2,1-*b*]phenanthrene-10,9'-fluorene] (39). With



33 (70 mg, 0.16 mmol) according to the general procedure. Column chromatography of the residue on silica gel (5/1 hexanes/EtOAc for the first reaction and 2/1 hexanes/CH_2Cl_2 for the second one) provided 66 mg (72%) of the title compound as a pale yellow solid: **mp** (decomp) 289.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 9.42 (d, *J* = 8.6 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 8.10 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.86 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.70 - 7.76 (m, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.44 - 7.52 (m, 3H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.27 (td, *J* = 7.5, 1.0 Hz, 2H), 7.17 (td, *J* = 7.5, 1.0 Hz, 1H), 7.10 (td, *J* = 7.5, 1.0 Hz, 2H), 6.87 (d, *J* = 7.6 Hz, 2H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.30 - 6.38 (m, 2H), 6.16 - 6.22 (m, 2H), 3.79 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.6, 149.9, 149.0, 144.4, 142.0, 141.3, 140.3, 137.2, 133.6, 133.5, 130.7, 130.6, 128.6, 128.44, 128.40, 128.1, 127.7, 127.6, 127.4, 127.2, 127.2, 126.7, 126.1, 126.0, 125.8, 125.4, 124.1, 123.9, 120.4, 119.7, 117.9, 112.4, 65.7, 55.2; **IR** (KBr) ν_{max} 3059, 3045, 3016, 2951, 2931, 2904, 2831, 1608, 1576, 1522, 1508, 1479, 1464, 1446, 1412, 1388, 1284, 1244, 1174, 1105, 1036, 901, 837, 773, 744, 727, 683, 638, 623, 538, 418 cm^{-1}; **HRMS** (CI) *m/z* for $C_{44}H_{29}O$ $[M+H]^+$ calcd: 573.22129, found: 573.22134; R_f (5/2 hexanes/CH_2Cl_2) = 0.15.

11,12,13,14-tetrafluoro-9-(4-methoxyphenyl)spiro[benzo[*g*]indeno[2,1-*b*]phenanthrene-10,9'-fluorene] (40). 

With **35** (49 mg, 0.10 mmol) according to the general procedure. Column chromatography of the residue on silica gel (5/1 hexanes/EtOAc for the first reaction and 5/1 hexanes/CH_2Cl_2 for the second one) provided 44 mg (70%) of the title compound as a pale yellow solid: **mp** (decomp) 210.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 9.34 (d, J = 8.6 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.83 (t, J = 8.1 Hz, 1H), 7.77 (d, J = 8.6 Hz, 1H), 7.72 (t, J = 7.3 Hz, 1H), 7.63 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 8.8 Hz, 1H), 7.28 (t, J = 7.3 Hz, 2H), 7.12 (t, J = 7.5 Hz, 2H), 6.89 (d, J = 7.6 Hz, 2H), 6.29 (d, J = 8.6 Hz, 2H), 6.08 (d, J = 8.6 Hz, 2H), 3.76 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.8, 145.5, 143.1, 143.2 (dd, $^{1,2}J_{C\text{-}F}$ = 252.1, 11.0 Hz), 142.2, 142.8 (dd, $^{1,2}J_{C\text{-}F}$ = 252.1, 11.1 Hz), 140.9 (dm, $^{1}J_{C\text{-}F}$ = 249.9 Hz), 140.2 (dm, $^{1}J_{C\text{-}F}$ = 258.7 Hz), 137.3, 135.2 (br s), 133.8, 133.7, 131.2 (d, $^{2}J_{C\text{-}F}$ = 13.3 Hz), 130.9, 130.8, 130.5, 130.4, 128.7, 128.0, 127.9, 127.8, 127.5, 127.4, 127.2, 126.5, 126.4, 126.2, 125.2, 125.1 (d, $^{2}J_{C\text{-}F}$ = 12.2 Hz), 123.4, 122.2 (d, $^{3}J_{C\text{-}F}$ = 6.6 Hz), 120.1, 112.5, 64.7, 55.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -145.04 (m, 1F), -147.03 (m, 1F), -157.14 (t, J = 20.4 Hz, 1F), -157.43 (dd, J = 20.4, 19.1 Hz, 1F); **IR** (KBr) ν_{max} 3059, 3043, 3016, 2960, 2927, 2839, 1612, 1577, 1512, 1491, 1448, 1415, 1408, 1388, 1363, 1325, 1302, 1242, 1174, 1105, 1078, 1039, 939, 904, 841, 816, 739, 648, 580, 526 cm^{-1}; **HRMS** (CI) *m/z* for $C_{44}H_{25}OF_4$ $[M+H]^+$ calcd: 645.18360, found: 645.18304; **R_f** (4/1 hexanes/CH_2Cl_2) = 0.21.

6 ABBREVIATIONS

Ac	acetyl
Acac	acetylacetone
Ac-Ile-OH	*N*-acetyl-L-isoleucine
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Bn	benzyl
Bu	butyl
Bz	benzoyl
CAN	Ceric Ammonium Nitrate
cat.	catalytic
CI	chemical ionization
Cy	cyclohexyl
cod	cyclooctadiene
Cp	cyclopentadienyl
Cp*	1,2,3,4,5-pentamethylcyclopentadiene
DavePhos	2-dicyclohexylphosphino-2'-(*N*,*N*-dimethylamino)biphenyl
dba	dibenzylideneacetone
DCB	dichlorobenzene
DCE	dichloroethane
DDAR	dehydro Diels-Alder reaction
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
DIFLUORPHOS	(2,2,2',2'-Tetrafluoro-4,4'-bi-1,3-benzodioxole-5,5'-diyl)bis(diphenylphosphine)
DFT	Density Functional theory
DMA	*N*,*N*-Dimethylacetamide
DMDC	dimethyl dicarbonate
DME	dimethoxyethane
DMF	*N*,*N*'-dimethylformamide
dmfu	dimethyl fumarate
DMSO	dimethyl sulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppp	1,3-bis(diphenylphosphino)propane
DQ	duroquinone
DSF-BIF	1',2',3',4'-tetrafluoro-6',7'-bis(4-methoxyphenyl) dispiro[fluorene-9,5'-benzo[*c*]indeno[1,2-*g*]fluorene-8',9''-fluorene]
DSF-IFs	6',7'-bis(4-methoxyphenyl)dispiro[fluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorenes]
ee	enantiomeric excess
e.g.	exempli gratia
EI	electron ionization
eq.	equivalent
ESI	electrospray ionization
Et	ethyl
et al.	et alia
F-dppe	1,2-bis[bis(pentafluorophenyl)phosphino]ethane
Flu	fluorenyl

GC	gas chromatography
HMPA	hexamethylphosphoramide
HPLC	high-performance liquid chromatography
HRMS	high-resolution mass spectrometry
HTMs	hole transport materials
i-	iso
IR	infrared spectrometry
Me	methyl
mp	melting point
MsOH	methanesulfonic acid
MW	microwave
n-	normal
NMR	nuclear magnetic resonance
OLEDs	organic light emitting diodes
OPVs	organic photovoltaic cells
ORTEP	Oak Ridge Thermal-Ellipsoid Plot
p-	para
Ph	phenyl
Piv	pivaloyl
ppy	polypyrrole
Pr	propyl
py	pyridine
QUINAP	1-(2-Diphenylphosphino-1-naphthyl)isoquinoline
rac	racemate
r.t	room temperature
sat.	saturated
SBF	spirobifluorene
SEGPHOS	5,5'-Bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole
sh	shoulder
sol.	solution
t-	tert
TEAB	tetraethylammonium bromide
TFA	trifluoroacetic acid
TFAA	trifluoroacetic anhydride
Tf	triflate
THF	tetrahydrofuran
TMS	trimethylsilyl
Tol	toluyl
Ts	tosyl
UV-Vis	ultraviolet-visible spectroscopy
xyl	xylene

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