Charles University

Faculty of Science

Department of Organic Chemistry

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Development of new syntheses of condensed aromatic compounds

Vývoj nových syntéz kondenzovaných aromatických sloučenin

PhD Thesis

Supervisor: Prof. RNDr. Martin Kotora, CSc.

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Prohlášení

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

V Praze dne

Reinhard Peter Kaiser

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1. Introduction

Since the first proposal of "spiro-concept" for organic material science by Salbeck *et al.* in the 1990s,[1] the following systematic studies have shown that compounds possessing spiro functionality are key substances for application in organic functional devices, such as organic semi-conductors, in monolayers, in light-emitting diodes (OLEDs) and in dye-sensitized solar cells.[2] The spiro concept is based on the connection of two or more more aromatic π-systems *via* an sp^3-hybridized atom (a typical example is 9,9'-spirobifluorene, Figure 1).

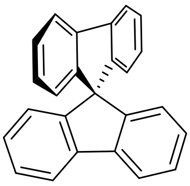


Figure 1. 9,9'-Spirobifluorene SBF

The spiro compounds have improved morphological and thermal stability in comparison with the individual parent π-systems. The perpendicular arrangement efficiently suppresses unwanted excimer (excited dimer) formation reactions, extended π-systems increase the solubility in organic non-polar solvents and stability of the molecule in excited state, leading to high-emission color stability.[1b,2a] In particular, the latter property is one of the key characteristics for continuous light-emitting devices. In the last decade, many studies on photophysical stability, electronic properties and applications of electroluminescent layers based on spiro compounds have been reported.[2b,3] Furthermore, several reports predict that such organic light-emitting diodes (OLEDs), phosphorescent organic light-emitting diodes (PhOLEDs),[3a] white organic light-emitting diodes (WOLEDs)[4] and other devices will become the future of illumination systems.[5]

Substituted 9,9'-spirobifluorenes and dispiroindenofluorenes constitute a class of polycyclic aromatic hydrocarbon spiro compounds (Figure 2) that significantly contribute to the aforementioned areas because of their unique physical and chemical properties.[1-6] The thesis will deal with development of new synthetic pathways for preparation of various 1,2,3,4-tetrasubstituted spirobifluorenes (SBFs), dispiroindeno[2,1-*c*]fluorenes (DS-IFs) and their derivatives as well as with possibilities for tuning of their photophysical properties.

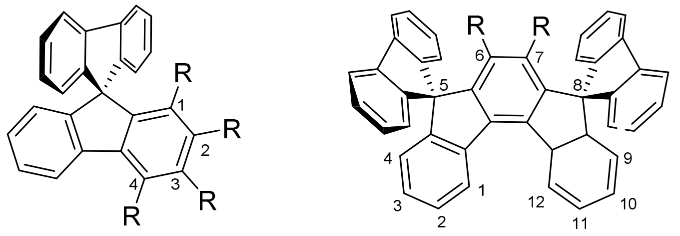
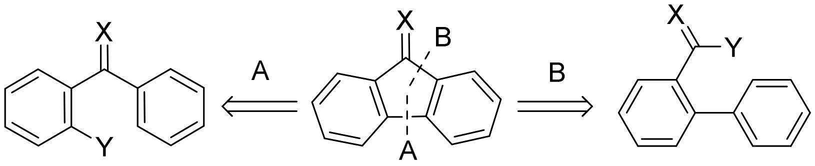


Figure 2. 1,2,3,4-Tetrasubstituted SBF and DS-IF compounds in comparison

2. Literature Review

2.1. Synthesis of fluorene compounds

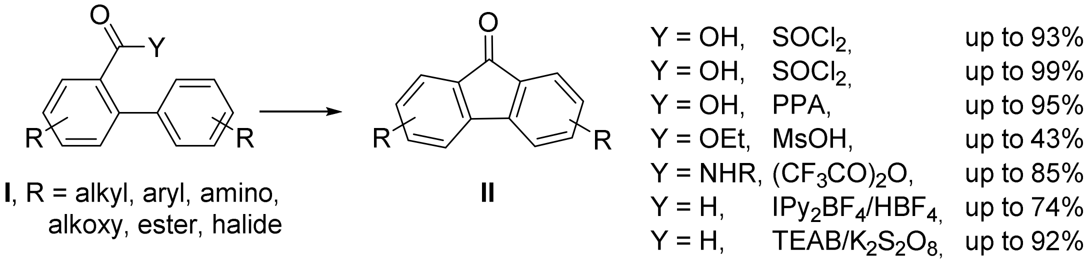
Polycyclic aromatic hydrocarbons (PAHs) are one of the most extensively studied organic substances for their unique properties and broad applications in many areas of chemistry, e.g. materials science. For the synthesis of fluorenes, mainly two disconnection approaches A and B have been used, leading to suitably substituted diphenyl methane compounds (Scheme 1, Disconnection A) or biphenyls as starting materials (Disconnection B). Ring-closing reactions can be performed under either transition metal-, Lewis acid-, or base-mediated or -catalyzed conditions.



Scheme 1. General disconnection approaches A and B of fluorenes

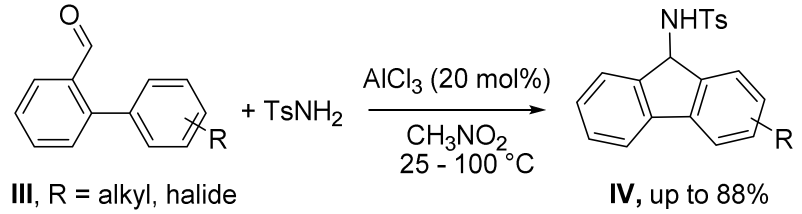
2.1.1. Acid- and base-catalyzed synthesis

One of the most used synthetic strategies, based on intramolecular Friedel-Crafts reaction starting from biphenyl or benzophenone precursors, was developed in the 1970s.[7] At present, a number of synthetic strategies utilizing substituted (1,1'-biphenyl)-2-carboxylic acids **I** and their derivatives (e.g. amides) are available (Scheme 2). As typical examples may serve reactions carried out in the presence of thionyl chloride ($SOCl_2$),[8a,b] polyphosphoric acid (PPA),[8c] methanesulfonic acid (MsOH)[8d] and trifluoroacetic anhydride ($(CF_3CO)_2O$)[8e] producing substituted fluorenones **II**. In addition, mixtures of bis(pyridine)iodonium(I) tetrafluoro-borate/HBF_4 (IPy_2BF_4/HBF_4)[8f] or tetraethylammonium bromide/potassium persulfate (TEAB/$K_2S_2O_8$)[8g] were also successfully used to perform ring closing Friedel-Crafts reaction of (1,1'-biphenyl)-2-carbaldehydes to fluorenones **II**.



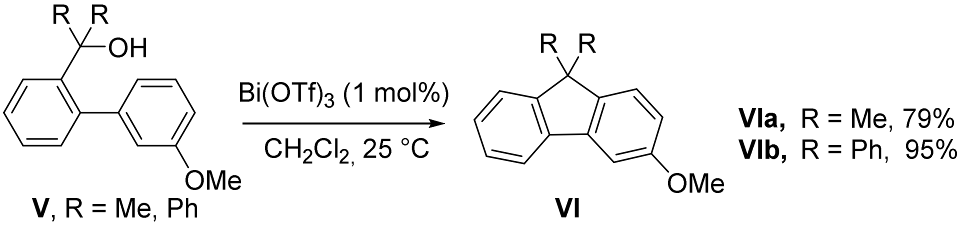
Scheme 2. Friedel-Crafts reactions of **I** to fluorenes **II**

Recently, $AlCl_3$-catalyzed reaction of differently substituted (1,1'-biphenyl)-2-carbaldehydes **III** in the presence of sulfonamide has been reported. It demonstrated that 9-aminofluorenes **IV** can be easily accessed in up to 88% (Scheme 3).[9]



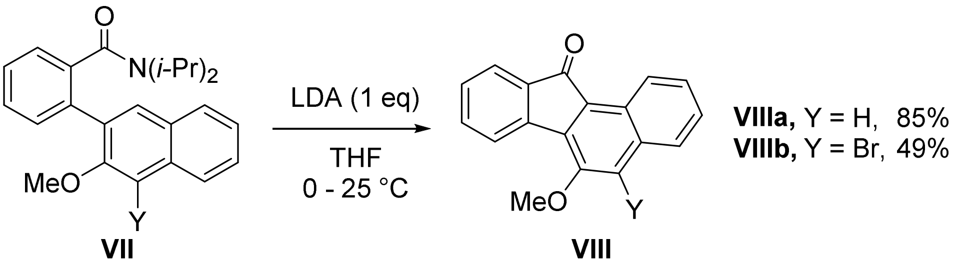
Scheme 3. $AlCl_3$-catalyzed condensation cyclization cascade from **III** to fluorenones **II**

In 2006, Rueping *et al.* introduced Friedel-Crafts benzylation of substituted 2-phenylbenzyl alcohols **V** with $Bi(OTf)_3$ as Lewis acid to promote cyclization to fluorenes **VI** in up to 95% yield (Scheme 4).[10]



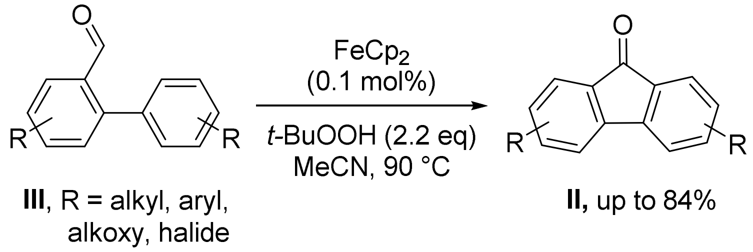
Scheme 4. $Bi(OTf)_3$-promoted intramolecular benzylation reaction of **V** to fluorenes **VI**

In addition to Lewis acids, base-mediated reactions have also been used to synthesize compounds with the fluorene scaffold. This method is based on the use of a sterically hindered base (LDA) in a combination with a tertiary amide **VII**, which undergoes cyclization to provide benzofluorenone **VIII**. However, this method suffers from a setback such as a limited functional group tolerance (Scheme 5).[11]



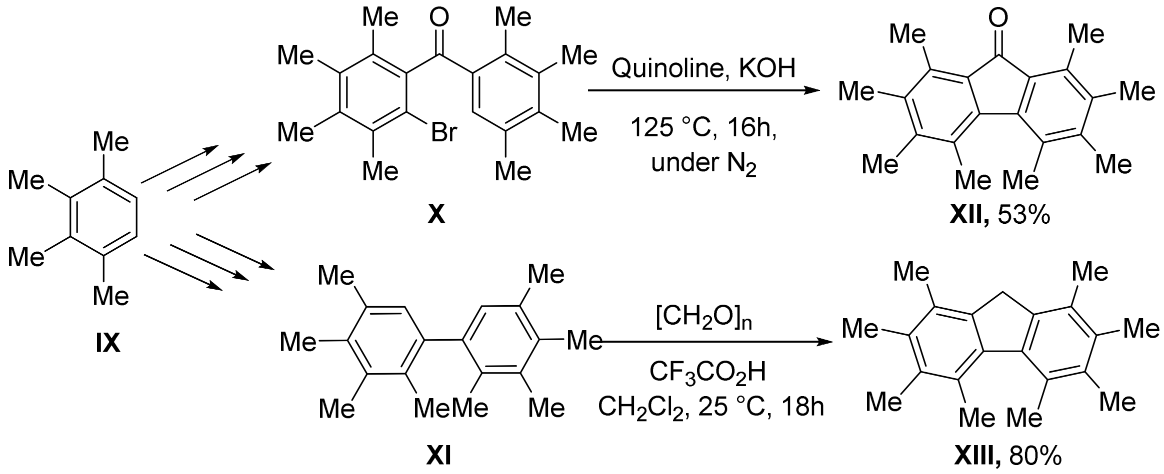
Scheme 5. LDA-mediated synthesis of benzofluorenes **VIII**

Another base-promoted synthetic approach was developed by Studer *et al.* They explored radical cross-dehydrogenative coupling *via* base-mediated homolytic aromatic substitution. They prepared fluorenones **II** in up to 84% from (1,1’-biphenyl)-2-carbaldehydes **III** using *t*-BuOOH as oxidant. $FeCp_2$ was the most effective radical chain initiator (Scheme 6).[12]



Scheme 6. Base-promoted radical cross-dehydrogenative coupling in (1,1’-biphenyl)-2-carbaldehydes **III** to fluorenones **II**

The syntheses of symmetrically octa- and nonamethylated fluorenes were studied as well, particularly by O’Hare[13a] and Tilley[13b]. Both synthetic procedures were based on the use of 1,2,3,4-tetramethylbenzene **IX** as the starting material. In the first case, O’Hare used highly alkaline conditions for cyclization of the monobrominated benzophenone **X** to fluorenone **XII** in 53% isolated yield. In the second approach, Tilley used electrophilic aromatic substitution and cyclization of **XI** with paraformaldehyde, producing the target fluorene **XIII** in 80% yield (Scheme 7).



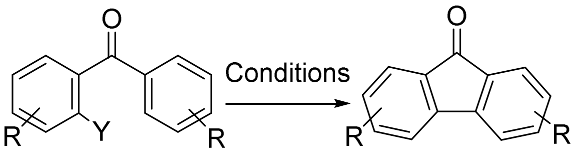
Scheme 7. Synthesis of octamethylfluorenone **XII** and octamethylfluorene **XIII**

2.1.2. Transition metal-catalyzed synthetic approaches

In addition to acid- and base-catalyzed synthetic approaches, many examples of transition metal-catalyzed reactions have emerged during the past several decades; however, many of them suffer from similar drawbacks and limitations as the aforementioned strategies.[14] As a typical starting material used in syntheses of functionalized fluorenes serve substituted benzophenones, diarylmethanes, or biaryl compounds. In addition to these precursors, also new methods based on utilization of various alkenes, alkynes and their derivatives for annulation have appeared.

2.1.2.1. Benzophenones/diarylmethanes as precursors

In the early 1980s, Ames and Opalko described the first pioneering studies on intramolecular dehydrogenative coupling of halogenated diaryl derivatives using catalytic Pd(II)-acetate under basic conditions, albeit with many side products.[15] As a representative of Rh-complex catalyzed formation of fluorenones, Blum *et al.* developed conversion of benzoic anhydride into fluorenones catalyzed by $RhCl(PPh_3)_3$ in the late 1960s.[16] More recently, numerous procedures based on intramolecular cyclization of substituted benzophenones **XIV** into target fluorenones **II** catalyzed by Pd-, Ag- or Cu-compounds have been reported (Scheme 8).



XIV, R = alkyl, aryl, alkoxy, halide

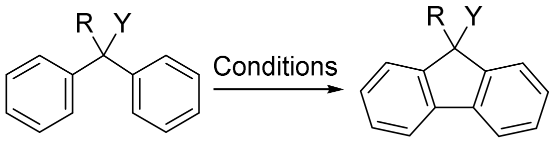
II

***A*^{1}**	Y = H	$Pd(OAc)_2$ (5 mol%), Ag_2O, K_2CO_3, TFA, 140 °C, 24h, up to 91%.
***A*^{2}**	Y = H	$Pd(OAc)_2$ (10 mol%), Ag_2O, TFA, 130 °C, 24h, up to 90%.
***A*^{3}**	Y = H	Pd(II) on MgLa (5 mol% Pd), Ag_2O, TFA:H_2O, 130 °C, 24h, up to 76%.
***B*^{1}**	Y = Br, I	$Pd(PPh_3)_4$ (6 mol%), KOAc, K_2CO_3, DMA, 110 °C, 23h, up to 96%.
***B*^{2}**	Y = Br, I	Cu(I) (15 mol%), K_3PO_4, DMF, 160 °C, MW, up to 90%.
C	Y = COOH	AgOAc (20 mol%), $K_2S_2O_8$, MeCN, 130 °C, MW, 1h, up to 84%.

Scheme 8. Synthetic pathways to fluorenones **II** from substituted benzophenones **XIV**

Shi[17a] and Cheng[17b] independently and concurrently developed Pd-catalyzed oxidative dehydrogenative dual C-H-functionalization of benzophenones in 2012 (Scheme 8, approach ***A*^{1}** and ***A*^{2}**). Recently, a heterogeneous catalytic dual C-H activation system (Pd on MgLa) have been also developed (Approach ***A*^{3}**).[17c] Direct intramolecular arylation of substituted halogenated benzophenones was carried out under Pd-[17d] or Cu-catalysis[17e] (Approach ***B*^{1}** and ***B*^{2}**). In addition to these approaches, radical decarboxylative C-H arylation under Ag-catalysis was reported as well (Approach ***C***).[17f]

Several other diarylmethane derivatives were applied in syntheses of fluorene compounds. Miura *et al.* presented Rh- and Ir-catalyzed dehydrogenative cyclization *via* double C-H bond cleavage of **XV** to form fluorene **XVI** in the presence of Cu salts (Scheme 9).[18]

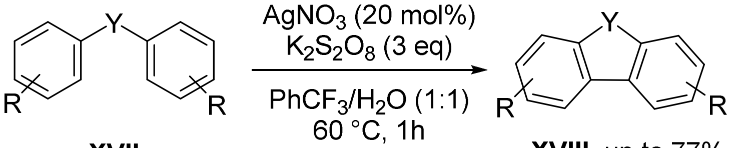


XV, **XVI**
R = alkyl, aryl, alkoxy, halide

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

Scheme 9. Rh- and Ir-catalyzed synthesis of fluorene **XVI** from diarylmethanes **XV**

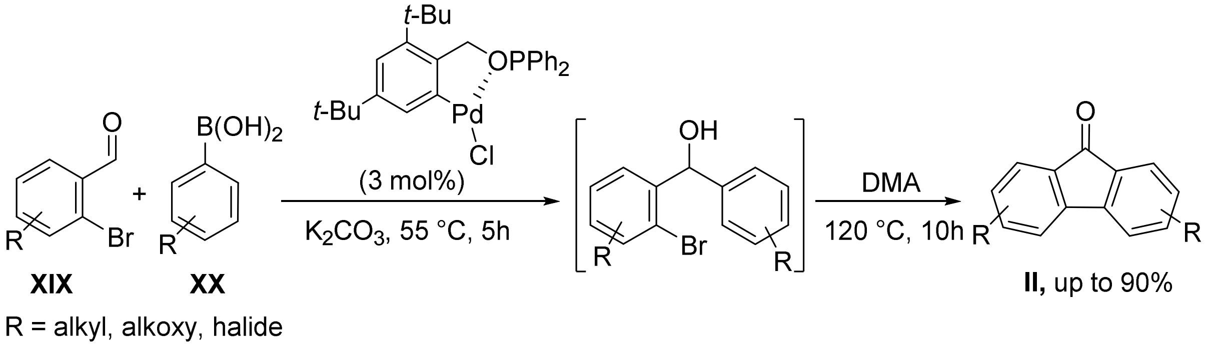
Another example of syntheses of compounds with the fluorene scaffold from diaryl ether, benzophenone, or diarylmethane derivatives consists of a Ag-catalyzed Pschorr-type radical cyclization. It furnished the target benzofurane, fluorenone, and fluorene compounds in up to 77% isolated yields (Scheme 10).[19]



XVII **XVIII,** up to 77%
R = alkoxy, ester, halide
Y = O, CH_2, CHOH, CO

Scheme 10. Ag-catalyzed synthesis fluorenes **XVIII** from diarylethers, benzophenones, or diarylmethanes

In addition to these approaches, a two-step Pd-complex catalyzed procedure starting from substituted bromobenzaldehydes and arylboronic acids was developed. In a one-pot reaction various arylboronic acids **XIX** were added to the carbonyl group of 2-bromobenzaldehydes **XX** initially forming intermediate benzylic alcohols and, upon heating, the intermediate underwent cyclization *via* a C-H activation and oxidation sequence, producing the target fluorenone compounds **II** in up to 90% (Scheme 11).[20]

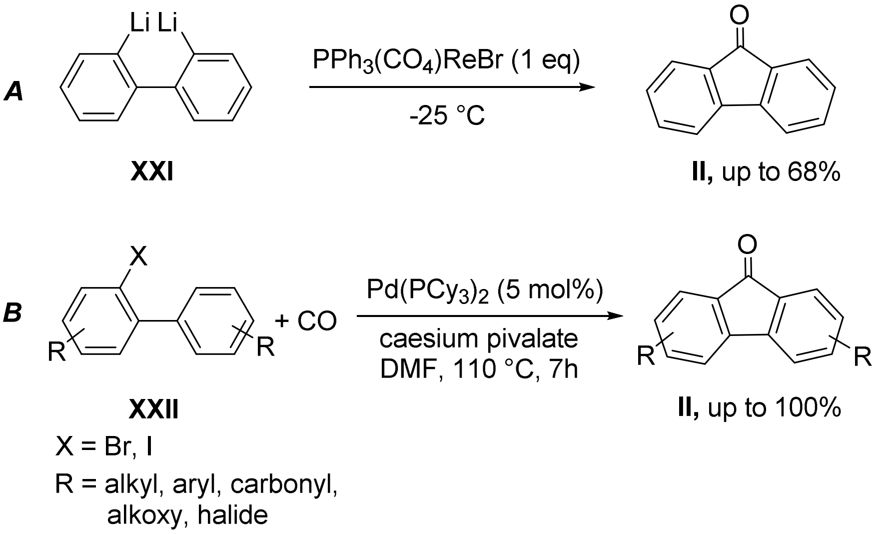


Scheme 11. One-step synthesis of 2-bromobenzaldehydes **XIX** with arylboronic acids **XX**

2.1.2.2. Syntheses starting from 1,1'-biphenyls and tandem reactions

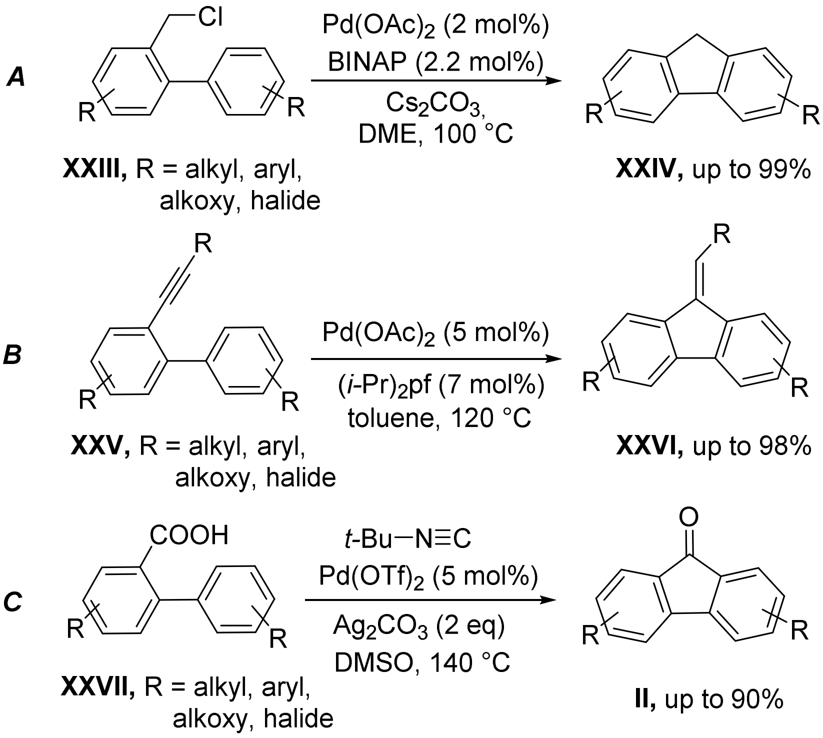
2.1.2.2.1. 1,1'-Biphenyls as precursors

The second approach, using transition metal-catalyzed reactions to provide fluorene and fluorenone compounds, is based on the use of appropriately substituted biphenyls. One of the first reports on the synthesis of fluorenes based on the use of transition metal compounds, albeit a stoichiometric one, appeared in the late 1980s. It was based on reactions of 2,2´-dilithiobiphenyls **XXI** with $PPh_3(CO_4)ReBr$ that served as the CO source. The corresponding substituted fluorenones **II** were obtained in up to 68% isolated yields (Scheme 12, ***A***).[21a] In 2000, Larock reported a Pd-complex catalyzed cyclocarbonylation of 2-halo-1,1'-biphenyls **XXII** with CO (1 atm) to synthesize fluorenones **II** in up to quantitative yields (Scheme 12, ***B***).[21b,c]



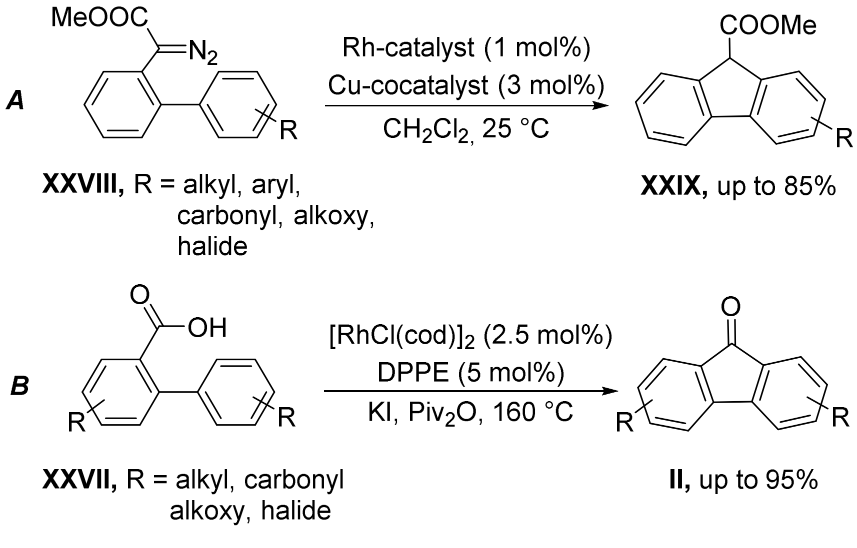
Scheme 12 Synthetic procedure for fluorenones **II** from (***A***) dilithiobiphenyl **XXI** or (***B***) 2-halo-1,1'-biphenyls **XXII**

Currently, many approaches to fluorenes are based on Pd-complex catalyzed C-H bond activation and functionalization. As typical examples may serve transformations of 2-(halomethyl)-1,1'-biphenyls **XXIII** or 2-alkynyl-1,1'-biphenyls **XXV** to fluorenes **XXIV** (Scheme 13, ***A***)[22a] and **XXVI** (Scheme 13, ***B***).[22b] The reactions proceed *via* an intramolecular dehydrogenative cyclization with good-to-excellent yields in all reactions. In addition, a Pd-catalyzed decarboxylative cyclization of (1,1'-biphenyl)-2-carboxylic acids **XXVII** using *t*-butyl isocyanide as the carbonyl source was also explored and it gave rise to substituted fluorenones **II** (Scheme 13, ***C***).[22c]



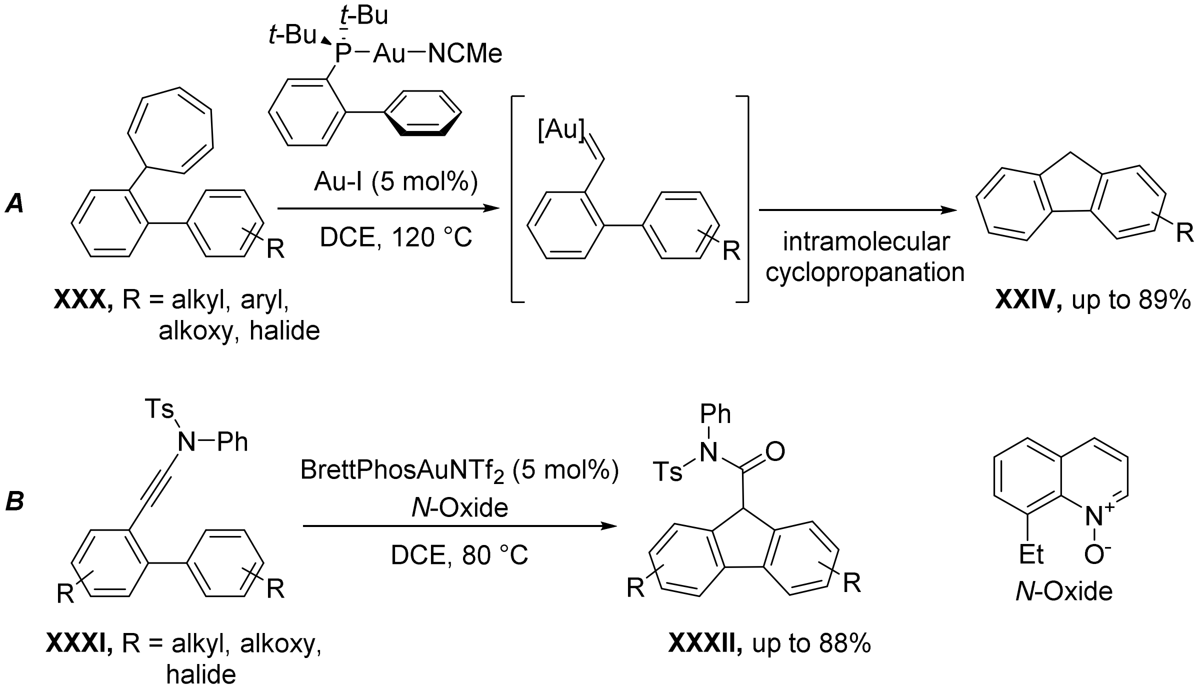
Scheme 13. Pd-catalyzed synthesis of fluorenones **II**

Although Pd-complex catalyzed methods have been the most commonly used for the synthesis of fluorene derivatives, also Rh-complex catalyzed procedures have been developed as well. These methods have found its application either in intramolecular insertion of carbenes in biaryldiazoacetates **XXVIII** to form fluorenyl carboxylates **XXIX** (Scheme 14, ***A***, the patent did not show any specific catalytic system)[23a] or in intramolecular acylation of biarylcarboxylic acids **XXVII** to form fluorenones **II** (Scheme 14, ***B***).[23b]



Scheme 14. Rh-catalyzed synthesis of fluorene-9-carboxylates **XXIX** and fluorenones **II**

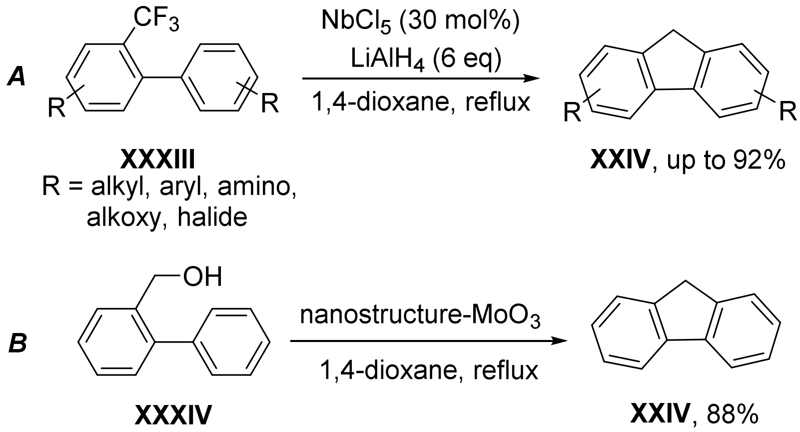
In 2014, the groups of Echavarren and Ye independently published two different Au-catalyzed synthetic procedures to form fluorenes. Echavarren showed that a Au-complex catalyzed retro-Buchner reaction of 2-(2,4,6-cycloheptatrien-1-yl)-1,1'-biphenyls **XXX** provided fluorenes **XXIV** (Scheme 15, ***A***).[24a] Ye *et al.* exploited a Au-complex intermolecular oxidative cyclization 2-alkynyl-1,1'-biphenyls **XXXI** in the presence of *N*-oxides to fluorene-9-carboxylic acid amides **XXXII** (Scheme 15, ***B***).[24b]



Scheme 15. Au-catalyzed formation of **XXIV** and fluorenylcaboxylic acid amides **XXXII**

The last examples of transition metal-catalyzed or -promoted strategies for the synthesis of fluorenes from the parent biaryl precursors are Mo- and Nb-catalyzed reactions.

Double activation of C-F and C-H bonds in substituted 2-trifluoromethylbiphenyls **XXXIII** with low valent Nb-compounds (prepared by reduction with $LiAlH_4$) was used for the synthesis of fluorenes **XXIV** in up to 92% yield (Scheme 16, ***A***).[25a] In the area of Mo-catalyzed reactions, nanostructured MoO_3 was used to initiate intramolecular benzylation (Friedel-Crafts reaction) of [(1,1'-biphenyl)-2-yl]methanol **XXXIV** forming fluorene **XXIV** in 88% yield (Scheme 16, ***B***).[25b]

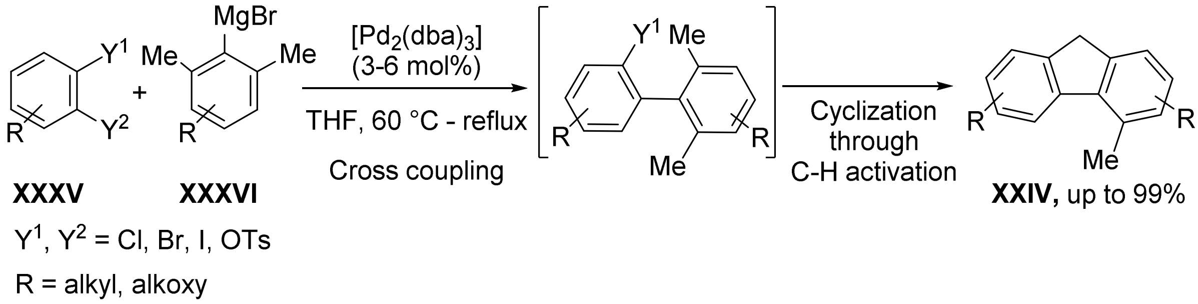


Scheme 16. Nb- and Mo-catalyzed formation of fluorenes **XXIV**

2.1.2.2.2. Tandem syntheses *via* biaryl intermediates

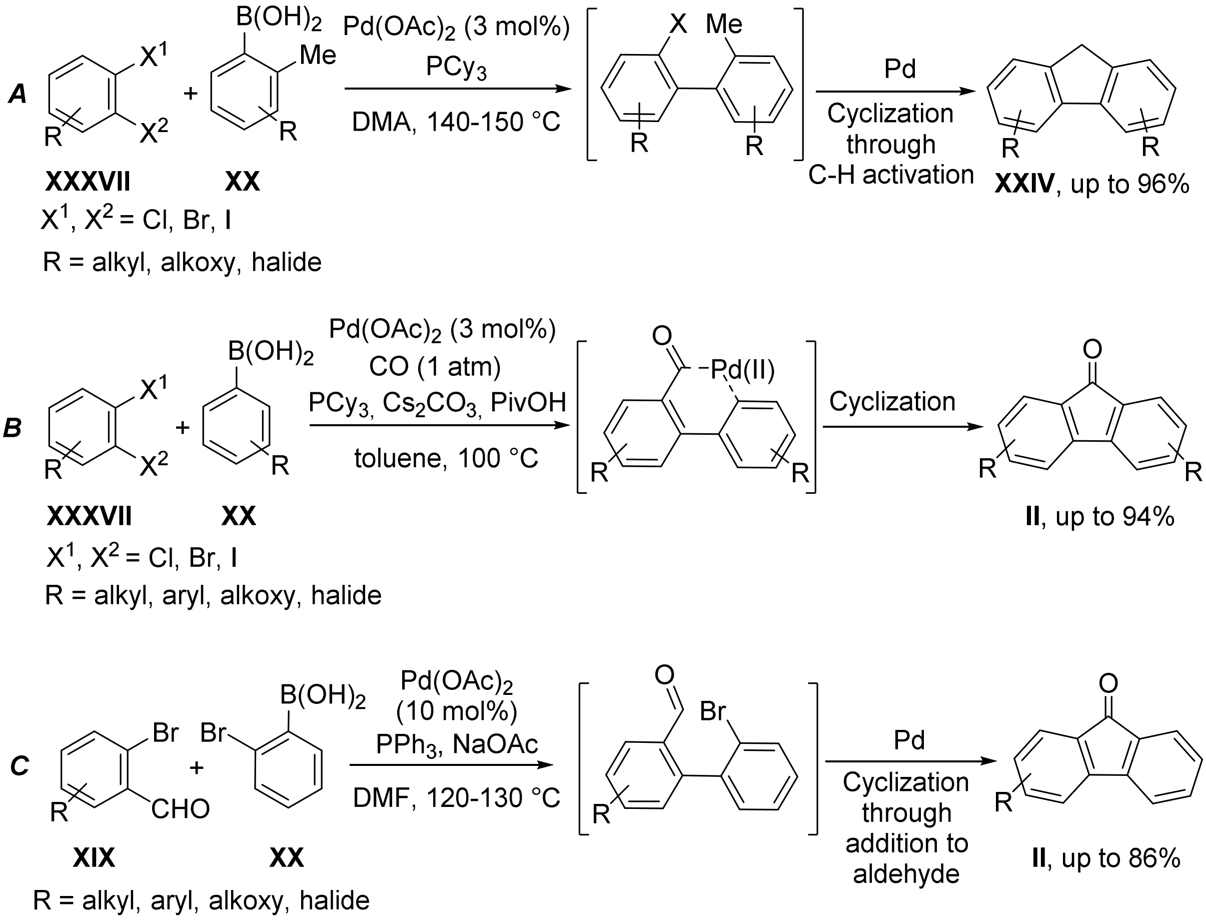
Development of tandem procedures for preparation of fluorenes *via* biphenyl intermediates is highly desirable, because they shorten the reaction sequence and avoid the need for the synthesis of the intermediate. The tandem procedures comprise two synthetic steps based on two reaction. In most cases the first step is a cross-coupling reaction that provides the intermediate biphenyls. These then, without isolation, undergo the second step: a ring-closing reaction.

In 2006, Hu *et al.* published a series of Pd-complex catalyzed reactions of variously substituted 1,2-dihaloarenes or tosylated haloarenes **XXXV** with sterically hindered Grignard reagents **XXXVI** forming the biphenyl intermediates. The subsequent cyclization proceeded *via* the C-H bond activation of the methyl group followed by cross coupling producing the desired fluorenes **XXIV** (Scheme 17).[26]



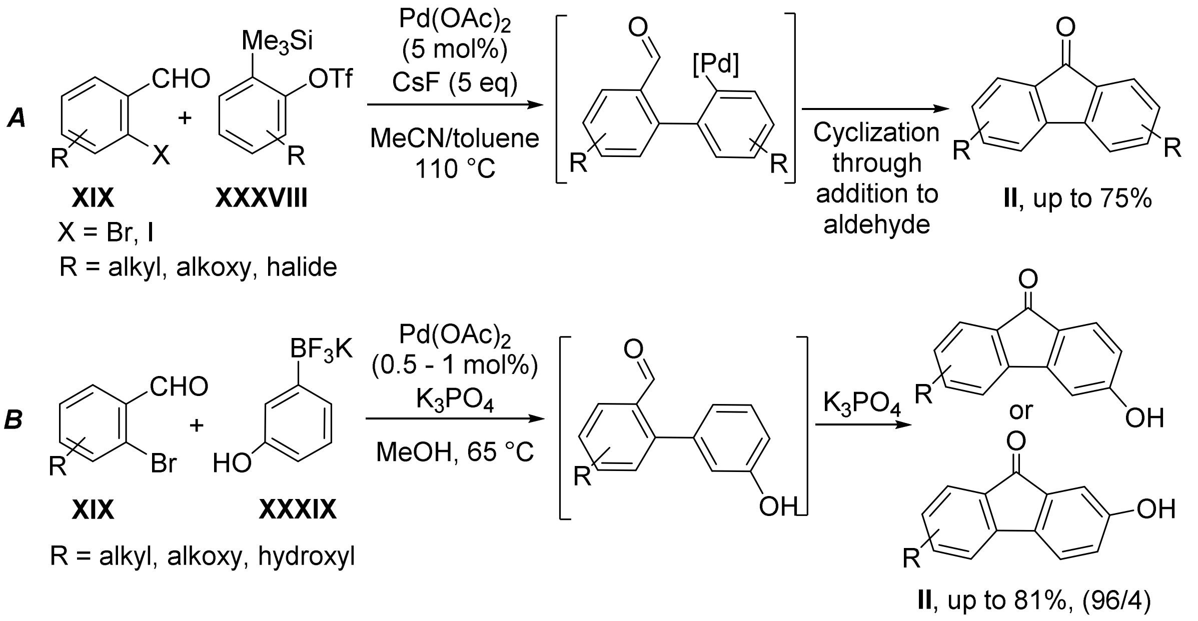
Scheme 17. Tandem Pd-catalyzed synthesis of fluorenes **XXIV**

In addition to Grignard reagents, various arylboronic acids were used in Suzuki cross-coupling with substituted haloarenes. Tandem Pd-catalyzed Suzuki cross-coupling of substituted 2-methylphenylboronic acids **XX** with 1,2-dihaloarenes **XXXVII** followed by cyclization through the C-H bond activation was used for synthesis of fluorenes **XXIV** (Scheme 18, ***A***).[27a] A similar approach was also used in the reaction of 1,2-dihaloarenes **XXXVII** and arylboronic acids **XX** under CO atmosphere in Pd-catalyzed synthesis to provide fluorenones **II** (Scheme 18, ***B***).[27b] Alternatively, Suzuki cross-coupling of 2-bromobenzaldehydes **XIX** and 2-bromophenylboronic acids **XX** giving rise to intermediate 2’-bromo-(1,1’-biphenyl)-2-carbaldehydes was also used as the first step. It was then followed by intramolecular addition of arylpalladium species to the carbonyl group forming fluorenones **II** (Scheme 18, ***C***).[27c]



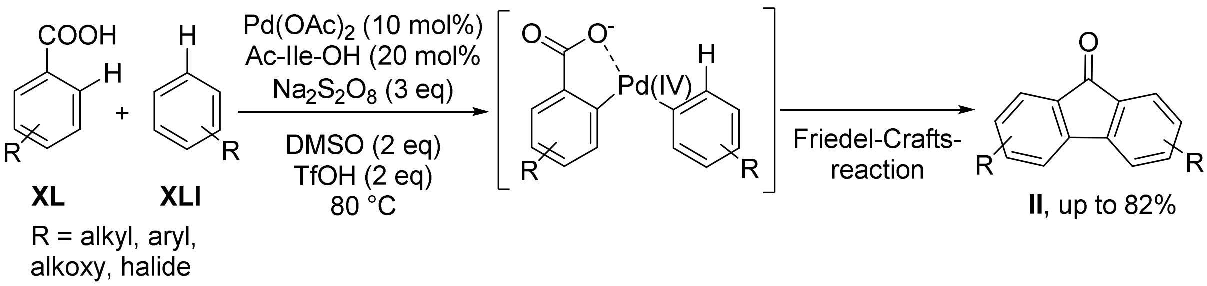
Scheme 18. Tandem Pd-catalyzed procedures for synthesis of various fluorenes **XXIV** and fluorenones **II**

In addition to this approach, 2-halobenzaldehydes have been often used for the Pd-catalyzed cross-coupling step with other substrates, e.g. silanes and boronates. In 2005, Larock *et al.* reported a Pd-catalyzed tandem annulation of 2-halobenzaldehydes **XIX** and 2-trimethylsilylaryl triflates **XXXVIII** to furnish fluorenones **II** in up to 75% yields. In this approach, the intermediate aryne was formed *in situ* and it was subsequently added to arylpalladium species, forming a new arylpalladium species. This intermediate was then intramolecularly added to the carbonyl group giving rise to fluorenones **II** (Scheme 19, ***A***).[28a,b] Another tandem cyclization based on Pd-catalyzed cross-coupling of 2-bromobenzaldehyde **XIX** and potassium 3-hydroxyphenyl trifluoroborate **XXXIX** followed by cyclization to fluorenones **II** was reported (Scheme 19, ***B***).[28c]



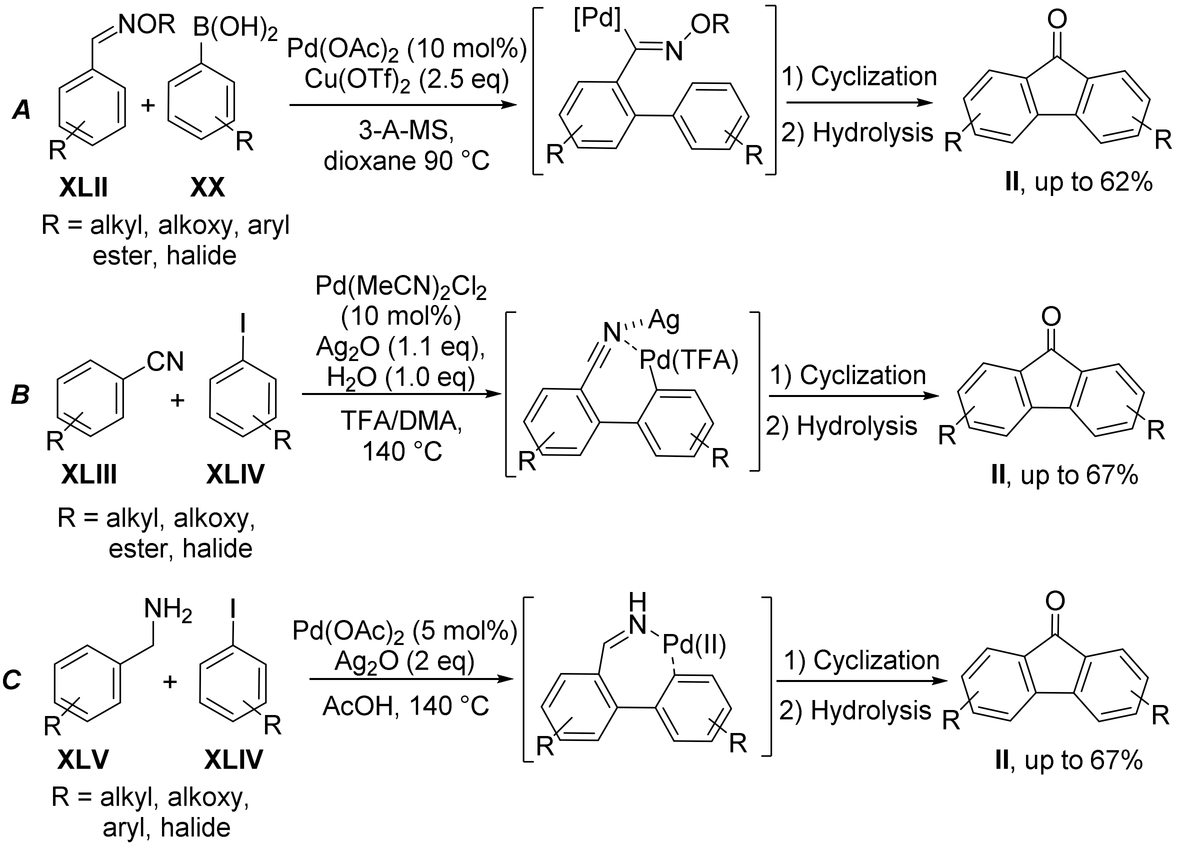
Scheme 19. Pd-catalyzed method for synthesis of fluorenones **II**

In 2016, You *et al.* successfully conducted, for the first time, chelation-assisted C-H activation of aromatic carboxylic acids. They used Pd-catalyzed *ortho*-selective oxidative C-H cross-coupling of benzoic acids **XL** with arenes **XLI**, followed by intramolecular Friedel-Crafts acylation to furnish target fluorenones **II** (Scheme 20).[29]



Scheme 20. Pd-catalyzed C-H cross-coupling of carboxylic acids **XL** followed by Friedel-Crafts reaction to fluorenes **II**

Finally, other examples of tandem Pd-catalyzed cross-coupling and cyclization procedures involved the use of oximes, nitriles or benzyl amines. Cheng[30a,b] and Shi[30c] reported a Pd-catalyzed functionalization of *ortho*-methyl oximes **XLII** with arylboronic acids **XX** to biphenyl aldoximes, followed by cyclization (Scheme 21, ***A***). The subsequent acidic hydrolysis yielded fluorenones **II**. This approach was similar to the previous mechanistic studies by Larock *et al.*[30d] The second approach used Pd-catalyzed remote nitriledirected dual C-H activation of substituted benzonitriles **XLIII** and subsequent reaction with aryl iodides **XXIV** (Scheme 21, ***B***).[30e,f] Interestingly, even reactions of simple benzylamines **XXXV** with aryl iodides **XXXIV** were suitable for tandem Pd-catalyzed synthesis of fluorenones **II** (Scheme 21, ***C***).[30g]

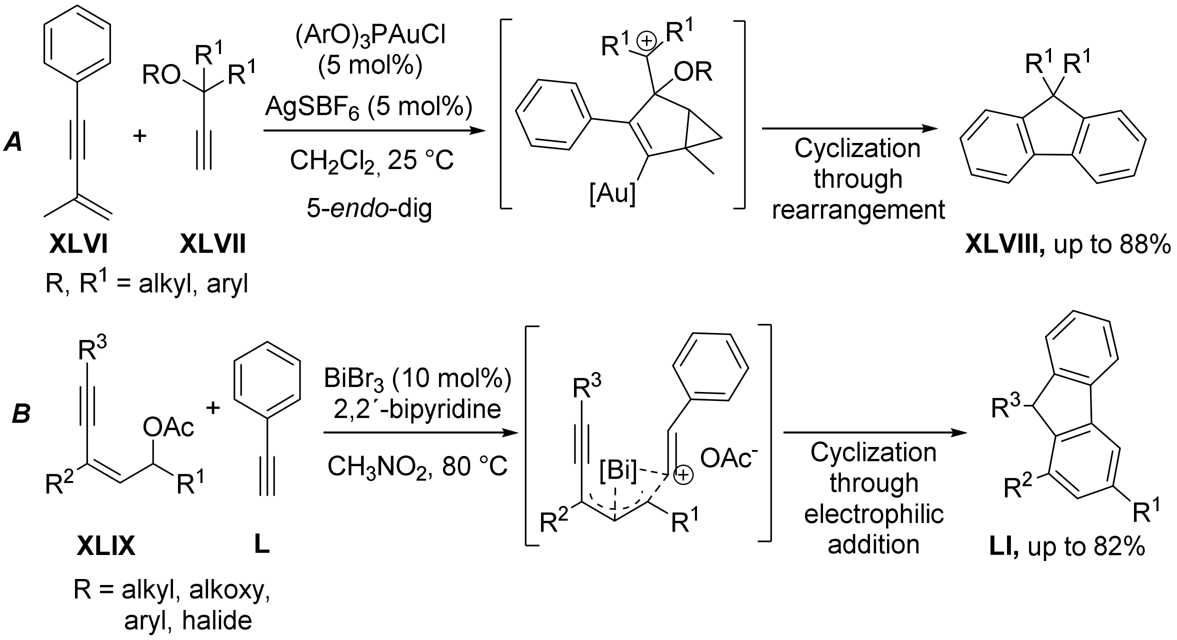


Scheme 21. Syntheses of fluorenones **II** by using Pd-catalyzed tandem reaction

2.1.2.3. Alkene and alkyne derivatives as precursors

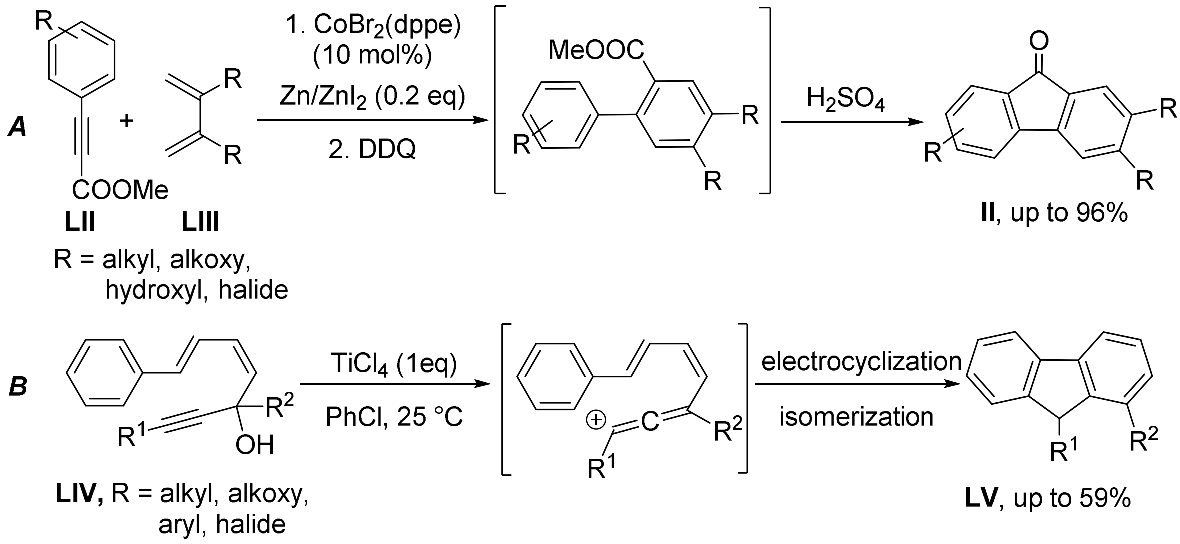
Following two previously described transition metal-catalyzed approaches that were based on the use of benzophenone/diarylmethane derivatives (Section 2.1.2.1) or various substituted biphenyl precursors (Section 2.1.2.2), other synthetic approaches using various substituted alkenes and alkynes as starting materials have also emerged in the last decades.

The first synthetic strategy is based on the annulation of enynes and alkynes. In the first method fluorenes **XLVIII** were synthesized under Au-catalysis from 1,3-enynes **XLVI** and propargyl esters **XLVII**. The reaction was initiated by intermolecular cyclopropanation of enynes *via* gold carbenoids, which were formed by rearrangement of propargyl esters. The rearrangement started with coordination of the cationic gold catalyst followed by 5-*endo*-dig cyclization that lead to formation of tertiary carbocation. Then, after several other skeletal rearrangements, cyclopropyl ring opening and nucleophilic substitution followed forming the target fluorene **XLVIII** (Scheme 22, ***A***).[31a] The second approach, using appropriately substituted enynes and alkynes as starting material, was reported by Liang *et al.* They successfully applied $BiCl_3$-catalyzed reaction of (*Z*)-pent-2-en-yl acetates **XLIX** with ethynylarenes **L** *via* tandem isomerization/Friedel-Crafts intermolecular electrophilic reaction/cycloisomerization/aromatization sequence to form substituted fluorenes **LI** (Scheme 22, ***B***).[31b,c]



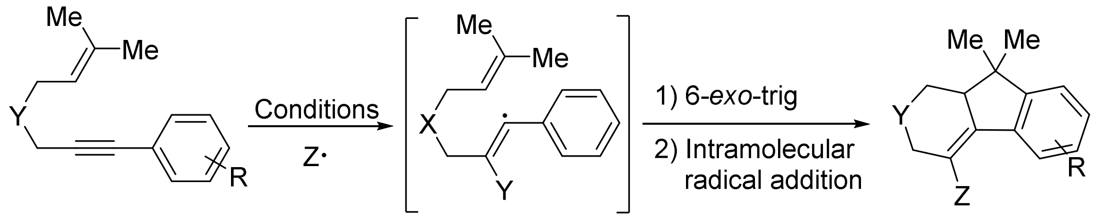
Scheme 22. Au- and Bi-catalyzed enyne and alkyne-based annulation reactions to fluorenes **XLVIII** and **LI**

In 2013, two new similar approaches were reported for the synthesis of fluorenes using reactions of dienes with alkynes. They involved either inter- or intramolecular reaction pathways. The intermolecular approach to fluorenones **II** was based on the following reaction sequence: Co-catalyzed Diels-Alder reaction of aryl-substituted propiolates **LII** and appropriately substituted dienes **LIII**, followed by DDQ oxidation providing *in situ* a biphenyl intermediate, followed by acidic Friedel-Crafts cyclization to form target fluorenone **II** (Scheme 23, ***A***).[32a] The intramolecular pathway utilized $TiCl_4$-mediated cyclization of substituted hept-4,6-diene-1-yn-3-ols **LIV**. The propargylic alcohol was converted in the presence of $TiCl_4$ into the diene-allenylic cation intermediate through Meyer-Schuster rearrangement, which underwent electrocyclization and isomerization, thereby forming the target fluorenes **LV** (Scheme 23, ***B***).[32b]



Scheme 23. Conversion of alkynes and dienes to fluorenes **II** and **LV**

Lastly, a class of not fully conjugated fluorenes, i.e. compounds with incomplete aromatic systems, can also be assembled using unsaturated molecular systems. Radical cyclization of 1,6-enynes **LVI** to unsaturated compounds with the fluorene scaffold **LVII** was conducted using either $AgSCF_3$[33a] or Ag(OAc) in the presence of diphenylphosphine oxide (Scheme 24).[33b] It underwent a regioselective radical intramolecular addition to the alkyne moiety through the same mechanistic pathway. The addition yielded an alkenyl radical intermediate, which subsequently formed the secondary radical by 6-*exo*-trig ring closing. Intramolecular addition of this intermediate to the aromatic ring formed the target compounds **LVII**.



LVI

LVII

Y = O, CH_2, NTs, $C(COOMe)_2$

R = alkyl, alkoxy, aryl, halide

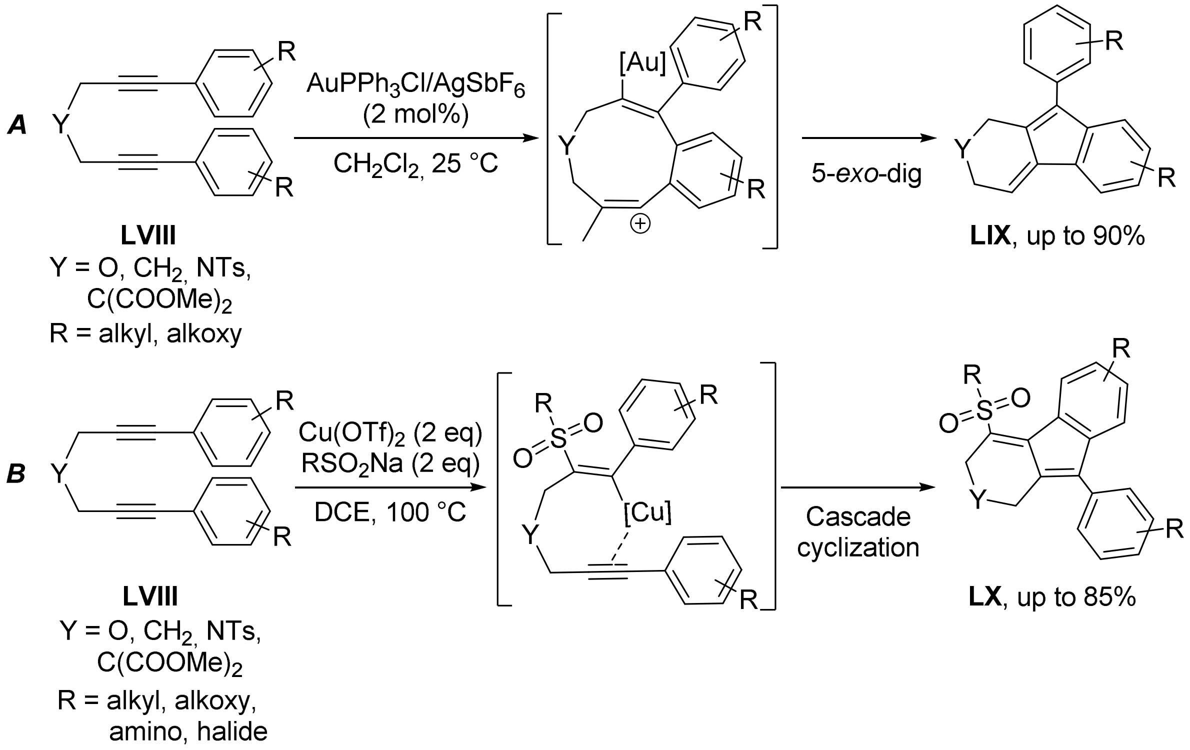
Conditions for:

Z = $\cdot SCF_3$: $AgSCF_3$ (1.5 eq), $K_2S_2O_8$ (3 eq), HMPA (0.5 eq), terpyridine (10 mol%), MeCN/DMF, 80 °C, up to 87%.

Z = $\cdot POR_2$: AgOAc (10 mol%), $HPOR_2$, $Zn(NO_3)_2$ (2 eq), MeCN, 100 °C, up to 85%.

Scheme 24. Ag-promoted radical formation of non-fully aromatic fluorenes **XLVII**

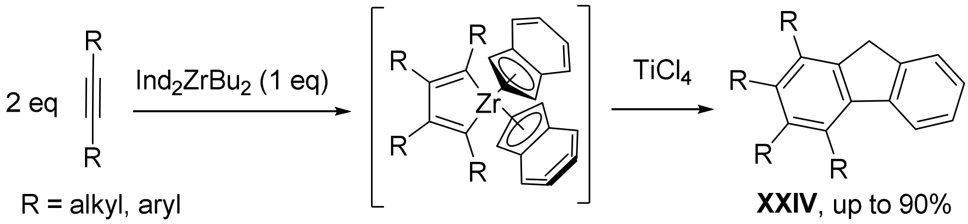
In addition to the Ag-mediated radical approach, also Au-catalysis and, very recently, Cu-mediated cyclization of 1,6-diynes were also reported. Au-catalysis of substituted, non-activated diynes **LVIII** promoted intramolecular [3+2] cycloaddition *via* a Au-(I)-containing π-alkyne moiety to form a vinylgold intermediate. Subsequently, this intermediate underwent either 5-*exo*-dig or Nazarov cyclization, thus forming the fluorenes **LIX** (Scheme 25, ***A***).[34a] In the second approach, treatment of substituted 1,6-diynes **LVIII** with Cu and sodium sulfonate led to the formation of two new C-C bonds and the assembly of fluorenes **LX**. The reaction involved tandem nucleophilic addition of sulfonate and the subsequent cascade cyclization *via* an ionic mechanism (Scheme 25, ***B***).[34b]



Scheme 25. Au-catalyzed and Cu-mediated annulations to of **LVIII** to **LIX** and **LX**

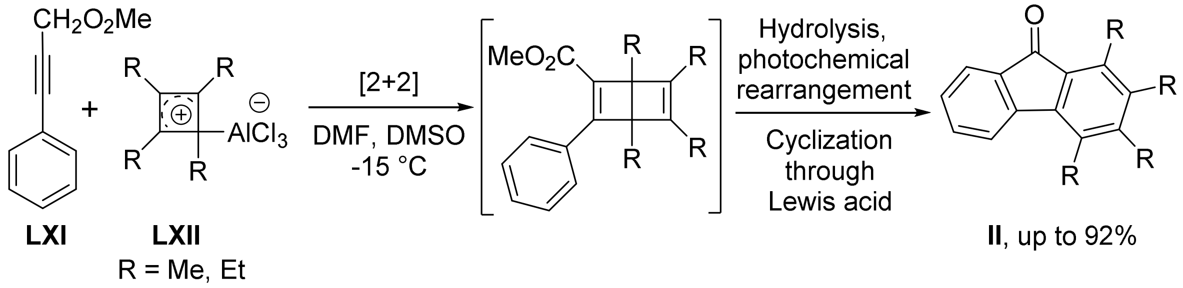
2.1.3. 1,2,3,4-Tetrasubstituted fluorenes

Synthesis of 1,2,3,4-tetrasubstituted fluorenes is quite challenging due to high level of substitution. In this respect only a handful of procedures have been developed so far. One of the first approaches to 1,2,3,4-tetrasubstituted fluorenes was developed in 2009 by Takahashi *et al.* and was based on Lewis-acid mediated rearrangement of homo-substituted bis(indenyl)zirconacyclopentadienes, prepared by reductive dimerization of the corresponding alkynes with reduced titanocene. The zirconacyclopentadienes were treated with an excess of $TiCl_4$ that promoted the skeletal rearrangement, formally addition of the ziconacyclopentadiene moiety to the indenyl ligand, resulting in the formation of 1,2,3,4-tetrasubstituted fluorenes **XXIV** in up to 90% yield (Scheme 26).[35]



Scheme 26. Zr-catalyzed formation of 1,2,3,4-tetrasubstituted fluorenes

The second approach, for the preparation of the same tetrasubstituted fluorene scaffold was based on the use of Dewar benzenes. The Dewar benzenes were prepared by a reaction of methyl phenylpropynoate **LXI** with tetraalkylcyclobutadiene-$AlCl_3$ complexes **LXII**. Then the ester moiety was hydrolyzed to free carboxylic acid and photochemically rearranged to substituted (1,1'-biphenyl)-2-carboxylic acids. The treatment of the acids with thionyl chloride furnished the 1,2,3,4-tetrasubstituted fluorenones **II** (Scheme 27).[8a]

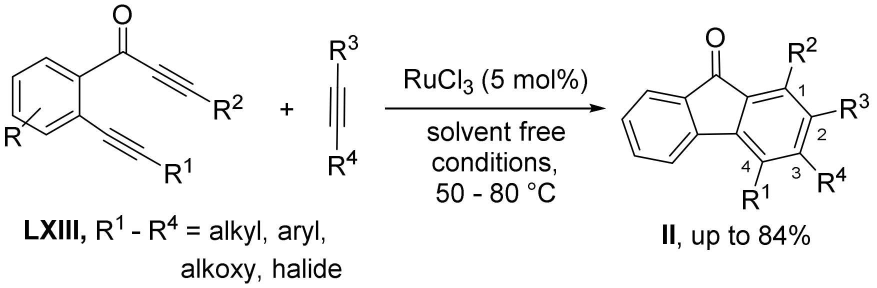


Scheme 27. Formation of a 1,2,3,4-tetrasubstituted fluorenones **II** from substituted cyclobutadienes

Since the above mentioned methods to 1,2,3,4-tetrasubstituted fluorene and fluorenones have limitations with respect to substituents R, development of other methods was desirable.

As a part of my previous project I studied a new reaction pathway for the synthesis of 1,2,3,4-tetrasubstituted fluorenes based on a transition metal catalyzed [2+2+2] cyclotrimerization of symmetrically substituted diynes with alkynes to provide various alkyl and aryl substituted 9*H*-fluorenes in up to 93% isolated yield (see section 4.1.1).[36]

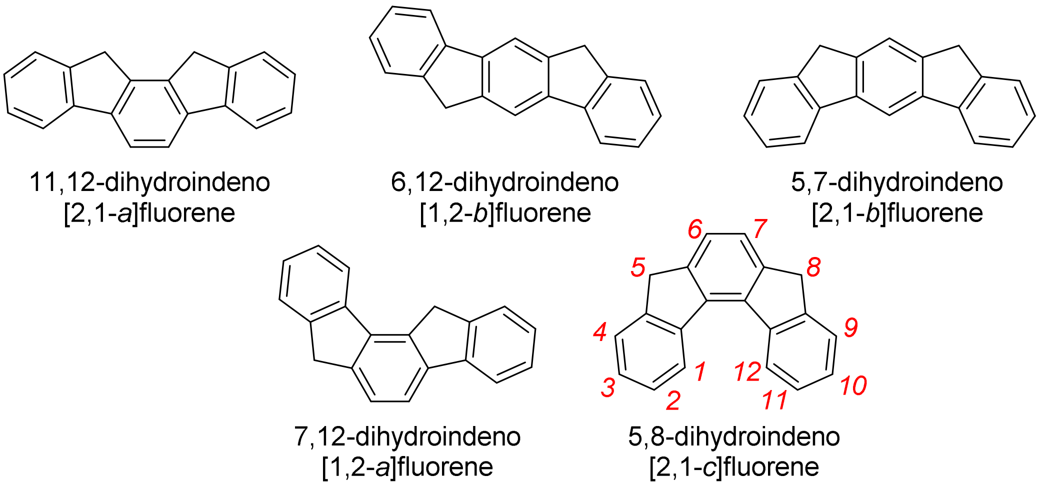
Soon after publishing of my study, the group of Ratovelomanana-Vidal *et al.* reported in 2016 modified [2+2+2] cyclotrimerization reaction of diynones **LXIII** with alkynes to furnish fluorenones **II** by using Ru-catalysis under simple conditions (solvent-free, no additional ligands, no additives) in up to 84% yield (Scheme 28).[37]



Scheme 28. Ru-catalyzed route to unsymmetrically substituted fluorenones **II**

2.2. Synthesis of indeno[2,1-*c*]fluorene compounds

In contrast to the vast research on syntheses of fluorenes conducted thus far, few synthetic strategies for indeno[2,1-*c*]fluorenes have been developed or are available. In fact, only a handful of studies have been published after the pioneering work of Ginsburg, Chardonnens and Stanfield, in the 1960s. They synthesized indeno[2,1-*c*]fluorenes *via* Lewis acid-assisted annulations of 3,3’-bi-(indenyl-cyclohepta-2,7-dienyls) or phenylcinnamalones.[38] The family of indenofluorenes consist of five different constitutional isomers,[39] chemistry and synthesis of which have been studied to different extents. These studies have mostly focused on the synthesis of indeno[1,2-*a*]fluorene, indeno[2,1-*a*]fluorene, indeno[1,2-*b*]fluorene and indeno[2,1-*b*]fluorene isomers, overlooking the indeno[2,1-*c*]fluorene isomer (Figure 3).


11,12-dihydroindeno [2,1-*a*]fluorene

6,12-dihydroindeno [1,2-*b*]fluorene

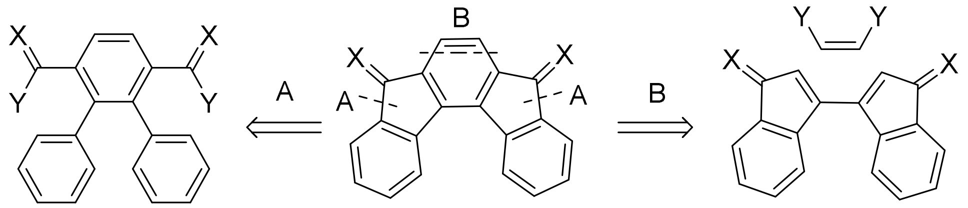
5,7-dihydroindeno [2,1-*b*]fluorene

7,12-dihydroindeno [1,2-*a*]fluorene

5,8-dihydroindeno [2,1-*c*]fluorene

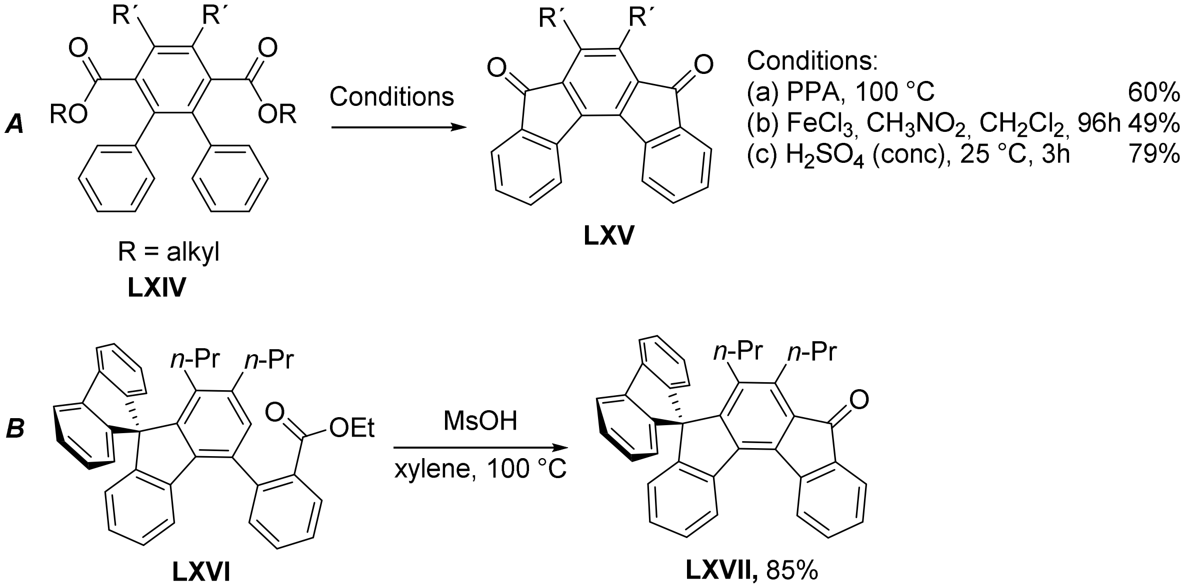
Figure 3. Isomers of the dihydroindenofluorene family

Furthermore, almost all known examples of the reported synthesis of indeno[2,1-*c*]fluorenes are based on either intramolecular Friedel-Crafts reaction (Scheme 29, Disconnection approach A), on intermolecular Diels-Alder reaction (Disconnection approach B) or on a combination of both.



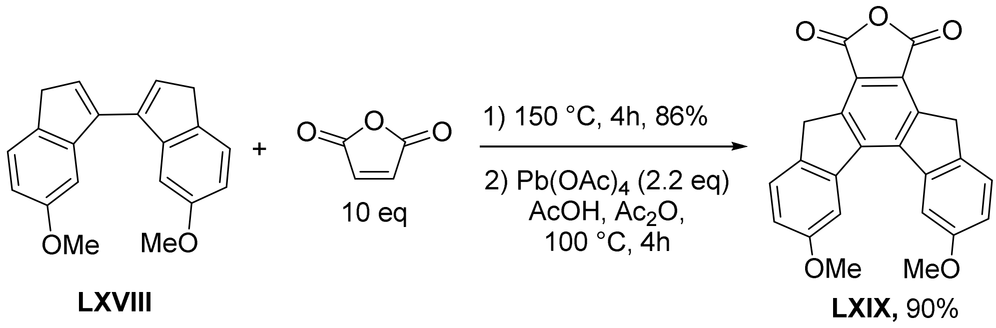
Scheme 29. General disconnection approaches A and B for indeno[2,1-*c*]fluorenes

The most intramolecular Friedel-Crafts reactions (Disconnection A) use substituted terphenyls bearing diester groups **LXIV** and acids, e.g. polyphosphoric acid (PPA),[6b] $FeCl_3$[6c] or H_2SO_4,[6d] to catalyze the double Friedel-Crafts reaction to furnish indeno[2,1-*c*]fluorendiones **LXV** (Scheme 30, ***A***). Moreover, a similar Friedel-Crafts reaction for the assembly of **LXVII** was also reported by Poriel *et al.*, in 2015. They started from substituted 9,9'-spirobifluorene **LXVI** bearing 2-ethyl benzoate functionality at position 4 of the core structure and used MsOH to mediate the cyclization (Scheme 30, ***B***).[6a]



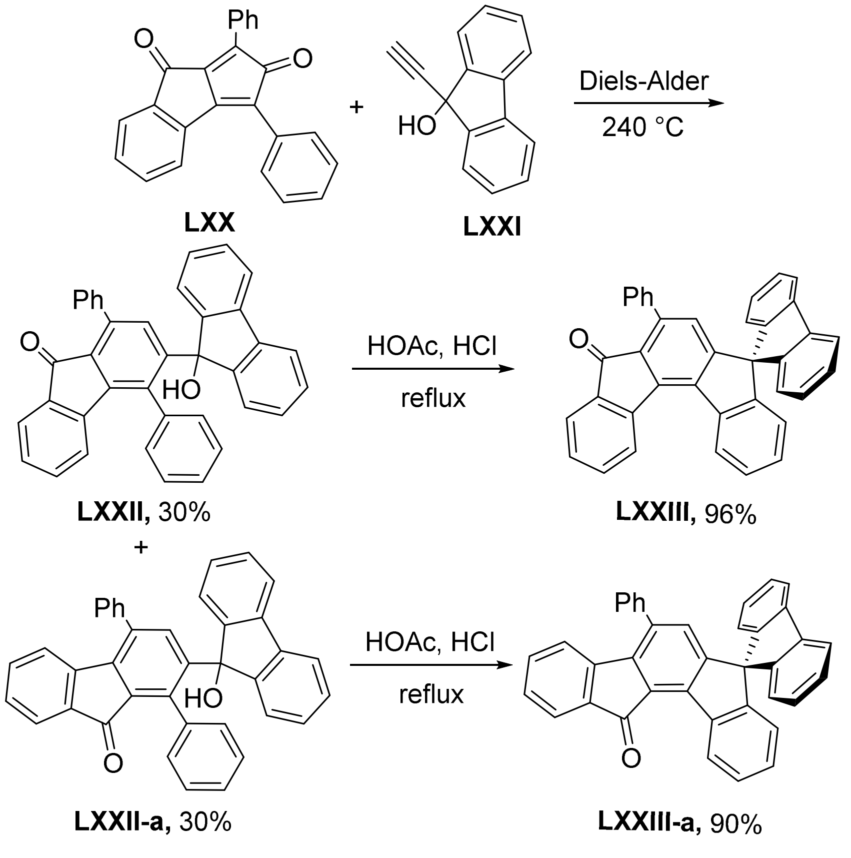
Scheme 30. Intramolecular Friedel-Crafts reaction for synthesis of indeno[2,1-*c*]fluorene **LXVII**

In 2014, Chen *et al.* presented another synthetic approach for the preparation of substituted indeno[2,1-*c*]fluorenes based on intermolecular Diels-Alder reaction. The reaction included Diels-Alder reaction of diene **LXVIII** with an excess of maleic anhydride. The subsequent aromatization with $Pb(OAc)_4$ led to the formation of indeno[2,1-*c*]fluorene **LXIX** in a high yield of 90% (Scheme 31).[6e]



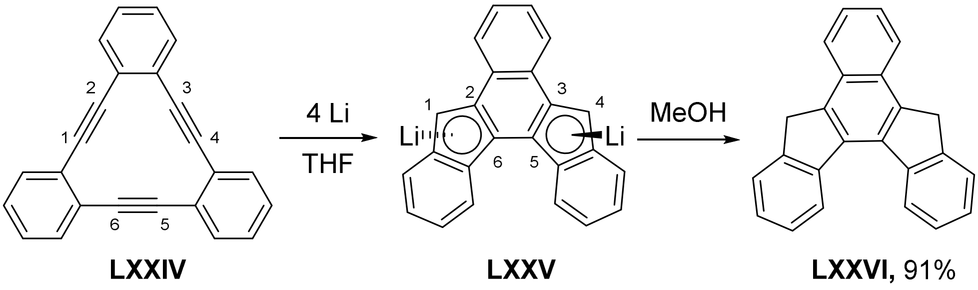
Scheme 31. Intermolecular Diels-Alder reaction to indeno[2,1-*c*]fluorene **LXIX**

Another strategy combining the two above mentioned synthetic approaches was also developed. The synthesis included intermolecular Diels-Alder reaction of indanocyclone **LXX** with 9-ethynyl-9-fluorenol **LXXI**, which led to the formation of a mixture of fluorenone **LXXII** and its structural isomer **LXXII-a** in a 1:1 ratio. Friedel-Crafts alkylation took place in the presence of HOAc/catalytic amount of HCl mixture under reflux and produced monospirobifluorene-indeno[2,1-*c*]fluorene **LXXIII** in a high yield of 96% (Scheme 32).[6f]



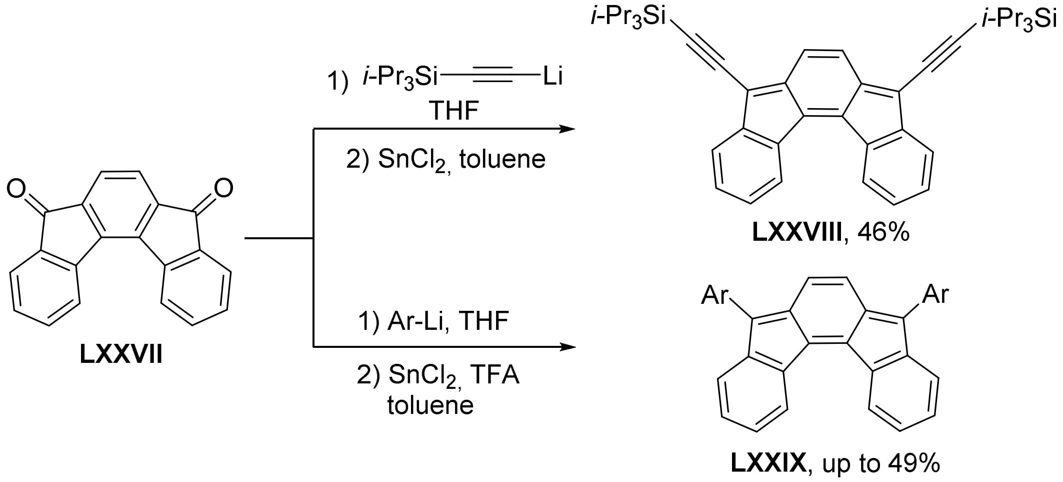
Scheme 32. Diels-Alder/intramolecular Friedel-Crafts reaction to indeno[2,1-*c*]fluorene **LXXIII**

An unusual synthetic strategy, significantly differing from pathways ***A*** and ***B***, was developed in the group of Tessier *et al.* in 1991. This approach consists of lithium-induced cyclization of tribenzocyclotriyne **LXXIV**. It was shown that combining 4 equivalents lithium with tribenzocyclotriyne **LXXIV** in THF under anaerobic conditions yielded dianion **LXXV**. Its methanolysis gave rise to the target indeno[2,1-*c*]fluorene **LXXVI** (Scheme 33).[40]



Scheme 33. Synthesis of indeno[2,1-*c*]fluorene **LXXVI** from tribenzocyclotriyne **LXXIV**

Using the parent indeno[2,1-*c*]fluorene-5,8-dione **LXXVII**, Haley *et al.* synthesized, for the first time, fully conjugated and antiaromatic indeno[2,1-*c*]fluorenes **LXXVIII** and **LXXIX** (Scheme 34).[6g,41] In their pioneering study, they found that indeno[2,1-*c*]fluorenes **LXXVIII** have high electron affinities and small HOMO-LUMO energy gaps, thus suggesting that these modified indeno[2,1-*c*]fluorenes **LXXVIII** and **LXXIX** are attractive candidates for applications in organic electronic devices.



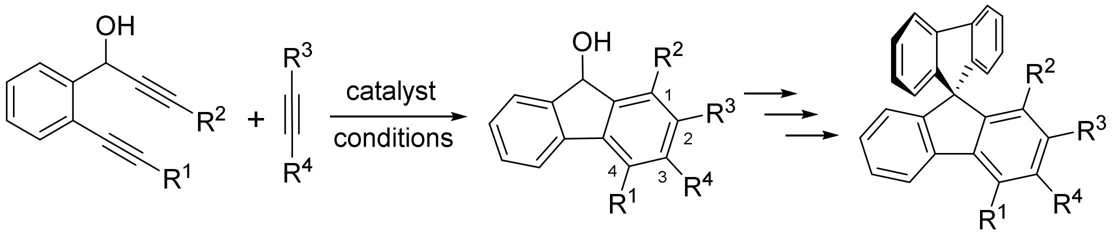
Scheme 34. Synthesis antiaromatic indeno[2,1-*c*]fluorene **LXXVIII** and **LXXIX**

All these synthetic approaches show that the preparation of indeno[2,1-*c*]fluorenes is still challenging task. With respect to the above said, it is possible to constitute that there has not been developed a general synthetic strategy for preparation of regioselectively substituted indeno[2,1-*c*]fluorenes yet. Moreover, the preparation of specifically substituted indeno[2,1-*c*]fluorenes is still challenging and requires specific methods. Therefore the area of synthesis of variously substituted fluorenes or indenofluorenes remains highly attractive and interesting field of organic synthesis.

3. Aim of the Work

As shown in the previous chapter, scientific literature describes numerous pathways for the synthesis of compounds containing the fluorene skeleton and the corresponding 9,9'-spirobifluorenes (SBFs). Nevertheless, a possibility of developing of a general method for the regioselective synthesis of unsymmetrically substituted fluorenes and their properties has not been explored thus far. Therefore, the aims of this thesis were the following:

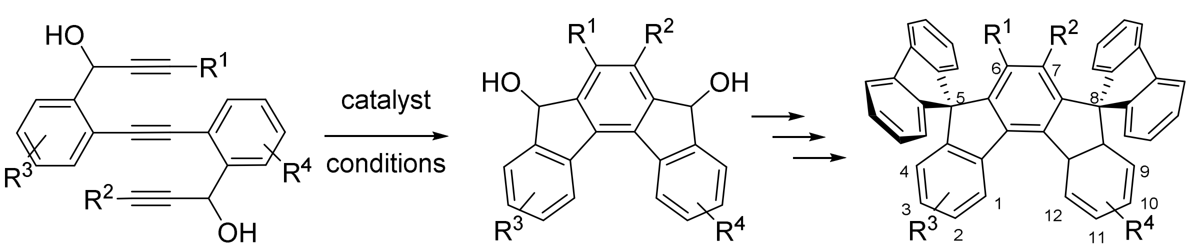
a) To develop a synthetic pathway for compounds with the fluorene scaffold using catalytic [2+2+2] cyclotrimerization of symmetrically or unsymmetrically substituted diynol precursors (R^1 and R^2) with alkynes to selectively form 1,2,3,4-tetrasubstituted fluorenols and their SBF derivatives (Scheme 35).



Scheme 35. Proposed synthetic pathway for SBF using transition metal-catalyzed [2+2+2] cyclotrimerization

b) To assess the effect of different alkyl, aromatic and extended π-aromatic hydrocarbon substituents (R^1 and R^2) at positions 1 and 4 on the photophysical properties of the corresponding SBFs.

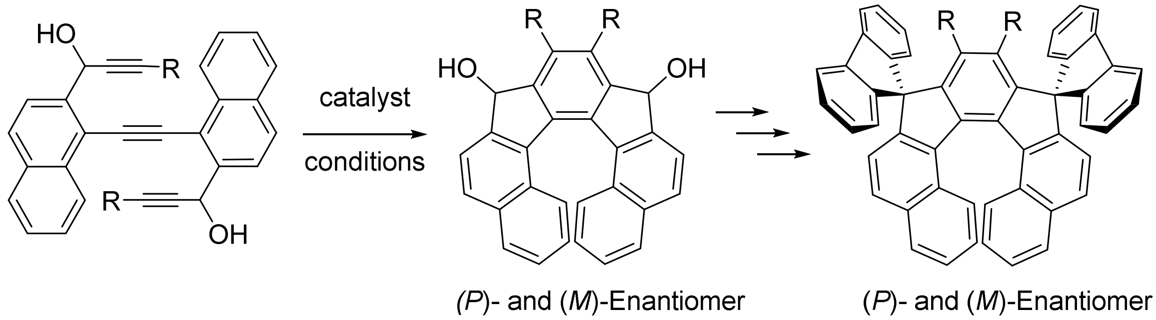
c) To extend the SBF synthetic method to the preparation of dispiroindeno[2,1-*c*] fluorenes (DS-IFs). They can be considered as extended SBF derivatives (Scheme 36).



Scheme 36. Proposed pathway of synthesis of DS-IFs using the synthetic approach developed

d) To assess substituent effects (R^1 and R^2 or substituents R^3 and R^4) on the photophysical properties of DS-IFs (Scheme 36), as performed for the SBFs.

e) To develop a synthesis route to a new class of [7]-helical DS-IFs by using the cyclotrimerization approach (Scheme 37).



Scheme 37. Proposed synthetic strategy for (*P*)- and (*M*)-[7]-helical DS-IFs

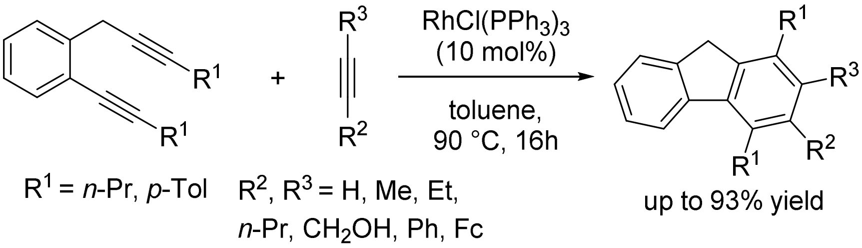
4. Results and Discussion

4.1. 9,9'-Spirobifluorenes (SBFs)

4.1.1. Study for the synthesis of 9*H*-fluorene

In my previous study, I was able to find suitable reaction conditions for a transition metal catalyzed [2+2+2] cyclotrimerization of substituted diynes with alkynes to provide 1,2,3,4-tetrasubstituted 9*H*-fluorenes.[36]

These fluorenes were synthesized using two sets of symmetrically substituted diynes. The diynes were prepared by one-step Negishi coupling of the corresponding alkynylzinc halides with 2-iodobenzyl bromide using a Pd catalyst.[42] Then, different catalytic systems for [2+2+2] cyclotrimerization containing Co, Ru, Ni and Rh complexes were studied. Excluding the Ru-catalysts, all other catalysts gave rise to the desired 9*H*-fluorenes. The rhodium complex (Wilkinson's catalyst, $RhCl(PPh_3)_3$, 10 mol%) proved to be the most powerful catalyst for [2+2+2] cyclotrimerization of the diynes with alkynes to provide various alkyl and aryl substituted 9*H*-fluorene derivatives in up to 93% isolated yield (Scheme 38). The substituent screening was then performed. Various symmetrically ($R^2 = R^3$ = Me, Et, *n*-Pr, CH_2OH) and unsymmetrically (R^2 = H, R^3 = Ph, Fc) substituted alkynes were applied in the cyclotrimerization reaction. The results showed that 3-hexyne ($R^2 = R^3$ = Et) was the most suitable reaction partner for Rh-catalyzed cyclotrimerization.[36]



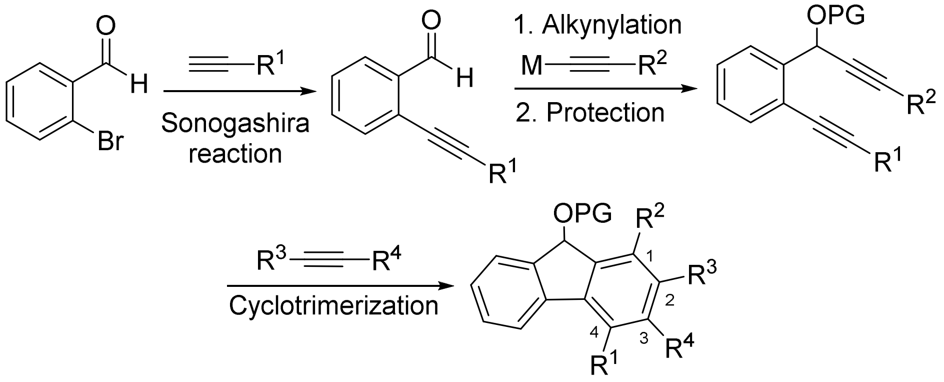
Scheme 38. General synthetic approach for 9*H*-fluorenes

These compounds were originally synthesized to serve as η^5- or η^6- ligands for several transition metals, because unsymmetrically substituted 9*H*-fluorenes are potential ligands for asymmetrical catalysis.[43] However, all attempts to form complexes of 1,2,3,4-tetrasubstituted 9*H*-fluorenes with transition metals, such as Mn and Fe, failed.

4.1.2. Study for the synthesis of 1,2,3,4-tetrasubstituted fluorenols

As shown above, the transition metal catalyzed reaction of diynes and alkynes was successfully used to synthesize tetrasubstituted 9*H*-fluorenes, but no further applications of these compounds were found. Therefore, the focus of this project shifted towards preparing the structurally related 1,2,3,4-tetrasubstituted fluorenols.

In contrast to 9*H*-fluorenes, fluorenols have the hydroxyl functional group at position 9. The presence of the hydroxyl group enables fluorenols to undergo conversion into the corresponding 9,9´-spirobifluorenes (SBFs). Moreover, I hypothesized that selective substitution at positions 1-4 of the SBFs framework could be used to tune their properties based on a recent research study on 2- and 4-substituted SBFs,[44] although a systematic study of substituent effects on SBFs has not been reported thus far. Therefore, I aimed to develop a general synthetic strategy for the regioselective synthesis of variously substituted SBFs using the cyclotrimerization method previously developed for the synthesis of tetrasubstituted 9*H*-fluorenes according to the reaction sequence below (Scheme 39).[36]



Scheme 39. General synthethic route for 1,2,3,4-tetrasubstituted fluorenols

Thus, the goal of this study was to assess whether the previously developed reaction pathway is also applicable for the synthesis of 1,2,3,4-tetrasubstituted fluorenols. For this purpose, the following objectives were considered:

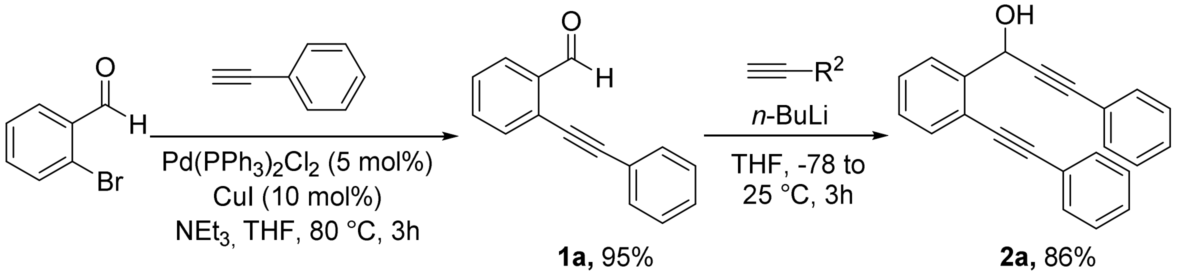
a) to find suitable diynol compounds for [2+2+2] cyclotrimerization reaction,

b) to study applicable catalytic systems for the [2+2+2] cyclotrimerization reaction,

c) to test different alkynes in the [2+2+2] cyclotrimerization reaction, and

d) to assess the effect of hydroxyl group protection.

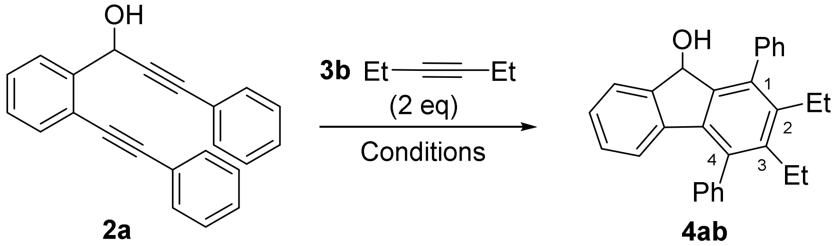
a) Either 2-bromobenzaldehyde or 2-iodobenzaldehyde could have been chosen as commercially available starting material; however, the former was used because of its lower price. In the first step, Sonogashira coupling of 2-bromobenzaldehyde with phenylacetylene using $PdCl_2(PPh_3)_2$ (5 mol%) and CuI (10 mol%) with triethylamine as base in THF at 80 °C for 3h yielded **1a** in 95% isolated yield. The subsequent alkynylation with lithium phenylacetylide in THF at -78 °C gave rise to the symmetrically substituted diynol **2a** in 86% isolated yield (82% after two steps, Scheme 40).



Scheme 40. Synthesis of diynol **2a**

b) Initially, diynol **2a** was applied as the model compound for the [2+2+2] cyclotrimerization study with different alkynes in the presence of various catalytic systems. The first task was to find suitable catalytic reaction conditions for the [2+2+2] cyclotrimerization of **2a** with alkynes. For this purpose, reactions of diynol **2a** and 3-hexyne **3b**, as a representative of internal alkynes, were performed using various transition metal-based (Co, Ru, Ni, Rh) catalytic systems (Table 1). Similar to the study of 9*H*-fluorene synthesis, the highest yield (76%) of the desired fluorenol **4ab** (Entry 1) was found when using the Wilkinson's catalyst ($RhCl(PPh_3)_3$). The other catalytic systems, consisting of $CpCo(CO)_2$ and $Ni(cod)_2/2PPh_3$, also furnished fluorenol **4ab**, albeit in lower yields of 11% and 19%, respectively (Entries 2 and 3). No product was formed only in the case of Cp*RuCl(cod), and the starting material was fully recovered. Subsequent attempts to change the reaction conditions also failed (Entries 4 and 5).

Table 1. Transition metal complex-catalyzed cyclotrimerization reactions of **2a** with **3b**

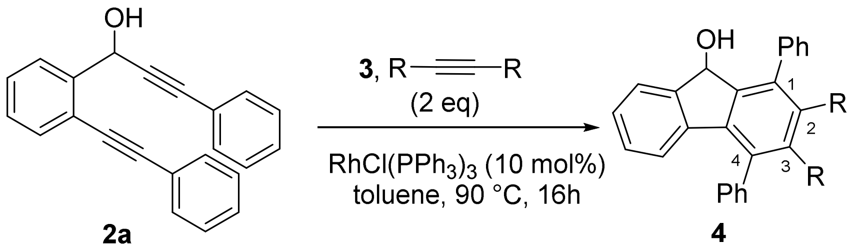


Entry	Catalyst (10 mol%)	Conditions	Yield (%)[a]
1	$RhCl(PPh_3)_3$	toluene, 90 °C, 16h	76
2	$CpCo(CO)_2$	THF, MW, 180 °C, 1h	11
3	$Ni(cod)_2/2PPh_3$	THF, 20 °C, 3h	19
4	Cp*RuCl(cod)	CH_2Cl_2, 25 °C, 2h	0
5	Cp*RuCl(cod)	toluene, 90 °C, 16h	0

[a] Isolated yields.

c) At this stage, the substituent effect of different symmetrically substituted internal alkynes **3** on cyclotrimerization with **2a** was tested. Therefore, alkynes were classified according to Charton steric parameters (upsilon steric parameter υ_{ef}) of the R substituents. Alkynes with small substituents such as **3a** (R = Me, $\upsilon_{ef} = 0.52$), **3b** (R = Et, $\upsilon_{ef} = 0.56$) and **3d** (R = CH_2OH, $\upsilon_{ef} = 0.53$), alkyne **3c** with a medium size substituent (R = *n*-Pr, $\upsilon_{ef} = 0.68$) and alkynes **3e-3g** with sterically more demanding aryl substituents (R = Ph, $\upsilon_{min} = 0.57$, $\upsilon_{max} = 2.15$) were chosen.[45] Interestingly, the product was formed only when using alkyl substituted alkynes (**3a-3d**). In detail, fluorenol **4aa** was synthesized in cyclotrimerization reaction with 2-butyne **3a**, albeit in a low yield (25%; Table 2, Entry 1). The low yield most likely resulted from the high volatility of the alkyne (27 °C boiling point). Thus, the concentration of the alkyne in the liquid phase was presumably low because the reaction was performed at 90 °C. Increasing the quantity of **3a** to 5 or 10 equivalents in a closed system failed to give fluorenol **4aa** in higher yields. The reactions of 3-hexyne and 4-octyne provided products **4ab** and **4ac** in 76% and 24% yield, respectively (Entries 2 and 3). Gratifyingly, the cyclotrimerization with 1,4-butynediol **3d** gave fluorenol **4ad** in 76% yield (Entry 4). However, the reactions of **2a** with arylalkynes **3e-3g** unexpectedly did not give aryl-substituted fluorenols **4ae-4ag**, most likely due to steric hindrance (Entries 5-7). The comparison of the reactions of **2a** with 3-hexyne **3b** or with 4-octyne **3c** shows that steric effects (**3b,** $\upsilon_{ef} = 0.56$; **3c,** $\upsilon_{ef} = 0.68$) decrease the product yield from 76 to 24% (Entries 2 and 3).

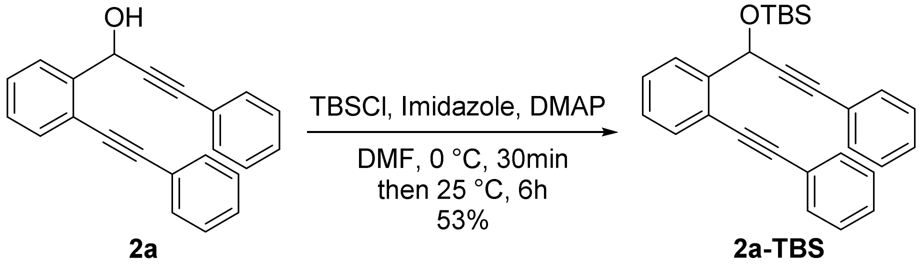
Table 2. Rh-catalyzed cyclotrimerization reactions of **2a** with alkynes **3**



Entry	R	Product	Yield (%)[a]
1	Me	**4aa**	25
2	Et	**4ab**	76
3	*n*-Pr	**4ac**	24
4	CH_2OH	**4ad**	76
5	Ph	**4ae**	0
6	*p*-Tol	**4af**	0
7	$C_6H_4CF_3$	**4ag**	0

[a] Isolated yields.

d) Lastly, the effect of the hydroxyl group protection at diynol **2a** for the Rh-catalyzed cyclotrimerization with various alkynes was assessed. The protection of the free hydroxyl group at **2a** was achieved using TBSCl and imidazole/DMAP at 0 °C. The product **2a-TBS** was obtained in a surprisingly low yield of 53% after isolation (Scheme 41). All attempts to improve these yields by changing reaction conditions such as time (up to 24h), temperature (up to 50 °C) and additives (bases) failed. The TBS group was chosen as the protecting group because it can be selectively removed with fluoride based reagents under mild reaction conditions.

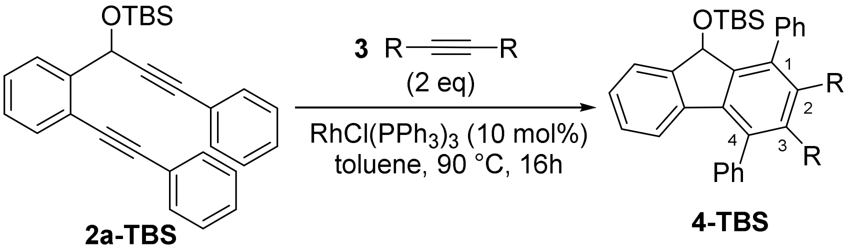


Scheme 41. Synthesis of protected diynol **2a-TBS**

The protected diynol **2a-TBS** was then subjected to Rh-catalyzed cyclotrimerization using different alkyl and aryl substituted internal alkynes, such as 2-butyne (**3a**), 3-hexyne (**3b**), 4-octyne (**3c**), 1,4-but-2-ynediol (**3d**), diphenylethyne (**3e**), di(4-tolyl)ethyne (**3f**), and bis(4-trifluoromethylphenyl)ethyne (**3g**) (Table 3).

The cyclotrimerization reaction of **2a-TBS** with alkyl substituted alkynes **3a-d** yielded 1,2,3,4-tetrasubstituted fluorenols **4a-d-TBS** (Entries 1-4). The reaction with **3a** gave **4aa-TBS** (R = Me, Entry 1) in 19% yield, with **3b** it furnished **4ab-TBS** (R = Et, Entry 2) in 71% yield, with **3c** it afforded **4ac-TBS** (R = *n*-Pr, Entry 3) in 6% yield, and with **3d** **4ad-TBS** (R = CH_2OH, Entry 4) was formed in 82% yield. In all cases, except **4ad-TBS**, the yields of products were slightly lower than those of the reaction with the unprotected diynol **2a** (see Table 2). No cyclotrimerization occurred and no products were detected in the reactions with aryl-substituted alkynes **3e-g** (Entries 5-7).

Table 3. Results from Rh-catalyzed cyclotrimerization reactions of **2a-TBS** with alkynes **3**



Entry	R	Product	Yield (%)[a]
1	Me	**4aa-TBS**	19
2	Et	**4ab-TBS**	71
3	*n*-Pr	**4ac-TBS**	6
4	CH_2OH	**4ad-TBS**	82
5	Ph	**4ae-TBS**	0
6	*p*-Tol	**4af-TBS**	0
7	$C_6H_4CF_3$	**4ag-TBS**	0

[a] Isolated yields.

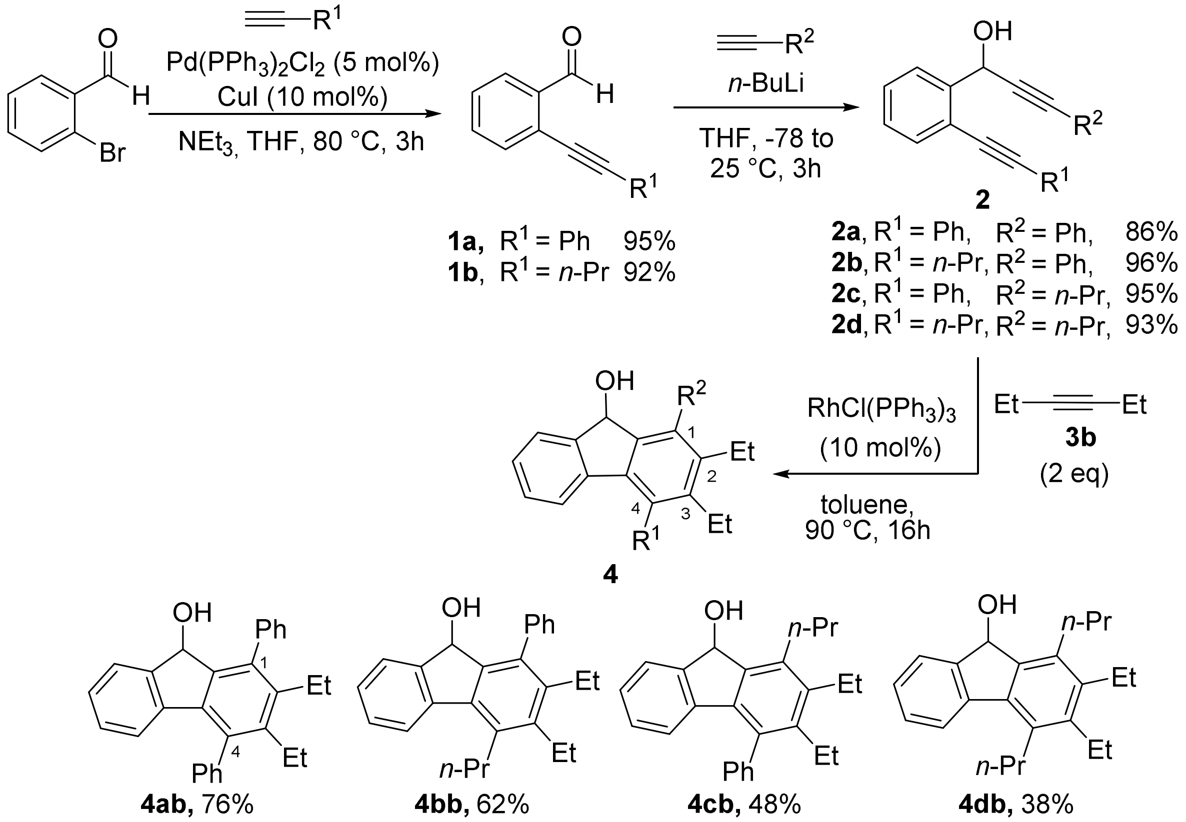
These results showed no significant effect of the hydroxyl group protection on the outcome of the cyclotrimerization reaction. Therefore, unprotected diynols were used in subsequent experiments. The results showed that 3-hexyne **3b** was the most suitable internal alkyne. Hence, this hexyne **3b** was selected for all further reactions. But-2-yne-1,4-diol **3d** yielded the corresponding fluorenols **4ad** and **4ad-TBS** in the same or in even higher yields than those of 3-hexyne **3b**, but the presence of two additional hydroxyl group could affect the subsequent steps of the synthesis.

4.1.3. Synthesis of 1,2,3,4-tetrasubstituted SBFs and analysis of the effect of the substituents at positions 1 and 4 on its photophysical properties

All synthesized fluorenols can be converted into the corresponding SBFs. The properties of the SBFs may be tuned by selective substitution at positions 1-4, yet no systematic study on the effect of the substituent on the photophysical properties of SBFs has been conducted thus far, as previously stated in section 4.1.2. This is particularly relevant when considering that SBFs have useful properties in organic optoelectronics, such as thermal and morphological stability, and their photophysical properties depend on their substituents.

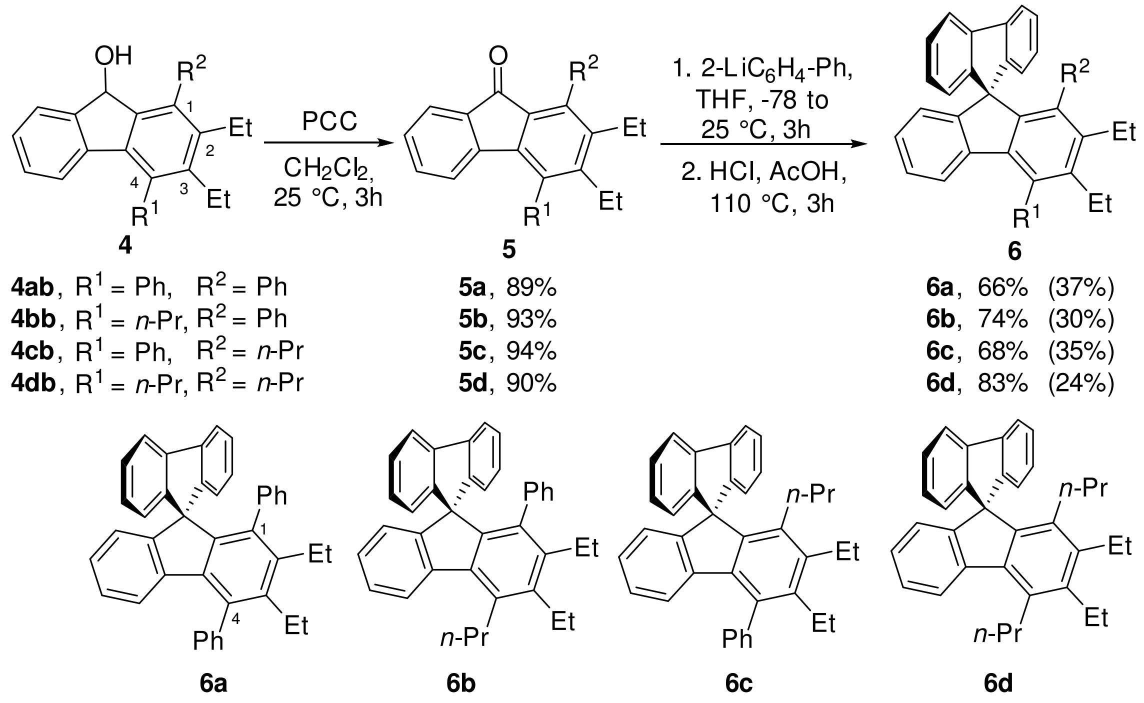
Initially, in addition to the previously obtained diynol **2a**, three other diynols **2b-d** with different combinations of substituents at the ends of the triple bond in symmetrical and unsymmetrical alignment were prepared. The synthesis started with Sonogashira coupling of 2-bromobenzaldehyde with pent-1-yne or phenylacetylene ($Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%), NEt_3, THF, 80 °C, 3h) producing **1a** and **1b** in 95 and 92% isolated yields, respectively. Their subsequent alkynylation with pent-1-yn-1-yllithium or lithium phenylacetylide in THF at -78 °C gave rise to the set of **2a**-**d**, again in very high isolated yields ranging from 86 to 96%.

Diynols **2a**-**d** were then cyclotrimerized with 3-hexyne **3b** in the presence of Wilkinson's catalyst (10 mol%) under the previously used conditions (toluene, 90 °C, 16h). Fluorenols **4ab**, **4bb**, **4cb** and **4db** were obtained in 38-76% isolated yields (Scheme 42). In some cases the formation of homo-coupled product from diynols **2a-d** was observed as minor side products (3-7%). Attempts to overcome the homocoupling reaction by slow addition of diynols **2a-d** into the reaction mixture and to increase the amount of the alkyne **3b** to 5 or even 10 equivalents failed.



Scheme 42. Synthesis of unsymmetrically 1,2,3,4-tetrasubstituted fluorenols **4**

Then, fluorenols **4ab**, **4bb**, **4cb** and **4db** were converted into the corresponding SBFs. Initially, fluorenols **4** were oxidized with pyridinium chlorochromate (PCC) in dichloromethane at 25 °C to the corresponding fluorenones **5a-d**. Fluorenones **5a**, **5b**, **5c**, and **5d** were isolated in 89, 94, 93 and 90% yields, respectively. Subsequently, fluorenones **5** were converted into the desired SBFs **6a-d** using a two-step approach[46] consisting of 2-lithiobiphenyl addition to **5a-d** that was followed by treatment with a mixture of acetic acid containing a catalytic amount of concentrated HCl at 110 °C. SBFs **6a**, **6b**, **6c**, and **6d** were obtained in 66, 74, 68, and 83% yields. In summary, regioselectively 1,2,3,4-tetrasubstituted SBFs **6a-d** were obtained, through the five-step synthetic pathway using the Rh-catalyzed cyclotrimerization as the key step, in overall yields ranging from 24 to 37% (Scheme 43, overall yields are in parenthesis). The structures of **6a** and **6c** were unequivocally confirmed by a single-crystal X-ray structure analysis (Figures 4 and 5).



Scheme 43. Synthesis of 1,2,3,4-tetrasubstituted SBFs **6a-d**

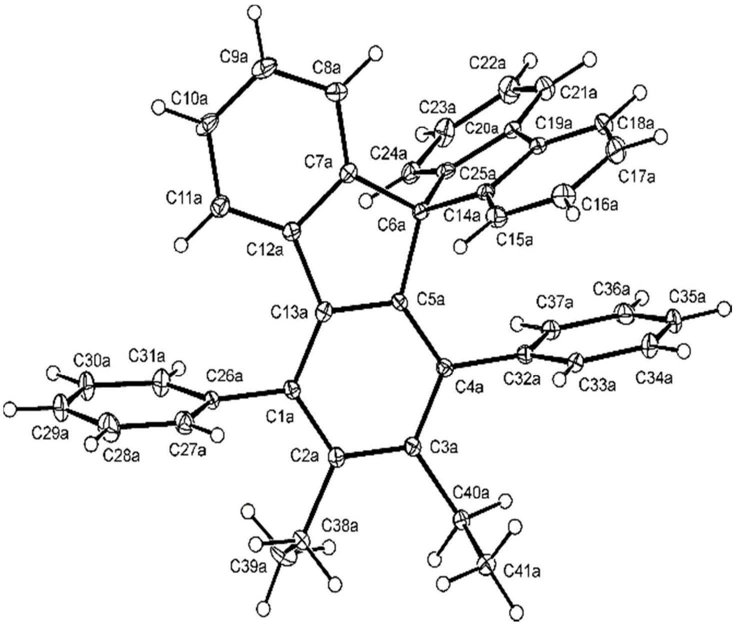


Figure 4. Platon plot of **6a** showing displacement ellipsoids at a 30% probability level

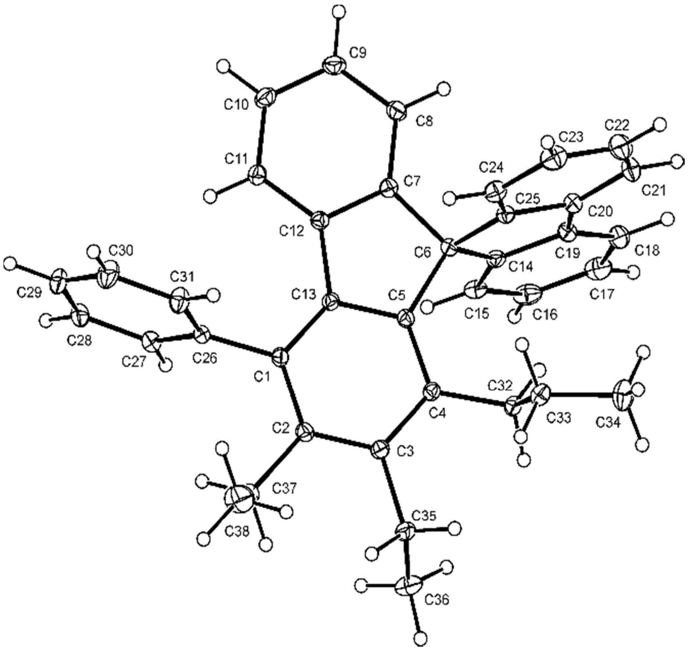


Figure 5. Platon plot of **6c** showing displacement ellipsoids at a 30% probability level

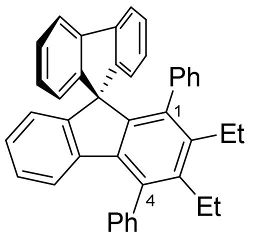
After preparing the set of SBFs **6a**-**d**, their photophysical properties were studied. Initially, the UV/Vis absorption spectra were recorded. Samples were measured in 10^{-6} M solutions in cyclohexane and the relative quantum yields Φ_s were determined using 9,10-diphenylanthracene (DPA) as the standard. To calculate the relative quantum yields Φ_s, DPA and the sample molecules must have the same absorption value at a certain wavelength. This specific wavelength, the isobestic point, is used as excitation wavelength λ_{exc} in the further measurement of fluorescence emission spectroscopy. In this case the comparison of absorption spectra show the isobestic points at 242 and 243 nm, respectively and were used as λ_{exc} for the emission spectroscopy.

The analysis of the fluorescence emission spectral data (Figure 6 and Table 4) showed that:

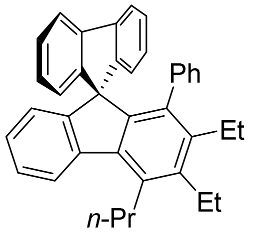
a) Compounds **6a** and **6c** with the phenyl substituents at position 4 show broad emission peaks at 330/333 nm after excitation at 242 nm and 243 nm, respectively.

b) Compounds **6b** and **6d** with the *n*-propyl substituent at position 4 have narrower emission patterns with emission maxima at 315 nm and smaller emission peaks at 328 nm after excitation at 243 nm and 242 nm, repectively.

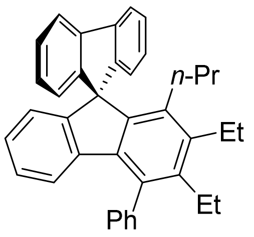
c) The quantum yields of all four compounds, namely **6a** ($\Phi_s = 0.62$), **6b** ($\Phi_s = 0.72$), **6c** ($\Phi_s = 0.48$) and **6d** ($\Phi_s = 0.87$), have similar values. These results show that substituted SBFs have good to high quantum yields.



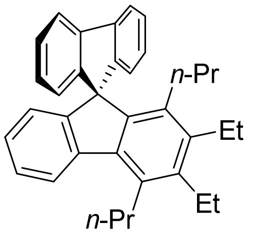
6a



6b



6c



6d

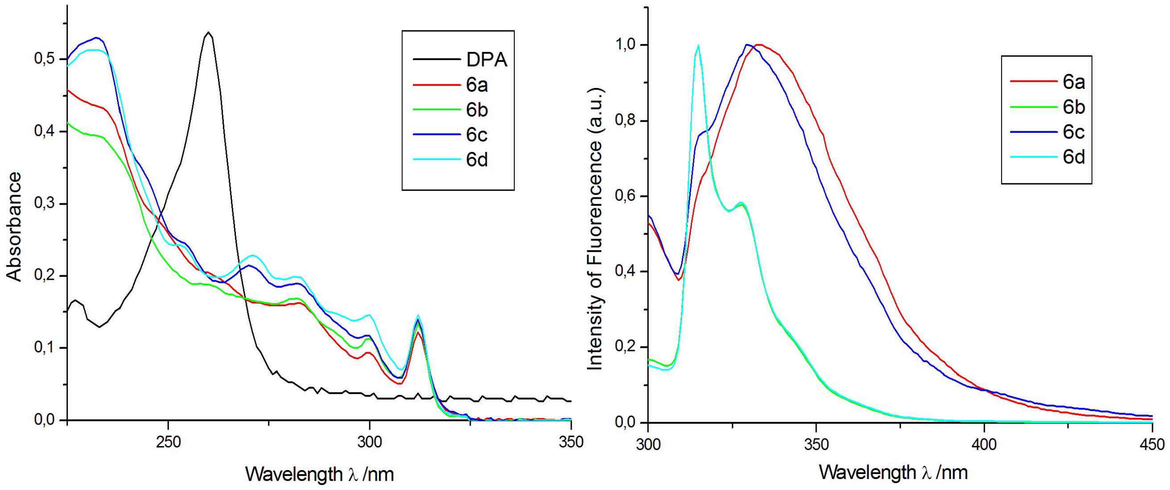


Figure 6. Absorption and emission spectral data of **6a-d** in 10^{-6} M samples

Table 4. Photophysical properties of **6a-d** (10^{-6} M in cyclohexane)

Sample	λ_{exc} /nm	λ_{em}^{max}/nm	Φ_s[a]
6a	242	333	0.62
6b	243	315/328	0.72
6c	243	330	0.48
6d	242	315/328	0.87

[a] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

These observations and comparisons led to the following conclusions:

a) Substituents at position 4 strongly affect the photophysical properties of SBFs. A significant difference was observed in the red shift of the fluorescence emission spectra caused by these substituents. The presence of the phenyl substituent at position 4 of **6a** and **6c** (λ_{max} = 333 and 330 nm) red-shifted the emission maxima by more than 15 nm in comparison with the propyl substituted SBFs **6b** and **6d** (λ_{max} = 315 nm for both).

b) The well-resolved profile with distinct peaks in the emission spectra of **6b** and **6d** match the spectra of similar compounds in the same solvent, such as the parent SBF (λ_{em} = 310, 323 nm),[44a] 2-phenyl-SBF (λ_{em} = 335, 351 nm) and 2-pyrimidyl-SBF (λ_{em} = 338, 355 nm).[44b] The broad emission band of **6a** and **6c** may be a characteristic property of aromatic substitution at position 4 of SBFs.

c) The measured emission spectra of **6a/6c** and **6b/6d** show that the substituent at position 1 of the SBF has negligible, if at all any, effect on the fluorescence emission shift or on the quantum yield. The quantum yields for all measured SBFs **6** ($\Phi_s = 0.48\text{-}0.87$) are also in accordance with previously reported results.[44]

In summary, I was able to synthesize selectively 1,2,3,4-tetrasubstituted SBFs in a five-step approach from commercially available compounds. The Rh-catalyzed [2+2+2] cyclotrimerization approach developed in this study was used as the key step. Furthermore, a preliminary analysis of the effect of the substituent at positions 1 and 4 on the photophysical properties of SBFs was conducted. The results indicate a connection between the aromatic substituents at position 4 of the SBF and a red shift of the fluorescence emission peak towards the visible light region. Therefore, substitution at this particular position is an interesting option for further synthetic modification.

4.1.4. Synthesis of SBFs bearing different substituents at position 4

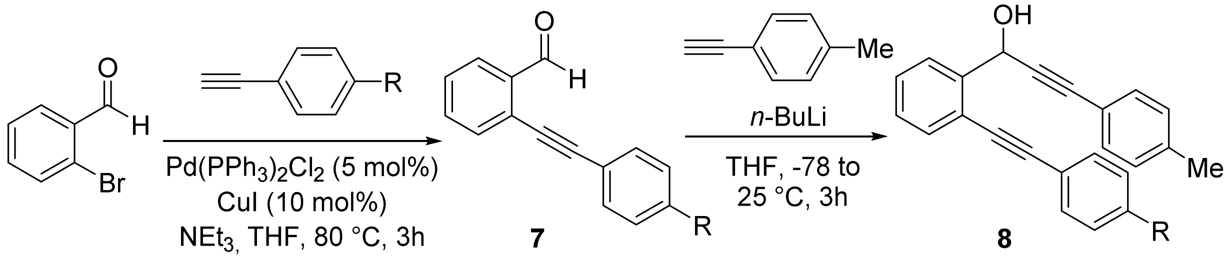
In the previous chapter, I showed that 4-aryl substituents of SBFs red shift the fluorescence emission wavelength of these compounds. Thus, the next step of this study on the modulation of photophysical properties of SBF derivatives was to use different substituents at position 4. This approach was divided into three stages:

a) to synthesize 4-substituted SBFs with 4-substituted phenyl groups bearing electron-donating and -withdrawing groups,
b) to synthesize the SBFs with extended aromatic moieties at position 4,
c) to attach fused π-aromatic hydrocarbons (PAHs) at position 4 of SBFs.

4.1.4.1. Synthesis of 4-substituted phenyl groups at position 4 of SBFs

In the first stage, a set of 4-substituted SBFs bearing 4-substituted phenyl groups was prepared. The 4-substituted phenyl groups encompassed moieties bearing electron-donating and -withdrawing functional groups. Because of structural similarity with compounds in section 4.1.3, the same five-step synthetic approach was applied.[47]

In the first step, 3-alkynylated benzaldehydes **7a-g** were synthesized by using Sonogashira coupling ($Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%), NEt_3, THF, 80 °C, 3h) of 2-bromobenzaldehyde with various 4-substituted phenylacetylenes having various electron-donating (OMe, Me, H) and -withdrawing (Ph, Cl, CF_3, CN) groups. The corresponding alkynylbenzaldehydes **7a-g** were obtained in good isolated yields in the range of 80 to 96%. The subsequent alkynylation of **7a-g** with lithium *p*-tolylacetylide at -78 °C in THF gave rise to diynols **8a-g** in 84 to 96% yields (Scheme 44).

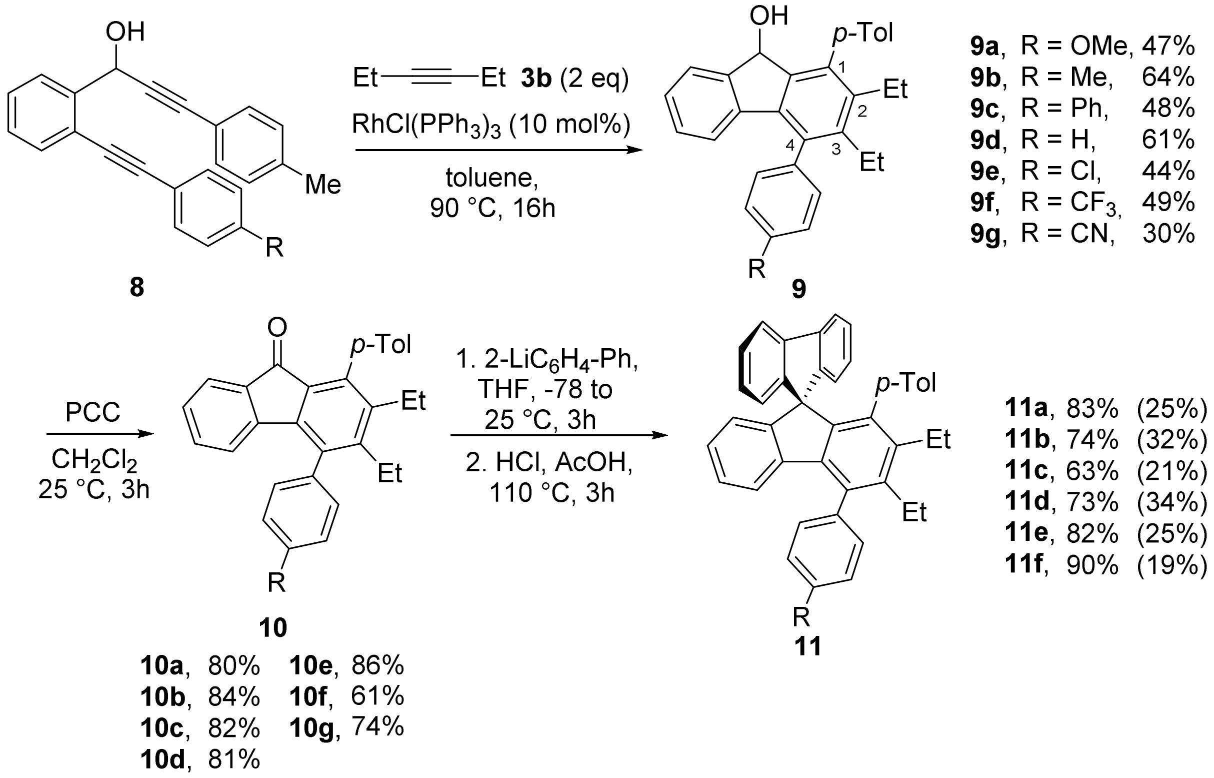


7a	R = C_6H_4-OMe,	96%	**8a**,	84%
7b	R = C_6H_4-Me,	96%	**8b**,	91%
7c,	R = C_6H_4-Ph,	92%	**8c**,	90%
7d,	R = C_6H_4-H,	97%	**8d**,	93%
7e,	R = C_6H_4-Cl,	90%	**8e**,	89%
7f,	R = C_6H_4-CF_3,	80%	**8f**,	90%
7g,	R = C_6H_4-CN,	84%	**8g**,	94%

Scheme 44. Synthesis of substituted diynols **8a-g**

In the third step, I applied the previously developed Wilkinson's complex catalyzed cyclotrimerization ($RhCl(PPh_3)_3$ (10 mol%), toluene, 90 °C, 16 h, for further details, see section 4.1.3) to mediate reactions of substituted diynols with small internal alkynes. As already mentioned, 3-hexyne **3b** was chosen as the most suitable compound for the cyclotrimerization reactions with diynols. The catalytic [2+2+2] cyclotrimerization of diynols **8a-g** with **3b** proceeded to provide the desired fluorenols **9a-g** in the range of 30 to 64% isolated yields (Scheme 45). These isolated yields matched the previously reported values obtained for **4ab**, **4bb**, **4cb** and **4db**, which were ranging from 38 to 76% (section 4.1.3.). Similar to the previous results also in this case the homo-coupling product of diynols **8a-g** was observed as minor side product (2-5%) and the same attempts (slow addition of diynol and increase of alkyne concentration, section 4.1.3) failed to suppress this unwanted side reaction.

In the next step, fluorenols **9a-g** were oxidized with PCC in dichloromethane at 25 °C uneventfully to fluorenones **10a-g** in good to high isolated yields (61-86%). Finally, the fluorenones **10a-g** were converted to SBFs **11a-f** by reaction with 2-lithiobiphenyl that was followed by treatment with a mixture of acetic acid containing a catalytic amount of concentrated HCl at 110 °C. The final SBFs **11a-f** were obtained in high isolated yields ranging from 63% to 90%. The overall yields from the commercially available starting material after five steps were in a reasonable range from 19 to 34% (Scheme 45, overall yields in parenthesis). Only in the case of **11g** (R = CN), 2-lithiobiphenyl added preferentially to the more reactive cyano group, thereby leading to the imine product. Changes in reaction conditions to suppress imine formation and to favor addition to the carbonyl group were not met with success. The structures of the SBFs **11a**, **11c** and **11e** were unequivocally confirmed by a single-crystal X-ray analysis (Figures 7-9).



Scheme 45. Synthesis of 4-aryl substituted SBFs **11a-f**

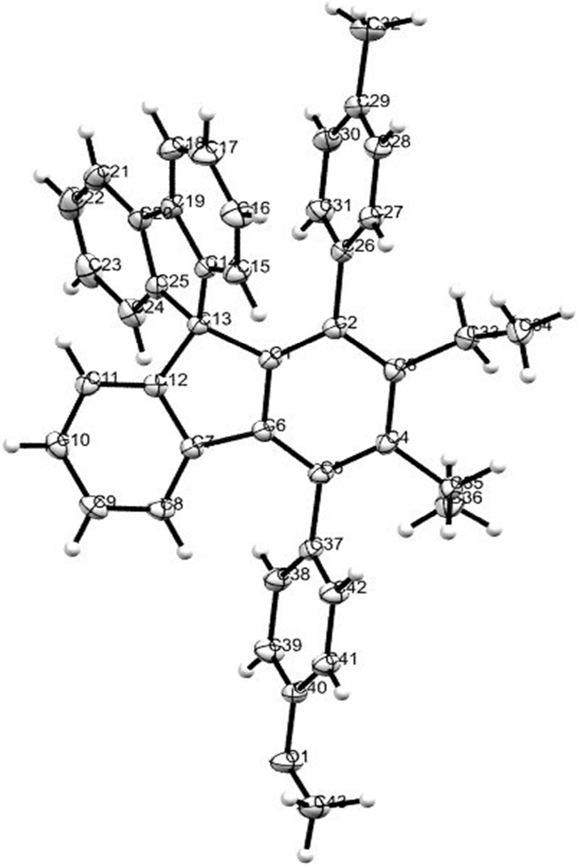


Figure 7. Platon plot of **11a** showing displacement ellipsoids at a 50% probability level

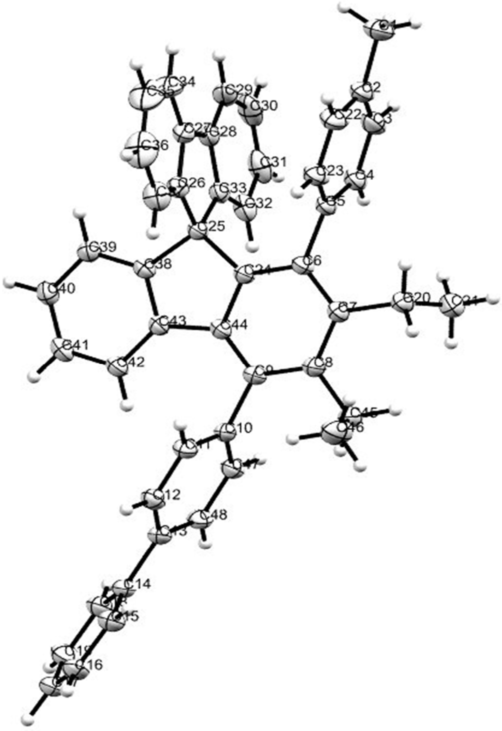


Figure 8. Platon plot of **11c** showing displacement ellipsoids at a 50% probability level

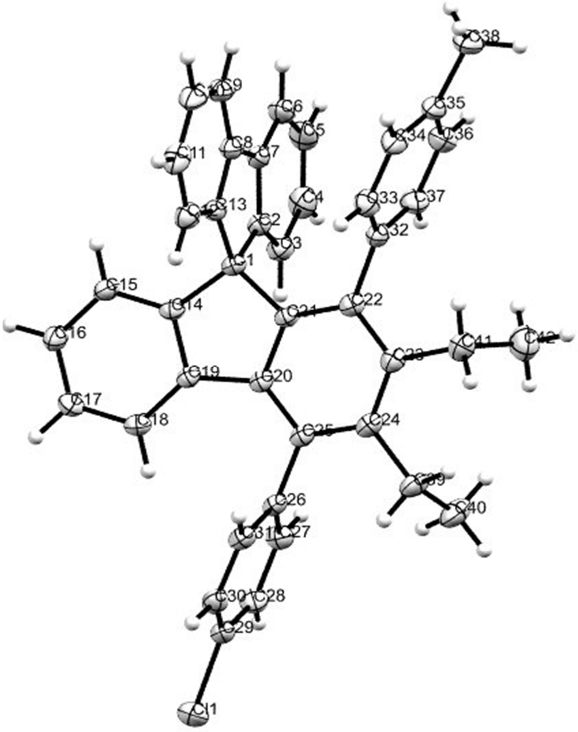


Figure 9. Platon plot of **11e** showing displacement ellipsoids at a 50% probability level

The X-ray diffraction data of all three SBFs showed large dihedral angles (almost perpendicular) between the SBF and the *para*-decorated aryl substituents at position 4. In detail, for **11a** the angles between C4-C5-C6 and C37-C38-C42 were 86°, for **11c** the angles between C8-C9-C44 and C10-C11-C47 were 94° and for **11e** the angles between C20-C24-C25 and C26-C27-C31 were 83°. This high rotation may be caused by the ethyl substituent at position 3 of the SBFs.

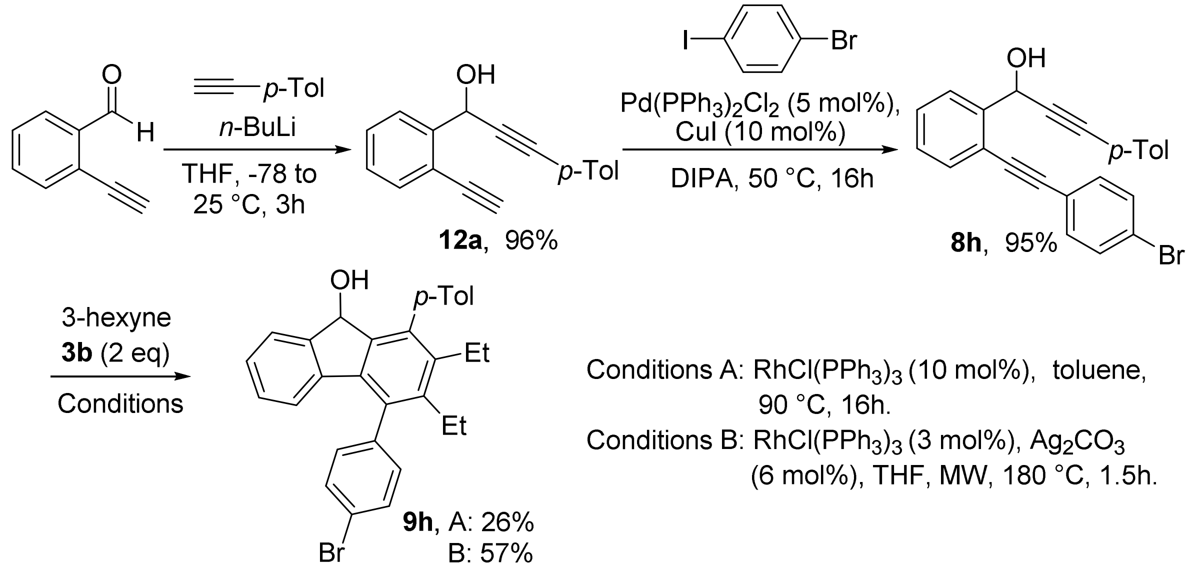
The almost perpendicular arrangement between the SBFs and the substituents at position 4 may affect the electron distribution within the molecule. This can in particular influence and lower the ability for a strong performance in photophysical properties, especially after excitation. Nevertheless, based on results obtained for 4-aryl-substituted SBFs[2,44,48] and our previous results regarding 1,2,3,4-tetrasubstituted SBFs,[36] these compounds presumably undergo planarization by stabilization of the excited state, which then improves the alignment and interaction of extended π-systems at the central carbon atoms.[44a,49]

Besides, also the aromatic substituent at position 1 of the SBF showed large dihedral angles. But in contrast to position 4, substituents at position 1 of the SBF are not influencing the photophysical properties at all, as found in the previous study (see section 4.1.3).

4.1.4.2. Synthesis of extended aromatic substituents at position 4 of SBFs

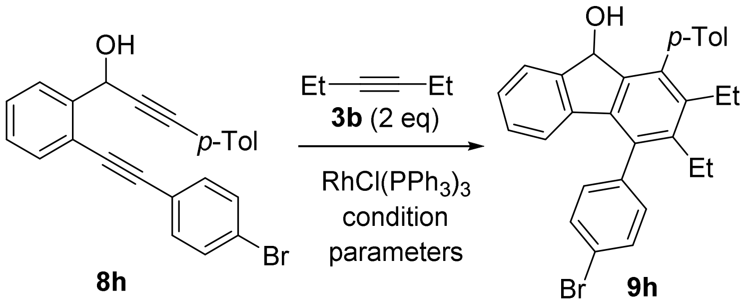
In the second stage, besides the effect of electron-donating and -withdrawing groups at the 4-substituted phenyl group of the SBFs at position 4, the effect on aromatic systems, such as biphenyl or diphenylethynyl moieties at the same position of the SBFs, was studied. In order to attach these substituents at position 4, 4-bromophenyl-substituted SBF **11h** was deemed the most suitable key intermediate to synthesize the desired 4-substituted SBF derivatives.

For the synthesis of the key compound **11h**, the above mentioned five-step synthetic approach was modified. Specifically, to avoid competing side reactions in the Pd-catalyzed Sonogashira cross-coupling of 2-bromobenzaldehyde and 1-bromo-4-ethynylbenzene, the approach to diynol **8h** had to be changed. First, 2-ethynylbenzaldehyde was allowed to react with lithium *p*-tolylacetylide at -78 °C in THF to furnish diynol **12a. 12a** was then reacted with 1-bromo-4-iodobenzene under Sonogashira coupling conditions ($Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%), NEt_3, THF, 80 °C, 3h) to give diynol **8h** that was isolated in excellent yield of 96%. Cyclotrimerization using $RhCl(PPh_3)_3$ (10 mol%) as the catalyst in toluene for 16h at 90 °C gave rise to fluorenol **9h** in an unsatisfactory isolated yield of 26% (Scheme 46, Conditions A). This rather low yield combined with a high catalytic loading led to optimization of the reaction conditions. An extensive screening of cyclotrimerization reactions with Wilkinson's catalyst under various conditions was carried out. It included different solvents, catalytic loadings, reaction temperatures, time and additives (Tables 5-11). After a lot of experiments, suitable catalytic conditions were found, which consisted of using the Wilkinson`s catalyst ($RhCl(PPh_3)_3$, 3 mol%) and the additive Ag_2CO_3 (6 mol%) in THF under microwave irradiation (MW, 1.5 h, 180 °C) (Conditions B). In this case the isolated yield of **9h** almost doubled to 57% (Table 11, Entry 4).



Scheme 46. Synthesis of 4-bromophenyl substituted fluorenol **9h**

Table 5. Reaction condition parameters screened for Rh-catalyzed cyclotrimerization of **9h**



Solvent	Catalyst (mol%)	T (°C)	time (h)	additive (6 mol%)
toluene	10	50	16	Ag_2CO_3
DMF	5	70	48	$AgSbF_6$
CH_2Cl_2	4	80	96	$AgNO_3$
Et_2O	3	110	1, MW	$AgCOOCF_3$
THF	2	150, MW	1.5, MW	AgOTf
	1	170, MW		Ag_3PO_4
		180, MW		$AgBF_4$
		190, MW		$AgCOOCH_3$
				$AgClO_4$
				Ag_2SO_4

Table 6. Variation of the catalyst loading and solvents

Entry	Solvent	Catalyst (mol%)	T (°C)	t (h)	Additive (6 mol%)	Recovered **8h** (%)[a]	**9h**, Yield (%)[a]
1	toluene	5	90	16			30
2	toluene	5	90	16	Ag_2CO_3		32
3	DMF	5	90	16			8
4	DMF	5	90	16	Ag_2CO_3		15
5	toluene	4	90	16			29
6	toluene	4	90	16	Ag_2CO_3		36
7	toluene	3	90	16		7	25
8	toluene	3	90	16	Ag_2CO_3	11	28
9	toluene	2	90	16		28	15
10	toluene	2	90	16	Ag_2CO_3	41	14
11	toluene	2	90	96		14	19
12	toluene	2	90	96	Ag_2CO_3	8	21
13	toluene	1	90	96		23	16
14	toluene	1	90	96	Ag_2CO_3	20	18

[a] Isolated yields

Table 7. Variation of additives

Entry	Solvent	Catalyst (mol%)	T (°C)	t (h)	Additive (6 mol%)	Recovered **8h** (%)[a]	**9h,** Yield (%)[a]
1	toluene	4	90	16	$AgSbF_6$		9
2	toluene	4	90	16	$AgNO_3$		37
3	toluene	4	90	16	$AgOOCCF_3$	13	21
4	toluene	4	90	16	AgOTf		0
5	toluene	4	90	16	Ag_3PO_4	16	21
6	toluene	4	90	16	$AgBF_4$		6
7	toluene	4	90	16	$AgOOCCH_3$		19
8	toluene	4	90	16	$AgClO_4$	31	7
9	toluene	4	90	16	Ag_2SO_4		31

[a] Isolated yields

Table 8. Variation of solvent

Entry	Solvent	Catalyst (mol%)	T (°C)	t (h)	Additive(6mol%)	Recovered **8h** (%)[a]	**9h,** Yield (%)[a]
1	CH_2Cl_2	4	90	16	Ag_2CO_3	5	30
2	Et_2O	4	90	16	Ag_2CO_3	10	32
3	THF	4	90	16	Ag_2CO_3		41

[a] Isolated yields

Table 9. Cyclotrimerization in THF in the presence of different additives

Entry	Solvent	Catalyst (mol%)	T (°C)	t (h)	Additive (6 mol%)	Recovered **8h** (%)[a]	**9h**, Yield (%)[a]
1	THF	4	90	16	-		48
2	THF	4	90	16	$AgNO_3$	38	29
2	THF	4	90	16	AgOTf		21
4	THF	4	90	16	$AgOOCCF_3$	93	5

[a] Isolated yields

Table 10. Effect of temperature

Entry	Solvent	Catalyst (mol%)	T (°C)	t (h)	Additive(6 mol%)	Recovered **8h** (%)[a]	**9h**, Yield (%)[a]
1	THF	4	50	16	Ag_2CO_3	67	15
2	THF	4	50	16	-	81	11
3	THF	4	70	16	Ag_2CO_3	29	26
4	THF	4	70	16	-	31	29
5	THF	4	80	16	Ag_2CO_3		42
6	THF	4	80	16	-		41
7	THF	4	110	16	Ag_2CO_3		35
8	THF	4	110	16	-		33
9	THF	4	150	1, MW	Ag_2CO_3	10	37
10	THF	4	150	1, MW	-		34

[a] Isolated yields

Table 10 (continued). Effect of temperature

Entry	Solvent	Catalyst (mol%)	T (°C)	t (h)	Additive(6 mol%)	Recovered **8h** (%)[a]	**9h**, Yield (%)[a]
11	THF	4	150	1.5, MW	Ag_2CO_3		41
12	THF	4	150	1.5, MW	-		29
13	THF	4	180	1, MW	Ag_2CO_3		51
14	THF	4	180	1, MW	-	6	40
15	THF	4	180	2, MW	Ag_2CO_3		32
16	THF	4	180	1, MW	AgOTf		3
17	THF	4	180	1, MW	$AgSbF_6$		4
18	THF	4	180	1, MW	$AgNO_3$		32
19	THF	4	180	1, MW	Ag_2SO_4		6

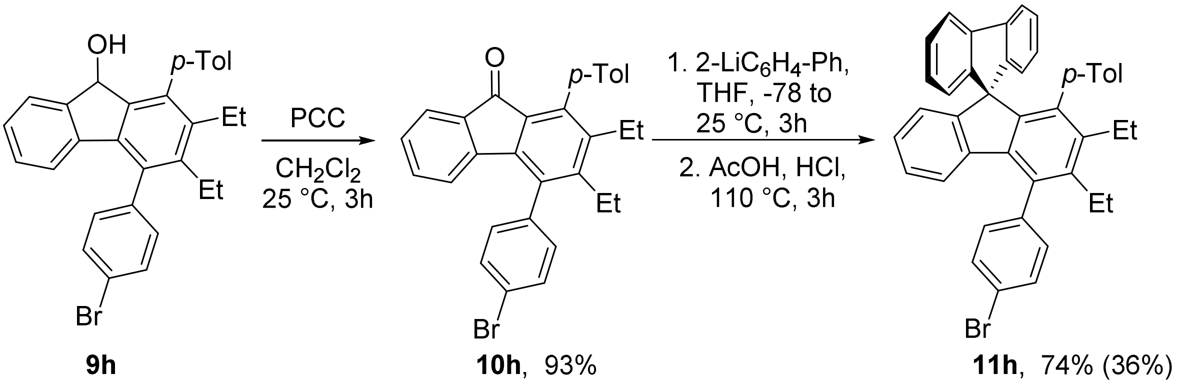
[a] Isolated yields

Table 11. Variation of the catalyst loading and temperature

Entry	Solvent	Catalyst (mol%)	T (°C)	t (h)	Additive (6 mol%)	Recovered **8h** (%)[a]	**9h**, Yield (%)[a]
1	THF	10	180	1, MW	Ag_2CO_3		47
2	THF	5	180	1, MW	Ag_2CO_3		43
3	THF	3	180	1, MW	Ag_2CO_3		49
4	THF	3	180	1.5, MW	Ag_2CO_3		57
5	THF	2	180	1, MW	Ag_2CO_3		32
6	THF	4	170	1, MW	Ag_2CO_3		51
7	THF	3	170	1, MW	Ag_2CO_3		37
8	THF	2	170	1, MW	Ag_2CO_3		27
9	THF	4	190	1, MW	Ag_2CO_3		43
10	THF	3	190	1, MW	Ag_2CO_3		40

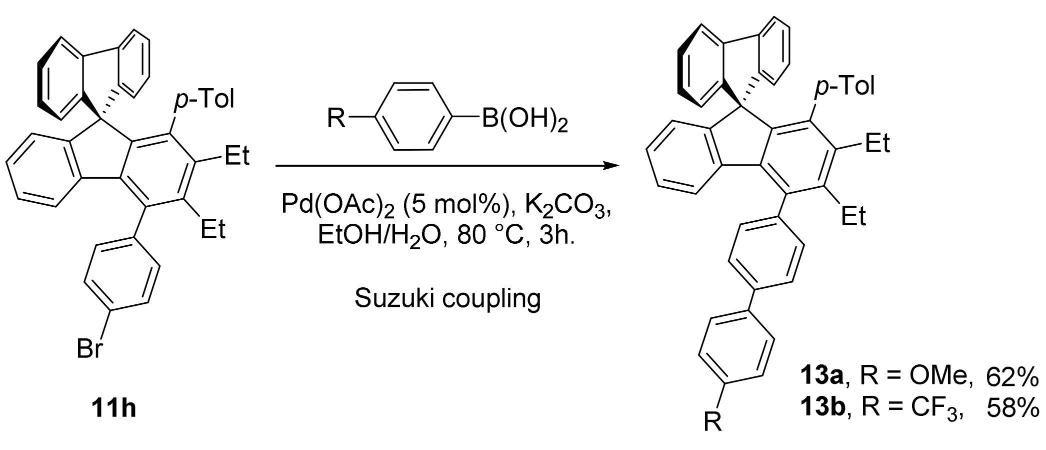
[a] Isolated yields

Having found suitable conditions for preparation of fluorenol **9h** in a good yield under catalytic conditions B, the next step was conducted. Fluorenol **9h** was subjected to oxidation with PCC in dichloromethane at 25 °C to give fluorenone **10h** in a nice 93% isolated yield. Its subsequent reaction **10h** with 2-lithiobiphenyl followed by treatment with a mixture of acetic acid and a catalytic amount of concentrated HCl at 110 °C gave SBF **11h** isolated in 74% yield. Thus SBF **11h** was formed in 36% overall yield after five steps (Scheme 47, the overall yield is in parenthesis).



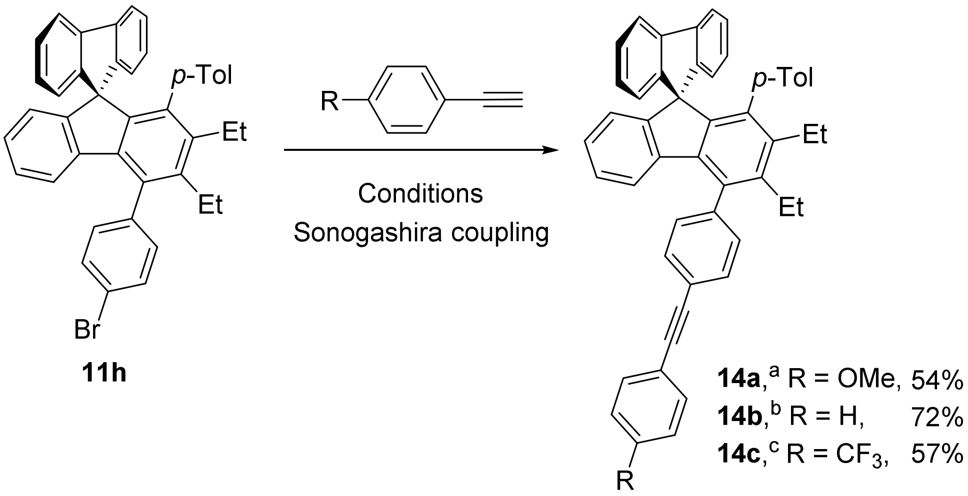
Scheme 47. Synthesis of 4-bromophenyl substituted SBF **11h**

SBF **11h** was then transformed by using a Pd-catalyzed Suzuki cross coupling reaction into **13a** and **13b**. The reactions with (4-methoxyphenyl)boronic acid or (4-(trifluoromethyl) phenyl)boronic acid were catalyzed by $Pd(OAc)_2$ in the presence of K_2CO_3 in a mixture of $EtOH/H_2O$ at 80 °C. The desired SBF **13a** with electron-donating (R = OMe) and SBF **13b** with electron-withdrawing (R = CF_3) substituents were obtained in 62 and 58% isolated yields, respectively (Scheme 48).



Scheme 48. Synthetic procedure for Pd-catalyzed Suzuki reactions to **13a** and **13b**

A similar approach was used for the synthesis of SBFs **14a-c** bearing 4-substituted diphenylethynyl substituents at position 4 of the SBF framework. In this instance Sonogashira cross coupling of **11h** with 4-substituted phenylacetylenes was used. First, the reaction of **11h** with 4-ethynylanisole (R = OMe) was carried out in the presence of $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%) and diisopropylamine as a base under microwave irradiation at 180 °C to give **14a** in 54% isolated yield. The reactions of **11h** with phenylacetylene (R = H) or 1-ethynyl-4-(trifluoromethyl)benzene (R = CF_3) proceeded already at 80 °C, albeit under slightly different reaction conditions. Specifically, SBF **14b** (R = H) was synthesized in 72% yield by using PEPPSI^{TM}-IPr (5 mol%), CuI (10 mol) and triethylamine in THF after 3h, whereas SBF **14c** (R = CF_3) was formed 57% isolated yield by using $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%) and triethylamine as base in DMF after 16h reaction time.(Scheme 49).



a) $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), diisopropylamine, MW, 180 °C, 1h.
b) PEPPSI^{TM}-IPr (5 mol%), CuI (10 mol%), triethylamine, THF, 80 °C, 3h.
c) $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), triethylamine, DMF, 80 °C, 16h.

Scheme 49. Synthetic procedure for Pd-catalyzed Sonogashira reactions to **14a-c**

The structures of **13a** and **14b** were unequivocally confirmed by a single-crystal X-ray analysis (Figures 10 and 11), and the diffraction data showed a similar behavior when analyzing the alignment of the aryl substituent at position 4, as previously observed in SBF **11c**. In the case of **13a** the twisting angle between the parent fluorene plane C4-C5-C6 and the phenyl moiety C37-C38-C42, which is connected to the SBF, had the angle of 83° and in the case of **14b** this angle was 75°. This may be explained by the same effect as previously described when discussing the anomaly in deformation of SBF **11a**, **11c** and **11e**.

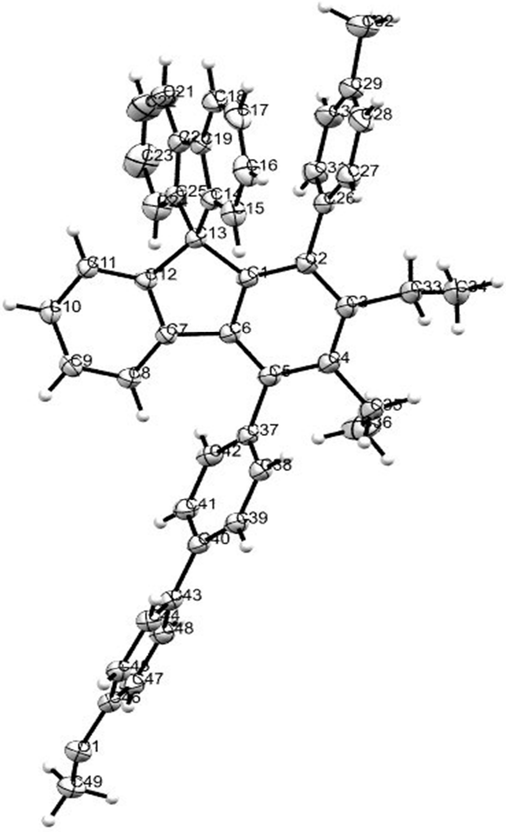


Figure 10. Platon plot of **13a** show displacement ellipsoids at a 50% probability level

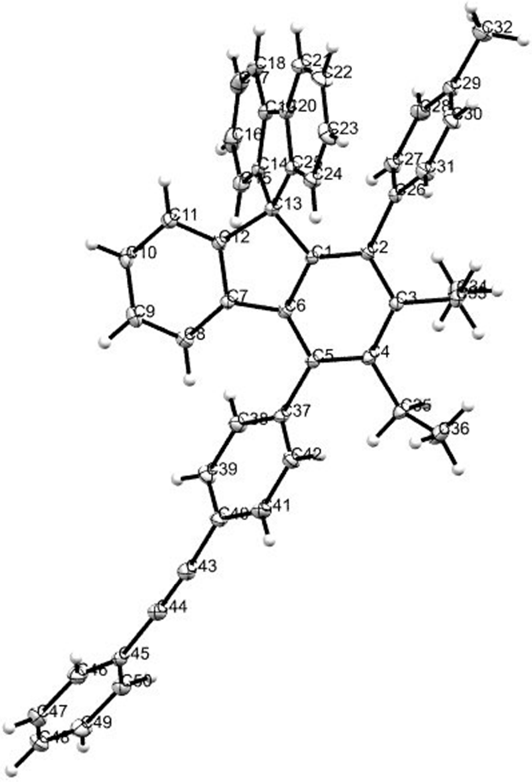
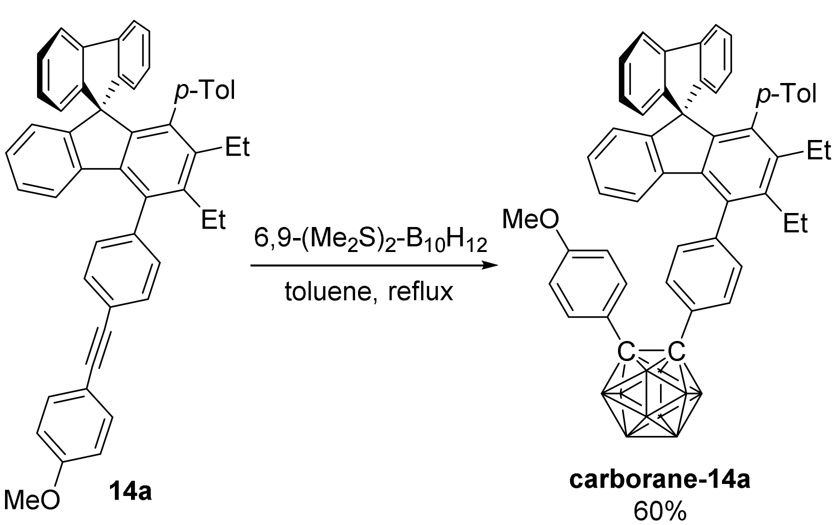


Figure 11. Platon plot of **14b** show displacement ellipsoids at a 50% probability level

SBFs **14** contain the internal triple bond. In general, alkynes are suitable reaction partners in the reaction with 6,9-(Me_2S)-*arachno*-$B_{10}H_{12}$ to form the corresponding 1,2-carboranes.[50] Thus SBFs **14** can be suitable substrates to form the corresponding carborane and the carborane itself might be an interesting target to study its photophysical properties. The previous studies have shown that 1,2-diaryl substituted carboranes exhibit interesting absorption and fluorescence emission properties due to their unique "face-on" conformation of the aryl substituents.[51] Accordingly, **14a** was converted with 6,9-(Me_2S)-*arachno*-$B_{10}H_{12}$ in toluene at 120 °C for 16h into **carborane-14a** containing the SBF moiety in 60% isolated yield (Scheme 50). Its structure was unequivocally confirmed by a single crystal X-ray analysis and showed indeed the "face-on" conformation of the 1,2-aryl substituents of the carborane structure (Figure 12).



14a

carborane-14a
60%

Scheme 50. Conversion of **14a** into carborane containing SBF **carborane-14a**

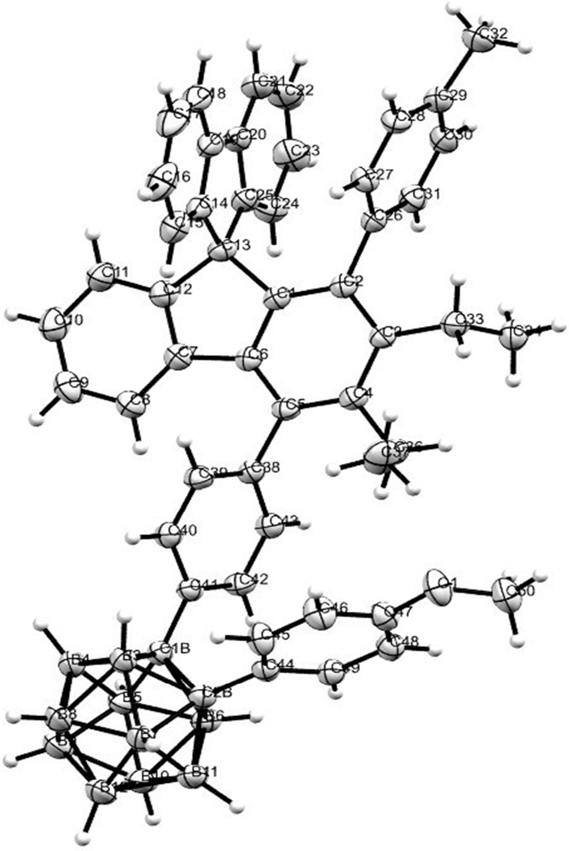


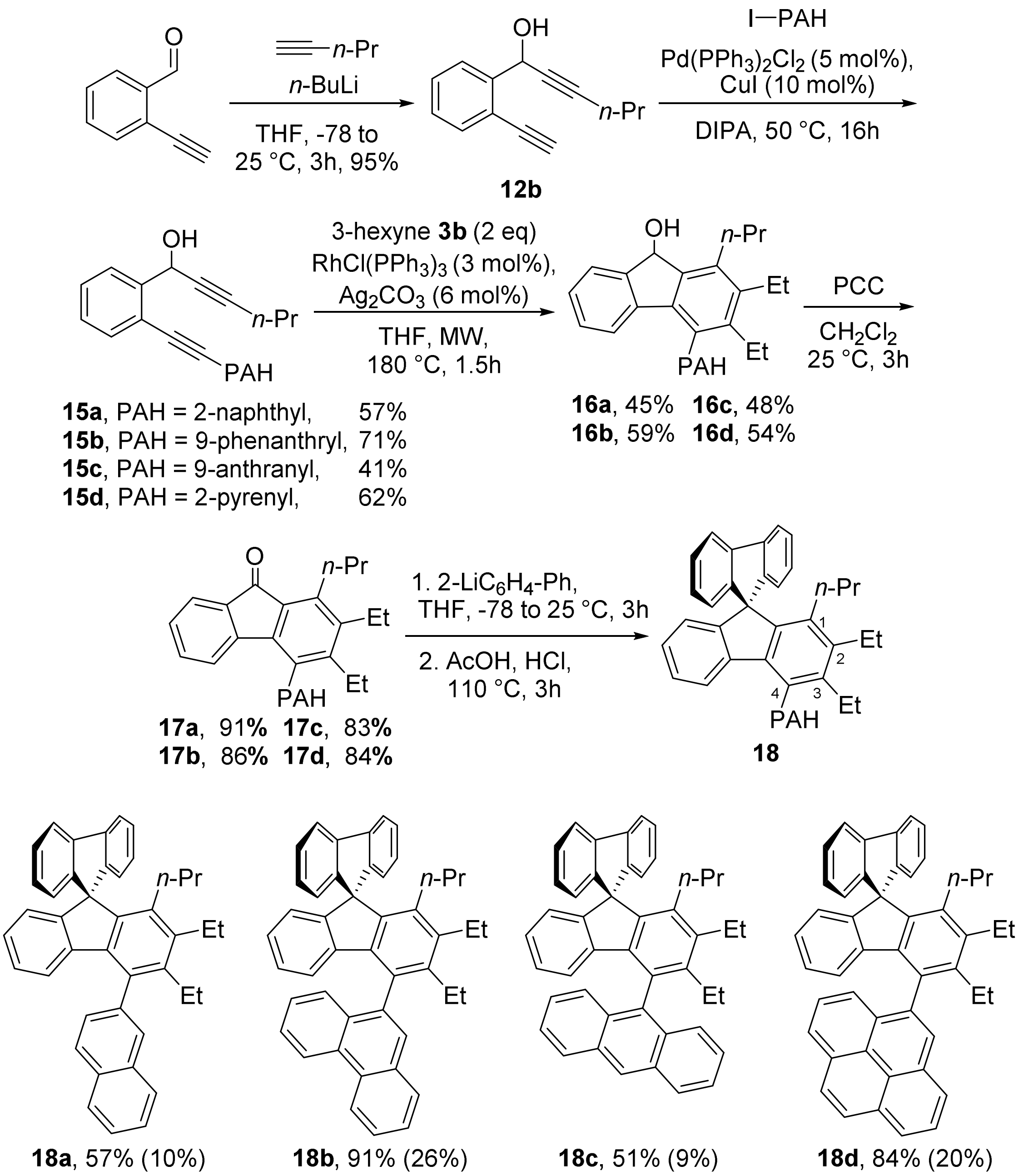
Figure 12. Platon plot of **carborane-14a** show displacement ellipsoids at a 50% probability level

4.1.4.3. Synthesis of fused π-aromatic hydrocarbons at position 4 of SBFs

Fused polyaromatic hydrocarbons (PAHs) represent another class of substituents that can be attached at position 4 of SBFs. PAHs, such as naphthalene, anthracene, phenanthrene or pyrene, have been studied since the 1970s and have shown interesting photophysical properties such as the fluorescence emission wavelength in the 350-420 nm range and reasonable quantum yields of $\Phi = 0.18\text{-}0.72$ in H_2O or ethanol.[52] Thus, SBFs having the PAH based substituents at position 4 seemed to be promising moieties to tune light emission wavelength and quantum yields.

In the first step, 2-ethynylbenzaldehyde was alkynylated with pent-1-yn-1-yllithium in THF at -78 °C to form diynol **12b** possessing the terminal triple bond in 95% isolated yield. The choice for the *n*-propyl substituent at position 1 was based on the fact that it has a negligible effect, if any, on the photophysical properties of the SBF at all (Section 4.1.3). In the next step, **12b** was converted to diynols **15a-d** with halo-PAHs (the use of ethynyl-substituted PAHs was also considered, but the above mentioned approach was chosen because of commercial availability of the halo-PAHs). The diynols **15a-d** were formed by Sonogashira coupling ($PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), NEt_3, THF, 80 °C, 3h) of **12b** with 2-iodonaphthalene, 9-iodoanthracene, 9-iodophenanthrene and 1-iodopyrene, respectively, in good isolated yields ranging from 41 to 71%. The yields were lower in comparison to the previous results of Sonogashira coupling with phenyl halides used for preparation of **7** (see section 4.1.4.1). This might be explained by a lower reactivity of diynol **12b** compared to aryl acetylenes, where the yields were ranging from 80 to 96%.

With diynols **15a-d** in hand, cyclotrimerization reactions were performed. All were reacted with 3-hexyne **3b** under the developed catalytic condition ($RhCl(PPh_3)_3$ (3 mol%), Ag_2CO_3 (6 mol%), THF, 180 °C, MW) into fluorenols **16a-d** in good isolated yields ranging from 45 to 59%, which were similar or even higher than previously observed results for **9a-g** (30-61%, section 4.1.4.1). The subsequent oxidation with PCC in dichloromethane at 25 °C gave rise to fluorenones **17a-d** uneventfully in very high yields ranging from 83 to 91%. In the last step, reactions of 2-lithiobiphenyl with fluorenones **17a-d,** followed by treatment with a mixture of acetic acid and a catalytic amount of concentrated HCl at 110 °C furnished SBFs **18a-d** with fused π-aromatic hydrocarbons at position 4 in high yields ranging from 51 to 91%. The overall yields were again in an acceptable range from 9 to 26% (Scheme 51, the overall yields are in parenthesis).



Scheme 51. Synthetic route of 4-PAH substituted SBF **18a-d**

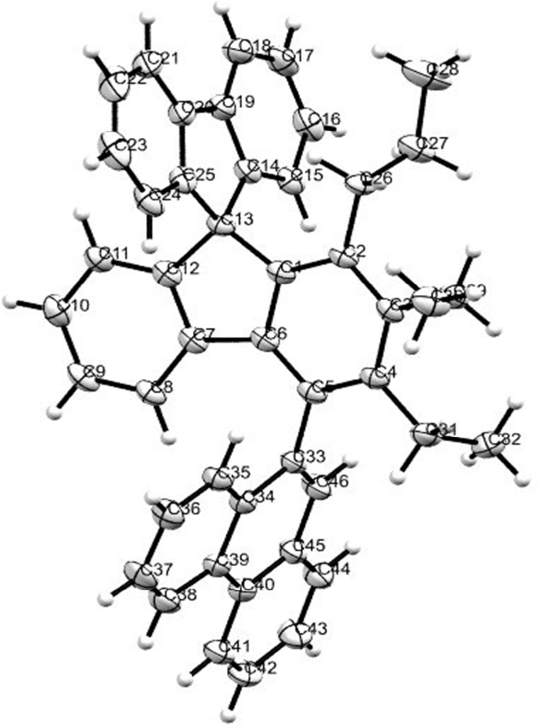


Figure 13. Platon plot of **18b** showing displacement ellipsoids at a 50% probability level

The structure of **18b** was confirmed by a single-crystal X-ray analysis (Figure 13) and showed an almost right angle of 91.8° between the plane of the attached phenanthryl moiety C34-C33-C46 and the fluorene part of the SBF with C4-C5-C6. Thus, also in this case, the molecular twist findings match the results previously observed for SBFs **11**, **13** and **14**.

4.1.5. Photophysical properties of 4-substituted SBFs

Until now, three different sets of 4-aryl substituted SBFs were prepared. They consisted of:

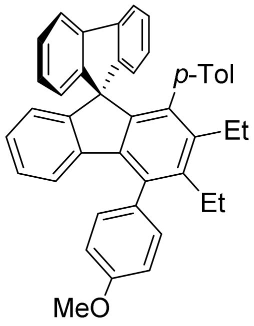
a) **11a-f** with electron-donating and -withdrawing groups at the 4-aryl substituent,

b) **13a** and **13b** with 4-substituted biphenyl moieties and **14a**-**c**, with 4-substituted 4-(2-(phen-1'-yl)ethynylphenyl moieties, one example of **carborane-14a** and,

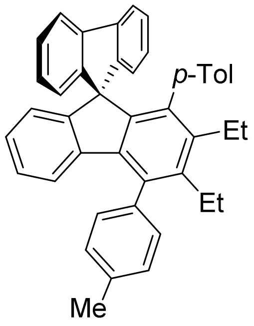
c) SBFs **18a-d** with the fused π-aromatic hydrocarbons at position 4.

All photophysical properties were measured under the same conditions, including a sample concentration of 10^{-6} M in cyclohexane, and the relative quantum yields Φ_s were calculated with DPA as the reference at the isobestic point.

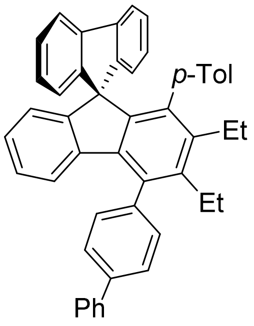
The first set, 4-aryl substituted SBFs **11a-f** was subjected to photophysical properties. After the absorption spectra were measured, the isobestic points of SBFs **11a-f** with the reference DPA (see section 4.1.3) were determined and were in the range of $\lambda = 240$-243 nm. These specific isobestic points then were used as excitation wavelengths λ_{exc} for the fluorescence emission spectroscopy and the results from the emission data are shown in Figures 14 and 15 and in Table 12.



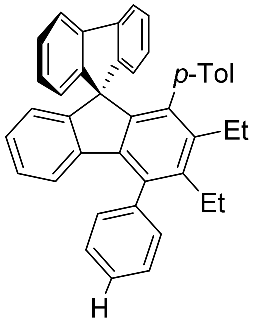
11a



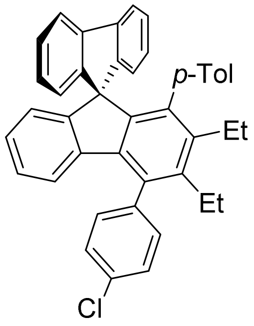
11b



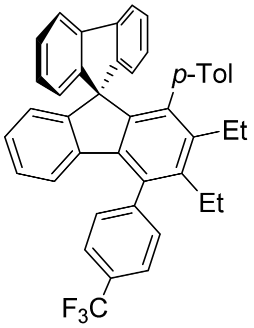
11c



11d



11e



11f

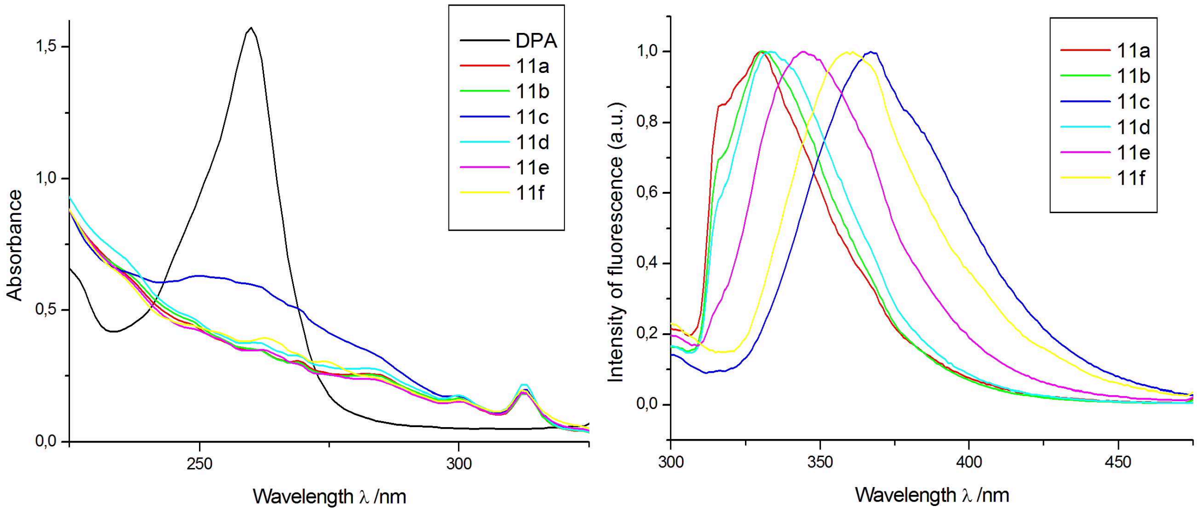


Figure 14. Absorption spectra (left) and normalized and corrected emission spectral data of **11** in 10^{-6} M samples (right)

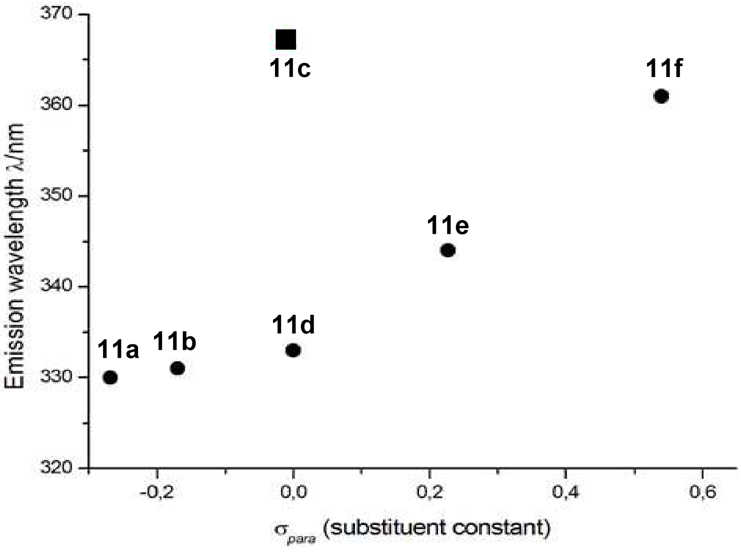


Figure 15. Plot of emission wavelength versus σ_{para} Hammett constants

Table 12. Photophysical properties (10^{-6} M in cyclohexane) of **11** and σ_{para} Hammett constants

Sample	R	λ_{exc} /nm	λ_{em}^{max}/nm	Φ_s[a]	σ_{para}
11a	OMe	241	330	0.50	-0.268
11b	Me	242	331	0.61	-0.17
11c	Ph	243	367	0.87	-0.01
11d	H	241	333	0.66	0
11e	Cl	241	344	0.61	0.227
11f	CF_3	240	361	0.64	0.54

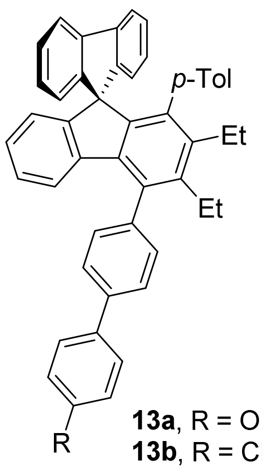
[a] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

The results showed that indeed electron-donating and -withdrawing groups had an effect on the emission wavelength maxima. Moreover there was a reasonable correlation of the emission wavelength maxima with the σ_{para} Hammett constants (Figure 15).[53] The obtained data indicate that the emission maxima were red-shifted in the presence of electron-deficient *para*-groups. This was clearly demonstrated by the difference of more than 30 nm between **11a** (λ_{em} = 330 nm, σ_{para} = -0.268) and **11f** (λ_{em} = 361 nm, σ_{para} = 0.54). The quantum yields of SBFs **11** were in general high (Φ_s = 0.50-0.87) and match those of other 4-aryl substituted SBF derivatives.[2,3a,8d,44,48] Notwithstanding, it should be noted that, in comparison with the parent 4-phenyl-substituted SBF (λ_{em} = 358 nm, Φ_s = 0.40)[2a] and with **11d**, which also have 4-phenyl substituent, the quantum yield, Φ_s = 0.66, was even better. Surprisingly, the difference of 25 nm in the emission maximum between 4-phenyl-substituted SBF and **11d** (λ_{em} = 333 nm) was rather high.

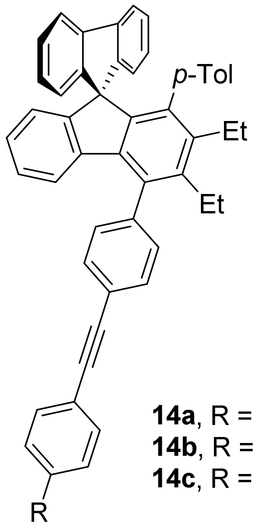
Additionally, the only exception to the linear correlation between σ_{para} and the emission wavelength maximum was observed in **11c** (σ_{para} = -0.01). The effect of one additional π-system on the SBF may explain the red-shifted emission wavelength (λ_{em} = 367 nm) and the very high quantum yield, Φ_s = 0.87.

After these results, samples **13a, 13b** and **14a-c** were also analyzed and compared with **11c** because the structure of **11c** is similar to that of the extended biaryl substituents at position 4 of SBFs without electron-donating or -withdrawing groups. The photophysical properties of **13** and **14** were measured under the same conditions and using DPA as reference as well. However, in contrast to the parent biphenyl substituted SBF **11c**, neither the biphenyl substituted derivatives SBF **13** nor the diphenylethynyl substituted derivatives SBF **14** showed a significant red shift. Only the relative quantum yields Φ_s increased (Figure 16 and Table 13). A detailed analysis of the results shows that the emissiom wavelength maxima λ_{em} of all samples ranged from 366 to 370 nm, thus matching the λ_{em} measured for **11c** (λ_{em} = 367 nm). The measured quantum yields Φ_s ranged from 0.65, for **13a,** to 1.00, for **14c** with the electron-withdrawing CF_3 substituent (Table 13), thereby showing that they are some of the most powerful 4-substituted SBFs prepared thus far regarding quantum yields.[2a,3a,8d,44,48,49]

The analysis of **carborane-14a** showed no fluorescence emission after excitation in the range of λ_{exc} = 250-330 nm, although the “face-on” conformation was confirmed based on X-ray data.



13a, R = OMe
13b, R = CF_3



14a, R = OMe
14b, R = H
14c, R = CF_3

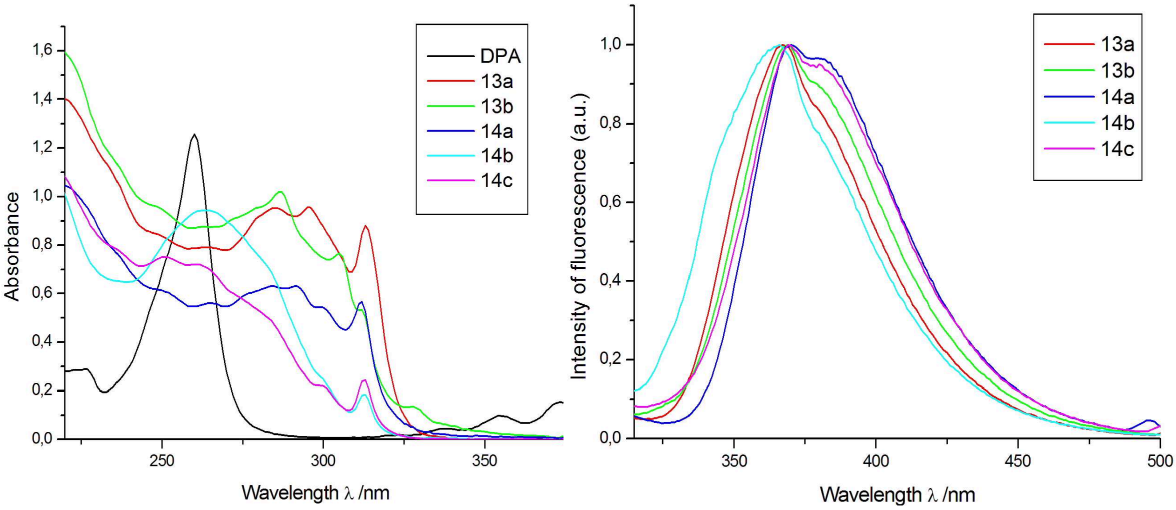


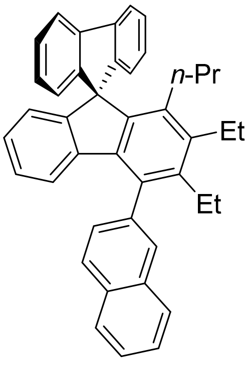
Figure 16. Absorption spectra (left) and normalized and corrected emission spectral data of **13** and **14** in 10^{-6} M samples (right)

Table 13. Photophysical properties of **13a-b** and **14a-c** (10^{-6} M in cyclohexane)

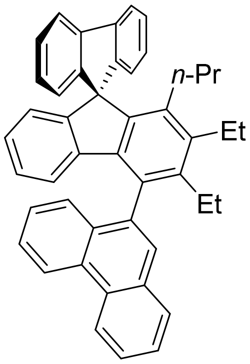
Sample	R	λ_{exc} /nm	λ_{em}^{max}/nm	$\Phi_s{}^a$
13a	OMe	254	366	0.65
13b	CF_3	251	369	0.99
14a	OMe	253	367	0.82
14b	H	254	369	0.79
14c	CF_3	248	370	1.00

[a] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

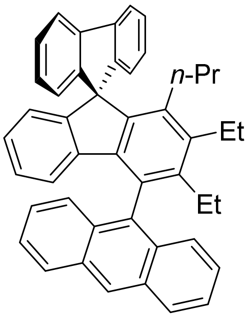
The photophysical properties of the last set with PAH-substituted SBFs **18a-d,** were also analyzed, and the results are shown in Figure 17. Although all four samples exhibit absorption spectra in the range of λ_{abs} = 250-330 nm, only **18b-d** also showed red-shifted emission (λ_{em} = 353-429 nm). The emission quantum yields were low for **18b** (Φ_s = 0.12, Table 14) and **18d** (Φ_s = 0.11), but very high in the case of the anthranyl-substituted SBF **18c** (Φ_s = 0.80). It is noteworthy that the fluorescence emission spectra of **18c** and **18d** show emission patterns similar to those of the parent π-aromatic hydrocarbons anthracene and pyrene, albeit red-shifted by almost 30 nm and 10 nm, respectively.[54,55]



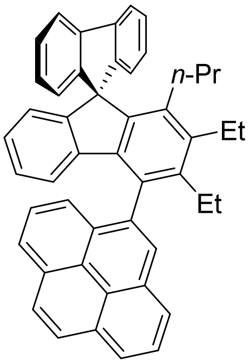
18a



18b



18c



18d

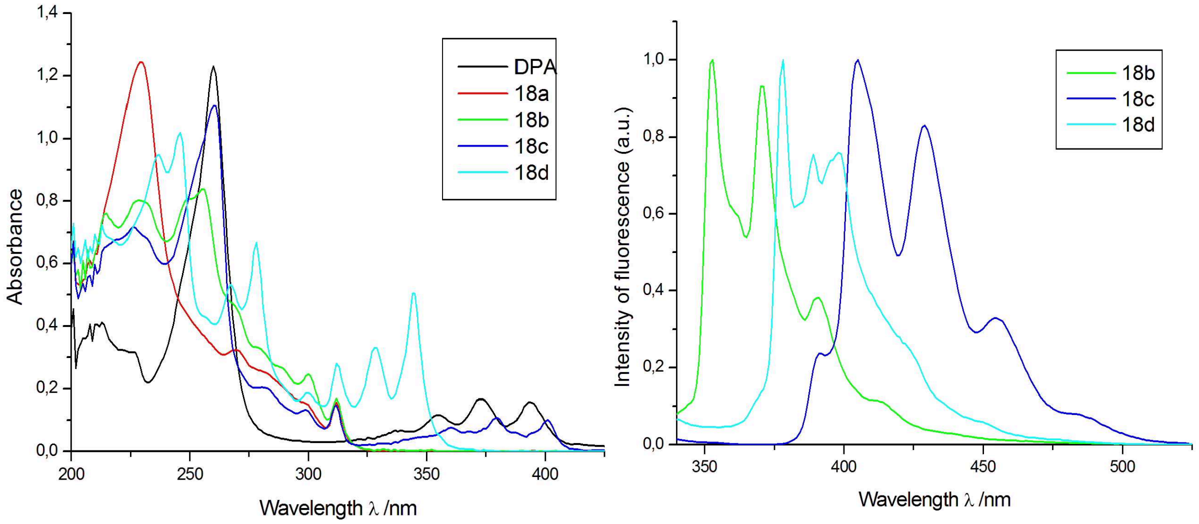


Figure 17. Absorption spectra (left) and normalized and corrected emission spectral data of **18** in 10^{-6} M samples (right)

Table 14. Photophysical properties for **18b-d** (10^{-6} M in cyclohexane)

Sample	R	λ_{exc} /nm	λ_{em}^{max}/nm	Φ_s[a]
18b	Ar = 9-phenanthryl	267	353, 370	0.12
18c	Ar = 9-anthranyl	270	405, 429	0.80
18d	Ar = 2-pyrenyl	267	378, 389	0.11

[a] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

4.1.6. Summary and outlook of 4-substituted SBFs

In the first part of the study, 19 different substituted SBFs at position 4 were synthesized. These substituents included various electron-donating and -withdrawing groups, aromatic substituents and even fused π-extended aromatic hydrocarbons (PAHs). The results showed the effect of different substituents on the photophysical properties of SBFs and indicate the existence of π-conjugation breaking between the 4-substituent and the fluorene, based on X-ray data. Indeed, the X-ray data of all analyzed substituted SBFs reveal a large and, in most cases, almost perpendicular arrangement between the aforementioned fragments. This unique property disrupts the electronic coupling between them,[48] which is presumably restored, at least partly, by planarization of the molecular structure during the stabilization of the excited state.[44a,49] This characteristic of steric hindrance may be used to tune the π-conjugation intensity in materials science for applications in electronic devices. Because of the spiro-framework, these 4-substituted SBFs also exhibit superior thermal and morphological stability,[1] which are key properties for a broad range of applications.[2] Although the effect on 4-substituted SBFs must be further studied, the results already show a high potential for key contributions to the fields of materials science and to organic electronics.

4.2. Dispiroindeno[2,1-*c*]fluorenes (DS-IFs)

4.2.1. Retrosynthesis of indeno[2,1-*c*]fluorenes

In the previous chapters, a new synthetic approach to 1,2,3,4-tetrasubstituted SBFs was described and their photophysical properties were studied (Section 4.1). In this chapter, the synthesis of structurally related indenofluorenes (IF), dihydroindenoflurenes and dispiroindenofluorenes was examined (DS-IF). DS-IFs, due to their structural similarity with SBFs, belong to the same class of condensed polyaromatic hydrocarbons. Similarly to SBFs, the DS-IFs are potential candidates for several applications, specifically in organic electronics, dyes and photovoltaic cells.[6a-g,41]

The indenofluorene framework is composed of the fluorene unit and the indene unit. The indene unit can be attached to different edges of the fluorene scaffold leading to 5-membered family of the corresponding regioisomers: 7,12-dihydroindeno[1,2-*a*]fluorene, 11,12-dihydroindeno[2,1-*a*]fluorene, 6,12-dihydroindeno[1,2-*b*]fluorene, 5,7-dihydroindeno[2,1-*b*]fluorene and 5,8-dihydroindeno[2,1-*c*]fluorene (Figure 18).[39]

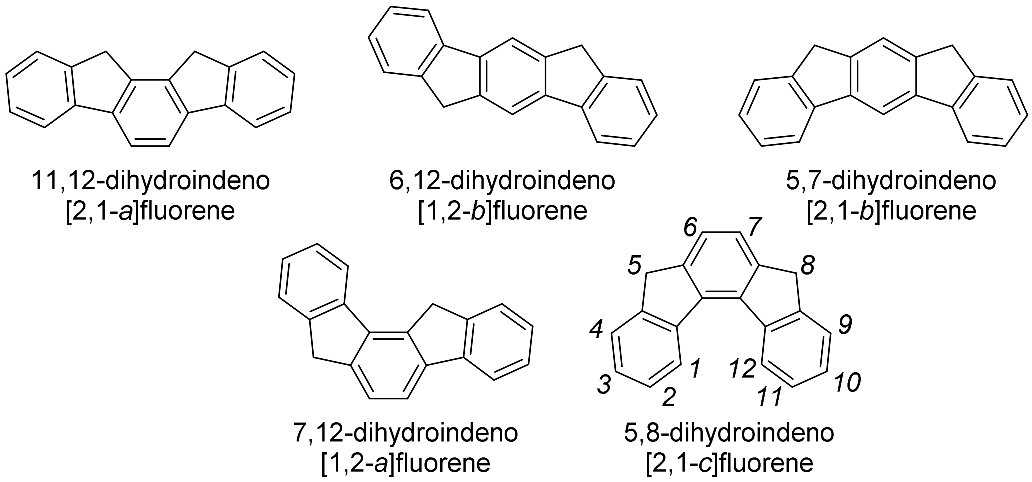
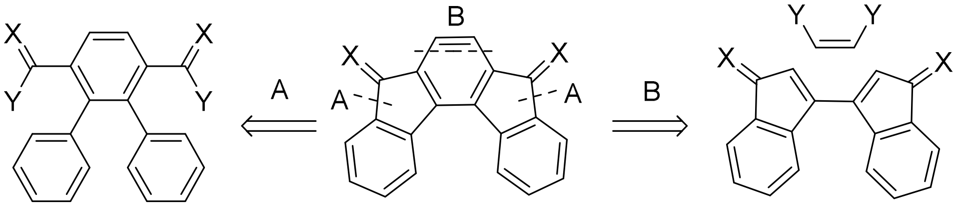


Figure 18. Isomers of the dihydroindenofluorene family

Synthetic approaches for the synthesis of the first four regioisomeric dihydroindenofluorenes have been extensively studied, yet only few reports on the synthesis of the last regioisomer - indeno[2,1-*c*]fluorene - are available. Furthermore, almost all known examples of the synthesis of indeno[2,1-*c*]fluorenes are based on intramolecular Friedel-Crafts-type cyclizations (Scheme 52, Disconnection approach A), on intermolecular Diels-

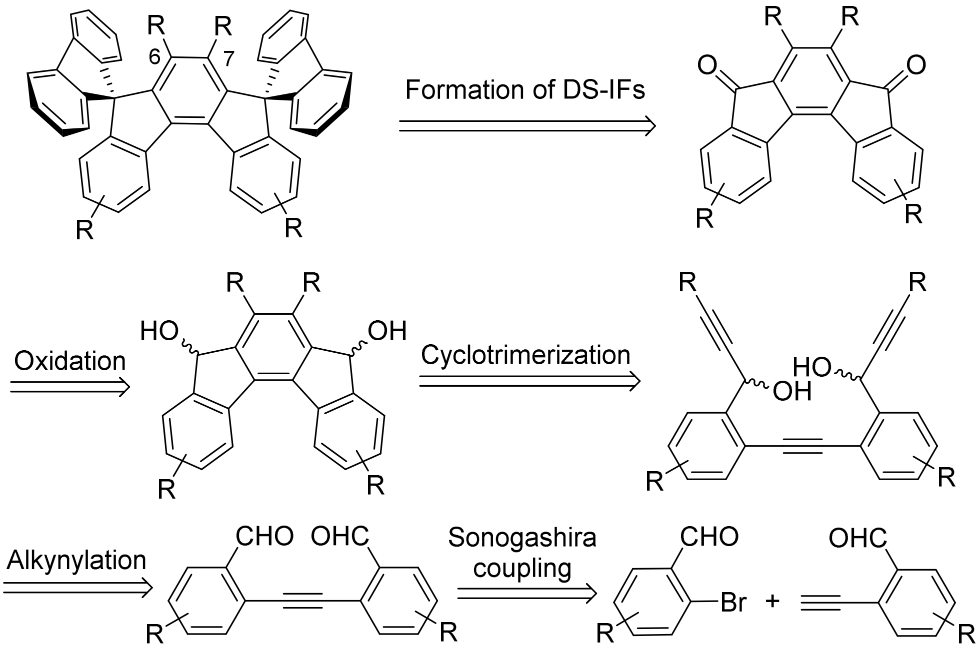
Alder cyclization (Disconnection approach B) or on a combination of both approaches (for further details, please see: 2.1. Synthesis of indeno[2,1-*c*]fluorene).



Scheme 52. General disconnection approaches A and B for indeno[2,1-*c*]fluorenes

The limited approaches for the synthesis of indeno[2,1-*c*]fluorenes narrow the choices of suitably substituted starting material. Moreover, no general approach for the selective synthesis of the substituted indenofluorenes and structure-property analysis has been developed thus far. However, the indeno[2,1,-*c*]fluorenes can be seen as more structurally complex congener of fluorenes. Thus, the previously developed synthetic approach to 1,2,3,4-tetrasubstituted SBFs based on catalytic [2+2+2] cyclotrimerization could also be used for preparation indeno[2,1-*c*]fluorenes (IFs) and their dispiro derivatives (DS-IFs).

The retrosynthetic approach indicates that the DS-IFs could be formed from diketones that can be obtained from substituted indeno[2,1-*c*]fluorenediols by oxidation. The diols can be formed in a transition metal-catalyzed intramolecular [2+2+2] cyclotrimerization as the key step from substituted triyndiols. The triyndiols can be formed using the alkynylation protocol with lithium acetylides from dialdehydes that in turn can be obtained by Sonogashira coupling, as shown in the previous chapters (Scheme 53).[36,47] The desired DS-IFs can then also be studied upon their photophysical properties.

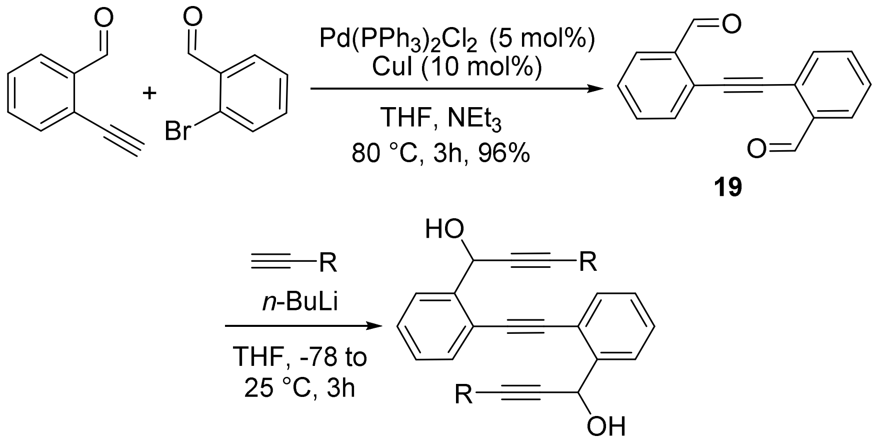


Scheme 53. Retrosynthetic approach for substituted indeno[2,1-*c*]fluorene-5,8-diols

4.2.2. Synthesis of substituted DS-IFs

4.2.2.1. Synthesis of symmetrically substituted DS-IFs

Preparation of triyndiols **19** consisted of 2 steps. The first step was the Sonogashira coupling of commercially available 2-bromobenzaldehyde and 2-ethynylbenzaldehyde using $PdCl_2(PPh_3)_2$ (5 mol%) and CuI (10 mol%) with triethylamine as a base in THF at 80 °C for 3h furnishing dialdehyde **19** in 96% isolated yield. In the second step, twofold alkynylation of the dialdehyde with various 4-substituted lithium phenylacetylides (R = MeO-, Me-, Ph-, Br-, CF_3-) or other acetylides (R = thienyl-, *n*-Pr-, TMS-, 1-naphthyl-) at -78 °C gave rise to nine symmetrically substituted triyndiols **20** in very high isolated yields ranging from 77 to 95% (Scheme 54).



19

20

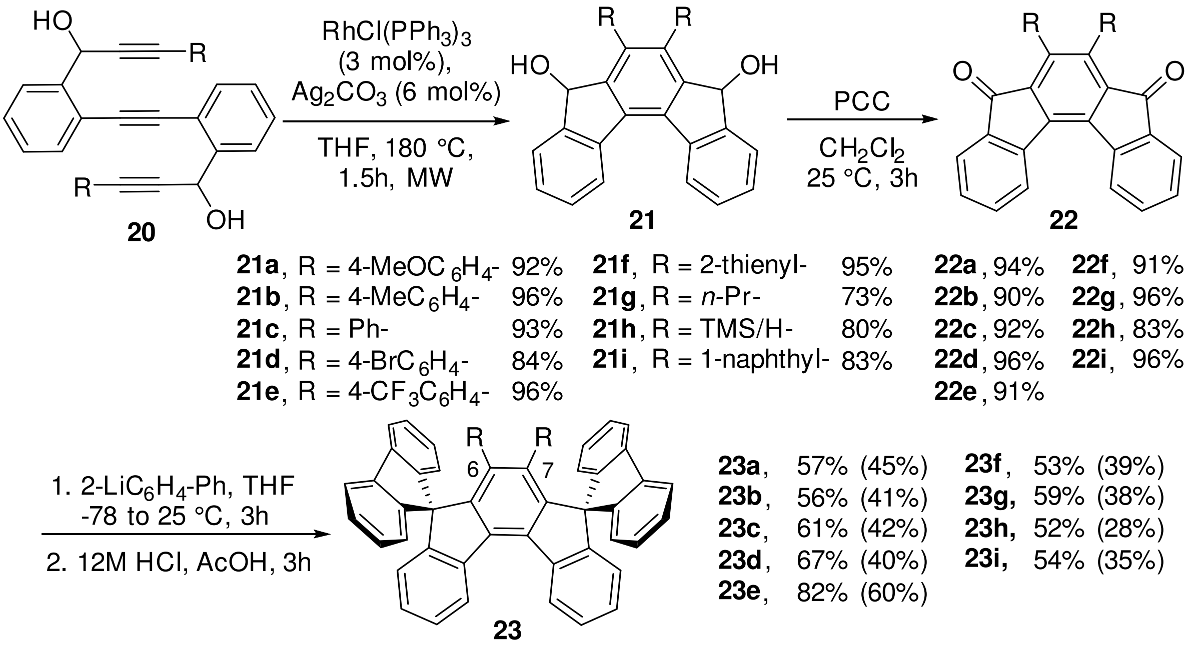
20a, R = 4-$MeOC_6H_4$- 94%
20b, R = 4-MeC_6H_4- 89%
20c, R = Ph- 84%
20d, R = 4-BrC_6H_4- 77%
20e, R = 4-$CF_3C_6H_4$- 86%
20f, R = 2-thienyl- 88%
20g, R = *n*-Pr- 95%
20h, R = TMS/H 84%
20i, R = 1-naphthyl- 85%

Scheme 54. Synthesis of symmetrically substituted triyndiols **20a-i**

Since the cyclotrimerization is the key step of DS-IF formation, the rhodium-complex catalyzed [2+2+2] cyclotrimerization to form indeno[2,1-*c*]fluorene-5,8-diols **21** in the third step was studied. Prior to the experiments, DFT calculations (B3LYP/6-311+G(d,p) at T = 453.15 K) were done to determine the free energy Δ*G* of the conversion of both *cis* and *trans* stereoisomers of triyndiols **20** into indeno[2,1-*c*]fluorene-5,8-diols **21**. The Δ*G* values of -381.78 kJ/mol (*cis*-isomer) and -378.04 kJ/mol (*trans*-isomer) showed that the conversion is energetically favorable despite the high torsional strain caused by steric hindrance in all five *ortho*-fused rings. Encouraged by the favorable computational results, experiments ensued.

Regarding intramolecular [2+2+2] cyclotrimerization reaction conditions of **20**, the ones previously used, based on Wilkinson's catalysts (3 mol%) and Ag_2CO_3 (6 mol%) as an additive in THF under microwave irradiation (1.5 h, 180 °C), were applied. Gratifyingly, the desired indeno[2,1-*c*]fluorene-5,8-diols **21** were formed in very high isolated yields (73-96%) as inseparable mixtures of diastereoisomers. In contrast to intermolecular cyclotrimerizations, no side reactions, such as homo-coupling (Section 4.1), occured in this step. In the cases of triyndiols **20a-c**, **20e** and **20f** a full conversion of the starting material into the target indeno[2,1-*c*]fluorene-5,8-diols was obtained. In the cases of compounds **21d** with 4-bromoaryl substituted and **21i** with naphthyl substituted indeno[2,1-*c*]fluorene-5,8-diols the yields were slightly lower (84% and 83%, respectively). The lowest yield of 73% was observed in the case of *n*-propyl substituted indeno[2,1-*c*]fluorene-5,8-diol **21g**. The only exception among the symmetrically substituted indeno[2,1-*c*]fluorene-5,8-diols was the monosilylated diol **21h**. The monosilylated diol **21h** was obtained after work-up of the reaction mixture as the result of protodesilylation. Similar mono-desilylation reactions have already been observed and explained by the effect of sterically driven protosilylation during the purification process on silica gel.[56]

Then, 2-step conversion of indeno[2,1-*c*]fluorene-5,8-diols into DS-IFs consisting of oxidation and the final formation of the target product ensued. In the fourth step, diols **21a-i** were subjected to oxidation with PCC in dichloromethane at 25 °C forming the corresponding indeno[2,1-*c*]fluorene-5,8-diones **22a-i** in almost quantitative isolated yields ranging from 83 to 96%. In the final step, the reaction of indeno[2,1-*c*]fluorene-5,8-diones **22a-i** with two equivalents of 2-lithiobiphenyl, followed by acidic cyclization using acetic acid and HCl at 110 °C furnished symmetrically substituted 5,8-dispiroindeno[2,1-*c*]fluorenes (DS-IFs) **23a-i** in very good yields (52-83%, Scheme 55). The overall yields of the successfully applied five-step synthesis of symmetrically substituted DS-IFs **23a-i** ranged from 28 to 60% (the overall yields are specified in parenthesis).



Scheme 55. Synthetic pathway of symmetrically substituted DS-IFs **23**

The structure of DS-IF **23b** was unequivocally determined by a single crystal X-ray structure analysis and showed a high degree of molecular twist in the altering *ortho*-fused five- and six-membered ring structure (Figure 19).

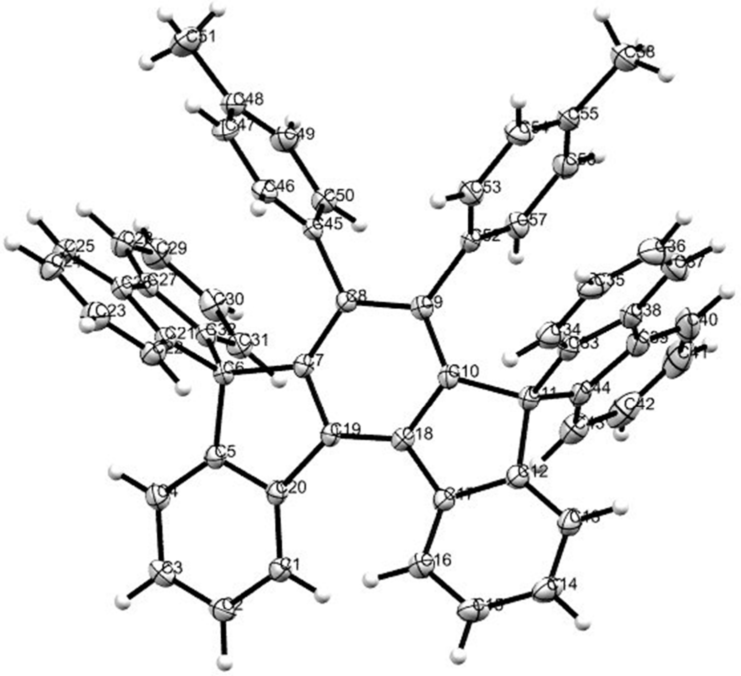


Figure 19. Platon plot of **23b** showing displacement ellipsoids at a 50% probability level

The derived dihedral angles add up to a high twisting angle of the backbone in which the dihedral angle of the fused ring system *1-2-3* was 15.5°, the angle of the fused ring system *2-3-4* was 18.3° and the dihedral angle of the ring system *3-4-5* was 3.2° (Figure 20). The total value of 32.4° was almost three times higher than the 13° backbone twisting of the parent 5,8-dispiroindeno[2,1-*c*]fluorene, as reported by Poriel *et.al.*[6a] Furthermore, the aromatic substituents at positions 6 and 7 are almost perpendicular to ring 3, as shown for SBF derivatives.

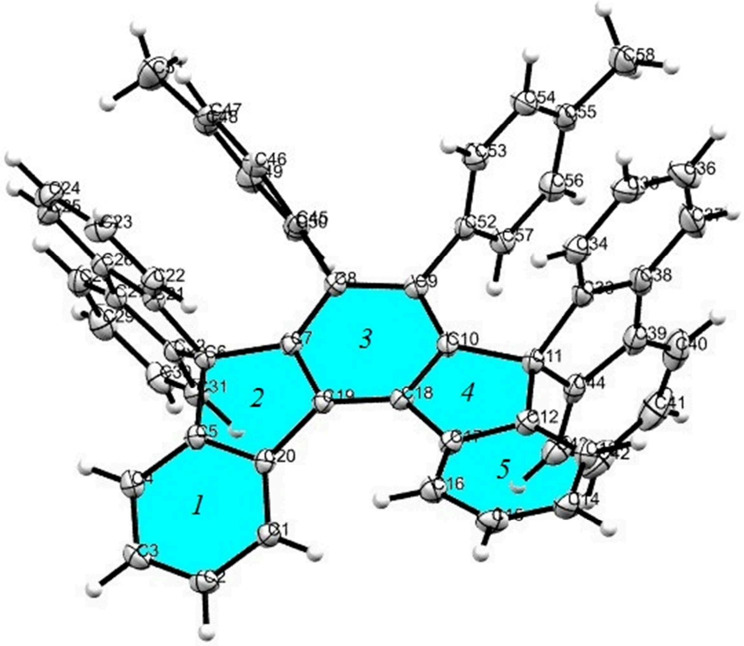


Figure 20. Visualization of DS-IF backbone twisting

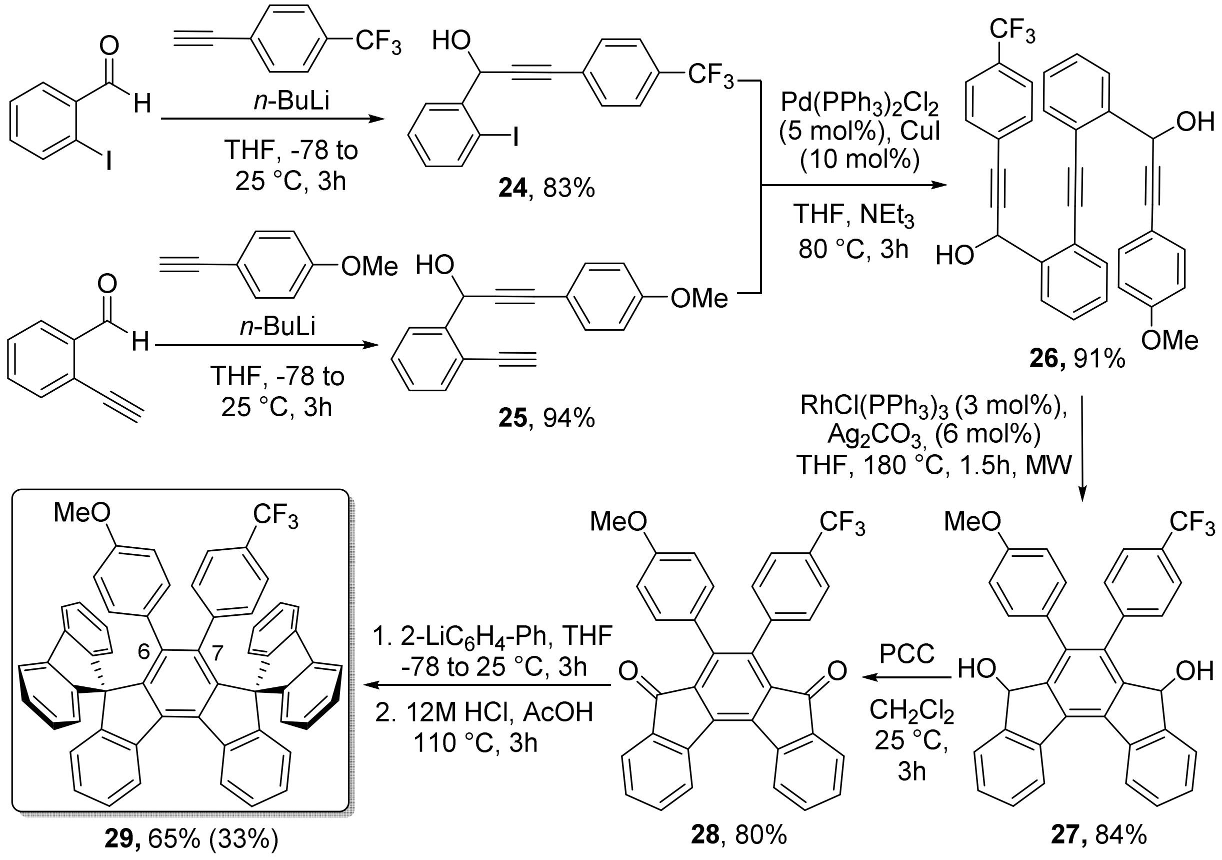
4.2.2.2. Synthesis of unsymmetrically substituted DS-IFs

In the previous chapter, the symmetrically substituted SD-IFs **23** were synthesized in good overall yields. In addition to symmetrically substituted **23**, it is assumed that the same methodology can be applied for synthesis of unsymmetrically substituted DS-IF derivatives. As far as properties of the unsymmetrically substituted DS-IFs are concerned, it is expected that they should exhibit interesting photophysical properties. For example, the interplay of electron-donating and -withdrawing groups within one molecule could result in dramatical change of their fluorescence emission spectra. With this goal in mind, strategies were developed for:

a) synthesis of DS-IF with different substituents at positions 6 and 7 and
b) synthesis of DS-IF with different substituents at positions 3 and 10.

a) Synthesis of DS-IF with different substituents at positions 6 and 7

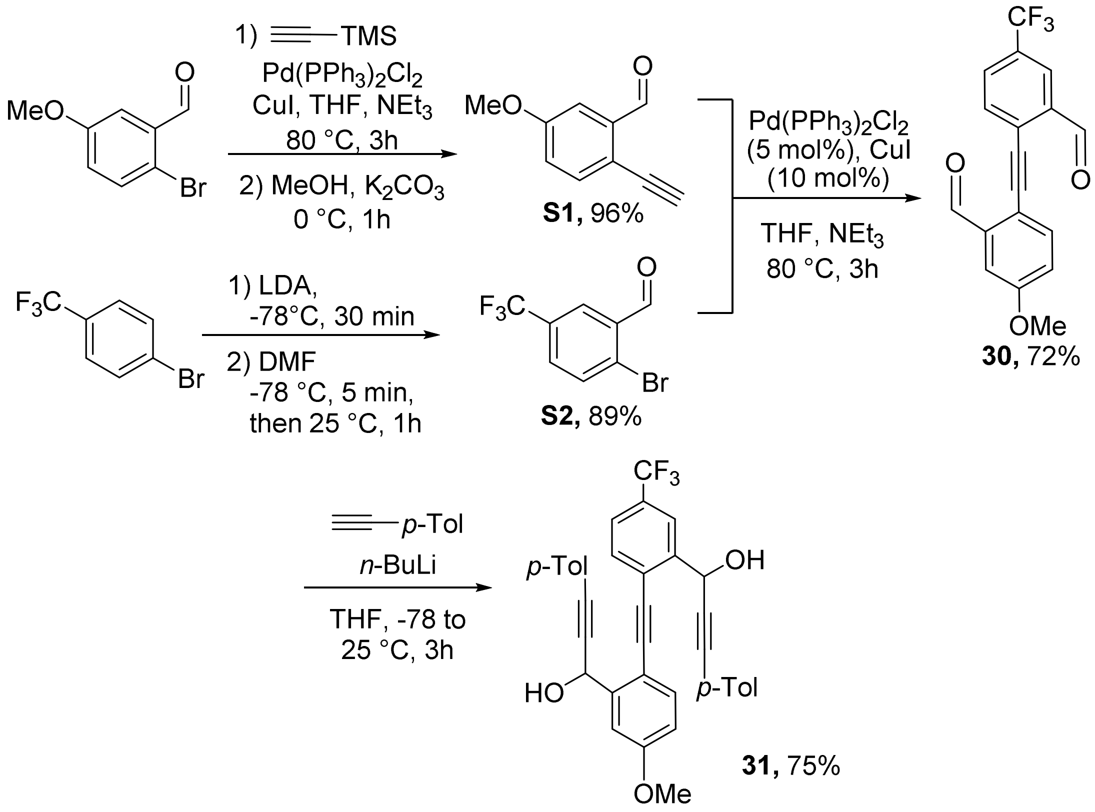
In the first step, unsymmetrically substituted indeno[2,1-*c*]fluorene-5,8-diols at positions 6 and 7 were prepared. For this purpose, alkyne **24** and diyne **25** were synthesized using alkynylation reaction of the commercially available starting materials. More specifically, alkyne **24** was formed by alkynylation reaction of 2-iodobenzaldehyde with lithium (4-trifluoromethylphenyl)acetylide at -78 °C in THF for 3h in 83% isolated yield. Diynol **25** was also synthesized by alkynylation reaction of 2-ethynylbenzaldehyde with lithium (4-methoxyphenyl)acetylide at -78 °C in THF for 3h in 94% isolated yield. Compounds **24** and **25** were then connected using the Sonogashira cross-coupling reaction ($PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), NEt_3, THF, 80 °C, 3h) to form triyndiol **26** in 91% isolated yield (Scheme 56). Gratifyingly, triyndiol **26** was cyclotrimerized in the presence of Wilkinson's catalyst under the previously studied conditions ($RhCl(PPh_3)_3$ (3 mol%), Ag_2CO_3 (6 mol%), THF, 180 °C, MW, 1.5h) into indeno[2,1-*c*]fluorene-5,8-diol **27** in a very high yield of 84%. Subsequently, oxidation to the corresponding indeno[2,1-*c*]fluorene-5,8-dione **28** with PCC in dichloromethane at 25 °C also furnished **28** in a high isolated yield of 80%. Lastly, the unsymmetrically substituted DS-IF **29** was synthesized by reaction of **28** with 2 equivalents of 2-lithiobiphenyl, followed by treatment with a mixture of acetic acid and a catalytic amount of concentrated HCl at 110 °C in a 65% isolated yield. The five-step synthetic pathway allowed synthesizing **29** in the overall yield of 33% (shown in parenthesis).



Scheme 56. Synthesis of unsymmetrically substituted DS-IF **29** (Pathway A)

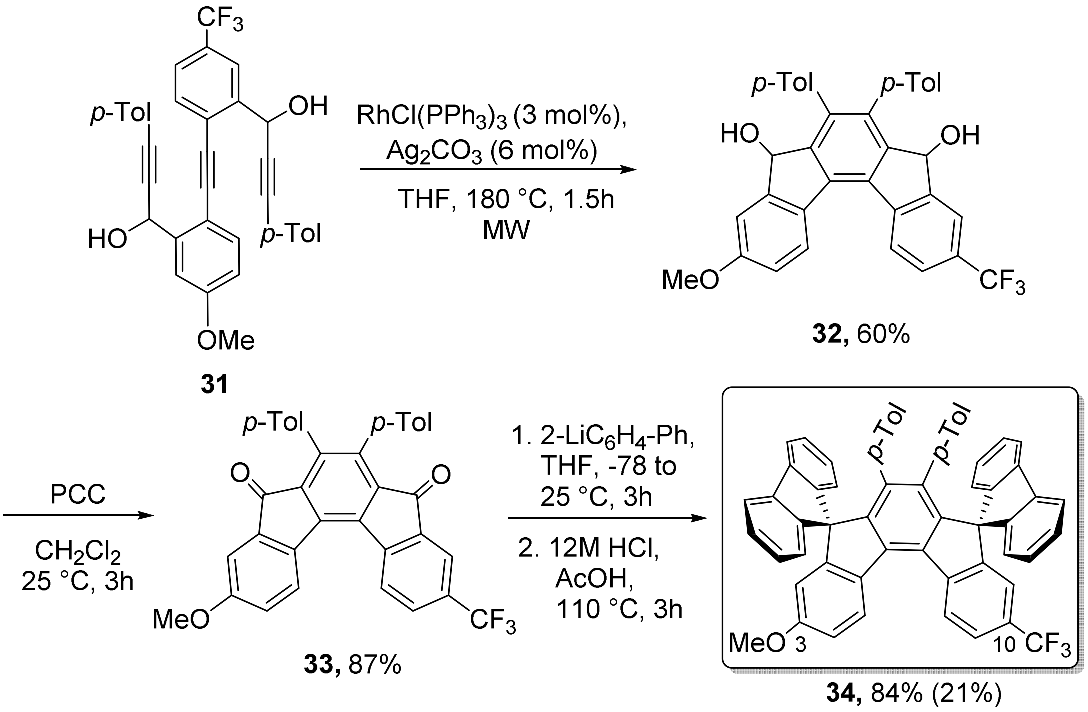
b) Synthesis of DS-IF with different substituents at positions 3 and 10.

The synthesis started with the preparation of substituted 3-ethynylbenzaldehyde **S1** and bromobenzaldehyde **S2.** 3-Ethynylbenzaldehyde **S1** was formed by Sonogashira reaction of 2-bromo-5-methoxybenzaldehyde with trimethylsilylacetylene using $PdCl_2(PPh_3)_2$ (5 mol%) and CuI (10 mol%) with triethylamine as base in THF at 80 °C for 3h. After filtration and evaporation of the solvents, the crude was subjected to deprotection of the TMS group under basic conditions using K_2CO_3 in a mixture of $MeOH/H_2O$ at 0 °C. It furnished **S1** with terminal triple bond in 96% isolated yield.[57] Bromobenzaldehyde **S2** was formed by metallation of 4-trifluoromethylbromobenzene with LDA at -78 °C for 30min, then addition of DMF followed and the reaction mixture was stirred additionally at 25 °C for 1h yielding **S2** in 89% yield after acidic work-up and isolation.[58] Sonogashira reaction of **S1** with **S2** ($PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), NEt_3, THF, 80 °C, 3h) gave rise to dialdehyde **30** in 72% isolated yield. The substituted dialdehyde **30** was alkynylated with lithium *p*-tolylacetylide at -78 °C in THF into triyndiol **31** in 75% isolated yield (Scheme 57).



Scheme 57. Synthesis of unsymmetrically substituted triyndiol **31**

Next, the intramolecular Rh-catalyzed cyclotrimerization was attempted. The previously used reaction conditions (Wilkinson's catalyst (3 mol%), Ag_2CO_3 (6 mol%), THF, 180 °C, MW, 1.5h) were applied and triyndiol **31** was converted into the desired unsymmetrically substituted indeno[2,1-*c*]fluorene-5,8-diol **32**, albeit in a slightly lower isolated yield of 60%. To understand why the yield of the reaction was somewhat lower than in the case of indeno[2,1-*c*]fluorene-5,8-diols **21a-i,** which showed almost full conversion (Section 4.2.2.1, Scheme 55), additional experiments were carried out. The reaction conditions, such as reaction time (30min–1.5h) and temperature (100–180 °C) were changed. Although in all experiments triyndiol **31** was fully consumed, judged by the disappearance of the starting material (TLC analysis), no change in yields of **32** were observed. Partial decomposition of **31** during the course of the reaction to undefined products cannot be excluded. Oxidation of **32** with PCC in dichloromethane at 25 °C furnished the corresponding unsymmetrically substituted indeno[2,1-*c*]fluorene-5,8-dione **32** in a high isolated yield of 87%. In the last step, reaction of **32** with 2 equivalents of 2-lithiobiphenyl, followed by treatment with a mixture of acetic acid and a catalytic amount of concentrated HCl at 110 °C provided the unsymmetrically substituted DS-IF **34** in 84% isolated yield. The overall yield of the six-step reaction procedure was 21% (Scheme 58).



Scheme 58. Synthesis of unsymmetrically substituted DS-IF **34** (Pathway B)

4.2.3. Preparation of [7]-helical DS-IFs

Until now, a set of nine symmetrically substituted DS-IFs, **23**, and two unsymmetrically substituted DS-IFs **29** bearing substituents at positions 6 and 7 and **34** at positions 3 and 10 were prepared. In this step the developed synthetic method for the preparation of DS-IFs was applied to DS-IFs with more than five *ortho*-fused rings. Although the synthetic strategy was the same, now 1-bromo-2-naphthaldehyde was used as the starting material to synthesize DS-IFs possessing the [7]- helical DS-IF scaffold. Such compounds are structurally related to [7]-helical fluorenes and their heterocyclic analogs.[59]

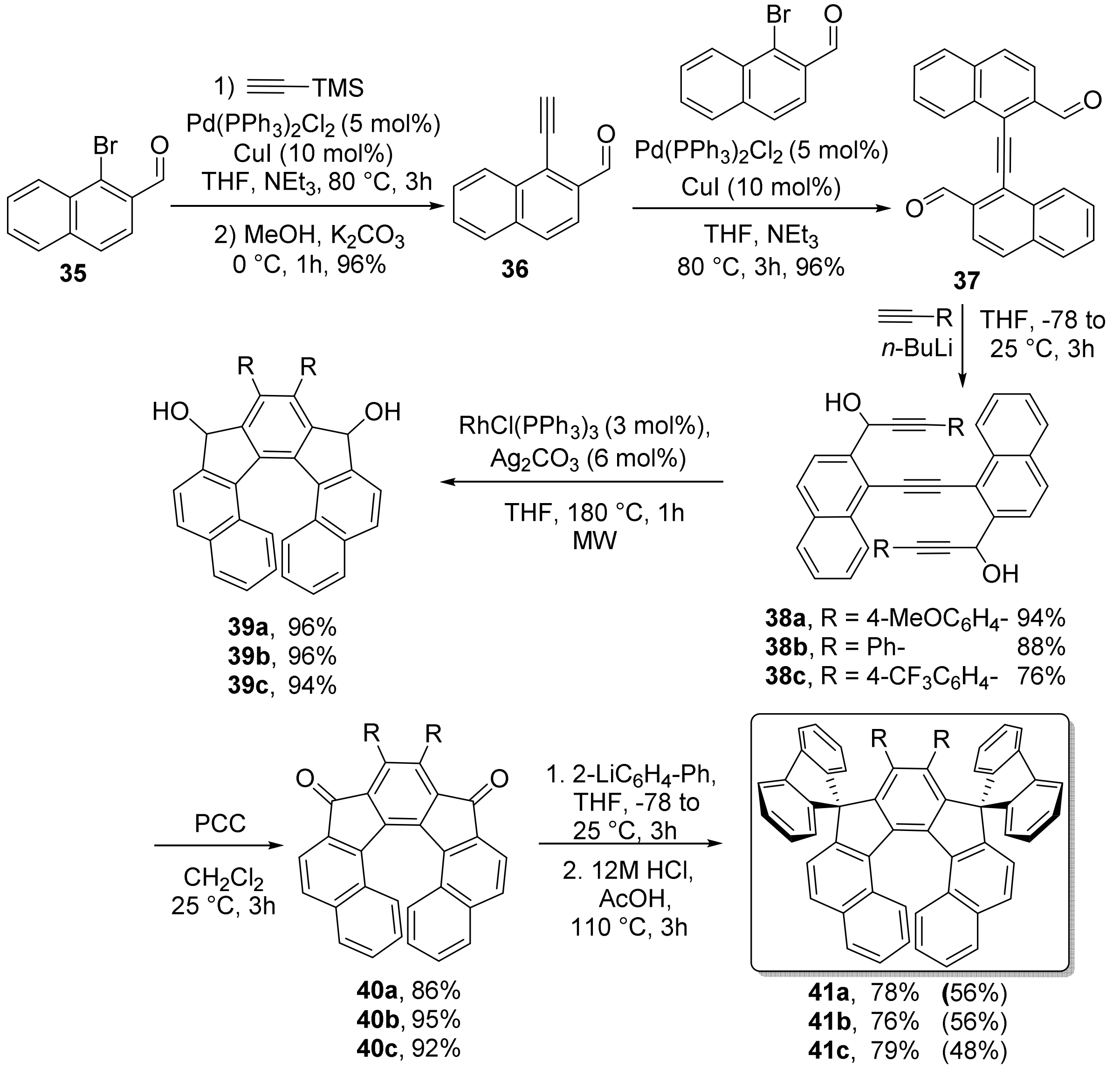
The reaction sequence started with Sonogashira coupling of 1-bromo-2-naphthaldehyde with ethynyltrimethylsilane and was performed using $PdCl_2(PPh_3)_2$ (5 mol%) and CuI (10 mol%) with triethylamine as a base in THF at 80 °C for 3h. The product was not isolated, but was instead filtered, and the solvents were removed. The subsequent removal of the TMS protection group under basic conditions with MeOH/K_2CO_3 at 0 °C furnished 1-ethynyl-2-naphthaldehyde **36** in almost quantitative yield of 96%. In the following step, the second Sonogashira reaction of 1-bromo-2-naphthaldehyde ($PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), NEt_3, THF, 80 °C, 3h) with **36** gave rise to dialdehyde **37**, again, in an almost quantitative isolated yield (96%). In the third step, the subsequent alkynylation of **37** with different 4-substituted lithium phenylacetylides (R = MeO-, H-, CF_3-) in THF at -78 °C provided three symmetrically substituted triyndiols **38a-c** in very high isolated yields ranging from 76 to 94%.

With triyndiols **38a-c** in hand, catalytic cyclotrimerization reactions followed. As in the previous cases, the [2+2+2] cyclotrimerization, catalyzed by $RhCl(PPh_3)_3$ (3 mol%) with Ag_2CO_3 (6 mol%) as additive in THF under MW irradiation at 180 °C, gave the desired [7]-helical indenofluorenediols **39a-c** in almost quantitative isolated yields (94-96%) as racemic mixtures of (*M*)- and (*P*)-helical enantiomers. Gratifyingly, these examples show the potential and efficiency of the Rh-catalyzed [2+2+2] cyclotrimerization. In particular, the excellent yield of the synthesis of the highly twisted helical systems (**39a-c**), consisting of all *ortho*-fused six- and five-membered rings, highlights the importance of the intramolecular [2+2+2] cyclotrimerization key step. In this study, no attempts were performed to synthesize enantiomerically enriched molecules **39** or to separate the racemic mixtures into individual enantiomers.

Finally, the [7]-helical indenofluorenediols **39a-c** were converted into [7]-helical DS-IFs by oxidation and formation of the dispiroderivatives (the final products). For this purpose,

39a-c were oxidized with PCC in dichloromethane at 25 °C forming [7]-helical indenofluorenediones **40a-c** in high isolated yields ranging from 82 to 95%. Then, the two-step conversion based on the reaction of **40a**-**c** with 2-lithiobiphenyl and followed by treatment with a mixture of acetic acid and a catalytic amount of concentrated HCl at 110 °C furnished [7]-helical DS-IFs **41a**-**c** in high yields ranging from 76 to 79%.

In summary, three [7]-helical DS-IFs **41a**-**c** were formed in six steps from the commercially available starting materials, the overall yields were in a very good range of 48-56% (Scheme 59, overall yields are shown in parenthesis).



Scheme 59. Synthesis of extended [7]-helical DS-IF **41**

The helical structures of **40a** and **41a** were unequivocally confirmed by a single crystal X-ray analysis (**41a**, Figure 21). The data show dihedral angles of 7.4° for the ring system *1-2-3*, 14.8° for *2-3-4*, 24.0° for *3-4-5*, 23.3° for *4-5-6* and 2.0° for *5-6-7* (Figure 22). The total sum of 64.1° reflects the high degree of molecular twist. The molecular twisting angles of structurally related [7]-helical compounds range from 82.8 to 97.8°.[59a,b] Thus, the degree of molecular twist in [7]-helical DS-IF **41a** is lower, most likely due to the presence of two cyclopentadiene rings.

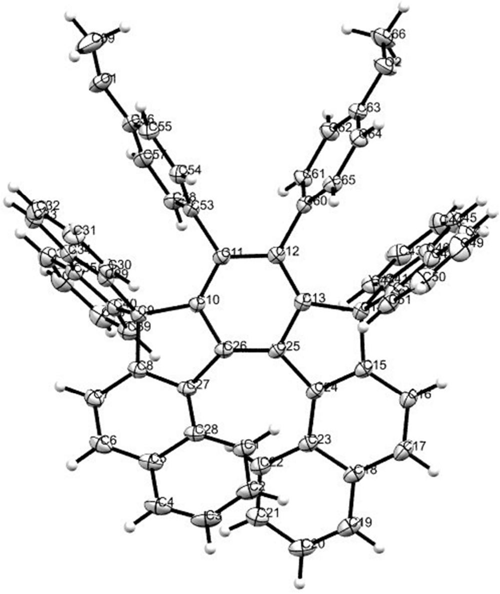


Figure 21. Platon plot of **41a** showing displacement ellipsoids at a 50% probability level

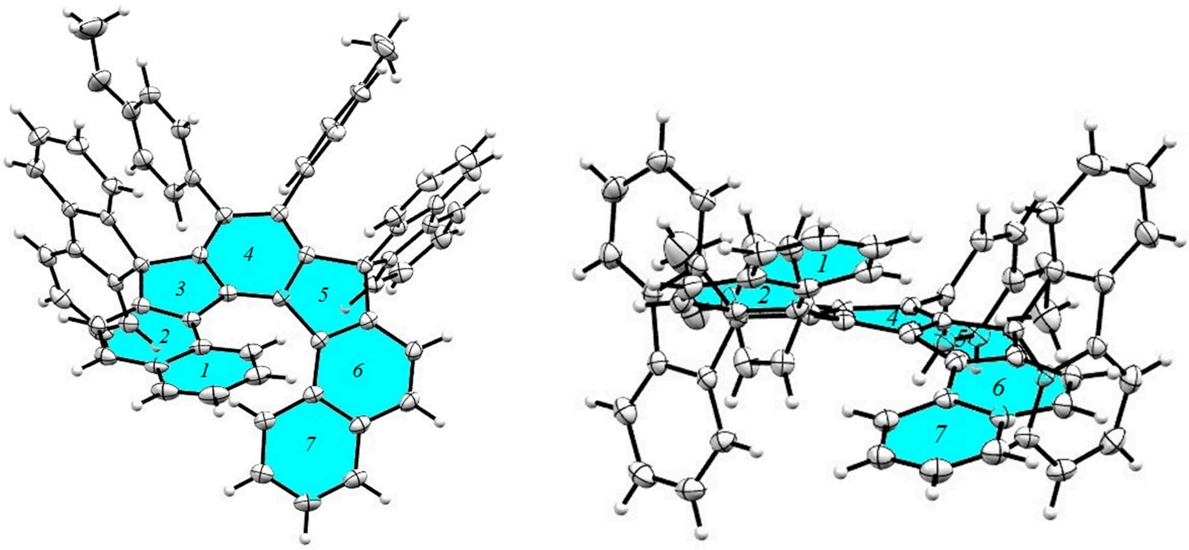


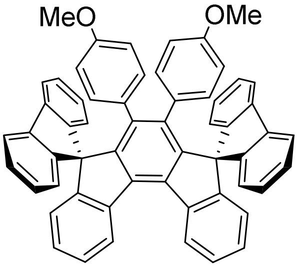
Figure 22. Colorized visualization of (P)-[7]-helical DS-IF **41a** backbone twisting

4.2.4. Analysis of photophysical properties

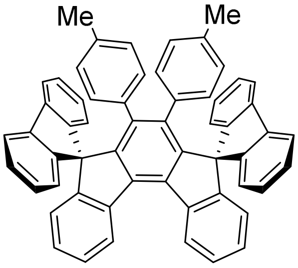
4.2.4.1. Photophysical properties of DS-IFs 23, 29 and 34

In the previous sections, a set of nine symmetrically substituted DS-IFs **23a-i,** two unsymmetrically substituted DS-IFs **29** and **34** and three [7]-helical DS-IFs **41a-c** were synthesized.

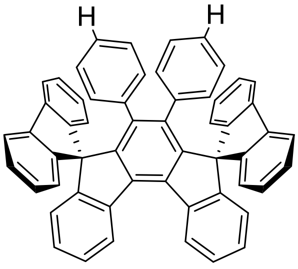
Firstly, the analysis of the absorption spectral data with DPA as the standard reference was conducted for the symmetrically substituted DS-IF **23a-i**. The data of the absorption spectroscopy show that the isobestic point for the further calculation of relative quantum yields of DS-IFs **23a-i** was best in the range from 264 to 271 nm. The subsequent fluorescence emission data after excitation at corresponding λ_{exc} = 264-271 nm showed a maximum in the very narrow range of 359-380 nm (Figure 23) and quantum yields ranging from Φ_s = 0.09-0.70 (Table 15) for all DS-IFs, except **23h** with TMS-substituent, which showed no emission in this area.



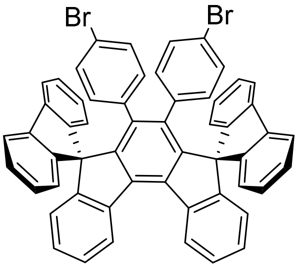
23a



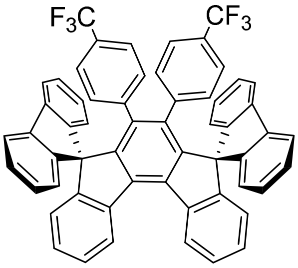
23b



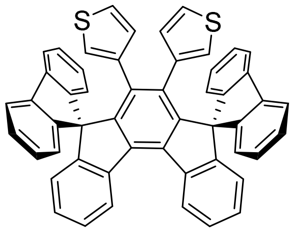
23c



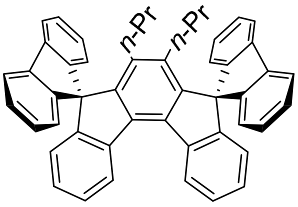
23d



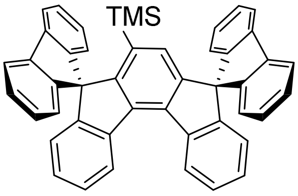
23e



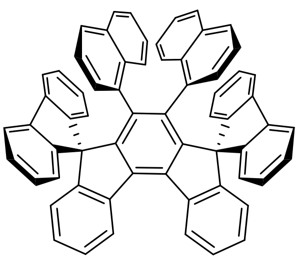
23f



23g



23h



23i

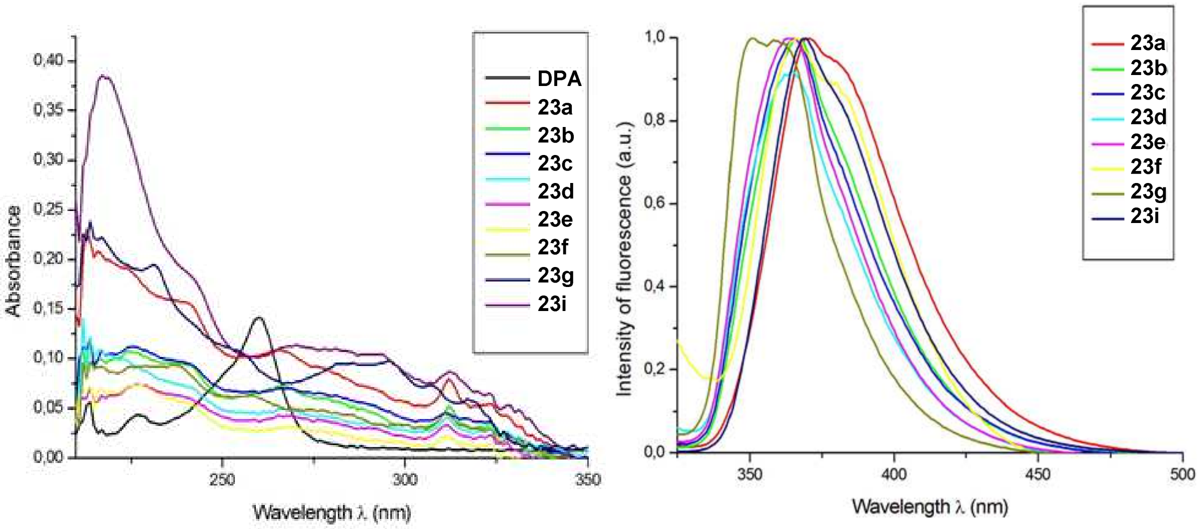


Figure 23. Absorption and normalized emission spectral data of symmetrically substituted DS-IFs **23** in10^{-6} M

Table 15. Photophysical properties for **23a-i** (10^{-6} M in cyclohexane)

Sample	R	λ_{exc} /nm	λ_{em}^{max}/nm	Φ_s[a]
23a	R = 4-MeOC_6H_4-	264	370, 380	0.31
23b	R = 4-MeC_6H_4-	266	366	0.09
23c	R = Ph-	266	366	0.67
23d	R = 4-BrC_6H_4-	269	365	0.33
23e	R = 4-$CF_3C_6H_4$-	269	364	0.70
23f	R = 2-thienyl-	271	366, 380	0.20
23g	R = *n*-Pr-	269	351, 359	0.63
23h	R = TMS/H-	266	-	0.00
23i	R = 1-naphthyl-	264	369	0.28

[a] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

The unsymmetrically substituted DS-IFs **29** and **34** showed, after excitation at the isobestic point λ_{exc} = 272 nm (for **29**) and λ_{exc} = 268 nm (for **34**), fluorescence emission maxima at λ_{em} = 370 nm and 389 nm (Figure 24) and quantum yields Φ_s = 0.54 and 0.60, respectively (Table 16).

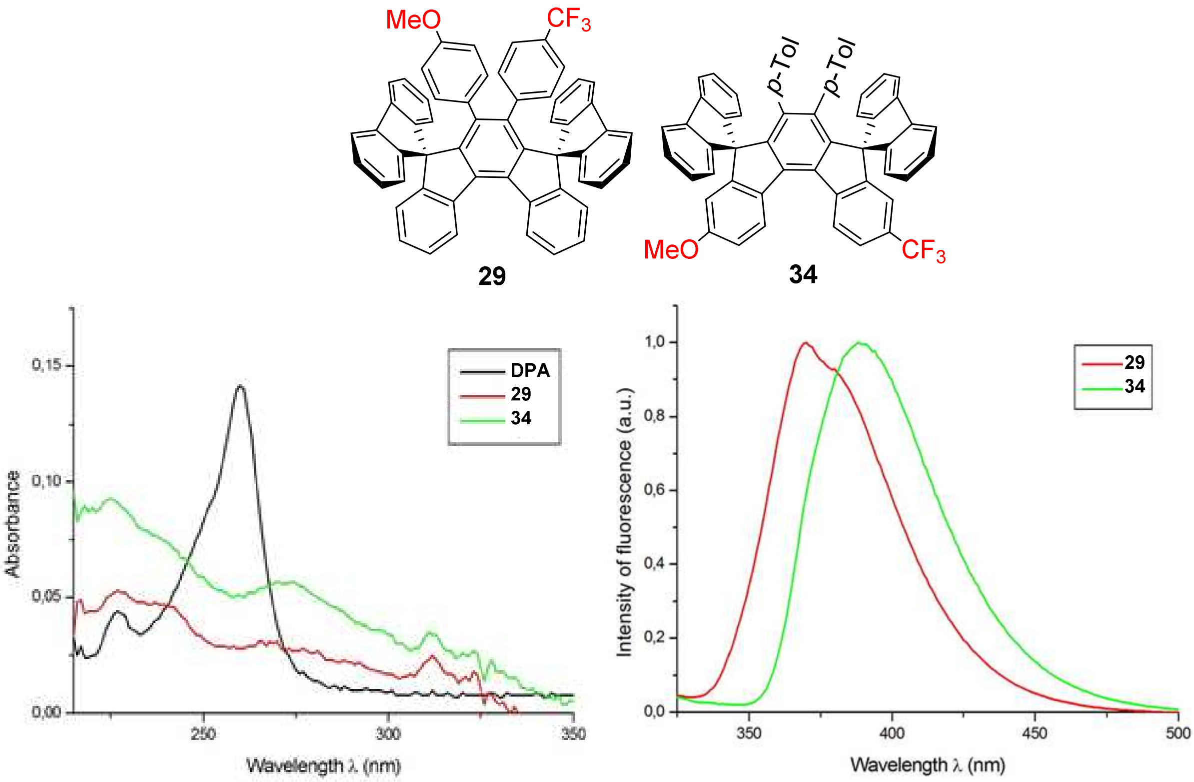


Figure 24. Absorption and normalized emission spectral data of unsymmetrically substituted DS-IF **29** and **34**

Table 16. Photophysical properties for **29** and **34** (10^{-6} M in cyclohexane)

Sample	λ_{exc} /nm	λ_{em}^{max}/nm	Φ_s[a]
29	272	370	0.54
34	268	389	0.60

[a] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

Comparative analysis with parent 5,8-dispiroindeno[2,1-*c*]fluorene showed that:[6a]

1) Instead of two distinct emission peaks, all substituted DS-IFs show only one maximum emission peak, which overlaps a second emission peak in some cases.

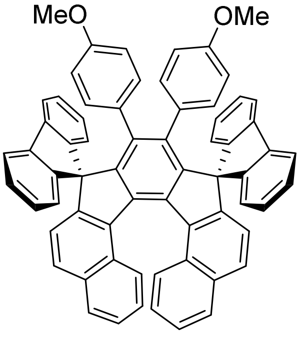
2) All symmetrically substituted compounds **23** show the emission maximum λ_{em} = 359-380 nm red-shifted by 1-22 nm in relation to the unsubstituted DS-IF (λ_{em} = 358 nm).

3) Electron-rich substituents apparently enhanced the red shift of the emission maxima, particularly 4-methoxyphenyl and thienyl substituents (**23a** and **23f**, both λ_{em} = 380 nm) at positions 6 and 7 of the DS-IF. They both show a 22 nm shift in relation to the parent DS-IF.

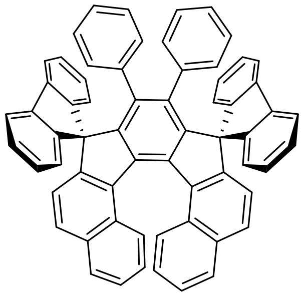
4) The effect of the electron-donating and -withdrawing substituents directly attached to the DS-IF (**34**, λ_{em} = 389 nm, substituents at positions 3 and 10) is stronger than that of 4-phenyl-substituted moieties at positions 6 and 7 of the DS-IF **29** (λ_{em} = 370 nm). This may be explained by the virtually perpendicular arrangement of the DS-IF and its substituents at positions 6 and 7, as shown by a X-ray single-crystal analysis of **23b** (for details, please see: 4.2.2.1). More specifically, this molecular twist may lead to weaker interactions between π-systems, thereby decreasing the effect of substituents on the photophysical properties of the DS-IFs. Nevertheless, partial restoration of the planar arrangement presumably occurs in the excited state. The actual effect of twisted π-systems and their interactions with parent DS-IFs is not yet fully clarified, thus requiring further studies.[2a,3a,8d,44,48,49]

4.2.4.2. Photophysical properties of [7]-helical DS-IFs 41

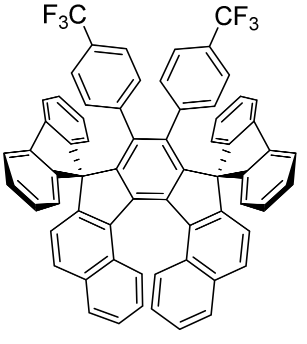
Similarly to the analysis of DS-IFs **23**, **29** and **34** above (Section 4.2.4.1), the photophysical properties of [7]-helical DS-IFs **41** were also analyzed. After excitation at the isobestic point $\lambda_{exc} = 269$ nm for all three compounds, the fluorescence emission data of **41a-c** showed red-shifted emission in the range of $\lambda_{em} = 398\text{-}428$ nm (Figure 25) with excellent quantum yields ranging from $\Phi_s = 0.75\text{-}0.88$ (Table 17).



41a



41b



41c

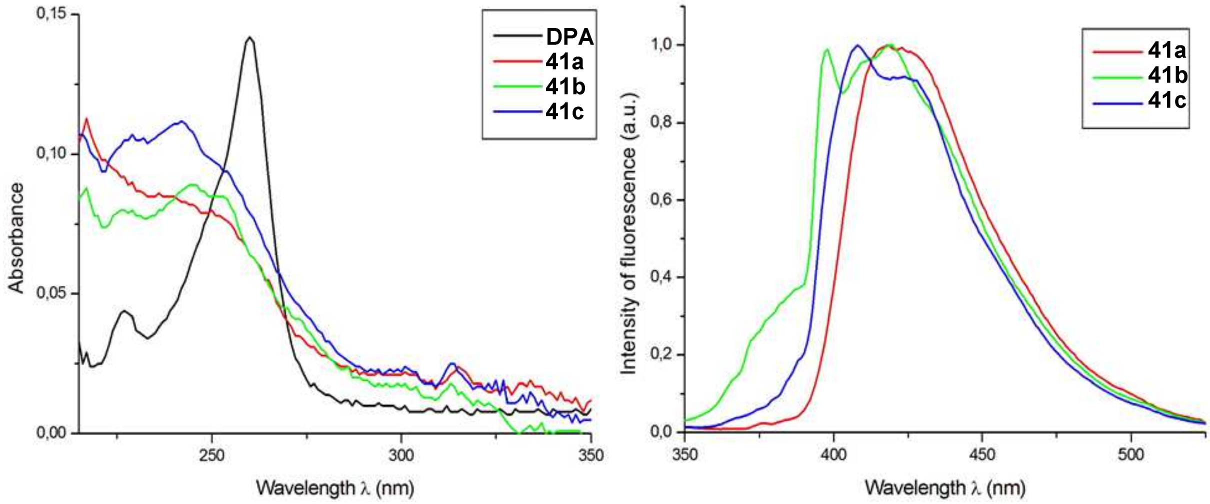


Figure 25. Absorption and emission spectral data of symmetrically substituted [7]-helical DS-IF **41** in10^{-6} M in cyclohexane

Table 17. Photophysical properties for **41a-c** (10^{-6} M in cyclohexane)

Sample	R	λ_{exc} /nm	λ_{em}^{max}/nm	Φ_s[a]
41a	R = 4-MeOC$_6$H$_4$-	269	418, 428	0.75
41b	R = Ph-	269	398, 428	0.87
41c	R = 4-CF$_3$C$_6$H$_4$-	269	408, 423	0.88

[a] Quantum yields calculated relative to DPA ($\Phi_r = 0.97$).

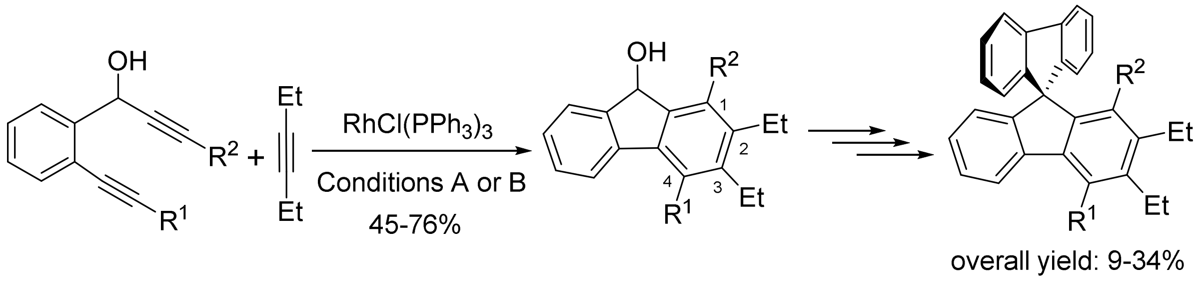
In comparison with the 5-ring containing DS-IFs **23a** (R = OMe, λ_{em} = 380 nm) **23c** (R = H, λ_{em} = 366 nm) and **23e** (R = CF_3, λ_{em} = 364 nm), the [7]-helical DSF-IFs **41a** (R = OMe, λ_{em} = 428 nm), **41b** (R = H, λ_{em} = 428 nm) and **41c** (R = CF_3, λ_{em} = 423 nm) show a shift in emission maxima by approximately 60 nm. This red shift of emission wavelength is cleary affected by the modulated π-extended structure. It is noteworthy that the compounds **41** showed the highest quantum yields (Φ_s = 0.75-0.88), whereas other [7]-helical molecules have quantum yields Φ = 0.30-0.40.[59]

In summary, it was possible to apply the previously developed reaction sequence for the preparation of 1,2,3,4-tetrasubstituted SBFs to synthesize a set of substituted DS-IFs. Thus, for the first time, 12 molecules were prepared containing symmetrically and unsymmetrically substituted DS-IFs and three molecules of [7]-helical DS-IFs. Furthermore, these π-extended [7]-helical DS-IFs **41** show very high quantum yields and fluorescence emission maxima in the blue region of visible light. Therefore, these DS-IFs could be, similarly to the SBFs, good candidates for applications materials science, such as in organic electronics and light-emitting devices (OLEDs), in dyes or even photovoltaic cells.[6a-g,41]

5. Conclusion

In this study a new synthetic method based on a Rh-complex catalyzed [2+2+2] cyclotrimerization of compounds with the triple bonds for preparation of fluorenes and its congeners was presented. The method was applied in syntheses of (a) selectively 1,2,3,4-tetrasubstituted SBFs, (b) symmetrically and unsymmetrically substituted DS-IFs, and (c) [7]-helical DS-IFs. This general reaction pathway consists of five or six steps and its length depended only on the availability of the starting materials.

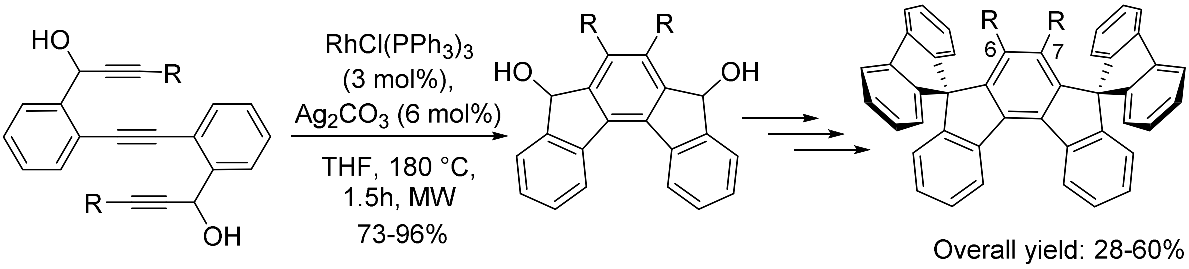
a) In total, 19 different 1,2,3,4-tetrasubstituted SBFs with various substituents at position 4 were prepared. These substituents included electron-donating and -withdrawing groups, aromatic substituents and π-extended aromatic hydrocarbon moieties. The key step was the catalytic cyclotrimerization of diynols with internal alkynes (the best results were obtained with 3-hexyne). All cyclotrimerization products were isolated in yields ranging from 45 to 76%. Additionally, an extensive screening of cyclotrimerization reactions with Wilkinson's catalyst under various reaction conditions (temperature, time, solvent and additives) was carried out as well. 1,2,3,4-Tetrasubstituted SBFs were synthesized in good overall yields (ranging from 9 to 34%) from the commercially available starting material (Scheme 52). The photophysical properties of all SBFs were analyzed by absorption and emission spectroscopy. Fluorescence emission maxima λ_{em} were in the range of 315-389 nm with quantum yields Φ_s up to 1.00.



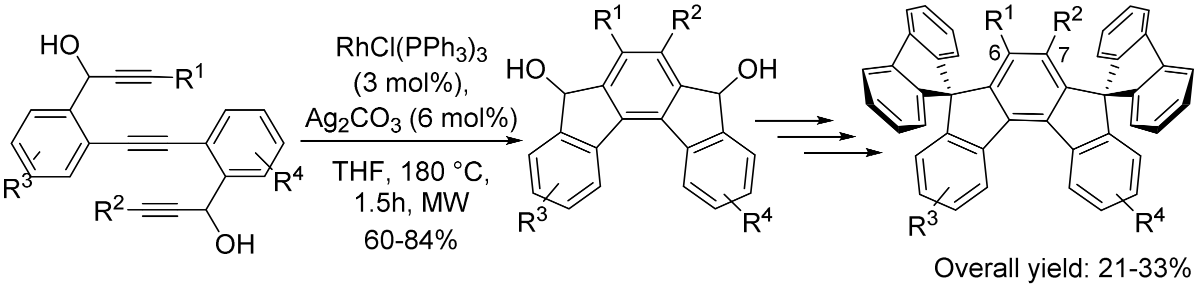
Conditions A: $RhCl(PPh_3)_3$ (10 mol%), toluene, 90 °C, 16h.
Conditions B: $RhCl(PPh_3)_3$ (3 mol%), Ag_2CO_3 (6 mol%), THF, MW, 180 °C, 1.5h.

Scheme 52. Synthetic pathway for SBFs using Rh-catalyzed [2+2+2] cyclotrimerization

b) 9 symmetrically and 2 unsymmetrically substituted DS-IFs at positions 6 and 7 were synthesized bearing various electron-donating and -withdrawing groups by using the same strategy. The Rh-complex catalyzed [2+2+2] cyclotrimerization of the prepared triyndiols gave rise to indeno[2,1-*c*]fluorene-5,8-diols that were isolated in yields ranging from 73 to 96% for symmetrically (Scheme 53) and from 60 to 84% for unsymmetrically substituted derivatives (Scheme 54). Subsequently, the corresponding DS-IFs were prepared from indeno[2,1-*c*]fluorene-5,8-diols in overall yields ranging from 21 to 60%. The photophysical properties of all DS-IFs were analyzed by absorption and emission spectroscopy. Fluorescence emission maxima were in the range of λ_{em} = 351-389 nm and quantum yields Φ_s were up to 0.70.

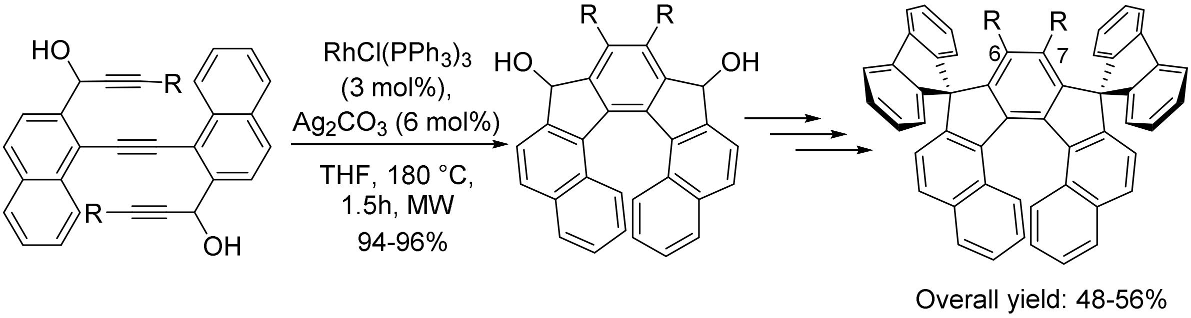


Scheme 53. Synthetic pathway for symmetrically substituted DS-IF using Rh-catalyzed [2+2+2] cyclotrimerization



Scheme 54. Synthetic pathway for unsymmetrically substituted DS-IF using Rh-catalyzed [2+2+2] cyclotrimerization

c) Finally, a set of three [7]-helical DS-IFs was prepared by using the same synthetic pathway from various commercially available starting compounds. The Rh-complex catalyzed [2+2+2] cyclotrimerization with triyndiols possessing the naphthalene units provided [7]-helical indenofluorenediols that were isolated in yields ranging from 94 to 96%. Subsequently, the corresponding [7]-helical DS-IFs were formed from [7]-helical indenofluorenediols with overall yields ranging from 48 to 56% (Scheme 55). The photophysical properties of [7]-helical DS-IFs were again analyzed by absorption and emission spectroscopy. Fluorescence emission maxima were in the range of λ_{em} = 423-428 nm with quantum yields Φ_s up to 0.80. These molecules have one of the highest measured quantum yields among the class of helicene like compounds recorded thus far.



Scheme 55. Synthetic pathway for [7]-helical DS-IFs using Rh-catalyzed [2+2+2] cyclotrimerization

In summary, this short and high-yielding five- or six-step synthetic pathway opens several possibilities for the preparation of new and selectively substituted SBFs and DS-IFs at different positions. The Rh-catalyzed [2+2+2] cyclotrimerization emerged as the key step of this synthesis using the Wilkinson's catalyst ($RhClPPh_3)_3$) as the most powerful catalyst. The systematic study provide useful guidelines for the future tuning and design of substituted 9,9'-spirobifluorenes and dispiroindeno[2,1-*c*]fluorenes with predefined properties and their application in materials science.

6. Experimental part

6.1. General

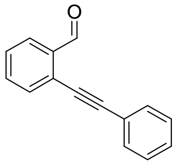
All reagents were commercially available and obtained from Sigma-Aldrich, Acros Organics, and Strem Chemicals companies. Solvents were purified and dried by distillation: tetrahydrofuran (THF) and toluene from sodium/benzophenone, dichloromethane from calcium hydride. Other solvents and all reagents were used without further purification. All reactions were performed under argon atmosphere unless otherwise noted. Chromatography was performed on Merck Silica gel 60. Thin layer chromatography was performed on Merck silica gel 60 F_{254} coated aluminium sheets. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III Spectrometer (^{1}H at 600 MHz and ^{13}C at 150 MHz) or on Bruker AVANCE III Spectrometer (^{1}H at 400 MHz and ^{13}C at 100 MHz) as solutions in $CDCl_3$, chemical shifts are given in δ-scale (^{1}H NMR spectra were referenced to residual peak of $CDCl_3$ at δ 7.26, ^{13}C NMR spectra to $CDCl_3$ at δ 77.00), coupling constants *J* are given in Hz. The following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, tt = triplet of triplet. Assignments of proton resonances were confirmed, when possible, by known literature data. The IR spectra were recorded on a Bruker IFS 55 spectrometer in KBr tablets and are reported in wave numbers (cm^{-1}). In case of liquids or oils the compounds were dissolved in acetone, mixed with KBr and the acetone evaporated. The MS spectra were recorded on a VG-Analytical ZAB-SEQ device. All melting points are uncorrected and were determined on a Kofler apparatus.

6.2. Synthesis of 9,9'-spirobifluorene scaffolds

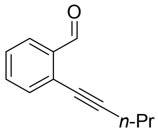
6.2.1. Synthesis of starting material 2, 8 and 12

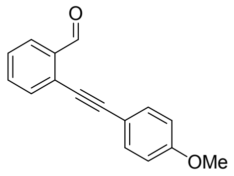
A: General procedure for Sonogashira reaction[60] (preparation of 1 and 7). 2-Bromobenzaldehyde (230 μL, 2.0 mmol), $PdCl_2(PPh_3)_2$ (69 mg, 0.1 mmol, 5 mol%) and CuI (38 mg, 0.2 mmol, 10 mol%) were dissolved in a Schlenk flask with reflux condensor in triethylamine (7 mL) and THF (7 mL), afterwards alkyne compound (2.4 mmol) was added and the reaction was stirred 3h under reflux. The reaction mixture was cooled down, filtered off with celite/silica and washed with diethyl ether. The organic fraction was concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (hexanes/EtOAc) provided products.

2-(Phenylethynyl)benzaldehyde (1a). With phenylacetylene (260 μL, 2.4 mmol) following the general procedure A. Column chromatography (5/1 hexanes/EtOAc) yielded 399 mg (96%) of the title compound as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.66 (d, J = 0.8 Hz, 1H), 7.95 (ddd, J = 7.8, 1.4, 0.6 Hz, 1H), 7.65 (ddd, J = 7.8, 1.3, 0.6 Hz, 1H), 7.59 (dt, J = 7.4, 1.4 Hz, 1H), 7.56-7.58 (m, 2H), 7.44-7.47 (m, 1H), 7.38-7.40 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.7, 135.8, 133.8, 133.2, 131.7, 129.1, 128.6, 128.5, 127.2, 126.9, 122.3, 96.3, 84.9. The spectral data were in accordance with previously published results.[45]

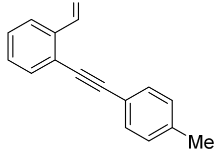


2-(Pent-1-yn-1-yl)benzaldehyde (1b). With 2-bromobenzaldehyde (500 μL, 4.0 mmol) and 1-pentyne (600 μL, 6.0 mmol) following the general procedure A. Column chromatography (5/1 hexanes/EtOAc) yielded 631 mg (92%) of the title compound as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.54 (d, J = 0.9 Hz, 1H), 7.87 (m, 1H), 7.49 (m, 2H), 7.35-7.38 (m, 1H), 2.45 (t, J = 7.1 Hz, 2H), 1.65 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.1, 135.9, 133.6, 133.3, 127.9, 127.8, 126.9, 98.0, 76.4, 22.0, 21.5, 13.6. The spectral data were in accordance with previously published results.[45]

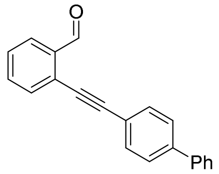




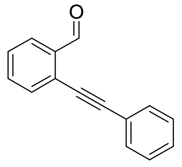
2-((4-Methoxyphenyl)ethynyl)benzaldehyde (7a). With 4-ethynylanisole (311 μL, 2.4 mmol) following the general procedure A. Column chromatography (10/1 hexanes/EtOAc) yielded 450 mg (96%) of the title compound as yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.65 (d, *J* = 0.8 Hz, 1H), 7.93 (ddd, *J* = 7.8, 1.3, 0.5 Hz, 1H), 7.61 (ddd, *J* = 7.8, 1.3, 0.5 Hz, 1H), 7.57 (dt, *J* = 7.3, 1.4 Hz, 1H), 7.51 (m, 2H), 7.43 (m, 1H), 6.91 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.9, 160.2, 135.7, 133.8, 133.2, 133.0, 128.2, 127.4, 127.2, 114.4, 114.2, 96.6, 83.8, 55.4. The spectral data were in accordance with previously published results.[61]



2-(*p*-Tolylethynyl)benzaldehyde (7b). With *p*-tolylacetylene (305 μL, 2.4 mmol) following the general procedure A. Column chromatography (10/1 hexanes/EtOAc) yielded 392 mg (89%) of the title compound as pale yellow solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.66 (d, *J* = 0.8 Hz, 1H), 7.95 (ddd, *J* = 7.8, 1.4, 0.5 Hz, 1H), 7.63 (ddd, *J* = 7.8, 1.3, 0.5 Hz, 1H), 7.58 (dt, *J* = 7.4, 1.4 Hz, 1H), 7.47 (m, 2H), 7.44 (m, 1H), 7.19 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.8, 139.4, 135.7, 133.7, 133.1, 131.6, 129.3, 128.4, 127.17, 127.15, 119.2, 96.6, 84.3, 21.6. The spectral data were in accordance with previously published results.[62]

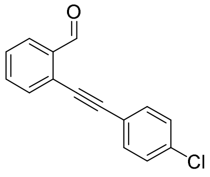


2-([1,1'-Biphenyl]-4-ylethynyl)benzaldehyde (7c). With 4-ethynylbiphenyl (428 mg, 2.4 mmol) following the general procedure A. Column chromatography (10/1 hexanes/EtOAc) yielded 520 mg (92%) of the title compound as a light yellow solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.68 (d, *J* = 0.8 Hz, 1H), 7.96 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.59-7.86 (m, 8H), 7.47 (m, 3H), 7.38 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.7, 141.8, 140.1, 135.8, 133.8, 133.2, 132.1, 128.9, 128.6, 127.8, 127.3, 127.2, 127.1, 126.9, 121.2, 96.3, 85.6. The spectral data were in accordance with previously published results.[63]

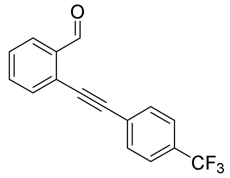


2-(Phenylethynyl)benzaldehyde (7d). With phenylacetylene (260 μL, 2.4 mmol) following the general procedure A. Column chromatography (5/1 hexanes/EtOAc) yielded 399 mg (96%) of the title compound as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.66 (d, *J* = 0.8 Hz, 1H), 7.95 (ddd, *J* = 7.8, 1.4, 0.6 Hz, 1H), 7.65 (ddd, *J* = 7.8, 1.3, 0.6 Hz, 1H), 7.59 (dt, *J* = 7.4, 1.4 Hz, 1H), 7.56-7.58

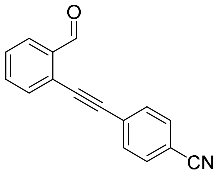
(m, 2H), 7.44-7.47 (m, 1H), 7.38-7.40 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.7, 135.8, 133.8, 133.2, 131.7, 129.1, 128.6, 128.5, 127.2, 126.9, 122.3, 96.3, 84.9. The spectral data were in accordance with previously published results.[60]



2-((4-Chlorophenyl)ethynyl)benzaldehyde (7e). With 1-chloro-4-ethynylbenzene (238 mg, 2.4 mmol) following the general procedure A. Column chromatography (10/1 hexanes/EtOAc) yielded 431 mg (90%) of the title compound as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.62 (d, *J* = 0.8 Hz, 1H), 7.95 (ddd, *J* = 7.8, 1.4, 0.6 Hz, 1H), 7.64 (ddd, *J* = 7.8, 1.3, 0.6 Hz, 1H), 7.60 (dt, *J* = 7.3, 1.4 Hz, 1H), 7.46-7.51 (m, 3H), 7.36-7.38 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.5, 133.8, 133.2, 132.9, 128.9, 128.8, 127.5, 126.4, 120.8, 95.1, 85.9. The spectral data were in accordance with previously published results.[64]

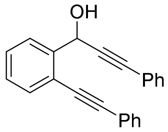


2-((4-(Trifluoromethyl)phenyl)ethynyl)benzaldehyde (7f). With 1-ethynyltrifluortoluene (392 µL, 2.4 mmol) following the general procedure A. Column chromatography (5/1 hexanes/EtOAc) yielded 442 mg (80%) of the title compound as a light brown solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.62 (d, *J* = 0.8 Hz, 1H), 7.97 (ddd, *J* = 7.8, 1.4, 0.5 Hz, 1H), 7.64-7.68 (m, 5H), 7.59 (dt, *J* = 7.4, 1.4 Hz, 1H), 7.50 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.2, 136.0, 133.8, 133.4, 131.9, 130.8 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 129.2, 127.6, 126.1, 125.8, 125.4 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 121.1-126.5 (q, $^1J_{C\text{-}F}$ = 272.3 Hz), 94.5, 87.2. The spectral data were in accordance with previously published results.[64]

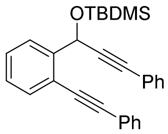


4-((2-Formylphenyl)ethynyl)benzonitrile (7g). With 4-ethynylbenzonitrile (305 mg, 2.4 mmol) following the general procedure A. Column chromatography (10/1 hexanes/EtOAc) yielded 392 mg (84%) of the title compound as a light yellow solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.59 (d, *J* = 0.8 Hz, 1H), 7.97 (ddd, *J* = 7.8, 1.3, 0.5 Hz, 1H), 7.65-7.69 (m, 5H), 7.63 (dt, *J* = 7.3, 1.4 Hz, 1H), 7.53 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.0, 136.0, 133.9, 133.5, 132.19, 132.16, 129.5, 127.9, 127.2, 125.3, 118.3, 112.3, 94.1, 89.1. The spectral data were in accordance with previously published results.[65]

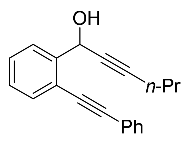
B: General procedure for alkynylation reaction[60] (preparation of 2, 8, 12). *n*-BuLi 1.6M (1.8 mL, 2.7 mmol) was added dropwise to a solution of 1-ethynyl-4-*p*-toluene (340 µL, 2.7 mmol) in anhydrous THF (15 mL), at -78 °C. After 30min of stirring, starting material **S** (1.78 mmol) in THF (5 mL) was added and the reaction mixture was stirred for 5 min at -78 °C, afterwards it was allowed to warm up to ambient temperature and the reaction was stirred 4h. Then NH_4Cl aq was used to quench the reaction mixture, it was extracted with diethyl ether (3 x 15 mL), the combined organic fractions were washed with a saturated solution of $NaHCO_3$ and brine, the organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes/EtOAc) provided products.



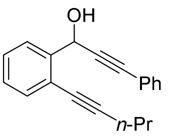
3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-ol (2a). With **1a** (0.64 g, 2.8 mmol) and phenylacetylene (3.3 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 0.73 g (86%) of the title compound as pale yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.59-7.61 (m, 3H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.35-7.38 (m, 4H), 7.30-7.33 (m, 3H), 6.19 (s, 1H), 2.89 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.2, 132.5, 131.7, 131.6, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 126.8, 122.8, 122.5, 121.4, 95.0, 88.3, 86.6, 86.5, 63.7. The spectral data were in accordance with previously published results.[65]



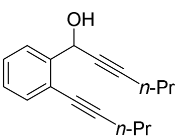
(3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl)oxy-*tert*-butyldimethylsilane (2a-TBS). **2a** (0.87 g, 3.3 mmol) was dissolved in anhydrous DMF (30 mL) and cooled to 0 °C. Imidazole (0.34 g, 4.9 mmol), DMAP (60.5 mg, 0.50 mmol) and afterwards TBDMSCl (0.59 g, 3.9 mmol) were added and the reaction was stirred for 30 min at 0 °C. Afterwards the reaction mixture was allowed to reach 25 °C and stirred for 6 h. The reaction mixture was quenched with a saturated solution of ammonium chloride and extracted by diethyl ether (3 × 20 mL), combined organic fractions were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated on vacuum evaporator. The residue was purified by column chromatography on silica gel (10/1 hexanes/EtOAc) to yield 0.61 g (53%) of the title compound as a light brown oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (m, 1H), 7.55-7.58 (m, 2H), 7.54 (m, 1H), 7.39-7.43 (m, 3H), 7.35-7.38 (m, 3H), 7.32 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.25-7.28 (m, 3H), 6.21 (s, 1H), 0.97 (s, 9H), 0.26 (s, 3H), 0.20 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.6, 132.0, 131.6, 131.5, 128.8, 128.42, 128.38, 128.13, 128.10, 127.6, 126.5, 123.3, 123.1, 120.8, 94.6, 90.1, 87.1, 85.0, 63.6, 25.8, 18.4, -4.4, -4.8; IR (KBr) ν_{max} 3058, 3028, 2956, 2926, 2854, 1598, 1488, 1473, 1443, 1323, 1251, 1111, 1075, 866, 842, 752 cm^{-1}; HRMS (*m/z*) for $C_{29}H_{30}OSiNa$ (M + Na) calcd: 445.19581, found: 445.19583; R_f (10/1 hexanes/EtOAc) = 0.67 (silica gel plate).



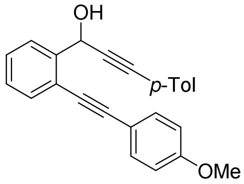
1-(2-(Phenylethynyl)phenyl)hex-2-yn-1-ol (2b). With **1a** (90 mg, 0.44 mmol) and 1-pentyne (65 μL, 0.65 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 115 mg (95%) of the title compound as a light yellow oil: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.74 (m, 1H), 7.55-7.57 (m, 3H), 7.39 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.35-7.37 (m, 3H), 7.31 (dt, *J* = 7.6, 1.4 Hz, 1H), 5.96 (m, 1H), 2.62 (d, *J* = 5.1 Hz, 1H), 2.25 (dt, *J* = 7.1, 2.1 Hz, 2H), 1.56 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 142.9, 132.4, 131.6, 128.8, 128.6, 128.4, 128.1, 126.6, 122.9, 121.3, 94.7, 87.5, 86.7, 79.5, 63.4, 22.0, 20.8, 13.5; IR (KBr) ν_{max} 3554, 3327, 3052, 3031, 2962, 2929, 2866, 2836, 2280, 2223, 1598, 1494, 1446, 1278, 1183, 1132, 1036, 994, 758 cm^{-1}; HRMS (*m/z*) for $C_{20}H_{18}O$ (M + Cl) calcd: 274.1358, found: 274.1360; R_f (1/1 hexanes/EtOAc) = 0.52 (silica gel plate).



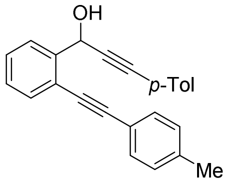
1-(2-(Pent-1-yn-1-yl)phenyl)-3-phenylprop-2-yn-1-ol (2c). With **1b** (172 mg, 1.0 mmol) and phenylacetylene (134 μL, 1.2 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 265 mg (96%) of the title compound as a yellow oil: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.73 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.47 (m, 2H), 7.45 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.34 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.30-7.32 (m, 3H), 7.28 (dt, *J* = 7.6, 1.4 Hz, 1H), 6.07 (d, *J* = 3.5 Hz, 1H), 2.84 (d, *J* = 4.7 Hz, 1H), 2.47 (t, *J* = 7.0 Hz, 2H), 1. 86 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 142.1, 132.6, 131.7, 128.4, 128.22, 128.18, 128.1, 126.7, 122.6, 122.2, 96.3, 88.3, 86.4, 78.7, 63.8, 22.1, 21.6, 13.6. The spectral data were in accordance with previously published results.[67]



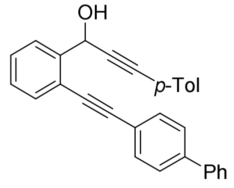
1-(2-(Pent-1-yn-1-yl)phenyl)hex-2-yn-1-ol (2d). With **1b** (172 mg, 1.0 mmol) and 1-pentyne (150 μL, 1.5 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 223 mg (93%) of the title compound as a slight yellow oil: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.67 (d, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.31 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.24 (dt, *J* = 7.6, 1.3 Hz, 1H), 5.85 (m, 1H), 2.63 (d, *J* = 5.5 Hz, 1H), 2.44 (t, *J* = 7.0 Hz, 2H), 2.25 (dt, *J* = 7.0, 2.0 Hz, 2H), 1.67 (m, 2H), 1.58 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.7, 132.5, 128.1, 128.0, 126.5, 122.1, 96.0, 87.4, 79.46, 78.1, 63.5, 22.2, 22.0, 21.6, 20.97, 13.6, 13.5. The spectral data were in accordance with previously published results.[60]



1-(2-((4-Methoxyphenyl)ethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (8a). With **7a** (450 mg, 1.9 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 560 mg (84%) of the title compound as pale yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.51 (m, 2H), 7.39 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.35 (m, 2H), 7.33 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.88 (m, 2H), 6.15 (d, *J* = 5.9 Hz, 1H), 3.83 (s, 3H), 2.84 (d, *J* = 5.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 142.1, 138.6, 133.1, 132.3, 131.6, 129.0, 128.5, 128.2, 126.8, 121.8, 119.4, 114.9, 114.1, 95.1, 87.6, 86.6, 85.4, 63.9, 55.3, 21.5. The spectral data were in accordance with previously published results.[67]

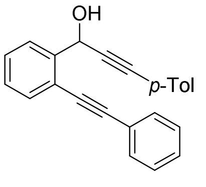


3-(*p*-Tolyl)-1-(2-(*p*-tolylethynyl)phenyl)prop-2-yn-1-ol (8b). With **7b** (392 mg, 1.78 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 545 mg (91%) of the title compound as pale yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.40 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.33 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.15 (d, *J* = 5.9 Hz, 1H), 2.77 (d, *J* = 5.9 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.3, 138.8, 138.6, 132.4, 131.7, 131.5, 129.2, 129.0, 128.7, 128.2, 126.8, 121.7, 119.7, 119.4, 95.3, 87.6, 86.7, 86.0, 63.9, 21.53, 21.46. The spectral data were in accordance with previously published results.[66]

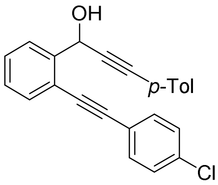


1-(2-([1,1'-Biphenyl]-4-yl-ethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (8c). With **7c** (540 mg, 1.8 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 650 mg (90%) of the title compound as a light yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (ddd, *J* = 7.8, 0.9, 0.4 Hz, 1H), 7.60-7.66 (m, 7H), 7.47 (m, 2H), 7.42 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.34-7.40 (m, 4H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.18 (d, *J* = 5.9 Hz, 1H), 2.78 (d, *J* = 5.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.4, 141.3, 140.2, 138.6, 132.5, 132.0, 131.7, 129.0, 128.9, 128.9, 128.3, 127.7, 127.1, 127.0, 126.8, 121.7, 121.5, 119.4, 95.0, 87.6, 87.3, 86.7, 63.9, 21.5; IR (KBr) ν_{max} 3548, 3342, 3060, 3028, 2947, 2920, 2866, 2211, 1595, 1512, 1494, 1446, 1404, 1374, 1275, 1224, 1183, 1108, 1027, 1009, 967, 842, 815, 764, 698 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{22}ONa$ (M + Na) calcd: 421.15629 found: 421.15630; R_f (2/1 hexanes/EtOAc) = 0.43 (silica gel plate).

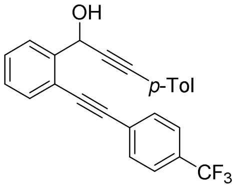
1-(2-(Phenylethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (8d). With **7d** (396 mg, 1.95 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 590 mg (93%) of the title compound as pale yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.57-7.60 (m, 3H), 7.42 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.33-7.37 (m, 6H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.16 (d, *J* = 5.9 Hz, 1H), 2.76 (d, *J* = 5.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.4, 138.6, 132.5, 131.64, 131.58, 129.0, 128.9, 128.6, 128.4, 128.3, 126.8, 122.8, 121.5, 119.4, 95.0, 87.5, 86.7, 86.6, 63.8, 21.5. The spectral data were in accordance with previously published results.[66]



1-(2-((4-Chlorophenyl)ethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (8e). With **7e** (434 mg, 1.8 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 570 mg (89%) of the title compound as colorless solid: mp (decomp) 126-131 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.56 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.48 (m, 2H), 7.42 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.32-7.36 (m, 5H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.12 (s, 1H), 2.67 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.4, 138.7, 134.6, 132.8, 132.5, 131.6, 129.1, 129.0, 128.8, 128.3, 126.8, 121.3, 121.2, 119.3, 93.8, 87.6, 87.5, 86.8, 63.8, 21.5; IR (KBr) ν_{max} 3276, 3189, 3066, 3034, 2989, 2914, 2864, 2851, 2217, 1568, 1512, 1488, 1470, 1392, 1284, 1219, 1186, 1090, 1027, 1015, 970, 830, 818, 749 cm^{-1}; HRMS (*m/z*) for $C_{24}H_{17}OClNa$ (M + Na) calcd: 379.08601, found: 379.08618; R_f (2/1 hexanes/EtOAc) = 0.45 (silica gel plate).

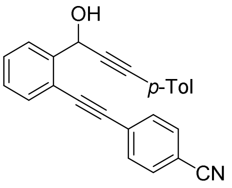


3-(*p*-Tolyl)-1-(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)prop-2-yn-1-ol (8f). With **7f** (442 mg, 1.6 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 564 mg (90%) of the title compound as colorless solid: mp (decomp) 133-138 °C; ^{1}H NMR (600

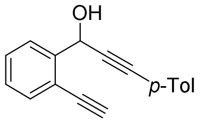


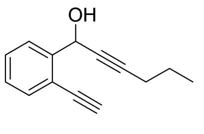
MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.60 (m, 3H), 7.45 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.36 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.13 (d, *J* = 5.9 Hz, 1H), 2.63 (d, *J* = 5.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.6, 138.8, 132.7, 131.8, 131.6, 130.2 (q, $^{2}J_{C\text{-}F}$ = 32.7 Hz), 129.5, 129.0, 128.4, 126.8, 126.7, 125.3 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 121.2-126.7 (q, $^{1}J_{C\text{-}F}$ = 272.3 Hz), 120.8, 119.3, 93.4, 89.0, 87.5, 86.8, 63.7, 21.5; IR (KBr) ν_{max} 3273, 3180, 3066, 3028, 2992, 2926, 2875, 2223, 1610, 1509, 1476, 1404, 1332, 1165, 1108, 1066, 1030, 967, 842, 815, 749 cm^{-1}; HRMS (*m/z*) for $C_{25}H_{18}OF_3$ (M + H) calcd: 391.13043, found: 391.13058; R_f (2/1 hexanes/EtOAc) = 0.47 (silica gel plate).

4-((2-(1-Hydroxy-3-(*p*-tolyl)prop-2-yn-1-yl)phenyl)ethynyl)benzonitrile (8g). With **7g** (392 mg, 1.7 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 556 mg (94%) of the title compound as light brown solid: mp (decomp) 151-156 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.63 (s, 4H), 7.58 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.46 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.37 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.32 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.10 (d, *J* = 5.1 Hz, 1H), 2.62 (d, *J* = 5.1 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.7, 138.9, 132.7, 132.1, 132.0, 131.6, 129.8, 129.1, 128.4, 127.8, 126.9, 120.5, 119.2, 118.4, 111.8, 93.1, 91.0, 87.4, 86.9, 63.6, 21.5; IR (KBr) ν_{max} 3279, 3324, 3192, 3060, 3028, 2992, 2914, 2881, 2857, 2226, 1598, 1504, 1473, 1455, 1407, 1290, 1183, 1120, 1105, 1027, 973, 839, 818, 752 cm^{-1}; HRMS (*m/z*) for $C_{25}H_{17}NO$ (M^+) calcd: 347.1310, found: 347.1311; R_f(2/1 hexanes/EtOAc) = 0.38 (silica gel plate).

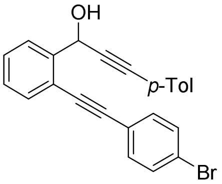


1-(2-Ethynylphenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (12a). With 2-ethynylbenzaldehyde (650 mg, 5.0 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 1.19 g (96%) of the title compound as light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.54 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.43 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.36 (m, 2H), 7.31 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.12 (d, *J* = 5.4 Hz, 1H), 3.41 (s, 1H), 2.74 (d, *J* = 5.4 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 138.7, 133.2, 131.6, 129.4, 129.0, 128.3, 126.9, 120.4, 119.3, 87.3, 86.8, 82.7, 81.0, 63.5, 21.5; IR (KBr) ν_{max} 3536, 3291, 3063, 3031, 2914, 2863, 2226, 1509, 1476, 1443, 1383, 1266, 1207, 1180, 1096, 1021, 967, 821, 761 cm^{-1}; HRMS (*m/z*) for $C_{18}H_{14}ONa$ (M + Na) calcd: 269.09369, found: 269.09360; R_f (2/1 hexanes/EtOAc) = 0.43 (silica gel plate).

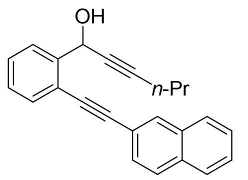




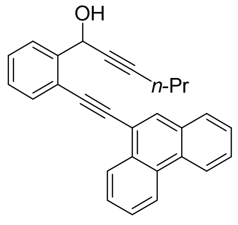
Preparation of 1-(2-Ethynylphenyl)hex-2-yn-1-ol (12b). With 2-ethynylbenzaldehyde (1.3 g, 10.0 mmol) and 1-pentyne (1.5 mL, 15 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 1.8 g (91%) of the title compound as light brown oil: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.50 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.40 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.29 (dt, *J* = 7.6, 1.3 Hz, 1H), 5.88 (s, 1H), 3.37 (s, 1H), 2.49 (d, *J* = 4.5 Hz, 1H), 2.25 (dt, *J* = 7.1, 2.0 Hz, 2H), 1.56 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.5, 133.1, 129.4, 128.1, 126.7, 120.3, 87.7, 82.5, 81.1, 79.2, 63.1, 22.0, 20.8, 13.5; IR (KBr) ν_{max} 3545, 3288, 3069, 3028, 2962, 2932, 2905, 2869, 2836, 2283, 2223, 1482, 1452, 1383, 1335, 1275, 1201, 1132, 1036, 991, 758 cm^{-1}; HRMS (*m/z*) for $C_{14}H_{14}O$ (M$^+$) calcd: 198.1045, found: 198.1044; R_f (5/1 hexanes/EtOAc) = 0.25 (silica gel plate).



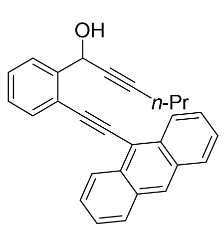
1-(2-((4-Bromophenyl)ethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (8h). 12a (736 mg, 4.6 mmol), 1-bromo-4-iodobenzene (1.1 g, 3.6 mmol), PdCl$_2$(PPh$_3$)$_2$ (104 mg, 0.15 mmol, 5 mol%) and CuI (57 mg, 0.3 mmol, 10 mol%) were dissolved in a flask in diisopropylamine (30 mL) and the reaction was stirred 16 h at 50 °C. The reaction mixture was cooled down, filtered off with celite/silica and washed with diethyl ether. The organic fraction was concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (2/1 hexanes/EtOAc) yielded 1.15 g (95%) of the title compound as brown solid: mp (decomp) 127-132 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.56 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.47-7.50 (m, 2H), 7.40-7.44 (m, 3H), 7.32-7.36 (m, 3H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.12 (d, *J* = 4.9 Hz, 1H), 2.74 (d, *J* = 4.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.4, 138.7, 133.0, 132.5, 131.7, 131.6, 129.1, 129.0, 128.3, 126.8, 122.9, 121.8, 121.1, 119.3, 93.9, 87.8, 87.5, 86.7, 63.7, 21.5; IR (KBr) ν_{max} 3548, 3342, 3060, 3022, 2914, 2863 2223, 1506, 1488, 1446, 1389, 1314, 1269, 1189, 1099, 1069, 1024, 1012, 961, 821, 758, 525 cm^{-1}; HRMS (*m/z*) for $C_{24}H_{17}OBrNa$ (M + Na) calcd: 423.03550, found: 423.03553; R_f (2/1 hexanes/EtOAc) = 0.46 (silica gel plate).



1-(2-(Naphthalen-2-ylethynyl)phenyl)hex-2-yn-1-ol (15a). With **12b** and 2-bromonaphthalene (397 mg, 2.0 mmol) following the general procedure A. Column chromatography (3/1 hexanes/EtOAc) yielded 434 mg (57%) of the title compound as a light brown oil: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (s, 1H), 7.82 (m, 3H), 7.75 (dd, J = 7.8, 0.9 Hz, 1H), 7.59 (m, 2H), 7.50 (m, 2H), 7.41 (dt, J = 7.5, 1.4 Hz, 1H), 7.34 (dt, J = 7.6, 1.3 Hz, 1H), 6.02 (s, 1H), 2.64 (s, 1H), 2.27 (dt, J = 7.1, 2.0 Hz, 2H), 1.56 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.9, 135.2 133.0, 132.4, 131.5, 128.9, 128.2, 128.12, 128.08, 127.80, 127.78, 126.8, 126.7, 126.6, 121.4, 120.2, 95.20, 87.56, 87.01, 79.49, 63.5, 22.0, 20.9, 13.5; IR (KBr) ν_{max} 3368, 3055, 2962, 2929, 2869, 2220, 1601, 1503, 1482, 1467, 1434, 1272, 1183, 1135, 1096, 1030, 997, 955, 896, 857, 815, 749, cm^{-1}; HRMS (*m/z*) for C$_{24}$H$_{20}$O (M$^+$) calcd: 324.1514 found: 324.1515; R_f (2/1 hexanes/EtOAc) = 0.44 (silica gel plate).



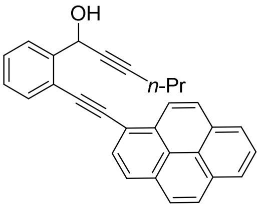
1-(2-(Phenanthren-9-ylethynyl)phenyl)hex-2-yn-1-ol (15b). With **12b** and 2-bromophenanthrene (40 mg, 0.2 mmol) following the general procedure A. Column chromatography (2/1 hexanes/EtOAc) yielded 53 mg (71%) of the title compound as a light brown oil: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.72 (dd, J = 5.9, 3.6 Hz, 1H), 8.67 (d, J = 8.3 Hz, 1H), 8.60 (m, 1H), 8.12 (s, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.67-7.74 (m, 4H), 7.62 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 6.12 (s, 1H), 2.64 (s, 1H), 2.28 (t, J = 7.1 Hz, 2H), 1.58 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.9, 132.7, 132.2, 131.2, 131.0, 130.4, 130.1, 129.0, 128.6, 128.2, 127.6, 127.2, 127.1, 127.01, 126.97, 126.6, 122.8, 122.6, 121.5, 119.4, 93.2, 91.1, 87.7, 79.6, 63.5, 22.0, 20.9, 13.5; IR (KBr) ν_{max} 3545, 3354, 3058, 2962, 2932, 2902, 2869, 2833, 2280, 2214, 1598, 1479, 1449, 1377, 1278, 1245, 1180, 1126, 1096, 1039, 1000, 955, 893, 755, 722 cm^{-1}; HRMS (*m/z*) for C$_{28}$H$_{22}$ONa (M + Na) calcd: 397.15629 found: 397.15631; R_f (2/1 hexanes/EtOAc) = 0.42 (silica gel plate).



1-(2-(Anthracen-9-ylethynyl)phenyl)hex-2-yn-1-ol (15c). With **12b** and 2-bromonaphthalene (257 mg, 1.0 mmol) following the general procedure A. Column chromatography (5/1 hexanes/EtOAc) yielded 153 mg (41%) of the title compound as a light brown oil: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (dd, J = 8.7, 0.9 Hz, 2H), 8.45 (s, 1H), 8.01 (d, J = 8.5 Hz, 2H), 7.86 (dd, J = 7.7, 1.4 Hz, 1H), 7.81 (dd, J = 7.5, 1.3 Hz, 1H), 7.62 (m, 2H), 7.52 (m, 2H), 7.47 (dt, J =

7.5, 1.5 Hz, 1H), 7.43 (dt, *J* = 7.5, 1.6 Hz, 1H), 6.21 (s, 1H), 2.64 (s, 1H), 2.27 (dt, *J* = 7.1, 2.1 Hz, 2H), 1.54 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 132.8, 132.7, 131.1, 129.0, 128.7, 128.2, 128.1, 126.8, 126.7, 126.5, 125.7, 121.8, 97.9, 91.7, 87.8, 79.8, 63.5, 22.0, 20.9, 13.5; IR (KBr) ν_{max} 3304, 3053, 2962, 2932, 2902, 2870, 2224, 2187, 1621, 1597, 1483, 1436, 1412, 1362, 1259, 1183, 1096, 1034, 1013, 999, 888, 845, 756, 739, 693 cm^{-1}; HRMS (*m/z*) for $C_{28}H_{22}ONa$ (M + Na) calcd: 397.25629 found: 397.25602; R_f (2/1 hexanes/EtOAc) = 0.41 (silica gel plate).

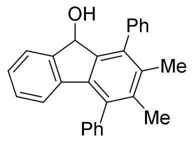
1-(2-(Pyren-2-ylethynyl)phenyl)hex-2-yn-1-ol (15d). With **12b** and 2-bromopyrene (281 mg, 1.0 mmol) following the general procedure A. Column chromatography (5/1 hexanes/EtOAc) yielded 246 mg (62%) of the title compound as a light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 9.1 Hz, 1H), 8.16-8.22 (m, 4H), 8.00-8.12 (m, 4H), 7.83 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.74 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.46 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.40 (dt, *J* = 7.5, 1.5 Hz, 1H), 6.19 (s, 1H), 2.73 (s, 1H), 2.30 (dt, *J* = 7.1, 2.1 Hz, 2H), 1.57 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 132.6, 131.9, 131.4, 131.2, 131.0, 129.7, 128.9, 128.5, 128.2, 128.2, 127.2, 126.6, 126.2, 125.7, 125.6, 125.4, 124.5, 124.4, 124.2, 121.7, 117.4, 94.1, 92.3, 87.7, 79.7, 63.6, 22.0, 20.9, 13.5; IR (KBr) ν_{max} 3545, 3291, 3044, 2961, 2932, 2902, 2871, 2206, 1927, 1600, 1508, 1486, 1448, 1435, 1379, 1275, 1242, 1184, 1133, 1033, 998, 848, 757, 717 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{22}ONa$ (M + Na) calcd: 421.15629 found: 421.15618; R_f (2/1 hexanes/EtOAc) = 0.40 (silica gel plate).



6.2.2. Cyclotrimerization reaction for 4, 9 and 16

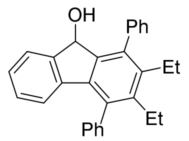
C^1: General procedure for cyclotrimerization with Wilkinson's catalyst $RhCl(PPh_3)_3$ under thermal conditions (Preparation of 4).[68] A dry flask was charged with starting diynol (0.5 mmol), alkyne **3** (1.0 mmol) and dissolved under argon atmosphere in toluene (15 mL). After addition of Wilkinson's catalyst (46 mg, 0.05 mmol, 10 mol%) the reaction mixture was heated up to 90 °C for 16h. The reaction mixture was cooled down to room temperature and the solvent was evaporated under reduced pressure. Column chromatography of the residue on silica gel yielded products.

C: General procedure for cyclotrimerization with Wilkinson's catalyst $RhCl(PPh_3)_3$ under MW irradiation (Preparation of 9 and 16). A dry microwave vial was charged with starting diynol (0.5 mmol), 3-hexyne **3b** (115 µL, 1.0 mmol) and dissolved under argon atmosphere in THF (15 mL). After addition of Wilkinson's catalyst (23 mg, 0.015 mmol, 3 mol%) and the additive Ag_2CO_3 (14 mg, 0.05 mmol, 10 mol%) the reaction mixture was sealed and heated up to 180 °C for 1.5h in a microwave reactor. The reaction mixture was cooled down to room temperature and the solvent was evaporated under reduced pressure. Column chromatography of the residue on silica gel yielded products.

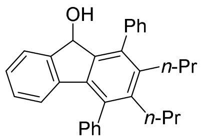


2,3-Dimethyl-1,4-diphenyl-9*H*-fluoren-9-ol (4aa). With **2a** (30.8 mg, 0.1 mmol) and 2-butyne **3a** (14.8 µL, 0.2 mmol) following the general procedure C^1. Column chromatography (5/1 hexanes/EtOAc) yielded 9 mg (25%) of the title compound as a slightly yellow solid: mp (decomp) 132-137 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.48-7.56 (m, 5H), 7.39-7.46 (m, 4H), 7.30-7.34 (m, 2H), 7.11 (dt, J = 7.4, 1.1 Hz, 1H), 6.95 (dt, J = 7.4, 1.2 Hz, 1H), 6.10 (d, J = 7.8 Hz, 1H), 5.53 (d, J = 5.2 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 1.63 (d, J = 5.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.3, 141.2, 140.6, 140.5, 139.6, 138.7, 136.5, 136.2, 135.4, 134.2, 130.0, 129.3, 129.2, 129.02, 128.96, 128.5, 128.42, 128.41, 127.44, 127.37, 126.8, 124.7, 122.5, 73.9, 17.40, 17.38; IR (KBr) ν_{max} 3563, 3559, 3052, 3025, 2926, 2863, 1601, 1571, 1497, 1440, 1359, 1296, 1180, 1099, 1060, 1027, 740, 701 cm^{-1}; HRMS (*m/z*) for $C_{27}H_{22}ONa$ (M + Na) calcd: 385.15629, found: 385.15633; R_f(5/1 hexanes/EtOAc) = 0.46 (silica gel plate).

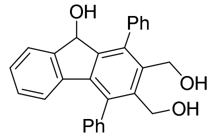
2,3-Diethyl-1,4-diphenyl-9*H*-fluoren-9-ol (4ab). With **2a** (30.8 mg, 0.1 mmol) and 3-hexyne **3b** (22.7 μL, 0.2 mmol) following the general procedure C^1. Column chromatography (5/1 hexanes/EtOAc) yielded 29 mg (76%) of the title compound as a slightly yellow solid: mp (decomp) 146-151 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49-7.55 (m, 5H), 7.44-7.48 (m, 2H), 7.35-7.45 (m, 4H), 7.09 (dt, J = 7.4, 1.1 Hz, 1H), 6.93 (dt, J = 7.4, 1.2 Hz, 1H), 5.94 (d, J = 7.8 Hz, 1H), 5.44 (s, 1H), 2.64 (dq, J = 15.0, 7.5 Hz, 1H), 2.59 (dq, J = 15.0, 7.5 Hz, 1H), 2.56 (dq, J = 15.0, 7.5 Hz, 1H), 2.54 (dq, J = 15.0, 7.5 Hz, 1H), 1.62 (s, 1H), 1.03 (t, J = 7.5 Hz, 3H), 1.02 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 141.6, 141.4, 140.5, 140.3, 139.8, 139.4, 139.1, 136.8, 135.8, 129.9, 129.5, 129.4, 129.0, 128.82, 128.80, 128.7, 128.4, 128.3, 127.44, 127.35, 126.7, 124.6, 122.5, 73.9, 22.9, 22.8, 15.82, 15.78; IR (KBr) ν_{max} 3566, 3058, 3022, 2965, 2935, 2872, 1604, 1470, 1443, 1377, 1227, 1072, 1030, 761, 698 cm^{-1}; HRMS (*m/z*) for $C_{29}H_{26}ONa$ (M + Na) calcd: 413.18759, found: 413.18784; R_f (5/1 hexanes/EtOAc) = 0.48 (silica gel plate).



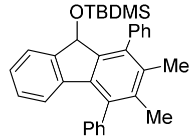
1,4-Diphenyl-2,3-dipropyl-9*H*-fluoren-9-ol (4ac). With **4a** (30.8 mg, 0.1 mmol) and 4-octyne **3c** (28.6 μL, 0.2 mmol) following the general procedure C^1. Column chromatography (5/1 hexanes/EtOAc) yielded 11 mg (26%) of the title compound as a slightly yellow solid: mp (decomp) 153-158 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48-7.54 (m, 5H), 7.43-7.46 (m, 2H), 7.39-7.41 (m, 2H), 7.33-7.37 (m, 2H), 7.09 (dt, J = 7.4, 1.1 Hz, 1H), 6.93 (dt, J = 7.4, 1.2 Hz, 1H), 5.95 (d, J = 7.9 Hz, 1H), 5.45 (d, J = 4.6 Hz, 1H), 2.49-2.54 (m, 1H), 2.42-2.46 (m, 2H), 2.37-2.41 (m, 1H), 1.62 (d, J = 4.7 Hz, 1H), 1.40-1.47 (m, 4H), 0.774 (t, J = 7.2 Hz, 3H), 0.772 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 141.4, 140.6, 140.5, 140.3, 139.4, 139.0, 138.7, 136.8, 135.7, 129.8, 129.4, 129.0, 128.8, 128.74, 128.69, 128.4, 128.3, 127.4, 127.3, 126.7, 124.6, 122.5, 73.9, 32.4, 32.3, 24.9, 24.8, 14.8, 14.7; IR (KBr) ν_{max} 3569, 3554, 3446, 3055, 2956, 2932, 2866, 1601, 1574, 1464, 1440, 1380, 1024, 749, 704 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{30}ONa$ (M + Na) calcd: 441.21889, found: 441.21886; R_f (5/1 hexanes/EtOAc) = 0.50 (silica gel plate).



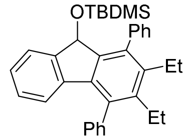
(9-Hydroxy-1,4-diphenyl-9*H*-fluorene-2,3-diyl)dimethanol (4ad). With **2a** (30.8 mg, 0.1 mmol) and 2-butyne-1,4-diol **3d** (8.6 mg, 0.1 mmol) following the general procedure C[1]. Column chromatography (2/1 hexanes/EtOAc) yielded 34 mg (86%) of the title compound as a slightly yellow solid: mp (decomp) 139-144 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44-7.53 (m, 8H), 7.41 (d, J = 7.3 Hz, 1H), 7.34 (m, 2H), 7.16 (t, J = 7.5 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.11 (d, J = 7.9 Hz, 1H), 5.56 (s, 2H), 4.57 (m, 4H), 3.14 (s, 2H, OH), 1.83 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.5, 143.8, 139.8, 139.7, 139.5, 138.6, 138.1, 137.9, 137.4, 137.3, 130.0, 129.3, 129.2, 129.07, 129.06, 128.96, 128.63, 128.59, 128.4, 127.93, 127.90, 127.6, 124.8, 123.0, 73.8, 60.0, 59.9; IR (KBr) ν_{max} 3569, 3327, 3055, 3022, 2926, 2887, 1503, 1473, 1443, 1347, 1296, 1111, 1009, 917, 860, 752, 707 cm^{-1}; HRMS (*m/z*) for $C_{27}H_{22}O_3Na$ (M + Na) calcd: 417.14612, found: 417.14604; R_f (1/1 hexanes/EtOAc) = 0.49 (silica gel plate).



(2,3-Dimethyl-1,4-diphenyl-9*H*-fluoren-9-yl)oxy-*tert*-butyl-dimethylsilane (4aa-TBS). With **2a-TBS** (42.3 mg, 0.1 mmol) and 2-butyne **3a** (14.8 μL, 0.2 mmol) following the general procedure C[1]. Column chromatography (30/1 hexanes/EtOAc) yielded 9 mg (19%) of the title compound as a pale yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52-7.55 (m, 2H), 7.40-7.50 (m, 5H), 7.33-7.38 (m, 3H), 7.28-7.30 (m, 1H), 7.05 (dt, J = 7.4, 1.1 Hz, 1H), 6.92 (dt, J = 7.4, 1.2 Hz, 1H), 6.05 (d, J = 7.8 Hz, 1H), 5.80 (s, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 0.63 (s, 9H), -0.32 (s, 3H), -0.66 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.7, 141.1, 141.0, 140.9, 140.0, 139.4, 136.19, 136.17, 135.6, 134.4, 131.2, 129.4, 129.3, 129.1, 128.9, 128.8, 128.4, 128.3, 128.0, 127.3, 126.8, 126.2, 125.8, 122.4, 74.9, 26.0, 18.1, 17.8, 17.6, -3.2, -3.8; IR (KBr) ν_{max} 3058, 3028, 2956, 2929, 2893, 2854, 1718, 1601, 1473, 1437, 1257, 1105, 1072, 833 cm^{-1}; HRMS (*m/z*) for $C_{33}H_{36}OSiNa$ (M + Na) calcd: 499.24276, found: 499.24283; R_f (20/1 hexanes/EtOAc) = 0.49 (silica gel plate).

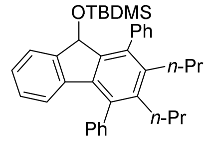


(2,3-Diethyl-1,4-diphenyl-9*H*-fluoren-9-yl)oxy-*tert*-butyl-dimethylsilane (4ab-TBS). With **2a-TBS** (42.3 mg, 0.1 mmol) and 3-hexyne **3b** (22.7 μL, 0.2 mmol) following the general procedure C[1]. Column chromatography (30/1 hexanes/EtOAc) yielded 36 mg (71%) of the title compound as a pale yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50-7.56 (m, 4H), 7.44-7.47 (m, 2H), 7.36-7.40 (m, 4H), 7.30-7.32 (m, 1H), 7.04 (dt, J = 7.4, 1.1 Hz, 1H), 6.91 (dt, J = 7.4, 1.2 Hz, 1H), 5.92 (d, J = 7.8 Hz, 1H), 5.66 (s, 1H), 2.69 (dq, J = 15.0, 7.5 Hz, 1H), 2.61 (dq, J = 15.0, 7.5 Hz,



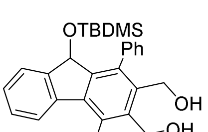
1H), 2.57 (dq, J = 15.0, 7.5 Hz, 1H), 2.50 (dq, J = 15.0, 7.5 Hz, 1H), 1.03 (t, J = 7.5 Hz, 3H), 0.98 (t, J = 7.5 Hz, 3H), 0.69 (s, 9H), -0.29 (s, 3H), -0.66 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 145.7, 141.6, 141.4, 141.0, 140.6, 140.2, 139.81, 139.75, 136.5, 135.9, 130.8, 129.7, 129.4, 129.2, 128.9, 128.7, 128.3, 128.2, 127.8, 127.3, 126.8, 126.2, 125.8, 122.4, 74.9, 26.1, 22.9, 22.8, 18.2, 15.9, 15.7, -3.2, -3.8; IR (KBr) ν_{max} 3055, 3022, 2968, 2929, 2851, 1718, 1601, 1559, 1473, 1440, 1257, 1105, 1078, 836 cm^{-1}; HRMS (m/z) for C$_{35}$H$_{41}$OSi (M + H) calcd: 505.2927, found: 505.2923; R_f (20/1 hexanes/EtOAc) = 0.51 (silica gel plate).

(1,4-Diphenyl-2,3-dipropyl-9*H*-fluoren-9-yl)oxy-*tert*-butyl-dimethylsilane (4ac-TBS).



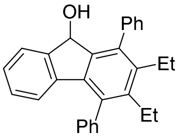
With **2a-TBS** (42.3 mg, 0.1 mmol) and 4-octyne **3c** (28.6 μL, 0.2 mmol) following the general procedure C^1. Column chromatography (30/1 hexanes/EtOAc) yielded 30 mg (56%) of the title compound as a colorless oil: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.47-7.54 (m, 4H), 7.42-7.45 (m, 2H), 7.33-7.39 (m, 4H), 7.28 (m, 1H), 7.03 (dt, J = 7.4, 1.1 Hz, 1H), 6.90 (dt, J = 7.4, 1.2 Hz, 1H), 5.91 (d, J = 7.6 Hz, 1H), 5.65 (s, 1H), 2.54-2.59 (m, 1H), 2.40-2.50 (m, 2H), 2.33-2.38 (m, 1H), 1.32-1.46 (m, 4H), 0.77 (t, J = 7.3 Hz, 3H), 0.75 (t, J = 7.3 Hz, 3H), 0.67 (s, 9H), -0.31 (s, 3H), -0.68 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 145.7, 141.3, 141.1, 140.6, 140.5, 139.83, 139.81, 139.1, 136.5, 135.8, 130.8, 129.7, 129.3, 129.2, 128.8, 128.6, 128.3, 128.1, 127.8, 127.2, 126.7, 126.2, 125.8, 122.4, 74.9, 32.4, 32.2, 26.1, 24.9, 24.7, 18.2, 14.7, 14.6, -3.2, -3.8; IR (KBr) ν_{max} 3058, 3022, 2953, 2932, 2854, 1598, 1500, 1476, 1440, 1317, 1257, 1108, 1063, 833 cm^{-1}; HRMS (m/z) for C$_{37}$H$_{44}$OSiNa (M + Na)calcd: 555.30536, found: 555.30535; R_f (20/1 hexanes/EtOAc) = 0.53 (silica gel plate).

[9-((*tert*-Butyldimethylsilyl)oxy]-1,4-diphenyl-9*H*-fluorene-2,3-diyl)dimethanol (4ad-TBS).

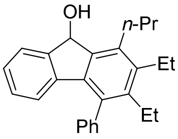


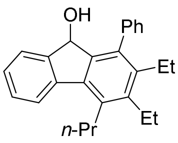
With **2a-TBS** (84 mg, 0.2 mmol) and 2-butyne-1,4-diol **3d** (26 mg, 0.3 mmol) following the general procedure C^1. Column chromatography (5/1 hexanes/EtOAc) yielded 83 mg (82%) of the title compound as a colorless oil: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.51-7.57 (m, 4H), 7.44-7.47 (m, 3H), 7.35-7.42 (m, 4H), 7.12 (dt, J = 7.4, 0.9 Hz, 1H), 6.96 (dt, J = 7.4, 0.6 Hz, 1H), 6.07 (d, J = 7.8 Hz, 1H), 5.84 (s, 1H), 4.67 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.59 (d, J = 12.0 Hz, 1H), 4.49 (d, J = 12.0 Hz, 1H), 3.00 (bs, 2H), 0.63 (s, 9H), -0.32 (s, 3H), -0.65 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 145.8, 143.8, 140.5, 140.1, 139.7, 138.9, 138.3, 138.2, 137.7, 137.1, 131.0, 129.4, 129.3, 129.1, 129.0, 128.8, 128.5, 128.4, 128.2, 127.9, 127.4, 127.0, 125.9, 123.0,74.8, 60.2, 60.1, 25.9, 18.1, -3.2, -3.8; IR (KBr) ν_{max} 3318, 3052, 3022, 2950, 2932, 2893, 2854, 1601, 1476, 1446, 1317, 1254, 1213, 1135, 1111, 1072, 1009, 833, 776, 701 cm^{-1}; HRMS (*m/z*) for $C_{33}H_{36}O_3SiNa$ (M + Na) calcd: 531.23259, found: 531.23254; *R$_f$* (2/1 hexanes/EtOAc) = 0.21 (silica gel plate).

2,3-Diethyl-1,4-diphenyl-9*H*-fluoren-9-ol (4ab). With **2a** (30.8 mg, 0.1 mmol) and 3-hexyne **3b** (22.7 μL, 0.2 mmol) following the general procedure C^1. Column chromatography (5/1 hexanes/EtOAc) yielded 29 mg (76%) of the title compound as a slightly yellow solid: mp (decomp) 146-151 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49-7.55 (m, 5H), 7.44-7.48 (m, 2H), 7.35-7.45 (m, 4H), 7.09 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.93 (dt, *J* = 7.4, 1.2 Hz, 1H), 5.94 (d, *J* = 7.8 Hz, 1H), 5.44 (s, 1H), 2.64 (dq, *J* = 15.0, 7.5 Hz, 1H), 2.59 (dq, *J* = 15.0, 7.5 Hz, 1H), 2.56 (dq, *J* = 15.0, 7.5 Hz, 1H), 2.54 (dq, *J* = 15.0, 7.5 Hz, 1H), 1.62 (s, 1H), 1.03 (t, *J* = 7.5 Hz, 3H), 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 141.6, 141.4, 140.5, 140.3, 139.8, 139.4, 139.1, 136.8, 135.8, 129.9, 129.5, 129.4, 129.0, 128.82, 128.80, 128.7, 128.4, 128.3, 127.44, 127.35, 126.7, 124.6, 122.5, 73.9, 22.9, 22.8, 15.82, 15.78; IR (KBr) ν_{max} 3566, 3058, 3022, 2965, 2935, 2872, 1604, 1470, 1443, 1377, 1227, 1072, 1030, 761, 698 cm^{-1}; HRMS (*m/z*) for $C_{29}H_{26}ONa$ (M + Na) calcd: 413.18759, found: 413.18784; *R$_f$* (5/1 hexanes/EtOAc) = 0.48 (silica gel plate).

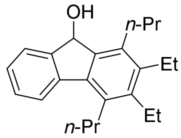


2,3-Diethyl-4-phenyl-1-propyl-9*H*-fluoren-9-ol (4bb). With **2b** (100 mg, 0.4 mmol) and 3-hexyne **3b** (90 μL, 0.8 mmol) following the general procedure C^1. Column chromatography (5/1 hexanes/EtOAc) yielded 65 mg (48%) of the title compound as a light brown solid: mp (decomp) 151-156 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 6.9 Hz, 1H), 7.45-7.51 (m, 3H), 7.31 (m, 1H), 7.28 (m, 1H), 7.12 (dt, *J* = 7.4, 1.0 Hz, 1H),), 6.92 (dt, *J* = 7.4, 0.8 Hz, 1H), 5.88 (d, *J* = 7.8 Hz, 1H), 5.64 (d, *J* = 10.2 Hz, 1H), 3.10-3.15 (m, 1H), 2.81-2.84 (m, 1H), 2.78 (m, 2H), 2.51 (m, 2H), 1.71-1.78 (m, 2H), 1.67 (d, *J* = 10.1 Hz, 1H), 1.26 (t, *J* = 7.5 Hz, 3H), 1.14 (t, *J* = 7.3 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.0, 141.8, 141.0, 140.6, 140.5, 140.3, 138.9, 135.9, 135.3, 129.6, 129.5, 128.7, 128.5, 127.2, 126.6, 124.5, 122.4, 74.6, 31.8, 25.0, 22.8, 21.8, 16.0, 15.8, 15.1; IR (KBr) ν_{max} 3536, 3392, 3055, 3019, 2962, 2932, 2869, 1601, 1494, 1464, 1437, 1377, 1281, 1189, 1066, 1039, 758, 704 cm^{-1}; HRMS (*m/z*) for $C_{29}H_{26}ONa$ (M + Na) calcd: 379.20324, found: 379.20331; *R$_f$* (5/1 hexanes/EtOAc) = 0.56 (silica gel plate).



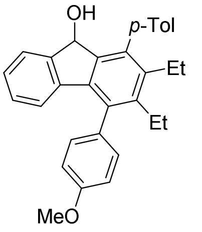


2,3-Diethyl-1-phenyl-4-propyl-9*H*-fluoren-9-ol (4cb). With **2c** (137 mg, 0.5 mmol) and 3-hexyne **3b** (120 μL, 1.0 mmol) following the general procedure C[1]. Column chromatography (5/1 hexanes/EtOAc) yielded 108 mg (62%) of the title compound as a light brown solid: mp (decomp) 137-142 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.47-7.52 (m, 3H), 7.43 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.39-7.42 (m, 1H), 7.34-7.39 (m, 2H), 7.25 (dt, *J* = 7.4, 0.9 Hz, 1H), 5.39 (d, *J* = 4.9 Hz, 1H), 3.03 (m, 2H), 2.81 (q, *J* = 7.5 Hz, 2H), 2.54-2.60 (m, 1H), 2.42-2.48 (m, 1H), 1.73-1.80 (m, 2H), 1.60 (d, *J* = 4.9 Hz, 1H), 1.27 (t, *J* = 7.6 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.5, 142.1, 141.4, 140.8, 139.9, 139.6, 137.5, 136.3, 135.8, 130.0, 129.0, 128.9, 128.2, 127.3, 126.6, 125.0, 122.8, 73.8, 31.7, 23.3, 23.0, 21.9, 16.0, 15.8, 14.7; IR (KBr) ν_{max} 3566, 3391, 3055, 3022, 2962, 2926, 2869, 1607, 1464, 1443, 1374, 1260, 1198, 1075, 1033, 761, 704 cm^{-1}; HRMS (*m/z*) for $C_{26}H_{28}ONa$ (M + Na) calcd: 379.20324, found: 379.20328; R_f (5/1 hexanes/EtOAc) = 0.51 (silica gel plate).

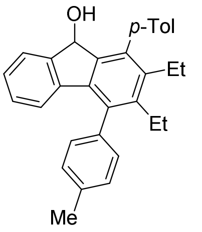


2,3-Diethyl-1,4-dipropyl-9*H*-fluoren-9-ol (4db). With **2d** (120 mg, 0.5 mmol) and 3-hexyne **3b** (120 μL, 1.0 mmol) following the general procedure C[1]. Column chromatography (5/1 hexanes/EtOAc) yielded 61 mg (38%) of the title compound as a slightly yellow solid: mp 122-127 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.61 (m, 1H), 7.38 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.28 (dt, *J* = 7.4, 1.0 Hz, 1H), 5.57 (d, *J* = 10.4 Hz, 1H), 3.04-3.09 (m, 1H), 2.95 (m, 2H), 2.71-2.78 (m, 5H), 1.65-1.73 (m, 4H), 1.64 (d, *J* = 10.4 Hz, 1H), 1.23 (t, *J* = 7.5 Hz, 3H), 1.22 (t, *J* = 7.5 Hz, 3H), 1.17 (t, *J* = 7.3 Hz, 3H), 1.11 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 141.8, 141.7, 140.9, 140.5, 137.2, 136.0, 134.6, 129.0, 126.5, 124.9, 122.7, 74.5, 31.8, 31.6, 25.0, 23.3, 21.9, 21.8, 16.0, 15.9, 15.1, 14.6; IR (KBr) ν_{max} 3518, 3392, 3069, 3043, 2959, 2926,2896, 2869, 1607, 1464, 1431, 1377, 1302, 1245, 1192, 1069, 1003, 764, 737 cm^{-1}; HRMS (*m/z*) for $C_{23}H_{30}ONa$ (M + Na) calcd: 345.21889, found: 345.21890; R_f (5/1 hexanes/EtOAc) = 0.63 (silica gel plate).

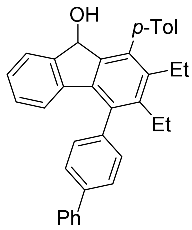
2,3-Diethyl-4-(4-methoxyphenyl)-1-(*p*-tolyl)-9*H*-fluoren-9-ol (9a). With **8a** (176 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 103 mg (47%) of the title compound as a brown oil: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40 (m, 1H), 7.25-7.36 (m, 6H), 7.10 (dt, J = 7.4, 1.0 Hz, 1H), 7.06-7.08 (m, 2H), 6.97 (dt, J = 7.4, 0.7 Hz, 1H), 6.07 (d, J = 7.8 Hz, 1H), 5.45 (d, J = 4.7 Hz, 1H), 3.94 (s, 3H), 2.60-2.66 (m, 1H), 2.55 (q, J = 7.5 Hz, 2H), 2.50-2.53 (m, 1H), 2.46 (s, 3H), 1.69 (d, J = 4.7 Hz, 1H), 1.03 (t, J = 7.5 Hz, 3H), 1.02 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 158.8, 145.2, 142.0, 141.5, 140.7, 139.9, 138.9, 137.0, 136.30, 136.27, 136.1, 132.5, 130.47, 130.45, 129.8, 129.6, 129.0, 128.6, 128.4, 126.7, 124.6, 122.6, 114.2, 114.1, 73.9, 55.3, 22.83, 22.81, 21.3, 15.9, 15.8; IR (KBr) ν_{max} 3566, 3452, 3069, 3040, 3022, 2968, 2929, 2869, 2839, 1607, 1571, 1515, 1467, 1428, 1374, 1284, 1245, 1177, 1105, 1033, 854, 824, 764, 746 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{30}O_2Na$ (M + Na) calcd: 457.21380, found: 457.21381; R_f (5/1 hexanes/EtOAc) = 0.36 (silica gel plate).



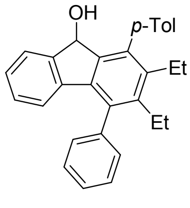
2,3-Diethyl-1,4-di-*p*-tolyl-9*H*-fluoren-9-ol (9b). With **8b** (168 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 133 mg (64%) of the title compound as a light brown viscous oil. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40 (d, J = 7.4, Hz, 1H), 7.30-7.36 (m, 6H), 7.23-7.27 (m, 2H), 7.10 (dt, J = 7.4, 1.0 Hz, 1H), 6.95 (dt, J = 7.6, 0.7 Hz, 1H), 6.02 (d, J = 7.8 Hz, 1H), 5.44 (d, J = 4.7 Hz, 1H), 2.60-2.66 (m, 1H), 2.55 (q, J = 7.5 Hz, 2H), 2.50-2.53 (m, 1H), 2.51 (s, 3H), 2.47 (s, 3H), 1.68 (d, J = 4.7 Hz, 1H), 1.03 (t, J = 7.5 Hz, 6H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 145.1, 141.7, 141.5, 140.7, 139.9, 138.9, 137.2, 137.0, 136.8, 136.7, 136.3, 135.8, 129.8, 129.7, 129.5, 129.4, 129.3, 129.2, 129.0, 128.7, 128.3, 126.6, 124.6, 122.6, 73.9, 22.84, 22.79, 21.4, 21.3, 15.9, 15.8; IR (KBr) ν_{max} 3425, 3058, 3019, 2968, 2926, 2890, 2869, 1598, 1556, 1470, 1437, 1374, 1290, 1195, 1177, 1072, 1024, 734, 758, 701 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{30}ONa$ (M + Na) calcd: 441.21889, found: 441.21893; R_f (5/1 hexanes/EtOAc) = 0.46 (silica gel plate).

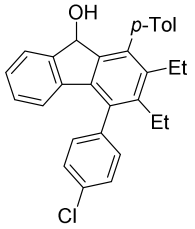


4-([1,1'-Biphenyl]-4-yl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-ol (9c). With **8c** (199.1 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 115 mg (48%) of the title compound as a viscous brown oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.82 (m, 4H), 7.52 (m, 2H), 7.40-7.47 (m, 4H), 7.32-7.38 (m, 4H), 7.11 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.94 (dt, *J* = 7.4, 0.8 Hz, 1H), 6.11 (d, *J* = 7.9 Hz, 1H), 5.47 (d, *J* = 4.7 Hz, 1H), 2.63-2.69 (m, 1H), 2.60 (q, *J* = 7.5 Hz, 2H), 2.51-2.57 (m, 1H), 2.48 (s, 3H), 1.71 (d, *J* = 4.7 Hz, 1H), 1.07 (t, *J* = 7.5 Hz, 3H), 1.05 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 141.7, 141.6, 140.7, 140.5, 140.0, 139.9, 139.4, 139.1, 137.1, 136.24, 136.23, 135.7, 129.93, 129.90, 129.8, 129.6, 129.1, 128.9, 128.6, 128.4, 127.4, 127.33, 127.27, 127.0, 126.74, 124.67, 122.5, 73.9, 22.9, 22.8, 21.3, 15.9 (2xCH_3); IR (KBr) ν_{max} 3566, 3440, 3049, 3028, 2968, 2926, 2866, 1598, 1515, 1488, 1473, 1449, 1431, 1371, 1311, 1290, 1251, 1180, 1141, 1102, 1066, 1021, 1012, 857, 839, 824, 767, 746, 698 cm^{-1}; HRMS (*m/z*) for $C_{36}H_{32}ONa$ (M + Na) calcd: 503.23454, found: 503.23464; R_f (5/1 hexanes/EtOAc) = 0.42 (silica gel plate).

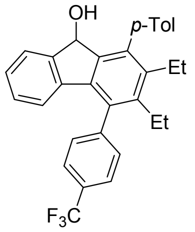


2,3-Diethyl-4-phenyl-1-(*p*-tolyl)-9*H*-fluoren-9-ol (9d). With **8d** (161 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 122 mg (61%) of the title compound as a light brown solid: mp (decomp) 70-75 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48-7.57 (m, 3H), 7.30-7.41 (m, 7H), 7.09 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.92 (dt, *J* = 7.4, 0.7 Hz, 1H), 5.93 (d, *J* = 7.9 Hz, 1H), 5.44 (d, *J* = 4.7 Hz, 1H), 2.60-2.66 (m, 1H), 2.55 (q, *J* = 7.5 Hz, 2H), 2.50-2.53 (m, 1H), 2.47 (s, 3H), 1.68 (d, *J* = 4.7 Hz, 1H), 1.03 (t, *J* = 7.5 Hz, 3H), 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 141.6, 141.5, 140.6, 140.3, 140.0, 139.0, 137.1, 136.6, 136.2, 135.7, 129.8, 129.6, 129.5, 129.4, 129.1, 128.8, 128.7, 128.6, 128.4, 127.3, 126.7, 124.6, 122.5, 73.9, 22.9, 22.8, 21.3, 15.9, 15.8; IR (KBr) ν_{max} 3572, 3443, 3078, 3049, 3022, 2968, 2932, 2866, 1598, 1515, 1470, 1446, 1431, 1371, 1308, 1242, 1180, 1141, 1099, 1069, 1036, 1021, 997, 830, 797, 743, 764, 707 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{28}ONa$ (M + Na) calcd: 427.20324, found: 427.20329; R_f (5/1 hexanes/EtOAc) = 0.44 (silica gel plate).

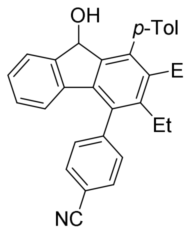




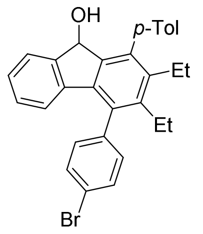
4-(4-Chlorophenyl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-ol (9e). With **8e** (178 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 97 mg (44%) of the title compound as a viscous brown oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51-7.53 (m, 2H), 7.41 (m, 1H), 7.28-7.35 (m, 6H), 7.12 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.98 (dt, *J* = 7.4, 0.7 Hz, 1H), 6.05 (d, *J* = 7.8 Hz, 1H), 5.44 (d, *J* = 4.6 Hz, 1H), 2.59-2.65 (m, 1H), 2.53 (q, *J* = 7.5 Hz, 2H), 2.47-2.53 (m, 1H), 2.46 (s, 3H), 1.68 (d, *J* = 4.7 Hz, 1H), 1.02 (t, *J* = 7.5 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 141.8, 141.5, 140.3, 140.1, 139.4, 138.8, 137.2, 136.1, 135.6, 135.2, 133.3, 131.0, 130.9, 129.8, 129.6, 129.10, 129.09, 129.0, 128.6, 128.5, 126.9, 124.8, 122.3, 73.8, 22.81, 22.77, 21.3, 15.9, 15.7; IR (KBr) ν_{max} 3563, 3437, 3066, 3049, 3022, 2962, 2929, 2866, 1607, 1565, 1518, 1491, 1470, 1461, 1425, 1392, 1371, 1248, 1204, 1183, 1141, 1087, 1069, 1018, 997, 857, 821, 803, 761, 749, 516 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{27}OClNa$ (M + Na) calcd: 461.16426, found: 461.16433; R_f (5/1 hexanes/EtOAc) = 0.43 (silica gel plate).



2,3-Diethyl-1-(*p*-tolyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (9f). With **8f** (195 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 115 mg (49%) of the title compound as a viscous brown oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (m, 2H), 7.50-7.54 (m, 2H), 7.41 (m, 1H), 7.29-7.36 (m, 4H), 7.12 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.95 (dt, *J* = 7.6, 1.1 Hz, 1H), 5.89 (d, *J* = 7.8 Hz, 1H), 5.45 (d, *J* = 4.6 Hz, 1H), 2.60-2.66 (m, 1H), 2.51 (q, *J* = 7.5 Hz, 2H), 2.47-2.54 (m, 1H), 2.47 (s, 3H), 1.70 (d, *J* = 4.6 Hz, 1H), 1.03 (t, *J* = 7.4 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 144.3, 141.9, 141.2, 140.2, 140.1, 139.6, 137.2, 136.0, 135.4, 135.0, 130.04, 130.01, 129.9, 129.8 (q, $^2J_{C\text{-}F}$ = 32.4 Hz), 129.53, 129.1, 128.6, 128.5, 127.0, 125.8 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.9, 121.6-127.0 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 122.1, 73.8, 22.8, 22.7, 21.3, 15.8, 15.7; IR (KBr) ν_{max} 3566, 3428, 3075, 3046, 3016, 2968, 2932, 2872, 1616, 1565, 1509, 1464, 1404, 1374, 1323, 1245, 1171, 1132, 1102, 1069, 1021, 866, 827, 767 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{27}OF_3Na$ (M + Na) calcd: 495.19062, found: 495.19065; R_f (5/1 hexanes/EtOAc) = 0.41 (silica gel plate).

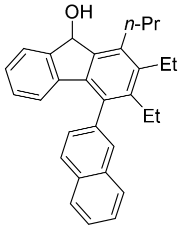


4-(2,3-Diethyl-9-hydroxy-1-(*p*-tolyl)-9*H*-fluoren-4-yl)benzonitrile (9g). With **8g** (178 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 65 mg (30%) of the title compound as a light brown solid: mp (decomp) 227-232 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.85 (m, 2H), 7.50-7.54 (m, 2H), 7.42 (m, 1H), 7.33-7.36 (m, 3H), 7.29 (m, 1H), 7.13 (dt, J = 7.4, 1.0 Hz, 1H), 6.97 (dt, J = 7.5, 0.8 Hz, 1H), 5.88 (d, J = 7.8 Hz, 1H), 5.44 (d, J = 4.6 Hz, 1H), 2.59-2.65 (m, 1H), 2.47-2.53 (m, 3H), 2.47 (s, 3H), 1.70 (d, J = 4.6 Hz, 1H), 1.02 (t, J = 7.5 Hz, 3H), 1.00 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 145.7, 145.2, 142.0, 140.8, 140.3, 139.9, 139.8, 137.3, 135.8, 135.2, 134.5, 132.7, 132.6, 130.63, 130.59, 129.9, 129.5, 129.2, 128.53, 128.50, 127.1, 125.0, 121.9, 118.9, 111.5, 73.7, 22.9, 22.7, 21.3, 15.8, 15.7; IR (KBr) ν_{max} 3476, 3090, 3075, 3049, 3028, 2971, 2926, 2866, 2235, 1607, 1515, 1473, 1428, 1395, 1371, 1308, 1263, 1192, 1144, 1099, 1069, 1033, , 860, 818, 761, 740, 567 cm^{-1}; HRMS (*m/z*) for C$_{31}$H$_{27}$NO (M$^+$) calcd: 429.2093, found: 429.2095; R_f (5/1 hexanes/EtOAc) = 0.31 (silica gel plate).

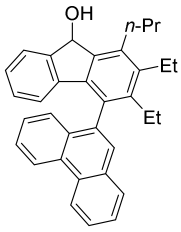


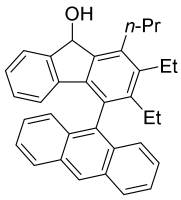
4-(4-Bromophenyl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-ol (9h). With **8h** (100 mg, 0.25 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 61 mg (51%) of the title compound as a brown solid: mp (decomp) 147-152 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.67 (m, 2H), 7.41 (m, 1H), 7.33 (m, 3H), 7.24-7.30 (m, 3H), 7.13 (dt, J = 7.4, 1.0 Hz, 1H), 6.99 (dt, J = 7.5, 0.8 Hz, 1H), 6.05 (d, J = 7.8 Hz, 1H), 5.44 (bs, 1H), 2.58-2.67 (m, 1H), 2.52 (q, J = 7.5 Hz, 2H), 2.48-2.53 (m, 1H), 2.47 (s, 3H), 1.69 (bs, 1H), 1.02 (t, J = 7.5 Hz, 3H), 1.01 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.2, 141.8, 141.4, 140.2, 140.1, 139.4, 139.3, 137.1, 136.1, 135.5, 135.2, 132.02, 131.96, 131.32, 131.29, 129.8, 129.6, 129.1, 128.6, 128.5, 126.9, 124.8, 122.3, 121.5, 73.8, 22.81, 22.75, 21.3, 15.84, 15.75; IR (KBr) ν_{max} 3563, 3047, 3025, 2962, 2929, 2869, 1601, 1512, 1488, 1467, 1431, 1392, 1371, 1263, 1183, 1099, 1069, 1012, 821, 764, 522 cm^{-1}; HRMS (*m/z*) for C$_{30}$H$_{27}$OBrNa (M + Na) calcd: 505.11375, found: 505.11368; R_f (5/1 hexanes/EtOAc) = 0.42 (silica gel plate).

2,3-Diethyl-4-(naphthalen-2-yl)-1-propyl-9*H*-fluoren-9-ol (16a). With **15a** (162 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 91 mg (45%) of the title compound as a light brown solid: mp (decomp) 93-98 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (m, 2H), 7.86 (m, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.53-7.60 (m, 3H), 7.45 (ddd, *J* = 13.1, 8.3, 1.6 Hz, 1H), 7.09 (dt, *J* = 7.4, 0.9 Hz, 1H), 6.81 (dt, *J* = 7.7, 0.9 Hz, 1H), 5.86 (d, *J* = 7.8 Hz, 1H), 5.67 (s, 1H), 3.15 (m, 1H), 2.86 (m, 1H), 2.82 (dq, *J* = 7.5, 2.2 Hz, 2H), 2.46-2.63 (m, 2H), 1.77 (m, 2H), 1.73 (s, 1H), 1.29 (t, *J* = 7.5 Hz, 3H), 1.17 (t, *J* = 7.3 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.0, 142.1, 141.1, 140.6, 140.5, 140.4, 139.1, 139.0, 138.0, 135.9, 135.0, 133.6, 132.5, 128.6, 128.3, 128.19, 128.16, 128.15, 128.13, 128.08, 128.0, 127.9, 126.7, 126.1, 125.9, 124.48, 124.47, 122.5, 74.6, 31.9, 31.8, 25.02, 24.96, 22.90, 22.88, 21.8, 16.0, 15.9, 15.1; IR (KBr) ν_{max} 3386, 3052, 2965, 2932, 2866, 1604, 1565, 1470, 1434, 1371, 1302, 1189, 1102, 1069, 1021, 964, 863, 806, 761, 752, cm^{-1}; HRMS (*m/z*) for C$_{30}$H$_{30}$O (M^{+}) calcd: 406.2297, found: 406.2295; R_f (5/1 hexanes/EtOAc) = 0.45 (silica gel plate).

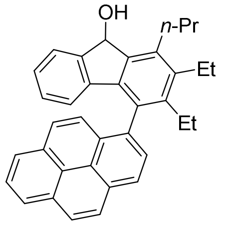


2,3-Diethyl-4-(phenanthren-9-yl)-1-propyl-9*H*-fluoren-9-ol (16b). With **15b** (94 mg, 0.25 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 67 mg (59%) of the title compound as a light brown solid: mp (decomp) 109-114 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.83 (m, 2H), 7.88 (m, 1H), 7.71-7.77 (m, 2H), 7.63-7.68 (m, 2H), 7.37-7.60 (m, 3H), 7.02 (m, 1H), 6.65 (dt, *J* = 7.8, 0.9 Hz, 1H), 5.83 (dd, *J* = 7.8, 2.5 Hz, 1H), 5.70 (d, *J* = 9.8 Hz, 1H), 3.11-3-31 (m, 1H), 2.91 (m, 1H), 2.83 (m, 2H), 2.55 (m, 1H), 2.27 (m, 1H), 1.79 (m, 2H), 1.73 (d, *J* = 9.9 Hz, 1H), 1.31 (dt, *J* = 7.3, 1.0 Hz, 3H), 1.19 (dt, *J* = 7.2, 2.2 Hz, 3H), 0.93 (dt, *J* = 7.4, 1.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.0, 142.86, 142.83, 141.4, 140.8, 140.24, 140.22, 139.29, 139.20, 136.54, 136.52, 136.51, 136.47, 132.58, 132.56, 131.8, 131.74, 131.73, 130.5, 130.20, 130.18, 128.79, 128.77, 128.68, 128.65, 127.8, 127.7, 126.9, 126.75, 126.73, 126.66, 126.63, 126.56, 126.53, 124.38, 124.35, 122.9, 122.7, 122.5, 122.4, 74.65, 74.62, 32.11, 31.61, 25.21, 24.91, 23.3, 21.84, 21.81, 16.23, 16.20, 16.17, 16.12, 15.13; IR (KBr) ν_{max} 3321, 3072, 2959, 2932, 2866, 1607, 1494, 1464, 1452, 1374, 1251, 1195, 1099, 1060, 1009, 908, 812, 770, 755, 725 cm^{-1}; HRMS (*m/z*) for C$_{34}$H$_{32}$ONa (M + Na) calcd: 479.23454, found: 479.23450; R_f (5/1 hexanes/EtOAc) = 0.38 (silica gel plate).





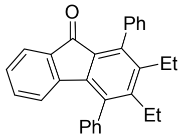
4-(Anthracen-9-yl)-2,3-diethyl-1-propyl-9*H*-fluoren-9-ol (16c). With **15c** (94 mg, 0.25 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 55 mg (48%) of the title compound as a light brown solid: mp (decomp) 104-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.08 (dd, *J* = 8.5, 3.9 Hz, 2H), 7.61 (dd, *J* = 8.8, 0.9 Hz, 1H), 7.41–7.50 (m, 4H), 7.22-7.28 (m 2H), 6.93 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.47 (dt, *J* = 7.6, 0.8 Hz, 1H), 5.73 (d, *J* = 8.4 Hz, 1H), 4.91 (d, *J* = 7.8 Hz, 1H), 3.24 (m, 1H), 2.96 (m, 1H), 2.85 (q, *J* = 7.6 Hz, 2H), 2.24 (q, *J* = 7.5 Hz, 2H), 1.86 (m, 2H), 1.78 (d, *J* = 9.2 Hz, 1H), 1.33 (t, *J* = 7.4 Hz, 3H), 1.21 (t, *J* = 7.3 Hz, 3H), 0.66 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 143.3, 141.7, 141.1, 140.1, 139.4, 137.1, 134.9, 131.6, 130.7, 130.5, 130.4, 128.6, 128.4, 126.64, 126.59, 126.5, 126.4, 125.6, 125.4, 125.3, 124.3, 121.8, 74.7, 31.9, 25.1, 23.5, 21.8, 16.2, 15.5, 15.1; IR (KBr) ν_{max} 3549, 3261, 2961, 2930, 2870, 2205, 1947, 1818, 1605, 1519, 1465, 1441, 1408, 1375, 1230, 1190, 1101, 1059, 1012, 973, 884, 845, 762, 738 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{32}ONa$ (M + Na) calcd: 479.23454, found: 479.23448; R_f (5/1 hexanes/EtOAc) = 0.39 (silica gel plate).



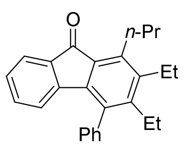
2,3-Diethyl-1-propyl-4-(pyren-2-yl)-9*H*-fluoren-9-ol (16d). With **15d** (100 mg, 0.25 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 64 mg (54%) of the title compound as a light brown solid: mp (decomp) 98-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 7.8, 4.7 Hz, 1H), 8.24 (m, 1H), 8.13-8.20 (m, 3H), 8.02 (dt, *J* = 7.6, 2.6 Hz, 1H), 7.94-8.00 (dd, *J* = 17.0, 7.8 Hz, 1H), 7.90 (dd, *J* = 9.2, 6.1 Hz, 1H), 7.64-7.78 (dd, *J* = 46.1, 9.2 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 6.98 (m, 1H), 6.53 (dt, *J* = 7.6, 0.5 Hz, 1H), 5.75 (dd, *J* = 9.7, 4.5 Hz, 1H), 5.21 (d, *J* = 7.8 Hz, 1H), 3.17-3.32 (m, 1H), 2.94 (m, 1H), 2.86 (m, 2H), 2.48 (m, 1H), 2.31 (m, 1H), 1.88 (m, 2H), 1.77 (d, *J* = 10.4 Hz, 1H), 1.34 (dt, *J* = 7.3, 1.2 Hz, 3H), 1.26 (dt, *J* = 7.2, 1.6 Hz, 3H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.97, 145.94, 142.85, 142.82, 141.35, 140.77, 140.76, 140.39, 139.33, 139.29, 136.67, 136.63, 135.63, 135.57, 133.18, 133.16, 131.38, 131.37, 131.22, 131.21, 130.75, 130.74, 129.62, 129.55, 128.60, 128.58, 127.97, 127.80, 127.61, 127.57, 127.46, 127.41, 126.55, 126.53, 126.02, 125.40, 125.28, 125.07, 125.05, 125.04, 124.95, 124.92, 124.38, 124.37, 122.15, 122.11, 74.69, 74.66, 32.05, 31.80, 25.16, 25.00, 23.2, 21.9, 16.19, 16.17, 15.77, 15.75, 15.16, 15.15; IR (KBr) ν_{max} 3545, 3349, 3043, 2961, 2930, 2869, 1697, 1602, 1464, 1374, 1306, 1191, 1178, 1099, 1057, 1022, 944, 847, 760, 743 cm^{-1}; HRMS (*m/z*) for $C_{36}H_{32}ONa$ (M + Na) calcd: 503.23454, found: 503.23448; R_f (5/1 hexanes/EtOAc) = 0.34 (silica gel plate).

6.2.3. Synthesis of 9,9'-spirobifluorenes 6, 11 and 18

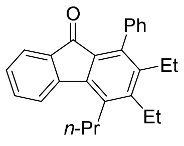
D: General procedure for Oxidation reaction with PCC (preparation of 5, 10 and 17). To a solution of pyridinium chlorochromate (PCC, 64 mg, 0.3 mmol) and celite (64 mg) in anhydrous CH_2Cl_2 (10 mL) the starting fluorenol (0.2 mmol) was added and the mixture was stirred for 3 h at rt. Afterwards, the residue was filtered through a celite/silica gel plug. Column chromatography of the residue on silica gel yielded products.



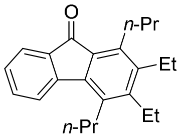
2,3-Diethyl-1,4-diphenyl-9*H*-fluoren-9-one (5a). With **4ab** (100 mg, 0.26 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 89 mg (89%) of the title compound as a bright yellow solid: mp (decomp) 75-80 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51-7.57 (m, 3H), 7.47-7.50 (m, 2H), 7.43-7.46 (m, 1H), 7.38-7.41 (m, 3H), 7.28-7.30 (m, 2H), 7.05 (dt, *J* = 7.4, 1.1 Hz, 1H), 7.01 (dt, *J* = 7.5, 1.4 Hz, 1H), 5.79 (d, *J* = 7.6 Hz, 1H), 2.52-2.57 (m, 4H), 1.04 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.2, 147.8, 144.0, 142.1, 140.9, 140.2, 139.2, 137.9, 137.3, 134.9, 133.8, 129.3, 129.03, 128.99, 128.7, 128.97, 127.95, 127.8, 127.2, 123.4, 122.6, 23.4, 22.4, 15.5, 15.4; IR (KBr) ν_{max} 3055, 3019, 2971, 2932, 2869, 1712, 1598, 1580, 1559, 1467, 1446, 1308, 1192, 1066, 764, 704 cm^{-1}; HRMS (*m/z*) for $C_{29}H_{24}ONa$ (M + Na) calcd: 411.17194, found: 411.17219; R_f (5/1 hexanes/EtOAc) = 0.55 (silica gel plate).



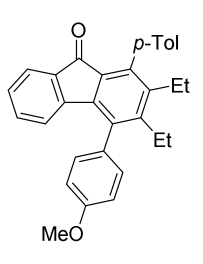
2,3-Diethyl-4-phenyl-1-propyl-9*H*-fluoren-9-one (5b). With **4bb** (95 mg, 0.27 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 89 mg (93%) of the title compound as a bright yellow solid: mp (decomp) 127-132 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47-7.53 (m, 4H), 7.31 (m, 2H), 7.07 (dt, *J* = 7.4, 0.8 Hz, 1H), 6.99 (dt, *J* = 7.6, 1.2 Hz, 1H), 5.74 (d, *J* = 7.6 Hz, 1H), 3.12 (m, 2H), 2.73 (q, *J* = 7.2 Hz, 2H), 2.48 (q, *J* = 7.5 Hz, 2H), 1.63 (m, 2H), 1.23 (t, *J* = 7.5 Hz, 3H), 1.14 (t, *J* = 7.3 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.0, 147.6, 144.0, 142.8, 142.0, 140.7, 139.5, 135.9, 135.1, 133.7, 129.4, 128.9, 128.8, 127.7, 127.6, 123.2, 122.5, 29.7, 24.6, 23.4, 21.4, 15.7, 15.3, 14.9; IR (KBr) ν_{max} 3060, 3016, 2965, 2929, 2869, 1703, 1604, 1559, 1464, 1452, 1320, 1186, 1060, 761, 710 cm^{-1}; HRMS (*m/z*) for $C_{26}H_{27}O$ (M + H) calcd: 355.20564, found: 355.20576; R_f (5/1 hexanes/EtOAc) = 0.64 (silica gel plate).



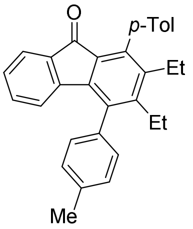
2,3-Diethyl-1-phenyl-4-propyl-9*H*-fluoren-9-one (5c). With **4cb** (70 mg, 0.2 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 66 mg (94%) of the title compound as a bright yellow solid: mp (decomp) 70-75 °C, ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.50 (m, 1H), 7.40-7.47 (m, 4H), 7.20-7.22 (m, 3H), 2.96 (m, 2H), 2.79 (q, *J* = 7.6 Hz, 2H), 2.47 (q, *J* = 7.5 Hz, 2H), 1.75 (m, 2H), 1.27 (t, *J* = 7.6 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 193.3, 147.9, 144.3, 142.2, 140.3, 139.6, 138.3, 137.1, 135.2, 134.2, 129.7, 128.7, 127.90, 127.89, 127.0, 123.7, 122.9, 31.5, 23.3, 22.5, 22.4, 15.6, 15.5, 14.6; IR (KBr) ν_{max} 3055, 3019, 2959, 2929, 2872, 1709, 1601, 1586, 1562, 1467, 1442, 1305, 1189, 1063, 764, 704 cm^{-1}; HRMS (*m/z*) for $C_{26}H_{27}O$ (M + H) calcd: 355.20564, found: 355.20590; R_f (5/1 hexanes/EtOAc) = 0.57 (silica gel plate).



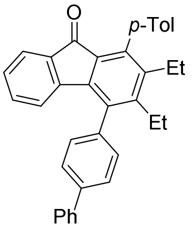
2,3-Diethyl-1,4-dipropyl-9*H*-fluoren-9-one (5d). With **4db** (61 mg, 0.20 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 55 mg (90%) of the title compound as a bright yellow yellow solid: mp (decomp) 76-81 °C, ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.62 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.44 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.23 (dt, *J* = 7.4, 0.7 Hz, 1H), 3.05 (m, 2H), 2.86 (m, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.67 (q, *J* = 7.5 Hz, 2H), 1.67 (m, 2H), 1.56 (m, 2H), 1.22 (t, *J* = 7.5 Hz, 3H), 1.18 (t, *J* = 7.5 Hz, 3H), 1.15 (t, *J* = 7.3 Hz, 3H), 1.09 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 195.1, 147.8, 144.3, 142.2, 141.3, 140.8, 135.5, 135.4, 134.1, 129.4, 127.7, 123.5, 122.8, 31.4, 29.6, 24.5, 23.3, 22.4, 21.5, 15.6, 15.5, 14.8, 14.6; IR (KBr) ν_{max} 3066, 3049, 2962, 2926, 2869, 1700, 1610, 1589, 1568, 1461, 1425, 1296, 1248, 1192, 1096, 1060, 994, 761, 716 cm^{-1}; HRMS (*m/z*) for $C_{23}H_{29}O$ (M + H) calcd: 321.22129, found: 321.22131; R_f (5/1 hexanes/EtOAc) = 0.66 (silica gel plate).



2,3-Diethyl-4-(4-methoxyphenyl)-1-(*p*-tolyl)-9*H*-fluoren-9-one (10a). With **9a** (87 mg, 0.26 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 69 mg (80%) of the title compound as a bright yellow solid: mp (decomp) 231-236 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40 (m, 1H), 7.28 (m, 4H), 7.16 (m, 2H), 7.08 (m, 2H), 7.05 (m, 2H), 5.92 (m, 1H), 3.95 (s, 3H), 2.55 (q, *J* = 7.5 Hz, 2H), 2.53 (q, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.03 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 193.3, 159.1, 148.4, 144.1, 142.3, 141.0, 140.6, 136.9, 136.6, 135.0, 134.9, 133.8, 131.4, 130.3, 129.1, 128.7, 128.5, 127.9, 123.4, 122.6, 114.3, 55.3, 23.4, 22.4, 21.4, 15.6, 15.4; IR (KBr) ν$_{max}$ 3022, 3001, 2962, 2932, 2893, 2869, 2836, 1712, 1613, 1586, 1562, 1512, 1461, 1422, 1302, 1284, 1242, 1192, 1186, 1066, 1030, 842, 824, 779 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{28}O_2$ (M^+) calcd: 432.2089, found: 432.2091; R_f (5/1 hexanes/EtOAc) = 0.39 (silica gel plate).

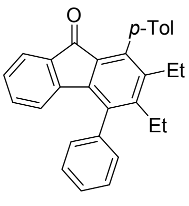


2,3-Diethyl-1,4-di-*p*-tolyl-9*H*-fluoren-9-one (10b). With **9b** (83 mg, 0.2 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 70 mg (84%) of the title compound as a bright yellow solid: mp (decomp) 76-81 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.39 (m, 1H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.05 (dt, *J* = 7.4, 1.2 Hz, 1H), 7.02 (dt, *J* = 7.5, 1.5 Hz, 1H), 5.87 (m, 1H), 2.55 (q, *J* = 7.5 Hz, 2H), 2.54 (q, *J* = 7.5 Hz, 2H), 2.51 (s, 3H), 2.47 (s, 3H), 1.03 (t, *J* = 7.4 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 193.3, 148.1, 144.1, 142.3, 141.0, 140.3, 137.4, 137.3, 136.6, 136.2, 135.0, 134.9, 133.7, 129.7, 129.11, 129.08, 128.7, 128.5, 127.9, 123.3, 122.6, 23.4, 22.4, 21.4 (2xCH_3), 15.6, 15.4; IR (KBr) ν$_{max}$ 3078, 3046, 3025, 2965, 2932, 2893, 2872, 1709, 1607, 1586, 1556, 1515, 1467, 1446, 1422, 1374, 1299, 1195, 1063, 875, 818, 779, 764, 725 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{28}O$ (M + Na) calcd: 416.2140, found: 416.2142; R_f (5/1 hexanes/EtOAc) = 0.49 (silica gel plate).

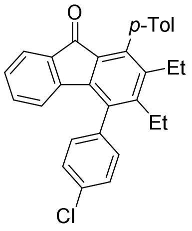


4-([1,1'-Biphenyl]-4-yl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-one (10c). With **9c** (96 mg, 0.2 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 78 mg (82%) of the title compound as a bright yellow solid: mp (decomp) 194-199 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.81 (m, 2H), 7.78 (m, 2H), 7.53 (m, 2H), 7.46 (m, 2H), 7.42 (m, 2H), 7.29 (m, 2H), 7.18 (m, 2H), 7.06 (dt, *J* = 7.4, 1.1 Hz, 1H), 7.02 (dt, *J* = 7.6, 1.4 Hz, 1H), 5.96 (d, *J* = 7.6 Hz, 1H), 2.59 (q, *J* = 7.5 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.04 (t, *J* = 7.5 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 193.2, 147.9, 144.0, 142.4, 141.2, 140.39, 140.37, 140.3, 138.3, 136.8, 136.7, 135.0, 134.9, 133.8, 129.8, 129.2, 128.9, 128.7, 128.5, 128.0, 127.6, 127.5, 127.0, 123.4, 122.6, 23.4, 22.4, 21.4, 15.6, 15.4; IR (KBr) ν$_{max}$ 3078, 3049, 3022, 2974, 2938, 2878, 1712, 1601, 1583, 1559, 1488, 1467, 1446, 1302, 1230, 1186, 1117, 1063, 1006, 872, 776, 752, 695 cm^{-1}; HRMS (*m/z*) for $C_{36}H_{30}O$ (M^+) calcd: 478.2297, found: 478.2296; R_f (5/1 hexanes/EtOAc) = 0.47 (silica gel plate).

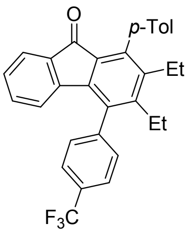
2,3-Diethyl-4-phenyl-1-(*p*-tolyl)-9*H*-fluoren-9-one (10d). With **9d** (81 mg, 0.2 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 69 mg (86%) of the title compound as a bright yellow solid: mp (decomp) 71-76 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.51-7.57 (m, 3H), 7.38-7.42 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.17 (m, 2H), 7.05 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.00 (dt, *J* = 7.6, 1.4 Hz, 1H), 5.79 (d, *J* = 7.6 Hz, 1H), 2.560 (q, *J* = 7.5 Hz, 2H), 2.559 (q, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.04 (t, *J* = 7.5 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 193.2, 147.7, 144.0, 142.3, 141.1, 140.2, 139.3, 137.2, 136.6, 134.9, 134.9, 133.7, 129.3, 129.1, 129.0, 128.7, 128.5, 127.9, 127.8, 123.4, 122.5, 23.4, 22.4, 21.4, 15.6, 15.3; IR (KBr) ν_{max} 3049, 3022, 2971, 2929, 2869, 1715, 1601, 1559, 1512, 1464, 1440, 1305, 1186, 1060, 1009, 952, 866, 764, 719, 707 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{26}O$ (M^+) calcd: 402.1984, found: 402.1988; R_f(5/1 hexanes/EtOAc) = 0.53 (silica gel plate).



4-(4-Chlorophenyl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-one (10e). With **9e** (87 mg, 0.2 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 75 mg (86%) of the title compound as a bright yellow solid: mp (decomp) 193-198 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.54 (m, 2H), 7.42 (m, 1H), 7.34 (m, 2H), 7.28 (m, 2H), 7.15 (m, 2H), 7.08 (m, 2H), 5.91 (m, 1H), 2.53 (q, *J* = 7.5 Hz, 2H), 2.52 (q, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.02 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 193.0, 147.6, 143.7, 142.5, 141.4, 140.2, 137.8, 136.7, 135.7, 134.9, 134.7, 133.9, 133.8, 130.8, 129.3, 129.2, 128.7, 128.4, 128.1, 123.6, 122.4, 23.3, 22.4, 21.4, 15.6, 15.3; IR (KBr) ν_{max} 3081, 3063, 3052, 3025, 2974, 2929, 2866, 1712, 1607, 1589, 1556, 1512, 1488, 1464, 1425, 1302, 1198, 1087, 955, 872, 821, 773, 725 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{26}OCl$ (M + H) calcd: 437.16667, found: 437.16665; R_f(5/1 hexanes/EtOAc) = 0.52 (silica gel plate).

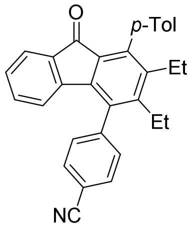


2,3-Diethyl-1-(*p*-tolyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (10f). With **9f** (95 mg, 0.2 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 57 mg (61%) of the title compound as a bright yellow solid: mp (decomp) 77-82 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.42 (m, 1H), 7.29 (m, 2H), 7.16 (m, 2H), 7.08 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.04 (dt, *J* = 7.6, 1.4 Hz, 1H), 5.76 (m, 1H), 2.54 (q, *J* = 7.5 Hz, 2H), 2.49 (q, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.02 (t, *J* = 7.5 Hz,

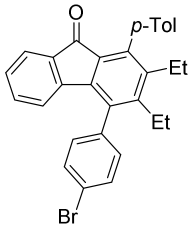


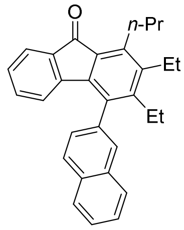
3H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 192.8, 147.2, 143.5, 143.3, 142.7, 141.7, 139.9, 136.8, 135.5, 134.9, 134.6, 133.9, 130.2 (q, $^{2}J_{\text{C-F}}$ = 32.6 Hz), 129.9, 129.3, 128.8, 128.4, 128.3, 126.0 (q, $^{3}J_{\text{C-F}}$ = 3.8 Hz), 121.5-126.9 (q, $^{1}J_{\text{C-F}}$ = 272.2 Hz), 123.7, 122.2, 23.4, 22.3, 21.4, 15.5, 15.3; IR (KBr) ν_{max} 3028, 2965, 2932, 2869, 1715, 1619, 1601, 1559, 1464, 1401, 1374, 1332, 1323, 1192, 1162, 1132, 1123, 1102, 1069, 1021, 872, 857, 824, 770, 719 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{26}OF_3$ (M + H) calcd: 471.19303, found: 471.19297; R_f (5/1 hexanes/EtOAc) = 0.54 (silica gel plate).

4-(2,3-Diethyl-9-oxo-1-(*p*-tolyl)-9*H*-fluoren-4-yl)benzonitrile (10g). With **9g** (65 mg, 0.15 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 47 mg (73%) of the title compound as a bright yellow solid: mp (decomp) 239-244 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.87 (m, 2H), 7.55 (m, 2H), 7.43 (m, 1H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.14 (m, 2H), 7.10 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.05 (dt, *J* = 7.6, 1.4 Hz, 1H), 5.76 (d, *J* = 7.6 Hz, 1H), 2.54 (q, *J* = 7.5 Hz, 2H), 2.48 (q, *J* = 7.5 Hz, 2H), 2.46 (s, 3H), 1.01 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 192.6, 146.8, 144.6, 143.2, 142.8, 141.9, 139.7, 136.9, 135.0, 134.9, 134.4, 133.9, 132.8, 130.5, 129.3, 128.8, 128.41, 128.35, 123.8, 122.0, 118.6, 112.1, 23.4, 22.3, 21.4, 15.5, 15.2; IR (KBr) ν_{max} 3120, 3081, 3066, 3046, 3022, 2977, 2926, 2893, 2872, 2229, 1718, 1604, 1559, 1512, 1467, 1422, 1371, 1320, 1169, 1069, 1021, 949, 872, 833, 764, 716 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{26}ON$ (M + H) calcd: 428.20089, found: 428.20087; R_f (5/1 hexanes/EtOAc) = 0.37 (silica gel plate).

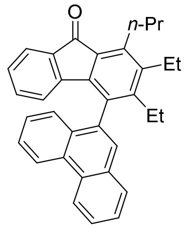


4-(4-Bromophenyl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-one (10h). With **9h** (510 mg, 1.1 mmol) following the general procedure D. Column chromatography (5/1 hexanes/EtOAc) yielded 475 mg (93%) of the title compound as a bright yellow solid: mp (decomp) 78-83 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.69 (m, 2H), 7.42 (m, 1H), 7.27-7.30 (m, 4H), 7.15 (m, 2H), 7.08 (m, 2H), 5.92 (m, 1H), 2.53 (q, *J* = 7.5 Hz, 2H), 2.51 (q, *J* = 7.5 Hz, 2H), 2.46 (s, 3H), 1.02 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 193.0, 147.6, 143.7, 142.5, 141.4, 140.1, 138.2, 136.8, 135.7, 134.9, 134.7, 133.9, 132.2, 131.1, 129.2, 128.7, 128.4, 128.2, 123.6, 122.4, 122.0, 23.3, 22.3, 21.4, 15.6, 15.3; IR (KBr) ν_{max} 3022, 2968, 2932, 2866, 1709, 1604, 1556, 1515, 1485, 1464, 1422, 1371, 1302, 1192, 1120, 1072, 1012, 949, 869, 824, 761, 719 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{26}OBr$ (M + H) calcd: 481.11615, found: 481.11621; R_f (5/1 hexanes/EtOAc) = 0.51 (silica gel plate).

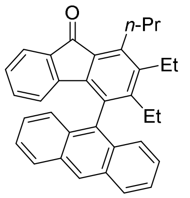




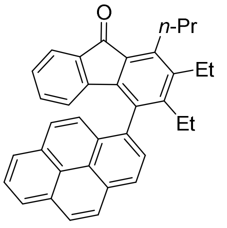
2,3-Diethyl-4-(naphthalen-2-yl)-1-propyl-9*H*-fluoren-9-one (17a). With **16a** (81 mg, 0.2 mmol) following the general procedure D. Column chromatography (5/1 hexanes/EtOAc) yielded 84 mg (91%) of the title compound as a bright yellow solid: mp (decomp) 69-74 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.00 (m, 2H), 7.87 (m, 1H), 7.81 (s, 1H), 7.56-7.61 (m, 2H), 7.53 (d, J = 7.2 Hz, 1H), 7.44 (dd, J = 8.3, 1.6 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 6.86 (dt, J = 7.6, 1.1 Hz, 1H), 5.71 (d, J = 7.6 Hz, 1H), 3.15 (m, 2H), 2.75 (q, J = 7.5 Hz, 2H), 2.45-2.53 (m, 2H), 1.65 (m, 2H), 1.25 (t, J = 7.4 Hz, 3H), 1.16 (t, J = 7.2 Hz, 3H), 0.99 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 194.9, 147.9, 144.0, 142.9, 142.2, 140.7, 136.9, 135.7, 135.1, 133.8, 133.5, 132.7, 128.8, 128.6, 128.14, 128.10, 127.9, 127.8, 127.7, 126.4, 126.2, 123.2, 122.5, 29.7, 24.7, 23.5, 21.4, 15.7, 15.4, 14.9; IR (KBr) ν_{max} 3052, 2962, 2929, 2866, 1700, 1601, 1562, 1467, 1428, 1374, 1299, 1186, 1102, 1063, 1012, 961, 860, 806, 764, 746, 716 cm^{-1}; HRMS (*m/z*) for C$_{30}$H$_{28}$O (M^{+}) calcd: 404.2140, found: 404.2141; R_f (5/1 hexanes/EtOAc) = 0.56 (silica gel plate).



2,3-Diethyl-4-(phenanthren-9-yl)-1-propyl-9*H*-fluoren-9-one (17b). With **16b** (100 mg, 0.22 mmol) following the general procedure D. Column chromatography (5/1 hexanes/EtOAc) yielded 85 mg (86%) of the title compound as a bright yellow solid: mp (decomp) 81-86 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.82 (d, J = 8.3 Hz, 2H), 7.90 (dd, J = 7.9, 1.3 Hz, 1H), 7.77 (dt, J = 7.1, 1.4 Hz, 1H), 7.75 (s, 1H), 7.66-7.71 (m, 2H), 7.59 (dd, J = 8.2, 1.1 Hz, 1H), 7.45-7.50 (m, 2H), 6.97 (dt, J = 7.5, 0.9 Hz, 1H), 6.72 (dt, J = 7.6, 1.3 Hz, 1H), 5.71 (d, J = 7.7 Hz, 1H), 3.33 (m, 1H), 3.11 (m, 1H), 2.79 (m, 2H), 2.53 (m, 1H), 2.25 (m, 1H), 1.73 (m, 2H), 1.28 (t, J = 7.5 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.0, 148.6, 143.6, 143.2, 142.6, 141.5, 135.4, 135.0, 133.9, 133.3, 131.6, 131.3, 130.6, 130.3, 129.2, 128.8, 127.9, 127.7, 127.1, 126.99, 126.95, 126.9, 126.3, 123.2, 123.0, 122.7, 122.5, 29.7, 24.7, 23.9, 21.5, 15.84, 15.82, 14; IR (KBr) ν_{max} 3075, 2965, 2935, 2869, 1703, 1604, 1562, 1491, 1470, 1449, 1377, 1257, 1192, 1060, 761, 746, 722 cm^{-1}; HRMS (*m/z*) for C$_{34}$H$_{31}$O (M + H) calcd: 455.23694, found: 455.23707; R_f (5/1 hexanes/EtOAc) = 0.49 (silica gel plate).

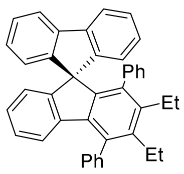


4-(Anthracen-9-yl)-2,3-diethyl-1-propyl-9*H*-fluoren-9-one (17c). With **16c** (100 mg, 0.23 mmol) following the general procedure D. Column chromatography (5/1 hexanes/EtOAc) yielded 84 mg (83%) of the title compound as a bright yellow solid: mp (decomp) 75-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.10 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.46–7.50 (m, 3H), 7.32 (m 2H), 6.89 (dt, J = 7.6, 0.6 Hz, 1H), 6.55 (dt, J = 7.6, 1.1 Hz, 1H), 4.82 (d, J = 7.7 Hz, 1H), 3.28 (m, 2H), 2.84 (q, J = 7.4 Hz, 2H), 2.25 (q, J = 7.5 Hz, 2H), 1.79 (m, 2H), 1.32 (t, J = 7.4 Hz, 3H), 1.24 (t, J = 7.3 Hz, 3H), 0.69 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 149.2, 143.34, 143.0, 142.2, 135.0, 133.8, 133.4, 131.6, 131.5, 130.3, 129.5, 128.5, 127.6, 127.2, 126.1, 126.0, 125.5, 123.0, 121.8, 29.8, 24.8, 24.0, 21.5, 15.9, 15.2, 14.9; IR (KBr) ν_{max} 3049, 2959, 2926, 2886, 1703, 1601, 1562, 1464, 1404, 1293, 1245, 1222, 1183, 1096, 1054, 1012, 973, 890, 848, 785, 761, 737, 716 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{31}O$ (M + H) calcd: 455.23694, found: 455.23681; R_f(5/1 hexanes/EtOAc) = 0.50 (silica gel plate).

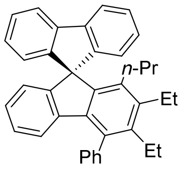


2,3-Diethyl-1-propyl-4-(pyren-2-yl)-9*H*-fluoren-9-one (17d). With **16d** (96 mg, 0.2 mmol) following the general procedure D. Column chromatography (5/1 hexanes/EtOAc) yielded 80 mg (84%) of the title compound as a bright yellow solid: mp (decomp) 87-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 7.8 Hz, 1H), 8.25 (dd, J = 7.6, 1.0 Hz, 1H), 8.16–8.22 (m, 3H), 8.04 (t, J = 7.6 Hz, 1H), 7.98 (d, J = 3.4 Hz, 1H), 7.95 (d, J = 4.8 Hz, 1H), 7.75 (d, J = 9.2 Hz, 1H), 7.50 (m 1H), 6.93 (dt, J = 7.5, 0.8 Hz, 1H), 6.58 (dt, J = 7.6, 1.2 Hz, 1H), 5.06 (d, J = 7.7 Hz, 1H), 3.31 (m, 1H), 3.18 (m, 1H), 2.81 (m, 2H), 2.48 (m, 1H), 2.29 (m, 1H), 1.73 (m, 2H), 1.31 (t, J = 7.4 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H), 0.85 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 148.6, 143.8, 143.2, 142.6, 141.6, 135.1, 134.3, 133.9, 133.8, 131.4, 131.2, 131.0, 129.5, 129.2, 128.0, 127.71, 127.68, 127.6, 127.5, 126.2, 125.33, 125.29, 125.1, 125.0, 124.9, 124.8, 123.2, 122.2, 29.8, 24.8, 23.8, 21.5, 15.9, 15.4, 14.9; IR (KBr) ν_{max} 3040, 2963, 2931, 2870, 1702, 1603, 1565, 1465, 1423, 1375, 1297, 1187, 1057, 1011, 952, 872, 849, 838, 761, 721 cm^{-1}; HRMS (*m/z*) for $C_{36}H_{31}O$ (M + H) calcd: 479.23694, found: 479.23680; R_f(5/1 hexanes/EtOAc) = 0.46 (silica gel plate).

E: General procedure for creation of 9,9'-spirobifluorene (preparation of 6, 11 and 18).[46] A solution of 2-bromobiphenyl (40 µL, 0.23 mmol) in anhydrous THF (3 mL) was cooled down to -78 °C and *n*-BuLi 1.6 M (140 µL, 0.23 mmol) was added dropwise. The resulted solution was stirred for 30 min, followed by the addition of fluorenone (0.15 mmol) in THF (3 mL) and stirred for 3 h first for 15 min at -78 °C, but during time it was allowed to reach ambient temperature. The reaction mixture was poured in a saturated solution of $NaHCO_3$ solution and extracted with diethyl ether (3 x 15 mL). The combined organic fractions were dried over $MgSO_4$ and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (10/1 hexanes/EtOAc) to yield desired alcohols. The alcohols were dissolved in acetic acid (10 mL) with a catalytic amount of HCl (12 mol/L) and the resulted solution stirred under reflux for 3 h. The reaction mixture was neutralized with H_2O and K_2CO_3 and extracted with diethyl ether (3 x 15 mL). Column chromatography of the residue on silica gel provided products.

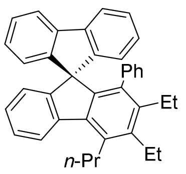


2,3-Diethyl-1,4-diphenyl-9,9'-spirobifluorene (6a). With **5a** (60 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 52 mg (66%) of the title compound as a colorless solid: mp (decomp) 115-120 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52-7.62 (m, 4H), 7.40-7.46 (m, 1H), 7.40 (m, 1H), 7.28-7.35 (m, 2H), 7.18 (dt, *J* = 7.3, 1.2 Hz, 2H), 7.05 (dt, *J* = 7.5, 1.2 Hz, 2H), 6.80-6.87 (m, 4H), 6.57-6.62 (m, 2H), 6.39-6.42 (m, 1H), 6.06-6.12 (m, 3H), 2.58 (q, *J* = 7.5 Hz, 2H), 2.28 (q, *J* = 7.5 Hz, 2H), 1.06 (t, *J* = 7.5 Hz, 3H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.7, 149.0, 143.3, 142.0, 141.8, 140.8, 140.3, 140.0, 139.3, 137.9, 137.1, 136.3, 133.1, 131.3, 129.8, 129.3, 128.8, 128.0, 127.6, 127.3, 127.0, 126.8, 126.7, 126.6, 126.2, 124.9, 123.8, 123.2, 122.5, 119.6, 65.5, 23.0, 22.9, 15.8, 15.6; IR (KBr) ν_{max} 3055, 3019, 2965, 2929, 2866, 1601, 1470, 1446, 1368, 1278, 1224, 1117, 1069, 1030, 752, 737 cm^{-1}; HRMS (*m/z*) for $C_{41}H_{32}Na$ (M + Na) calcd: 547.23962, found: 547.23933; R_f (20/1 hexanes/EtOAc) = 0.45 (silica gel plate).

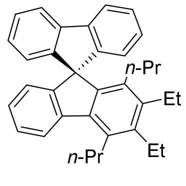


2,3-Diethyl-4-phenyl-1-propyl-9,9'-spirobifluorene (6b). With **5b** (87 mg, 0.25 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 88 mg (74%) of the title compound as a colorless solid: mp (decomp) 227-232 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ

7.87 (d, J = 7.6 Hz, 2H), 7.56 (m, 2H), 7.51 (m, 1H), 7.46 (m, 2H), 7.39 (dt, J = 7.5, 0.9 Hz, 2H), 7.13 (dt, J = 7.5, 1.0 Hz, 2H), 6.84 (d, J = 7.5 Hz, 2H), 6.81 (m, 2H), 6.38 (m, 1H), 5.98 (m, 1H), 2.60 (q, J = 7.4 Hz, 2H), 2.54 (q, J = 7.5 Hz, 2H), 1.47 (m, 2H), 1.11 (t, J = 7.4 Hz, 3H), 1.02 (t, J = 7.4 Hz, 3H), 0.65 (m, 2H), 0.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.8, 149.6, 143.1, 141.73, 141.70, 141.1, 140.52, 140.46, 138.4, 137.6, 135.1, 129.9, 128.7, 127.7, 127.4, 127.2, 126.6, 126.4, 124.2, 122.8, 122.5, 119.9, 66.0, 31.1, 23.6, 22.8, 21.7, 16.1, 15.8, 14.8; IR (KBr) ν_{max} 3055, 3016, 2962, 2932, 2869, 1598, 1470, 1449, 1374, 1278, 1260, 1150, 1105, 1063, 1027, 758, 740, 704 cm^{-1}; HRMS (*m/z*) for $C_{38}H_{35}$ (M + H) calcd: 591.27333, found: 591.27349; R_f (20/1 hexanes/EtOAc) = 0.48 (silica gel plate).

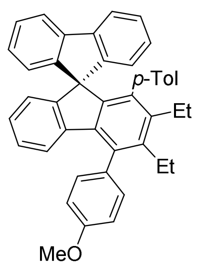


2,3-Diethyl-1-phenyl-4-propyl-9,9'-spirobifluorene (6c). With **5c** (66 mg, 0.2 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 67 mg (68%) of the title compound as a colorless solid: mp (decomp) 106-111 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, J = 8.0 Hz, 1H), 7.30-7.34 (m, 3H), 7.18 (t, J = 7.4 Hz, 2H), 7.04 (t, J = 7.4 Hz, 2H), 6.99 (t, J = 7.4 Hz, 1H), 6.82 (t, J = 7.4 Hz, 1H), 6.76 (d, J = 7.5 Hz, 2H), 6.57 (t, J = 7.6 Hz, 2H), 6.49 (d, J = 7.6 Hz, 1H), 6.04 (d, J = 7.5 Hz, 2H), 3.22 (m, 2H), 2.86 (q, J = 7.5 Hz, 2H), 2.26 (q, J = 7.4 Hz, 2H), 1.95 (m, 2H), 1.32 (t, J = 7.7 Hz, 3H), 1.31 (t, J = 7.5 Hz, 3H), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.0, 149.2, 143.7, 142.1, 141.9, 140.4, 139.9, 138.1, 137.8, 137.4, 135.7, 129.5, 127.2, 126.9, 126.7, 126.4, 126.0, 124.7, 123.8, 123.6, 122.8, 119.6, 65.5, 32.0, 23.5, 23.2, 22.0, 16.0, 15.6, 14.8; IR (KBr) ν_{max} 3058, 3034, 2962, 2932, 2872, 1598, 1473, 1449, 1368, 1266, 1236, 1108, 1072, 1027, 758, 731, 704 cm^{-1}; HRMS (*m/z*) for $C_{38}H_{35}$ (M + H) calcd: 491.27333, found: 491.27334; R_f (20/1 hexanes/EtOAc) = 0.52 (silica gel plate).

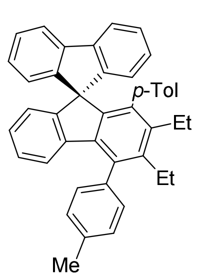


2,3-Diethyl-1,4-dipropyl-9,9'-spirobifluorene (6d). With **5d** (50 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 57 mg (83%) of the title compound as a colorless solid: mp (decomp) 101-106 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (m, 2H), 7.82 (d, J = 8.0 Hz, 1H), 7.37 (dt, J = 7.4, 1.1 Hz, 2H), 7.28 (dt, J = 7.4, 1.2 Hz, 1H), 7.11 (dt, J = 7.5, 1.1 Hz, 2H), 6.97 (dt, J = 7.5, 1.0 Hz, 1H), 6.78 (m, 2H), 6.46 (m, 1H), 3.11 (m, 2H), 2.80 (q, J = 7.5 Hz, 2H), 2.57 (q, J = 7.4 Hz, 2H), 1.86 (m, 2H), 1.70 (m, 2H), 1.28 (t, J = 7.7 Hz, 3H), 1.25 (t, J = 7.5 Hz, 3H), 1.09 (t, J = 7.5 Hz, 3H), 0.60 (m, 2H), 0.29 (t, J = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.69, 148.97, 143.25, 141.95, 141.78, 140.80, 140.27, 140.04, 139.31, 137.91, 137.11, 136.34, 133.09, 131.26, 129.79, 129.36, 129.32, 128.78, 127.95, 127.58, 127.33, 126.97, 126.80, 126.74, 126.60, 126.15, 124.89, 123.80, 123.22, 122.53, 119.63, 65.51, 22.99, 22.92, 15.77, 15.61; IR (KBr) ν_{max} 3058, 3037, 3016, 2953, 2929, 2896, 2869, 1598, 1476, 1446, 1365, 1284, 1219, 1114, 1069, 1030, 758, 740 cm^{-1}; HRMS (*m/z*) for $C_{35}H_{37}$ (M + H) calcd: 457.2895, found: 457.2895; R_f (20/1 hexanes/EtOAc) = 0.54 (silica gel plate).

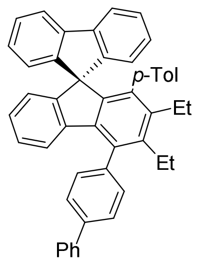
2,3-Diethyl-4-(4-methoxyphenyl)-1-(*p*-tolyl)-9,9'-spirobifluorene (11a). With 1**0a** (65 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 71 mg (83%) of the title compound as a colorless solid: mp (decomp) 260-265 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.18 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.14 (m, 2H), 7.04 (dt, *J* = 7.4, 1.0 Hz, 2H), 6.90 (dt, *J* = 7.3, 1.1 Hz, 1H), 6.84 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.40 (d, *J* = 7.4 Hz, 1H), 6.37 (d, *J* = 7.7 Hz, 2H), 6.19 (d, *J* = 7.8 Hz, 1H), 5.95 (d, *J* = 7.9 Hz, 2H), 3.98 (s, 3H), 2.59 (q, *J* = 7.4 Hz, 2H), 2.31 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.8, 149.7, 149.1, 143.7, 142.01, 141.99, 140.5, 140.3, 139.3, 138.3, 135.8, 134.2, 134.1, 133.1, 130.8, 129.1, 126.9, 126.8, 126.74, 126.70, 126.5, 123.8, 123.2, 122.6, 119.4, 114.1, 65.5, 55.3, 23.1, 22.9, 21.1, 15.8, 15.7; IR (KBr) ν_{max} 3063, 3040, 3022, 2956, 2932, 2869, 2839, 1613, 1574, 1512, 1476, 1467, 1440, 1425, 1371, 1290, 1245, 1177, 1111, 1063, 1033, 824, 815, 770, 737 cm^{-1}; HRMS (*m/z*) for $C_{43}H_{37}O$ (M + H) calcd: 569.28389, found: 569.28369; R_f (20/1 hexanes/EtOAc) = 0.36 (silica gel plate).



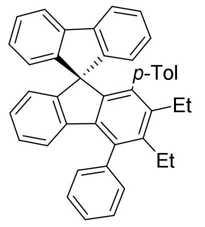
2,3-Diethyl-1,4-di-*p*-tolyl-9,9'-spirobifluorene (11b). With **11b** (62 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 61 mg (74%) of the title compound as a colorless solid: mp (decomp) 226-231 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (s, 4H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.18 (dt, *J* = 7.5, 1.0 Hz, 2H), 7.04 (dt, *J* = 7.5, 1.0 Hz, 2H), 6.88 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.83 (dt, *J* = 7.4, 1.2 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.39 (d, *J* = 7.5 Hz, 1H), 6.37 (d, *J* = 7.7 Hz, 2H), 6.14 (d, *J* = 7.8 Hz, 1H), 5.95 (d, *J* = 7.9 Hz, 2H), 2.57 (q, *J* = 7.4 Hz, 2H), 2.55 (s, 3H), 2.30 (q, *J* = 7.4 Hz, 2H), 2.16 (s, 3H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.7, 149.1, 143.7, 142.0, 140.3, 140.2, 139.2, 138.0, 137.7, 136.8, 136.2, 134.2, 134.0, 129.6, 129.4, 129.1, 126.9, 126.8, 126.7, 126.5, 123.8, 123.1,



122.6, 119.4, 65.5, 23.1, 22.9, 21.5, 21.1, 15.8, 15.7; IR (KBr) ν_{max} 3060, 3043, 3016, 2977, 2959, 2929, 2869, 1515, 1476, 1449, 1428, 1371, 1281, 1239, 1111, 1060, 1021, 863, 824, 755, 749, 734 cm^{-1}; HRMS (*m/z*) for $C_{43}H_{37}$ (M + H) calcd: 553.28898, found: 553.28902; R_f (20/1 hexanes/EtOAc) = 0.50 (silica gel plate).

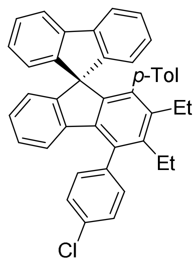


4-([1,1'-Biphenyl]-4-yl)-2,3-diethyl-1-(*p*-tolyl)-9,9'-spirobifluorene (11c). With **10c** (72 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 58 mg (63%) of the title compound as a colorless solid: mp (decomp) >270 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.86 (m, 2H), 7.83 (m, 2H), 7.60 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.42 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.19 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.05 (dt, *J* = 7.4, 1.0 Hz, 2H), 6.87 (dt, *J* = 7., 1.4 Hz, 1H), 6.84 (dt, *J* = 7.4, 1.4 Hz, 1H), 6.81 (d, *J* = 7.4 Hz, 2H), 6.40 (m, 1H), 6.38 (d, *J* = 7.6 Hz, 2H), 6.22 (m, 1H), 5.96 (d, *J* = 7.9 Hz, 2H), 2.62 (q, *J* = 7.4 Hz, 2H), 2.32 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.09 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 149.7, 149.1, 143.8, 142.0, 141.8, 140.8, 140.5, 140.1, 139.9, 139.8, 139.5, 137.9, 135.8, 134.11, 134.10, 130.3, 129.1, 128.9, 127.4, 127.3, 127.1, 126.9, 126.78, 126.77, 126.73, 126.6, 123.8, 123.2, 122.6, 119.4, 65.5, 29.7, 23.1, 23.0, 21.1, 15.9, 15.7; IR (KBr) ν_{max} 3078, 3058, 3043, 3016, 2968, 2929, 2869, 1601, 1518, 1491, 1440, 1386, 1368, 1111, 1060, 1006, 848, 824, 755, 737 cm^{-1}; HRMS (*m/z*) for $C_{48}H_{39}$ (M + H) calcd: 615.30463, found: 615.30474; R_f (20/1 hexanes/EtOAc) = 0.40 (silica gel plate).

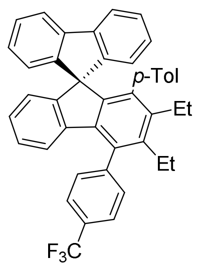


2,3-Diethyl-4-phenyl-1-(*p*-tolyl)-9,9'-spirobifluorene (11d). With **10d** (60 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 56 mg (73%) of the title compound as a colorless solid: mp (decomp) 238-243 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.60 (m, 2H), 7.54 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.18 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.04 (dt, *J* = 7.4, 1.0 Hz, 2H), 6.86 (dt, *J* = 7.4, 1.3 Hz, 1H), 6.83 (dt, *J* = 7.4, 1.4 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.39 (m, 1H), 6.37 (d, *J* = 7.6 Hz, 2H), 6.07 (m, 1H), 5.96 (d, *J* = 7.9 Hz, 2H), 2.58 (q, *J* = 7.4 Hz, 2H), 2.31 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 149.7, 149.1, 143.7, 142.0, 141.8, 140.9, 140.4, 139.9, 139.4, 137.8, 136.2, 134.13, 134.08, 129.8, 129.1, 128.8, 127.3, 126.9, 126.8, 126.72, 126.70, 126.5, 123.8, 123.2, 122.5, 119.4, 65.5, 23.0, 22.9, 21.1, 15.8, 15.7; IR (KBr) ν_{max} 3052, 3013, 2968, 2926, 2869, 1601, 1488, 1446, 1428, 1350, 1251, 1198, 1183, 1126, 1018, 860, 815, 758, 749, 701 cm^{-1};HRMS (*m/z*) for $C_{42}H_{35}$ (M + H) calcd: 539.27333, found: 539.27337; R_f (20/1 hexanes/EtOAc) = 0.44 (silica gel plate).

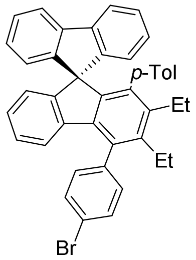
4-(4-Chlorophenyl)-2,3-diethyl-1-(*p*-tolyl)-9,9'-spirobifluorene (11e). With **10e** (65 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 72 mg (82%) of the title compound as a colorless solid: mp (decomp) 247-252 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (m, 2H), 7.48 (m, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.18 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.04 (dt, *J* = 7.4, 1.0 Hz, 2H), 6.92 (dt, *J* = 7.3, 1.1 Hz, 1H), 6.86 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 2H), 6.41 (d, *J* = 7.4 Hz, 1H), 6.37 (d, *J* = 7.7 Hz, 2H), 6.17 (d, *J* = 7.8 Hz, 1H), 5.94 (d, *J* = 7.9 Hz, 2H), 2.54 (q, *J* = 7.4 Hz, 2H), 2.30 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.8, 148.9, 143.9, 142.0, 141.5, 140.6, 140.0, 139.8, 139.3, 137.7, 134.7, 134.2, 134.0, 133.3, 131.3, 129.1, 129.0, 126.9, 126.82, 126.80, 126.78, 126.75, 123.8, 123.4, 122.3, 119.4, 65.5, 23.0, 22.9, 21.1, 15.7, 15.6; IR (KBr) ν_{max} 3060, 3040, 3016, 2971, 2965, 2929, 2866, 1598, 1512, 1494, 1476, 1443, 1368, 1281, 1223, 1090, 1060, 1015, 842, 821, 758, 740 cm^{-1}; HRMS (*m/z*) for $C_{42}H_{33}Cl$ (M + H) calcd: 573.23436, found: 573.23444; R_f (20/1 hexanes/EtOAc) = 0.57 (silica gel plate).



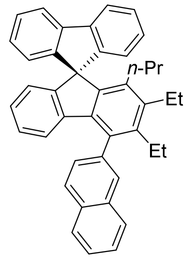
2,3-Diethyl-1-(*p*-tolyl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobifluorene (11f). With **10f** (47 mg, 0.1 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 55 mg (90%) of the title compound as a colorless solid: mp (decomp) 202-207 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.19 (dt, *J* = 7.5, 1.0 Hz, 2H), 7.05 (dt, *J* = 7.5, 1.0 Hz, 2H), 6.89 (dt, *J* = 7.4, 1.3 Hz, 1H), 6.85 (dt, *J* = 7.4, 1.5 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.42 (m, 1H), 6.38 (d, *J* = 7.6 Hz, 2H), 6.03 (m, 1H), 5.95 (d, *J* = 7.9 Hz, 2H), 2.53 (q, *J* = 7.4 Hz, 2H), 2.31 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.8, 148.8, 144.9, 144.1, 142.0, 141.3, 140.7, 140.0, 139.7, 137.4, 134.6, 134.2, 133.9, 126.9-133.1, (q, $^{1}J_{C-F}$ = 275.6 Hz), 130.36, 129.6, (q, $^{2}J_{C-F}$ = 32.6 Hz), 129.4, 129.0, 128.7, 127.9, 127.6, 127.0, 126.8, 125.7 (q, $^{3}J_{C-F}$ = 3.5 Hz), 123.8, 123.4, 122.1, 119.4, 65.5, 23.0, 22.9, 21.1, 15.71, 15.65; IR (KBr) ν_{max} 3060, 3037, 3013, 2968, 2932, 2869, 1613, 1512, 1473, 1452, 1374, 1320, 1165, 1129, 1108, 1069,



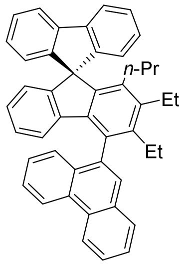
1021, 851, 758, 743, 728 cm^{-1}; HRMS (*m/z*) for $C_{43}H_{34}F_3$ (M + H) calcd: 607.26071, found: 607.26063; R_f (20/1 hexanes/EtOAc) = 0.46 (silica gel plate).



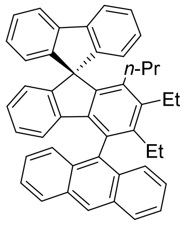
4-(4-Bromophenyl)-2,3-diethyl-1-(*p*-tolyl)-9,9'-spirobifluorene (11h). With **10h** (495 mg, 1.03 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 466 mg (74%) of the title compound as a slight yellow solid: mp (decomp) 111-116 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (m, 2H), 7.42 (m, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.19 (dt, *J* = 7.4, 1.1 Hz, 2H), 7.05 (dt, *J* = 7.5, 1.1 Hz, 2H), 6.93 (dt, *J* = 7.4, 1.3 Hz, 1H), 6.86 (dt, *J* = 7.4, 1.2 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 2H), 6.41 (d, *J* = 7.4 Hz, 1H), 6.38 (d, *J* = 7.7 Hz, 2H), 6.19 (d, *J* = 7.8 Hz, 1H), 5.94 (d, *J* = 7.9 Hz, 2H), 2.55 (q, *J* = 7.4 Hz, 2H), 2.30 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.7, 148.9, 144.0, 142.0, 141.5, 140.6, 139.9, 139.81, 139.79, 137.6, 134.7, 134.2, 133.9, 132.0, 131.7, 129.0, 126.9, 126.84, 126.80, 126.78, 126.76, 123.8, 123.4, 122.3, 121.4, 119.40, 65.47, 23.0, 22.9, 21.1, 15.74, 15.65; IR (KBr) ν_{max} 3066, 3013, 2959, 2926, 2866, 1512, 1491, 1449, 1425, 1371, 1156, 1111, 1069, 1003, 839, 824, 758, 752, 737, 522 cm^{-1}; HRMS (*m/z*) for $C_{42}H_{34}Br$ (M + H) calcd: 617.18384, found: 617.18402; R_f (20/1 hexanes/EtOAc) = 0.53 (silica gel plate).



2,3-Diethyl-4-(naphthalen-2-yl)-1-propyl-9,9'-spirobifluorene (18a). With **17a** (84 mg, 0.21 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 64 mg (57%) of the title compound as a colorless solid: mp (decomp) 154-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 8.02 (m, 1H), 7.98 (s, 1H), 7.93 (m, 1H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.58-7.63 (m, 3H), 7.39 (dt, *J* = 7.5, 0.8 Hz, 2H), 7.16 (m, 2H), 6.90 (t, *J* = 7.6 Hz, 2H), 6.79 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.70 (dt, *J* = 7.8, 1.2 Hz, 1H), 6.39 (d, *J* = 7.5 Hz, 1H), 5.98 (d, *J* = 7.7 Hz, 1H), 2.64 (q, *J* = 7.4 Hz, 2H), 2.60 (m, 1H), 2.52 (m, 1H), 1.81 (m, 2H), 1.15 (t, *J* = 7.4 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.69 (m, 2H), 0.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.6, 143.2, 141.72, 141.69, 141.65, 140.8, 140.6, 138.5, 138.4, 137.8, 134.8, 133.7, 132.6, 128.6, 128.4, 128.3, 128.2, 127.9, 127.7, 127.4, 126.7, 126.4, 126.1, 125.9, 124.3, 124.2, 122.8, 122.5, 120.0, 66.0, 31.1, 23.7, 22.9, 21.7, 16.1, 15.9, 14.8; IR (KBr) ν_{max} 3055, 3019, 2974, 2959, 2950, 2929, 2869, 1604, 1506, 1470, 1446, 1392, 1374, 1281, 905, 860, 833, 806, 755, 746 cm^{-1}; HRMS (*m/z*) for $C_{42}H_{37}$ (M + H) calcd: 541.28898, found: 541.28907; R_f (20/1 hexanes/EtOAc) = 0.46 (silica gel plate).



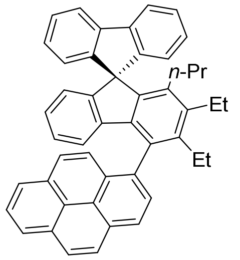
2,3-Diethyl-4-(phenanthren-9-yl)-1-propyl-9,9'-spirobifluorene (18b). With **17b** (65 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 81 mg (91%) of the title compound as a colorless solid: mp (decomp) >270°C °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (dd, *J* = 8.3, 2.6 Hz, 2H), 7.96 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.91 (s, 1H), 7.88 (dd, *J* = 7.6, 0.7 Hz, 2H), 7.78 (dt, *J* = 7.0, 1.4 Hz, 1H), 7.65-7.72 (m, 3H), 7.51 (m, 1H), 7.39 (ddt, *J* = 7.5, 2.8, 1.1 Hz, 2H), 7.18 (m, 2H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.70 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.53 (dt, *J* = 7.9, 1.2 Hz, 1H), 6.35 (d, *J* = 7.5 Hz, 1H), 5.97 (d, *J* = 7.8 Hz, 1H), 2.66 (q, *J* = 7.4 Hz, 2H), 2.60 (m, 1H), 2.32 (m, 1H), 1.85 (m, 2H), 1.16 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.73 (m, 2H), 0.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.7, 149.5, 143.4, 141.7, 141.6, 141.3, 141.1, 139.1, 138.0, 137.0, 132.4, 132.1, 131.9, 130.6, 130.3, 128.9, 127.9, 127.8, 127.7, 127.5, 127.4, 127.0, 126.78, 126.76, 126.7, 126.6, 126.4, 124.4, 124.0, 122.9, 122.8, 122.7, 122.5, 120.0, 66.1, 31.2, 23.7, 23.2, 21.7, 16.23, 16.18, 14.8; IR (KBr) ν_{max} 3071, 3015, 2965, 2931, 2869, 1599, 1472, 1447, 1426, 1373, 1281, 1154, 1059, 891, 866, 757, 745, 725 cm^{-1}; HRMS (*m/z*) for $C_{46}H_{38}$ (M + H) calcd: 591.30463, found: 591.30468; R_f (20/1 hexanes/EtOAc) = 0.38 (silica gel plate).



4-(Anthracen-9-yl)-2,3-diethyl-1-propyl-9,9'-spirobifluorene (18c). With **17c** (68 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 45 mg (51%) of the title compound as a light brown solid: mp (decomp) 251-256 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.64 (m, 2H), 7.39-7.44 (m, 4H), 7.28 (m, 1H), 7.19 (dt, *J* = 7.7, 1.2 Hz, 2H), 6.87 (d, *J* = 7.5 Hz, 2H), 6.64 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.40 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.31 (d, *J* = 7.5 Hz, 1H), 5.10 (d, *J* = 7.9 Hz, 1H), 2.66 (q, *J* = 7.4 Hz, 2H), 2.22 (q, *J* = 7.5 Hz, 2H), 1.88 (m, 2H), 1.16 (t, *J* = 7.4 Hz, 3H), 0.78 (m, 2H), 0.64 (t, *J* = 7.5 Hz, 3H), 0.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.7, 149.5, 143.4, 141.8, 141.6, 141.3, 141.1, 139.2, 138.1, 137.0, 132.4, 132.1, 132.0, 130.6, 130.3, 128.9, 127.9, 127.82, 127.76, 127.51, 127.46, 127.0, 126.81, 126.78, 126.7, 126.6, 126.4, 124.4, 124.0, 122.9, 122.8, 122.7, 122.5, 120.0, 68.1, 31.2, 23.8, 23.2, 21.7, 16.3, 16.2, 14.8; IR (KBr) ν_{max}

3064, 2963, 2871, 1525, 1468, 1446, 1372, 1345, 1262, 1241, 1155, 1055, 1027, 938, 755, 737 cm^{-1}; HRMS (*m/z*) for $C_{46}H_{39}$ (M + H) calcd: 591.30463, found: 591.30469; R_f (20/1 hexanes/EtOAc) = 0.43 (silica gel plate).

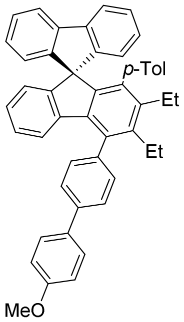
2,3-Diethyl-1-propyl-4-(pyren-2-yl)-9,9'-spirobifluorene (18d). With **17d** (72 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 54 mg (59%) of the title compound as a colorless solid: mp (decomp) 159-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.8 Hz, 1H), 8.21-8.27 (m, 3H), 8.17 (d, *J* = 6.9 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 8.04 (t, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 9.2 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.4 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.39 (t, *J* = 7.8 Hz, 1H), 6.34 (d, *J* = 7.5 Hz, 1H), 5.32 (d, *J* = 7.7 Hz, 1H), 2.68 (q, *J* = 7.4 Hz, 2H), 2.51 (m, 1H), 2.36 (m, 1H), 1.87 (m, 2H), 1.19 (t, *J* = 7.4 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H), 0.78 (m, 2H), 0.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 149.6, 149.5, 143.4, 141.8, 141.7, 141.6, 141.4, 141.1, 139.3, 138.1, 136.2, 133.0, 131.4, 131.3, 130.8, 129.9, 128.2, 127.83, 127.82, 127.76, 127.71, 127.65, 127.50, 127.46, 127.37, 126.7, 126.4, 126.0, 125.4, 125.2, 125.11, 125.07, 125.0, 124.4, 124.1, 122.7, 122.2, 120.03, 120.00, 66.1, 31.2, 23.7, 23.2, 21.8, 16.3, 15.7, 14.8; IR (KBr) ν_{max} 3039, 2963, 2929, 2870, 1601, 1584, 1470, 1446, 1424, 1374, 1282, 1242, 1177, 1154, 1056, 848, 820, 756, 740, 726 cm^{-1}; HRMS (*m/z*) for $C_{48}H_{39}$ (M + H) calcd: 615.30463, found: 615.30465; R_f (20/1 hexanes/EtOAc) = 0.37 (silica gel plate).



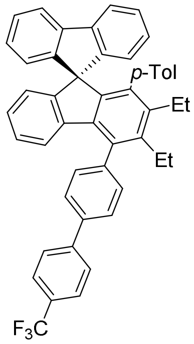
6.2.4. Synthesis of 9,9'-spirobifluorenes 13, 14, and carborane-14a

F: General procedure for Suzuki reaction (preparation of 13). Starting compound **11h** (0.1 mmol), boronic acid compound (0.12 mmol), Pd(OAc)$_2$ (1.3 mg, 5 mol%) and K$_2$CO$_3$ (17 mg, 0.12 mmol) were dissolved in a microwave vial ethanol (5 mL) and the reaction was stirred 3 h at 80 °C. The reaction mixture was cooled down, quenched with water and extracted with diethyl ether. The organic fraction was dried over Mg$_2$SO$_4$, filtered off and concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (hexanes/EtOAc) provided products.

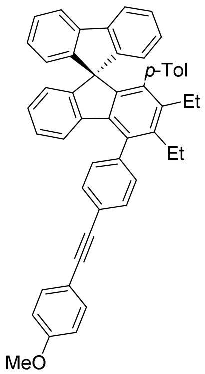
2,3-Diethyl-4-(4'-methoxy-[1,1'-biphenyl]-4-yl)-1-(*p*-tolyl)-9,9'-spirobifluorene (13a).



With **11h** (61 mg, 0.1 mmol) and 4-methoxyphenylboronic acid following the general procedure F. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 40 mg (62%) of the title compound as a colorless solid: mp (decomp) 138-143 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.20 (dt, *J* = 7.3, 0.7 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.06 (dt, *J* = 7.4, 0.8 Hz, 2H), 6.88 (dt, *J* = 7.3, 1.3 Hz, 1H), 6.82-6.85 (m, 3H), 6.39-6-43 (m, 3H), 6.25 (dd, *J* = 6.9, 1.1 Hz, 1H), 5.97 (d, *J* = 7.9 Hz, 2H), 3.92 (s, 3H), 2.63 (q, *J* = 7.4 Hz, 2H), 2.33 (q, *J* = 7.4 Hz, 2H), 2.19 (s, 3H), 1.10 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.3, 149.7, 149.1, 143.8, 142.0, 141.9, 140.5, 140.2, 139.5, 139.4, 139.3, 137.9, 135.9, 134.2, 134.1, 133.4, 130.2, 129.1, 128.1, 127.0, 126.9, 126.81, 126.76, 126.6, 123.9, 123.3, 122.6, 119.4, 114.4, 65.6, 55.5, 23.1, 23.0, 21.1, 15.9, 15.7; IR (KBr) ν_{max} 3069, 3037, 3013, 2953, 2836, 1604, 1500, 1470, 1437, 1278, 1251, 1086, 1039, 1009, 827, 809, 743 cm^{-1}; HRMS (*m/z*) for C$_{49}$H$_{41}$O (M + H) calcd: 645.31519, found: 645.31521; R_f(20/1 hexanes/EtOAc) = 0.30 (silica gel plate).

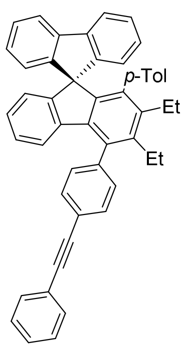


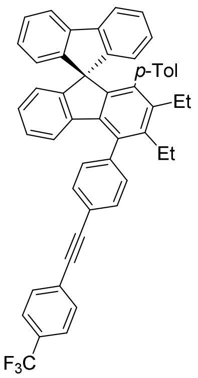
2,3-Diethyl-1-(*p*-tolyl)-4-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)-9,9'-spirobifluorene (13b). With **11h** (61 mg, 0.1 mmol) following the general procedure F. Column chromatography of the residue on silica gel (20/1 hexanes/ CH_2Cl_2) provided 39 mg (58%) of the title compound as a colorless solid: mp (decomp) 157-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.1 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 7.19 (dt, J = 7.4, 0.9 Hz, 2H), 7.06 (dt, J = 7.5, 1.0 Hz, 2H), 6.87 (dt, J = 7.3, 1.6 Hz, 1H), 6.84 (dt, J = 7.4, 1.4 Hz, 1H), 6.80 (d, J = 7.6 Hz, 2H), 6.43 (m, 1H), 6.38 (d, J = 7.8 Hz, 2H), 6.22 (m, 1H), 5.96 (d, J = 7.9 Hz, 2H), 2.61 (q, J = 7.4 Hz, 2H), 2.33 (q, J = 7.4 Hz, 2H), 2.18 (s, 3H), 1.09 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.0, 144.3, 143.9, 142.0, 141.7, 141.0, 140.6, 140.0, 139.7, 138.4, 137.7, 135.4, 134.2, 134.0, 130.6, 129.8, 129.1, 127.5, 127.4, 126.8 (q, $^2J_{C\text{-}F}$ = 16.8 Hz), 125.8, (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 123.2-126.5 , (q, $^1J_{C\text{-}F}$ = 160.1 Hz) 123.8, 123.3, 122.4, 119.4, 65.5, 23.1, 23.0, 21.1, 15.9, 15.7; IR (KBr) ν_{max} 3063, 3037, 3019, 2965, 2929, 2872, 1622, 1515, 1470, 1446, 1371, 1326, 1165, 1129, 1069, 1006, 836, 824, 758, 746, 737 cm^{-1}; HRMS (*m/z*) for $C_{49}H_{38}F_3$ (M + H) calcd: 683.29201, found: 683.29207; R_f (20/1 hexanes/EtOAc) = 0.52 (silica gel plate).



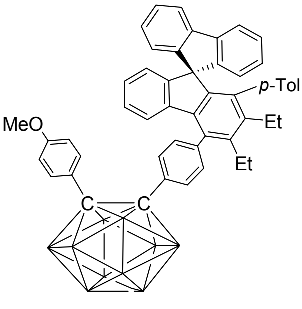
2,3-Diethyl-4-(4-((4-methoxyphenyl)ethynyl)phenyl)-1-(*p*-tolyl)-9,9'-spirobifluorene (14a). Starting compound **11h** (61 mg, 0.1 mmol), $PdCl_2(PPh_3)_2$ catalyst (8.5 mg, 5 mol%) and CuI (0.01 mmol, 10 mol%) were dissolved in a microwave vial in diisopropylamine (5 mL), afterwards 4-ethynylanisole (29 μL, 0.2 mmol) was added and the reaction was stirred at 180 °C in the microwave reactor for 1 h. The reaction mixture was cooled down, filtered off with celite/silica and washed with diethyl ether. The organic fraction was concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 36 mg (54%) of the title compound as a colorless solid: mp (decomp) 131-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.19 (dt, *J* = 7.4, 0.6 Hz, 2H), 7.05 (dt, *J* = 7.5, 0.6 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.91 (dt, *J* = 7.5, 0.9 Hz, 1H), 6.85 (dt, *J* = 7.4, 0.9 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.41 (d, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 7.8 Hz, 2H), 6.24 (d, *J* = 7.7 Hz, 1H), 5.95 (d, *J* = 7.9 Hz, 2H), 3.87 (s, 3H), 2.58 (q, *J* = 7.4 Hz, 2H), 2.31 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 149.7, 149.0, 143.9, 142.0, 141.6, 140.8, 140.5, 139.9, 139.7, 137.6, 135.5, 134.2, 134.1, 133.1, 131.9, 130.0, 129.1, 127.0, 126.9, 126.81, 126.78, 126.7, 123.8, 123.3, 122.6, 122.5, 119.4, 115.4, 114.1, 89.8, 88.2, 65.5, 55.4, 23.1, 22.9, 21.1, 15.8, 15.7; IR (KBr) ν_{max} 3040, 2971, 2872, 2836, 2211, 1604, 1565, 1518, 1446, 1371, 1287, 1251, 1171, 1105, 1030, 839, 755, 743 cm^{-1}; HRMS (*m/z*) for $C_{51}H_{41}O$ (M + H) calcd: 669.31519, found: 669.31522; R_f (20/1 hexanes/EtOAc) = 0.25 (silica gel plate).

2,3-Diethyl-4-(4-(phenylethynyl)phenyl)-1-(*p*-tolyl)-9,9'-spirobifluorene (14b). Starting compound **11h** (122 mg, 0.25 mmol), PEPPSI-IPr catalyst (8.5 mg, 5 mol%) and CuI (0.01 mmol, 10 mol%) were dissolved in a microwave vial in triethylamine (2 mL) and THF (3 mL), afterwards phenylacetylene (55 μL, 0.5 mmol) was added and the reaction was stirred 3 h at 80 °C. The reaction mixture was cooled down, filtered off with celite/silica and washed with diethyl ether. The organic fraction was concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 116 mg (72%) of the title compound as a colorless solid: mp (decomp) 167-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 2H), 7.62 (m, 2H), 7.53 (m, 2H), 7.35-7.43 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.18 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.04 (dt, *J* = 7.4, 1.0 Hz, 2H), 6.91 (dt, *J* = 7.3, 1.1 Hz, 1H), 6.86 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.40 (d, *J* = 7.5 Hz, 1H), 6.37 (d, *J* = 7.6 Hz, 2H), 6.22 (d, *J* = 7.9 Hz, 1H), 5.94 (d, *J* = 7.9 Hz, 2H), 2.56 (q, *J* = 7.4 Hz, 2H), 2.30 (q, *J* = 7.4 Hz, 2H), 2.17 (s, 3H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 149.0, 143.9, 142.0, 141.6, 141.2, 140.5, 139.9, 139.7, 137.6, 135.4, 134.2, 134.0, 132.5, 132.1, 131.7, 130.0, 129.2, 129.0, 128.43, 128.36, 126.94, 126.86, 126.80, 126.77, 126.7, 123.8, 123.31, 123.27, 122.5, 122.2, 119.4, 89.8, 89.5, 29.7, 23.0, 22.9, 21.1, 15.8, 15.7; IR (KBr) ν_{max} 3060, 2969, 2931, 2870, 2251, 2230, 1596, 1515, 1487, 1446, 1373, 1281, 1238, 1179, 1158, 1068, 1019, 913, 848, 823, 755, 742, 689 cm^{-1}; HRMS (*m/z*) for $C_{50}H_{38}Na$ (M + Na) calcd: 661.28657, found: 661.28601; R_f (20/1 hexanes/EtOAc) = 0.46 (silica gel plate).





2,3-Diethyl-1-(*p*-tolyl)-4-(4-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)-9,9'-spirobifluorene (14c). Starting compound **11h** (61 mg, 0.1 mmol), $PdCl_2(PPh_3)_2$ (3.5 mg, 5 mol%) and CuI (0.01 mmol, 10 mol%) were dissolved in a microwave vial in DMF (3 mL) and NEt_3 (2 mL), afterwards 1-ethynyl-trifluortoluene (65 μL, 0.15 mmol) was added and the reaction was stirred over night at 80 °C. The reaction mixture was cooled down, filtered off with celite/silica and washed with diethyl ether. The organic fraction was concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (10/1 hexanes/ CH_2Cl_2) provided 40 mg (57%) of the title compound as a light brown solid: mp (decomp) 151-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 7.4 Hz, 2H), 7.19 (dt, J = 7.4, 1.1 Hz, 2H), 7.05 (dt, J = 7.5, 1.1 Hz, 2H), 6.91 (dt, J = 7.4, 1.3 Hz, 1H), 6.86 (dt, J = 7.4, 1.3 Hz, 1H), 6.79 (d, J = 7.4 Hz, 2H), 6.41 (m, 1H), 6.38 (d, J = 7.7 Hz, 2H), 6.21 (m, 1H), 5.95 (d, J = 7.9 Hz, 2H), 2.56 (q, J = 7.4 Hz, 2H), 2.31 (q, J = 7.4 Hz, 2H), 2.18 (s, 3H), 1.06 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 148.9, 144.0, 142.0, 141.8, 141.5, 140.6, 139.81, 139.78, 137.5, 135.3, 134.2, 134.0, 132.2, 131.9, 130.1, 129.0, 127.0 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 126.8, 125.3 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 123.8, 123.4, 122.4, 121.5, 121.3-126.8, (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 119.4, 91.9, 88.4, 65.5, 23.0, 22.9, 21.1, 15.74, 15.66; IR (KBr) ν_{max} 3069, 3037, 2968, 2932, 2875, 2220, 1610, 1518, 1476, 1449, 1374, 1323, 1171, 1132, 1108, 1069, 1015, 845, 824, 758, 743 cm^{-1}; HRMS (*m/z*) for $C_{51}H_{38}F_3$ (M + H) calcd: 707.29201, found: 707.29211; R_f (20/1 hexanes/EtOAc) = 0.51 (silica gel plate).



1-[2,3-Diethyl-4-phenyl)-1-(*p*-tolyl)-9,9'-spirobifluorenyl]-2-(4-methoxyphenyl)-1,2-dicarba-*closo*-dicarborane (carborane-14a). Starting compound **14a** (67 mg, 0.1 mmol and 6,9-$(Me_2S)_2B_{10}H_{12}$ (70 mg, 0.15 mmol) were dissolved in a microwave vial under argon atmosphere in toluene (5 mL) and the reaction was stirred at 120 °C for 16 h. The reaction mixture was cooled down, quenched with MeOH and concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (2/1 hexanes/EtOAc) provided 47 mg (60%) of the title compound as a colorless solid: mp (decomp) 149-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.5 Hz, 2H), 7.53 (m, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 7.4 Hz, 2H), 7.18 (dt, J = 7.4, 1.0 Hz, 2H), 7.02 (dt, J = 7.5, 1.1 Hz, 2H), 6.82 (dt, J = 7.5, 1.0 Hz, 1H), 6.76 (d, J = 9.0 Hz, 2H), 6.72 (d, J = 7.5 Hz, 2H), 6.66 (dt, J = 7.9, 1.2 Hz, 1H), 6.36-6-39 (m, 3H), 5.91 (d, J = 8.0 Hz, 2H), 5.69 (d, J = 7.8 Hz, 1H), 3.74 (s, 3H), 2.35 (q, J = 7.4 Hz, 2H), 2.26 (q, J = 7.4 Hz, 2H), 2.17 (s, 3H), 0.90 (t, J = 7.4 Hz, 3H), 0.83 (t, J = 7.4 Hz, 3H); additional: ^{1}H-^{11}B NMR (400 MHz, $CDCl_3$) δ 3.41 (bs, 2H), 2.70 (bs, 2H), 2.61 (bs, 4H), 2.41 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 149.8, 148.8, 143.9, 143.1, 142.0, 141.2, 140.6, 139.9, 139.7, 137.1, 134.3, 134.2, 133.8, 132.3, 131.2, 130.0, 129.9, 128.9, 126.9, 126.8, 126.7, 126.6, 123.7, 123.4, 123.2, 122.0, 119.4, 113.6, 86.1, 85.6, 65.4, 55.2, 23.0, 22.7, 21.1, 15.60. 15.58; IR (KBr) ν_{max} 3219, 3063, 2966, 2932, 2870, 2592, 1607, 1514, 1462, 1447, 1374, 1301, 1260, 1184, 1075, 1032, 836, 824, 756, 744, 730 cm^{-1}; HRMS (*m/z*) for $C_{51}H_{50}OB_{10}Na$ (M + Na) calcd: 811.46844, found: 811.46871, for $C_{51}H_{50}O^{10}BB_9Na$ (M + Na) calcd: 810.47207, found: 810.47278, for $C_{51}H_{50}O^{10}B_2B_8Na$ (M + Na) calcd: 809.47571, found: 809.47651, for $C_{51}H_{50}O^{10}B_3B_7Na$ (M + Na) calcd: 808.47934, found: 808.48029; R_f (20/1 hexanes/EtOAc) = 0.27 (silica gel plate).

6.2.5. X-ray data of 9,9'-spirobifluorenes

Crystallographic data for **6a**, **6c, 11a**, **11c, 11e**, **13a**, **14b**, **carborane-14a** and **18b** were collected on Nonius KappaCCD diffractometer equipped with Bruker APEX-II CCD detector by monochromatized MoKα radiation (λ = 0.71073 Å) at a temperature either 120 K or 150(2) K. The structures were solved by direct methods (SHELXS)[69] and refined by full matrix least squares based on F^2 (SHELXL97). The absorption corrections were carried on using multi-scan method. The hydrogen atoms were found on difference Fourier map and were recalculated into idealized positions. All hydrogen atoms were refined as fixed (riding model) with assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or 1.5 U_{eq} for methyl moiety. The crystallographic data are summarized in Table Exp1-4.

Table Exp1. X-ray crystallographic data 9,9’-spirobifluorenes **6a** and **6c**

	6a	**6c**
Formula	$C_{41}H_{32}$	$C_{38}H_{34}$
M.w.	524.67	490.65
Crystal system	orthorhombic	triclinic
Space group [No.]	*Pca2*$_1$ (No 29)	*P*-1 (No 2)
a [Å]	29.4235 (18)	11.0066 (2)
b [Å]	11.4496 (7)	11.0845 (2)
c [Å]	17.2284 (14)	11.5394 (2)
α [°]		81.815 (1)
β [°]		87.544 (1)
γ [°]		80.909
Z	8	2
V $[Å^3]$	5804.0 (7)	1375.69 (4)
D_x [g cm^{-3}]	1.201	1.184
Crystal size [mm]	0.74×0.38×0.29	0.56×0.54×0.34
Crystal color, shape	a colorless prism	a colorless prism
μ [mm^{-1}]	0.07	0.07
$T_{\min}, T_{\max}$	0.952, 0.980	0.964, 0.978
Measured reflections	37907	20792
Independent diffractions (R_{int} ^{a})	9397 (0.049)	6299 (0.018)
Observed diffract. [$I>2\sigma(I)$]	8103	5492
No. of parameters	743	346
R^b	0.072	0.041
$wR(F^2)$ for all data	0.184	0.110
GOF^c	1.06	1.05
Residual electron density [e/Å^3]	0.62, -0.290	0.26, -0.24
CCDC no.	1403002	1403003

[a] $R_{\mathrm{int}} = \Sigma \left| F_o^2 - F_{o,\mathrm{mean}}^2 \right| / \Sigma F_o^2$

[b] $R(F) = \Sigma \left| |F_o| - |F_c| \right| / \Sigma |F_o|$, $wR(F^2) = [\Sigma (w(F_o^2 - F_c^2)^2) / (\Sigma w(F_o^2)^2)]^{½}$. [c] GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(N_{\mathrm{diffrs}} - N_{\mathrm{params}})]^{½}$

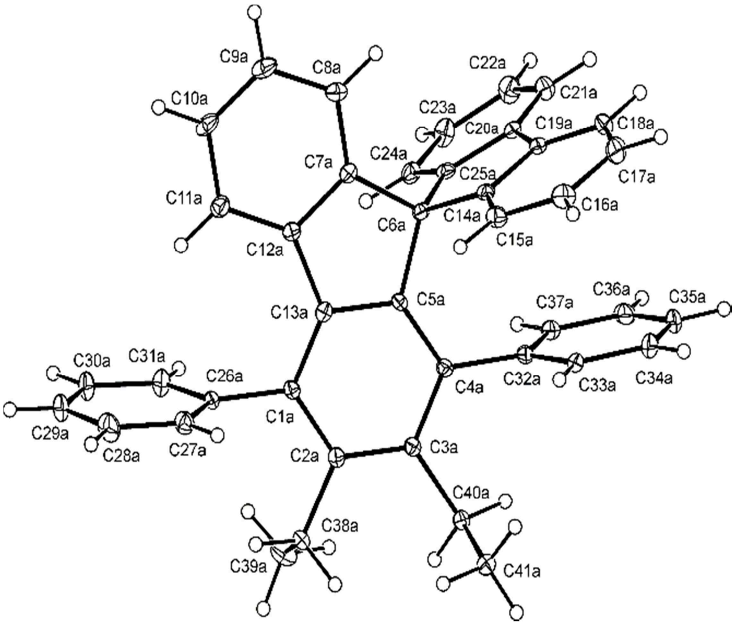


Figure Exp1. Platon plot of **6a** showing displacement ellipsoids at a 30% probability level

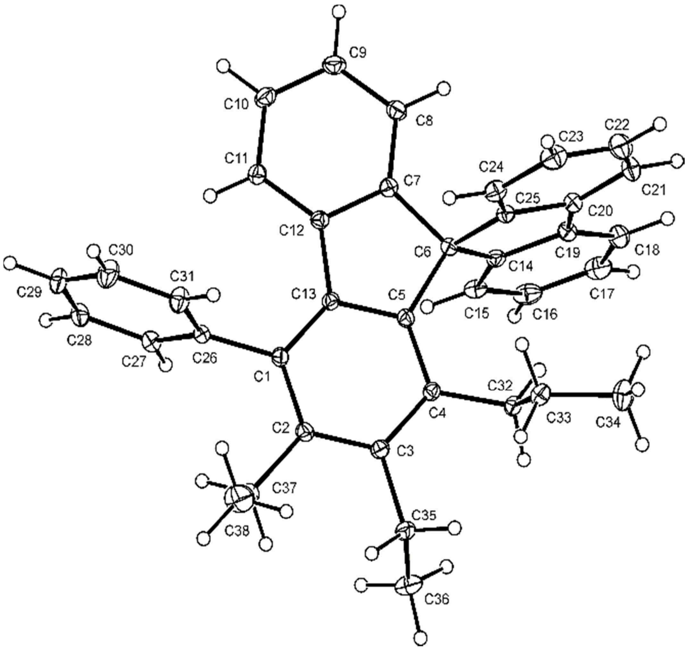


Figure Exp2. Platon plot of **6c** showing displacement ellipsoids at a 30% probability level

Table Exp2. X-ray crystallographic data for 9,9'-spirobifluorenes **11a**, **11c** and **11e**

	11a	**11c**	**11e**
Formula	$C_{43}H_{36}O$	$C_{48}H_{38}$	$C_{42}H_{33}Cl$
M.w.	568.72	614.78	573.13
Crystal system	monoclinic	triclinic	monoclinic
Space group [No.]	$P2_1$/n (No14)	$P1$ (No. 2)	$P2_1/n$ (No 14)
a [Å]	9.4308 (2)	8.3330 (2)	35.6573 (8)
b [Å]	17.6455 (3)	11.6908 (3)	9.6469 (2)
c [Å]	18.5101 (3)	18.3693 (4)	22.6588 (4)
a [°]		88.570 (1)	
β [°]	92.764 (1)	86.248 (1)	128.8580 (5)
γ [°]		72.826 (1)	
Z	4	2	8
V [$Å^3$]	3076.70 (10)	1706.04 (7)	6069.4 (2)
D_x [g cm^{-3}]	1.228	1.197	1.254
Crystal size [mm]	0.22×0.58×0.60	0.14×0.39×0.65	0.57×0.56×0.41
Crystal color, shape	a colorless prism	a colorless prism	a colorless prism
μ [mm^{-1}]	0.071	0.067	0.156
T_{min}, T_{max}	0.89, 0.98	0.93, 0.99	0.83, 0.94
Measured reflections	21163	18051	16117
Independent diffractions (R_{int} [a])	7059 (0.019)	7428 (0.024)	6626 (0.018)
Observed diffract. [I>2σ(I)]	5820	5525	5486
No. of parameters	401	436	391
R^b	0.041	0.0471	0.042
$wR(F^2)$ for all data	0.118	0.1366	0.111
GOF[c]	1.00	1.06	0.97
Residual electron density [e/Å^3]	0.28, -0.25	0.25, -0.22	0.61, -0.30
CCDC no.	1542107	1542108	1542109

[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$

[b] $R(F) = \Sigma \left| \left|F_o\right| - \left|F_c\right| \right| / \Sigma \left|F_o\right|$, $wR(F^2) = [\Sigma (w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$. [c] GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$

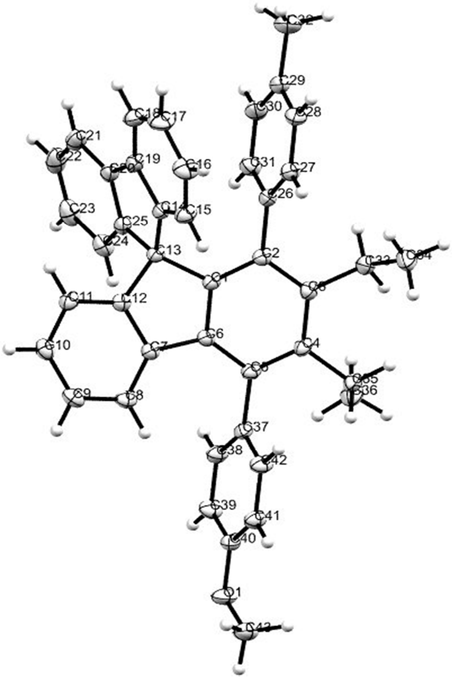


Figure Exp3. Platon plot of **11a** showing displacement ellipsoids at a 50% probability level

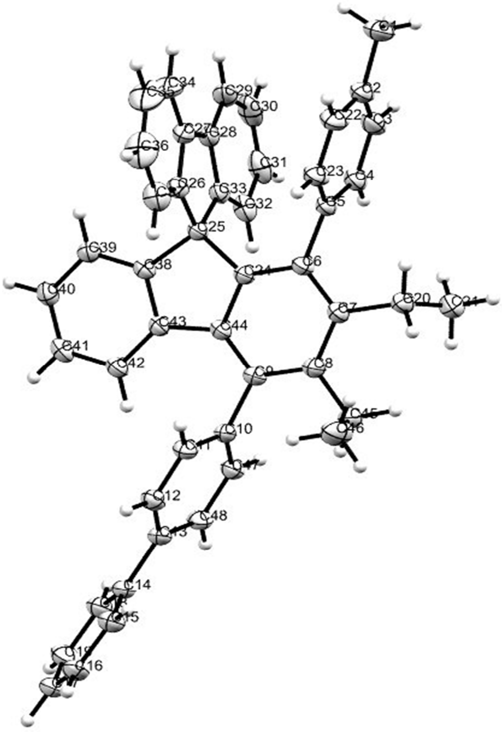


Figure Exp4. Platon plot of **11c** showing displacement ellipsoids at a 50% probability level

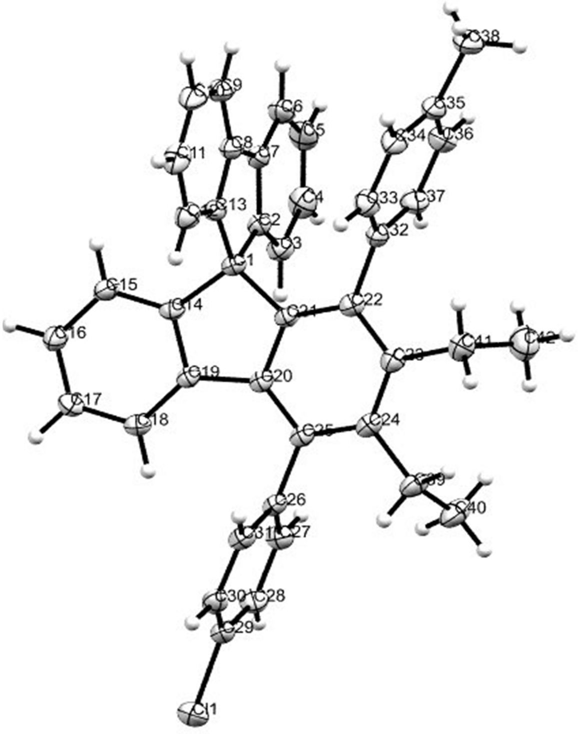


Figure Exp5. Platon plot of **11e** showing displacement ellipsoids at a 50% probability level

Table Exp3. X-ray crystallographic data for 9,9'-spirobifluorenes **13a** and **14b**

	13a	**14b**
Formula	$C_{49}H_{40}O$	$C_{50}H_{38}$, $CHCl_3$
M.w.	644.81	758.17
Crystal system	triclinic	triclinic
Space group [No.]	$P1$ (No 2)	$P1$ (No 2)
a [Å]	8.8276 (3)	9.9228(4)
b [Å]	11.6527 (3)	12.9083(6)
c [Å]	18.1740 (5)	16.2089(7)
a [°]	91.5340(10)	75.028(2)
β [°]	90.2770(10)	85.120(2)
γ[°]	107.9720(10)	71.846(2)
Z	2	2
V [$Å^3$]	1777.45(9)	1905.80(15)
D_x [g cm^{-3}]	1.205	1.321
Crystal size [mm]	0.24×0.16×0.15	0.15×0.17×0.27
Crystal color, shape	a colorless prism	a colorless prism
μ [mm^{-1}]	0.533	0.278
T_{min}, T_{max}	0.86, 0.96	0.93, 0.96
Measured reflections	34479	42155
Independent diffractions (R_{int} ^{a})	6986 (0.029)	8754 (0.067)
Observed diffract. [$I>2\sigma(I)$]	5694	7212
No. of parameters	455	490
R^b	0.043	0.042
$wR(F^2)$ for all data	0.110	0.124
GOF^c	1.04	1.05
Residual electron density [e/$Å^3$]	0.19, -0.21	0.43, -0.68
CCDC no.	1542110	1542111

[a] $R_{\mathrm{int}} = \Sigma \left| F_o^2 - F_{o,\mathrm{mean}}^2 \right| / \Sigma F_o^2$

[b] $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$, $wR(F^2) = [\Sigma\ (w(F_o^2 - F_c^2)^2)/(\ \Sigma w(F_o^2)^2)]^{½}$. [c] GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(N_{\mathrm{diffrs}} - N_{\mathrm{params}})]^{½}$

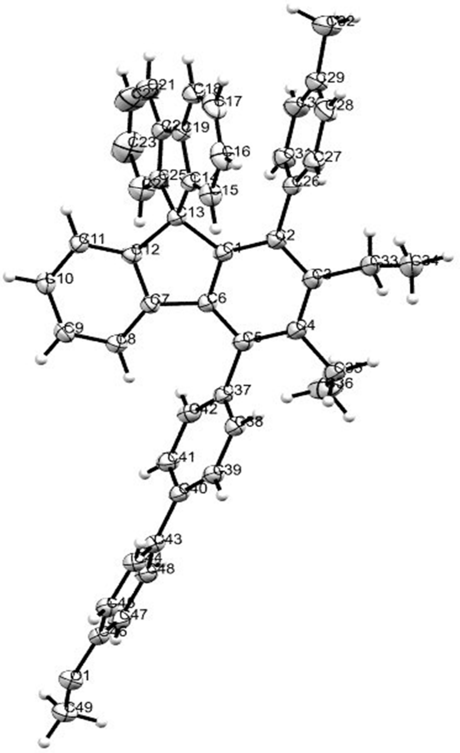


Figure Exp6. Platon plot of **13a** show displacement ellipsoids at a 50% probability level

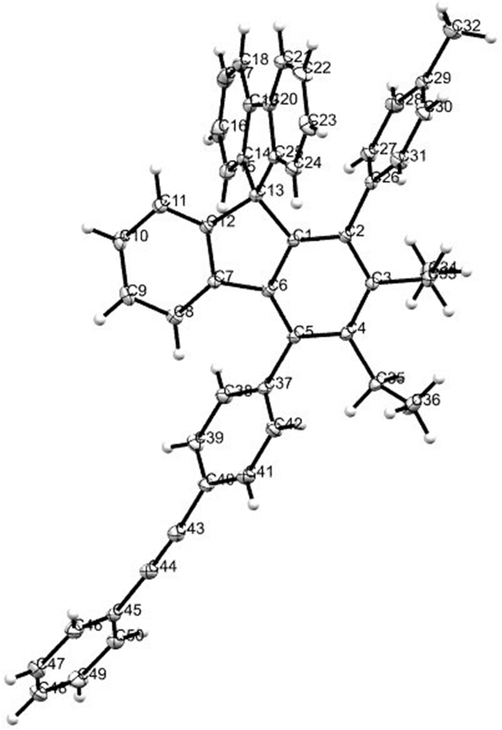


Figure Exp7. Platon plot of **14b** show displacement ellipsoids at a 50% probability level

Table Exp4. X-ray crystallographic data for 9,9'-spirobifluorenes **18b** and **carborane-14a**

	18b	**carborane-14a**
Formula	$C_{46}H_{38}$	$C_{51}H_{50}B_{10}O$
M.w.	590.76	787.01
Crystal system	monoclinic	monoclinic
Space group [No.]	*P1* (21/c1)	*P*21/c
a [Å]	16.8419(5)	16.9235(4)
b [Å]	8.6097(2)	9.1410(2)
c [Å]	23.3066(6)	28.7305(7)
a [°]		
β [°]	98.9400(10)	100.7280(10)
γ [°]		
Z	4	4
V $[Å^3]$	3338.49(15)	4366.86(18)
D_x [g cm^{-3}]	1.175	1.197
Crystal size [mm]	0.22×0.13×0.04	0.35×0.20×0.12
Crystal color, shape	a colorless bar	a colorless plate
μ [mm^{-1}]	0.498	0.489
T_{min}, T_{max}	0.82, 0.98	0.85, 0.94
Measured reflections	25788	48496
Independent diffractions (R_{int} ^{a})	6307 (0.051)	8591 (0.034)
Observed diffract. [$I>2\sigma(I)$]	5047	7272
No. of parameters	418	603
R^{b}	0.057	0.045
$wR(F^2)$ for all data	0.137	0.121
GOF^{c}	1.057	1.03
Residual electron density [e/Å^3]	0.43, -0.27	0.22, -0.24
CCDC no.	1542112	1542113

[a] $R_{\mathrm{int}} = \Sigma | F_o^2 - F_{o,\mathrm{mean}}^2 | / \Sigma F_o^2$

[b] $R(F) = \Sigma \, || F_o | - | F_c || / \Sigma | F_o |$, $wR(F^2) = [\Sigma \, (w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$. [c] GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(N_{\mathrm{diffrs}} - N_{\mathrm{params}})]^{½}$

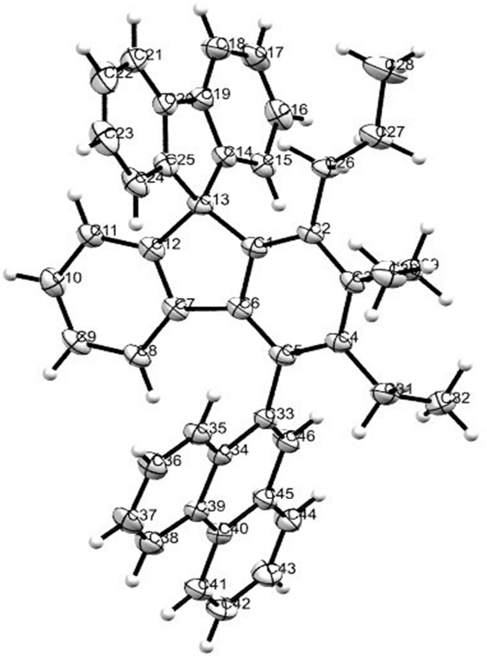


Figure Exp8. Platon plot of **18b** showing displacement ellipsoids at a 50% probability level

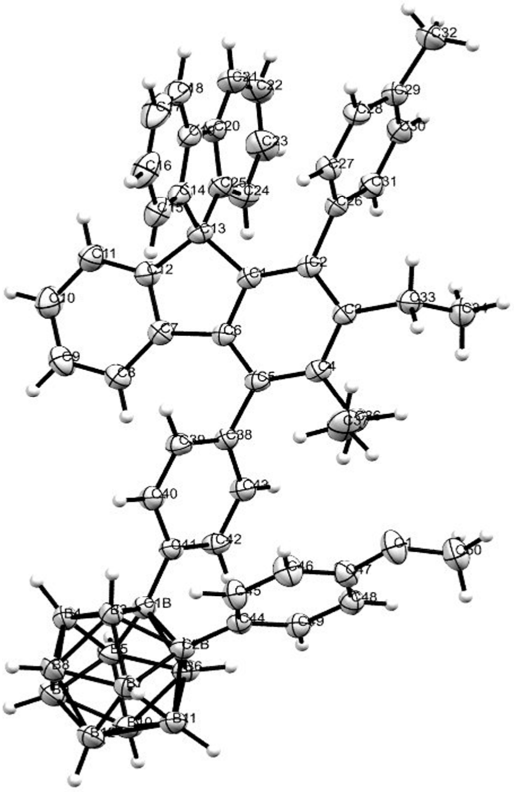


Figure Exp9. Platon plot of **carborane-14a** show displacement ellipsoids at a 50% probability level

6.2.6. Photophysical analysis of 9,9’-spirobifluorenes

Chemicals.

9,10-Diphenylanthracene (DPA) was purchased from Sigma-Aldrich.

The UV/Vis absorption spectra were recorded using Unicam 340 spectrometer. Corrected steady-state emission spectra were recorded on an Aminco Bowman (AB2) spectrometer.

Quantum yields of fluorescence of a sample (Φ_s) were calculated relative to diphenyleneanthracene DPA ($\Phi_{ref} = 0.97$ in cyclohexane) as a reference. Φ_s was determined according to the following equation.[70]

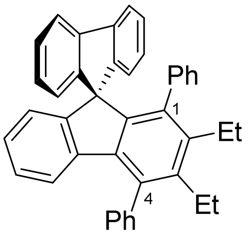
$$\Phi_s = \Phi_{ref} \times A_s / A_{ref} \qquad (1)$$

where A_s and A_{ref} represent integrated areas of the emission (in arbitrary units) of a sample and the reference, respectively.

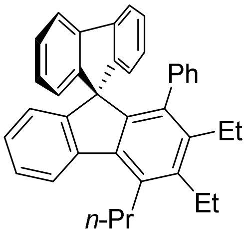
Micromolar solutions of the reference (DPA) and the samples were prepared in cyclohexane. The absorption of the reference and the samples were the same at the selected excitation wavelength ($A \leq 0.1$). Quantum yields were calculated from 5 independent measuring. The average value is reported.

The emission quantum yields (Φ_s) of the derivatives were determined in cyclohexane by standard procedures with DPA as reference (Figures Exp10-13 and tables Exp5-8).

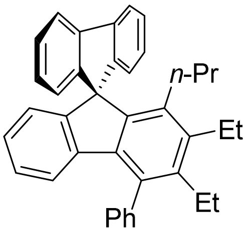
UV/Vis absorption and emission spectra of 6a-d.



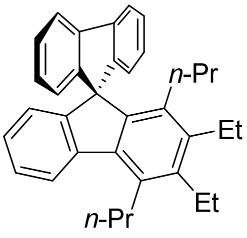
6a



6b



6c



6d

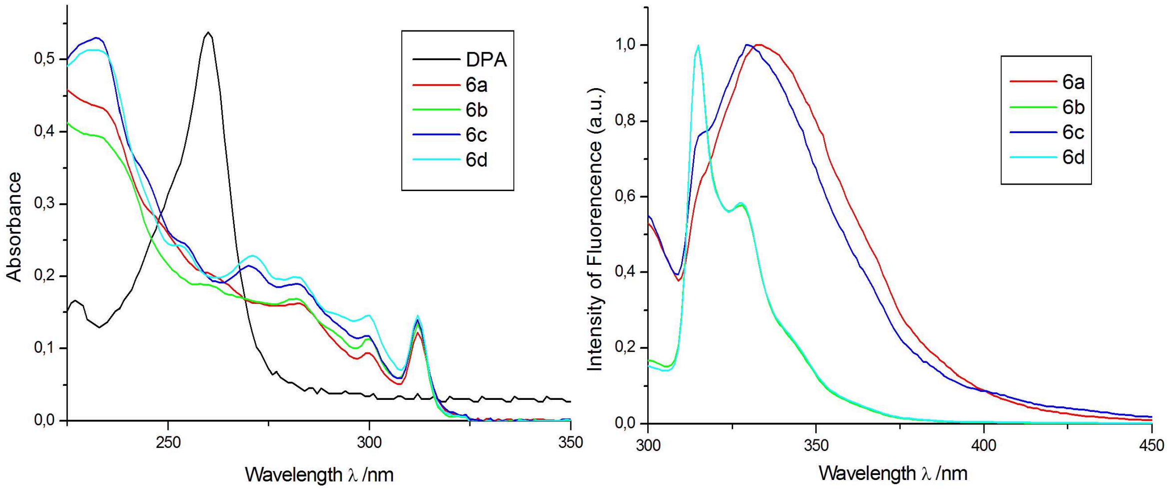


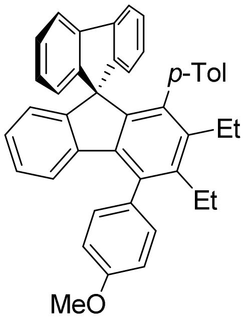
Figure Exp10. Absorption spectra of **6a-d** in cyclohexane (left). Normalized and corrected emission spectra of 10^{-6} M samples in cyclohexane. Emission after excitation at λ =240-243 nm (right).

Table Exp5. Photophysical properties of **6a-d** derivatives in cyclodexane

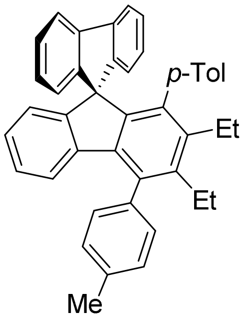
Sample	λ_{abs} **/nm (ε /10^4 mol^{-1} dm^3 cm^{-1})**	λ_{exc} **/nm**	λ_{em} **/nm**	Φ_s[a]
6a	217 (4.8)	241	333	0.62
	283 (1.6)			
	300 (0.9)			
	312 (1.2)			
6b	218 (5.0)	241	315, 328	0.72
	233 (5.1)			
	271 (2.3)			
	282 (2.0)			
	312 (1.5)			
6c	219 (4.4)	242	315, 328	0.87
	260 (1.9)			
	282 (1.7)			
	312 (1.3)			
6d	218 (5.1)	243	330	0.48
	232 (5.3)			
	270 (2.2)			
	282 (1.9)			
	312 (1.4)			

[a] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

UV/Vis absorption and emission spectra of 11a-g.



11a



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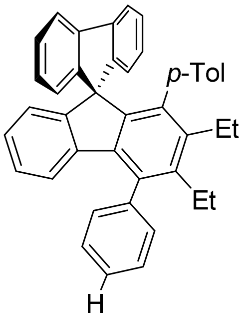
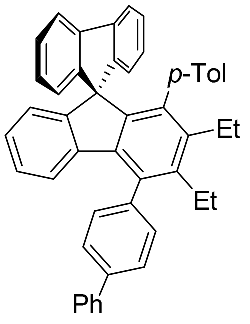
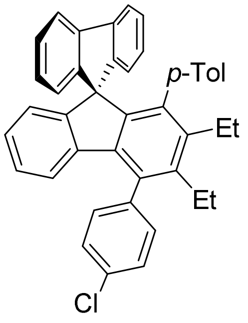


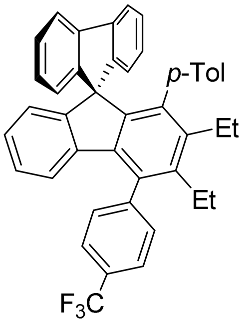
11c



11d



11e



11f

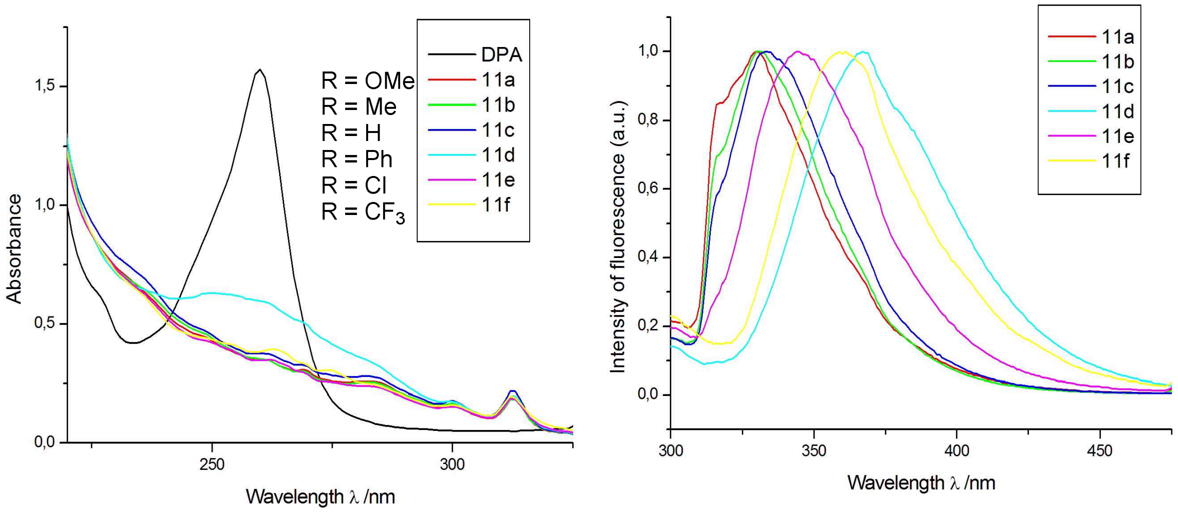


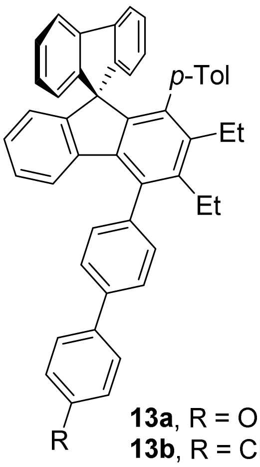
Figure Exp11. Absorption spectra of **11a-g** in cyclohexane (left). Normalized and corrected emission spectra of 10^{-6} M samples in cyclohexane. Emission after excitation at λ =240-243 nm (right).

Table Exp6. Photophysical properties of **11a-g** derivatives in cyclohexane

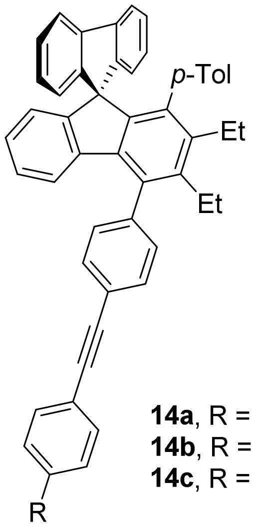
Sample	λ_{abs} /nm (ε /10^4 mol^{-1} dm^3 cm^{-1})	λ_{exc} /nm	λ_{em} /nm	Φ_s[a]
11a	262 (sh) 269 (sh) 300 (sh) 313 (1.6)	241	330	0.50
11b	262 (sh) 284 (sh) 300 (sh) 313 (1.6)	241	331	0.61
11c	250 (6.0) 255 (sh) 300 (sh) 313 (1.7)	243	367	0.87
11d	261 (sh) 284 (sh) 300 (sh) 313 (1.9)	242	333	0.66
11e	262 (sh) 284 (sh) 300 (sh) 313 (1.5)	241	344	0.61
11f	263 (sh) 274 (sh) 300 (sh) 313 (1.6)	240	361	0.64

[a] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

UV/Vis absorption and emission spectra of 13 and 14.



13a, R = OMe
13b, R = CF_3



14a, R = OMe
14b, R = H
14c, R = CF_3

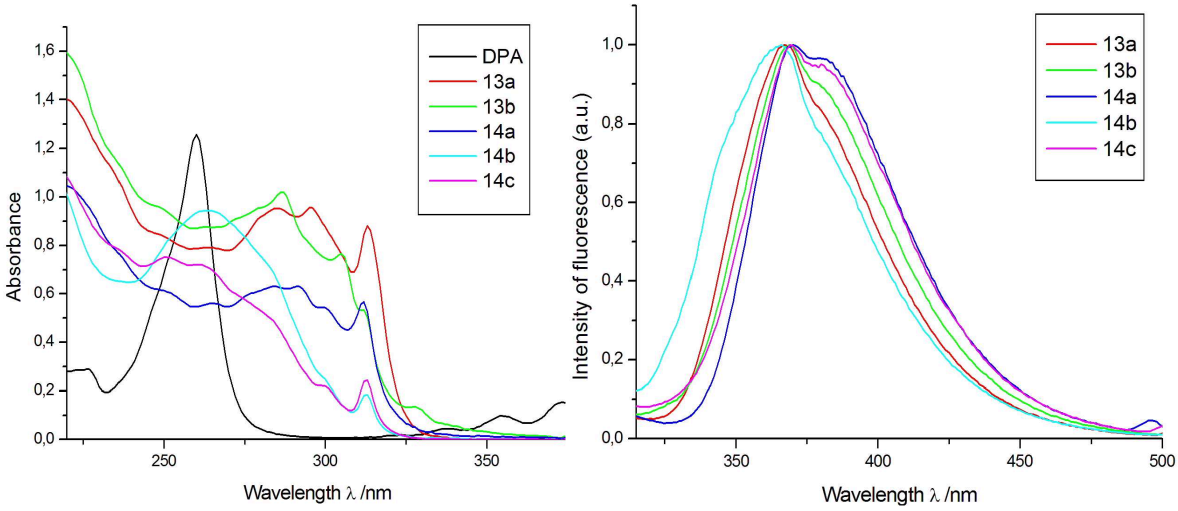


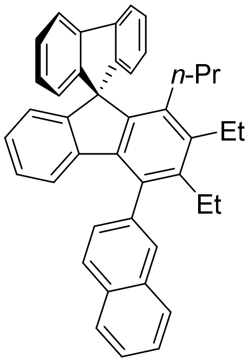
Figure Exp12. Absorption spectra of **13** and **14** in cyclohexane (left). Normalized and corrected emission spectra of 10^{-6} M samples in cyclohexane. Emission after excitation at λ = 248-255 nm (right).

Table Exp7. Photophysical properties of **13** and **14** derivatives in cyclohexane

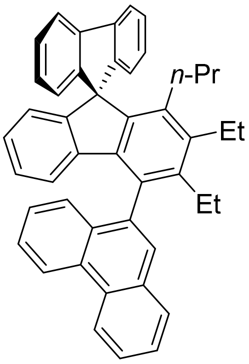
Sample	**λ_{abs} /nm (ε /10^5 mol^{-1} dm^3 cm^{-1})**	**λ_{exc} /nm**	**λ_{em} /nm**	**Φ_s[a]**
13a	216 (1.1)	254	366	0.65
	264 (0.9)			
	284 (sh)			
	313 (sh)			
13b	218 (1.1)	251	369	0.99
	250 (sh)			
	261 (sh)			
	300 (sh)			
14a	220 (1.4)	253	367	0.82
	285 (sh)			
	296 (sh)			
	313 (sh)			
14b	220 (1.6)	254	369	0.79
	305 (sh)			
	312 (sh)			
	328 (sh)			
14c	220 (1.0)	248	370	1.00
	266 (sh)			
	291 (sh)			
	300 (sh)			
	312 (sh)			

[a] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

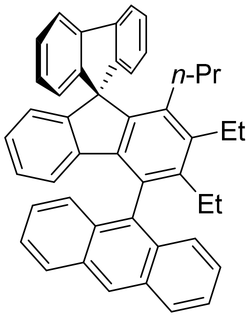
UV/Vis absorption and emission spectra of 18a-d.



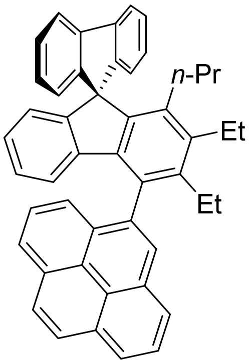
18a



18b



18c



18d

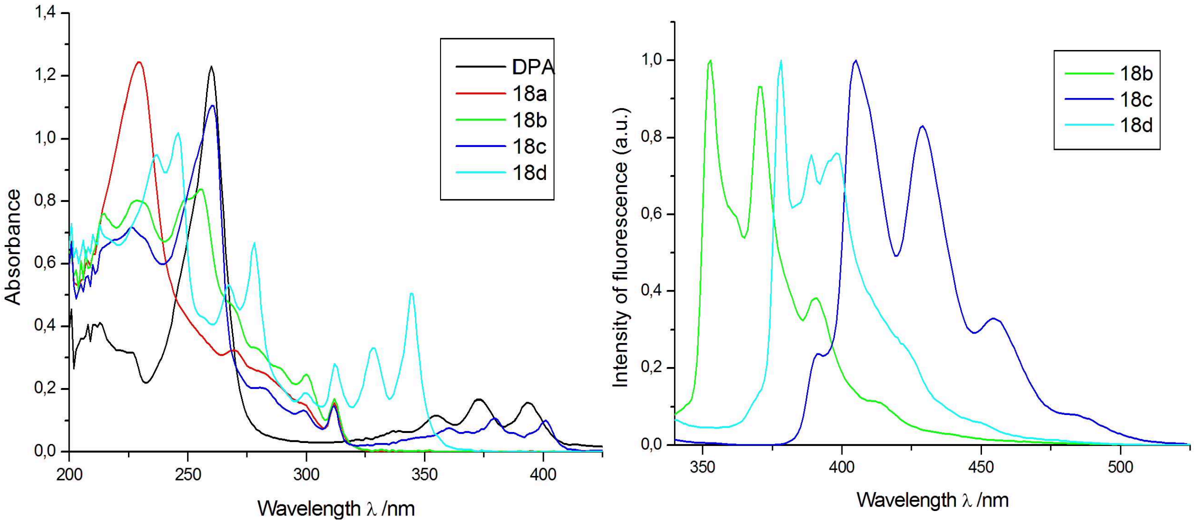


Figure Exp13. Absorption spectra of **18a-d** in cyclohexane (left). Normalized and corrected emission spectra of 10^{-6} M samples in cyclohexane. Emission after excitation at λ =269 nm (right).

Table Exp8. Photophysical properties of **18a-d** derivatives in cyclohexane

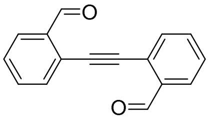
Sample	**λ_{abs} /nm (ε /10^5 mol^{-1} dm^3 cm^{-1})**	**λ_{exc} /nm**	**λ_{em} /nm**	**Φ_s[a]**
18a	229 (1.2)	-	-	0.00
	270 (sh)			
	282 (sh)			
	299 (sh)			
	312 (0.2)			
18b	215 (sh)	267	353	0.12
	228 (sh)		370	
	231 (sh)		391	
	300 (sh)		413	
	312 (0.1)			
18c	219 (sh)	270	392	0.80
	260 (1.1)		405	
	312 (0.1)		429	
	380 (0.1)		454	
	401 (0.1)		485	
18d	237 (sh)	267	378	0.11
	246 (1.0)		389	
	278 (0.7)		398	
	328 (0.3)			
	345 (0.5)			

[a] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

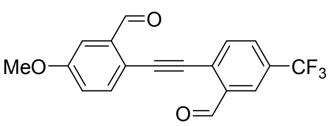
6.3. Synthesis of dispiroindeno[2,1-*c*]fluorenes

6.3.1. Synthesis of starting material

A: General procedure for Sonogashira reaction[60] (preparation of 19, 30 and 37). Starting halo-arylaldehyde (2.0 mmol), $PdCl_2(PPh_3)_2$ (69 mg, 0.1 mmol, 5 mol%) and CuI (38 mg, 0.2 mmol, 10 mol%) were dissolved in a Schlenk flask with reflux condensor in triethylamine (7 mL) and THF (7 mL), afterwards ethynyl-arylaldehyde (2.4 mmol) was added and the reaction was stirred 3 h under reflux. The reaction mixture was cooled down, filtered off with celite/silica and washed with diethyl ether. The organic fraction was concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (hexanes/EtOAc) provided products.

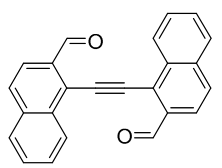


2,2'-(Ethyne-1,2-diyl)dibenzaldehyde (19). With 2-ethynylbenzaldehyde (650 mg, 5.0 mmol) and 2-bromobenzaldehyde (580 μL, 5.0 mmol) following the general procedure A. Column chromatography (5/1 hexanes/EtOAc) yielded 1.24 g (96%) of the title compound as a light brown solid: mp (decomp) 113-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (d, *J* = 0.7 Hz, 2H), 7.94 (ddd, *J* = 7.8, 1.3, 0.5 Hz, 2H), 7.67 (ddd, *J* = 7.7, 1.3, 0.5 Hz, 2H), 7.61 (dt, *J* = 7.4, 1.4 Hz, 2H), 7.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 136.0, 133.8, 133.5, 129.3, 128.0, 125.3, 91.6; IR (KBr) ν_{max} 3366, 3135, 3083, 3067, 3025, 2998, 2833, 2747, 1988, 1951, 1869, 1697, 1636, 1593, 1567, 1484, 1454, 1390, 1291, 1263, 1194, 1159, 1094, 954, 865, 814, 762, 642, 525, 434 cm^{-1}; HRMS (*m/z*) for $C_{16}H_{10}O_2$ (M^+) calcd: 234.0681, found: 234.0679; R_f (2/1 hexanes/EtOAc) = 0.38 (silica gel plate). The spectral data were in accordance with previously published results.[71]



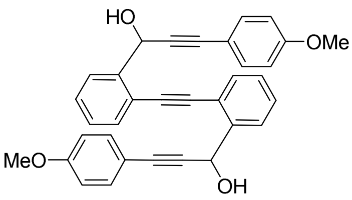
2-((2-Formyl-4-(trifluoromethyl)phenyl)ethynyl)-5-methoxybenzaldehyde (30). With 2-ethynyl-5-methoxybenzaldehyde[57] (235 mg, 1.4 mmol) and 2-bromo-5-(trifluoromethyl)benzaldehyde[58] (225 mg, 0.9 mmol) following the general procedure A. Column chromatography (5/1 hexanes/EtOAc) yielded 305 mg as a mixture of the title compound with inseparable side product in the ratio of 1:0.4 (217 mg, 73%) as a light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 10.56 (s, 1H), 8.22 (s, 1H), 7.84 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.81 (s, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 2.7 Hz, 1H), 7.18 (dd, *J* = 8.6, 2.7 Hz, 1H), 3.92 (s, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 190.5, 189.7, 160.9, 137.8, 135.8, 135.2, 134.7, 133.9, 125.1 (q, $^2J_{C\text{-}F}$ = 3.7 Hz), 121.7, 120.6-126.4 (q, $^1J_{C\text{-}F}$ = 382.4 Hz), 121.5, 111.4, 110.5, 105.0, 94.5, 90.4, 89.0, 78.9, 55.8; IR (KBr) ν_{max} 3363, 3083, 3064, 2953, 2865, 2761, 2206, 1697, 1600, 1557, 1505, 1489, 1433, 1392, 1330, 1286, 1252, 1228, 1190, 1122, 1094, 1068, 1026, 936, 879, 834, 730, 633 cm^{-1}; HRMS (*m/z*) for $C_{18}H_{11}O_3F_3$ (M^+) calcd: 332.0660, found: 332.0662; R_f (2/1 hexanes/EtOAc) = 0.44 (silica gel plate).

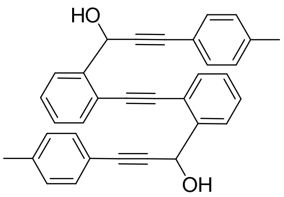


1,1'-(Ethyne-1,2-diyl)bis(2-naphthaldehyde) (37). With 1-ethynyl-2-naphthaldehyde[71] (350 mg, 1.5 mmol) and 1-bromo-2-naphthaldehyde (260 mg, 1.4 mmol) following the general procedure A. Filtration of the crude mixture with 5/1 hexanes/EtOAc yielded 490 mg (96%) of the title compound as a light yellow solid: mp (decomp) 126-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 10.97 (s, 1H), 8.66 (m, 2H), 8.06 (d, J = 8.6 Hz, 2H), 8.00 (d, J = 9.0 Hz, 2H), 7.96 (m, 2H), 7.72-7.75 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 135.8, 134.9, 133.3, 130.0, 129.6, 128.8, 128.3, 127.0, 125.8, 122.5, 95.4; IR (KBr) ν_{max} 3342, 3074, 2838, 2238, 1693, 1617, 1589, 1461, 1434, 1397, 1371, 1336, 1248, 1231, 867, 822, 780, 745 cm^{-1}; HRMS (*m/z*) for $C_{24}H_{14}O_2$ (M^+) calcd: 334.0994, found: 334.0995; R_f (2/1 hexanes/EtOAc) = 0.46 (silica gel plate). The spectral data were in accordance with previously published results.[73]

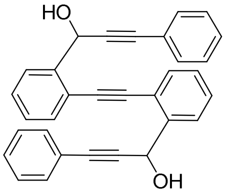
B: General procedure for alkynylation reaction[60] (preparation of 20, 24, 25 and 38). *n*-BuLi 1.6M (5.3 mmol, 3 eq) was added dropwise to a solution of alkyne compound (5.3 mmol, 3 eq) in anhydrous THF (15 mL), at -78 °C. After 30 min of stirring, dialdehyde compound (1.78 mmol) in THF (5 mL) was added and the reaction mixture was stirred for 5 min at -78 °C, afterwards it was allowed to warm up to ambient temperature and the reaction was stirred 3 h. Then NH_4Cl aq was used to quench the reaction mixture, it was extracted with diethyl ether (3 x 15 mL), the combined organic fractions were washed with a saturated solution of $NaHCO_3$ and brine, the organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes/EtOAc) provided products.



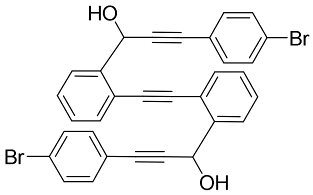
1,1'-(Ethyne-1,2-diylbis(2,1-phenylene))bis(3-(4-methoxyphenyl)prop-2-yn-1-ol) (20a). With **19** (234 mg, 1.0 mmol) and 4-ethynylanisole (390 μL, 3.0 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 470 mg (94%) of the title compound as a light brown solid: mp (decomp) 57-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.76 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.60 (dd, *J* = 7.3, 1.6 Hz, 2H), 7.35-7-41 (m, 6H), 7.32 (dt, *J* = 7.5, 1.6 Hz, 2H), 6.77 (m, 4H), 6.21 (s, 2H), 3.98 (s, 1H), 3.75 (s, 3H), 3.74 (s, 3H) 3.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.58, 159.56, 142.3, 142.2, 133.2, 132.7, 132.6, 128.9, 128.8, 128.19, 128.17, 127.2, 126.9, 121.7, 121.6, 114.5, 114.4, 113.8, 92.2, 86.9, 86.81, 86.80, 86.79, 63.7, 63.6, 55.1; IR (KBr) ν_{max} 3372, 3065, 2958, 2836, 2226, 1605, 1569, 1509, 1490, 1443, 1291, 1249, 1173, 1106, 1032, 963, 832, 761, 536 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{26}O_4Na$ (M + Na) calcd: 521.17233 found: 521.17222; R_f (1/1 hexanes/EtOAc) = 0.38 (silica gel plate).



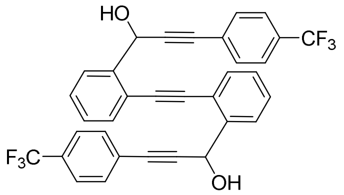
1,1'-(Ethyne-1,2-diylbis(2,1-phenylene))bis(3-(p-tolyl)prop-2-yn-1-ol) (20b). With **19** (106 mg, 0.45 mmol) and 1-ethynyl-4-*p*-toluene (170 μL, 1.35 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 187 mg (89%) of the title compound as a red solid: mp (decomp) 152-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.78 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.62 (m, 2H), 7.34-7-44 (m, 8H), 7.10 (m, 4H), 6.20 (s, 1H), 6.19 (s, 1H), 3.51 (s, 1H), 3.26 (s, 1H), 2.33 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 142.1, 138.71, 138.66, 132.8, 132.7, 131.7, 129.02, 129.00, 128.97, 128.39, 128.37, 127.3, 127.1, 121.83, 121.80, 119.3, 92.31, 92.26, 87.37, 87.31, 87.30, 87.2, 63.95, 63.88, 21.47, 21.46; IR (KBr) ν_{max} 3324, 3061, 3028, 2920, 2860, 2232, 2193, 1635, 1601, 1509, 1489, 1448, 1377, 1307, 1270, 1181, 1024, 964, 816, 760, 526 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{26}O_2Na$ (M + Na) calcd: 489.18250 found: 489.18242; R_f (2/1 hexanes/EtOAc) = 0.31 (silica gel plate).



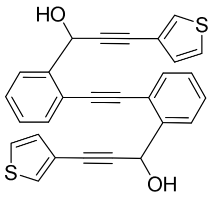
1,1'-(Ethyne-1,2-diylbis(2,1-phenylene))bis(3-phenylprop-2-yn-1-ol) (20c). With **19** (468 mg, 2.0 mmol) and phenylacetylene (660 μL, 6.0 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 730 mg (84%) of the title compound as a light brown solid: mp (decomp) 177-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.31-7-46 (m, 10H), 7.25 (m, 4H), 6.20 (s, 2H), 3.79 (s, 1H), 3.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 132.8, 131.8, 129.0, 128.5, 128.4, 128.2, 127.3, 127.0, 122.4, 121.8, 92.3, 88.1, 87.04, 86.97, 63.82, 63.75; IR (KBr) ν_{max} 3276, 3055, 2921, 2869, 2231, 1598, 1489, 1451, 1282, 1182, 1105, 1037, 970, 913, 752, 690, 525 cm^{-1}; HRMS (*m/z*) for $C_{32}H_{22}O_2Na$ (M + Na) calcd: 461.15120, found: 461.15127; R_f (2/1 hexanes/EtOAc) = 0.24 (silica gel plate).



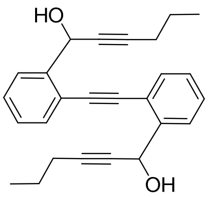
1,1'-(Ethyne-1,2-diylbis(2,1-phenylene))bis(3-(4-bromophenyl)prop-2-yn-1-ol) (20d). With **19** (234 mg, 1.0 mmol) and 1-bromo-4-ethynylbenzene (543 mg, 3.0 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 455 mg (77%) of the title compound as a light brown solid: mp (decomp) 181-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.87 (m, 2H), 7.62 (m, 2H), 7.35-7.48 (m, 10H), 7.28-7-33 (m, 4H), 6.21 (m, 1H), 6.18 (m, 1H), 3.44 (bs, 1H), 3.19 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 132.9, 132.8, 131.8, 129.1, 129.0, 128.6, 128.5, 128.47, 128.4, 128.3, 127.3, 127.1, 122.4, 121.8, 92.3, 88.0, 87.2, 63.94, 63.88; IR (KBr) ν_{max} 3286, 3064, 2883, 2229, 1587, 1570, 1487, 1451, 1394, 1283, 1181, 1071, 1027, 1013, 968, 822, 754, 690, 524 cm^{-1}; HRMS (*m/z*) for $C_{32}H_{20}O_2Br_2Na$ (M + Na) calcd: 616.97223 found: 616.97233; R_f (2/1 hexanes/EtOAc) = 0.29 (silica gel plate).



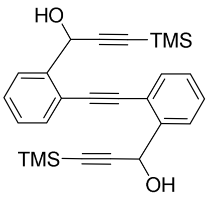
1,1'-(Ethyne-1,2-diylbis(2,1-phenylene))bis(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol) (20e). With **19** (234 mg, 1.0 mmol) and 1-ethynyl-4-(trifluoromethyl)benzene (490 μL, 3.0 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 483 mg (86%) of the title compound as a light brown solid: mp (decomp) 149-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.63 (dd, *J* = 7.3, 1.4 Hz, 2H), 7.52-7.57 (m, 8H), 7.42 (dt, *J* = 7.5, 1.6 Hz, 2H), 7.38 (dd, *J* = 7.5, 1.4 Hz, 2H), 6.21 (s, 2H), 3.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 133.0, 132.0, 129.2, 128.7, 127.3, 125.2 (q, $^{2}J_{C\text{-}F}$ = 3.8 Hz), 121.8, 120.6-126.4 (q, $^{1}J_{C\text{-}F}$ = 188.4 Hz), 92.3, 90.4, 85.6, 63.9; IR (KBr) ν_{max} 3281, 3089, 2945, 2927, 2861, 2230, 1615, 1489, 1453, 1405, 1328, 1161, 1118, 1070, 1027, 1018, 969, 843, 756 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{20}O_2F_6Na$ (M + Na) calcd: 597.12597 found: 597.12606; R_f (2/1 hexanes/EtOAc) = 0.38 (silica gel plate).



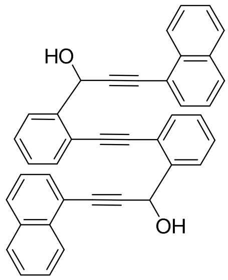
1,1'-(Ethyne-1,2-diylbis(2,1-phenylene))bis(3-(thiophen-3-yl)prop-2-yn-1-ol) (20f). With **19** (234 mg, 1.0 mmol) and 3-ethynyl-thiophene (300 μL, 3.0 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 398 mg (88%) of the title compound as a light brown solid: mp (decomp) 57-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.75 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.61 (dd, *J* = 7.5, 1.4 Hz, 2H), 7.47 (m, 2H), 7.38-7.43 (m, 2H), 7.35 (dt, *J* = 7.5, 1.5 Hz, 2H), 7.24 (t, *J* = 3.1 Hz, 1H), 7.22 (t, *J* = 3.1 Hz, 1H), 7.13 (ddd, *J* = 5.0, 2.2, 1.2 Hz, 2H), 6.19 (s, 1H), 6.18 (s, 1H), 3.62 (s, 1H), 3.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 142.0, 141.9, 132.9, 132.7, 129.9, 129.40, 129.38, 129.04, 129.00, 128.42, 128.40, 127.2, 127.0, 125.29, 125.26, 121.73, 121.68, 121.4, 92.28, 92.27, 87.70, 87.67, 82.3, 82.2, 63.9, 63.8; IR (KBr) ν_{max} 3527, 3334, 3106, 3061, 3022, 2869, 2231, 1599, 1520, 1489, 1449, 1358, 1270, 1177, 1027, 986, 864, 783, 760, 626 cm^{-1}; HRMS (*m/z*) for $C_{28}H_{18}O_2S_2Na$ (M + Na) calcd: 473.06404 found: 473.06415; R_f (2/1 hexanes/EtOAc) = 0.24 (silica gel plate).



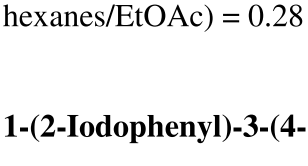
1,1'-(Ethyne-1,2-diylbis(2,1-phenylene))bis(hex-2-yn-1-ol) (20g). With **19** (234 mg, 1.0 mmol) and 1-pentyne (300 μL, 3.0 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 351 mg (95%) of the title compound as a light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.72 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.57 (m, 2H), 7.39 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.37 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.32 (m, 2H), 5.94 (m, 2H), 3.42 (s, 1H), 3.21 (s, 1H), 2.27 (m, 4H), 1.57 (m, 4H), 0.99 (t, *J* = 7.3 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 142.5, 132.6, 132.5, 128.8, 128.13, 128.10, 127.0, 126.8, 121.70, 121.68, 92.1, 92.0, 88.0, 87.9, 79.3, 79.2, 63.5, 63.4, 22.0, 20.84, 20.82, 13.53, 13.51; IR (KBr) ν_{max} 3558, 3063, 3022, 2962, 2933, 2899, 2871, 2833, 2277, 2226, 1598, 1565, 1489, 1449, 1379, 1328, 1276, 1189, 1133, 1033, 992, 807, 758, 630 cm^{-1}; HRMS (*m/z*) for $C_{26}H_{26}O_2Na$ (M + Na) calcd: 393.18250 found: 393.18269; R_f (2/1 hexanes/EtOAc) = 0.29 (silica gel plate).



1,1'-(Ethyne-1,2-diylbis(2,1-phenylene))bis(3-(trimethylsilyl)prop-2-yn-1-ol) (20h). With **19** (234 mg, 1.0 mmol) and ethynyltrimethylsilane (430 μL, 3.0 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 361 mg (84%) of the title compound as a light brown oil: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.77 (dd, J = 7.7, 1.2 Hz, 1H), 7.70 (dd, J = 7.6, 1.4 Hz, 1H), 7.58 (m, 2H), 7.39 (m, 2H), 7.34 (m, 2H), 3.55 (s, 1H), 3.25 (s, 1H), 0.21 (s, 9H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.7, 141.6, 132.8, 132.6, 128.92, 128.87, 128.4, 128.3, 127.3, 127.0, 121.9, 121.8, 104.2, 104.1, 92.2, 92.1, 63.8, 63.6, -0.20, -0.21; IR (KBr) ν_{max} 3346, 3058, 3025, 2959, 2898, 2173, 1598, 1490, 1449, 1408, 1374, 1250, 1188, 1038, 983, 844, 759 cm^{-1}; HRMS (*m/z*) for $C_{26}H_{30}O_2NaSi_2$ (M + Na) calcd: 453.16765 found: 453.16768; R_f (2/1 hexanes/EtOAc) = 0.30 (silica gel plate).



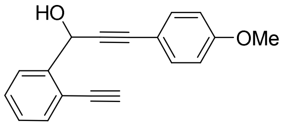
1,1'-(Ethyne-1,2-diylbis(2,1-phenylene))bis(3-(naphthalen-1-yl)prop-2-yn-1-ol) (20i). With **19** (234 mg, 1.0 mmol) and 1-ethynylnaphthalene (430 μL, 3.0 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 458 mg (85%) of the title compound as a light brown solid: mp (decomp) 86-91 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.30 (m, 1H), 8.25 (m, 1H), 7.91 (dd, J = 7.7, 1.3 Hz, 1H), 7.85 (dd, J = 7.6, 1.4 Hz, 1H), 7.76-7.81 (m, 4H), 7.68 (m, 2H), 7.66 (dt, J = 8.5, 1.2 Hz, 2H), 7.32-7-48 (m, 10H), 6.39 (s, 1H), 6.37 (s, 1H), 3.65 (s, 1H), 3.42 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.2, 142.1, 133.2, 133.03, 132.96, 132.9, 130.8, 129.13, 129.12, 129.0, 128.49, 128.46, 128.17, 128.15, 127.3, 127.1, 126.8, 126.4, 126.3, 126.12, 126.08, 125.1, 121.8, 121.7, 120.98, 119.95, 92.9, 92.5, 92.4, 85.2, 85.1, 64.2; IR (KBr) ν_{max} 3371, 3058, 2954, 2869, 2219, 1586, 1489, 1450, 1396, 1284, 1187, 1098, 1054, 1016, 950, 800, 773, 760 cm^{-1}; HRMS (*m/z*) for $C_{40}H_{26}O_2Na$ (M + Na) calcd: 561.18250, found: 561.18256; R_f (2/1 hexanes/EtOAc) = 0.28 (silica gel plate).



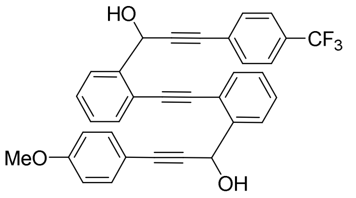
1-(2-Iodophenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol (24). With 2-iodo benzaldehyde (116 mg, 0.5 mmol) and 1-ethynyl-4-(trifluoromethyl)-benzene (82 μL, 0.5 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 195 mg (96%) of the title compound as a colorless liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (dd, J = 7.9, 1.2 Hz, 1H), 7.80 (dd, J = 7.8, 1.7 Hz, 1H), 7.58 (s, 4H), 7.43 (dt, J = 7.7, 1.2 Hz, 1H), 7.06 (dt, J = 7.6, 1.7 Hz, 1H), 5.90 (d, J = 5.0 Hz, 1H), 2.59 (d, J = 5.0 Hz, 1H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 142.1, 139.8, 132.0, 130.3, 128.8, 128.1, 122.6-130.6 (q, $^{1}J_{C\text{-}F}$ = 365.7 Hz), 125.2 (q, $^{2}J_{C\text{-}F}$ = 3.8 Hz), 97.9, 90.2, 85.5, 69.0; IR (KBr) ν_{max} 3285, 3180, 3061, 2887, 2229, 1614, 1497, 1464, 1436, 1405, 1326, 1279, 1170, 1137, 1114, 1070, 1053, 1012, 970, 840, 752, 731 cm^{-1}; HRMS (*m/z*) for $C_{16}H_{10}OF_3INa$ (M + Na) calcd: 424.96206, found: 424.96208; R_f (2/1 hexanes/EtOAc) = 0.52 (silica gel plate).

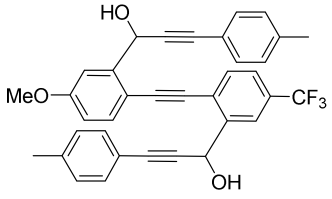
1-(2-Ethynylphenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (25). With 2-ethynyl benzaldehyde (260 mg, 2.0 mmol) and 4-ethynylanisole (260 µL, 2.0 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 436 mg (83%) of the title compound as a light brown liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.53 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.39-7.44 (m, 3H), 7.31 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.82 (m, 2H), 6.09 (s, 1H), 3.80 (s, 3H), 3.41 (s, 1H), 2.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 143.1, 133.3, 133.2, 132.8, 129.4, 129.2, 128.2, 127.4, 127.3, 126.9, 120.4, 114.5, 113.9, 86.7, 82.7, 81.9, 81.1, 63.8, 55.2; IR (KBr) ν_{max} 3427, 3288, 3066, 2935, 2837, 2227, 1606, 1509, 1479, 1446, 1291, 1248, 1174, 1107, 1029, 964, 832, 761, 663, 536 cm^{-1}; HRMS (*m/z*) for $C_{18}H_{14}O_2$ (M^+) calcd: 262.0994, found: 262.0999; R_f (2/1 hexanes/EtOAc) = 0.35 (silica gel plate).



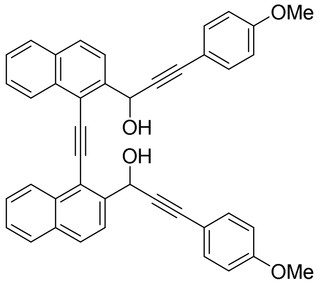
1-(2-((2-(1-Hydroxy-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)phenyl)ethynyl)-phenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (26). With **24** (200 mg, 0.5 mmol) and **25** (131 mg, 0.5 mmol) following the general procedure A. Column chromatography (2/1 hexanes/EtOAc) yielded 244 mg (91%) of the title compound as mixture as a light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.80 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.73 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.62 (dt, *J* = 6.9, 1.3 Hz, 2H), 7.52 (m, 4H), 7.34-7.44 (m, 6H), 6.77 (m, 2H), 6.22 (s, 1H), 6.18 (s, 1H), 3.95 (s, 1H), 3.76 (s, 3H), 3.54 (s, 1H), (minor) δ 7.83 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.76 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.62 (dt, *J* = 6.9, 1.3 Hz, 2H), 7.52 (m, 4H), 7.34-7.44 (m, 6H), 6.79 (m, 2H), 6.22 (s, 1H), 6.18 (s, 1H), 3.77 (s, 3H), 3.63 (s, 1H), 3.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (major) δ 159.8, 142.1, 141.8, 133.3, 132.92, 132.86, 132.0, 129.1, 128.6, 128.4, 127.3, 127.0, 119.8-126.2 (q, $^{1}J_{C\text{-}F}$ = 272.4 Hz), 125.2 (q, $^{2}J_{C\text{-}F}$ = 3.8 Hz), 121.7, 113.9, 92.4, 92.1, 90.7, 87.2, 86.6, 85.4, 64.0, 63.8, 55.2, (minor) δ 159.8, 142.1, 141.7, 133.3, 132.8, 132.7, 132.0, 129.1, 128.5, 128.4, 127.3, 127.0, 119.8-126.2 (q, $^{1}J_{C\text{-}F}$ = 272.4 Hz), 125.2 (q, $^{2}J_{C\text{-}F}$ = 3.8 Hz), 121.8, 114.3, 92.5, 92.1, 90.7, 87.2, 86.6, 85.5, 63.9, 63.7, 55.2; IR (KBr) ν_{max} 3348, 3064, 2928, 2871, 2234, 1606, 1509,



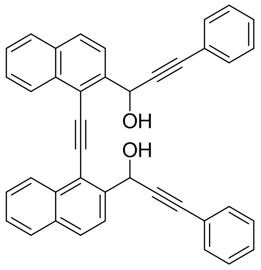
1490, 1443, 1323, 1291, 1249, 1171, 1125, 1068, 1032, 1018, 965, 833, 760 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{23}O_3F_3Na$ (M + Na) calcd: 559.14915, found: 559.14928; R_f (2/1 hexanes/EtOAc) = 0.28 (silica gel plate).



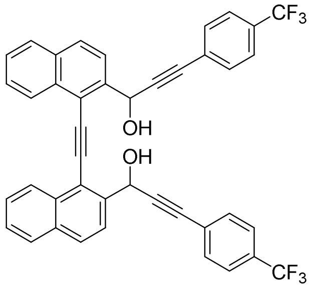
1-(2-((2-(1-Hydroxy-3-(*p*-tolyl)prop-2-yn-1-yl)-4-(trifluoromethyl)phenyl)ethynyl)-5-methoxyphenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (31). With **30** (270 mg, 0.8 mmol) and 1-ethynyl-4-*p*-toluene (310 μL, 2.4 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 345 mg (75%) of the title compound as mixture as a light brown solid: mp (decomp) 72-77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.49 (s, 1H), 7.31-7.39 (m, 6H), 7.07-7.12 (m, 4H), 6.85 (dt, *J* = 8.5, 2.7 Hz, 2H), 6.15 (d, *J* = 5.7 Hz, 1H), 6.04 (d, *J* = 5.2 Hz, 1H), 3.86 (s, 3H), 3.76 (s, 1H), 2.69 (s, 1H) 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 159.8, 145.7, 143.6, 138.7, 135.1, 134.0, 133.9, 131.7, 131.7, 129.0, 127.9-143.5 (q, $^1J_{C\text{-}F}$ = 254.8 Hz), 119.3, 114.3, 114.1, 114.0 (q, $^2J_{C\text{-}F}$ = 4.7 Hz), 113.9, 112.9, 112.6, 112.5, 112.1, 90.9, 87.3, 87.2, 86.9, 79.9, 77.9, 63.9, 63.4, 55.5, 21.5; IR (KBr) ν_{max} 3372, 3031, 3004, 2923, 2836, 2210, 1605, 1509, 1487, 1429, 1329, 1293, 1272, 1168, 1126, 1095, 1028, 973, 816, 527 cm^{-1}; HRMS (*m/z*) for $C_{36}H_{28}O_3F_3$ (M + H) calcd: 565.19851, found: 565.19818; R_f (2/1 hexanes/EtOAc) = 0.34 (silica gel plate).



1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(3-(4-methoxyphenyl)prop-2-yn-1-ol) (38a). With **37** (250 mg, 0.75 mmol) and 4-ethynylanisole (290 μL, 2.25 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 423 mg (94%) of the title compound as a light brown solid: mp (decomp) 97-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (m, 2H), 8.00 (dd, *J* = 8.6, 4.7 Hz, 2H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.56-7.63 (m, 4H), 7.40 (m, 4H), 6.78 (m, 4H), 6.62 (s, 2H), 3.76 (s, 6H), 3.47 (s, 1H), 3.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 141.4, 141.3, 133.4, 133.3, 133.0, 129.5, 128.3, 127.4, 126.8, 126.6, 124.3, 124.2, 118.9, 118.8, 114.4, 114.4, 113.88, 113.82, 95.6, 95.5, 87.3, 87.2, 87.1, 87.0, 64.14, 64.10, 55.2; IR (KBr) ν_{max} 3418, 3055, 3004, 2956, 2929, 2836, 2223, 1605, 1569, 1509, 1463, 1440, 1291, 1249, 1173, 1107, 1033, 979, 829, 802, 762 cm^{-1}; HRMS (*m/z*) for $C_{42}H_{30}O_4Na$ (M + Na) calcd: 621.20363, found: 621.20367; R_f (2/1 hexanes/EtOAc) = 0.16 (silica gel plate).



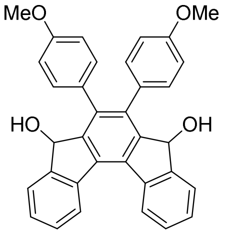
1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(3-phenylprop-2-yn-1-ol) (38b). With **37** (84 mg, 0.25 mmol) and phenylacetylene (83 μL, 0.75 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 119 mg (88%) of the title compound as a light brown solid: mp (decomp) 93-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (m, 2H), 8.03 (dd, *J* = 8.6, 3.4 Hz, 2H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.89 (m, 2H), 7.54-7.61 (m, 4H), 7.45 (m, 4H), 7.22-7.32 (m, 6H), 6.63 (s, 1H), 6.62 (s, 1H), 3.47 (s, 1H), 3.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 141.1, 133.4, 133.3, 133.03, 133.02, 131.8, 129.6, 128.5, 128.32, 128.26, 128.22, 128.19, 127.5, 126.8, 126.6, 124.3, 124.2, 122.4, 122.3, 119.0, 118.9, 95.6, 95.5, 88.6, 88.5, 87.26, 87.1, 64.10, 64.08.; IR (KBr) ν_{max} 3371, 3053, 2926, 2856, 2224, 1591, 1571, 1484, 1443, 1401, 1260, 1218, 1173, 1032, 980, 918, 824, 755, 693 cm^{-1}; HRMS (*m/z*) for $C_{40}H_{26}O_2Na$ (M + Na) calcd: 561.18250, found: 561.18256; R_f(2/1 hexanes/EtOAc) = 0.24 (silica gel plate).



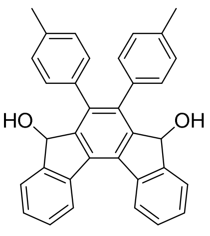
1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol) (38c). With **37** (84 mg, 0.25 mmol) and 1-ethynyl-4-(trifluoromethyl)-benzene (122 μL, 0.75 mmol) following the general procedure B. Column chromatography (2/1 hexanes/EtOAc) yielded 128 mg (76%) of the title compound as a light brown solid: mp (decomp) 98-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (m, 2H), 7.86-7.94 (m, 6H), 7.54-7.62 (m, 4H), 7.39-7.42 (m, 4H), 7.44-7.49 (m, 4H), 6.63 (s, 1H), 6.61 (s, 1H), 3.83 (s, 1H), 3.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.6, 133.4, 133.3, 133.1, 133.0, 132.0, 131.9, 129.8, 129.7, 128.4, 127.62, 127.60, 127.04, 127.00, 126.5, 126.4, 126.0 (q, $^3J_{C-F}$ = 1.4 Hz), 125.0 (q, $^2J_{C-F}$ = 3.8 Hz), 122.9-129.8 (q, $^1J_{C-F}$ = 261.6 Hz), 124.2, 124.1, 119.0, 118.9, 95.6, 95.5, 90.9, 90.8, 85.8, 85.7, 64.1, 64.0; IR (KBr) ν_{max} 3381, 3053, 2935, 2856, 2099, 1612, 1408, 1318, 1249, 1218, 1166, 1125, 1073, 1021, 983, 835, 762 cm^{-1}; HRMS (*m/z*) for $C_{42}H_{24}O_2F_6Na$ (M + Na) calcd: 697.15727, found: 697.15738; R_f(2/1 hexanes/EtOAc) = 0.25 (silica gel plate).

6.3.2. Cyclotrimerization reaction for 21, 27, 32 and 39

C: General procedure for cyclotrimerization with Wilkinson's catalyst $RhCl(PPh_3)_3$ (Preparation of 21, 27, 32 and 39). A dry microwave vial was charged with starting triyndiol (0.25 mmol), and dissolved under argon atmosphere in THF (5 mL). After addition of Wilkinson's catalyst (9 mg, 0.0075 mmol, 3 mol%) and the additive Ag_2CO_3 (4 mg, 0.015 mmol, 6 mol%) the reaction mixture was sealed and heated up to 180°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. Column chromatography of the residue on silica gel yielded products.

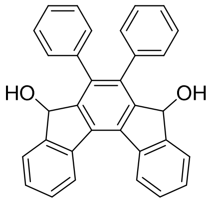


6,7-Bis(4-methoxyphenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (21a). With **20a** (125 mg, 0.25 mmol) following the general procedure C. Column chromatography (1/1 hexanes/EtOAc) yielded 114 mg (92%) of the title compound as a light brown solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.7, 3.7 Hz, 2H), 7.60 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 3H), 7.37 (m, 3H), 7.14 (m, 2H), 6.80 (m, 4H), 5.88 (s, 1H), 5.59 (s, 1H) 3.80 (s, 3H), 3.79 (s, 3H), 1.90 (s, 1H), 1.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 147.1, 145.8, 139.9, 137.3, 129.93, 129.89, 128.9, 128.8, 127.9, 125.5, 125.4, 123.51, 123.47, 114.1, 74.3, 74.1, 55.2, 55.1; IR (KBr) ν_{max} 3554, 3008, 2933, 2837, 1608, 1517, 1462, 1432, 1289, 1247, 1180, 1107, 1031, 837, 763, 736 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{26}O_4Na$ (M + Na) calcd: 521.17233, found: 521.17249; R_f (1/1 hexanes/EtOAc) = 0.43 (silica gel plate).

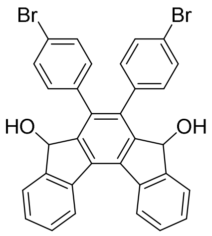


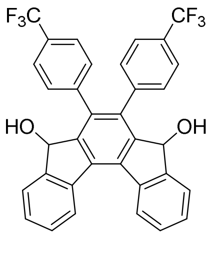
6,7-Di-*p*-tolyl-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (21b). With **20b** (45 mg, 0.1 mmol) following the general procedure C. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 45 mg (96%) of the title compound as a light brown solid: mp (decomp) 254-259 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.8 Hz, 2H), 8.23-8.32 (m, 2H), 7.59 (m, 3H), 7.49 (m, 3H), 7.34-7.43 (m, 4H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 5.85 (d, *J* = 2.9 Hz, 2H), 2.33 (s, 6H), 1.74 (d, *J* = 3.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 145.8, 139.9, 137.4, 136.9, 135.0, 134.7, 129.4, 129.3, 128.8, 128.2, 127.8, 125.4, 123.5, 74.3, 21.3; IR (KBr) ν_{max} 3575, 3550, 3518, 3460, 3046, 3023, 2947, 2921, 2868, 1605, 1515, 1464, 1431, 1328, 1247, 1184, 1105, 1071, 1022, 933, 830, 763, 735 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{26}O_2Na$ (M + Na) calcd: 489.18250, found: 489.18242; R_f (2/1 hexanes/EtOAc) = 0.40 (silica gel plate).

6,7-Diphenyl-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (21c). With **20c** (109 mg, 0.25 mmol) following the general procedure C. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 102 mg (93%) of the title compound as a light brown solid: mp (decomp) >260 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 7.8, 3.7 Hz, 2H), 7.64 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 3H), 7.40 (ddt, *J* = 7.4, 2.0. 0.9 Hz, 3H), 7.29-7.31 (m, 2H), 7.17-7.25 (m, 6H), 5.90 (s, 1H), 5.62 (s, 1H), 1.72-1.87 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 146.1, 145.81, 145.77, 139.8, 139.7, 138.6, 137.8, 137.7, 137.4, 135.1, 134.9, 128.9, 128.9, 128.0, 127.3, 127.2, 125.5, 125.4, 123.54, 123.49, 74.3, 74.1; IR (KBr) ν_{max} 3579, 3554, 3423, 3050, 3021, 2945, 2865, 1604, 1464, 1441, 1422, 1330, 1179, 1101, 1067, 1029, 848, 766, 742, 714, 704 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{26}O_2Na$ (M + Na) calcd: 461.15120, found: 461.15131; R_f (2/1 hexanes/EtOAc) = 0.26 (silica gel plate).

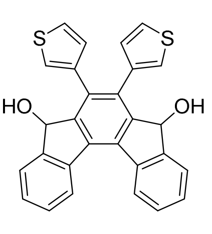


6,7-Bis(4-bromophenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (21d). With **20d** (148 mg, 0.25 mmol) following the general procedure C. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 124 mg (84%) of the title compound as a light brown solid: mp (decomp) 222-227 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.7, 2.4 Hz, 2H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 4H), 7.39 (m, 4H), 7.28-7-33 (m, 2H), 6.78 (m, 2H), 5.84 (m, 1H), 5.78 (s, 1H), 1.62 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 145.9, 145.8, 139.6, 139.5, 137.5, 137.4, 136.9, 136.6, 136.4, 135.5, 135.4, 135.2, 132.1, 131.7, 130.4, 129.1, 129.0, 128.9, 128.2, 128.1, 127.5, 125.4, 123.6, 121.6, 74.2, 74.1; IR (KBr) ν_{max} 3566, 3444, 3050, 2868, 1605, 1489, 1465, 1427, 1392, 1330, 1247, 1179, 1103, 1073, 1026, 1012, 833, 761, 736, 729 cm^{-1}; HRMS (*m/z*) for $C_{32}H_{22}O_2Br_2Na$ (M + Na) calcd: 616.97223, found: 616.97181; R_f (2/1 hexanes/EtOAc) = 0.38 (silica gel plate).

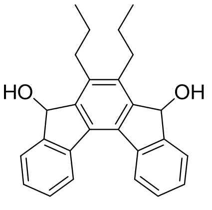




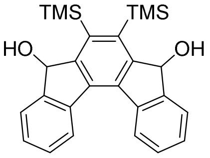
6,7-Bis(4-(trifluoromethyl)phenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (21e). With **20e** (143 mg, 0.25 mmol) following the general procedure C. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 138 mg (96%) of the title compound as a light brown solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 7.8 Hz, 2H), 7.64-7.72 (m, 2H), 7.61 (d, J = 7.1 Hz, 4H), 7.53 (m, 4H), 7.41 (t, J = 7.3 Hz, 4H), 7.02 (bs, 2H), 5.79 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 146.5, 145.9, 145.8, 139.7, 139.5, 137.5, 136.7, 136.4, 135.5, 129.1, 122.6-129.6 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 128.3, 128.1, 127.4, 125.5 (q, $^2J_{C\text{-}F}$ = 2.9 Hz), 123.5, 121.5, 74.2; IR (KBr) ν_{max} 3303, 3040, 2945, 2923, 1617, 1467, 1406, 1328, 1164, 1120, 1069, 1021, 849, 762, 741 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{20}O_2F_6Na$ (M + Na) calcd: 597.12597 found: 597.12610; R_f (2/1 hexanes/EtOAc) = 0.44 (silica gel plate).

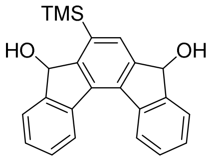


6,7-Di(thiophen-3-yl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (21f). With **20f** (113 mg, 0.25 mmol) following the general procedure C. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 108 mg (95%) of the title compound as a light brown solid: mp (decomp) 231-236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 7.8 Hz, 2H), 7.62 (d, J = 7.4 Hz, 2H), 7.50 (t, J = 7.4 Hz, 2H), 7.39 (ddt, J = 7.4, 2.8, 0.7 Hz, 2H), 7.31 (dd, J = 7.9, 3.0 Hz, 1H), 7.27 (m, 1H), 7.23 (dd, J = 2.9, 1.3 Hz, 1H), 7.16 (dd, J = 2.9, 1.2 Hz, 1H), 6.92 (dd, J = 4.9, 1.2 Hz, 2H), 5.88 (s, 1H), 5.64 (s, 1H), 1.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 146.7, 145.8, 145.7, 139.7, 139.6, 137.9, 137.8, 135.3, 135.1, 133.9, 132.8, 129.2, 129.0, 128.9, 128.6, 128.1, 126.1, 125.5, 125.41, 125.37, 124.2, 123.6, 123.54, 123.49, 74.3, 74.1; IR (KBr) ν_{max} 3546, 3393, 3103, 3029, 2869, 1605, 1466, 1440, 1353, 1264, 1192, 1070, 1024, 966, 856, 838, 802, 761, 732, 624 cm^{-1}; HRMS (*m/z*) for $C_{28}H_{18}O_2S_2Na$ (M + Na) calcd: 473.06404 found: 473.06409; R_f (2/1 hexanes/EtOAc) = 0.30 (silica gel plate).

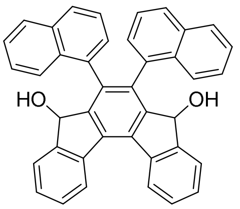


6,7-Dipropyl-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (21g). With **20g** (92 mg, 0.25 mmol) following the general procedure C. Column chromatography (2/1 hexanes/EtOAc) yielded 68 mg (73%) of the title compound as a light brown solid: mp (decomp) 204-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 7.7 Hz, 2H), 7.67 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.1 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 5.69 (s, 1H), 5.67 (s, 1H), 3.11 (m, 2H), 2.80 (m, 2H), 1.69 (m, 4H), 1.57 (s, 2H), 1.11 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 145.9, 140.1, 139.7, 128.9, 128.1, 127.5, 125.2, 123.1, 74.7, 31.1, 24.9, 15.0; IR (KBr) ν_{max} 3530, 3366, 3050, 2957, 2927, 2870, 1607, 1586, 1465, 1431, 1374, 1294, 1258, 1201, 1086, 1020, 933, 842, 763, 731, 724 cm^{-1}; HRMS (*m/z*) for $C_{26}H_{26}O_2Na$ (M + Na) calcd: 393.18250, found: 393.18264; R_f (2/1 hexanes/EtOAc) = 0.39 (silica gel plate).

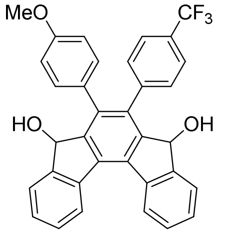




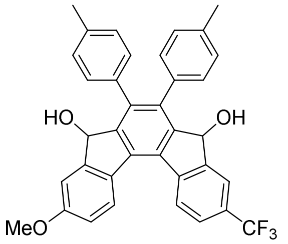
6,7-Bis(trimethylsilyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (major) (21h-TMS), 6-(Trimethylsilyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (minor) (21h). With **20h** (108 mg, 0.25 mmol) following the general procedure C. Column chromatography (2/1 hexanes/EtOAc) yielded 85 mg (80%) of the title compound as mixture as a light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 7.9, 2.1 Hz, 2H), 7.70 (m, 2H), 7.46 (m, 2H), 7.38 (dt, *J* = 7.4, 0.9 Hz, 2H), 5.72 (d, *J* = 8.0 Hz, 1H), 5.64 (m, 1H), 1.70 (s, 1H), 1.57 (s, 1H), 0.47 (s, 9H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 152.9, 147.4, 147.0, 146.3, 139.9, 139.8, 136.4, 130.1, 128.9, 128.5, 127.8, 127.7, 125.3, 125.18, 123.55, 123.4, 75.4, 75.1, 1.0, 0.1; δ (minor) 153.7, 147.9, 147.2, 146.6, 140.0, 139.9, 135.8, 134.7, 129.8, 128.8, 128.5, 127.7, 125.2, 125.0, 123.6, 75.6, 75.3, 1.0, 0.1; IR (KBr) ν_{max} 3540, 3393, 3067, 3046, 2954, 2896, 1606, 1465, 1407, 1380, 1248, 1198, 1117, 1039, 933, 843, 760, 736 cm^{-1}; HRMS (*m/z*) for $C_{26}H_{30}O_2NaSi_2$ (M + Na) (major) calcd: 453.16765, found: 453.16774, HRMS (*m/z*) for $C_{23}H_{22}O_2NaSi$ (M + Na) (minor) calcd: 381.12813, found: 381.12830; R_f (2/1 hexanes/EtOAc) (major) = 0.44 (silica gel plate), R_f (2/1 hexanes/EtOAc) (minor) = 0.26 (silica gel plate).



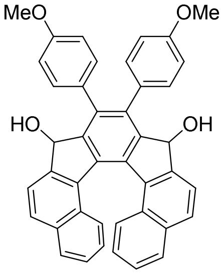
6,7-Di(naphthalen-1-yl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (21i). With **20i** (135 mg, 0.25 mmol) following the general procedure C. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 112 mg (83%) of the title compound as a light brown solid: mp (decomp) 217-222 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 4H), 7.58 (t, *J* = 8.5 Hz, 2H), 7.50-7.54 (m, 6H), 7.34-7.39 (m, 4H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 2H), 5.32 (s, 2H), 1.65 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 145.8, 139.8, 137.0, 134.1, 133.6, 130.9, 129.3, 128.9, 128.2, 128.1, 128.0, 125.9, 125.7, 125.6, 124.4, 123.6, 74.29; IR (KBr) ν_{max} 3553, 3422, 3053, 2953, 2869, 1593, 1507, 1465, 1390, 1330, 1189, 1040, 1019, 801, 780, 767, 733 cm^{-1}; HRMS (*m/z*) for $C_{40}H_{26}O_2Na$ (M + Na) calcd: 561.18250, found: 561.18255; R_f (2/1 hexanes/EtOAc) = 0.36 (silica gel plate).



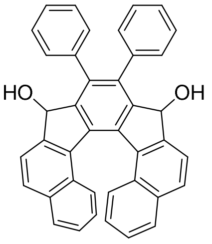
6-(4-Methoxyphenyl)-7-(4-(trifluoromethyl)phenyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (27). With **26** (134 mg, 0.25 mmol) following the general procedure C. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 113 mg (84%) of the title compound as a light brown solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 7.8 Hz, 2H), 7.61 (t, J = 7.9 Hz, 4H), 7.51 (dt, J = 7.4, 1.0 Hz, 4H), 7.37-7.41 (m, 6H), 5.86 (s, 1H), 5.81 (s, 1H), 3.79 (s, 3H), 1.78 (s, 1H), 1.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 146.5, 145.9, 145.8, 139.6, 136.6, 135.1, 122.9-129.2 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 129.1, 128.9, 128.2, 125.5, 125.4, 123.6 (q, $^2J_{C\text{-}F}$ = 3.9 Hz), 74.3, 74.2, 55.2; IR (KBr) ν_{max} 3566, 3221, 3040, 2952, 2921, 2861, 1609, 1513, 1463, 1434, 1405, 1323, 1249, 1163, 1125, 1107, 1065, 1032, 840, 764, 736 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{23}O_3F_3Na$ (M + Na) calcd: 559.14915, found: 559.14932; R_f (2/1 hexanes/EtOAc) = 0.34 (silica gel plate).



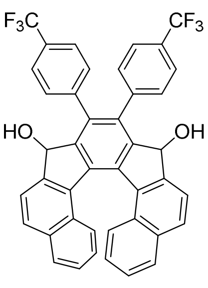
3-Methoxy-6,7-di-*p*-tolyl-10-(trifluoromethyl)-5,8-dihydroindeno[2,1-*c*]fluorene-5,8-diol (32). With **31** (134 mg, 0.25 mmol) following the general procedure C. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 84 mg (60%) of the title compound as a light brown solid: mp (decomp) 141-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.2 Hz, 1H), 8.20 (d, J = 8.6 Hz, 1H), 7.82 (s, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.34-7.41 (m, 3H), 7.16 (d, J = 2.1 Hz, 1H), 7.02 (dd, J = 8.6, 2.6 Hz, 2H), 7.00 (m, 2H), 6.76 (m, 2H), 5.89 (s, 1H), 5.81 (s, 1H), 3.88 (s, 3H), 2.33 (s, 6H), 1.80 (s, 1H), 1.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 148.1, 147.4, 146.8, 146.1, 143.5, 138.4, 137.0, 136.5, 135.7, 134.5, 134.4, 132.4, 132.1, 130.2, 129.5, 129.1, 128.4, 126.1, 126.0, 125.6-133.6 (q, $^1J_{C\text{-}F}$ = 194.6 Hz), 124.3, 123.1, 122.3 (q, $^2J_{C\text{-}F}$ = 3.8 Hz), 114.6, 110.9, 74.2, 74.0, 55.5, 21.2; IR (KBr) ν_{max} 3567, 3458, 3019, 2923, 2871, 1611, 1512, 1484, 1434, 1327, 1300, 1252, 1166, 1144, 1123, 1177, 1034, 833, 818, 527 cm^{-1}; HRMS (*m/z*) for $C_{36}H_{28}O_3F_3$ (M + H) calcd: 565.19851, found: 565.19819; R_f (2/1 hexanes/EtOAc) = 0.46 (silica gel plate).



8,9-Bis(4-methoxyphenyl)-7,10-dihydrobenzo[c]benzo[6,7]indeno[1,2-*g*]fluorene-7,10-diol (39a). With **38a** (150 mg, 0.25 mmol) following the general procedure C. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 145 mg (96%) of the title compound as diastereoisomers as a light brown solid: mp (decomp) 178-183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.39 (dd, *J* = 8.4, 0.8 Hz, 2H), 7.18 (m, 4H), 6.87 (m, 4H), 6.53 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2H), 5.84 (s, 2H), 3.81 (s, 6H), 2.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 145.3, 143.6, 138.0, 137.4, 134.6, 134.3, 129.6, 129.2, 129.1, 127.9, 127.7, 125.6, 124.5, 124.2, 122.2, 113.9, 74.4, 55.2; IR (KBr) ν_{max} 3548, 3053, 3001, 2954, 2835, 1608, 1511, 1462, 1362, 1287, 1247, 1176, 1033, 832, 800, 744 cm^{-1}; HRMS (*m/z*) for $C_{42}H_{30}O_4Na$ (M + Na) calcd: 621.20363, found: 621.20369; R_f (2/1 hexanes/EtOAc) = 0.22 (silica gel plate).



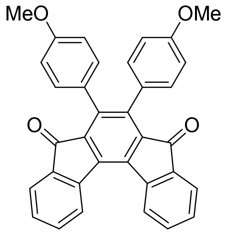
8,9-Diphenyl-7,10-dihydrobenzo[c]benzo[6,7]indeno[1,2-*g*]fluorene-7,10-diol (39b). With **38b** (107 mg, 0.2 mmol) following the general procedure C. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 103 mg (96%) of the title compound as diastereoisomers as a light brown solid: mp (decomp) 171-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 9.02 (d, *J* = 8.3 Hz, 1H), 8.95 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.93 (m, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.68-7.85 (m, 5H), 7.66 (s, 1H), 7.60-7.64 (m, 4H), 7.53-7.58 (m, 4H), 6.26 (d, *J* = 4.5 Hz, 1H), 5.84 (s, 1H), 1.88 (bs, 1H), 1.77 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.8, 129.6, 129.4, 129.3, 129.2, 128.7, 128.6, 128.1, 128.0, 127.3, 126.9, 126.8, 126.7, 126.0, 125.5, 124.5, 124.3, 124.1, 123.0, 122.7, 121.9, 116.2, 75.5, 74.1; IR (KBr) ν_{max} 3580, 3426, 3055, 2951, 1608, 1498, 1464, 1441, 1423, 1331, 1176, 1067, 1029, 766, 742, 714 cm^{-1}; HRMS (*m/z*) for $C_{40}H_{26}O_2Na$ (M + Na) calcd: 561.18250, found: 561.18267; R_f (2/1 hexanes/EtOAc) = 0.30 (silica gel plate).



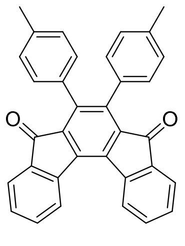
8,9-Bis(4-(trifluoromethyl)phenyl)-7,10-dihydrobenzo[c]benzo[6,7]indeno[1,2-*g*] fluorene-7,10-diol (39c). With **38c** (100 mg, 0.15 mmol) following the general procedure C. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 93 mg (94%) of the title compound as diastereoisomers as a light brown solid: mp (decomp) 189-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (m, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.67-7.79 (m, 4H), 7.57 (m, 4H), 7.48 (m, 2H), 7.40 (m, 2H), 7.21 (m, 2H), 6.65 (m, 1H), 6.56 (m, 1H), 5.73 (s, 2H), 1.96 (s, 1H), 1.59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 145.1, 144.2, 143.9, 142.0, 141.0, 137.4, 136.1, 135.4, 134.4, 134.1, 131.6, 130.1, 130.0, 129.7, 129.4, 129.2, 128.2, 128.1, 127.5, 127.2, 126.9, 125.9, 125.3 (q, $^{2}J_{C\text{-}F}$ = 4.7 Hz), 124.7, 124.6, 124.0, 122.6, 122.1, 121.8, 119.6-126.5 (q, $^{1}J_{C\text{-}F}$ = 305.7 Hz), 116.6, 75.5, 74.2; IR (KBr) ν_{max} 3478, 3053, 3018, 2929, 2846, 1626, 1598, 1446, 1301, 1270, 1232, 1177, 1049, 1028, 990, 824, 769, 696 cm^{-1}; HRMS (*m/z*) for $C_{42}H_{24}O_2F_6Na$ (M + Na) calcd: 697.15727, found: 697.15750; R_f (2/1 hexanes/EtOAc) = 0.38 (silica gel plate).

6.3.3. Synthesis of Dispiroindeno[2,1-*c*]fluorenes 23, 29, 34 and 41

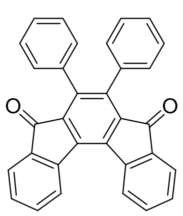
D: General procedure for Oxidation reaction with PCC (preparation of 22, 28, 33 and 40). To a solution of pyridinium chlorochromate (PCC, 64 mg, 0.3 mmol) and celite (64 mg) in anhydrous CH_2Cl_2 (10 mL) the starting indeno[2,1-*c*]fluorene-5,8-diol (0.2 mmol) was added and the mixture was stirred for 3h at rt. Afterwards the residue was filtered through a celite/silica gel plug. Column chromatography of the residue on silica gel yielded products.



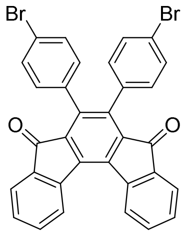
6,7-Bis(4-methoxyphenyl)indeno[2,1-*c*]fluorene-5,8-dione (22a). With **21a** (230 mg, 0.46 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 210 mg (94%) of the title compound as a bright yellow solid: mp (decomp) 245-250 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.7 Hz, 2H), 7.69 (dd, J = 7.3, 0.6 Hz, 2H), 7.66 (dt, J = 7.6, 1.3 Hz, 2H), 7.41 (dt, J = 7.5, 0.6 Hz, 2H), 6.90 (m, 4H), 6.77 (m, 4H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 158.8, 143.3, 142.7, 138.0, 136.2, 135.5, 134.8, 130.9, 129.6, 127.2, 124.8, 123.7, 113.0, 55.1; IR (KBr) ν_{max} 3073, 3046, 3007, 2959, 2837, 1714, 1609, 1517, 1466, 1426, 1302, 1288, 1246, 1200, 1179, 1030, 941, 835, 754, 721, cm^{-1}; HRMS (*m/z*) for $C_{34}H_{23}O_4$ (M + H) calcd: 495.15909, found: 495.15921; R_f (2/1 hexanes/EtOAc) = 0.47 (silica gel plate).



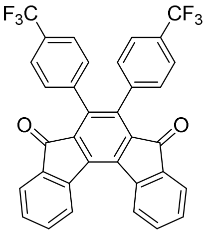
6,7-Di-*p*-tolylindeno[2,1-*c*]fluorene-5,8-dione (22b). With **21b** (140 mg, 0.3 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/ CH_2Cl_2) yielded 125 mg (90%) of the title compound as a bright yellow solid: mp (decomp) 167-172 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.7 Hz, 2H), 7.68 (dd, J = 7.3, 0.5 Hz, 2H), 7.65 (dt, J = 7.6, 1.3 Hz, 2H), 7.41 (dt, J = 7.5, 0.6 Hz, 2H), 7.02 (d, J = 7.8 Hz, 4H), 6.88 (m, 4H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 143.4, 142.7, 138.0, 136.9, 136.2, 135.4, 134.8, 132.0, 129.6, 129.3, 128.2, 124.8, 123.7, 21.4; IR (KBr) ν_{max} 3069, 3043, 3010, 2919, 2863, 1734, 1711, 1605, 1578, 1517, 1465, 1423, 1377, 1304, 1237, 1193, 1096, 1069, 1022, 931, 851, 826, 765, 753, 722, 665 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{23}O_2$ (M + H) calcd: 463.16926, found: 463.16927; R_f(2/1 hexanes/EtOAc) = 0.41 (silica gel plate).



6,7-Diphenylindeno[2,1-*c*]fluorene-5,8-dione (22c). With **21c** (285 mg, 0.65 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 257 mg (92%) of the title compound as a bright yellow solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.7 Hz, 2H), 7.69 (d, *J* = 7.3 Hz, 2H), 7.65 (dt, *J* = 7.6, 1.2 Hz, 2H), 7.41 (dt, *J* = 7.5, 0.6 Hz, 2H), 7.20-7.22 (m, 6H), 6.99-7.02 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 143.0, 142.7, 138.1, 136.1, 135.3, 135.0, 134.8, 129.7, 129.4, 127.4, 127.3, 124.8, 123.8; IR (KBr) ν_{max} 3055, 2921, 1711, 1607, 1571, 1466, 1417, 1379, 1302, 1198, 1076, 1027, 936, 830, 765, 752, 716, 702 cm^{-1}; HRMS (*m/z*) for $C_{32}H_{19}O_2$ (M + H) calcd: 435.13796, found: 435.13789; R_f (2/1 hexanes/EtOAc) = 0.36 (silica gel plate).

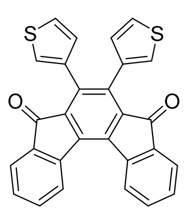


6,7-Bis(4-bromophenyl)indeno[2,1-*c*]fluorene-5,8-dione (22d). With **21d** (297 mg, 0.5 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/ CH_2Cl_2) yielded 285 mg (96%) of the title compound as a bright yellow solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (m, 2H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.68 (dt, *J* = 7.6, 1.2 Hz, 2H), 7.32-7.37 (m, 4H), 7.25 (m, 2H), 6.98 (m, 2H), 6.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 142.5, 141.3, 138.6, 136.3, 135.2, 135.1, 133.6, 131.1, 130.9, 130.0, 127.6, 125.0, 123.9, 122.0; IR (KBr) ν_{max} 3055, 3041, 3010, 1712, 1606, 1580, 1492, 1466, 1423, 1393, 1298, 1238, 1196, 1099, 1074, 1012, 933, 835, 756, 719 cm^{-1}; HRMS (*m/z*) for $C_{32}H_{17}O_2Br_2$ (M + H) calcd: 590.95898, found: 590.95892; R_f (2/1 hexanes/EtOAc) = 0.40 (silica gel plate).

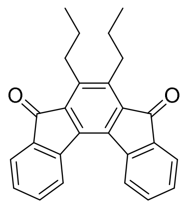


6,7-Bis(4-(trifluoromethyl)phenyl)indeno[2,1-*c*]fluorene-5,8-dione (22e). With **21e** (400 mg, 0.7 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 363 mg (91%) of the title compound as a bright yellow solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.7 Hz, 2H), 7.72 (d, *J* = 7.3 Hz, 2H), 7.70 (dt, *J* = 7.6, 1.3 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 4H), 7.46 (dt, *J* = 7.3, 0.5 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 142.5, 140.8, 138.8, 138.5, 136.3, 135.2, 135.1, 130.1, 129.9, 122.6-129.6 (q, $^1J_{C\text{-}F}$ = 272.1 Hz) 125.33, 125.05, 124.6 (q, $^2J_{C\text{-}F}$ = 3.8 Hz), 124.0; IR (KBr) ν_{max} 3067, 3040, 2922, 1712, 1606, 1467, 1409, 1328, 1171, 1127, 1111, 1067, 1020, 935, 850, 758, 721 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{17}O_2F_6$ (M + H) calcd: 571.11273 found: 571.11255; R_f (2/1 hexanes/EtOAc) = 0.34 (silica gel plate).

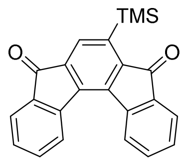
6,7-Di(thiophen-3-yl)indeno[2,1-*c*]fluorene-5,8-dione (22f). With **21f** (315 mg, 0.7 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 284 mg (91%) of the title compound as a light orange solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.7 Hz, 2H), 7.71 (dd, *J* = 7.3, 0.5 Hz, 2H), 7.65 (dt, *J* = 7.6, 1.2 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.22 (dd, *J* = 4.9, 2.9 Hz, 2H), 6.90 (dd, *J* = 2.9, 1.2 Hz, 2H) 6.78 (dd, *J* = 4.9, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 142.6, 138.5, 138.2, 136.5, 135.3, 134.9, 134.5, 129.7, 129.0, 124.8, 124.7, 124.1, 123.8; IR (KBr) ν_{max} 3114, 3085, 3049, 3013, 1709, 1607, 1583, 1465, 1437, 1349, 1314, 1275, 1204, 1189, 1071, 953, 832, 808, 763, 745, 718, 663 cm^{-1}; HRMS (*m/z*) for $C_{28}H_{15}O_2S_2$ (M + H) calcd: 447.05080 found: 447.05076; R_f (2/1 hexanes/EtOAc) = 0.34 (silica gel plate).



6,7-Dipropylindeno[2,1-*c*]fluorene-5,8-dione (22g). With **21g** (130 mg, 0.35 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 124 mg (96%) of the title compound as a bright yellow solid: mp (decomp) 181-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.59 (dt, *J* = 7.6, 1.1 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 3.12 (m, 4H), 1.54 (m, 4H), 0.99 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 146.0, 143.0, 140.1, 135.9, 135.4, 134.7, 129.1, 124.5, 123.5, 28.4, 24.4, 14.6; IR (KBr) ν_{max} 3082, 3052, 2970, 2926, 2868, 1701, 1608, 1588, 1466, 1419, 1313, 1293, 1253, 1209, 1157, 1113, 1086, 1016, 960, 923, 837, 756, 719 cm^{-1}; HRMS (*m/z*) for $C_{26}H_{22}O_2$ (M^+) calcd: 366.1620, found: 366.1625; R_f (2/1 hexanes/EtOAc) = 0.51 (silica gel plate).

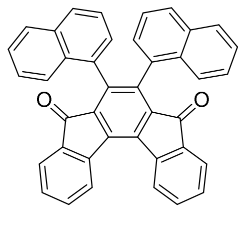


6-(Trimethylsilyl)indeno[2,1-*c*]fluorene-5,8-dione (22h). With **21h** (59 mg, 0.16 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 47 mg (83%) of the title compound as a bright yellow solid: mp (decomp) 260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (m, 2H), 7.82 (s, 1H), 7.78 (ddd, *J* = 7.4, 1.2, 0.6 Hz, 2H), 7.63 (m, 2H), 7.41 (ddt, *J* = 7.5, 2.0, 0.8 Hz, 2H), 0.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 192.9, 145.6, 143.7, 143.6, 142.6, 139.1, 139.0, 138.3, 135.1, 135.0, 134.9, 134.7, 130.8, 129.7, 129.5, 125.0, 124.7, 124.2, 123.9, -1.30; IR (KBr) ν_{max} 3082, 3005, 2953, 2896, 1714, 1611, 1580, 1471, 1413, 1323, 1246, 1207, 1096, 1084, 975, 929, 867, 843, 824, 758, 716 cm^{-1};

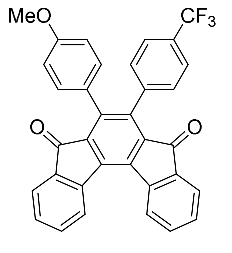


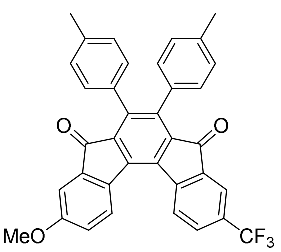
HRMS (*m/z*) for $C_{23}H_{19}O_2Si$ (M + H) calcd: 355.11488, found: 355.11493; R_f (2/1 hexanes/EtOAc) = 0.48 (silica gel plate).

6,7-Di(naphthalen-1-yl)indeno[2,1-*c*]fluorene-5,8-dione (22i). With **21i** (271 mg, 0.50 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 258 mg (96%) of the title compound as a bright yellow solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 7.7 Hz, 2H), 7.76 (dd, J = 7.7, 1.6 Hz, 2H), 7.76 (dt, J = 7.6, 1.2 Hz, 2H), 7.55-7-67 (m, 6H), 7.37-7.45 (m, 4H), 7.29 (t, J = 7.1 Hz, 1H), 7.23 (dd, J = 7.1, 1.2 Hz, 1H), 7.16 (dt, J = 8.1, 1.1 Hz, 1H), 7.04 (m, 1H), 6.97 (dd, J = 8.2, 7.1 Hz, 1H), 6.84 (dd, J = 7.1, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 142.90, 142.85, 141.9, 141.8, 138.5, 137.73, 137.71, 135.30, 135.25, 134.9, 133.4, 132.9, 132.8, 132.7, 132.5, 131.6, 129.8, 128.4, 128.0, 127.9, 127.8, 127.5, 125.9, 125.4, 125.3, 125.24, 125.21, 125.0, 124.7, 124.2, 123.98, 123.95; IR (KBr) ν_{max} 3052, 2919, 1712, 1608, 1507, 1467, 1375, 1317, 1296, 1202, 1003, 935, 799, 778, 759, 718 cm^{-1}; HRMS (*m/z*) for $C_{40}H_{23}O_2$ (M + H) calcd: 535.16926, found: 535.16938; R_f (2/1 hexanes/EtOAc) = 0.39 (silica gel plate).

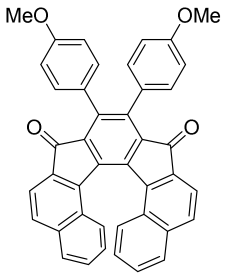


6-(4-Methoxyphenyl)-7-(4-(trifluoromethyl)phenyl)indeno[2,1-*c*]fluorene-5,8-dione (28). With **27** (188 mg, 0.35 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 149 mg (80%) of the title compound as a bright yellow solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.7 Hz, 2H), 7.63-7.72 (m, 4H), 7.47 (d, J = 8.0 Hz, 2H), 7.43 (dt, J = 7.5, 0.7 Hz, 1H), 7.41 (dt, J = 7.5, 0.7 Hz, 1H), 7.13 (d, J = 7.9 Hz, 2H), 6.87 (m, 2H), 6.73 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 191.5, 159.0, 142.7, 142.6, 142.4, 141.5, 139.1, 138.8, 137.9, 136.4, 136.1, 135.3, 135.1, 135.0, 125.6-136.2 (q, $^1J_{C\text{-}F}$ = 366.4 Hz), 134.9, 130.8, 130.0, 129.9, 129.8, 129.1, 126.4, 124.9, 124.4 (q, $^2J_{C\text{-}F}$ = 3.8 Hz), 123.9, 123.8, 113.1, 55.1; IR (KBr) ν_{max} 3073, 3004, 2952, 2952, 2905, 2836, 1712, 1608, 1514, 1467, 1425, 1325, 1302, 1247, 1166, 1121, 1074, 1035, 1020, 932, 837, 757, 719 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{20}O_3F_3$ (M + H) calcd: 533.13591, found: 533.13596; R_f(2/1 hexanes/EtOAc) = 0.38 (silica gel plate).

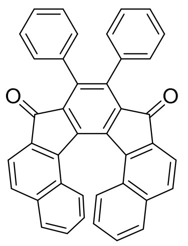




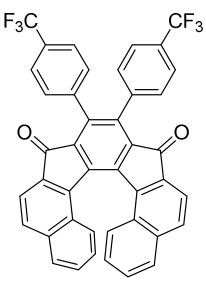
3-Methoxy-6,7-di-*p*-tolyl-10-(trifluoromethyl)indeno[2,1-*c*]fluorene-5,8-dione (33). With **32** (188 mg, 0.35 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 68 mg (87%) of the title compound as a bright yellow solid: mp (decomp) 109-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.91 (m, 2H), 7.21 (d, J = 2.6 Hz, 1H), 7.14 (dd, J = 8.4, 2.6 Hz, 1H), 7.04 (dd, J = 7.8, 1.8 Hz, 4H), 6.90 (dd, J = 8.1, 1.8 Hz, 4H), 3.88 (s, 3H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 190.2, 161.2, 145.8, 144.3, 143.0, 139.2, 137.5, 137.1, 137.0, 136.7, 136.1, 135.6, 135.2, 134.6, 131.7, 131.6, 131.5, 131.4, 129.3, 129.2, 128.3, 128.2, 124.8, 123.5, 121.4 (q, $^2J_{C\text{-}F}$ = 3.8 Hz), 120.6, 119.4-127.5 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 109.5, 55.7, 21.4; IR (KBr) ν_{max} 3022, 3001, 2924, 2869, 1713, 1622, 1608, 1487, 1434, 1329, 1302, 1246, 1169, 1130, 1071, 1021, 914, 835, 791, 754 cm^{-1}; HRMS (*m/z*) for $C_{36}H_{24}O_3F_3$ (M + H) calcd: 561.16721, found: 561.16724; R_f (2/1 hexanes/EtOAc) = 0.54 (silica gel plate).



8,9-Bis(4-methoxyphenyl)benzo[c]benzo[6,7]indeno[1,2-*g*]fluorene-7,10-dione (40a). With **39a** (272 mg, 0.45 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 229 mg (86%) of the title compound as a red solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 7.32 (m, 2H), 7.28 (d, J = 9.4 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 7.9 Hz, 2H), 6.84 (d, J = 7.7 Hz, 2H), 6.67 (ddd, J = 8.2, 6.9, 1.0 Hz, 2H), 3.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 158.9, 145.2, 142.3, 138.5, 137.8, 137.2, 134.2, 131.7, 130.8, 128.7, 128.6, 128.4, 127.0, 126.7, 125.7, 119.7, 113,1, 55.1; IR (KBr) ν_{max} 3052, 2930, 2833, 1704, 1609, 1516, 1441, 1291, 1249, 1178, 1109, 1035, 901, 835, 800, 777 cm^{-1}; HRMS (*m/z*) for $C_{42}H_{27}O_4$ (M + H) calcd: 595.19039, found: 595.19049; R_f(2/1 hexanes/EtOAc) = 0.32 (silica gel plate).

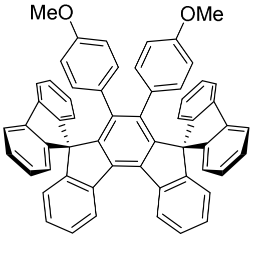


8,9-Diphenylbenzo[c]benzo[6,7]indeno[1,2-*g*]fluorene-7,10-dione (40b). With **39b** (103 mg, 0.19 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 96 mg (95%) of the title compound as a red solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.68 (m, 1H), 7.57 (m, 1H), 7.33 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 2H), 7.30 (m, 2H), 7.21-7.28 (m, 6H), 7.00 (d, *J* = 6.9 Hz, 2H), 6.69 (ddd, *J* = 8.3, 7.8, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 145.1, 142.1, 138.7, 137.7, 137.2, 134.8, 134.1, 130.9, 130.2, 130.1, 129.9, 129.6, 129.2, 128.9, 128.7, 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.3, 127.1, 126.6, 125.7, 125.5, 125.0, 123.4, 119.9, 119.7, 117.0; IR (KBr) ν_{max} 3054, 2919, 1710, 1617, 1570, 1464, 1419, 1375, 1304, 1197, 1074, 1025, 936, 830, 766, 752, 716, 701 cm^{-1}; HRMS (*m/z*) for $C_{40}H_{23}O_2$ (M + H) calcd: 535.16926, found: 535.16935; R_f (2/1 hexanes/EtOAc) = 0.40(silica gel plate).

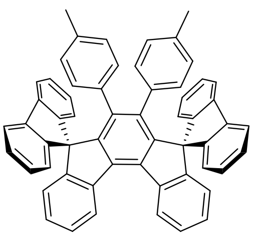


8,9-Bis(4-(trifluoromethyl)phenyl)benzo[c]benzo[6,7]indeno[1,2-*g*]fluorene-7,10-dione (40c). With **39c** (93 mg, 0.14 mmol) following the general procedure D. Column chromatography (2/1/1 hexanes/EtOAc/CH_2Cl_2) yielded 85 mg (92%) of the title compound as a red solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 6.9 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.37 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 2H), 7.30 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.67 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 145.0, 139.7, 139.2, 138.2, 138.0, 137.4, 133.9, 131.4, 130.6, 130.2, 130.01, 129.96, 129.7, 129.6, 129.0, 128.9, 128.5, 128.4, 126.6, 126.0, 117.5-125.5 (q, $^1J_{C\text{-}F}$ = 236.3 Hz), 125.4, 124.7 (q, $^2J_{C\text{-}F}$ = 3.5 Hz), 119.7; IR (KBr) ν_{max} 3072, 3041, 2920, 1711, 1605, 1469, 1404, 1329, 1170, 1127, 1067, 1019, 934, 855, 757, 721 cm^{-1} HRMS (*m/z*) for $C_{42}H_{21}O_2F_6$ (M + H) calcd: 671.14403, found: 671.14394; R_f (2/1 hexanes/EtOAc) = 0.42 (silica gel plate).

E: General procedure for creation of dispiroindeno[2,1-*c*]fluorenes (preparation of 23, 29, 34 and 41).[46] A solution of 2-bromobiphenyl (40 μL, 0.23 mmol) in anhydrous THF (3 mL) was cooled down to -78 °C and *n*-BuLi 1.6 M (140 μL, 0.23 mmol) was added dropwise. The resulted solution was stirred for 30 min, followed by the addition of fluorenone (0.07 mmol) in THF (3 mL) and stirred for 3h first for 15 min at -78 °C, but during time it was allowed to reach ambient temperature. The reaction mixture was poured in a saturated solution of $NaHCO_3$ solution and extracted with diethyl ether (3 x 15 mL). The combined organic fractions were dried over $MgSO_4$ and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (10/1 hexanes/EtOAc) to yield desired alcohols. The alcohols were dissolved in acetic acid (10 mL) with a catalytic amount of HCl (12 mol/L) and the resulted solution stirred under reflux for 3 h. The reaction mixture was neutralized with H_2O and K_2CO_3 and extracted with diethyl ether (3 x 15 mL). Column chromatography of the residue on silica gel provided products.

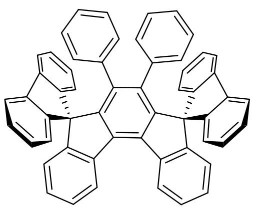


6',7'-bis(4-methoxyphenyl)dispirofluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene (23a). With **22a** (98 mg, 0.20 mmol) following the general procedure E. Column chromatography of the residue on silica gel (5/1/1 hexanes/EtOAc/CH_2Cl_2) provided 87 mg (57%) of the title compound as a colorless solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 7.9 Hz, 2H), 7.48 (dt, *J* = 7.9, 1.2 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 4H), 7.15 (dt, *J* = 7.4, 1.1 Hz, 4H), 7.13 (dt, *J* = 7.5, 0.9 Hz, 2H), 7.06 (dt, *J* = 7.5, 1.2 Hz, 4H), 6.91 (d, *J* = 7.4 Hz, 4H), 6.59 (dd, *J* = 7.6, 0.6 Hz, 2H), 5.73 (m, 4H), 5.57 (m, 4H), 3.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 150.5, 148.9, 147.1, 142.0, 141.4, 139.6, 136.4, 130.5, 128.8, 127.5, 127.1, 127.0, 126.9, 124.0, 123.7, 123.4, 119.7, 111.1, 66.2, 54.9; IR (KBr) ν_{max} 3040, 2953, 2931, 2827, 1612, 1516, 1465, 1447, 1418, 1283, 1243, 1174, 1106, 1036, 833, 765, 754, 740, 732 cm^{-1}; HRMS (*m/z*) for $C_{58}H_{38}O_2$ (M + H) calcd: 767.29446, found: 767.29447; R_f (1/1 hexanes/EtOAc) = 0.66 (silica gel plate).

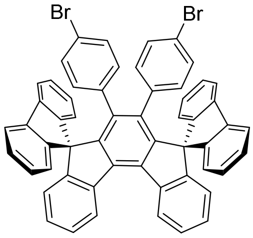


6',7'-Di-*p*-tolyldispirofluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene (23b). With **22b** (116 mg, 0.25 mmol) following the general procedure E. Column chromatography of the residue on silica gel (5/1/1 hexanes/EtOAc/CH_2Cl_2) provided 99 mg (56%) of the title compound as a colorless solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ

8.76 (d, *J* = 7.9 Hz, 2H), 7.47 (dt, *J* = 7.8, 1.2 Hz, 2H), 7.25-7.27 (m, 4H), 7.15 (dt, *J* = 7.4, 1.1 Hz, 4H), 7.12 (dt, *J* = 7.3, 0.9 Hz, 2H), 7.05 (dt, *J* = 7.5, 1.2 Hz, 4H), 6.90 (d, *J* = 7.5 Hz, 4H), 6.58 (dd, *J* = 7.6, 0.6 Hz, 2H), 5.96 (d, *J* = 7.8 Hz, 4H), 5.55 (m, 4H), 1.88 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.6, 148.9, 146.9, 142.0, 141.4, 139.7, 136.4, 133.3, 133.1, 129.3, 127.5, 127.1, 127.0, 126.8, 126.0, 124.0, 123.8, 123.4, 119.5, 66.2, 20.9; IR (KBr) ν_{max} 3042, 2917, 2866, 1600, 1510, 1446, 1415, 1367, 1282, 1244, 1155, 1109, 1020, 826, 810, 754, 741, 730 cm^{-1}; HRMS (*m/z*) for C$_{58}$H$_{39}$ (M + H) calcd: 735.30463, found: 735.30470; R_f (2/1 hexanes/EtOAc) = 0.56 (silica gel plate).

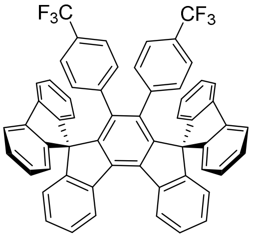


6',7'-Diphenyldispirofluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene (23c). With **22c** (109 mg, 0.25 mmol) following the general procedure E. Column chromatography of the residue on silica gel (5/1/1 hexanes/EtOAc/CH$_2$Cl$_2$) provided 108 mg (61%) of the title compound as a colorless solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.78 (d, *J* = 7.9 Hz, 2H), 7.49 (dt, *J* = 7.8, 1.2 Hz, 2H), 7.24-7.27 (m, 4H), 7.14 (m, 6H), 7.06 (dt, *J* = 7.5, 1.2 Hz, 4H), 6.93 (d, *J* = 7.2 Hz, 4H), 6.60 (dd, *J* = 7.6, 0.6 Hz, 2H), 6.42 (m, 2H), 6.18 (m, 4H), 5.67 (dd, *J* = 8.2, 1.2 Hz, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.5, 148.7, 146.4, 142.0, 141.3, 139.5, 136.6, 135.9, 129.6, 127.6, 127.2, 127.1, 126.9, 125.3, 124.3, 124.1, 123.8, 123.4, 119.7, 66.2; IR (KBr) ν_{max} 3058, 2953, 2927, 2866, 1601, 1463, 1445, 1412, 1367, 1155, 1071, 1029, 823, 753, 741, 702 cm^{-1}; HRMS (*m/z*) for C$_{56}$H$_{35}$ (M + H) calcd: 707.27333, found: 707.27344; R_f (2/1 hexanes/EtOAc) = 0.58 (silica gel plate).



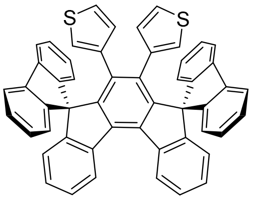
6',7'-Bis(4-bromophenyl)dispirofluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene (23d). With **22d** (59 mg, 0.1 mmol) following the general procedure E. Column chromatography of the residue on silica gel (5/1/1 hexanes/EtOAc/CH$_2$Cl$_2$) provided 58 mg (67%) of the title compound as a colorless solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.77 (d, *J* = 8.0 Hz, 2H), 7.50 (m, 2H), 7.34 (dd, *J* = 7.5, 0.7 Hz, 2H), 7.25 (m, 2H), 7.21 (dt, *J* = 7.5, 1.0 Hz, 2H), 7.20 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.13-7.18 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 4H), 6.91 (m, 4H), 6.62 (t, *J* = 7.6 Hz, 2H), 6.32 (m, 2H), 6.28 (m, 1H), 6.21 (m, 1H), 5.66 (m, 2H), 5.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.5, 150.2, 148.6, 148.5, 142.0, 141.9, 141.1, 131.1, 131.0, 129.6, 129.4, 128.6, 128.3, 127.8, 127.2, 127.0, 125.5, 125.3, 124.5, 124.0, 123.7, 123.5, 119.8; IR (KBr) ν_{max} 3041, 2932, 2839, 1601, 1485, 1446, 1414, 1386, 1282, 1155, 1072, 1011, 833, 756, 747, 738 cm^{-1}; HRMS (*m/z*) for

$C_{56}H_{32}Br_2$ (M + H) calcd: 863.09435, found: 863.09459; R_f (2/1 hexanes/EtOAc) = 0.62 (silica gel plate).

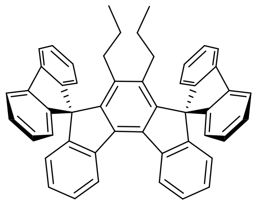


6',7'-Bis(4-(trifluoromethyl)phenyl)dispirofluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene (23e). With **22e** (57 mg, 0.10 mmol) following the general procedure E. Column chromatography of the residue on silica gel (5/1/1 hexanes/EtOAc/CH_2Cl_2) provided 69 mg (82%) of the title compound as a colorless solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 7.8 Hz, 2H), 7.53 (dt, J = 7.7, 1.1 Hz, 2H), 7.25 (d, J = 7.3 Hz, 4H), 7.17-7.19 (m, 6H), 7.09 (dt, J = 7.5, 1.2 Hz, 4H), 6.94 (d, J = 7.5 Hz, 4H), 6.64 (dd, J = 7.6, 0.5 Hz, 2H), 6.46 (d, J = 8.0 Hz, 4H), 5.80 (d, J = 7.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 148.1, 146.8, 141.9, 140.9, 139.3, 137.3, 137.2, 129.7, 122.0-129.1 (q, $^1J_{C\text{-}F}$ = 271.9 Hz), 128.1, 127.4, 127.3, 124.2, 123.8, 123.6, 122.4 (q, $^2J_{C\text{-}F}$ = 3.8 Hz), 119.9, 66.0; IR (KBr) ν_{max} 3064, 3023, 2932, 2839, 1617, 1448, 1404, 1328, 1168, 1121, 1109, 1065, 1020, 850, 841, 756, 745, 736 cm^{-1}; HRMS (*m/z*) for $C_{58}H_{33}F_6$ (M + H) calcd: 843.24810, found: 843.24886; R_f (2/1 hexanes/EtOAc) = 0.60 (silica gel plate).

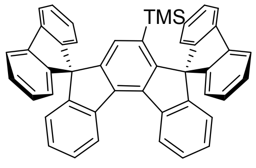
6',7'-Di(thiophen-3-yl)dispirofluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene (23f).



With **22f** (45 mg, 0.1 mmol) following the general procedure E. Column chromatography of the residue on silica gel (5/1/1 hexanes/EtOAc/CH_2Cl_2) provided 38 mg (53%) of the title compound as a colorless solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 7.9 Hz, 2H), 7.50 (dt, J = 7.6, 1.0 Hz, 4H), 7.40 (m, 2H), 7.24 (m, 2H), 7.15 (t, J = 7.4 Hz, 4H), 6.85-7.03 (m, 8H), 6.63 (d, J = 7.3 Hz, 2H), 6.19 (s, 2H), 5.39 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 148.2, 147.3, 142.0, 141.2, 136.9, 136.1, 135.1, 128.7, 127.8, 127.2, 127.1, 124.1, 123.5, 123.0, 122.5, 121.2, 119.8, 66.2; IR (KBr) ν_{max} 3062, 2949, 2871, 1598, 1464, 1447, 1349, 1281, 1225, 1154, 1069, 1005, 857, 803, 750, 739, 724, 390, 368 cm^{-1}; HRMS (*m/z*) for $C_{52}H_{31}S_2$ (M + H) calcd: 719.18617, found: 719.18622; R_f (2/1 hexanes/EtOAc) = 0.56 (silica gel plate).

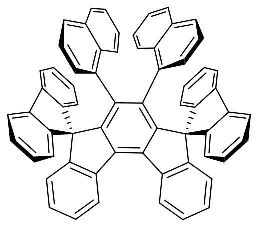


6',7'-Dipropyldispirofluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene (23g). With **22g** (37 mg, 0.1 mmol) following the general procedure E. Column chromatography of the residue on silica gel (5/1/1 hexanes/EtOAc/CH_2Cl_2) provided 38 mg (59%) of the title compound as a colorless solid: mp (decomp) 218-223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 7.9 Hz, 2H), 7.87 (d, J = 7.6 Hz, 4H), 7.42 (dt, J = 7.9, 1.2 Hz, 2H), 7.39 (dt, J = 7.5, 1.1 Hz, 4H), 7.15 (dt, J = 7.5, 1.1 Hz, 4H), 7.09 (dt, J = 7.6,0.8 Hz, 2H), 6.92 (d, J = 7.6 Hz, 4H), 6.58 (dd, J = 7.6, 0.7 Hz, 2H), 1.65 (m, 4H), 0.45 (m, 4H), 0.21 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 149.4, 146.7, 141.6, 141.4, 138.8, 135.7, 127.8, 127.5, 127.1, 126.9, 124.2, 123.6, 123.0, 120.0, 66.6, 30.3, 23.8, 14.5; IR (KBr) ν_{max} 3063, 3034, 3016, 2958, 2926, 2868, 1595, 1577, 1466, 1447, 1413, 1373, 1281, 1153, 1084, 1027, 752, 739 cm^{-1}; HRMS (*m/z*) for $C_{50}H_{39}$ (M + H) calcd: 639.30463, found: 639.30476; R_f (2/1 hexanes/EtOAc) = 0.59 (silica gel plate).



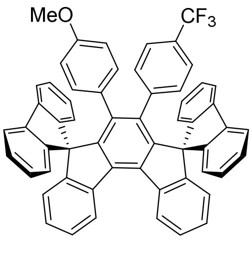
Dispirofluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluoren-6'-yltrimethylsilane (23h). With **22h** (42 mg, 0.12 mmol) following the general procedure E. Column chromatography of the residue on silica gel (5/1/1 hexanes/EtOAc/CH_2Cl_2) provided 39 mg (52%) of the title compound as a colorless solid: mp (decomp) 254-259 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 7.9 Hz, 1H), 8.32 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.74 (dd, J = 7.3, 0.5 Hz, 2H), 7.65 (dt, J = 7.6, 1.2 Hz, 2H), 7.44-7.52 (m, 4H), 7.37-7.42 (m, 4H), 7.20 (dt, J = 7.5, 1.0 Hz, 2H), 7.14 (dt, J = 7.5, 1.0 Hz, 2H), 7.00 (m, 1H), 6.78 (m, 3H), 6.71 (s, 1H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 149.9, 148.4, 144.9, 141.7, 140.4, 140.2, 138.4, 134.7, 134.5, 130.1, 128.81, 128.75, 128.0, 127.9, 127.8, 124.5, 124.3, 124.1, 123.9, 123.6, 120.2, -1.1; IR (KBr) ν_{max} 3065, 2956, 2930, 2861, 1604, 1549, 1465, 1449, 1413, 1347, 1285, 1245, 1151, 1081, 982, 932, 868, 842, 755, 734, 705 cm^{-1}; HRMS (*m/z*) for $C_{473}H_{35}Si$ (M + H) calcd: 626.24235, found: 626.24239; R_f(2/1 hexanes/EtOAc) = 0.64 (silica gel plate).

6',7'-Di(naphthalen-1-yl)dispiro[fluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene]

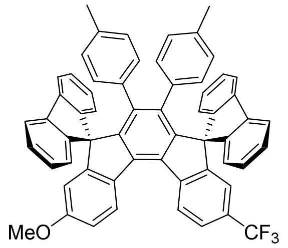


(23i). With **22i** (134 mg, 0.25 mmol) following the general procedure E. Column chromatography of the residue on silica gel (10/1/1 hexanes/EtOAc/CH_2Cl_2) provided 109 mg (54%) of the title compound as a colorless solid: mp (decomp) >260 °C; Due to lack of solubility in commom deuterated solvents only weak signals for ^{1}H and ^{13}C NMR were detectable: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, J = 7.9 Hz, 2H), 7.52 (dt, J = 7.9, 0.6 Hz, 2H), 7.06-7.23 (m, 12H), 6.85-6.93 (m, 6H), 6.80 (d, J = 7.7 Hz, 4H), 6.67 (d, J = 7.6 Hz, 2H), 6.58 (d, J = 7.5 Hz, 2H), 6.52 (dt, J = 7.5, 0.7 Hz, 2H), 6.38 (dt, J = 7.5, 1.0 Hz, 2H), 6.02 (t, J = 7.4 Hz, 2H), 5.59 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 149.8, 147.6, 145.6, 142.3, 141.3, 140.7, 137.4, 137.4, 132.9, 131.6, 131.4, 127.8, 127.3, 127.2, 127.1, 127.0, 126.7, 126.5, 126.2, 125.9, 124.1, 123.8, 123.7, 123.5, 123.0, 119.9, 118.4, 76.79, 66.3, 60.3; IR (KBr) ν_{max} 3059, 3038, 3010, 2959, 1601, 1508, 1447, 1379, 1364, 1282, 1158, 1030, 1005, 943, 800, 778, 752, 739, 727 cm^{-1}; HRMS (*m/z*) for $C_{64}H_{39}$ (M + H) calcd: 807.30463, found: 807.30505; R_f (2/1 hexanes/EtOAc) = 0.65 (silica gel plate).

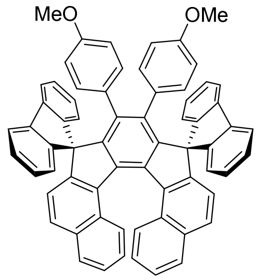
6'-(4-Methoxyphenyl)-7'-(4-(trifluoromethyl)phenyl)dispirofluorene-9,5'-indeno[2,1-*c*]-fluorene-8',9''-fluorene



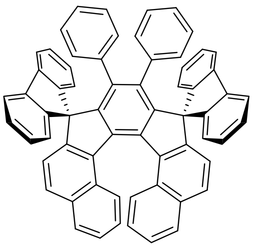
(29). With **28** (53 mg, 0.10 mmol) following the general procedure E. Column chromatography of the residue on silica gel (5/1/1 hexanes/EtOAc/CH_2Cl_2) provided 69 mg (82%) of the title compound as a colorless solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 7.9 Hz, 2H), 7.51 (t, J = 7.7 Hz, 2H), 7.32 (d, J = 7.6 Hz, 2H), 7.25 (d, J = 6.4 Hz, 2H), 7.14-7.20 (m, 6H), 7.08 (t, J = 7.5 Hz, 4H), 6.92 (d, J = 7.6 Hz, 4H), 6.62 (d, J = 7.6 Hz, 2H), 6.44 (d, J = 7.9 Hz, 2H), 5.81 (d, J = 7.9 Hz, 2H), 5.75 (d, J = 8.3 Hz, 2H) 5.58 (d, J = 8.3 Hz, 2H) 3.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 150.5, 150.1, 148.6, 148.4, 147.4, 146.5, 142.0, 141.9, 141.2, 140.0, 138.6, 138.3, 137.0, 136.7, 130.4, 129.8, 128.0, 127.82, 127.80, 127.31, 127.28, 127.2, 127.12, 127.07, 124.1, 123.8, 123.5-131.7 (q, $^1J_{C\text{-}F}$ = 271.9 Hz), 123.7, 123.53, 123.49, 122.2 (q, $^2J_{C\text{-}F}$ = 3.8 Hz), 119.8, 119.7, 111.3, 66.2, 66.0, 54.9; IR (KBr) ν_{max} 3062, 3037, 2951, 2831, 1614, 1510, 1465, 1448, 1418, 1323, 1244, 1165, 1119, 1107, 1070, 1019, 846, 829, 756, 738 cm^{-1}; HRMS (*m/z*) for $C_{58}H_{36}OF_3$ (M + H) calcd: 805.27128, found: 805.27179; R_f (2/1 hexanes/EtOAc) = 0.64 (silica gel plate).



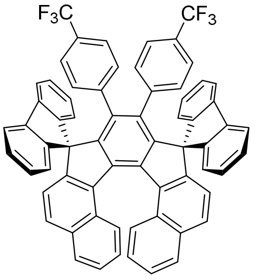
3'-Methoxy-6',7'-di-*p*-tolyl-10'-(trifluoromethyl)dispirofluorene-9,5'-indeno[2,1-*c*]fluorene-8',9''-fluorene (34). With **33** (30 mg, 0.05 mmol) following the general procedure E. Column chromatography of the residue on silica gel (5/1/1 hexanes/EtOAc/CH_2Cl_2) provided 35 mg (84%) of the title compound as a colorless solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, J = 8.3 Hz, 1H), 8.58 (d, J = 8.7 Hz, 1H), 7.71 (dd, J = 8.2, 0.9 Hz, 1H), 7.25 (m, 5H), 7.13-7.19 (m, 4H), 7.06 (m, 4H), 6.90 (d, J = 7.7 Hz, 2H), 6.88 (d, J = 7.7 Hz, 2H), 6.79 (s, 1H), 6.10 (d, J = 2.5 Hz, 1H), 5.96 (d, J = 7.9 Hz, 4H), 5.52 (dd, J = 8.0, 2.5 Hz, 4H), 3.64 (s, 3H), 1.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 152.9, 151.0, 148.7, 147.8, 147.5, 147.0, 145.1, 142.1, 142.0, 137.0-141.7 (q, $^1J_{C\text{-}F}$ = 267.7 Hz), 133.8, 133.7, 133.4, 132.8, 132.7, 129.2, 129.1, 127.1, 127.0, 126.9, 126.0, 125.9, 124.5, 124.1, 123.8, 123.7, 123.6, 123.0, 120.8 (q, $^2J_{C\text{-}F}$ = 3.2 Hz), 119.7, 119.5, 113.2, 109.3, 66.2, 66.1, 55.4, 29.7, 20.9; IR (KBr) ν_{max} 3067, 3039, 3018, 2920, 2834, 1605, 1518, 1481, 1447, 1369, 1329, 1266, 1242, 1166, 1126, 1078, 1033, 814, 740, 729 cm^{-1}; HRMS (*m/z*) for $C_{60}H_{39}OF_3$ (M + Na) calcd: 855.28452, found: 855.28494; R_f (2/1 hexanes/EtOAc) = 0.68 (silica gel plate).



8',9'-Bis(4-methoxyphenyl)dispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-*g*]-fluorene-10',9''-fluorene] (41a). With **40a** (59 mg, 0.1 mmol) following the general procedure E. Column chromatography of the residue on silica gel (5/1/1 hexanes/EtOAc/CH_2Cl_2) provided 67 mg (78%) of the title compound as a slight orange solid: mp (decomp) >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 7.4 Hz, 2H), 7.33 (d, J = 7.4 Hz, 2H), 7.30 (d, J = 7.3 Hz, 4H), 7.22 (m, 4H), 7.06 (t, J = 7.5 Hz, 2H), 6.92 (t, J = 7.5 Hz, 2H), 6.75 (m, 4H), 6.71 (d, J = 7.6 Hz, 2H), 5.89 (dd, J = 8.4, 2.7 Hz, 2H), 5.75 (dd, J = 8.3, 2.4 Hz, 2H), 5.68 (m, 4H), 3.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 148.4, 148.1, 147.6, 147.3, 142.7, 142.0, 138.9, 137.8, 136.2, 133.3, 131.4, 129.8, 129.6, 128.9, 128.8, 128.1, 127.34, 127.30, 127.2, 127.0, 126.9, 125.0, 124.4, 124.0, 123.8, 121.3, 120.2, 119.5, 111.5, 111.1, 66.9, 54.9; IR (KBr) ν_{max} 3052, 3052, 2832, 1611, 1516, 1448, 1364, 1285, 1244, 1175, 1107, 1035, 815, 739 cm^{-1}; HRMS (*m/z*) for $C_{66}H_{43}O_2$ (M + H) calcd: 867.32576, found: 867.32593; R_f (2/1 hexanes/EtOAc) = 0.52 (silica gel plate).



8',9'-Diphenyldispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-*g*]fluorene-10',9''-fluorene] (41b). With **40b** (53 mg, 0.1 mmol) following the general procedure E. Column chromatography of the residue on silica gel (5/1/1 hexanes/EtOAc/CH_2Cl_2) provided 61 mg (76%) of the title compound as a slight orange solid: mp (decomp) >260 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.5, 0.5 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.44 (m, 2H), 7.30-7.34 (m, 4H), 7.20-7.24 (m, 6H), 7.04 (dt, *J* = 7.5, 1.0 Hz, 2H), 6.91 (dt, *J* = 7.6, 1.1 Hz, 2H), 6.67-6.77 (m, 6H), 6.48 (m, 2H), 6.33 (m, 2H), 6.17 (m, 2H), 5.76 (dt, *J* = 6.9, 1.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 148.0, 147.5, 146.7, 146.6, 142.7, 141.9, 138.8, 137.7, 136.4, 135.9, 133.4, 130.3, 129.64, 129.61, 129.0, 128.9, 128.1, 127.4, 127.3, 127.0, 126.9, 125.6, 125.3, 125.1, 124.5, 124.4, 124.0, 123.8, 121.3, 120.2, 119.9, 119.6, 67.8.; IR (KBr) ν_{max} 3049, 3018, 2956, 2922, 2853, 1602, 1515, 1446, 1280, 1239, 1215, 1177, 1149, 1032, 810, 741, 696 cm^{-1}; HRMS (*m/z*) for $C_{64}H_{39}$ (M + H) calcd: 807.30463, found: 807.30471; R_f (2/1 hexanes/EtOAc) = 0.56 (silica gel plate).



8',9'-Bis(4-(trifluoromethyl)phenyl)dispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-*g*]-fluorene-10',9''-fluorene] (41c). With **40c** (67 mg, 0.1 mmol) following the general procedure E. Column chromatography of the residue on silica gel (5/1/1 hexanes/EtOAc/CH_2Cl_2) provided 74 mg (79%) of the title compound as a slight orange solid: mp (decomp) >260 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.4, 4.6 Hz, 4H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.36 (dt, *J* = 7.5, 1.0 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.21-7.28 (m, 6H), 7.09 (dt, *J* = 7.5, 0.7 Hz, 2H), 6.93 (dt, *J* = 7.5, 0.7 Hz, 2H), 6.76 (m, 4H), 6.70 (d, *J* = 7.6 Hz, 2H), 6.61 (d, *J* = 7.7 Hz, 2H), 6.45 (d, *J* = 7.9 Hz, 2H), 5.90 (t, *J* = 7.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 147.3, 146.9, 146.8, 142.6, 141.8, 139.3, 138.4, 137.0, 135.4, 133.4, 130.4, 129.7, 129.5, 129.1, 128.9, 128.2, 128.1, 127.8, 127.5, 127.4, 127.2, 127.1, 127.0, 126.8, 125.3, 125.2, 124.6, 124.0, 123.9, 122.6 (q, $^2J_{C\text{-}F}$ = 3.4 Hz), 121.2, 120.4, 119.8, 66.6; IR (KBr) ν_{max} 3056, 2922, 2866, 1619, 1446, 1405, 1325, 1246, 1166, 1125, 1079, 1018, 810, 738 cm^{-1}; HRMS (*m/z*) for $C_{66}H_{37}F_6$ (M + H) calcd: 943.27940, found: 943.27954; R_f (2/1 hexanes/EtOAc) = 0.58 (silica gel plate).

6.3.4. X-ray analysis of dispiroindeno[2,1-*c*]fluorenes

Crystallographic data was collected on Bruker D8 VENTURE Kappa Duo PHOTON100 by IμS micro-focus sealed tube at a temperature 150 K. The structures were solved by direct methods (XP) and refined by full matrix least squares based on F^2 (SHELXL2014).[69] The hydrogen atoms on carbons were fixed into idealised positions (riding model) and assigned temperature factors either $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or 1.5 for methyl moiety. PLATON/ SQUEEZE (Spek, A. L., *Acta Crystallographica Section D-Biological Crystallography* **2009**, *65*, 148) procedure was used to correct the diffraction data of **41** for the presence of the disordered solvents.

Table Exp9. X-ray crystallographic data for indenofluorenes **23b**, **40a**, and **41a**

	23b	**40a**	**41a**
Formula	$C_{58}H_{38}$	$C_{42}H_{26}O_2$	$C_{66}H_{42}O_2$
M.w.	734.88	594.63	866.99
λ [Å]	0.71073	0.71073	1.54178
Crystal system	monoclinic	triclinic	orthorhombic
Space group [No.]	$P2_1/n$ (No. 14)	P -1 (No. 2)	$Pna2_1$ (No 33)
a [Å]	13.4315(4)	9.7309(3)	16.3016(5)
b [Å]	13.7634(3)	12.1645(4)	13.3191(4)
c [Å]	20.9116(5)	14.1640(5)	21.3258 (6)
a [°]		65.993(1)	
β [°]	98.4780(10)	86.855(1)	
γ [°]		86.512(1)	
Z	4	2	4
V $[Å^3]$	3823.54(17)	1527.91(9)	4630.3(2)
D_x [g cm^{-3}]	1.277	1.293	1.244
Crystal size [mm]	0.09×0.20×0.19	0.09×0.27×0.28	0.03×0.17×0.52
Crystal color, shape	a colorless prism	a red plate	a colorless bar
μ [mm^{-1}]	0.072	0.082	0.567
$T_{\min}$, $T_{\max}$	0.89, 0.99	0.96, 0.98	0.88, 0.98
Measured reflections	41342	33305	41883
Independent diffract. (R_{int} [a])	7545 (0.034)	7039 (0.024)	8955 (0.029)
Observed diffract. [I>2σ(I)]	6313	6085	8711
No. of parameters	525	417	615
R^b	0.044	0.041	0.029
$wR(F^2)$ for all data	0.120	0.111	0.071
GOF[c]	1.04	1.03	1.05
Residual electron density [e/Å^3]	0.41, -0.24	0.27, -0.31	0.25, -0.18
CCDC no.	1548067	1548069	1548068

[a] $R_{\text{int}} = \Sigma \left| F_o^2 - F_{o,\text{mean}}^2 \right| / \Sigma F_o^2$

[b] $R(F) = \Sigma \left| |F_o| - |F_c| \right| / \Sigma |F_o|$, $wR(F^2) = [\Sigma (w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$. [c] $\text{GOF} = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{\text{diffrs}} - N_{\text{params}})]^{1/2}$

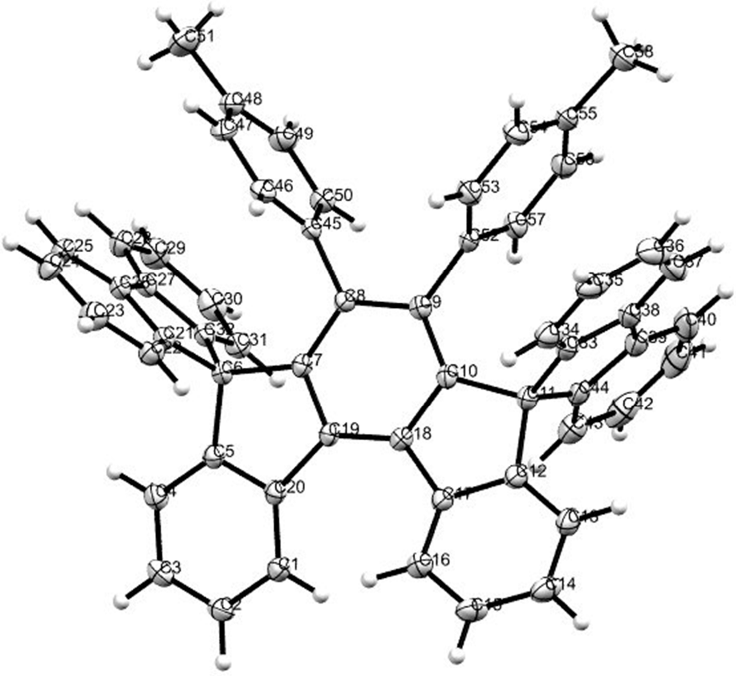


Figure Exp14. Platon plot of **23b** showing displacement ellipsoids at a 50% probability level

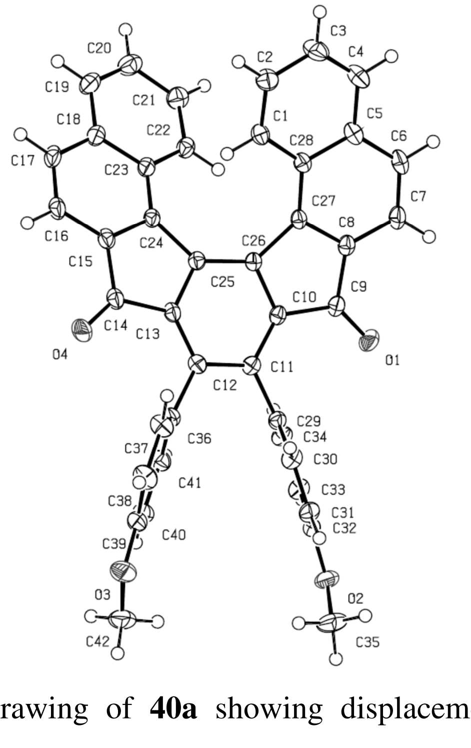


Figure Exp15. PLATON drawing of **40a** showing displacement ellipsoids on the 50% probability level

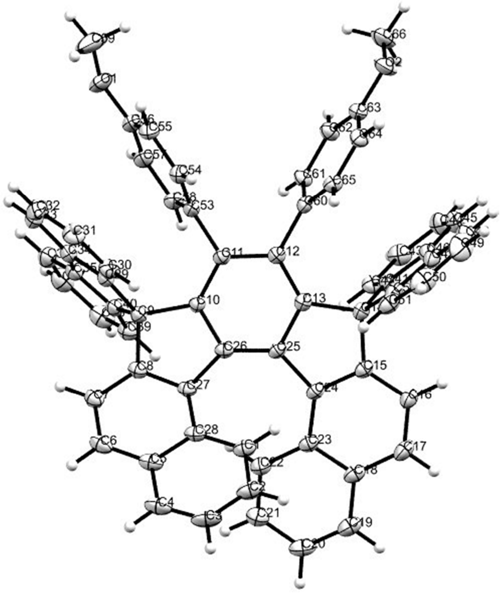


Figure Exp16. PLATON drawing of **41a** showing displacement ellipsoids on the 50% probability level

6.3.5. Photophysical analysis of dispiroindeno[2,1-*c*]fluorenes

Chemicals.

9,10-Diphenylanthracene (DPA) was purchased from Sigma-Aldrich.

The UV/Vis absorption spectra were recorded using Unicam 340 spectrometer. Corrected steady-state emission spectra were recorded on an Aminco Bowman (AB2) spectrometer.

Quantum yields of fluorescence of a sample (Φ_s) were calculated relative to DPA (Φ_{ref} = 0.97 in cyclohexane) as a reference. Φ_s was determined according to the following equation:[70]

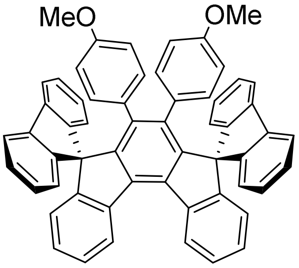
$$\Phi_s = \Phi_{ref} \times A_s / A_{ref} \qquad (1)$$

where A_s and A_{ref} represent integrated areas of the emission (in arbitrary units) of a sample and the reference, respectively.

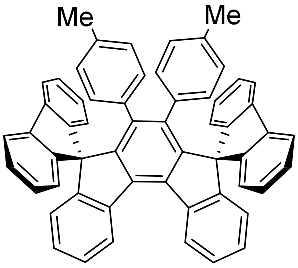
Micromolar solutions of the reference (DPA) and the samples were prepared in cyclohexane. The absorption of the reference and the samples were the same at the selected excitation wavelength ($A \leq 0.1$). Quantum yields were calculated from 5 independent measurments. The average value is reported.

The emission quantum yields (Φ_s) of the derivatives were determined in cyclohexane by standard procedures with DPA as reference (see Figures Exp17-19 and Tables Exp10-12).

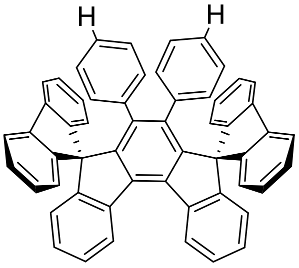
UV/Vis absorption and emission spectra of 23a-i.



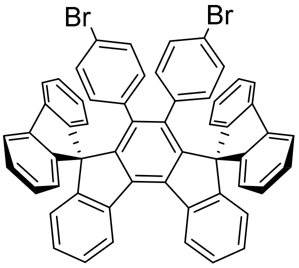
23a



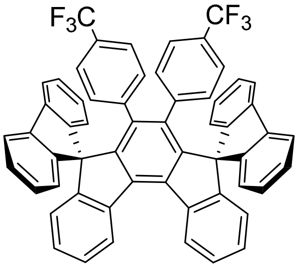
23b



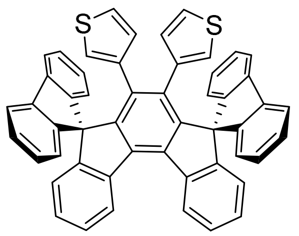
23c



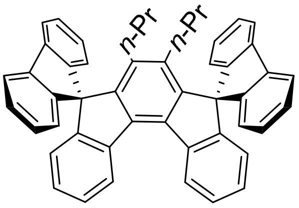
23d



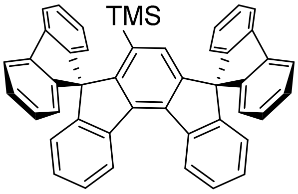
23e



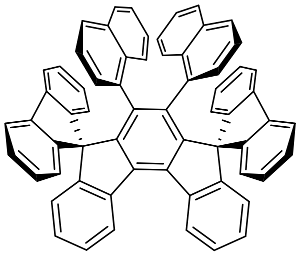
23f



23g



23h



23i

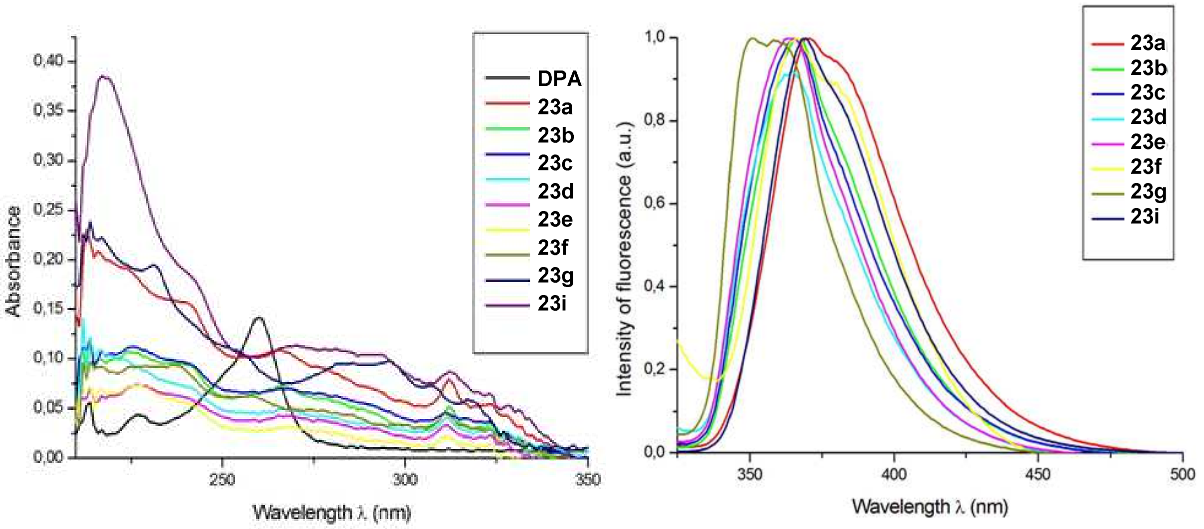


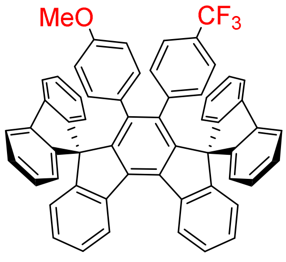
Figure Exp17. Absorption spectra of 10^{-6} M DPA and **23a-i** in cyclohexane (left). Normalized and corrected emission spectra of 10^{-6} M samples in cyclohexane. Excitation λ = 264-271 nm (right).

Table Exp10. Photophysical properties of **23a-i** derivatives in cyclohexane

Sample	λ_{abs}/nm (ε /10^5 mol^{-1} dm^3 cm^{-1})	λ_{exc} /nm	λ_{em} /nm	Φ_s[a]
23a	213 (0.2), 240 (sh), 265 (0.1), 612 (0.08)	264	370, 380	0.31
23b	207 (0.1), 240 (sh), 267 (0.07), 312 (0.05)	266	366	0.09
23c	225 (0.1), 239 (sh), 266 (0.07), 311 (0.05)	266	366	0.67
23d	217 (0.1), 223 (sh), 266 (0.05), 312 (0.04)	269	365	0.33
23e	226 (0.07), 239 (sh), 268 (0.04), 311 (0.03)	269	364	0.70
23f	226 (0.07), 238 (sh), 268 (0.03), 312 (0.02)	271	366, 380	0.20
23g	237 (0.09), 258 (sh), 277 (sh), 311 (0.05)	269	351, 359	0.63
23h	214 (0.2), 231 (sh), 282 (sh), 296 (0.1)	266	-	0.00
23i	217 (0.4), 242 (sh), 268 (0.1), 312 (0.09)	264	369	0.28

[a] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

UV/Vis absorption and emission spectra of 29 and 34.



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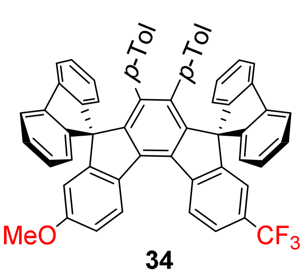


34

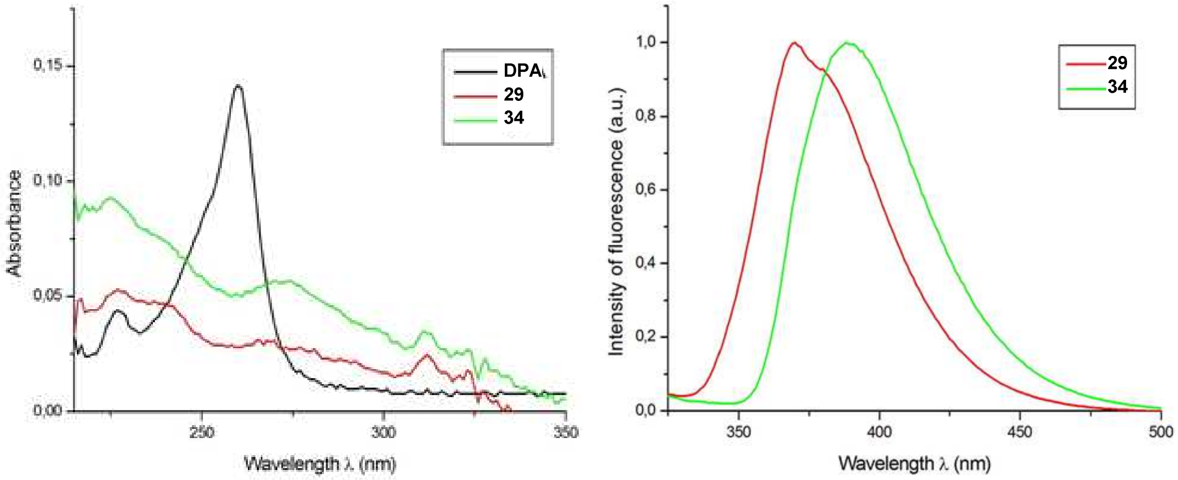


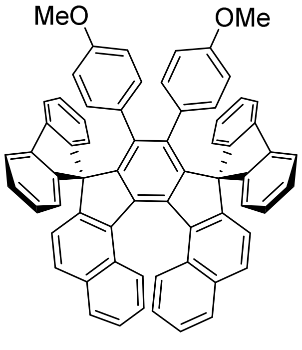
Figure Exp18. Absorption spectra of 10^{-6} M DPA, **29** and **34** in cyclohexane (left). Normalized and corrected emission spectra of 10^{-6} M samples in cyclohexane. Excitation λ = 268-272 nm (right).

Table Exp11. Photophysical properties of **29** and **34** in cyclohexane

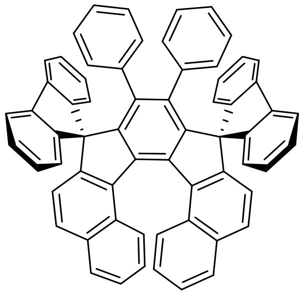
Sample	λ_{abs}/nm (ε /10^5 mol^{-1} dm^3 cm^{-1})	λ_{exc} /nm	λ_{em} /nm	Φ_s[a]
29	227 (0.05), 238 (sh), 266 (sh), 312 (0.03)	272	370	0.54
34	225 (0.09), 236 (sh), 274 (0.06), 311 (0.04)	268	389	0.60

[a] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

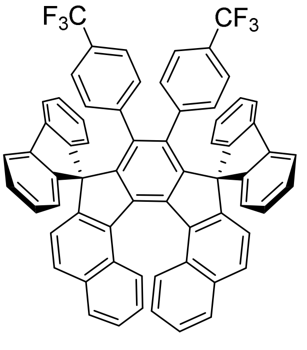
UV/Vis absorption and emission spectra of 41a-c.



41a



41b



41c

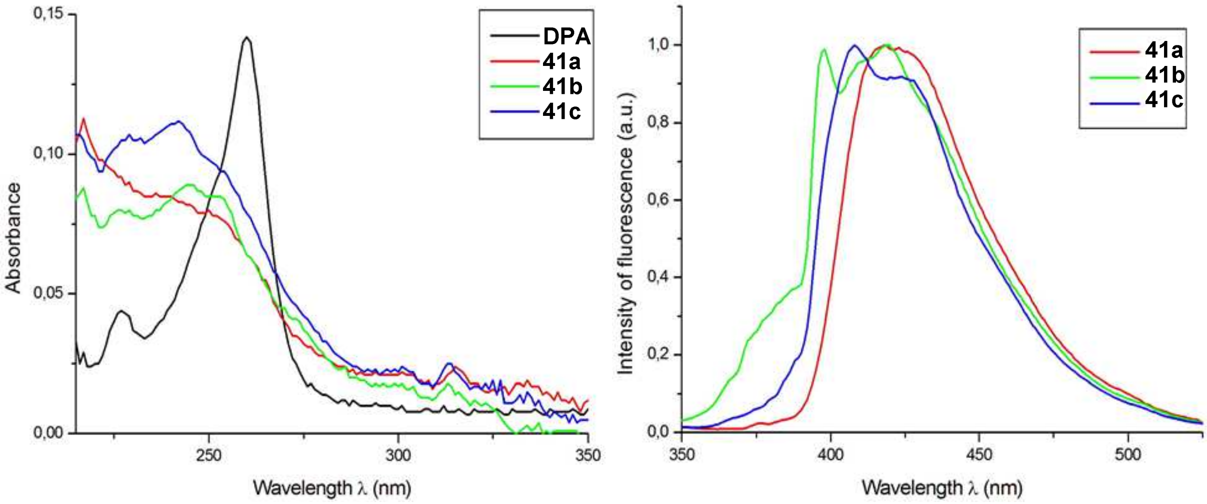


Figure Exp19. Absorption spectra of 10^{-6} M DPA and samples **41a-c** in cyclohexane (left). Normalized and corrected emission spectra of 10^{-6} M samples in cyclohexane. Excitation λ = 266-269 nm (right).

Table Exp12. Photophysical properties of **41a-c** derivatives in cyclohexane

Sample	λ_{abs}/nm (ε /10^5 mol^{-1} dm^3 cm^{-1})	λ_{exc} /nm	λ_{em} /nm	Φ_s[a]
41a	217 (0.1), 240 (sh), 315 (0.02)	269	418, 428	0.75
41b	217 (0.09), 225 (sh), 245 (0.09), 314 (0.02)	269	398, 419	0.87
41c	229 (sh), 242 (0.1), 314 (0.03)	269	408,423	0.88

[a] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

7. Author’s publications

Author’s Publications relevant to This Thesis

1. **A [2+2+2] Cyclotrimerization Approach to Selectively Substituted Fluorenes and Fluorenols, and Their Conversion to 9,9’- Spirobifluorenes**
   R. P. Kaiser, F. Hessler, J. Mosinger, I. Císařová, M. Kotora; *Chem. Eur. J.,* **2015**, *21*, 13577.
2. **Synthesis of selectively 4-substituted 9,9’-spirobifluorenes and modulation of their photophysical properties**
   R. P. Kaiser, J. Mosinger, I. Císařová, M. Kotora; *Org. Biomol. Chem.*, **2017**, *15*, 6913.

Other Publications

1. **Selective Borylation of [4]-helicene**
   D. Nečas, R. P. Kaiser, J. Ulč; *Eur. J. Org. Chem.,* **2016**, *21*, 5647.
2. **Direct regioselective C–H borylation of [5]-helicene**
   R. P. Kaiser, J. Ulč, I. Císařová, D. Nečas; *RSC Adv.*, **2018**, *8*, 580

8. Abstrakt

Disertační práce je rozdělena do dvou částí zabývajících se syntézou a analýzou strukturně příbuzných (i) 9,9´-spirobifluorenů (SBFs) a (ii) dispiroindeno[2,1-*c*]fluorenů (DS-IFs).

Disertační práce je rozdělena do dvou částí zaměřených na syntézu a fotofyzikální analýzu dvou skupin strukturně příbuzných látek: (i) 9,9´-spirobifluorenů (SBFs) a (ii) dispiroindeno[2,1-*c*]fluorenů (DS-IFs).

(i) V první části byla vyvinuta nová pětikroková syntéza SBFs, kde klíčovým krokem byla Rh-komplexy katalyzovaná [2+2+2] cyklotrimerizace symetricky či nesymetricky substituovaných diyn alkoholů s alkyny. Optimalizací této reakce (katalyzátor, teplota, čas, rozpouštědlo atd.) byly nalezeny ideální podmínky pro přípravu 1,2,3,4-substituovaných fluorenolů (klíčové intermediáty) a jako nejefektivnější se ukázal být Wilkinsonův katalyzátor ($RhCl(PPh_3)_3$). Tyto různě substituované fluorenoly byly následně ve dvou krocích převedeny na 19 nových SBFs, u kterých byl zkoumán vliv substituentu (elektronakceptorní, elektrondonorní) v poloze 4 na jejich spektroskopické vlastnosti. Získaná data ukazují emisní maxima λ_{em} v rozsahu 315 až 389 nm s excelentními kvantovými výtěžky Φ_s (až 1).

(ii) V druhé části byla tato nová metoda pro přípravu SBFs aplikována na přípravu DS-IFs. Rh-katalyzovaná [2+2+2] cyklotrimerizace triyndiolů poskytla indeno[2,1-*c*]fluorendioly ve vysokých výtěžcích. Tyto byly opět ve dvou krocích převedeny na odpovídající DS-IFs. Celkem bylo připraveno 9 symetricky substituovaných DS-IFs (pozice 6 a 7) a 2 nesymetricky substituované DS-IFs (pozice 3 a 10). Pro potvrzení syntetického potenciálu této reakční sekvence byly připraveny také 3 [7]helikální DS-IFs. Spektroskopická analýza všech produktů poskytla emisní maxima v rozsahu 351 až 428 nm s excelentními kvantovými výtěžky Φ_s (až 0.8). [7]helikální DS-IFs mají navíc nejvyšší dosud naměřené hodnoty kvantových výtěžků Φ_s pro tento tip látek.

9. Abstract

This work is divided into two parts that are focused on the synthesis and assessment of photophysical properties of two structurally related compounds: (i) 9,9´-spirobifluorenes (SBFs) and (ii) dispiroindeno[2,1-*c*]fluorenes (DS-IFs).

(i) In the first part, a five-step synthetic approach to SBFs was developed and as the crucial step was used an intermolecular [2+2+2] cyclotrimerization of symmetrically or unsymmetrically substituted diynols with alkynes catalyzed by Rh-complexes. Catalyst screening showed that Wilkinson's catalyst ($RhCl(PPh_3)_3$) had the highest efficiency in yielding 1,2,3,4-substituted fluorenols – the key intermediates. The fluorenols were then converted into SBFs bearing various electron-donating and -withdrawing groups, aromatic substituents, and π-extended aromatic hydrocarbon moieties (PAHs). Altogether 19 different SBFs were prepared and their photophysical properties screened. The fluorescent emission maxima λ_{em} were in the range of 315-389 nm with excellent quantum yields Φ_s (up to 1.00). As far as the substituent effect is concerned the presence of electron-withdrawing substituents on the SBF scaffold results in the red-shift of the emission maxima.

(ii) In the second part, a similar synthetic strategy was applied for synthesis DS-IFs. In this instance was utilized again the Rh-complex catalyzed intramolecular [2+2+2] cyclotrimerization of triyndiols, which provided indeno[2,1-*c*]fluorenr-5,8-diols in high yields. These were then converted into the corresponding DS-IFs. In total, 9 symmetrically substituted DS-IFs at positions 6 and 7 and 2 unsymmetrically substituted DS-IFs at positions 3 and 10 were synthesized. Furthermore, to demonstrate the potential of this synthetic approach, three [7]-helical DS-IFs were prepared. Photophysical properties of all compounds were evaluated as well. Their fluorescent emission maxima λ_{em} were in the range of 351-428 nm with excellent quantum yields Φ_s (up to 0.80). [7]-helical DS-IFs have the highest measured quantum yields among the class of helicene like compounds recorded thus far.

10. List of Abbreviations

DMAP	*N,N′*-Dimethylamino pyridine
DMA	*N,N′*-Dimethylacetamide
DMF	*N,N′*-Dimethylformamide
DPA	9,10-Diphenylanthracene
Et	Ethyl
eq	Equivalent
Fc	Ferrocenyl
h	Hour
HRMS	High Resolution Mass Spectroscopy
Hz	Hertz
IR	Infrared Spectroscopy
J	Coupling constant
LDA	Lithium diisopropylamide
Me	Methyl
mp	Melting Point
MS	Molecular sieve
NMR	Nuclear Magnetic Resonance
p-Tol	*para*-Tolyl
PCC	Pyridinium chlorochromate
PEPPSI^{TM}	Pyridine–enhanced precatalyst preparation stabilization and initiation ([1,3-Bis(2,6-Diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl) palladium(II) dichloride)
Ph	Phenyl
ppm	Parts per million
n-Pr	*n*-Propyl
THF	Tetrahydrofuran
TLC	Thin layer chromatography
UV	Ultraviolet

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