CHARLES UNIVERSITY

Faculty of Science

Department of Organic and Nuclear Chemistry

Organic chemistry

Diastereoselektivní syntéza helikálně chirálních látek pro enantioselektivní katalýzu

Diastereoselective synthesis of helically chiral compounds for enantioselective catalysis

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Ph.D. Thesis

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Prohlášení:

Prohlašuji, že jsem závěrečnou práci zpracovala samostatně a že jsem uvedla všechny použité informační zdroje a literaturu. Tato práce ani její podstatná část nebyla předložena k získání jiného nebo stejného akademického titulu.

V Praze dne 28.3.2012 Angelina Andronova

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ABBREVIATIONS AND SIGNS

Ac	acetyl
AIBN	azobisisobutyronitrile
Ar	aryl
BDMIM	1-butyl-2,3-dimethylimidazolium
Bu	butyl
cat.	catalytic amount
CD	circular dichroism
cod	1,5-cyclooctadiene
Cp	cyclopentadienyl
m-CPBA	*meta*-chloroperoxybenzoic acid
Cy	cyclohexyl
dba	dibenzylideneacetone
DCE	1,2-dichloroethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
de	diastereomeric excess
DFT	density functional theory
DIAD	diisopropyl azodicarboxylate
DIPA	diisopropylamine
DIPEA	*N*,*N*-diisopropylethylamine
DMAP	4-(dimethylamino)pyridine
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
dr	diastereomeric ratio
ECD	electronic circular dichroism
ee	enantiomeric excess
equiv.	equivalent
Et	ethyl

fum	dimethyl fumarate
hν	irradiation by a halogen lamp
HMPA	hexamethylphosphoramide
HPLC	high-performance liquid chromatography
HR	high resolution
i-Pr	isopropyl
IR	infrared spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
LDA	lithium diisopropylamide
LiHMDS	lithium bis(trimethylsilyl)amide
Me	methyl
Mes	mesityl
MW	microwave irradiation
M.p.	melting point
MS	mass spectroscopy
NBS	*N*-bromosuccinimide
NMR	nuclear magnetic resonace
NOE	nuclear Overhauser effect
Ph	phenyl
ROESY	rotational frame nuclear Overhauser effect spectroscopy
r.t.	room temperature
TAPA	*α*-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid
TBAF	tetra-*n*-butylammonium fluoride
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TMS	trimethylsilyl
TMSA	ethynyl(trimethyl)silane
p-Tol	*para*-tolyl
VAZO	2,2′-azobis(2-methylbutyronitrile)

1

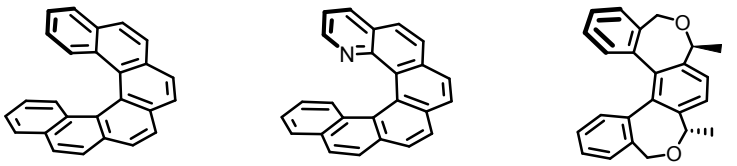
Introduction

1.1 Helicenes and helicene-like molecules

Helicenes are polycyclic aromatic compounds comprised of *ortho*-fused benzene rings. The chemistry of helicenes has attracted persistent attention due to their unique structural, spectral and optical features. Steric repulsion of the terminal benzene rings forces the molecule to adopt a helical non-planar shape. Thus helicenes are inherently chiral, while lacking chiral centres. The non-superimposable clockwise and counterclockwise helices represent an example of helical chirality. Apart from being aesthetic molecules, helicenes possess a rigid framework, which is very stable towards acids, bases and relatively high temperature. Their twisted shape offers applications in nanoscale molecular machinery as 'springs' or 'pawls'.[1] The large chiral π-electron system makes them an attractive target in search for new organic materials with useful optical and electronic properties. In particular, the non-racemic functionalised helicenes and their analogues are promising candidates for chiral ligands and auxiliaries in asymmetric synthesis.

With respect to their structure, helicenes can be divided into three main categories (Scheme 1.1). *Carbohelicenes* consist solely of *ortho*-fused benzene rings. *Heterohelicenes* have one or more heteroatoms incorporated in their structure. Finally, the *helicene-like* compounds are not fully aromatic compounds but possess the helical twisted shape.

Scheme 1.1



1 carbo[6]helicene

2 aza[6]helicene

3 [5]helicene-like

For simplification of the systematic names the IUPAC introduced a specific nomenclature for helicenes, where prefixes penta, hexa and hepta etc., are used for five, six and seven, etc. ring compounds.[2] The prefix could be written in brackets

before the helicene's name: *e.g*. [6]helicene. The stereochemical descriptors *P* (or plus) and *M* (or minus) can be assigned to the right-handed and left-handed helices, respectively.[3]

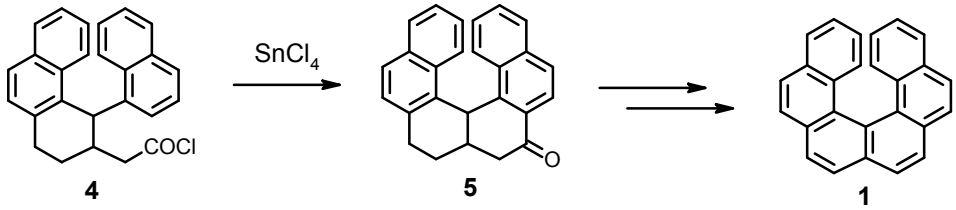
Although, the scientific community has a continuing interest in chemistry of helicenes, a general synthetic approach to the functionalised optically pure fully aromatic helicenes has not yet been discovered. Modification of the helical backbone, for instance, introduction of heteroatoms and substituents, might greatly simplify its synthesis. Besides, it provides new properties of these compounds, such as increased flexibility[4] and chiroptical properties[5-7]. In areas, where chirality is more important than the fully aromatic backbone, helicene-like compounds might represent an interesting option.[8] Therefore, it is not surprising that synthesis of the helicene-like structures started to attract considerable attention in recent years.

1.2 Synthesis of helicenes

1.2.1 Synthesis of racemic helicenes

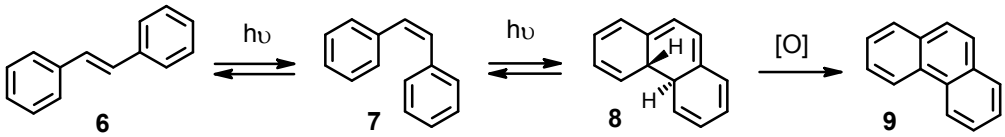
Interest in helicenes commenced in the early twentieth century.[9, 10] The first practical synthesis of helicenes was reported by Newman *et al*. in 1956 (Scheme 1.2).[11] The key annulation reaction was Friedel-Crafts acylation of the acyl chloride **4**.

Scheme 1.2



A decade later, Mallory *et al*. made an important breakthrough, when he used the stilbene photochemical dehydrocyclisation for the synthesis of helicenes.[12-14] Under UV-light irradiation *cis*/*trans* isomerisation of stilbene and its derivatives occurred and the intramolecular electrocyclisation of the *cis* isomer **7** produced the dihydroaromatic product **8**. In the presence of an oxidant, commonly a catalytic amount of iodine and atmospheric oxygen, the fully aromatic system **9** resulted (Scheme 1.3).[15, 16] As this oxidising system generated hydroiodic acid, which could cause side reactions, a very useful method was developed by Katz *et al*., in which an excess of iodine in the presence of propylene oxide – acting as HI scavenger – was employed.[17, 18]

Scheme 1.3

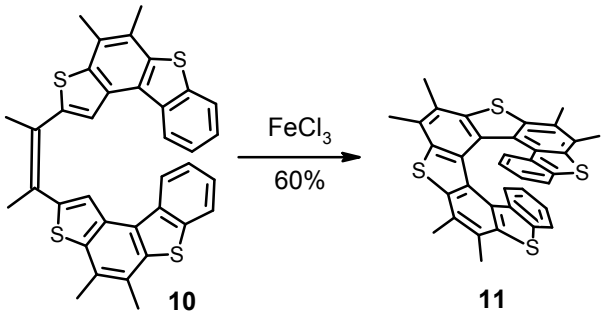


At the present time, 50 years after its discovery, the photochemical dehydrocyclisation still remains the most frequently used method to prepare helicenes. Recently it has proved to be useful in the syntheses of functionalised

carbo[5]- and [6]helicenes[19] as well as some aza[6]helicenes.[20] Diederich *et al*. adopted this method for the synthesis of new *helicopodand* receptors.[21, 22] The photochemical syntheses provided the longest helicenes existing up to date: namely, [14]helicene and thia[15]helicene with alternating benzene and thiophene rings.[15, 23-26] Nevertheless, the profound limitations, such as the high dilution (typically millimolar concentrations to prevent photodimerisation)[27] and incompatibility with some functional groups (typically iodo, amino, acetyl and nitro groups),[28-31] stimulated exploration of the non-photochemical methods of helicene synthesis.

Larsen *et al*. used non-photochemical cyclisation of stilbene precursors in the synthesis of thiahelicenes.[32] For example, the racemic thia[9]helicene **11** was obtained from the stilbene analogue **10** by oxidation with $FeCl_3$ (Scheme 1.4).

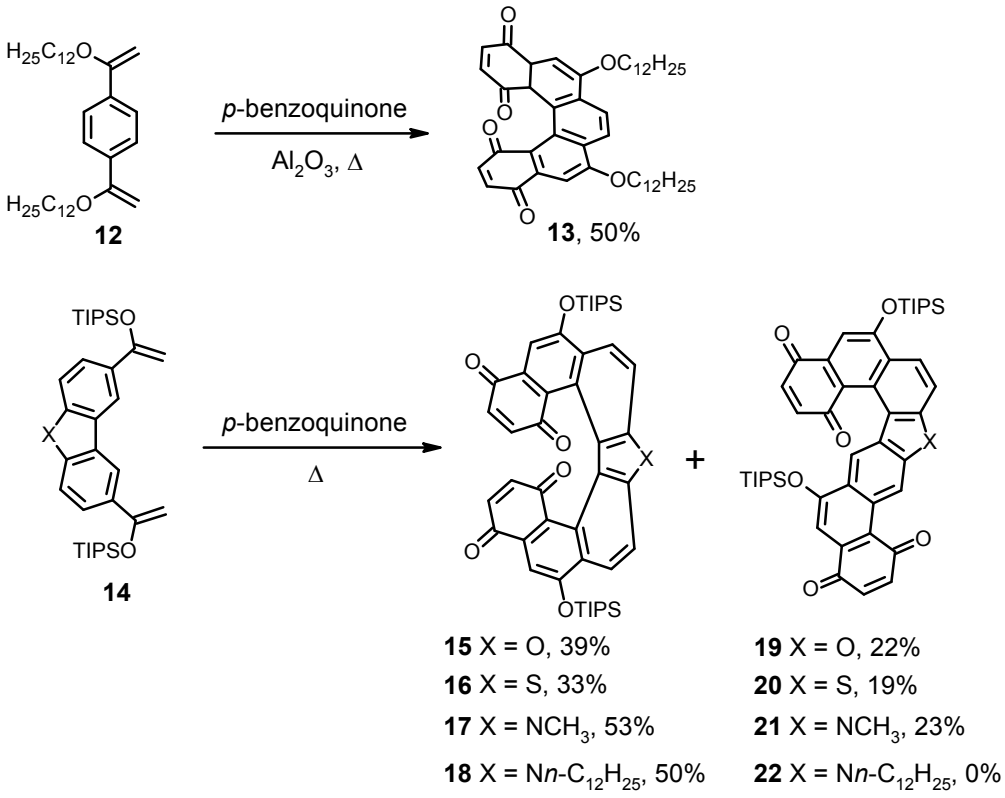
Scheme 1.4



In search for non-photochemical methods, Katz *et al.* developed an efficient and practical method for the multi-gram scale synthesis of helicene bisquinones based on Diels-Alder cyclisation. The moderate yields (usually 20-50%) of the key annulation reaction were compensated by simplicity of the synthesis and low cost of the starting materials.[33] Depending on the nature of the substrate, the cycloaddition was sometimes accompanied by the formation of the S-shaped by-product. The method was successfully applied to the preparation of functionalised [5]-, [6]- and [8]helicenes[34, 35] and hetero[7]helicenes **15**-**18** (Scheme 1.5).[36]

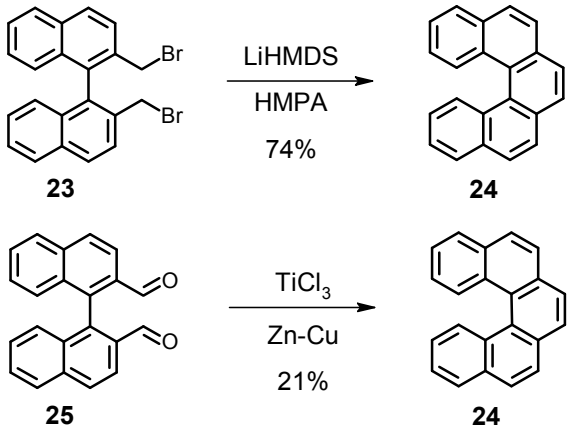
Later on, Minuti *et al.* applied Diels-Alder reaction in the two-step practical synthesis leading to the variety of substituted [5]- and [6]helicenes, including [5]helicene bisquinone and helicenes containing a cyclopentane ring.[37-40] Other non-photochemical methodologies include Hewett cyclisation in melted KOH,[41] oxidation of double phosphonium salts,[42] Wurtz-type coupling/Pd aromatisation[43] and coupling of aromatic bis-bromomethyl moieties with potassium amide in liquid ammonia.[44]

Scheme 1.5



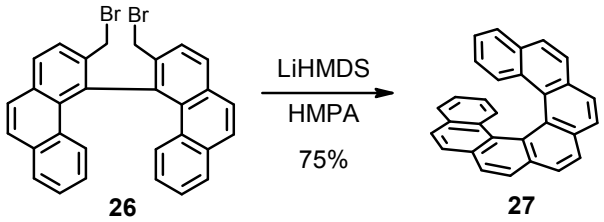
Dubois and Gingas developed one of the shortest gram-scale syntheses of unsubstituted [5]helicene **24** using either the carbenoid-type coupling methodology[45] or McMurry reaction (Scheme 1.6).[46]

Scheme 1.6



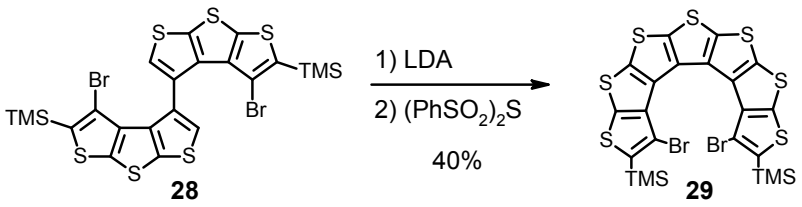
The carbenoid coupling methodology was extended to a short and efficient synthesis of [7]helicene **27** (Scheme 1.7).[47] In 2000 Rajca *et al*. used a related method for the construction of the annelated [7]thiophene helix **29** (Scheme 1.8).[48]

Scheme 1.7



26 **27**

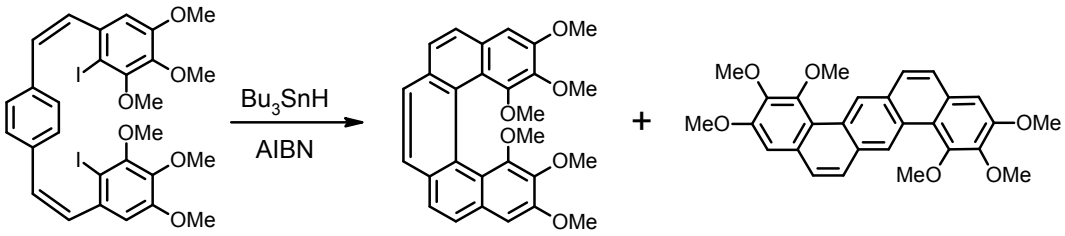
Scheme 1.8



28 **29**

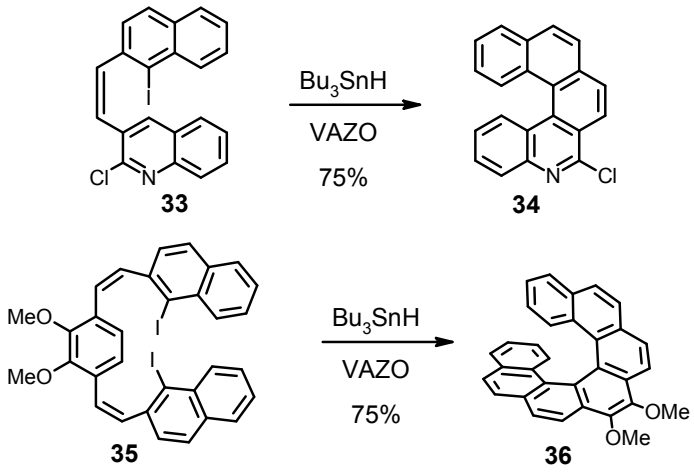
Harrowven *et al.* reported a novel route to functionalised [5]helicenes based on the regioselective tin hydride-mediated non-reducing tandem radical cyclisation of (*Z*,*Z*)-1,4-bis(2-iodostyryl)benzene derivatives.[49] The drawback of this method was formation of the S-shaped aromatic by-products, such as **32**, in some cases in a substantial amount (Scheme 1.9). This methodology was extended to the substituted aza[5]helicene **34** and [7]helicene **36** (Scheme 1.10).[50]

Scheme 1.9



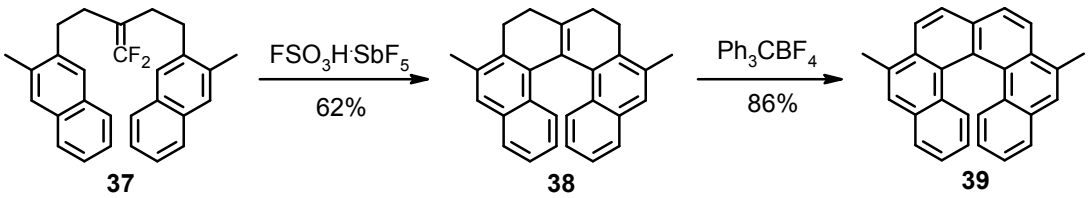
30 **31**, 35% **32**, 27%

Scheme 1.10



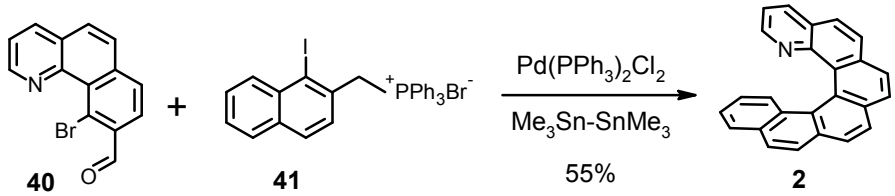
Recently, Ichikawa *et al.* developed a novel approach to substituted [5]- and [6]helicenes based on the electrophilic cyclisation of 1,1-difluoro-1-alkenes (Scheme 1.11). The authors exploited unique properties of the fluorine substituents, such as α-carbocation stabilizing effect and high electronegativity, in domino Friedel-Crafts-type cyclisation. The presence of methyl groups on the naphthalene units of **37** was necessary to control regioselectivity of the ring closure.[51]

Scheme 1.11



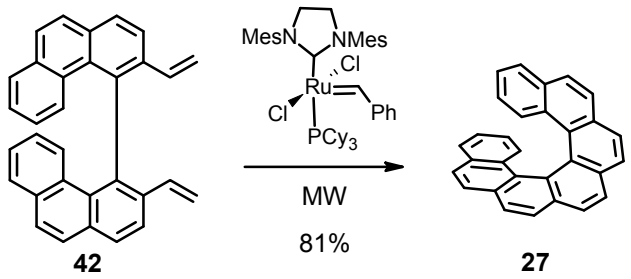
Takenaka *et al*. reported an original synthesis of the functionalised aza[5]- and [6]helicenes based on the highly *Z*-selective Wittig reaction and subsequent Stille-Kelly reaction as the key steps (Scheme 1.12).[52-55]

Scheme 1.12



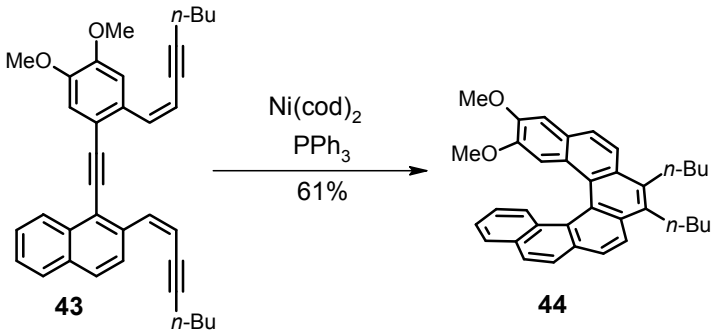
Numerous strategies utilising transition metal-catalysed reactions have emerged in recent years. Collins *et al*. developed a short and efficient method for the synthesis of carbo- and hetero[5]-, [6]- and [7]helicenes based on olefin metathesis using Grubbs 2nd generation catalyst and microwave irradiation (Scheme 1.13).[56, 57]

Scheme 1.13



In 1998 Starý and Stará and co-workers used intramolecular [2+2+2] cyclotrimerisation of aromatic alkynes as a straightforward route to helicenes.[58] The intramolecular triyne cyclisation proceeded with high regio- and chemoselectivity and tolerated presence of many functional groups.[59-65] Our group developed a modular synthetic approach, which allowed the preparation of an extensive library of functionalised helically chiral compounds.[66-68] For example, three aromatic rings were formed in a single step under mild reaction conditions in the Ni(0)-catalysed cyclotrimerisation of (*Z*,*Z*)-dienetriyne **43** to provide the fully aromatic [6]helicene derivative **44** (Scheme 1.14).[69]

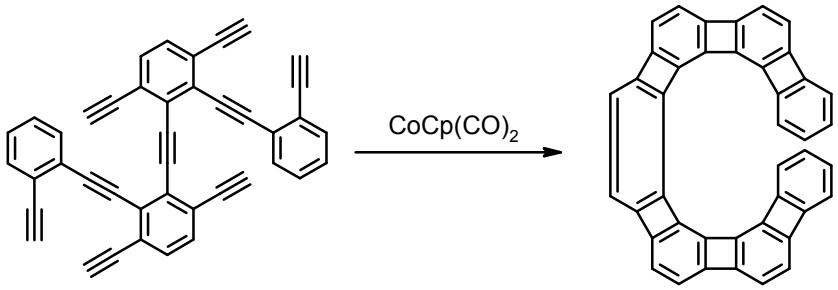
Scheme 1.14



This work inspired other groups to use the intramolecular cyclotrimerisation of triynes in the construction of helical scaffolds. Recently, Tanaka *et.al*.,[70-74] Carbery *et al*.[75] and Teplý *et al*.[76, 77] used the intramolecular triyne cyclotrimerisation for the syntheses of helically chiral compounds.

In 2002 Vollhardt *et al*. used intramolecular [2+2+2] cyclotrimerisation for the synthesis of helical phenylenes, called by the authors *heliphenes*.[78] The synthesis of **48** took advantage of the unprecedented triple cobalt-mediated cyclotrimerisation of the nonayne **47**, which enabled one-step formation of nine new cycles (Scheme 1.16).[79]

Scheme 1.16

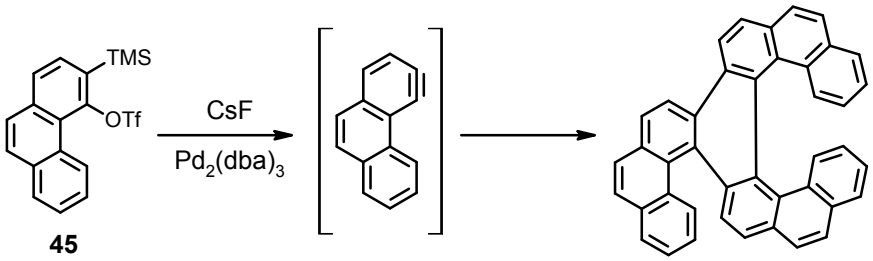


47

[7]heliphene
48, 2%

Later on, Guitián *et al.* reported palladium-catalysed intermolecular cyclotrimerisation of polycyclic arynes, which afforded the double-helicene structure **46** (Scheme 1.15).[80-82] By varying the reaction conditions, many different helical polycyclic aromatic structures were prepared.[79]

Scheme 1.15



45

46, 26%

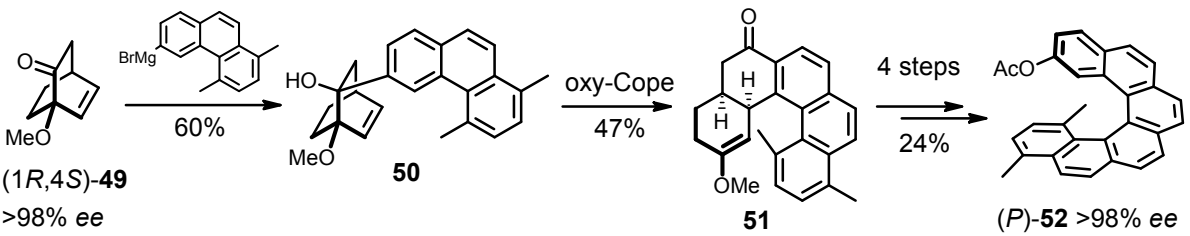
1.2.2 Asymmetric synthesis of helicenes

For many applications, for instance as ligands in enantioselective catalysis, helically chiral molecules have to be obtained in an optically pure form.[83] Therefore, several asymmetric protocols have emerged during the past few decades.[84]

There are three major approaches to non-racemic helicenes. Historically, the first attempt to obtain optically pure helicenes was based on the synthesis of racemic helicenes followed by chiral resolution. In 1956 Newman *et al*. reported preparation of the nonracemic [6]helicene, which was based on the repetitive co-crystallisation of the optically pure (-)-TAPA with the racemic [6]helicene.[85] Later on, more practical methods, based on resolution of diastereomeric derivatives, were developed. For example, Katz *et al*. transformed racemic helical bisquinones to diastereomeric camphanates, which were separable by column chromatography. The subsequent oxidative removal of the camphanoyl groups led to helical bisquinones in >98% optical purity.[86] Katz's method was recently employed in the resolution of thia[7]helicene[87] and triarylamine helicenes.[88] Resolutions of racemates based on chemical,[57, 89-91] enzymatic[26, 92] and chromatographic (using chiral stationary phases)[67, 93-95] protocols were reported as well.

The second approach includes a group of methods, which transform optically pure starting materials into nonracemic helicenes through a stereoselective transformation. Recently Ogawa *et al*. published an example of the central-to-helical chirality transfer based on the asymmetric aromatic oxy-Cope rearrangement (Scheme 1.17).[96-98]

Scheme 1.17

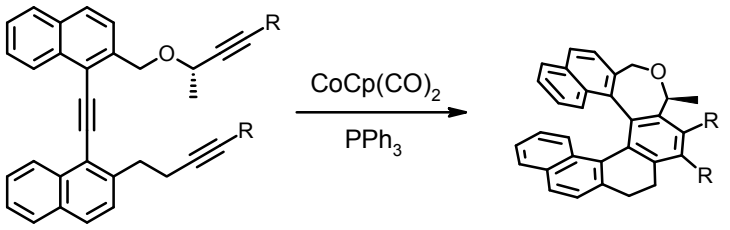


(1*R*,4*S*)-**49**
>98% *ee*

(*P*)-**52** >98% *ee*

Recently Starý and Stará and co-workers devised a diastereoselective synthesis of the nonracemic helicene-like structures based on helicity induction by the asymmetric centre present in the helical molecules (Scheme 1.18).[99] The presence of the methyl group causes the helical diastereomers to differ in energy. At high reaction temperatures, the stereochemical outcome of the [2+2+2] cycloisomerisation was controlled by the thermodynamic factors and, accordingly, the helicene-like compound with the lower free energy was formed predominantly. Thus, the chiral triyne **53** with the unsubstituted terminal alkyne moieties produced the (*M*,*S*)-**54** diastereomer with 92:8 *dr*. On the other hand, the triyne **55** substituted with *p*-tolyl groups at the triple bonds furnished the (*P*,*S*)-**56** diastereomer with 100% *de*.[100]

Scheme 1.18



(*S*)-**53** R = H

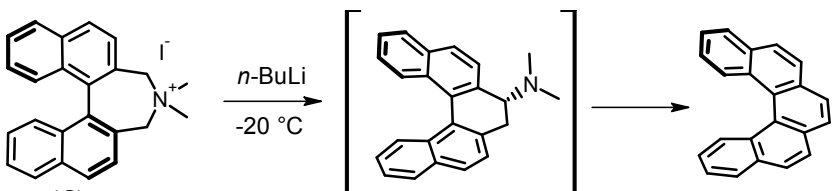
(*S*)-**55** R = *p*-Tol

(*M*,*S*)-**54** : (*P*,*S*)-**54** = 92 : 8 (R = H), 60%

(*M*,*S*)-**56** : (*P*,*S*)-**56** = 0 : 100 (R = *p*-Tol), 63%

Several approaches to nonracemic helicenes starting from axially chiral binaphthyls were reported. Stará *et al*. described Stevens rearrangement of the nonracemic binaphthyl dihydrodiazepinium salts to helical amines, which afforded (*P*)-[5]helicene as a single enantiomer upon treatment with a strong base via the base-induced 1,2-elimination (Scheme 1.19).[101] Other approaches utilised McMurry reaction of the enantiopure binaphthyl-2,2´-dicarbaldehyde[46] or oxidative cyclisation of the enantiopure 2,2´-bisphosphonium periodate to afford [5]helicene.[42]

Scheme 1.19



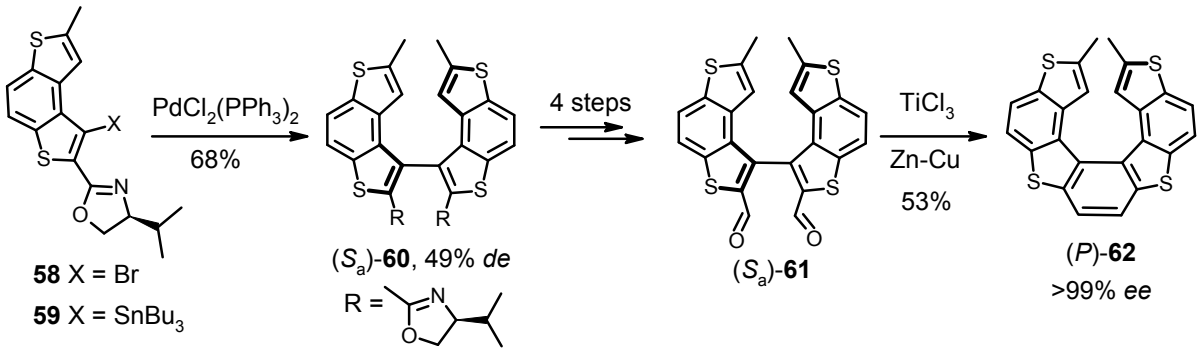
(*S*)-**57**

(*P*)-**25**

83%, 100% *ee*

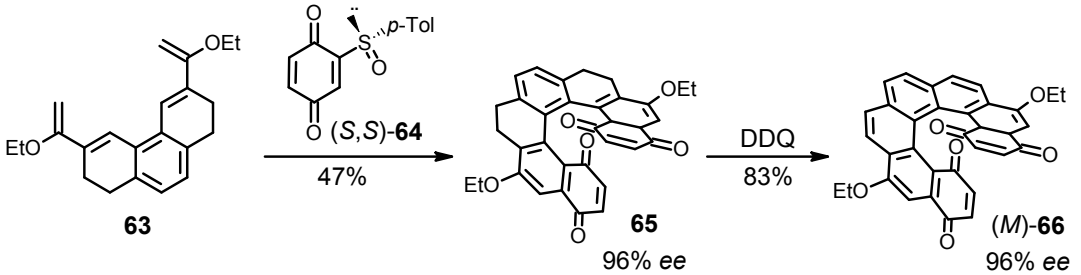
The axial-to-helical chirality transfer was recently employed in the synthesis of thia[7]helicenes.[102, 103] In the synthesis of thiahelicene (*P*)-**62**, the axially chiral precursor (S_a)-**60** was obtained in 49% *de* by Stille cross-coupling of the benzodithiophenes **58** and **59** with chiral oxazoline auxiliaries. After chromatographic separation of the diastereomers of **60** and several synthetic transformations, the intramolecular McMurry reaction of the optically pure dicarbaldehyde (S_a)-**61** gave thia[7]helicene **62** in >99% *ee* (Scheme 1.20).[103]

Scheme 1.20

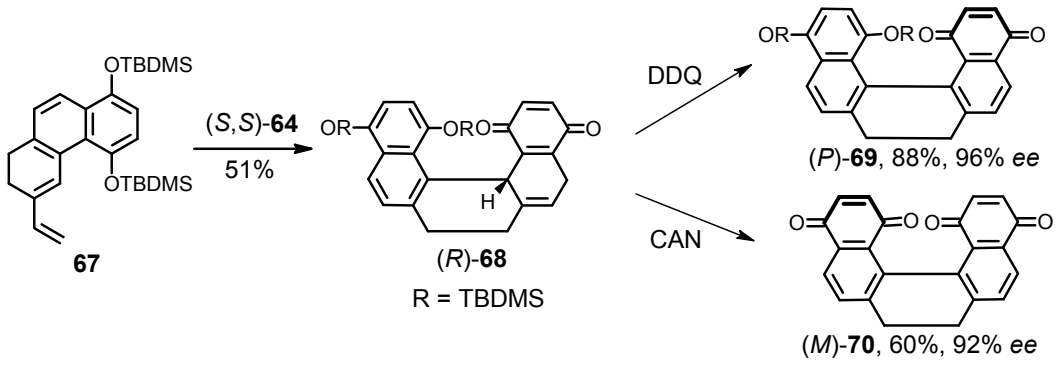


The third approach to nonracemic helicenes employs an asymmetric synthesis. Carreño *et al*. reported the asymmetric synthesis of the [7]helicene bisquinone **66**.[104, 105] The key step was the one-pot domino Diels–Alder reaction between the vinyl dihydrophenanthrene **63** and the enantiopure (*S*,*S*)-benzoquinone derivative **64** followed by a spontaneous sulfoxide elimination (Scheme 1.21). The versatility of this method was amplified by the enantio-divergent access to either the *P* or *M* helicene quinones **69** or **70** from the common intermediate (*R*)-**68** by simply selecting the aromatising agent – DDQ or CAN (Scheme 1.22).[106]

Scheme 1.21

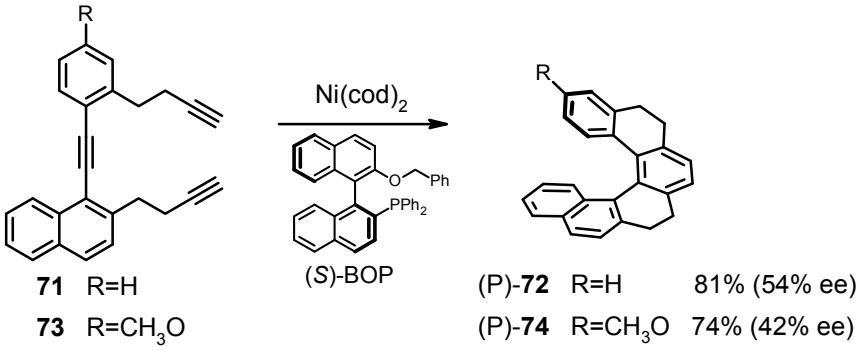


Scheme 1.22



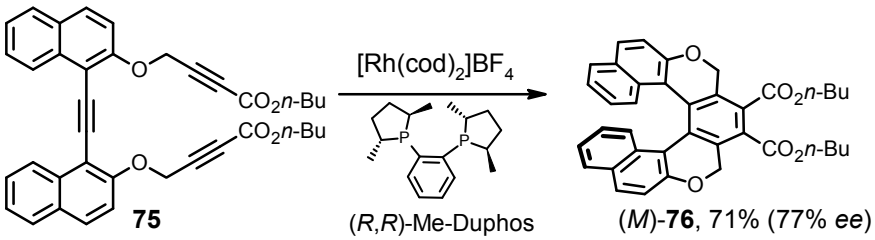
Starý and Stará *et al*. have developed the enantioselective [2+2+2] cyclotrimerisation reaction of triynes **71** and **73** to the corresponding tetrahydro[6]helicenes **72** and **74** in the presence of Ni(0) catalyst and the chiral ligand (*S*)-BOP (Scheme 1.23).[64]

Scheme 1.23



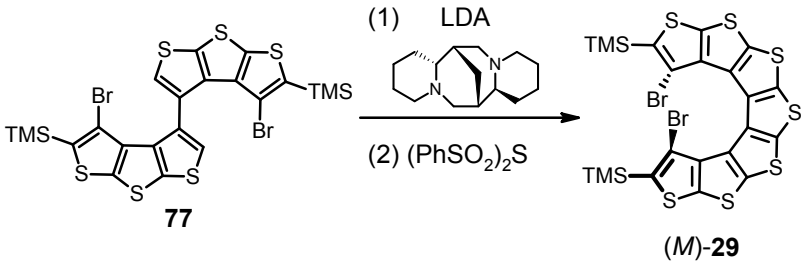
Later on, the enantioselective intramolecular [2+2+2] cyclisation was also studied by Tanaka *et al*.[74, 107] The cationic rhodium(I) complex and electron-rich diphosphine ligand (*R*,*R*)-Me-Duphos furnished the helicene-like molecule (*M*)-**76** in 77% *ee* (Scheme 1.24).

Scheme 1.24



The oligothiophene helix (*M*)-**29** was synthesised in 20-37% isolated yields and 19-47% *ee* by Rajca *et al*. using (-)-sparteine additive in the lithiation of the bis(dithienothiophene) **77** (Scheme 1.25).[48]

Scheme 1.25



77 (*M*)-**29**

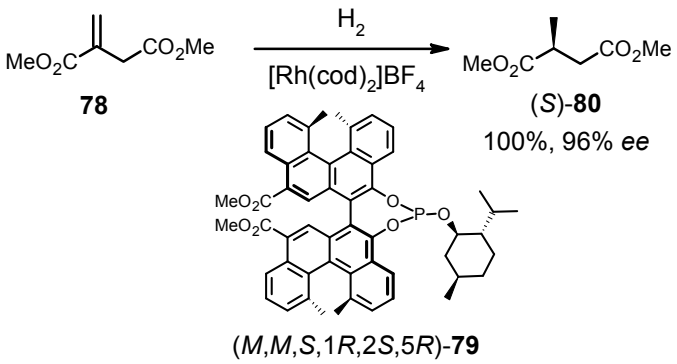
1.2 Applications of helicenes in asymmetric catalysis

The configurational stability of helicenes increases with an increasing number of the annelated rings. While, [5]helicene racemises readily at room temperature unless substituted in the position *1*, higher analogues with 6 rings and more are considered to be configurationally stable. This opens a possibility of using helicenes as chiral ligands or auxiliaries in the asymmetric synthesis.

In 1986 Martin *et al*. described the first successful application of an enantiopure helicene derivative, 2-cyano[7]helicene, as a catalyst in the asymmetric epoxidation of alkenes.[108] The group also reported the use of 2-hydroxy[7]helicene as a chiral auxiliary in the reduction of *α*-keto esters[109] and ene reaction.[110] Since the pioneering work by Martin *et al*., several other contributions appeared. Nevertheless, this field still remains largely unexplored, mainly due to the absence of the general asymmetric synthesis of functionalised helicenes.

Katz *et al.* prepared the dimeric bis[5]helicenediol ([5]HELOL)[111] in a nonracemic form and demonstrated its catalytic activity in the asymmetric addition of diethylzinc to aldehydes achieving up to 81% *ee*.[112] This finding inspired Yamaguchi in designing the bishelicenol phosphite ligands, which combined axial, central and helical chiralities.[113] For example, the ligand (*M*,*M*,1*R*,2*S*,5*R*)-**79** was successfully applied in the Rh-catalysed hydrogenation of dimethyl itaconate **78** (Scheme 1.26).[114]

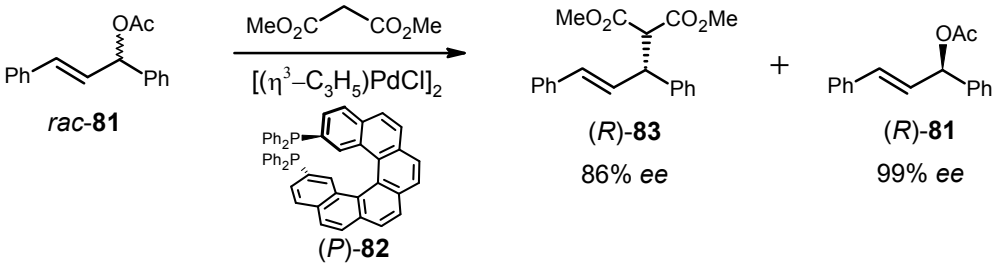
Scheme 1.26



(*M*,*M*,*S*,1*R*,2*S*,5*R*)-**79**

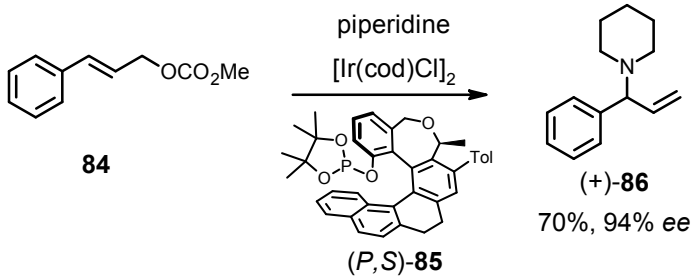
Reetz *at al*. tested [6]helicene diphosphine ligand (*P*)-**82** in the Rh-catalysed hydrogenation of dimethyl itaconate **78**, but only moderate enantioselectivity and reactivity was observed (54%, 39% *ee*).[115] The same (*P*)-**82** ligand was used in the Pd-catalysed kinetic resolution of the racemic allylic acetate **81** obtaining up to 99% *ee* for the starting material (*R*)-**81** and up to 86% *ee* for the substituted product (*R*)-**83** (Scheme 1.27).[116]

Scheme 1.27



Recently, Starý and Stará *et al*. achieved high enantioselectivity up to 94% *ee* in the Ir-catalysed allylic amination of the allyl carbonates using helically chiral phosphites (Scheme 1.28).[117] The enantioselectivity varied with the substitution on the phosphite, while the 4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2-yl derivative (*P*,*S*)-**85** was the most effective ligand. The same authors also explored asymmetric hydroformylation of the terminal alkenes catalysed by $Rh(acac)(CO)_2$ complexes. In this reaction the helical phosphites induced only moderate enantiomeric excesses (up to 32% *ee*).

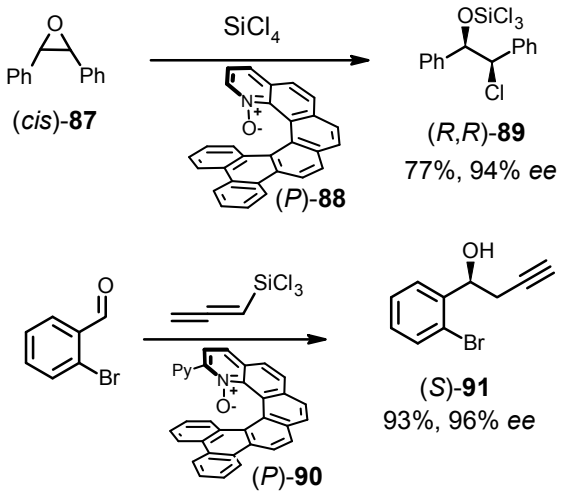
Scheme 1.28



In addition, helically chiral compounds began to appear as promising organocatalysts. Recently, Starý and Stará *et al.* have demonstrated the organocatalytic activity of 2-aza[6]helicene **2** in the asymmetric acyl transfer reaction with a moderate selectivity factor of up to 10.[91]

Takenaka *et al.* used the azahelicene *N*-oxides as organocatalysts in desymmetrisation of *meso*-epoxides[54, 118] and in enantioselective propargylation of aldehydes with allenyltrichlorosilane (Scheme 1.29).[119] The catalyst (*P*)-**88** was found to be more efficient in the ring-opening reaction of the *cis*-stilbene oxide **87** by $SiCl_4$ than aza[5]helicene and aza[6]helicene *N*-oxides. In the propargylation reaction the authors described the bidendate Lewis base catalyst (*P*)-**90** with the additional pyridine moiety, which exhibited greater selectivity and reactivity compared to the *N*-oxide (*P*)-**88**.

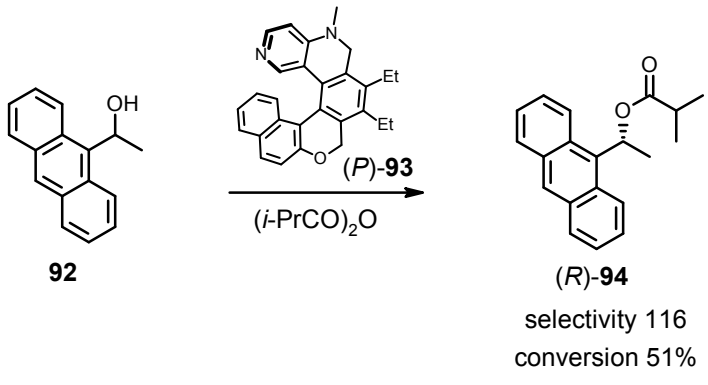
Scheme 1.29



Moreover, Takenaka *et al.* devised the helical 2-aminopyridinium ions as hydrogen-bond donor catalysts in the acid-catalysed asymmetric Friedel–Crafts reaction exhibiting high enantioselectivities of up to 96% *ee*.[55]

Recently, Carbery *et al*. developed the helically chiral Lewis base catalyst (*P*)-**93**, analogue of DMAP, which exhibited an excellent reactivity as well as selectivity in the kinetic resolution of chiral secondary alcohols with the selectivity factor of up to 116 (Scheme 1.30).[75]

Scheme 1.30



2

Goals

The main goals of the thesis were:

- *to develop a synthetic approach to the optically pure helicene-like compounds*.

  The main goal was to prepare the novel helicene-like compounds containing either two (2*S*)-2-methyl-2,7-dihydrooxepine rings, *oxepine-type compounds*, (Scheme 2.1) or two (2*R*)-2-methyl-2*H*-pyran rings, *pyran-type compounds*, (Scheme 2.2) using the diastereoselective synthesis. It was also necessary to investigate the role of various parameters in diastereoselectivity and efficiency of the synthesis. For example, the importance of aryl substituents at the terminal triple bonds of the triyne and the reaction conditions of the [2+2+2] cyclotrimerisation reaction had to be explored.

- *to functionalise the enantiopure helicene-like structures with specific functional groups for coordination to transition metals.*

  It was desirable to functionalise the helicene-like compounds with phosphine and phosphite groups because they could be tested as ligands in enantioselective transition-metal catalysis. The synthetic strategy aimed at the preparation of a common helical precursor, which could be transformed into various helical phosphines or phosphites. It was interesting to examine the relationship between the position of the phosphine group on the helical scaffold and the catalytic activity of the ligand.

- *to test the optically pure functionalised helicene-like compounds as ligands in the transition-metal enantioselective catalysis.*

  The activity of the synthesised ligands in the enantioselective Ni(0)-catalysed [2+2+2] cyclotrimerisation of triynes had to be explored because this reaction opens route to nonracemic fully aromatic helicenes. It was also desirable to check the efficiency of the novel helical ligands in other transition-metal catalysed reactions, in which high enantioselectivities had not been achieved yet, *e.g.*, the gold(I)-catalysed cyclisation of enynes.

- *to extend the scope of the diastereoselective synthesis of the helicene-like compounds.*

  An additional goal was to develop the synthesis of the helically chiral DMAP analogue **106**, which could be tested in as organocatalyst (Scheme 2.2).

- *to extend the scope of the intramolecular [2+2+2] cyclotrimerisation of alkynes to sufur-containing helicenes.*

Another goal was to apply the double intramolecular [2+2+2] cyclotrimerisation in the synthesis of thia[9]helicene **107** (Scheme 2.3).

Scheme 2.1 Synthesis of the optically pure *oxepine-type* helicene-like compounds.

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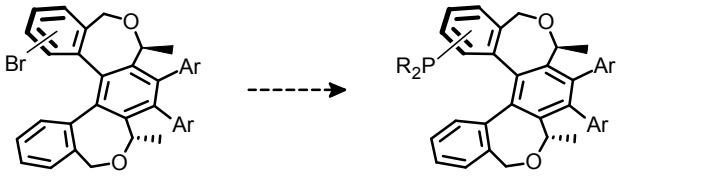

R = Ph, Cy, *i*-Pr, *t*-Bu, *o*-Tol etc.

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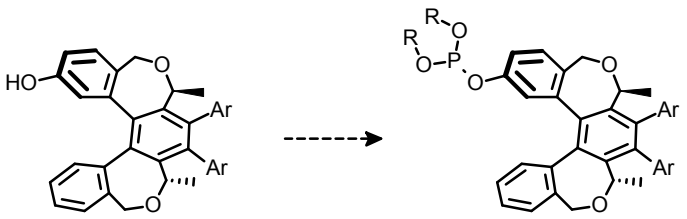

Scheme 2.2 Synthesis of the optically pure *pyran-type* helicene-like compounds

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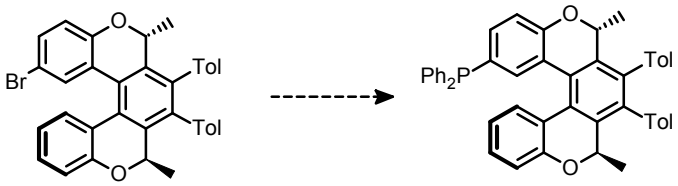
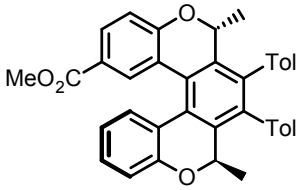


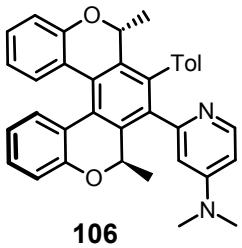
103 **104**

ESTER



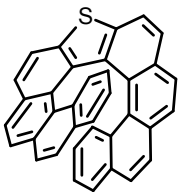
105

DMAP analogue



106

Scheme 2.3 Synthesis of thia[9]helicene



107

3

Results and discussion

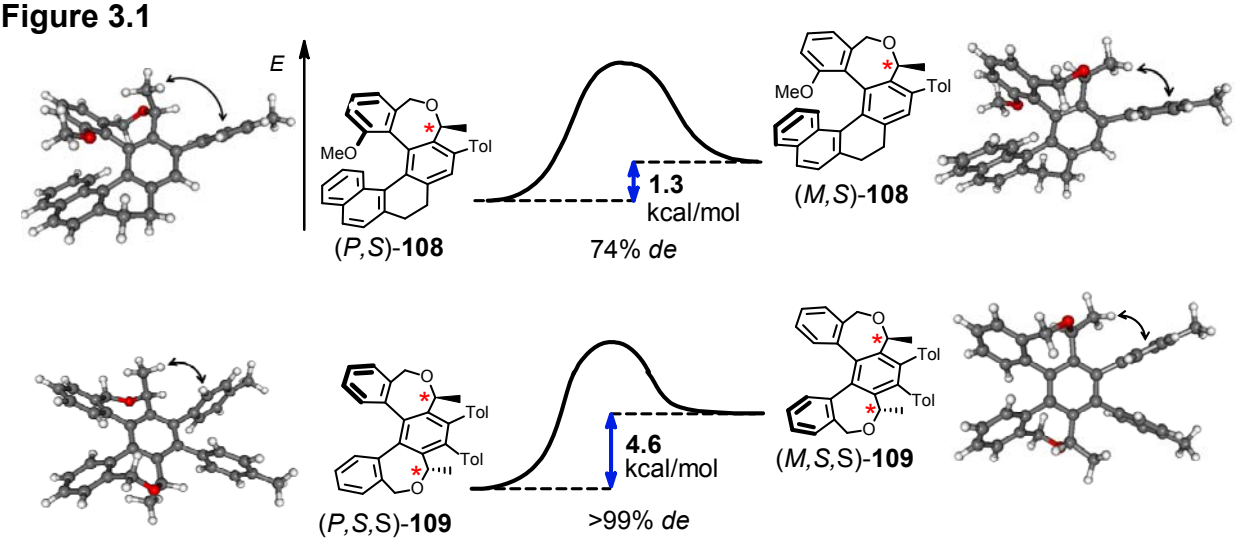
3.1 Diastereoselective synthesis of functionalised helicene-like compounds

3.1.1 Oxepine-type helicene-like compounds

As previously mentioned (Chapter 1.2.2), we have recently developed the diastereoselective synthesis of the helicene-like compounds possessing one (*S*)-methyl-2,7-dihydrooxepine ring.[99] It was found that the diastereoselectivity of the [2+2+2] cyclotrimerisation was governed by thermodynamic factors and was directly proportional to the difference in energy of the diastereomeric helical scaffolds formed (Figure 3.1). The steric interactions between the methyl and the tolyl substituents resulted in a predominant formation of the (*P*,*S*)-**108** configuration.

This approach to the optically pure helicenes was further elaborated by putting in the second (*S*)-methyl-2,7-dihydrooxepine ring into the [5]helicene scaffold. It was predicted by the DFT calculations (B3LYP/TZV+P) that this structural change would further increase the energy difference between the *P* and *M* helices.[120] The energy difference between (*P*,*S*,*S*)-**109** and (*M*,*S*,*S*)-**109** was calculated to be 4.6 kcal/mol, which would result in *dr* >99.96 : 0.04. The interconversion barrier between the two diastereomers was expected to be lower than the racemisation barrier of the configurationally unstable [5]helicene due to the flexibility given by the presence of two 7-membered rings.

Figure 3.1

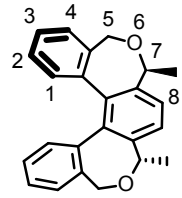


3.1.1.1 Synthesis of phosphines

As mentioned in the *Introduction* chapter helical ligands seem to be very promising in enantioselective catalysis applications. Phosphines are ubiquitous in transition metal chemistry and upon coordination to a transition-metal afford very efficient and versatile homogeneous catalysts. Therefore, we decided to develop the synthesis of phosphines based on the novel helical scaffold (*P*,*S*,*S*)-**3** and explore their potential in enantioselective catalysis. From the synthetic point of view the easiest approach was to place the phosphine substituent on the terminal or central aromatic rings, since the functionalisation of the flexible 7-membered rings was a more difficult task. This chapter describes the diastereoselective syntheses of the functionalised helical scaffolds derived from (*P*,*S*,*S*)-**3** with the phosphine substituents in different positions on the aromatic rings.

The position *1* of the helical scaffold (*P*,*S*,*S*)-**3** is the closest to the inner part of the helix and thus could be advantageous in a catalyst design (for numbering see IUPAC recommendation P-25.1.2.6). But the preliminary studies in our laboratory revealed that the synthetic access to the helical scaffolds functionalised in the position *1* was unviable. On the other hand, the substituents in the position *4* pointed away from the chiral scaffold. Therefore, the functionalised helicene-like compounds with substituents in the positions *2*, *3* and *8* were my initial targets.

Figure 3.2



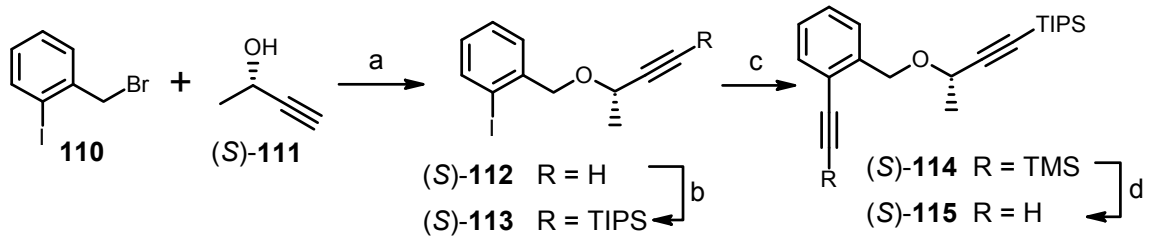
(*P,S,*S)-**3**

Helicene-like compounds with a phosphine group in the position *2*

The strategy was to access the phosphines from the 2-bromo[5]helicene-like precursor (*P*,*S*,*S*)-**124**. The synthesis of the *oxepine-type* helicene-like scaffold evolved from the modular synthesis of helicene-like compounds with one methyldihydrooxepine ring published earlier.[8, 60] The modular synthesis involved the preparation of the triyne structures by connecting two aryl building blocks and then intramolecular [2+2+2] cyclotrimerisation of the triynes, which regioselectively afforded the helical compounds.

The alkyne (*S*)-**112** was prepared by Williamson ether synthesis from the commercially available optically pure alcohol (*S*)-**111** and 2-iodobenzyl bromide **110** (Scheme 3.3). Then it was orthogonally protected with a bulky triisopopylsilyl group by treatment with LDA and triisopropylsilyl chloride. The subsequent Sonogashira cross-coupling of aryl iodide (*S*)-**113** with ethynyl(trimethyl)silane afforded (*S*)-**114**, which was then selectively deprotected to provide the TIPS-diyne (*S*)-**115** in good yield.

Scheme 3.3

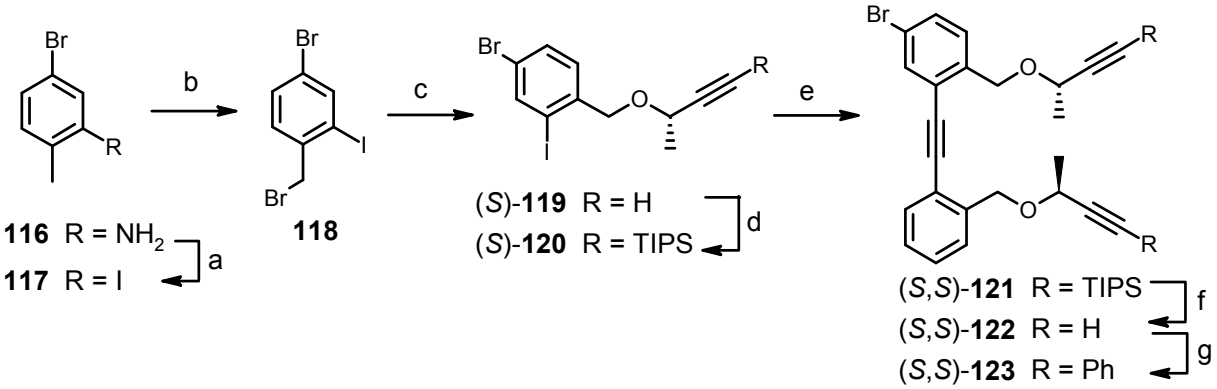


(a) KH (1.6 equiv.), (*S*)-**111** (1.7 equiv.), THF, 0 ºC→ r.t., overnight, 91%.
(b) 1). LDA (1.1 equiv.), THF, -78 ºC, 45 min; 2). TIPSCl (1.1 equiv.), -78 ºC→r.t., overnight, 84%.
(c) TMSA (1.0 equiv.), $Pd(PPh_3)_4$ (1 mol%), CuI (2 mol%), DIPA, r.t., 20 min, 99%.
(d) $NaOCH_3$ (1.0 equiv.), methanol, r.t., 30 min, 99%.

The synthesis of the second building block, bromoalkyne (*S*)-**120** started from the conversion of commercially available amine **116** to the benzyl bromide **118** by using literature procedures (Scheme 3.4).[121, 122] The nucleophilic substitution of **118** with the chiral alkoxide, derived from the optically pure (*S*)-**111** provided the alkyne (*S*)-**119**, which was then protected with the triisopropylsilyl group. Unfortunately, the compounds **118**, (*S*)-**119** and (*S*)-**120** were contaminated by the inseparable impurity

(the iodine-bromine exchange product), formed in minor amount during the radical bromination step **117**→**118**. It was chromatographically separated from the main compound only after the key Sonogashira cross-coupling of the two building blocks (*S*)-**115** and (*S*)-**120** at low temperature, which provided the protected triyne (*S*,*S*)-**121** in excellent yield. The cross-coupling reaction was performed at -2 ºC in order to avoid the concurrent reaction taking place on the C-Br bond. The reaction with tetrabutylammonium fluoride afforded the triyne (*S*,*S*)-**122** in good yield after chromatography. Then the two phenyl substituents were introduced into the (*S*,*S*)-**122** in order not only to control the stereochemical outcome of the cyclisation but also to increase the yield of the cyclisation by increasing the stability of the triyne against degradation.[123]

Scheme 3.4

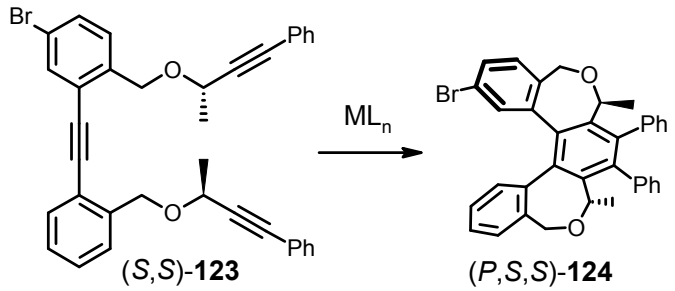


(a) 1) $NaNO_2$ (1.0 equiv.), H_2SO_4 (aq., 5.2 equiv.), 0 ºC, 10 min; 2) KI (2.1 equiv.), 110 ºC, 2 h, 65%.
(b) NBS (2.0 equiv.), AIBN (cat.), K_2CO_3 (cat.), CCl_4, IR lamp, reflux, 5 h; 77%.
(c) KH (1.5 equiv.), (*S*)-**111** (1.5 equiv.), THF, 0 ºC→ r.t., 1.5 h, 95%.
(d) 1) LDA (1.0 equiv.), THF, -78 ºC, 1 h; 2) TIPSCl (1.3 equiv.), -78 ºC→r.t., overnight, 61%.
(e) (*S*)-**115** (1.0 equiv.), $Pd(PPh_3)_4$ (2.7 mol%), CuI (5.5 mol%), DIPA, -2 ºC, 2 h, 94%.
(f) TBAF (0.9 equiv.), THF, r.t., 1 h, 88%.
(g) PhI (3.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), CuI (10 mol%), DIPA (8.0 equiv.), toluene, 0 ºC→ r.t., overnight, 89%.

The [2+2+2] cyclotrimerisation of the triyne (*S*,*S*)-**123** proceeded in good yield and with >99% diastereoselectivity providing only (*P*,*S*,*S*)-**124** diastereomer. The other diastereomer (*M*,*S*,*S*)-**124** was not detected by NMR experiments. In addition, the helical bromide (*P*,*S*,*S*)-**124** was a sufficiently stable compound and thus could

serve as the suitable precursor in the synthesis of phosphines. The conditions for the cyclotrimerisation reaction are summarised in Table 3.1.

Table 3.1



(*S*,*S*)-**123** (*P*,*S*,*S*)-**124**

Entry	Transition metal complex (equiv.)	Solvent	Temperature, time	Heating mode	Isolated yield
1	$CoCp(CO)_2$ (1), PPh_3 (2)	decane	140 ºC, 2 h	hν	80%
2	$CoCp(CO)_2$ (1), PPh_3 (2)	THF	180 ºC, 1 h	MW	77%
3	$RhCp(C_2H_2)_2$ (1)	decane	140 ºC, 1 h	hν	46%

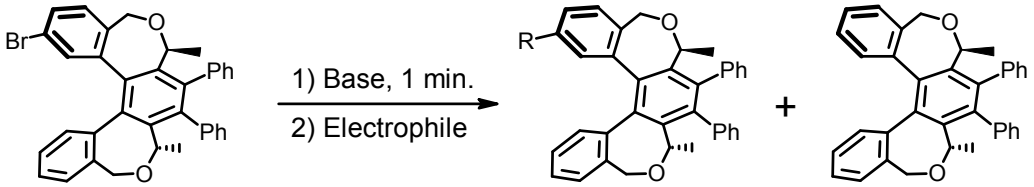
The best conditions for a gram scale synthesis employed the microwave-assisted synthesis at 180 ºC and $CoCp(CO)_2$ complex (Entry 2). The classical Vollhartd's conditions using a halogen lamp irradiation and decane as the solvent (Entry 1) worked well on a small scale (40 mg, 80% yield), but scale-up to 250 mg batch decreased the yield to 60%. Utilising the rhodium(I) complex in decane and the halogen lamp irradiation gave the product in the lower yield probably due to higher by-products formation or decomposition of the starting material/product (Entry 3). In all cases stoichiometric amount of the transition-metal complex had to be used because of the low reactivity of the triyne (*S*,*S*)-**123**.

The optically pure helical bromide (*P*,*S*,*S*)-**124** was used to prepare phosphines by lithium-halogen exchange reaction. Recently, Aloui *et al.* described a successful conversion of the (±)-3-bromo-14-methoxy[6]helicene into (±)-3-diphenylphosphino-14-methoxy[6]helicene using *n*-BuLi in THF at -78 ºC for 1.5 h.[124] However, when these conditions were applied to (*P*,*S*,*S*)-**124**, no phosphine was formed and the reduced helicene-like compound (*P*,*S*,*S*)-**126** was obtained as the only product in 84% isolated yield.

The lithiation step was explored by varying the reaction conditions (Table 3.2). In order to simplify the ^{1}H NMR spectra analysis of the crude reaction mixture, iodine was used as an electrophile. The NMR analysis of the mixture of products was the most suitable method since the compounds (*P*,*S*,*S*)-**124**, (*P*,*S*,*S*)-**125a** and (*P*,*S*,*S*)-**126** had nearly the same R_f factors and hence could not be separated chromatographically. The presence of the compounds was also confirmed using the ESI-MS analysis of the crude mixture.

Since the lithium-halogen exchange reaction was known to be extremely fast even at low temperatures, the reaction time was reduced to 1 min.[125, 126] As shown in Table 3.2, using *n*-BuLi and *s*-BuLi in THF at -78 °C (Entries 1-2) did not drive the reaction to full conversion and the iodinated product (*P*,*S*,*S*)-**125a** was not detected either.

Table 3.2



(*P*,*S*,*S*)-**124**

(*P*,*S*,*S*)-**125a** R = I
(*P*,*S*,*S*)-**125b** R = TMS
(*P*,*S*,*S*)-**125c** R = PPh_2

(*P*,*S*,*S*)-**126**

Entry	RLi (equiv.)	Solvent	Temp.	Electrophile[a]	**125** : **126** : **124**[b]
1	*n*-BuLi (1.0)	THF	-78 ºC	I_2	0 : 1 : 5
2	*s*-BuLi (1.0)	THF	-78 ºC	I_2	0 : 2 : 3
3	*n*-BuLi (1.0)	Et_2O	-78 ºC	I_2	0 : 0 : 1
4	*t*-BuLi (2.0)	Et_2O	-78 ºC	I_2	0 : 1 : 0
5	*t*-BuLi (2.0)	Et_2O	-95 ºC	I_2	2 : 1 : 0
6	*t*-BuLi (2.0)	Et_2O	-95 ºC	TMSCl	9 : 1 : 0[c]
7	*t*-BuLi (2.0)	Et_2O	-110 ºC	Ph_2PCl	1 : 0 : 0

[a] 1.2-1.6 equiv.
[b] The ratio of products determined from ^{1}H NMR.
[c] Isolated.

Then diethyl ether was used instead of tetrahydrofuran because it could slow down the concurrent protonation of the lithiated species.[127, 128] However, this hindered the bromine-lithium exchange step too (Entry 3). Therefore, a more potent

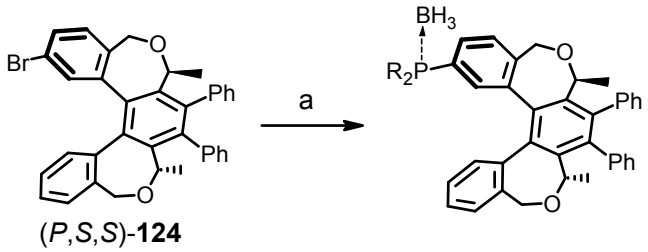
reagent *t*-BuLi[129, 130] was used in order to achieve the complete conversion in diethyl ether. However, this again led to the exclusive formation of the reduced product (*P*,*S*,*S*)-**126** (Entry 4).The iodinated product (*P*,*S*,*S*)-**125a** appeared only when the reaction was carried out at temperatures lower than -78 ºC (Entries 5-7). The possible rationale to this observation could be the stabilisation of the lithiated intermediate at low temperatures, which permitted its further reaction with the electrophile.[131, 132]

The reaction also took place with other electrophilic reagents. The helicene-like silane (*P*,*S*,*S*)-**125b** was obtained in 65% yield (Entry 6) along with only *ca* 10% of the hydrogen transfer product (*P*,*S*,*S*)-**126**. Finally, the reaction with chlorodiphenylphosphine provided the desired helically chiral phosphine (*P*,*S*,*S*)-**125c** as a single product in 84% isolated yield (Entry 7). It was observed that generally the reaction temperatures below -105 ºC were sufficient for the formation of the phosphine in good yields.

Phosphine (*P*,*S*,*S*)-**125c** was prone to oxidation and was protected with borane for practical reasons (Scheme 3.5).[133-135] The resultant phosphine-borane complex (*P*,*S*,*S*)-**127** was a stable compound, which allowed chromatographic purification. The borane moiety could be easily removed by heating with an excess of diethylamine.[134, 136, 137]

In order to tune the electronic and steric parameters of the phosphorous ligands, the substituents on the phosphorus were varied. Dicyclohexylphosphine (*P*,*S*,*S*)-**128** and diisopropylphosphine (*P*,*S*,*S*)-**129** were prepared in acceptable yields using the corresponding dialkylchlorophosphines under the optimised conditions (Scheme 3.5). However, when using di(*t*-butyl)chlorophosphine or di(*o*-tolyl)chlorophosphine, the desired derivatives (*P*,*S*,*S*)-**130** and (*P*,*S*,*S*)-**131** were not obtained probably due to larger steric requirements of these substituents and only the hydrogen-transfer product (*P*,*S*,*S*)-**126** was obtained instead.

Scheme 3.5



(*P*,*S*,*S*)-**124**

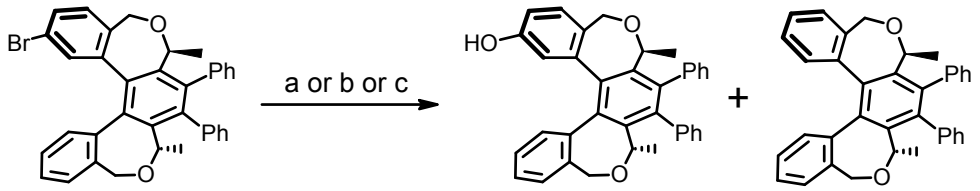
(*P*,*S*,*S*)-**127** R = Ph, 87%
(*P*,*S*,*S*)-**128** R = Cy, 64%
(*P*,*S*,*S*)-**129** R = *i*-Pr, 50%
(*P*,*S*,*S*)-**130** R = *t*-Bu, 0%
(*P*,*S*,*S*)-**131** R = *o*-Tol, 0%

(a) 1) *t*-BuLi (2.0-2.1 equiv.), Et_2O, -110 ºC, 1-2 min; 2) R_2PCl (1.5-1.9 equiv.), -110 ºC → 0 °C, 30 min; 3) BH_3-$S(CH_3)_2$ (5.0 equiv.), 0 °C, 1 h.

The alternative methods for phosphine (*P*,*S*,*S*)-**127** preparation were also tested. The procedure by Liese *et al.* using tetrakis(triphenylphosphine)palladium and diphenylphosphine for phosphination of arylbromides[138] was performed but bromide (*P*,*S*,*S*)-**124** was unreactive under these conditions. Furthermore, no bromine-magnesium exchange reaction occurred with (*P*,*S*,*S*)-**124** when magnesium turnings or isopropylmagnesium halide were used in the reaction.[139, 140]

As it was advantageous to use bromide (*P*,*S*,*S*)-**124** as a common precursor of the phosphites as well, the transformation of (*P*,*S*,*S*)-**124** to the hydroxy substituted helicene (*P*,*S*,*S*)-**132** was explored (Scheme 3.6). However, the palladium-catalysed reaction employing potassium hydroxide as a nucleophile provided the desired helicenol (*P*,*S*,*S*)-**132** in the negligible 9% isolated yield.[141] The copper-catalysed hydroxylation using tetrabutylammonium hydroxide was also unsuccessful leaving the bromide unreacted.[142] The bromine-magnesium exchange reaction of the helical bromide (*P*,*S*,*S*)-**124** with dibutylisopropylmagnesium ate complex (*i*-$PrBu_2MgLi$)[143] at 0 ºC and the subsequent reaction with gaseous oxygen at -78 °C furnished helicenol (*P*,*S*,*S*)-**132** in 37% isolated yield together with 42% yield of the hydrogen-transfer product (*P*,*S*,*S*)-**126**. In this case, the decrease of the bromine-magnesium exchange reaction temperature left bromide (*P*,*S*,*S*)-**124** unreacted. The halogen-lithium exchange reaction of bromide (*P*,*S*,*S*)-**124** with two equivalents of *t*-butyllithium at -105 ºC, followed by the reaction with gaseous oxygen at the same temperature, provided helicenol (*P*,*S*,*S*)-**132** and the reduced product (*P*,*S*,*S*)-**126** in 32% and 43% isolated yields, respectively.

Scheme 3.6



(*P*,*S*,*S*)-**124** (*P*,*S*,*S*)-**132** (*P*,*S*,*S*)-**126**

(a) KOH (5.1 equiv.), $Pd(dba)_2$ (7 mol%), XPhos (16 mol%), water/1,4-dioxane (1:1), 100 ºC, 16 h, 9% for **132**.
(b) 1) *i*-$PrBu_2MgLi$ (1.25 equiv.), THF, 0 ºC, 15 min; 2) O_2 (g), - 78 ºC, 30 min; 3) HCl, - 78 ºC →r.t., 37% for **132**, 42% for **126**.
(c) 1) *t*-BuLi (2.1 equiv.), Et_2O, -105 ºC, 1 min.; 2) O_2 (g), -105 ºC, 1.5 h, 3) HCl, - 105 ºC →r.t., 32% for **132**, 43% for **126**.

These initial results demonstrated that the diastereoselective synthesis of helically chiral molecules, which took advantage of the thermodynamic energy difference between the two possible diastereomers, was viable and indeed provided exclusively the lower energy (*P*,*S*,*S*)-diastereomer in >99% *de* as predicted by the theoretical calculations. In addition, the synthesis allowed preparation of the functionalised helical compound (*P*,*S*,*S*)-**124**, which could serve as the precursor of phosphines and phosphites (see Chapter 3.1.1.2 for information on the synthesis of the phosphites from the respective helicenols). Because of the low yields obtained in the transformation of the helical bromide (*P*,*S*,*S*)-**124** to helicenol (*P*,*S*,*S*)-**132**, an alternative synthesis of methoxy substituted helicene scaffolds was pursued (Chapter 3.1.1.2). The successful transformation of the bromide (*P*,*S*,*S*)-**124** to the phosphines (*P*,*S*,*S*)-**127**-**129** encouraged us in pursuit of the synthesis of regioisomeric 3-bromo[5]helicene-like compound (*P*,*S*,*S*)-**142** and its transformation to the phosphines.

Helicene-like compounds with phosphine group in position *3*

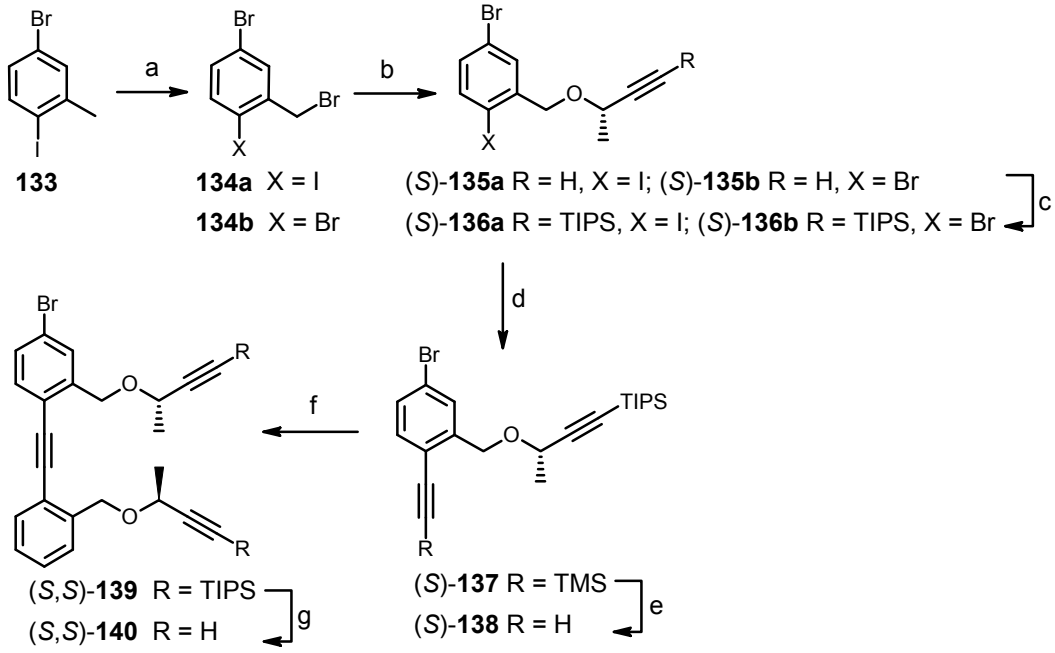
The preparation of 3-bromo[5]helicene-like compound (*P*,*S*,*S*)-**142** followed the same synthetic protocol which was elaborated for the 2-bromo[5]helicene-like compound (*P*,*S*,*S*)-**124**. However, due to the different reactivity of the regioisomer **133** (Scheme 3.7) towards the radical bromination, commercially available bromoiodide **133** afforded dibromoiodide **134a**[121, 144] contaminated with 30% of the inseparable tribromide **134b**[226] resulting from the iodine-bromine exchange reaction. This impurity could not be removed until the polarity of the product of one of the subsequent reactions had changed significantly later in the synthesis. The following nucleophilic substitution of **134** with the chiral alkoxide, derived from the enantiopure alcohol (*S*)-**111**, afforded alkynes (*S*)-**135a** and (*S*)-**135b**, which were subsequently protected with triisopropylsilyl group to provide silanes (*S*)-**136a** and (*S*)-**136b**. Sonogashira cross-coupling of iodide (*S*)-**136a** with ethynyl(trimethyl)silane was carried out at 0 °C providing diyne (*S*)-**137**. Bromide (*S*)-**136b** remained unreacted as an impurity in this and the following reaction as well. The subsequent selective deprotection of the TMS group in diyne (*S*)-**137** afforded the monosilylated diyne (*S*)-**138**. The increased polarity of alkyne (*S*)-**138** permitted an efficient chromatographic purification and removal of the impurity **136b**. Nevertheless, the bromo substituted diynes (*S*)-**137** and (*S*)-**138** were unstable and had to be used in the next reactions soon after preparation.

Sonogashira cross-coupling of the two building blocks – diyne (*S*)-**138** and aryl iodide (*S*)-**113** – was carried out at 0 ºC in order to avoid the concurrent reaction on the C-Br bond. The resulting triyne (*S*,*S*)-**139** was deprotected using tetrabutylammonium fluoride to give triyne (*S*,*S*)-**140** in good yield. The yield of the desilylation reaction was strongly temperature dependent: adding the fluoride solution at -78 ºC and leaving the reaction mixture to warm-up slowly to room temperature instead of performing the whole reaction at room temperature, increased the yield from 62% to 95%.

Two phenyl substituents were introduced into triyne (*S*,*S*)-**140** in good yield by the double Sonogashira cross-coupling with iodobenzene (Scheme 3.8).[118] The bisarylated triyne (*S*,*S*)-**141** was then subjected to [2+2+2] cyclotrimerisation under microwave irradiation in the presence of cyclopentadienylcobalt(I) complexes –

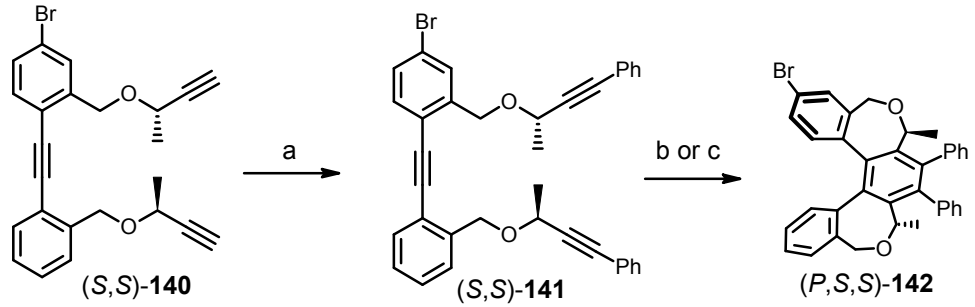
$CoCp(CO)_2$ and CoCp(CO)(fum). Both complexes provided the helicene-like (*P*,*S*,*S*)-**142** in high yield as a single diastereomer. The optical purity was established from the fact that no racemisation took place on the chiral centre during the synthesis and the other diastereomers of the final helicene-like compounds were not detected by the NMR analysis.

Scheme 3.7



(a) NBS (1.2 equiv.), AIBN (cat.), K_2CO_3 (cat.), CCl_4, IR lamp, reflux, 10 h, 45% for **134a** and **134b** (2:1).
(b) KH (1.1 equiv.), (*S*)-**111** (1.1 equiv.), THF, 0 ºC→r.t., 1.5 h, 95% for **135a** and **135b** (2:1).
(c) 1) LDA (1.0 equiv.), THF, -78 ºC, 1 h; 2) TIPSCl (1.0 equiv.), -78 ºC→r.t., overnight, 63% for **136a** and **136b** (2:1).
(d) TMSA (1.1 equiv.), $Pd(PPh_3)_4$ (0.6 mol%), CuI (2 mol%), DIPA, 0 ºC, 30 min, 98% for **137** and **136b** (3:1).
(e) $NaOCH_3$ (1.0 equiv.), methanol-THF (2:1), r.t., 30 min, 61%.
(f) (*S*)-**113** (1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (1 mol%), CuI (2 mol%), DIPA, 0 ºC, 2 h, 80%.
(g) TBAF (1.0 equiv.), THF, -78 ºC, 1 h, then r.t., overnight, 95%.

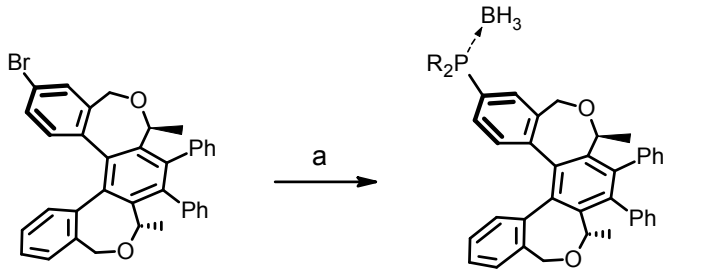
Scheme 3.8



(a) PhI (4.0 equiv.), $Pd(PPh_3)_4$ (1 mol%), CuI (2 mol%), DIPA, 0 ºC, 1h, then r.t., overnight, 92%.
(b) $CoCp(CO)_2$ (1.3 equiv.), PPh_3 (2.0 equiv.), THF, ionic liquid, MW, 180 ºC, 30 min, 92%.
(c) CoCp(CO)(fum) (1.1 equiv.), THF, SiC, MW, 180 ºC, 10 min, 94%.

The helical diphenyl- and dicyclohexylphosphino borane complexes (*P*,*S*,*S*)-**143** and (*P*,*S*,*S*)-**144** were prepared under the optimised conditions of bromine-lithium exchange reaction using two equivalents of *t*-butyllithium at the temperature carefully kept below -110 ^{o}C in good yields (Scheme 3.9). Without protection with borane, even diphenylphosphino derivative (*P*,*S*,*S*)-**143** easily oxidised while being exposed to air in solution as was observed in ^{31}P NMR spectra.

Scheme 3.9

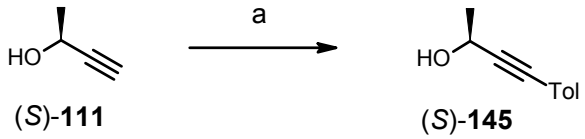


(a) 1) *t*-BuLi (2.0 equiv.), Et_2O, <-110 ºC, 1 min; 2) $ClPR_2$ (2.3-2.9 equiv.), -110 ºC → -80 ºC, 1 h (for **143**) or -110 ºC, 15 min (for **144**), then 0 ºC, 15 min; 3) BH_3-$S(CH_3)_2$ (10-26 equiv.), 0 ºC→r.t., overnight.

Helicene-like compound with phosphine group in position *8*

The diastereoselective synthetic methodology developed for the functionalised helicene-like compounds with substituents on the terminal aromatic ring was then extended to the synthesis of optically pure helicene-like compound with the phosphine group on the central aromatic ring. The synthesis of the helicene-like compound (*P*,*S*,*S*)-**153** with the diphenylphosphine group directly attached to the helical scaffold in position *8* started with the preparation of the chiral alcohol (*S*)-**145** from the commercial alcohol (*S*)-**111** by Sonogashira cross-coupling with *p*-iodotoluene (Scheme 3.10).[66]

Scheme 3.10



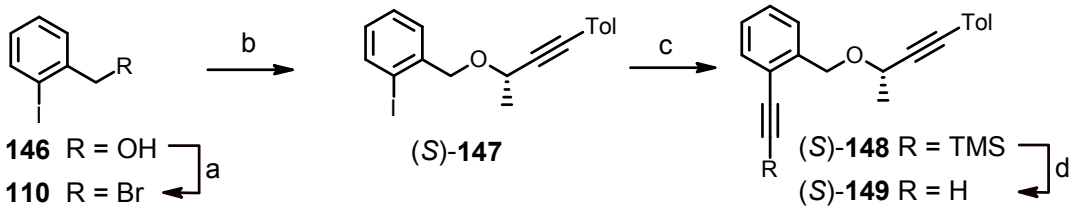
(*S*)-**111** (*S*)-**145**

(a) *p*-iodotoluene (1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (8 mol%), DIPA (5.0 equiv.), toluene, r.t., overnight, 99%.

The synthesis of the unsubstituted building block (*S*)-**149** (Scheme 3.11) started from the benzyl bromide **110**, which could be easily prepared from benzyl alcohol **146**.[145] The reaction of the bromide **110** with the alkoxide derived from (*S*)-**145** afforded the aryl iodide (*S*)-**147** in good yield. It was then converted into diyne (*S*)-**149** by Sonogashira cross-coupling with ethynyl(trimethyl)silane and the subsequent desilylation with potassium carbonate in a mixture of dichloromethane-methanol afforded (*S*)-**149** in an excellent isolated yield.

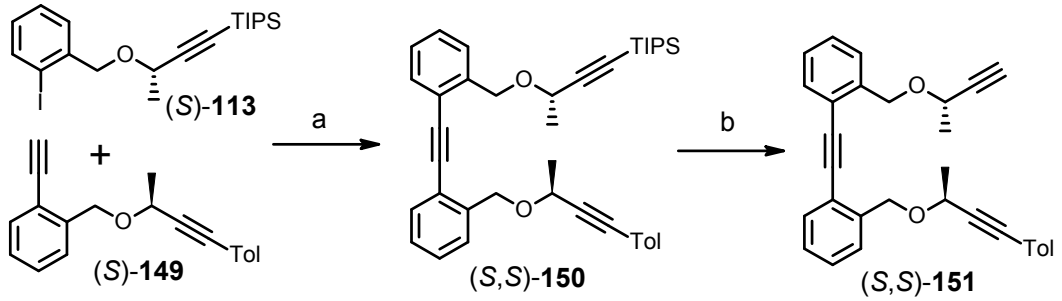
Sonogashira cross-coupling of the building blocks (*S*)-**113** and (*S*)-**149** provided the triyne (*S*,*S*)-**150** in good yield (Scheme 3.12). The following removal of the triisopropylsilyl group with tetrabutylammonium fluoride provided the triyne (*S*,*S*)-**151** in excellent yield.

Scheme 3.11



(a) PBr_3 (1.5 equiv.), THF, 0 °C, 30 min, 95%.
(b) (*S*)-**145** (1.0 equiv.), KH (1.5 equiv.), THF, 0 °C→r.t., overnight, 76%.
(c) TMSA (1.1 equiv.), $Pd(PPh_3)_4$ (2 mol%), CuI (4 mol%), DIPA, r.t., 15 h , 94%.
(d) K_2CO_3 (2.0 equiv.), CH_3OH/CH_2Cl_2 (1:5), r.t., 30 min, 94%.

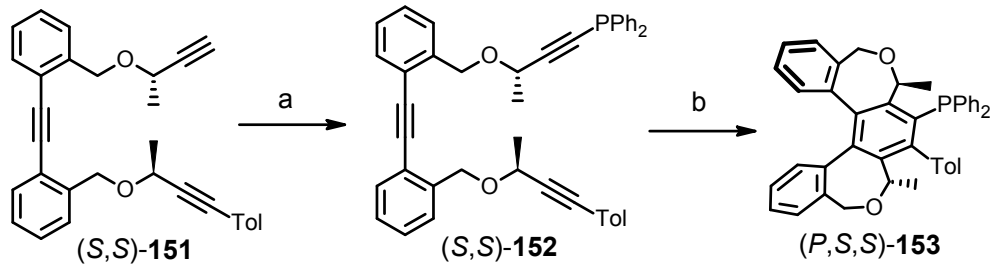
Scheme 3.12



(a) (*S*)-**113** (1.0 equiv.), (*S*)-**149** (1.1 equiv.), $Pd(PPh_3)_4$ (5 mol%), CuI (10 mol%), DIPA (6.3 equiv.), toluene, r.t., overnight, 77%.
(b) TBAF (1.05 equiv.), THF, 0 ºC, 10 min, then r.t., 30 min, 93%.

Introduction of the diphenylphosphino group into the triyne (*S*,*S*)-**151** was accomplished using *n*-butyllithium at -78 °C followed by the addition of chlorodiphenylphosphine (*S*,*S*)-**151** → (*S*,*S*)-**152** (Scheme 3.13). Reaction with LDA was also examined but the results were not reproducible. The resulting phosphine (*S*,*S*)-**152** was surprisingly stable towards the oxidation in air but decomposed on silica gel (even on silica gel deactivated with 2% of triethylamine). Thus, (*S*,*S*)-**152** was purified using the reversed phase chromatography in order to obtain acceptable yields.

Scheme 3.13

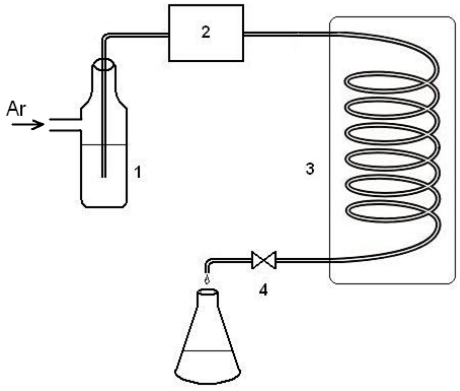


(a) 1) *n*-BuLi (1.1 equiv.), THF, -78 ºC, 2 min; 2) Ph_2PCl (1.3 equiv.), -78 ºC, 10 min, then →r.t., 30 min, 59%.
(b) $CoCp(CO)_2$ (0.6 equiv.), THF, 250 ºC, 70 bar, continuous flow reactor, 42%.

Attempts to cyclotrimerise triyne (*S*,*S*)-**152** with methods previously used, *i.e.* $CoCp(CO)_2/PPh_3$ combined with a halogen lamp or with microwave irradiation, failed due to decomposition of the starting compound (*S*,*S*)-**152**.

However, we have recently successfully applied a continuous flow reactor (Figure 3.2) to various problematic cyclotrimerisation reactions. When the pressurised mixture of (*S*,*S*)-**152** and a substoichiometric amount of $CoCp(CO)_2$ in tetrahydrofuran passed through a heated steel capillary at 250 ºC and 70 bar, the helical phosphine (*P*,*S*,*S*)-**153** was readily obtained in 42% yield and >99% *de*. The main by-product was cyclobutadienylcobalt complex[146-151] as determined from LC-MS analysis.

Figure 3.2 Schematic representation of the continuous flow reactor.



Legend: 1 – Schlenk flask with a reaction mixture connected to an argon line; 2 – HPLC pump; 3 – heated stainless steel capillary; 4 – backpressure valve.

The NMR spectrum of phosphine (*P*,*S*,*S*)-**153** deserves special attention. The signal of one methyl group was shifted unusually upfield to the value of -0.08 ppm

(doublet A in Figure 3.3). In addition, ^{31}P-NMR showed a magnetic shielding of the phosphorus as compared to the previously prepared helical phosphines. The single-crystal X-ray diffraction analysis (Figure 3.4, Appendix A) revealed that the shielding originated from the close proximity of the phosphorus atom to the tolyl substituent (the distance is approximately 3 Å). The anisotropic shielding of the methyl protons, on the other hand, resulted from the proximity of one methyl group to the phenyl ring of the diphenylphosphino substituent.

Figure 3.3 A fragment of the HSQC NMR spectrum of (*P*,*S*,*S*)-**153**. The two doublets (A and B) correspond to the methyl groups on the dihydrooxepine rings and the singlet C belongs to the methyl of the tolyl substituent.

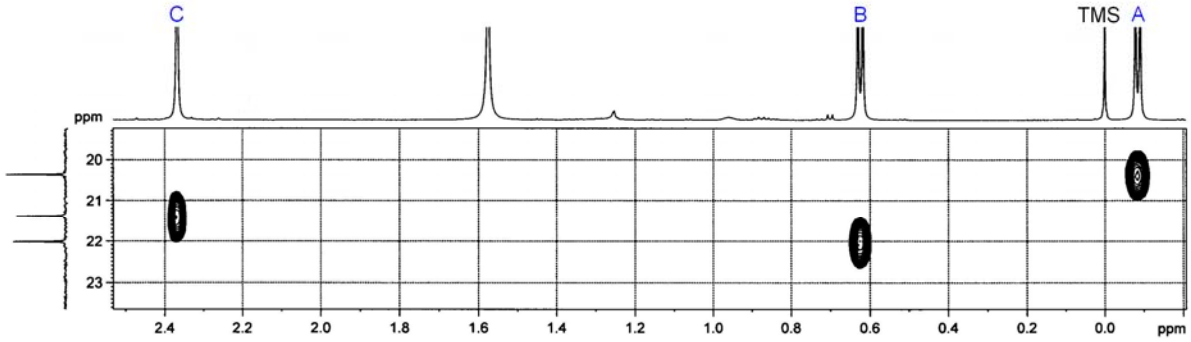
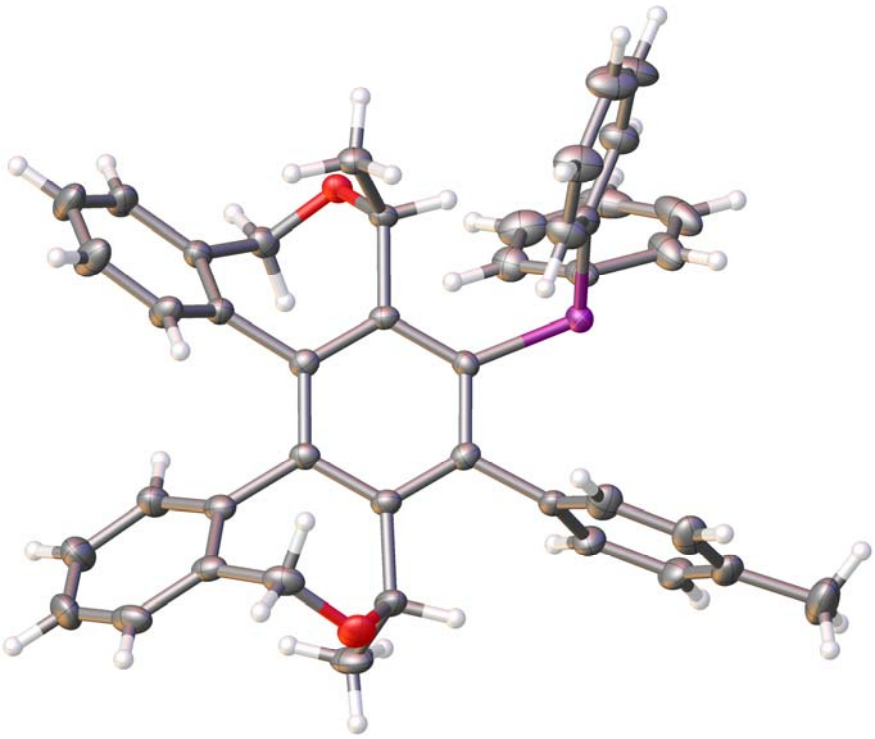


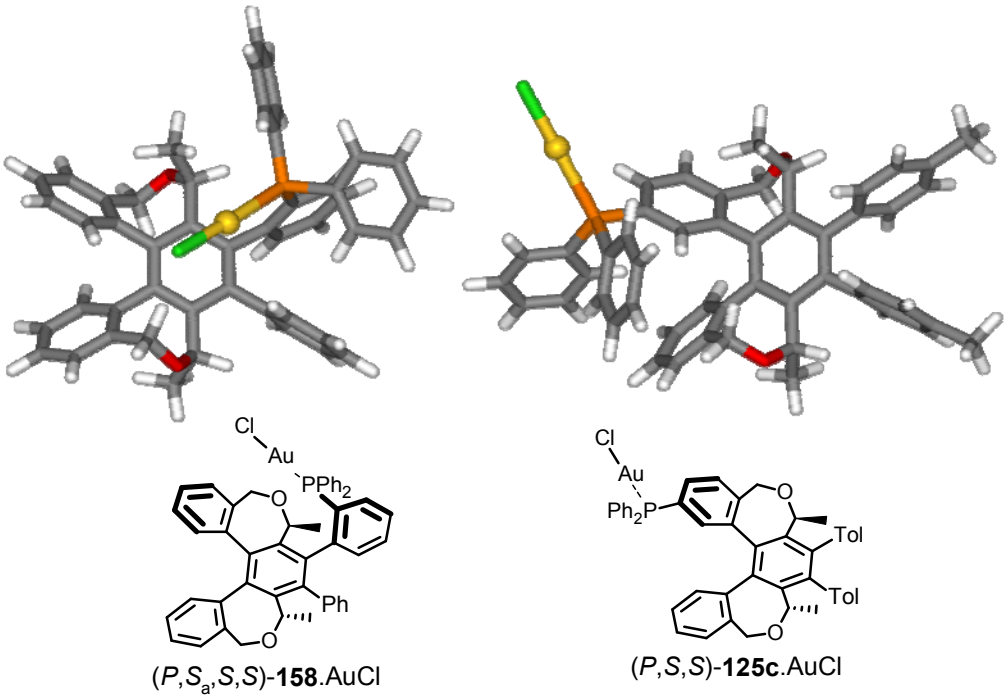
Figure 3.4 X-ray structure of phosphine (*P*,*S*,*S*)-**153** with thermal ellipsoids at 50% probability level.



Atropisomeric helicene-like phosphines

Inspired by the success in highly diastereoselective synthesis of the functionalised helicenes with phosphine groups in positions *2*, *3* and *8*, we decided to synthesise a more complex structure, which would have the phosphine group positioned just above or below the helical cavity, depending on the configuration of the chiral axis, which arises from *ortho*-substitution on the phenyl ring. The models of the gold(I) complex with phosphine (*P*,S_a,*S*,*S*)-**158** and the already synthesised phosphine (*P*,*S*,*S*)-**125c** show the advantageous orientation of the transition metal in the first compound (Figure 3.5). It is known that the linear geometry of gold(I) complexes makes the enantioselective gold(I)-catalysed reactions particularly challenging because of the increased distance between the substrate and the chiral phosphine ligand.[152-154]

Figure 3.5 Molecular models of gold(I) chloride complexes of phosphines (*P*,S_a,*S*,*S*)-**158** and (*P*,*S*,*S*)-**125c**.



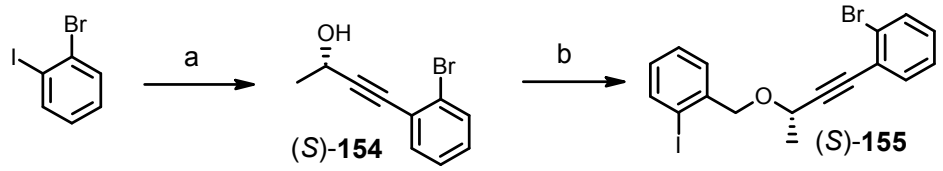
(*P*,S_a,*S*,*S*)-**158**.AuCl (*P*,*S*,*S*)-**125c**.AuCl

The first attempt to synthesise (*P*,S_a,*S*,*S*)-**158** was based upon the preparation of the helical bromide (*P*,S_a,*S*,*S*)-**157** and its subsequent conversion to the phosphine-borane complex (*P*,S_a,*S*,*S*)-**158** using bromine-lithium exchange reaction.

The synthesis of the bromide (*P*,S_a,*S*,*S*)-**157** started with the preparation of the chiral bromo alcohol (*S*)-**154**, which was readily obtained from the commercial

optically pure alcohol (*S*)-**111** by Sonogashira cross-coupling reaction (Scheme 3.14). The cross-coupling was carried out at 0 °C to suppress the concurrent reaction on the C-Br bond. The following deprotonation of (*S*)-**154** and the reaction with benzyl bromide **110** provided the building block (*S*)-**155** in good yield.

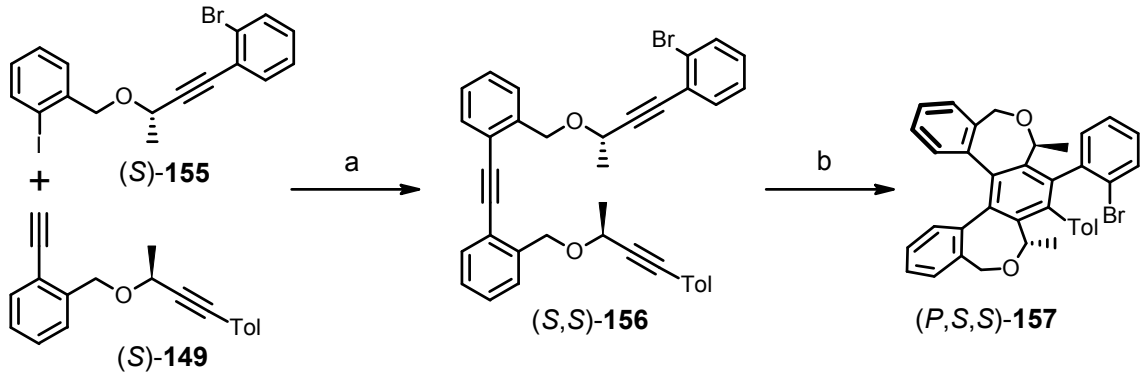
Scheme 3.14



(a) (*S*)-**111** (1.06 equiv.), $Pd(PPh_3)_4$ (2 mol%), CuI (4 mol%), DIPA, 0 ºC→r.t., overnight, 99%.
(b) 1) KH (1.8 equiv.), THF, 0 ºC, 20 min; 2) **110** (1.36 equiv.), THF, 0 ºC, 30 min, 85%.

The aryl iodide (*S*)-**155** then reacted with the diyne building block (*S*)-**149** under the Sonogashira cross-coupling conditions again at 0 ºC to provide (*S*,*S*)-**156** in good yield (Scheme 3.15).

Scheme 3.15

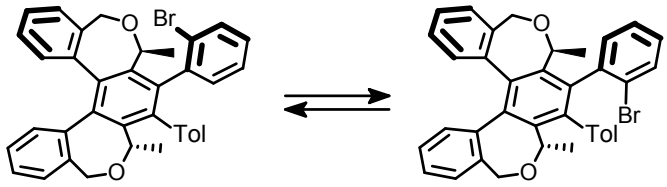


(a) $Pd(PPh_3)_4$ (5 mol%), CuI (10 mol%), DIPA, 0 ºC, 1 h, then →r.t., 2 h, 75%.
(b) $CoCp(CO)_2$ (1.3 equiv.), PPh_3 (2.0 equiv.), THF, MW, 200 ºC, 10 min, 60%.

As expected, the cyclotrimerisation of triyne (*S*,*S*)-**156** provided the helical bromide (*P*,*S*,*S*)-**157** as a 56:44 mixture of atropisomers (*P*,S_a,*S*,*S*)-**157** and (*P*,R_a,*S*,*S*)-**157**, which were formed as the result of the *ortho*-substitution on the phenyl ring (Scheme 3.16). No change of the atropisomer ratio was observed after heating the mixture in DMF at 250 ºC for 1 hour. The high interconversion barrier

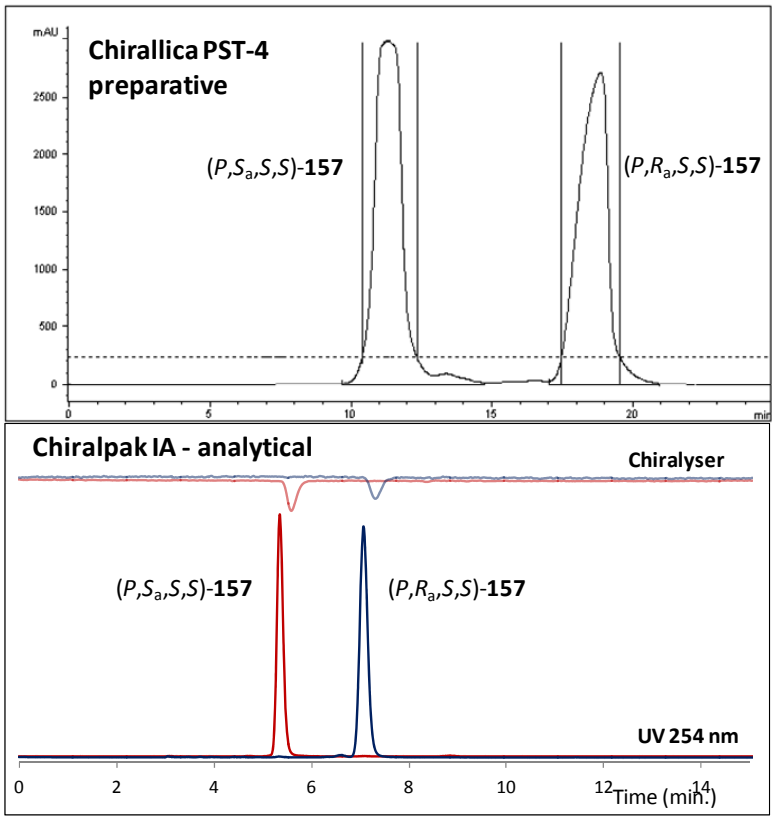
allowed separation of the atropisomers by HPLC chromatography using a chiral stationary phase (Figure 3.6). The chiral HPLC column was necessary for the effective separation because the atropisomers were inseparable on a normal and reversed phase. The elucidation of the structure was done on the basis of the single-crystal X-ray diffraction analysis of atropisomer (*P*,S_a,*S*,*S*)-**157** (Figure 3.7, Appendix A). The other atropisomer (*P*,R_a,*S*,*S*)-**157** did not provide single crystals but the spectroscopic data (NMR, IR, MS) confirmed that this compound differed from (*P*,S_a,*S*,*S*)-**157** only in the conformation.

Scheme 3.16



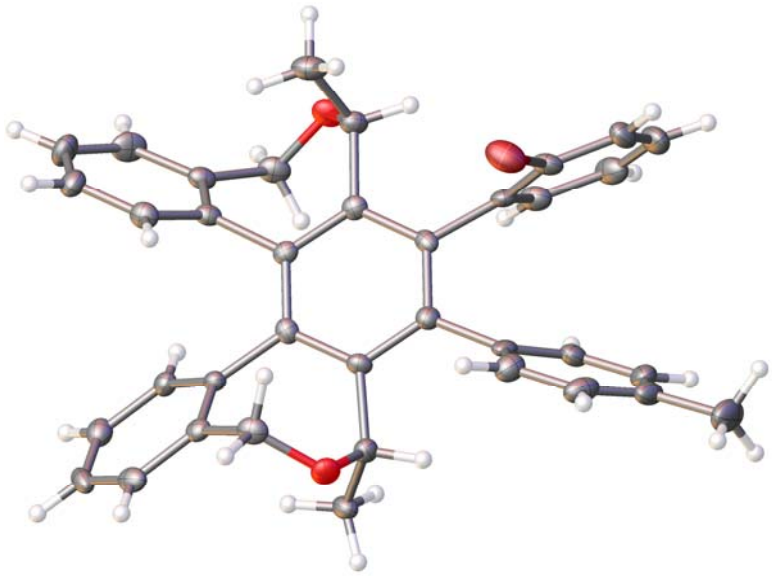
(*P*,S_a,*S*,*S*)-**157** (*P*,R_a,*S*,*S*)-**157**

Figure 3.6 Chromatogram of the preparative HPLC separation of the two atropisomers on Chirallica PST-4 column and the demonstration of their purity on the analytical Chiralpak IA column.



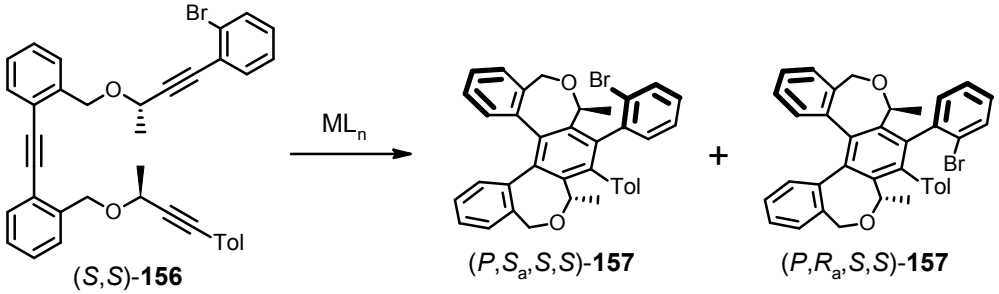
The barrier of interconversion of the two atropisomers was not established experimentally as it required temperatures higher than 250 ºC. The value of the interconversion barrier between (*P*,S_a,*S*,*S*)-**157** and (*P*,R_a,*S*,*S*)-**157** was calculated to be 45.65 kcal/mol (B3LYP/cc-pVDZ level, Appendix B). The difference in the free energies between (*P*,S_a,*S*,*S*)-**157** and (*P*,R_a,*S*,*S*)-**157** was found to be insignificant (0.34 kcal/mol).[155]

Figure 3.7 X-ray structure of bromide (*P*,S_a,*S*,*S*)-**157** with thermal ellipsoids at the 50% probability level.



The influence of the reaction conditions on the ratio of atropisomers was examined (Table 3.3). The cyclotrimerisation reaction was investigated using $CoCp(CO)_2$, CoCp(CO)(fum) and $RhCp^*(C_2H_2)_2$ complexes, since the iridium[156] and the cationic rhodium[107]complexes were unreactive. Initially, the microwave-assisted synthesis using $CoCp(CO)_2$ and PPh_3 in a ratio of 1:2 was carried out at 140 and 200 °C (Entries 1-2). Higher yield was obtained at 140 °C and the atropisomer ratio was nearly the same in both reactions. Carrying out the reaction under halogen lamp irradiation and with a prolonged reaction period decreased the isolated yield to 34% without affecting the atropisomer ratio (Entry 3). Furthermore, the use of CoCp(CO)(fum) complex, which was more air and temperature stable[157, 211] compared to $CoCp(CO)_2$, was also investigated. Heating at 180 °C was required for the cyclotrimerisation to proceed and the mixture of atropisomers was obtained in excellent yield and unchanged ratio (Entry 4).

Table 3.3



(*S*,*S*)-**156** (*P*,S_a,*S*,*S*)-**157** (*P*,R_a,*S*,*S*)-**157**

Entry	ML_n[a]	Solvent	Heating mode	Temperature, Time[b]	Isolated yield	Atropisomer ratio S_a:R_a[c]
1	$CoCp(CO)_2/PPh_3$	THF	MW	140 ºC,20 min	83%	59 : 41
2	$CoCp(CO)_2/PPh_3$	THF	MW	200 ºC,10 min	60%	56 : 44
3	$CoCp(CO)_2/PPh_3$	decane	hν	140 ºC, 2 h	34%	60 : 40
4	CoCp(CO)(fum)	THF	MW	180 ºC,10 min	96%	60 : 40
5	$RhCp^*(C_2H_2)_2$	THF	MW	140 ºC,15 min	42%	72 : 28
6	$RhCp^*(C_2H_2)_2$	THF	MW	200 ºC,10 min	88%	1 : 1[d]
7	$RhCp^*(C_2H_2)_2$	decane	hν	140 ºC, 1 h	50%	60 : 40

[a] Stoichiometric amount of the transition-metal complex and 2 equiv. of PPh_3 was used in all cases due to the low reactivity of the triyne. Use of substoichiometric amounts resulted only in partial conversion of the substrate.

[b] The reaction proceeded until all the triyne was consumed according to the TLC analysis.

[c] The ratio of the products was determined using HPLC and NMR techniques.

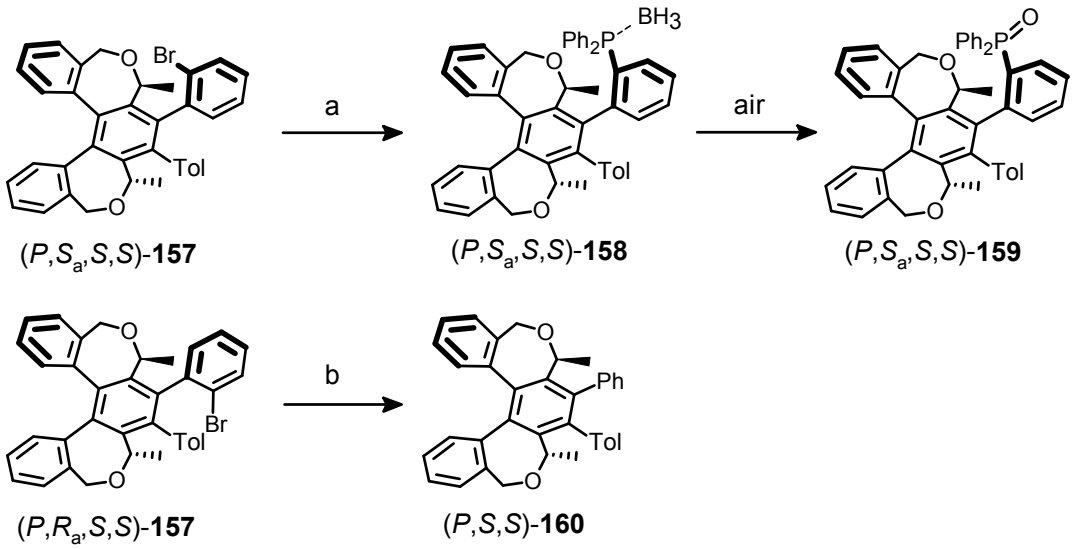
[d] Isolated product contained 33% of (*P*,*S*,*S*)-**160**.

Reactivity of $RhCp^*(C_2H_2)_2$ complex was also examined at different temperatures (Entries 5-7). The microwave-assisted reaction at 140 °C provided the helicene-like compound in moderate yield. In contrast to the cobalt-mediated reactions, the atropisomer ratio shifted in favour of the S_a isomer (Entry 5). Raising the temperature to 200 °C provided the atropisomers in a 1:1 ratio, but they were contaminated with the product of the reductive dehalogenation (*P*,*S*,*S*)-**160** (Entry 6). The yield of cyclotrimerisation with $RhCp^*(C_2H_2)_2$ complex under halogen lamp irradiation at 140 °C was comparable to the microwave-assisted reaction at the same temperature (*cf.* Entries 5 and 7). However, the atropisomer ratio was closer to that obtained from the cobalt-mediated cyclotrimerisations (*cf.* Entries 1-4 and 7).

On the whole, the cobalt complexes were the most suitable for the cyclotrimerisation of triyne (*S*,*S*)-**156**. Compared to the rhodium complex, cobalt complexes afforded reaction mixtures with fewer by-products. In addition, the reductive dehalogenation by-product (*P*,*S*,*S*)-**160** was never observed in the case of cobalt-mediated reactions. Generally, the atropisomer ratio S_a:R_a was roughly 2:1 except for the case, when the $RhCp^*(C_2H_2)_2$ complex and microwave irradiation were used. Counterintuitively, the ratio was mostly shifted in favour of the atropisomer (*P*,S_a,*S*,*S*)-**157**, which had the higher calculated free energy (Appendix B).

The separated atropisomers of (*P*,*S*,*S*)-**157** exhibited the different reactivity with respect to the lithium-halogen exchange reaction. At -110 ºC the atropisomer (*P*,S_a,*S*,*S*)-**157** provided the phosphine-borane complex (*P*,S_a,*S*,*S*)-**158** in acceptable yield. The other atropisomer (*P*,R_a,*S*,*S*)-**157** under the same reaction conditions provided only the reduced product (*P*,*S*,*S*)-**160** (Scheme 3.17).

Scheme 3.17



(*P*,S_a,*S*,*S*)-**157** (*P*,S_a,*S*,*S*)-**158** (*P*,S_a,*S*,*S*)-**159**

(*P*,R_a,*S*,*S*)-**157** (*P*,*S*,*S*)-**160**

(a) 1) *t*-BuLi (2.0 equiv.), Et_2O, -110 ºC, 1 min; 2) Ph_2PCl (2.8 equiv.), -110 ºC→0 °C, 2 h; 3) BH_3·THF (66 equiv.), 0 °C→r.t., 30 min, 55%.

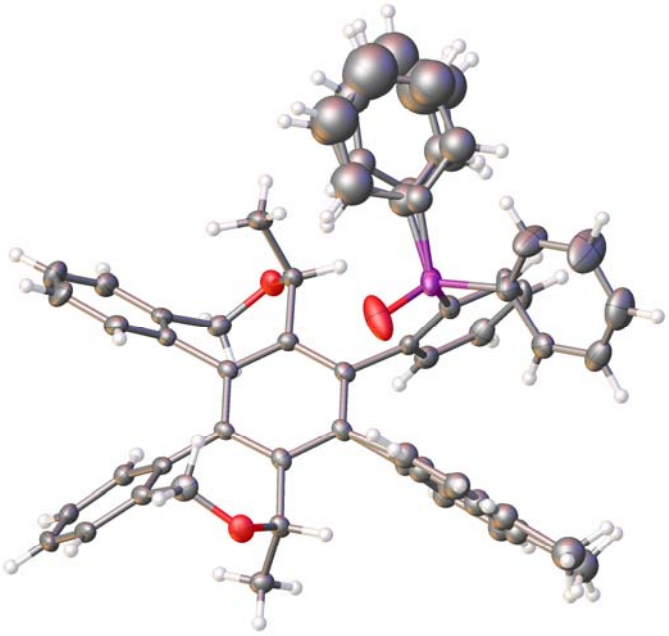
(b) 1) *t*-BuLi (2.0 equiv.), Et_2O, -110 ºC, 1 min; 2) Ph_2PCl (2.8 equiv.), -110→0 °C, 2 h; 3) BH_3·THF (66 equiv.), 0 °C→r.t., 30 min, 82%.

This result is counterintuitive since the lithiated intermediate resulting from the bromine-lithium exchange with (*P*,R_a,*S*,*S*)-**157** atropisomer could be stabilised by coordination to the proximate oxygen atom of the 7-membered ring.

Furthermore, it was surprising that the phosphine-borane complex (*P*,S_a,*S*,*S*)-**158** was very air-sensitive. In contrast to the previously prepared phosphine-borane

complexes, the borane protected phosphine (*P*,S_a,*S*,*S*)-**158** readily oxidised in a solution and upon the contact with silica gel to the phosphine oxide (*P*,S_a,*S*,*S*)-**159**. In addition, the decomposition was observed during chromatography on silica gel. Due to these complications it was not prepared on a larger scale and accordingly was not tested in asymmetric catalysis. The single-crystal X-ray diffraction analysis of (*P*,S_a,*S*,*S*)-**159** was unfortunately flawed by the crystal structure disorders (Figure 3.8, Appendix A). Nevertheless, this structure combined with the evidence from the NMR analysis demonstrated that there was no epimerisation during the bromine-lithium exchange reaction (Figure 3.8).

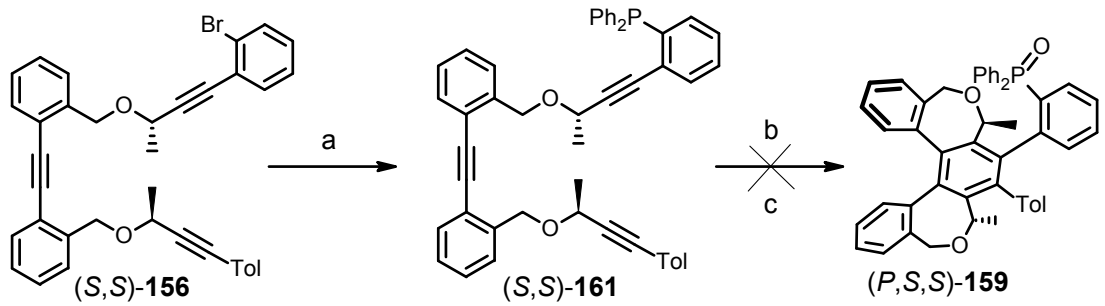
Figure 3.8 X-ray structure of (*P*,S_a,*S*,*S*)-**159** with thermal ellipsoids at the 50% probability level.



An alternative synthetic route leading to both atropisomers of the phosphine (*P*,*S*,*S*)-**158** was also pursued. In this approach (Scheme 3.18), the phosphine group was introduced into the triyne (*S*,*S*)-**156** by the bromine-lithium exchange reaction to provide phosphine (*S*,*S*)-**161** in acceptable yield. Unfortunately, the triyne (*S*,*S*)-**161** was unstable and was prone to decomposition during purification both by silica gel and reversed phase chromatography. Therefore, only a small amount of pure (*S*,*S*)-**161** was obtained. This result could be rationalised by a recent report by Fukazawa *et al.*, in which he described the spontaneous cyclisation of similar phosphines with alkynyl substituents in *ortho* position.[158] The cyclotrimerisation experiments using $CoCp(CO)_2$ complex were performed under microwave irradiation conditions and in

the continuous flow reactor. In neither case the helical phosphine oxide (*P*,*S*,*S*)-**159** was obtained, as the triyne decomposed to a complex mixture of unidentified products.

Scheme 3.18



(a) 1) *n*-BuLi (1.0 equiv.), THF, -85 ºC, 1 min.; 2) Ph_2PCl (1.6 equiv.), -85 ºC, 5 min, 45%.
(b) $CoCp(CO)_2$ (1.0 equiv.), PPh_3 (2.0 equiv.), THF, 180 ºC, 15 min, MW, decomposition.
(c) $CoCp(CO)_2$ (1.0 equiv.), THF, 250 ºC, 80 bar, continuous flow reactor, decomposition.

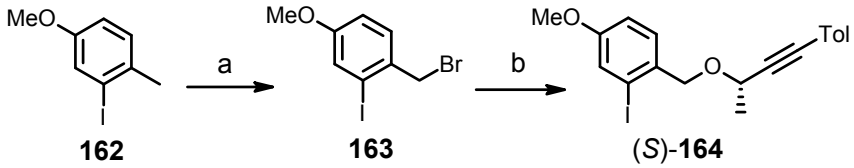
3.1.1.2 Synthesis of phosphites

Helical phosphites have recently proved to be promising ligands in enantioselective transition metal-catalysed reactions. For example, they were recently successfully applied to Rh-catalysed hydroformylation and Ir-catalysed allylic amination reactions.[117]

2-Hydroxyhelicene-like compound as a precursor of phosphites

Phosphites are usually prepared from the corresponding alcohols. Since the access to the hydroxy helicenes from the helical bromides was not viable (*cf*. Scheme 3.6), an alternative synthetic approach via the methoxy substituted helicene-like compounds was pursued. The synthesis started with the preparation of the building block (*S*)-**164** (Scheme 3.19) from aryl iodide **162**.[65] The radical bromination of this compound with NBS provided **163**,[65] which was not contaminated by the iodine-bromine exchange product (*cf*. the preparation of the compound **134**, Scheme 3.7). The following reaction with alkoxide, prepared from (*S*)-**145**, provided the building block (*S*)-**164** in moderate yield.

Scheme 3.19

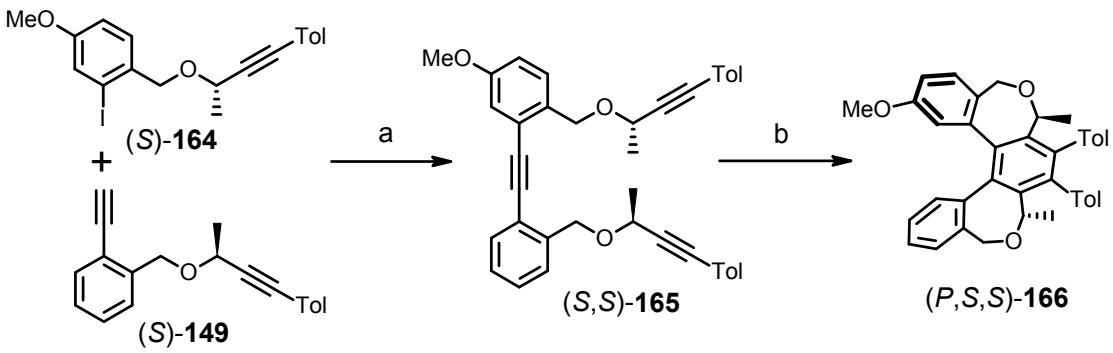


162 **163** (*S*)-**164**

(a) NBS (1.2 equiv.), AIBN (cat.), K_2CO_3 (cat.), CCl_4, IR lamp, reflux, 2h, 98%.
(b) (*S*)-**145** (1.0 equiv.), KH (1.5 equiv.), THF, 0 °C, 1 h, then r.t., overnight, 52%.

The synthesis continued with Sonogashira cross-coupling of the building blocks (*S*)-**149** and (*S*)-**164**, which furnished triyne (*S*,*S*)-**165** in good yield (Scheme 3.20). Finally, the cyclotrimerisation reaction of the methoxy substituted triyne (*S*,*S*)-**165** was performed by the microwave-assisted synthesis in the presence of a cobalt complex and provided the helicene-like compound (*P*,*S*,*S*)-**166**, which was obtained as a single diastereomer.

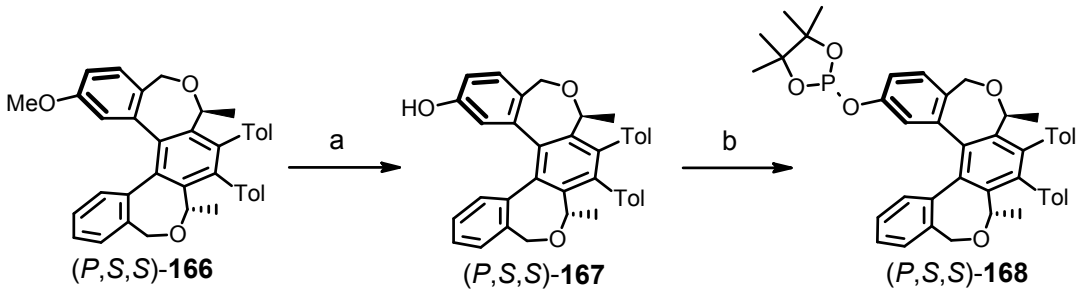
Scheme 3.20



(a) (*S*)-**164** (1.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), CuI (11 mol%), DIPA, 80 ºC, 30 min, 73%.
(b) $CoCp(CO)_2$ (1.0 equiv.), PPh_3 (2.0 equiv.), ionic liquid, THF, MW, 200 ºC, 15 min, 70%.

The methoxy substituted helicene-like compound (*P*,*S*,*S*)-**166** was then demethylated using a large excess of sodium ethanethiolate to give the hydroxy derivative (*P*,*S*,*S*)-**167** in almost quantitative yield (Scheme 3.21). Then it was converted into phosphite (*P*,*S*,*S*)-**168** in the presence of triethylamine and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. The dioxaphospholanyl derivative (*P*,*S*,*S*)-**168** was prepared for an initial testing in enantioselective catalysis because it was found to be successful in the catalytic reactions explored before in our lab.[117]

Scheme 3.21

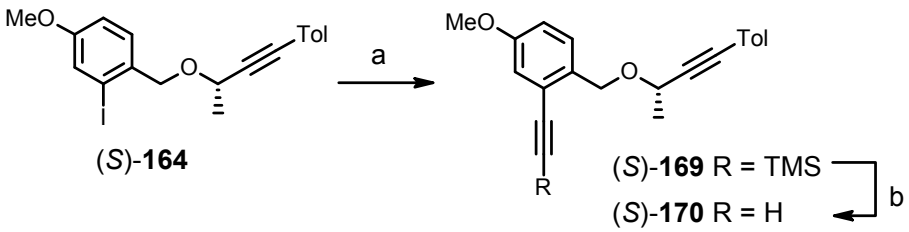


(a) NaSEt (19.2 equiv.), DMF, 130 ºC, 18 h, 98%.
(b) Et_3N (40 equiv.), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (1.2 equiv.), Et_2O, r.t., 1 h, 74%.

2,15-Dihydroxy helicene-like compound as a precursor of helical phosphites/phosphonites

The MeO-substituted aryl iodide (*S*)-**164** was used for the synthesis of diyne (*S*)-**170** (Scheme 3.22). Sonogashira cross-coupling with ethynyl(trimethyl)silane afforded silane (*S*)-**169**, and the subsequent deprotection of the trimethylsilyl group with potassium carbonate in methanol provided diyne (*S*)-**170** in good yield.

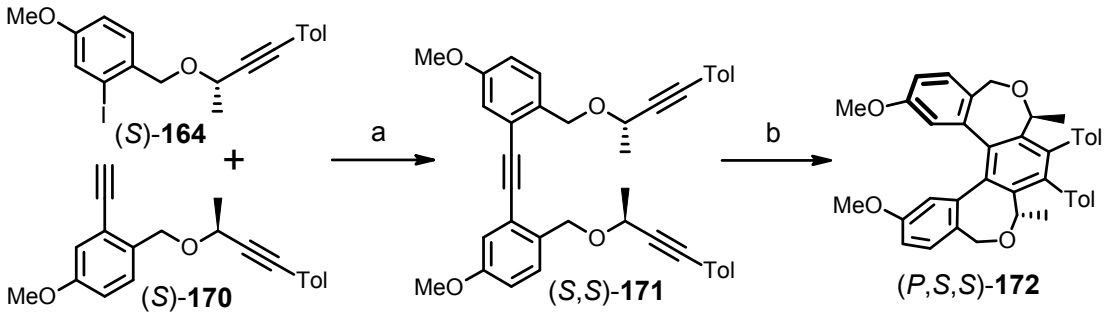
Scheme 3.22



(a) TMSA (1.2 equiv.), $Pd(PPh_3)_4$ (6 mol%), CuI (12 mol%), DIPA, 80 ºC, 45 min., 85%.
(b) K_2CO_3 (3.5 equiv.), methanol, r.t., 2 h, 60%.

Finally, the building blocks (*S*)-**164** and (*S*)-**170** were connected under Sonogashira cross-coupling conditions to give triyne (*S*,*S*)-**171** in high yield (Scheme 3.23). Triyne (*S*,*S*)-**171** was not obtained by a double Sonogashira cross-coupling of aryl iodide (*S*)-**164** with gaseous acetylene since the complex mixture of products including the dimeric by-product (tetrayne) was formed instead.

Scheme 3.23

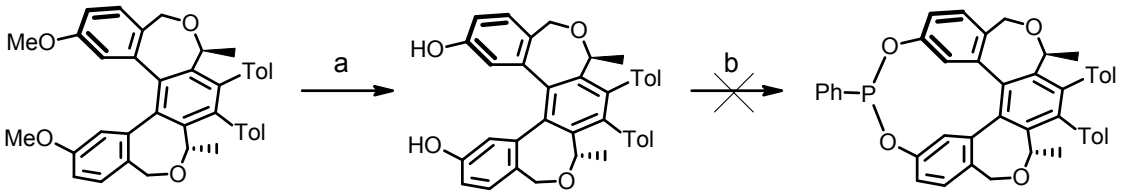


(a) (*S*)-**164** (1.0 equiv.), $Pd(PPh_3)_4$ (2 mol%), CuI (5 mol%), DIPA, r.t., 1.5 h, 82%.
(b) $CoCp(CO)_2$ (1.4 equiv.), PPh_3 (2.0 equiv.), ionic liquid, THF, MW, 200 ºC, 20 min, 88%.

The triyne was then cyclotrimerised in the presence of $CoCp(CO)_2/PPh_3$ and microwave irradiation to give the helicene-like compound (*P*,*S*,*S*)-**172** as a single diastereomer. When the same reaction was carried out in decane under halogen-lamp irradiation, the yield dropped to 53% due to the decomposition of the starting material/product.

Demethylation of (*P*,*S*,*S*)-**172** with an excess of sodium ethanethiolate provided the dihydroxy helicene-like compound (*P*,*S*,*S*)-**173** in excellent yield (Scheme 3.24). Nevertheless, the cyclic phosphonite or bisphosphite compounds were not obtained. Reaction of (*P*,*S*,*S*)-**173** with phenylphosphonous dichloride in the presence of a base resulted in a complex mixture of compounds. The fact that the cyclic product was not formed could be explained by the large distance between the oxygen atoms of the hydroxyl groups, which was 5.2 Å as determined from the X-ray structure of (*P*,*S*,*S*)-**172** (Figure 3.13 in Chapter 3.1.3 (p. 72), Appendix A). According to the Cambridge Structural Database[159] the length of the P-O bond of aromatic cyclic phosphites varied between 1.5-1.7 Å and accordingly the distance between the oxygen atoms corresponded to 2.4-2.7 Å. This is half the distance separating the hydroxy groups in (*P*,*S*,*S*)-**172**. Although one can argue that the conformation of the molecule (*P*,*S*,*S*)-**172** could be determined by crystal packing, the oxepine-type structures appear to be fairly rigid on the NMR time scale probably due to the fixation of the conformation by the methyl group on the 7-membered rings. Nevertheless, helicenol (*P*,*S*,*S*)-**173** is being currently explored as a precursor of helical phosphoramidites by the group of Prof. A. Alexakis (University of Geneva, Switzerland) as a part of the collaboration between our teams.

Scheme 3.24



(*P*,*S*,*S*)-**172** (*P*,*S*,*S*)-**173** (*P*,*S*,*S*)-**174**

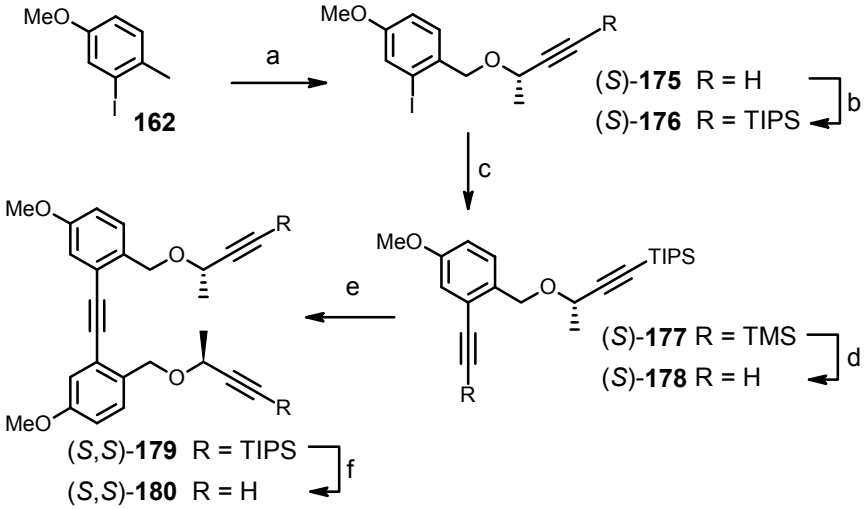
(a) NaSEt (40 equiv.), DMF, 140 ºC, 6 h, 90%.
(b) NaH (4 equiv.), $PhPCl_2$ (0.5 equiv.), THF, r.t., 30 min.

3.1.1.3 Influence of triyne substituents on [2+2+2] cyclotrimerisation reaction

The initially designed triyne structures were substituted with aryl groups at the terminal triple bonds, because their presence ensured high diastereoselectivity of the cyclisation, increased the triyne's stability along with the yield of the cyclotrimerisation reaction. In this work the effect of the electronic nature of the aryl substituents on the yield and diastereoselectivity of the cyclotrimerisation reaction was further explored. Thus, a library of triynes bearing aryl substituents with electron-donating as well as electron-withdrawing groups was prepared and screened.

Triyne (*S*,*S*)-**180** was prepared from the toluene derivative **162** (Scheme 3.25). The bromination of **162** and subsequent nucleophilic substitution with the alkoxide, derived from (*S*)-**111** provided alkyne (*S*)-**175**, which was then orthogonally protected to give silane (*S*)-**176** in good yield. Transformation to diyne (*S*)-**178** by Sonogashira cross-coupling and the following desilylation with a weak base provided diyne (*S*)-**178**. Finally, Sonogashira cross-coupling of iodide (*S*)-**176** and diyne (*S*)-**178** followed by desilylation with TBAF provided the triyne (*S*,*S*)-**180** in high isolated yield.

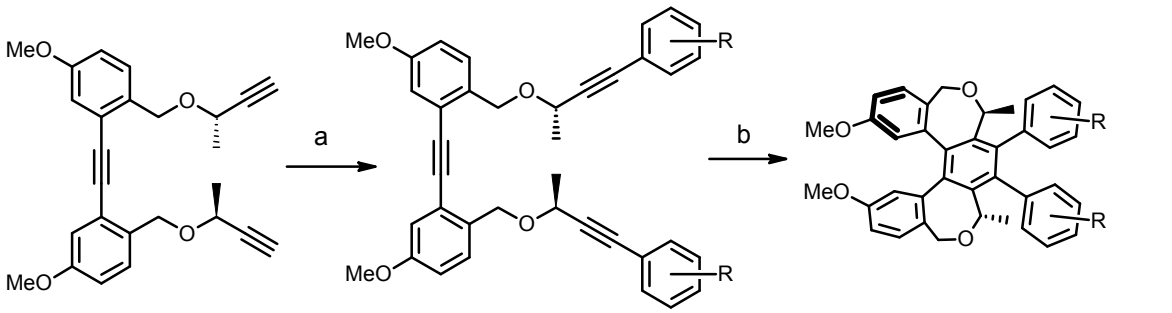
Scheme 3.25



(a) 1) NBS (1.2 equiv.), AIBN (cat.), K_2CO_3 (cat.), CCl_4, IR lamp, reflux, 2.5 h; 2) KH (1.5 equiv.), (*S*)-**111** (1.0 equiv.), THF, 0 ºC, 1 h, then r.t. overnight, 28%.
(b) 1) LDA (1.8 equiv.), THF, -78 ºC, 1 h; 2) TIPSCl (1.8 equiv.), -78 ºC→r.t., overnight, 84%.
(c) TMSA (1.1 equiv.), $Pd(PPh_3)_4$ (6 mol%), CuI (12 mol%), DIPA, r.t., 1.5 h, 99%.
(d) K_2CO_3 (3.5 equiv.), methanol, r.t., 45 min, 93%.
(e) (*S*)-**176** (0.9 equiv.), $Pd(PPh_3)_4$ (5 mol%), CuI (11 mol%), DIPA, r.t., 1 h, 83%.
(f) TBAF (2.0 equiv.), THF, r.t., 30 min, 94%.

Sonogashira cross-coupling of triyne (*S*,*S*)-**180** with a series of aryl iodides proceeded smoothly with moderate to high yields. As was expected, aryl iodides possessing electron-withdrawing groups were more reactive (Scheme 3.26). The subsequent cyclotrimerisation reaction provided in all cases exclusively (*P*,*S*,*S*)-diastereomers of the helicene-like compounds (*P*,*S*,*S*)-**172** and (*P*,*S*,*S*)-**188**-**193**. It was found that some functional groups were not suitable for the reaction rendering the cyclic product unstable, *e.g.* cyano and nitro derivatives, while the other, *e.g.* 3,5-bis(trifluoromethyl), made the reaction to proceed in quantitative yield. A clear correlation between the electronic nature of the aryl substituents and efficiency of the cyclotrimerisation reaction was not observed.

Scheme 3.26



(*S*,*S*)-**180**

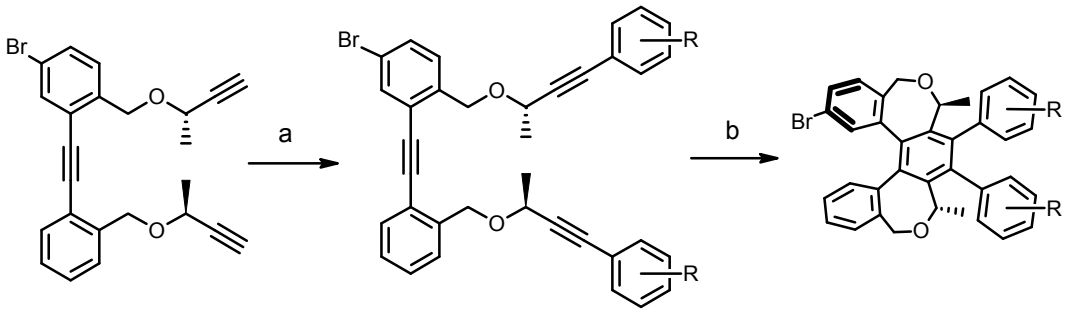
(*S*,*S*)-**171**	R = 4-CH_3, 73%	(*P*,*S*,*S*)-**172**	R = 4-CH_3, 88%
(*S*,*S*)-**181**	R = 4-OCH_3, 47%	(*P*,*S*,*S*)-**188**	R = 4-OCH_3, 61%
(*S*,*S*)-**182**	R = H, 50%	(*P*,*S*,*S*)-**189**	R = H, 87%
(*S*,*S*)-**183**	R = 4-CN, 75%	(*P*,*S*,*S*)-**190**	R = 4-CN, 45%
(*S*,*S*)-**184**	R = 4-Cl, 51%	(*P*,*S*,*S*)-**191**	R = 4-Cl, 76%
(*S*,*S*)-**185**	R = 4-CF_3, 89%	(*P*,*S*,*S*)-**192**	R = 4-CF_3, 74%
(*S*,*S*)-**186**	R = 3,5-CF_3, 60%	(*P*,*S*,*S*)-**193**	R = 3,5-CF_3, 99%
(*S*,*S*)-**187**	R = 4-NO_2, 52%	(*P*,*S*,*S*)-**194**	R = 4-NO_2, decomp.

(a) $Pd(CH_3CN)_2Cl_2$ (10-16 mol%), PPh_3 (20-26 mol%), CuI (15-23 mol%), aryl iodide (2.5-6.4 equiv.), DIPA (2.5 equiv.), toluene, 80 ºC, 5 min.
(b) $CoCp(CO)_2$ (1.0-1.1 equiv.), PPh_3 (2.0 equiv.), decane, halogen lamp, 140 ºC, 45 min-2 h.

A similar study was carried out on the bromo substituted triyne (*S*,*S*)-**122** (Scheme 3.27). Due to the presence of the bromo substituent, the reaction temperature was decreased to 0 ºC and a more reactive $Pd(PPh_3)_4$ complex was employed (*cf*. a catalytic system of $Pd(CH_3CN)Cl_2/PPh_3$, Scheme 3.26). Nitro and cyano derivatives were not studied due to their failure in the previous experiments. Sonogashira coupling of triyne (*S*,*S*)-**122** with a series of aryl iodides afforded (*S*,*S*)-

123 and (*S*,*S*)-**195**-**199** with good yields. Surprisingly, when the previously favourable 4-trifluoromethylphenyl and 3,5-bis(trifluoromethyl)phenyl substituents were introduced in the triyne (*S*,*S*)-**122** structure, it led to decomposition of the reaction mixture (**195**→**203**) and the low isolated yield of the helicene-like compound (*P*,*S*,*S*)-**204** were observed. The most efficacious substituent was phenyl. All helicene-like compounds **124**, **200**-**202** and **204** were obtained as single (*P*,*S*,*S*) diastereomers.

Scheme 3.27



(*S*,*S*)-**122**

(*S*,*S*)-**123** R = H, 75%
(*S*,*S*)-**195** R = 4-OCH_3, 65%
(*S*,*S*)-**196** R = 4-CH_3, 80%
(*S*,*S*)-**197** R = 4-Cl, 85%
(*S*,*S*)-**198** R = 4-CF_3, 70%
(*S*,*S*)-**199** R = 3,5-CF_3, 91%

(*P*,*S*,*S*)-**124** R = H, 80%
(*P*,*S*,*S*)-**200** R = 4-OCH_3, 72%
(*P*,*S*,*S*)-**201** R = 4-CH_3, 49%
(*P*,*S*,*S*)-**202** R = 4-Cl, 72%
(*P*,*S*,*S*)-**203** R = 4-CF_3, decomp.
(*P*,*S*,*S*)-**204** R = 3,5-CF_3, 20%

(a) $Pd(PPh_3)_4$ (10 mol%), CuI (20-22 mol%), aryl iodide (2.5-5.2 equiv.), DIPA (9-12 equiv.), toluene, 0 ºC→r.t., overnight.
(b) $CoCp(CO)_2$ (1.0 equiv.), PPh_3 (2.0 equiv.), halogen lamp, decane, 140 ºC, 30 min-2.5 h.

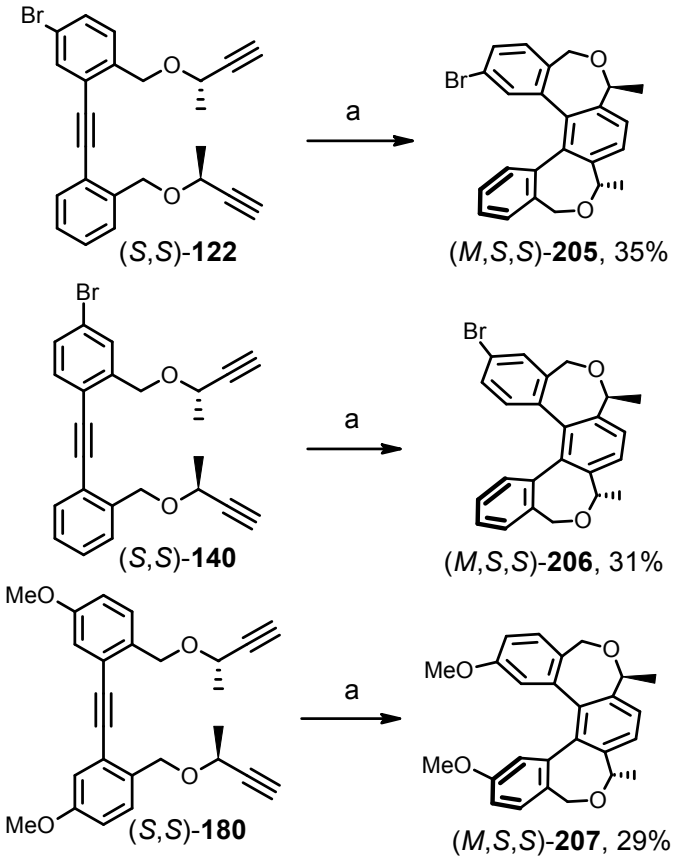
These results demonstrate that it was generally difficult to draw any conclusion about the electronic nature of the alkyne substituents to support the cyclotrimerisation reactions. But it is evident that the yield of the cyclotrimerisation strongly depended on the triyne structure and a simple correlation could not be found.

In contrast, cyclotrimerisation of the unsubstituted triynes (*S*,*S*)-**122**, (*S*,*S*)-**140** and (*S*,*S*)-**180** provided exclusively (*M*,*S*,*S*)-**205**, (*M*,*S*,*S*)-**206**, (*M*,*S*,*S*)-**207** diastereomers (Scheme 3.28). It was also observed that the helicene scaffolds without aryl substituents on the central benzene ring were formed in lower yields and were generally less stable than the substituted ones.

In addition, several other catalytic systems were examined in cyclotrimerisation of triyne (*S*,*S*)-**122**. Under catalyst-free conditions reported by Ley *et al.*[160] triyne

(*S*,*S*)-**122** was completely unreactive. Other complexes used in cyclotrimerisation reaction were also tested: Wilkinson catalyst,[161] 1st gen. Grubbs catalyst,[162] RuCp*Cl(cod),[163] $[Ir(dppe)Cl]_2$,[161] $NiCl_2(dppe)/Zn$[161] and $Co(PPh_3)_3Br$.[161] However, none of them provided the desired helicene-like compound (*M*,*S*,*S*)-**205**. The most suitable was $CoCp(CO)_2/PPh_3$ catalytic system, which provided the helical compound (*M*,*S*,*S*)-**205** in 35% yield.

Scheme 3.28



(a) $CoCp(CO)_2$ (1.0-1.1 equiv.), PPh_3 (2.0 equiv.), THF, MW, 190 °C, 5-10 min.

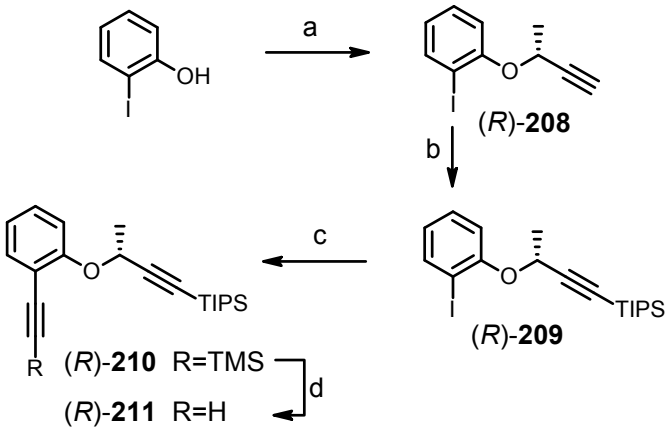
3.2 Pyran-type helicene-like compounds

The scope and limitations of the asymmetric synthesis of the helically chiral compounds employing the diastereoselective [2+2+2] cyclotrimerisation were further investigated on triynes, which cyclised to a novel type of helical scaffold with two 6-membered (*R*)-methyl-2*H*-pyran rings. These molecules were an attractive target because of their resemblance to the fully aromatic helicenes. The DFT calculations predicted the energy difference between these *pyran-type* diastereomers to be twice as much as in the *oxepine-type* series (9.2 *vs*. 4.6 kcal/mol).[164,165]

Helicene-like compound with phosphine substituent in position *2*

The synthetic route to the *pyran-type* derivatives was shorter than the route to the *oxepine-type* compounds because it used Mitsunobu reaction for the ether bond formation instead of the two-step preparation of the benzyl ether derivatives (*cf*. Chapter 3.1.1). Thus, the enantiopure commercial alcohol (*S*)-**111** reacted smoothly with 2-iodophenol to provide the ether (*R*)-**208** in excellent yield (Scheme 3.29).[166] After orthogonal protection with triisopropylsilyl group, Sonogashira cross-coupling of (*R*)-**209** with ethynyl(trimethyl)silane gave the optically pure diyne (*R*)-**210**. The sterically bulky triisopopylsilyl group was necessary to suppress the competing carbopalladation. In the case of the *p*-tolyl substituted alkyne, after the formation of an arylpalladium intermediate, intramolecular Heck-type coupling could be faster than the reaction with ethynyl(trimethyl)silane. Desilylation with sodium methanolate provided diyne (*R*)-**211** in good yield.

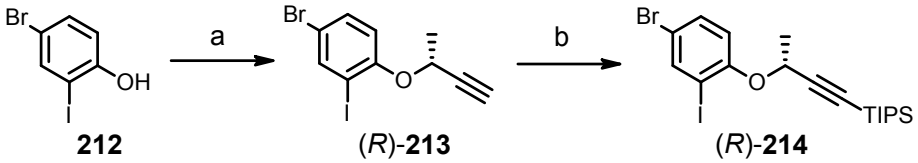
Scheme 3.29



(a) (*S*)-**111** (1.0 equiv.), PPh_3 (1.0 equiv.), DIAD (1.0 equiv.), THF, 0 ºC→r.t., overnight, 93%.
(b) 1) LDA (1.2 equiv.), THF, -80 ºC, 1 h; 2) TIPSCl (2.2 equiv.), -80 ºC, 1 h, then r.t., 1 h, 89%.
(c) TMSA (1.2 equiv.), $Pd(PPh_3)_4$ (5 mol%), CuI (10 mol%), DIPA, r.t., 2 h, 99%.
(d) $NaOCH_3$ (1.0 equiv.), methanol-CH_2Cl_2 (1:2), r.t., 30 min, 86%.

The bromo substituted building block (*R*)-**214** was synthesised from the phenol derivative **212**, readily prepared from commercial 4-bromophenol by the published procedure.[167] Then Mitsunobu reaction of **212** with the commercial alcohol (*S*)-**111** afforded alkyne (*R*)-**213** in excellent yield, which was then protected with triisopropylsilyl group (Scheme 3.30).

Scheme 3.30



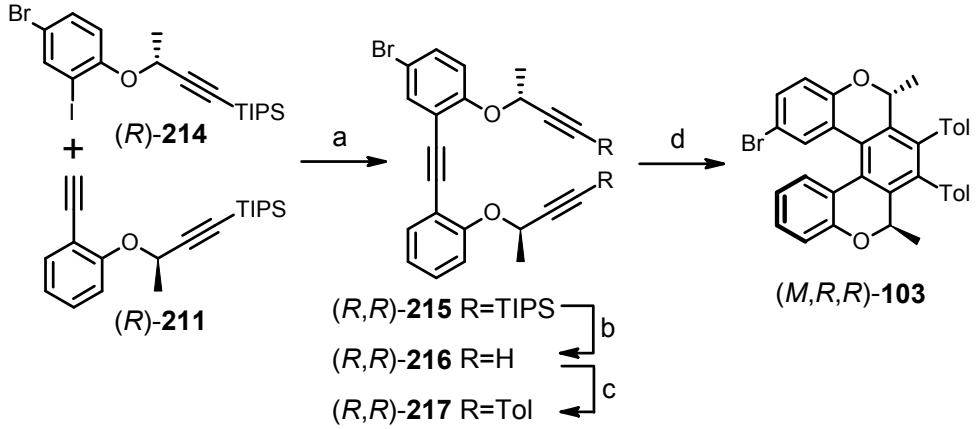
212 (*R*)-**213** (*R*)-**214**

(a) (*S*)-**111** (1.0 equiv.), PPh_3 (1.2 equiv.), DIAD (1.0 equiv.), THF, 0 ºC→r.t., 1 h, 96%.
(b) 1) LDA (1.1 equiv.), THF, -78 ºC, 1 h; 2) TIPSCl (1.0 equiv.), -78 ºC, 1 h, then r.t., 1 h, 86%.

Sonogashira cross-coupling of diyne (*R*)-**211** and aryl iodide (*R*)-**214** provided the bromo substituted triyne (*R*,*R*)-**215** (Scheme 3.31), which was then transformed to the *p*-tolyl-substituted triyne (*R*,*R*)-**217**. Cyclotrimerisation in the presence of cyclopentadienylcobalt(I) or nickel(0) complexes proceeded with >99% *de* while only (*M*,*R*,*R*)-**103** diastereomer was obtained (Table 3.4). Unfortunately, the triyne (*R*,*R*)-

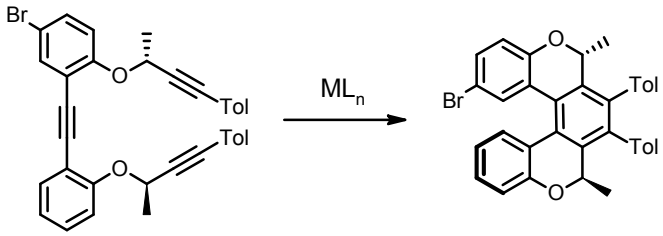
217 was rather unreactive and many by-products were formed during the cyclotrimerisation reaction.

Scheme 3.31



(a) (*R*)-**214** (1.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), CuI (10 mol%), DIPA, 0 ºC, 1 h→r.t., overnight, 98%.
(b) TBAF (2.0 equiv.), THF, r.t., 30 min, 98%.
(c) *p*-iodotoluene (2.4 equiv.), $Pd(PPh_3)_4$ (10 mol%), CuI (20 mol%), DIPA, 0 ºC, 30 min, then r.t., 30 min, 90%.
(d) $CoCp(CO)_2$ (1.0 equiv.), PPh_3 (2.0 equiv.), decane, hν, 140 ºC, 50 min, 53%.

Table 3.4 Cyclotrimerisation of the triyne (*R*,*R*)-**217**.



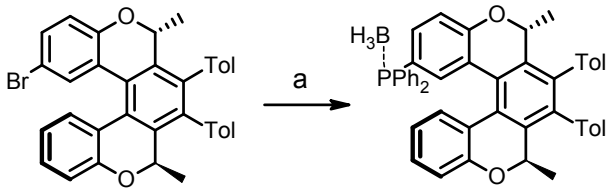
Entry	Metal complex	Solvent	Temperature, time	Heating mode	Isolated yield
1	$CoCp(CO)_2$ (1.0), PPh_3 (2.0)	decane	140 ºC, 50 min	hν	53%
2	CoCp(CO)(fum) (1.0), PPh_3 (2.0)	THF	180 ºC, 20 min	MW	66%
3	$Ni(cod)_2$ (0.2), PPh_3 (0.4)	THF	r.t., overnight	–	18%[a]

[a] 77% conversion.

Finally, the helicene-like bromide (*M*,*R*,*R*)-**103** was converted into the phosphine-borane complex (*M*,*R*,*R*)-**218** using the halogen-lithium exchange reaction

(Scheme 3.32). The reaction proceeded in high yield but required temperatures below -110 ºC, the same as in the case of the *oxepine-type* helicenes.

Scheme 3.32



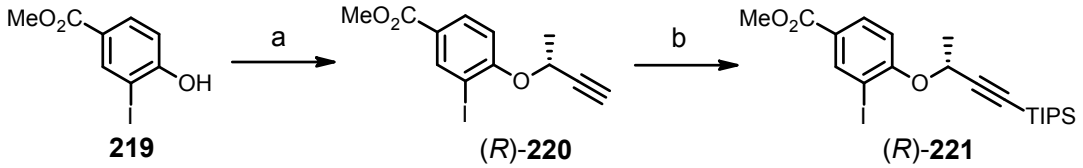
(*M*,*R*,*R*)-**103** (*M*,*R*,*R*)-**218**

(a) 1). *t*-BuLi (2.1 equiv.), Et_2O, -115 ºC, 1 min.; 2). Ph_2PCl (5.2 equiv.), -110 ºC → -80 ºC; 3). BH_3-THF (9.6 equiv.), r.t., 30 min, 98%.

Helicene-like compound with an ester group in the position *2*

The synthesis of helical ester (*M*,*R*,*R*)-**105** followed the same synthetic route developed for bromide (*M*,*R*,*R*)-**103** providing comparable yields (*cf.* Scheme 3.30 and 3.33). The commercially available compound **219** was transformed into ether (*R*)-**220** by Mitsunobu reaction with the optically pure alcohol (*S*)-**111**. The protection of alkyne (*R*)-**220** with the triisopropylsilyl group afforded the building block (*R*)-**221** in good yield (Scheme 3.33). Sonogashira cross-coupling of aryl iodide (*R*)-**221** with alkyne (*R*)-**211** produced the silylated triyne (*R*,*R*)-**222** in excellent yield (Scheme 3.34). After desilylation, the *p*-tolyl groups were introduced into the triyne providing the triyne (*R*,*R*)- **224** in almost quantitative yield.

Scheme 3.33

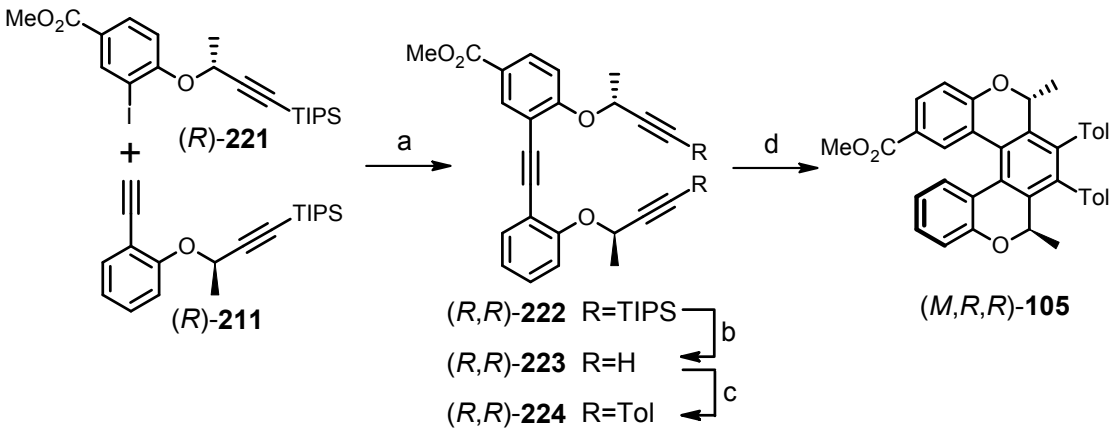


219 (*R*)-**220** (*R*)-**221**

(a) (*S*)-**111** (1.0 equiv.), PPh_3 (1.0 equiv.), DIAD (1.0 equiv.), THF, 0 ºC, 15 min, then r.t., overnight, 86%.
(b) 1) LDA (1.2 equiv.), THF, -80 ºC, 1 h; 2) TIPSCl (1.2 equiv.), -80 ºC, 1h, then→r.t., 1 h, 61%.

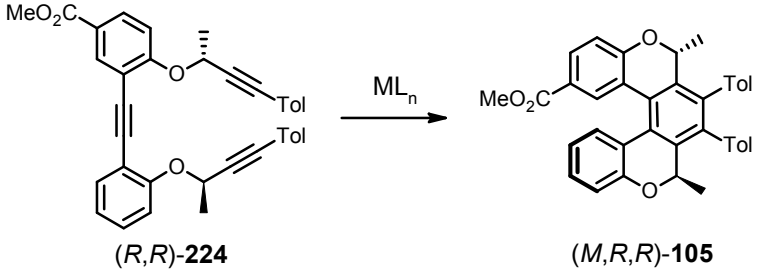
The ester substituted triyne (*R*,*R*)-**224** was more reactive in the cyclotrimerisation reaction than bromide (*R*,*R*)-**217**. Thus a catalytic amount of cobalt or nickel complexes was sufficient to drive the reaction to completion (Table 3.5). The helical ester (*M*,*R*,*R*)-**105** was obtained in good yield and >99% *de*. The utilisation of the commercial $CoCp(CO)_2$ was more effective than the zero-valent nickel complex (Entries 1-3 *vs*. Entry 4).

Scheme 3.34



(a) (*R*)-**211** (1.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), CuI (10 mol%), DIPA, r.t., 1 h, 95%.
(b) TBAF (2.0 equiv.), THF, r.t., 30 min, 91%.
(c) *p*-iodotoluene (2.2 equiv.), $Pd(PPh_3)_4$ (10 mol%), CuI (26 mol%), DIPA, r.t., 1h, 95%.
(d) $CoCp(CO)_2$ (22 mol%), PPh_3 (44 mol%), THF, MW, 140 ºC, 30 min, 81%.

Table 3.5 Cyclotrimerisation of the triyne (*R*,*R*)-**224**.



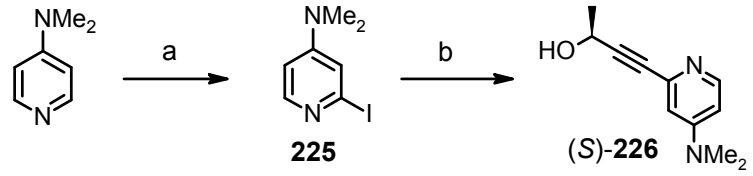
Entry	Catalytic system (equiv.)	Solvent	Temperature, time	Heating mode	Isolated yield
1	$CoCp(CO)_2$ (0.1), PPh_3 (0.2)	decane	140 ºC, 1 h	hν	72%
2	$CoCp(CO)_2$ (1), PPh_3 (2)	decane	140 ºC, 1 h	hν	68%
3	$CoCp(CO)_2$ (0.2), PPh_3 (0.4)	THF	140 ºC, 30 min	MW	81%
4	$Ni(cod)_2$ (0.2), PPh_3 (0.4)	THF	r.t., 16 h	–	59%[a]

[a] 65% conversion.

Helical DMAP-analogue

The optically pure helical DMAP-analogue was prepared from 4-(dimethylamino)pyridine using diastereoselective synthetic methodology developed earlier. Dimethylaminopyridine was iodinated according to the literature procedure[168] to provide iodide **225** (Scheme 3.35). The following Sonogashira cross-coupling with the optically pure (*S*)-**111** provided the DMAP substituted alkyne (*S*)-**226** in high yield.

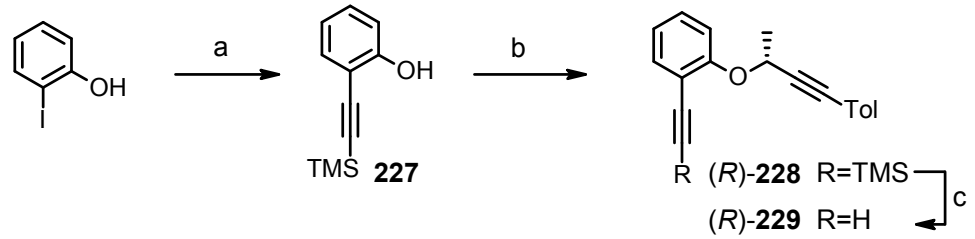
Scheme 3.35



(a) 1) BF_3-Et_2O (1.1 equiv.), THF, 0 ºC, 40 min; 2) LiTMP (1.2 equiv.), THF, -78 ºC, 45 min; 3) I_2 (1.5 equiv.), THF, -78 ºC, 1 h→r.t., 1 h, 78%.
(b) (*S*)-**111** (1.1 equiv.), $Pd(PPh_3)_4$ (5 mol%), CuI (10 mol%), DIPA, r.t., 1h, 89%.

The second building block (*R*)-**229** was prepared from commercial 2-iodophenol. Sonogashira cross-coupling with ethynyl(trimethyl)silane had to precede Mitsunobu reaction with the optically pure alcohol (*S*)-**145** due to the possible concurrent Heck-type carbopalladation on the tolyl substituted alkyne moiety (Scheme 3.36).

Scheme 3.36

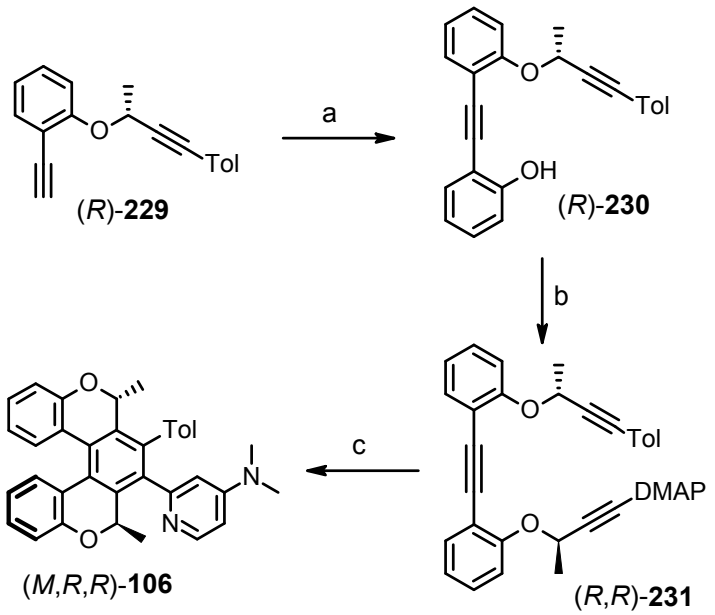


(a) TMSA (1.5 equiv.), $Pd(PPh_3)_4$ (4 mol%), CuI (9 mol%), DIPA (1.5 equiv.), benzene, r.t., 3 h, 98%.
(b) (*S*)-**145** (1.2 equiv.), PPh_3 (1.1 equiv.), DIAD (1.2 equiv.), benzene, r.t., 3 h, 75%.
(c) K_2CO_3 (2.0 equiv.), r.t., 1.5 h, methanol, 83%.

Sonogashira cross-coupling of the desilylated diyne (*R*)-**229** and 2-iodophenol afforded the phenol derivative (*R*)-**230** in quantitative yield (Scheme 3.37). Mitsunobu reaction of (*R*)-**230** and (*S*)-**226** was slow and required prolonged heating. Finally, cyclotrimerisation of triyne (*R*,*R*)-**231** provided the helical DMAP-analogue (*M*,*R*,*R*)-**106** with good yield and >99% *de*. The structure was confirmed by a single-crystal X-ray analysis (Figure 3.9, Appendix A). The rotation barrier of the DMAP substituent was estimated to be 18.7 kcal/mol (AM1, Gaussian). According to the ^{1}H and ^{13}C NMR spectra, (*M*,*R*,*R*)-**106** existed as a mixture of two atropisomers at room temperature. However, when heated at 100 ºC in DMSO, it appeared as one compound on the NMR time scale.

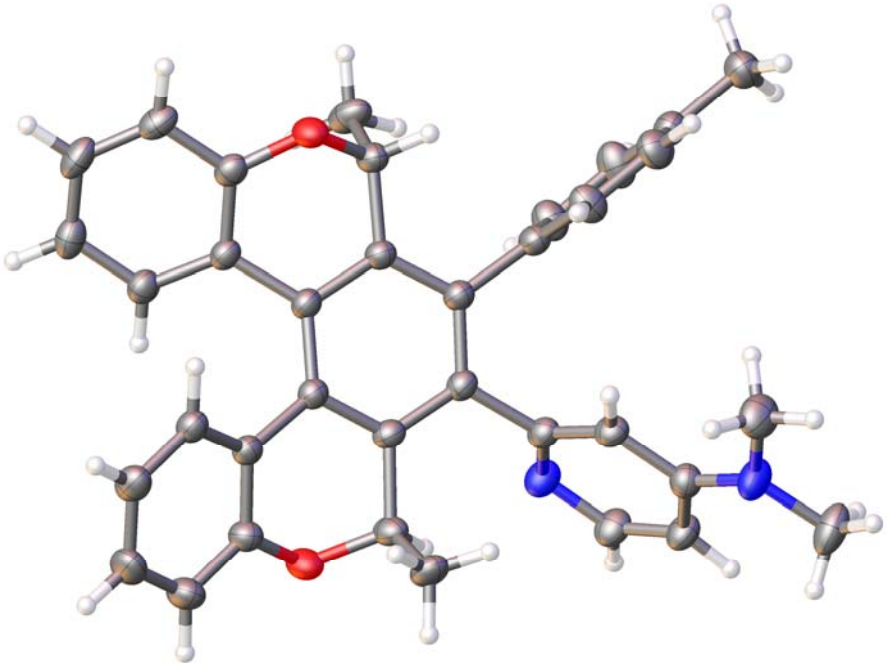
This enantiopure helicene-like DMAP-analogue (*M*,*R*,*R*)-**106** was further studied in the group of Prof. P. R. Schreiner (Justus-Liebig University, Giessen, Germany) as a possible organocatalyst in the enantioselective acyl transfer reaction.

Scheme 3.37



(a) 2-iodophenol (1.3 equiv.), $Pd(PPh_3)_4$ (5 mol%), CuI (10 mol%), DIPA (15 equiv.), toluene, r.t., 1h, 99%.
(b) (*S*)-**226** (1.0 equiv.), PPh_3 (1.0 equiv.), DIAD (1.0 equiv.), THF, 50 ºC, 2 d, 88%.
(c) $CoCp(CO)_2$ (1.0 equiv.), PPh_3 (2.0 equiv.), ionic liquid, THF, MW, 180 ºC, 25 min, 89%.

Figure 3.9 X-ray structure of (*M*,*R*,*R*)-**106** with thermal ellipsoids at the 50% probability level.



3.1.3 Helicity assignment

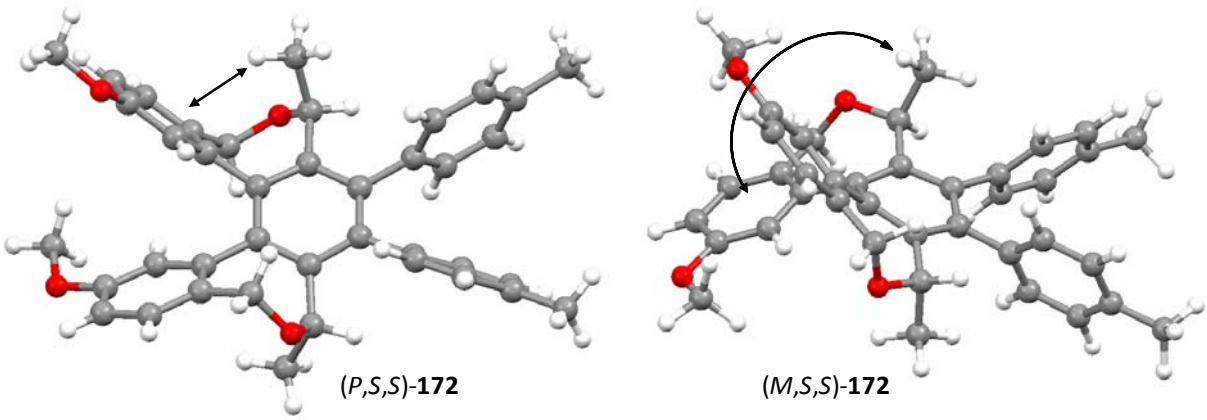
A combination of methods was used to assign the relative configuration of the synthesised helicene-like compounds.

NMR techniques

The NMR spectroscopy was a primary tool in analysis of the synthesised diastereomeric helicene-like compounds. With the exception of the atropisomeric bromide (*P*,*S*,*S*)-**157** and DMAP-analogue (*M*,*R*,*R*)-**106**, only one set of signals corresponding to a single compound was observed in ^{1}H NMR spectra in different solvents. This indicated the presence of only one diastereomer, assuming that the NMR spectra of the (*P*,*S*,*S*) and (*M*,*S*,*S*) diastereomers were not identical.

As mentioned in Chapter 3.1.1, the steric interaction between the methyl groups on the dihydrooxepine rings and the adjacent aromatic rings (Figure 3.1) was crucial for the induction of diastereoselectivity. The chemical shift of these methyl protons was indicative of the helicity due to its position relative to the aromatic parts of the molecule.[8, 99, 169] It fell within an interval of 0.54-0.62 ppm for the (*P*)-helices and within an interval of 1.58-1.67 ppm for the (*M*)-helices.[99] Similarly, the methyl protons (δ=0.67 ppm) of the compound (*P*,*S*,*S*)-**172** (Figure 3.10) were shielded by the ring current of the proximate aromatic ring. Such shielding could not arise in the case of the (*M*,*S*,*S*)-**172** structure, in which the methyl hydrogens were located outside of the shielding cone of the aromatic rings.

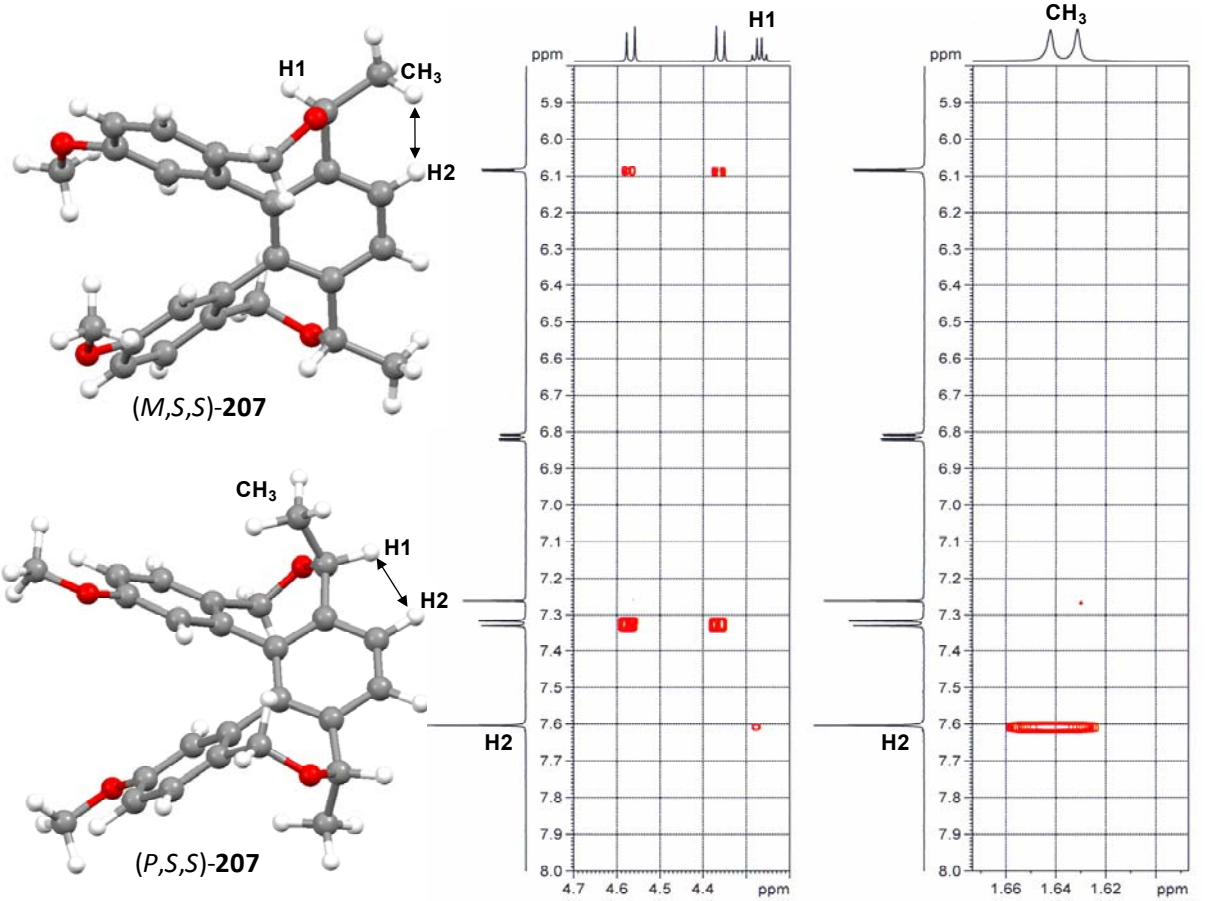
Figure 3.10 Molecular models of the two possible diastereomers of **172.**



(*P*,*S*,*S*)-**172** (*M*,*S*,*S*)-**172**

Helicity of the compounds without aryl substituents was assigned by measuring NOE interactions (Figure 3.11). For instance, in the compound (*M*,*S*,*S*)-**207**, a strong coupling in the ROESY spectrum arose from the spatial proximity of the methyl group (CH_3) and the H2 hydrogen, whereas the interaction between H1 and H2 hydrogens was weak. If the helicene had the (*P*,*S*,*S*)-**207** configuration, a strong H1-H2 interaction and a weak CH_3-H2 would be observed. The same method was applied in the assignment of the relative configurations of the compounds (*M*,*S*,*S*)-**205** and (*M*,*S*,*S*)-**206**.

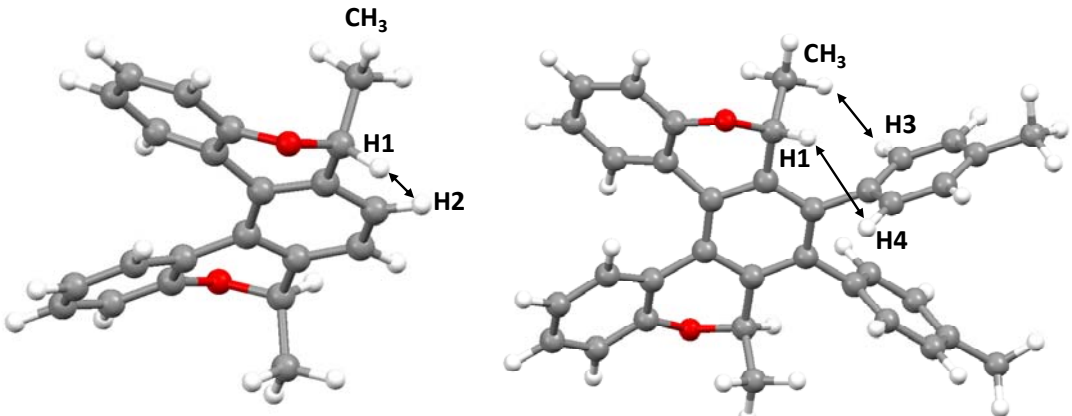
Figure 3.11 Comparison of the experimentally observed ROESY NMR spectrum of (*M*,*S*,*S*)-**207** and molecular models of the two possible diastereomers (*M*,*S*,*S*)-**207** and (*P*,*S*,*S*)-**207**.



The helicity assignment in the *pyran-type* series was done by measuring the NOE interactions in the model unsubstituted pyran-type compound (*M*,*R*,*R*)-**232** synthesised in our group by Mgr. J. Žádný (Figure 3.12). ROESY spectrum of (*M*,*R*,*R*)-**232** showed strong coupling of the hydrogens H1-H2, whereas the NOE between the H2 and the methyl group (CH_3) was negligible. This method, however, could not be used in the case of the *p*-tolyl substituted compounds (*M*,*R*,*R*)-**103**,

(*M*,*R*,*R*)-**105** and (*M*,*R*,*R*)-**106**, since both NOE interactions H1-H4 and CH_3-H3 were observed in the ROESY spectrum. These results will be presented in our collective paper.[165]

Figure 3.12 Molecular models of the helicene-like compounds containing (*R*)-methyl-2*H*-pyran rings. The arrows indicate the observed NOE interactions.

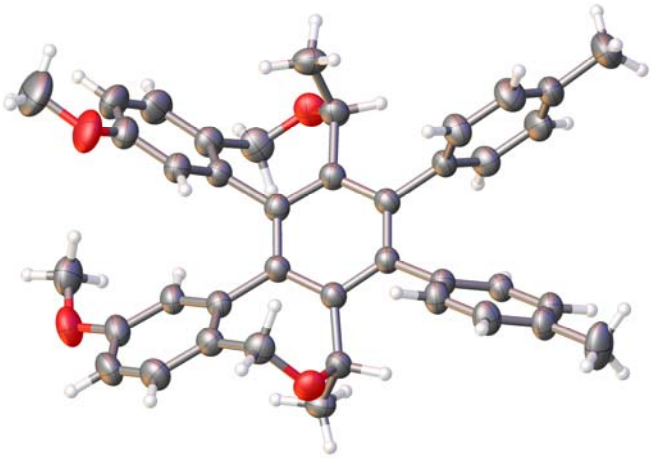


(*M*,*R*,*R*)-**232**

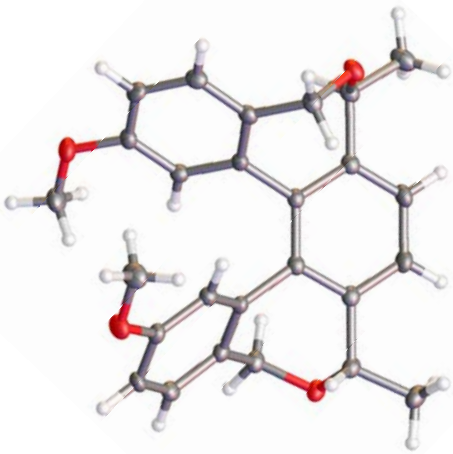
Single-crystal X-ray diffraction

In some cases the single-crystal X-ray diffraction analysis was used to determine helicity of the synthesised compounds. The *oxepine-type* helicenes crystallised more readily than the *pyran-type* compounds. The layer diffusion technique and using the combination of dichloromethane-heptane solvents proved to be the most successful in obtaining monocrystals of the *oxepine-type* helicenes. For polar compounds, such as (*P*,*S*,*S*)-**167** and (*M*,*R*,*R*)-**106**, slow evaporation from a concentrated acetonitrile solution was used. In addition to the structures already presented in the text, three other helicene-like compound (*P*,*S*,*S*)-**167**, (*P*,*S*,*S*)-**172** and (*M*,*S*,*S*)-**207** were analysed (Figure 3.13).

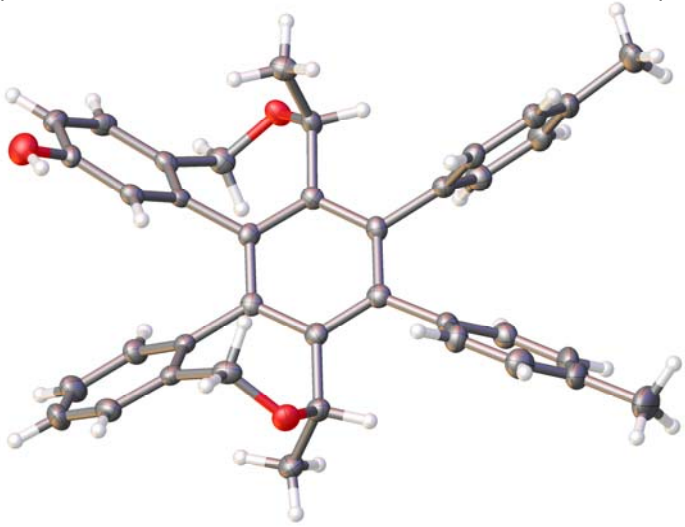
Figure 3.13 X-ray structures of (*P*,*S*,*S*)-**172**, (*M*,*S*,*S*)-**207** and (*P*,*S*,*S*)-**167** with thermal ellipsoids at the 50% probability level.



(*P*,*S*,*S*)-**172**



(*M*,*S*,*S*)-**207**



(*P*,*S*,*S*)-**167**

Circular dichroism

Circular dichroism (CD) spectroscopy is an established technique for studying molecular chirality.[99, 169] The absolute configuration of helicenes and heterohelicenes was determined using CD spectroscopy either in UV-vis (ECD) or in infrared spectral regions (VCD).[170-173, 173, 174] For assigning the absolute configuration, experimental CD spectra are often compared with the *in silico* calculated CD spectra.[174-178] However, in spite of large strides in computational methods in the last decades,[179, 180] the cost of such calculations is prohibitive in the case of large molecules. Therefore, in this work the structure characterisation by the experimental ECD spectroscopy was compared with that obtained by the NMR and X-ray experiments. It is well known that the sign of the Cotton effect of simple helicenes is related to the sense of the helix.[172,181] Therefore, a qualitative comparison of the CD spectrum of a compound in question with the spectrum of the compound of known configuration can be used to ascertain the helicity. For small helicenes the sense of optical rotation is indicative of the helicity: $[\alpha]^{22}_{D}>0$ for (*P*)-helicity and $[\alpha]^{22}_{D}<0$ for (*M*)-helicity.[182] However, it was observed that the sign of the optical rotation of the helicene-like molecules, which possessed more than one element of chirality, was not related to their helicity. For example, the compounds (*M*,*R*,*R*)-**205**, (*M*,*R*,*R*)-**206** and (*M*,*R*,*R*)-**207** had $[\alpha]^{22}_{D}$ values -8°, +124° and -62°, respectively.

The CD spectrum of the helicene-like alcohol of the *oxepine-type* (*P*,*S*,*S*)-**167** possessed an intensive couplet of positive (235 nm) and negative (252 nm) spectral bands accompanied with a shoulder at 246 nm (Figure 3.14). Additional negative bands at 222 nm together with a broad negative spectral band around 270 nm were observed. According to the X-ray diffraction analysis, the alcohol (*P*,*S*,*S*)-**167** had (*P*)-helicity (Figure 3.13). The CD spectrum of the structurally related bromide (*P*,*S*,*S*)-**124** was similar with respect to the positions and signs of the principal spectral bands (couplet of positive (225 nm) and negative (254 nm) bands with a shoulder at 247 nm). Therefore, (*P*)-helicity was assigned to bromide (*P*,*S*,*S*)-**124**.

Bromide (*P*,*S*,*S*)-**124** was then compared to the structurally similar bromide (*P*,*S*,*S*)-**142** and also to their corresponding phosphine-borane complexes (*P*,*S*,*S*)-**127** and (*P*,*S*,*S*)-**143** (Figure 3.15). The CD spectra of all four compounds possessed characteristic couplets of positive and negative spectral bands at (+)225 nm and

(-)254 nm for bromide (*P*,*S*,*S*)-**124**; (+)220 nm and (-)256 nm for bromide (*P*,*S*,*S*)-**142**; (+)227 nm and (-)247 nm for phosphine-borane complex (*P*,*S*,*S*)-**127**; (+)224 nm and (-)261 nm for phosphine-borane complex (*P*,*S*,*S*)-**143** accompanied by broad negative low intensity bands around 290 nm. Consequently, helicity of all these compounds was expected to be the same. (*P*)-Helicity was assigned on a basis of the spectral similarity to bromide (*P*,*S*,*S*)-**124**.

Figure 3.14 CD spectra of (*P*,*S*,*S*)-**124** and (*P*,*S*,*S*)-**167**.

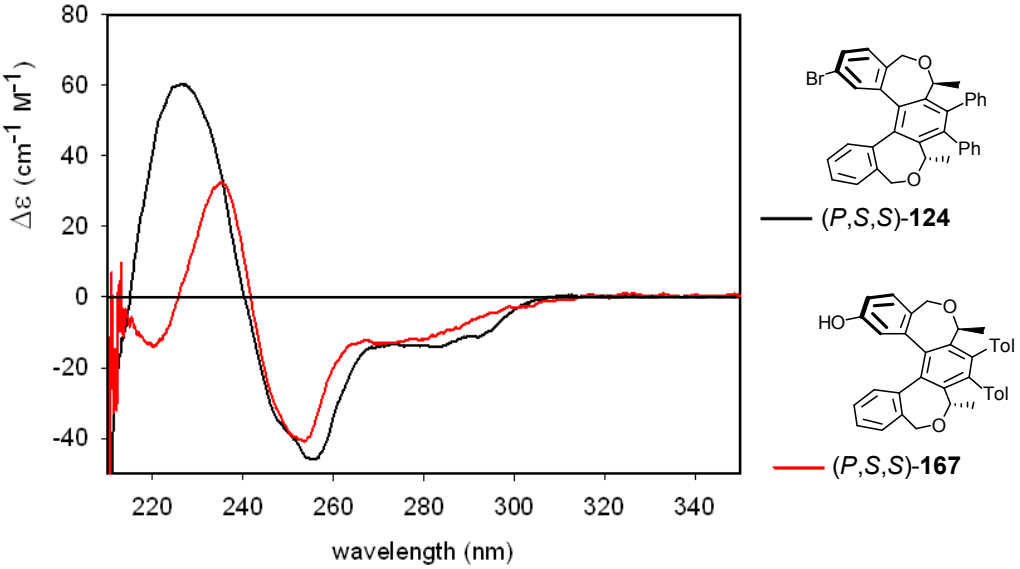


Figure 3.15 CD spectra of (*P*,*S*,*S*)-**124**, (*P*,*S*,*S*)-**127**, (*P*,*S*,*S*)-**142** and (*P*,*S*,*S*)-**143**.

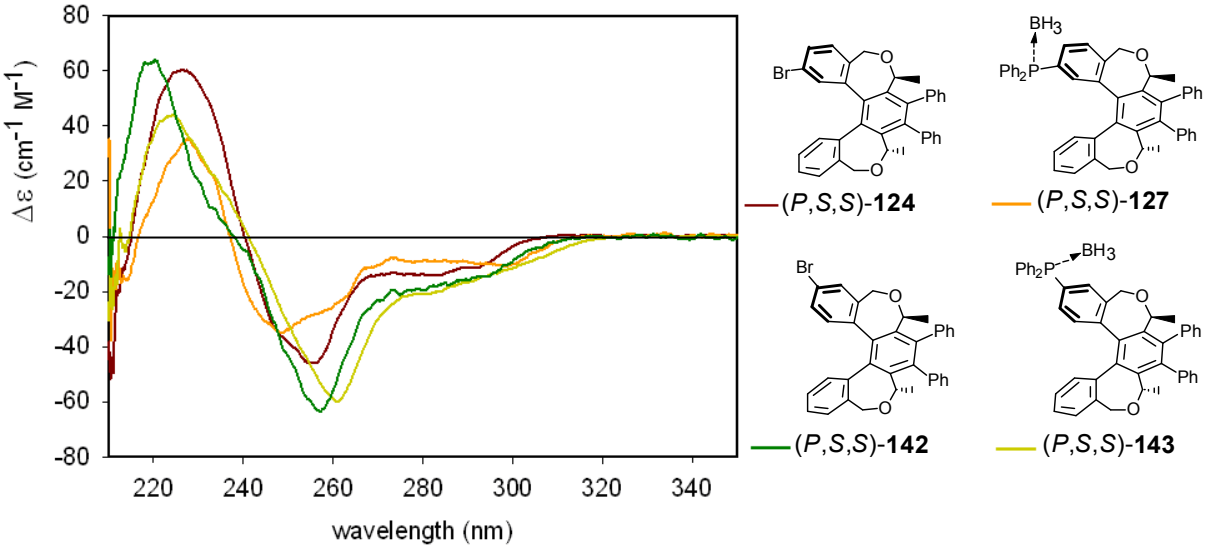
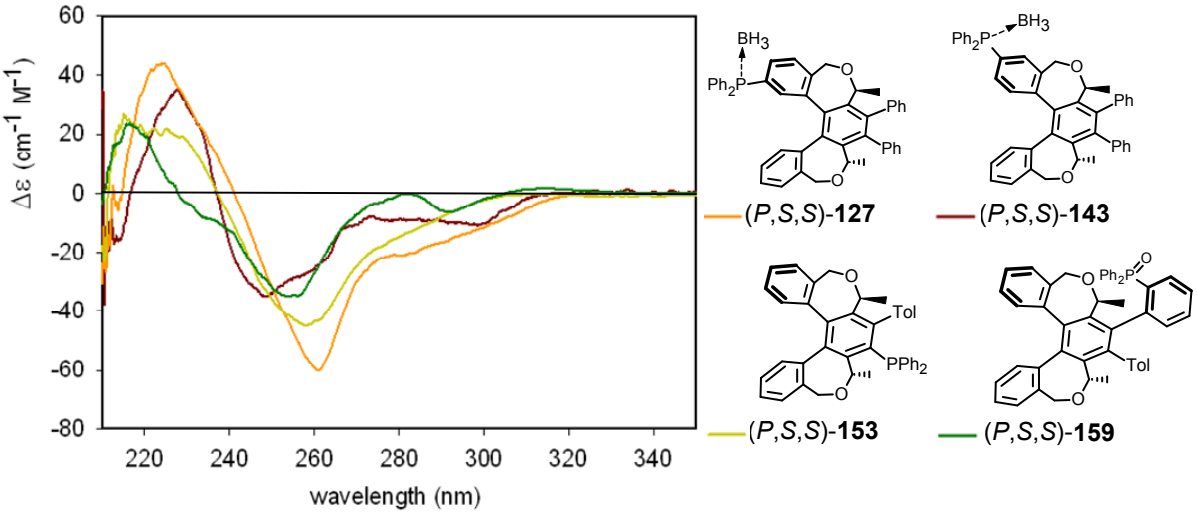


Figure 3.16 shows the ECD spectra of the synthesised phosphine derivatives (*P*,*S*,*S*)-**127**, (*P*,*S*,*S*)-**143**, (*P*,*S*,*S*)-**153** and (*P*,*S*,*S*)-**159**. As in the previous case, the CD spectra were characterised by positive and negative couplet bands at (+)227 nm and (-)261 nm for (*P*,*S*,*S*)-**127**, (+)224 nm and (-)247 nm for (*P*,*S*,*S*)-**143**, (+)229 nm

and (-)257 nm for (*P*,*S*,*S*)-**153** and (+)217 nm and (-)255 nm and an additional low intensity negative band at 290 nm for (*P*,*S*,*S*)-**159**. The helicity of (*P*,*S*,*S*)-**153** and (*P*,*S*,*S*)-**159** was determined by X-ray diffraction analysis. The spectral similarity between the phosphines of known helicity and (*P*,*S*,*S*)-**127** and (*P*,*S*,*S*)-**143** led to a conclusion that all these compounds had the same helicity.

Figure 3.16 CD spectra of (*P*,*S*,*S*)-**127**, (*P*,*S*,*S*)-**143**, (*P*,*S*,*S*)-**153** and (*P*,*S*,*S*)-**159**.



The helicity of (*P*,*S*,*S*)-**172** and (*M*,*S*,*S*)-**207** was determined by X-ray analysis. The ECD spectra of these compounds were almost in a mirror image relationship (Figure 3.17). Both compounds had opposite maxima at 219 nm (negative in the case (*P*,*S*,*S*)-**172**, positive in the case of (*M*,*S*,*S*)-**207**) and at 237 nm (positive for (*P*,*S*,*S*)-**172** and negative slightly blue-shifted at 233 nm with a shoulder at 247 nm for (*M*,*S*,*S*)-**207**). The additional spectral bands, negative at 265 nm for (*P*,*S*,*S*)-**172** and positive slightly red-shifted at 266 nm for (*M*,*S*,*S*)-**207**, were also observed. The opposite signs of the Cotton effects indicated the opposite helicity of these compounds. The experimental CD spectra showed a number of subtle differences but the additional negative band at 250 nm for the compound (*P*,*S*,*S*)-**207** was a distinctive one, which probably originated from the structural difference between these compounds.

The opposite sense of helicity of bromides (*P*,*S*,*S*)-**124**, (*P*,*S*,*S*)-**142** and (*M*,*S*,*S*)-**205**, (*M*,*S*,*S*)-**206** is demonstrated in Figure 3.18. These compounds have opposite sign of their Cotton effects in range of 270-300 nm (negative for compounds (*P*,*S*,*S*)-**124**, (*P*,*S*,*S*)-**142** and positive for (*M*,*S*,*S*)-**205**, (*M*,*S*,*S*)-**206**). The presence of

the additional negative maxima at 254 nm ((*P*,*S*,*S*)-**124**) and 256 nm ((*P*,*S*,*S*)-**142**) and the positive maxima at 230 nm ((*P*,*S*,*S*)-**124**) and 220 nm ((*P*,*S*,*S*)-**142**) could be caused by the presence of phenyl substituents. Intensity of the CD signals of (*M*,*S*,*S*)-**205**, (*M*,*S*,*S*)-**206** is comparable to the intensity of the spectrum of the similar compound (*M*,*S*,*S*)-**207** (Δε in range of 10-20 $cm^{-1}M^{-1}$, *cf*. Figure 3.17).

Figure 3.17 CD spectra of (*P*,*S*,*S*)-**172** and (*P*,*S*,*S*)-**207.**

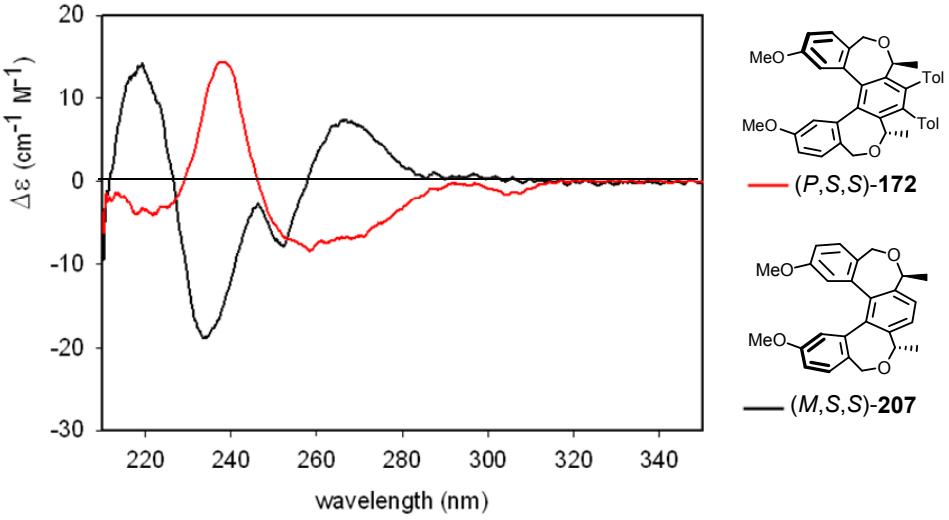
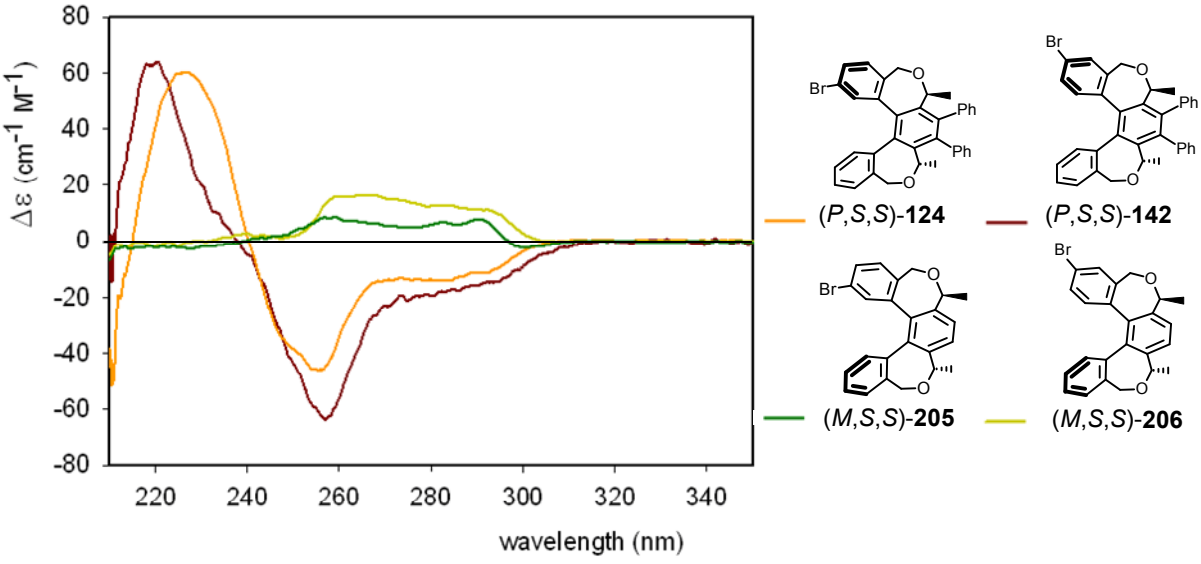


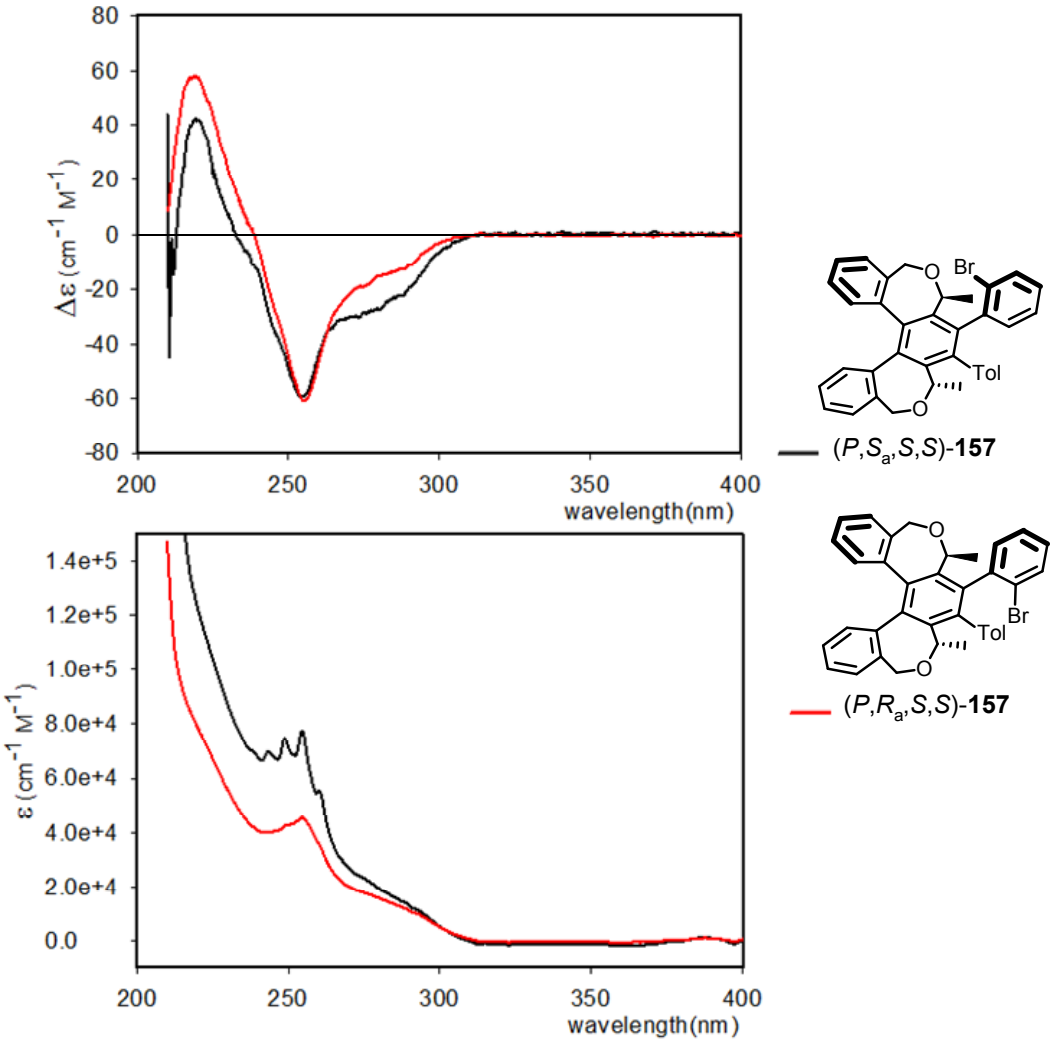
Figure 3.18 CD spectra of (*P*,*S*,*S*)-**124**, (*P*,*S*,*S*)-**142**, (*P*,*S*,*S*)-**205** and (*P*,*S*,*S*)-**206**.



The CD and UV-vis absorption spectra of the atropisomeric helical bromides (*P*,S_a,*S*,*S*)-**157** and (*P*,R_a,*S*,*S*)-**157** are shown in Figure 3.19. Both compounds possessed the characteristic couplets at 219 nm (positive and more intensive for the R_a isomer) and 254 nm (negative, the same for both compounds) spectral bands

accompanied with a shoulder at 283 nm (more distinct for the S_a compound). The UV-visible absorption spectra of both compounds possessed the absorption maximum at 254 nm, which in the case of the (*P*,S_a,*S*,*S*)-**157** atropisomer had a more distinctive vibronic structure compared to the other R_a-isomer.

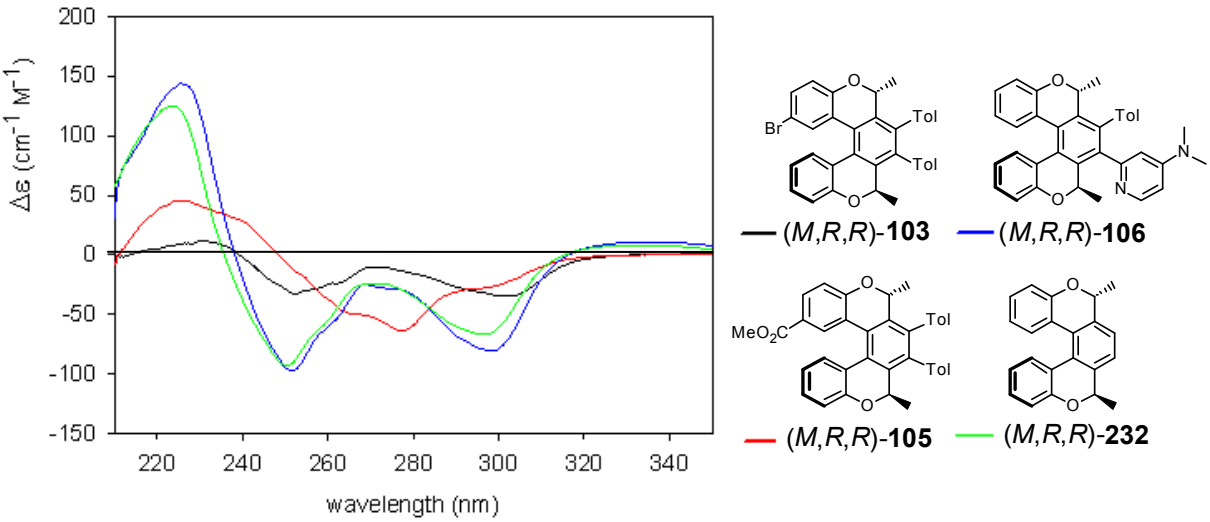
Figure 3.19 CD and UV-vis spectra of (*P*,S_a,S,*S*)-**157** and (*P*,R_a,*S*,*S*)-**157**.



The helicity of the *pyran-type* helicene-like compound (*M*,*R*,*R*)-**106** was determined by the X-ray analysis. Its CD spectrum was in an excellent agreement with the spectrum of (*M*,*S*,*S*)-**232**, whose helicity was determined using the NMR methods (Figure 3.20).[165] The spectrum of the DMAP-analogue (*M*,*R*,*R*)-**106** contained a positive maximum at 225 nm and two negative minima at 252 nm and 298 nm, while the spectrum of (*M*,*S*,*S*)-**232** was slightly blue-shifted. The CD spectrum of bromide (*M*,*R*,*R*)-**103**, which was characterised by a positive band at 231 nm and two negative bands at 252 nm and 302 nm, respectively, resembled the

spectrum of the DMAP-analogue (*M*,*R*,*R*)-**106**. The CD spectrum of ester (*M*,*R*,*R*)-**105** showed positive maxima at 225 nm and 241 nm and negative minima at 263 nm and 277 nm. The observed spectral shifts of these couplets probably arose from the difference in substitution on these helicene-like skeletons. Nevertheless, the similarity of the general sense of the Cotton effects of these four compounds implied that it was highly probable that they possessed the same (*M*)-helicity.

Figure 3.20 CD spectra of (*M*,*R*,*R*)-**103**, (*M*,*R*,*R*)-**106**, (*M*,*R*,*R*)-**105** and (*M*,*R*,*R*)-**232**.

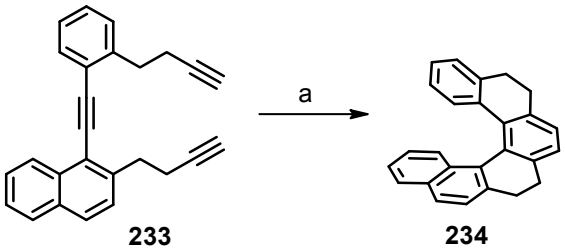


3.2 Enantioselective catalysis

Enantioselective Ni-catalysed cyclotrimerisation of alkynes

The enantioselective [2+2+2] cyclotrimerisation of aromatic alkynes would provide an efficient and atom-economic access to the nonracemic helicenes. Therefore, the synthesised phosphines and phosphites were tested as ligands in the Ni(0)-catalysed cyclotrimerisation of triyne **233**[183] under mild reaction conditions using 20 mol% of $Ni(cod)_2$ and 40 mol% of *P*-ligand in tetrahydrofuran at room temperature (Tab. 3.7 and Figure 3.21). The phosphines were easily obtained from the respective phosphine-borane complexes by treatment with an excess of diethylamine.

Table 3.7



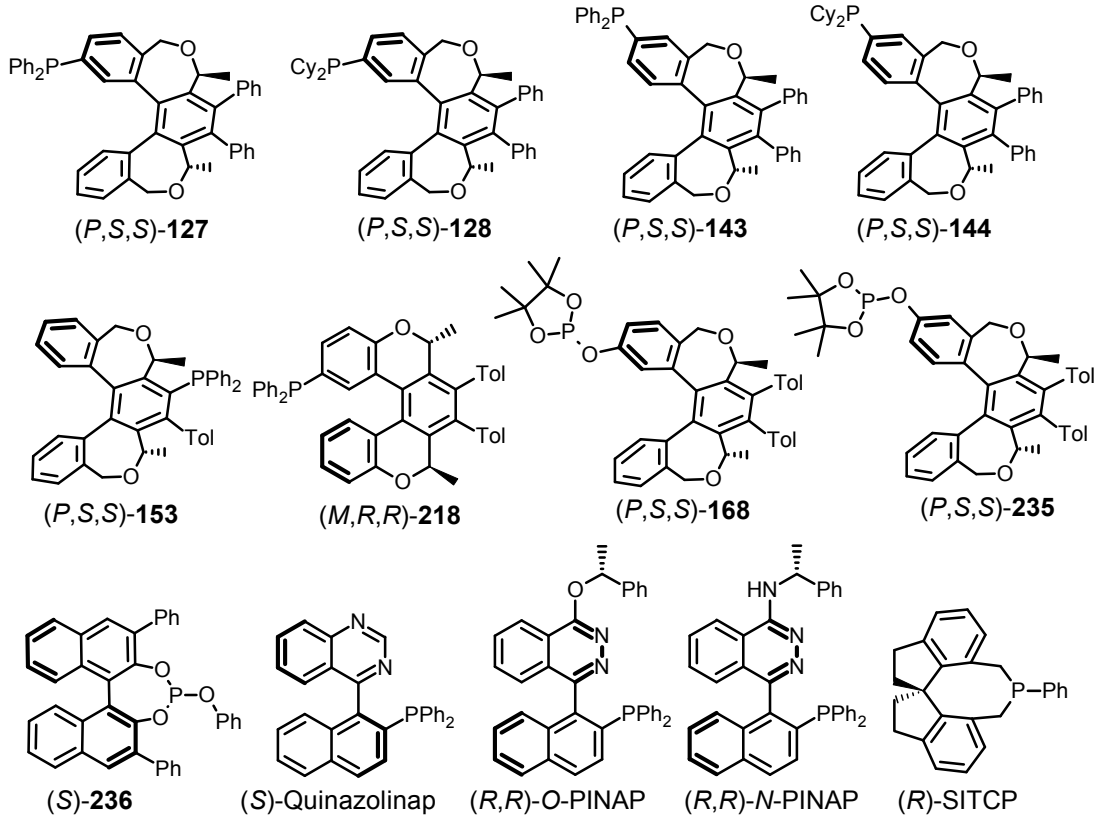
233 **234**

(a) $Ni(cod)_2$ (20 mol%), ligand (40 mol%), THF, r.t., 15 min.

Entry	Ligand	Isolated yield[a]	*ee* (configuration)
1	(*P*,*S*,*S*)-**127**	17%	30% (-)
2	(*P*,*S*,*S*)-**128**	99%	0%
3	(*P*,*S*,*S*)-**143**	67%	28% (+)
4	(*P*,*S*,*S*)-**144**	99%	0%
5	(*P*,*S*,*S*)-**153**	94%	7% (+)
6	(*M*,*R*,*R*)-**218**	75%	10% (+)
7	(*P*,*S*,*S*)-**168**	92%	0%
8	(*P*,*S*,*S*)-**235**[184]	62%	0%
9	(*S*)-**236**[185-187]	<5%	n/a
10	(*S*)-Quinazolinap[188]	75%	40% (+)
11	(*R*,*R*)-*O*-PINAP	33%	9% (+)
12	(*R*,*R*)-*N*-PINAP	26%	22% (+)
13	(*R*)-SITCP	35%	5% (+)

[a] the isolated yield was equivalent to conversion of the triyne **233**.

Figure 3.21



Apart from the helically chiral ligands (Entries 1-8), binaphthyl-type phosphite (*S*)-**236**[185-187] (Entry 9, provided by Prof. H. Yamamoto (University of Chicago, USA)), (*S*)-Quinazolinap[188] (Entry 10, provided by Prof. P. C. Guiry (University College Dublin, Ireland)), commercially available (*R*,*R*)-*O*-PINAP (Entry 11), (*R*,*R*)-*N*-PINAP (Entry 12) and spiro ligand (*R*)-SITCP (Entry 13) were tested.

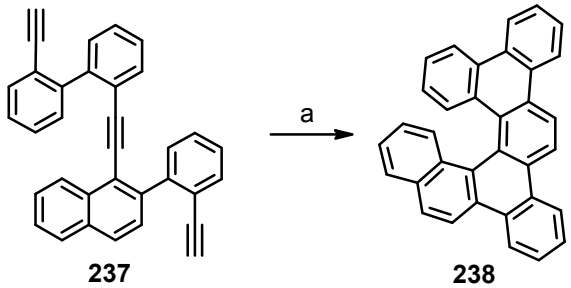
Moderate yields and enantioselectivities were observed when helical diphenylphosphine ligands were used in the cyclotrimerisation reaction (Entries 1, 3, 5-6). Initially, phosphine (*P*,*S*,*S*)-**127** from the dihydrooxepine series afforded 4*H*-[6]helicene **234** in 30% *ee* but the conversion was low (Entry 1). Using electron-donating cyclohexyl substituents increased reactivity but decreased enantioselectivity of the reaction with (*P*,*S*,*S*)-**128** (Entry 2). When the diphenylphosphino substituent was shifted further from the helical cavity to the position *3*, the yield increased dramatically and the enantioselectivity dropped slightly (Entry 3). Surprisingly, a change in the position of the phosphine substituent inverted the helicity of the product **234** (Entries 1 and 3). Similarly, the exchange of the phenyl substituents on the phosphorus to the cyclohexyl groups provided the racemic 4*H*-[6]helicene **234** in

quantitative yield (Entry 4). Therefore, further study was conducted on the diphenylphosphino helicene-like ligands. Almost quantitative conversion of the triyne **233** was observed when the diphenylphosphino group was placed on the central benzene ring of the scaffold (Entry 5). This position was however less favourable for the enantioselectivity of the reaction. The *pyran-type* (*M*,*R*,*R*)-**218** ligand was moderately reactive affording 4*H*-[6]helicene **234** in 75% yield and 10% *ee* (Entry 6). The more electrophilic phosphites (*P*,*S*,*S*)-**168** and (*P*,*S*,*S*)-**235**[184] increased reactivity of the catalyst, but the racemic product **234** was obtained (Entries 7-8).

Binaphthyl-type ligands were even less reactive (Entries 9, 11-12). The phosphite (*S*)-**236** dramatically retarded the reactivity of the nickel catalyst, so only <5% of **234** were produced (Entry 9). The most successful was (*S*)-quinazolinap[189] (Entry 10) with 40% *ee* (75% yield). However, the structurally similar (*R*,*R*)-O-PINAP and (*R*,*R*)-*N*-PINAP ligands provided 4*H*-[6]helicene **234** in 9% *ee* (33% yield) and 22% *ee* (26% yield), respectively (Entries 11-12). The spiro-ligand (*R*)-SITCP (Entry 13) exhibited very low reactivity and enantioselectivity.

The enantioselective [2+2+2] cyclotrimerisation was also examined on a more reactive substrate **237**[190] available in our laboratory (Table 3.8). In the case of (*P*,*S*,*S*)-**127** and (*P*,*S*,*S*)-**143**, the fully aromatic dibenzo[6]helicene **238** was formed in higher yields compared to 4*H*-[6]helicene **234** and enantioselectivity up to 25% *ee* was observed (Entry 2).

Table 3.8



237 **238**

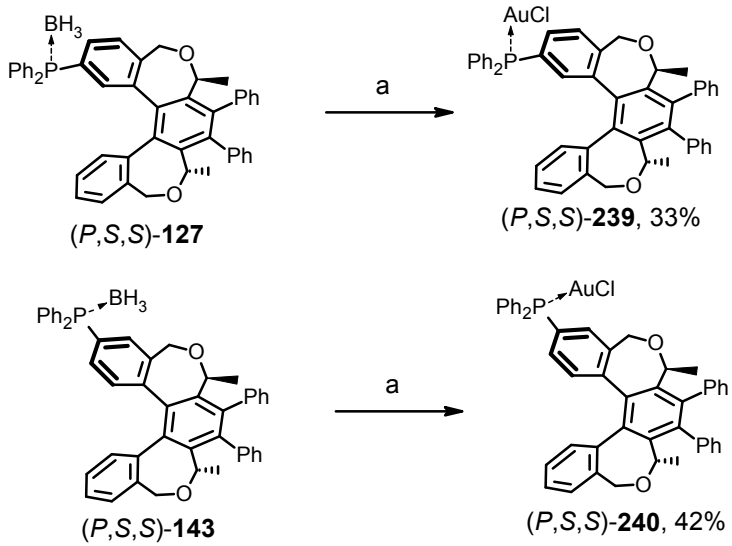
(a) $Ni(cod)_2$ (20 mol%), ligand (40 mol%), THF, r.t., 15 min.

Entry	Ligand	Isolated yield	*ee* (configuration)
1	(*P*,*S*,*S*)-**127**	98%	16% (-)
2	(*P*,*S*,*S*)-**143**	73%	25% (-)

Gold(I)-catalysed cyclisation of enynes

Gold-catalysed cyclisation of enynes is a great challenge in asymmetric catalysis due to the linear geometry of gold(I) complexes, which increases the distance between the ligand and a prochiral substrate.[152, 191] Recently, Echavarren and co-workers reported on the cationic gold(I) complexes, which were exceedingly effective in promoting alkoxycarbocyclisations of a wide range of 1,6-enynes.[192, 193] The active catalytic species in these reactions was the cationic gold(I) complex $[(Ph_3P)Au]^+$, generated *in situ* from $[(Ph_3P)AuCH_3]$ after treatment with a strong acid.[194, 195] This method of generation of cationic gold(I) species was not suitable for our elaborate helical phosphines since heating in acidic media was required. Therefore, another well-known procedure was used – the corresponding chlorophosphinegold(I) complexes were treated *in situ* with a silver salt, thus precipitating silver chloride and forming the desired cationic complex.[196] The chlorophosphinegold(I) complexes (*P*,*S*,*S*)-**239** and (*P*,*S*,*S*)-**240** were prepared from the corresponding phosphine-borane complexes (*P*,*S*,*S*)-**127** and (*P*,*S*,*S*)-**143** (Scheme 3.38).[197-199] Sodium tetrachloroaurate was initially reduced by 2,2´-thiodiethanol and then mixed with the deprotected phosphine.

Scheme 3.38

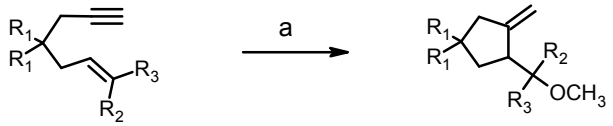


(a) 1) Et_2NH, 50 ºC, 15 h; 2) $NaAuCl_4$ (2.0-2.5 equiv.), 2,2´-thiodiethanol (5.9-6.7 equiv.), H_2O; 3) phosphine (1.0 equiv.), THF, r.t., 30 min.

The complexes with phosphites (*P*,*S*,*S*)-**168** and (*P*,*S*)-**85** were generated *in situ* from the thioether complex [AuCl(SMe_2)], in which dimethylsulfide was easily displaced by the phosphite ligand.[200]

The prepared helical gold(I) complexes (*P*,*S*,*S*)-**239** and (*P*,*S*,*S*)-**240** were efficient catalysts for methoxycarbocyclisation of 1,6-enynes **241-244** (Scheme 3.39). The cyclised products were obtained in quantitative (95-99%) yields but no enantioselectivity was observed in these reactions. The more reactive bis(phenylsulfonyl) derivatives **241** and **242** were reactive at room temperature whereas the malonates **243** and **244** required heating to 80 °C. The gold(I) complex of the phosphite (*P*,*S*,*S*)-**168** provided (±)-**245** in 95% yield while the gold(I) complex of the [7]helicene-like (*P*,*S*)-**85** afforded (-)-**245** in 92% yield and 15% *ee*. The reaction did not proceed in THF, dichloromethane or toluene employing only 10% of methanol.

Scheme 3.39



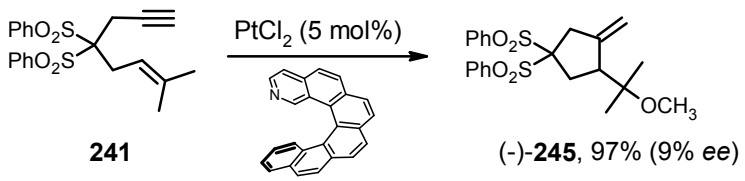
241 $R_1 = PhSO_2$, $R_2 = R_3 = CH_3$
242 $R_1 = PhSO_2$, $R_2 = H$, $R_3 = Ph$
243 $R_1 = CH_3O_2C$, $R_2 = R_3 = CH_3$
244 $R_1 = CH_3O_2C$, $R_2 = H$, $R_3 = Ph$

245 $R_1 = PhSO_2$, $R_2 = R_3 = CH_3$
246 $R_1 = PhSO_2$, $R_2 = H$, $R_3 = Ph$
247 $R_1 = CH_3O_2C$, $R_2 = R_3 = CH_3$
248 $R_1 = CH_3O_2C$, $R_2 = H$, $R_3 = Ph$

(a) AuCl(L*) (2 mol%), $AgSbF_6$ (2 mol%), methanol, r.t. or 80 ºC, 95-99%.[199]

The methoxycarbocyclisation of 1,6-enynes could be also catalysed by a less reactive platinum dichloride.[199, 201] Azahelicenes prepared in our group were tested as *N*-donor ligands in this reaction. The best result was obtained with (-)-2-aza[6]helicene[202] (Scheme 3.40). The cycloaddition product (-)-**245** was formed with an excellent regioselectivity in 97% yield and 9% *ee*.

Scheme 3.40



241

(10 mol%)

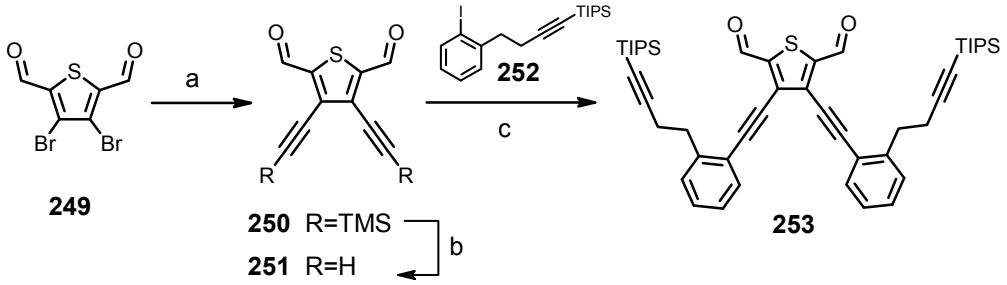
(-)-**245**, 97% (9% *ee*)

3.3 Synthesis of thia[9]helicene

Electron-rich aromatic compounds are strong candidates for applications in molecular electronics as organic semiconductors.[203] Helical aromatic molecules, different from the widely used acene and coronene molecules, could be particularly interesting because of their twisted π-conjugated system.[204] In order to extend the application of [2+2+2] cyclotrimerisation to the synthesis of sulfur-containing heterohelicenes, the synthesis of **107** was pursued.

The compound **249** was provided by Prof. V. G. Nenajdenko (Moscow State University, Russia) as a part of the collaboration. The double Sonogashira cross-coupling reaction of the thiophene **249**, activated by the presence of the aldehydic groups, readily reacted with ethynyl(trimethyl)silane to provide the diyne **250** in high yield (Scheme 3.41). The reaction proceeded only in toluene, whereas in amines, DMF or THF decomposition took place. Silane **250** was then deprotected with potassium carbonate in methanol. Unfortunately, diyne **251** was very unstable and decomposed during the reaction with aryl iodide **252**.[60] Therefore, some *in situ* TMS-deprotection procedures were examined,[205] for instance a recent procedure by Pale *et.al*.,[206] but no desired product **253** was observed either.

Scheme 3.41

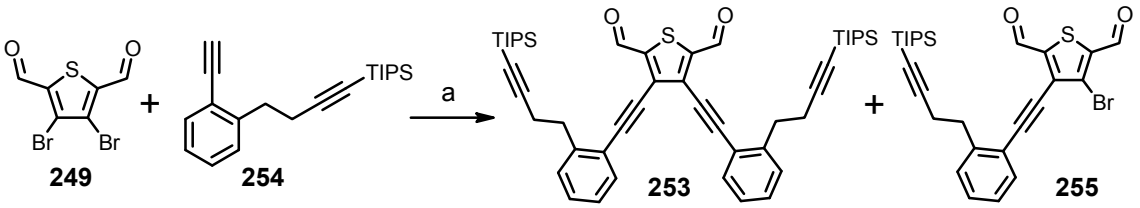


(a) TMSA (2.6 equiv.), $Pd(CH_3CN)_2Cl_2$ (10 mol%), PPh_3 (20 mol%), CuI (10 mol%), DIPEA (2.0 equiv.), toluene, r.t., 2 h, 90%.
(b) K_2CO_3 (5 equiv.), methanol (10 equiv.), $CHCl_3$, r.t., 30 min., decomposition.
(c) **252** (1.1 equiv.), $Pd(PPh_3)_4$ (10 mol%), $AgSbF_6$ (20 mol%), K_2CO_3 (8.0 equiv.), CH_3OH (8.0 equiv.), DMF, 50 ºC, decomposition.

Therefore, an alternative synthetic route was explored where bromide **249** reacted with diyne **254**[69] under Sonogashira cross-coupling conditions to provide tetrayne **253** in acceptable yield together with diyne **255** (Table 3.9). In order to

decrease the amount of **255** formed, different conditions of the cross-coupling were examined. When the reaction was carried out at higher temperature (Entries 1 *vs*. 2), the less stable bromide **255** decomposed. Then, several electron-rich phosphines were examined as ligands in the cross-coupling reaction. Indeed, they decreased the amount of bromide **255** in the reaction mixture, but the yield of the desired tetrayne **253** also dropped (Entries 3-5). Finally, the initial conditions with triphenylphosphine as a ligand at room temperature were found to be the best.

Table 3.9



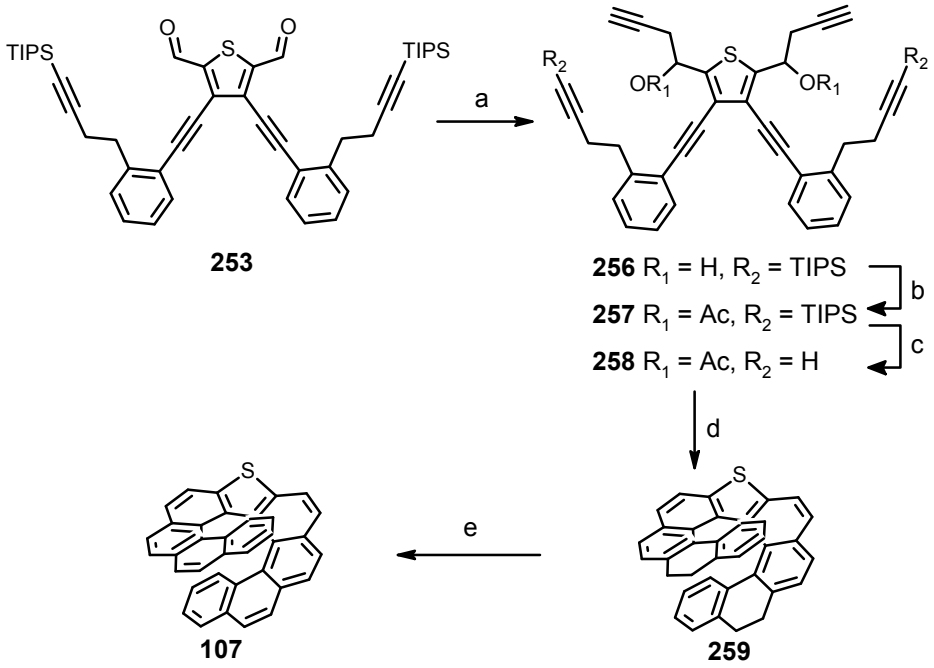
a) **254** (2.4 equiv.), $Pd(CH_3CN)_2Cl_2$ (10-11 mol%), Ligand (20-26 mol%), CuI (11 mol%), DIPEA (4.0-4.3 equiv.), toluene, overnight.

Entry	Ligand	Temperature	Isolated yields, %	
			253	**255**
1	PPh_{3f}	r.t.	48	20 - 6
2	PPh_3	reflux	47	8
3	XPhos	80 ºC	27	1
4	P(*t*-Bu)$_3$	80 ºC	20	0
5	P(*o*-Tol)$_3$	80 ºC	13	1

The following step in the synthesis was the regioselective propargylation of dicarbaldehyde **253** in the presence of gallium and indium (Scheme 3.42).[207] In this reaction no product with an allenyl structure was detected. The instability of the resultant diol **256** was circumvented by its *in situ* conversion into the more stable acetate **257**. In the next step, the silyl groups were removed using tetrabutylammonium fluoride to provide hexayne **258** in a good yield. The intramolecular [2+2+2] cyclotrimerisation of hexayne **258** in the presence of a stoichiometric amount of cobalt complex was accompanied by elimination of acetic acid and afforded tetrahydrothia[9]helicene **259** in 30% yield. Due to the small amount of the compound **259** available, the last aromatisation step was carried out

on a micromolar scale. In the presence of an excess of tritylium tetrafluoroborate the fully aromatic **107** was obtained, as confirmed by the high-resolution mass spectroscopy analysis.

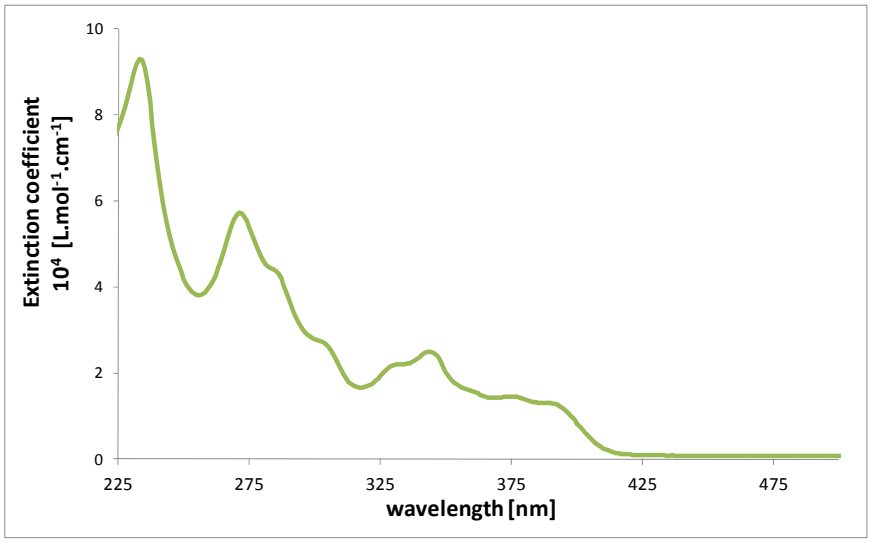
Scheme 3.42



(a) Propargyl bromide (8.2 equiv.), Ga (4.1 equiv.), In (20 mol%), THF, 0 ºC, 1 h → r.t., 20 min sonification, then 0 ºC, 30 min.
(b) DMAP (1.2 equiv.), Ac_2O (4.8 equiv.), THF, r.t., 30 min, 60% after two steps
(c) TBAF (1.5 equiv.), THF, r.t., overnight, 63%.
(d) $CoCp(CO)_2$ (1.0 equiv.), PPh_3 (2.0 equiv.), decane, halogen lamp, 160 ºC, 30 min, 30%.
(e) Ph_3CBF_4 (10 equiv.), DCE, 80 ºC, 6h.

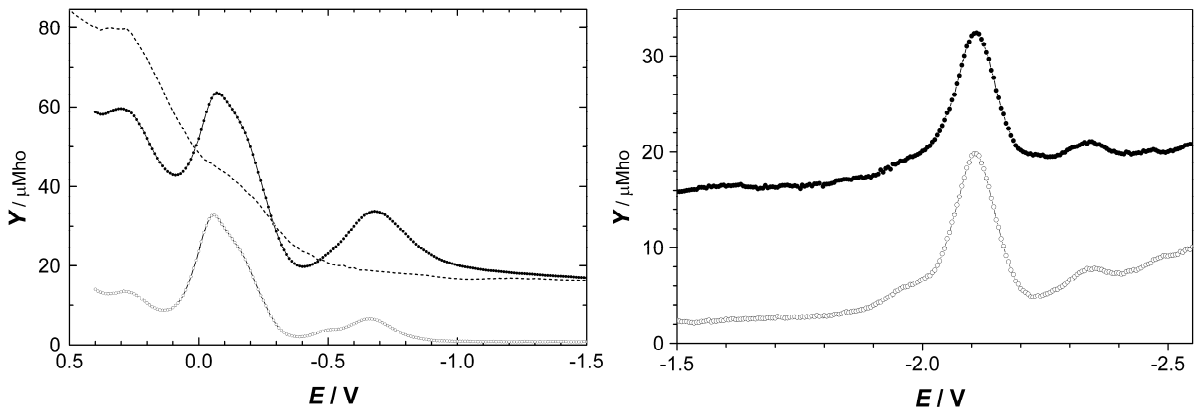
The absorption spectrum of tetrahydrothia[9]helicene **259** in UV-vis spectral region is shown in Figure 3.22. The extremely high molar extinction coefficient (ε = $93 \cdot 10^3$ $Lmol^{-1}cm^{-1}$) is a result of the large twisted π-conjugated system. The UV spectrum contains strong absorption bands at 233 nm and 271 nm (overlapping bands at 285 nm and 302 nm). The weaker bands at 331 nm, 343 nm and a wide band at 375-390 nm were also observed.

Figure 3.22 UV-Vis absorption spectrum of tetrahydrothia[9]helicene **259** in THF (analyte concentration $7 \cdot 10^{-5}$ M).



In addition, tetrahydrothia[9]helicene **259** was analysed by electrochemical methods. Figure 3.23 shows AC polarogram of **259** solution in acetonitrile. The same size of the real and imaginary admittance components indicated a fast reversible electron transfer at the formal redox potentials -2.11 V *vs*. Ag/AgCl (calibrated using Fc/Fc^+ = 0.484 V *vs*. Ag/AgCl). On the contrary, the following reduction at -2.3 V was irreversible and afforded only a small but distinctive maximum on both admittance vectors. No oxidation wave was detected at positive potentials using DC polarography. AC polarography in region -0.7 to +0.5 V showed distinctive minima, which corresponded to absorption-desorption processes or a change in the structure of the adsorbed film.

Figure 3.23 AC polarograms of **259** in CH_3CN (analyte concentration 0.35 mM) with 0.1 M Bu_4NPF_6 *vs*. Ag/AgCl. Frequency of AC sinusoidal signal 160 Hz, amplitude 10 mV p-p. Admittance parts: real (empty dots), imaginary (full dots).



4

Conclusion

A general diastereoselective synthetic approach to functionalised nonracemic helicene-like compounds was developed. This methodology was successfully applied to the synthesis of two types of helical scaffolds: one contained two (*S*)-methyldihydrooxepine rings and the other two (*R*)-methyl-2*H*-pyran rings.

The study also confirmed that the aryl substituents at the triyne indeed played a crucial role in the formation of the helical scaffold. They allowed „switching“ the stereoselectivity of the [2+2+2] cyclotrimerisation providing either (*P*) or (*M*) helicene-like structures. Generally, the aryl substituents were beneficial in both increasing yield of cyclotrimerisation and stability of the final helicene-like products. However, it was difficult to predict which type of an aryl substituent would provide the best yields in the cyclotrimerisation reaction for a specific triyne.

The synthesis of the nonracemic *oxepine-type* bromo substituted helicene-like compounds (*P*,*S*,*S*)-**124** and (*P*,*S*,*S*)-**142** as efficient precursors of various phosphines and phosphites was developed. The synthetic methodology for the transformation of the helical bromides to phosphines was worked out and the phoshine-borane complexes (*P*,*S*,*S*)-**127**, (*P*,*S*,*S*)-**128**, (*P*,*S*,*S*)-**129**, (*P*,*S*,*S*)-**143** and (*P*,*S*,*S*)-**144** were obtained in good yields. In addition, the *oxepine-type* helical compound (*P*,*S*,*S*)-**153** with the diphenylphosphino group in the position *8* was synthesised. The atropisomeric phosphine oxide (*P*,S_a,*S*,*S*)-**159** was obtained by the synthesis and chromatographic separation of the atropisomeric bromides (*P*,R_a,*S*,*S*)-**157** and (*P*,S_a,*S*,*S*)-**157**.

The hydroxy derivatives, which were precursors of phosphites, could be obtained either from the corresponding bromides or by the alternative synthetic pathway via the methoxy substituted helicene-like scaffolds. It was found that the synthesis of hydroxy substituted helicene-like compound through the corresponding methoxy derivatives brought less problems and higher yields. The hydroxy substituted helicenes (*P*,*S*,*S*)-**132**, (*P*,*S*,*S*)-**167** and (*P*,*S*,*S*)-**173** were prepared and some of them were successfully transformed to the corresponding phosphites.

The functionalised *pyran-type* helical scaffolds bearing the bromo, methoxycarbonyl and 4-dimethylaminopyridyl substituents were successfully prepared. The bromo derivative (*M*,*R*,*R*)-**103** was transformed to the phosphine borane complex (*M*,*R*,*R*)-**218**.

The synthesised phosphines and phosphites were tested as ligands in the enantioselective Ni-catalysed [2+2+2] cyclotrimerisation reaction. In addition, other binaphthyl-type ligands were also tested. Moderate enantioselectivities up to 40% *ee* were obtained. The prepared ligands were also used in the Au-catalysed enyne cyclisation, where low enantioselectivities up to 15% *ee* were obtained.

The synthetic route to thia[9]helicene **107** was explored. Tetrahydrothia[9]helicene **259** was successfully prepared and characterised by polarography, NMR, IR, MS and UV-Vis spectroscopy. Thia[9]helicene **107** was prepared from **259** but its identity was confirmed only by mass spectroscopy.

To conclude, the results demonstrate that the diastereoselective synthesis of helically chiral compounds based on [2+2+2] cyclotrimerisation is a general, flexible and practical method, which provides access to nonracemic helically chiral phosphines and phosphites. Although the observed enantioselectivities in the Ni- and Au-catalysed cyclisations were moderate, it is hoped that this study will stimulate further investigations in this field.

5

Experimental section

- Melting points were determined on Mikro-Heiztisch Polytherm A (Hund, Wetzlar) apparatus and are uncorrected.
- The NMR spectra were measured in $CDCl_3$, CD_2Cl_2, d_6-acetone, d_6-DMSO on Bruker Avance: ^1H NMR spectra at 400.1 MHz, 500.1 MHz and 600.1 MHz; ^{13}C NMR spectra at 100.6 MHz, 125.8 MHz and 150.9 MHz; ^{31}P NMR spectra at 162.0 MHz and 202.3 MHz; ^{11}B NMR spectra at 160.4 MHz; ^{19}F NMR spectra at 470.6 MHz. ^1H Chemical shifts in $CDCl_3$ (in ppm, δ scale) were referenced to tetramethylsilane. In ^{31}P NMR spectra phosphoric acid was used as an external standard. In ^{11}B NMR spectra BF_3-Et_2O was used as an external standard. In ^{19}F NMR spectra hexafluorobenzene was used as an external standard. The coupling constants (J) are given in Hz. The HMBC experiments were set up for J_{C-H} = 5 Hz. Assignment of ^1H and ^{13}C NMR spectra of the key compounds was performed using COSY, HMQC and HMBC experiments.
- The IR spectra were measured in $CHCl_3$ or KBr on FT-IR spectrometer Bruker Equinox 55.
- FAB mass spectra (ionisation by Xe, thioglycerol, 2-hydroxyethyl disulfide and 3-nitrobenzyl alcohol matrices) were measured on ZAB-EQ (VG Analytical) spectrometer. The EI mass spectra were determined on GCT Premier (Waters) at an ionising voltage of 70 eV, the *m/z* values are given along with their relative intensities (%). For exact mass measurement, the spectra were internally calibrated using perfluorotri-*n*-butylamine (Heptacosa). ESI and APCI mass spectra were measured on LCQ Fleet (Thermo Fisher Scientific) with a 3D ion trap mass spectrometer and Q-Tof micro (Waters) mass spectrometer. High resolution spectra were obtained from LTQ Orbitrap XL (Thermo Fisher Scientific).
- Optical rotations were measured in CH_2Cl_2 or acetone on Autopol IV (Rudolph Research Analytical) instrument.
- UV-Vis spectra were recorded on Cary 50 (Varian Inc.) with pure solvent (distilled THF) as a baseline.
- Circular dichroism spectra were recorded on a J-815 CD spectrometer (Jasco Analytical Instruments, Inc.) in freshly distilled THF using a 10 mm quartz sample cell.

- Cyclic voltametry was performed on a fast rise-time potentiostat, a lock-in amplifier (Stanford Research, model SRS830). The instruments were interfaced to a personal computer via an IEEE–interface card (PC–Lab, AdvanTech Model PCL–848) and a data acquisition card (PCL–818) using 12–bit precision for both A/D and D/A conversion. A three-electrode electrochemical cell was used. The reference electrode, Ag|AgCl|1M LiCl, was separated from the test solution by a non-aqueous salt bridge. The potential of the ferrocene/ferrocenium redox couple (Fc/Fc^{+}) was 0.484 V. The working electrode was a computer controlled valve-operated mercury drop (model SMDE2, Laboratorní přístroje, Prague). The auxiliary electrode was a platinum wire. Oxygen was removed from the solvent (anhydrous acetonitrile) by passing a stream of argon.

- Single-crystal X-ray analyses of compounds (*P*,*S*,*S*)-**132**, (*P*,S_a,*S*,*S*)-**137**, (*P*,S_a,*S*,*S*)-**138**, (*P*,*S*,*S*)-**146**, (*M*,*S*,*S*)-**166** were performed on Bruker Apex II diffractometer by monochromatised MoK_α radiation (λ = 0.71073 Å) at 150 K. Data collection: *Apex II* (Bruker); cell refinement: *SAINT* (Bruker); data reduction: *SAINT* (Bruker); program used to solve structure: *SHELXS97* (Sheldrick, 2008); program used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2*.[208]

- Single-crystal X-ray analyses of compounds (*P*,*S*,*S*)-**151**, (*M*,*R*,*R*)-**192** were performed on Xcalibur X-ray diffractometer with CuK_α radiation (λ=1.54180 Å) at 170 K. Data collection: *Xcalibur* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED* (Oxford Diffraction, 2002); program used to solve structure: *Superflip* (Palatinus & Chapuis, 2007); program used to refine structure: *CRYSTALS* (Betteridge *et al*.,[209] 2003); molecular graphics: *OLEX2.*[208]

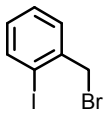
- Reaction progress was monitored by thin-layer chromatography (TLC) on Silica gel 60 F_{254}-coated aluminium sheets (Merck) and Silica gel 60 RP-18 F_{254}s aluminium sheets (Merck). Spots were detected either using UV light or the following solutions: (1) $Ce(SO_4)_2{\cdot}4H_2O$ (1%) and $H_3P(Mo_3O_{10})_4$ (2%) in sulfuric acid (10%); (2) *p*-anisaldehyde (2%), acetic acid (2%) and sulfuric acid (7%) in 99% ethanol; (3) 2,4-dinitrophenylhydrazine (2%) and sulfuric acid (4%) in 60% ethanol.

- Column chromatography was carried out on Silica gel 60 (0.040-0.063 mm), Fluka). Flash chromatography was carried out on Isolera One HPFC system (Biotage, Inc.) using Biotage KP-Sil® Silica cartridges (0.040-0.063 mm), Silica gel 60 (0.040-0.063 mm) or Silica gel 60 (0.015-0.040 mm). Aluminium oxide 90 active neutral (activity stage I, 0.063-0.200 mm, Merck) was used for filtration. Reversed phase flash chromatography was performed on Isolera One HPFC system (Biotage, Inc.) using Biotage KP-C18-HS® Silica cartridges.
- Analytical HPLC was carried out using an isocratic HPLC pump (Knauer), UV-Vis detector (Knauer) and polarimetric detector Chiralyser (IBZ Messtechnik). Preparative HPLC was carried out on Agilent 1100 using UV detector.
- Continuous-flow reactor was composed of an HPLC pump, backpressure regulator and a heated capillary (length 10 m, ID 1.0 mm, OD 1/16“, stainless steel).
- Microwave-assisted reactions were carried out in Biotage Initiator EXP EU (300 W) in Biotage Microwave Vials. Silicon carbide (400 mesh particle size) or ionic liquid (1-butyl-2,3-dimethylimidazolium tetrafluoroborate, [BDMIM][BF_4]) were used to increase absorption of the microwave irradiation.
- IR lamp (250 W, Polam) was used in bromination reactions. Two 250 W halogen lamps were used in cyclotrimerisation reactions.
- All reactions were carried out under argon. Air and moisture sensitive compounds ($Ni(cod)_2$) were manipulated in glove-box MBraun Unilab.
- The bath with temperature below -95 °C was prepared by adding dry ice (crushed to powder) to *n*-propanol (p.a.) in a bowl-shaped Dewar flask until a thick suspension was formed. Then liquid nitrogen was added in small portions to the thoroughly stirred suspension until its temperature, measured using digital thermometer, reached the required value.
- The commercially available catalysts and reagent grade materials were purchased and used as received. Solvents (diisopropylamine, toluene) were degassed by three freeze-pump-thaw cycles before use. Diisopropylamine, diethylamine and *N*,*N*-diisopropylethylamine were distilled from calcium hydride under argon. Tetrahydrofuran and diethyl ether were freshly distilled from sodium/benzophenone under argon. *n*-BuLi, *sec*-BuLi, *t*-BuLi, $Pd(PPh_3)_4$,

$Pd(PPh_3)_2Cl_2$, $Pd(dba)_2$, $Ni(cod)_2$, and $CoCp(CO)_2$ were purchased. $RhCp^*(C_2H_2)_2$[210] and $CoCp(CO)(fum)$[157] were prepared in our lab by Mgr. J. Žádný using literature procedures. NBS was recrystallised from water. 2-iodobenzyl bromide was used as received (Sigma-Aldrich, 97%) or recrystallised from methanol (Alfa Aesar, 96%). Sodium hydride was used as 60% w/w dispersion in mineral oil (Sigma-Aldrich). Potassium hydride was used as 30 wt% dispersion in mineral oil (Sigma-Aldrich). Optically pure (-)-(*S*)-3-butyn-2-ol **111** was purchased (Sigma-Aldrich, 97%). Boron trifluoride diethyl etherate was distilled under vacuum before use. Borane dimethyl sulfide complex and borane tetrahydrofuran complex solution were purchased from Sigma Aldrich.

- Sodium methoxide solution was freshly prepared by dissolving the weighted amount of sodium metal in absolute methanol at 0 ºC. Lithium diisopropylamide solution was always freshly prepared by mixing equimolar amounts of distilled diisopropylamine (CaH_2) and *n*-butyllithium in THF at 0 ºC for 30 min.
- Data for the molecular models presented in the figures were either taken from X-ray analysis or optimised by AM1 calculations in Gaussian 03.[212] The figures were prepared using Molekel[213] and Mercury[214] software.

2-Iodobenzyl bromide 110

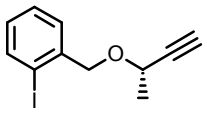


2-Iodobenzyl alcohol (5.51 g, 23.5 mmol) was dissolved in THF (35 ml) and cooled to 0 ºC. Phosphorus tribromide (3.35 ml, 35.25 mmol, 1.5 equiv.) was slowly added over a period of 30 min and the reaction mixture stirred at 0 ºC for 30 min. Then a saturated aqueous solution of $NaHCO_3$ (50 ml) was added and THF removed *in vacuo*. Then diethyl ether (100 ml) was added and washed with water (3 x 100 ml) and then dried over anhydrous $MgSO_4$. The product was purified by flash chromatography on silica gel (hexane) to provide **110** (6.66 g, 95%) as a white solid.

^{1}H NMR and ^{13}C NMR were in agreement with the published data.[215]

^{1}H NMR (400 MHz, $CDCl_3$): 4.60 (2H, s), 6.98 (1H, td, *J* = 7.7, 7.7, 1.5), 7.34 (1H, td, *J* = 7.5, 0.9), 7.47 (1H, dd, *J* = 7.6, 1.5), 7.86 (1H, d, *J* = 7.8).

2-Iodobenzyl (1*S*)-1-methylprop-2-yn-1-yl ether (*S*)-**112**



Potassium hydride (dispersion in mineral oil, 1.22 g, 30.4 mmol, 1.6 equiv.) was washed with hexane under argon and dried under vacuum. Then it was suspended in THF (20 ml) and cooled to 0 ºC. Then (*S*)-**111** was added slowly (2.5 ml, 31.9 mmol, 1.7 equiv.) and the solution was stirred at 0 ºC for 30 min. Then a solution of **110** (5.72 g, 19.3 mmol, 1.0 equiv.) in THF (20 ml) was added and the reaction was stirred at room temperature overnight. After filtration through a sintered glass (hexane), the volatiles were removed *in vacuo*. The residue was dissolved in dichloromethane (100 ml) and washed with water (3 x 100 ml) and then dried over anhydrous $MgSO_4$. Column chromatography on silica gel (hexane) afforded product (*S*)-**112** (5.1 g, 91%) as a colourless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): 1.53 (3H, d, *J* = 6.6), 2.48 (1H, d, *J* = 2.0), 4.30 (1H, dq, *J* = 6.6, 6.6, 6.6, 2.0), 4.49 (1H, d, *J* = 12.5), 4.76 (1H, d, *J* = 12.5), 6.98 (1H, dddt, *J* = 7.9, 7.3, 1.8, 0.6, 0.6), 7.34 (1H, dt, *J* = 7.5, 7.5, 1.3), 7.45 (1H, ddt, *J* = 7.7, 1.8, 0.7, 0.7), 7.82 (1H, dd, *J* = 7.9, 1.3).

^{13}C NMR (126 MHz, $CDCl_3$): 22.01 (q), 65.05 (d), 73.41 (d), 74.42 (t), 83.45 (s), 97.97 (s), 128.17 (d), 129.03 (d), 129.22 (d), 139.20 (d), 140.20 (s).

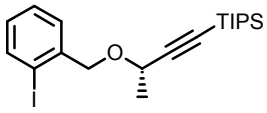
IR ($CHCl_3$): 3306 s, 3061 w, 2992 m, 2938 w, 2870 m, 2112 w, 1583 m, 1566 m, 1466 m, 1440 m, 1374 m, 1326 m, 1273 m, 1161 w, 1116 s, 1098 vs, 1067 s, 1045 m, 1015 vs, 983 w, 946 w, 694 w, 649 m, 638 s, 531 w, 511 vw, 429 w cm^{-1}.

ESI MS: 309 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{11}H_{11}OINa$ 308.9747, found 308.9747.

Optical rotation: $[\alpha]^{22}_D$ -55° (c 1.357, CH_2Cl_2).

{(3*S*)-3-[(2-Iodobenzyl)oxy]but-1-yn-1-yl}[tris(1-methylethyl)]silane (*S*)-**113**



To a solution of diisopropylamine (5.0 ml, 0.035 mol, 2.0 equiv.) in THF (5 ml) cooled to -78 ºC a solution of *n*-BuLi (1.6 M in hexanes, 12.1 ml, 0.019 mol, 1.1 equiv.) was added and the solution was stirred at -78 ºC for 1 h. Then this solution was added to a solution of alkyne (*S*)-**112** (5.05 g, 0.018 mol) in THF (10 ml) at -78 ºC via a cannula (over a period of 15 min). After stirring for 45 min at -78 ºC triisopropylsilyl chloride (4.2 ml, 0.019 mol, 1.1 equiv.) was added dropwise. The reaction mixture was stirred at -78 ºC for 10 min and then allowed to warm up to room temperature and stirred overnight. The solvents were removed *in vacuo* and the residue dissolved in dichloromethane (100 ml) and washed with water (3 x 100 ml) and then dried over anhydrous $MgSO_4$. Column chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) afforded product (*S*)-**113** (6.34 g, 84%) as a colourless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): 1.04-1.13 (21H, m), 1.52 (3H, d, *J* = 6.6), 4.33 (1H, q, *J* = 6.6), 4.51 (1H, d, *J* = 12.7), 4.79 (1H, d, *J* = 12.7), 6.97 (1H, ddd, *J* = 7.9, 7.4, 1.8), 7.33 (1H, td, *J* = 7.5, 7.5, 1.3), 7.45 (1H, ddt, *J* = 7.6, 1.8, 0.8, 0.8), 7.81 (1H, dd, *J* = 7.9, 1.3).

^{13}C NMR (126 MHz, $CDCl_3$): 11.18 (d), 18.64 (q), 22.30 (q), 65.69 (d), 74.27 (t), 86.22 (s), 97.88 (s), 107.25 (s), 128.12 (d), 128.96 (d), 129.09 (d), 139.16 (d), 140.55 (s).

IR ($CHCl_3$): 3060 vw, 2959 s, 2945 vs, 2892 m, 2867 vs, 2165 w, 2149 w, 1583 w, 1566 w, 1464 s, 1439 m, 1384 w, 1371 w, 1325 w, 1273 vw, 1163 vw, 1116 m, 1097

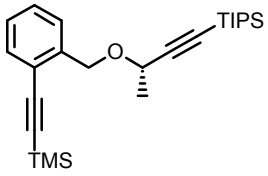
s, 1071 m, 1044 m, 1015 s, 997 m, 980 w, 945 w, 883 s, 696 w, 680 m, 662 m, 650 w, 527 vw, 507 vw cm^{-1}.

ESI MS: 465 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{20}H_{31}OINaSi$ 465.1081, found 465.1078.

Optical rotation: $[\alpha]^{22}_D$ -36° (c 1.262, CH_2Cl_2).

Trimethyl({2-[({(1*S*)-1-methyl-3-[tris(1-methylethyl)silyl]prop-2-yn-1-yl}oxy)methyl]phenyl}ethynyl)silane (*S*)-**114**



Tetrakis(triphenylphosphine)palladium(0) (157 mg, 0.136 mmol, 1 mol%), copper iodide (52 mg, 0.273 mmol, 2 mol%), aryl iodide (*S*)-**113** (6.0 g, 13.56 mmol) were suspended in diisopropylamine (50 ml) and ethynyl(trimethyl)silylane (2.0 ml, 14.15 mmol, 1.0 equiv.) was added at room temperature. After stirring for 20 min at room temperature, the reaction mixture was filtered through a sintered glass (hexane) and solvents were removed *in vacuo*. Column chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) afforded product (*S*)-**114** (5.54 g, 99%) as an oil.

^{1}H NMR (600 MHz, $CDCl_3$): 0.25 (9H, s), 1.05-1.10 (21H, m), 1.52 (3H, d, *J* = 6.6), 4.34 (1H, q, *J* = 6.6), 4.71 (1H, dq, *J* = 12.7, 0.5, 0.5, 0.5), 4.89 (1H, bd, *J* = 12.7), 7.20 (1H, dtt, *J* = 7.6, 7.6, 1.5, 0.6, 0.6), 7.30 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.45 (1H, ddd, *J* = 7.6, 1.4, 0.5), 7.46 (1H, ddq, *J* = 7.6, 1.5, 0.7, 0.7, 0.7).

^{13}C NMR (151 MHz, $CDCl_3$): -0.01 (q), 11.17 (d), 18.62 (q), 22.41 (q), 65.95 (d), 68.70 (t), 85.69 (s), 98.94 (s), 102.66 (s), 107.75 (s), 121.59 (s), 127.01 (d), 127.37 (d), 128.59 (d), 132.36 (d), 140.63 (s).

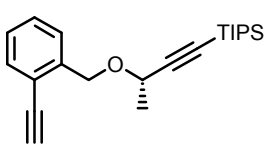
IR ($CHCl_3$): 3097 vw, 3071 w, 2960 vs, 2945 vs, 2892 s, 2866 vs, 2156 s, 1599 vw, 1570 vw, 1483 m, 1463 s, 1450 s, 1408 w, 1388 m, 1384 m, 1371 m, 1324 s, 1288 vw, 1262 m, 1251 vs, 1159 vw, 1118 s, 1110 s, 1095 s, 1070 s, 1019 m, 997 s, 883 vs, 869 vs, 845 vs, 695 m, 679 s, 663 s, 595 m, 519 w, 495 vw, 452 m cm^{-1}.

ESI MS: 435 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{25}H_{40}ONaSi_2$ 435.2510, found 435.2509.

Optical rotation: $[\alpha]^{22}_D$ -86° (c 0.981, CH_2Cl_2).

{(3*S*)-3-[(2-Ethynylbenzyl)oxy]but-1-yn-1-yl}[tris(1-methylethyl)]silane (*S*)-**115**



Sodium methoxide was prepared by dissolving sodium (310 mg, 13.5 mmol, 1.0 equiv.) in methanol (20 ml) at 0 ºC. Then it was added to a solution of silane (*S*)-**114** (5.8 g, 13.5 mmol) in methanol (50 ml) and stirred at room temperature for 30 min. The solvent was removed *in vacuo* and the residue dissolved in diethyl ether (100 ml) and washed with water (3 x 100 ml) and then dried over anhydrous $MgSO_4$. The product (*S*)-**115** (4.57 g, 99%) was a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.03-1.12 (21H, m), 1.51 (3H, d, *J* = 6.6), 3.25 (1H, s), 4.32 (1H, q, *J* = 6.6), 4.74 (1H, dd, *J* = 12.9, 0.8), 4.96 (1H, dd, *J* = 12.9, 0.8), 7.23 (1H, dtt, *J* = 7.6, 7.6, 1.4, 0.6, 0.6), 7.34 (1H, dt, *J* = 7.6, 7.6, 1.5), 7.48 (1H, bdd, *J* = 7.6, 1.5), 7.49 (1H, ddq, *J* = 7.6, 1.4, 0.7, 0.7, 0.7).

^{13}C NMR (151 MHz, $CDCl_3$): 11.17 (d), 18.61 (q), 22.32 (q), 65.65 (d), 68.39 (t), 81.20 (s), 81.59 (d), 85.86 (s), 107.56 (s), 120.66 (s), 127.13 (d), 127.62 (d), 128.89 (d), 132.65 (d), 140.81 (s).

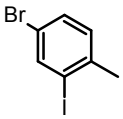
IR ($CHCl_3$): 3306 s, 3099 vw, 3072 w, 2959 vs, 2945 vs, 2925 s, 2892 s, 2866 vs, 2165 w, 2106 w, 1601 w, 1572 vw, 1482 s, 1463 s, 1451 m, 1388 m, 1384 m, 1371 m, 1325 s, 1288 w, 1255 w, 1157 w, 1113 s, 1108 s, 1094 s, 1069 s, 1019 m, 997 m, 950 w, 883 s, 867 w, 679 s, 663 s, 655 s, 615 s, 519 w, 495 vw, 454 w cm^{-1}.

ESI MS: 363 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{22}H_{32}ONaSi$ 363.2115, found 363.2114.

Optical rotation: $[\alpha]^{22}_D$ -79° (c 0.819, CH_2Cl_2).

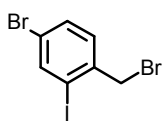
4-Bromo-2-iodo-1-methylbenzene 117



To an aqueous solution of sulfuric acid (1.25 M, 50 ml, 0.062 mol, 5.2 equiv.) in a 250 ml round-bottom flask 4-bromo-2-iodo-1-methylbenzene (1.5 ml, 12.0 mmol, 1.0 equiv.) was added and a white suspension was formed. The suspension was cooled to -2 °C and $NaNO_2$ (0.84 g, 12.2 mmol, 1.0 equiv.) was carefully added in small portions. The resulting yellow suspension was stirred at 0 °C for 10 min and then potassium iodide (4.1 g, 24.7 mmol, 2.1 equiv.) was added. The reaction mixture was then heated at 110 °C for 2 h and then at r.t. overnight. Then it was extracted with dichloromethane (2 x 100 ml) and the combined organic phases were washed with a saturated aqueous solution of $Na_2S_2O_3$ (1 x 100 ml), saturated aqueous solution of $KHCO_3$ (1 x 100 ml), water (3 x 100 ml) and then dried over anhydrous $MgSO_4$. Flash chromatography on silica gel (hexane) afforded product (2.28 g, 65%) as a yellow liquid.
^{1}H NMR and ^{13}C NMR were in agreement with the published data.[216]

^{1}H NMR (400 MHz, $CDCl_3$): 2.38 (3H, s), 7.10 (1H, d, *J* = 8.2), 7.36 (1H, dd, *J* = 8.1, 2.1), 7.94 (1H, d, *J* = 2.1).

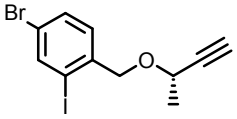
4-Bromo-1-(bromomethyl)-2-iodobenzene 118



In a 250 ml round-bottom flask **117** (4.41 g, 14.85 mmol, 1.0 equiv.), NBS (3.97 g, 22.28 mmol, 1.5 equiv.), CCl_4 (100 ml) and a catalytic amount of AIBN and K_2CO_3 were flushed with nitrogen and the suspension was refluxed using IR lamp for 3 h. Then an additional amount of NBS (1.32 g, 7.42 mmol, 0.05 equiv.) and AINB (cat.) were added and the reaction mixture was heated for another 2 h. Then the reaction mixture was washed with a saturated solution of $Na_2S_2O_3$ (2 x 50 ml), water (3 x 50 ml) and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (hexane). The product **118** (4.28 g, 77%, with <10% I-Br exchange impurity) was obtained as a white solid.
^{1}H NMR and ^{13}C NMR were in agreement with the published data.[121]

^{1}H NMR (400 MHz, $CDCl_3$): 4.54 (2H, s), 7.33 (1H, d, *J* = 8.2), 7.47 (1H, dd, *J* = 8.2, 2.0), 8.00 (1H, d, *J* = 2.0).

4-Bromo-2-iodobenzyl (1*S*)-1-methylprop-2-yn-1-yl ether (*S*)-**119**

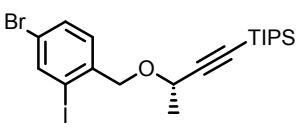


In a flame-dried Schlenk flask potassium hydride (dispersion in mineral oil, 1.01 g, 0.025 mol, 1.5 equiv.) was washed with hexane under argon, then dried under vacuum and flushed with argon. After that THF (20 ml) was added to hydride and the suspension was cooled to 0 ºC, (*S*)-**111** (1.98 ml, 0.025 mol, 1.5 equiv.) was added and the reaction mixture was stirred at 0 ºC for 1 h. Then a solution of the benzyl bromide **118** (6.32 g, 0.017 mol) in THF (20 ml) was added at 0 ºC and the reaction mixture was allowed to warm up to room temperature and stirred for 1.5 h. The reaction was quenched by an addition of a saturated aqueous solution of NH_4Cl (5 ml) and an aqueous phase was washed with diethyl ether (4 x 100 ml), the combined organic phases were washed with water (2 x 50 ml) and dried over anhydrous Na_2SO_4. The volatiles were removed *in vacuo* and the residue was purified by chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) to provide product (*S*)-**119** (5.8 g, 95%, with <10% I-Br exchange impurity) as an amorphous solid.

^{1}H NMR and ^{13}C NMR were in agreement with the published data.[217]

^{1}H NMR (400 MHz, $CDCl_3$): 1.52 (3H, d, *J* = 6.6), 2.49 (1H, d, *J* = 2.0), 4.29 (1H, dq, *J* = 6.6, 6.6, 6.6, 2.0), 4.43 (1H, d, *J* = 12.7), 4.70 (1H, dd, *J* = 12.7, 0.8), 7.31 (1H, dt, *J* = 8.2, 0.8, 0.8), 7.47 (1H, dd, *J* = 8.2, 2.0), 7.97 (1H, d, *J* = 2.0).

{(3*S*)-3-[(4-Bromo-2-iodobenzyl)oxy]but-1-yn-1-yl}[tris(1-methylethyl)] silane (*S*)-**120**

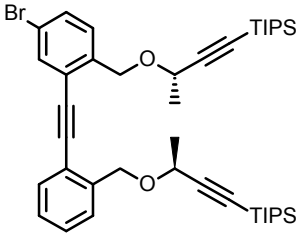


A solution of lithium diisopropylamide was freshly prepared: In a flame-dried Schlenk flask diisopropylamine (5.0 ml, 35.5 mmol, 2.2 equiv.) in THF (10 ml) was cooled to 0 ºC under argon and a solution of *n*-BuLi (1.6 M in hexanes, 10.0 ml, 16.0 mmol, 1.0 equiv) was added. The solution was stirred at 0 ºC for 1 h. A flame-dried Schlenk flask was filled with a solution of alkyne (*S*)-**119** (5.80 g, 15.9 mmol) in THF (20 ml) under argon and cooled to -78 ºC. A solution of lithium diisopropylamide (25 ml, 16.0 mmol, 1.0 equiv) in THF was slowly added and the reaction mixture stirred at -78 ºC for 1 h. Then triisopropylsilyl chloride (4.4 ml, 20.7 mmol, 1.3 equiv.) was added and the solution

was stirred at -78 ºC for 30 min, then allowed to warm up to room temperature and stirred overnight. The volatiles were removed *in vacuo*, the residue was dissolved in dichloromethane (100 ml) and washed with water (3 x 50 ml). The combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) to provide product (*S*)-**120** (5.06 g, 61%, with <10% I-Br exchange impurity) as a colourless oil.
^{1}H NMR and ^{13}C NMR were in agreement with the published data.[217]

^{1}H NMR (400 MHz, $CDCl_3$): 1.03-1.11 (21H, m), 1.51 (3H, d, *J* = 6.6), 4.32 (1H, q, *J* = 6.6), 4.44 (1H, bd, *J* = 13.0), 4.72 (1H, dd, *J* = 13.0, 0.8), 7.31 (1H, dt, *J* = 8.2, 0.8, 0.8), 7.46 (1H, dd, *J* = 8.2, 2.0), 7.96 (1H, d, *J* = 2.0).

[(3*S*)-3-{[2-({5-Bromo-2-[({(1*S*)-1-methyl-3-[tris(1-methylethyl)silyl]prop-2-yn-1-yl}oxy)methyl]phenyl}ethynyl)benzyl]oxy}but-1-yn-1-yl][tris(1-methylethyl)] silane (*S,S*)-**121**



A flame-dried 500 ml three-neck flask with thermometer was filled with tetrakis(triphenylphosphine)palladium(0) (303 mg, 0.262 mmol, 2.7 mol%) and copper iodide (100 mg, 0.525 mmol, 5.5 mol%), flushed with argon and a degassed solution of aryl iodide (*S*)-**120** (4.94 g, 9.47 mmol) in diisopropylamine (60 ml) was added. The solution was cooled to -2 ºC and a degassed solution of alkyne (*S*)-**115** (3.23 g, 9.47 mmol, 1.0 equiv.) in diisopropylamine (20 ml) was added dropwise over a period of 2 h using a syringe pump. Then the reaction mixture was allowed to warm up to room temperature, filtered through a sintered glass (hexane) and the volatiles were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane) to provide the product (*S,S*)-**121** (6.41 g, 94%) as an oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.52 (6H, d, *J* = 6.6), 0.98-1.06 (42H, m), 4.34 (2H, q, *J* = 6.6), 4.74 (1H, bd, *J* = 13.0), 4.79 (1H, bd, *J* = 12.8), 4.96 (1H, dd, *J* = 13.0, 0.8), 5.02 (1H, bd, *J* = 12.8), 7.26 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.36 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.40

(1H, dt, *J* = 8.3, 0.9, 0.9), 7.46 (1H, dd, *J* = 8.3, 2.0), 7.50 (1H, ddd, *J* = 7.6, 1.4, 0.4), 7.53 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7), 7.63 (1H, d, *J* = 2.0).

^{13}C NMR (151 MHz, $CDCl_3$): 11.07 (d), 11.09 (d), 18.51 (q), 18.54 (q), 22.41 (q), 22.42 (q), 65.65 (d), 65.86 (d), 68.16 (t), 68.59 (t), 86.01 (s), 86.15 (s), 89.84 (s), 92.71 (s), 107.31 (s), 107.45 (s), 120.54 (s), 121.08 (s), 123.45 (s), 127.13 (d), 127.48 (d), 128.83 (d), 128.90 (d), 131.45 (d), 132.15 (d), 134.26 (d), 139.19 (s), 140.18 (s).

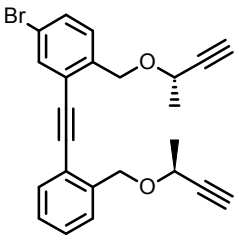
IR ($CHCl_3$): 2945 vs, 2866 vs, 2216 w, 2165 m, 1602 w, 1589 s, 1556 m, 1490 s, 1463 vs, 1450 s, 1384 s, 1371 s, 1325 s, 1310 m, 1244 m, 1154 m, 1118 vs, 1096 vs, 1071 vs, 1019 s, 997 s, 949 m, 884 vs, 830 m, 679 vs, 664 vs, 575 m, 454 m cm^{-1}.

ESI MS: 796 ($[M+H_2O+CH_3OH]^+$, with ^{81}Br), 794 ($[M+H_2O+CH_3OH]^+$, with ^{79}Br), 752 ($[M+H_2O]^+$, with ^{81}Br), 750 ($[M+H_2O]^+$, with ^{79}Br), 735 ($[M]^+$, with ^{81}Br), 733 ($[M]^+$, with ^{79}Br).

HR ESI MS: calculated for $C_{42}H_{62}O_2{}^{79}BrSi_2$ 733.3472, found 733.3462.

Optical rotation: $[\alpha]^{22}_D$ -120° (c 0.067, CH_2Cl_2).

4-Bromo-1-({[(1*S*)-1-methylprop-2-yn-1-yl]oxy}methyl)-2-{[2-({[(1*S*)-1-methylprop-2-yn-1-yl]oxy}methyl)phenyl]ethynyl}benzene (*S,S*)-**122**



In a 250 ml round-bottom flask flushed with argon silane (*S*,*S*)-**121** (6.31 g, 8.59 mmol) was dissolved in THF (80 ml) and a solution of tetrabutylammonium fluoride trihydrate (0.964 M in THF, 8.0 ml, 7.71 mmol, 0.9 equiv.) was added at room temperature and stirred for 1 h. The volatiles were evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 85:15) to provide product (*S,S*)-**122** (3.20 g, 88%) as an oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.52 (6H, d, *J* = 6.6), 2.46 (1H, d, *J* = 2.0), 2.48 (1H, d, *J* = 2.0), 4.32 (1H, dq, *J* = 6.6, 6.6, 6.6, 2.0), 4.33 (1H, q, *J* = 6.6), 4.74 (1H, d, *J* = 12.8), 4.78 (1H, bd, *J* = 12.8), 4.96 (1H, dd, *J* = 0.8, 12.8), 5.02 (1H, bd, *J* = 12.8), 7.29 (1H, dt, *J* = 7.7, 7.7, 1.3), 7.38 (1H, dt, *J* = 7.7, 7.7, 1.4), 7.40 (1H, dddt, *J* = 7.6,

1.4, 0.8, 0.8, 0.4), 7.47 (1H, dd, *J* = 8.3, 2.0), 7.53 (1H, ddq, *J* = 7.6, 1.3, 0.7, 0.7, 0.7), 7.53 (1H, d, *J* = 8.3), 7.69 (1H, d, *J* = 2.0).

^{13}C NMR (151 MHz, $CDCl_3$): 22.06 (q), 22.11 (q), 64.97 (d), 65.11 (d), 68.24 (t), 68.77 (t), 73.38 (d), 73.48 (d), 83.54 (s), 83.75 (s), 89.90 (s), 92.75 (s), 120.75 (s), 121.32 (s), 123.61 (s), 127.43 (d), 127.85 (d), 128.95 (d), 129.11 (d), 131.55 (d), 132.18 (d), 134.48 (d), 138.68 (s), 139.76 (s).

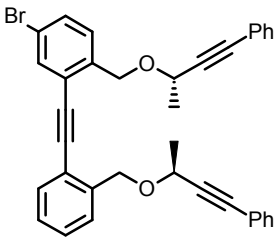
IR ($CHCl_3$): 3306 s, 3072 w, 2215 w, 2112 w, 1600 w, 1589 m, 1556 w, 1491 m, 1477 m, 1469 m, 1453 m, 1392 m, 1374 m, 1327 s, 1314 m, 1247 w, 1153 w, 1135 s, 1118 s, 1098 vs, 1080 s, 1066 s, 1020 m, 951 w, 702 w, 639 s, 574 w, 454 w cm^{-1}.

ESI MS: 445 ($[M+Na]^+$, with ^{81}Br), 443 ($[M+Na]^+$, with ^{79}Br).

HR ESI MS: calculated for $C_{24}H_{21}O_2Na^{79}Br$ 443.0623, found 443.0620.

Optical rotation: $[\alpha]^{22}_D$ -79° (c 0.832, CH_2Cl_2).

4-Bromo-1-({[(1*S*)-1-methyl-3-phenylprop-2-yn-1-yl]oxy}methyl)-2-{[2-({[(1*S*)-1-methyl-3-phenylprop-2-yn-1-yl]oxy}methyl)phenyl]ethynyl}benzene (*S,S*)-**123**



A flame-dried Schlenk flask was filled with tetrakis(triphenylphosphine)palladium(0) (290 mg, 0.25 mmol, 5 mol%), copper iodide (96 mg, 0.50 mmol, 10 mol%) and flushed with argon. Then toluene (35 ml), diisopropylamine (5.7 ml, 4.08 g, 0.04 mol, 8.0 equiv.) and iodobenzene (1.68 ml, 0.015 mol, 3.0 equiv.) were added. The reaction mixture was cooled to 0 ºC and a degassed solution of alkyne (*S*,*S*)-**122** (2.12 g, 5.04 mmol) in toluene (20 ml) was added dropwise over a period of 1.5 h. The reaction mixture was stirred at 0 ºC for 2 h and then at room temperature overnight. The reaction mixture was filtered through a sintered glass (hexane) and the volatiles were evaporated under reduced pressure. The residue was purified by flash chromatography (hexane-diethyl ether 100:0 to 85:15) to provide product (*S,S*)-**123** (2.58 g, 89%) as an oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.56 (6H, d, *J* = 6.6), 4.50 (1H, q, *J* = 6.6), 4.51 (1H, q, *J* = 7.1), 4.80 (1H, d, *J* = 12.8), 4.85 (1H, d, *J* = 12.5), 4.99 (1H, d, *J* = 12.8), 5.04 (1H, d, *J* = 12.5), 7.19 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.23-7.29 (6H, m), 7.35 (1H, dt, *J* = 7.6,

7.6, 1.4), 7.37 (4H, m), 7.40 (1H, d, *J* = 8.3), 7.45 (1H, dd, *J* = 8.3, 2.0), 7.49 (1H, dd, *J* = 7.7, 1.4), 7.54 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7), 7.65 (1H, d, *J* = 2.0).

^{13}C NMR (151 MHz, $CDCl_3$): 22.22 (q), 22.24 (q), 65.56 (d), 65.75 (d), 68.29 (t), 68.77 (t), 85.40 (s), 85.47 (s), 88.84 (s), 88.96 (s), 89.95 (s), 92.81 (s), 120.75 (s), 121.37 (s), 122.55 (s), 122.58 (s), 123.71 (s), 127.37 (d), 127.92 (d), 128.21 (d), 128.25 (d), 128.29 (d), 128.89 (d), 129.26 (d), 131.54 (d), 131.66 (s), 131.70 (d), 132.24 (d), 134.33 (d), 138.98 (s), 139.97 (s).

IR ($CHCl_3$): 2868 m, 2226 w, 1599 w, 1589 m, 1574 w, 1556 w, 1490 s, 1477 w, 1452 m, 1444 m, 1392 w, 1373 m, 1330 s, 1313 m, 1277 w, 1255 w, 1177 w, 1154 w, 1129 m, 1094 vs, 1064 vs, 1029 m, 1020 w, 999 w, 951 w, 833 w, 819 m, 691 s, 576 w, 446 w cm^{-1}.

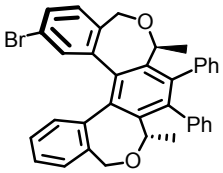
ESI MS: 597 ($[M+Na]^+$, with ^{81}Br), 595 ($[M+Na]^+$, with ^{79}Br).

HR ESI MS: calculated for $C_{36}H_{29}O_2{}^{79}BrNa$ 595.1249, found 595.1241.

Optical rotation: $[\alpha]^{22}_D$ -122° (c 0.263, CH_2Cl_2).

(*P*,3*S*,6*S*)-11-Bromo-3,6-dimethyl-4,5-diphenyl-1,3,6,8-tetrahydrodibenzo[*e*,*e'*] benzo[1,2-*c*:4,3-*c'*]bisoxepine (*P*,*S*,*S*)-**124**

Preparation using halogen lamp irradiation and $CoCp(CO)_2$ complex:



A flame-dried Schlenk flask was filled with triyne (*S*,*S*)-**123** (36.3 mg, 0.0633 mmol), triphenylphosphine (33.2 mg, 0.127 mmol, 2.0 equiv.) and flushed with argon. Then dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (8.5 µl, 0.063 mmol, 1.0 equiv.) and decane (4 ml) were added and the reaction mixture was heated under halogen lamp irradiation at 140 ºC for 2 h. The reaction mixture was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 85:15) and then it was further purified by washing (hexane) to provide the product (*P*,*S*,*S*)-**124** (28.8 mg, 80%) as a white solid.

Microwave-assisted preparation with $CoCp(CO)_2$ complex:

In a 20 ml Biotage microwave vial triyne (*S*,*S*)-**123** (1.12 g, 1.95 mmol), $CoCp(CO)_2$ (0.26 ml, 1.95 mmol, 1.0 equiv.), triphenylphosphine (1.03 g, 3.91 mmol, 2.0 equiv.), silicon carbide (200 mg) and THF (40 ml) were heated at 180 ºC in a microwave reactor for 1h. The reaction mixture was filtered through a sintered glass (THF) and the volatiles were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) to provide the product (*P*,*S*,*S*)-**124** (860 mg, 77%) as a yellowish solid.

Preparation using halogen lamp irradiation and $RhCp(C_2H_2)_2$ complex:

In a Schlenk flask triyne (*S*,*S*)-**123** (16.8 mg, 0.029 mmol), (η^5-cyclopentadienyl)(di-η^2-ethene)rhodium(I) (6.6 mg, 0.029 mmol, 1.0 equiv.) and decane (5 ml) were heated under halogen lamp irradiation at 140 ºC for 1 h. Then the reaction mixture was allowed to cool down to room temperature and subjected to column chromatography on silica gel (hexane-diethyl ether 100:0 to 80:20) to provide product (*P*,*S*,*S*)-**124** (7.6 mg, 46%) as a yellowish solid.

M.p.: 137-140°C (hexane).

^{1}H NMR (600 MHz, $CDCl_3$): 0.64 (3H, d, *J* = 7.1), 0.68 (3H, d, *J* = 7.1), 4.56 (1H, d, *J* = 11.5), 4.62 (1H, d, *J* = 11.5), 4.81 (1H, d, *J* = 11.5), 4.87 (1H, d, *J* = 11.5), 4.94 (2H, q, *J* = 7.1), 6.56 (1H, dd, *J* = 7.7, 1.1), 6.70 (1H, d, *J* = 2.0), 6.84 (2H, m), 7.16 (2H, m), 7.04 (1H, dt, *J* = 7.6, 7.6, 1.2), 7.04-7.10 (4H, m), 7.21 (2H, m), 7.27 (1H, dt, *J* = 7.6, 7.6, 1.1), 7.28 (1H, d, *J* = 8.0), 7.34 (1H, dd, *J* = 8.0, 2.0), 7.44 (1H, dd, *J* = 7.5, 1.2).

^{13}C NMR (151 MHz, $CDCl_3$): 22.22 (q), 22.55 (q), 66.83 (t), 67.57 (t), 72.78 (d), 72.82 (d), 121.36 (s), 126.51 (d), 126.83 (d), 127.47 (d), 127.51 (d), 127.56 (d), 127.80 (d), 127.82 (d), 128.15 (d), 128.44 (d), 129.71 (d), 129.72 (d), 130.02 (d), 130.09 (d), 130.13 (d), 130.65 (d), 131.90 (d), 134.90 (d), 135.71 (s), 136.80 (s), 137.42 (s), 137.46 (s), 137.64 (s), 137.82 (s), 139.39 (s), 139.80 (s), 139.83 (s), 142.21 (s), 142.26 (s), 142.64 (s).

IR ($CHCl_3$): 2928 s, 1600 w, 1593 w, 1570 w, 1555 w, 1496 w, 1485 w, 1443 m, 1393 w, 1371 m, 1177 w, 1128 w, 1113 m, 1080 vs, 1070 s, 1028 w, 1001 w, 949 w, 914 w, 819 w, 705 vs cm^{-1}.

EI MS: 574 ($M^{+\bullet}$, with ^{81}Br, 31), 572 ($M^{+\bullet}$, with ^{79}Br, 30), 559 (55), 557 (53), 541 (9), 539 (9), 529 (16), 527 (18), 511 (20), 509 (17), 448 (30), 432 (20), 417 (16), 405 (18), 403 (7), 387 (5), 341 (20), 327 (27), 326 (28), 313 (17), 289 (8), 252 (10), 215 (7), 178 (5), 149 (87), 105 (13), 91 (14), 77 (40), 57 (42), 43 (100).

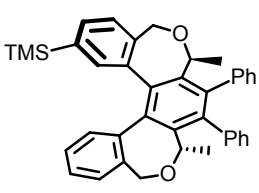
HR EI MS: calculated for $C_{36}H_{29}O_2{}^{79}Br$ 572.1351, found 572.1359.

Optical rotation: $[\alpha]^{22}_D$ -97° (c 0.144, CH_2Cl_2).

General procedure for iodination of (*P*,*S*,*S*)-124:

In a flame-dried Schlenk flask helicene (*P*,*S*,*S*)-**124** (1.0 equiv.) was dissolved in THF or diethyl ether (0.1 mmol/ml) and cooled down to -78 ºC. A solution of BuLi (1.0 equiv.) was added at -78 ºC and the reaction mixture was stirred at -78 ºC for 1 min. Then a solution of iodine (1.2 equiv.) in THF or diethyl ether (0.05 mmol/ml) was added. After stirring at -78 ºC for 15 min and at room temperature for 15 min, the volatiles were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 75:25) to provide a mixture of (*P*,*S*,*S*)-**124**, (*P*,*S*,*S*)-**125** and (*P*,*S*,*S*)-**126** as an amorphous solid.

[(*P*,3*S*,6*S*)-3,6-Dimethyl-4,5-diphenyl-1,3,6,8-tetrahydrodibenzo[*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepin-11-yl](trimethyl)silane (*P*,*S*,*S*)-**125b**



In a flame-dried Schlenk flask starting bromide (*P*,*S*,*S*)-**124** (43.2 mg, 0.0753 mmol) was flushed with argon and dissolved in diethyl ether (7 ml). Then the solution was cooled to -95 ºC and a solution of *t*-BuLi (1.7 M in pentane, 90 µl, 0.153 mmol, 2.0 equiv.) was added so that its drops run down the cooled walls of the Schlenk flask. After 1 min chlorotrimethylsilane (15 µl, 0.12 mmol, 1.6 equiv.) was added and after stirring at -95 ºC for 30 min the reaction mixture was allowed to warm up to room temperature. The volatiles were removed *in vacuo* and the residue was purified by

flash chromatography (hexane-acetone 100:0 to 80:20) to provide product (*P*,*S*,*S*)-**125b** (27.4 mg, 65%) as an oil together with the reduced product (*P*,*S*,*S*)-**126** (1.7 mg, 5%) as an amorphous solid.

^{1}H NMR (600 MHz, $CDCl_3$): -0.06 (9H, s), 0.64 (3H, d, *J* = 7.1), 0.66 (3H, d, *J* = 7.1), 4.58 (1H, d, *J* = 11.4), 4.63 (1H, d, *J* = 11.4), 4.88 (1H, d, *J* = 11.4), 4.91 (1H, d, *J* = 11.4), 4.95 (2H, q, *J* = 7.1), 6.53 (1H, dd, *J* = 7.8, 1.3), 6.73 (1H, d, *J* = 1.2), 6.85 (2H, m), 6.94 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.05 (2H, m), 7.05 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.08 (2H, m), 7.18 (2H, m), 7.21 (2H, m), 7.33 (1H, dd, *J* = 7.3, 1.2), 7.37 (1H, d, *J* = 7.3), 7.41 (1H, dd, *J* = 7.5, 1.3).

^{13}C NMR (151 MHz, $CDCl_3$): -1.47 (q), 22.17 (q), 22.30 (q), 67.37 (t), 67.43 (t), 72.71 (d), 72.80 (d), 126.27 (d, 2C), 127.32 (d, 2C), 127.58 (d), 127.64 (d, 2C), 128.36 (d), 130.01 (d), 130.04 (d), 132.06 (d), 132.15 (d), 137.25 (s), 137.33 (s), 137.35 (s), 137.42 (s), 137.52 (d), 137.76 (s), 138.09 (s), 138.87 (s), 139.36 (s), 140.00 (s), 140.02 (s), 140.21 (s), 141.79 (s), 141.90 (s).

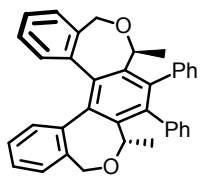
IR ($CHCl_3$): 2928 s, 2858 s, 1601 w, 1577 w, 1554 vw, 1496 w, 1443 m, 1394 w, 1249 w, 1186 w, 1080 vs, 1072 s, 1028 w, 948 w, 835 m, 704 vs, 693 w cm^{-1}.

ESI MS: 589 ($[M+Na]^+$), 567 ($[M+H]^+$).

HR ES MS: calculated for $C_{39}H_{39}O_2Si$ 567.2719, found 567.2735.

Optical rotation: $[\alpha]^{22}_D$ -102° (c 0.352, CH_2Cl_2).

(*P*,3*S*,6*S*)-3,6-Dimethyl-4,5-diphenyl-1,3,6,8-tetrahydrodibenzo[*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepine (*P*,*S*,*S*)-**126**



In a flame-dried Schlenk flask helicene (*P*,*S*,*S*)-**124** (81 mg, 0.14 mmol) was dissolved in THF (5 ml) and cooled down to -78 ºC. A solution of *n*-BuLi (1.6 M in hexanes, 0.10 ml, 0.16 mmol, 1.1 equiv.) in THF (2 ml) was cooled down to -78 ºC and added to the solution of bromide via cannula (over a period of 1 min). The reaction mixture was stirred at -78 ºC for 1.5 h and then chlorodiphenylphosphine (30 µl, 0.16 mmol, 1.1 equiv.) was added. After stirring at -78 ºC for 15 min and at room temperature for 15 min, the volatiles were removed *in vacuo* and the residue purified by flash chromatography on

silica gel (hexane-diethyl ether 100:0 to 85:15) to provide product (*P*,*S*,*S*)-**106** (58.6 mg, 84%) as a white solid.

M.p.: >340 °C (chloroform)

^{1}H NMR (600 MHz, $CDCl_3$): 0.62 (6H, d, *J* = 7.1), 4.60 (2H, d, *J* = 11.4), 4.89 (2H, d, *J* = 11.4), 4.94 (2H, q, *J* = 7.1), 6.60 (2H, dd, *J* = 7.8, 1.3), 6.85 (2H, m), 6.98 (2H, dt, *J* = 7.6, 7.6, 1.3), 7.04-7.09 (4H, m), 7.18 (2H, m), 7.20 (2H, dt, *J* = 7.6, 7.6, 1.3), 7.21 (2H, m), 7.40 (2H, dd, *J* = 7.5, 1.3).

^{13}C NMR (151 MHz, $CDCl_3$): 22.14 (q), 67.45 (d), 72.71 (t), 126.30 (d), 127.33 (d), 127.55 (d), 127.57 (d), 127.66 (d), 128.51 (d), 129.68 (d), 130.02 (d), 132.04 (d), 137.12 (s), 137.32 (s), 137.72 (s), 139.97 (s), 140.07 (s), 141.92 (s).

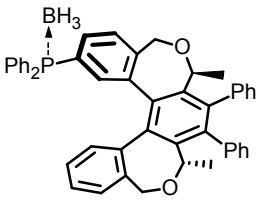
IR ($CHCl_3$): 2964 vs, 2863 s, 1729 m, 1624 w, 1602 w, 1578 w, 1496 w, 1443 m, 1306 w, 1109 s, 1080 vs, 1070 vs, 1027 s, 1017 s, 704 vs cm^{-1}.

ESI MS: 495 ($[M+H]^+$).

HR ES MS: calculated for $C_{36}H_{31}O_2$ 495.2324, found 495.2341.

Optical rotation: $[\alpha]^{22}_D$ -105° (c 0.060, CH_2Cl_2).

[(*P*,3*S*,6*S*)-3,6-Dimethyl-4,5-diphenyl-1,3,6,8-tetrahydrodibenzo[*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepin-11-yl](diphenyl)phosphane-borane complex (*P*,*S*,*S*)-**127**



In a flame-dried Schlenk flask starting bromide (*P*,*S*,*S*)-**124** (30.3 mg, 0.0528 mmol) was flushed with argon and dissolved in diethyl ether (5 ml). Then the solution was cooled to -110 ºC and solution of *t*-BuLi (1.7 M in pentane, 62 µl, 0.105 mmol, 2.0 equiv.) was added so that drops run down the cooled walls of the Schlenk flask. After 1 min chlorodiphenylphosphine (15 µl, 0.08 mmol, 1.5 equiv.) was added and after stirring at -110 ºC for 30 min the reaction mixture was allowed to warm up to 0 ºC. Then a solution of borane-dimethylsulfide complex (2.0 M in THF, 130 µl, 0.26 mmol, 5.0 equiv.) was added and the reaction mixture was stirred at 0 ºC for 1 h. The volatiles were removed *in vacuo* and the residue was purified by flash

chromatography (hexane-acetone 100:0 to 80:20) to provide product (*P*,*S*,*S*)-**127** (31.8 mg, 87%) as a white solid.

M.p.: 130-133°C (hexane).

^{1}H NMR (500 MHz, $CDCl_3$): 0.55 (3H, d, *J* = 7.1), 0.63 (3H, d, *J* = 7.1), 4.40 (1H, d, *J* = 11.5), 4.50 (1H, d, *J* = 11.5), 4.64 (1H, d, *J* = 11.4), 4.87 (1H, q, *J* = 7.1), 4.92 (1H, d, *J* = 11.4), 4.94 (1H, q, *J* = 7.1), 6.58 (1H, dd, *J* = 7.7, 1.3), 6.68 (1H, m), 6.80-6.84 (2H, m), 7.02-7.14 (6H, m), 7.07 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.14 (1H, dt, *J* = 7.5, 7.5, 1.3), 7.17-7.26 (2H, m), 7.18-7.26 (6H, m), 7.31 (1H, dd, *J* = 7.5, 1.3), 7.37 (4H, dt, *J* = 7.7, 7.7, 2.3), 7.52-7.54 (2H, m). The BH_3 signal was not determined because it was broad.

^{13}C NMR (126 MHz, $CDCl_3$): 21.99 (q), 22.42 (q), 67.22 (t), 66.90 (t), 72.56 (d), 72.83 (d), 126.41 (d), 126.44 (d), 127.36 (d), 127.51 (d), 127.51 (d), 127.66 (s, J_{PC} = 47.8), 127.70 (d, 2C), 127.74 (d), 128.61 (d, J_{PC} = 10.0), 128.74 (s, J_{PC} = 82.9), 129.08 (d), 129.28 (d, J_{PC} = 11.2), 129.50 (d), 129.52 (d), 129.84 (d), 129.93 (d), 131.04 (d, J_{PC} = 2.0), 131.12 (d, J_{PC} = 2.3), 131.95 (d), 132.10 (d, J_{PC} = 12.0), 133.19 (d, J_{PC} = 17.5), 133.30 (d, J_{PC} = 17.5), 135.89 (s), 136.46 (d, J_{PC} = 7.8), 137.12 (s), 137.32 (s), 137.49 (s), 137.67 (s), 139.55 (s), 139.61 (s), 139.65 (s), 140.59 (s, J_{PC} = 2.2), 140.69 (s, J_{PC} = 11.0), 142.03 (s), 142.39 (s).

^{31}P NMR (202 MHz, $CDCl_3$): 20.85 (s).

^{11}B NMR (160 MHz, $CDCl_3$): -2.16 (bs).

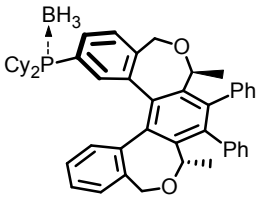
IR ($CHCl_3$): 2965 vs, 2929 vs, 2866 s, 2388 s, 2348 m, 1601 m, 1589 w, 1577 w, 1557 w, 1495 m, 1488 m, 1438 s, 1179 m, 1079 vs, 1072 vs, 1060 s, 1029 s, 1000 m, 827 m, 704 vs, 694 s, 496 m cm^{-1}.

ESI MS: 715 ($[M+Na]^+$), 693 ($[M+H]^+$).

HR ESI MS: calculated for $C_{48}H_{42}O_2BNaP$ 715.2913, found 715.2936.

Optical rotation: $[\alpha]^{22}_D$ -136° (c 0.350, CH_2Cl_2).

[(*P*,3*S*,6*S*)-3,6-Dimethyl-4,5-diphenyl-1,3,6,8-tetrahydrodibenzo[*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepin-11-yl](dicyclohexyl)phosphane-borane complex (*P*,*S*,*S*)-**128**



In a flame-dried Schlenk flask bromide (*P*,*S*,*S*)-**124** (39.8 mg, 0.0694 mmol) was flushed with argon and dissolved in diethyl ether (7 ml). Then the solution was cooled to -110 ºC and a solution of *t*-BuLi (1.7 M in pentane, 82 µl, 0.139 mmol, 2.0 equiv.) was added so that drops run down the cooled walls of the Schlenk flask. After 2 min chlorodicyclohexylphosphine (30 µl, 0.136 mmol, 1.9 equiv.) was added. After stirring at -110 ºC for 30 min the reaction mixture was allowed to warm up to 0 ºC. Then a solution of borane dimethylsulfide complex (2.0 M in THF, 173 µl, 0.347 mmol, 5.0 equiv.) was added and the reaction mixture was stirred at 0 ºC for 1 h. The volatiles were removed *in vacuo* and the residue was purified by flash chromatography (hexane-diethyl ether 100:0 to 85:15) to provide product (*P*,*S*,*S*)-**128** (31.2 mg, 64%) as a white amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): 0.57 (6H, d, *J* = 7.1), 0.80-1.79 (20H, m), 4.64 (1H, d, *J* = 11.4), 4.66 (1H, d, *J* = 11.4), 4.94 (1H, d, *J* = 11.4), 4.94 (1H, q, *J* = 7.1), 4.95 (1H, d, *J* = 11.4), 4.97 (1H, q, *J* = 7.1), 6.58 (1H, dd, *J* = 7.8, 1.3), 6.83 (1H, m), 6.86 (1H, m), 6.97 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.03-7.10 (6H, m), 7.11 (1H, dd, *J* = 10.3, 1.5), 7.14-7.23 (2H, m), 7.18 (1H, dt, *J* = 7.5, 7.5, 1.3), 7.45 (1H, dd, *J* = 7.5, 1.3), 7.48 (1H, dt, *J* = 7.8, 7.8, 1.5), 7.51 (1H, dd, *J* = 7.6, 2.2). The BH_3 signal was not determined because it was broad and/or obscured by the aliphatic signals.

^{13}C NMR (126 MHz, $CDCl_3$): 22.05 (q), 22.08 (q), 25.74 (t, J_{PC} = 6.1), 25.79 (t, J_{PC} = 11.7, 2C), 26.13 (t, J_{PC} = 3.5), 26.32 (t, 2C), 26.56 (t, J_{PC} = 14.3), 26.63 (t, J_{PC} = 5.3), 26.70 (t, J_{PC} = 7.2), 26.93 (t, J_{PC} = 10.7), 30.24 (d, J_{PC} = 34.0), 31.60 (d, J_{PC} = 33.4), 66.98 (t), 67.34 (t), 72.62 (s), 72.82 (d), 125.05 (d, J_{PC} = 47.3), 126.39 (d), 126.41 (d), 127.33 (d), 127.34 (d), 127.44 (d), 127.66 (d), 127.72 (d), 127.76 (d), 128.49 (d, J_{PC} = 8.5), 129.15 (d), 129.57 (d), 129.65 (d), 129.91 (d), 130.05 (d), 131.68 (d, J_{PC} = 4.8), 131.89 (d), 136.13 (s), 137.22 (s), 137.26 (s), 137.71 (s), 137.94 (d, J_{PC} = 9.9), 138.23 (s), 139.70 (s), 139.74 (s), 139.77 (s), 140.40 (s, J_{PC} = 2.4), 140.87 (s, J_{PC} = 10.4), 141.92 (s), 142.39 (s).

^{31}P NMR (202 MHz, $CDCl_3$): 27.00 (s).

^{11}B NMR (160 MHz, $CDCl_3$): -2.40 (bs).

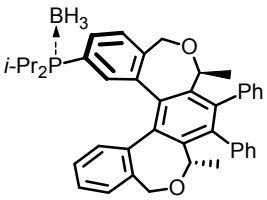
IR ($CHCl_3$): 2934 vs, 2856 vs, 2380 m, 2347 m, 1601 w, 1577 w, 1557 w, 1497 w, 1491 w, 1450 s, 1443 m, 1395 w, 1181 w, 1079 s, 1072 s, 1029 m, 1004 w, 948 w, 824 m, 705 s cm^{-1}.

ESI MS: 743 ($[M+K]^+$), 727 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{48}H_{54}O_2BNaP$ 727.3852, found 727.3859.

Optical rotation: $[\alpha]^{22}_D$ -103° (c 0.43, CH_2Cl_2).

[(*P*,3*S*,6*S*)-3,6-Dimethyl-4,5-diphenyl-1,3,6,8-tetrahydrodibenzo[*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepin-11-yl][bis(1-methylethyl)]phosphane-borane complex (*P*,*S*,*S*)-**129**



In a flame-dried Schlenk flask starting bromide (*P*,*S*,*S*)-**124** (28.2 mg, 0.0492 mmol) was flushed with argon and dissolved in diethyl ether (6 ml). Then the solution was cooled to -110 ºC and solution of *t*-BuLi (1.7 M in pentane, 60 µl, 0.102 mmol, 2.1 equiv.) was added so that drops run down the cooled walls of the Schlenk flask. After 1 min chlorodiisopropylphosphine (15 µl, 0.094 mmol, 1.9 equiv.) was added and after stirring at -110 ºC for 30 min the reaction mixture was allowed to warm up to 0 ºC. Then a solution of borane dimethylsulfide complex (2.0 M in THF, 125 µl, 0.25 mmol, 5.0 equiv.) was added and the reaction mixture was stirred at 0 ºC for 1 h. The volatiles were removed *in vacuo* and the residue was purified by flash chromatography (hexane-acetone 100:0 to 85:15) to provide product (*P*,*S*,*S*)-**129** (15.2 mg, 50%) as a white amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): 0.57 (3H, d, *J* = 7.1), 0.58 (3H, d, *J* = 7.1), 0.67 (3H, dd, J_{HH} = 7.0, J_{PH} = 14.3), 0.87 (3H, dd, J_{HH} = 7.0, J_{PH} = 13.8), 0.89 (3H, dd, J_{HH} = 7.0, J_{PH} = 15.5), 1.00 (3H, dd, J_{HH} = 7.0, J_{PH} = 15.5), 1.95-2.03 (1H, m), 2.04-2.10 (1H, m), 4.64 (1H, d, *J* = 11.4), 4.66 (1H, d, *J* = 11.4), 4.93 (1H, d, *J* = 11.4), 4.94 (1H, q, *J* = 7.1), 4.95 (1H, d, *J* = 11.4), 4.95 (1H, q, *J* = 7.1), 6.58 (1H, dd, *J* = 7.7, 1.2), 6.83-6.87 (2H, m), 6.98 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.04-7.10 (6H, m), 7.07-7.09 (1H, m), 7.15-7.23 (2H, m), 7.18 (1H, dt, *J* = 7.6, 7.6, 1.2), 7.44 (1H, dd, *J* = 7.5, 1.3), 7.52

(1H, dd, J = 7.7, 2.1), 7.58 (1H, ddd, J = 9.0, 7.7, 1.5). The BH_3 signal was not determined because it was broad and/or obscured by the aliphatic signals.

^{13}C NMR (126 MHz, $CDCl_3$): 16.64 (dq, J_{PC} = 1.5), 16.70 (dq, J_{PC} = 1.2), 16.80 (dq, J_{PC} = 1.4), 16.83 (dq, J_{PC} = 1.5), 21.31 (d, J_{PC} = 34.2), 21.65 (d, J_{PC} = 34.4), 22.03 (q), 22.05 (q), 66.96 (t), 67.30 (t), 72.63 (d), 72.78 (d), 125.36 (s, J_{PC} = 47.4), 126.40 (d), 126.42 (d), 127.35 (d), 127.43 (d), 127.61 (d), 127.68 (d), 128.73 (d), 128.00 (d), 128.70 (d, J_{PC} = 9.4), 129.14 (d), 129.58 (d), 129.60 (d), 129.91 (d), 129.98 (d), 131.90 (d), 132.51 (d, J_{PC} = 7.4), 136.05 (s), 137.13 (d, J_{PC} = 8.0), 137.19 (s), 137.27 (s), 137.70 (s), 138.15 (s), 139.65 (s), 139.73 (s), 139.74 (s), 140.68 (s, J_{PC} = 2.3), 140.73 (s, J_{PC} = 9.6), 142.02 (s), 142.45 (s).

^{31}P NMR (202 MHz, $CDCl_3$): 34.76 (s).

^{11}B NMR (160 MHz, $CDCl_3$): -3.03 (bs).

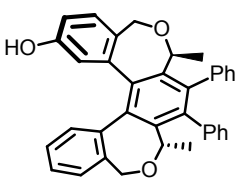
IR ($CHCl_3$): 2967 vs, 2874 s, 2381 s, 2349 m, 1601 m, 1577 w, 1556 w, 1496 m, 1443 m, 1387 m, 1371 s, 1179 w, 1080 vs, 1072 vs, 1029 m, 999 w, 947 w, 827 m, 705 vs, 690 m cm^{-1}.

ESI MS: 647 ($[M+Na]^+$), 625 ($[M+H]^+$).

HR ESI MS: calculated for $C_{42}H_{47}O_2BP$ 625.3407, found 625.3395.

Optical rotation: $[\alpha]^{22}_D$ -94° (c 0.046, CH_2Cl_2).

(*P*,3*S*,6*S*)-3,6-Dimethyl-4,5-diphenyl-1,3,6,8-tetrahydrodibenzo[*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepin-11-ol (*P*,*S*,*S*)-**132**



Palladium-catalysed hydroxylation:

In a Carius flask bromide (*P*,*S*,*S*)-**124** (30.1 mg, 0.052 mmol), bis(dibenzylideneacetone)palladium(0) (2.0 mg, 3.5 µmol, 7 mol%), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (3.9 mg, 8.2 µmol, 16 mol%), potassium hydroxide (15.0 mg, 0.27 mmol, 5.1 equiv.) were suspended in mixture of water-1,4-dioxane (1:1, 1 ml) and stirred at 100 °C for 16 h. Then an aqueous solution of HCl was added (1M, 5 ml) and the reaction was washed with ethyl acetate (3 x 10 ml). The combined organic phases were dried over

anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 100:0 to 50:50) to provide product (*P*,*S*,*S*)-**132** (2.4 mg, 9%) as a white solid.

Halogen-magnesium exchange using organomagnesium ate complex:

In a flame-dried Schlenk flask dibutylisopropylmagnesium ate complex was prepared by mixing an isopropylmagnesium chloride lithium chloride complex (1.3 M in THF, 50 µl, 0.065 mmol, 1.25 equiv.), a solution of *n*-BuLi (1.6 M in hexanes, 81 µl, 0.130 mmol, 2.5 equiv.) in THF (1 ml) at 0 °C and stirring the solution for 15 min. To this solution a solution of bromide (*P*,*S*,*S*)-**124** (30.0 mg, 0.052 mmol) in THF (1 ml) was added and the solution was stirred at 0 °C for 15 min. Then the reaction mixture was cooled to -78 °C and oxygen gas (99.9991%) was bubbled through the solution for 30 min. After that the reaction mixture was allowed to warm up to room temperature and an aqueous solution of HCl (1M, 5 ml) was added. Then THF was removed *in vacuo*, the aqueous phase was washed with ethyl acetate (3 x 5 ml). The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 100:0 to 50:50) to provide product (*P*,*S*,*S*)-**132** (9.7 mg, 37%) as a white solid and (*P*,*S*,*S*)-**126** (10.7 mg, 42%) as a white solid.

Bromine-lithium exchange using *t*-butyllithium:

In a flame-dried Schlenk flask starting bromide (*P*,*S*,*S*)-**124** (23.5 mg, 0.041 mmol) was flushed with argon and dissolved in diethyl ether (1 ml). Then the solution was cooled to -105 ºC and solution of *t*-BuLi (1.7 M in pentane, 50 µl, 0.085 mmol, 2.1 equiv.) was added so that drops run down the cooled walls of the Schlenk flask. After 1 min, gaseous oxygen (99.9991%) was bubbled through the reaction mixture at -105 °C for 1.5 h. Then the cooling bath was removed and the solution was allowed to warm up to room temperature. An aqueous solution of HCl (1M, 1 ml) was added and then extracted with ethyl acetate (3 x 3 ml). The combined organic phases were concentrated *in vacuo* and the residue purified by flash chromatography on silica gel (hexane-ethyl acetate 100:0 to 50:50) to provide product (*P*,*S*,*S*)-**132** (6.7 mg, 32%) as a white solid and (*P*,*S*,*S*)-**126** (8.6 mg, 43%) as a white solid.

M.p.: 273-276 °C (hexane)

^{1}H NMR (500 MHz, d_6-acetone, ref=2.09): 0.59 (3H, d, *J* = 7.1), 0.67 (3H, d, *J* = 7.1), 4.52 (1H, d, *J* = 11.5), 4.59 (1H, d, *J* = 11.3), 4.75 (1H, d, *J* = 11.5), 4.80 (1H, d, *J* = 11.3), 4.88 (1H, q, *J* = 7.1), 4.89 (1H, q, 7.1), 6.21 (1H, d, *J* = 2.5), 6.76 (1H, dd, *J* = 7.8, 1.3), 6.76 (1H, dd, *J* = 8.1, 2.5), 7.02-7.05 (2H, m), 7.09 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.11-7.17 (4H, m), 7.19-7.23 (2H, m), 7.23-7.27 (2H, m), 7.30 (1H, d, *J* = 8.1), 7.30 (1H, dt, *J* = 7.4, 7.4, 1.3), 7.48 (1H, ddd, *J* = 7.5, 1.4, 0.4).

^{13}C NMR (125 MHz, d_6-acetone, ref=29.8): 22.48 (q), 22.50 (q), 67.13 (t), 67.68 (t), 72.77 (d), 73.04 (d), 115.58 (d), 119.41 (d), 127.17 (d), 127.18 (d), 128.16 (d), 128.19 (d), 128.20 (d), 128.32 (d), 128.33 (d), 128.55 (d), 129.23 (d), 130.42 (s), 130.48 (d), 130.50 (d), 130.52 (d), 131.04 (d), 131.06 (d), 132.58 (d), 137.77 (s), 137.80 (s), 138.07 (s), 138.19 (s), 138.23 (s), 141.04 (s), 141.14 (s), 141.16 (s), 142.19 (s), 142.65 (s), 142.72 (s), 157.61 (s).

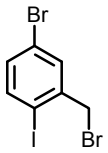
IR ($CHCl_3$): 3594 w, 3387 vw, 3080 w, 3061 w, 2966 m, 2928 m, 2863 w, 1603 m, 1585 w, 1554 vw, 1499 w, 1461 w, 1451 vw, 1444 w, 1371 m, 1304 vw, 1288 w, 1250 m, 1179 m, 1151 m, 1109 w, 1079 s, 1072 s, 1045 w, 1028 w, 1000 vw, 949 vw, 939 w, 916 vw, 857 w, 846 w, 705 vs, 616 w, 560 w, 533 w, 480 vw, 462 vw cm^{-1}.

ESI MS: 533 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{36}H_{30}O_3Na$ 533.2087, found 533.2087.

Optical rotation: $[\alpha]^{22}_D$ -192° (c 0.088, CH_2Cl_2).

4-Bromo-2-(bromomethyl)-1-iodobenzene 134a

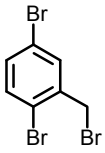


In a 500 ml round-bottom flask NBS (22.4 g, 0.125 mol, 1.2 equiv.), 5-bromo-2-iodotoluene (15 ml, 0.105 mol) and catalytic amount of AIBN and K_2CO_3 were suspended in CCl_4 (200 ml), flushed with nitrogen and refluxed for 10 h using IR lamp irradiation. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (hexane) to provide product as a 2:1 mixture of **134a** and **134b** (17g, 45%) as a solid.
^{1}H NMR and ^{13}C NMR were in agreement with the published data.[121, 217]

^{1}H NMR (500 MHz, $CDCl_3$): 4.52 (2H, s), 7.12 (1H, dd, *J* = 8.4, 2.4), 7.60 (1H, d, *J* = 2.4), 7.69 (1H, d, *J* = 8.4).

^{13}C NMR (126 MHz, $CDCl_3$): 37.47 (t), 97.86 (s), 122.79 (s), 133.11 (d), 133.22 (d), 141.26 (d), 142.14 (s).

1,4-Dibromo-2-(bromomethyl)benzene 134b

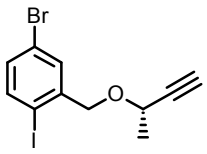


^{1}H NMR (500 MHz, $CDCl_3$): 4.53 (2H, s), 7.29 (1H, dd, *J* = 8.5, 2.4), 7.44 (1H, d, *J* = 8.5), 7.59 (1H, d, *J* = 2.4).

^{13}C NMR (126 MHz, $CDCl_3$): 32.15 (t), 121.44 (s), 123.03 (s), 133.10 (d), 133.95 (d), 134.65 (d), 138.93 (s).

^{1}H NMR and ^{13}C NMR were in agreement with the published data.[217, 226]

5-Bromo-2-iodobenzyl (1*S*)-1-methylprop-2-yn-1-yl ether (*S*)-135a



In a flame-dried Schlenk flask potassium hydride (dispersion in mineral oil, 1.92 g, 0.048 mol, 1.1 equiv.) was washed (hexane) under argon, dried under vacuum and flushed with argon. THF (20 ml) was added to the hydride and the flask was cooled to 0 ºC, alcohol (*S*)-**111** (3.8 ml, 0.048 mol, 1.1 equiv.) was added and the reaction mixture was stirred at 0 ºC for 1 h. Then a solution of benzyl bromide **134** (17.0 g, 0.047 mol) in THF (20 ml) was added at 0 ºC and the reaction mixture was allowed to warm up to room temperature and stirred for 1.5 h. The reaction was quenched by addition of a saturated solution of NH_4Cl (5 ml) and the aqueous phase was extracted with diethyl ether (4 x 200 ml), the combined organic phases were washed with water (2 x 150 ml) and dried over anhydrous Na_2SO_4. The volatiles were removed *in vacuo* and the residue was purified by chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) to provide product as a 2:1 mixture of (*S*)-**135a** and (*S*)-**135b** (12.7 g, 95%) as an oil.

^{1}H NMR and ^{13}C NMR were in agreement with the published data.[217]

^{1}H NMR (500 MHz, $CDCl_3$): 1.55 (3H, d, *J* = 6.6), 2.50 (1H, d, *J* = 2.0), 4.31 (1H, dq, *J* = 6.6, 6.6, 6.6, 2.0), 4.42 (1H, dt, *J* = 12.9, 1.7, 1.7), 4.71 (1H, dt, *J* = 12.9, 0.8, 0.8), 7.12 (1H, ddt, *J* = 8.3, 2.5, 0.7, 0.7), 7.59 (1H, dt, *J* = 2.5, 0.8, 0.8), 7.65 (1H, d, *J* = 8.3).

^{13}C NMR (126 MHz, $CDCl_3$): 22.00 (q), 65.38 (d), 73.73 (d), 73.81 (t), 83.11 (s), 95.15 (s), 122.74 (s), 131.66 (d), 132.14 (d), 140.26 (d), 142.39 (s).

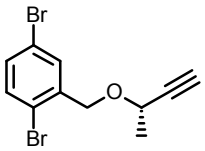
IR ($CHCl_3$, mixture of **135a** and **135b**): 3307 s, 3090 vw, 3066 vw, 2992 m, 2962 w, 2938 m, 2870 m, 2113 vw, 1584 w, 1551 w, 1461 m, 1451 s, 1438 m, 1376 m, 1327 s, 1282 w, 1262 m, 1199 m, 1101 vs, 1090 vs, 1023 s, 1011 vs, 949 vw, 883 m, 872 m, 811 s, 639 s, 570 w, 525 w, 432 w cm^{-1}.

EI MS: 366 ($M^{+\bullet}$, **135a** with ^{81}Br, 22), 364 ($M^{+\bullet}$, **135a** with ^{79}Br, 23), 320 ($M^{+\bullet}$, **135b** with $^{81}Br^{81}$Br, 3), 318 ($M^{+\bullet}$, **135b** with $^{81}Br^{79}$Br, 5), 316 ($M^{+\bullet}$, **135b** with $^{79}Br^{79}$Br, 3), 311 (8), 293 (25), 295 (28), 265 (5), 263 (6), 249 (22), 217 (18), 195 (10), 169 (38), 156 (23), 149 (10), 128 (13), 89 (51), 75 (37), 53 (100), 43 (49).

HR EI MS: calculated for **135a** $C_{11}H_{10}O^{79}BrI$ 363.8959, found 363.8956.

Optical rotation: $[\alpha]^{22}_D$ -48° (c 0.124, CH_2Cl_2, mixture of **135a**:**135b** = 2:1).

1,4-Dibromo-2-({[(1S)-1-methylprop-2-yn-1-yl]oxy}methyl)benzene (*S*)-**135b**

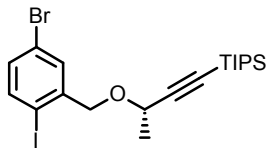


^{1}H NMR (500 MHz, $CDCl_3$): 1.55 (3H, d, *J* = 6.6), 2.49 (1H, d, *J* = 2.0), 4.31 (1H, dq, *J* = 6.5, 6.5, 6.5, 2.0), 4.52 (1H, dt, *J* = 13.2, 0.7, 0.7), 4.78 (1H, dt, *J* = 13.2, 0.8, 0.8), 7.27 (1H, ddt, *J* = 8.4, 2.5, 0.7, 0.7), 7.39 (1H, d, *J* = 8.4), 7.64 (1H, dt, *J* = 2.5, 0.8, 0.8).

^{13}C NMR (126 MHz, $CDCl_3$): 22.00 (q), 65.41 (s), 73.67 (d), 73.73 (t), 120.89 (s), 121.45 (s), 131.78 (d), 131.80 (s), 133.74 (d), 139.54 (s).

^{1}H NMR and ^{13}C NMR were in agreement with the published data.[217]

{(3*S*)-3-[(5-Bromo-2-iodobenzyl)oxy]but-1-yn-1-yl}[tris(1-methylethyl)]silane (*S*)-**136a**



A flame-dried Schlenk flask was filled with a solution of alkyne (*S*)-**135** (12.5 g, 0.036 mol) in THF (50 ml) under argon and cooled to -78 ºC. A solution of lithium diisopropylamide, prepared from a solution of *n*-BuLi (1.6 M in hexanes, 22.5 ml, 0.036 mmol, 1.0 equiv.) and diisopropylamine (7.0 ml, 0.050 mol, 1.4 equiv.) in THF

(10 ml), was cooled to -78 ºC and then slowly added (over a period of 30 min) to the solution of alkyne (*S*)-**136** via a cannula. The reaction mixture was then stirred at -78 ºC for 1 h. Triisopropylsilyl chloride (7.6 ml, 0.036 mol, 1.0 equiv.) was added and the solution was stirred at -78 ºC for 15 min, then allowed to warm up to room temperature and stirred overnight. The volatiles were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 99:1) to provide product as a 2:1 mixture of (*S*)-**136a** and (*S*)-**136b** (11.5 g, 63%) as an amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): 1.53 (3H, d, *J* = 6.6), 1.04-1.12 (21H, m), 4.34 (1H, q, *J* = 6.6), 4.45 (1H, dt, *J* = 13.2, 0.7, 0.7) 4.74 (1H, dt, *J* = 13.2, 0.7, 0.7), 7.11 (1H, ddt, *J* = 8.3, 2.5, 0.7, 0.7), 7.59 (1H, dt, *J* = 2.5, 0.9, 0.9), 7.64 (1H, d, *J* = 8.3).

^{13}C NMR (126 MHz, $CDCl_3$): 11.12 (d), 18.63 (q), 22.26 (q), 65.98 (d), 73.62 (t), 86.64 (s), 95.02 (s), 106.77 (s), 122.72 (s), 131.61 (d), 132.00 (d), 140.20 (d), 142.73 (s).

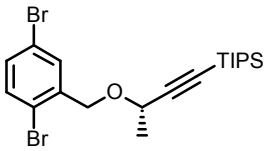
IR ($CHCl_3$, mixture of **136a** and **136b**,): 3088 vw, 3065 vw, 2989 m, 2960 vs, 2866 vs, 2164 w, 1582 w, 1575 w, 1558 vw, 1551 w, 1463 s, 1452 s, 1438 m, 1384 m, 1373 m, 1325 s, 1289 w, 1262 s, 1198 w, 1098 vs, 1086 vs, 1076 s, 1023 s, 1011 s, 997 s, 883 vs, 810 s, 700 w, 679 s, 665 s, 638 m, 575 m, 525 w, 433 w cm^{-1}.

ESI MS: 545 ($[M+Na]^+$, **136a** with ^{81}Br), 543 ($[M+Na]^+$, **136a** with ^{79}Br), 495 ($[M+Na]^+$, **136b** with $^{81}Br^{79}$Br).

HR ESI MS: calculated for **136a** $C_{20}H_{29}O^{79}BrINaSi$ 543.0186, found 543.0183.

Optical rotation: $[\alpha]^{22}_D$ -103° (c 0.352, CH_2Cl_2, mixture of **136a**:**136b**=2:1).

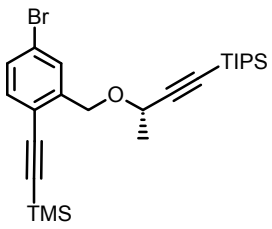
{(3S)-3-[(2,5-Dibromobenzyl)oxy]but-1-yn-1-yl}[tris(1-methylethyl)]silane (*S*)-**136b**



^{1}H NMR (500 MHz, $CDCl_3$): 1.04-1.12 (21H, m), 1.53 (3H, d, *J* = 6.6), 4.34 (1H, q, *J* = 6.6), 4.55 (1H, dt, *J* = 13.4, 0.8, 0.8), 4.82 (1H, dt, *J* = 13.4, 0.8, 0.8), 7.26 (1H, ddt, *J* = 8.4, 2.5, 0.7, 0.7), 7.38 (1H, d, *J* = 8.4), 7.64 (1H, dt, *J* = 2.5, 0.9, 0.9).

^{13}C NMR (126 MHz, $CDCl_3$): 11.11 (d), 18.59 (q), 22.26 (q), 66.00 (d), 69.15 (t), 86.61 (s), 106.80 (s), 120.89 (s), 121.42 (s), 131.66 (d), 131.85 (d), 133.69 (d), 139.88 (s).

({4-Bromo-2-[({(1*S*)-1-methyl-3-[tris(1-methylethyl)silyl]prop-2-yn-1-yl}oxy) methyl]phenyl}ethynyl)(trimethyl)silane (*S*)-**137**



A flame-dried Schlenk flask was charged with tetrakis(triphenylphosphine)palladium(0) (108 mg, 0.093 mmol, 0.6 mol%), copper iodide (59 mg, 0.309 mmol, 2 mol%) and diisopropylamine (30 ml) under argon. The mixture was cooled to 0 ºC and a degassed solution of (*S*)-**136** (8.02 g, 0.015 mol) in diisopropylamine (30 ml) was added. Then ethynyl(trimethyl)silane (2.3 ml, 0.016 mmol, 1.1 equiv.) was slowly added and the reaction mixture was stirred at 0 ºC for 30 min. The reaction mixture was filtered through a short pad of silica gel (hexane) and the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane) to provide the silane (*S*)-**137** (7.80 g, 98%) contaminated with 25% of (*S*)-**136b** inseparable unreacted impurity as an amorphous material.

^{1}H NMR (500 MHz, $CDCl_3$): 0.24 (9H, s), 1.04-1.10 (21H, m), 1.54 (3H, d, *J* = 6.6), 4.34 (1H, q, *J* = 6.6), 4.65 (1H, dt, *J* = 13.3, 0.7, 0.7), 4.86 (1H, dt, *J* = 13.3, 0.7, 0.7), 7.29 (1H, d, *J* = 8.2), 7.34 (1H, ddt, *J* = 8.2, 2.1, 0.7, 0.7), 7.63 (1H, ddd, *J* = 2.1, 1.1, 0.8).

^{13}C NMR (126 MHz, $CDCl_3$): 11.09 (d), 18.60 (q), 22.38 (q), 66.17 (d), 67.93 (t), 86.06 (s), 100.49 (s), 101.36 (s), 107.24 (s), 120.02 (s), 122.98 (s), 130.03 (d), 130.08 (d), 133.49 (d), 142.74 (s).

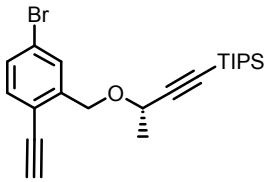
IR ($CHCl_3$): 2945 vs, 2866 vs, 2157 m, 1586 w, 1555 w, 1472 s, 1464 s, 1401 m, 1384 m, 1371 m, 1325 m, 1252 s, 1119 s, 1097 s, 1083 s, 1070 s, 997 m, 883 s, 847 vs, 823 m, 679 s, 661s cm^{-1}.

ESI LC-MS: 493 ($[M+H]^{+\cdot}$, with ^{81}Br), 491 ($[M+H]^{+\cdot}$, with ^{79}Br).

HR ESI MS: calculated for $C_{25}H_{40}O^{79}BrSi_2$ 491.1796, found 491.1781.

Optical rotation: $[\alpha]^{22}_{D}$ -29° (c 0.035, CH_2Cl_2).

{(3*S*)-3-[(5-Bromo-2-ethynylbenzyl)oxy]but-1-yn-1-yl}[tris(1-methylethyl)]silane (*S*)-**138**



In a 250 ml round-bottom flask sodium (354 mg, 15.4 mmol, 1.0 equiv.) was dissolved in methanol (200 ml) under cooling to 0 ºC. After stirring for 15 min at 0 ºC the silane (*S*)-**137** (7.80 g, 15.8 mmol) in THF (100 ml) was added and the reaction mixture was stirred at room temperature for 30 min. The solvents were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (heptane) to provide alkyne (*S*)-**138** (3.63 g, 61%) as an amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): 1.05-1.15 (21H, m), 1.54 (3H, d, *J* = 6.6), 3.33 (1H, s), 4.35 (1H, q, *J* = 6.6), 4.70 (1H, dt, *J* = 13.3, 0.7, 0.7), 4.95 (1H, dt, *J* = 13.3, 0.8, 0.8), 7.34 (1H, d, *J* = 8.2), 7.38 (1H, ddt, *J* = 8.2, 2.0, 0.6, 0.6), 7.68 (1H, ddd, *J* = 2.0, 1.2, 0.8).

^{13}C NMR (126 MHz, $CDCl_3$): 11.10 (d), 18.60 (q), 22.28 (q), 65.93 (d), 67.69 (t), 80.14 (s), 82.85 (d), 86.28 (s), 107.03 (s), 119.11 (s), 123.38 (s), 130.21 (d), 130.38 (d), 133.79 (d), 142.95 (s).

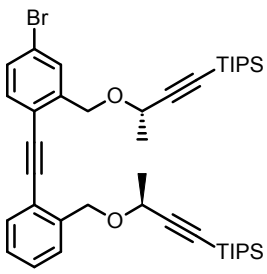
IR ($CHCl_3$): 3305 vs, 2866 vs, 2165 w, 2107 w, 1697 w, 1588 s, 1557 w, 1472 s, 1464 vs, 1401 m, 1385 s, 1371 s, 1325 s, 1259 m, 1197 vs, 1138 s, 1116 vs, 1081 vs, 1068 vs, 997 s, 883 vs, 823 s, 679 vs, 663 vs, 620 s cm^{-1}.

APCI MS: 421 ($[M+H]^{+\cdot}$, with ^{81}Br), 419 ($[M+H]^{+\cdot}$, with ^{79}Br).

HR APCI MS: calculated for $C_{22}H_{32}O^{79}BrSi$ 419.1400, found 419.1400.

Optical rotation: $[\alpha]^{22}_{D}$ -31° (c 0.101, CH_2Cl_2).

[(3*S*)-3-{[2-({4-Bromo-2-[({(1*S*)-1-methyl-3-[tris(1-methylethyl)silyl]prop-2-yn-1-yl}oxy)methyl]phenyl}ethynyl)benzyl]oxy}but-1-yn-1-yl][tris(1-methylethyl)] silane (*S*,*S*)-**139**



A flame-dried Schlenk flask was charged with bis(triphenylphosphine)palladium(II) dichloride (60 mg, 0.0854 mmol, 1 mol%), copper iodide (33 mg, 0.171 mmol, 2 mol%) and flushed with argon. Then diisopropylamine (20 ml) and a degassed solution of aryl iodide (*S*)-**113** (3.85 g, 8.72 mmol, 1.01 equiv.) in diisopropylamine (20 ml) were added and the mixture was stirred at room temperature for 10 min. Then it was cooled to 0 ºC, a degassed solution of alkyne (*S*)-**138** (3.63 g, 8.65 mmol) in diisopropylamine (25 ml) was added dropwise (over a period of 1 h) and the reaction mixture was stirred at 0 ºC for 2 h. Then it was filtered through a short pad of silica gel (hexane) and the solvent was removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane) to obtain product (*S*,*S*)-**139** (5.06 g, 80%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$): 0.98-1.07 (42H, m), 1.51 (3H, d, *J* = 6.6), 1.54 (3H, d, *J* = 6.6), 4.34 (1H, q, *J* = 6.6), 4.36 (1H, q, *J* = 6.6), 4.76 (1H, dt, *J* = 13.3, 0.7, 0.7), 4.77 (1H, d, *J* = 12.7), 5.00 (1H, dt, *J* = 13.3, 0.7, 0.7) 5.01 (1H, d, *J* = 12.7), 7.26 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.35 (1H, d, *J* = 8.2), 7.37 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.38 (1H, bdd, *J* = 8.2, 2.0), 7.50 (1H, bdd, *J* = 7.6, 1.4), 7.52 (1H, ddq, *J* = 7.7, 1.4, 0.6, 0.6, 0.6), 7.69 (1H, ddd, *J* = 2.0, 1.1, 0.7).

^{13}C NMR (126 MHz, $CDCl_3$): 11.06 (d), 11.09 (d), 18.52 (q), 22.39 (q), 22.42 (q), 65.68 (d), 66.01 (d), 68.04 (t), 68.69 (t), 85.98 (s), 86.30 (s), 90.29 (s), 92.69 (s), 107.17 (s), 107.48 (s), 120.20 (s), 121.33 (s), 122.79 (s), 127.16 (d), 127.57 (d), 128.70 (d), 130.12 (d), 130.21 (d), 132.03 (d), 133.13 (d), 140.03 (s), 142.22 (s).

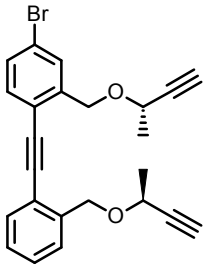
IR ($CHCl_3$): 3071 w, 2866 vs, 2215 vw, 2164 w, 1599 vw, 1586 w, 1572 vw, 1555 vw, 1493 m, 1471 s, 1463 s, 1452 m, 1401 w, 1384 m, 1371 m, 1325 m, 1255 w, 1118 s, 1138 m, 1096 s, 1080 s, 1069 s, 1019 m, 997 m, 949 w, 883 s, 822 m, 679 s, 661 m cm^{-1}.

APCI MS: 735 ($[M+H]^+$, with ^{81}Br), 733 ($[M+H]^+$, with ^{79}Br).

HR ESI MS: calculated for $C_{42}H_{62}O_2{}^{79}BrSi_2$ 733.3466, found 733.3482.

Optical rotation: $[\alpha]^{22}_{D}$ -60° (c 0.176, CH_2Cl_2).

4-Bromo-2-({[(1*S*)-1-methylprop-2-yn-1-yl]oxy}methyl)-1-{[2-({[(1*S*)-1-methylprop-2-yn-1-yl]oxy}methyl)phenyl]ethynyl}benzene (*S*,*S*)-**140**



A flame-dried Schlenk flask was charged with silane (*S*,*S*)-**139** (2.75 g, 3.74 mmol), flushed with argon and THF (30 ml) was added. The solution was cooled to -78 ºC and a solution of tetrabutylammonium fluoride trihydrate (0.914 M in THF, 4.0 ml, 3.74 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at -78 ºC for 1 h and then it was left to warm up to room temperature and stirred overnight. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) to obtain product (*S*,*S*)-**140** (1.49 g, 95%) as a yellow solid.

M.p.: 71-73°C (heptane).

^{1}H NMR (500 MHz, $CDCl_3$): 1.52 (3H, d, *J* = 6.6), 1.54 (3H, d, *J* = 6.6), 2.45 (1H, d, *J* = 2.0), 2.47 (1H, d, *J* = 2.0), 4.32 (1H, dq, *J* = 6.6, 6.6, 6.6, 2.0), 4.34 (1H, dq, *J* = 6.6, 6.6, 6.6, 2.0), 4.78 (1H, bd, *J* = 12.5), 4.76 (1H, dt, *J* = 12.0, 0.6, 0.6), 5.00 (1H, dt, *J* = 12.0, 0.6, 0.6), 5.01 (1H, bd, *J* = 12.5), 7.29 (1H, dt, *J* = 7.5, 7.5, 1.4), 7.37 (1H, dt, *J* = 7.7, 7.7, 1.4), 7.39 (1H, dd, *J* = 8.2, 0.6), 7.41 (1H, bdd, *J* = 8.2, 2.0), 7.53 (1H, ddt, *J* = 7.4, 1.4, 0.7, 0.7), 7.54 (1H, ddd, *J* = 7.6, 1.4, 0.5), 7.69 (1H, dq, *J* = 2.0, 0.8, 0.8, 0.8).

^{13}C NMR (126 MHz, $CDCl_3$): 22.08 (q), 22.11 (q), 64.31 (d), 64.95 (d), 65.31 (d), 68.18 (t), 68.79 (t), 73.60 (d), 83.46 (s), 83.75 (s), 90.37 (s), 92.70 (s), 120.31 (s), 121.48 (s), 122.89 (s), 127.42 (d), 127.79 (d), 128.83 (d), 130.37 (d), 130.67 (d), 132.12 (d), 133.24 (d), 139.63 (s), 141.77 (s).

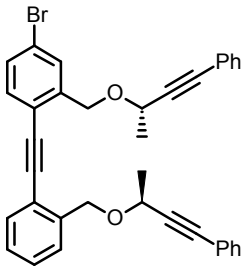
IR ($CHCl_3$): 3306 s, 3071 w, 2214 vw, 2112 vw, 1600 vw, 1586 w, 1571 vw, 1555 vw, 1493 m, 1472 m, 1453 m, 1401 m, 1390 m, 1374 m, 1327 s, 1153 w, 1137 s, 1117 vs, 1100 vs, 1081 s, 1066 s, 1020 m, 950 w, 822 m, 639 s cm^{-1}.

APCI MS: 423 ($[M+H]^+$, with ^{81}Br), 421 ($[M+H]^+$, with ^{79}Br).

HR APCI MS: calculated for $C_{24}H_{22}O_2{}^{79}Br$ 421.0798, found 421.0793.

Optical rotation: $[\alpha]^{22}_{D}$ -101° (c 0.043, CH_2Cl_2).

4-Bromo-2-({[(1S)-1-methyl-3-phenylprop-2-yn-1-yl]oxy}methyl)-1-{[2-({[(1S)-1-methyl-3-phenylprop-2-yn-1-yl]oxy}methyl)phenyl]ethynyl}benzene (*S*,*S*)-**141**



A flame-dried Schlenk flask was charged with tetrakis(triphenylphosphine)palladium(0) (36 mg, 0.0308 mmol, 1 mol%), copper iodide (12 mg, 0.0616 mmol, 2 mol%), flushed with argon and diisopropylamine (20 ml) and iodobenzene (1.2 ml, 0.011 mol, 4.0 equiv.) were added at room temperature. The mixture was cooled to 0 ºC and a degassed solution of alkyne (*S*,*S*)-**140** (1.30 g, 3.08 mmol) in diisopropylamine (25 ml) was slowly added. The reaction mixture was stirred at 0 ºC for 1 h and then allowed to warm up to room temperature and stirred overnight. The reaction mixture was filtered through a sintered glass (hexane) and the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 99:1) to provide product (*S*,*S*)-**141** (1.58 g, 92%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$): 1.55 (3H, d, *J* = 6.6), 1.58 (3H, d, *J* = 6.6), 4.50 (1H, q, *J* = 6.6), 4.52 (1H, q, *J* = 6.6), 4.81 (1H, dt, *J* = 12.6, 0.7, 0.7), 4.83 (1H, bd, *J* = 12.5), 5.02 (1H, dt, *J* = 12.6, 0.7, 0.7), 5.04 (1H, bd, *J* = 12.5), 7.19 (1H, dt, *J* = 7.5, 7.5, 1.3), 7.23-7.29 (6H, m), 7.27 (1H, dd, *J* = 8.2, 2.0), 7.31 (1H, d, *J* = 8.2), 7.34-7.36 (2H, m), 7.35 (1H, dt, *J* = 7.7, 7.7, 1.4), 7.37-7.39 (2H, m), 7.48 (1H, ddd, *J* = 7.6, 1.4, 0.5), 7.53 (1H, ddt, *J* = 7.8, 1.4, 0.7, 0.7), 7.68 (1H, dq, *J* = 2.0, 0.7, 0.7, 0.7).

^{13}C NMR (126 MHz, $CDCl_3$): 22.21 (q), 22.23 (q), 65.53 (d), 65.95 (d), 68.22 (t), 68.79 (t), 85.33 (s), 85.57 (s), 88.73 (s), 89.02 (s), 90.39 (s), 92.74 (s), 120.38 (s), 121.64 (s), 122.51 (s), 122.56 (s), 122.79 (s), 127.40 (d), 128.05 (d), 128.21 (d), 128.28 (d), 128.30 (d), 128.77 (d), 130.29 (d), 130.51 (d), 131.69 (d), 131.72 (d), 132.09 (d), 133.21 (d), 139.79 (s), 141.96 (s).

IR ($CHCl_3$): 3083 w, 3066 w, 3036 w, 2227 w, 1599 w, 1586 w, 1573 w, 1555 vw, 1497 m, 1490 s, 1472 w, 1451 m, 1444 m, 1401 w, 1389 w, 1373 m, 1329 s, 1255 w, 1152 w, 1131 m, 1116 s, 1097 vs, 1063 s, 1029 m, 1019 w, 950 w, 822 m, 692 s cm^{-1}.

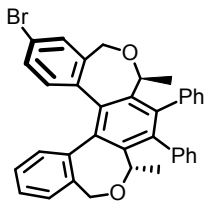
APCI MS: 575 ([M+H]$^+$, with ^{81}Br), 573 ([M+H]$^+$, with ^{79}Br).

HR APCI MS: calculated for $C_{36}H_{30}O_2{}^{79}Br$ 573.1424, found 573.1408.

Optical rotation: $[\alpha]^{22}_D$ -90° (c 0.138, CH_2Cl_2).

(*P*,3*S*,6*S*)-10-Bromo-3,6-dimethyl-4,5-diphenyl-1,3,6,8-tetrahydrodibenzo[*e*,*e'*] benzo[1,2-*c*:4,3-*c'*]bisoxepine (*P*,*S*,*S*)-**142**

Procedure using $CoCp(CO)_2$ complex:



A 20 ml microwave vial was charged with ionic liquid [BDMIM][BF_4] (~100 mg), dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (108 µl, 0.815 mmol, 1.3 equiv.), triyne (*S*,*S*)-**141** (344 mg, 0.599 mmol), triphenylphosphine (315 mg, 1.199 mmol, 2.0 equiv.) and THF (20 ml) and the solution was heated in a microwave reactor at 180 ºC for 30 min. Then the solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 90:10) to provide product (*P*,*S*,*S*)-**142** (317 mg, 92%) as an off-white solid.

Procedure using CoCp(CO)(fum) complex:

A 20 ml microwave vial was charged with silicon carbide (100 mg), carbonyl(η^5-cyclopentadienyl)(η^2-dimethylfumarate)cobalt(I) complex (434 mg, 1.44 mmol, 1.1 equiv), triyne (*S*,*S*)-**141** (750 mg, 1.31 mmol) and THF (20 ml) and the solution was heated in a microwave reactor at 180 ºC for 10 min. Then solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 90:10) and the obtained solid was washed (hexane) to provide product (*P*,*S*,*S*)-**142** (1.34 g, 94%) as a white solid.

M.p.: 273-277°C (heptane).

^{1}H NMR (500 MHz, $CDCl_3$): 0.61 (3H, d, *J* = 7.1), 0.67 (3H, d, *J* = 7.1), 4.54 (1H, d, *J* = 11.3), 4.59 (1H, d, *J* = 11.3), 4.83 (1H, d, *J* = 11.3), 4.86 (1H, d, *J* = 11.3), 4.94 (1H, q, *J* = 7.1), 4.95 (1H, q, *J* = 7.1), 6.47 (1H, d, *J* = 8.4), 6.59 (1H, bd, *J* = 7.7), 6.84 (2H, m), 7.03 (1H, bt, *J* = 7.6), 7.04-7.09 (4H, m), 7.11 (1H, dd, *J* = 8.4, 2.0), 7.16

(2H, m), 7.19-7.21 (2H, m), 7.24 (1H, bt, *J* = 7.4), 7.41 (1H, bt, *J* = 7.3), 7.58 (1H, bd, *J* = 2.0).

^{13}C NMR (126 MHz, $CDCl_3$): 22.10 (q), 22.39 (q), 66.91 (t), 67.44 (t), 72.70 (d), 72.85 (d), 121.26 (s), 126.42 (d), 127.39 (d), 127.41 (d), 127.64 (d), 127.70 (d), 127.71 (d), 127.86 (d), 128.70 (d), 129.67 (d, 2C), 130.00 (d), 130.05 (d), 130.45 (d), 131.53 (d), 132.01 (d), 133.58 (d), 135.94 (s), 137.20 (s), 137.36 (s), 137.63 (s), 137.86 (s), 139.18 (s), 139.68 (s, 2C), 139.80 (s), 139.83 (s), 142.19 (s), 142.39 (s).

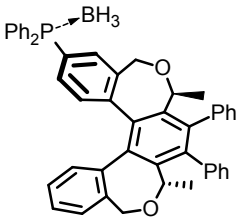
IR ($CHCl_3$): 3082 w, 3062 w, 3034 w, 2967 m, 2928 m, 1602 w, 1592 w, 1577 vw, 1496 w, 1483 w, 1443 w, 1410 w, 1371 m, 1114 m, 1081 s, 1072 s, 1046 w, 1028 w, 1000 vw, 949 w, 914 w, 705 vs, 626 w, 563 w, 416 vw cm^{-1}.

ESI MS: 597 ($[M+Na]^+$, with ^{81}Br), 595 ($[M+Na]^+$, with ^{79}Br), 575 ($[M+H]^+$, with ^{81}Br), 573 ($[M+H]^+$, with ^{79}Br),.

HR ESI MS: calculated for $C_{36}H_{30}O_2{}^{79}Br$ 573.1424, found 573.1416; calculated for $C_{36}H_{29}{}^{79}BrO_2Na$ 595.1243, found 595.1239.

Optical rotation: $[\alpha]^{22}_D$ -164° (c 0.059, CH_2Cl_2).

[(*P*,3*S*,6*S*)-3,6-Dimethyl-4,5-diphenyl-1,3,6,8-tetrahydrodibenzo[*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepin-10-yl]diphenylphosphane-borane complex (*P*,*S*,*S*)-**143**



A flame-dried Schlenk flask was filled with a solution of bromide (*P*,*S*,*S*)-**142** (54.0 mg, 0.094 mmol) in diethyl ether (4 ml) under argon. Then it was cooled to -110 ºC and a solution of *t*-BuLi (1.7 M in pentane, 114 µl, 0.188 mmol, 2.0 equiv) was added so that drops fell down on the wall of the Schlenk flask. After stirring at -110 ºC for 1 min chlorodiphenylphosphine (40 µl, 0.223 mmol, 2.3 equiv.) was added and the reaction mixture was stirred at -110 ºC to -80 ºC for 1 h. Then the Schlenk flask was removed from a dry-ice bath and immersed into an ice-water bath and allowed to warm up to 0 ºC over a period of 15 min. Then a solution of borane dimethylsulfide complex (2.0 M in THF, 50 µl, 0.1 mmol, 10.0 equiv.) was added and the reaction mixture was stirred at 0 ºC for 1h and at room temperature overnight. The volatiles were removed *in vacuo* and the residue was purified by flash

chromatography (hexane-ethyl acetate 100:0 to 90:10) to provide product (*P*,*S*,*S*)-**143** (62.4 mg, 96%) as a white solid.

M.p.:143-147°C (chloroform).

^{1}H NMR (500 MHz, $CDCl_3$): 0.63 (3H, d, *J* = 7.1), 0.68 (3H, d, *J* = 7.1), 4.58 (2H, d, *J* = 11.5), 4.86 (1H, d, *J* = 11.5), 4.88 (1H, dd, *J* = 11.5, 0.9), 4.94 (1H, q, *J* = 7.1), 4.96 (1H, q, *J* = 7.1), 6.54 (1H, dd, *J* = 7.7, 1.3), 6.68 (1H, dd, *J* = 8.0, 2.2), 6.84-6.86 (2H, m), 7.01 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.04-7.11 (4H, m), 7.14-7.17 (2H, m), 7.17 (1H, ddd, *J* = 10.4, 8.0, 1.7), 7.19-7.22 (2H, m), 7.25 (1H, dt, *J* = 7.5, 7.5, 1.3), 7.40 (1H, ddd, *J* = 7.4, 1.4, 0.5), 7.41-7.46 (5H, m), 7.49-7.54 (5H, m), 7.63 (1H, ddd, *J* = 10.8, 1.7, 0.5).

^{13}C NMR (125 MHz, $CDCl_3$): 22.14 (q), 22.53 (q), 67.10 (t), 67.36 (t), 72.70 (d), 72.76 (d), 126.45 (d), 126.48 (d), 127.26 (d), 127.39 (d), 127.43 (d), 127.72 (d), 127.74 (d), 127.98 (d), 128.02 (s, J_{PC} = 57.5), 128.70 (s, J_{PC} = 58.0), 128.74 (d), 128.78 (d, J_{PC} = 5.5), 128.85 (d, J_{PC} = 5.6), 129.21 (s, J_{PC} = 58.1), 129.56 (d), 129.64 (d), 129.92 (d), 129.97 (d), 131.24 (d, J_{PC} = 2.4), 131.31 (d, J_{PC} = 2.4), 131.91 (d, J_{PC} = 9.1), 132.03 (d), 132.30 (d, J_{PC} = 10.1), 133.04 (d, J_{PC} = 9.7, 2C), 133.21 (d, J_{PC} = 9.7), 135.92 (s), 137.42 (s), 137.45 (s), 137.61 (s), 137.86 (s), 138.30 (s, J_{PC} = 10.2), 139.58 (s, 2C), 139.67 (s), 142.11 (s), 142.69 (s), 143.72 (s, J_{PC} = 2.5).

^{31}P NMR (202 MHz, $CDCl_3$): 20.73 (s).

^{11}B NMR (160 MHz, $CDCl_3$): -2.90 (bs).

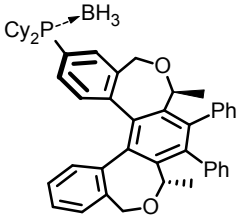
IR ($CHCl_3$): 3080 w, 3062 w, 3037 w, 2968 m, 2928 w, 2389 m, 2348 w, 1600 w, 1577 vw, 1494 w, 1488 w, 1438 m, 1370 m, 1238 w, 1188 w, 1119 w, 1105 s, 1077 s, 1060 m, 1046 w, 1028 w, 999 w, 949 w, 704 vs, 694 m, 628 w, 623 w, 610 w, 572 w, 512 w, 497 w, 429 vw, 415 vw cm^{-1}.

ESI MS: 715 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{48}H_{42}O_2BNaP$ 715.2908, found 715.2917.

Optical rotation: $[\alpha]^{22}_D$ -218° (c 0.051, CH_2Cl_2).

[(*P*,3*S*,6*S*)-3,6-Dimethyl-4,5-diphenyl-1,3,6,8-tetrahydrodibenzo[*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepin-10-yl]dicyclohexylphosphane-borane complex (*P*,*S*,*S*)-**144**



A flame-dried Schlenk flask was filled with a solution of bromide (*P*,*S*,*S*)-**142** (44.7 mg, 0.078 mmol) in diethyl ether (5 ml) under argon. Then it was cooled to -116 ºC and a solution of *t*-BuLi (1.7 M in pentane, 95 µl, 0.157 mmol, 2.0 equiv.) was added so that drops fell down on the wall of the Schlenk flask. After stirring at -110 ºC for 1 min chlorodicyclohexylphosphine (50 µl, 0.226 mmol, 2.9 equiv.) was added and the reaction mixture was stirred at -110 ºC for 15 min. The Schlenk flask was removed from a dry-ice bath and immersed into an ice-water bath and allowed to warm up to 0 ºC. Then a solution of borane-THF complex (2 M in THF, 1 ml, 2 mmol, 26 equiv.) was added and the reaction mixture was stirred at 0 ºC for 30 min and at room temperature overnight. The volatiles were removed *in vacuo* and the residue was purified by flash chromatography (hexane-diethyl ether 100:0 to 85:15) to provide product (*P*,*S*,*S*)-**144** (47.2 mg, 85%) as a white amorphous material.

^{1}H NMR (500 MHz, $CDCl_3$): 0.64 (6H, d, *J* = 7.2), 1.10-2.10 (20H, m), 4.59 (1H, d, *J* = 11.4), 4.67 (1H, d, *J* = 11.6), 4.87 (1H, d, *J* = 11.4), 4.89 (1H, d, *J* = 11.6), 4.96 (2H, q, *J* = 7.2), 6.49 (1H, dd, *J* = 7.7, 1.3), 6.66 (1H, dd, *J* = 8.0, 1.8), 6.83-6.86 (2H, m), 7.03-7.06 (2H, m), 7.06-7.09 (2H, m), 7.07 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.15-7.18 (2H, m), 7.18 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.18-7.21 (2H, m), 7.25 (1H, ddd, *J* = 8.6, 8.0, 1.5), 7.40 (1H, dd, *J* = 7.5, 1.3), 7.73 (1H, dd, *J* = 9.4, 1.5).

^{13}C NMR (126 MHz, $CDCl_3$): 22.21 (q), 22.41 (q), 26.01 (t), 26.33 (t, J_{PC} = 2.4), 26.35 (t, J_{PC} = 2.9), 26.67 (t, J_{PC} = 7.8), 26.78 (t, J_{PC} = 8.3), 31.34 (s, J_{PC} = 33.7), 31.46 (s, J_{PC} = 33.4), 67.28 (t), 67.43 (t), 72.74 (d), 72.77 (d), 125.00 (s, J_{PC} = 47.6), 126.45 (d), 126.48 (d), 127.15 (d), 127.39 (d), 127.41 (d), 127.70 (d), 127.72 (d), 127.84 (d), 128.64 (d), 129.69 (d), 129.76 (d), 130.05 (d), 130.07 (d), 131.74 (d, J_{PC} = 6.3), 131.91 (d, J_{PC} = 8.9), 132.03 (d), 133.61 (d, J_{PC} = 8.7), 136.18 (s), 137.37 (s), 137.55 (s), 137.71 (s), 138.02 (s), 138.13 (s, J_{PC} = 9.3), 139.70 (s), 139.74 (s), 139.80 (s), 142.13 (s), 142.62 (s), 143.41 (s, J_{PC} = 2.4).

^{31}P NMR (202 MHz, $CDCl_3$): 26.43 (s).

^{11}B NMR (160 MHz, $CDCl_3$): -2.38 (bs).

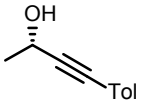
IR ($CHCl_3$): 3082 vw, 3063 w, 3036 vw, 2934 vs, 2857 s, 2381 m, 2348 w, 1601 w, 1577 vw, 1553 vw, 1496 w, 1462 w, 1450 m, 1445 m, 1370 m, 1299 w, 1238 w, 1120 w, 1112 w, 1104 m, 1077 s, 1028 w, 1004 w, 948 vw, 833 vw, 705 s, 695 w, 574 w, 511 w, 421 vw cm^{-1}.

ESI MS: 728 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{48}H_{54}O_2BNaP$ 727.3850, found 727.3847.

Optical rotation: $[\alpha]^{22}_D$ -214° (c 0.035, CH_2Cl_2).

(2*S*)-4-(4-Methylphenyl)but-3-yn-2-ol (*S*)-**145**

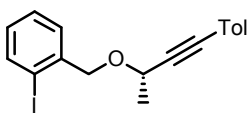


The Schlenk flask was charged with bis(triphenylphosphine)palladium(II) dichloride (80 mg, 0.114 mmol, 4 mol%), copper iodide (44 mg, 0.231 mmol, 8 mol%) and purged with argon. Then 4-iodotoluene (603 mg, 2.76 mmol), toluene (30 ml) and diisopropylamine (2 ml, 1.43 g, 14.2 mmol, 5.0 equiv.) were added and the mixture was stirred at room temperature for 5 min. Then alcohol (*S*)-**111** (215 µl, 2.76 mmol.) was added dropwise over a period of 30 min and the reaction mixture was allowed to stir overnight. The reaction mixture was then filtered through a short pad of silica gel (hexane-ethyl acetate 1:1) and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (hexane-ethyl acetate 95:5 to 90:10) to obtain product (*S*)-**145** (441.9 mg, 99%) as a yellow solid.

^{1}H NMR and ^{13}C NMR were in agreement with the published data.[66]

^{1}H NMR (400 MHz, $CDCl_3$): 1.55 (3H, d, *J* = 6.6), 2.34 (3H, bs), 4.75 (1H, q, *J* = 6.6), 7.11 (m, 2H), 7.32 (m, 2H).

2-Iodobenzyl (1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl ether (*S*)-**147**



Potassium hydride (dispersion in mineral oil, 490 mg, 12.2 mol, 1.5 equiv.) in THF (10 ml) was cooled to 0 ºC. Then tolyl alcohol (*S*)-**145** (1.30 g, 8.14 mmol, 1.0 equiv.) in THF (5 ml) was slowly added and the reaction mixture was stirred at 0 ºC for 1 h. Then benzyl bromide **110**

(2.39 g, 8.14 mmol) in THF (6 ml) was added at 0 °C and the reaction mixture was allowed to warm up to room temperature and stirred overnight. A saturated aqueous solution of NH_4Cl (100 ml) was added to quench the excess of potassium hydride and the product was extracted with diethyl ether (3 x 80 ml), the combined organic layers washed with water (3 x 40 ml) and dried over anhydrous Na_2SO_4. The solvents were removed *in vacuo* to give a yellow oil, which was purified by chromatography on silica gel (hexane-diethyl ether 95:5) to give the product (*S*)-**147** (2.32 g, 76%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): 1.59 (3H, d, *J* = 6.6), 2.34 (3H, bs), 4.52 (1H, q, *J* = 6.6), 4.57 (1H, d, *J* = 12.5), 4.83 (1H, d, *J* = 12.5), 6.98 (1H, ddd, *J* = 7.8, 7.4, 1.8), 7.12 (2H, m), 7.34 (1H, ddd, *J* = 7.7, 7.4, 1.3), 7.35 (2H, m), 7.49 (1H, ddt, *J* = 7.7, 1.8, 0.8, 0.8), 7.82 (1H, dd, *J* = 7.8, 1.3).

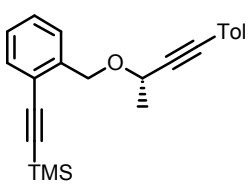
^{13}C NMR (126 MHz, $CDCl_3$): 21.45 (q), 22.21 (q), 65.75 (d), 74.44 (t), 85.60 (s), 88.05 (s), 98.13 (s), 119.61 (s), 128.17 (d), 129.01 (d), 129.13 (d), 129.18 (d), 131.63 (d), 138.42 (s), 139.18 (d), 140.44 (s).

IR ($CHCl_3$): 3059 v, 3033 w, 2226 w, 1609 w, 1588 w, 1566 m, 1510 vs, 1466 m, 1452 m, 1407 w, 1373 m, 1329 s, 1313 m, 1273 w, 1259 m, 1181 w, 1160 w, 1114 s, 1095 vs, 1045 m, 1014 s, 819 vs, 649 w cm^{-1}.

EI MS: 376 ($M^{+\bullet}$, 2), 361 (5), 346 (2), 256 (2), 217 (25), 205 (100), 143 (50), 129 (90), 115 (23), 90 (22), 43 (44).

HR EI MS: calculated for $C_{18}H_{17}OI$ 376.0324; found 376.0314.
Optical rotation: $[\alpha]^{22}_D$ -95° (c 0.20, CH_2Cl_2).

Trimethyl{[2-({[(1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}methyl) phenyl]ethynyl}silane (*S*)-**148**



A flame-dried Schlenk flask was charged with iodide (*S*)-**147** (2.56 g, 6.80 mmol), tetrakis(triphenylphosphine)palladium(0) (149 mg, 0.129 mmol, 2 mol%), copper iodide (49 mg, 0.257 mmol, 4 mol%) and diisopropylamine (25 ml) was added. Ethynyl(trimethyl)silane (1.0 ml, 7.22 mmol, 1.1 equiv.) was added and the reaction mixture was stirred at room temperature for 15 h. The inorganic material was filtered

off through a sintered glass (hexane) and the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane) to give product (*S*)-**148** (2.2 g, 94%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$): 0.23 (9H, s), 1.59 (3H, d, *J* = 6.6), 2.34 (3H, s), 4.53 (1H, q, *J* = 6.6), 4.78 (1H, d, *J* = 12.7), 4.96 (1H, d, *J* = 12.7), 7.10 (1H, m), 7.21 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.32 (1H, dt, *J* = 7.6, 7.6, 1.5), 7.33 (1H, m), 7.45 (1H, dd, *J* = 7.5, 1.5), 7.50 (1H, ddq, *J* = 7.7, 1.4, 0.6, 0.6, 0.6).

^{13}C NMR (126 MHz, $CDCl_3$): -0.06 (q), 21.43 (q), 22.22 (q), 65.86 (d), 68.76 (t), 85.27 (s), 88.30 (s), 99.03 (s), 102.67 (s), 119.69 (s), 121.67 (s), 127.08 (d), 127.47 (d), 128.63 (d), 128.94 (d), 131.64 (d), 132.24 (d), 138.32 (s), 140.54 (s).

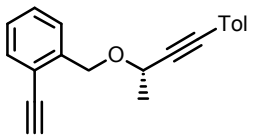
IR ($CHCl_3$): 3071 w, 3033 w, 2901 m, 2226 w, 2156 s, 1607 w, 1602 w, 1570 w, 1510 s, 1484 m, 1450 s, 1408 w, 1372 m, 1328 s, 1312 m, 1289 w, 1261 s, 1251 vs, 1178 w, 1159 w, 1130 m, 1108 s, 1094 vs, 1041 m, 1029 m, 1022 m, 869 vs, 845 vs, 819 vs, 699 m, 595 w cm^{-1}.

EI MS: 346 ($M^{+\bullet}$, 3), 331 (6), 273 (9), 203 (12), 188 (32), 179 (38), 173 (42), 143 (15), 128 (14), 115 (9), 86 (11), 73 (100), 59 (11), 43 (10).

HR EI MS: calculated for $C_{23}H_{26}OSi$ 346.1753; found 346.1756.

Optical rotation: $[\alpha]^{22}_D$ -127° (c 0.70, CH_2Cl_2).

2-Ethynylbenzyl (1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl ether (*S*)-**149**



To a solution of silane (*S*)-**148** (2.2 g, 6.41 mmol) in dichloromethane (125 ml) and anhydrous K_2CO_3 (1.77g, 12.8 mmol, 2.0 equiv.) in methanol (25 ml) was added. After stirring at room temperature for 30 min, the reaction mixture was washed with water (2 x 150 ml) and the combined organic phases were dried over anhydrous $MgSO_4$. The volatiles were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 90:10) to give product (*S*)-**149** (1.65 g, 94%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$): 1.58 (3H, d, *J* = 6.6), 2.35 (3H, s), 3.27 (1H, s), 4.51 (1H, q, *J* = 6.6), 4.80 (1H, d, *J* = 12.5), 4.99 (1H, d, *J* = 12.5), 7.12 (2H, m), 7.24 (1H, dt, *J*

= 7.6, 7.6, 1.4), 7.34 (2H, m), 7.36 (1H, dt, *J* = 7.6, 7.6, 1.5), 7.50 (1H, dd, *J* = 7.7, 1.5), 7.53 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7).

^{13}C NMR (126 MHz, $CDCl_3$): 21.45 (q), 22.21 (q), 65.68 (d), 68.58 (t), 81.29 (s), 81.65 (d), 85.33 (s), 88.34 (s), 119.72 (s), 120.82 (s), 127.25 (d), 127.86 (d), 128.93 (d), 128.99 (d), 131.61 (d), 132.68 (d), 138.36 (s), 140.66 (s).

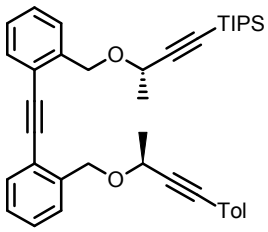
IR ($CHCl_3$): 3305 vs, 3072 m, 3032 m, 2226 w, 2106 w, 1602 w, 1571 w, 1510 vs, 1483 m, 1449 s, 1406 w, 1372 s, 1328 vs, 1312 m, 1288 w, 1258 m, 1180 m, 1160 w, 1130 s, 1108 vs, 1093 vs, 1041 s, 1028 m, 1022 s, 819 vs, 699 w, 655 s, 618 s cm^{-1}.

EI MS: 274 ($M^{+\bullet}$, 2), 273 (8), 259 (37), 231 (31), 215 (17), 158 (17), 143 (100), 129 (71), 115 (94), 91 (83), 43 (56).

HR EI MS: calculated for $C_{20}H_{18}O$ 274.1358; found 274.1359.

Optical rotation: $[\alpha]^{22}_D$ -151° (c 0.24, CH_2Cl_2).

Tris(1-methylethyl){(3*S*)-3-[(2-{[2-({[(1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}methyl)phenyl]ethynyl}benzyl)oxy]but-1-yn-1-yl}silane (*S*,*S*)-**150**



A flame-dried Schlenk flask was charged with tetrakis(triphenylphosphine)palladium(0) (131 mg, 0.113 mmol, 5 mol%), copper iodide (43 mg, 0.226 mmol, 10 mol%) and toluene (10 ml) was added. Then diisopropylamine (2 ml, 14.2 mmol, 6.3 equiv.) and a degassed solution of aryl iodide (*S*)-**113** (1.086 g, 2.26 mmol, 1.0 equiv.) in toluene (20 ml) were added and the reaction mixture was stirred at room temperature for 5 min. Then a degassed solution of the alkyne (*S*)-**149** (674 mg, 2.45 mmol, 1.1 equiv.) in toluene (10 ml) was added dropwise and the reaction mixture was stirred at room temperature overnight. The reaction mixture was filtered through a short pad of silica gel (hexane-diethyl ether 9:1) and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane) to provide product (*S*,*S*)-**150** (1.03 g, 77%) as a colourless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): 1.04 (21H, m), 1.49 (3H, d, *J* = 6.6), 1.59 (3H, d, *J* = 6.6), 2.33 (3H, bs), 4.34 (1H, q, *J* = 6.6), 4.55 (1H, q, *J* = 6.6), 4.81 (1H, dd, *J* = 12.6, 0.6),

4.87 (1H, d, *J* = 12.5), 5.01 (1H, dd, *J* = 12.6, 0.6), 5.07 (1H, d, *J* = 12.5), 7.03-7.06 (2H, m), 7.17 (1H, bdt, *J* = 7.5, 7.5, 1.4), 7.26-7.28 (2H, m), 7.27 (1H, dt, *J* = 7.5, 7.5, 1.4), 7.32 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.36 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.48 (1H, ddd, *J* = 7.6, 1.4, 0.5), 7.50 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7), 7.52 (1H, ddd, *J* = 7.6, 1.4, 0.5), 7.57 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7).

^{13}C NMR (151 MHz, $CDCl_3$): 11.09 (s), 18.54 (q), 21.44 (q), 22.31 (q), 22.41 (q), 65.68 (d), 65.69 (d), 68.73 (t), 68.82 (t), 85.42 (s), 85.81 (s), 88.35 (s), 91.44 (s), 91.52 (s), 107.62 (s), 119.58 (s), 121.69 (s), 121.88 (s), 127.13 (d), 127.20 (d), 127.52 (d), 127.72 (d), 128.39 (d), 128.51 (d), 128.93 (d), 131.61 (d), 132.04 (d), 132.11 (d), 138.26 (s), 139.94 (s), 139.98 (s).

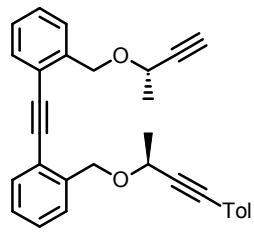
IR ($CHCl_3$): 3071 w, 2989 m, 2959 s, 2944 vs, 2892 s, 2866 vs, 2226 w, 2165 w, 1571 vw, 1510 s, 1492 m, 1463 m, 1454 m, 1407 vw, 1384 w, 1372 m, 1327 s, 1112 s, 1095 vs, 1066 s, 1062 w, 1040 m, 1021 m, 997 m, 945 w, 884 m, 819 s, 679 m, 650 w cm^{-1}.

ESI MS: 627 ($[M+K]^+$), 611 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{40}H_{48}O_2NaSi$ 611.3316, found 611.3314.

Optical rotation: $[\alpha]^{22}_D$ -220° (c 0.139, CH_2Cl_2).

1-({[(1*S*)-1-Methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}methyl)-2-{[2-({[(1*S*)-1-methylprop-2-yn-1-yl]oxy}methyl)phenyl]ethynyl}benzene (*S*,*S*)-**151**



In a Schlenk flask tetrabutylammonium fluoride trihydrate (711 mg, 2.25 mmol, 1.05 equiv.) was dissolved in THF (10 ml) under argon, cooled to 0 ºC and a solution of silane (*S*,*S*)-**150** (1.26 g, 2.14 mmol) in THF (15 ml) was added dropwise. The reaction mixture was stirred at 0 ºC for 10 min and then at room temperature for 30 min. The solution was filtered through a short pad of silica gel (ethyl acetate) and the solvents were removed *in vacuo*. The residue was dried on a membrane pump at room temperature overnight. After that it was purified by flash chromatography on silica gel (hexane) to provide product (*S*,*S*)-**151** (856 mg, 93%) as a colourless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): 1.49 (3H, d, *J* = 6.6), 1.59 (3H, d, *J* = 6.6), 2.32 (3H, bs), 2.44 (1H, d, *J* = 2.0), 4.30 (1H, dq, *J* = 6.6, 6.6, 6.6, 2.0), 4.56 (1H, q, *J* = 6.6), 4.79 (1H, dd, *J* = 12.6, 0.5), 4.90 (1H, d, *J* = 12.5), 5.00 (1H, dd, *J* = 12.6, 0.5), 5.08 (1H, d, *J* = 12.5), 7.03-7.06 (2H, m), 7.19 (1H, bdt, *J* = 7.5, 7.5, 1.4), 7.26-7.28 (2H, m), 7.28 (1H, bdt, *J* = 7.5, 7.5, 1.4), 7.33 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.36 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.50 (1H, ddd, *J* = 7.6, 1.4, 0.6), 7.50 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7), 7.55 (1H, ddd, *J* = 7.6, 1.4, 0.5), 7.60 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7).

^{13}C NMR (151 MHz, $CDCl_3$): 21.44 (q), 22.07 (q), 22.32 (q), 64.93 (d), 65.71 (d), 68.81 (t), 68.84 (t), 73.22 (d), 83.78 (s), 85.45 (s), 88.37 (s), 91.46 (s), 91.55 (s), 119.56 (s), 121.81 (s), 121.84 (s), 127.26 (d), 127.29 (d), 127.64 (d), 127.76 (d), 128.47 (d), 128.56 (d), 128.94 (d), 131.60 (d), 132.06 (d), 132.13 (d), 138.30 (s), 139.61 (s), 139.95 (s).

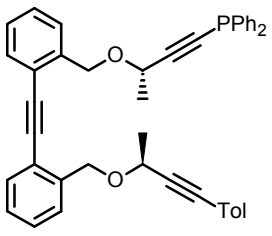
IR ($CHCl_3$): 3306 s, 3071 w, 2991 s, 2868 m, 2225 w, 2112 vw, 1602 w, 1571 w, 1510 s, 1493 m, 1452 m, 1406 vw, 1373 m, 1328 s, 1180 vw, 1113 vs, 1098 vs, 1042 m, 1022 m, 945 w, 819 s, 638 m cm^{-1}.

ESI MS: 471 ($[M+K]^+$), 455 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{31}H_{28}O_2Na$ 455.1982, found 455.1986.

Optical rotation: $[\alpha]^{22}_D$ -223° (c 0.244, CH_2Cl_2).

{(3*S*)-3-[(2-{[2-({[(1*S*)-1-Methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}methyl) phenyl]ethynyl}benzyl)oxy]but-1-yn-1-yl}(diphenyl)phosphane (*S*,*S*)-**152**



In a flame-dried Schlenk flask alkyne (*S*,*S*)-**151** (85 mg, 0.197 mmol) was dissolved in THF (6 ml) under argon and was cooled to -78 ºC. To this solution a solution of *n*-BuLi (1.6 M in hexanes, 135 µl, 0.216 mmol, 1.1 equiv.) was added dropwise and after 2 min chlorodiphenylphosphine (46 µl, 0.25 mmol, 1.3 equiv.) was added and the reaction mixture was stirred at -78 ºC for 10 min. Then it was allowed to warm up to room temperature and was stirred for additional 30 min. The reaction was quenched with a few drops of ethanol and solvents were removed

in vacuo. The residue was purified by flash chromatography on reversed phase silica gel (methanol) to provide product (*S*,*S*)-**152** (73 mg, 59%) as an oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.56 (6H, d, *J* = 6.6), 2.31 (3H, bs), 4.51 (2H, q, *J* = 6.6), 4.81 (1H, d, *J* = 12.6), 4.85 (1H, d, *J* = 12.5), 5.02 (1H, d, *J* = 12.6), 5.05 (1H, d, *J* = 12.5), 7.02-7.05 (2H, m), 7.17 (1H, dt, *J* = 7.5, 7.5, 1.4), 7.19 (1H, dt, *J* = 7.5, 7.5, 1.4), 7.25-7.28 (2H, m), 7.25-7.29 (6H, m), 7.30 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.33 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.46 (1H, bdd, *J* = 7.6, 1.4), 7.48 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7), 7.49 (1H, bdd, *J* = 7.7, 1.4), 7.53 (1H, ddq, *J* = 7.8, 1.4, 0.7, 0.7, 0.7), 7.54-7.29 (4H, m).

^{13}C NMR (151 MHz, $CDCl_3$): 21.43 (q), 22.05 (q), 22.30 (q), 65.66 (d), 66.02 (d), 68.81 (t), 69.12 (t), 81.99 (s, J_{PC}=9.0), 85.42 (s), 85.42 (s), 88.41 (s), 91.42 (s), 108.65 (s, J_{PC}=1.3), 119.56 (s), 121.73 (s), 121.79 (s), 127.26 (d), 127.28 (d), 127.65 (d), 127.72 (d), 128.44 (d, J_{PC}=11.9), 128.51 (d), 128.53 (d, J_{PC}=7.7), 128.56 (d), 128.94 (d), 128.95 (d, J_{PC}=7.4), 131.59 (d), 132.06 (d), 132.15 (d), 132.36 (d, J_{PC}=10.3), 132.50 (d, J_{PC}=10.5), 136.00 (s, J_{PC}=4.3), 136.03 (s, J_{PC}=4.3), 138.27 (s), 139.63 (s), 139.90 (s).

^{31}P NMR (162 MHz, $CDCl_3$): -34.39 (s).

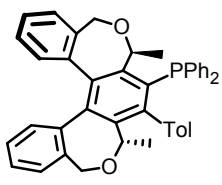
IR ($CHCl_3$): 3061 w, 2991 m, 2936 w, 2868 m, 2225 w, 2187 vw, 1602 w, 1586 vw, 1572 w, 1510 m, 1492 m, 1480 m, 1452 m, 1436 m, 1406 vw, 1389 w, 1372 m, 1327 s, 1287 vw, 1181 w, 1112 s, 1096 vs, 1041 m, 1026 m, 1000 w, 949 w, 819 m, 696 s cm^{-1}.

ESI MS: 655 ($[M+K]^+$), 639 ($[M+Na]^+$), 617 ($[M+H]^+$).

HR ESI MS: calculated for $C_{43}H_{38}O_2P$ 617.2604, found 617.2604.

Optical rotation: $[\alpha]^{22}_D$ -208° (c 0.550, CH_2Cl_2).

[(*P*,3*S*,6*S*)-3,6-Dimethyl-5-(4-methylphenyl)-1,3,6,8-tetrahydrodibenzo[*e*,*e'*]benzo [1,2-*c*:4,3-*c'*]bisoxepin-4-yl](diphenyl)phosphane (*P*,*S*,*S*)-**153**



A solution of triyne (*S*,*S*)-**152** (40 mg, 0.064 mmol) and dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (5 µl, 0.038 mmol, 0.6 equiv.) in THF (18 ml) was passing through a continuous-flow

reactor at temperature of 250 ºC, pressure 70 bar with a flow rate of 0.5 ml/min. Then volatiles were removed *in vacuo* and the product was purified by flash chromatography on reversed phase silica gel (methanol) to provide product (*P*,*S*,*S*)-**153** (17 mg, 42%) as yellow crystals. Single crystal was grown by layer-diffusion technique and slow evaporation form a saturated dichlorometane solution layered by heptane.

M.p.: 144 ºC (decomposition, heptane).

^{1}H NMR (600 MHz, $CDCl_3$): -0.09 (3H, d, *J* = 7.1), 0.62 (3H, d, *J* = 7.1), 2.37 (3H, bs), 4.37 (1H, d, *J* = 11.5), 4.78 (2H, d, *J* = 11.5), 4.84 (1H, d, *J* = 11.5), 4.97 (1H, q, *J* = 7.1), 5.29 (1H, dq, *J* = 7.1, 7.1, 7.1, 1.6), 6.48 (1H, dd, *J* = 7.7, 1.3), 6.50 (1H, dd, *J* = 7.7, 1.3), 6.89 (1H, dt, *J* = 7.6, 7.6, 1.3), 6.91 (1H, dd, *J* = 7.7, 1.8), 6.95 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.07 (1H, bdd, *J* = 7.7, 1.8), 7.18-7.23 (2H, m), 7.19-7.24 (6H, m), 7.20-7.22 (2H, m), 7.24-7.33 (2H, m), 7.31 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.38-7.40 (1H, m), 7.42-7.45 (2H, m).

^{13}C NMR (151 MHz, $CDCl_3$): 20.36 (q), 21.39 (q), 22.02 (q), 67.07 (t), 67.37 (t), 72.75 (d, J_{PC} = 4.4), 73.65 (d), 127.12 (d), 127.26 (d), 127.34 (d), 127.68 (d), 127.81 (d), 128.10 (d, J_{PC} = 5.2), 128.17 (d), 128.22 (d, J_{PC} = 5.0), 128.48 (d), 128.50 (d), 128.66 (d, J_{PC}=4.5), 129.14 (d, 2C), 129.56 (d, J_{PC} = 5.2), 131.12 (d, J_{PC} = 18.9), 131.81 (d), 131.86 (d), 131.90 (d, J_{PC} = 18.4), 135.46 (s, J_{PC} = 6.5), 136.10 (s, J_{PC} = 21.9), 136.77 (s), 137.56 (s, J_{PC} = 13.6), 137.96 (s, J_{PC} = 8.1), 138.37 (s, J_{PC} = 21.1), 138.85 (s), 139.52 (s, J_{PC} = 13.0), 139.53 (s), 139.88 (s), 140.30 (s), 143.93 (s, J_{PC}= 3.9), 151.56 (s, J_{PC} = 41.2).

^{31}P NMR (162 MHz, $CDCl_3$): -11.76 (s).

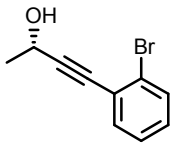
IR ($CHCl_3$): 3073 w, 3058 w, 2969 m, 2927 m, 2863 w, 1711 w, 1603 vw, 1585 w, 1512 w, 1487 w, 1480 w, 1462 w, 1453 w, 1435 m, 1407 w, 1385 w, 1370 m, 1304 w, 1182 w, 1120 w, 1111 m, 1089 s, 1078 vs, 1046 m, 1028 w, 1020 w, 994 w, 948 w, 836 m, 697 s, 495 m cm^{-1}.

ESI MS: 655 ($[M+K]^+$), 639 ($[M+Na]^+$), 617 ($[M+H]^+$).

HR ESI MS: calculated for $C_{43}H_{38}O_2P$ 617.26039, found 617.26044.

Optical rotation: $[\alpha]^{22}_D$ -144° (c 0.152, CH_2Cl_2).

(2*S*)-4-(2-Bromophenyl)but-3-yn-2-ol (*S*)-**154**



A flame-dried Schlenk flask was charged with tetrakis(triphenylphosphine)palladium(0) (152 mg, 0.132 mmol, 2 mol%), copper iodide (56 mg, 0.294, 4 mol%), 1-bromo-2-iodobenzene (1.0 ml, 7.79 mmol) and diisopropylamine (15 ml) was added under argon, then the reaction mixture as was cooled to 0 ºC. (*S*)-Butyn-2-ol (*S*)-**111** (650 µl, 8.29 mmol, 1.06 equiv.) was added dropwise and the reaction mixture was stirred at room temperature overnight. Then it was filtered through a sintered glass (hexane), concentrated *in vacuo* and dried at a membrane pump. The residue was purified by flash chromatography on silica gel (hexane-diethyl ether 95:5 to 90:10) to provide product (*S*)-**154** (1.75 g, 99%) as an orange oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.59 (3H, d, *J* = 6.6), 4.81 (1H, q, *J* = 6.6), 7.17 (1H, ddd, *J* = 8.1, 7.4, 1.7), 7.26 (1H, ddd, *J* = 7.6, 7.6, 1.2), 7.46 (1H, ddd, *J* = 7.7, 1.7, 0.4), 7.58 (1H, ddd, *J* = 8.1, 1.2, 0.4).

^{13}C NMR (151 MHz, $CDCl_3$): 24.22 (q), 58.93 (d), 82.61 (s), 95. 53 (s), 124.64 (s), 125.55 (s), 126.98 (d), 129.57 (d), 132.37 (d), 133.37 (d).

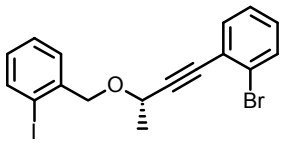
IR ($CHCl_3$): 3602 m, 3442 w, 3072 w, 3058 w, 2988 m, 2234 vw, 1587 w, 1559 w, 1470 vs, 1449 w, 1435 m, 1376 m, 1359 m, 1331 m, 1280 w, 1255 m, 1161 vw, 1122 m, 1077 m, 1051 m, 1027 s, 935 m, 854 m, 732 vs, 655 m, 586 w, 507 w, 445 m cm^{-1}.

EI MS: 226 ($M^{+\bullet}$, with ^{81}Br, 17), 224 ($M^{+\bullet}$, with ^{79}Br, 18), 211 (26), 209 (32), 183 (17), 181 (25), 145 (100), 128 (11), 115 (16), 102 (56), 75 (18), 63 (10), 51 (7), 43 (15).

HR EI MS: calculated for $C_{10}H_9O^{79}Br$ 223.9837, found 223.9843.

Optical rotation: $[\alpha]^{22}_D$ -28° (c 0.081, CH_2Cl_2).

(1*S*)-3-(2-Bromophenyl)-1-methylprop-2-yn-1-yl 2-iodobenzyl ether (*S*)-**155**



In a flame-dried Schlenk flask potassium hydride (dispersion in mineral oil, 227 mg, 5.67 mmol, 1.8 equiv.) was washed with hexane under argon and then dried under vacuum. THF (10 ml) was added and the suspension was cooled to 0 ºC. A solution of alcohol (*S*)-**154**

(712 mg, 3.16 mmol) in THF (8 ml) was slowly added and the mixture was stirred at 0 ºC for 20 min. Then a solution of 2-iodobenzyl bromide **110** (1.28 mg, 4.32 mmol, 1.36 equiv.) in THF (5 ml) was added and the reaction mixture was stirred at 0 ºC for 30 min. After the reaction completion the solvent was removed *in vacuo*, the residue was dissolved in dichloromethane (100 ml), washed with water (2 x 100 ml) and brine (50 ml). The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was evaporated *in vacuo* and the compound was purified by flash chromatography on silica gel (hexane:acetone 100:0 to 95:5) to provide product (*S*)-**155** (1.18 g, 85%) as an oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.63 (3H, d, *J* = 6.6), 4.58 (1H, q, *J* = 6.6), 4.62 (1H, bd, *J* = 12.5), 4.91 (1H, bd, *J* = 12.5), 6.99 (1H, dtt, *J* = 7.6, 7.6, 1.7, 0.6, 0.6), 7.17 (1H, ddd, *J* = 7.9, 7.5, 1.7), 7.25 (1H, dt, *J* = 7.6, 7.6, 1.2), 7.35 (1H, dt, *J* = 7.5, 7.5, 1.2), 7.48 (1H, ddd, *J* = 7.7, 1.7, 0.4), 7.51 (1H, dddd, *J* = 7.6, 1.7, 0.9, 0.7), 7.59 (1H, ddd, *J* = 7.9, 1.2, 0.4), 7.83 (1H, dd, *J* = 7.9, 1.2).

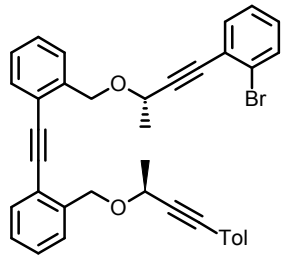
^{13}C NMR (151 MHz, $CDCl_3$): 22.00 (q), 65.70 (d), 74.56 (t), 84.00 (s), 93.55 (s), 98.11 (s), 124.83 (s), 125.68 (s), 126.96 (d), 128.18 (d), 129.12 (d), 129.22 (d), 129.52 (d), 132.37 (d), 133.44 (d), 139.20 (d), 140.36 (s).

IR ($CHCl_3$): 3069 w, 3060 w, 2230 vw, 1587 w, 1566 w, 1560 w, 1470 vs, 1453 m, 1436 s, 1373 m, 1328 s, 1314 m, 1273 w, 1161 w, 1121 s, 1114 s, 1096 vs, 1048 m, 1044 s, 1027 s, 1014 s, 946 w, 921 w, 863 w, 656 m, 650 w, 581 w, 527 w, 445 w, 429 w cm^{-1}.

ESI MS: 465 ($[M+Na]^+$, with ^{81}Br), 463 ($[M+Na]^+$, with ^{79}Br).

HR ESI MS: calculated for $C_{17}H_{14}O^{79}BrINa$ 462.9165, found 462.9163.

Optical rotation: $[\alpha]^{22}_D$ -90° (c 0.202, CH_2Cl_2).



1-Bromo-2-{(3*S*)-3-[(2-{[2-({[(1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}methyl)phenyl] ethynyl}benzyl)oxy]but-1-yn-1-yl}benzene (*S*,*S*)-**156**

In a Schenk flask tetrakis(triphenylphosphine)palladium(0)

(105 mg, 0.091 mmol, 5 mol%) and copper iodide (35 mg, 0.184 mmol, 10 mol%) were flushed with argon and a solution of aryl iodide (*S*)-**155** (800 mg, 1.81 mmol) in diisopropylamine (20 ml) at 0 ºC was added. After stirring for 10 min at 0 ºC alkyne (*S*)-**149** (507 mg, 1.85 mmol, 1.02 equiv.) in diisopropylamine (20 ml) was added and left stirring at 0 ºC for 1 h. The reaction mixture was allowed to warm up to room temperature and stirred for additional 2 h. Then it was filtered through a sintered glass (hexane) and the volatiles were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) to afford product (*S*,*S*)-**156** (804 mg, 75%) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.56 (3H, d, *J* = 6.6), 1.60 (3H, d, *J* = 6.6), 2.32 (3H, bs), 4.53 (1H, q, *J* = 6.6), 4.58 (1H, q, *J* = 6.6), 4.88 (1H, d, *J* = 12.6), 4.91 (1H, d, *J* = 12.5), 5.07 (1H, d, *J* = 12.6), 5.13 (1H, d, *J* = 12.5), 7.04 (2H, m), 7.12 (1H, ddd, *J* = 8.0, 7.4, 1.8), 7.17 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.19 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.27 (2H, m), 7.29 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.32 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.34 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.39 (1H, bdd, *J* = 7.7, 1.8), 7.50 (1H, ddd, *J* = 7.7, 1.4, 0.5), 7.51 (1H, ddd, *J* = 7.7, 1.4, 0.5), 7.53 (1H, ddd, *J* = 8.0, 1.3, 0.5), 7.53 (1H, ddq, *J* = 7.6, 1.4, 0.7, 0.7, 0.7), 7.55 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7).

^{13}C NMR (151 MHz, $CDCl_3$): 21.44 (q), 22.07 (q), 22.29 (q), 65.61 (d), 65.67 (d), 68.83 (t), 69.00 (t), 83.80 (s), 85.41 (s), 88.38 (s), 91.54 (s), 91.55 (s), 93.92 (s), 119.58 (s), 121.83 (s), 121.92 (s), 124.82 (s), 125.58 (s), 126.87 (d), 127.21 (d), 127.28 (d), 127.73 (d), 127.83 (d), 128.46 (d), 128.49 (d), 128.93 (d), 129.37 (d), 131.61 (d), 132.10 (d), 132.13 (d), 132.28 (d), 133.44 (d), 138.26 (s), 139.78 (s), 139.91 (s).

IR ($CHCl_3$): 3306 w, 3071 w, 2226 w, 1602 w, 1588 vw, 1571 vw, 1559 vw, 1510 m, 1493 m, 1470 s, 1452 m, 1435 m, 1407 vw, 1372 m, 1329 s, 1259 w, 1180 vw, 1160 w, 1130 m, 1113 s, 1095 vs, 1064 s, 1027 m, 948 w, 865 w, 819 s cm^{-1}.

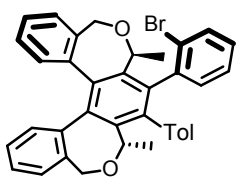
ESI MS: 611 ($[M+Na]^+$, with ^{81}Br), 609 ($[M+Na]^+$, with ^{79}Br).

HR ESI MS: calculated for $C_{37}H_{31}O_2{}^{79}BrNa$ 609.1400, found 609.1393.

Optical rotation: $[\alpha]^{22}_D$ -201° (c 0.065, acetone).

(*P*,S_a,3*S*,6*S*)-4-(2-Bromophenyl)-3,6-dimethyl-5-(4-methylphenyl)-1,3,6,8-tetrahydrodibenzo[*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepine (*P*,S_a,*S*,*S*)-**157**

Procedure using $CoCp(CO)_2$ complex and microwave irradiation



In a microwave vial triyne (*S*,*S*)-**156** (51.9 mg, 0.088 mmol) and triphenylphosphine (47 mg, 0.18 mmol, 2.0 equiv.) were dissolved in THF (5 ml) and dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (15 µl, 0.11 mmol, 1.3 equiv.) was added under argon. The reaction was heated in a microwave reactor at 200 ºC for 10 min and then the volatiles were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-acetone 100:0 to 95:5) to provide product (*P*,*S*,*S*)-**157** (30.5 mg, 60%, R_a:S_a = 44:56) as a solid. The atropisomers were separated on the preparative HPLC column Chirallica PST-4 (5 µm, 250 x 4.6 mm, chiral stationary phase: cellulose tris(phenylcarbamate, heptane-2-propanol 9:1, flow rate: 5 ml/min, (S_a)-atropisomer t_R = 11.2 min, (R_a)-atropisomer t_R = 18.5 min). The single crystal of (*P*,S_a,*S*,*S*)-**157** was grown by slow evaporation from a saturated acetonitrile solution.

M.p.: 230-233 ºC (heptane).

^{1}H NMR (600 MHz, $CDCl_3$, T = 280 K): 0.51 (3H, d, *J* = 7.1), 0.65 (3H, d, *J* = 7.1), 2.16 (3H, bs), 4.51 (1H, d, *J* = 11.4), 4.53 (1H, d, *J* = 11.5), 4.68 (1H, q, *J* = 7.1), 4.75 (1H, d, *J* = 11.5), 4.82 (1H, q, *J* = 7.1), 4.82 (1H, d, *J* = 11.4), 6.50 (1H, dd, *J* = 7.7, 1.3), 6.56 (1H, dd, *J* = 7.8, 1.3), 6.65 (1H, dd, *J* = 7.7, 1.9), 6.78 (1H, ddq, *J* = 7.7, 1.9, 0.7, 0.7, 0.7), 6.91 (1H, dt, *J* = 7.6, 7.6, 1.3), 6.92 (1H, dt, *J* = 7.5, 7.5, 1.2), 6.93 (1H, dt, *J* = 7.7, 7.7, 1.4), 6.96 (1H, ddq, *J* = 7.7, 1.9, 0.7, 0.7, 0.7), 7.13 (1H, ddd, *J* = 8.0, 7.4, 1.8), 7.14 (1H, dt, *J* = 7.5, 7.5, 1.3), 7.16 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.17 (1H, dd, *J* = 7.6, 1.8), 7.27 (1H, dd, *J* = 8.0, 1.2), 7.32 (1H, dd, *J* = 7.7, 1.9), 7.34 (1H, dd, *J* = 7.4, 1.3), 7.35 (1H, dd, *J* = 7.5, 1.4).

^{13}C NMR (151 MHz, $CDCl_3$): 21.18 (q), 21.99 (q), 22.26 (q), 67.33 (t), 67.37 (t), 72.44 (d), 72.80 (d), 124.17 (s), 126.73 (d), 127.07 (d), 127.23 (d), 127.29 (d), 127.60 (d), 127.62 (d), 127.67 (d), 128.31 (d), 128.50 (d), 128.54 (d, 2C), 129.74 (d), 131.57 (d), 131.91 (d), 132.04 (d), 132.09 (d), 135.99 (s), 136.86 (s), 136.86 (s), 136.91 (s),

137.47 (s), 137.55 (s), 137.57 (s), 137.67 (s), 139.77 (s), 139.83 (s), 140.63 (s), 140.86 (s), 141.69 (s).

IR ($CHCl_3$): 3067 w, 2966 s, 2927 vs, 2861 s, 1615 vw, 1604 w, 1591 vw, 1581 vw, 1562 w, 1514 m, 1489 vw, 1473 m, 1462 m, 1436 w, 1405 vw, 1371 s, 1308 w, 1299 w, 1254 m, 1183 w, 1164 w, 1149 m, 1121 m, 1078 vs, 1027 m, 1020 w, 948 w, 838 m, 804 w, 696 w, 685 w, 572 vw, 453 w, 422 w cm^{-1}. Compared to atropisomer (*P*,R_a,*S*,*S*)-**157**: weaker band 1615 vw, band 1254 m instead of 1261 m, additional band 685 w.

EI MS: 588 ($M^{+\bullet}$, with ^{81}Br, 46), 586 ($M^{+\bullet}$, with ^{79}Br, 45), 573 (98), 571 (100), 555 (12), 543 (27), 541 (34), 525 (37), 507 (13), 492 (7), 474 (13), 462 (27), 446 (45), 434 (49), 419 (31), 403 (15), 400 (12), 387 (8), 376 (5), 339 (20), 326 (23), 313 (12), 302 (6), 289 (5), 252 (3), 215 (5), 207 (5), 200 (4), 155 (5), 145 (13), 113 (10), 85 (17), 71 (22), 57 (22), 55 (6).

HR EI MS: calculated for $C_{37}H_{31}O_2{}^{79}Br$ 586.1507, found 586.1502.

Optical rotation: $[\alpha]^{22}_D$ -217° (c 0.248, CH_2Cl_2).

(*P*,S_a,3*S*,6*S*)-4-(2-Bromophenyl)-3,6-dimethyl-5-(4-methylphenyl)-1,3,6,8-tetrahydrodibenzo[*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepine (*P*,S_a,*S*,*S*)-**157**

Procedure using $CoCp(CO)_2$ complex and halogen lamp irradiation

In a Schlenk flask triyne (*S*,*S*)-**156** (29 mg, 0.049 mmol), dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (6.5 µl, 0.050 mmol, 1.0 equiv.) and triphenylphosphine (26 mg, 0.099 mmol, 2.0 equiv.) were suspended in decane (4 ml) and heated at 140 ºC for 2 h. Then the reaction mixture was purified by chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) to provide a yellow solid, which was further recrystallised (hexane) to give product (10 mg, 35%) as a 3:2 mixture of (*P*,S_a,*S*,*S*)-**157** and (*P*,R_a,*S*,*S*)-**157**.

Procedure using CoCp(CO)(fum) complex and microwave irradiation

In a 5 ml Biotage microwave vial triyne (*S*,*S*)-**156** (156 mg, 0.197 mmol), carbonyl(η^5-cyclopentadienyl)(η^2-dimethylfumarate)cobalt(I) (60 mg, 0.201 mmol, 1.0 equiv.) and

silicon carbide (50 mg) were suspended in THF (5 ml) and heated in a microwave reactor at 180 ºC for 10 min. The volatiles were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 85:5) to provide product (111 mg, 96%) as a 3:2 mixture of (*P*,S_a,*S*,*S*)-**157** and (*P*,R_a,*S*,*S*)-**157**.

Procedure using RhCp*$(C_2H_2)_2$ complex and halogen lamp irradiation

In a Schlenk flask triyne (*S*,*S*)-**156** (21 mg, 0.035 mmol), (pentamethyl-η^5-cyclopentadienyl)(di-η^2-ethene)rhodium(I) (10.5 mg, 0.035 mmol, 1.0 equiv.) were suspended in decane (4 ml) and heated by halogen lamp irradiation at 140 ºC for 1 h. Then the reaction mixture was purified by chromatography on silica gel (hexane-ethyl acetate 100:0 to 90:10) to provide a yellow solid (10 mg, 50%) as a 3:2 mixture of (*P*,S_a,*S*,*S*)-**157** and (*P*,R_a,*S*,*S*)-**157**.

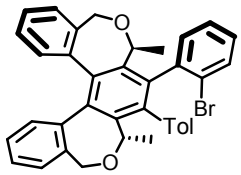
Procedure using RhCp*$(C_2H_2)_2$ complex and microwave irradiation at 140°C

In a 5 ml Biotage microwave vial triyne (*S*,*S*)-**156** (70 mg, 0.119 mmol), (pentamethyl-η^5-cyclopentadienyl)(di-η^2-ethene)rhodium(I) (33 mg, 0.112 mmol, 0.9 equiv.) were dissolved in THF (5 ml) and heated in a microwave reactor at 140 ºC for 15 min. Then the volatiles were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 85:15) to provide product (27 mg, 42%) as a 7:3 mixture of (*P*,S_a,*S*,*S*)-**157** and (*P*,R_a,*S*,*S*)-**157**.

Procedure using RhCp*$(C_2H_2)_2$ complex and microwave irradiation at 200°C

In a 5 ml Biotage microwave vial triyne (*S*,*S*)-**156** (19 mg, 0.032 mmol), (pentamethyl-η^5-cyclopentadienyl)(di-η^2-ethene)rhodium(I) (9.5 mg, 0.032 mmol, 1.0 equiv.) were dissolved in THF (5 ml) and heated in a microwave reactor at 200 ºC for 10 min. Then the volatiles were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 100:0 to 90:10) to provide product (19.4 mg, 88%) as a 1:1:1 mixture of (*P*,S_a,*S*,*S*)-**157** and (*P*,R_a,*S*,*S*)-**157** and (*P*,*S*,*S*)-**160**.

(*P*,*R*$_a$,3*S*,6*S*)-4-(2-Bromophenyl)-3,6-dimethyl-5-(4-methylphenyl)-1,3,6,8-tetrahydrodibenzo[*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepine (*P*,*R*$_a$,*S*,*S*)-**157**



M.p.: 295-300 ºC (heptane).

^{1}H NMR (600 MHz, $CDCl_3$, T=280 K): 0.54 (6H, d, *J* = 6.6), 2.16 (3H, bs), 4.49 (1H, d, *J* = 11.5), 4.53 (1H, d, *J* = 11.4), 4.68 (1H, q, *J* = 6.6), 4.81 (1H, d, *J* = 11.4), 4.84 (1H, q, *J* = 6.6), 4.85 (1H, d, *J* = 11.5), 6.51 (1H, dd, *J* = 7.8, 1.4), 6.54 (1H, dd, *J* = 7.8, 1.4), 6.81 (1H, ddt, *J* = 7.7, 1.9, 0.7, 0.7), 6.86 (1H, dd, *J* = 7.5, 1.8), 6.90 (1H, dt, *J* = 7.6, 7.6, 1.3), 6.91 (1H, dt, *J* = 7.4, 7.4, 1.2), 6.91 (1H, dt, *J* = 7.6, 7.6, 1.3), 6.93 (1H, dd, *J* = 7.7, 1.9), 6.95 (1H, ddt, *J* = 7.7, 1.9, 0.7, 0.7), 6.98 (1H, dd, *J* = 7.7, 1.9), 6.98 (1H, ddd, *J* = 8.0, 7.3, 1.8), 7.14 (2H, dt, *J* = 7.5, 7.5, 1.4), 7.34 (2H, dd, *J* = 7.5, 1.3), 7.40 (1H, dd, *J* = 8.0, 1.2).

^{13}C NMR (151 MHz, $CDCl_3$): 21.17 (q), 22.07 (q), 22.19 (q), 66.93 (t), 67.40 (t), 72.62 (d), 73.06 (d), 124.24 (s), 126.55 (d), 127.18 (d), 127.24 (d), 127.57 (d), 127.57 (d), 128.16 (d), 128.27 (d), 128.31 (d, 2C), 128.48 (d), 128.52 (d), 129.04 (d), 131.72 (d), 131.91 (d), 132.01 (d), 132.17 (d), 136.10 (s), 136.47 (s), 136.83 (s), 136.98 (s), 137.56 (s), 137.57 (s), 137.79 (s), 137.90 (s), 139.54 (s), 139.90 (s), 140.70 (s), 140.79 (s), 141.33 (s).

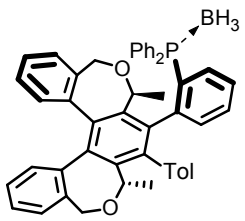
IR ($CHCl_3$): 3067 w, 2965 s, 2927 vs, 2858 s, 1616 vw, 1604 w, 1604 w, 1590 vw, 1581 vw, 1562 w, 1514 m, 1489 w, 1471 m, 1462 m, 1452 m, 1437 w, 1404 vw, 1371 m, 1308 w, 1299 w, 1261 m, 1183 w, 1164 w, 1149 m, 1120 m, 1112 s, 1079 vs, 1027 m, 1020 m, 948 w, 837 m, 804 w, 695 w, 572 vw, 455 w, 421 vw cm^{-1}. Compared to isomer (*P*,*S*$_a$,*S*,*S*)-**157**: stronger band 1616 vw, band 1261 m instead of 1254 m, band 685 w missing.

EI MS: 588 ($M^{+\bullet}$, with ^{81}Br, 38), 586 ($M^{+\bullet}$, with ^{79}Br, 37), 573 (98), 571 (100), 555 (8), 543 (31), 541 (30), 525 (35), 507 (49), 492 (7), 477 (17), 462 (35), 446 (39), 434 (57), 419 (39), 403 (15), 401 (13), 387 (8), 357 (5), 355 (10), 343 (15), 339 (19), 326 (26), 313 (12), 302 (6), 289 (5), 265 (3), 252 (6), 222 (5), 219 (11), 200 (4), 193 (5), 150 (3), 131 (6), 119 (3), 100 (2), 69 (15), 43 (6).

HR EI MS: calculated for $C_{37}H_{31}O_2{}^{79}Br$ 586.1507, found 586.1515.

Optical rotation: $[\alpha]^{22}_{D}$ -173° (c 0.258, CH_2Cl_2).

{2-[(*P*,S_a,3*S*,6*S*)-3,6-Dimethyl-5-(4-methylphenyl)-1,3,6,8-tetrahydrodibenzo [*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepin-4-yl]phenyl}(diphenyl)phosphane-borane complex (*P*,S_a,*S*,*S*)-**158**



In flame-dried Schlenk flask a solution of bromide (*P*,S_a,*S*,*S*)-**157** (18 mg, 0.030 mmol) in diethyl ether (1.5 ml) was cooled to -110 ºC and a solution of *t*-BuLi (1.7 M in pentane, 38 µl, 0.060 mmol, 2.0 equiv.) was added dropwise. The solution was stirred at -110 ºC for 1 min and then chlorodiphenylphosphine (15 µl, 0.084 mmol, 2.8 equiv.) was added dropwise. The reaction mixture was allowed to warm up to 0 ºC over a period of 2 h. Then a solution of borane-THF complex (2 M in THF, 2.0 ml, 2.0 mmol, 66 equiv.) was added and the reaction was stirred at room temperature for 30 min. Then the reaction mixture was filtered through a short pad of alumina (diethyl ether) and the volatiles were evaporated *in vacuo*. The column chromatography on silica gel (hexane-diethyl ether 95:5) afforded product (*P*,S_a,*S*,*S*)-**158** (11.5 mg, 55%) as a solid.

^{1}H NMR (600 MHz, $CDCl_3$): 0.35 (3H, d, *J* = 7.1), 0.47 (3H, d, *J* = 7.1), 2.15 (3H, bs), 4.56 (1H, d, *J* = 11.3), 4.56 (1H, d, *J* = 11.4), 4.68 (1H, q, *J* = 7.1), 4.78 (1H, d, *J* = 11.3), 4.88 (1H, q, *J* = 7.1), 4.98 (1H, d, *J* = 11.4), 6.48 (1H, bdd, *J* = 7.8, 2.0), 6.55 (1H, dd, *J* = 7.7, 1.3), 6.65 (1H, bdd, *J* = 7.8, 2.0), 6.65 (1H, dd, *J* = 7.7, 1.4), 6.74 (1H, bdd, *J* = 7.8, 2.0), 6.93 (1H, dt, *J* = 7.6, 7.6, 1.4), 6.96 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.14 (1H, bdt, *J* = 7.9, 7.9, 1.4), 7.17-7.25 (4H, m), 7.19 (1H, dt, *J* = 7.5, 7.5, 1.3), 7.19 (1H, dt, *J* = 7.5, 7.5, 1.4), 7.20-7.22 (1H, m), 7.29-7.33 (4H, m), 7.36 (1H, dd, *J* = 7.5, 1.4), 7.39 (1H, dd, *J* = 7.4, 1.4), 7.43-7.48 (2H, m), 7.49 (1H, tt, *J* = 7.3, 1.5), 7.53 (1H, ddd, *J* = 7.8, 4.4, 1.2), 7.54 (1H, bdd, *J* = 7.8, 2.0). The BH_3 signal was not determined because it was broad.

^{13}C NMR (151 MHz, $CDCl_3$): 20.99 (q), 21.09 (q), 21.92 (q), 67.30 (t), 67.53 (t), 72.11 (d), 72.61 (d), 125.78 (s, J_{PC} = 50.9), 126.45 (d, J_{PC} = 6.4), 126.76 (d), 127.27 (d), 127.46 (d), 127.53 (d), 127.91 (d), 128.26 (s, J_{PC} = 60.6, 2C), 128.33 (d, J_{PC} = 9.9, 2C), 128.36 (d), 128.46 (d, J_{PC} = 9.8, 2C), 128.63 (d), 130.30 (d, J_{PC} = 2.1), 130.37

(d, J_{PC} = 2.1), 130.41 (d, J_{PC} = 7.7), 130.85 (d), 131.14 (d), 131.88 (d), 132.29 (d), 132.53 (d, J_{PC} = 9.0, 2C), 132.71 (d, J_{PC} = 9.3, 2C), 134.17 (d, J_{PC} = 9.7), 135.44 (s), 135.79 (s), 136.76 (s), 137.09 (d), 137.09 (s), 137.35 (s), 137.45 (s), 137.57 (s), 138.39 (s), 139.66 (s), 139.80 (s, J_{PC} = 2.3), 140.45 (s), 141.96 (s), 146.75 (s, J_{PC} = 5.7).

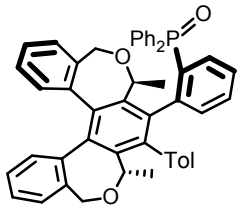
^{31}P NMR (202 MHz): 21.45 (s).

IR ($CHCl_3$): 3062 vw, 2958 s, 2442 vw, 2412 vw, 2356 vw, 2344 vw, 1603 vw, 1588 vw, 1514 w, 1486 w, 1464 m, 1437 w, 1379 w, 1370 w, 1186 vw, 1146 vw, 1127 vw, 1111 vw, 1098 vw, 1073 m, 1028 vw, 1021 vw, 1002 vw, 947 w, 838 w, 698 w, 494 w cm^{-1}.

ESI MS: 1436 ($[2M+Na]^+$), 729 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{49}H_{44}O_2BNaP$ 729.3064, found 729.3064.

Optical rotation: $[\alpha]^{22}_D$ -124° (c 0.160, CH_2Cl_2).



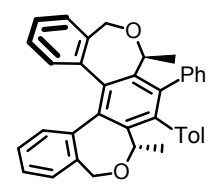
(2-((*P*,*S*$_a$,3*S*,6*R*)-3,6-dimethyl-5-(4-methylphenyl)-1,3,6,8-tetrahydrodibenzo[e,e']benzo[1,2-c:4,3-c']bisoxepin-4-yl)phenyl)(diphenyl)phosphane oxide (*P*,*S*$_a$,*S*,*S*)-**159**

^{31}P NMR (202 MHz): -14.70 (s).

ESI MS: 731 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{49}H_{41}O_3NaP$ 731.2686, found 731.2680.

Single crystal was grown from a saturated solution of isopropanol and dichloromethane.



(*P*,3*S*,6*S*)-3,6-Dimethyl-4-(4-methylphenyl)-5-phenyl-1,3,6,8-tetrahydrodibenzo [*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepine (*P*,*S*,*S*)-**160**

Prepared following the same procedure as for (*P*,*S*$_a$,*S*,*S*)-**158**. Bromide (*P*,*R*$_a$,*S*,*S*)-**157** (18 mg, 0.030 mmol), *t*-BuLi (38 µl, 0.060 mmol, 2.0 equiv.),

chlorodiphenylphosphine (15 µl, 0.084 mmol, 2.8 equiv.), diethyl ether (1.5 ml), solution of borane-THF complex (2 M in THF, 2.0 ml, 2.0 mmol, 66 equiv.). Chromatography: hexane- diethyl ether (1:0 to 95:5). Yield: 12.5 mg, 82%, as a solid.

^{1}H NMR (600 MHz, $CDCl_3$): 0.61 (6H, d, *J* = 7.1), 2.23 (3H, bs), 4.59 (2H, d, *J* = 11.4), 4.88 (2H, d, *J* = 11.4), 4.93 (1H, q, *J* = 7.1), 4.94 (1H, q, *J* = 7.1), 6.58 (2H, dd, *J* = 7.7, 1.2), 6.72 (1H, dd, *J* = 7.7, 1.9), 6.84-6.86 (2H, m), 6.96 (2H, dt, *J* = 7.6, 7.6, 1.3), 6.99-7.01 (2H, m), 7.04-7.10 (2H, m), 7.16-7.18 (1H, m), 7.20 (2H, dt, *J* = 7.6, 7.6, 1.2), 7.20-7.22 (1H, m), 7.40 (2H, dd, *J* = 7.5, 1.3).

^{13}C NMR (151 MHz, $CDCl_3$): 21.10 (q), 22.17 (q, 2C), 67.48 (t, 2C), 72.70 (d), 72.74 (d), 126.24 (d), 127.29 (d), 127.30 (d), 127.34 (d), 127.54 (d, 2C), 127.64 (d), 128.04 (d), 128.36 (d), 128.50 (d, 2C), 129.55 (d), 129.73 (d), 129.89 (d), 130.07 (d), 132.07 (d, 2C), 135.73 (s), 136.93 (s), 136.96 (s), 137.10 (s), 137.35 (s), 137.63 (s), 137.81 (s), 137.84 (s), 140.19 (s, 3C), 142.01 (s), 142.05 (s).

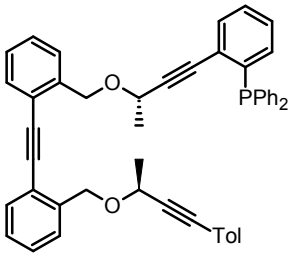
IR ($CHCl_3$): 3063 w, 3063 w, 2963 m, 2927 s, 2858 m, 1603 w, 1603 w, 1603 w, 1579 vw, 1557 vw, 1515 w, 1493 w, 1493 w, 1461 m, 1455 w, 1443 w, 1405 vw, 1371 m, 1298 vw, 1183 vw, 1162 vw, 1121 w, 1112 m, 1079 vs, 1071 s, 1046 m, 1026 w, 1026 w, 948 w, 838 w, 703 m cm^{-1}.

ESI MS: 531 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{37}H_{32}O_2Na$ 531.2295, found 531.2301.

Optical rotation: $[\alpha]^{22}_D$ -179° (c 0.183, CH_2Cl_2).

(2-{(3*S*)-3-[(2-{[2-({[(1*S*)-1-Methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}methyl) phenyl]ethynyl}benzyl)oxy]but-1-yn-1-yl}phenyl)(diphenyl)phosphane (*S*,*S*)-**161**



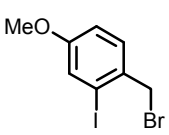
In a flame-dried Schlenk flask bromide (*S*,*S*)-**156** (28 mg, 0.048 mmol) was dissolved in THF (1.5 ml) and cooled to -85 °C. Then a solution of *n*-BuLi (1.6 M in hexanes, 30 µl, 0.048 mmol, 1.0 equiv.) was added and the solution was stirred at -85 °C for 1 min. After that chlorodiphenylphosphine (20 µl, 0.076 mmol, 1.6 equiv.) was added and the reaction mixture was stirred at -85 °C for

5 min. Then a cooling bath was removed and the solution was allowed to warm up to room temperature. The solvents were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 100:0 to 95:5) to provide the product (*S*,*S*)-**161** (15 mg, 45%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 1.31 (3H, d, *J* = 6.6 Hz), 1.56 (3H, d, *J* = 6.6 Hz), 2.32 (3H, s), 4.36 (1H, q, *J* = 6.6 Hz), 4.53 (1H, q, *J* = 6.6 Hz), 4.62 (1H, d, *J* = 12.3 Hz), 4.79 (1H, d, *J* = 12.3 Hz), 4.86 (1H, d, *J* = 12.6 Hz), 5.05 (1H, d, J = 12.6 Hz), 6.76 – 6.71 (1H, m), 7.04 (2H, d, *J* = 7.8 Hz), 7.21 – 7.13 (5H, m), 7.21 (1H, d, *J* = 1.6 Hz), 7.29 – 7.22 (8H, m), 7.31 (1H, s), 7.33 (1H, dd, *J* = 7.6, 1.3 Hz), 7.40 (1H, d, *J* = 7.7 Hz), 7.45 – 7.42 (2H, m), 7.49 (3H, td, *J* = 7.6, 1.0 Hz), 7.55 (1H, d, *J* = 7.7 Hz).

^{31}P NMR (162 MHz): -8.72 (s).

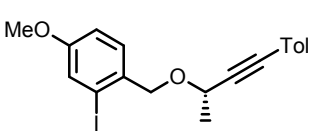
1-(Bromomethyl)-2-iodo-4-methoxybenzene 163



In a 500 ml round-bottom flask 2-iodo-4-bromo-methylbenzene **162** (2.74 g, 11.0 mmol), NBS (2.28 g, 12.8 mmol, 1.16 equiv.), catalytic amount of AIBN and K_2CO_3 were suspended in CCl_4 (30 ml) and heated to reflux for 2 h using an IR lamp. The reaction mixture was filtered through a short pad of silica gel (hexane-diethyl ether 9:1) and the solvents were removed *in vacuo* to afford product **163** (3.6 g, 98%) as an amorphous solid.
^{1}H NMR and ^{13}C NMR were in agreement with the published data.[65]

^{1}H NMR (400 MHz, $CDCl_3$): 3.80 (3H, s), 4.60 (2H, s), 6.87 (1H, dd, *J* = 8.5, 2.6), 7.36 (1H, d, *J* = 6.4), 7.38 (1H, s).

2-Iodo-4-methoxy-1-({[(1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy} methyl)benzene (*S*)-**164**



Potassium hydride (dispersion in mineral oil, 1.37 g, 34.0 mmol, 1.5 equiv.) was suspended in THF (20 ml) and cooled to 0 ºC. Then tolyl alcohol (*S*)-**145** (3.63 g, 22.67 mmol, 1.0 equiv.) in THF (10 ml) was added slowly and the reaction mixture was stirred at 0 ºC

for 1 h. Then **163** (6.84 g, 20.85 mmol, 0.9 equiv.) in THF (20 ml) was added and the reaction mixture allowed to warm up to room temperature and stirred overnight. A saturated aqueous solution of NH_4Cl (50 ml) was added to quench the excess of potassium hydride, then the product was extracted with ether (3 x 150 ml), the combined organic layers washed with water (3 x 150 ml) and dried over anhydrous Na_2SO_4. The solvents were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 92:8) to give the product (*S*)-**164** (4.81 g, 52%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): 1.57 (3H, d, *J* = 6.6), 2.35 (3H, s), 3.77 (3H, s), 4.53 (1H, d, *J* = 11.8), 4.79 (1H, d, *J* = 11.8), 4.89 (1H, q, *J* = 6.6), 6.89 (1H, dd, *J* = 8.5, 2.6), 7.12 (2H, m), 7.36 (2H, m), 7.36 (1H, d, *J* = 8.5), 7.38 (1H, d, *J* = 2.6).

^{13}C NMR (126 MHz, $CDCl_3$): 21.46 (q), 22.22 (q), 55.50 (q), 65.39 (d), 73.89 (t), 85.47 (s), 88.23 (s), 98.89 (s), 114.08 (d), 119.69 (s), 124.51 (d), 129.00 (d), 130.06 (d), 131.63 (d), 132.56 (s), 138.38 (s), 159.32 (s).

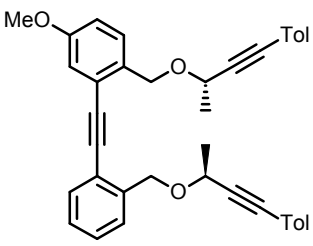
IR ($CHCl_3$): 3084 w, 3052 w, 3032 m, 2839 m, 2226 w, 1599 vs, 1566 s, 1510 vs, 1491 vs, 1465 s, 1440 s, 1401 m, 1372 m, 1328 s, 1313 s, 1284 s, 1250 s, 1182 m, 1153 w, 1128 s, 1119 s, 1106 vs, 1094 vs, 1037 vs, 1021 vs, 863 m, 819 vs, 647 w cm^{-1}.

EI MS: 406 ($M^{+\bullet}$, 16), 292 (24), 262 (16), 247 (53), 236 (32), 206 (18), 191 (86), 158 (29), 143 (100), 129 (47), 115 (29), 89 (25), 77 (23), 57 (28), 41 (24).

HR EI MS: calculated for $C_{19}H_{19}O_2I$ 406.0430; found 406.0439.

Optical rotation: $[\alpha]^{22}_D$ -80° (c 0.52, CH_2Cl_2).

4-Methoxy-1-({[(1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}methyl)-2-{[2-({[(1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}methyl)phenyl] ethynyl}benzene (*S*,*S*)-**165**



A Schlenk flask was charged with aryl iodide (*S*)-**164** (3.07 g, 7.55 mmol), tetrakis(triphenylphosphine)palladium(0) (470 mg, 0.407 mmol, 5 mol%), copper iodide (162 mg, 0.85 mmol,

11 mol%) and diisopropylamine (35 ml) was added and the reaction mixture was heated at 80 ºC under argon. A solution of alkyne (*S*)-**149** (2.17 g, 7.87 mmol, 1.04 equiv.) in diisopropylamine (20 ml) was added and the reaction mixture stirred at 80 ºC for 30 min. The reaction mixture was filtered through a sintered glass (hexane) and the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-diethyl ether 95:5) to give product (*S*,*S*)-**144** (3.00 g, 73%) as an orange oil.

^{1}H NMR (500 MHz, $CDCl_3$): 1.53 (3H, d, *J* = 6.6), 1.56 (3H, d, *J* = 6.6), 2.30 (3H, s), 2.31 (3H, s), 3.74 (3H, s), 4.49 (1H, q, *J* = 6.6), 4.52 (1H, q, *J* = 6.6), 4.79 (1H, d, *J* = 11.8), 4.87 (1H, d, *J* = 12.6), 4.97 (1H, d, *J* = 11.8), 5.04 (1H, d, *J* = 12.6), 6.89 (1H, dd, *J* = 8.5, 2.7), 7.03 (4H, m), 7.03 (1H, d, *J* = 2.7), 7.18 (1H, dt, *J* = 7.5, 7.5, 1.4), 7.25 (4H, m), 7.33 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.42 (1H, d, *J* = 8.5), 7.50 (1H, bdd, *J* = 7.7, 1.4), 7.53 (1H, ddq, *J* = 7.7, 1.4, 0.6, 0.6, 0.6).

^{13}C NMR (126 MHz, $CDCl_3$): 21.41 (q, 2C), 22.27 (q), 22.30 (q), 55.28 (q), 65.30 (d), 65.64 (d), 68.50 (t), 68.81 (t), 85.27 (s), 88.36 (s), 91.06 (s), 91.63 (s), 115.11 (d), 116.51 (d), 119.58 (s), 119.66 (s), 121.78 (s), 123.33 (s), 127.21 (d), 127.73 (d), 128.48 (d), 128.90 (d, 2C), 129.74 (d), 131.57 (d), 131.60 (d), 132.16 (d), 132.18 (s), 138.18 (s), 138.22 (s), 139.98 (s), 158.64 (s).

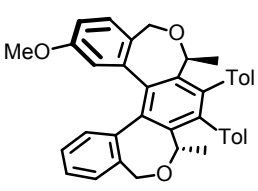
IR ($CHCl_3$): 2989 s, 2935 s, 2840 m, 2225 w, 1604 s, 1571 s, 1510 vs, 1502 s, 1485 m, 1452 s, 1444 s, 1420 m, 1389 m, 1372 s, 1328 vs, 1277 m, 1258 s, 1160 w, 1130 s, 1115 vs, 1108 vs, 1095 vs, 1060 vs, 1022 s, 947 m, 856 m, 819 vs, 708 m, 647 w, 545 m cm^{-1}.

ESI MS: 591 ($[M+K]^+$), 575 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{39}H_{36}O_3Na$ 575.2557; found 575.2555.

Optical rotation: $[\alpha]^{22}_D$ -198° (c 0.58, CH_2Cl_2).

(*P*,3*S*,6*S*)-11-Methoxy-3,6-dimethyl-4,5-bis(4-methylphenyl)-1,3,6,8-tetrahydro dibenzo[*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepine (*P*,*S*,*S*)-**166**



A flame-dried 20 ml microwave vial was charged with triyne (*S*,*S*)-**165** (236.8 mg, 0.428 mmol), dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (57 µl, 77.5 mg, 0.429 mmol, 1.0 equiv), triphenylphosphine (225.0 mg, 0.858 mmol, 2.0 equiv), ionic liquid [BDMIM][BF_4] (~100 mg) and THF (20 ml) and the resultant solution was heated in a microwave reactor at 200 ºC for 15 min. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 85:15) to give product (*P*,*S*,*S*)-**166** (163.6 mg, 70%) as a solid.

Mp: 122-124 ºC (hexane).

^{1}H NMR (500 MHz, $CDCl_3$): 0.62 (3H, d, *J* = 7.1), 0.65 (3H, d, *J* = 7.1), 2.24 (6H, s), 3.32 (3H, s), 4.54 (1H, d, *J* = 11.5), 4.58 (1H, d, *J* = 11.4), 4.80 (1H, d, *J* = 11.5), 4.87 (1H, d, *J* = 11.4), 4.91 (1H, q, *J* = 7.1), 4.93 (1H, q, *J* = 7.1), 6.09 (1H, d, *J* = 2.6), 6.62 (1H, dd, *J* = 7.7, 1.3), 6.72 (2H, m), 6.74 (1H, dd, *J* = 8.3, 2.6), 6.86 (2H, m), 7.01 (2H, m), 7.01 (1H, dt, *J* = 7.5, 7.5, 1.4), 7.05 (2H, m), 7.21 (1H, dt, *J* = 7.4, 7.4, 1.3), 7.28 (1H, d, *J* = 8.3), 7.40 (1H, dd, *J* = 7.5, 1.4).

^{13}C NMR (126 MHz, $CDCl_3$): 21.14 (q, 2C), 22.22 (q), 22.27 (q), 55.02 (q), 66.79 (t), 67.40 (t), 72.50 (d), 72.71 (d), 114.40 (d), 116.59 (d), 127.49 (d), 127.53 (d), 128.05 (d), 128.08 (d), 128.33 (d), 128.35 (d, 2C), 129.47 (d), 129.49 (d), 129.57 (d), 129.80 (d), 129.82 (d), 130.65 (s), 131.99 (d), 135.63 (s, 2C), 136.84 (s), 137.02 (s, 2C), 137.04 (s), 137.50 (s), 137.60 (s, 2C), 140.25 (s), 141.24 (s), 142.14 (s), 142.17 (s), 158.64 (s).

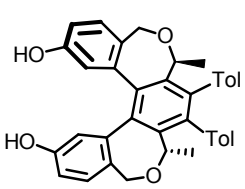
IR ($CHCl_3$): 2961 m, 2926 m, 2859 m, 2838 m,1615 m,1607 s, 1588 m, 1580 m, 1516 s, 1501 s, 1491 m, 1466 s, 1461 s,1445 m, 1430 m, 1404 w, 1370 s, 1317 m, 1283 m, 1183 m, 1146 s, 1130 m, 1123 m, 1111 s, 1077 vs, 1043 s, 1038 s, 1022 m, 859 s, 818 m, 698 w.

EI MS: 552 ($M^{+\bullet}$, 5), 537 (3), 519 (1), 149 (10), 111 (12), 97 (22), 85 (35), 71 (62), 57 (96), 43 (100).

HR EI MS: calculated for $C_{39}H_{36}O_3$ 552.2664; found 552.2678.

Optical rotation: $[\alpha]^{22}_{D}$ -127° (c 0.52, CH_2Cl_2).

(*P*,3*S*,6*S*)-3,6-Dimethyl-4,5-bis(4-methylphenyl)-1,3,6,8-tetrahydrodibenzo [*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepin-11-ol (*P*,*S*,*S*)-**167**



In a flame-dried Schlenk flask sodium hydride (dispersion in mineral oil, 921 mg, 23.0 mmol, 19.2 equiv.) was washed with hexane, dried under vacuum and then suspended in DMF (20 ml). It was cooled to 0 ºC, then ethanethiol (2.5 ml, 2.1 g, 33.8 mmol, 28.2 equiv.) was added and the mixture was stirred at room temperature for 30 min until all hydride was dissolved. Then the sodium ethanethiolate solution was cooled to 0 ºC and a solution of methoxy derivative (*P*,*S*,*S*)-**166** (636.3 mg, 1.2 mmol) in DMF (15 ml) was added and the reaction mixture was heated at 130 ºC for 18 h. The reaction mixture was diluted with an aqueous solution of HCl (1M, 100 ml) and extracted with dichloromethane (3 x 200 ml). The combined organic phases were washed with water (2 x 100 ml), brine (100 ml) and dried over anhydrous Na_2SO_4. The solvents were removed *in vacuo*, the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 1:1) to obtain product (*P*,*S*,*S*)-**167** (607 mg, 98%) as a white solid. Single crystal was grown by slow evaporation from a saturated acetonitrile solution.

Mp: 307-309°C (hexane).

^{1}H NMR (500 MHz, $CDCl_3$): 0.59 (3H, d, *J* = 7.1), 0.66 (3H, d, *J* = 7.1), 2.24 (6H, s), 4.53 (2H, d, *J* = 11.5), 4.79 (2H, d, *J* = 11.5), 4.81 (1H, d, *J* = 11.5), 4.91 (1H, q, *J* = 7.1), 4.92 (1H, q, *J* = 7.1), 6.05 (1H, d, *J* = 2.6), 6.65 (1H, dd, *J* = 7.8, 1.3), 6.67 (1H, dd, *J* = 8.1, 2.6), 6.72 (2H, m), 6.86 (2H, m), 7.01 (1H, dt, *J* = 7.7, 1.3), 7.01 (2H, m), 7.03 (2H, m), 7.21 (1H, dt, *J* = 7.4, 7.4, 1.3), 7.25 (1H, d, *J* = 8.1), 7.37 (1H, dd, *J* = 7.5, 1.3).

^{13}C NMR (126 MHz, $CDCl_3$): 21.14 (q, 2C), 22.13 (q), 22.21 (q), 66.73 (t), 67.39 (t), 72.49 (d), 72.73 (d), 114.63 (d), 118.65 (d), 127.47 (d), 127.67 (d), 128.08 (d, 2C), 128.34 (d), 128.36 (d), 128.54 (d), 129.41 (d), 129.44 (d), 129.78 (d), 129.88 (d), 130.47 (s), 131.92 (d), 135.66 (s, 2C), 136.75 (s), 136.95 (s, 3C), 137.42 (s), 137.46 (s), 137.50 (s), 140.05 (s), 141.70 (s), 142.17 (s), 142.22 (s), 154.96 (s).

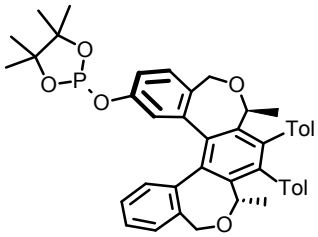
IR ($CHCl_3$): 3593 w, 3535 w, 3212 w, 1617 w, 1607 m, 1597 w, 1587 w, 1516 m, 1500 w, 1490 w, 1461 m, 1424 w, 1405 w, 1371 m, 1182 m, 1146 m, 1124 w, 1111 m, 1077 vs, 1022 m, 861 m, 698 w cm^{-1}.

EI MS: 538 ($M^{+\bullet}$, 2), 523 (1), 434 (5), 248 (4), 206 (3), 151 (37), 97 (27), 83 (38), 69 (50), 55 (84), 41 (100).

HR EI MS: calculated for $C_{38}H_{34}O_3$ 538.2508; found 538.2501.

Optical rotation: $[\alpha]^{22}_D$ -120° (c 0.56, CH_2Cl_2).

(*P*,3*S*,6*S*)-3,6-Dimethyl-4,5-bis(4-methylphenyl)-11-[(4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2-yl)oxy]-1,3,6,8-tetrahydrodibenzo[*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepine (*P*,*S*,*S*)-**168**



A flame-dried Schlenk flask was charged with the alcohol (*P*,*S*,*S*)-**167** (29.2 mg, 0.054 mmol), flushed with argon and triethylamine (300 µl, 2.15 mmol, 40 equiv.) and diethyl ether (5 ml) were added while stirred. Then 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (10 µl, 11.5 mg, 0.063 mmol, 1.2 equiv.) was added at room temperature. After stirring for 1 h the reaction mixture was filtered through a short pad of alumina (diethyl ether) and the volatiles were removed *in vacuo*. The product (*P*,*S*,*S*)-**168** (27.4 mg, 74%) was obtained as a colourless oil.

^{1}H NMR (500 MHz, CD_2Cl_2): 0.57 (3H, d, *J* = 7.1), 0.61 (3H, d, *J* = 7.1), 1.23 (6H, bs), 1.27 (3H, d, *J* = 0.7), 1.32 (3H, d, *J* = 0.7), 2.26 (6H, bs), 4.52 (1H, d, *J* = 11.5), 4.55 (1H, d, *J* = 11.4), 4.76 (1H, d, *J* = 11.5), 4.79 (2H, q, *J* = 7.1), 4.82 (1H, d, *J* = 11.4), 6.28 (1H, dd, *J* = 2.5, 0.8), 6.62 (1H, dd, *J* = 7.8, 1.3), 6.79-6.81 (2H, m), 6.86 (1H, ddd, *J* = 8.1, 2.5, 0.9), 6.91-6.94 (2H, m), 7.00 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.02-7.06 (4H, m), 7.23 (1H, dt, *J* = 7.4, 7.4, 1.3), 7.31 (1H, d, *J* = 8.1), 7.40 (1H, ddd, *J* = 7.5, 1.4, 0.6).

^{13}C NMR (126 MHz, CD_2Cl_2): 21.20 (q, 2C), 22.27 (q), 22.39 (q), 24.92 (q), 25.02 (q), 25.46 (q, J_{PC} = 3.4), 25.57 (q, J_{PC} = 3.2), 66.91 (t), 67.61 (t), 72.68 (d), 72.78 (d), 85.69 (s, J_{PC} = 7.4), 85.82 (s, J_{PC} = 7.6), 120.27 (d, J_{PC} = 7.4), 124.64 (d, J_{PC} = 8.7),

127.66 (d), 128.11 (d), 128.40 (d), 128.41 (d), 128.59 (d), 128.82 (d), 129.74 (d), 129.75 (d), 129.92 (d), 130.29 (d), 130.33 (d), 132.18 (d), 133.96 (s), 136.25 (s, 2C), 136.78 (s), 137.38 (s), 137.68 (s), 137.70 (s), 137.94 (s), 137.97 (s), 138.31 (s), 140.30 (s), 142.09 (s), 142.22 (s), 142.39 (s), 151.25 (d, J_{PC} = 7.1).

^{31}P NMR (202 MHz, CD_2Cl_2): 138.30 (s).

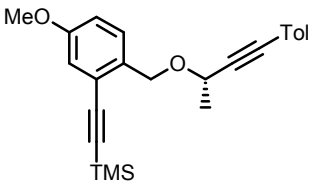
IR ($CHCl_3$): 2983 s, 1604 m, 1581 w, 1559 w, 1515 m, 1500 m, 1490 m, 1480 w, 1461 m, 1448 m, 1434 m, 1405 w, 1393 m, 1373 s, 1300 w, 1241 m, 1233 m, 1165 m, 1151 m, 1137 s, 1125 w, 1110 m, 1077 s, 1023 w, 961 s, 944 m, 899 s, 862 m, 845 s, 836 s, 819 m, 697 vw, 689 vw, 647 w, 594 w, 495 w cm^{-1}.

ESI MS: 707 ($[M+Na]^+$), 685 ($[M]^+$).

HR ESI MS: calculated for $C_{44}H_{45}O_5NaP$ 707.2897; found 707.2896.

Optical rotation: $[\alpha]^{22}_D$ -127° (c 0.340, CH_2Cl_2).

{[5-Methoxy-2-({[(1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}methyl) phenyl]ethynyl}(trimethyl)silane (*S*)-**169**



A flame-dried Schlenk flask was charged with iodide (*S*)-**164** (3.76 g, 9.26 mmol), tetrakis(triphenylphosphine)-palladium(0) (642 mg, 0.555 mmol, 6 mol%), copper iodide (211 mg, 1.11 mmol, 12 mol%) and then diisopropylamine (100 ml) was added under argon. Ethynyl(trimethyl)silane (1.6 ml, 11.1 mmol, 1.2 equiv) was added and the reaction mixture was heated at 80 ºC for 45 min. The inorganic material was filtered off on a sintered glass (hexane) and the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-diethyl ether 99:1) to give product (*S*)-**169** (2.96 g, 85%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$): 0.23 (9H, s), 1.56 (3H, d, *J* = 6.6), 2.34 (3H, s), 3.78 (3H, s), 4.50 (1H, q, *J* = 6.6), 4.70 (1H, d, *J* = 11.8), 4.88 (1H, dd, *J* = 11.8, 0.6), 6.85 (1H, dd, *J* = 8.5, 2.7), 6.98 (1H, d, *J* = 2.7), 7.10 (2H, m), 7.34 (2H, m), 7.38 (1H, bd, *J* = 8.5).

^{13}C NMR (126 MHz, $CDCl_3$): -0.07 (q), 21.43 (q), 22.23 (q), 55.36 (q), 65.60 (d), 68.51 (t), 85.13 (s), 88.47 (s), 98.54 (s), 102.75 (s), 115.40 (d), 116.67 (d), 119.74 (s), 123.08 (s), 128.94 (d), 129.46 (d), 131.63 (d), 132.77 (s), 138.28 (s), 158.53 (s).

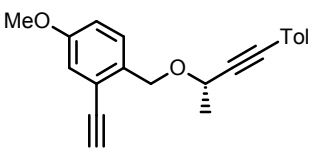
IR ($CHCl_3$): 2962 s, 2902 m, 2839 m, 2225 w, 2154 m, 1605 s, 1571 m, 1510 s, 1503 s, 1443 m, 1409 w, 1389 w, 1372 m, 1327 s, 1285 s, 1263 s, 1251 vs, 1163 s, 1131 m, 1120 s, 1096 s, 1058 s, 1037 s, 1022 m, 856 vs, 846 vs, 819 s, 701 w, 550 w cm^{-1}.

EI MS: 376 ($M^{+\bullet}$, 24), 361 (52), 303 (42), 245 (52), 217 (43), 203 (23), 143 (66), 129 (100), 115 (27), 73 (83).

HR EI MS: calculated for $C_{24}H_{28}O_2Si$ 376.1859; found 376.1842.

Optical rotation: $[\alpha]^{22}_D$ -93° (c 0.70, CH_2Cl_2).

2-Ethynyl-4-methoxy-1-({[(1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy} methyl)benzene (*S*)-**170**



To a solution of silane (*S*)-**169** (4.16 g, 9.26 mmol) anhydrous K_2CO_3 (4.48 g, 32.41 mmol, 3.5 equiv.) in methanol (30 ml) was added and the reaction mixture was stirred at room temperature for 2 h. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 92:8) to give product (*S*)-**170** (1.68 g, 60%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$): 1.55 (3H, d, *J* = 6.6), 2.35 (3H, s), 3.24 (1H, s), 3.79 (3H, s), 4.47 (1H, q, *J* = 6.6), 4.71 (1H, d, *J* = 11.8), 4.91 (1H, d, *J* = 11.8), 6.90 (1H, dd, *J* = 8.5, 2.7), 7.02 (1H, d, *J* = 2.7), 7.11 (2H, m), 7.34 (2H, m), 7.41 (1H, d, *J* = 8.5).

^{13}C NMR (126 MHz, $CDCl_3$): 21.44 (q), 22.20 (q), 55.36 (q), 65.31 (d), 68.25 (t), 81.18 (d), 81.37 (s), 85.19 (s), 88.50 (s), 115.47 (d), 117.30 (d), 119.77 (s), 122.29 (s), 128.98 (d), 129.86 (d), 131.59 (d), 132.80 (s), 138.31 (s), 158.62 (s).

IR ($CHCl_3$): 3305 vs, 2839 s, 2225 w, 2106 w, 1605 vs, 1572 s, 1510 vs, 1503 vs, 1444 s, 1415 m, 1389 m, 1372 s, 1327 vs, 1285 vs, 1257 vs, 1248 vs, 1181 w, 1159

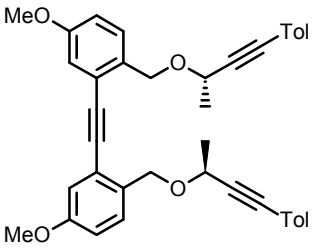
s, 1130 s, 1111 vs, 1095 vs, 1057 vs, 1037 vs, 1022 s, 945 w, 858 s, 819 vs, 655 s, 628 s, 545 w cm^{-1}.

EI MS: 304 ($M^{+\bullet}$, 11), 303 (10), 289 (55), 276 (12), 261 (66), 245 (12), 145 (89), 143 (70), 129 (100), 128 (65), 115 (34), 102 (27), 83 (41), 57 (22), 43 (20).

HR EI MS: calculated for $C_{21}H_{20}O_2$ 304.1463; found 304.1454.

Optical rotation: $[\alpha]^{22}_D$ -104° (c 0.46, CH_2Cl_2).

1,1'-Ethyne-1,2-diylbis[5-methoxy-2-({[(1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}methyl)benzene] (*S*,*S*)-**171**



A flame-dried Schlenk flask was charged with the iodide (*S*)-**164** (2.25 g, 5.53 mmol), tetrakis(triphenylphosphine)-palladium(0) (147 mg, 0.127 mmol, 2 mol%), copper iodide (57 mg, 0.290 mmol, 5 mol%) and diisopropylamine (20 ml) was added under argon. Then a degassed solution of alkyne (*S*)-**170** (1.68 g, 5.53 mmol, 1.0 equiv.) in diisopropylamine (20 ml) was added and the reaction mixture was stirred at room temperature for 1.5 h. The precipitate was filtered off (diisopropylamine) and the solvent was removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 85:15) to give product (*S*,*S*)-**171** (2.62 g, 82%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$): 1.54 (6H, d, *J* = 6.6), 2.31 (6H, s), 3.74 (6H, s), 4.49 (2H, q, *J* = 6.6), 4.80 (2H, d, *J* = 11.8), 4.96 (2H, d, *J* = 11.8), 6.89 (2H, dd, *J* = 8.6, 2.7), 7.02 (4H, m), 7.04 (2H, d, *J* = 2.7), 7.24 (4H, m), 7.41 (2H, d, *J* = 8.6).

^{13}C NMR (126 MHz, $CDCl_3$): 21.41 (q), 22.29 (q), 55.28 (q), 65.28 (d), 68.50 (t), 85.27 (s), 88.49 (s), 91.12 (s), 115.15 (d), 116.54 (d), 119.60 (s), 123.24 (s), 128.87 (d), 129.72 (s), 129.72 (d), 132.20 (s), 138.66 (d), 158.62 (s).

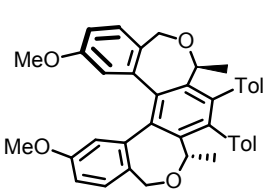
IR ($CHCl_3$): 2935 s, 2839 m, 2225 w, 1604 vs, 1571 s, 1510 vs, 1503 s, 1446 m, 1427 m, 1406 w, 1388 m, 1372 m, 1328 vs, 1281 m, 1130 s, 1117 s, 1107 s, 1094 vs, 1037 vs, 1022 s, 856 m, 819 vs, 647 vw, 544 w cm^{-1}.

ESI MS: 621 ($[M+K]^+$), 605 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{40}H_{38}O_4Na$ 605.2662; found 605.2661.

Optical rotation: $[\alpha]^{22}_D$ -178° (c 0.34, CH_2Cl_2).

(*P*,3*S*,6*S*)-11,14-Dimethoxy-3,6-dimethyl-4,5-bis(4-methylphenyl)-1,3,6,8-tetrahydrodibenzo[*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepine (*P*,*S*,*S*)-**172**



A flame-dried 20 ml microwave vial was charged with triyne (*S*,*S*)-**171** (321 mg, 0.551 mmol), dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (100 µl, 0.753 mmol, 1.37 equiv.), triphenylphosphine (289 mg, 1.10 mmol, 2.0 equiv.), ionic liquid [BDMIM][BF_4] (ca 100 mg) and THF (20 ml) and the solution was heated in a microwave reactor at 200 ºC for 20 min. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 100:0 to 85:15) to give product (*P*,*S*,*S*)-**172** (282.5 mg, 88%) as a yellow solid. Single crystal was grown by layer-diffusion technique from a saturated dichloromethane solution layered with heptane.

Mp: 221-223 ºC (hexane).

^{1}H NMR (500 MHz, $CDCl_3$): 0.67 (6H, d, *J* = 7.1), 2.24 (6H, s), 3.35 (6H, s), 4.54 (2H, d, *J* = 11.6), 4.80 (2H, d, *J* = 11.6), 4.91 (2H, q, *J* = 7.1), 6.14 (2H, d, *J* = 2.6), 6.71 (2H, dd, *J* = 7.7, 1.9), 6.76 (2H, dd, *J* = 8.2, 2.6), 6.86 (2H, ddq, *J* = 7.7, 1.9, 0.9, 0.9, 0.9), 7.01 (2H, ddq, *J* = 7.8, 1.9, 0.8, 0.8, 0.8), 7.04 (2H, dd, *J* = 7.8, 1.9), 7.29 (2H, d, *J* = 8.2).

^{13}C NMR (126 MHz, $CDCl_3$): 21.14 (q), 22.33 (q), 55.08 (q), 66.74 (t), 72.52 (d), 114.51 (d), 116.38 (d), 128.07 (d), 128.35 (d), 129.46 (2 x d), 129.78 (d), 130.44 (s), 135.65 (s), 136.97 (s), 136.99 (s), 137.60 (s), 141.33 (s), 142.21 (s), 158.80 (s).

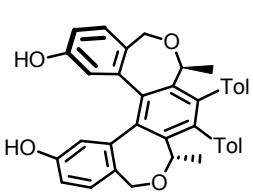
IR ($CHCl_3$): 2961 s, 2927 vs, 2856 s, 2838 m, 1607 vs, 1578 m, 1516 s, 1501 s, 1431 m, 1369 s, 1283 s, 1183 m, 1146 s, 1125 m, 1108 s, 1077 vs, 1040 s, 858 s, 821 m, 695 vw cm^{-1}.

EI MS: 582 ($M^{+\bullet}$, 35), 567 (13), 537 (16), 509 (9), 149 (7), 119 (7), 97 (11), 84 (80), 71 (20), 57 (36), 43 (100).

HR EI MS: calculated for $C_{40}H_{38}O_4$ 582.2770; found 582.2786.

Optical rotation: $[\alpha]^{22}_D$ -66° (c 0.64, CH_2Cl_2).

(*P*,3*S*,6*S*)-3,6-Dimethyl-4,5-bis(4-methylphenyl)-1,3,6,8-tetrahydrodibenzo [*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepine-11,14-diol (*P*,*S*,*S*)-**173**



Sodium hydride (dispersion in mineral oil, 285 mg, 7.3 mmol, 40.0 equiv.) was suspended in DMF (5 ml) and cooled to 0 ºC. Ethanethiol (0.54 ml, 0.45 g, 7.3 mmol, 40 equiv.) was added and the mixture was stirred at room temperature for 30 min until all hydride was dissolved. Then dimethoxy derivative (*P*,*S*,*S*)-**172** (104 mg, 0.179 mmol) in DMF (5 ml) was added and the reaction mixture was heated at 140 ºC for 6 h. Then the reaction mixture was diluted with an aqueous solution of HCl (1M, 100 ml) and extracted with dichloromethane (3 x 100 ml). The combined organic phases were washed with water (2 x 100 ml), brine (100 ml) and dried over anhydrous Na_2SO_4. Then the volatiles were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 1:1) to obtain product (*P*,*S*,*S*)-**173** (89.5 mg, 90%) as a white solid.

Mp: 189-190 °C (acetone).

^{1}H NMR (600 MHz, d_6-acetone, rfp=2.09 ppm): 0.65 (6H, d, *J* = 7.1), 2.26 (6H, s), 4.49 (2H, d, *J* = 11.4), 4.71 (2H, d, *J* = 11.4), 4.87 (2H, q, *J* = 7.1), 6.30 (2H, d, *J* = 2.5), 6.77 (2H, dd, *J* = 8.1, 2.5), 6.89-6.91 (2H, m), 6.96-6.98 (2H, m), 7.05-7.09 (4H, m), 7.28 (2H, d, *J* = 8.1).

^{13}C NMR (151 MHz, d_6-acetone, rfp=29.8 ppm): 21.09 (q), 22.57 (q), 67.25 (t), 72.82 (d), 115.71 (d), 119.36 (d), 128.87 (d), 129.00 (d), 130.40 (d), 130.43 (s), 130.50 (d), 131.01 (d), 136.48 (s), 137.93 (s), 138.45 (s), 138.48 (s), 142.52 (s), 142.73 (s), 157.70 (s).

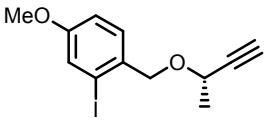
IR ($CHCl_3$): 3598 m, 3399 m, 2961 s, 1604 vs, 1586 m, 1562 w, 1543 vw, 1515 m, 1498 m, 1459 m, 1449 m, 1400 vw, 1370 m, 1287 m, 1256 m, 1184 s, 1148 s, 1117 m, 1107 s, 1077 s, 1022 m, 858 m, 848 m, 818 m, 697 m cm^{-1}.

ESI MS: 577 ([M+Na]$^+$).

HR ESI MS: calculated for $C_{38}H_{34}O_4Na$ 577.23493; found 577.23506.

Optical rotation: $[\alpha]^{22}_D$ -128° (c 0.553, acetone).

2-Iodo-4-methoxy-1-({[(1*S*)-1-methylprop-2-yn-1-yl]oxy}methyl)benzene (*S*)-**175**



In a 250 ml round-bottom flask 2-iodo-4-methoxy-1-methylbenzene **162** (4.70 g, 18.9 mmol), NBS (4.05 g, 22.7 mmol, 1.2 equiv.), catalytic amount of AIBN and K_2CO_3 in CCl_4 (100 ml) were refluxed using an IR lamp for 2.5 h. Then the reaction mixture was filtered through a short pad of alumina (diethyl ether), concentrated *in vacuo* and the crude 1-(bromomethyl)-2-iodo-4-methoxybenzene **163** was used in the next reaction without purification. To potassium hydride (20% dispersion in mineral oil, 1.14 g, 28.4 mol, 1.5 equiv.) distilled THF (20 ml) was added at 0 ºC under argon. Then (*S*)-but-3-yn-2-ol (*S*)-**111** (1.5 ml, 18.9 mmol, 1.0 equiv.) was added dropwise and the reaction mixture was stirred at 0 ºC for 1 h. Then the solution of the crude benzyl bromide in THF (10 ml) was added and the reaction mixture was allowed to warm up to room temperature and stirred overnight. A saturated aqueous solution of NH_4Cl (50 ml) was added to quench the excess of potassium hydride, then the product was extracted with ether (3 x 200 ml), the combined organic layers were washed with water (3 x 200 ml) and dried over anhydrous Na_2SO_4. The solvents were removed *in vacuo* the residue was purified by chromatography on silica gel (hexane-diethyl ether 95:5) to give product (*S*)-**175** (1.67 g, 28%) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$): 1.50 (3H, d, *J* = 6.8), 2.48 (1H, d, *J* = 2.0), 3.78 (3H, s), 4.26 (1H, qd, *J* = 6.8, 6.8, 6.8, 2.0), 4.45 (1H, d, *J* = 11.6), 4.73 (1H, d, *J* = 12.0), 6.88 (1H, dd, *J* = 8.4, 2.8), 7.32 (1H, d, *J* = 8.8), 7.38 (1H, d, *J* = 2.8).

^{13}C NMR (101 MHz, $CDCl_3$): 22.03 (q), 55.51 (q), 64.70 (d), 73.29 (d), 73.89 (t), 83.59 (s), 98.76 (s), 114.06 (d), 124.57 (d), 129.99 (d), 132.32 (s), 159.38 (s).

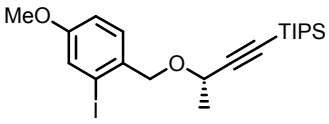
IR (KBr): 3293 m, 3247 w, 2838 w, 1598 vs, 1566 m, 1490 s, 1467 w, 1457 m, 1440 m, 1400 w, 1373 w, 1326 w, 1285 m, 1235 s, 1183 w, 1135 w, 1100 s, 1063 m, 1035 m, 1021 s, 911 w, 859 w, 811 w, 760 w, 667 w, 639 w, 608 w, 444 w cm^{-1}.

EI MS: 316 ($M^{+\bullet}$, 60), 286 (39), 271 (7), 261 (59), 247 (100), 215 (5), 174 (5), 159 (34), 145 (15), 134 (24), 121 (46), 108 (72), 91 (24), 77 (51), 63 (44), 53 (52).

HR EI MS: calculated for $C_{12}H_{13}O_2I$ 315.9960; found 315.9953.

Optical rotation: $[\alpha]^{22}_D$ -42° (c 0.050, CH_2Cl_2).

{(3S)-3-[(2-Iodo-4-methoxybenzyl)oxy]but-1-yn-1-yl}[tris(1-methylethyl)]silane (*S*)-**176**



In a flame-dried Schlenk flask an LDA solution was prepared from diisopropylamine (1.3 ml, 9.54 mmol, 1.8 equiv.) and a solution of *n*-BuLi (1.6 M in hexanes, 5.95 ml, 9.54 mmol, 1.8 equiv.) in THF (6 ml) by stirring at 0 ºC for 30 min. In a flame-dried Schlenk flask alkyne (*S*)-**175** (1.67 g, 5.3 mmol) was dissolved in THF (10 ml) and cooled down to -78 ºC under argon. The freshly prepared lithium diisopropylamide solution (9.54 mmol, 1.8 equiv.) was added dropwise and the solution was stirred at -78 ºC for 1 h. Then triisopropylsilyl chloride (2.0 ml, 9.44 mmol, 1.8 equiv.) was added and the reaction mixture was allowed to warm up to room temperature and stirred overnight. A saturated aqueous solution of NH_4Cl (10 ml) was added to quench the excess of the base, the product was extracted with ether (3 x 200 ml), the combined organic layers washed with water (3 x 200 ml) and dried over anhydrous Na_2SO_4. The solvents were removed *in vacuo*, the residue was purified by chromatography on silica gel (hexane-diethyl ether 99:1) to give product (*S*)-**176** (2.10 g, 84%) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$): 1.09 (21H, m), 1.49 (3H, d, *J* = 6.8), 3.78 (3H, s), 4.28 (1H, q, *J* = 6.8), 4.47 (1H, d, *J* = 11.6), 4.76 (1H, d, *J* = 11.6), 6.88 (1H, dd, *J* = 8.5, 2.6), 7.31 (1H, d, *J* = 8.6), 7.37 (1H, d, *J* = 2.5).

^{13}C NMR (101 MHz, $CDCl_3$): 11.18 (d), 18.65 (q), 22.34 (q), 55.52 (q), 65.33 (d), 73.72 (t), 86.02 (s), 98.65 (s), 107.39 (s), 114.04 (d), 124.51 (d), 129.91 (d), 132.64 (s), 159.29 (s).

IR (KBr): 2958 s, 2943 vs, 2865 vs, 2865 vs, 2838 w, 2165 w, 1598 s, 1566 w, 1490 s, 1464 s, 1440 m, 1400 w, 1382 w, 1368 w, 1324 m, 1285 m, 1234 s, 1181 w, 1137

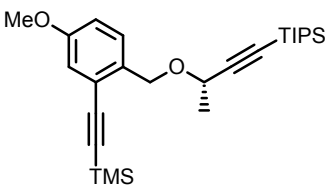
w, 1099 s, 1069 m, 1038 m, 1020 m, 997 w, 922 m, 883 m, 807 w, 761 w, 679 s, 667 m, 636 w, 599 w, 444 w cm^{-1}.

EI MS: 472 ($M^{+\bullet}$, 3), 429 (50), 399 (5), 259 (6), 247 (100), 236 (56), 215 (5), 188 (8), 167 (8), 121 (16), 83 (5), 59 (6), 43 (5).

HR EI MS: calculated for $C_{21}H_{33}O_2ISi$ 472.1295; found 472.1307.

Optical rotation: $[\alpha]^{22}_D$ -44° (c 0.088, CH_2Cl_2).

({5-Methoxy-2-[({(1S)-1-methyl-3-[tris(1-methylethyl)silyl]prop-2-yn-1-yl}oxy)methyl]phenyl}ethynyl)(trimethyl)silane (*S*)-**177**



A Schlenk flask was charged with aryl iodide (*S*)-**176** (1.13 g, 2.4 mmol), tetrakis(triphenylphosphine)palladium(0) (166 mg, 0.143 mmol, 6 mol%), copper iodide (55 mg, 0.280 mmol, 12 mol%) and diisopropylamine (20 ml) was added under argon. Ethynyl(trimethyl)silane (370 µl, 2.64 mmol, 1.1 equiv.) was added dropwise at room temperature and the reaction mixture was stirred for 1.5 h. The reaction mixture was filtered through a sintered glass (hexane) and solvents were removed *in vacuo*, the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 95:5) to afford product (*S*)-**177** (1.05 g, 99%) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$): 0.25 (9H, m), 1.09 (21H, m), 1.49 (3H, d, *J* = 6.8), 3.79 (3H, s), 4.31 (1H, q, *J* = 6.6), 4.63 (1H, d, *J* = 11.9), 4.81 (1H, d, *J* = 11.8), 6.86 (1H, dd, *J* = 8.5, 2.7), 6.98 (1H, d, *J* = 2.8), 7.34 (1H, d, *J* = 8.6).

^{13}C NMR (101 MHz, $CDCl_3$): -0.02 (q), 11.16 (d), 18.62 (q), 22.41 (q), 55.40 (q), 65.72 (d), 68.46 (t), 85.52 (s), 98.46 (s), 102.75 (s), 107.87 (s), 115.32 (d), 116.84 (d), 123.01 (s), 129.39 (d), 132.85 (s), 158.52 (s).

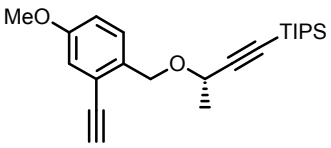
IR ($CHCl_3$): 2959 s, 2944 s, 2866 vs, 2837 w, 2156 m, 1605 m, 1572 w, 1500 m, 1464 m, 1443 m, 1417 w, 1410 w, 1383 w, 1368 w, 1323 m, 1285 m, 1262 m, 1250 s, 1162 m, 1139 w, 1119 s, 1100 s, 1071 m, 1038 m, 1021 m, 997 w, 883 m, 855 vs, 845 vs, 760 w, 699 w, 679 m, 668 m, 652 m cm^{-1}.

EI MS: 442 ($M^{+\bullet}$, 7), 399 (10), 369 (8), 313 (6), 270 (10), 255 (8), 236 (84), 218 (42), 203 (24), 187 (14), 167 (18), 133 (18), 97 (20), 73 (100), 59 (62), 43 (27).

HR EI MS: calculated for $C_{26}H_{42}O_2Si_2$ 442.2723; found 442.2712.

Optical rotation: $[\alpha]^{22}_D$ -45° (c 0.078, CH_2Cl_2).

{(3S)-3-[(2-Ethynyl-4-methoxybenzyl)oxy]but-1-yn-1-yl}[tris(1-methylethyl)] silane (*S*)-**178**



In a 250 ml round-bottom flask silane (*S*)-**177** (1.05 g, 2.37 mmol) and K_2CO_4 (1.14 g, 8.28 mmol, 3.5 equiv.) were suspended in methanol (30 ml) and the reaction mixture was stirred at room temperature for 45 min. The reaction mixture was filtered through a sintered glass (diethyl ether) and the volatiles were removed *in vacuo.* The residue was dissolved in diethyl ether (100 ml) and washed with water (3 x 150 ml) and brine (100 ml). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 96:4) to afford the product (*S*)-**178** (816 mg, 93%) as an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$): 1.06 (21H, m), 1.48 (3H, d, *J* = 6.7), 3.23 (1H, s), 3.79 (3H, s), 4.29 (1H, q, *J* = 6.6), 4.66 (1H, d, *J* = 12.0), 4.89 (1H, d, *J* = 12.0), 6.90 (1H, dd, *J* = 8.5, 2.7), 7.02 (1H, d, *J* = 2.7), 7.37 (1H, d, *J* = 8.5).

^{13}C NMR (101 MHz, $CDCl_3$): 11.18 (d), 18.63 (q), 22.37 (q), 55.40 (q), 65.33 (d), 68.10 (t), 81.14 (d), 81.31 (s), 85.67 (s), 107.71 (s), 115.46 (d), 117.31 (d), 122.10 (s), 129.65 (d), 132.95 (s), 158.58 (s).

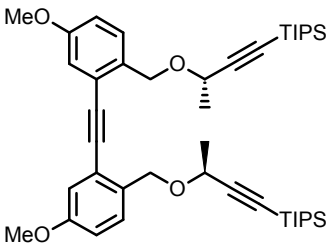
IR ($CHCl_3$): 3306 m, 2961 s, 2945 vs, 2866 vs, 2840 m, 2165 w, 2106 vw, 1605 m, 1572 m, 1501 m, 1464 s, 1444 m, 1417 w, 1383 w, 1371 w, 1324 m, 1284 m, 1256 m, 1158 w, 1138 m, 1111 s, 1098 s, 1037 m, 1020 m, 997 m, 883 m, 858 w, 826 w, 679 s, 650 m cm^{-1}.

EI MS: 370 ($M^{+\bullet}$, 3), 368 (5), 327 (38), 283 (22), 255 (10), 236 (8), 236 (52), 213 (16), 197 (67), 178 (2), 167 (18), 145 (100), 136 (10), 121 (15), 102 (13), 83 (15), 75 (18), 59 (20), 43 (10).

HR EI MS: calculated for $C_{23}H_{34}O_2Si$ 370.2328; found 370.2341.

Optical rotation: $[\alpha]^{22}_D$ -70° (c 0.064, CH_2Cl_2).

{Ethyne-1,2-diylbis[(4-methoxybenzene-2,1-diyl)methanediyloxy(3S)but-1-yne-3,1-diyl]}bis[tris(1-methylethyl)silane] (*S*,*S*)-**179**



To tetrakis(triphenylphosphine)palladium(0) (127 mg, 0.110 mmol, 5 mol%) and copper iodide (42 mg, 0.220 mmol, 11 mol%) in a Schlenk flask a solution of aryl iodide (*S*)-**176** (931 mg, 1.97 mmol) in diisopropylamine (10 ml) was added under argon. After stirring at room temperature for 5 min a solution of alkyne (*S*)-**178** (810 mg, 2.18 mmol, 1.1 equiv.) in diisopropylamine (10 ml) was added dropwise at room temperature and the reaction mixture was stirred for 1 h. The reaction mixture was filtered through a sintered glass (hexane) and solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-diethyl ether 95:5) to afford product (*S*,*S*)-**179** (1.13 g, 83%) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$): 1.04 (42H, m), 1.49 (6H, d, *J* = 6.6), 3.81 (6H, s), 4.31 (2H, q, *J* = 6.6), 4.73 (2H, d, *J* = 11.8), 4.92 (2H, d, *J* = 11.9), 6.89 (2H, dd, *J* = 8.5, 2.7), 7.05 (2H, d, *J* = 2.7), 7.40 (2H, d, *J* = 8.6).

^{13}C NMR (101 MHz, $CDCl_3$): 11.14 (d), 18.56 (q), 22.46 (q), 55.39 (q), 65.39 (d), 68.48 (t), 85.71 (s), 91.04 (s), 107.80 (s), 114.87 (d), 116.88 (d), 123.21 (s), 129.63 (d), 132.33 (s), 158.64 (s).

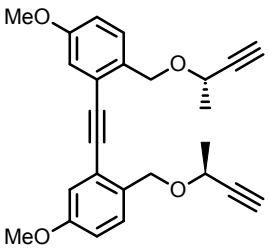
IR ($CHCl_3$): 2960 s, 2944 vs, 2866 vs, 2837 w, 2165 w, 1604 s, 1571 m, 1504 m, 1465 s, 1446 w, 1427 w, 1384 w, 1371 w, 1324 m, 1282 w, 1245 m, 1173 m, 1137 w, 1121 m, 1096 s, 1037 m, 1019 m, 997 w, 883 m, 856 w, 825 w, 679 m cm^{-1}.

ESI MS: 737 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{44}H_{66}O_4NaSi_2$ 737.4392; found 737.4391.

Optical rotation: $[\alpha]^{22}_D$ -159° (c 0.022, CH_2Cl_2).

1,1'-Ethyne-1,2-diylbis[5-methoxy-2-({[(1S)-1-methylprop-2-yn-1-yl]oxy}methyl) benzene] (*S*,*S*)-**180**



In a 250 ml flask silane (*S*,*S*)-**179** (1.13 g, 1.58 mmol) was dissolved in THF (20 ml) under argon. A solution of tetrabutylammonium fluoride trihydrate (0.964 M in THF, 3.30 ml, 3.18 mmol, 2.0 equiv.) was added dropwise and the reaction mixture was stirred at room temperature for 30 min. Then solvent was evaporated *in vacuo* and the residue was purified by chromatography on silica gel (hexane-diethyl ether 100:0 to 90:10) to provide product (*S*,*S*)-**180** (602 mg, 94%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$): 1.49 (6H, d, *J* = 6.6), 2.43 (2H, d, *J* = 2.0), 3.82 (6H, s), 4.30 (2H, dq, *J* = 6.6, 6.6, 6.6, 2.0), 4.73 (2H, d, *J* = 11.8), 4.94 (2H, bd, *J* = 11.8), 6.91 (2H, dd, *J* = 8.5, 2.7), 7.08 (2H, d, *J* = 2.7), 7.41 (2H, dq, *J* = 8.5, 0.4, 0.4, 0.4).

^{13}C NMR (126 MHz, $CDCl_3$): 22.13 (q), 55.42 (q), 64.66 (d), 68.55 (t), 73.13 (d), 83.96 (s), 91.10 (s), 115.06 (d), 116.85 (d), 123.25 (s), 129.68 (d), 131.93 (s), 158.73 (s).

IR ($CHCl_3$): 3306 s, 2839 m, 2210 vw, 2112 w, 1604 vs, 1571 s, 1504 vs, 1466 s, 1447 s, 1427 m, 1374 s, 1327 s, 1282 s, 1247 s, 1173 s, 1139 s, 1098 vs, 1060 s, 1038 vs, 1018 s, 856 m, 825 m, 638 s cm^{-1}.

EI MS: 402 ($M^{+\bullet}$, 2), 319 (10), 301 (10), 279 (100), 264 (17), 237 (5), 208 (10), 189 (5), 178 (10), 165 (22), 152 (12), 121 (6), 69 (8), 53 (35), 43 (18).

HR EI MS: calculated for $C_{26}H_{26}O_4$ 402.1831; found 402.1839.

Optical rotation: $[\alpha]^{22}_D$ -106° (c 0.303, CH_2Cl_2).

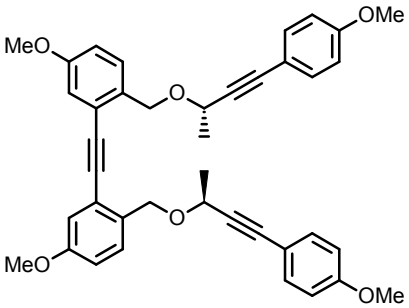
General procedure for Sonogashira coupling of triyne (*S*,*S*)-**180 to prepare substituted triynes** (*S*,*S*)-**171**, (*S*,*S*)-**181** – (*S*,*S*)-**187:**

Triyne (*S*,*S*)-**180** (0.14-0.33 mmol), bis(acetonitrile)palladium(II) dichloride (10-15 mol%), triphenylphosphine (20-26 mol%), copper iodide (15-21 mol%) and aryl iodide (2.5-6.4 equiv.) were dissolved in toluene (5-10 ml, c~22µmol/ml) and diisopropylamine (2.5 equiv.) was added. After the reaction mixture was stirred at 80 ºC for 5 min, it was filtered through a sintered glass (diethyl ether) and solvents were removed *in vacuo*. The flash chromatography on silica gel (hexane-diethyl ether 100:0 to 85:15) provided products (*S*,*S*)-**171**, (*S*,*S*)-**181 -** (*S*,*S*)-**187** as amorphous solids.

1,1'-Ethyne-1,2-diylbis[5-methoxy-2-({[(1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}methyl)benzene] (*S*,*S*)-**171**

Triyne (*S*,*S*)-**180** (74.2 mg, 0.18 mmol), bis(acetonitrile)-palladium(II) dichloride (4.7 mg, 0.018 mmol, 10 mol%), triphenylphosphine (9.4 mg, 0.036 mmol, 20 mol%), copper iodide (6.9 mg, 0.036 mmol, 20 mol%), aryl iodide (98.1 mg, 0.45 mmol, 2.5 equiv.), diisopropylamine (63 µl, 0.45 mmol, 2.5 equiv.), toluene (8 ml). Yield: 76.6 mg, 73%. (For spectra, see above).

1,1'-Ethyne-1,2-diylbis[5-methoxy-2-({[(1*S*)-3-(4-methoxyphenyl)-1-methylprop-2-yn-1-yl]oxy}methyl)benzene] (*S*,*S*)-**181**



Triyne (*S*,*S*)-**180** (93.1 mg, 0.23 mmol), bis(acetonitrile)-palladium(II) dichloride (6.0 mg, 0.023 mmol, 10 mol%), triphenylphosphine (12.6 mg, 0.048 mmol, 20 mol%), copper iodide (9.0 mg, 0.047 mmol, 20 mol%), aryl iodide (135.0 mg, 0.575 mmol, 2.5 equiv.), diisopropylamine (80 µl, 0.575 mmol, 2.5 equiv.), toluene (10 ml). Yield: 66.0 mg, 47%.

^{1}H NMR (600 MHz, $CDCl_3$): 1.53 (6H, d, *J* = 6.6), 3.76 (6H, s), 3.78 (6H, s), 4.48 (2H, q, *J* = 6.6), 4.80 (2H, d, *J* = 11.9), 4.96 (2H, dd, *J* = 11.9, 0.5), 6.74 (4H, m), 6.89 (2H, dd, *J* = 8.5, 2.7), 7.04 (2H, d, *J* = 2.7), 7.29 (4H, m), 7.41 (2H, d, *J* = 8.5).

^{13}C NMR (151 MHz, $CDCl_3$): 22.37 (q), 55.24 (q), 55.35 (q), 65.33 (d), 68.49 (t), 85.10 (s), 87.81 (s), 91.16 (s), 113.76 (d), 114.85 (s), 115.19 (d), 116.61 (d), 123.29 (s), 129.75 (d), 132.29 (s), 133.16 (d), 158.66 (s), 159.45 (s).

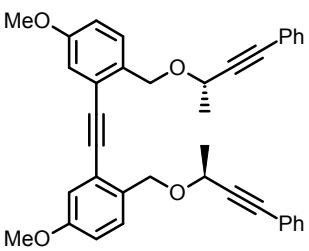
IR ($CHCl_3$): 3076 w, 3026 m, 2840 m, 2224 w, 2200 w, 1606 vs, 1572 s, 1572 s, 1510 vs, 1443 s, 1425 m, 1413 m, 1372 m, 1328 s, 1303 s, 1291 vs, 1250 vs, 1173 s, 1130 s, 1119 s, 1107 s, 1094 s, 1057 s, 1034 vs, 1020 s, 856 m, 834 s, 695 vw cm^{-1}.

APCI MS: 615 ($[M+H]^+$).

HR APCI MS: calculated for $C_{40}H_{39}O_6$ 615.2747, found 615.2726.

Optical rotation: $[\alpha]^{22}_D$ -150° (c 0.163, CH_2Cl_2).

1,1'-Ethyne-1,2-diylbis[5-methoxy-2-({[(1*S*)-1-methyl-3-phenylprop-2-yn-1-yl]oxy}methyl)benzene] (*S*,*S*)-**182**



Triyne (*S*,*S*)-**180** (56.4 mg, 0.14 mmol), bis(acetonitrile)-palladium(II) dichloride (4.0 mg, 0.015 mmol, 10 mol%), triphenylphosphine (8.2 mg, 0.030 mmol, 20 mol%), copper iodide (6.1 mg, 0.32 mmol, 23 mol%), aryl iodide (183 mg, 0.897 mmol, 6.4 equiv.), diisopropylamine (50 µl, 0.35 mmol, 2.5 equiv.), toluene (6 ml). Yield: 39.1 mg, 50%.

^{1}H NMR (500 MHz, $CDCl_3$): 1.54 (6H, d, *J* = 6.6), 3.75 (6H, s), 4.49 (2H, q, *J* = 6.6), 4.80 (2H, d, *J* = 11.8), 4.97 (2H, d, *J* = 11.8), 6.89 (2H, dd, *J* = 8.6, 2.7), 7.05 (2H, d, *J* = 2.7), 7.19-7.28 (6H, m), 7.34-7.36 (4H, m), 7.41 (2H, d, *J* = 8.6).

^{13}C NMR (126 MHz, $CDCl_3$): 21.28 (q), 55.33 (q), 65.27 (d), 68.58 (t), 85.16 (s), 89.26 (s), 91.15 (s), 115.20 (d), 116.63 (d), 122.73 (s), 123.29 (s), 128.14 (d, 2C), 129.78 (d), 131.69 (d), 132.19 (s), 158.69 (s).

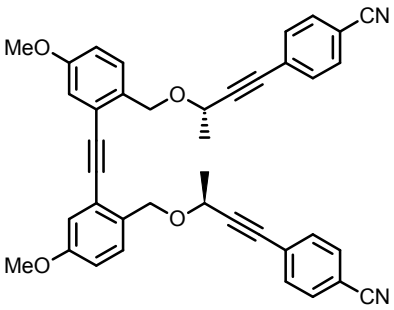
IR ($CHCl_3$): 3083 w, 3058 w, 2839 m, 2226 w, 1604 s, 1572 m, 1503 s, 1490 s, 1444 m, 1427 w, 1382 s, 1373 m, 1328 s, 1280 vs, 1174 s, 1143 s, 1108 s, 1095 vs, 1070 s, 1036 s, 1029 s, 1000 w, 917 m, 856 m, 700 w, 692 s, 524 w, 426 w cm^{-1}.

FAB MS: 577 ($[M+Na]^+$).

HR FAB MS: calculated for $C_{38}H_{34}O_4Na$ 577.2355, found 577.2354.

Optical rotation: $[\alpha]^{22}_D$ -172° (c 0.236, CH_2Cl_2).

4,4'-{Ethyne-1,2-diylbis[(4-methoxybenzene-2,1-diyl)methanediyloxy(3*S*)but-1-yne-3,1-diyl]}dibenzonitrile (*S*,*S*)-**183**



Triyne (*S*,*S*)-**180** (133.3 mg, 0.33 mmol), bis(acetonitrile)-palladium(II) dichloride (8.6 mg, 0.033 mmol, 10 mol%), triphenylphosphine (17.4 mg, 0.066 mmol, 20 mol%), copper iodide (12.6 mg, 0.066 mmol, 20 mol%), aryl iodide (189.0 mg, 0.83 mmol, 2.5 equiv.), diisopropylamine (115 µl, 0.83 mmol, 2.5 equiv.), toluene (14 ml). Yield: 153 mg, 75%.

^{1}H NMR (600 MHz, $CDCl_3$): 1.53 (6H, d, *J* = 6.6), 3.77 (6H, s), 4.47 (2H, q, *J* = 6.6), 4.77 (2H, d, *J* = 11.7), 4.92 (2H, d, *J* = 11.7), 6.89 (2H, dd, *J* = 8.5, 2.7), 6.99 (2H, d, *J* = 2.7), 7.36 (4H, m), 7.37 (2H, d, *J* = 8.5), 7.46 (4H, m).

^{13}C NMR (151 MHz, $CDCl_3$): 21.99 (q), 55.37 (q), 64.94 (d), 68.66 (t), 83.67 (s), 93.77 (s), 111.46 (s), 114.80 (d), 117.07 (d), 118.44 (s), 123.39 (s), 127.48 (s), 129.94 (d), 131.62 (s), 131.81 (d), 132.12 (d), 158.80 (s).

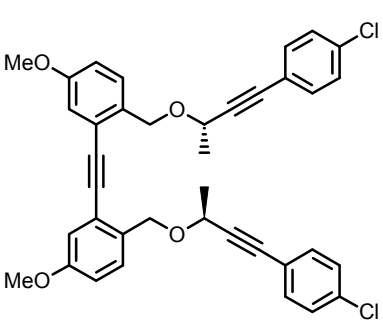
IR ($CHCl_3$): 2840 m, 2230 s, 1605 vs, 1571 m, 1501 s, 1445 m, 1427 w, 1406 m, 1373 m, 1327 s, 1281 m, 1241 s, 1174 s, 1131 m, 1118 s, 1095 vs, 1057 s, 1037 s, 1020 m, 856 m, 840 vs, 817 m, 642 w cm^{-1}.

FAB MS: 627 ($[M+Na]^+$).

HR FAB MS: calculated for $C_{40}H_{32}N_2NaO_4$ 627.2260, found 627.2237.

Optical rotation: $[\alpha]^{22}_D$ -166° (c 0.102, CH_2Cl_2).

1,1'-Ethyne-1,2-diylbis[2-({[(1*S*)-3-(4-chlorophenyl)-1-methylprop-2-yn-1-yl]oxy}methyl)-5-methoxybenzene] (*S*,*S*)-**184**



Triyne (*S*,*S*)-**180** (87.6 mg, 0.22 mmol), bis(acetonitrile)-palladium(II) dichloride (6.0 mg, 0.023 mmol, 10 mol%), triphenylphosphine (12.5 mg, 0.046 mmol, 20 mol%), copper iodide (9.0 mg, 0.047 mmol, 21 mol%), aryl iodide (131.2 mg, 0.55 mmol, 2.5 equiv.), diisopropylamine (80 µl, 0.55 mmol, 2.5 equiv.), toluene (10 ml). Yield: 69.7 mg, 51%.

^{1}H NMR (500 MHz, $CDCl_3$): 1.53 (6H, d, *J* = 6.6), 3.76 (6H, s), 4.46 (2H, q, *J* = 6.6), 4.77 (2H, d, *J* = 11.8), 4.93 (2H, d, *J* = 11.8), 6.89 (2H, dd, *J* = 8.5, 2.7), 7.02 (2H, d, *J* = 2.7), 7.16 (4H, m), 7.24 (4H, m), 7.39 (2H, d, *J* = 8.5).

^{13}C NMR (126 MHz, $CDCl_3$): 21.17 (q), 55.33 (q), 65.10 (d), 68.56 (t), 84.09 (s), 91.05 (s), 114.96 (d), 116.85 (d), 121.15 (s), 123.32 (s), 128.45 (d), 129.83 (d), 131.97 (s), 132.88 (d), 134.13 (s), 158.73 (s).

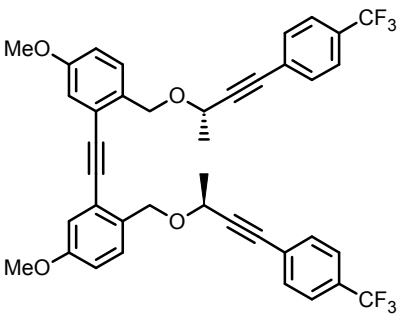
IR ($CHCl_3$): 3078 w, 3058 w, 2839 m, 2229 w, 2208 w, 1604 vs, 1571 s, 1490 vs, 1446 m, 1427 m, 1398 m, 1372 m, 1327 vs, 1281 s, 1256 s, 1243 s, 1173 s, 1119 s, 1098 vs, 1058 s, 1037 vs, 1016 vs, 856 m, 829 vs, 707 vw, 694 w, 617 w, 542 m, 525 m cm^{-1}.

FAB MS: 645 ($[M+Na]^+$).

HR FAB MS: calculated for $C_{38}H_{32}O_4Cl_2Na$ 645.1575, found 645.1601.

Optical rotation: $[\alpha]^{22}_D$ -128° (c 0.165, CH_2Cl_2).

1,1'-Ethyne-1,2-diylbis{5-methoxy-2-[({(1*S*)-1-methyl-3-[4-(trifluoromethyl) phenyl]prop-2-yn-1-yl}oxy)methyl]benzene} (*S*,*S*)-**185**



Triyne (*S*,*S*)-**180** (66.1 mg, 0.16 mmol), bis(acetonitrile)-palladium(II) dichloride (4.2 mg, 0.016 mmol, 10 mol%), triphenylphosphine (8.8 mg, 0.032 mmol, 20 mol%), copper iodide (6.2 mg, 0.032 mmol, 20 mol%), aryl iodide (112 mg, 0.415 mmol, 2.5 equiv.), diisopropylamine (60 µl, 0.410 mmol, 2.5 equiv.), toluene (7 ml). Yield: 101.0 mg, 89%.

^{1}H NMR (600 MHz, $CDCl_3$): 1.54 (6H, d, *J* = 6.6), 3.75 (6H, s), 4.47 (2H, q, *J* = 6.6), 4.79 (2H, d, *J* = 11.7), 4.94 (2H, d, *J* = 11.7), 6.88 (2H, dd, *J* = 8.5, 2.7), 7.02 (2H, d, *J* = 2.7), 7.39 (4H, m), 7.38 (2H, d, *J* = 8.5), 7.44 (4H, m).

^{13}C NMR (151 MHz, $CDCl_3$): 22.07 (q), 55.27 (q), 64.99 (d), 68.62 (t), 83.89 (s), 91.00 (s), 91.74 (s), 114.90 (d), 116.93 (d), 123.37 (s), 123.85 (s, J_{CF} = 272.1), 125.02 (d, J_{CF} = 3.8), 126.42 (s), 129.76 (s, J_{CF} = 32.5), 129.89 (d), 131.78 (s), 131.85 (d), 158.76 (s).

^{19}F NMR (471 MHz, $CDCl_3$): -59.02 (s).

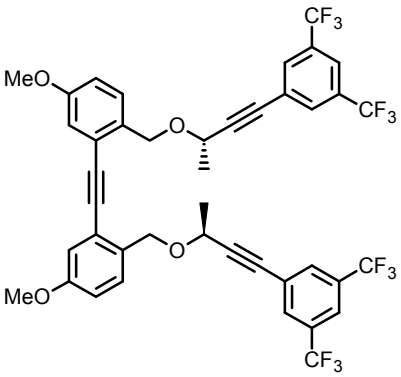
IR ($CHCl_3$): 2840 m, 2210 vw, 1615 s, 1605 s, 1572 s, 1503 s, 1446 m, 1427 w, 1405 m, 1373 m, 1322 vs, 1300 s, 1283 s, 1252 s, 1241 s, 1172 vs, 1131 vs, 1106 vs, 1097 vs, 1068 vs, 1057 s, 1037 s, 1017 s, 943 w, 855 m, 844 vs, 827 m, 817 m, 725 s, 651 m, 598 m, 520 w cm^{-1}.

FAB MS: 713 ($[M+Na]^+$).

HR FAB MS: calculated for $C_{40}H_{32}O_4F_6Na$ 713.2102, found 713.2075.

Optical rotation: $[\alpha]^{22}_D$ -197° (c 0.066, CH_2Cl_2).

1,1'-Ethyne-1,2-diylbis{2-[({(1*S*)-3-[3,5-bis(trifluoromethyl)phenyl]-1-methylprop-2-yn-1-yl}oxy)methyl]-5-methoxybenzene} (*S*,*S*)-**186**



Triyne (*S*,*S*)-**180** (63.5 mg, 0.16 mmol), bis(acetonitrile)-palladium(II) dichloride (4.1 mg, 0.016 mmol, 10 mol%), triphenylphosphine (8.0 mg, 0.032 mmol, 20 mol%), copper iodide (6.0 mg, 0.032 mmol, 20 mol%), aryl iodide (161 mg, 0.47 mmol, 2.9 equiv.), diisopropylamine (56 µl, 0.40 mmol, 2.5 equiv.), toluene (7 ml). Yield: 78.3 mg, 60%.

^{1}H NMR (500 MHz, $CDCl_3$): 1.55 (6H, d, *J* = 6.6), 3.74 (6H, s), 4.49 (2H, q, *J* = 6.6), 4.79 (2H, d, *J* = 11.7), 4.93 (2H, d, *J* = 11.7), 6.83 (2H, dd, *J* = 8.6, 2.7), 7.00 (2H, d, *J* = 2.7), 7.34 (2H, d, *J* = 8.6), 7.75 (6H, bs).

^{13}C NMR (126 MHz, $CDCl_3$): 22.03 (q), 55.22 (q), 64.95 (d), 68.99 (t), 82.19 (s), 91.04 (s), 93.12 (s), 114.77 (d), 116.95 (d), 122.85 (s, J_{CF} = 272.8), 123.44 (s), 124.99 (s), 130.08 (d), 131.51 (s), 131.51 (d, J_{CF} = 3.7), 131.73 (s, J_{CF} = 33.6), 158.84 (s).

^{19}F NMR (471 MHz, $CDCl_3$): −59.31 (s).

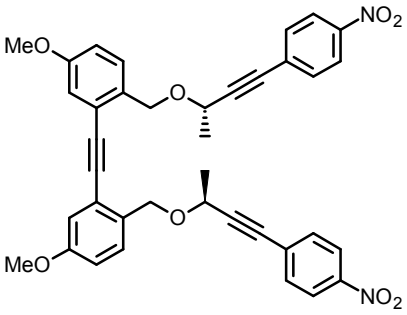
IR ($CHCl_3$): 2840 w, 2230 vw, 1610 w, 1604 m, 1571 w, 1503 w, 1464 w, 1428 w, 1400 w, 1382 s, 1327 m, 1280 vs, 1235 w, 1183 s, 1144 vs, 1107 m, 1095 m, 1037 m, 899 m, 857 w, 848 w, 700 m, 684 m, 426 w cm^{-1}.

ESI MS: 849 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{42}H_{30}O_4F_{12}Na$ 849.1845, found 849.1845.

Optical rotation: $[\alpha]^{22}_D$ -130° (c 0.087, CH_2Cl_2).

1,1'-Ethyne-1,2-diylbis[5-methoxy-2-({[(1*S*)-1-methyl-3-(4-nitrophenyl)prop-2-yn-1-yl]oxy}methyl)benzene] (*S*,*S*)-**187**



Triyne (*S*,*S*)-**180** (86.4 mg, 0.22 mmol), bis(acetonitrile)-palladium(II) dichloride (9.0 mg, 0.034 mmol, 16 mol%), triphenylphosphine (15.1 mg, 0.057 mmol, 26 mol%), copper iodide (6.3 mg, 0.033 mmol, 15 mol%), aryl iodide (150 mg, 0.60 mmol, 2.7 equiv.), diisopropylamine (80 µl, 0.55 mmol, 2.5 equiv.), toluene (10 ml). Yield: 73.5 mg, 52%.

^{1}H NMR (600 MHz, $CDCl_3$): 1.55 (6H, d, *J* = 6.6), 3.76 (6H, s), 4.48 (2H, q, *J* = 6.6), 4.78 (2H, d, *J* = 11.7), 4.94 (2H, d, *J* = 11.7), 6.87 (2H, dd, *J* = 8.5, 2.7), 6.98 (2H, d, *J* = 2.7), 7.37 (2H, d, *J* = 8.5), 7.42 (4H, m), 8.03 (4H, m).

^{13}C NMR (151 MHz, $CDCl_3$): 21.94 (q), 55.32 (q), 64.90 (d), 68.66 (t), 83.52 (s), 90.91 (s), 94.66 (s), 114.64 (d), 117.18 (d), 123.42 (s), 123.35 (d), 129.43 (s), 129.98 (d), 132.33 (d), 146.90 (s), 158.81 (s).

IR ($CHCl_3$): 3107 w, 3082 w, 3029 w, 2839 w, 2230 vw, 2215 vw, 1602 s, 1596 s, 1574 m, 1571 m, 1521 s, 1506 m, 1493 m, 1447 w, 1428 w, 1404 w, 1374 w, 1346 vs, 1326 s, 1308 m, 1286 m, 1256 m, 1174 m, 1130 m, 1120 m, 1108 m, 1096 s, 1037 m, 1015 m, 855 s, 689 w, 543 vw cm^{-1}.

ESI MS: 667 ($[M+Na]^+$).

HR FAB MS: calculated for $C_{38}H_{32}O_8N_2Na$ 667.2056, found 667.2053.

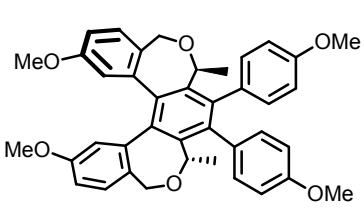
Optical rotation: $[\alpha]^{22}_D$ -150° (c 0.458, CH_2Cl_2).

General procedure for cyclotrimerisation of triynes (*S,S*)-**171 and** (*S*,*S*)-**181** - (*S*,*S*)-**187 to helicene-like products** (*P*,*S*,*S*)-**172 and** (*P*,*S*,*S*)-**188** - (*P*,*S*,*S*)-**194:**

Triyne (*S*,*S*)-**181** - (*S*,*S*)-**187** (0.04-0.07 mmol), triphenylphosphine (2.0 equiv.) and dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (1.0 equiv.) were flushed with argon in a Schlenk flask and decane (4 ml) was added. The reaction mixture was heated at 140 ºC using a halogen lamp until the starting material disappeared (according to TLC).

Then the reaction mixture was purified by chromatography on silica gel (hexane-acetone 100:0 to 95:5 or 70:30, depending on the substrate) to provide products (*P*,*S*,*S*)-**188** - (*P*,*S*,*S*)-**194** as amorphous material.

(*P*,3*R*,6*S*)-11,14-Dimethoxy-4,5-bis(4-methoxyphenyl)-3,6-dimethyl-1,3,6,8-tetrahydrodibenzo[*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepine (*P*,*S*,*S*)-**188**



Triyne (*S*,*S*)-**181** (33.0 mg, 0.054 mmol), triphenylphosphine (29.1 mg, 0.111 mmol, 2.0 equiv.), dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (7.2 µl, 0.054 mmol, 1.0 equiv.), reaction period: 2 h. Chromatography: hexane → hexane-acetone 1:1. Yield: 20.0 mg, 61%.

^{1}H NMR (600 MHz, $CDCl_3$): 0.61 (6H, d, *J* = 7.1), 3.29 (6H, s), 3.67 (6H, s), 4.48 (2H, d, *J* = 11.6), 4.74 (2H, d, *J* = 11.6), 4.88 (2H, q, *J* = 7.1), 6.07 (2H, d, *J* = 2.7), 6.54 (2H, dd, *J* = 8.4, 2.7), 6.66 (2H, dd, *J* = 8.3, 2.2), 6.69 (2H, dd, *J* = 8.3, 2.7), 6.70 (2H, dd, *J* = 8.4, 2.7), 7.01 (2H, dd, *J* = 8.3, 2.2), 7.23 (2H, d, *J* = 8.3).

^{13}C NMR (151 MHz, $CDCl_3$): 22.32 (q), 55.07 (q), 66.75 (t), 72.57 (d), 113.00 (d), 113.07 (d), 114.52 (d), 116.38 (d), 129.49 (d), 130.41 (s), 130.64 (d), 130.97 (d), 132.41 (s), 137.02 (s), 137.81 (s), 141.29 (s), 142.14 (s), 157.79 (s), 158.81 (s).

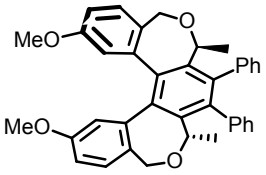
IR ($CHCl_3$): 3026 m, 2961 s, 2839 m, 1608 s, 1578 m, 1515 vs, 1502 m, 1466 s, 1443 m, 1431 m, 1370 m, 1306 m, 1285 s, 1245 vs, 1177 s, 1148 m, 1126 m, 1108 m, 1077 s, 1043 s, 1034 s, 858 m, 848 m, 821 m, 696 w, 635 w cm^{-1}.

FAB MS: 614 ($[M]^+$).

HR FAB MS: calculated for $C_{40}H_{38}O_6$ 614.2659, found 614.2668.

Optical rotation: $[\alpha]^{22}_D$ -77° (c 0.313, CH_2Cl_2).

(*P*,3*R*,6*S*)-11,14-Dimethoxy-3,6-dimethyl-4,5-diphenyl-1,3,6,8-tetrahydrodibenzo [*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepine (*P*,*S*,*S*)-**189**



Triyne (*S*,*S*)-**182** (22.5 mg, 0.041 mmol), triphenylphosphine (21.3 mg, 0.081 mmol, 2.0 equiv.), dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (5.4 µl, 0.041 mmol, 1.0 equiv.), reaction period: 1.5 h. Chromatography: hexane → hexane-acetone 9:1. Yield: 19.5 mg, 87%.

^{1}H NMR (600 MHz, $CDCl_3$): 0.69 (6H, d, *J* = 7.1), 3.37 (6H, s), 4.56 (2H, d, *J* = 12.6), 4.83 (2H, d, *J* = 12.6), 4.93 (2H, q, *J* = 7.1), 6.16 (2H, d, *J* = 2.6), 6.78 (2H, dd, *J* = 8.2, 2.6), 6.84 (2H, dt, *J* = 7.5, 1.7, 1.7), 7.05 (2H, dt, *J* = 7.5, 1.7, 1.7), 7.08 (2H, tt, *J* = 7.4, 1.5), 7.17 (2H, dt, *J* = 7.5, 1.7, 1.7), 7.21 (2H, dt, *J* = 7.5, 1.7, 1.7), 7.31 (2H, d, *J* = 8.2).

^{13}C NMR (151 MHz, $CDCl_3$): 22.32 (q), 55.09 (q), 66.76 (t), 72.57 (d), 114.59 (d), 126.33 (d), 127.34 (d), 127.67 (d), 129.52 (d), 129.68 (d), 130.00 (d), 130.40 (s), 137.21 (s), 137.43 (s), 139.92 (s), 141.20 (s), 142.08 (s), 158.84 (s).

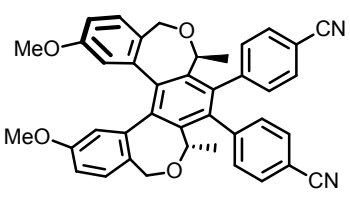
IR ($CHCl_3$): 3082 w, 3060 w, 2963 m, 2928 m, 2859 m, 2837 w, 1606 vs, 1578 m, 1502 s, 1467 m, 1443 m, 1431 m, 1370 m, 1283 m, 1256 s, 1238 s, 1175 m, 1078 vs, 1071 vs, 1037 m, 1000 w, 821 w, 705 vs, 694 w cm^{-1}.

FAB MS: 554 ($[M]^+$).

HR FAB MS: calculated for $C_{38}H_{34}O_4$ 554.2457, found 554.2462.

Optical rotation: $[\alpha]^{22}_D$ -69° (c 0.079, CH_2Cl_2).

4,4'-[(3*R*,6*S*)-11,14-Dimethoxy-3,6-dimethyl-1,3,6,8-tetrahydrodibenzo[*e*,*e*'] benzo[1,2-*c*:4,3-*c*']bisoxepine-4,5-diyl]dibenzonitrile (*P*,*S*,*S*)-**190**



Triyne (*S*,*S*)-**183** (42.8 mg, 0.071 mmol), triphenylphosphine (37.2 mg, 0.142 mmol, 2.0 equiv.), dicarbonyl(η^5-cyclopentadienyl)-cobalt(I) (9.4 µl, 0.071 mmol, 1.0 equiv.), reaction period: 45 min. Chromatography: hexane → hexane-acetone 9:1. Yield: 19.8 mg, 45%.

^{1}H NMR (600 MHz, $CDCl_3$): 0.60 (6H, d, *J* = 7.1), 3.32 (6H, s), 4.50 (2H, d, *J* = 11.7), 4.65 (2H, q, *J* = 7.1), 4.71 (2H, d, *J* = 11.7), 6.07 (2H, d, *J* = 2.6), 6.74 (2H, dd, *J* = 8.2, 2.6), 6.88 (2H, dd, *J* = 7.9, 1.6), 7.26 (2H, dd, *J* = 7.9, 1.6), 7.26 (2H, d, *J* = 8.2), 7.33 (2H, dd, *J* = 7.9, 1.6), 7.50 (2H, dd, *J* = 7.9, 1.6).

^{13}C NMR (151 MHz, $CDCl_3$): 22.10 (q), 55.12 (q), 66.75 (t), 72.35 (d), 111.13 (s), 114.92 (d), 116.40 (d), 118.31 (s), 129.81 (d), 130.06 (s), 130.49 (d), 130.58 (d), 131.60 (d), 131.89 (d), 137.37 (s), 138.55 (s), 139.49 (s), 140.36 (s), 144.39 (s), 159.00 (s).

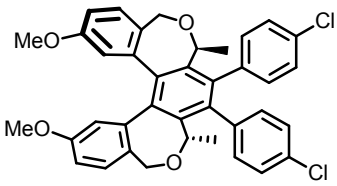
IR ($CHCl_3$): 2964 s, 2929 s, 2857 m, 2839 m, 1607 vs, 1578 m, 1502 s, 1432 m, 1409 m, 1301 m, 1284 s, 1257 s, 1250 m, 1238 vs, 1180 m, 1174 s, 1136 m, 1126 m, 1037 s, 1020 m, 979 m, 822 m, 822 m, 695 w, 636 m, 544 m cm^{-1}.

FAB MS: 604 ($[M]^+$).

HR FAB MS: calculated for $C_{40}H_{32}O_4N_2$ 604.2362, found 604.2386.

Optical rotation: $[\alpha]^{22}_D$ -64° (c 0.139, CH_2Cl_2).

(*P*,3*R*,6*S*)-4,5-Bis(4-chlorophenyl)-11,14-dimethoxy-3,6-dimethyl-1,3,6,8-tetrahydrodibenzo[*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepine (*P*,*S*,*S*)-**191**



Triyne (*S*,*S*)-**184** (44.0 mg, 0.071 mmol), triphenylphosphine (37.1 mg, 0.141 mmol, 2.0 equiv.), dicarbonyl(η^5-cyclopentadienyl)-cobalt(I) (9.4 µl, 0.071 mmol, 1.0 equiv.), reaction period: 1 h 40 min. Chromatography: hexane → hexane-acetone 7:3. Yield: 33.2 mg, 76%.

^{1}H NMR (600 MHz, $CDCl_3$): 0.67 (6H, d, *J* = 7.1), 3.37 (6H, s), 4.55 (2H, d, *J* = 11.7), 4.78 (2H, d, *J* = 11.7), 4.84 (2H, q, *J* = 7.1), 6.14 (2H, d, *J* = 2.6), 6.77 (2H, dd, *J* = 8.2, 2.2), 6.78 (2H, dd, *J* = 8.3, 2.6), 7.08 (2H, dd, *J* = 8.2, 2.2), 7.11 (2H, dd, *J* = 8.2, 2.2), 7.23 (2H, dd, *J* = 8.2, 2.2), 7.31 (2H, d, *J* = 8.3).

^{13}C NMR (151 MHz, $CDCl_3$): 22.20 (q), 55.19 (q), 66.74 (t), 72.42 (d), 114.71 (d), 116.39 (d), 127.93 (d), 128.18 (d), 129.63 (d), 130.26 (s), 130.93 (d), 131.17 (d), 132.67 (s), 137.62 (s), 137.73 (s), 138.16 (s), 140.86 (s), 140.65 (s), 158.90 (s).

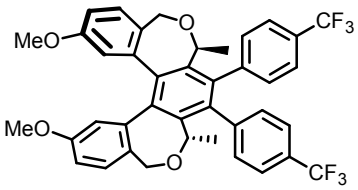
IR ($CHCl_3$): 3030 w, 2836 m, 1606 s, 1595 m, 1579 m, 1499 vs, 1432 m, 1396 vs, 1370 s, 1283 m, 1256 vs, 1199 m, 1175 m, 1146 m, 1125 m, 1107 s, 1090 s, 1077 vs, 1036 s, 1017 s, 859 m, 831 m, 693 w, 570 w cm^{-1}.

EI MS: 622 ($M^{+\bullet}$, 100), 607 (83), 591 (24), 577 (84), 561 (32), 549 (48), 526 (8), 514 (25), 499 (12), 316 (23), 277 (52), 262 (17), 191 (27), 175 (24), 149 (12), 139 (11), 121 (7), 77 (5), 57 (5).

HR EI MS: calculated for $C_{38}H_{32}O_4Cl_2$ 622.1678, found 622.1673.

Optical rotation: $[\alpha]^{22}_D$ -53° (c 0.289, CH_2Cl_2).

(*P*,3*R*,6*S*)-11,14-Dimethoxy-3,6-dimethyl-4,5-bis[4-(trifluoromethyl)phenyl]-1,3,6,8-tetrahydrodibenzo[*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepine (*P*,*S*,*S*)-**192**



Triyne (*S*,*S*)-**185** (27.0 mg, 0.039 mmol), triphenylphosphine (21.1 mg, 0.080 mmol, 2.0 equiv.), dicarbonyl(η^5-cyclopentadienyl)-cobalt(I) (5.2 µl, 0.039 mmol, 1.0 equiv.), reaction period: 1 h 15 min. Chromatography: hexane → hexane-acetone 9:1. Yield: 18.6 mg, 74%.

^{1}H NMR (600 MHz, $CDCl_3$): 0.69 (6H, d, *J* = 7.1), 3.39 (6H, s), 4.57 (2H, d, *J* = 11.7), 4.79 (2H, q, *J* = 7.1), 4.80 (2H, d, *J* = 11.7), 6.16 (2H, d, *J* = 2.6), 6.80 (2H, dd, *J* = 8.3, 2.6), 6.96 (2H, m), 7.32 (2H, m), 7.33 (2H, d, *J* = 8.3), 7.34 (2H, m), 7.51 (2H, m).

^{13}C NMR (151 MHz, $CDCl_3$): 22.20 (q), 55.12 (q), 66.76 (d), 72.42 (t), 114.81 (d), 116.41 (d), 123.88 (s, J_{CF} = 272.1), 124.61 (d), 124.96 (d), 129.04 (s, J_{CF} = 32.6), 129.73 (d), 130.05 (d), 130.10 (s), 130.21 (d), 137.47 (s), 138.11 (s), 140.28 (s), 140.66 (s), 143.33 (s), 158.96 (s).

^{19}F NMR (471 MHz, $CDCl_3$): -58.88 (J_{CF} = 3.6) (s).

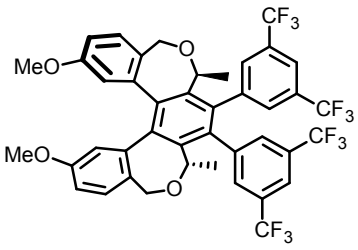
IR ($CHCl_3$): 3435 s, 1638 m, 1614 m, 1579 w, 1501 w, 1433 w, 1406 w, 1369 w, 1327 vs, 1301 w, 1284 w, 1256 w, 1169 m, 1148 m, 1126 m, 1109 m, 1071 m, 1038 w, 1021 w, 935 vw, 866 w, 849 w, 735 w, 696 w, 639 w cm^{-1}.

FAB MS: 690 ($[M]^+$), 675 ($[M\text{-}CH_3]^+$), 659 ($[M\text{-}O]^+$).

HR FAB MS: calculated for $C_{40}H_{32}O_4F_6$ 690.2205, found 690.2192.

Optical rotation: $[\alpha]^{22}_D$ -72° (c 0.517, CH_2Cl_2).

(*P*,3*R*,6*S*)-4,5-Bis[3,5-bis(trifluoromethyl)phenyl]-11,14-dimethoxy-3,6-dimethyl-1,3,6,8-tetrahydrodibenzo[*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepine (*P*,*S*,*S*)-**193**



Triyne (*S*,*S*)-**186** (51.5 mg, 0.062 mmol), triphenylphosphine (34.2 mg, 0.130 mmol, 2.0 equiv.), dicarbonyl(η^5-cyclopentadienyl)-cobalt(I) (9.0 µl, 0.067 mmol, 1.1 equiv.), reaction period: 1 h 15 min. Chromatography: hexane → hexane-acetone 95:5. Yield: 50.8 mg, 99%.

^{1}H NMR (600 MHz, $CDCl_3$): 0.75 (6H, d, *J* = 7.1), 3.41 (6H, s), 4.59 (2H, d, *J* = 11.8), 4.78 (2H, d, *J* = 11.8), 4.83 (2H, q, *J* = 7.1), 6.15 (2H, d, *J* = 2.6), 6.83 (2H, dd, *J* = 8.3, 2.6), 7.33 (2H, bs), 7.34 (2H, d, *J* = 8.3), 7.60 (2H, bs), 7.65 (2H, bs).

^{13}C NMR (151 MHz, $CDCl_3$): 22.13 (q), 55.16 (q), 66.75 (t), 72.58 (d), 115.02 (d), 116.44 (d), 120.93 (s, J_{CF} = 3.8), 122.75 (s, J_{CF} = 273.1), 129.73 (d), 129.93 (d), 129.87 (d), 130.08 (s), 131.76 (s, J_{CF} = 33.6), 131.49 (s, J_{CF} = 33.8), 137.74 (s), 138.94 (s), 139.12 (s, J_{CF} = 3.8), 140.12 (s), 141.47 (s), 159.13 (s).

^{19}F NMR (471 MHz, $CDCl_3$): -59.37 (s), -59.57 (s).

IR ($CHCl_3$): 3087 vw, 2840 w, 1618 w, 1606 m, 1594 m, 1580 w, 1501 w, 1466 m, 1434 w, 1382 m, 1371 m, 1281 vs, 1239 m, 1185 s, 1139 vs, 1107 m, 1086 m, 1035 m, 893 w, 857 w, 848 w, 705 w, 683 m, 429 vw cm^{-1}.

APCI MS: 827 ($[M+H]^+$).

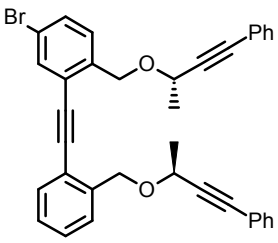
HR APCI MS: calculated for $C_{42}H_{31}O_4F_{12}$ 827.2031, found 827.2060.

Optical rotation: $[\alpha]^{22}_D$ -168° (c 0.121, CH_2Cl_2).

General procedure for Sonogashira coupling of triyne (*S*)-**122 to prepare substituted triynes** (*S,S*)-**123 and** (*S*,*S*)-**195** - (*S*,*S*)-**199:**

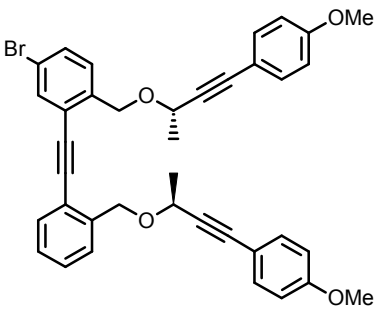
Triyne (*S*)-**122** (0.13-0.24 mmol), tetrakis(triphenylphosphine)palladium(0) (10 mol%), copper iodide (20 mol%), aryl iodide (2.2-5.2 equiv.) were dissolved in toluene and diisopropylamine (9-12 equiv.) was added. After the reaction mixture was stirred at 0 ºC and then at room temperature overnight, it was filtered through a sintered glass (diethyl ether) and solvents were removed *in vacuo*. The flash chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5 or 85:15, depending on compound) provided products (*S,S*)-**123** and (*S*,*S*)-**195** - (*S*,*S*)-**199** as amorphous solids.

4-Bromo-1-({[(1*S*)-1-methyl-3-phenylprop-2-yn-1-yl]oxy}methyl)-2-{[2-({[(1*S*)-1-methyl-3-phenylprop-2-yn-1-yl]oxy}methyl)phenyl]ethynyl}benzene (*S,S*)-**123**



Triyne (*S*)-**122** (84.9 mg, 0.20 mmol), tetrakis(triphenylphosphine)palladium(0) (23.0 mg, 0.020 mmol, 10 mol%), copper iodide (8.0 mg, 0.040 mmol, 20 mol%), aryl iodide (165 mg, 0.807 mmol, 4.0 equiv.), diisopropylamine (300 µl, 2.14 mmol, 11 equiv.), toluene (5 ml). Chromatography: hexane → hexane-diethyl ether 85:15. Yield: 86.1 mg, 75%.

4-Bromo-1-({[(1*S*)-3-(4-methoxyphenyl)-1-methylprop-2-yn-1-yl]oxy}methyl)-2-{[2-({[(1*S*)-3-(4-methoxyphenyl)-1-methylprop-2-yn-1-yl]oxy}methyl)phenyl] ethynyl}benzene (*S*,*S*)-**195**



Triyne (*S*)-**122** (81.0 mg, 0.192 mmol), tetrakis(triphenyl-phosphine)palladium(0) (22.0 mg, 0.019 mmol, 10 mol%), copper iodide (7.3 mg, 0.038 mmol, 20 mol%), aryl iodide (100 mg, 0.427 mmol, 2.2 equiv.), diisopropylamine (300 µl, 2.14 mmol, 11 equiv.), toluene (5 ml). Chromatography: hexane → hexane-diethyl ether 95:5. Yield: 78.5 mg, 65%.

^{1}H NMR (600 MHz, $CDCl_3$): 1.55 (6H, d, *J* = 6.6), 3.78 (6H, s), 4.50 (2H, q, *J* = 6.6), 4.80 (1H, d, *J* = 12.9), 4.85 (1H, d, *J* = 12.5), 4.98 (1H, d, *J* = 12.9), 5.03 (1H, d, *J* = 12.5), 6.75 (4H, m), 7.20 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.30 (4H, m), 7.35 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.40 (1H, bd, *J* = 8.3), 7.44 (1H, dd, *J* = 8.3, 2.0), 7.49 (1H, dd, *J* = 7.7, 1.4), 7.54 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7), 7.63 (1H, d, *J* = 2.0).

^{13}C NMR (151 MHz, $CDCl_3$): 22.31 (q, 2C), 55.24 (q, 2C), 65.58 (d), 65.81 (d), 68.19 (t), 68.64 (t), 85.34 (s), 85.40 (s), 87.41 (s), 87.51 (s), 89.95 (s), 92.81 (s), 113.80 (d, 2C), 114.65 (s), 114.67 (s), 121.38 (s), 120.68 (s), 123.70 (s), 127.31 (d), 127.89 (d), 128.86 (d), 129.24 (d), 131.48 (d), 132.23 (d), 133.11 (d), 133.16 (d), 134.30 (d), 139.11 (s), 140.08 (s), 159.49 (s), 159.53 (s).

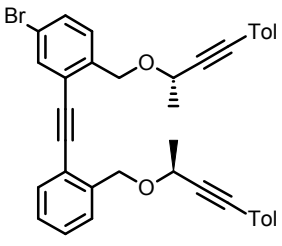
IR ($CHCl_3$): 2936 s, 2840 m, 2225 w, 1607 s, 1589 m, 1573 m, 1556 w, 1510 vs, 1491 m, 1477 m, 1466 m, 1457 m, 1443 m, 1414 w, 1393 w, 1372 m, 1329 s, 1304 m, 1291 s, 1250 vs, 1173 s, 1154 w, 1129 m, 1117 s, 1106 s, 1093 s, 1063 s, 1034 s, 951 w, 834 s, 820 m, 612 w, 573 w cm^{-1}.

FAB MS: 657 ($[M+Na]^+$, with ^{81}Br), 655 ($[M+Na]^+$, with ^{79}Br).

HR FAB MS: calculated for $C_{38}H_{33}O_4{}^{79}BrNa$ 655.1460, found 655.1465.

Optical rotation: $[\alpha]^{22}_D$ -171° (c 0.191, CH_2Cl_2).

4-Bromo-1-({[(1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}methyl)-2-{[2-({[(1*S*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}methyl)phenyl]ethynyl} benzene (*S*,*S*)-**196**



Triyne (*S*)-**122** (100.0 mg, 0.237 mmol), tetrakis(triphenyl-phosphine)palladium(0) (28.3 mg, 0.024 mmol, 10 mol%), copper iodide (10.1 mg, 0.053 mmol, 22 mol%), aryl iodide (140.2 mg, 0.643 mmol, 2.7 equiv.), diisopropylamine (300 µl, 2.14 mmol, 9 equiv.), toluene (5 ml). Chromatography: hexane → hexane-diethyl ether 9:1. Yield: 114.2 mg, 80%.

^{1}H NMR (600 MHz, $CDCl_3$): 1.55 (6H, d, *J* = 6.6), 2.32 (6H, bs), 4.50 (2H, q, *J* = 6.6), 4.79 (1H, d, *J* = 12.9), 4.85 (1H, d, *J* = 12.6), 4.98 (1H, dd, *J* = 12.8, 0.8), 5.03 (1H, d,

J = 12.6), 7.04 (4H, m), 7.19 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.26 (4H, m), 7.35 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.40 (1H, ddt, *J* = 8.3, 0.8, 0.8, 0.5), 7.44 (1H, dd, *J* = 8.3, 2.0), 7.49 (1H, ddd, *J* = 7.7, 1.4, 0.3), 7.54 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7), 7.63 (1H, d, *J* = 2.0).

^{13}C NMR (151 MHz, $CDCl_3$): 21.44 (q, 2C), 22.27 (q, 2C), 65.59 (d), 65.81 (d), 68.24 (t), 68.70 (t), 85.56 (s), 85.61 (s), 88.14 (s), 88.25 (s), 89.97 (s), 92.83 (s), 119.49 (s), 119.51 (s), 120.70 (s), 121.39 (s), 123.70 (s), 127.31 (d), 127.90 (d), 128.84 (d), 128.96 (d, 2C), 129.23 (d), 131.47 (d), 131.56 (d), 131.60 (d), 132.24 (d), 134.32 (d), 138.30 (s), 138.36 (s), 139.09 (s), 140.06 (s).

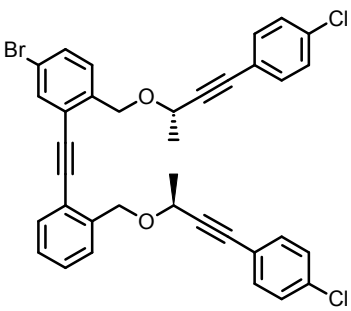
IR ($CHCl_3$): 2936 m, 2868 m, 2225 w, 1607 w, 1600 w, 1589 w, 1556 w, 1510 s, 1491 m, 1477 w, 1451 w, 1408 w, 1392 w, 1373 m, 1329 s, 1314 w, 1274 w, 1258 w, 1180 w, 1154 w, 1130 m, 1117 s, 1105 s, 1093 vs, 1022 m, 950 w, 819 vs, 574 w, 445 w cm^{-1}.

ESI MS: 603 ($[M+H]^+$, with ^{81}Br), 601 ($[M+H]^+$, with ^{79}Br).

HR ESI MS: calculated for $C_{38}H_{34}O_2{}^{79}Br$ 601.1742, found 601.1758.

Optical rotation: $[\alpha]^{22}_D$ -175° (c 0.077, CH_2Cl_2).

4-Bromo-1-({[(1*S*)-3-(4-chlorophenyl)-1-methylprop-2-yn-1-yl]oxy}methyl)-2-{[2-({[(1*S*)-3-(4-chlorophenyl)-1-methylprop-2-yn-1-yl]oxy}methyl)phenyl]ethynyl} benzene (*S*,*S*)-**197**



Triyne (*S*)-**122** (77.2 mg, 0.183 mmol), tetrakis(triphenyl-phosphine)palladium(0) (21.0 mg, 0.018 mmol, 10 mol%), copper iodide (7.0 mg, 0.037 mmol, 20 mol%), aryl iodide (131 mg, 0.55 mmol, 3.0 equiv.), diisopropylamine (300 µl, 2.14 mmol, 12 equiv.), toluene (5 ml). Chromatography: hexane → hexane-diethyl ether 85:15. Yield: 99 mg, 85%.

^{1}H NMR (600 MHz, $CDCl_3$): 1.55 (6H, d, *J* = 6.6), 4.47 (2H, q, *J* = 6.6), 4.78 (1H, d, *J* = 12.8), 4.83 (1H, d, *J* = 12.5), 4.95 (1H, d, *J* = 12.8), 5.00 (1H, d, *J* = 12.5), 7.19 (4H, m), 7.21 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.26 (4H, m), 7.37 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.38

(1H, d, *J* = 8.3), 7.46 (1H, dd, *J* = 8.3, 2.1), 7.47 (1H, dd, *J* = 7.7, 1.3), 7.52 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7), 7.62 (1H, d, *J* = 2.0).

^{13}C NMR (151 MHz, $CDCl_3$): 22.12 (q), 22.14 (q), 65.41 (d), 65.61 (d), 68.28 (t), 68.76 (t), 84.32 (s), 84.40 (s), 89.79 (s), 89.89 (s), 89.92 (s), 92.73 (s), 120.86 (s), 120.96 (s), 120.99 (s), 121.41 (s), 123.71 (s), 127.45 (d), 128.01 (d), 128.53 (d), 128.54 (d), 128.97 (d), 129.32 (d), 131.59 (d), 132.18 (d), 132.85 (d), 132.90 (d), 134.28 (s), 134.32 (s), 134.34 (d), 138.78 (s), 139.81 (s).

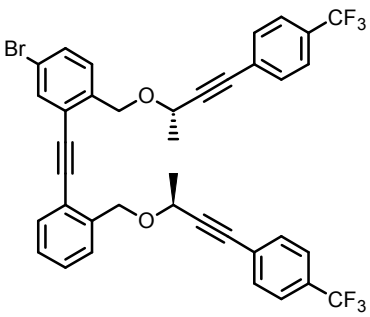
IR ($CHCl_3$): 2990 m, 2867 m, 2226 w, 1601 w, 1589 m, 1556 w, 1490 vs, 1453 m, 1397 m, 1373 m, 1328 s, 1310 m, 1257 m, 1176 w, 1154 w, 1129 m, 1120 s, 1098 vs, 1015 s, 951 w, 830 vs, 576 w, 451 w cm^{-1}.

FAB MS: 665 ($[M+Na]^+$, with ^{81}Br), 663 ($[M+Na]^+$, with ^{79}Br).

HR FAB MS: calculated for $C_{36}H_{27}O_2{}^{79}BrNaCl_2$ 663.0469, found 663.0462.

Optical rotation: $[\alpha]^{22}_D$ -196° (c 0.217, CH_2Cl_2).

4-Bromo-1-[({(1*S*)-1-methyl-3-[4-(trifluoromethyl)phenyl]prop-2-yn-1-yl}oxy) methyl]-2-({2-[({(1*S*)-1-methyl-3-[4-(trifluoromethyl)phenyl]prop-2-yn-1-yl}oxy) methyl]phenyl}ethynyl)benzene (*S*,*S*)-**198**



Triyne (*S*)-**122** (54.5 mg, 0.129 mmol), tetrakis(triphenyl-phosphine)palladium(0) (15.0 mg, 0.013 mmol, 10 mol%), copper iodide (4.9 mg, 0.026 mmol, 20 mol%), aryl iodide (185 mg, 0.680 mmol, 5.2 equiv.), diisopropylamine (180 µl, 1.29 mmol, 10 equiv.), toluene (4 ml). Chromatography: hexane → hexane-diethyl ether 9:1. Yield: 64.3 mg, 70%.

^{1}H NMR (600 MHz, $CDCl_3$): 1.56 (6H, d, *J* = 6.6), 4.49 (2H, q, *J* = 6.6), 4.79 (1H, d, *J* = 12.7), 4.84 (1H, d, *J* = 12.4), 4.96 (1H, d, *J* = 12.7), 5.01 (1H, d, *J* = 12.4), 7.20 (1H, dt, *J* = 7.5, 7.5, 1.4), 7.36 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.36 (1H, d, *J* = 8.3), 7.42 (4H, m), 7.44 (1H, dd, *J* = 8.3, 2.0), 7.46 (4H, m), 7.47 (1H, ddt, *J* = 7.5, 1.4, 0.7, 0.7), 7.51 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7), 7.62 (1H, d, *J* = 2.0).

^{13}C NMR (151 MHz, $CDCl_3$): 22.02 (q), 22.05 (q), 65.30 (d), 65.47 (d), 68.33 (t), 68.83 (t), 84.07 (s), 84.18 (s), 89.83 (s), 91.24 (s), 91.39 (s), 92.65 (s), 120.92 (s), 121.43 (s), 123.74 (s), 123.80 (s, J_{FC} = 272.1), 125.11 (d, J_{FC} = 3.8), 126.22 (s), 126.22 (s), 127.51 (d), 128.08 (d), 129.04 (d), 129.36 (d), 129.90 (s, J_{FC} = 32.6), 131.66 (d), 131.82 (d), 131.87 (d), 132.15 (d), 134.35 (d), 138.55 (s), 139.60 (s).

^{19}F NMR (471 MHz, $CDCl_3$): -59.02 (s), -59.04 (s).

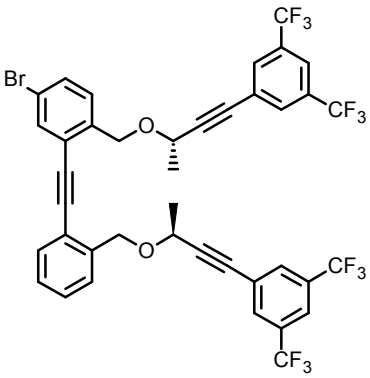
IR ($CHCl_3$): 2990 m, 2936 m, 2868 m, 2216 w, 1616 s, 1601 w, 1589 m, 1575 w, 1556 w, 1515 w, 1491 m, 1478 w, 1451 m, 1404 m, 1394 m, 1373 m, 1321 vs, 1287 m, 1253 m, 1171 vs, 1132 vs, 1095 vs, 1068 vs, 844 vs, 708 m, 623 w, 598 m cm^{-1}.

ESI MS: 733 ($[M+Na]^+$, with ^{81}Br), 731 ($[M+Na]^+$, with ^{79}Br).

HR ESI MS: calculated for $C_{38}H_{27}O_2{}^{79}BrF_6Na$ 731.0991, found 731.0990.

Optical rotation: $[\alpha]^{22}_D$ -177° (c 0.171, CH_2Cl_2).

1-[({(1*S*)-3-[3,5-Bis(trifluoromethyl)phenyl]-1-methylprop-2-yn-1-yl}oxy)methyl]-2-({2-[({(1*S*)-3-[3,5-bis(trifluoromethyl)phenyl]-1-methylprop-2-yn-1-yl}oxy) methyl]phenyl}ethynyl)-4-bromobenzene (*S*,*S*)-**199**



Triyne (*S*)-**122** (63.7 mg, 0.151 mmol), tetrakis(triphenyl-phosphine)palladium(0) (17.0 mg, 0.015 mmol, 10 mol%), copper iodide (5.9 mg, 0.031 mmol, 20 mol%), aryl iodide (205.6 mg, 0.603 mmol, 4.0 equiv.), diisopropylamine (210 µl, 1.51 mmol, 10 equiv.), toluene (5 ml). Chromatography: hexane → hexane-diethyl ether 9:1. Yield: 116.2 mg, 91%.

^{1}H NMR (600 MHz, $CDCl_3$): 1.57 (3H, d, *J* = 6.6), 1.58 (3H, d, *J* = 6.6), 4.50 (1H, q, *J* = 6.6), 4.51 (1H, q, *J* = 6.6), 4.80 (1H, d, *J* = 12.6), 4.84 (1H, d, *J* = 12.3), 4.96 (1H, d, *J* = 12.6), 5.00 (1H, d, *J* = 12.3), 7.20 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.33 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.36 (1H, bd, *J* = 8.3), 7.42 (1H, dd, *J* = 8.3, 2.0), 7.47 (1H, bdd, *J* = 7.5, 1.4), 7.49 (1H, ddq, *J* = 7.7, 1.4, 0.7, 0.7, 0.7), 7.61 (1H, d, *J* = 2.0), 7.75-7.77 (6H, m).

^{13}C NMR (151 MHz, $CDCl_3$): 21.96 (q), 22.01 (q), 65.36 (d), 65.45 (d), 68.65 (t), 69.26 (t), 82.39 (s), 82.45 (s), 89.87 (s), 92.57 (s), 92.74 (s), 92.78 (s), 121.05 (s), 121.48 (s), 121.76 (d, J_{FC} = 3.7), 122.81 (s, J_{FC} = 272.8), 123.77 (s), 124.79 (s), 124.81 (s), 127.64 (d), 128.28 (d), 129.04 (d), 129.46 (d), 131.52 (d, J_{FC} = 3.7), 131.68 (d), 131.80 (s, J_{FC} = 33.8), 132.07 (d), 134.39 (d), 138.33 (s), 139.44 (s).

^{19}F NMR (471 MHz, $CDCl_3$): -59.31 (s), -59.32 (s).

IR ($CHCl_3$): 3086 vw, 2230 vw, 1615 w, 1600 vw, 1589 w, 1556 w, 1491 w, 1462 w, 1400 w, 1382 s, 1327 w, 1280 vs, 1233 w, 1183 s, 1144 vs, 1107 m, 1095 m, 1025 w, 953 w, 899 m, 848 w, 820 w, 700 m, 684 m, 426 w cm^{-1}.

ESI MS: 847 ($[M+H]^+$, with ^{81}Br), 845 ($[M+H]^+$, with ^{79}Br).

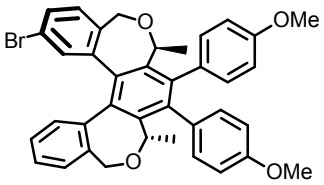
HR ESI MS: calculated for $C_{40}H_{26}O_2{}^{79}BrF_{12}$ 845.0925, found 845.0904.

Optical rotation: $[\alpha]^{22}_D$ -154° (c 0.374, CH_2Cl_2).

General procedure for cyclotrimerisation of triynes (*S*,*S*)-**195** – (*S*,*S*)-**197 and** (*S*,*S*)-**123 to helicene-like products** (*P*,*S*,*S*)-**200** – (*P*,*S*,*S*)-**204 and** (*P*,*S*,*S*)-**124:**

Triyne (*S*,*S*)-**195** – (*S*,*S*)-**197** and (*S*,*S*)-**199** (0.07 mmol), triphenylphosphine (2.0 equiv.) and dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (1.0 equiv.) were flushed with argon in a Schlenk flask and decane (4 ml) was added. The reaction mixture was heated at 140 ºC using a halogen lamp until the starting material disappeared (according to TLC analysis). Then the reaction mixture was purified by chromatography on silica gel (hexane-diethyl ether 100:0 to 9:1 or 75:25, depending on the substrate) to provide products (*P*,*S*,*S*)-**200** – (*P*,*S*,*S*)-**202** and (*P*,*S*,*S*)-**204** as amorphous material.

Cyclotrimerisation (*S*,*S*)-**123** → (*P*,*S*,*S*)-**124** is on page 106.



(*P*,3*S*,6*S*)-11-Bromo-4,5-bis(4-methoxyphenyl)-3,6-dimethyl-1,3,6,8-tetrahydro dibenzo[*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepine (*P*,*S*,*S*)-**200**

Triyne (*S*,*S*)-**195** (69.2 mg, 0.109 mmol), triphenylphosphine (57.3 mg, 0.219 mmol, 2.0 equiv.), dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (14.5 µl, 0.109 mmol, 1.0 equiv.), reaction period: 2 h 40 min. Chromatography: hexane → hexane-diethyl ether 75:25. Yield: 50.1 mg, 72%.

^{1}H NMR (600 MHz, $CDCl_3$): 0.62 (3H, d, *J* = 7.1), 0.67 (3H, d, *J* = 7.1), 3.74 (6H, s), 4.96 (2H, q, *J* = 7.1), 4.55 (1H, d, *J* = 11.5), 4.61 (1H, d, *J* = 11.5), 4.78 (1H, d, *J* = 11.5), 5.84 (1H, d, *J* = 11.5), 6.54 (1H, dd, *J* = 7.7, 1.2), 6.62 (2H, dd, *J* = 8.5, 2.2), 6.68 (1H, d, *J* = 2.0), 6.73 (2H, dd, *J* = 8.5, 2.2), 6.77 (2H, dd, *J* = 8.5, 2.2), 7.03 (1H, dt, *J* = 7.6, 7.6, 1.2), 7.07 (2H, dd, *J* = 8.5, 2.2), 7.26 (1H, dt, *J* = 7.4, 7.4, 1.2), 7.27 (1H, d, *J* = 8.0), 7.33 (1H, dd, *J* = 8.0, 2.0), 7.44 (1H, dd, *J* = 7.5, 1.2).

^{13}C NMR (151 MHz, $CDCl_3$): 22.12 (q), 22.45 (q), 55.08 (q, 2C), 66.72 (t), 67.45 (t), 72.68 (d), 72.72 (d), 113.03 (d), 113.05 (d), 113.10 (d, 2C), 121.21 (s), 127.42 (d), 127.97 (d), 128.70 (d), 129.99 (d), 130.46 (d), 130.57 (d), 130.59 (d), 130.89 (d), 130.96 (d), 131.79 (d), 132.17 (s), 132.21 (s), 134.79 (d), 135.41 (s), 136.70 (s), 137.11 (s), 137.72 (s), 137.75 (s), 137.92 (s), 139.38 (s), 142.17 (s), 142.25 (s), 142.61 (s), 157.84 (s), 157.85 (s).

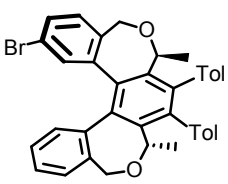
IR ($CHCl_3$): 2929 vs, 2857 m, 2840 m, 1611 s, 1594 m, 1576 m, 1570 m, 1554 w, 1514 vs, 1494 m, 1484 m, 1484 m, 1443 m, 1410 m, 1393 m, 1304 m, 1286 s, 1246 vs, 1178 s, 1128 m, 1110 s, 1079 vs, 1033 s, 1014 m, 949 m, 840 m, 817 m cm^{-1}.

EI MS: 634 ($M^{+\bullet}$, with ^{81}Br, 96), 632 ($M^{+\bullet}$, with ^{79}Br, 100), 619 (49), 617 (55), 601 (14), 599 (15), 587 (19), 571 (31), 569 (18), 557 (13), 520 (8), 508 (37), 492 (26), 477 (15), 466 (27), 435 (3), 401 (6), 359 (8), 326 (7), 316 (9), 252 (6), 245 (8), 200 (4), 193 (5), 187 (4), 149 (42), 135 (9), 101 (10), 97 (16), 71 (17), 59 (18), 57 (26), 43 (37).

HR EI MS: calculated for $C_{38}H_{33}O_4{}^{79}Br$ 632.1562, found 632.1550.

Optical rotation: $[\alpha]^{22}_D$ -86° (c 0.295, CH_2Cl_2).

(*P*,3*S*,6*S*)-11-Bromo-4,5-bis(4-methylphenyl)-3,6-dimethyl-1,3,6,8-tetrahydro dibenzo[*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepine (*P*,*S*,*S*)-**201**



Triyne (*S*,*S*)-**196** (37.8 mg, 0.063 mmol), triphenylphosphine (32.5 mg, 0.124 mmol, 2.0 equiv.), dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (8.3 µl, 0.063 mmol, 1.0 equiv.), reaction period: 1 h. Chromatography: hexane → hexane-diethyl ether 8:2. Yield: 18.7 mg, 49%.

^{1}H NMR (600 MHz, $CDCl_3$): 0.62 (3H, d, *J* = 7.1), 0.66 (3H, d, *J* = 7.1), 2.24 (6H, bs), 4.92 (2H, q, *J* = 7.1), 4.55 (1H, d, *J* = 11.5), 4.61 (1H, d, *J* = 11.5), 4.79 (1H, d, *J* = 11.5), 5.84 (1H, d, *J* = 11.5), 6.54 (2H, m), 6.86-6.87 (2H, m), 7.01-7.05 (4H, m), 6.54 (1H, dd, *J* = 7.7, 1.2), 6.68 (1H, d, *J* = 2.0), 7.03 (1H, dt, *J* = 7.6, 7.6, 1.2), 7.25 (1H, dt, *J* = 7.5, 7.5, 1.2), 7.26 (1H, d, *J* = 8.0), 7.32 (1H, dd, *J* = 8.0, 2.0), 7.43 (1H, dd, *J* = 7.5, 1.2).

^{13}C NMR (151 MHz, $CDCl_3$): 21.14 (q, 2C), 22.12 (q), 22.45 (q), 66.70 (t), 67.43 (t), 72.64 (d), 72.68 (d), 121.20 (s), 127.41 (d), 127.94 (d), 128.09 (d), 128.13 (d), 128.39 (d), 128.69 (d), 129.37 (d), 129.38 (d), 129.69 (d), 129.77 (d), 129.99 (d), 130.44 (d), 131.79 (d), 134.79 (d), 135.36 (s), 135.75 (s), 135.77 (s), 136.70 (s), 136.74 (s), 136.78 (s), 137.06 (s), 137.52 (s), 137.69 (s), 137.71 (s), 139.40 (s), 142.24 (s), 142.27 (s), 142.68 (s).

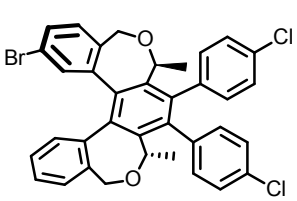
IR ($CHCl_3$): 2968 s, 2927 vs, 2867 m, 1606 m, 1606 m, 1593 m, 1584 m, 1559 m, 1515 s, 1484 m, 1415 m, 1307 m, 1285 m, 1183 m, 1128 m, 1113 s, 1079 vs, 1022 s, 818 m cm^{-1}.

ESI MS: 625 ($[M+Na]^+$, with ^{81}Br), 623 ($[M+Na]^+$, with ^{79}Br).

HR ESI MS: calculated for $C_{38}H_{34}O_4{}^{79}Br$ 623.1556, found 623.1553.

Optical rotation: $[\alpha]^{22}_D$ -96° (c 0.216, CH_2Cl_2).

(*P*,3*S*,6*S*)-11-Bromo-4,5-bis(4-chlorophenyl)-3,6-dimethyl-1,3,6,8-tetrahydro dibenzo[*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepine (*P*,*S*,*S*)-**202**



Triyne (*S*,*S*)-**183** (28.5 mg, 0.044 mmol), triphenylphosphine (24.0 mg, 0.088 mmol, 2.0 equiv.), dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (5.9 µl, 0.044 mmol, 1.0 equiv.), reaction period: 30 min. Chromatography: hexane → hexane-diethyl ether 75:15. Yield: 20.4 mg, 72%. Note: the product is prone to decomposition on silica gel and in solution.

^{1}H NMR (600 MHz, $CDCl_3$): 0.59 (3H, d, *J* = 7.1), 0.64 (3H, d, *J* = 7.1), 4.83 (2H, q, *J* = 7.1), 4.53 (1H, d, *J* = 11.6), 4.59 (1H, d, *J* = 11.6), 4.73 (1H, d, *J* = 11.6), 5.79 (1H, d, *J* = 11.6), 6.51 (1H, dd, *J* = 7.7, 1.3), 6.65 (1H, d, *J* = 2.0), 6.74 (2H, dd, *J* = 8.2, 2.2), 7.01 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.07 (4H, dd, *J* = 8.2, 2.2), 7.21 (2H, dd, *J* = 8.2, 2.2), 7.25 (1H, dt, *J* = 7.5, 7.5, 1.3), 7.25 (1H, d, *J* = 8.0), 7.32 (1H, dd, *J* = 8.0, 2.0), 7.42 (1H, dd, *J* = 7.5, 1.3).

^{13}C NMR (151 MHz, $CDCl_3$): 22.01 (q), 22.35 (q), 66.72 (t), 67.45 (t), 72.53 (d), 72.56 (d), 121.36 (s), 127.58 (d), 127.97 (d), 128.00 (d), 128.23 (d), 128.29 (d), 128.83 (d), 130.12 (d), 130.79 (d), 130.85 (d), 130.87 (d), 131.08 (d), 131.16 (d), 131.71 (d), 132.77 (s), 132.79 (s), 134.72 (d), 136.14 (s), 136.57 (s), 137.57 (s), 137.60 (s), 137.75 (s), 137.86 (s), 137.93 (s), 137.97 (s), 138.96 (s), 140.69 (s), 141.11 (s), 141.79 (s).

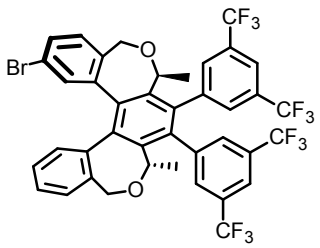
IR ($CHCl_3$): 2966 s, 2928 s, 2857 m, 1603 w, 1594 m, 1570 w, 1557 w, 1495 s, 1485 m, 1472 w, 1396 m, 1127 w, 1113 m, 1090 s, 1079 vs, 1016 s, 949 w, 832 m, 816 m cm^{-1}.

FAB MS: 665 ($[M+Na]^+$, with ^{81}Br), 663 ($[M+Na]^+$, with ^{79}Br).

HR FAB MS: calculated for $C_{36}H_{27}O_2{}^{79}BrCl_2Na$ 663.0469, found 663.0480.

Optical rotation: $[\alpha]^{22}_D$ -101° (c 0.099, CH_2Cl_2).

(*P*,3*S*,6*S*)-4,5-Bis[3,5-bis(trifluoromethyl)phenyl]-11-bromo-3,6-dimethyl-1,3,6,8-tetrahydrodibenzo[*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepine (*P*,*S*,*S*)-**204**



Triyne (*S*,*S*)-**183** (44.0 mg, 0.052 mmol), triphenylphosphine (27.3 mg, 0.104 mmol, 2.0 equiv.), dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (7.0 µl, 0.052 mmol, 1.0 equiv.), reaction period: 2 h. Chromatography: hexane → hexane-diethyl ether 9:1. Yield: 8.8 mg, 20%. Note: the compound was unstable in solution.

^{1}H NMR (600 MHz, $CDCl_3$): 0.69 (3H, d, *J* = 7.1), 0.75 (3H, d, *J* = 7.1), 4.84 (2H, q, *J* = 7.1), 4.60 (1H, d, *J* = 11.7), 4.66 (1H, d, *J* = 11.7), 4.77 (1H, d, *J* = 11.7), 5.82 (1H, d, *J* = 11.7), 6.55 (1H, dd, *J* = 7.7, 1.2), 6.69 (1H, d, *J* = 2.0), 7.09 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.31 (1H, d, *J* = 8.0), 7.32 (1H, dt, *J* = 7.6, 7.6, 1.2), 7.33 (2H, m), 7.40 (1H, dd, *J* = 8.0, 2.0), 7.48 (1H, dd, *J* = 7.5, 1.3), 7.59 (2H, m), 7.65 (2H, bs).

^{13}C NMR (151 MHz, $CDCl_3$): 21.95 (q), 22.30 (q), 66.73 (t), 67.45 (t), 72.68 (d), 72.79 (d), 121.04 (d), 121.67 (s), 122.72 (s, J_{FC} = 273.0), 127.90 (d), 128.85 (d), 129.03 (d), 129.67 (d), 129.87 (d), 131.39 (d), 131.49 (s, J_{FC} = 35.0), 131.56 (d), 134.54 (d), 136.42 (s), 137.43 (s), 137.51 (s), 137.69 (s), 137.86 (s), 138.21 (s), 139.00 (s), 139.29 (s), 139.38 (s), 141.22 (s), 141.25 (s).

^{19}F NMR (471 MHz, $CDCl_3$): -59.35 (s), -59.56 (s).

IR ($CHCl_3$): 2967 s, 2928 s, 2857 s, 2967 s, 2928 s, 1618 m, 1593 m, 1593 m, 1571 w, 1560 w, 1495 w, 1495 w, 1484 m, 1484 m, 1464 m, 1396 s, 1382 vs, 1316 s, 1278 vs, 1238 s, 1187 vs, 1140 vs, 1108 s, 1088 vs, 1077 vs, 950 m, 905 vs, 889 m, 683 s, 432 w cm^{-1}.

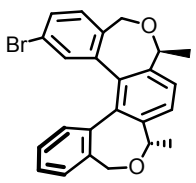
FAB MS: due to decomposition molecular peak was not observed.

Optical rotation: $[\alpha]^{22}_D$ -68° (c 0.259, CH_2Cl_2).

General procedure for cyclotrimerisation of triynes (*S*,*S*)-**122**, (*S*,*S*)-**140 and** (*S*,*S*)-**180 to helicene-like products** (*P*,*S*,*S*)-**205** – (*P*,*S*,*S*)-**207:**

Triyne (*S*,*S*)-**122**, (*S*,*S*)-**140** and (*S*,*S*)-**180** (0.031-0.174 mmol), triphenylphosphine (2.0 equiv.) and dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (1.0 equiv.) were dissolved in THF (3-5 ml) in a 5 ml microwave reactor under argon and heated at 190 ºC for 5-10 min. Then the volatiles were removed *in vacuo* and the residue purified by flash chromatography on silica gel (hexane-ethyl acetate 10:0 to 9:1) to provide product (*M*,*S*,*S*)-**205** - (*M*,*S*,*S*)-**207** as a colourless oil or white crystals.

(*M*,3*S*,6*S*)-11-Bromo-3,6-dimethyl-1,3,6,8-tetrahydrodibenzo[*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepine (*M*,*S*,*S*)-**205**



Triyne (*S*,*S*)-**122** (20 mg, 0.047 mmol), triphenylphosphine (25 mg, 0.095 mmol, 2.0 equiv.), dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (7 µl, 0.052 mmol, 1.1 equiv.), THF (3 ml), reaction period: 5 min. Yield: 6.6 mg, 35%, a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.64 (6H, d, *J* = 6.4), 4.22 (1H, q, *J* = 6.4), 4.24 (1H, q, *J* = 6.4), 4.34 (1H, d, *J* = 11.3), 4.39 (1H, d, *J* = 11.3), 4.58 (1H, d, *J* = 11.3), 4.63 (1H, d, *J* = 11.3), 6.50 (1H, dd, *J* = 7.7, 1.3), 6.61 (1H, d, *J* = 2.0), 7.07 (1H, dt, *J* = 7.5, 7.5, 1.3), 7.29 (1H, d, *J* = 8.0), 7.32 (1H, dt, *J* = 7.4, 7.4, 1.3), 7.39 (1H, dd, *J* = 8.0, 2.0), 7.45 (1H, bdd, *J* = 7.5, 1.7), 7.60 (1H, d, *J* = 8.1), 7.63 (1H, d, *J* = 8.1).

^{13}C NMR (151 MHz, $CDCl_3$): 17.82 (q), 17.83 (q), 67.28 (t), 68.01 (t), 68.65 (d), 68.73 (d), 121.31 (s), 125.19 (d), 125.61 (d), 127.50 (d), 128.28 (d), 129.08 (d), 130.39 (d), 130.59 (d), 130.81 (d), 133.65 (d), 134.41 (s), 135.62 (s), 136.46 (s), 137.78 (s), 138.00 (s), 138.04 (s), 138.65 (s), 141.49 (s).

IR ($CHCl_3$): 3072 w, 2982 m, 2963 m, 2928 s, 2860 m, 1604 vw, 1591 w, 1577 vw, 1558 vw, 1495 w, 1482 m, 1463 m, 1450 w, 1424 m, 1403 vw, 1377 m, 1364 m, 1308 vw, 1157 w, 1130 w, 1109 w, 1087 vs, 1047 m, 949 w, 830 m, 822 w, 418 w cm^{-1}.

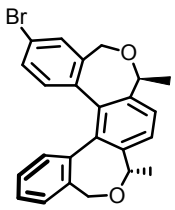
EI MS: 422 ($M^{+\bullet}$, with ^{81}Br, 32), 420 ($M^{+\bullet}$, with ^{79}Br, 31), 407 (30), 405 (32), 377 (13), 361 (6), 347 (5), 308 (7), 296 (18), 280 (20), 268 (22), 253 (52), 239 (18), 226 (7),

202 (4), 189 (5), 178 (6), 164 (10), 149 (53), 126 (7), 111 (9), 97 (35), 95 (37), 85 (16), 83 (17), 69 (100), 67 (39), 57 (36), 41 (30).

HR EI MS: calculated for $C_{24}H_{21}O_2{}^{79}Br$ 420.0725, found 420.0735.

Optical rotation: $[\alpha]^{22}_D$ -8° (c 0.063, CH_2Cl_2).

(*M*,3*S*,6*S*)-10-Bromo-3,6-dimethyl-1,3,6,8-tetrahydrodibenzo[*e*,*e*']benzo[1,2-*c*:4,3-*c*']bisoxepine (*M*,*S*,*S*)-**206**



Triyne (*S*,*S*)-**140** (13 mg, 0.031 mmol), triphenylphosphine (16 mg, 0.062 mmol, 2.0 equiv.), dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (4 µl, 0.031 mmol, 1.0 equiv.), THF (3 ml), reaction period: 5 min. Yield: 4 mg, 31%, a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.63 (3H, d, *J* = 6.5), 1.64 (3H, d, *J* = 6.5), 4.21 (2H, q, *J* = 6.5), 4.37 (1H, d, *J* = 11.2), 4.39 (1H, d, *J* = 11.2), 4.56 (1H, d, *J* = 11.2), 4.61 (1H, d, *J* = 11.2), 6.39 (1H, d, *J* = 8.3), 6.53 (1H, dd, *J* = 7.7, 1.3), 7.05 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.12 (1H, dd, *J* = 8.3, 2.1), 7.29 (1H, dt, *J* = 7.6, 7.6, 1.3), 7.43 (1H, dd, *J* = 7.7, 1.3), 7.58 (1H, d, *J* = 2.1), 7.60 (1H, d, *J* = 8.2), 7.62 (1H, d, *J* = 8.2).

^{13}C NMR (151 MHz, $CDCl_3$): 17.84 (q, 2C), 67.39 (t), 67.93 (t), 68.64 (d), 68.86 (d), 121.50 (s), 125.24 (d), 125.42 (d), 127.66 (d), 128.06 (d), 129.00 (d), 130.47 (d), 130.73 (d), 131.82 (d), 132.35 (d), 135.61 (s), 136.78 (s), 137.52 (s), 137.68 (s), 137.92 (s), 138.03 (s), 138.46 (s), 138.99 (s).

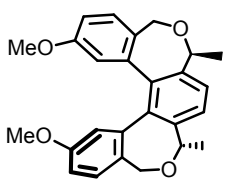
IR ($CHCl_3$): 3100 vw, 3071 w, 2982 m, 1604 vw, 1593 w, 1590 w, 1575 w, 1560 w, 1482 m, 1463 m, 1449 w, 1424 m, 1403 vw, 1377 m, 1364 m, 1308 vw, 1157 w, 1130 w, 1109 w, 1087 vs, 1047 m, 949 w, 830 m, 822 w, 694 w, 493 vw, 418 w cm^{-1}.

EI MS: 422 ($M^{+\bullet}$, with ^{81}Br, 50), 420 ($M^{+\bullet}$, with ^{79}Br, 52), 407 (54), 405 (58), 391 (10), 389 (10), 377 (28), 375 (22), 361 (14), 347 (10), 308 (14), 296 (57), 280 (39), 268 (48), 253 (100), 239 (38), 226 (14), 202 (8), 189 (10), 178 (7), 165 (9), 141 (10), 126 (18), 86 (63), 84 (97), 43 (35).

HR EI MS: calculated for $C_{24}H_{21}O_2{}^{79}Br$ 420.0725, found 420.0727.

Optical rotation: $[\alpha]^{22}_D$ +124 (c 0.102, CH_2Cl_2).

(*M*,3*S*,6*S*)-11,14-Dimethoxy-3,6-dimethyl-1,3,6,8-tetrahydrodibenzo[*e*,*e*']benzo [1,2-*c*:4,3-*c*']bisoxepine (*M*,*S*,*S*)-**207**



Triyne (*S*,*S*)-**180** (70 mg, 0.174 mmol), triphenylphosphine (91 mg, 0.347 mmol, 2.0 equiv.), dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (23 µl, 0.174 mmol, 1.0 equiv.), THF (5 ml), reaction period: 10 min. Yield: 20 mg, 29%, white crystals. The single crystal was grown by solvent diffusion and evaporation from heptane-dichloromethane.

M.p.: 179-181 ºC (hexane).

^{1}H NMR (600 MHz, $CDCl_3$): 1.64 (6H, d, *J* = 6.5), 3.36 (6H, s), 4.27 (2H, q, *J* = 6.5), 4.36 (2H, d, *J* = 11.4), 4.57 (2H, d, *J* = 11.4), 6.08 (2H, d, *J* = 2.7), 6.81 (2H, dd, *J* = 8.2, 2.7), 7.32 (2H, d, *J* = 8.2), 7.60 (2H, s).

^{13}C NMR (151 MHz, $CDCl_3$): 17.84 (q), 55.07 (q), 67.27 (t), 68.54 (d), 114.55 (d), 115.43 (d), 125.15 (d), 128.26 (s), 129.88 (d), 137.90 (s), 137.93 (s), 140.55 (s), 158.71 (s).

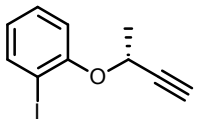
IR ($CHCl_3$): 3077 w, 3028 w, 2984 s, 2962 m, 2837 m, 1609 vs, 1591 m, 1573 m, 1559 w, 1498 s, 1466 s, 1455 m, 1431 m, 1376 m, 1319 s, 1289 vs, 1264 m, 1253 m, 1231 s, 1190 w, 1178 s, 1152 m, 1124 m, 1082 s, 1034 vs, 934 w, 863 m, 855 m, 689 vw cm^{-1}.

ESI MS: 425 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{26}H_{26}O_4Na$ 425.1723, found 425.1721.

Optical rotation: $[\alpha]^{22}_D$ -62° (c 0.215, CH_2Cl_2).

1-Iodo-2-{[(1*R*)-1-methylprop-2-yn-1-yl]oxy}benzene (*R*)-**208**



A solution of 2-iodophenol (562 mg, 2.55 mmol), triphenylphosphine (669 mg, 2.55 mmol, 1.0 equiv.), and (*S*)-**111** (200 µl, 2.55 mmol, 1.0

equiv.) in THF (10 ml) in a Schlenk flask was cooled to 0 °C under argon and diisopropyl azodicarboxylate (502 µl, 2.55 mmol, 1.0 equiv.) was slowly added. The reaction mixture was stirred at 0 °C for 15 min, then left to warm up to room temperature and stirred overnight. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (hexane) to provide the product (*S*)-**208** (646 mg, 93%) as white crystals, which melt at room temperature.

^{1}H NMR (400 MHz, $CDCl_3$): 1.75 (3H, d, *J* = 6.6), 2.50 (1H, d, *J* = 2.0), 4.86 (1H, dq, *J* = 6.6, 6.6, 6.6, 2.0), 6.75 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.07 (1H, dd, *J* = 8.2, 1.3), 7.30 (1H, ddd, *J* = 8.2, 7.3, 1.6), 7.78 (1H, dd, *J* = 7.8, 1.6).

^{13}C NMR (101 MHz, $CDCl_3$): 22.21 (q), 65.34 (d), 74.41 (d), 82.48 (s), 87.64 (s), 114.92 (d), 123.48 (d), 129.20 (d), 139.55 (d), 156.37 (s).

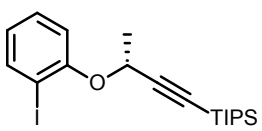
IR ($CHCl_3$): 3307 vs, 3086 vw, 3067 w, 2119 w, 1582 s, 1571 s, 1470 vs, 1453 m, 1439 vs, 1377 s, 1328 s, 1286 s, 1277 vs, 1259 m, 1241 vs, 1164 m, 1129 s, 1091 vs, 1047 s, 1036 s, 1019 vs, 944 s, 923 m, 836 w, 707 w, 652 s, 643 s, 586 w, 434 w cm^{-1}.

EI MS: 272 ($M^{+\bullet}$, 47), 221 (9), 220 (100), 190 (10), 145 (10), 115 (12), 91 (14), 92 (14), 65 (16), 64 (16), 63 (16), 53 (5).

HR EI MS: calculated for $C_{10}H_9OI$ 271.9698, found 271.9694.

Optical rotation: $[\alpha]^{22}_D$ +60° (c 0.316, CH_2Cl_2).

[(3*R*)-3-(2-Iodophenoxy)but-1-yn-1-yl][tris(1-methylethyl)]silane (*R*)-**209**



Lithium diisopropylamide was freshly prepared before the reaction: to a solution of diisopropylamine (0.4 ml, 2.84 mmol, 1.3 equiv.) in THF (5 ml) cooled to 0 °C under argon a solution of *n*-BuLi (1.6 M in hexanes, 1.65 ml, 2.64 mmol, 1.2 equiv.) was slowly added and stirred at 0 °C for 1 h. A Schlenk flask filled with a solution of alkyne (*R*)-**208** (590 mg, 2.16 mmol) and THF (5 ml) was cooled to -82 °C under argon. The prepared LDA solution (2.64 mmol, 1.2 equiv.) was slowly added to the alkyne and the reaction

mixture was stirred at -80 °C for 1 h. Then triisopropylsilyl chloride (460 µl, 2.17 mmol) was added dropwise and the reaction mixture was stirred at -80 °C for 1 h. Then it was left to warm up to room temperature and stirred for another 1 h. The reaction was carefully quenched by adding ethanol (0.5 ml) and solvents were removed under reduced pressure. The residue was purified by chromatography on silica gel (hexane) to afford the desired product (*R*)-**209** (823 mg, 89%) as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): 1.01 (21H, s), 1.74 (3H, d, *J* = 6.6), 4.88 (1H, q, *J* = 6.6), 6.72 (1H, dt, *J* = 7.7, 7.7, 1.4), 7.14 (1H, dd, *J* = 8.3, 1.5), 7.25 (1H, ddd, *J* = 8.2, 7.3, 1.5), 7.76 (1H, dd, *J* = 7.8, 1.6).

^{13}C NMR (101 MHz, $CDCl_3$): 11.11 (d), 18.49 (q), 22.46 (q), 66.23 (d), 87.69 (s), 87.94 (s), 106.09 (s), 115.75 (d), 123.32 (d), 129.00 (d), 139.31 (d), 156.62 (s).

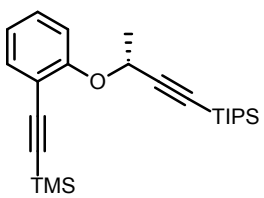
IR ($CHCl_3$): 3066 w, 2959 s, 2945 vs, 2892 s, 2867 vs, 2169 w, 1582 m, 1571 m, 1470 vs, 1462 s, 1439 s, 1384 w, 1375 m, 1327 m, 1285 m, 1277 m, 1258 w, 1241 s, 1163 w, 1132 s, 1091 s, 1075 m, 1046 s, 1019 s, 997 m, 950 s, 921 m, 884 s, 842 vw, 679 s, 659 s, 583 m, 433 w cm^{-1}.

EI MS: 428 ($M^{+\bullet}$, 10), 385 (23), 333 (20), 329 (10), 305 (10), 277 (15), 263 (12), 220 (14), 216 (30), 208 (55), 187 (15), 167 (25), 165 (100), 125 (30), 111 (30), 109 (25), 83 (20), 59 (20).

HR EI MS: calculated for $C_{19}H_{29}OISi$ 428.1032, found 428.1042.

Optical rotation: $[\alpha]^{22}_D$ +43° (c 0.299, CH_2Cl_2).

Trimethyl{[2-({(1*R*)-1-methyl-3-[tris(1-methylethyl)silyl]prop-2-yn-1-yl}oxy) phenyl]ethynyl}silane (*R*)-**210**



A Schlenk flask was charged with tetrakis-(triphenylphosphine)palladium(0) (66.0 mg, 0.094 mmol, 5 mol%) and copper iodide (36.0 mg, 0.187 mmol, 10 mol%). The degassed solution of aryl iodide (*R*)-**209** (802 mg, 1.87 mmol) in diisopropylamine (20 ml) and ethynyl(trimethyl)silane (300 µl, 2.20 mmol, 1.2 equiv.)

were added at room temperature under argon. After stirring at room temperature for 2 h, the reaction mixture was filtered through a sintered glass (hexane) and the solvents were removed *in vacuo*. The residue was purified by chromatography on silica gel (hexane) to obtain the product (*R*)-**210** (736 mg, 99%) as an off-white oil.

^{1}H NMR (400 MHz, $CDCl_3$): 0.25 (9H, s), 1.01 (21H, s), 1.70 (3H, d, *J* = 6.6), 4.94 (1H, q, *J* = 6.6), 6.92 (1H, td, *J* = 7.5, 7.5, 1.2), 7.16 (1H, dd, *J* = 8.3, 1.0), 7.23 (1H, m), 7.41 (1H, dd, *J* = 7.6, 1.6).

^{13}C NMR (101 MHz, $CDCl_3$): 0.01 (q), 11.13 (d), 18.50 (q), 22.41 (q), 66.17 (d), 87.21 (s), 98.49 (s), 101.42 (s), 106.57 (s), 114.39 (s), 116.75 (d), 121.60 (d), 129.44 (d), 133.50 (d), 158.89 (s).

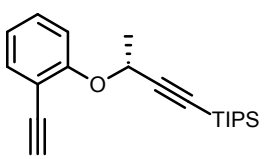
IR ($CHCl_3$): 3076 vw, 2961 s, 2945 s, 2867 s, 2157 m, 2110 vw, 2067 w, 1596 w, 1573 w, 1463 m, 1446 m, 1409 vw, 1384 w, 1374 w, 1328 w, 1289 w, 1261 m, 1250 s, 1163 w, 1131 m, 1075 w, 1042 m, 1018 w, 997 w, 951 m, 935 w, 884 s, 862 vs, 846 vs, 700 w, 679 m, 661 m, 594 w, 455 w cm^{-1}.

EI MS: 398 ($M^{+\bullet}$, 6), 355 (8), 313 (8), 271 (9), 190 (60), 175 (100), 159 (32), 125 (18), 111 (16), 109 (13), 95 (10), 83 (15), 73 (38), 59 (21).

HR EI MS: calculated for $C_{24}H_{38}OSi_2$ 398.2461, found 398.2466.

Optical rotation: $[\alpha]^{22}_D$ +21° (c 0.267, CH_2Cl_2).

[(3*R*)-3-(2-Ethynylphenoxy)but-1-yn-1-yl][tris(1-methylethyl)]silane (*R*)-**211**



To a solution of silane (*R*)-**210** (710 mg, 1.78 mmol) in dichloromethane (20 ml) at room temperature a freshly prepared solution of sodium methoxide (1.84 mmol, 1.0 equiv.) in methanol (10 ml) was added and left stirring at room temperature for 30 min. The reaction mixture was filtered through a short pad of silica gel (dichloromethane) and solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) to provide the alkyne product (*R*)-**211** (502 mg, 86%) as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): 1.01 (21H, s), 1.72 (3H, d, *J* = 6.6), 3.25 (1H, s), 4.93 (1H, q, *J* = 6.6), 6.92 (1H, dt, *J* = 7.5, 7.5, 1.1), 7.18 (1H, dd, *J* = 8.4, 1.1), 7.23-7.29 (1H, m), 7.44 (1H, dd, *J* = 7.6, 1.7).

^{13}C NMR (101 MHz, $CDCl_3$): 11.10 (d), 18.47 (q), 22.37 (q), 65.76 (d), 80.08 (s) 81.00 (s), 87.45 (s), 106.31 (s), 112.85 (d), 115.66 (s), 121.29 (d), 129.67 (d), 133.94 (d), 158.89 (s).

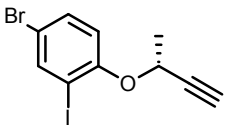
IR ($CHCl_3$): 3307 s, 3078 w, 3062 vw, 2959 s, 2945 vs, 2892 s, 2867 vs, 2169 w, 2108 w, 1596 m, 1575 w, 1487 vs, 1463 s, 1446 s, 1384 w, 1375 w, 1326 m, 1288 m, 1268 w, 1246 vs, 1164 w, 1131 s, 1109 m, 1091 s, 1074 m, 1043 s, 1018 w, 997 m, 951 s, 937 m, 884 s, 650 s, 679 s, 660 s, 614 m, 592 m, 452 w cm^{-1}.

EI MS: 326 ($M^{+\bullet}$, 3), 311 (18), 283 (18), 241 (42), 225 (16), 213 (26), 199 (30), 165 (100), 137 (14), 125 (17), 109 (16), 95 (13), 83 (11), 59 (8).

HR EI MS: calculated for $C_{21}H_{30}OSi$ 326.2066, found 326.2061.

Optical rotation: $[\alpha]^{22}_D$ +39° (c 0.25, CH_2Cl_2).

4-Bromo-2-iodo-1-{[(1*R*)-1-methylprop-2-yn-1-yl]oxy}benzene (*R*)-**213**



A solution of 4-bromo-2-iodophenol **212** (522 mg, 1.75 mmol), triphenylphosphine (544 mg, 2.07 mmol, 1.2 equiv.) and alcohol (*S*)-**111** (140 µl, 1.78 mmol, 1.0 equiv.) in tetrahydrofuran (15 ml) was cooled to 0 °C under argon in a Schlenk flask and diisopropyl azodicarboxylate (350 µl, 1.78 mmol, 1.0 equiv.) was slowly added. The reaction mixture was stirred at 0 °C for 15 min and then left to warm up to room temperature while stirring continued for 1 h. The reaction was quenched with an excess of methyl iodide (3 ml) and the volatiles were evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane) to provide product (*R*)-**213** (592 mg, 96%) as white crystals.

M.p.: 75-77 °C (chloroform)**.**

^{1}H NMR (400 MHz, $CDCl_3$): 1.74 (3H, d, *J* = 6.6), 2.51 (1H, d, *J* = 2.0), 4.81 (1H, qd, *J* = 6.6, 6.6, 6.6, 2.0), 6.93 (1H, d, *J* = 8.7), 7.40 (1H, dd, *J* = 8.7, 2.4), 7.89 (1H, d, *J* = 2.4).

^{13}C NMR (101 MHz, $CDCl_3$): 22.11 (q), 65.62 (d), 74.84 (d), 81.95 (s), 88.34 (s), 114.63 (s), 115.87 (d), 131.97 (d), 141.29 (d), 155.69 (s).

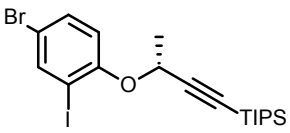
IR ($CHCl_3$): 3307 s, 3089 vw, 3068 vw, 2118 w, 1572 m, 1561 m, 1464 vs, 1412 w, 1377 s, 1328 m, 1277 vs, 1265 s, 1240 vs, 1151 m, 1127 m, 1090 vs, 1034 vs, 943 m, 875 m, 837 w, 805 m, 702 w, 642 s, 596 w, 538 w, 430 w cm^{-1}.

EI MS: 352 ($M^{+\bullet}$, with ^{81}Br, 20), 350 ($M^{+\bullet}$, with ^{79}Br, 19), 300 (98), 298 (100), 271 (10), 269 (10), 219 (22), 172 (10), 144 (15), 131 (18), 115 (16), 100 (5), 91 (5), 74 (5), 69 (28), 63 (25), 53 (16), 44 (7).

HR EI MS: calculated for $C_{10}H_8O^{79}BrI$ 349.8803, found 349.8807.

Optical rotation: $[\alpha]^{22}_D$ +72° (c 0.33, CH_2Cl_2).

4-Bromo-2-iodo-1-{[(1*R*)-1-methylprop-2-yn-1-yl]oxy}benzene (*R*)-**214**



Lithium diisopropylamide was freshly prepared before the reaction: To a solution of diisopropylamine (300 µl, 2.13 mmol, 1.3 equiv.) in tetrahydrofuran (5 ml) cooled to 0 °C under argon a solution of *n*-BuLi (1.6 M in hexanes, 1.10 ml, 1.76 mmol, 1.1 equiv.) was slowly added and the reaction mixture was stirred at 0 °C for 30 min. A Schlenk flask filled with a solution of alkyne (*R*)-**213** (561 mg, 1.60 mmol) in THF (5 ml) was cooled to -78 °C under argon and the prepared LDA solution was slowly added. The reaction mixture was stirred at -78 °C for 1 h. Then triisopropylsilyl chloride was added dropwise (345 µl, 1.61 mmol, 1.0 equiv.) and the reaction mixture was stirred at -78 °C for 1 h. It was left to warm up to room temperature and stirred at the same temperature for another 1 h. The reaction mixture was diluted with diethyl ether (100 ml) and extracted with a saturated aqueous solution of NH_4Cl (100 ml), water (100 ml) and brine (100 ml). The combined organic phases were dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure and the residue was

purified by chromatography on silica gel (hexane) to give product (*R*)-**214** (698 mg, 86%) as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): 1.01 (21H, s), 1.72 (3H, d, *J* = 6.6), 4.83 (1H, q, *J* = 6.6), 7.00 (1H, d, *J* = 8.8), 7.36 (1H, dd, *J* = 8.7, 2.4), 7.87 (1H, d, *J* = 2.4).

^{13}C NMR (101 MHz, $CDCl_3$): 11.08 (d), 18.48 (q), 22.39 (q), 66.56 (d), 88.35 (s), 88.65 (s), 105.49 (s), 114.44 (s), 116.61 (d), 131.72 (d), 141.08 (d), 155.98 (s).

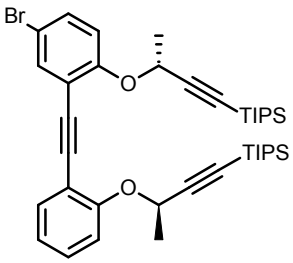
IR ($CHCl_3$): 2959 s, 2945 s, 2867 s, 2169 w, 1571 w, 1561 w, 1464 vs, 1411 vw, 1388 w, 1377 m, 1327 m, 1278 m, 1265 w, 1240 s, 1150 w, 1133 m, 1090 m, 1076 w, 1043 m, 1032 s, 1019 w, 997 w, 950 m, 933 w, 884 m, 875 m, 836 vw, 809 w, 704 vw, 679 s, 664 m, 591 w, 539 w, 432 vw cm^{-1}.

EI MS: 508 ($M^{+\bullet}$, with ^{81}Br, 6), 506 ($M^{+\bullet}$, with ^{79}Br, 6), 463 (6), 461 (3), 434 (3), 431 (3), 413 (5), 411 (5), 385 (3), 383 (3), 357 (4), 355 (4), 342 (94), 298 (18), 265 (8), 253 (6), 208 (50), 165 (100), 153 (10), 139 (14), 125 (24), 111 (21), 96 (18), 83 (17), 73 (19), 59 (16).

HR EI MS: calculated for $C_{19}H_{28}O^{79}BrISi$ 506.0138, found 506.0133.

Optical rotation: $[\alpha]^{22}_D$ +68° (c 0.68, CH_2Cl_2).

[(3*R*)-3-(2-{[5-Bromo-2-({(1*R*)-1-methyl-3-[tris(1-methylethyl)silyl]prop-2-yn-1-yl}oxy)phenyl]ethynyl} phenoxy)but-1-yn-1-yl][tris(1-methylethyl)]silane (*R*,*R*)-**215**



A Schlenk flask filled with tetrakis(triphenylphosphine)-palladium(0) (40.0 mg, 0.035 mmol, 5 mol%), copper iodide (13.1 mg, 0.069 mmol, 10 mol%) and diisopropylamine (3 ml) was cooled to 0 °C and a degassed solution of aryl iodide (*R*)-**214** (357 mg, 0.704 mmol, 1.0 equiv.) in diisopropylamine (10 ml) was added. To this mixture a degassed solution of alkyne (*R*)-**211** (229 mg, 0.702 mmol) in diisopropylamine (10 ml) was added dropwise and the reaction mixture was stirred at 0 °C for 1 h and then at room temperature overnight. The reaction mixture was filtered through a short pad of silica gel (diethyl

ether), the solvents were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane) to give product (*R*,*R*)-**215** (483 mg, 98%) as a yellowish oil.

^{1}H NMR (600 MHz, $CDCl_3$): 0.99-1.02 (42H, m), 1.73 (3H, d, *J* = 6.6), 1.74 (3H, d, *J* = 6.6), 4.97 (1H, q, *J* = 6.6), 4.99 (1H, q, *J* = 6.6), 6.96 (1H, dt, *J* = 7.5, 7.5, 1.1), 7.07 (1H, d, *J* = 8.8), 7.19 (1H, dd, *J* = 8.3, 1.1), 7.26 (1H, ddd, *J* = 8.3, 7.4, 1.7), 7.33 (1H, dd, *J* = 8.8, 2.5), 7.47 (1H, ddd, *J* = 7.5, 1.7, 0.4), 7.59 (1H, d, *J* = 2.5).

^{13}C NMR (151 MHz, $CDCl_3$): 11.03 (d), 11.04 (d), 18.47 (q), 18.47 (q), 22.49 (q), 22.53 (q), 65.76 (d), 66.19 (d), 87.33 (s), 87.80 (s), 88.38 (s), 91.31 (s), 105.93 (s), 106.32 (s), 113.52 (s), 113.94 (s), 115.91 (d), 116.79 (s), 117.81 (d), 121.42 (d), 129.44 (d), 131.63 (d), 133.42 (d), 135.49 (d), 157.20 (s), 158.15 (s).

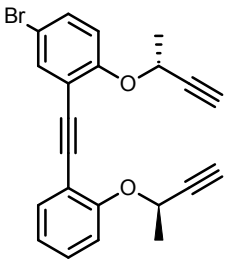
IR ($CHCl_3$): 3076 vw, 3010 w, 2960 s, 2945 vs, 2867 vs, 2219 vw, 2168 w, 1597 w, 1586 w, 1575 w, 1560 w, 1494 s, 1478 s, 1464 s, 1448 m, 1393 w, 1388 w, 1374 w, 1326 m, 1279 m, 1261 m, 1238 s, 1163 w, 1131 s, 1091 s, 1075 m, 1042 m, 1018 w, 997 m, 950 s, 937 m, 883 s, 863 w, 831 w, 805 w, 679 s, 661 m, 591 w, 569 w cm^{-1}.

EI MS: 706 ($M^{+\bullet}$, with ^{81}Br, 2), 704 ($M^{+\bullet}$, with ^{79}Br, 1), 691 (5), 689 (4), 663 (12), 661 (12), 619 (15), 582 (12), 539 (50), 497 (97), 495 (99), 455 (29), 453 (31), 411 (39), 373 (32), 331 (38), 290 (91), 288 (100), 259 (12), 208 (10), 181 (7), 167 (55), 157 (62), 139 (33), 125 (91), 111 (96), 97 (41), 83 (48), 73 (75), 59 (65).

HR EI MS: calculated for $C_{40}H_{57}O_2{}^{79}BrSi_2$ 704.3080, found 704.3087.

Optical rotation: $[\alpha]^{22}_D$ -64° (c 0.061, CH_2Cl_2).

4-Bromo-1-{[(1*R*)-1-methylprop-2-yn-1-yl]oxy}-2-[(2-{[(1*R*)-1-methylprop-2-yn-1-yl]oxy}phenyl)ethynyl]benzene (*R*,*R*)-**216**



To a solution of silane (*R*,*R*)-**215** (465 mg, 0.658 mmol) in THF (10 ml) in a Schlenk flask under argon a solution of tetrabutylammonium fluoride trihydrate (423 mg, 1.34 mmol, 2.0 equiv.) in THF (10 ml) was added and the reaction mixture was stirred at room temperature for 30 min. Then it was filtered through

a short pad of silica gel (diethyl ether) and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 90:10) to afford product (*R*,*R*)-**216** (255 mg, 98%) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.74 (3H, d, *J* = 6.6), 1.75 (3H, d, *J* = 6.6), 2.49 (2H, d, *J* = 2.0), 4.96 (1H, dq, *J* = 6.6, 6.6, 6.6, 2.0), 4.98 (1H, dq, *J* = 6.6, 6.6, 6.6, 2.0), 7.00 (1H, d, *J* = 8.8), 7.00 (1H, dt, *J* = 7.5, 7.5, 1.1), 7.13 (1H, dd, *J* = 8.3, 1.1), 7.31 (1H, ddd, *J* = 8.3, 7.5, 1.7), 7.37 (1H, dd, *J* = 8.8, 2.5), 7.50 (1H, dd, *J* = 7.6, 1.7), 7.62 (1H, d, *J* = 2.5).

^{13}C NMR (151 MHz, $CDCl_3$): 22.18 (q), 22.24 (q), 64.93 (d), 65.32 (d), 74.19 (d), 74.51 (d), 82.36 (s), 82.72 (s), 88.37 (s), 91.22 (s), 113.80 (s), 113.92 (s), 115.32 (d), 116.71 (s), 117.28 (d), 121.71 (d), 129.66 (d), 131.92 (d), 133.61 (d), 135.71 (d), 156.85 (s), 157.86 (s).

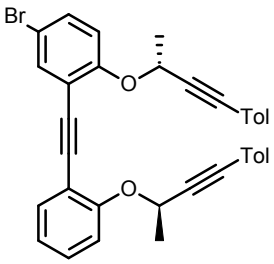
IR ($CHCl_3$): 3307 s, 3076 vw, 3064 vw, 2219 w, 2118 w, 1598 w, 1586 w, 1575 w, 1561 w, 1494 vs, 1479 s, 1448 m, 1393 m, 1377 m, 1327 m, 1279 s, 1261 m, 1239 vs, 1163 w, 1152 vw, 1130 s, 1113 m, 1100 m, 1091 vs, 1039 s, 944 m, 924 w, 830 w, 806 w, 644 s, 572 vw cm^{-1}.

EI MS: 394 ($M^{+\bullet}$, with ^{81}Br, 17), 392 ($M^{+\bullet}$, with ^{79}Br, 17), 379 (47), 377 (51), 364 (28), 362 (30), 341 (43), 339 (45), 325 (17), 297 (35), 287 (42), 260 (64), 245 (36), 231 (75), 218 (14), 208 (30), 202 (40), 189 (29), 180 (47), 163 (24), 152 (100), 133 (7), 126 (10), 99 (13), 71 (22), 57 (48), 53 (46), 51 (30).

HR EI MS: calculated for $C_{22}H_{17}O_2{}^{79}Br$ 392.0412, found 392.0408.

Optical rotation: $[\alpha]^{22}_D$ -24° (c 0.184, CH_2Cl_2).

4-Bromo-1-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}-2-[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl) ethynyl]benzene (*R*,*R*)-**217**



A flame-dried Schlenk flask was charged with *p*-iodotoluene (333 mg, 1.52 mmol, 2.4 equiv.), tetrakis(triphenylphosphine)-palladium(0) (72.0 mg, 0.062 mmol, 10 mol%) and copper iodide

(23.0 mg, 0.125 mmol, 20 mol%) under argon and diisopropylamine (5 ml) was added. The reaction mixture was cooled to 0 °C and stirred for 10 min, then a degassed solution of alkyne (*R*,*R*)-**216** (245 mg, 0.623 mmol) in diisopropylamine (20 ml) was slowly added over a period of 10 min. After stirring for 30 min at 0 °C, the solution was allowed to warm up to room temperature and left stirring for additional 30 min. Then the reaction mixture was filtered through a short pad of silica gel (diethyl ether) and the solvents were removed *in vacuo*. Flash chromatography on silica gel (hexane-diethyl ether 95:5) provided product (*R*,*R*)-**217** (320 mg, 90%) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.80 (3H, d, *J* = 6.6), 1.81 (3H, d, *J* = 6.6), 2.30 (3H, bs), 2.31 (3H, bs), 5.15 (1H, q, *J* = 6.6), 5.18 (1H, q, *J* = 6.6), 6.97 (1H, dt, *J* = 7.5, 7.5, 1.1), 7.05-7.09 (2H, m), 7.05-7.09 (2H, m), 7.07 (1H, d, *J* = 8.8), 7.20 (1H, dd, *J* = 8.3, 1.1), 7.24-7.26 (2H, m), 7.26 (1H, d, *J* = 2.5), 7.26-7.27 (2H, m), 7.29 (1H, ddd, *J* = 8.3, 7.4, 1.7), 7.36 (1H, dd, *J* = 8.8, 2.5), 7.50 (1H, ddd, *J* = 7.6, 1.7, 0.7).

^{13}C NMR (151 MHz, $CDCl_3$): 21.45 (q), 21.46 (q), 22.40 (q), 22.48 (q), 65.94 (d), 66.29 (d), 86.15 (s), 86.47 (s), 87.05 (s), 87.45 (s), 88.51 (s), 91.36 (s), 113.58 (s), 114.04 (s), 115.63 (d), 116.80 (s), 117.47 (d), 119.17 (s), 119.31 (s), 121.52 (d), 128.96 (d), 128.99 (d), 129.64 (d), 131.58 (d), 131.88 (d), 133.58 (d), 135.65 (d), 138.56 (s), 138.69 (s), 157.19 (s), 158.20 (s).

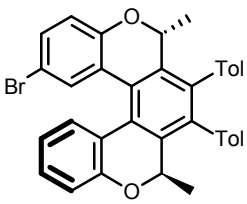
IR ($CHCl_3$): 3081 w, 3057 vw, 2236 w, 2220 w, 1609 w, 1597 w, 1585 m, 1574 w, 1563 w, 1510 vs, 1494 vs, 1478 vs, 1447 s, 1409 vw, 1394 m, 1375 m, 1330 s, 1280 s, 1259 s, 1237 vs, 1180 vw, 1163 w, 1152 vw, 1124 s, 1099 m, 1086 vs, 1036 s, 1020 m, 946 s, 928 w, 832 w, 819 vs, 805 m, 708 vw, 645 w, 571 w, 539 w, 411 w cm^{-1}.

EI MS: 574 ($M^{+\bullet}$, with ^{81}Br, 15), 572 ($M^{+\bullet}$, with ^{79}Br, 14), 559 (49), 557 (51), 544 (10), 542 (9), 428 (17), 430 (19), 417 (41), 415 (48), 401 (13), 399 (14), 290 (19), 288 (20), 143 (100), 128 (48), 115 (25), 89 (2).

HR EI MS: calculated for $C_{36}H_{29}O_2{}^{79}Br$ 572.1351, found 572.1360.

Optical rotation: $[\alpha]^{22}_D$ -294° (c 0.327, CH_2Cl_2).

(*M*,2*R*,5*R*)-9-Bromo-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c*']dichromene (*M*,*R*,*R*)-**103**



By $CoCp(CO)_2$, stoichiometric method: The Schlenk flask charged with triyne (*R*,*R*)-**217** (53.0 mg, 0.092 mmol) and triphenylphosphine (48.5 mg, 0.185 mmol, 2.0 equiv.) was purged with argon. Decane (3.5 ml) was added and then a solution of dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (12.2 µl, 0.092 mmol, 1.0 equiv.) in decane (0.5 ml). The reaction mixture was heated at 140 °C under simultaneous irradiation with a 500 W halogen lamp for 50 min. Then the mixture was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 90:10) to afford the desired product (*M*,*R*,*R*)-**103** (28.0 mg, 53%) as an oil.

By CoCp(CO)(fum), stoichiometric method: A flame-dried microwave vial was charged with triyne (*R*,*R*)-**217** (34.0 mg, 0.059 mmol), carbonyl(η^5-cyclopentadienyl)(η^2-dimethylfumarate)cobalt(I) (17.6 mg, 0.059 mmol, 1.0 equiv.) and triphenylphosphine (31.1 mg, 0.119 mmol, 2.0 equiv.) and dissolved in THF (3 ml). The reaction mixture was heated at 180 °C in a microwave reactor for 20 min. Then the solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 99:1) to furnish the desired cyclic product (*M*,*R*,*R*)-**103** (22.5 mg, 66%) as a yellow oil.

By $Ni(cod)_2$, catalytic method: In a flame-dried Schlenk flask bis(cyclooctadiene)nickel(0) (5.1 mg, 0.019 mmol, 20 mol%) and triphenylphosphine (9.8 mg, 0.037 mmol, 40 mol%) were dissolved in THF (1 ml). Then a solution of triyne (*R*,*R*)-**217** (53 mg, 0.093 mmol) in THF (1 ml) was added at room temperature and the reaction mixture was stirred overnight. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (0.015-0.040 mm, hexane-diethyl ether 100:0 to 90:10) to provide product (*M*,*R*,*R*)-**103** (9.6 mg, 18%) as a yellow oil.

^{1}H NMR (600.1 MHz, $CDCl_3$): 0.88 (3H, d, *J* = 6.7), 0.91 (3H, d, *J* = 6.7), 2.22 (6H, s), 5.15 (1H, q, *J* = 6.7), 5.17 (1H, q, *J* = 6.7), 6.78-6.82 (2H, m), 6.87 (1H, ddd, *J* = 7.9, 7.3, 1.2), 6.92-6.95 (2H, m), 6.97 (1H, d, *J* = 8.5), 7.01 (1H, ddd, *J* = 8.0, 1.2, 0.5), 7.13-7.16 (2H, m), 7.17-7.20 (2H, m), 7.25 (1H, ddd, *J* = 8.0, 7.3, 1.6), 7.34 (1H, dd, *J* = 8.5, 2.4), 7.38 (1H, ddt, *J* = 7.9, 1.6, 0.5, 0.5), 7.48 (1H, dd, *J* = 2.4, 0.7).

^{13}C NMR (151 MHz, $CDCl_3$): 18.48 (q), 18.57 (q), 21.10 (q), 21.11 (q), 73.33 (d), 73.73 (d), 113.60 (s), 120.23 (d), 121.78 (d), 121.99 (d), 123.51 (s), 124.42 (s), 126.13 (s), 126.24 (s), 129.38 (d), 129.39 (d), 129.54 (d), 129.87 (d), 130.52 (d), 131.61 (d), 131.69 (d), 132.11 (d), 132.61 (d), 135.56 (s), 135.59 (s), 137.12 (s), 137.13 (s), 138.32 (s), 138.95 (s), 139.86 (s), 140.18 (s), 153.56 (s), 154.52 (s).

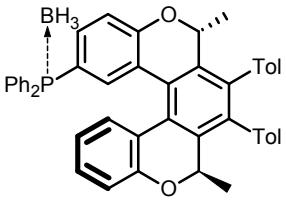
IR ($CHCl_3$): 3082 w, 3047 m, 3029 m, 2985 s, 2928 s, 2868 m, 1605 w, 1584 w, 1569 vw, 1517 m, 1486 m, 1480 s, 1446 m, 1428 vs, 1407 w, 1379 w, 1368 m, 1294 vw, 1183 w, 1160 w, 1122 w, 1110 m, 1063 s, 1023 m, 1011 m, 838 m, 827 m, 813 w, 695 vw, 572 vw cm^{-1}.

EI MS: 574 ($M^{+\bullet}$, with ^{81}Br, 43), 572 ($M^{+\bullet}$, with ^{79}Br, 43), 559 (94), 557 (100), 544 (20), 542 (20), 513 (6), 479 (5), 463 (5), 419 (4), 239 (6).

HR EI MS: calculated for $C_{36}H_2O_{29}{}^{79}Br$ 572.1351, found 572.1355.

Optical rotation: $[\alpha]^{22}_D$ -552° (c 0.086, CH_2Cl_2).

[(*M*,2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-c:4,3-c'] dichromen-9-yl](diphenyl)phosphane borane complex (*M*,*R*,*R*)-**218**



In a flame-dried Schlenk flask helicene (*M*,*R*,*R*)-**103** (30.0 mg, 0.0523 mmol) was dissolved in diethyl ether (2 ml) and cooled to -115 °C under argon. Then a solution of *t*-BuLi (1.7 M in pentane, 70 µl, 0.112 mmol, 2.1 equiv.) was added so that the drops fell down on the glass wall of the Schlenk flask. The reaction mixture was stirred for 1 min at -115 °C and then chlorodiphenylphosphine (50 µl, 0.27 mmol, 5.2 equiv.) was added dropwise. The reaction was left in a cooling bath to warm up slowly to -80 °C (over a period of 40 min) and then the Schenk was removed from the bath to warm up the reaction to room temperature. Then a solution of borane-THF complex (1 M in THF, 0.5 ml, 0.5 mmol, 9.6 equiv.) was added and the reaction stirred at room temperature for 30 min. The reaction mixture was purified by filtration through a short pad of silica gel (hexane-diethyl ether 1:1) and the solvents were removed *in vacuo*. The residue was further purified by flash chromatography on silica

gel (0.015-0.040 mm, hexane-diethyl ether 98:2 to 90:10) to give product (*M*,*R*,*R*)-**218** (35.6 mg, 98%) as an amorphous white material.

^{1}H NMR (600 MHz, $CDCl_3$): 0.86 (3H, d, *J* = 6.6), 0.93 (3H, d, *J* = 6.6), 2.25 (3H, bs), 2.26 (3H, bs), 5.18 (1H, q, *J* = 6.6), 5.30 (1H, q, *J* = 6.6), 6.41 (1H, ddd, *J* = 7.8, 7.3, 1.2), 6.59-6.63 (2H, m), 6.83-6.87 (2H, m), 6.94 (1H, dd, *J* = 8.1, 1.2), 7.03 (1H, ddd, *J* = 8.1, 7.3, 1.6), 7.06-7.09 (2H, m), 7.10-7.12 (2H, m), 7.13 (1H, dd, *J* = 8.3, 2.3), 7.28 (1H, bdd, *J* = 7.8, 1.6), 7.36-7.48 (10H, m), 7.53 (1H, dd, *J* = 11.0, 2.0), 7.57 (1H, ddd, *J* = 10.4, 8.3, 2.0). The BH_3 signal was very broad and thus was not measured.

^{13}C NMR (151 MHz, $CDCl_3$): 18.20 (q), 18.61 (q), 21.16 (q, 2C), 72.77 (d), 73.55 (d), 119.37 (d), 119.98 (s, J_{PC} = 61.1), 120.24 (d, J_{PC} = 12.1), 121.53 (d), 123.07 (s), 123.92 (s, J_{PC} = 10.7), 124.12 (s), 125.55 (s), 128.41 (d), 128.45 (d), 128.48 (d), 128.51 (d), 128.59 (d, 2C), 128.62 (d), 128.66 (d, J_{PC} = 3.5), 128.84 (d, J_{PC} = 2.5), 129.12 (d), 130.18 (s, J_{PC} = 58.3), 130.53 (d), 130.64 (d), 130.70 (d, J_{PC} = 13.3), 130.85 (d, J_{PC} = 2.3), 131.13 (d, J_{PC} = 2.3), 132.83 (d, J_{PC} = 9.7), 133.46 (d, J_{PC} = 9.7), 133.77 (d, J_{PC} = 8.4), 134.42 (s), 134.46 (s), 136.18 (s), 136.22 (s), 137.13 (s), 137.70 (s), 138.86 (s), 139.37 (s), 153.33 (s), 156.16 (s, J_{PC} = 2.5).

^{31}P NMR (202 MHz, $CDCl_3$): 20.56 (s).

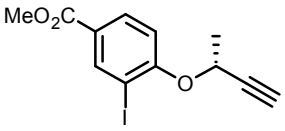
IR ($CHCl_3$): 3061 w, 3061 w, 2985 m, 2387 m, 2349 w, 1603 w, 1603 w, 1595 m, 1584 w, 1573 w, 1518 m, 1492 w, 1492 w, 1486 m, 1486 m, 1483s, 1446 m, 1438 s, 1430 m, 1405 vw, 1377 w, 1368 m, 1237 m, 1183 w, 1162 w, 1148 s, 1148 s, 1126 m, 1107 s, 1107 s, 1107 s, 1086 s, 1073 m, 1062 vs, 1029 w, 1022 m, 1012 w, 1001 m, 947 w, 840 m, 821 w, 808 m, 703 s, 694 s, 694 s, 583 w, 498 m cm^{-1}.

EI MS: 1408 ($[2M+Na]^+$), 715 ($[M+Na]^+$).

HR EI MS: calculated for $C_{48}H_{42}O_2BNaP$ 715.2908, found 715.2909.

Optical rotation: $[\alpha]^{22}_D$ -43° (c 0.024, CH_2Cl_2).

Methyl 3-iodo-4-{[(1*R*)-1-methylprop-2-yn-1-yl]oxy}benzoate (*R*)-**220**



A mixture of phenol **219** (426 mg, 1.53 mmol), triphenylphosphine (402 mg, 1.53 mmol, 1.0 equiv.) and (*S*)-**111** (120 µl, 1.53 mmol, 1.0 equiv.) in THF (10 ml) was cooled to 0 °C and diisopropyl azodicarboxylate (300 µl, 1.53 mmol, 1.0 equiv.) was slowly added. The reaction mixture was stirred at 0 °C for 15 min and then left to warm up to room temperature while stirred overnight. The solvent was evaporated under the reduced pressure and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) to provide product (*R*)-**220** (433 mg, 86%) as white crystals.

M.p.: 104-107°C (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): 1.78 (3H, d, *J* = 6.6), 2.53 (1H, d, *J* = 2.0), 3.89 (3H, s), 4.93 (1H, qd, *J* = 6.6, 6.6, 6.6, 2.0), 7.05 (1H, d, *J* = 8.7), 8.01 (1H, dd, *J* = 8.7, 2.1), 8.47 (1H, d, *J* = 2.2).

^{13}C NMR (101 MHz, $CDCl_3$): 22.04 (q), 52.11 (q), 65.21 (d), 75.05 (d), 81.61 (s), 86.38 (s), 112.88 (d), 124.96 (s), 131.22 (d), 141.09 (d), 159.74 (s), 165.45 (s).

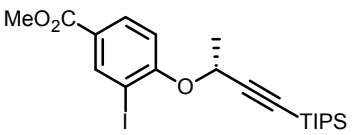
IR ($CHCl_3$): 3307 m, 3073 vw, 3029 w, 2120 vw, 1718 vs, 1594 s, 1564 w, 1485 s, 1453 w, 1437 s, 1395 m, 1379 w, 1326 m, 1303 s, 1292 s, 1260 vs, 1235 m, 1152 m, 1120 s, 1090 s, 1040 s, 1030 m, 973 w, 943 m, 911 w, 854 vw, 825 w, 706 vw, 683 m, 645 m, 537 vw, 434 w cm^{-1}.

EI MS: 330 ($M^{+\bullet}$, 34), 315 (100), 278 (17), 247 (20), 189 (11), 188 (10), 128 (6), 115 (13), 63 (5).

HR EI MS: calculated for $C_{12}H_{11}O_3I$ 329.9753, found 329.9763.

Optical rotation: $[\alpha]^{22}_D$ +95° (c 0.122, CH_2Cl_2).

Methyl 3-iodo-4-({(1*R*)-1-methyl-3-[tris(1-methylethyl)silyl]prop-2-yn-1-yl}oxy) benzoate (*R*)-**221**



Lithium diisopropylamide was freshly prepared before the reaction: To a solution of diisopropylamine (0.400 ml, 2.84 mmol, 2.2 equiv.) in THF (5 ml) cooled to 0 °C under argon a solution of *n*-BuLi (1.6 M in hexanes, 0.950 ml, 1.52 mmol, 1.2 equiv.) was slowly added and stirred at 0 °C for 1 h. The prepared LDA solution was slowly added to a solution of the alkyne (*R*)-**220** (420 mg, 1.27 mmol) in THF (5 ml), which was cooled to -82 °C under argon in a Schlenk flask, and the reaction mixture was stirred at -80 °C for 1 h. Then triisopropylsilyl chloride (275 µl, 1.29 mmol, 1.2 equiv.) was added dropwise and the reaction mixture was stirred at -80 °C for 1 h. It was left to warm up to room temperature and stirred at this temperature for another 1 h. The reaction was carefully quenched by adding ethanol (1 ml) and the solvents were removed under the reduced pressure. The residue was purified by chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) to give the desired product (*R*)-**221** (379 mg, 61%) as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): 1.00 (21H, s), 1.77 (3H, d, *J* = 6.6), 3.89 (3H, s), 4.94 (1H, q, *J* = 6.6), 7.13 (1H, d, *J* = 8.6), 7.97 (1H, dd, *J* = 8.6, 2.2), 8.45 (1H, d, *J* = 2.2).

^{13}C NMR (101 MHz, $CDCl_3$): 11.05 (d), 18.47 (q), 22.29 (q), 52.07 (q), 66.08 (d), 86.54 (s), 88.65 (s), 105.12 (s), 113.49 (d), 124.73 (s), 130.99 (d), 140.94 (d), 160.04 (s), 165.56 (s).

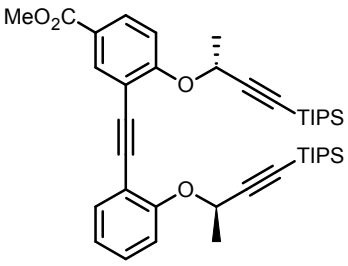
IR ($CHCl_3$): 3307 vw, 3073 vw, 3031 w, 2946 vs, 2892 s, 2867 vs, 2170 w, 1717 vs, 1593 vs, 1563 vs, 1485 s, 1463 s, 1437 vs, 1395 m, 1385 m, 1377 m, 1324 s, 1302 vs, 1292 vs, 1261 vs, 1151 m, 1119 vs, 1091 vs, 1075 m, 1040 vs, 997 m, 973 m, 949 vs, 910 m, 884 s, 824 m, 681 s, 435 m cm^{-1}.

EI MS: 486 ($M^{+\bullet}$, 6), 443 (74), 391 (40), 363 (12), 335 (12), 278 (20), 273 (15), 247 (100), 209 (23), 208 (32), 167 (30), 165 (85), 125 (20), 111 (18), 96 (15), 83 (15), 73 (15), 59 (16).

HR EI MS: calculated for $C_{21}H_{31}O_3ISi$ 486.1087, found 486.1094.

Optical rotation: $[\alpha]^{22}_D$ +63° (c 0.45, CH_2Cl_2).

Methyl 4-({(1*R*)-1-methyl-3-[tris(1-methylethyl)silyl]prop-2-yn-1-yl}oxy)-3-{[2-({(1*R*)-1-methyl-3-[tris(1-methylethyl)silyl]prop-2-yn-1-yl}oxy)phenyl]ethynyl}-benzoate (*R*,*R*)-**222**



A Schlenk flask was charged with tetrakis-(triphenylphosphine)palladium(0) (45.7 mg, 0.040 mmol, 5 mol%), copper iodide (14.7 mg, 0.077 mmol, 10 mol%) and diisopropylamine (5 ml) and a degassed solution of aryl iodide (*R*)-**221** (359 mg, 0.737 mmol) in diisopropylamine (5 ml) was added at room temperature under argon. To this mixture a degassed solution of alkyne (*R*)-**211** (244.1 mg, 0.747 mmol, 1.01 equiv.) in diisopropylamine (5 ml) was added dropwise and the reaction mixture was stirred at room temperature for 1 h. Then the reaction mixture was filtered through a short pad of silica gel (hexane-ethyl acetate 8:2), the solvents were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 90:10) to give product (*R*,*R*)-**222** (480 mg, 95%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 0.99-1.02 (42H, m), 1.76 (3H, d, *J* = 6.6), 1.78 (3H, d, *J* = 6.6), 3.90 (3H, s), 5.01 (1H, q, *J* = 6.6), 5.02 (1H, q, *J* = 6.6), 6.97 (1H, dt, *J* = 7.5, 7.5, 1.2), 7.20 (1H, bdd, *J* = 8.3, 1.2), 7.22 (1H, d, *J* = 8.7), 7.26 (1H, ddd, *J* = 8.3, 7.3, 1.7), 7.5 (1H, ddd, *J* = 7.6, 1.7, 0.4), 7.94 (1H, dd, *J* = 8.7, 2.2), 8.19 (1H, d, *J* = 2.2).

^{13}C NMR (101 MHz, $CDCl_3$): 11.01 (d), 11.05 (d), 18.47 (2 x q), 22.39 (d), 22.57 (q), 52.02 (q), 65.74 (d), 65.85 (d), 87.30 (s), 88.20 (s), 88.85 (s), 90.64 (s), 105.47 (s), 106.40 (s), 114.05 (d), 114.10 (s), 114.17 (s), 116.09 (d), 121.47 (d), 122.93 (s), 129.31 (d), 130.74 (d), 133.46 (d), 135.02 (d), 158.15 (s), 161.38 (s), 166.40 (s).

IR ($CHCl_3$): 3077 vw, 3030 w, 2960 s, 2945 s, 2867 s, 2214 vw, 2169 w, 1716 s, 1602 m, 1595 m, 1577 w, 1498 m, 1487 m, 1463 m, 1448 m, 1438 s, 1410 w, 1384 w, 1375 w, 1321 s, 1290 m, 1277 m, 1253 vs, 1235 s, 1163 w, 1131 s, 1112 m, 1091 s, 1075 s, 1043 m, 1019 w, 997 m, 950 s, 935 m, 919 m, 883 s, 827 w, 679 s, 666 m, 591 vw cm^{-1}.

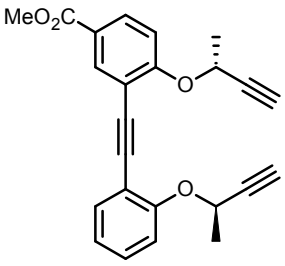
EI MS: 684 ($M^{+\bullet}$, 3), 669 (20), 641 (24), 597 (28), 555 (3), 527 (5), 495 (7), 475 (100), 453 (10), 433 (52), 417 (5), 401 (11), 391 (28), 389 (25), 373 (8), 359 (12), 347 (17),

337 (14), 309 (41), 287 (37), 268 (70), 237 (30), 208 (12), 167 (33), 139 (22), 125 (68), 111 (73), 97 (43), 83 (48), 73 (58), 59 (60).

HR EI MS: calculated for $C_{42}H_{60}O_4Si_2$ 684.4030, found 684.4031.

Optical rotation: $[\alpha]^{22}_D$ -69° (c 0.89, CH_2Cl_2).

Methyl 4-{[(1*R*)-1-methylprop-2-yn-1-yl]oxy}-3-[(2-{[(1*R*)-1-methylprop-2-yn-1-yl]oxy}phenyl)ethynyl]benzoate (*R*,*R*)-**223**



In a Schlenk flask a solution of tetrabutylammonium fluoride trihydrate (191 mg, 0.604 mmol, 2.0 equiv.) in THF (2 ml) a solution of silane (*R*,*R*)-**222** (207 mg, 0.302 mmol) in THF (5 ml) was added under argon. The reaction mixture was stirred at room temperature for 30 min. Then it was filtered through a short pad of silica gel (ethyl acetate) and the solvents were removed under the reduced pressure. The residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 90:10) to give product (*R*,*R*)-**223** (102 mg, 91%) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.76 (3H, d, *J* = 6.6), 1.78 (3H, d, *J* = 6.6), 2.50 (1H, d, *J* = 2.0), 2.52 (1H, d, *J* = 2.0), 3.90 (3H, s), 5.01 (1H, dq, *J* = 6.6, 6.6, 6.6, 2.0), 5.03 (1H, dq, *J* = 6.6, 6.6, 6.6, 2.0), 7.01 (1H, dt, *J* = 7.7, 7.7, 1.1), 7.14 (1H, dd, *J* = 8.3, 1.1), 7.14 (1H, d, *J* = 8.7), 7.31 (1H, ddd, *J* = 8.3, 7.6, 1.7), 7.52 (1H, bdd, *J* = 7.8, 1.7), 7.98 (1H, dd, *J* = 8.7, 2.2), 8.21 (1H, d, *J* = 2.2).

^{13}C NMR (151 MHz, $CDCl_3$): 22.12 (q), 22.28 (q), 52.06 (q), 64.64 (d), 65.05 (d), 74.75 (2x d), 81.98 (s), 82.81 (s), 88.86 (s), 90.56 (s), 113.64 (d), 114.14 (s), 114.21 (s), 115.55 (d), 121.77 (d), 123.27 (s), 129.53 (d), 130.98 (d), 133.67 (d), 135.21 (d), 157.86 (s), 161.02 (s), 166.26 (s).

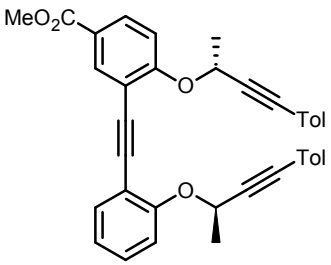
IR ($CHCl_3$): 3307 s, 3077 vw, 3028 w, 2954 w, 2213 vw, 2119 vw, 1717 s, 1602 m, 1595 m, 1577 w, 1498 m, 1488 m, 1447 m, 1439 s, 1410 w, 1377 w, 1321 s, 1290 m, 1277 s, 1253 vs, 1235 s, 1163 w, 1130 s, 1112 m, 1091 s, 1038 s, 944 m, 924 w, 828 w, 644 m cm^{-1}.

EI MS: 372 ($M^{+\bullet}$, 22), 357 (100), 342 (48), 329 (8), 319 (74), 313 (13), 305 (30), 298 (7), 287 (14), 268 (14), 260 (31), 259 (30), 245 (15), 231 (39), 218 (13), 208 (23), 202 (20), 181 (20), 180 (33), 179 (33), 168 (16), 165 (11), 152 (48), 149 (37), 139 (10), 126 (6), 97 (4), 71 (3), 69 (3), 57 (9), 53 (20).

HR EI MS: calculated for $C_{24}H_{20}O_4$ 372.1362, found 372.1355.

Optical rotation: $[\alpha]^{22}_D$ -31° (c 0.082, CH_2Cl_2).

Methyl 4-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}-3-[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)ethynyl]benzoate (*R*,*R*)-**224**



A flame-dried Schlenk flask was charged with *p*-iodotoluene (118 mg, 0.541 mmol, 2.2 equiv.), tetrakis-(triphenylphosphine)palladium(0) (30.0 mg, 0.025 mmol, 10 mol%), copper iodide (12.2 mg, 0.064 mmol, 26 mol%) and diisopropylamine (5 ml) at room temperature under argon. The reaction mixture was stirred for 5 min and then a degassed solution of alkyne (*R*,*R*)-**223** (92 mg, 0.247 mmol) in diisopropylamine (5 ml) was slowly added over a period of 10 min. After stirring at room temperature for 1 h, the reaction mixture was filtered through a short pad of silica gel (diethyl ether) and the solvents were removed *in vacuo*. Flash chromatography on silica gel (hexane-ethyl acetate 95:5) provided product (*R*,*R*)-**224** (125 mg, 95%) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.85 (3H, d, *J* = 6.6), 1.86 (3H, d, *J* = 6.6), 2.31 (3H, bs), 2.32 (3H, bs), 3.89 (3H, s), 5.21 (1H, q, *J* = 6.6), 5.23 (1H, q, *J* = 6.6), 6.99 (1H, dt, *J* = 7.5, 7.5, 1.2), 7.06-7.08 (2H, m), 7.08-7.10 (2H, m), 7.22 (1H, bdd, *J* = 8.4, 1.2), 7.24 (1H, d, *J* = 8.8), 7.26-7.27 (2H, m), 7.27-7.29 (2H, m), 7.30 (1H, ddd, *J* = 8.4, 7.4, 1.7), 7.54 (1H, ddd, *J* = 7.6, 1.7, 0.3), 7.99 (1H, dd, *J* = 8.8, 2.2), 8.22 (1H, d, *J* = 2.2).

^{13}C NMR (151 MHz, $CDCl_3$): 21.45 (q), 21.46 (q), 22.33 (q), 22.50 (q), 52.01 (q), 65.57 (d), 65.99 (d), 86.12 (s), 86.63 (s), 86.68 (s), 87.53 (s), 88.98 (s), 90.69 (s), 113.78 (d), 114.14 (s), 114.27 (s), 115.78 (d), 119.36 (s), 121.56 (d), 123.00 (s),

128.94 (d), 129.00 (d), 129.51 (d), 130.97 (d), 131.57 (d), 131.60 (d), 133.63 (d), 135.16 (d), 138.53 (s), 138.79 (s), 158.17 (s), 161.38 (s), 166.36 (s), 199.00 (s).

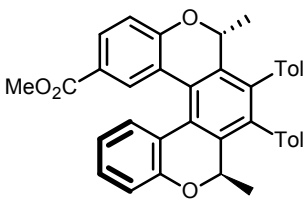
IR ($CHCl_3$): 3081 vw, 3060 vw, 3031 w, 2955 m, 2235 w, 2212 vw, 1716 s, 1602 m, 1595 m, 1576 w, 1510 m, 1497 m, 1487 m, 1448 m, 1439 m, 1409 w, 1376 w, 1321 m, 1290 m, 1278 m, 1252 vs, 1235 s, 1181 w, 1163 w, 1110 m, 1085 s, 1036 m, 1024 m, 1020 w, 983 vw, 946 m, 919 w, 819 m, 707 w, 542 m cm^{-1}.

EI MS: 552 ($M^{+\bullet}$, 60), 537 (100), 522 (13), 493 (10), 461 (7), 431 (5), 410 (17), 395 (52), 379 (10), 363 (8), 350 (5), 335 (8), 319 (6), 277 (11), 268 (15), 237 (28), 209 (5), 181 (8), 142 (3), 114 (2), 59 (5).

HR EI MS: calculated for $C_{38}H_{32}O_4$ 552.2301, found 552.2298.

Optical rotation: $[\alpha]^{22}_D$ -217° (c 0.211, CH_2Cl_2).

Methyl (2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c*']dichromene-9-carboxylate (*M*,*R*,*R*)-**105**



By $CoCp(CO)_2$, catalytic method using halogen lamp:

A Schlenk flask charged with triyne (*R*,*R*)-**224** (69 mg, 0.125 mmol) and triphenylphosphine (6.6 mg, 0. 025 mmol, 0.2 equiv.) was purged with argon. Decane (3.5 ml) was added and then a solution of dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (1.7 µl, 0.012 mmol, 0.1 equiv.) in decane (1.5 ml). The reaction mixture was heated at 140 °C under simultaneous irradiation with a 500 W halogen lamp for 1 h. Then the mixture was subjected to column chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) to afford the desired product (*M*,*R*,*R*)-**105** (50 mg, 72%) as a yellow solid.

By $CoCp(CO)_2$, stoichiometric method using halogen lamp: A Schlenk flask charged with triyne (*R*,*R*)-**224** (57.0 mg, 0.103 mmol) and triphenylphosphine (54.0 mg, 0.206 mmol, 2.0 equiv.) was purged with argon. Decane (3.5 ml) was added and then a solution of dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (13.7 µl, 0.103 mmol, 1.0 equiv.) in decane (1.5 ml). The reaction mixture was heated at 140 °C under simultaneous irradiation with a 500 W halogen lamp for 1 h. Then the mixture was

purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 90:1) to afford the desired product (*M*,*R*,*R*)-**105** (39.0 mg, 68%) as a yellow solid.

By $CoCp(CO)_2$, catalytic method with microwave irradiation: A flame-dried microwave vial charged with triyne (*R*,*R*)-**224** (50.0 mg, 0.091 mmol) and triphenylphosphine (10.5 mg, 0.04 mmol, 44 mol%) was purged with argon. THF (3 ml) and dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (3 µl, 0.02 mmol, 22 mol%) were added. The reaction mixture was heated in a microwave reactor at 140 °C for 30 min. Then the solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) to afford the desired product (*M*,*R*,*R*)-**105** (43.0 mg, 81%) as a yellow solid.

By $Ni(cod)_2$, catalytic method: In a flame-dried Schlenk flask bis(cyclooctadiene)nickel(0) (6.1 mg, 0.022 mmol, 20 mol%) and triphenylphosphine (11.4 mg, 0.043 mmol, 40 mol%) were dissolved in THF (1 ml). Then a solution of triyne (*R*,*R*)-**224** (60 mg, 0.109 mmol) in THF (1.5 ml) was added at room temperature and the reaction mixture was stirred overnight. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 80:20) to provide product (*M*,*R*,*R*)-**105** (35.4 mg, 59%) as a yellow oil.

M.p.: 111-113 °C (hexane).

^{1}H NMR (600 MHz, *d6*-acetone, rfp=2.09 ppm): 0.95 (3H, d, *J* = 6.7), 0.98 (3H, d, *J* = 6.7), 2.29 (6H, bs), 3.77 (3H, s), 5.23 (1H, q, *J* = 6.7), 5.30 (1H, q, *J* = 6.7), 6.83 (1H , ddd, *J* = 7.9, 7.3, 1.3), 6.85-6.89 (2H, m), 6.99-7.02 (2H, m), 7.08 (1H, ddd, *J* = 8.0, 1.3, 0.3), 7.15 (1H, dd, *J* = 8.4, 0.3), 7.21-7.23 (2H, m), 7.25-7.28 (2H, m), 7.28 (1H, ddd, *J* = 8.0, 7.3, 1.6), 7.37 (1H, ddt, *J* = 7.9, 1.6, 0.5, 0.5), 7.91 (1H, dd, *J* = 8.4, 2.1), 8.18 (1H, dt, *J* = 2.1, 0.5, 0.5).

^{13}C NMR (151 MHz, d_6-acetone, rfp=29.8 ppm): 18.47 (q), 18.77 (q), 21.10 (q), 51.96 (q), 73.32 (d), 74.14 (d), 120.08 (d), 120.19 (d), 121.99 (d), 123.72 (s), 123.87 (s), 123.91 (s), 124.79 (s), 126.23 (s), 129.27 (d), 129.36 (d), 129.37 (d), 129.40 (d), 129.87 (d), 129.90 (d), 130.30 (d), 131.26 (d), 131.49 (d), 131.63 (d), 131.72 (d), 135.56 (s), 135.62 (s), 137.10 (s), 137.13 (s), 138.23 (s), 138.80 (s), 139.47 (s), 140.31 (s), 154.39 (s), 158.52 (s), 166.50 (s).

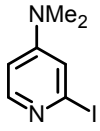
IR ($CHCl_3$): 3081 w, 1714 vs, 1605 m, 1585 m, 1518 m, 1486 m, 1443 m, 1433 s, 1423 m, 1406 vw, 1380 w, 1368 m, 1333 m, 1258 vs, 1184 w, 1160 w, 1125 m, 1115 s, 1062 s, 1022 m, 836 m cm^{-1}.

EI MS: 552 ($M^{+\bullet}$, 41), 537 (100), 522 (14), 493 (16), 479 (8), 463 (5), 435 (4), 419 (4), 395 (3), 371 (2), 343 (2), 313 (2), 261 (2), 253 (2), 245 (2), 191 (1).

HR EI MS: calculated for $C_{38}H_{32}O_4$ 552.2301, found 552.2305.

Optical rotation: $[\alpha]^{22}_D$ -601° (c 0.211, CH_2Cl_2).

2-Iodo-*N*,*N*-dimethylpyridin-4-amine 225

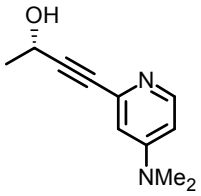


In a flame-dried Schlenk flask 4-(dimethylamino)pyridine (203 mg, 1.66 mmol) was dissolved in THF (4 ml) and cooled to 0 ºC. Boron trifluoride diethyl etherate (220 µl, 1.78 mmol, 1.1 equiv.) was added and the solution was stirred at 0 ºC for 40 min. In another flame-dried Schlenk flask a solution of 2,2,6,6-tetramethylpiperidine (330 µl, 1.96 mmol, 1.2 equiv.) in THF (3 ml) at -78 ºC was treated with a solution of *n*-BuLi (1.6 M in hexanes, 1.2 ml, 1.92 mmol, 1.15 equiv.) and then warmed to room temperature over ca 20 min. The DMAP-BF_3 adduct solution in the first flask was cooled down to -78 ºC and the solution of TMP-Li from the second flask was added to it via a cannula over a period of 5 min with a vigorous stirring. The resulting solution was stirred at -78 ºC for 45 min. A solution of iodine (623 mg, 2.45 mmol, 1.47 equiv.) in THF (1 ml) was added to the reaction mixture and it was stirred at -78 ºC for 1 h. Then it was allowed to warm up to room temperature. The reaction mixture was diluted with diethyl ether (100 ml) and was washed with a saturated aqueous solution of $Na_aS_2O_3$ (1 x 100 ml) and then water (2 x 100 ml). The combined organic phases were dried over anhydrous $MgSO_4$. The volatiles were removed *in vacuo*, the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate gradient 90:10 to 70:30) to provide product **225** (320 mg, 78%) as a white solid.
^{1}H NMR and ^{13}C NMR were in agreement with the published data.[218]

^{1}H NMR (400 MHz, $CDCl_3$): 2.98 (6H, s), 6.45 (1H, dd, *J* = 2.5, 6.0), 6.90 (1H, d, *J* = 2.5), 7.91 (1H, d, *J* = 6.0).

ESI: 249 ($[M+H]^+$).

(2*S*)-4-[4-(Dimethylamino)pyridin-2-yl]but-3-yn-2-ol (*S*)-**226**



A flame-dried Schlenk flask was charged with tetrakis(triphenylphosphine)palladium(0) (75.1 mg, 0.065 mmol, 5 mol%), copper iodide (24.7 mg, 0.13 mmol, 10 mol%) and diisopropylamine (5 ml) was added under argon. Then a degassed solution of **225** (320 mg, 1.29 mmol) in diisopropylamine (5 ml) was added dropwise at room temperature. After stirring for 2 min (*S*)-**111** (110 µl, 98.3 mg, 1.40 mmol, 1.08 equiv.) was added to the reaction mixture and it was stirred at room temperature for 1 h. Then solvents were removed *in vacuo* and the residue was purified by chromatography on silica gel (hexane-ethyl acetate-ethanol 45:45:10). It was further purified by recrystallisation (acetone) to provide the product (*S*)-**226** (219 mg, 89%) as white crystals.

M.p.: 130-132 °C (acetone).

^{1}H NMR (600 MHz, d_6-acetone, rfp=2.09): 1.49 (3H, d, *J* = 6.6), 3.05 (6H, s), 4.71 (1H, q, *J* = 6.6), 4.60 (1H, bs), 6.59 (1H, dd, *J* = 6.0, 2.7), 6.71 (1H, dd, *J* = 2.7, 0.6), 8.12 (1H, dd, *J* = 6.0, 0.6).

^{13}C NMR (151 MHz, d_6-acetone, rfp=29.8): 24.79 (q), 39.10 (q), 58.21 (d), 84.32 (s), 90.44 (s), 106.80 (d), 110.45 (d), 143.99 (s), 150.42 (d), 155.13 (s).

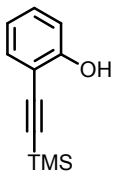
IR ($CHCl_3$): 3601 w, 3100 w, 3094 w, 2987 m, 2821 w, 2237 vw, 1597 vs, 1540 s, 1505 m, 1450 m, 1428 m, 1415 w, 1376 s, 1329 m, 1295 m, 1167 m, 1128 w, 1106 m, 1075 m, 1066 m, 1048 m, 997 s, 936 w, 811 m cm^{-1}.

ESI MS: 402 ($[2M-H+Na]^+$), 191 ($[M+H]^+$).

HR ESI MS: calculated for $C_{11}H_{15}ON_2$ 191.1179, found 191.1180.

Optical rotation: $[\alpha]^{22}_D$ -30° (c 0.240, CH_2Cl_2).

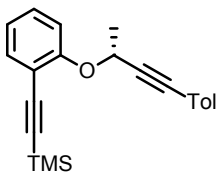
2-[(Trimethylsilyl)ethynyl]phenol 227



A Schlenk flask was charged with 2-iodophenol (150 mg, 0.680 mmol), tetrakis(triphenylphosphine)palladium(0) (31 mg, 0.027 mmol, 4 mol%) and copper iodide (11.7 mg, 0.061 mmol, 9 mol%) and then it was flushed with argon. Benzene (3.5 ml) and diisopropylamine (144 µl, 1.02 mmol, 1.5 equiv.) were added and the reaction mixture was degassed 3 times. The mixture was then stirred for 10 min, ethynyl(trimethyl)silane (142 µl, 1.02 mmol, 1.5 equiv.) was added and the mixture was stirred at room temperature for 3 h. The organic solvents were evaporated *in vacuo*. The residue was purified by chromatography on silica gel (hexane-ethyl acetate 10:1) to afford the desired product **227** (127 mg, 98%) as an oil.

^{1}H NMR and ^{13}C NMR were in agreement with the published data.[219, 220]

Trimethyl[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)-ethynyl]silane (*R*)-**228**



A dry Schlenk flask was charged with 2-[(trimethylsilyl)ethynyl]phenol **227** (87.0 mg, 0.460 mmol), triphenylphosphine (131 mg, 0.500 mmol, 1.1 equiv.), alcohol (*S*)-**145** (88 mg, 0.550 mmol, 1.2 equiv.), and dry benzene (4.5 ml) was added under argon. Diethyl azodicarboxylate (86 µl, 0.550 mmol, 1.2 equiv.) was added dropwise over a period of 5 min. The reaction mixture was stirred at room temperature for 3 h. The precipitated diethyl 1,2-hydrazinedicarboxylate was filtered off through a paper filter and the organic solvent was evaporated *in vacuo*. The residue was purified by chromatography on silica gel (hexane-ethyl acetate 50:1) to afford the desired product (*R*)-**228** (114 mg, 75%) as oil.

^{1}H NMR (400 MHz, $CDCl_3$): 0.26 (9H, s), 1.77 (3H, d, *J* = 6.6), 2.33 (3H, s), 5.12 (1H, q, *J* = 6.5), 6.94 (1H, td, *J* = 7.5, 7.5, 1.1), 7.09 (2H, d, *J* = 7.9), 7.18 (1H, dd, *J* = 7.9, 0.9), 7.24-7.23 (3H, m), 7.43 (1H, dd, *J* = 7.6, 1.6).

^{13}C NMR (101 MHz, $CDCl_3$): 0.25 (q), 21.66 (q), 22.57 (q), 66.47 (d), 86.40 (s), 87.81 (s), 99.92 (s), 101.57 (s), 114.55 (s), 116.49 (d), 119.67 (s), 121.81 (d), 129.19 (d), 129.83 (d), 131.79 (d), 133.80 (d), 138.76 (s), 159.17 (s).

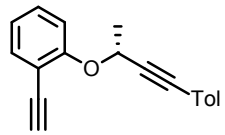
IR ($CHCl_3$): 3077 w, 3057 vw, 2962 m, 2900 w, 2236 w, 2157 m, 1609 vw, 1596 w, 1574 w, 1510 s, 1486 s, 1446 s, 1409 w, 1375 w, 1332 m, 1290 m, 1281 w, 1260 m, 1250 vs, 1181 vw, 1164 w, 1121 m, 1110 m, 1086 s, 1036 m, 1020 w, 947 m, 929 w, 863 vs, 845 vs, 819 s, 720 vw, 700 w, 645 w, 536 w, 416 vw cm^{-1}.

EI MS: 332 ($M^{+\bullet}$, 7), 317 (18), 259 (6), 190 (12), 175 (48), 159 (30), 143 (100), 128 (50), 115 (42), 73 (12).

HR EI MS: calculated for $C_{22}H_{24}OSi$ 332.1596, found 332.1594.

Optical rotation: $[\alpha]^{22}_D$ -25° (c 0.21, $CHCl_3$).

1-Ethynyl-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}benzene (*R*)-**229**



To a solution of trimethylsilyl derivative (*R*)-**228** (110 mg, 0.330 mmol) in methanol (3 ml) anhydrous K_2CO_3 (91 mg, 0.660 mmol, 2.0 equiv.) was added in one portion. The reaction mixture was stirred at room temperature for 1.5 h. Then it was diluted with water (20 ml), extracted with diethyl ether (3 x 15 ml) and the combined organic portions were dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel (hexane-ethyl acetate 50:1) to give the product (*R*)-**229** (71 mg, 83%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 1.79 (3H, d, *J* = 6.6), 2.32 (3H, s), 3.27 (1H, s), 5.12 (1H, q, *J* = 6.6), 6.94 (1H, td, *J* = 7.5, 7.5, 1.0), 7.08 (2H, d, *J* = 7.9), 7.19 (1H, dd, *J* = 7.8, 0.9), 7.24-7.34 (3H, m), 7.47 (1H, dd, *J* = 6.6, 1.7).

^{13}C NMR (101 MHz, $CDCl_3$): 21.66 (q), 22.58 (q), 66.08 (d), 80.28 (s), 81.38 (d), 86.48 (s), 87.57 (s), 113.07 (s), 115.45 (d), 119.58 (s), 121.55 (d), 129.19 (d), 130.12 (d), 131.81 (d), 134.29 (d), 138.63 (s), 159.17 (s).

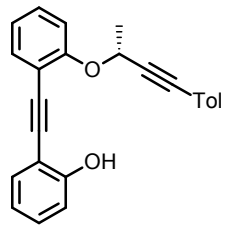
IR ($CHCl_3$): 3307 s, 3079 w, 3057 vw, 2236 w, 2108 w, 1609 w, 1597 m, 1576 w, 1510 s, 1486 vs, 1446 s, 1409 vw, 1332 m, 1288 m, 1268 m, 1260 w, 1245 vs, 1186 w, 1164 w, 1122 m, 1107 m, 1086 s, 1036 s, 1020 m, 946 m, 819 s, 655 m, 613 m, 541 w, 410 w cm^{-1}.

ESI MS: 283 ([M + Na]$^+$).

HR ESI MS: calculated for $C_{19}H_{16}ONa$ 283.1093, found 283.1093.

Optical rotation: $[\alpha]^{22}_D$ +1.0° (c 0.45, $CHCl_3$).

2-[(2-{[(1*R*)-1-Methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)ethynyl] phenol (*R*)-**230**



In a flame-dried Schlenk flask filled with 2-iodophenol (381 mg, 1.73 mmol, 1.28 equiv.), tetrakis(triphenylphosphine)palladium(0) (77.6 mg, 0.067 mmol, 5 mol %) and copper iodide (25.6 mg, 0.134 mmol, 10 mol %), toluene (10 ml) and diisopropylamine (2.8 ml, 19.8 mmol, 15 equiv.) were added under argon. Then a degassed solution of the alkyne (*R*)-**229** (350 mg, 1.344 mmol) in toluene (15 ml) was added at room temperature and allowed to stir for 1 h. Then the reaction mixture was filtered through a sintered glass (hexane) and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane-ethyl acetate 100:0 to 90:10) to obtain the product (*R*)-**230** (468.1 mg, 99%) as white crystals.

M.p.: 122-123°C (hexane).

^{1}H NMR (600 MHz, d_6-acetone, rfp=2.09): 1.82 (3H, d, *J* = 6.5), 2.35 (3H, bs), 5.44 (1H, q, *J* = 6.5), 6.94 (1H, dt, *J* = 7.5, 7.5, 1.1), 7.02 (1H, ddd, *J* = 8.3, 1.1, 0.5), 7.08 (1H, dt, *J* = 7.5, 7.5, 1.1), 7.19-7.21 (2H, m), 7.31 (1H, ddd, *J* = 8.3, 7.4, 1.7), 7.32-7.35 (2H, m), 7.37 (1H, ddt, *J* = 8.4, 1.1, 0.5, 0.5), 7.44 (1H, ddd, *J* = 8.4, 7.4, 1.7), 7.47 (1H, ddd, *J* = 7.6, 1.7, 0.5), 7.56 (1H, ddd, *J* = 7.6, 1.7, 0.5).

^{13}C NMR (151 MHz, d_6-acetone, rfp=29.8): 21.33 (q), 22.65 (q), 66.15 (d), 86.65 (s), 88.31 (s), 90.00 (s), 91.91 (s), 111.24 (s), 114.53 (s), 115.93 (d), 115.98 (d), 120.09 (s), 120.63 (d), 122.32 (d), 129.98 (d), 130.52 (d), 130.95 (d), 132.32 (d), 132.72 (d), 133.41 (d), 139.72 (s), 158.63 (s), 158.86 (s).

IR ($CHCl_3$): 3516 w, 3457 m, 3085 w, 3064 vw, 3063 vw, 2995 w, 2871 w, 2237 w, 2220 vw, 2202 vw, 1615 w, 1596 m, 1576 m, 1510 s, 1494 s, 1480 vs, 1448 m, 1409

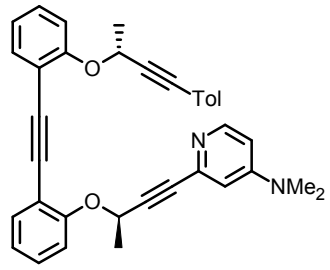
vw, 1377 w, 1331 m, 1279 m, 1246 vs, 1180 vw, 1164 w, 1148 m, 1122 m, 1109 m, 1086 s, 1034 m, 1020 w, 944 m, 819 s cm^{-1}.

ESI MS: 351 ($[M-H]^-$).

HR ESI MS: calculated for $C_{25}H_{19}O_2$ 351.1391, found 351.1389.

Optical rotation: $[\alpha]^{22}_D$ -440° (c 0.104, CH_2Cl_2).

***N*,*N*-Dimethyl-2-[(3*R*)-3-{2-[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)ethynyl]phenoxy}but-1-yn-1-yl]pyridin-4-amine** (*R*,*R*)-**231**



In a flame-dried Schlenk flask diyne (*R*)-**230** (205 mg, 0.582 mmol), alcohol (*S*)-**226** (112.2 mg, 0.589 mmol, 1.0 equiv.) and triphenylphosphine (155 mg, 0.591 mmol, 1.0 equiv.) were flushed with argon and dissolved in THF (45 ml). The solution was cooled to 0 °C and diisopropyl azodicarboxylate (116 µl, 0.589 mmol, 1.0 equiv.) was added dropwise. The reaction mixture was stirred at 50 °C for 2 d under positive pressure of argon. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 90:10 to 20:80) to provide product (*R*,*R*)-**231** (268 mg, 88%) as a yellow oil.

^{1}H NMR (600 MHz, d_6-acetone, rfp=2.09): 1.83 (3H, d, *J* = 6.5), 1.84 (3H, d, *J* = 6.5), 2.34 (3H, bs), 2.99 (6H, s), 5.42 (2H, q, *J* = 6.5), 6.58 (1H, dd, *J* = 6.0, 2.7), 6.70 (1H, dd, *J* = 2.7, 0.5), 7.08 (2H, dt, *J* = 7.5, 7.5, 1.2), 7.18-7.20 (2H, m), 7.31-7.33 (2H, m), 7.34 (1H, dd, *J* = 8.4, 1.2), 7.35 (1H, dd, *J* = 8.4, 1.2), 7.41 (1H, dt, *J* = 7.4, 1.6, 1.6), 7.42 (1H, dt, *J* = 7.4, 1.6, 1.6), 7.58 (2H, ddd, *J* = 8.4, 7.6, 1.6), 8.10 (1H, dd, *J* = 6.0, 0.5).

^{13}C NMR (151 MHz, d_6-acetone, rfp=29.8): 21.32 (q), 22.64 (q), 22.79 (q), 39.06 (q), 66.05 (d), 66.13 (d), 86.18 (s), 86.49 (s), 87.40 (s), 88.50 (s), 90.74 (s), 90.80 (s), 107.09 (d), 110.82 (d), 115.16 (s), 115.22 (s), 116.38 (d), 116.44 (d), 120.15 (s), 122.37 (d), 122.46 (d), 129.95 (d), 130.36 (d), 130.41 (d), 132.28 (d), 134.09 (d), 134.13 (d), 139.61 (s), 143.25 (s), 150.47 (d), 155.04 (s), 158.85 (s), 158.88 (s).

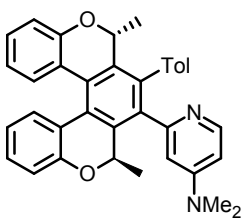
IR ($CHCl_3$): 3076 vw, 3060 vw, 2994 m, 2821 w, 2234 w, 1595 vs, 1575 m, 1540 m, 1510 m, 1497 s, 1481 m, 1449 m, 1428 w, 1414 w, 1376 m, 1330 m, 1295 m, 1286 m, 1236 s, 1164 m, 1121 m, 1111 m, 1087 m, 1065 w, 1039 m, 1020 w, 997 m, 946 m, 935 w, 818 m, 811 w cm^{-1}.

ESI MS: 1049 ($[2M-H]^+$).

HR ESI MS: calculated for $C_{36}H_{33}O_2N_2$ 525.2537, found 525.2526.

Optical rotation: $[\alpha]^{22}_D$ -356° (c 0.025, CH_2Cl_2).

2-[(*M*,2*R*,5*R*)-2,5-Dimethyl-4-(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-3-yl]-*N*,*N*-dimethylpyridin-4-amine (*M*,*R*,*R*)-**106**



In a flame dried 20 ml microwave vial triphenylphosphine (135 mg, 0.515 mmol, 2.0 equiv.) and ionic liquid [BDMIM][BF_4] (ca 100 mg) were flushed with argon and a solution of triyne (*R*,*R*)-**231** (114 mg, 0.218 mmol) in THF (16 ml) was added. Then dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (30 µl, 0.228 mmol, 1.0 equiv.) was added to the mixture and it was heated at 180 °C for 25 min under microwave irradiation. The reaction mixture was filtered through a short pad of silica gel (ethyl acetate) and solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 95:5 to 20:80) to provide product (*M*,*R*,*R*)-**106** (203.3 mg, 89%), which was further recrystallised (hexane-diethyl ether 1:1) to provide white crystals (56%). Single crystal was grown by slow evaporation from a saturated acetonitrile solution.

M.p.: 244-245°C (hexane-diethyl ether).

^{1}H NMR (600 MHz, d_6-DMSO, rfp=2.50, T=373.3 K): 0.92 (3H, d, *J* = 6.7), 0.99 (3H, d, *J* = 6.7), 2.26 (3H, bs), 2.80 (6H, s), 5.18 (1H, q, *J* = 6.7), 5.41 (1H, bq, *J* = 6.7), 6.28 (1H, d, *J* = 2.7), 6.38 (1H, dd, *J* = 6.0, 2.7), 6.80 (2H, ddd, *J* = 7.8, 7.2, 1.3), 6.84-6.87 (1H, m), 6.96-6.99 (1H, m), 7.02 (2H, dd, *J* = 8.0, 1.3), 7.13-7.16 (1H, m), 7.20-7.23 (1H, m), 7.22 (2H, ddd, *J* = 8.0, 7.2, 1.6), 7.32 (2H, dd, *J* = 7.8, 1.6), 8.06 (1H, d, *J* = 6.0).

^{13}C NMR (151 MHz, d_6-DMSO, rfp=39.50, T=373.3 K): 17.51 (q), 17.65 (q), 20.01 (q), 37.90 (q), 71.19 (d), 71.58 (d), 104.59 (d), 108.80 (d), 118.53 (d), 118.51 (d), 120.25 (d), 120.30 (d), 122.51 (d), 122.54 (s), 124.11 (s), 124.26 (s), 127.61 (d), 127.96 (d), 128.03 (d), 128.69 (d), 128.77 (d), 128.77 (d), 129.96 (d), 133.93 (s), 135.35 (s), 135.78 (s), 136.61 (s), 138.27 (s), 138.27 (s), 147.87 (d), 152.54 (s), 152.59 (s), 153.45 (s), 155.64 (s).

IR ($CHCl_3$): 3081 vw, 3064 vw, 2983 w, 2817 vw, 1599 vs, 1585 m, 1558 w, 1542 m, 1515 w, 1505 w, 1488 m, 1452 w, 1435 m, 1420 w, 1369 m, 1331 w, 1291 w, 1247 w, 1179 w, 1153 m, 1118 w, 1107 w, 1087 w, 1066 m, 1037 w, 1022 w, 993 m, 946 vw, 833 w, 811 w cm^{-1}.

ESI MS: 525 ($[M+H]^+$).

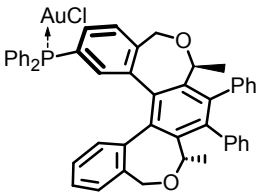
HR ESI MS: calculated for $C_{36}H_{33}O_2N_2$ 525.2537, found 525. 2536.

Optical rotation: $[\alpha]^{22}_D$ -457° (c 0.163, CH_2Cl_2).

General procedure for Ni-catalysed enantioselective cyclotrimerisation of triynes 233 and 237 to products 234 and 238:

In a Schlenk flask $Ni(cod)_2$ (0.01 mmol, 20 mol%) and chiral ligand (0.02 mmol, 40 mol%) were dissolved in THF (1 ml) under argon. After stirring for 5 min at room temperature a solution of triyne **233** or **237** (0.05 mmol) in THF (1 ml) was added and the reaction mixture was stirred at room temperature for 15 min. The volatiles were removed *in vacuo* and the residue purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 95:5) to provide product **234** or **238** as an off-white solid. The product was then analysed on the analytical chiral HPLC (*R*,*R*)-Whelk-O1 column. Retention times were: (-)-**234** 5.5 min, (+)-**234** 6.4 min (heptane, 1 ml/min); (-)-**238** 14.2 min, (+)-**238** 21.2 min (heptane-2-propanol=98:2, 1 ml/min).

Chloro{[(*P*,3*S*,6*S*)-3,6-dimethyl-4,5-diphenyl-1,3,6,8-tetrahydrodibenzo[*e*,*e'*]benzo[1,2-*c*:4,3-*c'*]bisoxepin-11-yl](diphenyl)phosphane-κ*P*}gold (*P*,*S*,*S*)-**239**



A solution of phosphine borane complex (*P*,*S*,*S*)-**127** (57 mg, 0.082 mmol) in diethylamine (1.5 ml) was heated at 50 ºC for 15 h. The volatiles were removed *in vacuo* and the residue dried at 50 ºC for 1 h. Sodium tetrachloroaurate (65 mg, 0.163 mmol, 2.0 equiv.) was dissolved in water (4 ml) and thiodiethanol (50 µl, 0.484 mmol, 5.9 equiv.) was added. A solution of deprotected phosphine (54 mg, 0.072 mmol) in THF (3 ml) was added to the aqueous gold solution at room temperature and the reaction mixture was stirred for 30 min. The solvents were removed *in vacuo* and the residue purified by flash chromatography on silica gel (hexane-diethyl ether-ethyl acetate 8:1:1) to provide gold complex (*P*,*S*,*S*)-**239** (48 mg, 33%) as a grey powder.

^{1}H NMR (600 MHz, $CDCl_3$): 0.56 (3H, d, *J* = 7.1), 0.66 (3H, d, *J* = 7.1), 4.44 (1H, d, *J* = 11.6), 4.50 (1H, d, *J* = 11.6), 4.65 (1H, d, *J* = 11.5), 4.88 (1H, q, *J* = 7.1), 4.92 (1H, d, *J* = 11.5), 4.95 (1H, q, *J* = 7.1), 6.56 (1H, dd, *J* = 7.7, 1.3), 6.68 (1H, dd, *J* = 13.4, 1.7), 6.80-6.85 (4H, m), 7.02-7.14 (4H, m), 7.07 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.15-7.24 (2H, m), 7.16 (1H, dt, *J* = 7.5, 7.5, 1.3), 7.16-7.25 (4H, m), 7.35 (1H, dd, *J* = 7.5, 1.4), 7.38-7.42 (4H, m), 7.46 (1H, ddd, *J* = 13.3, 7.8, 1.7), 7.49-7.54 (2H, m), 7.55 (1H, dd, *J* = 7.8, 2.6).

^{13}C NMR (151 MHz, $CDCl_3$): 22.02 (q), 22.63 (q), 66.73 (t), 67.22 (t), 72.52 (d), 72.86 (d), 126.45 (d), 126.50 (d), 127.37 (d), 127.45 (d), 127.51 (d), 127.71 (d), 127.89 (s, J_{PC} = 61.6), 127.89 (s, J_{PC} = 63.3), 127.90 (d), 128.37 (s, J_{PC} = 62.4), 129.00 (d), 129.02 (d), 129.08 (d), 129.10 (d), 129.48 (d), 129.59 (d, J_{PC} = 12.9), 129.86 (d, J_{PC} = 7.9), 131.76 (d, J_{PC} = 2.5), 131.83 (d, J_{PC} = 2.5), 131.90 (d), 133.02 (d, J_{PC} = 15.4), 134.13 (d, J_{PC} = 13.9), 134.53 (d, J_{PC} = 13.9), 135.37 (s), 137.15 (s), 137.35 (s), 137.37 (d, J_{PC} = 2.9), 137.68 (s), 137.83 (s), 139.42 (s), 139.49 (s), 139.57 (s), 141.40 (s, J_{PC} = 11.9), 141.50 (s, J_{PC} = 2.5), 142.15 (s), 142.67 (s).

^{31}P NMR (202 MHz, $CDCl_3$): 33.22 (s).

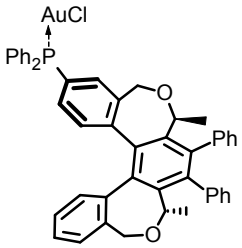
IR ($CHCl_3$): 3079 w, 3061 w, 3034 w, 1601 w, 1588 w, 1577 w, 1556 vw, 1495 w, 1483 w, 1438 s, 1409 w, 1393 w, 1370 m, 1309 w, 1178 w, 1115 m, 1103 s, 1080 vs, 1071 s, 1028 w, 999 w, 906 w, 705 vs, 693 s, 483 w, 434 vw cm^{-1}.

APCI MS: 944 ($[M+CH_3OH_2]^+$), 875 ($[M-Cl]^+$).

HR APCI MS: calculated for $C_{48}H_{39}O_2AuP$ 875.2348, found 875.2312.

Optical rotation: $[\alpha]^{22}_D$ -143° (c 0.065, CH_2Cl_2).

Chloro{[(*P*,3*S*,6*S*)-3,6-dimethyl-4,5-diphenyl-1,3,6,8-tetrahydrodibenzo[*e*,*e'*] benzo[1,2-*c*:4,3-*c'*]bisoxepin-10-yl](diphenyl)phosphane-κ*P*}gold (*P*,*S*,*S*)-**240**



A solution of phosphine borane complex (*P*,*S*,*S*)-**143** (50 mg, 0.072 mmol) in diethylamine (1.0 ml) was heated at 50 ºC for 15 h. The volatiles were removed *in vacuo* and the residue dried at 50 ºC for 1 h. Sodium tetrachloroaurate (69 mg, 0.178 mmol, 2.5 equiv.) was dissolved in water (4 ml) and thiodiethanol (50 µl, 0.484 mmol, 6.7 equiv.) was added. A solution of the phosphine (48.9 mg, 0.072 mmol) in THF (3 ml) was added to the aqueous gold solution and the reaction mixture was stirred at room temperature for 30 min. The solvents were removed *in vacuo* and the residue purified by flash chromatography on silica gel (diethyl ether) to provide the gold complex (*P*,*S*,*S*)-**240** (61 mg, 42%) as a grey powder.

^{1}H NMR (600 MHz, $CDCl_3$): 0.63 (3H, d, *J* = 7.1), 0.69 (3H, d, *J* = 7.1), 4.55 (1H, d, *J* = 11.6), 4.59 (1H, d, *J* = 11.6), 4.86 (1H, d, *J* = 11.6), 4.88 (1H, dd, *J* = 11.6, 0.8), 4.94 (1H, q, *J* = 7.1), 4.97 (1H, q, *J* = 7.1), 6.54 (1H, dd, *J* = 7.7, 1.3), 6.72 (1H, dd, *J* = 8.0, 2.4), 6.83-6.86 (2H, m), 7.04-7.12 (4H, m), 7.04 (1H, dt, *J* = 7.6, 7.6, 1.4), 7.12 (1H, ddd, *J* = 12.8, 8.0, 1.8), 7.13-7.17 (2H, m), 7.19-7.23 (2H, m), 7.27 (1H, dt, *J* = 7.5, 7.5, 1.3), 7.41 (1H, dd, *J* = 7.5, 1.4), 7.45-7.49 (8H, m), 7.52-7.56 (2H, m), 7.56 (1H, dd, *J* = 13.2, 1.8).

^{13}C NMR (151 MHz, $CDCl_3$): 22.17 (q), 22.68 (q), 66.97 (t), 67.37 (t), 72.73 (d), 72.82 (d), 126.56 (d), 126.60 (d), 127.41 (d), 127.44 (s, J_{PC} = 62.1), 127.47 (d), 127.51 (d), 127.80 (d), 127.82 (d), 128.22 (d), 128.22 (s, J_{PC} = 62.6), 128.82 (s, J_{PC} = 62.4), 128.88 (d), 129.24 (d, J_{PC} = 7.4), 129.32 (d, J_{PC} = 7.4), 129.55 (d), 129.64 (d), 129.92

(d), 129.98 (d), 132.02 (d), 132.04 (d, J_{PC} = 2.5), 132.13 (d, J_{PC} = 2.5), 132.66 (d, J_{PC} = 13.4), 132.81 (d, J_{PC} = 12.0), 134.04 (d, J_{PC} = 13.8), 134.26 (d, J_{PC} = 13.8), 135.50 (s), 137.48 (s), 137.52 (s), 137.76 (s), 137.95 (s), 139.00 (s, J_{PC} = 11.8), 139.49 (s), 139.60 (s), 142.26 (s), 142.99 (s), 144.74 (s, J_{PC} = 2.5).

^{31}P NMR (202 MHz, $CDCl_3$): 32.72 (s).

IR ($CHCl_3$): 3079 w, 3062 w, 3034 w, 1600 w, 1577 vw, 1553 vw, 1494 w, 1483 w, 1438 w, 1407 w, 1393 w, 1370 m, 1309 w, 1115 m, 1103 s, 1079 s, 1073 s, 1028 w, 999 w, 704 s, 639 s, 479 w, 432 vw cm^{-1}.

APCI MS: 916 ($[M\text{-}Cl+CH_3CN]^+$), 875 ($[M\text{-}Cl]^+$).

HR APCI MS: calculated for $C_{50}H_{42}O_2NAuP$ 916.2613, found 916.2578.

Optical rotation: $[\alpha]^{22}_D$ -152° (c 0.023, CH_2Cl_2).

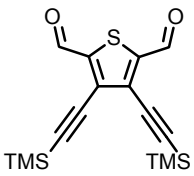
General procedure for enantioselective cyclisation of enynes 241-244 using helical phosphinegold(I) complexes to products 245-248:

In a Schlenk flask phosphinegold(I) complex (*P*,*S*,*S*)-**239** or (*P*,*S*,*S*)-**240** (2 µmol, 2 mol%) was dissolved in methanol (2 ml) and $AgSbF_6$ (2 µmol, 2 mol%) was added. After stirring at room temperature for 15 min, a solution of enyne (0.1 mmol) in methanol (1 ml) was added and the reaction mixture was stirred at room temperature (or at 80 °C for **243** and **244**) until the starting material was completely consumed. Then the reaction mixture was filtered through a short pad of silica gel (hexane-ethyl acetate 70:30) to provide products as an off-white solid. The compounds were analysed on the analytical chiral HPLC Daicel Chiralpak AD-H column. Retention times were: (-)-**245** 34.8 min, (+)-**245** 45.0 min (heptane-2-propanol=5:1, flow 0.5 ml/min); (-)-**246** 53.8 min, (+)-**246** 64.6 min (heptane-2-propanol=6:1, flow 0.5 ml/min); (-)-**247** 17.4 min, (+)-**247** 21.4 min (heptane-2-propanol=98:2, flow 0.5 ml/min); (-)-**248** 17.1 min, (+)-**248** 18.7 min (heptane-2-propanol=98:2, flow 0.5 ml/min).

Procedure for enantioselective cyclisation of enyne 241 using $PtCl_2$ and (-)-2-aza[6]helicene:

In a Schlenk flask enyne **241** (33.5 mg, 0.083 mmol), $PtCl_2$ (1.0 mg, 3.76 μmol, 4.5 mol%) and (-)-2-aza[6]helicene (2.6 mg, 7.84 μmol, 9.4 mol%) were dissolved in methanol (3 ml) and heated at 80 ºC for 22 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (hexane-ethyl acetate 7:3) to provide product (-)-**245** (35.7 mg, 97%, 9% *ee*) as a solid, which was analysed on the analytical chiral HPLC Daicel Chiralpak AD-H column (heptane-2-propanol = 5:1, flow 0.5 ml/min, (-)-**245** 34.8 min, (+)-**245** 45.0 min).

3,4-Bis[(trimethylsilyl)ethynyl]thiophene-2,5-dicarbaldehyde 250



In a Schlenk flask 3,4-dibromothiophene-2,5-dicarbaldehyde **249** (300 mg, 1.01 mmol), bis(acetonitrile)palladium(II) dichloride (26.1 mg, 0.101 mmol, 10 mol%), triphenylphosphine (53.4 mg, 0.204 mmol, 20 mol%) and copper iodide (20.2 mg, 0.106 mmol, 10 mol%) were flushed with argon and toluene (10 ml) and diisopropylethylamine (0.350 ml, 2.01 mmol, 2.0 equiv.) were added. Ethynyl(trimethyl)silane (0.360 ml, 2.55 mmol, 2.6 equiv.) was added to the solution and it was stirred at room temperature for 2 h. Then the reaction mixture was filtered through a short pad of silica gel (hexane-ethyl acetate 90:10) and the volatiles were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-diethyl ether 100:0 to 90:10) to provide product **250** (290 mg, 90%) as a yellow solid.

M.p.: 167-170 ºC (hexane).

^{1}H NMR (600 MHz, $CDCl_3$): 0.31 (18H, s), 10.18 (2H, s).

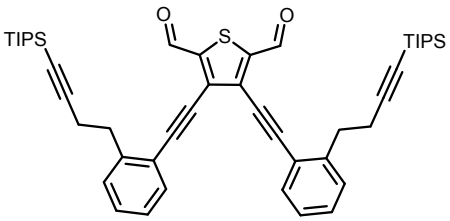
^{13}C NMR (151 MHz, $CDCl_3$): -0.34 (q), 93.71 (s), 106.45 (s), 133.20 (s), 147.66 (s), 183.41 (d).

IR ($CHCl_3$): 2901 w, 2816 vw, 2710 vw, 2161 w, 1685 vs, 1674 vs, 1506 vw, 1411 w, 1352 w, 1252 s, 1243 s, 850 vs, 699 m, 557 vw, 437 w cm^{-1}.

APCI MS: 333 ($[M+H]^+$).

HR APCI MS: calculated for $C_{16}H_{21}O_2SSi_2$ 333.0806, found 333.0796.

3,4-Bis[(2-{4-[tris(1-methylethyl)silyl]but-3-yn-1-l}phenyl)ethynyl]thiophene-2,5-dicarbaldehyde 253



In a Schlenk flask 3,4-dibromothiophene-2,5-dicarbaldehyde **249** (53.4 mg, 0.161 mmol), bis(acetonitrile)palladium(II) dichloride (4.8 mg, 0.018 mmol, 10 mol%), triphenylphosphine (10.9 mg, 0.041 mmol, 26 mol%) and copper iodide (3.3 mg, 0.017 mmol, 11 mol%) were suspended in toluene (5 ml) and diisopropylethylamine (120 µl, 0.69 mmol, 4.3 equiv.) under argon. After stirring at room temperature for 15 min a solution of diyne **254** (118.3 mg, 0.381 mmol, 2.4 equiv.) in toluene (5 ml) was added and the reaction mixture was stirred at room temperature overnight. The reaction mixture was filtered through the short pad of silica gel (ethyl acetate) and the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 100:0 to 95:5) to give product **253** (58 mg, 48%) as a yellow amorphous solid and product **255** (10 mg, 6 %) as an amorphous solid.

^{1}H NMR (600 MHz, $CDCl_3$): 0.93-1.00 (42H, m), 2.60 (4H, t, *J* = 7.0), 3.08 (4H, t, *J* = 7.0), 7.25 (2H, ddd, *J* = 7.7, 7.1, 1.7), 7.35 (2H, ddd, *J* = 7.7, 7.1, 1.4), 7.38 (4H, ddd, *J* = 7.7, 1.7, 0.5), 7.58 (2H, ddd, *J* = 7.7, 1.4, 0.5), 10.31 (2H, s).

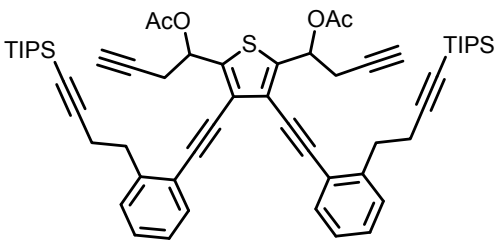
^{13}C NMR (151 MHz, $CDCl_3$): 11.20 (d), 18.52 (q), 20.89 (t), 33.76 (t), 81.76 (s), 83.33 (s), 98.07 (s), 107.07 (s), 120.77 (s), 126.56 (d), 129.60 (d), 129.88 (d), 132.76 (d), 132.86 (s), 143.01 (s), 146.87 (s), 182.98 (d).

IR ($CHCl_3$): 3064 w, 3031 w, 2959 s, 2865 s, 2205 m, 2171 m, 1683 vs, 1672 s, 1599 vw, 1514 vw, 1495 w, 1480 w, 1463 m, 1452 w, 1400 vw, 1386 w, 1374 w, 1349 w, 1298 w, 1162 vw, 1127 vw, 1103 w, 1074 w, 1017 w, 996 m, 948 w, 884 m, 860 w, 677 s, 661 m, 589 w, 417 w cm^{-1}.

ESI MS: 1545 ($[2M+CH_3OH+H]^+$), 1485 ($[2M-CHO]^+$), 756 (M^+).

HR ESI MS: calculated for $C_{48}H_{60}O_2SSi_2$ 756.3858, found 756.3854.

{3,4-Bis[(2-{4-[tris(1-methylethyl)silyl]but-3-yn-1-yl}phenyl)ethynyl]thiene-2,5-diyl}dibut-1-yne-4,4-diyl diacetate 257



In a Schenk flask indium (7.8 mg, 0.068 mmol, 20 mol%) and gallium (95.4 mg, 1.37 mmol, 4.1 equiv.) were suspended in THF (10 ml) under argon. The suspension was cooled down to 0 ºC and propargyl bromide (80% solution in toluene, 300 µl, 2.7 mmol, 8.2 equiv.) was added dropwise. After stirring at 0 ºC for 1 h the suspension was sonicated at room temperature for 20 min until gallium was completely dissolved. Then a solution of aldehyde **253** (250 mg, 0.330 mmol) in THF (10 ml) was added at 0ºC and the reaction mixture was stirred for 30 min. After the reaction was completed it was diluted with diethyl ether (100 ml) and extracted with water (3 x 100 ml). The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was evaporated from benzene (3 x) and dried on oil pump at room temperature for 1 h before the next reaction. Then it was dissolved in THF (15 ml) under argon and 4-(dimethylamino)pyridine (46 mg, 0.38 mmol, 1.15 equiv.) was added. Acetic anhydride (150 µl, 1.59 mmol, 4.8 equiv.) was added dropwise and the reaction mixture was stirred at room temperature for 30 min. After the reaction was complete diethyl ether (100 ml) was added and the solution was washed with water (3 x 100 ml). The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 90:10 to 85:15) to give product **257** (183 mg, 60%) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): 0.90-1.06 (42H, m), 2.06 (2H, t, *J* = 2.6), 2.16 (6H, s), 2.61 (4H, t, *J* = 6.8), 2.89* (2H, ddd, *J* = 17.0, 6.8, 2.6), 2.90* (2H, ddd, *J* = 17.0, 6.8, 2.6), 2.91* (2H, ddd, *J* = 17.0, 5.8, 2.6), 2.97* (2H, ddd, *J* = 17.0, 5.8, 2.6), 3.06 (4H, t, *J* = 6.8), 6.41* (2H, dd, *J* = 6.8, 5.8), 6.42* (2H, dd, *J* = 6.8, 5.8), 7.20 (2H, dt, *J* = 7.5, 7.5, 1.4), 7.26 (2H, dt, *J* = 7.5, 7.5, 1.5), 7.36 (2H, ddt, *J* = 7.6, 1.4, 0.6, 0.6), 7.53 (2H, ddd, *J* = 7.6, 1.5, 0.5).

^{13}C NMR (151 MHz, $CDCl_3$): 11.22 (d), 18.55 (q), 20.70 (q), 20.70 (t), 20.88 (q), 25.99* (t), 26.03* (t), 33.57 (t), 68.69* (d), 68.82* (d), 71.60* (d), 71.64* (d), 78.37 (s), 81.28 (s), 85.12 (s), 94.45 (s), 107.81 (s), 121.84 (s), 122.48 (s), 126.30 (d), 128.65

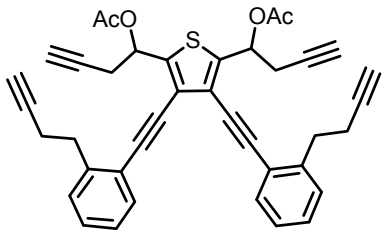
(d), 129.69 (d), 132.51 (d), 142.32 (s), 142.70* (s), 142.76* (s), 169.41 (s), 169.43 (s). *Diastereomeric species

IR ($CHCl_3$): 3310 m, 3064 w, 3031 w, 2958 s, 2892 m, 2865 s, 2207 vw, 2170 m, 2127 vw, 1746 s, 1599 vw, 1499 w, 1483 w, 1464 m, 1451 m, 1382 m, 1372 m, 1339 w, 1292 w, 1231 vs, 1170 w, 1123 vw, 1101 w, 1072 w, 1040 s, 1020 m, 996 m, 947 vw, 884 m, 678 s, 660 s, 639 m, 620 m, 604 w, 589 w, 416 vw cm^{-1}.

ESI MS: 959 ($[M+K]^+$), 943 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{58}H_{72}O_4NaSSi_2$ 943.4582, found 943.4555.

{3,4-Bis[(2-but-3-yn-1-ylphenyl)ethynyl]thiene-2,5-diyl}dibut-1-yne-4,4-diyl diacetate 258



In a Schlenk flask silane **257** (310 mg, 0.33 mmol) was dissolved in THF (10 ml) at room temperature under argon and a solution of tetrabutylammonium fluoride trihydrate (1 M in THF, 0.5 ml, 0.5 mmol, 1.5 equiv.) was added and the reaction mixture was stirred at room temperature overnight. Then solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (gradient hexane-ethyl acetate 90:10 to 80:20) to afford product **258** (125 mg, 63%) as an amorphous solid.

^{1}H NMR (600 MHz, $CDCl_3$): 1.90 (2H, t, *J* = 2.6), 2.07 (2H, t, *J* = 2.7), 2.16 (6H, s), 2.54 (4H, dt, *J* = 7.3, 7.3, 2.6), 2.90 (2H, ddd, *J* = 17.0, 6.7, 2.7), 2.91* (2H, ddd, *J* = 17.0, 6.7, 2.7), 2.96 (2H, ddd, *J* = 17.0, 5.8, 2.7), 2.97* (2H, ddd, *J* = 17.0, 5.8, 2.7), 3.08 (4H, t, *J* = 7.3), 6.44 (2H, dd, *J* = 6.7, 5.8), 6.45* (2H, dd, *J* = 6.7, 5.8), 7.30-7.32 (4H, m), 7.21-7.24 (2H, m), 7.55 (2H, dd, *J* = 7.6, 1.1).

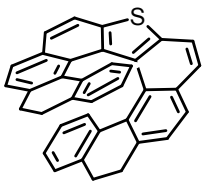
^{13}C NMR (151 MHz, $CDCl_3$): 19.42 (t), 20.89 (q), 26.04 (t), 26.08* (t), 33.41 (t), 68.66 (d), 68.78* (d), 69.17 (d), 71.62 (d), 71.67* (d), 78.40 (s), 83.56 (s), 83.57* (s), 85.23 (s), 94.21 (s), 122.03 (s), 122.45 (s), 126.48 (d), 128.82 (d), 129.16 (d), 132.68 (d), 142.16 (s), 142.95 (s), 143.00* (s), 169.42 (s), 169.45* (s). *Diastereomeric species

IR ($CHCl_3$): 3309 s, 3065 w, 3029 w, 2958 w, 2208 vw, 2119 w, 1746 s, 1600 w, 1500 w, 1484 w, 1449 m, 1372 s, 1350 w, 1341 w, 1294 w, 1230 vs, 1170 w, 1124 vw, 1102 w, 1044 m, 1029 m, 945 w, 640 s, 607 w, 596 w cm^{-1}.

ESI MS: 647 ($[M+K]^+$), 631 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{40}H_{32}O_4NaS$ 631.1914, found 631.1901.

1,2,12,13-Tetrahydrobisbenzo[5,6]phenanthro[3,4-*b*:4',3'-*d*]thiophene 259



A Schlenk flask was charged with hexayne **258** (50.0 mg, 0.082 mmol) and triphenylphosphine (43.6 mg, 0.164 mmol, 2.0 equiv.) The Schlenk flask was closed with septum containing a thermometer and filled with argon. Then decane (4 ml) and dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (11 µl, 0.082 mmol, 1.0 equiv.) were added and the reaction mixture was stirred and heated at 160 °C by two 250 W halogen lamps for 30 min. The reaction mixture was allowed to cool down to room temperature and dissolved in chloroform (10 ml). Then an excess of methyl iodide (1 ml) was added and the solution was stirred at room temperature for 30 min. The solvents were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 100:0 to 90:10) to furnish product **259** (12 mg, 30%) as amorphous solid.

^{1}H NMR (600 MHz, $CDCl_3$): 2.52 (2H, dt, *J* = 16.1, 16.1, 5.9), 2.66 (2H, ddd, *J* = 14.3, 5.7, 1.7), 2.86 (2H, ddd, *J* = 15.9, 5.7, 1.7), 3.29 (2H, dddt, *J* = 16.2, 14.3, 5.9, 1.1, 1.1), 5.90 (2H, dd, *J* = 7.9, 1.3), 6.02 (2H, dddd, *J* = 7.9, 7.2, 1.4, 0.9), 6.57 (2H, dt, *J* = 7.3, 7.3, 1.3), 6.76 (2H, ddt, *J* = 7.4, 1.4, 0.7, 0.7), 7.02 (2H, dt, *J* = 8.0, 0.7, 0.7), 7.38 (2H, bd, *J* = 8.0), 7.66 (2H, dd, *J* = 8.3, 0.4), 7.80 (2H, d, *J* = 8.3).

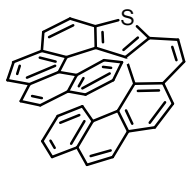
^{13}C NMR (151 MHz, $CDCl_3$): 29.02 (t), 29.15 (t), 118.83 (d), 123.65 (d), 124.47 (d), 125.40 (d), 125.69 (d), 126.51 (d), 126.77 (s), 126.88 (d), 126.94 (d), 129.63 (s), 131.65 (s), 132.11 (s), 133.86 (s), 135.89 (s), 135.90 (s), 138.68 (s).

IR ($CHCl_3$): 3056 w, 2928 vs, 1628 vw, 1593 w, 1574 w, 1536 vw, 1502 w, 1482 w, 1464 w, 1454 m, 1442 w, 1306 w, 1251 w, 1175 w, 1159 w, 1018 vw, 1003 vw, 974 vw, 945 vw, 880 vw, 830 m, 708 vw, 586 m cm^{-1}.

EI MS: 488 ($M^{+\bullet}$, 25), 322 (8), 285 (10), 257 (12), 239 (7), 185 (5), 153 (5), 149 (20), 139 (9), 125 (15), 111 (28), 97 (40), 83 (55), 71 (67), 57(100), 43 (48).

HR EI MS: calculated for $C_{36}H_{24}S$ 488.1599, found 488.1603.

Bisbenzo[5,6]phenanthro[3,4-*b*:4',3'-*d*]thiophene 107



To a solution of helicene **259** (2.5 mg, 4.5 μmol) in dichloroethane (0.5 ml) tritylium tetrafluoroborate (15.1 mg, 45 μmol, 10.0 equiv.) was added in a Schlenk flask under argon and the solution was stirred at 80 °C for 6 h. The reaction mixture was allowed to cool down to room temperature and then triethylamine (2 ml) was added for neutralisation. The solvents were removed *in vacuo* and the residue was purified by thin layer chromatography on silica gel (hexane-ethyl acetate 90:10) to give product **107** (~1 mg) as an amorphous material.

EI MS: 484 ($M^{+\bullet}$, 100), 467 (4), 450 (6), 306 (6), 240 (9), 150 (6).

HR EI MS: calculated for $C_{36}H_{20}S$ 484.1286, found 484.1284.

Appendix A: Single-crystal X-ray diffraction analysis

Compound	(*P*,*S*,*S*)-**153**	(*P*,*S*$_a$,*S*,*S*)-**157**	(*P*,*S*$_a$,*S*,*S*)-**159**	(*P*,*S*,*S*)-**167**
Formula	$C_{43}H_{37}O_2P$	$C_{37}H_{31}BrO_2$	$C_{49}H_{41}O_3P{\cdot}½CH_2Cl_2$	$C_{38}H_{34}O_3$
***M*$_r$**	616.7	587.53	751.25	538.65
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*P* 2_1 2_1 2_1	*P* 2_1 2_1 2_1	*P* 2_1 2_1 2_1	*P* 2_1 2_1 2_1
a, Å	13.3839(5)	10.1911(5)	9.7151(3)	9.8458(6)
b, Å	15.0953(6)	10.6235(4)	16.6419(5)	12.4322(8)
c, Å	16.0521(6)	26.2466(12)	24.8997(8)	23.5830(16)
α, °	90.00	90.00	90.00	90.00
β, °	90.00	90.00	90.00	90.00
γ, °	90.00	90.00	90.00	90.00
Crystal size (mm^3)	0.52 x 0.42 x 0.41	0.24 x 0.22 x 0.17	0.53 x 0.41 x 0.32	0.36 x 0.31 x 0.18
Appearance	colourless prism	colourless prism	colourless prism	colourless prism
Cell volume (Å^3)	3243.1(2)	2841.6(2)	4025.7(2)	2886.7(3)
Z	4	4	4	4
Temperature (K)	150(2)	150(2)	150(2)	150(2)
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α
Radiation wavelength, Å	0.71073	0.71073	0.71073	0.71073
S	1.028	1.010	1.047	1.039
***R*-factor (%)**	3.69	4.13	6.51	4.59
***wR* (%)**	7.96	8.07	16.43	9.54
Number of parameters	418	364	403	374
Flack parameter	0.01(7)	-0.004(8)	0.01(13)	-0.1(15)
X-ray diffractometer	Bruker Apex II	Bruker Apex II	Bruker Apex II	Bruker Apex II
Software	SHELXS	SHELXS	SHELXS	SHELXS

Compound	(*P*,*S*,*S*)-**172**	(*M*,*S*,*S*)-**207**	(*M*,*R*,*R*)-**106**
Formula	$C_{40}H_{38}O_4$	$C_{26}H_{26}O_4$	$C_{36}H_{32}N_2O_2{\cdot}CH_3CN$
***M*$_r$**	582.74	402.47	565.71
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	*P* 2_1	*P* 2_1 2_1 2	*P* 2_1 2_1 2_1
a, Å	6.05682(18)	12.9543(10)	10.7586(3)
b, Å	16.3534(5)	8.0220(7)	14.6318(5)
c, Å	16.0720(5)	9.9226(7)	19.0604(6)
α, °	90.00	90.00	90.00
β, °	97.699(3)	90.00	90.00
γ, °	90.00	90.00	90.00
Crystal size (mm^3)	0.18 x 0.23 x 0.57	0.58 x 0.51 x 0.38	0.13 x 0.25 x 0.62
Appearance	colourless prism	colourless prism	colourless plate
Cell volume (Å^3)	1577.58(8)	1031.15(14)	3000.46(16)
Z	2	2	4
Temperature (K)	170(2)	150(2)	170(2)
Radiation type	CuK_α	MoK_α	CuK_α
Radiation wavelength, Å	1.54184	0.71073	1.54184
S	1.065	1.040	1.104
***R*-factor (%)**	3.69	3.31	4.79
***wR* (%)**	4.56	8.11	5.64
Number of parameters	399	138	390
Flack parameter	-0.09(15)	0.20(10)	-0.1(2)
X-ray diffractometer	Xcalibur	Bruker Apex II	Xcalibur
Software	CRYSTALS	SHELXS	CRYSTALS

Appendix B: Quantum mechanical calculations

Rotation energy barrier involved in the interconversion of the atropisomeric bromides (*P*,S_a,*S*,*S*)-**157** and (*P*,R_a,*S*,*S*)-**157** was first estimated by calculating relaxed potential energy surface (PES) scan using semi-empirical AM1[221] model in Gaussian 03, where the changing parameter was the dihedral angle between the helical scaffold and the phenyl ring bearing the bromo substituent (Figure 8.1). This helped to indentify the potential minima (R_a and S_a) and transition state structures (TS1 and TS2). The geometries of these structures were optimised using DFT on the B3LYP/cc-pVDZ[222-224] level of theory in Gaussian 03.[212] The transition states were located using STQN method[225] (QST3 option). Unfortunately, calculation of the transition state TS2 did not converge on the DFT level. However, semiempirical AM1 method predicts the TS1 to be more stable by ~6 kcal/mol and thus it could be used in the calculation of the rotation barrier. Identity of the minima and the transition state TS1 were confirmed by vibrational frequency calculations at the same computational level (B3LYP, cc-pVDZ). Vibrational analysis also allowed calculating thermodynamic energy values (Table 8.1, Figure 8.2).

Figure 8.1 PES scan of the bromide (*P*,*S*,*S*)-**157** using AM1 in Gaussian 03. Scan step 2°.

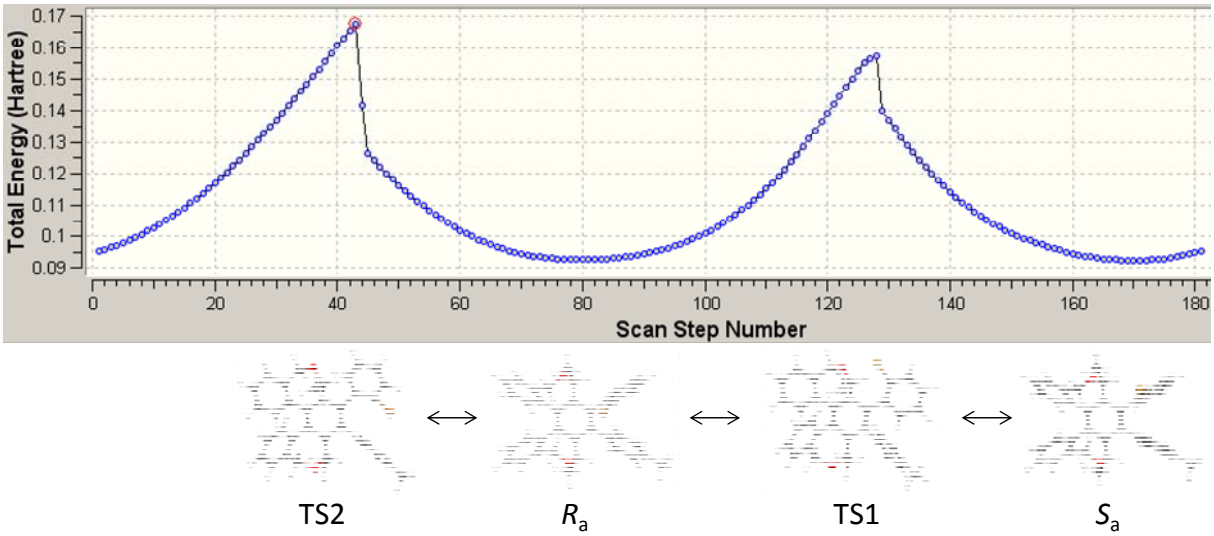
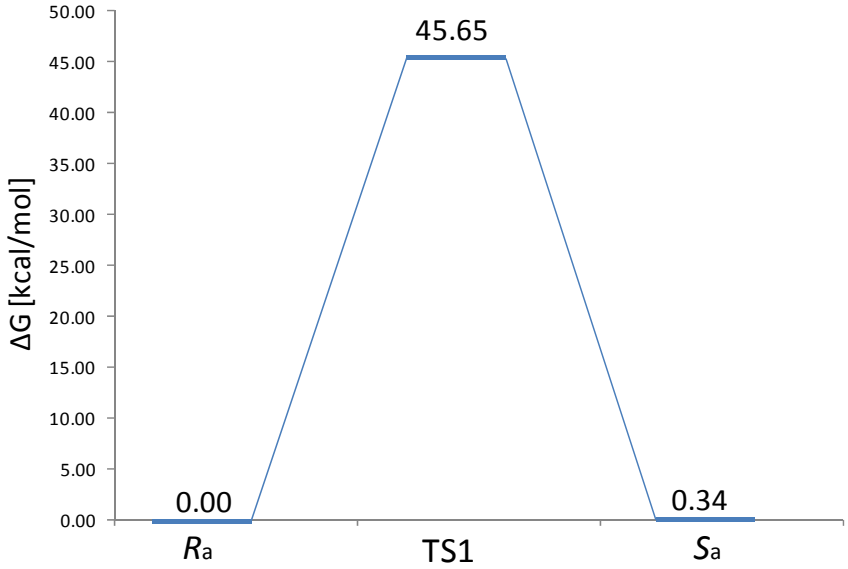


Table 8.1 The computed energies (B3LYP, cc-pVDZ, in Hartree units).

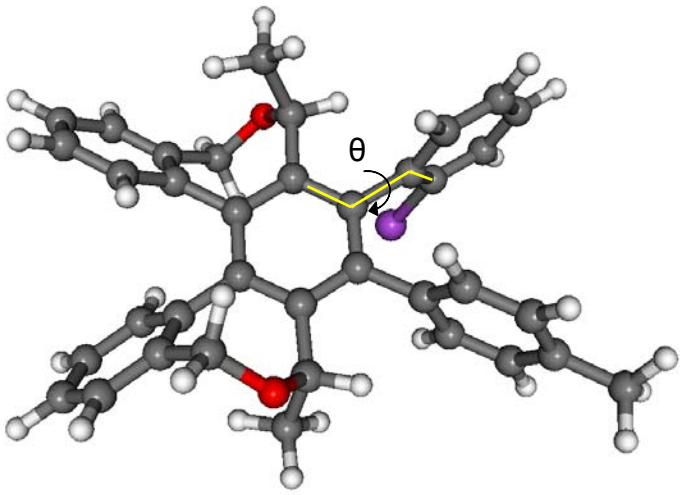
Species	Potential energy, PE	PE+ZPE	PE+thermal energy[a]	PE+thermal enthalpy[a]	PE+thermal free energy[a]
R_a	-4153.28280	-4152.70751	-4152.60570	-4152.67261	-4152.77466
S_a	-4153.28241	-4152.70709	-4152.67314	-4152.67220	-4152.77412
TS1	-4153.21297	-4152.63848	-4152.67356	-4152.60476	-4152.70192

[a] at 298.150 K, 1.000 Atm.

Figure 8.2 Free energy differences between the atropisomers and the calculated transition state (B3LYP, cc-pVDZ).



Computed data for (*P*,R_a,*S*,*S*)-157:



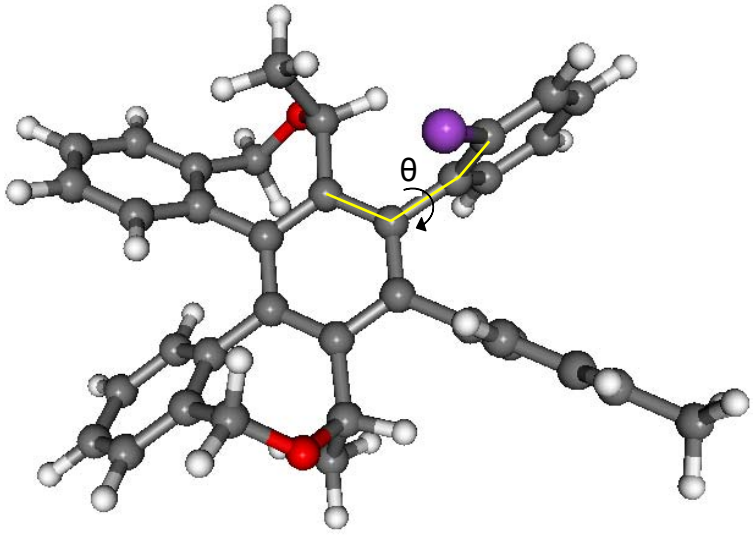
Dihedral angle θ = -85.03° (the arrow indicates positive sense of rotation)

XYZ Coordinates:

C	-3.882505	-0.653845	-1.379934
C	-2.908596	-1.183530	-0.516134
C	-3.169578	-2.407134	0.134666
C	-4.396168	-3.052553	-0.064334
C	-5.364376	-2.508068	-0.910434
C	-5.098395	-1.308863	-1.578634
H	-3.681019	0.280058	-1.906734
H	-4.587653	-4.000256	0.446066
H	-6.316968	-3.021982	-1.057334
H	-5.839801	-0.880875	-2.257134
C	-2.080168	-3.030417	0.970166
C	-1.588107	-0.502909	-0.326034
H	-2.472355	-3.875023	1.554966
H	-1.668979	-2.288410	1.681266
C	-0.397395	-1.250991	-0.490634
O	-1.034459	-3.585801	0.180666
C	-0.970867	-3.068800	-2.220234
H	-0.955350	-4.160699	-2.360634
H	-1.998073	-2.715915	-2.379834
H	-0.323974	-2.612690	-2.988134
C	-1.520528	0.878292	-0.006334
C	-0.270039	1.542711	0.013866
C	0.847994	-0.590771	-0.416334
C	0.912873	0.806730	-0.218734
C	-2.759640	1.650573	0.326466
C	-3.003260	2.892669	-0.296434
C	-3.666533	1.188759	1.295466
C	-4.150371	3.623651	0.035866
C	-4.802445	1.928641	1.625766
H	-3.474819	0.240962	1.800466
C	-5.054664	3.146337	0.986766
H	-4.329086	4.584948	-0.453434
H	-5.492339	1.552230	2.384466
H	-5.945572	3.726923	1.237066
O	-0.800075	3.908503	-0.612034
C	-1.977868	3.437585	-1.258534

H	-2.374982	4.310479	-1.796734
H	-1.718356	2.666989	-2.010634
H	-1.571063	3.114891	2.052866
C	-0.544367	3.395207	1.785466
H	0.145240	2.896218	2.486466
H	-0.438584	4.483709	1.914166
H	2.849671	0.911260	1.733166
C	3.132863	1.454364	0.829266
C	4.373053	2.094683	0.767066
C	2.248862	1.494950	-0.259234
C	4.775842	2.796289	-0.378534
H	5.043154	2.044194	1.629866
C	2.648351	2.197056	-1.408334
C	3.889641	2.832976	-1.465934
H	1.972950	2.249946	-2.265534
H	4.174933	3.368880	-2.375534
C	6.104731	3.511310	-0.430834
H	6.944542	2.814123	-0.287434
H	6.176319	4.276611	0.362366
H	6.248723	4.026512	-1.393134
C	2.127606	-1.354052	-0.615934
C	2.730307	-1.387842	-1.886334
C	2.778017	-2.050842	0.416966
C	3.917217	-2.083124	-2.119034
C	3.967528	-2.752323	0.202466
C	4.537828	-2.768014	-1.071534
H	4.356618	-2.088717	-3.118534
H	4.439636	-3.281016	1.030866
C	-0.158362	3.035113	0.341866
H	0.896734	3.307929	0.235666
C	-0.422772	-2.747991	-0.819834
H	0.616633	-3.095075	-0.815334
H	5.467137	-3.316600	-1.239634
H	2.245598	-0.849350	-2.703034
Br	2.041517	-2.071053	2.192766

Computed data for (*P*,S_a,*S*,*S*)-157:



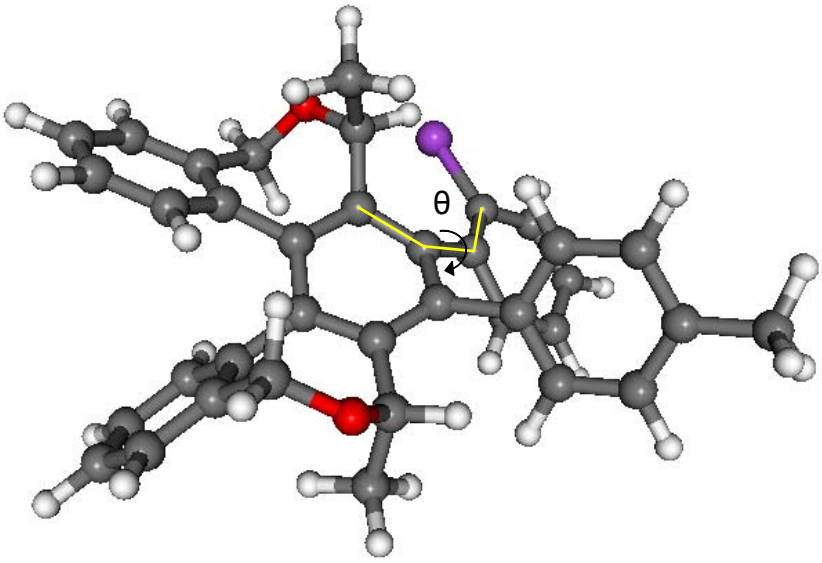
Dihedral angle θ = 93.82° (the arrow indicates positive sense of rotation)

XYZ Coordinates:

C	3.803145	-0.969071	1.073093
C	2.945147	-1.263451	0.000150
C	3.307879	-2.285657	-0.901605
C	4.520435	-2.964753	-0.731230
C	5.374444	-2.652012	0.328473
C	5.005947	-1.656759	1.238829
H	3.520395	-0.196965	1.790027
H	4.791242	-3.755754	-1.435786
H	6.317298	-3.189946	0.450690
H	5.656491	-1.414657	2.082271
C	2.339345	-2.667483	-1.992457
C	1.634379	-0.558343	-0.163907
H	2.817880	-3.339292	-2.719966
H	2.009685	-1.761022	-2.537084
C	0.456811	-1.329584	-0.318159
O	1.208772	-3.389536	-1.513712
C	0.947718	-3.542287	0.933219
H	0.936767	-4.632155	0.775348
H	1.953954	-3.254549	1.262462
H	0.235461	-3.301820	1.738648
C	1.560541	0.857938	-0.153631
C	0.300492	1.504906	-0.189217
C	-0.791089	-0.675490	-0.397497
C	-0.875818	0.732153	-0.305037
C	2.804518	1.691901	-0.131761
C	2.925128	2.746838	0.796417
C	3.839476	1.483550	-1.059226
C	4.077023	3.542872	0.799009
C	4.979774	2.287811	-1.054594
H	3.746483	0.685381	-1.797089
C	5.107721	3.315561	-0.115133
H	4.158855	4.357982	1.522948
H	5.770680	2.110174	-1.786681
H	6.001001	3.944220	-0.103113

O	0.668227	3.650175	1.048965
C	1.766841	3.038333	1.716540
H	2.060180	3.755868	2.496631
H	1.438478	2.108146	2.219667
H	1.796468	3.530839	-1.603109
C	0.735223	3.735540	-1.412467
H	0.156716	3.423467	-2.297853
H	0.610710	4.822292	-1.286315
H	-2.373036	1.328447	-2.519799
C	-2.860775	1.635218	-1.591802
C	-4.108827	2.260526	-1.644264
C	-2.224025	1.396343	-0.364420
C	-4.766053	2.669919	-0.475191
H	-4.581331	2.431807	-2.615561
C	-2.879517	1.805108	0.808021
C	-4.127602	2.428041	0.750607
H	-2.403823	1.633357	1.774933
H	-4.615649	2.731729	1.680874
C	-6.101198	3.372786	-0.532322
H	-6.856174	2.765750	-1.054894
H	-6.022358	4.333528	-1.071361
H	-6.482190	3.597759	0.476144
C	-2.052557	-1.467745	-0.603032
C	-2.875984	-1.913783	0.444032
C	-2.452003	-1.795602	-1.912089
C	-4.049557	-2.635782	0.207077
C	-3.616355	-2.519307	-2.167080
H	-1.816280	-1.475677	-2.740142
C	-4.421197	-2.936497	-1.103902
H	-4.661311	-2.962642	1.048245
H	-3.894152	-2.757344	-3.195918
C	0.181936	3.032678	-0.162377
H	-0.886748	3.269623	-0.132165
C	0.501614	-2.860879	-0.370563
H	-0.522405	-3.205015	-0.553961
H	-5.337123	-3.501909	-1.288540
Br	-2.400572	-1.577941	2.276669

Transition state 1:



Dihedral angle θ = 18.37° (the arrow indicates positive sense of rotation)

XYZ Coordinates:

C	3.695083	-0.526917	1.246980
C	2.642106	-1.207952	0.613980
C	2.802151	-2.575947	0.332980
C	4.018172	-3.213906	0.593980
C	5.070149	-2.511872	1.176980
C	4.897105	-1.172877	1.523980
H	3.569048	0.531079	1.524980
H	4.135208	-4.280903	0.351980
H	6.026166	-3.016840	1.377980
H	5.712086	-0.620850	2.015980
C	1.626177	-3.356986	-0.145020
C	1.411082	-0.491993	0.257980
H	1.899212	-4.421977	-0.380020
H	1.161161	-2.879001	-1.049020
C	0.131101	-1.078035	0.401980
O	0.673181	-3.480017	0.898980
C	0.374130	-1.941027	2.709980
H	0.265160	-2.851031	3.346980
H	1.433119	-1.594992	2.760980
H	-0.294897	-1.137049	3.097980
C	1.525038	0.829011	-0.221020
C	0.394011	1.666974	-0.150020
C	-1.005922	-0.363073	-0.047020
C	-0.862970	1.067932	0.006980
C	2.792021	1.344053	-0.748020
C	3.348982	2.518071	-0.210020
C	3.431042	0.705074	-1.817020
C	4.536965	3.030111	-0.731020
C	4.616025	1.226113	-2.336020
H	2.997073	-0.212940	-2.241020
C	5.170987	2.384132	-1.793020
H	4.970935	3.948125	-0.306020
H	5.113042	0.718130	-3.175020
H	6.106973	2.791163	-2.203020

O	1.436939	3.818008	0.582980
C	2.648961	3.174048	0.930980
H	3.265933	4.008069	1.369980
H	2.433986	2.410041	1.730980
H	1.685963	3.095016	-2.131020
C	0.759948	3.568986	-1.727020
H	-0.108042	3.258957	-2.356020
H	0.875911	4.677990	-1.783020
H	-2.161040	3.184889	-1.280020
C	-2.586031	2.913875	-0.300020
C	-3.670055	3.633839	0.195980
C	-2.035996	1.852893	0.433980
C	-4.232044	3.312820	1.436980
H	-4.090082	4.462825	-0.393020
C	-2.603985	1.532874	1.677980
C	-3.688009	2.253838	2.171980
H	-2.184957	0.701888	2.266980
H	-4.120000	1.986824	3.147980
C	-5.373070	4.094783	1.961980
H	-6.124076	4.288758	1.156980
H	-5.013103	5.081794	2.348980
H	-5.884052	3.556766	2.797980
C	-2.235907	-0.836114	-0.723020
C	-2.785939	0.151868	-1.596020
C	-2.842865	-2.100134	-0.851020
C	-3.995935	0.017828	-2.254020
C	-4.099860	-2.229175	-1.481020
C	-4.704895	-1.178195	-2.147020
H	-4.384962	0.842815	-2.868020
H	-4.611828	-3.207192	-1.464020
C	0.512961	3.160978	-0.281020
H	-0.451055	3.650946	0.064980
C	-0.021858	-2.289040	1.276980
H	-1.109848	-2.607076	1.289980
H	-5.691891	-1.298228	-2.614020
H	-2.211970	1.065887	-1.819020
Br	-2.229808	-3.801113	-0.366020

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