SYNTHESIS OF METHOXY SUBSTITUTED CENTRALLY CHIRAL TRIYNES AS PRECURSORS OF FUNCTIONALISED NONRACEMIC HELICENE-LIKE COMPOUNDS

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A modular synthesis of a series of methoxy substituted optically pure aromatic triynes (–)-(*S*)-**5**-**9** and (–)-(*R*)-**10** is presented. It relies on key operations such as substitution of benzylic bromine with an alkoxy group and aryl-alkyne coupling reaction to combine appropriate methoxy substituted benzene/naphthalene building blocks and chiral alkynol synthons such as (–)-(2*S*)-but-3-yn-2-ol and (–)-(1*R*)-1-phenylprop-2-yn-1-ol. The triyne molecules comprise a diphenylacetylene, 1-(phenylethynyl)naphthalene or 1,1′-ethyne-1,2-diyldinaphthalene core unit. They are intended to serve as [2+2+2] cyclisation precursors of methoxy substituted nonracemic helicene-like compounds with a penta-, hexa- and heptacyclic helical scaffold.

Keywords: Alkynes; Arenes; Helical chirality; Sonogashira reaction; Cross-coupling; Helical structures; Helicenes; Heterohelicenes.

Asymmetric synthesis of helicenes[1] and their analogues could be, from a conceptual as well as practical point of view, the most straightforward method for obtaining these attractive molecules in a nonracemic form. Along with other authors, who contributed to the solution of this general problem[2], we have recently published an independent way to nonracemic helicene-like compounds, based on diastereoselective Co(I)-mediated [2+2+2] cycloisomerisation of aromatic triynes containing an asymmetric carbon atom[3]. We have found that highly stereoselective cyclisation of such triynes takes place producing a [7]helicene-like scaffold in diastereomeric ratios up to 100:0 (Scheme 1). However, for the future utilisa-

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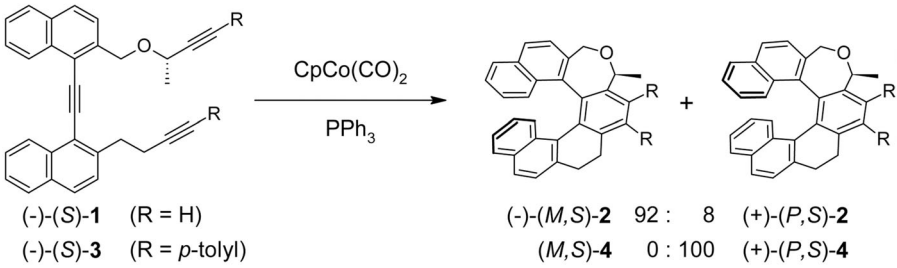
tion of these compounds for instance in asymmetric catalysis the presence of proper functional groups is essential. Thus, we have decided to further develop the diastereoselective synthesis of helicene-like compounds bearing substituents. We have paid attention to the regioselective introduction of the masked hydroxy groups and varying the length of the helical backbone. We have observed in accordance with the previous findings[3] that diastereoselective Co(I)-mediated [2+2+2] cycloisomerisation of methoxy substituted optically pure aromatic triynes leads to nonracemic oxygenated penta-, hexa- and heptacyclic helicene-like compounds. In this parallel study we have been mostly focused on the cyclisation step and its stereochemical outcome[4]. Herein, we report a detailed description of the synthesis of a series of aforementioned, optically pure functionalised aromatic triynes.

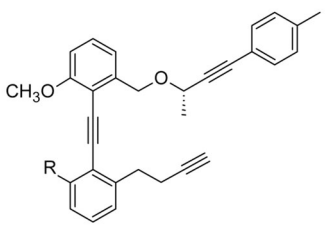


(-)-(*S*)-**1** (R = H) (-)-(*M*,*S*)-**2** 92 : 8 (+)-(*P*,*S*)-**2**
(-)-(*S*)-**3** (R = *p*-tolyl) (*M*,*S*)-**4** 0 : 100 (+)-(*P*,*S*)-**4**

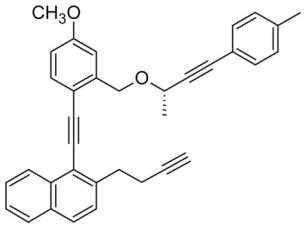
SCHEME 1

RESULTS AND DISCUSSION

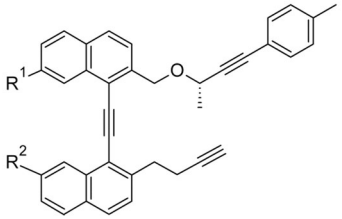
Synthesis of a series of optically pure aromatic triynes (–)-(*S*)-**5**–**9** and (–)-(*R*)-**10** (Chart 1) relies on assembling the [2+2+2] cyclisation precursors from methoxy substituted phenyl or naphthyl building blocks by means of Sonogashira coupling. We have applied the same methodology we explored previously in the case of unfunctionalised triynes[5], however, this time we have proven its versatility as it can be easily adapted to the preparation of methoxy derivatives required. We have experienced the methodology transfer from unsubstituted to CH_3O substituted triynes has not been routine since in specific cases synthetic modifications were necessary. A short synthesis of starting building blocks (–)-(*S*)-**11** [4], **12** [6], **14**, **21** [7], (–)-(*S*)-**22** [5], **25** [8], (–)-(*S*)-**27** [5], **28** [9], **30** [9], **36** [8,10], **38** [10] and (–)-(*R*)-**39** has been already described in literature by us or other authors or they are commercially available. Finally, it is worth noting that both enantiomers of but-3-yn-2-ol, which can serve as key chiral synthons, are commercially available at a reasonable price if supplied in bulk.



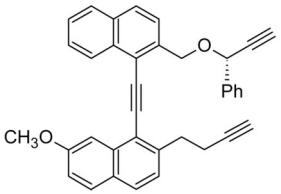
(-)-(*S*)-**5** R = H
(-)-(*S*)-**6** R = CH_3O



(-)-(*S*)-**7**



(-)-(*S*)-**8** R^1 = H, R^2 = CH_3O
(-)-(*S*)-**9** R^1 = CH_3O, R^2 = H

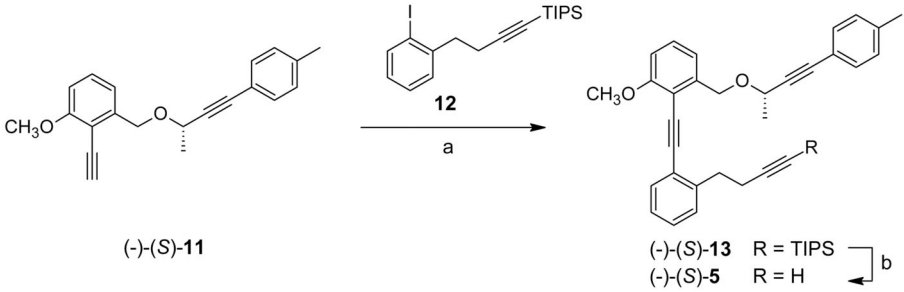


(-)-(*R*)-**10**

CHART 1

*Synthesis of Triyne (–)-(S)-**5***

The preparation of methoxy substituted optically pure triyne (–)-(*S*)-**5** with a tolane core unit was short and straightforward (Scheme 2). The known triyne precursors such as the optically pure diyne (–)-(*S*)-**11** [4] and iodobenzene **12** [6] were subjected to Pd(0)/Cu(I)-catalysed Sonogashira coupling followed by desilylation of (–)-(*S*)-**13** with tetrabutylammonium fluoride to obtain the required model triyne (–)-(*S*)-**5** in good overall yield.



(-)-(*S*)-**11**

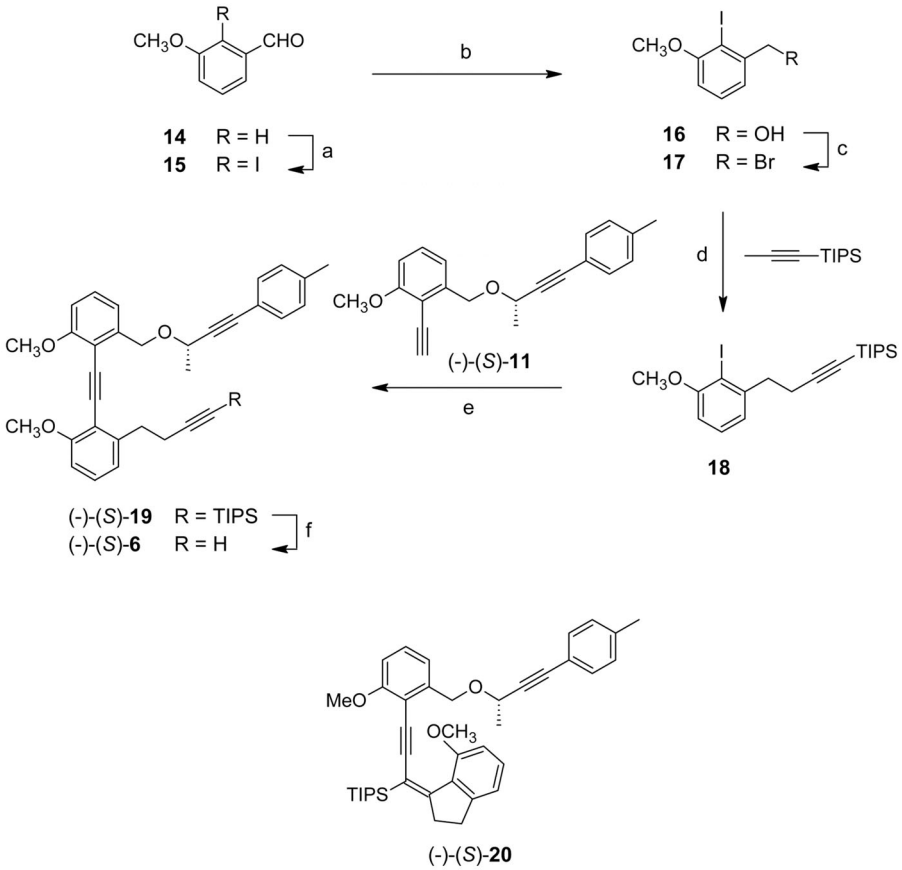
(-)-(*S*)-**13** R = TIPS
(-)-(*S*)-**5** R = H

SCHEME 2

(a) **12** (1.1 equiv.), [$Pd(PPh_3)_4$] (5 mole %), CuI (10 mole %), diisopropylamine, r.t., 2 h, 72%; (b) Bu_4NF (1.2 equiv.), THF, r.t., 30 min, 86%

*Synthesis of Triyne (–)-(S)-**6***

The dimethoxy substituted optically pure triyne (–)-(*S*)-**6** with a tolane core unit was prepared as follows. The directed *ortho* metallation of *m*-anisaldehyde **14** followed by iodination was the key to success in obtaining the 1,2,3-trisubstituted benzene building block (Scheme 3). Using the literature



SCHEME 3

(a) *N*,*N*,*N*′-Trimethylethane-1,2-diamine (1.1 equiv.), BuLi (1.1 equiv.), benzene, 0 °C–r.t., 15 min, then PhLi (3.0 equiv.), 0 °C–r.t., 8 h, then iodine (5.9 equiv) in THF, –78 °C–r.t., 10 min, 67%; (b) DIBAL-H® (1.5 equiv.), toluene, –78 °C, 45 min, 72%; (c) PBr_3 (1.1 equiv.), THF, 0 °C, 1 h, 89%; (d) TIPS–C≡C–CH_3 (1.2 equiv.), BuLi (1.3 equiv.), THF, –78 °C, 1.5 h, then **17**, –78 °C, 1 h, 80%; (e) (–)-(*S*)-**11** (0.9 equiv.), $[Pd(PPh_3)_4]$ (6 mole %), CuI (24 mole %), diisopropylamine, 80 °C, 1 h, 73% of (–)-(*S*)-**19**, 13% of (–)-(*S*)-**20**; (f) Bu_4NF (1.3 equiv.), THF, r.t., 30 min, 99%

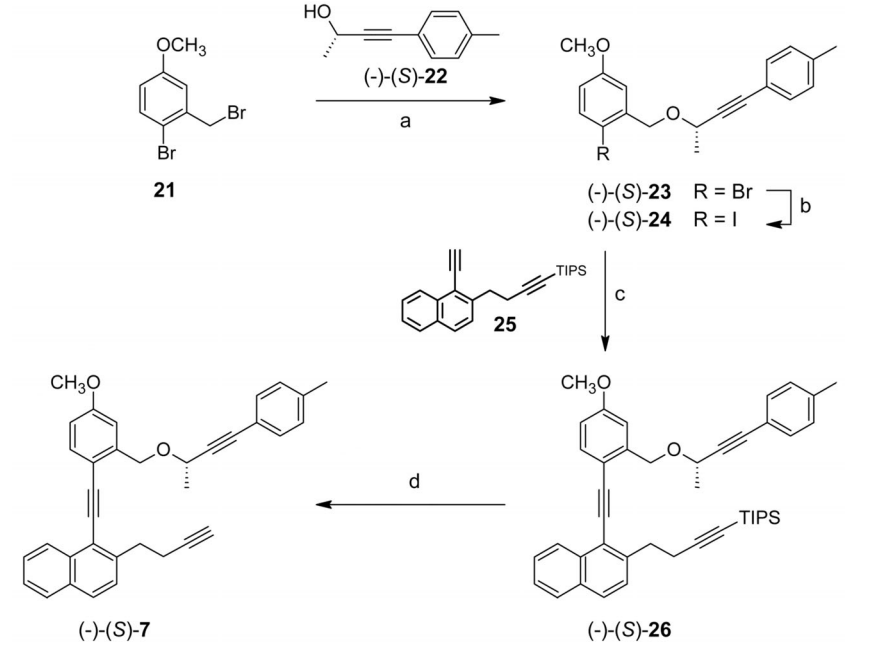
procedure[11], deprotonation proceeded exclusively between the directing substituents and iodide **15** was obtained in good yield. Then, the formyl group was reduced to the hydroxymethyl group by the treatment with diisobutylaluminium hydride to afford **16** in good yield. Bromination with phosphorus tribromide led to the bromomethyl derivative **17** in high yield, which was then reacted with lithiated 1-(triisopropylsilyl)prop-1-yne generated in situ to attach the alkyne sidearm in good yield. Having the properly functionalised iodide **18** in hand, we were able to couple it with the optically pure diyne (–)-(*S*)-**11** [4] under Pd(0)/Cu(I) catalysis. We obtained the desired triyne (–)-(*S*)-**19** in good yield as a major Sonogashira reaction-type product. However, it was accompanied by a minor Heck reaction-type product (–)-(*S*)-**20**, which could be separated by flash chromatography. This side product was formed despite the presence of a bulky triisopropylsilyl group at the tethered alkyne unit. The final step of the reaction sequence leading to the model triyne (–)-(*S*)-**6** was tetrabutylammonium fluoride-mediated desilylation affording the product in quantitative yield.

*Synthesis of Triyne (–)-(S)-**7***

The synthesis of the methoxy substituted optically pure triyne (–)-(*S*)-**7** containing a 1-(phenylethynyl)naphthalene core unit started with nucleophilic substitution of benzylic bromine in **21** [7] with sodium alkoxide derived from the optically pure alcohol (–)-(*S*)-**22** [5] to obtain (–)-(*S*)-**23** in good yield (Scheme 4). After attaching the alkyne sidearm, it was necessary to perform a bromine-to-iodine displacement in order to enable the planned Sonogashira reaction. Thus, bromide (–)-(*S*)-**23** was treated with sodium iodide under Cu(I) catalysis in the presence of a Buchwald diamine ligand[12] to obtain iodide (–)-(*S*)-**24** in nearly quantitative yield. Afterwards, assembling the triyne backbone was attempted utilising Sonogashira reaction with **25** [8] under Pd(0)/Cu(I) catalysis to afford (–)-(*S*)-**26** in high yield. Finally, desilylation with tetrabutylammonium fluoride led to model triyne (–)-(*S*)-**7** in good yield.

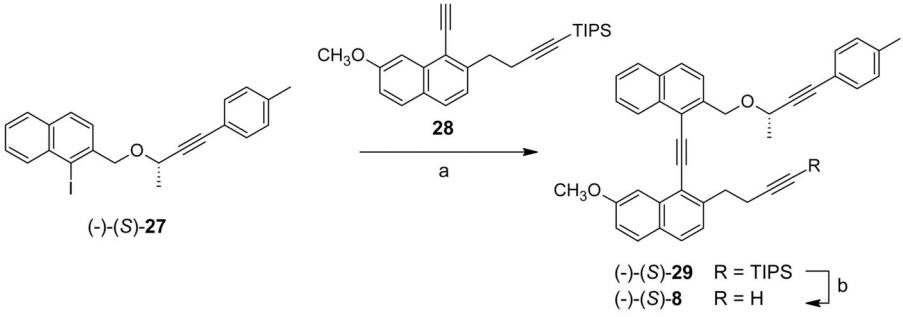
*Synthesis of Triyne (–)-(S)-**8***

The preparation of the methoxy substituted optically pure triyne (–)-(*S*)-**8** comprising a 1,1′-ethynediyldinaphthalene core unit started with Sonogashira coupling of the optically pure iodide (–)-(*S*)-**27** [5] with diyne **28** under Pd(0)/Cu(I) catalysis to afford chiral triyne (–)-(*S*)-**29** in moderate yield (Scheme 5). The subsequent removal of the triisopropylsilyl protect-



SCHEME 4

(a) (–)-(*S*)-**22** (1.1 equiv.), NaH (2.8 equiv.), THF, 0 °C, 2 h, then **21**, 50 °C, 1 h, 77%; (b) NaI (2.4 equiv.), CuI (11 mole %), (±)-*trans*-*N*,*N*′-dimethylcyclohexane-1,2-diamine (13 mole %), pentan-1-ol, 130 °C, 37 h, in a pressure glass tube, 98%; (c) **25** (1.1 equiv.), $[Pd(PPh_3)_4]$ (5 mole %), CuI (9 mole %), diisopropylamine, 80 °C, 10 min, 91%; (d) Bu_4NF (1.2 equiv.), THF, r.t., 1 h, 69%



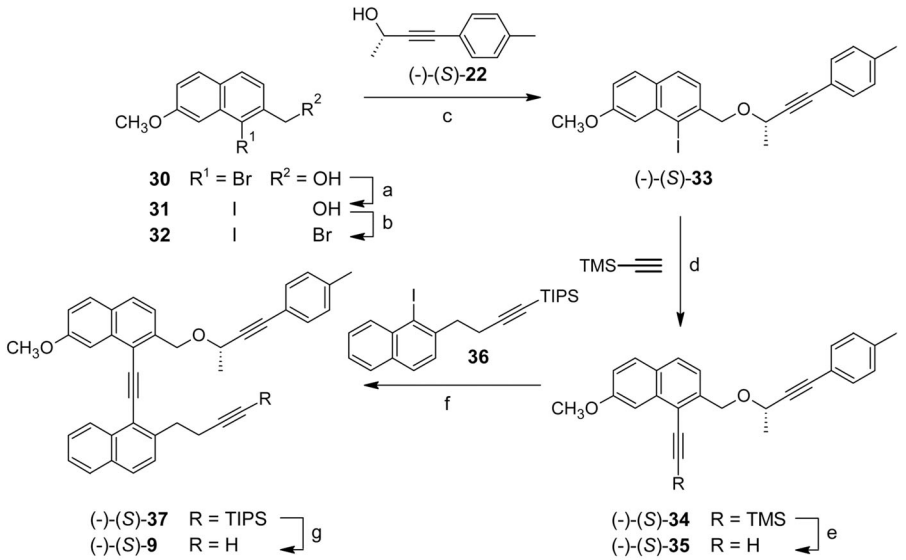
SCHEME 5

(a) **28** (1.1 equiv.), $[Pd(PPh_3)_4]$ (5 mole %), CuI (9 mole %), diisopropylamine, r.t., 2 h, 44%; (b) Bu_4NF (1.2 equiv.), THF, r.t., 15 min, 99%

ing group by treatment with tetrabutylammonium fluoride provided the model triyne (–)-(*S*)-**8** in quantitative yield.

*Synthesis of Triyne (–)-(S)-**9***

The preparation of the methoxy substituted optically pure triyne (–)-(*S*)-**9** derived from a 1,1′-ethynediyldinaphthalene core unit started with lithiation/iodination of bromoalcohol **30** [9] to obtain iodoalcohol **31** in high yield. After its smooth conversion to the benzylic bromide **32** by treatment with phosphorus tribromide, a chiral alkyne sidearm was attached in the reaction with the lithium salt of the optically pure (–)-(*S*)-**22** [5] to afford (–)-(*S*)-**33** in good yield (Scheme 6). The subsequent Sonogashira coupling with (trimethylsilyl)acetylene under Pd(0)/Cu(I) catalysis led to diyne (–)-(*S*)-**34** in high yield which was then desilylated with sodium methoxide to obtain the free diyne (–)-(*S*)-**35** in high yield. To build the triyne back-



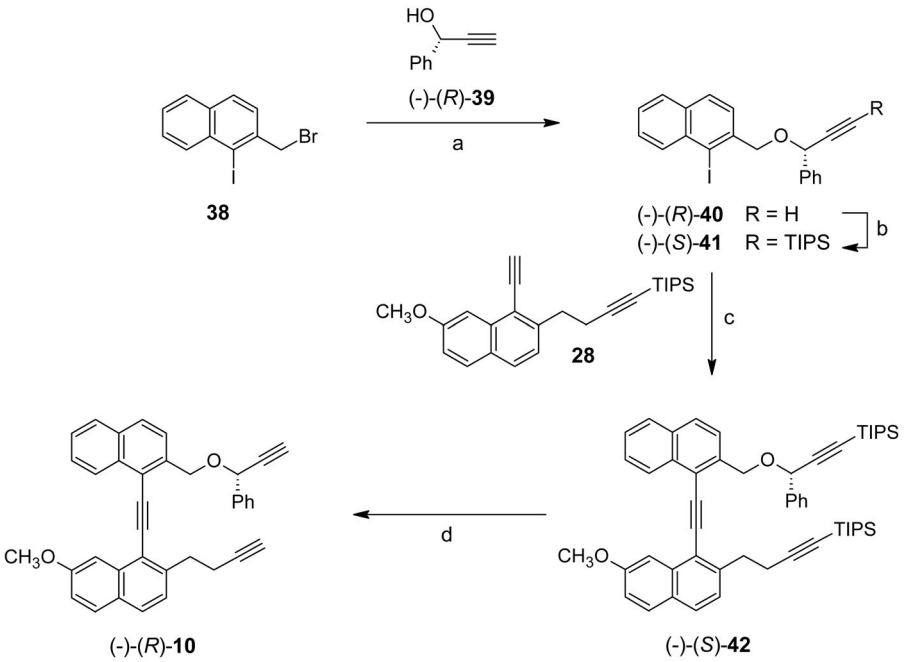
SCHEME 6

(a) BuLi (2.2 equiv.), THF, –90 °C, 30 min, then iodine (2.5 equiv.), THF, –90 °C, 40 min, 93%; (b) PBr_3 (1.6 equiv.), THF, 0 °C, 1 h, 79%; (c) (–)-(*S*)-**22** (1.5 equiv.), BuLi (1.5 equiv.), THF–DMSO 13:1, –35–0 °C, 10 min, then **32**, 40 °C, 20 h, 65%; (d) TMS–C≡CH (1.2 equiv.), $[Pd(PPh_3)_4]$ (5 mole %), CuI (10 mole %), diisopropylamine, 80 °C, 4 h, in a pressure glass tube, 89%; (e) CH_3ONa in methanol (1.9 equiv.), THF, r.t., 2 h, 87%; (f) **36** (1.1 equiv.), $[Pd(PPh_3)_4]$ (6 mole %), CuI (22 mole %), diisopropylamine, r.t., 1.5 h, 64%; (g) Bu_4NF (1.3 equiv.), THF, r.t., 15 min, 87%

bone, the compound **35** was coupled with iodide **36** [8,13] under Pd(0)/Cu(I) catalysis to provide triyne (–)-(*S*)-**37** in moderate yield. The final removal of the triisopropylsilyl group with tetrabutylammonium fluoride resulted in the formation of the model triyne (–)-(*S*)-**9** in high yield.

*Synthesis of Triyne (–)-(R)-**10***

The methoxy substituted optically pure triyne (–)-(*R*)-**10** containing a 1,1′-ethynediyldinaphthalene core unit was synthesised using a different chiral synthon from the model substrates discussed above (Scheme 7). Displacement of benzylic bromine in **38** [10] by alkoxide derived from the commercially available optically pure alkyne building block (–)-(*R*)-**39** provided iodide (–)-(*R*)-**40** with a tethered alkyne unit in good yield. Subsequently,



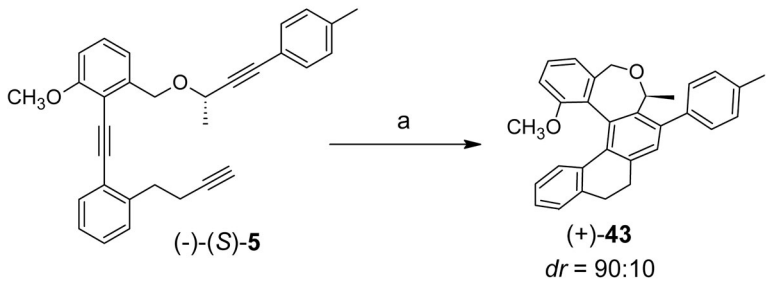
SCHEME 7

(a) (–)-(*R*)-**39** (1.5 equiv.), BuLi (1.5 equiv.), THF–DMSO 16:1, –35–0 °C, 30 min, then **38**, 50 °C, 20 h, 67%; (b) LDA (1.3 equiv.), THF, –78 °C, 1 h, then TIPSCl (2.0 equiv.), –78 °C–r.t., 4 h, 73%; (c) **28** (1.1 equiv.), $[Pd(PPh_3)_4]$ (6 mole %), CuI (10 mole %), diisopropylamine, r.t., 3 h, 85%; (d) Bu_4NF (8.8 equiv.), THF–methanol 100:1, r.t., 24 h, 90%

the protection of the terminal alkyne via its deprotonation by lithium diisopropylamide and silylation with triisopropylsilyl chloride afforded iodide (–)-(*S*)-**41** in good yield. This operation did not affect the aromatic iodide or the chiral centre[14]. Then, the assembly of triyne (–)-(*S*)-**42** could be performed in high yield by coupling the aforementioned iodide with diyne **28**[9] under Pd(0)/Cu(I) catalysis. The whole reaction pathway was completed by the desilylation step using tetrabutylammonium fluoride to obtain the desired model triyne (–)-(*R*)-**10** in high yield[15].

CONCLUSION

The modular synthesis of a series of the methoxy substituted optically pure aromatic triynes (–)-(*S*)-**5**–**9** and (–)-(*R*)-**10** relied on key operations such as benzylic bromine-to-alkoxide substitution and aryl-alkyne coupling reaction to combine appropriate methoxy substituted benzene/naphthalene building blocks and chiral alkynol synthons. We have proven the versatility of this synthetic methodology that can be easily adapted to the preparation of functionalised derivatives. In parallel, diastereoselective Co(I)-mediated [2+2+2] cycloisomerisation of these triynes to obtain methoxy substituted nonracemic helicene-like compounds (comprising a penta-, hexa- and heptacyclic helical scaffold) has been studied. The preliminary results have shown good stereocontrol in cyclisation (**5**→**43**; Scheme 8). The helicity assignment of **43** as well as outputs of cyclotrimerisation of the other triynes **6**–**10** will be published separately in a more comprehensive study[4].



SCHEME 8
(a) $CpCo(CO)_2$ (1.0 equiv.), PPh_3 (2.0 equiv.), decane, irradiated with a halogen lamp, 140 °C, 4 h, 56%

EXPERIMENTAL

General

^{1}H NMR spectra were measured at 499.8 or 500.13 MHz and ^{13}C NMR spectra at 125.7 MHz in $CDCl_3$ with TMS as an internal standard. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) are given in Hz. HMBC experiments were set up for J_{C-H} = 5 Hz. For correct assignment of both ^{1}H and ^{13}C NMR spectra of key compounds, the COSY, ROESY, HMQC, HMBC and CIGAR-HMBC experiments were performed. For all the other compounds, the general semiempirical equations were applied to the chemical shift assignments. IR spectra (wavenumbers in cm^{-1}) were measured in CCl_4 or $CHCl_3$. EI MS spectra were determined at an ionising voltage of 70 eV, *m/z* values are given along with their relative intensities (%). FAB MS spectra were measured using the bis(2-hydroxyethyl) disulfide matrix, *m/z* values are given. In the case of APCI+ MS spectra, the samples were dissolved in acetone and directly infused into the APCI source (probe temperature 300 °C, source block temperature 120 °C, corona current 3.0 μA, cone voltage 25 V). HR MS spectra were obtained by the EI, APCI+ or FAB technique. Compounds (–)-(*S*)-**11** [4], **12** [6], **21** [7], (–)-(*S*)-**22** [5], **25** [8], (–)-(*S*)-**27** [5], **28** [9], **30** [9], **36** [8,10] and **38** [10] were prepared according to the literature procedures. Commercially available building blocks **14** and (–)-(*R*)-**39** and other reagent grade materials were used as received. Diisopropylamine and pentan-1-ol were distilled and degassed by three freeze-pump-thaw cycles before use; benzene and toluene were distilled from calcium hydride under argon before use; THF was freshly distilled from sodium/benzophenone under nitrogen; methanol was distilled with sodium under nitrogen and stored over 5 Å molecular sieves. TLC was performed on silica gel 60 F_{254}-coated aluminium sheets (Merck) and spots were detected with a solution of $Ce(SO_4)_2 \cdot 4H_2O$ (1%) and $H_3P(Mo_3O_{10})_4$ (2%) in sulfuric acid (10%). Flash chromatography was performed on silica gel 60 (0.040–0.063 or <0.063 mm, Merck) or on Biotage KP-Sil® silica cartridges (0.040–0.063 mm) used in Sp1® HPFC system (Biotage, Inc.).

(–)-2-{[2-(3-Butynyl)phenyl]ethynyl}-1-methoxy-3-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)benzene (**5**)

A Schlenk flask was charged with a solution of triyne (–)-(*S*)-**13** (60 mg, 0.102 mmol) in THF (3 ml) under argon. A tetrabutylammonium fluoride solution (0.96 M in THF, 127 μl, 0.122 mmol, 1.20 equiv.) was added and the reaction mixture was stirred at room temperature for 15 min. Solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 95:5) to provide triyne (–)-(*S*)-**5** (38 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$): 1.59 (3 H, d, *J* = 6.6), 1.96 (1 H, t, *J* = 2.6), 2.33 (3 H, bs), 2.62 (2 H, dt, *J* = 7.5, 7.5, 2.6), 3.12 (2 H, t, *J* = 7.5), 3.93 (3 H, s), 4.56 (1 H, q, *J* = 6.6), 4.89 (1 H, dd, *J* = 12.7, 0.4), 5.06 (1 H, bd, *J* = 12.7), 6.85 (1 H, dd, *J* = 8.3, 1.0), 7.05 (1 H, m), 7.11 (1 H, ddd, *J* = 7.7, 6.8, 2.0), 7.18 (1 H, ddt, *J* = 7.7, 1.0, 0.8, 0.8), 7.24 (1 H, ddd, *J* = 7.7, 6.8, 1.4), 7.26 (1 H, dd, *J* = 7.7, 2.0), 7.29 (1 H, m), 7.31 (2 H, dd, *J* = 8.3, 7.7), 7.48 (1 H, ddd, *J* = 7.7, 1.4, 0.7). ^{13}C NMR (125 MHz, $CDCl_3$): 19.42 (t), 21.45 (q), 22.30 (q), 33.92 (t), 55.94 (q), 65.66 (d), 68.68 (d), 68.76 (t), 84.31 (s), 85.40 (s), 87.23 (s), 88.39 (s), 96.73 (s), 109.42 (d), 111.19 (s), 119.65 (d), 119.80 (s), 123.02 (s), 126.30 (d), 128.18 (d), 128.93 (d), 129.11 (d), 129.26 (d), 131.65 (d), 132.26 (d), 138.27 (s), 141.58 (s), 142.15 (s), 160.37 (s). IR ($CHCl_3$): 3308 m, 3066 w, 3031 w, 2840 w, 2226 w, 2117 w, 1596 w, 1577 m, 1510 s, 1490 m, 1473 vs, 1460 m, 1451 m (sh), 1438 m, 1408 w, 1388 w, 1372 w, 1329 m,

1298 m, 1271 s, 1130 m (sh), 1119 m (sh), 1106 m (sh), 1096 s (sh), 1087 s, 1031 m (sh), 1022 w (sh), 867 w, 819 s, 639 m, 544 w, 495 w. EI MS: 432 ($M^{\bullet+}$) (2), 417 (10), 399 (3), 379 (6), 357 (4), 341 (3), 302 (3), 289 (4), 273 (8), 256 (7), 245 (6), 223 (10), 215 (11), 189 (9), 165 (7), 149 (100), 143 (33), 115 (20), 103 (16), 81 (15), 69 (29), 57 (55), 41 (41). HR EI MS: for $C_{31}H_{28}O_2$ 432.2089; found 432.2081. α_D^{22} –140 (*c* 0.10, CH_2Cl_2).

(–)-2-{[2-(3-Butynyl)-6-methoxyphenyl]ethynyl}-1-methoxy-3-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)benzene (**6**)

A 50 ml flask was charged with triyne (–)-(*S*)-**19** (254 mg, 0.411 mmol) and filled with argon. THF (5 ml) was added and the resulting solution was treated with a tetrabutylammonium fluoride solution (1.07 M in THF, 500 µl, 0.536 mmol, 1.30 equiv.). After stirring at room temperature for 30 min, solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 95:5) to provide triyne (–)-(*S*)-**6** (191 mg, 99%) as an amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): 1.59 (3 H, d, *J* = 6.6), 1.96 (1 H, t, *J* = 2.6), 2.31 (3 H, s), 2.64 (2 H, dt, *J* = 7.7, 7.7, 2.6), 3.13 (2 H, t, *J* = 7.7), 3.84 (3 H, s), 3.94 (3 H, s), 4.59 (1 H, q, *J* = 6.6), 4.99 (1 H, d, *J* = 13.2), 5.08 (1 H, d, *J* = 13.2), 6.74 (1 H, dd, *J* = 8.3, 1.0), 6.83 (1 H, dd, *J* = 8.3, 1.0), 6.88 (1 H, dd, *J* = 7.6, 1.0), 7.03 (2 H, m), 7.19 (1 H, dd, *J* = 7.7, 1.0), 7.20 (1 H, dd, *J* = 8.3, 7.6), 7.29 (1 H, t, *J* = 7.9), 7.29 (2 H, m). ^{13}C NMR (125 MHz, $CDCl_3$): 19.27 (t), 21.41 (q), 22.30 (q), 34.04 (t), 55.84 (q), 55.99 (q), 65.78 (d), 68.52 (d), 68.85 (t), 84.51 (s), 85.22 (s), 88.69 (s), 91.95 (s), 93.12 (s), 108.65 (d), 109.30 (d), 111.49 (s), 112.62 (s), 119.35 (d), 119.82 (s), 121.43 (d), 128.80 (d), 128.89 (d), 129.03 (d), 131.63 (d), 138.17 (s), 141.89 (s), 144.03 (s), 160.25 (s), 160.39 (s). IR (CCl_4): 3314 s, 3084 w, 3066 w, 3031 w, 2837 m, 2227 w, 2119 w, 1599 w, 1577 s, 1510 s, 1482 s, 1472 vs, 1462 s (sh), 1453 m (sh), 1438 s, 1408 vw, 1371 m, 1329 s, 1293 s, 1265 vs, 1187 w, 1165 w, 1115 s, 1085 vs, 1062 s, 1030 m, 1023 m (sh), 818 s, 722 w, 709 w, 634 s, 455 w. EI MS: 462 ($M^{\bullet+}$) (2), 447 (30), 429 (19), 419 (46), 409 (22), 388 (16), 303 (38), 171 (53), 143 (78), 128 (100), 115 (52), 83 (53), 69 (61), 57 (80), 43 (50). HR EI MS: calculated for $C_{32}H_{30}O_3$ 462.2195; found 462.2200. α_D^{22} –149 (*c* 0.10, CH_2Cl_2).

(–)-2-(3-Butynyl)-1-{[4-methoxy-2-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)phenyl]ethynyl}naphthalene (**7**)

A Schlenk flask was charged with a solution of triyne (–)-(*S*)-**26** (748 mg, 1.17 mmol) in THF (9 ml) under argon. A tetrabutylammonium fluoride solution (1.07 M in THF, 1.3 ml, 1.39 mmol, 1.19 equiv.) was added and the reaction mixture was stirred at room temperature for 1 h. Solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 90:10). The obtained product was triturated with petroleum ether (4 × 1 ml) to provide triyne (–)-(*S*)-**7** (392 mg, 69%) as an amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): 1.62 (3 H, d, *J* = 6.6), 1.98 (1 H, t, *J* = 2.6), 2.29 (3 H, s), 2.65 (2 H, dt, *J* = 7.6, 7.6, 2.6), 3.28 (2 H, t, *J* = 7.6), 3.87 (3 H, s), 4.60 (1 H, q, *J* = 6.6), 5.00 (1 H, d, *J* = 12.9), 5.16 (1 H, d, *J* = 12.9), 6.87 (1 H, dd, *J* = 8.5, 2.7), 6.96 (2 H, m), 7.19 (1 H, bd, *J* = 2.7), 7.21 (2 H, m), 7.40 (1 H, d, *J* = 8.4), 7.44 (1 H, ddd, *J* = 8.1, 6.8, 1.4), 7.49 (1 H, ddd, *J* = 8.4, 6.8, 1.4), 7.60 (1 H, d, *J* = 8.5), 7.75 (1 H, bd, *J* = 8.4), 7.81 (1 H, ddt, *J* = 8.1, 1.4, 0.8, 0.8), 8.45 (1 H, ddt, *J* = 8.4, 1.4, 0.8, 0.8). ^{13}C NMR (125 MHz, $CDCl_3$): 19.68 (t), 21.39 (q), 22.33 (q), 34.52 (t), 55.42 (q), 65.81 (d), 68.94 (t), 69.07 (d), 83.86 (s), 85.62 (s), 88.26 (s), 88.98 (s), 96.63 (s), 112.99 (d), 113.35 (d), 114.03 (s), 119.56 (s), 119.80 (s), 125.79 (d), 126.24 (d), 126.84 (d), 127.28 (d), 128.00 (d), 128.03 (d), 128.86 (d),

131.60 (d), 132.04 (s), 133.55 (s), 133.71 (d), 138.24 (s), 140.89 (s), 141.84 (s), 160.10 (s). IR ($CHCl_3$): 3309 m, 3058 w, 2991 m, 2937 m, 2841 w, 2225 w, 2201 w, 2118 w, 1621 w (sh), 1606 vs, 1592 w (sh), 1566 m, 1510 vs, 1498 vs, 1466 m, 1445 m, 1431 m, 1420 w (sh), 1408 vw, 1390 w, 1373 w, 1328 m, 1313 m (sh), 1296 s, 1278 m, 1259 m, 1233 s, 1192 w, 1163 m, 1130 m (sh), 1117 m, 1107 m, 1093 s, 1058 s, 1036 m, 1025 m, 921 w, 882 w, 865 w, 819 vs, 640 m, 524 w, 438 w. EI MS: 482 ($M^{\bullet+}$) (1), 467 (4), 449 (3), 439 (9), 429 (4), 339 (5), 321 (7), 311 (6), 295 (7), 285 (7), 276 (16), 265 (22), 252 (16), 239 (46), 226 (34), 215 (14), 202 (18), 189 (15), 165 (16), 143 (52), 128 (100), 115 (50), 91 (25), 43 (54). HR EI MS: calculated for $C_{35}H_{30}O_2$ 482.2246; found 482.2222. α_D^{22} –145 (*c* 0.32, CH_2Cl_2).

(–)-2-(3-Butynyl)-7-methoxy-1-{[2-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)-1-naphthyl]ethynyl}naphthalene (**8**)

A Schlenk flask was charged with a solution of triyne (–)-(*S*)-**29** (64 mg, 92.9 μmol) in THF (4 ml) under argon. A tetrabutylammonium fluoride solution (0.96 M in THF, 116 μl, 0.112 mmol, 1.20 equiv.) was added and the reaction mixture was stirred at room temperature for 15 min. Solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 95:5) to provide triyne (–)-(*S*)-**8** (49 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$): 1.60 (3 H, d, *J* = 6.6), 2.00 (1 H, t, *J* = 2.6), 2.26 (3 H, s), 2.70 (2 H, dt, *J* = 7.6, 7.6, 2.6), 3.39 (2 H, t, *J* = 7.6), 3.98 (3 H, s), 4.58 (1 H, q, *J* = 6.6), 5.34 (1 H, d, *J* = 12.8), 5.38 (1 H, d, *J* = 12.8), 6.88 (2 H, m), 7.12 (2 H, m), 7.15 (1 H, dd, *J* = 8.8, 2.6), 7.31 (1 H, d, *J* = 8.4), 7.54 (1 H, ddd, *J* = 8.1, 6.8, 1.2), 7.60 (1 H, ddd, *J* = 8.3, 6.8, 1.4), 7.74 (1 H, d, *J* = 8.4), 7.74 (1 H, d, *J* = 8.8), 7.79 (1 H, d, *J* = 8.5), 7.90 (1 H, bd, *J* = 8.5), 7.90 (1 H, ddt, *J* = 8.1, 1.4, 0.7, 0.7), 7.93 (1 H, d, *J* = 2.6), 8.68 (1 H, dq, *J* = 8.3, 1.0, 1.0, 1.0). ^{13}C NMR (125 MHz, $CDCl_3$): 20.00 (t), 21.38 (q), 22.38 (q), 34.78 (t), 55.48 (q), 65.55 (d), 69.19 (d), 69.24 (t), 83.78 (s), 85.74 (s), 88.30 (s), 94.30 (s), 96.29 (s), 104.55 (d), 118.35 (s), 118.87 (d), 119.23 (s), 119.41 (s), 124.97 (d), 125.57 (d), 126.25 (d), 126.29 (d), 126.96 (d), 127.53 (s), 128.38 (d), 128.38 (d), 128.65 (d), 128.77 (d), 129.68 (d), 131.47 (d), 132.47 (s), 133.42 (s), 135.23 (s), 138.15 (s), 138.93 (s), 141.89 (s), 158.91 (s). IR ($CHCl_3$): 3308 m, 3061 w, 3032 w, 2225 w, 2118 w, 1623 vs, 1596 w, 1568 w, 1510 vs, 1462 s, 1445 m (sh), 1423 m, 1381 m, 1328 m, 1262 vs, 1177 m, 1129 m (sh), 1095 vs, 1028 s, 868 m, 841 s, 819 vs, 697 w, 640 m, 435 w. ESI+ MS: 413 (8), 373 (47), 316 (46), 288 (82), 242 (100), 186 (7). HR EI MS: calculated for $C_{39}H_{32}O_2$ 532.2402; found 532.2395. α_D^{22} –128 (*c* 0.05, CH_2Cl_2).

(–)-1-{[2-(3-Butynyl)-1-naphthyl]ethynyl}-7-methoxy-2-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)naphthalene (**9**)

A Schlenk flask was charged with a solution of triyne (–)-(*S*)-**37** (40 mg, 58.1 μmol) in THF (4 ml) under argon. A tetrabutylammonium fluoride solution (0.964 M in THF, 75 μl, 72.3 μmol, 1.25 equiv.) was added and the reaction mixture was stirred at room temperature for 15 min. Solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 95:5) to provide triyne (–)-(*S*)-**9** (27 mg, 87%) as an amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): 1.62 (3 H, d, *J* = 6.6), 1.97 (1 H, t, *J* = 2.6), 2.28 (3 H, s), 2.70 (2 H, dt, *J* = 7.5, 7.5, 2.6), 3.37 (1 H, dd, *J* = 14.8, 7.5), 3.43 (1 H, dd, *J* = 14.8, 7.5), 4.00 (3 H, s), 4.61 (1 H, q, *J* = 6.6), 5.25 (1 H, d, *J* = 12.6), 5.36 (1 H, d, *J* = 12.6), 6.93 (2 H, m), 7.16 (2 H, m), 7.21 (1 H, dd, *J* = 8.9, 2.5), 7.46 (1 H, d, *J* = 8.4), 7.49 (1 H,

ddd, *J* = 8.1, 6.8, 1.4), 7.53 (1 H, ddd, *J* = 8.4, 6.8, 1.4), 7.64 (1 H, d, *J* = 8.3), 7.79 (1 H, d, *J* = 8.9), 7.81 (1 H, bd, *J* = 8.4), 7.83 (1 H, bd, *J* = 8.3), 7.86 (1 H, ddt, *J* = 8.1, 1.4, 0.7, 0.7), 7.95 (1 H, d, *J* = 2.5), 8.69 (1 H, ddt, *J* = 8.4, 1.4, 0.8, 0.8). ^{13}C NMR (125 MHz, $CDCl_3$): 19.84 (t), 21.40 (q), 22.38 (q), 34.48 (t), 55.48 (q), 65.64 (d), 69.39 (d), 69.49 (t), 83.62 (s), 85.60 (s), 88.39 (s), 94.81 (s), 95.73 (s), 104.48 (d), 117.84 (s), 119.24 (d), 119.54 (s), 119.73 (s), 123.32 (d), 125.93 (d), 126.26 (d), 126.91 (d), 127.31 (d), 128.16 (s), 128.23 (d), 128.48 (d), 128.53 (d), 128.81 (d), 129.85 (d), 131.54 (d), 132.12 (s), 133.72 (s), 134.92 (s), 138.15 (s), 139.61 (s), 141.13 (s), 158.90 (s). IR ($CHCl_3$): 3308 m, 3059 w, 3034 w, 2225 vw, 2200 vw, 2119 vw, 1623 s, 1595 w, 1573 w, 1510 s, 1462 m, 1446 m, 1424 w, 1381 m, 1375 m, 1329 m, 1310 w, 1278 m (sh), 1268 m, 1176 m, 1126 m (sh), 1106 m (sh), 1095 s, 1041 m, 1029 m, 1021 m, 868 w, 843 m, 819 m, 702 vw, 640 w, 525 w, 435 vw. ESI+ MS: 461 (4), 415 (5), 372 (14), 316 (55), 288 (100), 242 (26), 186 (4). HR EI MS: calculated for $C_{39}H_{32}O_2$ 532.2402; found 532.2383. α_D^{22} –69 (*c* 0.50, CH_2Cl_2).

(–)-2-(3-Butynyl)-7-methoxy-1-{[2-({[(1*R*)-1-phenyl-2-propynyl]oxy}methyl)-1-naphthyl]ethynyl}naphthalene (**10**)

A Schlenk flask was charged with a solution of triyne (–)-(*S*)-**42** (45 mg, 55.1 μmol) in a mixture of THF (5 ml) and methanol (50 μl) under argon. A tetrabutylammonium fluoride solution (0.964 M in THF, 504 μl, 0.486 mmol, 8.82 equiv.) was added and the reaction mixture was stirred at room temperature for 24 h. Solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 95:5) to provide triyne (–)-(*R*)-**10** (25 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): 2.01 (1 H, t, *J* = 2.6), 2.62 (1 H, d, *J* = 2.2), 2.69 (2 H, dt, *J* = 7.6, 7.6, 2.6), 3.37 (2 H, t, *J* = 7.6), 3.94 (3 H, s), 5.33 (2 H, s), 5.36 (1 H, bd, *J* = 2.2), 7.18 (1 H, dd, *J* = 8.9, 2.6), 7.24–7.32 (3 H, m), 7.36 (1 H, d, *J* = 8.3), 7.54–7.56 (2 H, m), 7.55 (1 H, ddd, *J* = 8.1, 6.8, 1.3), 7.61 (1 H, ddd, *J* = 8.4, 6.8, 1.3), 7.77 (1 H, d, *J* = 8.3), 7.78 (1 H, d, *J* = 8.9), 7.78 (1 H, d, *J* = 8.5), 7.90 (1 H, d, *J* = 8.5), 7.90 (1 H, ddt, *J* = 8.1, 1.3, 0.8, 0.8), 7.91 (1 H, d, *J* = 2.6), 8.69 (1 H, ddt, *J* = 8.4, 1.4, 0.9, 0.9). ^{13}C NMR (125 MHz, $CDCl_3$): 19.99 (t), 34.73 (t), 55.47 (q), 68.93 (t), 69.29 (d), 70.82 (d), 76.19 (d), 81.54 (s), 83.79 (s), 94.16 (s), 96.40 (s), 104.55 (d), 118.26 (s), 118.89 (d), 119.39 (s), 125.01 (d), 125.57 (d), 125.57 (d), 126.22 (d), 126.41 (d), 127.03 (d), 127.39 (d), 127.50 (s), 128.40 (d), 128.51 (d), 128.51 (d), 128.72 (d), 129.78 (d), 132.75 (s), 133.36 (s), 135.19 (s), 138.01 (s), 138.25 (s), 141.88 (s), 158.88 (s). IR ($CHCl_3$): 3307 s, 3063 w, 2832 w (sh), 2193 vw, 2118 w, 1623 vs, 1596 w, 1570 w, 1511 m, 1494 w, 1455 m (sh), 1430 w, 1423 m, 1318 w, 1262 vs, 1139 m, 1095 s, 1086 s, 1040 s, 1029 s, 868 w, 841 s, 820 s, 699 s, 648 s, 640 m (sh). EI MS: 504 ($M^{\bullet+}$) (15), 389 (11), 289 (12), 278 (14), 221 (8), 191 (17), 171 (11), 149 (13), 129 (17), 115 (40), 97 (39), 83 (48), 69 (86), 55 (96), 43 (100). HR EI MS: calculated for $C_{37}H_{28}O_2$ 504.2089; found 504.2073. α_D^{22} –17 (*c* 0.20, CH_2Cl_2).

(–)-Triisopropyl[4-(2-{[2-methoxy-6-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)phenyl]ethynyl}phenyl)-1-butynyl]silane (**13**)

A Schlenk flask was charged with iodide **12** (67 mg, 0.161 mmol, 1.09 equiv.), [$Pd(PPh_3)_4$] (10.0 mg, 8.28 μmol, 5 mole %) and CuI (3.0 mg, 16.4 μmol, 10 mole %) and filled with argon. Diisopropylamine (2 ml) was added and the resulting solution was stirred at room temperature for 5 min. A solution of diyne (–)-(*S*)-**11** (50 mg, 0.148 mmol) in diisopropylamine (2 ml) was added and the reaction was stirred at room temperature for 2 h. Solvent

was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 95:5) to provide triyne (–)-(*S*)-**13** (63 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): 0.96–1.06 (21 H, m), 1.58 (3 H, d, *J* = 6.6), 2.33 (3 H, s), 2.71 (2 H, t, *J* = 7.3), 3.10 (2 H, t, *J* = 7.3), 3.92 (3 H, s), 4.54 (1 H, q, *J* = 6.6), 4.88 (1 H, d, *J* = 12.7), 5.05 (1 H, d, *J* = 12.7), 6.84 (1 H, dd, *J* = 8.4, 1.1), 7.05 (1 H, m), 7.09 (1 H, dt, *J* = 7.5, 7.5, 1.4), 7.17 (1 H, dq, *J* = 7.7, 0.9, 0.9, 0.9), 7.21 (1 H, dt, *J* = 7.5, 7.5, 1.4), 7.29 (1 H, m), 7.30 (1 H, dd, *J* = 8.4, 7.7), 7.30 (1 H, bdd, *J* = 7.4, 1.4), 7.47 (1 H, bdd, *J* = 7.6, 1.3). ^{13}C NMR (125 MHz, $CDCl_3$): 11.28 (d), 18.59 (q), 20.80 (t), 21.45 (q), 22.29 (q), 34.16 (t), 55.98 (q), 65.62 (d), 68.76 (t), 84.31 (s), 80.72 (s), 85.39 (s), 87.04 (s), 88.37 (s), 96.96 (s), 108.55 (s), 109.43 (d), 111.33 (s), 119.66 (s), 119.82 (d), 122.87 (s), 126.12 (d), 128.07 (d), 128.93 (d), 129.18 (d), 129.54 (d), 131.65 (d), 132.19 (d), 138.26 (s), 141.53 (s), 142.35 (s), 160.33 (s). IR ($CHCl_3$): 3063 w, 3030 w, 2866 vs, 2840 m (sh), 2226 w, 2169 m, 1596 w, 1577 m, 1510 s, 1489 m, 1473 vs, 1463 s, 1450 m (sh), 1438 m, 1407 w, 1388 m, 1383 m, 1372 m, 1367 w (sh), 1329 m, 1299 m (sh), 1270 s, 1131 m (sh), 1119 m (sh), 1106 m (sh), 1098 s (sh), 1087 s, 1075 s (sh), 1029 m (sh), 1020 m (sh), 996 m, 919 w, 884 s, 865 w (sh), 819 s, 678 m, 662 s, 619 w, 542 w, 499 w. EI MS: 588 ($M^{\bullet+}$) (3), 573 (1), 545 (7), 487 (5), 445 (15), 415 (6), 401 (34), 379 (7), 359 (5), 271 (10), 239 (12), 215 (8), 159 (14), 143 (100), 128 (42), 115 (35), 87 (16), 73 (21), 55 (32), 43 (59). HR EI MS: calculated for $C_{40}H_{48}O_2Si$ 588.3424; found 588.3443. α_D^{22} –105 (*c* 0.10, CH_2Cl_2).

2-Iodo-3-methoxybenzaldehyde (**15**)

A 250 ml three-neck flask was charged with *N*,*N*,*N*′-trimethylethane-1,2-diamine (2.0 ml, 16.1 mmol, 1.06 equiv.) and benzene (33 ml). The stirred solution was cooled to 0 °C and a butyllithium solution (1.6 M in hexanes, 10.0 ml, 16.0 mmol, 1.05 equiv.) was added. The reaction mixture was stirred at room temperature for 15 min and cooled to 0 °C. 3-Methoxybenzaldehyde **14** (1.85 ml, 15.2 mmol) was added and the reaction mixture was stirred at room temperature for 15 min. After cooling to 0 °C, a phenyllithium solution (25.0 ml, 45.0 mmol, 2.96 equiv.) was added and the reaction mixture was stirred at room temperature for 8 h. The reaction mixture was cooled to –78 °C and a solution of iodine (22.80 g, 89.8 mmol, 5.90 equiv.) in THF (60 ml) was added. After keeping the mixture at –78 °C for 10 min, it was allowed to warm to room temperature. The reaction mixture was poured into a mixture of ice (200 g) in 5% HCl (50 ml). After extraction with ether (2 × 100 ml) and a sodium thiosulfate solution (2 × 100 ml), the organic phase was evaporated in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 95:5 to 90:10) to provide iodoaldehyde **15** (2.65 g, 67%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): 3.95 (3 H, s), 7.05 (1 H, dd, *J* = 8.0, 1.4), 7.39 (1 H, ddd, *J* = 8.0, 7.7, 0.8), 7.49 (1 H, dd, *J* = 7.7, 1.4), 10.19 (1 H, d, *J* = 0.8). ^{13}C NMR (125 MHz, $CDCl_3$): 56.85 (q), 93.87 (s), 116.04 (d), 122.33 (d), 129.48 (d), 136.82 (s), 158.34 (s), 196.42 (d). IR ($CHCl_3$): 3070 w, 2841 w, 2801 w, 2738 w, 1696 vs, 1675 m, 1567 s, 1464 s, 1428 m, 1380 m, 1336 s, 1298 s, 1268 vs, 1186 w, 1101 w, 1065 m, 1015 s, 903 m, 703 w, 504 w. EI MS: 262 ($M^{\bullet+}$, 100), 247 (2), 234 (4), 230 (2), 218 (7), 212 (3), 203 (7), 133 (20), 119 (8), 104 (16), 92 (11), 76 (28), 63 (14), 50 (8). HR EI MS: calculated for $C_8H_7IO_2$ 261.9491; found 261.9491.

(2-Iodo-3-methoxyphenyl)methanol (**16**)

A Schlenk flask was charged with iodoaldehyde **15** (1.21 g, 4.61 mmol) and filled with argon. Toluene (20 ml) was added and the solution was cooled to –78 °C. A diisobutyl-

aluminium hydride solution (1.5 M in toluene, 3.20 ml, 4.80 mmol, 1.04 equiv.) was added dropwise. After stirring at –78 °C for 30 min, a second portion of diisobutylaluminium hydride solution (1.50 ml, 2.25 mmol, 0.49 equiv.) was added and stirring was continued at –78 °C for 45 min. The reaction mixture was treated with water (5 ml) and filtered through sintered glass. The filtrate was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. Chromatography of the crude product on silica gel (petroleum ether–ether–acetone, 80:10:10) provided alcohol **16** (879 mg, 72%) as a crystalline solid. ^{1}H NMR (500 MHz, $CDCl_3$): 3.90 (3 H, s), 4.72 (2 H, bs), 6.77 (1 H, dd, *J* = 8.1, 1.5), 7.09 (1 H, ddt, *J* = 7.6, 1.5, 0.7, 0.7), 7.31 (1 H, dd, *J* = 8.1, 7.6). ^{13}C NMR (125 MHz, $CDCl_3$): 56.57 (q), 69.72 (t), 89.46 (s), 110.14 (d), 120.93 (d), 129.40 (d), 144.60 (s), 157.96 (s). IR ($CHCl_3$): 3610 w, 3458 w, 3073 w, 2840 w, 1588 m, 1569 s, 1468 vs, 1430 s, 1382 w, 1291 s, 1269 vs, 1191 w, 1173 w, 1102 w, 1077 m, 1040 s, 1013 s, 910 w, 714 w, 637 w, 597 w. EI MS: 264 ($M^{\bullet+}$, 100), 135 (15), 107 (18), 94 (17), 77 (27), 51 (12). HR EI MS: calculated for $C_8H_9IO_2$ 263.9647; found 263.9653.

1-(Bromomethyl)-2-iodo-3-methoxybenzene (**17**)

A Schlenk flask was charged with alcohol **16** (201 mg, 0.760 mmol) and filled with argon. THF (1 ml) was added and the solution was cooled to 0 °C. Phosphorus tribromide (80 µl, 0.842 mmol, 1.11 equiv.) was added dropwise and the reaction mixture was stirred at 0 °C for 1 h. Solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether–acetone, 80:10:10) to provide bromide **17** (222 mg, 89%) as a crystalline solid. ^{1}H NMR (500 MHz, $CDCl_3$): 3.90 (3 H, s), 4.67 (2 H, s), 6.73 (1 H, dd, *J* = 8.2, 1.4), 7.11 (1 H, dd, *J* = 7.6, 1.4), 7.28 (1 H, dd, *J* = 8.2, 7.6). ^{13}C NMR (125 MHz, $CDCl_3$): 39.37 (t), 56.65 (q), 92.59 (s), 110.62 (d), 122.85 (d), 129.52 (d), 142.01 (s), 158.64 (s). IR ($CHCl_3$): 3073 w, 3062 w, 2840 w, 1588 w, 1570 s, 1466 s, 1439 m, 1428 m, 1299 s, 1268 vs, 1253 w, 1188 w, 1102 w, 1067 s, 1016 s, 926 w, 713 m, 609 w, 558 w. EI MS: 328 ($M^{\bullet+}$ with ^{81}Br, 26), 326 ($M^{\bullet+}$ with ^{79}Br, 26), 247 (100), 105 (25), 90 (17), 51 (15). HR EI MS: calculated for $C_8H_8O^{79}BrI$ 325.8803; found 325.8835.

[4-(2-Iodo-3-methoxyphenyl)-1-butynyl](triisopropyl)silane (**18**)

A Schlenk flask was charged with 1-(triisopropylsilyl)prop-1-yne (980 µl, 4.09 mmol, 1.20 equiv.) and filled with argon. THF (17 ml) was added and the solution was cooled to –78 °C. A butyllithium solution (2.66 ml, 4.26 mmol, 1.25 equiv.) was added and the reaction was stirred at –78 °C for 1.5 h. A solution of bromide **17** (1.11 g, 3.41 mmol) in THF (17 ml) was added dropwise and the reaction mixture was stirred at –78 °C for 1 h. Solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 99:1) to provide compound **18** (1.21 g, 80%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): 1.00–1.06 (21 H, m), 2.57 (2 H, t, *J* = 7.3), 3.02 (2 H, t, *J* = 7.3), 3.88 (3 H, s), 6.67 (1 H, dd, *J* = 8.2, 1.4), 6.95 (1 H, dd, *J* = 7.6, 1.4), 7.19 (1 H, dd, *J* = 8.2, 7.6). ^{13}C NMR (125 MHz, $CDCl_3$): 11.28 (d), 18.61 (q), 20.44 (t), 40.42 (t), 56.51 (q), 81.17 (s), 92.55 (s), 107.59 (s), 108.83 (d), 122.66 (d), 128.80 (d), 144.94 (s), 158.12 (s). IR ($CHCl_3$): 3061 w, 2866 s, 2841 m, 2171 m, 1588 w, 1567 m, 1466 vs, 1428 m, 1383 w, 1367 w, 1337 w, 1293 m, 1264 s, 1189 w, 1075 s, 1041 w, 1014 m, 996 m, 919 w, 884 m, 713 w, 678 m, 662 m, 528 w. EI MS: 442 ($M^{\bullet+}$, 1), 399 (100), 357 (11), 329 (5), 273 (16), 229 (17), 187 (15), 59 (7). HR EI MS: calculated for $C_{17}H_{24}IOSi$ ($[M - CH(CH_3)_2]^{\bullet+}$) 399.0641; found 399.0534.

(–)-Triisopropyl[4-(3-methoxy-2-{[2-methoxy-6-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)phenyl]ethynyl}phenyl)-1-butynyl]silane (**19**)

A Schlenk flask was charged with diyne (–)-(*S*)-**11** (179 mg, 0.588 mmol), iodide **18** (275 mg, 0.622 mmol, 1.06 equiv.), [$Pd(PPh_3)_4$] (38 mg, 33.1 μmol, 6 mole %) and CuI (27 mg, 0.142 mmol, 24 mole %) and filled with argon. Diisopropylamine (8 ml) was added and the reaction mixture was stirred at room temperature for 10 min and then heated to 80 °C for 60 min. Solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 95:5) to provide the desired triyne (–)-(*S*)-**19** (267 mg, 73%) as an oil and compound (–)-(*S*)-**20** (47 mg, 13%) as an amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): 1.19 (18 H, d, *J* = 7.5), 1.44 (3 H, d, *J* = 6.6), 1.62 (3 H, m), 2.33 (3 H, s), 2.88 (4 H, s), 3.65 (3 H, s), 3.73 (3 H, s), 4.20 (1 H, q, *J* = 6.6), 4.60 (1 H, d, *J* = 12.9), 4.75 (1 H, d, *J* = 12.9), 6.71 (1 H, bd, *J* = 8.3), 6.73 (1 H, dd, *J* = 8.4, 1.0), 6.85 (1 H, d, *J* = 7.8), 7.07 (2 H, m), 7.10 (1 H, dd, *J* = 7.9, 1.0), 7.16 (1 H, dd, *J* = 8.4, 7.9), 7.19 (1 H, dd, *J* = 8.4, 7.8), 7.26 (2 H, m). ^{13}C NMR (125 MHz, $CDCl_3$): 12.77 (d), 19.10 (q), 21.42 (q), 22.14 (q), 31.75 (t), 37.66 (t), 54.79 (q), 55.52 (q), 65.84 (d), 68.94 (t), 84.83 (s), 88.88 (s), 90.28 (s), 90.28 (s), 104.04 (s), 109.14 (d), 109.94 (d), 113.26 (s), 113.49 (s), 116.59 (d), 119.10 (d), 119.92 (s), 127.44 (d), 128.87 (d), 130.09 (d), 131.59 (d), 138.09 (s), 141.04 (s), 149.06 (s), 156.70 (s), 159.64 (s). IR (CCl_4): 3084 w, 3065 w, 3031 w, 2866 vs, 2837 m, 2227 w, 2169 m, 1599 w, 1576 s, 1510 s, 1482 m, 1472 vs, 1462 s (sh), 1438 s, 1409 vw, 1387 w, 1383 w, 1371 m, 1329 m, 1311 m (sh), 1294 s, 1265 vs, 1241 w (sh), 1186 w, 1163 w, 1115 m, 1085 vs, 1042 m, 1030 m (sh), 1021 m, 997 m, 919 w, 884 m, 818 m, 723 w, 709 w, 677 s, 660 m, 613 w. EI MS: 618 ($M^{\bullet+}$) (5), 575 (7), 475 (11), 431 (12), 301 (31), 239 (8), 215 (8), 173 (11), 157 (24), 143 (100), 128 (57), 115 (46), 59 (53). HR EI MS: calculated for $C_{41}H_{50}O_3Si$ 618.3529; found 618.3542. α_D^{22} –111 (*c* 0.17, CH_2Cl_2).

(–)-Triisopropyl{(1*E*)-1-(7-methoxy-2,3-dihydro-1*H*-inden-1-ylidene)-3-[2-methoxy-6-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)phenyl]-2-propynyl}silane (**20**)

^{1}H NMR (500 MHz, $CDCl_3$): 1.19 (18 H, d, *J* = 7.5), 1.43 (3 H, d, *J* = 6.6), 1.61 (3 H, m), 2.33 (3 H, s), 2.88 (4 H, s), 3.65 (3 H, s), 3.74 (3 H, s), 4.20 (1 H, q, *J* = 6.6), 4.60 (1 H, d, *J* = 12.8), 4.74 (1 H, d, *J* = 12.8), 6.71 (1 H, dd, *J* = 8.2, 0.8), 6.73 (1 H, dd, *J* = 8.1, 1.2), 6.85 (1 H, dd, *J* = 7.3, 0.8), 7.07 (2 H, m), 7.10 (1 H, ddt, *J* = 7.8, 1.2, 0.8, 0.8), 7.19 (1 H, dd, *J* = 8.2, 7.3), 7.26 (2 H, m), 7.61 (1 H, t, *J* = 8.0). ^{13}C NMR (125 MHz, $CDCl_3$): 12.79 (d), 19.11 (q), 21.42 (q), 22.14 (q), 31.76 (t), 37.67 (t), 54.81 (q), 55.55 (q), 65.86 (d), 68.95 (t), 84.85 (s), 88.90 (s), 90.30 (s), 104.05 (s), 109.17 (d), 109.97 (d), 113.29 (s), 113.52 (s), 116.61 (d), 119.14 (d), 119.95 (s), 127.45 (d), 128.88 (d), 130.10 (d), 131.26 (s), 131.60 (d), 138.10 (d), 141.06 (s), 149.07 (s), 156.72 (s), 159.66 (s), 160.65 (s). IR (CCl_4): 3084 w, 3065 w, 3030 w, 2865 vs, 2836 s, 2227 w, 2171 w, 1596 m, 1583 s, 1577 s (sh), 1551 m, 1510 s, 1480 vs, 1471 vs, 1464 s (sh), 1460 s (sh), 1438 m, 1407 vw (sh), 1388 m, 1384 m (sh), 1370 m, 1328 s, 1304 m, 1273 vs, 1185 w, 1162 w, 1107 s, 1088 s, 1070 s, 1063 vs, 1022 m, 996 w, 884 m, 818 s, 724 w, 708 w, 672 m, 663 m (sh), 614 w, 458 w. EI MS: 618 ($M^{\bullet+}$) (10), 575 (15), 475 (11), 432 (35), 316 (16), 291 (21), 279 (100). HR FAB MS: calculated for $C_{41}H_{51}O_3Si$ 619.3607; found 619.3589. α_D^{22} –83 (*c* 0.12, CH_2Cl_2).

(–)-1-Bromo-4-methoxy-2-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)benzene (**23**)

A Schlenk flask was charged with NaH (80% suspension in mineral oil, 218 mg, 7.27 mmol, 2.77 equiv.) and filled with argon. THF (5 ml) was added and the stirred suspension was cooled to 0 °C. A solution of alcohol (–)-(*S*)-**22** (465 mg, 2.85 mmol, 1.09 equiv.) in THF (7 ml) was added dropwise and the reaction mixture was stirred at room temperature for 2 h. A solution of bromide **21** (734 mg, 2.62 mmol) in THF (8 ml) was added and the reaction was heated at 50 °C for 1 h. Solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 95:5) to provide (–)-(*S*)-**23** (724 mg, 77%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): 1.60 (3 H, d, *J* = 6.6), 2.35 (3 H, s), 3.80 (3 H, s), 4.52 (1 H, q, *J* = 6.6), 4.63 (1 H, d, *J* = 13.0), 4.84 (1 H, d, *J* = 13.0), 6.71 (1 H, dd, *J* = 8.7, 3.1), 7.11 (1 H, d, *J* = 3.1), 7.12 (2 H, m), 7.34 (2 H, m), 7.41 (1 H, d, *J* = 8.7). ^{13}C NMR (125 MHz, $CDCl_3$): 21.44 (q), 22.23 (q), 55.49 (q), 65.89 (d), 69.98 (t), 85.61 (s), 88.10 (s), 113.03 (s), 114.77 (d), 114.77 (d), 119.68 (s), 129.02 (d), 131.66 (d), 133.05 (d), 138.45 (s), 138.68 (s), 159.12 (s). IR ($CHCl_3$): 3084 w, 2991 m, 2841 m, 2225 w, 1596 m, 1575 m, 1510 vs, 1476 vs, 1465 vs, 1456 s (sh), 1444 m, 1419 m, 1409 m, 1389 m, 1373 m, 1329 s, 1313 m, 1298 s, 1273 s, 1259 m, 1193 w, 1165 s, 1131 m (sh), 1119 s, 1108 s (sh), 1096 vs, 1056 s, 1021 s, 947 w, 920 w, 879 w, 862 w, 819 vs, 600 m, 525 w, 440 w, 410 w. FAB MS (bis(2-hydroxyethyl) disulfide matrix): 383 (M with ^{81}Br + Na^+), 381 (M with ^{79}Br + Na^+), 311, 297, 279, 253, 235, 207, 143. HR FAB MS: calculated for ($C_{19}H_{19}{}^{79}BrO_2$ + Na^+) 381.0466; found 381.0472. α_D^{22} –84 (*c* 0.24, CH_2Cl_2).

(–)-1-Iodo-4-methoxy-2-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)benzene (**24**)

A sealed tube was charged with NaI (63 mg, 0.417 mmol, 2.40 equiv.), dried in vacuo at 130 °C for 10 min and allowed to cool to room temperature under argon. CuI (4 mg, 20.0 μmol, 11 mole %), (±)-*trans*-*N*,*N*′-dimethylcyclohexane-1,2-diamine (3 mg, 22.5 μmol, 13 mole %), bromide (–)-(*S*)-**23** (63 mg, 0.174 mmol) and pentan-1-ol (1 ml) were added and the reaction mixture was heated to 130 °C for 37 h. The resulting mixture was filtered through a short pad of silica and the crude product was obtained from the solid residue by extracting with a mixture of petroleum ether–ether (95:5). Chromatography on silica gel (petroleum ether–ether, 95:5) provided iodide (–)-(*S*)-**24** (70 mg, 98%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): 1.60 (3 H, d, *J* = 6.6), 2.35 (3 H, s), 3.79 (3 H, s), 4.52 (1 H, q, *J* = 6.6), 4.54 (1 H, d, *J* = 12.8), 4.78 (1 H, d, *J* = 12.8), 6.59 (1 H, dd, *J* = 8.6, 3.1), 7.10 (1 H, d, *J* = 3.1), 7.12 (2 H, m), 7.35 (2 H, m), 7.67 (1 H, d, *J* = 8.6). ^{13}C NMR (125 MHz, $CDCl_3$): 21.44 (q), 22.22 (q), 55.38 (q), 65.85 (d), 74.35 (t), 85.67 (s), 86.11 (s), 88.07 (s), 114.90 (d), 115.35 (d), 119.66 (s), 129.02 (d), 131.66 (d), 138.45 (s), 139.57 (d), 141.57 (s), 160.09 (s). IR ($CHCl_3$): 3083 w, 2991 m, 2937 m, 2840 w, 2225 w, 1590 m, 1571 m, 1510 s, 1467 vs, 1456 m (sh), 1444 m, 1415 m, 1408 w, 1387 w, 1373 w, 1328 s, 1308 m, 1295 s, 1273 m, 1258 m, 1237 s, 1194 w, 1131 m (sh), 1117 m, 1095 vs, 1054 s, 1021 w, 1011 m, 920 w, 878 w, 862 w, 819 vs, 590 w, 545 w, 525 w, 463 vw. EI MS: 405 ($M^{\bullet+}$, 1), 287 (1), 279 (2), 263 (2), 247 (47), 235 (34), 143 (100), 128 (27), 109 (14), 97 (22), 83 (36), 69 (78), 57 (99). HR FAB MS: calculated for ($C_{19}H_{19}IO_2$ + Na^+) 429.0328; found 429.0337. α_D^{22} –76 (*c* 0.21, CH_2Cl_2).

(–)-Triisopropyl[4-(1-{[4-methoxy-2-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)phenyl]ethynyl}-2-naphthyl)-1-butynyl]silane (**26**)

A Schlenk flask was charged with iodide (–)-(*S*)-**24** (528 mg, 1.30 mmol), [$Pd(PPh_3)_4$] (68 mg, 58.8 μmol, 5 mole %) and CuI (21 mg, 0.112 mmol, 9 mole %) and filled with argon. A solution of diyne **25** (517 mg, 1.43 mmol, 1.10 equiv.) in diisopropylamine (13 ml) was added and the reaction mixture was stirred at 80 °C for 10 min. After cooling to room temperature, the reaction mixture was filtered through sintered glass and the solid residue was washed with a mixture of petroleum ether–ether (99:1). Solvents were removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 95:5) to provide triyne (–)-(*S*)-**26** (755 mg, 91%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): 0.89–1.04 (21 H, m), 1.61 (3 H, d, *J* = 6.6), 2.29 (3 H, s), 2.73 (2 H, t, *J* = 7.4), 3.27 (2 H, t, *J* = 7.4), 3.87 (3 H, s), 4.58 (1 H, q, *J* = 6.6), 4.99 (1 H, d, *J* = 12.9), 5.16 (1 H, d, *J* = 12.9), 6.85 (1 H, dd, *J* = 8.5, 2.7), 6.97 (2 H, m), 7.17 (1 H, d, *J* = 2.7), 7.22 (2 H, m), 7.42 (1 H, ddd, *J* = 8.1, 6.8, 1.4), 7.44 (1 H, d, *J* = 8.4), 7.47 (1 H, ddd, *J* = 8.4, 6.8, 1.4), 7.59 (1 H, d, *J* = 8.5), 7.72 (1 H, bd, *J* = 8.4), 7.80 (1 H, ddt, *J* = 8.1, 1.4, 0.7, 0.7), 8.45 (1 H, ddt, *J* = 8.4, 1.4, 0.8, 0.8). ^{13}C NMR (125 MHz, $CDCl_3$): 11.32 (d), 18.60 (q), 21.12 (t), 21.40 (q), 22.33 (q), 34.90 (t), 55.42 (q), 65.75 (d), 68.96 (t), 81.13 (s), 85.62 (s), 88.23 (s), 89.20 (s), 96.61 (s), 108.19 (s), 112.96 (d), 113.38 (d), 114.21 (s), 119.58 (s), 119.72 (s), 125.65 (d), 126.22 (d), 126.73 (d), 127.55 (d), 127.88 (d), 127.96 (d), 128.87 (d), 131.61 (d), 132.03 (s), 133.52 (s), 133.73 (d), 138.28 (s), 141.28 (s), 141.72 (s), 160.03 (s). IR ($CHCl_3$): 3058 w, 2989 m, 2866 vs, 2225 w, 2201 w, 2170 m, 1620 w (sh), 1606 s, 1592 w (sh), 1566 m, 1510 s, 1498 s, 1465 s, 1445 m, 1430 w, 1420 w (sh), 1390 w (sh), 1383 w, 1373 w, 1368 w (sh), 1328 m, 1315 m (sh), 1296 m, 1279 m, 1259 m, 1234 m, 1192 w, 1163 m, 1130 w (sh), 1117 m, 1107 m (sh), 1094 m, 1059 m, 1035 m, 1025 m, 996 w, 920 w, 884 m, 866 w, 819 s, 678 m, 660 m, 616 w, 599 w (sh), 524 w, 440 w, 408 w. EI MS: 638 ($M^{\bullet+}$) (8), 595 (3), 565 (5), 495 (11), 465 (4), 429 (8), 321 (13), 239 (10), 173 (13), 159 (21), 143 (100), 129 (41), 115 (49), 87 (32), 73 (42), 59 (36). HR EI MS: calculated for $C_{44}H_{50}O_2Si$ 638.3580; found 638.3567. α_D^{22} –72 (*c* 0.15, CH_2Cl_2).

(–)-Triisopropyl[4-(7-methoxy-1-{[2-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)-1-naphthyl]ethynyl}-2-naphthyl)-1-butynyl]silane (**29**)

A Schlenk flask was charged with iodide (–)-(*S*)-**27** (95 mg, 0.223 mmol), [$Pd(PPh_3)_4$] (14 mg, 12.1 μmol, 5 mole %) and CuI (4 mg, 21.0 μmol, 9 mole %) and filled with argon. Diisopropylamine (3 ml) was added and the resulting solution was stirred at room temperature for 5 min. A solution of diyne **28** (95 mg, 0.243 mmol, 1.09 equiv.) in diisopropylamine (4 ml) was added and the reaction was stirred at room temperature for 2 h. Solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 95:5) to provide triyne (–)-(*S*)-**29** (67 mg, 44%). ^{1}H NMR (500 MHz, $CDCl_3$): 0.94–1.01 (21 H, m), 1.59 (3 H, d, *J* = 6.6), 2.26 (3 H, s), 2.78 (2 H, t, *J* = 7.2), 3.37 (2 H, dt, *J* = 7.2, 7.2, 2.3), 3.97 (3 H, s), 4.57 (1 H, q, *J* = 6.6), 5.30 (1 H, d, *J* = 12.7), 5.37 (1 H, d, *J* = 12.7), 6.88 (2 H, m), 7.12 (2 H, m), 7.14 (1 H, dd, *J* = 8.8, 2.6), 7.36 (1 H, d, *J* = 8.3), 7.53 (1 H, ddd, *J* = 8.1, 6.8, 1.2), 7.59 (1 H, ddd, *J* = 8.4, 6.8, 1.4), 7.70 (1 H, bd, *J* = 8.3), 7.73 (1 H, d, *J* = 8.8), 7.78 (1 H, d, *J* = 8.5), 7.89 (1 H, bd, *J* = 8.5), 7.89 (1 H, ddt, *J* = 8.1, 1.4, 0.7, 0.7), 7.93 (1 H, d, *J* = 2.6), 8.68 (1 H, ddt, *J* = 8.4, 1.2, 0.9, 0.9). ^{13}C NMR (125 MHz, $CDCl_3$): 11.29 (d), 18.57 (q), 21.36 (t), 21.38 (q), 22.37 (q), 34.94 (t), 55.46 (q), 65.55 (d), 69.23 (t), 81.32 (s), 85.71 (s), 88.27 (s), 94.20 (s), 96.46 (s), 104.53 (d), 107.97 (s), 118.23 (s), 118.71 (d), 119.36 (s), 119.42 (s), 125.41 (d), 125.60 (d), 126.22 (d), 126.24 (d),

126.93 (d), 127.53 (s), 128.18 (d), 128.35 (d), 128.57 (d), 128.77 (d), 129.63 (d), 131.47 (d), 132.73 (s), 133.42 (s), 135.21 (s), 138.13 (s), 138.81 (s), 142.28 (s), 158.79 (s). IR ($CHCl_3$): 3060 w, 2865 vs, 2226 w, 2170 m, 1623 s, 1596 w, 1570 w, 1510 s, 1462 s, 1423 m, 1382 m, 1368 w (sh), 1328 m, 1316 m, 1262 s, 1177 m, 1095 s, 1035 s, 1022 s, 997 m, 884 m, 867 w (sh), 839 s, 819 s, 702 w, 524 w, 435 vw. EI MS: 688 ($M^{\bullet+}$) (1), 544 (4), 530 (5), 501 (7), 427 (1), 339 (3), 296 (11), 255 (12), 227 (26), 200 (6), 178 (42), 149 (62), 97 (37), 69 (74), 57 (97), 43 (100). HR EI MS: calculated for $C_{48}H_{52}O_2Si$ 688.3737; found 688.3703. α_D^{22} –97 (*c* 0.06, CH_2Cl_2).

(1-Iodo-7-methoxynaphthalen-2-yl)methanol (**31**)

Butyllithium (1.6 M in hexanes, 780 µl, 1.247 mmol, 2.22 equiv.) was added to bromide **30** (150 mg, 0.562 mmol) in THF (3 ml) at –90 °C under argon. The mixture was stirred 30 min at –90 °C. Iodine (349 mg, 1.376 mmol, 2.45 equiv.) in THF (2 ml) was added and the reaction mixture was stirred at –90 °C for 40 min. The solvent was evaporated in vacuo and the residue was partitioned between dichloromethane and water. The organic layer was separated, washed with aqueous $Na_2S_2O_3$ (2 ×), water and dried over anhydrous Na_2SO_4. Volatiles were removed in vacuo to afford **31** (164 mg, 93%) as an amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): 2.12 (1 H, t, *J* = 6.0), 3.99 (3 H, s), 4.94 (2 H, d, *J* = 6.0), 7.16 (1 H, dd, *J* = 8.9, 2.5), 7.48 (1 H, d, *J* = 8.3), 7.56 (1 H, d, *J* = 2.5), 7.70 (1 H, d, *J* = 8.9), 7.77 (1 H, bd, *J* = 8.3). ^{13}C NMR (125 MHz, $CDCl_3$): 55.44 (q), 71.11 (t), 101.63 (s), 110.88 (d), 119.32 (d), 123.72 (d), 128.78 (d), 129.02 (s), 130.03 (d), 136.05 (s), 142.23 (s), 159.42 (s). IR ($CHCl_3$): 3611 w, 3064 w, 2840 w, 1626 vs, 1598 w, 1552 w, 1510 vs, 1460 s, 1441 m, 1414 w, 1377 m, 1262 m, 1179 m, 1124 m, 1061 m, 1034 m, 982 w, 962 w, 841 vs, 698 w, 650 w, 520 w. EI MS: 314 ($M^{\bullet+}$, 100), 256 (10), 186 (10), 156 (12), 144 (33), 127 (20), 115 (40), 97 (9), 83 (12), 69 (20), 55 (30), 43 (38). HR EI MS: calculated for $C_{12}H_{11}IO_2$ 313.9804; found 313.9815.

2-(Bromomethyl)-1-iodo-7-methoxynaphthalene (**32**)

A Schlenk flask was charged with alcohol **31** (150 mg, 0.478 mmol) and filled with argon. THF (4 ml) was added and the solution was cooled to 0 °C. Phosphorus tribromide (24 µl, 0.255 mmol, 1.60 equiv.) was added dropwise and the reaction mixture was stirred at 0 °C for 1 h. The solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether–acetone, 80:10:10) to provide bromide **32** (142 mg, 79%) as an amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): 3.99 (3 H, s), 4.69 (2 H, s), 7.17 (1 H, dd, *J* = 8.8, 2.5), 7.42 (1 H, d, *J* = 8.3), 7.58 (1 H, bd, *J* = 2.5), 7.68 (1 H, dt, *J* = 8.8, 0.5, 0.5), 7.72 (1 H, dt, *J* = 8.3, 0.6, 0.6). ^{13}C NMR (125 MHz, $CDCl_3$): 41.33 (t), 55.48 (q), 104.87 (s), 111.86 (d), 119.86 (d), 124.95 (d), 128.79 (s), 129.07 (d), 129.95 (d), 136.60 (s), 139.69 (s), 159.64 (s). IR ($CHCl_3$): 3062 w, 2838 w, 1624 vs, 1600 w, 1553 w, 1511 vs, 1459 s, 1439 m, 1407 w, 1378 m, 1262 m, 1179 m, 1127 m, 1034 m, 986 m, 965 m, 840 vs, 693 m, 650 w, 628 w, 546 w, 518 w. EI MS: 378 ($M^{\bullet+}$ with ^{81}Br, 29), 376 ($M^{\bullet+}$ with ^{79}Br, 29), 297 (100), 256 (7), 170 (24), 155 (26), 127 (27), 97 (8), 83 (9), 69 (19), 55 (22), 41 (28). HR EI MS: calculated for $C_{12}H_{10}{}^{79}BrIO$ 375.8960; found 325.8962.

(–)-1-Iodo-7-methoxy-2-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)naphthalene (**33**)

A Schlenk flask was charged with a solution of alcohol (–)-(*S*)-**22** (83 mg, 0.518 mmol, 1.50 equiv.) in THF (2 ml) under argon. The solution was cooled to –35 °C and DMSO (150 µl) and a butyllithium solution (1.6 M in hexanes, 325 µl, 0.520 mmol, 1.51 equiv.) were added. After stirring at 0 °C for 10 min, a solution of bromide **32** (130 mg, 0.345 mmol) in THF (2 ml) was added and the reaction mixture was stirred at 40 °C for 20 h. Solvents were removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 95:5) to provide (–)-(*S*)-**33** (103 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): 1.62 (3 H, d, *J* = 6.6), 2.35 (3 H, s), 3.99 (3 H, s), 4.56 (1 H, q, *J* = 6.6), 4.88 (1 H, d, *J* = 12.7), 5.02 (1 H, d, *J* = 12.7), 7.11 (2 H, m), 7.15 (1 H, dd, *J* = 8.9, 2.6), 7.35 (2 H, m), 7.50 (1 H, d, *J* = 8.3), 7.59 (1 H, d, *J* = 2.6), 7.68 (1 H, d, *J* = 8.9), 7.74 (1 H, bd, *J* = 8.3). ^{13}C NMR (125 MHz, $CDCl_3$): 21.46 (q), 22.27 (q), 55.43 (q), 65.75 (d), 76.19 (t), 85.67 (s), 88.20 (s), 102.24 (s), 111.22 (d), 119.15 (d), 119.70 (s), 124.25 (d), 128.41 (d), 129.02 (d), 129.07 (s), 129.97 (d), 131.67 (d), 136.14 (s), 138.43 (s), 140.31 (s), 159.31 (s). IR ($CHCl_3$): 3083 w, 3063 w, 3031 w, 2840 w (sh), 2225 w, 1626 s, 1612 m (sh), 1600 w, 1553 w, 1510 vs, 1460 s, 1441 m, 1375 m, 1327 m, 1306 m, 1270 m (sh), 1258 m, 1230 s, 1178 m, 1124 s, 1108 s (sh), 1094 s, 1035 m, 1022 w, 962 m, 841 s, 819 s, 702 w, 654 w, 518 w. FAB MS: 479 (M + Na^+), 457, 297, 285, 263, 253, 171, 143, 128, 79, 61. HR FAB MS: calculated for $C_{23}H_{21}IO_2$ 457.0665; found 457.0677. α_D^{22} –102 (*c* 0.16, CH_2Cl_2).

(–)-{[7-Methoxy-2-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)-1-naphthyl]ethynyl}(trimethyl)silane (**34**)

A tube was charged with iodide (–)-(*S*)-**33** (95 mg, 0.208 mmol), [$Pd(PPh_3)_4$] (13 mg, 11.3 µmol, 5 mole %) and CuI (4 mg, 21.0 µmol, 10 mole %), filled with argon and sealed. Diisopropylamine (2 ml) and (trimethylsilyl)acetylene (34 µl, 0.241 mmol, 1.16 equiv.) were added and the reaction mixture was stirred at 80 °C for 4 h. Volatiles were removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 95:5) to provide diyne (–)-(*S*)-**34** (79 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): 0.30 (9 H, s), 1.60 (3 H, d, *J* = 6.6), 2.34 (3 H, s), 3.95 (3 H, s), 4.56 (1 H, q, *J* = 6.6), 5.02 (1 H, d, *J* = 12.7), 5.13 (1 H, d, *J* = 12.7), 7.10 (2 H, m), 7.15 (1 H, dd, *J* = 8.9, 2.6), 7.33 (2 H, m), 7.52 (1 H, d, *J* = 8.4), 7.68 (1 H, d, *J* = 2.6), 7.71 (1 H, d, *J* = 8.9), 7.75 (1 H, bd, *J* = 8.4). ^{13}C NMR (125 MHz, $CDCl_3$): 0.13 (q), 21.44 (q), 22.27 (q), 55.14 (q), 65.76 (d), 69.29 (t), 85.27 (s), 88.47 (s), 100.99 (s), 104.59 (d), 104.88 (s), 117.53 (s), 118.87 (d), 119.78 (s), 123.08 (d), 127.92 (s), 128.44 (d), 128.95 (d), 129.62 (d), 131.67 (d), 134.99 (s), 138.31 (s), 139.92 (s), 158.67 (s). IR ($CHCl_3$): 3062 w, 3031 w, 2225 w, 2145 m, 1624 s, 1597 w, 1572 w, 1511 s, 1462 s, 1446 m, 1423 m, 1409 w, 1373 m, 1328 m, 1271 s, 1251 s, 1176 m, 1129 m (sh), 1106 s (sh), 1096 s, 1031 s, 1020 m (sh), 873 m (sh), 853 vs, 844 vs, 819 s, 701 w, 648 w, 527 w, 429 w. ESI+ MS: 383 (18), 317 (24), 311 (34), 279 (100), 233 (6). HR EI MS: calculated for $C_{28}H_{30}O_2Si$ 426.2015; found 426.2021. α_D^{22} –135 (*c* 0.08, CH_2Cl_2).

(–)-1-Ethynyl-7-methoxy-2-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)naphthalene (**35**)

A Schlenk flask was charged with a solution of diyne (–)-(*S*)-**34** (50 mg, 0.117 mmol) in THF (2 ml) under argon. A sodium methoxide solution (prepared by dissolving sodium (5 mg, 0.217 mmol, 1.86 equiv.) in dry methanol (1 ml) under argon) was added. After stirring at room temperature for 2 h, solvents were removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 95:5) to provide diyne (–)-(*S*)-**35** (36 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$): 1.59 (3 H, d, *J* = 6.6), 2.35 (3 H, s), 3.71 (1 H, s), 3.96 (3 H, s), 4.54 (1 H, q, *J* = 6.6), 5.06 (1 H, d, *J* = 12.5), 5.16 (1 H, d, *J* = 12.5), 7.11 (2 H, m), 7.16 (1 H, dd, *J* = 8.9, 2.6), 7.34 (2 H, m), 7.54 (1 H, d, *J* = 8.4), 7.68 (1 H, d, *J* = 2.6), 7.73 (1 H, d, *J* = 8.9), 7.78 (1 H, bd, *J* = 8.4). ^{13}C NMR (125 MHz, $CDCl_3$): 21.45 (q), 22.26 (q), 55.34 (q), 65.60 (d), 69.13 (t), 79.57 (s), 85.37 (s), 87.06 (d), 88.48 (s), 104.46 (d), 116.63 (s), 119.02 (d), 119.81 (s), 123.24 (d), 127.94 (s), 128.74 (d), 128.99 (d), 129.67 (d), 131.64 (d), 135.06 (s), 138.35 (s), 140.44 (s), 158.82 (s). IR ($CHCl_3$): 3035 m, 3030 w, 2225 w, 2099 vw, 1625 s, 1604 m, 1573 w, 1511 s, 1462 s, 1446 m, 1423 m, 1389 m, 1374 m, 1328 m, 1310 m (sh), 1270 s, 1179 m, 1105 s (sh), 1095 s, 1029 m, 1027 m (sh), 1020 m (sh), 872 w, 843 s, 819 m, 708 w, 656 w, 611 w, 525 w, 444 vw. ESI+ MS: 355 ($M + H^+$) (15), 316 (69), 288 (100), 279 (67), 213 (8). HR EI MS: calculated for $C_{25}H_{22}O_2$ 354.1620; found 354.1621. α_D^{22} –200 (*c* 0.02, CH_2Cl_2).

(–)-Triisopropyl[4-(1-{[7-methoxy-2-({[(1*S*)-1-methyl-3-(4-methylphenyl)-2-propynyl]oxy}methyl)-1-naphthyl]ethynyl}-2-naphthyl)-1-butynyl]silane (**37**)

A Schlenk flask was charged with iodide **36** (49 mg, 0.106 mmol, 1.10 equiv.), [$Pd(PPh_3)_4$] (7 mg, 6.06 μmol, 6 mole %) and CuI (4 mg, 21.0 μmol, 22 mole %) and filled with argon. Diisopropylamine (1 ml) was added and the resulting solution was stirred at room temperature for 5 min. A solution of diyne (–)-(*S*)-**35** (34 mg, 95.9 μmol) in diisopropylamine (2.5 ml) was added and the reaction was stirred at room temperature for 1.5 h. The solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 95:5) to provide triyne (–)-(*S*)-**37** (42 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$): 0.92–0.98 (21 H, m), 1.61 (3 H, d, *J* = 6.6), 2.28 (3 H, s), 2.78 (2 H, t, *J* = 7.3), 3.37 (1 H, dd, *J* = 13.2, 7.3), 3.42 (1 H, dd, *J* = 13.2, 7.3), 3.99 (3 H, s), 4.59 (1 H, q, *J* = 6.6), 5.23 (1 H, d, *J* = 12.6), 5.35 (1 H, d, *J* = 12.6), 6.93 (2 H, m), 7.17 (2 H, m), 7.20 (1 H, dd, *J* = 8.9, 2.6), 7.47 (1 H, ddd, *J* = 8.1, 6.8, 1.3), 7.51 (1 H, d, *J* = 8.4), 7.51 (1 H, ddd, *J* = 8.4, 6.8, 1.2), 7.63 (1 H, d, *J* = 8.4), 7.78 (1 H, d, *J* = 8.9), 7.78 (1 H, bd, *J* = 8.4), 7.82 (1 H, bd, *J* = 8.4), 7.85 (1 H, ddt, *J* = 8.1, 1.2, 0.7, 0.7), 7.95 (1 H, d, *J* = 2.6), 8.68 (1 H, ddt, *J* = 8.4, 1.3, 0.8, 0.8). ^{13}C NMR (125 MHz, $CDCl_3$): 11.27 (d), 18.54 (q), 21.30 (q), 21.41 (t), 22.38 (q), 34.71 (t), 55.42 (q), 65.59 (d), 69.49 (t), 81.58 (s), 85.58 (s), 88.38 (s), 94.74 (s), 95.90 (s), 104.44 (d), 107.78 (s), 118.02 (s), 119.25 (d), 119.57 (s), 119.64 (s), 123.35 (d), 125.79 (d), 126.24 (d), 126.78 (d), 127.70 (d), 128.17 (d), 128.17 (s), 128.29 (d), 128.44 (d), 128.82 (d), 129.81 (d), 131.55 (d), 132.13 (s), 133.72 (s), 134.95 (s), 138.14 (s), 139.47 (s), 141.55 (s), 158.88 (s). IR ($CHCl_3$): 3059 w, 3033 w, 2865 s, 2225 w, 2170 w, 1624 s, 1595 w, 1572 w, 1510 s, 1462 s, 1445 m (sh), 1425 m, 1382 m, 1375 m (sh), 1368 w (sh), 1329 m, 1311 m, 1292 m (sh), 1279 m (sh), 1262 s, 1176 m, 1128 m (sh), 1095 s, 1039 s (sh), 1027 s, 1021 s, 997 m (sh), 884 m, 867 w, 842 s, 818 s, 702 w, 526 w, 435 w. ESI+ MS: 663 (100), 607 (22), 551 (17), 495 (11), 413 (9), 391 (19), 371 (16), 317 (24), 288 (51), 279 (36), 242 (3). HR EI MS: calculated for $C_{48}H_{52}O_2Si$ 688.3737; found 688.3707. α_D^{22} –103 (*c* 0.07, CH_2Cl_2).

(–)-1-Iodo-2-({[(1*R*)-1-phenyl-2-propynyl]oxy}methyl)naphthalene (**40**)

A Schlenk flask was charged with a solution of alcohol (–)-(*R*)-**39** (172 mg, 1.297 mmol, 1.50 equiv.) in THF (3 ml) under argon. The solution was cooled to –35 °C and DMSO (375 μl) and a butyllithium solution (1.6 M in hexanes, 811 μl, 1.297 mmol, 1.50 equiv.) were added. After stirring at 0 °C for 10 min, a solution of bromide **38** (300 mg, 0.865 mmol) in THF (4 ml) was added and the reaction mixture was stirred at 40 °C for 20 h. Solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 95:5) to provide (–)-(*R*)-**40** (235 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$): 2.73 (1 H, d, *J* = 2.2), 4.95 (1 H, d, *J* = 12.6), 5.02 (1 H, d, *J* = 12.6), 5.35 (1 H, d, *J* = 2.2), 5.43 (1 H, s), 7.29–7.43 (5 H, m), 7.50 (1 H, ddd, *J* = 8.1, 6.8, 1.3), 7.57 (1 H, ddd, *J* = 8.6, 6.8, 1.5), 7.63 (1 H, d, *J* = 8.4), 7.77 (1 H, bdd, *J* = 8.1, 1.5), 7.81 (1 H, bd, *J* = 8.4), 8.25 (1 H, bd, *J* = 8.6). ^{13}C NMR (125 MHz, $CDCl_3$): 71.12 (d), 75.73 (t), 81.35 (s), 103.70 (s), 126.46 (d), 126.59 (d), 127.50 (d), 127.76 (d), 128.31 (d), 128.59 (d), 128.64 (d), 128.80 (d), 132.39 (d), 133.75 (s), 134.72 (s), 137.92 (s), 139.41 (s). IR ($CHCl_3$): 3306 s, 3088 w, 3064 m, 3036 w, 3010 s, 2118 vw, 1622 w, 1597 w, 1584 vw, 1552 m, 1501 s, 1494 m, 1448 m, 1320 s, 1258 s, 1178 w, 1089 vs, 1060 s (sh), 1031 s, 1003 m, 863 m, 817 vs, 699 vs, 646 m, 523 m. EI MS: 398 ($M^{\bullet+}$) (3), 284 (5), 267 (30), 253 (4), 241 (3), 215 (3), 165 (13), 155 (7), 141 (100), 115 (69), 105 (49), 97 (13), 77 (34), 69 (21), 57 (44), 43 (29). HR EI MS: calculated for $C_{20}H_{15}IO$ 398.0167; found 398.0155. α_D^{22} –15 (*c* 0.22, CH_2Cl_2).

(–)-{(3*S*)-3-[(1-Iodo-2-naphthyl)methoxy]-3-phenyl-1-propynyl}(triisopropyl)silane (**41**)

A Schlenk flask was charged with a solution of iodide (–)-(*R*)-**40** (200 mg, 0.502 mmol) in THF (5 ml) under argon. The solution was cooled to –78 °C and a lithium diisopropylamide solution (2 M in THF, 326 μl, 0.653 mmol, 1.30 equiv.) was added. After stirring at –78 °C for 1 h, chlorotriisopropylsilane (215 μl, 1.004 mmol, 2.0 equiv.) was added and the reaction mixture was allowed to warm to room temperature while stirring for 4 h. The solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 95:5) to provide (–)-(*S*)-**41** (203 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): 1.04–1.17 (21 H, m), 5.01 (1 H, d, *J* = 12.8), 5.05 (1 H, d, *J* = 12.8), 5.43 (1 H, s), 7.31–7.42 (5 H, m), 7.50 (1 H, ddd, *J* = 8.1, 6.8, 1.2), 7.57 (1 H, ddd, *J* = 8.4, 6.8, 1.5), 7.64 (1 H, d, *J* = 8.4), 7.77 (1 H, ddt, *J* = 8.1, 1.5, 0.8, 0.8), 7.80 (1 H, bd, *J* = 8.4), 8.25 (1 H, ddt, *J* = 8.4, 1.2, 0.8, 0.8). ^{13}C NMR (125 MHz, $CDCl_3$): 11.26 (d), 18.70 (q), 71.79 (d), 75.42 (t), 89.97 (s), 103.48 (s), 104.35 (s), 126.47 (d), 126.48 (d), 127.68 (d), 127.71 (d), 128.27 (d), 128.38 (d), 128.41 (d), 128.70 (d), 132.33 (d), 133.72 (s), 134.71 (s), 138.33 (s), 139.81 (s). IR ($CHCl_3$): 3089 w, 3065 w, 3036 w, 3010 m, 2867 vs, 2170 w, 1602 w, 1552 w, 1501 w, 1495 w, 1464 s, 1455 m (sh), 1384 m, 1369 m, 1334 s, 1258 m, 1137 w, 1085 m (sh), 1071 m, 1026 m, 999 m, 884 s, 863 w, 817 m, 699 s, 681 m, 664 m, 628 w (sh), 523 w. EI MS: 554 ($M^{\bullet+}$) (3), 511 (6), 481 (1), 439 (1), 427 (10), 384 (6), 341 (26), 331 (14), 287 (19), 267 (30), 258 (100), 254 (55), 227 (10), 199 (15), 159 (13), 141 (80), 128 (16), 115 (23), 83 (6), 73 (15), 59 (30), 43 (19). HR EI MS: calculated for $C_{29}H_{35}IOSi$ 554.1501; found 554.1474. α_D^{22} –41 (*c* 0.21, CH_2Cl_2).

(–)-Triisopropyl((3*S*)-3-{[1-({7-methoxy-2-[4-(triisopropylsilyl)-3-butynyl]-1-naphthyl}ethynyl)-2-naphthyl]methoxy}-3-phenyl-1-propynyl)silane (**42**)

A Schlenk flask was charged with $[Pd(PPh_3)_4]$ (11 mg, 9.52 μmol, 6 mole %) and CuI (3 mg, 15.8 μmol, 10 mole %) and filled with argon. A solution of iodide (–)-(*S*)-**41** (91 mg, 0.164 mmol) in diisopropylamine (1.5 ml) was added and the resulting mixture was stirred at room temperature for 10 min. A solution of diyne **28** (70 mg, 0.179 mmol, 1.09 equiv.) in diisopropylamine (1.5 ml) was added and the reaction was stirred at room temperature for 3 h. The solvent was removed in vacuo and the crude product was chromatographed on silica gel (petroleum ether–ether, 100:0 to 95:5) to provide triyne (–)-(*S*)-**42** (114 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): 0.95–1.02 (21 H, m), 0.95–1.02 (21 H, m), 2.72 (2 H, t, *J* = 7.2), 3.33 (2 H, t, *J* = 7.2), 3.89 (3 H, s), 5.32 (1 H, d, *J* = 12.7), 5.35 (1 H, d, *J* = 12.7), 5.40 (1 H, s), 7.16 (1 H, dd, *J* = 8.8, 2.6), 7.22–7.31 (3 H, m), 7.41 (1 H, d, *J* = 8.3), 7.54 (1 H, ddd, *J* = 8.1, 6.8, 1.3), 7.59 (2 H, m), 7.60 (1 H, ddd, *J* = 8.4, 6.8, 1.3), 7.72 (1 H, bd, *J* = 8.3), 7.76 (1 H, d, *J* = 8.8), 7.78 (1 H, d, *J* = 8.5), 7.87 (1 H, d, *J* = 2.6), 7.89 (1 H, bd, *J* = 8.5), 7.89 (1 H, ddt, *J* = 8.1, 1.3, 0.7, 0.7), 8.66 (1 H, dq, *J* = 8.4, 0.9, 0.9, 0.9). ^{13}C NMR (125 MHz, $CDCl_3$): 11.13 (d), 11.27 (d), 18.48 (q), 18.57 (q), 21.35 (t), 34.98 (t), 55.37 (q), 68.63 (t), 71.50 (d), 81.32 (s), 89.72 (s), 94.08 (s), 96.47 (s), 104.56 (s), 107.96 (s), 108.44 (d), 118.18 (s), 118.72 (d), 119.47 (s), 125.42 (d), 125.74 (d), 125.74 (d), 126.17 (d), 126.28 (d), 126.97 (d), 127.49 (s), 127.57 (d), 128.23 (d), 128.25 (d), 128.32 (d), 128.51 (d), 129.66 (d), 132.72 (s), 133.41 (s), 135.22 (s), 138.42 (s), 138.54 (s), 142.25 (s), 158.75 (s). IR ($CHCl_3$): 3063 w, 2866 vs, 2170 m, 1623 s, 1596 w, 1568 w, 1511 w, 1494 w, 1462 s, 1454 m (sh), 1423 w, 1383 m, 1367 w, 1316 w, 1265 m, 1093 m, 1071 m, 1036 s, 1025 m, 997 m, 884 s, 866 w (sh), 839 m, 821 m, 699 m, 679 s, 659 s, 634 w. APCI+ MS: 817 ($M + H^+$) (92), 546 (100). HR APCI+ MS: calculated for $C_{55}H_{69}O_2Si_2$ 817.4836; found 817.4828. α_D^{22} –23 (*c* 0.06, CH_2Cl_2).

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REFERENCES AND NOTES

1. For selected reviews, see: a) Urbano A.: *Angew. Chem., Int. Ed.* **2003**, *42*, 3986; b) Hopf H.: *Classics in Hydrocarbon Chemistry: Syntheses, Concepts, Perspectives*, Chap. 12.2, p. 323. VCH, Weinheim 2000; c) Katz T. J.: *Angew. Chem., Int. Ed.* **2000**, *39*, 1921; d) Oremek G., Seiffert U., Janecka A.: *Chem.-Ztg.* **1987**, *111*, 69; e) Vögtle F.: *Fascinating Molecules in Organic Chemistry*, p. 156. Wiley, New York 1992; f) Meurer K. P., Vögtle F.: *Top. Curr. Chem.* **1985**, *127*, 1; g) Laarhoven W. H., Prinsen W. J. C.: *Top. Curr. Chem.* **1984**, *125*, 63.
2. a) Caeiro J., Peña D., Cobas A., Perez D., Guitian E.: *Adv. Synth. Catal.* **2006**, *348*, 2466; b) Carreño M. C., Gonzales-Lopez M., Urbano A.: *Chem. Commun.* **2005**, 611; c) El Abed R., Ben Hassine B., Genet J. P., Gorsane M., Madec J., Ricard L., Marinetti A.: *Synthesis* **2004**, 2513; d) Rajca A., Miyasaka M., Pink M., Wang H., Rajca S.: *J. Am. Chem. Soc.* **2004**, *126*, 15211; e) Miyasaka M., Rajca A., Pink M., Rajca S.: *Chem. Eur. J.* **2004**, *10*, 6531;

f) Ogawa Y., Toyama M., Karikomi M., Seki K., Haga K., Uyehara T.: *Tetrahedron Lett.* **2003**, *44*, 2167; g) Carreño M. C., Garcia-Cerrada S., Urbano A.: *Chem. Eur. J.* **2003**, *9*, 4118; h) Carreño M. C., Garcia-Cerrada S., Urbano. A.: *J. Am. Chem. Soc.* **2001**, *123*, 7929; i) Tanaka K., Suzuki H., Osuga H.: *J. Org. Chem.* **1997**, *62*, 4465; j) Stará I. G., Starý I., Tichý M., Závada J., Hanuš V.: *J. Am. Chem. Soc.* **1994**, *116*, 5084; k) Katz T. J., Sudhakar A., Teasley M. F., Gilbert A. M., Geiger W. E., Robben M. P., Wuensch M., Ward M. D.: *J. Am. Chem. Soc.* **1993**, *115*, 3182; l) Vanest J., Martin R. H.: *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 113; m) Bestmann H. J., Both W.: *Chem. Ber.* **1974**, *107*, 2923.

3. Stará I. G., Alexandrová Z., Teplý, F., Sehnal P., Starý I., Šaman D., Buděšínský M., Cvačka J.: *Org. Lett.* **2005**, *7*, 2547.
4. Sehnal P., Krausová Z., Teplý F., Stará I. G., Starý I., Rulíšek L., Šaman D., Císařová I.: *J. Org. Chem.*, in press.
5. Alexandrová Z., Stará I. G., Sehnal P., Teplý F., Starý I., Šaman D., Fiedler P.: *Collect. Czech. Chem. Commun.* **2004**, *69*, 2193.
6. Teplý F., Stará I. G., Starý I., Kollárovič A., Šaman D., Fiedler P.: *Tetrahedron* **2002**, *58*, 9007.
7. a) Fang A. G., Mello J. V., Finney N. S.: *Tetrahedron* **2004**, *60*, 11075; b) Speicher A.: *J. Prakt. Chem.* **2000**, *342*, 162.
8. Teplý F., Stará I. G., Starý I., Kollárovič A., Šaman D., Fiedler P., Vyskočil Š.: *J. Org. Chem.* **2003**, *68*, 5193.
9. Teplý F., Stará I. G., Starý I., Kollárovič A., Luštinec D., Krausová Z., Šaman D., Fiedler P.: *Eur. J. Org. Chem.* **2007**, 4244.
10. Stará I. G., Kollárovič A., Teplý F., Starý I., Šaman D., Fiedler P.: *Collect. Czech. Chem. Commun.* **2000**, *65*, 577.
11. a) Meyers A. I., Moorlag H.: *Tetrahedron Lett.* **1993**, *34*, 6993; b) Comins D. L., Brown J. D.: *J. Org. Chem.* **1989**, *54*, 3730.
12. Klapars A., Buchwald S. L.: *J. Am. Chem. Soc.* **2002**, *124*, 14844.
13. Stará I. G., Kollárovič A., Teplý F., Starý I., Šaman D., Fiedler P.: *Collect. Czech. Chem. Commun.* **2000**, *65*, 577.
14. Although the chiral centre was untouched and, accordingly, the same sense of absolute stereochemistry at the asymmetric carbon atom was maintained, the CIP notation assigned an opposite configuration.
15. Note, the CIP stereodescriptor was changed from (*S*) back to (*R*) without touching chemically the chiral centre.