

SYNTHETIC STUDIES TOWARD CHIRAL AROMATIC TRIYNES AS KEY SUBSTRATES FOR THE ASYMMETRIC SYNTHESIS OF HELICENE-LIKE MOLECULES

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Dedicated to Professor Otto Exner on the occasion of his 80th birthday.

We have developed the synthesis of model nonracemic aromatic triynes (–)-(S)-**1–4** containing the 1-[[2-(but-3-yn-1-yl)-1-naphthyl]ethynyl]-2-[[((S)-1-methylprop-2-yn-1-yl)oxy]-methyl]naphthalene unit. The common 1,2-di(2-substituted-1-naphthyl)acetylene part was constructed via Sonogashira coupling of appropriate 1-iodonaphthalenes with 1-ethynyl-naphthalenes both bearing tethered acetylene units in positions 2. The chirality of triynes (–)-(S)-**1–4** was introduced by incorporating commercially available (–)-(S)-but-3-yn-2-ol (**10**) into tethered acetylene units. The nonracemic triynes are intended to be used as substrates in stereoselective [2+2+2] triyne cycloisomerization catalyzed by transition metal complexes. **Keywords:** Alkynes; Arenes; Chirality; Copper; Cross-coupling; Helical structures; Palladium; Synthesis design.

Asymmetric synthesis of helicenes and related systems¹ which are inherently chiral is a challenging task not entirely fulfilled so far. Different strategies have emerged during the last decades ranging from practical to curious. The most remarkable achievements were published by Martin², Katz³, Tanaka⁴, and Carreño⁵ who successfully used chiral auxiliaries, reactants or reagents in the stoichiometric asymmetric synthesis of helicenes⁶. Moreover, we have recently disclosed basic principles of the alternative catalytic asymmetric synthesis of helicene backbones that relies on intramolecular [2+2+2] cycloisomerization of triynes under catalysis with chiral Ni(0) complexes⁷. In spite of these significant achievements⁸, the resolution of racemates has so far played a dominant role in producing optically enriched/pure helicenes⁹.

It is obvious that the accessibility of nonracemic helicenes and helicene-like compounds via stoichiometric asymmetric synthesis has not been fully explored. To control helicity of such systems, we have suggested that central-to-helical chirality transfer might be efficient in [2+2+2] cycloisomerization¹⁰ of chiral triynes. Thus, we have designed model triynes **1–4** containing an asymmetric carbon center in their molecules (Chart 1). In this report, we describe the synthesis of such key aromatic triynes. The detailed study of diastereoselective [2+2+2] triyne cycloisomerization, which is now under way, will be published separately¹¹.

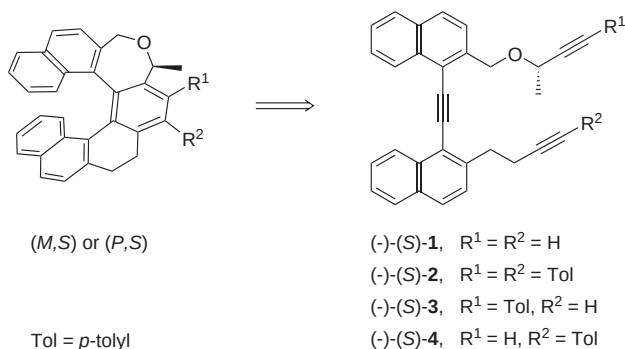


CHART 1

RESULTS AND DISCUSSION

The modular synthesis of chiral triynes (-)-(S)-**1–4** was started from common building blocks **5–13** (Chart 2). Concerning naphthyl derivatives, **5** is commercially available and the preparations of compounds **6** (lit.¹²), **7** (lit.^{7a}), **8** (lit.^{7a}), and **9** (lit.^{7a}) have recently been described by us in previous

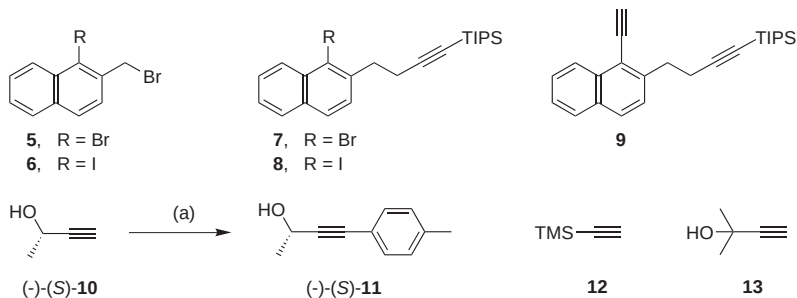


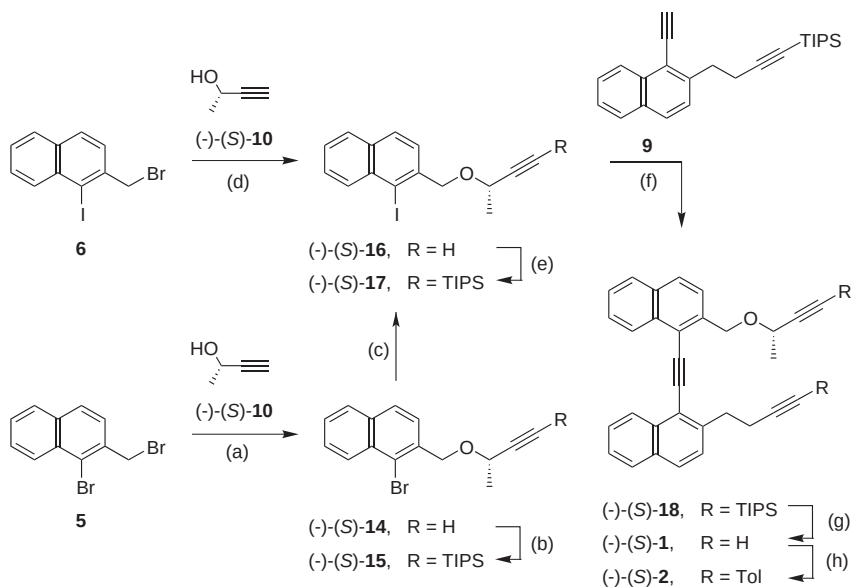
CHART 2

(a) 4-Iodotoluene (1.0 equiv.), $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (0.8 mole %), CuI (1.5 mole %), PPh_3 (1.5 mole %), diisopropylamine (1.0 equiv.), toluene, 0 °C to room temperature, 3 h, 83%

papers. Both chiral alkyne (–)-(S)-**10** and its (*R*) enantiomer are commercially available. The former was routinely transformed to (–)-(S)-**11** (lit.¹³) using Pd(II)/Cu(I)-catalyzed Sonogashira coupling with 4-iodotoluene. The monoprotected acetylenes **12** and **13** are also commercially available.

Synthesis of Triynes (–)-(S)-**1** and **2**

We proposed alternative synthesis routes to get (–)-(S)-**1** and **2** (Scheme 1). First, we explored the route starting from readily available benzylic bromide **5** because the conversion to its counterpart **6** requires three additional steps¹². Compound **5** was treated with a sodium salt of optically pure (–)-(S)-**10** to give rise to (–)-(S)-**14** in high yield. The subsequent silylation reaction with LDA/triisopropylsilyl chloride led to (–)-(S)-**15**, again in high



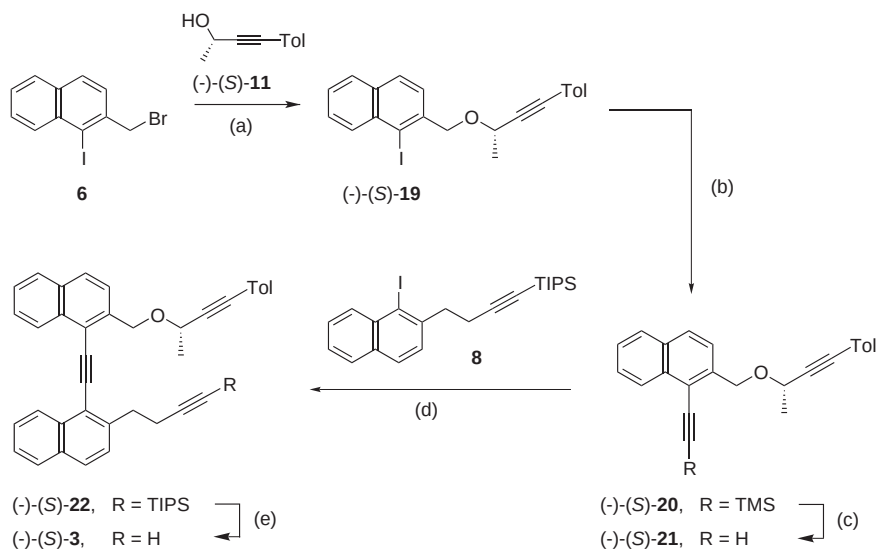
SCHEME 1

(a) (–)-(S)-**10** (1.3 equiv.), NaH (1.3 equiv.), THF, 0 °C, 30 min, then **5** (1.0 equiv.), room temperature to 50 °C, 3 h, 96%; (b) LDA (1.1 equiv.), THF, –78 °C, 45 min, then TIPSCl (1.1 equiv.), –78 °C to room temperature, 1 h, 95%; (c) BuLi (1.0 equiv.), THF, –78 °C, 15 min, then I₂ (1.1 equiv.), –78 °C, 1 h, 41%; (d) (–)-(S)-**10** (1.6 equiv.), BuLi (1.7 equiv.), THF–DMSO, –30 °C to –5 °C, 45 min, then **6** (1.0 equiv.), 40 °C, 3.5 h, 81%; (e) LDA (1.0 equiv.), THF, –78 °C, 45 min, then TIPSCl (2.0 equiv.), –78 °C to room temperature, overnight, 84%; (f) **9** (1.1 equiv.), [Pd(PPh₃)₄] (5 mole %), CuI (10 mole %), diisopropylamine, room temperature, 1 h, 81%; (g) Bu₄NF (2.4 equiv.), THF, room temperature, 15 min, 82%; (h) 4-iodotoluene (2.1 equiv.), [Pd(PPh₃)₄] (10 mole %), CuI (20 mole %), diisopropylamine, 80 °C, 30 min, 82%

yield. Note, the use of lithiumdiisopropylamide as a base was essential¹⁴ because sodium hydride was ineffective in the reaction and butyllithium preferred a bromine/lithium exchange to the terminal acetylene deprotonation. The Sonogashira coupling of (–)-(S)-**15** with diyne **9** under [Pd(PPh₃)₄]/CuI catalysis in diisopropylamine did not proceed and, therefore, we decided to convert naphthyl bromide (–)-(S)-**15** to a more reactive naphthyl iodide (–)-(S)-**17**. A routine lithiation/iodination protocol allowed us to produce (–)-(S)-**17** but only in moderate yield as the major iodide was accompanied by numerous side products. Therefore, we took benzylic bromide **6** as a starting material that underwent smooth reaction with a sodium salt of (–)-(S)-**10** to furnish (–)-(S)-**16** in good yield. The subsequent silylation with triisopropylsilyl chloride in the presence of lithiumdiisopropylamide afforded (–)-(S)-**17** in high yield. Then, the Sonogashira coupling of naphthyl iodide (–)-(S)-**17** with diyne **9** proceeded smoothly to furnish silylated triyne (–)-(S)-**18** in good yield. Desilylation with tetrabutylammonium fluoride produced model unprotected triyne (–)-(S)-**1** in good yield. On reaction of (–)-(S)-**1** with 4-iodotoluene under Pd(0)/Cu(I) catalysis, double Sonogashira coupling took place to give, in high yield, another model triyne (–)-(S)-**2** with two tethered acetylene units capped with *p*-tolyl groups.

Synthesis of Triyne (–)-(S)-**3**

The critical step for the successful preparation of triyne (–)-(S)-**3** was the assembly of the core dinaphthylacetylene unit (Scheme 2). The reaction of the benzylic bromide **6** with a sodium salt of (–)-(S)-**11** furnished (–)-(S)-**19** in good yield. The subsequent coupling of (–)-(S)-**19** with diyne **9** in diisopropylamine under [Pd(PPh₃)₄]/CuI catalysis, however, yielded a complex product mixture instead of the expected (–)-(S)-**22**. Therefore, we attempted to build the dinaphthylacetylene unit in a complementary way. Iodide (–)-(S)-**19** reacted with (trimethylsilyl)acetylene under Pd(0)/Cu(I) catalysis to produce (–)-(S)-**20** in good yield. After smooth desilylation of (–)-(S)-**20** using sodium methoxide, diyne (–)-(S)-**21** was successfully coupled with naphthyl iodide **8** under Pd(0)/Cu(I) catalysis to afford triyne (–)-(S)-**22** in reasonable yield. The final deprotection of (–)-(S)-**22** with tetrabutylammonium fluoride which was not further optimized, led to the desired triyne (–)-(S)-**3** in moderate yield.



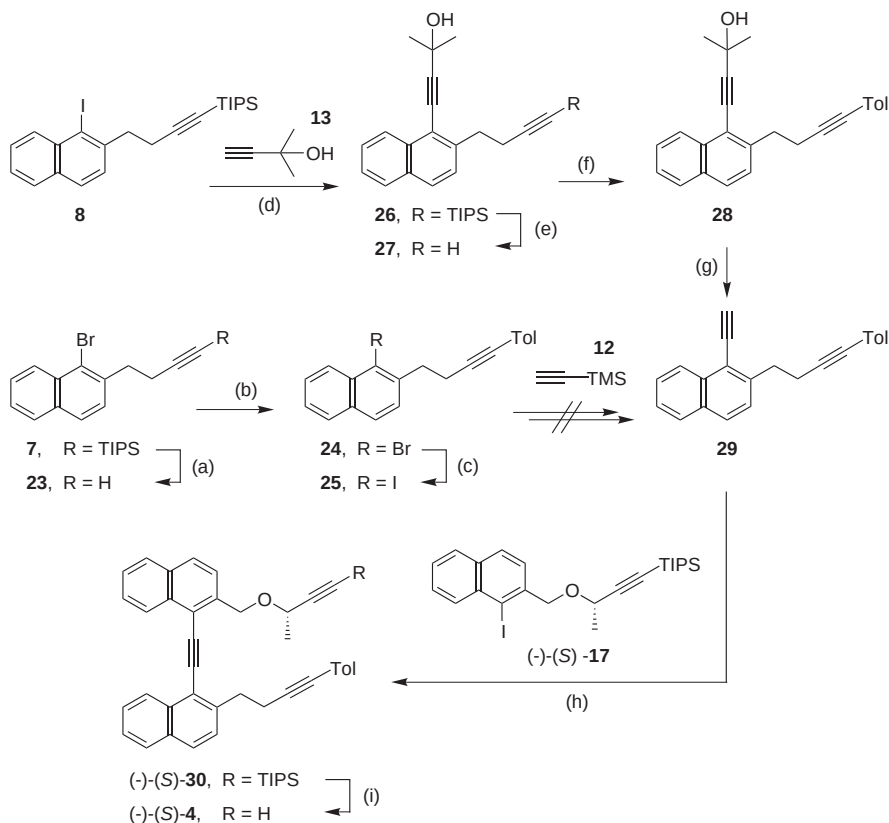
SCHEME 2

(a) $(-)-(S)$ -**11** (1.5 equiv.), BuLi (1.5 equiv.), THF–DMSO, -30 to 0 °C, 10 min, then **6** (1.0 equiv.), 40 °C, 16 h, 66%; (b) $\text{TMSC}\equiv\text{CH}$ (1.2 equiv.), $[\text{Pd}(\text{PPh}_3)_4]$ (5 mole %), CuI (10 mole %), diisopropylamine, 80 °C, 2 h, 81%; (c) CH_3ONa (1.7 equiv.), methanol, room temperature, 1 h, 81%; (d) **8** (1.1 equiv.), $[\text{Pd}(\text{PPh}_3)_4]$ (5 mole %), CuI (10 mole %), diisopropylamine, room temperature, 1 h, 58%; (e) Bu_4NF (2.4 equiv.), THF, room temperature, 30 min, 35%

Synthesis of Triyne $(-)-(S)$ -**4**

The first attempts at synthesizing $(-)-(S)$ -**4** started from the readily available building block **7** (Scheme 3). To cap the tethered acetylene unit with a *p*-tolyl group, alkyne **7** was quantitatively desilylated with tetrabutylammonium fluoride and unprotected alkyne **23** reacted with 4-iodotoluene under $\text{Pd}(0)/\text{Cu}(\text{I})$ catalysis to selectively produce **24** in nearly quantitative yield. Note, no formation of oligomeric products originating from the self-coupling of **23** was observed, as aryl bromides are generally much less reactive than aryl iodides in Sonogashira coupling-type reactions. In order to ensure clean subsequent coupling with (trimethylsilyl)acetylene, bromide **24** was transformed via routine lithiation/iodination into iodide **25** in excellent yield. To our dismay, however, coupling of **25** with (trimethylsilyl)acetylene under $[\text{Pd}(\text{PPh}_3)_4]/\text{CuI}$ catalysis in diisopropylamine yielded a complex product mixture that precluded the synthesis of **29** via such a route. We reasoned the tethered acetylene unit capped with the tolyl

group was reactive enough to participate in the undesirable intramolecular Heck-type addition. Therefore, we decided to interchange the introduction of the *p*-tolyl group and ethynyl one. First, taking advantage of the triisopropylsilyl group bulkiness and the unreactivity of the adjacent tethered acetylene unit, we successfully coupled iodide **8** with acetylene **13** under Pd(0)/Cu(I) catalysis to furnish orthogonally protected diyne **26** in high



SCHEME 3

(a) Bu₄NF (1.1 equiv.), THF, room temperature, 15 min, 99%; (b) 4-Iodotoluene (1.0 equiv.), [Pd(PPh₃)₄] (5 mole %), CuI (10 mole %), diisopropylamine, room temperature, 2 h, 97%; (c) BuLi (1.0 equiv.), THF, -78 °C, 15 min, then I₂ (1.1 equiv.), -78 °C, 1 h, 93%; (d) **13** (3.6 equiv.), [Pd(PPh₃)₄] (5 mole %), CuI (10 mole %), diisopropylamine, 80 °C, 2 h, 86%; (e) Bu₄NF (3.3 equiv.), THF, room temperature, 45 min, 74%; (f) 4-iodotoluene (1.1 equiv.), [Pd(PPh₃)₄] (5 mole %), CuI (10 mole %), diisopropylamine, room temperature, 30 min, 78%; (g) NaH (2.5 equiv.), toluene, 110 °C, 40 min, 78%; (h) (-)-(S)-**17** (1.0 equiv.), [Pd(PPh₃)₄] (5 mole %), CuI (10 mole %), diisopropylamine, room temperature, 1 h, then 80 °C, 2 h, 76%; (i) Bu₄NF (1.1 equiv.), THF, room temperature, 10 min, 84%

yield. Then, by reacting with tetrabutylammonium fluoride, we selectively removed the triisopropylsilyl group to produce monoprotected diyne **27** in good yield. The subsequent coupling of **27** with 4-iodotoluene under Pd(0)/Cu(I) catalysis proceeded smoothly to give diyne **28** with a capped tethered acetylene unit in good yield. The 2-(2-hydroxypropyl) protecting group was removed by treating of **28** with sodium hydride to produce diyne **29** in good yield. Sonogashira coupling of **29** with (–)-(S)-**17** under Pd(0)/Cu(I) catalysis allowed us to assemble triyne (–)-(S)-**30** in good yield. The preparation of (–)-(S)-**4** was finalized by desilylation of (–)-(S)-**30** with tetrabutylammonium fluoride that delivered the target in high yield.

CONCLUSION

We have developed the synthesis of a series of model nonracemic aromatic triynes (–)-(S)-**1–4**. Their successful preparation has benefited from the modular character of the general synthesis scheme and the variability of the approaches explored. The common core 1,2-di(2-substituted-1-naphthyl)-acetylene unit was constructed via Sonogashira coupling of 1-iodonaphthalenes with 1-ethynylnaphthalenes both bearing tethered acetylene units in positions 2. The chirality of triynes (–)-(S)-**1–4** was easily introduced by incorporating commercially available (–)-(S)-but-3-yn-2-ol (**10**) into the tethered acetylene units. The nonracemic triynes (–)-(S)-**1–4** are intended to be used as key substrates for stereoselective [2+2+2] triyne cycloisomerization catalyzed by transition metal complexes. This study is under way and will be published separately.

EXPERIMENTAL

General

^1H NMR spectra were measured at 499.8 or 500.13 MHz, ^{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 $J_{\text{C-H}} = 5$ Hz. For correct assignment of both ^1H and ^{13}C NMR spectra of key compounds, COSY, ROESY, HMQC, HMBC, and CIGAR-HMBC experiments were performed. For all the other compounds, the general semiempirical equations were used for the chemical shift assignment. IR spectra (in cm^{-1}) were measured in CHCl_3 . EI MS spectra were determined at an ionizing voltage of 70 eV, m/z values are given along with their relative intensities (%). FAB MS spectra were measured using the thioglycerol-glycerol 3:1 matrix, m/z values are given. HR MS spectra were obtained by the EI or APCI. Optical rotations (in $10^{-1} \text{ deg cm}^3 \text{ g}^{-1}$) were measured in CH_2Cl_2 . Commercially available reagent-grade materials were used as received. Diisopropylamine was degassed by three freeze-pump-thaw cycles before use; dimethyl sulfoxide was distilled from calcium hydride in vacuo; methanol was distilled from sodium under

argon; THF was freshly distilled from sodium/benzophenone under nitrogen; toluene was distilled from calcium hydride under argon. TLC was performed on Silica gel 60 F₂₅₄-coated aluminium sheets (Merck) and spots were detected with a solution of Ce(SO₄)₂·4H₂O (1%) and H₃P(Mo₃O₁₀)₄ (2%) in sulfuric acid (10%). Flash chromatography was performed on Silica gel 60 (0.040–0.063 mm or <0.063 mm, Merck) or on Biotage KP-Sil® Silica cartridges (0.040–0.063 mm) used in Horizon® HPFC system (Biotage, Inc.).

1-[[2-(But-3-yn-1-yl)-1-naphthyl]ethynyl]-2-[[((S)-1-methylprop-2-yn-1-yl)oxy]methyl]-naphthalene (**1**)

Tetrabutylammonium fluoride (1 M solution in tetrahydrofuran, 2.17 ml, 2.34 mmol, 2.40 equiv.) was added to silylated triyne (–)-(S)-**18** (700 mg, 0.960 mmol) in tetrahydrofuran (20 ml) under argon. The mixture was stirred at room temperature for 15 min. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel (petroleum ether–ether 100:0 to 95:5) to afford unprotected triyne (–)-(S)-**1** (323 mg, 82%) as an oil. ¹H NMR: 1.56 (3 H, d, *J* = 6.6); 2.03 (1 H, t, *J* = 2.7); 2.43 (1 H, d, *J* = 2.1); 2.75 (2 H, dt, *J* = 7.7, 7.7, 2.7); 3.65 (2 H, t, *J* = 7.7); 4.41 (1 H, dq, *J* = 6.6, 6.6, 6.6, 2.1); 5.19 (1 H, d, *J* = 12.6); 5.35 (1 H, d, *J* = 12.6); 7.51 (1 H, d, *J* = 8.4); 7.52 (1 H, ddd, *J* = 8.1, 6.8, 1.2); 7.55 (1 H, ddd, *J* = 8.1, 6.8, 1.2); 7.62 (1 H, ddd, *J* = 8.4, 6.8, 1.4); 7.64 (1 H, ddd, *J* = 8.4, 6.8, 1.4); 7.74 (1 H, d, *J* = 8.5); 7.84 (1 H, dd, *J* = 8.4, 0.8); 7.87 (1 H, ddt, *J* = 8.2, 1.4, 0.8, 0.8); 7.89 (1 H, ddt, *J* = 8.1, 1.4, 0.6, 0.6); 7.90 (1 H, dt, *J* = 8.5, 0.6, 0.6); 8.59 (1 H, dq, *J* = 8.4, 0.9, 0.9, 0.9); 8.62 (1 H, ddt, *J* = 8.4, 1.2, 0.9, 0.9). ¹³C NMR: 20.04 (t), 22.15 (q), 34.70 (t), 65.00 (d), 69.28 (s), 69.43 (t), 73.46 (d), 83.70 (s), 83.72 (s), 94.30 (s), 95.91 (s), 119.07 (s), 119.60 (s), 125.40 (d), 125.98 (d), 126.27 (d), 126.33 (d), 126.42 (d), 127.07 (d), 127.18 (d), 127.35 (d), 128.22 (d), 128.29 (d), 128.77 (d), 128.71 (d), 132.10 (s), 132.69 (s), 133.42 (s), 133.71 (s), 138.80 (s), 141.36 (s). IR: 3307 vs, 3060 m, 2190 vw, 2118 w, 1621 w, 1593 w, 1570 w, 1508 m, 1375 w, 1261 w, 1098 s, 867 w, 820 s, 638 s. EI MS: 412 (M⁺, 100), 385 (12), 368 (10), 359 (32), 341 (31), 331 (37), 319 (51), 315 (41), 302 (40), 289 (71), 276 (29), 257 (8), 239 (7), 215 (9), 203 (15), 191 (47), 179 (20), 165 (40), 151 (36), 141 (38), 125 (13), 115 (15), 97 (28), 83 (31), 69 (37), 57 (61), 43 (66). HR EI MS: calculated for C₃₁H₂₄O 412.1827; found 412.1807. [α]_D²² –57 (c 0.45).

2-[[((S)-1-Methyl-3-*p*-tolylprop-2-yn-1-yl)oxy]methyl]-1-[[2-(4-*p*-tolylbut-3-yn-1-yl)-1-naphthyl]ethynyl]naphthalene (**2**)

A Schlenk flask was charged with [Pd(PPh₃)₄] (10 mg, 0.009 mmol, 10 mole %), CuI (3 mg, 0.0016 mmol, 20 mole %), 4-iodotoluene (38 mg, 0.174 mmol, 2.10 equiv.), and flushed with argon. Alkyne **1** (34 mg, 0.082 mmol) in diisopropylamine (3 ml) was added and the mixture was stirred at 80 °C for 30 min. Volatiles were removed in vacuo and the residue was chromatographed on silica gel (hexanes–ether 95:5) to afford **2** (40 mg, 82%) as an amorphous solid. M.p. 156 °C (petroleum ether–ether). ¹H NMR: 1.60 (3 H, d, *J* = 6.6); 2.26 (3 H, brs); 2.31 (3 H, brs); 2.92 (2 H, t, *J* = 7.7); 3.48 (2 H, t, *J* = 7.5); 4.61 (1 H, q, *J* = 6.6); 5.28 (1 H, d, *J* = 12.7); 5.40 (1 H, d, *J* = 12.7); 6.91 (2 H, m); 7.04 (2 H, m); 7.15 (2 H, m); 7.23 (2 H, m); 7.48 (1 H, ddd, *J* = 8.1, 6.8, 1.2); 7.51 (1 H, d, *J* = 8.5); 7.52 (1 H, ddd, *J* = 8.0, 6.8, 1.2); 7.56 (1 H, ddd, *J* = 8.3, 6.8, 1.4); 7.60 (1 H, ddd, *J* = 8.3, 6.8, 1.4); 7.78 (1 H, d, *J* = 8.5); 7.82 (1 H, dd, *J* = 8.5, 0.7); 7.85 (1 H, ddt, *J* = 8.0, 1.4, 0.6, 0.6); 7.88 (1 H, ddt, *J* = 8.1, 1.4, 0.6, 0.6); 7.90 (1 H, dd, *J* = 8.5, 0.7); 8.63 (2 H, dt, *J* = 8.3, 1.0, 1.0). ¹³C NMR: 21.08 (t), 21.38 (2 × q), 22.35 (q), 35.02 (t), 65.69 (d), 69.42 (t), 81.63 (s), 85.63 (s), 88.32 (s),

88.61 (s), 94.28 (s), 95.98 (s), 119.22 (s), 119.51 (s), 119.60 (s), 120.78 (s), 125.59 (d), 125.85 (d), 126.26 (d), 126.31 (d), 126.34 (d), 127.06 (d), 127.15 (d), 127.53 (d), 128.10 (d), 128.23 (d), 128.50 (d), 128.69 (d), 128.78 (d), 128.89 (d), 131.42 (d), 131.54 (d), 132.07 (s), 132.68 (s), 133.75 (2 × s), 137.51 (s), 138.11 (s), 139.09 (s), 141.74 (s). IR: 3059 m, 3011 s, 2226 w, 2203 vw (sh), 1620 w, 1610 w, 1593 m, 1570 m, 1510 vvs, 1399 s, 1373 m, 1328 s, 1260 m, 1180 w, 1094 w, 1022 m, 867 m, 819 vvs. EI MS: 592 (M^{+} , 0.2), 496 (0.4), 467 (0.3), 449 (66), 421 (25), 289 (20), 143 (40), 129 (50), 97 (40), 91 (32), 83 (48), 73 (70), 57 (96), 43 (100). HR APCI MS: calculated for $C_{45}H_{37}O$ ($M^{+} + 1$) 593.2844; found 593.2855. $[\alpha]_D^{22}$ -80 (c 0.15).

1-[[2-(But-3-yn-1-yl)-1-naphthyl]ethynyl]-2-[[((S)-1-methyl-3-*p*-tolylprop-2-yn-1-yl)oxy]-methyl]naphthalene (**3**)

Tetrabutylammonium fluoride (1 M solution in tetrahydrofuran, 350 μ l, 0.380 mmol, 2.40 equiv.) was added to silylated triyne (–)-(S)-**22** (100 mg, 0.160 mmol) in tetrahydrofuran (3 ml) under argon. The mixture was stirred at room temperature for 30 min. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel (petroleum ether–ether 98:2) to afford unprotected triyne (–)-(S)-**3** (27 mg, 35%) as an oil. 1H NMR: 1.62 (3 H, d, J = 6.6); 2.01 (1 H, t, J = 2.6); 2.28 (3 H, s); 2.71 (2 H, dt, J = 7.6, 7.6, 2.6); 3.71 (2 H, t, J = 7.6); 4.62 (1 H, d, J = 6.6); 5.28 (1 H, d, J = 12.8); 5.39 (1 H, d, J = 12.8); 6.91 (2 H, m); 7.14 (2 H, m); 7.46 (1 H, d, J = 8.4); 7.48 (1 H, ddd, J = 8.1, 6.8, 1.2); 7.55 (1 H, ddd, J = 8.1, 6.8, 1.2); 7.55 (1 H, ddd, J = 8.4, 6.8, 1.4); 7.64 (1 H, ddd, J = 8.4, 6.8, 1.4); 7.79 (1 H, d, J = 8.5); 7.82 (1 H, brd, J = 8.4); 7.85 (1 H, brdd, J = 8.1, 1.4); 7.89 (1 H, brdd, J = 8.1, 1.4); 7.91 (1 H, brd, J = 8.5); 8.60 (1 H, brdd, J = 8.4, 1.2); 8.62 (1 H, brdd, J = 8.4, 1.2). ^{13}C NMR: 19.99 (t), 21.39 (q), 22.37 (q), 34.66 (t), 65.69 (d), 69.22 (d), 69.41 (t), 83.71 (s), 85.64 (s), 88.30 (s), 94.38 (s), 95.82 (s), 119.18 (s), 119.50 (s), 119.61 (s), 125.63 (d), 125.92 (d), 126.29 (d), 126.31 (d), 126.32 (d), 127.12 (d), 127.13 (d), 127.29 (d), 128.11 (d), 128.28 (d), 128.59 (d), 128.74 (d), 128.79 (d), 131.53 (d), 132.09 (s), 132.70 (s), 133.45 (s), 133.75 (s), 138.14 (s), 139.11 (s), 141.36 (s). IR: 3308 m, 3059 m, 2226 w, 2195 vw (sh), 2118 w, 1620 vw, 1608 vw, 1593 w, 1570 w, 1510 s, 1328 m, 1260 w, 1127 m (sh), 1105 s (sh), 1094 s, 1075 m, 1022 m, 867 w, 819 vs, 640 m, 524 w, 428 w. EI MS: 502 (M^{+} , 7), 487 (15), 459 (32), 449 (14), 406 (5), 368 (6), 359 (21), 341 (29), 331 (31), 315 (40), 302 (44), 289 (65), 276 (23), 265 (7), 231 (8), 203 (13), 191 (68), 165 (34), 153 (15), 141 (61), 128 (100), 115 (40), 105 (11), 91 (17), 65 (8), 55 (11), 43 (53). HR EI MS: calculated for $C_{38}H_{30}O$ 502.2297; found 502.2278. $[\alpha]_D^{22}$ -108 (c 0.08).

1-[[2-(4-*p*-Tolylbut-3-yn-1-yl)-1-naphthyl]ethynyl]-2-[[((S)-1-methylprop-2-yn-1-yl)oxy]-methyl]naphthalene (**4**)

Tetrabutylammonium fluoride (1 M solution in tetrahydrofuran, 95 μ l, 0.100 mmol, 1.10 equiv.) was added to silylated triyne (–)-(S)-**30** (60 mg, 0.090 mmol) in tetrahydrofuran (3 ml) under argon. The mixture was stirred at room temperature for 10 min. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel (petroleum ether–ether 93:7) to afford unprotected triyne (–)-(S)-**4** (39 mg, 84%) as an oil. 1H NMR: 1.54 (3 H, d, J = 6.6); 2.32 (3 H, s); 2.42 (1 H, d, J = 2.0); 2.95 (2 H, t, J = 7.5); 3.53 (2 H, t, J = 7.5); 4.40 (1 H, dq, J = 6.6, 6.6, 6.6, 2.0); 5.20 (1 H, d, J = 12.6); 5.36 (1 H, d, J = 12.6); 7.05 (2 H, m); 7.24 (2 H, m); 7.52 (1 H, ddd, J = 8.1, 6.8, 1.2); 7.53 (1 H, ddd, J = 8.1, 6.8, 1.2); 7.56 (1 H, d, J = 8.4); 7.61 (1 H, ddd, J = 8.4, 6.8, 1.4); 7.62 (1 H, ddd, J = 8.4, 6.8, 1.4); 7.74 (1 H, d, J = 8.5); 7.85 (1 H, brd, J = 8.4); 7.88 (1 H, brdd, J = 8.1, 1.4); 7.88 (1 H, brdd, J =

8.1, 1.4); 7.89 (1 H, brd, $J = 8.5$); 8.63 (1 H, ddt, $J = 8.4, 1.0, 0.8, 0.8$); 8.64 (1 H, ddt, $J = 8.4, 1.0, 0.8, 0.8$). ^{13}C NMR: 21.13 (t), 21.38 (q), 22.13 (q), 35.08 (t), 65.01 (d), 69.43 (t), 73.46 (d), 81.68 (s), 83.73 (s), 88.57 (s), 94.21 (s), 96.08 (s), 119.12 (s), 119.62 (s), 120.75 (s), 125.37 (d), 125.92 (d), 126.31 (d), 126.31 (d), 126.42 (d), 127.02 (d), 127.20 (d), 127.57 (d), 128.21 (d), 128.25 (d), 128.62 (d), 128.72 (d), 128.91 (d), 131.43 (d), 132.10 (s), 132.68 (s), 133.43 (s), 133.74 (s), 137.56 (s), 138.80 (s), 141.74 (s). IR: 3307 m, 3060 w, 2225 vw, 2196 vw, 2112 vw, 1620 vw, 1593 w, 1571 w, 1510 s, 1452 w, 1431 w, 1399 m, 1375 w, 1326 m, 1313 w, 1275 w, 1264 w (sh), 1181 w, 1146 w (sh), 1135 w (sh), 1110 s (sh), 1098 s, 1063 m, 1040 w, 1023 w, 867 w, 819 vs, 638 m, 530 w, 427 w. EI MS: 502 (M^{++} , 4), 487 (15), 459 (4), 449 (79), 434 (8), 421 (100), 411 (28), 393 (7), 357 (11), 339 (19), 329 (26), 315 (23), 302 (41), 289 (79), 276 (30), 265 (13), 255 (19), 191 (8), 165 (23), 155 (15), 141 (70), 129 (38), 119 (24), 105 (27), 83 (18), 69 (25), 57 (37), 53 (20), 43 (37). HR EI MS: calculated for $\text{C}_{38}\text{H}_{30}\text{O}$ 502.2297; found 502.2306. $[\alpha]_{\text{D}}^{22} -58$ (c 0.11).

(S)-4-(4-Methylphenyl)but-3-yn-2-ol (**11**)

A modified procedure was used¹³: A Schlenk flask was charged with 4-iodotoluene (1.50 g, 6.88 mmol, 1.00 equiv.), $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (14 mg, 0.060 mmol, 0.8 mole %), CuI (20 mg, 0.100 mmol, 1.5 mole %), triphenylphosphine (28 mg, 0.110 mmol, 1.5 mole %), and flushed with argon. Toluene (7 ml) was added, the mixture was cooled to 0 °C, and propargylic alcohol (–)-(S)-**10** (540 µl, 6.88 mmol) in degassed diisopropylamine (970 µl, 6.90 mmol, 1.00 equiv.) was added. The mixture was stirred at 0 °C for 5 min and then at room temperature for 3 h. Volatiles were removed in vacuo and the residue was extracted with ether. The solvent was removed in vacuo and the residue was chromatographed on silica gel (hexanes) to afford (–)-(S)-**11** (910 mg, 83%) as an oil. ^1H NMR, ^{13}C NMR, and IR spectra were in agreement with the literature data¹³. $[\alpha]_{\text{D}}^{22} -27$ (c 0.13).

1-Bromo-2-[[[(S)-1-methylprop-2-yn-1-yl]oxy]methyl]naphthalene (**14**)

A Schlenk flask was charged with NaH (80% suspension in mineral oil, 250 mg, 8.33 mmol, 1.25 equiv.), flushed with argon, and hydride was washed with hexane (3×). THF (40 ml) was added and the mixture was cooled to 0 °C. Alcohol (–)-(S)-**10** (675 µl, 8.54 mmol, 1.30 equiv.) was added and the mixture was stirred at 0 °C for 30 min. Bromide **5** (2 g, 6.67 mmol) in THF (40 ml) was added and the mixture was stirred at room temperature for 1 h and then at 50 °C for 2 h. The solvent was evaporated in vacuo and the residue was partitioned between ether and water. Organic layer was separated, washed with water (3×), and dried over anhydrous Na_2SO_4 . The solvent was removed in vacuo to afford (–)-(S)-**14** (1.86 g, 96%) as an oil. ^1H NMR: 1.55 (3 H, d, $J = 6.6$); 2.50 (1 H, d, $J = 2.1$); 4.33 (1 H, dq, $J = 6.6, 6.6, 6.6, 2.1$); 4.87 (1 H, d, $J = 12.8$); 5.05 (1 H, d, $J = 12.8$); 7.51 (1 H, ddd, $J = 8.1, 6.8, 1.2$); 7.59 (1 H, ddd, $J = 8.5, 6.8, 1.3$); 7.63 (1 H, brd, $J = 8.4$); 7.81 (1 H, ddd, $J = 8.4, 0.8, 0.6$); 7.82 (1 H, ddt, $J = 8.1, 1.3, 0.7, 0.7$); 8.32 (1 H, ddt, $J = 8.5, 1.2, 0.7, 0.7$). ^{13}C NMR: 22.08 (q), 65.14 (d), 70.80 (t), 73.38 (d), 83.59 (s), 122.74 (s), 126.25 (d), 126.45 (d), 127.10 (d), 127.36 (d), 127.64 (d), 128.11 (d), 132.25 (s), 134.07 (s), 135.61 (s). IR: 3307 vs, 2113 w, 1625 w, 1599 w, 1559 m, 1503 s, 1259 s, 1112 vs, 1099 vs, 1032 m, 864 m, 818 vs, 666 s, 639 s. EI MS: 290 (M^{++} with ^{81}Br , 30), 288 (M^{++} with ^{79}Br , 30), 236 (21), 221 (33), 207 (5), 179 (17), 165 (23), 157 (14), 141 (100), 128 (79), 115 (5), 63 (6), 53 (16), 43 (11). HR EI MS: calculated for $\text{C}_{15}\text{H}_{13}^{81}\text{BrO}$ 290.0129 and for $\text{C}_{15}\text{H}_{13}^{79}\text{BrO}$ 288.0149; found 290.0115 and 288.0122, respectively. $[\alpha]_{\text{D}}^{22} -87$ (c 0.10).

{(S)-3-[(1-Bromo-2-naphthyl)methoxy]but-1-yn-1-yl}(triisopropyl)silane (15**)**

Lithium diisopropylamide (2 M solution in tetrahydrofuran, 2 ml, 4.0 mmol, 1.10 equiv.) was added to (–)-(S)-**14** (1.62 g, 3.64 mmol) in tetrahydrofuran (40 ml) at –78 °C under argon. The mixture was stirred at –78 °C for 45 min and chlorotriisopropylsilane (0.85 ml, 4.0 mmol, 1.10 equiv.) was added. The reaction mixture was stirred at –78 °C for additional 15 min and then at room temperature for 45 min. Volatiles were removed in vacuo and the residue was partitioned between dichloromethane and water. The organic layer was separated, washed with water (3×), and dried over anhydrous Na₂SO₄. The solvent was removed in vacuo to afford (–)-(S)-**15** (2.60 g, 95%) as an oil. ¹H NMR: 1.05–1.11 (21 H, m); 1.53 (3 H, d, *J* = 6.6); 4.37 (1 H, q, *J* = 6.6); 4.90 (1 H, d, *J* = 13.0); 5.09 (1 H, d, *J* = 13.0); 7.51 (1 H, ddd, *J* = 8.1, 6.8, 1.2); 7.58 (1 H, ddd, *J* = 8.4, 6.8, 1.4); 7.64 (1 H, d, *J* = 8.5); 7.81 (1 H, brd, *J* = 8.5); 7.82 (1 H, ddt, *J* = 8.1, 1.4, 0.6, 0.6); 8.32 (1 H, ddt, *J* = 8.4, 1.2, 0.9, 0.9). ¹³C NMR: 11.17 (d), 18.61 (q), 22.36 (q), 65.73 (d), 70.60 (t), 86.24 (s), 107.32 (s), 122.69 (s), 126.31 (d), 126.37 (d), 127.07 (d), 127.29 (d), 127.57 (d), 128.09 (d), 132.23 (s), 134.02 (s), 135.89 (s). IR: 3059 m, 2866 vs, 2165 m, 1623 w, 1599 m, 1558 m, 1503 s, 1463 vs, 1427 w, 1383 s, 1372 s, 1325 vs, 1258 s, 1115 vs (sh), 1097 vs, 1071 vs, 997 s, 969 s, 884 vs, 865 s, 816 vs, 681 s, 660 s, 646 s, 532 s, 413 m. EI MS: 446 (M⁺ with ⁸¹Br, 12), 444 (M⁺ with ⁷⁹Br, 12), 403 (62), 373 (39), 359 (8), 321 (15), 307 (23), 279 (55), 251 (6), 235 (18), 219 (100), 207 (10), 192 (31), 167 (21), 141 (52), 125 (24), 115 (12), 97 (17), 83 (23), 69 (16), 59 (20), 41 (9). HR EI MS: calculated for C₂₄H₃₃⁸¹BrOSi 446.1463 and for C₂₄H₃₃⁷⁹BrOSi 444.1484; found 446.1481 and 444.1470, respectively. [α]_D²⁵ –73 (c 0.20).

1-Iodo-2-[(S)-1-methylprop-2-yn-1-yl]oxy)methyl]naphthalene (16**)**

A Schlenk flask was charged with (–)-(S)-**10** (1.60 ml, 20.32 mmol, 1.60 equiv.) and flushed with argon. Tetrahydrofuran (30 ml) and dimethyl sulfoxide (5.7 ml) were added and the solution was cooled to –30 °C. Then butyllithium (1.6 M solution, 2.40 ml, 3.89 mmol, 1.70 equiv.) was added. The mixture was stirred at –30 °C for 30 min and at –5 °C for 15 min. Bromide **6** (4.23 g, 12.20 mmol) in tetrahydrofuran (15 ml) was added and the reaction mixture was stirred at 40 °C for 3.5 h. Volatiles were removed in vacuo and the residue was chromatographed on silica gel (petroleum ether–ether 99:1 to 97:3) to afford (–)-(S)-**16** (3.32 g, 81%) as an oil. ¹H NMR: 1.56 (3 H, d, *J* = 6.6); 2.51 (1 H, d, *J* = 2.1); 4.35 (1 H, dq, *J* = 6.6, 6.6, 6.6, 2.1); 4.81 (1 H, d, *J* = 12.7); 5.03 (1 H, d, *J* = 12.7); 7.50 (1 H, ddd, *J* = 8.1, 6.9, 1.2); 7.57 (1 H, ddd, *J* = 8.5, 6.9, 1.5); 7.59 (1 H, d, *J* = 8.4); 7.77 (1 H, ddt, *J* = 8.1, 1.5, 0.5, 0.5); 7.81 (1 H, brdt, *J* = 8.4, 0.7, 0.7); 8.25 (1 H, ddt, *J* = 8.5, 1.2, 0.8, 0.8). ¹³C NMR: 22.07 (q), 65.12 (d), 73.47 (d), 76.03 (t), 83.55 (s), 103.44 (s), 126.27 (d), 126.50 (d), 127.71 (d), 128.28 (d), 128.74 (d), 132.33 (d), 133.73 (d), 134.72 (d), 139.66 (s). IR: 3306 s, 3059 m, 2112 w, 1621 w, 1596 w, 1552 m, 1502 s, 1374 m, 1257 s, 1113 vs (sh), 1099 vvs, 1031 m, 863 m, 817 s, 638 s, 523 m. EI MS: 336 (M⁺, 53), 306 (6), 282 (20), 267 (22), 179 (11), 165 (36), 141 (100), 128 (44), 115 (5), 83 (5), 53 (16), 43 (14). HR EI MS: calculated for C₁₅H₁₃IO 336.0011; found 336.0008. [α]_D²² –75 (c 0.37).

{(S)-3-[(1-Iodo-2-naphthyl)methoxy]but-1-yn-1-yl}(triisopropyl)silane (17**)**

Method 1: Butyllithium (1.6 M solution, 3.8 ml, 6.05 mmol, 1.04 equiv.) was added to (–)-(S)-**15** (2.59 g, 5.81 mmol) in tetrahydrofuran (15 ml) at –78 °C under argon. The mixture was stirred at –78 °C for 15 min. Iodine (1.62 g, 6.38 mmol, 1.10 equiv.) in tetra-

hydrofuran (10 ml) was added and the reaction mixture was stirred at -78°C for 1 h. The solvent was evaporated in vacuo and the residue was partitioned between ether and water. The organic layer was separated, washed with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (3 $\times$), water (2 $\times$), and dried over anhydrous Na_2SO_4 . Volatiles were removed in vacuo and the residue was chromatographed on silica gel (petroleum ether–ether 99.5:0.5) to afford iodide (–)-(S)-**17** (1.17 g, 41%) as an oil.

Method 2: Lithium diisopropylamide (2 M solution in tetrahydrofuran, 670 μL , 1.34 mmol, 1.04 equiv.) was added to (–)-(S)-**16** (435 mg, 1.29 mmol) in tetrahydrofuran (6 ml) at -78°C under argon. The mixture was stirred at -78°C for 45 min and chlorotriisopropylsilane (560 μL , 2.62 mmol, 2.03 equiv.) was added. The reaction mixture was stirred at -78°C to room temperature overnight. Volatiles were removed in vacuo and the residue was chromatographed on silica gel (petroleum ether–ether 100:0 to 98:2) to afford (–)-(S)-**17** (535 mg, 84%) as an oil.

^1H NMR: 1.07–1.12 (21 H, m); 1.55 (3 H, d, $J = 6.6$); 4.38 (1 H, q, $J = 6.6$); 4.83 (1 H, d, $J = 12.9$); 5.06 (1 H, d, $J = 12.9$); 7.49 (1 H, ddd, $J = 8.0, 6.8, 1.2$); 7.56 (1 H, ddd, $J = 8.5, 6.8, 1.4$); 7.60 (1 H, d, $J = 8.4$); 7.76 (1 H, ddt, $J = 8.0, 1.4, 0.7, 0.7$); 7.80 (1 H, dt, $J = 8.4, 0.6, 0.6$); 8.24 (1 H, ddt, $J = 8.5, 1.2, 0.7, 0.7$). ^{13}C NMR: 11.17 (d), 18.65 (q), 22.37 (q), 65.75 (d), 75.85 (t), 86.29 (s), 103.26 (s), 107.28 (s), 126.26 (d), 126.41 (d), 127.64 (d), 128.26 (d), 128.67 (d), 132.28 (d), 133.69 (s), 134.70 (s), 139.97 (s). IR: 3059 w, 2891 s, 2866 vvs, 2164 w, 1620 vw, 1596 vw, 1552 w, 1501 m, 1463 s, 1383 w, 1372 m, 1256 m, 1097 s, 1031 w, 997 m, 883 s, 863 w, 815 s, 679 s, 664 m, 523 w. EI MS: 492 (M^{++} , 27), 449 (87), 419 (12), 353 (15), 325 (13), 307 (8), 279 (68), 267 (100), 251 (9), 237 (6), 227 (17), 208 (8), 199 (19), 192 (42), 182 (7), 167 (17), 141 (56), 125 (22), 111 (19), 97 (14), 83 (19), 69 (15), 59 (21), 41 (10). FAB MS: 449, 353, 325, 307, 289, 279, 267, 165, 141, 125, 115, 73, 59. HR EI MS: calculated for $\text{C}_{24}\text{H}_{33}\text{IOSi}$ 492.1345; found 492.1327. $[\alpha]_{\text{D}}^{22} -86$ (c 0.27).

Triisopropyl((S)-3-[[1-(2-[4-(triisopropylsilyl)but-3-yn-1-yl]-1-naphthyl)-ethynyl]-2-naphthyl]methoxy)but-1-yn-1-yl)silane (**18**)

A Schlenk flask was charged with $[\text{Pd}(\text{PPh}_3)_4]$ (56 mg, 0.050 mmol, 5 mole %), CuI (18 mg, 0.100 mmol, 10 mole %), and flushed with argon. Iodide (–)-(S)-**17** (473 mg, 0.960 mmol) in diisopropylamine (14 ml) was added and the mixture was stirred at room temperature for 10 min. Then diyne **9** (380 mg, 1.05 mmol, 1.10 equiv.) in diisopropylamine (10 ml) was added and the mixture was stirred at room temperature for 1 h. Volatiles were removed in vacuo and the residue was chromatographed on silica gel (hexanes–ether 99:1) to afford (–)-(S)-**18** (564 mg, 81%) as an oil. ^1H NMR: 0.90–1.02 (42 H, m); 1.55 (3 H, d, $J = 6.6$); 2.81 (2 H, t, $J = 7.3$); 3.42 (2 H, t, $J = 7.3$); 4.42 (1 H, q, $J = 6.6$); 5.18 (1 H, d, $J = 12.4$); 5.31 (1 H, d, $J = 12.4$); 7.50 (1 H, ddd, $J = 8.0, 6.8, 1.2$); 7.53 (1 H, ddd, $J = 8.1, 6.8, 1.2$); 7.55 (1 H, d, $J = 8.4$); 7.59 (1 H, ddd, $J = 8.3, 6.8, 1.3$); 7.62 (1 H, ddd, $J = 8.4, 6.8, 1.4$); 7.73 (1 H, d, $J = 8.4$); 7.80 (1 H, brd, $J = 8.4$); 7.86 (1 H, ddt, $J = 8.0, 1.4, 0.7, 0.7$); 7.88 (1 H, dt, $J = 8.4, 0.8, 0.8$); 7.88 (1 H, ddt, $J = 8.1, 0.7, 0.7$); 8.57 (1 H, ddt, $J = 8.3, 1.2, 0.8, 0.8$); 8.58 (1 H, ddt, $J = 8.4, 1.2, 0.8, 0.8$). ^{13}C NMR: 11.08 (d), 11.27 (d), 18.47 (q), 18.56 (q), 21.39 (t), 22.51 (q), 34.90 (t), 65.69 (d), 69.33 (t), 81.42 (s), 86.08 (s), 94.23 (s), 95.84 (s), 107.56 (s), 107.88 (s), 119.28 (s), 119.48 (s), 125.74 (d), 125.78 (d), 126.21 (d), 126.24 (d), 126.34 (d), 126.90 (d), 127.08 (d), 127.68 (d), 128.11 (d), 128.21 (d), 128.44 (d), 128.59 (d), 132.08 (s), 132.67 (s), 133.44 (s), 133.78 (s), 139.01 (s), 141.69 (s). IR: 3059 w, 2891 m, 2866 vs, 2169 w, 1620 vw, 1593 w, 1570 w, 1508 w, 1463 m, 1399 w, 1383 w, 1372 w, 1367 w, 1251 w, 1096 m,

996 m, 883 s, 867 w, 818 m, 678 s, 661 m, 617 w. EI MS: 725 (M^{++} , 2), 724 (3), 682 (0.8), 613 (1.6), 530 (1.2), 515 (32), 492 (18), 449 (78), 419 (12), 353 (14), 341 (10), 325 (12), 307 (10), 289 (6), 279 (72), 267 (100), 251 (9), 235 (10), 227 (20), 208 (10), 199 (24), 192 (44), 181 (16), 167 (24), 157 (16), 141 (67), 125 (36), 111 (38), 97 (37), 83 (50), 73 (62), 59 (58), 41 (54). HR EI MS: calculated for $C_{36}H_{39}OSi$ ($M^{++} - 210$) 515.2770; found 515.2789. $[\alpha]_D^{22} -110$ (c 1.21).

1-Iodo-2-[[[(*S*)-1-methyl-3-*p*-tolylprop-2-yn-1-yl]oxy]methyl]naphthalene (**19**)

A Schlenk flask was charged with (–)-(*S*)-**11** (623 mg, 3.89 mmol, 1.50 equiv.) and flushed with argon. Tetrahydrofuran (10 ml) was added and the solution was cooled to $-30\text{ }^{\circ}\text{C}$. Dimethyl sulfoxide (1.10 ml) was added followed by butyllithium (1.6 M solution, 2.4 ml, 3.89 mmol, 1.50 equiv.). The reaction mixture was stirred at $0\text{ }^{\circ}\text{C}$ for 10 min. Bromide **6** (900 mg, 2.59 mmol) in tetrahydrofuran (7 ml) was added and the reaction mixture was stirred at $40\text{ }^{\circ}\text{C}$ for 16 h. Volatiles were removed in vacuo and the residue was chromatographed on silica gel (hexanes–ether 99:1 to 95:5) to afford (–)-(*S*)-**19** (730 mg, 66%) as an oil. ^1H NMR: 1.62 (3 H, d, $J = 6.6$); 2.35 (3 H, s); 4.57 (1 H, q, $J = 6.6$); 4.91 (1 H, d, $J = 12.8$); 5.16 (1 H, d, $J = 12.8$); 7.11 (2 H, m); 7.35 (2 H, m); 7.50 (1 H, ddd, $J = 8.0, 6.8, 1.2$); 7.57 (1 H, ddd, $J = 8.6, 6.8, 1.5$); 7.64 (1 H, d, $J = 8.4$); 7.77 (1 H, brdd, $J = 8.0, 1.5$); 7.82 (1 H, brd, $J = 8.4$); 8.26 (1 H, ddt, $J = 8.6, 1.2, 0.9, 0.9$). ^{13}C NMR: 21.46 (q), 22.26 (q), 65.79 (d), 76.04 (t), 85.70 (s), 88.14 (s), 103.57 (s), 119.65 (s), 126.40 (d), 126.46 (d), 127.67 (d), 128.27 (d), 128.73 (d), 129.02 (d), 131.67 (d), 132.36 (d), 133.72 (s), 134.72 (s), 138.45 (s), 139.91 (s). IR: 3058 w, 2226 w, 1620 vw, 1551 w, 1546 vw, 1510 m, 1502 w, 1425 w, 1374 w, 1327 m, 1095 vs, 1020 s, 863 m, 817 vs, 704 vw, 523 w. EI MS: 340 (6), 279 (2), 267 (18), 255 (100), 157 (7), 149 (18), 141 (39), 140 (26), 129 (42), 115 (15), 95 (10), 83 (15), 71 (23), 57 (43), 43 (34). FAB MS: 267, 255, 239, 215, 189, 165, 152, 143, 141, 115, 91, 77, 69, 55. $[\alpha]_D^{22} -112$ (c 0.20).

Trimethyl[(2-[[[(*S*)-1-methyl-3-*p*-tolylprop-2-yn-1-yl]oxy]methyl]-1-naphthyl)ethynyl]silane (**20**)

A pressure glass tube with a side arm and a PTFE stopcock was charged with $[\text{Pd}(\text{PPh}_3)_4]$ (12 mg, 0.011 mmol, 5 mole %), CuI (4 mg, 0.021 mmol, 10 mole %), iodide (–)-(*S*)-**19** (90 mg, 0.210 mmol), and flushed with argon. Degassed diisopropylamine (2 ml) was added followed by (trimethylsilyl)acetylene (36 μl , 0.250 mmol, 1.20 equiv.). The tube was tightly closed and the reaction mixture was stirred at $80\text{ }^{\circ}\text{C}$ for 2 h. Volatiles were removed in vacuo and the residue was chromatographed on silica gel (hexanes–ether 99:1) to afford (–)-(*S*)-**20** (68 mg, 81%) as an oil. ^1H NMR: 0.30 (9 H, s); 1.60 (3 H, d, $J = 6.6$); 2.34 (3 H, brs); 4.56 (1 H, q, $J = 6.6$); 5.03 (1 H, d, $J = 12.7$); 5.15 (1 H, d, $J = 12.7$); 7.10 (2 H, m); 7.33 (2 H, m); 7.49 (1 H, ddd, $J = 8.1, 6.8, 1.2$); 7.56 (1 H, ddd, $J = 8.4, 6.8, 1.4$); 7.67 (1 H, d, $J = 8.5$); 7.82 (1 H, brd, $J = 8.5$); 7.82 (1 H, ddt, $J = 8.1, 1.4, 0.7, 0.7$); 8.35 (1 H, ddt, $J = 8.4, 1.2, 0.8, 0.8$). ^{13}C NMR: 0.08 (q), 21.44 (q), 22.28 (q), 65.83 (d), 69.16 (t), 85.30 (s), 88.42 (s), 100.52 (s), 105.09 (s), 118.78 (s), 119.75 (s), 125.31 (d), 126.15 (d), 126.24 (d), 126.87 (d), 128.07 (d), 128.67 (d), 128.95 (d), 131.67 (d), 132.44 (s), 133.38 (s), 138.32 (s), 139.67 (s). IR: 3060 w, 3009 s, 2900 m, 2226 w, 2148 m, 1621 vw, 1607 vw, 1593 w, 1568 w, 1510 s, 1408 w, 1374 m, 1328 s, 1260 m, 1251 s, 1181 w, 1130 m (sh), 1095 s, 1027 m (sh), 1021 m, 872 vs, 846 vs, 820 vs, 701 w, 644 m, 570 w, 525 w, 405 w. EI MS: 396 (M^{++} , 2), 381 (5), 323 (10), 310 (3), 279 (2), 265 (34), 253 (4), 237 (8), 178 (6), 165 (9), 143 (16), 129

(31), 115 (6), 73 (100), 59 (14). HR EI MS: calculated for $C_{27}H_{28}OSi$ 396.1909; found 396.1922. $[\alpha]_D^{22}$ -128 (c 0.14).

1-Ethynyl-2-[[[(*S*)-1-methyl-3-*p*-tolylprop-2-yn-1-yl]oxy]methyl]naphthalene (**21**)

Sodium methoxide (3.3 M solution in methanol, 70 μ l, 0.230 mmol, 1.70 equiv.) was added to (*-*)-(*S*)-**20** (53 mg, 0.130 mmol) in tetrahydrofuran (2 ml) under argon. The reaction mixture was stirred at room temperature for 1 h. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel (hexanes–ether 99:1) to afford (*-*)-(*S*)-**21** (35 mg, 81%) as an oil. 1H NMR: 1.59 (3 H, d, J = 6.6); 2.35 (3 H, brs); 3.70 (1 H, s); 4.54 (1 H, q, J = 6.6); 5.07 (1 H, d, J = 12.5); 5.18 (1 H, d, J = 12.5); 7.11 (2 H, m); 7.34 (2 H, m); 7.51 (1 H, ddd, J = 8.1, 6.8, 1.3); 7.57 (1 H, ddd, J = 8.4, 6.8, 1.4); 7.69 (1 H, d, J = 8.5); 7.76 (1 H, brd, J = 8.5); 7.84 (1 H, ddt, J = 8.1, 1.4, 0.7, 0.7); 8.38 (1 H, ddt, J = 8.4, 1.3, 0.8, 0.8). ^{13}C NMR: 21.45 (q), 22.26 (q), 65.65 (d), 68.99 (t), 79.27 (s), 85.41 (s), 87.18 (d), 88.43 (s), 117.93 (s), 119.78 (s), 125.53 (d), 126.13 (d), 126.28 (d), 127.00 (d), 128.12 (d), 128.99 (2 $\times$ d), 131.64 (d), 132.47 (s), 133.58 (s), 138.37 (s), 139.98 (s). IR: 3304 s, 3061 w, 3033 w, 2226 w, 2100 vw, 1621 vw, 1608 vw, 1594 w, 1569 w, 1510 s, 1431 w (sh), 1407 vw (sh), 1373 m, 1328 s, 1259 w, 1175 w, 1106 s (sh), 1095 vs, 1022 m, 869 w, 835 w, 820 vs, 658 m, 617 m, 438 w. EI MS: 324 (M^{+} , 4), 323 (13), 309 (26), 281 (23), 265 (15), 193 (100), 165 (61), 152 (24), 143 (28), 129 (53), 115 (22), 91 (7), 63 (6), 51 (5), 43 (17). HR EI MS: calculated for $C_{24}H_{20}O$ 324.1514; found 324.1504. $[\alpha]_D^{22}$ -169 (c 0.09).

Triisopropyl(4-[1-[(2-[[[(*S*)-1-methyl-3-*p*-tolylprop-2-yn-1-yl]oxy]methyl]-1-naphthyl]ethynyl]-2-naphthyl]but-1-yn-1-yl)silane (**22**)

A Schlenk flask was charged with $[Pd(PPh_3)_4]$ (5 mg, 0.005 mmol, 5 mole %), CuI (2 mg, 0.009 mmol, 10 mole %), iodide **8** (45 mg, 0.095 mmol, 1.10 equiv.), and flushed with argon. Degassed diisopropylamine (1 ml) was added followed by diyne (*-*)-(*S*)-**21** (28 mg, 0.086 mmol) in diisopropylamine (1 ml). The reaction mixture was stirred at room temperature for 1 h. Volatiles were removed in vacuo and the residue was chromatographed on silica gel (hexanes–ether 98:2) to afford (*-*)-(*S*)-**22** (33 mg, 58%) as an oil. 1H NMR: 0.86–1.02 (21 H, m); 1.62 (3 H, d, J = 6.6); 2.28 (3 H, s); 2.89 (2 H, t, J = 5.7); 3.92 (2 H, t, J = 5.7); 4.60 (1 H, d, J = 6.6); 5.26 (1 H, d, J = 12.6); 5.37 (1 H, d, J = 12.6); 6.91 (2 H, m); 7.15 (2 H, m); 7.47 (1 H, ddd, J = 8.0, 6.9, 1.3); 7.52 (1 H, d, J = 8.4); 7.54 (1 H, ddd, J = 8.1, 6.8, 1.2); 7.54 (1 H, ddd, J = 8.4, 6.9, 1.4); 7.63 (1 H, ddd, J = 8.4, 6.8, 1.4); 7.77 (1 H, d, J = 8.5); 7.78 (1 H, brd, J = 8.4); 7.84 (1 H, ddt, J = 8.0, 1.4, 0.8, 0.8); 7.89 (1 H, ddt, J = 8.1, 1.4, 0.8, 0.8); 7.90 (1 H, brd, J = 8.5); 8.59 (1 H, ddt, J = 8.4, 1.2, 0.8, 0.8); 8.60 (1 H, ddt, J = 8.4, 1.3, 0.8, 0.8). ^{13}C NMR: 11.28 (d), 18.56 (q), 21.34 (t), 21.39 (q), 22.36 (q), 34.83 (t), 65.64 (d), 69.39 (t), 81.39 (s), 85.62 (s), 88.29 (s), 94.28 (s), 95.98 (s), 107.90 (s), 119.32 (s), 119.46 (s), 119.51 (s), 125.65 (d), 125.78 (d), 126.24 (d), 126.27 (d), 126.30 (d), 126.96 (d), 127.11 (d), 127.67 (d), 128.06 (d), 128.24 (d), 128.39 (d), 128.66 (d), 128.79 (d), 131.53 (d), 132.08 (s), 132.70 (s), 133.44 (s), 133.74 (s), 138.13 (s), 138.98 (s), 141.75 (s). IR: 3059 w, 3008 m, 2864 vs, 2226 w, 2170 m, 1620 vw, 1608 vw, 1593 w, 1570 w, 1510 s, 1463 s, 1399 m, 1380 m, 1368 w (sh), 1375 m (sh), 1327 m, 1265 m, 1129 w (sh), 1105 m (sh), 1094 s, 1075 m, 1021 m, 997 m, 884 m, 867 w, 819 s, 679 m, 660 m, 616 w, 524 w, 427 w. EI MS: 658 (M^{+} , 2), 615 (3), 515 (8), 449 (6), 341 (16), 326 (8), 302 (10), 289 (11), 187 (6), 173 (15), 159 (23), 143 (100), 129 (23), 115 (36), 103 (10), 87 (26), 73 (48), 59 (52), 43 (35). HR EI MS: calculated for $C_{47}H_{50}OSi$ 658.3631; found 658.3661. $[\alpha]_D^{22}$ -59 (c 0.10).

1-Bromo-2-(but-3-yn-1-yl)naphthalene (**23**)

Tetrabutylammonium fluoride (1 M solution in tetrahydrofuran, 371 μ l, 0.400 mmol, 1.10 equiv.) was added to silylated alkyne **7** (150 mg, 0.360 mmol) in tetrahydrofuran (5 ml) under argon. The mixture was stirred at room temperature for 20 min. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel (petroleum ether–ether 99:1) to afford unprotected alkyne **23** (93 mg, 99%) as an oil. ^1H NMR: 1.99 (1 H, t, $J = 2.6$); 2.61 (2 H, dt, $J = 7.6, 7.6, 2.6$); 3.23 (2 H, t, $J = 7.6$); 7.41 (1 H, d, $J = 8.4$); 7.49 (1 H, ddd, $J = 8.1, 6.9, 1.2$); 7.58 (1 H, ddd, $J = 8.6, 6.9, 1.4$); 7.76 (1 H, brd, $J = 8.4$); 7.81 (1 H, ddt, $J = 8.1, 1.4, 0.7, 0.7$); 8.32 (1 H, ddt, $J = 8.6, 1.0, 0.9, 0.9$). ^{13}C NMR: 18.93 (t), 36.38 (t), 69.19 (d), 83.38 (s), 123.89 (s), 126.10 (d), 127.27 (d), 127.38 (d), 127.55 (d), 128.04 (d), 128.20 (d), 132.54 (s), 133.46 (s), 137.74 (s). IR: 3308 vs, 3058 w, 3013 m, 2944 w, 2918 w, 2871 w, 2842 w, 2119 w, 1624 w, 1598 w, 1558 w, 1502 m, 1463 w, 1453 w, 1431 w, 1353 m, 1329 m, 1259 m, 1253 m, 1146 w, 1135 w, 1031 w, 1016 w, 969 m, 928 w, 905 w, 864 w, 816 s, 643 vs, 639 vs (sh), 480 vw, 470 w, 411 w. EI MS: 260 (M^{++} with ^{81}Br , 30), 258 (M^{++} with ^{79}Br , 30), 221 (97), 219 (100), 179 (67), 152 (7), 140 (50), 89 (8), 76 (8), 63 (9). FAB MS: 259, 232, 221, 215, 197, 186, 181, 165, 152, 141, 123, 115, 110, 105, 91, 75. HR EI MS: calculated for $\text{C}_{14}\text{H}_{11}^{81}\text{Br}$ 260.0024 and for $\text{C}_{14}\text{H}_{11}^{79}\text{Br}$ 258.0044; found 260.0014 and 258.0043, respectively.

1-Bromo-2-(4-*p*-tolylbut-3-yn-1-yl)naphthalene (**24**)

A Schlenk flask was charged with $[\text{Pd}(\text{PPh}_3)_4]$ (18 mg, 0.016 mmol, 5 mole %), CuI (6 mg, 0.031 mmol, 10 mole %), 4-iodotoluene (67 mg, 0.310 mmol, 1.00 equiv.), and flushed with argon. Alkyne **23** (80 mg, 0.310 mmol) in diisopropylamine (3 ml) was added and the mixture was stirred at room temperature for 2 h. Volatiles were removed in vacuo and the residue was chromatographed on silica gel (hexanes–ether 98:2) to afford **24** (105 mg, 97%) as an oil. ^1H NMR: 2.32 (3 H, s); 2.81 (2 H, t, $J = 7.5$); 3.30 (2 H, t, $J = 7.5$); 7.06–7.09 (2 H, m); 7.24–7.27 (2 H, m); 7.46 (1 H, d, $J = 8.3$); 7.49 (1 H, ddd, $J = 8.1, 6.8, 1.2$); 7.58 (1 H, ddd, $J = 8.5, 6.8, 1.3$); 7.76 (1 H, brd, $J = 8.3$); 7.81 (1 H, ddt, $J = 8.1, 1.3, 0.7, 0.7$); 8.33 (1 H, ddt, $J = 8.5, 1.0, 0.8, 0.8$). ^{13}C NMR: 20.00 (t), 21.39 (q), 36.71 (t), 81.61 (s), 88.24 (s), 120.68 (s), 123.92 (s), 126.03 (d), 127.31 (d), 127.33 (d), 127.45 (d), 128.03 (d), 128.41 (d), 128.95 (d), 131.40 (d), 132.57 (s), 133.46 (s), 137.64 (s), 138.11 (s). IR: 3075 m (sh), 3056 s, 3035 m, 3011 vs, 2235 vw, 2225 vw, 1623 w, 1609 w, 1599 m, 1558 s, 1510 vs, 1502 vs, 1463 m, 1452 s, 1430 s, 1407 w, 1375 m, 1354 s, 1344 s, 1331 s, 1308 w (sh), 1273 m, 1258 s, 1181 w, 1146 w, 1135 w, 1119 w, 1043 w (sh), 1031 m, 1022 m, 1013 m, 969 s, 946 w, 932 m, 907 m, 863 m, 818 vs, 642 m, 531 vs, 477 w, 469 w, 413 m. EI MS: 350 (M^{++} with ^{81}Br , 0.95), 348 (M^{++} with ^{79}Br , 1), 269 (100), 254 (14), 221 (23), 219 (24), 140 (28), 129 (33), 85 (9), 77 (6), 71 (12), 57 (22), 43 (20). FAB MS: 349, 307, 289, 279, 271, 257, 232, 215, 197, 181, 165, 147, 141, 131, 123, 110, 91, 75, 57. HR EI MS: calculated for $\text{C}_{21}\text{H}_{17}^{81}\text{Br}$ 350.0493 and $\text{C}_{21}\text{H}_{17}^{79}\text{Br}$ 348.0513; found 350.0507 and 348.0511, respectively.

1-Iodo-2-(4-*p*-tolylbut-3-yn-1-yl)naphthalene (**25**)

Butyllithium (1.6 M solution, 147 μ l, 0.240 mmol, 1.04 equiv.) was added to **24** (80 mg, 0.230 mmol) in tetrahydrofuran (2 ml) at -78°C under argon. The mixture was stirred 15 min at -78°C . Iodine (63 mg, 0.250 mmol, 1.10 equiv.) in tetrahydrofuran (1.5 ml) was added and the reaction mixture was stirred at -78°C for 1 h. The solvent was evaporated in

vacuo and the residue was partitioned between ether and water. The organic layer was separated, washed with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (2×), water, and dried over anhydrous Na_2SO_4 . Volatiles were removed in vacuo and the residue was chromatographed on silica gel (petroleum ether–ether 98:2) to afford iodide **25** (83 mg, 93%) as an oil. ^1H NMR: 2.33 (3 H, s); 2.80 (2 H, t, $J = 7.5$); 3.34 (2 H, t, $J = 7.5$); 7.08 (2 H, m); 7.27 (2 H, m); 7.47 (1 H, d, $J = 8.5$); 7.48 (1 H, ddd, $J = 8.1, 6.8, 1.2$); 7.56 (1 H, ddd, $J = 8.5, 6.8, 1.4$); 7.76 (1 H, brd, $J = 8.5$); 7.76 (1 H, ddt, $J = 8.1, 1.4, 0.7, 0.7$); 8.26 (1 H, ddt, $J = 8.5, 1.2, 0.8, 0.8$). ^{13}C NMR: 20.31 (t), 21.40 (q), 41.98 (t), 81.69 (s), 88.08 (s), 105.39 (s), 120.67 (s), 126.06 (d), 127.70 (d), 127.82 (d), 128.16 (d), 128.56 (d), 128.95 (d), 131.42 (d), 132.76 (d), 132.95 (s), 135.13 (s), 137.65 (s), 142.59 (s). IR: 3081 w (sh), 3055 m, 3033 w, 3011 s, 2233 vw, 1621 w, 1599 w, 1551 m, 1510 vs, 1501 s, 1452 m, 1429 m, 1407 w, 1379 w, 1351 w, 1342 w, 1326 m, 1271 w, 1257 m, 1180 w, 1145 w, 1132 w, 1119 w, 1042 w (sh), 1032 w, 1022 w, 1011 w, 960 m, 947 w (sh), 928 w, 901 w, 862 w, 819 vs, 636 w, 524 m, 478 w, 465 vw, 410 w. EI MS: 396 (M^{+} , 12), 269 (67), 255 (16), 239 (6), 141 (100), 129 (28), 115 (16), 71 (6), 57 (10), 43 (7). FAB MS: 397, 377, 307, 289, 271, 257, 232, 215, 197, 181, 165, 149, 142, 131, 123, 110, 91, 75. HR EI MS: calculated for $\text{C}_{21}\text{H}_{17}\text{I}$ 396.0375; found 396.0370.

2-Methyl-4-{2-[4-(triisopropylsilyl)but-3-yn-1-yl]-1-naphthyl}but-3-yn-2-ol (**26**)

A Schlenk flask was charged with $[\text{Pd}(\text{PPh}_3)_4]$ (63 mg, 0.050 mmol, 5 mole %), CuI (21 mg, 0.110 mmol, 10 mole %), iodide **8** (500 mg, 1.08 mmol), and flushed with argon. Diisopropylamine (8 ml) was added followed by alkyne **13** (380 μl , 3.89 mmol, 3.60 equiv.). The mixture was stirred at 80 °C for 2 h. Volatiles were removed in vacuo and the residue was chromatographed on silica gel (hexanes–ether–acetone 98:2:0 to 80:10:10) to afford **26** (390 mg, 86%) as an oil. ^1H NMR: 0.98–1.06 (21 H, m); 1.75 (6 H, s); 2.67 (2 H, t, $J = 7.5$); 3.21 (2 H, t, $J = 7.5$); 7.41 (1 H, d, $J = 8.4$); 7.46 (1 H, ddd, $J = 8.1, 6.8, 1.2$); 7.54 (1 H, ddd, $J = 8.4, 6.8, 1.4$); 7.74 (1 H, brd, $J = 8.4$); 7.80 (1 H, ddt, $J = 8.1, 1.4, 0.7, 0.7$); 8.28 (1 H, ddt, $J = 8.4, 1.2, 0.8, 0.8$). ^{13}C NMR: 11.27 (d), 18.59 (q), 20.95 (t), 31.69 (q), 34.95 (t), 66.04 (s), 78.56 (s), 81.01 (s), 103.46 (s), 108.08 (s), 118.67 (s), 125.73 (d), 125.91 (d), 126.76 (d), 127.28 (d), 128.02 (d), 128.31 (d), 131.92 (s), 133.47 (s), 141.75 (s). IR: 3599 m, 3059 w, 2865 vs, 2217 vw, 2170 m, 1621 w, 1595 w (sh), 1567 w, 1508 w, 1463 s, 1429 w, 1383 s, 1365 m, 1328 m, 1273 w, 1115 m, 1026 w, 996 m, 886 w, 884 s, 821 m, 679 m, 660 s, 627 m. EI MS: 418 (M^{+} , 12), 375 (46), 333 (14), 317 (13), 303 (7), 287 (8), 273 (16), 261 (27), 245 (32), 229 (30), 215 (16), 202 (23), 191 (30), 178 (18), 165 (41), 152 (16), 131 (25), 115 (11), 103 (70), 75 (100), 61 (66), 43 (48). HR EI MS: calculated for $\text{C}_{28}\text{H}_{38}\text{OSi}$ 418.2691; found 418.2675.

4-[2-(But-3-yn-1-yl)-1-naphthyl]-2-methylbut-3-yn-2-ol (**27**)

Tetrabutylammonium fluoride (1 M solution in tetrahydrofuran, 450 μl , 0.480 mmol, 3.30 equiv.) was added to silylated diyne **26** (61 mg, 0.150 mmol) in tetrahydrofuran (2.5 ml) under argon. The mixture was stirred at room temperature for 45 min. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel (petroleum ether–ether–acetone 80:10:10) to afford diyne **27** (28 mg, 74%) as an oil. ^1H NMR: 1.75 (6 H, s); 1.99 (1 H, t, $J = 2.7$); 2.61 (2 H, dt, $J = 7.5, 7.5, 2.7$); 3.21 (2 H, t, $J = 7.5$); 7.39 (1 H, d, $J = 8.5$); 7.47 (1 H, ddd, $J = 8.1, 6.8, 1.3$); 7.55 (1 H, ddd, $J = 8.4, 6.8, 1.4$); 7.76 (1 H, brd, $J = 8.5$); 7.81 (1 H, ddt, $J = 8.1, 1.4, 0.6, 0.6$); 8.28 (1 H, ddt, $J = 8.4, 1.3, 0.8, 0.8$). ^{13}C NMR: 19.54 (t), 31.69 (q), 34.47 (t), 66.04 (s), 68.95 (d), 78.49 (s), 83.81 (s), 103.55 (s), 118.81 (s),

125.86 (d), 125.94 (d), 126.88 (d), 127.17 (d), 128.07 (d), 128.41 (d), 131.94 (s), 133.48 (s), 141.42 (s). IR: 3598 w, 3308 m, 3059 w, 2218 vw, 2118 vw, 1621 vw, 1593 w, 1567 vw, 1508 w, 1463 w, 1455 w, 1431 w, 1383 m, 1365 m, 1329 m, 1273 w, 1115 w, 1026 vw, 868 w, 820 m, 650 m. EI MS: 262 (M^{++} , 19), 247 (22), 229 (12), 219 (15), 209 (7), 202 (22), 189 (21), 178 (25), 165 (50), 152 (9), 141 (50), 115 (7), 83 (6), 69 (9), 57 (17), 43 (100). HR EI MS: calculated for $C_{19}H_{18}O$ 262.1357; found 262.1348.

2-Methyl-4-[2-(4-*p*-tolylbut-3-yn-1-yl)-1-naphthyl]but-3-yn-2-ol (**28**)

A Schlenk flask was charged with $[Pd(PPh_3)_4]$ (9 mg, 0.008 mmol, 5 mole %), CuI (3 mg, 0.016 mmol, 10 mole %), 4-iodotoluene (37 mg, 0.170 mmol, 1.10 equiv.), and flushed with argon. Alkyne **27** (40 mg, 0.150 mmol) in diisopropylamine (1.5 ml) was added and the mixture was stirred at room temperature for 30 min. Volatiles were removed in vacuo and the residue was chromatographed on silica gel (petroleum ether–ether–acetone 80:10:10) to afford **28** (42 mg, 78%) as an oil. 1H NMR: 1.74 (6 H, s) 2.32 (3 H, s); 2.81 (2 H, t, $J = 7.5$); 3.27 (2 H, t, $J = 7.5$); 7.07 (2 H, m); 7.25 (2 H, m); 7.44 (1 H, d, $J = 8.4$); 7.47 (1 H, ddd, $J = 8.1, 6.8, 1.2$); 7.56 (1 H, ddd, $J = 8.4, 6.8, 1.3$); 7.77 (1 H, brd, $J = 8.4$); 7.81 (1 H, ddt, $J = 8.1, 1.4, 0.6, 0.6$); 8.30 (1 H, ddt, $J = 8.4, 1.2, 0.8, 0.8$). ^{13}C NMR: 20.64 (t), 21.38 (q), 31.67 (q), 34.76 (t), 66.03 (s), 78.63 (s), 81.46 (s), 88.63 (s), 103.39 (s), 118.86 (s), 120.74 (s), 125.78 (d), 125.95 (d), 126.82 (d), 127.36 (d), 128.06 (d), 128.31 (d), 128.94 (d), 131.39 (d), 131.93 (s), 133.51 (s), 137.61 (s), 141.77 (s). IR: 3598 m, 3080 w, 3059 w, 2219 vw, 1621 vw, 1593 w, 1567 w, 1510 vs, 1451 w, 1435 w, 1408 w (sh), 1383 m, 1365 m, 1329 m, 1274 w, 1179 m, 1162 m, 1146 m, 1116 m, 1041 vw, 1022 w, 956 m, 868 w, 846 w, 819 vs, 531 m. EI MS: 352 (M^{++} , 1), 337 (100), 276 (7), 262 (8), 211 (8), 205 (12), 179 (14), 165 (40), 149 (7), 141 (14), 128 (10), 119 (17), 97 (11), 83 (14), 69 (19), 57 (30), 43. FAB MS: 353, 335, 319, 305, 289, 279, 265, 239, 226, 215, 202, 193, 186, 179, 165, 152, 141, 129, 115, 105, 93, 73. HR EI MS: calculated for $C_{26}H_{24}O$ ($M^{++} - CH_3$) 337.1592; found 337.1588.

1-Ethynyl-2-(4-*p*-tolylbut-3-yn-1-yl)naphthalene (**29**)

Sodium hydride (80% suspension in mineral oil, 30 mg, 1.17 mmol, 2.50 equiv.) was added to diyne **28** (138 mg, 0.390 mmol) in toluene (6 ml) under argon. The mixture was stirred at 110 °C for 40 min, then cooled to room temperature, and partitioned between ether and water. The organic layer was separated, washed with brine (2×), and dried over anhydrous Na_2SO_4 . Volatiles were removed in vacuo and the residue was chromatographed on silica gel (petroleum ether–ether–acetone 80:10:10) to afford **29** (90 mg, 78%) as an oil. 1H NMR: 2.33 (3 H, s); 2.82 (2 H, t, $J = 7.5$); 3.32 (2 H, t, $J = 7.5$); 3.72 (1 H, s); 7.09 (2 H, m); 7.26 (2 H, m); 7.47 (1 H, d, $J = 8.4$); 7.48 (1 H, ddd, $J = 8.1, 6.8, 1.2$); 7.57 (1 H, ddd, $J = 8.4, 6.8, 1.4$); 7.80 (1 H, brd, $J = 8.4$); 7.82 (1 H, ddt, $J = 8.1, 1.4, 0.8, 0.8$); 8.38 (1 H, ddt, $J = 8.4, 1.2, 0.9, 0.9$). ^{13}C NMR: 20.66 (t), 21.40 (q), 34.55 (t), 79.98 (s), 81.46 (s), 86.41 (d), 88.62 (s), 118.28 (s), 120.78 (s), 125.87 (d), 126.03 (d), 126.98 (d), 127.36 (d), 128.09 (d), 128.73 (d), 128.94 (d), 131.41 (d), 131.86 (s), 133.90 (s), 137.58 (s), 141.64 (s). IR: 3304 s, 3081 w, 3059 w, 2228 vw, 2098 w, 1621 w, 1602 w, 1593 w, 1568 w, 1510 vs, 1451 w, 1431 w, 1407 vw, 1374 w, 1343 w, 1328 w, 1275 vw, 1268 w, 1181 w, 1146 w, 1118 w, 1041 vw, 1022 w, 868 w, 819 vs, 654 m, 613 m, 557 w, 529 m. EI MS: 294 (M^{++} , 61), 279 (40), 202 (9), 189 (8), 165 (100), 139 (14), 129 (26), 115 (9), 77 (6), 69 (9), 57 (11), 43 (10). FAB MS: 295, 279, 257, 232, 215, 197, 186, 181, 165, 149, 131, 119, 110, 91, 75. HR EI MS: calculated for $C_{23}H_{18}$ 294.1408; found 294.1402.

Triisopropyl[(S)-3-[(1-[[2-(4-*p*-tolylbut-3-yn-1-yl)-1-naphthyl]ethynyl]-2-naphthyl)methoxy]-but-1-yn-1-yl]silane (**30**)

A Schlenk flask was charged with [Pd(PPh₃)₄] (9 mg, 0.010 mmol, 5 mole %), CuI (3.5 mg, 0.020 mmol, 10 mole %), iodide (–)-(S)-**17** (85 mg, 0.170 mmol, 1.01 equiv.), and flushed with argon. Degassed diisopropylamine (2 ml) was added followed by diyne **29** (50 mg, 0.170 mmol) in diisopropylamine (2 ml). The reaction mixture was stirred at room temperature for 1 h and then at 80 °C for 2 h. Volatiles were removed in vacuo and the residue was chromatographed on silica gel (hexanes–ether 99:1) to afford (–)-(S)-**30** (85 mg, 76%) as an oil. ¹H NMR: 0.90–1.00 (21 H, m); 1.54 (3 H, d, *J* = 6.6); 2.32 (3 H, s); 2.94 (2 H, t, *J* = 7.5); 3.50 (2 H, t, *J* = 7.5); 4.43 (1 H, q, *J* = 6.6); 5.21 (1 H, d, *J* = 12.4); 5.31 (1 H, d, *J* = 12.4); 7.05 (2 H, m); 7.24 (2 H, m); 7.52 (2 H, ddd, *J* = 8.1, 6.8, 1.2); 7.55 (1 H, d, *J* = 8.4); 7.59 (1 H, ddd, *J* = 8.4, 6.8, 1.4); 7.61 (1 H, ddd, *J* = 8.4, 6.8, 1.4); 7.74 (1 H, d, *J* = 8.5); 7.84 (1 H, brd, *J* = 8.4); 7.87 (1 H, brdd, *J* = 8.1, 1.4); 7.88 (1 H, brd, *J* = 8.5); 7.88 (1 H, brdd, *J* = 8.1, 1.4); 8.61 (2 H, brd, *J* = 8.4). ¹³C NMR: 11.09 (d), 18.49 (q), 21.12 (t), 21.38 (q), 22.49 (q), 35.07 (t), 65.75 (d), 69.37 (t), 81.64 (s), 86.08 (s), 88.58 (s), 94.26 (s), 95.86 (s), 107.61 (s), 119.22 (s), 119.64 (s), 120.78 (s), 125.72 (d), 125.86 (d), 126.24 (d), 126.33 (d), 126.38 (d), 127.00 (d), 127.12 (d), 127.52 (d), 128.15 (d), 128.20 (d), 128.55 (d), 128.62 (d), 128.89 (d), 131.43 (d), 132.09 (s), 132.68 (s), 133.47 (s), 133.82 (s), 137.52 (s), 139.13 (s), 141.70 (s). IR: 3083 w (sh), 3060 w, 3011 s, 2866 vs, 2230 vvw, 2200 vvw (sh), 2165 w, 1621 w, 1593 w, 1571 w, 1510 s, 1463 s, 1452 w, 1431 w, 1400 m, 1383 w, 1373 w, 1325 m, 1310 w (sh), 1275 w, 1181 w, 1096 s, 1071 m, 1043 w, 1021 m, 997 m, 884 s, 867 w, 819 vs, 680 s, 663 m, 628 w (sh), 530 w, 428 w. EI MS: 658 (M⁺, 0.3), 505 (0.7), 485 (0.3), 471 (0.2), 449 (100), 421 (31), 329 (7), 302 (9), 289 (11), 255 (9), 141 (14), 129 (8), 105 (9), 73 (13), 59 (15), 43 (12). HR EI MS: calculated for C₃₄H₂₅OSi (M⁺ – 209) 449.1905; found 449.1912. [α]_D²² –58 (c 0.11).

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