Supporting Information

Synthesis of 3-Hexahelicenol and Its Transformation to 3-Hexahelicenyl Amines, Diphenylphosphine, Methyl Carboxylate, and Dimethylthiocarbamate

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Experimental Section (For references, see the article)

General. ^1H NMR spectra were measured at 499.8 MHz or 500.13 MHz, ^{13}C NMR spectra at 125.7 MHz, in CDCl_3 with TMS as an internal standard. ^{19}F NMR spectrum was measured at 470.3 MHz in CDCl_3 with CFCl_3 as an internal standard. Chemical shifts are given in δ -scale, coupling constants J are given in Hz. HMBC experiments were setup for $J_{\text{C-H}} = 5$ Hz. For correct assignment of both ^1H and ^{13}C NMR spectra of key compounds, the H COSY and HMQC experiments were performed. For all the other compounds, the general semiempirical equations were applied to the chemical shift assignments. IR spectra 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 or nitrobenzyl alcohol matrix, m/z values are given. HR MS spectra were obtained by the EI or FAB technique. Commercially available reagent grade materials were used as received. Solid $\text{Ni}(\text{cod})_2$ was handled in a glovebox. Decane and diisopropylamine were degassed by three freeze-pump-thaw cycles before use; 1,2-dichloroethane, dichloromethane, toluene, and xylene were distilled from calcium hydride under argon; DMF and DMSO were distilled from calcium hydride under vacuum and stored over 4 Å molecular sieves; methanol was distilled with sodium under argon and stored over 4 Å molecular sieves; THF was freshly distilled from sodium/benzophenone under nitrogen. TLC was performed on Silica gel 60 F₂₅₄-coated aluminium sheets (Merck) and spots were detected by the solution of $\text{Ce}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$ (1 %) and $\text{H}_3\text{P}(\text{Mo}_3\text{O}_{10})_4$ (2 %) in sulfuric acid (10 %). Flash chromatography was performed on Silica gel 60 (0.040-0.063 mm or <0.063 mm, Merck).

4-Bromo-3-[4-(triisopropylsilyl)-3-butynyl]phenyl Methyl Ether **3**. A

mixture of 1-methoxy-3-methylbenzene **1** (6.30 g, 51.57 mmol) and N-bromosuccinimide (19.30 g, 108.43 mmol, 2.1 equiv) in dichloromethane (250 mL) under nitrogen was heated to reflux with an IR lamp for 4 h. After cooling to rt, precipitate was filtered off and rinsed with dichloromethane (200 mL). The filtrate was washed with water (200 mL), dried over Na₂SO₄, and evaporated *in vacuo* to dryness to afford crude **2** (14.30 g, 99 %).¹¹

n-Butyllithium (1.6 M, 21.0 mL, 33.60 mmol, 1.05 equiv) was added to a solution of triisopropyl(1-propynyl)silane (8.05 mL, 33.61 mmol, 1.05 equiv) in THF (180 mL) at -78 °C under argon. After stirring at -78 °C for 1.5 h, **2** (9.01 g, 32.17 mmol) in THF (100 mL) was added and the mixture was kept at -78 °C for 15 min. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel (petroleum ether-ether 99:1 to 95:5) to obtain **3** (12.10 g, 95 %) as an oil. IR: 2959 s, 2944 vs, 2922 s, 2892 m, 2866 vs, 2838 m (sh), 2171 m, 1596 m, 1574 m, 1473 s, 1465 s, 1444 m (sh), 1430 m, 1416 m, 1406 vw (sh), 1387 w (sh), 1382 w, 1367 w, 1337 w, 1304 m, 1292 m, 1278 m, 1252 m, 1192 w, 1161 m, 1130 w, 1117 w, 1072 w, 1058 m, 1043 m, 1021 s, 996 m, 921 w, 884 s, 872 w (sh), 813 w, 678 s, 665 s, 647 m (sh), 601 m. ¹H NMR: 0.99-1.05 (21 H, m, 3 x (CH₃)₂CH), 2.59 (2 H, t, *J* = 7.3, CH₂CH₂C≡C), 2.92 (2 H, t, *J* = 7.3, CH₂CH₂C≡C), 3.77 (3 H, s, CH₃O), 6.64 (1 H, dd, *J* = 8.8, 3.1, 4-H), 6.85 (1 H, d, *J* = 3.1, 6-H), 7.40 (1 H, d, *J* = 8.8, 3-H). ¹³C NMR: 11.3 (d, 3 x (CH₃)₂CH), 18.6 (q, 3 x (CH₃)₂CH), 20.1 (t, CH₂CH₂C≡C), 35.7 (t, CH₂CH₂C≡C), 55.4 (q, CH₃O), 81.2 (s, CH₂CH₂C≡C), 107.5 (s, CH₂CH₂C≡C), 113.4 (d, C-4), 114.7 (s, C-2), 116.8 (d, C-6), 133.2 (d, C-3), 140.6 (s, C-1), 158.8 (s, C-5). EI MS: 396 (M⁺ with ⁸¹Br, 10), 394 (M⁺ with ⁷⁹Br, 9), 353 (100), 351 (99), 325 (11), 323 (11), 311 (14), 309 (14), 272 (10), 256 (7), 229 (25), 215 (9), 201 (22), 187 (11),

173 (8), 149 (21), 97 (8), 83 (15), 55 (12), 43 (17). HR EI MS: calculated for $C_{20}H_{31}^{79}BrOSi$ 394.1328; found 394.1255.

4-Iodo-3-[4-(triisopropylsilyl)-3-butynyl]phenyl Methyl Ether 4. *n*-

Butyllithium (1.6 M solution in hexanes, 29.50 mL, 47.20 mmol, 1.05 equiv) was added dropwise to a stirred solution of aryl bromide **3** (17.78 g, 44.96 mmol) in THF (100 mL) at $-78\text{ }^{\circ}\text{C}$ under argon. After the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 10 min, iodine (12.85 g, 50.62 mmol, 1.13 equiv) in THF (60 mL) was added dropwise. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 20 min and then warmed to room temperature. The reaction mixture was evaporated to dryness *in vacuo*, the residue was diluted with dichloromethane (100 mL), washed with $Na_2S_2O_3$ (2 x), water (1 x), and dried over anhydrous Na_2SO_4 . The solvent was removed *in vacuo* to afford pure iodide **4** as an oil (19.09 g, 96 %). IR: 3077 vw, 3065 vw, 2960 vs, 2944 vs, 2922 s, 2892 s, 2866 vs, 2840 m (sh), 2171 s, 1591 m, 1568 s, 1467 vs, 1429 m, 1412 m, 1383 m, 1366 w, 1336 w, 1302 s, 1293 s, 1277 s, 1238 vs, 1173 m (sh), 1162 m, 1112 w, 1072 m, 1056 s, 1043 s, 996 m, 953 w, 884 s, 678 s, 661 s, 611 m, 593 m. 1H NMR: 0.94-1.10 (21 H, m, 3 x $(CH_3)_2CH$), 2.56 (2 H, t, $J = 7.3$, $CH_2CH_2C\equiv C$), 2.90 (2 H, t, $J = 7.3$, $CH_2CH_2C\equiv C$), 3.77 (3 H, s, CH_3O), 6.51 (1 H, dd, $J = 8.7, 3.0$, 4-H), 6.87 (1 H, d, $J = 3.0$, 6-H), 7.66 (1 H, d, $J = 8.7$, 3-H). ^{13}C NMR: 11.3 (d, 3 x $(CH_3)_2CH$), 18.6 (q, 3 x $(CH_3)_2CH$), 20.4 (t, $CH_2CH_2C\equiv C$), 40.1 (t, $CH_2CH_2C\equiv C$), 55.3 (q, CH_3O), 81.3 (s, $CH_2CH_2C\equiv C$), 88.7 (s, C-2), 107.4 (s, $CH_2CH_2C\equiv C$), 113.9 (d, C-6), 116.3 (d, C-4), 139.8 (d, C-3), 143.9 (s, C-1), 159.9 (s, C-5). EI MS: 442 (M^+ , 10), 399 (100), 371 (9), 351 (15), 329 (9), 273 (29), 247 (9), 229 (30), 215 (9), 201 (18), 171 (11), 121 (14), 73 (8), 59 (18). HR EI MS: calculated for $C_{20}H_{31}IOSi$ 442.1189; found 442.1191.

[4-(1-Bromo-2-naphthyl)-1-butyne](triisopropyl)silane 6. *n*-Butyllithium (1.6 M solution in hexanes, 57.90 mL, 92.64 mmol, 1.04 equiv) was added dropwise to a solution of triisopropyl(1-propynyl)silane (22.20 mL, 92.68 mmol, 1.04 equiv) in THF (100 mL) at $-78\text{ }^{\circ}\text{C}$ under argon. After the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 2.5 h, dibromide **5** (26.65 g, 88.84 mmol) in THF (130 mL) was added dropwise. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h and then warmed to room temperature. The solvents were removed *in vacuo*. The residue was suspended in petroleum ether, solids were filtered off, and the solution was concentrated *in vacuo*. Flash chromatography on silica gel (petroleum ether) gave alkyne **6** (33.83 g, 91 %) as an oil. IR: 3057 w, 3037 vw, 3009 vw, 2959 s, 2944 vs, 2924 s, 2891 m, 2866 vs, 2171 m, 1624 vw, 1599 vw, 1558 w, 1503 w, 1463 m, 1452 w (sh), 1429 w, 1383 w, 1366 w, 1358 w, 1327 w, 1146 vw, 1073 w, 1029 w, 996 w, 884 m, 861 w, 678 s, 660 m, 622 m, 531 m. ^1H NMR: 0.99-1.04 (21 H, m, 3 x $(\text{CH}_3)_2\text{CH}$), 2.67 (2 H, t, $J = 7.3$, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 3.22 (2 H, t, $J = 7.3$, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 7.45 (1 H, d, $J = 8.3$, 3-H), 7.48 (1 H, ddd, $J = 8.0, 6.9, 1.2$, 6-H), 7.57 (1 H, ddd, $J = 8.4, 6.9, 1.3$, 7-H), 7.72 (1 H, brd, $J = 8.3$, 4-H), 7.80 (1 H, brd, $J = 8.0$, 5-H), 8.31 (1 H, dq, $J = 8.4, 0.9, 0.9, 0.9$, 8-H). ^{13}C NMR: 11.3 (d, 3 x $(\text{CH}_3)_2\text{CH}$), 18.6 (q, 3 x $(\text{CH}_3)_2\text{CH}$), 20.4 (t, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 36.7 (t, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 81.4 (s, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 107.6 (s, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 123.8 (s, C-1), 126.0 (d, C-6), 126.3 (d, C-4), 127.3 (d, C-8), 127.4 (d, C-7), 128.0 (d, C-5), 128.5 (d, C-3), 132.5 (s, C-4a), 133.5 (s, C-8a), 138.1 (s, C-2). EI MS: 416 (M^{++} with ^{81}Br , 12), 414 (M^{++} with ^{79}Br , 12), 373 (100), 371 (98), 343 (8), 293 (7), 249 (23), 235 (8), 221 (56), 219 (26), 207 (28), 205 (27), 191 (11), 178 (19), 159 (14), 140 (17), 73 (8), 59 (14). HR EI MS: calculated for $\text{C}_{23}\text{H}_{31}^{79}\text{BrSi}$ 414.1378; found 414.1435.

[4-(1-Iodo-2-naphthyl)-1-butynyl](triisopropyl)silane 7. *n*-Butyllithium (1.6 M solution in hexanes, 53.0 mL, 84.80 mmol, 1.04 equiv) was added dropwise to a stirred solution of aryl bromide **6** (33.83 g, 81.43 mmol) in THF (120 mL) at -78°C under argon. After the mixture was stirred at -78°C for 15 min, iodine (22.68 g, 89.36 mmol, 1.1 equiv) in THF (100 mL) was added dropwise. The mixture was stirred at -78°C for 20 min and then warmed to room temperature. The reaction mixture was evaporated to dryness *in vacuo*, the residue was diluted with ether (100 mL), washed with $\text{Na}_2\text{S}_2\text{O}_3$ (2 x), water (1 x), and dried over anhydrous Na_2SO_4 . The solvent was removed *in vacuo* to afford pure iodide **7** (36.88 g, 98 %) as an oil. ^1H NMR spectrum was in agreement with the literature data.¹²

Triisopropyl(4-{1-[(trimethylsilyl)ethynyl]-2-naphthyl}-1-butynyl)silane 8. A teflon autoclave was charged with aryl iodide **7** (13.11 g, 28.35 mmol), $\text{Pd}(\text{PPh}_3)_4$ (344 mg, 0.298 mmol, 1 mol %), CuI (110 mg, 0.578 mmol, 2 mol %), and flushed with argon. Diisopropylamine (60 mL) and $\text{TMS-C}\equiv\text{CH}$ (4.70 mL, 33.26 mmol, 1.17 equiv) were added and the reaction was stirred at 80°C for 1.5 h. The precipitate was filtered off and washed with petroleum ether (5 x 10 mL). The combined fractions were evaporated to dryness *in vacuo* and the residue was chromatographed on a short pad of silica gel (petroleum ether) to obtain **8** (12.15 g, 99 %) as an oil. IR: 3059 w, 3012 vw, 2866 s, 2171 m, 2153 m, 2143 m, 1623 vw, 1592 w, 1508 w, 1463 m, 1408 w, 1381 w, 1367 w, 1262 w, 1251 s, 1146 w, 1074 m, 1026 w, 996 w, 883 s, 877 s, 845 vs, 820 m, 698 w, 676 s, 660 m, 629 m, 523 w. ^1H NMR: 0.34 (9 H, s, $(\text{CH}_3)_3\text{Si}$), 0.90-1.12 (21 H, m, 3 x $(\text{CH}_3)_2\text{CH}$), 2.67 (2 H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 3.23 (2 H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 7.41 (1 H, d, $J = 8.4$, 3-H), 7.46 (1 H, ddd, $J = 8.1$, 6.8, 1.3, 6-H), 7.55 (1 H, ddd, $J = 8.4$, 6.8, 1.3, 7-H), 7.73 (1 H, d, $J = 8.4$, 4-H), 7.79

(1 H, brd, $J = 8.1$, 5-H), 8.33 (1 H, dq, $J = 8.4$, 0.9, 0.9, 0.9, 8-H). ^{13}C NMR: 0.1 (q, $(\text{CH}_3)_3\text{Si}$), 11.3 (d, 3 x $(\text{CH}_3)_2\text{CH}$), 18.6 (q, 3 x $(\text{CH}_3)_2\text{CH}$), 20.8 (t, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 33.0 (t, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 80.9 (s, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 101.3 (s, $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}$), 104.3 (s, $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}$), 108.2 (s, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 119.3 (s, C-1), 125.7 (d, C-3), 126.1 (d, C-8), 126.8 (d, C-6), 127.3 (d, C-7), 128.0 (d, C-5), 128.4 (d, C-4), 131.9 (s, C-4a), 133.6 (s, C-8a), 142.4 (s, C-2). EI MS: 432 (M^+ , 43), 389 (100), 359 (5), 347 (12), 336 (13), 315 (11), 293 (35), 273 (7), 245 (20), 219 (16), 205 (10), 141 (16), 101 (12), 87 (14), 73 (68), 59 (47). HR EI MS: calculated for $\text{C}_{28}\text{H}_{40}\text{Si}_2$ 432.2669; found 432.2699; calculated for $\text{C}_{25}\text{H}_{33}\text{Si}_2$ (M- C_3H_7) 389.2121; found 389.2140.

[4-(1-Ethynyl-2-naphthyl)-1-butynyl](triisopropyl)silane 9. Sodium

methanolate generated from sodium (1.94 g, 84.39 mmol, 1.7 equiv) and methanol (40 mL) was added to TMS derivative **8** (21.49 g, 49.67 mmol) in methanol (500 mL) under argon and the mixture was stirred at room temperature for 16 h. The solution was evaporated *in vacuo* to dryness and the residue was chromatographed on silica gel (petroleum ether) to obtain **9** (17.73 g, 99 %) as an oil. IR: 3311 m, 3060 w, 3014 vw, 2866 vs, 2171 m, 2099 vw, 1623 vw, 1593 w, 1508 w, 1463 m, 1451 w (sh), 1430 w, 1383 w, 1367 w, 1325 w, 1268 w, 1072 w, 1026 w, 996 w, 884 m, 865 w, 678 s, 660 s, 650 s, 607 m. ^1H NMR: 0.92-1.07 (21 H, m, 3 x $(\text{CH}_3)_2\text{CH}$), 2.69 (2 H, t, $J = 7.4$, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 3.25 (2 H, t, $J = 7.4$, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 3.70 (1 H, s, $\text{C}\equiv\text{CH}$), 7.45 (1 H, d, $J = 8.4$, 3-H), 7.47 (1 H, ddd, $J = 8.2$, 6.9, 1.3, 6-H), 7.55 (1 H, ddd, $J = 8.4$, 6.9, 1.3, 7-H), 7.76 (1 H, brd, $J = 8.4$, 4-H), 7.81 (1 H, brd, $J = 8.1$, 5-H), 8.36 (1 H, brdq, $J = 8.4$, 1.0, 1.0, 1.0, 8-H). ^{13}C NMR: 11.3 (d, 3 x $(\text{CH}_3)_2\text{CH}$), 18.6 (q, 3 x $(\text{CH}_3)_2\text{CH}$), 21.0 (t, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 34.5 (t, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 80.0 (s, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 81.2 (s, $\text{C}\equiv\text{CH}$), 86.4 (d, $\text{C}\equiv\text{CH}$), 108.0 (s, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 118.2 (s, C-1), 125.8 (d, C-3), 126.0 (d, C-

8), 126.9 (d, C-6), 127.4 (d, C-7), 128.0 (d, C-5), 128.7 (d, C-4), 131.8 (s, C-4a), 133.9 (s, C-8a), 142.6 (s, C-2). EI MS: 360 (M^+ , 52), 317 (35), 275 (100), 259 (14), 247 (30), 233 (67), 219 (23), 202 (22), 189 (11), 165 (38), 139 (7), 130 (15), 73 (17), 59 (54). HR EI MS: calculated for $C_{25}H_{32}Si$ 360.2273; found 360.2233.

Methyl 3-[4-(Triisopropylsilyl)-3-butynyl]-4-({2-[4-(triisopropylsilyl)-3-butynyl]-1-naphthyl}ethynyl)phenyl Ether 10. A Schlenk flask was charged with phenyl iodide **4** (5.54 g, 12.52 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (302 mg, 0.261 mmol, 2 mol %), CuI (99 mg, 0.519 mmol, 4 mol %), and flushed with argon. Diisopropylamine (20 mL) and then naphthyl acetylene **9** (4.52 g, 12.53 mmol, 1.0 equiv) in diisopropylamine (20 mL) were added and the reaction mixture was stirred at 80 °C for 15 min. The precipitate was filtered off and washed with petroleum ether (5 x 10 mL). The combined fractions were evaporated to dryness *in vacuo* and the residue was chromatographed on silica gel (petroleum ether-ether 99:1) to obtain **10** (7.61 g, 90 %) as an oil. IR: 3058 w, 2958 vs, 2944 vs, 2920 s (sh), 2891 s, 2865 vs, 2198 w, 2170 s, 1605 s, 1564 m, 1508 m (sh), 1499 s, 1464 s, 1428 m, 1383 m, 1366 w, 1306 m, 1297 m, 1282 m, 1239 s, 1166 m, 1160 m, 1111 m, 1072 w, 1059 m, 1025 m, 1037 m, 996 m, 951 w, 884 s, 866 w, 816 m, 678 s, 661 s, 598 m. 1H NMR: 1.0-1.05 (42 H, m, 6 x $(CH_3)_2CH$), 2.75 (2 H, t, $J = 7.4$, $NphCH_2CH_2C\equiv C$), 2.77 (2 H, t, $J = 7.3$, $PhCH_2CH_2C\equiv C$), 3.17 (2 H, t, $J = 7.3$, $PhCH_2CH_2C\equiv C$), 3.31 (2 H, t, $J = 7.4$, $NphCH_2CH_2C\equiv C$), 3.84 (3 H, s, CH_3O), 6.80 (1 H, dd, $J = 8.6, 2.6$, 6-H (Ph)), 6.91 (1 H, d, $J = 2.6$, 2-H (Ph)), 7.47 (1 H, d, $J = 8.4$, 3-H (Nph)), 7.47 (1 H, ddd, $J = 8.2, 6.8, 1.2$, 6-H (Nph)), 7.57 (1 H, ddd, $J = 8.3, 6.8, 1.3$, 7-H), 7.60 (1 H, d, $J = 8.6$, 5-H (Ph)), 7.73 (1 H, brd, $J = 8.4$, 4-H (Nph)), 7.82 (1 H, ddt, $J = 8.2, 1.3, 0.8, 0.8$, 5-H (Nph)), 8.42 (1 H, dq, $J = 8.4, 1.1, 1.1, 1.1$, 8-H). ^{13}C NMR: 11.29 (d, $((CH_3)_2CH)_3Si$ -

C≡C-CH₂CH₂-Ph), 11.31 (d, ((CH₃)₂CH)₃Si-C≡C-CH₂CH₂-Nph), 18.6 (q, 6 x (CH₃)₂CH), 21.1 (t, C≡C-CH₂CH₂-Nph), 21.3 (t, C≡C-CH₂CH₂-Ph), 34.7 (t, C≡C-CH₂CH₂-Nph), 35.0 (t, C≡C-CH₂CH₂-Ph), 55.3 (q, CH₃O), 81.1 (s, C≡C-CH₂CH₂-Nph), 81.2 (s, C≡C-CH₂CH₂-Ph), 88.5 (s, Ph-C≡C-Nph), 97.5 (s, Ph-C≡C-Nph), 107.8 (s, C≡C-CH₂CH₂-Nph), 108.1 (s, C≡C-CH₂CH₂-Ph), 112.1 (d, C-6 (Ph)), 115.19 (s, C-4 (Ph)), 115.21 (d, C-2 (Ph)), 119.8 (s, C-1 (Nph)), 125.7 (d, C-6 (Nph)), 126.1 (d, C-7), 126.7 (d, C-4 (Nph)), 127.55 (d, C-5 (Nph)), 127.57 (d, C-8), 128.1 (d, C-3 (Nph)), 132.0 (s, C-8a), 133.5 (s, C-4a), 134.0 (d, C-5 (Ph)), 141.1 (s, C-2 (Nph)), 143.8 (s, C-3 (Ph)), 159.8 (s, C-1 (Ph)).

EI MS: 674 (M⁺, 12), 631 (10), 517 (5), 368 (13), 327 (7), 264 (12), 236 (12), 157 (44), 115 (86), 73 (88), 57 (93), 43 (100). FAB MS (nitrobenzyl alcohol matrix): 675 ((M+H)⁺), 674 (M⁺), 589, 517. HR FAB MS: calculated for C₄₅H₆₂OSi₂ 674.4339; found 674.4321.

2-(3-Butynyl)-1-[[2-(3-butynyl)-4-methoxyphenyl]ethynyl]naphthalene **11.**

Tetrabutylammonium fluoride (1.07 M solution in THF, 17.70 mL, 18.97 mmol, 2.4 equiv) was added to silylated triyne **10** (5.33 g, 7.89 mmol) in THF (50 mL) under argon and the mixture was stirred at rt for 15 min. The solution was evaporated *in vacuo* to dryness and the residue was chromatographed on silica gel (petroleum ether-ether 95:5) to obtain **11** (2.12 g, 74 %) as an oil. IR: 3308 s, 3059 w, 2840 w, 2253 vw, 2199 w, 2118 w, 1718 w, 1605 s, 1565 m, 1497 s, 1466 m, 1457 m, 1430 m, 1307 s, 1298 m, 1283 s, 1239 vs, 1160 m, 1112 m, 1057 m, 1038 m, 1025 w, 955 w, 867 w, 819 s, 812 m, 640 s, 539 w, 449 w. ¹H NMR: 2.00 (1 H, t, *J* = 2.7, PhCH₂CH₂C≡CH), 2.03 (1 H, t, *J* = 2.6, NphCH₂CH₂C≡CH), 2.68 (2 H, dt, *J* = 7.7, 7.7, 2.6, NphCH₂CH₂C≡CH), 2.68 (2 H, dt, *J* = 7.6, 7.6, 2.7, PhCH₂CH₂C≡CH), 3.20

(2 H, t, $J = 7.6$, $\text{PhCH}_2\text{CH}_2\text{C}\equiv\text{CH}$), 3.31 (2 H, t, $J = 7.7$, $\text{NphCH}_2\text{CH}_2\text{C}\equiv\text{CH}$), 3.86 (3 H, s, CH_3O), 6.83 (1 H, dd, $J = 8.4, 2.6$, 5-H (Ph)), 6.91 (1 H, d, $J = 2.6$, 3-H (Ph)), 7.44 (1 H, d, $J = 8.4$, 3-H (Nph)), 7.49 (1 H, ddd, $J = 8.1, 6.9, 1.2$, 6-H (Nph)), 7.59 (1 H, ddd, $J = 8.3, 6.9, 1.3$, 7-H), 7.61 (1 H, d, $J = 8.4$, 6-H (Ph)), 7.77 (1 H, brd, $J = 8.4$, 4-H (Nph)), 7.83 (1 H, ddt, $J = 8.0, 1.3, 0.5, 0.5$, 5-H (Nph)), 8.44 (1 H, ddt, $J = 8.4, 1.2, 0.8, 0.8$, 8-H). ^{13}C NMR: 19.77 (t, $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_2-\text{Nph}$), 19.79 (t, $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_2-\text{Ph}$), 34.3 (t, $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_2-\text{Nph}$), 34.6 (t, $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_2-\text{Ph}$), 55.4 (q, CH_3O), 69.1 (d, $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_2-\text{Ph}$), 69.2 (d, $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_2-\text{Nph}$), 83.6 (s, $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_2-\text{Nph}$), 83.8 (s, $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_2-\text{Ph}$), 88.4 (s, $\text{Ph}-\text{C}\equiv\text{C}-\text{Nph}$), 97.3 (s, $\text{Ph}-\text{C}\equiv\text{C}-\text{Nph}$), 112.2 (d, C-5 (Ph)), 114.9 (d, C-3 (Ph)), 115.2 (s, C-1 (Ph)), 119.8 (s, C-1 (Nph)), 125.8 (d, C-8), 126.2 (d, C-3 (Nph)), 126.9 (d, C-6 (Nph)), 127.3 (d, C-7), 128.07 (d, C-5 (Nph)), 128.12 (d, C-4 (Nph)), 132.0 (s, C-4a), 133.5 (s, C-8a), 134.0 (d, C-6 (Ph)), 140.8 (s, C-2 (Nph)), 143.6 (s, C-2 (Ph)), 159.8 (s, C-4 (Ph)). EI MS: 362 (M^+ , 100), 347 (36), 331 (13), 303 (19), 289 (19), 277 (28), 265 (27), 252 (18), 239 (40), 226 (14), 215 (17), 202 (18), 189 (16), 165 (15), 138 (20), 126 (18), 121 (37), 91 (7), 55 (11), 43 (13). HR EI MS: calculated for $\text{C}_{27}\text{H}_{22}\text{O}$ 362.1671; found 362.1687.

3-Methoxy-5,6,9,10-tetrahydrohexahelicene 12. *Catalysis with $\text{CpCo}(\text{CO})_2$:*

A Schlenk flask was charged with triyne **11** (1.0 g, 2.76 mmol) and flushed with argon. The substrate was dissolved in decane (15 mL) at 90 °C. Then a solution of triphenylphosphine (292 mg, 1.11 mmol, 40 mol %) in hot decane (5 mL) and $\text{CpCo}(\text{CO})_2$ (75 μL , 0.567 mmol, 20 mol %) in decane (2 mL) were added and the mixture was stirred at 140 °C for 2.5 h under concomitant irradiation with a halogen lamp. The crude reaction mixture was chromatographed on silica gel (petroleum ether-ether 95:5 to 80:20) to obtain **12** (675 mg, 68 %) as solid, mp 194.5-195 °C

(petroleum ether). *Catalysis with $\text{Co}_2(\text{CO})_8$* : A Schlenk flask was charged with triyne **11** (107 mg, 0.295 mmol) and flushed with argon. Dioxane (2 mL) was added, the solution was heated to 100 °C, and $\text{Co}_2(\text{CO})_8$ (40 mg, 0.123 mmol, 40 mol %) in dioxane (3 mL) was added in two portions. The reaction mixture was stirred at 100 °C for 1 h and then filtered through a short pad of silica gel (eluted with petroleum ether-ether 95:5) to obtain **12** (57.6 mg, 54 %). *Catalysis with $\text{Ni}(\text{cod})_2$ and (S)-(-)-BOP*: A Schlenk flask was charged with (S)-(-)-BOP (12 mg, 0.022 mmol, 40 mol %), flushed with argon, the ligand was dissolved in THF (1.5 mL) and the solution was cooled to -20 °C. Then $\text{Ni}(\text{cod})_2$ (3.1 mg, 0.011 mmol, 20 mol %) in THF (0.5 mL) was added and the solution was stirred at -20 °C for 5 min. Triyne **11** (20 mg, 0.055 mmol) in THF (1 mL) was added dropwise and the mixture was stirred at -20 °C for 0.1 h. To destroy the phosphine ligand that might interfere during a chiral HPLC on an analytical Chiracel OD-H column, the excess of methyl iodide was added. The mixture was stirred at rt for 1 h, volatiles were removed *in vacuo* and the residue was chromatographed on silica gel (petroleum ether-ether 100:0 to 99:1) to obtain **12** (14.8 mg, 74 %). IR: 2943 m, 2899 m, 2837 m, 1610 m, 1587 w, 1569 w, 1560 w, 1509 w, 1500 s, 1466 m, 1436 m, 1423 w, 1417 w, 1308 m, 1188 w, 1039 m. ^1H NMR: 2.66 (1 H, tdt, $J = 15.0, 15.0, 4.6, 1.5, 1.5$, 9-H), 2.72 (1 H, tdt, $J = 15.4, 15.4, 4.2, 1.3, 1.3$, 5-H), 2.83 (1 H, ddd, $J = 15.4, 4.6, 2.0$, 5-H), 2.84 (1 H, ddd, $J = 15.0, 4.2, 2.3$, 9-H), 2.90 (1 H, ddd, $J = 14.2, 4.2, 2.0$, 6-H), 2.91 (1 H, ddd, $J = 14.9, 4.6, 2.3$, 10-H), 2.99 (1 H, td, $J = 14.9, 14.9, 4.2$, 10-H), 3.02 (1 H, dddt, $J = 15.4, 14.2, 4.6, 1.0, 1.0$, 6-H), 3.61 (3 H, s, CH_3O), 5.90 (1 H, ddd, $J = 8.7, 2.8, 0.9$, 2-H), 6.28 (1 H, d, $J = 8.7$, 1-H), 6.70 (1 H, dd, $J = 2.8, 0.9$, 4-H), 6.86 (1 H, ddd, $J = 8.3, 6.7, 1.3$, 15-H), 7.11 (1 H, ddd, $J = 8.1, 6.7, 1.2$, 14-H), 7.17 (1 H, dd, $J = 7.5, 1.0$, 8-H), 7.20 (1 H, dd, $J = 7.5, 1.0$, 7-H), 7.46 (1 H, d, $J = 8.1$, 11-H), 7.47 (1 H, dq, $J = 8.3, 0.9$,

0.9, 0.9, 16-H), 7.63 (1 H, brd, $J = 8.1$, 12-H), 7.68 (1 H, brd, $J = 8.1$, 13-H). ^{13}C NMR: 29.9 (t, C-9), 30.4 (t, C-6), 30.7 (t, C-10), 31.1 (t, C-5), 55.0 (q, CH_3O), 110.6 (d, C-2), 112.4 (d, C-4), 124.2 (d, C-11), 124.8 (d, C-13), 125.4 (d, C-15), 126.1 (d, C-14, 16), 126.2 (d, C-12), 127.4 (d, C-7), 127.5 (d, C-8), 128.4 (s, C-6a), 129.23 (s, C-8a), 129.28 (d, C-1), 130.5 (s, C-16d), 132.2 (s, C-16c), 132.9 (s, C-16e), 134.2 (s, C-10a), 137.3 (s, C-12a), 138.0 (s, C-16b), 139.5 (s, C-16a), 140.6 (s, C-4a), 157.8 (s, C-3). EI MS: 362 (M^+ , 100), 181 (6), 150 (5). HR EI MS: calculated for $\text{C}_{27}\text{H}_{22}\text{O}$ 362.1671; found 362.1658.

5,6,9,10-Tetrahydro-3-hexahelicenol 13. A Schlenk flask was charged with methyl ether **12** (110 mg, 0.303 mmol) and flushed with argon. The material was dissolved in dichloromethane (5 mL) and BBr_3 (1.0 M solution in dichloromethane, 1.40 mL, 1.40 mmol, 4.6 equiv) was added dropwise. The mixture was stirred at room temperature for 40 min and quenched with aqueous KHCO_3 (saturated, 10 mL). The product was extracted with dichloromethane (3 x 15 mL), organic portions were combined and dried over anhydrous Na_2SO_4 . The solvent was evaporated *in vacuo* and the residue was chromatographed on silica gel (petroleum ether-ether 90:10) to get **13** (94 mg, 89 %) as an amorphous solid. IR: 3597 m, 2944 m, 2899 m, 2838 m, 1612 m, 1588 m, 1574 w, 1562 w, 1509 m, 1500 s, 1471 w, 1462 w, 1436 s, 1425 m, 1415 w, 1187 s. ^1H NMR: 2.66 (1 H, tdt, $J = 15.0, 15.0, 4.5, 1.5, 1.5$, 5-H), 2.72 (1 H, tdt, $J = 15.0, 15.0, 4.5, 1.5, 1.5$, 9-H), 2.81 (1 H, ddd, $J = 15.0, 4.3, 2.0$, 5-H), 2.85 (1 H, ddd, $J = 14.8, 4.2, 2.1$, 9-H), 2.90 (1 H, ddd, $J = 14.5, 4.5, 2.2$, 6-H), 2.92 (1 H, ddd, $J = 15.1, 4.5, 2.1$, 10-H), 2.99 (1 H, td, $J = 15.0, 15.0, 4.2$, 10-H), 3.00 (1 H, dddt, $J = 15.0, 14.5, 4.3, 1.0, 1.0$, 6-H), 5.82 (1 H, ddd, $J = 8.5, 2.8, 0.8$, 2-H), 6.23 (1 H, d, $J = 8.5$, 1-H), 6.64 (1 H, ddt, $J = 2.8, 1.0, 0.6, 0.6$, 4-H), 6.89 (1 H, ddd, $J = 8.7$,

6.7, 1.4, 15-H), 7.13 (1 H, ddd, $J = 8.0, 6.7, 1.2$, 14-H), 7.18 (1 H, dd, $J = 7.2, 1.2$, 8-H), 7.21 (1 H, dd, $J = 7.2, 1.2$, 7-H), 7.46 (1 H, brd, $J = 8.2$, 11-H), 7.47 (1 H, ddt, $J = 8.6, 1.2, 0.7, 0.7$, 16-H), 7.64 (1 H, ddt, $J = 8.1, 1.4, 0.6, 0.6$, 12-H), 7.69 (1 H, ddt, $J = 8.0, 1.4, 0.6, 0.6$, 13-H). ^{13}C NMR: 29.8 (t, C-10), 30.2 (t, C-6), 30.6 (t, C-9), 31.1 (t, C-5), 112.2 (d, C-2), 113.8 (d, C-4), 124.2 (d, C-11), 124.8 (d, C-13), 125.4 (d, C-15), 126.10 (d, C-16), 126.13 (d, C-14), 126.2 (d, C-12), 127.4 (d, C-8), 127.5 (d, C-7), 128.5 (s, C-6a), 129.3 (s, C-8a), 129.4 (d, C-1), 130.5 (s, C-16d), 132.1 (s, C-16c), 133.0 (s, C-16e), 134.1 (s, C-10a), 137.3 (s, C-12a), 138.0 (s, C-16b), 140.0 (s, C-16a), 140.6 (s, C-4a), 153.7 (s, C-3). EI MS: 348 (M^+ , 100), 331 (7), 265 (8), 174 (7), 149 (11), 97 (8), 91 (13), 73 (22), 69 (23), 57 (20), 41 (23). HR EI MS: calculated for $\text{C}_{26}\text{H}_{20}\text{O}$ 348.1514; found 348.1501.

3-Methoxyhexahelicene 14. A solution of **12** (200 mg, 0.552 mmol) and Ph_3CBF_4 (613 mg, 1.86 mmol, 3.4 equiv) in 1,2-dichloroethane (5 mL) was stirred under argon at 80 °C for 2 hours. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel (petroleum ether-ether 99:1) to obtain **14** (196 mg, 99 %) as solid, mp 223-224 °C (petroleum ether-ether). IR: 3051 m, 2960 w, 2837 w, 1621 s, 1610 s, 1585 w, 1556 w, 1524 w, 1513 m, 1500 m, 1487 m, 1463 s, 1455 m, 1437 m, 1432 m, 1401 w, 1297 m, 1276 s, 1256 s, 1237 vs, 1166 m, 1158 m, 1116 m, 1037 s, 909 s, 853 vs, 841 vs, 834 m, 634 s, 535 m, 527 m. ^1H NMR: 3.83 (3 H, s, CH_3O), 6.33 (1 H, dd, $J = 9.3, 2.8$, 2-H), 6.72 (1 H, ddd, $J = 8.5, 6.8, 1.4$, 15-H), 7.17 (1 H, bd, $J = 2.8$, 4-H), 7.23 (1 H, ddd, $J = 8.0, 6.8, 1.2$, 14-H), 7.49 (1 H, dt, $J = 9.3, 0.7, 0.7$, 1-H), 7.62 (1 H, ddt, $J = 8.5, 1.2, 0.7, 0.7$, 16-H), 7.82 (1 H, dd, $J = 8.0, 1.4$, 13-H), 7.84 (1 H, dt, $J = 8.5, 0.6, 0.6$, 5-H), 7.90 (1 H, dt, $J = 8.6, 0.5, 0.5$, 12-H), 7.92 (1 H, d, $J = 8.5$, 6-H), 7.93 (1 H, d, $J = 8.0$, 7-H), 7.93 (1 H, d, $J = 8.6$, 11-

H), 7.95 (2 H, d, $J = 8.0$ Hz, 8,10-H), 7.98 (1 H, d, $J = 8.0$ Hz, 9-H). ^{13}C NMR: 55.2 (q, CH_3O), 107.0 (d, C-4), 115.6 (d, C-2), 123.8 (s, C-8a), 124.75 (d, C-15), 124.79 (s, C-6a), 125.6 (d, C-14), 125.9 (d, C-7), 126.1 (d, C-9), 126.8 (d, C-11), 126.9 (d, C-5), 127.2 (d, C-16), 127.26 (d, C-13), 127.28 (d, C-12), 127.5 (d, C-10), 127.7 (d, C-8), 127.8 (d, C-6), 128.1 (s, C-16b), 128.3 (s, C-16d), 129.3 (d, C-1), 129.8 (s, C-16e), 130.14 (s, C-16a), 131.18 (s, C-10a), 131.8 (s, C-12a), 133.22 (s, C-16c), 133.27 (s, C-4a), 157.2 (s, C-3). EI MS: 358 (M^+ , 100), 313 (17), 300 (27), 287 (6), 162 (7), 156 (14), 150 (16), 144 (9). HR EI MS: calculated for $\text{C}_{27}\text{H}_{18}\text{O}$ 358.1358; found 358.1366.

3-Hexahelicenol 15. A Schlenk flask was charged with methyl ether **14** (459 mg, 1.28 mmol) and flushed with nitrogen. The material was dissolved in dichloromethane (20 mL), cooled to -78°C , and BBr_3 (1.0 M solution in dichloromethane, 1.30 mL, 1.30 mmol, 3.0 equiv) was added dropwise. The mixture was allowed to reach room temperature and stirring was continued at room temperature for 2 days. The mixture was diluted with water, extracted with dichloromethane (150 mL), organic layer was washed with water (10 mL) and dried over anhydrous Na_2SO_4 . The solvent was evaporated *in vacuo* to obtain crude **15** (437 mg, 99 %), which was sufficiently pure for further elaboration. Alternatively, crude **15** was chromatographed on silica gel (petroleum ether-ether-acetone 80:10:10) to afford **15** (335 mg, 76 %) as an amorphous solid. IR: 3594 m, 3507 vw, 1621 m, 1584 w, 1558 w, 1525 w, 1513 w, 1502 w, 1486 w, 1445 m, 1435 w, 1407 w, 1275 m, 1257 m, 1240 m, 1173 s, 1156 m, 868 m, 854 m, 842 vs, 670 vs, 634 m, 535 m, 526 m. ^1H NMR: 6.38 (1 H, dd, $J = 9.1, 2.7$, 2-H), 6.83 (1 H, ddd, $J = 8.5, 6.8, 1.4$, 15-H), 7.33 (1 H, dt, $J = 2.7, 0.6, 0.6$, 4-H), 7.35 (1 H, ddd, $J = 8.0, 6.8, 1.2$, 14-H), 7.51 (1 H, dt, $J = 9.1, 0.7, 0.7$, 1-H), 7.70 (1 H, ddt, $J = 8.5, 1.2, 0.8, 0.8$, 16-H), 7.94

(1 H, dt, J = 8.6, 0.7, 0.7, 5-H), 7.99 (1 H, ddt, J = 8.0, 1.4, 0.6, 0.6, 13-H), 8.05 (1 H, d, J = 8.6, 6-H), 8.08 (1 H, dt, J = 8.5, 0.6, 0.6, 12-H), 8.10 (1 H, d, J = 8.1, 7-H), 8.12 (1 H, d, J = 8.1, 8-H), 8.12 (1 H, d, J = 8.5, 11-H), 8.14 (1 H, d, J = 8.2, 10-H), 8.17 (1 H, d, J = 8.2, 9-H). ^{13}C NMR: 111.0 (d, C-2), 116.6 (d, C-4), 124.2 (s, C-8a), 124.8 (s, C-6a), 125.5 (d, C-15), 126.4 (d, C-14), 126.5 (d, C-7), 127.1 (d, C-9), 127.5 (d, C-11), 127.8 (d, C-5), 128.0 (d, C-16), 128.1 (d, C-13), 128.2 (d, C-10), 128.3 (d, C-12), 128.57 (d, C-8), 128.63 (d, C-6), 128.8 (s, C-16d), 129.1 (s, C-16b), 129.8 (d, C-1), 130.6 (s, C-16e), 130.9 (s, C-16a), 132.1 (s, C-10a), 132.8 (s, C-12a), 134.2 (s, C-16c), 134.7 (s, C-4a), 156.0 (s, C-3). EI MS: 344 (M^+ , 100), 324 (5), 313 (10), 300 (25), 287 (6), 162 (10), 150 (13), 144 (8). HR EI MS: calculated for $\text{C}_{26}\text{H}_{16}\text{O}$ 344.1201; found 344.1189.

3-Hexahelicenyl Trifluoromethanesulfonate 16. *n*-Butyllithium (1.6 M in hexanes, 830 μL , 1.33 mmol, 1.04 equiv) was added dropwise to alcohol **15** (440 mg, 1.28 mmol) in THF (15 mL) under argon and the mixture was stirred at -78°C for 10 min. Triflic anhydride (300 μL , 1.78 mmol, 1.4 equiv) was added dropwise and the reaction mixture was stirred at -78°C for 20 min. To prevent decomposition of the product, triethylamine (410 μL , 2.94 mmol, 2.3 equiv) was added and the reaction mixture was allowed to reach room temperature. Solvents were removed *in vacuo* and the residue was chromatographed on silica gel (petroleum ether-ether-aceton 80:10:10) to obtain triflate **16** (272 mg, 45 %) as an amorphous solid. IR: 1616 w, 1557 w, 1523 w, 1511 w, 1502 w, 1484 w, 1471 w, 1443 m, 1423 vs, 1246 s, 1228 s, 1203 m, 1128 m, 1141 vs. ^1H NMR: 6.52 (1 H, dd, J = 9.4, 2.7, 2-H), 6.70 (1 H, ddd, J = 8.5, 6.9, 1.4, 15-H), 7.24 (1 H, ddd, J = 8.0, 6.9, 1.2, 14-H), 7.45 (1 H, ddt, J = 8.5, 1.2, 0.5, 0.5, 16-H), 7.64 (1 H, dt, J = 9.4, 0.7, 0.7, 1-H), 7.73 (1 H, bd, J = 2.7, 4-

H), 7.84 (1 H, ddd, $J = 8.0, 1.4, 0.6$, 13-H), 7.91 (1 H, dt, $J = 8.6, 0.7, 0.7$, 5-H), 7.94 (1 H, s, 11, 12-H), 8.00 (1 H, dd, $J = 8.2, 0.4$, 7-H), 8.01 (1 H, d, $J = 8.2$, 10-H), 8.03 (1 H, d, $J = 8.2$, 9-H), 8.04 (1 H, d, $J = 8.6$, 6-H), 8.07 (1 H, d, $J = 8.2$, 8-H). ^{13}C NMR: 117.34 (d, C-2), 118.75 (q, CF_3), 118.76 (d, C-4), 123.90 (s, C-8a), 124.95 (d, C-15), 125.89 (d, C-14), 126.15 (d, C-7), 126.94 (d, C-9), 127.08 (d, C-5, 11), 127.41 (s, C-16d), 127.50 (d, C-16), 127.54 (s, C-16b), 127.74 (d, C-13), 127.81 (d, C-10), 127.85 (d, C-12), 128.22 (d, C-8), 128.33 (d, C-6), 129.28 (s, C-16a), 129.38 (s, C-16e), 130.12 (d, C-1), 131.52 (s, C-6a), 131.56 (s, C-10a), 131.89 (s, C-12a), 132.27 (s, C-4a), 133.36 (s, C-16c), 146.64 (s, C-3). ^{19}F NMR: -147.48 (d, $J_{\text{CF}} = 282.1$). EI MS: 476 (M^+ , 100), 447 (3), 343 (25), 325 (6), 313 (44), 300 (59), 287 (12), 157 (14), 150 (18), 144 (12), 101 (10), 85 (5), 71 (25), 55 (10). HR EI MS: calculated for $\text{C}_{27}\text{H}_{15}\text{F}_3\text{O}_3\text{S}$ 476.0694; found 476.0699.

3-Hexahelicenyl 1,1,2,2,3,3,4,4,4-Nonafluoro-1-butanefluoride **17**. A

Schlenk flask was charged with sodium hydride (80 % in mineral oil, 3.8 mg, 0.127 mmol, 2.2 equiv), flushed with argon, and solution of **15** (20 mg, 0.058 mmol) in DMF (1 mL) was added. The mixture was stirred at room temperature for 20 min, cooled to 0 °C, and nonaflate fluoride (21 μL , 0.117 mmol, 2.0 equiv) was added. The flask was stirred for 30 min to reach room temperature. The mixture was diluted with water (5 mL) and extracted with ether (2 x 10 mL). The combined fractions were dried over anhydrous Na_2SO_4 , the solvent was removed *in vacuo*, and the residue was chromatographed on silica gel (petroleum ether-ether 95:5) to receive nonaflate **17** (31 mg, 85 %) as an amorphous solid. IR: 3052 w, 1611 vw, 1582 vw, 1556 w, 1523 w, 1511 w, 1502 w, 1425 s, 1243 vs, 1146 s, 844 m, 587 w, 528 w. ^1H NMR: 6.53 (1 H, dd, $J = 9.4, 2.7$, 2-H), 6.70 (1 H, ddd, $J = 8.5, 6.9, 1.4$, 15-H), 7.23 (1 H, ddd, $J =$

8.0, 6.9, 1.2, 14-H), 7.45 (1 H, ddt, $J = 8.5, 1.2, 0.6, 0.6$, 16-H), 7.64 (1 H, dt, $J = 9.4, 0.6, 0.6$, 1-H), 7.74 (1 H, brd, $J = 2.7$, 4-H), 7.84 (1 H, ddd, $J = 8.0, 1.4, 0.8$, 13-H), 7.91 (1 H, dt, $J = 8.6, 0.6, 0.6$, 5-H), 7.94 (2 H, s, 11,12-H), 8.00 (1 H, d, $J = 8.2$, 7-H), 8.01 (1 H, d, $J = 8.2$, 10-H), 8.03 (1 H, d, $J = 8.2$, 9-H), 8.04 (1 H, brd, $J = 8.6$, 6-H), 8.07 (1 H, d, $J = 8.2$, 8-H). ^{13}C NMR: 117.3 (d, C-2), 118.7 (d, C-4), 123.9 (s, C-8a), 125.0 (d, C-15), 125.9 (d, C-14), 126.2 (d, C-11), 126.9 (d, C-9), 127.08 (d, C-7), 127.12 (d, C-5), 127.4 (s, C-16d), 127.5 (d, C-16), 127.6 (s, C-16b), 127.7 (d, C-13), 127.8 (d, C-10), 127.9 (d, C-8), 128.2 (d, C-12), 128.3 (d, C-6), 129.3 (s, C-16e), 129.4 (s, C-16a), 130.1 (d, C-1), 131.5 (s, C-6a), 131.6 (s, C-10a), 131.9 (s, C-12a), 132.3 (s, C-4a), 133.4 (s, C-16c), 147.0 (s, C-3), the signals of nonaflate carbon atoms were not observed. EI MS: 626 (M^+ , 100), 343 (41), 325 (16), 313 (42), 300 (64), 287 (11), 150 (22), 95 (12), 83 (12), 71 (15), 57 (24), 43 (15). HR EI MS: calculated for $\text{C}_{30}\text{H}_{15}\text{F}_9\text{O}_3\text{S}$ 626.0598; found 626.0607.

Methyl 3-Hexahelicenecarboxylate 18. *From triflate 16:* A Schlenk flask was charged with $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.0049 mmol, 10 mol %) and dppp (2 mg, 0.0048 mmol, 10 mol %), flushed with argon, and methanol (1 mL) with triethylamine (20 μL , 0.144 mmol, 3.0 equiv) were added. Triflate **16** (23 mg, 0.048 mmol) in DMSO (1.5 mL) was added and the mixture was stirred at 70 $^\circ\text{C}$ for 1.5 h while carbon monoxide was slowly bubbled throughout the solution. The reaction mixture was diluted with water, extracted with ether (3 x 5 mL), etheral portions were combined and dried over anhydrous Na_2SO_4 . Solvents were removed *in vacuo* and the residue was chromatographed on silica gel (petroleum ether-ether 90:10) to provide methyl ester **18** (11 mg, 59 %) as an amorphous solid. *From nonaflate 17:* The reaction was carried out in the same way starting from **17** (18 mg, 0.029 mmol), $\text{Pd}(\text{OAc})_2$ (0.6

mg, 0.0029 mmol, 10 mol %), dppp (1.2 mg, 0.0029 mmol, 10 mol %), triethylamine (12 μ L, 0.086 mmol, 3.0 equiv), DMSO (1.5 mL), and methanol (1 mL) to obtain methyl ester **18** (9.9 mg, 89 %). IR: 3052 w, 3028 w, 2953 w, 1716 vs, 1623 w, 1606 w, 1559 w, 1521 w, 1507 w, 1497 w, 1487 w, 1468 w, 1457 w, 1447 w, 1436 m, 1345 w, 1302 s, 1282 s, 1265 s, 1175 w, 1148 m, 1146 w, 1123 m, 1109 m, 1090 w, 994 w, 982 w, 910 w, 869 w, 845 vs, 829 w, 825 w, 624 m, 606 w, 523 m, 501 w. ^1H NMR: 3.89 (3 H, s, CH_3O), 6.67 (1 H, ddd, $J = 8.6, 6.9, 1.5$, 15-H), 7.21 (1 H, ddd, $J = 8.0, 6.9, 1.2$, 14-H), 7.26 (1 H, dd, $J = 8.9, 1.9$, 2-H), 7.54 (1 H, brd, $J = 8.6$, 16-H), 7.62 (1 H, brd, $J = 8.9$, 1-H), 7.83 (1 H, ddd, $J = 8.0, 1.5, 0.7$, 13-H), 7.94 (2 H, s, 11, 12-H), 7.98 (1 H, d, $J = 8.2$, 10-H), 7.99 (2 H, s, 5, 6-H), 8.01 (2 H, s, 7, 8-H), 8.05 (1 H, d, $J = 8.2$, 9-H), 8.56 (1 H, dd, $J = 1.9, 0.6$, 4-H). ^{13}C NMR: 52.0 (q, CH_3O), 124.2 (s, C-8a), 124.95 (d, C-1, 15), 125.9 (d, C-14), 126.1 (d, C-11), 126.6 (s, C-3), 126.8 (d, C-9), 127.10 (d, C-7), 127.12 (d, C-5), 127.3 (d, C-2), 127.58 (s, C-16d), 127.61 (d, C-16), 127.7 (d, C-8, 10), 127.8 (s, C-16b), 128.0 (d, C-13), 128.2 (d, 12), 128.4 (d, C-6), 129.8 (s, C-16a), 130.2 (d, C-4), 131.0 (s, C-4a), 131.4 (s, C-10a), 131.8 (s, C-6a, 12a), 132.7 (s, C-16e), 133.2 (s, C-16c), 167.1 (s, C=O). EI MS: 386 (M^{+} , 100), 324 (17), 300 (32), 223 (6), 205 (5), 162 (24), 149 (82), 125 (10), 111 (16), 97 (21), 83 (26), 69 (31), 57 (54), 43 (56). HR EI MS: calculated for $\text{C}_{28}\text{H}_{18}\text{O}_2$ 386.1307; found 386.1322.

N-Phenyl-3-hexahelicenamine 19. Aniline (22 μ L, 0.241 mmol, 3.1 equiv) was added to triflate **16** (37 mg, 0.078 mmol), $\text{Pd}(\text{dba})_2$ (2.7 mg, 0.0047 mmol, 6 mol %), (R)-(+)-BINAP (3.5 mg, 0.0056 mmol, 7 mol %), and cesium carbonate (59 mg, 0.181 mmol, 2.4 equiv) in toluene (2 mL) under argon and the mixture was stirred at 90 $^\circ\text{C}$ for 14 h. The solvent was removed *in vacuo* and the residue was

chromatographed on silica gel (petroleum ether-ether 90:10) to afford amine **19** (22 mg, 69 %) as an amorphous solid. IR: 3428 w, 3050 w, 1623 s, 1599 vs, 1570 w, 1558 w, 1530 m, 1512 m, 1497 vs, 1468 w, 1448 m, 1433 w, 1159 w, 695 w. ^1H NMR: 5.74 (1 H, s, NH), 6.43 (1 H, dd, $J = 9.1, 2.5$, 2-H), 6.79 (1 H, ddd, $J = 8.5, 6.9, 1.5$, 15-H), 6.93 (1 H, tt, $J = 7.3, 1.1$, H_{para} of Ph), 6.98-7.01 (2 H, m, 2 x H_{ortho} of Ph), 7.24-7.27 (2 H, m, 2 x H_{meta} of Ph), 7.28 (1 H, ddd, $J = 7.9, 6.9, 1.1$, 14-H), 7.42 (1 H, brd, $J = 2.5$, 4-H), 7.45 (1 H, dt, $J = 9.1, 0.6, 0.6$, 1-H), 7.68 (1 H, ddt, $J = 8.5, 1.1, 0.7, 0.7$, 16-H), 7.76 (1 H, dt, $J = 8.5, 0.6, 0.6$, 5-H), 7.84 (1 H, ddd, $J = 7.9, 1.5, 0.5$, 13-H), 7.88 (1 H, d, $J = 8.5$, 6-H), 7.90 (1 H, brdd, $J = 8.6, 0.6$, 12-H), 7.92 (1 H, d, $J = 8.6$, 11-H), 7.93 (1 H, d, $J = 8.1$, 7-H), 7.94 (1 H, d, $J = 8.1$, 8-H), 7.95 (1 H, d, $J = 8.2$, 9-H), 7.98 (1 H, d, $J = 8.2$, 10-H). ^{13}C NMR: 112.7 (d, C-2), 117.7 (d, 2 x C_{ortho} of Ph), 117.8 (d, C-4), 121.1 (d, C_{para} of Ph), 123.8 (s, C-8a), 124.7 (d, C-15), 125.0 (s, C-6a), 125.5 (d, C-14), 125.9 (d, C-7), 126.2 (d, C-9), 126.8 (d, C-11), 126.9 (d, C-5), 127.09 (d, C-10), 127.11 (d, C-16), 127.3 (d, C-13), 127.5 (d, C-12), 127.7 (d, C-8), 127.9 (d, C-6), 128.1 (s, C-16b), 129.0 (s, C-16d), 129.1 (d, C-1), 129.3 (d, 2 x C_{meta} of Ph), 129.9 (s, C-16e), 130.2 (s, C-16a), 131.2 (s, C-10a), 131.8 (s, C-12a), 133.2 (s, C-16c), 133.3 (s, C-4a), 140.4 (s, C-3), 143.3 (s, C_{ipso} of Ph). EI MS: 419 (M^{+} , 100), 326 (8), 300 (19), 248 (13), 234 (6), 210 (5), 118 (5), 77 (7), 57 (8). HR EI MS: calculated for $\text{C}_{32}\text{H}_{21}\text{N}$ 419.1674; found 419.1660.

***N*-(Diphenylmethylene)-3-hexahelicenamine 20.** A Schlenk flask was charged with triflate **16** (32 mg, 0.067 mmol), $\text{Pd}(\text{OAc})_2$ (1.0 mg, 0.0045 mmol, 6 mol %), (R)-(+)-BINAP (2.6 mg, 0.0042 mmol, 6 mol %), and cesium carbonate (31 mg, 0.094 mmol, 1.4 equiv) and flushed with argon. THF (1 mL) and benzophenone imine (17 μL , 0.101 mmol, 1.5 equiv) were added. The mixture was heated to reflux for 40

h. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel (petroleum ether-ether 97:3) to furnish imine **20** (29 mg, 85 %) as an amorphous solid. IR: 3084 w, 3052 m, 3011 m, 1659 m, 1616 s, 1599 s, 1577 m, 1556 w, 1513 w, 1495 m, 1390 w, 1318 s, 1291 m, 1281 s, 1252 m, 974 m, 910 s, 873 m, 843 vs, 823 m, 701 vs, 655 m, 638 m, 629 m, 606 m, 535 m, 526 m, 505 m. ^1H NMR: 6.21 (1 H, dd, $J = 9.0, 2.3$, 2-H), 6.71 (1 H, ddd, $J = 8.5, 6.8, 1.4$, 15-H), 7.02-7.05 (4 H, m, 4 x H_{ortho} of Ph), 7.08 (1 H, brd, $J = 2.3$, 4-H), 7.27 (1 H, ddd, $J = 8.0, 6.8, 1.2$, 14-H), 7.36-7.51 (4 H, m, 4 x H_{meta} of Ph), 7.38 (1 H, dt, $J = 9.0, 0.7, 0.7$, 1-H), 7.57-7.61 (2 H, m, 2 x H_{para} of Ph), 7.61 (1 H, ddt, $J = 8.5, 1.2, 0.6, 0.6$, 16-H), 7.70 (1 H, dt, $J = 8.6, 0.6, 0.6$, 5-H), 7.81 (1 H, ddd, $J = 8.0, 1.4, 0.6$, 13-H), 7.84 (1 H, d, $J = 8.6$, 6-H), 7.88 (1 H, dd, $J = 8.6, 0.5$, 12-H), 7.91 (1 H, d, $J = 8.2$, 7-H), 7.91 (1 H, d, $J = 8.6$, 11-H), 7.93 (1 H, d, $J = 8.2$, 8-H), 7.94 (1 H, d, $J = 8.2$, 10-H), 7.96 (1 H, d, $J = 8.2$, 9-H). ^{13}C NMR: 117.4 (d, C-4), 120.1 (d, C-2), 123.9 (s, C-8a), 124.9 (d, C-15), 125.5 (d, C-14), 126.1 (d, C-11), 126.2 (d, C-8), 126.3 (d, C-6), 126.5 (s, C-16e), 126.8 (d, C-10), 127.1 (d, C-9), 127.3 (d, C-7), 127.5 (d, C-13), 127.77 (d, C-16), 127.78 (d, C-5), 127.80 (d, C-12), 127.9 and 128.3 (2 x d, 4 x C_{ortho} of Ph), 128.06 (s, C-16b), 128.10 (d, C-1), 128.2 (s, C-16d), 128.3 and 130.1 (d, 2 x C_{para} of Ph), 129.3 and 129.5 (2 x d, 4 x C_{meta} of Ph), 129.8 (s, C-16a), 130.6 (s, C-6a), 131.2 (s, C-10a), 131.7 (s, C-12a), 132.5 (s, C-4a), 133.2 (s, C-16c), 136.0 and 139.8 (2 x s, 2 x C_{ipso} of Ph), 148.6 (s, C-3), 152.2 (s, C=N). EI MS: 507 (M^+ , 100), 430 (6), 324 (10), 300 (20), 254 (6), 214 (6), 162 (12), 149 (14), 105 (13), 71 (9), 57 (17). FAB MS (thioglycerine/glycerine matrix): 508 ($(\text{M}+1)^+$), 459, 405, 369, 341, 327, 307, 291, 257, 215, 201. HR EI MS: calculated for $\text{C}_{39}\text{H}_{25}\text{N}$ 507.1987; found 507.1997.

3-Hexahelicenamine 21. A Schlenk flask was charged with Pd(OAc)₂ (0.7 mg, 0.0031 mmol, 4 mol %), (R)-(+)-BINAP (3.3 mg, 0.0053 mmol, 6 mol %), and cesium carbonate (41 mg, 0.126 mmol, 1.4 equiv) and flushed with argon. Triflate **16** (43 mg, 0.090 mmol) in THF (2 mL) and benzophenone imine (18 μ L, 0.107 mmol, 1.2 equiv) were added. The mixture was heated to reflux for 40 h, then treated with aqueous hydrochloric acid (2 M, 200 μ L) at room temperature for 10 min, diluted with aqueous hydrochloric acid (0.5 M, 20 mL), and extracted with ether (2 x 5 mL). The aqueous portion was treated with aqueous sodium hydroxide (2 M, 4 mL), extracted with ether (3 x 5 mL), ethereal portions were combined, dried over anhydrous Na₂SO₄, and the solvent was removed *in vacuo*. The residue was chromatographed on silica gel (petroleum ether-acetone 85:15) to provide amine **21** (18 mg, 57 %) as an amorphous solid. IR: 3484 w, 3453 w, 3399 w, 3378 w, 3085 w, 3050 m, 1627 vs, 1605 m (sh), 1583 w, 1557 w, 1525 w, 1514 w, 1502 m, 1487 w, 1471 w, 1447 m, 1435 w, 1419 w, 1410 w, 1365 m, 1306 m, 1274 m, 1263 m, 1246 m, 1189 m, 1171 m, 1160 m, 1120 m, 858 s, 841 vs, 831 m, 822 m, 634 m. ¹H NMR: 3.71 (2 H, brs, NH₂), 6.12 (1 H, dd, *J* = 9.0, 2.6, 2-H), 6.76 (1 H, ddd, *J* = 8.5, 6.9, 1.4, 15-H), 6.99 (1 H, dt, *J* = 2.6, 0.5, 0.5, 4-H), 7.23 (1 H, ddd, *J* = 8.0, 6.9, 1.2, 14-H), 7.38 (1 H, dt, *J* = 9.0, 0.6, 0.6, 1-H), 7.68 (1 H, ddt, *J* = 8.5, 1.2, 0.6, 0.6, 16-H), 7.71 (1 H, dt, *J* = 8.6, 0.7, 0.7, 5-H), 7.81 (1 H, ddt, *J* = 8.0, 1.4, 0.5, 0.5, 13-H), 7.84 (1 H, d, *J* = 8.6, 6-H), 7.88 (1 H, dd, *J* = 8.6, 0.6, 10-H), 7.88 (1 H, dd, *J* = 8.1, 0.3, 12-H), 7.91 (1 H, brd, *J* = 8.1, 11-H), 7.92 (1 H, brd, *J* = 8.2, 7-H), 7.92 (1 H, d, *J* = 8.6, 9-H), 7.95 (1 H, dd, *J* = 8.2, 0.3, 8-H). ¹³C NMR: 109.5 (d, C-4), 115.6 (d, C-2), 123.6 (s, C-6a), 123.7 (s, C-8a), 124.7 (d, C-15), 125.3 (d, C-14), 125.5 (d, C-7), 126.2 (d, C-9), 126.6 (d, C-11), 126.8 (d, C-5), 126.9 (d, C-10), 127.0 (d, C-16), 127.3 (d, C-13), 127.4 (d, C-12), 127.6 (d, C-6), 128.0 (d, C-8), 128.2 (s, C-16b), 128.6 (s, C-16d), 129.1 (d, C-1),

129.7 (s, C-16e), 129.9 (s, C-16a), 131.1 (s, C-10a), 131.7 (s, C-12a), 133.2 (s, C-16c), 133.5 (s, C-4a), 143.9 (s, C-3). EI MS: 343 (M^+ , 100), 324 (11), 300 (34), 287 (7), 262 (7), 149 (8), 109 (15), 95 (20), 83 (22), 69 (29), 57 (54), 43 (40). HR EI MS: calculated for $C_{26}H_{17}N$ 343.1361; found 343.1358.

3-Hexahelicenyl(diphenyl)phosphine Oxide 22. A Schlenk flask was charged with triflate **16** (149 mg, 0.313 mmol), diphenylphosphine oxide (129 mg, 0.638 mmol, 2.0 equiv), $Pd(OAc)_2$ (4.2 mg, 0.019 mmol, 6 mol %), and dppb (7.6 mg, 0.018 mmol, 6 mol %) and flushed with argon. Ethyldiisopropylamine (300 μ L, 1.72 mmol, 5.5 equiv) and DMSO (4 mL) were added and the mixture was stirred at 100 $^{\circ}C$ for 1 h. The reaction mixture was diluted with water (15 mL) and dichloromethane (50 mL) and acidified with aqueous hydrochloric acid (5 %) to pH 2-3. The organic layer was separated, the aqueous layer was extracted with dichloromethane (3 x 20 mL), organic portions were combined, and dried over anhydrous Na_2SO_4 . The solvent was removed *in vacuo* and the residue was chromatographed on silica gel (petroleum ether-ethyl acetate 40:60) to receive phosphine oxide **22** (122 mg, 74 %) as an amorphous solid. IR: 3079 w, 3059 w, 1619 w, 1603 w, 1592 w, 1484 w, 1466 w, 1438 s, 1174 s, 1097 m, 1070 w, 1028 w, 998 w, 694 s. 1H NMR: 6.72 (1 H, ddd, J = 10.3, 8.7, 1.7, 2-H), 6.73 (1 H, ddd, J = 8.5, 6.9, 1.5, 15-H), 7.28 (1 H, ddd, J = 8.0, 6.9, 1.2, 14-H), 7.32-7.60 and 7.64-7.76 (10 H, m, 2 x Ph), 7.53 (1 H, dd, J = 8.5, 1.2, 16-H), 7.60 (1 H, brdd, J = 8.7, 1.2, 1-H), 7.83 (1 H, dd, J = 8.0, 1.5, 13-H), 7.90 (1 H, brd, J = 8.6, 12-H), 7.93 (1 H, d, J = 8.6, 11-H), 7.95 (1 H, brd, J = 8.5, 5-H), 8.00 (1 H, d, J = 8.2, 11-H), 7-H), 8.01 (1 H, d, J = 8.2, 10-H), 8.01 (1 H, d, J = 8.5, 6-H), 8.03 (1 H, d, J = 8.2, 9-H), 8.08 (1 H, d, J = 8.2, 8-H), 8.40 (1 H, dd, J = 13.3, 1.7, 4-H). ^{13}C NMR: 124.2 (s, C-8a), 124.6 (d, C-15), 125.4 (d, C-14), 126.0 (dd, J_{C-P} = 10.9, C-

2), 126.3 (d, C-11, 13), 127.0 (d, C-9), 127.2 (d, C-5), 127.4 (d, C-10), 127.6 (d, C-7), 127.7 (d, C-16), 128.07 (d, C-6, 8), 128.08 (d, C-12), 128.21 (s, C-16b), 128.26 (dd, $J_{C-P} = 13.1$, C-1), 128.32 (s, C-16d), 128.32 (dd, $J_{C-P} = 8.3$, 2 x C_{meta} of Ph), 128.4 (dd, $J_{C-P} = 8.4$, 2 x C_{meta} of Ph), 129.9 (s, C-12a), 130.9 (d, $J_{C-P} = 12.6$, C-4a), 131.5 (s, C-10a), 131.60 (d, $J_{C-P} = 104.8$, C_{ipso} of Ph), 131.66 (s, C-16e), 131.69 (dd, $J_{C-P} = 105.6$, C_{ipso} of Ph), 131.75 (dd, $J_{C-P} = 2.8$, C_{para} of Ph), 131.87 (dd, $J_{C-P} = 2.8$, C_{para} of Ph), 131.93 (s, C-6a), 132.0 (dd, $J_{C-P} = 10.0$, 2 x C_{ortho} of Ph), 132.2 (dd, $J_{C-P} = 10.0$, 2 x C_{ortho} of Ph), 132.3 (s, C-16a), 132.9 (d, $J_{C-P} = 103.8$, C-3), 133.2 (dd, $J_{C-P} = 9.9$, C-4), 133.3 (s, C-16c). EI MS: 528 (M^{+} , 100), 324 (12), 300 (14), 257 (6), 217 (66), 199 (41), 152 (9), 97 (14), 77 (42). HR EI MS: calculated for $C_{38}H_{25}OP$ 528.1643; found 528.1653.

3-Hexahelicenyl(diphenyl)phosphine 23. A mixture of phosphine oxide **22** (113 mg, 0.214 mmol), trichlorosilane (260 μ L, 2.58 mmol, 12.0 equiv), and triethylamine (270 μ L, 1.94 mmol, 9.0 equiv) in xylene (5 mL) was stirred under argon at 120 °C for 3 h. The reaction mixture was quenched with water (200 μ L), loaded on a silica gel column, and the product was eluted under argon (petroleum ether-ethyl acetate 98:2 to 50:50) to afford phosphine **23** (80 mg, 73 %) as an amorphous solid. 1H NMR: 6.51 (1 H, ddd, $J = 8.7, 6.6, 1.7$, 2-H), 6.72 (1 H, ddd, $J = 8.4, 6.8, 1.4$, 15-H), 7.06-7.33 (10 H, m, 2 x Ph), 7.24 (1 H, ddd, $J = 8.0, 6.8, 1.1$, 14-H), 7.43 (1 H, ddt, $J = 8.7, 1.2, 0.7, 0.7$, 1-H), 7.52 (1 H, ddt, $J = 8.4, 1.1, 0.7, 0.7$, 16-H), 7.72 (1 H, dd, $J = 8.9, 1.7$, 4-H), 7.74 (1 H, dd, $J = 8.5, 0.5$, 5-H), 7.74 (1 H, brdd, $J = 8.0, 1.4$, 13-H), 7.81 (1 H, dd, $J = 8.6, 0.6$, 12-H), 7.84 (1 H, d, $J = 8.6$, 11-H), 7.85 (1 H, d, $J = 8.5$, 6-H), 7.89 (2 H, d, $J = 8.2$, 7, 10-H), 7.93 (1 H, d, $J = 8.2$, 8-H), 7.94 (1 H, d, $J = 8.2$, 9-H). ^{13}C NMR: 124.1 (s, C-8a), 124.6 (d, C-15), 125.4 (d, C-14), 126.2 (d, C-

11), 126.6 (d, C-5), 126.9 (d, C-9), 127.2 (d, C-10), 127.3 (d, C-8), 127.4 (d, C-7), 127.6 (dd, J_{CP} = 6.0, C-1), 127.72 (d, C-13), 127.74 (d, C-6), 127.74 (s, C-16d), 127.84 (d, C-16), 127.87 (s, C-16b), 127.9 (d, C-12), 128.3 and 128.4 (2 x dd, J_{CP} = 6.9, 4 x C_{meta} of Ph), 128.7 (d, 2 x C_{para} of Ph), 129.0 (dd, J_{CP} = 14.6, C-2), 129.9 (s, C-16a), 130.2 (s, C-16e), 131.3 (s, C-6a), 131.5 (d, J_{CP} = 8.3, C-4a), 131.6 (s, C-10a), 131.9 (s, C-12a), 133.2 (s, C-16c), 133.5 and 133.9 (2 x dd, J_{CP} = 19.5, 4 x C_{ortho} of Ph), 133.7 (dd, J_{CP} = 24.3, C-4), 134.0 (d, J_{CP} = 10.0, C-3), 137.5 (d, J_{CP} = 10.1, 2 x C_{ipso} of Ph). EI MS: 512 (M^{+} , 100), 324 (7), 300 (9), 256 (6), 183 (11), 151 (27), 136 (7), 122 (11), 111 (13), 97 (17), 83 (21), 69 (38), 57 (48), 43 (47). HR EI MS: calculated for $C_{38}H_{25}P$ 512.1694; found 512.1714.

O-(3-Hexahelicenyl) Dimethylthiocarbamate 24. A Schlenk flask was charged with sodium hydride (80 % suspension in mineral oil, 23 mg, 0.767 mmol, 2.2 equiv) and flushed with argon. Alcohol **15** (121 mg, 0.351 mmol) in DMF (2 mL) was added and the mixture was stirred at room temperature for 20 min. Dimethylthiocarbamoyl chloride (55 mg, 0.444 mmol, 1.3 equiv) in DMF (1.5 mL) was added and the mixture was stirred at 85 °C for 20 min. The reaction mixture was diluted with water (5 mL), extracted with dichloromethane (2 x 10 mL), the organic portions were combined, dried over anhydrous Na_2SO_4 , and the solvent was evaporated *in vacuo*. The residue was chromatographed on silica gel (petroleum ether-ether-acetone 80:10:10) to provide thiocarbamate **24** (126 mg, 83 %) as an amorphous solid. IR: 3051 w, 2981 m, 1621 w, 1535 s, 1526 s, 1513 s, 1500 s, 1444 m, 1288 s, 1269 m, 1250 s, 1182 vs, 1172 s, 1155 s, 1144 s, 1133 s, 1114 m, 1047 w, 960 w, 878 m, 843 vs. 1H NMR: 2.57 (3 H, s, CH_3N), 3.02 (3 H, s, CH_3N), 6.53 (1 H, dd, J = 9.2, 2.6, 2-H), 6.85 (1 H, ddd, J = 8.4, 6.9, 1.4, 15-H), 7.22 (1 H, ddd, J =

8.0, 6.9, 1.1, 14-H), 7.65 (1 H, d, $J = 2.6$, 4-H), 7.73 (1 H, dd, $J = 8.5$, 0.7, 5-H), 7.73 (1 H, ddd, $J = 8.0$, 1.4, 0.7, 13-H), 7.78 (1 H, d, $J = 8.5$, 6-H), 7.80 (2 H, s, 7,12-H), 7.81 (1 H, brd, $J = 8.2$, 11-H), 7.83 (1 H, d, $J = 8.2$, 10-H), 7.85 (2 H, d, $J = 8.2$, 8,9-H), 7.91 (1 H, dt, $J = 9.2$, 0.6, 0.6, 1-H), 8.00 (1 H, brdd, $J = 8.4$, 1.1, 16-H). ^{13}C NMR: 37.6 (q, CH_3N), 42.6 (q, CH_3N), 120.3 (d, C-4), 121.2 (d, C-2), 124.5 (s, C-8a), 125.9 (d, C-15), 126.3 (d, C-14), 126.4 (d, C-7), 127.13 (d, C-9), 127.16 (d, C-5), 127.21 (d, C-11), 127.5 (d, C-6), 127.7 (d, C-8), 127.9 (d, C-10,13), 128.1 (d, C-16), 128.3 (d, C-12), 128.43 (s, C-16b), 128.48 (s, C-16e), 128.54 (s, C-16a,d), 129.2 (d, C-1), 131.5 (s, C-10a), 131.8 (s, C-6a), 132.2 (s, C-12a), 132.9 (s, C-4a), 133.7 (s, C-16c), 152.0 (s, C-3), 187.8 (s, C=S). EI MS: 431 (M^+ , 12), 313 (6), 301 (6), 88 (100), 72 (94), 56 (6), 42 (12). HR EI MS: calculated for $\text{C}_{29}\text{H}_{21}\text{NOS}$ 431.1344; found 431.1274.

S-(3-Hexahelicenyl) Dimethylthiocarbamate 25. Neat thiocarbamate **24** (36 mg, 0.083 mmol) was heated under argon to 280 °C for 30 min. The crude product was chromatographed on silica gel (petroleum ether-ether-acetone 80:10:10) to afford isomeric thiocarbamate **25** (31 mg, 86 %) as an amorphous solid. IR: 3051 w, 1663 s, 1622 w, 1559 vw, 1492 w, 1407 w, 1365 s, 1261 m, 1096 s, 855 m, 843 vs, 627 m, 607 w, 531 w, 525 w, 509 w. ^1H NMR: 3.02 (6 H, brs, 2 x CH_3), 6.72 (1 H, dd, $J = 8.8$, 2.0, 2-H), 6.74 (1 H, ddd, $J = 8.4$, 6.9, 1.4, 15-H), 7.24 (1 H, ddd, $J = 8.0$, 6.9, 1.1, 14-H), 7.55 (1 H, dt, $J = 8.8$, 0.7, 0.7, 1-H), 7.58 (1 H, ddt, $J = 8.4$, 1.1, 0.7, 0.7, 16-H), 7.81 (1 H, ddd, $J = 8.0$, 1.4, 0.6, 13-H), 7.88 (1 H, dt, $J = 8.5$, 0.6, 0.6, 12-H), 7.90 (1 H, brdd, $J = 8.5$, 0.6, 5-H), 7.92 (1 H, d, $J = 8.5$, 6-H), 7.93 (1 H, d, $J = 8.5$, 11-H), 7.95 (1 H, d, $J = 8.2$, 9-H), 7.97 (1 H, d, $J = 8.0$, 7-H), 7.99 (1 H, d, $J = 8.0$, 8-H), 8.00 (1 H, brd, $J = 2.0$, 4-H), 8.00 (1 H, d, $J = 8.2$, 10-H). ^{13}C NMR: 36.9 (q, 2 x CH_3), 124.2 (s, C-16c), 125.1 (d, C-15), 125.7 (s, C-6a), 125.8 (d, C-7), 126.1 (d, C-

14), 126.8 (d, C-5), 126.9 (d, C-10), 127.2 (d, C-12), 127.35 (d, C-16), 127.41 (d, C-13), 127.58 (d, C-11), 127.59 (d, C-9), 127.7 (d, C-6), 127.86 (s, C-8a), 127.96 (s, C-3), 128.02 (d, C-1, 8), 129.9 (s, C-16d), 130.1 (s, C-16e), 130.7 (d, C-2), 131.4 (s, C-16a), 131.75 (s, C-10a), 131.84 (s, C-12a), 132.1 (s, C-16b), 133.2 (s, C-4a), the signal of C=O was not observed. EI MS: 431 (M^{+} , 24), 415 (8), 393 (1), 359 (4), 326 (6), 300 (8), 149 (58), 111 (10), 97 (16), 72 (100), 57 (28), 43 (21). HR EI MS: calculated for $C_{29}H_{21}NOS$ 431.1344; found 431.1353.

2-(6-Hepten-3-ynyl)-1-[[2-(6-hepten-3-ynyl)-4-methoxyphenyl]ethynyl]naphthalene 26. A solution of triyne **11** (74 mg, 0.204 mmol) and ethylmagnesium bromide (3 M solution in ether, 165 μ L, 0.495 mmol, 2.4 equiv) in THF (3 mL) was added to CuCl (40 mg, 0.404 mmol, 2.0 equiv) under argon placed in a pressure tube. Allyl bromide (70 μ L, 0.809 mmol, 4.0 equiv) was added, the tube was tightly closed and heated to 70 °C for 45 min under stirring. Solvents were removed *in vacuo* and the residue was chromatographed on silica gel (petroleum ether-ether 95:5) to receive bisallylated triyne **26** (60 mg, 67 %) as an oil. IR: 3086 w, 3059 m, 2960 m, 2936 m, 2914 m, 2864 w, 2840 m, 2215 w, 2200 w, 1641 m, 1605 vs, 1564 m, 1510 m (sh), 1498 s, 1466 m, 1428 m, 1308 s, 1283 s, 1260 m (sh), 1239 vs, 1167 m, 1160 m, 1099 m, 1057 s, 1037 m, 1025 m, 994 m, 919 m, 867 w, 816 s. 1H NMR: 2.68 (4 H, m, 2 x $CH_2CH_2C\equiv C$), 2.93 (4 H, m, $CH_2CH=CH_2$), 3.17 (2 H, t, $J = 7.6$, $CH_2CH_2C\equiv C$ (Ph)), 3.29 (2 H, t, $J = 7.6$, $CH_2CH_2C\equiv C$ (Nph)), 3.85 (3 H, s, CH_3O), 5.05 (2 H, dq, $J = 10.0$, 1.7, 1.7, 1.7, 2 x $CH_2CH=CHH$), 5.26 (2 H, dq, $J = 16.9$, 1.8, 1.8, 1.8, $CH_2CH=CHH$), 5.79 (1 H, dddt, $J = 16.9$, 10.0, 5.4, 5.4, 0.8, $CH_2CH=CH_2$), 5.79 (1 H, ddt, $J = 16.9$, 10.0, 5.4, 5.4, $CH_2CH=CH_2$), 6.81 (1 H, dd, $J = 8.4$, 2.7, 6-H (Ph)), 6.90 (1 H, d, $J = 2.7$, 2-H (Ph)),

7.43 (1 H, d, $J = 8.3$, 3-H (Nph)), 7.47 (1 H, ddd, $J = 8.1$, 6.8, 1.2, 6-H (Nph)), 7.56 (1 H, ddd, $J = 8.4$, 6.8, 1.4, 7-H), 7.60 (1 H, d, $J = 8.4$, 5-H (Ph)), 7.75 (1 H, brd, $J = 8.3$, 4-H (Nph)), 7.81 (1 H, ddt, $J = 8.1$, 1.4, 0.7, 0.7, 5-H (Nph)), 8.44 (1 H, ddt, $J = 8.4$, 1.2, 0.8, 0.8, 8-H). ^{13}C NMR: 20.2 (t, 2 x $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$), 23.16 (t, $\text{CH}_2\text{CH}=\text{CH}_2$ (Nph)), 23.19 (t, $\text{CH}_2\text{CH}=\text{CH}_2$ (Ph)), 34.8 (t, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$ (Ph)), 35.2 (t, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$ (Nph)), 55.3 (q, CH_3O), 77.5 (s, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$ (Ph)), 77.6 (s, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$ (Nph)), 81.8 (s, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$ (Ph)), 82.0 (s, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$ (Nph)), 88.3 (s, $\text{Ph-C}\equiv\text{C-Nph}$), 97.3 (s, $\text{Ph-C}\equiv\text{C-Nph}$), 112.3 (d, C-6 (Ph)), 114.8 (d, C-2 (Ph)), 115.3 (s, C-4 (Ph)), 115.67 (t, $\text{CH}_2\text{CH}=\text{CH}_2$ (Nph)), 115.73 (t, $\text{CH}_2\text{CH}=\text{CH}_2$ (Ph)), 119.8 (s, C-1 (Nph)), 125.7 (d, C-6 (Nph)), 126.2 (d, C-8), 126.8 (d, C-7), 127.9 (d, C-4 (Nph)), 128.1 (d, C-5 (Nph)), 128.4 (d, C-3 (Nph)), 132.0 (s, C-4a), 133.5 (s, C-8a), 133.5 (d, $\text{CH}_2\text{CH}=\text{CH}_2$ (Ph)), 134.0 (d, C-5 (Ph)), 141.3 (s, C-2 (Nph)), 144.2 (s, C-3 (Ph)), 159.7 (s, C-1 (Ph)). EI MS: 442 (M^+ , 92), 427 (14), 415 (33), 401 (36), 386 (90), 371 (74), 360 (77), 345 (45), 321 (43), 303 (33), 289 (59), 276 (53), 265 (40), 252 (47), 239 (100), 226 (41), 202 (32), 191 (26), 178 (23), 165 (41), 151 (19), 165 (41), 141 (34), 121 (32), 97 (20), 77 (31), 57 (36), 41 (20). HR EI MS: calculated for $\text{C}_{33}\text{H}_{30}\text{O}$ 442.2297; found 442.2288.

7,8-Diallyl-3-methoxy-5,6,9,10-tetrahydrohexahelicene 27. A Schlenk flask was charged with triyne **26** (47 mg, 0.106 mmol) and flushed with argon. The substrate was dissolved in decane (5 mL) at 140 °C. Then a solution of triphenylphosphine (11.2 mg, 0.043 mmol, 40 mol %) in hot decane (3 mL) and $\text{CpCo}(\text{CO})_2$ (3 μL , 0.023 mmol, 20 mol %) in decane (800 μL) were added and the mixture was stirred at 140 °C for 3 h under concomitant irradiation with a halogen lamp. The solvent was evaporated *in vacuo* and the residue was chromatographed

on silica gel (petroleum ether-ether 99:1 to 95:5) to obtain **27** (35 mg, 74 %) as an amorphous solid. IR: 3081 w, 3056 w, 3008 s, 2838 m, 1636 m, 1609 s, 1581 m, 1510 m (sh), 1500 vs, 1404 m, 1307 m, 1191 w, 1041 s, 995 m, 916 s, 866 w, 814 s. ^1H NMR: 2.40 (1 H, m, $\Sigma J = 25.0$, 9-H), 2.48 (1 H, ddt, $J = 15.0, 15.0, 4.8, 1.6$, 6-H), 2.85 (1 H, brddd, $J = 14.9, 4.8, 2.5$, 5-H), 2.88-2.92 (2 H, m, 10-H), 2.93 (1 H, brdt, $J = 14.8, 14.8, 4.7$, 5-H), 3.05 (1 H, ddd, $J = 14.9, 3.9, 2.6$, 9-H), 3.11 (1 H, ddd, $J = 15.3, 4.7, 2.5$, 6-H), 3.49 (2 H, ddt, $J = 17.2, 5.4, 1.7, 1.7$, 2 x CHHCH=CH₂), 3.54 (2 H, ddt, $J = 17.2, 5.4, 1.7, 1.7$, 2 x CHHCH=CH₂), 3.59 (3 H, s, CH₃O), 4.96 (1 H, dq, $J = 17.1, 1.9, 1.9, 1.9$, C₇-CH₂CH=CHH), 4.99 (1 H, dq, $J = 17.1, 1.9, 1.9, 1.9$, C₈-CH₂CH=CHH), 5.05 (1 H, dq, $J = 10.2, 1.9, 1.9, 1.9$, C₇-CH₂CH=CHH), 5.08 (1 H, dq, $J = 10.2, 1.9, 1.9, 1.9$, C₈-CH₂CH=CHH), 5.90 (1 H, ddd, $J = 8.6, 2.7, 0.7$, 2-H), 6.037 (1 H, ddt, $J = 17.1, 10.2, 5.4, 5.4$, C₇-CH₂CH=CH₂), 6.041 (1 H, ddt, $J = 17.1, 10.2, 5.4, 5.4$, C₈-CH₂CH=CH₂), 6.26 (1 H, d, $J = 8.6$, 1-H), 6.66 (1 H, dd, $J = 2.7, 0.9$, 4-H), 6.87 (1 H, ddd, $J = 8.6, 6.7, 1.4$, 15-H), 7.09 (1 H, ddd, $J = 8.1, 6.7, 1.2$, 14-H), 7.45 (1 H, d, $J = 8.1$, 11-H), 7.50 (1 H, ddt, $J = 8.6, 1.2, 0.9, 0.9$, 16-H), 7.61 (1 H, ddt, $J = 8.1, 1.4, 0.7, 0.7$, 13-H), 7.66 (1 H, brd, $J = 8.1$, 12-H). ^{13}C NMR: 26.2 (t, C-6), 26.8 (t, C-9), 30.4 (t, C-5), 31.1 (t, C-10), 33.7 (t, C₈-CH₂CH=CH₂), 33.9 (t, C₇-CH₂CH=CH₂), 55.0 (q, CH₃O), 110.6 (d, C-2), 111.9 (d, C-4), 115.29 (t, C₈-CH₂CH=CH₂), 115.32 (t, C₇-CH₂CH=CH₂), 124.1 (d, C-14), 124.8 (d, C-15), 125.7 (d, C-11), 126.0 (d, C-16), 127.1 (d, C-12), 127.5 (d, C-13), 128.2 (s, C-16c), 129.0 (s, C-16b), 129.1 (s, C-16e), 129.4 (s, C-16a), 129.5 (d, C-1), 132.88 (s, C-12a), 132.93 (s, C-8), 133.3 (s, C-16d), 133.8 (s, C-7), 135.7 (s, C-6a), 136.4 (d, C₈-CH₂CH=CH₂), 136.6 (d, C₇-CH₂CH=CH₂), 137.5 (s, C-10a), 139.0 (s, C-4a), 139.4 (s, C-8a), 157.7 (s, C-3). EI MS: 442 (M⁺, 100), 221 (4), 199 (5), 149 (6), 121 (7), 101 (8), 91 (38), 77

(5), 69 (8), 59 (20), 43 (48). HR EI MS: calculated for $C_{33}H_{30}O$ 442.2297; found 442.2317.