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A Convenient Route to 2-Hydroxy- and 2,15-Dihydroxyhexahelicene

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2-Hydroxy- and 2,15-dihydroxyhexahelicene were synthesised from simple benzene and naphthalene building blocks by intramolecular Co^{I}- or Ni^{0}-catalysed [2+2+2] cycloisomerisation of CH_3O-substituted aromatic triynes. This approach avoids vexing photodehydrocyclisation of stilbene-type precursors, providing thus a useful alternative to classical procedures.

Introduction

Helicenes as unique chiral three-dimensional aromatics have attracted continuous attention for decades.[1] In spite of this, recently there have been only scattered efforts to exploit helicenes in enantioselective catalysis.[2] Reetz's HELIXOL, 2,15-dihydroxyhexahelicene **1**, was expected to play an important role in this arena,[3] but only its use as an excellent enantioselective fluorescent sensor has been published so far.[4b] For broader exploitation of helically chiral ligand **1** and its congener **2**,[5] they should be accessible in a convenient way. Note, en route to **1** the key photodehydrocyclisation of a stilbene-type precursor requires impractical high dilution conditions and provides rather low yield owing to its incompleteness and some side product formation.[3,4] The synthesis of **2** has never been described in detail (Figure 1).

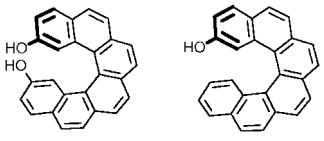
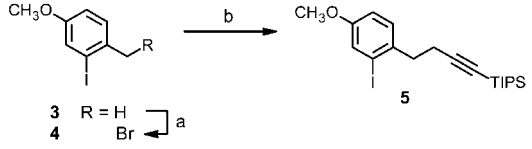


Figure 1. 2-Hydroxy- and 2,15-dihydroxyhexahelicene.

In this paper, we report a new method to synthesise **1** and **2** by using intramolecular transition-metal catalysed [2+2+2] cycloisomerisation of CH_3O-substituted aromatic triynes that circumvents disputed photochemistry. The basis of this organometallic approach has been established by our previous syntheses of helicenes and related compounds.[6,7] Now we show the method can be easily adapted to the alternative preparation of hexahelicene alcohols **1** and **2**.

Results and Discussion

The convergent synthesis of diol **1** relies on the utilisation of CH_3O-substituted benzene and naphthalene building blocks and de novo construction of three centrally fused benzene rings. First, we carried out a simple preparation of **5** (Scheme 1). Radical bromination of **3** with NBS provided known **4** in high yield.[8] Note, bromide **4** is very unstable even in a pure state. However, when treated immediately after its separation with $LiCH_2C{\equiv}CTIPS$, the building block **5** was produced in good yield.



Scheme 1. Synthesis of the benzene building block **5**. Reagents and conditions: (a) NBS (1.1 equiv.), AIBN (cat.), K_2CO_3 (cat.), CCl_4, reflux, 1 h, 99%; (b) $LiCH_2C{\equiv}CTIPS$ (1.0 equiv.), THF, –78 °C, 10 min, 74%.

As only a limited set of trisubstituted naphthalenes is commercially available, we had to prepare **14** from known **6** (Scheme 2).[9] To displace the hydroxy group with a carbon moiety, we initially treated **6** with *n*-butyllithium/triflic anhydride to obtain reactive triflate **7**. Attempts to regioselectively introduce a bromomethyl group by Ni^{II}-catalysed coupling[10] of **7** with CH_3MgBr followed by radical bromination totally failed due to a complex mixture formed in the first step. Therefore, we turned our attention to an alternative Pd^{II}-catalysed methoxycarbonylation route[11] of **7** to distinguish between the Br and TfO groups. Indeed, the more reactive TfO group was preferentially transformed

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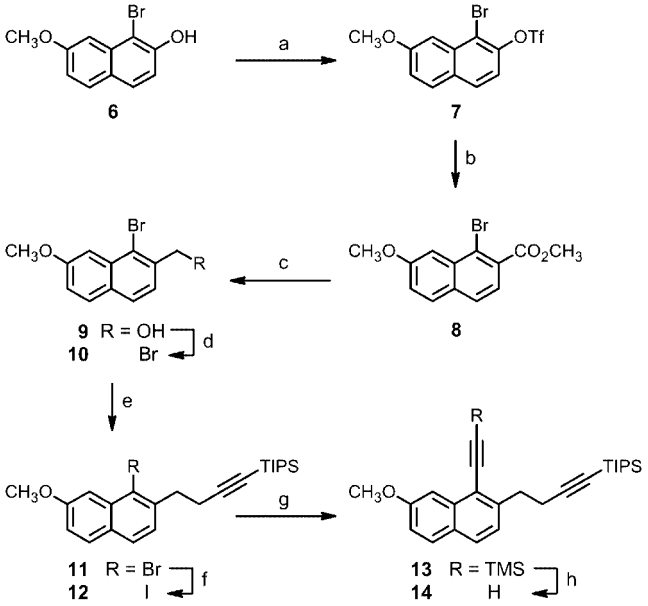
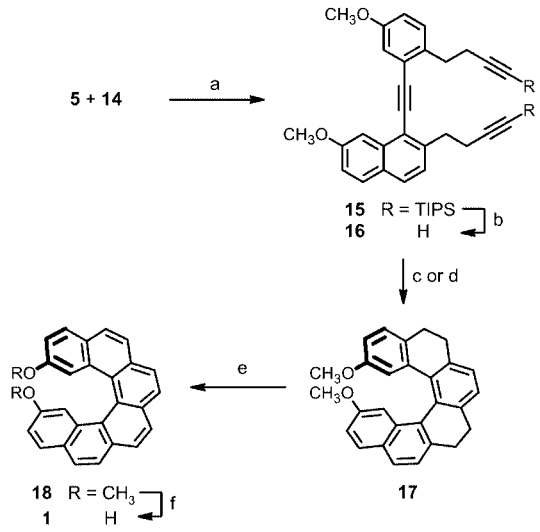
into **8** in acceptable yield. Clean reduction with lithium aluminium hydride without any debromination provided alcohol **9** in high yield that was easily converted to bromide **10** in good yield on reaction with PBr_3. Similarly as for **5**, the side arm in **11** was attached by treatment of **10** with $LiCH_2C{\equiv}CTIPS$. To preclude any Heck-type participation of the tethered acetylene unit in the following Sonogashira coupling, bromide **11** was transformed to the more reactive iodide **12** in good yield by a routine lithiation/iodination protocol. Pd^0/Cu^I-catalysed coupling of **12** with trimethylsilylacetylene afforded **13** in excellent yield. Finally, smooth partial desilylation with sodium methoxide led to the desired naphthalene building block **14** in quantitative yield.



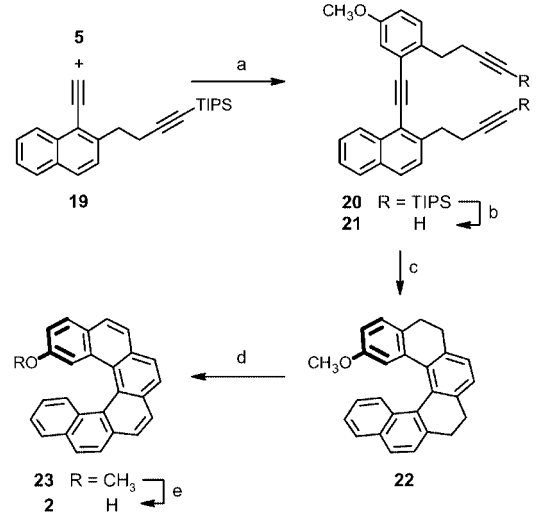
Scheme 2. Synthesis of the naphthalene building block **14**. Reagents and conditions: (a) *n*BuLi (1.0 equiv.), THF, –78 °C, 5 min, then Tf_2O (1.3 equiv.), –78 °C, 40 min, 67%; (b) CO, $Pd(OAc)_2$ (5%), dppp (5%), Et_3N (2.5 equiv.), DMSO/CH_3OH, 3:2, 70 °C, 2 h, 58%; (c) $LiAlH_4$ (0.6 equiv.), THF, 0 °C, 1 h, 90%; (d) PBr_3 (1.3 equiv.), THF, 0 °C, 2.5 h, 67%; (e) $LiCH_2C{\equiv}CTIPS$ (1.0 equiv.), THF, –78 °C, 1 h, 77%; (f) *n*BuLi (1.1 equiv.), THF, –78 °C, 10 min, then I_2 (1.5 equiv.), –78 °C, 20 min, 95%; (g) $TMSC{\equiv}CH$ (1.6 equiv.), $Pd(PPh_3)_4$ (5%), CuI (10%), *i*Pr_2NH, in a sealed tube, 80 °C, 1 h, 99%; (h) CH_3ONa (2.4 equiv.), CH_3OH, r.t., 2 h, 99%.

Having obtained both the key building blocks **5** and **14**, we could complete the convergent synthesis of **1** (Scheme 3). First, we carried out Sonogashira coupling of **5** and **14** to receive triyne **15** in good yield. Subsequent desilylation with *n*Bu_4NF provided unprotected triyne **16**, which was a suitable substrate for the key [2+2+2] cycloisomerisation reaction. Indeed, under Co^I catalysis, tetrahydrohelicene **17** was produced in reasonable yield. It should be noted that halogen lamp irradiation and the addition of triphenylphosphane were not essential, but the former promoted the reaction through catalyst activation and the latter kept the active catalyst alive for a longer period.[12] Alternatively, Ni^0-catalysed cyclisation led to an almost identical yield of **17**. To obtain a fully aromatic helicene backbone, **17** reacted with Ph_3CBF_4[13] to give known **18** in high yield.[4a,14,15] An alternative aromatisation of **17** with triphenylmethanol in trifluoroacetic acid[16] heated at reflux was similarly efficient (69% yield). The removal of CH_3 groups with BBr_3 completed the whole reaction sequence to provide **1**.



Scheme 3. Synthesis of 2,15-dihydroxyhexahelicene **1**. Reagents and conditions: (a) **5** (1.0 equiv.), **14** (1.0 equiv.), $Pd(PPh_3)_4$ (5%), CuI (10%), *i*Pr_2NH, 80 °C, 10 min, 79%; (b) *n*Bu_4NF (2.4 equiv.), THF, r.t., 1 h, 84%; (c) $CpCo(CO)_2$ (20%), PPh_3 (40%), *n*-decane, halogen lamp, 140 °C, 1 h, 56%; (d) $Ni(cod)_2$ (20%), PPh_3 (40%), THF, r.t., 24 h, 53%; (e) Ph_3CBF_4 (3.0 equiv.), 1,2-dichloroethane, 85 °C, 12 h, 64%; (f) BBr_3 (10 equiv.), CH_2Cl_2, 0 °C to r.t., 2 h, 52%.

As a logical extension, we prepared monohydroxy derivative **2**. By simply following the synthetic scheme for **1**, the preparation of **2** demonstrated an advantageous modular



Scheme 4. Synthesis of 2-hydroxyhexahelicene **2**. Reagents and conditions: (a) **5** (1.0 equiv.), **19** (1.0 equiv.), $Pd(PPh_3)_4$ (2.5%), CuI (5%), *i*Pr_2NH, 80 °C, 10 min, 86%; (b) *n*Bu_4NF (2.4 equiv.), THF, r.t., 1 h, 60%; (c) $CpCo(CO)_2$ (20%), PPh_3 (40%), *n*-decane, halogen lamp, 140 °C, 3 h, 77%; (d) Ph_3CBF_4 (3.0 equiv.), 1,2-dichloroethane, 80 °C, 3 h, 96%; (e) BBr_3 (4.5 equiv.), CH_2Cl_2, r.t., 1 h, 95%.

characteristic of our general methodology. Thus, iodide **5** was coupled with naphthyl acetylene[7] **19** under Pd^0/Cu^I catalysis to easily produce protected triyne **20** in high yield (Scheme 4). After desilylation with nBu_4NF, triyne **21** was produced in acceptable yield. The key Co^I-catalysed cycloisomerisation furnished CH_3O-substituted tetrahydrohelicene **22** in good yield. To accomplish the whole synthetic sequence, the last two steps were executed. Both the aromatisation with Ph_3CBF_4 to afford known[14] **23** and the subsequent demethylation with BBr_3 to afford final **2** proceeded well and rendered the products in excellent yields.

Conclusions

A new method was developed for the preparation of 2-hydroxy- and 2,15-dihydroxyhexahelicene **1** and **2**, respectively, from simple building blocks. The significance of the current investigation is that it provides a useful alternative to the classic photochemistry-based approach, which has hindered broader exploitation of 2-substituted hexahelicenes.

Experimental Section

General Remarks: ^1H and ^{13}C NMR spectra were recorded with TMS as an internal standard. HMBC experiments were set up for $J_{C,H}$ = 5 Hz. For the correct assignment of both ^1H and ^{13}C NMR spectra of key compounds, the COSY, ROESY, HMQC, HMBC and CIGAR-HMBC experiments were performed. For all the other compounds, the general semiempirical equations were applied to the chemical shift assignments. Electron impact (EI) mass spectra were determined at an ionising voltage of 70 eV. Fast atom bombardment (FAB) mass spectra were measured by using the thioglycerol/glycerol 3:1 matrix or bis(2-hydroxyethyl) disulfide matrix. HRMS spectra were obtained by the EI or FAB technique. Compounds **6**[9] and **19**[7] were prepared according to the literature procedure. Commercially available reagent grade materials were used as received. Solid $Ni(cod)_2$ was handled in a glove box. Decane and diisopropylamine were degassed by three freeze–pump–thaw cycles before use; 1,4-dichloroethane and dichloromethane were distilled from calcium hydride under an atmosphere of argon before use; DMSO was distilled from calcium hydride under vacuum and stored over 5 Å molecular sieves; THF was freshly distilled from sodium/benzophenone under an atmosphere of nitrogen; tetrachloromethane was filtered through alumina before use; methanol was distilled with sodium under an atmosphere of nitrogen and stored over 5 Å molecular sieves. TLC was performed on Silica gel 60 F_{254}-coated aluminium sheets (Merck) and spots were detected by the solution of $Ce(SO_4)_2$. 4 H_2O (1%) and $H_3P(Mo_3O_{10})_4$ (2%) in sulfuric acid (10%). Flash chromatography was performed on Silica gel 60 (0.040–0.063 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.).

2,15-Hexahelicenediol (1): A Schlenk flask was charged with dimethoxy derivative **18** (66 mg, 0.170 mmol) and flushed with argon. The material was dissolved in dichloromethane (10 mL) and BBr_3 (1.0 M in dichloromethane, 1.70 mL, 1.70 mmol, 10.0 equiv.) was added dropwise. The mixture was stirred at r.t. for 1 h. The mixture was diluted with water (10 mL), extracted with dichloromethane (3 × 10 mL), the combined organic portions were dried with anhydrous Na_2SO_4 and the solvent was evaporated in vacuo. The residue was chromatographed on silica gel (petroleum ether/ethyl acetate, 75:25) to afford **1** (32 mg, 52%) as an amorphous solid. ^1H NMR, ^{13}C NMR and HR EI MS spectra were in agreement with the literature data.[4] MS (EI): *m*/*z* (%) = 360 (29) $[M]^{+\cdot}$, 340 (11), 243 (3), 149 (11), 97 (23), 83 (35), 69 (48), 57 (99), 41 (100).

2-Hexahelicenol (2): A Schlenk flask was charged with methyl ether **23** (137 mg, 0.382 mmol) and flushed with argon. The material was dissolved in dichloromethane (10 mL) and BBr_3 (1.0 M in dichloromethane, 1.70 mL, 1.70 mmol, 4.5 equiv.) was added dropwise. The mixture was stirred at r.t. for 1 h. The mixture was diluted with water (10 mL), extracted with dichloromethane (3 × 20 mL), the combined organic portions were dried with anhydrous Na_2SO_4 and the solvent was evaporated in vacuo. The residue was chromatographed on silica gel (petroleum ether/diethyl ether/acetone, 80:10:10) to afford **2** (125 mg, 95%) as an amorphous solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.75 (ddd, J = 8.5, 6.8, 1.4 Hz, 1 H), 6.83 (dd, J = 8.6, 2.5 Hz, 1 H), 6.92 (dt, J = 2.5, 0.7, 0.7 Hz, 1 H), 7.29 (ddd, J = 8.0, 6.8, 1.1 Hz, 1 H), 7.66 (ddt, J = 8.5, 1.1, 0.7, 0.7 Hz, 1 H), 7.73 (dt, J = 8.6, 0.5, 0.5 Hz, 1 H), 7.80 (d, J = 8.5 Hz, 1 H), 7.82 (ddd, J = 8.0, 1.4, 0.5 Hz, 1 H), 7.86 (dt, J = 8.5, 0.6, 0.6 Hz, 1 H), 7.91 (br. dd, J = 8.6, 0.5 Hz, 1 H), 7.93 (d, J = 8.6 Hz, 1 H), 7.96 (d, J = 8.2 Hz, 2 H), 7.98 (dd, J = 8.2, 0.4 Hz, 1 H), 8.00 (dd, J = 8.2, 0.4 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 111.58 (d), 115.95 (d), 123.87 (d), 124.20 (s), 124.78 (d), 125.93 (d), 126.34 (d), 126.85 (s), 126. 98 (d), 127.00 (d), 127.01 (d), 127.22 (d), 127.36 (d), 127.37 (d), 127.51 (s), 127.62 (d), 127.73 (d), 129.39 (d), 130.04 (s), 131.28 (s), 131.30 (s), 131.56 (s), 131.85 (s), 132.95 (s), 153.11 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3592 (m), 1623 (m), 1612 (m), 1585 (vw), 1558 (vw), 1531 (w), 1526 (w), 1507 (w), 1477 (w), 1416 (w), 1182 (m), 851 (s), 841 (vs) cm^{-1}. MS (EI): *m*/*z* (%) = 344 (100) $[M]^{+\cdot}$, 326 (24), 313 (23), 300 (45), 287 (11), 163 (15), 150 (17), 95 (12), 83 (14), 69 (18), 57 (26), 43 (24). HRMS (EI): calcd. for $C_{26}H_{16}O$ 344.1201; found 344.1187.

1-(Bromomethyl)-2-iodo-4-methoxybenzene (4): 5-Methoxy-2-methylaniline (5.0 g, 36.45 mmol) was dissolved in concentrated sulfuric acid (8.0 mL) and water (120 mL). The solution was cooled to 0 °C (measured with an internal thermometer), and the anilinium salt precipitated. Sodium nitrite (2.67 g, 38.70 mmol, 1.06 equiv.) in water (8 mL) was added dropwise under vigorous stirring at such a rate to maintain a temperature between 0–5 °C. The resulting orange-brown solution was treated with potassium iodide (6.07 g, 36.56 mmol, 1.0 equiv.) in water (8 mL) at r.t. for 1 h while nitrogen evolution was observed. Then the mixture was stirred at 100 °C for an additional 1 h until the nitrogen evolution deceased. The reaction mixture was extracted with dichloromethane (3 × 50 mL), and the organic portions were combined, washed with aqueous $KHCO_3$ (4×), aqueous $Na_2S_2O_3$ (5×), water (1×) and dried with anhydrous Na_2SO_4. The solvent was removed in vacuo, and the residue was filtered through a short pad of silica gel (petroleum ether/diethyl ether, 95:5) to afford iodide **3** (6.77 g, 75%) as a yellow orange oil. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 3.76 (s, 3 H), 6.80 (dd, J = 8.2, 2.6 Hz, 1 H), 7.11 (d, J = 8.2 Hz, 1 H), 7.35 (d, J = 2.6 Hz, 1 H) ppm. The mixture of iodide **3** (3.95 g, 15.92 mmol), *N*-bromosuccinimide (3.12 g, 17.53 mmol, 1.1 equiv.) and catalytic amounts of AIBN and K_2CO_3 in tetrachloromethane (100 mL) was heated to reflux for 1 h with use of an IR lamp. The precipitate was filtered off, washed with tetrachloromethane and the portions were combined. The solvent was evaporated in vacuo, and the residue was quickly filtered through a short pad of silica gel (petroleum ether/diethyl ether, 90:10) to receive bromide **4** (5.15 g, 99%) as an amorphous solid.[8] The substance was immediately used owing to its instability (it may rapidly darken during the evaporation of the solvent and evolve fumes but these changes may

not influence the next reaction with organolithium). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.80 (s, 3 H), 4.61 (s, 2 H), 6.88 (dd, J = 8.6, 2.4 Hz, 1 H), 7.38 (d, J = 8.6 Hz, 1 H), 7.39 (d, J = 2.4 Hz, 1 H) ppm. IR: $\tilde{\nu}$ = 3084 (w), 3064 (w), 2839 (m), 1595 (vs), 1565 (s), 1492 (vs), 1464 (s), 1439 (s), 1342 (w), 1309 (s), 1201 (s), 1182 (s), 1022 (vs), 611 (m) cm^{-1}. MS (EI): m/z (%) = 328 (4) $[M]^{+\cdot}$ with ^{81}Br, 326 (5) $[M]^{+\cdot}$ with ^{79}Br, 262 (12), 247 (100), 201 (5), 199 (6), 120 (18), 105 (7), 91 (8), 77 (11), 63 (8), 51 (15), 41 (13). HRMS (EI): calcd. for $C_8H_8{}^{79}BrIO$ 325.8803; found 325.8811.

[4-(2-Iodo-4-methoxyphenyl)-1-butynyl](triisopropyl)silane (5): *n*-Butyllithium (1.6 M in hexanes, 10.40 mL, 16.64 mmol, 1.05 equiv.) was added dropwise to a solution of triisopropyl(prop-1-yn-1-yl)-silane (4.0 mL, 16.70 mmol, 1.06 equiv.) in THF (60 mL) at –78 °C under an atmosphere of argon. After the mixture was stirred at –78 °C for 1.5 h, bromide **4** (5.18 g, 15.84 mmol) in THF (20 mL) was added dropwise. The mixture was stirred at –78 °C for 10 min and then warmed to r.t. The solvents were removed in vacuo. Flash chromatography on silica gel (petroleum ether/diethyl ether, 99:1) gave alkyne **5** (5.22 g, 74%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98–1.06 (m, 21 H), 2.52 (t, J = 7.3 Hz, 2 H), 2.89 (t, J = 7.3 Hz, 2 H), 3.76 (s, 3 H), 6.81 (dd, J = 8.4, 2.7 Hz, 1 H), 7.20 (d, J = 8.4 Hz, 1 H), 7.34 (d, J = 2.7 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 11.27 (d), 18.61 (q), 20.79 (t), 38.93 (t), 55.49 (q), 81.25 (s), 99.95 (s), 107.58 (s), 114.26 (d), 124.34 (d), 130.14 (d), 135.08 (s), 158.31 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2959 (s), 2944 (s), 2865 (s), 2839 (s), 2170 (m), 1599 (s), 1563 (m), 1491 (s), 1464 (s), 1441 (m), 1428 (w), 1383 (w), 1366 (w), 1336 (w), 1323 (w), 1313 (w), 1286 (m), 1182 (w), 1159 (w), 1072 (w), 1062 (w), 1021 (s), 996 (m), 920 (w), 884 (w), 678 (m) cm^{-1}. MS (EI): m/z (%) = 442 (1) $[M]^{+\cdot}$, 399 (100), 371 (9), 357 (10), 273 (6), 247 (18), 229 (17), 201 (10), 153 (17), 121 (7), 97 (9), 83 (12), 73 (6), 59 (12). MS [FAB, bis(2-hydroxyethyl) disulfide]: m/z (%) = 399 [M – C_3H_7]$^+$, 371, 357, 343, 328, 273, 246, 229, 215, 201, 187, 171, 121, 87.

1-Bromo-7-methoxy-2-naphthyl Trifluoromethanesulfonate (7): *n*-Butyllithium (1.6 M in hexanes, 35 mL, 56.0 mmol, 1.0 equiv.) was added dropwise to alcohol **6** (14.21 g, 56.15 mmol)[9] in THF (360 mL) under an atmosphere of argon, and the mixture was stirred at –78 °C for 5 min. Triflic anhydride (12.0 mL, 71.33 mmol, 1.3 equiv.) was added dropwise, and the reaction mixture was stirred at –78 °C for 40 min. To prevent decomposition of the product, triethylamine (12 mL, 86.10 mmol, 1.5 equiv.) was added, and the reaction mixture was allowed to reach r.t. The solvents were removed in vacuo, and the residue was chromatographed on alumina (petroleum ether/diethyl ether/acetone, 80:10:10) to obtain triflate **7** (13.06 g, 67%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.98 (s, 3 H), 7.23 (dd, J = 8.9, 2.5 Hz, 1 H), 7.28 (d, J = 8.9 Hz, 1 H), 7.54 (d, J = 2.5 Hz, 1 H), 7.75 (d, J = 8.9 Hz, 1 H), 7.78 (br. d, J = 8.9 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 55.54 (q), 105.88 (d), 114.55 (s), 117.28 (d), 118.68 (q, $J_{C,F}$ = 320.5 Hz), 120.71 (d), 128.35 (s), 129.23 (d), 129.98 (d), 134.29 (s), 145.59 (s), 160.03 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3070 (vw), 3009 (w), 2962 (w), 2938 (w), 2910 (w), 2845 (vw), 2830 (vw), 1628 (s), 1599 (w), 1572 (w), 1507 (s), 1464 (m), 1460 (m), 1432 (vs), 1419 (s), 1384 (s), 1260 (m), 1228 (vs), 1217 (vs), 1189 (s), 1174 (s), 1142 (vs), 1036 (m), 991 (s), 978 (s), 867 (vs), 836 (s), 627 (s), 592 (s) cm^{-1}. MS (EI): m/z (%) = 386 (99) $[M]^{+\cdot}$ with ^{81}Br, 384 (98) $[M]^{+\cdot}$ with ^{79}Br, 253 (41), 351 (40), 225 (100), 223 (97), 210 (15), 208 (16), 182 (20), 180 (21), 172 (32), 160 (14), 157 (14), 129 (5), 113 (10), 101 (20), 75 (12), 69 (15), 63 (7), 51 (7). HRMS (EI): calcd. for $C_{12}H_8{}^{79}BrF_3O_4S$ 383.9279; found 383.9280.

Methyl 1-Bromo-7-methoxy-2-naphthoate (8): A Schlenk flask was charged with $Pd(OAc)_2$ (385 mg, 1.72 mmol, 5 mol-%) and dppp (708 mg, 1.72 mmol, 5 mol-%) and flushed with argon. Methanol (200 mL) with triethylamine (12 mL, 86.10 mmol, 2.5 equiv.) were added to the reaction mixture. Triflate **7** (12.0 g, 34.37 mmol) in DMSO (300 mL) was added, and the mixture was stirred at 70 °C for 2 h while carbon monoxide was slowly bubbled throughout the solution. The reaction mixture was diluted with water and extracted with diethyl ether (4 × 80 mL). Ethereal portions were combined, washed with water and dried with anhydrous Na_2SO_4. The solvents were removed in vacuo, and the residue was chromatographed on silica gel (petroleum ether/diethyl ether/acetone, 90:10:0 to 80:10:10) to provide methyl ester **8** (5.86 g, 58%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.99 (s, 3 H), 4.00 (s, 3 H), 7.25 (dd, J = 8.9, 2.5 Hz, 1 H), 7.54 (d, J = 8.4 Hz, 1 H), 7.72 (d, J = 2.5 Hz, 1 H), 7.74 (d, J = 8.9 Hz, 1 H), 7.76 (br. d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 52.66 (q), 55.48 (q), 106.61 (d), 120.87 (s), 121.09 (d), 123.49 (d), 127.47 (d), 129.80 (d), 130.61 (s), 131.72 (s), 133.69 (s), 159.48 (s), 168.05 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3067 (w), 1729 [vs (br)], 1626 (vs), 1603 (s), 1557 (m), 1510 (vs), 1443 (vs), 1434 [s (sh)], 1384 (s), 1273 (s), 1247 (vs), 1034 (s), 975 (m), 865 (w), 845 (vs), 528 (m) cm^{-1}. MS (EI): m/z (%) = 296 (98) $[M]^{+\cdot}$ with ^{81}Br, 294 (100) $[M]^{+\cdot}$ with ^{79}Br, 265 (51), 263 (56), 237 (16), 235 (18), 222 (9), 220 (9), 216 (33), 196 (7), 194 (7), 185 (22), 156 (25), 113 (33), 97 (16), 81 (25), 69 (52), 57 (41), 43 (57). HRMS (EI): calcd. for $C_{13}H_{11}{}^{79}BrO_3$ 293.9892; found 293.9879.

(1-Bromo-7-methoxy-2-naphthyl)methanol (9): Lithium aluminium hydride (1.0 M in THF, 17.0 mL, 17.0 mmol, 0.6 equiv.) was added dropwise to methyl ester **8** (8.21 g, 27.82 mmol) in THF (160 mL) under an atmosphere of argon, and the mixture was stirred at 0 °C for 1 h. Then anhydrous Na_2SO_4 (10 g) was added, and the excess hydride was decomposed by the careful addition of a saturated solution of Na_2SO_4 in water. The reaction mixture was filtered through a short pad of silica gel (ether), and the solvents were removed in vacuo to provide pure alcohol **9** (6.66 g, 90%) as an amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.06 (t, J = 6.0 Hz, 1 H), 3.98 (s, 3 H), 4.97 (J = 6.0 Hz, 2 H), 7.18 (dd, J = 8.9, 2.5 Hz, 1 H), 7.49 (d, J = 8.3 Hz, 1 H), 7.59 (d, J = 2.5 Hz, 1 H), 7.73 (d, J = 8.9 Hz, 1 H), 7.76 (br. d, J = 8.3 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 55.43 (q), 66.11 (t), 105.34 (d), 119.42 (d), 121.15 (s), 123.70 (d), 127.68 (d), 129.51 (s), 129.82 (d), 133.53 (s), 138.25 (s), 159.13 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3608 (m), 3461 (w), 3066 (w), 2841 (w), 1627 (vs), 1603 (m), 1559 (w), 1512 (vs), 1461 (s), 1414 (w), 1381 (s), 1313 (m), 1263 (s), 1034 (s), 842 (vs), 527 (m) cm^{-1}. MS (EI): m/z (%) = 268 (95) $[M]^{+\cdot}$ with ^{81}Br, 266 (100) $[M]^{+\cdot}$ with ^{79}Br, 256 (9), 188 (32), 158 (36), 144 (53), 127 (25), 115 (48), 93 (12), 69 (10), 57 (16), 43 (19). HRMS (EI): calcd. for $C_{12}H_{11}{}^{79}BrO$ 265.9942; found 265.9938.

1-Bromo-2-(bromomethyl)-7-methoxynaphthalene (10): Phosphorus tribromide (1.20 mL, 12.63 mmol, 1.3 equiv.) was added dropwise to alcohol **9** (7.86 g, 29.43 mmol) in THF (200 mL) under an atmosphere of argon, and the mixture was stirred at 0 °C for 2.5 h. The solvent was evaporated in vacuo, and the residue was chromatographed on silica gel (petroleum ether/diethyl ether, 90:10 to 80:20) to furnish bromide **10** (6.49 g, 67%) as an amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.98 (s, 3 H), 4.84 (s, 2 H), 7.19 (dd, J = 8.9, 2.5 Hz, 1 H), 7.38 (d, J = 8.3 Hz, 1 H), 7.62 (d, J = 2.5 Hz, 1 H), 7.71 (d, J = 8.9 Hz, 1 H), 7.71 (d, J = 8.3 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 35.00 (t), 55.47 (q), 106.14 (d), 120.00 (d), 123.56 (s), 125.36 (d), 127.95 (d), 129.59 (s), 129.78 (d), 133.91 (s), 135.40 (s), 159.35 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3064 (w), 2840 (w), 1625 (vs), 1601 (m), 1559 (m), 1512 (vs), 1460 (vs), 1413 (m), 1382 (s), 1317 (m), 1263 (vs), 1034 (s), 841 (vs), 657 (m), 628 (m), 527 (m) cm^{-1}. MS (EI): m/z (%) = 332 (15) $[M]^{+\cdot}$ with ^{81}Br/^{81}Br, 330 (31) $[M]^{+\cdot}$ with ^{79}Br/^{81}Br, 328 (16) $[M]^{+\cdot}$ with ^{79}Br/^{79}Br,

251 (98), 249 (100), 208 (8), 206 (10), 171 (35), 155 (18), 139 (9), 127 (33), 98 (14), 83 (15), 69 (23), 57 (34), 55 (29), 43 (33). HRMS (EI): calcd. for $C_{12}H_{10}{}^{79}Br_2O$ 327.9098; found 327.9110.

[4-(1-Bromo-7-methoxy-2-naphthyl)-1-butynyl](triisopropyl)silane (11): *n*-Butyllithium (1.6 M in hexanes, 18.0 mL, 28.8 mmol, 1.06 equiv.) was added dropwise to a solution of triisopropyl(prop-1-yn-1-yl)silane (6.90 mL, 28.81 mmol, 1.06 equiv.) in THF (80 mL) at –78 °C under an atmosphere of argon. After the mixture was stirred at –78 °C for 2 h, bromide **10** (8.93 g, 27.06 mmol) in THF (120 mL) was added dropwise. The mixture was stirred at –78 °C for 1 h and then warmed to r.t. The solvents were removed in vacuo. Flash chromatography on silica gel (petroleum ether) gave alkyne **11** (9.29 g, 77%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98–1.07 (m, 21 H), 2.66 (t, J = 7.3 Hz, 2 H), 3.20 (t, J = 7.3 Hz, 2 H), 3.97 (s, 3 H), 7.14 (dd, J = 8.9, 2.6 Hz, 1 H), 7.30 (d, J = 8.2 Hz, 1 H), 7.61 (d, J = 2.6 Hz, 1 H), 7.61 (d, J = 8.2 Hz, 1 H), 7.69 (d, 1 H, 8.9) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 11.29 (d), 18.59 (q), 20.39 (t), 36.87 (t), 55.41 (q), 81.29 (s), 105.82 (d), 107.66 (s), 118.72 (d), 122.57 (s), 126.15 (d), 127.11 (d), 128.84 (s), 129.65 (d), 133.81 (s), 138.55 (s), 158.95 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3062 (w), 2866 (vs), 2171 (s), 1627 (s), 1603 (m), 1558 (w), 1512 (vs), 1461 (vs), 1412 (m), 1381 (s), 1367 (m), 1317 (m), 1261 (s), 1073 (w), 1035 (s), 996 (m), 884 (s), 838 (s), 678 (s), 660 (s), 624 (m), 618 (m), 526 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 446 (66) $[M]^{+\cdot}$ with ^{81}Br, 444 (65) $[M]^{+\cdot}$ with ^{79}Br, 403 (100), 401 (96), 366 (16), 347 (21), 323 (24), 305 (61), 279 (29), 263 (17), 251 (76), 237 (44), 274 (47), 265 (35), 139 (29), 96 (42), 89 (38), 73 (41), 59 (76), 43 (41). HRMS (EI): calcd. for $C_{24}H_{33}{}^{79}BrOSi$ 444.1484; found 444.1497.

[4-(1-Iodo-7-methoxy-2-naphthyl)-1-butynyl](triisopropyl)silane (12): *n*-Butyllithium (1.6 M in hexanes, 7.0 mL, 11.20 mmol, 1.01 equiv.) was added dropwise to a stirred solution of aryl bromide **11** (4.94 g, 11.10 mmol) in THF (100 mL) at –78 °C under an atmosphere of argon. After the mixture was stirred at –78 °C for 20 min, iodine (3.64 g, 14.40 mmol, 1.3 equiv.) in THF (20 mL) was added dropwise. The mixture was stirred at –78 °C for 30 min and then warmed to r.t. The reaction mixture was evaporated to dryness in vacuo, and the residue was diluted with dichloromethane (100 mL), washed with water (1 ×), $Na_2S_2O_3$ (2 ×), water (1 ×) and dried with anhydrous Na_2SO_4. The solvent was removed in vacuo, and the residue was chromatographed on silica gel (petroleum ether) to afford pure iodide **12** (3.34 g, 61%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98–1.07 (m, 21 H), 2.65 (t, J = 7.4 Hz, 2 H), 3.24 (t, J = 7.4 Hz, 2 H), 3.98 (s, 3 H), 7.12 (dd, J = 8.8, 2.6 Hz, 1 H), 7.31 (d, J = 8.2 Hz, 1 H), 7.58 (d, J = 2.6 Hz, 1 H), 7.64 (br. d, J = 8.2 Hz, 1 H), 7.66 (d, J = 8.8 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 11.29 (q), 18.61 (q), 20.71 (t), 42.23 (t), 55.43 (q), 81.39 (s), 104.04 (s), 107.51 (s), 111.67 (d), 118.60 (d), 125.66 (d), 128.23 (d), 128.24 (s), 129.84 (d), 136.46 (s), 142.97 (s), 159.28 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3060 (w), 2866 (vs), 2170 (m), 1626 (vs), 1601 (w), 1552 (w), 1511 (vs), 1460 (s), 1407 (w), 1377 (s), 1365 [w (sh)], 1315 (w), 1260 (s), 1035 (s), 1073 (w), 996 (m), 884 (s), 839 (s), 678 (s), 660 (s), 628 (m), 618 (m), 518 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 492 (56) $[M]^{+\cdot}$, 449 (100), 407 (12), 323 (14), 279 (23), 251 (24), 237 (26), 197 (36), 189 (19), 59 (19). HRMS (EI): calcd. for $C_{24}H_{33}IOSi$ 492.1345; found 492.1352.

Triisopropyl(4-{7-methoxy-1-[(trimethylsilyl)ethynyl]-2-naphthyl}-1-butynyl)silane (13): A teflon autoclave was charged with aryl iodide **12** (1.75 g, 3.55 mmol), $Pd(PPh_3)_4$ (205 mg, 0.177 mmol, 5 mol%) and CuI (67 mg, 0.352 mmol, 10 mol%) and then flushed with argon. Diisopropylamine (20 mL) and TMS-C≡CH (800 μL, 5.66 mmol, 1.6 equiv.) were added, and the reaction was stirred at 80 °C for 1 h. The precipitate was filtered off and washed with petroleum ether (3 × 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/diethyl ether, 99:1) to obtain **13** (1.63 g, 99%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.34 (s, 9 H), 0.99–1.06 (m, 21 H), 2.66 (t, J = 7.7 Hz, 2 H), 3.21 (t, J = 7.7 Hz, 2 H), 3.95 (s, 3 H), 7.12 (dd, J = 8.8, 2.5 Hz, 1 H), 7.26 (d, J = 8.5 Hz, 1 H), 7.66 (br. d, J = 2.5 Hz, 1 H), 7.68 (d, J = 8.5 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 0.14 (q), 11.28 (d), 18.60 (q), 20.89 (t), 35.09 (t), 55.14 (q), 80.76 (s), 101.70 (s), 104.11 (s), 104.48 (d), 108.26 (s), 117.93 (s), 118.40 (d), 125.01 (d), 127.31 (s), 128.18 (d), 129.55 (d), 135.13 (s), 142.68 (s), 158.62 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3053 (w), 2865 (s), 2170 (m), 2146 (w), 1623 (s), 1598 (w), 1570 (w), 1511 (m), 1462 (s), 1388 (w), 1367 (w), 1251 (s), 1072 (w), 1032 (m), 996 (w), 884 (m), 853 (vs), 843 (vs), 678 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 462 (100) $[M]^{+\cdot}$, 447 (7), 419 (93), 389 (6), 379 (11), 345 (10), 319 (11), 290 (8), 275 (22), 251 (10), 219 (8), 158 (11), 115 (14), 101 (10), 87 (15), 73 (67), 59 (41), 45 (6). HRMS (EI): calcd. for $C_{29}H_{42}OSi_2$ 462.2774; found 462.2772.

[4-(1-Ethynyl-7-methoxy-2-naphthyl)-1-butynyl](triisopropyl)silane (14): Sodium methoxide generated from sodium (277 mg, 12.04 mmol, 2.4 equiv.) and methanol (10 mL) was added to TMS derivative **13** (2.32 g, 5.01 mmol) in methanol (20 mL) under an atmosphere of argon, and the mixture was stirred at r.t. for 2 h. The solution was evaporated in vacuo to dryness, and the residue was chromatographed on silica gel (petroleum ether/diethyl ether, 99:1 to 90:10) to afford **14** (1.94 g, 99%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99–1.06 (m, 21 H), 2.68 (t, J = 7.4 Hz, 2 H), 3.23 (t, J = 7.4 Hz, 2 H), 3.71 (s, 1 H), 3.96 (s, 3 H), 7.13 (dd, J = 9.0, 2.6 Hz, 1 H), 7.30 (d, J = 8.4 Hz, 1 H), 7.65 (d, 1 H, 2.6), 7.68 (d, J = 8.4 Hz, 1 H), 7.70 (d, J = 9.0 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 11.28 (d), 18.58 (q), 21.00 (t), 34.61 (t), 55.33 (q), 80.26 (s), 81.06 (s), 86.29 (d), 104.34 (d), 108.07 (s), 116.89 (s), 118.50 (d), 125.07 (d), 127.29 (s), 128.43 (d), 129.59 (d), 135.32 (s), 143.10 (s), 158.75 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3305 (m), 3052 (w), 2865 (vs), 2170 (m), 2098 (w), 1624 (s), 1598 (w), 1571 (w), 1511 (m), 1462 (s), 1387 (m), 1367 (w), 1070 (w), 1030 (m), 996 (m), 883 (s), 678 (m), 660 (s), 610 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 390 (100) $[M]^{+\cdot}$, 379 (20), 347 (42), 289 (23), 275 (21), 263 (49), 247 (14), 202 (20), 182 (23), 158 (20), 152 (28), 146 (21), 139 (18), 115 (31), 87 (14), 73 (38), 59 (43), 41 (11). HRMS (EI): calcd. for $C_{26}H_{34}OSi$ 390.2379; found 390.2391.

Triisopropyl{4-[4-methoxy-2-({7-methoxy-2-[4-(triisopropylsilyl)-3-butynyl]-1-naphthyl}ethynyl)phenyl]-1-butynyl}silane (15): A Schlenk flask was charged with phenyl iodide **5** (1.73 g, 3.91 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (113 mg, 0.098 mmol, 2.5 mol%), CuI (37 mg, 0.194 mmol, 5 mol%) and flushed with argon. Diisopropylamine (10 mL) and then naphthyl acetylene **14** (1.53 g, 3.92 mmol, 1.0 equiv.) in diisopropylamine (10 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 × 10 mL). The combined fractions were evaporated to dryness in vacuo, and the residue was chromatographed on silica gel (petroleum ether/diethyl ether, 99:1) to obtain **15** (1.82 g, 66%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.97–1.04 (m, 42 H), 2.71 (t, J = 7.2 Hz, 2 H), 2.75 (t, J = 7.4 Hz, 2 H), 3.18 (t, J = 7.2 Hz, 2 H), 3.29 (t, J = 7.4 Hz, 2 H), 3.83 (s, 3 H), 3.99 (s, 3 H), 6.86 (dd, J = 8.5, 2.8 Hz, 1 H), 7.14 (d, J = 2.8 Hz, 1 H), 7.14 (dd, J = 8.9, 2.5 Hz, 1 H), 7.29 (d, J = 8.5 Hz, 1 H), 7.34 (d, J = 8.3 Hz, 1 H), 7.68 (br. d, J = 8.3 Hz, 1 H), 7.72 (d, J = 8.9 Hz, 1 H), 7.76 (d, J = 2.5 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 11.29 (d), 18.57 (q), 18.59 (q), 21.29 (t), 21.48 (t), 33.40 (t), 35.02 (t), 55.27 (q), 55.38 (q), 81.19 (s), 81.28 (s), 89.73 (s), 97.16 (s), 104.39 (d), 107.88 (s), 107.95 (s), 114.54 (d), 117.31 (d), 118.00 (s), 118.49 (d), 123.77 (s),

125.30 (d), 127.49 (s), 128.12 (d), 129.65 (d), 130.57 (d), 134.37 (s), 135.05 (s), 142.07 (s), 157.97 (s), 158.67 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3053 (w), 2865 (vs), 2170 (m), 1623 (s), 1604 (m), 1569 (w), 1511 (m), 1500 (m), 1462 (s), 1426 (m), 1387 (w), 1383 (w), 1366 (w), 1316 (w), 1180 (w), 1176 (w), 1072 (w), 1038 (m), 996 (m), 883 (m), 678 (m) cm^{-1}. MS (EI): *m/z* (%) = 704 (4) $[M]^{+\cdot}$, 661 (7), 462 (5), 399 (100), 353 (14), 323 (15), 271 (11), 229 (26), 201 (18), 149 (17), 115 (29), 87 (16), 59 (29). HRMS (EI): calcd. for $C_{46}H_{64}O_2Si_2$ 704.4445; found 704.4462.

2-(3-Butynyl)-1-{[2-(3-butynyl)-5-methoxyphenyl]ethynyl}-7-methoxynaphthalene (16): Tetrabutylammonium fluoride (1.07 M in THF, 1.06 mL, 1.13 mmol, 2.5 equiv.) was added to silylated triyne **15** (320 mg, 0.454 mmol) in THF (15 mL) under an atmosphere of argon, and the mixture was stirred at r.t. for 1 h. The solution was evaporated in vacuo to dryness, and the residue was chromatographed on silica gel (petroleum ether/diethyl ether, 95:5) to obtain **16** (178 mg, 99%) as an oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.98 (t, *J* = 2.6 Hz, 1 H), 2.00 (t, *J* = 2.7 Hz, 1 H), 2.63 (dt, *J* = 7.5, 7.5, 2.6 Hz, 2 H), 2.68 (dt, *J* = 7.6, 7.6, 2.7 Hz, 2 H), 3.17 (t, *J* = 7.5 Hz, 2 H), 3.30 (t, *J* = 7.6 Hz, 2 H), 3.84 (s, 3 H), 4.00 (s, 3 H), 6.90 (dd, *J* = 8.5, 2.7 Hz, 1 H), 7.16 (dd, *J* = 8.8, 2.6 Hz, 1 H), 7.18 (d, *J* = 2.7 Hz, 1 H), 7.26 (d, *J* = 8.5 Hz, 1 H), 7.30 (d, *J* = 8.3 Hz, 1 H), 7.72 (br. d, *J* = 8.3 Hz, 1 H), 7.73 (d, *J* = 8.9 Hz, 1 H), 7.75 (br. d, *J* = 2.6 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 19.83 (t), 20.00 (t), 33.03 (t), 34.73 (t), 55.39 (q), 69.05 (d), 69.19 (d), 83.71 (s), 83.78 (s), 89.71 (s), 97.15 (s), 104.36 (d), 114.92 (d), 117.27 (d), 118.08 (s), 118.70 (d), 123.81 (s), 124.96 (d), 127.47 (s), 128.35 (d), 129.73 (d), 130.16 (d), 133.97 (s), 134.98 (s), 141.89 (s), 158.00 (s), 158.79 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3307 (s), 3052 (w), 2838 (w), 2117 (w), 1623 (vs), 1604 (m), 1569 (m), 1510 (s), 1501 (s), 1462 (s), 1426 (m), 1176 (m), 1036 (s), 640 (s) cm^{-1}. MS (EI): *m/z* (%) = 392 (100) $[M]^{+\cdot}$, 377 (12), 361 (19), 354 (43), 345 (21), 307 (18), 289 (42), 279 (23), 263 (18), 252 (17), 239 (25), 226 (23), 217 (15), 189 (20), 171 (33), 149 (54), 138 (18), 121 (32), 97 (15), 83 (17), 71 (26), 57 (37), 43 (23). HRMS (EI): calcd. for $C_{28}H_{24}O_2$ 392.1776; found 392. 1776.

2,15-Dimethoxy-5,6,9,10-tetrahydrohexahelicene (17): A Schlenk flask was charged with triyne **16** (99 mg, 0.253 mmol) and flushed with argon. The substrate was dissolved in decane (4 mL) at 90 °C. Then a solution of triphenylphosphane (27 mg, 0.101 mmol, 40 mol%) in hot decane (1.5 mL) and $CpCo(CO)_2$ (7 µL, 0.53 mmol, 20 mol%) in decane (0.5 mL) were added, and the mixture was stirred at 140 °C for 1 h under concomitant irradiation with a halogen lamp. The solvent was evaporated in vacuo, and the residue was chromatographed on silica gel (petroleum ether/diethyl ether, 95:5) to obtain **17** (55 mg, 56%) as amorphous solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.63–2.78 (m, 2 H), 2.81–3.02 (m, 2 H), 2.88 (s, 3 H), 3.48 (s, 3 H), 6.12 (d, *J* = 2.6 Hz, 1 H), 6.44 (dd, *J* = 6.8, 2.6 Hz, 1 H), 6.78 (br. d, *J* = 2.6 Hz, 1 H), 6.83 (dd, *J* = 8.8, 2.6 Hz, 1 H), 7.05 (br. d, *J* = 8.1 Hz, 1 H), 7.21 (dd, *J* = 7.4, 1.1 Hz, 1 H), 7.27 (dd, *J* = 7.4, 1.1 Hz, 1 H), 7.34 (br. d, *J* = 8.0 Hz, 1 H), 7.55 (d, *J* = 8.8 Hz, 1 H), 7.62 (br. d, *J* = 8.1 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 29.29 (t), 30.46 (t), 30.85 (t), 31.44 (t), 54.53 (q), 54.58 (q), 104.15 (d), 112.17 (d), 114.52 (d), 117.78 (d), 124.06 (d), 127.27 (d), 127.97 (d), 128.34 (d), 128.35 (d), 128.63 (s), 129.07 (d), 129.79 (s), 130.93 (s), 130.94 (s), 131.28 (s), 133.59 (s), 136.22 (s), 138.11 (s), 139.07 (s), 140.94 (s), 157.42 9s), 157.46 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3050 (w), 2899 (m), 2836 (m), 1624 (vs), 1609 (s), 1598 [m (sh)], 1561 (w), 1571 (m), 1514 (vs), 1498 (vs), 1445 (m), 1411 (m), 1380 (m), 1323 (m), 1307 (m), 1256 (m), 1184 (m), 1175 (s), 1165 [m (sh)], 1050 [w (sh)], 1035 (s), 942 (w), 909 (s), 857 (s), 838 (vs), 825 (s), 811 (w), 636 (w), 516 (w), 558 (w), 431 (vw) cm^{-1}. MS (EI): *m/z* (%) = 392 (100) $[M]^{+\cdot}$, 363 (3), 277 (4), 261 (5), 196 (6), 171 (6), 127 (8), 69 (10) 57 (13), 43 (10). HRMS (EI): calcd. for $C_{28}H_{24}O_2$ 392.1776; found 392.1767.

2,15-Dimethoxyhexahelicene (18): A solution of **17** (68 mg, 0.173 mmol) and Ph_3CBF_4 (170 mg, 0.515 mmol, 3.0 equiv.) in 1,2-dichloroethane (6 mL) was stirred under an atmosphere of argon at 85 °C for 12 h. The solvent was removed in vacuo, and the residue was chromatographed on silica gel (petroleum ether/diethyl ether, 95:5) to obtain **18** (57 mg, 85%) as an amorphous solid. ^1H NMR and ^{13}C NMR spectra were in agreement with the literature data.[15]

Triisopropyl{4-[4-methoxy-2-({2-[4-(triisopropylsilyl)-3-butynyl]-1-naphthyl}ethynyl)phenyl]-1-butynyl}silane (20): A Schlenk flask was charged with phenyl iodide **5** (2.06 g, 4.66 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (135 mg, 0.117 mmol, 2.5 mol%) and CuI (44 mg, 0.231 mmol, 5 mol%) and flushed with argon. Diisopropylamine (10 mL) and then naphthyl acetylene **19** (1.68 g, 4.66 mmol, 1.0 equiv.)[7] in diisopropylamine (8 mL) were added, and the reaction mixture was stirred at 80 °C for 10 min. The precipitate was filtered off and washed with petroleum ether (5 × 10 mL). The combined fractions were evaporated to dryness in vacuo, and the residue was chromatographed on silica gel (petroleum ether/diethyl ether, 99:1 to 95:5) to obtain **20** (2.70 g, 86%) as an oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.97–1.05 (m, 42 H), 2.71 (t, *J* = 7.3 Hz, 2 H), 2.75 (t, *J* = 7.3 Hz, 2 H), 3.13 (t, *J* = 7.3 Hz, 2 H), 3.31 (t, *J* = 7.3 Hz, 2 H), 3.85 (s, 3 H), 6.86 (dd, *J* = 8.5, 2.8 Hz, 1 H), 7.17 (d, *J* = 2.8 Hz, 1 H), 7.29 (d, *J* = 8.5 Hz, 1 H), 7.48 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1 H), 7.49 (d, *J* = 8.5 Hz, 1 H), 7.58 (ddd, *J* = 8.3, 6.7, 1.4 Hz, 1 H), 7.76 (d, *J* = 8.5 Hz, 1 H), 7.83 (dt, *J* = 8.1, 1.4, 0.7, 0.7 Hz, 1 H), 8.42 (ddt, *J* = 8.4, 1.2, 0.8, 0.8 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 11.27 (d), 11.29 (d), 18.58 (q), 18.61 (q), 21.30 (t), 21.54 (t), 33.51 (t), 34.86 (t), 55.47 (q), 81.10 (s), 81.27 (s), 89.40 (s), 97.19 (s), 107.84 (s), 108.01 (s), 114.74 (s), 117.29 (d), 119.24 (s), 123.61 (s), 125.75 (d), 126.00 (d), 126.87 (d), 127.61 (d), 128.11 (d), 128.32 (d), 130.58 (d), 132.01 (s), 133.58 (s), 134.54 (s), 141.57 (s), 157.91 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3058 (w), 2958 (s), 2944 (vs), 2865 (vs), 2837 [w (sh)], 2170 (m), 1603 (m), 1569 (w), 1500 (m), 1491 (m), 1464 (s), 1444 (w), 1430 (w), 1383 (w), 1366 (w), 1337 (w), 1324 (w), 1291 (w), 1156 (w), 1181 (w), 1073 (w), 1062 (w), 1024 (m), 996 (m), 919 (w), 883 (s), 852 (w), 817 (w), 679 (s) cm^{-1}. MS (EI): *m/z* (%) = 674 (7) $[M]^{+\cdot}$, 631 (24), 516 (5), 473 (7), 157 (66), 129 (17), 115 (100), 101 (14), 87 (48), 73 (49), 59 (60), 41 (7). HRMS (EI): calcd. for $C_{45}H_{62}OSi_2$ 674.4339; found 674.4316.

2-(3-Butynyl)-1-{[2-(3-butynyl)-5-methoxyphenyl]ethynyl}naphthalene (21): Tetrabutylammonium fluoride (1.07 M in THF, 3.20 mL, 3.43 mmol, 2.4 equiv.) was added to silylated triyne **20** (956 mg, 1.42 mmol) in THF (25 mL) under an atmosphere of argon, and the mixture was stirred at r.t. for 1 h. The solution was evaporated in vacuo to dryness, and the residue was chromatographed on silica gel (petroleum ether/diethyl ether, 95:5) to obtain **21** (307 mg, 60%) as an amorphous solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.00 (t, *J* = 2.6 Hz, 1 H), 2.02 (t, *J* = 2.7 Hz, 1 H), 2.64 (dt, *J* = 7.6, 7.6, 2.6 Hz, 2 H), 2.69 (dt, *J* = 7.6, 7.6, 2.7 Hz, 2 H), 3.16 (t, *J* = 7.6 Hz, 2 H), 3.33 (t, *J* = 7.6 Hz, 2 H), 3.86 (s, 3 H), 6.90 (dd, *J* = 8.5, 2.7 Hz, 1 H), 7.20 (d, *J* = 7.7 Hz, 1 H), 7.26 (d, *J* = 8.5 Hz, 1 H), 7.45 (d, *J* = 8.5 Hz, 1 H), 7.50 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1 H), 7.60 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1 H), 7.80 (br. d, *J* = 8.5 Hz, 1 H), 7.84 (ddt, *J* = 8.1, 1.3, 0.7, 0.7 Hz, 1 H), 8.43 (ddt, *J* = 8.3, 1.3, 0.8, 0.8 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 19.82 (t), 20.15 (t), 33.23 (t), 34.59 (t), 55.46 (q), 69.05 (d), 69.12 (s), 83.71 (s), 83.81 (s), 89.39 (s), 97.17 (s), 115.07 (d), 117.23 (d), 119.36 (s), 123.69 (s), 125.94 (d), 126.08 (d), 127.05 (d), 127.28 (d), 128.17 (d), 128.55 (d), 130.26 (d), 132.03 (s), 133.56 (s), 134.28 (s), 141.33 (s), 158.01 (s) ppm. IR

($CHCl_3$): $\tilde{\nu}$ = 3308 (s), 3059 (w), 2937 (w), 2915 (w), 2864 (w), 2838 (w), 2200 (vw), 2117 (w), 1604 (s), 1569 (w), 1500 (s), 1492 (m), 1466 (m), 1444 (w), 1433 (w), 1382 (w), 1322 (w), 1293 (w), 1284 (w), 1262 (m), 1235 (m), 1182 (w), 1156 (w), 1116 (w), 1038 (m), 867 (w), 820 (m), 640 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 362 (2) $[M]^{+\cdot}$, 286 (21), 247 (100), 201 (3), 199 (3), 120 (10), 115 (8), 51 (6). HRMS (EI): calcd. for $C_{27}H_{22}O$ 362.1671; found 362.1678.

2-Methoxy-5,6,9,10-tetrahydrohexahelicene (22): A Schlenk flask was charged with triyne **21** (193 mg, 0.532 mmol) and flushed with argon. The substrate was dissolved in decane (5 mL) at 90 °C. Then a solution of triphenylphosphane (52 mg, 0.214 mmol, 40 mol%) in hot decane (3 mL) and $CpCo(CO)_2$ (14 μL, 0.0106 mmol, 20 mol%) 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/diethyl ether, 99:1 to 95:5) to obtain **22** (148 mg, 77%) as amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.68–3.02 (m, 8 H), 2.87 (s, 3 H), 6.00 (d, *J* = 2.6 Hz, 1 H), 6.39 (dd, *J* = 8.2, 2.6 Hz, 1 H), 6.89 (ddd, *J* = 8.7, 6.7, 1.4 Hz, 1 H), 7.05 (dd, *J* = 8.2, 1.1 Hz, 1 H), 7.14 (ddd, *J* = 8.1, 6.7, 1.1 Hz, 1 H), 7.21 (dd, *J* = 7.4, 1.1 Hz, 1 H), 7.26 (dd, *J* = 7.4, 1.2 Hz, 1 H), 7.47 (d, *J* = 8.2 Hz, 1 H), 7.48 (dq, *J* = 7.8, 1.0, 1.0, 1.0 Hz, 1 H), 7.65 (ddt, *J* = 8.1, 1.4, 0.6, 0.6 Hz, 1 H), 7.68 (br. d, *J* = 8.2 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 29.02 (t), 30.27 (t), 30.59 (t), 31.07 (t), 54.54 (q), 112.34 (d), 114.02 (d), 124.45 (d), 124.93 (d), 125.88 (d), 126.18 (d), 126.26 (d), 126.38 (d), 127.38 (d), 127.46 (d), 127.83 (d), 129.66 (s), 130.32 (s), 130.95 (s), 132.03 (s), 132.97 (s), 134.28 (s), 136.02 (s), 138.12 (s), 140.60 (s), 157.18 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2942 (s), 2899 (m), 2837 (m), 1608 (s), 1596 (m), 1570 (m), 1509 [m (sh)], 1497 (s), 1419 (w), 1408 (w), 1306 (m), 1183 (m), 1176 (m), 1036 (m), 825 (vs) cm^{-1}. MS (EI): *m*/*z* (%) = 362 (100) $[M]^{+\cdot}$, 213 (10), 199 (17), 149 (11), 121 (26), 101 (10), 91 (12), 83 (8), 75 (14), 59 (24), 43 (44). HRMS (EI): calcd. for $C_{27}H_{22}O$ 362.1671; found 362.1672.

2-Methoxyhexahelicene (23): A solution of **22** (143 mg, 0.395 mmol) and Ph_3CBF_4 (391 mg, 1.18 mmol, 3.0 equiv.) in 1,2-dichloroethane (6 mL) was stirred under an atmosphere of argon at 80 °C for 3 h. The solvent was removed in vacuo, and the residue was chromatographed on silica gel (petroleum ether/diethyl ether, 95:5) to obtain **23** (136 mg, 96%)[14] as an amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.90 (s, 3 H), 6.74 (ddd, *J* = 8.6, 6.9, 1.4 Hz, 1 H), 6.87 (dd, *J* = 8.7, 2.6 Hz, 1 H), 6.99 (br. d, *J* = 2.6 Hz, 1 H), 7.27 (ddd, *J* = 7.9, 6.9, 1.1 Hz, 1 H), 7.66 (ddt, *J* = 8.6, 1.1, 0.7, 0.7 Hz, 1 H), 7.75 (br. d, *J* = 8.7 Hz, 1 H), 7.85 (ddd, *J* = 7.9, 1.4, 0.6 Hz, 1 H), 7.83 (d, *J* = 8.4 Hz, 1 H), 7.88 (dt, *J* = 8.4, 0.6, 0.6 Hz, 1 H), 7.89 (dt, *J* = 8.5, 0.6, 0.6 Hz, 1 H), 7.96 (d, *J* = 8.5 Hz, 1 H), 7.98 (d, *J* = 8.2 Hz, 2 H), 8.00 (d, *J* = 8.2 Hz, 1 H), 8.02 (d, *J* = 8.2 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 54.23 (q), 107.71 (d), 117.53 (d), 123.86 (d), 124.18 (s), 124.87 (d), 125.94 (d), 126.28 (d), 126.80 (s), 126.86 (d), 126.97 (d), 127.04 (d), 127.26 (d), 127.37 (s), 127.40 (s), 127.44 (d), 127.57 (d), 127.70 (d), 127.82 (d), 129.45 (d), 130.25 (s), 131.05 (s), 131.23 (s), 131.63 (s), 131.84 (s), 133.07 (s), 157.13 (s) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3087 (w), 3051 (m), 3030 (w), 1621 (m), 1612 (m), 1584 (w), 1522 (w), 1507 (m), 1495 (m), 1479 (m), 1466 (m), 1454 (m), 1449 [w (sh)], 1438 (w), 1430 (m), 1404 (w), 1368 (m), 1292 (w), 1275 (w), 1258 (w), 1231 (s), 1183 (m), 1160 (w), 1153 (w), 1138 (m), 1115 (w), 1091 (w), 1073 [w (sh)], 1050 (w), 1037 (w), 1031 (m), 1002 (w), 870 (m), 849 (vs), 837 (s), 819 (w), 802 (m), 684 (w), 640 (w), 633 (vw), 624 (w), 612 (w), 606 (w), 587 (m), 533 (m), 511 (m), 501 (w), 483 (w), 436 (vw), 429 (vw) cm^{-1}. MS (EI): *m*/*z* (%) = 358 (100) $[M]^{+\cdot}$, 342 (6), 327 (15), 313 (17), 300 (21), 179 (5), 163 (12), 150 (18), 143 (8), 57 (15), 43 (9). MS (FAB, thioglycerol/glycerol): *m*/*z* = 358 $[M]^+$, 327, 313, 300, 282, 276, 263, 256, 242, 218, 185, 165, 149, 115, 93, 69, 55. HRMS (FAB): calcd. for $C_{27}H_{18}O$ 358.1358; found 358.1315.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for compounds **2**, **5**, **7**–**17** and **20**–**23** and ^{1}H NMR spectrum for compound **4**.

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[1] For selected reviews, see: a) A. Urbano, *Angew. Chem. Int. Ed.* **2003**, *42*, 3986; b) H. Hopf, *Classics in Hydrocarbon Chemistry: Syntheses, Concepts, Perspectives*, VCH, Weinheim, **2000**, p. 323; c) T. J. Katz, *Angew. Chem. Int. Ed.* **2000**, *39*, 1921; d) F. Vögtle, *Fascinating Molecules in Organic Chemistry*, Wiley, New York, **1992**, p. 156; e) G. Oremek, U. Seiffert, A. Janecka, *Chem.-Ztg.* **1987**, *111*, 69; f) K. P. Meurer, F. Vögtle, *Top. Curr. Chem.* **1985**, *127*, 1; g) W. H. Laarhoven, W. J. C. Prinsen, *Top. Curr. Chem.* **1984**, *125*, 63.

[2] a) D. Nakano, M. Yamaguchi, *Tetrahedron Lett.* **2003**, *44*, 4969; b) I. Sato, R. Yamashima, K. Kadowaki, J. Yamamoto, T. Shibata, K. Soai, *Angew. Chem. Int. Ed.* **2001**, *40*, 1096; c) S. D. Dreher, T. J. Katz, K. C. Lam, A. L. Rheingold, *J. Org. Chem.* **2000**, *65*, 815; d) M. T. Reetz, S. Sostmann, *J. Organomet. Chem.* **2000**, *603*, 105; e) M. T. Reetz, E. W. Beuttenmüller, R. Goddard, *Tetrahedron Lett.* **1997**, *38*, 3211.

[3] M. T. Reetz, S. Sostmann, R. Goddard, *Helixol – A New Ligand with Helical Chirality for Asymmetric Catalysis*, 10th IUPAC Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS), P-444, Versailles, France, **1999**.

[4] a) C. Wachsmann, E. Weber, M. Czugler, W. Seichter, *Eur. J. Org. Chem.* **2003**, 2863; b) M. T. Reetz, S. Sostmann, *Tetrahedron* **2001**, *57*, 2515.

[5] B. Ben Hassine, M. Gorsane, F. Geerts-Evrard, J. Pecher, R. H. Martin, D. Castelet, *Bull. Soc. Chim. Belg.* **1986**, *95*, 557.

[6] a) I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, D. Šaman, P. Fiedler, *Collect. Czech. Chem. Commun.* **2003**, *68*, 917; b) F. Teplý, I. G. Stará, I. Starý, A. Kollárovič, D. Šaman, L. Rulíšek, P. Fiedler, *J. Am. Chem. Soc.* **2002**, *124*, 9175; c) I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, Š. Vyskočil, D. Šaman, *Tetrahedron Lett.* **1999**, *40*, 1993.

[7] For 3-hexanelicenol, see: F. Teplý, I. G. Stará, I. Starý, A. Kollárovič, D. Šaman, Š. Vyskočil, P. Fiedler, *J. Org. Chem.* **2003**, *68*, 5193.

[8] S. M. Kupchan, H. C. Wormser, M. Sesso, *J. Org. Chem.* **1965**, *30*, 3935.

[9] K. Takahashi, T. Tanaka, T. Suzuki, M. Hirama, *Tetrahedron* **1994**, *50*, 1327.

[10] Y. Uozumi, A. Tanahashi, S.-Y. Lee, T. Hayashi, *J. Org. Chem.* **1993**, *58*, 1945.

[11] R. E. Dolle, S. J. Schmidt, L. I. Kruse, *J. Chem. Soc. Chem. Commun.* **1987**, 904.

[12] I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, D. Šaman, M. Tichý, *J. Org. Chem.* **1998**, *68*, 4046.

[13] D. F. Lindow, R. G. Harvey, *J. Am. Chem. Soc.* **1971**, *93*, 3786.

[14] J. M. Brown, I. P. Field, P. J. Sidebottom, *Tetrahedron Lett.* **1981**, *22*, 4867.

[15] F. Furche, R. Ahlrichs, C. Wachsmann, E. Weber, A. Sobanski, F. Vögtle, S. Grimme, *J. Am. Chem. Soc.* **2000**, *122*, 1717.

[16] P. P. Fu, R. G. Harvey, *Tetrahedron Lett.* **1974**, *36*, 3217.

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