Highly Efficient Chirality Inducers in Nematic Liquid Crystals: Synthesis of 7,7′-Disubstituted 2,2′-methylenedioxy-1,1′-binaphthyls

Christian Kühn, Matthias Bremer* and Peter R. Schreiner*

Institute of Organic Chemistry, Justus Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen and Merck KGaA, Frankfurter Str. 250, 64295 Darmstadt, Germany.

Supporting Information

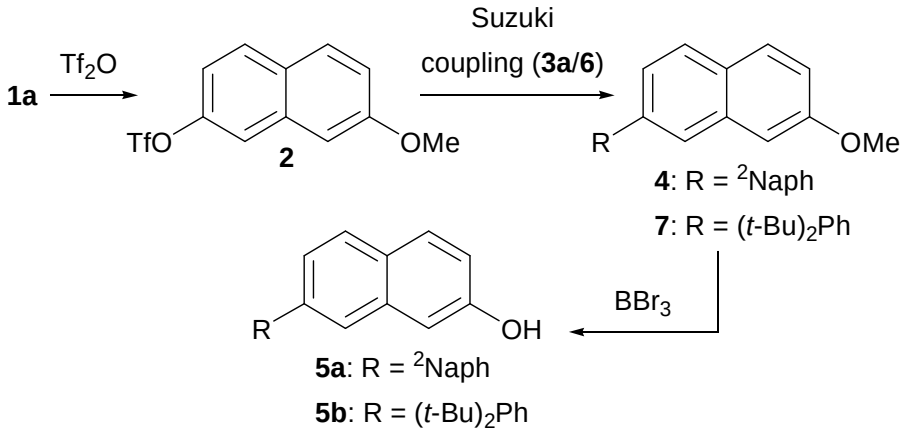
Table of contents

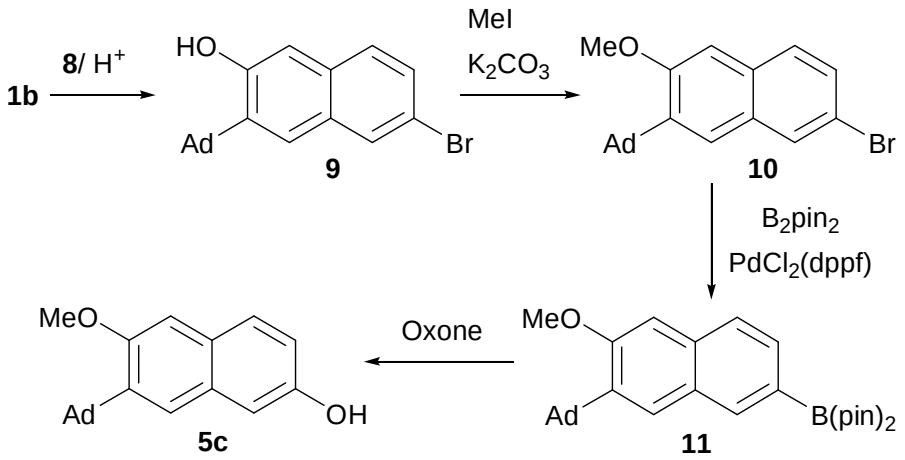
1. General remarks

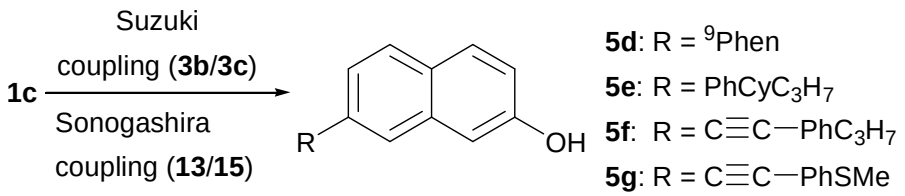
Chemicals were purchased from ABCR, Aldrich, Alfa Aesar or Merck at the highest purity grade available and were used without further purifications. Solvents were purchased from Merck (SeccoSolv®). These high-purity dried solvents with lowest water content were used without prior distillation. Unless otherwise noted, all reactions were carried out under a nitrogen-atmosphere. Column chromatography was conducted using Merck silica gel (0.063 – 0.200 mm). For thin layer chromatography (TLC) analysis throughout this work, Merck TLC plates were used. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV500 spectrometer using TMS as the internal standard with chemical shifts given in ppm. Mass spectrometry was performed on a Agilent 7000 Triple Quad. High resolution mass spectrometry (HRMS) was performed on a Thermo Scientific LTQ-XL mass spectrometer. The purity of the synthesized products was determined by high performance liquid chromatography (HPLC) and gas chromatography (GC). HPLC was performed on Hitachi LaChrom system with phenomenex synergi Max-RP and Merck RP-18 Supersher columns. GC analyses were performed by using a Varian 430 gas chromatograph. The resolution of the racemic compounds into their enantiomers was performed on LaPrep Sigma or SFC minigram with Chiralcel and Chiralpak columns. Optical rotations were measured on an Anton Paar MCP 500 polarimeter. Elemental analyses were conducted with a Carlo Erba CHN analyzer.

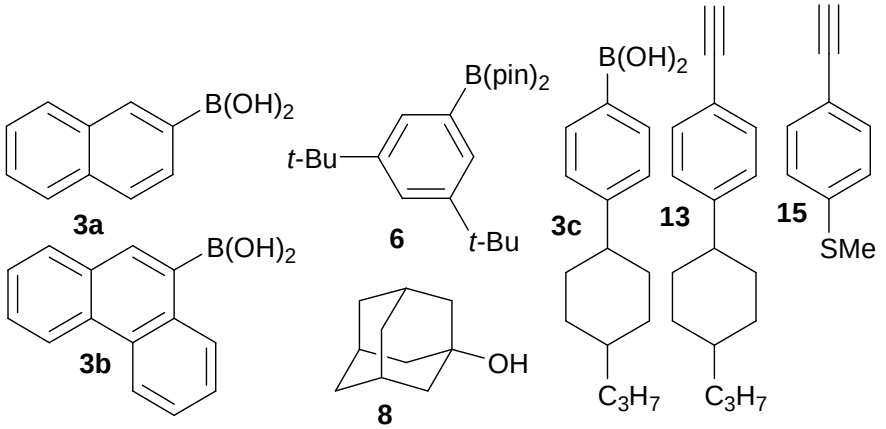
2. Synthetic procedures

Preparation of the 7-substituted 2-naphthols

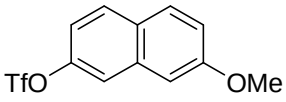








7-Methoxy-2-trifluoromethanesulfonyloxy-naphthalene (2)

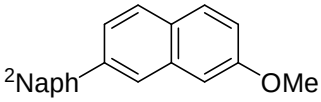


2

7-methoxy-2-naphthol (**1a**, 25.0 g, 144 mmol) and DMAP (0.70 g, 5.70 mmol) were suspended in CH_2Cl_2 (400 mL) at room temperature. Then, triethylamine (30 mL, 216 mmol) was added. The yellow reaction mixture was stirred and cooled to 0 °C using an ice bath. Subsequently, triflic anhydride (33 mL, 200 mmol) was added slowly. The mixture was warmed to room temperature and stirred overnight. Then, the mixture was poured onto ice-water and the whole was stirred. The organic phase was separated, washed with water (1 x 200 mL) and dried over anhydrous sodium sulfate. The solvent was removed by rotational evaporation. The residue was purified by column chromatography on silica gel using a mixture of heptane/toluene (1:1) as eluent. Concentration followed by recrystallization from heptane afforded **2** (38.1 g, 87%) as colorless crystals. Analytical data were identical with those reported in the literature.[1]

GC (%): 100. **MS** (EI): *m/z* (%) = 306 (58) [M^+], 173 (22) [M^+–133], 145 (100) [M^+–161], 130 (15) [M^+–176], 102 (22) [M^+–204], 69 (5) [M^+–237]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 3.93 (s, 3 H), 7.13 (d, 1 H, *J* = 2.5 Hz), 7.19 – 7.23 (m, 2 H), 7.63 (d, 1 H, *J* = 2.5 Hz), 7.76 (d, 1 H, *J* = 9.0 Hz), 7.82 (d, 1 H, *J* = 8.9 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 55.4, 105.8, 117.0, 118.0, 119.1 (q, 321 Hz), 120.3, 127.9, 129.4, 130.2, 134.9, 147.8, 158.9.

7-Methoxy-2,2'-binaphthalene (4)

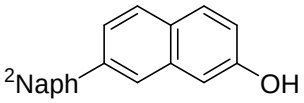


4

2 (60.0 g, 196 mmol) and 2-naphthylboronic acid (**3a**, 41.7 g, 235 mmol) were dissolved in THF (700 mL). Subsequently, a solution of $NaBO_2 \cdot 4H_2O$ (41.3 g, 294 mmol) in 180 mL H_2O was added. After addition of $PdCl_2(PPh_3)_2$ (2.75 g, 3.90 mmol) and N_2H_5OH (2-3 drops), the reaction mixture was heated to 60 °C and stirred for 20 h. The black mixture was cooled to room temperature and diluted with water (300 mL). The organic materials were extracted with MTBE (600 mL). The organic phase was separated, washed with water (1 x 400 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using heptane/toluene (1:1) as eluent, to afford the product. Recrystallization from heptane gave **4** (39.9 g, 72%) as a white solid.

GC (%): 98.7. **MS** (EI): *m/z* (%) = 284 (100) [M^+], 241 (34) [M^+–43], 142 (14) [M^+–142], 126 (7) [M^+–158], 119 (11) [M^+–165]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 3.95 (s, 3 H), 7.16 (dd, 1 H, *J* = 8.9, 2.5 Hz), 7.23 (d, 1 H, *J* = 2.6 Hz), 7.46 – 7.55 (m, 2 H), 7.73 (dd, 1 H, *J* = 8.4, 1.8 Hz), 7.77 (d, 1 H, *J* = 8.9 Hz), 7.84 – 7.97 (m, 5 H), 8.05 – 8.09 (m, 1 H), 8.13 – 8.18 (m, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 55.4, 106.1, 118.9, 123.5, 125.1, 125.8, 126.0, 126.1, 126.3, 127.7, 128.2, 128.3, 128.5, 129.2, 132.7, 133.8, 135.0, 138.6, 139.0, 158.1. **HRMS** *m/z* calcd. for $C_{21}H_{17}O$: 285.12717; found: 285.12794.

7-Hydroxy-2,2'-binaphthalene (5a)

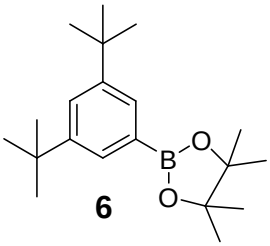


5a

A solution of **4** (1.50 g, 5.20 mmol) in CH_2Cl_2 (30 mL) was stirred and cooled to 5 °C using an ic e bath. Then, BBr_3 (0.75 mL, 7.90 mmol) was carefully added dropwise. The reaction mixture turned reddish and was stirred for 3 h at this temperature. After stirring overnight at room temperature, the mixture was poured onto ice-water. The organic materials were extracted with CH_2Cl_2 (100 mL) and MTBE (10 mL). The separated organic phase was washed with saturated $NaHCO_3$ solution (2 x 50 mL) and water (1 x 50 mL). The organic solvent was dried over anhydrous sodium sulfate and removed under reduced pressure. The recrystallization (toluene) of the remaining yellow solid afforded **5a** (1.30 g, 92%) as white crystals.

GC (%): 99.9. **MS** (EI): *m/z* (%) = 270 (100) [M^+], 252 (6) [M^+–18], 239 (14) [M^+–31], 135 (14) [M^+–135], 119 (8) [M^+–151]. **^{1}H NMR** (500 MHz, DMSO): δ/ppm = 7.11 (dd, 1 H, *J* = 8.8, 2.4 Hz), 7.26 (d, 1 H, *J* = 2.3 Hz), 7.55 (m, 2 H), 7.72 – 7.83 (m, 2 H), 7.88 – 8.07 (m, 5 H), 8.12 – 8.17 (m, 1 H), 8.32 – 8.37 (m, 1 H), 9.81 (s, 1 H). **^{13}C NMR** (100 MHz, DMSO): δ/ppm = 109.1, 118.9, 122.0, 123.9, 125.3, 125.4, 126.1, 126.4, 127.0, 127.5, 128.2, 128.3, 128.4, 129.0, 132.2, 133.4, 135.0, 137.4, 137.6, 155.7. **HRMS** *m/z* calcd. for $C_{21}H_{15}O$: 271.11229; found: 271.11184.

2-(3,5-Di-*tert*.-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)



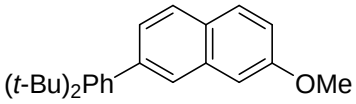
6

A mixture of 1-bromo-3,5-di-*tert*.-butyl-benzol (25.0 g, 91.9 mmol), bis(pinacolato)diboron (36.1 g, 138 mmol), potassium acetate (27.1, 276 mmol), $PdCl_2$(dppf) (3.37 g, 4.60 mmol) and dioxane (200 mL) was stirred at room temperature. The dark red suspension was heated under reflux for 16 h. After cooling to room temperature, the black reaction mixture was poured onto water (300 mL) and the organic materials were extracted with MTBE (400 mL). Then, the insoluble particles were removed by filtration over celite. The separated organic phase was washed with water (1 x 200 mL) and brine (1 x 100 mL) and dried over anhydrous sodium sulfate. Removing of the solvent afforded a black oil, which was purified by column chromatography on silica gel using toluene as eluent. The organic fractions were collected and evaporated under reduced pressure. The recrystallization (heptane) of the resulting solid afforded **6** (20.2 g, 69%) as colorless crystals. Analytical data were identical with those reported in the literature.[2]

GC (%): 99.8. **MS** (EI): *m/z* (%) = 316 (13) [M^+], 301 (100) [M^+–15], 217 (5) [M^+–99], 201 (8) [M^+–115], 57 (7) [M^+–259]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 1.30 – 1.39 (m, 30 H), 7.54 (t, 1 H, *J* = 2.0 Hz),

7.67 (d, 2 H, *J* = 2.0 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 24.9, 31.5, 34.8, 83.5, 125.5, 128.8, 149.8. **HRMS** *m/z* calcd. for $C_{20}H_{33}BO_2$: 316.25736; found: 316.25702.

2-(3,5-Di-*tert.*-butylphenyl)-7-methoxy-naphthalene (7)

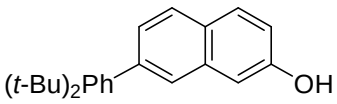


7

2 (14.0 g, 45.6 mmol) and **6** (17.4 g, 54.8 mmol) were dissolved in THF (200 mL). Then, $NaBO_2 \cdot 4H_2O$ (9.63 g, 68.4 mmol), 40 mL H_2O, $PdCl_2(PPh_3)_2$ (0.96 g, 1.40 mmol) and 2-3 drops of N_2H_5OH were added. The reaction mixture was heated to 60 °C for 20 h under stirring. After cooling to room temperature, the black mixture was diluted with water (200 mL) and extracted with MTBE (300 mL). The separated organic phase was washed with water (1 x 200 mL) and dried over anhydrous sodium sulfate. Concentration followed by column chromatography using a mixture of heptane/toluene (1:1) as eluent afforded the product. Recrystallization from heptane gave **7** (13.0 g, 82%) as a white solid.

GC (%): 99.9. **MS** (EI): *m/z* (%) = 346 (100) [M^+], 331 (71) [M^+–15], 275 (5) [M^+–71], 165 (12) [M^+–181], 151 (8) [M^+–195], 57 (12) [M^+–289]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 1.41 (s, 18 H), 3.94 (s, 3 H), 7.14 (dd, 1 H, *J* = 8.9, 2.5 Hz), 7.21 (d, 1 H, *J* = 2.5 Hz), 7.47 (t, 1 H, *J* = 1.8 Hz), 7.54 (d, 2 H, *J* = 1.8 Hz), 7.60 (dd, 1 H, *J* = 8.4, 1.8 Hz), 7.75 (d, 1 H, *J* = 9.0 Hz), 7.82 (d, 1 H, *J* = 8.4 Hz), 7.89 – 7.95 (m, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 31.6, 35.1, 55.4, 106.1, 118.7, 121.5, 122.0, 123.9, 124.9, 128.0, 128.1, 129.2, 134.9, 140.4, 140.7, 151.2, 158.0. **HRMS** *m/z* calcd. for $C_{25}H_{30}O$: 346.22967; found: 346.22919. **Anal.** calcd. (%) for $C_{25}H_{30}O$: C 86.66, H 8.73; found: C 86.90, H 8.60.

7-(3,5-Di-*tert.*-butylphenyl)-2-hydroxy-naphthalene (5b)



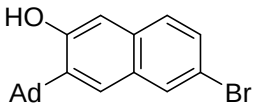
5b

A solution of **7** (11.0 g, 31.7 mmol) in CH_2Cl_2 (150 mL) was stirred and cooled to 5 °C using an ice bath. Then, BBr_3 (4.5 mL, 47.4 mmol) was dissolved in 25 mL CH_2Cl_2 and added dropwise (slowly). The reaction mixture turned brown and was stirred for 3 h at this temperature. After stirring overnight at room temperature, the mixture was poured onto ice-water (500 mL). The organic materials were extracted with CH_2Cl_2 (200 mL) and MTBE (20 mL). The separated organic phase was washed with saturated $NaHCO_3$ solution (2 x 100 mL) and water (1 x 150 mL). The organic solution was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The remaining white-yellow solid was recrystallized from a mixture of heptane/toluene to afford **5b** (10.0 g, 94%) as a white powder.

GC (%): 99.5. **MS** (EI): *m/z* (%) = 332 (99) [M^+], 317 (100) [M^+–15], 261 (6) [M^+–71], 231 (6) [M^+–101], 158 (8) [M^+–174], 144 (6) [M^+–188], 57 (13) [M^+–275]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 1.41

(s, 18 H), 4.96 (s, 1 H), 7.09 (dd, 1 H, *J* = 8.8, 2.5 Hz), 7.22 (d, 1 H, *J* = 2.5 Hz), 7.46 (t, 1 H, *J* = 1.8 Hz), 7.52 (d, 2 H, *J* = 1.8 Hz), 7.59 (dd, 1 H, *J* = 8.4, 1.8 Hz), 7.77 (d, 1 H, *J* = 8.8 Hz), 7.81 – 7.88 (m, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm = 31.6, 35.0, 109.7, 117.6, 121.6, 122.0, 124.0, 124.4, 128.0, 128.1, 129.6, 134.9, 140.6, 151.2, 153.7. **HRMS** *m/z* calcd. for $C_{24}H_{28}O$: 332.21402; found: 332.21387. **Anal.** calcd. (%) for $C_{24}H_{28}O$: C 86.70, H 8.49; found: C 86.20, H 8.90.

3-(1-Adamantyl)-6-bromo-2-naphthol (9)

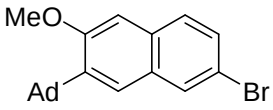


9

6-Bromo-2-naphthol (**1b**, 11.5 g, 50.0 mmol) and 1-adamantanol (**8**, 7.69 g, 50.0 mmol) were suspended in a solution of 60 mL heptane and 40 mL CH_2Cl_2. Subsequently, conc. H_2SO_4 (3 mL, 56.3 mmol) was added and the whole was stirred for 48 h at room temperature. After this reaction time, the mixture turned from yellow to brown. The insoluble material was filtered off and the solid was washed with heptane (3 x 20 mL). The resulting ocher-colored solid was dissolved in MTBE (200 mL) and the organic solution was washed with water (1 x 75 mL) and dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using a mixture of heptane/toluene (1:1) as eluent. **9** (8.05 g, 45%) could be isolated as a white powder.

GC (%): 100. **MS** (EI): *m/z* (%) = 356 (100) [M^+], 315 (5) [M^+–41], 301 (5) [M^+–55], 262 (6) [M^+–94], 235 (6) [M^+–121], 220 (42) [M^+–136], 202 (14) [M^+–154], 165 (5) [M^+–191]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 1.78 – 1.85 (m, 6 H), 2.08 – 2.15 (m, 3 H), 2.17 – 2.23 (m, 6 H), 5.07 (s, 1 H), 6.94 (s, 1 H), 7.38 – 7.48 (m, 2 H), 7.53 (s, 1 H), 7.89 (d, 1 H, *J* = 1.7 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 29.0, 37.0, 37.4, 40.6, 110.8, 116.8, 125.5, 126.7, 129.0, 129.8, 130.3, 131.2, 139.8, 153.9. **HRMS** *m/z* calcd. for $C_{20}H_{21}BrO$: 356.07758; Found: 356.07721. **Anal.** calcd. (%) for $C_{20}H_{21}BrO$: C 67.23, H 5.92; found: C 67.30, H 6.00.

3-(1-Adamantyl)-6-bromo-2-methoxynaphthalene (10)

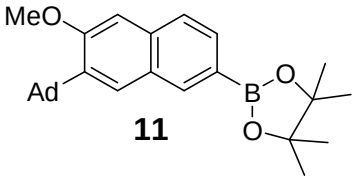


10

A mixture oft sodium hydride (60% oil dispersion, 0.17 g, 4.20 mmol) in THF (20 mL) was cooled to 0 °C using an ice bath. To the grey suspension was slowly added **9** (1.00 g, 2.80 mmol) in THF (10 mL). The mixture was stirred for 30 min at 0 °C. After addition of iodomethane (0.25 mL, 4.0 mmol), the reaction was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with water and extracted with MTBE (100 mL). The separated organic phase was washed with water (1 x 50 mL) and dried over anhydrous sodium sulfate. After removing the organic solvent under reduced pressure, the yellow oil was purified by column chromatography on silica gel using heptane as eluent. **9** (0.60 g, 58%) could be isolated as a white solid.

GC (%): 100. **MS** (EI): *m/z* (%) = 370 (100) [M^+], 315 (6) [M^+–55], 300 (14) [M^+–70], 278 (5) [M^+–92], 234 (33) [M^+–136], 219 (5) [M^+–151], 202 (8) [M^+–168], 182 (5) [M^+–188], 165 (5) [M^+–205]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 1.76 – 1.84 (m, 6 H), 2.07 – 2.14 (m, 3 H), 2.14 – 2.19 (m, 6 H), 3.93 (s, 3 H), 7.06 (s, 1 H), 7.43 (dd, 1 H, *J* = 8.7, 2.0 Hz), 7.50 – 7.57 (m, 2 H), 7.89 (d, 1 H, *J* = 2.0 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 29.0, 37.1, 37.6, 40.7, 54.9, 106.0, 116.8, 124.9, 127.4, 128.9, 129.7, 130.0, 131.4, 141.2, 158.2. **HRMS** *m/z* calcd. for $C_{21}H_{23}BrO$: 370.09323; found: 370.09277. **Anal.** calcd. (%) for $C_{21}H_{23}BrO$: C 67.93, H 6.24; found: C 68.00, H 6.20.

2-(7-Adamantyl-6-methoxy-naphthyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11)

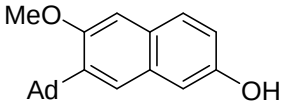


11

A mixture of **10** (14.0 g, 37.7 mmol), bis(pinacolato)diboron (14.8 g, 56.5 mmol), potassium acetate (11.1 g, 113 mmol), $PdCl_2$(dppf) (1.38 g, 1.90 mmol) and dioxane (200 mL) was stirred at room temperature. The dark red suspension was heated under reflux for 16 h. After cooling to room temperature, the black reaction mixture was poured onto water (200 mL) and the organic materials were extracted with MTBE (300 mL). Then, the insoluble particles were removed by filtration over celite. The separated organic phase was washed with water (1 x 200 mL) and brine (1 x 200 mL) and dried over anhydrous sodium sulfate. Concentration afforded a black oil, which was purified by column chromatography on silica gel using a mixture of heptane/toluene (1:1) as eluent. The organic fractions were collected and evaporated under reduced pressure. The recrystallization (heptane) of the resulting solid afforded **10** (11.0 g, 70%) as colorless crystals.

GC (%): 99.9. **MS** (EI): *m/z* (%) = 418 (100) [M^+], 346 (9) [M^+–72], 332 (5) [M^+–86], 319 (8) [M^+–99], 246 (5) [M^+–172]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 1.37 (s, 12 H), 1.75 – 1.84 (m, 6 H), 2.05 – 2.12 (m, 3 H), 2.17 (m, 6 H), 3.94 (s, 3 H), 7.09 (s, 1 H), 7.62 – 7.69 (m, 2 H), 7.74 (dd, 1 H, *J* = 8.1, 1.2 Hz), 8.28 (d, 1 H, *J* = 1.1 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 24.9, 29.2, 37.2, 37.5, 40.8, 54.8, 83.7, 105.9, 124.8, 126.6, 128.2, 130.4, 134.8, 136.2, 139.9, 159.0. **HRMS** *m/z* calcd. for $C_{27}H_{35}BO_3$: 418.26793; found: 418.26755. **Anal.** calcd. (%) for $C_{27}H_{35}BO_3$: C 77.51, H 8.43; found: C 77.40, H 8.40.

7-(1-Adamantyl)-6-methoxy-2-hydroxynaphthalene (5c)



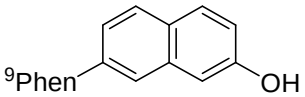
5c

11 (1.50 g, 3.60 mmol) was dissolved in acetone (40 mL) and added to a stirred mixture of oxone (2.31 g, 3.80 mmol) in H_2O (10 mL) at 5 °C using an ice bath. After 30 min, the ice bath was removed and the mixture was stirred at room temperature overnight. The brown colored suspension was filtered off and the solid was washed with acetone. The organic filtrate was concentrated under reduced pressure and the residue was dissolved in MTBE (75 mL). The organic solution was washed with

water (3 x 25 mL), dried over anhydrous sodium sulfate and concentrated to dryness. The subsequent column chromatography on silica gel using toluene as eluent and recrystallization from heptane afforded **5c** (0.73 g, 63%) as a white solid.

GC (%): 100. **MS** (EI): *m/z* (%) = 308 (100) [M^+], 251 (8) [M^+–57], 236 (23) [M^+–72], 214 (5) [M^+–94], 173 (5) [M^+–135]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 1.75 – 1.83 (m, 6 H), 2.06 – 2.13 (m, 3 H), 2.14 – 2.20 (m, 6 H), 3.90 (s, 3 H), 4.80 (s, 1 H), 7.00 (dd, 1 H, *J* = 8.7, 2.5 Hz), 7.04 – 7.10 (m, 2 H), 7.45 (s, 1 H), 7.58 (d, 1 H, *J* = 8.7 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 29.2, 37.2, 37.5, 40.8, 54.9, 106.3, 109.8, 117.3, 124.2, 127.5, 128.1, 129.7, 140.8, 151.7, 156.5. **HRMS** *m/z* calcd. for $C_{21}H_{24}O_2$: 308.17763; found: 308.17742. **Anal.** calcd. (%) for $C_{21}H_{24}O_2$: C 81.78, H 7.84; found: C 81.80, H 7.80.

7-(Phenanthren-9-yl)naphthalen-2-ol (5d)

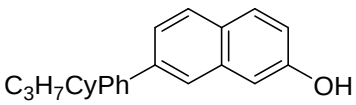


5d

7-Bromo-2-naphthol (**1c**, 10.0 g, 44.4 mmol) and 9-phenanthrylboronic acid (**3b**, 10.4 g, 46.8 mmol) were dissolved in THF (100 mL). Subsequently, a solution of $NaBO_2 \cdot 4H_2O$ (9.36 g, 66.6 mmol) in 30 mL H_2O was added. After addition of $PdCl_2(PPh_3)_2$ (1.56 g, 2.20 mmol) and N_2H_5OH (2-3 drops), the reaction mixture was heated to 60 °C and stirred for 20 h. The black mixture was cooled to room temperature and diluted with water (200 mL). The organic materials were extracted with MTBE (300 mL). Insoluble particles were removed by filtration over celite and the organic phase was separated, washed with water (1 x 100 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using toluene as eluent, to afford the product. Recrystallization from a mixture of heptane/toluene (1:2) gave **5d** (8.40 g, 59%) as a white solid.

GC (%): 100. **MS** (EI): *m/z* (%) = 320 (100) [M^+], 303 (10) [M^+–17], 289 (27) [M^+–31], 276 (10) [M^+–44], 160 (13) [M^+–160], 151 (17) [M^+–169], 144 (22) [M^+–176], 131 (10) [M^+–189], 84 (10) [M^+–236], 49 (14) [M^+–271]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 5.03 (s, 1 H), 7.13 – 7.23 (m, 2 H), 7.48 – 7.55 (m, 2 H), 7.59 – 7.71 (m, 3 H), 7.76 (s, 1 H), 7.82 – 7.98 (m, 5 H), 8.71 – 8.83 (m, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 109.7, 118.0, 122.6, 122.9, 126.3, 126.5, 126.6, 126.7, 126.9, 127.1, 127.2, 127.5, 127.7, 128.2, 128.7, 129.8, 130.1, 130.7, 131.2, 131.6, 134.7, 138.8, 139.1, 153.8. **HRMS** *m/z* calcd. for $C_{24}H_{16}O$: 320.12012; found: 321.12064. **Anal.** calcd. (%) for $C_{24}H_{16}O$: C 89.97, H 5.03; found: C 90.20, H 4.90.

7-(4-(4-Propyl-cyclohexyl)phenyl)naphthalen-2-ol (5e)



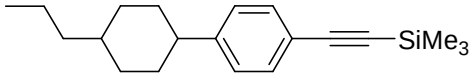
5e

7-Bromo-2-naphthol (**1c**, 10.5 g, 46.6 mmol) and 4-(4-propyl-cyclohexyl)phenylboronic acid (**3c**, 13.8 g, 55.9 mmol) were dissolved in THF (100 mL). Subsequently, a solution of $NaBO_2 \cdot 4H_2O$

(9.83 g, 69.9 mmol) in 30 mL H_2O was added. After addition of $PdCl_2(PPh_3)_2$ (1.64 g, 2.30 mmol) and N_2H_5OH (2-3 drops), the reaction mixture was heated to 60 °C and stirred for 5 h. The black mixture was cooled to room temperature and diluted with water (250 mL). The organic materials were extracted with MTBE (300 mL). Insoluble particles were removed by filtration over celite and the organic phase was separated, washed with water (1 x 100 mL) and dried over anhydrous sodium sulfate. Concentration followed by recrystallization (heptane/ethanol 10:1) gave **5e** (10.5 g, 65%) as white needles.

GC (%): 99.9. **MS** (EI): *m/z* (%) = 344 (100) [M^+], 315 (5) [M^+–29], 259 (25) [M^+–85], 246 (35) [M^+–98], 233 (27) [M^+–111], 215 (10) [M^+–129], 189 (5) [M^+–155], 129 (11) [M^+–215], 116 (7) [M^+–228], 84 (15) [M^+–260], 49 (20) [M^+–295], 41 (10) [M^+–303], 28 (5) [M^+–316]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 0.95 (t, 3 H, *J* = 7.2 Hz), 1.03 – 1.18 (m, 2 H), 1.21 – 1.59 (m, 7 H), 1.87 – 2.05 (m, 4 H), 2.56 (tt, 1 H, *J* = 12.2, 3.4 Hz), 4.95 (s, 1 H), 7.11 (dd, 1 H, *J* = 8.8, 2.5 Hz), 7.21 (d, 1 H, *J* = 2.5 Hz), 7.31 – 7.38 (m, 2 H), 7.59 – 7.69 (m, 3 H), 7.79 (d, 1 H, *J* = 8.8 Hz), 7.84 (d, 1 H, *J* = 8.5 Hz), 7.87 – 7.90 (m, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 14.4, 20.1, 33.6, 34.4, 37.1, 39.8, 44.4, 109.8, 117.6, 123.5, 124.0, 127.3, 127.3, 128.0, 128.2, 129.6, 134.9, 138.7, 139.3, 147.3, 153.7. **HRMS** *m/z* calcd. for $C_{25}H_{28}O$: 344.21402; found: 344.21395. **Anal.** calcd. (%) for $C_{25}H_{28}O$: C 87.16, H 8.19; found: C 87.30, H 8.20.

Trimethyl(2-(4-(4-propylcyclohexyl)phenyl)ethynyl)silane (12)

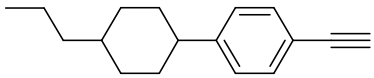


12

To a mixture of 1-bromo-4-(4-propylcyclohexyl)benzene (20.0 g, 71.1 mmol) in triethylamine (250 mL) was added ethynyltrimethylsilane (15 mL, 107 mmol) and $PdCl_2(PPh_3)_2$ (2.50 g, 3.60 mmol). The yellow suspension was stirred for 15 min at room temperature. After addition of Cu(I)-iodide (0.68 g, 3.60 mmol), the reaction mixture was heated to 50 °C and stirred overnight. After cooling down, the reaction was poured onto water (300 mL) and the organic materials were extracted with MTBE (250 mL). The organic phase was separated, dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using heptane as eluent. Removal of the solvent and subsequent recrystallization from ethanol gave **12** (18.2 g, 86%) as white crystals.

GC (%): 99.8. **MS** (EI): *m/z* (%) = 298 (33) [M^+], 283 (100) [M^+–15], 185 (12) [M^+–113], 99 (5) [M^+–199], 73 (7) [M^+–225]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 0.26 (s, 9 H), 0.93 (t, 3 H, *J* = 7.2 Hz), 0.98 – 1.14 (m, 2 H), 1.18 – 1.53 (m, 7 H), 1.79 – 1.97 (4 H), 2.39 – 2.56 (m, 1 H), 7.11 – 7.19 (m, 2 H), 7.36 – 7.45 (m, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 14.4, 20.0, 33.4, 34.1, 37.0, 39.7, 44.5, 93.2, 105.4, 120.4, 126.7, 131.9, 148.5. **HRMS** *m/z* calcd. for $C_{20}H_{30}Si$: 298.21168; found: 298.21030. **Anal.** calcd. (%) for $C_{20}H_{30}Si$: C 80.46, H 10.13; found: C 80.50, H 10.10.

1-Ethynyl-4-(4-propylcyclohexyl)benzene (13)

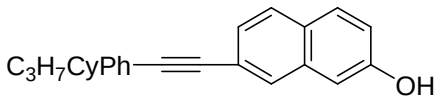


13

12 (23.5 g, 78.7 mmol) was dissolved in THF (150 mL). Then, 1 M TBAF (86 mL, 86.0 mmol) was added dropwise. After stirring the colorless solution for 3 h at room temperature, the reaction was poured onto water (200 mL) and the organic materials were extracted with MTBE (200 mL). The organic phase was separated, washed with water (1 x 100 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel using a mixture of heptane/toluene (9:1) as eluent. Removal of the solvent and recrystallization from ethanol gave **13** (13.4 g, 75%) as colorless crystals. Analytical data were identical with those reported in the literature.[3]

GC (%): 99.8. **MS** (EI): *m/z* (%) = 226 (72) [M^+], 155 (8) [M^+–71], 141 (53) [M^+–85], 128 (100) [M^+–98], 122 (5) [M^+–104], 115 (60) [M^+–111], 102 (12) [M^+–124], 89 (5) [M^+–137], 81 (6) [M^+–145], 77 (5) [M^+–149], 67 (5) [M^+–159], 55 (9) [M^+–171], 41 (9) [M^+–165]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 0.93 (t, 3 H, *J* = 7.2 Hz), 1.00 – 1.15 (m, 2 H), 1.20 – 1.53 (m, 7 H), 1.83 – 1.97 (m, 4 H), 2.49 (m, 1 H), 3.04 (s, 1 H), 7.16 – 7.22 (m, 2 H), 7.41 – 7.47 (m, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 14.4, 20.0, 33.5, 34.1, 37.0, 39.7, 44.6, 83.9, 119.4, 126.9, 132.1, 148.9. **HRMS** *m/z* calcd. for $C_{17}H_{22}$: 226.17215; found: 226.17164. **Anal.** calcd. (%) for $C_{20}H_{30}Si$: C 90.20, H 9.80; found: C 90.10, H 9.80.

7-((4-(4-Propylcyclohexyl)phenyl)ethynyl)naphthalen-2-ol (5f)

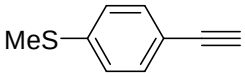


5f

A mixture of 7-bromo-2-naphthol (**1c**, 6.30 g, 27.9 mmol), **13** (6.98 g, 30.8 mmol), triethylamine (150 mL) and $PdCl_2(PPh_3)_2$ (0.98 g, 1.40 mmol) was stirred for 15 min at room temperature. After addition of Cu(I)-iodide (0.27 g, 1.4 mmol), the reaction mixture was heated to 60 °C and stirred overnight. After cooling down, the reaction was poured onto water (200 mL) and extracted with MTBE (200 mL). The organic phase was separated, dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using toluene and toluene/ethyla acetate (9:1) as eluent. Recrystallization from toluene gave **5f** (6.45 g, 62 %) as a beige-colored solid.

GC (%): 98.7. **MS** (EI): *m/z* (%) = 368 (100) [M^+], 283 (9) [M^+–85], 270 (21) [M^+–98], 239 (8) [M^+–129], 128 (10) [M^+–240], 55 (6) [M^+–313], 41 (6) [M^+–327]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 0.94 (t, 3 H, *J* = 7.2 Hz), 1.01 – 1.17 (m, 2 H), 1.19 – 1.55 (m, 7 H), 1.84 – 2.02 (m, 4 H), 2.45 – 2.59 (m, 1 H), 5.00 (s, 1 H), 7.10 – 7.15 (m, 2 H), 7.21 – 7.26 (m, 2 H), 7.45 (dd, 1 H, *J* = 8.4, 1.6 Hz), 7.49 – 7.55 (m, 2 H), 7.75 (dd, 2 H, *J* = 8.3, 1.4 Hz), 7.90 (m, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 14.4, 20.1, 33.5, 34.2, 37.0, 39.7, 44.6, 89.2, 90.1, 109.4, 118.4, 120.6, 121.6, 126.4, 126.9, 127.8, 128.3, 129.7, 131.6, 134.3, 148.4, 153.9. **HRMS** *m/z* calcd. for $C_{27}H_{28}O$: 368.21402; found: 368.21337. **Anal.** calcd. (%) for $C_{27}H_{28}O$: C 88.00, H 7.66; found: C 87.40, H 7.60.

4-Ethynyl-thioanisole (15)

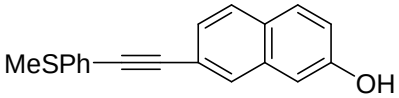


15

To a mixture of 4-bromothioanisole (**14**, 22.6 g, 111 mmol) in triethylamine (250 mL) was added ethynyltrimethylsilane (23 mL, 166 mmol) and $PdCl_2(PPh_3)_2$ (3.91 g, 5.60 mmol). The yellow suspension was stirred for 15 min at room temperature. After addition of Cu(I)-iodide (1.06 g, 5.60 mmol), the reaction mixture was heated to 50 °C and stirred overnight. After cooling down, the organic solvent was removed under reduced pressure. The resulting residue was purified by column chromatography using heptane as eluent. Evaporation of the solvent gave 17.1 g of a brown oil, which was dissolved in methanol (120 mL). After addition of potassium carbonate (5.33 g, 38.6 mmol), the suspension was stirred for 2 h at room temperature. The solvent was evaporated under reduced pressure and to the residue was added MTBE (150 mL) and water (100 mL). The organic phase was separated, washed with water (1 x 75) and dried over anhydrous sodium sulfate. Purification by column chromatography using a mixture of heptane/toluene (1:1) as eluent, gave **15** (10.2 g, 62%) as a light yellow oil. Analytical data were identical with those reported in the literature.[4]

GC (%): 98.8. **MS** (EI): *m/z* (%) = 148 (100) [M^+], 133 (32) [M^+–15], 115 (10) [M^+–33], 102 (13) [M^+–46], 89 (43) [M^+–59], 74 (12) [M^+–74], 69 (6) [M^+–79], 63 (10) [M^+–85], 51 (5) [M^+–97]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 2.51 (s, 3 H), 3.09 (s, 1 H), 7.20 (d, 2 H, *J* = 8.2 Hz), 7.43 (d, 2 H, *J* = 8.2 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 15.3, 83.5, 118.4, 125.8, 132.4, 140.1. **HRMS** *m/z* calcd. for C_9H_9S: 149.04250; found: 149.04167.

7-(4-Methylsulfanyl-phenylethinyl)naphthalen-2-ol (5g)

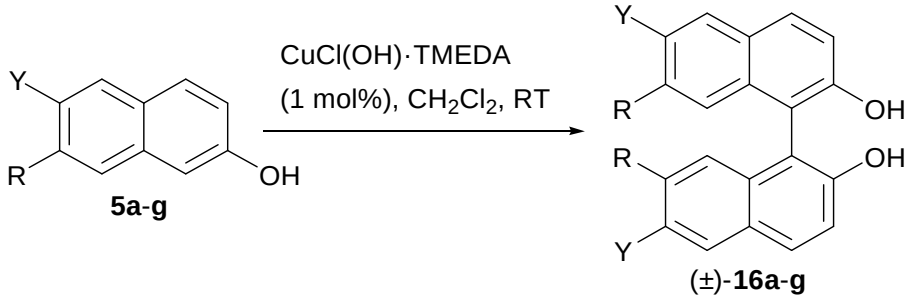


5g

A mixture of 7-bromo-2-naphthol (**1c**, 5.60 g, 24.9 mmol), **15** (4.47 g, 29.8 mmol), triethylamine (150 mL) and $PdCl_2(PPh_3)_2$ (0.87 g, 1.20 mmol) was stirred for 15 min at room temperature. After addition of Cu(I)-iodide (0.24 g, 1.20 mmol), the reaction mixture was heated under reflux and stirred overnight. After cooling down, the organic solvent was removed under reduced pressure. The resulting residue was purified by column chromatography using toluene and toluene/ethyl acetate (9:1) as eluent. The combined product fractions were evaporated under reduced pressure. Recrystallization from toluene (two times) afforded **5g** (3.90 g, 54%) as a beige-colored solid.

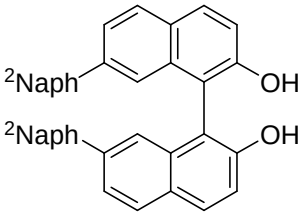
GC (%): 99.6. **MS** (EI): *m/z* (%) = 290 (100) [M^+], 275 (44) [M^+–15], 245 (10) [M^+–45], 213 (8) [M^+–77], 203 (8) [M^+–87], 145 (18) [M^+–145], 137 (5) [M^+–153], 122 (5) [M^+–168], 101 (5) [M^+–189]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 2.35 (s, 3H), 6.95 – 7.03 (m, 2 H), 7.04 – 7.11 (m, 2 H), 7.18 (dd, 1 H, *J* = 8.4, 1.7 Hz), 7.27 – 7.35 (m, 2 H), 7.52 (dd, 2 H, *J* = 9.0, 6.3 Hz), 7.66 – 7.71 (m, 1 H), 9.12 (s, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 15.2, 89.2, 90.2, 109.0, 119.4, 120.5, 125.2, 125.8, 127.5, 127.7, 129.1, 129.5, 131.7, 134.4, 139.2, 155.8. **HRMS** *m/z* calcd. for $C_{19}H_{14}OS$: 290.07654; found: 290.07609. **Anal.** calcd. (%) for $C_{49}H_{30}O_2$: C 78.59, H 4.86; found: C 78.60, H 5.00.

Oxidative coupling of the 2-naphthol derivatives (5a-g) with CuCl(OH)·TMEDA[5]



(±)-**16a-g**

Typical procedure: (±)-7,7'-Di(2-naphthyl)-1,1'-bi-2-naphthol (16a)

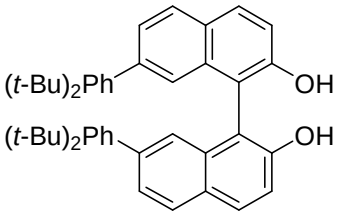


16a

5a (1.00 g, 3.70 mmol) was added to a mixture of CuCl(OH)·TMEDA (20 mg, 0.04 mmol) in CH_2Cl_2 (40 mL) and the whole was stirred at room temperature for 20 h in open air. The dark reaction mixture was concentrated and purified by column chromatography on silica gel (toluene to toluene/ethyl acetate 9:1). The combined organic fractions were evaporated to dryness, and the subsequent recrystallization (toluene) afforded **16a** (0.60 g, 54%) as a white powder.

GC (%): 89.0. **MS** (EI): *m/z* (%) = 538 (100) [M^+], 269 (9) [M^+–269], 241 (9) [M^+–297].]. **^{1}H NMR** (500 MHz, DMSO): δ/ppm = 7.39 – 7.55 (m, 10 H), 7.73 (dd, 2 H, *J* = 8.4, 1.8 Hz), 7.82 – 7.91 (m, 6 H), 7.97 (dd, 4 H, *J* = 5.3, 3.6 Hz), 8.03 (d, 2 H, *J* = 8.5 Hz), 9.44 (s, 2 H). **^{13}C-NMR** (100 MHz, DMSO): δ ppm = 115.7, 118.9, 121.9, 122.6, 124.9, 125.2, 126.0, 126.4, 127.4, 127.5, 128.0, 128.5, 128.7, 128.9, 132.0, 133.1, 134.2, 137.4, 138.1. **HRMS** *m/z* calcd. for $C_{21}H_{15}O$: 538.19328; found: 538.19152.

(±)-7,7'-Bis-(3,5-di-*tert.*-butylphenyl)-2,2'-dihydroxy-1,1'-binaphthyl (16b) from 5b



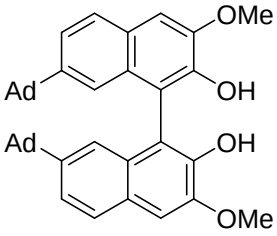
16b

Reaction time: 3 h; yield: 4.02 g (46%); beige-colored solid, recrystallization from ethanol.

HPLC (%): 97.2. **MS** (EI): *m/z* (%) = 662 (100) [M^+], 316 (13) [M^+–346], 57 (9) [M^+–605]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 1.21 (s, 36 H), 5.23 (s, 2 H), 7.18 (d, 4 H, *J* = 1.8 Hz), 7.29 – 7.41 (m, 6 H), 7.60 (dd, 2 H, *J* = 8.4, 1.8 Hz), 7.94 (dd, 4 H, *J* = 10.8, 8.7 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 31.3, 34.8, 111.2, 117.5, 121.5, 122.0, 123.2, 124.1, 128.5, 131.1, 133.7, 140.6, 141.5, 151.0, 153.0.

HRMS *m/z* calcd. for $C_{48}H_{54}O_2$: 662.41238; found: 662.4111. **Anal.** calcd. (%) for $C_{48}H_{54}O_2$: C 86.96, H 8.21; found: C 85.90, H 8.50.

(±)-7,7'-Di(1-adamantyl)-2,2'-dihydroxy-6,6'-dimethoxy-1,1'-binaphthyl (16c) from 5c

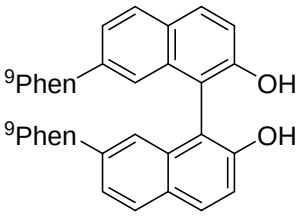


16c

Reaction time: 3.5 h; yield: 0.31 g (62%); white solid (purification after column chromatography: stirring in acetone).

HPLC (%): 98.2. **MS** (EI): *m/z* (%) = 614 (34) [M^+], 135 (100) [M^+–479], 107 (12) [M^+–507], 93 (23) [M^+–521], 67 (9) [M^+–547], 28 (14) [M^+–586]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 1.60 – 1.99 (m, 30 H) 3.95 (s, 6 H), 4.91 (s, 2 H), 7.07 (s, 2 H), 7.19 (s, 2 H), 7.30 (d, 2 H, *J* = 8.9 Hz), 7.80 (d, 2 H, *J* = 8.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 29.0, 37.0, 37.6, 40.3, 54.9, 107.1, 111.6, 117.4, 122.5, 127.8, 128.7, 128.9, 141.3, 150.7, 156.5. **HRMS** *m/z* calcd. for $C_{42}H_{46}O_4$: 614.33961; found: 614.33752. **Anal.** calcd. (%) for $C_{42}H_{46}O_4$: C 82.05, H 7.54; found: C 82.20, H 7.80.

(±)-2,2‘-Dihydroxy-7,7'-diphenanthren-9-yl-1,1'-binaphthyl (16d) from 5d

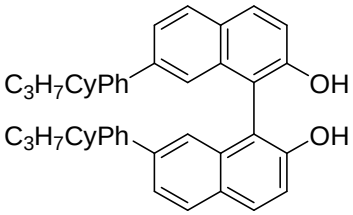


16d

Reaction time: 4 h; yield: 5.30 g (82%); white solid (purification after column chromatography: stirring in acetone).

HPLC (%): 97.4. **MS** (EI): *m/z* (%) = 638 (100) [M^+], 319 (15) [M^+–319], 289 (9) [M^+–349]. **^{1}H NMR** (500 MHz, DMSO): δ/ppm = 7.26 – 7.30 (m, 2 H), 7.34 – 7.50 (m, 6 H), 7.56 – 7.73 (m, 8 H), 7.79 – 7.93 (m, 6 H), 7.98 (d, 2 H, *J* = 8.3 Hz), 8.74 – 8.91 (m, 4 H), 9.49 (s, 2 H). **^{13}C NMR** (100 MHz, DMSO): δ/ppm = 115.4, 118.8, 122.7, 123.3, 124.4, 125.3, 126.0, 126.6, 126.7, 126.9, 127.0, 127.3, 128.2, 128.5, 128.6, 128.8, 129.2, 130.1, 130.8, 133.9, 137.1, 138.2, 153.6. **HRMS** *m/z* calcd. for $C_{48}H_{30}O_2$: 638.22458; found: 638.22371. **Anal.** calcd. (%) for $C_{48}H_{30}O_2$: C 90.26, H 4.73; found: C 89.90, H 4.80.

(±)-2,2'-Dihydroxy-7,7'-bis-(4-(4-propyl-cyclohexyl)phenyl]-1,1'-binaphthyl (16e) from 5e

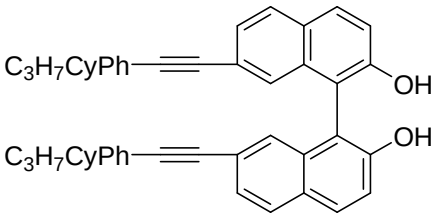


16e

Reaction time: 4 h; yield: 0.52 g (52%); white solid, recrystallization from heptane/ethanol (1:1) with few drops of toluene.

HPLC (%): 99.9. **MS** (EI): *m/z* (%) = 686 (100) [M^+], 638 (6) [M^+–48], 258 (5) [M^+–428], 83 (7) [M^+–603], 69 (13) [M^+–617], 55 (7) [M^+–631]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 0.81 (t, 6 H, *J* = 7.3 Hz), 0.89 – 0.98 (m, 4 H), 1.07 – 1.37 (m, 14 H), 1.69 – 1.81 (m, 8 H), 2.34 (tt, 2 H, *J* = 12.2, 3.3 Hz), 5.01 (s, 2 H), 7.06 – 7.10 (m, 4 H), 7.24 – 7.31 (m, 8 H), 7.53 (dd, 2 H, *J* = 8.5, 1.8 Hz), 7.86 (d, 2 H, *J* = 8.5 Hz), 7.90 (d, 2 H, *J* = 8.9 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 14.4, 20.0, 33.5, 34.3, 37.0, 39.7, 44.3, 111.0, 117.6, 121.9, 124.0, 127.2, 127.4, 128.6, 128.9, 131.2, 133.7, 138.6, 140.4, 147.2, 153.2. **HRMS** *m/z* calcd. for $C_{50}H_{54}O_2$: 686.41238; found: 686.41173. **Anal.** calcd. (%) for $C_{50}H_{54}O_2$: C 87.42, H 7.92; found: C 87.30, H 7.90.

(±)-2,2‘-Dihydroxy-7,7'-bis-((4-(4-propylcyclohexyl)phenyl)ethinyl)-1,1'-binaphthyl (16f) from 5f

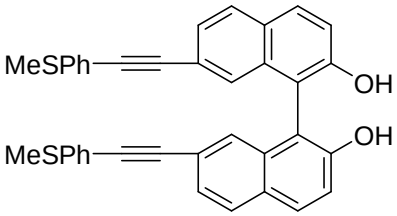


16f

Reaction time: 5 h; yield: 1.80 g (62%); white solid, recrystallization (both toluene and ethanol).

HPLC (%): 99.7. **MS** (EI): *m/z* (%) = 734 (100) [M^+], 367 (5) [M^+–367], 83 (6) [M^+–651], 69 (10) [M^+–665], 55 (10) [M^+–679]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 0.92 (t, 6 H, *J* = 7.2 Hz), 0.98 – 1.14 (m, 4 H), 1.18 – 1.50 (m, 14 H), 1.81 – 1.94 (m, 8 H), 2.40 – 2.53 (m, 2 H), 5.06 (s, 2 H), 7.10 – 7.19 (m, 4 H), 7.31 – 7.35 (m, 2 H), 7.36 – 7.45 (m, 6 H), 7.52 (dd, 2 H, *J* = 8.4, 1.5 Hz), 7.89 (d, 2 H, *J* = 8.4 Hz), 8.00 (d, 2 H, *J* = 8.9 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 14.4, 20.0, 33.5, 34.1, 37.0, 39.7, 44.6, 89.1, 90.7, 110.4, 118.4, 120.2, 122.8, 126.8, 127.1, 127.1, 128.6, 128.8, 131.4, 131.6, 133.3, 148.4, 153.4. **HRMS** *m/z* calcd. for $C_{54}H_{54}O_2$: 734.41238; found: 734.41215. **Anal.** calcd. (%) for $C_{54}H_{54}O_2$: C 88.24, H 7.41; found: C 87.80, H 7.30.

(±)-2,2‘-Dihydroxy-7,7'-bis-(4-methylsulfanyl-phenylethinyl)-1,1'-binaphthyl (16g) from 5g

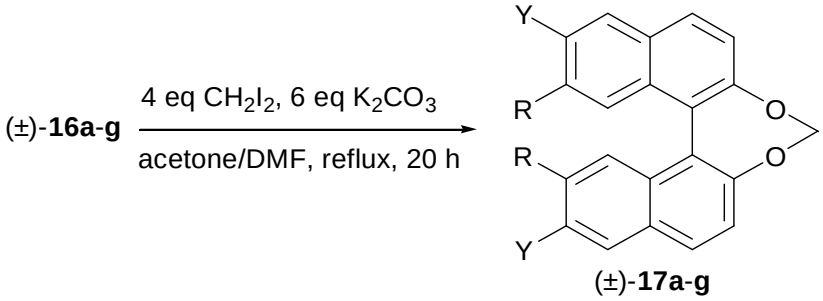


16g

Reaction time: 5 h; yield: 1.43 g (66%); white solid, recrystallization (both toluene and ethanol).

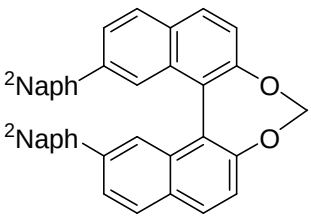
HPLC (%): 96.4. **MS** (EI): *m/z* (%) = 578 (11) [M^+], 372 (6) [M^+–206], 330 (6) [M^+–248], 318 (18) [M^+–260], 304 (100) [M^+–274], 292 (12) [M^+–286], 275 (5) [M^+–303], 248 (18) [M^+–330], 231 (6) [M^+–347], 219 (19) [M^+–359], 189 (16) [M^+–389], 165 (11) [M^+–413], 152 (17) [M^+–426], 142 (40) [M^+–436], 127 (21) [M^+–451], 101 (16) [M^+–477], 95 (11) [M^+–483], 86 (31) [M^+–492], 69 (37) [M^+–509], 55 (11) [M^+–523], 41 (53) [M^+–537], 28 (7) [M^+–558]. **^{1}H NMR** (500 MHz, DMSO): δ/ppm = 2.46 (s, 6 H), 7.07 – 7.12 (m, 2 H), 7.17 – 7.23 (m, 4 H), 7.34 – 7.44 (m, 8 H), 7.87 – 8.00 (m, 4 H), 9.50 (s, 2 H). **^{13}C NMR** (100 MHz, DMSO): δ/ppm = 14.2, 89.3, 90.1, 114.8, 118.0, 119.6, 119.8, 124.7, 125.5, 127.0, 127.6, 128.7, 129.0, 131.7, 133.7, 139.6, 153.8. **HRMS** *m/z* calcd. for $C_{38}H_{26}O_2S_2$: 578.13742; found: 578.13613. **Anal.** calcd. (%) for $C_{38}H_{26}O_2S_2$: C 78.86, H 4.53; found: C 78.10, H 4.50.

<u>Preparation of the 7,7’-disubstituted methylenedioxy-bridged binaphthyls</u>



(±)-**17a-g**

Typical procedure: (±)-2,2'-Methylenedioxy-7,7'-di(2-naphthyl)-1,1'-binaphthyl (17a)



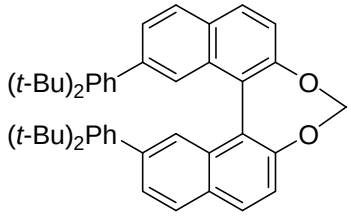
17a

A mixture of **16a** (1.00 g, 1.90 mmol), diiodomethane (1.49 g, 5.60 mmol), potassium carbonate (1.54 g, 11.1 mmol) and 50 mL acetone was stirred and heated under reflux for

20 h. After cooling down, the reaction mixture was poured onto water (100 mL) and the organic materials were extracted with MTBE (100 mL). The organic phase was separated, washed with water (1 x 50 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed under reduced pressure and the resulting yellow solid was purified by column chromatography using toluene as eluent. Recrystallization from a mixture of heptane/toluene (2:1) afforded **17a** (0.52 g, 50%) as a white solid.

HPLC (%): 99.3. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 5.77 (s, 2 H), 7.33 – 7.40 (m, 4 H), 7.48 – 7.54 (m, 4 H), 7.61 – 7.73 (m, 6 H), 7.80 – 7.91 (m, 4 H), 7.98 – 8.11 (m, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 103.3, 121.1, 125.0, 125.5, 125.9, 126.1, 126.3, 126.3, 127.5, 128.1, 128.4, 129.3, 130.2, 131.1, 132.5, 132.5, 133.5, 138.3, 138.8, 151.9. **HRMS** *m/z* calcd. for $C_{41}H_{26}O_2$: 550.19328; found: 550.19216. **Anal.** calcd. (%) for $C_{41}H_{26}O_2$: C 89.43, H 4.76; found: C 88.80, H 4.60.

(±)-7,7'-Bis(3,5-di-*tert.*-butylphenyl)-2,2'-methylenedioxy-1,1'-binaphthyl (17b) from 16b

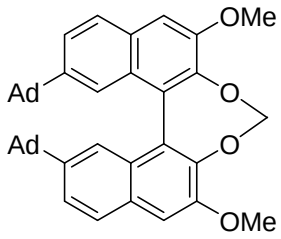


17b

Yield: 0.53 g (58%); white solid, recrystallization from acetone.

HPLC (%): 99.2. **MS** (EI): *m/z* (%) = 674 (100) [M^+], 646 (22) [M^+–28], 457 (5) [M^+–217], 322 (13) [M^+–352], 308 (6) [M^+–366], 287 (5) [M^+–387], 259 (6) [M^+–415], 231 (8) [M^+–443], 57 (99) [M^+–617]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 1.11 (s, 36 H), 5.74 (s, 2 H), 7.20 – 7.24 (m, 6 H), 7.45 (d, 2 H, *J* = 8.7 Hz), 7.76 (dd, 2 H, *J* = 8.5, 1.8 Hz), 7.90 (d, 2 H, *J* = 1.7 Hz), 7.98 (dd, 4 H, *J* = 11.7, 8.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 31.3, 34.8, 103.2, 120.7, 121.4, 121.6, 125.0, 125.3, 126.3, 128.6, 129.8, 130.8, 132.4, 139.7, 139.9, 150.9, 151.6. **HRMS** *m/z* calcd. for $C_{49}H_{54}O_2$: 674.41238; found: 674.41119. **Anal.** calcd. (%) for $C_{49}H_{54}O_2$: C 87.20, H 8.06; found: C 87.10, H 8.00.

(±)-7,7'-Di(1-adamantyl)-6,6'-dimethoxy-2,2'-methylenedioxy-1,1'-binaphthyl (17c) from 16c

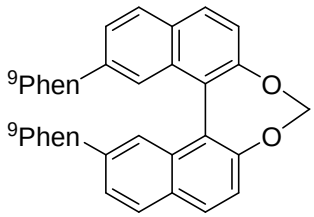


17c

Yield: 0.50 g (70%); white solid, recrystallization from ethanol.

HPLC (%): 99.4. **MS** (EI): *m/z* (%) = 626 (100) [M$^+$], 598 (15) [M$^+$–28], 313 (10) [M$^+$–313], 135 (94) [M$^+$–491], 107 (16) [M$^+$–519], 93 (28) [M$^+$–533], 67 (11) [M$^+$–559], 55 (6) [M$^+$–571]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 1.54 – 1.60 (m, 12 H), 1.77 – 1.81 (m, 6 H), 1.82 – 1.89 (m, 12 H), 3.90 (s, 6 H), 5.55 (s, 2 H), 7.13 (s, 2 H), 7.28 – 7.33 (m, 4 H), 7.73 (d, 2 H, *J* = 8.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 27.9, 35.9, 36.5, 53.9, 102.1, 105.7, 119.4, 123.8, 125.5, 126.0, 126.8, 130.3, 138.9, 148.4, 156.0. **HRMS** *m/z* calcd. for $C_{43}H_{46}O_4$: 626.33961; found: 626.33870. **Anal.** calcd. (%) for $C_{43}H_{46}O_4$: C 82.39, H 7.40; found: C 82.30, H 7.40.

(±)-2,2'-Methylenedioxy-7,7'-diphenanthren-9-yl-1,1'-binaphthyl (17d) from 16d

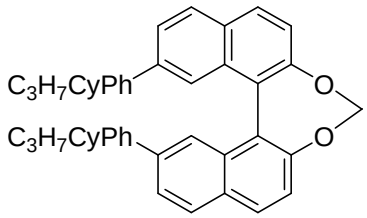


17d

The reaction was performed in DMF. Yield: 1.80 g (73%); white solid (purification after column chromatography: stirring in acetone).

HPLC (%): 100. **MS** (EI): *m/z* (%) = 650 (100) [M$^+$], 622 (35) [M$^+$–28], 445 (8) [M$^+$–205], 413 (5) [M$^+$–237], 325 (8) [M$^+$–325], 302 (9) [M$^+$–348], 289 (7) [M$^+$–361]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 5.69 (s, 2 H), 6.97 – 7.21 (m, 4 H), 7.29 – 7.61 (m, 14 H), 7.72 – 7.78 (m, 2 H), 7.86 (d, 2 H, *J* = 8.4 Hz), 7.94 (d, 2 H, *J* = 8.7 Hz), 8.53 – 8.68 (m, 4 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 103.2, 121.0, 122.4, 122.6, 126.2, 126.4, 126.5, 126.6, 126.6, 126.7, 126.9, 127.4, 127.7, 128.1, 128.8, 129.9, 130.3, 130.9, 131.0, 131.2, 132.4, 138.5, 138.9, 151.6. **HRMS** *m/z* calcd. for $C_{49}H_{30}O_2$: 650.22458; found: 650.22439. **Anal.** calcd. (%) for $C_{49}H_{30}O_2$: C 90.44, H 4.65; found: C 90.40, H 4.80.

(±)-2,2'-Methylenedioxy-7,7'-bis-(4-(4-propyl-cyclohexyl)phenyl)-1,1'-binaphthyl (17e) from 16e



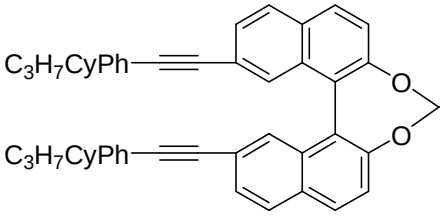
17e

Yield: 1.50 g (74%); white crystals, recrystallization from heptane.

HPLC (%): 100. **MS** (EI): *m/z* (%) = 698 (100) [M$^+$], 670 (15) [M$^+$–28], 83 (10) [M$^+$–615], 69 (18) [M$^+$–629], 55 (10) [M$^+$–643], 32 (12) [M$^+$–666], 28 (55) [M$^+$–670]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 0.80 (t, 6 H, *J* = 7.3 Hz), 0.85 – 0.99 (m, 4 H), 1.06 – 1.37 (m, 12 H), 1.67 – 1.79 (m, 10 H), 2.31 (tt, 2 H, *J* = 12.3, 3.1 Hz), 5.64 (s, 2 H), 6.99 – 7.04 (m, 4 H), 7.17 – 7.22 (m, 4 H), 7.38 (d, 2 H, *J* = 8.7 Hz), 7.64 (dd, 2 H, *J* = 8.5, 1.7 Hz), 7.74 (d, 2 H, *J* = 1.7 Hz), 7.91 (dd, 4 H, *J* = 8.6, 7.4 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 14.4, 20.0, 33.5, 34.2, 34.3, 37.0, 39.7, 44.2, 103.2, 120.8, 124.9, 125.0, 126.3, 127.2, 127.3, 129.0, 130.1, 130.9, 132.4, 138.6, 139.0, 147.0, 151.7. **HRMS** *m/z* calcd.

for $C_{51}H_{54}O_2$: 698.41238; found: 698.41143. **Anal.** calcd. (%) for $C_{51}H_{54}O_2$: C 87.64, H 7.79; found: C 87.50, H 7.70.

(±)-2,2'-Methylenedioxy-7,7'-bis-((4-(4-propylcyclohexyl)phenyl)ethynyl)-1,1'-binaphthyl (17f) from 16f

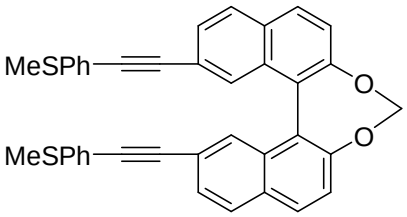


17f

The reaction was performed in DMF. Yield: 1.10 g (77%); white solid, recrystallization from 1-chlorobutane.

HPLC (%): 99.8. **MS** (EI): *m/z* (%) = 746 (100) [M^+], 718 (10) [M^+–28], 320 (5) [M^+–426], 83 (8) [M^+–663], 69 (14) [M^+–677], 55 (12) [M^+–691]. **^{1}H**-NMR (500 MHz, $CDCl_3$): δ/ppm = 0.93 (t, 6 H, *J* = 7.3 Hz), 1.00 – 1.11 (m, 4 H), 1.19 – 1.48 (m, 14 H), 1.83 – 1.92 (m, 8 H), 2.37 – 2.51 (m, 2 H), 5.70 (s, 2 H), 7.11 – 7.16 (m, 4 H), 7.35 – 7.39 (m, 4 H), 7.50 (d, 2 H, *J* = 8.7 Hz), 7.58 (dd, 2 H, *J* = 8.5, 1.5 Hz), 7.69 – 7.72 (m, 2 H), 7.93 (d, 2 H, *J* = 8.5 Hz), 8.00 (d, 2 H, *J* = 8.5 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 14.4, 20.0, 33.5, 34.1, 37.0, 39.7, 44.6, 89.2, 90.4, 103.1, 120.4, 121.4, 121.7, 125.7, 126.8, 128.1, 128.5, 129.5, 130.3, 131.1, 131.6, 132.0, 148.3, 151.8. **HRMS** *m/z* calcd. for $C_{55}H_{54}O_2$: 746.41238; found: 746.41240. **Anal.** calcd. (%) for $C_{55}H_{54}O_2$: C 88.43, H 7.29; found: C 87.50, H 7.30.

(±)-2,2'-Methylenedioxy-7,7'-bis-(4-methylsulfanyl-phenylethynyl)-1,1'-binaphthyl (17g) from 16g



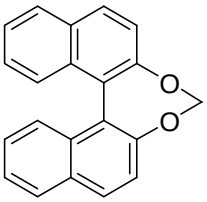
17g

The reaction was performed in DMF. Yield: 0.52 g (50%); white solid (purification after column chromatography: stirring in acetone).

HPLC (%): 98.0. **MS** (EI): *m/z* (%) = 590 (100) [M^+], 562 (23) [M^+–28], 320 (5) [M^+–270], 295 (5) [M^+–295], 233 (5) [M^+–357]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 2.23 (s, 6 H), 5.45 (s, 2 H), 6.86 – 6.94 (m, 4 H), 7.06 – 7.14 (m, 4 H), 7.28 (d, 2 H, *J* = 8.7 Hz), 7.34 (dd, 2 H, *J* = 8.5, 1.5 Hz), 7.39 – 7.43 (m, 2 H), 7.73 (d, 2 H, *J* = 8.4 Hz), 7.79 (d, 2 H, *J* = 8.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 20.0, 94.6, 107.8, 123.8, 126.1, 126.4, 130.3, 130.4, 132.6, 133.5, 134.0, 135.2, 135.9, 136.6, 144.3, 156.6. **HRMS** *m/z* calcd. for $C_{39}H_{26}O_2S_2$: 590.13742; found: 590.13656. **Anal.** calcd. (%) for $C_{39}H_{26}O_2S_2$: C 79.29, H 4.44; found: C 79.00, H 4.30.

Preparation of unsubstituted binaphthyls from commercially available (–)-BINOL

(–)-2,2'-Methylenedioxy-1,1'-binaphthyl (18)

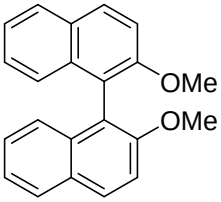


18

The identical procedure as before gave **18** (7.98 g, 79%) as colorless crystals; recrystallization from 2-propanol/toluene (5:1). Analytical data were identical with those reported in the literature.[6]

GC (%): 100. **MS** (EI): *m/z* (%) = 298 (100) [M^+], 281 (6) [M^+–17], 269 (87) [M^+–29], 253 (22) [M^+–45], 239 (42) [M^+–59], 226 (6) [M^+–72], 213 (6) [M^+–85], 134 (13) [M^+–164], 119 (17) [M^+–179], 106 (5) [M^+–192]. $[\alpha]_D^{20}$ = +783 (c = 8.15, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 5.69 (s, 2 H), 7.29 (ddd, 2 H, *J* = 8.3, 6.7, 1.3 Hz), 7.41 – 7.54 (m, 6 H), 7.89 – 8.00 (m, 4 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 103.1, 120.9, 125.0, 126.0, 126.1, 126.9, 128.4, 130.3, 131.8, 132.1. **HRMS** *m/z* calcd. for $C_{21}H_{14}O_2$: 298.09938; found: 298.09850.

(–)-2,2'-Dimethoxy-1,1'-binaphthyl (19)



19

A mixture of (–)-BINOL (10.0 g, 33.9 mmol), iodomethane (13 mL, 209 mmol), potassium carbonate (16.4 g, 119 mmol) and 150 mL acetone was stirred and heated under reflux for 20 h. After cooling down, the reaction mixture was poured onto water (250 mL). The insoluble material was filtered off and washed with water (2 x 50 mL). The resulting white solid was dried under vacuum. Recrystallization from 1-chlorobutane afforded **19** (8.90 g, 82%) as white crystals. Analytical data were identical with those reported in the literature.[7]

GC (%): 98.4. **MS** (EI): *m/z* (%) = 314 (100) [M^+], 268 (49) [M^+–46], 255 (9) [M^+–59], 239 (18) [M^+–75], 226 (9) [M^+–88]. $[\alpha]_D^{20}$ = –93 (c = 7.51, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 3.75 (s, 6 H), 7.07 – 7.12 (m, 2 H), 7.20 (ddd, 2 H, *J* = 8.1, 6.7, 1.3 Hz), 7.30 (ddd, 2 H, *J* = 8.1, 6.7, 1.2 Hz), 7.45 (d, 2 H, *J* = 9.1 Hz), 7.85 (dd, 2 H, *J* = 8.3, 0.9 Hz), 7.96 (dd, 2 H, *J* = 9.1, 0.7 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ/ppm = 56.9, 114.2, 119.6, 123.5, 125.2, 126.3, 127.9, 129.2, 129.4, 134.0, 155.0. **HRMS** *m/z* calcd. for $C_{22}H_{18}O_2$: 314.13068; found: 314.13017.

3. Separation of racemic binaphthyls into enantiomers

Racemic **17a** was resolved by repeated SFC separation on a Chiralcel OD-H column by using a SFC minigram (CO_2/2-propanol + 0.5% DEA, 60:40; flow rate 0.5 mL/min; 75 mg/4 mL dioxane, total 7 injections). Evaporation of the solvents gave fraction 1 (211 mg, t_r = 7.6 min, *ee* = 98%) and fraction 2 (200 mg, t_r = 16.7 min, *ee* = 96%).

Racemic **16b** was resolved by repeated SFC separation on a Chiralpak AS-H column by using a SFC minigram (CO_2/methanol, 85:15; flow rate 1.0 mL/min; 168 mg/2.5 mL methanol, total 13 injections). Evaporation of the solvents gave fraction 1 (815 mg, t_r = 4.5 min, *ee* = 93%) and fraction 2 (858 mg, t_r = 7.4 min, *ee* = 94%).

Racemic **16c** was resolved by repeated HPLC separation on a Chiralpak IA column by using a Laprep Sigma (*n*-heptane/2-propanol, 85:15; flow rate 0.8 mL/min; 125 mg/7 mL CH_2Cl_2, total 24 injections). Evaporation of the solvents gave fraction 1 (1490 mg, t_r = 9.1 min, *ee* = 90%) and fraction 2 (1270 mg, t_r = 15.0 min, *ee* = 98%).

Racemic **17d** was resolved by repeated HPLC separation on a Chiralcel OD-H column by using a Laprep Sigma (*n*-heptane/2-propanol, 85:15; flow rate 0.8 mL/min; 100 mg/4 mL CH_2Cl_2, total 13 injections). Evaporation of the solvents gave fraction 1 (540 mg, t_r = 11.8 min, *ee* = 98%) and fraction 2 (480 mg, t_r = 19.5 min, *ee* = 90%).

Racemic **17e** was resolved by repeated SFC separation on a Chiralcel OD-H column by using a SFC minigram (CO_2/2-propanol, 75:25; flow rate 0.6 mL/min; 48 mg/0.9 mL dioxane, total 28 injections). Evaporation of the solvents gave fraction 1 (482 mg, t_r = 4.7 min, *ee* = 100%) and fraction 2 (502 mg, t_r = 8.1 min, *ee* = 94%).

Racemic **17f** was resolved by repeated HPLC separation on a Chiralcel OD-H column by using a Laprep Sigma (*n*-heptane/ethanol, 10:90; flow rate 0.8 mL/min; 100 mg/5 mL CH_2Cl_2, total 9 injections). Evaporation of the solvents gave fraction 1 (274 mg, t_r = 15.4 min, *ee* = 97%) and fraction 2 (228 mg, t_r = 20.4 min, *ee* = 98%).

Racemic **17g** was resolved by repeated HPLC separation on a Chiralcel OD-H column by using a Laprep Sigma (*n*-hexane/2-propanol, 80:20; flow rate 0.8 mL/min; 100 mg/8 mL dioxane, total 5 injections). Evaporation of the solvents gave fraction 1 (140 mg, t_r = 13.1 min, *ee* = 94%) and fraction 2 (105 mg, t_r = 24.7 min, *ee* = 90%).

4. Specific rotations

An Anton Paar MCP 500 polarimeter was used to determine the optical rotations of the synthesized binaphthyls. Conditions: D-line of a sodium lamp (589 nm), 20 °C, c = [mg mL $^{-1}$].

The absolute configurations of the methylenedioxy-bridged binaphthyls **17a**-**g** were not determined, so the sign of optical rotation was not taken into account.

Compound	Specific rotation [°]
17a	1325 (c = 0.20, CH_2Cl_2, *ee* = 98%)
17b	937 (c = 5.22, CH_2Cl_2, *ee* = 94%)
17c	607 (c = 6.02, CH_2Cl_2, *ee* = 98%)
17d	583 (c = 5.46, CH_2Cl_2, *ee* = 98%)
17e	932 (c = 6.97, CH_2Cl_2, *ee* = 100%)
17f	1522 (c = 10.6, CH_2Cl_2, *ee* = 98%)
17g	1449 (c = 6.62, CH_2Cl_2, *ee* = 94%)
18	783 (c = 8.15, CH_2Cl_2).
19	93 (c = 7.51, CH_2Cl_2)

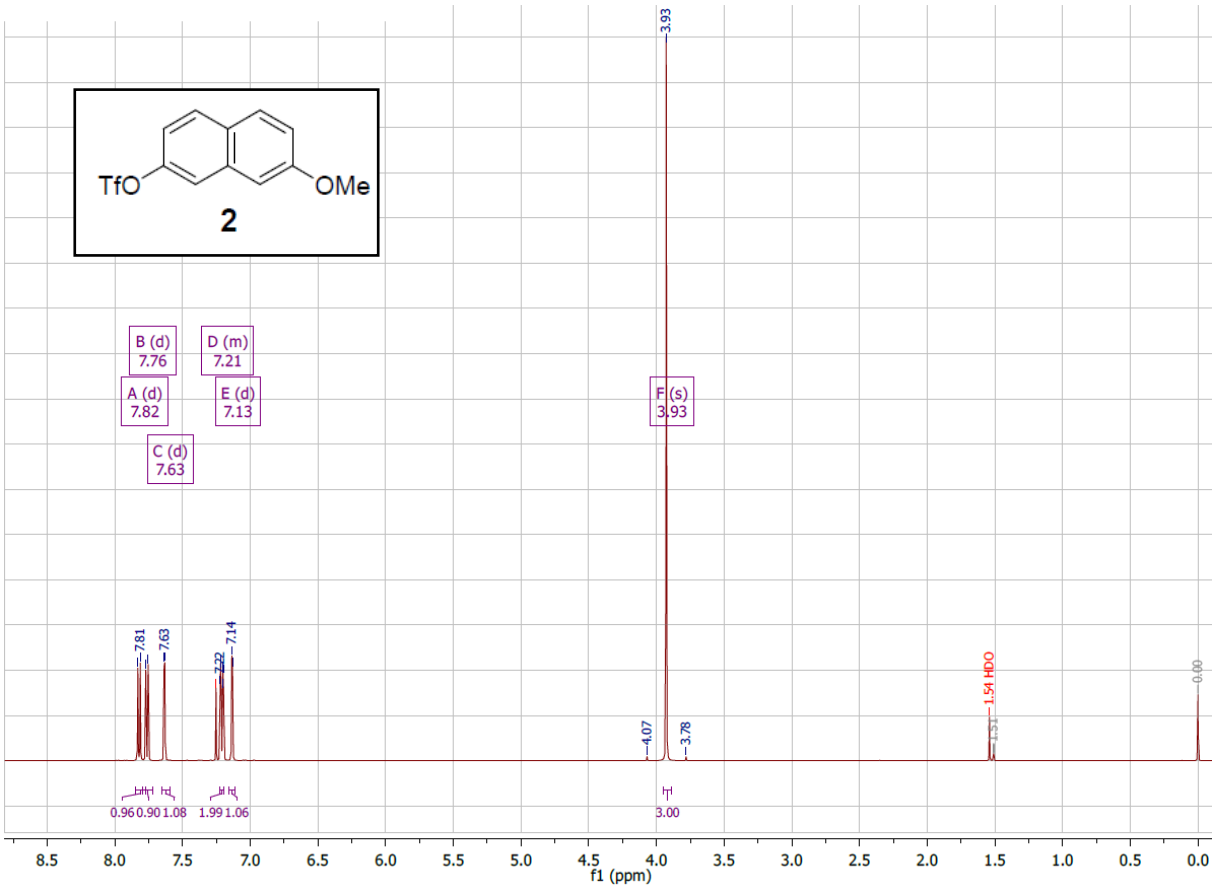
5. Helical Twisting Powers (HTP's)

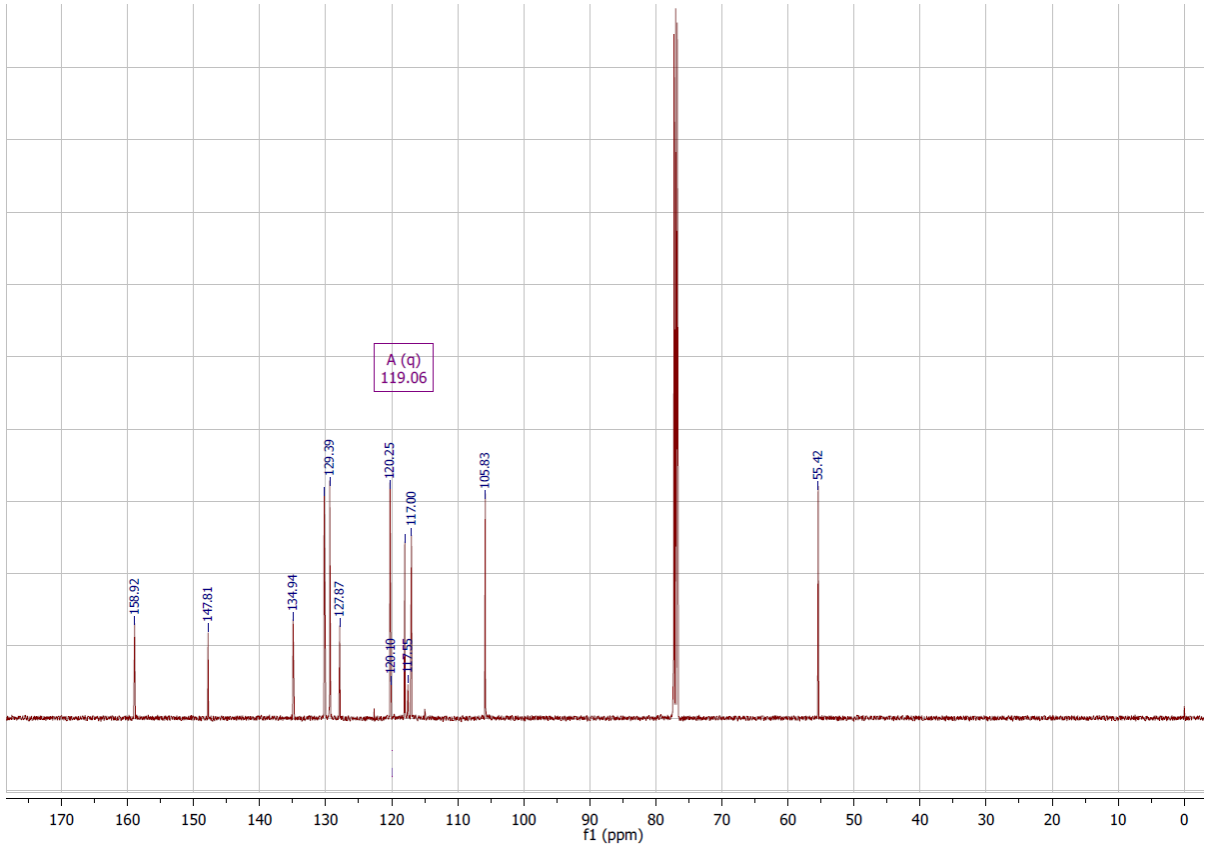
The HTP's were measured in MLC-6260 (Merck, commercial nematic mixture of 16 liquid crystalline compounds) by the Grandjean-Cano method. After dissolving the chiral dopant in MLC-6260, the cholesteric phase (N*) was inserted between a plano-convex lens and a glass plate. Both lens and plate were appropriately rubbed to obtain the necessary alignment. Then, the cholesteric pitch *p* (distance between observed disclination lines) was measured with an optical microscope in linearly polarized light. Due to the known dopant molar fraction *c* and enantiomeric excess *r*, the HTP-values (β) could be calculated with the following equation: $\beta = (pcr)^{-1}$.

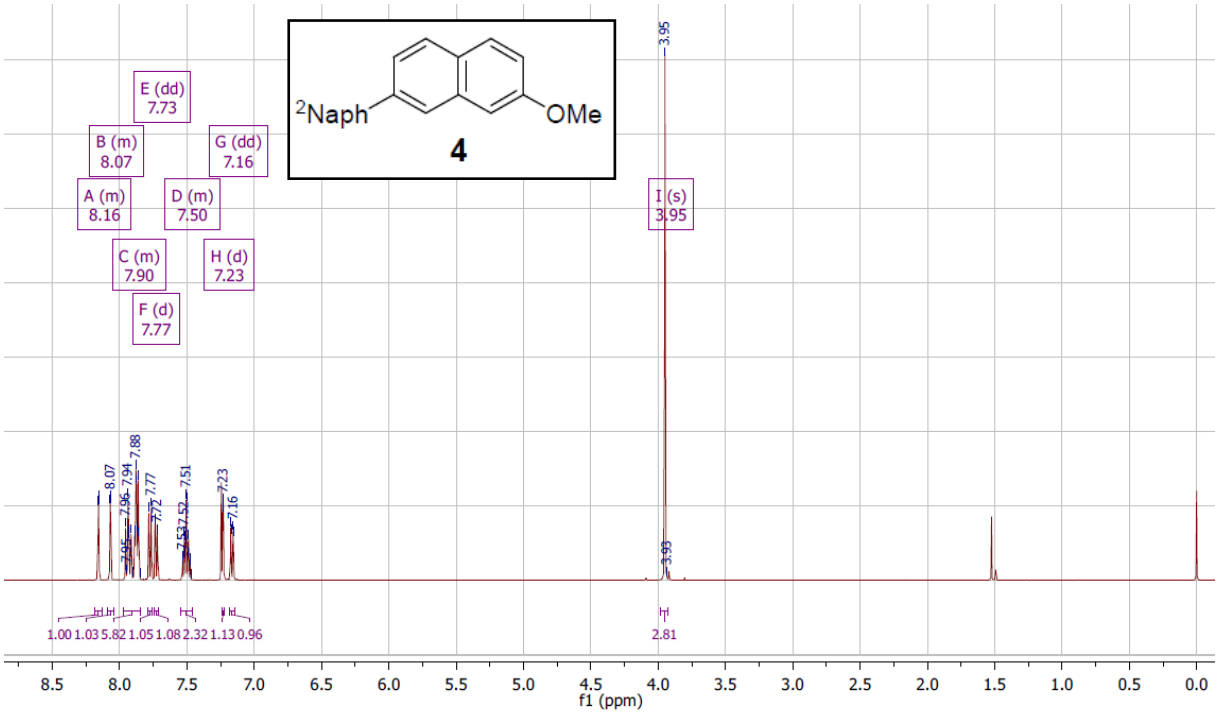
Compound	HTP [µm^{-1}] (MLC-6260)
17a	65
17b	3
17c	14
17d	63
17e	102
17f	114
17g	56
18	41
19	4

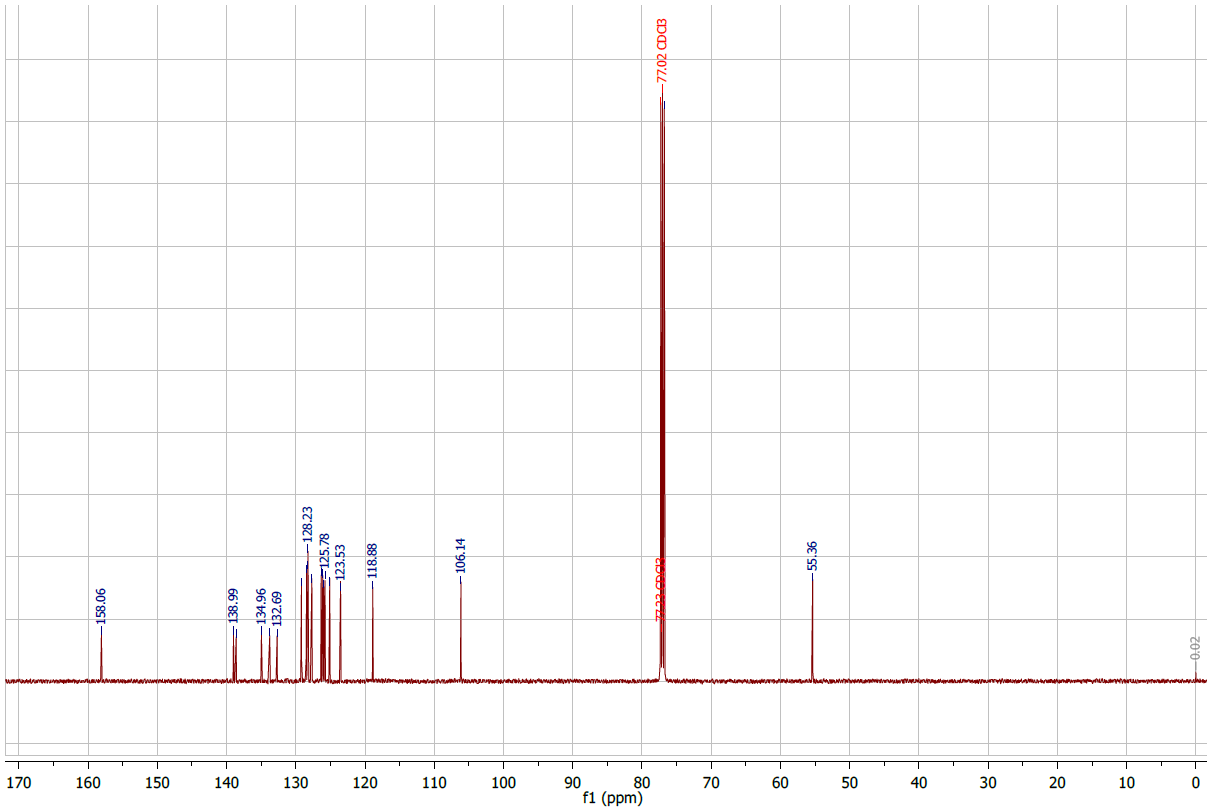
The sign of β was not taken into account.

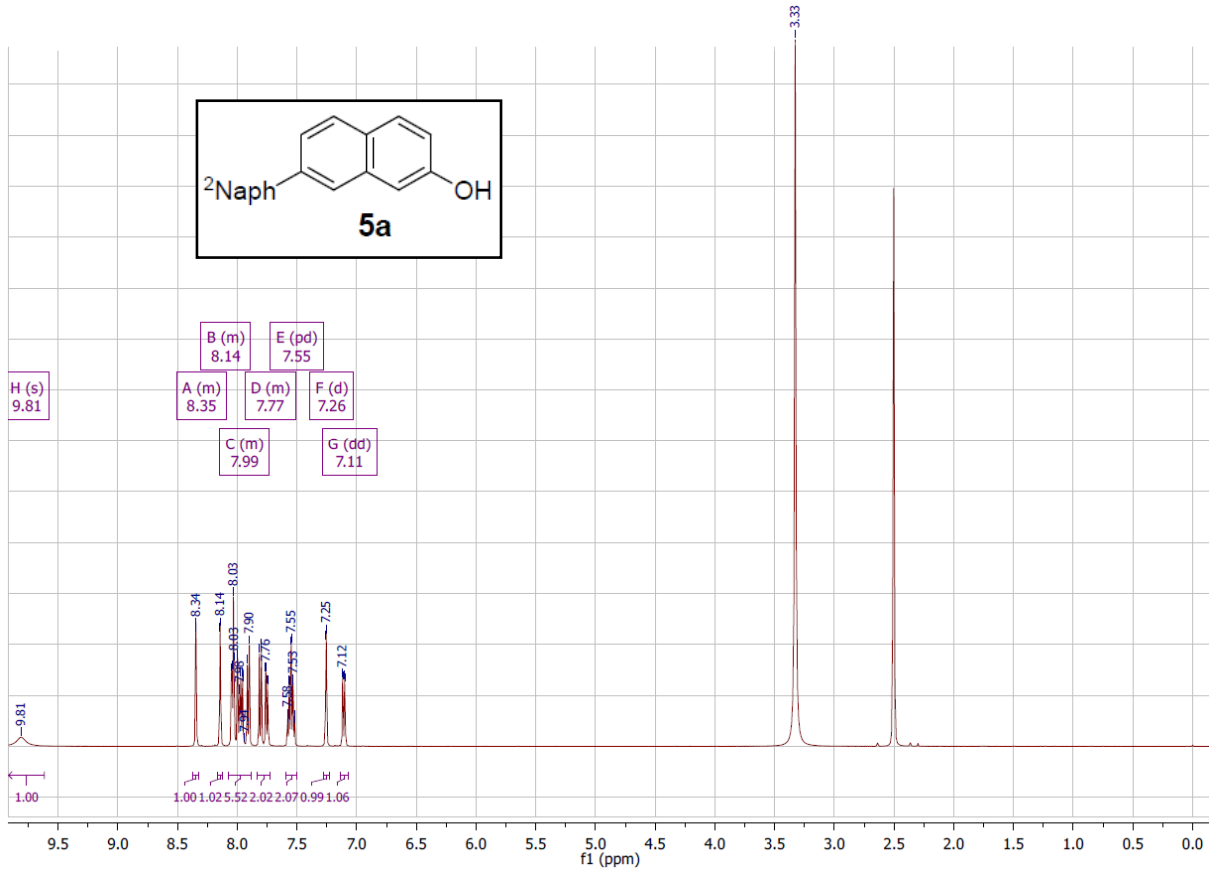
6. NMR spectra

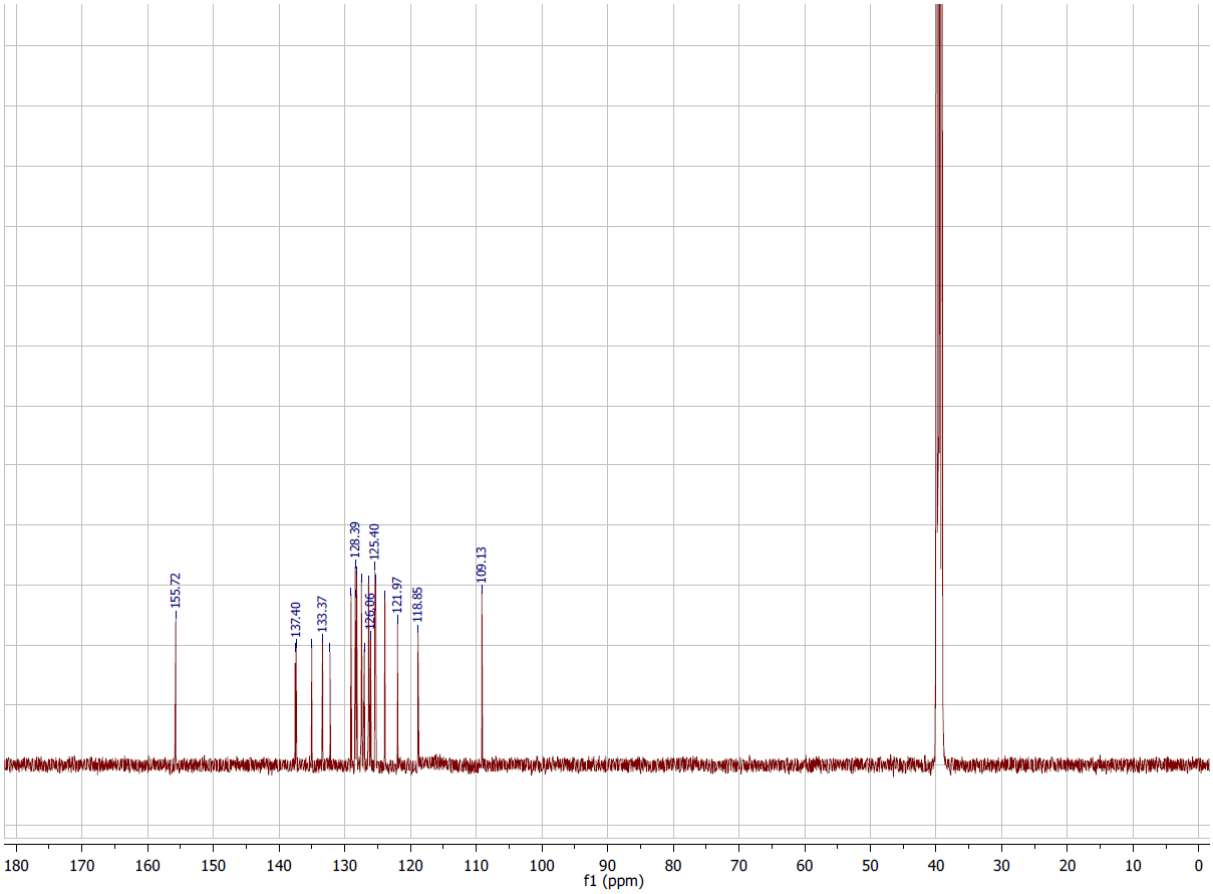


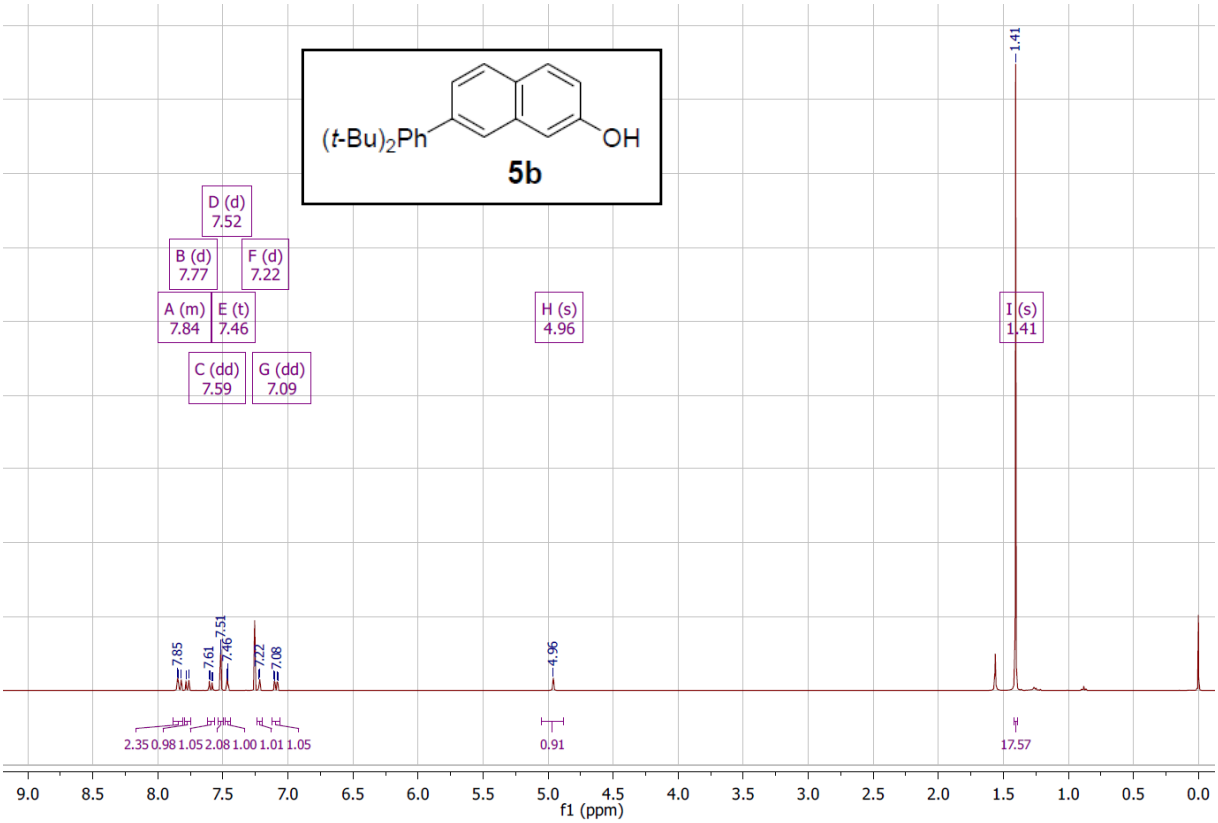


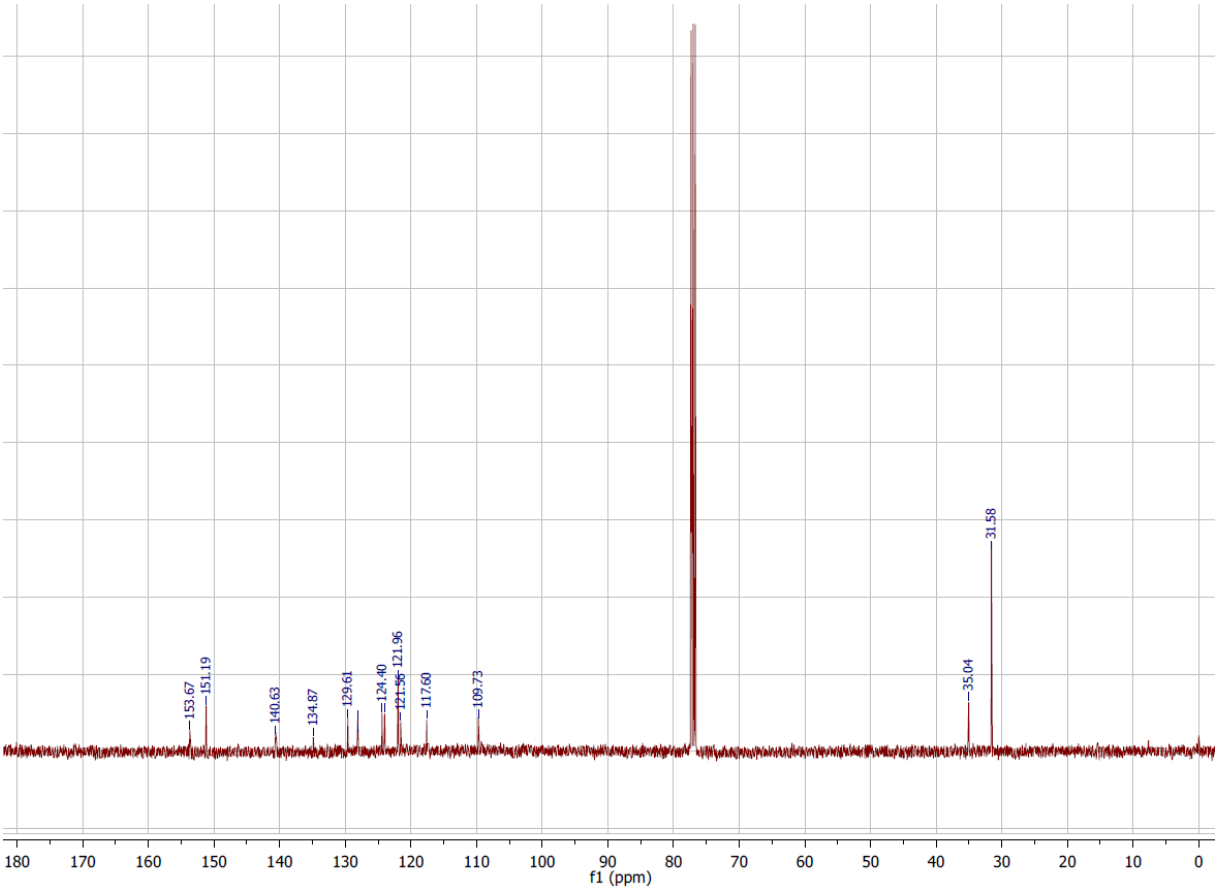

E (dd)
7.73
B (m)
8.07
G (dd)
7.16
A (m)
8.16
D (m)
7.50
C (m)
7.90
H (d)
7.23
F (d)
7.77
2Naph
OMe
4
I (s)
3.95
1.00 1.03 5.82 1.05 1.08 2.32 1.13 0.96
2.81
f1 (ppm)

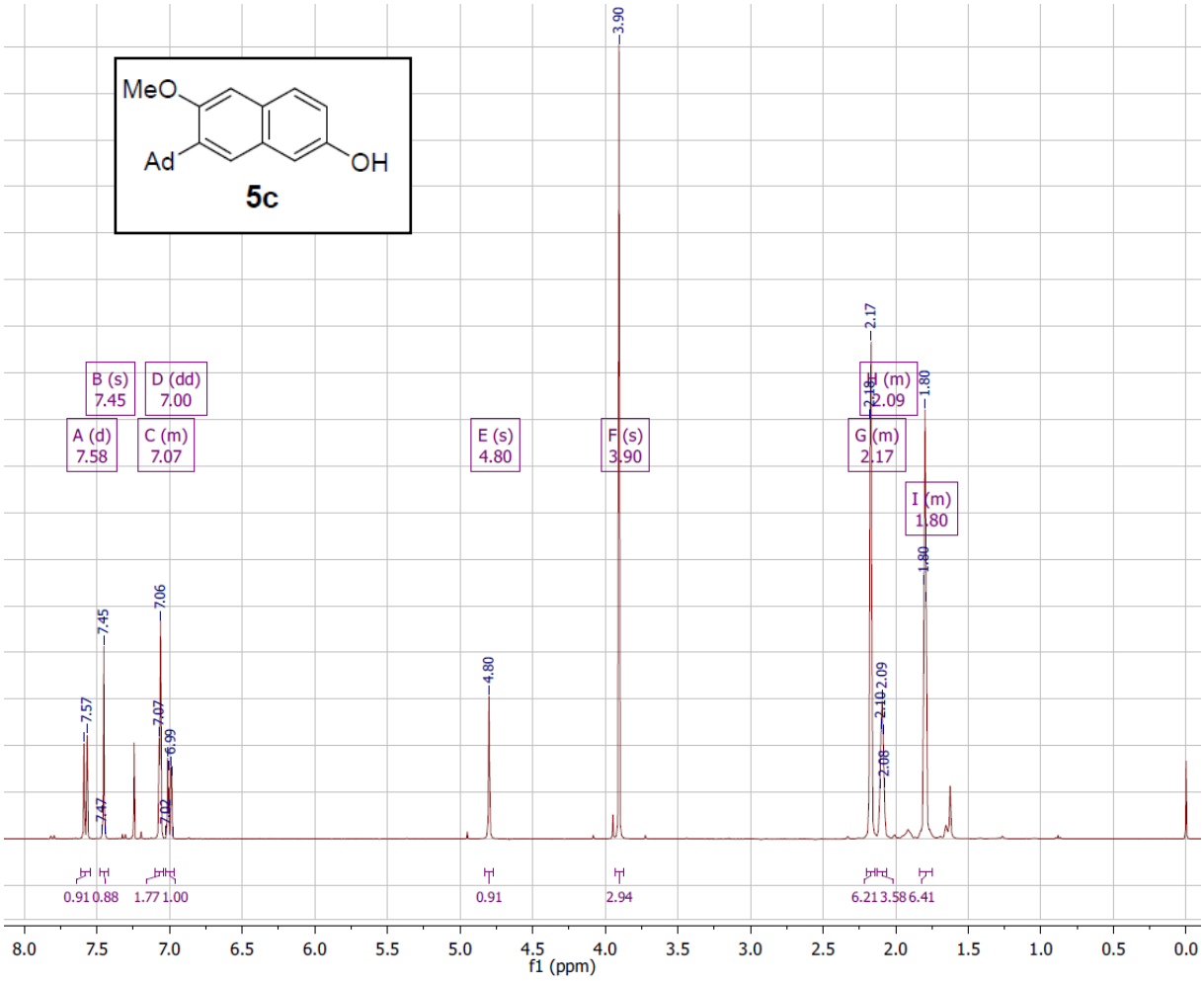

77.02 CDCl3
158.06
138.99
134.96
132.69
128.23
125.78
123.53
118.88
106.14
55.36
f1 (ppm)

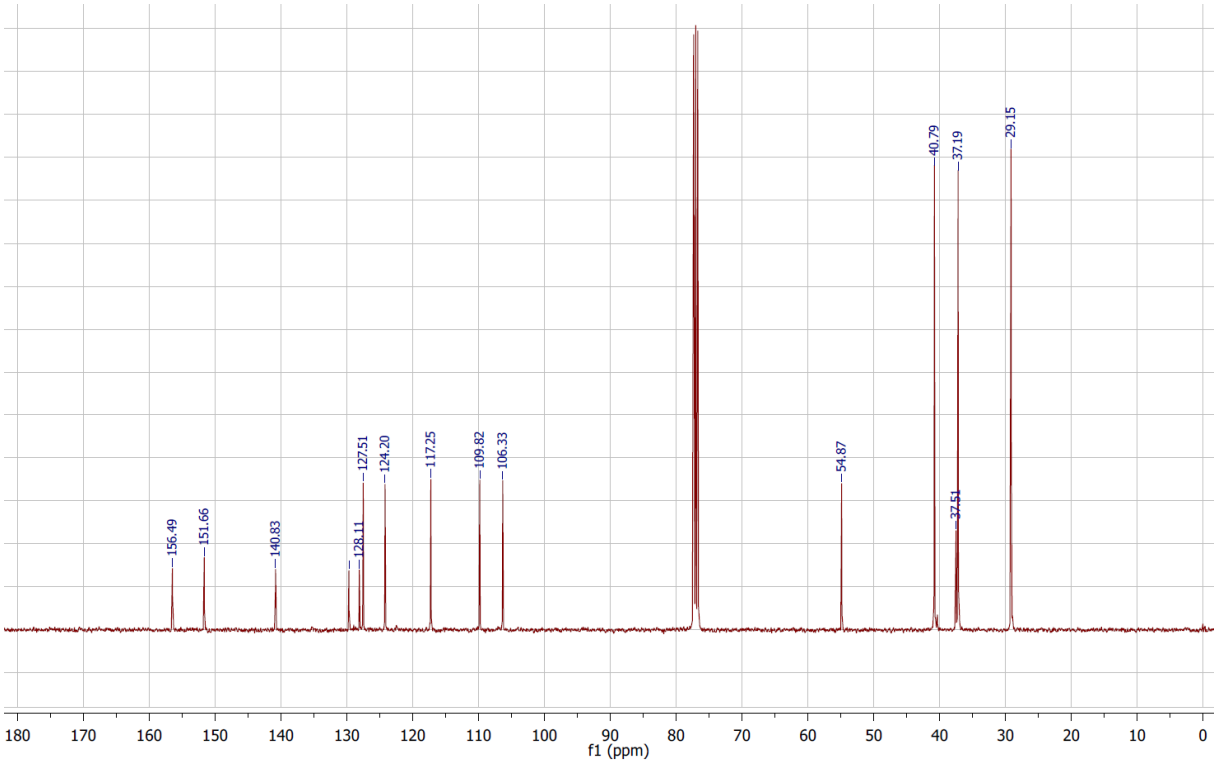

2Naph
OH
5a
H (s) 9.81
A (m) 8.35
B (m) 8.14
C (m) 7.99
D (m) 7.77
E (pd) 7.55
F (d) 7.26
G (dd) 7.11
3.33
8.34
8.14
8.03
7.90
7.76
7.55
7.25
7.12
9.81
1.00
1.00 1.02 5.52 2.02 2.07 0.99 1.06
f1 (ppm)

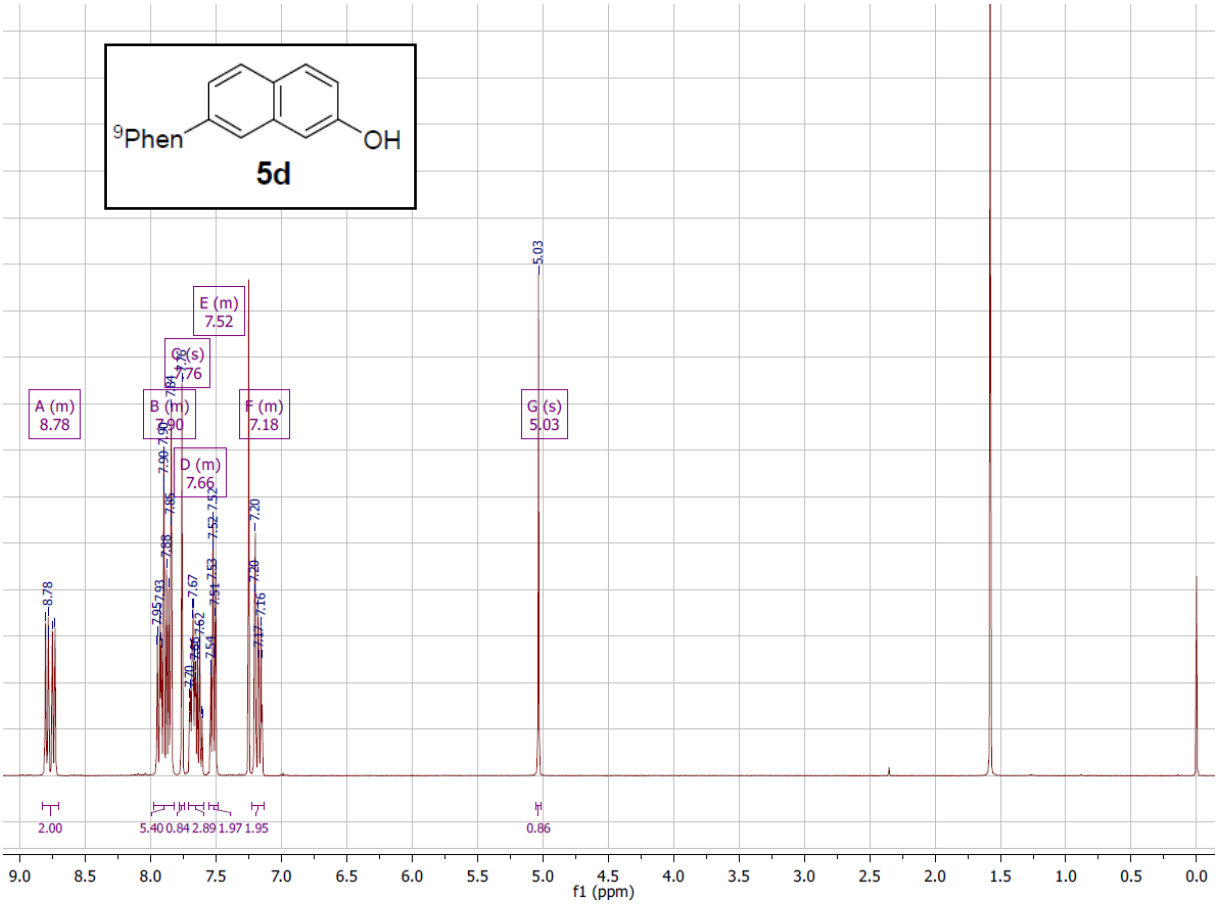

155.72
137.40
133.37
128.39
125.40
126.06
121.97
118.85
109.13
f1 (ppm)

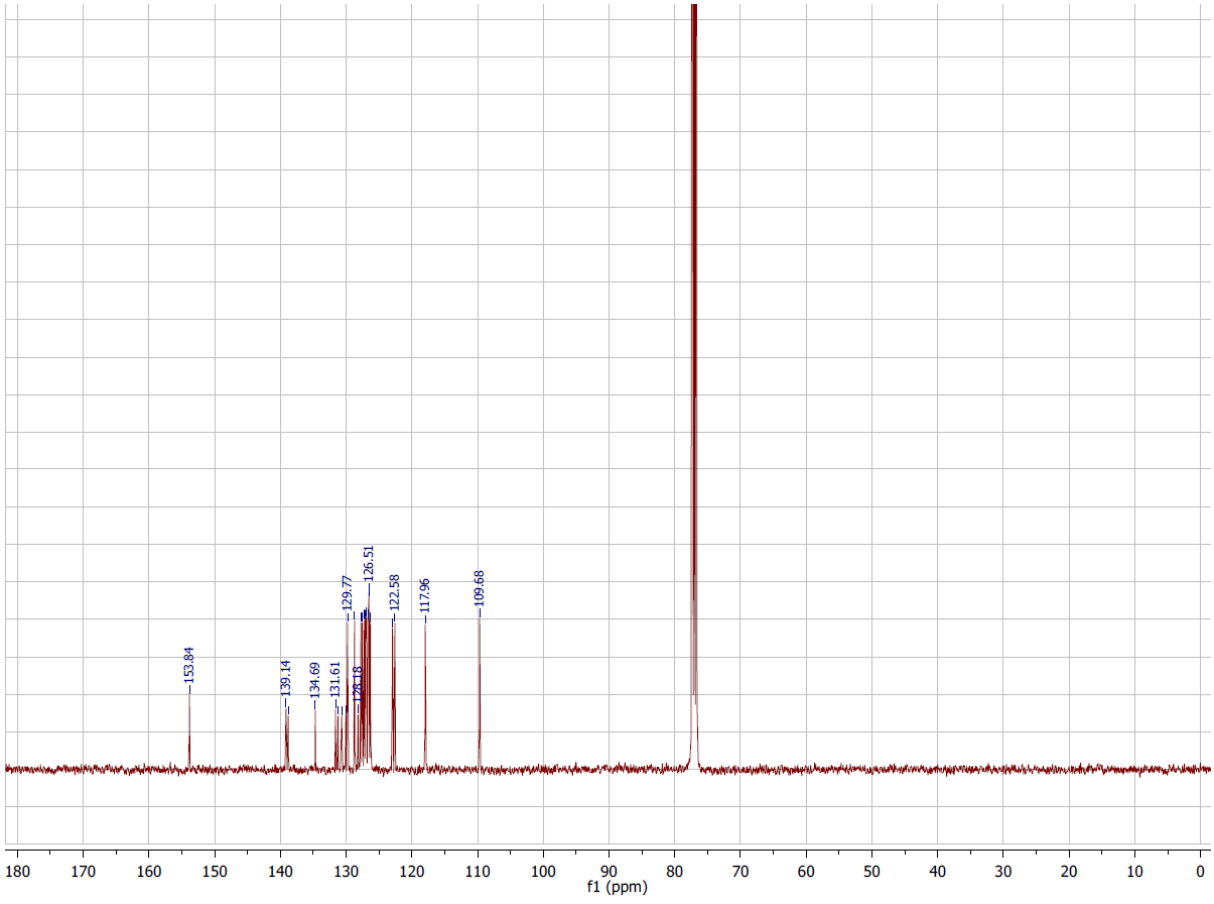

(t-Bu)2Ph
OH
5b
D (d) 7.52
B (d) 7.77
F (d) 7.22
A (m) 7.84
E (t) 7.46
H (s) 4.96
I (s) 1.41
C (dd) 7.59
G (dd) 7.09
1.41
7.85
7.61
7.51
7.46
7.22
7.08
4.96
2.35 0.98 1.05 2.08 1.00 1.01 1.05
0.91
17.57
f1 (ppm)

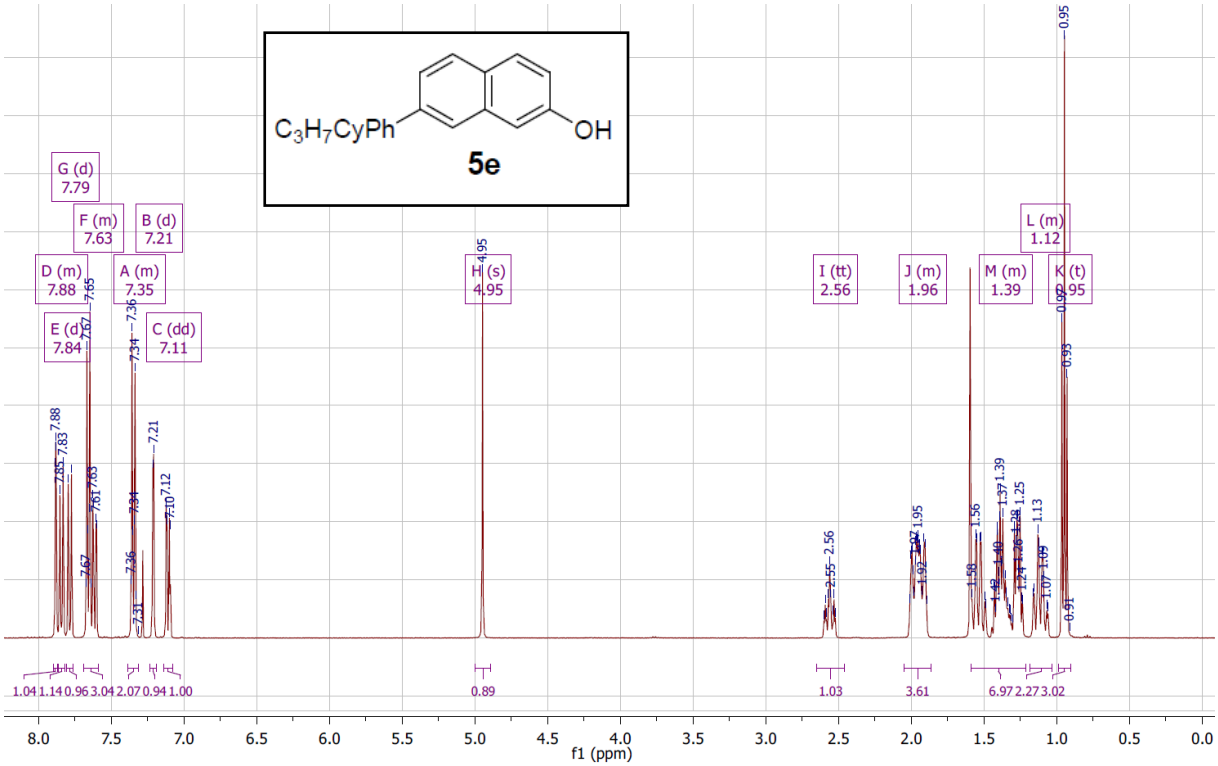

153.67
151.19
140.63
134.87
129.61
124.40
121.96
121.56
117.60
109.73
35.04
31.58
f1 (ppm)

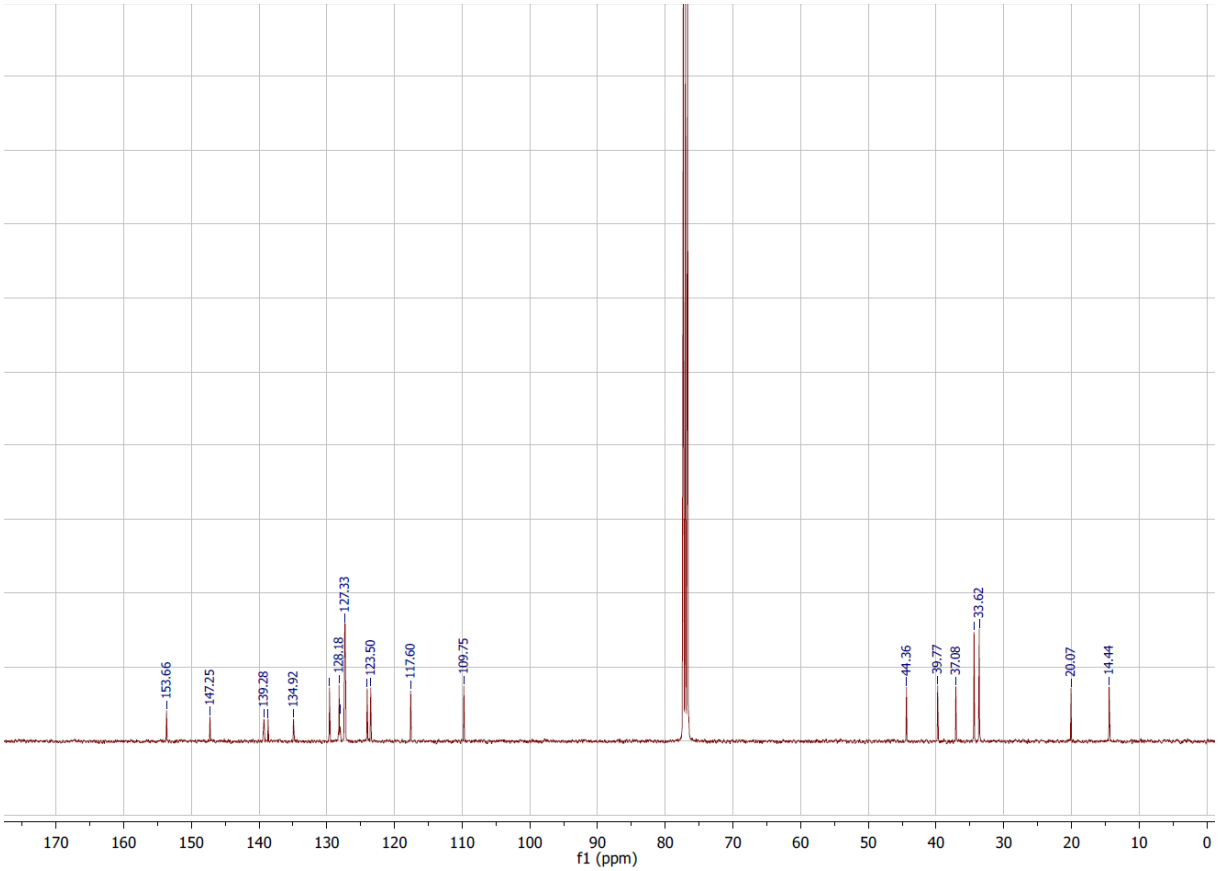

MeO
Ad
OH
5c
B (s) 7.45
D (dd) 7.00
A (d) 7.58
C (m) 7.07
E (s) 4.80
F (s) 3.90
G (m) 2.17
H (m) 2.09
I (m) 1.80
f1 (ppm)

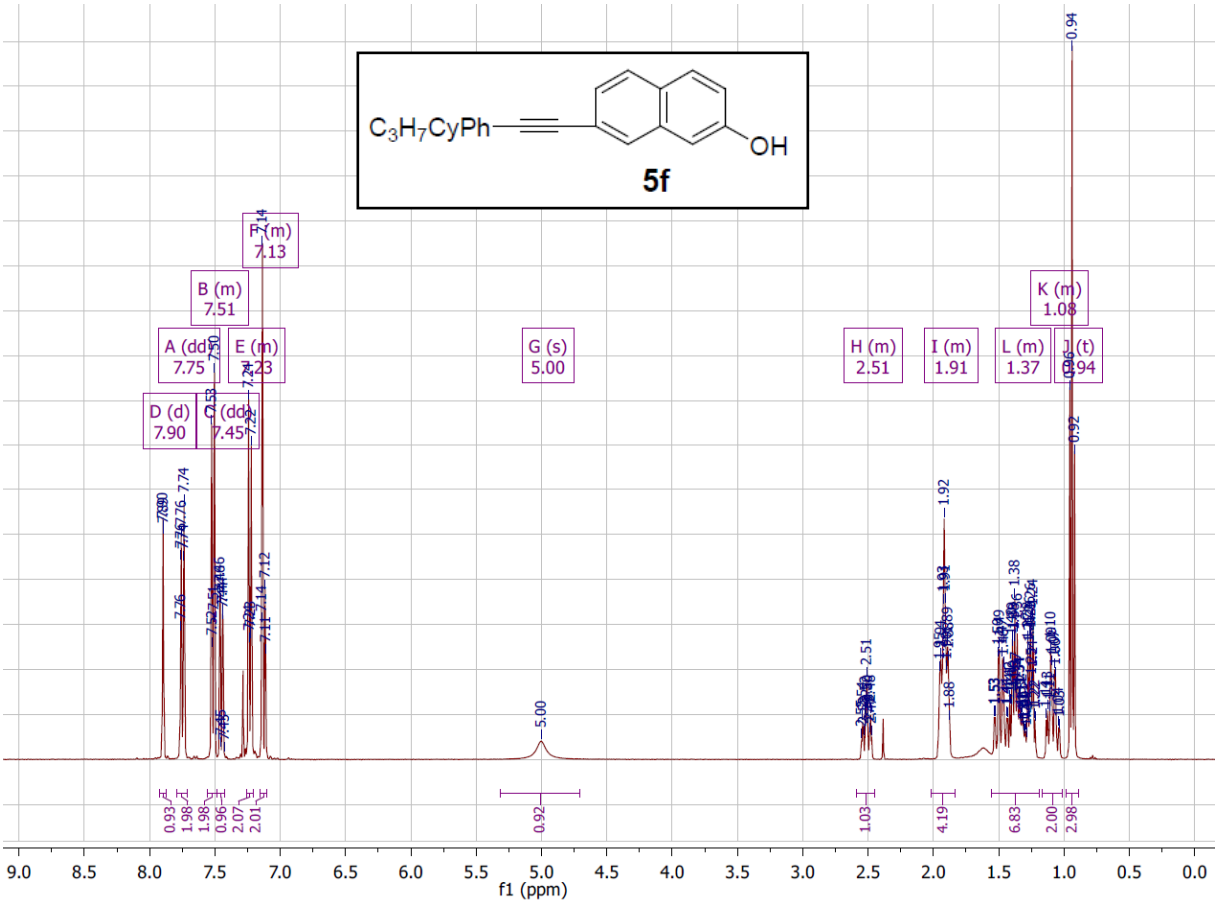

f1 (ppm)

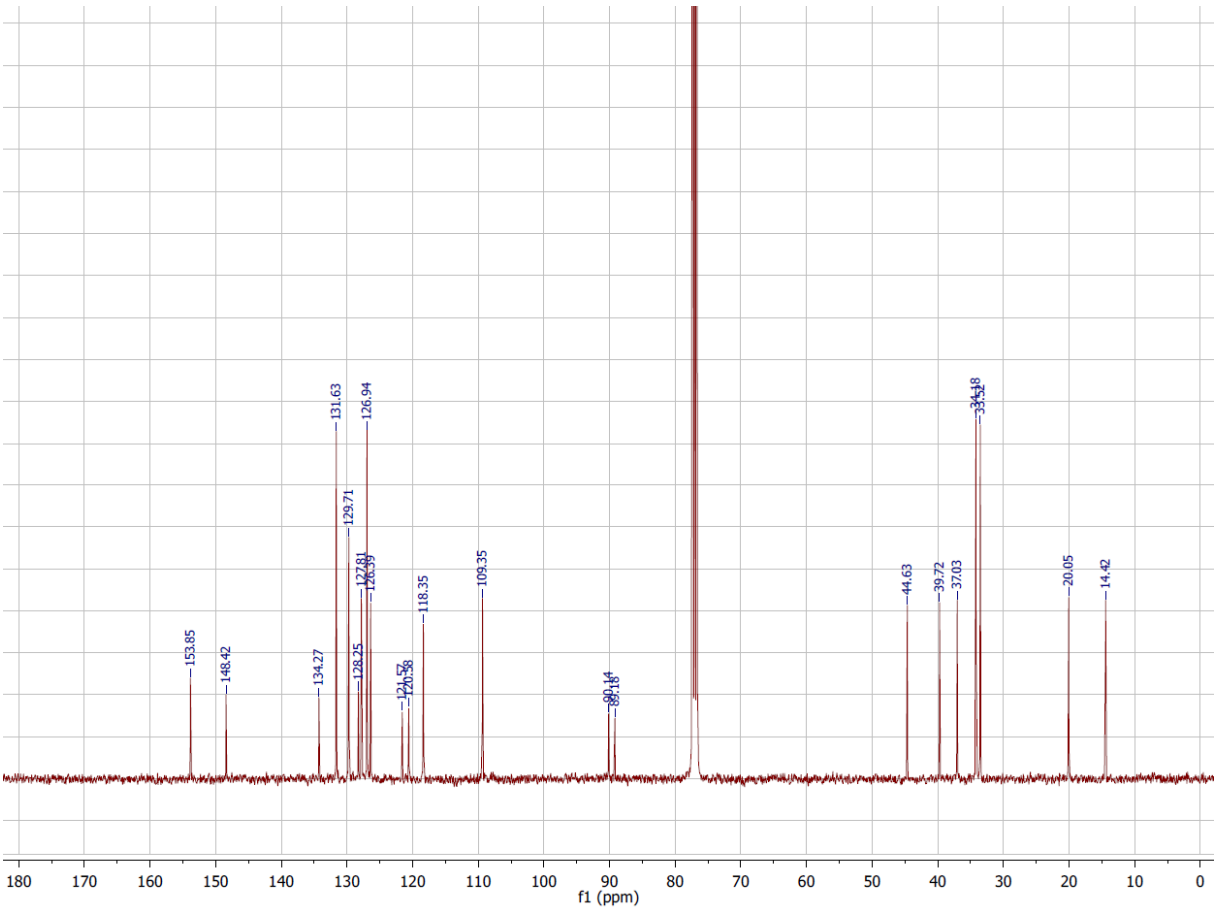

9Phen
OH
5d
A (m) 8.78
B (m) 7.90
C (s) 7.76
D (m) 7.66
E (m) 7.52
F (m) 7.18
G (s) 5.03
2.00
5.40
0.84
2.89
1.97
1.95
0.86
f1 (ppm)

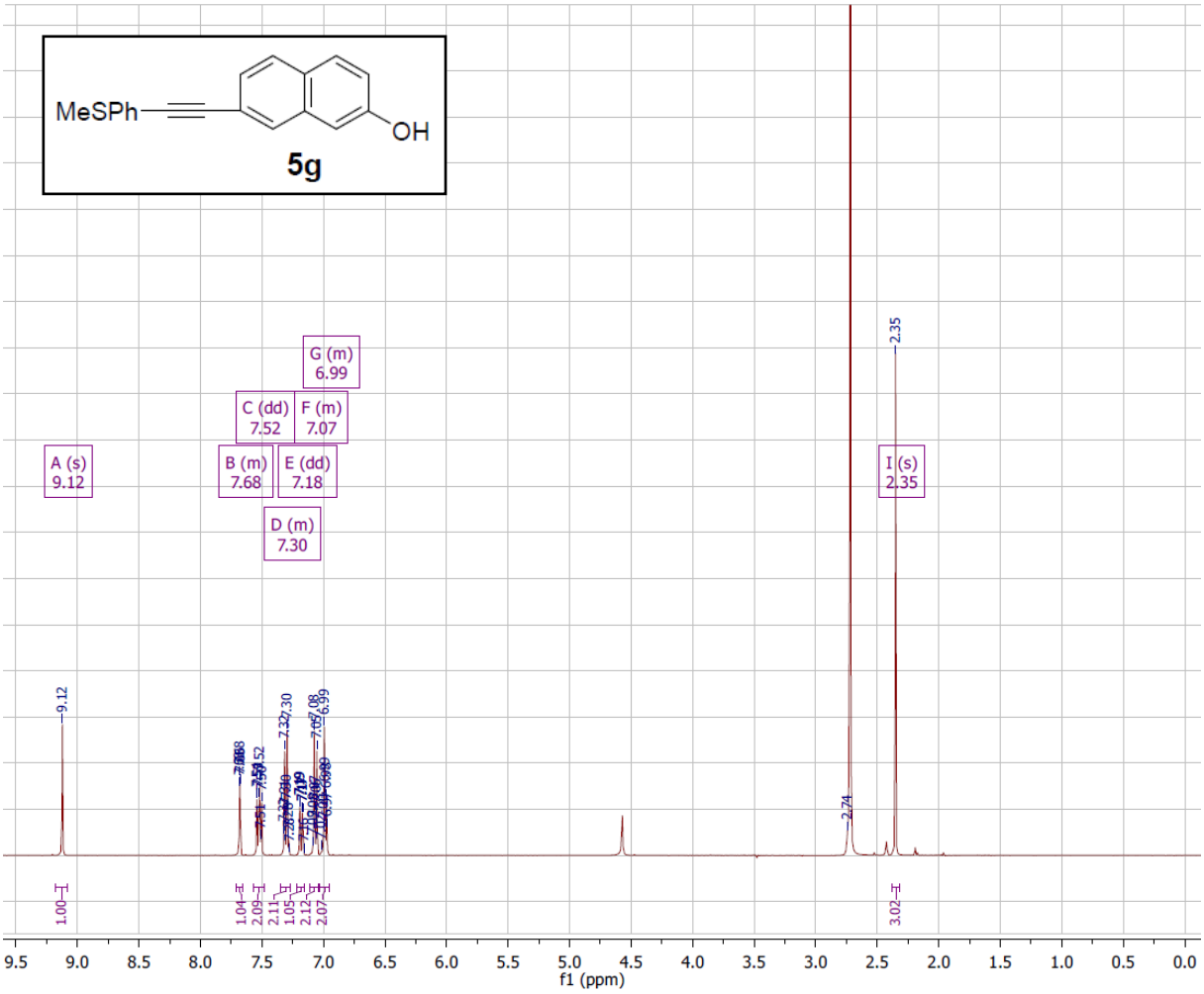

153.84
139.14
134.69
131.61
129.77
126.51
122.58
117.96
109.68
f1 (ppm)

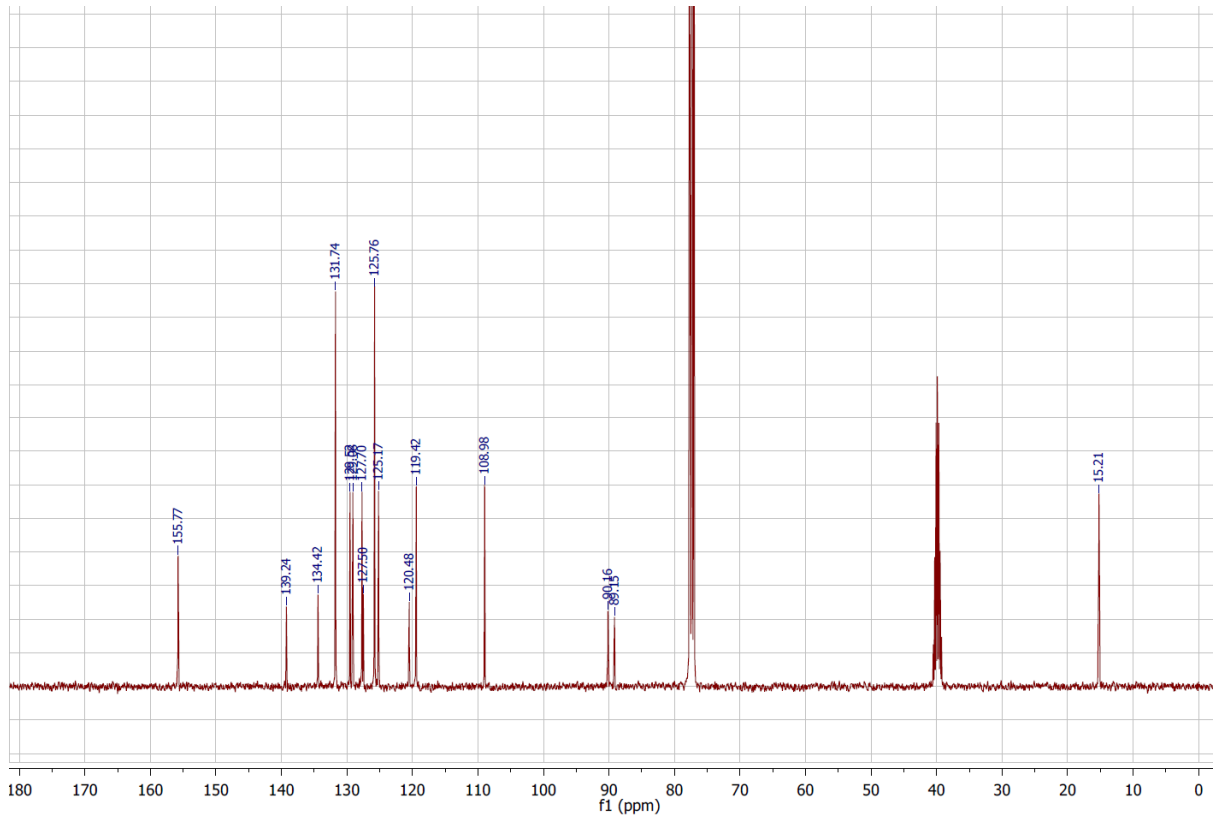

C3H7CyPh
OH
5e
G (d) 7.79
F (m) 7.63
B (d) 7.21
D (m) 7.88
A (m) 7.35
H (s) 4.95
I (tt) 2.56
J (m) 1.96
M (m) 1.39
L (m) 1.12
K (t) 0.95
E (d) 7.84
C (dd) 7.11
1.04 1.14 0.96 3.04 2.07 0.94 1.00
0.89
1.03
3.61
6.97 2.27 3.02
f1 (ppm)

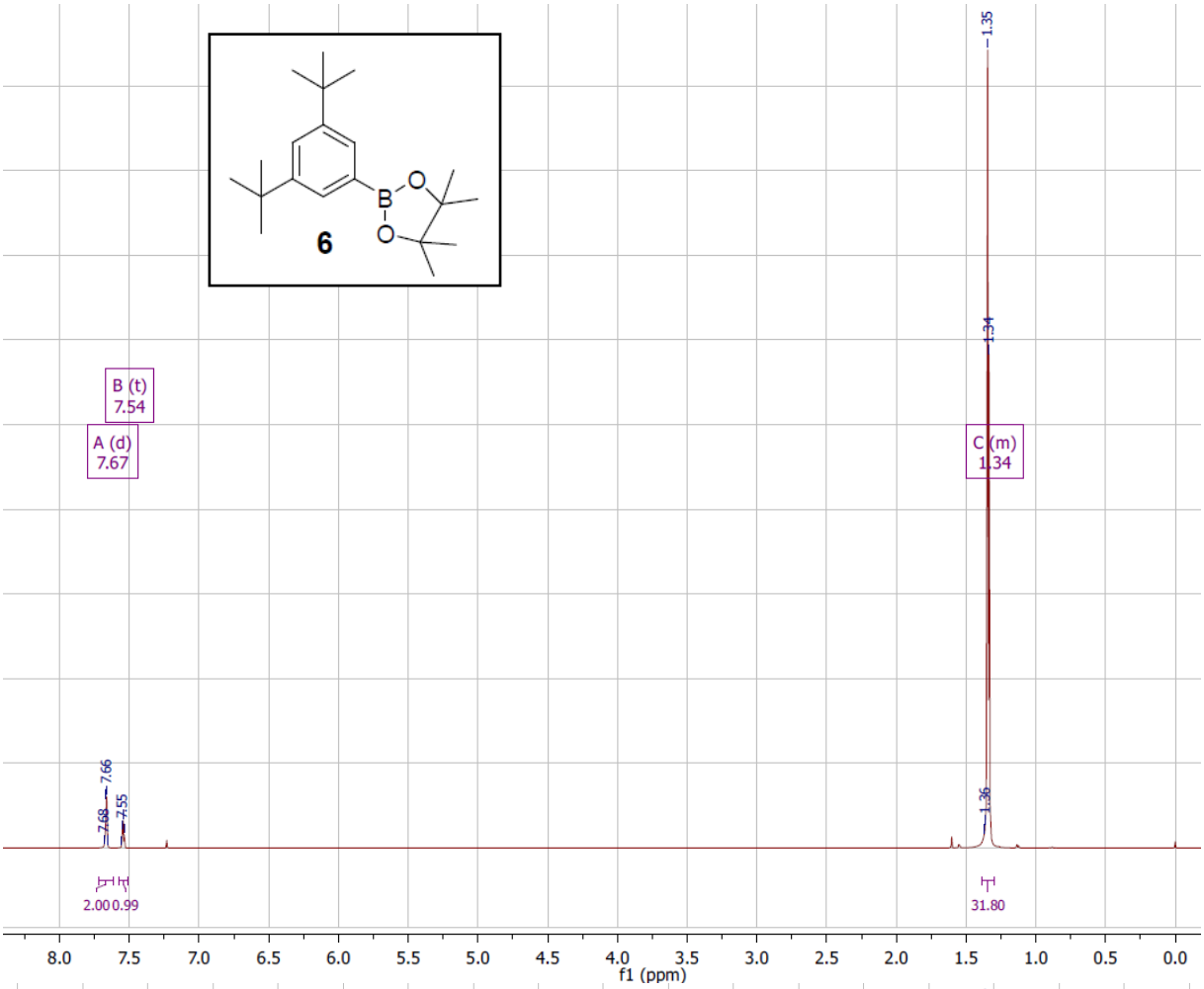

153.66
147.25
139.28
134.92
128.18
127.33
123.50
117.60
109.75
44.36
39.77
37.08
33.62
20.07
14.44
f1 (ppm)

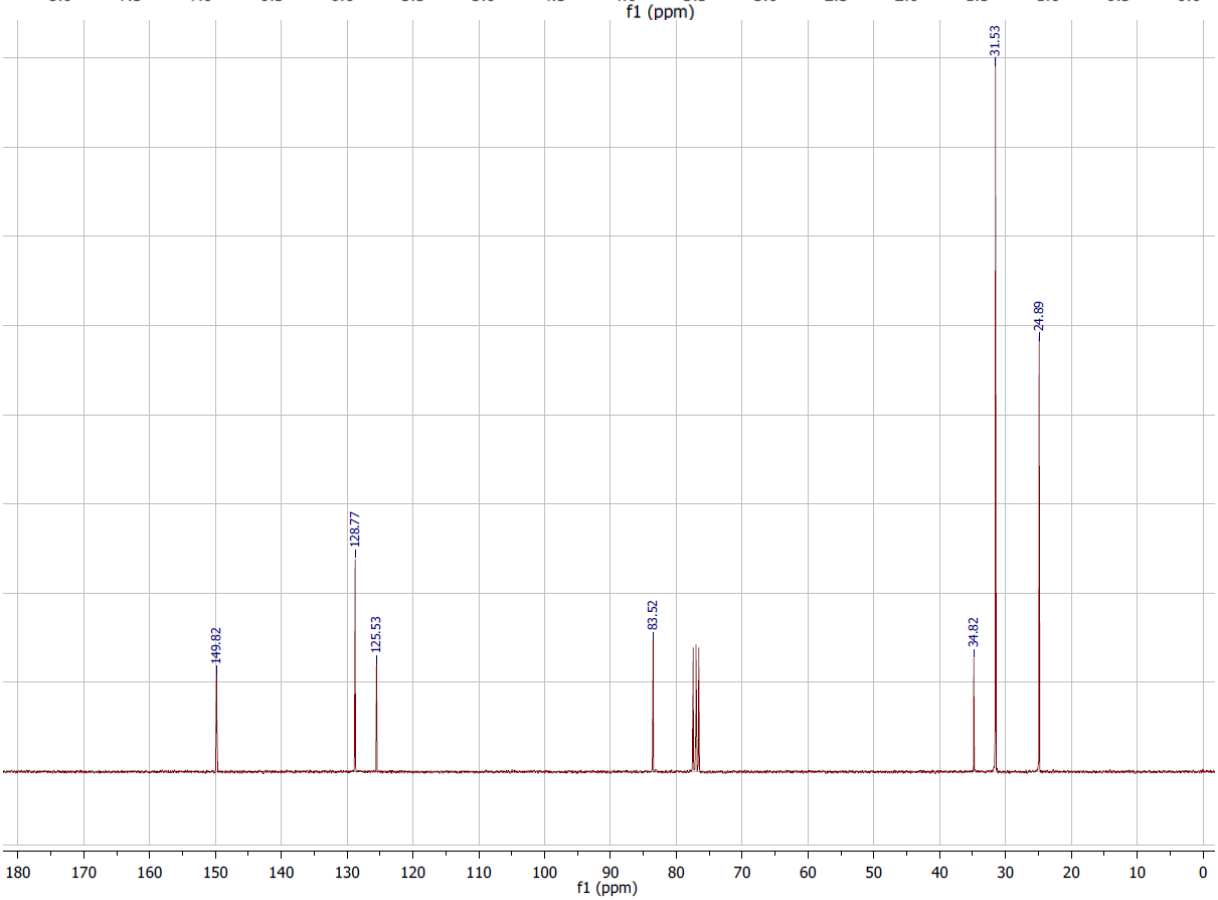

C3H7CyPh
OH
5f
F (m) 7.13
B (m) 7.51
A (dd) 7.75
E (m) 7.23
D (d) 7.90
C (dd) 7.45
G (s) 5.00
H (m) 2.51
I (m) 1.91
L (m) 1.37
K (m) 1.08
J (t) 0.94
f1 (ppm)

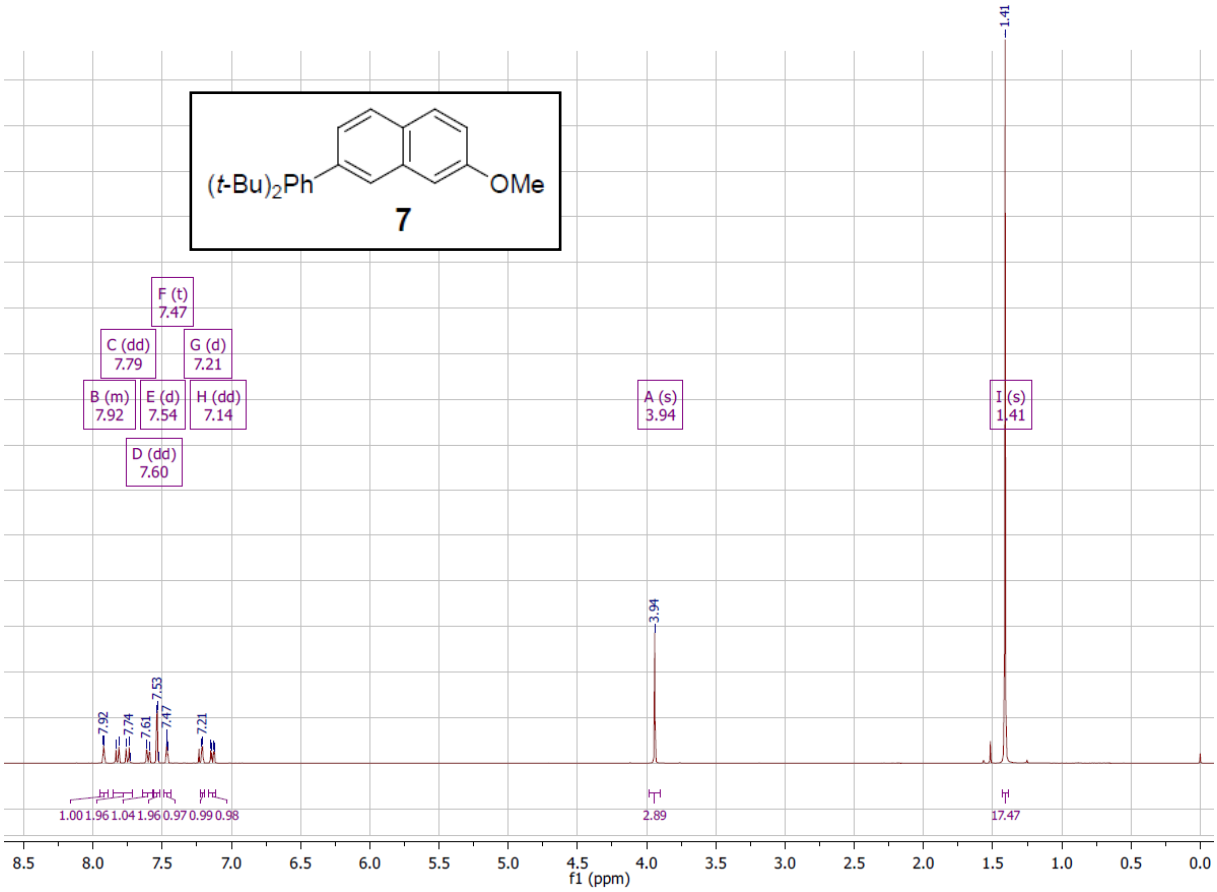

153.85
148.42
134.27
131.63
129.71
128.25
127.81
126.94
126.39
121.57
120.58
118.35
109.35
90.14
89.18
44.63
39.72
37.03
35.18
34.52
20.05
14.42
f1 (ppm)

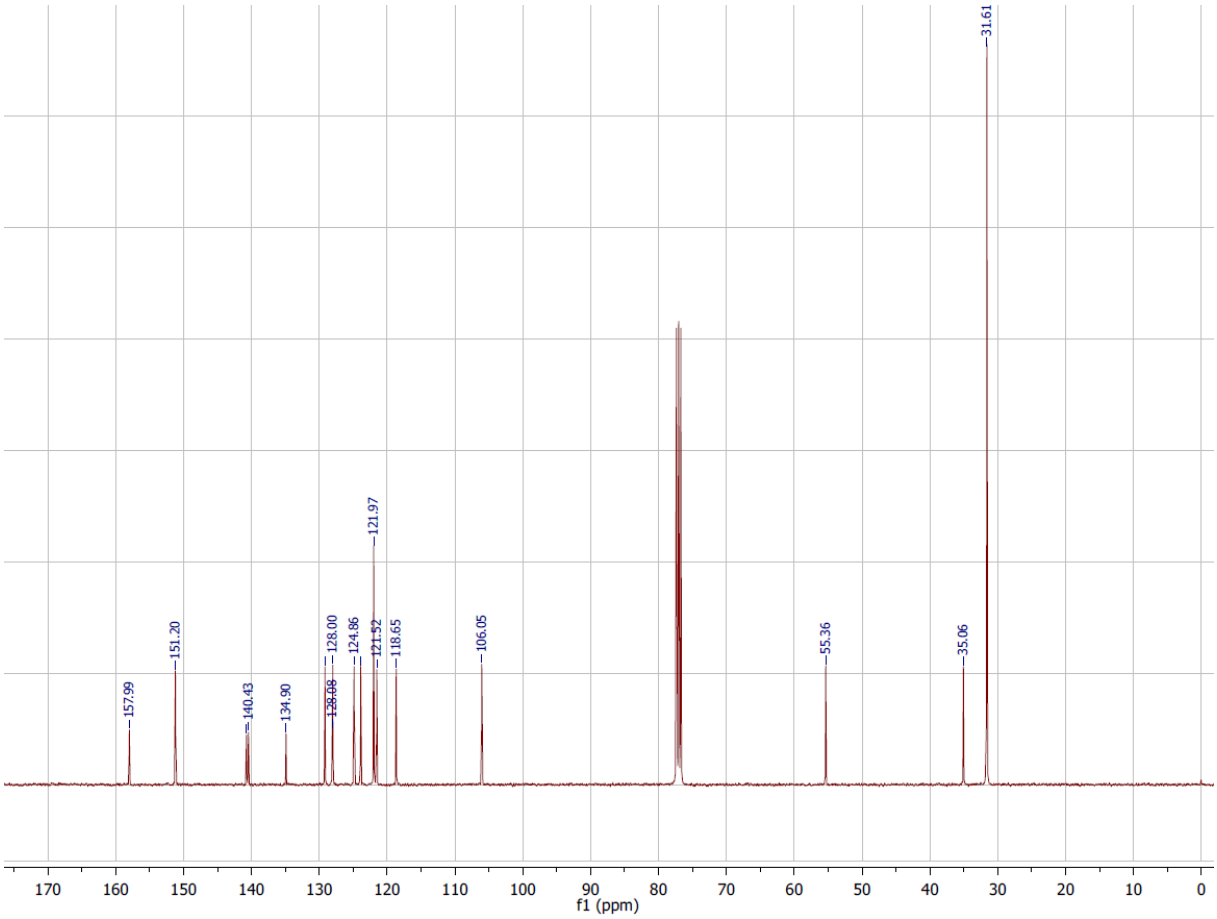

MeSPh
OH
5g
A (s) 9.12
B (m) 7.68
C (dd) 7.52
D (m) 7.30
E (dd) 7.18
F (m) 7.07
G (m) 6.99
I (s) 2.35
f1 (ppm)

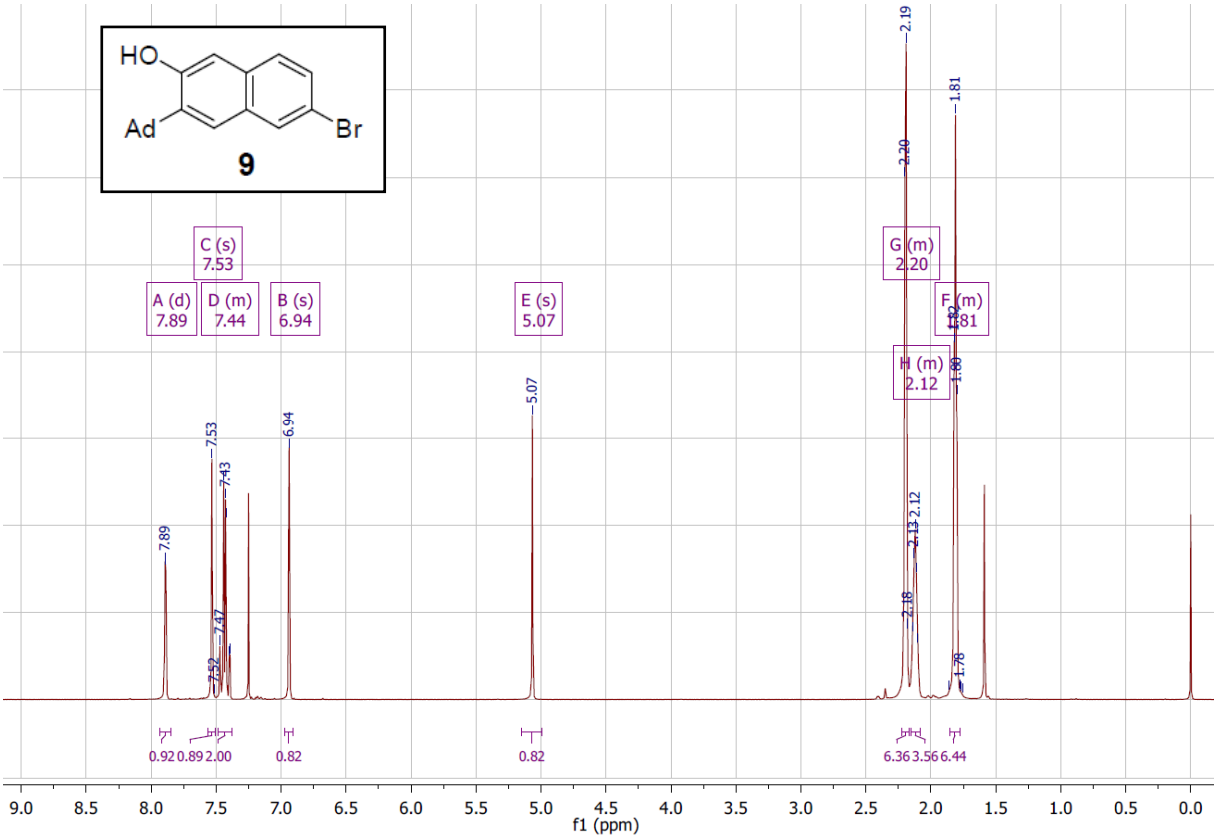

155.77
139.24
134.42
131.74
127.50
125.76
125.17
120.48
119.42
108.98
90.16
89.15
15.21
f1 (ppm)

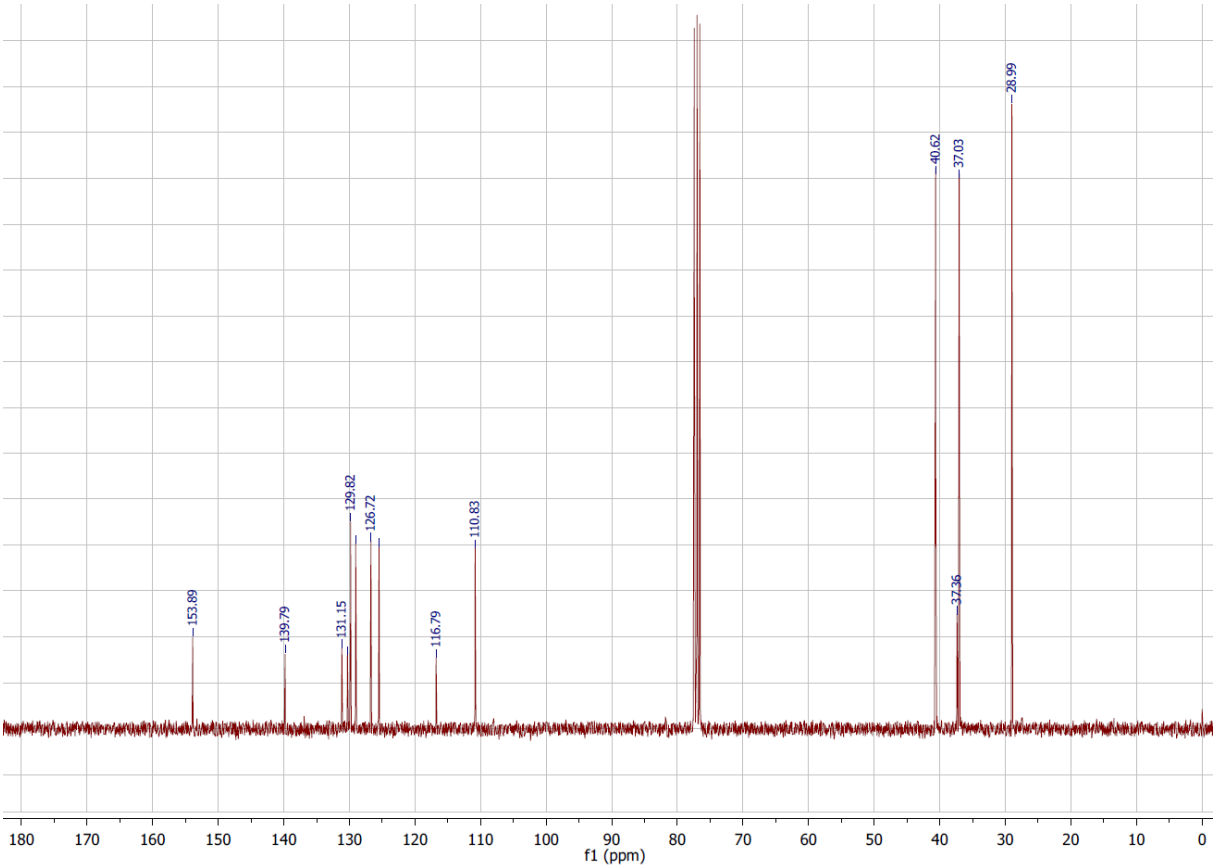

6
B (t)
7.54
A (d)
7.67
C (m)
1.34
1.35
1.34
7.66
7.55
7.68
1.36
2.00
0.99
31.80
f1 (ppm)

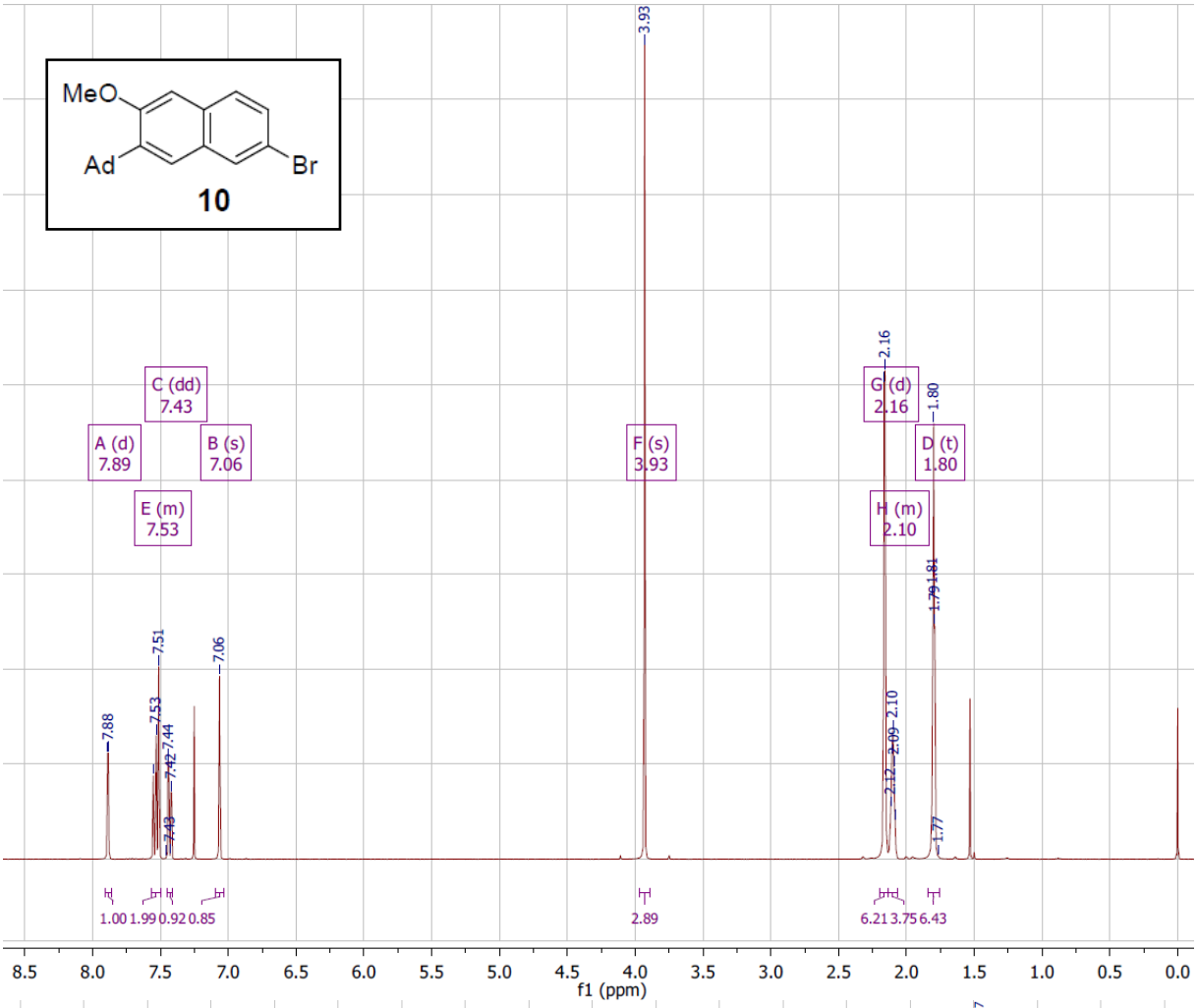

31.53
24.89
128.77
125.53
149.82
83.52
34.82
f1 (ppm)

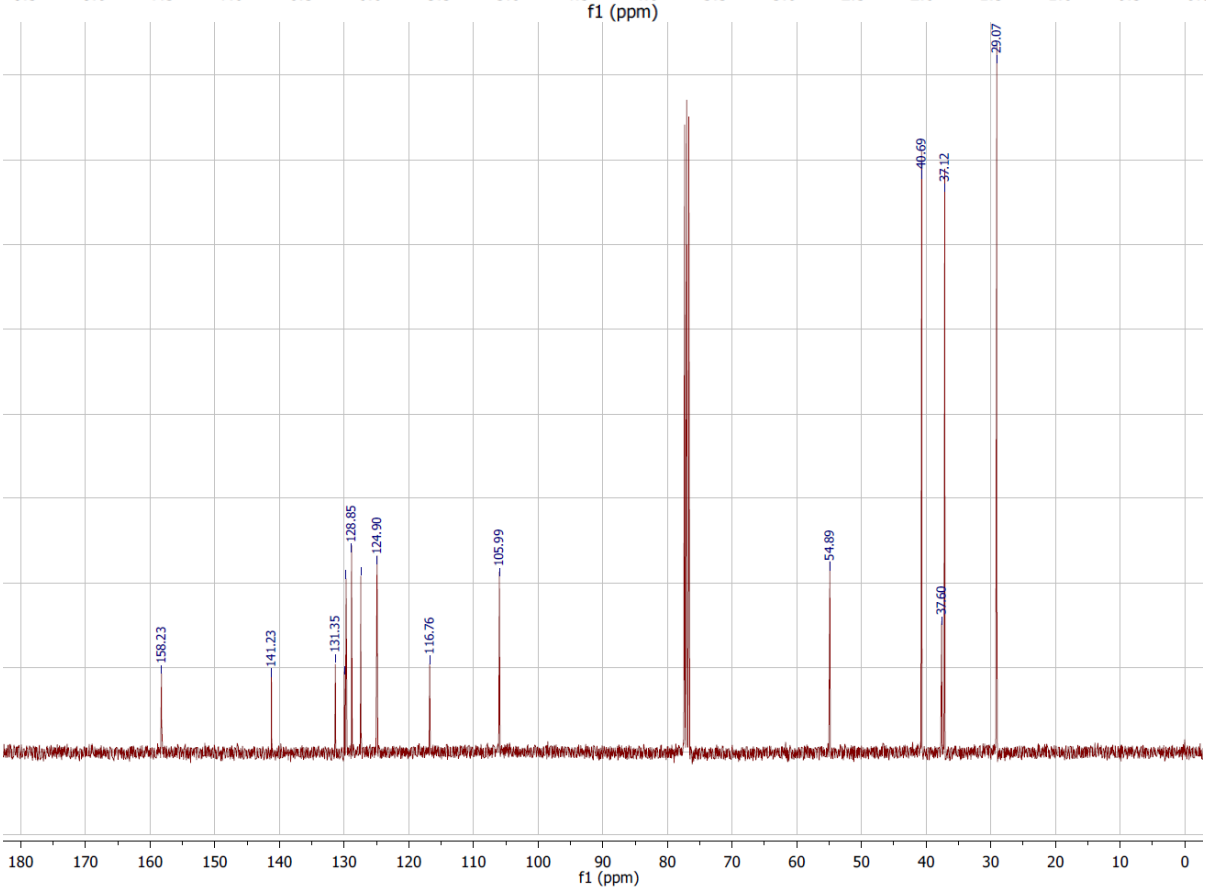

(t-Bu)2Ph
OMe
7
F (t) 7.47
C (dd) 7.79
G (d) 7.21
B (m) 7.92
E (d) 7.54
H (dd) 7.14
D (dd) 7.60
A (s) 3.94
I (s) 1.41
1.41
3.94
7.92
7.74
7.61
7.53
7.47
7.21
1.00 1.96 1.04 1.96 0.97 0.99 0.98
2.89
17.47
f1 (ppm)

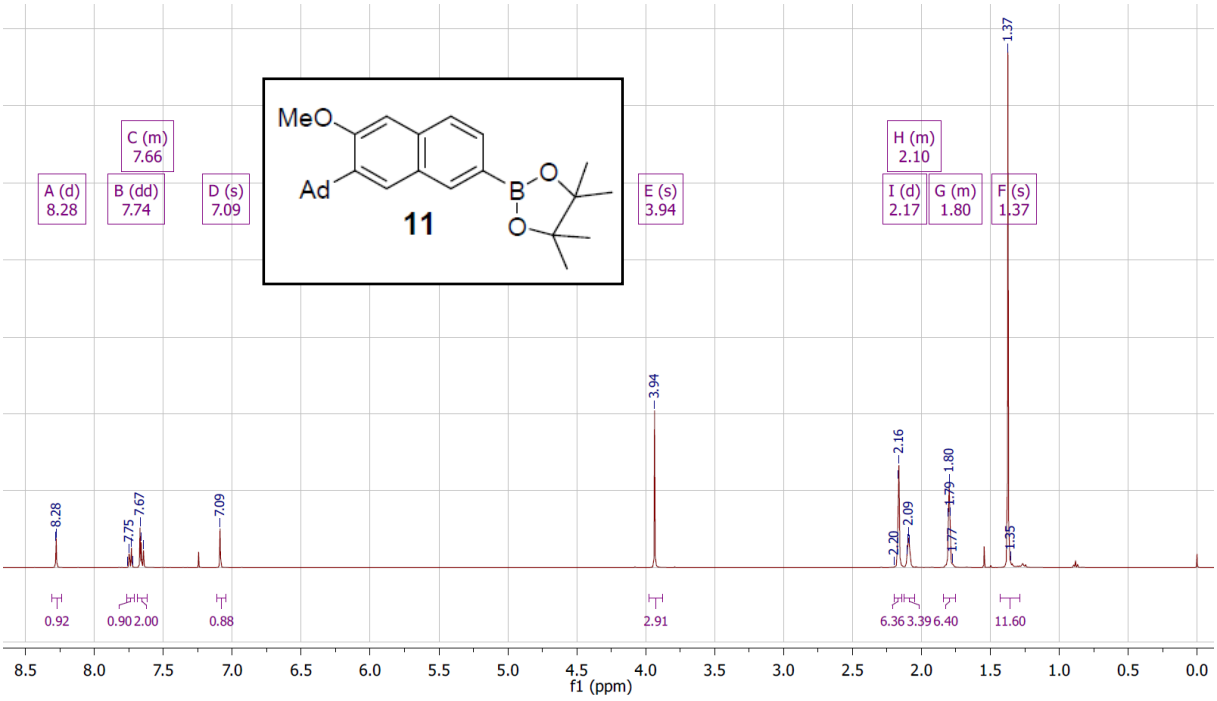

31.61
157.99
151.20
140.43
134.90
128.00
128.08
124.86
121.97
121.52
118.65
106.05
55.36
35.06
f1 (ppm)

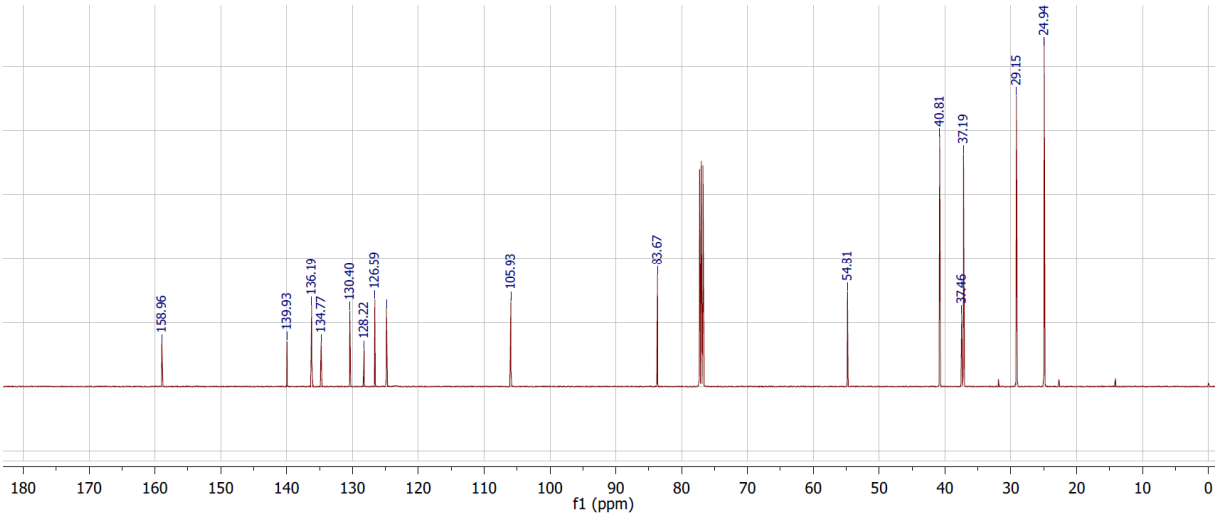

HO
Ad
Br
9
C (s) 7.53
A (d) 7.89
D (m) 7.44
B (s) 6.94
E (s) 5.07
G (m) 2.20
F (m) 1.81
H (m) 2.12
7.89
7.53
7.44
7.43
7.47
7.32
6.94
5.07
2.19
2.20
2.13
2.12
2.18
1.81
1.78
0.92 0.89 2.00 0.82 0.82 6.36 3.56 6.44
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

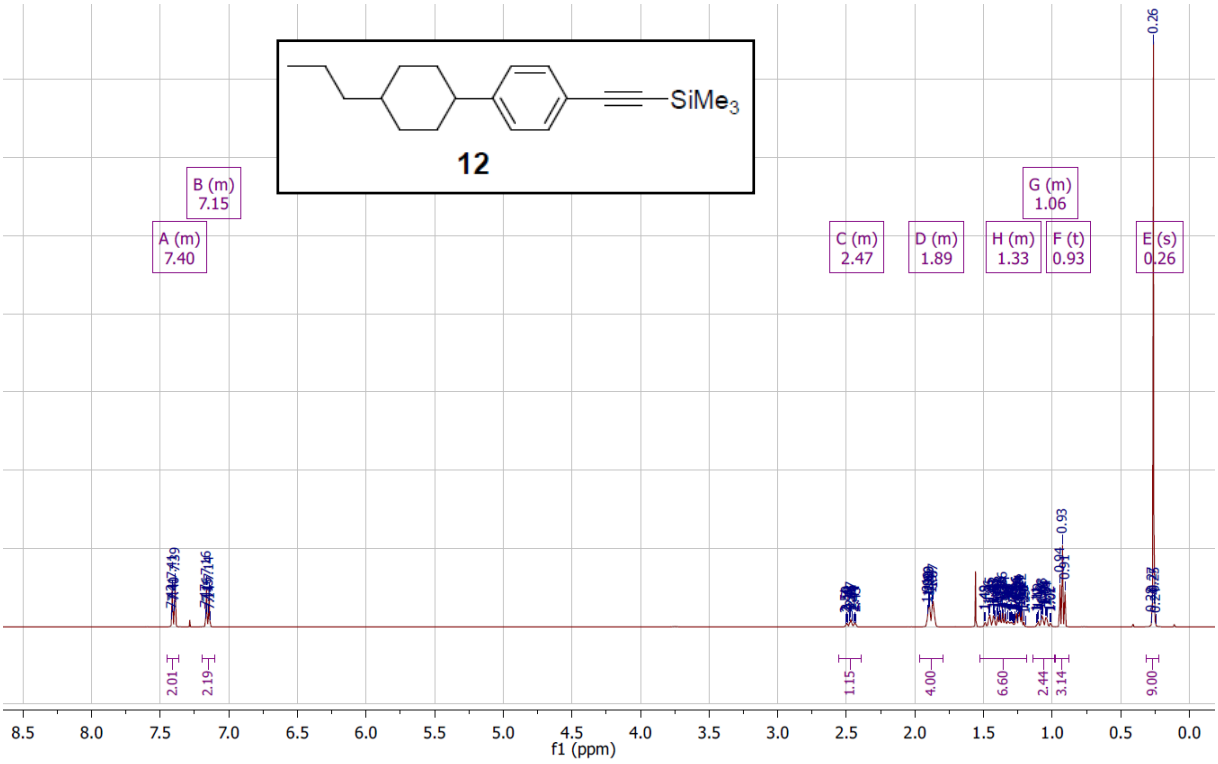

153.89
139.79
131.15
129.82
126.72
116.79
110.83
40.62
37.03
37.36
28.99
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

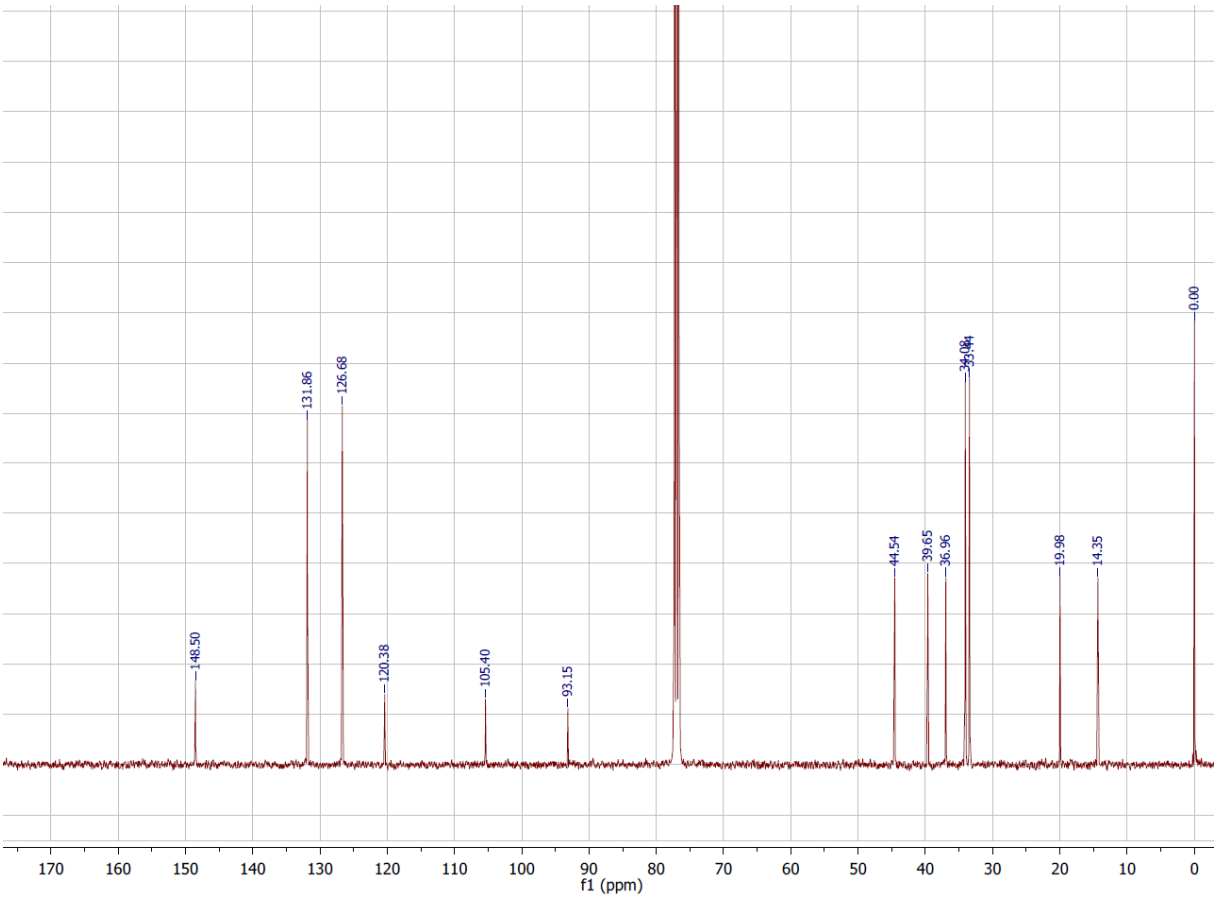

MeO
Ad
Br
10
A (d) 7.89
B (s) 7.06
C (dd) 7.43
E (m) 7.53
F (s) 3.93
G (d) 2.16
D (t) 1.80
H (m) 2.10
1.00 1.99 0.92 0.85
2.89
6.21 3.75 6.43
f1 (ppm)

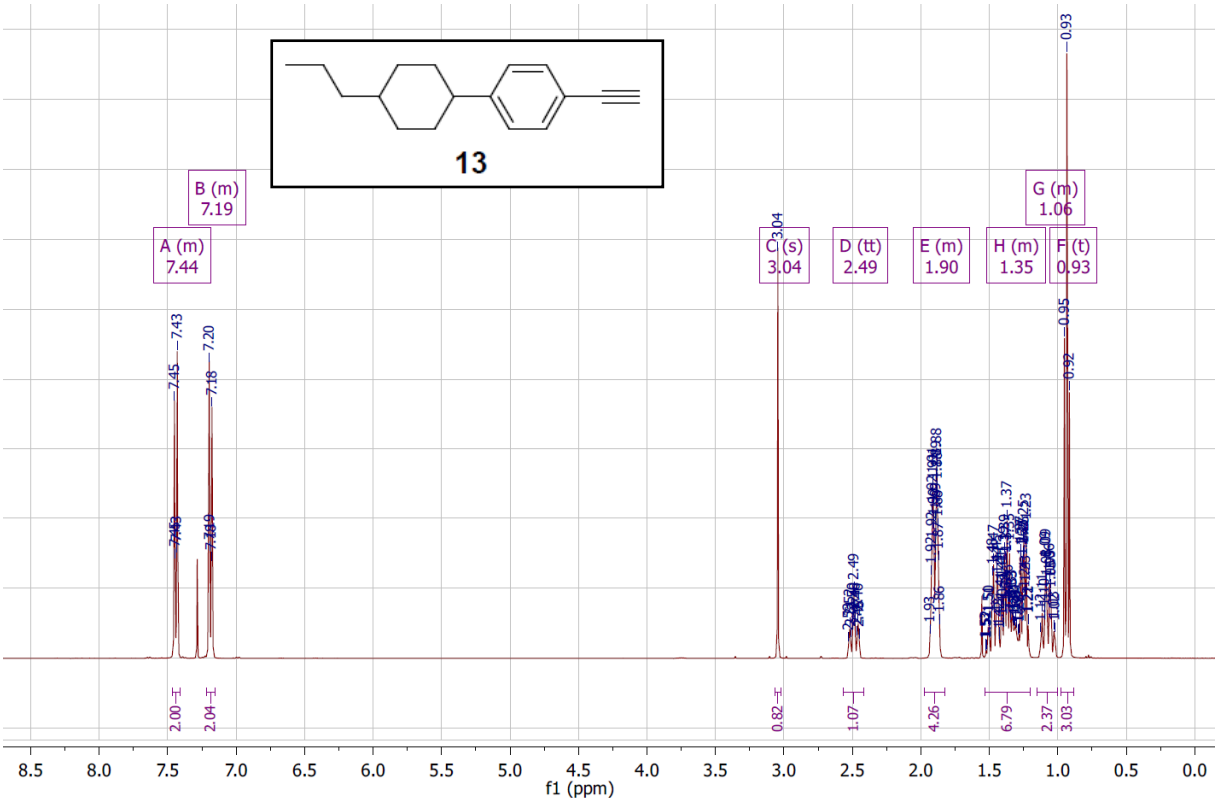

158.23
141.23
131.35
128.85
124.90
116.76
105.99
54.89
40.69
37.12
37.60
29.07
f1 (ppm)

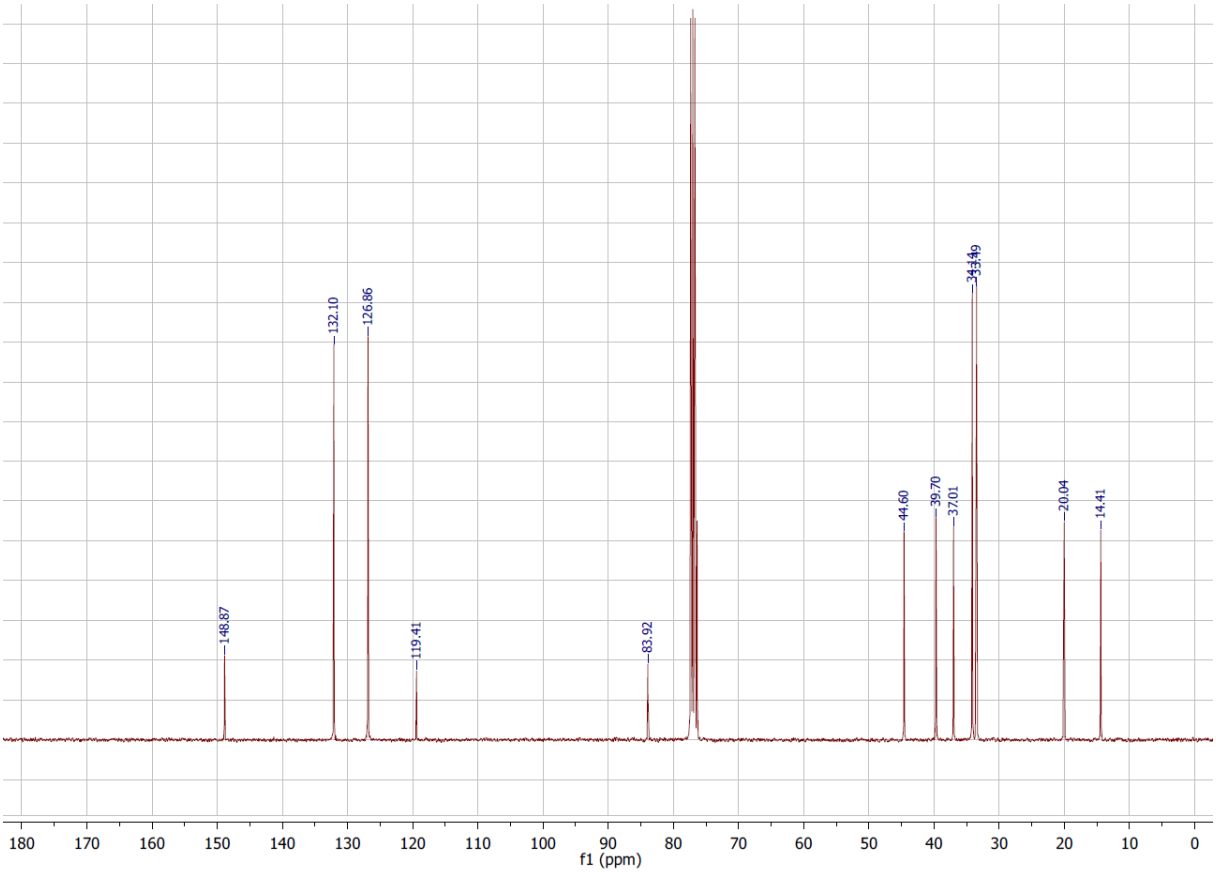

A (d)
8.28
B (dd)
7.74
C (m)
7.66
D (s)
7.09
E (s)
3.94
F (s)
1.37
G (m)
1.80
H (m)
2.10
I (d)
2.17
MeO
Ad
11
B
O
O
8.28
7.75
7.67
7.09
3.94
2.20
2.16
2.09
1.79
1.77
1.80
1.35
1.37
0.92
0.90
2.00
0.88
2.91
6.36
3.39
6.40
11.60
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

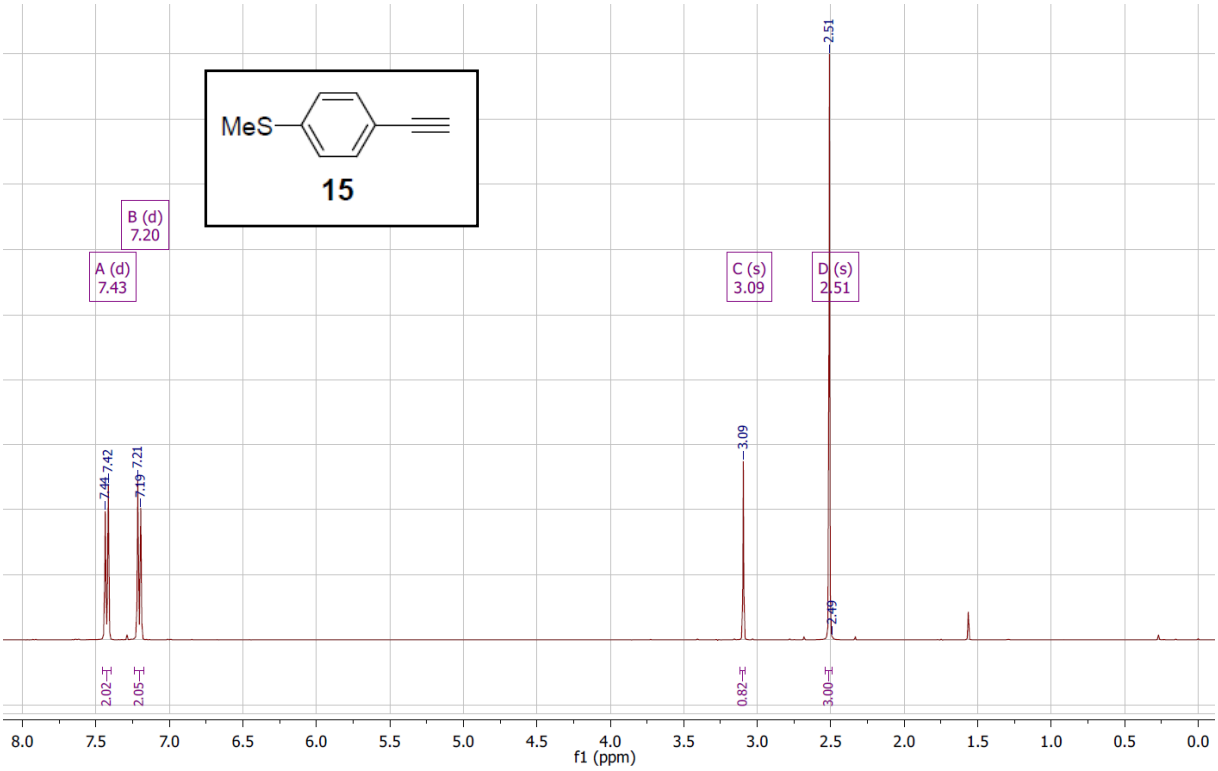

158.96
139.93
136.19
134.77
130.40
128.22
126.59
105.93
83.67
54.81
40.81
37.19
37.46
29.15
24.94
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

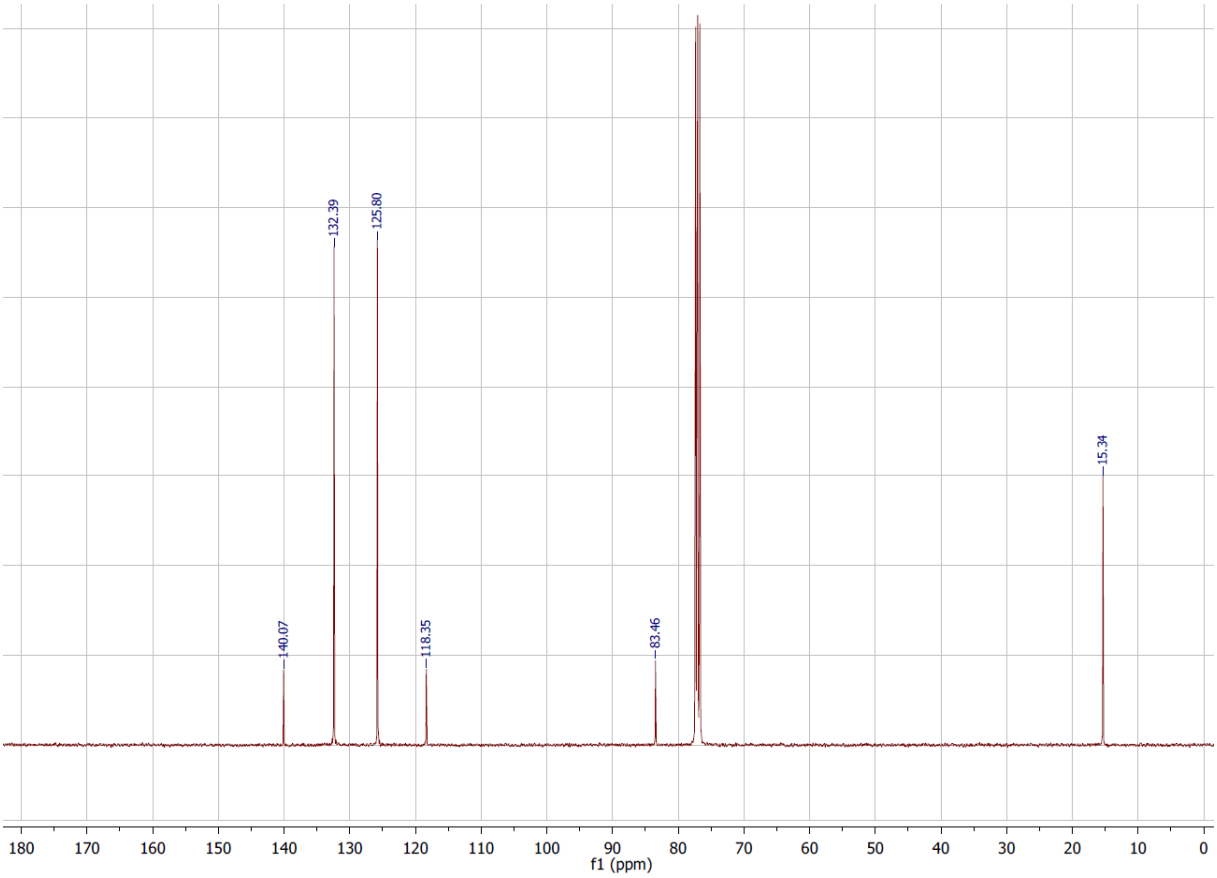

SiMe3
12
A (m) 7.40
B (m) 7.15
C (m) 2.47
D (m) 1.89
H (m) 1.33
F (t) 0.93
G (m) 1.06
E (s) 0.26
2.01
2.19
1.15
4.00
6.60
2.44
3.14
9.00
f1 (ppm)

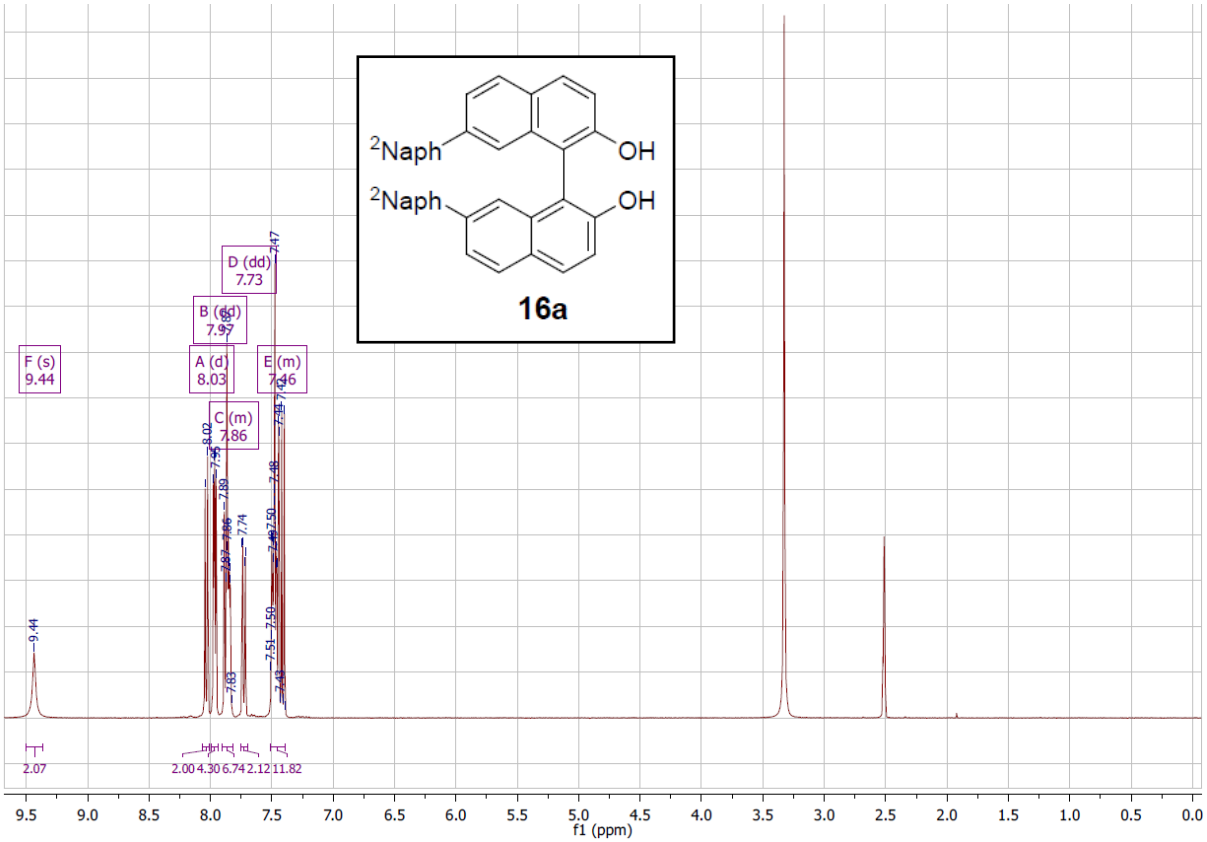

148.50
131.86
126.68
120.38
105.40
93.15
44.54
39.65
36.96
34.08
19.98
14.35
0.00
f1 (ppm)

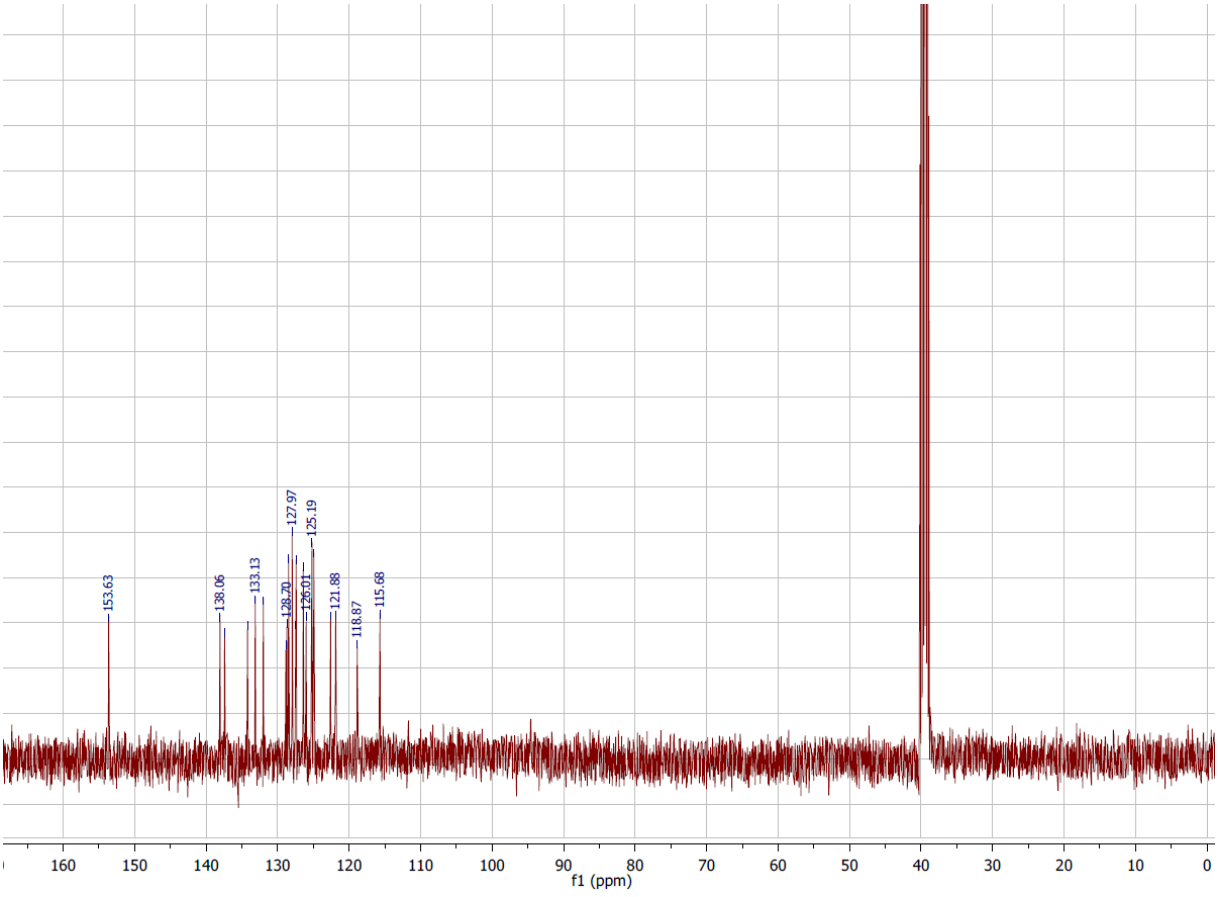

13
A (m)
7.44
B (m)
7.19
C (s)
3.04
D (tt)
2.49
E (m)
1.90
H (m)
1.35
F (t)
0.93
G (m)
1.06
f1 (ppm)

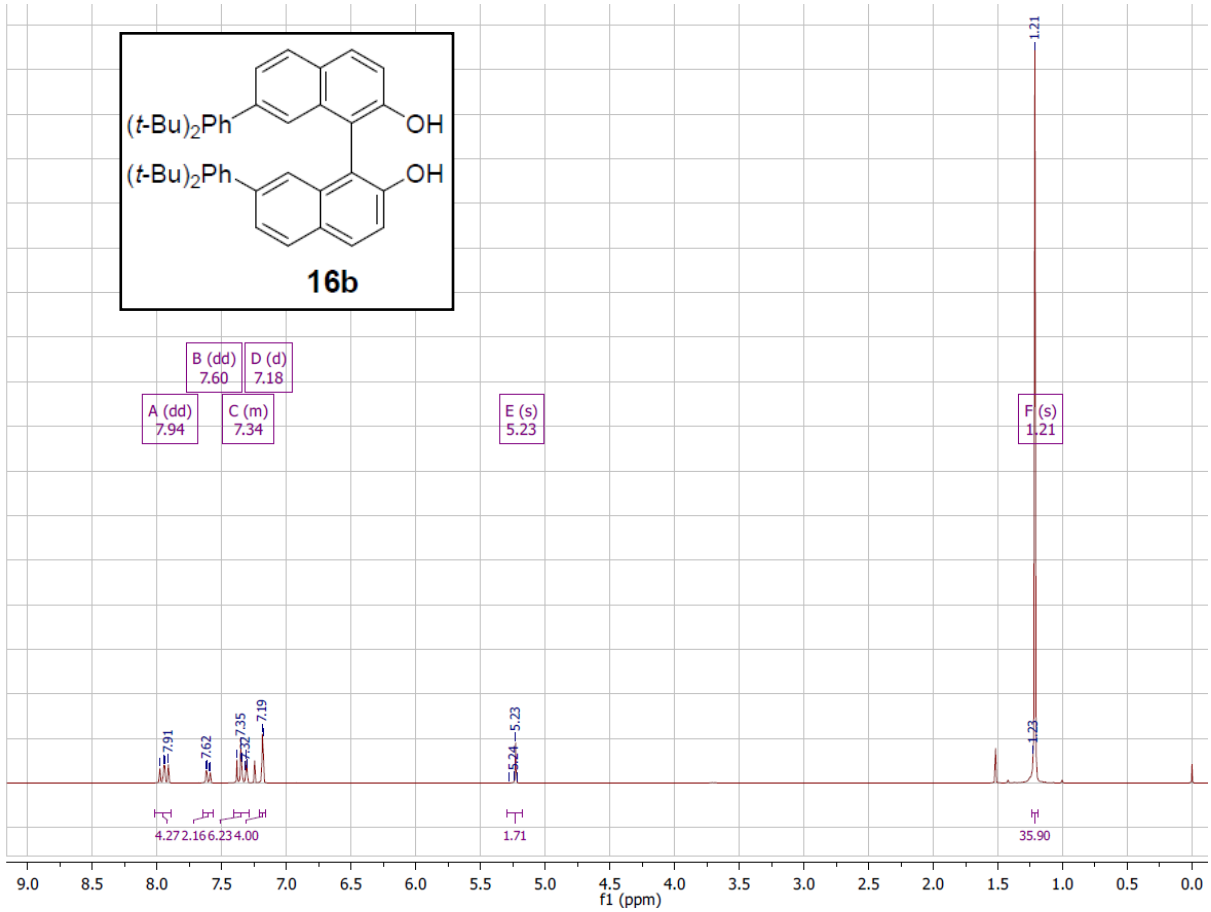

148.87
132.10
126.86
119.41
83.92
44.60
39.70
37.01
33.49
20.04
14.41
f1 (ppm)

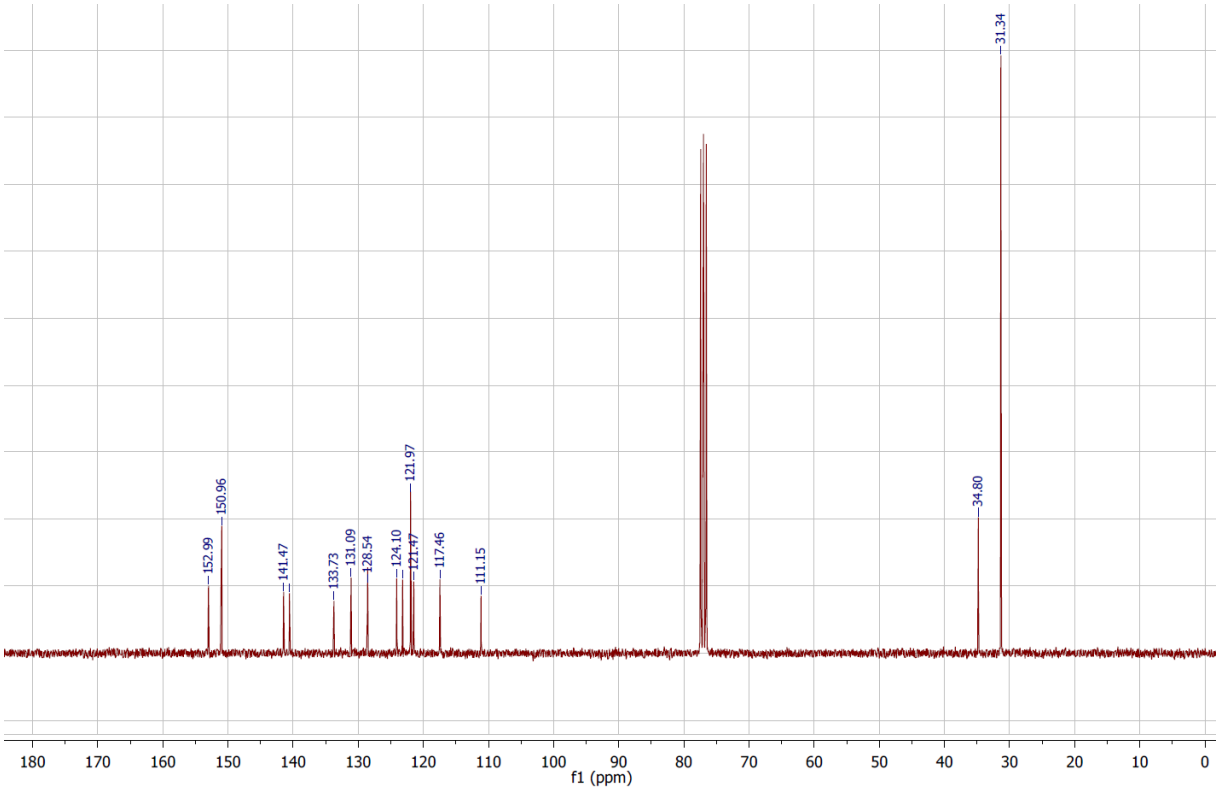

MeS
15
B (d)
7.20
A (d)
7.43
C (s)
3.09
D (s)
2.51
7.44
7.42
7.19
7.21
3.09
2.51
2.49
2.02
2.05
0.82
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

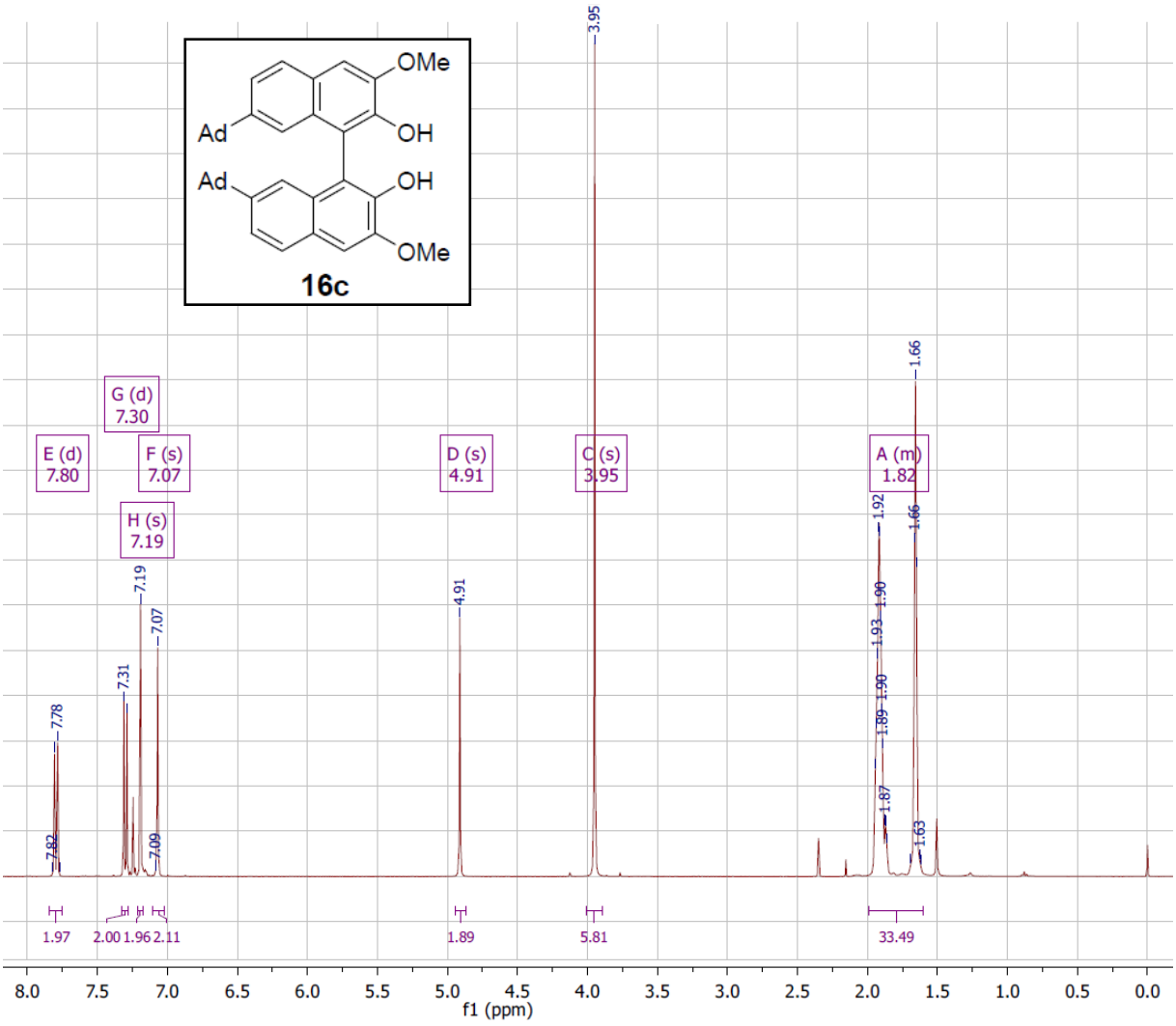

140.07
132.39
125.80
118.35
83.46
15.34
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

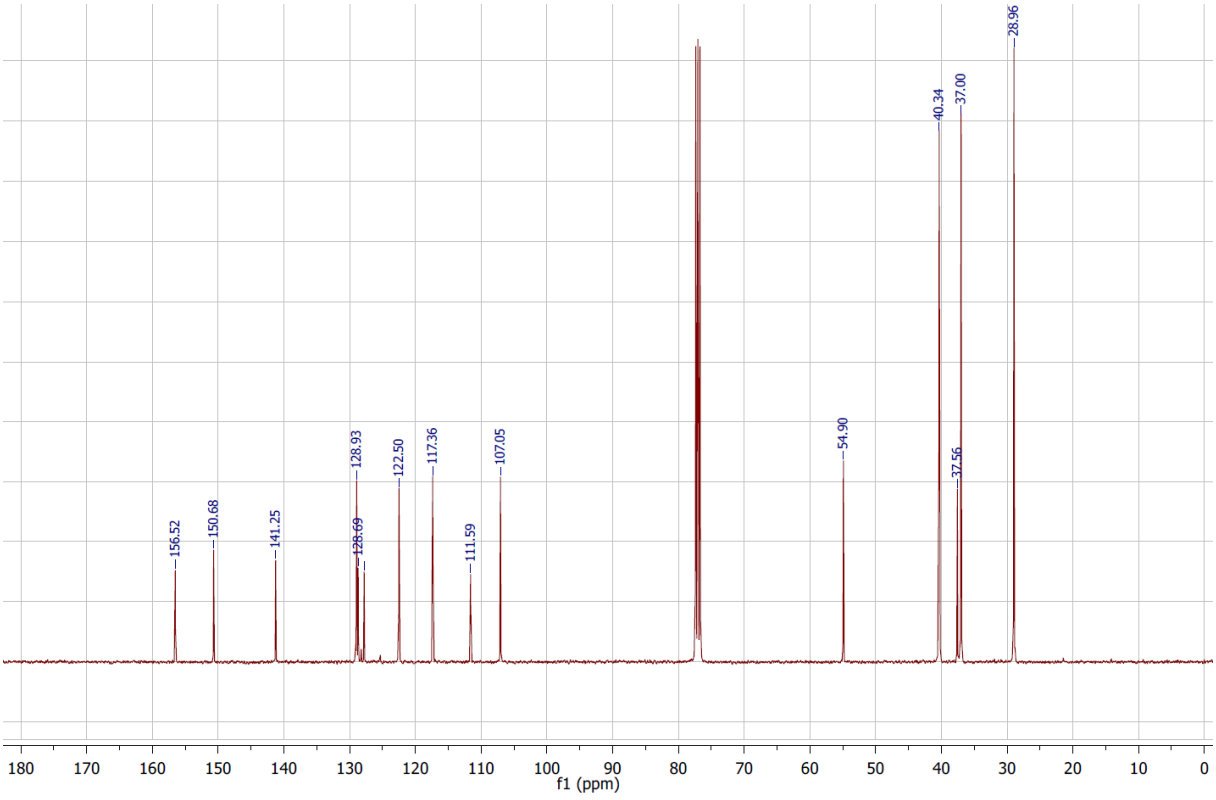

2Naph
OH
2Naph
OH
16a
D (dd)
7.73
B (dd)
7.97
F (s)
9.44
A (d)
8.03
E (m)
7.46
C (m)
7.86
9.44
2.07
2.00 4.30 6.74 2.12 11.82
f1 (ppm)

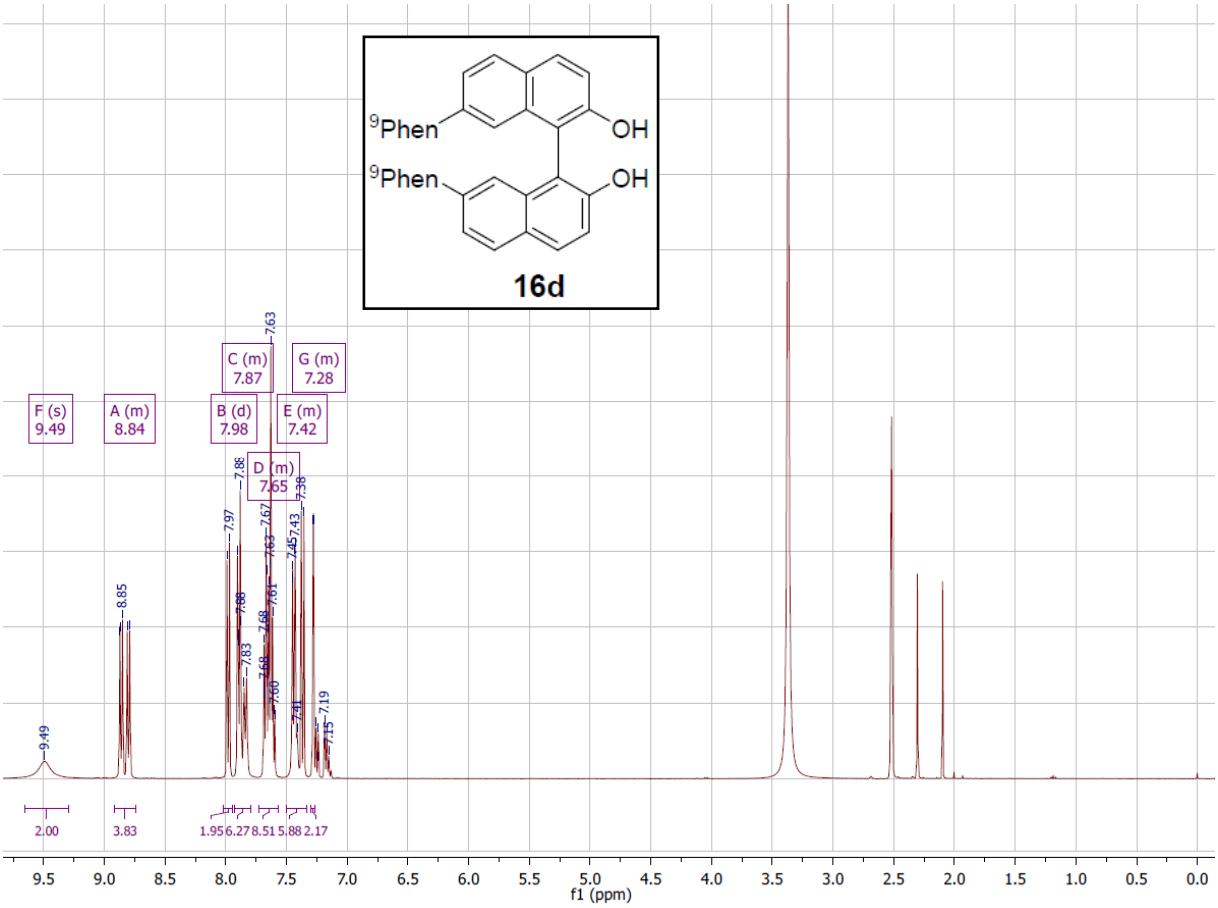

153.63
138.06
133.13
128.70
127.97
126.01
125.19
121.88
118.87
115.68
f1 (ppm)

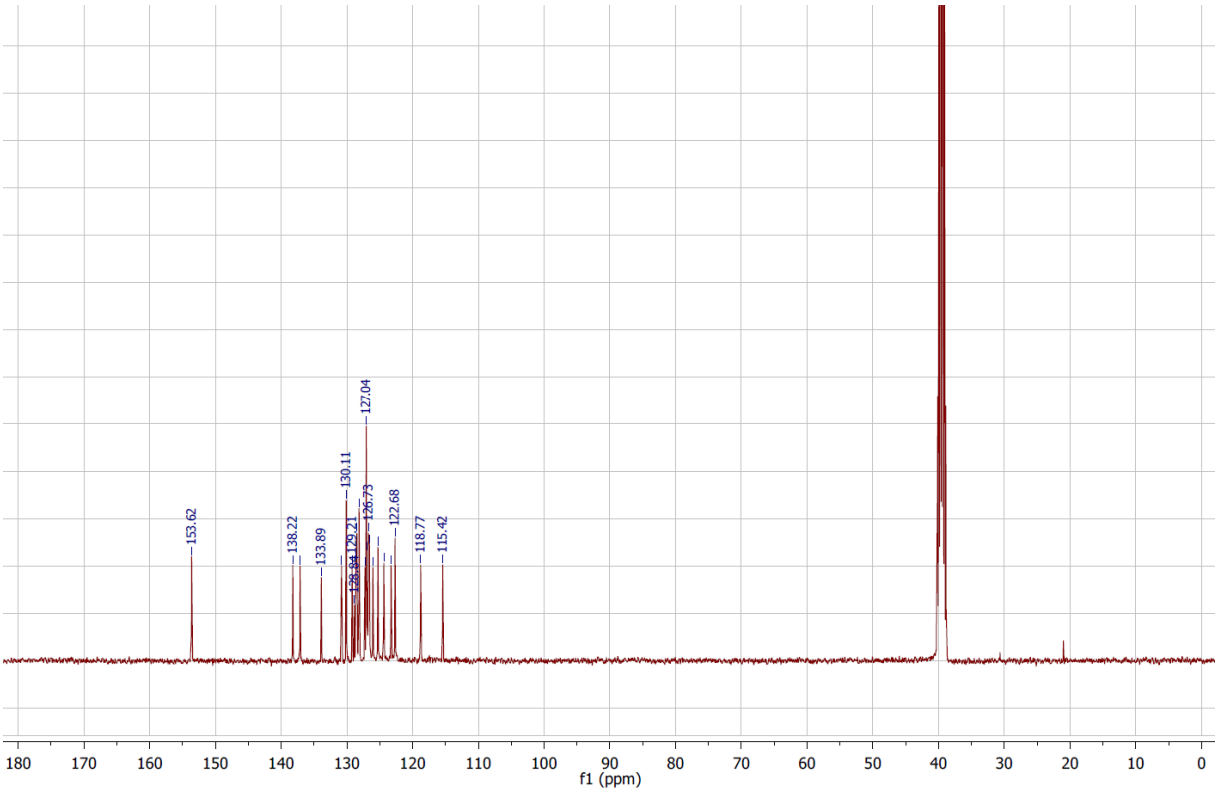

(t-Bu)2Ph
OH
(t-Bu)2Ph
OH
16b
B (dd) 7.60
D (d) 7.18
A (dd) 7.94
C (m) 7.34
E (s) 5.23
F (s) 1.21
7.91
7.62
7.35
7.32
7.19
5.24
5.23
1.23
1.21
4.27 2.16 6.23 4.00
1.71
35.90
f1 (ppm)

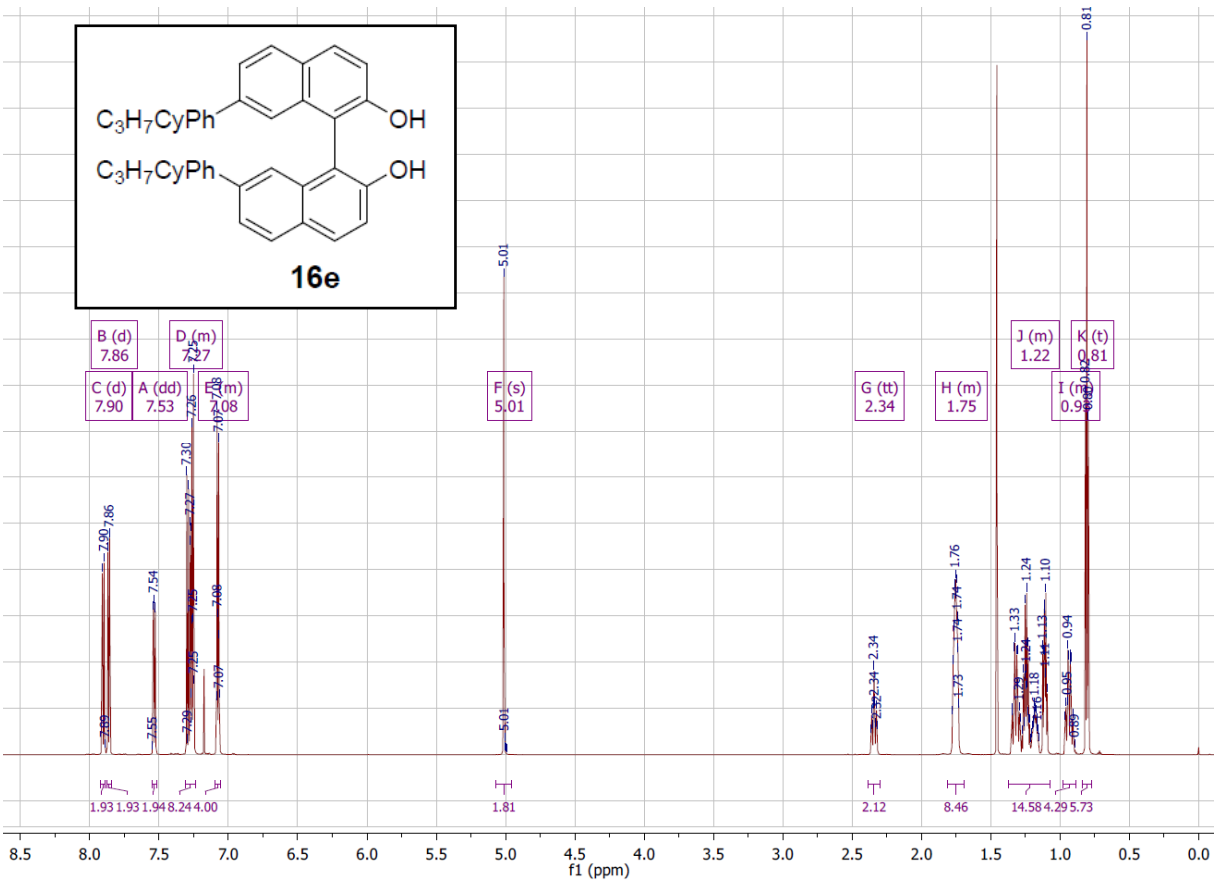

152.99
150.96
141.47
133.73
131.09
128.54
124.10
121.97
121.47
117.46
111.15
34.80
31.34
f1 (ppm)

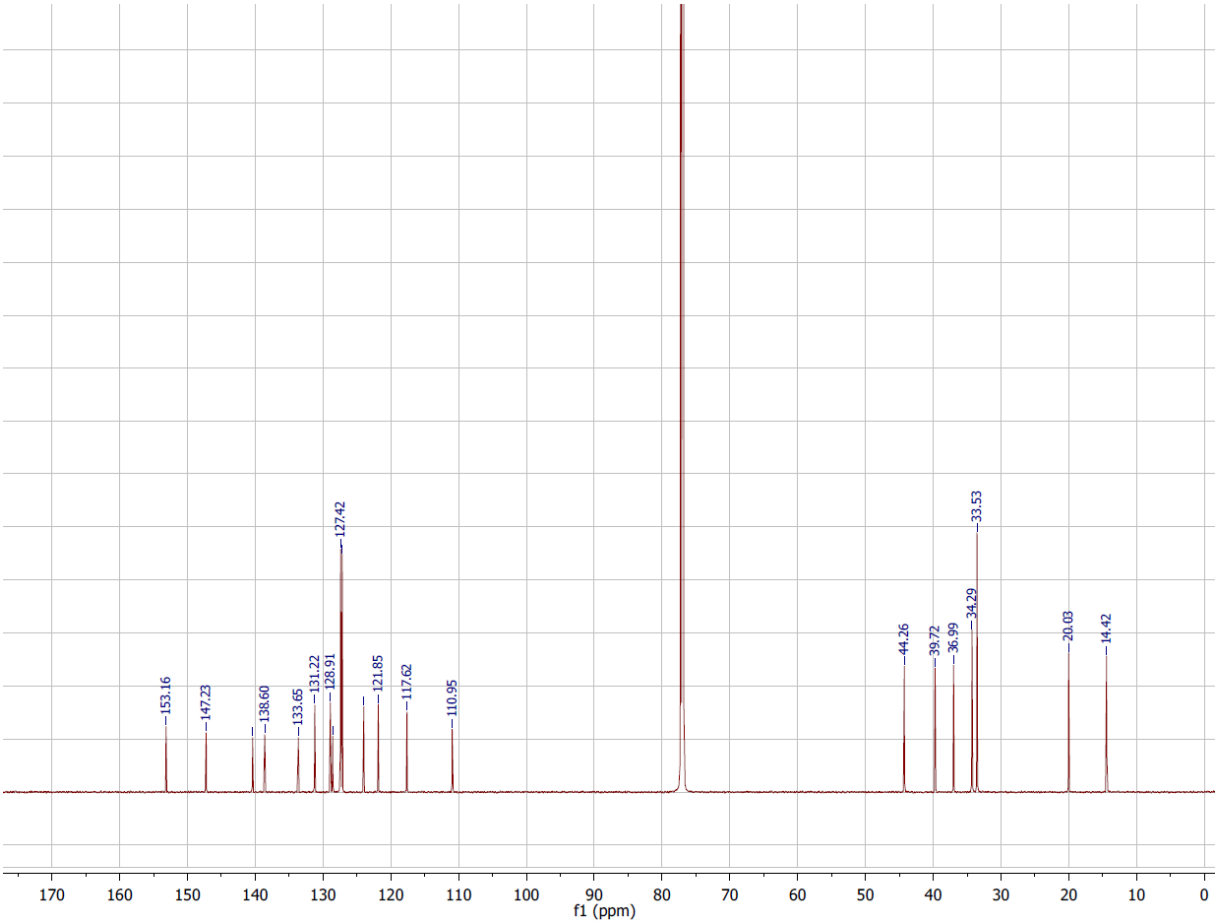

OMe
Ad
OH
Ad
OH
OMe
16c
G (d)
7.30
E (d)
7.80
F (s)
7.07
H (s)
7.19
D (s)
4.91
C (s)
3.95
A (m)
1.82
7.78
7.82
7.31
7.19
7.09
7.07
4.91
3.95
1.92
1.90
1.93
1.90
1.89
1.87
1.66
1.66
1.63
1.97
2.00
1.96
2.11
1.89
5.81
33.49
f1 (ppm)

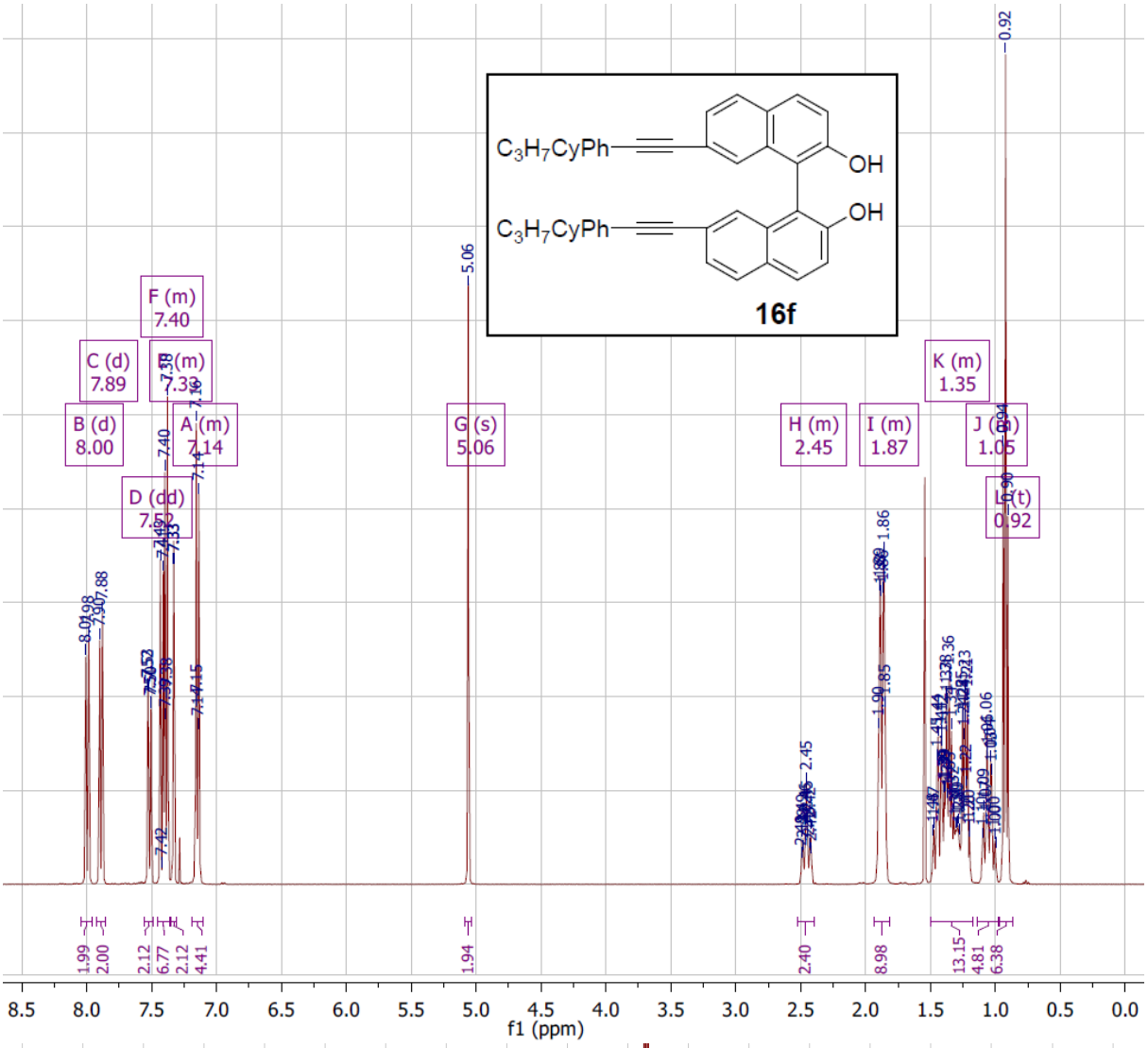

156.52
150.68
141.25
128.93
128.69
122.50
117.36
111.59
107.05
54.90
40.34
37.56
37.00
28.96
f1 (ppm)

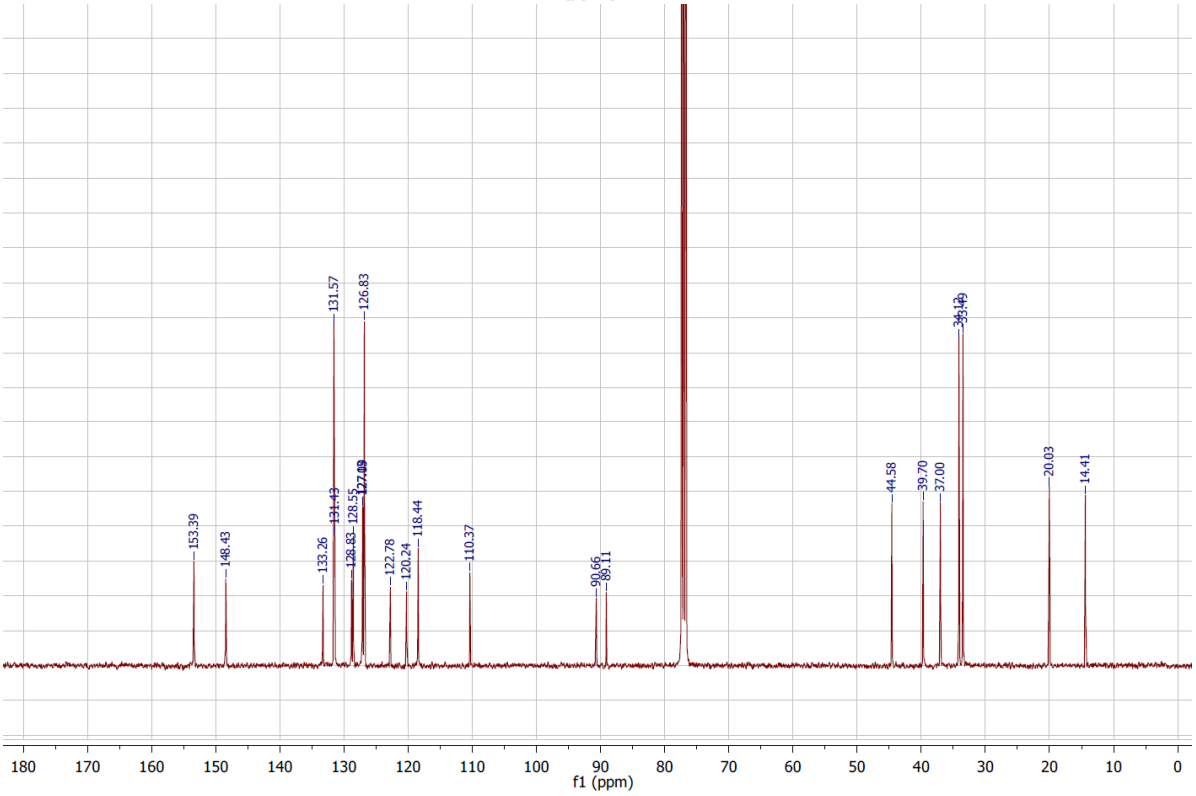

9Phen
OH
9Phen
OH
16d
F (s) 9.49
A (m) 8.84
B (d) 7.98
C (m) 7.87
D (m) 7.65
E (m) 7.42
G (m) 7.28
2.00
3.83
1.95
6.27
8.51
5.88
2.17
f1 (ppm)

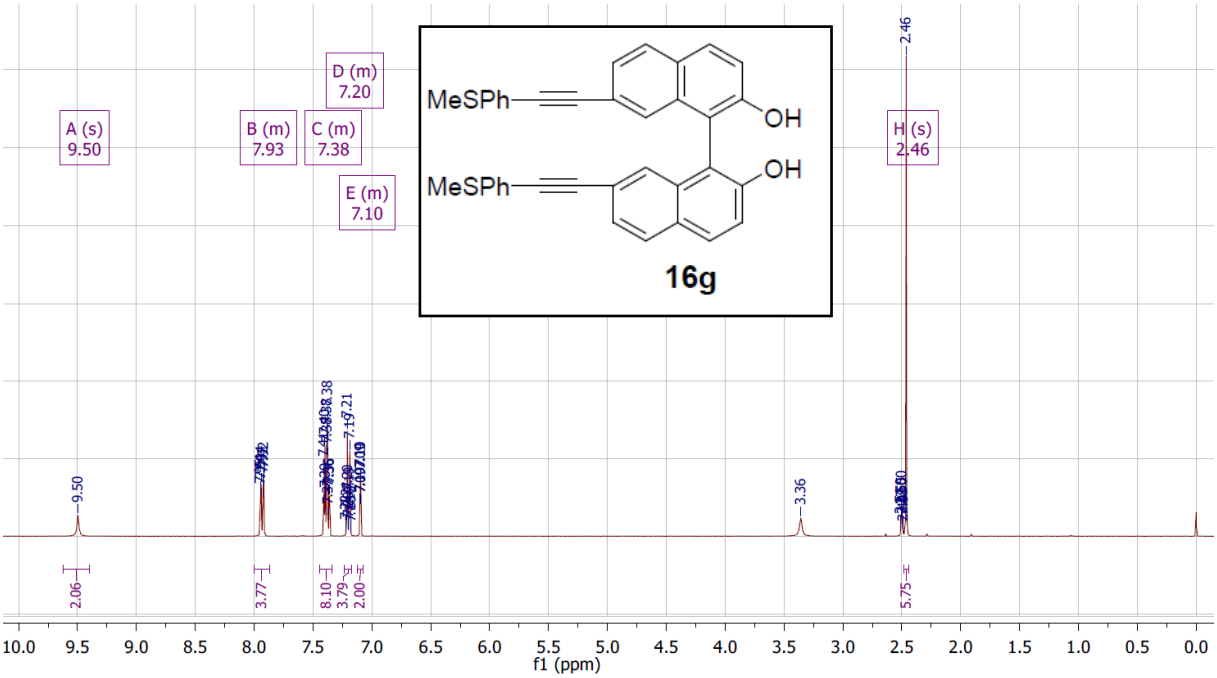

153.62
138.22
133.89
130.11
129.21
127.04
126.73
122.68
118.77
115.42
f1 (ppm)

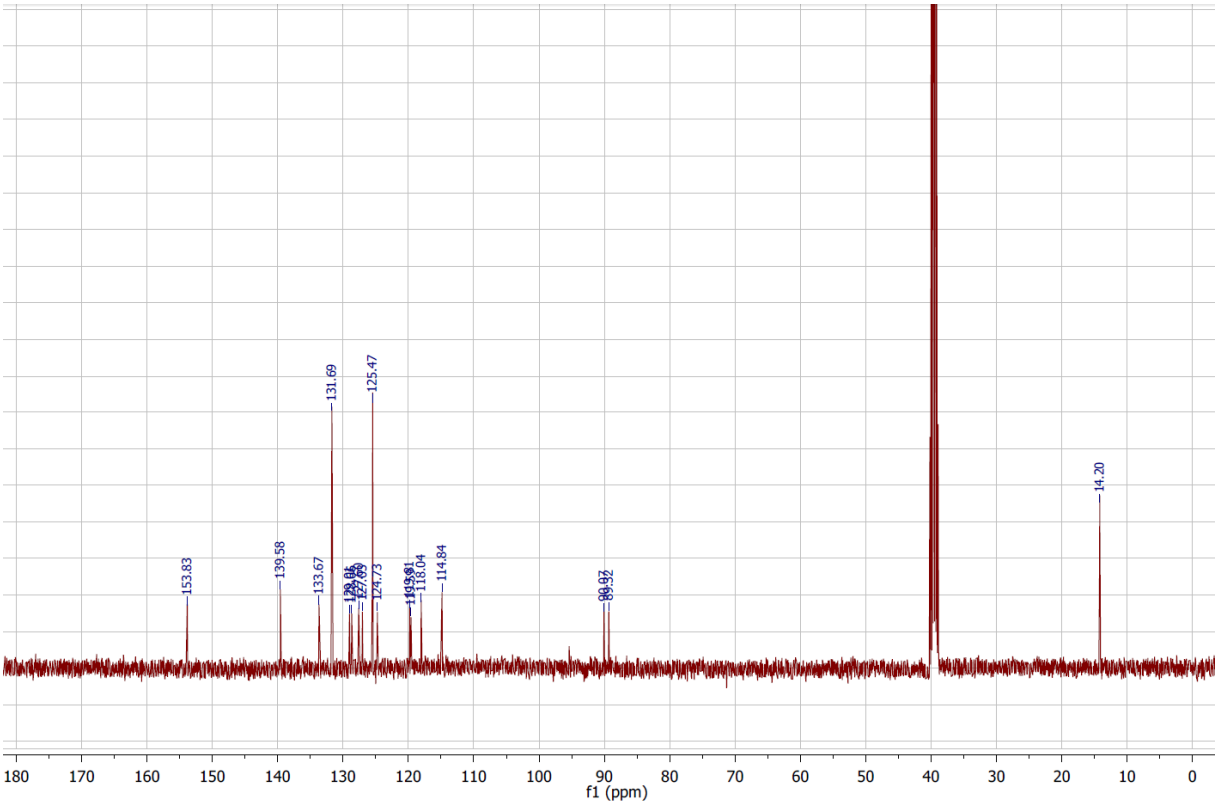

C3H7CyPh
OH
C3H7CyPh
OH
16e
B (d) 7.86
D (m) 7.27
C (d) 7.90
A (dd) 7.53
E (m) 7.08
F (s) 5.01
G (tt) 2.34
H (m) 1.75
J (m) 1.22
K (t) 0.81
I (m) 0.93
1.93 1.93 1.94 8.24 4.00
1.81
2.12
8.46
14.58 4.29 5.73
f1 (ppm)

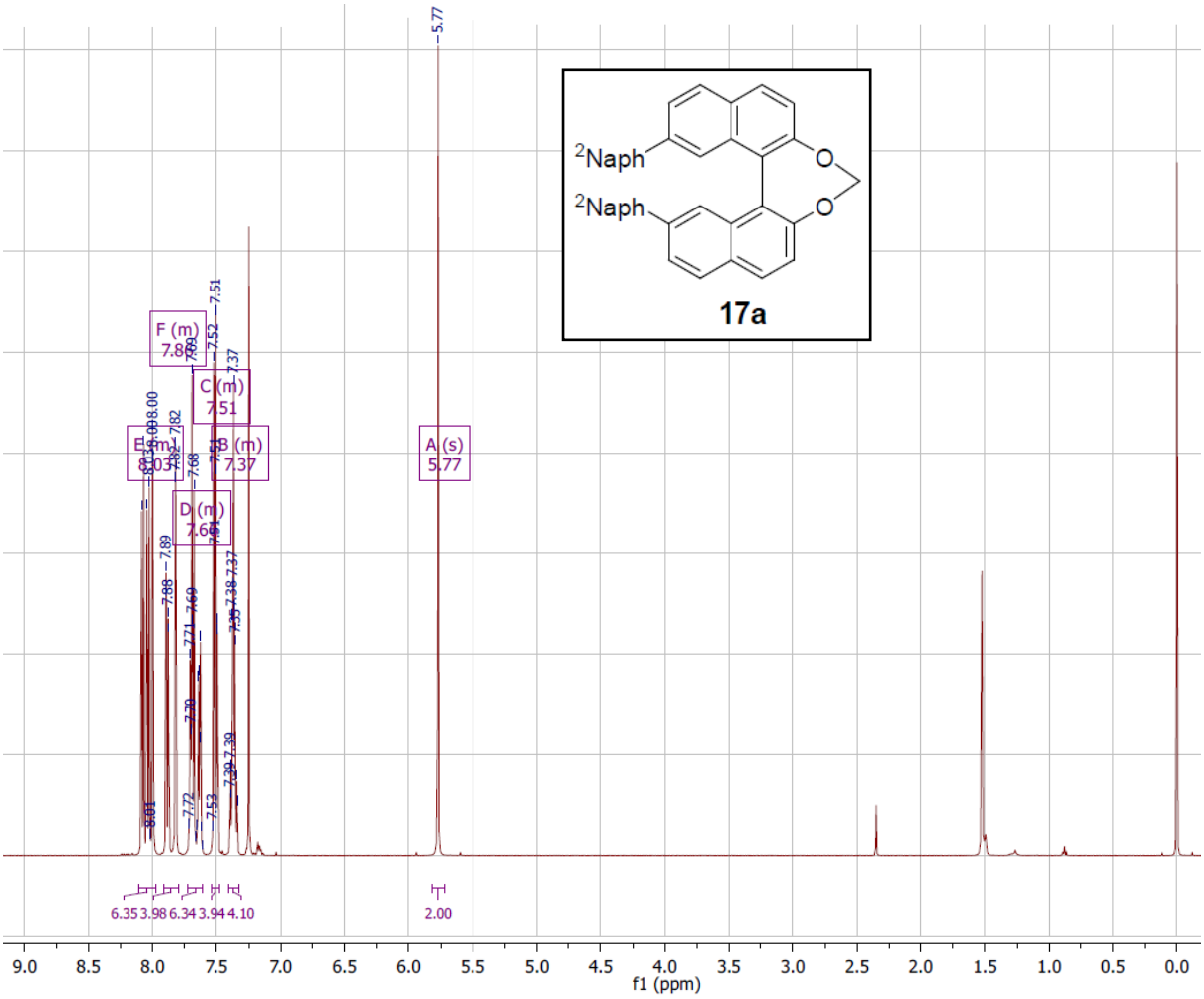

153.16
147.23
138.60
133.65
131.22
128.91
127.42
121.85
117.62
110.95
44.26
39.72
36.99
34.29
33.53
20.03
14.42
f1 (ppm)

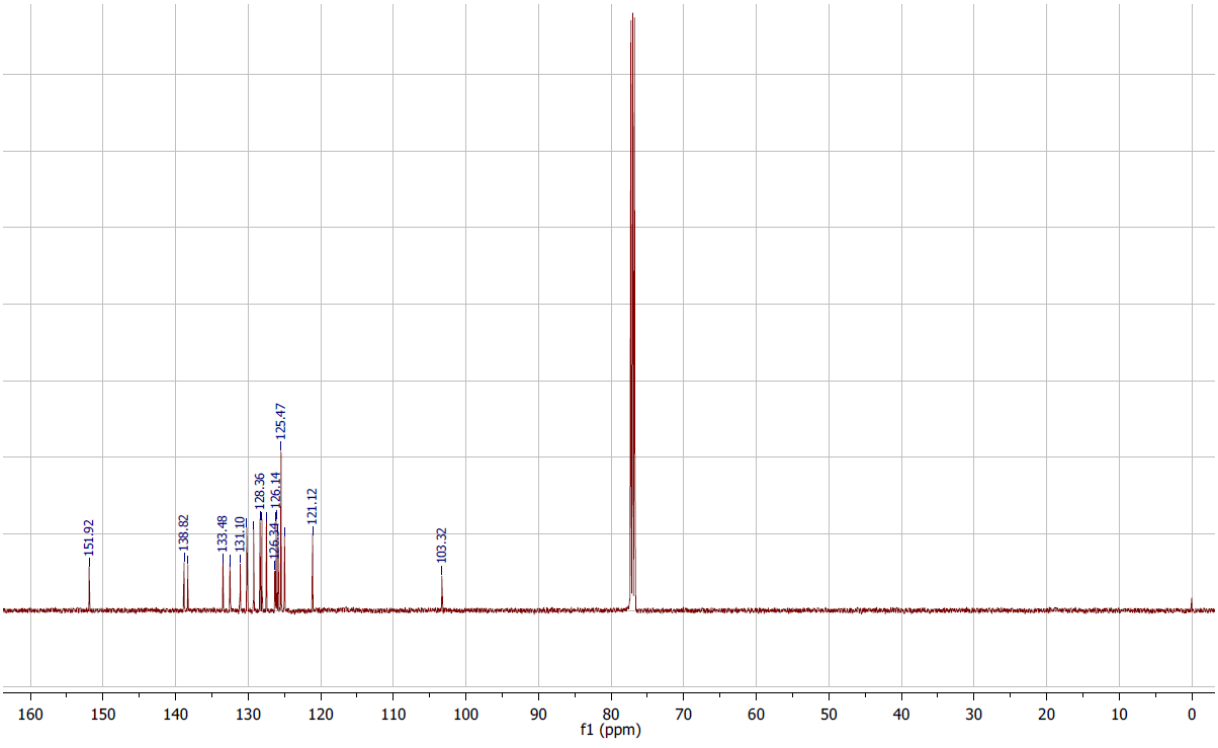

C3H7CyPh
OH
C3H7CyPh
OH
16f
F (m)
7.40
C (d)
7.89
E (m)
7.33
B (d)
8.00
A (m)
7.14
D (dd)
G (s)
5.06
H (m)
2.45
I (m)
1.87
K (m)
1.35
J (t)
0.92
f1 (ppm)

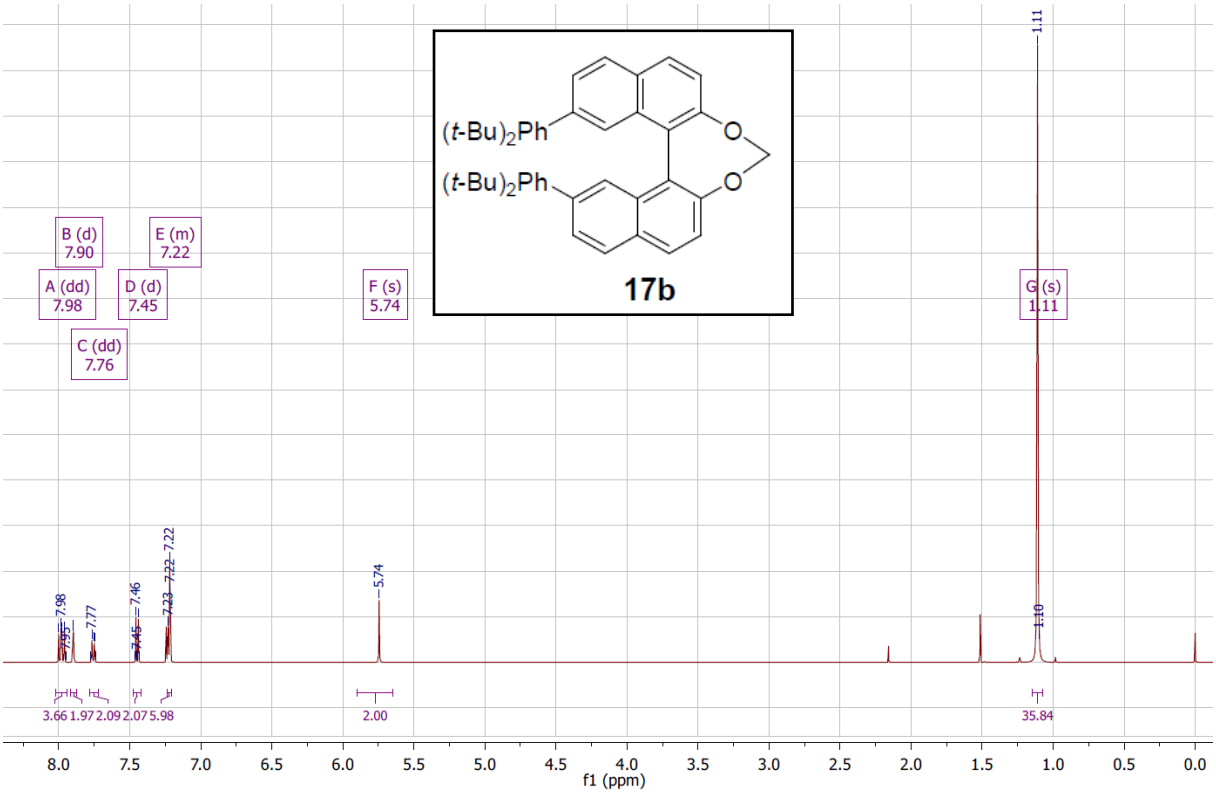

153.39
148.43
133.26
131.57
131.43
128.83
128.55
126.83
122.78
120.24
118.44
110.37
90.66
89.11
44.58
39.70
37.00
35.19
20.03
14.41
f1 (ppm)

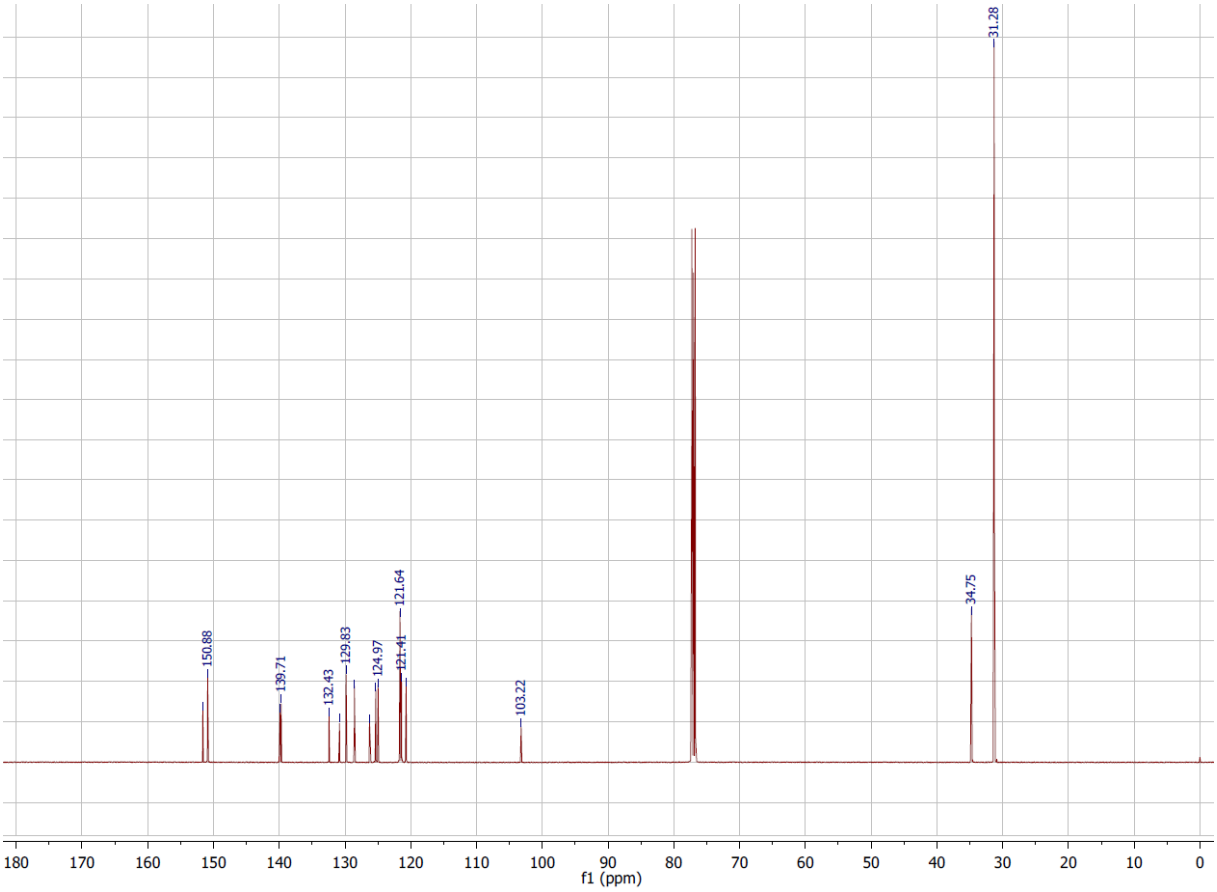

A (s)
9.50
B (m)
7.93
C (m)
7.38
D (m)
7.20
E (m)
7.10
H (s)
2.46
MeSPh
OH
MeSPh
OH
16g
9.50
3.36
2.46
2.06
3.77
8.10
3.79
2.00
5.75
f1 (ppm)

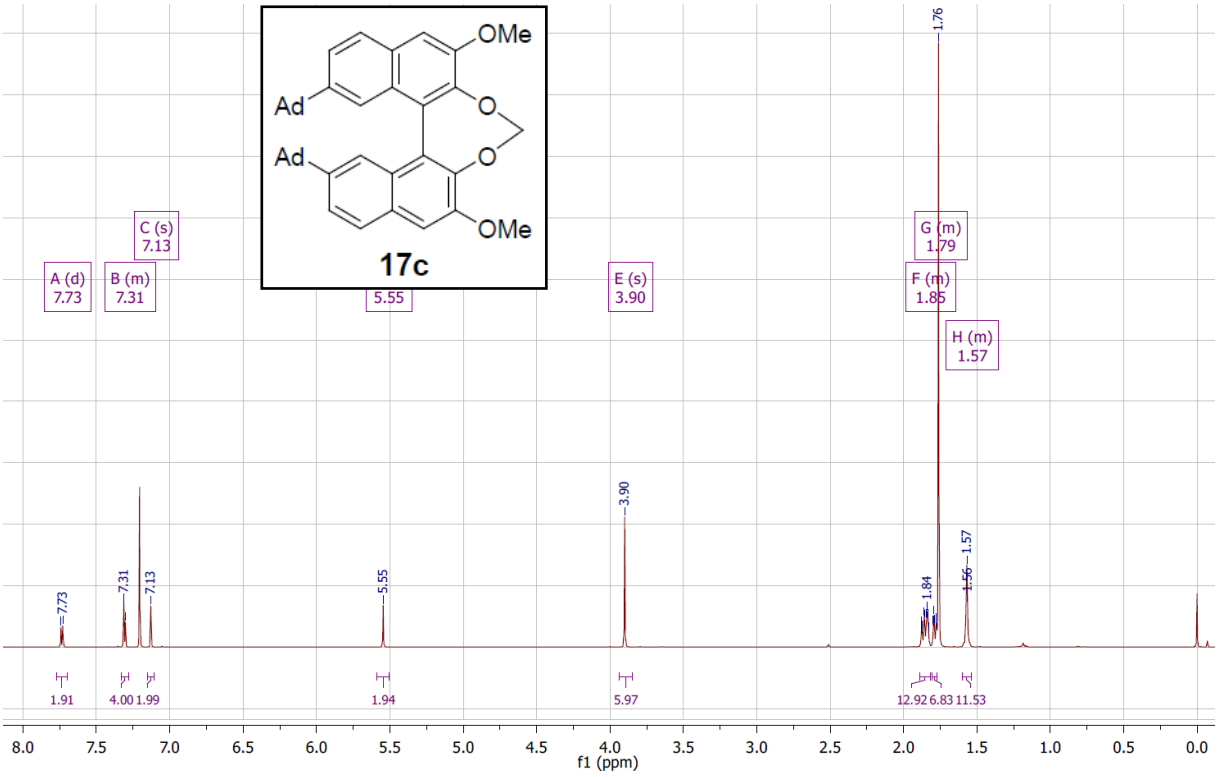

153.83
139.58
133.67
131.69
125.47
124.73
118.04
114.84
14.20
f1 (ppm)

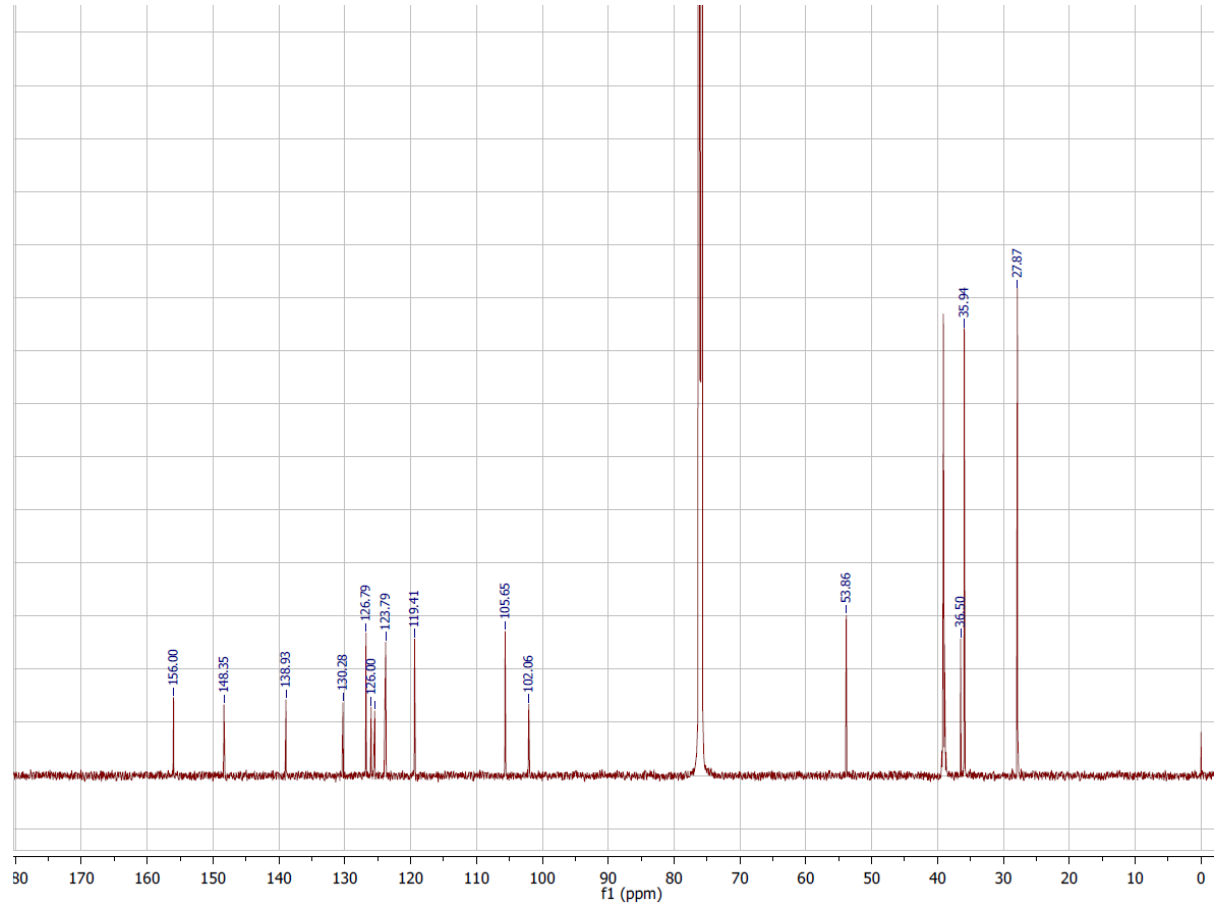

5.77
2Naph
2Naph
O
O
17a
F (m)
7.88
C (m)
7.51
B (m)
7.37
A (s)
5.77
D (m)
7.61
6.35 3.98 6.34 3.94 4.10
2.00
f1 (ppm)

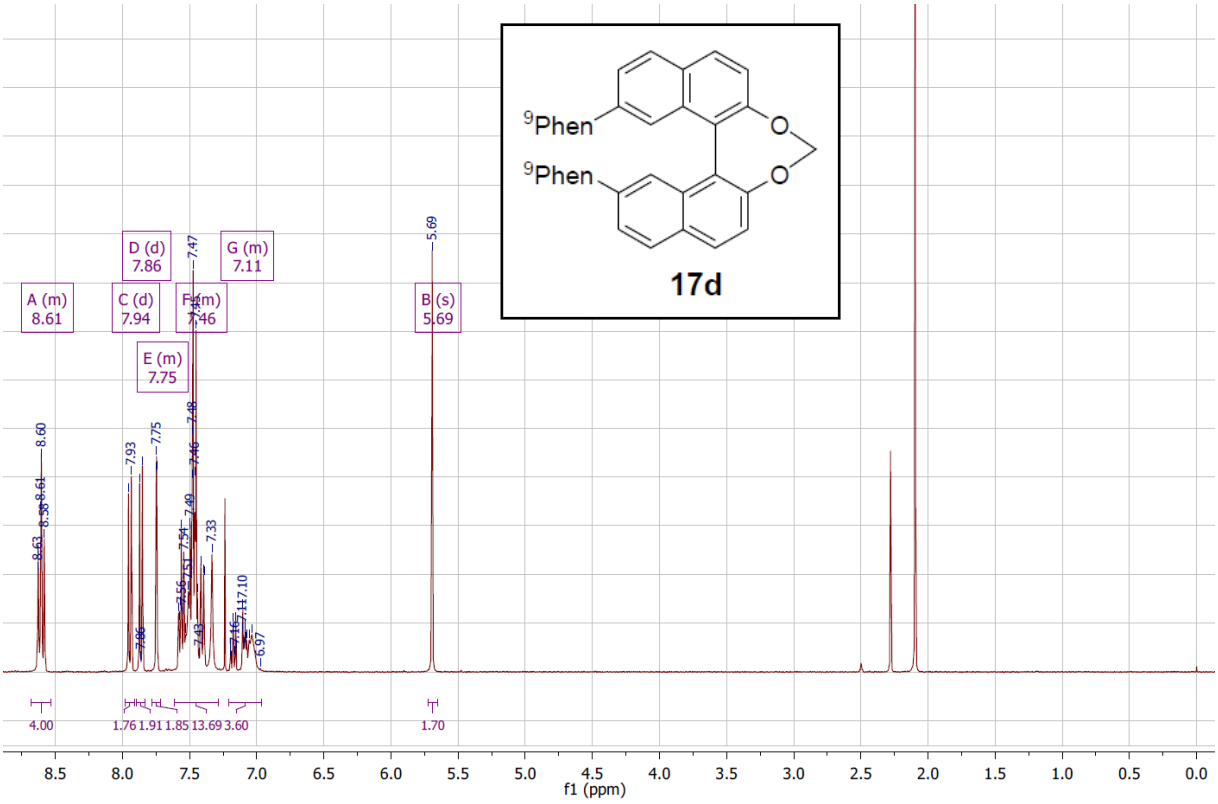

151.92
138.82
133.48
131.10
128.36
126.34
126.14
125.47
121.12
103.32
f1 (ppm)

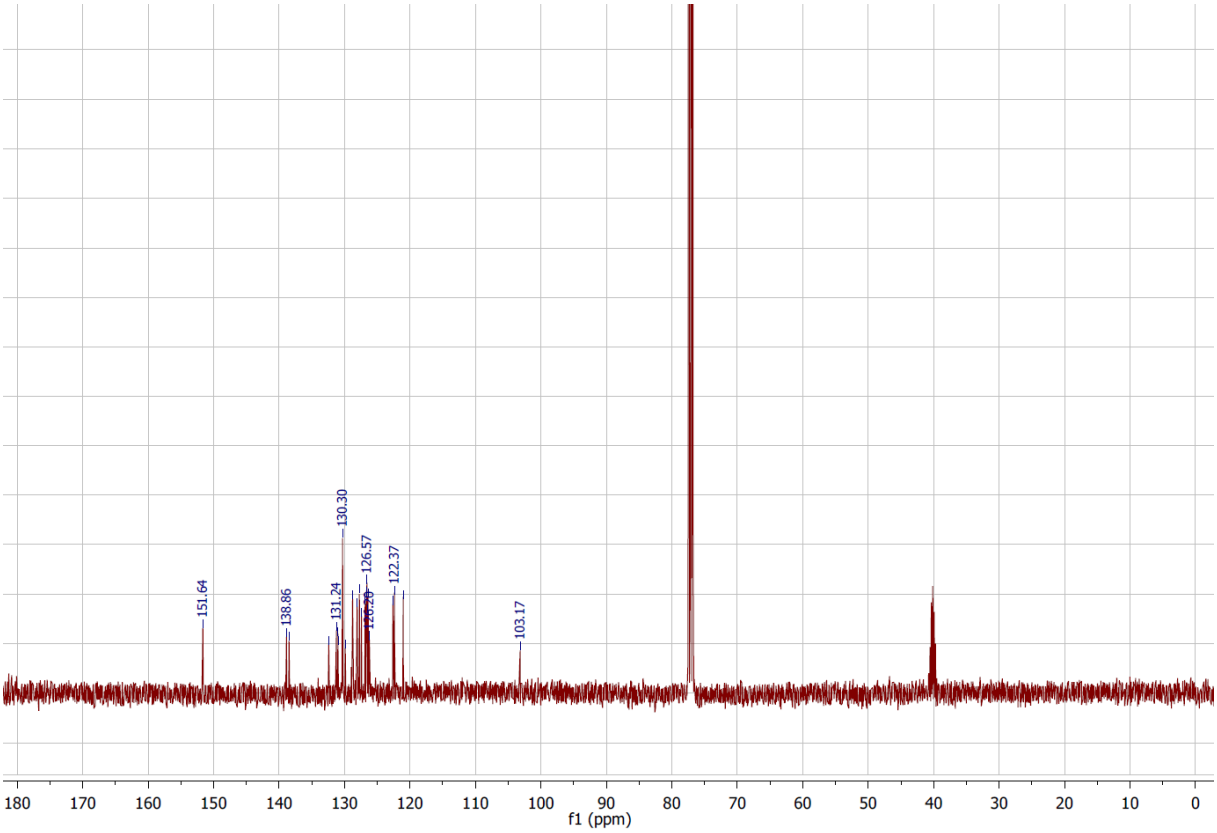

(t-Bu)2Ph
(t-Bu)2Ph
O
O
17b
B (d) 7.90
E (m) 7.22
A (dd) 7.98
D (d) 7.45
C (dd) 7.76
F (s) 5.74
G (s) 1.11
7.98
7.77
7.46
7.22
5.74
1.11
3.66 1.97 2.09 2.07 5.98
2.00
35.84
f1 (ppm)

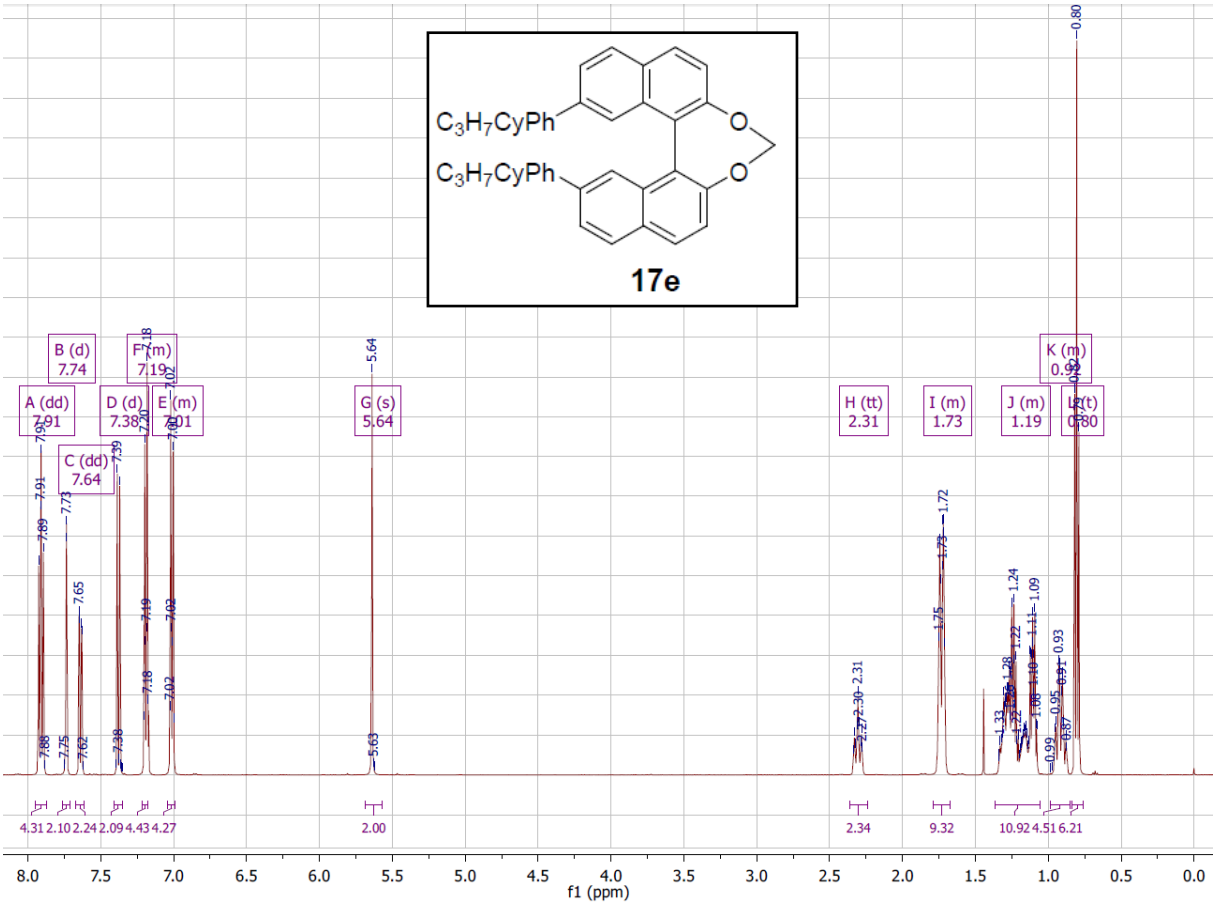

31.28
150.88
139.71
132.43
129.83
124.97
121.64
121.41
103.22
34.75
f1 (ppm)

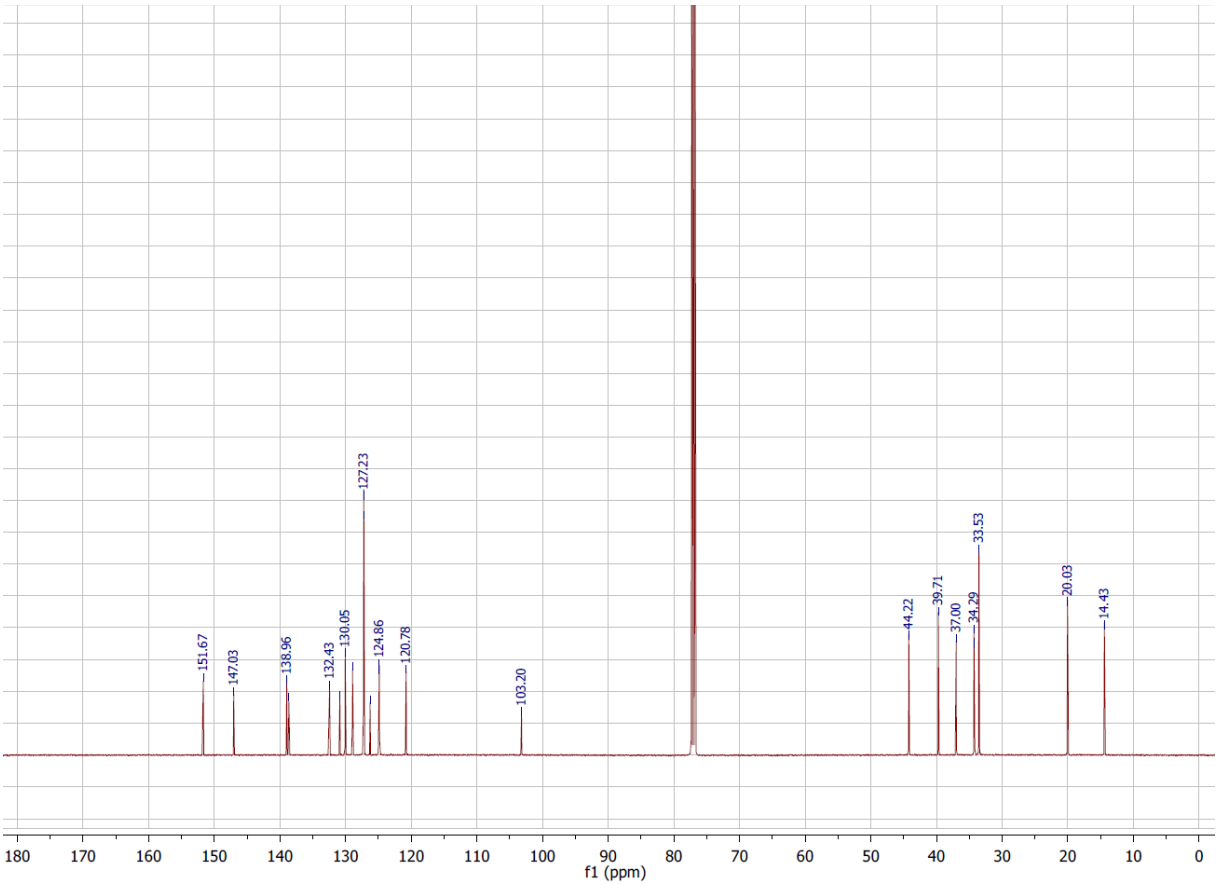

OMe
Ad
O
O
Ad
OMe
17c
A (d)
7.73
B (m)
7.31
C (s)
7.13
5.55
E (s)
3.90
G (m)
1.79
F (m)
1.85
H (m)
1.57
1.76
7.73
7.31
7.13
5.55
3.90
1.84
1.57
1.56
1.91
4.00
1.99
1.94
5.97
12.92
6.83
11.53
f1 (ppm)

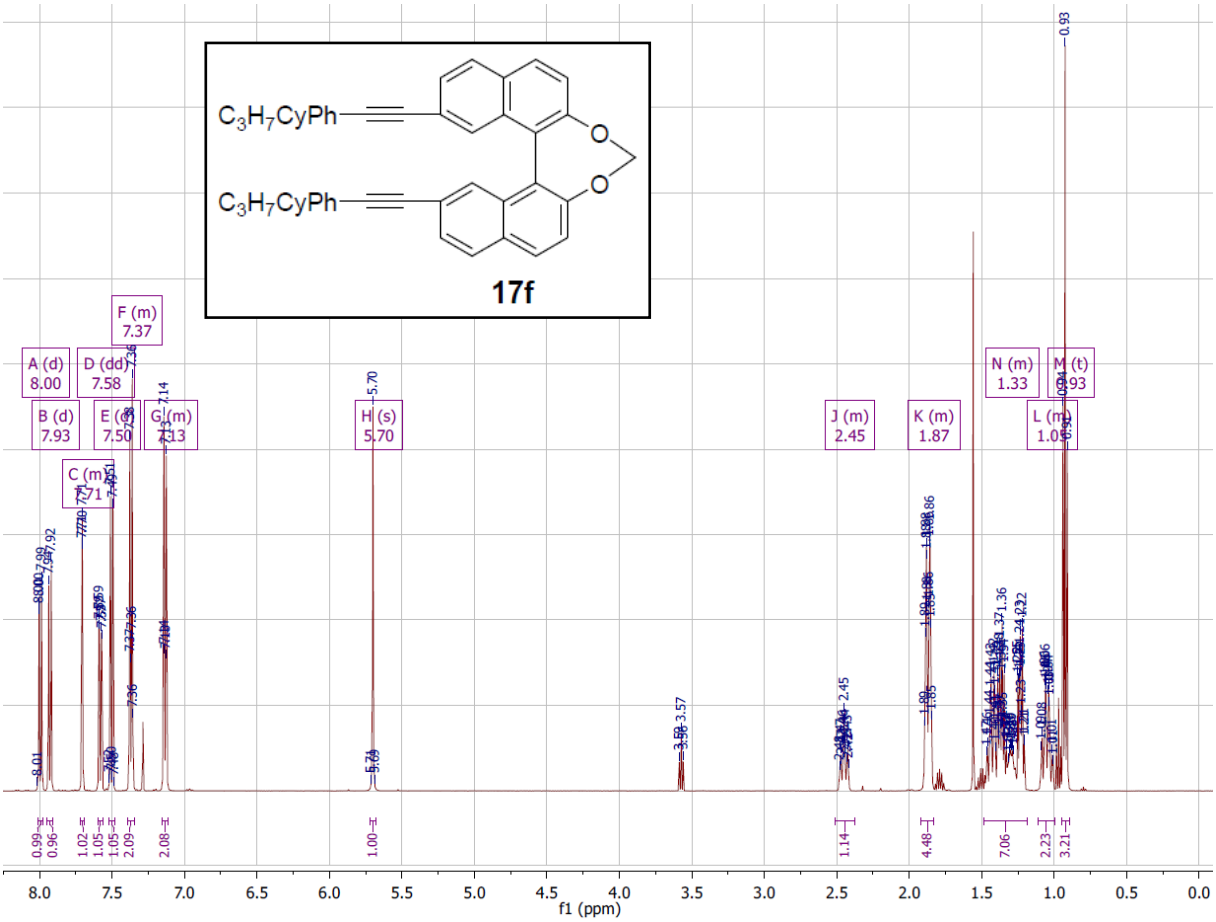

156.00
148.35
138.93
130.28
126.79
126.00
123.79
119.41
105.65
102.06
53.86
35.94
36.50
27.87
f1 (ppm)

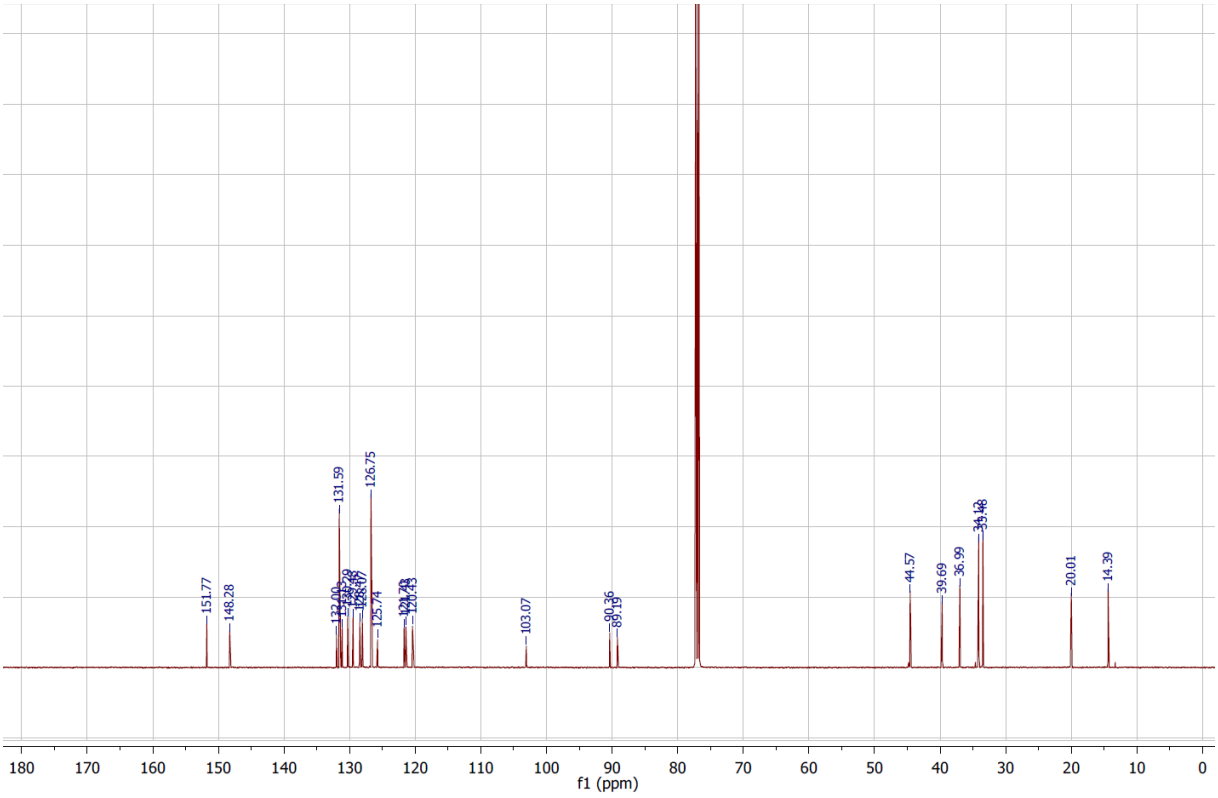

9Phen
9Phen
O
O
17d
A (m) 8.61
C (d) 7.94
F (m) 7.46
D (d) 7.86
G (m) 7.11
E (m) 7.75
B (s) 5.69
4.00
1.76 1.91 1.85 13.69 3.60
1.70
f1 (ppm)

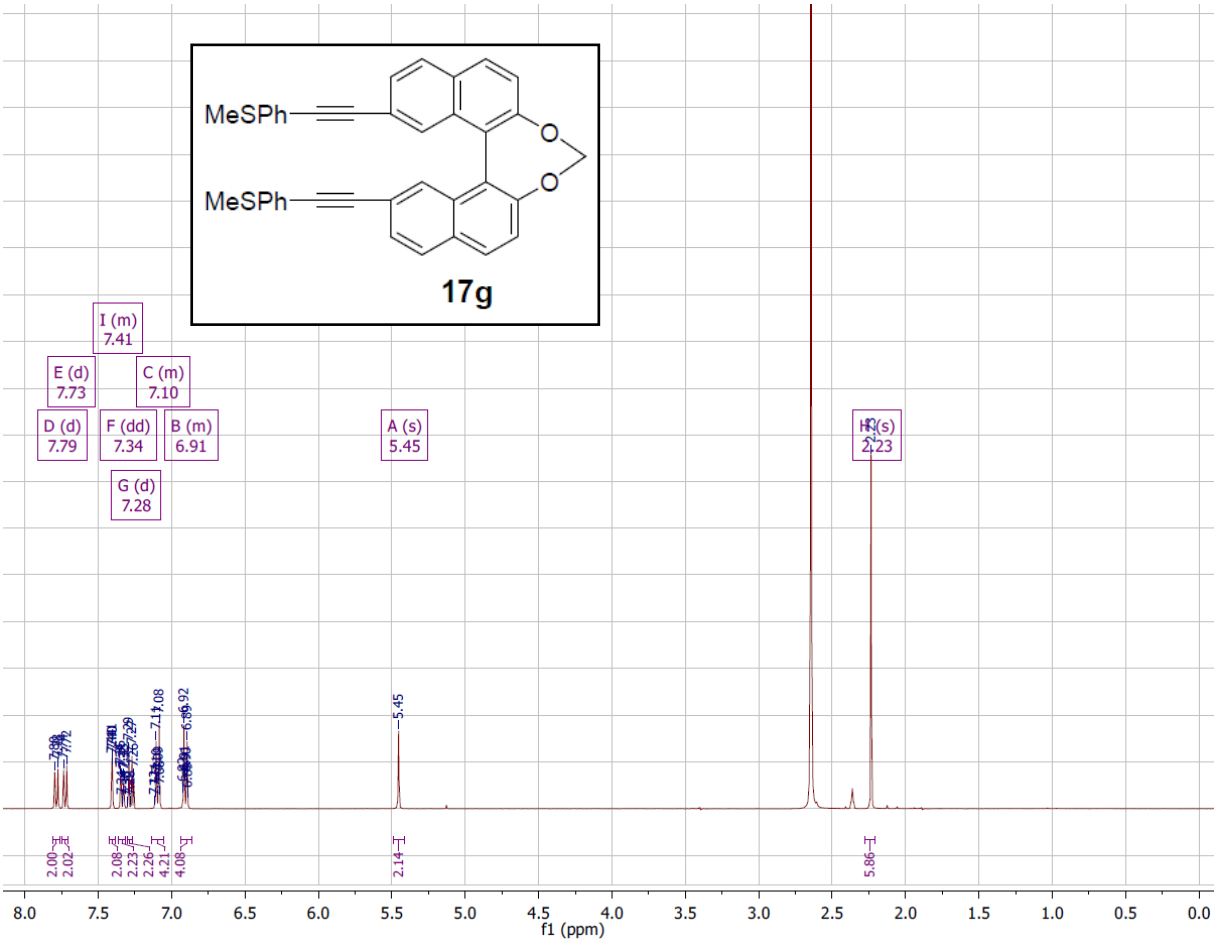

151.64
138.86
131.24
130.30
126.57
122.37
103.17
f1 (ppm)

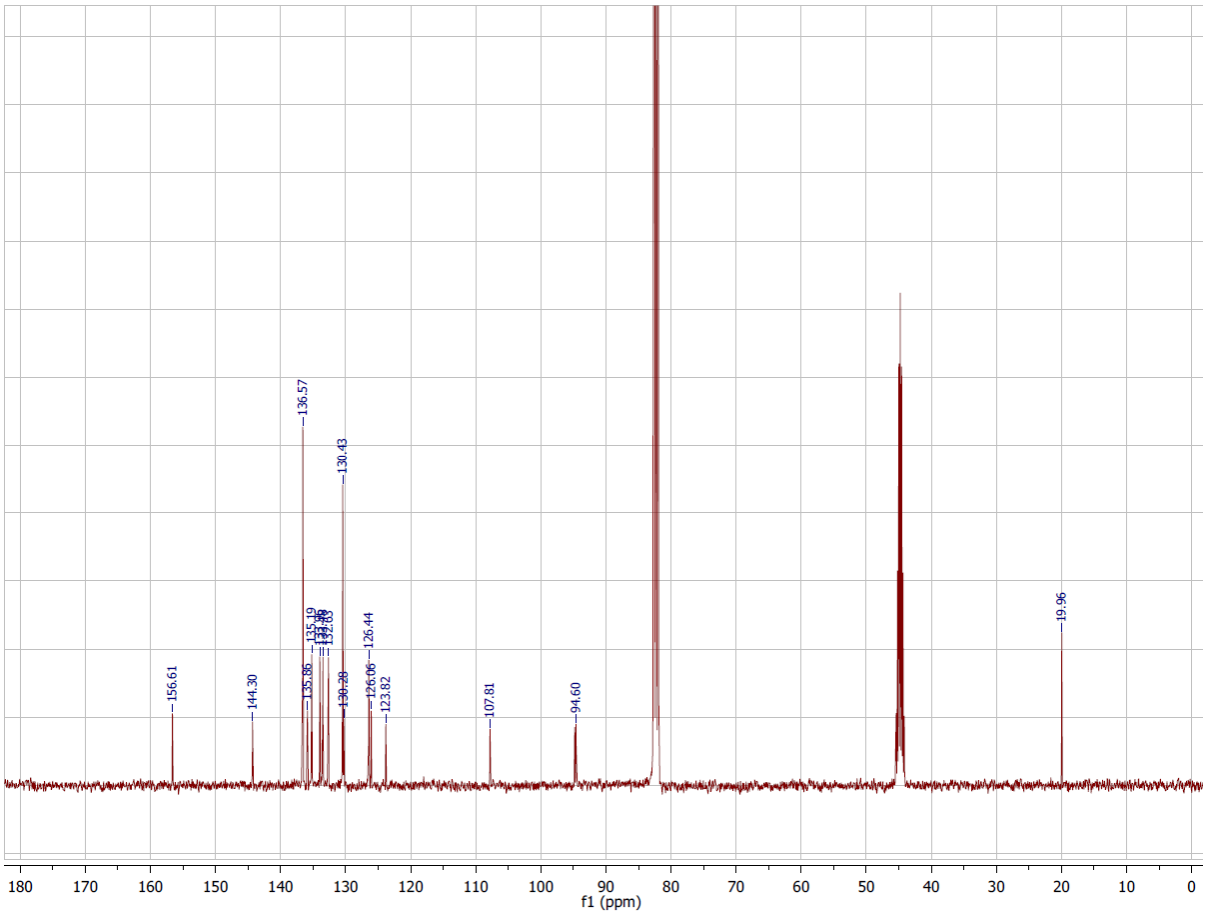

C3H7CyPh
C3H7CyPh
O
O
17e
A (dd) 7.91
B (d) 7.74
C (dd) 7.64
D (d) 7.38
E (m) 7.01
F (m) 7.19
G (s) 5.64
H (tt) 2.31
I (m) 1.73
J (m) 1.19
K (m) 0.93
L (t) 0.80
4.31 2.10 2.24 2.09 4.43 4.27
2.00
2.34
9.32
10.92 4.51 6.21
f1 (ppm)

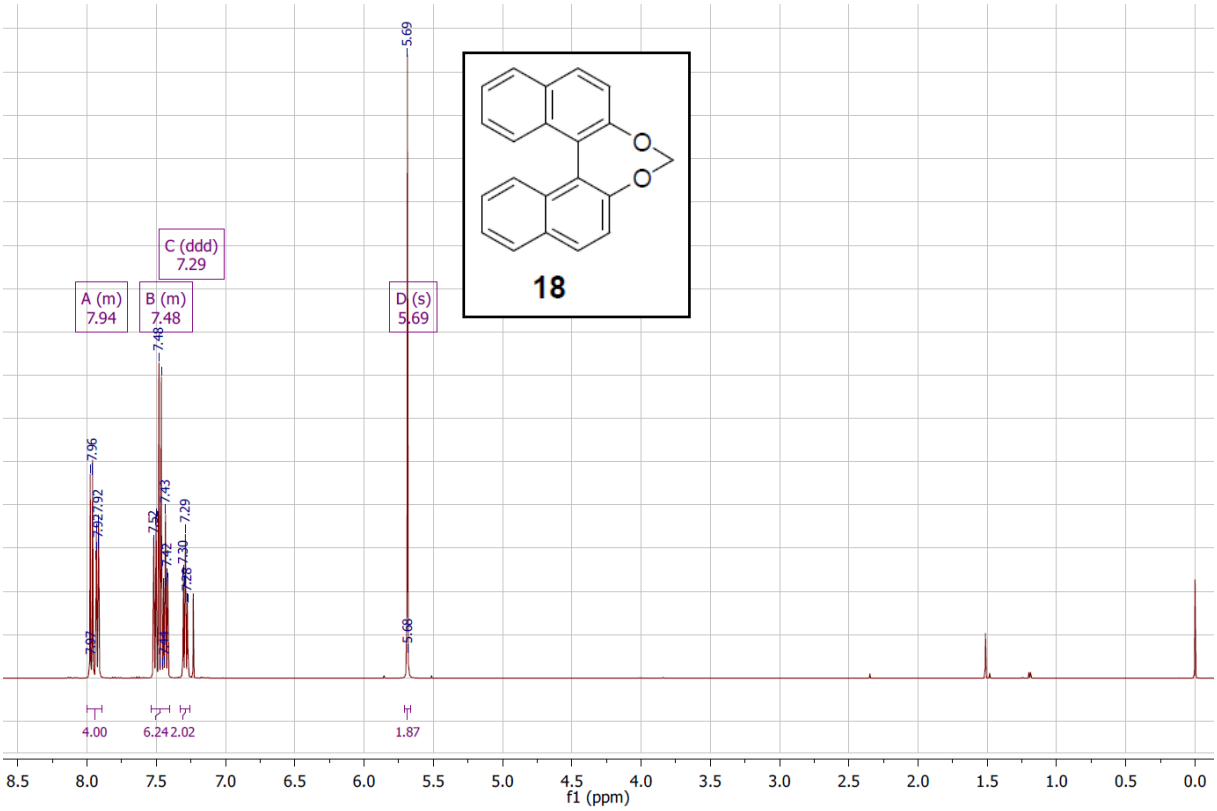

151.67
147.03
138.96
132.43
130.05
127.23
124.86
120.78
103.20
44.22
39.71
37.00
34.29
33.53
20.03
14.43
f1 (ppm)

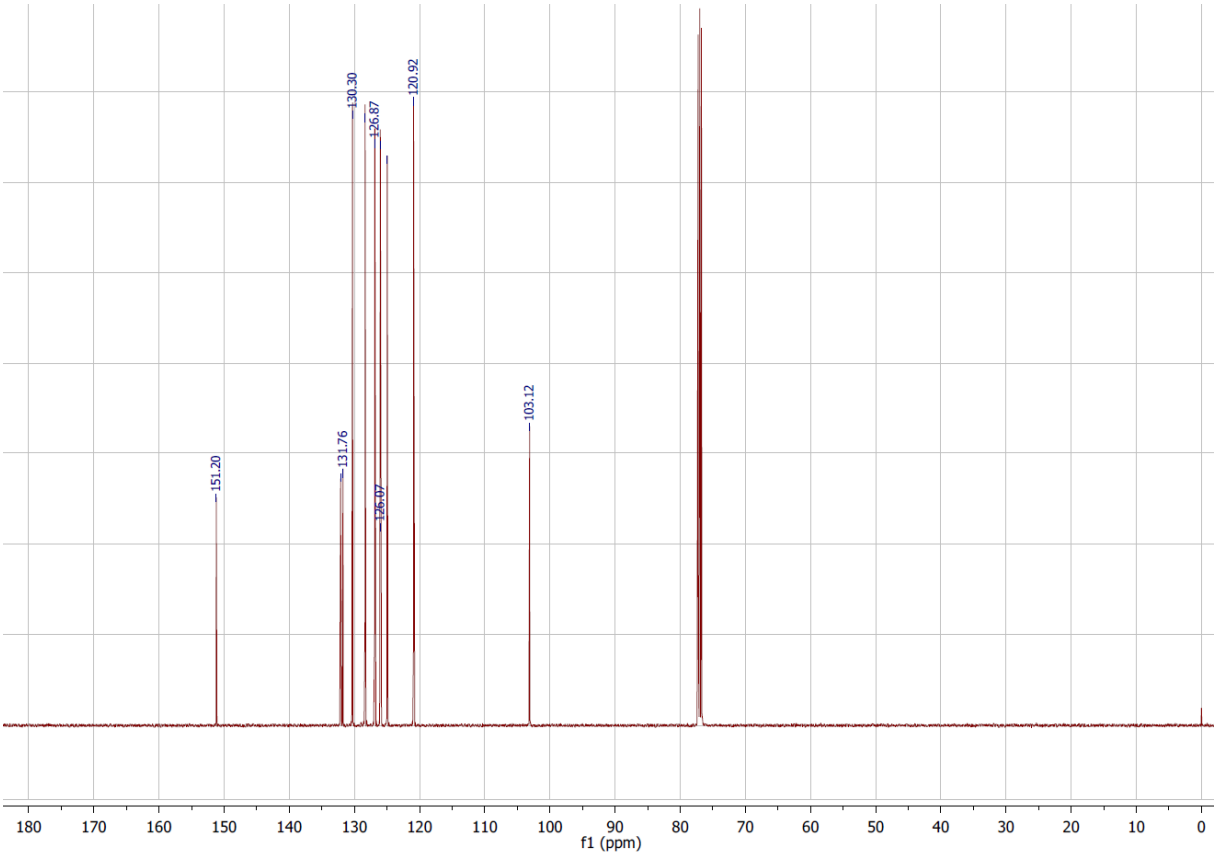

C3H7CyPh
C3H7CyPh
O
O
17f
A (d) 8.00
B (d) 7.93
C (m) 7.71
D (dd) 7.58
E (d) 7.50
F (m) 7.37
G (m) 7.13
H (s) 5.70
J (m) 2.45
K (m) 1.87
L (m) 1.05
M (t) 0.93
N (m) 1.33
f1 (ppm)

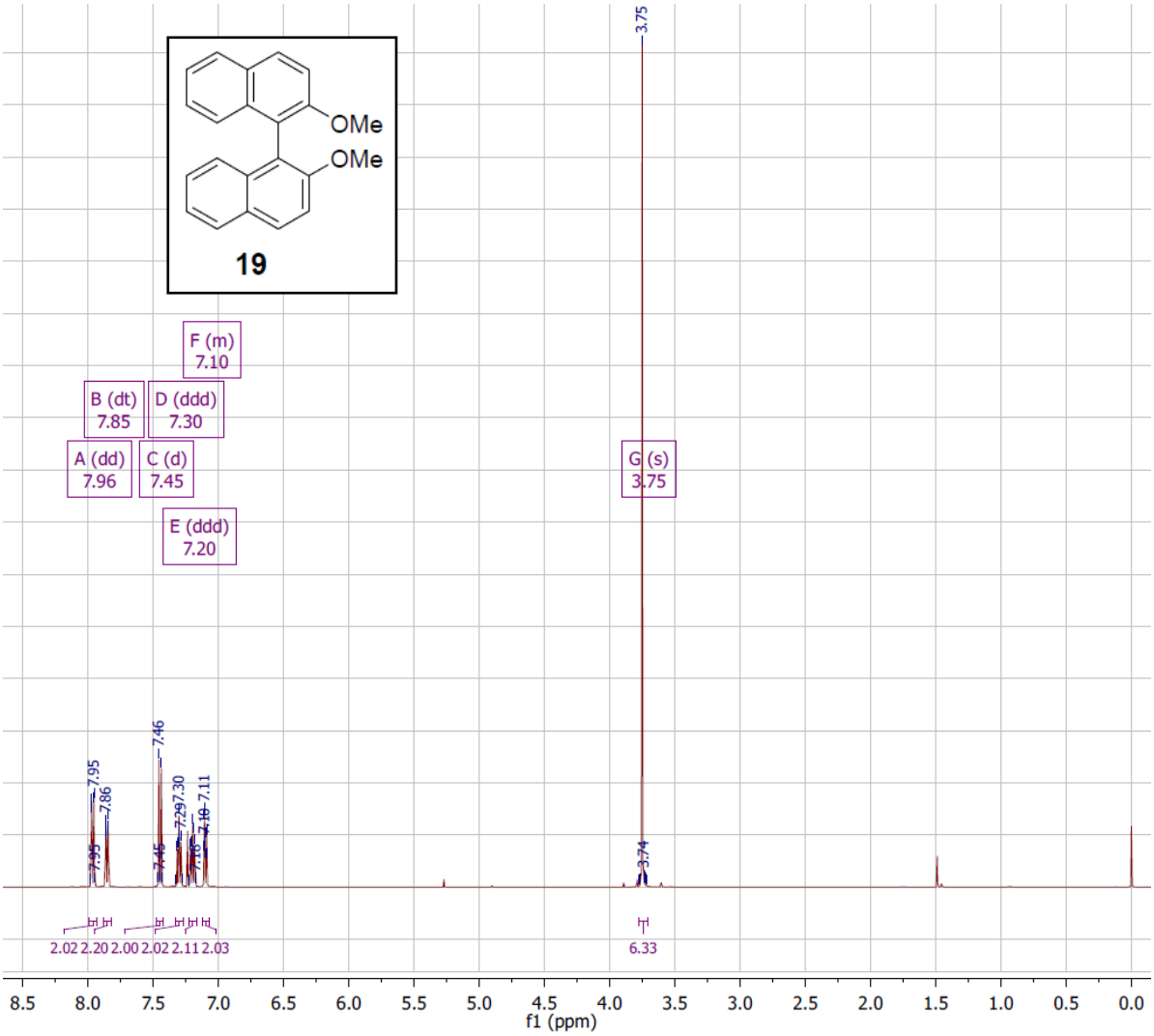

151.77
148.28
131.59
126.75
125.74
103.07
90.36
89.19
44.57
39.69
36.99
20.01
14.39
f1 (ppm)

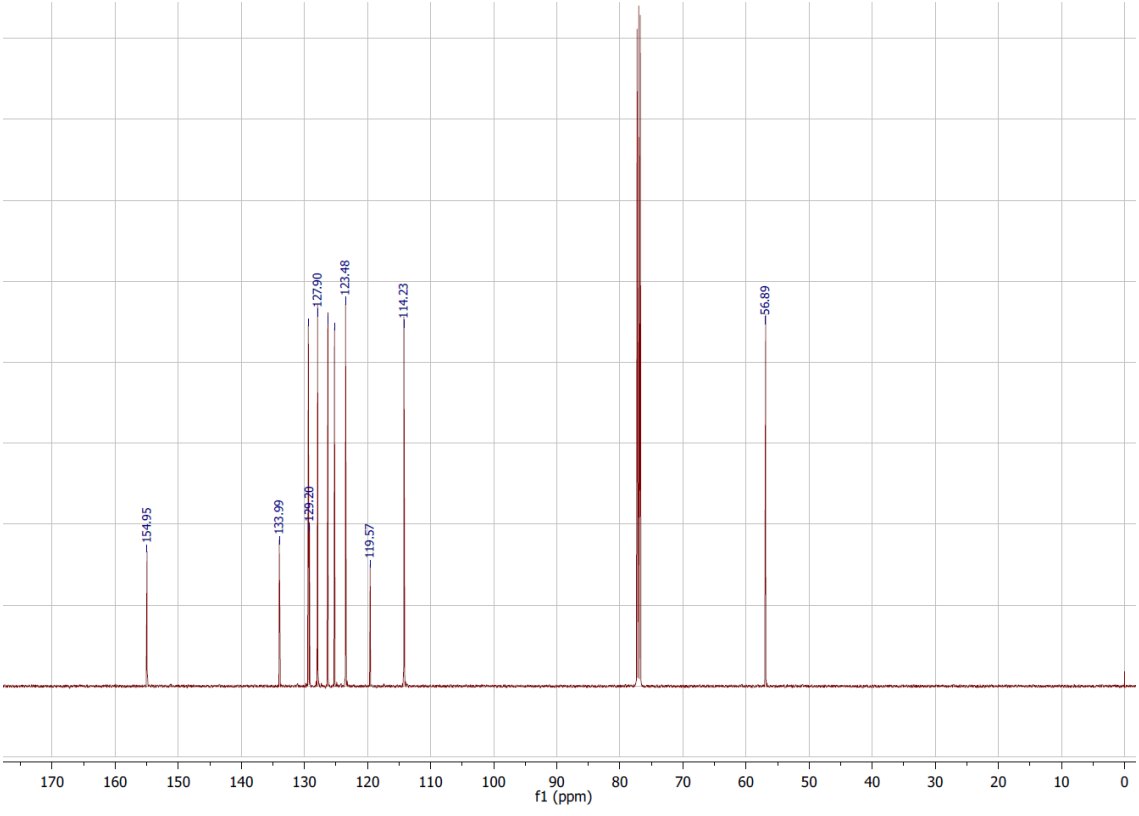

MeSPh
MeSPh
O
O
17g
I (m)
7.41
E (d)
7.73
C (m)
7.10
D (d)
7.79
F (dd)
7.34
B (m)
6.91
G (d)
7.28
A (s)
5.45
H (s)
2.23
f1 (ppm)


136.57
130.43
126.44
156.61
144.30
135.86
130.28
126.06
123.82
107.81
94.60
19.96
f1 (ppm)


5.69
C (ddd)
7.29
A (m)
7.94
B (m)
7.48
D (s)
5.69
18
7.96
7.92
7.52
7.43
7.29
7.30
5.68
4.00
6.24
2.02
1.87
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


130.30
126.87
120.92
151.20
131.76
126.07
103.12
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
OMe
19
F (m)
7.10
B (dt)
7.85
D (ddd)
7.30
A (dd)
7.96
C (d)
7.45
E (ddd)
7.20
G (s)
3.75
3.75
7.95
7.86
7.46
7.30
7.11
2.02 2.20 2.00 2.02 2.11 2.03
6.33
f1 (ppm)


154.95
133.99
129.28
127.90
123.48
119.57
114.23
56.89
f1 (ppm)

7. References

[1] T. R. Kelly, R. A. Silva, H. De Silva, S. Jasmin, Y. Zhao, *J. Am. Chem. Soc.* **2000**, *122*, 6935–6949.

[2] A. Efimov, T. Kumpulainen, H. Lemmetyinen, J. Ranta, *J. Org. Chem.* **2010**, *75*, 5178–5194.

[3] L. Wang, D. Tan, S. Liang, G. Liang, CN Patent 103755530 A, **2014**.

[4] C. J. Wong, Y.-L. Zeller, A. D. Hunter, Z. Xu, *Angew. Chem. Int. Ed.* **2014**, *53*, 14438–14442.

[5] M. Noji, M. Nakajima, K. Koga, *Tetrahedron Lett.* **1994**, *35*, 7983–7984.

[6] Y. Li, M. Wang, A. Urbas, Q. Li, *J. Mater. Chem. C.* **2013**, *1*, 3917–3923.

[7] G. Gottarelli, G. P. Spada, *J. Org. Chem.* **1991**, *56*, 2096–2098.