

Chemistry–A European Journal

Supporting Information

Rhodium-Catalyzed Enantioselective Synthesis of Highly Fluorescent and CPL-Active Dispiroindeno[2,1-c]fluorenes

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I General Information

All reagents were commercially available and purchased from Sigma-Aldrich, Acros Organics, Fluorochem, Alfa Aesar, and Strem Chemicals companies formed. Solvents were purified and dried by distillation: tetrahydrofuran (THF) and toluene from sodium/benzophenone, dichloromethane and 1,2-dichloroethane from calcium hydride. Other solvents and all reagents were used without further purification. All reactions were per under argon atmosphere unless otherwise noted. Chromatography was performed on Silica gel 60A (40-60 μm) from Acros Organics. Thin layer chromatography was performed on Merck silica gel 60 F₂₅₄ pre-coated aluminum sheets. NMR spectra were recorded on Bruker AVANCE III Spectrometer (¹H at 400 MHz and ¹³C at 101 MHz, and ¹⁹F at 376 MHz). All NMR spectra were measured in CDCl₃, C₆D₆ or *d*₆-DMSO solutions and referenced to residual solvent signal: CDCl₃ (¹H, $\delta_{\text{H}} = 7.26$; ¹³C, $\delta_{\text{C}} = 77.16$), C₆D₆ (¹H, $\delta_{\text{H}} = 7.16$; ¹³C, $\delta_{\text{C}} = 128.06$), *d*₆-DMSO (¹H, $\delta_{\text{H}} = 2.50$; ¹³C, $\delta_{\text{C}} = 39.52$). Coupling constants *J* are given in Hz. The IR samples were recorded in KBr powder and measured on spectrometer Thermo Nicolet AVATAR 370 FT-IR and are reported in wave numbers (cm⁻¹). The MS spectra were recorded on an Agilent 5975 Inert MSD or GC \times GC-TOFMS LECO Pegasus IVD device. All melting points are uncorrected and were determined on a Kofler apparatus KB T300. Optical rotations were measured on automatic polarimeter Autopol III and are given in deg.mL.g⁻¹.dm⁻¹ with accuracy ± 2 and the mass concentrations in g/100 mL. HPLC analyses were performed with YMC Chiral ART Cellulose-SB (4.6 mm \times 250 mm) or Daicel Chiralpak® (4.6 mm \times 250 mm) columns and carried out on an Ecom instrument using LCP4100 pump and LCD2083 UV detector. SFC conditions: Waters Acquity Ultra Performance Convergence Chromatography system, column YMC CHIRAL ART Cellulose-SB (150 \times 3 mm I.D., particle size 3 μm). The values obtained from the enantiomeric ratio were rounded to the whole numbers.

II Synthesis of Starting Material

1,1'-(Ethyne-1,2-diyl)bis(2-naphthaldehyde) (**S**) was synthesized by using the previously reported procedures.¹

1-Ethynyl-2-naphthaldehyde (S2a). In a Schlenk flask were dissolved PdCl₂(PPh₃)₂ (0.5 mmol, 351 mg), CuI (1.0 mmol, 190 mg) and 1-bromo-2-naphthaldehyde **S1a** (10.0 mmol, 2.35 g) in THF (40 mL) followed by addition of trimethylsilylethyne (15.0 mmol, 2.1 mL) and Et₃N (40 mL). The reaction mixture was stirred at reflux for 3 hours and then it was cooled down to 25 °C, filtered through a pad of Celite®/silica, which was washed with Et₂O. The filtrate was concentrated under reduced pressure. The residue was treated with K₂CO₃ pellets in a mixture of MeOH/water at 0 °C for 1 h. The resulting mixture was quenched with 1M HCl, extracted with CH₂Cl₂ (3× 100 mL), the combined organic fractions were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (19/1 hexanes/EtOAc) furnished 1.75 g (97%) of the title compound as a yellow solid.

¹H NMR (400 MHz; CDCl₃) δ 10.79 (d, *J* = 0.9 Hz, 1H), 8.56-8.52 (m, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.92-7.88 (m, 2H), 7.70-7.65 (m, 2H), 3.92 (s, 1H).

¹³C NMR (101 MHz; CDCl₃) δ 192.1, 135.8, 135.4, 133.5, 129.62, 129.57, 128.6, 128.0, 127.2, 126.2, 122.0, 90.3, 77.3.

The recorded spectral data were in accordance with the previously published values.²

1,1'-(Ethyne-1,2-diyl)bis(2-naphthaldehyde) (S3a). In a flask was dissolved PdCl₂(PPh₃)₂ (0.46 mmol, 323 mg), CuI (0.74 mmol, 141 mg), 1-bromo-2-naphthaldehyde **S1a** (9.3 mmol, 2.18 g) and 1-ethynyl-2-naphthaldehyde **S2a** (9.3 mmol, 1.68 g) in THF (37 mL) and Et₃N (37 mL) was added. The reaction mixture was stirred at reflux for 3 hours. Then the reaction mixture was cooled down to 25 °C and filtered. The precipitate was dissolved in CH₂Cl₂ (250 mL), washed with H₂O (3 times), dried over Na₂SO₄, filtered, and concentrated under reduced pressure to provide 2.3 g (74%) of the title compound as a yellow solid.

Mp = 129-131 °C (CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ 11.00 (s, 1H), 10.99 (s, 1H), 8.69-8.64 (m, 2H), 8.08 (d, *J* = 8.6 Hz, 2H), 8.02-7.95 (m, 4H), 7.72-7.75 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 191.4 (2C), 136.0 (2C), 135.1 (2C), 133.4 (2C), 130.2 (2C), 129.8 (2C), 128.9 (2C), 128.5 (2C), 127.2 (2C), 126.0 (2C), 122.6 (2C), 95.5 (2C).

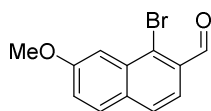
IR (KBr) ν 3342, 3074, 2838, 2238, 1693, 1617, 1589, 1461, 1434, 1397, 1371, 1336, 1248, 1231, 867, 822, 780, 745 cm⁻¹.

HRMS (EI): *m/z* calcd for C₂₄H₁₄O₂ [(M)⁺]: 334.0994, found: 334.0995.

¹ D. Peña, D. Pérez, E. Guitián, L. Castedo, *Eur. J. Org. Chem.* **2003**, 1238-1243.

² D. Schweinfurth, M. Zalibera, M. Kathan, C. Shen, M. Mazzolini, N. Trapp, J. Crassous, G. Gescheidt, F. Diederich, *J. Am. Soc. Chem.* **2014**, *136*, 13045-13052.

1-Bromo-7-methoxy-2-naphthaldehyde (S1b). To a solution of dry DMF (85 mmol, 6.6 mL) in dry CH₂Cl₂ (100 mL) was dropwise added PBr₃ (71 mmol, 6.7 mL) at 0 °C. After 1 hour of stirring, 7-methoxy-1-tetralone (14.2 mmol, 2.5 g) in CH₂Cl₂ (50 mL) was added and the reaction mixture was stirred under reflux for 4 h. Then the reaction mixture was cooled to 0 °C and quenched with a saturated aqueous solution of NaHCO₃ (250 mL). After the end of the



gas generation, the layers were separated. The aqueous phase was extracted with CH₂Cl₂ (3 × 200 mL). The combined organic phases were washed with H₂O, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. A solution of the crude product in dry toluene (50 mL) was heated with DDQ (31.2 mmol, 7.1 g) at 120 °C and stirred for 16 h. The mixture was diluted with hexanes (50 mL), filtered, and concentrated under reduced pressure.

Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) furnished 2.8 g (74%) of the title compound as a yellow solid.

R_f (20/1 hexanes/EtOAc) = 0.23.

Mp = 89.6 °C (CH₂Cl₂).

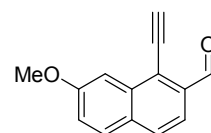
¹H NMR (400 MHz, CDCl₃) δ_H 10.65 (s, 1H), 7.81-7.71 (m, 4H), 7.31 (ddd, J = 8.9, 2.5, 1.0 Hz, 1H), 4.00 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ_C 193.2, 159.6, 133.7, 132.8, 131.8, 130.2, 129.5, 128.0, 122.6, 122.2, 106.3, 55.7.

IR (KBr) ν 3336, 3007, 2965, 2935, 2905, 2869, 2857, 2830, 1673, 1595, 1455, 1308, 1269, 1237, 1216, 1201, 1186, 1135, 1045, 1033, 975, 848, 842 cm⁻¹.

HRMS (EI): m/z calcd for C₉H₁₂BrO₂ [(M)⁺]: 263.9786, found: 263.9788.

1-Ethynyl-7-methoxy-2-naphthaldehyde (S2b). In a Schlenk flask was dissolved PdCl₂(PPh₃)₂ (0.2 mmol, 134 mg), CuI (0.38 mmol, 72 mg) and 1-bromo-7-methoxy-2-naphthaldehyde **S1b** (3.8 mmol, 1 g) in THF (15 mL). To the solution was added trimethylsilylethyne (5.7 mmol, 790 μ L) and Et₃N (15 mL). The reaction mixture was stirred at reflux for 3 h. Then the mixture was cooled down to 25 °C, filtered through a pad of Celite[®]/silica gel, and washed with Et₂O. The filtrate was concentrated under reduced pressure. The residue was treated with K₂CO₃ pellets in a mixture of MeOH/water at 0 °C for 1 h. The resulting mixture was quenched with 1M HCl, extracted with CH₂Cl₂ (3 × 100 mL), the combined organic fractions were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (19/1 hexanes/EtOAc) furnished 574 mg (72%) of the title compound as a yellow solid.



R_f (19/1 hexanes/EtOAc) = 0.28.

Mp = 114.4 °C (CH₂Cl₂).

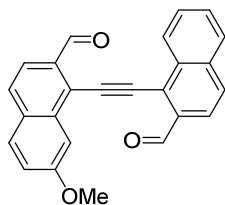
¹H NMR (400 MHz, CDCl₃) δ 10.77 (s, 1H), 7.84-7.78 (m, 4H), 7.32 (dd, J = 8.9, 2.5 Hz, 1H), 4.00 (s, 3H), 3.93 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 192.3, 159.5, 135.8, 135.2, 131.3, 130.1, 129.3, 124.4, 122.3, 120.0, 105.2, 90.0, 55.6.

IR (KBr) ν 3279, 3261, 3240, 3064, 3010, 2962, 2941, 2863, 2830, 1739, 1685, 1625, 1595, 1509, 1461, 1320, 1216, 1051, 1027, 842 cm⁻¹.

HRMS (EI): m/z calcd for C₁₄H₁₀O₂ [(M)⁺]: 210.0681, found: 210.0680.

1-((2-Formylnaphthalen-1-yl)ethynyl)-7-methoxy-2-naphthaldehyde (S3b). In a flask were dissolved PdCl₂(PPh₃)₂ (0.25 mmol, 175 mg), CuI (0.3 mmol, 57 mg), 1-bromo-7-methoxy-2-naphthaldehyde **S2b** (5 mmol, 1.32 g) and 1-ethynyl-2-naphthaldehyde **S1a** (5 mmol, 900 mg) in THF (20 mL) followed by addition of Et₃N (20 mL). The reaction mixture was stirred at reflux for 3 hours.



Then the reaction mixture was cooled down to 25 °C and filtered. The precipitate was dissolved in CH₂Cl₂ (250 mL), washed with H₂O (3 times), dried over Na₂SO₄, filtered, and concentrated under reduced pressure to provide 1.4 g (77%) of the title compound as a yellow solid.

Mp = 184.9 °C (CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ 11.04 (s, 1H), 10.98 (s, 1H), 8.75-8.72 (m, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 8.00-7.91 (m, 5H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.76-7.71 (m, 2H), 7.37 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.99 (s, 3H).

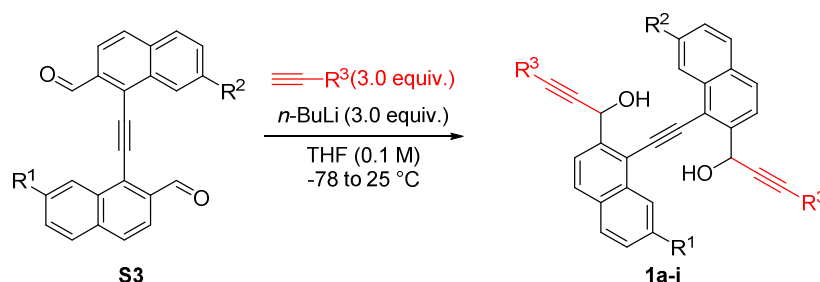
¹³C NMR (101 MHz, CDCl₃) δ 191.6, 191.4, 159.8, 136.0, 135.4, 135.3, 135.0, 133.5, 131.5, 130.4, 130.0, 129.9, 129.8, 129.0, 128.4, 127.2, 126.1, 124.1, 122.8, 122.7, 120.8, 105.1, 96.3, 95.5, 55.8.

IR (KBr) ν 3411, 3267, 3004, 2848, 1691, 1679, 1589, 1455, 1278, 1240, 1216, 836, 824 cm⁻¹.

HRMS (EI): *m/z* calcd for C₂₅H₁₆O₃ [(M)⁺]: 364.0994, found: 364.1101.

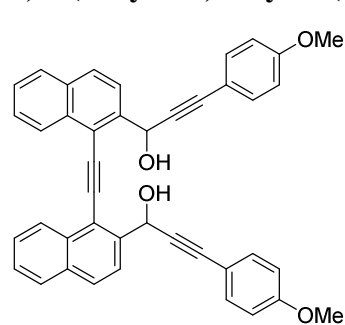
For synthesis of **S3c**, see synthesis of **1i**.

General procedure for alkylation reaction (A).¹ *n*-BuLi 1.6 M (3 mmol, 2 mL) was added dropwise to a solution of the corresponding alkyne (3 mmol) in anhydrous THF (40 mL) at -78 °C. After 1 hour of stirring was added dialdehyde **S3** (1.0 mmol) and the reaction mixture was stirred for 5 min at -78 °C and then it was allowed to warm up to 25 °C and stirred for 3 hours. It was quenched with a saturated aqueous solution NH₄Cl, extracted with Et₂O (3 × 100 mL), the combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes/EtOAc) provided products **1**.



Note: In all cases the respective triynediols were obtained as mixtures of *rac* (and *meso*) diastereoisomers. In some cases full assignment of NMR signals was possible, but in other ones it was not feasible (the signals were often covered by each other). Therefore, in those cases the peaks are listed as observed and in the respective ¹H NMR spectra are listed and displayed without integration.

1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(3-(4-methoxyphenyl)prop-2-yn-1-ol)



(1a). According to the general procedure A with **S3a** (5.7 mmol, 1.9 g), 4-ethynylanisole (17.1 mmol, 2.1 mL), *n*-BuLi (17.1 mmol, 10.7 mL) in THF (150 mL). Column chromatography of the residue on silica gel (2.5/1 hexanes/EtOAc) furnished 3.2 g (94%) of the title compound (an inseparable 2:1 mixture of diastereoisomers) as a light brown solid.

R_f (4/1 hexanes/EtOAc) = 0.12.

Mp = 97-102 °C (CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ 8.67 (d, J = 8.3 Hz, 2H), 8.01 (dd, J = 8.6, 4.6 Hz, 2H), 7.92-7.86 (m, 4H), 7.53-7.63 (m, 4H), 7.40-7.35 (m, 4H), 6.77-6.72 (m, 4H), 6.62 (d, J = 4.4 Hz, 2H), 3.75 (s, 6H), 3.62 (d, J = 4.8 Hz, 1H), 3.44 (d, J = 5.0 Hz, 1H).

Major isomer: ¹³C NMR (101 MHz, CDCl₃) δ 159.82 (2C), 141.6 (2C), 133.6 (2C), 133.5 (4C), 133.1 (2C), 129.6 (2C), 128.4 (2C), 127.6 (2C), 126.9 (2C), 126.7 (2C), 124.5 (2C), 119.01 (2C), 114.60 (2C), 113.94 (4C), 95.6 (2C), 87.40 (2C), 87.24 (2C), 64.25 (2C), 55.3 (2C).

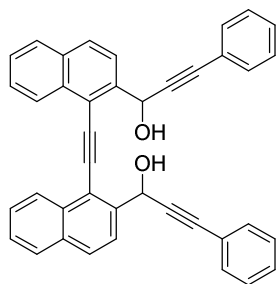
Minor isomer: ¹³C NMR (101 MHz, CDCl₃) δ 159.80 (2C), 141.4 (2C), 133.51 (2C), 124.4 (2C), 118.96 (2C), 114.57 (2C), 113.92 (4C), 95.7 (2C), 87.44 (2C), 87.22 (2C), 64.21 (2C); other peaks are covered by signals of the major isomer.

IR (KBr) ν 3418, 3055, 3004, 2956, 2929, 2836, 2223, 1605, 1569, 1509, 1463, 1440, 1291, 1249, 1173, 1107, 1033, 979, 829, 802, 762 cm⁻¹.

HRMS (ESI⁺): m/z calcd for C₄₂H₃₀O₄Na [(M+Na)⁺]: 621.20363, found: 621.20367.

The spectral data were in accordance with previously published results.³

1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(3-phenylprop-2-yn-1-ol) (1b).



According to the general procedure **A** with **S3a** (1.5 mmol, 502 mg), phenylacetylene (4.5 mmol, 495 μ L) and *n*-BuLi (4.5 mmol, 2.8 mL) in THF (40 mL). Column chromatography of the residue on silica gel (4/1 hexanes/EtOAc) furnished 544 mg (67%) of the title compound (an inseparable 2:1 mixture of diastereoisomers) as a light brown solid.

R_f (4/1 hexanes/EtOAc) = 0.14.

Mp = 93-98 °C (CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ 8.70-8.67 (m, 2H), 8.04-8.00 (m, 2H), 7.94-7.87 (m, 4H), 7.61-7.55 (m, 4H), 7.48-7.44 (m, 4H), 7.30-7.22 (m, 6H), 6.64 (br s, 2H), 3.61 (br s, 1H), 3.45 (br s, 1H).

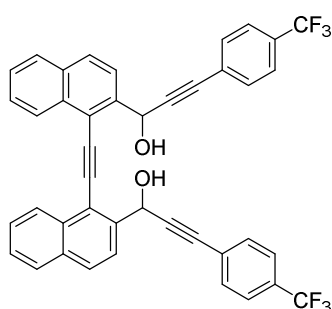
Major isomer: ¹³C NMR (101 MHz, CDCl₃) δ 141.28 (2C), 133.56 (2C), 133.18 (2C), 132.0 (4C), 129.8 (2C), 128.7 (2C), 128.5 (2C), 128.36 (4C), 127.7 (2C), 126.98 (2C), 126.7 (2C), 124.4 (2C), 122.48 (2C), 119.06 (2C), 95.7 (2C), 88.71 (2C), 87.29 (2C), 64.2 (2C);

Minor isomer: ¹³C NMR (101 MHz, CDCl₃) δ 141.34 (2C), 133.59 (2C), 133.20 (2C), 128.38 (4C), 127.0 (2C), 124.5 (2C), 122.50 (2C), 119.14 (2C), 95.6 (2C), 88.68 (2C), 87.32 (2C), 64.3 (2C); other peaks are covered by signals of the major isomer.

IR (KBr) ν 3371, 3053, 2926, 2856, 2224, 1591, 1571, 1484, 1443, 1401, 1260, 1218, 1173, 1032, 980, 918, 824, 755, 693 cm⁻¹.

HRMS (ESI⁺): m/z calcd for C₄₀H₂₆O₂Na [(M + Na)⁺]: 561.18250, found: 561.18256.

1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol) (1c).



According to the general procedure **A** with **S3a** (1.5 mmol, 502 mg), 1-ethynyl-4-(trifluoromethyl)-benzene (4.5 mmol, 740 μ L) and *n*-BuLi (4.5 mmol, 2.8 mL) in THF (40 mL). Column chromatography of the residue on silica gel (3/1 hexanes/EtOAc) furnished 930 mg (92%) of the title compound (an inseparable 2:1 mixture of diastereoisomers) as a brownish solid.

R_f (3/1 hexanes/EtOAc) = 0.28.

Mp = 98-103 °C (CH₂Cl₂).

¹H NMR (400 MHz, C₆D₆) δ 8.77 (d, J = 8.4 Hz, 2H), 8.10-8.06 (m, 2H), 7.63-7.54 (m, 4H), 7.46-7.38 (m, 2H), 7.33-7.28 (m, 2H), 7.19-7.13 (m, 5H), 7.05-6.98 (m, 4H), 6.94 (s, 1H), 5.28 (br s, 2H).

Major isomer: ¹³C NMR (101 MHz, CDCl₃) δ 140.8 (2C), 133.4 (2C), 133.1 (2C), 132.0 (4C), 130.26 (q, ² J_{C-F} = 32.6 Hz) (2C), 129.8 (2C), 128.5 (2C), 127.7 (2C), 127.1 (2C), 126.5 (2C), 126.0 (m) (2C), 125.0 (q, ³ J_{C-F} = 3.8 Hz) (2C), 124.4 (2C), 123.7 (q, ¹ J_{C-F} = 272.3 Hz) (2C), 119.0 (2C), 95.5 (2C), 91.1 (2C), 85.8 (2C), 64.1 (2C);

Minor isomer: ¹³C NMR (101 MHz, CDCl₃) δ 140.7 (2C), 133.3 (2C), 133.04 (2C), 130.21 (q, ² J_{C-F} = 32.8 Hz) (2C), 129.7 (2C), 127.6 (2C), 127.0 (2C), 125.05 (q, ² J_{C-F} = 3.8 Hz) (2C),

³ R. P. Kaiser, D. Nečas, T. Cadart, R. Gyepes, I. Císařová, J. Mosinger, L. Pospíšil, M. Kotora, *Angew. Chem. Int. Ed.* **2019**, *58*, 17169-17174.

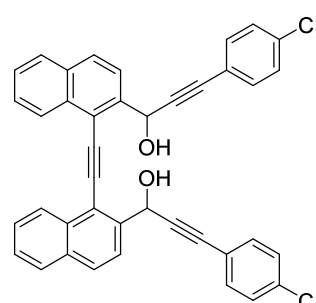
124.2 (2C), 118.9 (2C), 95.7 (2C), 91.2 (2C), 85.7 (2C), 64.0 (2C); other peaks are covered by signals of the major isomer.

^{19}F NMR (376.5 MHz, CDCl_3) δ -62.93, -62.91.

IR (KBr) ν 3381, 3053, 2935, 2856, 2099, 1612, 1408, 1318, 1249, 1218, 1166, 1125, 1073, 1021, 983, 835, 762 cm^{-1} .

HRMS (ESI $^+$): m/z calcd for $\text{C}_{42}\text{H}_{24}\text{O}_2\text{F}_6\text{Na}$ [(M+Na) $^+$]: 697.15727, found: 697.15738.

1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(3-(4-chlorophenyl)prop-2-yn-1-ol) (1d).



(**1d**). According to the general procedure A with **S3a** (1.5 mmol, 502 mg), (4-chlorophenyl)acetylene (4.5 mmol, 615 mg) and *n*-BuLi (4.5 mmol, 2.8 mL) in THF (40 mL). Column chromatography of the residue on silica gel (3/1 hexanes/EtOAc) furnished 806 mg (88%) of the title compound (an inseparable 2:1 mixture of diastereoisomers) as a brownish solid.

R_f (3/1 hexanes/EtOAc) = 0.33.

Mp = 173-175 °C (CH_2Cl_2).

^1H NMR (400 MHz, CDCl_3) δ 8.67-8.65 (m, 2H), 7.97-7.90 (m, 6H), 7.64-7.56 (m, 4H), 7.37-7.32 (m, 4H), 7.24-7.19 (m, 4H), 6.60-6.58 (m, 2H), 3.37 (d, J = 5.4 Hz, 1H), 3.17 (d, J = 5.3 Hz, 1H).

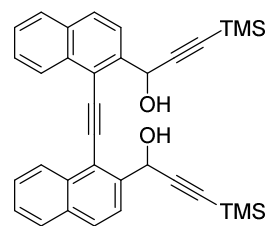
Major isomer: ^{13}C NMR (101 MHz, CDCl_3) δ 141.0 (2C), 134.7 (2C), 133.44 (2C), 133.1 (2C), 133.0 (4C), 129.7 (2C), 128.58 (4C), 128.4 (2C), 127.6 (2C), 126.97 (2C), 126.5 (2C), 124.3 (2C), 120.78 (2C), 119.0 (2C), 95.5 (2C), 89.48 (2C), 86.1 (2C), 64.11 (2C);

Minor isomer: ^{13}C NMR (101 MHz, CDCl_3) δ 140.9 (2C), 134.6 (2C), 133.37 (2C), 133.1 (2C), 128.55 (4C), 128.4 (2C), 126.95 (2C), 124.2 (2C), 120.75 (2C), 118.9 (2C), 95.6 (2C), 89.53 (2C), 86.0 (2C), 64.05 (2C); other peaks are covered by signals of the major isomer.

IR (KBr) ν 3369, 3061, 2226, 1703, 1592, 1568, 1488, 1401, 1263, 1222, 1093, 1012, 979, 827, 764 cm^{-1} .

HRMS (ESI $^+$): m/z calcd for $\text{C}_{40}\text{H}_{24}\text{O}_2\text{Cl}_2\text{Na}$ [(M+Na) $^+$]: 629.10456, found: 629.10394.

1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(3-(trimethylsilyl)prop-2-yn-1-ol) (1e).



According to the general procedure A with **S3a** (1.5 mmol, 502 mg), trimethylsilyl acetylene (4.5 mmol, 630 μL) and *n*-BuLi (4.5 mmol, 2.8 mL) in THF (40 mL). Column chromatography of the residue on silica gel (5/1 hexanes/EtOAc) furnished 738 mg (93%) of the title compound (an inseparable 2:1 mixture of diastereoisomers) as a light brown solid.

R_f (5/1 hexanes/EtOAc) = 0.29.

Mp = 79-84 °C (CH_2Cl_2).

^1H NMR (400 MHz, CDCl_3) δ 8.66-8.62 (m, 2H), 8.01-7.89 (m, 6H), 7.69-7.64 (m, 2H), 7.58 (ddd, J = 8.1, 6.8, 1.3 Hz, 2H), 6.37 (s, 1H), 6.36 (s, 1H), 0.198 (s, 9H), 0.195 (s, 9H).

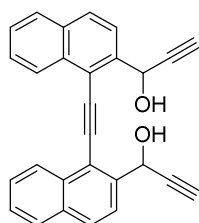
Major isomer: ^{13}C NMR (101 MHz, CDCl_3) δ 141.0 (2C), 133.54 (2C), 133.20 (2C), 129.6 (2C), 128.5 (2C), 127.6 (2C), 127.0 (2C), 126.69 (2C), 124.6 (2C), 119.4 (2C), 104.67 (2C), 95.6 (2C), 92.5 (2C), 64.2 (2C), -0.3 (6C);

Minor isomer: ^{13}C NMR (101 MHz, CDCl_3) δ 140.9 (2C), 133.49 (2C), 133.18 (2C), 129.7 (2C), 126.72 (2C), 124.4 (2C), 119.3 (2C), 104.74 (2C), 92.4 (2C), 64.1 (2C); other peaks are covered by signals of the major isomer.

IR (KBr) ν 3515, 3461, 3336, 3061, 2956, 2932, 2896, 2170, 1649, 1509, 1401, 1329, 1251, 1148, 1030, 1000, 842, 758 cm^{-1} .

HRMS (ESI⁺): m/z calcd for $\text{C}_{34}\text{H}_{34}\text{O}_2\text{Si}_2\text{Na}$ [(M+Na)⁺]: 553.19895, found: 553.19903.

1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(prop-2-yn-1-ol) (1f). K_2CO_3 (4.0



mmol, 553 mg) was added to a solution of **1e** (1.32 mmol, 700 mg) in a mixture of MeOH (40 mL) and H_2O (2 mL). The heterogeneous mixture was stirred for 2 hours at 0 °C. Then, the reaction mixture was quenched by HCl (1M), extracted with CH_2Cl_2 (3 × 100 mL), the combined organic fractions were washed with brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. Without further purification, the title compound was

obtained as a mixture of diastereoisomers and as a brownish solid (484 mg, 96%).

R_f (4/1 hexanes/EtOAc) = 0.14.

Mp = 169-171 °C (CH_2Cl_2).

^1H NMR (400 MHz, CDCl_3) δ 8.62 (d, J = 8.2 Hz, 2H), 7.97 (s, 4H), 7.93-7.90 (m, 2H), 7.69-7.63 (m, 2H), 7.61-7.57 (m, 2H), 6.39-6.37 (m, 2H), 2.96 (br s, 1H), 2.75 (s, 2H), 1.57 (br s, 1H).

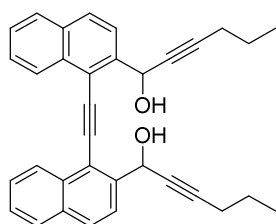
Major isomer: ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 143.1 (2C), 132.81 (2C), 132.80 (2C), 130.3 (2C), 129.1 (2C), 128.4 (2C), 127.6 (2C), 126.1 (2C), 124.26 (2C), 117.0 (2C), 95.2 (2C), 85.3 (2C), 76.71 (2C), 61.8 (2C);

Minor isomer: ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 143.0 (2C), 132.83 (2C), 128.5 (2C), 124.33 (2C), 117.1 (2C), 85.2 (2C), 76.73 (2C), 61.9 (2C); other peaks are covered by signals of the major isomer.

IR (KBr) ν 3511, 3458, 3069, 2958, 2894, 2171, 1612, 1507, 1405, 1250, 1148, 1035, 845, 759 cm^{-1} .

HRMS (ESI⁺): m/z calcd for $\text{C}_{28}\text{H}_{18}\text{O}_2\text{Na}$ [(M+Na)⁺]: 409.11990, found: 409.11999.

1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(hex-2-yn-1-ol) (1g). According to the



general procedure A with **S3a** (1.5 mmol, 502 mg), 1-pentyne (4.5 mmol, 450 μL) and $n\text{-BuLi}$ (4.5 mmol, 2.8 mL) in THF (40 mL). Column chromatography of the residue on silica gel (4/1 hexanes/EtOAc) furnished 627 mg (89%) of the title compound (an inseparable 2:1 mixture of diastereoisomers) as a yellow solid.

R_f (4/1 hexanes/EtOAc) = 0.21.

Mp = 154-159 °C (CH_2Cl_2).

^1H NMR (400 MHz, CDCl_3) δ 8.67-8.64 (m, 2H), 7.98-7.95 (m, 2H), 7.89-7.84 (m, 4H), 7.67-7.62 (m, 2H), 7.55 (ddd, J = 8.3, 6.9, 1.3 Hz, 2H), 6.43-6.41 (m, 2H), 3.76 (br s, 2H), 2.27 (td, J = 7.1, 2.1 Hz, 4H), 1.56 (sext, J = 7.3 Hz, 4H), 0.97 (td, J = 7.4, 1.1 Hz, 6H).

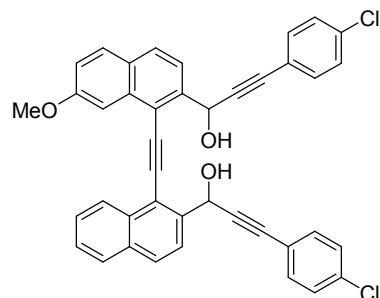
Major isomer: ^{13}C NMR (101 MHz, CDCl_3) δ 141.9 (2C), 133.4 (2C), 132.93 (2C), 129.4 (2C), 128.3 (2C), 127.3 (2C), 126.7 (2C), 126.56 (2C), 124.4 (2C), 118.8 (2C), 95.35 (2C), 88.04 (2C), 79.98 (2C), 63.7 (2C), 22.0 (2C), 20.9 (2C), 13.6 (2C);

Minor isomer: ^{13}C NMR (101 MHz, CDCl_3) δ 141.8 (2C), 133.3 (2C), 132.91 (2C), 126.64 (2C), 124.2 (2C), 118.7 (2C), 95.41 (2C), 87.96 (2C), 80.04 (2C), 63.6 (2C); other peaks are covered by signals of the major isomer.

IR (KBr) ν 3411, 3363, 3330, 3061, 2965, 2929, 2908, 2869, 2171, 1616, 1589, 1461, 1374, 1329, 1281, 1225, 1135, 1096, 1036, 994, 866, 830, 764 cm^{-1} .

HRMS (MALDI): m/z calcd for $\text{C}_{34}\text{H}_{30}\text{O}_2$ [M^+]: 470.2245, found: 470.2240.

3-(4-Chlorophenyl)-1-(1-((2-(3-(4-chlorophenyl)-1-hydroxyprop-2-yn-1-yl)-7-



methoxynaphthalen-1-yl)ethynyl)naphthalen-2-yl)prop-2-yn-1-ol (1h). Following the general procedure A with **S3b** (1.5 mmol, 547 mg), (4-chlorophenyl)acetylene (4.5 mmol, 615 mg) and *n*-BuLi (4.5 mmol, 2.8 mL) in THF (40 mL). Column chromatography of the residue on silica gel (3/1 hexanes/EtOAc) furnished 850 mg (89%) of the title compound (an inseparable 2:1 mixture of diastereoisomers) as a brownish solid.

R_f (3/1 hexanes/EtOAc) = 0.28.

Mp = 221.7 °C (CH_2Cl_2).

^1H NMR (400 MHz, CDCl_3) δ 8.75-8.70 (m, 1H), 7.99-7.76 (m, 7H), 7.59-7.53 (m, 2H), 7.35-7.30 (m, 4H), 7.24-7.16 (m, 5H), 6.63-6.61 (m, 1H), 6.57-6.54 (m, 1H), 3.98 (s, 3H), 3.65-3.57 (m, 1H), 3.46-3.40 (m, 1H).

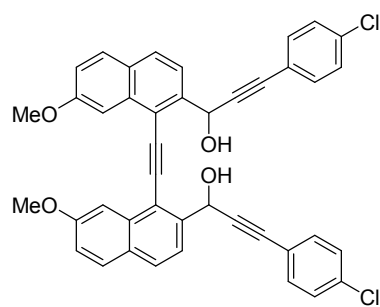
Major isomer: ^{13}C NMR (101 MHz, CDCl_3) δ 159.34, 141.5, 141.0, 135.3, 134.9, 134.80, 133.6, 133.3, 133.19 (2C), 133.17 (2C), 130.1, 129.7, 129.5, 128.8 (2C), 128.73 (2C), 127.5, 127.09, 126.5, 124.7, 122.2, 120.92, 120.86, 120.1, 119.4, 117.8, 104.69, 96.2, 95.8, 89.56, 89.49, 86.22, 86.14, 64.5, 64.32, 55.64 (2 carbon signals are probably covered by other signals);

Minor isomer: ^{13}C NMR (101 MHz, CDCl_3) δ 159.32, 141.4, 140.9, 135.1, 134.83, 134.78, 133.5, 133.25, 133.1, 128.70, 128.65, 127.4, 127.07, 124.5, 122.0, 119.35, 117.7, 104.71, 95.75, 89.59, 89.51, 86.24, 64.35, 64.2, 55.62; other peaks are covered by signals of the major isomer.

IR (KBr) ν 3315, 3055, 3004, 2941, 2911, 2830, 1706, 1619, 1491, 1269, 1225, 1180, 1096, 1036, 1018, 830, 761 cm^{-1} .

HRMS (ESI $^+$): m/z calcd for $\text{C}_{41}\text{H}_{26}\text{O}_3\text{Cl}_2\text{Na}$ [($\text{M}+\text{Na}$) $^+$]: 659.11512, found: 659.11424.

1,1'-(Ethyne-1,2-diylbis(7-methoxynaphthalene-1,2-diyl))bis(3-(4-chlorophenyl)prop-2-



yn-1-ol) (1i). In a flask were dissolved $\text{PdCl}_2(\text{PPh}_3)_2$ (0.21 mmol, 147 mg), CuI (0.42 mmol, 80 mg), 1-bromo-7-methoxy-2-naphthaldehyde **S1b** (4.2 mmol, 1.1 g) and 1-ethynyl-7-methoxy-2-naphthaldehyde **S2b** (4.2 mmol, 882 mg) in THF (17 mL) followed by addition of Et_3N (17 mL). The reaction mixture was stirred at reflux for 3 hours. Then, the reaction mixture was cooled down to 25 °C and filtered. The crude precipitate was, because of its low solubility, used

directly in the next step. According to the general procedure A with the precipitate of **S3c** (4.2

mmol, 1.7 g), (4-chlorophenyl)acetylene (12.6 mmol, 1.7 g) and *n*-BuLi (12.6 mmol, 7.9 mL) in THF (110 mL). Column chromatography of the residue on silica gel (linear gradient: 4/1 to 2/1 hexanes/EtOAc) furnished 1.3 g (46%) of the title compound (an inseparable 2:1 mixture of diastereoisomers) as a brown solid.

R_f (3/1 hexanes/EtOAc) = 0.25.

Mp = 192.8 °C (CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ 8.00 (br s, 2H), 7.91-7.81 (m, 6H), 7.37-7.33 (m, 4H), 7.29-7.21 (m, 6H), 6.62 (s, 2H), 3.97 (s, 6H), 3.19 (br s, 1H), 2.98 (br s, 1H).

Major isomer: ¹³C NMR (101 MHz, (CD₃)₂CO) δ 160.3 (2C), 143.78 (2C), 135.7 (2C), 134.84 (2C), 133.93 (4C), 131.01 (2C), 130.17 (2C), 129.52 (4C), 129.3 (2C), 122.79 (2C), 122.4 (2C), 120.2 (2C), 117.9 (2C), 105.8 (2C), 96.4 (2C), 92.13 (2C), 85.15 (2C), 64.10 (2C), 56.16 (2C);

Minor isomer: ¹³C NMR (101 MHz, (CD₃)₂CO) δ 143.80 (2C), 135.6 (2C), 134.83 (2C), 133.92 (4C), 131.03 (2C), 130.18 (2C), 129.50 (4C), 122.81 (2C), 120.1 (2C), 117.8 (2C), 105.9 (2C), 92.06 (2C), 85.14 (2C), 64.07 (2C), 56.14 (2C); other peaks are covered by signals of the major isomer.

IR (KBr) ν 3419, 3052, 2995, 2935, 2839, 2226, 2196, 1736, 1712, 1622, 1512, 1491, 1464, 1392, 1380, 1269, 1234, 1174, 1087, 1030, 1018, 845, 833, 719 cm⁻¹.

HRMS (ESI⁺): *m/z* calcd for C₄₂H₂₈O₄Cl₂Na [(M+Na)⁺]: 689.12569, found: 689.12601.

Note: Attempts to oxidize the prepared diol **1a** to the corresponding ketone failed. Although numerous oxidation procedures were applied (PCC in CH₂Cl₂; MnO₂ in Et₂O; IBX in THF/DMSO; NaOCl, Et₃NBnCl in CH₂Cl₂; Collins reagent in CH₂Cl₂), a complex reactions mixture was obtained each time. In most of the cases, formation of a mono-oxidation reaction products and some degradation products of the starting material were observed.

III: Optimization of Cyclotrimerization Reaction

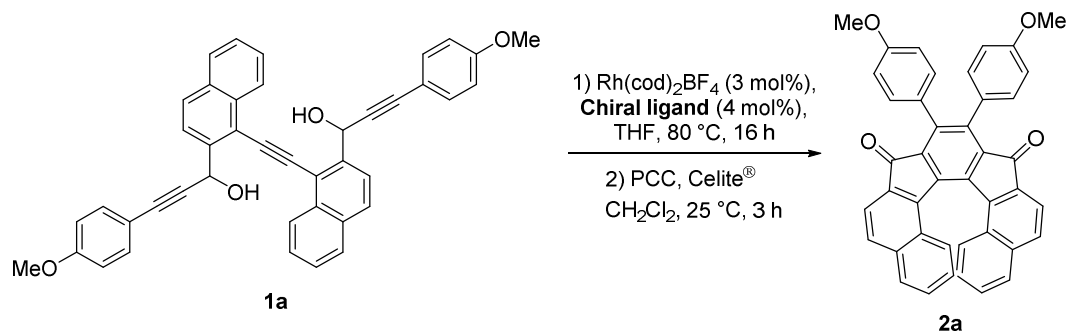
III.1. Screening of chiral ligands in enantioselective cyclotrimerization of **1a** in THF

Triynediol **1a** was chosen as a representative substrate to study catalytic enantioselective cyclotrimerization under different conditions by using combinations of $\text{Rh}(\text{cod})_2\text{BF}_4$ with various chiral ligands in THF at 80 °C for 16 h. Since upon cyclotrimerization a mixture of meso and rac diols was formed, the crude diols were directly oxidized with PCC in CH_2Cl_2 to the corresponding diketone **2a** to obtain a product with element of helical chirality only. The oxidation proceeded without erosion of its ee value. Although asymmetric induction of up to 60% ee (80:20 e.r.) was observed when BINAP or (R)-DBTM-Segphos were used (SI-Table 1), the reaction proved to be rather irreproducible with no obvious reason, as far as yields and asymmetric induction were concerned.

Representative procedure for enantioselective cyclotrimerization using rhodium catalyst and chiral ligand.

A dry microwave vial was charged with $\text{Rh}(\text{cod})_2\text{BF}_4$ (2.4 mg, 0.006 mmol), a chiral ligand (0.008 mmol), and were dissolved under argon atmosphere in THF (2 mL). Afterwards H_2 gas was bubbled through the reaction to activate the catalytic system (3 × 5 min). Then starting material **1a** (120 mg, 0.2 mmol) was added, the reaction vessel was sealed and heated up to 80°C for 16 h while stirring. The reaction mixture was cooled down to 25 °C and the solvent was evaporated under reduced pressure. The crude diol was added to a solution of pyridinium chlorochromate (130 mg, 0.6 mmol) and Celite® (120 mg) in anhydrous CH_2Cl_2 (20 mL) and the reaction mixture was stirred for 3 h at 25 °C. Then the reaction mixture was filtered through a Celite®/silica gel plug and the filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica gel yielded product **2a**.

Table S1. Screening of ligand for catalytic enantioselective cyclotrimerization of **1a** in THF and subsequent oxidation to **2a**.

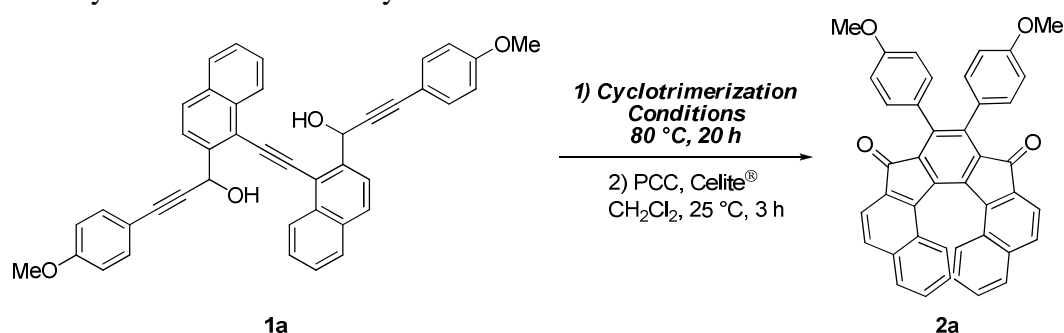


Entry	Ligand	e.r. ^a
1	(<i>R</i>)-BINAP	80:20
2	(<i>R</i>)-DM-BINAP	78:22
3	(<i>R</i>)-DM-Segphos	76:24
4	(<i>R</i>)-DBTM-Segphos	80:20
5	(<i>R</i>)-MeO-BIPHEP	71:29
6	(<i>R</i>)-DM-Garphos	77:23
7	(<i>R</i>)-DBTM-Garphos	61:39
8	(<i>R</i>)-Ph-Garphos	75:25
9	(<i>R</i>)-DMM-Garphos	75:25
10	(<i>R</i>)-DTFM-Garphos	55:45
11	SL J001-1	66:34
12	SL J003-1	54:46
13	SL T002-1	56:44
14	SL W002-1	49:51
15	SL M001-1	39:61

^a ees (e.r.) were determined by HPLC using a column with a chiral stationary phase

III.2. Representative screening of cyclotrimerization of **1a** in various solvents.

In order to avoid irreproducibility of yields of the aforementioned cyclotrimerizations in THF, various reaction media were screened (SI-Table 2). Cyclotrimerizations were catalyzed by a combination of Rh(cod)₂BF₄ (5 mol%) and dppb (6 mol%) in various solvents at 80 °C on 0.1 mmol scale. It was found that the aforementioned problem regarding reproducibility of yields disappeared when CH₂ClCH₂Cl was used and yields were significantly increased.

Table S2. Cyclotrimerization of triynediol **1a** to **2a** in various solvents.

Entry	Catalyst (mol%)	Ligand (mol%)	Solvent	Yield (%) ^a
1	Cp*Ru(cod)Cl (5)		CH ₂ ClCH ₂ Cl	traces
2	[Rh(cod) ₂]BF ₄ (5)	dppb (8)	THF	17
3	[Rh(cod) ₂]BF ₄ (5)	dppb (8)	MTBE	0
4	[Rh(cod) ₂]BF ₄ (5)	dppb (8)	Me-THF	traces
5	[Rh(cod) ₂]BF ₄ (5)	dppb (8)	CH ₂ Cl ₂	<20 ^b
6	[Rh(cod) ₂]BF ₄ (5)	dppb (8)	CH ₂ ClCH ₂ Cl	59

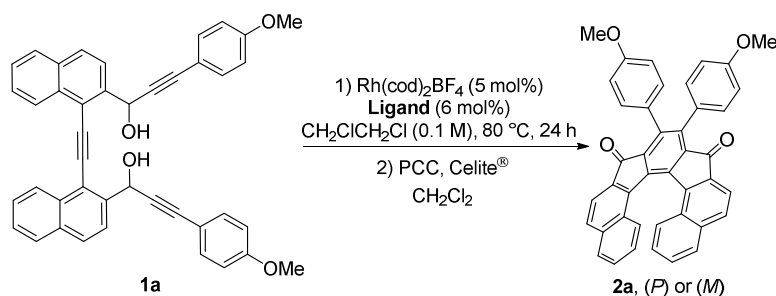
^a Isolated yield. ^b Isolated with 90% purity.

III.3. Screening of different chiral phosphines.

Thus further reactions were run in the presence of mixtures of Rh(cod)₂BF₄ (5 mol%) and chiral phosphines (6 or 12 mol%) in CH₂ClCH₂Cl at 80 °C on 0.1 mmol scale. Once again the crude diol was oxidized to diketone **2a** prior to analysis (Table 3).

The use of monodentate (*R*)-PROPOS, phosphoramidite based ligands such as (*S*)-MonoPhos and (*S*)-*H*₈-MonoPhos, and (*R,R*)-Tartrate provided **2a** with unsatisfactory results: the yields as well as asymmetric induction did not exceed 20% and 36% ee (32:68 e.r) (Entries 1-4).

Then, BINAP based ligands were screened (Entries 5-8). In general, diketone **2a** was obtained in good isolated yields ranging from 42 to 62% and, gratifyingly, with excellent enantioselectivity up to 92% (96:4 e.r.) when the (*R*)-*H*₈-BINAP ligand was used (Entry 7). In addition, other chiral ligands such as GarphosTM, DIFLUOROPHOS and BIPHEP derivatives were evaluated as well (Entries 9-14). Unfortunately, none of these ligands provided better results than (*R*)-*H*₈-BINAP in terms of yields and asymmetric induction (ees up to 90%, e.r. up to 95:5). Finally, SEGPHOS[®] based ligands were tested (Entries 15-17). One of the best result was obtained with (*S*)-SEGPHOS[®] and giving rise to **2a** in a very good isolated yield of 74% and 90% ee (e.r. of 5:95) (Entry 15). The use (*S*)-DM-SEGPHOS[®] which have substituted phenyl rings on the phosphorus atom did not have substantial effect on asymmetric induction (Entry 16). However, application of a more bulkier ligand such as (*R*)-DTBM-SEGPHOS[®] gave **2a** with drastically decreased asymmetric induction as well as the yield (Entry 17).

Table S3. Ligand screening for the enantioselective [2+2+2] cyclotrimerization of triynediol **1a**.

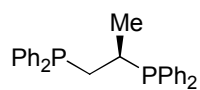
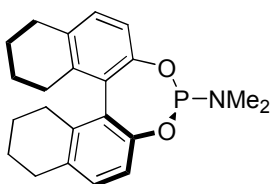
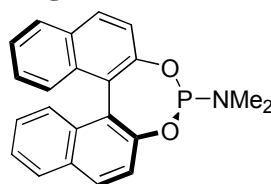
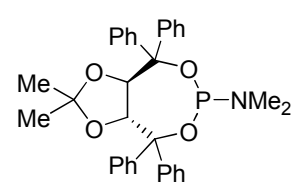
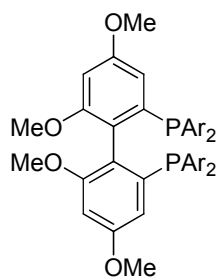
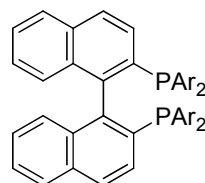
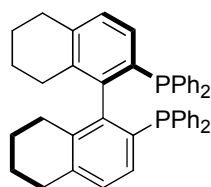
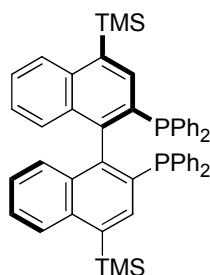
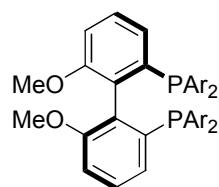
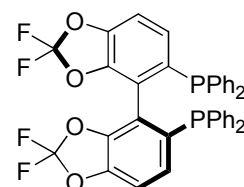
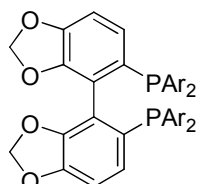
Entry ^a	Ligand	Yield (%) ^b	ee (%) ^c	e.r. (%) ^c	Config. ^d
1	(<i>R</i>)-PROPHOS	10	8	54:46	<i>M</i>
2	(<i>S</i>)-MonoPhos	20	36	32:68	<i>P</i>
3	(<i>S</i>)- <i>H</i> ₈ -MonoPhos	20	34	67:33	<i>M</i>
4	(<i>R,R</i>)-Tartrate	20	22	61:39	<i>M</i>
5	(<i>R</i>)-BINAP	55	76	88:12	<i>M</i>
6	(<i>S</i>)-DM-BINAP	55	86	7:93	<i>P</i>
7	(<i>R</i>)- <i>H</i> ₈ -BINAP	62	92	96:4	<i>M</i>
8	(<i>R</i>)-TMS-BINAP	42	90	95:5	<i>M</i>
9	(<i>R</i>)-Garphos TM	45	84	92:8	<i>M</i>
10	(<i>R</i>)-Tol-Garphos TM	51	86	93:7	<i>M</i>
11	(<i>S</i>)-DM-Garphos TM	50	90	5:95	<i>P</i>
12	(<i>R</i>)-DMM-Garphos TM	62	70	85:15	<i>M</i>
13	(<i>S</i>)-DIFLUOROPHOS	48	86	7:93	<i>P</i>
14	(<i>R</i>)-DM-MeO-BIPHEP	49	90	95:5	<i>M</i>
15	(<i>S</i>)-SEGPHOS [®]	74	90	5:95	<i>P</i>
16	(<i>S</i>)-DM-SEGPHOS [®]	50	88	6:94	<i>P</i>
17	(<i>R</i>)-DTBM-SEGPHOS [®]	20	26	62:38	<i>M</i>

^a Reaction conditions: **1a** (0.1 mmol), Rh(cod)₂BF₄ (5 mol%), Ligand (6 mol%) in CH₂ClCH₂Cl (1 mL) at 80 °C for 24 h. ^b Isolated yields. ^c ees (e.r.) were determined by HPLC using a column with a chiral stationary phase. ^d Configuration of the major enantiomer. Absolute configuration was assigned retrospectively on the basis of X-ray diffraction analysis of **2d** (vide infra).

Although the best result in terms of asymmetric induction was obtained with (*R*)-*H*₈-BINAP (Entry 5), the SEGPHOS[®] ligands (*S* or *R*) (Entry 15), were used for further experiments because of good combination of high enantioselectivity and conversion of the starting material to products.

Note: It should be stressed that for a successful course of the reaction it is necessary to use meticulously dried and purified dichloroethane. If this condition is not met, both yield as well as asymmetric induction drops down.

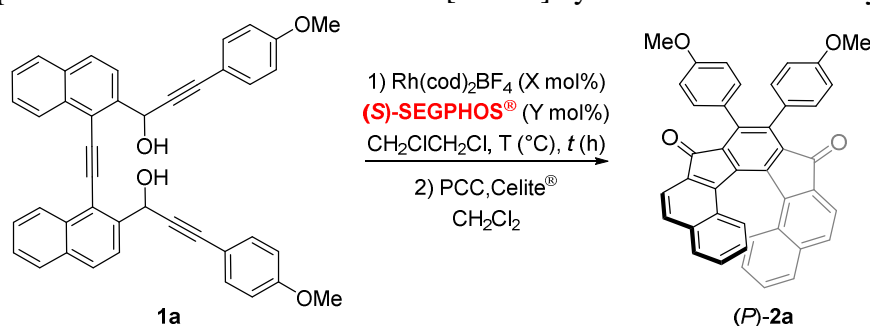
List of chiral ligands

*(R)*-PROPHOS*(S)*-H₈-MonoPhos*(S)*-Phosphoramidite*(R,R)*-tartrateAr = xyl
(S)-xyl-GarphosAr = 3,5-(Me)₂-4-MeO-C₆H₂
(R)-DMM-GarphosAr = Ph
(R)-BINAPAr = xyl
(S)-xyl-BINAP*(R)*-H₈-BINAP*(R)*-TMS-BINAPAr = xyl
(R)-MeO-BIPHEP*(S)*-DIFLUORPHOSAr = Ph
(S)-SEGPHOSAr = 3,5-(*t*-Bu)₂-4-MeO-C₆H₂
(R)-DTBM-SEGPHOS

III.4. Screening of different chiral phosphines.

Next, we focused our attention on other factors such as solvent, temperature or catalytic loading in order to increase asymmetric induction in the [2+2+2] cyclotrimerization (SI-Table 4). It is important to highlight that $\text{CH}_2\text{ClCH}_2\text{Cl}$ is a crucial parameter, in fact the reaction did not proceed in other solvents or gave lower isolated yield (see SI-Table 2). Then temperature effect on the course of reaction was evaluated. We were pleased to notice that running the reaction at 60 °C, the desired product (*P*)-**2a** was obtained in 76% isolated yield and the excellent enantiomeric ratio of 3:97 (Entry 2). Decreasing temperature to 50 °C substantially reduced the reaction rate giving **2a** in trace amounts only as detected by ^1H NMR analysis of the crude reaction mixture (Entry 3). Trace amounts of **2a** were also detected when 1 mol% of the catalyst was used at 60 or 70 °C (Entries 4 and 5).

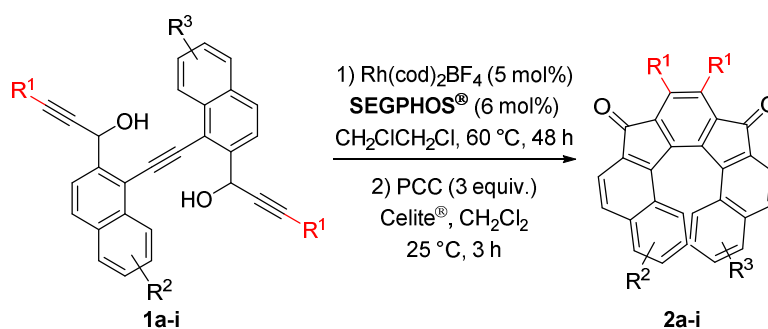
Table S4. Optimization of the enantioselective [2+2+2] cyclotrimerization of triynediol **1a**.



Entry	Cat. (mol%)	Ligand (mol%)	T (°C)	t (h)	Yield (%) ^a	ee (%) ^b	e.r. (%) ^b
1	5	6	80	24	74 ^c	90	5:95
2	5	6	60	48	76 ^c	94	3:97
3	5	6	50	48	traces	n.d.	-
4	1	1.5	60	48	traces	n.d.	-
5	1	1.5	70	48	traces	n.d.	-

^a Isolated yield. ^b ees were determined by HPLC using a column with a chiral stationary phase. n.d.: not determined. ^c Full consumption of **2a**.

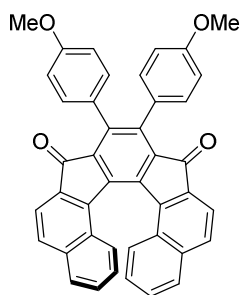
IV Enantioselective [2+2+2] Cyclotrimerization and Oxidation Reactions



General procedure for enantioselective [2+2+2] cyclotrimerization followed by oxidation reaction (GP-A). A dry microwave vial was charged with Rh(cod)₂BF₄ (0.05 mmol, 20.3 mg) and (*S*)- or (*R*)-SEGPHOS[®] (0.06 mmol, 36.6 mg) in dry CH₂ClCH₂Cl (11 mL) under argon atmosphere. H₂ gas was bubbled into the reaction mixture for 45 min.⁴ Afterwards, the corresponding triynediol **1** (1 mmol) was added under argon atmosphere. The reaction was stirred at 60 °C for 48 hours unless otherwise mentioned. Then, the reaction mixture was concentrated under reduced pressure. The crude diols were directly oxidized to the corresponding diketone **2** without any further purification. To a solution of the crude diols in dry CH₂Cl₂ (100 mL) under argon atmosphere, pyridinium chlorochromate (3.0 mmol, 647 mg) and Celite[®] (700 mg) were added. The resulting mixture was stirred at 25 °C for 3 hours. Afterwards, the reaction mixture was filtered through a pad of 1:4 silica gel/Celite[®]. Then, the pad was washed using CH₂Cl₂ and the filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica gel provided products **2**.

The absolute configuration of helical **3d** possessing two *para*-chlorophenyl moieties was determined to be *P* by the anomalous dispersion method. This find allowed us to retrospectively assess configuration of all obtained helical compounds.

⁴ I. Thiel, M. Horstmann, P. Jungk, S. Keller, F. Fisher, H.-J. Drexler, D. Heller, M. Hapke, *Chem. Eur. J.*, **2017**, *23*, 17048-17057.

(P)-8,9-Bis(4-methoxyphenyl)benzo[c]benzo[6,7]indeno[1,2-g]fluorene-7,10-dione ((P)-

2a). According to the general procedure **GP-A** with **1a** (1.0 mmol, 600 mg) and (*S*)-SEGPHOS[®] (0.06 mmol, 36.6 mg). Column chromatography on silica gel (5/1/1 hexanes/EtOAc/CH₂Cl₂) furnished 416 mg (70%) of the title compound as a red solid.

R_f (5/1/1 hexanes/EtOAc/CH₂Cl₂) = 0.33.

Mp (decomp) >260 °C (CH₂Cl₂).

$[\alpha]_D^{20} +1939$ (*c* 0.56, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.85-7.80 (m, 4H), 7.33-7.24 (m, 4H), 7.17-7.15 (m, 2H), 6.90-6.84 (m, 4H), 6.78-6.76 (m, 2H), 6.65 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2H), 3.81 (s, 6H).

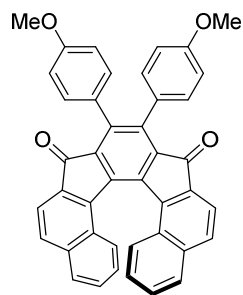
¹³C NMR (101 MHz, CDCl₃) δ 191.4 (2C), 159.0 (2C), 145.1 (2C), 142.3 (2C), 138.6 (2C), 137.8 (2C), 137.2 (2C), 134.2 (2C), 131.8 (2C), 130.9 (2C), 128.8 (2C), 128.7 (2C), 128.5 (2C), 128.4 (2C), 127.1 (2C), 126.7 (2C), 125.7 (2C), 119.8 (2C), 113.2 (2C), 113.0 (2C), 55.1 (2C).

IR (KBr) ν 3052, 2930, 2833, 1704, 1609, 1516, 1441, 1291, 1249, 1178, 1109, 1035, 901, 835, 800, 777 cm⁻¹.

HRMS (ESI⁺): *m/z* calcd for C₄₂H₂₇O₄ [(M+H)⁺]: 595.19039, found: 595.19049.

HPLC analysis: 8:92 e.r. (column YMC CHIRAL Cellulose-SB (Heptane/*i*-PrOH = 80/20, flow rate 1 mL/min, UV 254 nm, *t*_{min} = 14.5 min; *t*_{major} = 21.1 min).

Racemic			(<i>S</i>)-SEGPHOS [®] , 8:92 e.r		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	14.6	49.6	1	14.5	7.7
2	21.2	50.4	2	21.1	92.3

(M)-8,9-Bis(4-methoxyphenyl)benzo[c]benzo[6,7]indeno[1,2-g]fluorene-7,10-dione ((M)-

2a). According to the general procedure **GP-A** with **1a** (1.0 mmol, 600 mg) and (*R*)-SEGPHOS[®] (0.06 mmol, 36.6 mg). Column chromatography on silica gel (5/1/1 hexanes/EtOAc/CH₂Cl₂) furnished 315 mg (53%) of the title compound as a red solid.

R_f (5/1/1 hexanes/EtOAc/CH₂Cl₂) = 0.33.

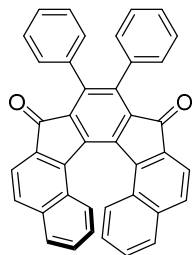
$[\alpha]_D^{20}$ -2784 (*c* 0.23, CHCl₃).

HPLC analysis: 94:6 e.r. (column YMC CHIRAL Cellulose-SB (Heptane/*i*-PrOH = 80/20, flow rate 1 mL/min, UV 254 nm, t_{major} = 14.6

min; t_{min} = 21.5 min).

Racemic			(<i>R</i>)-SEGPHOS [®] , 94:6 e.r		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	14.6	49.6	1	14.6	93.5
2	21.2	50.4	2	21.5	6.5

(P)-8,9-Diphenylbenzo[*c*]benzo[6,7]indeno[1,2-*g*]fluorene-7,10-dione ((P)-2b). According to the general procedure **GP-A** with **1b** (1.0 mmol, 539 mg) and (*S*)-SEGPHOS® (0.06 mmol, 36.6 mg). Column chromatography on silica gel (8/1/1 hexanes/EtOAc/CH₂Cl₂) furnished 470 mg (88%) of the title compound as a red solid. *R_f*(8/1/1 hexanes/EtOAc/CH₂Cl₂) = 0.40.



Mp (decomp) >260 °C (CH₂Cl₂).

[α]_D²⁰ +1824 (*c* 0.39, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.36-7.30 (m, 4H), 7.29-7.20 (m, 8H), 7.01 (d, *J* = 6.9 Hz, 2H), 6.69 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 2H).

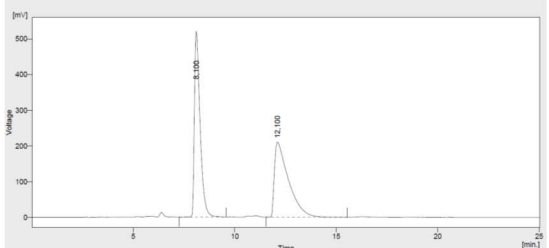
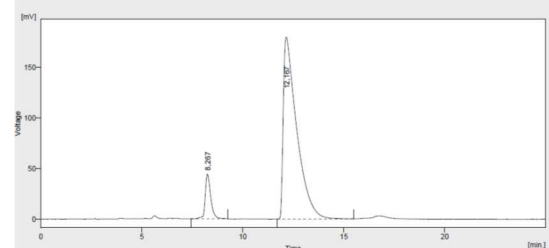
¹³C NMR (101 MHz, CDCl₃) δ 191.3, 145.3, 142.2, 138.8, 137.9, 137.4, 135.0, 134.2, 131.0, 130.3, 129.4, 128.9, 128.8, 128.6, 127.7, 127.61, 127.55, 126.8, 125.8, 119.9.

IR (KBr) ν 3054, 2919, 1710, 1617, 1570, 1464, 1419, 1375, 1304, 1197, 1074, 1025, 936, 830, 766, 752, 716, 701 cm⁻¹.

HRMS (ESI⁺): *m/z* calcd for C₄₀H₂₃O₂ [(M+H)⁺]: 535.16926, found: 535.16935.

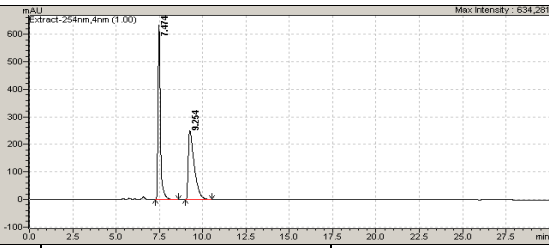
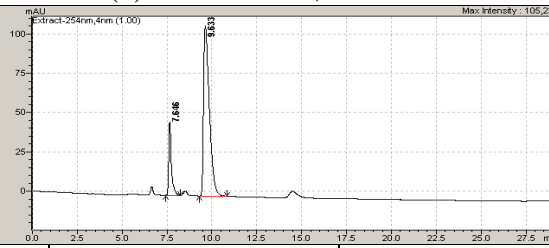
1st batch:

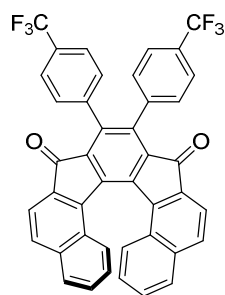
HPLC analysis: 9:91 e.r. (column YMC Chiral Cellulose-SB, Heptane/CH₂Cl₂ = 80/20, flow rate 1.0 mL/min, UV 254 nm, *t*_{min} = 8.3 min; *t*_{major} = 12.2 min).

Racemic			<i>(S)</i> -SEGPHOS® , 9:91 e.r.		
					
N°	Retention time (min)	Relative area (%)	N°	Retention time (min)	Relative area (%)
1	8.1	50.1	1	8.3	9.1
2	12.1	49.9	2	12.2	90.9

2nd batch:

HPLC analysis: 16:84 e.r. (Column Daicel Chiralpak IB, Heptane/CH₂Cl₂ = 80:20, flow rate 1.0 mL/min, UV 254 nm).

Racemic			<i>(S)</i> -SEGPHOS® , 16:84 e.r.		
					
N°	Retention time (min)	Relative area (%)	N°	Retention time (min)	Relative area (%)
1	7.5	50.0	1	7.6	16.2
2	9.3	50.0	2	9.2	83.8

(P)-8,9-Bis(4-(trifluoromethyl)phenyl)benzo[c]benzo[6,7]indeno[1,2-g]fluorene-7,10-

dione ((P)-2c). According to the general procedure GP-A with **1c** (1.0 mmol, 675 mg) and (*S*)-SEGPHOS[®] (0.06 mmol, 36.6 mg). Column chromatography on silica gel (8/1/1 hexanes/EtOAc/CH₂Cl₂) furnished 536 mg (80%) of the title compound as a red solid.

R_f (8/1/1 hexanes/EtOAc/CH₂Cl₂) = 0.42.

Mp (decomp) >260 °C (CH₂Cl₂).

$[\alpha]_D^{20} +1573$ (*c* 0.53, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.61-7.46 (m, 4H), 7.45-7.22 (m, 6H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.71 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 191.0 (2C), 145.2 (2C), 139.9 (2C), 139.4 (2C), 138.4 (2C), 138.1 (2C), 137.5 (2C), 134.0 (2C), 131.6 (2C), 130.7 (2C), 130.0 (q, ²*J*_{C-F} = 32.4 Hz) (2C), 129.8 (2C), 129.1 (2C), 129.0 (2C), 128.6 (2C), 126.7 (2C), 126.1 (2C), 124.9 (q, ³*J*_{C-F} = 5.8 Hz) (2C), 124.1 (q, ¹*J*_{C-F} = 272.2 Hz) (2C), 119.9 (2C); one signal of two carbons is missing probably due to the overlapped signals.

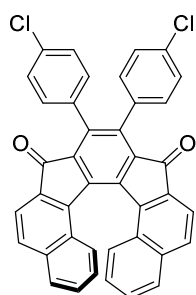
¹⁹F NMR (376.5 MHz, CDCl₃) δ -62.57.

IR (KBr) ν 3072, 3041, 2920, 1711, 1605, 1469, 1404, 1329, 1170, 1127, 1067, 1019, 934, 855, 757, 721 cm⁻¹.

HRMS (ESI⁺): *m/z* calcd for C₄₂H₂₁O₂F₆ [(M+H)⁺]: 671.14403, found: 671.14394.

HPLC analysis: 90:10 e.r. (column YMC Chiral Cellulose-SB (Heptane/CH₂Cl₂ = 80/20, flow rate 1 mL/min, UV 254 nm, *t*_{major} = 5.6 min; *t*_{min} = 8.1 min).

Racemic			(<i>S</i>)-SEGPHOS [®] , 90:10 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	5.7	50.4	1	5.6	89.9
2	8.0	49.6	2	8.1	10.1

(P)-8,9-Bis(4-chlorophenyl)benzo[c]benzo[6,7]indeno[1,2-g]fluorene-7,10-dione ((P)-2d).

According to the general procedure **GP-A** with **1d** (1.0 mmol, 608 mg) and (*S*)-SEGPHOS[®] (0.06 mmol, 36.6 mg). Column chromatography on silica gel (10/1/1 hexanes/EtOAc/CH₂Cl₂) furnished 341 mg (57%) of the title compound as a red solid.

R_f (10/1/1 hexanes/EtOAc/CH₂Cl₂) = 0.35.

Mp (decomp) >260 °C (CH₂Cl₂).

$[\alpha]_D^{20}$ +2026 (*c* 1.00, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.33 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 2H), 7.29-7.26 (m, 2H), 7.24-7.20 (m, 4H), 7.10 (dd, *J* = 8.2, 2.2 Hz, 2H), 6.91 (dd, *J* = 8.2, 2.2 Hz, 2H), 6.66 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 2H).

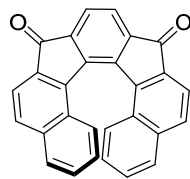
¹³C NMR (101 MHz, CDCl₃) δ 190.9 (2C), 144.9 (2C), 140.3 (2C), 138.9 (2C), 137.8 (2C), 137.3 (2C), 133.9 (2C), 133.8 (2C), 133.0 (2C), 131.7 (2C), 131.2 (2C), 130.7 (2C), 128.9 (2C), 128.8 (2C), 128.4 (2C), 128.01 (2C), 127.97 (2C), 126.5 (2C), 125.8 (2C), 119.7 (2C).

IR (KBr) ν 3061, 2923, 2851, 1706, 1616, 1583, 1440, 1371, 1302, 1266, 1237, 1096, 1015, 905, 833, 776 cm⁻¹.

HRMS (APCI): *m/z* calcd for C₄₀H₂₁Cl₂O₂ [(M+H)⁺]: 603.09131, found: 603.09092.

HPLC analysis: 4:96 e.r. (column YMC CHIRAL Cellulose-SB (Heptane/*i*-PrOH = 80/20, flow rate 1 mL/min, UV 254 nm, t_{\min} = 8.2 min; t_{major} = 11.0 min).

Racemic			(S)-SEGPHOS [®] , 4:96 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	8.2	50.1	1	8.2	3.8
2	11.3	49.9	2	11.0	96.2

(P)-Benzo[c]benzo[6,7]indeno[1,2-g]fluorene-7,10-dione ((P)-2f). (Pathway A)

to the general procedure **GP-A** with **1e** (1.0 mmol, 531 mg) and (*S*)-SEGPHOS[®] (0.06 mmol, 36.6 mg). Afterwards, the crude mixture was concentrated under reduced pressure, then dissolved in MeOH/H₂O (40/1) and stirred in presence of K₂CO₃ (3.0 mmol, 415 mg) for 2 hours at 0 °C. Then, the reaction mixture was quenched by using HCl (1M), extracted with

CH₂Cl₂ (3× 100 mL). The combined organic fractions were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Column chromatography on silica gel (7/1/1 hexanes/CH₂Cl₂/EtOAc) furnished 76 mg (20%) of the title compound as a red solid.

[α]_D²⁰ -327 (*c* 0.39, CHCl₃).

Mp (decomp) >260 °C (CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ 7.95-7.90 (m, 4H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.72 (s, 2H), 7.34 (ddd, *J* = 8.2, 6.8, 1.1 Hz, 2H), 7.28-7.26 (m, 2H), 6.67 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 191.9 (2C), 146.4 (2C), 142.3 (2C), 139.1 (2C), 137.7 (2C), 133.9 (2C), 131.2 (2C), 129.1 (2C), 128.8 (2C), 128.7 (2C), 127.0 (2C), 125.9 (2C), 124.0 (2C), 120.1 (2C).

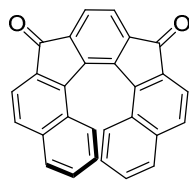
IR (KBr) ν 3052, 2929, 2854, 1700, 1622, 1455, 1401, 1272, 1242, 1195, 1099, 1039, 994, 872, 830, 767 cm⁻¹.

HRMS (APCI): *m/z* calcd for C₂₈H₁₅O₂ [(M+H)⁺]: 383.10666, found: 383.10667.

HPLC analysis: 69:31 e.r. (column YMC Chiral Cellulose-SB, Heptane/CH₂Cl₂ = 50/50, flow rate 0.5 mL/min, UV 254 nm, *t*_{major} = 7.7 min; *t*_{min} = 10.0 min).

Racemic			<i>(S)</i> -SEGPHOS [®] , 69:31 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	7.6	49.8	1	7.7	68.7
2	9.7	50.2	2	10.0	31.3

(P)-Benzo[c]benzo[6,7]indeno[1,2-g]fluorene-7,10-dione ((P)-2f). (Pathway B) According to the general procedure **GP-A** with **1f** (1.0 mmol, 387 mg) and (*S*)-SEGPHOS[®] (0.06 mmol, 36.6 mg). Column chromatography on silica gel (7/1/1 hexanes/CH₂Cl₂/EtOAc) furnished 164 mg (43%) of the title compound as a red solid.

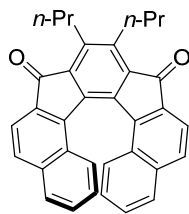


$[\alpha]_D^{20}$ -307 (*c* 0.14, CHCl₃).

HPLC analysis: 61:39 e.r. (column YMC Chiral Cellulose-SB, Heptane/CH₂Cl₂ = 50/50, flow rate 0.5 mL/min, UV 254 nm, t_{major} = 7.6 min; t_{min} = 9.7 min).

Racemic			<i>(S)</i> -SEGPHOS [®] , 61:39 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	7.6	49.8	1	7.6	60.8
2	9.7	50.2	2	9.7	39.2

(P)-8,9-Dipropylbenzo[*c*]benzo[6,7]indeno[1,2-*g*]fluorene-7,10-dione ((P)-2g). According to the general procedure GP-A with **1g** (1.0 mmol, 471 mg) and (*S*)-SEGPPOS® (0.06 mmol, 36.6 mg). Column chromatography on silica gel (3/2 hexanes/CH₂Cl₂) furnished 304 mg (65%) of the title compound as a red solid.



R_f (3/2 hexanes/CH₂Cl₂) = 0.35.

Mp = 108-113 °C (CH₂Cl₂).

$[\alpha]_D^{20}$ +1478 (*c* 0.18, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.88-7.83 (m, 4H), 7.79 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.28-7.24 (m, 2H), 7.18 (dd, *J* = 8.5, 1.1 Hz, 2H), 6.59 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 2H), 3.35-3.27 (m, 2H), 3.11-3.04 (m, 2H), 1.75-1.55 (m, 4H), 1.15 (t *J* = 7.3 Hz, 6H).

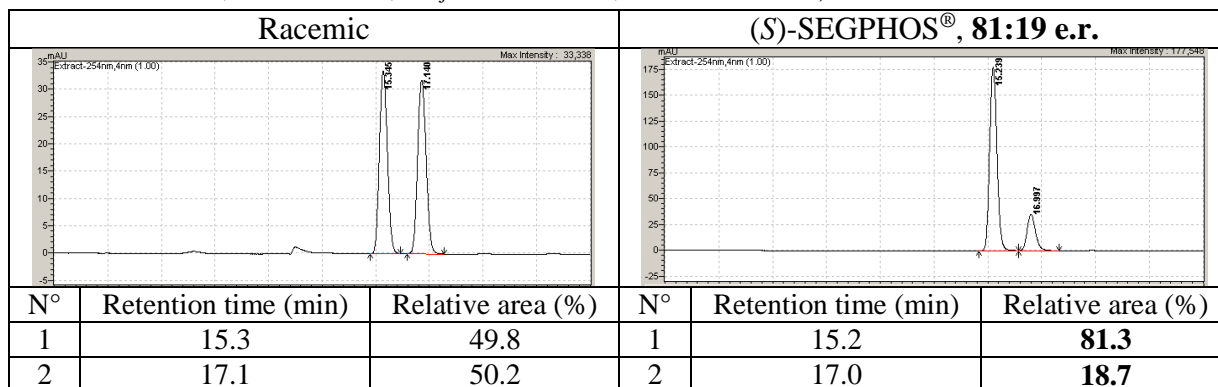
¹³C NMR (101 MHz, CDCl₃) δ 193.4 (2C), 145.4 (2C), 145.2 (2C), 137.7 (2C), 137.4 (2C), 137.3 (2C), 134.1 (2C), 130.5 (2C), 128.7 (2C), 128.6 (2C), 128.4 (2C), 126.8 (2C), 125.6 (2C), 119.7 (2C), 28.4 (2C), 24.6 (2C), 14.8 (2C).

IR (KBr) ν 3046, 2965, 2929, 2869, 1703, 1619, 1589, 1452, 1365, 1269, 1237, 1204, 1030, 982, 869, 833, 779, 755 cm⁻¹.

HRMS (MALDI): *m/z* calcd for C₃₄H₂₆O₂ [M⁺]: 466.19273, found: 466.19270.

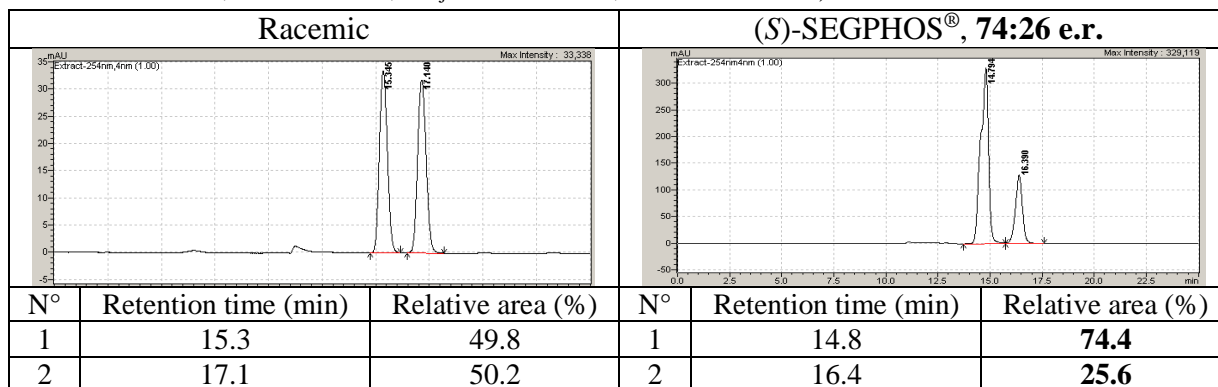
1st batch:

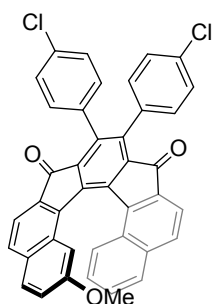
HPLC analysis: 81:19 e.r. (column Daicel Chiralpak® AD-H (Heptane/*i*-PrOH = 98/2, flow rate 0.3 mL/min, UV 254 nm, *t*_{major} = 15.2 min; *t*_{min} = 17.0 min).



2nd batch:

HPLC analysis: 74:26 e.r. (column Daicel Chiralpak® AD-H (Heptane/*i*-PrOH = 98/2, flow rate 0.3 mL/min, UV 254 nm, *t*_{major} = 14.8 min; *t*_{min} = 16.4 min).



(P)-8,9-Bis(4-chlorophenyl)-2-methoxybenzo[*c*]benzo[6,7]indeno[1,2-*g*]fluorene-7,10-

dione ((P)-2h). According to the general procedure **GP-A** with **1h** (1.0 mmol, 638 mg) and (*S*)-SEGPHOS[®] (0.06 mmol, 36.6 mg) at 80 °C for 48 hours. Column chromatography of the residue on silica gel (9/1/1 hexanes/EtOAc/CH₂Cl₂) furnished 158 mg (25%) of the title compound as a red solid.

R_f (9/1/1 hexanes/EtOAc/CH₂Cl₂) = 0.32.

Mp (decomp) 161 °C (CH₂Cl₂).

$[\alpha]_D^{20} +796$ (c 0.14, CHCl₃).

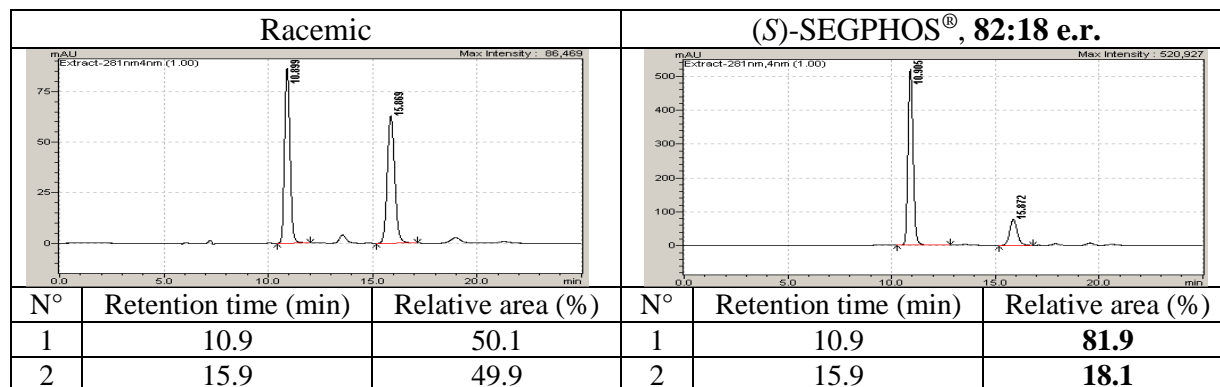
¹H NMR (400 MHz, CDCl₃) δ 7.92-7.86 (m, 3H), 7.81 (d, J = 8.2 Hz, 1H), 7.75 (dd, J = 9.1, 1.5 Hz, 1H), 7.69 (dd, J = 8.0, 1.5 Hz, 1H), 7.43-7.39 (m, 2H), 7.29-7.21 (m, 4H), 7.14-7.10 (m, 2H), 6.99 (dd, J = 8.9, 2.5 Hz, 1H), 9.95-6.90 (m, 2H), 6.80 (ddd, J = 8.3, 7.0, 1.2 Hz, 1H), 6.57 (d, J = 2.5 Hz, 1H), 2.69 (s, 3H).

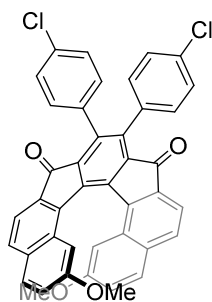
¹³C NMR (101 MHz, CDCl₃) δ 191.3, 191.2, 158.1, 145.3, 143.6, 140.5, 140.3, 139.8, 138.6, 138.3, 138.2, 137.5, 134.7, 134.0, 133.95 (2C), 133.2, 133.13, 133.12, 131.7, 131.1, 130.81 (2C), 130.79, 130.7, 130.4, 130.0, 129.5, 129.1, 128.7, 128.2 (2C), 128.1, 126.6, 126.2, 122.4, 120.1, 117.9, 104.9, 76.8, 54.1.

IR (KBr) ν 3058, 3025, 2998, 2956, 2926, 2833, 1709, 1628, 1580, 1494, 1467, 1431, 1395, 1371, 1314, 1299, 1266, 1234, 1222, 1204, 1171, 1096, 1030, 1015, 845, 833, 767, 743 cm⁻¹.

HRMS (APCI): m/z calcd for C₄₁H₂₃Cl₂O₃ [(M+H)⁺]: 633.10188, found: 633.10151.

HPLC analysis: 82:18 e.r. (column Chiralpak IA (Heptane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, UV 281 nm, t_{maj} = 10.9 min; t_{min} = 15.9 min).



(P)-8,9-Bis(4-chlorophenyl)-2,15-dimethoxybenzo[c]benzo[6,7]indeno[1,2-g]fluorene-

7,10-dione ((P)-2i). According to the general procedure **GP-A** with **1i** (1.0 mmol, 668 mg) and (*S*)-SEGPHOS[®] (0.06 mmol, 36.6 mg) at 80 °C for 7 days. Column chromatography of the residue on silica gel (linear gradient: 10/1/1 to 8/1/1 hexanes/EtOAc/CH₂Cl₂) furnished 164 mg (23%) of the title compound as a red solid. *R_f* (8/1/1 hexanes/EtOAc/CH₂Cl₂) = 0.35.

Mp = 371 °C (CH₂Cl₂).

$[\alpha]_D^{20}$ +1297 (*c* 0.29, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 9.1 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.28-7.21 (m, 4H), 7.12 (dd, *J* = 8.1, 2.2 Hz, 2H), 7.06 (dd, *J* = 9.0, 2.5 Hz, 2H), 6.92 (dd, *J* = 8.2, 2.2 Hz, 2H), 6.70 (d, *J* = 2.5 Hz, 2H), 2.74 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 191.3 (2C), 158.2 (2C), 143.6 (2C), 140.3 (2C), 139.3 (2C), 138.4 (2C), 134.6 (2C), 134.0 (2C), 133.23 (2C), 133.15 (2C), 131.7 (2C), 130.8 (2C), 130.6 (2C), 130.5 (2C), 130.2 (2C), 128.24 (2C), 128.16 (2C), 123.0 (2C), 118.1 (2C), 104.7 (2C), 54.3 (2C).

IR (KBr) ν 3061, 3001, 2956, 2932, 2830, 1709, 1622, 1583, 1467, 1431, 1377, 1302, 1272, 1225, 1204, 1177, 1162, 1132, 1093, 1015, 848, 815 cm⁻¹.

HRMS (APCI): *m/z* calcd for C₄₂H₂₅Cl₂O₄ [(M+H)⁺]: 663.11244, found: 663.11227.

1st batch:

HPLC analysis: 81:19 e.r. (column Chiralpak IA (Heptane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, UV 285 nm, *t*_{maj} = 11.1 min; *t*_{min} = 21.1 min).

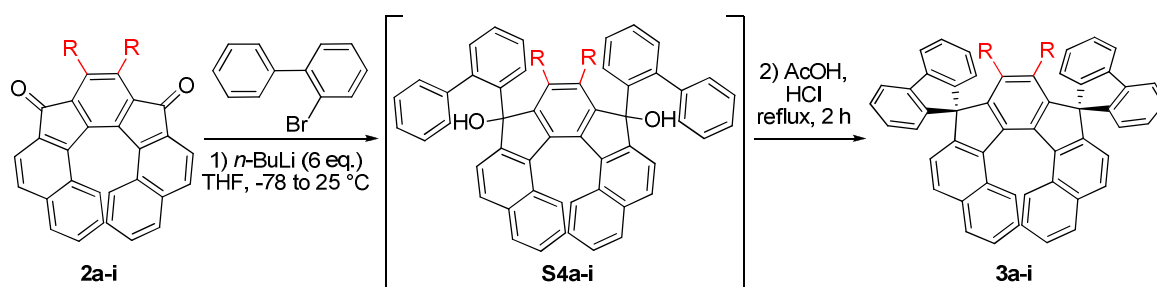
Racemic			(<i>S</i>)-SEGPHOS [®] , 81:19 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	11.0	50.1	1	11.1	81.3
2	21.1	49.9	2	21.1	18.7

2nd batch:

HPLC analysis: 88:12 e.r. (column Chiralpak IA (Heptane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, UV 285 nm, *t*_{maj} = 11.1 min; *t*_{min} = 21.1 min).

Racemic			(<i>S</i>)-SEGPHOS [®] , 88:12 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	11.0	50.1	1	11.1	88.5
2	21.1	49.9	2	21.1	11.5

V Synthesis of Dispiro-9,5'-indeno[2,1-c]fluorene-8',9''-fluorenes



The conversion of **2** to **3** was carried out in two steps. In the first step was arylated **2** to alcohol **S4** (**GP-B**). The crude alcohol **S4** was without characterization and further purification converted to spiro compounds **3** under various conditions (**GP-C1-4**).

General procedure for conversion of 2 to S4 (GP-B).⁵ *n*-BuLi 1.6 M (6.0 equiv.) was added dropwise to a solution of 2-bromobiphenyl (6.0 equiv.) in dry THF at -78 °C. The resulting mixture was stirred for 1 hour at the same temperature, followed by the dropwise addition of **2** (1.0 equiv.) in dry THF and stirred for 30 min at -78 °C and afterwards, it was allowed to reach ambient temperature and stirred overnight. Then, the reaction mixture was poured into a saturated aqueous NH₄Cl solution and extracted with CH₂Cl₂ (3 times). The combined organic fractions were dried over Na₂SO₄, filtered and concentrated under reduced pressure. Flash column chromatography on silica gel was performed to yield the corresponding crude alcohol **S4**.

General procedures for conversion of S4 to 3 (GP-C). Preparative scale carried out with the 1st batch of 2.

GP-C1 The alcohol **S4** was dissolved in acetic acid (25 mL) and HCl (12 M, 0.5 mL) and refluxed for 2 hours. The resulting mixture was neutralized with a saturated aqueous K₂CO₃ solution, extracted with CH₂Cl₂ (3 times), dried over Na₂SO₄, filtered and concentrated under reduced pressure. Column chromatography on silica gel of the residue afforded desired bispiro-compounds **3**.

Reaction on analytical scale were carried out with crude alcohols S4 obtained from the 2nd batch of 2.

GP-C2 The alcohol **S4** (0.1 mmol) was dissolved in acetic acid (5 mL) and HCl (12 M, 0.1 mL) and refluxed for 2 hours. The resulting mixture was neutralized with the saturated aqueous K₂CO₃ solution, extracted with CH₂Cl₂ (3 times), dried over Na₂SO₄, filtered and concentrated under reduced pressure.

Column chromatography on silica gel of the residue afforded **3**.

GP-C3 The alcohol **S4** (0.1 mmol) was dissolved in acetic acid (5 mL) and HCl (12 M, 0.1 mL) and refluxed for 2 hours. The resulting mixture was neutralized with the saturated

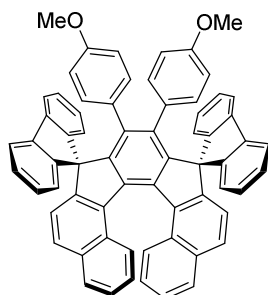
⁵ Z. Jiang, H. Yao, Z. Zhang, C. Yang, Z. Liu, Y. Tao, J. Qin, D. Ma; *Org. Lett.* **2009**, *11* 2607-2610.

aqueous K_2CO_3 solution, extracted with CH_2Cl_2 (3 times), dried over Na_2SO_4 , filtered and concentrated under reduced pressure.

Preparative thin layer chromatography on silica gel of the residue afforded **3**.

GP-C4 The alcohol **S4** (0.1 mmol) was dissolved in CH_2Cl_2 (2 mL) then trifluoroacetic anhydride (0.22 mmol, 40 μL) was added at 0 °C and stirred for 1 hour. Afterwards, the reaction was heated at 50 °C for 2 hours. After complete consumption of the alcohol, the reaction was cooled down to room temperature and washed by H_2O , dried over Na_2SO_4 , filtered and concentrated under reduced pressure.

Preparative thin layer chromatography on silica gel of the residue afforded **3**.

(P)-8',9'-Bis(4-methoxyphenyl)dispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-g]-

fluorene-10',9''-fluorene] ((P)-3a). According to the GP-B and GP-C1 with (P)-2a (0.25 mmol, 150 mg), *n*-BuLi (1.5 mmol, 0.94 mL) and 2-bromobiphenyl (1.5 mmol, 260 μ L) in THF (15 mL). Column chromatography of the residue on silica gel (8/1 hexanes/EtOAc) furnished 178 mg (82%) of the title compound as a yellowish solid.

R_f (8/1 hexanes/EtOAc) = 0.28. Mp (decomp) >260 °C (CH₂Cl₂);

$[\alpha]_D^{20} +363$ (*c* 0.63, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.36-7.30 (m, 6H), 7.26-7.20 (m, 4H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.92 (t, *J* = 7.5 Hz, 2H), 6.78-6.70 (m, 6H), 5.90 (dd, *J* = 8.4, 2.8 Hz, 2H), 5.77 (dd, *J* = 8.4, 2.6 Hz, 2H), 5.69 (m, 4H), 3.52 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 156.6 (2C), 148.6 (2C), 148.3 (2C), 147.8 (2C), 147.4 (2C), 142.9 (2C), 142.1 (2C), 139.1 (2C), 138.0 (2C), 136.4 (2C), 133.5 (2C), 131.6 (2C), 129.9 (2C), 129.7 (2C), 129.0 (2C), 128.9 (2C), 128.2 (2C), 127.5 (2C), 127.4 (2C), 127.3 (2C), 127.2 (2C), 127.1 (2C), 125.2 (2C), 124.6 (2C), 124.2 (2C), 124.0 (2C), 121.4 (2C), 120.3 (2C), 119.6 (2C), 111.6 (2C), 111.2 (2C), 67.0 (2C), 55.1 (2C).

IR (KBr) ν 3052, 3052, 2832, 1611, 1516, 1448, 1364, 1285, 1244, 1175, 1107, 1035, 815, 739 cm⁻¹.

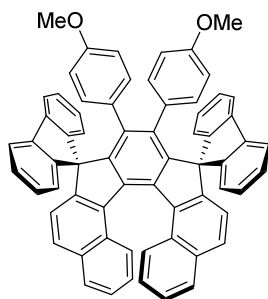
HRMS (ESI⁺): *m/z* calcd for C₆₆H₄₃O₂ [(M+H)⁺]: 867.32576, found: 867.32593.

HPLC analysis: 93:7 e.r. (column YMC CHIRAL Cellulose-SB (Heptane/*i*-PrOH = 80/20, flow rate 1 mL/min, UV 254 nm, t_{major} = 4.5 min; t_{min} = 5.2 min).

Racemic			(S)-SEGPHOS [®] , 93:7 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	4.5	48.8	1	4.5	92.6
2	5.3	51.2	2	5.2	7.4

After precipitation from the CH₂Cl₂ solution by MeOH:

Racemic			(S)-SEGPHOS [®] , 97:3 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	5.4	49.1	1	5.4	97.3
2	6.4	50.9	2	6.4	2.7

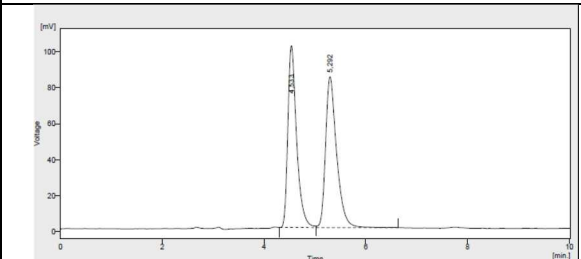
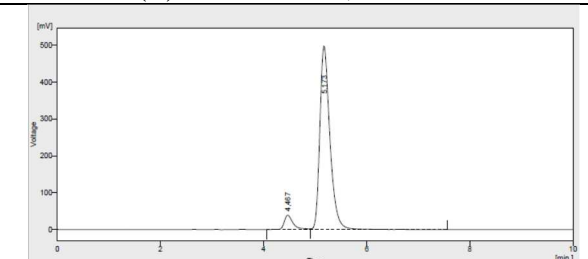
(M)-8',9'-Bis(4-methoxyphenyl)dispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-g]-

fluorene-10',9''-fluorene] ((M)-3a). According to GP-B and GP-C1 with (M)-2a (0.25 mmol, 150 mg), *n*-BuLi (1.5 mmol, 0.94 mL) and 2-bromobiphenyl (1.5 mmol, 260 μ L) in THF (15 mL). Column chromatography of the residue on silica gel (8/1 hexanes/EtOAc) furnished 147 mg (68%) of the title compound as a yellowish solid.

$[\alpha]_D^{20}$ -258 (*c* 0.88, CHCl₃).

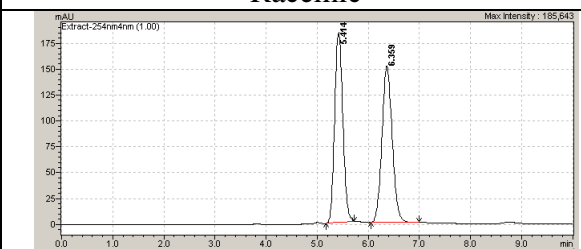
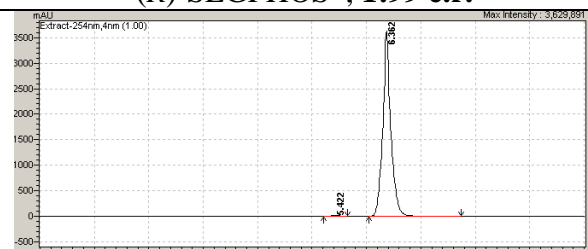
HPLC analysis: 6:94 e.r. (column YMC CHIRAL Cellulose-SB (Heptane/*i*-PrOH = 80/20, flow rate 1 mL/min, UV 254 nm, t_{\min} = 4.5

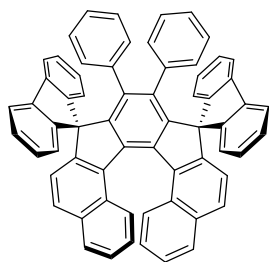
min; t_{major} = 5.2 min).

Racemic			(R)-SEGPHOS[®], 6:94 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	4.5	48.8	1	4.5	6.5
2	5.3	51.2	2	5.2	93.5

After precipitation from the CH₂Cl₂ solution by MeOH:

Column Chiralpak IB, Heptane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, UV 254 nm

Racemic			(R)-SEGPHOS[®], 1:99 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	5.4	49.1	1	5.4	0.6
2	6.4	50.9	2	6.4	99.4

(P)-8',9'-Diphenyldispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-g]fluorene-10',9''-

fluorene] ((*P*)-**3b**). According to the GP-B and GP-C1 with (*P*)-**2b** (0.20 mmol, 120 mg), *n*-BuLi (1.2 mmol, 0.75 mL) and 2-bromobiphenyl (1.2 mmol, 210 μ L) in THF (12 mL). Column chromatography of the residue on silica gel (10/1 hexanes/EtOAc) furnished 72.6 mg (45%) of the title compound as a yellowish solid.

R_f (10/1 hexanes/EtOAc) = 0.58.

Mp (decomp) >260 °C (CH₂Cl₂).

$[\alpha]_D^{20}$ +140 (*c* 0.43, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.37-7.31 (m, 4H), 7.27-7.21 (m, 6H), 7.05 (dt, *J* = 7.5, 1.1 Hz, 2H), 6.91 (dt, *J* = 7.5, 1.1 Hz, 2H), 6.79-6.71 (m, 6H), 6.50 (dt, *J* = 7.5, 1.1 Hz, 2H), 6.34 (t, *J* = 7.4 Hz, 2H), 6.18 (dt, *J* = 7.5 Hz, 2H), 5.78 (t, *J* = 7.4 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 148.6 (2C), 148.2 (2C), 147.6 (2C), 146.8 (2C), 142.9 (2C), 142.1 (2C), 139.0 (2C), 137.9 (2C), 136.5 (2C), 136.1 (2C), 133.5 (2C), 130.5 (2C), 129.7 (2C), 129.2 (2C), 129.1 (2C), 128.2 (2C), 127.5 (2C), 127.45 (2C), 127.38 (2C), 127.2 (2C), 127.1 (2C), 125.7 (2C), 125.5 (2C), 125.2 (2C), 124.7 (2C), 124.6 (2C), 124.2 (2C), 124.0 (2C), 121.4 (2C), 120.4 (2C), 119.7 (2C), 67.0 (2C).

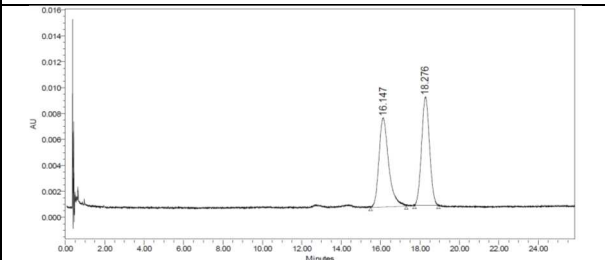
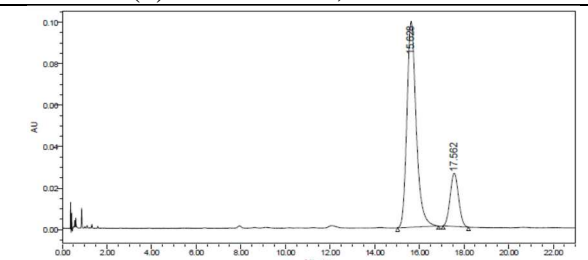
IR (KBr) ν 3049, 3018, 2956, 2922, 2853, 1602, 1515, 1446, 1280, 1239, 1215, 1177, 1149, 1032, 810, 741, 696 cm⁻¹.

HRMS (APCI): *m/z* calcd for C₆₄H₃₉ [(M+H)⁺]: 807.30463, found: 807.30471.

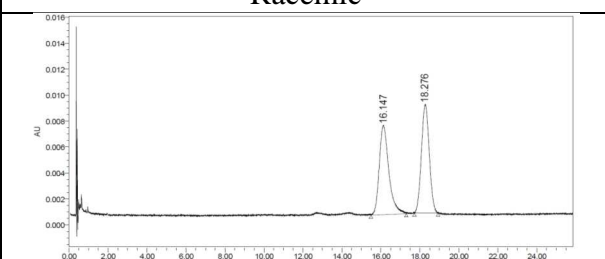
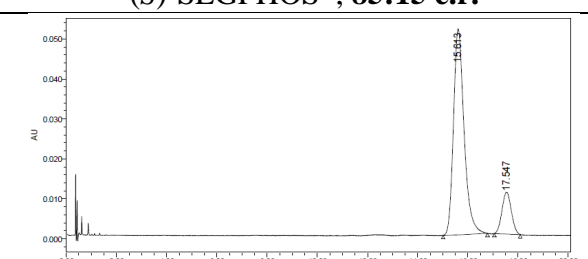
SFC analysis: 66:34 e.r. (Column CHIRAL ART Cellulose-SB (150 x 3 mm I.D., particle size 3 μ m), column temperature 40 °C, sample temperature 10 °C, back pressure 2000 psi, carbone dioxide/*i*-PrOH = 80:20, flow rate 2.0 mL/min, UV 254 nm, t_{major} = 16.2 min; t_{min} = 18.4 min).

Racemic			(S)-SEGPHOS [®] , 66:34 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	16.1	50.06	1	16.2	65.8
2	18.3	49.94	2	18.4	34.2

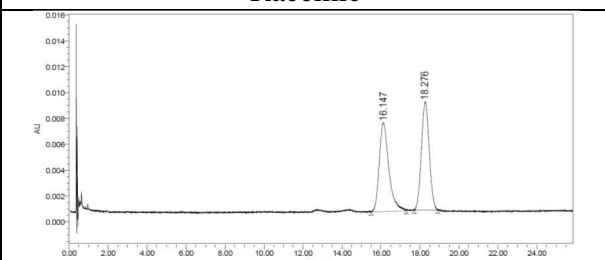
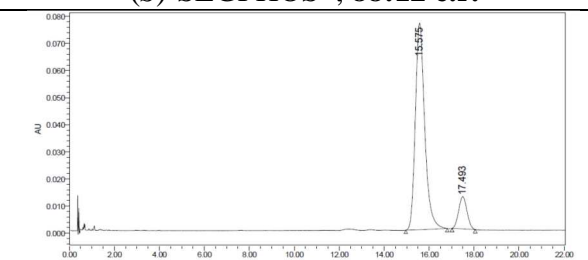
According to the **GP-C2**.

Racemic			<i>(S)</i> -SEGPHOS [®] , 81:19 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	16.1	50.06	1	15.6	81.0
2	18.3	49.94	2	17.6	19.0

According to the **GP-C3**.

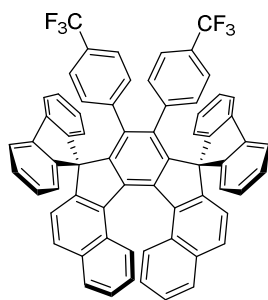
Racemic			<i>(S)</i> -SEGPHOS [®] , 85:15 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	16.1	50.06	1	15.6	84.8
2	18.3	49.94	2	17.5	15.2

According to the **GP-C4**.

Racemic			<i>(S)</i> -SEGPHOS [®] , 88:12 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	16.1	50.06	1	15.6	87.9
2	18.3	49.94	2	17.5	12.1

(P)-8',9'-Bis(4-(trifluoromethyl)phenyl)dispiro[fluorene-9,7'-

benzo[*c*]benzo[6,7]indeno[1,2-*g*]fluorene-10',9''-fluorene] ((P)-3c). According to the **GP-B** and **GP-C1** with **(P)-2c** (0.30 mmol, 120 mg), *n*-BuLi (1.8 mmol, 1.13 mL) and 2-bromobiphenyl (1.8 mmol, 310 μ L) in THF (15 mL). Column chromatography of the residue on silica gel (15/1 hexanes/Acetone) furnished 219 mg (77%) of the title compound as a yellowish solid.



R_f (15/1 hexanes/Acetone) = 0.30.

Mp (decomp) >260 °C (CH₂Cl₂).

$[\alpha]_D^{20}$ +246 (*c* 0.36, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.44-7.32 (m, 4H), 7.32-7.18 (m, 6H), 7.13 (td, *J* = 7.5, 1.2 Hz, 2H), 6.97 (td, *J* = 7.5, 1.2 Hz, 2H), 6.86-6.77 (m, 4H), 6.74 (d, *J* = 7.5 Hz, 2H), 6.67 (m, 2H), 6.55-6.44 (m, 2H), 5.95 (t, *J* = 7.4 Hz, 4H).

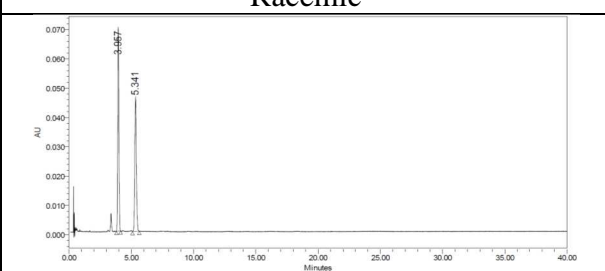
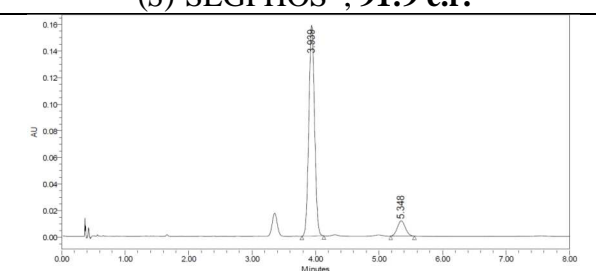
¹³C NMR (101 MHz, CDCl₃) δ 148.4 (2C), 147.5 (2C), 147.2 (2C), 147.1 (2C), 142.8 (2C), 142.0 (2C), 139.5 (2C), 138.6 (2C), 137.2 (2C), 135.6 (2C), 133.6 (2C), 130.6 (2C), 129.72 (2C), 129.67 (2C), 129.3 (2C), 128.4 (2C), 128.0 (2C), 127.6 (4C), 127.35 (2C), 127.31 (2C), 127.0 (q, ²*J*_{C-F} = 32.0 Hz) (2C), 125.5 (2C), 125.45 (2C), 124.8 (2C), 124.14 (2C), 124.11 (q, ¹*J*_{C-F} = 272.0 Hz) (2C), 124.08 (2C), 122.8 (q, ³*J*_{C-F} = 3.4 Hz) (2C), 121.4 (2C), 120.5 (2C), 120.0 (2C), 66.8 (2C).

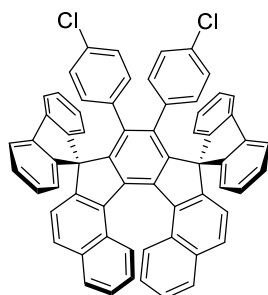
¹⁹F NMR (376.5 MHz, CDCl₃) δ -62.93.

IR (KBr) ν 3056, 2922, 2866, 1619, 1446, 1405, 1325, 1246, 1166, 1125, 1079, 1018, 810, 738 cm⁻¹.

HRMS (APCI): *m/z* calcd for C₆₆H₃₇F₆ [(M+H)⁺]: 943.27940, found: 943.27954.

SFC analysis: 91:9 e.r. (Column CHIRAL ART Cellulose-SB (150 x 3 mm I.D., particle size 3 μ m), column temperature 40 °C, sample temperature 10 °C, back pressure 2000 psi, carbone dioxide/*i*-PrOH = 80:20, flow rate 2.0 mL/min, UV 254 nm, *t*_{major} = 3.9 min; *t*_{min} = 5.3 min).

Racemic			(S)-SEGPHOS[®], 91:9 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	4.0	52.07	1	3.9	90.9
2	5.3	47.93	2	5.3	9.1

(P)-8',9'-Bis(4-chlorophenyl)dispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-

g]fluorene-10',9''-fluorene] ((P)-3d). According to the GP-B and GP-C1 with (P)-2d (0.20 mmol, 120 mg), *n*-BuLi (1.2 mmol, 0.75 mL) and 2-bromobiphenyl (1.2 mmol, 210 μ L) in THF (12 mL). Column chromatography of the residue on silica gel (10/1 hexanes/EtOAc) furnished 71 mg (40%) of the title compound as a yellowish solid.

R_f (10/1 hexanes/EtOAc) = 0.42.

Mp (decomp) >260 °C (CH₂Cl₂).

$[\alpha]_D^{20} +396$ (*c* 0.40, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.86-7.81 (m, 4H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.52 (dt, *J* = 7.6, 1.0 Hz, 2H), 7.38-7.32 (m, 4H), 7.29-7.20 (m, 6H), 7.12 (td, *J* = 7.5, 1.1 Hz, 2H), 6.92 (td, *J* = 7.5, 1.1 Hz, 2H), 6.77-6.73 (m, 4H), 6.68 (d, *J* = 7.6 Hz, 2H), 6.33 (dd, *J* = 8.4, 2.3 Hz, 2H), 6.18 (dd, *J* = 8.5, 2.3 Hz, 2H), 5.68 (ddt, *J* = 6.4, 4.3, 2.0 Hz, 4H).

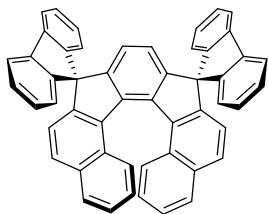
¹³C NMR (101 MHz, CDCl₃) δ 148.4 (2C), 147.7 (2C), 147.4 (2C), 147.3 (2C), 142.9 (2C), 142.1 (2C), 138.8 (2C), 136.9 (2C), 136.2 (2C), 134.4 (2C), 133.5 (2C), 131.7 (2C), 131.1 (2C), 130.3 (2C), 129.7 (2C), 129.5 (2C), 128.3 (2C), 127.8 (2C), 127.53 (2C), 127.49 (2C), 127.34 (2C), 127.26 (2C), 126.1 (2C), 125.8 (2C), 125.4 (2C), 124.7 (2C), 124.2 (2C), 124.0 (2C), 121.4 (2C), 120.5 (2C), 119.8 (2C), 66.9 (2C).

IR (KBr) ν 3049, 2498, 1715, 1497, 1449, 1395, 1365, 1222, 1093, 1021, 815, 737 cm⁻¹.

HRMS (APCI): *m/z* calcd for C₆₄H₃₇Cl₂ [(M+H)⁺]: 875.22668, found: 875.22685.

SFC analysis: 99:1 e.r. (Column CHIRAL ART Cellulose-SB (150 x 3 mm I.D., particle size 3 μ m), column temperature 40 °C, sample temperature 10 °C, back pressure 2000 psi, carbone dioxide/*i*-PrOH = 80:20, flow rate 2.0 mL/min, UV 254 nm, t_{major} = 12.7 min; t_{min} = 16.9 min).

Racemic			(S)-SEGPPOS [®] , 99:1 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	12.6	50.41	1	12.7	99.4
2	16.6	49.59	2	16.9	0.6

(P)-Dispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-g]fluorene-10',9''-fluorene] ((*P*)-**3f**).

According to the GP-B and GP-C1 with (*P*)-**2f** (0.4 mmol, 150 mg), *n*-BuLi (2.4 mmol, 1.5 mL) and 2-bromobiphenyl (2.4 mmol, 410 μ L) in THF (20 mL). Column chromatography of the residue on silica gel (9/1/1 hexanes/EtOAc/CH₂Cl₂) furnished 78.6 mg (30%) of the title compound as a colorless solid.

R_f (9/1/1 hexanes/EtOAc/CH₂Cl₂) = 0.47.

Mp (decomp) >260 °C (CH₂Cl₂).

$[\alpha]_D^{20}$ -174 (*c* 0.35, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.95 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.91-7.84 (m, 6H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.40 (tt, *J* = 7.5, 1.3 Hz, 4H), 7.30-7.26 (m, 2H), 7.21-7.14 (m, 4H), 7.10 (dt, *J* = 7.5, 1.2 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.8 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 2H), 6.74 (m, 2H), 6.58 (s, 2H).

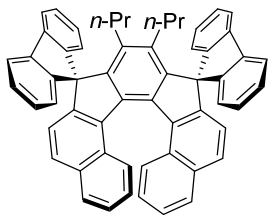
¹³C NMR (101 MHz, CDCl₃) δ 150.4 (2C), 148.3 (2C), 148.1 (2C), 147.9 (2C), 142.5 (2C), 141.9 (2C), 139.8 (2C), 136.8 (2C), 133.7 (2C), 129.7 (2C), 129.2 (2C), 128.3 (2C), 128.1 (2C), 128.03 (2C), 127.98 (2C), 127.9 (2C), 127.6 (2C), 125.4 (2C), 124.7 (4C), 124.0 (2C), 121.6 (2C), 121.5 (2C), 120.5 (2C), 120.1 (2C), 66.9 (2C).

IR (KBr) ν 3055, 2974, 2929, 2851, 1580, 1476, 1449, 1437, 1359, 1269, 1213, 1177, 1111, 1078, 815, 749, 698 cm⁻¹.

HRMS (MALDI): *m/z* calcd for C₅₂H₃₀ [M⁺]: 654.23475, found: 654.23480.

SFC analysis: 27.5:72.5 e.r. (Column CHIRAL ART Cellulose-SB (150 x 3 mm I.D., particle size 3 μ m), column temperature 40 °C, sample temperature 10 °C, back pressure 2000 psi, carbone dioxide/*i*-PrOH = 80:20, flow rate 2.0 mL/min, UV 254 nm, t_{\min} = 12.8 min; t_{\max} = 14.6 min).

Racemic			<i>(S)</i> -SEGPPOS [®] , 27.5:72.5 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	12.7	50.0	1	12.8	27.5
2	14.4	50.0	2	14.6	72.5

(P)-8',9'-Dipropyldispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-g]fluorene-10',9''-

fluorene] ((*P*)-**3g**). According to the GP-B and GP-C1 with (*P*)-**2g** (0.30 mmol, 140 mg), *n*-BuLi (1.8 mmol, 1.15 mL) and 2-bromobiphenyl (1.8 mmol, 310 μ L) in THF (18 mL). Column chromatography of the residue on silica gel (15/1 hexanes/EtOAc) furnished 154 mg (69%) of the title compound as a orange solid.

R_f (15/1 hexanes/EtOAc) = 0.40.

Mp = 238-240 °C (CH₂Cl₂).

$[\alpha]_D^{20}$ +38 (*c* 0.54, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.94 (ddt, *J* = 7.6, 3.1, 0.9 Hz, 4H), 7.77 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.72 (dd, *J* = 8.5, 1.1 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.47-7.36 (m, 4H), 7.24-7.14 (m, 6H), 7.11 (td, *J* = 7.5, 1.1 Hz, 2H), 6.80 (d, *J* = 7.6 Hz, 2H), 6.73 (d, *J* = 8.3 Hz, 2H), 6.67 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2H), 1.94-1.79 (m, 2H), 1.72-1.65 (m, 2H), 0.76-0.65 (m, 2H), 0.28-0.17 (m, 8H).

¹³C NMR (101 MHz, CDCl₃) δ 148.9 (2C), 148.5 (2C), 148.2 (2C), 147.1 (2C), 142.5 (2C), 141.8 (2C), 139.0 (2C), 137.2 (2C), 135.7 (2C), 133.3 (2C), 129.5 (2C), 128.6 (2C), 128.08 (2C), 128.06 (2C), 128.0 (2C), 127.9 (2C), 127.8 (2C), 127.4 (2C), 125.1 (2C), 124.5 (2C), 124.4 (4C), 121.1 (2C), 120.5 (2C), 120.1 (2C), 67.3 (2C), 30.4 (2C), 24.1 (2C), 14.7 (2C).

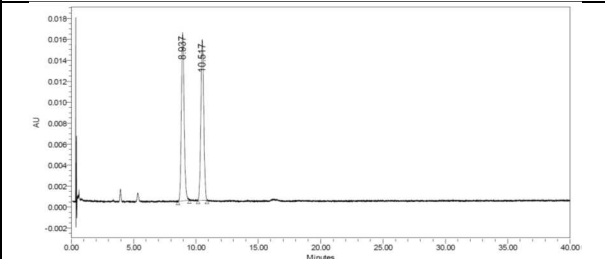
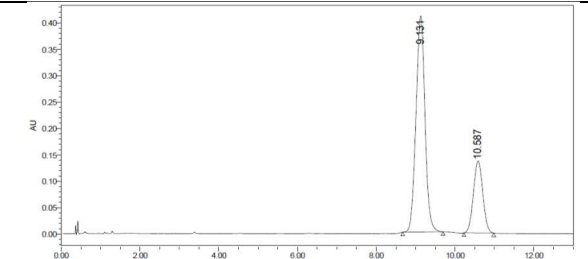
IR (KBr) ν 3052, 3016, 2959, 2920, 2869, 1718, 1619, 1601, 1583, 1571, 1515, 1452, 1365, 1281, 1245, 1222, 1159, 1084, 1033, 1006, 818, 737 cm⁻¹.

HRMS (APCI): *m/z* calcd for C₅₈H₄₃ [(M+H)⁺]: 739.33593, found: 739.33548.

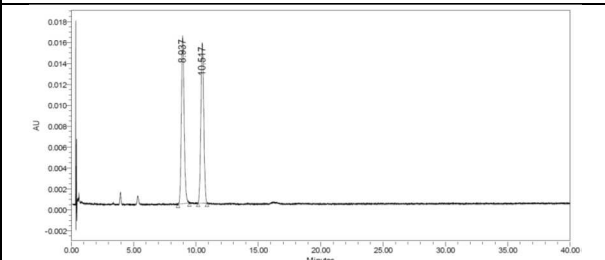
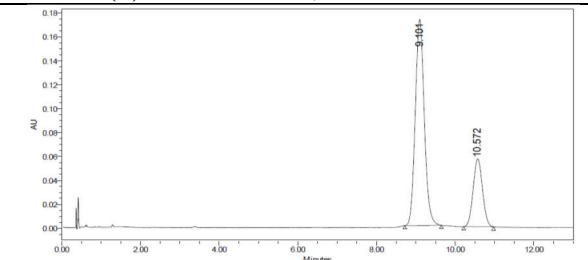
SFC analysis: 63:37 e.r. (Column CHIRAL ART Cellulose-SB (150 x 3 mm I.D., particle size 3 μ m), column temperature 40 °C, sample temperature 10 °C, back pressure 2000 psi, carbone dioxide/*i*-PrOH = 80:20, flow rate 2.0 mL/min, UV 254 nm, t_{major} = 9.0 min; t_{min} = 10.6 min).

Racemic			<i>(S)</i> -SEGPHOS [®] , 63:37 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	8.9	49.94	1	9.0	62.6
2	10.5	50.06	2	10.5	37.4

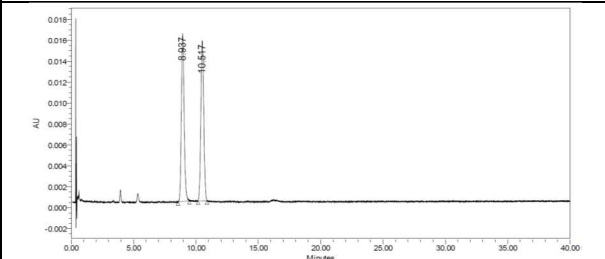
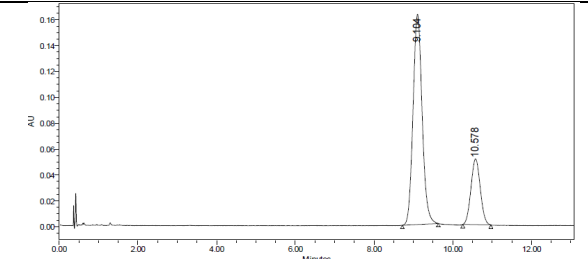
According to the **GP-C2**.

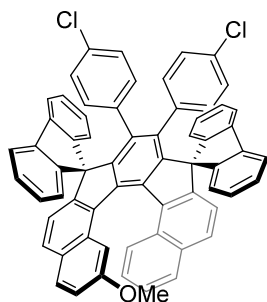
Racemic			<i>(S)</i> -SEGPHOS [®] , 74:26 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	8.9	49.94	1	9.1	74.2
2	10.5	50.06	2	10.6	25.8

According to the **GP-C3**.

Racemic			<i>(S)</i> -SEGPHOS [®] , 74.5:25.5 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	8.9	49.94	1	9.1	74.5
2	10.5	50.06	2	10.6	25.5

According to the **GP-C4**.

Racemic			<i>(S)</i> -SEGPHOS [®] , 76:24 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	8.9	49.94	1	9.1	75.8
2	10.5	50.06	2	10.6	24.2

(P)-8',9'-Bis(4-chlorophenyl)-2'-methoxydispiro[fluorene-9,7'-**benzo[c]benzo[6,7]indeno[1,2-g]fluorene-10',9''-fluorene] ((P)-3h).**

According to the **GP-B** and **GP-C1** with **(P)-2h** (0.2 mmol, 130 mg), *n*-BuLi (1.2 mmol, 0.75 mL) and 2-bromobiphenyl (1.2 mmol, 210 μ L) in THF (12 mL). Column chromatography of the residue on silica gel (linear gradient: 4/1 to 3/1 hexanes/ CH_2Cl_2) furnished 54 mg (30%) of the title compound as a yellowish solid.

R_f (3/1 hexanes/ CH_2Cl_2) = 0.17.

Mp (decomp) > 350 $^\circ\text{C}$ (CH_2Cl_2).

$[\alpha]_D^{20}$ +183 (*c* 0.39, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.62 (dd, J = 14.3, 8.3 Hz, 2H), 7.57-7.48 (m, 2H), 7.40-7.28 (m, 7H), 7.26-7.12 (m, 3H), 7.12 (tdd, J = 7.6, 4.0, 1.1 Hz, 2H), 6.97-6.84 (m, 4H), 6.75 (d, J = 8.3 Hz, 1H), 6.72-6.60 (m, 3H), 6.37-6.29 (m, 2H), 6.18 (dt, J = 8.9, 2.4 Hz, 2H), 5.73-5.62 (m, 4H), 2.76 (s, 3H).

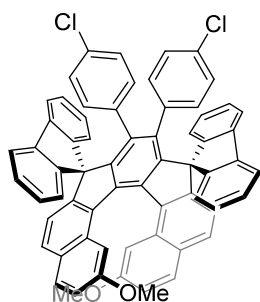
^{13}C NMR (101 MHz, CDCl_3) δ 157.2 (C), 149.1 (C), 148.7 (C), 148.0 (C), 147.9 (C), 147.6 (C), 147.33 (C), 147.29 (C), 147.2 (C), 142.9 (C), 142.8 (C), 142.1 (C), 138.9 (C), 138.0 (C), 137.2 (C), 136.5 (C), 136.1 (C), 135.8 (C), 134.4 (C), 134.4 (C), 133.6 (C), 131.8 (C), 131.7 (C), 131.13 (C), 131.10 (C), 130.9 (C), 130.2 (2C), 130.1 (C), 129.8 (C), 129.2 (C), 129.04 (C), 128.96 (C), 128.2 (C), 127.9 (C), 127.8 (C), 127.6 (C), 127.53 (2C), 127.46 (C), 127.3 (C), 127.2 (C), 127.0 (C), 126.19 (C), 126.16 (C), 125.8 (2C), 125.1 (C), 124.3 (C), 124.2 (C), 124.0 (C), 123.5 (C), 121.72 (C), 120.66 (C), 120.5 (C), 119.84 (C), 119.78 (C), 119.2 (C), 118.5 (C), 106.0 (C), 67.00 (C), 66.96 (C), 53.9 (3C).

IR (KBr) ν 3061, 3052, 3034, 3010, 2953, 2932, 1619, 1512, 1494, 1461, 1426, 1392, 1362, 1228, 1210, 1168, 1087, 1027, 1015, 888, 824, 740 cm^{-1} .

HRMS (APCI): m/z calcd for $\text{C}_{65}\text{H}_{39}\text{Cl}_2\text{O}$ $[(\text{M}+\text{H})^+]$: 905.23725, found: 905.23761.

SFC analysis: 85:15 e.r. (Column CHIRAL ART Cellulose-SB (150 x 3 mm I.D., particle size 3 μm), column temperature 40 $^\circ\text{C}$, sample temperature 10 $^\circ\text{C}$, back pressure 2000 psi, carbone dioxide/*i*-PrOH = 80:20, flow rate 2.0 mL/min, UV 254 nm, t_{major} = 12.8 min; t_{min} = 16.5 min).

Racemic			(S)-SEGPHOS[®], 85:15 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	12.8	50.12	1	12.8	84.7
2	16.3	49.88	2	16.5	15.3

(P)-8',9'-Bis(4-chlorophenyl)-2',15'-dimethoxydispiro[fluorene-9,7'-

benzo[c]benzo[6,7]indeno[1,2-g]fluorene-10',9''-fluorene] ((P)-3i).

According to the **GP-B** and **GP-C1** with **(P)-2i** (0.2 mmol, 130 mg), *n*-BuLi (1.2 mmol, 0.75 mL) and 2-bromobiphenyl (1.2 mmol, 210 μ L) in THF (12 mL). Column chromatography of the residue on silica gel (25/1 hexanes/EtOAc) furnished 50 mg (36%) of the title compound as a yellowish solid.

R_f (25/1 hexanes/EtOAc) = 0.26.

M_p = 255 $^{\circ}$ C (CH_2Cl_2).

$[\alpha]_D^{20}$ +18 (*c* 0.17, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, J = 9.0 Hz, 2H), 7.56 (t, J = 7.5 Hz, 4H), 7.46 (d, J = 2.5 Hz, 2H), 7.43-7.27 (m, 6H), 7.26-7.18 (m, 4H), 7.12 (td, J = 7.5, 1.1 Hz, 2H), 7.01-6.88 (m, 4H), 6.66 (dd, J = 15.9, 7.8 Hz, 4H), 6.40-6.32 (m, 2H), 6.23-6.16 (m, 2H), 5.75-5.62 (m, 4H), 2.83 (s, 6H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.7 (2C), 149.7 (2C), 148.3 (2C), 147.7 (2C), 147.5 (2C), 143.1 (2C), 142.3 (2C), 138.3 (2C), 137.2 (2C), 135.9 (2C), 134.9 (2C), 132.2 (2C), 131.6 (2C), 131.3 (2C), 130.6 (2C), 129.9 (2C), 129.2 (2C), 129.0 (2C), 128.2 (2C), 127.9 (2C), 127.8 (2C), 127.6 (2C), 126.3 (2C), 126.1 (2C), 124.5 (2C), 123.8 (2C), 120.9 (2C), 120.1 (2C), 119.4 (2C), 119.0 (2C), 105.9 (2C), 67.4 (2C), 54.3 (2C).

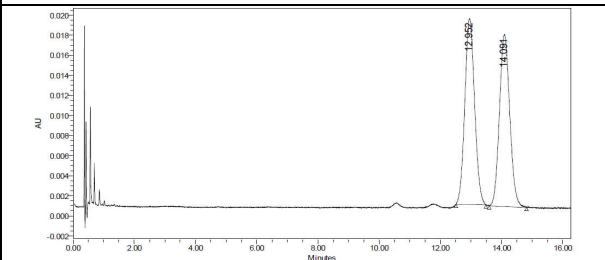
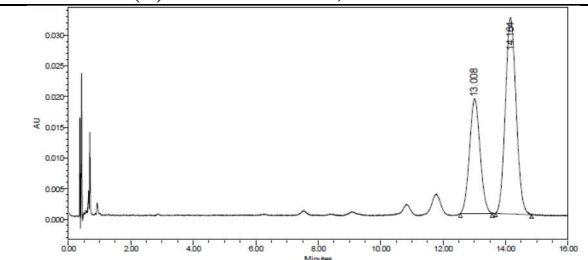
IR (KBr) ν 3058, 3031, 3010, 2962, 2923, 2851, 2830, 1625, 1586, 1500, 1473, 1449, 1434, 1326, 1272, 1234, 1210, 1171, 1156, 1102, 1072, 1042, 1012, 830, 758, 731, 701 cm^{-1} .

HRMS (APCI): m/z calcd for $\text{C}_{66}\text{H}_{41}\text{Cl}_2\text{O}_2$ [($\text{M}+\text{H}$) $^+$]: 935.24781, found: 935.24771.

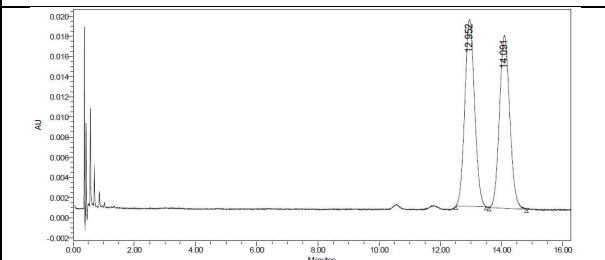
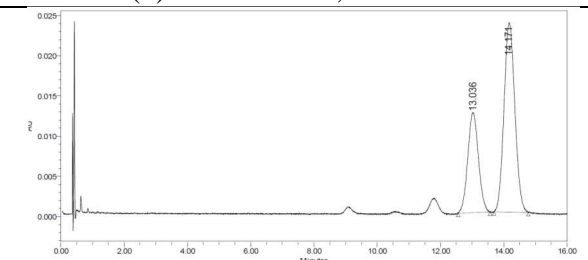
SFC analysis: 56:44 e.r. (Column CHIRAL ART Cellulose-SB (150 x 3 mm I.D., particle size 3 μ m), column temperature 40 $^{\circ}$ C, sample temperature 10 $^{\circ}$ C, back pressure 2000 psi, carbone dioxide/*i*-PrOH = 80:20, flow rate 2.0 mL/min, UV 254 nm, t_{major} = 13.0 min; t_{min} = 14.2 min).

Racemic			(S)-SEGPHOS [®] , 56:44 e.r.		
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	13.0	50.66	1	13.0	55.7
2	14.1	49.34	2	14.2	44.3

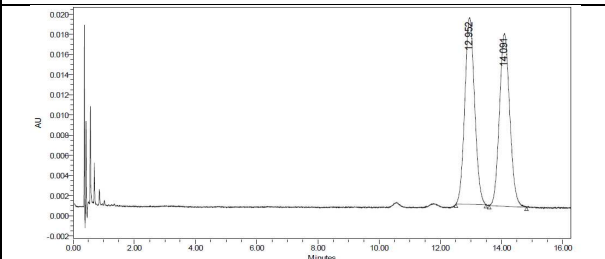
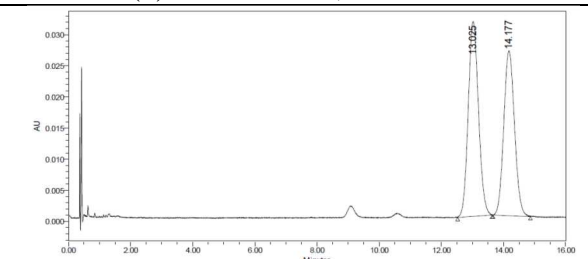
According to the **GP-C2**.

Racemic			<i>(S)</i> -SEGPHOS [®] , 37:63 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	13.0	50.66	1	13.0	36.5
2	14.1	49.34	2	14.2	63.5

According to the **GP-C3**.

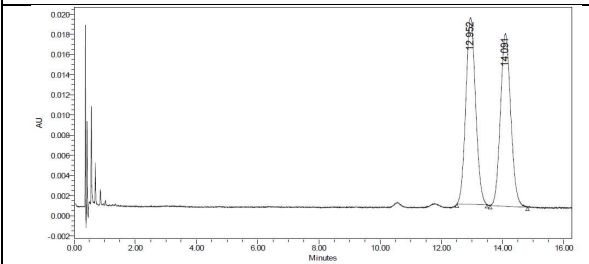
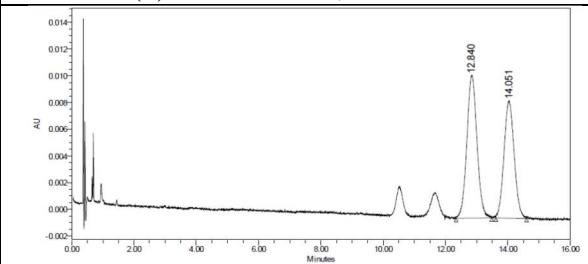
Racemic			<i>(S)</i> -SEGPHOS [®] , 34:66 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	13.0	50.66	1	13.0	34.1
2	14.1	49.34	2	14.2	65.9

According to the **GP-C4**.

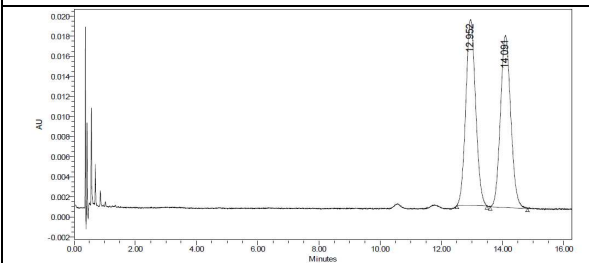
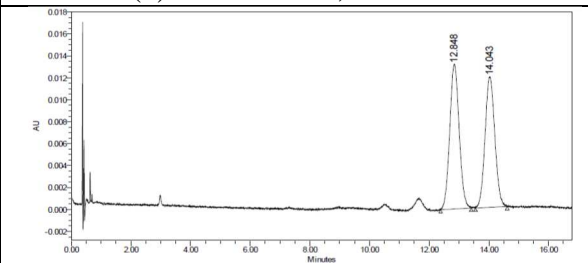
Racemic			<i>(S)</i> -SEGPHOS [®] , 53:47 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	13.0	50.66	1	13.0	53.0
2	14.1	49.34	2	14.2	47.0

Chromatographic charts from column chromatography of *P-3i*

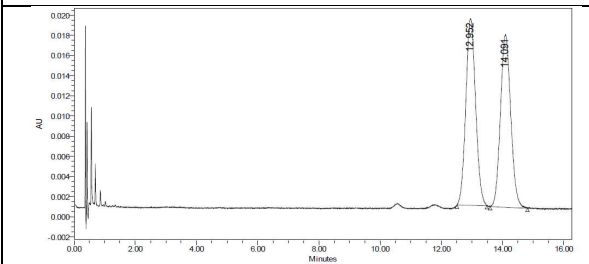
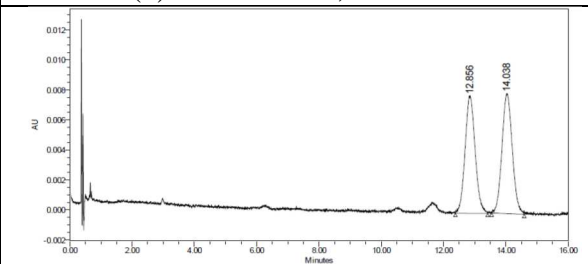
a) Fraction X1 (25/1 hexanes/EtOAc)

Racemic			<i>(S)</i> -SEGPHOS [®] , 55:45 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	13.0	50.66	1	12.8	54.7
2	14.1	49.34	2	14.1	45.3

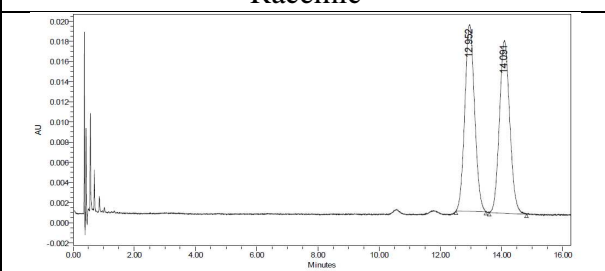
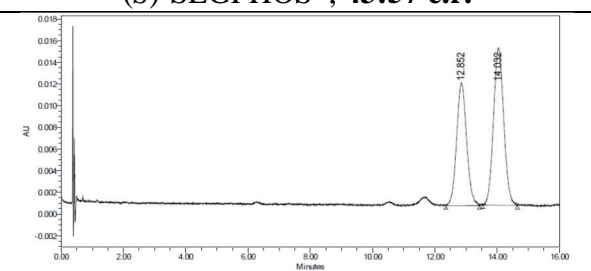
b) Fraction X2 (25/1 hexanes/EtOAc)

Racemic			<i>(S)</i> -SEGPHOS [®] , 52:48 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	13.0	50.66	1	12.8	51.6
2	14.1	49.34	2	14.0	48.4

c) Fraction X3 (20/1 Hexanes/EtOAc)

Racemic			<i>(S)</i> -SEGPHOS [®] , 49:51 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	13.0	50.66	1	12.9	48.8
2	14.1	49.34	2	14.0	51.2

d) Fraction X4 (elution of the column with neat EtOAc)

Racemic			<i>(S)</i> -SEGPHOS [®] , 43:57 e.r.		
					
N ^o	Retention time (min)	Relative area (%)	N ^o	Retention time (min)	Relative area (%)
1	13.0	50.66	1	12.9	43.2
2	14.1	49.34	2	14.0	56.8

VI Determination of the Racemization Barrier of 2a and 3a

General procedure. A solution of compound **2a** or **3a** (1.2 mg) in a solvent (5 mL) was refluxed under the argon atmosphere. In time intervals, a small sample (0.1 mL) of the solution was taken. It was cooled to r.t. and immediately analysed using HPLC on a chiral column (YMC Chiral Cellulose SB, 250 x 4.6 mm). Dependences of % of the major enantiomer on time are shown in SI-Figures 1 and 3).

Enantiomerization rate constant k_{enant} was calculated using first order kinetics with the equation:

$$\ln \frac{[M]_0 - [M]_{eq}}{[M]_t - [M]_{eq}} = 2k_{enant}t$$

where $[M]_0$ is initial concentration of major enantiomer, $[M]_{eq}$ is equilibrium concentration, $[M]_t$ is concentration of major enantiomer at time t .

Dependences of $\ln \frac{[M]_0 - [M]_{eq}}{[M]_t - [M]_{eq}}$ on time t are shown in SI-Figures 2 and 4. Activation energy ΔG^\ddagger for interconversion of enantiomers was calculated from the Eyring equation. Experimental conditions and results are summarized in SI-Table 5.

Table S5. Experimental conditions and results of determination of racemisation barrier

Compound	Solvent	Temperature (K)	Mobile phase for HPLC analysis	k_{enant} (s ⁻¹)	ΔG^\ddagger (kJ · mol ⁻¹)
(<i>P</i>)- 2a	toluene	383.75	heptane/propan-2-ol 8/2 flowrate 1.0 ml/min	2.602×10^{-6}	135.8
(<i>P</i>)- 3a	o-xylene	417.65	heptane/propan-2-ol 9/1 flowrate 0.5 ml/min	8.466×10^{-5}	136.0

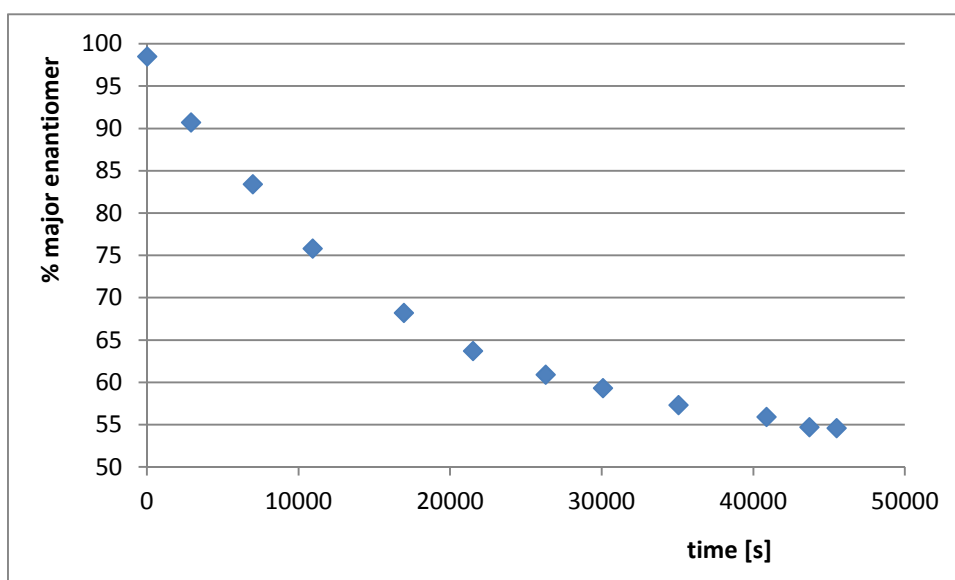


Figure S1. Dependence of % of the major enantiomer of **2a** on time.

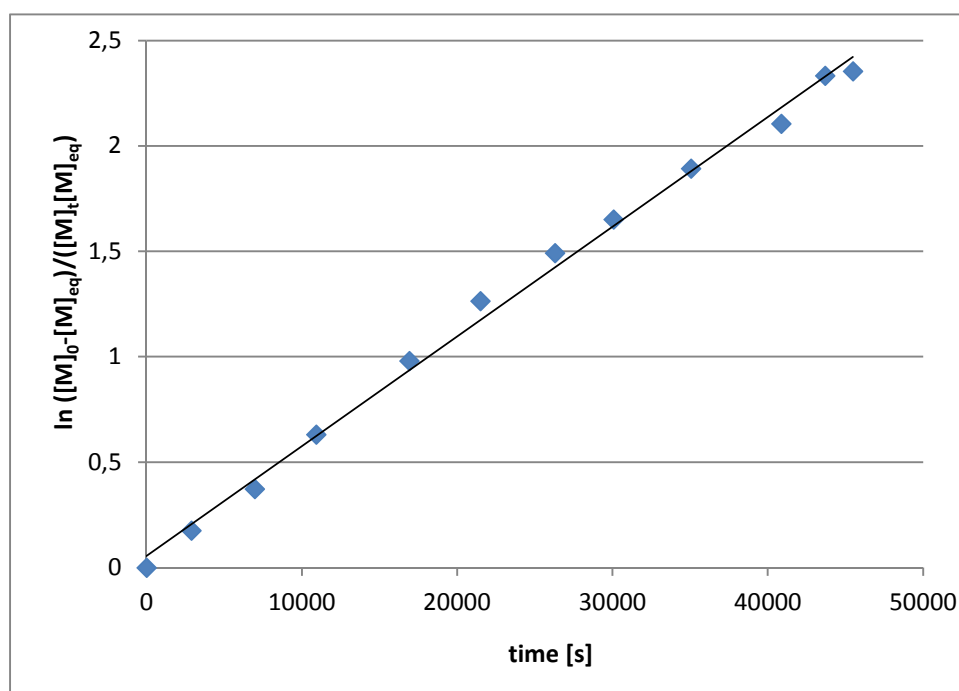


Figure S2. Dependence of $\ln \frac{[M]_0 - [M]_{eq}}{[M]_t - [M]_{eq}}$ on time t for compound **2a**.

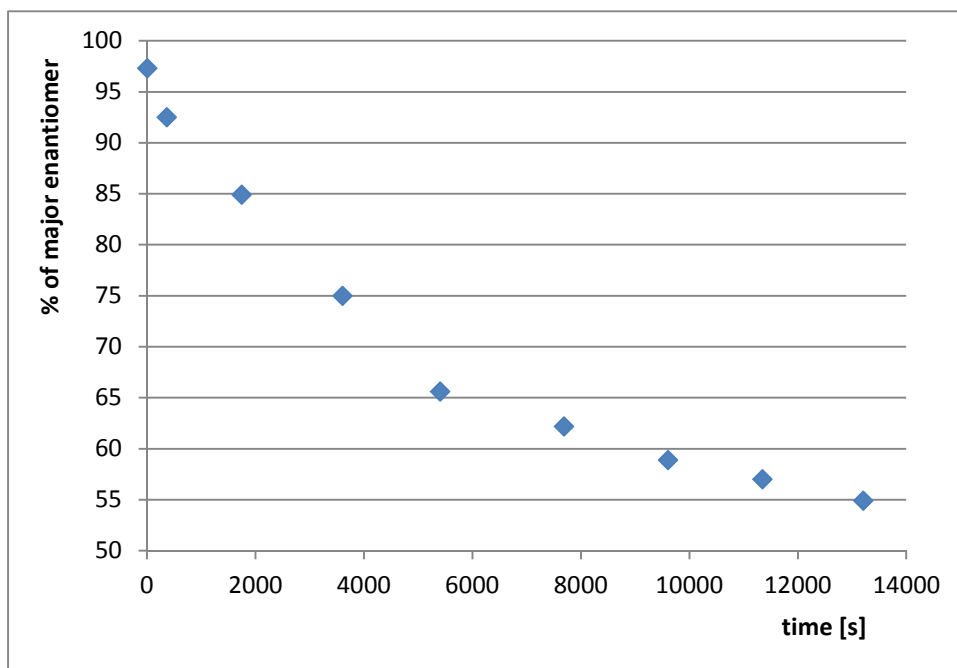


Figure S3. Dependence of % of the major enantiomer of **3a** on time.

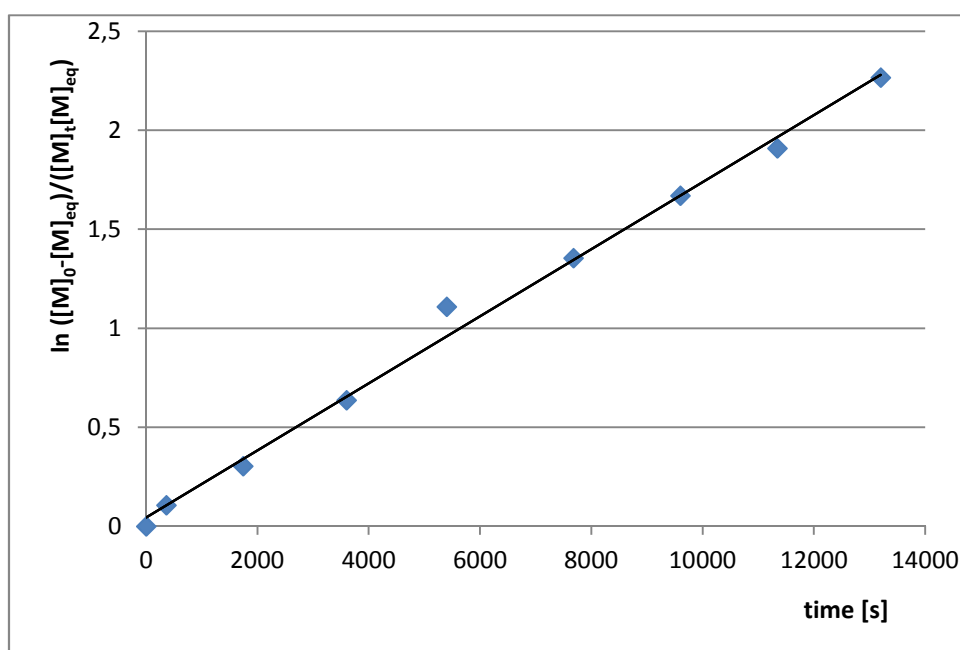


Figure S4. Dependence of $\ln \frac{[M]_0 - [M]_{eq}}{[M]_t - [M]_{eq}}$ on time t for compound **3a**.

VII X-Ray Diffraction Analysis

The crystal structures of **2a**, **2d**, **3d** and **3f** were determined by x-ray diffraction experiment carried on Bruker D8 VENTURE Kappa Duo PHOTON100 by μ S micro-focus sealed tube $\text{CuK}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) at low temperature. The structures were solved by direct methods (XT^3)⁶ and refined by full matrix least squares based on F^2 (SHELXL2018^{39b}).⁶ The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors either $H_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{pivot atom})$ or $H_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{pivot atom})$ for methyl moiety. Crystals of **3f** and **3d** contain in their unit cells molecules of solvents so seriously disordered that position of individual atoms can not be properly resolved and refined. To improve the precision of main molecules, the contribution of solvents were removed from diffraction pattern using SQUEEZE procedure of PLATON^{40 7} software before final refinement.

The structure determination of **3d** requires more detailed explanation. The crystal was measured at temperature 200K since at lower temperature undergoes phase transition accompany by destruction of the crystal probably due to a change of disordered solvent arrangement. The space group symmetry enables the presence of only one enantiomer in the crystal, therefore the absolute structure determination was point of interest, even if the disorder of dichloromethane solvent significantly hampered the precision of refined parameters. Two means of improving the resulting model were applied. In the first approach, the contribution of solvents was removed by SQUEEZE procedure as described above. The chirality parameter was refined to the value $0.042(7)^{418}$ confirming well the model chirality. In the second approach the atomistic solvent model was used to describe electron density in the voids. The partially occupied positions of atoms were added to the model without any aspiration on the correct geometry of the solvent until residual electron density was below $0.70\text{e}/\text{\AA}^3$. The obtained value of chirality parameter $0.002(3)$ leads to the conclusion, that presented enantiomer is correct.

X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under deposition number CCDC 2024649, 2024650, 2024651 and 2024652 for **2a**, **2d**, **3d** and **3f**, respectively and can be obtained free of charge from the Centre *via* its website (www.ccdc.cam.ac.uk/getstructures).

⁶ SHELXT: G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8.

⁷ A. L. Speck, *Acta Cryst.* **2015**, *C71*, 9-18-

⁸ S. Parsons, H. D. Flack, T. Wagner, *Acta Cryst.* **2013**, *B69*, 249-259

Table S6. X-Ray crystallographic data

Compound	2a	2d	3f	3d
Formula	2(C ₄₂ H ₂₆ O ₄)·CH ₂ Cl ₂	C ₄₀ H ₂₀ Cl ₂ O ₂	C ₅₂ H ₃₀ [+solvent]	C ₆₄ H ₃₆ Cl ₂ [+solvent]
M.w.	1274.18	603.46	654.76	437.91
Crystal system	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group [No.]	<i>P</i> ⁻ 1 (No 2)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>Pbca</i> (No 61)	<i>P</i> 2 ₁ 2 ₁ 2 (No 18)
<i>a</i> [Å]	9.7177 (3)	14.3954 (5)	18.6716 (5)	14.2931 (4)
<i>b</i> [Å]	12.1649 (4)	13.0354 (4)	15.5429 (4)	28.0024 (7)
<i>c</i> [Å]	14.1681 (5)	14.9474 (5)	23.7224 (7)	12.9710 (3)
α [°]	65.924 (1)			
β [°]	86.865 (1)	92.861 (2)		
γ [°]	86.516 (1)			
Z	1	4	8	8
V [Å ³]	1525.53 (9)	2801.38 (16)	6884.5 (3)	5191.5 (2)
<i>D</i> _x [g cm ⁻³]	1.387	1.431	1.263	1.121
Crystal size [mm]	0.32×0.30×0.05	0.13×0.07×0.05	0.33×0.23×0.15	0.26×0.25×0.10
Crystal shape, colour	Plate, red	Bar, purple	Plate, colourless	Prism, violet
μ [mm ⁻¹]	1.48	2.38	0.55	1.41
θ _{max} [°]	72.1	72.3	72.2	70.2
Measured reflections	27096	20007	58107	58886
Independent diffractions (<i>R</i> _{int} ^a)	5978 (0.028)	2753 (0.123)	6775 (0.058)	9878 (0.027)
Observed diffract. [<i>I</i> >2σ(<i>I</i>)]	5426	2198	6482	9571
<i>T</i> _{min} , <i>T</i> _{max}	0.79, 0.93	0.74, 0.90	0.83, 0.92	0.70, 0.88
No. of parameters	444	199	469	595
<i>w</i> ₁ , <i>w</i> ₂ ^b	0.0485, 0.6397	0.0302, 9.1237	0.0547, 12.3426	0.0606, 0.835
Absolut. structure param. (Flack)				0.042 (7)
<i>R</i> ^c [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.039	0.067	0.067	0.034
w <i>R</i> (<i>F</i> ²) for all data	0.100	0.128	0.164	0.096
GOF ^d	1.02	1.15	1.07	1.04
Residual electron density [e/Å ³]	0.35, -0.43	0.36, -0.35	0.89, -0.31	0.35, -0.34
CCDC	2024649	2024650	2024651	2024652

^a $R_{\text{int}} = \Sigma |F_o^2 - F_{o,\text{mean}}^2| / \Sigma F_o^2$, ^b Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^2$, where $P = \frac{1}{3}[\max(F_o^2, 0) + 2F_c^2]$. ^c $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2) / (\Sigma w(F_o^2)^2)]^{1/2}$. ^d $\text{GOF} = [\Sigma(w(F_o^2 - F_c^2)^2) / (N_{\text{diffs}} - N_{\text{params}})]^{1/2}$

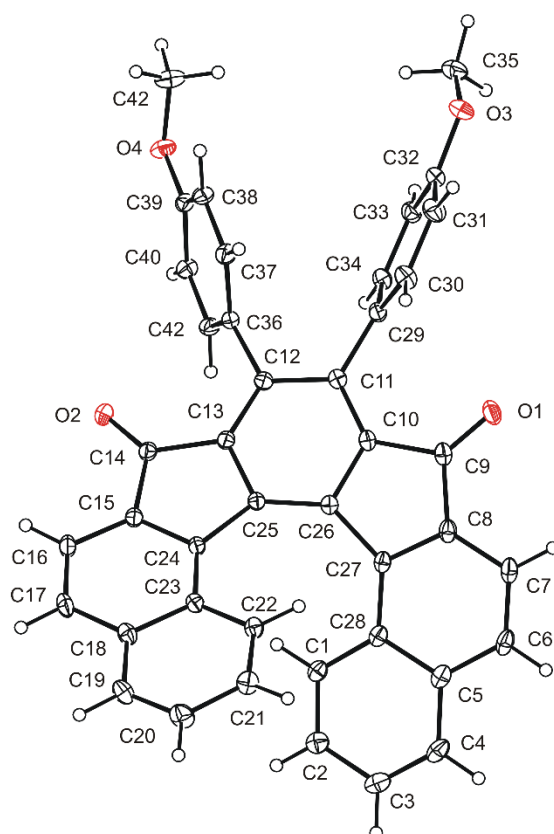


Figure S5. The ORTEP plot of **2a**. Ellipsoids are shown with 30% probability.

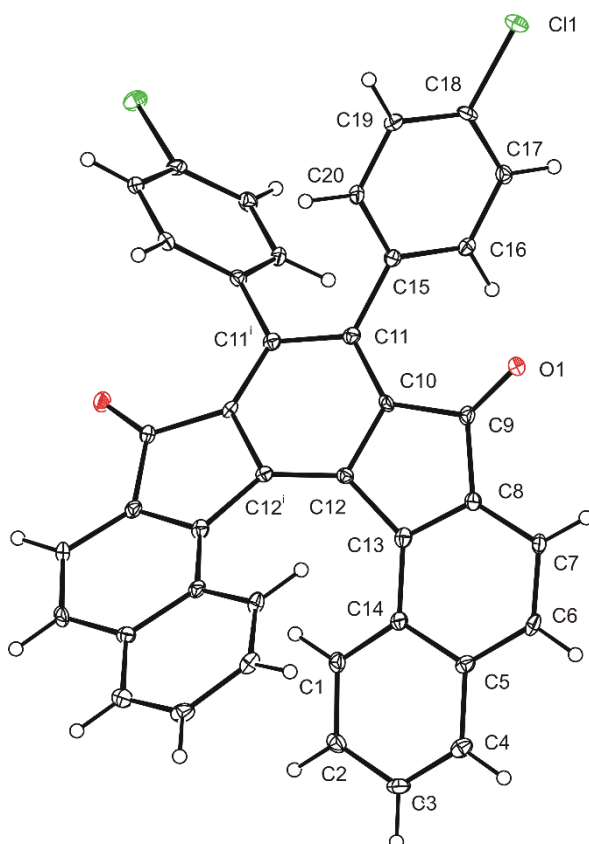


Figure S6. The ORTEP plot of **2d**. Ellipsoids are shown with 30% probability.

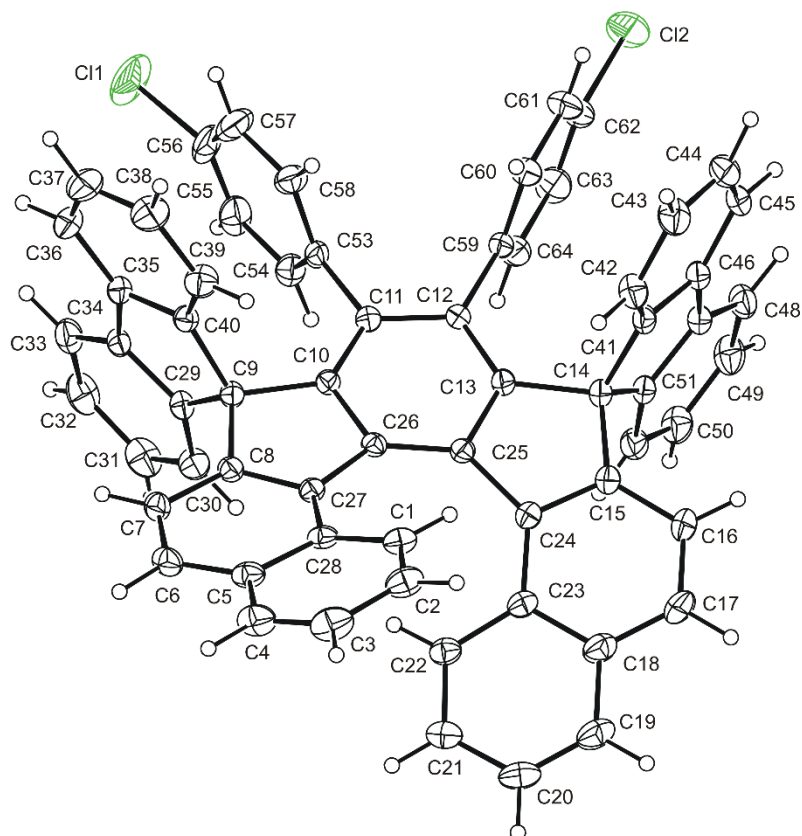


Figure S7. The ORTEP plot of **3d**. Ellipsoids are shown with 30% probability.

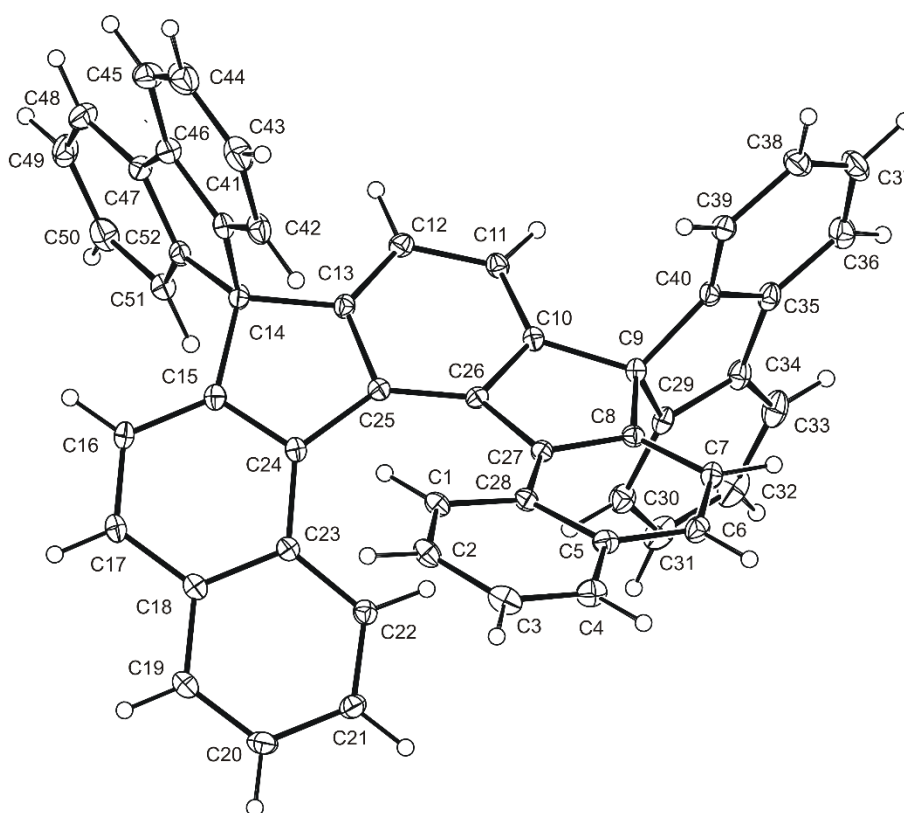


Figure S8. The ORTEP plot of **3f**. Ellipsoids are shown with 30% probability.

VIII Photophysical Properties

The UV/Vis absorption spectra were recorded using Thermo Helios Beta spectrometer as a CH_2Cl_2 solutions (10^{-5} M). Fluorescence emission spectra and emission absolute quantum yields were measured using Hamamatsu Quantaurs-QY Plus UV-NIR absolute PL quantum yield spectrometer C13534 with integrating sphere as a CH_2Cl_2 solutions (10^{-6} M, $\lambda_{\text{exc}} = 350$ nm).

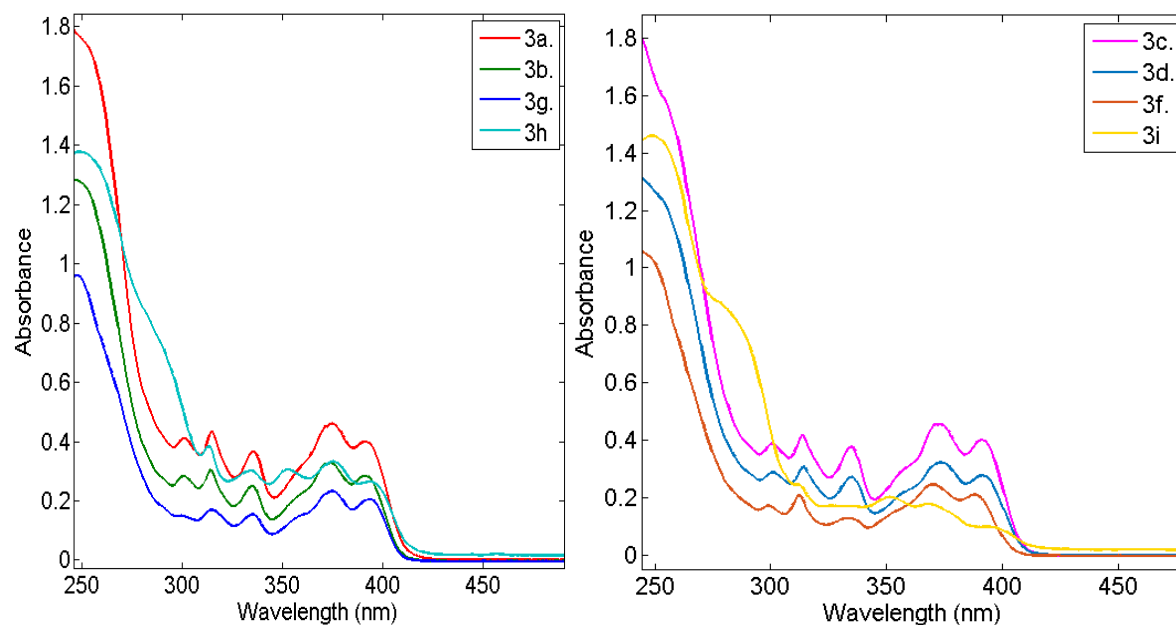


Figure S9. Absorption spectra (10^{-5} M) of **3a-d**, **3f-g** in CH_2Cl_2 .

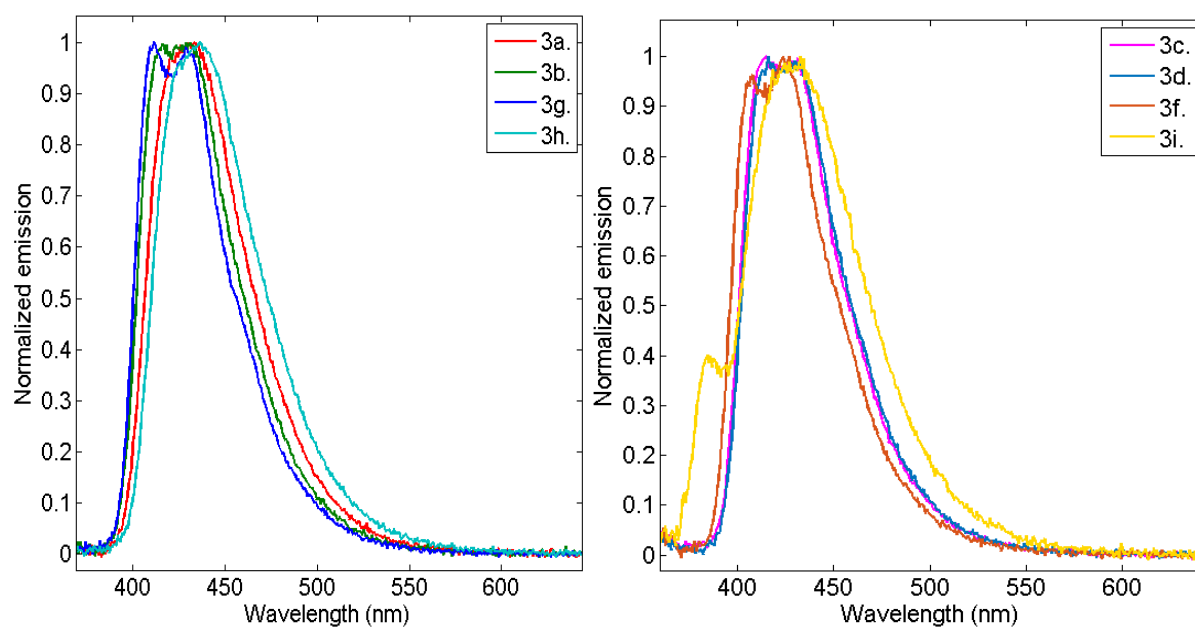


Figure S10. Normalized and corrected emission spectra (10^{-6} M) of **3a-d**, **3f-g** in CH_2Cl_2 using $\lambda_{\text{exc}} = 350$ nm.

Table S7. Photophysical properties of **3a-d**, **3f-g** in CH₂Cl₂.

3	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon/10^4 \text{ mol}^{-1}\cdot\text{dm}^3\cdot\text{cm}^{-1}$)	$\lambda_{\text{em}}/\text{nm}$	Φ_{s}^a
3a	301 (4.11), 314 (4.32), 335 (3.67), 374 (4.60), 391 (3.99)	431	0.85
3b	301 (2.84), 314 (3.04), 335 (2.49), 374 (3.27), 391 (2.84)	417, 430	0.87
3c	301(3.87), 314 (4.16), 335 (3.77), 371 (4.57), 391 (4.00)	415, 430	0.78
3d	301 (2.86), 314 (3.06), 335 (2.71), 373 (3.22), 391 (2.76)	415, 429	0.75
3f	299 (1.71), 312 (2.06), 333 (1.27), 370 (2.45), 388 (2.10)	409, 423	0.87
3g	314 (1.70), 335 (1.54), 374 (2.32), 393 (2.05)	412, 428	0.86
3h	313 (3.83), 334 (3.02), 352 (3.06), 375 (3.33), 395 (2.65)	437	0.97
3i	312 (2.44), 352 (2.01), 368 (1.78), 393 (0.98)	433	0.82

^a Absolute quantum yields of **3** (10^{-6} M in CH₂Cl₂), $\lambda_{\text{exc}} = 350$ nm.

IX Circular Dichroism Measurement of (*P*)- and (*M*)-3a

The ECD, absorption and fluorescence spectra were measured on a Jasco 1500 spectropolarimeter equipped with a fluorescence emission monochromator (FMO522) and separate fluorescence emission detector (FDT-538). The ECD and absorption spectra were measured over a spectral range of 210 nm to 500 nm in dichloromethane (1.0×10^{-4} solutions). Measurements were made in a quartz cell with a 0.1 cm path length using a scanning speed of 20 nm/min, a response time of 4 seconds, standard instrument sensitivity. After a baseline subtraction, spectra were expressed in terms of differential molar extinction ($\Delta\epsilon$). Fluorescence spectra were measured with constant emission slit (10 nm) and excitation slit (5 nm) with excitation wavelength 390nm.

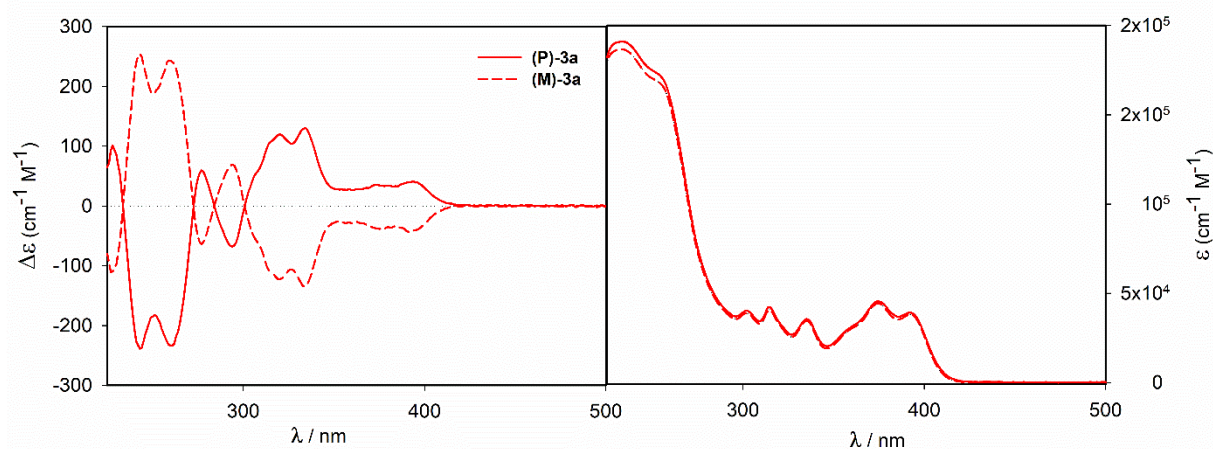


Figure S11. ECD (left) and absorption (right) spectra of heptahelicenic derivatives (*P*)- and (*M*)-3a in CH_2Cl_2 .

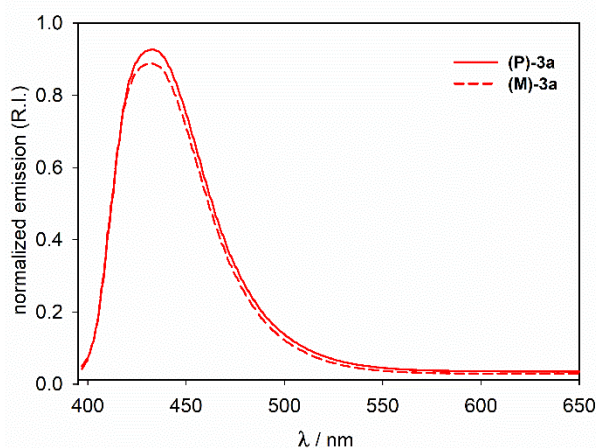


Figure S12. Normalized emission spectra (10^{-4} M) of (*P*)- (black) and (*M*)-3a (red) in dichloromethane using $\lambda_{\text{exc}} = 390$ nm

X. Circularly Polarized Luminescence (CPL) measurements of (*P*)- and (*M*)-3a

The circularly polarized luminescence (CPL) measurements were performed using a home-built CPL spectrofluoropolarimeter. The samples were excited using a 90° geometry with a Xenon ozone-free lamp 150 W LS. The following parameters were used: emission slit width ≈ 2 nm, integration time = 4 sec, scan speed = 50 nm/min, accumulations = 5. The concentration of all the samples was $\sim 10^{-5}$ M. Excitation of the samples were performed at 360 nm.

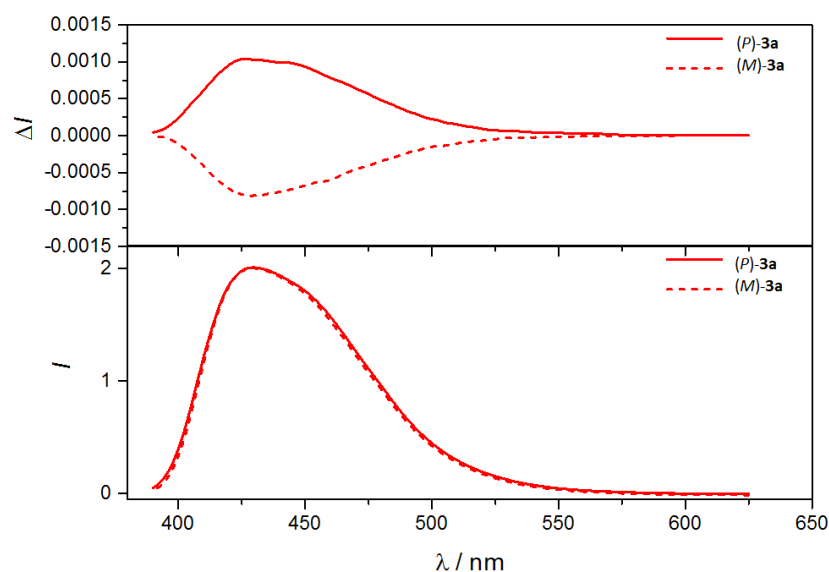


Figure S13a. CPL (upper) and emission (bottom) spectra of heptahelicenic derivatives (*P*)- and (*M*)-3a in CH₂Cl₂.

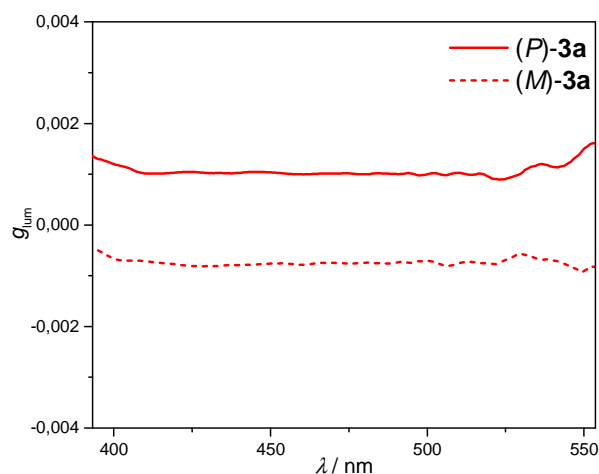


Figure S13b. g_{lum} spectra for (*P*) and (*M*)-3a.

XI Calculations

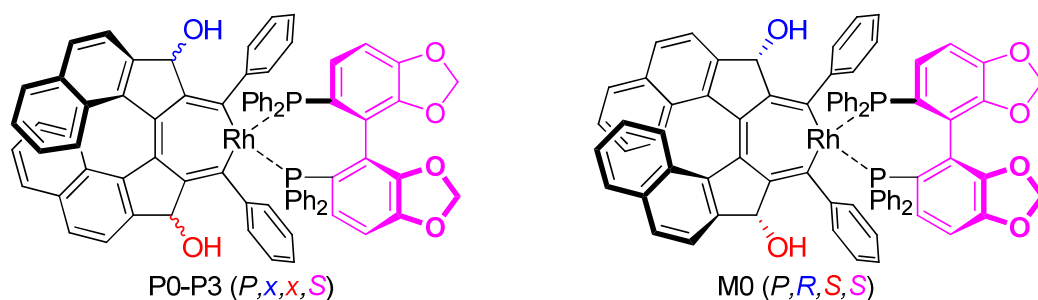


Table S8. Energies of intermediates

Isomer	Total energy [a.u.]	Relative energy WRT P0 [kJ/mol]/ Boltzmann ratio WRT P0 at 298.15 K
P0	-4245.97803323	0.000/100.000%
P1	-4245.97180006	16.365/0.136%
P2	-4245.96999825	21.096/0.020%
P3	-4245.97656023	3.867/17.400%
M0	-4245.92993924	126.271/0.000%

Experimental

Computational studies were carried out using Gaussian16, Revision C.01.⁹ All computations utilized the M11 functional,¹⁰ the LANL2DZ core potential¹¹ for the Rh atoms and the 6-31+G(d,p) basis set¹² for all other atoms. Geometry optimizations utilized Hessians estimated prior the first optimization steps.

⁹ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

¹⁰ R. Peverati, D. G. Truhlar, "Improving the Accuracy of Hybrid Meta-GGA Density Functionals by Range Separation," *J. Phys. Chem. Lett.* **2011**, 2, 2810-2817.

¹¹ P. J. Hay, W. R. Wadt, "Ab initio effective core potentials for molecular calculations – potentials for the transition-metal atoms Sc to Hg," *J. Chem. Phys.* **1985**, **82**, 270-283.

¹² R. Ditchfield, W. J. Hehre, J. A. Pople, "Self-Consistent Molecular Orbital Methods. 9. Extended Gaussian-type basis for molecular-orbital studies of organic molecules," *J. Chem. Phys.* **1971**, **54**, 724.

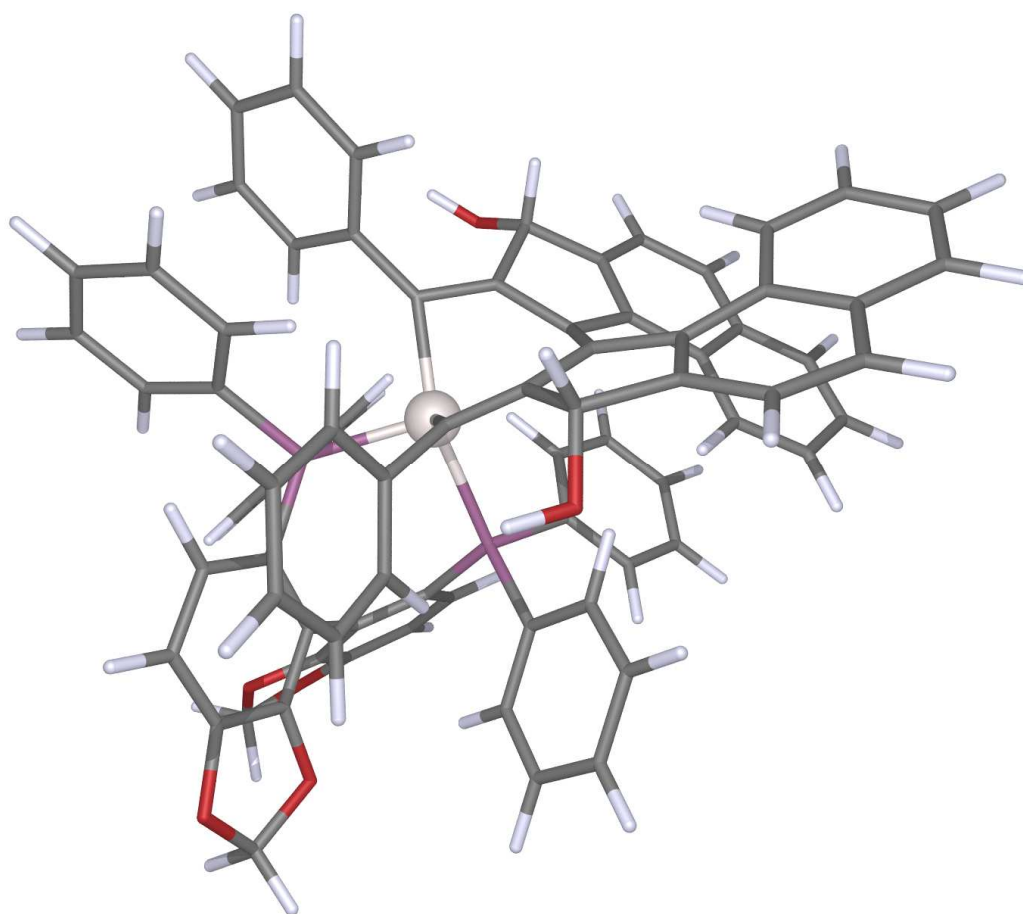


Figure S14. Drawing of P0-(*P, S, R, Sligand*)-isomer.

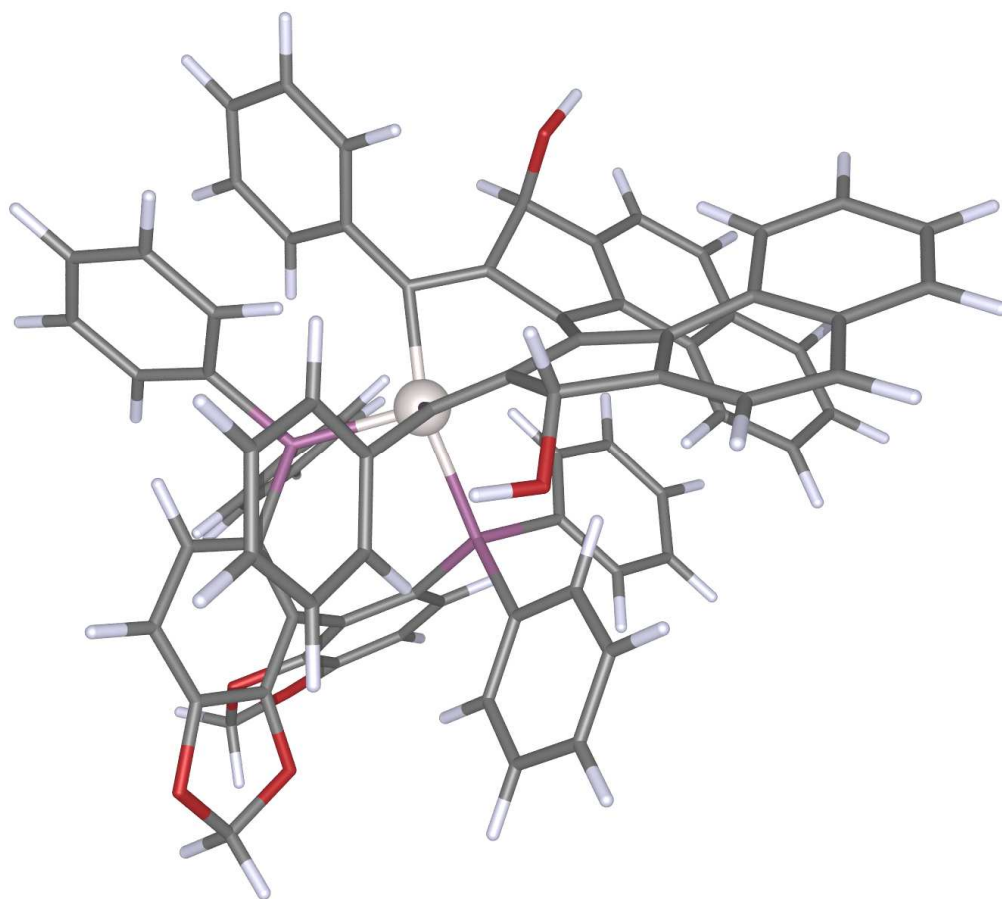


Figure S15. Drawing of P1-(*P, S, S, S_{ligand}*)-isomer.

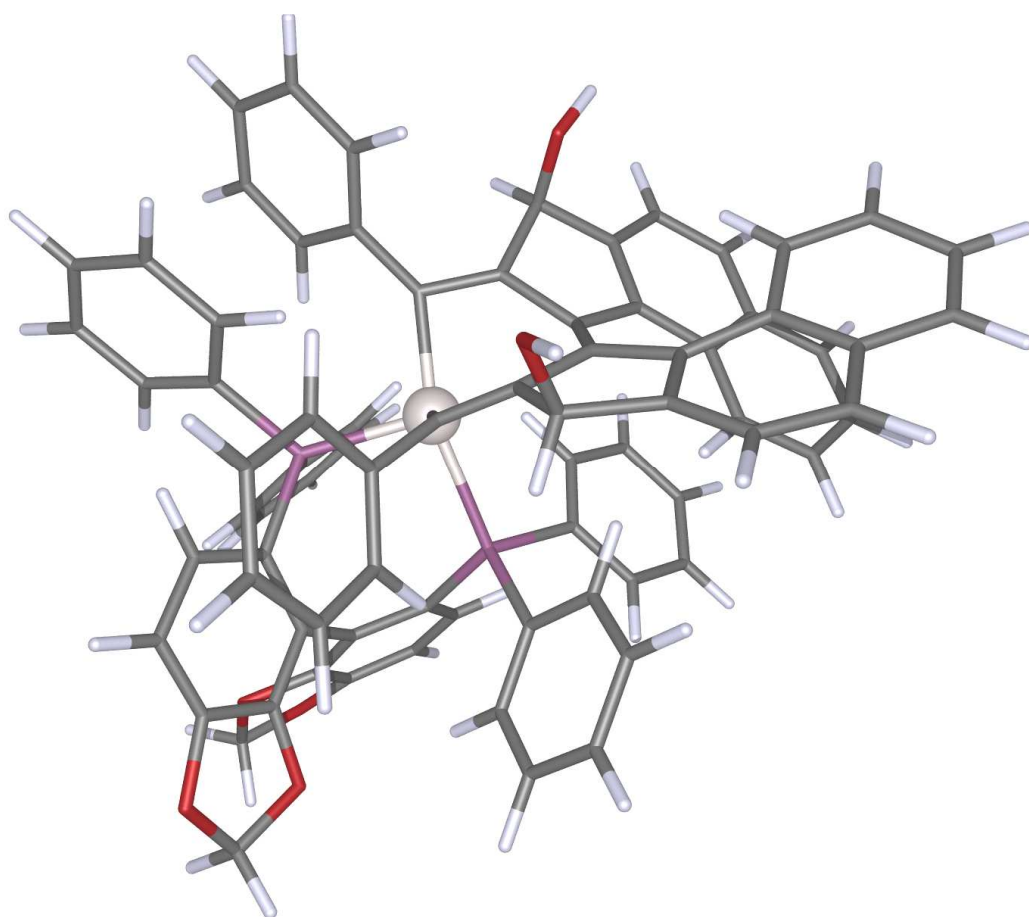


Figure S16. Drawing of P2-(*P, R, S, ligand*)-isomer.

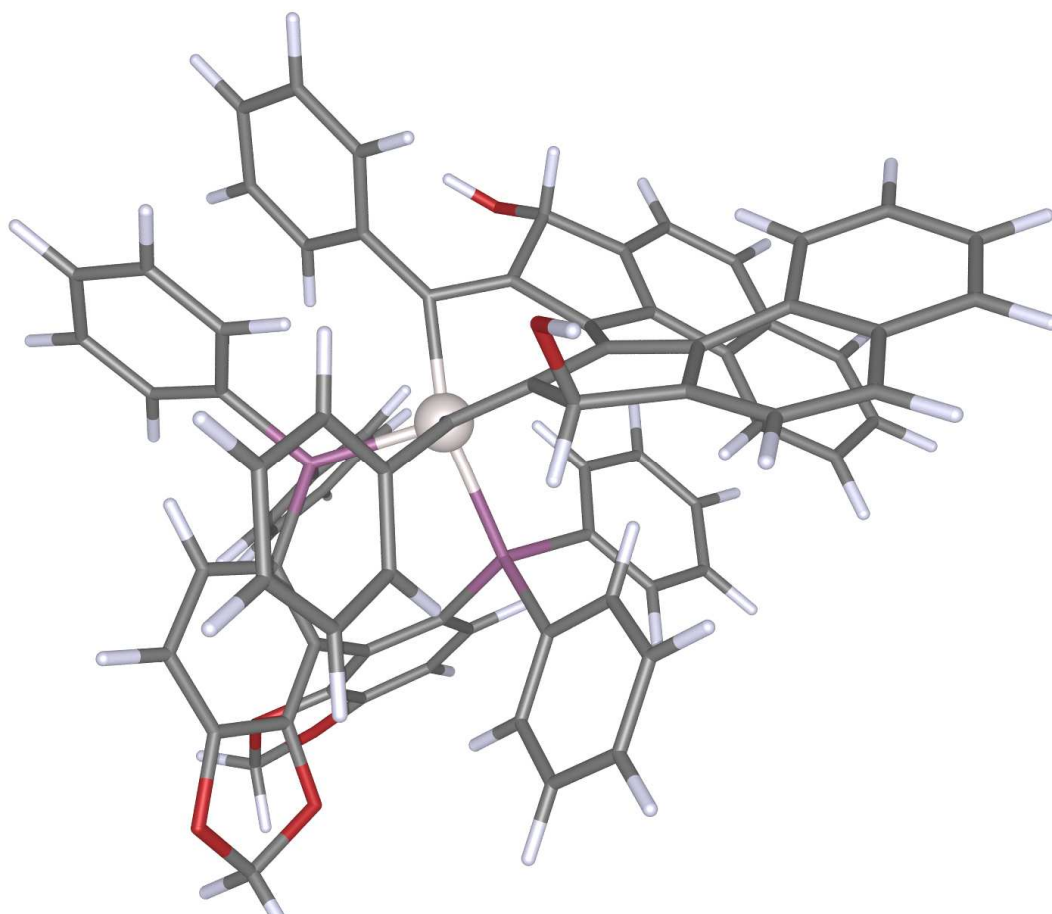


Figure S17. Drawing of P3-(*P, R, R, S_{ligand}*)-isomer.

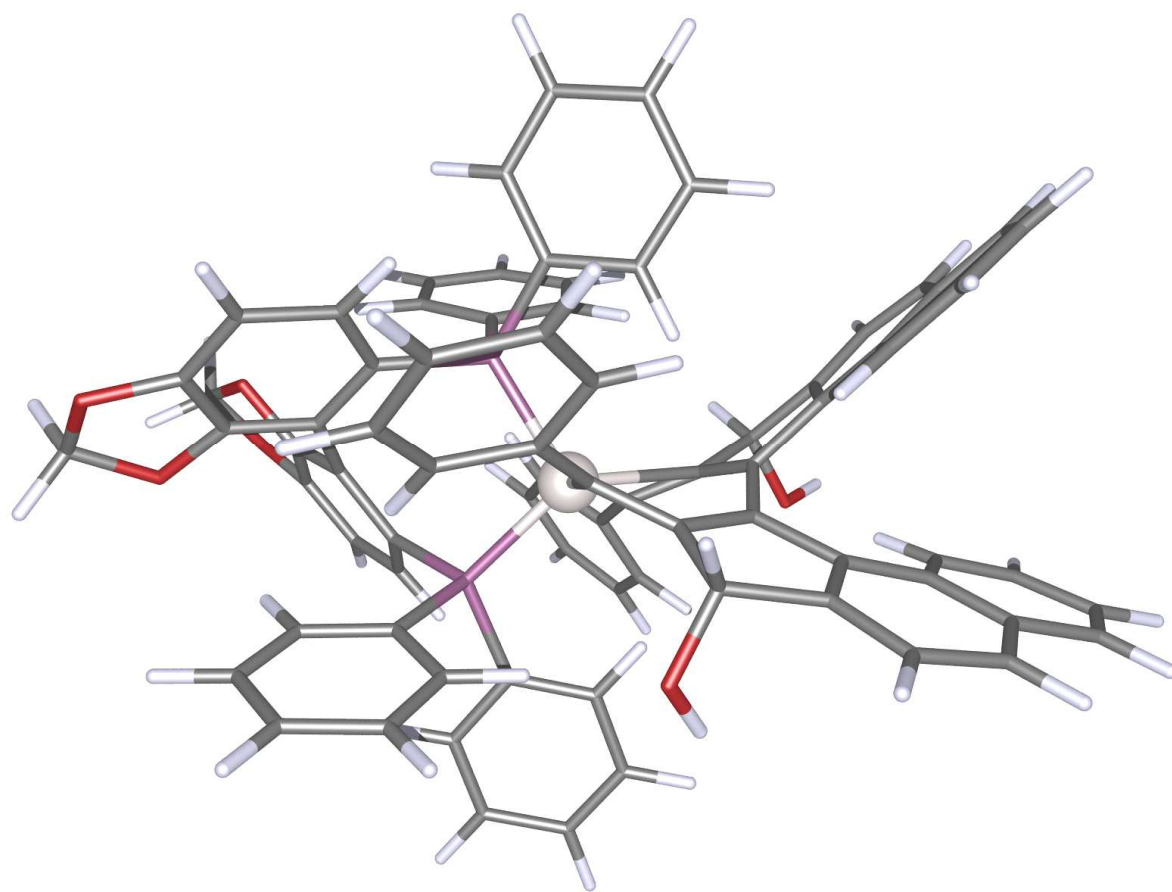
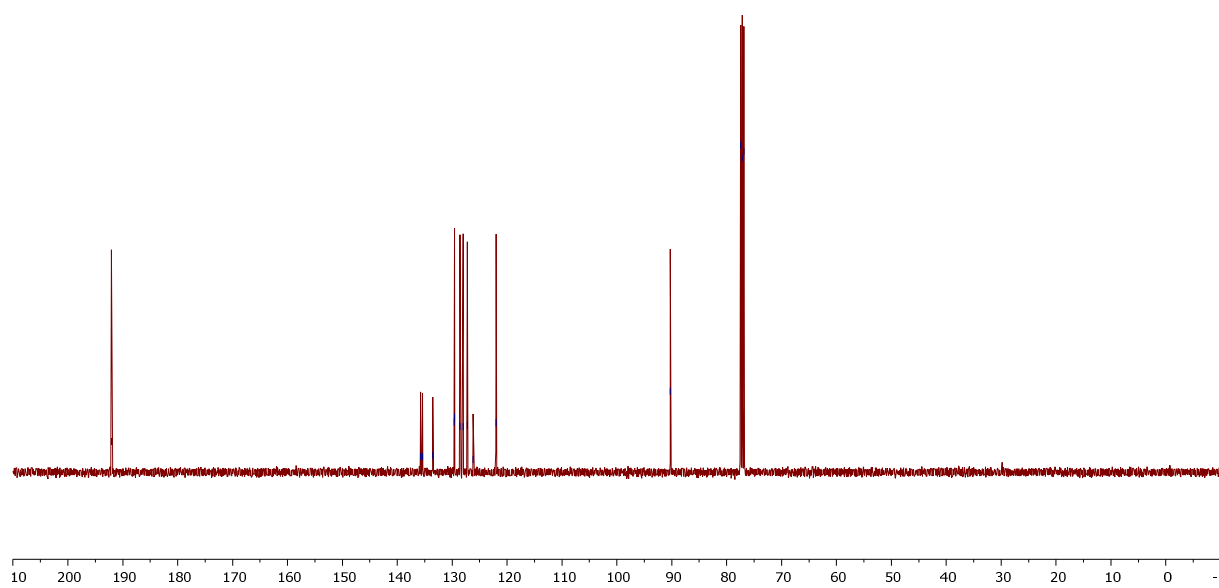
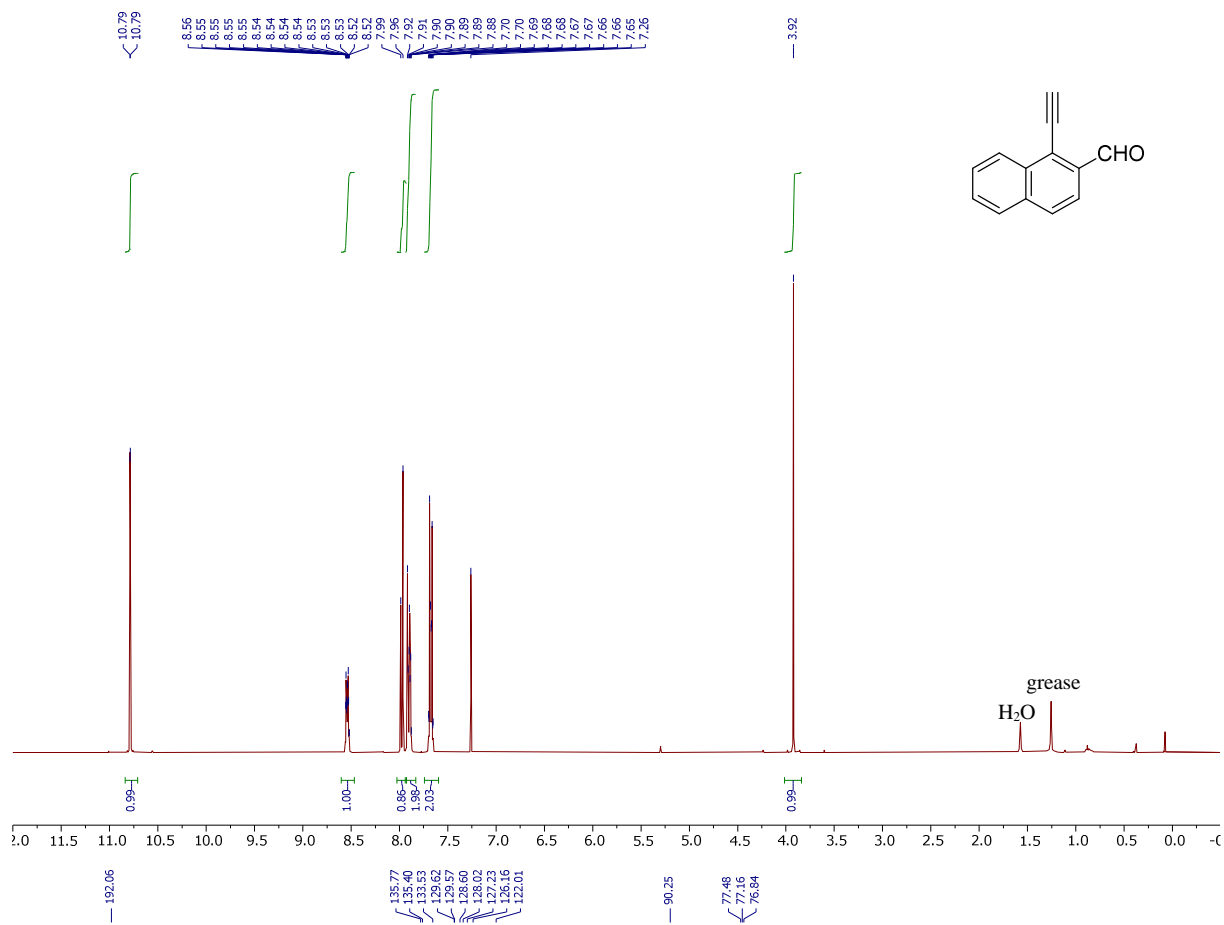
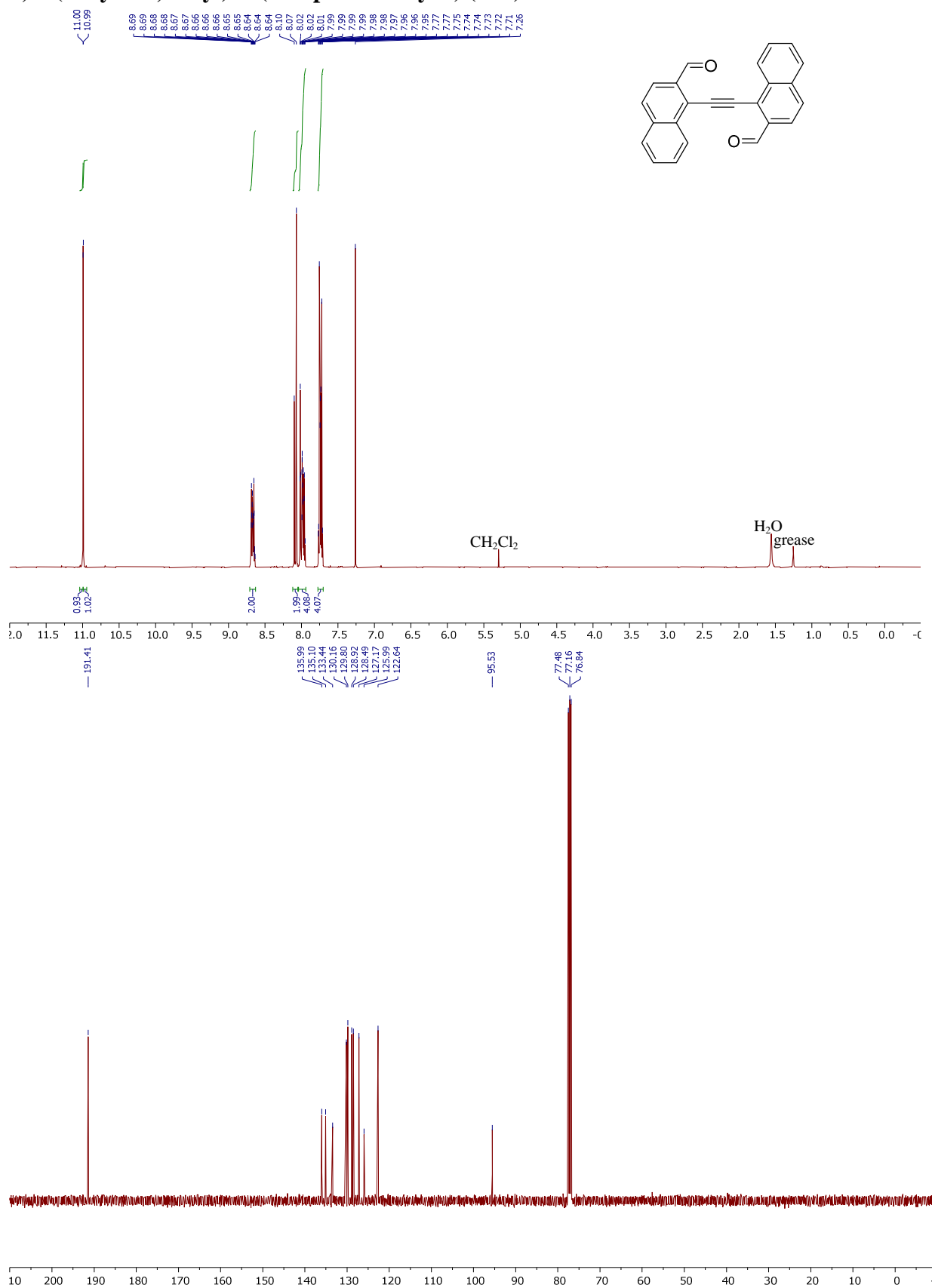


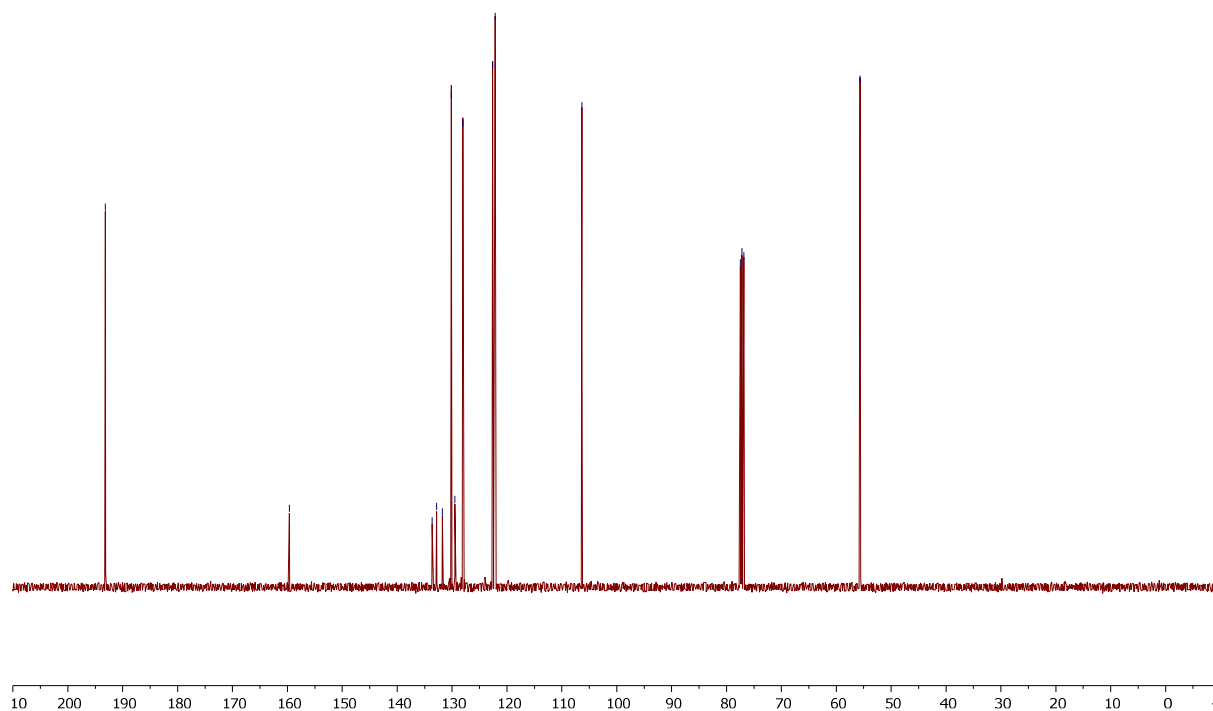
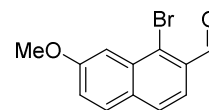
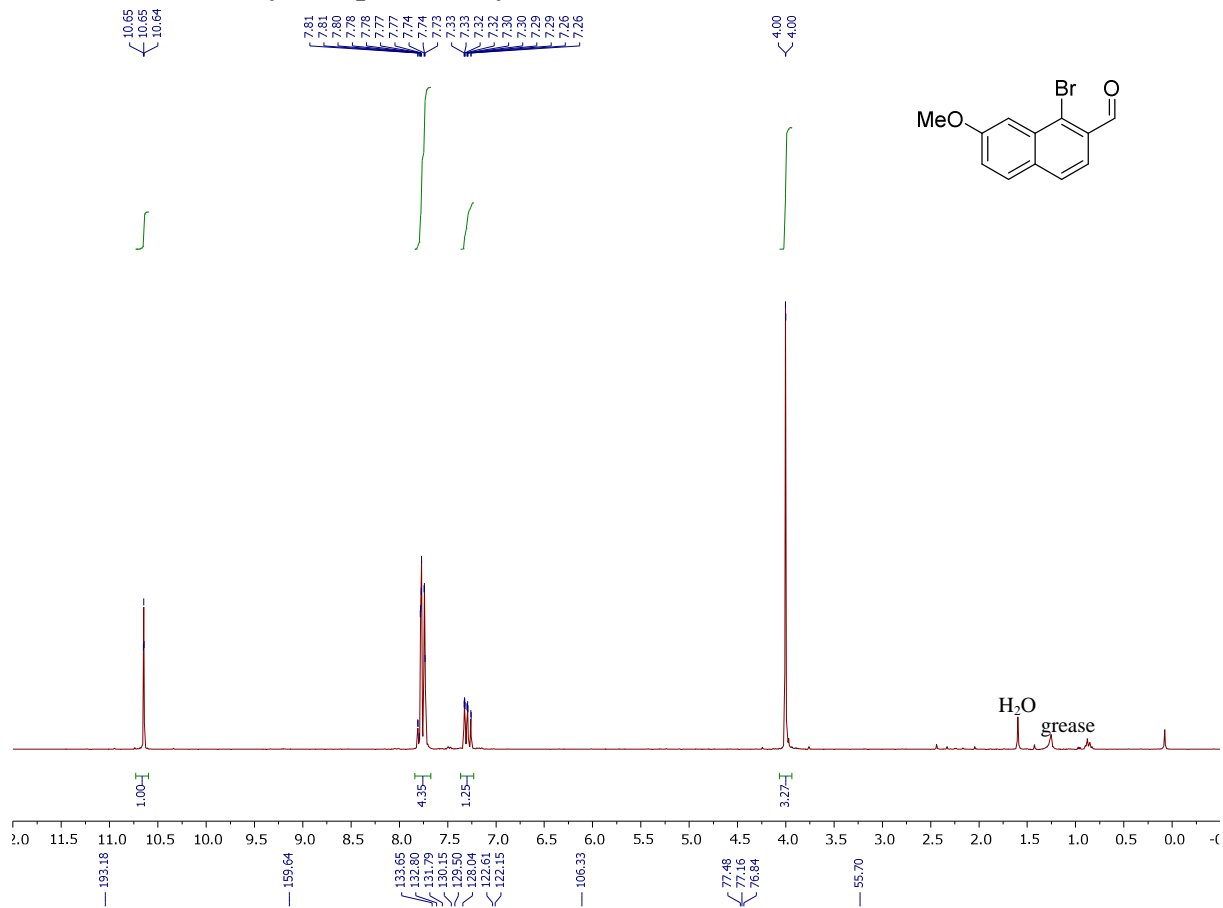
Figure S18. Drawing of M0-(*P, S, R, S_{ligand}*)-isomer.

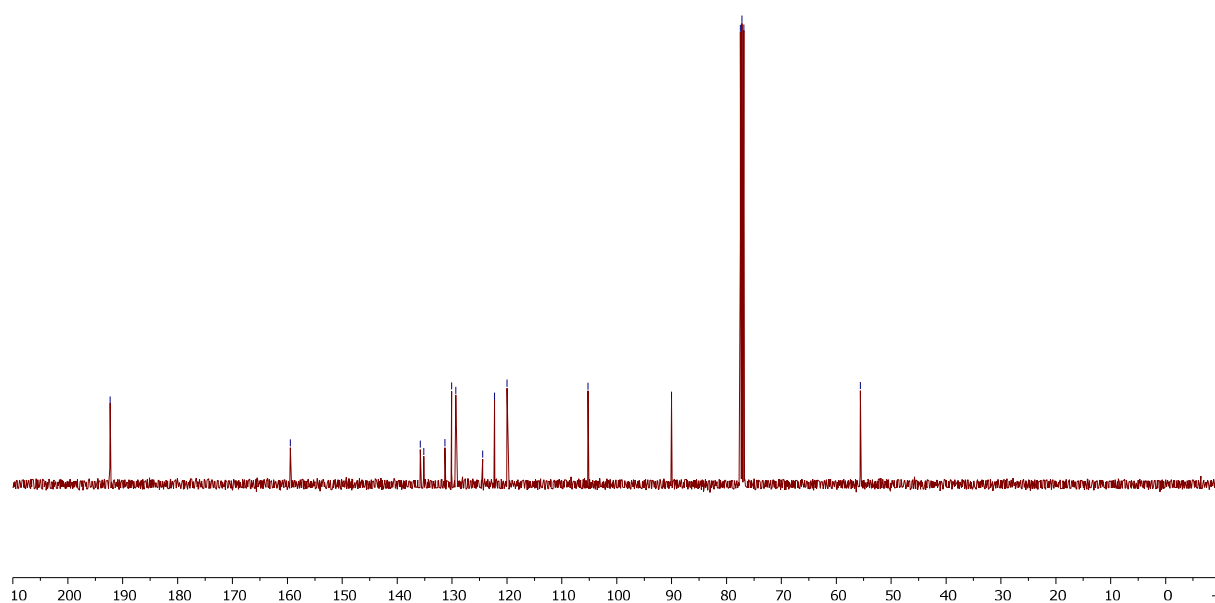
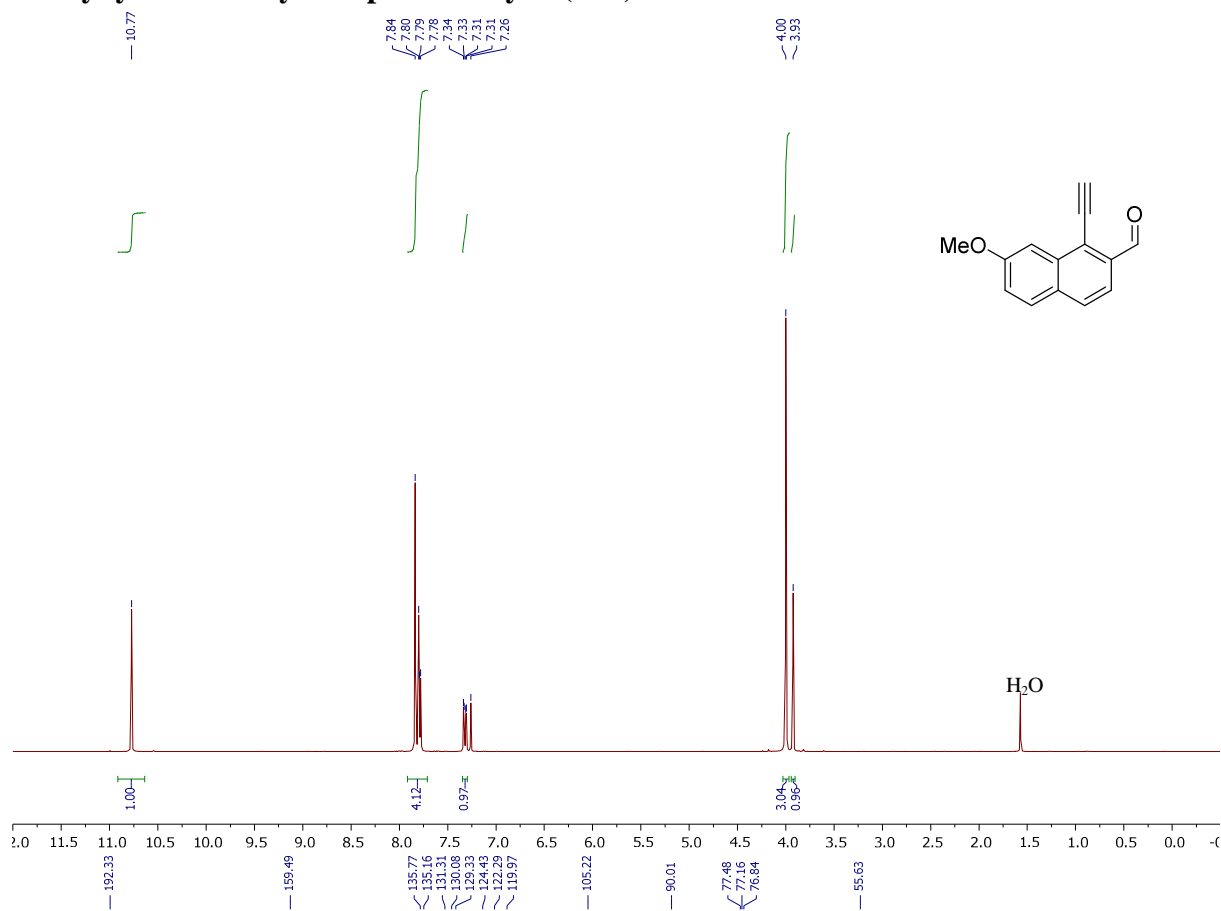
XII Copies of ^1H and ^{13}C NMR spectra

1-ethynyl-2-naphthaldehyde (S2a).

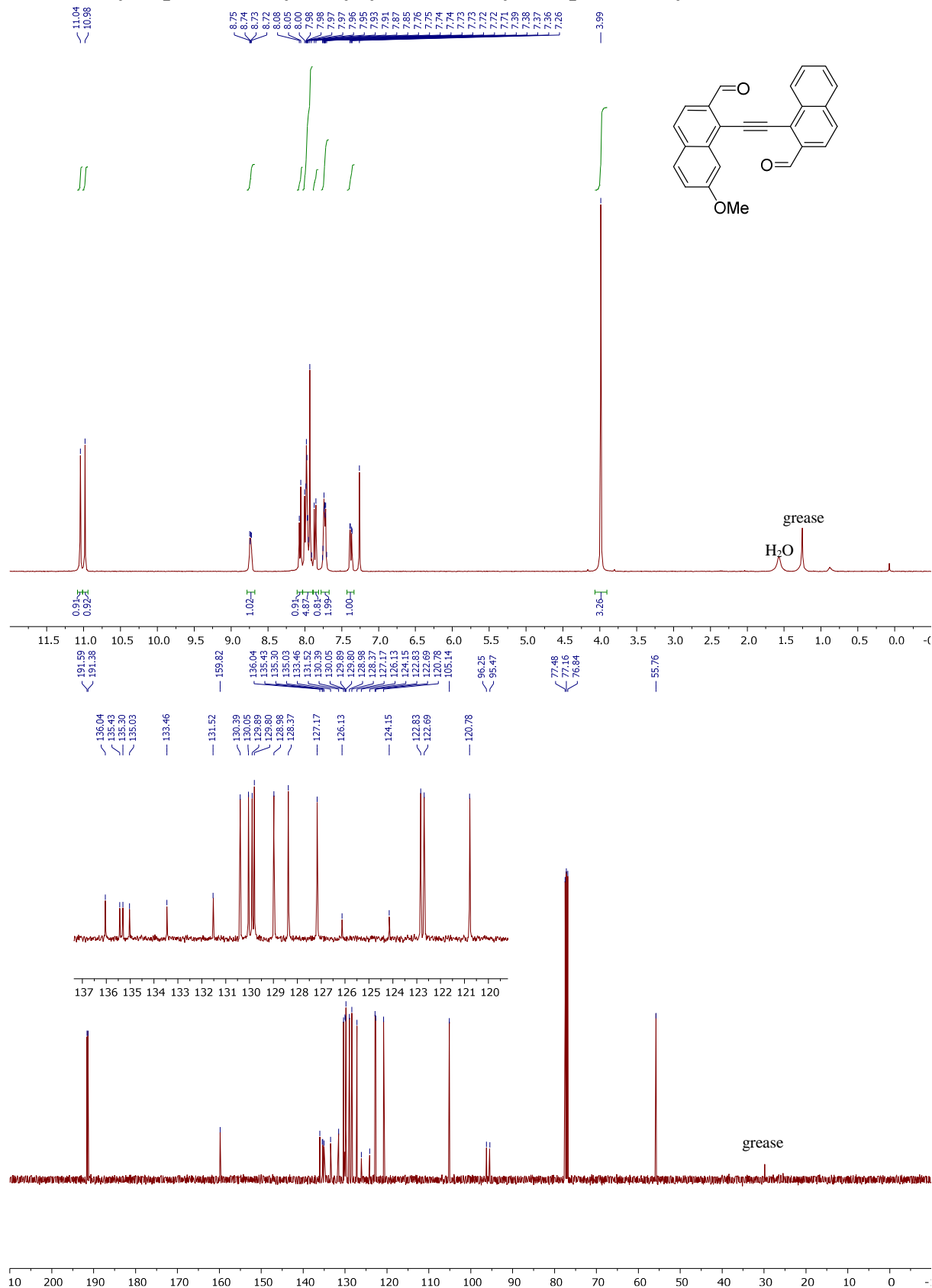


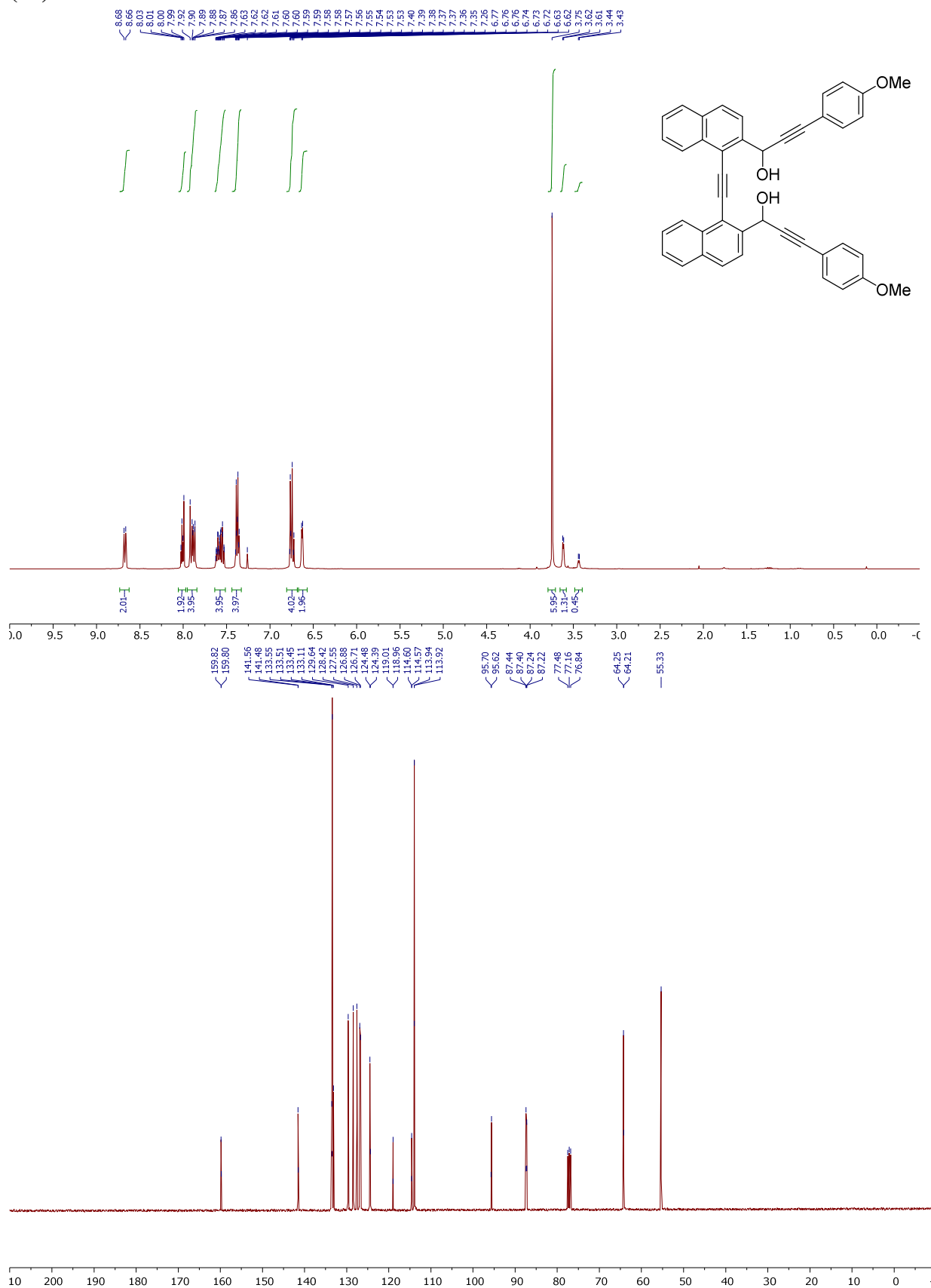
1,1'-(Ethyne-1,2-diyl)bis(2-naphthaldehyde) (S3a).

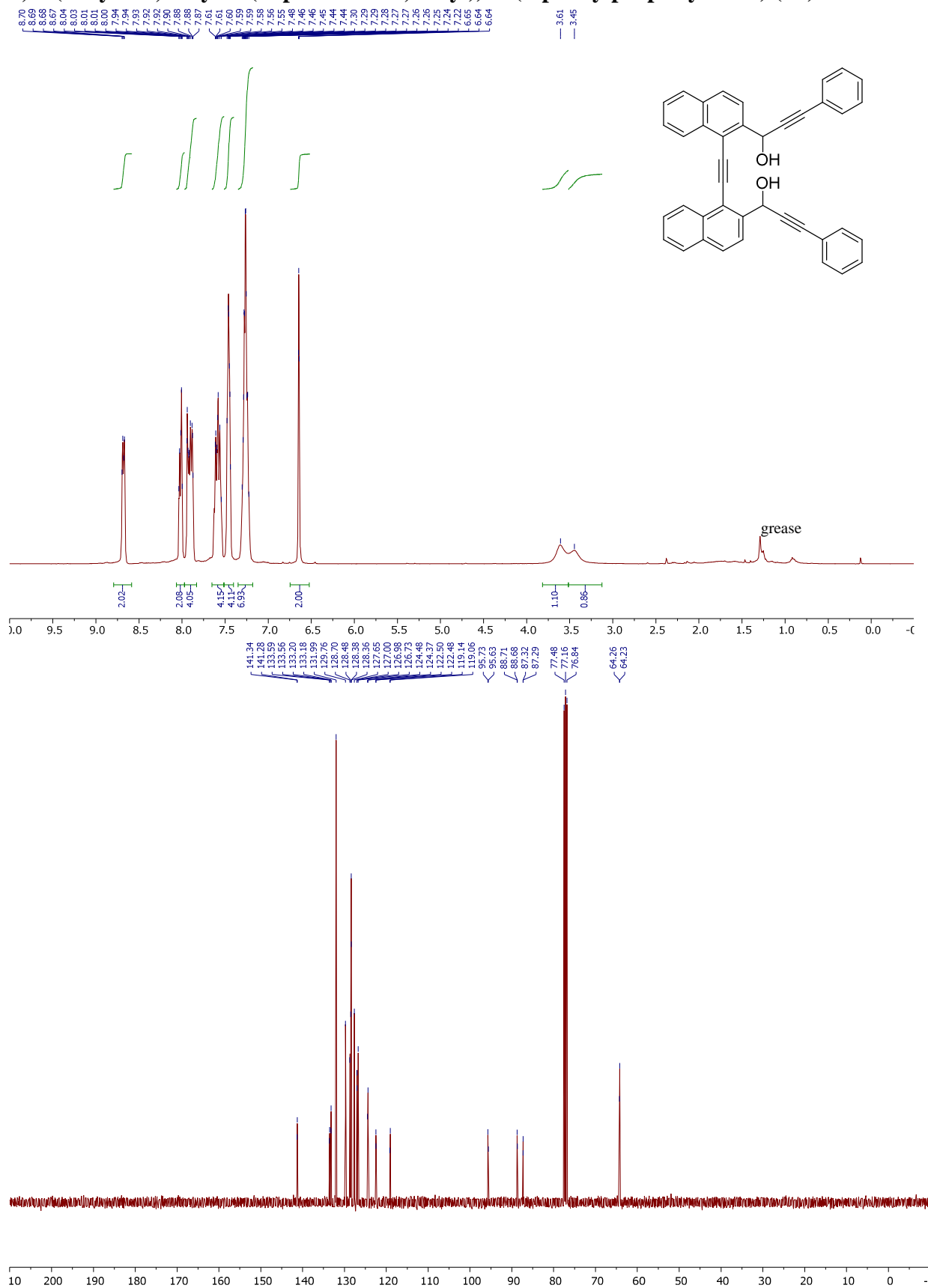
1-bromo-7-methoxy-2-naphthaldehyde (S1b).

1-ethynyl-7-methoxy-2-naphthaldehyde (S2b).

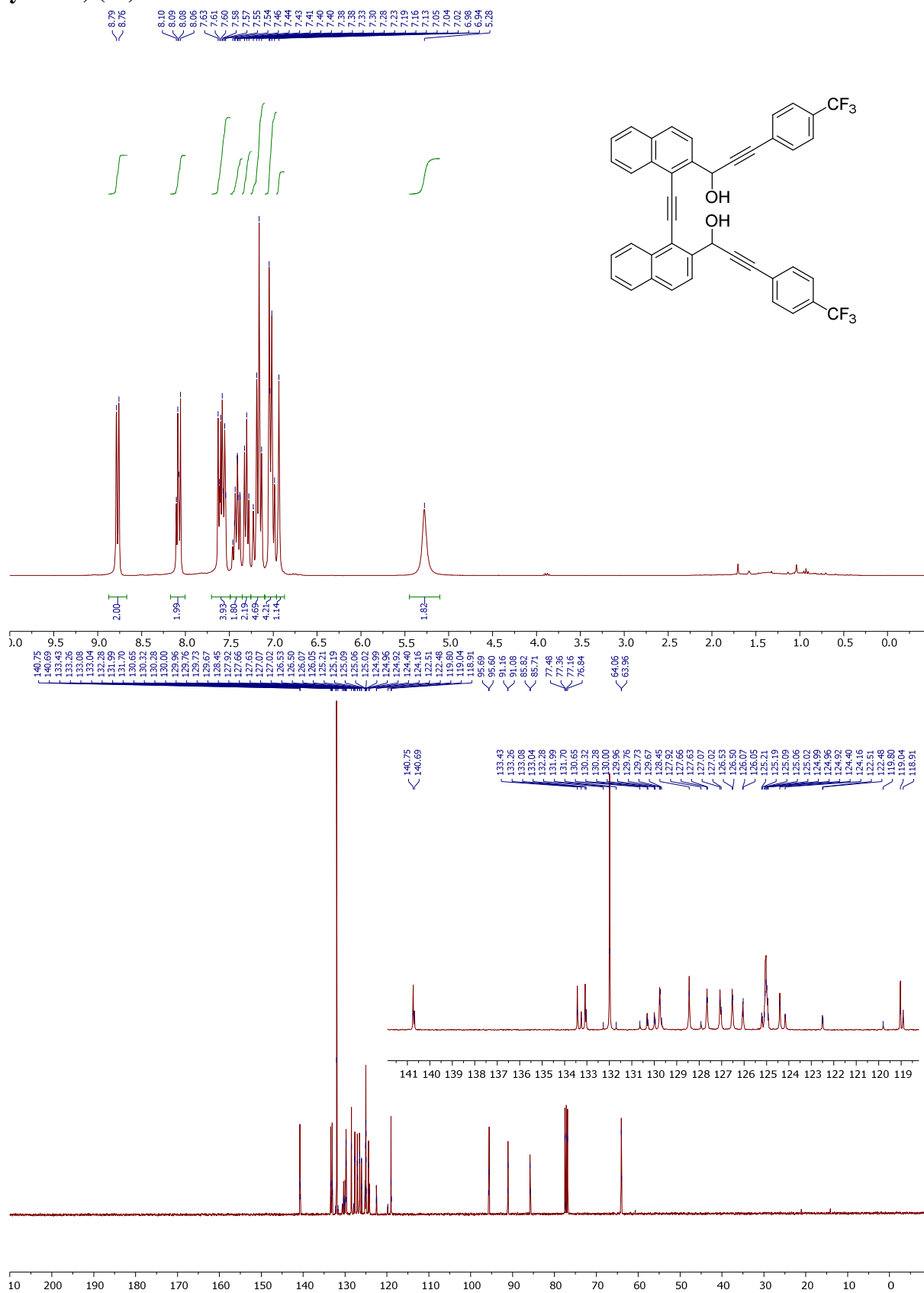
1-((2-formylnaphthalen-1-yl)ethynyl)-7-methoxy-2-naphthaldehyde (S3b).



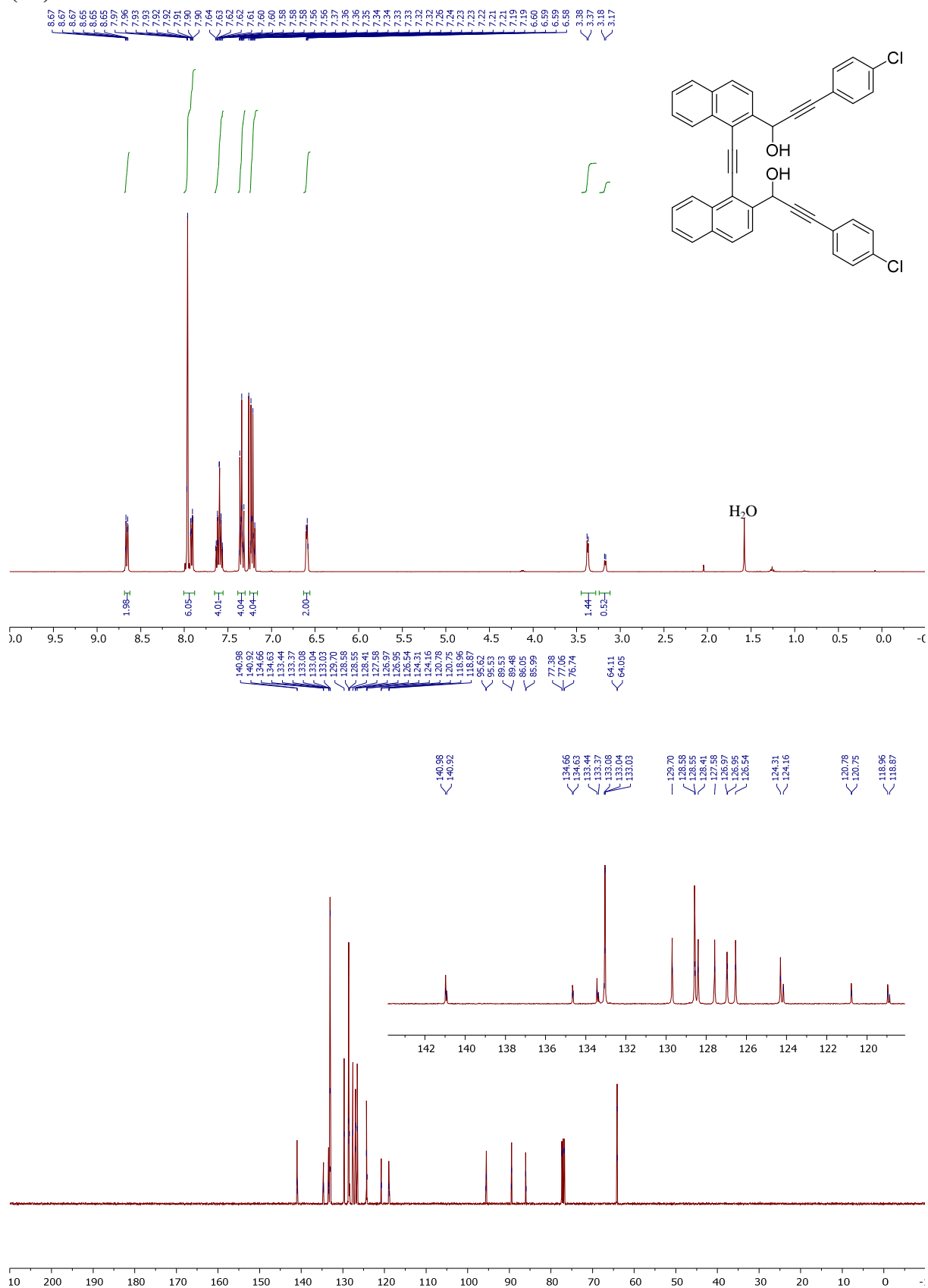
1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(3-(4-methoxyphenyl)prop-2-yn-1-ol)
(1a).

1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(3-phenylprop-2-yn-1-ol) (1b).

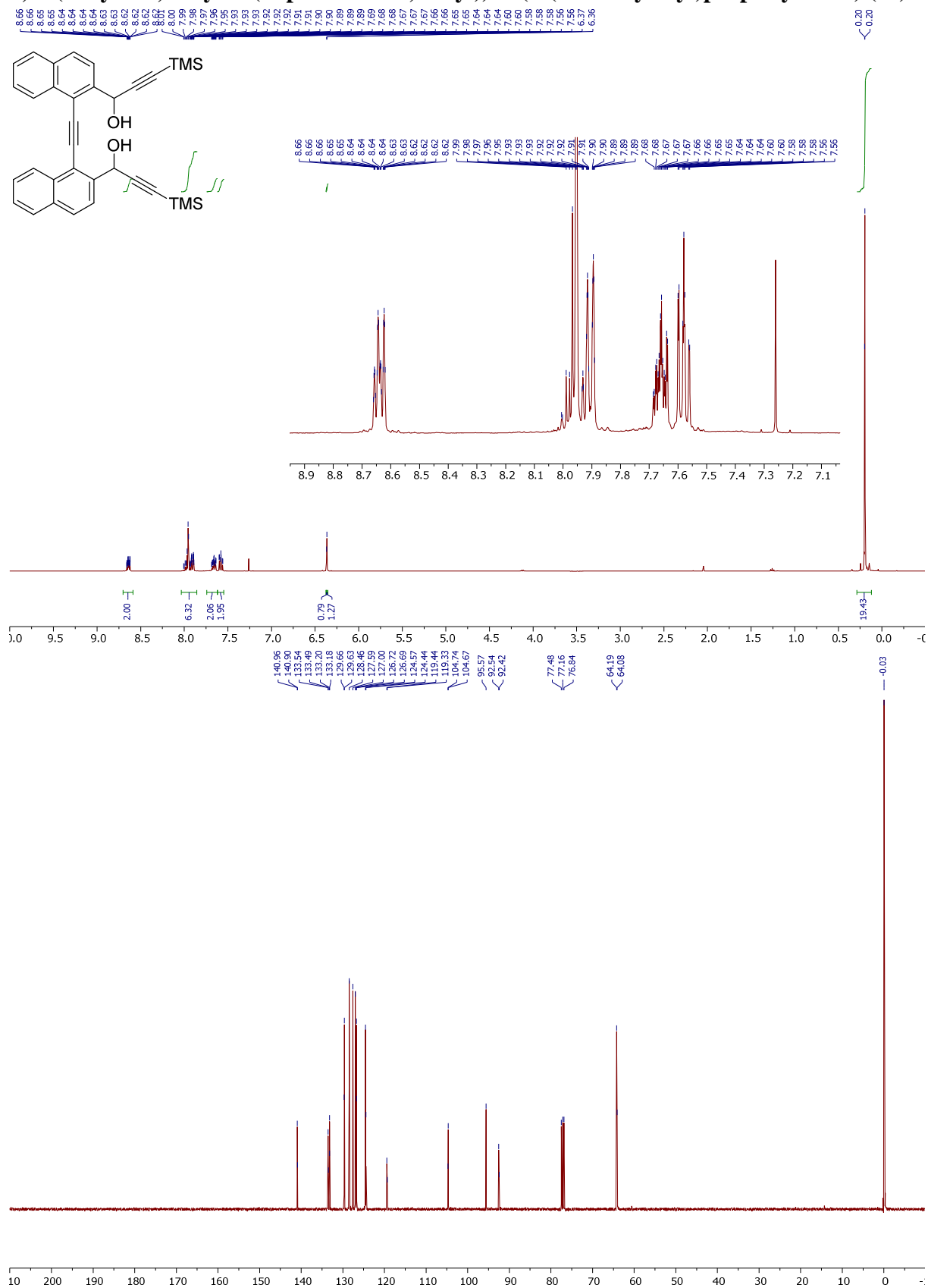
1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol) (1c).



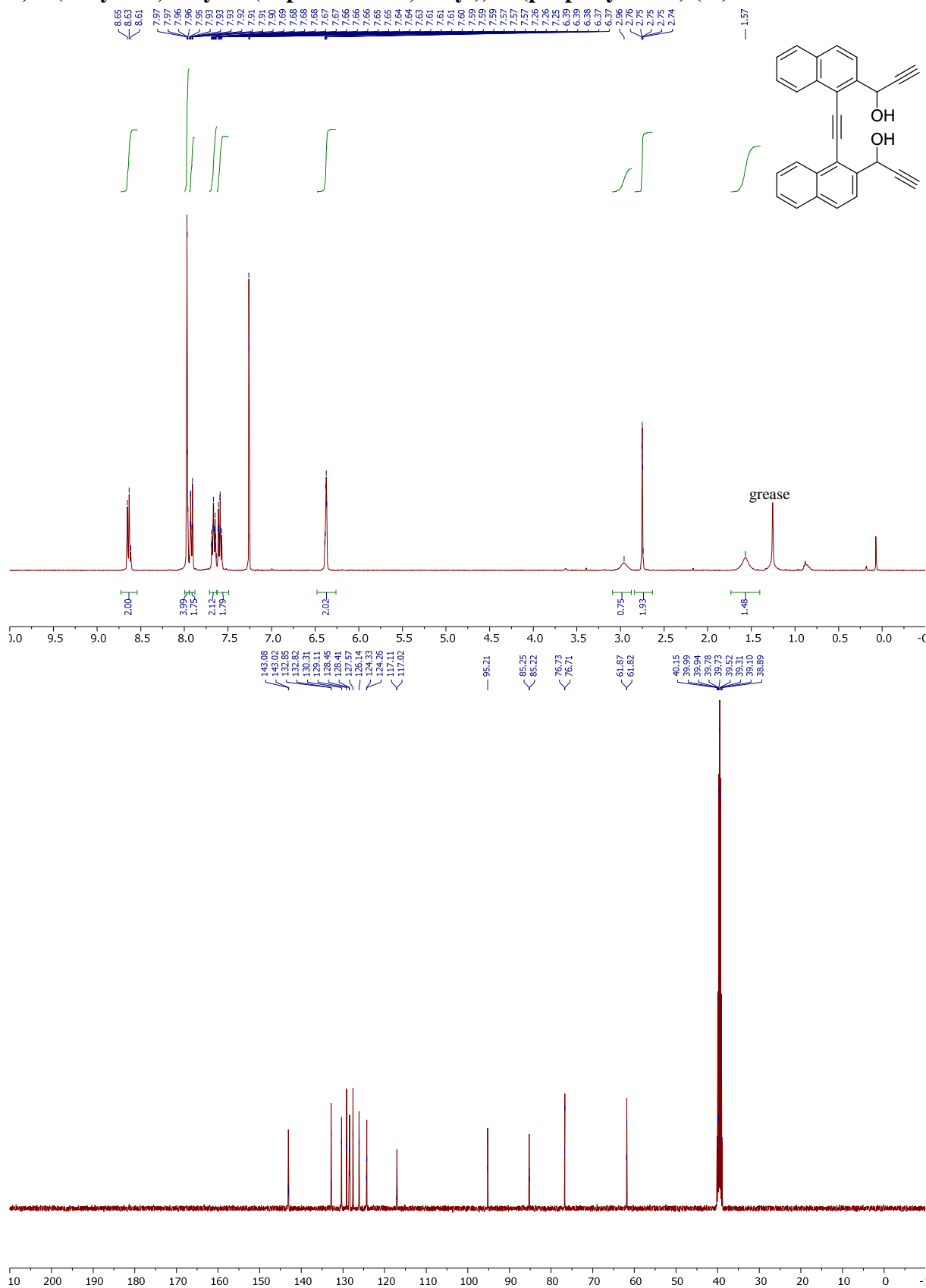
1,1'-(ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(3-(4-chlorophenyl)prop-2-yn-1-ol)
(1d).



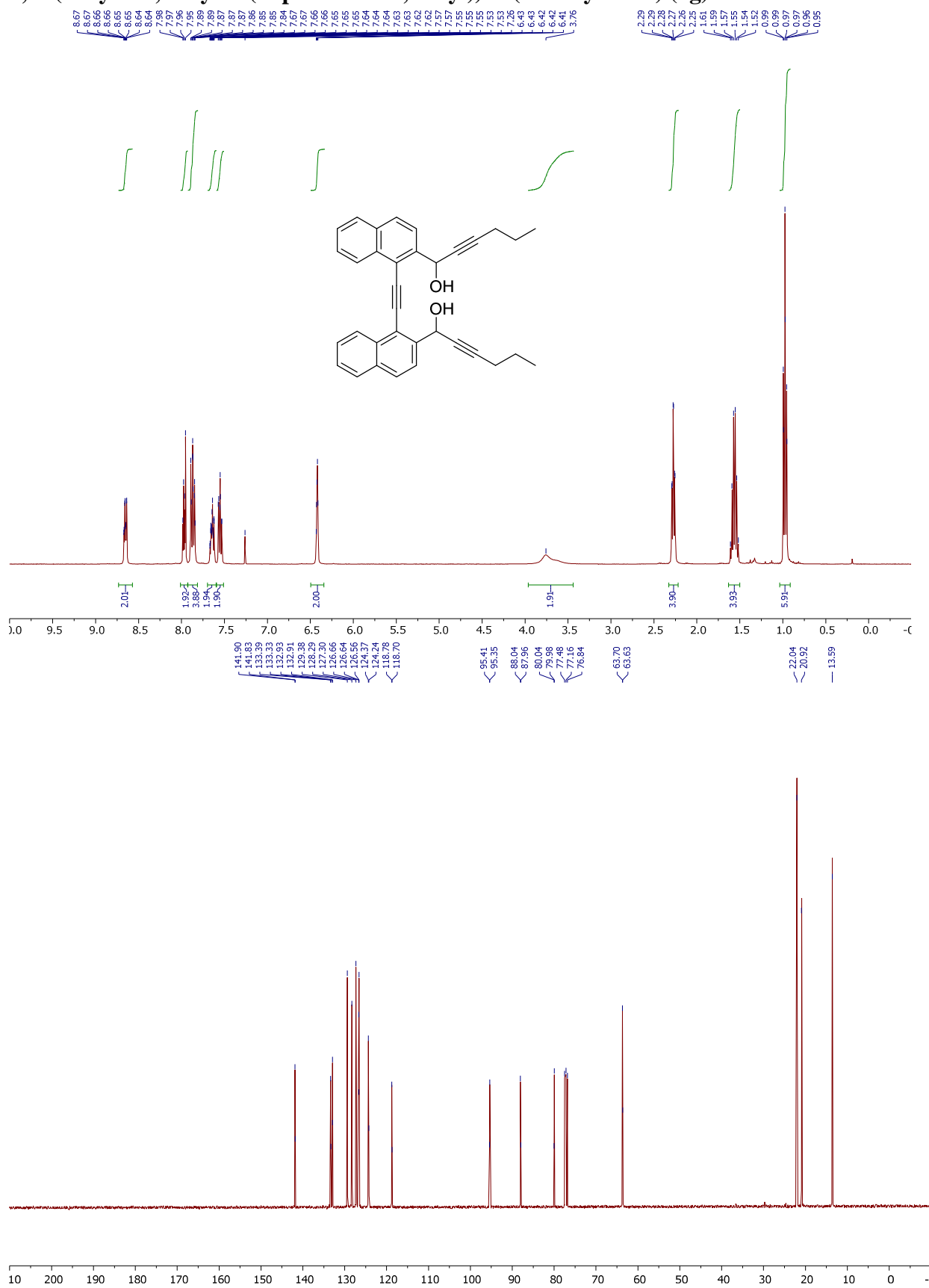
1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(3-(trimethylsilyl)prop-2-yn-1-ol) (1e).



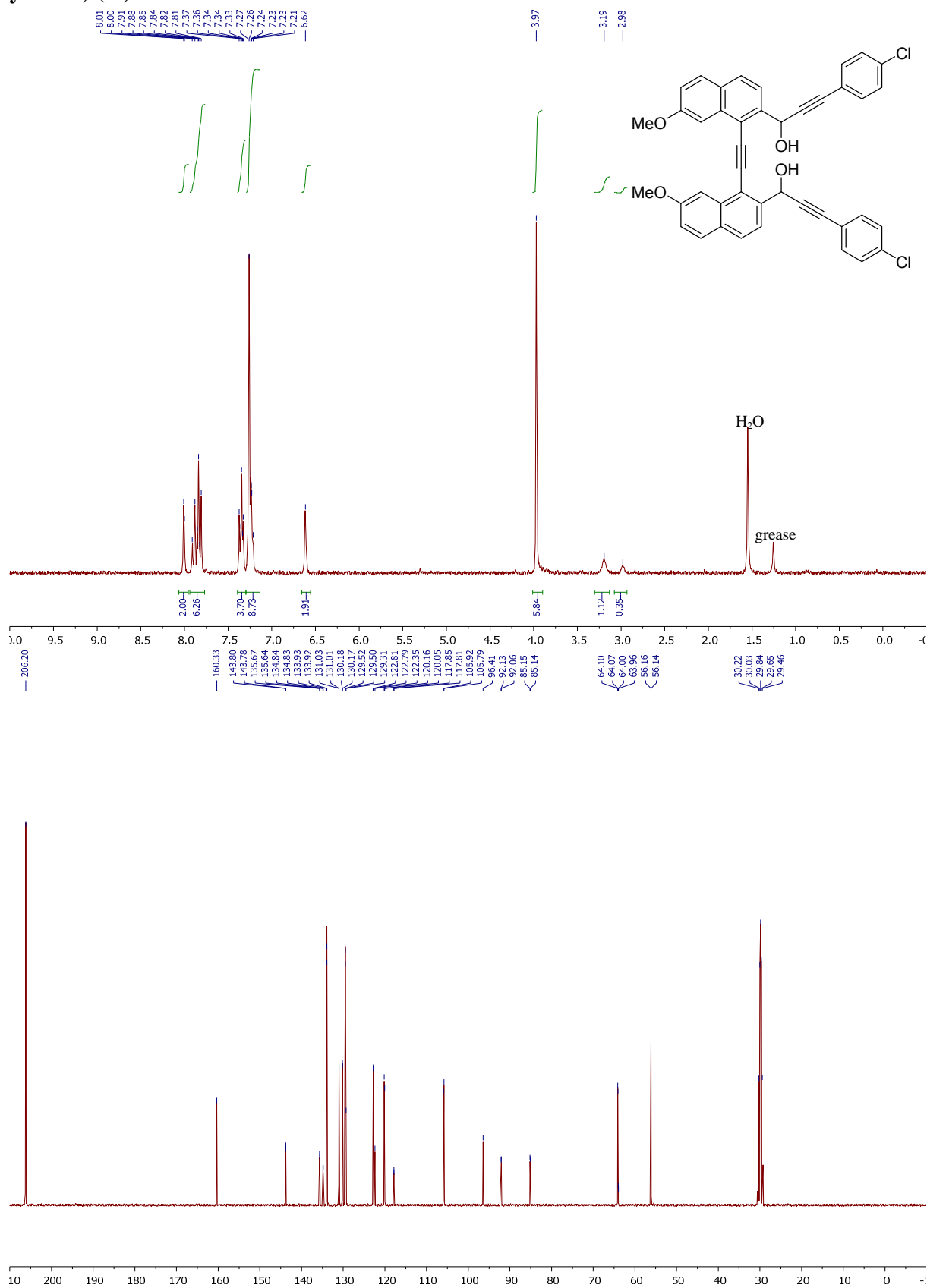
1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(prop-2-yn-1-ol) (1f).



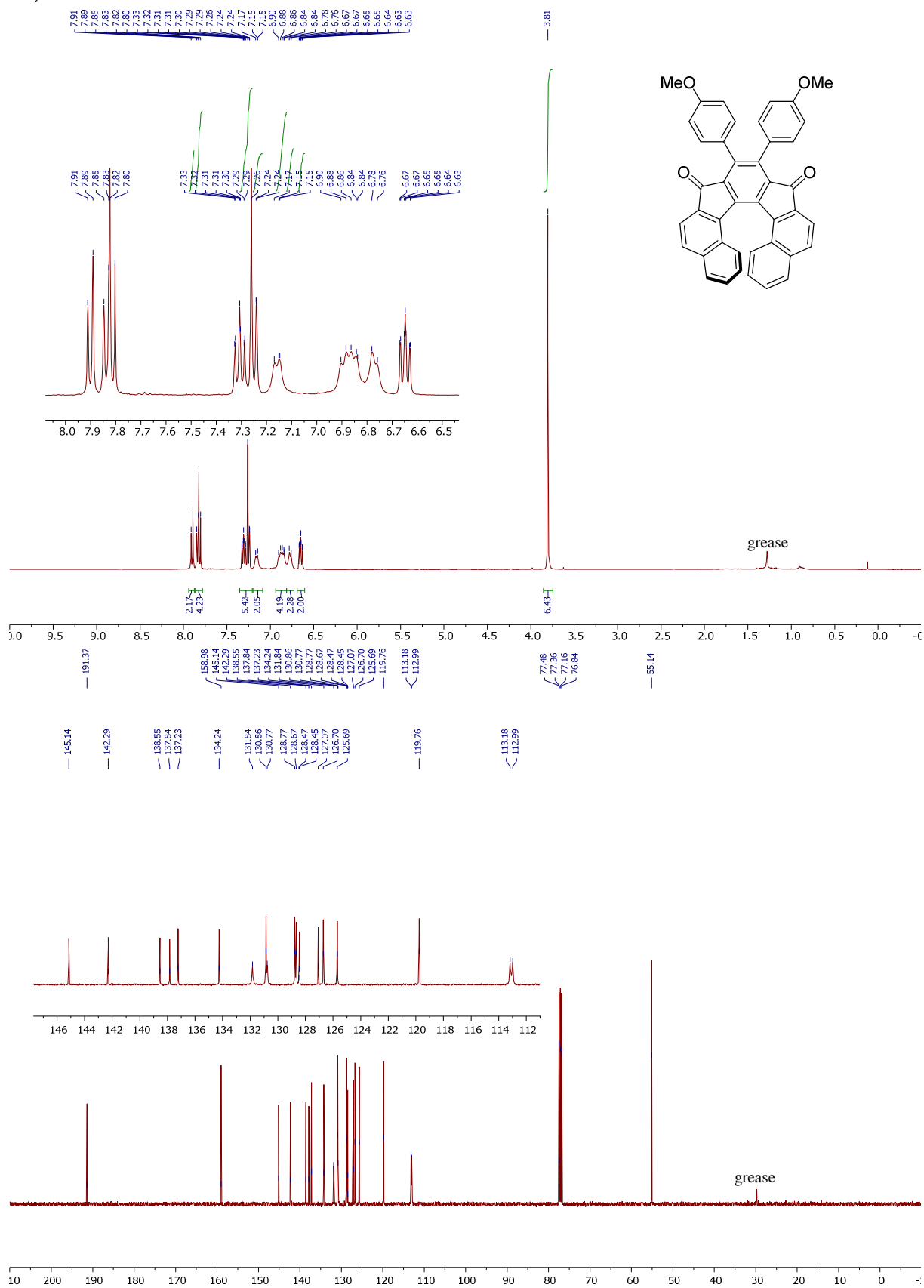
1,1'-(Ethyne-1,2-diylbis(naphthalene-1,2-diyl))bis(hex-2-yn-1-ol) (1g).

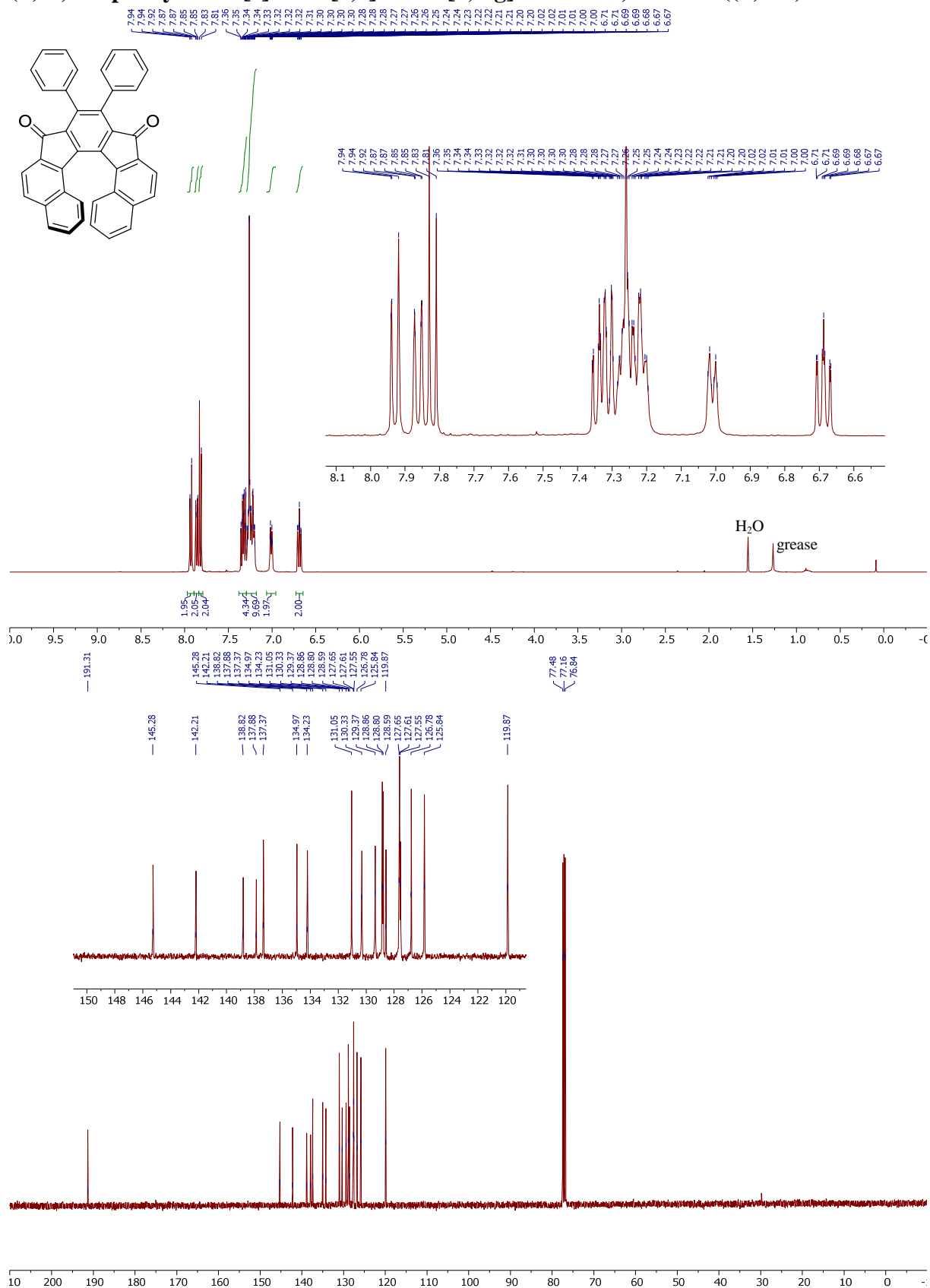


1,1'-(ethyne-1,2-diylbis(7-methoxynaphthalene-1,2-diyl))bis(3-(4-chlorophenyl)prop-2-yn-1-ol) (1i).

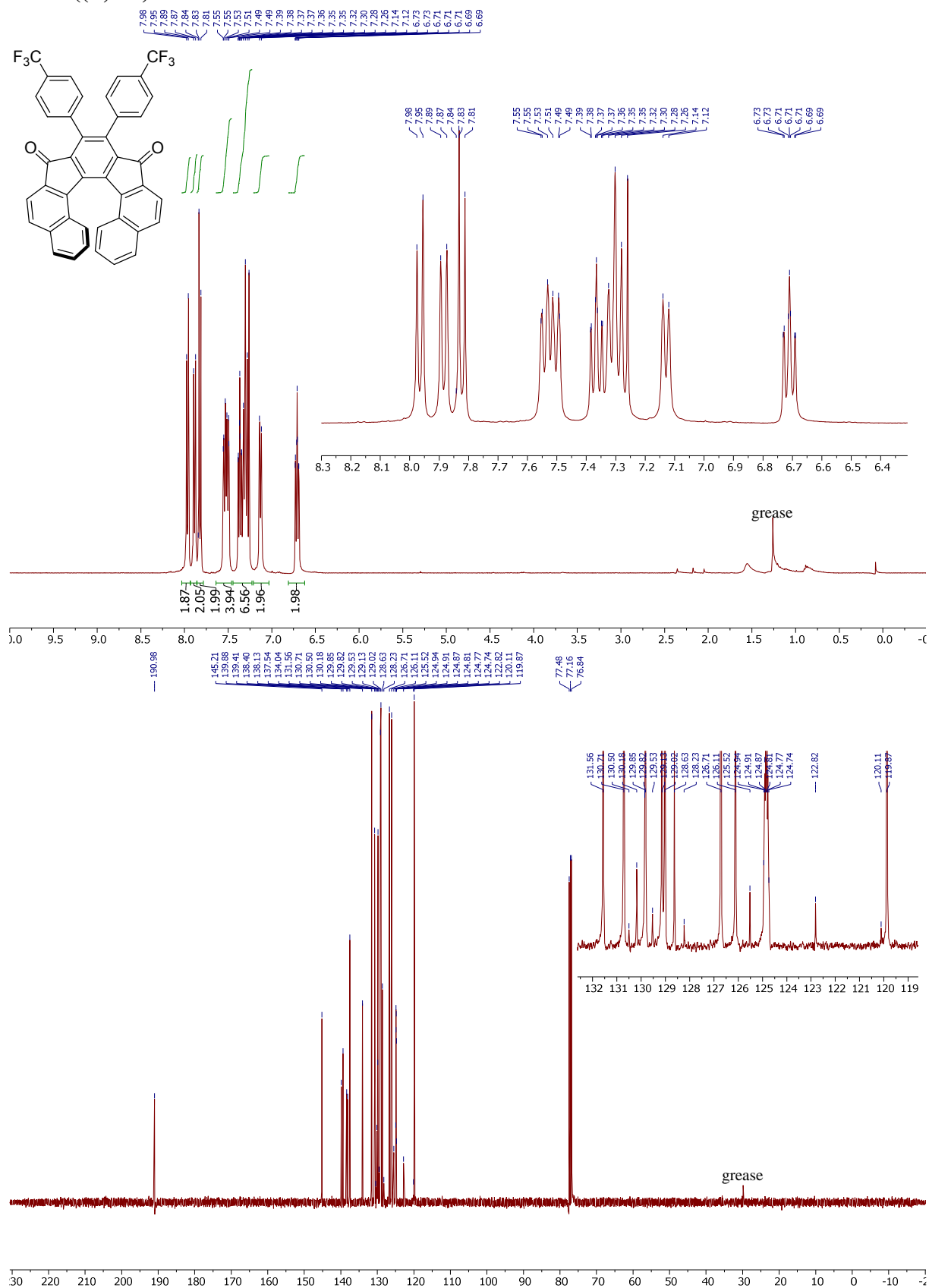


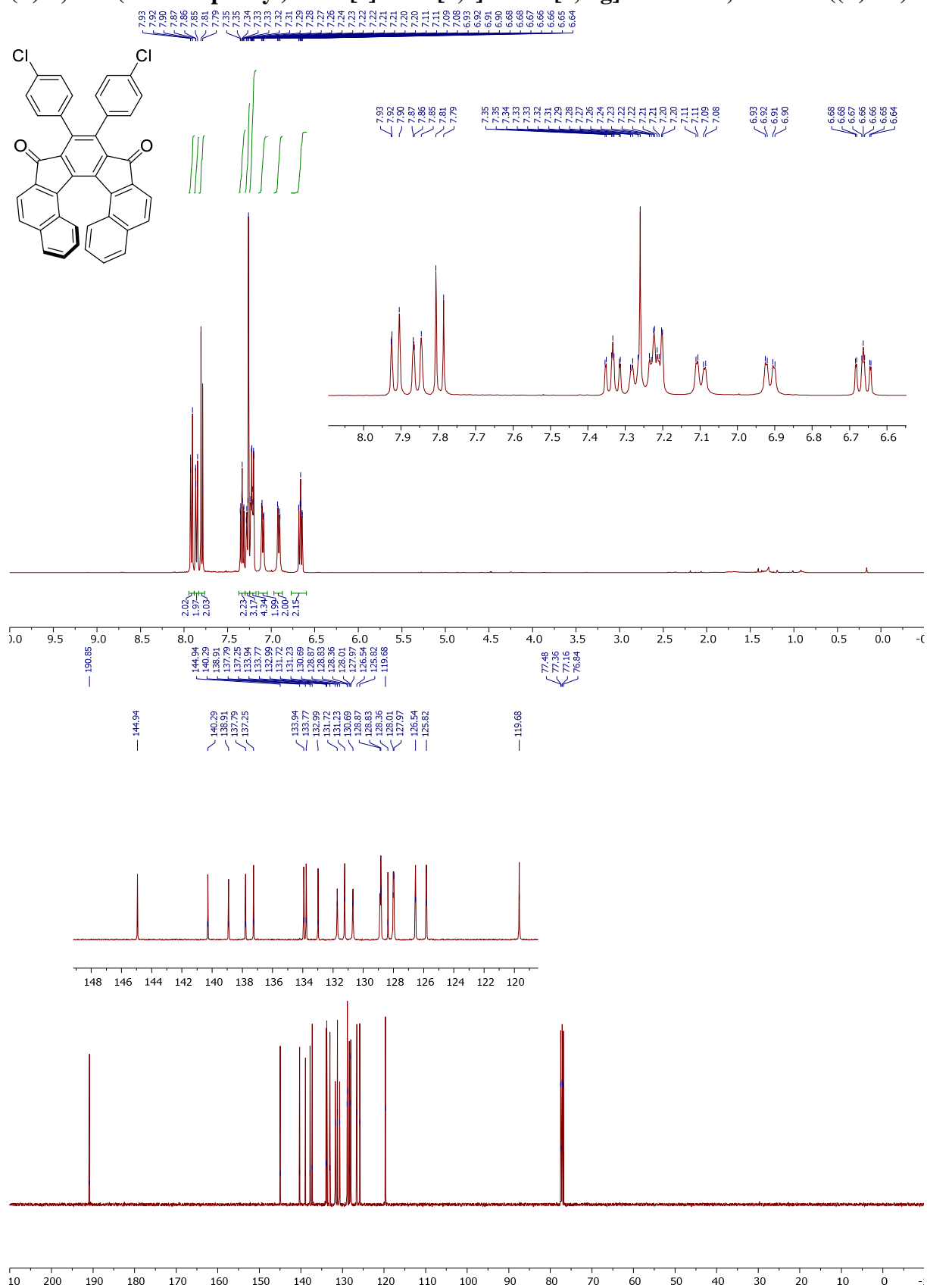
(P)-8,9-Bis(4-methoxyphenyl)benzo[c]benzo[6,7]indeno[1,2-g]fluorene-7,10-dione ((P)-2a).

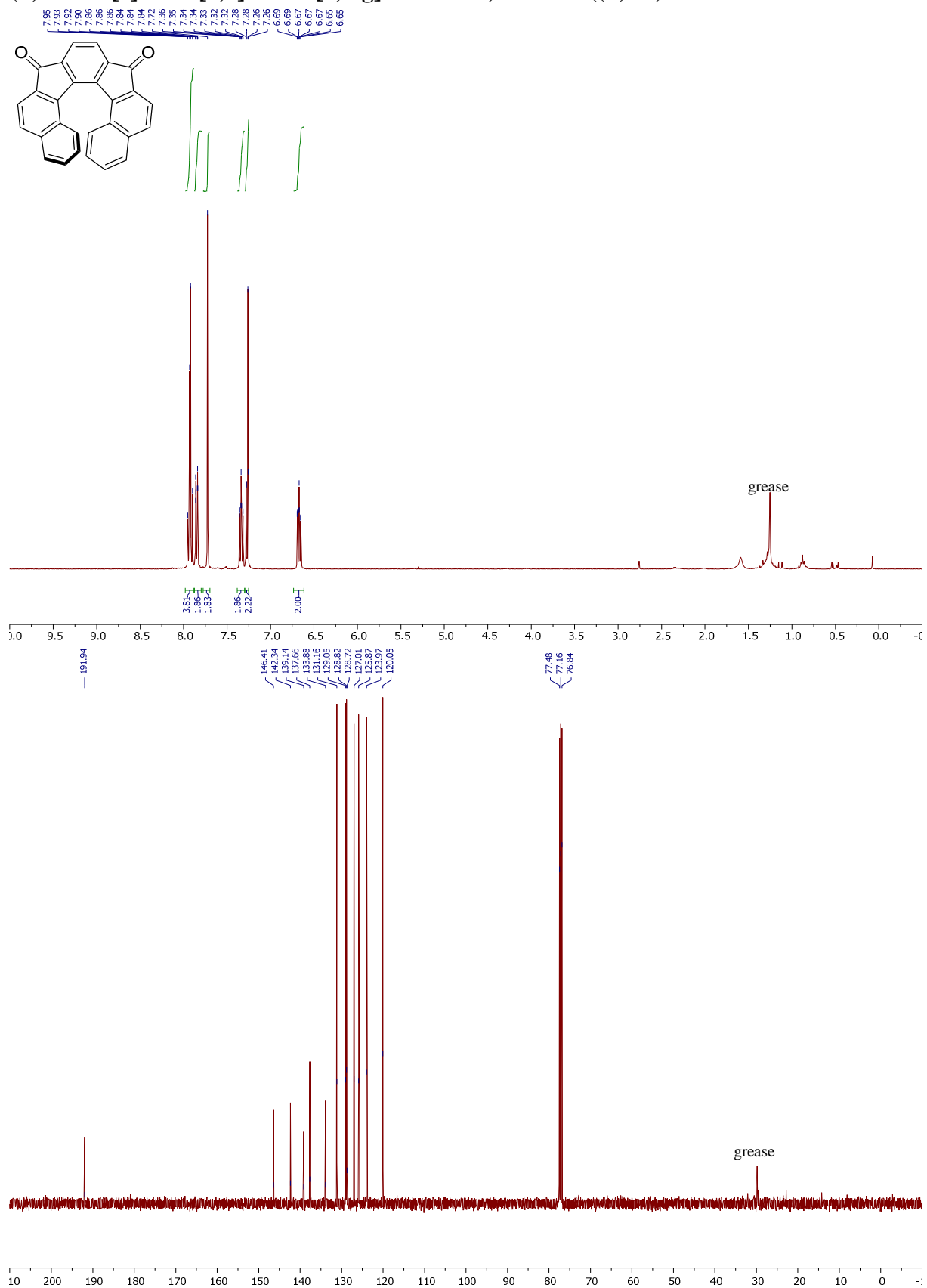


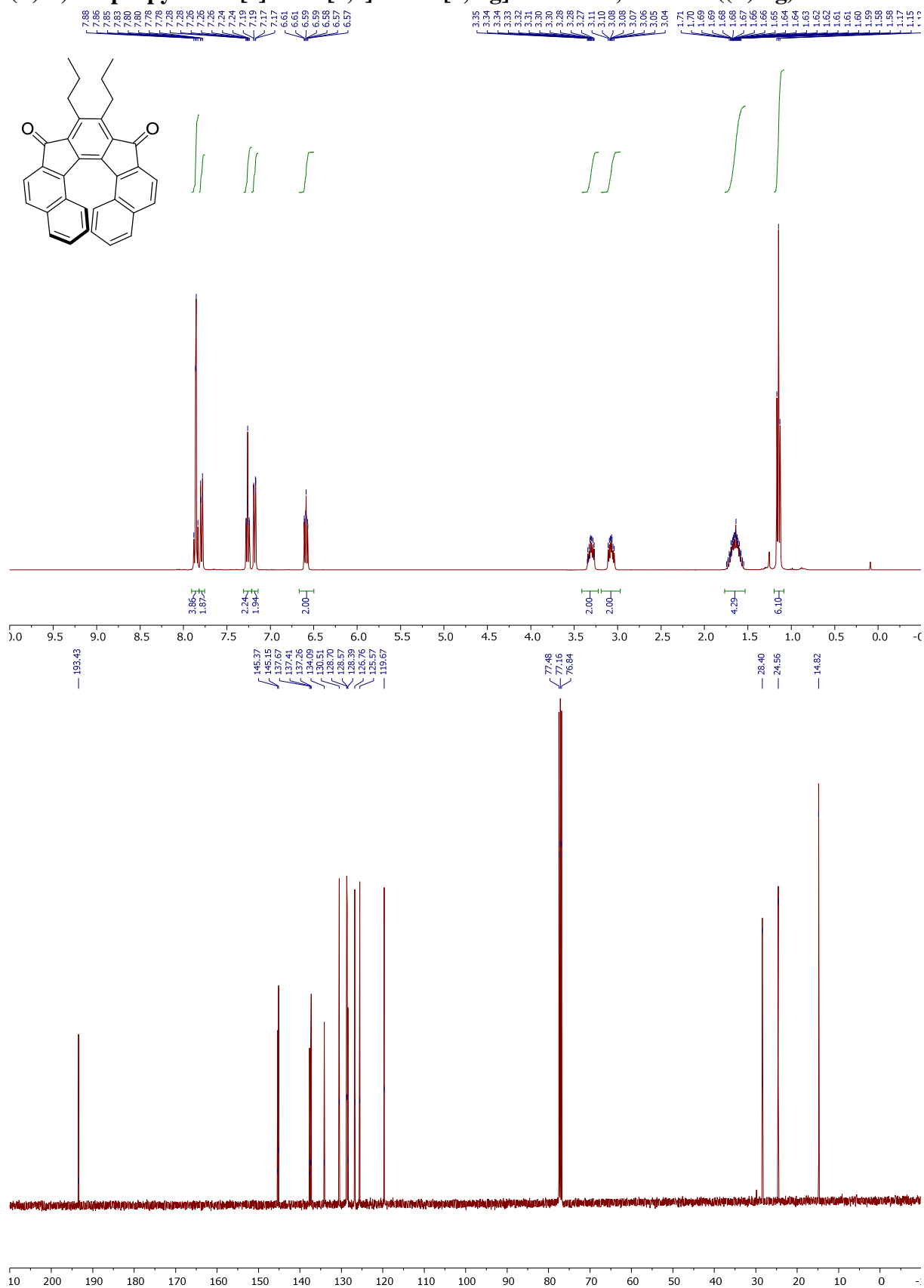
(P)-8,9-Diphenylbenzo[*c*]benzo[6,7]indeno[1,2-*g*]fluorene-7,10-dione ((P)-2b).

(P)-8,9-Bis(4-(trifluoromethyl)phenyl)benzo[c]benzo[6,7]indeno[1,2-g]fluorene-7,10-dione ((P)-2c).

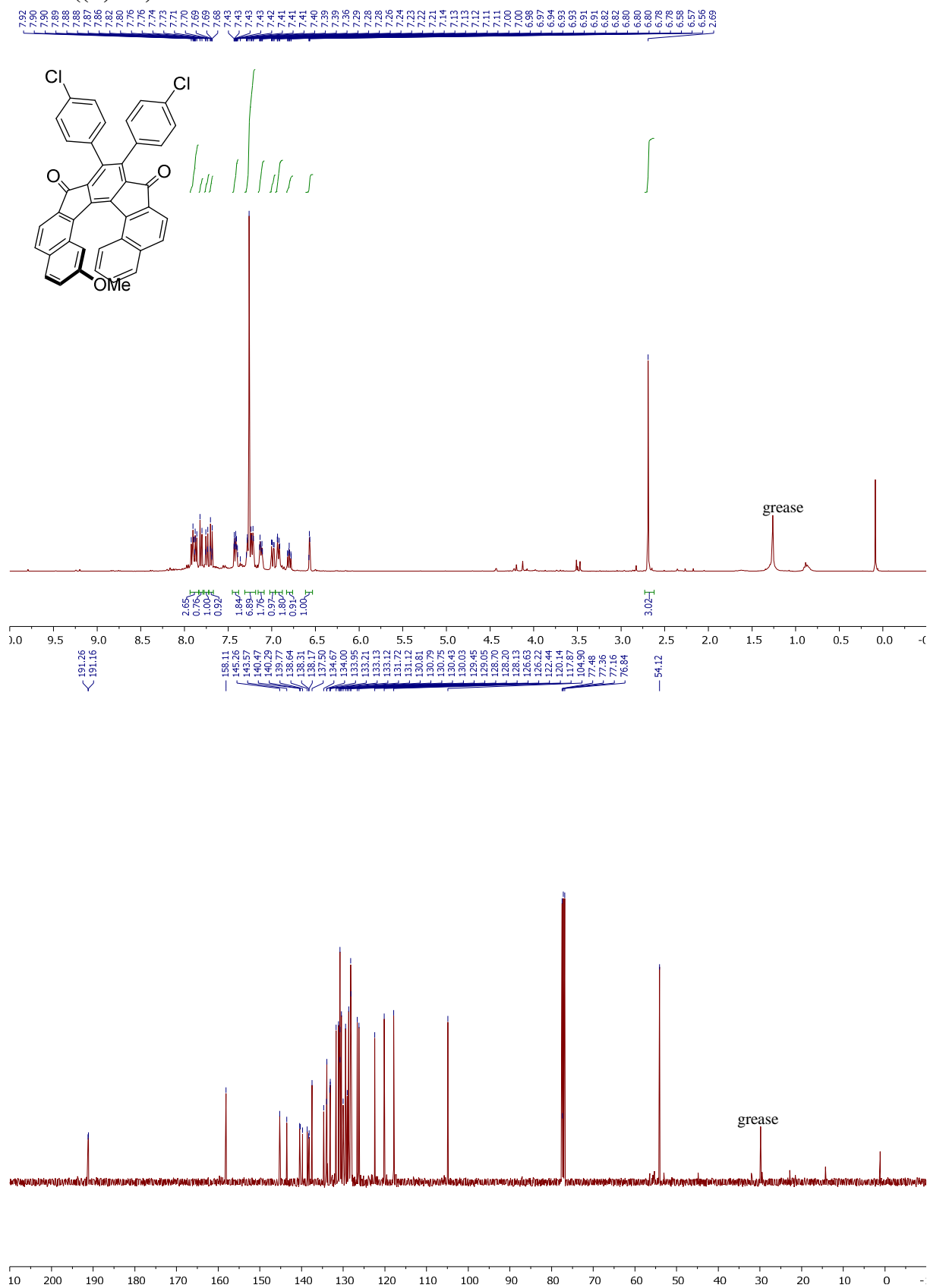


(P)-8,9-bis(4-chlorophenyl)benzo[c]benzo[6,7]indeno[1,2-g]fluorene-7,10-dione ((P)-2d).

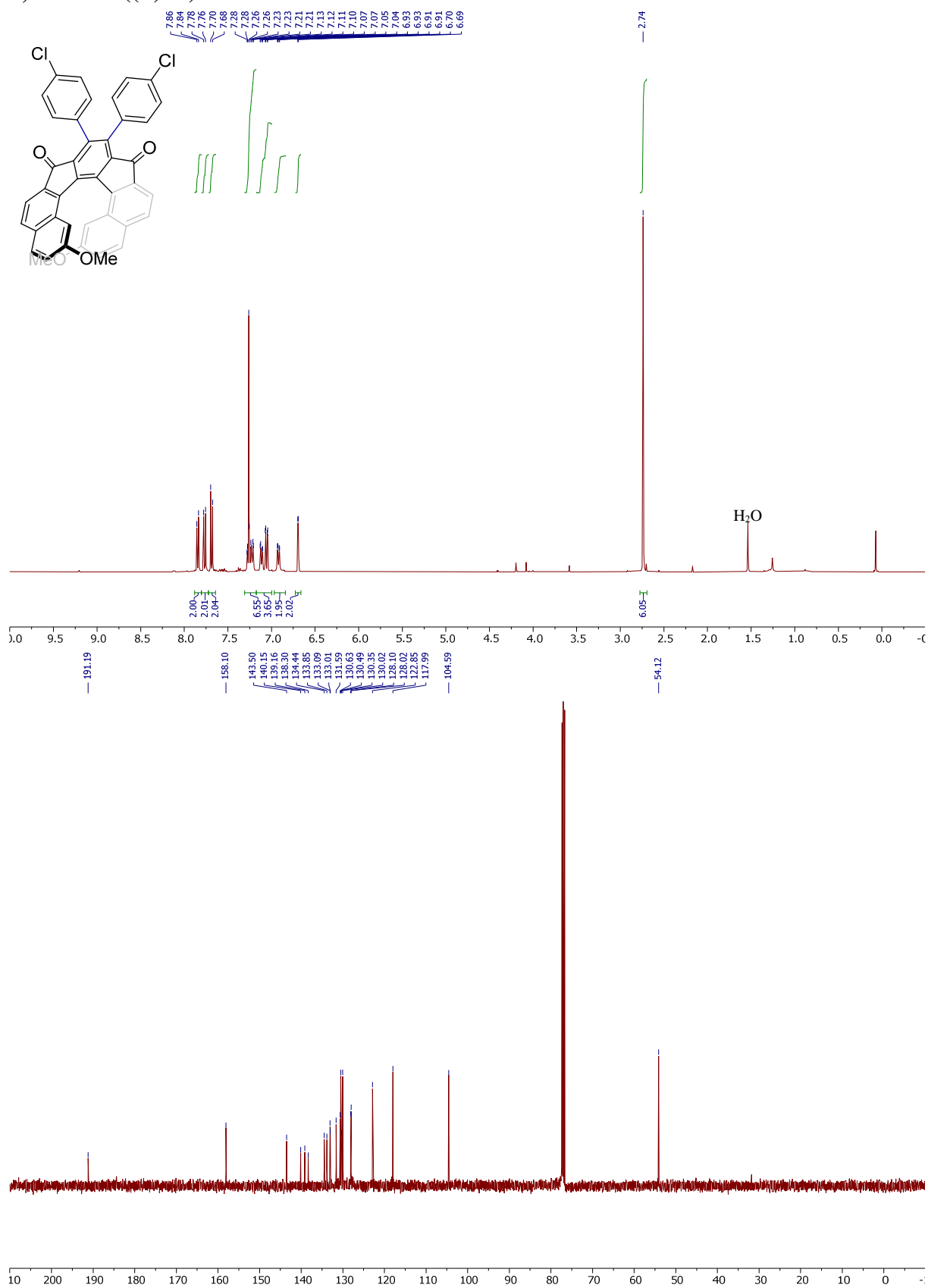
(P)-Benzo[c]benzo[6,7]indeno[1,2-g]fluorene-7,10-dione ((P)-2f).

(P)-8,9-Dipropylbenzo[c]benzo[6,7]indeno[1,2-g]fluorene-7,10-dione ((P)-2g).

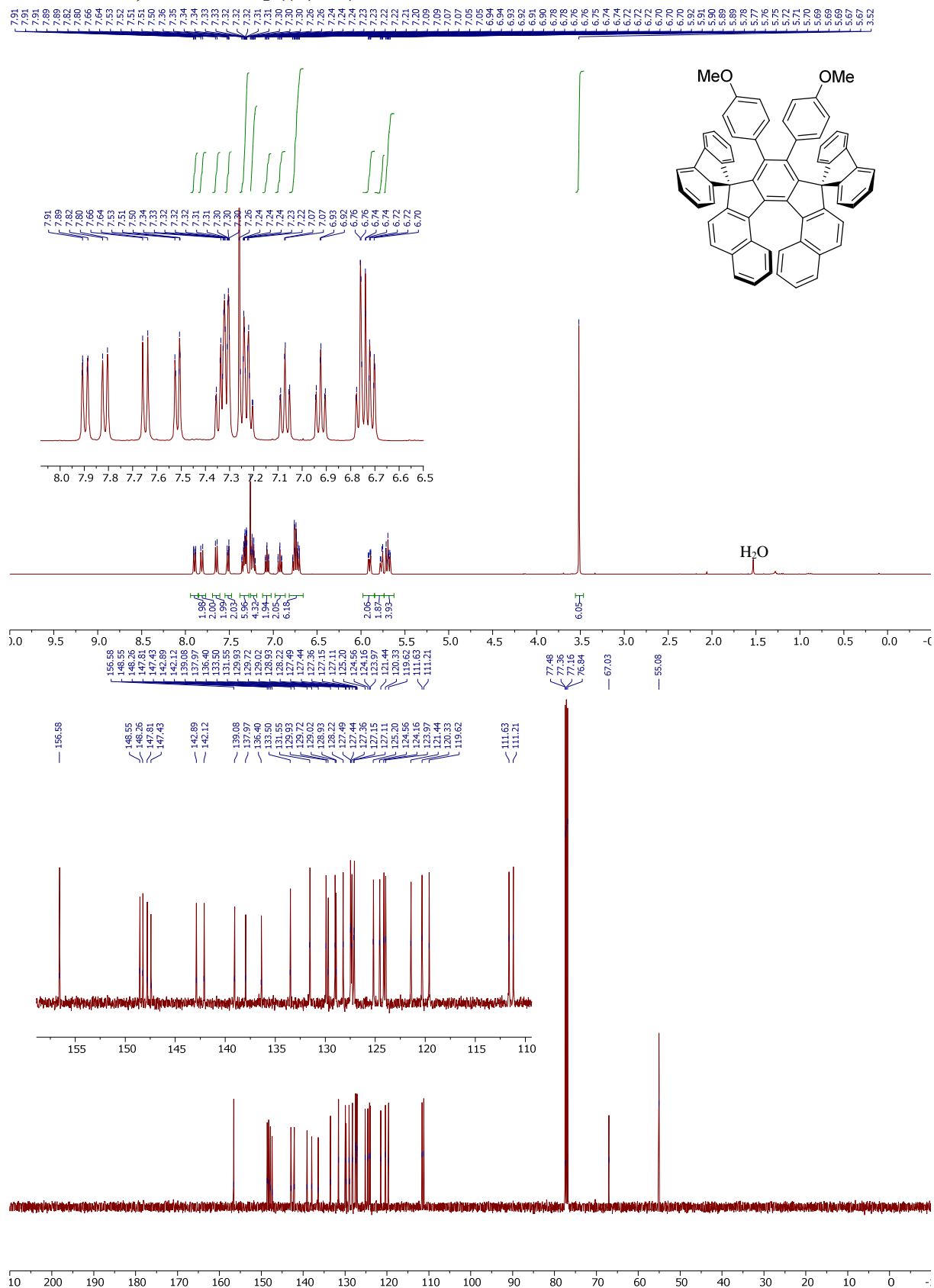
(P)- 8,9-bis(4-chlorophenyl)-2-methoxybenzo[c]benzo[6,7]indeno[1,2-g]fluorene-7,10-dione ((P)-2h).



(P)-8,9-bis(4-chlorophenyl)-2,15-dimethoxybenzo[c]benzo[6,7]indeno[1,2-g]fluorene-7,10-dione ((P)-2i).

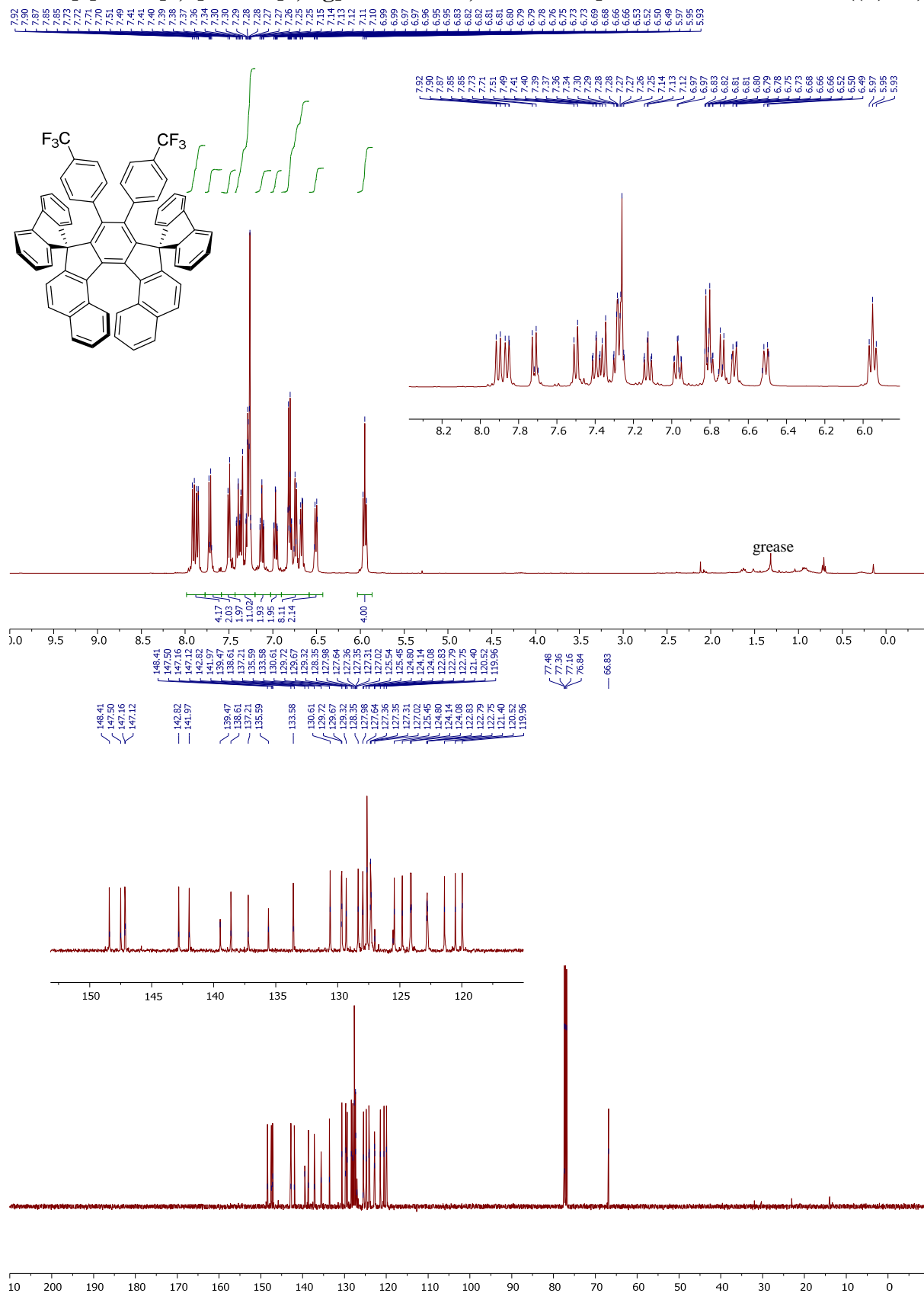


(P)-8',9'-Bis(4-methoxyphenyl)dispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-g]-fluorene-10',9''-fluorene] ((P)-3a).

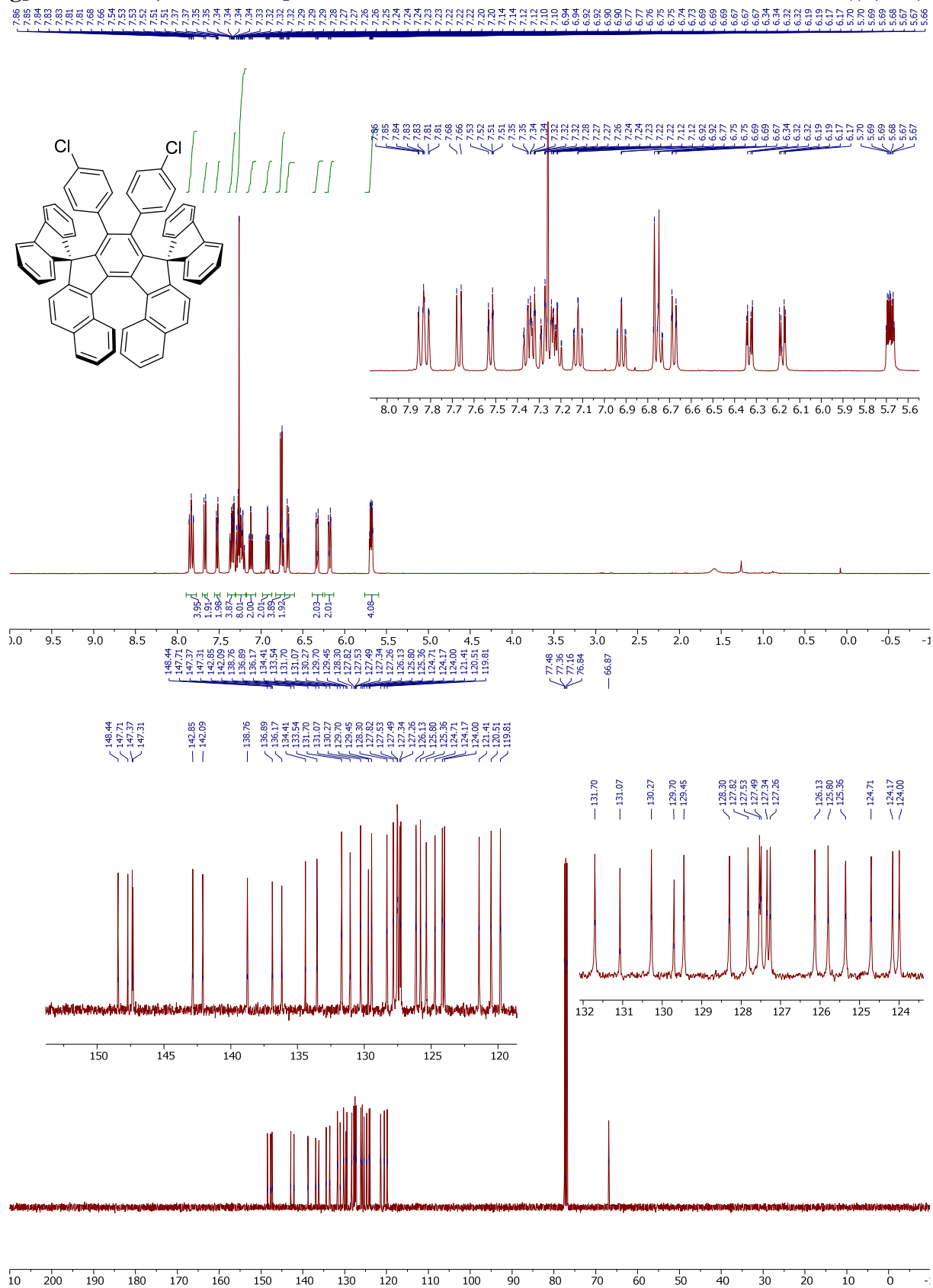


(P)-8',9'-bis(4-(trifluoromethyl)phenyl)dispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-g]fluorene-10',9''-fluorene]

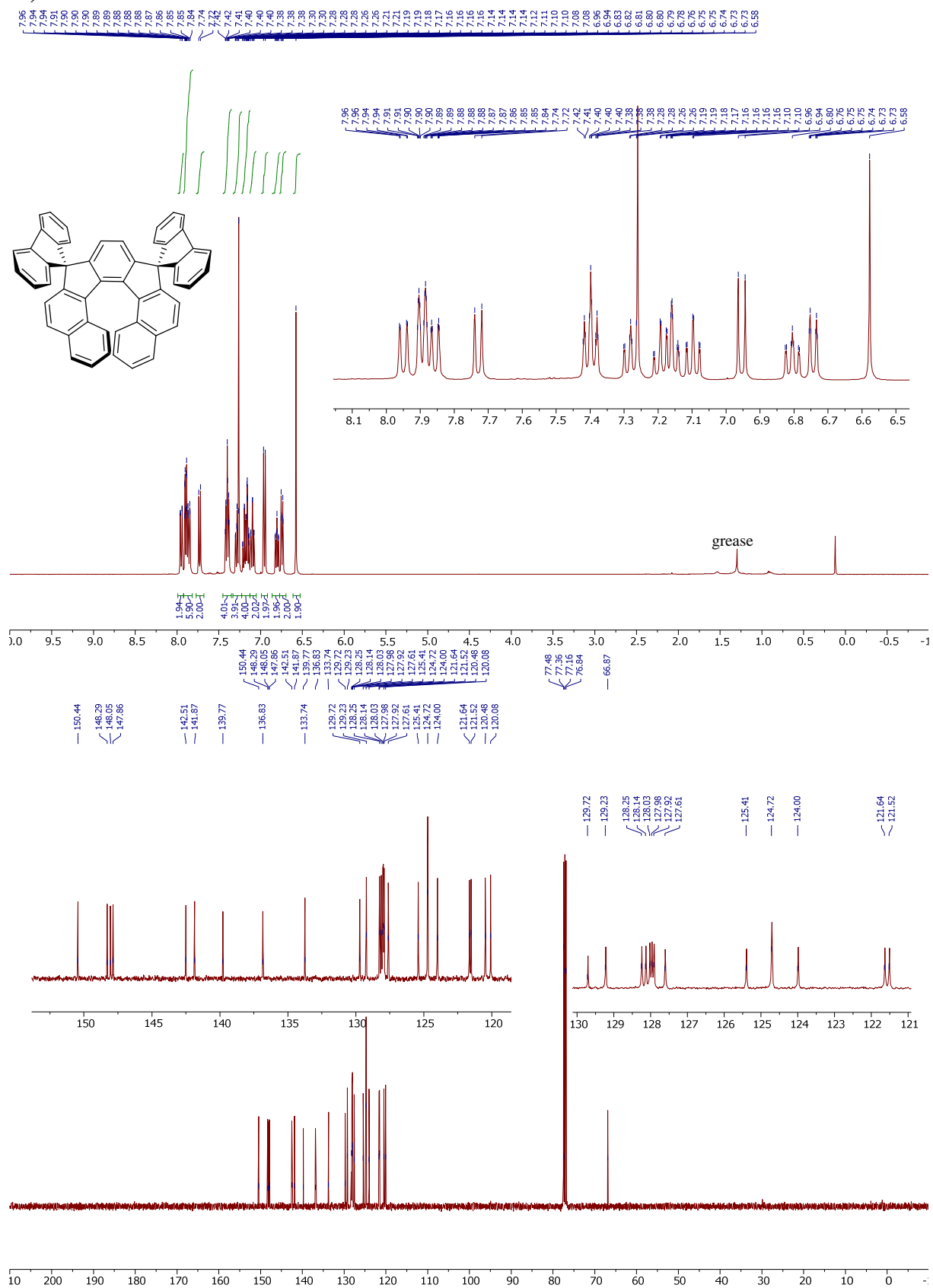
((P)-3c).



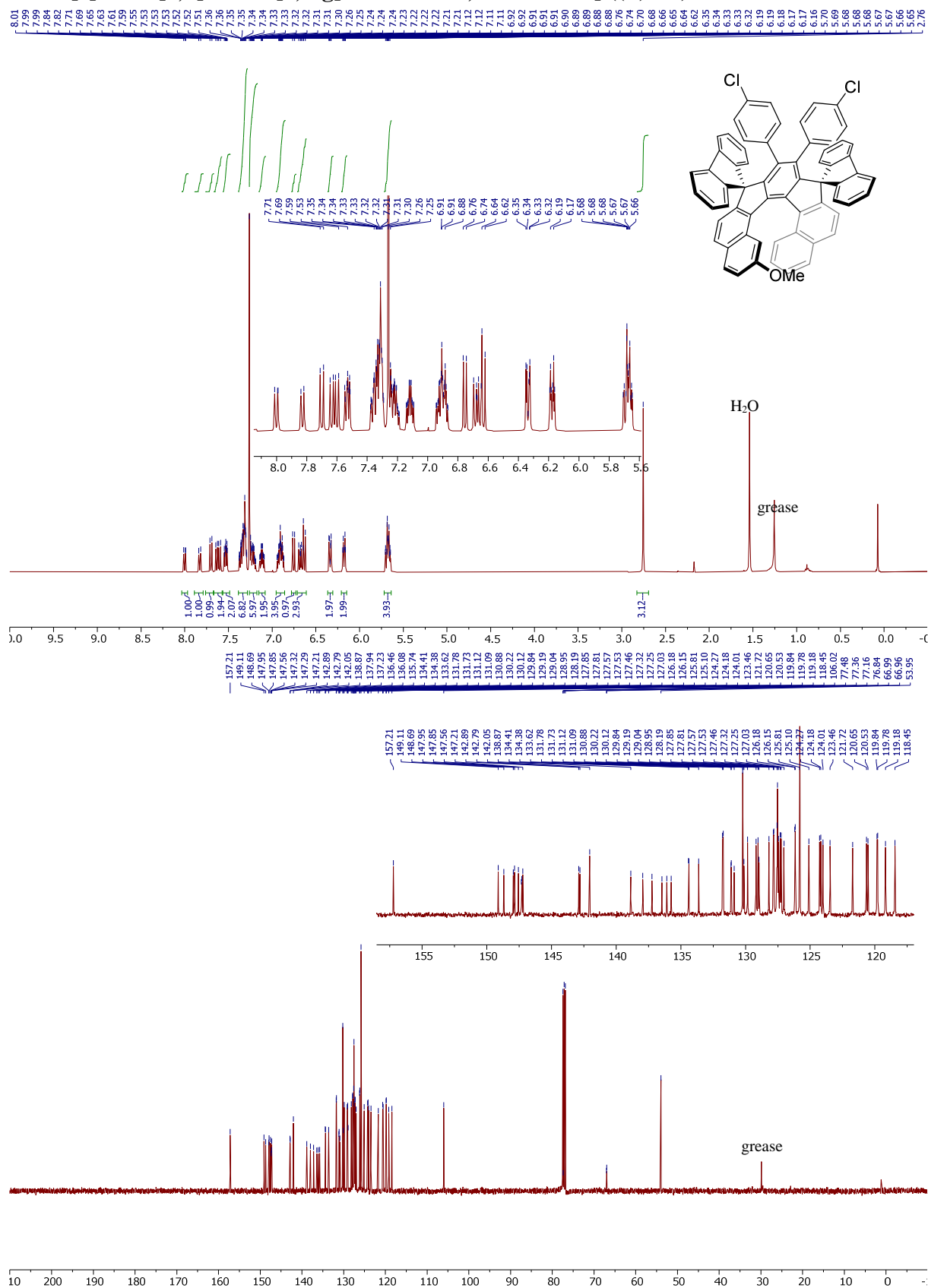
(P)-8',9'-bis(4-chlorophenyl)dispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-g]fluorene-10',9''-fluorene] **((P)-3d).**



(P)-Dispiro[fluorene-9,7'-benzo[*c*]benzo[6,7]indeno[1,2-*g*]fluorene-10',9''-fluorene] ((P)-3f).



(P)-8',9'-bis(4-chlorophenyl)-2'-methoxydispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-g]fluorene-10',9''-fluorene] ((P)-3h).



(P)-8',9'-bis(4-chlorophenyl)-2',15'-dimethoxydispiro[fluorene-9,7'-benzo[c]benzo[6,7]indeno[1,2-g]fluorene-10',9''-fluorene] ((P)-3i).

