

Supporting Information

***Helicene Quinones: Redox-Triggered Chiroptical Switching
and Chiral Recognition of the Semiquinone Radical Anion
Lithium Salt by ENDOR Spectroscopy***

David Schweinfurth, Michal Zalibera, Michael Kathan, Chengshuo Shen, Marcella Mazzolini, Nils Trapp, Jeanne Crassous, Georg Gescheidt, and François Diederich**

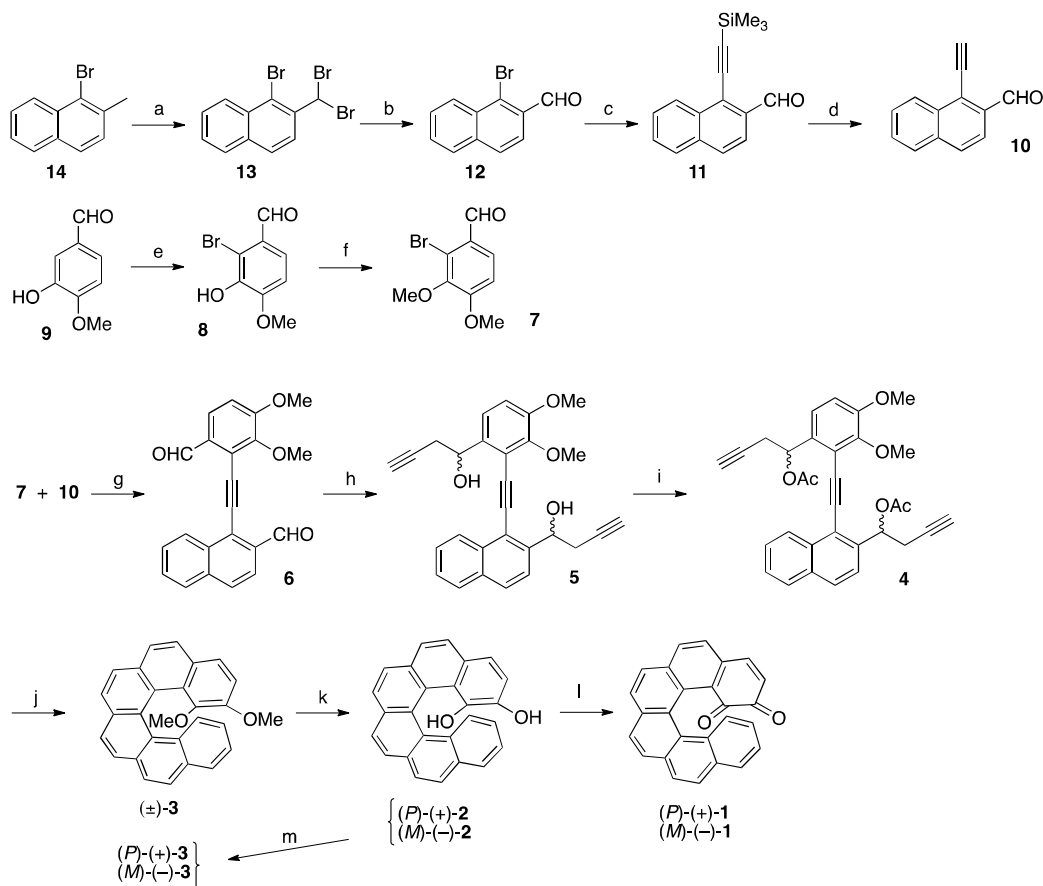
Table of Contents

1SI	Materials and Methods	S3
2SI	Synthetic Procedures	S4
3SI	X-ray Data	S16
3.1SI	General Information	S16
3.2SI	Crystal Data for (±)-1 and (±)-2	S17
3.3SI	Crystal Packing in (±)-1 and (±)-2	S18
4SI	Electrochemistry and Spectroelectrochemistry	S21
4.1SI	Cyclic Voltammetry	S21
4.2SI	UV/Vis and ECD Spectroelectrochemistry	S21
5SI	EPR and ENDOR Spectroscopy	S25
5.1SI	General Information	S25
5.2SI	Sample Preparation	S25
5.3SI	Experimental Data	S26
6SI	DFT Calculations	S31
6.1SI	General Information	S31
6.2SI	Results from (TD-)DFT calculations	S32
6.3SI	Coordinate Geometries	S36
7SI	NMR Spectra of New Compounds	S54
8SI	References	S67

1SI Materials and Methods

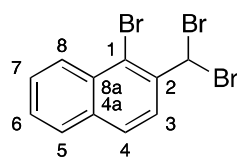
All starting materials and reagents were purchased from commercial sources and used without further purification, unless otherwise stated. Solvents were purified by a solvent drying system from *LC Technology Solutions Inc. SP-105* under a nitrogen atmosphere. All reactions were carried out under an argon or nitrogen atmosphere, unless otherwise stated. Reactions were monitored by thin layer chromatography (*Merck* silica gel F254, 0.25 mm) and visualized under UV irradiation at 254 nm. Flash chromatography was performed using silica gel (*Silicycle*, 60 Å, 230-400 mesh). Flash chromatography was performed by a *Teledyne ISCO Combi Flash R_f 300* system. Liquid chromatography/mass spectrometry (LC/MS) for reaction control was performed on an *Ultimate 3000* series LC instrument combined with a *MSQ Plus* mass spectrometer from *Dionex*, using *Zorbax Eclipse Plus C18* columns (30 x 3 mm; 3.5 mm pore size) from *Agilent*. Melting points were obtained on a *Büchi B-540* capillary melting point apparatus. ¹H and ¹³C NMR were taken on a *Bruker DRX 400* spectrometer. Spectra were referenced to residual solvent peaks. Chemical shifts are expressed in parts per million (δ). Coupling constants (*J*) are expressed in Hz. Coupling patterns are designated as s, singlet; d, doublet; t, triplet; dd, doublet of doublets; td, triplet of doublets; m, multiplet. UV/Vis spectra were recorded on a *Varian Cary-500* spectrophotometer, and ECD spectra were recorded on a *JASCO J-715* spectrophotometer; path lengths of 1 cm were used. Wavelengths reported in nanometers. Optical rotatory dispersion (ORD) was recorded on a *Perkin-Elmer 241* polarimeter using a 10.0 cm cell. IR spectra were recorded on a *Perkin Elmer BX FT-IR* spectrophotometer; peaks are reported in wavenumbers (cm^{-1}). Mass spectrometry was performed by the MS-service at ETH Zürich. Elemental analysis was performed at the Mikrolabor of the Laboratorium für Organische Chemie at ETH Zürich. High resolution matrix-assisted laser-desorption-ionization (HR-MALDI) mass spectra were measured on a *Varian Ionspec Ultima MALDI-FTICR* mass spectrometer using *trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile* (DCTB) as matrix. Electrospray ionization mass spectrometry (ESI-MS) was performed on a *Bruker Daltonics maXis* (UHR-TOF). All calculations were performed on the Brutus cluster of the Competence Center for Computational Chemistry (C4) at ETH Zürich.

2SI Synthetic Procedures



Scheme 1SI. General synthetic scheme. (a) NBS, AIBN, benzene, 80 °C, 24 h, 87%. (b) AgNO₃, EtOH/H₂O, 22 °C, 2 h, 82%. (c) Ethynyltrimethylsilane, CuI, [Pd(PPh₃)₂Cl₂], THF/DIPA, 50 °C, 18 h, 68%. (d) NEt₃·3 HF, THF, 22 °C, 1 h, 94%. (e) Br₂, Fe powder, NaOAc, AcOH, 22 °C, 16 h, 69%. (f) CH₃I, K₂CO₃, acetone, 60 °C, 4 h, 75%. (g) CuI, [Pd(PPh₃)₂Cl₂], THF/DIPA, 80 °C, 18 h, 77%. (h) Propargyl bromide, Ga metal, In powder, THF, 0 °C, 5 min, 51%. (i) Ac₂O, DMAP, pyridine, 22 °C, 3 h, 94%. (j) 1. [Ni(COD)₂], PPh₃, THF, 22 °C, 12 h, 2. TsOH·H₂O, toluene, 80 °C, 3 h, 46%. (k) BBr₃, CH₂Cl₂, -78 °C, 3 h, 70%. (l) Ag₂O, CH₃CN, 20 min, 22 °C, 99% of (P)-(+)-1, 99% of (M)-(-)-1. (m) MeI, K₂CO₃, acetone, 50 °C, 8 h, 68% of (P)-(+)-3, 52% of (M)-(-)-3. NBS = *N*-Bromosuccinimide; AIBN = Azobisisobutyronitrile; DIPA = Diisopropylamine; DMAP = 4-Dimethylaminopyridine; COD = 1,5-Cyclooctadiene; TsOH = *p*-Toluenesulfonic acid.

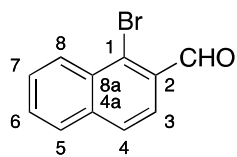
1-Bromo-2-(dibromomethyl)naphthalene (13).¹ According to a published



procedure, 1-bromo-2-methylnaphthalene (25.0 g, 0.114 mol) and *N*-bromosuccinimide (60.7 g, 0.341 mol) were dissolved in hot benzene (350 mL) at 50 °C. AIBN (612 mg, 3.73 mmol) was added in small portions over 3 h yielding an orange solution.

The mixture was stirred at 80 °C for 24 h, cooled to 22 °C, and filtered. The filtrate was evaporated, and the residue was dissolved in CH₂Cl₂ (300 mL), and filtered through a pad of SiO₂. Evaporation of the filtrate gave **13** (37.7 g, 87%) as a light yellow solid, which was used in the next step without further purification. M.p. 73–76 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.49 (s, 1 H; CHBr₂), 7.58 (t, *J* = 7.7 Hz, 1 H; H–C(6)), 7.64 (t, *J* = 7.7 Hz, 1 H; H–C(7)), 7.83 (d, *J* = 8.0 Hz, 1 H; H–C(5)), 7.90 (d, *J* = 8.7 Hz, 1 H; H–C(3)), 8.06 (d, *J* = 8.7 Hz, 1 H; H–C(4)), 8.31 ppm (d, *J* = 8.5 Hz, 1 H; H–C(8)); ¹³C NMR (101 MHz, CDCl₃): δ = 41.37 (CHBr₂), 119.68 (C(1)), 127.90 (C(4)), 128.09/128.39/128.46/128.54/129.15 (C(3,5,6,7,8)), 131.35 (C(8a)), 134.78 (C(4a)), 138.08 ppm (C(2)); IR (ATR): $\tilde{\nu}$ = 3034 (w), 1619 (w), 1596 (w), 1557 (w), 1501 (m), 1460 (w), 1382 (w), 1351 (w), 1324 (m), 1302 (w), 1258 (m), 1218 (m), 1205 (m), 1167 (w), 1140 (m), 1033 (w), 974 (m), 906 (m), 865 (m), 806 (s), 771 (w), 750 (s), 733 (s), 678 (s), 666 (s), 646 cm⁻¹ (s); HR-EI-MS: *m/z* (%): 381.8014 (29, [M]⁺, calcd. for C₁₁H₇⁸¹Br₃⁺: 381.8031), 379.8034 (97, [M]⁺, calcd. for C₁₁H₇⁷⁹Br⁸¹Br₂⁺: 379.8051), 377.8067 (100, [M]⁺, calcd. for C₁₁H₇⁷⁹Br₂⁸¹Br⁺: 377.8072), 375.8081 (26, [M]⁺, calcd. for C₁₁H₇⁷⁹Br₃⁺: 375.8092); elemental analysis calcd. (%) for C₁₁H₇Br₃ (378.89): C 34.87, H 1.86; found: C 35.15, H 1.83.

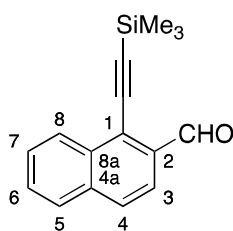
1-Bromo-2-naphthaldehyde (12).² According to a published procedure, 1-bromo-2-



(dibromomethyl)naphthalene (37.0 g, 97.7 mmol) was dissolved in EtOH (1 L). AgNO₃ (83.6 g, 0.492 mol) was dissolved in H₂O (250 mL) and added to the solution. The resulting mixture was stirred for 2 h, and then NaCl (28.9 g, 0.495 mol) was added, which caused the reaction mixture to warm up and to change colour from light green to yellow. The cloudy solution was filtered through Celite, and the filtrate was evaporated. The addition of water led to a precipitate, which was filtered off. A solution of the solid in CH₂Cl₂ (200 mL) was washed with water (3 x 50 mL), dried over Na₂SO₄, and evaporated to yield **12** (18.9 g, 82%) as a light yellow solid. M.p. 115–117 °C; ¹H

NMR (400 MHz, CDCl₃): δ = 7.66–7.71 (m, 2 H; H–C(6,7)), 7.85 (br. d, J = 8.6 Hz, 1 H; H–C(3)), 7.87–7.89 (m, 1 H; H–C(5)), 7.94 (d, J = 8.5 Hz, 1 H; H–C(4)), 8.51 (d with virtual coupling, J = 9.8 Hz, 1 H, H–C(8)), 10.67 ppm (d, J = 0.7 Hz, 1 H; CHO); ¹³C NMR (101 MHz, CDCl₃): δ = 124.23 (C(3)), 128.25/128.35/128.42/128.61 (C(5,6,7,8)), 129.85 (C(4)), 131.32/131.45/132.24 (C(1,4a,8a)), 137.37 (C(2)), 192.95 ppm (CHO); IR (ATR): $\tilde{\nu}$ = 3058 (w), 2867 (w), 1682 (m), 1641 (m), 1616 (m), 1595 (m), 1552 (m), 1497 (w), 1454 (m), 1423 (w), 1349 (w), 1321 (m), 1307 (m), 1279 (w), 1254 (m), 1214 (m), 1156 (w), 1141 (w), 1030 (w), 969 (m), 887 (m), 868 (m), 808 (s), 769 (m), 749 (s), 666 (m), 629 (m), 612 cm⁻¹ (m); HR-EI-MS: m/z (%): 235.9655 (95, [M]⁺, calcd. for C₁₁H₇⁸¹BrO⁺: 235.9680), 233.9669 (100, [M]⁺, calcd. for C₁₁H₇⁷⁹BrO⁺: 233.9675); elemental analysis calcd. (%) for C₁₁H₇BrO (235.08): C 56.20, H 3.00; found: C 56.09, H 2.97.

1-[(Trimethylsilyl)ethynyl]-2-naphthaldehyde (11).³ In accordance with a

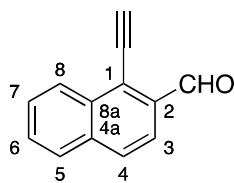


published procedure, **12** (2.0 g, 8.51 mmol), CuI (82.0 mg, 0.431 mmol), [Pd(PPh₃)₂Cl₂] (308 mg, 0.439 mmol), and ethynyltrimethylsilane (6.0 mL, 42.2 mmol) were dissolved in a degassed mixture of THF (25 mL) and DIPA (25 mL) under a nitrogen atmosphere. After stirring for 18 h at 50 °C, the mixture

was filtered over SiO₂. Evaporation of the filtrate and flash chromatography (SiO₂; pentane/EtOAc 97:3) gave **11** (1.47 g, 68%) as a colorless solid. R_f = 0.62 (SiO₂; pentane/EtOAc 97:3); M.p. 63–65 °C; ¹H NMR (400 MHz, CDCl₃): δ = 0.37 (s, 9 H; SiMe₃), 7.64–7.69 (m, 2 H; H–C(6,7)), 7.87 (d, J = 8.8 Hz, 1 H; H–C(3)), 7.87–7.89 (m, 1 H; H–C(5)), 7.95 (d, J = 8.6 Hz, 1 H; H–C(4)), 8.51 (d with virtual coupling, J = 9.7 Hz, 1 H, H–C(8)), 10.79 ppm (d, J = 0.8 Hz, 1 H; CHO); ¹³C NMR (101 MHz, CDCl₃): δ = 0.04 (SiMe₃), 98.06 (C≡CSiMe₃), 109.06 (C≡CSiMe₃), 121.97 (C(3)), 127.47 (C(1)), 127.39/127.89/128.57/129.20/129.50 (C(4,5,6,7,8)), 133.39/134.87/135.84 (C(2,4a,8a)), 192.49 ppm (CHO). IR (ATR): $\tilde{\nu}$ = 3251 (w), 3056 (w), 2955 (w), 2897 (w), 2846 (w), 2151 (w), 1682 (s), 1618 (w), 1591 (m), 1567 (w), 1459 (w), 1431 (w), 1402 (w), 1376 (m), 1332 (m), 1248 (m), 1232 (s), 1141 (w), 1068 (m), 1026 (w), 918 (w), 870 (s), 838 (s), 812 (s), 759 (s), 745 (s), 736 (s), 699 (m), 651 (s), 637 cm⁻¹ (w); HR-MALDI-TOF-MS: m/z (%): 252.0965 (100, [M]⁺, calcd. for

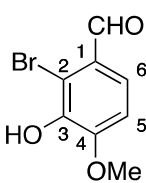
C₁₆H₁₆OSi⁺: 252.0965); elemental analysis calcd. (%) for C₁₆H₁₆OSi (252.38): C 76.14, H 6.39; found: 76.37, 6.19.

1-Ethynyl-2-naphthaldehyde (10). Under a nitrogen atmosphere, protected



naphthalene **11** (526 mg, 2.08 mmol) was dissolved in THF (5 mL). NEt₃·3 HF (3.0 mL, 18.4 mmol) was added dropwise. The solution was stirred for 1 h, diluted with Et₂O (15 mL), washed with a 1 M NaOH solution (3 x 20 mL), dried over Na₂SO₄, and evaporated to yield **10** (348 mg, 94%) as a brown solid. M.p. 123–125 °C; ¹H NMR (400 MHz, CDCl₃): δ = 3.92 (s, 1 H; C≡CH), 7.65–7.70 (m, 2 H; H–C(6,7)), 7.87–7.93 (m, 2 H; H–C(3,5)), 7.98 (d, *J* = 8.6 Hz, 1 H; H–C(4)), 8.52–8.57 (d with virtual coupling, *J* = 9.7 Hz, 1 H, H–C(8)), 10.79 ppm (d, *J* = 0.8 Hz, 1 H; CHO); ¹³C NMR (101 MHz, CDCl₃): δ = 77.28 (C≡CH), 90.25 (C≡CH), 122.05 (C(3)), 126.18 (C(1)), 127.25/128.04/128.62/129.58/129.64 (C(4,5,6,7,8)), 133.56, 135.43, 135.80 (C(2,4a,8a)), 192.08 ppm (CHO); IR (ATR): $\tilde{\nu}$ = 3248 (m), 3061 (w), 2846 (w), 1670 (s), 1617 (w), 1590 (m), 1566 (w), 1457 (w), 1431 (m), 1375 (w), 1333 (m), 1264 (w), 1230 (m), 1169 (w), 1152 (w), 1139 (w), 1054 (w), 1026 (w), 915 (w), 870 (m), 813 (s), 784 (m), 756 (s), 718 (s), 659 (s), 638 cm⁻¹ (s); HR-MALDI-TOF-MS: *m/z* (%): 181.0648 (100, [*M*]⁺, calcd. for C₁₃H₉O⁺: 181.0648).

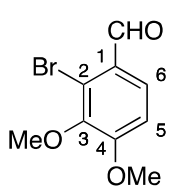
2-Bromo-3-hydroxy-4-methoxybenzaldehyde (8).⁴ According to a published



procedure, isovanillin (25.0 g, 0.164 mol), NaOAc (27.0 g, 0.329 mol), and iron powder (750 mg, 13.4 mmol) were dissolved in glacial acetic acid (250 mL) under a nitrogen atmosphere. A solution of bromine (9.12 mL, 0.178 mol) in glacial acetic acid (30 mL) was added dropwise. The mixture was stirred at 22 °C for 16 h and poured into ice water (500 mL). The precipitate was filtered off and washed with ice water (150 mL). Crystallization from EtOH gave **8** (26.3 g, 69%) as a white solid. M.p. 208–210 °C; ¹H NMR (400 MHz, CDCl₃): δ = 4.01 (s, 3 H; OMe), 6.08 (s, 1 H; OH), 6.93 (dd, *J* = 8.5, 0.7 Hz, 1 H; H–C(6)), 7.58 (d, *J* = 8.6 Hz, 1 H; H–C(5)), 10.26 ppm (d, *J* = 0.8 Hz, 1 H; CHO); ¹³C NMR (101 MHz, CDCl₃): δ = 56.75 (OCH₃), 109.42 (C(5)), 113.01 (C(2)), 122.91 (C(6)), 127.41 (C(1)), 143.35 (C(3)), 151.83 (C(4)), 191.01 ppm (CHO). IR (ATR): $\tilde{\nu}$ = 3202 (w), 2950 (w), 2890 (w), 1666 (s), 1591 (m), 1562 (m), 1493 (m), 1461 (m), 1449 (m), 1435 (m), 1386 (w), 1335 (w), 1275 (s), 1231 (s),

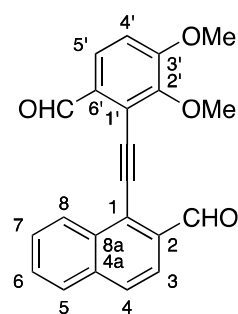
1199 (s), 1165 (s), 1131 (s), 1014 (s), 987 (s), 818 (s), 804 (s), 783 (s), 657 cm^{-1} (s); HR-EI-MS: m/z (%): 231.9551 (96, $[M]^+$, calcd. for $\text{C}_8\text{H}_7^{81}\text{BrO}_3^+$: 231.9553), 229.9569 (100, $[M]^+$, calcd. for $\text{C}_8\text{H}_7^{79}\text{BrO}_3^+$: 229.9573); elemental analysis calcd. (%) for $\text{C}_8\text{H}_7\text{BrO}_3$ (231.05): C 41.59, H 3.05; found: C 41.60, H 2.99.

2-Bromo-3,4-dimethoxybenzaldehyde (7).⁵ According to a published procedure,

 **8** (2.0 g, 8.66 mmol) was dissolved in acetone (35 mL). K_2CO_3 (2.30 g, 16.6 mmol) and methyl iodide (2.0 mL, 32.1 mmol) were subsequently added at 22 °C to the solution, whereas the color changed to yellow. The suspension was stirred 4 h at 60 °C,

evaporated, and the remaining solid dissolved in EtOAc (50 mL). The solution was washed with water (3 x 150 mL), dried over Na_2SO_4 , and the solvent was evaporated. Flash chromatography (SiO_2 ; cyclohexane/EtOAc 85:15) gave **7** (1.60 g, 75%) as a colorless solid. $R_f = 0.27$ (SiO_2 ; cyclohexane/EtOAc 4:1); M.p. 85–86 °C; ^1H NMR (400 MHz, CDCl_3): $\delta = 3.91$ (s, 3 H; OMe), 3.99 (s, 3 H; OMe), 6.99 (dd, $J = 8.7, 0.8$ Hz, 1 H; H-C(6)), 7.76 (d, $J = 8.7$ Hz, 1 H; H-C(5)), 10.28 (d, $J = 0.8$ Hz, 1 H; CHO); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 56.43$ (OCH₃), 60.78 (OCH₃), 111.07 (C(5)), 123.20 (C(2)), 126.61 (C(6)), 127.48 (C(1)), 146.51 (C(3)), 158.77 (C(4)), 191.04 ppm (CHO); IR (ATR): $\tilde{\nu} = 2942$ (w), 2862 (w), 1677 (m), 1580 (m), 1488 (m), 1456 (w), 1446 (w), 1435 (w), 1410 (w), 1377 (w), 1303 (m), 1277 (m), 1256 (m), 1216 (m), 1190 (w), 1140 (w), 1020 (s), 928 (s), 826 (w), 809 (s), 779 (s), 657 (m), 639 cm^{-1} (m); HR-MALDI-TOF-MS: m/z (%): 246.9787 (97, $[M + \text{H}]^+$, calcd. for $\text{C}_9\text{H}_{10}^{81}\text{BrO}_3^+$: 246.9787), 244.9806 (100, $[M + \text{H}]^+$, calcd. for $\text{C}_9\text{H}_{10}^{79}\text{BrO}_3^+$: 244.9808); elemental analysis calcd. (%) for $\text{C}_9\text{H}_9\text{BrO}_3$ (245.07): calcd. C 44.11, H 3.70; found: C 44.07, H 3.64.

1-[(6-Formyl-2,3-dimethoxyphenyl)ethynyl]-2-naphthaldehyde (6). Under a

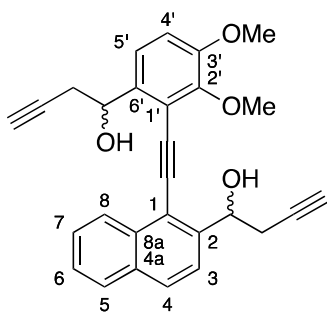


nitrogen atmosphere, bromide **7** (272 mg, 1.11 mmol), naphthalene **10** (220 mg, 1.22 mmol), $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (39.0 mg, 0.056 mmol), and CuI (10.7 mg, 0.056 mmol) were dissolved in a degassed mixture of THF (10 mL) and DIPA (10 mL). After stirring for 18 h at 80 °C, the black mixture was filtered over SiO_2 . Evaporation of the filtrate and flash

chromatography (SiO_2 ; cyclohexane/EtOAc 80:20) gave **6** (294 mg, 77%) as a brown

solid. $R_f = 0.21$ (SiO₂; cyclohexane/EtOAc 4:1); M.p. 191–193 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 4.02$ (s, 3 H; OMe), 4.06 (s, 3 H; OMe), 7.10 (dd, $J = 8.6, 0.6$ Hz, 1 H; H–C(5')), 7.67–7.76 (m, 2 H; H–C(6,7)), 7.79 (d, $J = 8.6$ Hz, 1 H; H–C(4')), 7.91–7.96 (m, 2 H; H–C(3,5)), 8.03 (d, $J = 8.6$ Hz, 1 H; H–C(4)), 8.81 (d with virtual coupling, $J = 7.8$ Hz, 1 H, H–C(8)), 10.51 (d, $J = 0.7$ Hz, 1 H; OCH–C(6')), 10.99 ppm (d, $J = 0.9$ Hz, 1 H; OCH–C(2)); ¹³C NMR (101 MHz, CDCl₃): $\delta = 56.40$ (OMe), 61.50 (OMe), 93.68 and 94.20 (C≡C), 112.92 (C(4')), 120.03 (C(1')), 122.34 (C(3)), 126.82 (C(1)), 126.55/127.55/128.25/128.66/129.64/129.82 (C(4,5,6,7,8,5')), 129.86 (C(6')), 133.53/135.06/135.93 (C(2,4a,8a)), 151.46 (C(2')), 157.80 (C(3')), 189.61 (OCH–C(6')), 192.37 ppm (OCH–C(2)); IR (ATR): $\tilde{\nu} = 3080$ (w), 2838 (w), 1685 (s), 1673 (s), 1616 (w), 1585 (s), 1570 (m), 1486 (m), 1459 (m), 1440 (w), 1424 (w), 1390 (w), 1334 (w), 1314 (m), 1290 (s), 1260 (s), 1229 (m), 1207 (m), 1154 (w), 1093 (m), 1032 (m), 947 (w), 921 (m), 892 (w), 867 (w), 831 (m), 818 (s), 780 (m), 770 (m), 740 (s), 684 (w), 655 (w), 637 (w) cm⁻¹; HR-MALDI-TOF-MS: m/z (%): 345.1121 (100, [M + H]⁺, calcd. for C₂₂H₁₇O₄⁺: 345.1121); elemental analysis calcd. (%) for C₂₂H₁₆O₄ (344.37): C 76.73, H 4.68; found: C 76.75, H 4.80.

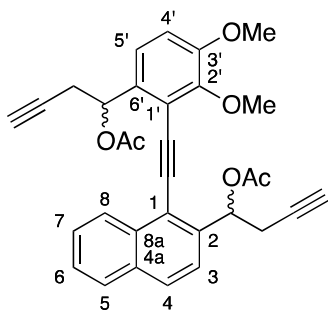
1-(1-{6-(1-Hydroxybut-3-yn-1-yl)-2,3-dimethoxyphenyl}ethynyl)naphth-2-



yl)but-3-yn-1-ol (5). Under a nitrogen atmosphere, a 80% solution of propargyl bromide in toluene (0.57 mL, 5.1 mmol) was added to a mixture of gallium metal (207 mg, 2.97 mmol) and indium powder (17.0 mg, 0.148 mmol) in dry THF (10 mL). After stirring for 5 h at 0 °C, the metals were completely dissolved and a solution of dialdehyde **6** (205 mg, 0.595 mmol) in dry THF (25 mL) was added. The brown solution was stirred for 5 min, washed with a 1 M NaOH solution (300 mL), diluted with EtOAc (100 mL), dried over Na₂SO₄, and evaporated. Flash chromatography (SiO₂; cyclohexane/EtOAc 75:25) gave **5** (129 mg, 51 %) as a brown solid. $R_f = 0.22$ (SiO₂; cyclohexane/EtOAc 3:2); M.p. 61–64 °C; ¹H NMR (400 MHz, CDCl₃, 1:1 mixture of diastereoisomers): $\delta = 2.09$ and 2.10 (t, $J = 2.6$ Hz, 1 H; C≡CH), 2.15 and 2.17 (t, $J = 2.6$ Hz, 1 H; C≡CH), 2.68 and 2.72 (dt, $J = 8.3, 2.8$ Hz, 2 H; CH₂), 2.79 and 2.84 (ddd, $J = 7.9, 2.7, 1.4$ Hz, 1 H; CH_aCHOH), 2.89–3.06 (m, 3 H; CH_bCHOH,OH), 3.910 and 3.914 (s, 3 H; OMe), 4.048 and

4.054 (s, 3 H; OMe), 5.47–5.53 (m, 1 H; *CHOH*), 5.66–5.80 (m, 1 H; *CHOH*), 6.99 (dd, $J = 8.6, 2.2$ Hz, 1 H; H–C(5')), 7.35 (d, $J = 8.6$ Hz, 1 H; H–C(4')), 7.53 (ddd, $J = 8.2, 6.8, 1.3$ Hz, 1 H; H–C(6)), 7.63 (ddd, $J = 8.2, 6.8, 1.2$ Hz, 1 H; H–C(7)), 7.74 (d, $J = 8.6$ Hz, 1 H; H–C(3)), 7.86 (d, $J = 8.1$ Hz, 1 H; H–C(5)), 7.89 (d, $J = 8.6$ Hz, 1 H; H–C(4)), 8.60 ppm (d, $J = 8.4$ Hz, 1 H; H–C(8)) ppm; ^{13}C NMR (101 MHz, CDCl_3 , 1:1 mixture of diastereoisomers): $\delta = 27.07/28.55/28.92$ (CH_2), 56.14 (OMe), 61.34/61.36 (OMe), 70.40/70.48/70.95/71.09/71.18/71.30/71.32/71.40 ($\text{C}\equiv\text{CH}$, *CHOH*), 80.85/81.00/81.02/81.23 ($\text{C}\equiv\text{CH}$), 93.78/93.87/94.32/94.37 ($\text{C}\equiv\text{C}$ –C(1)), 113.25/113.27 (C(4')), 116.07/116.09 (C(1')), 117.98/118.03 (C(1)), 121.14/121.20 (C(3)), 123.26/123.29/126.52/126.55/126.66/127.47/128.35/129.37/129.38 (C(4,5,6,7,8,5')), 132.83/133.46 (C(4a,8a)), 136.69/136.73 (C(6')), 143.06/143.08 (C(2)), 150.46 (C(2')), 152.16/152.17 ppm (C(3')); IR (ATR): $\tilde{\nu} = 3411$ (m), 3290 (m), 2937 (w), 2837 (w), 2119 (w), 1729 (m), 1595 (m), 1569 (m), 1484 (s), 1452 (m), 1419 (m), 1374 (m), 1271 (s), 1248 (s), 1097 (s), 1071 (s), 1034 (s), 1008 (s), 952 (m), 852 (m), 820 (s), 785 (m), 752 (s), 725 (m), 634 cm^{-1} (s); HR-MALDI-TOF-MS: m/z (%): 447.1566 (100, $[M + \text{Na}]^+$, calcd. for $\text{C}_{28}\text{H}_{24}\text{NaO}_4^+$: 447.1567).

1-(1-{[6-(1-Acetoxybut-3-yn-1-yl)-2,3-dimethoxyphenyl]ethynyl}naphthalen-2-

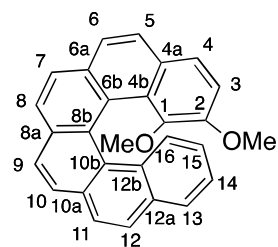


yl)but-3-yn-1-yl Acetate (4). Under a nitrogen atmosphere, diol **5** (200 mg, 0.471 mmol) and DMAP (2.9 mg, 0.024 mmol) were dissolved in a mixture of dry pyridine/acetic anhydride (3/6 mL). After stirring for 3 h at 22 °C, the solvent was evaporated. Flash chromatography (cyclohexane/EtOAc 85:15), gave **4** (225 mg, 94%) as a yellow solid. $R_f = 0.15$ (SiO_2 ; cyclohexane/EtOAc 4:1); M.p. 129–130 °C; ^1H NMR (400 MHz, CDCl_3 , 1:1 mixture of diastereoisomers): $\delta = 1.97$ and 1.98 (t, $J = 2.6$ Hz, 1 H; $\text{C}\equiv\text{CH}$), 2.02 and 2.02 (t, $J = 2.3$ Hz, 1 H; $\text{C}\equiv\text{CH}$), 2.15 and 2.16 (s, 3 H; COAc), 2.175 and 2.178 (s, 3 H; COAc), 2.82–3.13 (m, 4 H; CH_2), 3.91 (s, 3 H; OMe), 4.06 and 4.07 (s, 3 H; OMe), 6.49 (t, $J = 5.5$ Hz, 1 H; CHOAc), 6.77 (t, $J = 5.8$ Hz, 1 H; CHOAc), 6.97 (dd, $J = 8.6, 1.0$ Hz, 1 H; H–C(4')), 7.24 (d, $J = 8.7$ Hz, 1 H; H–C(5')), 7.53 (ddd, $J = 8.1, 6.8, 1.2$ Hz, 1 H; H–C(6)), 7.63 (t, $J = 7.3$ Hz, 1 H; H–C(7)), 7.666 and 7.671 (d,

of diastereoisomers): $\delta = 1.97$ and 1.98 (t, $J = 2.6$ Hz, 1 H; $\text{C}\equiv\text{CH}$), 2.02 and 2.02 (t, $J = 2.3$ Hz, 1 H; $\text{C}\equiv\text{CH}$), 2.15 and 2.16 (s, 3 H; COAc), 2.175 and 2.178 (s, 3 H; COAc), 2.82–3.13 (m, 4 H; CH_2), 3.91 (s, 3 H; OMe), 4.06 and 4.07 (s, 3 H; OMe), 6.49 (t, $J = 5.5$ Hz, 1 H; CHOAc), 6.77 (t, $J = 5.8$ Hz, 1 H; CHOAc), 6.97 (dd, $J = 8.6, 1.0$ Hz, 1 H; H–C(4')), 7.24 (d, $J = 8.7$ Hz, 1 H; H–C(5')), 7.53 (ddd, $J = 8.1, 6.8, 1.2$ Hz, 1 H; H–C(6)), 7.63 (t, $J = 7.3$ Hz, 1 H; H–C(7)), 7.666 and 7.671 (d,

$J = 8.7$ Hz, 1 H; H-C(3)), 7.80–7.91 (m, 2 H; H-(C4,5)), 8.68 and 8.72 ppm (dd, $J = 8.5, 1.0$ Hz, 1 H; H-C(8)); ^{13}C NMR (101 MHz, CDCl_3 , 1:1 mixture of diastereoisomers): $\delta = 21.24/25.96/26.10/26.13$ (CH_2), 56.11 (OMe), 61.40/61.41 (OMe), 70.81/70.88/71.03/71.09 ($\text{C}\equiv\text{CH}$), 71.81/72.05/72.18 (CHOAc), 79.59/79.67/79.75/79.85 ($\text{C}\equiv\text{CH}$), 93.85/93.94/94.00/94.10 ($\text{C}\equiv\text{C}-\text{C}(1)$), 113.02/113.04 ($\text{C}(4')$), 116.74/116.76 ($\text{C}(1')$), 118.70/118.71 ($\text{C}(1)$), 122.05 ($\text{C}(3)$), 123.27/123.29/126.82/126.94/127.50/127.52/128.19/128.20/129.12 ($\text{C}(4,5,6,7,8,5')$), 132.85/132.86/133.41/133.44/133.52 ($\text{C}(4a,8a,6')$), 139.62/139.69 ($\text{C}(2)$), 150.68/150.70 ($\text{C}(2')$), 152.54 ($\text{C}(3')$), 169.84/169.90 ppm ($\text{C}=\text{O}$); IR (ATR): $\tilde{\nu} = 3269$ (m), 2939 (w), 2837 (w), 2121 (w), 1735 (s), 1596 (w), 1574 (w), 1508 (w), 1486 (m), 1465 (w), 1454 (w), 1420 (m), 1370 (m), 1352 (w), 1228 (s), 1149 (w), 1099 (m), 1041 (s), 942 (w), 905 (w), 863 (w), 818 (m), 785 (w), 757 (m), 664 (m), 647 cm^{-1} (m); HR-MALDI-TOF-MS: m/z (%): 508.1880 (100, $[M]^+$, calcd. for $\text{C}_{32}\text{H}_{28}\text{O}_6^+$: 508.1880); elemental analysis calcd. (%) for $\text{C}_{32}\text{H}_{28}\text{O}_6$ (508.56): C 75.57, H 5.55; found: C 75.40, H 5.47.

***rac*-1,2-Dimethoxy-[6]helicene ((±)-3).** Under a nitrogen atmosphere, triene



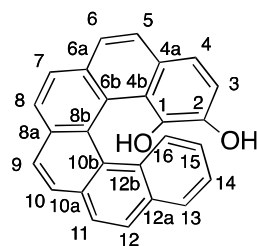
4 (250 mg, 0.492 mmol) was dissolved in dry THF (10 mL), and was slowly added to a red solution of $[\text{Ni}(\text{COD})_2]$ (135 mg, 0.492 mmol) and PPh_3 (258 mg, 0.984 mmol) in dry THF (30 mL). The brown solution was stirred for 12 h at 22 °C and filtered over a pad of SiO_2 . After evaporation, a solution of the brown residue in toluene (50 mL) was treated with $\text{TosOH}\cdot\text{H}_2\text{O}$ (1.40 g, 7.36 mmol). The suspension was stirred at 80 °C for 3 h and filtered. The filtrate was washed with a 1 M NaOH solution (3 x 150 mL), dried over Na_2SO_4 , and evaporated. Flash chromatography (SiO_2 ; cyclohexane/EtOAc 95:5) gave ((±)-**3** (88.5 mg, 46%) as a yellow, sticky oil. $R_f = 0.41$ (SiO_2 ; cyclohexane/EtOAc 4:1); ^1H NMR (400 MHz, CDCl_3 , assignment based on DQF-COSY, HSQC, and HMBC spectroscopy): $\delta = 2.26$ (s, 3 H; MeO-C(1)), 3.35 (s, 3 H; MeO-C(2)), 6.58 (ddd, $J = 8.4, 6.9, 1.4$ Hz, 1 H; H-C(15)), 7.07 (d, $J = 8.6$ Hz, 1 H; H-C(3)), 7.17 (ddd, $J = 8.0, 6.9, 1.2$ Hz, 1 H; H-C(14)), 7.19 (dd, $J = 8.5, 1.0$ Hz, 1 H; H-C(16)), 7.66 (d, $J = 8.7$ Hz, 1 H; H-C(4)), 7.78 (dd, $J = 7.9, 1.6$ Hz, 1 H; H-C(13)), 7.83 (d, $J = 8.5$ Hz, 1 H; H-C(6)), 7.89 (br. d, $J = 8.4$ Hz, 2 H; H-C(5,12)), 7.94 (d, $J = 8.5$ Hz, 1 H; H-C(11)), 7.97 (d, $J = 8.3$ Hz, 1 H; H-C(9)), 8.00 (d,

$J = 8.3$ Hz, 2 H; H-C(7,10)), 8.09 ppm (d, $J = 8.1$ Hz, 1 H; H-C(8)); ^{13}C NMR (101 MHz, CDCl_3 , assignment based on HSQC, and HMBC spectroscopy): $\delta = 58.57$ (OMe), 58.63 (OMe), 116.75 (C(3)), 123.22 (C(15)), 123.64 (C(4)), 123.90 (C(6b)), 124.79/124.81 (C(6,14)), 125.08 (C(8b)), 125.37 (C(9)), 125.85 (C(4b)), 126.27/126.29 (C(11,16)), 126.48 (C(10)), 127.01 (C(7)), 127.14 (C(13)), 127.40 (C(8)), 127.60 (C(12)), 127.67 (C(5)), 128.94 (C(4a)), 129.04 (C(10b)), 129.12 (C(12b)), 130.55 (C(10a)), 131.86 (C(6a)), 131.90 (C(8a)), 132.24 (C(12a)), 146.78 (C(1)), 150.48 ppm (C(2)); IR (ATR): $\tilde{\nu} = 3042$ (w), 2930 (w), 1734 (w), 1635 (w), 1598 (m), 1550 (w), 1520 (w), 1503 (m), 1474 (m), 1444 (m), 1416 (w), 1401 (w), 1351 (w), 1318 (m), 1287 (w), 1274 (m), 1251 (m), 1200 (w), 1187 (w), 1174 (m), 1151 (m), 1136 (m), 1120 (w), 1086 (m), 1072 (m), 1039 (m), 996 (w), 970 (w), 952 (w), 905 (w), 884 (w), 832 (s), 814 (s), 765 (m), 744 388.1459 (100, $[M]^+$, calcd. for $\text{C}_{28}\text{H}_{20}\text{O}_2^+$: 388.1458).

(*P*)-(+)-1,2-Dimethoxy-[6]helicene ((*P*)-(+)-3). (*P*)-(+)-[6]Helicene-1,2-diol (*P*)-(+)-2 (20.0 mg, 0.055 mmol) was dissolved in dry and degassed acetone (15 mL). K_2CO_3 (76 mg, 0.550 mmol) and MeI (0.5 mL, 0.8 mmol) were added. The mixture was stirred at 50 °C for 8 h, filtered, and evaporated. A solution of the residue in CH_2Cl_2 (50 mL) was washed with H_2O (150 mL), brine (50 mL), dried over Na_2SO_4 , and evaporated. Flash chromatography (SiO_2 , cyclohexane/EtOAc 98:2) gave (*P*)-(+)-3 (14.5 mg, 68%) as a yellow wax. $[\alpha]_{\text{D}}^{22} = +2947 \pm 40$ ($c = 0.21$ in CH_3CN).

(*M*)-(-)-1,2-Dimethoxy-[6]helicene ((*M*)-(-)-3). (*M*)-(-)-3 was prepared in an analogous manner from (*M*)-(-)-[6]helicene-1,2-diol (*M*)-(-)-2. $[\alpha]_{\text{D}}^{22} = -2879 \pm 40$ ($c = 0.22$ in CH_3CN).

(*P*)-(+)-[6]Helicene-1,2-diol ((*P*)-(+)-2) and (*M*)-(-)-[6]helicene-1,2-diol ((*M*)-(-)-2).



Under a nitrogen atmosphere, a solution of 1 M BBr_3 in CH_2Cl_2 (2.30 mL, 2.30 mmol) was added slowly to a yellow solution of (\pm)-3 (300 mg, 0.772 mmol) in dry CH_2Cl_2 (15 mL) at -78 °C. During a reaction time of 3 h, the mixture was allowed to warm to 0 °C. The black solution was poured into

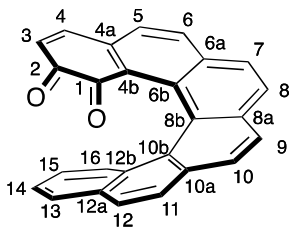
ice water. The organic yellow layer was separated, dried over Na_2SO_4 , and evaporated. Flash chromatography (cyclohexane/EtOAc 90:10) gave (\pm)-3 (195 mg, 70%) as a brown solid. The enantiomers were separated by preparative HPLC on a

chiral phase, using a Pirkle covalent (*S,S*)-Whelk-O 1 (Kromasil silica (10 μm , 100 \AA), 25 cm x 21.1 mm) column (Regis Technologies Inc., Morton Grove, IL, USA) with *n*-hexane/*i*PrOH/THF (90:9.5:0.5) as eluent (15 mL min⁻¹ flow rate): 4 mL of a solution of racemic (\pm)-**2** (*n*-hexane/*i*PrOH/THF (80:19:1), *c* = 3.47 mM) were injected every 12 min. The compounds are moderately stable towards oxygen as a solid, but oxidize rapidly in solution. Therefore, the solutions for the UV/Vis and ECD spectroscopy, and for the optical rotation measurements were prepared in the glove box under oxygen-free conditions.

Data for (*P*)-(+)-**2**: $R_f = 0.22$ (SiO₂; cyclohexane/EtOAc 4:1); M.p. 233–236 °C (decomp.); prep. HPLC: $t_R = 18.0$ min (*n*-hexane/*i*PrOH/THF (90:9.5:0.5)); $[\alpha]_D^{22} = +3129 \pm 40$ (*c* = 0.27 in CH₃CN); ¹H NMR (400 MHz, CD₂Cl₂, assignment based on DQF-COSY, HSQC, and HMBC spectroscopy): $\delta = 4.22$ (s, 1 H; HO–C(1)), 5.10 (s, 1 H; HO–C(2)), 6.61 (ddd, $J = 8.4, 6.9, 1.4$ Hz, 1 H; H–C(15)), 7.02 (d, $J = 8.5$ Hz, 1 H; H–C(3)), 7.06 (ddd, $J = 8.5, 1.2, 0.6$ Hz, 1 H; H–C(16)), 7.27 (ddd, $J = 8.0, 6.9, 1.1$ Hz, 1 H; H–C(14)), 7.54 (d, $J = 8.5$ Hz, 1 H; H–C(4)), 7.80 (d, $J = 8.5$ Hz, 1 H; H–C(6)), 7.85 (dd, $J = 7.9, 1.2$ Hz, 1 H; H–C(13)), 7.92 (d, $J = 8.5$ Hz, 1 H; H–C(5)), 7.98 (d, $J = 8.6$ Hz, 1 H; H–C(12)), 8.01 (d, $J = 8.6$ Hz, 1 H; H–C(11)), 8.06 (d, $J = 8.3$ Hz, 1 H; H–C(10)), 8.09 (d, $J = 8.2$ Hz, 1 H; H–C(7)), 8.14 ppm (d, $J = 8.2$ Hz, 2 H; H–C(8) and H–C(9)); ¹³C NMR (101 MHz, CD₂Cl₂, assignment based on HSQC, and HMBC spectroscopy): $\delta = 115.92$ (C(3)), 121.60 (C(4)), 121.81 (C(4b)), 123.32 (C(6b)), 123.58 (C(8b)), 124.05 (C(6)), 124.35 (C(15)), 126.34 and 126.36 (C(14,16)), 126.49 (C(10b)), 126.64 (C(11)), 127.63/127.66/127.81/127.91/127.96 (C(7,8,9,10,13)), 127.95 (C(4a)), 128.77 (C(12b)), 129.09 (C(5)), 129.20 (C(12)), 131.41 (C(10a)), 132.73 (C(12a)), 132.87 (C(8a)), 133.24 (C(6a)), 138.32 (C(1)), 142.83 ppm (C(2)); IR (ATR): $\tilde{\nu} = 3488$ (w), 3415 (w), 3314 (w), 3044 (w), 1698 (w), 1617 (w), 1600 (w), 1556 (w), 1526 (w), 1505 (w), 1474 (w), 1423 (w), 1397 (w), 1348 (w), 1365 (w), 1281 (w), 1242 (m), 1201 (m), 1156 (w), 1111(w), 1079 (w), 1029 (w), 1002 (w), 974 (w), 952 (w), 931 (w), 889 (w), 840 (s), 811 (m), 792 (w), 764 (w), 746 (m), 728 (w), 719 (w), 693 (w), 611 (w) cm⁻¹. HR-MALDI-TOF-MS: m/z (%): 360.1145 (100, $[M]^+$, calcd. for C₂₆H₁₆O₂⁺: 360.1145).

Data for (*M*)-(-)-**2**: prep. HPLC: $t_R = 21.0$ min (*n*-hexane/*i*PrOH/THF (90:9.5:0.5)); $[\alpha]_D^{22} = -3086 \pm 40$ ($c = 0.18$ in CH_3CN).

(*P*)-(+)-[6]Helicene-1,2-dione ((*P*)-(+)-**1**). Under a nitrogen atmosphere, a suspension

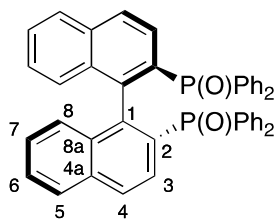


of (*P*)-(+)-**2** (80.0 mg, 0.222 mmol) and silver(II) oxide (40.0 mg, 0.323 mmol) in dry MeCN (20 mL) was stirred at 0 °C for 20 min. The red mixture was filtered over celite. The filtrate was evaporated to yield (*P*)-(+)-**1** (79.0 mg, 99%) as a red, crystalline solid. $R_f = 0.16$ (SiO₂;

cyclohexane/EtOAc 4:1); M.p. 182–185 °C (decomp.); $[\alpha]_D^{22} = +6293 \pm 60$ ($c = 0.19$ in CH_3CN); ¹H NMR (400 MHz, CDCl_3 , assignment based on DQF-COSY, HSQC, and HMBC spectroscopy): $\delta = 6.11$ (d, $J = 9.9$ Hz, 1 H; H-C(3)), 7.16 (ddd, $J = 8.4, 6.9, 1.4$ Hz, 1 H; H-C(15)), 7.33 (ddd, $J = 8.0, 6.9, 1.1$ Hz, 1 H; H-C(14)), 7.39 (d, $J = 8.0$ Hz, 1 H; H-C(5)), 7.40 (d, $J = 9.9$ Hz, 1 H; H-C(4)), 7.74 (d, $J = 8.4$ Hz, 1 H; H-C(7)), 7.78 (d, $J = 8.4$ Hz, 2 H; H-C(9,11)), 7.83 (d, $J = 8.3$ Hz, 1 H; H-C(12)), 7.87 (d, $J = 8.4$ Hz, 1 H; H-C(8)), 7.90 (d, $J = 8.3$ Hz, 1 H; H-C(10)), 7.91 (dd, $J = 8.1, 1.4$ Hz, 1 H; H-C(13)), 8.03 (d, $J = 8.0$ Hz, 1 H; H-C(6)), 8.39 ppm (br. d, $J = 8.5$ Hz, 1 H; H-C(16)); ¹³C NMR (101 MHz, CDCl_3 , assignment based on HSQC, and HMBC spectroscopy): $\delta = 124.56$ (C(8b)), 125.58 (C(15)), 126.23 (C(16)), 126.41 (C(7)), 126.52/126.67/126.88 (C(9,11,14)), 127.00 (C(3)), 127.17 (C(5)), 128.32 (C(12)), 129.02 (C(6b)), 129.22 (C(10b)), 129.68 (C(8)), 129.84/129.90 (C(10,13)), 130.12 (C(12b)), 131.69 (C(10a)), 132.69 (C(4a)), 132.80 (C(12a)), 134.11 (C(6a)), 134.23 (C(8a)), 134.41 (C(6)), 135.32 (C(4b)), 146.26 (C(4)), 181.31 (C(1)), 183.76 ppm (C(2)); IR (ATR): $\tilde{\nu} = 3047$ (w), 2924 (w), 2853 (w), 1663 (s), 1606 (m), 1546 (w), 1513 (w), 1474 (w), 1437 (w), 1402 (w), 1374 (m), 1332 (m), 1269 (w), 1248 (m), 1200 (w), 1187 (m), 1154 (w), 1136 (m), 1109 (m), 1088 (w), 1042 (m), 995 (w), 953 (w), 929 (w), 879 (w), 846 (s), 816 (s), 767 (m), 743 (s), 725 (m), 698 (m), 651 (m), 635 cm^{-1} (m); HR-MALDI-TOF-MS: m/z (%): 359.1066 (100, $[M + H]^+$, calcd. for $\text{C}_{26}\text{H}_{15}\text{O}_2^+$: 359.1067).

(*M*)-(-)-[6]Helicene-1,2-dione ((*M*)-(-)-**1**). (*M*)-(-)-**1** was prepared in an analogous way from (*M*)-(-)-**2**. $[\alpha]_D^{22} = +6280 \pm 60$ ($c = 0.25$ in CH_3CN).

(R)-(+)-2,2'-Bis(diphenylphosphanyl)-1,1'-binaphthyldioxide ((R)-(+)-BINAPO).⁶



According to a published procedure, a solution of (R)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene (500 mg, 0.803 mol) in CH₂Cl₂ (17 mL) was cooled to 0 °C and H₂O₂ (30 %, 2 mL) was added dropwise. The mixture was stirred at 0 °C for 4 h and diluted with H₂O (50 mL). The aqueous phase was extracted with CH₂Cl₂ (3 x 20 mL). The combined phases were washed with H₂O (30 mL), dried over Na₂SO₄, and evaporated to yield (R)-(+)-BINAPO (501 mg, 95%) as a white solid. M.p. 259–261 °C; [α]_D²² = +199.5 (*c* = 1 in CHCl₃) (+198.1 (*c* = 1 in benzene))⁶; ¹H NMR (400 MHz, CD₂Cl₂, assignment based on COSY spectroscopy): δ = 6.65 (dd, *J* = 8.6, 1.1 Hz, 2 H; 2 H–C(8)), 6.73 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 2 H; 2 H–C(7)), 7.25 (td, *J* = 8.0, 2.9 Hz, 4 H; 4 H–C(4) of Ph), 7.31–7.49 (m, 16 H; 4 H–C(3,6) and 12 H of Ph), 7.73 (dd, *J* = 12.2, 1.4 Hz, 2 H; 2 H–C(2,6) of Ph), 7.76 (d, *J* = 12.2 Hz, 2 H; 2 H–C(2,6) of Ph), 7.84 (d, *J* = 8.2 Hz, 2 H; 2 H–C(5)), 7.88 ppm (dd, *J* = 8.6, 2.5 Hz, 2 H; 2 H–C(4)); ³¹P NMR (162 MHz, CD₂Cl₂) δ = 27.82 ppm; IR (ATR): $\tilde{\nu}$ = 3048 (w), 1588 (w), 1553 (w), 1502 (w), 1482 (w), 1434 (m), 1371 (w), 1339 (w), 1308 (w), 1260 (w), 1202 (m), 1166 (w), 1150 (w), 1140 (w), 1116 (m), 1101 (m), 1025 (w), 997 (w), 947 (w), 883 (w), 870 (w) 845 (w), 814 (m), 751 (m), 745 (m), 738 (m), 721 (m), 695 (s), 641 (m), 628 (m), 617 cm⁻¹ (w); HR-MALDI-TOF-MS: *m/z* (%): 677.1770 (100, [M + Na]⁺, calcd. for C₄₄H₃₂NaO₂P₂⁺: 677.1770); elemental analysis calcd. (%) for C₄₄H₃₂O₂P₂ (654.68): C 80.72, H 4.93; found: C 80.61, H 4.86.

3SI X-ray Data

3.1SI General Information

Single crystals of (\pm)-**2** suitable for X-ray diffraction were grown by slow diffusion of *n*-hexane into a chloroform solution at -30 °C under a nitrogen atmosphere. In contrast, (\pm)-**1** is stable under ambient conditions and could also be crystallized by slow diffusion of *n*-hexane into a chloroform solution at -30 °C. Crystals of compounds were measured on a Bruker Kappa Apex2 Duo ((\pm)-**2**) and a Bruker/Nonius Kappa Apex2 ((\pm)-**1**) diffractometer. The structures were solved by direct methods with SHELXS-2013/14 and refined by full-matrix least-squares analysis (SHELXL-2013/14).⁷ Data were corrected for absorption effects using the multi-scan method (SADABS).⁸ Unless otherwise indicated below, all non-hydrogen atoms were refined anisotropically. Hydrogen positions were calculated based on a riding model and included in the structure factor calculation. CCDC (1004335 ((\pm)-**2**) and 1004336 ((\pm)-**1**)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk), or *via* <http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/DataRequest.aspx?>.

3.2SI Crystal Data for (±)-1 and (±)-2

Table 1SI. Crystallographic details.

	(±)-1·CHCl ₃	(±)-2
formula	C ₂₇ H ₁₅ Cl ₃ O ₂	C ₂₆ H ₁₆ O ₂
M_r	477.74	360.39
crystal color, shape	metallic black, irregular	dull brown, block
crystal size	0.12 x 0.30 x 0.36	0.07 x 0.12 x 0.17
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	$Pbca$
a (Å)	8.1039(3)	9.898(1)
b (Å)	19.8611(6)	16.198(2)
c (Å)	14.8094(5)	21.268(2)
α (deg)	90	90
β (deg)	119.708(2)	90
γ (deg)	90	90
V (Å ³)	2070.3(1)	3409.8(6)
Z	4	8
D_{calc} (g cm ⁻³)	1.533	1.404
T (K)	100(1)	100(1)
radiation source	Mo K α	Cu K α
λ (Å)	0.71073	1.54178
μ (mm ⁻¹)	0.467	0.694
F(000)	976	1504
meas./indep. refl.	12433/4771	12948/2875
obsvd. [$I > 2\sigma(F^2)$]	4108	2452
$R(\text{int})$	0.0188	0.1436
$R[F^2 > 2\sigma(F^2)]$	0.0364	0.0850
$wR(F^2)$	0.0982	0.2393
S	1.041	1.068
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.527, -0.516	0.644, -0.288

3.3SI Crystal Packing in (\pm)-1 and (\pm)-2

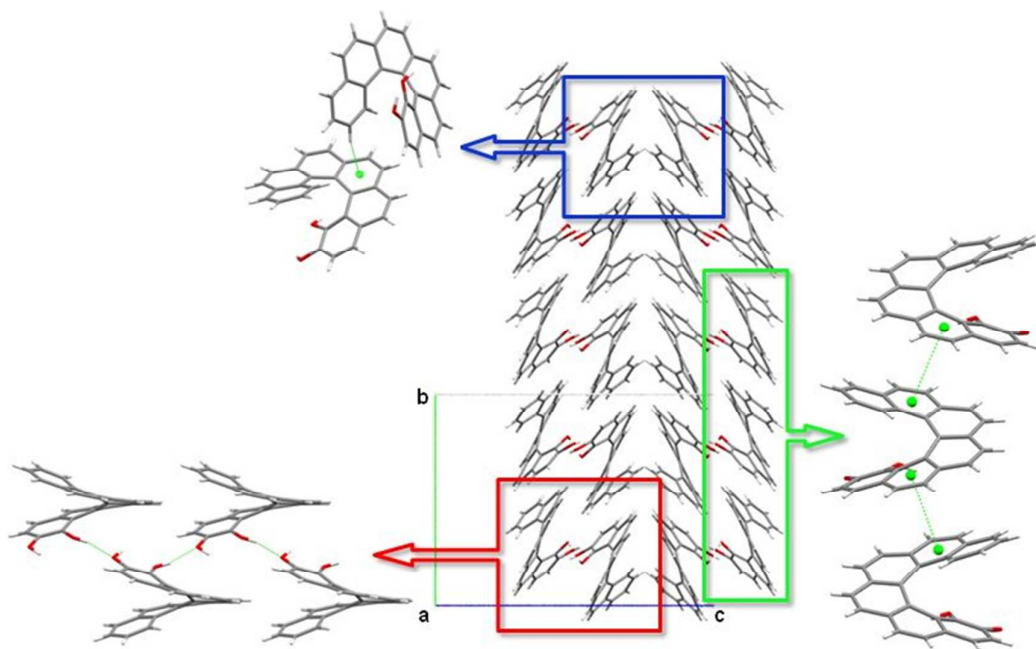


Figure 1SI. Packing motif of catechol (\pm)-2. Hydrogen bonding along a -axis (red, 1.905 Å), parallel displaced π - π stacking interactions along b -axis (green, 3.894 Å), and T-shaped π - π stacking interactions along b -axis (blue, 3.639 Å).

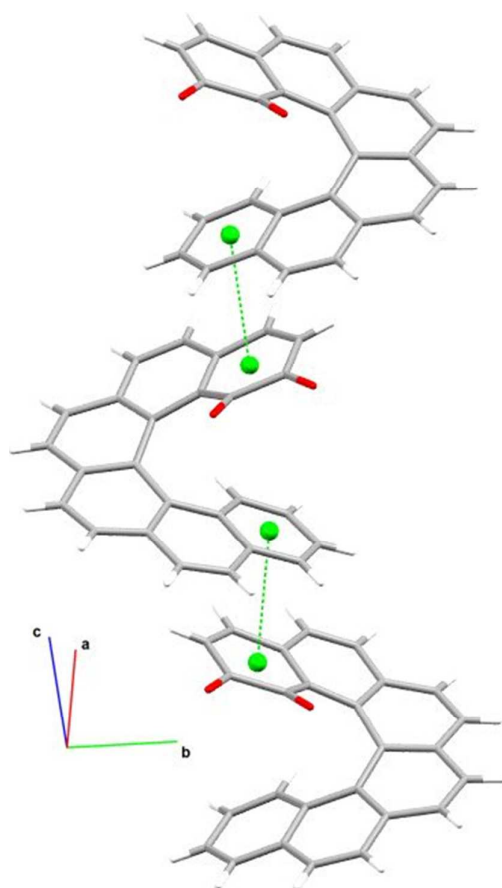


Figure 2SI. Packing motif of (\pm)-**1** governed by parallel displaced π - π stacking interactions (3.365 Å).

Table 2SI. Structural parameters that describe the helicity in (±)-**1** and (±)-**2**.

Parameters	(±)- 1	(±)- 2	[6]helicene ⁹
d [C(1)–C(16)] / Å	3.227(2)	3.153(5)	3.215
d [C(2)–C(15)] / Å	4.283(2)	4.013(5)	4.576
θ [C(1)–C(4B)–C(6B)–C(8B)] / °	20.0(2)	24.3(5)	11.3 / 15.2 ^a
θ [C(4B)–C(6B)–C(8B)–C(10B)] / °	28.8(2)	23.9(5)	30.0 / 30.3 ^a
θ [C(6B)–C(8B)–C(10B)–C(12B)] / °	27.0(2)	25.4(5)	30.0 / 30.3 ^a
θ [C(8B)–C(10B)–C(12B)–C(16)] / °	13.9(2)	20.4(5)	11.3 / 15.2 ^a

^a pairs of different values were reported due to the deviation from the C_2 point group

4SI Electrochemistry and Spectroelectrochemistry

4.1SI Cyclic Voltammetry

The cyclic voltammogram (CV) was obtained with a *PG 580* potentiostat (Uniscan, UK) using a Pt disc working electrode, glassy carbon rod counter electrode, and Ag wire pseudo-reference electrode. The sample solution with approximate concentration of 1 mM, prepared with 0.1 M tetrabutylammonium hexafluorophosphate (NBu₄PF₆) supporting electrolyte in CH₃CN, was purged with Ar for 15 min before each experiment and the CV was recorded at a scan rate of 100 mV s⁻¹. Ferrocene served as internal potential standard.

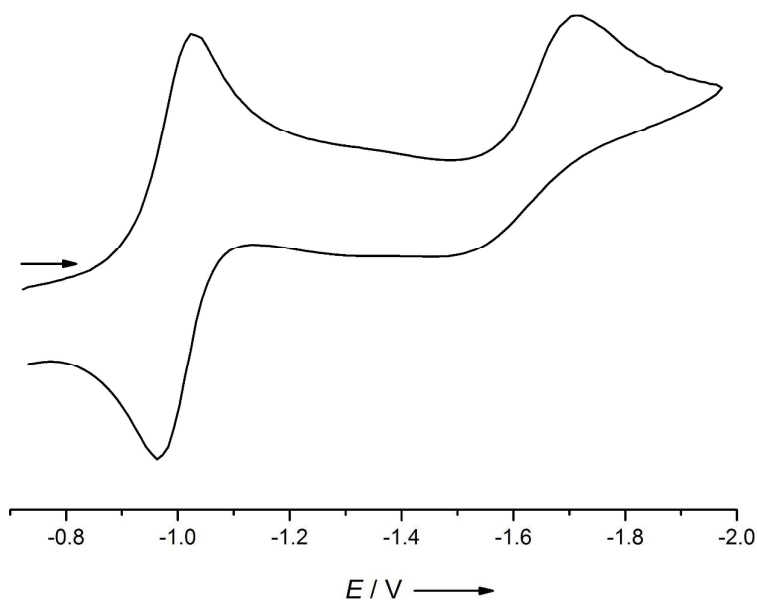


Figure 3SI. Cyclic voltammogram of (±)-**1** in CH₃CN and 0.1 M NBu₄PF₆. A sweep rate of 100 mV/s was used and the potential is referenced against Fc⁺⁰.

4.2SI UV/Vis and ECD Spectroelectrochemistry

UV/Vis and ECD spectroelectrochemistry (SEC) experiments were performed at 20 °C, under argon, with a home-made Optically Transparent Thin-Layer

Electrosynthetic (OTTLE) cell, using a *Varian CARY 5000* spectrometer (UV/Vis), a *Jasco J-815* circular dichroism spectrometer (IFR140 facility - Biosit platform - Université de Rennes 1), and an *EG&G PAR model 362* potentiostat. A Pt mesh was used as the working electrode, a Pt wire as the counter electrode, and a Pt wire as a pseudo-reference electrode. The electrodes were arranged in the cell such that the Pt mesh was in the optical path of the quartz cell. The anhydrous freeze-pump-thaw degassed sample-electrolyte solution (0.2 M NBu₄PF₆) was cannula-transferred under argon into the cell previously thoroughly deoxygenated. Stable isobestic points were observed during oxidation or reduction. In every case, re-reduced or re-oxidized samples displayed in the spectral region of interest no features other than those of the parent material.

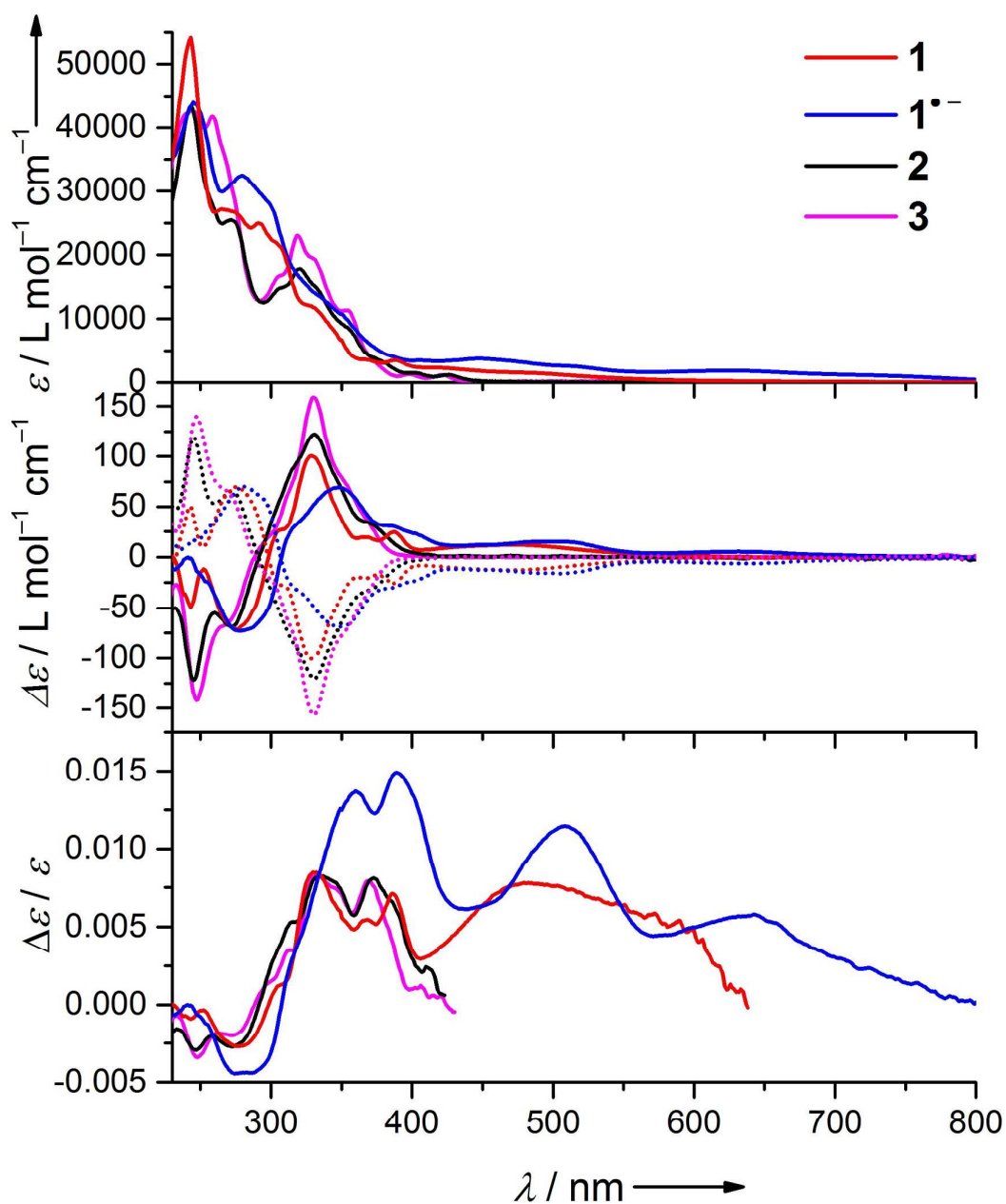


Figure 4SI. UV/Vis (top) and ECD spectra (middle) in acetonitrile. $\Delta\epsilon/\epsilon$ (bottom) was calculated for the (*P*)-(+)-enantiomers only. Spectra of 1^- were generated electrochemically with an OTTLE cell (0.2 M NBu_4PF_6 was used as an electrolyte). In the ECD spectra, solid lines represent spectra of (*P*)-(+)-enantiomers, while dotted lines show spectra of the (*M*)-(-)-enantiomers.

Table 3SI. ECD spectra in acetonitrile. Only the spectral characterization for the (*M*)-(-) enantiomers is listed (see Table 1 for ECD spectral data of the (*P*)-(+) enantiomers). Spectra of (*M*)-(-)-**1**⁺ were generated electrochemically with an OTTLE cell (0.1 M NBu₄PF₆ was used as an electrolyte).

Compound	λ/nm ($\Delta\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$)
(<i>M</i>)-(-)- 1	243 (50), 276 (70), 307 sh (-28), 329 (-100), 367 (-21), 387 (-26), 471 (-13)
(<i>M</i>)-(-)- 1 ⁺	277 (68), 318 sh (-32), 348 (-69), 385 (-30), 505 (-16), 628 (-6)
(<i>M</i>)-(-)- 2	245 (119), 272 (65), 331 (-120), 370 sh (-33)
(<i>M</i>)-(-)- 3	247 (140), 271 (62), 330 (-157), 357 sh (-63)

5SI EPR and ENDOR Spectroscopy

5.1SI General Information

EPR and ENDOR spectra were recorded using two ESP300 (Bruker, Germany) X-band spectrometers (one equipped with an ENDOR unit). Temperature control was achieved using the EUROTHERM variable temperature units. Typical spectrometer settings for recording the solution EPR spectra were: microwave power = 0.2 mW, modulation amplitude = 0.015 mT, modulation frequency = 100 kHz, conversion time = 40.96 ms, time constant = 10.24 ms, and number of points = 2048. ENDOR spectra were recorded with microwave power = 10 mW, modulation amplitude = 0.1 mT, modulation frequency = 12.5 kHz, pump frequency = 10 MHz, modulation depth = 100 kHz, and field locked at the maximum of the EPR line. Spectra were analyzed with the WinEPR software provided by the spectrometers manufacturer, and the EPR simulations were performed with EasySpin.¹⁰

5.2SI Sample Preparation

Reductions were performed in dry THF with the use of Li metal. The solvents were heated to reflux over a Na/K alloy and stored over a Na/K alloy under high vacuum. Samples were prepared in a special three compartment EPR sample tube connected to the vacuum line. Small pieces of Li metal were placed inside the tube, and about 0.4 mL of the solvent was freshly condensed to dissolve the investigated compound. The sample was successively degassed by three freeze-pump-thaw cycles and sealed under high vacuum. Reductions were performed by contact of the THF solution of the parent molecule with the Li metal in the evacuated sample tube. The sample tubes were either stored at 190 K (isopropanol/dry ice bath) or immediately transferred into the microwave cavity of the EPR spectrometer.

For the chiral recognition experiments, the samples were carefully reduced by Li metal in THF. After the generation of the desired radical was confirmed by EPR, the solution was mixed with an excess of (*R*)-(+)-BINAPO, which was placed in a different compartment of the EPR sample tube. Contact of (*R*)-(+)-BINAPO and Li metal was strictly avoided.

5.3SI Experimental Data

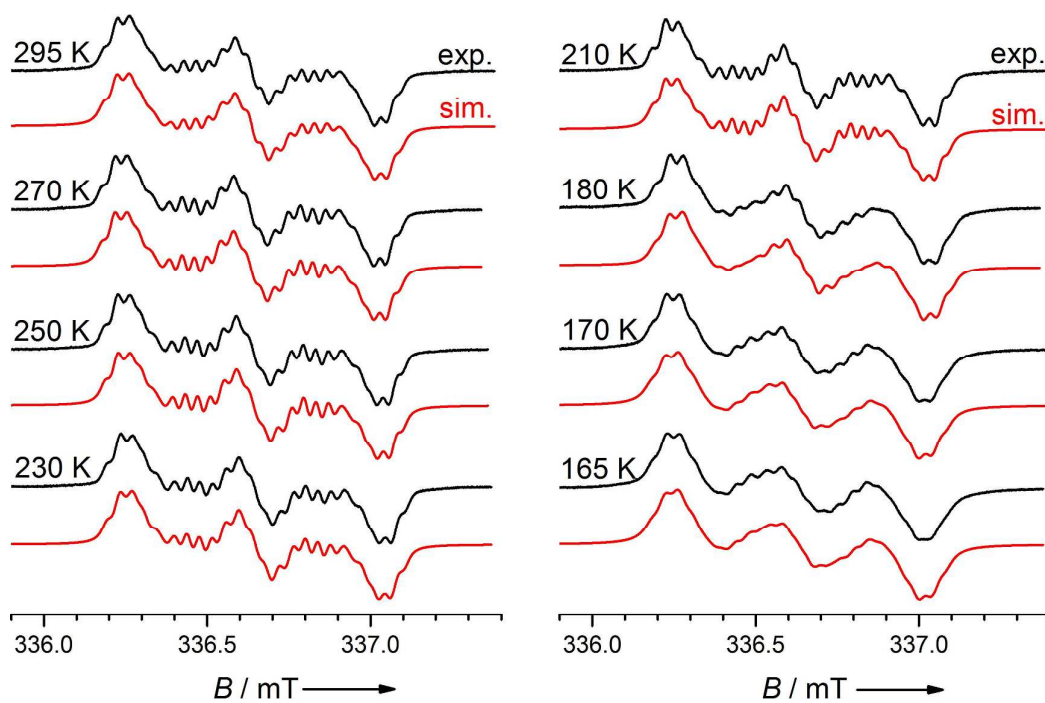


Figure 5SI. Variable temperature X-band (9.4506 GHz) EPR spectra of $[\text{Li}^+(\pm)\text{-}\mathbf{1}^*]$ in THF (black) together with simulations (red). Natural abundances of 7.5% for ${}^6\text{Li}$ ($S = 1$) and 92.5% for ${}^7\text{Li}$ ($S = 3/2$), and corresponding g_n ratio were taken into account for EPR simulations. For hyperfine coupling constants see Table 3SI.

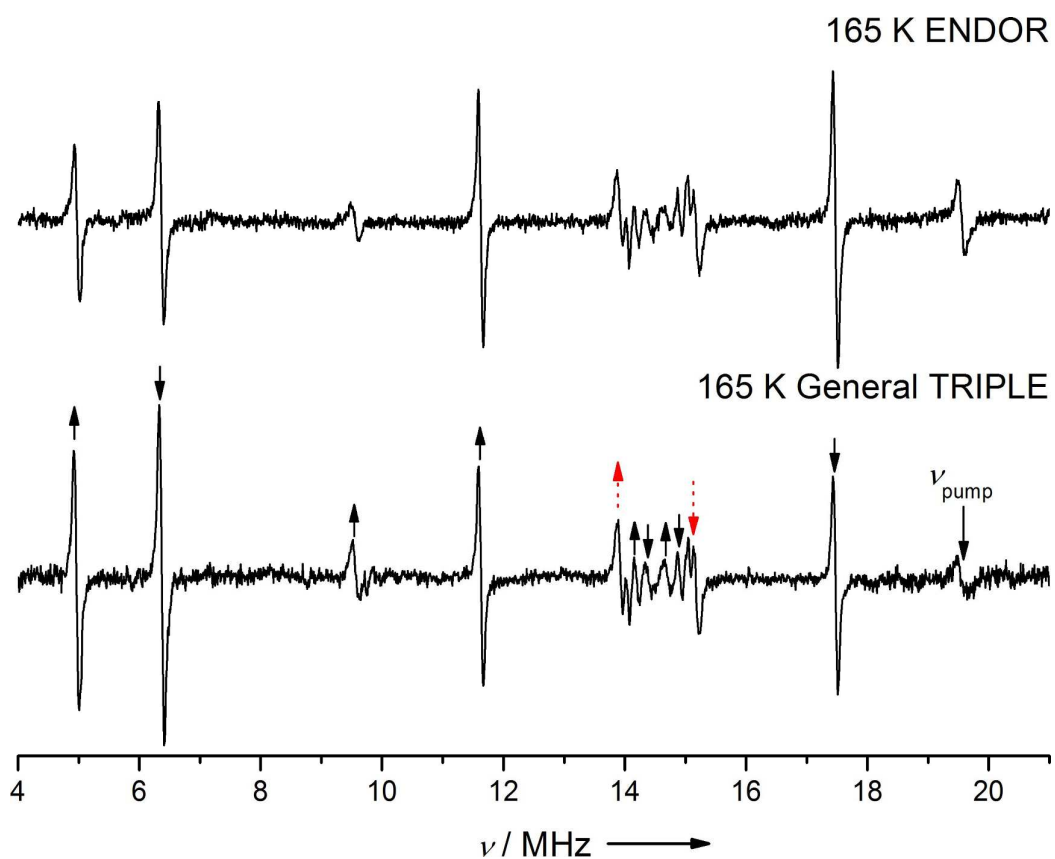
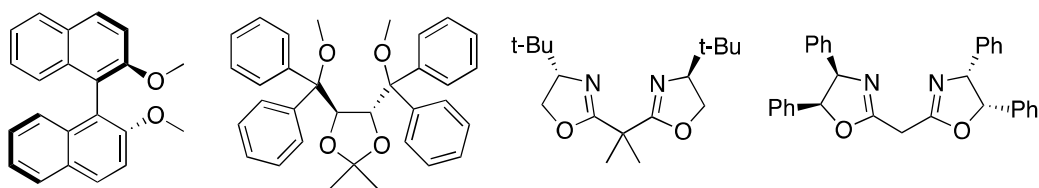


Figure 6SI. ENDOR (top) and general TRIPLE (bottom) spectroscopy of $[\text{Li}^+\{(\pm)\text{-1}^-\}]$ in THF at 165 K. Arrows indicate the relative intensity changes used for sign assignment of hyperfine coupling constants (red dotted arrows – ambiguous change due to line overlap).

Table 4SI. Hyperfine coupling constants from simulations of X-band (9.4506 GHz) EPR spectra of $[\text{Li}^+\{\pm\text{-I}^-\}]$ in THF, together with hyperfine couplings determined from ENDOR spectroscopy. Natural abundances of 7.5% for ${}^6\text{Li}$ ($S = 1$) and 92.5% for ${}^7\text{Li}$ ($S = 3/2$), and corresponding g_n ratio were taken into account for EPR simulations. Relative signs of hyperfine coupling constants were determined by TRIPLE spectroscopy (\pm marks ambiguous assignment), while atom assignment is based on DFT results. Hyperfine coupling to H3 and H11–H16 is negligible according to DFT.

Method	T/K	A/MHz							
		${}^7\text{Li}$	H4	H5	H6	H7	H8	H9	H10
EPR	295	-1.57	-10.19	± 1.23	-5.84	± 1.03	-0.73	+0.33	± 1.14
EPR	270	-1.57	-10.19	± 1.24	-5.84	± 1.01	-0.72	+0.31	± 1.15
EPR	250	-1.58	-10.19	± 1.23	-5.84	± 1.01	-0.72	+0.31	± 1.15
ENDOR	250	-1.56	-10.19	^a	-5.84	± 1.07	^a	+0.24	^a
EPR	230	-1.58	-10.13	± 1.23	-5.82	± 1.00	-0.72	+0.31	± 1.17
ENDOR	230	-1.55	-10.13	^a	-5.82	± 1.07	^a	+0.28	^a
EPR	210	-1.55	-10.11	± 1.19	-5.84	± 1.00	-0.71	+0.29	± 1.17
ENDOR	210	-1.53	-10.11	± 1.15	-5.84	± 0.98	-0.71	+0.28	^a
EPR	180	-1.45	-10.08	± 1.27	-5.83	± 1.13	-0.72	+0.31	± 1.16
ENDOR	180	-1.45	-10.05	± 1.22	-5.84	± 1.04	-0.72	+0.32	^a
EPR	170	-1.41	-10.05	± 1.26	-5.83	± 1.10	-0.71	+0.30	± 1.18
ENDOR	170	-1.41	-10.01	± 1.24	-5.85	± 1.05	-0.72	+0.32	^a
EPR	165	-1.40	-10.01	± 1.27	-5.83	± 1.06	-0.72	+0.29	± 1.21
ENDOR	165	-1.39	-10.00	± 1.24	-5.85	± 1.04	-0.72	+0.32	^a

^a not resolved



Scheme 2SI. Enantiopure ligands that were unsuccessfully used to bind to $[\text{Li}^+\{(\pm)\text{-1}^{\bullet-}\}]$ in THF.

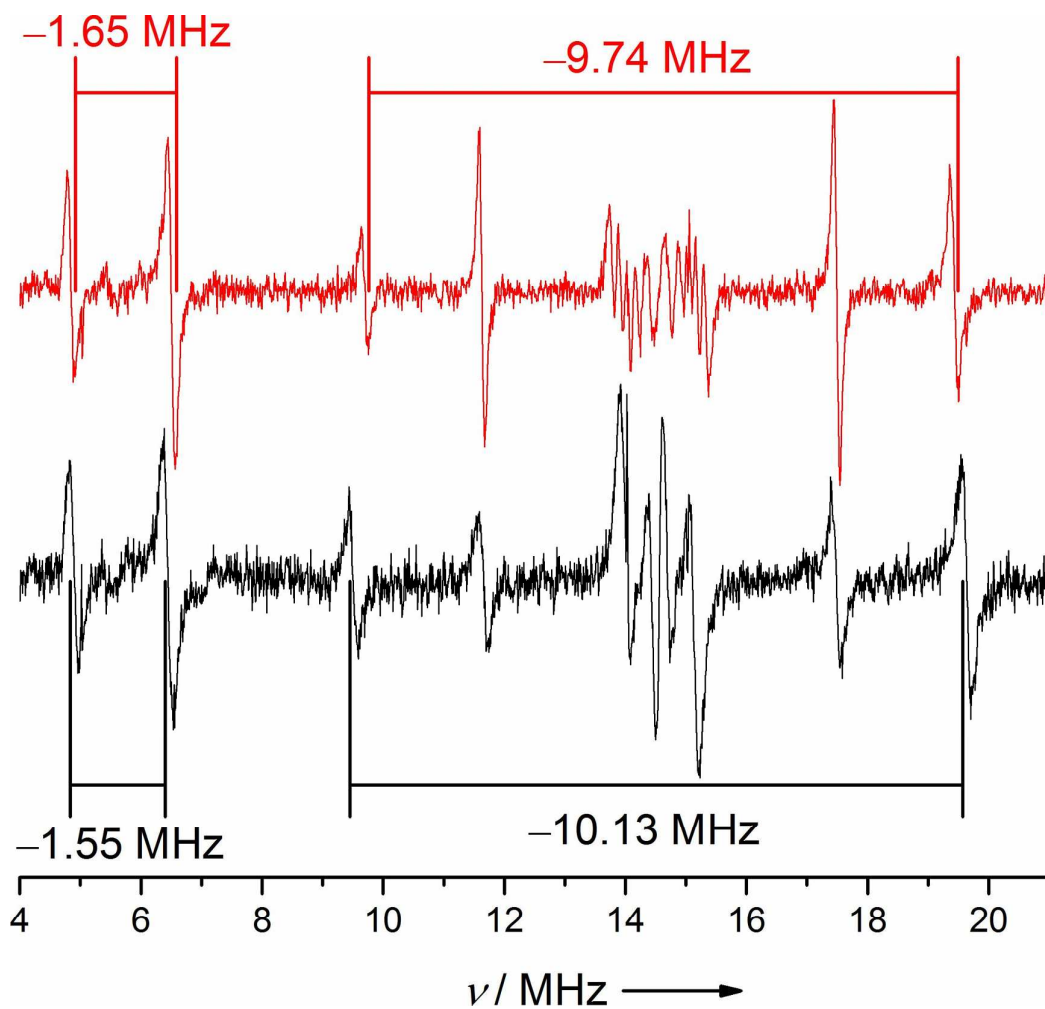


Figure 7SI. ENDOR spectra of $[\text{Li}^+\{(\pm)\text{-1}^{\bullet-}\}]$ (black) and $[\{(R)\text{-}(+)\text{-BINAPO}\}\text{Li}^+\{(\pm)\text{-1}^{\bullet-}\}]$ (red) in THF at 230 K.

Table 5SI. Hyperfine couplings from ENDOR spectroscopy in THF.

Species	<i>T</i> /K	⁷ Li	<i>A</i> /MHz						
			H4	H5	H6	H7	H8	H9	H10
[Li ⁺ ((±)- 1 ⁺)]	230	-1.55	-10.13	- ^a	-5.82	±1.07	- ^a	+0.28	- ^a
	210	-1.53	-10.11	±1.15	-5.84	±0.98	-0.71	+0.28	- ^a
[{(<i>R</i>)-(+)-BINAPO}Li ⁺ {(±)- 1 ⁺ }]	230	-1.64	-9.74	±1.53	-5.86	±1.05	-0.75	+0.32	±1.27
	210	-1.69	-9.73	±1.54	-5.86	±1.04	-0.74	+0.32	±1.26
[{(<i>R</i>)-(+)-BINAPO}Li ⁺ {(<i>P</i>)-(+)- 1 ⁺ }]	230	-1.70	-9.78	±1.52	-5.84	±1.04	-0.72	+0.32	±1.25
	210	-1.76	-9.80	±1.53	-5.84	±1.06	-0.75	+0.34	±1.24
[{(<i>R</i>)-(+)-BINAPO}Li ⁺ {(<i>M</i>)-(-)- 1 ⁺ }]	230	-1.58	-9.67	±1.54	-5.87	±1.05	-0.77	+0.32	±1.27
	210	-1.62	-9.71	±1.54	-5.87	±1.06	-0.75	+0.33	±1.25

^a not resolved

6SI DFT Calculations

6.1SI General Information

All calculations were conducted with the Gaussian 09 suite of programs.¹¹ The geometry optimizations were performed with the functional ω B97X-D and the 6-31G(d,p) basis set. ω B97X-D is a hybrid GGA functional including dispersion correction,¹² which is important to calculate the structure and properties of helicenes.¹³ Furthermore, it was shown that ω B97X-D describes the geometry of helicenes with high accuracy.¹⁴ Fermi contact couplings were calculated using the ω B97X-D functional with the 6-31G(d,p) basis set. For the TD-DFT calculations, the CAM-B3LYP functional¹⁵ with the 6-31G(d,p) basis set was used; 40 states were calculated. Calculated UV/Vis and ECD spectra of singlet species were bathochromically shifted by 2500 cm^{-1} , while the corresponding spectra of doublet species were bathochromically shifted by 1000 cm^{-1} . The Polarizable Continuum Model (PCM)¹⁶ was used for all calculations, including the solvent effects of either THF (Fermi contact coupling calculations) or acetonitrile (TD-DFT).

6.2SI Results from (TD-)DFT calculations

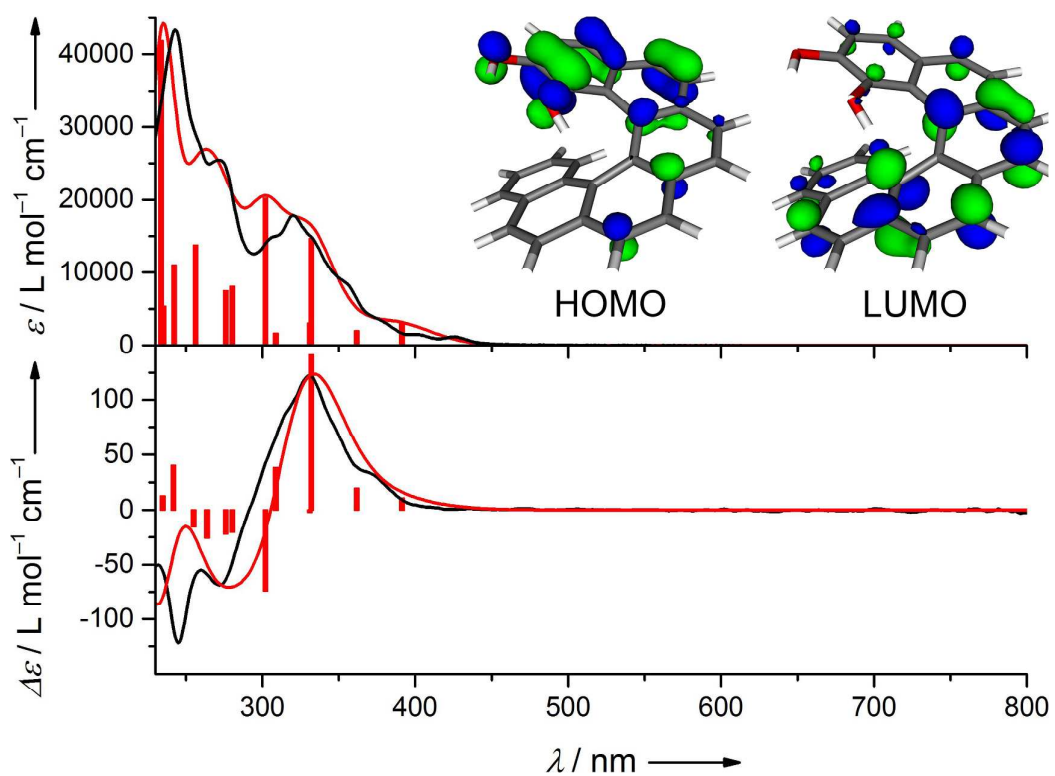


Figure 8SI. TD-DFT calculations [CAM-B3LYP/6-31g(d,p)] on (*P*)-(+)-**2** in acetonitrile. Calculated (red) and experimental (black) UV/Vis (top) and ECD (bottom) spectra are shown. Red bars indicate major calculated transitions. In the inset, the calculated frontier orbitals are shown.

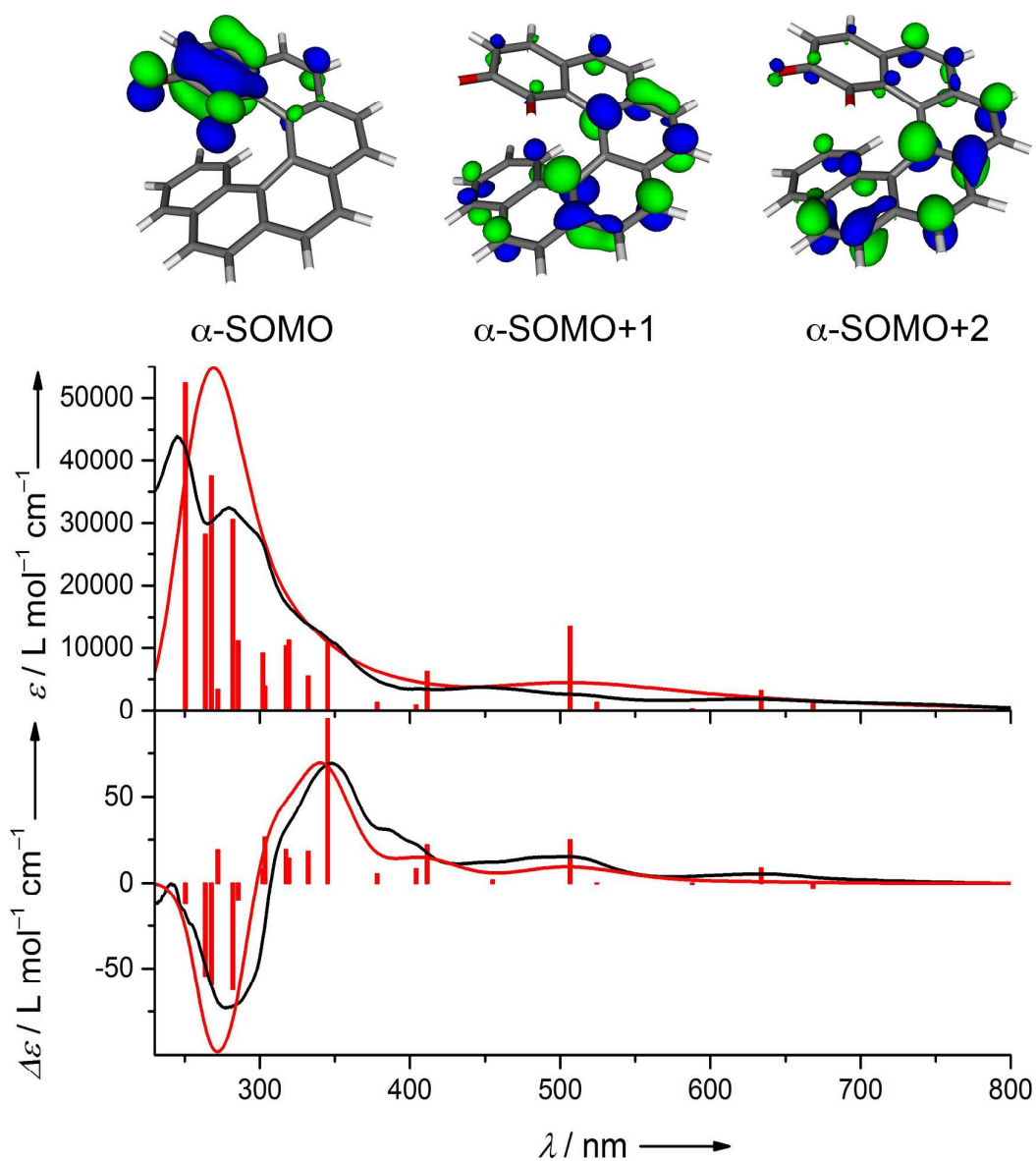


Figure 9SI. TD-DFT calculations [UCAM-B3LYP/6-31g(d,p)] on $(P)\text{-}(+)\text{-1}^-$ in acetonitrile. Calculated (red) and experimental (black) UV/Vis (top) and ECD (bottom) spectra are shown. Red bars indicate major calculated transitions. In the inset, the calculated frontier orbitals are shown.

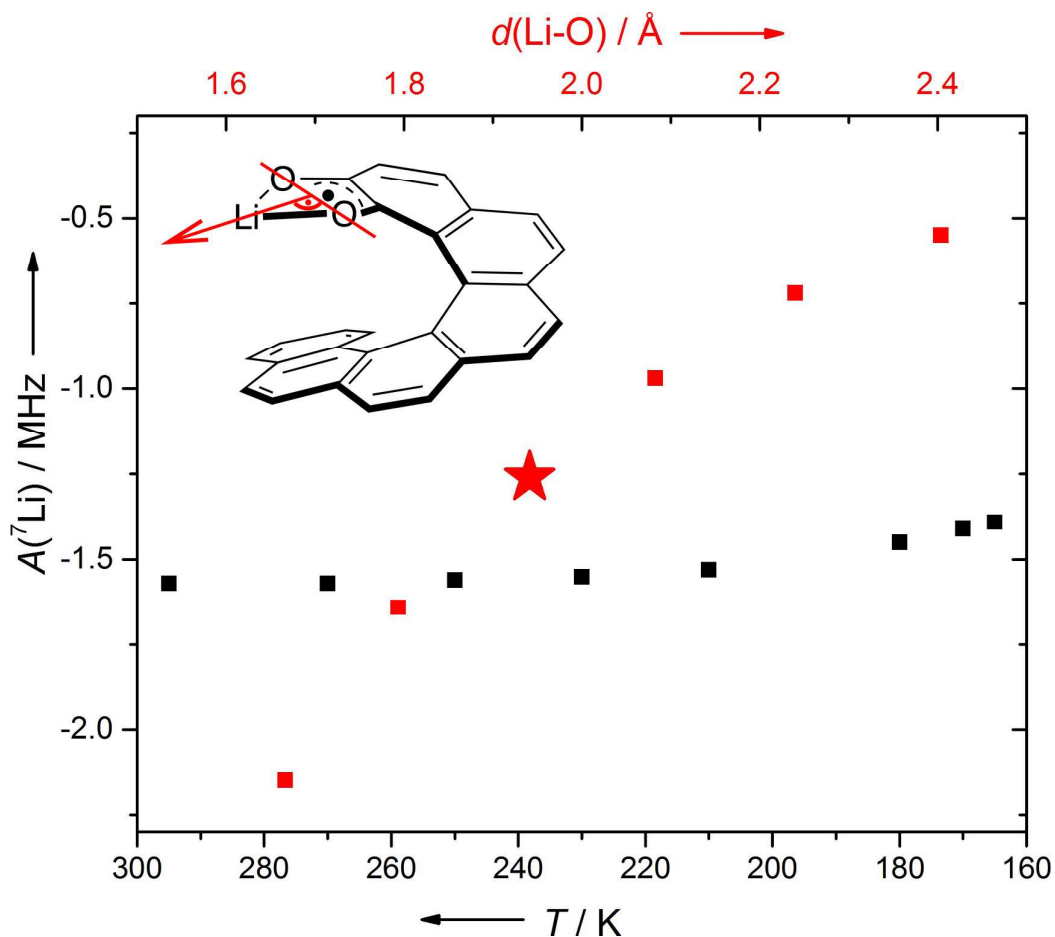


Figure 10SI. Experimental lithium hyperfine couplings from EPR spectroscopy of $[\text{Li}^+\{\text{(-)-1}^-\}]$ in THF (black). In red, calculated lithium hyperfine couplings [uωB97X-D/6-31g(d,p)] are shown. The asterisk shows the value from the optimized structure without restraints. All other values were calculated from a scan, in which the lithium atom was moved along the red axis. The distances $d(\text{Li-O})$ are an average of the two single Li-O distances.

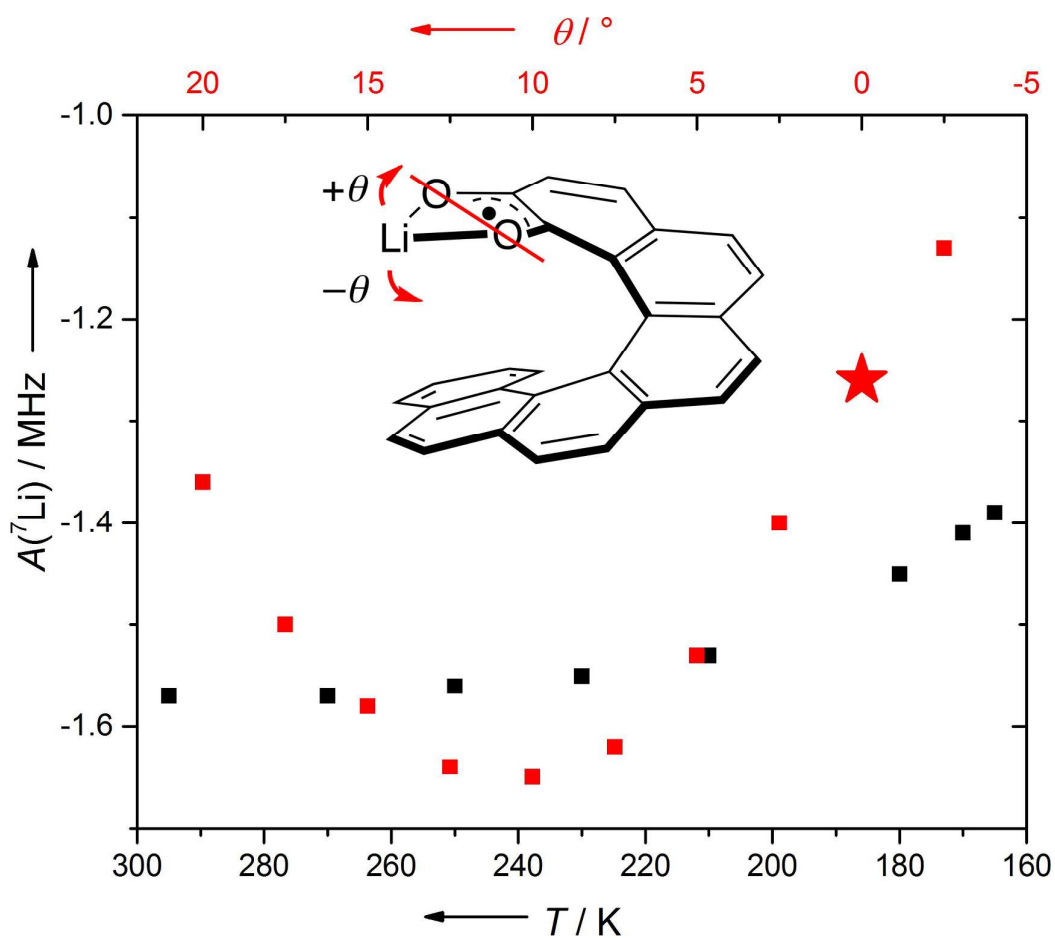


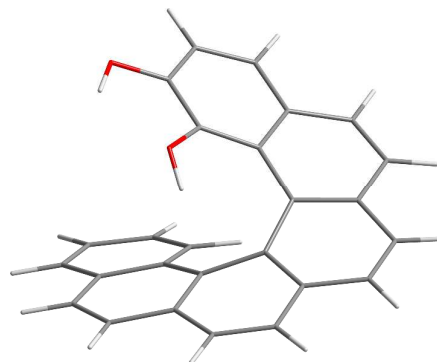
Figure 11SI. Experimental lithium hyperfine couplings from EPR spectroscopy of $[\text{Li}^+\{(\pm)\text{-1}^-\}]$ in THF (black). In red, calculated lithium hyperfine couplings [uωB97X-D/6-31g(d,p)] are shown. The asterisk shows the value from the optimized structure without restraints. All other values were calculated from a scan, in which the lithium atom was moved along a circle with constant distances $d(\text{Li-O})$.

6.3SI Coordinate Geometries

(*P*)-(+)-2 [ω B97X-D/6-31g(d,p), PCM solvation in acetonitrile]

Atom type, (x,y,z) coordinates:

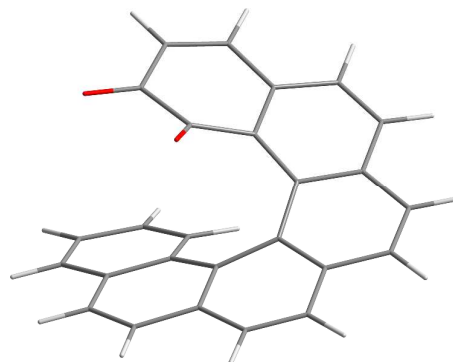
O	1.13362600	-3.01269800	-2.25704100
H	0.27688500	-2.65545800	-2.53086300
O	-0.06713400	-0.73342000	-1.99153900
H	-0.68492200	-0.09370100	-1.61671000
C	2.93832000	-2.36042700	-0.85439100
H	3.41375600	-3.31609600	-1.04530600
C	3.54727500	-1.38628900	-0.09635400
H	4.54184200	-1.55080500	0.30591000
C	2.91334000	-0.15234800	0.14277100
C	1.59395700	0.09079200	-0.34134300
C	0.93269000	1.33362700	0.04580600
C	-0.49595900	1.56734700	0.00290600
C	-1.51866200	0.53917500	0.10439000
C	-1.33017900	-0.74785000	0.76663800
C	-2.30101900	-1.76708300	0.58186700
C	-2.10967900	-3.03661300	1.17323900
H	-2.85269600	-3.80887300	0.99635900
C	-1.02750300	-3.28232000	1.98490400
H	-0.89343600	-4.25744100	2.44126600
C	1.69856300	-2.09036600	-1.43994100
C	3.63265800	0.90541900	0.78787500
H	4.63900400	0.70285000	1.14210100
C	3.10946400	2.15174900	0.86382400
H	3.69096300	2.97899900	1.25874700
C	1.75281100	2.39889800	0.47284600
C	1.05149800	-0.87620700	-1.22138400
C	-0.93801300	2.90831000	-0.13086100
C	-2.28088900	3.18062800	-0.51880100
H	-2.57560900	4.21427200	-0.67216300
C	-3.15626800	2.16529400	-0.74547100
H	-4.15658400	2.36268100	-1.11779800
C	-2.80479000	0.82813600	-0.40297500
C	-3.77413200	-0.21727700	-0.54703800
H	-4.72590100	0.02580900	-1.00922500
C	-3.50720100	-1.47972600	-0.13415600
H	-4.23291800	-2.27490900	-0.27577700
C	-0.11911700	-2.24402700	2.25760200
H	0.70142300	-2.40946400	2.94805500
C	-0.26931000	-1.01058300	1.66531400
H	0.42769200	-0.22197200	1.91589200
C	-0.04009900	3.98100200	0.12618100
H	-0.41007700	4.99909700	0.05410900
C	1.23669000	3.72460100	0.51997200
H	1.90196200	4.53078200	0.81352600



(P)-(+)-1 [uωB97X-D/6-31g(d,p), PCM solvation in acetonitrile]

Atom type, (x,y,z) coordinates:

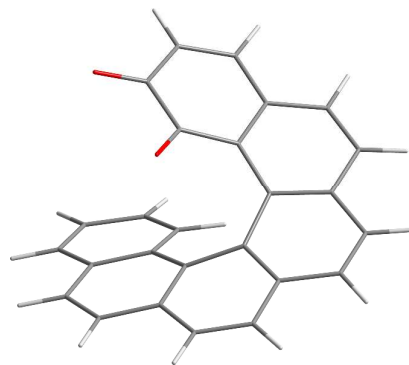
O	-0.55944600	-0.19659700	-2.03291100
O	-2.89569800	-1.58244300	-1.62209700
C	-0.59189400	-1.10005100	-1.22322600
C	-1.83645800	-2.01924100	-1.21381100
C	-1.62072800	-3.39885600	-0.78131600
H	-2.44193700	-4.10058200	-0.87443400
C	-0.41963600	-3.75980500	-0.29967000
H	-0.24849200	-4.79100800	-0.00334300
C	0.68986900	-2.82722700	-0.07313400
C	0.55351700	-1.46482700	-0.34609800
C	1.90053700	-3.31981000	0.45630300
H	2.00347600	-4.37994600	0.66265600
C	2.95803800	-2.46697000	0.63862000
H	3.92124900	-2.85114100	0.95965500
C	2.81957400	-1.07584500	0.42604200
C	1.56115300	-0.53776800	0.04932100
C	3.95869000	-0.21652900	0.53076900
H	4.91669100	-0.65074200	0.79798800
C	3.84698300	1.09699600	0.21803100
H	4.72197000	1.73954100	0.20064800
C	2.56648000	1.68827200	-0.03159000
C	1.39324900	0.90949100	0.05776400
C	2.48169200	3.07130000	-0.35889900
H	3.40052700	3.64034800	-0.46021100
C	1.27184100	3.64568700	-0.59640800
H	1.20124100	4.67749500	-0.92709900
C	0.07000900	2.92726500	-0.33559400
C	0.12588600	1.59887500	0.12881200
C	-1.19617900	3.56888100	-0.53392300
H	-1.20365000	4.56747600	-0.96034500
C	-2.35585000	2.93846800	-0.22882600
H	-3.31433600	3.41128100	-0.41998500
C	-2.33243400	1.67261400	0.44035200
C	-1.09147600	1.03600000	0.69647500
C	-3.53171900	1.09181200	0.91522600
H	-4.47283400	1.58108900	0.68149700
C	-3.51215200	-0.04912000	1.68114600
H	-4.43759300	-0.48501400	2.04219900
C	-2.27640200	-0.61799600	2.03943400
H	-2.24613500	-1.47229500	2.70769500
C	-1.09880200	-0.08184700	1.56736000
H	-0.16174500	-0.51281200	1.89419100



(P)-(+)-1⁺ [ω B97X-D/6-31g(d,p), PCM solvation in acetonitrile]

Atom type, (x,y,z) coordinates:

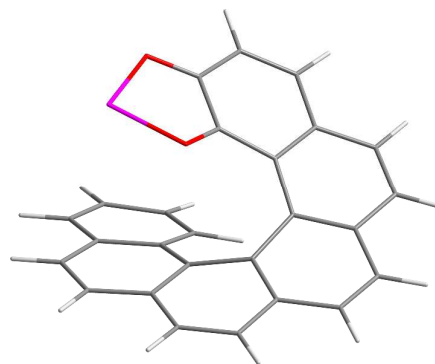
O	-0.06895300	-0.61749600	-1.94957600
O	0.94842600	-3.14821500	-2.12305900
C	0.94515200	-0.91429300	-1.28250100
C	1.54863500	-2.27275300	-1.45377400
C	2.84280700	-2.50844000	-0.86692600
H	3.29173000	-3.48514200	-1.02929800
C	3.50485900	-1.53709700	-0.17655800
H	4.50668800	-1.71759400	0.20589600
C	2.91787200	-0.25597000	0.06400200
C	1.59552100	0.02174400	-0.36063700
C	3.69363000	0.75838400	0.69057500
H	4.70940800	0.52414600	0.99820700
C	3.20491800	2.02180900	0.82309300
H	3.82738600	2.82282400	1.21158500
C	1.85175800	2.31337200	0.47925500
C	0.99200000	1.27841600	0.03410100
C	1.38326800	3.65796600	0.55352600
H	2.07930200	4.43406400	0.85892400
C	0.11682500	3.96656200	0.16987100
H	-0.21870200	4.99854700	0.12298200
C	-0.81995600	2.92926000	-0.10970500
C	-0.43272800	1.57065100	-0.00525300
C	-2.15261600	3.26917100	-0.48655000
H	-2.40283200	4.31801100	-0.61745700
C	-3.07034800	2.29563800	-0.72381100
H	-4.06624200	2.54083100	-1.08147000
C	-2.76764700	0.93759200	-0.41318700
C	-1.49337300	0.58599400	0.07181800
C	-3.78066200	-0.06322400	-0.57294400
H	-4.72358700	0.23032900	-1.02584100
C	-3.56898200	-1.34511500	-0.18771900
H	-4.32843500	-2.10667500	-0.33977400
C	-2.37218200	-1.69285100	0.51667800
C	-1.35939300	-0.71630100	0.70681800
C	-2.22780800	-2.97879300	1.08721600
H	-3.00129600	-3.71897800	0.90135600
C	-1.15195000	-3.28198100	1.88810800
H	-1.05381400	-4.26953800	2.32734700
C	-0.20333700	-2.28346400	2.17360100
H	0.61278000	-2.49191400	2.85815800
C	-0.31016800	-1.03556000	1.60199600
H	0.41524300	-0.27750900	1.86390400



[Li{(P)-(+)-1⁺}] $\theta = 0^\circ$ [ω B97X-D/6-31g(d,p), PCM solvation in THF]

Atom type, (x,y,z) coordinates:

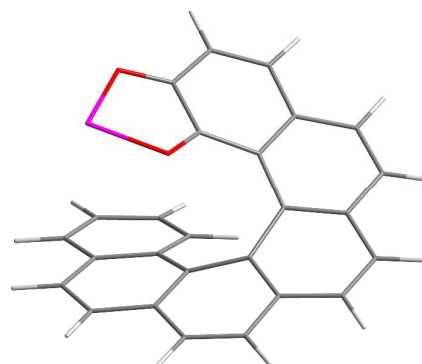
O	-0.56295400	-0.38083500	-1.83880400
O	-1.71367600	-2.78598600	-1.87513000
C	3.76533900	-0.88803000	0.69807000
H	4.79276800	-0.78207300	1.03356300
C	-1.39723800	0.49713000	0.77735500
C	3.19127000	-2.11840600	0.59123700
H	3.74134000	-3.01310300	0.86799300
C	1.66053500	0.19892600	0.02672300
C	0.13805000	-3.76700900	-0.75942300
H	-0.28196500	-4.76042500	-0.88117000
C	1.58499100	2.64483600	-0.10603100
C	3.02275100	0.29115500	0.40249400
C	-0.56442300	1.50562800	0.13909000
C	-0.88468300	-0.48499400	1.65787300
H	0.16544700	-0.46966200	1.91743200
C	-3.39811500	1.64240100	-0.09836200
H	-4.47553800	1.65815200	-0.23668500
C	-0.59681000	-2.65786800	-1.28255900
C	1.89156500	-2.25664100	0.03525900
C	-0.00971000	-1.30656500	-1.17703000
C	-3.61626000	-0.48075700	1.14474500
H	-4.68801100	-0.44327800	0.96902900
C	1.16239800	-1.10738800	-0.34258500
C	-2.80409200	0.53547900	0.58934700
C	2.99348100	2.68748400	0.11675100
H	3.49927500	3.64650600	0.05686200
C	3.66911700	1.56119500	0.45935900
H	4.72385600	1.59815100	0.71529300
C	-1.20636600	2.66607800	-0.33330200
C	-0.44794800	3.82846500	-0.65454800
H	-0.97072700	4.71740900	-0.99484100
C	-2.63199900	2.69439300	-0.47818600
H	-3.08523200	3.58049700	-0.91353800
C	0.87747300	1.42565600	0.02184500
C	1.34691600	-3.56895800	-0.16501600
H	1.93000400	-4.41661100	0.18427900
C	0.89562900	3.84286400	-0.45277100
H	1.47125600	4.75280100	-0.59364000
C	-1.69555200	-1.45066400	2.21082400
H	-1.26901400	-2.18993300	2.88093300
C	-3.07233100	-1.47442300	1.92476400
H	-3.70546300	-2.24616800	2.35022600
Li	-2.29295800	-1.01920900	-2.43993200



[Li{(P)-(+)-1⁺}] $\theta = 2.5^\circ$ [u ω B97X-D/6-31g(d,p), PCM solvation in THF]

Atom type, (x,y,z) coordinates:

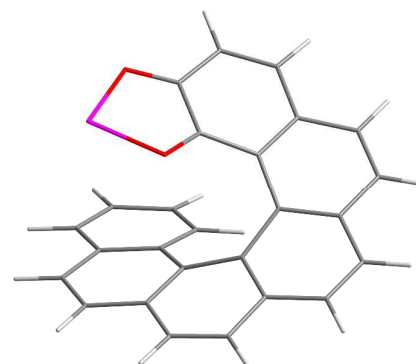
O	-0.57592900	-0.37428000	-1.82365200
O	-1.74427100	-2.77102200	-1.85261200
C	3.76190800	-0.91250700	0.69446900
H	4.78968300	-0.81266700	1.03082400
C	-1.39386100	0.50682700	0.77806300
C	3.18204800	-2.13975400	0.58303300
H	3.72776900	-3.03797400	0.85699300
C	1.66264600	0.18775000	0.02652100
C	0.11576800	-3.76836500	-0.76377400
H	-0.31053900	-4.75927200	-0.88426000
C	1.60266500	2.63438000	-0.10429500
C	3.02555900	0.27138600	0.40223000
C	-0.55405600	1.50945900	0.14002800
C	-0.88813000	-0.47828500	1.65896700
H	0.16202800	-0.46973800	1.91896500
C	-3.38624300	1.66278200	-0.10274600
H	-4.46323200	1.68445600	-0.24367900
C	-0.61733200	-2.65347100	-1.27703900
C	1.88142200	-2.26959000	0.02733800
C	-0.01931400	-1.30672300	-1.17497600
C	-3.61914600	-0.45752000	1.14245100
H	-4.69036100	-0.41390800	0.96486300
C	1.15732800	-1.11537100	-0.34526600
C	-2.80010300	0.55333200	0.58757400
C	3.01113400	2.66820400	0.11979000
H	3.52282000	3.62418700	0.06121800
C	3.67951700	1.53742400	0.46173800
H	4.73425100	1.56762100	0.71856700
C	-1.18810500	2.67335300	-0.33449900
C	-0.42199000	3.83052000	-0.65622400
H	-0.93867900	4.72221400	-0.99866100
C	-2.61323000	2.70979400	-0.48238100
H	-3.06035700	3.59779400	-0.92020800
C	0.88729800	1.41967100	0.02322200
C	1.32912900	-3.57834200	-0.17555400
H	1.90945600	-4.43016100	0.16823800
C	0.92136800	3.83660400	-0.45260200
H	1.50303900	4.74265800	-0.59370100
C	-1.70573100	-1.43861900	2.21147700
H	-1.28459400	-2.18037200	2.88225800
C	-3.08227100	-1.45390300	1.92390700
H	-3.72066400	-2.22151500	2.34899700
Li	-2.29622700	-1.00837500	-2.45633700



[Li{(P)-(+)-1⁺}] $\theta = 5^\circ$ [ω B97X-D/6-31g(d,p), PCM solvation in THF]

Atom type, (x,y,z) coordinates:

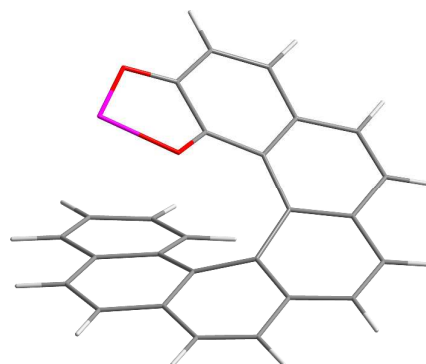
O	-0.58774600	-0.36472700	-1.81814500
O	-1.79773100	-2.74079300	-1.84005300
C	3.74756100	-0.97716300	0.68938800
H	4.77758800	-0.89487000	1.02361200
C	-1.38482900	0.53107500	0.77780300
C	3.14698200	-2.19428600	0.57794200
H	3.67810800	-3.10185600	0.84970100
C	1.66582300	0.15919000	0.02615200
C	0.04936400	-3.77003800	-0.75921300
H	-0.39422100	-4.75358600	-0.87767300
C	1.64850800	2.60679400	-0.10273200
C	3.03060800	0.21910200	0.39987800
C	-0.52735900	1.51936800	0.14096100
C	-0.89692000	-0.46189400	1.65982900
H	0.15308900	-0.47178600	1.92050800
C	-3.35594100	1.72036900	-0.10599400
H	-4.43218700	1.76050100	-0.24840300
C	-0.66613800	-2.64277800	-1.27031100
C	1.84298200	-2.30155600	0.02542900
C	-0.04428500	-1.30654500	-1.17194700
C	-3.62668400	-0.39501000	1.13959200
H	-4.69672700	-0.33312600	0.96049900
C	1.13764700	-1.13507000	-0.34513800
C	-2.78962400	0.60093000	0.58470500
C	3.05747800	2.61605300	0.12040600
H	3.58531300	3.56329300	0.06284100
C	3.70650000	1.47348000	0.46004900
H	4.76188300	1.48472600	0.71578200
C	-1.14092400	2.69412100	-0.33366600
C	-0.35494700	3.83829600	-0.65394400
H	-0.85619400	4.73890200	-0.99601500
C	-2.56500100	2.75460800	-0.48359100
H	-2.99665500	3.65024200	-0.92142100
C	0.91211000	1.40448000	0.02423600
C	1.26804000	-3.60071800	-0.17571900
H	1.83491400	-4.46230700	0.16615500
C	0.98825700	3.82100000	-0.44986800
H	1.58576600	4.71684600	-0.59002600
C	-1.73167700	-1.40745600	2.21226700
H	-1.32414100	-2.15576600	2.88417800
C	-3.10787900	-1.39930800	1.92308300
H	-3.75991300	-2.15538000	2.34818400
Li	-2.29691300	-0.98131300	-2.49664300



[Li{(P)-(+)-1⁺}] $\theta = 7.5^\circ$ [u ω B97X-D/6-31g(d,p), PCM solvation in THF]

Atom type, (x,y,z) coordinates:

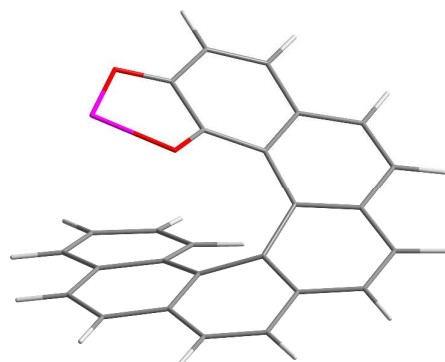
O	-0.56967700	-0.36420500	-1.83929700
O	-1.77204200	-2.74385300	-1.88321300
C	3.74067900	-0.96469100	0.70281500
H	4.76980800	-0.88116300	1.03940300
C	-1.38378000	0.52526900	0.78416000
C	3.13990000	-2.18258200	0.59766900
H	3.67031700	-3.08813900	0.87722200
C	1.66126700	0.16639300	0.02728800
C	0.05424000	-3.76541600	-0.75983900
H	-0.38547300	-4.75036000	-0.88126800
C	1.63656300	2.61274400	-0.10992100
C	3.02446900	0.22985100	0.40412800
C	-0.53455800	1.51681600	0.14158500
C	-0.88704600	-0.46414000	1.66543900
H	0.16413300	-0.46926700	1.92143800
C	-3.36422000	1.70467800	-0.09035100
H	-4.44143000	1.73906600	-0.22670300
C	-0.65405800	-2.64140100	-1.28758300
C	1.83834000	-2.29326800	0.03962200
C	-0.03869300	-1.30295900	-1.17839400
C	-3.61902400	-0.41058200	1.15969800
H	-4.69009700	-0.35555800	0.98456800
C	1.13536900	-1.12907900	-0.34073900
C	-2.78966900	0.58866100	0.59913400
C	3.04559300	2.62602200	0.11285700
H	3.57192900	3.57395500	0.05239900
C	3.69729400	1.48632800	0.45853300
H	4.75188500	1.50160200	0.71714400
C	-1.15513800	2.68802700	-0.33218400
C	-0.37427200	3.83446800	-0.65730200
H	-0.88053100	4.73274300	-0.99828100
C	-2.58020300	2.74195800	-0.47414900
H	-3.01841500	3.63501100	-0.91081300
C	0.90453400	1.40873700	0.02123200
C	1.26543400	-3.59330100	-0.16142900
H	1.82883100	-4.45324900	0.19017600
C	0.97001200	3.82317300	-0.45843000
H	1.56378200	4.72095200	-0.60232700
C	-1.71412000	-1.41256000	2.22397000
H	-1.29862200	-2.15818900	2.89394300
C	-3.09180400	-1.41148300	1.94174300
H	-3.73760000	-2.17039300	2.37126500
Li	-2.23247200	-1.00084100	-2.60846700



[Li{(P)-(+)-1⁺}] $\theta = 10^\circ$ [u ω B97X-D/6-31g(d,p), PCM solvation in THF]

Atom type, (x,y,z) coordinates:

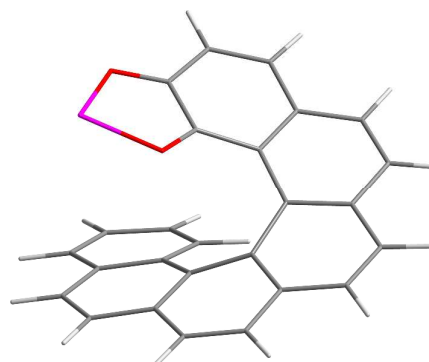
O	-0.57354700	-0.36635000	-1.83680800
O	-1.76998700	-2.74899500	-1.87887500
C	3.74220200	-0.96075900	0.70324600
H	4.77114600	-0.87561100	1.04009900
C	-1.38504500	0.52505200	0.78518700
C	3.14251400	-2.17902000	0.59815900
H	3.67349000	-3.08432700	0.87767700
C	1.66113600	0.16765900	0.02829000
C	0.05830900	-3.76651900	-0.75640300
H	-0.38166000	-4.75149500	-0.87647000
C	1.63431400	2.61411400	-0.10993100
C	3.02468500	0.23294500	0.40432100
C	-0.53603900	1.51670600	0.14235500
C	-0.88859600	-0.46315500	1.66815000
H	0.16213000	-0.46652700	1.92580800
C	-3.36566300	1.70323600	-0.09126800
H	-4.44272200	1.73725400	-0.22900200
C	-0.65111800	-2.64376700	-1.28566900
C	1.84088400	-2.29158400	0.04042600
C	-0.03851100	-1.30389600	-1.17712000
C	-3.62045400	-0.41106000	1.15918000
H	-4.69136700	-0.35532700	0.98346900
C	1.13599100	-1.12826800	-0.33997200
C	-2.79072100	0.58809400	0.59921500
C	3.04348700	2.62887300	0.11236400
H	3.56831100	3.57751600	0.05031300
C	3.69631100	1.49003200	0.45818700
H	4.75145300	1.50638200	0.71467400
C	-1.15698100	2.68722600	-0.33283400
C	-0.37694900	3.83389400	-0.65927100
H	-0.88343800	4.73130700	-1.00208600
C	-2.58206000	2.74059300	-0.47556700
H	-3.02038800	3.63292800	-0.91352000
C	0.90325500	1.40944700	0.02212000
C	1.26952300	-3.59253800	-0.15888700
H	1.83358700	-4.45157300	0.19386700
C	0.96717200	3.82383300	-0.45961400
H	1.55960800	4.72233500	-0.60434000
C	-1.71610300	-1.41161300	2.22609000
H	-1.30205100	-2.15607700	2.89831100
C	-3.09357000	-1.41119500	1.94228000
H	-3.73990600	-2.17006400	2.37110200
Li	-2.20592300	-1.02131800	-2.65421700



[Li{(P)-(+)-1⁻}] $\theta = 12.5^\circ$ [u ω B97X-D/6-31g(d,p), PCM solvation in THF]

Atom type, (x,y,z) coordinates:

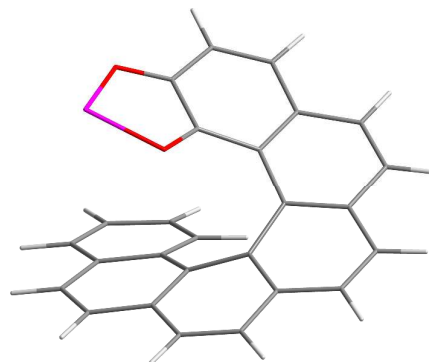
O	-0.57058900	-0.36594200	-1.84077700
O	-1.76798700	-2.74806500	-1.88503200
C	3.73984500	-0.96108900	0.70663200
H	4.76861500	-0.87640800	1.04414400
C	-1.38492700	0.52522900	0.78684400
C	3.13904900	-2.17897100	0.60297500
H	3.66897700	-3.08431800	0.88434600
C	1.66019500	0.16781800	0.02896900
C	0.05534500	-3.76549200	-0.75421500
H	-0.38542800	-4.75017700	-0.87370600
C	1.63375700	2.61399400	-0.11120500
C	3.02349600	0.23282800	0.40565200
C	-0.53658600	1.51663200	0.14272000
C	-0.88772600	-0.46241400	1.67008600
H	0.16317900	-0.46562100	1.92698500
C	-3.36620600	1.70304300	-0.08831600
H	-4.44336300	1.73680400	-0.22529900
C	-0.65109200	-2.64299200	-1.28800700
C	1.83782700	-2.29130400	0.04410100
C	-0.03828000	-1.30325800	-1.17847300
C	-3.62001300	-0.41027300	1.16385100
H	-4.69103100	-0.35473700	0.98878600
C	1.13447200	-1.12791800	-0.33873200
C	-2.79074000	0.58838200	0.60243600
C	3.04297000	2.62850000	0.11108300
H	3.56809900	3.57692300	0.04816700
C	3.69545900	1.48982000	0.45828700
H	4.75053000	1.50622100	0.71506600
C	-1.15784000	2.68685100	-0.33274900
C	-0.37786800	3.83323900	-0.66044800
H	-0.88453700	4.73046400	-1.00351400
C	-2.58305500	2.74016200	-0.47411900
H	-3.02180600	3.63215400	-0.91235800
C	0.90259300	1.40957800	0.02187400
C	1.26542800	-3.59194300	-0.15423100
H	1.82774600	-4.45105100	0.20112500
C	0.96641000	3.82341100	-0.46154500
H	1.55868300	4.72188000	-0.60717900
C	-1.71477100	-1.41033100	2.22954300
H	-1.30014000	-2.15433100	2.90193100
C	-3.09253700	-1.40991200	1.94709500
H	-3.73851300	-2.16851700	2.37693400
Li	-2.16788100	-1.03625900	-2.71320200



[Li{(P)-(+)-1⁻}] $\theta = 15^\circ$ [u ω B97X-D/6-31g(d,p), PCM solvation in THF]

Atom type, (x,y,z) coordinates:

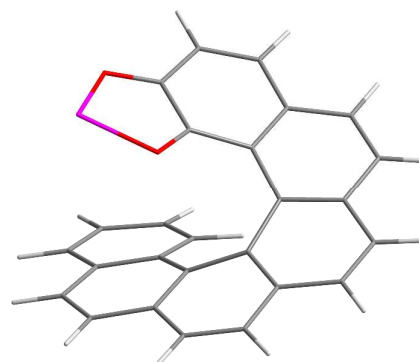
O	-0.55749400	-0.36465700	-1.85422100
O	-1.75406500	-2.74702000	-1.90711800
C	3.73572100	-0.95286300	0.71487900
H	4.76391100	-0.86743300	1.05387800
C	-1.38496300	0.52078300	0.78973700
C	3.13535800	-2.17147800	0.61424900
H	3.66521500	-3.07542200	0.90005600
C	1.65743800	0.17263600	0.02964800
C	0.05773600	-3.76153600	-0.75396800
H	-0.38103000	-4.74703500	-0.87429500
C	1.62544900	2.61792500	-0.11424600
C	3.01944600	0.23993200	0.40908600
C	-0.54169800	1.51426700	0.14231700
C	-0.88202100	-0.46434700	1.67255000
H	0.16983600	-0.46492700	1.92574400
C	-3.37187700	1.69146600	-0.08072500
H	-4.44955100	1.72120800	-0.21432400
C	-0.64424500	-2.64074100	-1.29686200
C	1.83575200	-2.28585800	0.05186300
C	-0.03336600	-1.30050500	-1.18353500
C	-3.61573900	-0.42078500	1.17611800
H	-4.68737500	-0.37023400	1.00336500
C	1.13409400	-1.12385800	-0.33684400
C	-2.79149000	0.57940200	0.61005300
C	3.03448000	2.63532200	0.10900600
H	3.55851500	3.58437400	0.04584000
C	3.68892800	1.49845100	0.45955200
H	4.74313100	1.51759800	0.71952400
C	-1.16747600	2.68212600	-0.33265900
C	-0.39090300	3.83040100	-0.66208900
H	-0.90096100	4.72612100	-1.00420700
C	-2.59317000	2.73064600	-0.47003600
H	-3.03613400	3.62079800	-0.90785300
C	0.89735800	1.41214900	0.02022400
C	1.26407900	-3.58680400	-0.14640200
H	1.82450600	-4.44512000	0.21384900
C	0.95388900	3.82484500	-0.46534900
H	1.54384900	4.72466600	-0.61224400
C	-1.70414300	-1.41348800	2.23686600
H	-1.28403700	-2.15559900	2.90790500
C	-3.08284800	-1.41754500	1.95929700
H	-3.72469800	-2.17752600	2.39285900
Li	-2.10914600	-1.05377000	-2.79192600



[Li{(P)-(+)-1⁺}] $\theta = 17.5^\circ$ [u ω B97X-D/6-31g(d,p), PCM solvation in THF]

Atom type, (x,y,z) coordinates:

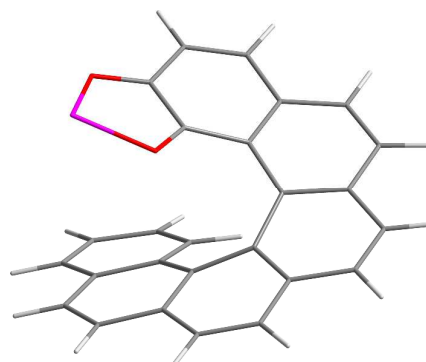
O	-0.56646900	-0.36762000	-1.84463900
O	-1.75648000	-2.75338400	-1.89195100
C	3.73939100	-0.94874600	0.71226200
H	4.76761400	-0.86112400	1.05070300
C	-1.38707200	0.52148200	0.78914100
C	3.14123100	-2.16814100	0.61078000
H	3.67276700	-3.07169600	0.89487900
C	1.65786000	0.17368900	0.03058000
C	0.06383800	-3.76425800	-0.74988700
H	-0.37471900	-4.75007700	-0.86818400
C	1.62399000	2.61935700	-0.11322600
C	3.02060800	0.24296900	0.40813800
C	-0.54280100	1.51508000	0.14308100
C	-0.88573000	-0.46337900	1.67323300
H	0.16539100	-0.46279100	1.92925500
C	-3.37289400	1.69192700	-0.08509600
H	-4.45023400	1.72160600	-0.22148700
C	-0.64216800	-2.64478300	-1.29045200
C	1.84094800	-2.28470100	0.05034200
C	-0.03390000	-1.30286700	-1.17952700
C	-3.61864400	-0.42037600	1.17011800
H	-4.68991700	-0.36881100	0.99552600
C	1.13568500	-1.12368900	-0.33602100
C	-2.79319800	0.58007500	0.60647300
C	3.03316200	2.63822300	0.10920700
H	3.55558500	3.58805200	0.04484500
C	3.68889700	1.50202900	0.45873700
H	4.74379000	1.52204900	0.71601100
C	-1.16822500	2.68270800	-0.33322800
C	-0.39202300	3.83112700	-0.66292300
H	-0.90181900	4.72633500	-1.00667100
C	-2.59376500	2.73123700	-0.47298700
H	-3.03593100	3.62117200	-0.91198800
C	0.89657700	1.41293900	0.02164500
C	1.27171400	-3.58691900	-0.14642300
H	1.83458900	-4.44407400	0.21274800
C	0.95248200	3.82606200	-0.46495800
H	1.54161100	4.72636700	-0.61205900
C	-1.70912600	-1.41305600	2.23495500
H	-1.29141000	-2.15481800	2.90793000
C	-3.08723100	-1.41725800	1.95407900
H	-3.73029900	-2.17747500	2.38544800
Li	-2.08702200	-1.07702700	-2.81749600



[Li{(P)-(+)-1⁺}] $\theta = 20^\circ$ [u ω B97X-D/6-31g(d,p), PCM solvation in THF]

Atom type, (x,y,z) coordinates:

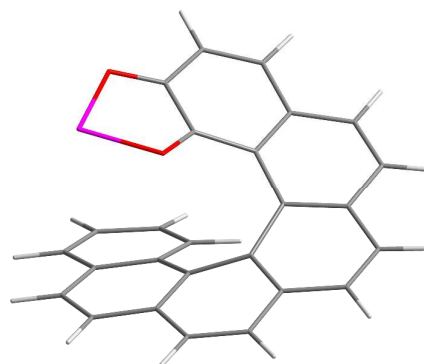
O	-0.56513700	-0.36757900	-1.84616100
O	-1.75502400	-2.75339300	-1.89407400
C	3.73816000	-0.94743700	0.71481500
H	4.76621800	-0.85965400	1.05372400
C	-1.38761700	0.52135100	0.78997100
C	3.13983100	-2.16683300	0.61419800
H	3.67105900	-3.07020000	0.89949200
C	1.65706200	0.17447000	0.03136800
C	0.06318700	-3.76363300	-0.74762700
H	-0.37570400	-4.74940600	-0.86504900
C	1.62252800	2.61992700	-0.11388800
C	3.01963400	0.24413700	0.40939000
C	-0.54394100	1.51497800	0.14319000
C	-0.88564300	-0.46281000	1.67451700
H	0.16554100	-0.46161900	1.93027900
C	-3.37402800	1.69075600	-0.08414500
H	-4.45139400	1.71981800	-0.22045200
C	-0.64139400	-2.64469100	-1.29110300
C	1.83986600	-2.28381800	0.05302600
C	-0.03333900	-1.30256100	-1.17997400
C	-3.61871500	-0.42083200	1.17237400
H	-4.69002000	-0.36985300	0.99784900
C	1.13506900	-1.12303900	-0.33486600
C	-2.79379100	0.57947500	0.60782000
C	3.03167600	2.63919800	0.10873300
H	3.55390500	3.58909900	0.04384300
C	3.68761900	1.50339100	0.45926200
H	4.74242500	1.52390800	0.71686400
C	-1.16985200	2.68215500	-0.33354400
C	-0.39401200	3.83061200	-0.66403600
H	-0.90413500	4.72548600	-1.00818600
C	-2.59545900	2.73017200	-0.47279600
H	-3.03805800	3.61969800	-0.91219400
C	0.89545400	1.41342300	0.02167400
C	1.27042900	-3.58604600	-0.14289000
H	1.83254200	-4.44299900	0.21795700
C	0.95055000	3.82616900	-0.46630500
H	1.53927000	4.72664700	-0.61402000
C	-1.70855100	-1.41235400	2.23714600
H	-1.29042000	-2.15358000	2.91046200
C	-3.08676600	-1.41706100	1.95675400
H	-3.72948100	-2.17725200	2.38870800
Li	-2.04607000	-1.09563700	-2.86526000



[Li{(P)-(+)-1⁺}] $\theta = -2.5^\circ$ [u ω B97X-D/6-31g(d,p), PCM solvation in THF]

Atom type, (x,y,z) coordinates:

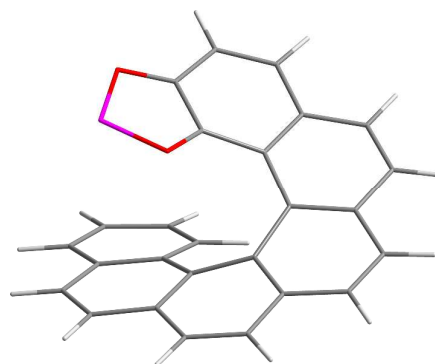
O	-0.49375700	-0.46685300	-1.83050100
O	-1.22058100	-3.03076000	-1.92180500
C	3.84883700	-0.27855800	0.72115400
H	4.84412800	-0.01001000	1.06291700
C	-1.46230000	0.27523900	0.78281800
C	3.48069800	-1.58522300	0.61220200
H	4.16672900	-2.37891200	0.89297600
C	1.60142500	0.45736100	0.03594600
C	0.75534300	-3.70210200	-0.78647600
H	0.51407400	-4.75098800	-0.92705700
C	1.14156400	2.85980200	-0.11631200
C	2.92987000	0.76621000	0.41643900
C	-0.80048900	1.39704800	0.13462000
C	-0.79916200	-0.60446700	1.67069900
H	0.23639800	-0.42188200	1.92514900
C	-3.61822300	1.07813600	-0.10356100
H	-4.68395900	0.92021300	-0.24257500
C	-0.14952500	-2.72601100	-1.30791700
C	2.22422900	-1.92985200	0.04606700
C	0.19896200	-1.29609200	-1.17269100
C	-3.49727800	-1.03865400	1.16632000
H	-4.56111100	-1.17589300	0.99225400
C	1.31991700	-0.91302800	-0.33154200
C	-2.85724400	0.08731000	0.59693600
C	2.52435500	3.12586100	0.11091000
H	2.87406700	4.15180200	0.04360700
C	3.36744800	2.12297000	0.46572600
H	4.40223500	2.32688800	0.72424200
C	-1.61753500	2.43622900	-0.34869600
C	-1.05176200	3.70131200	-0.67980300
H	-1.70863700	4.49260500	-1.02882600
C	-3.02881000	2.23457300	-0.49512700
H	-3.61687400	3.03204600	-0.94054900
C	0.63532100	1.54526500	0.02023600
C	1.90611500	-3.31189500	-0.17163000
H	2.61868400	-4.05442100	0.17679200
C	0.27196800	3.93024700	-0.47605900
H	0.69838800	4.91781500	-0.62463000
C	-1.44567500	-1.67978500	2.23708300
H	-0.90430200	-2.33523600	2.91136600
C	-2.80187300	-1.92410000	1.95640000
H	-3.30318900	-2.78167200	2.39306300
Li	-2.10633000	-1.37274500	-2.41424400



[Li{(P)-(+)-1⁺}] $d(\text{Li-O}) = 1.67 \text{ \AA}$ [u ω B97X-D/6-31g(d,p), PCM solvation in THF]

Atom type, (x,y,z) coordinates:

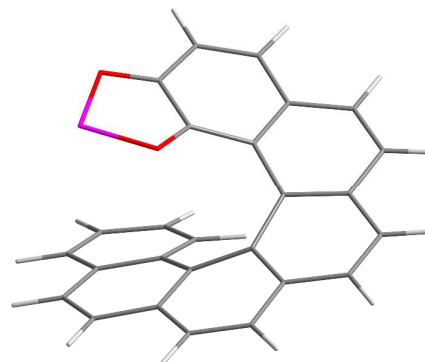
O	-0.63585800	-0.28070900	-1.82503500
O	-2.13723800	-2.48417800	-1.85356500
C	3.58756800	-1.44039900	0.68938100
H	4.62046600	-1.49186200	1.02063000
C	-1.31156500	0.70750700	0.77249300
C	2.83635900	-2.57191500	0.58296500
H	3.24884300	-3.53875200	0.85490700
C	1.66818000	-0.04550400	0.03063500
C	-0.43623500	-3.74550100	-0.75245700
H	-0.99850700	-4.66592600	-0.86935100
C	1.96368400	2.38270300	-0.09838700
C	3.03008100	-0.16244500	0.40092600
C	-0.33351200	1.58208200	0.14380700
C	-0.95722600	-0.34182700	1.65296500
H	0.08127400	-0.48003900	1.92404100
C	-3.11209800	2.13283300	-0.12491300
H	-4.17352600	2.30338800	-0.27981300
C	-0.99672900	-2.54115100	-1.26865200
C	1.52951800	-2.51027200	0.03211900
C	-0.20759400	-1.28608100	-1.16637300
C	-3.65214100	0.05821700	1.10499800
H	-4.70488300	0.24747600	0.91371800
C	0.98100700	-1.26298600	-0.33859000
C	-2.69522000	0.95025500	0.56704100
C	3.36265000	2.21094500	0.12209000
H	4.00781200	3.08259100	0.06537900
C	3.86196200	0.99498600	0.45916700
H	4.91054200	0.87043800	0.71180700
C	-0.79207800	2.82494800	-0.33200000
C	0.13393800	3.85989100	-0.64875300
H	-0.24863700	4.81670600	-0.99165800
C	-2.19637500	3.06240200	-0.49113600
H	-2.51018400	4.00425800	-0.93196400
C	1.07897600	1.28518800	0.02916900
C	0.79349200	-3.72672500	-0.16726300
H	1.24597300	-4.65113900	0.17999400
C	1.46390200	3.67152200	-0.44402300
H	2.17232800	4.48260100	-0.58328100
C	-1.90577100	-1.18354600	2.18929100
H	-1.59851200	-1.97918100	2.86006100
C	-3.26748600	-1.00743700	1.88490700
H	-4.01019400	-1.68402500	2.29477900
Li	-2.14058400	-0.86119400	-2.23896000



[Li{(P)-(+)-1⁺}] $d(\text{Li-O}) = 1.79 \text{ \AA}$ [u ω B97X-D/6-31g(d,p), PCM solvation in THF]

Atom type, (x,y,z) coordinates:

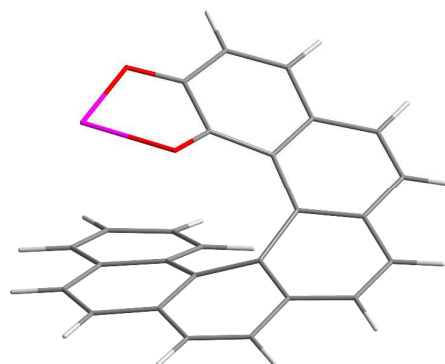
O	-0.61783000	-0.26030000	-1.84771600
O	-2.19245600	-2.41203300	-1.87661300
C	3.54665900	-1.53647900	0.68868100
H	4.57726100	-1.61754700	1.02129900
C	-1.28519500	0.73105500	0.78073900
C	2.76192100	-2.64536600	0.58385600
H	3.14545500	-3.62340100	0.85891200
C	1.66864900	-0.09031300	0.02576500
C	-0.54479000	-3.71807100	-0.75703000
H	-1.13594800	-4.62051100	-0.87403700
C	2.02369200	2.33017400	-0.09884200
C	3.02579500	-0.24301300	0.39820600
C	-0.29125000	1.58299000	0.14607600
C	-0.95009300	-0.32365800	1.66251300
H	0.08629200	-0.48411900	1.92904400
C	-3.05690400	2.19742700	-0.10682300
H	-4.11513800	2.39260300	-0.25514100
C	-1.06561900	-2.49653700	-1.28130100
C	1.45745100	-2.54774300	0.03063800
C	-0.23883400	-1.27274300	-1.18033100
C	-3.63836900	0.13793600	1.12997400
H	-4.68761100	0.35111100	0.94442900
C	0.94739500	-1.28638800	-0.34572600
C	-2.66380600	1.00578800	0.58419300
C	3.41805000	2.12245500	0.12049600
H	4.08581700	2.97699800	0.06442400
C	3.88625300	0.89341200	0.45662500
H	4.93157100	0.74278100	0.70894900
C	-0.72264900	2.83673400	-0.32611300
C	0.22695800	3.85027000	-0.64356400
H	-0.13393500	4.81659200	-0.98356500
C	-2.12204700	3.10591900	-0.47871200
H	-2.41649800	4.05498100	-0.91755300
C	1.11350600	1.25420800	0.02724100
C	0.68271300	-3.74004900	-0.16701200
H	1.10348400	-4.67820900	0.18370600
C	1.55282600	3.63093600	-0.44155000
H	2.27910900	4.42618800	-0.58058500
C	-1.91482400	-1.14052100	2.20788100
H	-1.62207700	-1.94077900	2.87965100
C	-3.27391300	-0.93381500	1.91101300
H	-4.02954200	-1.59167600	2.32773900
Li	-2.28246800	-0.68466500	-2.35800000



[Li{(P)-(+)-1⁻}] $d(\text{Li-O}) = 2.08 \text{ \AA}$ [ω B97X-D/6-31g(d,p), PCM solvation in THF]

Atom type, (x,y,z) coordinates:

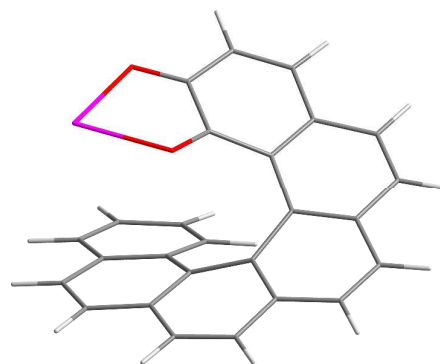
O	-0.59576100	-0.35438900	-1.81244800
O	-1.83355700	-2.71605000	-1.83812800
C	3.74006900	-1.02645400	0.67761400
H	4.77209700	-0.95776300	1.00885900
C	-1.37088900	0.54463200	0.78120600
C	3.12395400	-2.23543000	0.56398000
H	3.64500300	-3.15042300	0.83072400
C	1.67043100	0.13657000	0.02247500
C	0.00367300	-3.76804100	-0.76963600
H	-0.45075700	-4.74631800	-0.89238500
C	1.68353100	2.58554200	-0.10118100
C	3.03663800	0.17927000	0.39321000
C	-0.50398900	1.52316100	0.14254600
C	-0.89271600	-0.45136200	1.66499600
H	0.15768200	-0.47277100	1.92334500
C	-3.32970000	1.75255500	-0.10445300
H	-4.40570300	1.80447300	-0.24544900
C	-0.70368200	-2.62981800	-1.27235800
C	1.81649900	-2.32564300	0.01575400
C	-0.06614700	-1.30273300	-1.17192100
C	-3.62217600	-0.35688800	1.14671000
H	-4.69181900	-0.28337600	0.96921700
C	1.12332300	-1.14988100	-0.34942400
C	-2.77462100	0.62810000	0.58804800
C	3.09273600	2.57708300	0.11943500
H	3.63234700	3.51778100	0.06309500
C	3.72785100	1.42518700	0.45453200
H	4.78401600	1.42241500	0.70754000
C	-1.10493600	2.70459000	-0.33121700
C	-0.30638300	3.84058200	-0.65005300
H	-0.79762400	4.74708800	-0.99111300
C	-2.52821700	2.77893900	-0.48219200
H	-2.95113100	3.67891800	-0.91975100
C	0.93351700	1.39153100	0.02424500
C	1.22600500	-3.61674300	-0.18868900
H	1.78398000	-4.48678200	0.14673700
C	1.03660800	3.80777200	-0.44592900
H	1.64430000	4.69694900	-0.58503300
C	-1.73719400	-1.38614900	2.22103200
H	-1.33699800	-2.13719600	2.89428100
C	-3.11347800	-1.36404800	1.93325300
H	-3.77326200	-2.11147100	2.36171200
Li	-2.51394300	-0.84398400	-2.45302700



[Li{(P)-(+)-1⁺}] $d(\text{Li-O}) = 2.24 \text{ \AA}$ [$\omega\text{B97X-D/6-31g(d,p)}$, PCM solvation in THF]

Atom type, (x,y,z) coordinates:

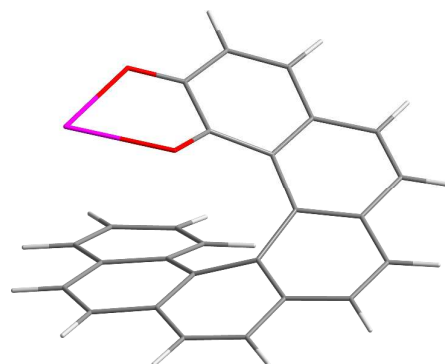
O	-0.57761000	-0.36035300	-1.81980900
O	-1.78599600	-2.73730300	-1.83216800
C	3.76334600	-0.95778400	0.67283500
H	4.79360600	-0.87027100	1.00529600
C	-1.37691300	0.51172000	0.78474000
C	3.17008300	-2.17796600	0.55555900
H	3.70833400	-3.08348400	0.82108200
C	1.67231800	0.16594300	0.01851400
C	0.07274600	-3.76146700	-0.77600300
H	-0.36699100	-4.74685800	-0.89726400
C	1.63414400	2.61487400	-0.09840200
C	3.03680200	0.23537600	0.39125600
C	-0.53113200	1.50663900	0.14279600
C	-0.87573900	-0.47560000	1.66562400
H	0.17653500	-0.47830300	1.91693100
C	-3.36208100	1.68179400	-0.09278600
H	-4.43968500	1.71393500	-0.22843900
C	-0.65685900	-2.63401300	-1.27591000
C	1.86450400	-2.29269300	0.00670900
C	-0.03587500	-1.29952100	-1.18319100
C	-3.60986100	-0.42909900	1.16589400
H	-4.68182800	-0.37469700	0.99522900
C	1.15032000	-1.12923200	-0.35788700
C	-2.78348000	0.57004600	0.60082800
C	3.04300500	2.63495500	0.12344200
H	3.56348900	3.58652300	0.06936400
C	3.70156800	1.49532100	0.45652200
H	4.75741900	1.51443900	0.71040600
C	-1.15647100	2.67629300	-0.32874700
C	-0.38146500	3.82887600	-0.64692800
H	-0.89129600	4.72563400	-0.98658100
C	-2.58134000	2.72238200	-0.47608400
H	-3.02293200	3.61360400	-0.91325200
C	0.90941800	1.40517900	0.02358600
C	1.29488700	-3.59260300	-0.19847300
H	1.86769400	-4.45441900	0.13364100
C	0.96177100	3.82385300	-0.44205900
H	1.55054500	4.72593000	-0.57973000
C	-1.70004000	-1.42437600	2.22816900
H	-1.28218700	-2.16813000	2.89879100
C	-3.07848800	-1.42633100	1.95005000
H	-3.72218600	-2.18467600	2.38377300
Li	-2.65755700	-0.79112500	-2.52458500



[Li{(P)-(+)-1⁺}] $d(\text{Li-O}) = 2.40 \text{ \AA}$ [ω B97X-D/6-31g(d,p), PCM solvation in THF]

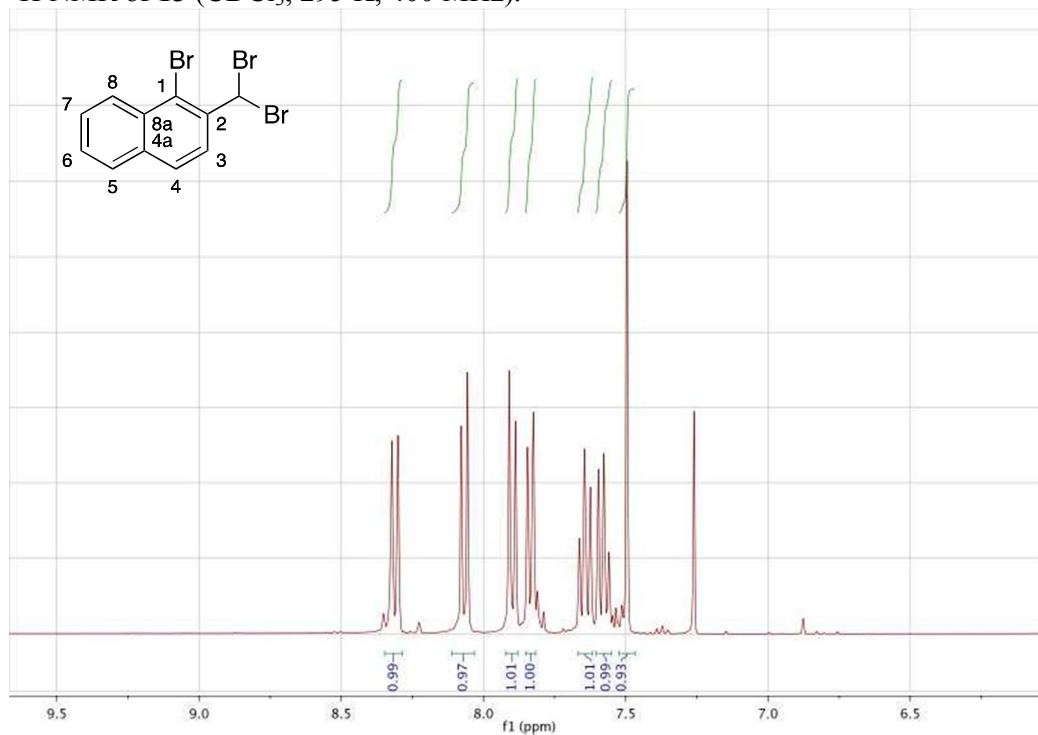
Atom type, (x,y,z) coordinates:

O	-0.56906800	-0.36424700	-1.82686600
O	-1.76908100	-2.74546300	-1.83010300
C	3.77332400	-0.93412300	0.66643400
H	4.80343900	-0.84009600	0.99769000
C	-1.37505900	0.49775200	0.78723000
C	3.18691400	-2.15779900	0.55068700
H	3.73096500	-3.05988300	0.81658000
C	1.67451700	0.17560100	0.01341200
C	0.09520900	-3.75865100	-0.77465700
H	-0.33991900	-4.74655500	-0.89377400
C	1.61807900	2.62462200	-0.09994300
C	3.03871200	0.25459700	0.38526000
C	-0.53855600	1.49985800	0.14416300
C	-0.86391900	-0.48778500	1.66444900
H	0.18928600	-0.48378700	1.91154400
C	-3.37241200	1.65919600	-0.07308300
H	-4.45129300	1.68651800	-0.20018600
C	-0.64236800	-2.63560200	-1.27652600
C	1.88111900	-2.28155500	0.00367800
C	-0.02577200	-1.29821500	-1.18917100
C	-3.60022100	-0.45804600	1.17730700
H	-4.67341300	-0.40977700	1.01214200
C	1.15996800	-1.12250800	-0.36272800
C	-2.78290700	0.54769300	0.61071700
C	3.02710700	2.65469000	0.11904700
H	3.54081600	3.60995200	0.06481900
C	3.69434600	1.51923500	0.45000400
H	4.75052500	1.54598000	0.70207600
C	-1.17390000	2.66692600	-0.32064200
C	-0.40805800	3.82562200	-0.63925700
H	-0.92540600	4.71985600	-0.97428000
C	-2.59998700	2.70544300	-0.45832200
H	-3.04955400	3.59623600	-0.88829100
C	0.90272400	1.40921400	0.02095200
C	1.31772900	-3.58405800	-0.19876100
H	1.89524300	-4.44297400	0.13313500
C	0.93590800	3.82938400	-0.43947900
H	1.51776200	4.73595700	-0.57731600
C	-1.67954100	-1.44265800	2.22928400
H	-1.25379900	-2.18467700	2.89686400
C	-3.05905400	-1.45348600	1.95690800
H	-3.69584200	-2.21688400	2.39200700
Li	-2.81234200	-0.72142300	-2.60634400

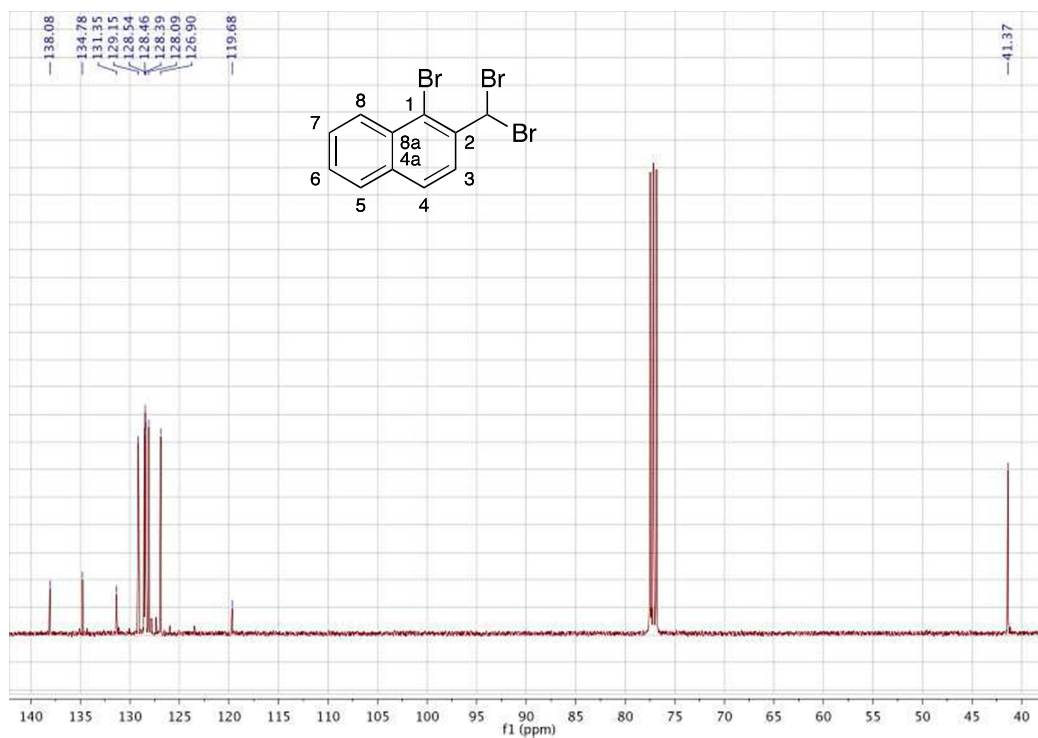


7SI NMR Spectra of New Compounds

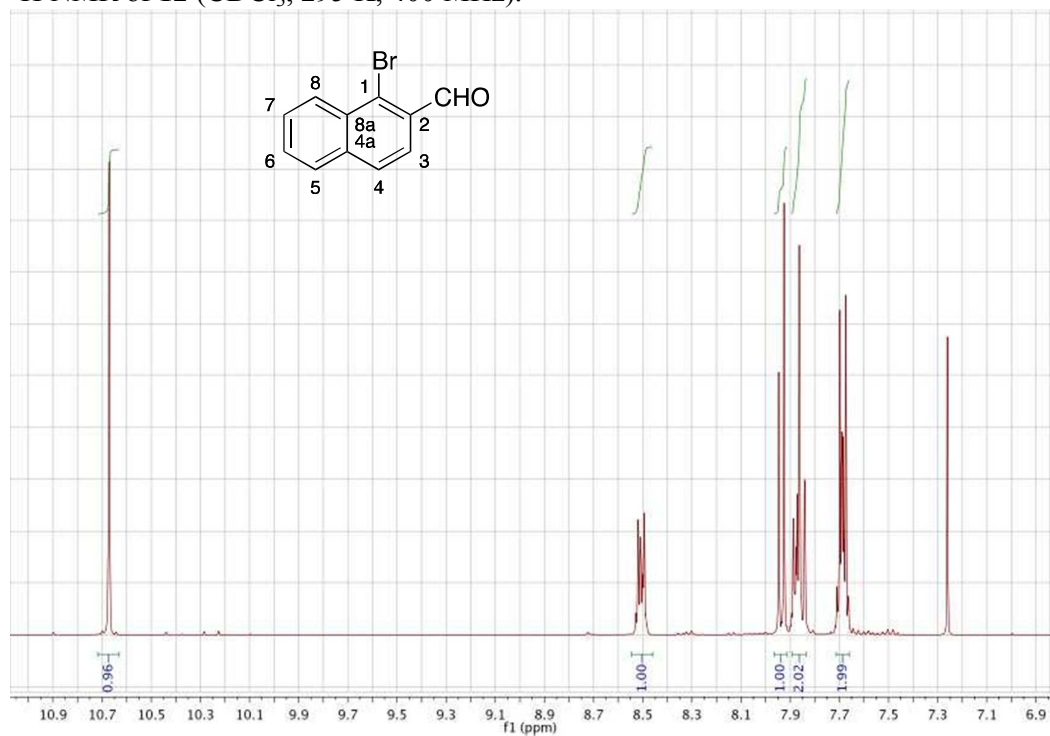
^1H NMR of **13** (CDCl_3 , 295 K, 400 MHz).



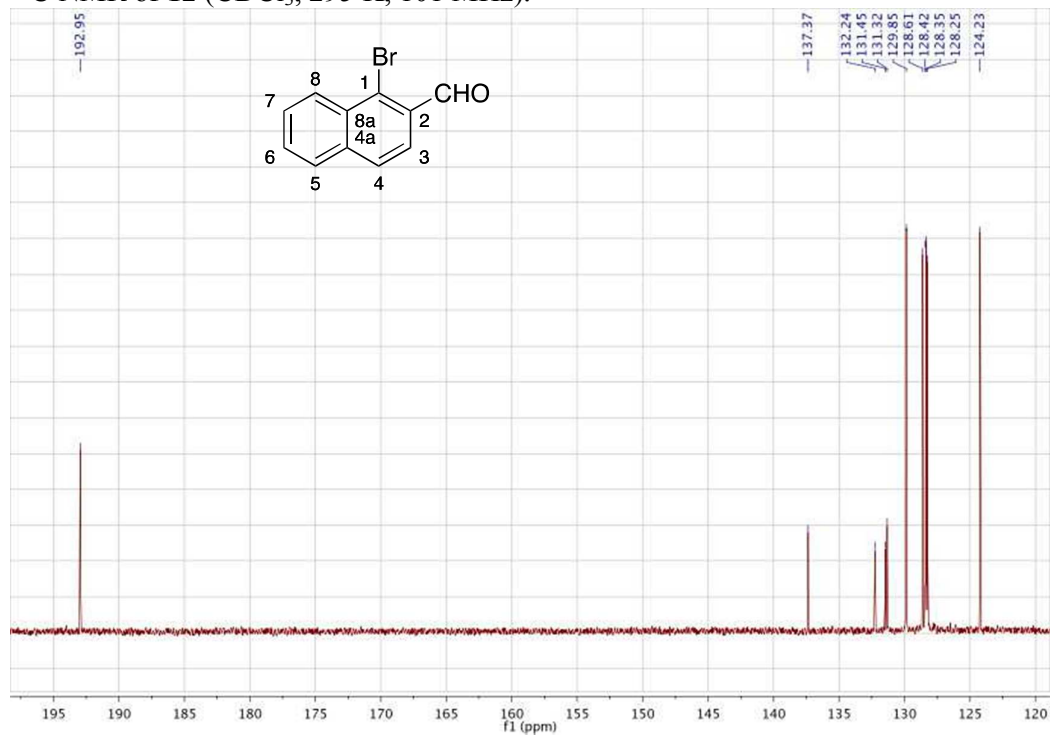
^{13}C NMR of **13** (CDCl_3 , 295 K, 101 MHz).



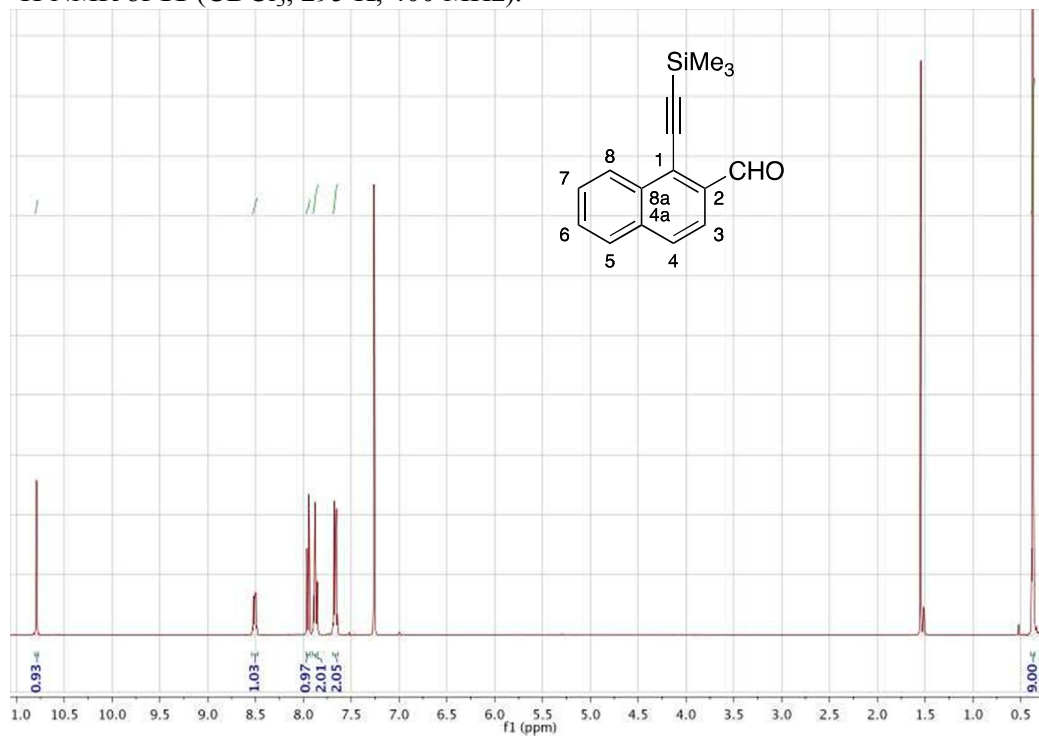
^1H NMR of **12** (CDCl_3 , 295 K, 400 MHz).



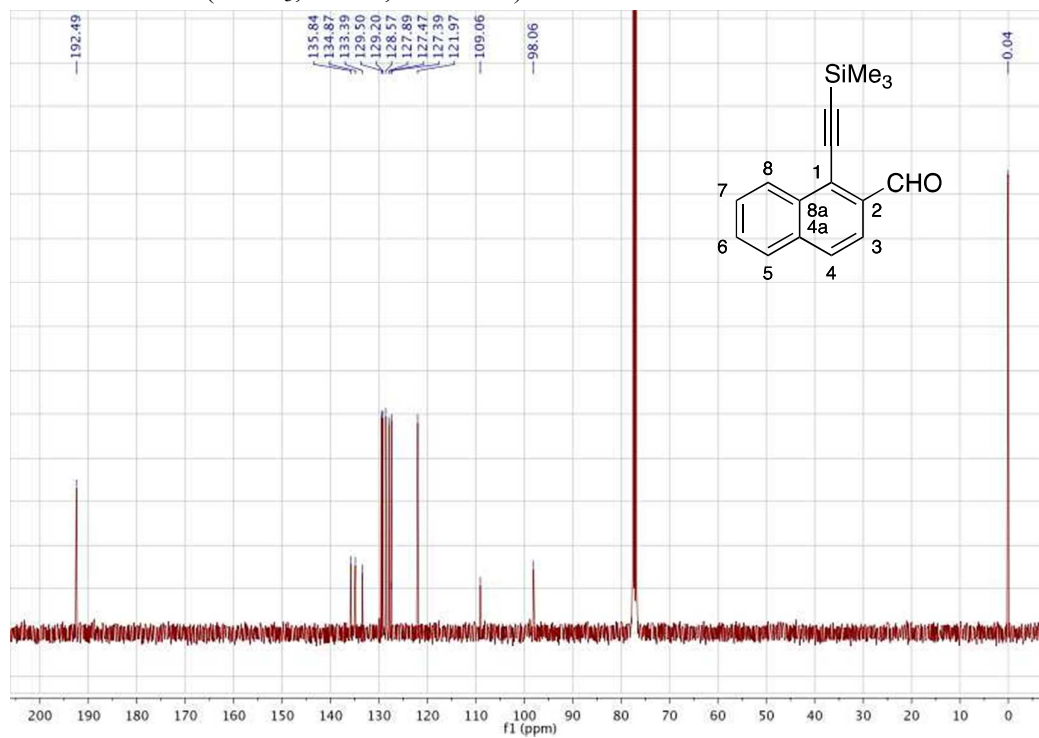
^{13}C NMR of **12** (CDCl_3 , 295 K, 101 MHz).



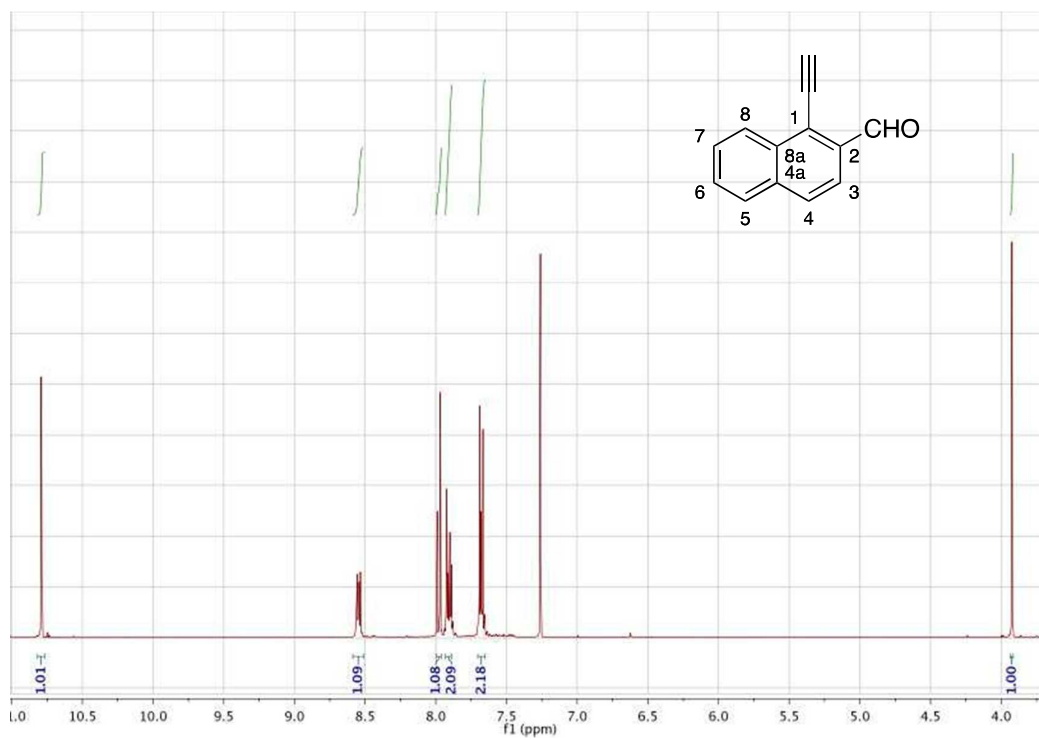
^1H NMR of **11** (CDCl_3 , 295 K, 400 MHz).



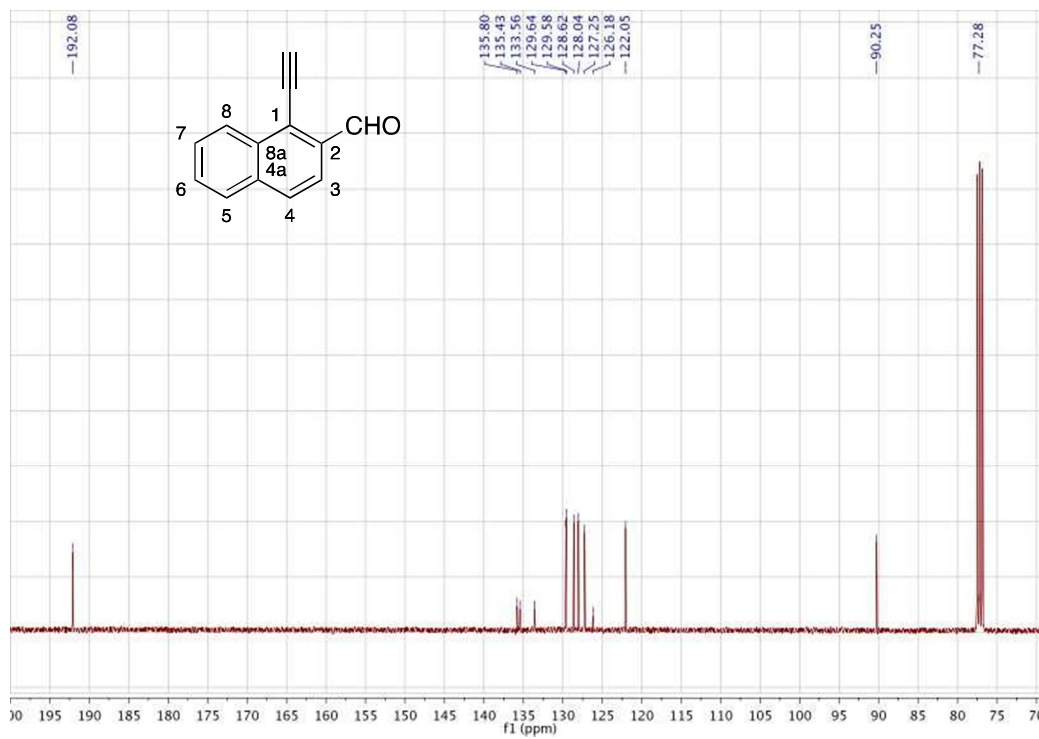
^{13}C NMR of **11** (CDCl_3 , 295 K, 101 MHz).



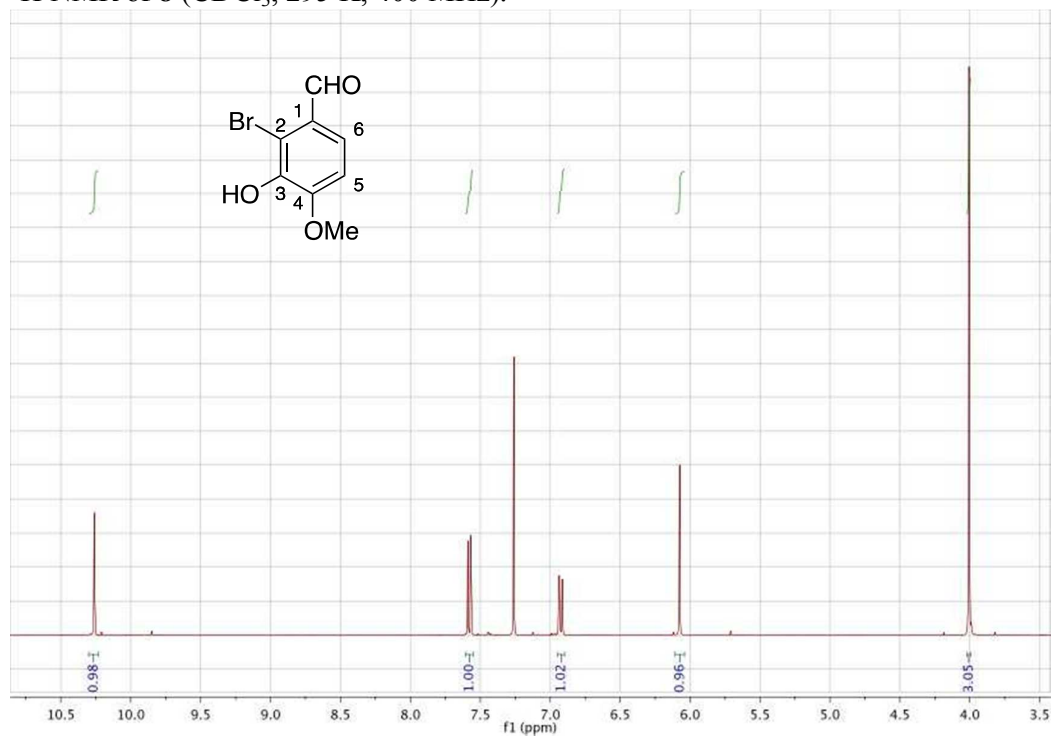
^1H NMR of **10** (CDCl_3 , 295 K, 400 MHz).



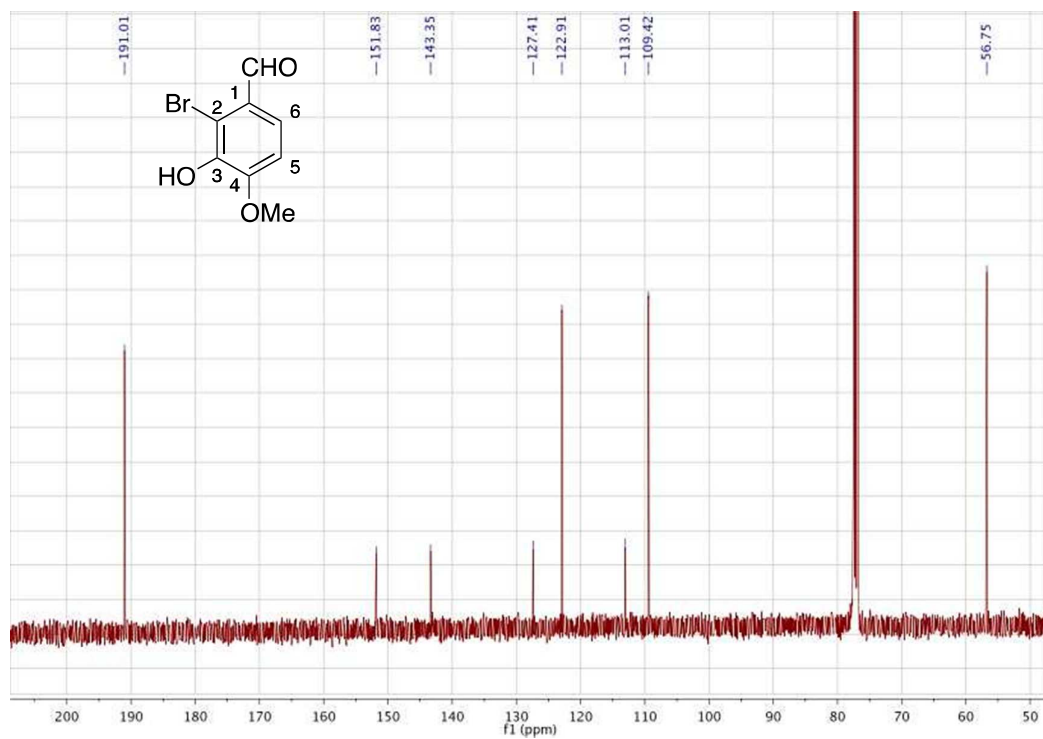
^{13}C NMR of **10** (CDCl_3 , 295 K, 101 MHz).



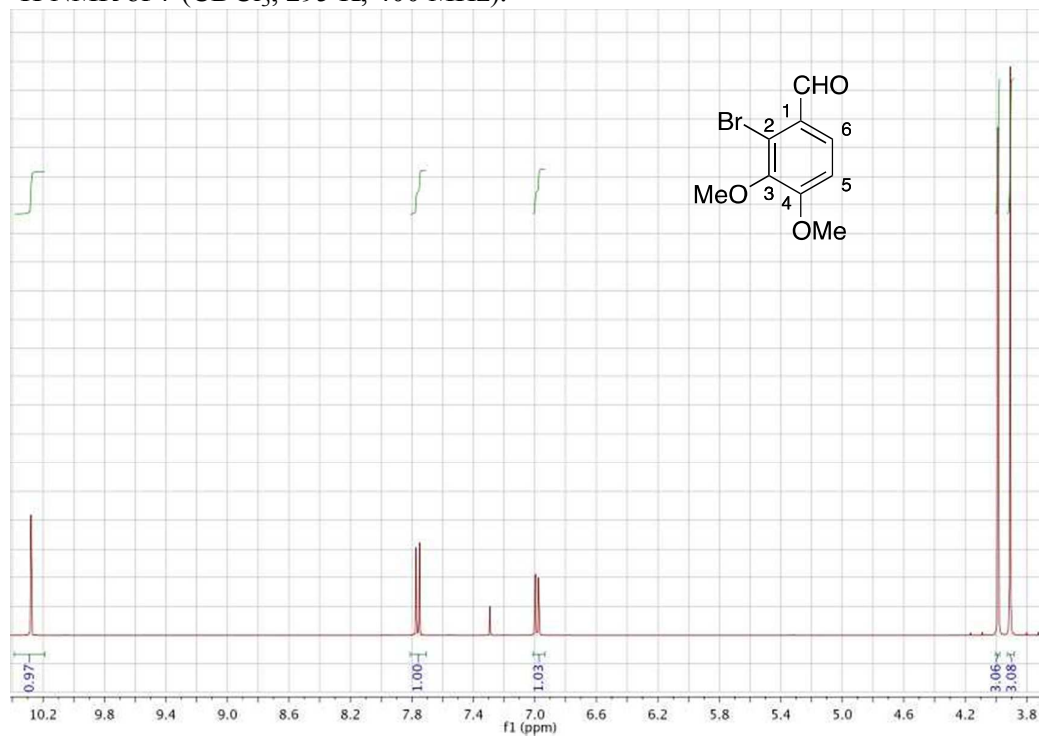
^1H NMR of **8** (CDCl_3 , 295 K, 400 MHz).



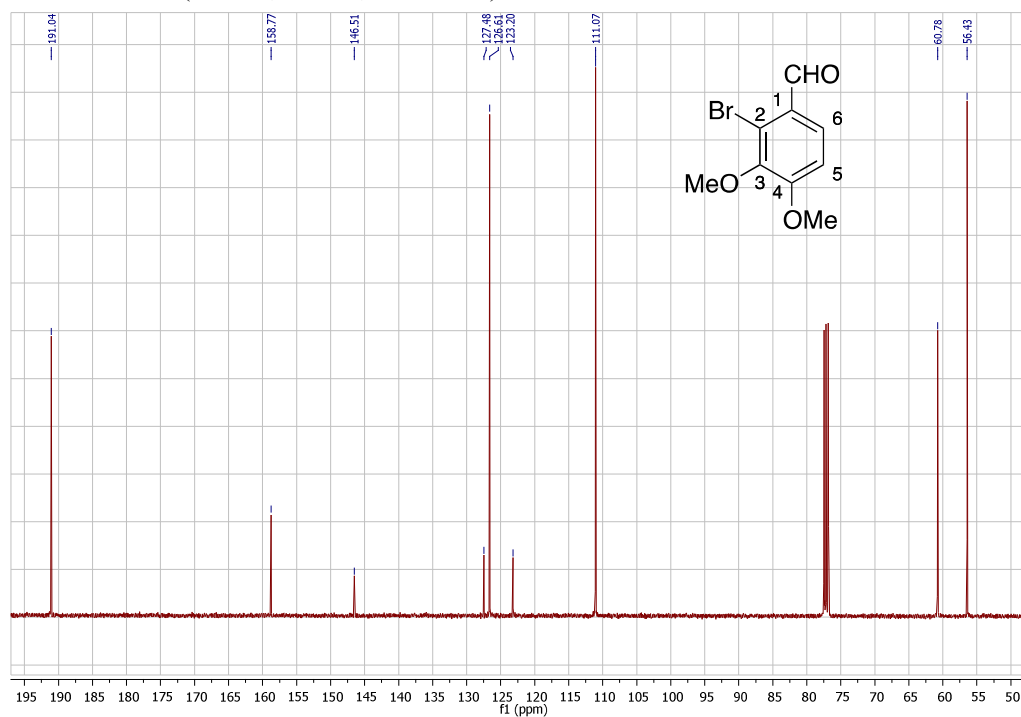
^{13}C NMR of **8** (CDCl_3 , 295 K, 101 MHz).



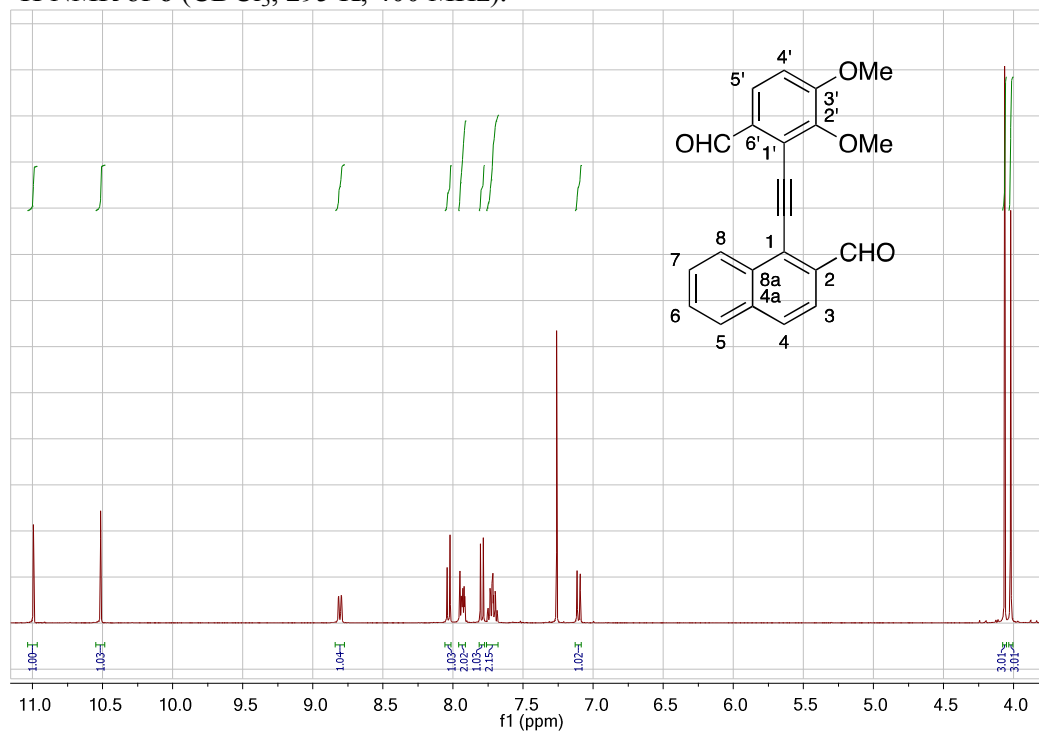
^1H NMR of **7** (CDCl_3 , 295 K, 400 MHz).



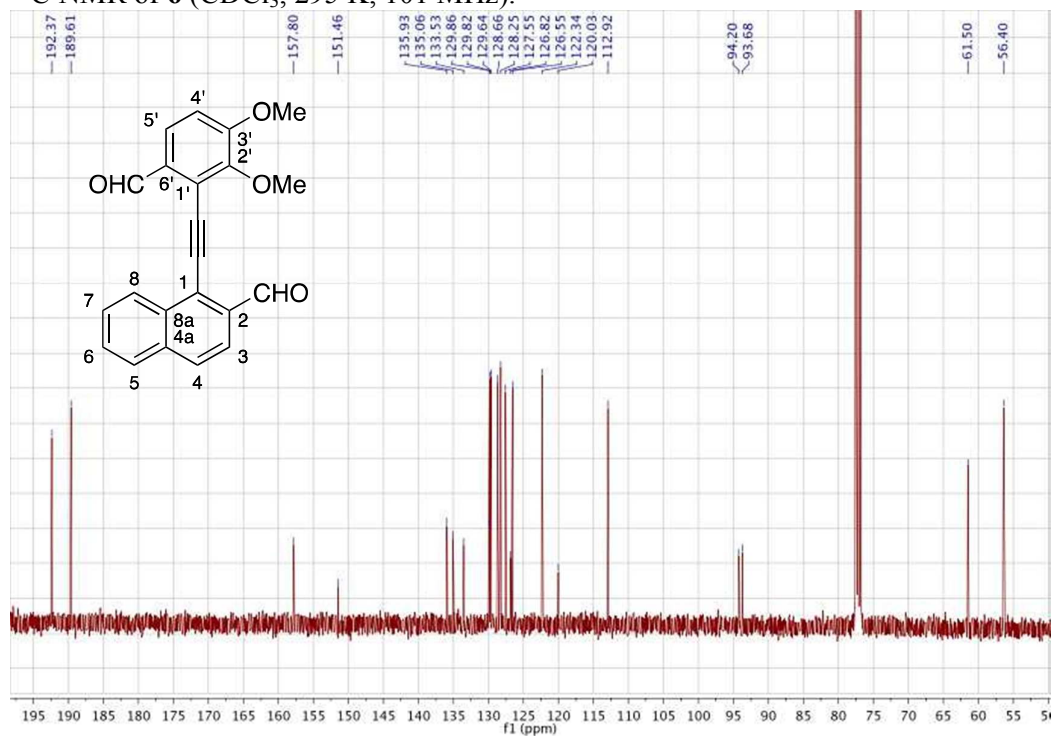
^{13}C NMR of **7** (CDCl_3 , 295 K, 101 MHz).



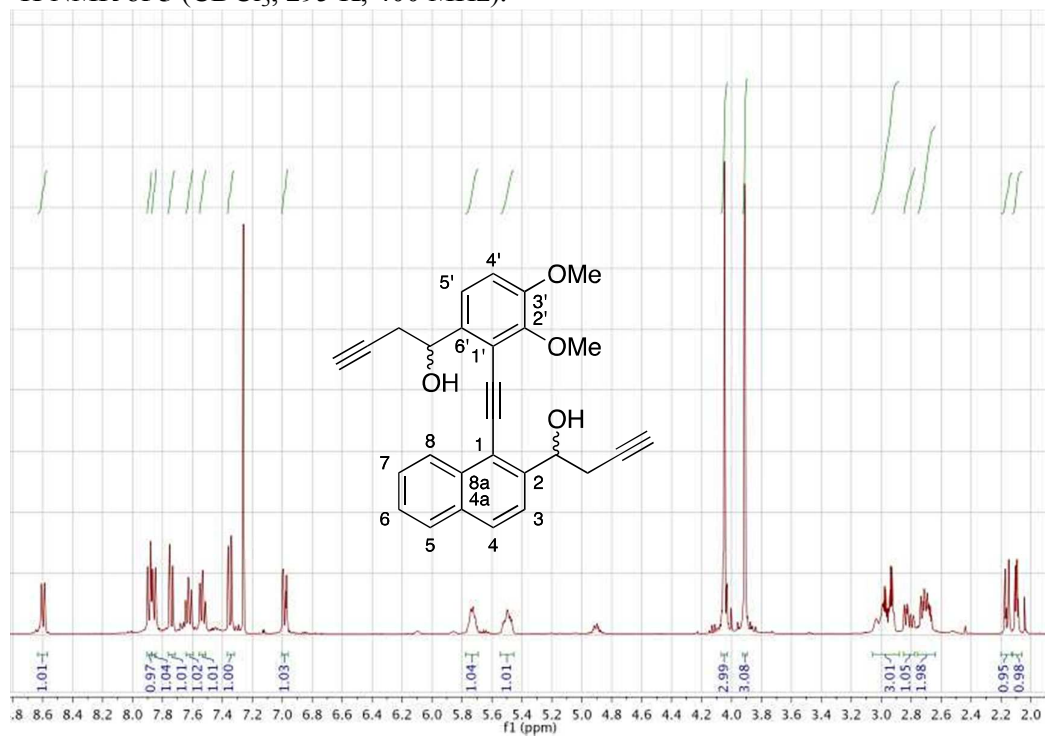
^1H NMR of **6** (CDCl_3 , 295 K, 400 MHz).



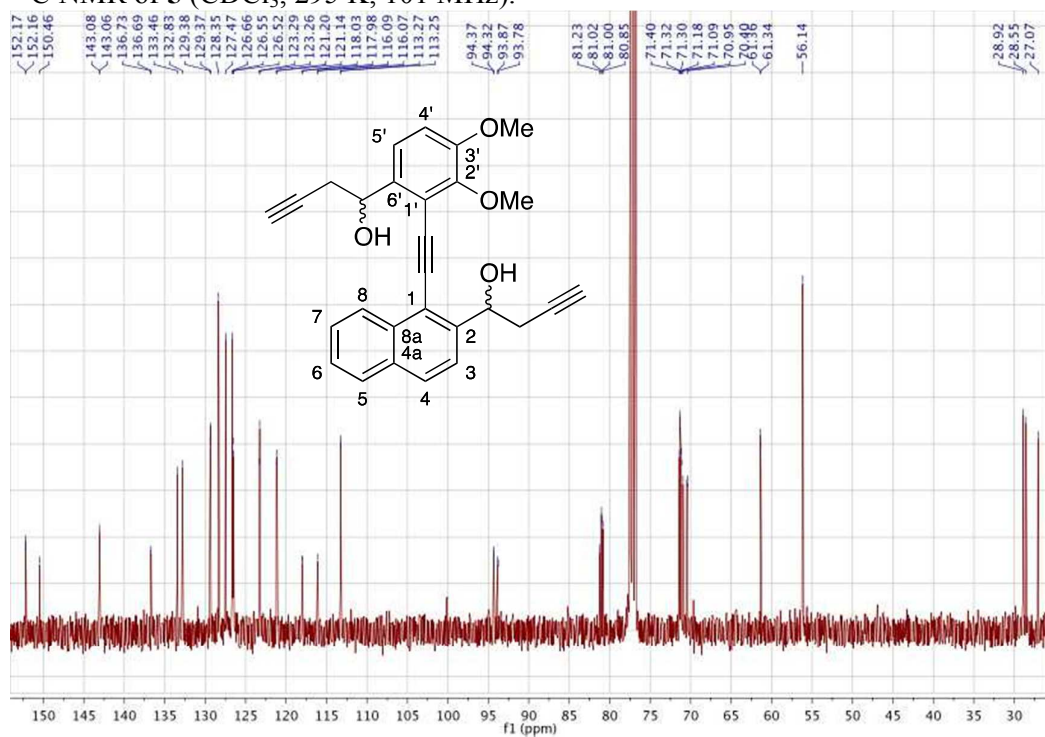
^{13}C NMR of **6** (CDCl_3 , 295 K, 101 MHz).



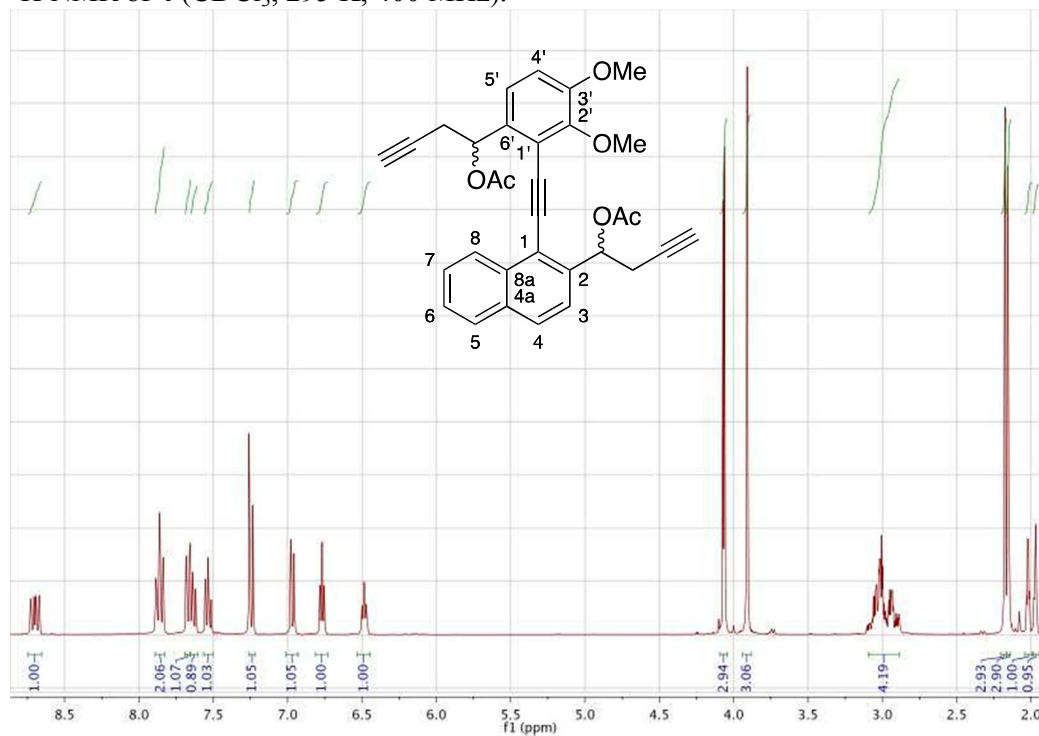
^1H NMR of **5** (CDCl_3 , 295 K, 400 MHz).



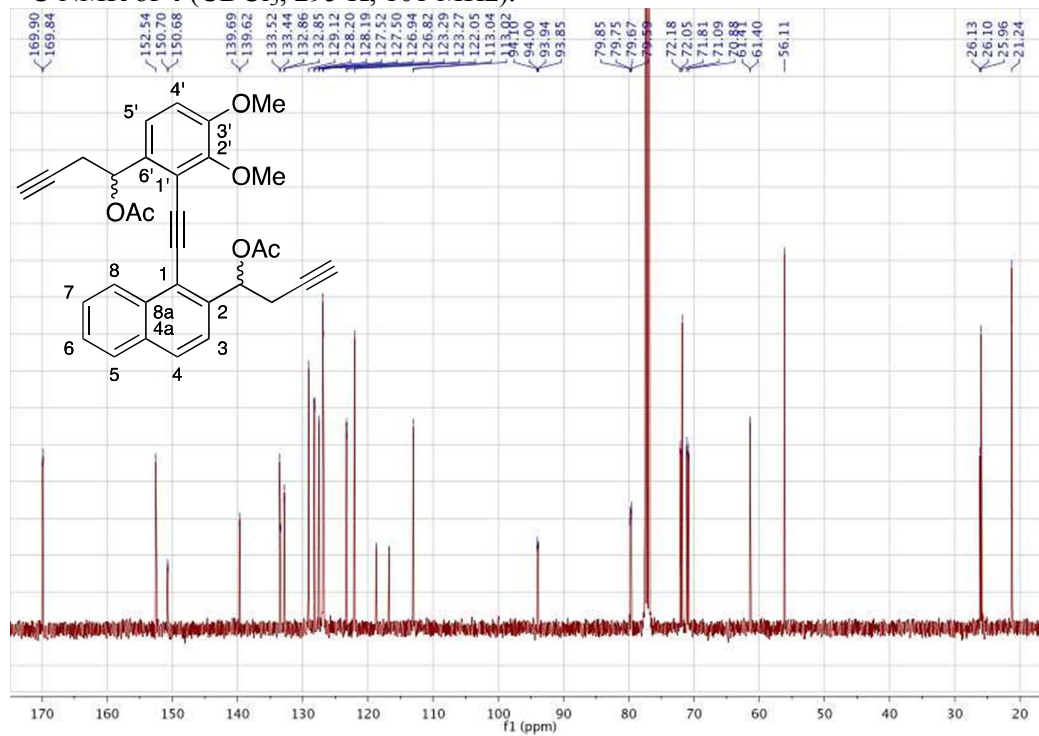
^{13}C NMR of **5** (CDCl_3 , 295 K, 101 MHz).



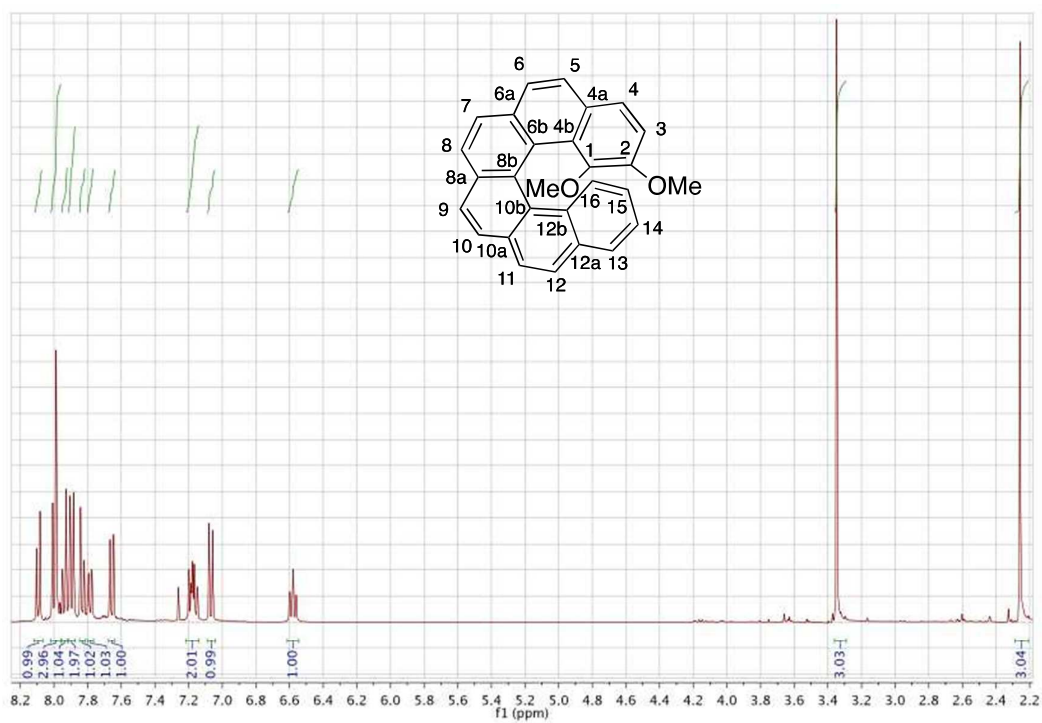
^1H NMR of **4** (CDCl_3 , 295 K, 400 MHz).



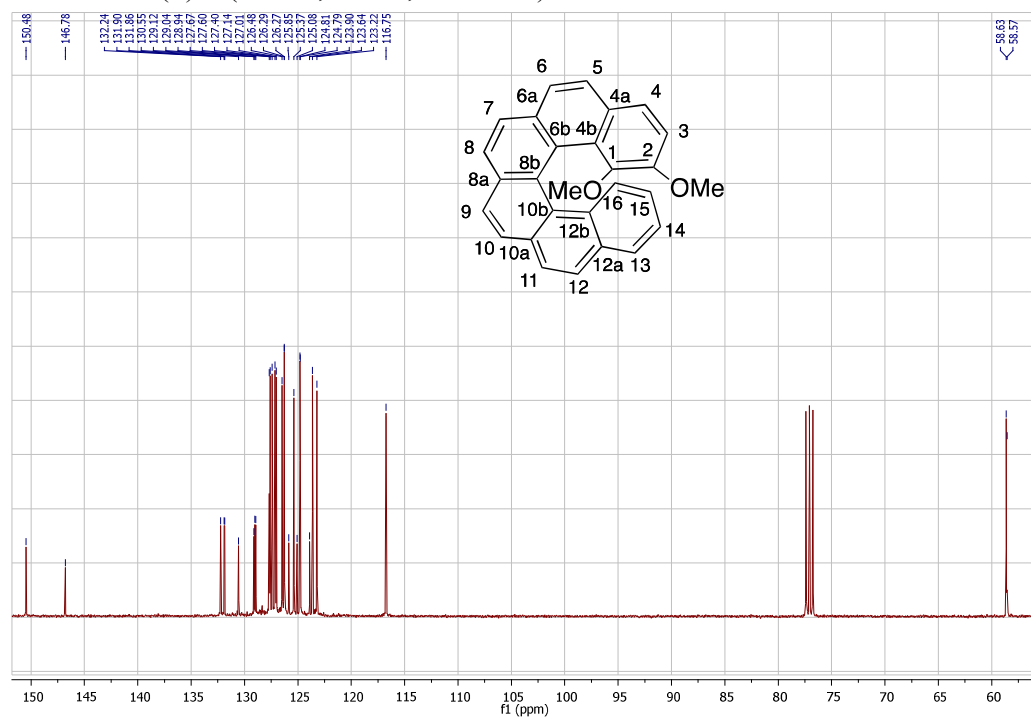
^{13}C NMR of **4** (CDCl_3 , 295 K, 101 MHz).



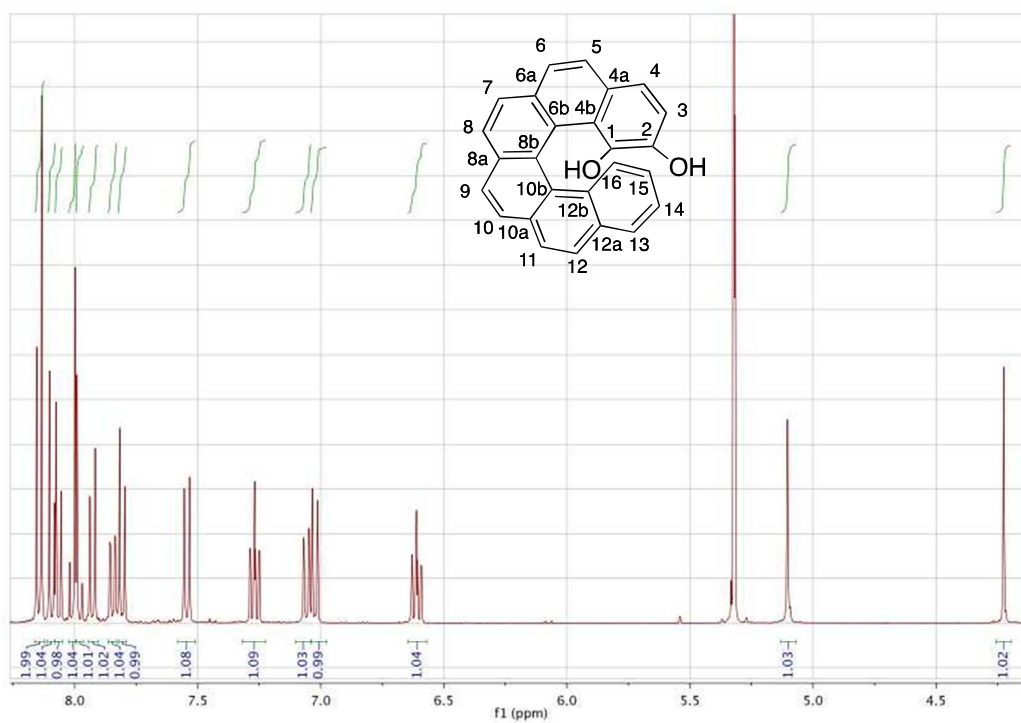
^1H NMR of (\pm)-**3** (CDCl_3 , 295 K, 400 MHz).



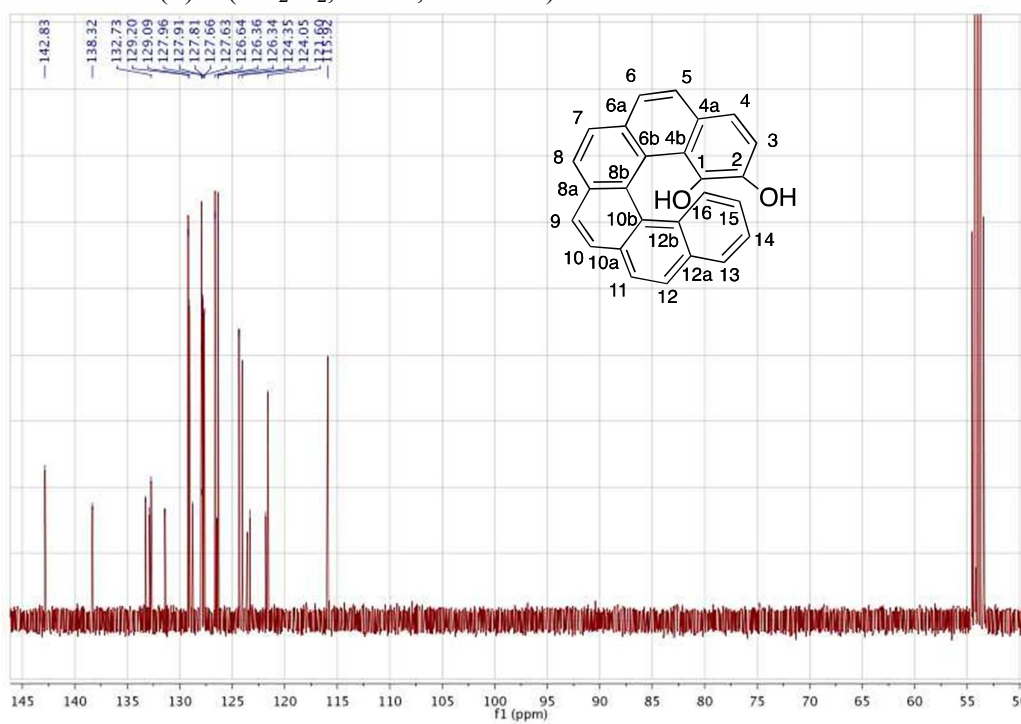
^{13}C NMR of (\pm)-**3** (CDCl_3 , 295 K, 101 MHz).



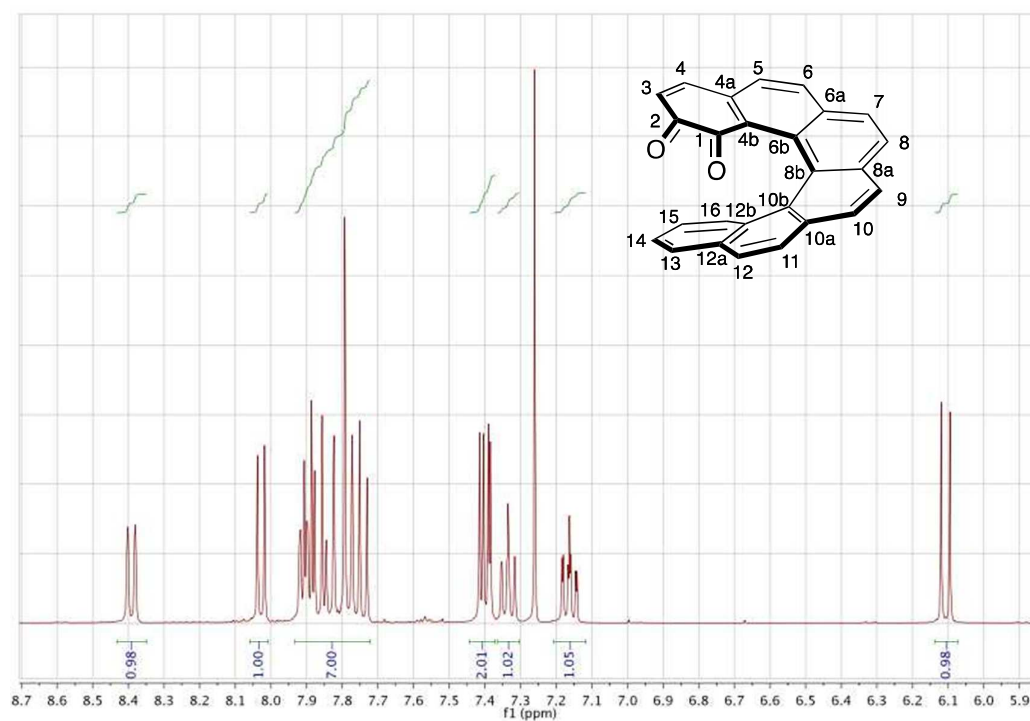
^1H NMR of (\pm)-**2** (CD_2Cl_2 , 295 K, 400 MHz).



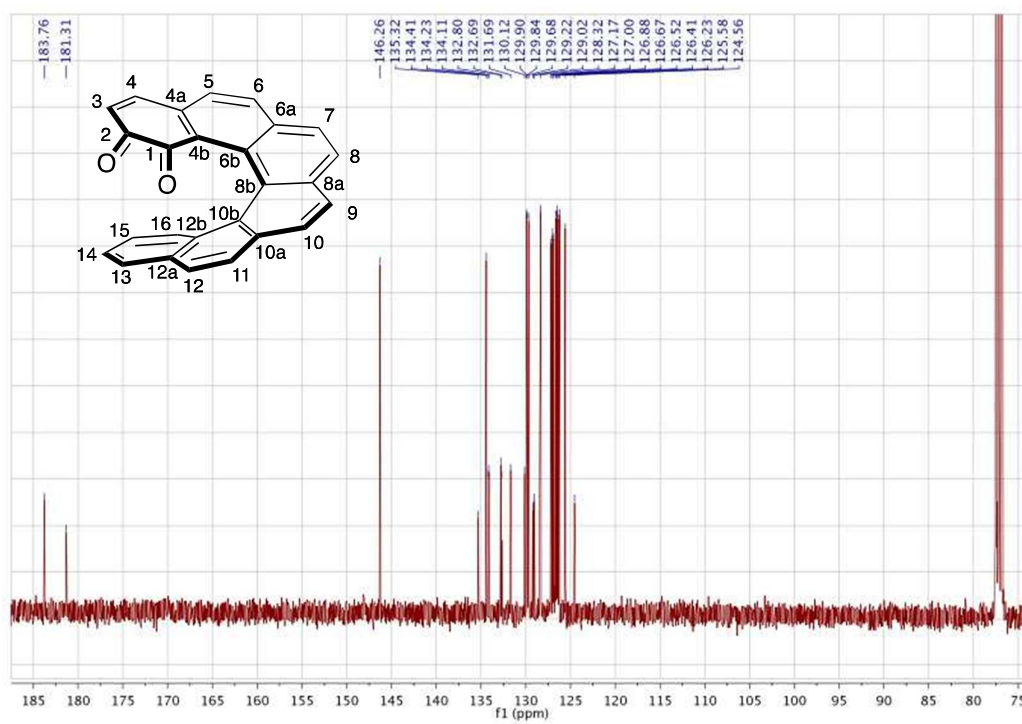
^{13}C NMR of (\pm)-**2** (CD_2Cl_2 , 295 K, 101 MHz).



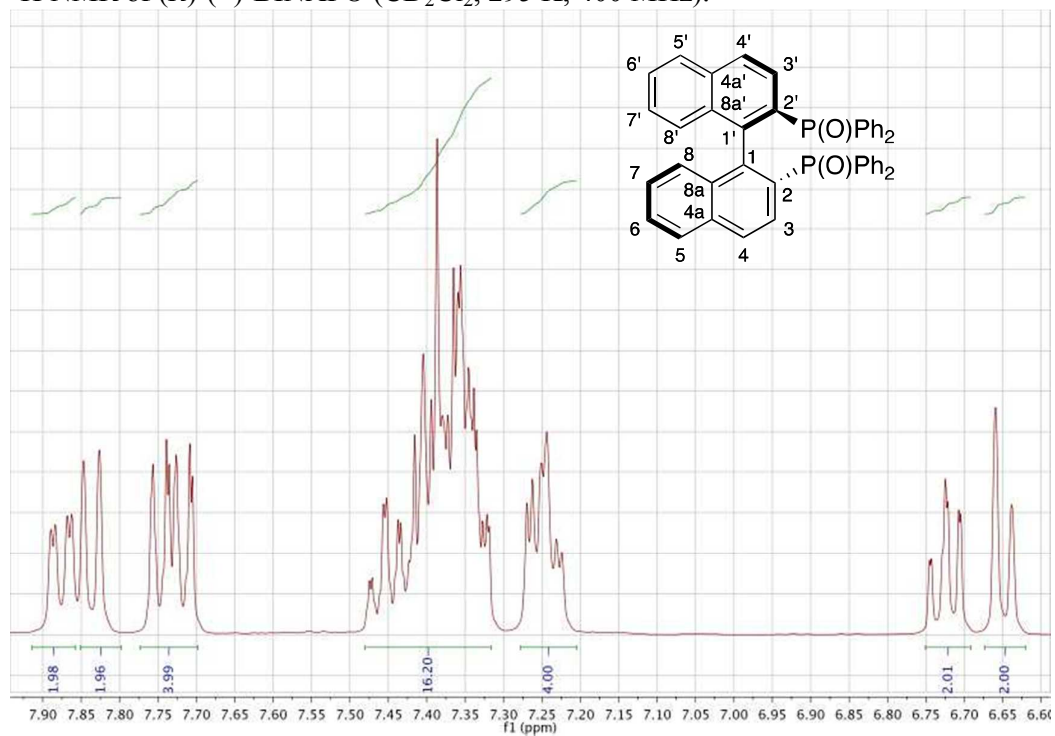
^1H NMR of (*P*)-(+)-1 (CDCl_3 , 295 K, 400 MHz).



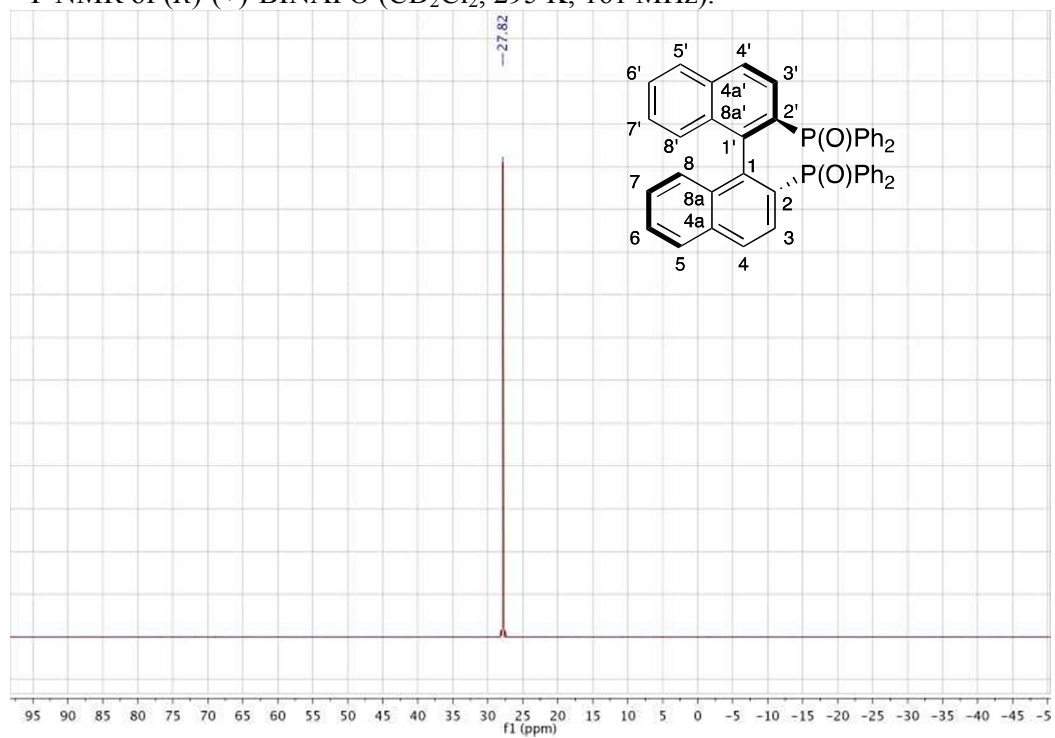
^{13}C NMR of (*P*)-(+)-1 (CDCl_3 , 295 K, 101 MHz).



^1H NMR of (*R*)-(+)-BINAPO (CD_2Cl_2 , 295 K, 400 MHz).



^{31}P NMR of (*R*)-(+)-BINAPO (CD_2Cl_2 , 295 K, 161 MHz).



8SI References

- (1) Vautravers, N. R.; Regent, D. D.; Breit, B. *Chem. Commun.* **2011**, 47, 6635–6637.
- (2) Demir, A. S.; Reis, Ö. *Tetrahedron* **2004**, 60, 3803–3811.
- (3) Zi, W.; Toste, F. D. *J. Am. Chem. Soc.* **2013**, 135, 12600–12603.
- (4) Toth, J. E.; Hamann, P. R.; Fuchs, P. L. *J. Org. Chem.* **1988**, 53, 4694–4708.
- (5) Singidi, R. R.; RajanBabu, T. V. *Org. Lett.* **2008**, 10, 3351–3354.
- (6) Berthod, M.; Saluzzo, C.; Mignani, G.; Lemaire, M. *Tetrahedron: Asymmetry* **2004**, 15, 639–645.
- (7) Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112–122.
- (8) Sheldrick, G. M. *SADABS. Program for Absorption Correction*. University of Göttingen, Germany, 1996.
- (9) De Rango, C.; Tsoucaris, G.; Delerq, J. P.; Germain, G.; Putzeys, J. P. *Cryst. Struct. Commun.* **1973**, 2, 189–192.
- (10) Stoll, S.; Schweiger, A. *J. Magn. Res.* **2006**, 178, 42–55.
- (11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.1*; Gaussian, Inc.: Wallingford, CT, 2009.
- (12) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, 10, 6615–6620.
- (13) Rulišek, L.; Exner, O.; Cwiklik, L.; Jungwirth, P.; Starý, I.; Pospíšil, L.; Havlas, Z. *J. Phys. Chem. C* **2007**, 111, 14948–14955.
- (14) Roose, J.; Achermann, S.; Dumele, O.; Diederich, F. *Eur. J. Org. Chem.* **2013**, 3223–3231.
- (15) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, 393, 51–57.

(16) (a) Pascual-Ahuir, J. L.; Silla, E.; Tuñon, I. *J. Comp. Chem.* **1994**, *15*, 1127–1138; (b) Tomasi, J.; Mennucci, B.; Cancès, E. *J. Mol. Struct.* **1999**, *464*, 211–226.