Supporting Information

Transformation from triple helicene to double helicene embedding adjacent stereogenic carbon atoms and axial stereogenicity

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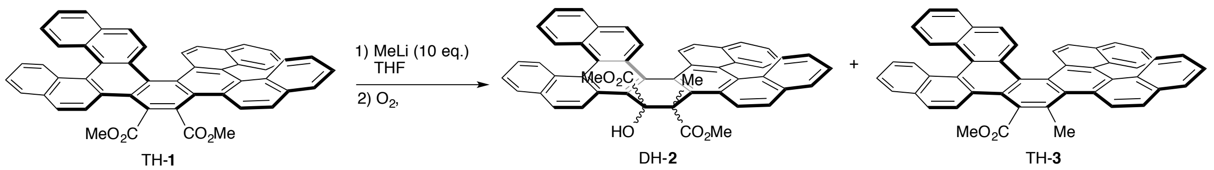
1. Experimental Details.

General.

Triple Helicene (TH-**1**),[S1] dimethyl [5]helicene-7,8-dicarboxylate (**5**),[S2] dimethyl phenanthrene-9,10-dicarboxylate (**9**)[S3] were prepared according to the reported procedure. All the other chemicals were obtained from commercial sources and used without further purification unless otherwise noted.

Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS400 (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) or a JEOL EXZ500 (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) spectrometer with Me_4Si as a standard. Fast atom bombardment (FAB)-MS spectra were measured on a JEOL JMS-700 spectrometer.

Synthesis of Double Helicene (DH-2) and Triple Helicene (TH-3). (Table 1)



A solution of triple helicene (TH-**1**, 50 mg, 72 μmol) in THF (6 mL) was added dropwise MeLi (1.2 M in ether, 0.60 mL, 0.72 mmol) at 0 °C under N_2 atmosphere. The mixture was stirred for 30 min at 0 °C (and slowly warmed to 80 °C (for entry 1) or 60 °C (for entry 2)). Then, O_2 (excess) was added to the mixture with bubbling. After stirring for 15 min, the resulting mixture was poured into sat. NH_4Cl *aq*, and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtered, and then evaporated under reduced pressure.

Reaction temperature at 80 ℃ (entry 1)

The crude mixture was purified by preparative thin-layer chromatography with CH_2Cl_2/hexane = 9/2 to give the title compound DH-**2a** (R_f = 0.13) as yellow solid (13.5 mg, 19 μmol, 26%) and TH-**3** (R_f = 0.75) as yellow solid (7.5 mg, 12 μmol, 16%).

Reaction temperature at 60 ℃ (entry 2)

The crude mixture was purified by preparative thin-layer chromatography with CH_2Cl_2/hexane = 9/2 to give the title compound DH-**2b** (R_f = 0.18) as yellow solid (13.6 mg, 19 μmol, 26%), DH-**2c** (R_f = 0.075) as yellow solid (4.7 mg, 6.5 μmol, 9 %), TH-**3** (R_f = 0.75) as yellow solid (1.9 mg, 2.9 μmol, 4%), and mixture of DH-**2a** (R_f = 0.125) and DH-**2d** (R_f = 0.125). Then, mixture of DH-**2a** and DH-**2d** was purified by preparative thin-layer chromatography with hexane/EtOAc = 5/3 to give the title compound DH-**2a** (R_f = 0.425) as yellow solid (23.0 mg, 32 μmol, 44%) and DH-**2d** (R_f = 0.575) as yellow solid (1.0 mg, 1.4 μmol, 2%).

Reaction temperature at 0 ℃ (entry 3)

The crude mixture was purified by preparative thin-layer chromatography with CH_2Cl_2/hexane = 9/2 to give the title compound DH-**2a** (R_f = 0.125) as yellow solid (16.2 mg, 22 µmol, 31%) and DH-**2b** (R_f = 0.175) as yellow solid (16.2 mg, 22 µmol, 31%).

DH-**2a**

Mp. 257.2 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (s, 3H), 3.89 (s, 3H), 4.06 (s, 3H), 7.23-7.35 (m, 4H), 7.44 (t, J = 7.0 Hz, 1H), 7.49 (t, J = 7.0 Hz, 1H), 7.53 (t, J = 7.0 Hz, 2H), 7.63-7.69 (m, 4H), 7.81 (d, J = 8.4 Hz, 2H), 7.85 (t, J = 8.4 Hz, 2H), 7.95-7.99 (m, 4H), 8.39 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 8.4 Hz, 1H), 8.56 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 53.2, 53.3, 58.1, 80.6, 119.4, 120.0, 123.8, 124.0, 124.8, 124.9, 125.1, 125.1, 126.3, 126.5, 126.5, 126.6, 127.0, 127.3, 127.6, 127.6, 127.8, 127.8, 127.8, 127.8, 127.9 (x 2), 128.0 (x 2), 128.2 (x 3), 128.4, 129.4 (x 2), 129.6 (x 4), 129.8 (x 2), 130.8 (x 2), 131.0, 131.3, 131.5, 131.9, 132.1, 132.2, 175.3, 175.7; IR ($CHCl_3$): v 1239, 1431, 1736, 3199 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{51}H_{34}O_5$ [M]$^+$: 726.2406, found: 726.2415.

DH-**2b**

Mp. 267.4 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (s, 3H), 3.02 (s, 3H), 3.79 (s, 3H), 4.08 (s, 1H), 7.28 (t, J = 8.4 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.35 (t, J = 8.4 Hz, 1H), 7.46 (t, J = 8.4 Hz, 1H), 7.48 (t, J = 8.4 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.61 (d, J = 7.4 Hz, 1H), 7.64 (d, J = 7.4 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.83 (d, J = 7.4 Hz, 1H), 7.84 (d, J = 7.4 Hz, 1H), 7.95-7.99 (m, 5H), 8.04 (d, J = 9.2 Hz, 1H), 8.41 (d, J = 8.4 Hz, 1H), 8.46 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 8.4 Hz, 1H), 8.58 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 52.7, 53.7, 56.2, 79.8, 119.5, 121.6, 123.8, 124.0, 124.6, 125.0 (x 2), 125.1, 126.3 (x 3), 126.4, 126.7, 126.9, 127.5, 127.7 (x 2), 127.9, 128.0 (x 4), 128.5, 129.1, 129.4 (x 2), 129.5 (x 2), 129.6 (x 4), 130.2, 130.7, 130.9, 131.1, 131.3, 131.6, 131.7, 131.8, 132.0, 132.2 (x 2), 133.3, 173.8 (x 2); IR ($CHCl_3$): v 1249, 1637, 1725, 2089, 3440 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{51}H_{34}O_5$ [M]$^+$: 726.2406, found: 726.2401.

DH-**2c**

Mp. 255.5 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H), 3.02 (s, 3H), 3.09 (s, 3H), 4.88 (s, 1H), 7.23-7.36 (m, 4H), 7.45-7.57 (m, 6H), 7.61 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 9.2 Hz, 2H), 7.98 (d, J = 9.2 Hz, 2H), 8.26 (d, J = 9.2 Hz, 1H), 8.40 (d, J = 8.8 Hz, 1H), 8.45 (d, J = 8.8 Hz, 1H), 8.49 (d, J = 8.8 Hz, 1H), 8.54 (d, J = 8.8 Hz, 1H) 8.66 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 52.7, 53.5, 55.9, 81.3, 121.7, 122.3, 123.7 (x 2), 124.8 (x 3), 125.0, 126.3 (x 5), 126.8, 127.5 (x 2), 127.7, 127.8, 127.9 (x 4), 128.0 (x 2), 129.0, 129.3, 129.4 (x 2), 129.6 (x 3), 129.7, 130.2, 130.7, 130.8, 131.0, 131.1, 131.5, 131.6, 131.7, 131.9, 132.0, 132.2, 133.1, 172.7, 173.4; IR ($CHCl_3$): v 1232, 1734, 2949, 3484 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{51}H_{34}O_5$ [M]$^+$: 726.2406, found: 726.2401.

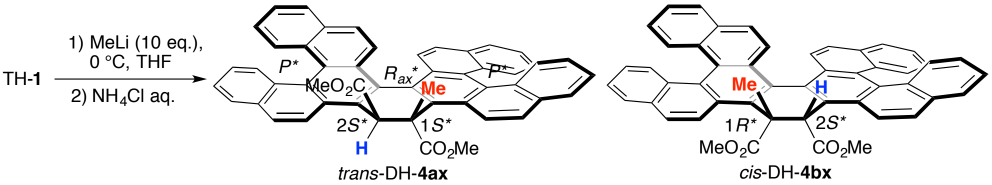
DH-2d

Mp. 254.8 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (s, 3H), 2.95 (s, 3H), 3.75 (s, 3H), 4.37 (s, 1H), 7.29 (t, *J* = 8.4 Hz, 1H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.32 (t, *J* = 8.4 Hz, 1H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 9.0 Hz, 2H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.94-7.99 (m, 4H), 8.41 (d, *J* = 9.0 Hz, 1H), 8.46 (d, *J* = 9.0 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.54 (d, *J* = 9.0 Hz, 1H), 8.59 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 52.8, 53.6, 59.5, 81.4, 119.7, 122.2, 123.6, 123.9, 124.7, 124.9, 125.0, 125.0, 126.2, 126.4 (x 2), 126.5, 126.8, 127.5, 127.6 (x 2), 127.7, 127.9 (x 3), 128.0 (x 2), 128.2, 128.3, 128.5, 129.3 (x 3), 129.6 (x 2), 129.7 (x 2), 130.7, 130.8 (x 2), 130.9, 131.3 (x 2), 131.6, 131.7, 131.9, 132.1, 132.6, 133.0, 175.4, 175.4; IR ($CHCl_3$): *ν* 1234, 1268, 1728, 3045, 3471 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{51}H_{34}O_5$ [M]$^+$: 726.2406, found: 726.2405.

TH-**3**

Mp. 119.5 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.20 (s, 3H), 4.11 (s, 3H), 7.21 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.30 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 8.01-8,12 (m, 5H), 8.25 (d, *J* = 8.8 Hz, 1H), 8.38 (d, *J* = 8.8 Hz, 1H), 8.43 (d, *J* = 8.8 Hz, 1H), 8.45 (d, *J* = 8.8 Hz, 1H), 8.47 (d, *J* = 7.2 Hz, 1H), 8.50 (d, *J* = 8.8 Hz, 1H), 8.57 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 52.8, 121.8, 124.3, 124.3, 124.6, 125.0 (x 2), 125.2 (x 2), 126.3 (x 2), 126.4, 126.5 (x 2), 126.6, 126.8, 126.9, 127.2, 127.4, 127.5, 127.6 (x 2), 127.7, 128.0 (x 2), 128.2, 129.4, 129.5 (x 3), 129.7 (x 2), 130.0, 130.6 (x 2), 130.7 (x 2), 130.9, 131.1, 131.6, 131.9, 132.0, 132.2 (x 2), 132.4, 132.9, 172.8 (x 2); IR ($CHCl_3$): *ν* 1217, 1506, 1726, 2920, 3449 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{49}H_{30}O_2$ [M]$^+$: 650.2246, found: 650.2248.

Synthesis of *trans*-(*P, *P**, *R*$_{ax}$*, 1*S**, 2*S**)-DH-4ax and *cis*-(*P**, *P**, *R*$_{ax}$*, 1*R**, 2*S**)-DH-4bx.**



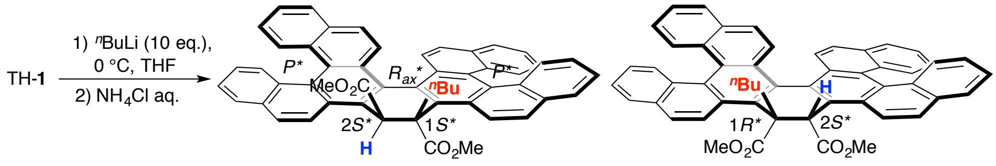
A solution of triple helicene (TH-**1**, 50 mg, 72 µmol) in THF (6 mL) was added dropwise MeLi (1.2 M in ether, 0.60 mL, 0.72 mmol, 10 eq) at 0 °C under N_2 atmosphere. The mixture was stirred for 30 min at 0 °C. Then, sat. NH_4Cl *aq*. was added to the mixture. After stirring for 15 min, the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtered, and then evaporated under reduced pressure. The crude mixture was purified by preparative thin-layer chromatography with CH_2Cl_2/hexane = 9/2 to give the title compound *trans*-DH-**4ax** (R_f = 0.65) as yellow solid (38.4 mg, 54 μmol, 75%) and *cis*-DH-**4bx** (R_f = 0.50) as yellow solid (12.8 mg, 18 μmol, 25%).

***trans*-(*P**, *P**, *R*$_{ax}$*, 1*S**, 2*S**)-DH-4ax**

Mp. 148.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.02 (s, 3H), 3.18 (s, 3H), 5.27 (s, 1H), 7.23 (t, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 6.8 Hz, 1H), 7.46 (t, *J* = 6.8 Hz, 1H), 7.52 (t, *J* = 6.8 Hz, 1H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.68-7.74 (m, 3H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.96-8.01 (m, 3H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 8.43 (d, *J* = 8.8 Hz, 2H), 8.46 (d, *J* = 8.8 Hz, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 8.58 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 50.6, 51.8, 52.8, 53.8, 120.6, 123.1, 124.0, 124.3, 124.6, 124.7, 124.8 (x 2), 126.1, 126.2, 126.3, 126.4, 126.7, 127.2 (x 3), 127.5, 127.6, 127.8 (x 2), 128.0 (x 3), 128.3, 129.1, 129.3, 129.4 (x 2), 129.5, 129.7, 129.9, 130.1, 130.2, 130.7, 130.9, 131.2, 131.3, 131.6 (x 2), 131.9, 132.1 (x 2), 134.7, 135.0, 170.1, 174.8; IR ($CHCl_3$): *v* 1235, 1432, 1727, 2951, 3013, 3046 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{51}H_{34}O_4$ $[M]^+$: 710.2457, found: 710.2449.

***cis*-(*P**, *P**, *R*$_{ax}$*, 1*R**, 2*S**)-DH-4bx**

Mp. 168.2 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (s, 3H), 3.27 (s, 3H), 3.72 (s, 3H), 4.74 (s, 1H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.60 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 52.1, 52.4, 52.8, 53.7, 119.4, 120.0, 124.3, 124.4, 124.7, 124.8, 125.0, 125.1, 126.1, 126.3, 126.4, 126.5 (x 2), 127.3 (x 3), 127.5, 127.6, 127.7 (x 2), 127.9, 128.0, 128.1 (x 2), 128.8, 129.1, 129.3 (x 3), 129.5, 129.7 (x 2), 129.8, 130.2, 130.7, 130.8, 131.0, 131.3 (x 2), 131.5, 132.0, 132.1, 132.2, 133.8, 170.8, 176.6; IR ($CHCl_3$): *v* 1242, 1432, 1735, 2949, 3018, 3049 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{51}H_{34}O_4$ $[M]^+$: 710.2457, found: 710.2450.



trans-DH-**4ay**

cis-DH-**4by**

Synthesis of *trans*-(*P, *P**, *R*$_{ax}$*, 1*S**, 2*S**)-DH-4ay and *cis*-(*P**, *P**, *R*$_{ax}$*, 1*R**, 2*S**)-DH-4by.**

A solution of triple helicene **1** (100 mg, 0.14 mmol) in THF (12 mL) was added dropwise ^{n}BuLi (1.58 M in hexane, 0.91 mL, 1.44 mmol, 10 eq) at −78 °C under N_2 atmosphere. The mixture was stirred for 3 min at −78 °C, then warmed to 0 °C and stirred for 7 min. The aqueous solution of NH_4Cl was added to the mixture. After stirring for 15 min, the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtered, and then evaporated under reduced pressure. The crude mixture was purified by preparative thin-layer chromatography with hexane/EtOAc = 5/1 to give the title compound *trans*-DH-**4ay** (R_f = 0.40) as yellow solid (36.8 mg, 49 μmol, 34%) and *cis*-DH-**4by** (R_f = 0.43) as yellow solid (43.3 mg, 58 μmol, 40%) (It is difficult to separate each diastereomer completely).

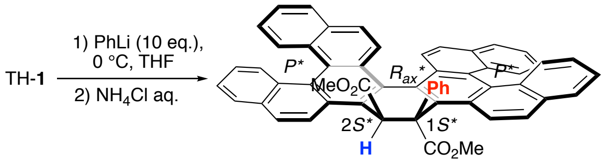
***trans*-(*P**, *P**, *R*$_{ax}$*, 1*S**, 2*S**)-DH-4ay**

Mp. 103.5 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 0.00 (m, 3H), 0.39-0.44 (m, 1H), 0.66 (q, *J* = 7.6 Hz, 2H), 0.88 (m, 1H), 2.08-2.11 (m, 1H), 2.28 (dt, *J* = 3.2, 13.2 Hz, 1H), 3.80 (m, 3H), 3.93 (s, 3H), 5.13 (s, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.62-7.63 (m, 3H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.73 (m, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.92-7.98 (m, 5H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 8.58 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 23.2, 27.9, 32.3, 52.5, 53.0, 55.9 (x 2), 120.4, 120.9, 123.5, 124.0, 124.8, 124.9, 125.0 (x 2), 126.2, 126.3 (x 2), 126.5, 126.9, 127.6, 127.7 (x 4), 127.9 (x 5), 128.1, 129.2, 129.4, 129.5 (x 2), 129.6, 130.0 (x 2), 130.1, 130.8, 130.9, 131.0, 131.3, 131.5 (x 2), 131.8 (x 3), 131.9, 132.0, 132.8, 177.6 (x 2); IR ($CHCl_3$): *v* 1222, 1733, 2953, 3016, 3047 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{54}H_{40}O_4$ $[M]^+$: 752.2927, found: 752.2933

***cis*-(*P**, *P**, *R*$_{ax}$*, 1*R**, 2*S**)-DH-4by**

Mp. 143.2 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 0.41 (t, *J* = 7.4 Hz, 3H), 0.82-0.93 (m, 2H), 1.13-1.15 (m, 1H), 1.45-1.52 (m, 1H), 1.91 (dt, *J* = 3.6, 12.8 Hz, 1H), 2.28 (dt, *J* = 3.6, 12.8 Hz, 1H), 3.23 (s, 3H), 3.69 (s, 3H), 4.93 (s, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.32-7.37 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 9.2 Hz, 1H), 7.73 (d, *J* = 9.2 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.82-7.87 (m, 4H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 9.2 Hz, 1H), 8.20 (d, *J* = 9.2 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H) , 8.46 (d, *J* = 8.4 Hz, 1H) , 8.54 (d, *J* = 8.4 Hz, 1H) , 8.58 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 22.9, 28.3, 37.1, 51.0, 52.3, 52.5, 55.3, 119.3, 120.8, 124.3, 124.4, 124.7 (x 2), 124.9, 125.1, 126.1, 126.3, 126.4, 126.5 (x 2), 127.2, 127.3, 127.4 (x 2), 127.6 (x 4), 127.9, 128.0, 128.1, 128.3, 128.8, 129.2, 129.3, 129.5 (x 2), 129.6, 129.7, 129.9, 130.2, 130.7, 130.8, 131.3, 131.4, 131.9, 132.0, 132.1, 132.2, 132.6, 133.8, 171.1, 176.4; IR ($CHCl_3$): *v* 1222, 1733, 2953, 3016, 3047 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{54}H_{40}O_4$ $[M]^+$: 752.2927, found: 752.2934

Synthesis of *trans*-(*P, *P**, *R*$_{ax}$*, 1*S**, 2*S**)-DH-4az.**



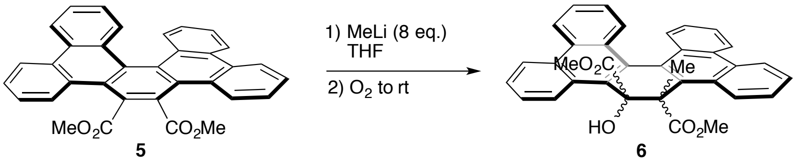
trans-DH-**4az**

A solution of triple helicene **1** (100 mg, 0.14 mmol) in THF (12mL) was added dropwise PhLi (1.0 M in THF, 1.44 mL, 1.44 mmol, 10 eq) at −78 °C under N_2 atmosphere. The mixture was stirred for 3 min at −78 °C, stirred for 7 min at 0 °C. Then, sat. NH_4Cl *aq* was added to the mixture. After stirring for 15 min, the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtered, and then evaporated under reduced pressure. The crude mixture was purified by preparative thin-layer chromatography with CH_2Cl_2/hexane = 9/2 to give the title compound *trans*-DH-**4az** (R_f = 0.53) as yellow solid (78.0 mg, 54 µmol, 70%).

***trans*-(*P**, *P**, *R*$_{ax}$*, 1*S**, 2*S**)-DH-4az**

Mp. 276.1 °C. (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (s, 3H), 3.34 (s, 3H), 5.61 (s, 1H), 6.69 (d, J = 7.6 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 7.21-7.35 (m, 6H), 7.43-7.54 (m, 5H), 7.58 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.73-7.75 (m, 3H), 7.83 (m, 3H), 7.88 (d, J = 8.8 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 8.02 (d, J = 8.8 Hz, 1H), 8.33 (d, J = 8.8 Hz, 1H), 8.45 (d, J = 8.8 Hz, 1H), 8.52 (d, J = 8.8 Hz, 2H), 8.60 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.8, 53.1, 54.7, 61.1, 120.0, 124.3, 124.4, 124.5, 124.6, 124.7, 124.8, 125.3, 126.0 (x 2), 126.2 (x 2), 126.3, 126.4, 127.1, 127.3, 127.4, 127.5, 127.6 (x 2), 127.7, 127.8, 127.9 (x 2), 128.1 (x 2), 128.5, 129.1, 129.3, 129.4 (x 2), 129.5, 129.7 (x 2), 129.8, 130.1, 130.3, 130.5, 130.8, 130.9 (x 2), 131.1, 131.3 (x 2), 132.0, 132.1, 132.3, 132.4, 135.6, 140.2, 170.4, 171.8; IR ($CHCl_3$): *ν* 1233, 1728, 2949, 3015, 3047 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{56}H_{36}O_4$ [M]$^+$: 772.2614, found: 772.2621

Synthesis of dimethyl-1-hydroxy-2-methyl-1,2-dihydrodibenzo[*f,j*]picene-1,2-dicarboxylate (6). (Scheme 3A)



A solution of dibenzo[*f,j*]picene-9,10-dicarboxylic acid, 9,10-dimethyl ester (**5**, 50 mg, 0.10 mmol) in THF (6 mL) was added dropwise MeLi (1.2 M in ether, 0.68 mL, 0.81 mmol, 8 eq.) at 0 °C under N_2 atmosphere. The mixture was stirred for 30 min at same temperature. Then, to the mixture was added O_2 (excess) with bubbling. After stirring for 15 min, the resulting mixture was poured into sat. NH_4Cl *aq*, and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtered, and then evaporated under reduced pressure. The crude mixture was purified by preparative thin-layer chromatography with hexane/THF =

3/1 to give the title compound *trans*-**6a** ($R_f = 0.48$) as yellow solid (23.0 mg, 44 μmol, 43%) and *cis*-**6b** ($R_f = 0.35$) as yellow solid (24.6 mg, 47 μmol, 46%).

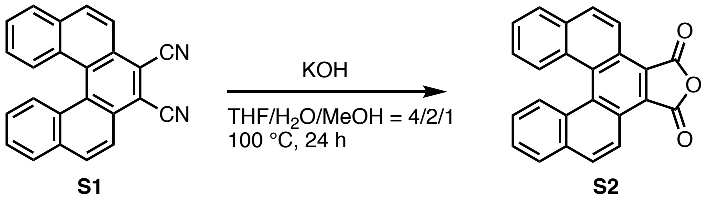
***trans*-dimethyl-1-hydroxy-2-methyl-1,2-dihydrodibenzo[*f,j*]picene-1,2-dicarboxylate 6a**

Mp. 125.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, D_2O was added) δ 1.71 (s, 3H), 3.75 (s, 3H), 3.97 (s, 3H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.66 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.67 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 2H), 8.68 (d, *J* = 8.0 Hz, 1H), 8.70 (d, *J* = 8.0 Hz, 1H), 8.74 (d, *J* = 8.0 Hz, 1H), 8.79 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 53.2 (x 2), 58.6, 81.3, 123.1, 123.2, 123.6, 123.7, 124.1, 124.7, 125.6, 126.1, 126.3, 126.5, 126.6, 127.1, 127.9, 128.0, 128.1, 128.4, 128.7, 128.9, 129.3, 129.5, 129.8, 129.9, 130.3, 130.8, 130.9, 131.2, 131.4, 132.0, 175.3, 175.8; IR ($CHCl_3$): *ν* 1081, 1720, 2345, 2374, 3202 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{35}H_{26}O_5$ [M]$^+$: 526.1780, found: 526.1777.

***cis*-dimethyl-1-hydroxy-2-methyl-1,2-dihydrodibenzo[*f,j*]picene-1,2-dicarboxylate 6b**

Mp. 251.0 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.93 (s, 3H), 3.17 (s, 3H), 3.64 (s, 3H), 4.15 (s, 1H), 7.18-7.28 (m, 4H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 2H), 7.64 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.66 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.73 (d, *J* = 7.6 Hz, 1H), 8.75 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.4, 52.7, 53.6, 56.2, 80.2, 122.8 (x 3), 123.6, 123.7, 125.4, 125.8, 125.9 (x 2), 126.0, 126.1, 126.5, 126.8 (x 3), 128.2, 128.6, 129.6, 129.7, 129.9, 130.0, 130.3 (x 2), 130.7, 131.5, 131.7, 131.8, 133.3, 173.7, 176.3; IR ($CHCl_3$): *ν* 1236, 1734, 2344, 2372, 3483 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{35}H_{26}O_5$ [M]$^+$: 526.1780, found: 526.1789.

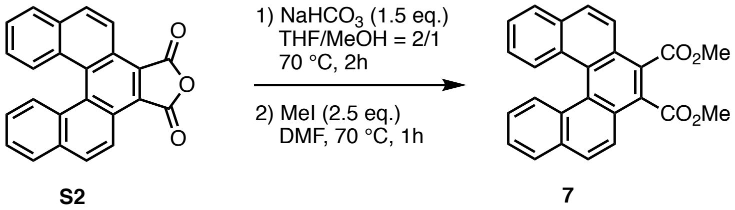
Synthesis of [5]helicene-7,8-dicarboxylic anhydride (S2).



A solution of 7,8-dicyano-[5]helicene (**S1**, 100 mg, 0.30 mmol)[S3], KOH (342 mg, 6.1 mmol, 20 eq), H_2O (6 mL), MeOH (3 mL) in THF (12 mL) was stirred for 24 h at 100 °C. Then, to the mixture was added H_2O and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtered, and then evaporated under reduced pressure. The crude mixture was washed with MeOH to give the title compound **S2** as yellow solid (72.1 mg, 0.21 mmol, 68%).

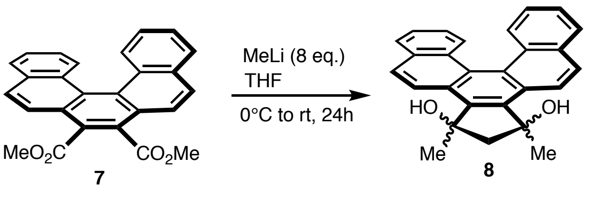
Mp. 267.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 8.4 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 2H), 8.38 (d, *J* = 8.4 Hz, 2H), 8.90 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.9, 125.7, 126.3, 126.4, 128.3, 128.8, 129.5, 130.4, 131.0, 132.9, 133.7, 163.5; IR ($CHCl_3$): *ν* 1761, 1838, 2368, 2919 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{24}H_{12}O_3$ $[M]^+$: 348.0786, found: 348.0790.

Synthesis of [5]helicene 7,8-carboxylic acid dimethyl ester 7.



A solution of [5]helicene-7,8-dicarboxylic anhydride **S2** (100 mg, 0.29 mmol) , $NaHCO_3$ (37.1 mg, 0.43 mmol, 1.5 eq), and MeOH (5 mL) in THF (10 mL) was stirred for 2 h at 70 °C. After removal of the solvent, the obtained [5]helicene-8-methoxycarbonyl-7-carboxylic acid was dissolved in DMF. MeI (44.9μL, 0.72 mmol, 2.5eq) was added dropwise to the mixture at room temperature under N_2 atmosphere. After stirring for 1 h at 70 °C, H_2O was added and the aqueous phase was extracted with DCM. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtered, and then evaporated under reduced pressure. The crude mixture was purified by preparative thin-layer chromatography with hexane/EtOAc = 5/1 to give the title compound **7** as yellow solid (88.9 mg, 0.24 mmol, 85%). The synthesis of compound **7** was previously reported.[S4] However, the reported protocol involving a Pd-catalyzed [2+2+2] cross-cyclotrimerization reaction afforded some isomers that are difficult to separate. Considering the overall efficiency of synthesis, compound **7** was synthesized from **S1** for this study.

Synthesis of 1,3-dimethyl-2,3-dihydro-1*H*-dibenzo[*c,g*]cyclopenta[*l*]phenanthrene-1,3-diol (8). (Scheme 3B)



A solution of [5]helicene 7,8-carboxylic acid dimethyl ester (**7**, 50 mg, 0.13 mmol) in THF (6 mL) was added dropwise MeLi (1.2 M in ether, 0.87 mL, 1.04 mmol, 8 eq) at 0 °C under N_2 atmosphere. The mixture was stirred for 24 h at room temperature and poured into sat. NH_4Cl *aq*. The mixture was extracted with dichloromethane and the combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtered, and then evaporated under reduced pressure. The crude mixture was purified by GPC to give the title compound *trans*-**8** as colorless solid (22.5 mg, 60 μmol, 47%) and *cis*-**8** as colorless solid (6.2 mg, 16 μmol, 13%).

***trans*-1,3-dimethyl-2,3-dihydro-1*H*-dibenzo[*c*,*g*]cyclopenta[*l*]phenanthrene-1,3-diol 8**

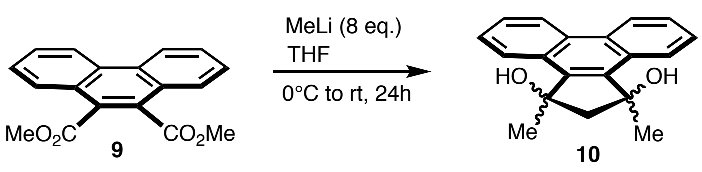
Two inseparable *trans*-isomers based on a helicity of [5]helicene unit are detected and the ratio of the two (*trans*-**8**_major/*trans*-**8**_minor = 62/38) was determined by ^{1}H NMR.

Mp. 126.5 °C. *trans*-**8**_major: ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.01 (s, 6H), 2.14 (s, 2H), 2.71 (s, 2H), 7.20 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.93 (d, J = 9.2 Hz, 4H), 8.28 (d, J = 7.6 Hz, 2H), 8.61 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ30.9, 62.2, 80.8, 122.1, 124.5, 126.3, 127.7, 127.7, 128.0, 129.0, 129.5, 131.3, 132.0, 140.2; *trans*-**8**_minor: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.97 (s, 6H), 2.16 (s, 2H), 2.71 (s, 2H), 7.20 (t, J = 8.0 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.96 (d, J = 8.8 Hz, 4H), 8.26 (d, J = 8.0 Hz, 2H), 8.59 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 30.9, 62.7, 80.2, 122.7, 124.4, 126.3, 127.1, 127.5, 128.0, 128.8, 129.6, 131.1, 132.0, 139.9; IR (CHCl$_3$): *v* 1143, 2929, 2970, 3375 cm^{-1}. HRMS (FAB) *m/z* calcd for C$_{27}$H$_{22}$O$_2$ [M]$^+$: 378.1620, found: 378.1615.

***cis*-1,3-dimethyl-2,3-dihydro-1*H*-dibenzo[*c*,*g*]cyclopenta[*l*]phenanthrene-1,3-diol 8**

Mp. 138.7 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.76 (s, 3H), 1.81 (s, 3H), 2.43 (m, 2H), 2.50 (d, J = 14.6 Hz, 1H), 2.78 (d, J = 14.6 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 8.25 (d, J = 7.4 Hz, 1H), 8.26 (d, J = 7.4 Hz, 1H), 8.63 (d, J = 8.4 Hz, 1H), 8.66 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 28.1, 28.3, 63.3, 78.4, 79.4, 122.4, 122.8, 124.3, 124.3, 126.2 (x 2), 127.1 (x 2), 127.6 (x 2), 127.8, 127.9, 128.0, 129.0, 129.3, 129.5, 131.0, 131.1, 131.9 (x 2), 139.4, 139.7; IR (CHCl$_3$): *v* 1135, 2932, 2976, 3370 cm^{-1}. HRMS (FAB) *m/z* calcd for C$_{27}$H$_{22}$O$_2$ [M]$^+$: 378.1620, found: 378.1628.

Synthesis of 1,3-dimethyl-2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene-1,3-diol (10). (Scheme 3B)



A solution of dimethyl phenanthrene-9,10-dicarboxylate **9** (50 mg, 0.17 mmol) in THF (6 mL) was added dropwise MeLi (1.2 M in ether, 1.1 mL, 1.36 mmol, 8 eq) at 0 °C under N$_2$ atmosphere. The mixture was stirred for 24 h at room temperature and poured into sat. NH$_4$Cl *aq*. The mixture was extracted with dichloromethane and the combined organic layers were washed with brine and dried over anhydrous MgSO$_4$, filtered, and then evaporated under reduced pressure. The crude mixture was purified by preparative thin-layer chromatography with hexane/EtOAc = 5/3 to give the title compound *trans*-

10 (R_f = 0.38) as colorless solid (10.9 mg, 39 μmol, 23%) and *cis*-**10** (R_f = 0.28) as colorless solid (18.4 mg, 66 μmol, 39%).

***trans*-1,3-dimethyl-2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene-1,3-diol 10**

Mp. 133.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.95 (s, 6H), 2.67 (s, 2H), 7.62 (dt, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 2H), 7.66 (dt, *J* = 7.6 Hz, 1H), 8.61 (d, *J* = 7.6 Hz, 1H), 8.61 (d, *J* = 7.6 Hz, 1H), 8.72 (d, *J* = 7.6 Hz, 1H), 8.72 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5, 61.9, 80.8, 123.4, 125.6, 126.7, 126.7, 180.0, 132.1, 139.4; IR ($CHCl_3$): *v* 1128, 1145, 2930, 2970, 3369 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{19}H_{18}O_2$ [M]$^+$: 278.1307, found: 278.1305.

***cis*-1,3-dimethyl-2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene-1,3-diol 10**

Mp. 182.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (s, 3H), 1.70 (s, 3H), 2.28-2.31 (m, 3H), 2.64-2.69 (m, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 8.56-8.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.7, 63.2, 79.3, 123.2, 125.7, 126.6, 126.6, 127.8, 131.7, 138.8; IR ($CHCl_3$): *v* 1148, 1375, 1622, 3431, cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{19}H_{18}O_2$ [M]$^+$: 278.1307, found: 278.1312.

2. Spectral Data

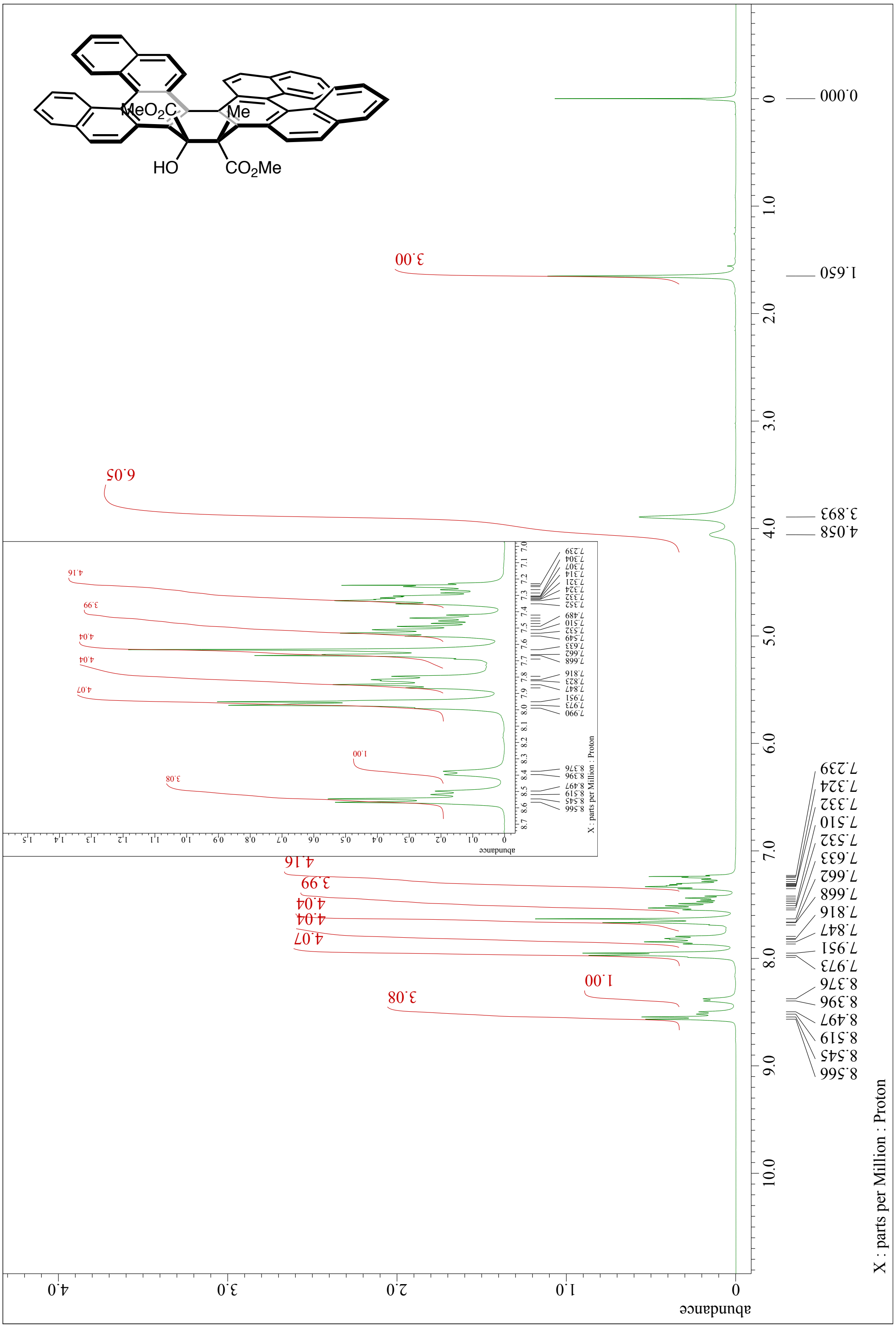


Figure S1. ^{1}H NMR spectrum of *trans*-(*P**, *P**, *R$_{ax}$**, 1*R**, 2*S**)-DH-2a.

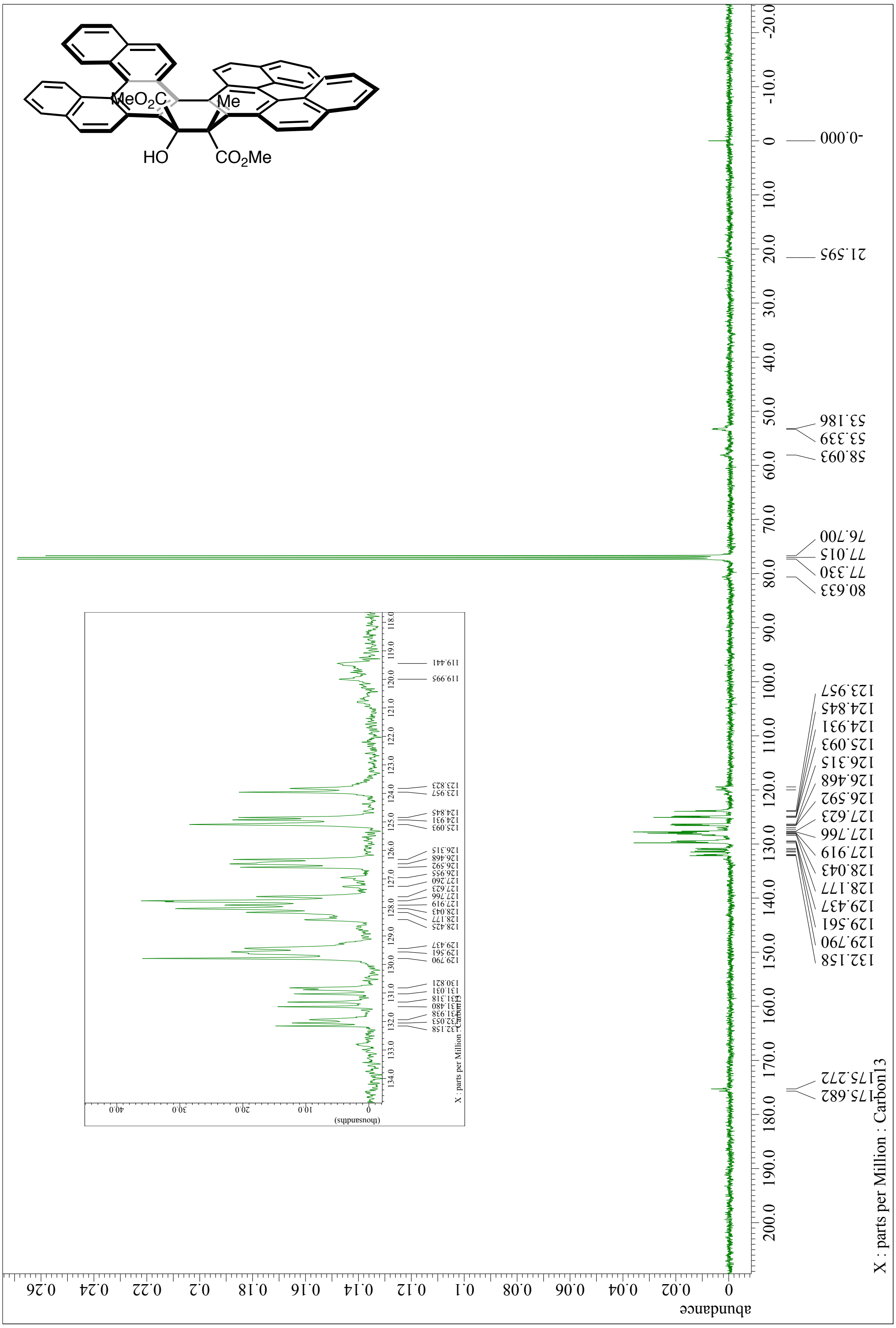


Figure S2. ^{13}C NMR spectrum of *trans*-$(P^*, P^*, R_{ax}^*, 1R^*, 2S^*)$-DH-2a.

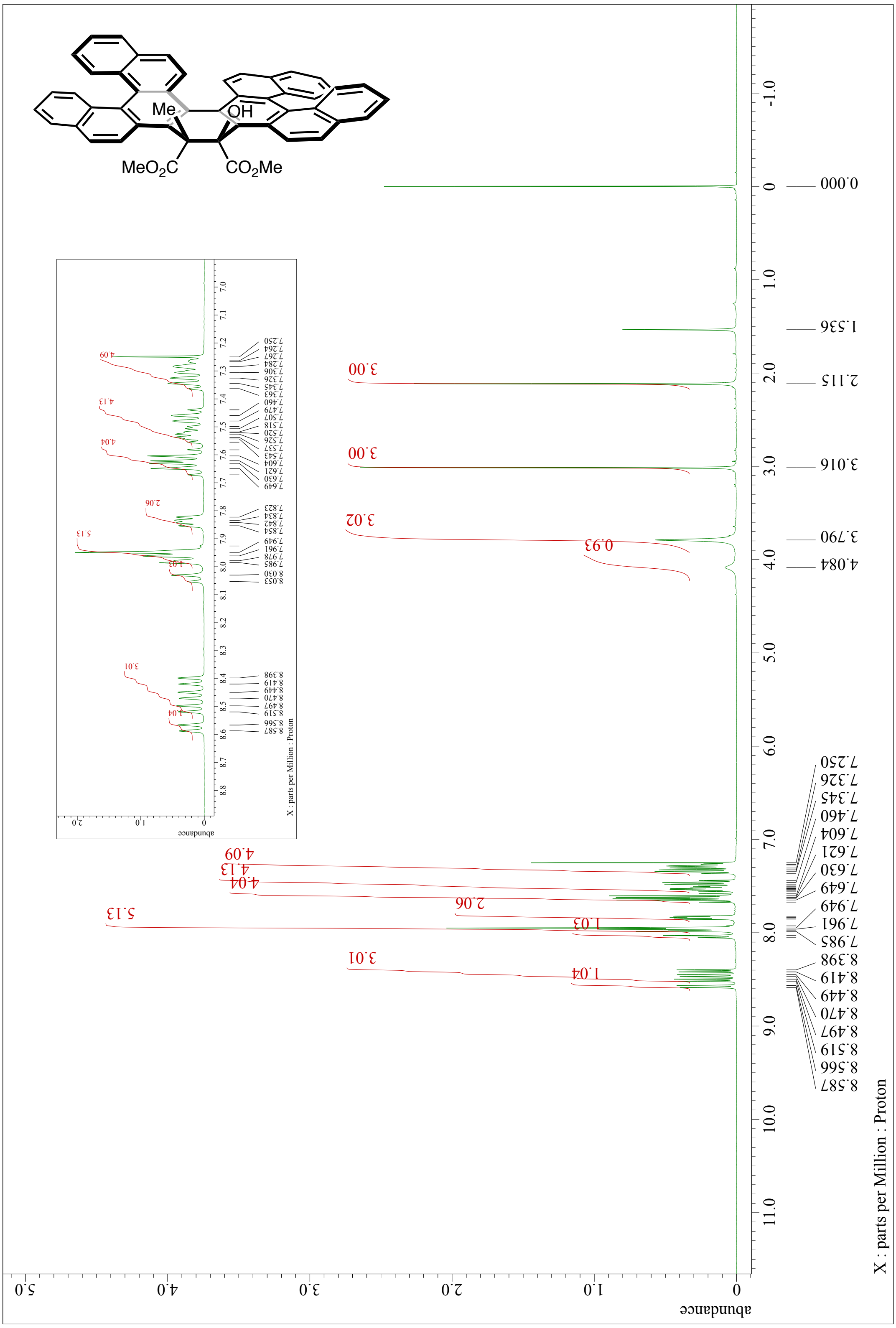


Figure S3. ^{1}H NMR spectrum of *cis*-(*P**, *P**, *R*$_{ax}$*, 1*R**, 2*R**)-DH-2b.

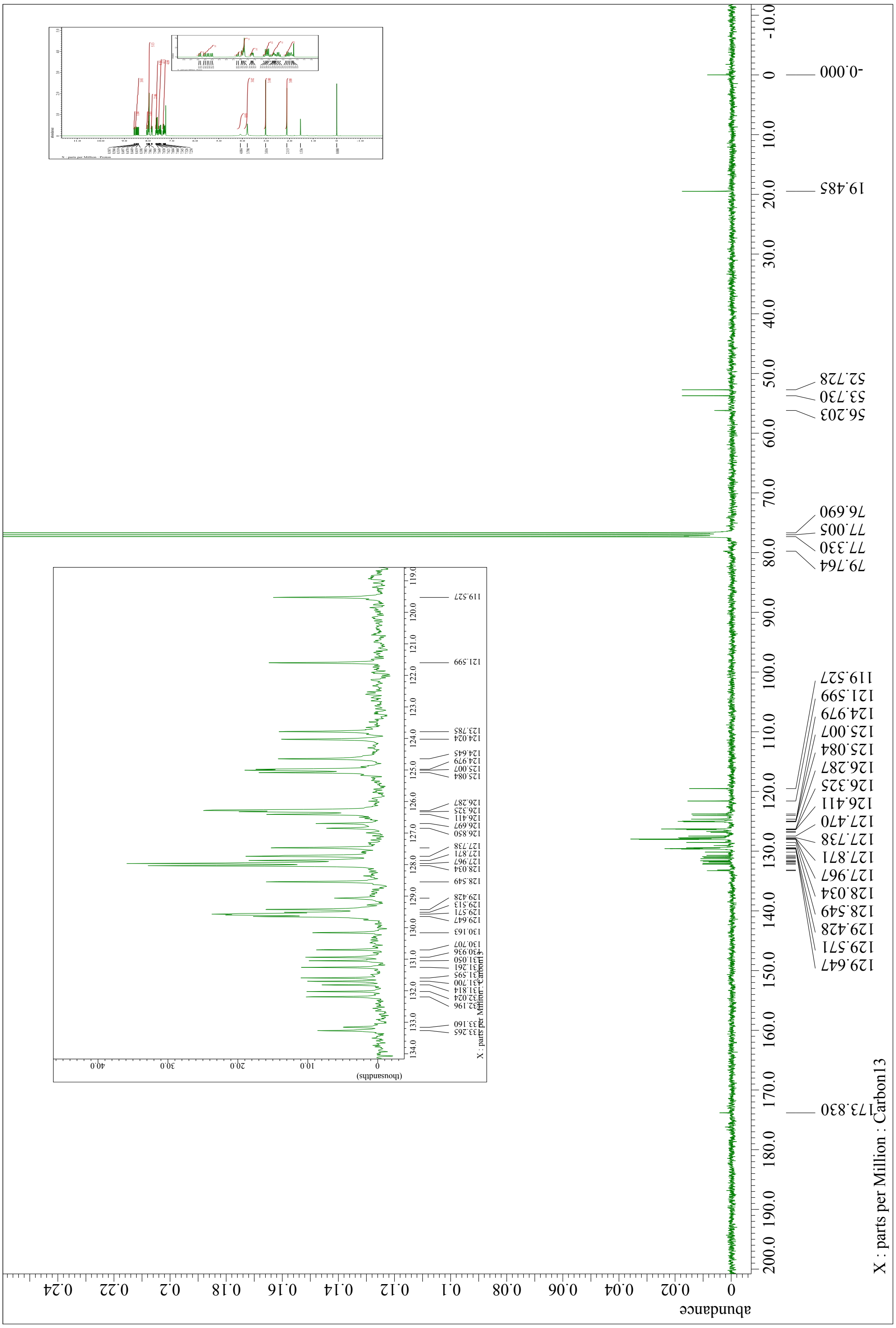


Figure S4. ^{13}C NMR spectrum of *cis*-(*P**, *P**, *R*$_{ax}$*, 1*R**, 2*R**)-DH-2b.

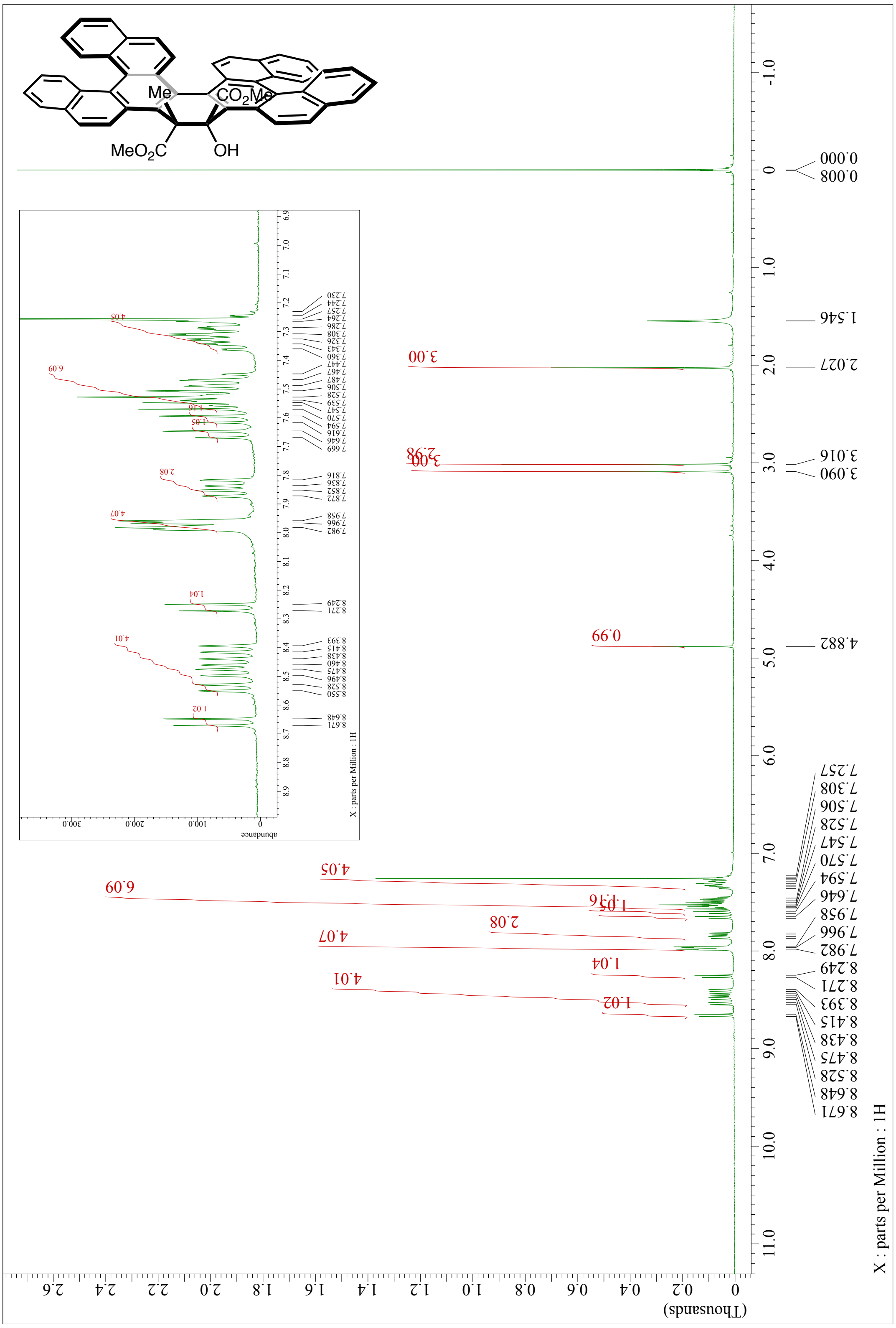


Figure S5. ^{1}H NMR spectrum of *trans*-(P*, P*, R_{ax}*, 1R*, 2R*)-DH-2c.

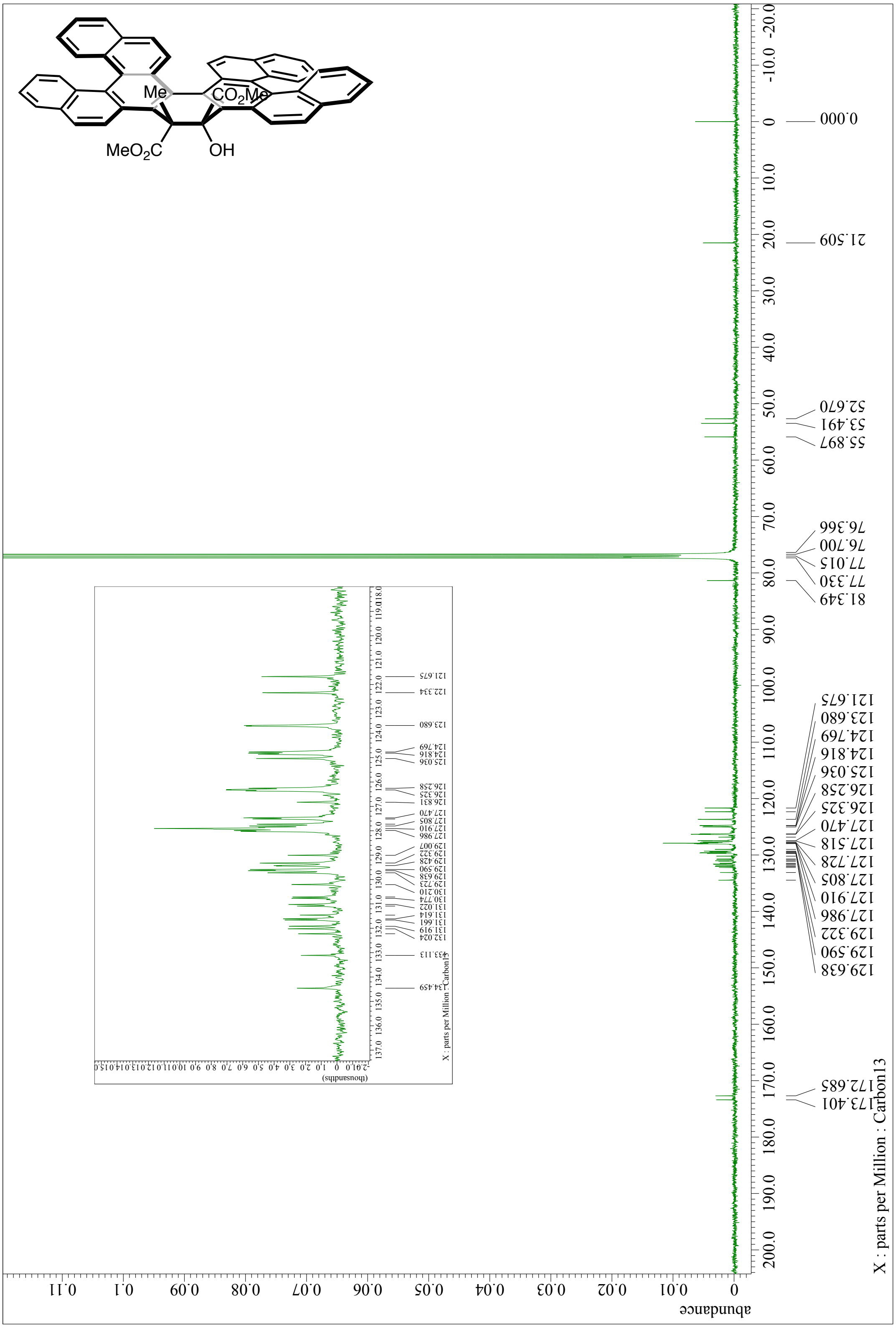


Figure S6. ^{13}C NMR spectrum of *trans*-(*P, *P**, *R$_{ax}$**, 1*R**, 2*R**)-DH-2c.**

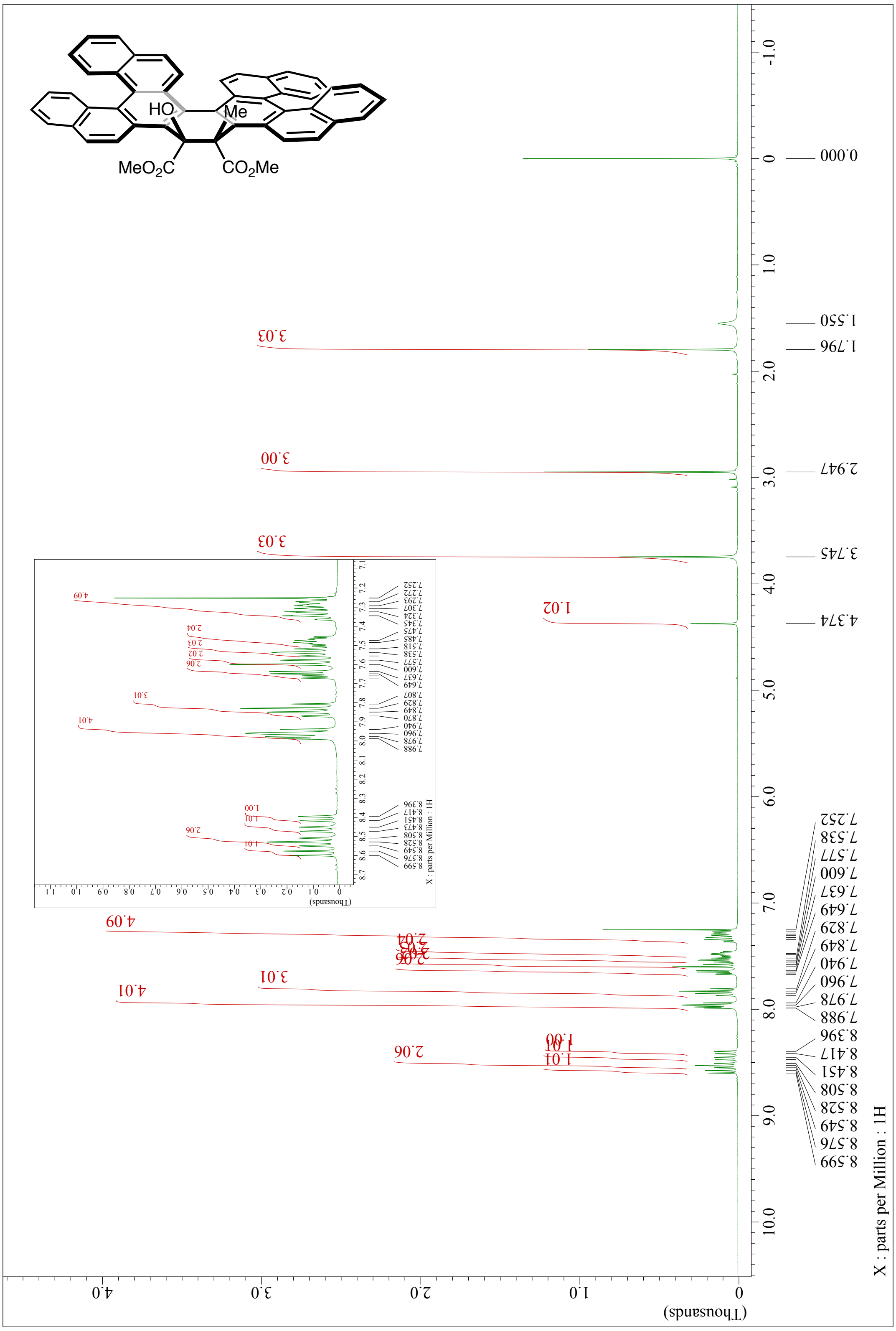


Figure S7. ^{1}H NMR spectrum of *cis*-(*P**, *P**, *R$_{ax}$**, 1*S**, 2*S**)-DH-2d.

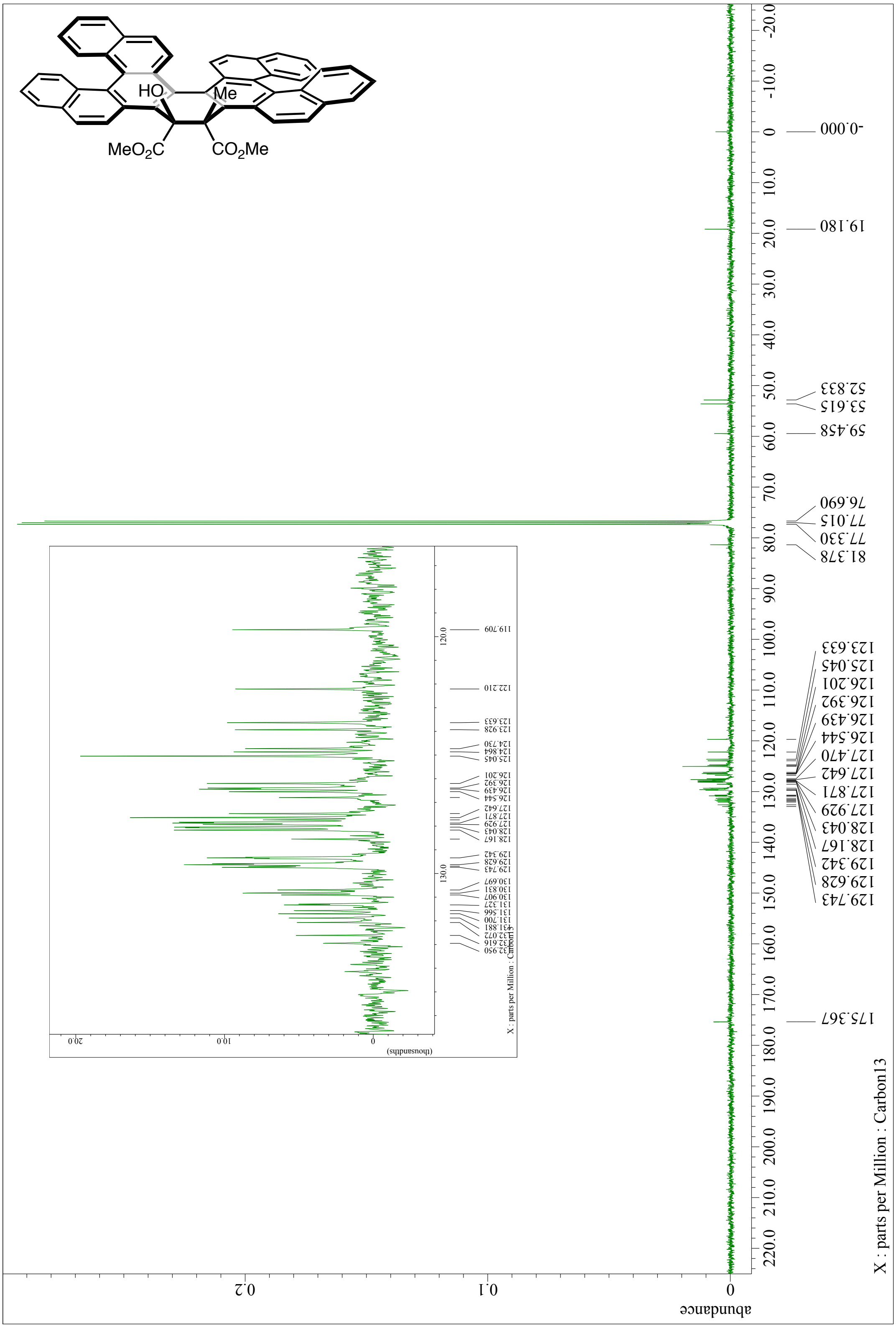


Figure S8. ^{13} **NMR spectrum of *cis*-(*P**, *P**, *R*$_{ax}$*, 1*S**, 2*S**)-DH-2d.**

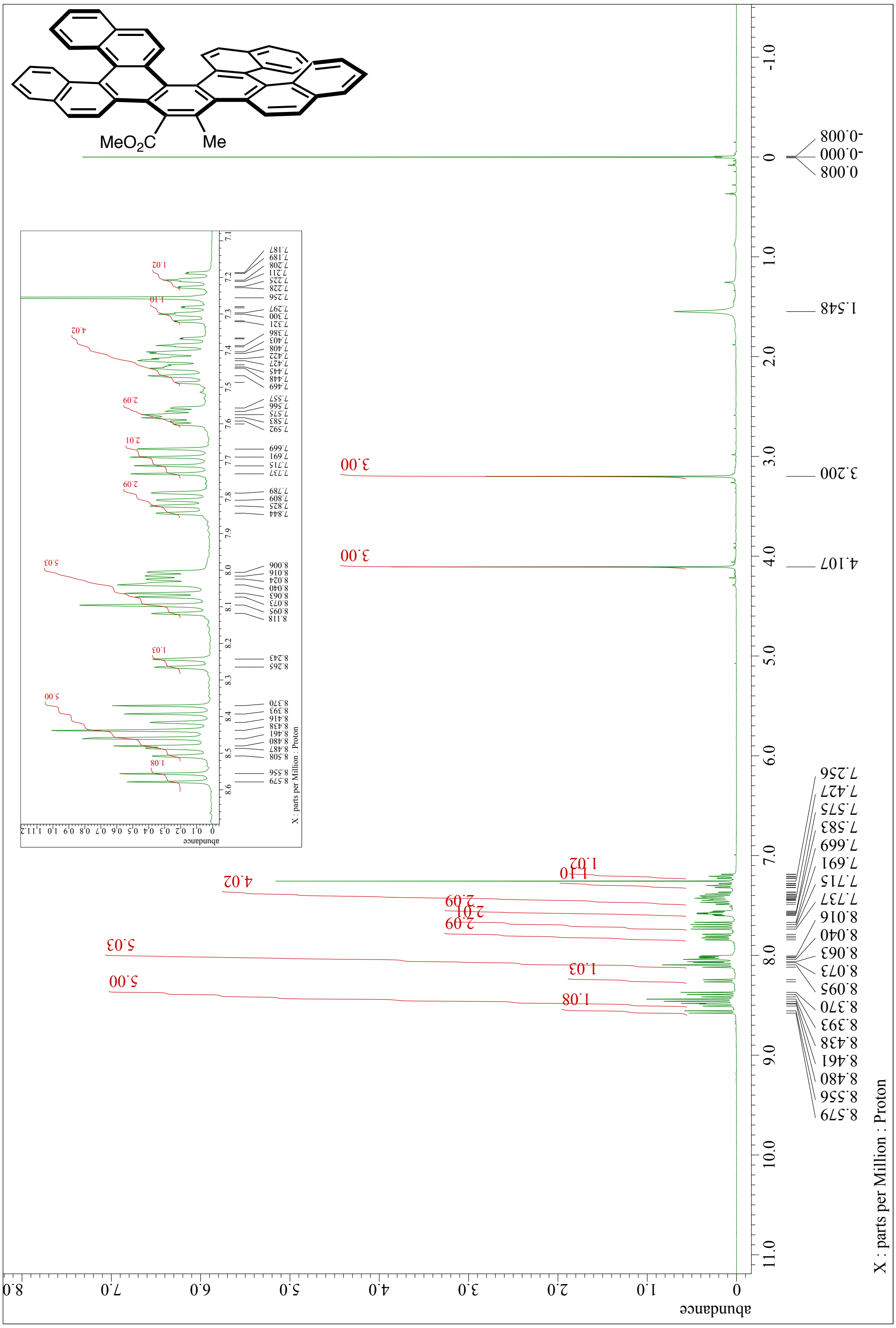


Figure S9. ^{1}H NMR spectrum of TH-3.

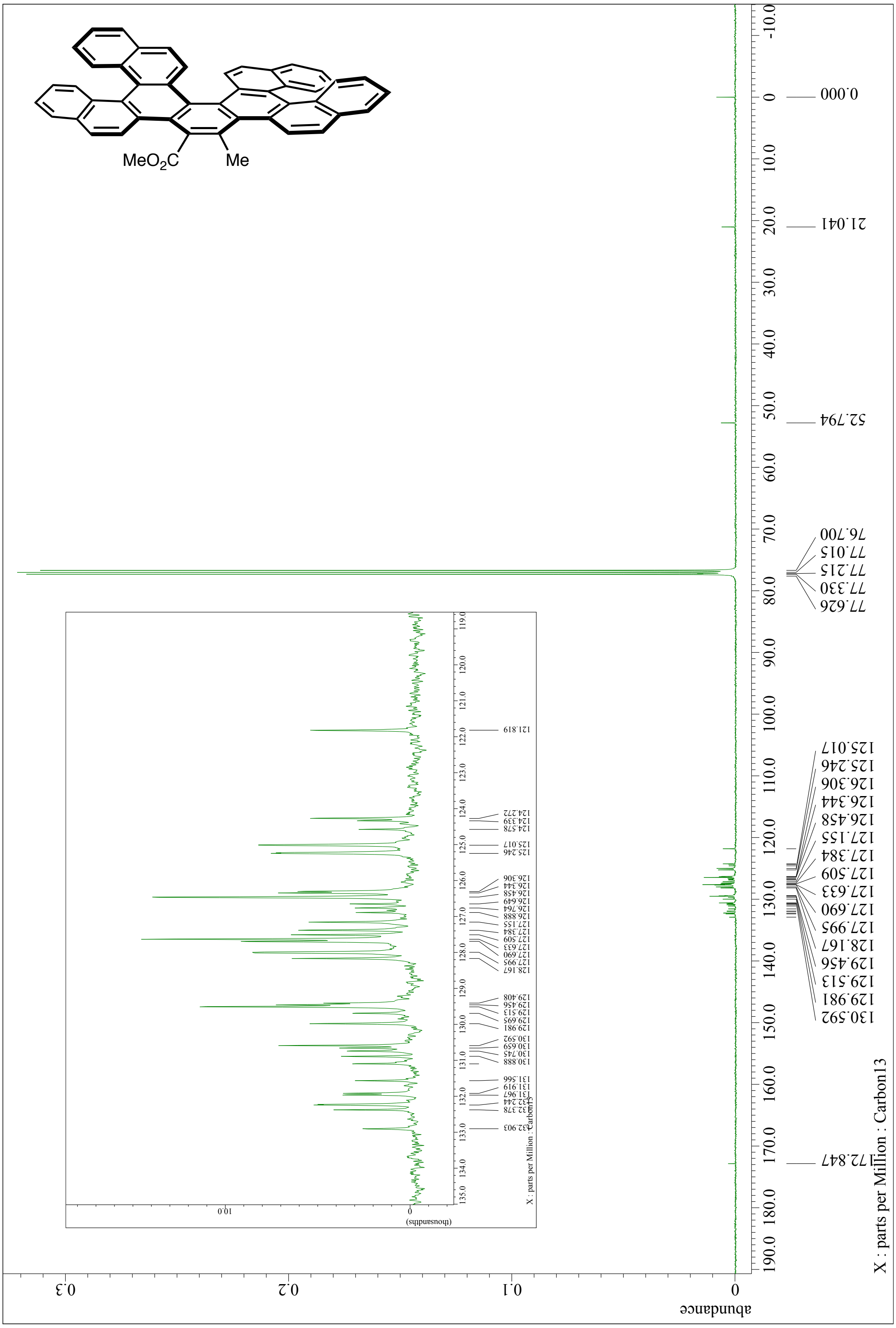


Figure S10. ^{13}C NMR spectrum of TH-3.

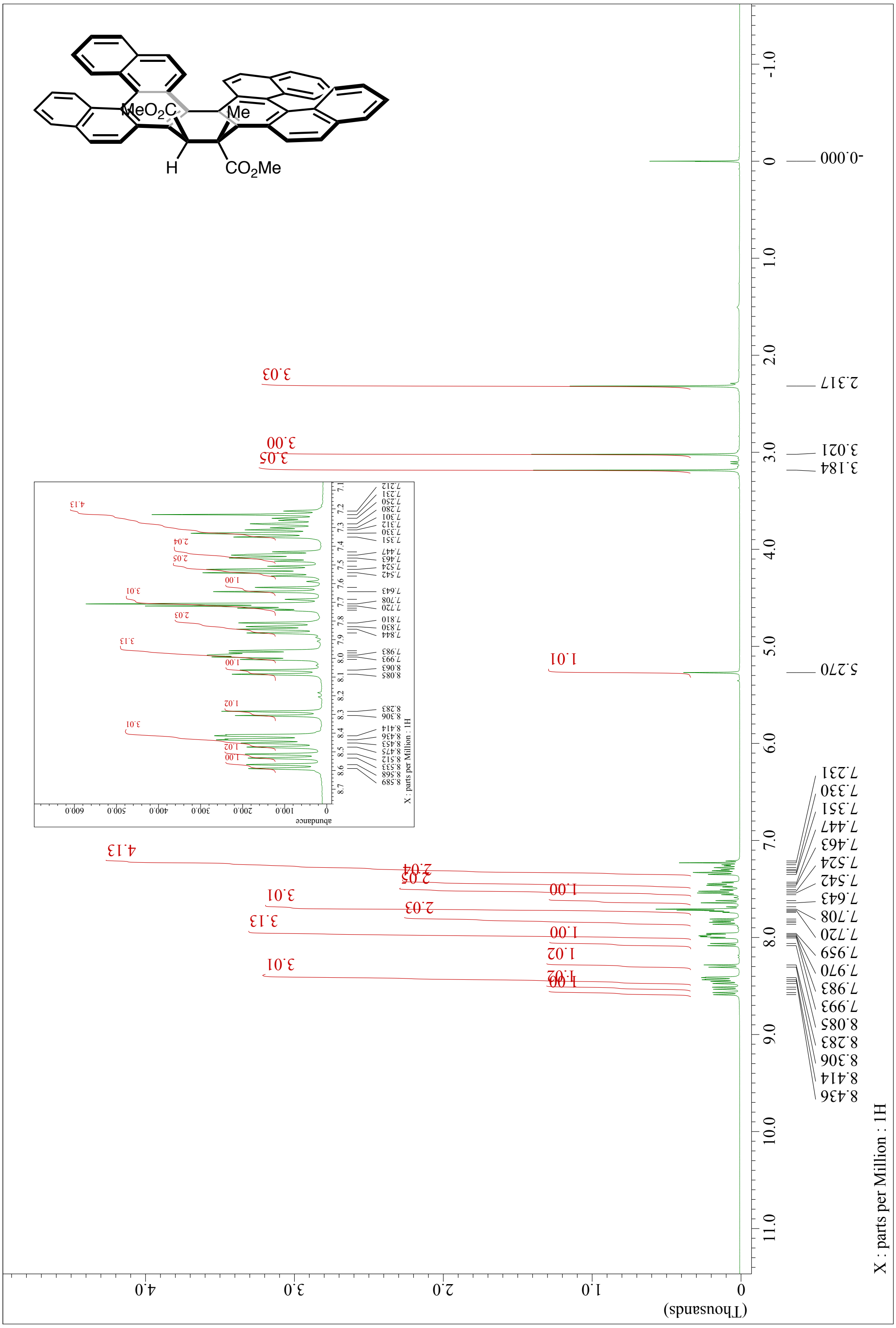


Figure S11. ^{1}H NMR spectrum of *trans*-(*P**, *P**, *R*$_{ax}$*, 1*S**, 2*S**)-DH-4ax.

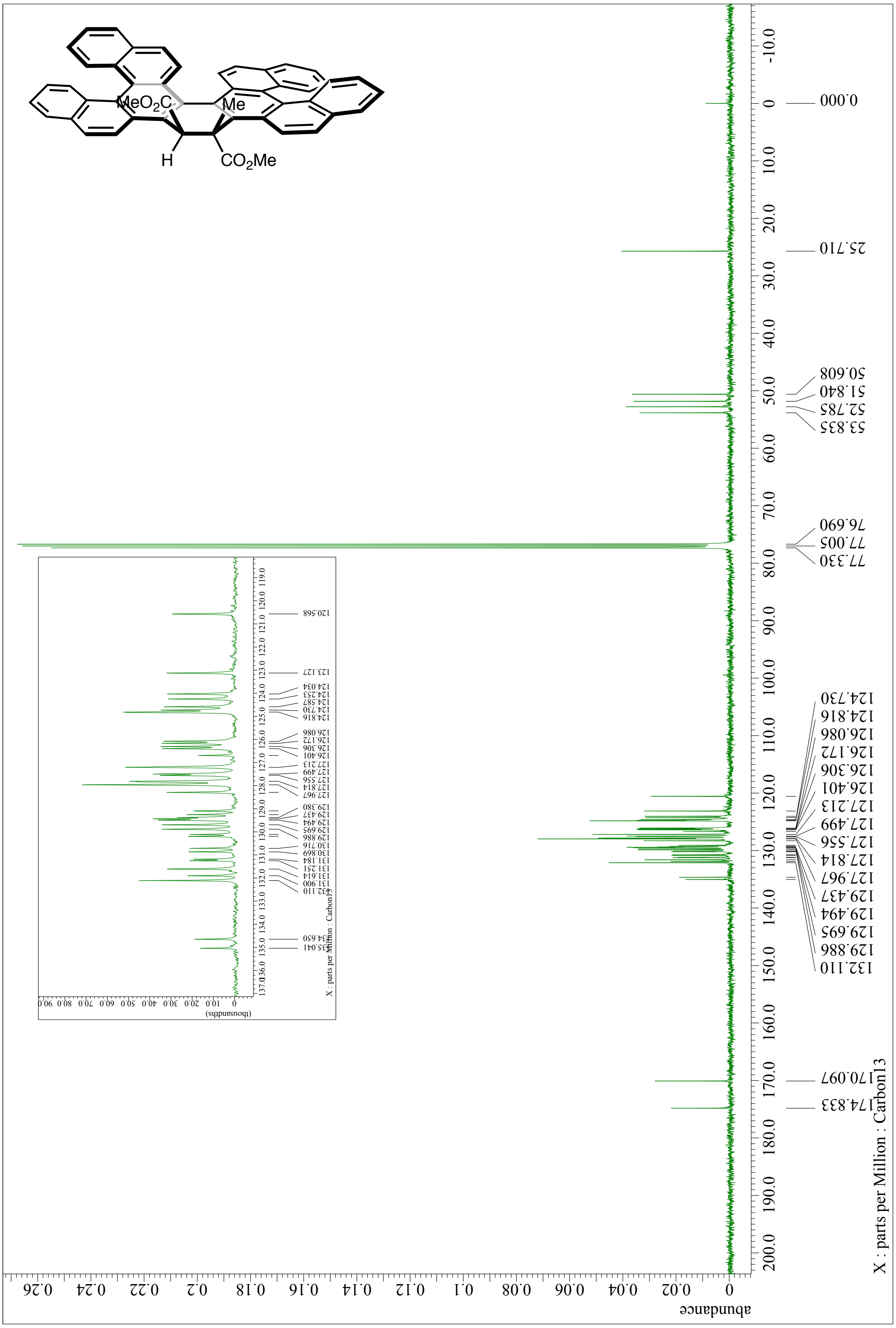


Figure S12. ^{13}C **NMR spectrum of** ***trans*-(*P**, *P**, *R*$_{ax}$*, 1*S**, 2*S**)-DH-4ax.**

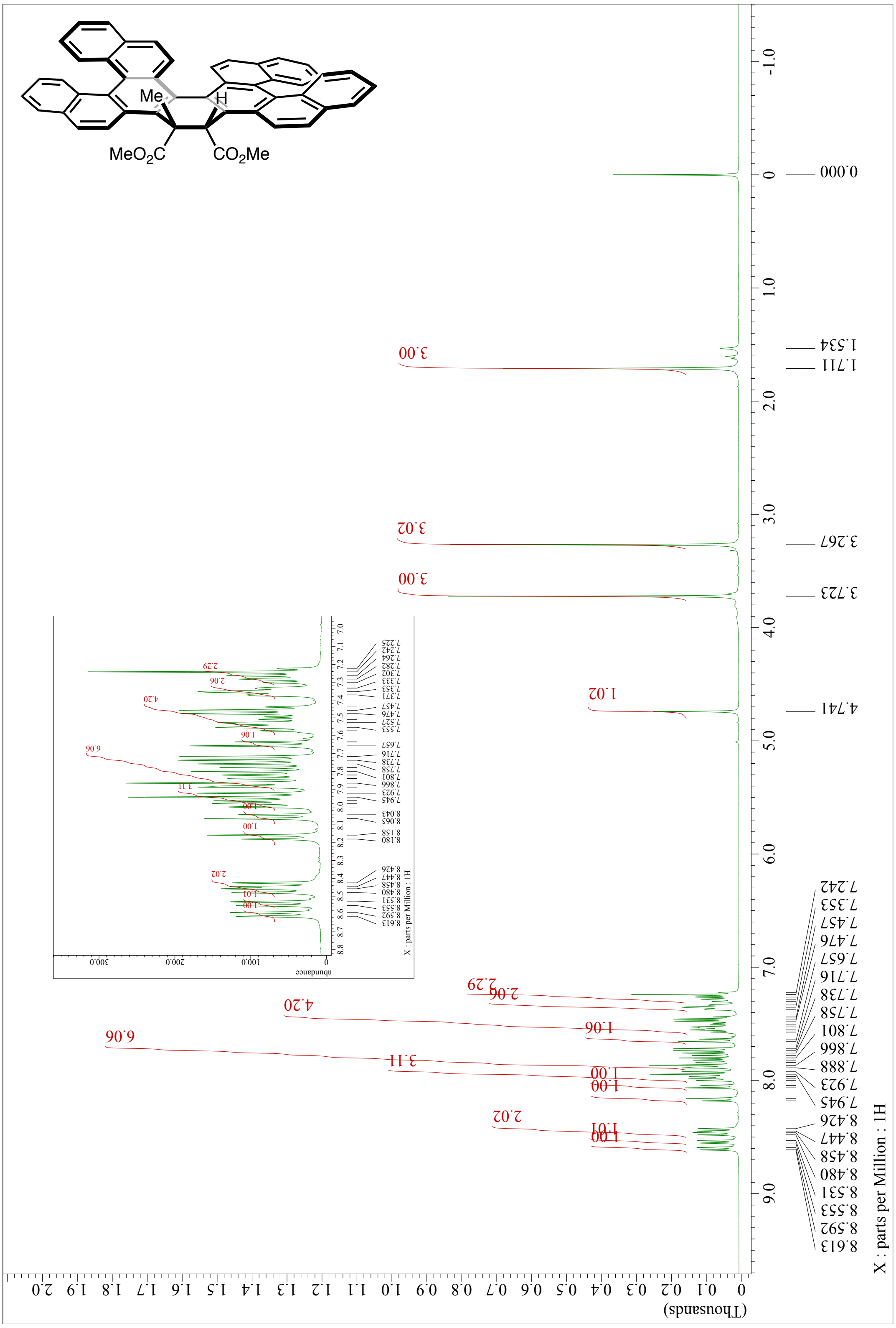


Figure S13. ^{1}H NMR spectrum of *cis*-(*P**, *P**, *R*$_{ax}$*, 1*R**, 2*S**)-DH-4bx.

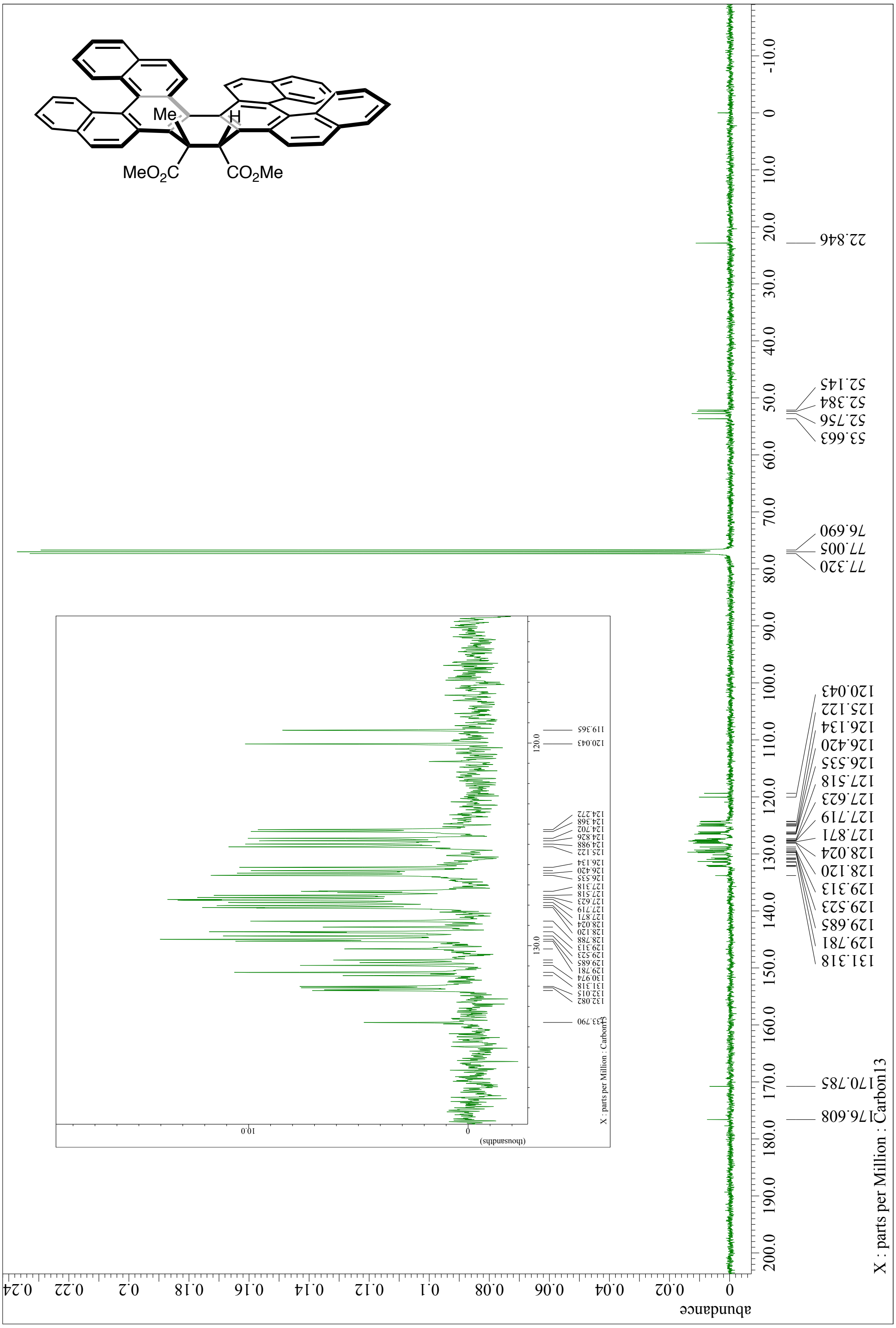


Figure S14. ^{13}C NMR spectrum of *cis*-(*P**, *P**, *R*$_{ax}$*, 1*R**, 2*S**)-DH-4bx.

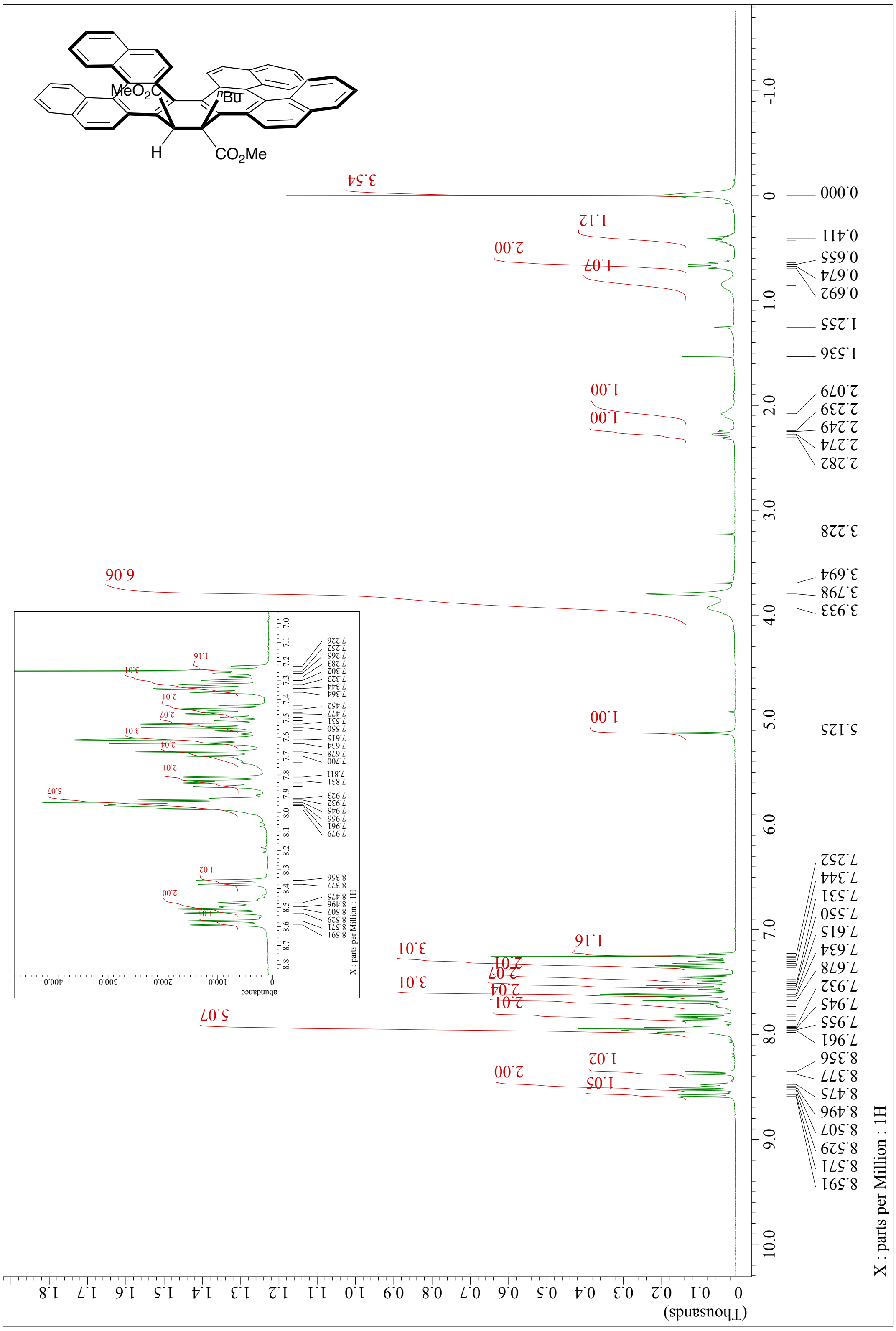


Figure S15. ^{1}H NMR spectrum of *trans*-(*P**, *P**, *R*$_{ax}$*, 1*S**, 2*S**)-DH-4ay.

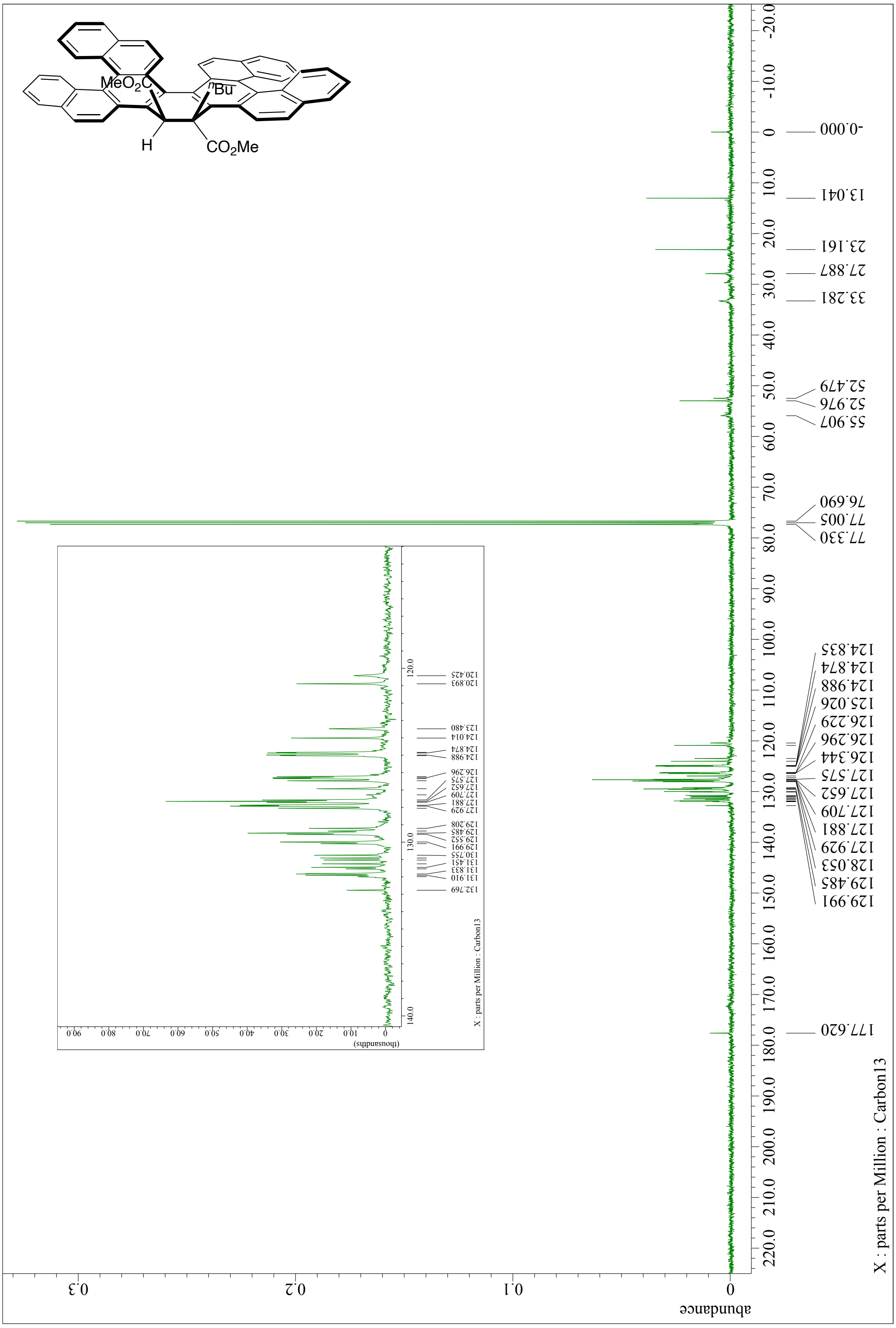


Figure S16. ^{13}C NMR spectrum of ***trans*-(*P**, *P**, R_{ax}*, 1*S**, 2*S**)-DH-4ay.**

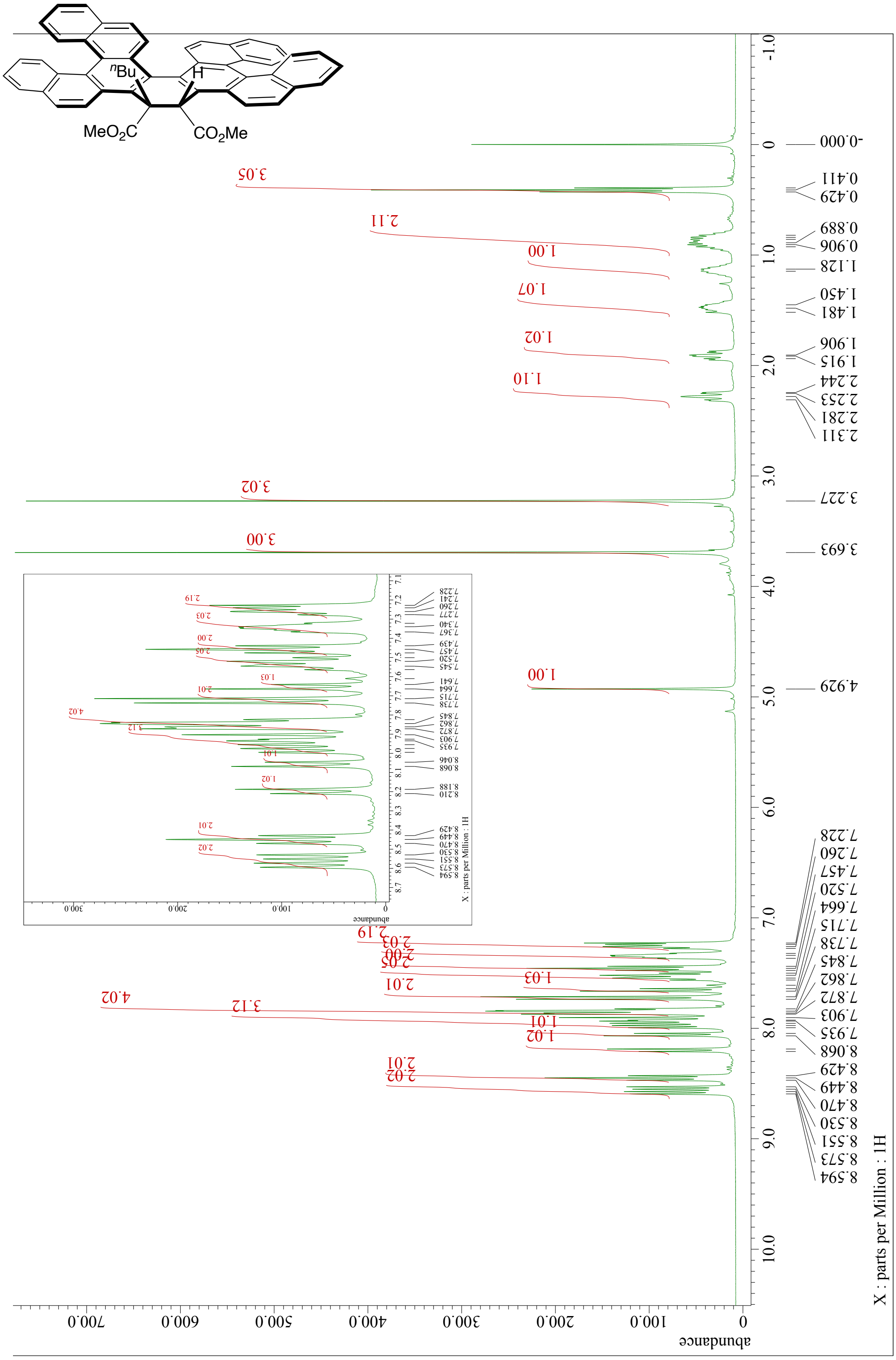


Figure S17. ^{1}H NMR spectrum of *cis*-(*P**, *P**, R_{ax}*, 1*R**, 2*S**)-DH-4by.

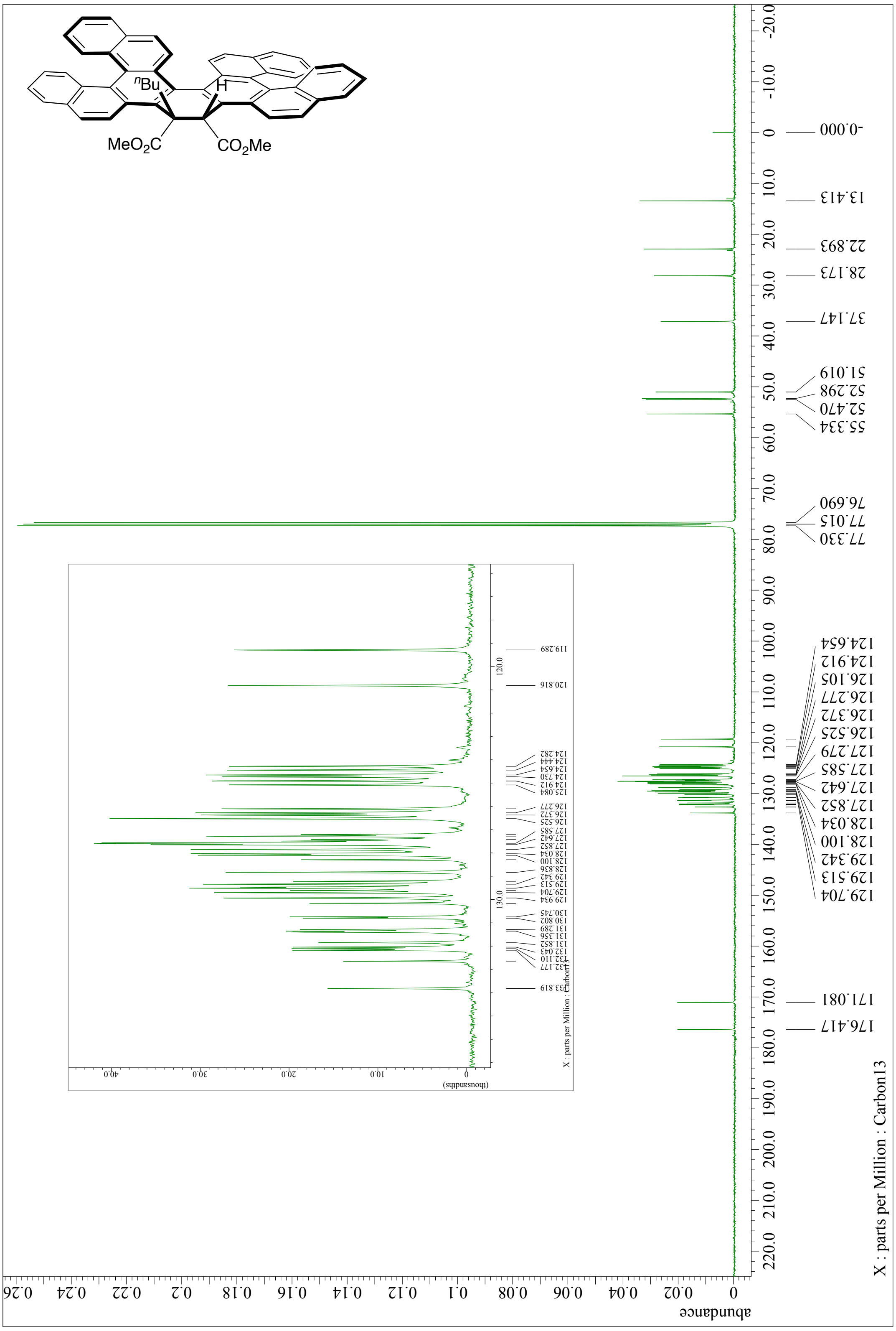


Figure S18. ^{13}C NMR spectrum of *cis*-(*P**, *P**, *R*$_{ax}$*, 1*R**, 2*S**)-DH-4by.

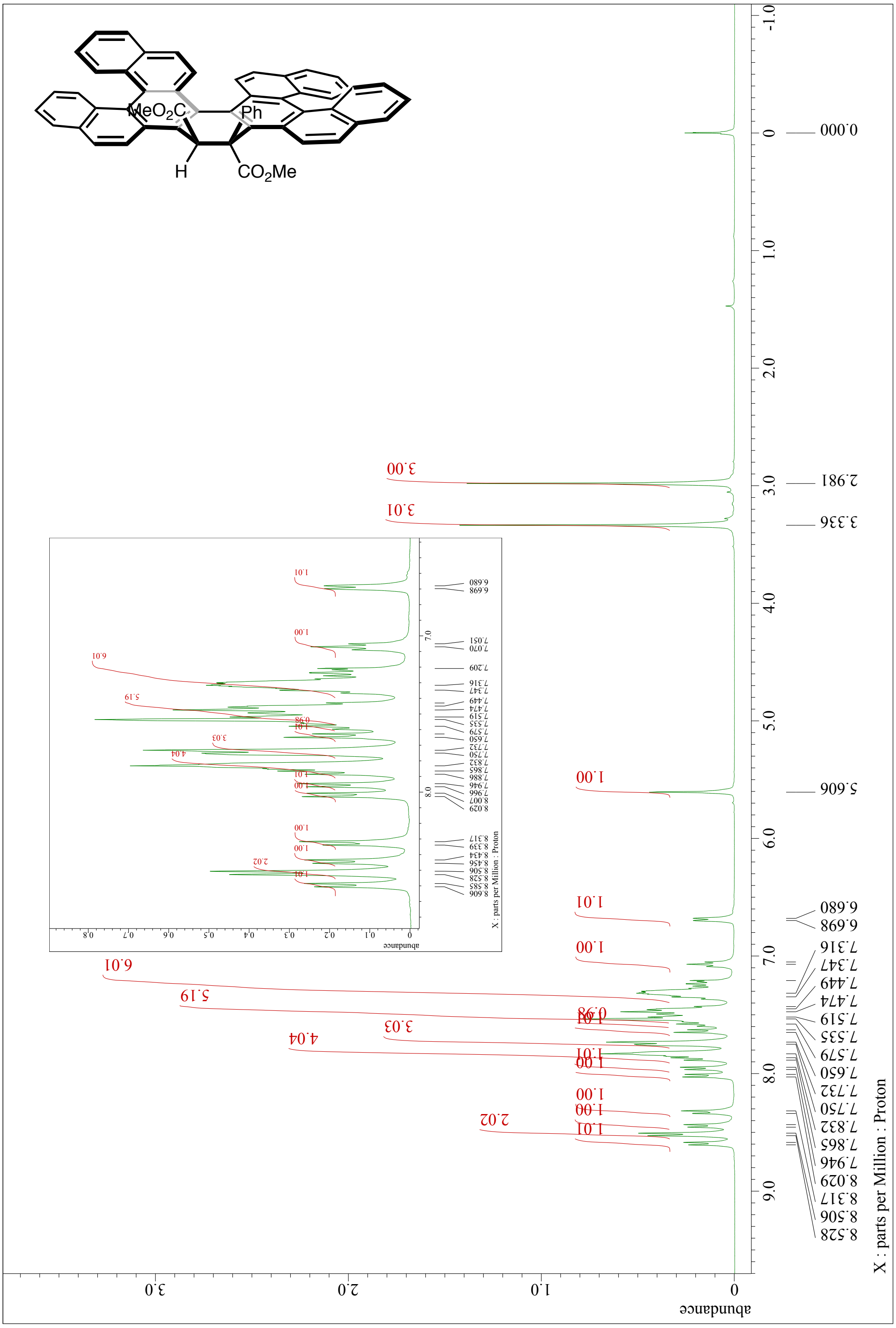


Figure S19. ^{1}H NMR spectrum of *trans*-(*P**, *P**, R_{ax}*, 1*S**, 2*S**)-DH-4az.

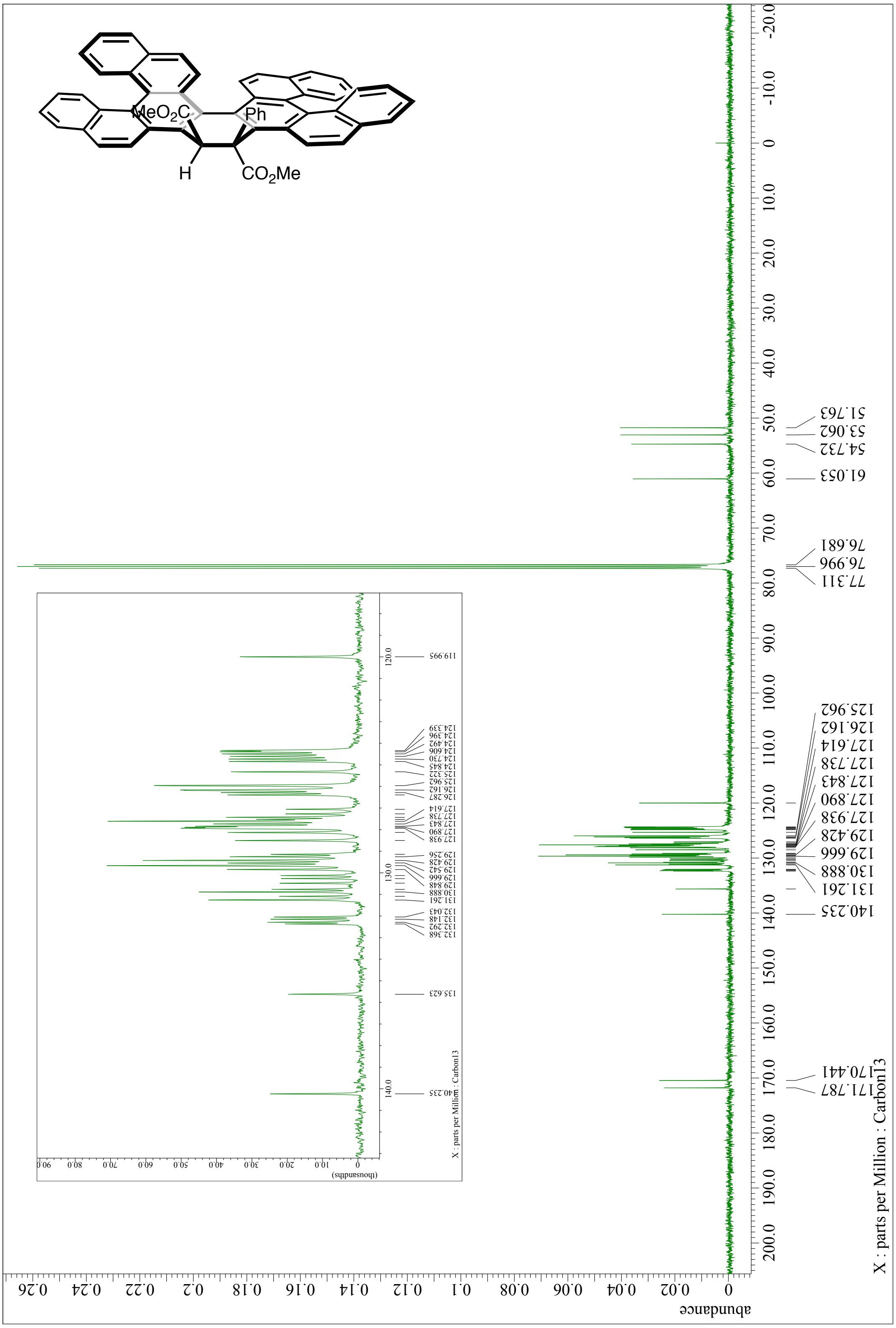


Figure S20. ^{13}C NMR spectrum of ***trans*-(*P**, *P**, R_{ax}*, 1*S**, 2*S**)-DH-4az.**

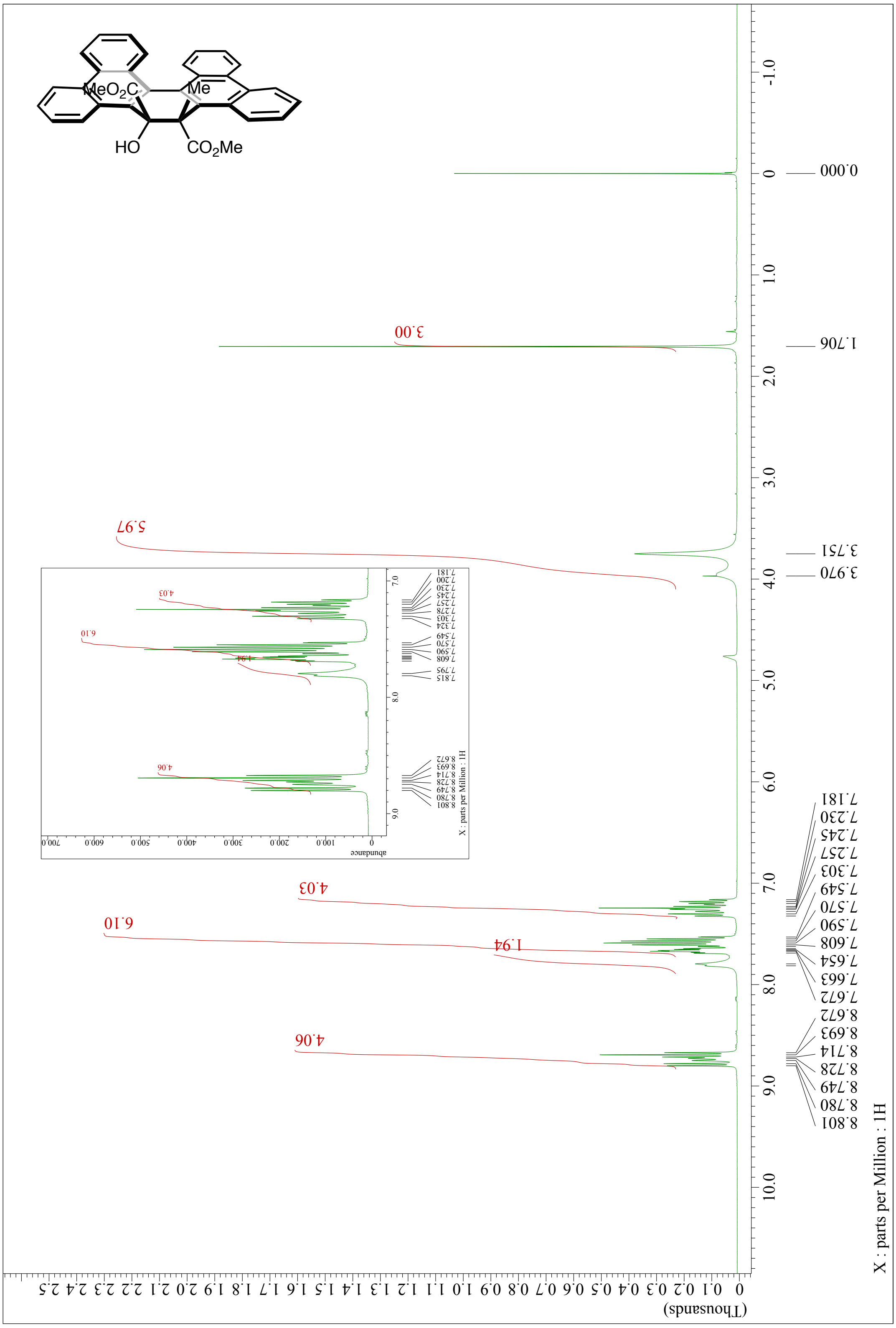


Figure S21. ^{1}H NMR spectrum of *trans*-dimethyl-1-hydroxy-2-methyl-1,2-dihydrodibenzo[*f*,*j*]picene-1,2-dicarboxylate 6a.

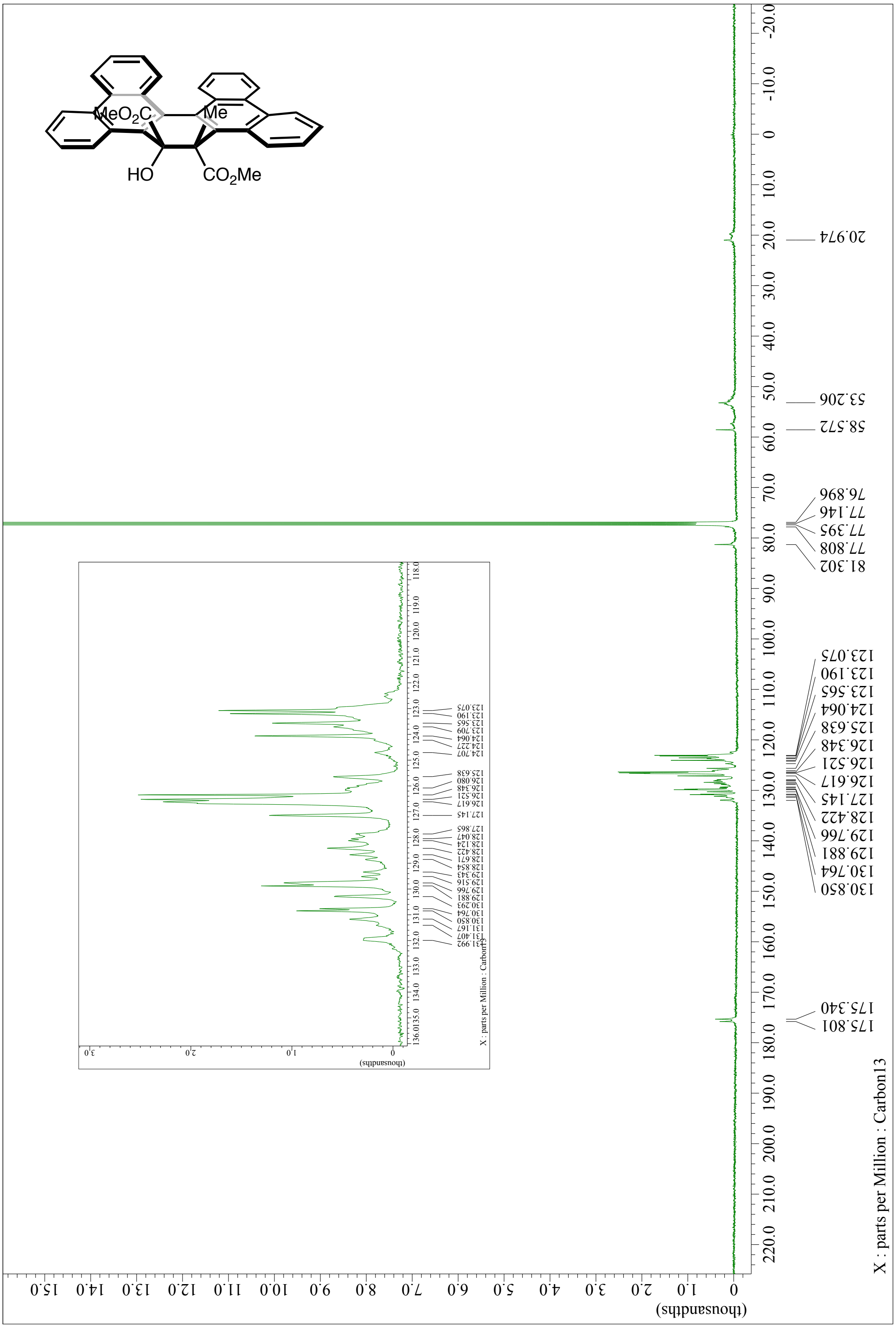


Figure S22. **^{13}C NMR spectrum of *trans*-dimethyl-1-hydroxy-2-methyl-1,2-dihydrodibenzo[*f,j*]picene-1,2-dicarboxylate 6a.**

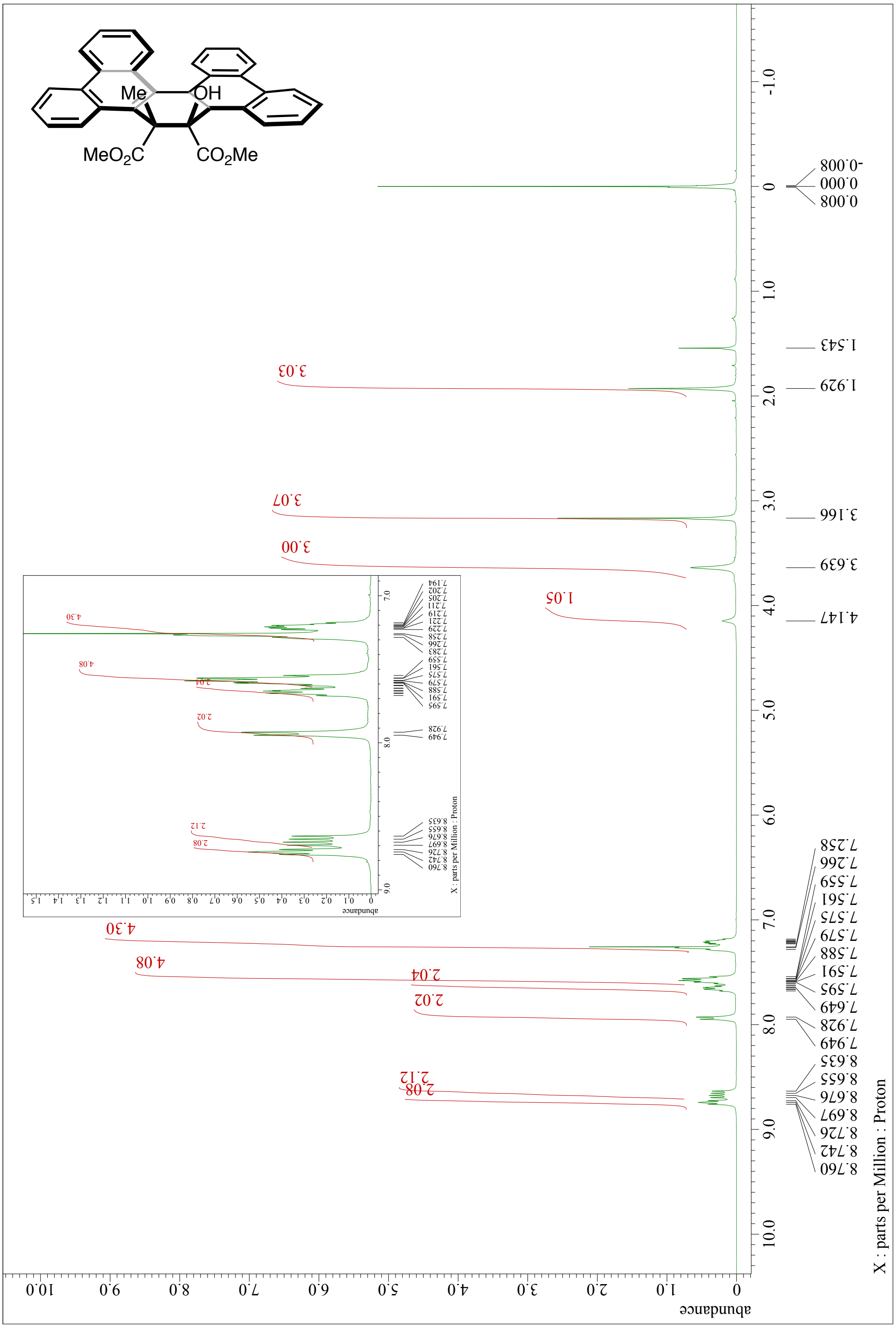


Figure S23. **^{1}H NMR spectrum of *cis*-dimethyl-1-hydroxy-2-methyl-1,2-dihydrodibenzo[*f,j*]picene-1,2-dicarboxylate 6b**

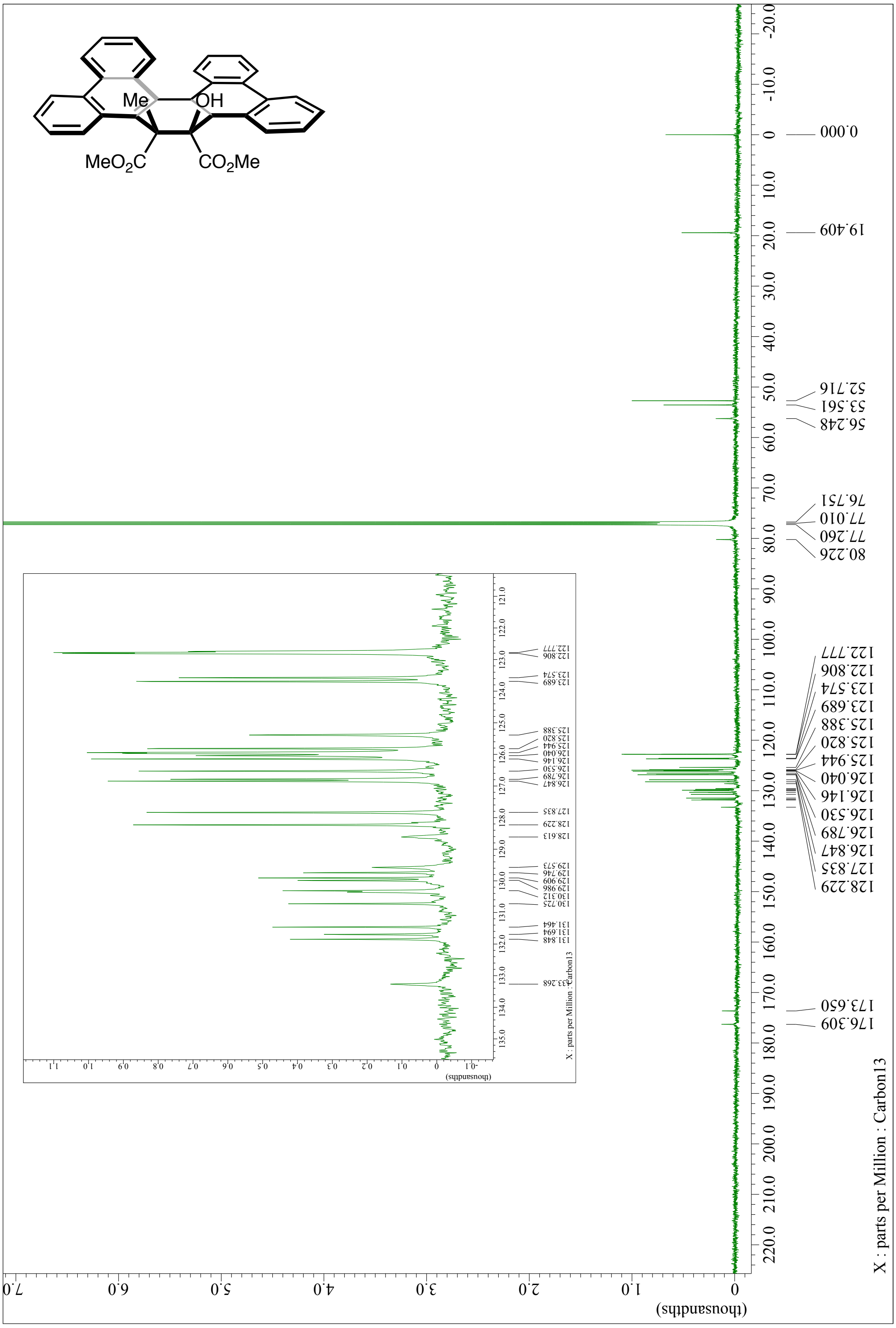


Figure S24. **^{13}C NMR spectrum of *cis*-dimethyl-1-hydroxy-2-methyl-1,2-dihydrodibenzo[*f,j*]picene-1,2-dicarboxylate 6b.**

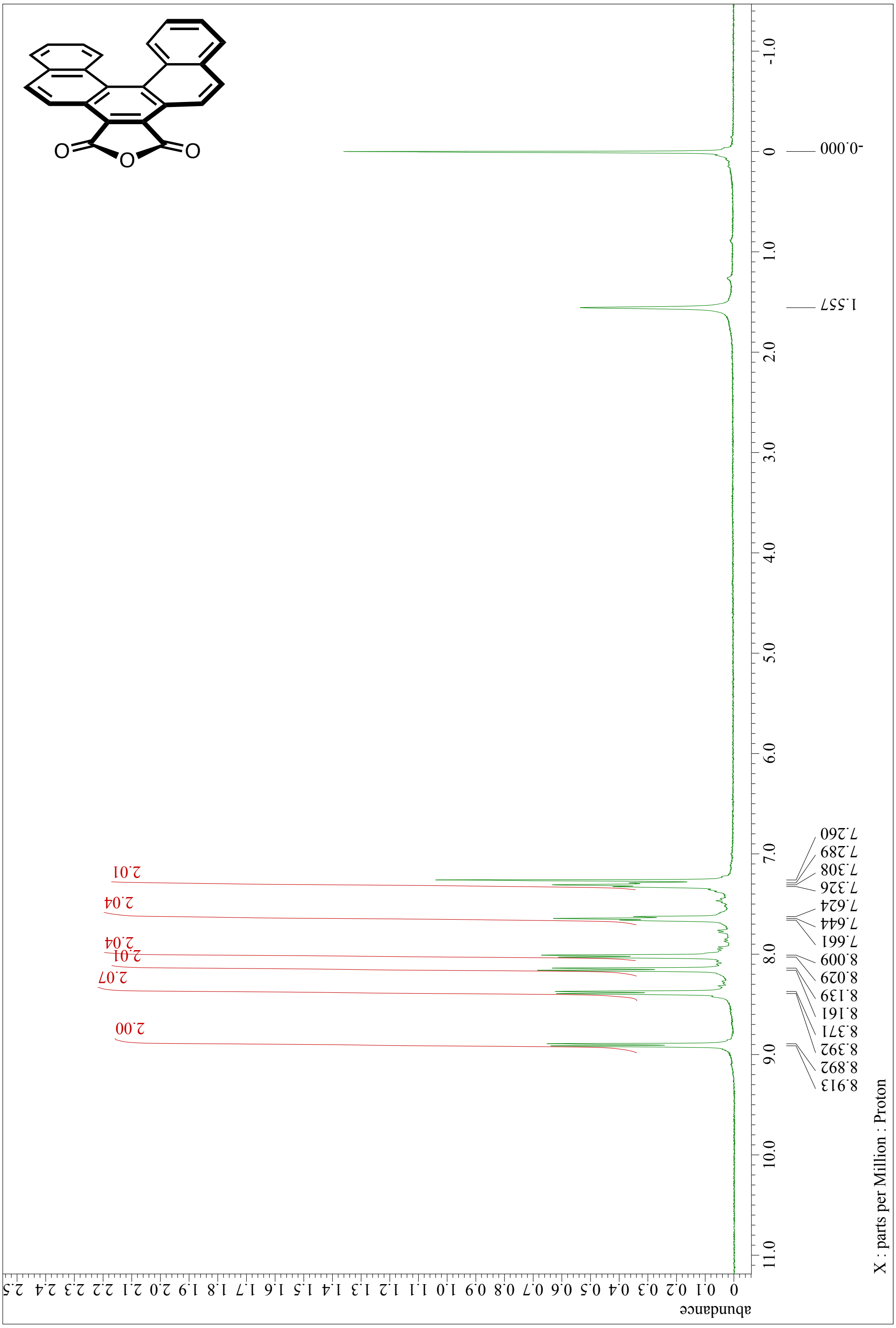


Figure S25. ^{1}H NMR spectrum of S2.

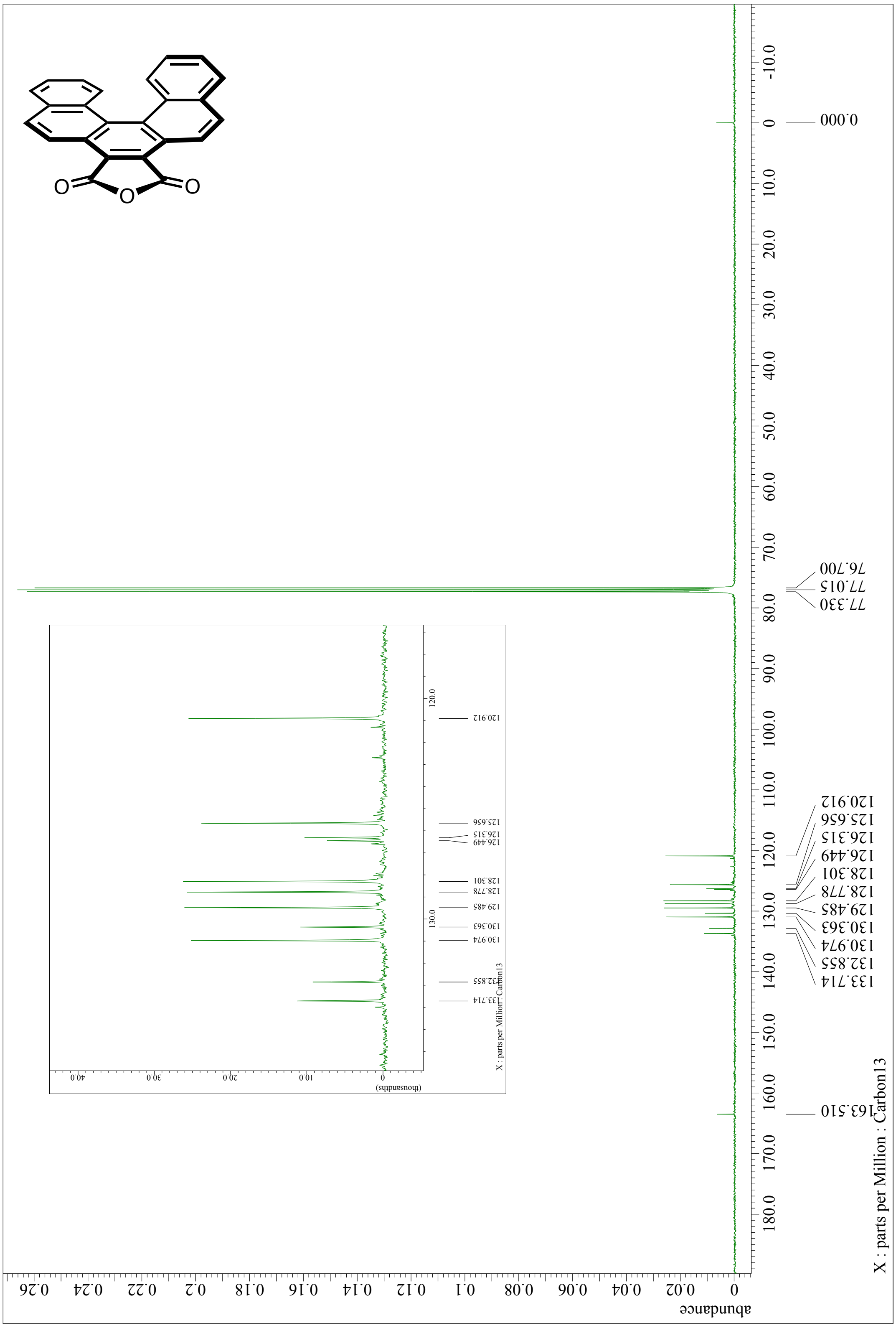


Figure S26. ^{13}**C NMR spectrum of S2.**

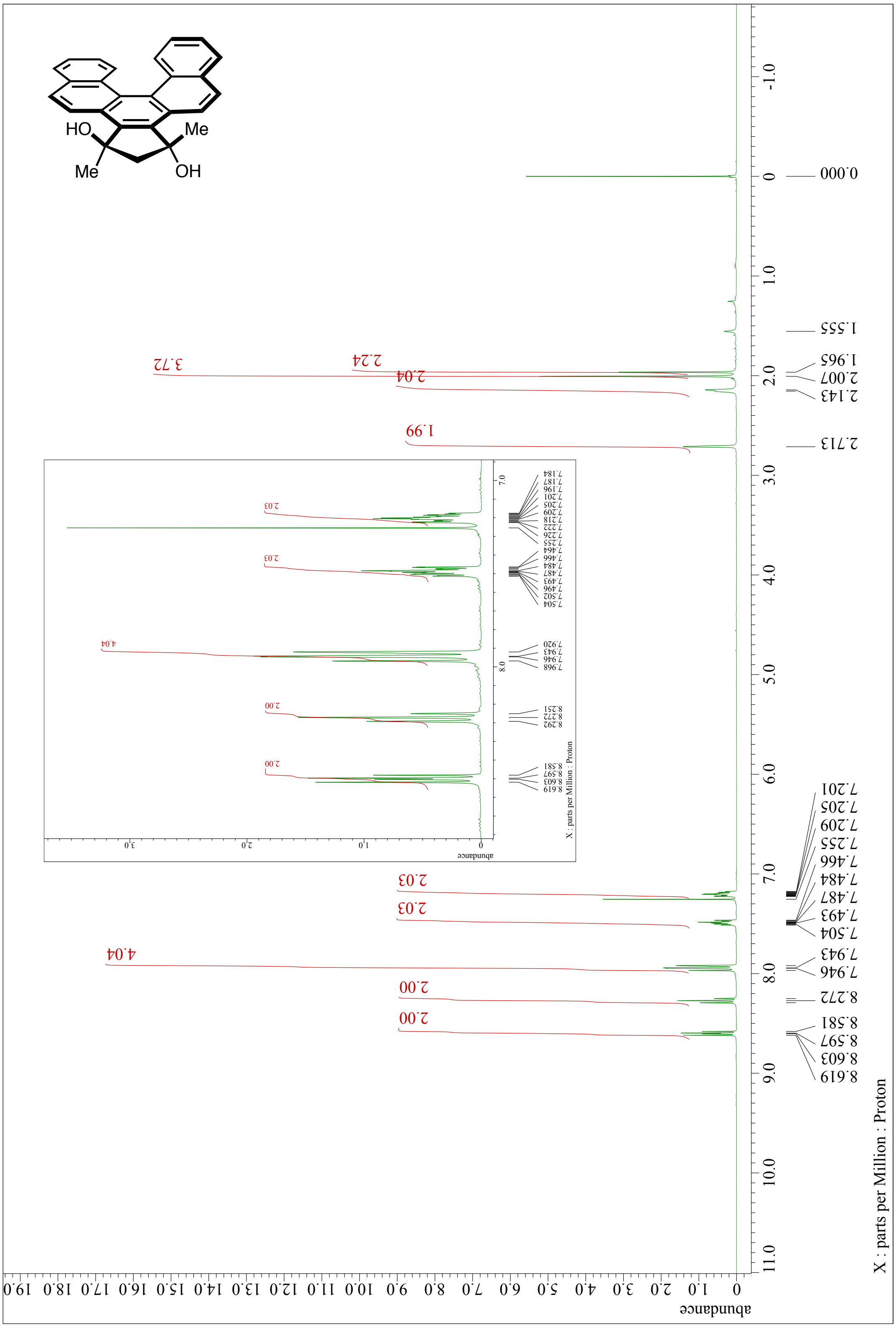


Figure S29. **^{1}H NMR spectrum of *trans*-1,3-dimethyl-2,3-dihydro-1*H*-dibenzo[*c*,*g*]cyclopenta[*l*]phenanthrene-1,3-diol 8.**

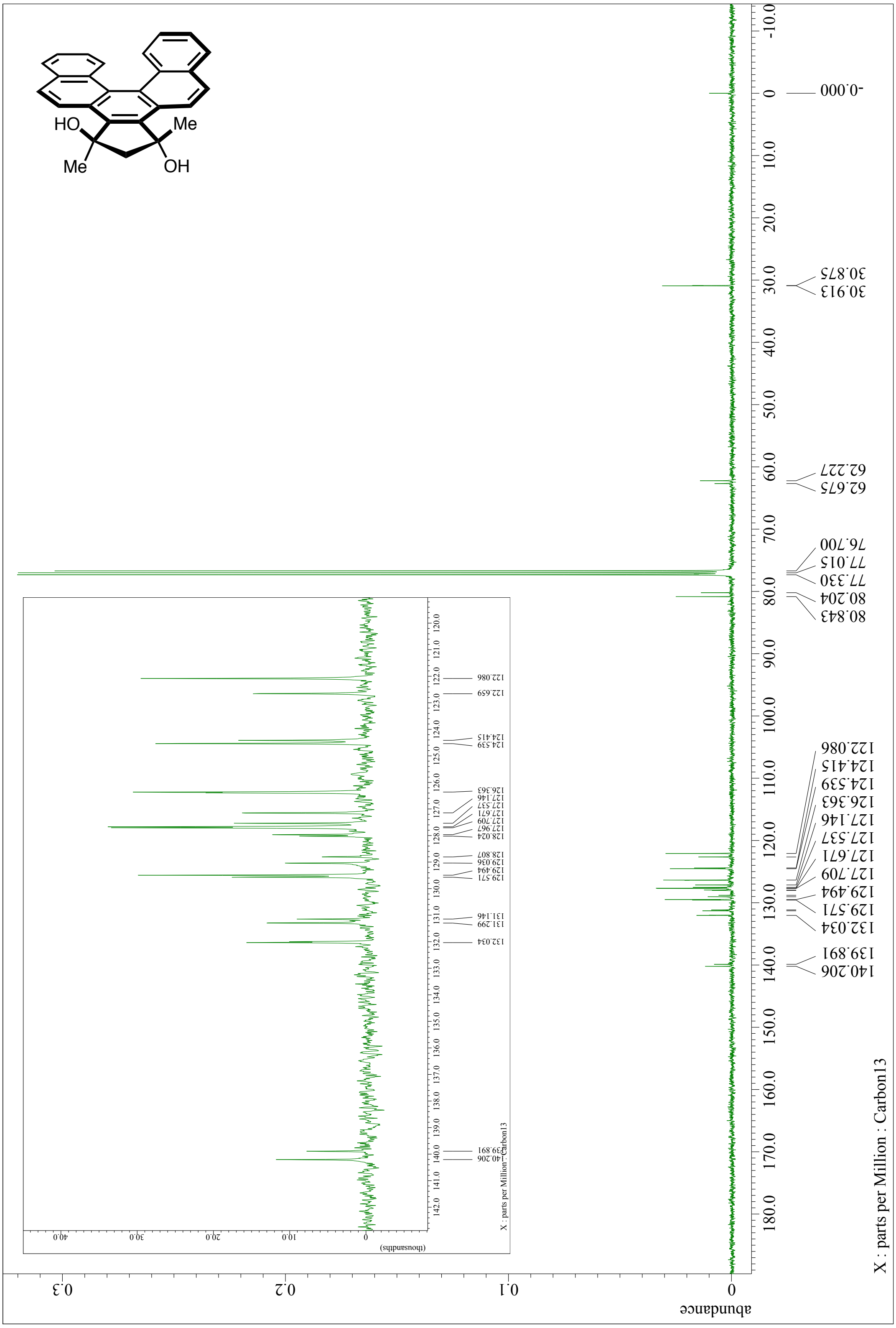


Figure S30. ^{13}C NMR spectrum of ***trans***-1,3-dimethyl-2,3-dihydro-1***H***-dibenzo[***c***,***g***]cyclopenta[***l***]phenanthrene-1,3-diol 8.

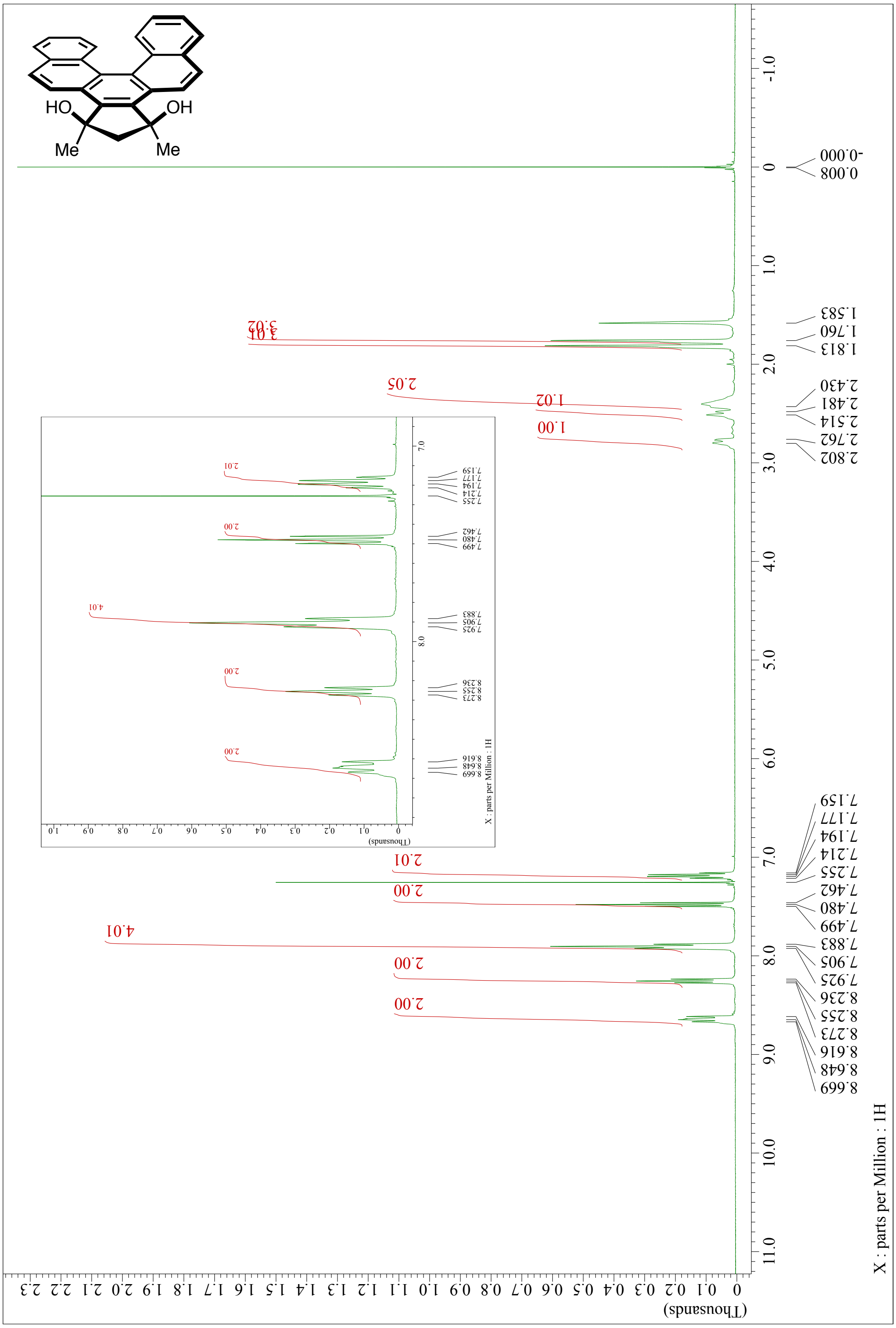


Figure S27. ^{1}**H NMR spectrum of *cis*-1,3-dimethyl-2,3-dihydro-1*H*-dibenzo[*c*,*g*]cyclopenta[*l*]phenanthrene-1,3-diol 8.**

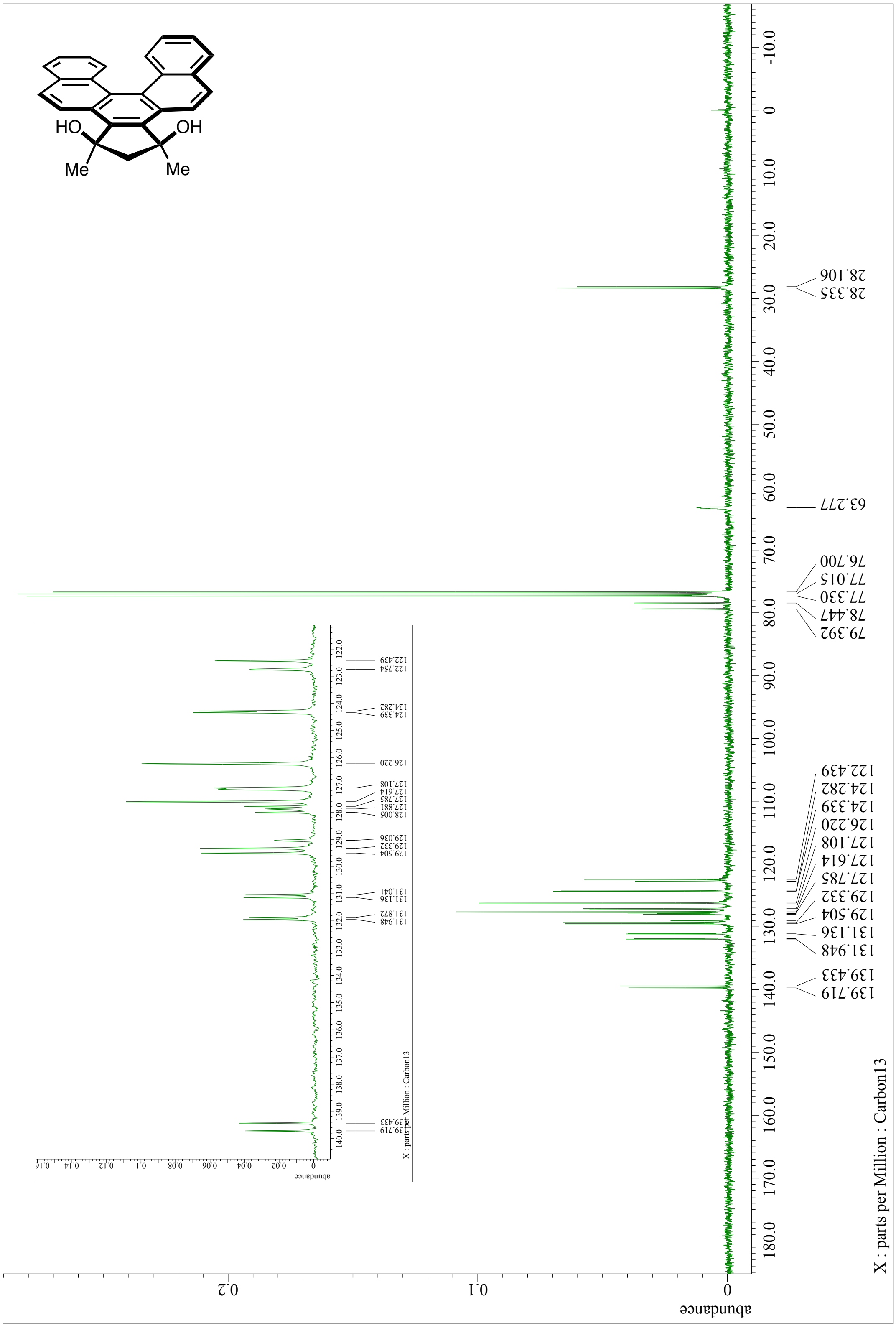


Figure S28. **^{13}C NMR spectrum of *cis*-1,3-dimethyl-2,3-dihydro-1*H*-dibenzo[*c*,*g*]cyclopenta[*l*]phenanthrene-1,3-diol 8.**

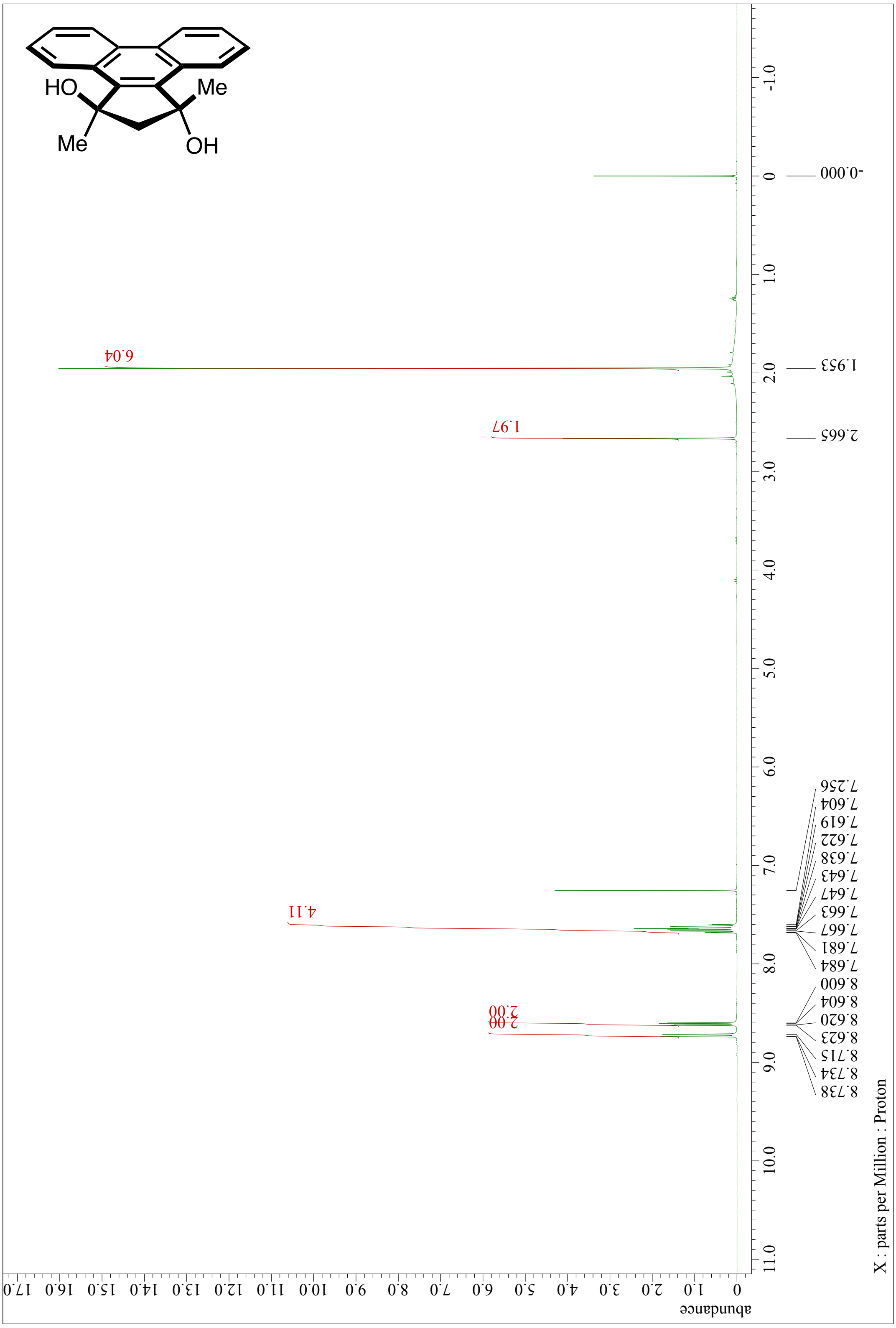


Figure S33. ^{1}H NMR spectrum of *trans*-1,3-dimethyl-2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene-1,3-diol 10.

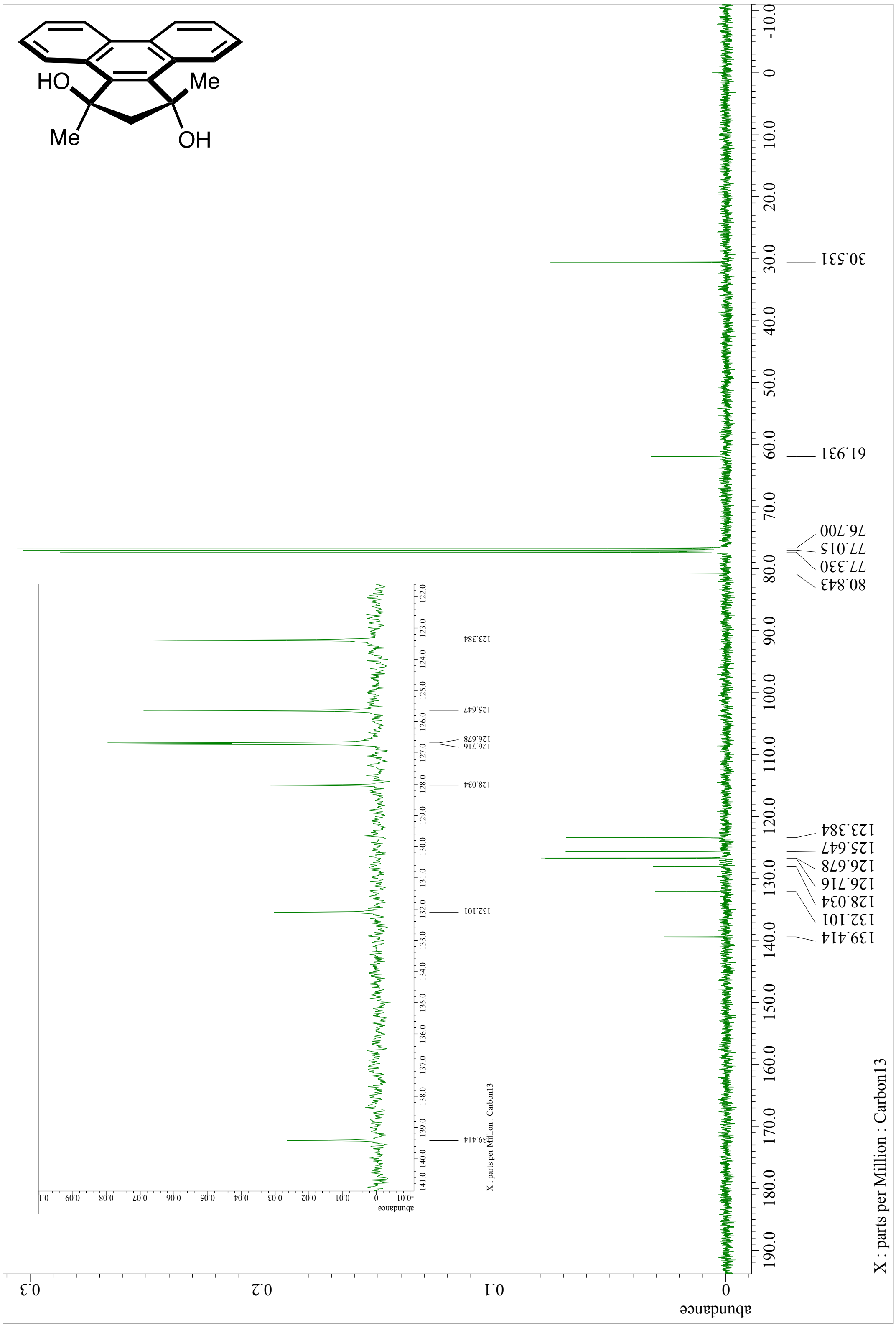


Figure S34. ^{13}C NMR spectrum of ***trans*-1,3-dimethyl-2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene-1,3-diol 10.**

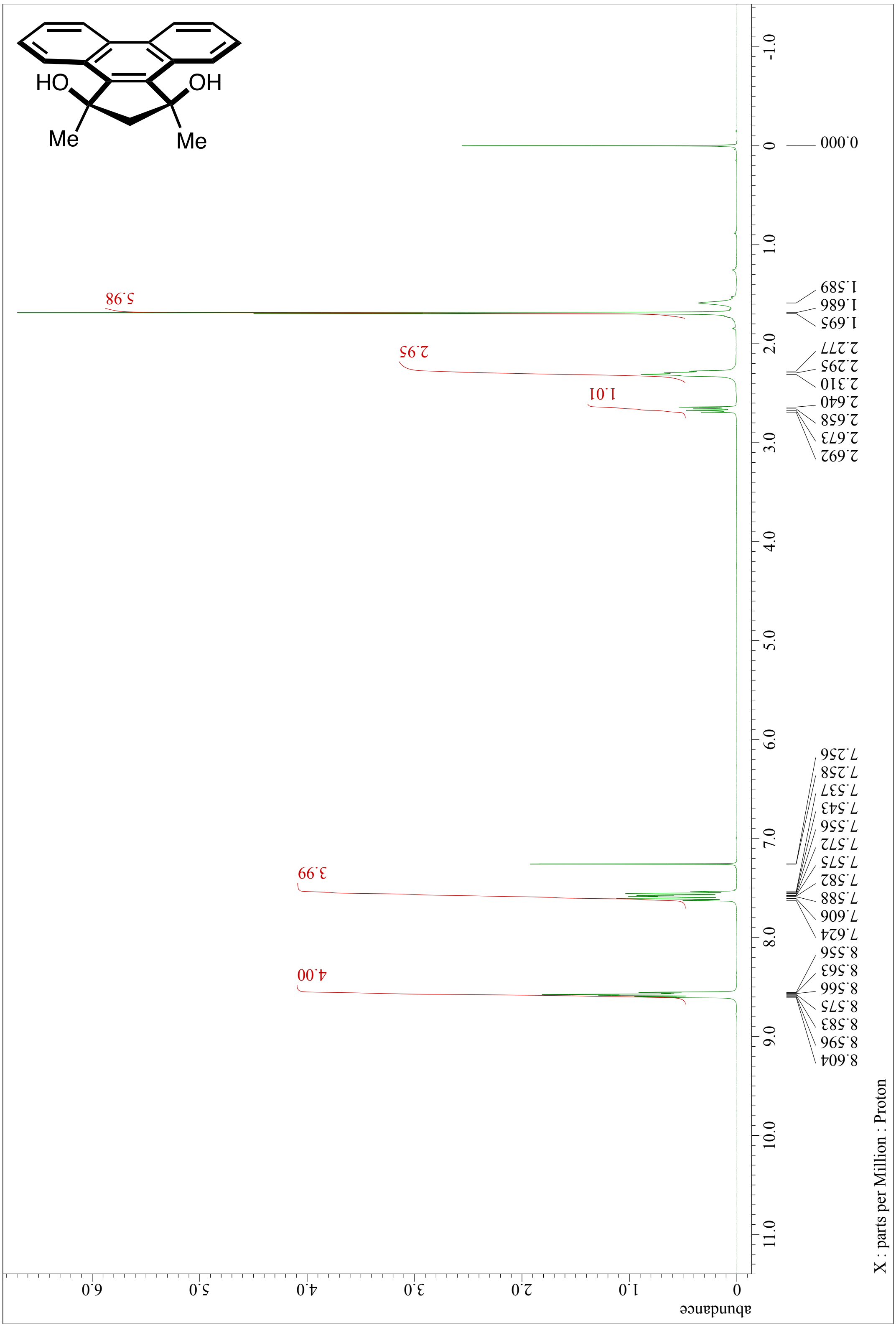


Figure S31. **^{1}H NMR spectrum of *cis*-1,3-dimethyl-2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene-1,3-diol 10a.**

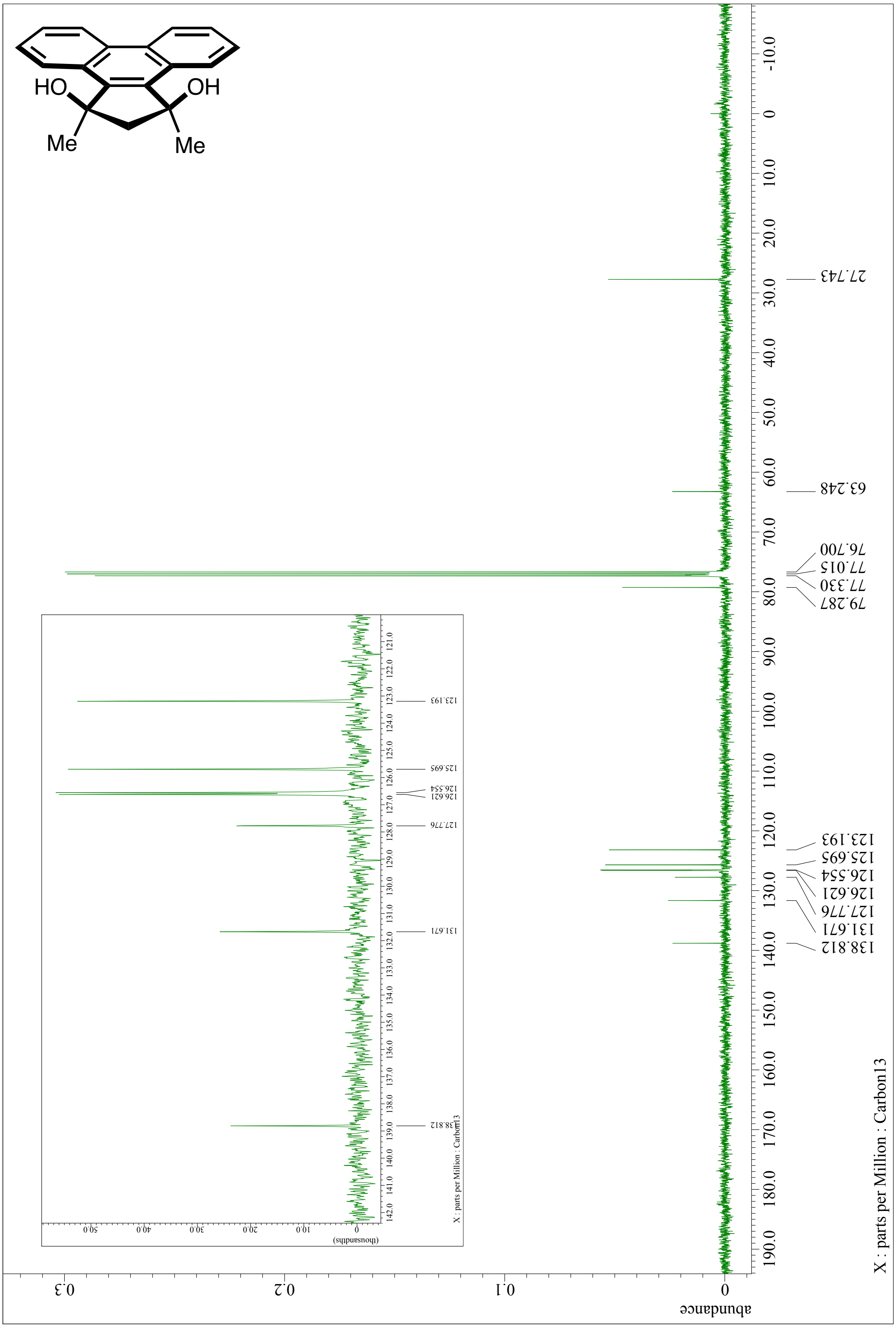
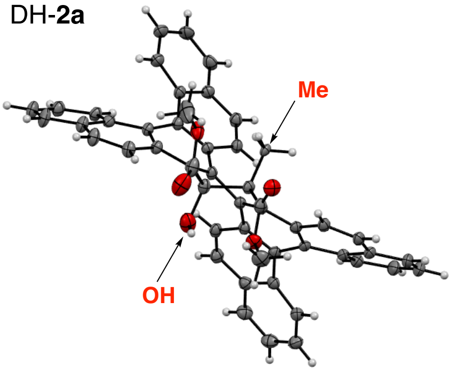


Figure S32. **^{13}C NMR spectrum of *cis*-1,3-dimethyl-2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene-1,3-diol 10a.**

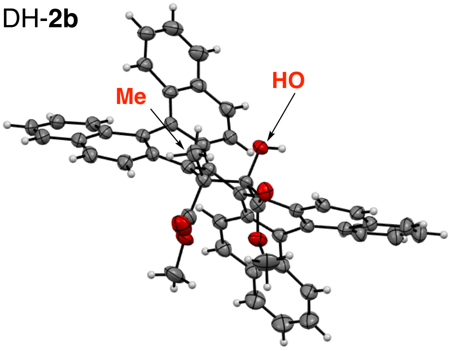
3. X-ray Crystallographic Analysis

Single crystals of **2a**, **2b**, **2c**, and **2d** were grown by CS_2/Et_2O at −20 °C (for **2a**), CH_2Cl_2/Et_2O at −20 °C (for **2b** and **2c**), and CH_2Cl_2/MeOH at −20 °C (for **2d**). X-Ray data were collected on a Rigaku Saturn diffractometer with VariMax multi-layer mirror monochromated Mo-Kα radiation (λ = 0.71073 Å) at −170 °C. The data were corrected for Lorentz and polarization effects. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the REQABS program in CrystalClear software. The structures were solved by direct methods (SIR2014[S5] for **2a** and **2b** or SHELXS-2013[S6] for **2c** and **2d**) and refined by full-matrix least squares against F^2 using all data. Non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were generated by AFIX instructions. The major isomer DH-**2a** crystallized with three independent molecules in the unit cell. The contribution of severely disordered solvent molecules in **2a** and **2b** was subtracted from the reflection data using the SQUEEZE routine in PLATON software package.[S7] All calculations were performed using Yadokari-XG 2009[S8] software package except for refinement, which was performed using SHELXL-2013.[S9]

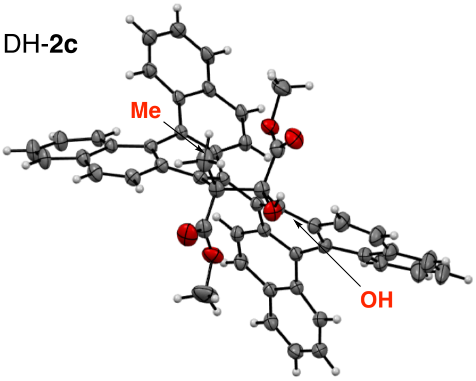
DH-**2a**



DH-**2b**



DH-**2c**



DH-**2d**

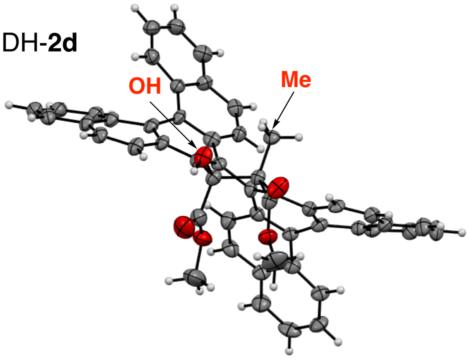
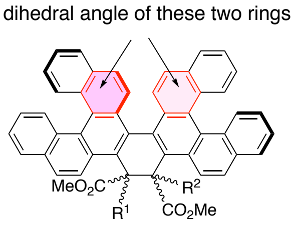


Table S1. Crystal Data for **2a**–**d**.

	2a	**2b**	**2c**	**2d**
Formula	$C_{156}H_{102}O_{15}S_6$	$C_{51}H_{34}O_5$	$C_{59}H_{54}O_7$	$C_{53}H_{36}Cl_2O_6$
Formula weight	2408.73	726.78	875.02	839.72
Crystal Size/mm	0.23 × 0.18 × 0.14	0.19 × 0.13 × 0.10	0.25 × 0.22 × 0.11	0.14 × 0.06 × 0.04
Temperature/ °C	−170	−170	−170	−170
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	*P*-1 (#2)	*P*-1 (#2)	*P*-1 (#2)	*P*-1 (#2)
Lattice parameters				
a/Å	14.695(3)	11.493(9)	11.541(4)	11.523(6)
b/Å	20.709(4)	13.905(10)	14.334(7)	12.874(7)
c/Å	22.202(4)	15.123(10)	15.473(6)	14.864(6)
α/°	79.292(4)	69.85(3)	94.345(16)	75.48(3)
β/°	80.514(4)	68.97(2)	108.46(2)	75.27(3)
γ/°	89.184(5)	83.25(3)	110.631(14)	87.03(4)
V/Å^3	6547(2)	2118(3)	2221.1(16)	2064.3(18)
Z	2	2	2	2
D_{calc} /g cm^{-3}	1.222	1.140	1.308	1.351
μ (cm^{-1})	0.169	0.073	0.085	0.211
$2\theta_{max}$/°	55.0	55.0	55.0	55.0
No. of reflections	68195	20986	22810	16632
Independent reflections	29547	9445	9989	8983
No. of parameters	1787	511	597	564
R_{int}	0.0471	0.0499	0.0334	0.0436
Completeness to θ (%)	99.2	99.0	98.9	97.9
R_1 [I>2σ(I)]	0.0834	0.0627	0.0760	0.1047
wR_2 (all data)	0.2473	0.1881	0.2486	0.3464
Largest diff. peak (e.Å^{-3})	0.820	0.325	0.760	0.703
Largest diff. hole (e.Å^{-3})	−1.236	−0.409	−0.669	−0.862
Goodness-of-fit	1.065	0.905	1.066	1.039

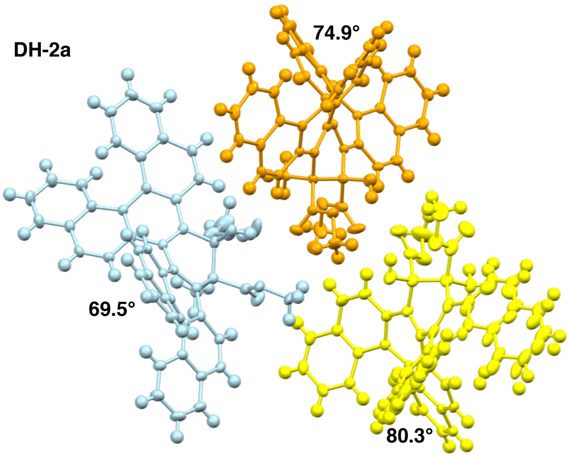
Table S2. Dihedral angles of internal biaryl unit for DH-**2a**–**d**.



$R^1 \neq R^2$: Me or OH

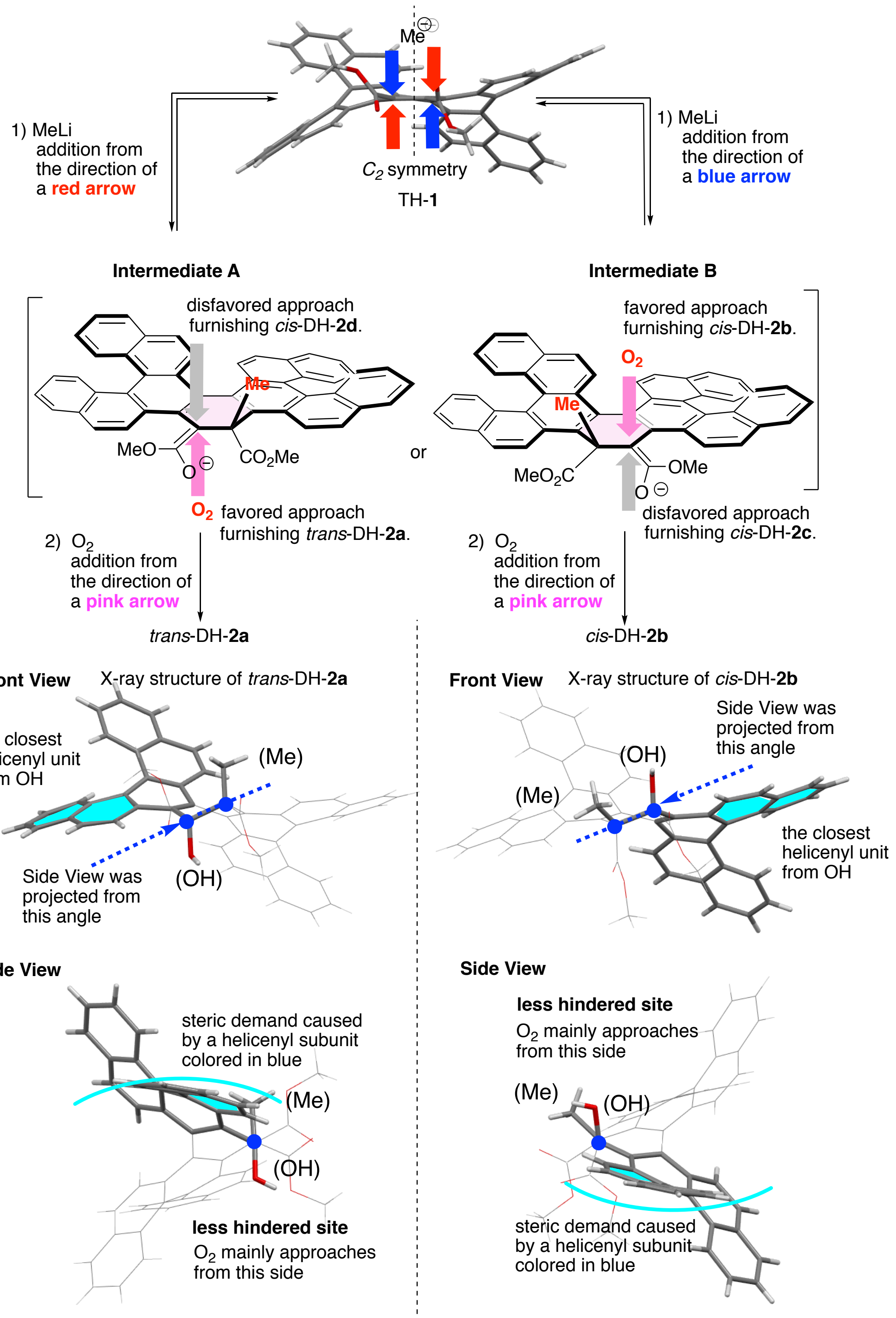
DH-2a	DH-2b	DH-2c	DH-2d
69.5° 74.9° 80.3°	84.2°	81.8°	78.8°

DH-2a



4. Stereochemical outcome for the formation of DH-2a-2d.

Figure S33.



5. HPLC analysis of optically active DH-2a and DH-2b

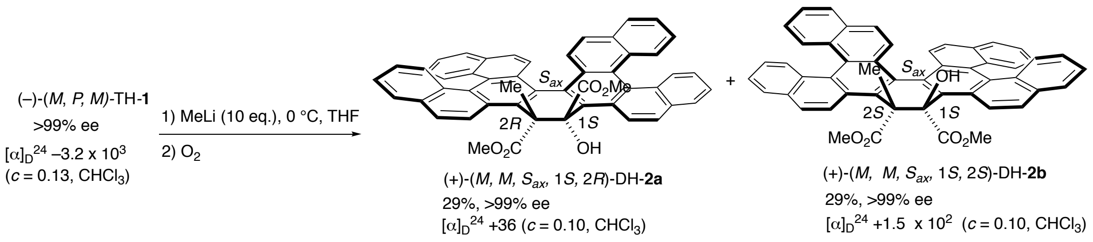
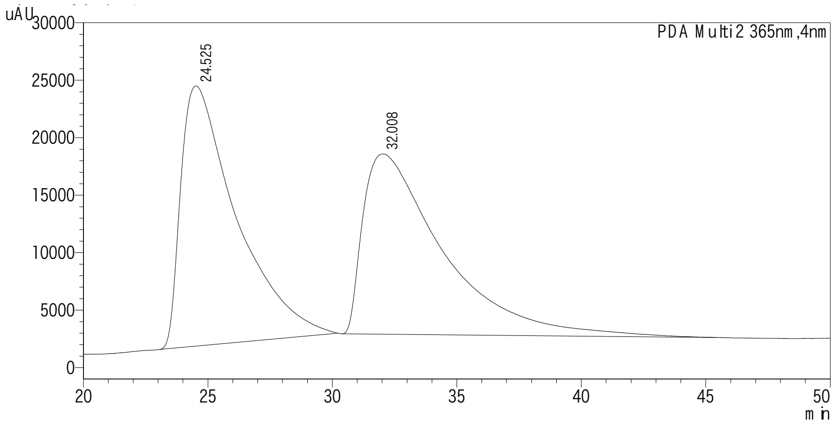
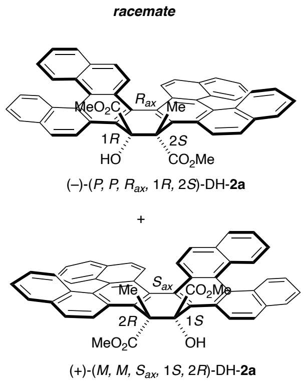


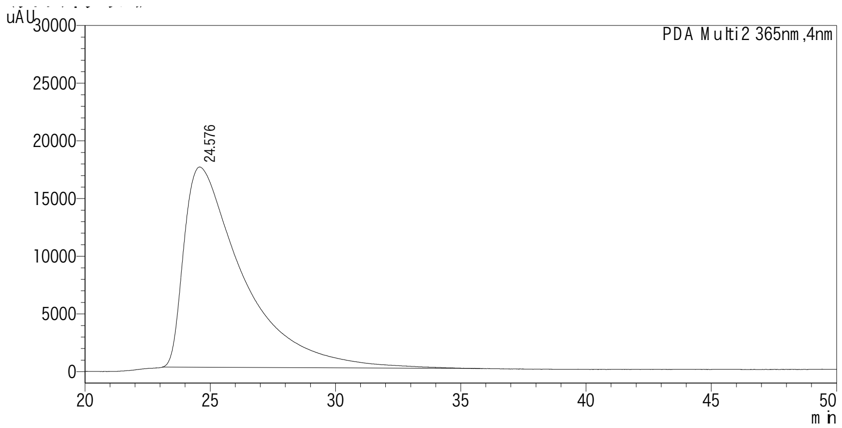
Figure S34. HPLC of DH-**2a**

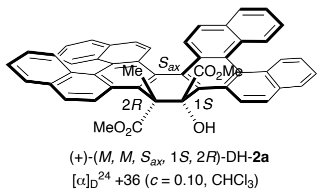
Condition: CHIRALPAK IB, Hexane/^{i}PrOH = 19/1, 0.5 mL/min, 365 nm





peak#	retention time (min)	area	height	area%
1	24.525	3512921	22630	49.965
2	32.008	3517803	15671	50.035
total	–	7030723	38301	100.000

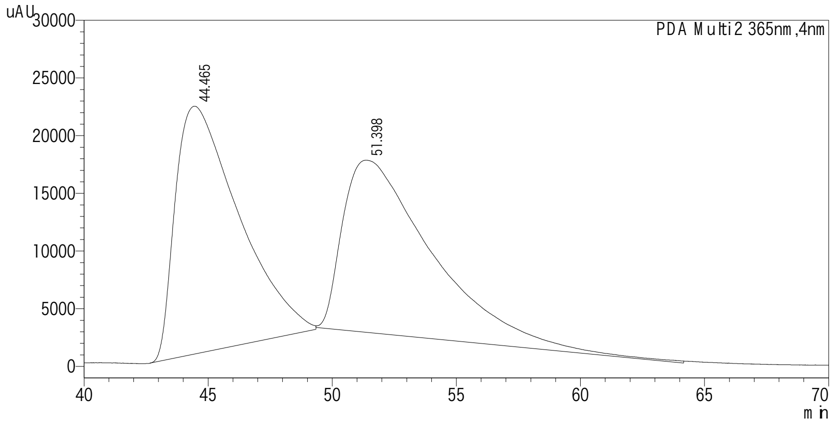




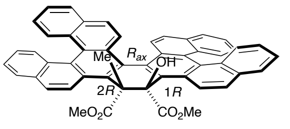
peak#	retention time (min)	area	height	area%
1	24.576	2869272	17365	100.000
–	not detected	–	–	–
total	–	2869272	17365	100.000

Figure S35. HPLC analysis of DH-**2b**

Condition: CHIRALPAK IB, Hexane/^{i}PrOH = 19/1, 1.0mL/min, 365 nm

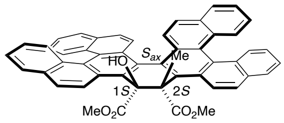


racemate



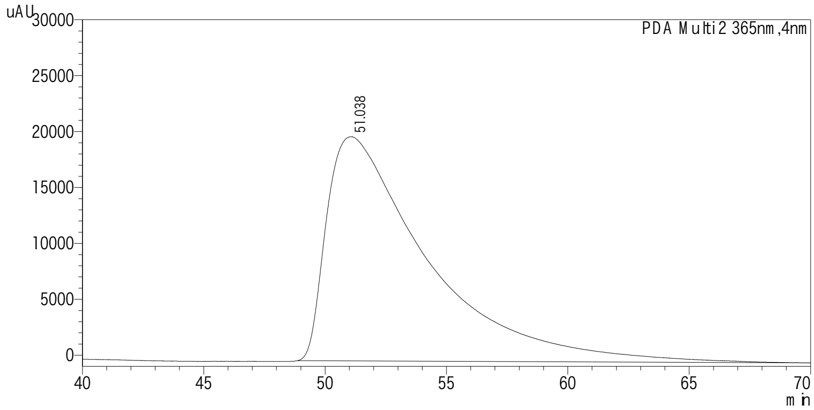
(–)-(*P*, *P*, R_{ax}, 1*R*, 2*R*)-DH-**2b**

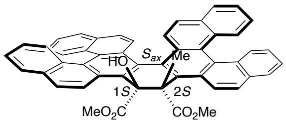
+



(+)-(*M*, *M*, S_{ax}, 1*S*, 2*S*)-DH-**2b**

peak#	retention time (min)	area	height	area%
1	44.465	3817587	21482	50.245
2	51.398	3780353	14936	49.755
total	–	7597939	36418	100.000





(+)-(*M*, *M*, S_{ax}, 1*S*, 2*S*)-DH-**2b**

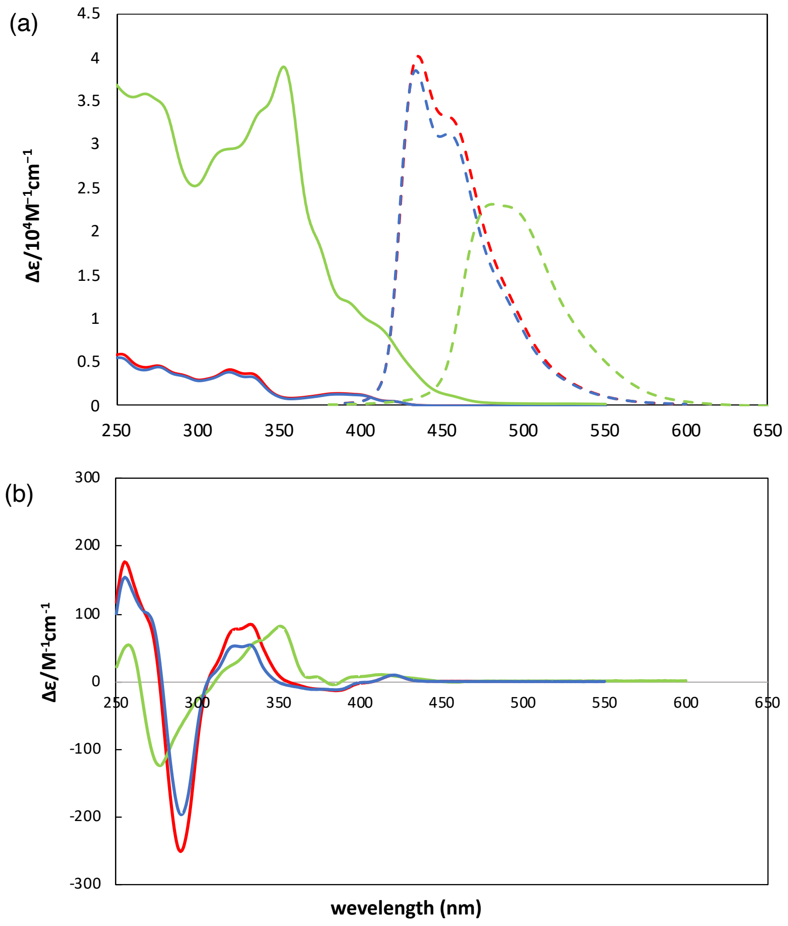
$[\alpha]_D^{24}$ +1.5 x 10^2 (*c* = 0.10, $CHCl_3$)

peak#	retention time (min)	area	height	area%
–	not detected	–	–	–
1	51.038	5807572	20042	100.000
total	–	5807572	20042	100.000

6. Photophysical Study

UV-Vis absorption spectra were measured on a JASCO V-670 spectrophotometer with dilute chloroform solution in spectral grade solvent at room temperature with a 1 cm square quarts cell. Emission spectra were measured on a JASCO FP-6200 spectrofluorometer with dilute solutions in spectral grade solvent in a 1 cm square quartz cell upon the excitation at 320 nm. Circular dichroism (CD) spectra were measured on a JASCO J-820 spectrometer at 20 ºC (PTC-423L thermostat, JASCO) with a dilute chloroform solution in a 1 mm quartz cell.

Figure S36. (a) UV-vis absorption (solid line) and photoluminescence (dashed line) spectra, (b) CD spectra of (–)-TH-**1** (green), (+)-DH-**2a** (red) and (+)-DH-**2b** (blue) in $CHCl_3$.



7. Theoretical Calculations

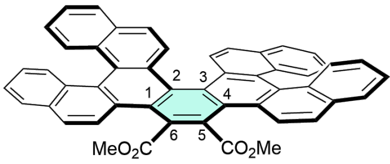
Theoretical calculations were performed using the Gaussian 09[S10] programs on a NEC LX 110Rh-1 system of the Research Center for Computational Science, Japan. All structures were optimized without any symmetry assumptions unless otherwise noted. Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated from the gas-phase studies. The structure of local minimums of (*M,P,M*)-**TH-1**, (*P*)-**5**, (*P*)-**7**, and **9** were optimized at B3LYP/6-31G(d) level,[S11] and the GIAO calculations were carried out at B3LYP/6-311+G(2d,p) level. Molecular orbitals are visualized by the use of GaussView 5.0.9 software.

Table S3. Uncorrected and thermal-corrected (298 K) energies of stationary points (Hartree).[a]

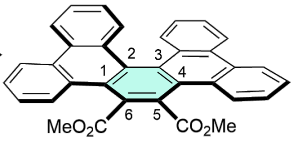
Structure	*E*	*E* + *ZPE*	*H*	G
(*M*,*P*,*M*)-**TH-1**	-2224.35865269	-2223.703879	-2223.662571	-2223.776016
(*P*)-**5**	-1609.81737841	-1609.349398	-1609.318904	-1609.409043
(*P*)-**7**	-1302.54102203	-1302.167296	-1302.142112	-1302.222394
9	-995.273557394	-994.993289	-994.973385	-995.042725

a) *E*: electronic energy; *ZPE*: zero-point energy; H (= $E + ZPE + E_{\mathrm{vib}} + E_{\mathrm{rot}} + E_{\mathrm{trans}} + RT$): sum of electronic and thermal enthalpies; G (= $H - TS$): sum of electronic and thermal free energies.

Table S4. HOMA and GIAO values of benzene ring **A** of **TH-1**, **5**, **7**, and **9**.



TH-**1**



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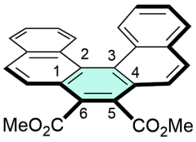

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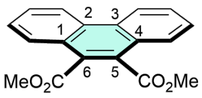


9

	Bond length (R_i, Å)						HOMA	NICS(0)
	C1−C2	C2−C3	C3−C4	C4−C5	C5−C6	C6−C1		
TH-1 (x-ray)[a]	1.404(4)	1.439(4)	1.420(4)	1.424(4)	1.385(4)	1.426(4)	0.715	−
TH-1 (calc)	1.416	1.435	1.416	1.424	1.392	1.424	0.726	−5.61
5	1.415	1.437	1.415	1.423	1.392	1.423	0.728	−5.80
7	1.424	1.445	1.424	1.431	1.381	1.431	0.588	−7.09
9	1.427	1.456	1.427	1.444	1.372	1.444	0.390	−6.22
[5]helicene	−	−	−	−	−	−	0.584	−7.32
phenanthrene[b,c]	−	−	−	−	−	−	0.435	−6.82

a) Ref S1. b) Ref S12. c)

Calculated at B3LYP/6-31G(d) level.

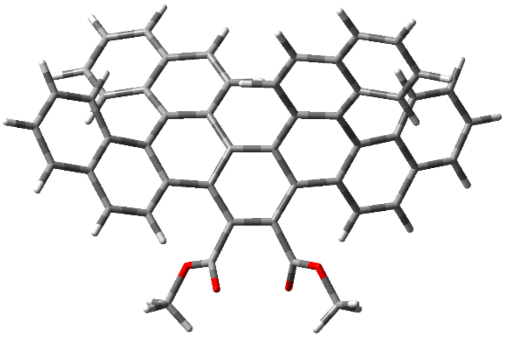
The definition of HOMA index[S13]

$$\mathrm{HOMA} = 1 - \frac{257.7}{6} \sum_{i=1}^{6} (1.388 - R_i)^2$$

The individual C−C bond length : R_i
Number of bonds: $n = 6$
Empirical constant: $\alpha = 257.7$
Optimal value: $R_{opt} = 1.388$

Table S5. Atomic coordinates of the optimized structures.

(*M*,*P*,*M*)-**TH-1**



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C	-2.83659300	1.05058200	-0.47971900
C	-4.73970500	1.89763400	-1.75161100
C	-2.87322600	-1.13091100	0.64416200
C	-0.71263500	-0.03974900	0.08133100
C	-1.46338600	-1.16890400	0.62988200
C	-2.87812800	-3.01106500	2.27053100
C	-6.53556200	-1.91329100	-1.71005500
H	-6.94796800	-2.91648400	-1.77576200
C	-4.94633400	-1.76715700	1.93936700
H	-5.48773600	-0.93721300	1.50335600
C	-6.63770700	0.41701500	-2.30722200
H	-7.11026000	1.24910300	-2.82394000
C	-3.58638100	-1.97749900	1.57988900
C	-5.35551600	-1.70752200	-1.02738100
C	-5.58487700	-2.58152900	2.85081900
C	-7.20403500	-0.83710800	-2.33435700
H	-8.14135600	-1.00683900	-2.85704500
C	-0.78504800	-2.19737300	1.35792600
C	-1.46943400	-3.11666800	2.09907300
C	-3.56728200	-3.85631500	3.17693100
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H	-5.41659700	-4.30270900	4.16330100
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H	2.14066700	5.94478000	-1.10966500
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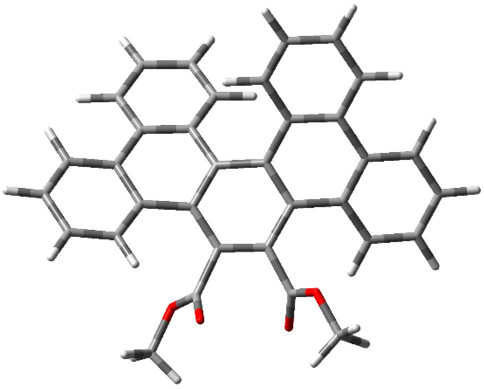
H	-3.46436900	5.08280200	1.96704600

(*P*)-**5**



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H	2.04401500	5.15782700	-1.13014700
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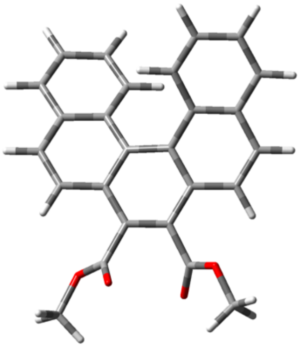
(*P*)-**7**



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H	2.98709000	4.79356100	0.23740700
H	0.68854100	4.52999500	1.00451200
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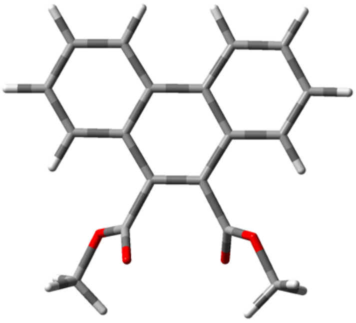

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C	0.76629100	-2.83601500	-0.28731800
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H	4.11312700	3.38761600	0.42901900
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