

Supporting Information

Synthesis of Polycyclic Spirocarbocycles via Acid-Promoted Ring-Contraction/Dearomative Ring-Closure Cascade of Oxapropellanes

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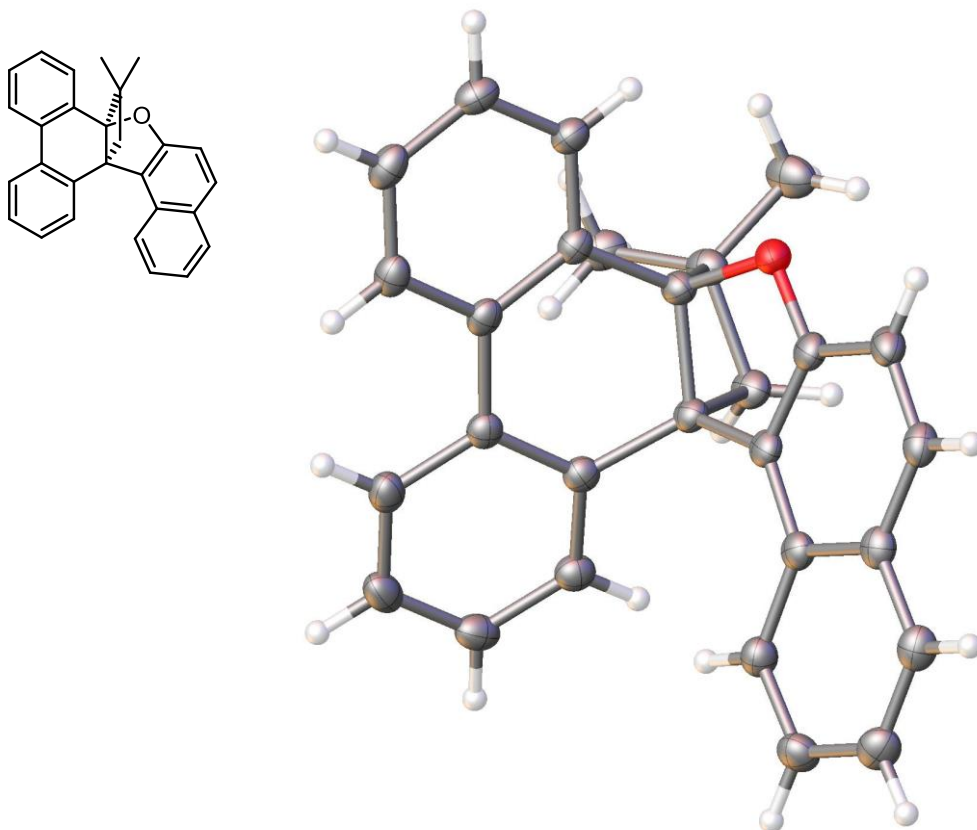
1. General Information

All non-aqueous reactions were carried out in dried glassware under an atmosphere of dry argon unless otherwise noted. For reactions that require heating, oil bath was used as a heat source. 1,2-Dichloroethane (DCE) was refluxed with and distilled from CaH_2 prior to use. Ethyl acetate (EtOAc) and *N,N*-dimethylformamide (DMF) for reaction solvents were dried over molecular sieves 4A prior to use. All other dehydrated solvents for the reactions were purchased and used without further desiccation. All reagents were purchased and used without further purifications. Analytical TLC was performed on pre-coated silica gel plate (Wako Silicagel 70 F254). Flash column chromatography was performed on Wakogel 60N unless otherwise stated. ^1H , ^{13}C NMR spectra were recorded on a JEOL JNM-LA 500 at 500 and 125 MHz, respectively. Chemical shifts (δ) and coupling constants (J) are presented in parts per million and hertz, respectively. Tetramethylsilane (δ 0.0 ppm) was used as internal standard for ^1H NMR. Residual CDCl_3 (δ 77.0 ppm) was used as internal standard for ^{13}C NMR. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). High-resolution mass spectra (HRMS) were recorded on a JEOL MS700 spectrometer (FAB) or a SHIMADZU LCMS-IT-TOF fitted with an ESI. IR spectra were recorded on a Shimadzu IRAffinity-1, and the wave numbers of maximum absorption peaks are reported in cm^{-1} . Melting points were determined on YANACO micro melting point apparatus. X-Ray single crystal diffraction analyses were performed on a Rigaku XtaLAB P200 apparatus. High performance liquid chromatography (HPLC) analyses were performed on a SHIMADZU analytical system equipped with two LC-20AT pumps and a SPD-20A UV/Vis detector using YMC CHIRAL Amylose-SA column (250×4.6 mm), Daicel Chiralpak AD-H column (250×4.6 mm), or Daicel Chiralpak AS-H column (250×4.6 mm). Preparative HPLC was performed on a YMC LC-forte/R using YMC YMC-GPC T-2000 (600×21.2 mm) and YMC-GPC T-4000 (600×21.2 mm), or YMC CHIRAL Amylose-SA column (250×20 mm). Optical rotations were obtained on a JASCO P-1030 polarimeter. CD spectrum were recorded on JASCO J-820 CD spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-2600. Fluorescence spectra were recorded on a JASCO FP-6200.

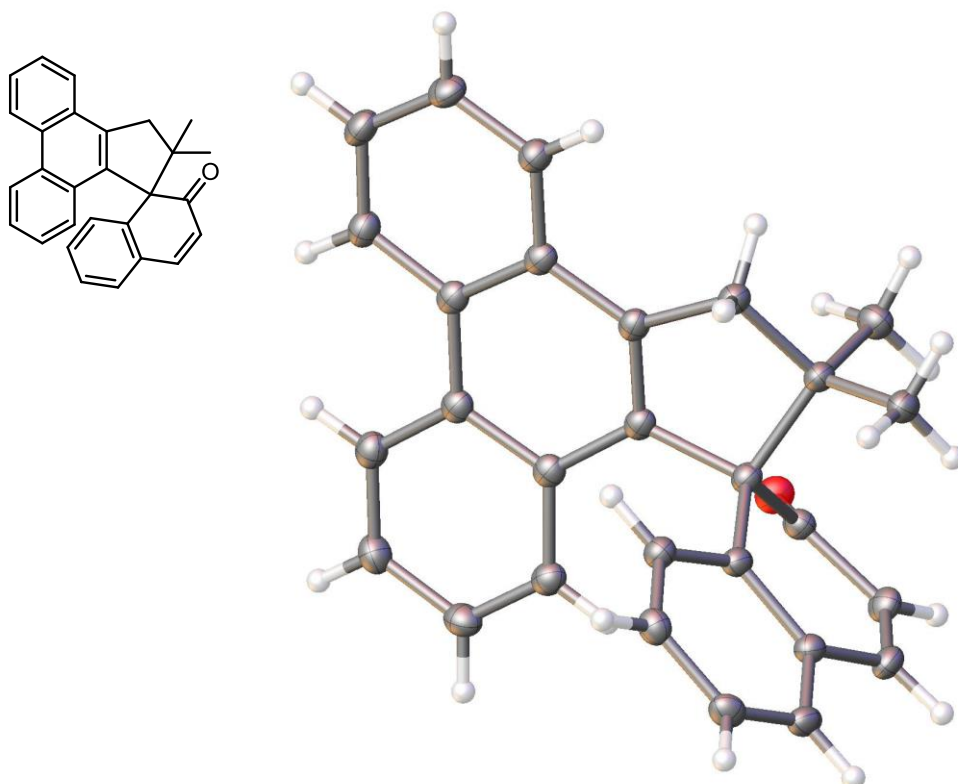
2. X-ray crystallographic data

ORTEP drawing of compounds (+)-**1a**, **4a**, (+)-**4a**, (+)-**4f**, **5a**, **6**, and **7** (50% probability).

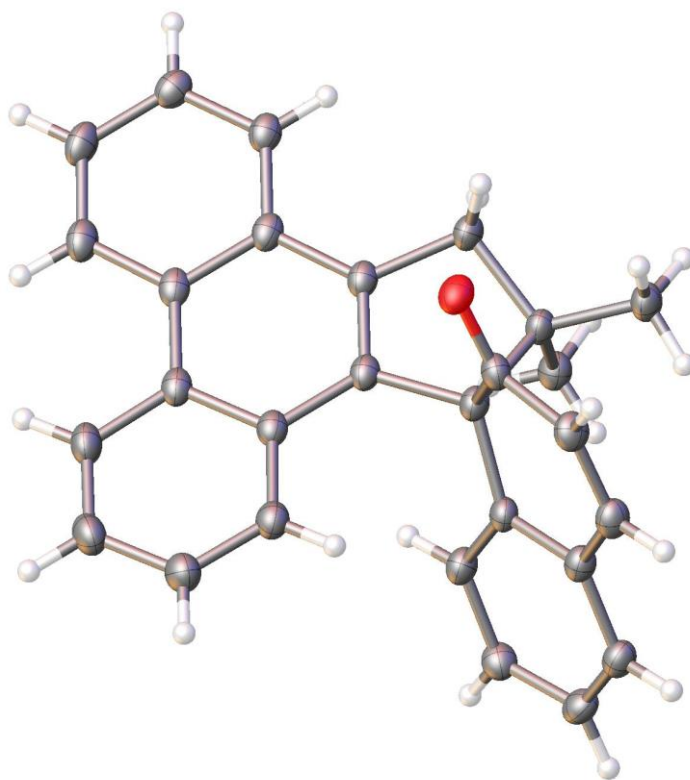
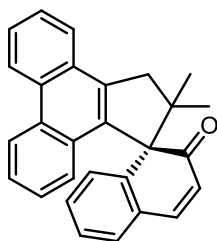
Compound (+)-**1a**



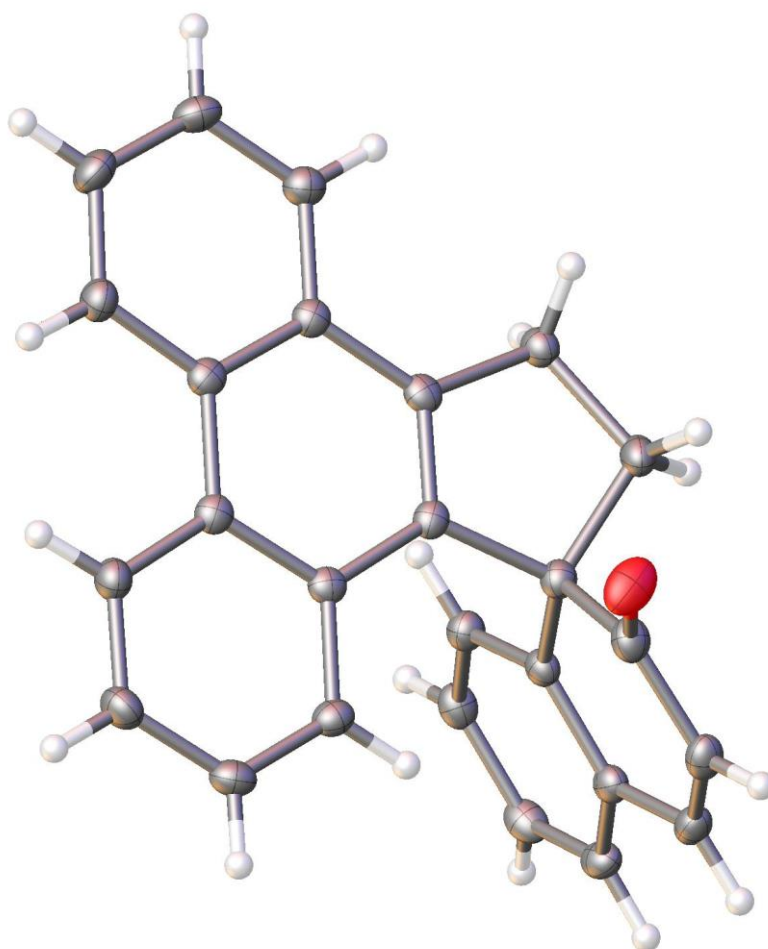
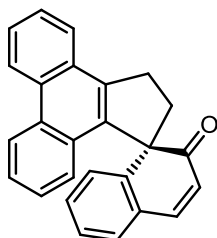
Compound **4a**



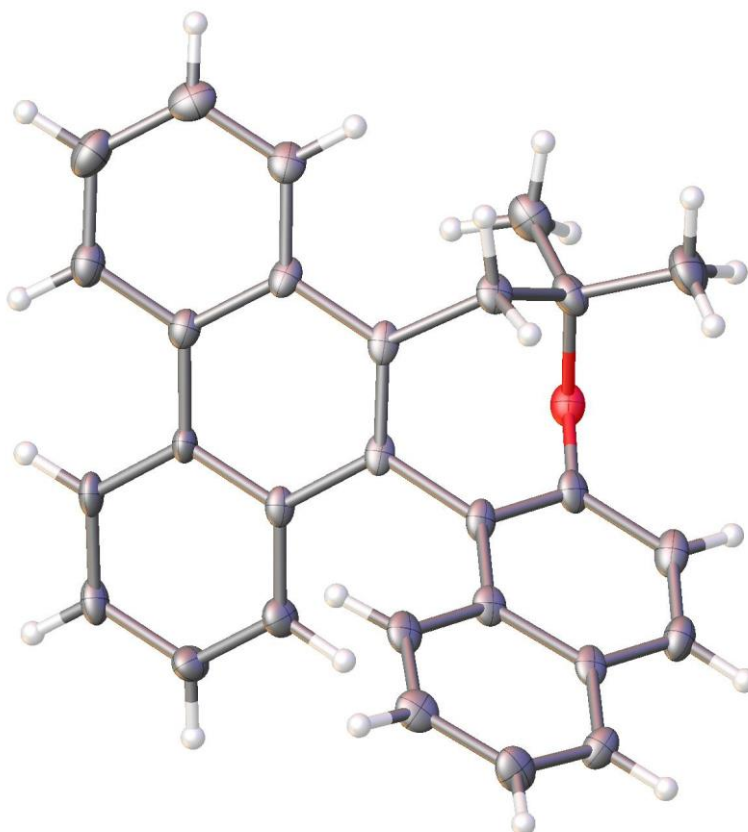
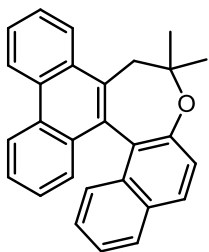
Compound (+)-4a



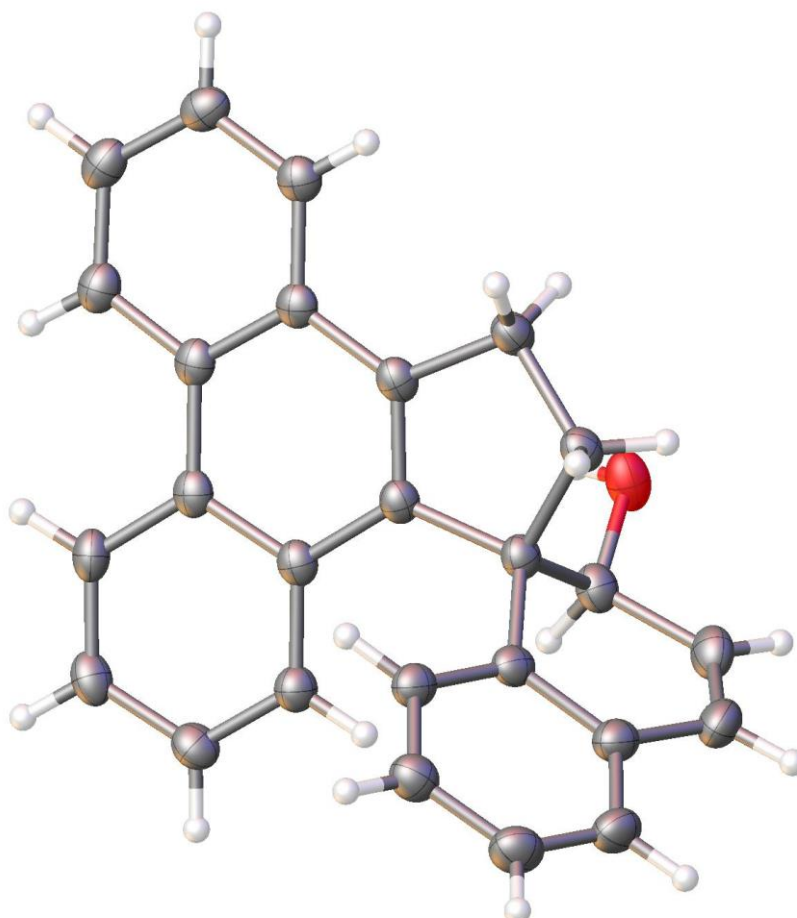
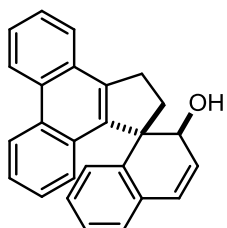
Compound (+)-4f



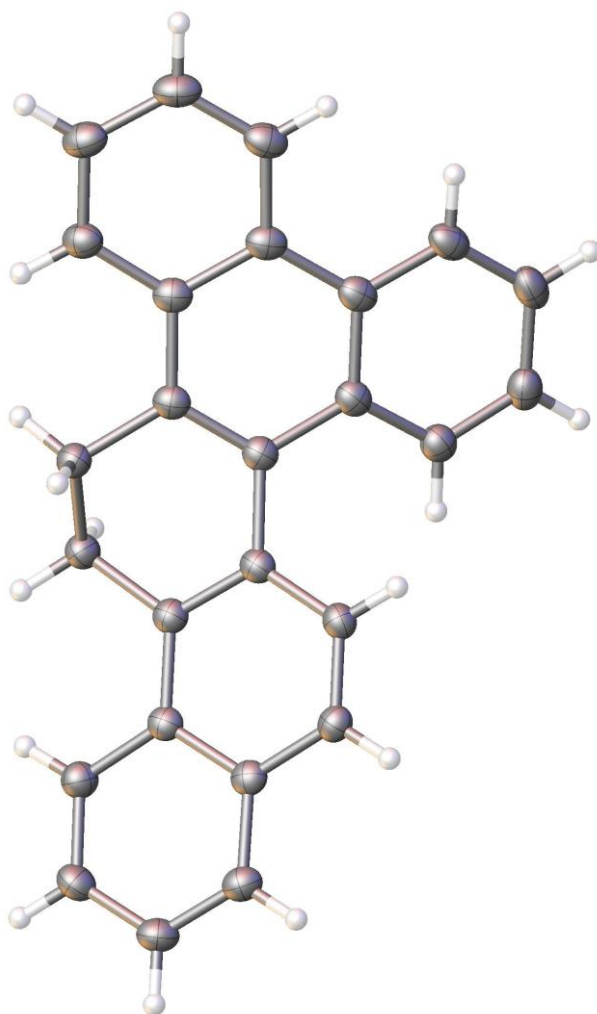
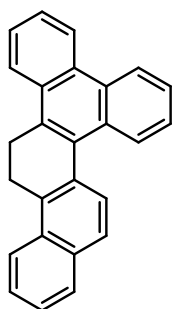
Compound 5a



Compound 6



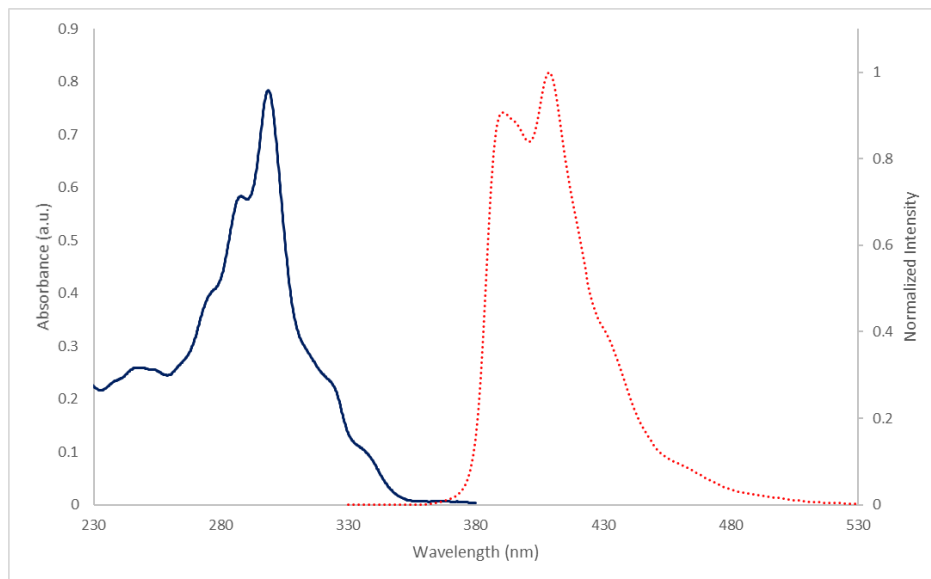
Compound 7



CCDC 1944323 ((+)-**1a**), 1944319 (**4a**), 1944324 ((+)-**4a**), 1944325 ((+)-**4f**), 1944320 (**5a**), 1944321 (**6**), and 1944322 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

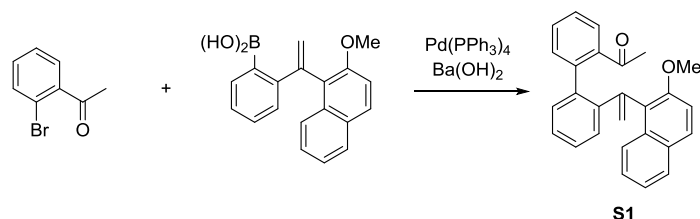
3. Optical Properties of Compound 9

UV-vis absorption spectra (solid line) and fluorescence spectra (dashed line, excited at 280 nm) in dichloromethane (10 μ M)



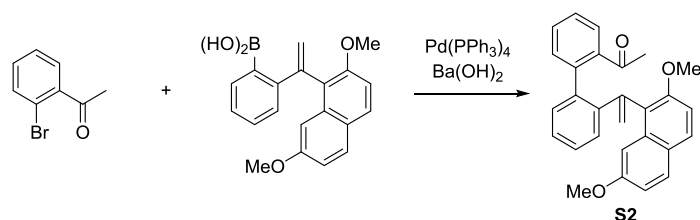
4. Preparation of Substrates

Synthesis of Compound S1



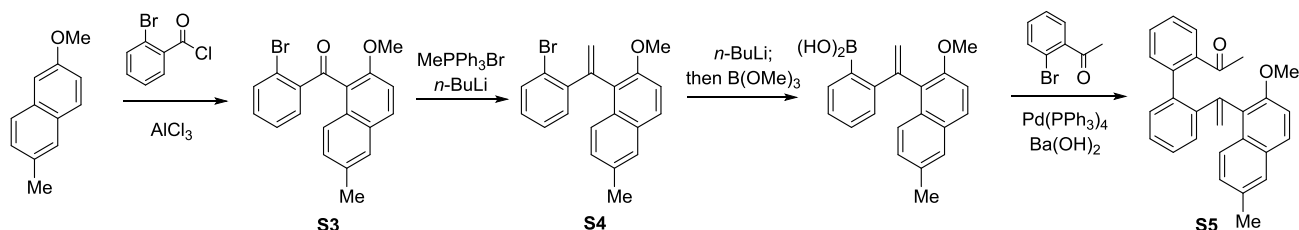
To a solution of 2'-bromoacetophenone (3.98 g, 20.0 mmol) in DME (86 mL) and water (14 mL) was added Ba(OH)₂ (5.14 g, 30.0 mmol), (2-(1-(2-methoxynaphthalen-1-yl)vinyl)phenyl)boronic acid¹ (6.08 g, 20.0 mmol), and Pd(PPh₃)₄ (1.16 g, 1.00 mmol) and the resulting solution was heated to 80 °C. After stirring for 16 h, the reaction mixture was cooled to 0 °C, quenched with 1 M aq. HCl, and diluted with EtOAc. Phases were separated, and the organic layer was washed with water followed by brine, dried over MgSO₄ and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc) to give the title compound (6.74 g, 89%) as white solids: mp 85–86 °C; ¹H NMR (500 MHz, CDCl₃, 50 °C) δ 1.97 (s, 3H), 3.62 (s, 3H), 5.33 (d, J = 1.4 Hz, 1H), 5.65 (s, 1H), 6.87–7.34 (m, 9H), 7.37–7.49 (m, 2H), 7.62–7.69 (m, 2H), 7.80 (d, J = 7.5 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃, 50 °C) δ 29.6, 56.1, 113.6, 122.9, 123.2, 125.4, 125.9, 126.1, 126.4, 126.8, 127.6, 127.7, 128.2, 129.05, 129.14, 130.0, 130.2, 130.7, 131.1, 133.1, 138.9, 139.3, 141.3, 143.1, 153.7, 201.7 ppm; IR (neat) 3055, 3012, 2935, 2839, 1678 cm⁻¹; HRMS–ESI (m/z) [M+Na]⁺ calcd for C₂₇H₂₂O₂Na 401.1512, found 401.1516.

Synthesis of Compound S2



To a solution of 2'-bromoacetophenone (597 mg, 3.00 mmol) in DME (18 mL) and water (3 mL) was added Ba(OH)₂ (771 mg, 4.50 mmol), (2-(1-(2,7-dimethoxynaphthalen-1-yl)vinyl)phenyl)boronic acid¹ (1.00 g, 3.00 mmol), and Pd(PPh₃)₄ (173 mg, 0.150 mmol) and the resulting solution was heated to 80 °C. After stirring for 5 h, the reaction mixture was cooled to 0 °C, quenched with 1 M aq. HCl, and diluted with EtOAc. Phases were separated, and the organic layer was washed with water followed by brine, dried over MgSO₄ and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc) to give the title compound (834 mg, 68%) as white solids: mp 111–112 °C; ¹H NMR (500 MHz, CDCl₃, 50 °C) δ 1.93 (s, 3H), 3.57 (s, 3H), 3.74 (s, 3H), 5.40 (d, *J* = 1.7 Hz, 1H), 5.72 (d, *J* = 1.4 Hz, 1H), 6.69–7.02 (m, 6H), 7.07 (d, *J* = 2.3 Hz, 1H), 7.21–7.27 (m, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.40–7.55 (m, 4H) ppm; ¹³C NMR (125 MHz, CDCl₃, 50 °C) δ 29.6, 55.0, 55.8, 104.1, 110.7, 115.9, 122.6, 124.5, 124.6, 126.2, 126.8, 127.7, 128.0, 128.7, 129.1, 129.8, 130.3, 130.5, 130.7, 134.2, 138.8, 139.4, 141.0, 142.2, 143.8, 154.3, 157.8, 201.5 ppm; IR (neat) 3059, 3012, 2935, 2835, 1678 cm⁻¹; HRMS–ESI (*m/z*) [M+Na]⁺ calcd for C₂₈H₂₄O₃Na 431.1617, found 431.1617.

Preparation of Compound S5



Synthesis of Compound S3

To a stirred solution of 2-methoxy-6-methylnaphthalene (6.89 g, 40 mmol) and AlCl₃ (11.7 g, 87.7 mmol) in dry DCM (130 mL) was added 2-bromobenzoyl chloride (6.3 mL, 48 mmol) at –20 °C. After stirring for 30 min, the reaction mixture was poured into iced 3 M aq. HCl. Phases were separated and the organic layer was washed with water, dried over MgSO₄ and concentrated. The resulting solids were washed with hexanes and dried under reduced pressure to give the title compound (10.3 g, 72%) as white solids: mp 94–95 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.49 (s, 3H), 3.68 (s, 3H), 7.21 (d, *J* = 8.9 Hz, 1H), 7.27–7.31 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.44–7.47 (m, 1H), 7.60 (s, 1H), 7.64–7.67 (m, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 9.2 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 21.3, 56.7, 113.5, 120.4, 123.1, 124.1, 127.0, 127.1, 129.3, 130.1, 130.3, 131.1, 131.9, 132.1, 133.9, 134.1, 141.4, 155.3, 196.9 ppm; IR (neat) 3008, 2939, 2916, 1678 cm⁻¹; HRMS–ESI (*m/z*) [M+Na]⁺ calcd for C₁₉H₁₅BrO₂Na 377.0147, found 377.0153.

Synthesis of Compound S4

To a stirred solution of MePPh₃Br (18.6 g, 52.1 mmol) in dry THF (65 mL) was added *n*-BuLi (1.6 M in hexane, 31 mL, 50 mmol) at 0 °C. After stirring for 20 min, **S3** (9.24 g, 26.0 mmol) was added and the resulting solution was allowed to warm to room temperature. After stirring for 16 h, the reaction was quenched by water and diluted with EtOAc. Phases were separated, and the organic layer was washed with water followed by brine, dried over MgSO₄ and

concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc), and the resulting solids were washed with MeOH and dried under reduced pressure to give the title compound (7.94 g, 86%) as white solids: mp 102–103 °C; ^1H NMR (500 MHz, CDCl_3) δ 2.47 (s, 3H), 3.68 (s, 3H), 5.64 (d, J = 1.4 Hz, 1H), 6.01 (d, J = 1.4 Hz, 1H), 7.02 (ddd, J = 8.0, 7.2, 2.0 Hz, 1H), 7.11 (td, J = 7.5, 1.4 Hz, 1H), 7.15–7.17 (m, 1H), 7.19 (d, J = 8.9 Hz, 1H), 7.30 (dd, J = 8.6, 1.7 Hz, 1H), 7.55 (s, 1H), 7.57 (dd, J = 7.9, 1.0 Hz, 1H), 7.71 (d, J = 8.9 Hz, 1H), 8.09 (d, J = 8.6 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 21.3, 56.7, 114.2, 121.7, 123.6, 125.3, 125.8, 126.8, 126.9, 128.0, 128.6, 128.9, 129.5, 130.6, 131.5, 133.0, 133.4, 142.2, 143.0, 153.4 ppm; IR (neat) 3059, 3008, 2935, 2916, 2835 cm^{-1} ; HRMS–ESI (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{18}\text{BrO}$ 353.0536, found 353.0540.

Synthesis of Compound S5

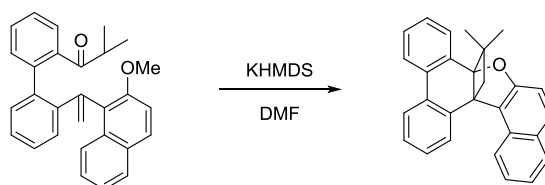
To a stirred solution of **S4** (6.44 g, 18.2 mmol) in dry THF (100 mL) was added *n*-BuLi (1.6 M in hexane, 14 mL, 22 mmol) dropwise at -78°C . After stirring for 50 min, $\text{B}(\text{OMe})_3$ (16 mL, 146 mmol) was added and the resulting solution was allowed to warm to room temperature. After stirring for 14 h, the reaction was quenched with sat. aq. NH_4Cl and diluted with Et_2O . Phases were separated, and the organic layer was washed with water followed by brine, dried over MgSO_4 and concentrated. The resulting boronic acid was used without further purifications.

To a solution of 2'-bromoacetophenone (597 mg, 3.00 mmol) in DME (13 mL) and water (2 mL) was added $\text{Ba}(\text{OH})_2$ (771 mg, 4.50 mmol), the crude boronic acid above (955 mg, 3.00 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (173 mg, 0.150 mmol) and the resulting solution was heated to 80°C . After stirring for 5 h, the reaction mixture was cooled to 0°C , quenched with 1 M aq. HCl, and diluted with EtOAc. Phases were separated, and the organic layer was washed with water followed by brine, dried over MgSO_4 and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc) to give the title compound (586 mg, 50%) as pale yellow paste: ^1H NMR (500 MHz, CDCl_3 , 50°C) δ 1.99 (s, 3H), 2.42 (s, 3H), 3.60 (s, 3H), 5.31 (s, 1H), 5.61 (s, 1H), 6.95–7.29 (m, 8H), 7.36 (d, J = 6.9 Hz, 1H), 7.41–7.51 (m, 2H), 7.58 (d, J = 9.2 Hz, 1H), 7.71 (d, J = 8.6 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3 , 50°C) δ 21.2, 29.6, 56.1, 113.7, 122.8, 125.3, 125.9, 126.4, 126.5, 126.7, 127.6, 128.2, 128.3, 128.5, 129.4, 130.1, 130.7, 131.1, 131.4, 132.7, 139.1, 139.3, 141.4, 143.1, 153.1, 201.8 ppm; IR (neat) 3059, 3012, 2916, 2835, 1678 cm^{-1} ; HRMS–ESI (m/z) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{24}\text{O}_2\text{Na}$ 415.1668, found 415.1672.

General Procedure for the Preparations of Oxapropellanes 5

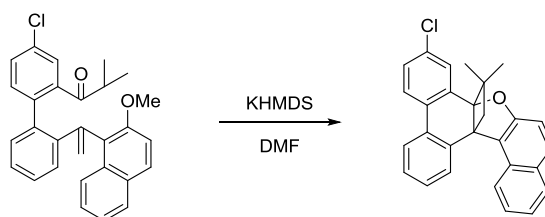
To a stirred solution of biaryl ketones in dry DMF (0.1 M) was added KHMDS (1 M in THF, 2.0 equiv). After stirring for 30 min, the reaction was quenched with 1 M aqueous HCl and diluted with Et_2O . Phases were separated, and the organic layer was washed three times with water followed by brine, dried over MgSO_4 and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc) to give the desired oxapropellanes.

Compound 1a



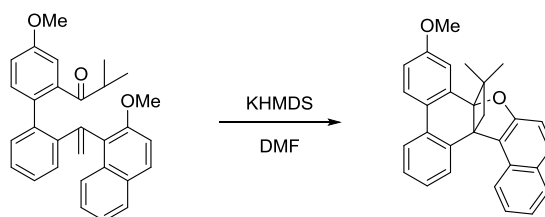
The general procedure using 1-(2'-(1-(2-methoxynaphthalen-1-yl)vinyl)-[1,1'-biphenyl]-2-yl)-2-methylpropan-1-one¹ (3.0 mmol) gave the title compound (989 mg, 88%) as white solids. The spectroscopic data were in good agreement with those reported.

Compound 1b



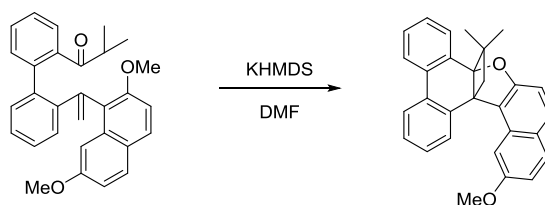
The general procedure using 1-(4-chloro-2'-(1-(2-methoxynaphthalen-1-yl)vinyl)-[1,1'-biphenyl]-2-yl)-2-methylpropan-1-one² (1.5 mmol) gave the title compound (539 mg, 88%) as white solids: mp 202–203 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.85 (s, 3H), 1.30 (s, 3H), 2.61 (d, *J* = 11.5 Hz, 1H), 2.83 (d, *J* = 11.5 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 1H), 7.21–7.27 (m, 1H), 7.27–7.34 (m, 2H), 7.35–7.42 (m, 2H), 7.45 (d, *J* = 2.3 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.77–7.81 (m, 2H), 8.10 (d, *J* = 7.2 Hz, 1H), 8.24 (d, *J* = 8.6 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 24.2, 26.6, 44.4, 49.4, 51.8, 93.2, 112.5, 122.4, 124.1, 124.3, 124.5, 126.3, 127.4, 127.6, 127.8, 128.7, 129.3, 130.2, 130.3, 130.6, 130.8, 131.1, 131.4, 133.9, 134.5, 137.4, 159.7 ppm; IR (neat) 3059, 3016, 2958, 2931 cm⁻¹; HRMS–FAB (*m/z*) [*M*+*H*]⁺ calcd for C₂₈H₂₂ClO 409.1354, found 409.1359.

Compound 1c



The general procedure using 1-(4-methoxy-2'-(1-(2-methoxynaphthalen-1-yl)vinyl)-[1,1'-biphenyl]-2-yl)-2-methylpropan-1-one² (395 mg, 0.905 mmol) gave the title compound (217 mg, 59%) as white solids: mp 185–186 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.85 (s, 3H), 1.29 (s, 3H), 2.58 (d, *J* = 11.5 Hz, 1H), 2.82 (d, *J* = 11.5 Hz, 1H), 3.86 (s, 3H), 6.89 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.97 (d, *J* = 2.9 Hz, 1H), 7.16 (d, *J* = 8.9 Hz, 1H), 7.20–7.24 (m, 1H), 7.25–7.32 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.76–7.83 (m, 2H), 8.06 (d, *J* = 8.6 Hz, 1H), 8.27 (d, *J* = 8.6 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 24.3, 26.9, 44.4, 49.5, 51.4, 55.4, 93.7, 111.8, 112.5, 114.8, 122.3, 122.7, 123.6, 124.1, 124.8, 125.4, 126.2, 126.5, 127.4, 129.3, 130.08, 130.13, 130.2, 130.9, 132.3, 134.1, 136.7, 159.6, 159.9 ppm; IR (neat) 3059, 3016, 2958, 2931, 2866 cm⁻¹; HRMS–FAB (*m/z*) [*M*+*H*]⁺ calcd for C₂₉H₂₅O₂ 405.1849, found 405.1855.

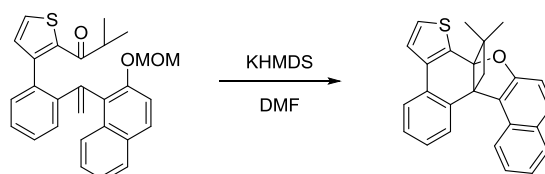
Compound 1d



The general procedure using 1-(2'-(1-(2,7-dimethoxynaphthalen-1-yl)vinyl)-[1,1'-biphenyl]-2-yl)-2-methylpropan-1-one¹ (1.5 mmol) gave the title compound (557 mg, 92%) as white solids: mp 163–165 °C; ¹H NMR (500 MHz,

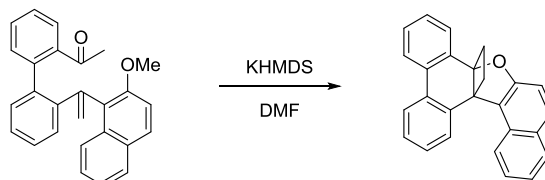
CDCl₃) δ 0.86 (s, 3H), 1.35 (s, 3H), 2.69 (d, J = 11.2 Hz, 1H), 2.82 (d, J = 11.2 Hz, 1H), 3.82 (s, 3H), 6.87 (dd, J = 8.9, 2.3 Hz, 1H), 7.01 (d, J = 8.9 Hz, 1H), 7.30–7.41 (m, 4H), 7.48 (d, J = 9.2 Hz, 1H), 7.53–7.58 (m, 2H), 7.62 (d, J = 8.9 Hz, 1H), 7.83–7.93 (m, 2H), 8.14 (dd, J = 7.2, 1.4 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 24.2, 26.4, 44.2, 49.1, 52.1, 55.3, 94.3, 101.2, 110.0, 114.8, 122.4, 123.7, 124.6, 125.4, 126.8, 127.3, 127.6, 128.4, 128.6, 129.7, 130.6, 130.7, 132.0, 132.5, 132.8, 133.0, 137.8, 157.9, 160.5 ppm; IR (neat) 2931 cm⁻¹; HRMS–ESI (m/z): [M+H]⁺ calcd for C₂₉H₂₅O₂ 405.1849, found, 405.1850.

Compound 1e



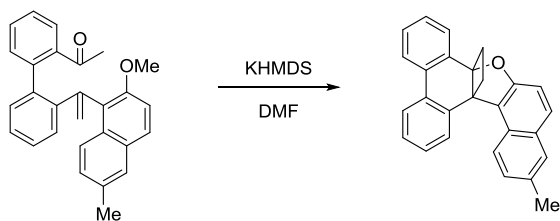
The general procedure using 1-(3-(2-(1-(2-(methoxymethoxy)naphthalen-1-yl)vinyl)phenyl)thiophen-2-yl)-2-methylpropan-1-one¹ (324 mg, 0.732 mmol) gave the title compound (106 mg, 38%) as pale yellow solids: mp 169–170 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.98 (s, 3H), 1.18 (s, 3H), 2.46 (d, J = 11.5 Hz, 1H), 2.93 (d, J = 11.5 Hz, 1H), 7.16 (d, J = 8.9 Hz, 1H), 7.19–7.31 (m, 3H), 7.41 (d, J = 5.2 Hz, 1H), 7.44 (d, J = 5.2 Hz, 1H), 7.48 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.64 (dd, J = 7.5, 1.6 Hz, 1H), 7.67 (d, J = 8.9 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 8.06 (dd, J = 7.5, 1.0 Hz, 1H), 8.29 (d, J = 8.6 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 24.2, 28.0, 45.8, 49.7, 51.9, 91.7, 112.5, 122.5, 123.4, 124.4, 124.6, 126.3, 126.9, 127.1, 127.4, 128.7, 129.4, 130.0, 130.41, 130.43, 130.9, 133.0, 136.2, 137.2, 160.0 ppm; IR (neat) 3059, 3016, 2958, 2927 cm⁻¹; HRMS–FAB (m/z) [M+H]⁺ calcd for C₂₆H₂₁OS 381.1308, found 381.1313.

Compound 1f



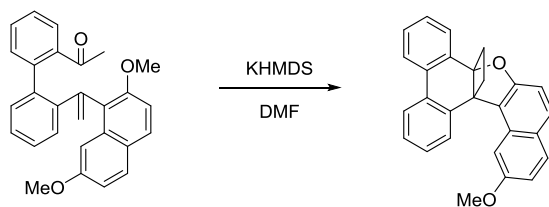
The reaction was carried out according to the general procedure at 80 °C for 20 min using **S1** (2.4 mmol) to give the title compound (703 mg, 85%) as white solids: mp 89–91 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.26–2.35 (m, 1H), 2.38–2.44 (m, 1H), 2.87–2.95 (m, 1H), 3.03–3.12 (m, 1H), 7.13 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 8.9 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.44–7.51 (m, 2H), 7.60 (t, J = 7.7 Hz, 1H), 7.69–7.77 (m, 2H), 7.87 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 8.03–8.12 (m, 1H), 8.30 (d, J = 8.3 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 28.8, 36.0, 53.3, 85.9, 113.3, 122.8, 123.0, 124.3, 125.1, 126.6, 127.5, 127.8, 128.3, 128.8, 128.9, 129.2, 129.5, 130.4, 130.5, 130.7, 132.1, 132.3, 132.4, 137.1, 158.8 ppm; IR (neat) 3059, 3016, 2989, 2943 cm⁻¹; HRMS–FAB (m/z) [M+H]⁺ calcd for C₂₆H₁₉O 347.1431, found 347.1436.

Compound 1g



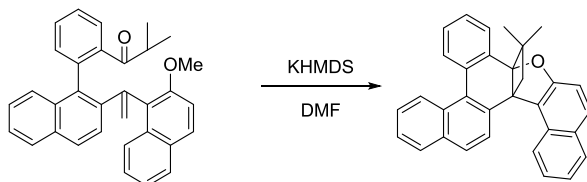
The reaction was carried out according to the general procedure at 80 °C for 20 min using **S5** (0.81 mmol) to give the title compound (147 mg, 50%) as white solids: mp 88–90 °C; ^1H NMR (500 MHz, CDCl_3) δ 2.29 (td, J = 10.6, 8.9 Hz, 1H), 2.40 (ddd, J = 11.4, 8.9, 2.0 Hz, 1H), 2.53 (s, 3H), 2.88 (ddd, J = 11.0, 9.3, 2.0 Hz, 1H), 3.06 (dt, J = 11.5, 10.0 Hz, 1H), 7.11–7.16 (m, 2H), 7.25–7.29 (m, 1H), 7.43–7.51 (m, 3H), 7.63–7.67 (m, 2H), 7.70–7.73 (m, 1H), 7.89 (d, J = 7.2 Hz, 1H), 7.99 (d, J = 7.5 Hz, 1H), 8.04–8.07 (m, 1H), 8.21 (d, J = 8.6 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 21.4, 28.8, 36.0, 53.4, 85.8, 113.3, 123.0, 124.2, 124.3, 125.0, 127.5, 127.8, 128.2, 128.5, 128.8, 128.86, 128.90, 129.2, 129.6, 130.2, 130.8, 132.2, 132.3, 132.5, 137.2, 158.2 ppm; IR (neat) 3062, 3012, 2989, 2943, 2920 cm^{-1} ; HRMS–ESI (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{21}\text{O}$ 361.1587, found 361.1582.

Compound 1h



The reaction was carried out according to the general procedure at 80 °C for 20 min using **S2** (1.0 mmol) to give the title compound (184 mg, 49%) as white solids: mp 157–158 °C; ^1H NMR (500 MHz, CDCl_3) δ 2.31 (td, J = 10.4, 8.6 Hz, 1H), 2.42 (ddd, J = 11.5, 8.9, 2.3 Hz, 1H), 2.91 (ddd, J = 11.0, 9.2, 2.1 Hz, 1H), 3.07 (dt, J = 11.7, 9.8 Hz, 1H), 3.98 (s, 3H), 7.01–7.06 (m, 2H), 7.14–7.19 (m, 1H), 7.28–7.33 (m, 1H), 7.46–7.53 (m, 2H), 7.57 (d, J = 2.3 Hz, 1H), 7.67 (d, J = 8.6 Hz, 1H), 7.72–7.74 (m, 1H), 7.77 (d, J = 8.9 Hz, 1H), 7.98 (d, J = 7.7 Hz, 1H), 8.01 (d, J = 7.5 Hz, 1H), 8.06–8.09 (m, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 28.5, 36.0, 53.1, 55.4, 85.8, 103.2, 110.9, 115.2, 123.0, 124.2, 124.4, 125.9, 127.6, 127.7, 128.2, 128.82, 128.85, 129.2, 130.1, 130.8, 131.0, 132.2, 132.5, 133.3, 137.3, 158.1, 159.4 ppm; IR (neat) 3066, 3012, 2993, 2939, 2877 cm^{-1} ; HRMS–ESI (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{21}\text{O}_2$ 377.1536, found 377.1539.

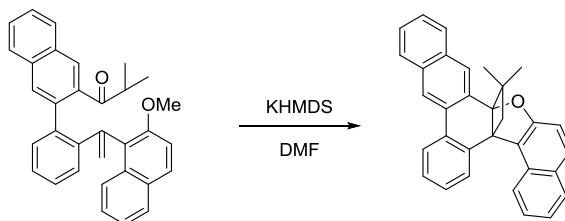
Compound 1i



The general procedure using 1-(2-(2-(1-(2-methoxynaphthalen-1-yl)vinyl)naphthalen-1-yl)phenyl)-2-methylpropan-1-one¹ (238 mg, 0.521 mmol) gave the title compound (215 mg, 97%) as white solids: mp 204–205 °C; ^1H NMR (500 MHz, CDCl_3) δ 0.85 (s, 3H), 1.40 (s, 3H), 2.65 (d, J = 11.7 Hz, 1H), 2.80 (d, J = 11.7 Hz, 1H), 7.15–7.21 (m, 2H), 7.31–7.40 (m, 3H), 7.45–7.52 (m, 2H), 7.62 (d, J = 8.6 Hz, 1H), 7.65 (dd, J = 7.4, 1.4 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.87–7.93 (m, 2H), 7.99 (d, J = 8.3 Hz, 1H), 8.24 (d, J = 8.3 Hz, 1H), 8.43 (d, J = 8.6 Hz, 1H), 8.54–8.60 (m, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 24.6, 25.5, 43.6, 50.3, 53.3, 94.9, 112.7, 122.3, 122.5, 124.3, 125.7, 126.21, 126.23, 126.25,

127.0, 127.2, 127.9, 128.2, 128.57, 128.63, 129.0, 129.2, 129.95, 129.97, 130.01, 130.9, 132.0, 132.8, 134.1, 134.9, 135.8, 160.1 ppm; IR (neat) 3055, 3012, 2974, 2931 cm^{-1} ; HRMS–FAB (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{25}\text{O}$ 425.1900, found 425.1905.

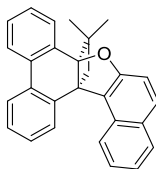
Compound 1j



The general procedure using 1-(3-(2-(1-(2-methoxynaphthalen-1-yl)vinyl)phenyl)naphthalen-2-yl)-2-methylpropan-1-one² (1.5 mmol) gave the title compound (613 mg, 96%) as pale yellow solids: mp $>250\text{ }^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 0.84 (s, 3H), 1.42 (s, 3H), 2.71 (d, $J = 11.5\text{ Hz}$, 1H), 2.86 (d, $J = 11.5\text{ Hz}$, 1H), 7.16 (d, $J = 8.6\text{ Hz}$, 1H), 7.21 (t, $J = 7.6\text{ Hz}$, 1H), 7.33–7.48 (m, 5H), 7.62 (d, $J = 8.9\text{ Hz}$, 1H), 7.72 (d, $J = 8.3\text{ Hz}$, 1H), 7.81–7.90 (m, 2H), 7.99 (s, 1H), 8.06 (d, $J = 7.5\text{ Hz}$, 1H), 8.15 (d, $J = 7.5\text{ Hz}$, 1H), 8.29 (d, $J = 8.6\text{ Hz}$, 1H), 8.33 (s, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 24.2, 26.6, 44.1, 49.6, 51.9, 94.3, 112.6, 121.5, 122.29, 122.31, 124.6, 125.1, 126.16, 126.24, 126.3, 126.5, 127.5, 127.7, 127.8, 128.3, 129.3, 130.05, 130.08, 130.8, 130.9, 131.0, 131.8, 132.7, 133.3, 133.5, 137.8, 160.0 ppm; IR (neat) 3055, 3020, 2962, 2931 cm^{-1} ; HRMS–FAB (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{25}\text{O}$ 425.1900, found 425.1905.

Preparation of Enantiopure Substrates

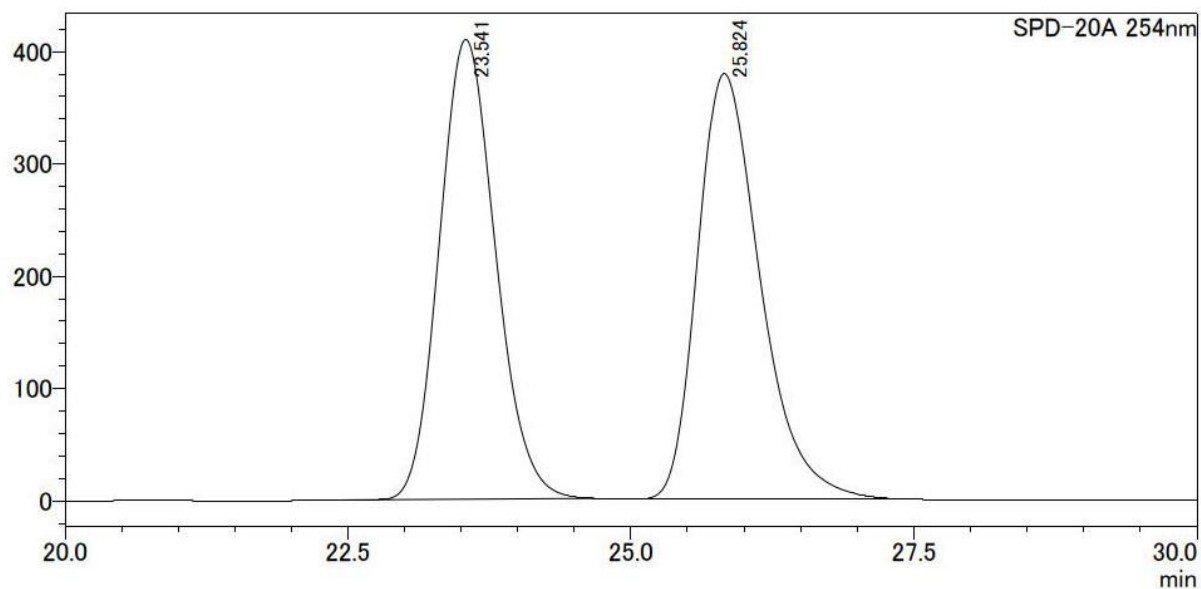
(+)-1a



Racemic mixtures of **1a** was separated by preparative chiral HPLC (column: YMC CHIRAL Amylose-SA, eluent: hexane/*i*-PrOH = 99.5/0.5), flow rate: 25 mL/min, detection: UV 254 nm). Analytical HPLC (column: YMC CHIRAL Amylose-SA, eluent: hexane/*i*-PrOH = 99.5/0.5, flow rate: 0.20 mL/min, detection: UV 254 nm, temperature: 25 $^{\circ}\text{C}$) (+)-**1a** 23.5 min, (–)-**4a** 25.8 min. $[\alpha]_D^{25} +232$ (c 0.74, CHCl_3 , 99% ee). Recrystallization from hexanes/EtOAc afforded colorless, clear plates suitable for X-ray crystallography. The absolute configuration was determined by X-ray crystallography.

Chromatogram of racemic 1a

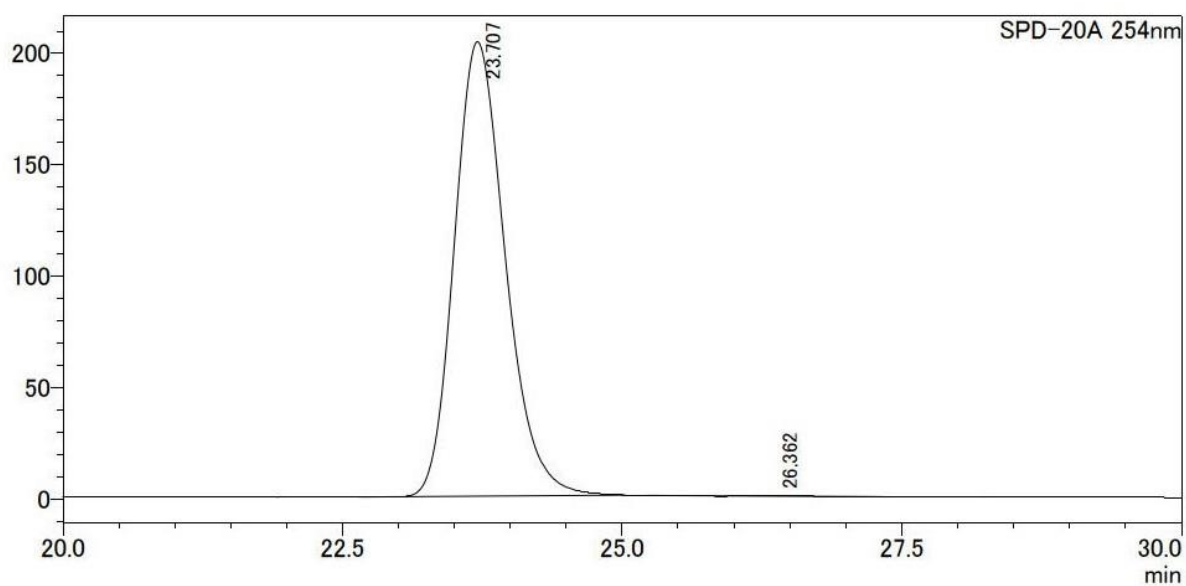
mV



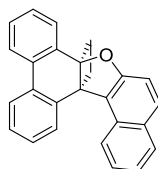
peak#	time	area	height	area%
1	23.541	14156618	409269	49.202
2	25.824	14615945	378830	50.798
合計		28772562	788100	100.000

Chromatogram of (+)-**1a** (99% ee)

mV

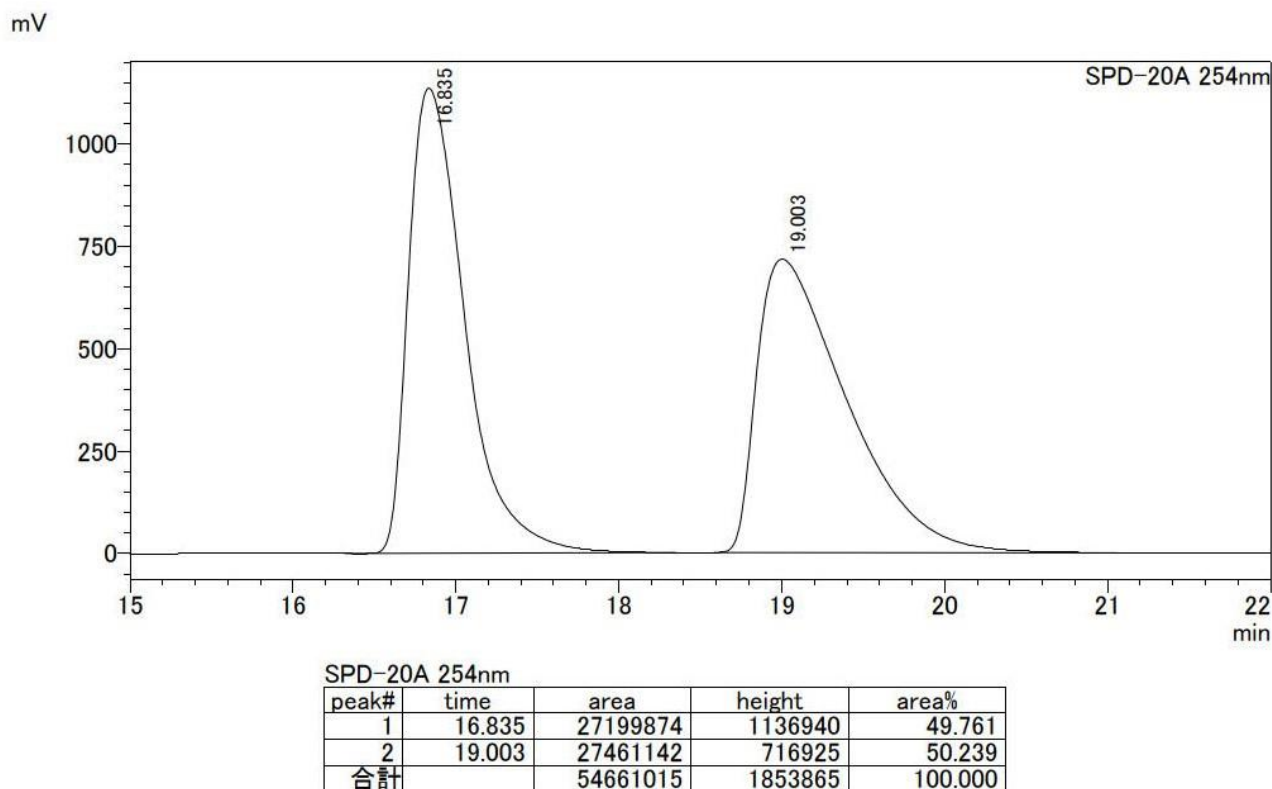


peak#	time	area	height	area%
1	23.707	6465490	203995	99.968
2	26.362	2095	305	0.032
合計		6467584	204299	100.000

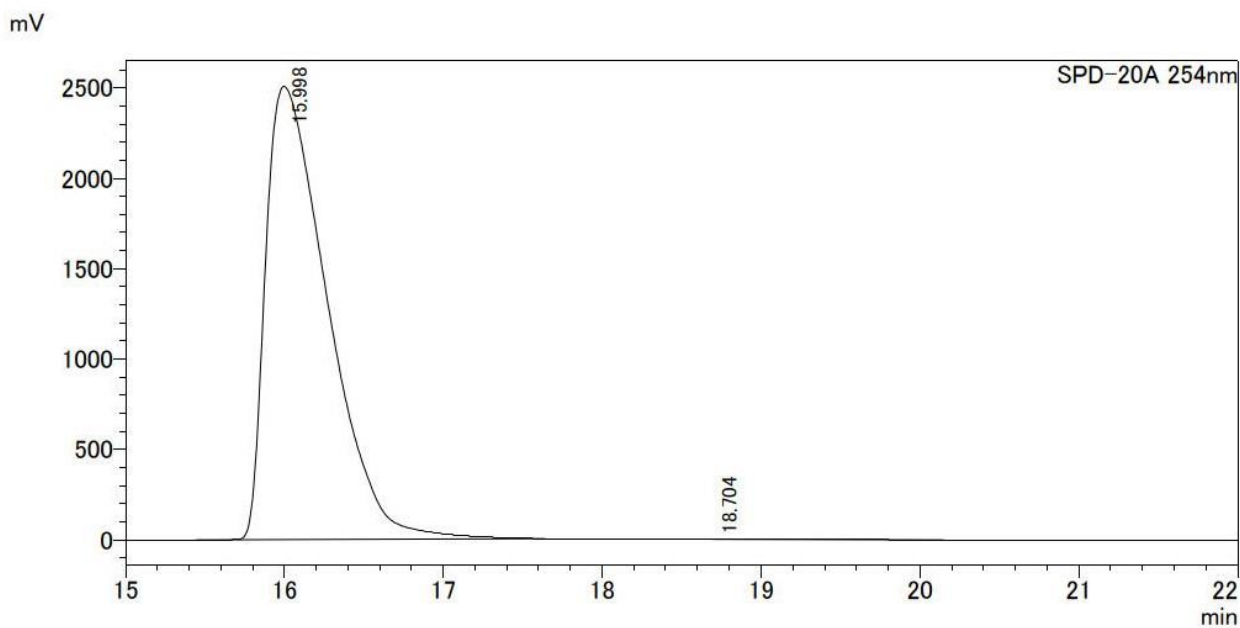
(+) -**1f**

Racemic mixtures of **1f** was separated by preparative chiral HPLC (column: YMC CHIRAL Amylose-SA, eluent: hexane/*i*-PrOH = 99.5/0.5), flow rate: 25 mL/min, detection: UV 254 nm). Analytical HPLC (column: YMC CHIRAL Amylose-SA, eluent: hexane/*i*-PrOH = 99.5/0.5, flow rate: 0.40 mL/min, detection: UV 254 nm, temperature: 25 °C) (+)-**1f** 16.8 min, (–)-**1f** 19.0 min. $[\alpha]_D^{21} +742$ (c 0.55, CHCl₃, 99% ee). The absolute configuration was determined by comparing the CD spectra with that of (+)-**1a**, whose absolute configuration was determined by X-ray crystallography.

Chromatogram of Racemic **1f**

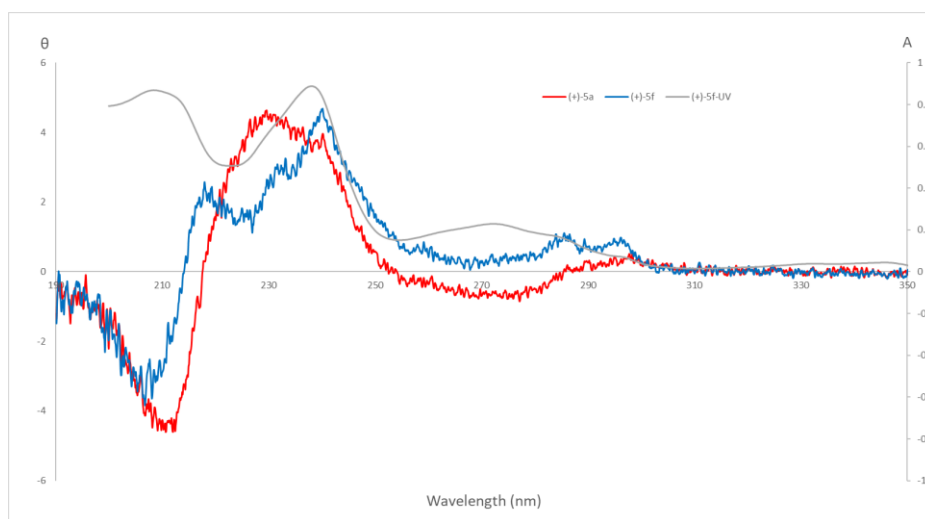


Chromatogram of (+)-**1f** (99% ee)



SPD-20A 254nm				
peak#	time	area	height	area%
1	15.998	67680097	2507641	100.060
2	18.704	-40783	8	-0.060
合計		67639314	2507649	100.000

CD Spectra of (+)-**1a** (red line) and (+)-**1f** (blue line), and UV-vis spectra of (+)-**1f** (gray line) in MeCN (17 μ M). The spectral patterns suggest that the absolute configurations of these two compounds are identical.

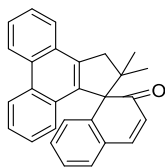


5. Acid-promoted Rearrangement of Oxapropellanes

General Procedure for Spirocyclizations of Oxapropellanes

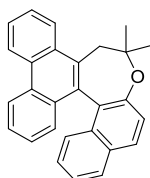
To a stirred solution of oxapropellane **1** in dry 1,2-dichloroethane (0.05 M) was added TfOH (2.0 equiv) at -20°C . After stirring for 20 min, the reaction was quenched with Et_3N and diluted with CHCl_3 . Phases were separated and the organic layer was washed with 1 M aqueous HCl followed by water, dried over MgSO_4 and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc) to give the desired spirocycles **4**.

Compound 4a



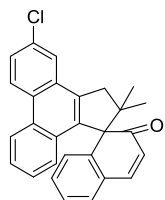
The general procedure using **1a** (1.00 mmol) gave the title compound (347 mg, 93%) as pale yellow solids. WRecrystallization from EtOAc/CHCl₃ gave colorless, clear plates suitable for X-ray crystallography: mp 219–220 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.87 (s, 3H), 1.23 (s, 3H), 3.25 (d, *J* = 15.8 Hz, 1H), 3.29 (d, *J* = 15.8 Hz, 1H), 6.34 (d, *J* = 9.7 Hz, 1H), 6.48 (d, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 7.00 (td, *J* = 7.5, 1.4 Hz, 1H), 7.22 (td, *J* = 7.5, 1.1 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 9.7 Hz, 1H), 7.64–7.73 (m, 2H), 7.91 (dd, *J* = 7.8, 1.3 Hz, 1H), 8.70 (d, *J* = 8.3 Hz, 1H), 8.76 (d, *J* = 7.7 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 25.5, 31.0, 46.7, 50.1, 72.8, 123.2, 123.3, 125.0, 125.4, 126.3, 126.48, 126.54, 126.6, 127.1, 128.1, 128.6, 129.3, 129.4, 129.5, 130.4, 131.1, 131.3, 137.3, 139.4, 142.2, 145.3, 201.9 ppm; IR (neat) 3062, 3020, 2962, 2927, 1662 cm⁻¹; HRMS–FAB (*m/z*) [M+H]⁺ calcd for C₂₈H₂₃O 375.1744, found 375.1749.

Compound 5a



The reaction was carried out at room temperature for 2 h using **1a** (18.7 mg, 0.0500 mmol) according to the general procedure to give the title compound (4.1 mg, 22%) as white solids. Recrystallization from CH₂Cl₂/hexane gave colorless, clear prisms suitable for X-ray crystallography: mp 202–203 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.28 (s, 3H), 1.49 (s, 3H), 2.78 (d, *J* = 14.6 Hz, 1H), 3.42 (d, *J* = 14.6 Hz, 1H), 7.18–7.24 (m, 1H), 7.27–7.35 (m, 2H), 7.36–7.45 (m, 3H), 7.6 (t, *J* = 7.6 Hz, 1H), 7.68–7.77 (m, 2H), 7.91–7.98 (m, 2H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.79 (d, *J* = 8.3 Hz, 1H), 8.87 (d, *J* = 8.0 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 26.8, 27.1, 37.8, 91.0, 122.7, 123.3, 124.3, 124.45, 124.50, 125.6, 125.9, 126.1, 126.3, 126.8, 127.2, 127.9, 128.1, 128.3, 129.3, 129.7, 130.4, 130.6, 131.0, 131.8, 132.8, 152.5 ppm; IR (neat) 2974 cm⁻¹; HRMS–ESI (*m/z*) [M+H]⁺ calcd for C₂₈H₂₃O 375.1744, found 375.1745.

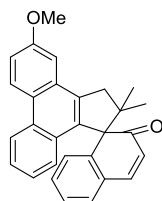
Compound 4b



The general procedure using **1b** (0.20 mmol) gave the title compound (71.9 mg, 88%) as white solids: mp 133–135 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.86 (s, 3H), 1.22 (s, 3H), 3.23 (s, 2H), 6.34 (d, *J* = 10.0 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 6.84 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.02 (td, *J* = 7.6, 1.3 Hz, 1H), 7.21–7.25 (m, 1H), 7.28 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.43 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.49 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.60 (d, *J* = 10.0 Hz, 1H), 7.63 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.88 (d, *J* = 2.0 Hz, 1H), 8.62 (d, *J* = 8.3 Hz, 1H), 8.66 (d, *J* = 8.9 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 25.5, 30.9, 46.5, 50.1, 72.8, 123.2, 124.3, 124.9, 125.8, 126.4, 126.59, 126.63, 126.9, 127.3, 128.0, 128.6,

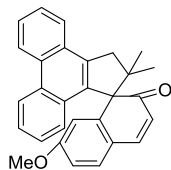
129.5, 129.6, 130.3, 130.4, 130.9, 132.5, 138.5, 138.7, 141.9, 145.4, 201.6 ppm; IR (neat) 3066, 3016, 2962, 2927, 1658 cm^{-1} ; HRMS–FAB (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{22}\text{ClO}$ 409.1354, found 409.1359.

Compound 4c



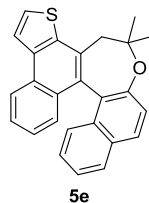
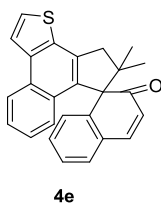
The general procedure using **1c** (40.5 mg, 0.100 mmol) gave the title compound (31.5 mg, 78%) as white solids: mp 200–201 °C; ^1H NMR (500 MHz, CDCl_3) δ 0.87 (s, 3H), 1.23 (s, 3H), 3.24 (s, 2H), 3.99 (s, 3H), 6.34 (d, $J = 9.7$ Hz, 1H), 6.48 (d, $J = 7.7$ Hz, 1H), 6.81 (d, $J = 8.3$ Hz, 1H), 7.01 (td, $J = 7.6, 1.1$ Hz, 1H), 7.18–7.26 (m, 3H), 7.32 (dd, $J = 9.2, 2.6$ Hz, 1H), 7.42 (dd, $J = 7.4, 1.1$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.60 (d, $J = 10.0$ Hz, 1H), 8.59 (d, $J = 8.3$ Hz, 1H), 8.66 (d, $J = 9.2$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 25.6, 31.0, 46.9, 50.0, 55.4, 72.9, 105.7, 116.5, 122.8, 124.9, 125.3, 125.4, 125.5, 126.5, 127.1, 127.5, 128.2, 129.4, 130.4, 130.6, 131.4, 137.9, 138.8, 142.2, 145.3, 158.3, 201.8 ppm; IR (neat) 3066, 3008, 2962, 2931, 1658 cm^{-1} ; HRMS–FAB (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{25}\text{O}_2$ 405.1849, found 405.1855.

Compound 4d



The general procedure using **1d** (0.20 mmol) gave the title compound (74.2 mg, 92%) as white solids: mp 204–206 °C; ^1H NMR (500 MHz, CDCl_3) δ 0.89 (s, 3H), 1.21 (s, 3H), 3.27 (s, 2H), 3.49 (s, 3H), 6.04 (d, $J = 2.6$ Hz, 1H), 6.22 (d, $J = 9.7$ Hz, 1H), 6.72 (dd, $J = 8.3, 2.6$ Hz, 1H), 6.88 (d, $J = 7.5$ Hz, 1H), 7.29 (ddd, $J = 8.1, 7.0, 1.1$ Hz, 1H), 7.35 (d, $J = 8.3$ Hz, 1H), 7.48 (ddd, $J = 8.3, 7.02, 1.3$ Hz, 1H), 7.54 (d, $J = 9.7$ Hz, 1H), 7.64 (td, $J = 7.3, 1.3$ Hz, 1H), 7.68 (ddd, $J = 8.1, 6.8, 1.6$ Hz, 1H), 7.89 (dd, $J = 7.7, 1.1$ Hz, 1H), 8.69 (d, $J = 8.3$ Hz, 1H), 8.74 (d, $J = 7.7$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 25.3, 31.0, 46.5, 50.0, 55.0, 72.8, 110.9, 115.4, 123.20, 123.25, 123.9, 124.1, 125.0, 125.4, 126.3, 126.49, 126.54, 126.6, 128.6, 129.3, 131.0, 131.2, 131.3, 137.4, 139.3, 144.5, 145.2, 160.7, 201.5 ppm; IR (neat) 3059, 3020, 2962, 2927, 1654 cm^{-1} ; HRMS–FAB (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{25}\text{O}_2$ 405.1849, found 405.1855.

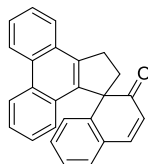
Compound 4e



The general procedure using **1e** (38.1 mg, 0.100 mmol) gave compounds **4e** (23.6 mg, 62%) and **5e** (11.9 mg, 31%). **4e**: pale yellow solids; mp 187–188 °C; ^1H NMR (500 MHz, CDCl_3) δ 0.87 (s, 3H), 1.22 (s, 3H), 3.09 (d, $J = 15.8$ Hz, 1H), 3.22 (d, $J = 15.8$ Hz, 1H), 6.34 (d, $J = 9.7$ Hz, 1H), 6.42 (d, $J = 7.7$ Hz, 1H), 6.89 (d, $J = 8.3$ Hz, 1H), 7.02 (td, $J = 7.5,$

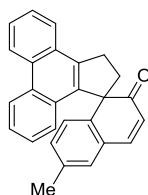
1.1 Hz, 1H), 7.19–7.25 (m, 2H), 7.40–7.47 (m, 2H), 7.60 (d, $J = 10.0$ Hz, 1H), 7.61 (d, $J = 5.4$ Hz, 1H), 8.06 (d, $J = 5.4$ Hz, 1H), 8.35 (d, $J = 8.3$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 25.5, 30.6, 47.4, 51.0, 72.3, 122.8, 124.5, 125.1, 125.2, 125.4, 126.37, 126.41, 127.2, 127.8, 128.3, 129.4, 129.9, 130.4, 134.1, 135.9, 136.1, 137.0, 142.3, 145.3, 201.8 ppm; IR (neat) 3062, 3008, 2962, 2924, 1658 cm^{-1} ; HRMS–FAB (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{21}\text{OS}$ 381.1308, found 381.1313. **5e**: pale yellow solids; mp 118–119 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 1.34 (s, 3H), 1.48 (s, 3H), 2.90 (d, $J = 14.0$ Hz, 1H), 2.96 (d, $J = 14.4$ Hz, 1H), 7.22 (ddd, $J = 8.4, 6.9, 1.3$ Hz, 1H), 7.24–7.28 (m, 1H), 7.36–7.42 (m, 3H), 7.49 (d, $J = 8.3$ Hz, 1H), 7.54 (ddd, $J = 8.2, 7.0, 1.1$ Hz, 1H), 7.63 (d, $J = 5.4$ Hz, 1H), 7.90–7.96 (m, 2H), 8.12 (d, $J = 5.4$ Hz, 1H), 8.41 (d, $J = 8.3$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 27.1, 27.2, 43.2, 90.7, 123.1, 123.8, 124.4, 124.5, 124.9, 125.4, 125.6, 125.7, 127.2, 127.4, 128.1, 128.2, 128.6, 129.2, 129.3, 130.2, 130.4, 131.1, 132.9, 135.7, 139.2, 152.3 ppm; IR (neat) 3059, 3008, 2974, 2927 cm^{-1} ; HRMS–ESI (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{21}\text{OS}$ 381.1308, found 381.1310.

Compound 4f



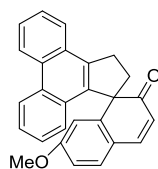
The general procedure using **1f** (0.22 mmol) gave the title compound (65.8 mg, 87%) as white solids: mp 190–191 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 2.40–2.48 (m, 1H), 2.86–2.95 (m, 1H), 3.53–3.70 (m, 2H), 6.43 (d, $J = 10.0$ Hz, 1H), 6.82 (d, $J = 7.7$ Hz, 1H), 6.84 (d, $J = 8.3$ Hz, 1H), 7.12 (td, $J = 7.5, 1.4$ Hz, 1H), 7.22–7.29 (m, 2H), 7.42–7.50 (m, 2H), 7.65–7.74 (m, 3H), 7.95–8.03 (m, 1H), 8.67 (d, $J = 8.3$ Hz, 1H), 8.70–8.76 (m, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 30.8, 43.2, 66.3, 123.2, 123.3, 125.2, 125.3, 125.6, 126.6, 126.75, 126.81, 127.0, 127.4, 128.2, 128.4, 129.4, 129.5, 130.5, 131.2, 131.4, 138.6, 141.7, 145.5, 146.7, 202.9 ppm; IR (neat) 3062, 3012, 2939, 2846, 1654 cm^{-1} ; HRMS–FAB (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{19}\text{O}$ 347.1431, found 347.1436.

Compound 4g



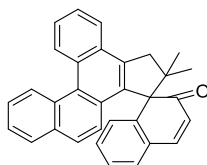
The general procedure using **1g** (0.10 mmol) gave the title compound (26.6 mg, 74%) as pale yellow solids: mp 77–78 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 2.32 (s, 3H), 2.41 (ddd, $J = 13.1, 8.4, 5.2$ Hz, 1H), 2.87 (ddd, $J = 12.9, 8.9, 6.0$ Hz, 1H), 3.53–3.67 (m, 2H), 6.40 (d, $J = 9.7$ Hz, 1H), 6.70 (d, $J = 8.0$ Hz, 1H), 6.85 (d, $J = 8.3$ Hz, 1H), 6.93 (d, $J = 8.0$ Hz, 1H), 7.23–7.28 (m, 2H), 7.45–7.49 (m, 1H), 7.64–7.71 (m, 3H), 7.97–8.00 (m, 1H), 8.66 (d, $J = 8.3$ Hz, 1H), 8.70–8.74 (m, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 20.8, 30.7, 43.3, 66.0, 123.2, 123.3, 125.2, 125.3, 125.4, 125.6, 126.6, 126.7, 126.8, 127.3, 128.3, 129.4, 130.0, 131.2, 131.3, 136.6, 138.8, 141.6, 143.8, 145.7, 203.2 ppm; IR (neat) 3062, 3012, 2920, 2850, 1654 cm^{-1} ; HRMS–ESI (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{21}\text{O}$ 361.1587, found 361.1592.

Compound 4h



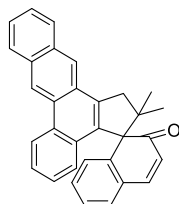
The general procedure using **1h** (0.20 mmol) gave the title compound (59.4 mg, 79%) as white solids: mp 103–105 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.44 (ddd, *J* = 13.0, 8.7, 5.3 Hz, 1H), 2.89 (ddd, *J* = 12.9, 9.2, 6.3 Hz, 1H), 3.54 (s, 3H), 3.56–3.68 (m, 2H), 6.30 (d, *J* = 9.7 Hz, 1H), 6.36 (d, *J* = 2.6 Hz, 1H), 6.76 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.89 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.25–7.29 (m, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.45–7.49 (m, 1H), 7.63–7.71 (m, 3H), 7.96–7.99 (m, 1H), 8.66 (d, *J* = 8.3 Hz, 1H), 8.70–8.74 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 30.8, 43.5, 55.2, 66.4, 111.6, 114.0, 121.9, 122.7, 123.2, 123.3, 125.36, 125.44, 125.6, 126.6, 126.8, 128.2, 129.4, 131.1, 131.2, 131.4, 138.9, 141.6, 145.4, 149.1, 161.6, 202.9 ppm; IR (neat) 3062, 3008, 2939, 2846, 1651 cm⁻¹; HRMS–ESI (*m/z*) [M+H]⁺ calcd for C₂₇H₂₁O₂ 377.1536, found 377.1540.

Compound 4i



The general procedure using **1i** (42.5 mg, 0.100 mmol) gave the title compound (35.7 mg, 84%) as white solids: 204–205 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.89 (s, 3H), 1.24 (s, 3H), 3.34 (s, 2H), 6.35 (d, *J* = 10.0 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 1H), 6.98 (td, *J* = 7.5, 1.4 Hz, 1H), 7.22 (td, *J* = 7.5, 1.3 Hz, 1H), 7.43 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.51–7.57 (m, 2H), 7.60–7.64 (m, 2H), 7.66–7.73 (m, 2H), 7.86 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.99–8.03 (m, 1H), 9.06 (d, *J* = 8.6 Hz, 1H), 9.15 (d, *J* = 7.7 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 25.5, 31.0, 46.5, 50.4, 73.0, 124.5, 124.8, 125.5, 125.76, 125.82, 126.0, 126.4, 126.9, 127.2, 127.7, 128.17, 128.25, 128.3, 128.6, 128.9, 129.5, 130.1, 130.3, 130.6, 131.0, 132.7, 137.6, 140.0, 142.4, 145.3, 202.1 ppm; IR (neat) 3062, 3012, 2962, 2927, 1662 cm⁻¹; HRMS–FAB (*m/z*) [M+H]⁺ calcd for C₃₂H₂₅O 425.1900, found 425.1905.

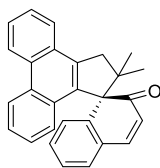
Compound 4j



The general procedure using **1j** (0.20 mmol) gave the title compound (66.8 mg, 79%) as white solids: mp 228–230 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.89 (s, 3H), 1.26 (s, 3H), 3.32 (d, *J* = 15.8 Hz, 1H), 3.37 (d, *J* = 15.8 Hz, 1H), 6.35 (d, *J* = 10.0 Hz, 1H), 6.59 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 7.19–7.24 (m, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.54–7.62 (m, 3H), 8.03–8.09 (m, 1H), 8.11–8.18 (m, 1H), 8.36 (s, 1H), 8.84 (d, *J* = 8.3 Hz, 1H), 9.22 (s, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 25.5, 31.1, 47.0, 50.0, 73.0, 122.2, 123.3, 123.5, 125.7, 125.9, 126.5, 126.7, 127.2, 127.8, 128.0, 128.1, 128.6, 128.7, 129.5, 129.7, 130.4, 131.6, 131.8, 131.9, 137.2, 139.5, 142.1, 145.3, 201.9 ppm; IR (neat) 3055, 3012, 2962, 2927, 1658 cm⁻¹; HRMS–FAB (*m/z*) [M+H]⁺ calcd for C₃₂H₂₅O 425.1900, found 425.1905.

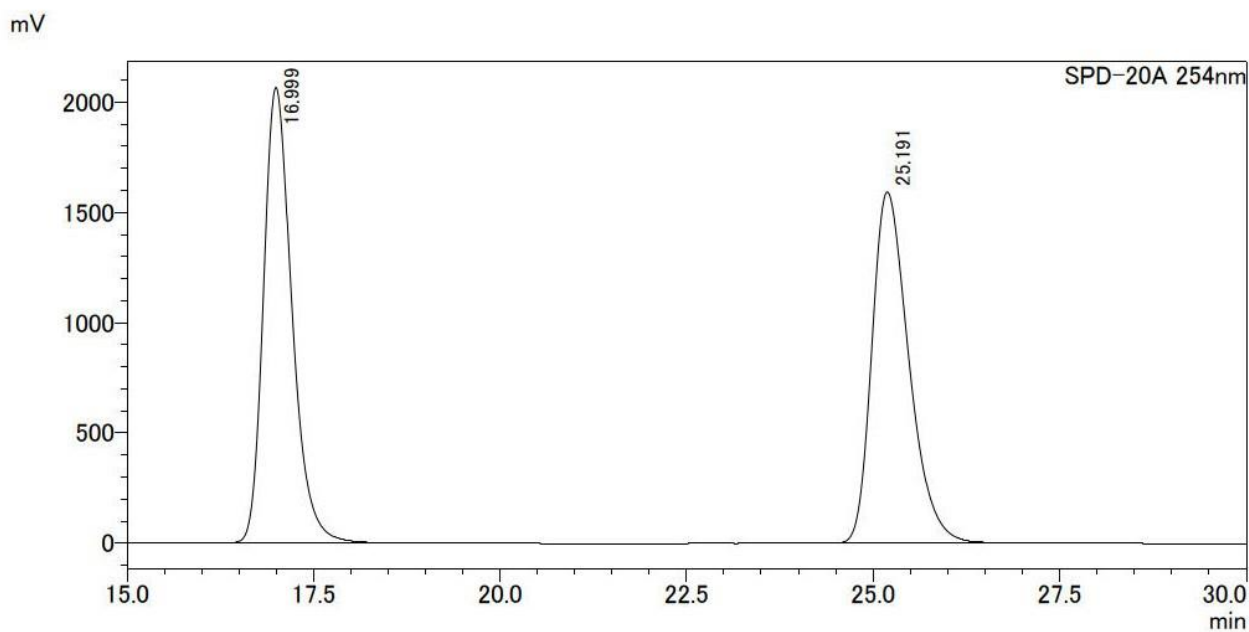
Chirality Transfer Experiments

(+)-**4a**



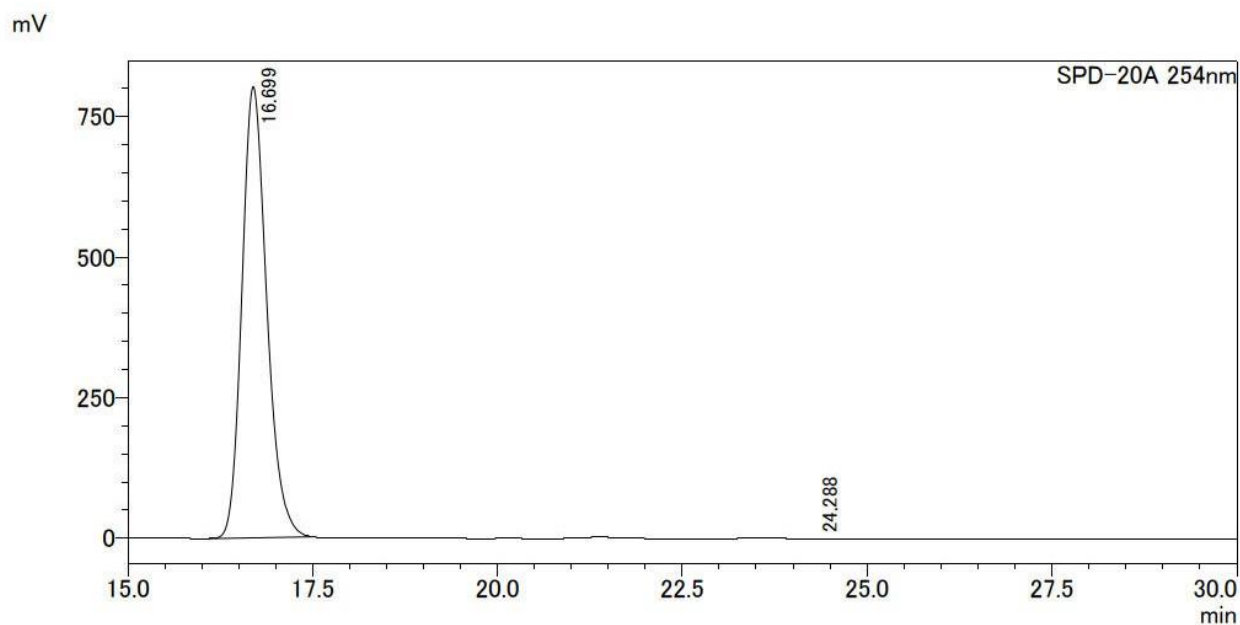
The general procedure using (+)-**1a** (14.8 mg, 0.0395 mmol, 99% ee) gave the title compound (12.8 mg, 86% yield, 99% ee) as white solids. Analytical HPLC (column: Daicel Chiralpak AD-H, eluent: hexane/*i*-PrOH = 90/10, flow rate: 0.75 mL/min, detection: UV 254 nm, temperature: 25 °C) (+)-**4a** 17.0 min, (–)-**4a** 25.2 min. $[\alpha]_D^{21} +37.2$ (c 1.28, CHCl₃, 99% ee). Recrystallization from CHCl₃ gave colorless, clear plates suitable for X-ray crystallography. The absolute configuration was determined by X-ray crystallography.

Racemic Sample of **4a**



SPD-20A 254nm				
peak#	time	area	height	area%
1	16.999	54545608	2066424	49.804
2	25.191	54975082	1593477	50.196
合計		109520690	3659901	100.000

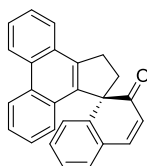
Optically Active Sample of (+)-**4a** (99% ee)



SPD-20A 254nm

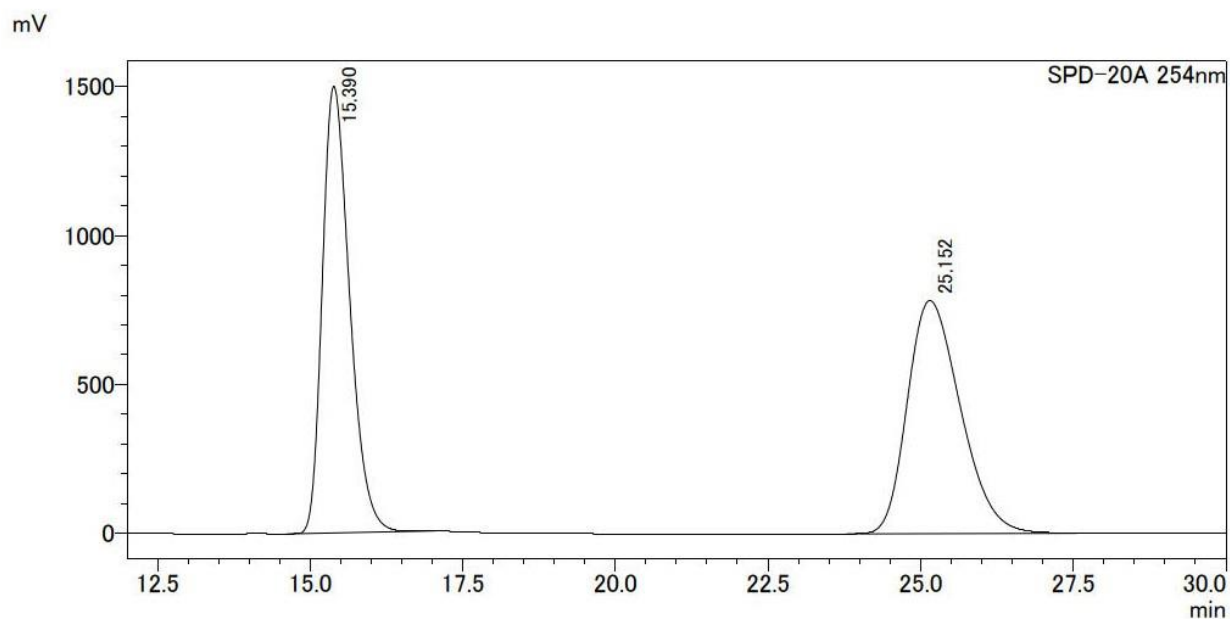
peak#	time	area	height	area%
1	16.699	18745275	802299	100.003
2	24.288	-477	0	-0.003
合計		18744798	802299	100.000

(+)-**4f**



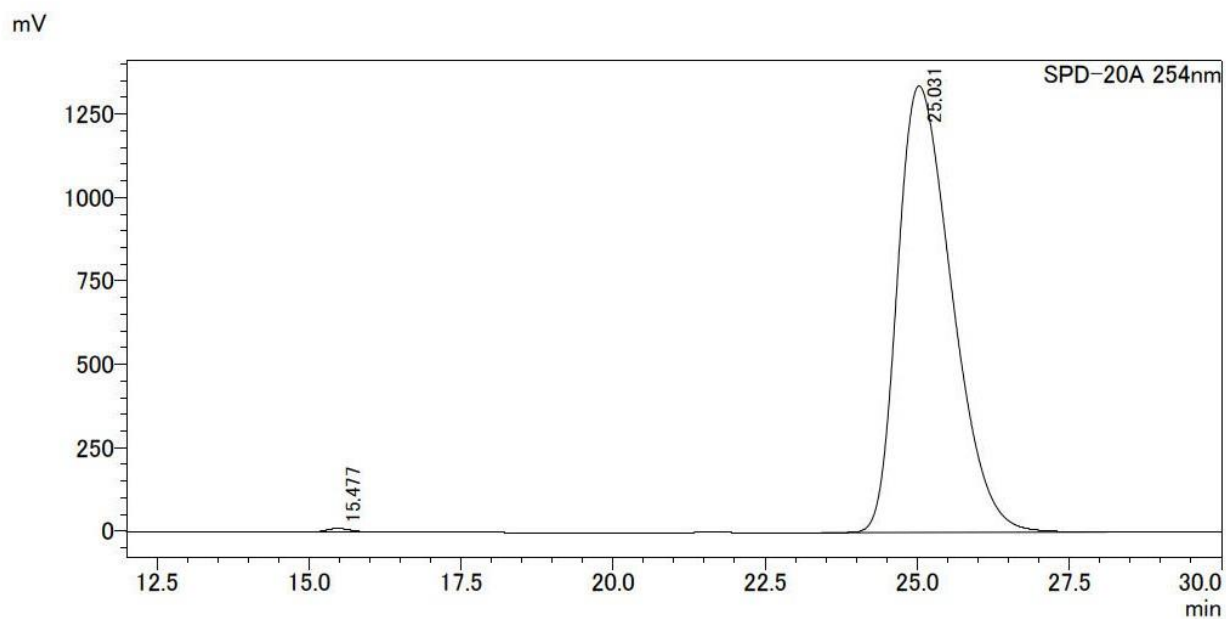
The general procedure using (+)-**1f** (7.3 mg, 0.021 mmol, 99% ee) gave the title compound (6.0 mg, 82% yield, 99% ee) as white solids. Analytical HPLC (column: Daicel Chiralpak AS-H, eluent: hexane/*i*-PrOH = 90/10, flow rate: 0.75 mL/min, detection: UV 254 nm, temperature: 25 °C) (+)-**4f** 25.2 min, (–)-**4f** 15.4 min. $[\alpha]_D^{21} +39.8$ (c 0.59, CHCl₃, 99% ee). Recrystallization from hexanes/EtOH gave colorless, clear plates suitable for X-ray crystallography. The absolute configuration was determined by X-ray crystallography.

Chromatogram of racemic **4f**



SPD-20A 254nm				
peak#	time	area	height	area%
1	15.390	46601304	1501138	49.622
2	25.152	47310817	783175	50.378
合計		93912121	2284313	100.000

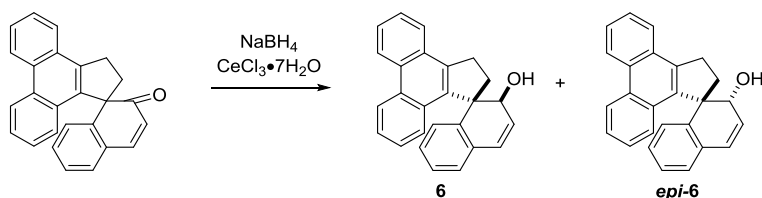
Chromatogram of (+)-**4f** (99% ee)



SPD-20A 254nm				
peak#	time	area	height	area%
1	15.477	332918	11436	0.400
2	25.031	82962814	1338405	99.600
合計		83295732	1349841	100.000

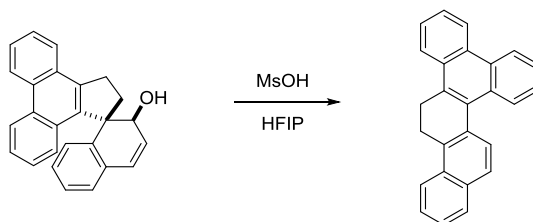
6. Derivertizations of Products

Compound 6 and *epi*-6



To a stirred solution of compound **4f** (69.3 mg, 0.200 mmol) and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (112 mg, 0.300 mmol) in THF (0.6 mL) and MeOH (1.4 mL) was added five portions of NaBH_4 (11.3 mg, 0.300 mmol each, totally 1.50 mmol) every 5 min. After stirring another 5 min, the reaction was quenched with sat. aqueous NH_4Cl and diluted with EtOAc. Phases were separated, and the aqueous phase was extracted three times with EtOAc. The combined organic phases were washed with brine, dried over MgSO_4 and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc) to give compound **6** (57.0 mg, 82%) along with *epi-6* (9.2 mg, 13%). Recrystallization of compound **6** from $\text{CHCl}_3/\text{EtOH}$ gave colorless, clear plates suitable for X-ray crystallographic studies. **6**: white solids; mp 85–87 °C; ^1H NMR (500 MHz, CDCl_3) δ 1.40 (d, $J = 3.4$ Hz, 1H), 1.94–2.04 (m, 1H), 3.35–3.49 (m, 3H), 5.58–5.62 (m, 1H), 5.99 (dd, $J = 10.0, 1.7$ Hz, 1H), 6.51 (dd, $J = 9.9, 2.7$ Hz, 1H), 6.78 (d, $J = 7.5$ Hz, 1H), 6.91–6.98 (m, 1H), 7.13–7.19 (m, 2H), 7.33–7.39 (m, 1H), 7.51–7.58 (m, 1H), 7.65–7.74 (m, 2H), 7.77 (d, $J = 8.3$ Hz, 1H), 7.91–7.97 (m, 1H), 8.71–8.79 (m, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 31.6, 33.1, 62.7, 74.0, 123.0, 123.7, 125.32, 125.34, 125.9, 126.7, 126.76, 126.85, 126.9, 127.0, 127.1, 127.5, 128.1, 128.4, 129.4, 131.0, 131.5, 131.67, 131.70, 135.9, 142.4, 142.9 ppm; IR (neat) 3564, 3062, 3016, 2939, 2924, 2846 cm^{-1} ; HRMS-ESI (m/z) [$\text{M}+\text{Na}$] $^+$ calcd for $\text{C}_{26}\text{H}_{20}\text{ONa}$ 371.1406, found 371.1403. *epi-6*: white solids; mp 165–166 °C; ^1H NMR (500 MHz, CDCl_3) δ 1.44 (d, $J = 4.9$ Hz, 1H), 2.04 (dt, $J = 12.9, 10.2$ Hz, 1H), 2.76 (dd, $J = 12.9, 7.2$ Hz, 1H), 3.33–3.49 (m, 2H), 4.34 (t, $J = 5.0$ Hz, 1H), 6.24 (dd, $J = 9.6, 5.6$ Hz, 1H), 6.80 (d, $J = 9.4$ Hz, 1H), 6.91 (d, $J = 7.5$ Hz, 1H), 7.06 (td, $J = 7.5, 1.1$ Hz, 1H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.23–7.33 (m, 2H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.63–7.76 (m, 3H), 7.88–8.02 (m, 1H), 8.73 (d, $J = 8.3$ Hz, 1H), 8.76 (d, $J = 8.0$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 29.3, 38.7, 60.1, 69.7, 122.8, 123.1, 125.1, 125.5, 125.6, 126.46, 126.48, 126.5, 126.7, 127.6, 128.2, 128.5, 128.9, 129.7, 130.3, 130.5, 130.7, 130.8, 130.9, 137.0, 141.1, 141.4 ppm; IR (neat) 3545, 3062, 3016, 3020, 2924, 2850 cm^{-1} ; HRMS-ESI (m/z) [$\text{M}+\text{Na}$] $^+$ calcd for $\text{C}_{26}\text{H}_{20}\text{ONa}$ 371.1406, found 371.1411.

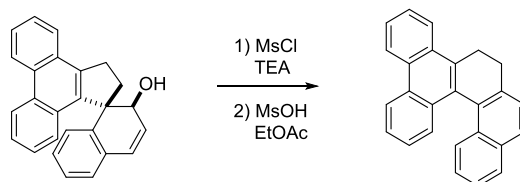
Compound 7



To a stirred solution of compound **6** (34.8 mg, 0.100 mmol) in HFIP (1.0 mL) was added three portions of MsOH (20 μL , 0.30 mmol each, totally 0.90 mmol) every 10 min. After stirring another 10 min, the reaction was quenched with sat. aqueous NaHCO_3 and diluted with CHCl_3 . Phases were separated and the organic phase was washed with water, dried over MgSO_4 and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc) followed by preparative HPLC (column: YMC-GPC T-2000 and YMC-GPC T-4000, eluent: CHCl_3) to give the title compound (25.1 mg, 76%) as white solids. Recrystallization from cyclohexane/ CHCl_3 gave colorless, clear plates suitable for X-ray crystallography: mp 91–92 °C; ^1H NMR (500 MHz, CDCl_3) δ 3.08–3.65 (m, 4H), 7.49–7.54 (m, 1H), 7.56–7.62 (m, 2H), 7.63–7.70 (m, 3H), 7.83 (d, $J = 8.6$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.97 (d, $J = 8.6$ Hz, 1H), 8.21–8.29 (m, 2H), 8.47

(dd, $J = 8.3, 0.9$ Hz, 1H), 8.72–8.81 (m, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 23.9, 25.5, 123.0, 123.2, 123.7, 124.0, 125.2, 125.5, 125.8, 126.1, 126.2, 126.4, 126.5, 126.9, 127.2, 128.5, 129.2, 130.0, 130.5, 130.6, 131.2, 131.3, 131.9, 132.7, 133.6, 134.5 ppm; IR (neat) 3066, 3012, 2958, 2885, 2827 cm^{-1} ; HRMS–FAB (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{19}$ 331.1482, found 331.1487.

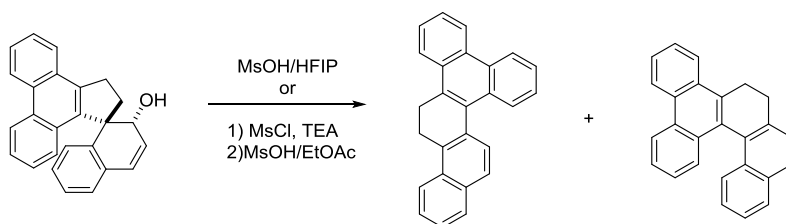
Compound 8



To a stirred solution of compound **9** (69.7 mg, 0.200 mmol) and Et_3N (69 μL , 0.50 mmol) in dry DCM (2.0 mL) was added MsCl (31 μL , 0.40 mmol) at 0 $^\circ\text{C}$. After stirring for 1.5 h, the reaction was quenched with water and diluted with EtOAc and Et_2O (1/1). Phases were separated and the organic layer was washed with water followed by brine, dried over MgSO_4 and concentrated. The resulting crude product was used without further purifications.

To a stirred solution of the crude product above in dry EtOAc was added silica gel (Wakogel 60N, dried at 100 $^\circ\text{C}$ under reduced pressure prior to use, 400 mg). After stirring for 20 h, the reaction mixture was diluted with CHCl_3 , the silica gel was filtered off, washed with CHCl_3 , and the filtrate was concentrated. The resulting solids were washed with hexanes/ Et_2O to give the title compound (40.4 mg, 61%) as white solids: mp 207–209 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 2.89 (td, $J = 14.75, 5.2$ Hz, 1H), 2.95–3.09 (m, 2H), 3.55–3.63 (m, 1H), 7.15–7.20 (m, 1H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.37–7.45 (m, 2H), 7.56–7.64 (m, 3H), 7.64–7.73 (m, 2H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.3$ Hz, 1H), 8.22–8.28 (m, 1H), 8.75 (d, $J = 8.3$ Hz, 1H), 8.77–8.83 (m, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 26.2, 30.6, 122.9, 123.1, 124.0, 124.6, 124.8, 125.4, 125.6, 126.0, 126.3, 126.8, 127.2, 127.7, 128.0, 128.3, 129.6, 129.9, 130.0, 130.2, 130.6, 130.8, 131.2, 133.2, 136.4, 138.2 ppm; IR (neat) 3051, 3008, 2943, 2889, 2831 cm^{-1} ; HRMS–FAB (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{19}$ 331.1482, found 331.1487.

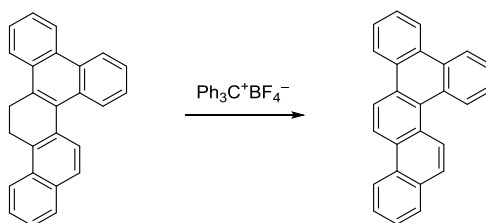
Formations of Compounds 7 and 8 from *epi-6*



Analogous procedure to that for the synthesis compound **7** using *epi-6* (7.0 mg, 0.020 mmol) instead of compound **6** yielded compound **7** (53%) and **8** (16%) along with recovered starting material (31%). Yields were determined by NMR using triphenylmethane as an internal standard.

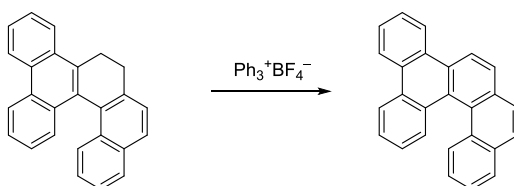
On the other hand, analogous procedure to that for the synthesis compound **8** using *epi-6* (7.0 mg, 0.020 mmol) instead of compound **6** yielded compound **7** (9%) and **8** (60%). Yields were determined by NMR using triphenylmethane as an internal standard.

Compound 9



To a test tube containing compound **7** (33.0 mg, 0.100 mmol) and triphenylcarbenium tetrafluoroborate (99.0 mg, 0.300 mmol) was added dry DCE (3.0 mL), and the resulting solution was heated to 80 °C. After stirring for 2 h, the reaction was quenched with water and diluted with CHCl₃. Phases were separated and the organic phase was washed with water, dried over MgSO₄ and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc) and the resulting solids were washed with hexanes/Et₂O to give the title compound (25.3 mg, 77%) as white solids: mp 152–153 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.62–7.79 (m, 6H), 7.90 (d, *J* = 9.2 Hz, 1H), 7.99 (dd, *J* = 7.73, 1.1 Hz, 1H), 8.68–8.78 (m, 3H), 8.79–8.88 (m, 4H), 8.91 (d, *J* = 8.9 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 121.0, 122.1, 123.1, 123.2, 123.5, 123.6, 125.9, 126.1, 126.66, 126.69, 126.82, 126.85, 127.2, 127.4, 128.11, 128.14, 128.4, 128.5, 129.4, 129.7, 130.0, 130.1, 130.23, 130.25, 131.1, 131.6 ppm; IR (neat) 3059, 3028, 2924 cm⁻¹; UV–vis (CH₂Cl₂) λ_{max} (ε) 298 (78400), 288 (58400), 247 (25900) nm (L mol⁻¹ cm⁻¹); Fluorescence (CH₂Cl₂) λ_{max} (normalized intensity) 409 (1.0), 390 (0.91) nm; HRMS–FAB (*m/z*) [M+H]⁺ calcd for C₂₆H₁₇ 329.1325, found 329.1330.

Compound 10



To a test tube containing compound **8** (16.5 mg, 0.0500 mmol) and triphenylcarbenium tetrafluoroborate (49.5 mg, 0.150 mmol) was added dry DCE (1.5 mL), and the resulting solution was heated to 80 °C. After stirring for 5 h, the reaction was quenched with water and diluted with CHCl₃. Phases were separated and the organic phase was washed with water, dried over MgSO₄ and concentrated. The residue was purified by silica gel column chromatography (hexanes/EtOAc). The resulting solids were washed with hexanes/Et₂O to give the title compound (14.1 mg, 86%) as white solids. The spectroscopic data were in good agreement with those reported.³

7. DFT Calculations

All the calculations were performed using Gaussian 16 program.⁴ Geometry optimizations were performed at B3LYP/6–31G(d,p)/CPCM(DCE) level of theory. The TS geometries were verified by vibrational frequency analysis and intrinsic reaction coordinate calculations were also performed at the same level of theory. Single point energies were calculated at the mPW1PW91/6–311+G(2d,p)/CPCM (DCE) theoretical level for the optimized geometries. This level of theory was previously applied for the rearrangements of carbocations in literature.⁵

1f-H⁺

Zero-point correction= 0.373024 (Hartree/Particle)

Thermal correction to Energy=	0.391748
Thermal correction to Enthalpy=	0.392692
Thermal correction to Gibbs Free Energy=	0.328271
Sum of electronic and zero-point Energies=	-1076.885335
Sum of electronic and thermal Energies=	-1076.866611
Sum of electronic and thermal Enthalpies=	-1076.865667
Sum of electronic and thermal Free Energies=	-1076.930087

C	1.01095	-1.18636	0.4928
O	0.37913	-2.0436	-0.77781
C	0.5745	-1.78798	1.82811
C	2.43859	-0.96169	0.21861
C	-0.97965	-1.57583	-0.87172
C	-1.23012	-0.52805	-0.02226
C	-1.91212	-2.24097	-1.67531
C	0.04626	-0.00799	0.64766
C	0.55772	1.32565	0.12176
C	0.08435	-0.35264	2.19112
H	-1.6201	-3.06185	-2.3194
C	-3.21178	-1.79515	-1.58948
C	-3.58438	-0.76797	-0.67881
H	-3.98195	-2.25904	-2.19713
C	-2.59234	-0.12953	0.14781
C	-4.9459	-0.38202	-0.54645
H	-5.68364	-0.85868	-1.18497
C	-5.32806	0.5614	0.37878
C	-4.36102	1.1553	1.22291
H	-6.37188	0.84215	0.47401
C	-3.02905	0.82123	1.11131
H	-4.67162	1.87809	1.97052
H	-2.31035	1.27947	1.7804
H	-0.25443	-2.49055	1.73144
H	1.36554	-2.22937	2.43279
H	-0.86132	-0.28237	2.72696
H	0.8487	0.23145	2.70525
C	3.33414	-2.0384	0.32617
C	2.88357	0.33861	-0.11165
C	4.26864	0.50697	-0.29823
C	-0.30175	2.41907	-0.03688
C	1.92508	1.46729	-0.23082

C	2.36063	2.70995	-0.72797
H	-1.35089	2.31896	0.20283
C	0.15579	3.64571	-0.51178
C	1.49671	3.79009	-0.86163
H	3.39048	2.83869	-1.03615
H	1.86915	4.73375	-1.24702
H	-0.53607	4.47522	-0.61649
C	5.15113	-0.56409	-0.20466
H	4.67656	1.48691	-0.50952
H	6.21148	-0.39201	-0.36009
H	2.95686	-3.02269	0.58642
C	4.68998	-1.84926	0.09831
H	5.38096	-2.68182	0.1729
H	0.89825	-1.89756	-1.59632

TS1

Zero-point correction=	0.372077 (Hartree/Particle)
Thermal correction to Energy=	0.390390
Thermal correction to Enthalpy=	0.391335
Thermal correction to Gibbs Free Energy=	0.327721
Sum of electronic and zero-point Energies=	-1076.884461
Sum of electronic and thermal Energies=	-1076.866147
Sum of electronic and thermal Enthalpies=	-1076.865203
Sum of electronic and thermal Free Energies=	-1076.928816

C	1.04717	-1.16597	0.54241
O	0.35793	-2.07288	-0.89067
C	0.5714	-1.82817	1.81854
C	2.45199	-0.9442	0.26184
C	-0.96885	-1.57089	-0.93444
C	-1.21691	-0.55322	-0.04196
C	-1.92978	-2.18134	-1.75489
C	0.05109	-0.02962	0.64453
C	0.54993	1.312	0.12717
C	0.06674	-0.39675	2.19341
H	-1.65056	-2.9754	-2.43748
C	-3.22544	-1.73488	-1.63974
C	-3.58241	-0.74526	-0.68348
H	-4.00407	-2.16787	-2.2596

C	-2.5751	-0.14923	0.15502
C	-4.93937	-0.3539	-0.52295
H	-5.68677	-0.80129	-1.17153
C	-5.30542	0.55892	0.43875
C	-4.32354	1.11627	1.29029
H	-6.34587	0.84443	0.55486
C	-2.99577	0.7743	1.15279
H	-4.61838	1.81809	2.06391
H	-2.26795	1.21055	1.82647
H	-0.25921	-2.51923	1.67266
H	1.33987	-2.28733	2.43831
H	-0.89362	-0.34627	2.70389
H	0.8161	0.18387	2.73173
C	3.36077	-2.01119	0.3995
C	2.88232	0.35159	-0.11929
C	4.26217	0.52235	-0.33504
C	-0.32021	2.39842	-0.02388
C	1.91382	1.46785	-0.23659
C	2.33559	2.71621	-0.7333
H	-1.36639	2.28952	0.22417
C	0.12371	3.62967	-0.49874
C	1.461	3.7878	-0.85853
H	3.36278	2.85637	-1.0449
H	1.8216	4.73623	-1.24329
H	-0.57594	4.45363	-0.59491
C	5.15211	-0.53988	-0.21606
H	4.66156	1.49521	-0.58992
H	6.20829	-0.36658	-0.39663
H	2.99239	-2.98839	0.69518
C	4.70864	-1.81852	0.14503
H	5.41017	-2.64001	0.23874
H	0.85865	-1.88684	-1.70879

2

Zero-point correction=	0.371561 (Hartree/Particle)
Thermal correction to Energy=	0.390974
Thermal correction to Enthalpy=	0.391918
Thermal correction to Gibbs Free Energy=	0.325830
Sum of electronic and zero-point Energies=	-1076.892450

Sum of electronic and thermal Energies=	-1076.873037
Sum of electronic and thermal Enthalpies=	-1076.872093
Sum of electronic and thermal Free Energies=	-1076.938181

C	1.06905	-1.1726	0.61099
O	0.19594	-1.60807	-1.76697
C	0.4287	-1.99312	1.66196
C	2.45334	-0.99241	0.4311
C	-1.07339	-1.29737	-1.3741
C	-1.22379	-0.51242	-0.23601
C	-2.18773	-1.77548	-2.10501
C	0.0668	-0.09024	0.48099
C	0.62216	1.2428	0.04737
C	-0.02116	-0.54575	2.06287
H	-2.02228	-2.38936	-2.9857
C	-3.45618	-1.46756	-1.68862
C	-3.67346	-0.64907	-0.5496
H	-4.31466	-1.84356	-2.23693
C	-2.54554	-0.13837	0.18266
C	-4.99294	-0.31787	-0.14237
H	-5.82411	-0.72141	-0.71385
C	-5.2212	0.5002	0.94009
C	-4.12109	1.03323	1.64722
H	-6.23387	0.74738	1.24146
C	-2.82644	0.7279	1.28141
H	-4.29241	1.70059	2.48624
H	-2.01784	1.19202	1.83213
H	-0.43376	-2.57897	1.34832
H	1.08057	-2.5467	2.33232
H	-1.03954	-0.49193	2.43827
H	0.68898	-0.01689	2.69392
C	3.33612	-2.08189	0.66079
C	2.94213	0.27539	-0.01802
C	4.32543	0.37789	-0.24727
C	-0.23485	2.32568	-0.19639
C	2.01779	1.40497	-0.176
C	2.49323	2.67005	-0.58328
H	-1.30231	2.20262	-0.07367
C	0.25834	3.56398	-0.58941
C	1.63235	3.73792	-0.77898

H	3.55074	2.82427	-0.7545
H	2.02727	4.70007	-1.0879
H	-0.42702	4.38967	-0.75058
C	5.16985	-0.70677	-0.04542
H	4.76176	1.30834	-0.58486
H	6.23155	-0.58831	-0.23748
H	2.93177	-3.02837	1.00175
C	4.68369	-1.94656	0.40895
H	5.36178	-2.77848	0.5608
H	0.17867	-2.25161	-2.48955

TS2

Zero-point correction=	0.370718 (Hartree/Particle)
Thermal correction to Energy=	0.389768
Thermal correction to Enthalpy=	0.390712
Thermal correction to Gibbs Free Energy=	0.325439
Sum of electronic and zero-point Energies=	-1076.893345
Sum of electronic and thermal Energies=	-1076.874295
Sum of electronic and thermal Enthalpies=	-1076.873351
Sum of electronic and thermal Free Energies=	-1076.938624

C	-1.04989	-1.20158	-0.46718
O	0.0689	-1.77312	1.93522
C	-0.4344	-2.1423	-1.43087
C	-2.46981	-0.99208	-0.39099
C	1.26737	-1.38133	1.42304
C	1.26505	-0.53773	0.31375
C	2.47853	-1.82974	2.00652
C	-0.09725	-0.14127	-0.22007
C	-0.64365	1.18723	0.15081
C	-0.12301	-0.73098	-1.94828
H	2.4386	-2.48949	2.86837
C	3.67967	-1.44141	1.47471
C	3.73873	-0.56616	0.35822
H	4.60735	-1.79816	1.91188
C	2.51735	-0.08166	-0.2222
C	4.98796	-0.15587	-0.17599
H	5.8953	-0.54079	0.28086
C	5.05596	0.71322	-1.24148

C	3.86173	1.21874	-1.79991
H	6.01641	1.02029	-1.64213
C	2.63049	0.8377	-1.30629
H	3.90892	1.92548	-2.6226
H	1.74227	1.28626	-1.73571
H	0.45806	-2.67415	-1.11603
H	-1.11483	-2.74932	-2.0174
H	0.91351	-0.54928	-2.2095
H	-0.85507	-0.24615	-2.58477
C	-3.34516	-2.08074	-0.6069
C	-2.97734	0.29252	-0.04978
C	-4.37478	0.43059	0.05472
C	0.22032	2.23562	0.51734
C	-2.04992	1.4055	0.1792
C	-2.5213	2.69607	0.49604
H	1.28722	2.06227	0.54868
C	-0.27027	3.49347	0.83393
C	-1.64975	3.72738	0.80815
H	-3.58452	2.89858	0.50692
H	-2.04285	4.71039	1.04606
H	0.4169	4.28976	1.09987
C	-5.22139	-0.64873	-0.15521
H	-4.81386	1.38588	0.31057
H	-6.29342	-0.50766	-0.06207
H	-2.93866	-3.05731	-0.84347
C	-4.71138	-1.91534	-0.48006
H	-5.38121	-2.75465	-0.63033
H	0.20557	-2.37368	2.68175

3

Zero-point correction=	0.371362 (Hartree/Particle)
Thermal correction to Energy=	0.391052
Thermal correction to Enthalpy=	0.391996
Thermal correction to Gibbs Free Energy=	0.325138
Sum of electronic and zero-point Energies=	-1076.915051
Sum of electronic and thermal Energies=	-1076.895362
Sum of electronic and thermal Enthalpies=	-1076.894418
Sum of electronic and thermal Free Energies=	-1076.961275

C	-0.90164	-1.23068	0.23411
O	0.89387	-0.08584	2.91471
C	-0.46217	-2.46837	1.16783
C	-2.34244	-1.12001	-0.07223
C	1.82823	-0.14372	1.92385
C	1.37328	-0.14957	0.61201
C	3.21382	-0.2044	2.21618
C	-0.09587	-0.05083	0.34461
C	-0.68625	1.22585	0.18726
C	-0.15002	-2.56323	-0.23654
H	3.53695	-0.20549	3.25324
C	4.12869	-0.25597	1.19546
C	3.71669	-0.2431	-0.16394
H	5.18964	-0.30269	1.42204
C	2.31677	-0.17943	-0.46834
C	4.65932	-0.28034	-1.22493
H	5.71592	-0.32974	-0.97736
C	4.24849	-0.25165	-2.5387
C	2.86879	-0.18083	-2.84149
H	4.97757	-0.27992	-3.34197
C	1.92603	-0.14444	-1.8362
H	2.54732	-0.1523	-3.87806
H	0.87373	-0.083	-2.09431
H	0.31414	-2.22949	1.88135
H	-1.32772	-2.97912	1.57293
H	0.86913	-2.40472	-0.56446
H	-0.76608	-3.16185	-0.8969
C	-3.15853	-2.26008	-0.20431
C	-2.92341	0.16536	-0.23557
C	-4.30526	0.25405	-0.53019
C	0.11556	2.40204	0.31479
C	-2.09285	1.35251	-0.09688
C	-2.61596	2.65395	-0.23388
H	1.17092	2.29161	0.52778
C	-0.43404	3.6526	0.17383
C	-1.8113	3.7727	-0.1024
H	-3.66634	2.80074	-0.44543
H	-2.2522	4.75809	-0.21474
H	0.18201	4.53906	0.27415
C	-5.08634	-0.87802	-0.65767

H	-4.77215	1.2214	-0.66181
H	-6.14297	-0.78442	-0.88451
H	-2.74186	-3.25327	-0.08264
C	-4.50812	-2.1455	-0.49275
H	-5.11421	-3.03997	-0.59123
H	1.32633	-0.09134	3.78078

TS3

Zero-point correction=	0.369378 (Hartree/Particle)
Thermal correction to Energy=	0.388875
Thermal correction to Enthalpy=	0.389819
Thermal correction to Gibbs Free Energy=	0.323330
Sum of electronic and zero-point Energies=	-1076.882344
Sum of electronic and thermal Energies=	-1076.862847
Sum of electronic and thermal Enthalpies=	-1076.861902
Sum of electronic and thermal Free Energies=	-1076.928391

C	-0.85794	-1.19977	0.00554
O	0.71958	0.23936	2.81698
C	0.36823	-2.57946	1.28038
C	-2.29871	-1.18928	-0.1349
C	1.69833	0.06374	1.89496
C	1.31824	-0.07505	0.55461
C	3.06609	0.04981	2.26963
C	-0.13573	-0.02831	0.20425
C	-0.78772	1.24638	0.05357
C	-0.07408	-2.52569	-0.09244
H	3.32986	0.13849	3.31941
C	4.0397	-0.06617	1.31019
C	3.71102	-0.15647	-0.07127
H	5.0856	-0.07877	1.60185
C	2.33175	-0.14095	-0.45948
C	4.71502	-0.2537	-1.0664
H	5.75588	-0.27203	-0.75627
C	4.3809	-0.32073	-2.40326
C	3.02312	-0.29503	-2.79009
H	5.15709	-0.39255	-3.15813
C	2.02076	-0.2142	-1.84351
H	2.76333	-0.34124	-3.84304

H	0.98294	-0.19598	-2.1595
H	-0.3674	-2.64791	2.07585
H	1.41218	-2.55346	1.56652
H	0.73549	-2.48678	-0.81949
H	-0.76029	-3.3334	-0.35721
C	-3.06669	-2.37664	-0.17397
C	-2.96617	0.06861	-0.25052
C	-4.36655	0.06948	-0.42899
C	-0.04761	2.45311	0.15536
C	-2.19405	1.30403	-0.19165
C	-2.78823	2.57495	-0.34669
H	1.01501	2.40284	0.36053
C	-0.65807	3.6788	-0.0103
C	-2.03981	3.73685	-0.26422
H	-3.85011	2.65973	-0.53904
H	-2.52792	4.6979	-0.39115
H	-0.07652	4.59188	0.06086
C	-5.09347	-1.10781	-0.4726
H	-4.89814	1.00704	-0.53156
H	-6.16988	-1.07199	-0.60484
H	-2.59388	-3.34192	-0.0395
C	-4.43993	-2.34096	-0.339
H	-5.00563	-3.26649	-0.3582
H	1.10527	0.31639	3.7018

4f-H⁺

Zero-point correction=	0.373877 (Hartree/Particle)
Thermal correction to Energy=	0.392880
Thermal correction to Enthalpy=	0.393824
Thermal correction to Gibbs Free Energy=	0.328407
Sum of electronic and zero-point Energies=	-1076.948119
Sum of electronic and thermal Energies=	-1076.929116
Sum of electronic and thermal Enthalpies=	-1076.928172
Sum of electronic and thermal Free Energies=	-1076.993590

C	-1.03165	-1.22314	0.44016
O	0.94283	0.51675	2.88278
C	1.04879	-2.00427	1.35278
C	-2.42421	-1.10615	0.10708

C	1.80115	0.27717	1.92071
C	1.23938	-0.511	0.7755
C	3.14602	0.64848	2.00507
C	-0.20544	-0.13731	0.4221
C	-0.66558	1.17203	0.04659
C	-0.30176	-2.49293	0.79347
H	3.52287	1.12861	2.90227
C	3.97343	0.42324	0.92317
C	3.5248	-0.14553	-0.3035
H	5.01584	0.72054	0.9975
C	2.16815	-0.55185	-0.42986
C	4.41314	-0.26538	-1.39711
H	5.44409	0.05255	-1.27713
C	3.96473	-0.77313	-2.60449
C	2.62377	-1.16029	-2.73021
H	4.64098	-0.86432	-3.44711
C	1.73616	-1.05248	-1.65692
H	2.26248	-1.54705	-3.67772
H	0.70159	-1.34732	-1.78869
H	0.99496	-1.95266	2.44139
H	1.89685	-2.63262	1.08039
H	-0.17134	-3.12725	-0.09215
H	-0.82748	-3.09776	1.53895
C	-3.28116	-2.23119	0.12097
C	-2.94417	0.17914	-0.23539
C	-4.32245	0.27219	-0.53929
C	0.19834	2.28916	-0.02225
C	-2.05055	1.33474	-0.27114
C	-2.49922	2.62829	-0.62551
H	1.2543	2.16584	0.19725
C	-0.2728	3.53875	-0.37774
C	-1.63557	3.70814	-0.67667
H	-3.54234	2.79059	-0.86895
H	-2.01338	4.68735	-0.95342
H	0.40708	4.38336	-0.42655
C	-5.14426	-0.84118	-0.51531
H	-4.75829	1.22928	-0.79961
H	-6.19797	-0.73539	-0.75409
H	-2.87474	-3.20406	0.37714
C	-4.62274	-2.10488	-0.18577

H	-5.27075	-2.97553	-0.17099
H	1.35465	0.96813	3.64063

TS4

Zero-point correction=	0.369510 (Hartree/Particle)
Thermal correction to Energy=	0.388801
Thermal correction to Enthalpy=	0.389745
Thermal correction to Gibbs Free Energy=	0.323766
Sum of electronic and zero-point Energies=	-1076.877221
Sum of electronic and thermal Energies=	-1076.857930
Sum of electronic and thermal Enthalpies=	-1076.856986
Sum of electronic and thermal Free Energies=	-1076.922965

C	0.94965	-1.1378	0.3225
O	-0.6845	-1.62997	-2.30017
C	0.44262	-3.16248	-0.6532
C	2.37028	-0.92562	0.49151
C	-1.70927	-1.12565	-1.52832
C	-1.33865	-0.40938	-0.40301
C	-3.06336	-1.37653	-1.84801
C	0.11749	-0.14315	-0.16803
C	0.65274	1.16053	-0.46792
C	0.34705	-2.51115	0.63983
H	-3.31072	-1.93624	-2.74544
C	-4.05007	-0.90645	-1.01533
C	-3.73223	-0.19156	0.1697
H	-5.09291	-1.09084	-1.25503
C	-2.35499	0.06128	0.48761
C	-4.74529	0.27765	1.04807
H	-5.78358	0.08292	0.79469
C	-4.42184	0.9609	2.19835
C	-3.06415	1.20439	2.51718
H	-5.20364	1.31359	2.86345
C	-2.05603	0.76936	1.68514
H	-2.81534	1.74101	3.42761
H	-1.0207	0.96368	1.94343
H	-0.39568	-3.66302	-1.12124
H	1.39756	-3.20653	-1.16858
H	-0.67592	-2.45938	1.00994

H	0.95433	-3.03409	1.39271
C	3.2349	-1.94935	0.94886
C	2.9174	0.36246	0.20847
C	4.29703	0.56751	0.4262
C	-0.18696	2.18929	-0.97052
C	2.0461	1.42122	-0.28553
C	2.52986	2.70669	-0.61184
H	-1.24025	1.98453	-1.11581
C	0.31916	3.43435	-1.28165
C	1.68851	3.69358	-1.0965
H	3.57997	2.9403	-0.4905
H	2.09311	4.67166	-1.33674
H	-0.33628	4.20832	-1.66703
C	5.11976	-0.44913	0.88164
H	4.73538	1.53991	0.24058
H	6.17688	-0.25885	1.03569
H	2.85571	-2.94501	1.14337
C	4.58621	-1.71876	1.14201
H	5.22611	-2.52134	1.49349
H	-1.04366	-2.1041	-3.06665

5f-H⁺

Zero-point correction= 0.374775 (Hartree/Particle)

Thermal correction to Energy= 0.393466

Thermal correction to Enthalpy= 0.394410

Thermal correction to Gibbs Free Energy= 0.329848

Sum of electronic and zero-point Energies= -1076.912908

Sum of electronic and thermal Energies= -1076.894217

Sum of electronic and thermal Enthalpies= -1076.893273

Sum of electronic and thermal Free Energies= -1076.957835

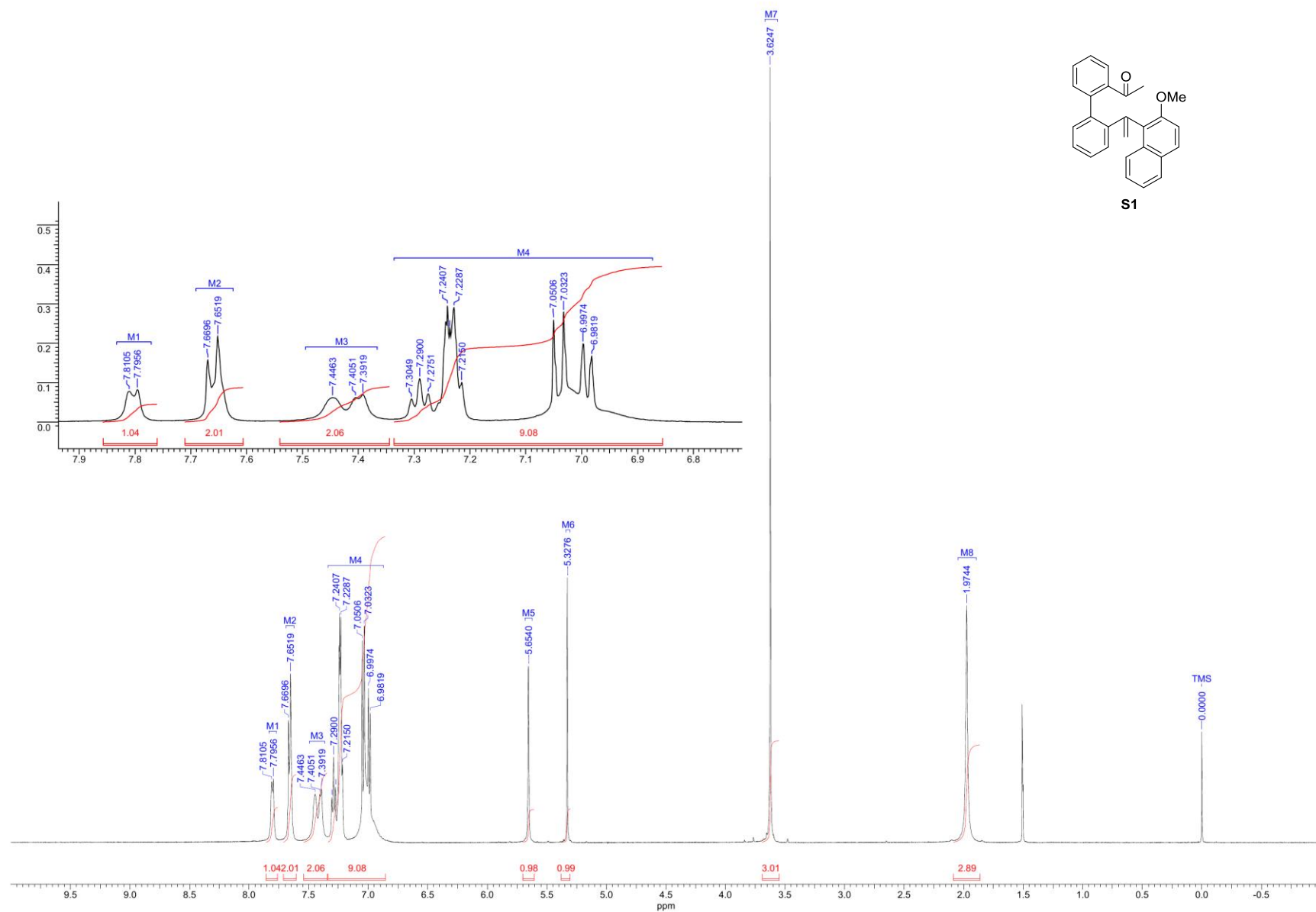
C	1.01466	-1.15182	0.30791
O	-0.65319	-2.35306	-1.6331
C	0.16742	-3.28506	-0.72787
C	2.41997	-0.86158	0.49765
C	-1.71674	-1.57719	-1.02464
C	-1.30584	-0.5061	-0.26402
C	-3.03939	-1.98931	-1.23996
C	0.1493	-0.17888	-0.14449
C	0.63894	1.12313	-0.55411

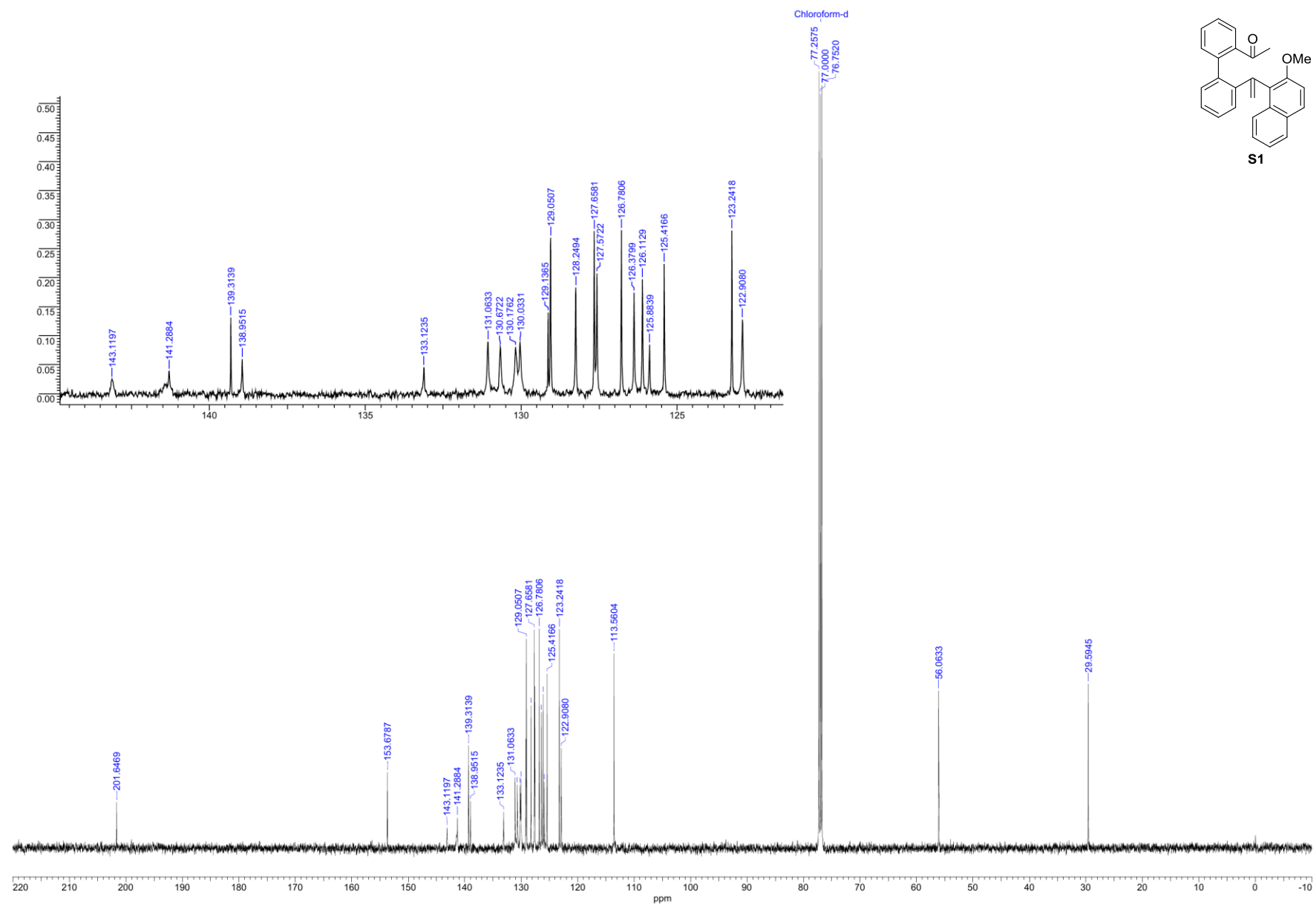
C	0.45003	-2.53884	0.56129
H	-3.26344	-2.84788	-1.86381
C	-4.03342	-1.25872	-0.63328
C	-3.71696	-0.17147	0.22407
H	-5.07321	-1.52972	-0.78369
C	-2.34544	0.20182	0.43552
C	-4.74254	0.53975	0.90411
H	-5.77564	0.25513	0.72853
C	-4.43419	1.55679	1.7772
C	-3.08207	1.90154	2.01353
H	-5.2247	2.08987	2.29557
C	-2.06346	1.2441	1.3603
H	-2.84551	2.69028	2.72061
H	-1.03329	1.51487	1.55641
H	-0.43086	-4.18616	-0.59242
H	1.05158	-3.46909	-1.33567
H	-0.46471	-2.48138	1.15678
H	1.12832	-3.18116	1.12494
C	3.32935	-1.83153	0.99254
C	2.91233	0.44796	0.20453
C	4.27685	0.72677	0.45493
C	-0.20578	2.06905	-1.18762
C	2.01539	1.44304	-0.36579
C	2.46908	2.7193	-0.77928
H	-1.24245	1.81549	-1.37216
C	0.27023	3.30135	-1.58876
C	1.61895	3.63343	-1.3714
H	3.50901	2.99211	-0.64964
H	1.99909	4.60165	-1.68178
H	-0.39498	4.00705	-2.07627
C	5.13549	-0.23583	0.95004
H	4.67015	1.71662	0.25987
H	6.17683	0.01059	1.13192
H	2.98986	-2.83664	1.20975
C	4.65874	-1.53067	1.21454
H	5.32955	-2.29325	1.59727
H	-0.92539	-2.79003	-2.46292

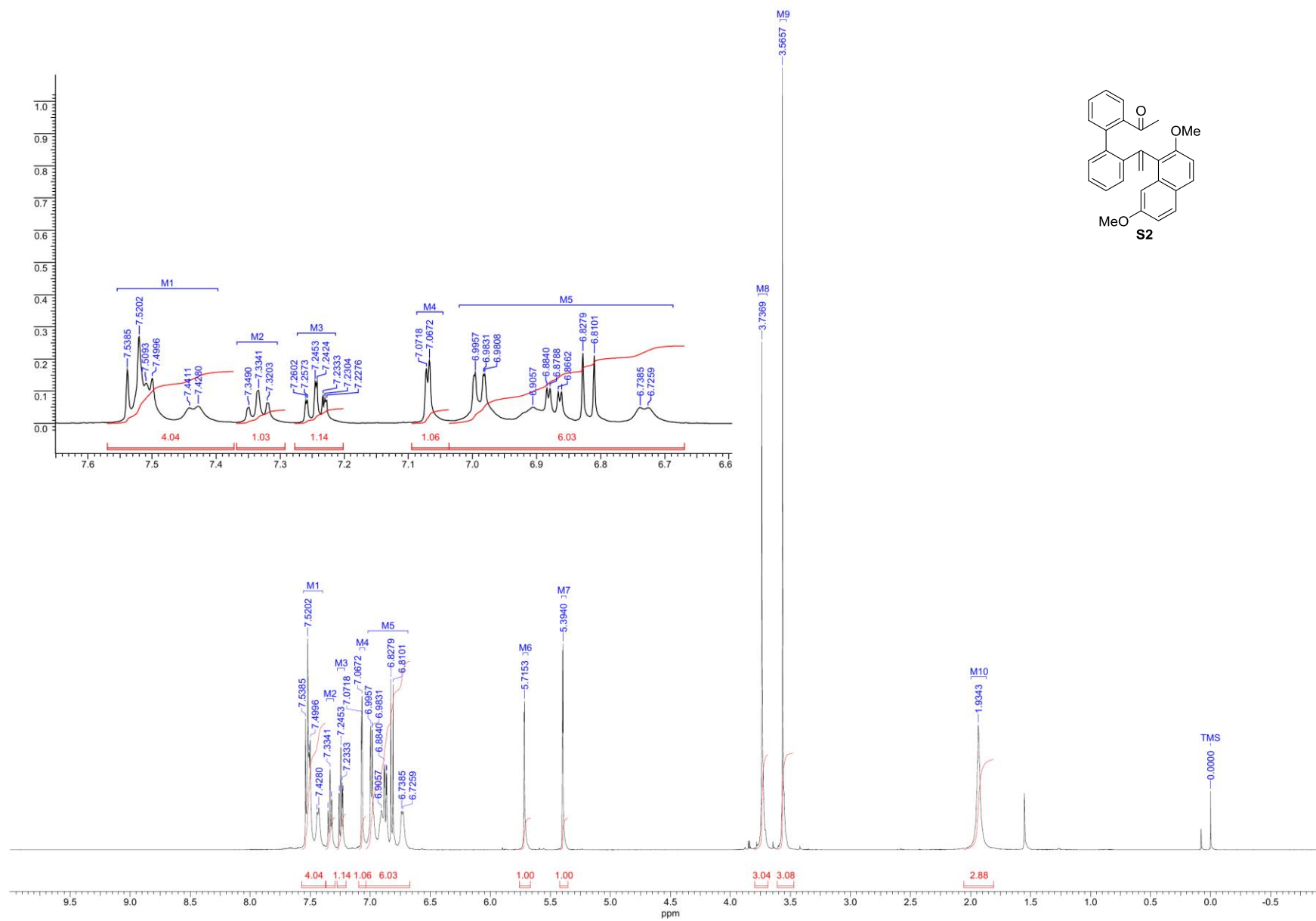
8. References

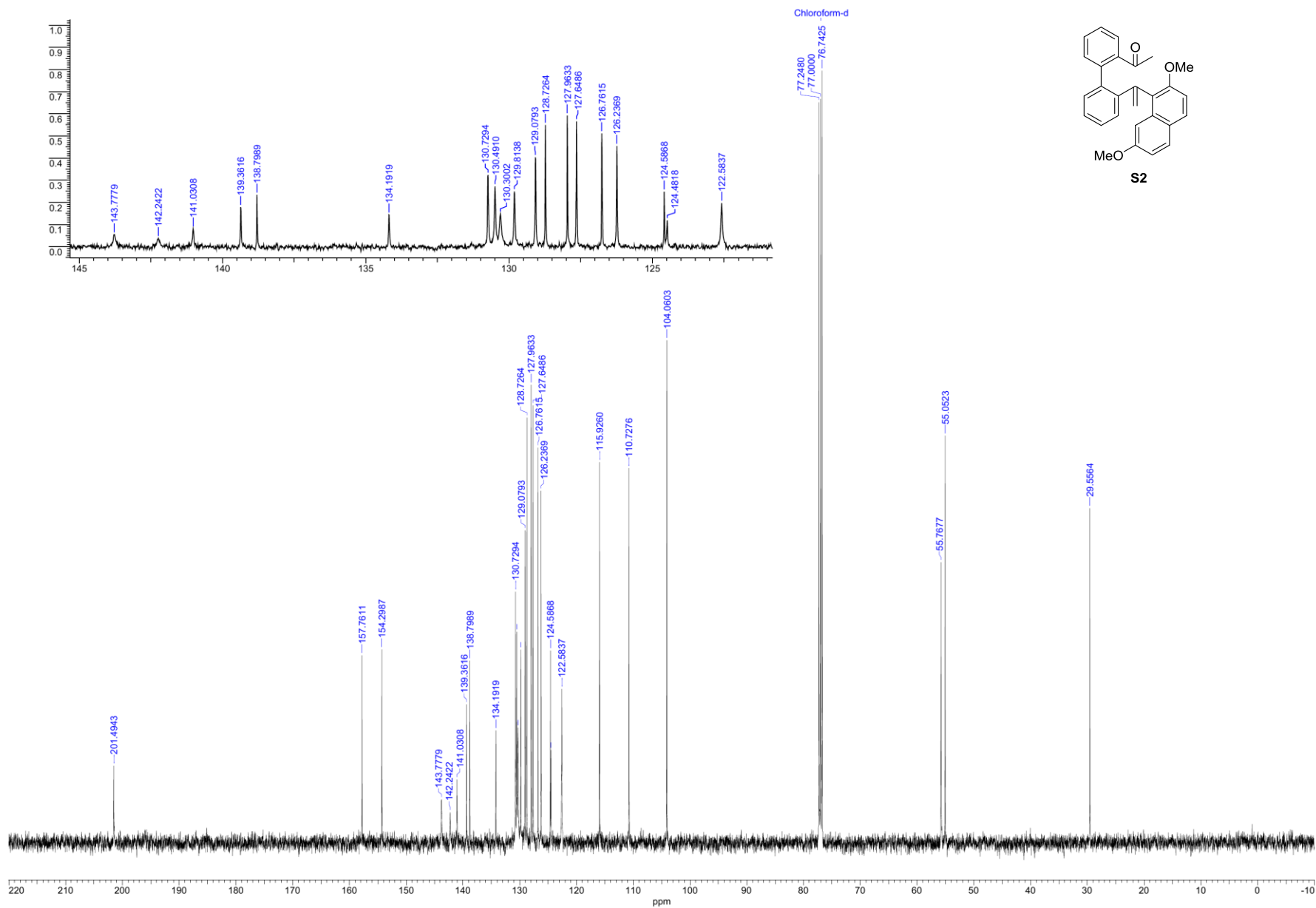
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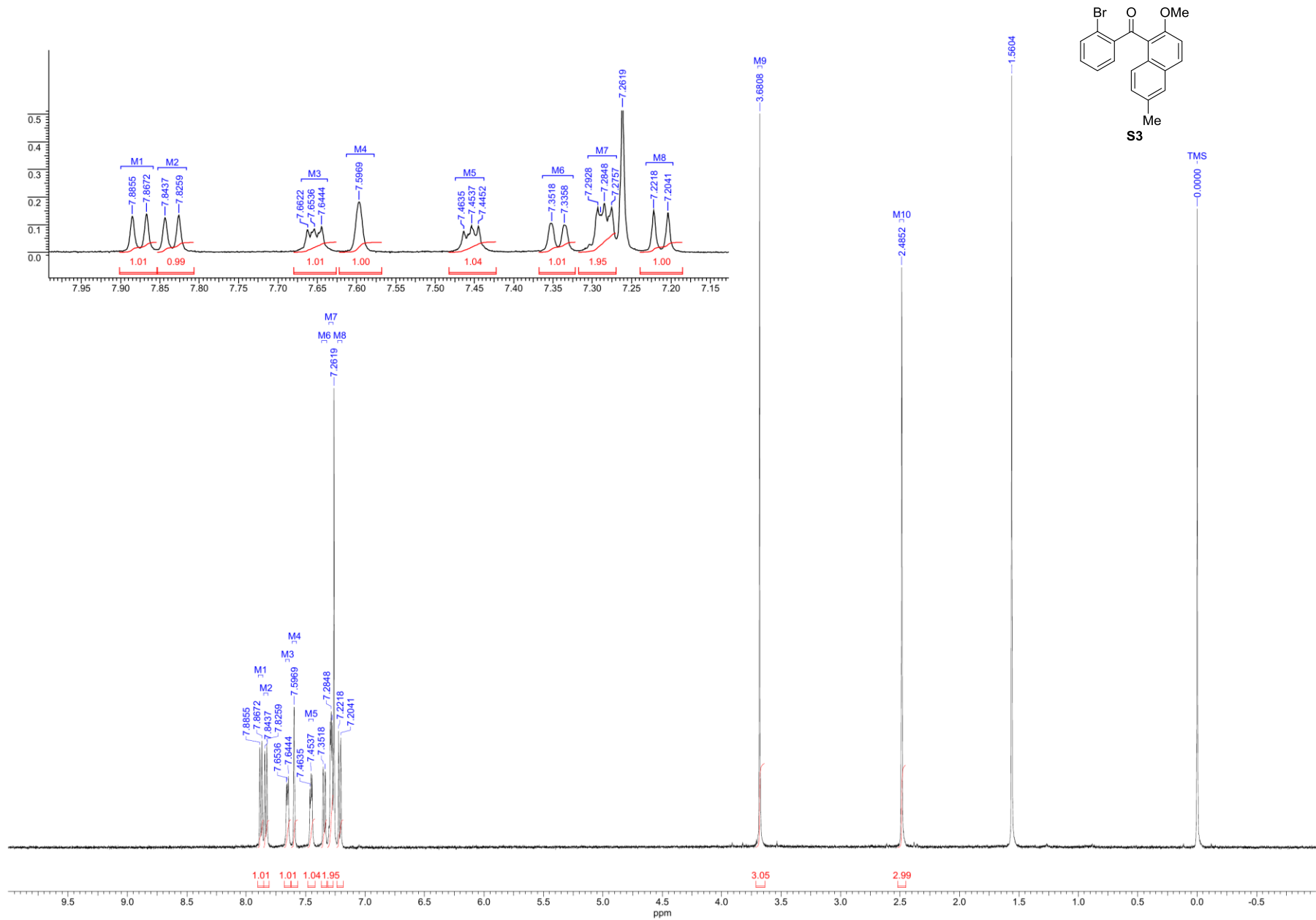
9. NMR Spectra

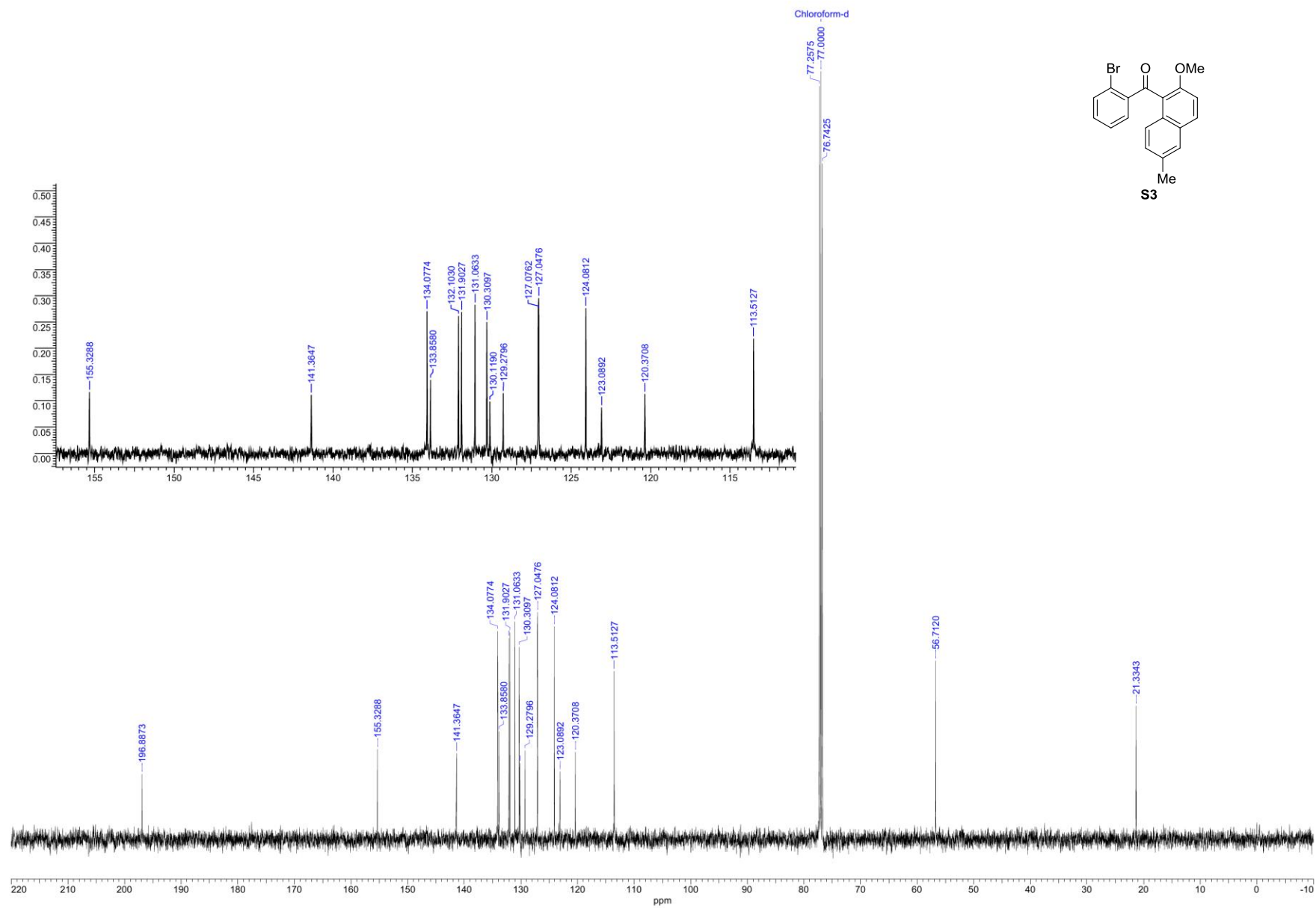


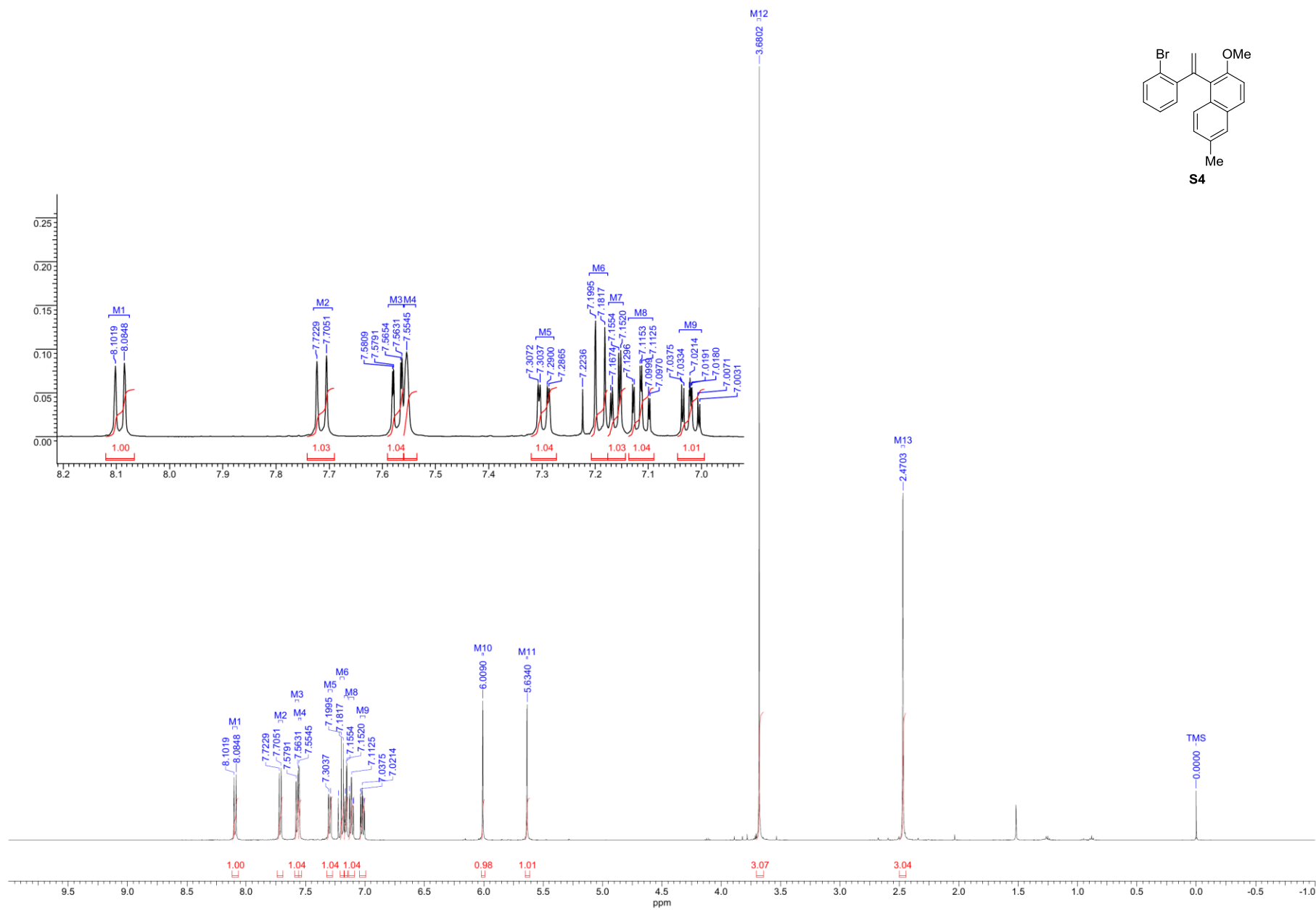
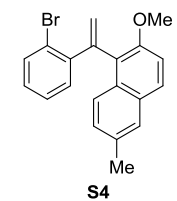


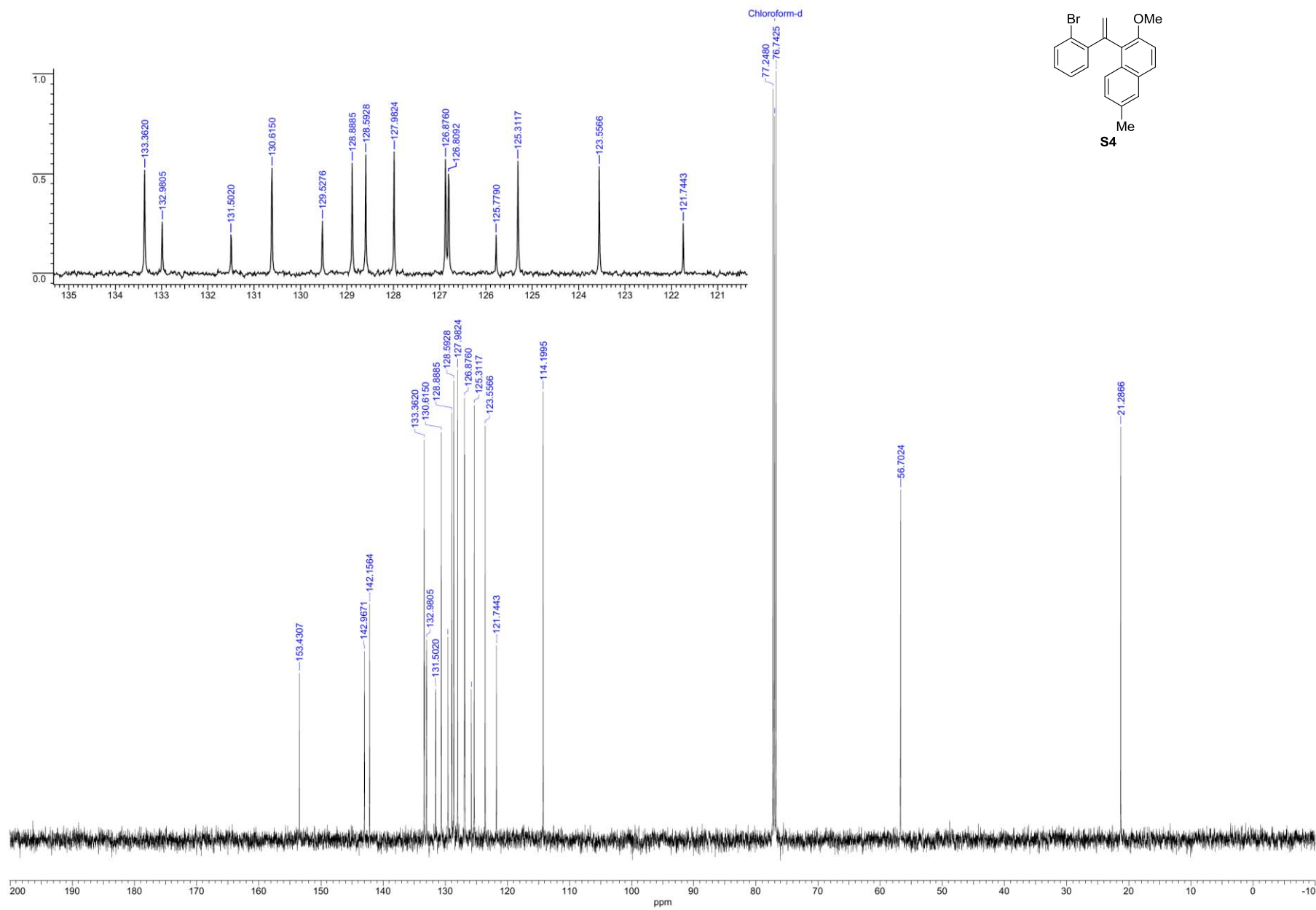


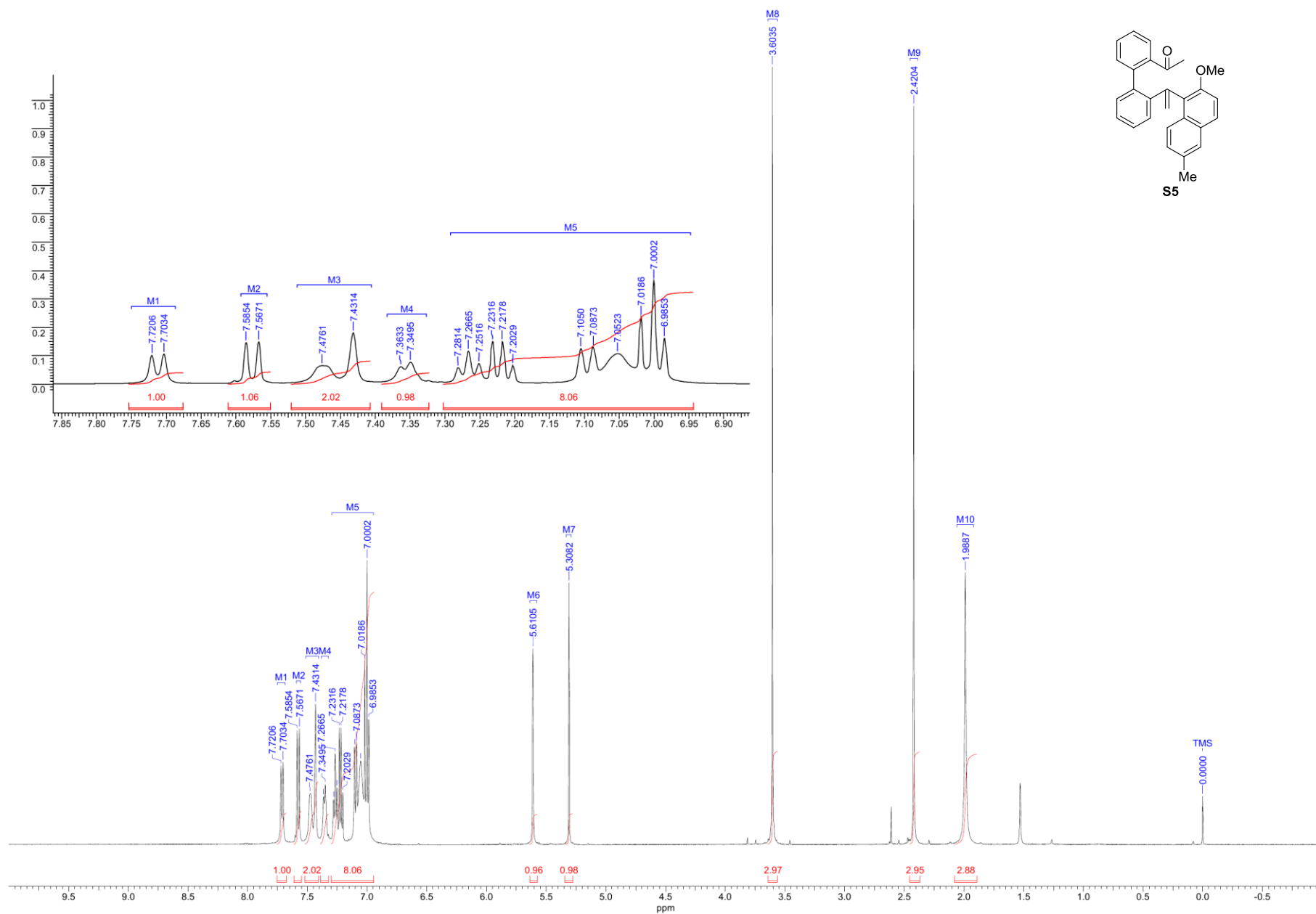


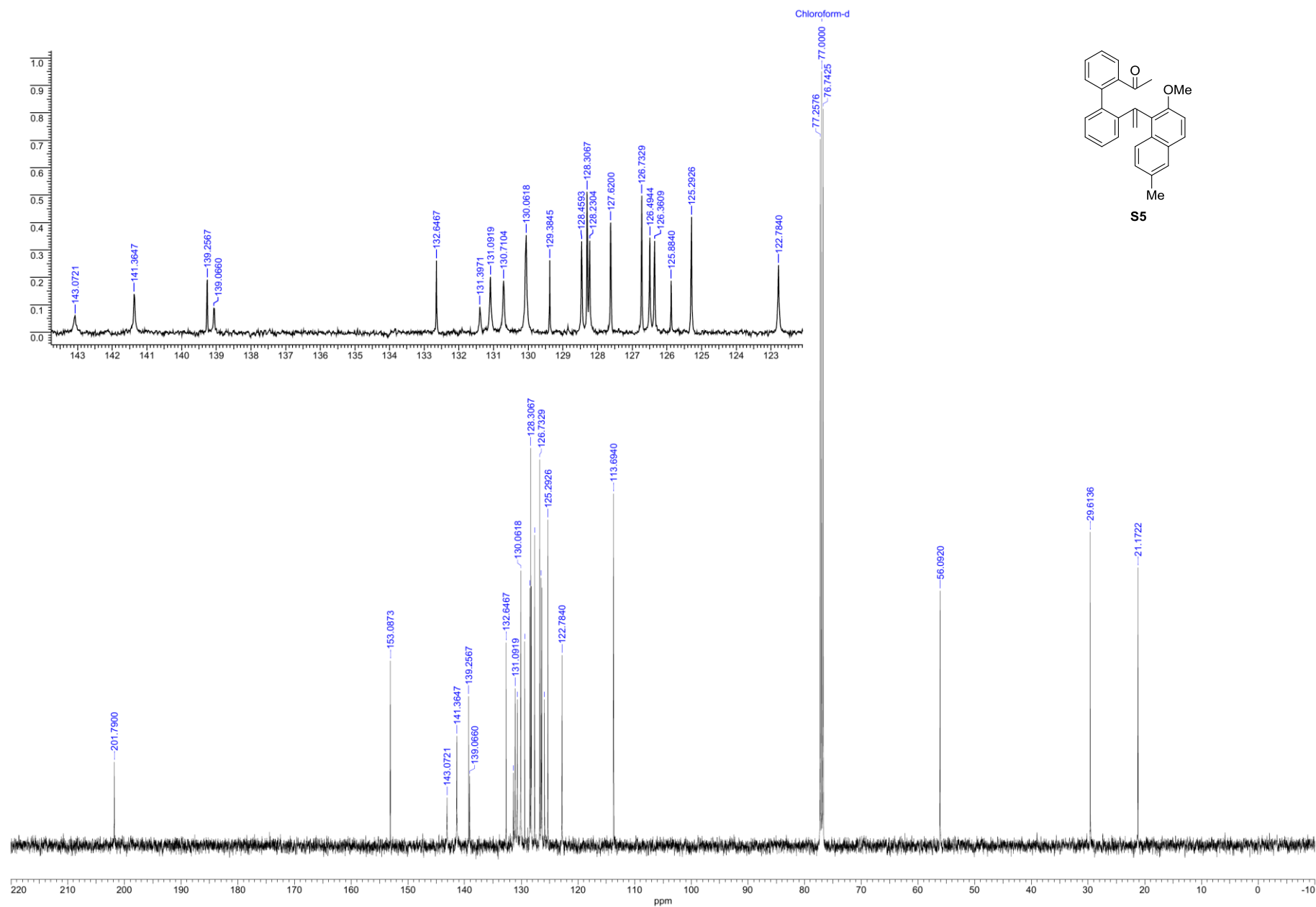


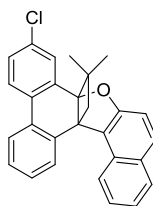




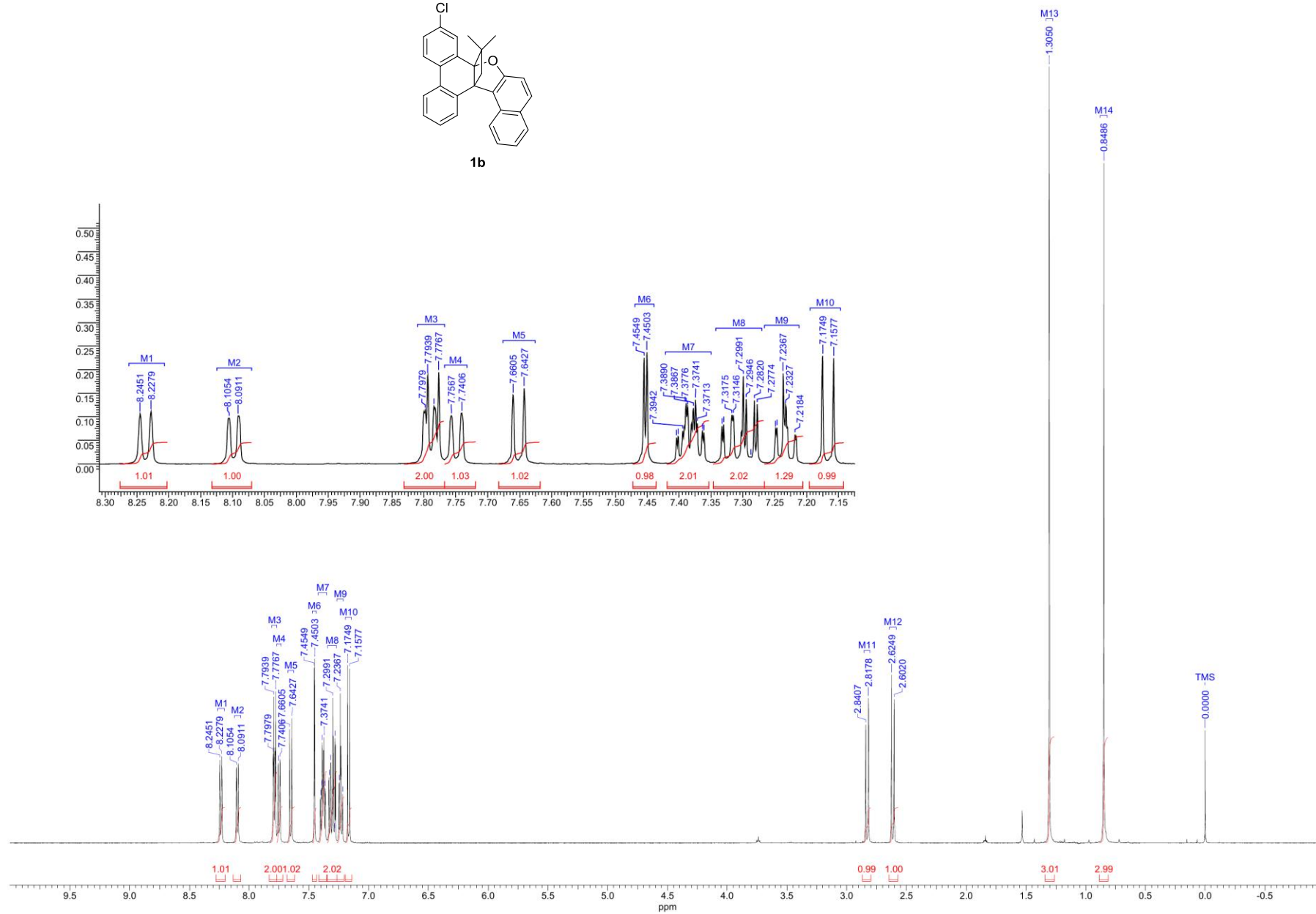


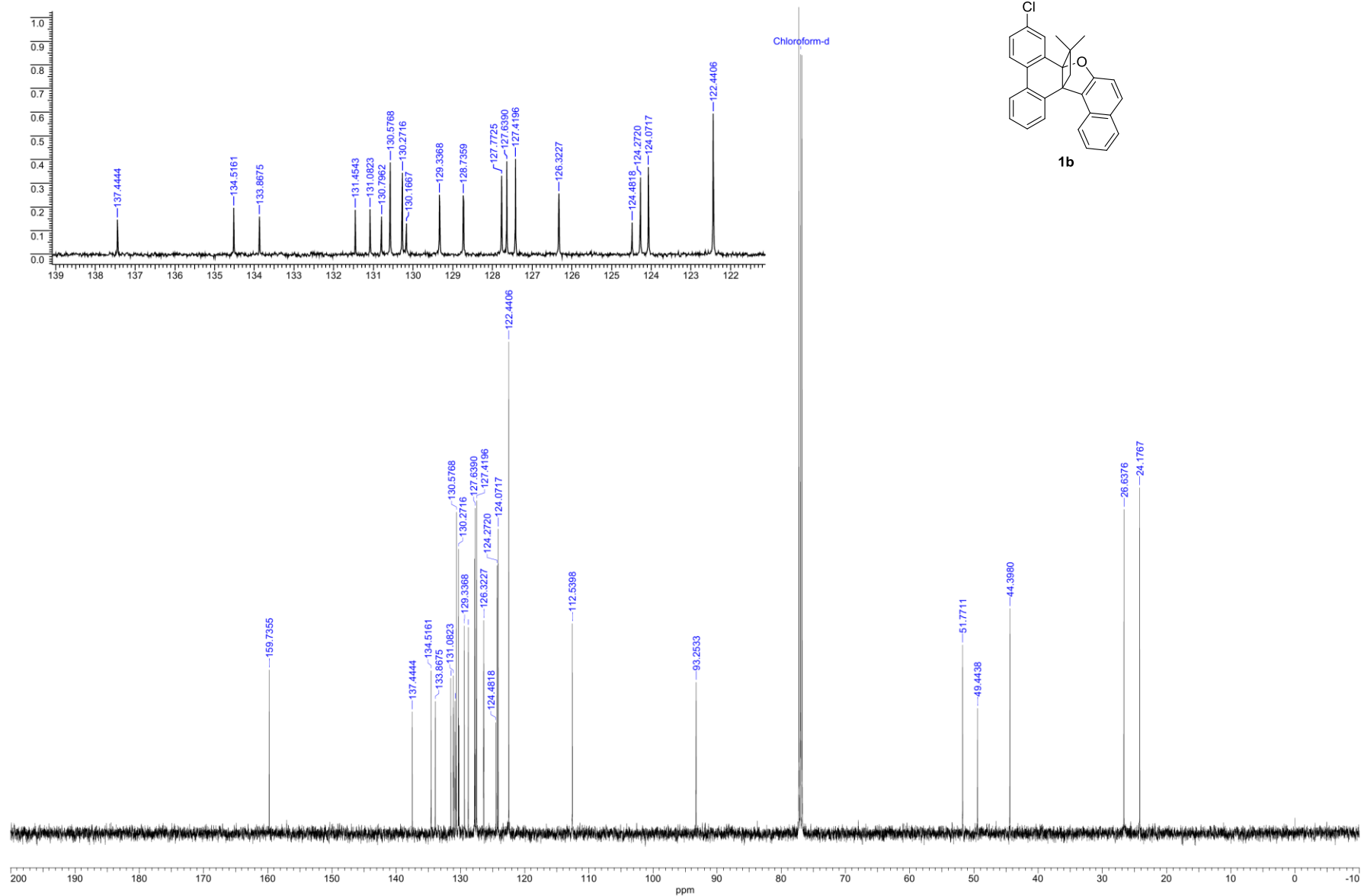


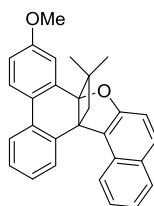




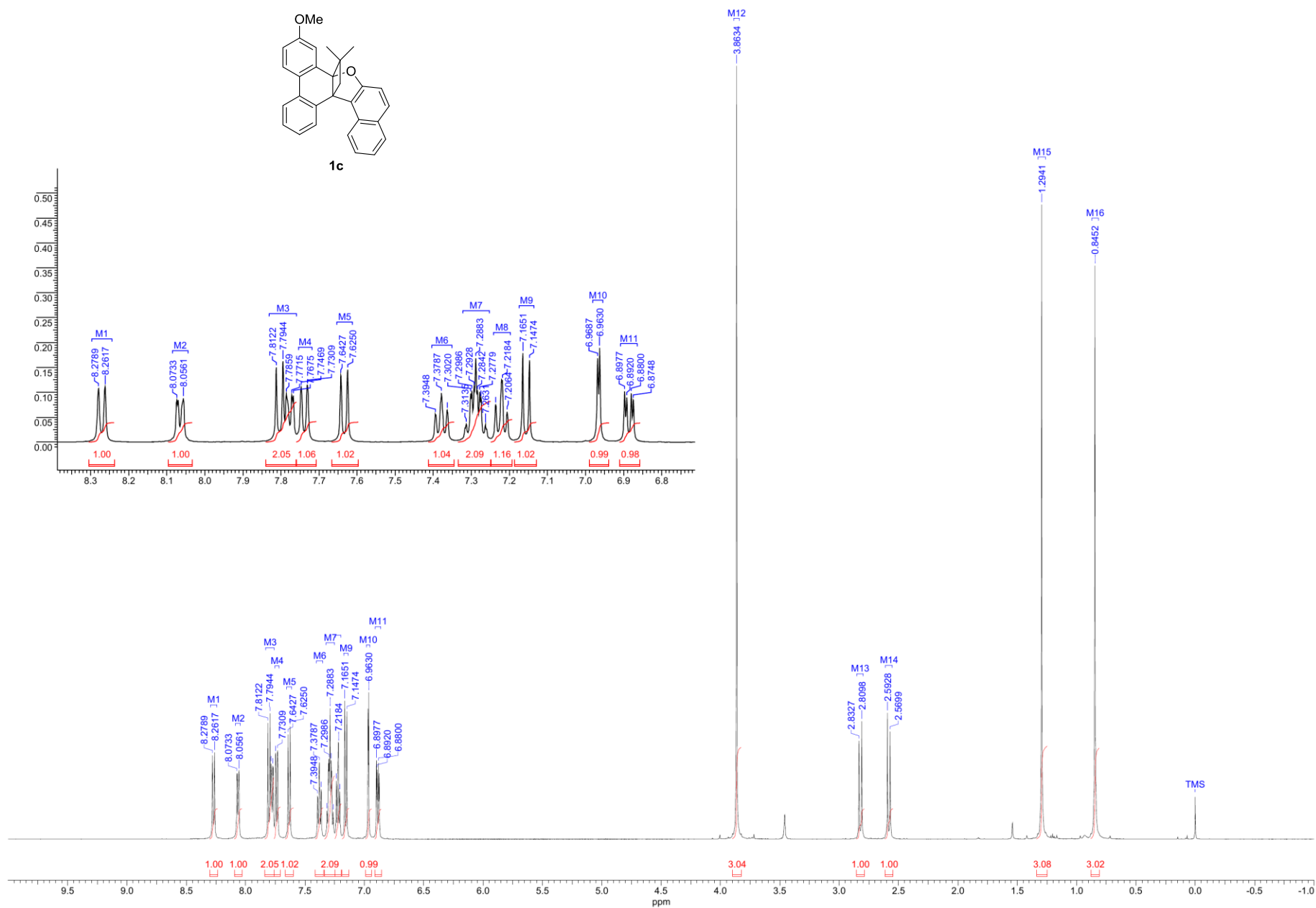
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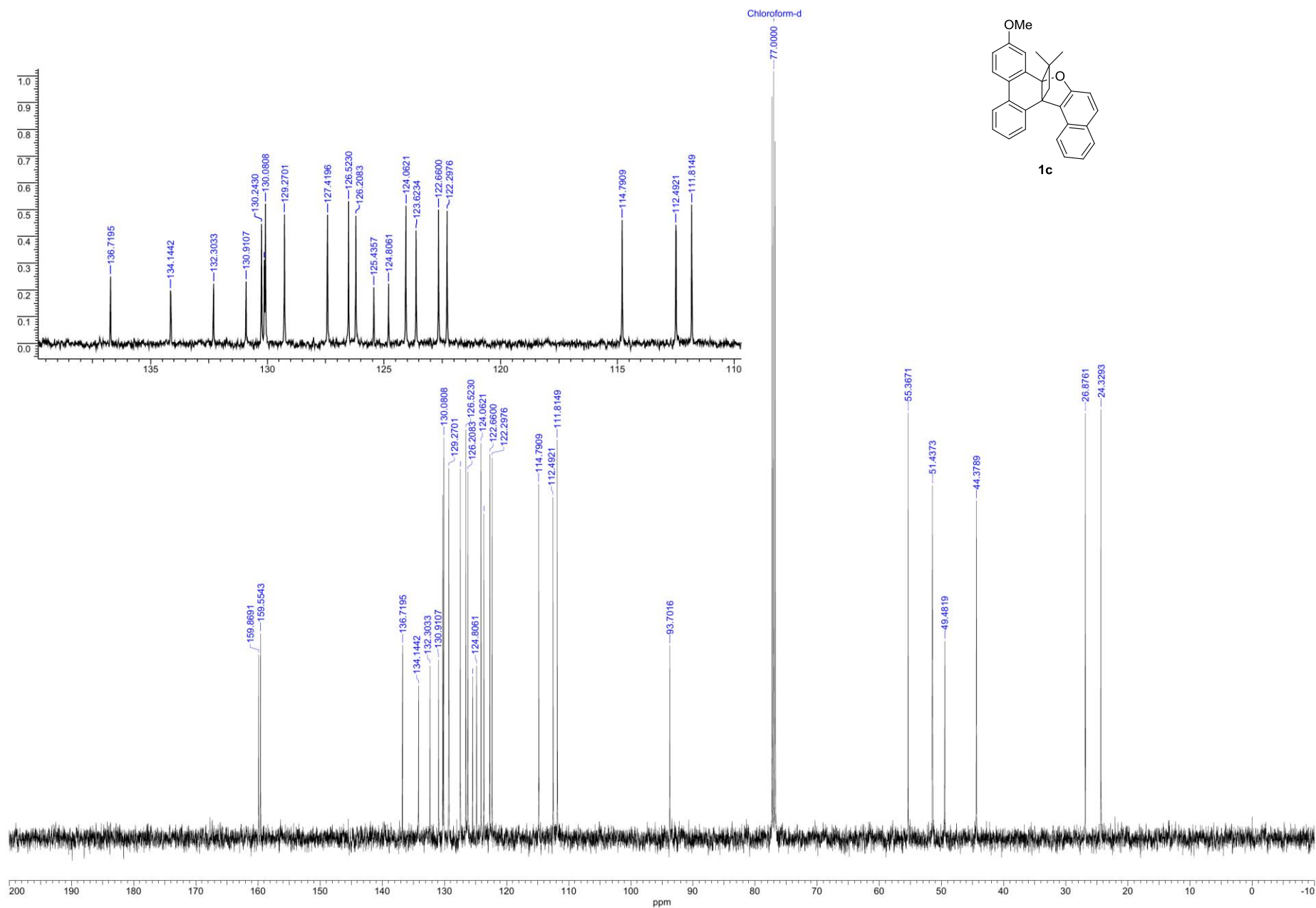


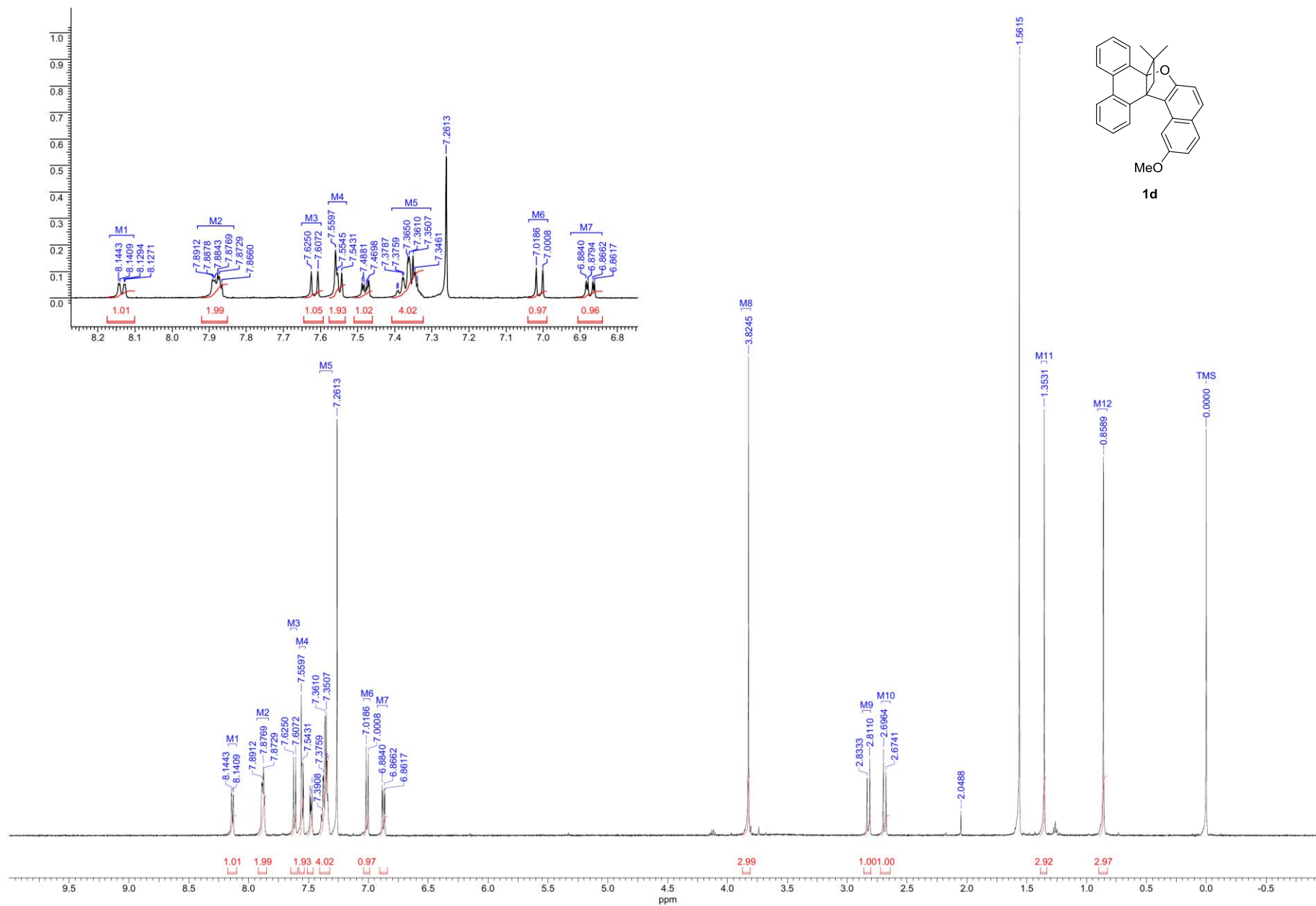


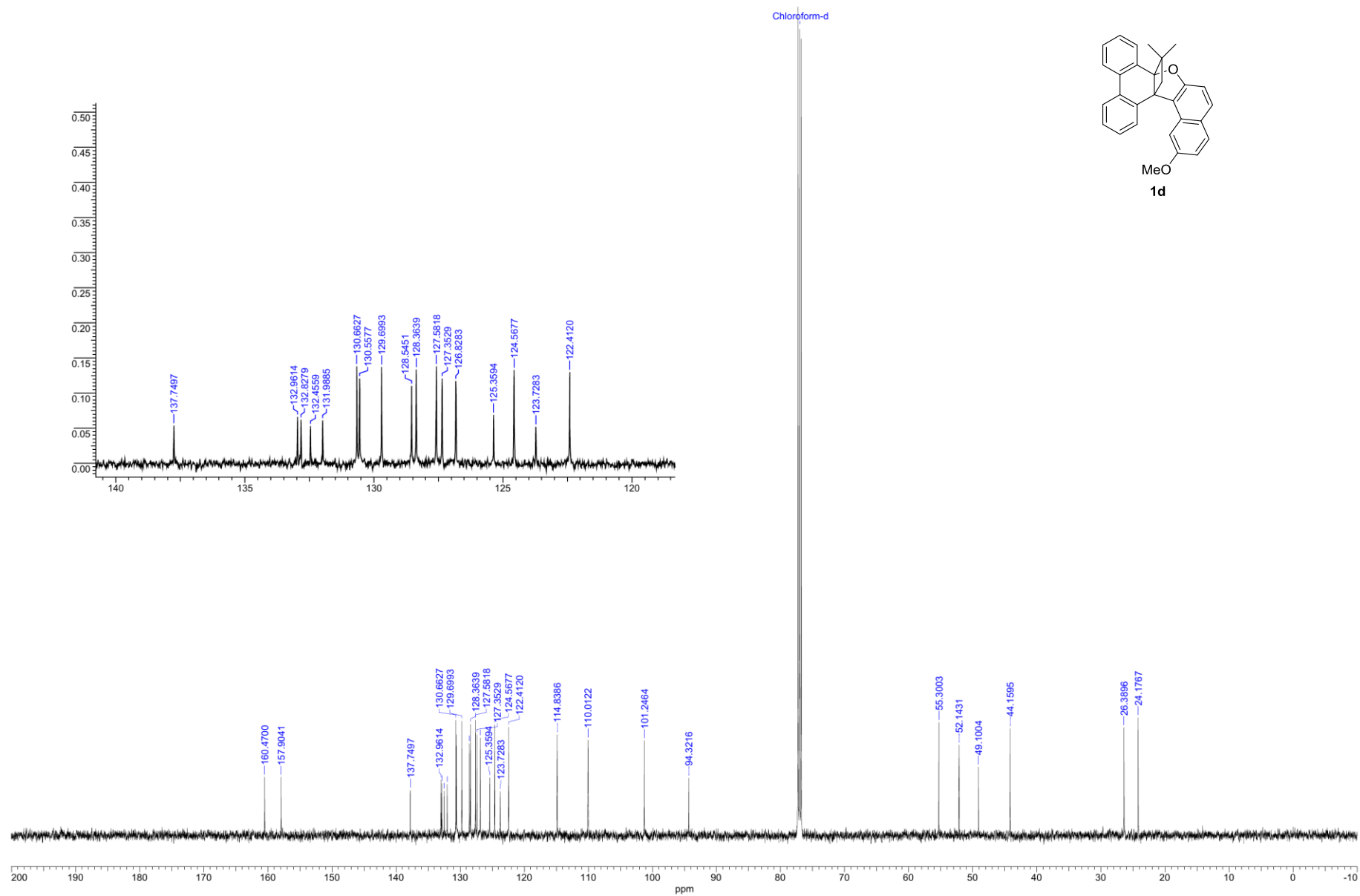


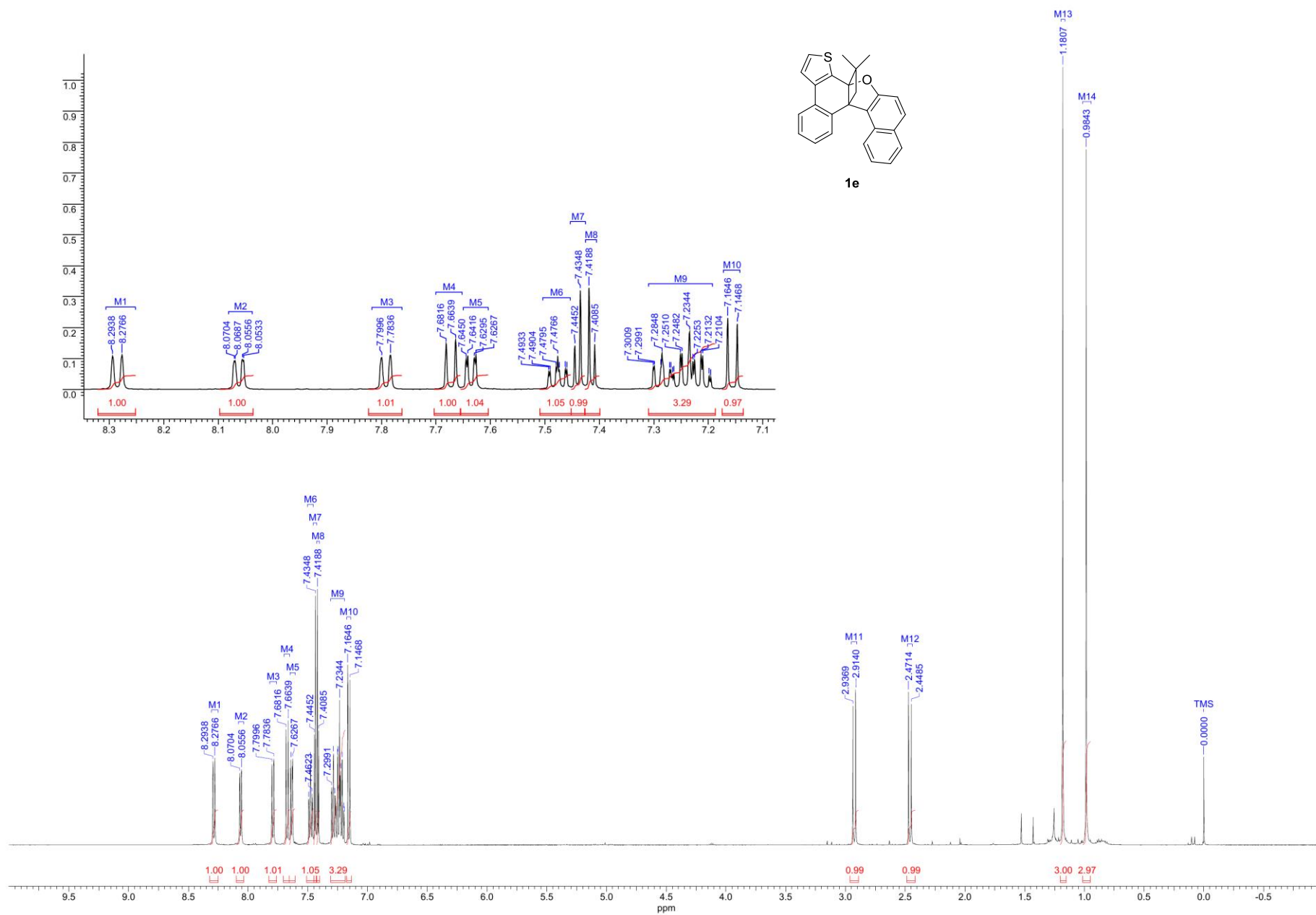
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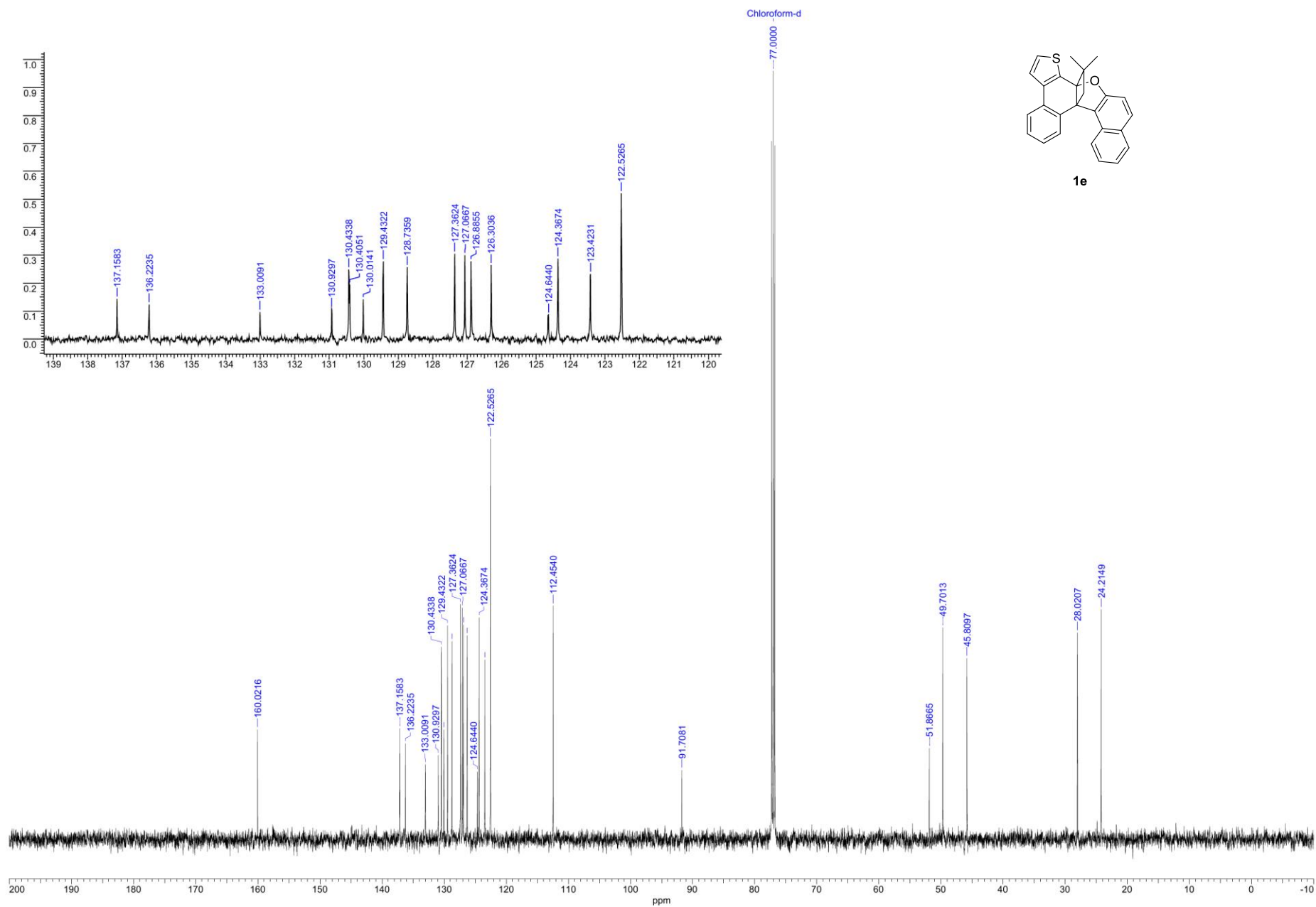


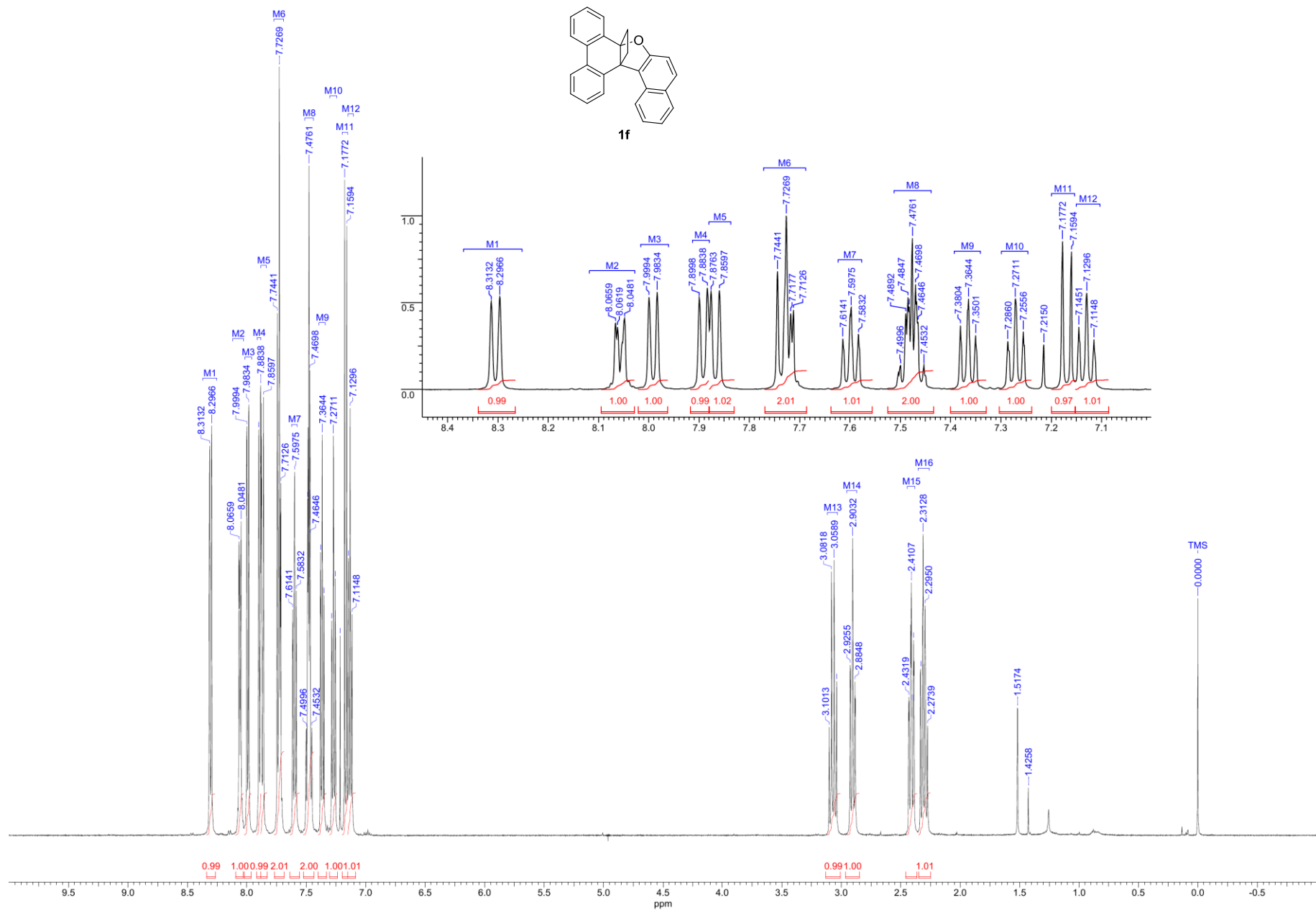


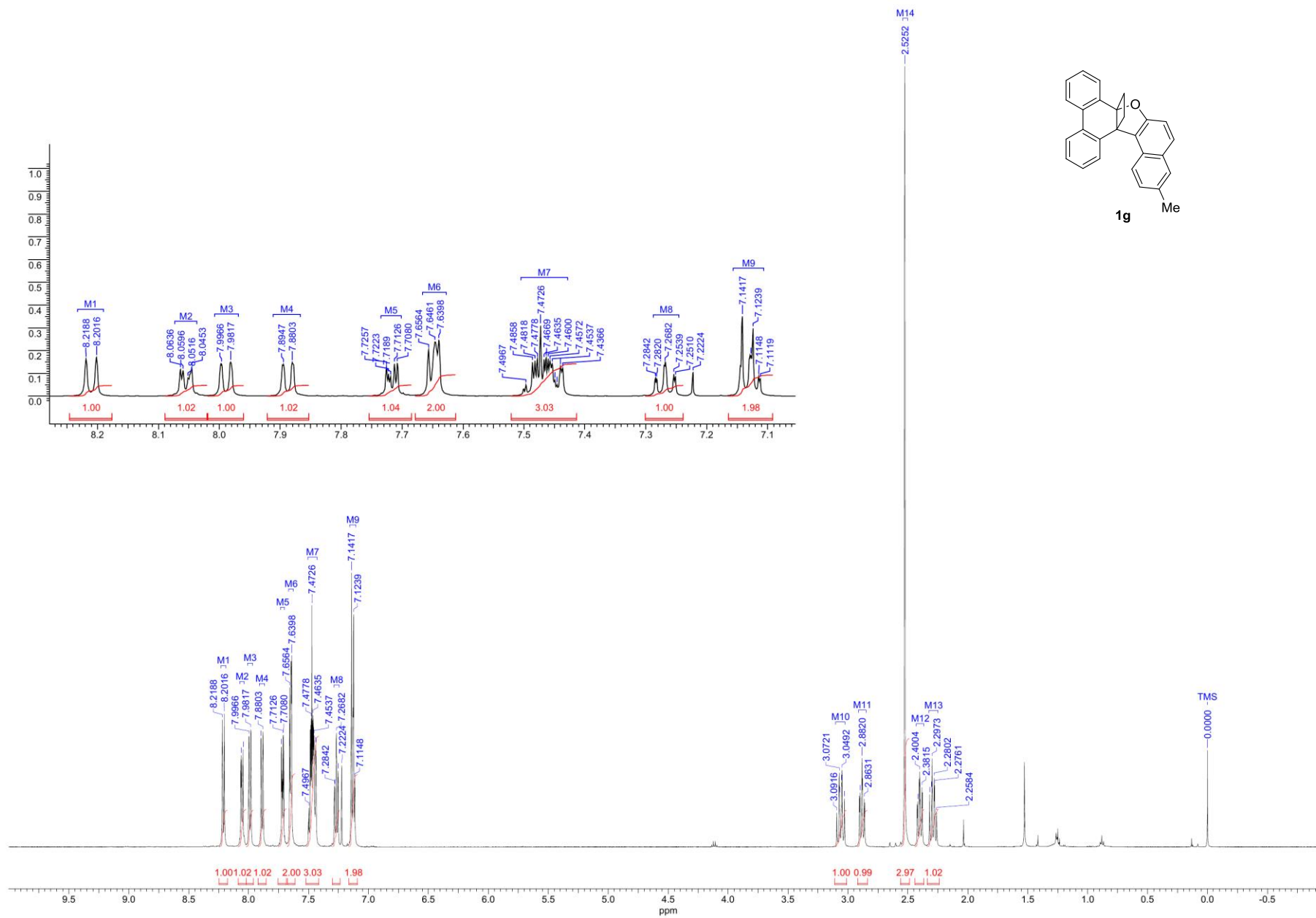


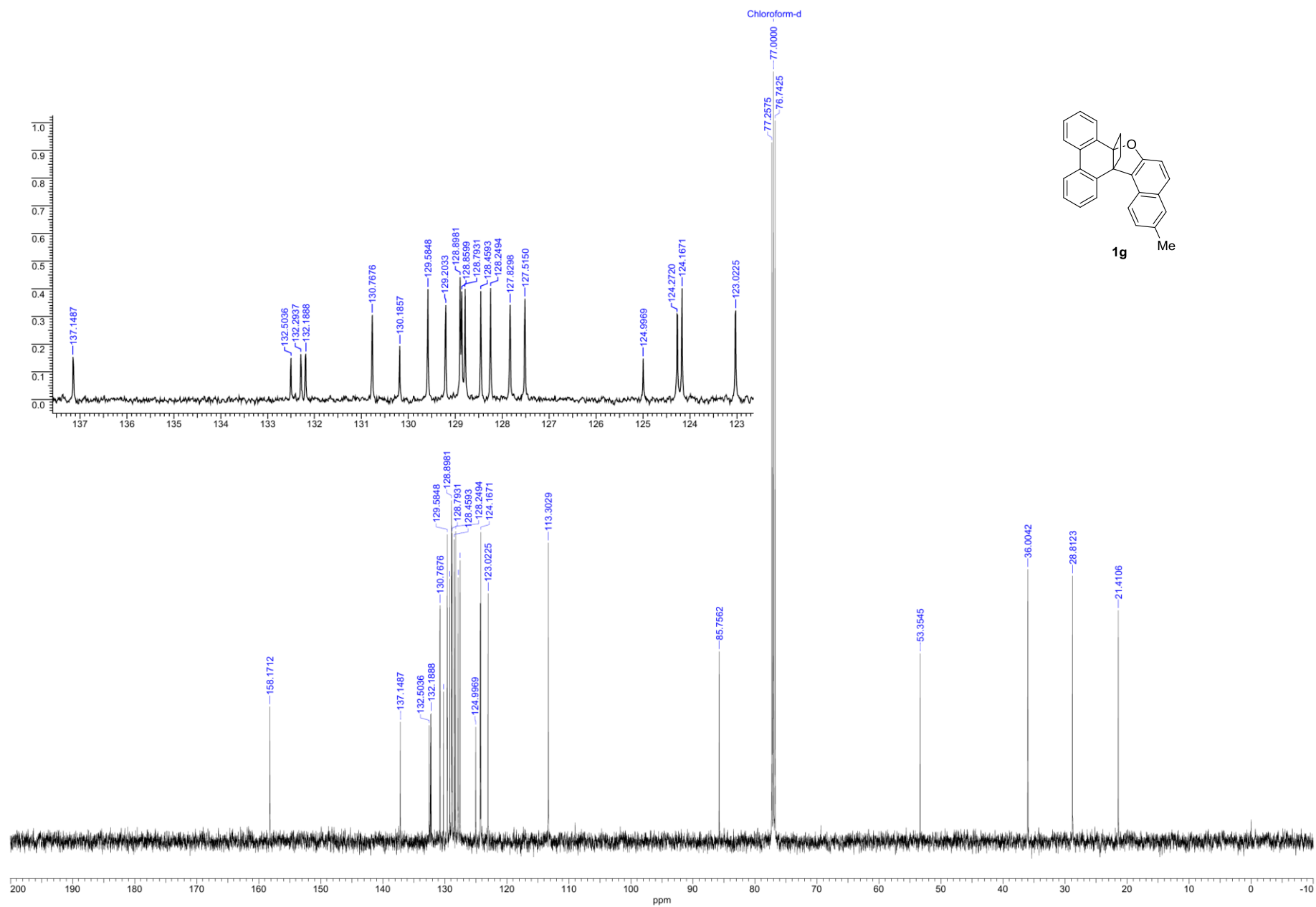


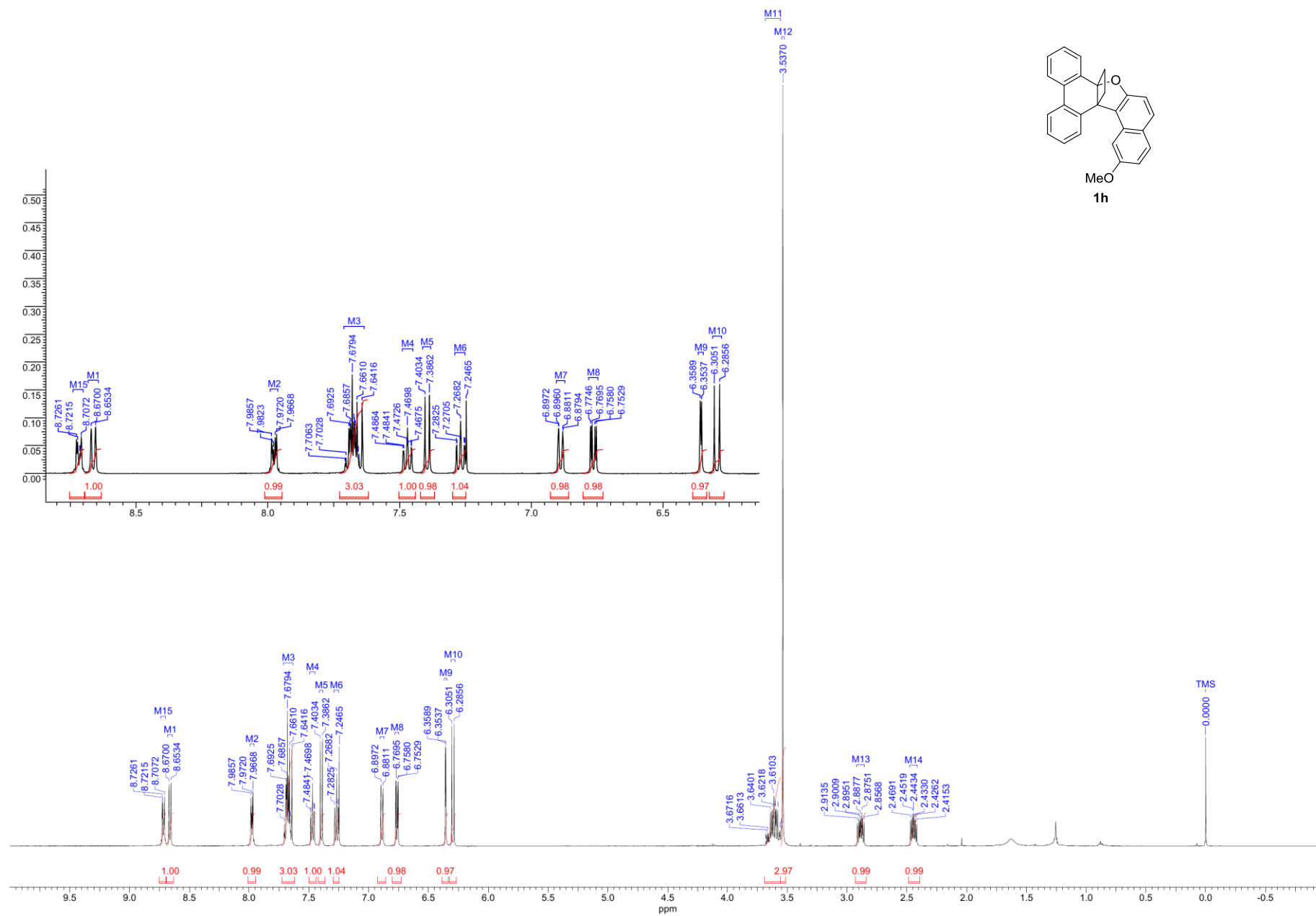


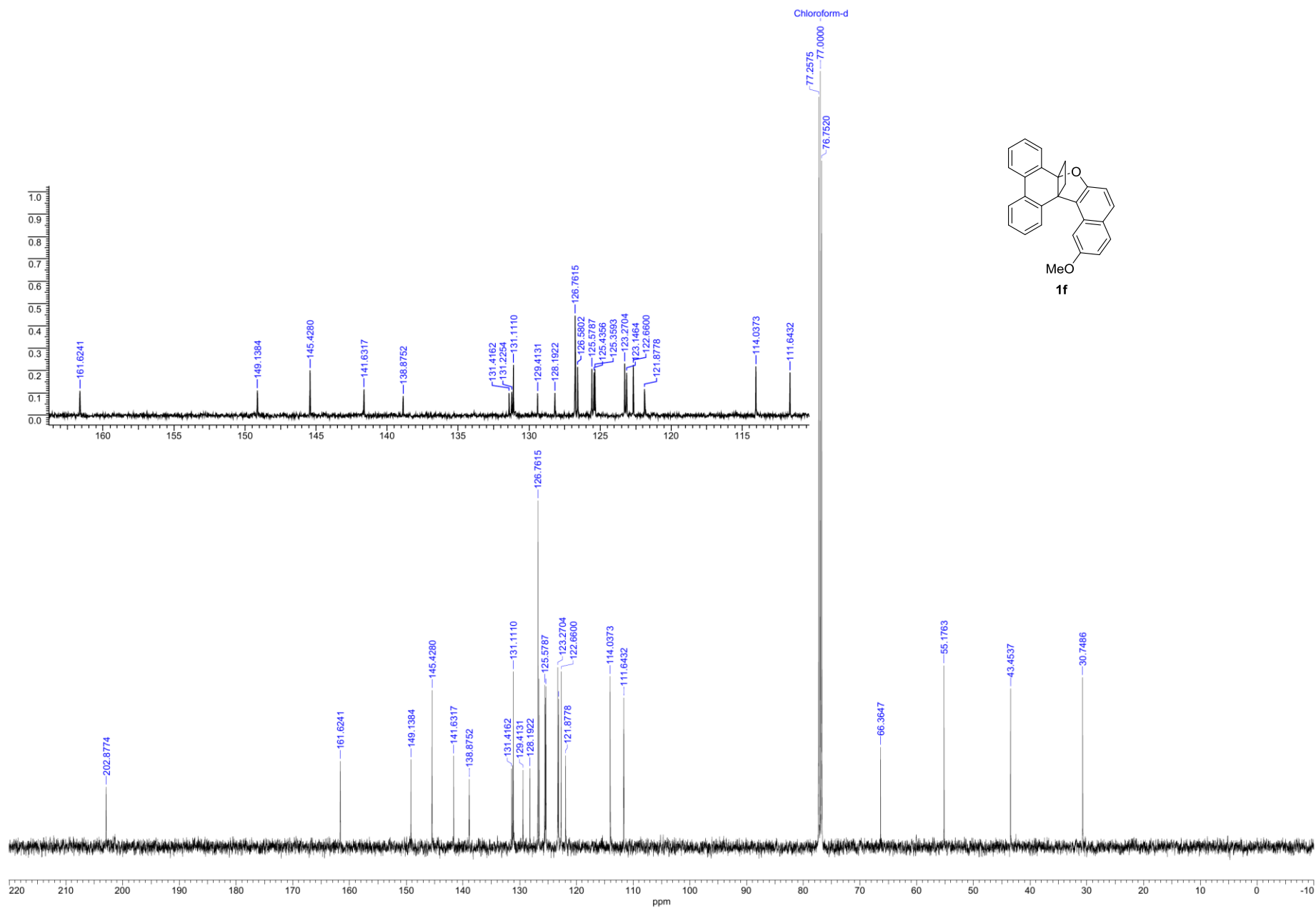


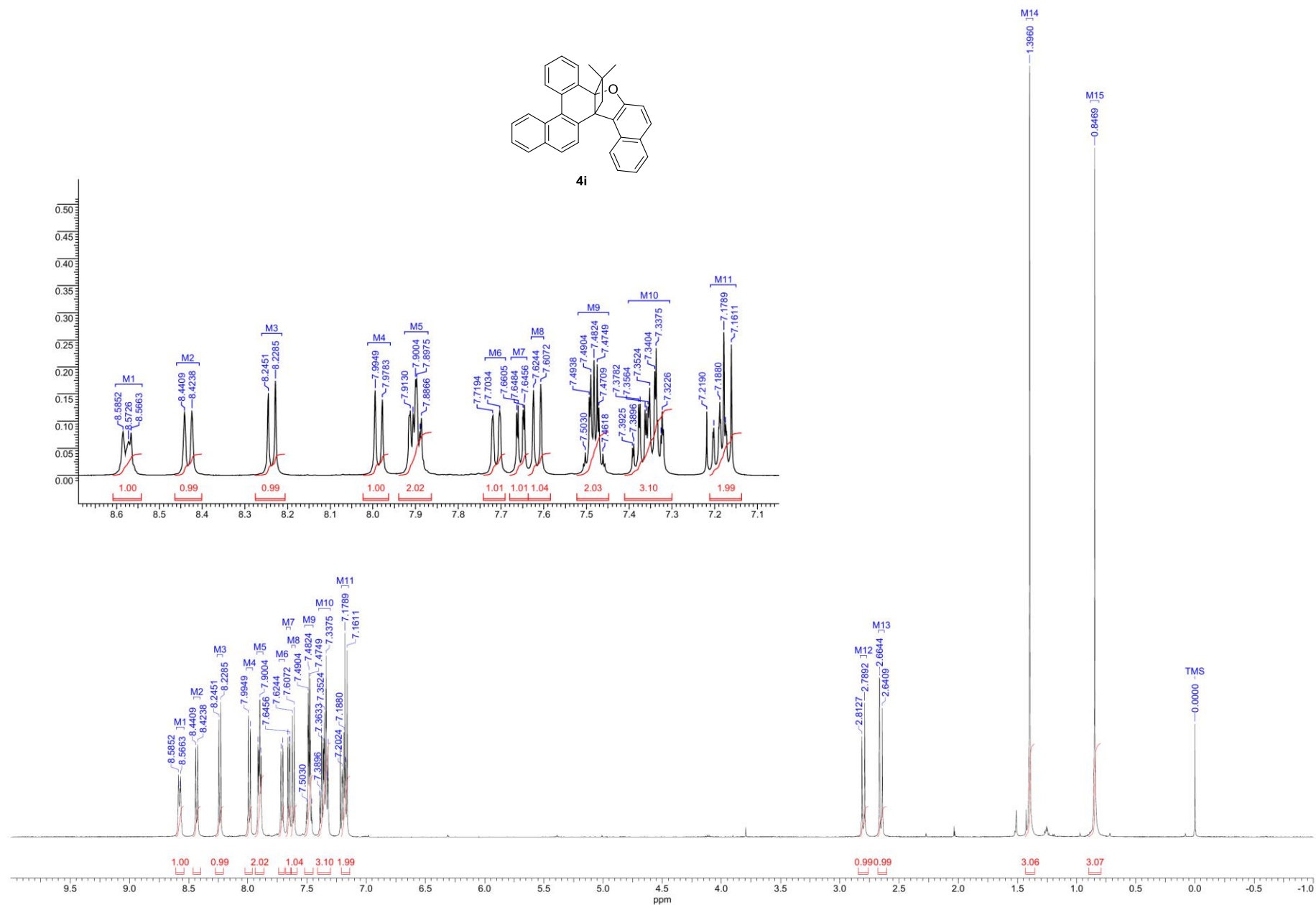


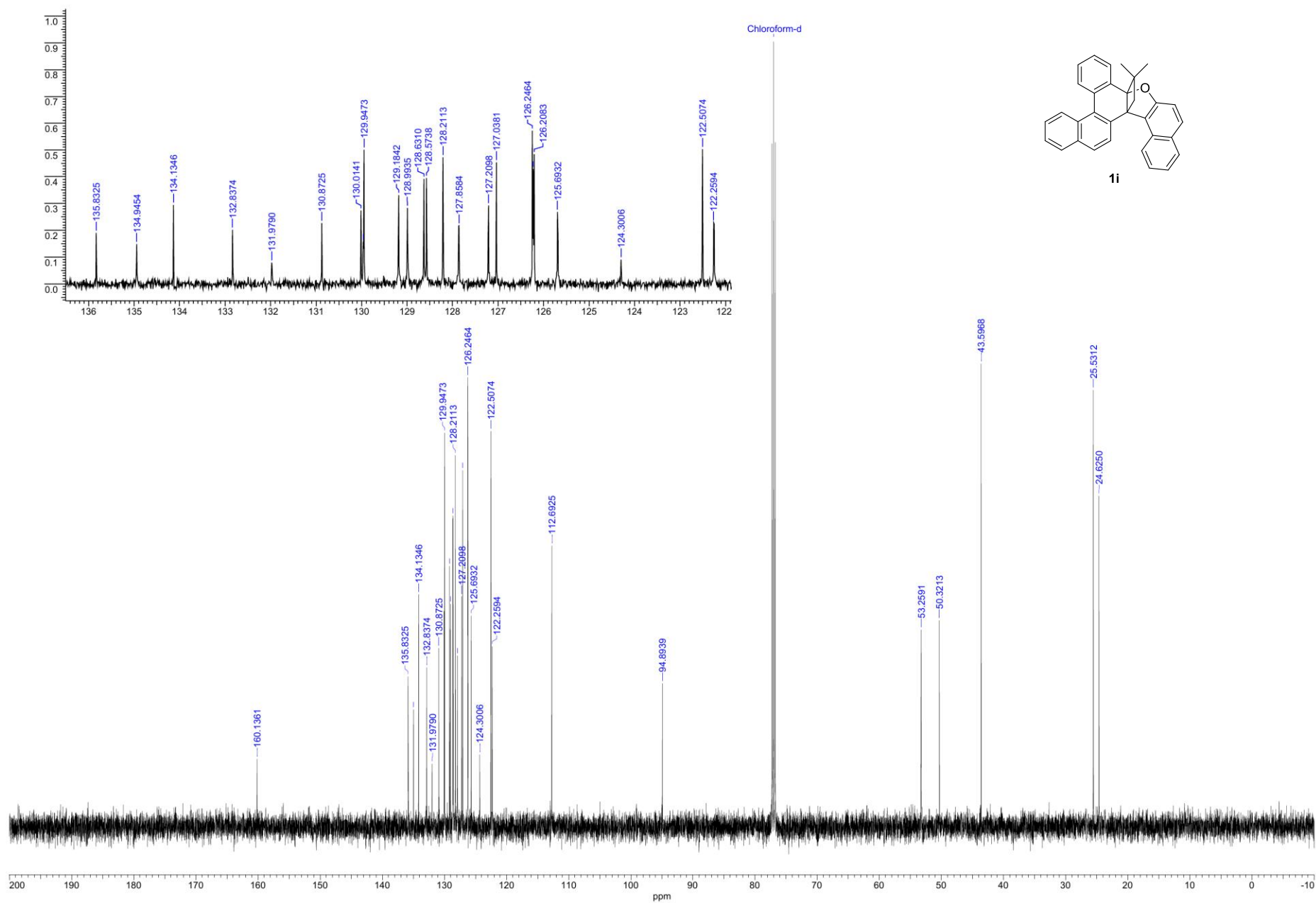


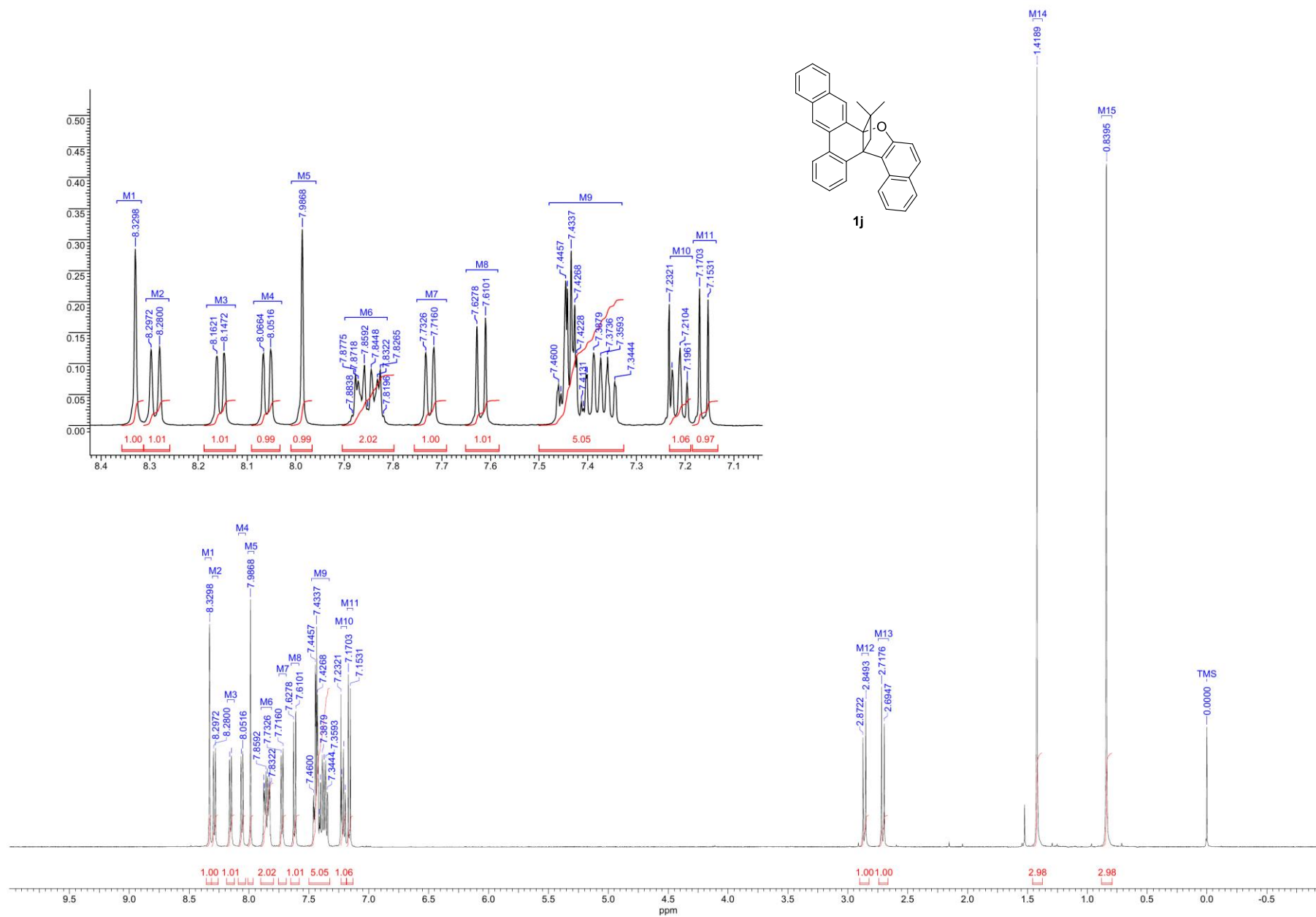


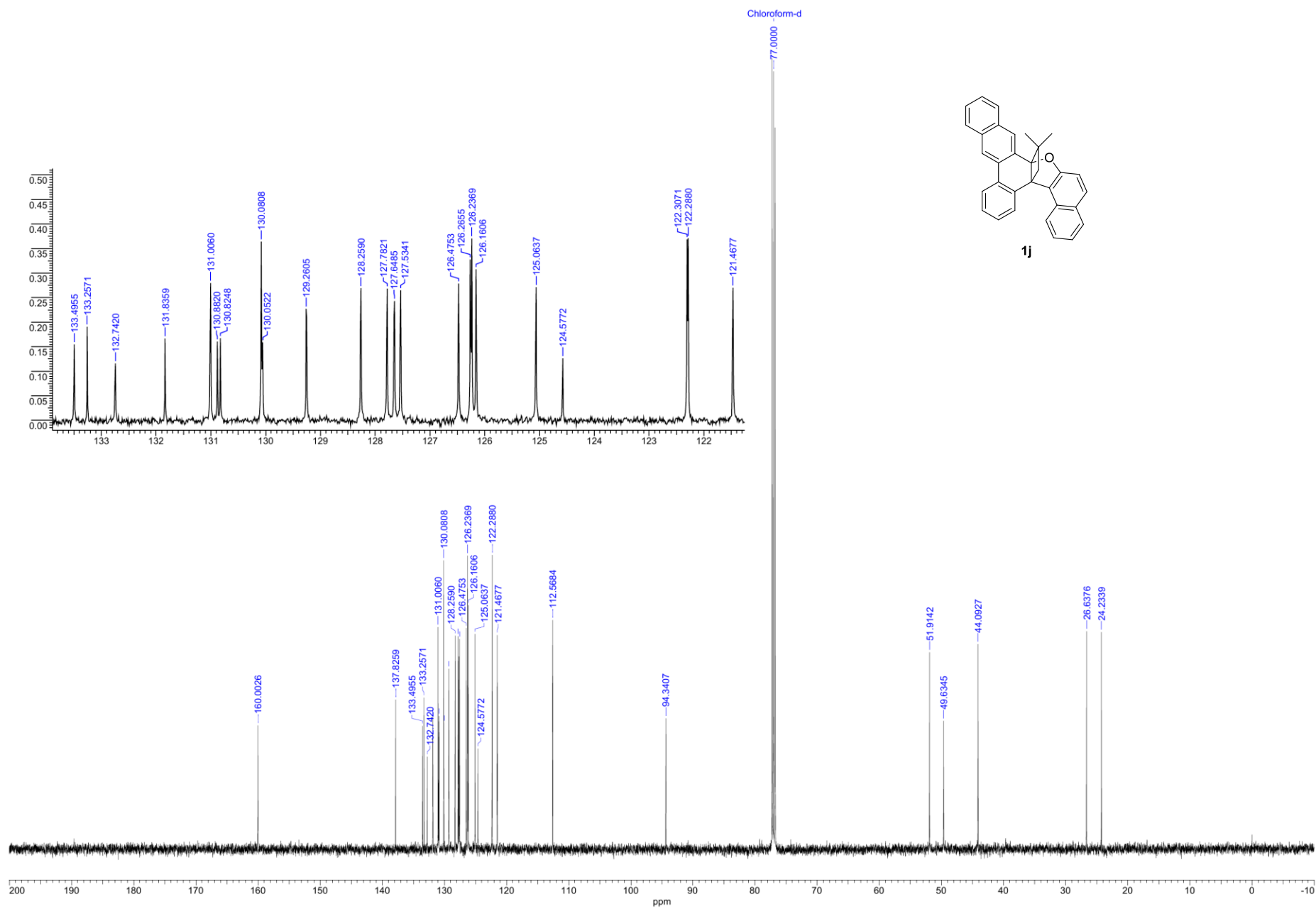


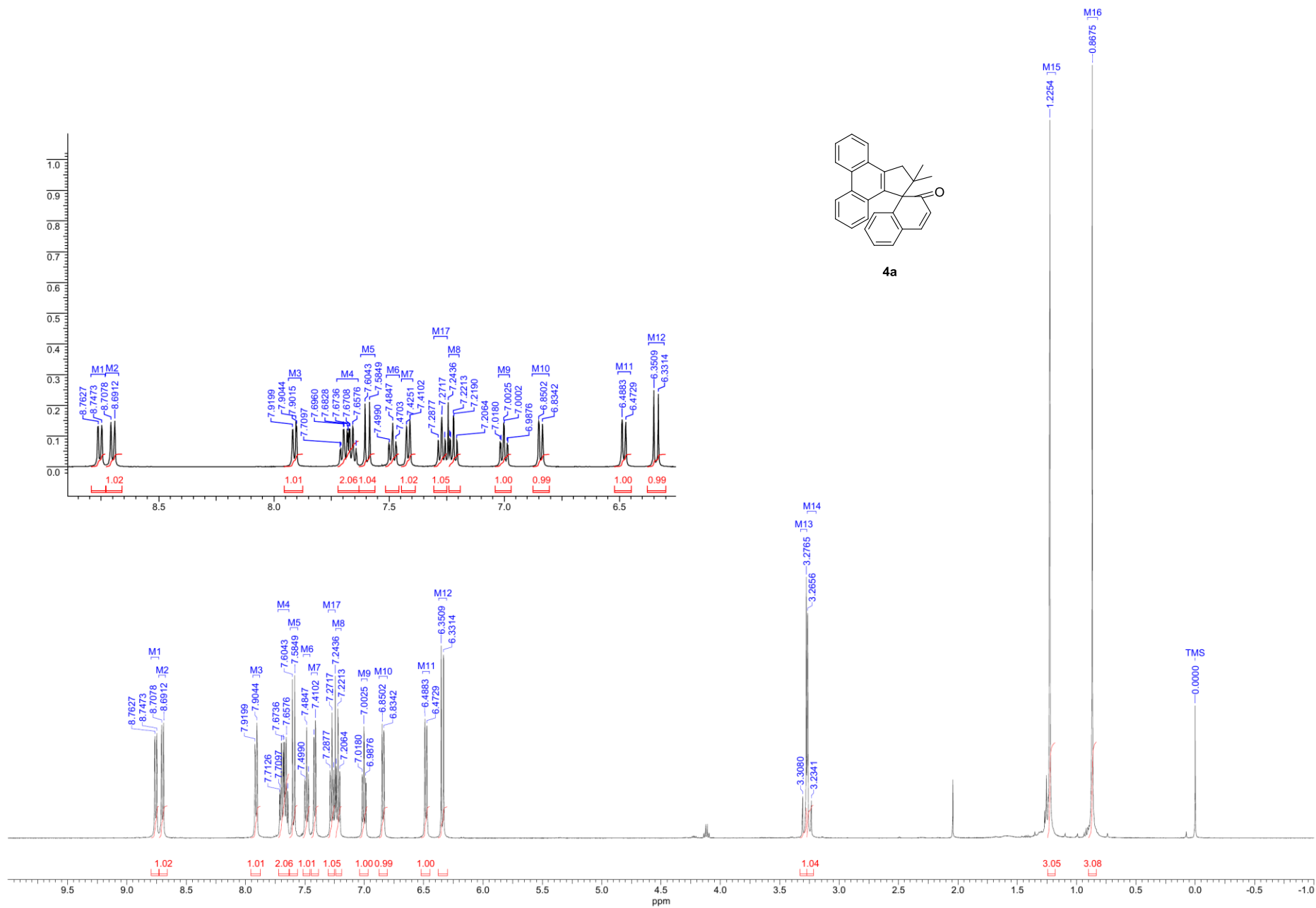


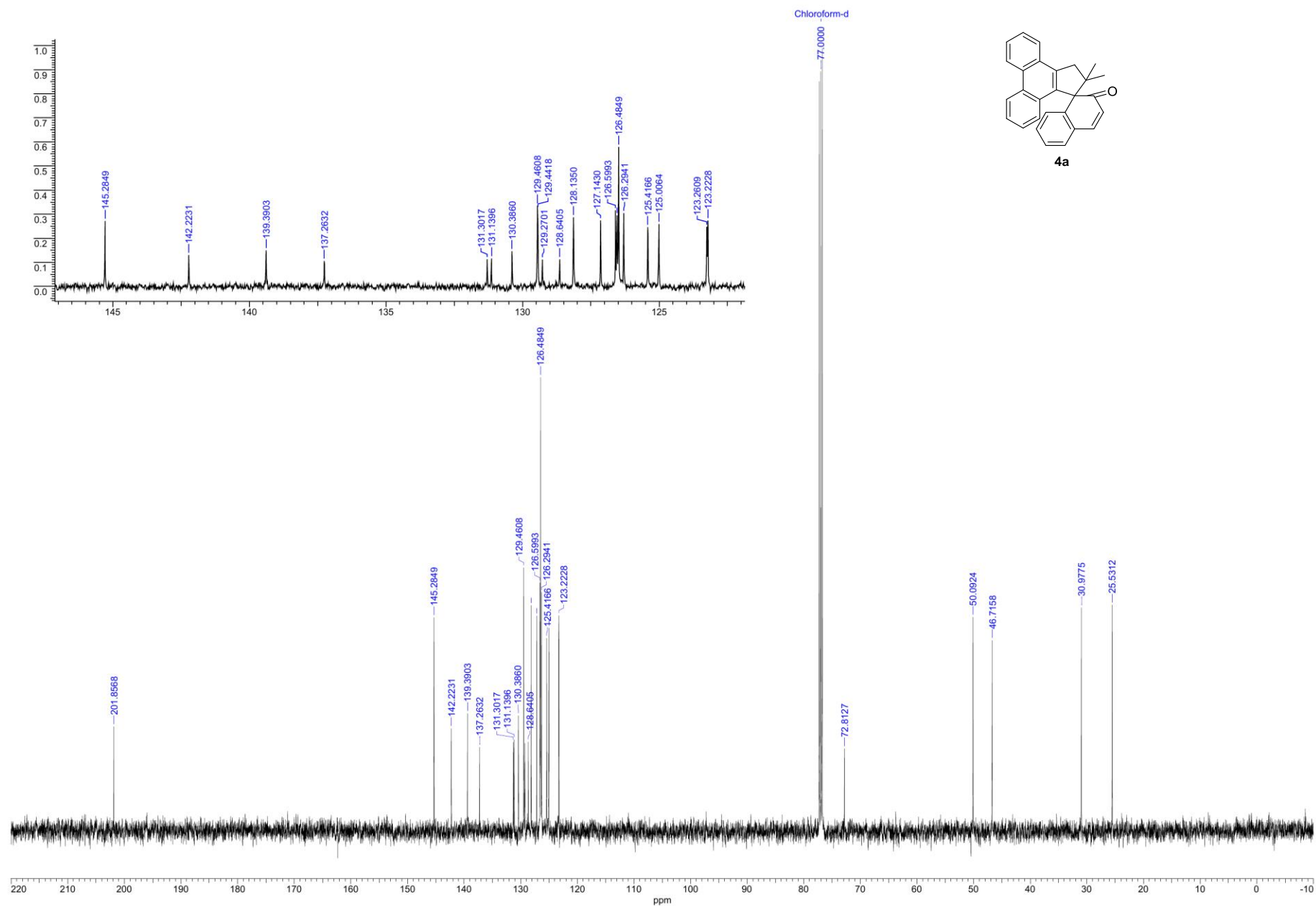


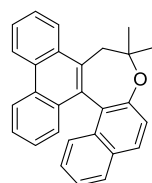




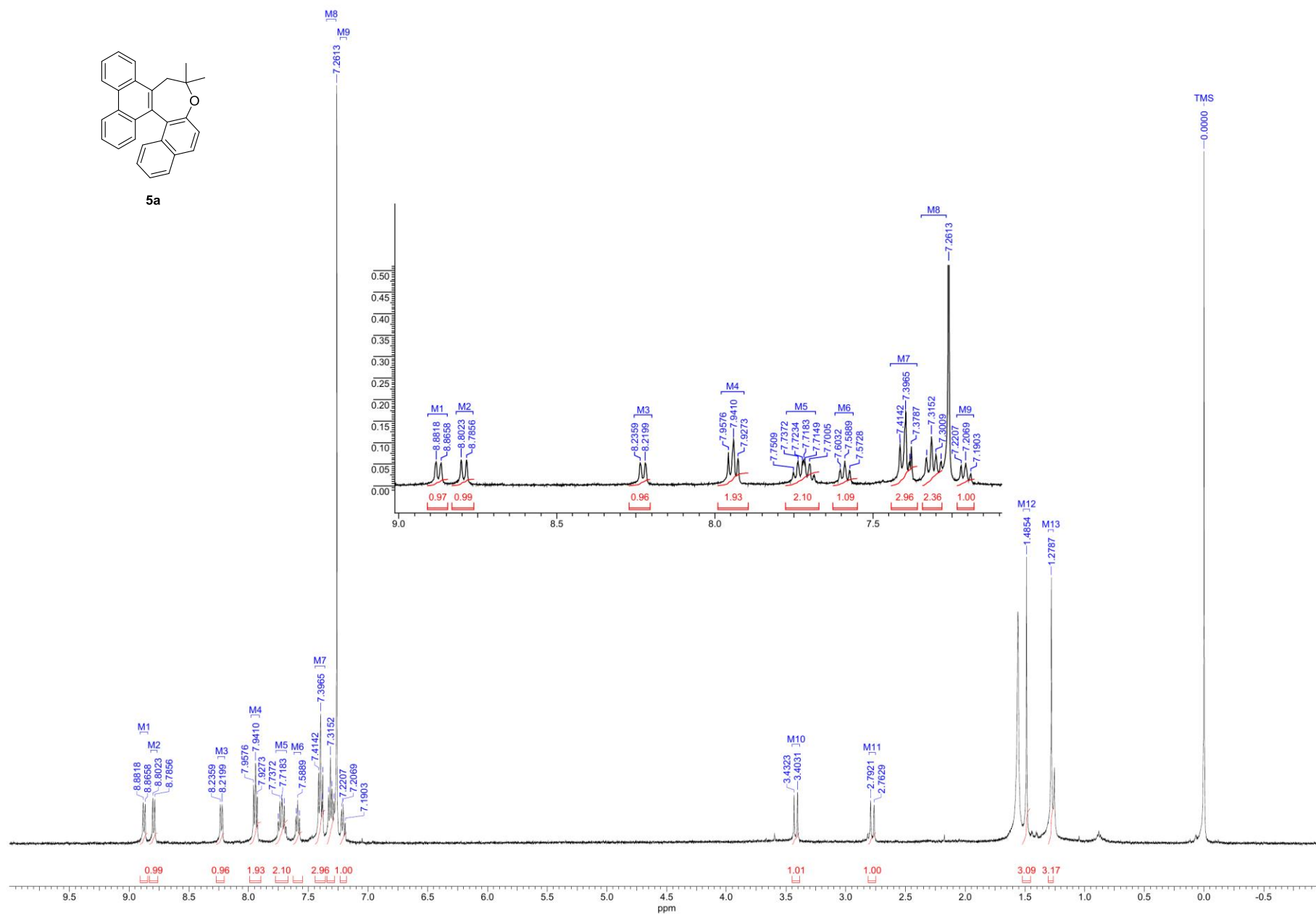


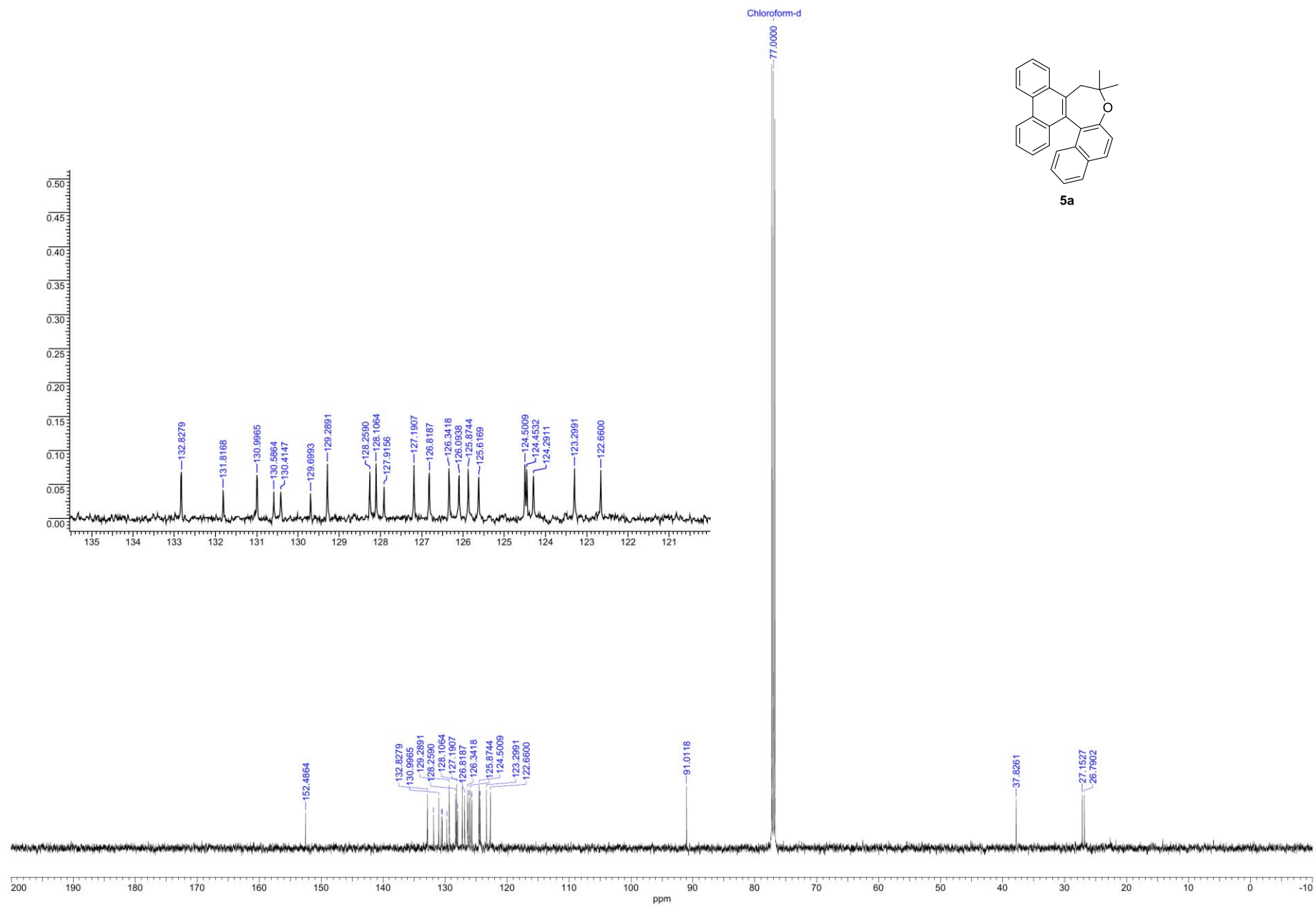


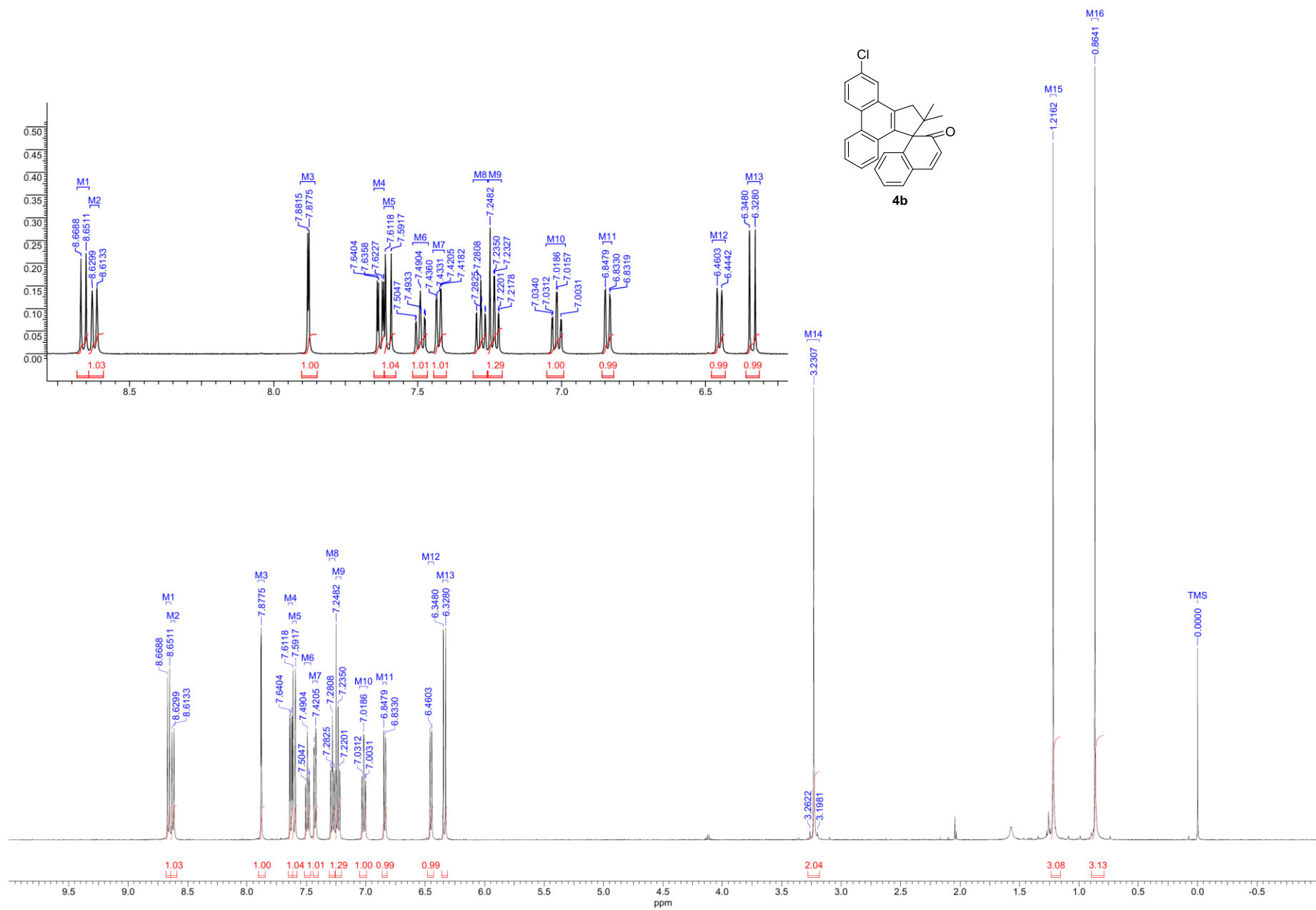


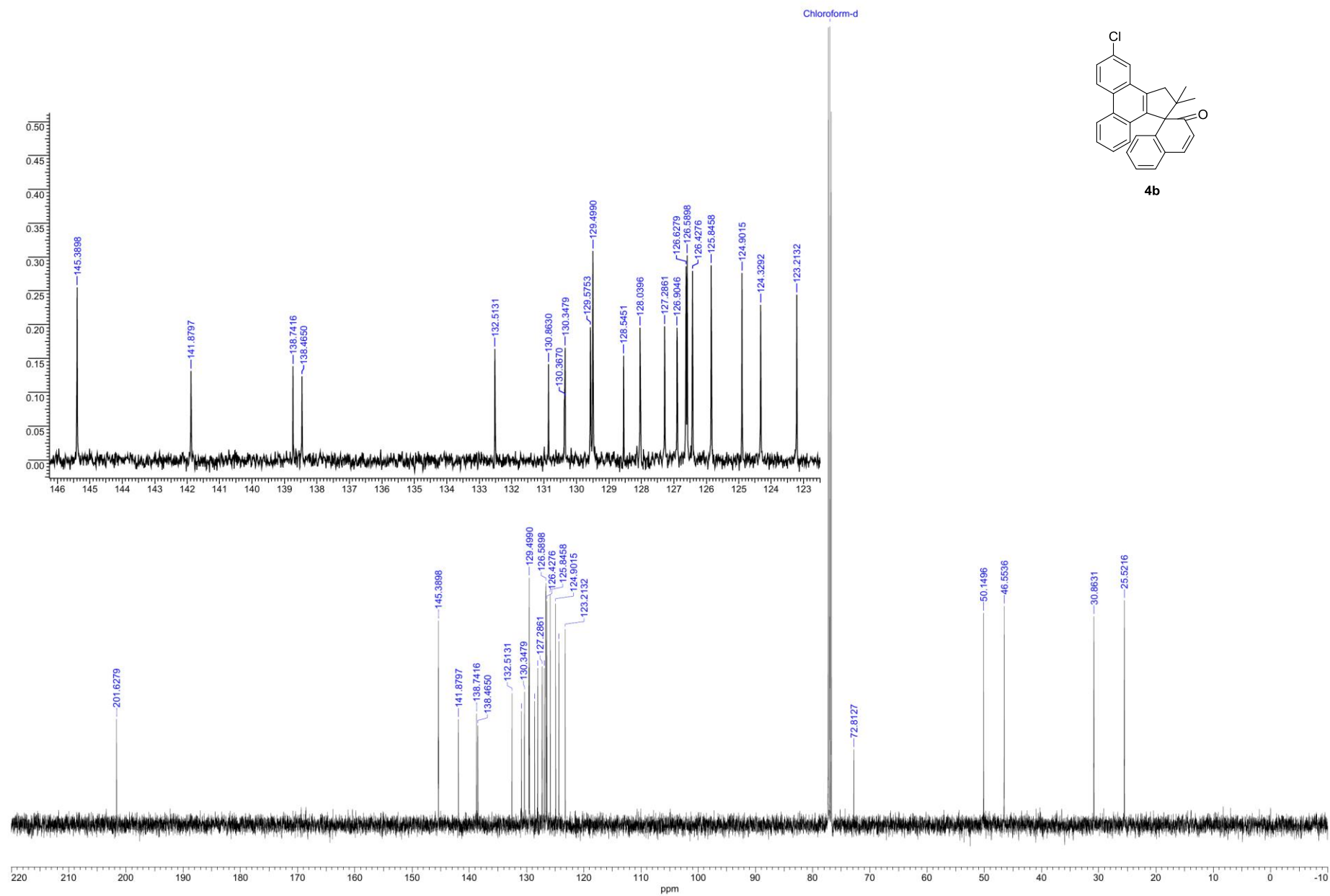


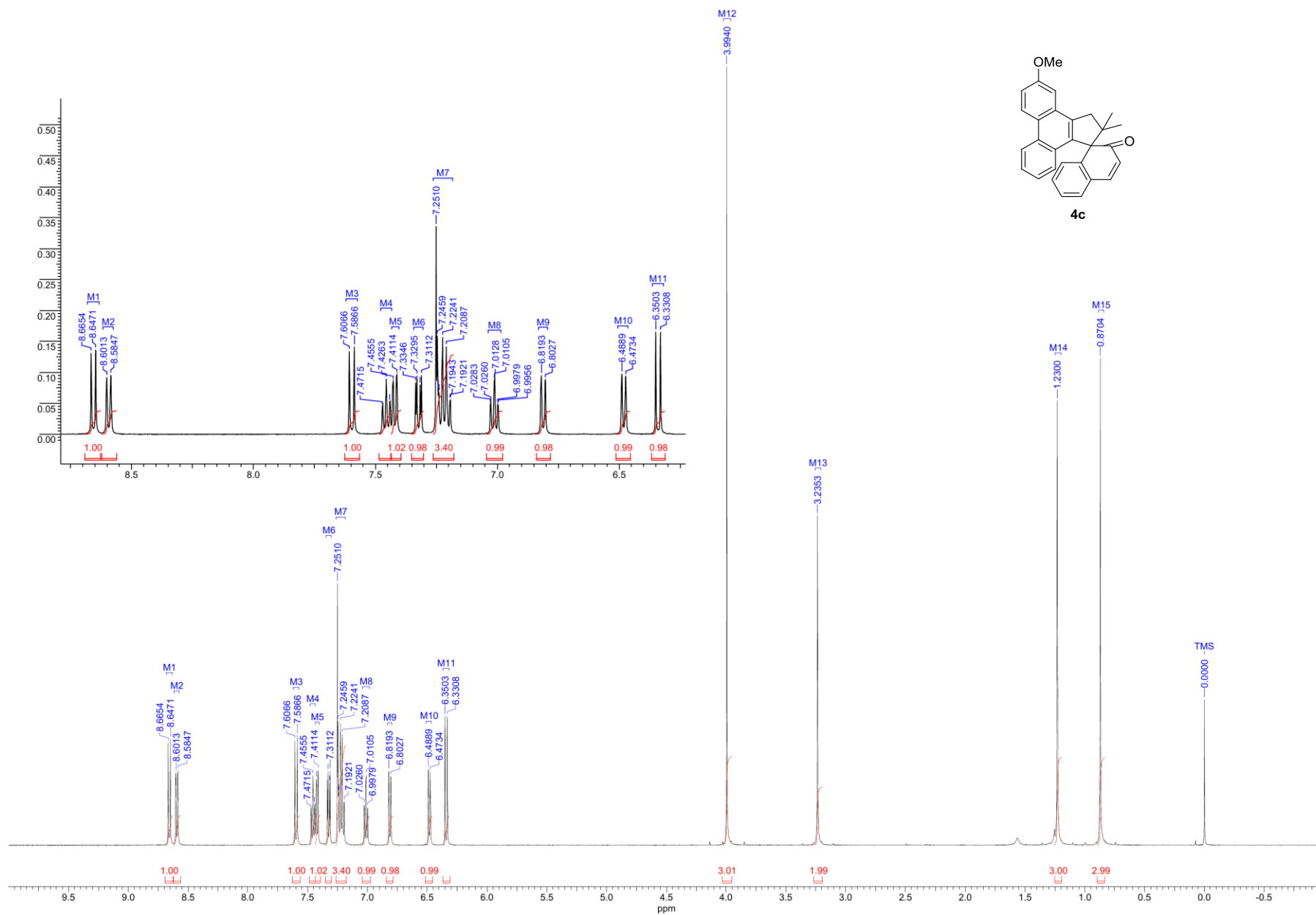
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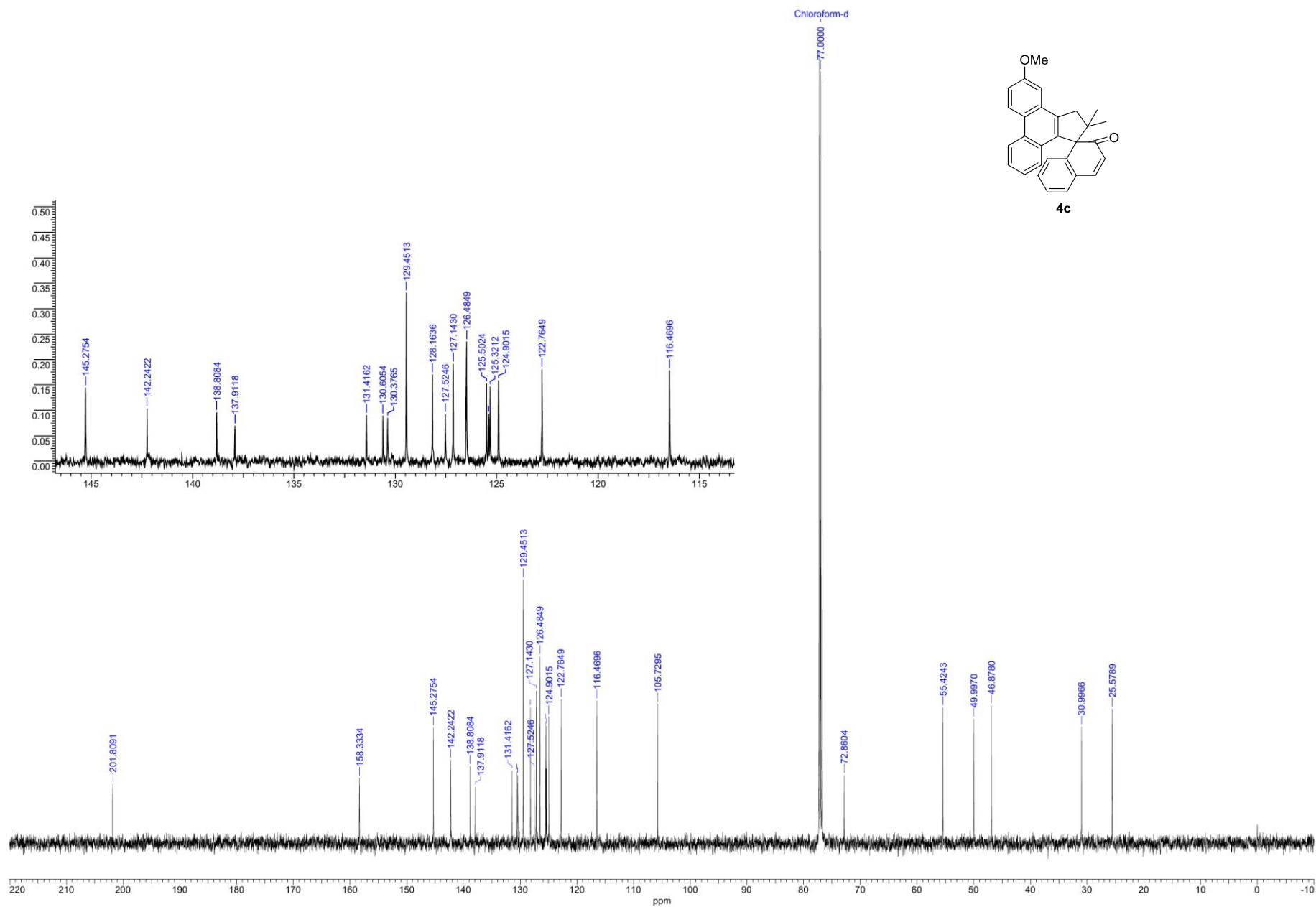


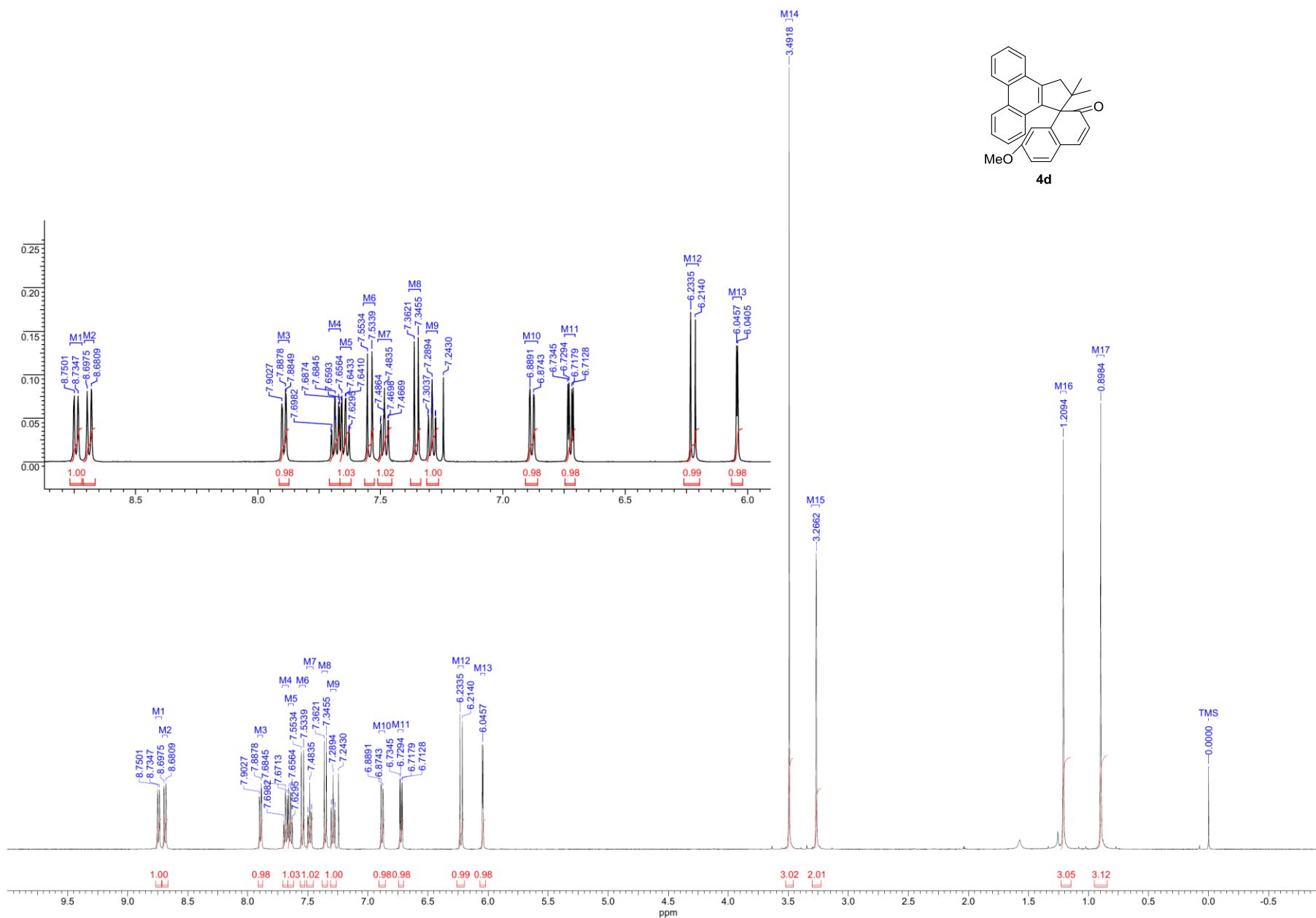
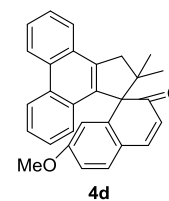


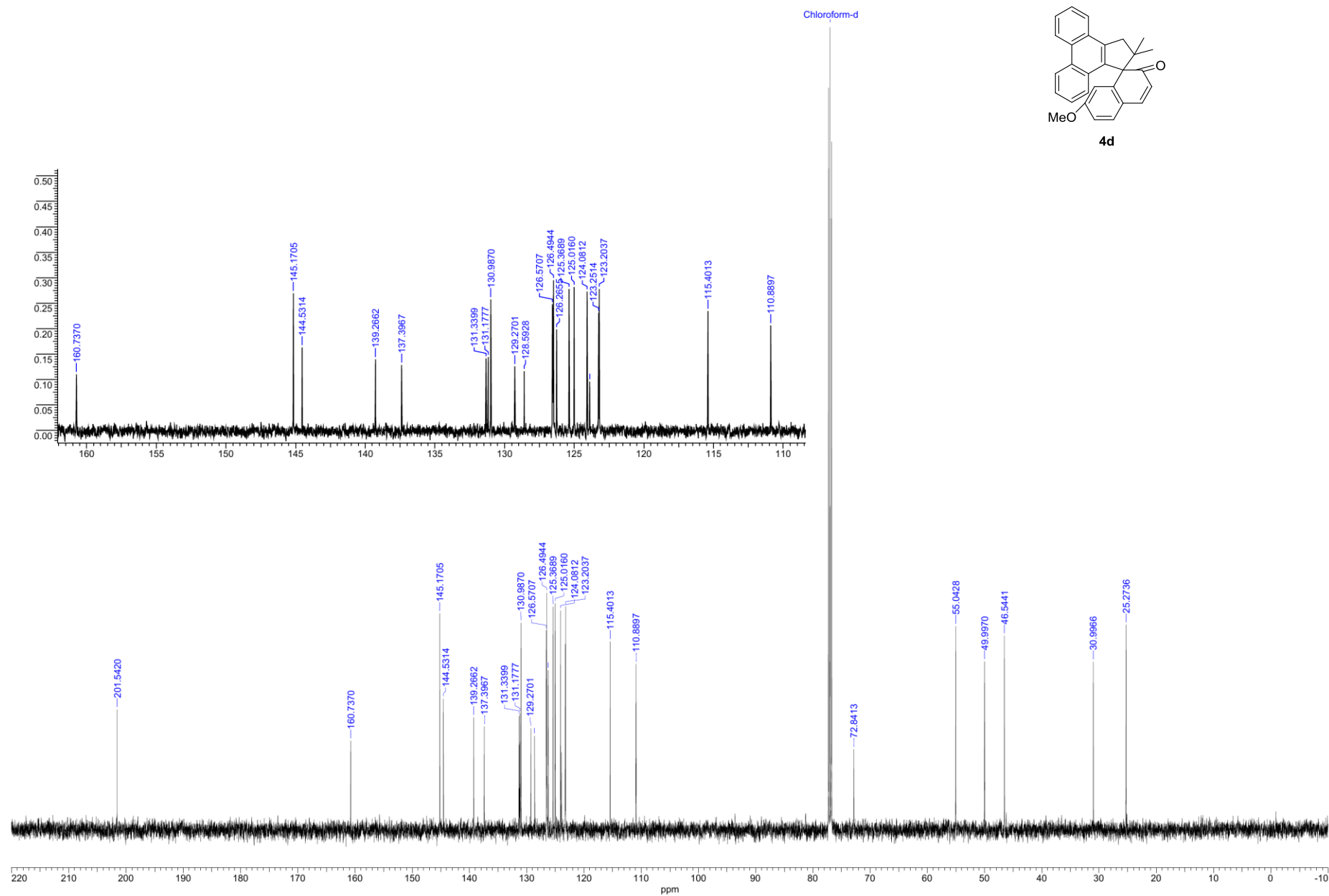


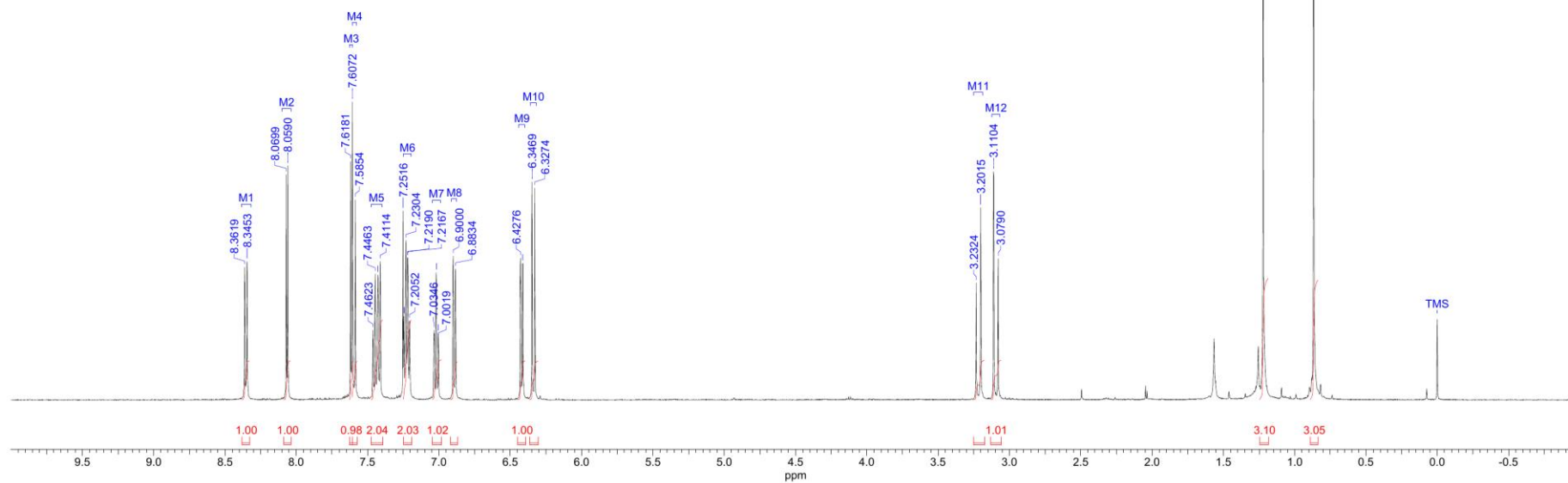
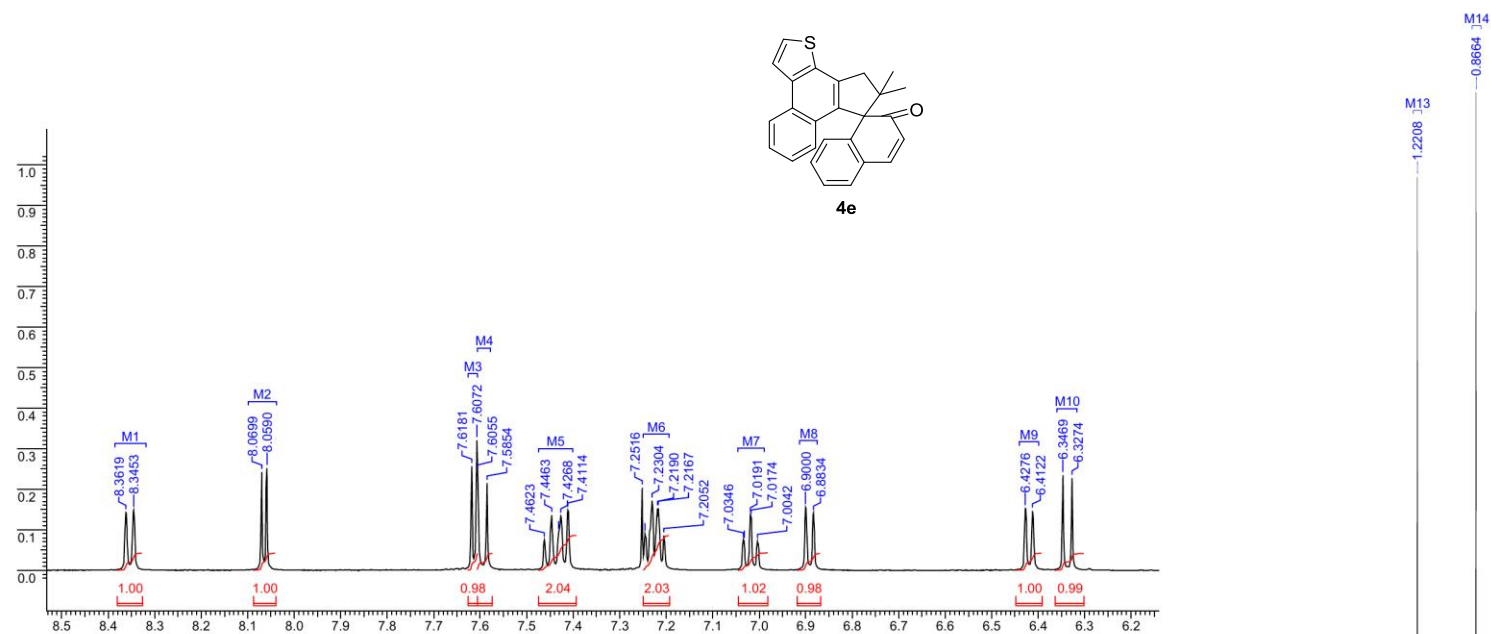
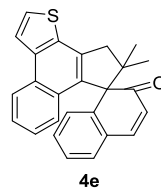


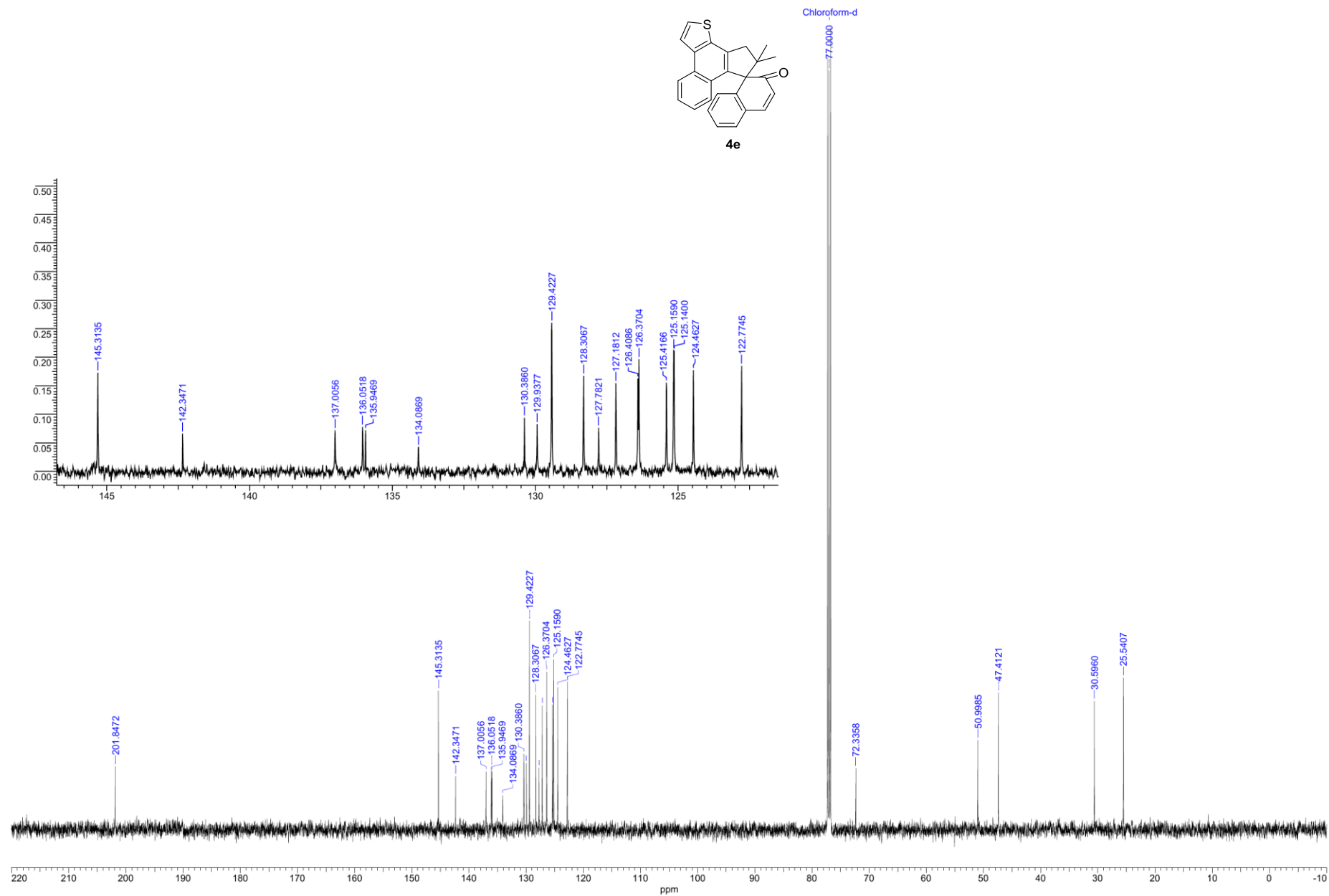


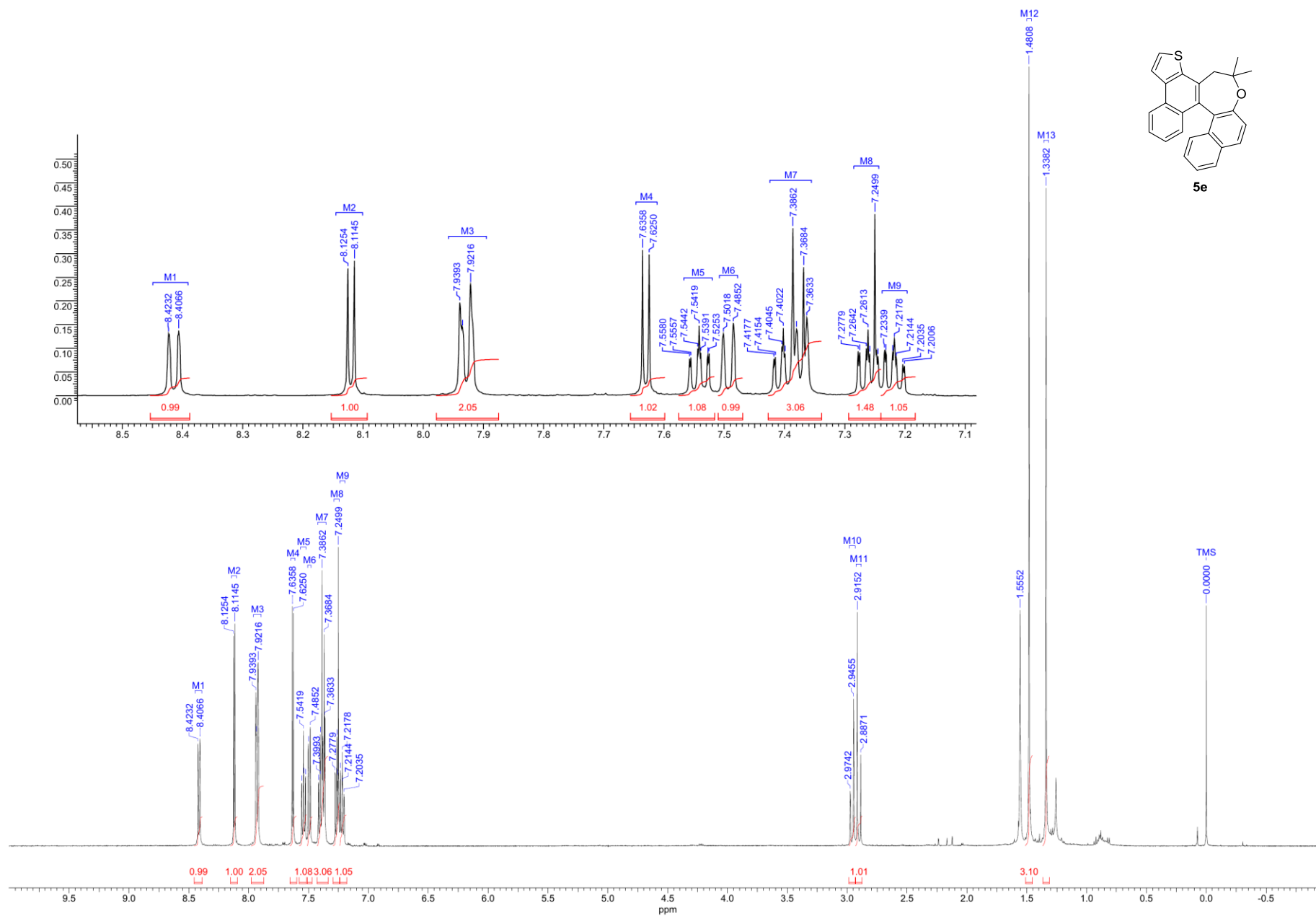


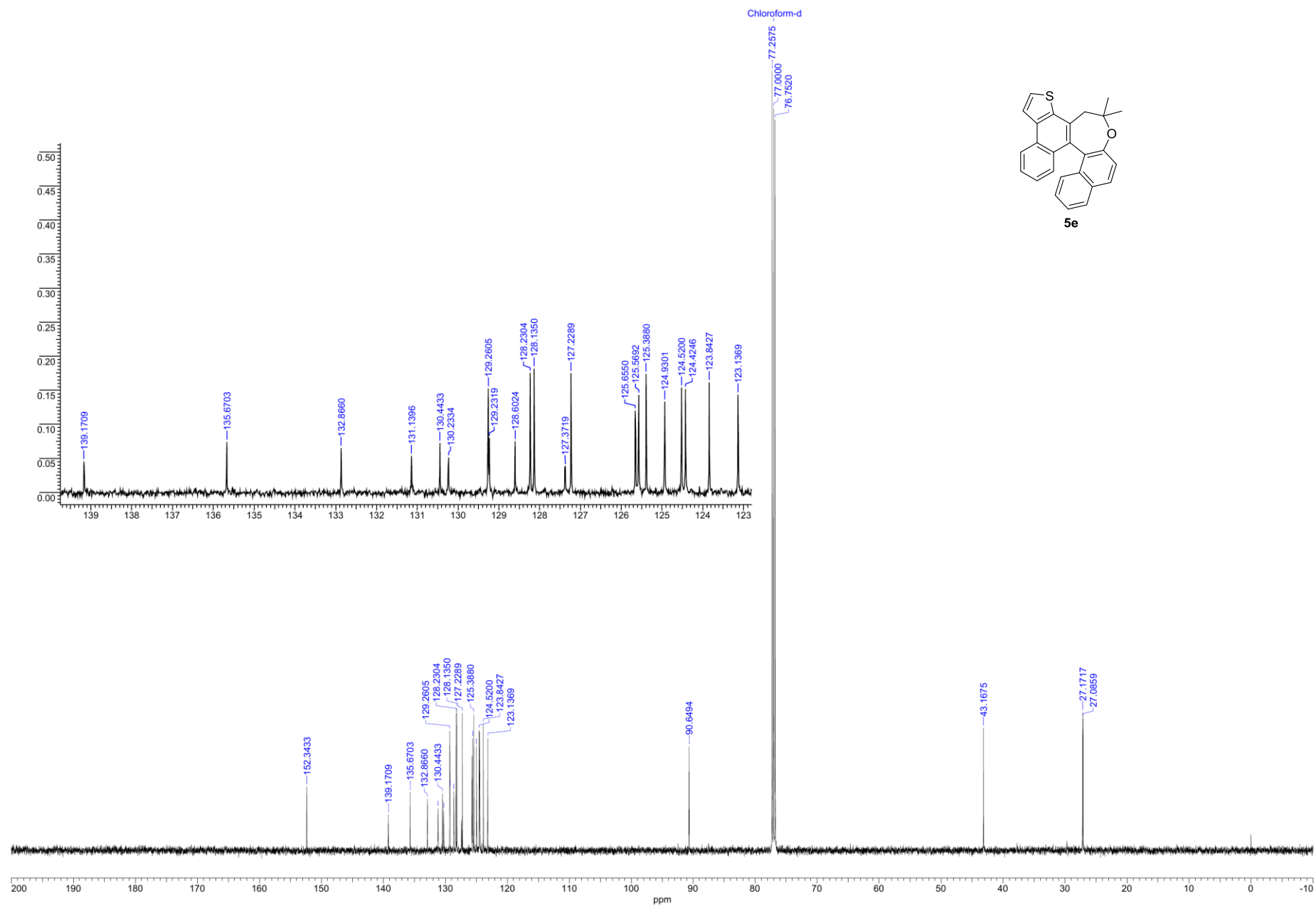


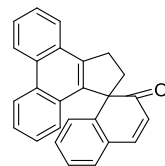




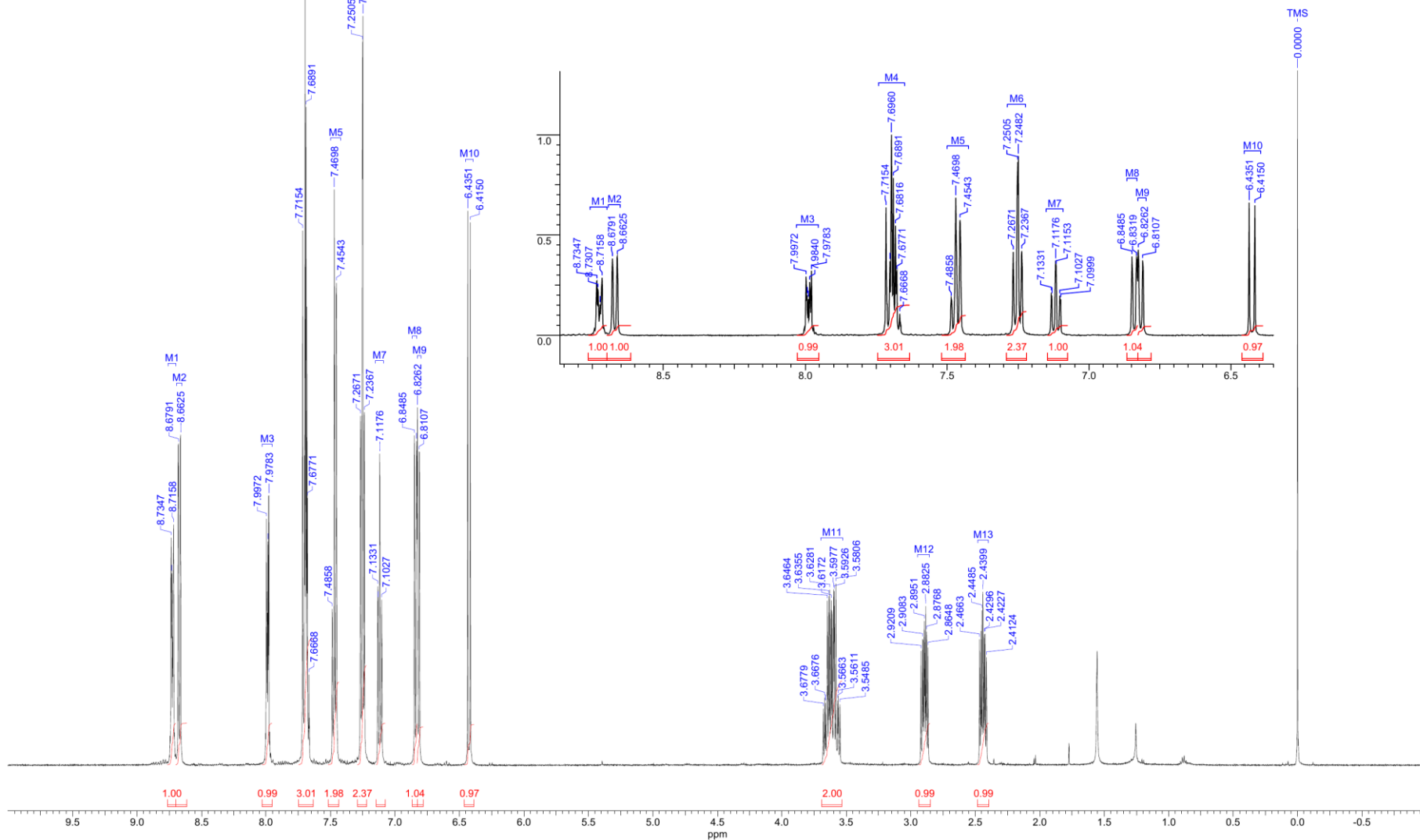


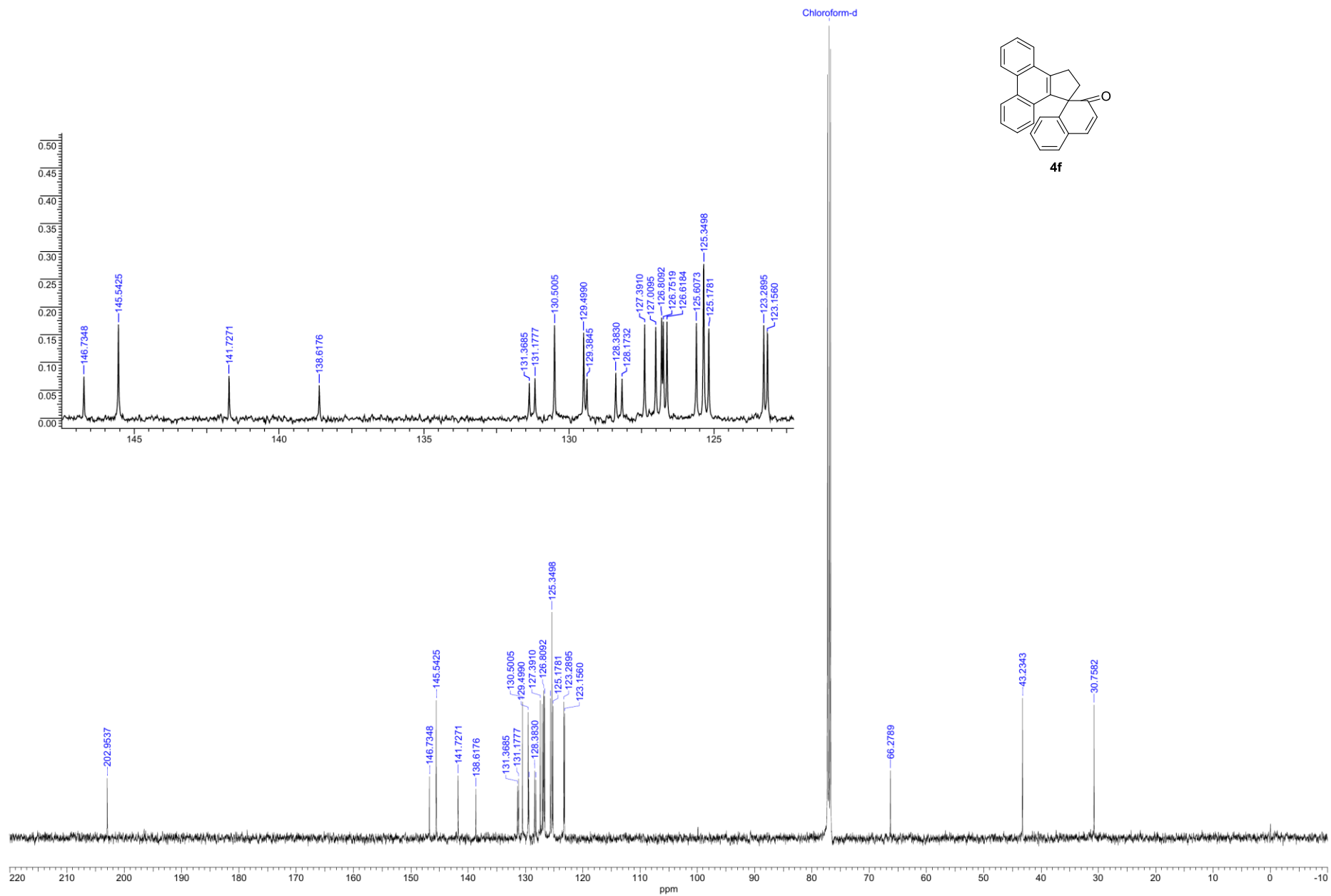


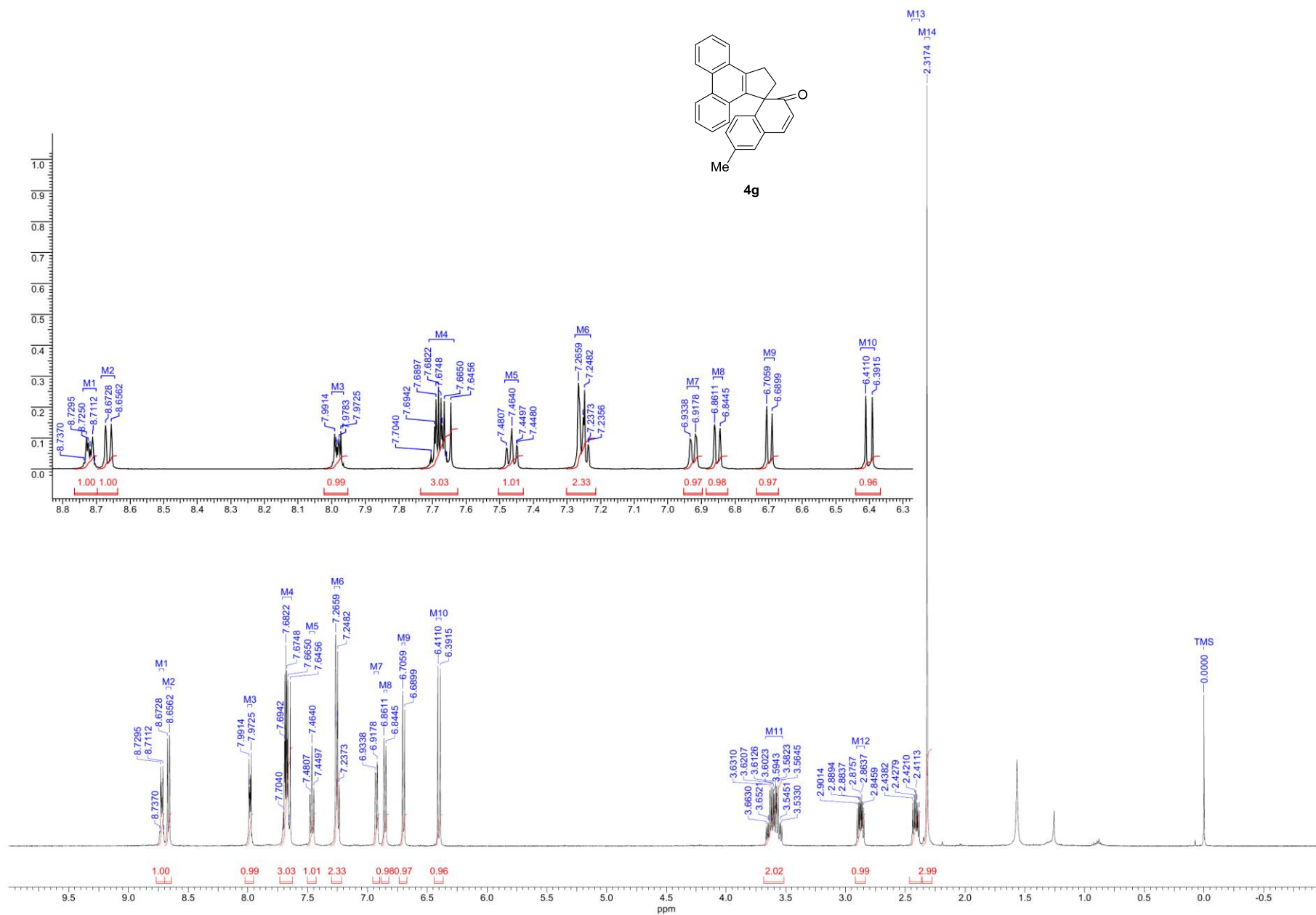


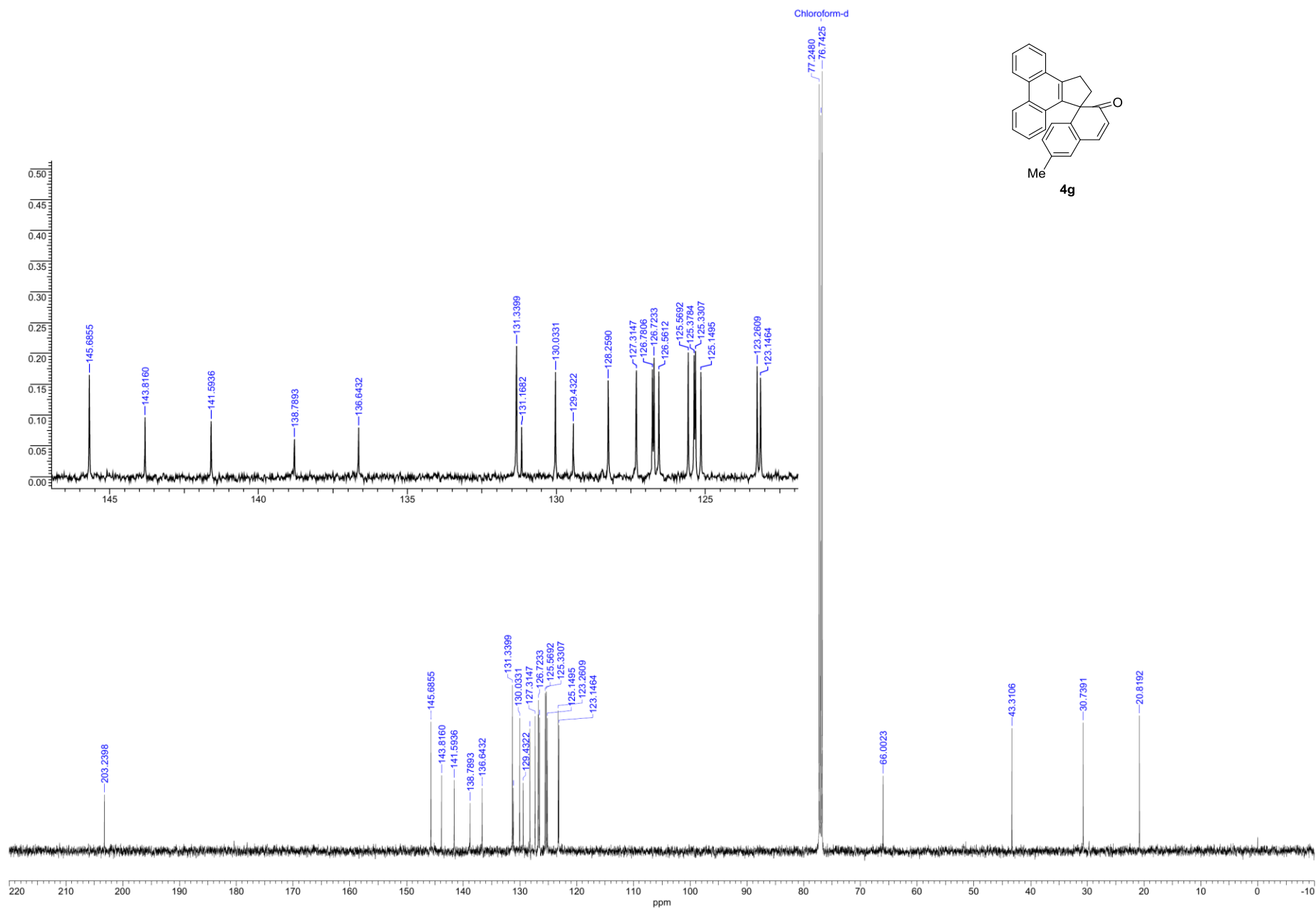


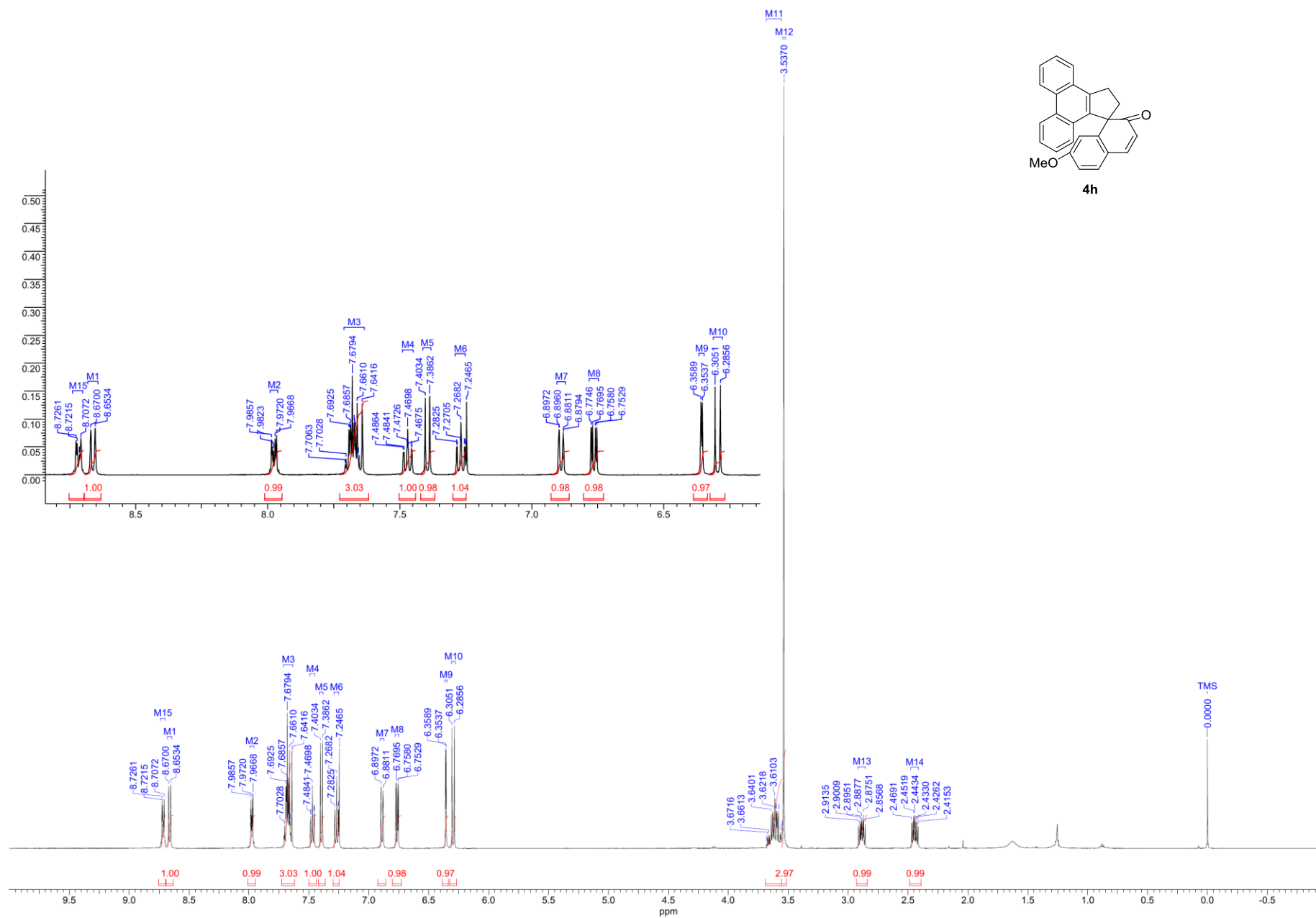
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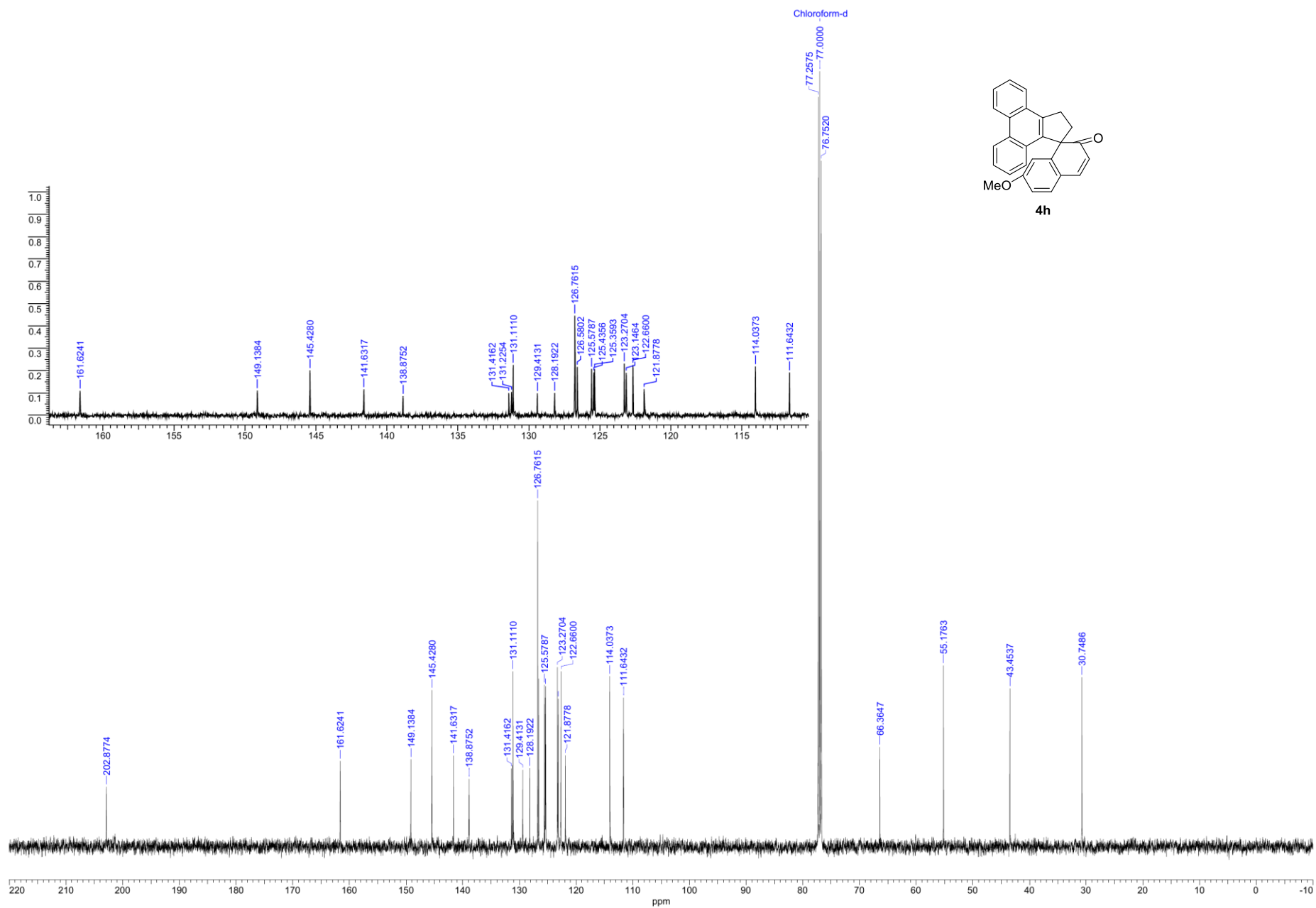


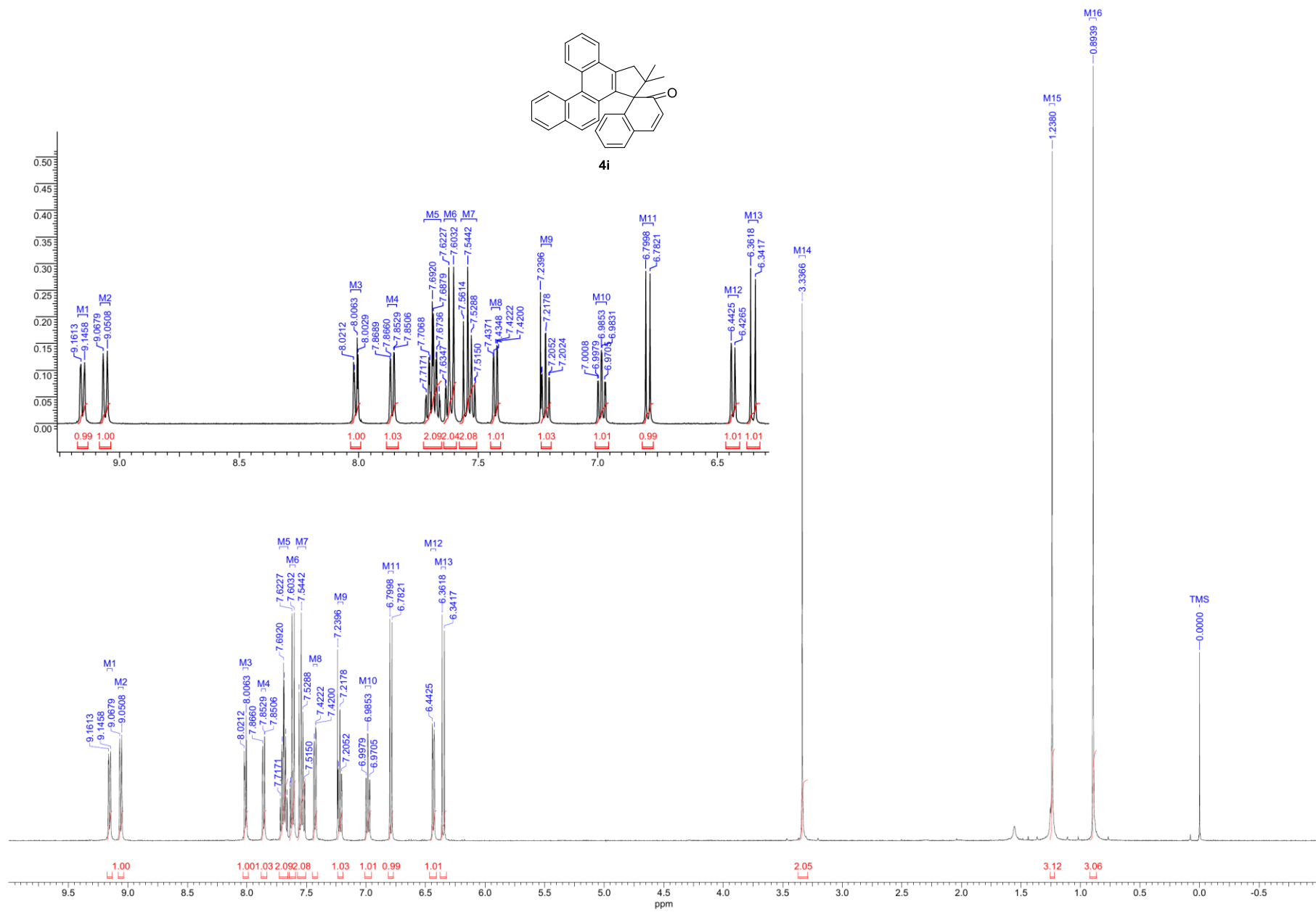


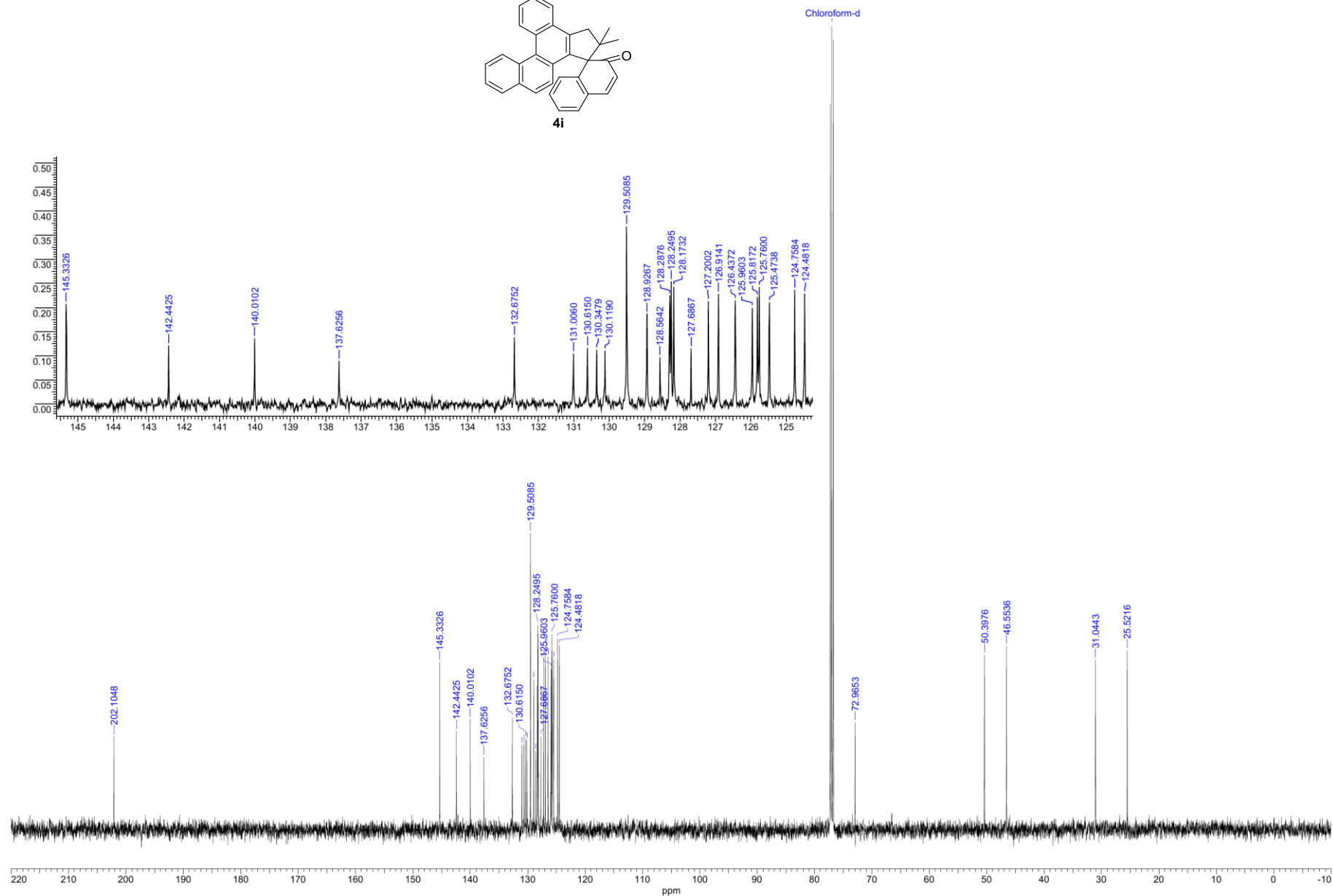
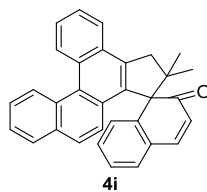


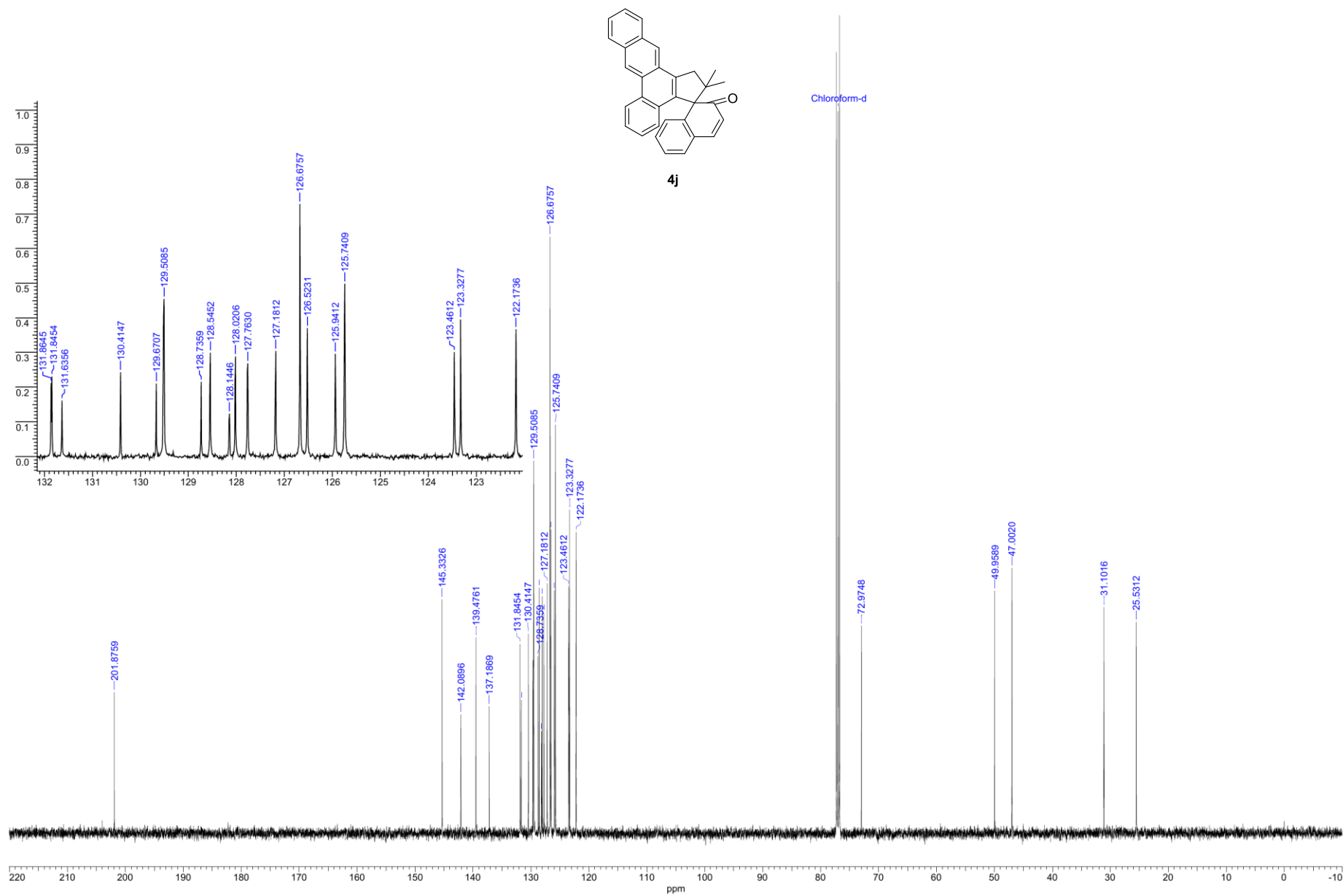


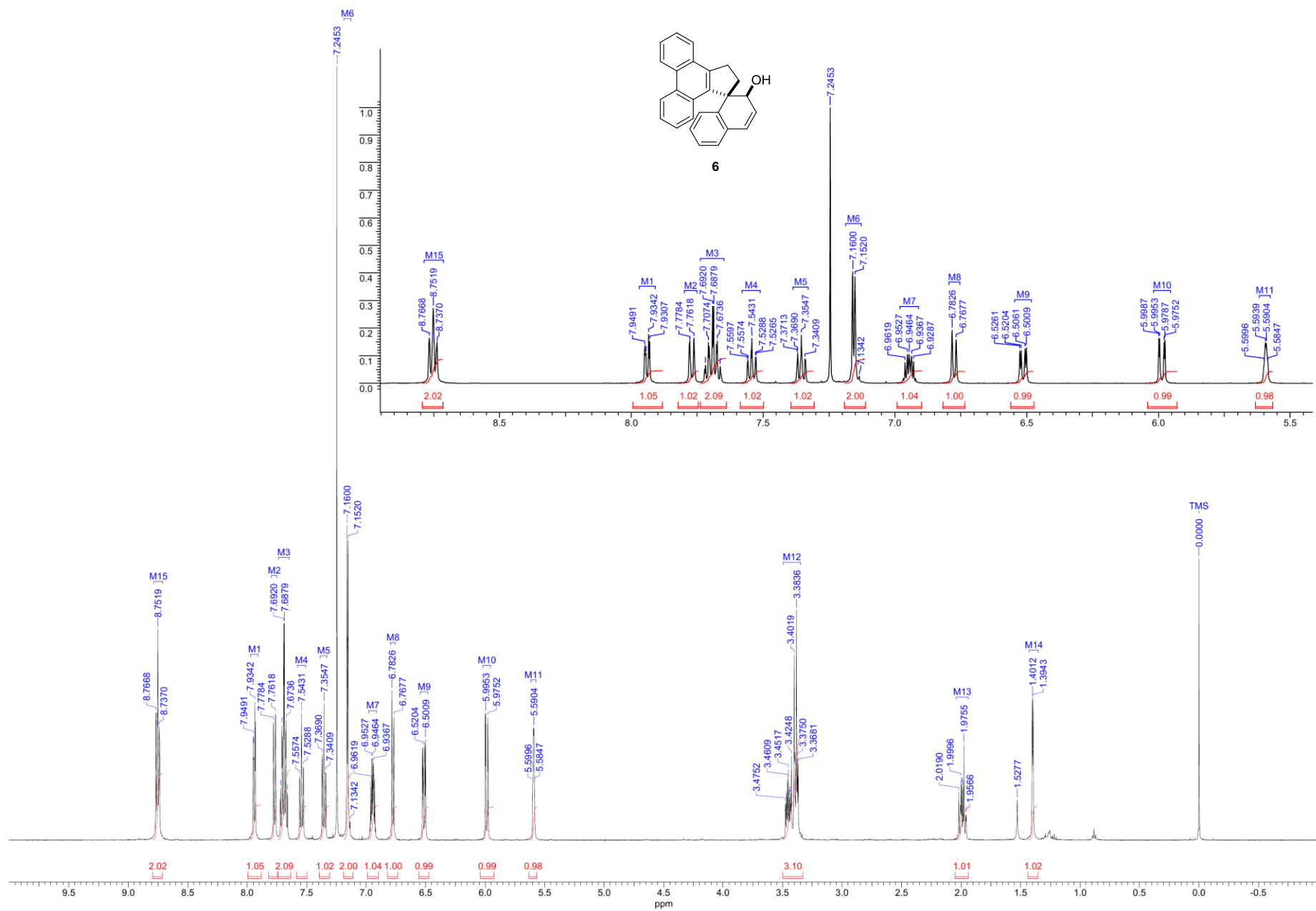


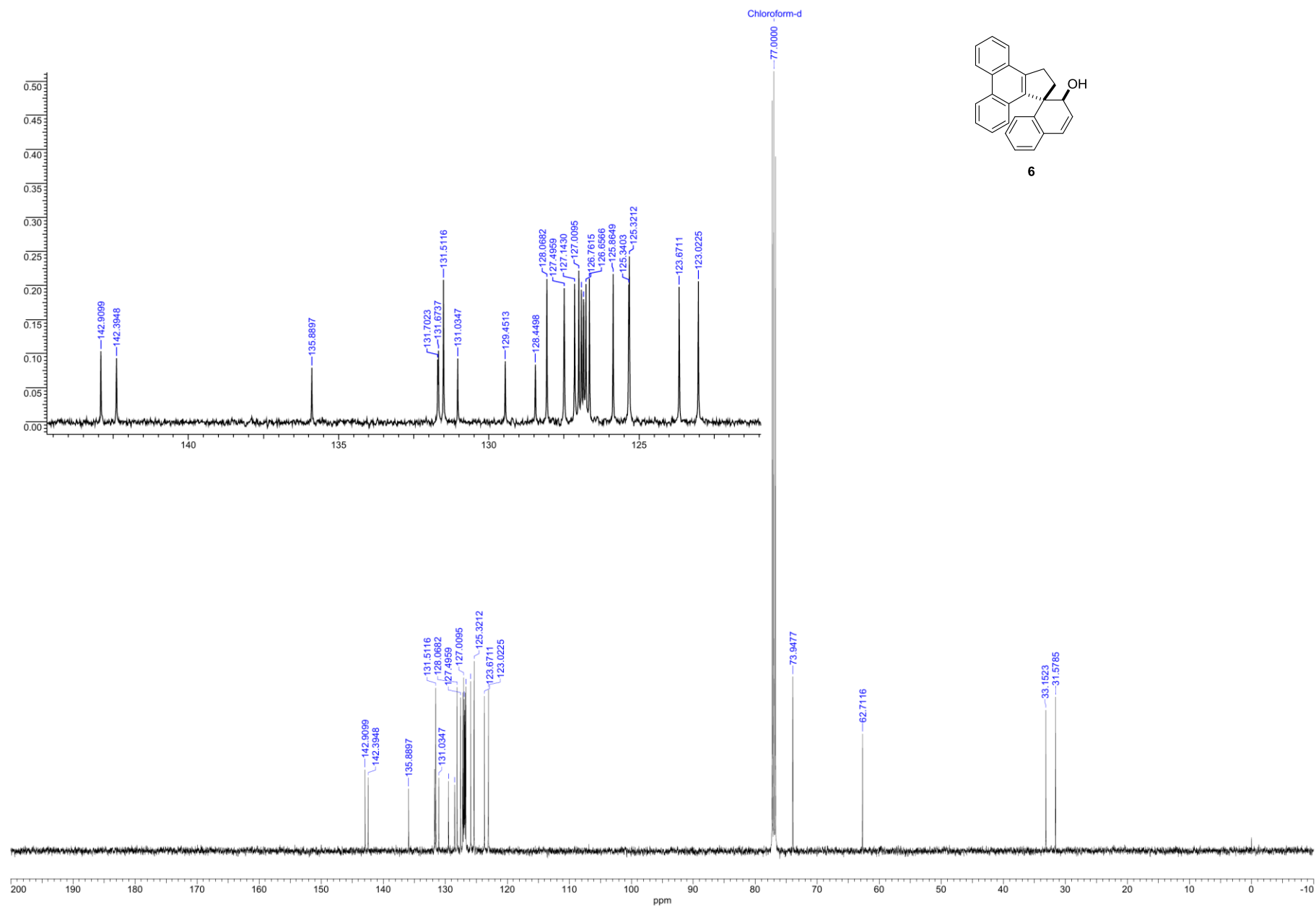


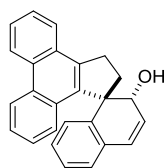




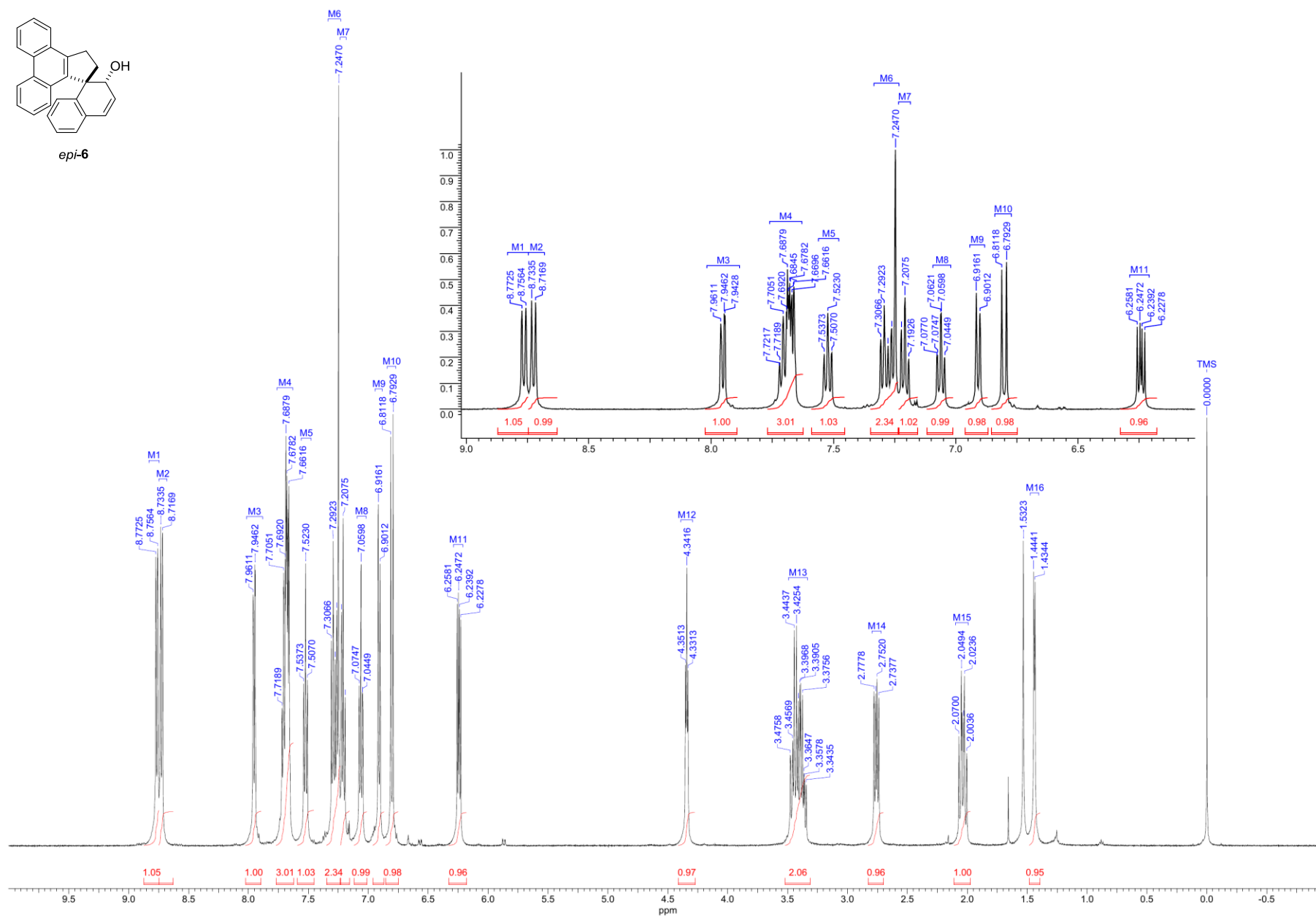


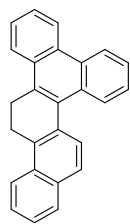




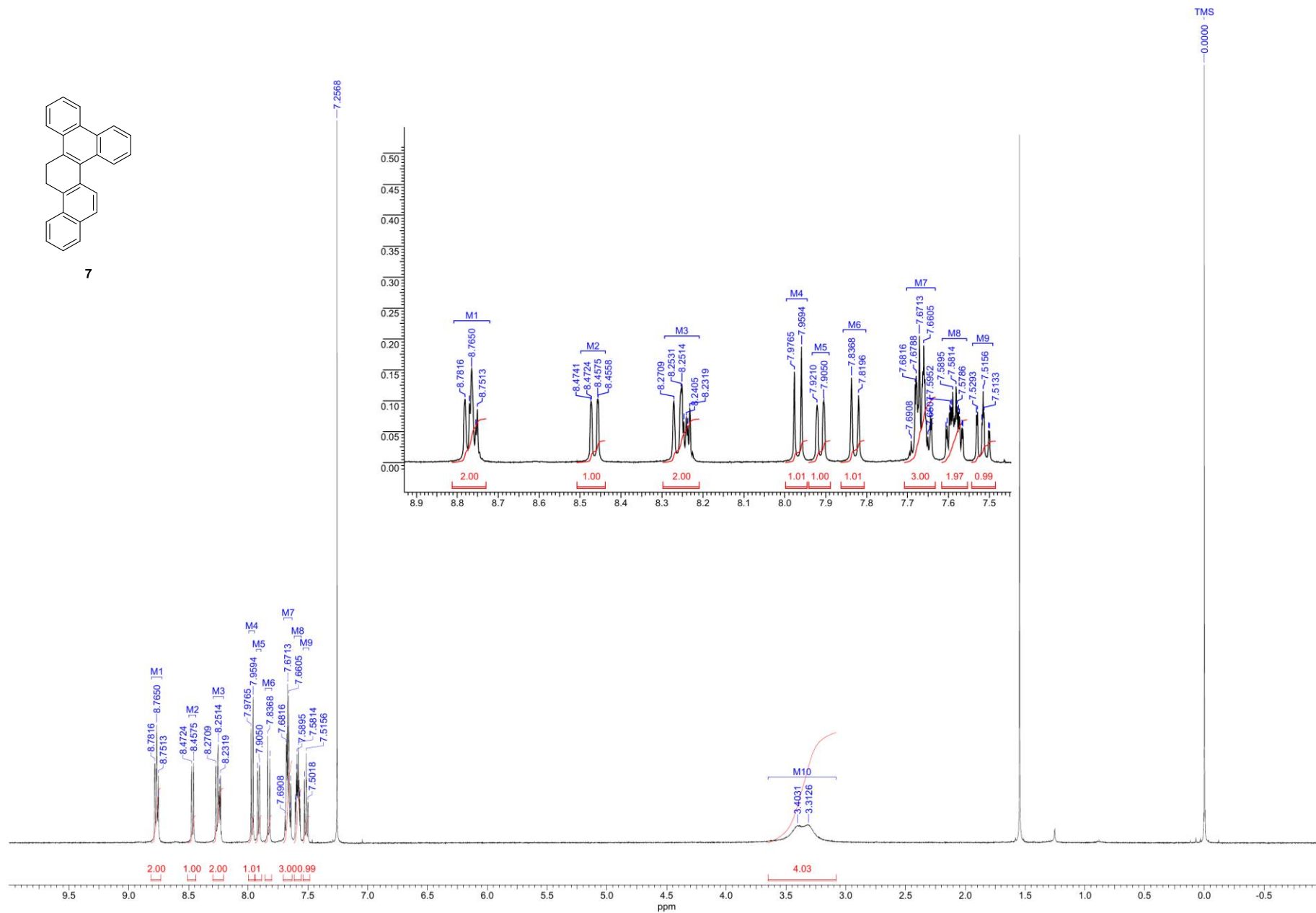


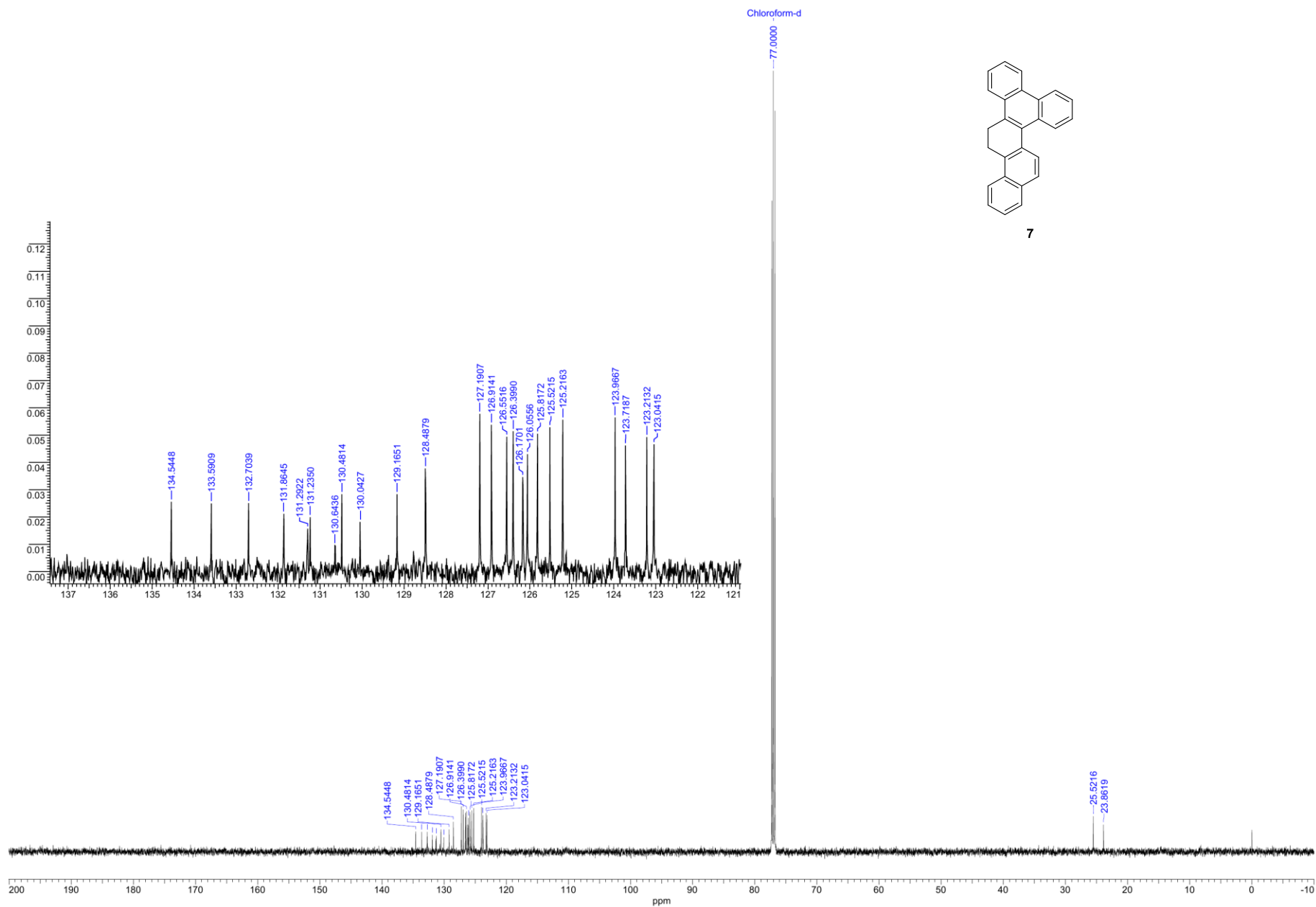
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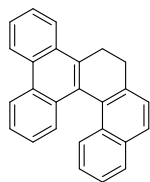




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