

Supporting Information

MnSO₄-Promoted S-O Bond Cleavage to Synthesize Functionalized Sulfonium Ylides from Activated Alkynes and Sulfoxides

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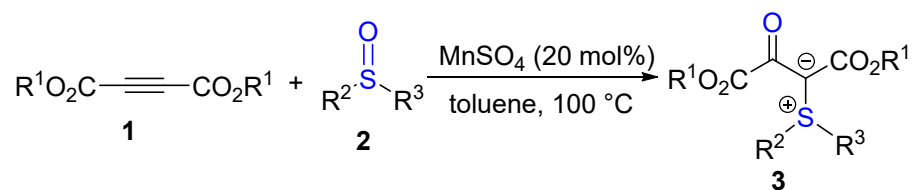
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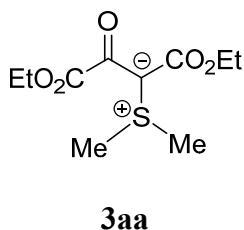
1. General Experimental Information

^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 400 and 500 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were acquired on an LTQ FT spectrometer, and were obtained by peak matching. Melting points are reported uncorrected. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Chromatography was performed using with 300-400 mesh silica gel (SiO_2). Unless otherwise noted, all reagents and solvents were obtained from commercial sources and, where appropriate, purified prior to use. Mn catalysts, acetylenedicarboxylates **1a-b**, **1f**, **1g**, **1m**, **1n**, and sulfoxides **2a-2k** were purchased directly from Sigma-Aldrich. Acetylenedicarboxylates **1c**¹, **1d-1e**², and **1h-1j**² were prepared according to literature methods and their spectral data matched literature values.

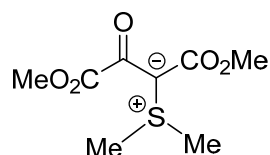
2. Synthesis of sulfonium ylides **3**



General procedure: In a 25-mL Teflon-sealed flask was charged with acetylenedicarboxylates **1** (0.5 mmol), sulfoxides **2** (5 mmol, 10.0 equiv.) and MnSO_4 (0.1 mmol, 20 mol%) under air atmosphere. Toluene (2.0 mL) was added. The reaction vessel was sealed with a Teflon cap and stirred vigorously at $100\text{ }^\circ\text{C}$ for 6–24 h until the substrate **1** disappeared (monitored by TLC). At this time, the reaction was quenched with H_2O (10 mL). The water was extracted by EtOAc ($3 \times 10\text{ mL}$). The organic layers were combined together, washed with brine ($1 \times 10\text{ mL}$), dried with Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 2/1) to give the corresponding sulfonium ylide **3**.

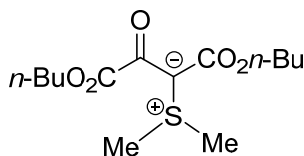


(1,4-Diethoxy-1,3,4-trioxobutan-2-yl)dimethylsulfonium ylide (3aa). $R_f = 0.2$, 0.107 g (86% yield); yellow solid; mp 89–90 °C. ^1H NMR (400 MHz, CDCl_3): δ 4.25 (q, $J = 7.2$ Hz, 2H), 4.11 (q, $J = 7.2$ Hz, 2H), 2.94 (s, 6H), 1.31 (t, $J = 7.2$ Hz, 3H), 1.20 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 180.7, 166.5, 165.0, 72.1, 61.1, 59.8, 25.9, 14.2, 13.8. IR (thin film): 2983, 2936, 1710, 1678, 1381, 1277 1202, 1080 cm^{-1} . HRMS (ESI): m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{10}\text{H}_{17}\text{O}_5\text{S}$: 249.0791; found: 249.0793.



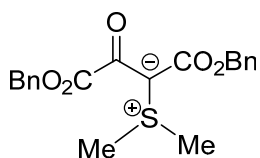
3ba

(1,4-Dimethoxy-1,3,4-trioxobutan-2-yl)dimethylsulfonium ylide (3ba).^[3] 0.087 g (79% yield); yellow solid. ^1H NMR (400 MHz, CDCl_3): δ 3.79 (s, 3H), 3.63 (s, 3H), 2.96 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 180.6, 166.9, 165.4, 72.0, 52.0, 51.1, 25.9.



3ca

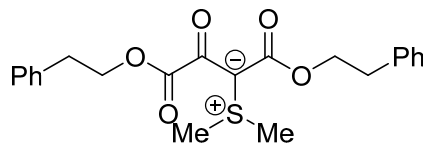
(1,4-Dibutoxy-1,3,4-trioxobutan-2-yl)dimethylsulfonium ylide (3ca). $R_f = 0.3$, 0.119 g (78% yield); white solid; mp 41–42 °C. ^1H NMR (400 MHz, CDCl_3): δ 4.16 (t, $J = 6.8$ Hz, 2H), 4.03 (d, $J = 6.8$ Hz, 2H), 2.94 (s, 6H), 1.67–1.60 (m, 2H), 1.57–1.49 (m, 2H), 1.38–1.27 (m, 4H), 0.89–0.84 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 180.6, 166.6, 165.0, 72.2, 64.9, 63.8, 30.7, 30.2, 25.9, 18.9, 18.8, 13.5, 13.5. IR (thin film): 2959, 2873, 1734, 1668, 1464, 1397, 1200, 1075 cm^{-1} . HRMS (ESI): m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{14}\text{H}_{25}\text{O}_5\text{S}$: 305.1417; found: 305.1413.



3da

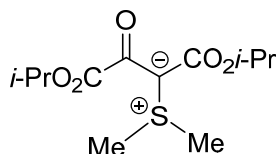
(1,4-Bis(benzyloxy)-1,3,4-trioxobutan-2-yl)dimethylsulfonium ylide (3da). $R_f = 0.2$, 0.147 g (69% yield), white solid; mp 80–81 °C. ^1H NMR (400 MHz, CDCl_3): δ

7.27–7.16 (m, 10H), 4.99 (s, 2H), 4.86 (s, 2H), 2.85 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 180.3, 166.1, 164.8, 136.0, 135.2, 128.6, 128.4, 128.4, 128.3, 128.1, 128.1, 72.5, 66.7, 66.1, 25.9. IR (thin film): 3033, 2959, 1725, 1659, 1423, 1220, 1065, 737 cm^{-1} . HRMS (ESI): m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{20}\text{H}_{21}\text{O}_5\text{S}$: 373.1104; found: 373.1111.



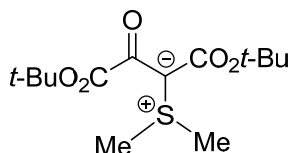
3ea

Dimethyl(1,3,4-trioxo-1,4-diphenethoxybutan-2-yl)sulfonium ylide (3ea). R_f = 0.3, 0.142 g (71% yield); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.24–7.12 (m, 10H), 4.36 (t, J = 7.2 Hz, 2H), 4.24 (t, J = 7.2 Hz, 2H), 2.98 (t, J = 7.6 Hz, 2H), 2.85 (t, J = 7.2 Hz, 8H). ^{13}C NMR (100 MHz, CDCl_3): δ 180.7, 166.4, 164.8, 137.8, 137.5, 128.9, 128.7, 128.4, 128.3, 128.3, 126.4, 71.9, 65.6, 64.4, 35.1, 34.7, 26.0. IR (thin film): 3028, 2974, 2928, 1720, 1663, 1583, 1461, 1194, 1083, 729 cm^{-1} . HRMS (ESI): m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{O}_5\text{S}$: 401.1417; found: 401.1413.



3fa

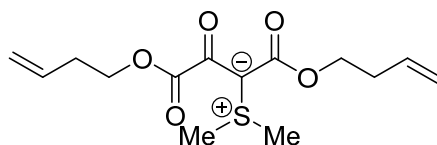
(1,4-Diisopropoxy-1,3,4-trioxobutan-2-yl)dimethylsulfonium ylide (3fa). R_f = 0.2, 0.097 g (69% yield); yellow solid; mp 123–124 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 5.08–5.02 (m, 1H), 4.99–4.93 (m, 1H), 2.92 (s, 6H), 1.27 (d, J = 6.4 Hz, 6H), 1.16 (d, J = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 180.8, 166.0, 164.5, 72.3, 68.7, 67.3, 25.9, 21.9, 21.5. IR (thin film): 2984, 2938, 1725, 1666, 1459, 1377, 1202, 1070 cm^{-1} . HRMS (ESI): m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{12}\text{H}_{21}\text{O}_5\text{S}$: 277.1104; found: 277.1101.



3ga

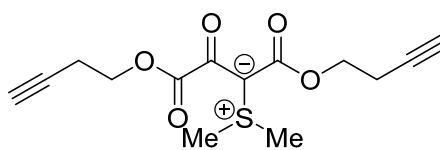
(1,4-Di-tert-butoxy-1,3,4-trioxobutan-2-yl)dimethylsulfonium ylide (3ga). R_f = 0.3, 0.062 g (38% yield); white solid; mp 144–145 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 2.96 (s, 6H), 1.55 (s, 9H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 181.4, 165.8,

164.5, 82.3, 80.5, 72.0, 28.7, 28.2, 26.2. IR (thin film): 2979, 2929, 1717, 1658, 1382, 1214, 1079 cm^{-1} . HRMS (ESI): m/z ($M + H$)⁺ calcd for $\text{C}_{14}\text{H}_{25}\text{O}_5\text{S}$: 305.1417; found: 305.1414.



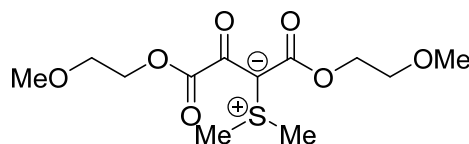
3ha

(1,4-Bis(but-3-enyloxy)-1,3,4-trioxobutan-2-yl)dimethylsulfonium ylide (3ha). R_f = 0.3, 0.108 g (72% yield); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 5.79–5.67 (m, 2H), 5.10–4.98 (m, 4H), 4.21 (t, J = 7.2 Hz, 2H), 4.10 (t, J = 7.2 Hz, 2H), 2.93 (s, 6H), 2.44 (q, J = 13.6 Hz, 2H), 2.36 (q, J = 13.6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 180.5, 166.4, 164.8, 134.0, 133.5, 117.1, 116.9, 72.1, 64.1, 63.0, 33.0, 32.5, 26.0. IR (thin film): 2960, 1732, 1668, 1393, 1200, 1076, 994 cm^{-1} . HRMS (ESI): m/z ($M + H$)⁺ calcd for $\text{C}_{14}\text{H}_{21}\text{O}_5\text{S}$: 301.1104; found: 301.1102.



3ia

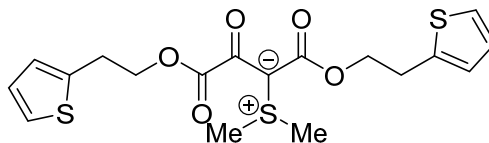
(1,4-Bis(but-3-ynyloxy)-1,3,4-trioxobutan-2-yl)dimethylsulfonium ylide (3ia). R_f = 0.3, 0.120 g (81% yield); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 4.37 (t, J = 7.2 Hz, 2H), 4.22 (t, J = 6.8 Hz, 2H), 3.00 (s, 6H), 2.66–2.62 (m, 2H), 2.55–2.51 (m, 2H), 2.01 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 180.4, 166.0, 164.7, 80.5, 79.8, 71.9, 70.1, 69.9, 62.9, 61.9, 26.2, 19.1, 18.7. IR (thin film): 3286, 3014, 2918, 2852, 1740, 1676, 1179, 1080 cm^{-1} . HRMS (ESI): m/z ($M + H$)⁺ calcd for $\text{C}_{14}\text{H}_{17}\text{O}_5\text{S}$: 297.0791; found: 297.0768.



3ja

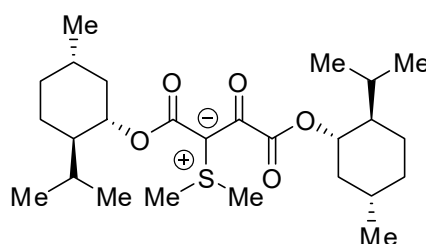
Dimethyl(6,8,9-trioxo-2,5,10,13-tetraoxatetradecan-7-yl)sulfonium ylide (3ja). R_f = 0.1, 0.100 g (65% yield); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 4.37 (t, J = 4.8 Hz, 2H), 4.22 (t, J = 4.4 Hz, 2H), 3.66 (t, J = 4.8 Hz, 2H), 3.55 (t, J = 4.8 Hz, 2H),

3.36 (s, 3H), 3.33 (s, 3H), 2.96 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 180.5, 166.4, 164.9, 72.0, 70.5, 70.0, 64.0, 62.8, 58.8, 58.7, 26.1. IR (thin film): 2932, 1734, 1672, 1452, 1387, 1200, 1075 cm^{-1} . HRMS (ESI): m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{12}\text{H}_{21}\text{O}_5\text{S}$: 309.1003; found: 309.1000.



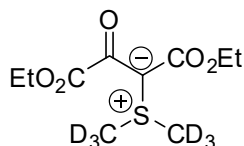
3ka

Dimethyl(1,3,4-trioxo-1,4-bis(2-(thiophen-2-yl)ethoxy)butan-2-yl)sulfonium ylide (3ka). R_f = 0.2, 0.131 g (64% yield); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.01 (brs, 2H), 6.86–6.84 (m, 2H), 6.81 (brs, 1H), 6.77–6.76 (m, 1H), 4.36 (t, J = 7.2 Hz, 2H), 4.23 (t, J = 6.8 Hz, 2H), 3.18 (t, J = 7.2 Hz, 2H), 3.05 (t, J = 6.8 Hz, 2H), 2.85 (s, 6H); ^{13}C NMR (100MHz, CDCl_3): δ 180.5, 166.2, 164.7, 139.9, 139.4, 126.8, 125.5, 125.4, 123.8, 123.8, 71.6, 65.2, 64.1, 29.3, 28.8, 25.9. IR (thin film): 3094, 3029, 2963, 2929, 1737, 1720, 1389, 1197, 1090 cm^{-1} . HRMS (ESI): m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{18}\text{H}_{21}\text{O}_5\text{S}_3$: 413.0546; found: 413.0535.



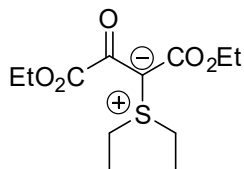
3la

(1,4-Bis((1S,2R,5S)-2-isopropyl-5-methylcyclohexyloxy)-1,3,4-trioxobutan-2-yl)dimethylsulfonium ylide (3la). R_f = 0.1, 0.162 g (69% yield); colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 4.82–4.70 (s, 2H), 2.96 (d, J = 4.0 Hz, 6H), 2.23 (d, J = 12.0 Hz, 1H), 2.02–1.96 (m, 2H), 1.86–1.82 (m, 1H), 1.65 (t, J = 6.8 Hz, 4H), 1.49–1.30 (m, 4H), 1.09–0.94 (m, 4H), 0.89 (d, J = 6.8 Hz, 3H), 0.85 (d, J = 6.8 Hz, 10H), 0.78 (d, J = 7.2 Hz, 4H), 0.71 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 181.2, 166.1, 164.5, 74.8, 73.6, 71.5, 47.1, 47.0, 41.2, 40.6, 34.2, 34.1, 26.1, 25.9, 25.6, 23.3, 23.2, 22.0, 21.9, 20.8, 20.7, 16.2, 16.1. IR (thin film): 2955, 2933, 2869, 1729, 1671, 1385, 1202, 1070 cm^{-1} . HRMS (ESI): m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{26}\text{H}_{45}\text{O}_5\text{S}$: 469.2982; found: 469.2977.



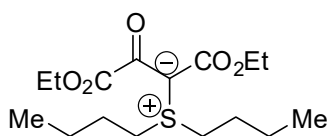
3ab

(1,4-Diethoxy-1,3,4-trioxobutan-2-yl)dimethylsulfonium-D₆ ylide (3ab). $R_f = 0.2$, 0.104 g (82% yield); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 4.26 (q, $J = 7.2$ Hz, 2H), 4.12 (q, $J = 7.2$ Hz, 2H), 1.32 (d, $J = 7.2$ Hz, 3H), 1.21 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 180.8, 166.5, 160.0, 72.0, 61.1, 60.0, 25.6 (q, $J = 21.1$ Hz), 14.2, 13.9. IR (thin film): 2983, 2936, 1709, 1677, 1381, 1202, 1081 cm^{-1} . HRMS (ESI): m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{D}_6\text{O}_5\text{S}$: 255.1168; found: 255.1166.



3ac

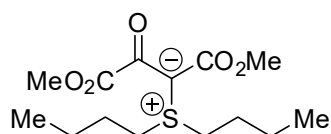
1-(1,4-Diethoxy-1,3,4-trioxobutan-2-yl)tetrahydro-1H-thiophenium ylide (3ac). $R_f = 0.3$, 0.088 g (63% yield); white solid; mp 64–65 °C. ^1H NMR (400 MHz, CDCl_3): δ 4.29 (q, $J = 7.2$ Hz, 2H), 4.15 (d, $J = 7.2$ Hz, 2H), 3.58–3.53 (m, 2H), 3.26–3.21 (m, 2H), 2.71–2.67 (m, 2H), 2.03–1.98 (m, 2H), 1.34 (t, $J = 7.2$ Hz, 3H), 1.23 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 180.2, 166.9, 165.3, 72.6, 61.1, 60.0, 41.4, 28.7, 14.3, 13.9. IR (thin film): 2944, 1733, 1667, 1373, 1193, 1090, 1066 cm^{-1} . HRMS (ESI): m/z ($\text{M} + \text{H}$) $^+$ calcd for $\text{C}_{12}\text{H}_{19}\text{O}_5\text{S}$: 275.0948; found: 275.0943.



3ad

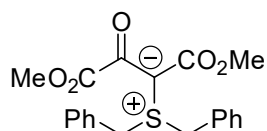
Dibutyl(1,4-diethoxy-1,3,4-trioxobutan-2-yl)sulfonium ylide (3ad). $R_f = 0.2$, 0.087 g (53% yield); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 4.25 (q, $J = 14.4$ Hz, 2H), 4.10 (d, $J = 14.0$ Hz, 2H), 3.78–3.71 (m, 2H), 2.98–2.91 (m, 2H), 1.65–1.56 (m, 4H), 1.46–1.34 (m, 4H), 1.30 (t, $J = 7.2$ Hz, 3H), 1.19 (t, $J = 7.2$ Hz, 3H), 0.89 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 181.5, 166.6, 165.9, 67.4, 60.9, 59.6, 39.5, 26.4, 21.3, 14.2, 13.8, 13.3. IR (thin film): 2962, 2737, 1738, 1668, 1375, 1279, 1198,

1075 cm^{-1} . HRMS (ESI): m/z ($M + H$)⁺ calcd for $\text{C}_{16}\text{H}_{29}\text{O}_5\text{S}$: 333.1730; found: 333.1727.



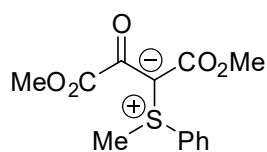
3bd

Dibutyl(1,4-dimethoxy-1,3,4-trioxobutan-2-yl)sulfonium ylide (3bd).^[3] 0.115 g (76% yield); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 3.81 (s, 3H), 3.80–3.75 (m, 2H), 3.64 (s, 3H), 3.00–2.93 (m, 2H), 1.67–1.59 (m, 4H), 1.47–1.38 (m, 4H), 0.93 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 181.3, 166.9, 166.5, 67.1, 51.9, 51.0, 39.5, 26.5, 21.3, 13.3.



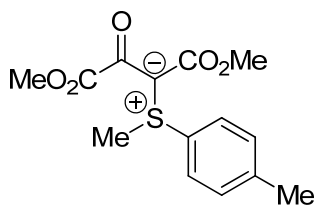
3be

Dibenzyl(1,4-dimethoxy-1,3,4-trioxobutan-2-yl)sulfonium ylide (3be).^[3] 0.143 g (77% yield); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.38–7.30 (m, 10H), 4.96 (d, $J = 12.0$ Hz, 2H), 4.51 (d, $J = 8.0$ Hz, 2H), 3.86 (s, 3H), 3.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 181.6, 166.9, 166.3, 130.3, 130.1, 130.1, 129.4, 129.2, 129.1, 128.9, 128.3, 67.8, 57.2, 52.1, 51.0, 44.1.



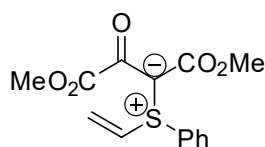
3bf

Benzyl(1,4-dimethoxy-1,3,4-trioxobutan-2-yl)(methyl)sulfonium ylide (3bf). $R_f = 0.1$, 0.087 g (62% yield); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.74–7.72 (m, 2H), 7.54–7.51 (m, 3H), 3.85 (s, 3H), 3.68 (s, 3H), 3.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 180.6, 167.0, 165.7, 131.9, 130.1, 130.0, 127.9, 72.9, 52.1, 51.3, 25.8. IR (thin film): 2955, 2850, 1737, 1679, 1369, 1285, 1078, 805 cm^{-1} . HRMS (ESI): m/z ($M + H$)⁺ calcd for $\text{C}_{13}\text{H}_{15}\text{O}_5\text{S}$: 283.0635; found: 283.0635.



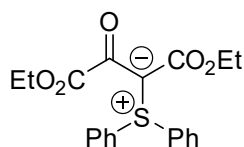
3bg

(1,4-Dimethoxy-1,3,4-trioxobutan-2-yl)(methyl)(p-tolyl)sulfonium ylide (3bg). R_f = 0.2, 0.111 g (74% yield); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 3.84 (s, 3H), 3.68 (s, 3H), 3.35 (s, 3H), 2.39 (s, 3H). IR (thin film): 2956, 2852, 1737, 1679, 1368, 1284, 1078, 807 cm^{-1} . ^{13}C NMR (100 MHz, CDCl_3): δ 180.5, 167.0, 165.8, 142.8, 130.7, 128.0, 126.7, 73.5, 52.1, 51.3, 25.8, 21.3. HRMS (ESI): m/z ($M + \text{H}$) $^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{NaO}_5\text{S}$: 319.0611; found: 319.0590.



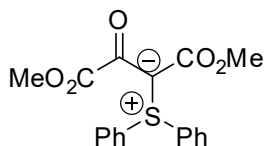
3bh

(1,4-Dimethoxy-1,3,4-trioxobutan-2-yl)(phenyl)(vinyl)sulfonium ylide (3bh). R_f = 0.2, 0.094 g (61% yield); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.63–7.61 (m, 2H), 7.53–7.51 (m, 3H), 7.41 (dd, J = 16.8 Hz, 8.8 Hz, 1H), 6.33 (dd, J = 16.8 Hz, 1.2 Hz, 1H), 6.22 (dd, J = 9.2 Hz, 1.2 Hz, 1H), 3.86 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 179.9, 166.9, 165.6, 132.0, 131.6, 130.1, 129.1, 127.3, 125.8, 73.6, 52.1, 51.4. IR (thin film): 2956, 2852, 1739, 1682, 1575, 1367, 1077, 765 cm^{-1} . HRMS (ESI): m/z ($M + \text{H}$) $^+$ calcd for $\text{C}_{14}\text{H}_{15}\text{O}_5\text{S}$: 295.0635; found: 295.0658.



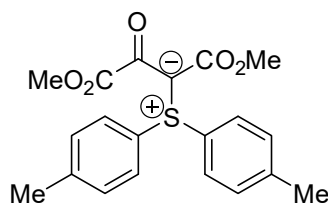
3ai

(1,4-Diethoxy-1,3,4-trioxobutan-2-yl)diphenylsulfonium ylide (3ai). R_f = 0.3, 0.118 g (64% yield); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.68 (d, J = 7.2 Hz, 4H), 7.56–7.48 (m, 6H), 4.34 (q, J = 7.2 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 180.3, 166.8, 165.4, 131.9, 129.8, 129.7, 128.3, 73.7, 61.3, 60.2, 14.3, 14.0. IR (thin film): 2982, 2932, 1735, 1676, 1586, 1373, 1069, 748 cm^{-1} . HRMS (ESI): m/z ($M + \text{H}$) $^+$ calcd for $\text{C}_{20}\text{H}_{21}\text{O}_5\text{S}$: 373.1104; found: 373.1117.



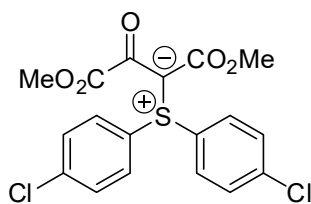
3bi

(1,4-Dimethoxy-1,3,4-trioxobutan-2-yl)diphenylsulfonium ylide (3bi).^[3] 0.118 g (68% yield); yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 7.6 Hz, 4H), 7.55–7.48 (m, 6H), 3.84 (s, 3H), 3.68 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 180.0, 167.0, 165.9, 131.9, 129.8, 129.7, 128.2, 73.3, 52.1, 51.3.



3bj

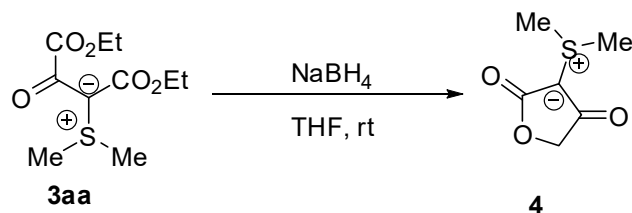
(1,4-Dimethoxy-1,3,4-trioxobutan-2-yl)di-p-tolylsulfonium ylide (3bj). *R*_f = 0.3, 0.122 g (65% yield); yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.56 (d, *J* = 8.4 Hz, 4H), 7.30 (d, *J* = 8.4 Hz, 4H), 3.84 (s, 3H), 3.68 (s, 3H), 2.41 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 180.0, 167.2, 166.0, 142.7, 130.5, 129.6, 125.0, 74.0, 52.0, 51.3, 21.4. IR (thin film): 2921, 1734, 1662, 1577, 1367, 1076, 865 cm⁻¹. HRMS (ESI): *m/z* (*M* + *H*)⁺ calcd for C₂₀H₂₀NaO₅S: 395.0924; found: 395.0917.



3bk

Bis(4-chlorophenyl)(1,4-dimethoxy-1,3,4-trioxobutan-2-yl)sulfonium ylide (3bk). *R*_f = 0.3, 0.137 g (66% yield); yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, *J* = 8.4 Hz, 4H), 7.43 (d, *J* = 8.4 Hz, 4H), 3.78 (s, 3H), 3.63 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 180.0, 166.7, 165.5, 139.0, 131.0, 130.3, 126.2, 72.7, 52.2, 51.6. IR (thin film): 2924, 2853, 1739, 1645, 1365, 1262, 1087, 806 cm⁻¹. HRMS (ESI): *m/z* (*M* + *H*)⁺ calcd for C₁₈H₁₅Cl₂O₅S: 413.0012; found: 413.0011.

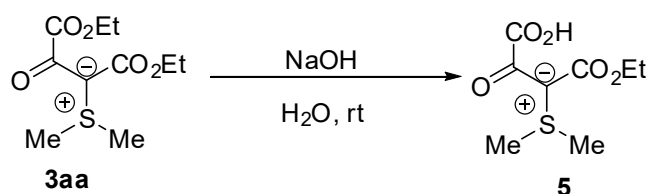
3. Procedure for preparing compound 4



A dry Teflon-sealed flask equipped with a stir bar was charged with sulfonium ylide **3aa** (0.128 g, 0.5 mmol) and NaBH₄ (0.024 g, 1.0 mmol, 2.0 equiv.) under an air atmosphere. THF (5 mL) was added. The reaction vessel was sealed with a Teflon cap and stirred vigorously at room temperature for 12 h until substrate **3aa** disappeared completely (monitored by TLC). At this time, the reaction was quenched with H₂O (10 mL). The water was extracted by EtOAc (3 × 10 mL). The organic layers were combined together, washed with brine (1 × 10 mL), dried with Na₂SO₄ and filtered. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (ethyl acetate/ methanol = 1/4) to give sulfonium ylide **4**.

(2,4-Dioxotetrahydrofuran-3-yl)dimethylsulfonium ylide (4). $R_f = 0.4$, 0.096 g (60% yield); white solid, mp 133–134 °C. ¹H NMR (400 MHz, CDCl₃): δ 4.29 (s, 2H), 2.95 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 191.2, 172.6, 71.5, 65.2, 26.3. IR (thin film): 2958, 1719, 1629, 1425, 1373, 1241, 1303 cm⁻¹. HRMS (ESI): m/z (M + H)⁺ calcd for C₆H₉O₃S: 161.0267; found: 161.0266.

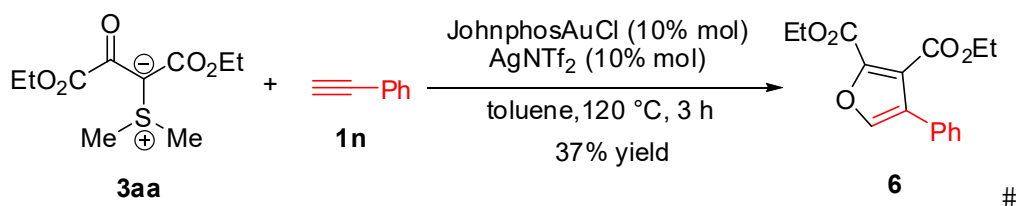
4. Procedure for preparing compound 5



In a 25-mL round-bottom flask was charged with sulfonium ylide **3aa** (0.128g, 0.5 mmol) and NaOH (2.0 mmol, 4.0 equiv.) under an air atmosphere. H₂O (5 mL) was added. The reaction mixture was stirred vigorously at 30 °C for 15 h. At this time, the reaction was quenched with H₂O (10 mL). The water was extracted by EtOAc (3 × 10 mL). The organic layers were combined together, washed with brine (1 × 10 mL), dried with Na₂SO₄ and filtered. The solvent was removed under reduced pressure and the residue was purified by using medium pressure flash column chromatography (elunets: MeOH) to afford ylide **5**.

1-(Carboxy-3-ethoxy-1,3-dioxopropan-2-yl)dimethylsulfonium ylide (5). $R_f = 0.1$, 0.110 g (100% yield); white solid, mp 91–92 °C. ^1H NMR (400 MHz, CDCl_3): δ 4.17 (q, $J = 13.6$ Hz, 2H), 3.00 (s, 6H), 1.29 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 191.0, 176.3, 167.8, 73.5, 60.8, 26.5, 14.7. IR (thin film): 3367, 2926, 1663, 1580, 1426, 1276, 1071 cm^{-1} . HRMS (ESI): m/z ($M + H$) $^+$ calcd for $\text{C}_8\text{H}_{13}\text{O}_5\text{S}$: 221.0478; found: 221.0485.

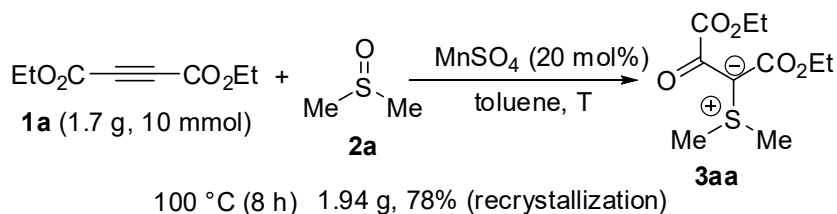
5. Procedure for preparing compound 6



To a dry 10 mL Schlenk tube with a stir bar was added with JohnPhosAuCl (10 mol%, 0.03 mmol, 16 mg) and AgNTf_2 (10 mol%, 0.03 mmol, 12 mg) and toluene (2 mL, 0.1 M) under nitrogen. After stirring at room temperature for 15 min, **3aa** (0.2 mmol, 50 mg) and phenylacetylene **1n** (1 mmol, 5 equiv) was added. When the reaction was complete (TLC analysis), the solvent was evaporated and the residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/20) to afford the furan **6**.

Diethyl 4-phenylfuran-2,3-dicarboxylate (6). $R_f = 0.5$, 0.026 g (37% yield); a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.65 (s, 1H), 7.40–7.35 (m, 5H), 4.42 (q, $J = 7.2$ Hz, 2H), 4.36 (q, $J = 7.2$ Hz, 2H), 1.40 (t, $J = 7.2$ Hz, 3H), 1.31 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.0, 157.7, 142.4, 141.9, 129.7, 128.8, 128.2, 127.5, 124.9, 62.0, 61.6, 14.1, 13.9. HRMS (ESI): m/z ($M + H$) $^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{O}_5$: 289.1071; found: 289.1071.

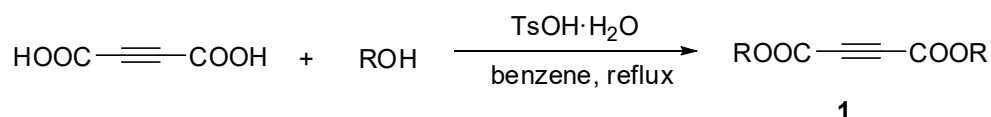
6. Procedure for gram scalable preparations of 3aa



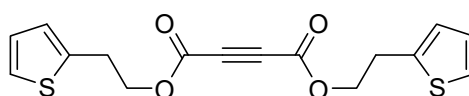
In a 100-mL Teflon-sealed flask was charged with acetylenedicarboxylate **1a** (1.7 g, 10 mmol), sulfoxide **2a** (100 mmol, 10.0 equiv) and MnSO_4 (2 mmol, 20 mol%) under air atmosphere. Toluene (40.0 mL) was added. The flask was sealed with a Teflon cap and stirred vigorously at 100 °C for 8 h until substrate **1a** disappeared

(monitored by TLC). At this time, the reaction was quenched with H₂O (40 mL). The water layer was extracted by EtOAc (3 × 40 mL). The organic layers were combined together, washed with brine (1 × 40 mL), dried with Na₂SO₄ and filtered. The solvent was removed under reduced pressure and the crude solid was recrystallized by MeOH to give sulfonium ylide **3aa** (1.94 g, 78% yield).

7. Procedure for preparing acetylenedicarboxylates **1**

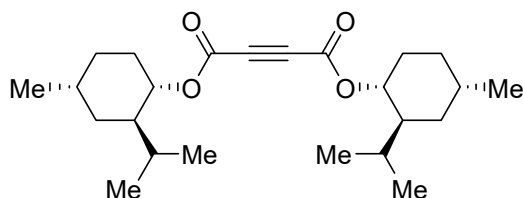


A suspension of acetylenedicarboxylic acid (10.0 mmol), alcohol (22.0 mmol, 2.2 equiv) and TsOH·H₂O (1.0 mmol, 0.1 equiv.) in benzene (20 mL, 2 mL/mmol) was heated under reflux with a Dean–Stark trap in an oil bath maintained at 100 °C. The solids were dissolved within 1 h and formed a clear light-yellow solution. The reaction was monitored until the substrate acetylenedicarboxylic acid disappeared (by TLC). At this time, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1/50) to give the corresponding acetylenedicarboxylate **1**.



1k

Bis(2-(thiophen-2-yl)ethyl) but-2-ynedioate (1k). *R_f* = 0.6, 3.34 g (91% yield); white solid; mp 63–64 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.20 (q, *J* = 5.2 Hz, 2H), 6.98–6.95 (m, 2H), 6.89 (t, *J* = 2.8 Hz, 2H), 4.47 (t, *J* = 6.8 Hz, 4H), 3.24 (t, *J* = 7.2 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 151.5, 138.5, 127.0, 125.9, 124.3, 74.6, 66.8, 28.1. IR (thin film): 3112, 2965, 2930, 2862, 1702, 1388, 1257 cm^{−1}. HRMS (ESI): *m/z* (M + Na)⁺ calcd for C₁₆H₁₄O₄NaS₂: 357.0226, found: 357.0244.



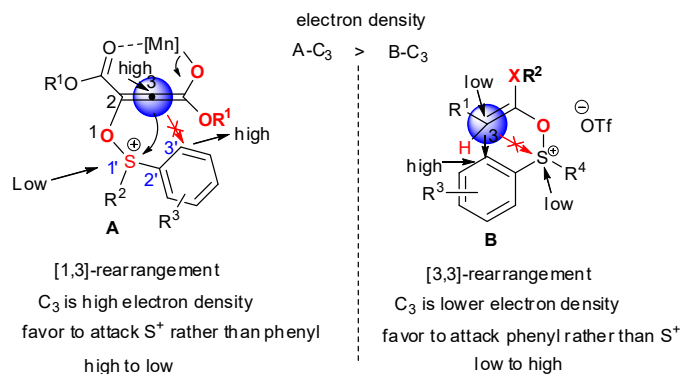
1l

Bis((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) but-2-ynedioate (1l). *R_f* = 0.6, 3.40 g (87% yield); white solid; mp 136–137 °C. ¹H NMR (400 MHz, CDCl₃): δ

4.89–4.80 (m, 2H), 2.05–2.00 (m, 2H), 1.92–1.87 (m, 2H), 1.72–1.67 (m, 4H), 1.49–1.41 (m, 4H), 1.10–1.01 (m, 4H), 0.92 (q, $J = 7.2$ Hz, 13H), 0.86 (d, $J = 3.6$ Hz, 1H), 0.77 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 151.6, 74.9, 46.8, 40.4, 34.0, 31.4, 26.0, 23.2, 21.9, 20.7, 16.1. IR (thin film): 3405, 2963, 2926, 2871, 1712, 1456, 1378, 1258 cm^{-1} . HRMS (ESI): m/z ($\text{M} + \text{Na}$) $^{+}$ calcd for $\text{C}_{24}\text{H}_{38}\text{O}_4\text{Na}$: 413.2662; found: 413.2689.

8. Explanation for 1,3 and 3,3-rearrangement of S-O-vinyl moiety

We think that the factor favors 1,3-rearrangement over 3,3-rearrangement in our system **A** is owing to the substituent electronic effect on the S-O-vinyl moieties. In our system **A**, the Mn-catalyst promoted the enolation of carbonyl groups and the electron density of C3 in system **A** is higher than C3 of S-O-vinyl moiety in system **B** (Scheme 1-A and 1-B) owing to p- π conjugation of the three O-atom. In O-S-phenyl moiety, S^{+} is lower electron density than phenyl group. Therefore, in system **A**, the higher electron density of **A**-C3 is favor to attack the lower electron density of S^{+} center rather than phenyl while in system **B**, the low electron density of **B**-C3 is favor to attack the high electron density of phenyl rather than S^{+} center due to electric matches for bond formation. That is why our system of S-O bond undergoes [1,3]-rearrangement rather than [3,3]-rearrangement.



9. References

- [1] A. Earla, and R. Braslau, *Macromol. Rapid Commun.* **2014**, *35*, 666.
- [2] A. A. Kislukhin, C. J. Higginson, and M. G. Finn, *Org. Lett.* **2011**, *13*, 1832.
- [3] T. J. Chow, U.-K. Tan, and S.-M. Peng, *Synth. Commun.* **1988**, *18*, 519.

10. X-ray structure of compound **3aa**

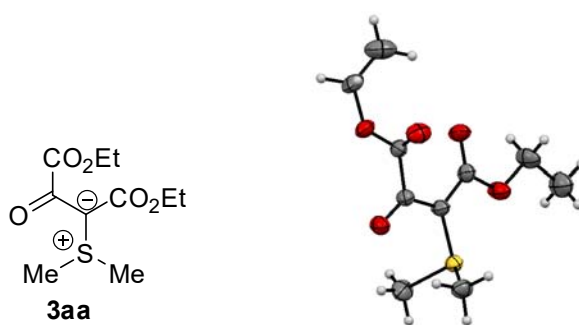
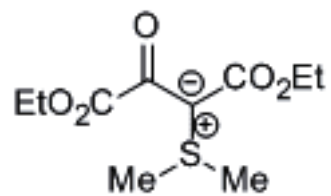
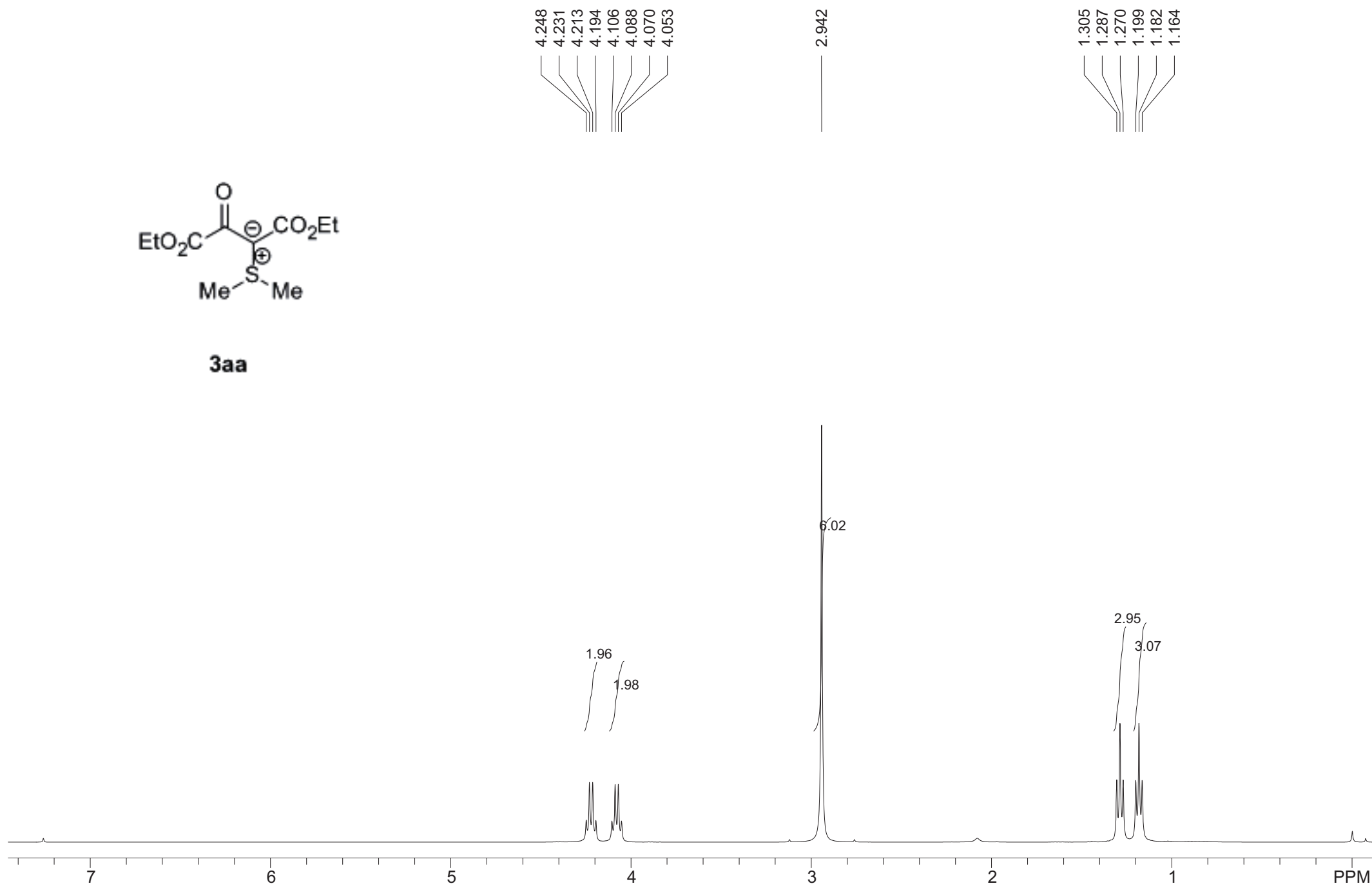


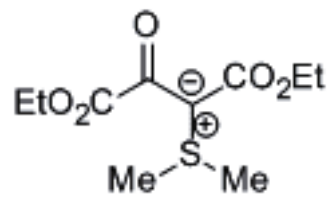
Figure S1: ORTEP diagram of **3aa** at 50% ellipsoid probability

11. NMR spectra of compounds **3**, **4**, **5**, **6**, and **1k-1l**

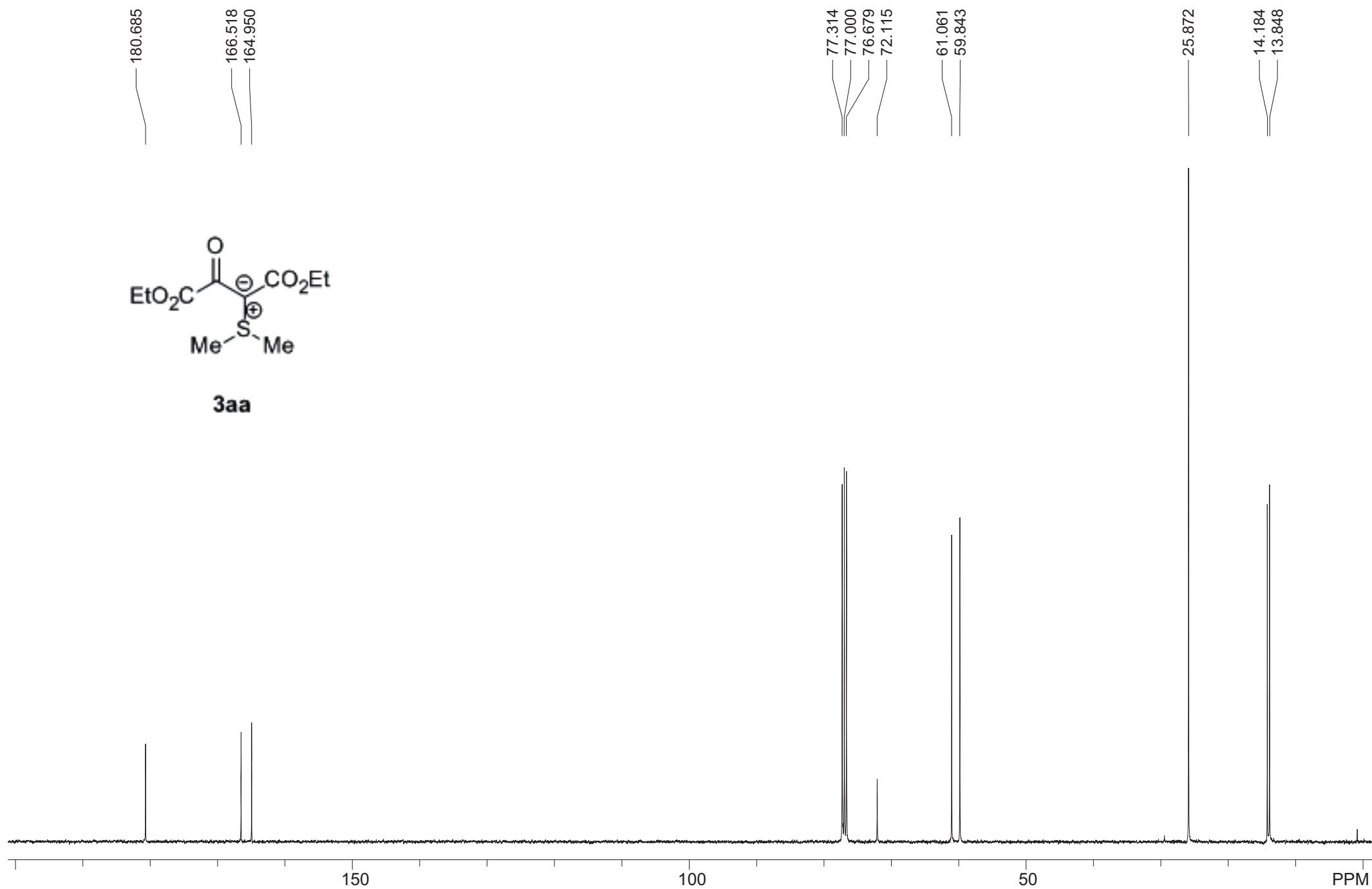


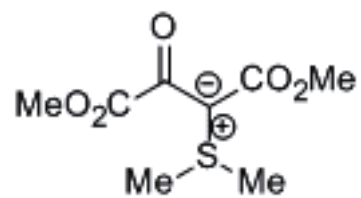
3aa



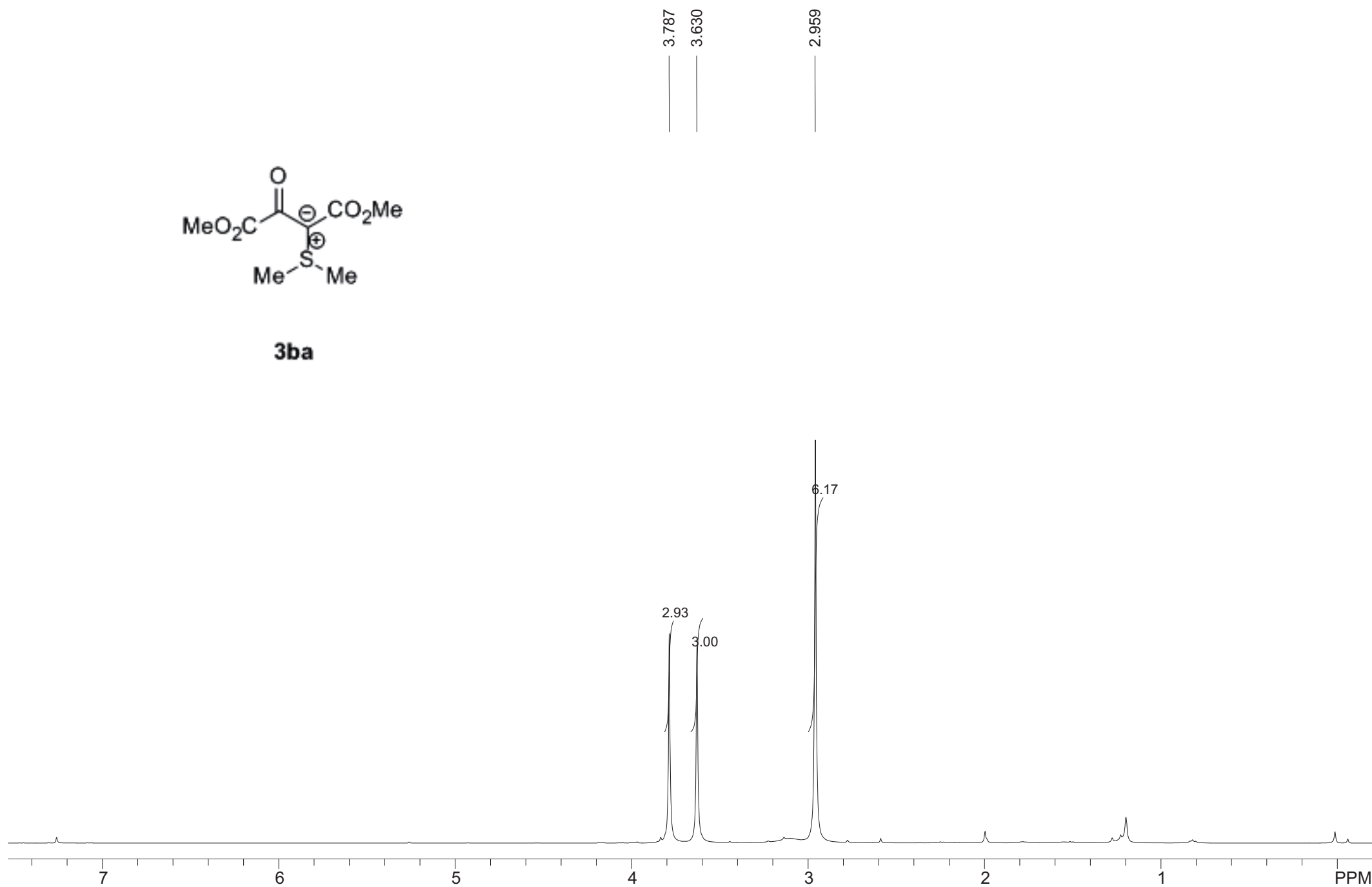


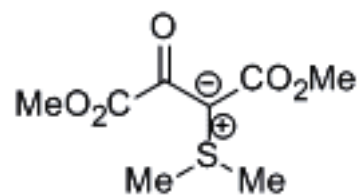
3aa



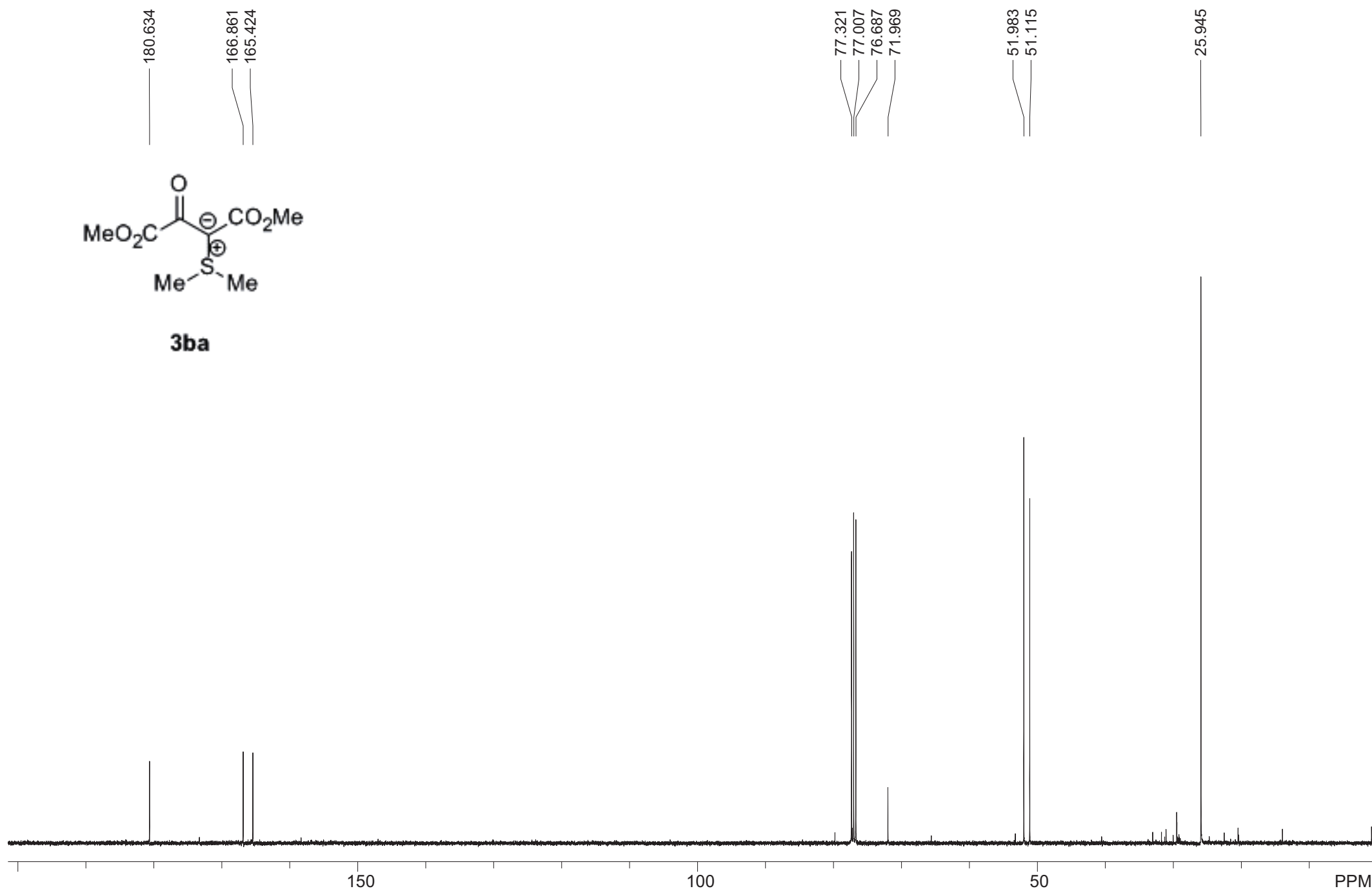


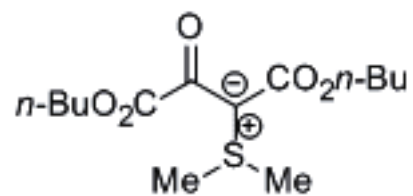
3ba



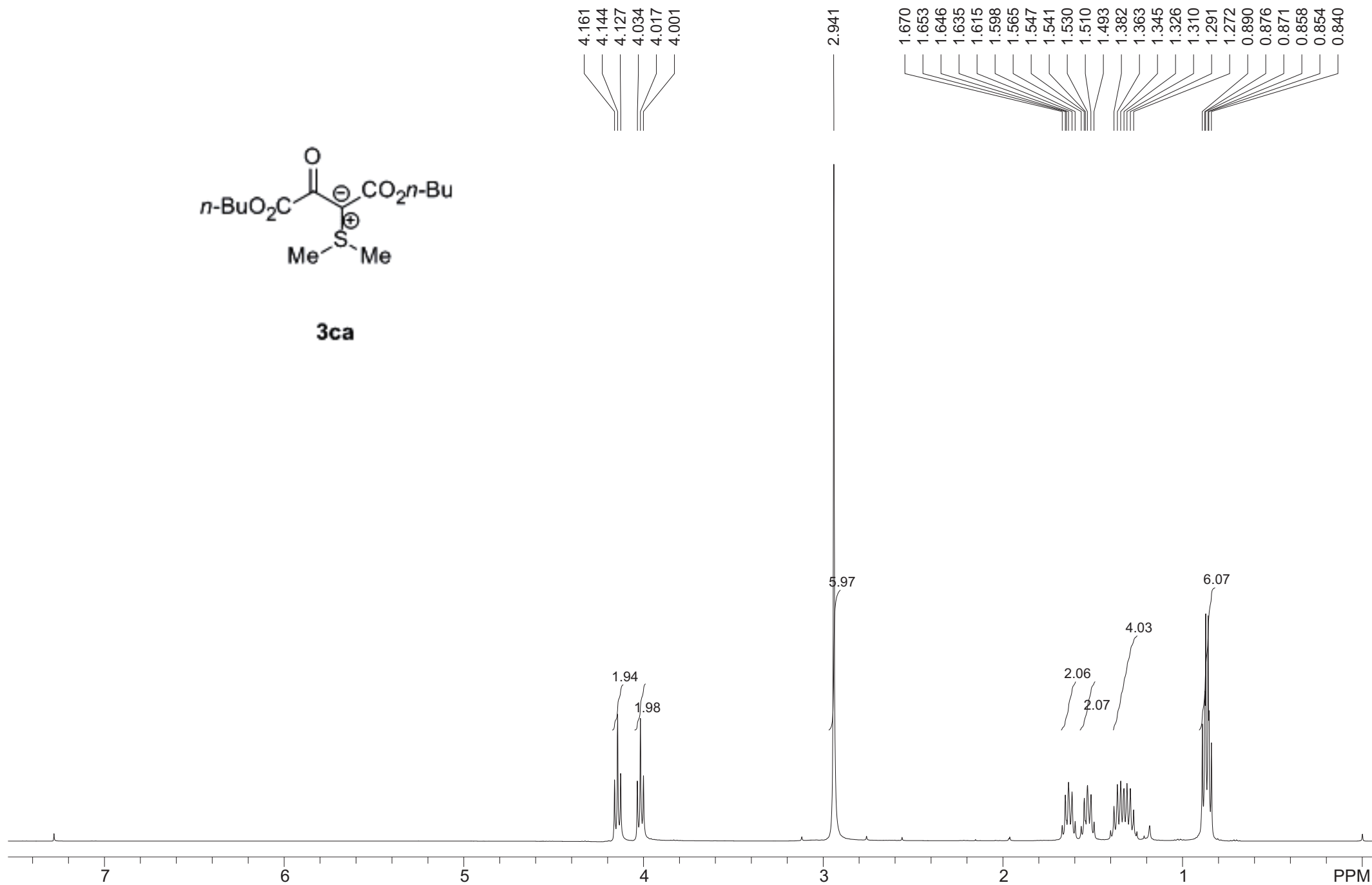


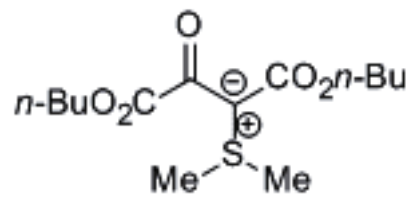
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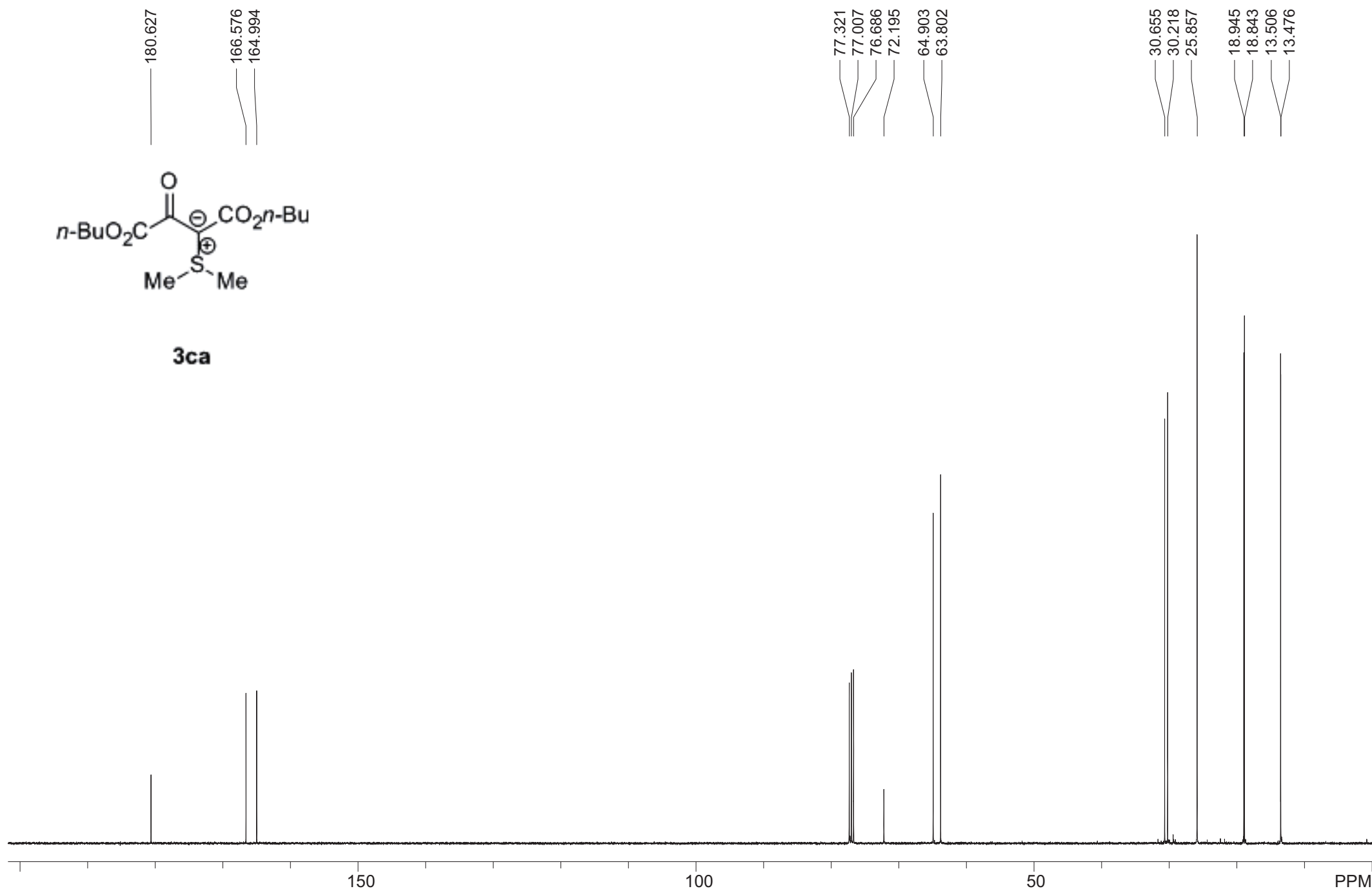


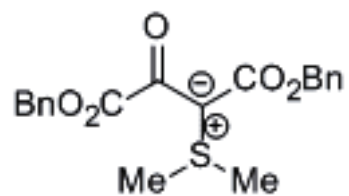
3ca





3ca



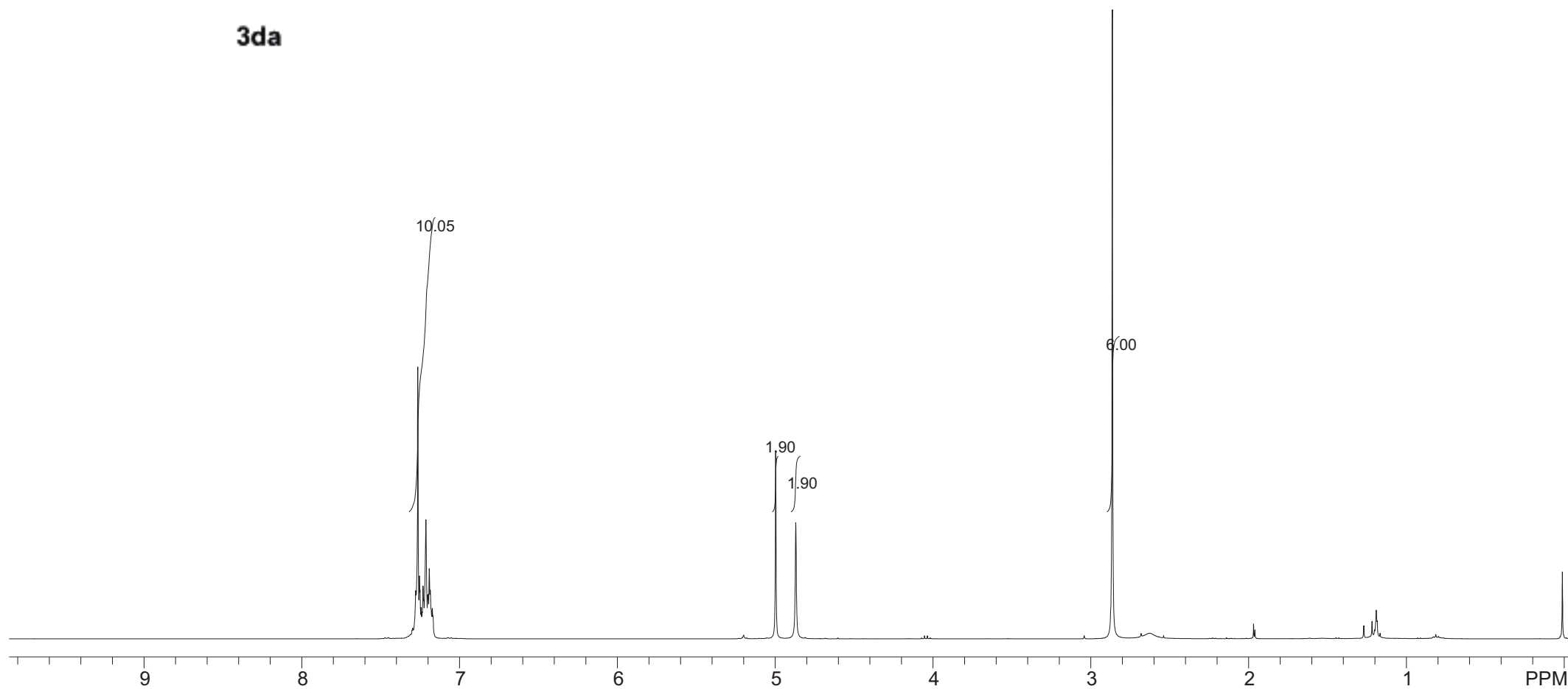


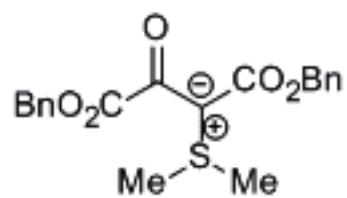
3da

7.267
7.264
7.253
7.243
7.239
7.232
7.226
7.220
7.215
7.202
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7.187
7.181
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7.157

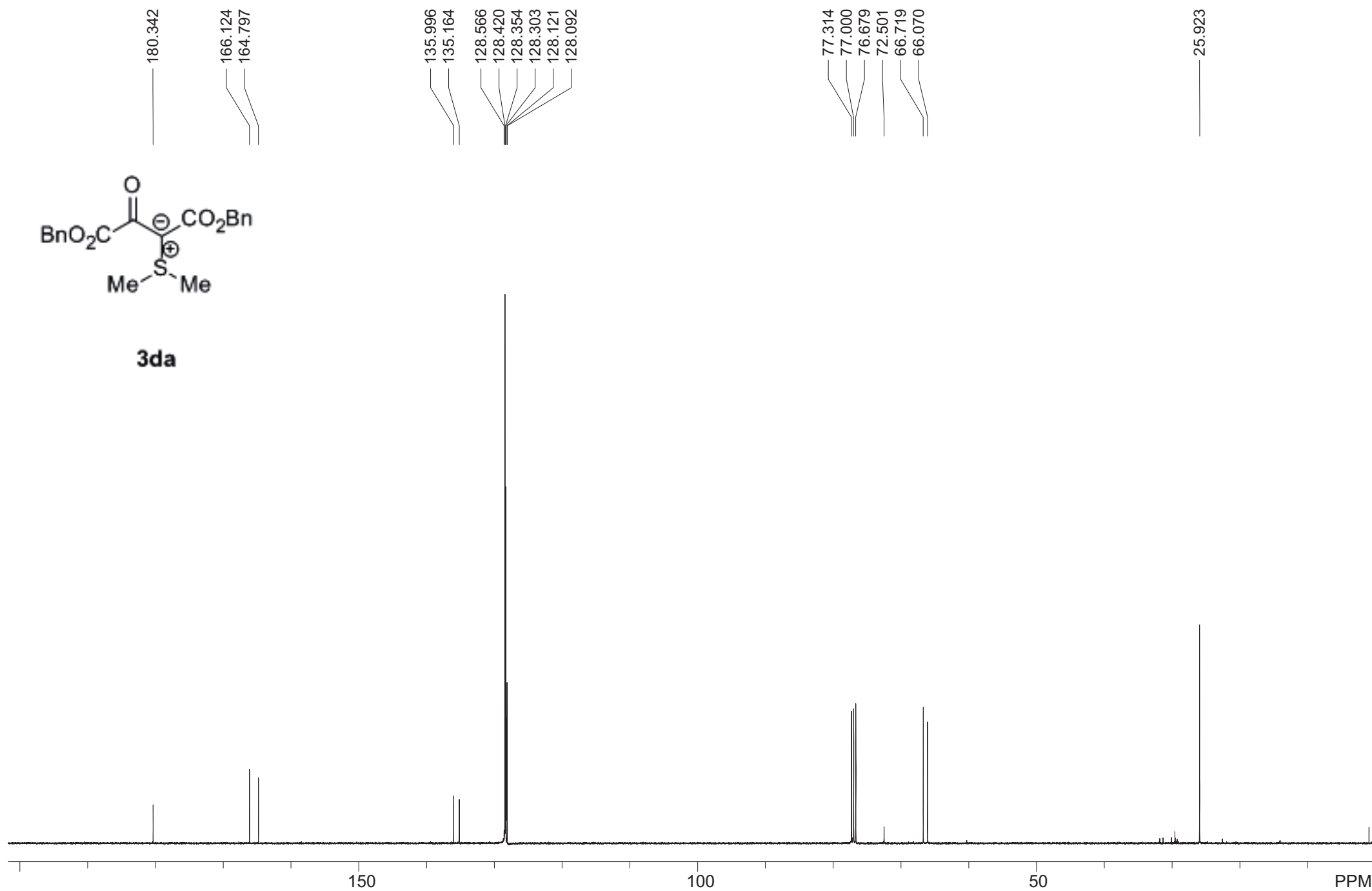
4.986
4.859

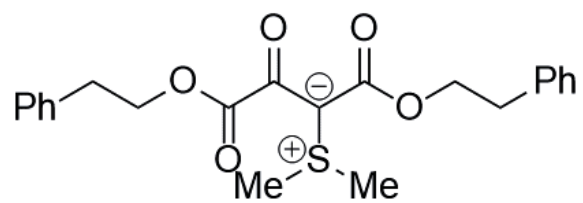
2.852



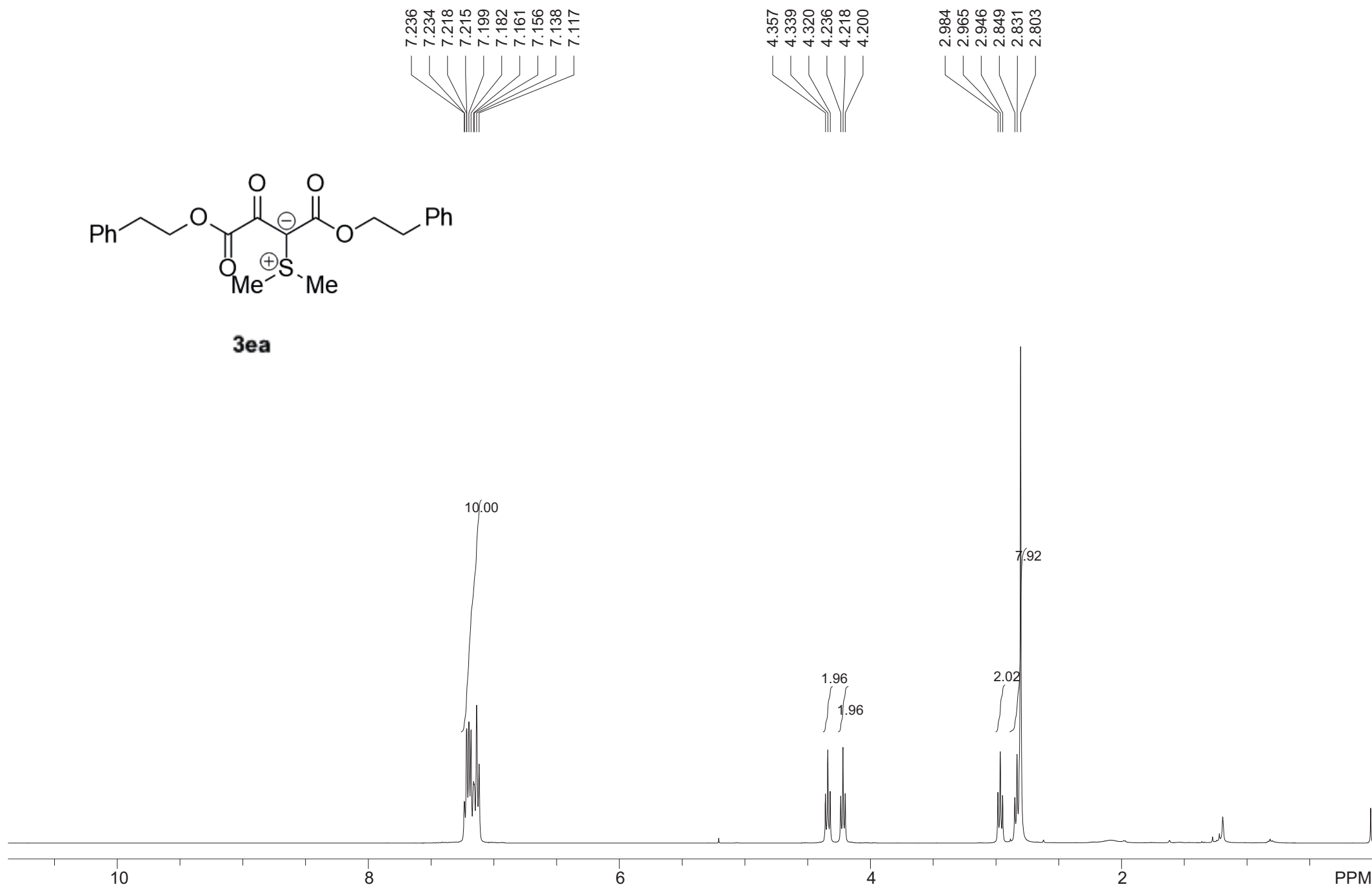


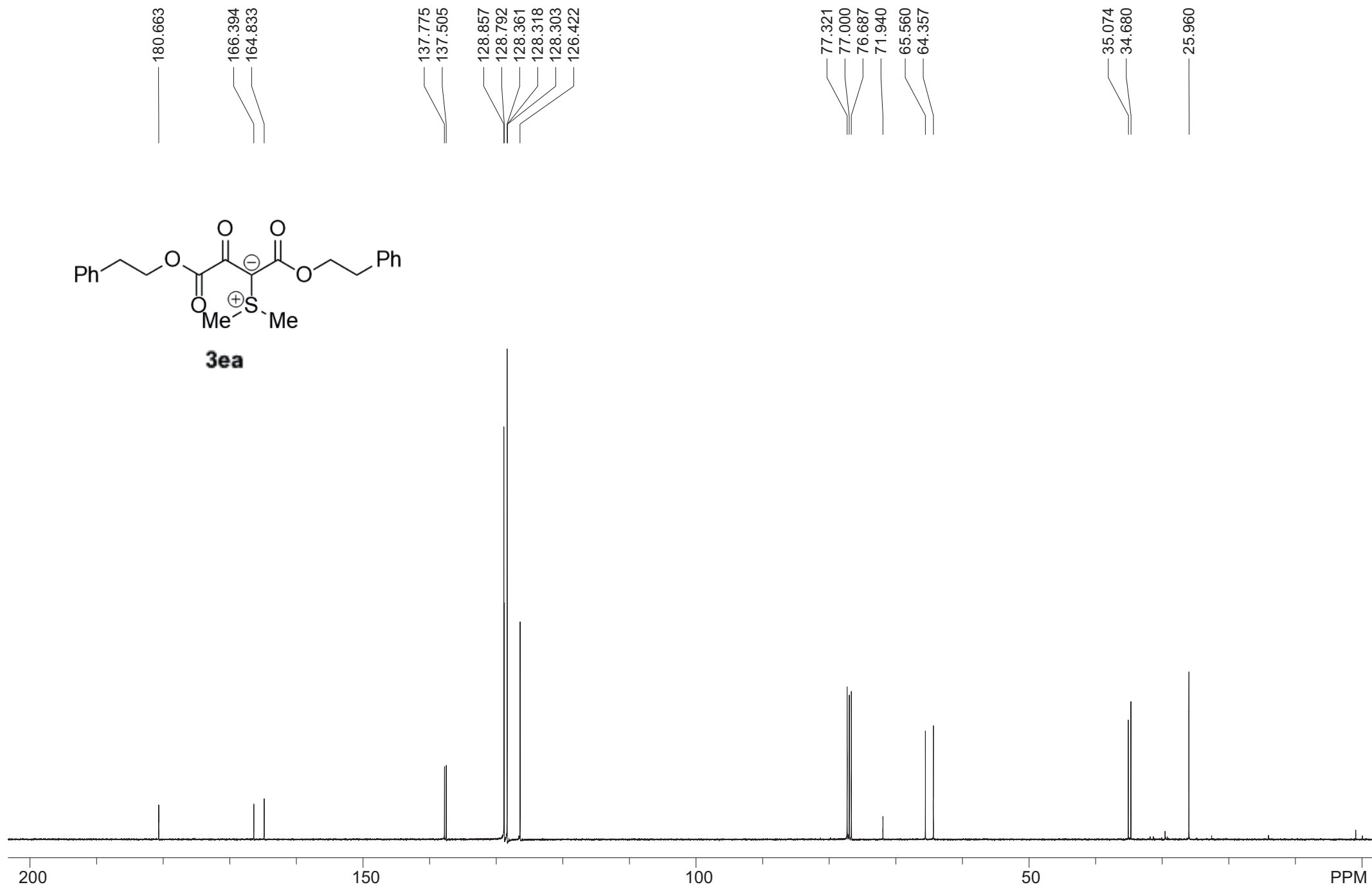
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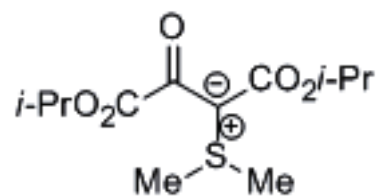




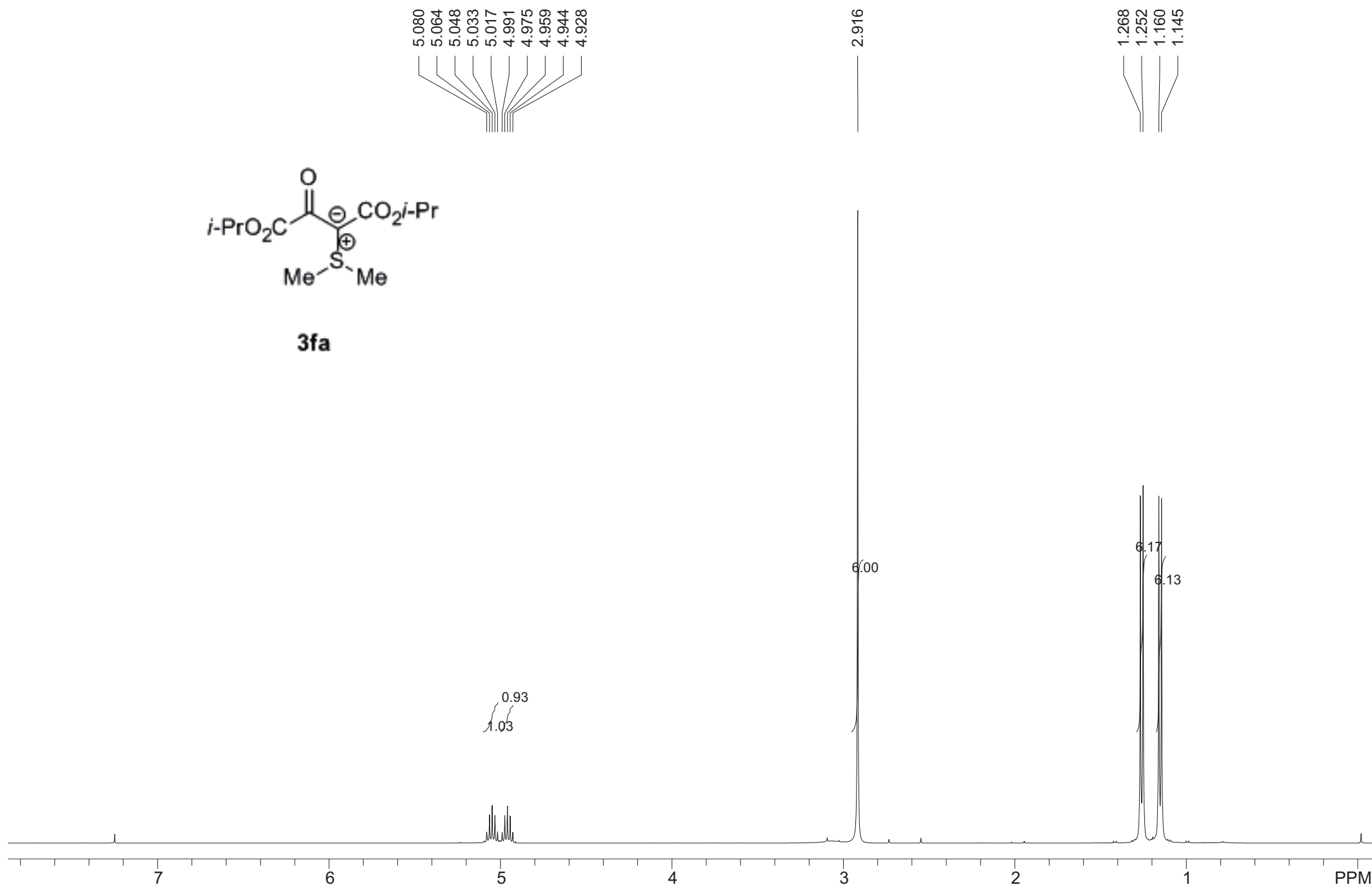
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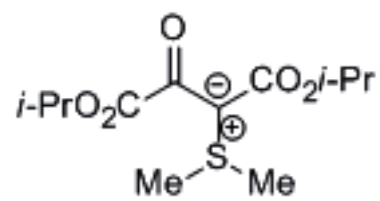




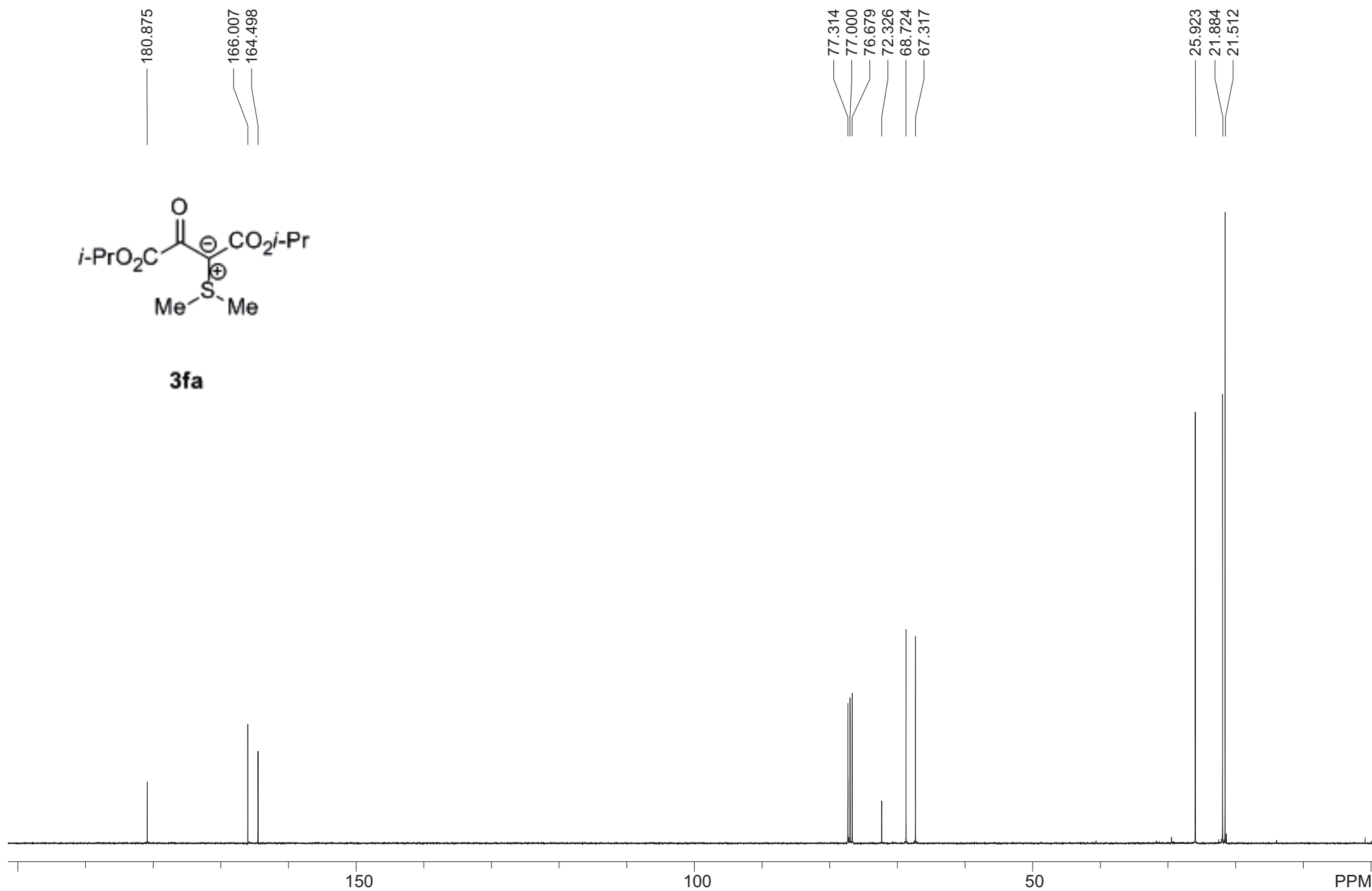


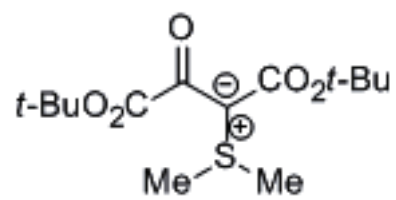
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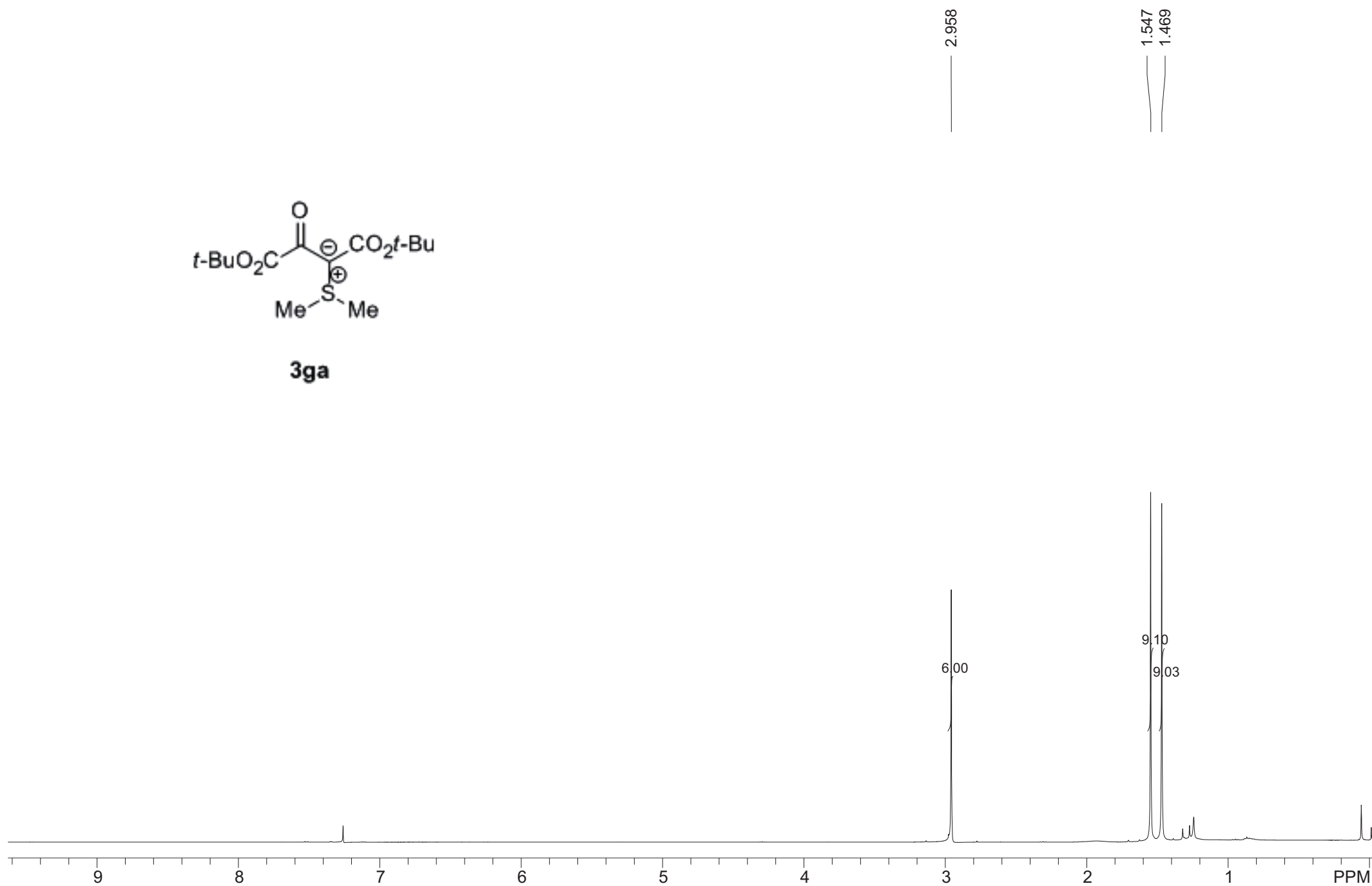


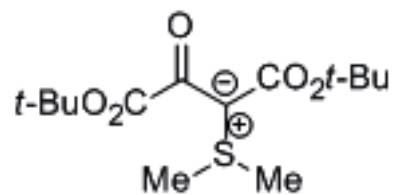
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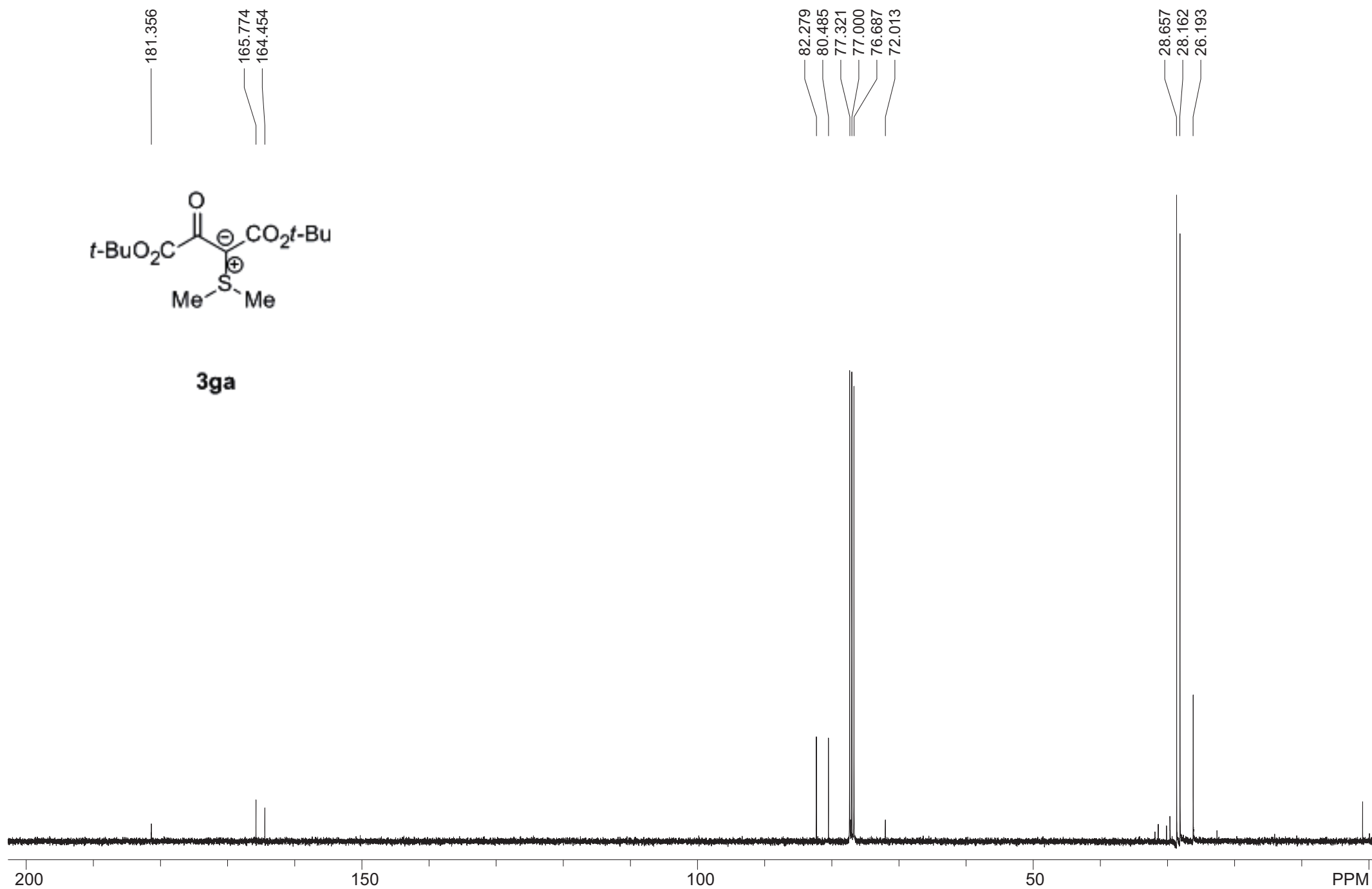


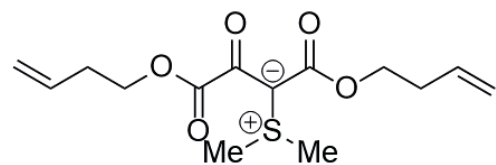
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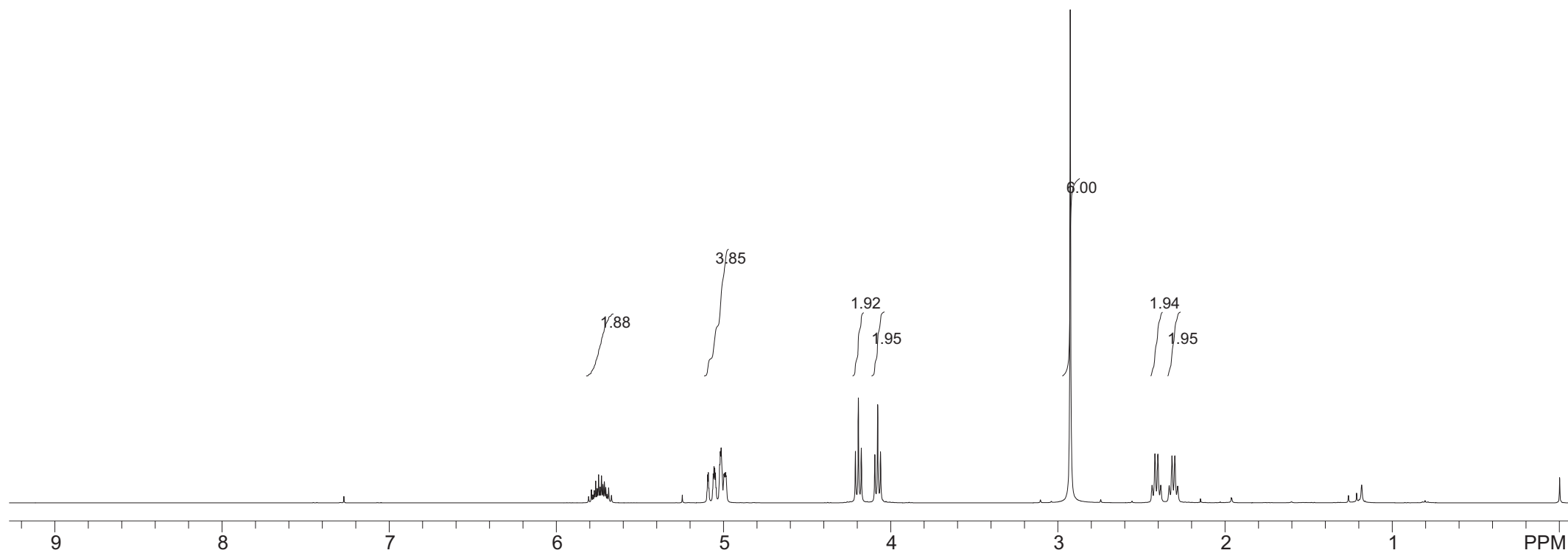
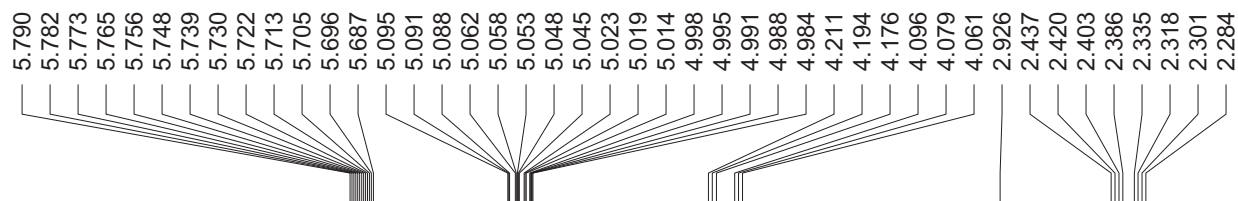


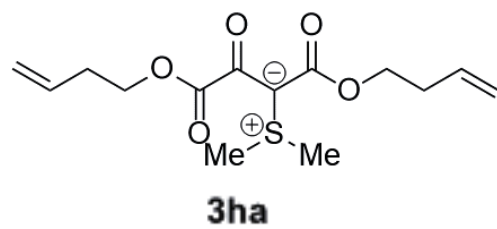
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3ha





180.503

166.357
164.804

134.020
133.516

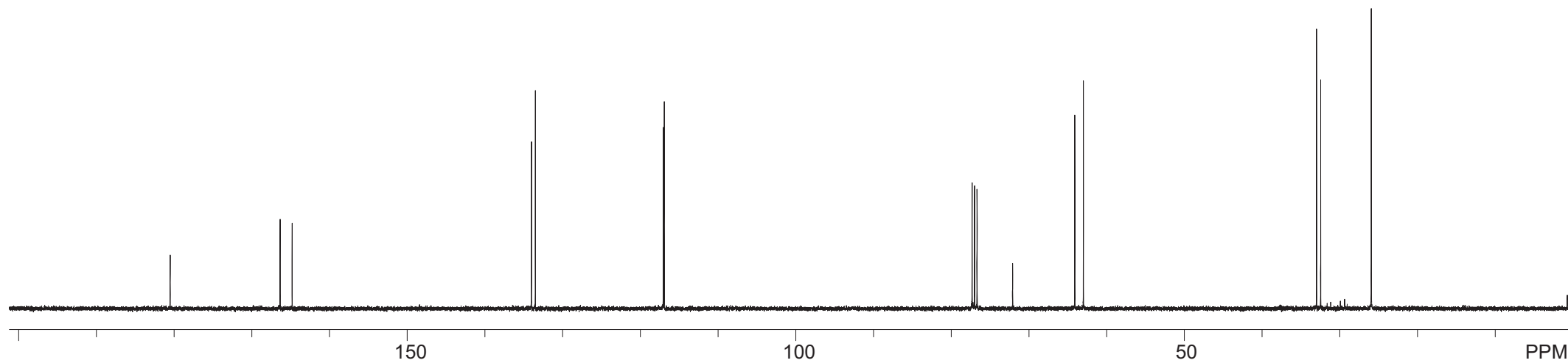
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116.928

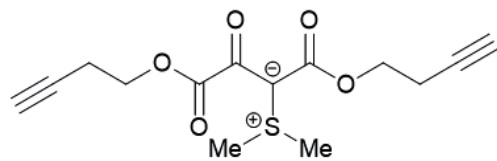
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72.107

64.109
63.000

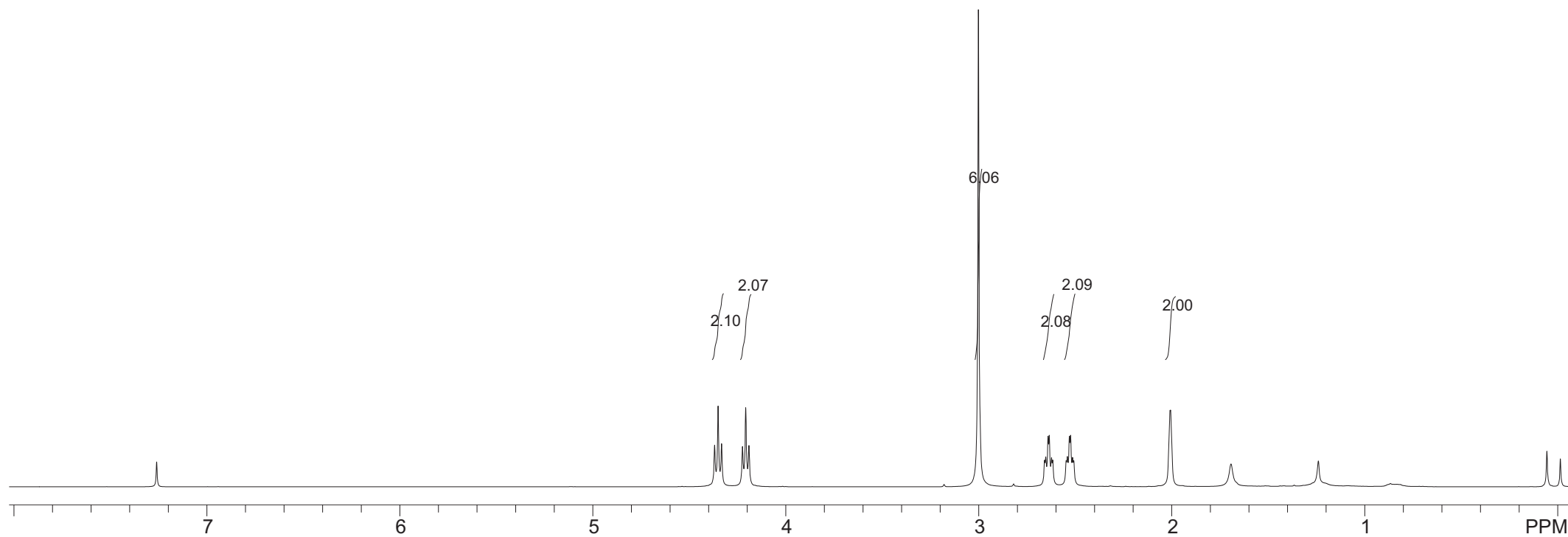
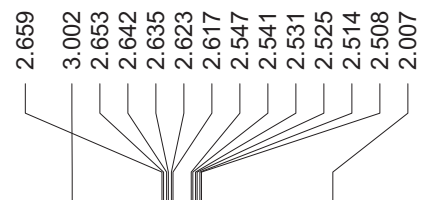
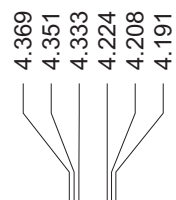
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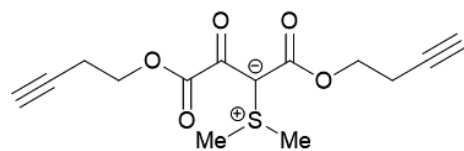
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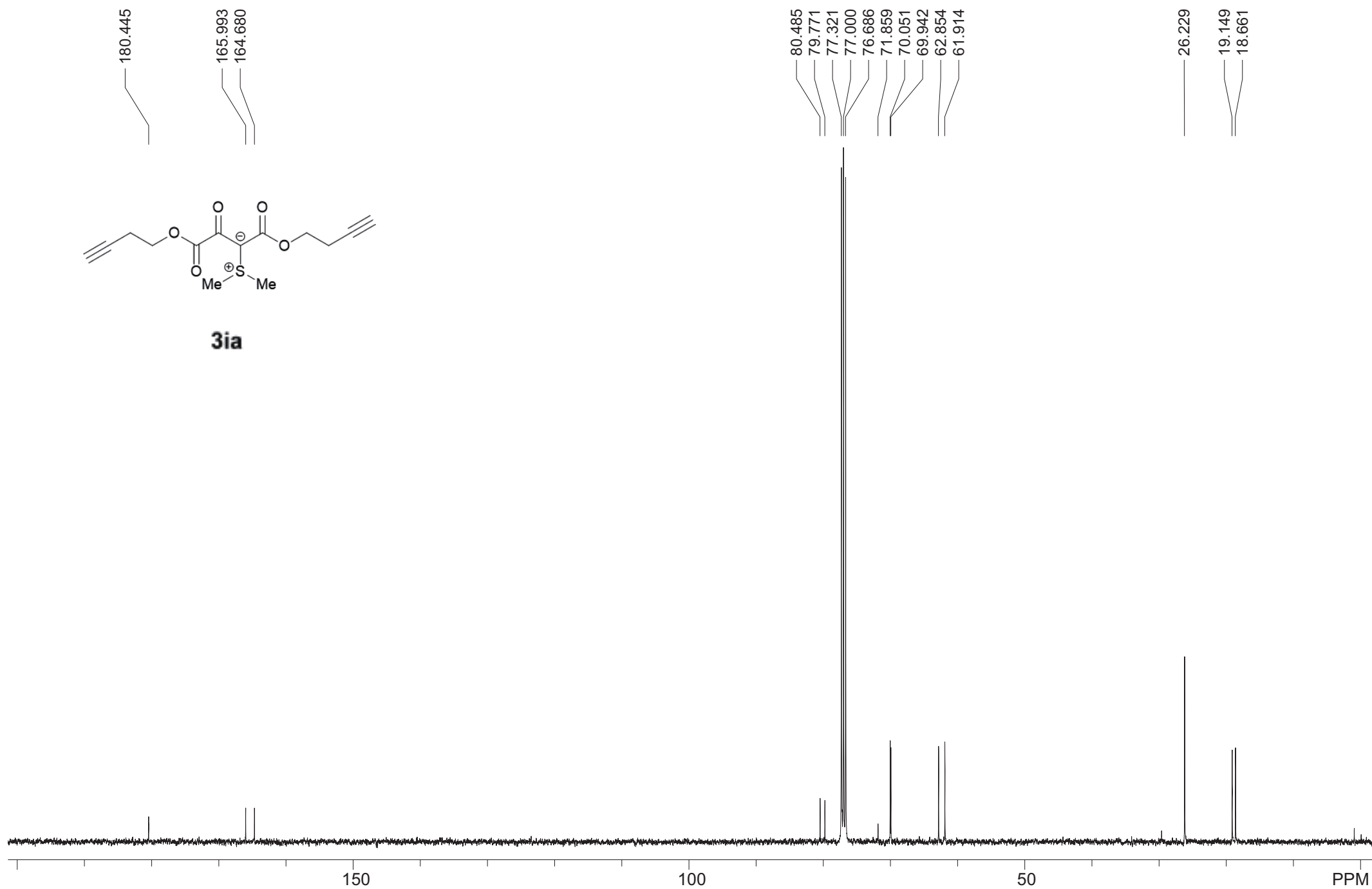


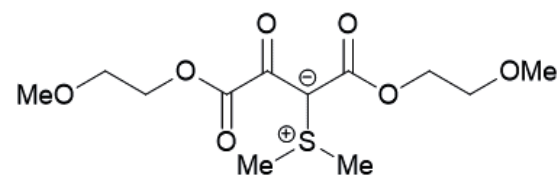
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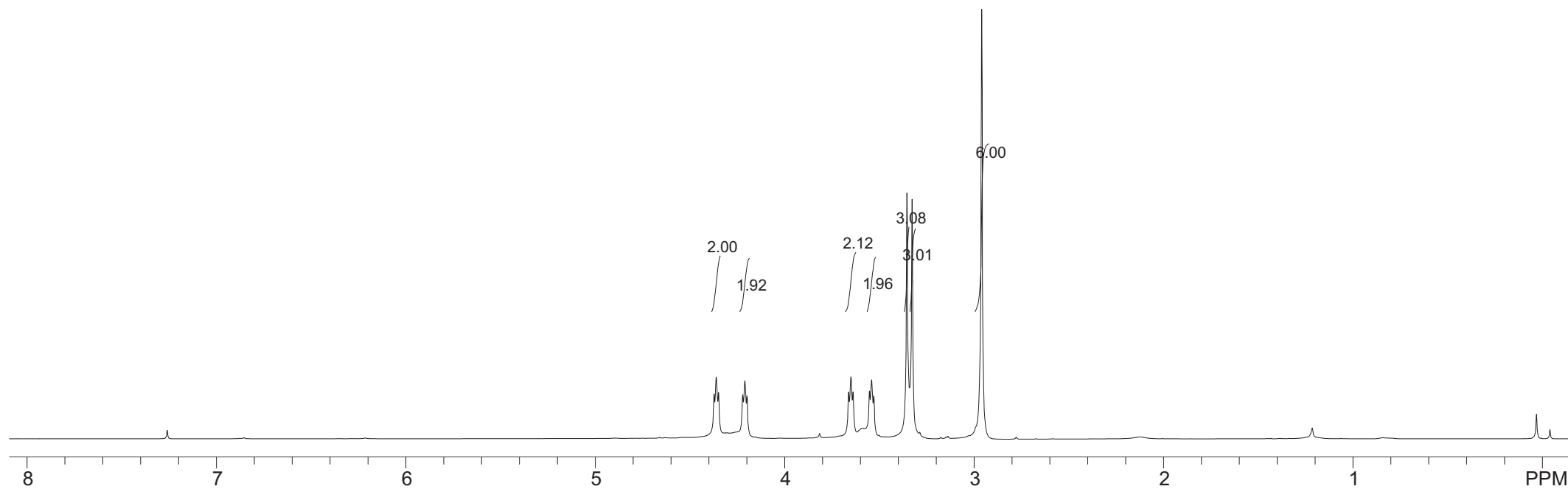
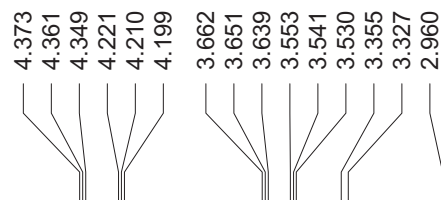


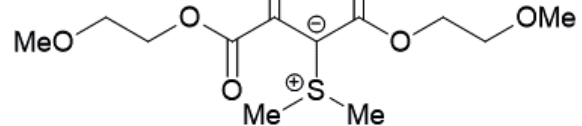
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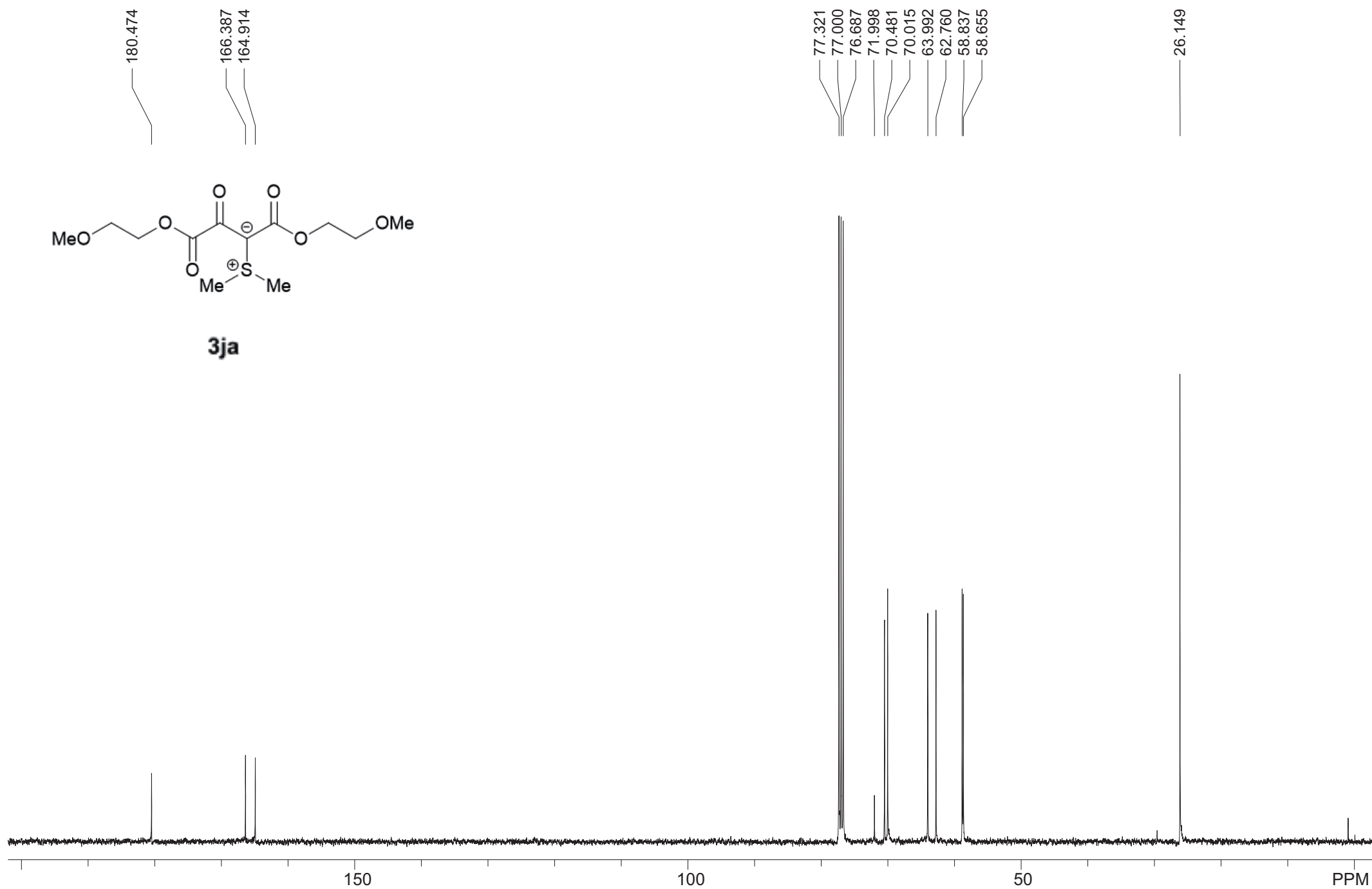


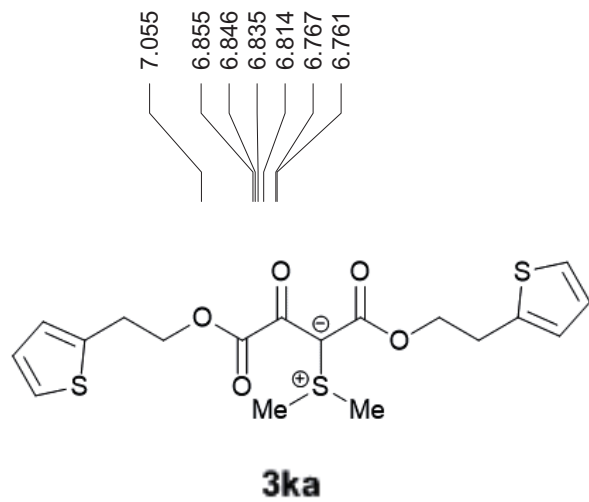
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3ja

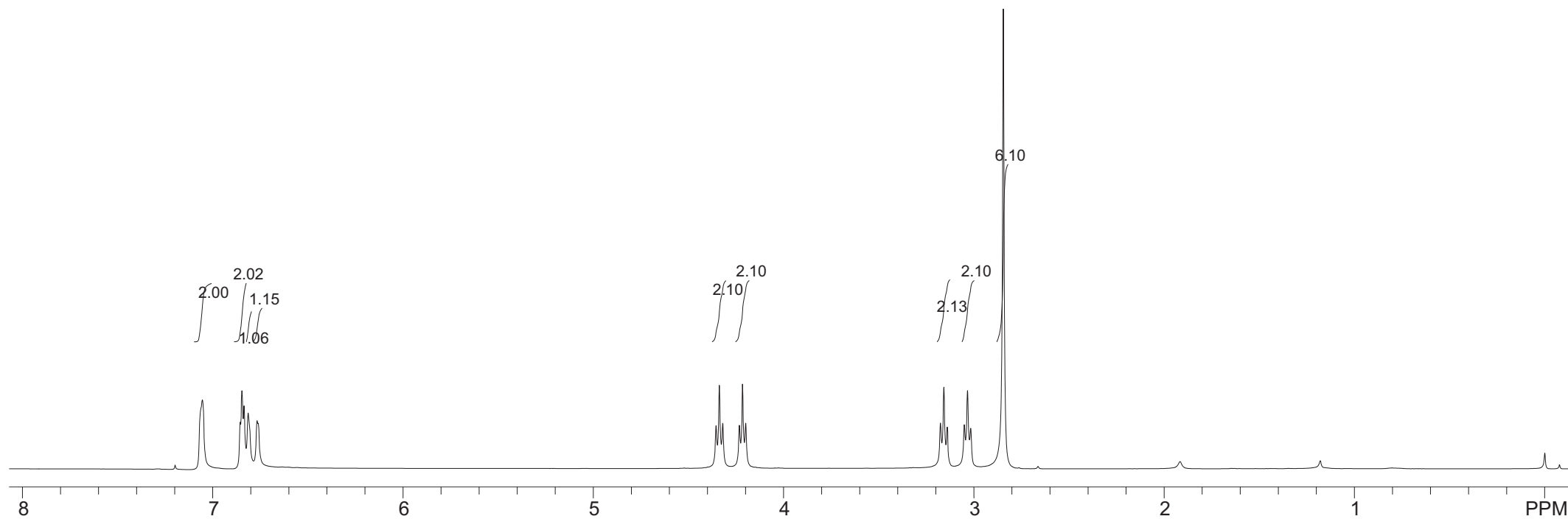


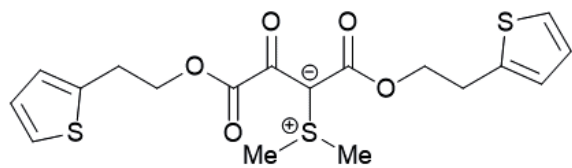


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6.767
6.761

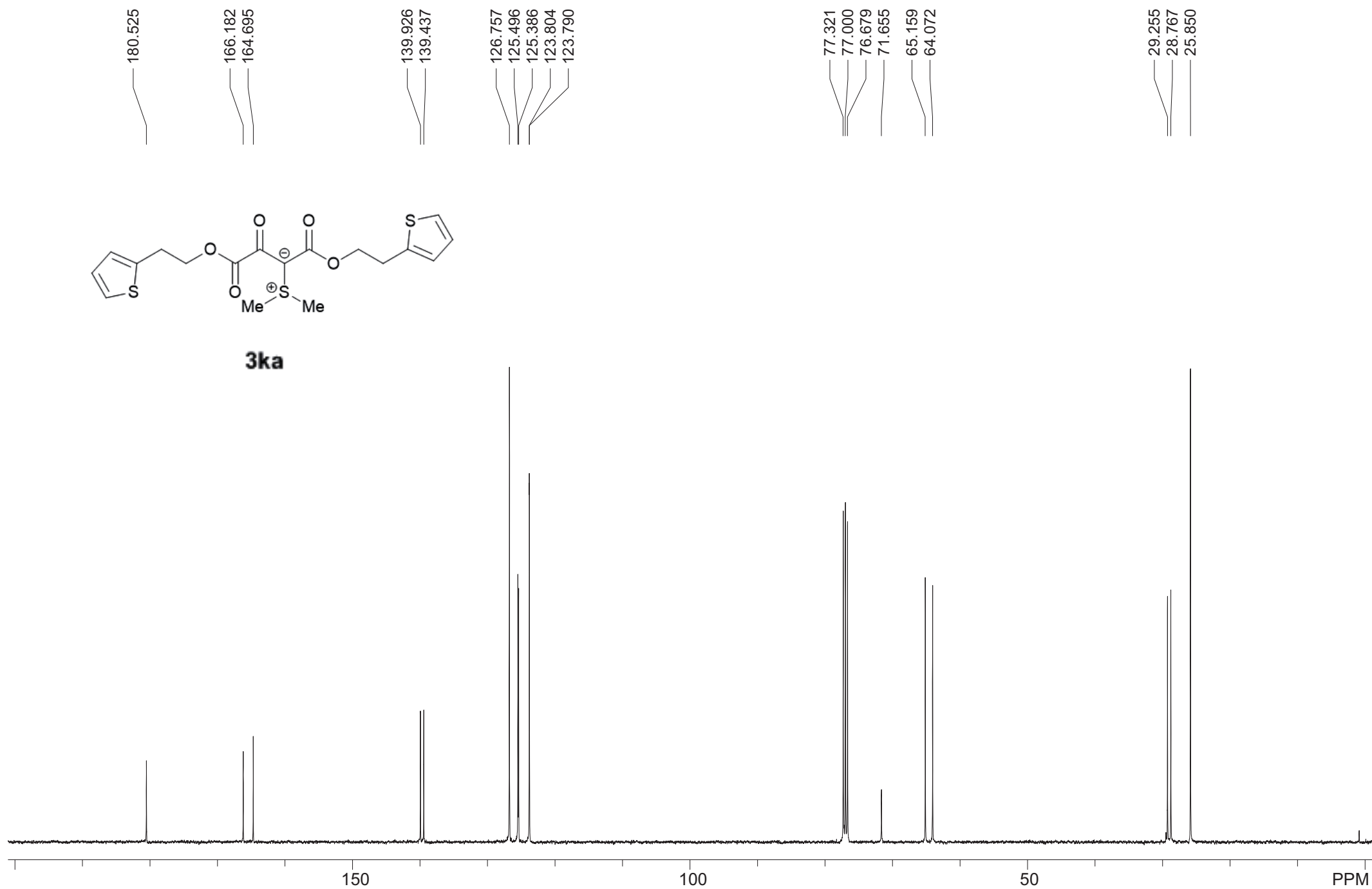
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4.199

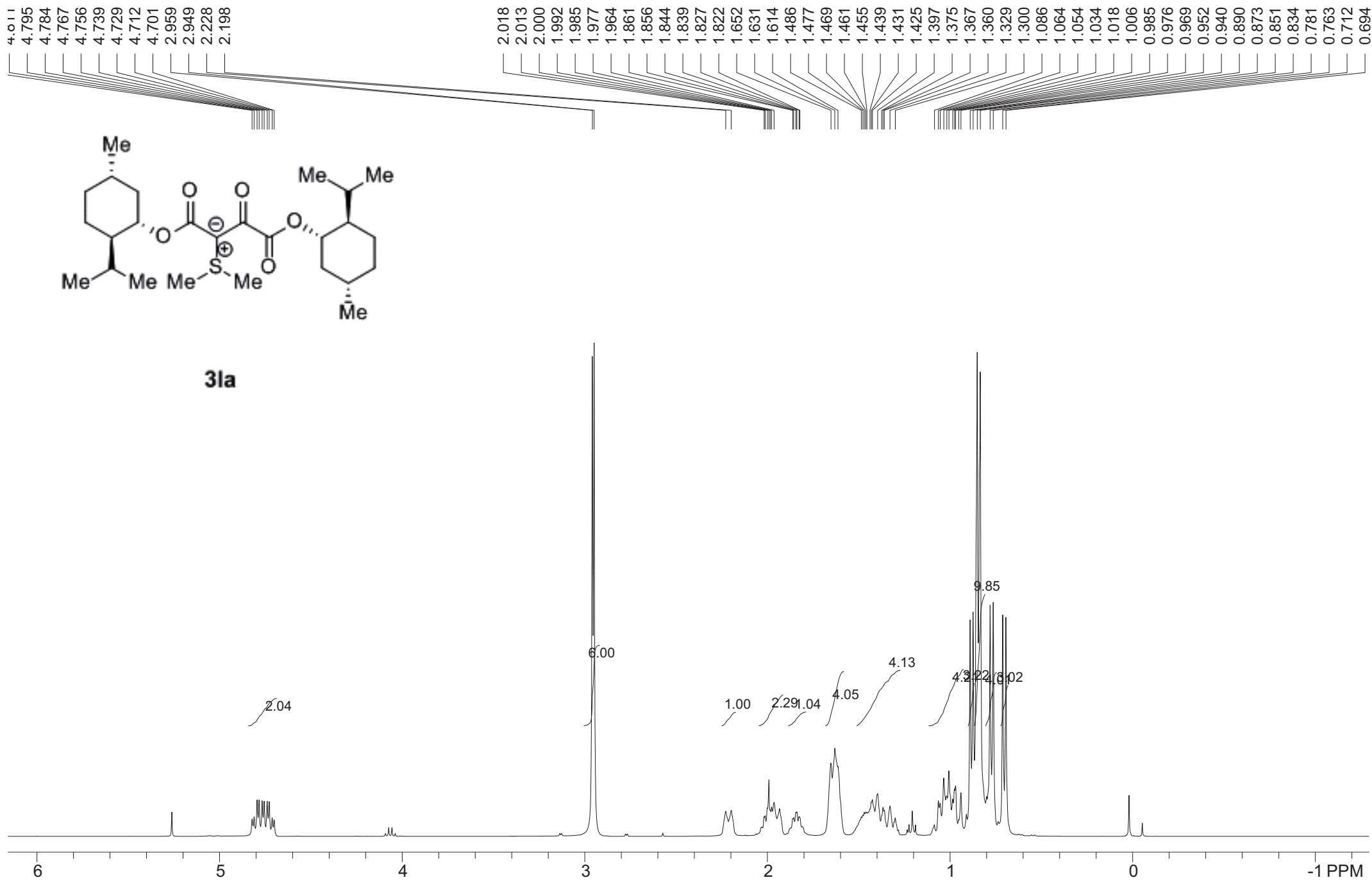
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2.845

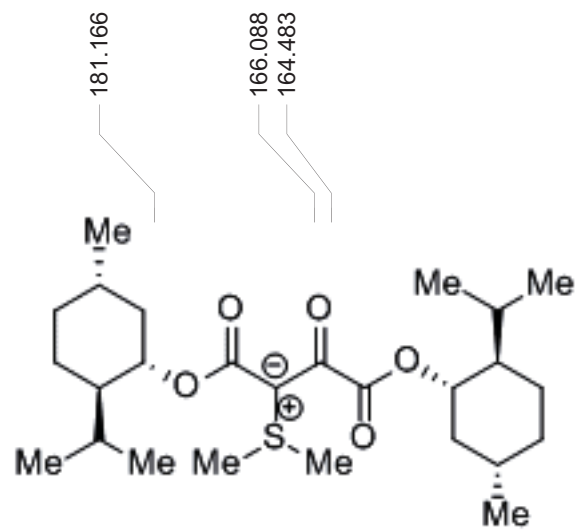




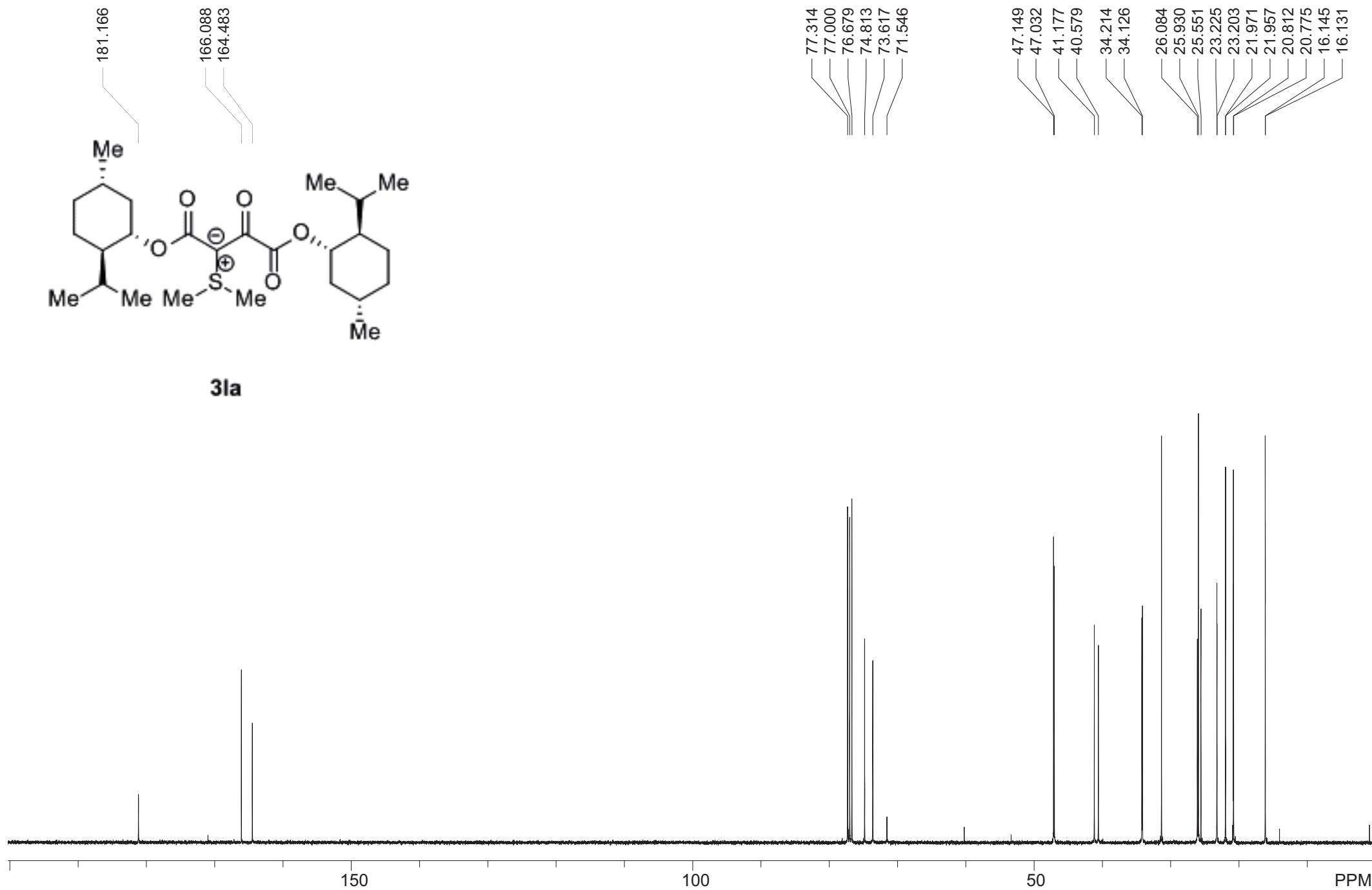
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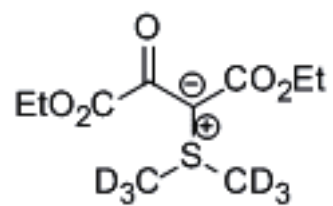




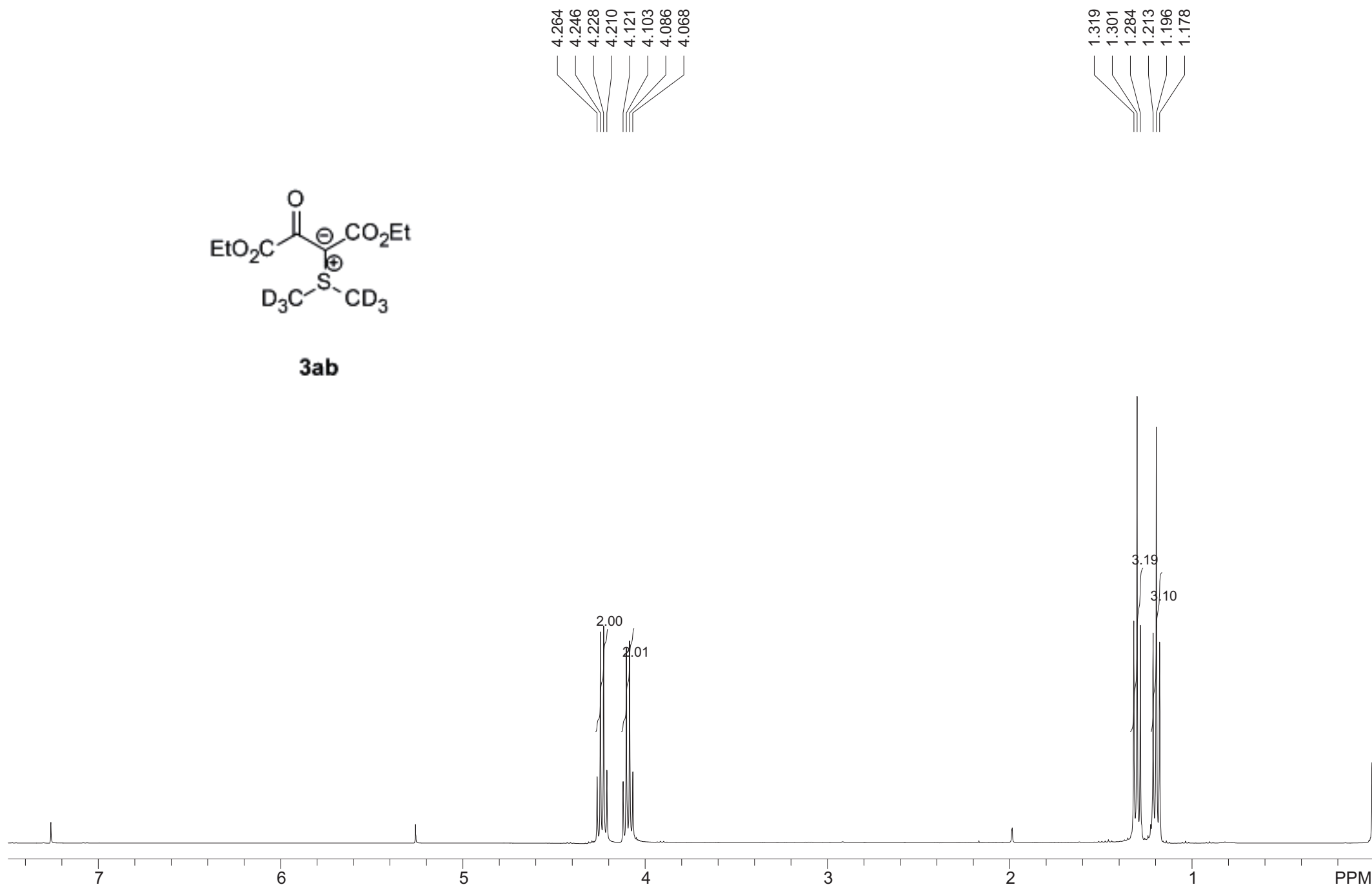


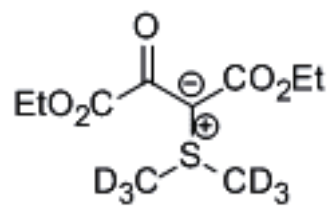
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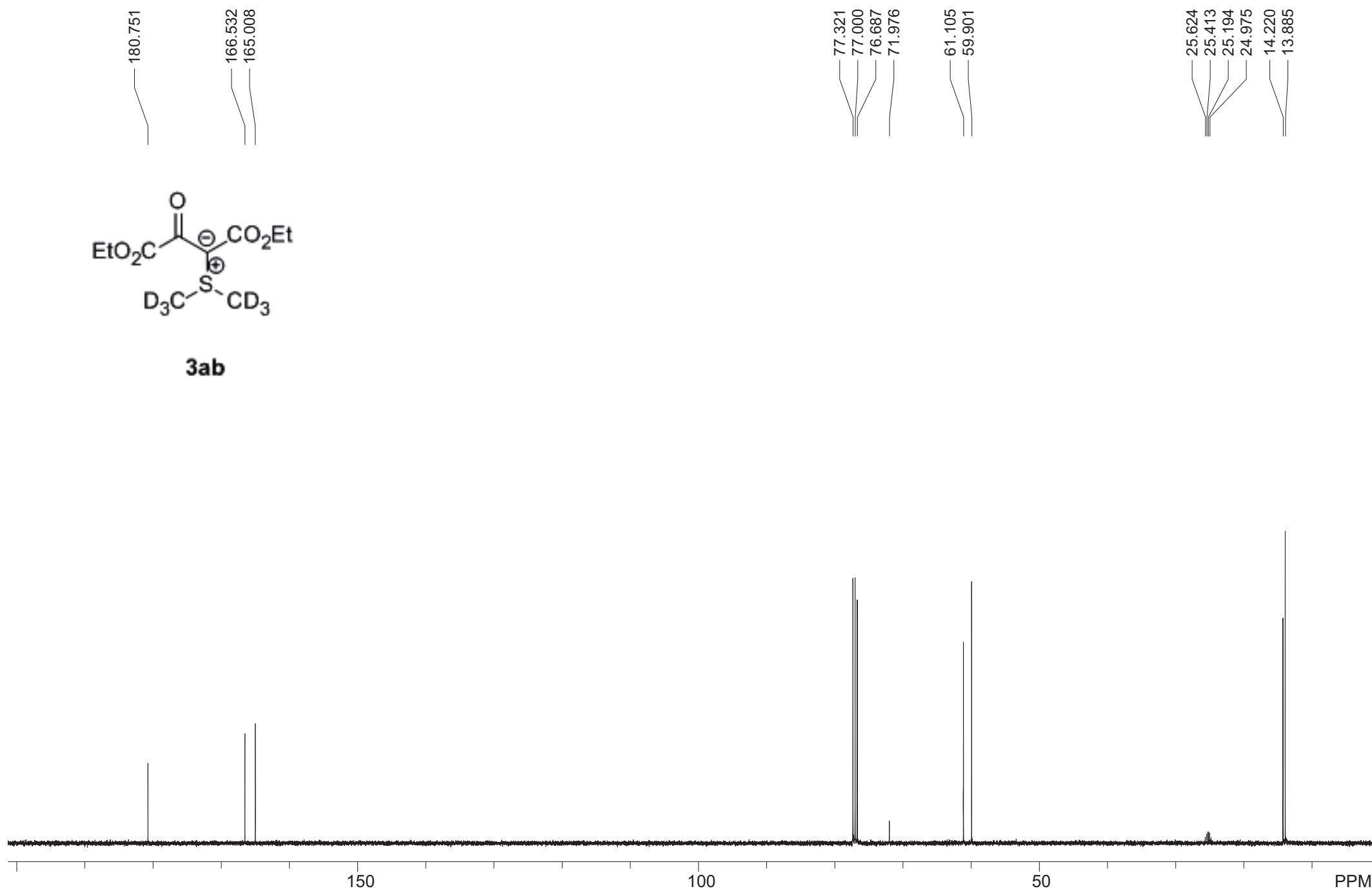


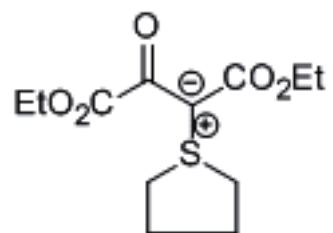
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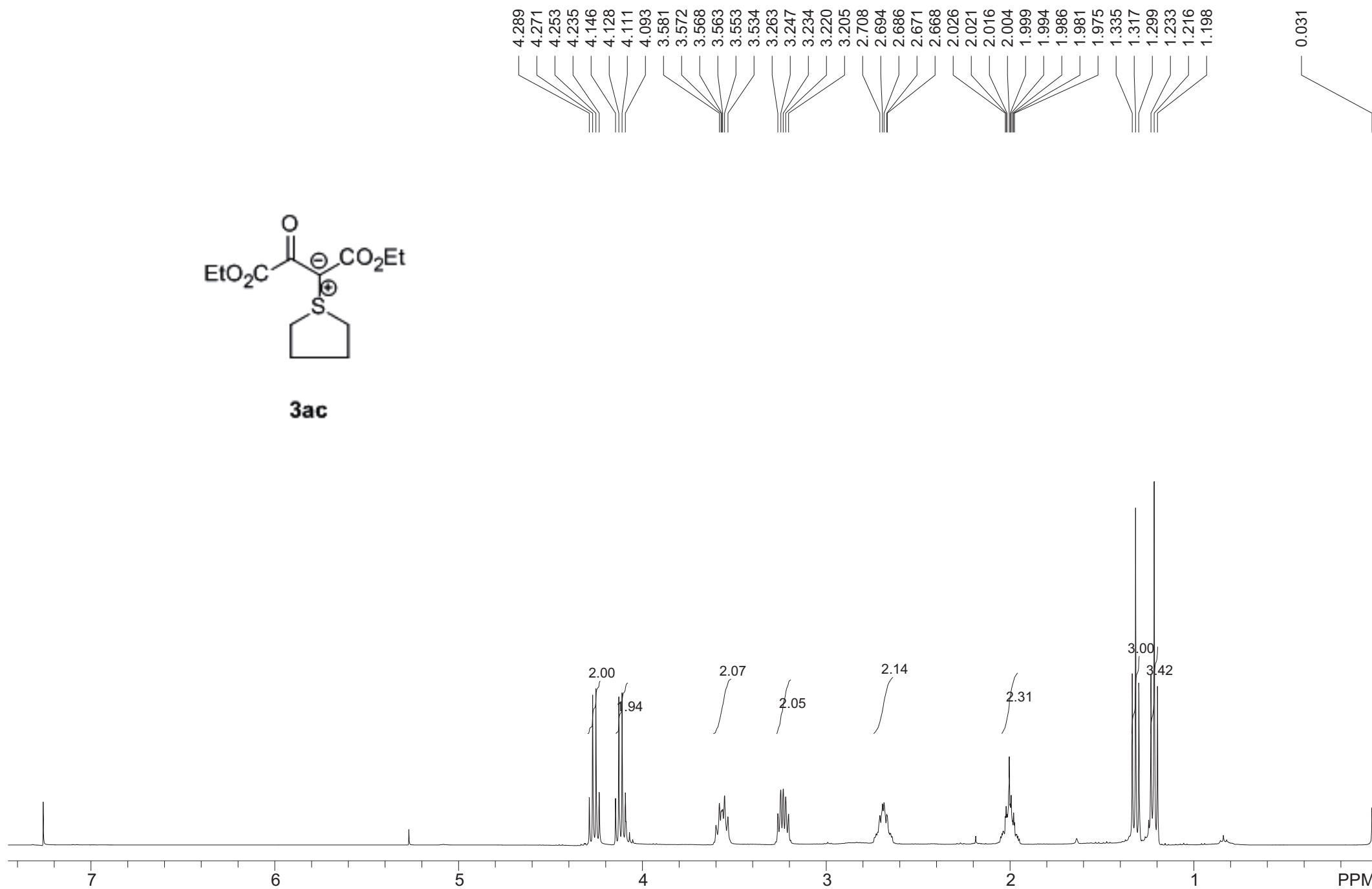


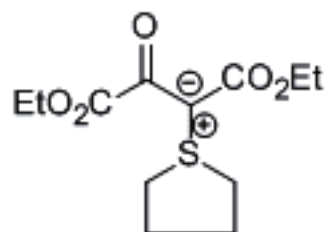
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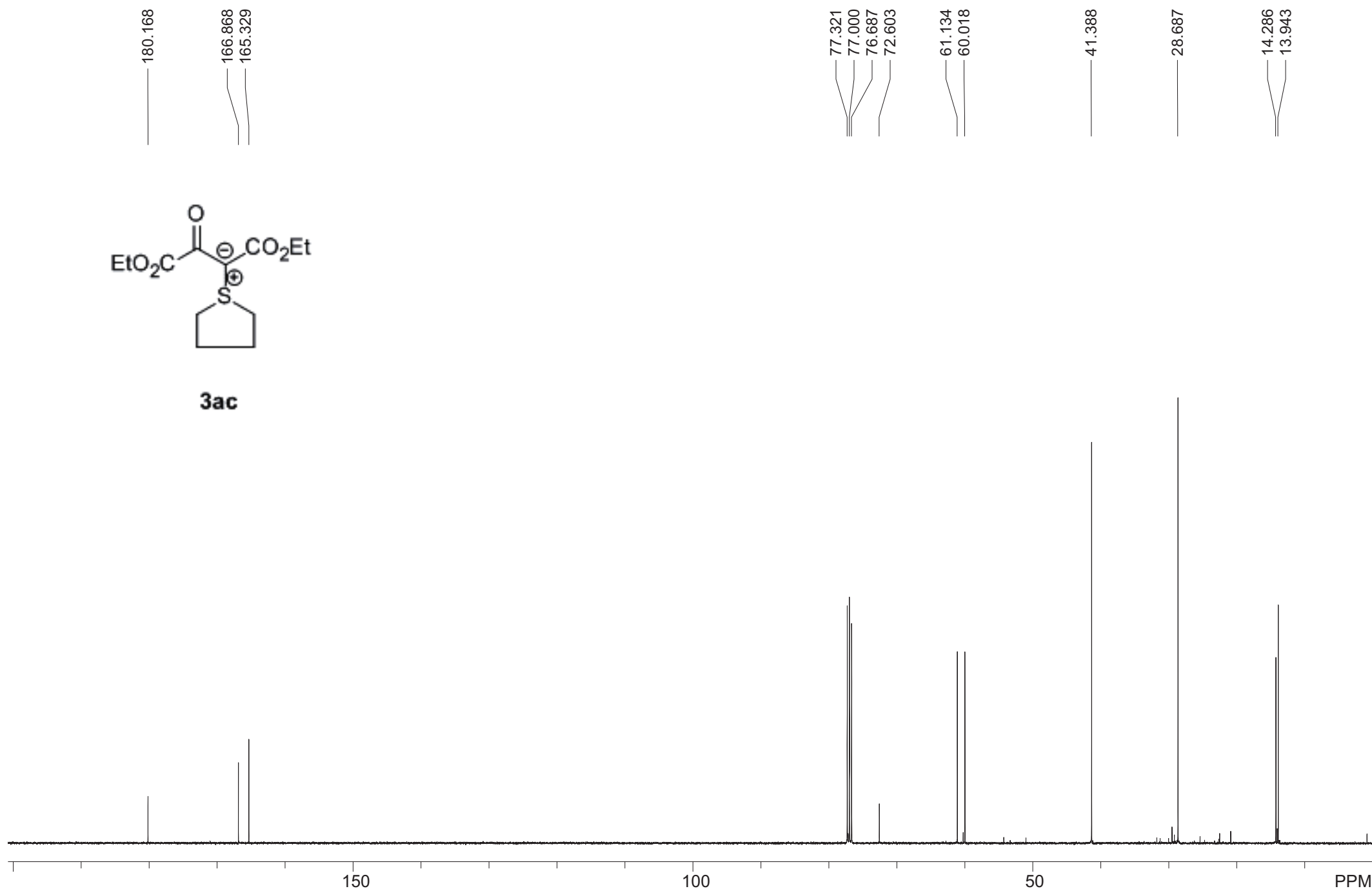


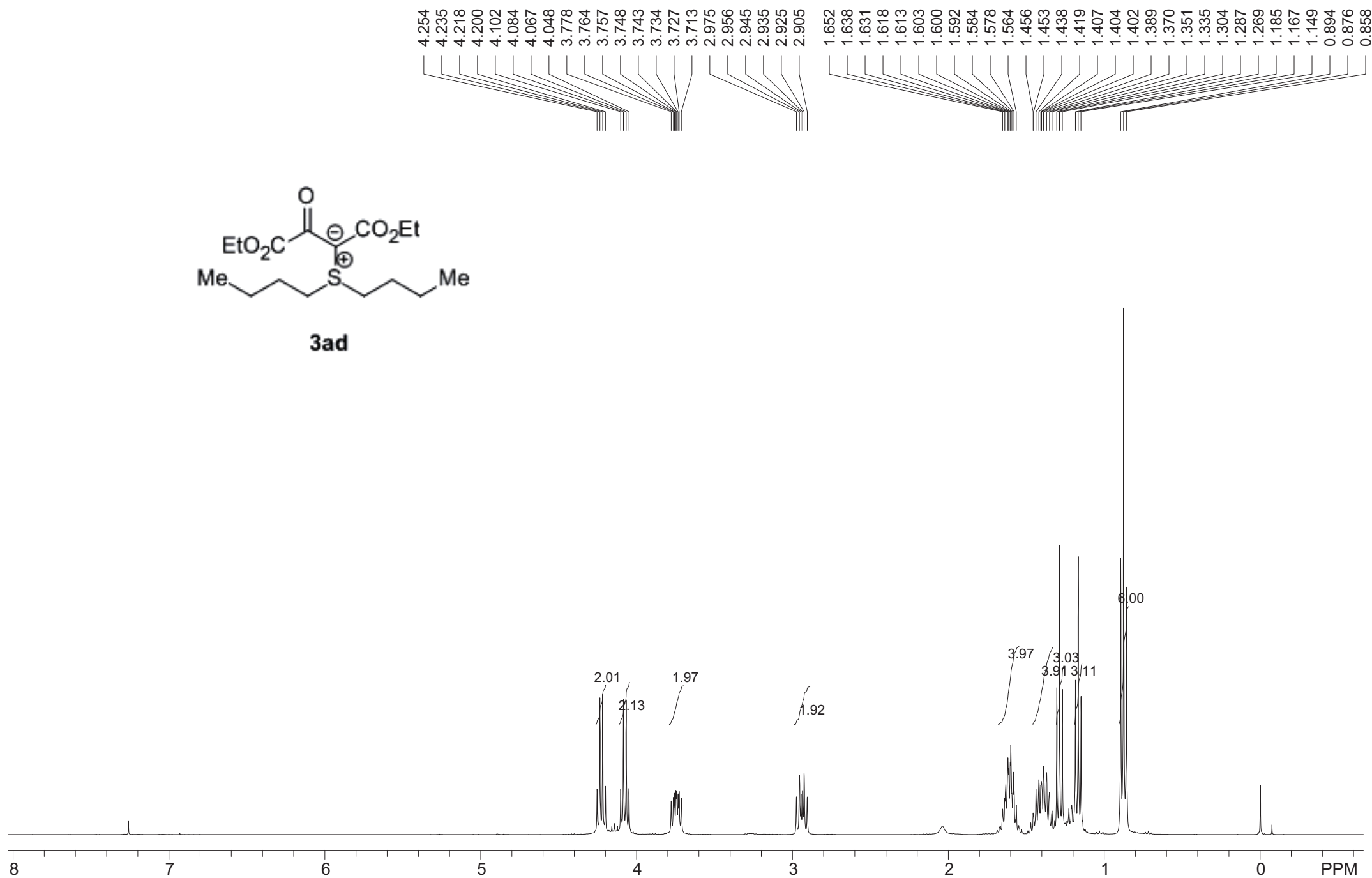
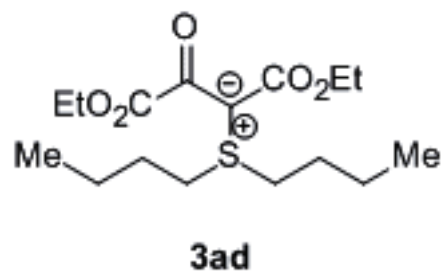
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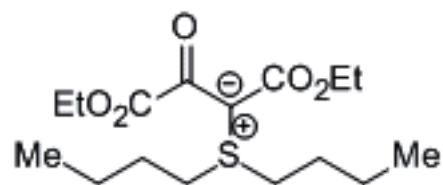




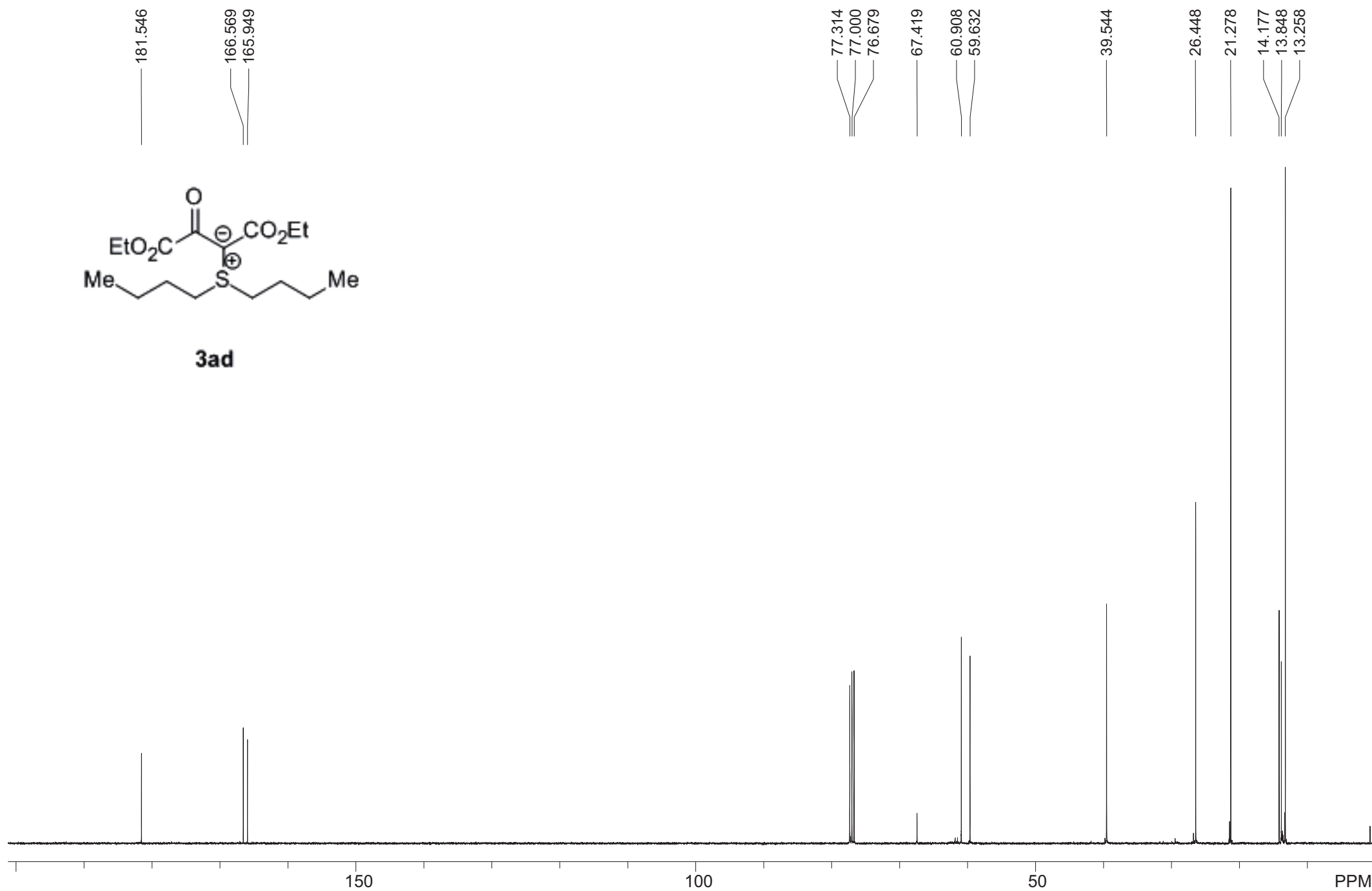
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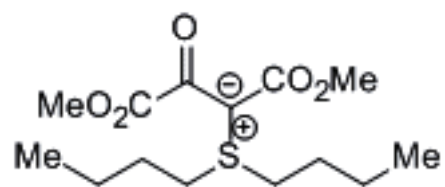




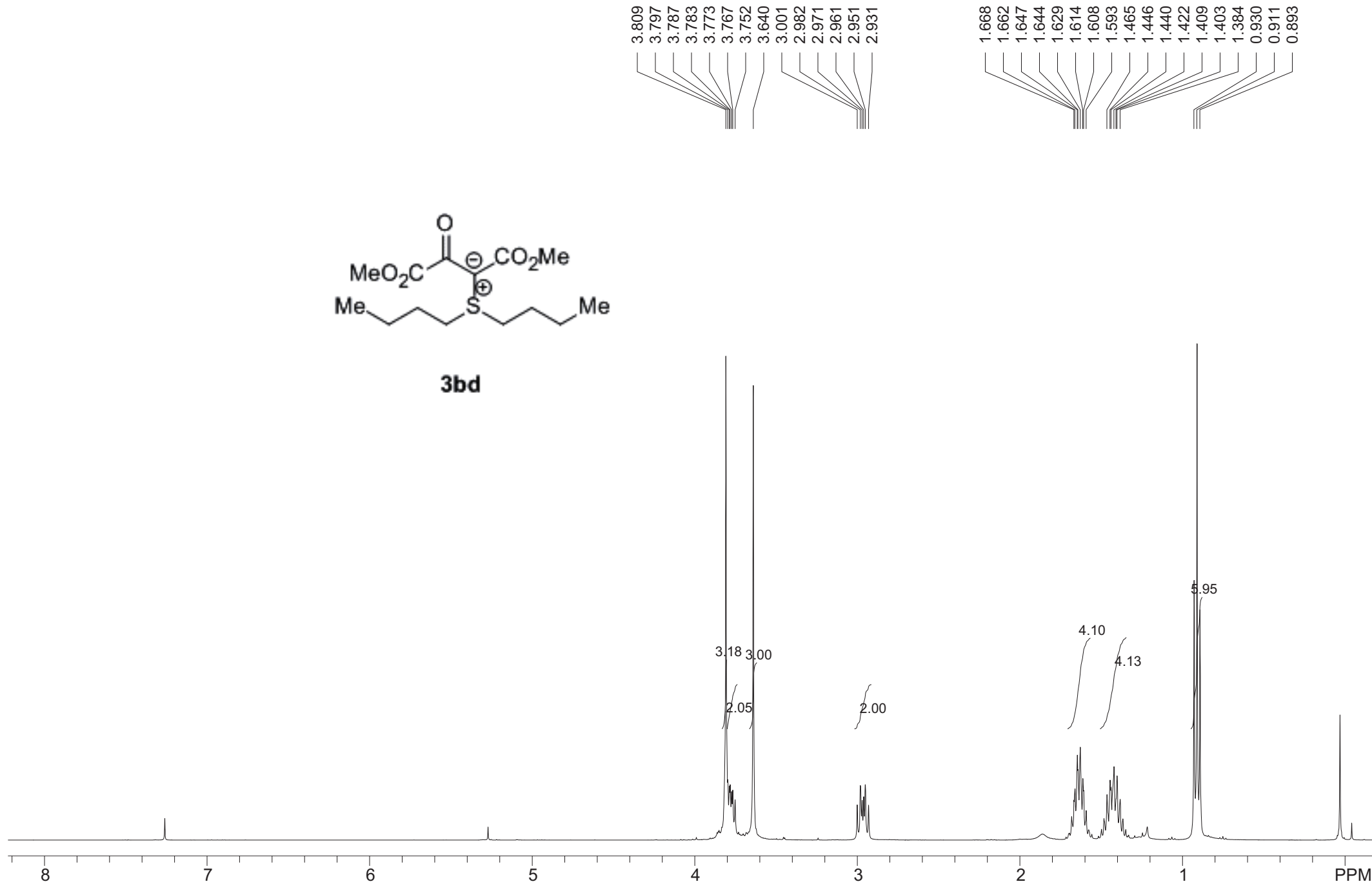


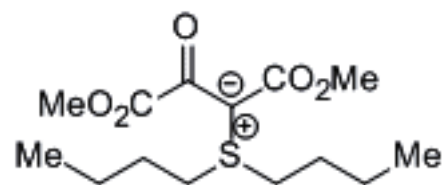
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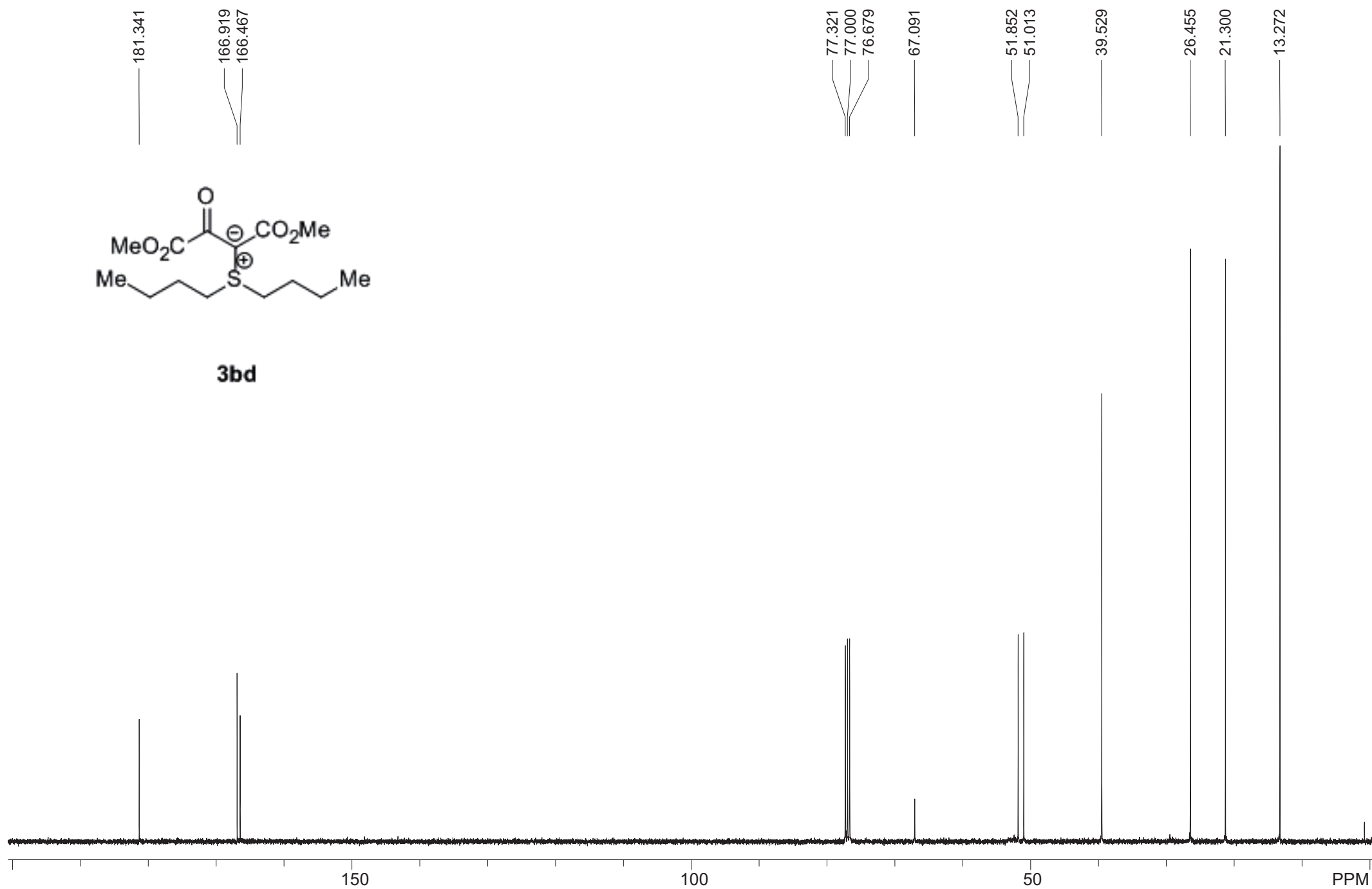


3bd





3bd



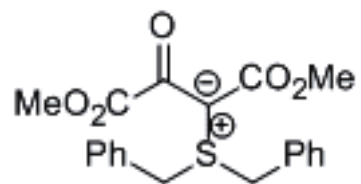
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7.302

4.958
4.928

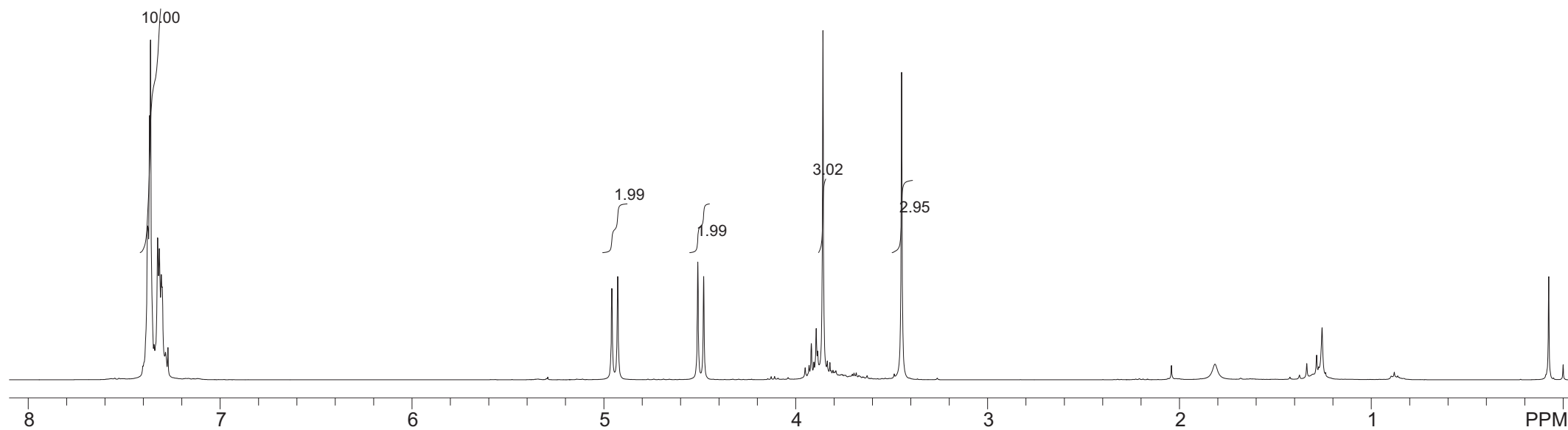
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4.480

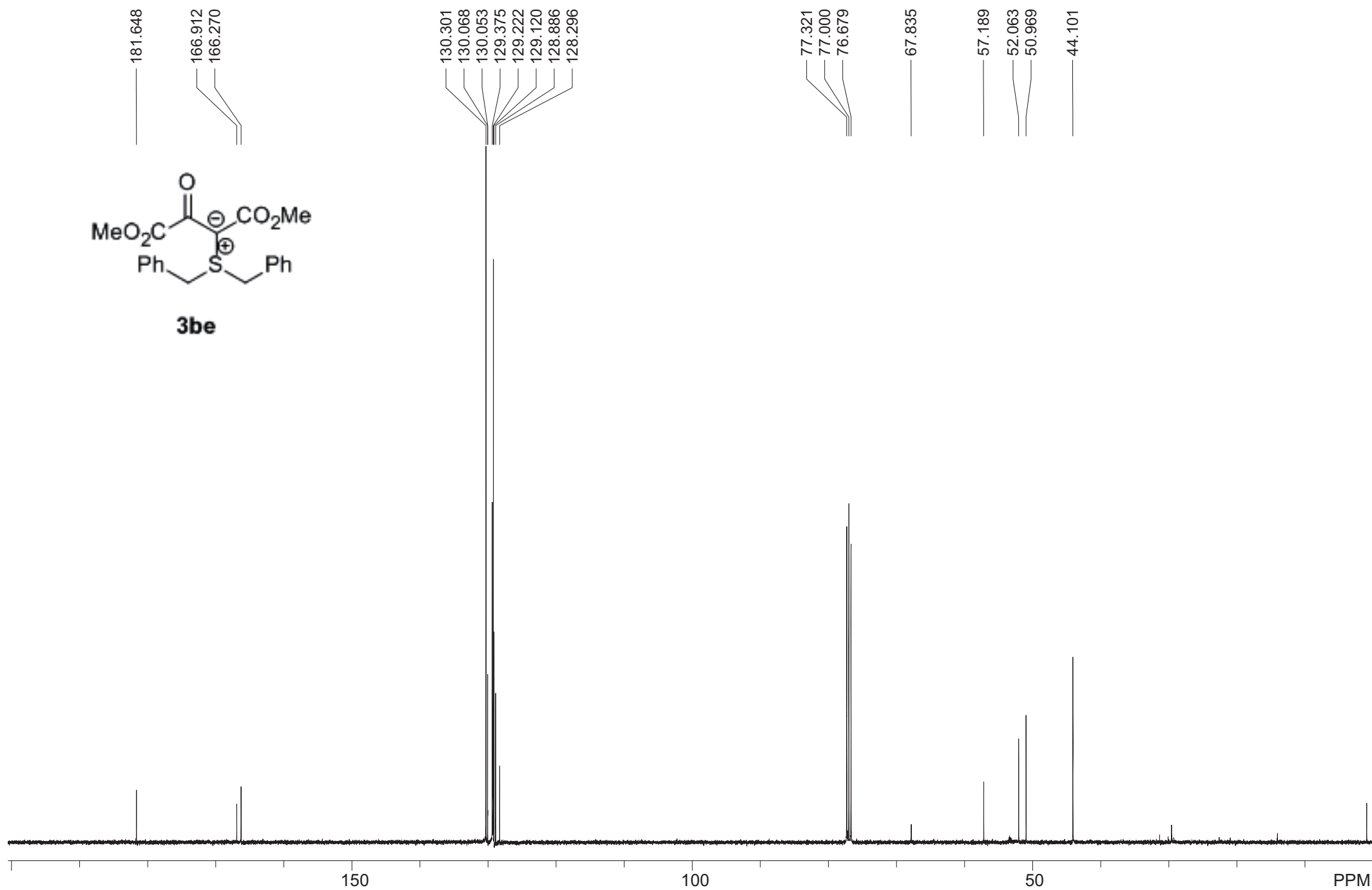
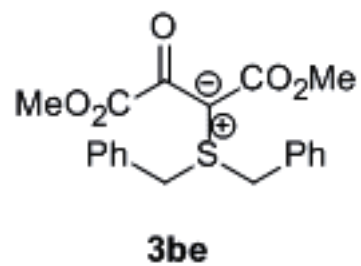
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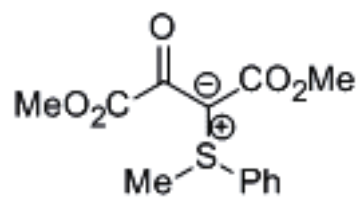
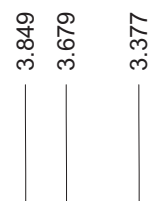
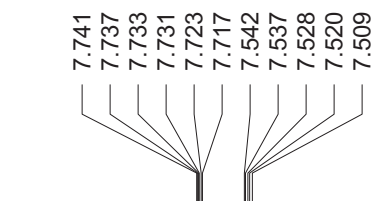
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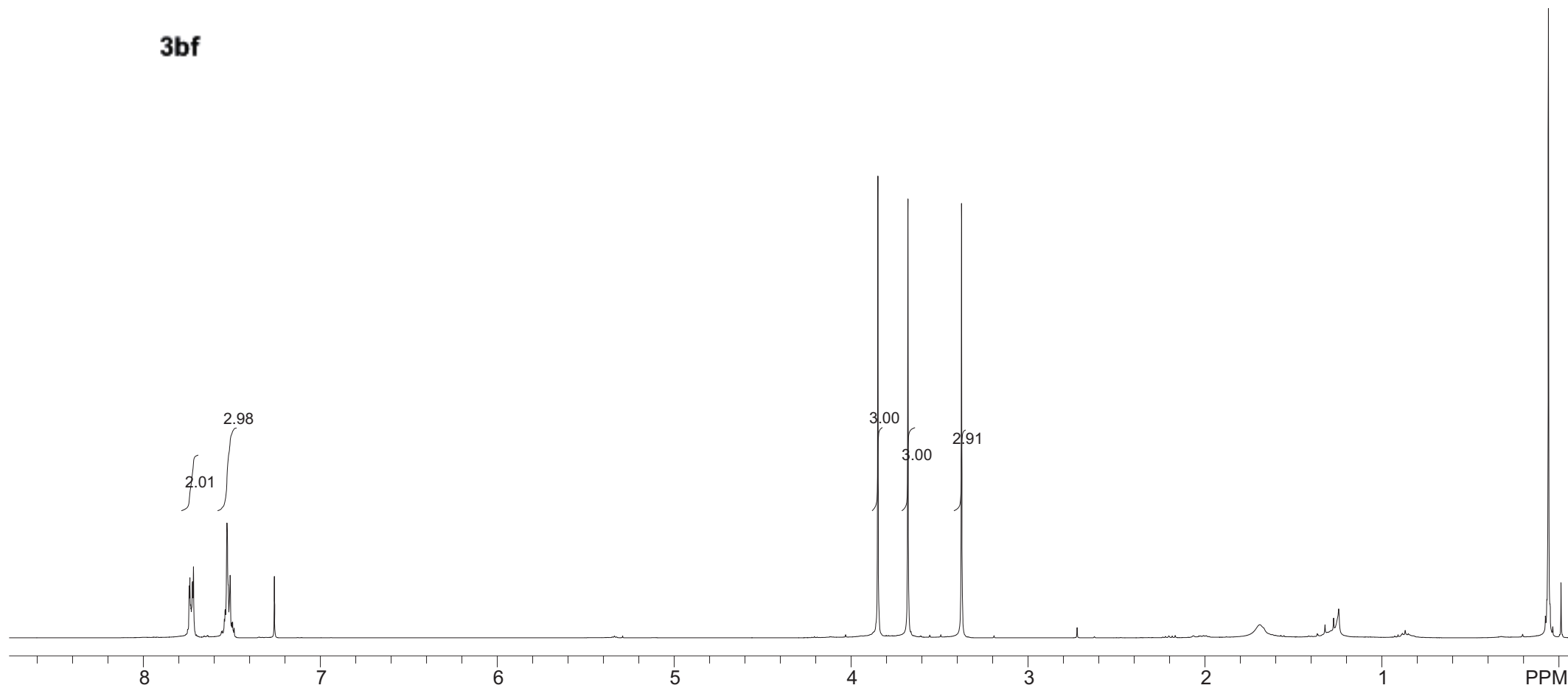
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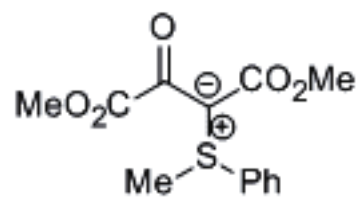




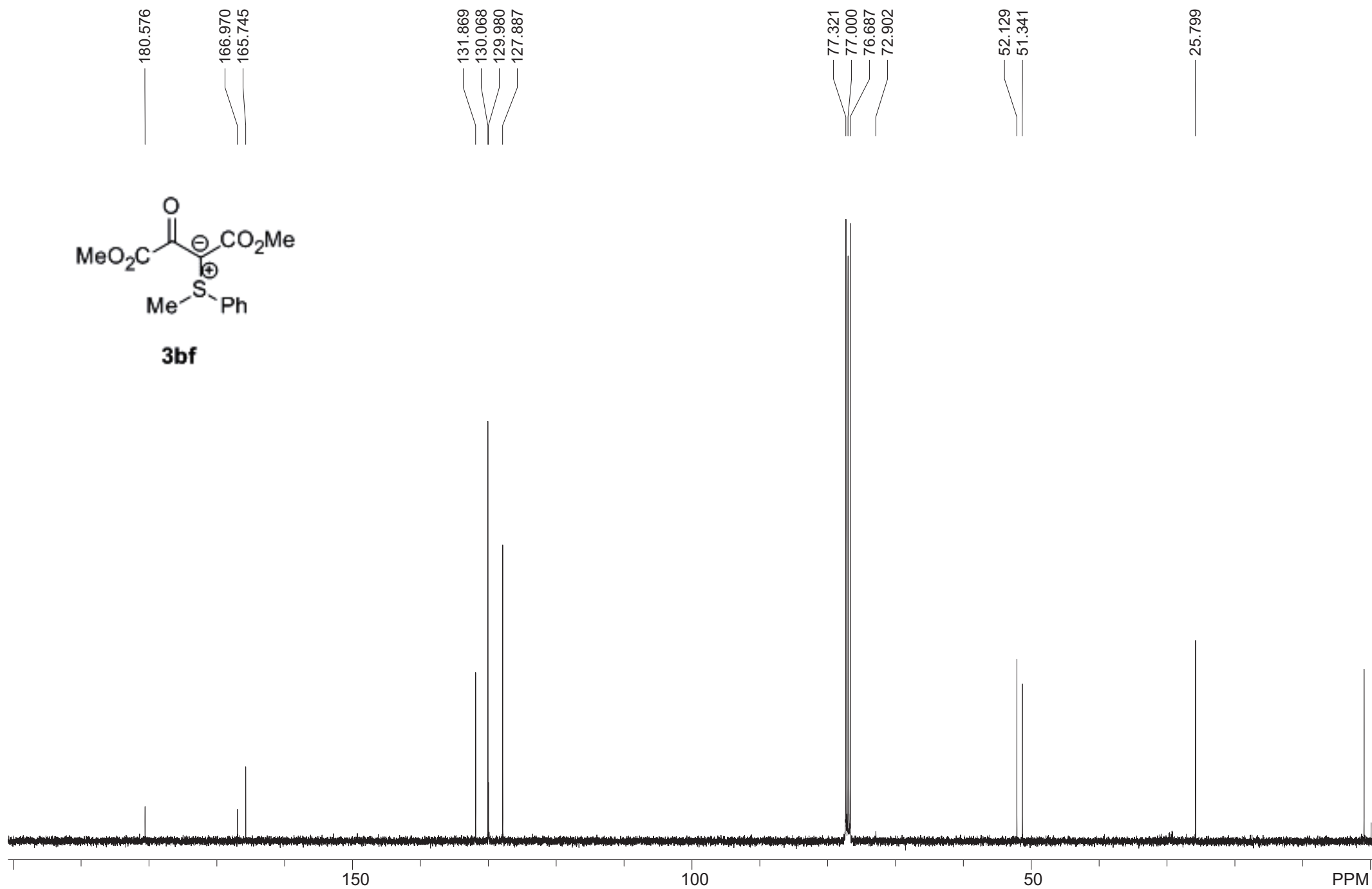


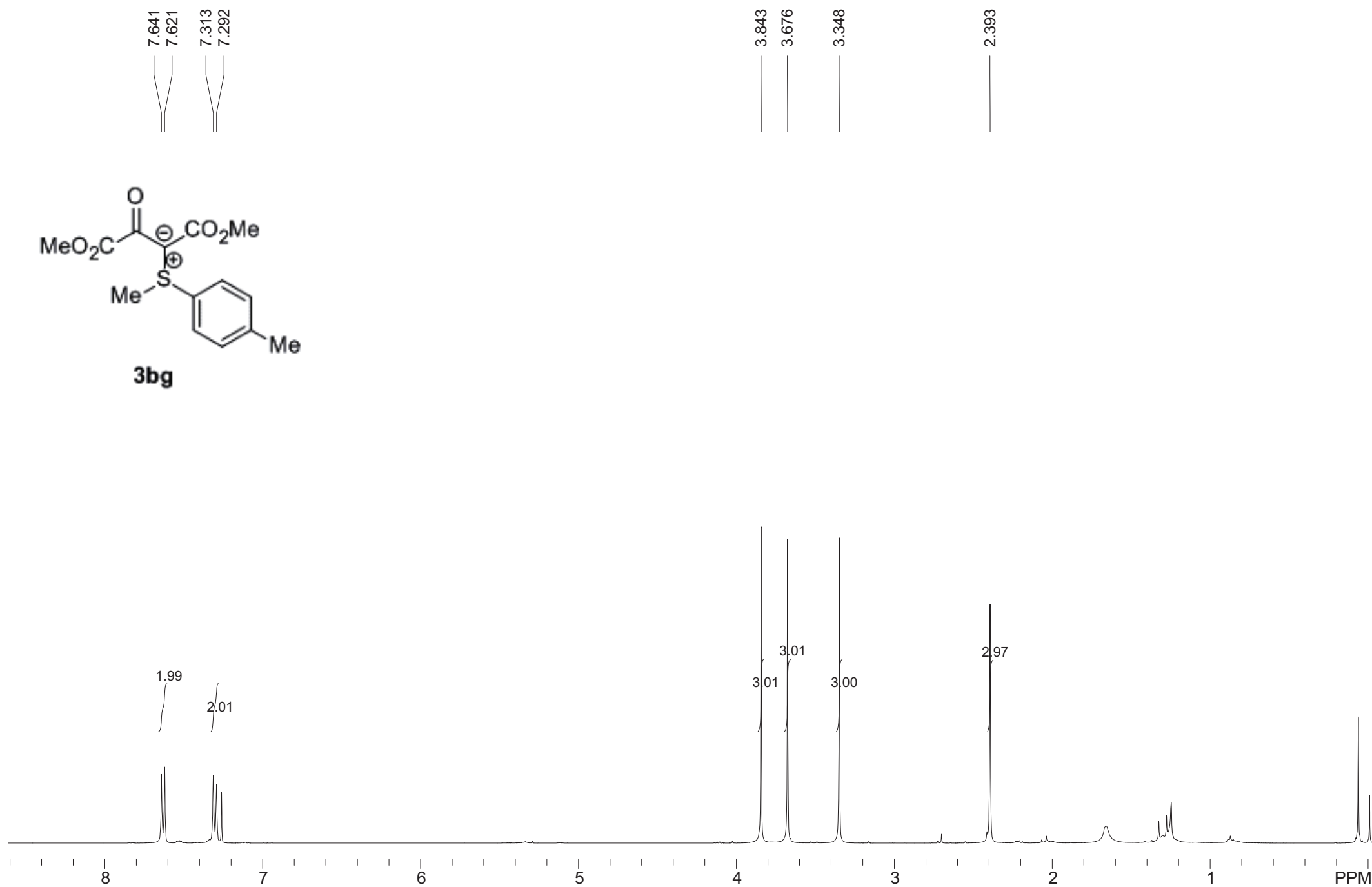
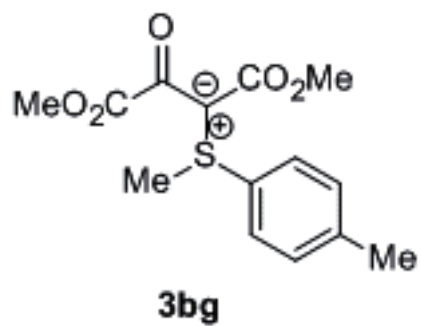
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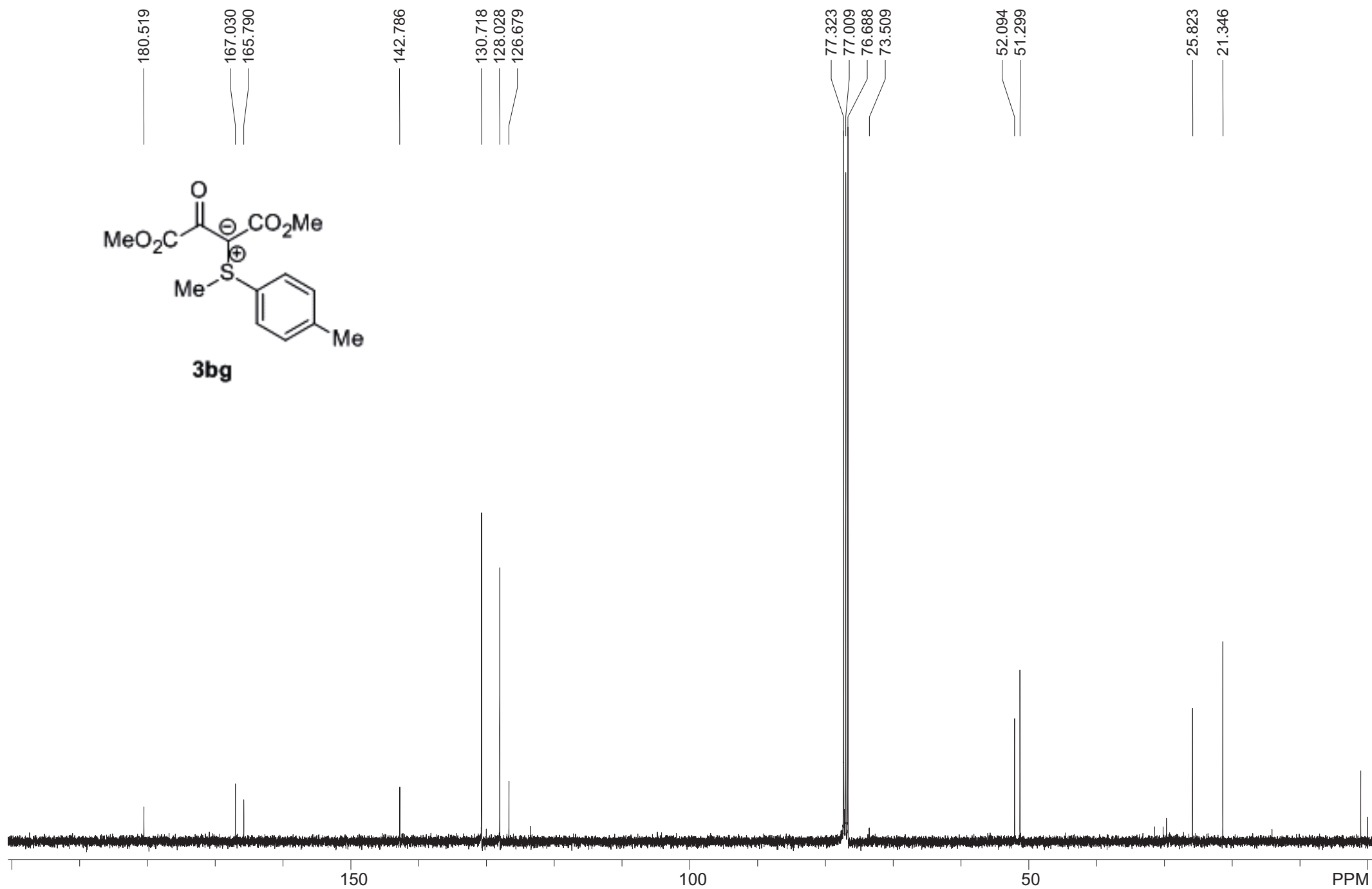


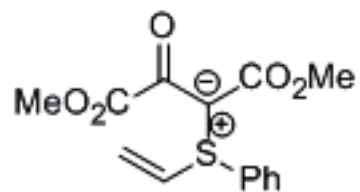
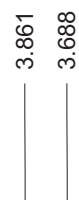
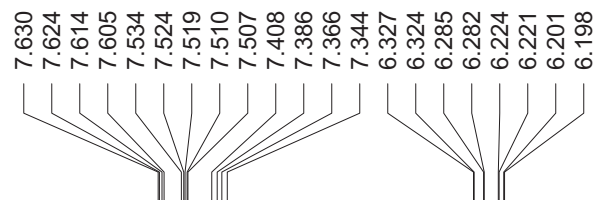


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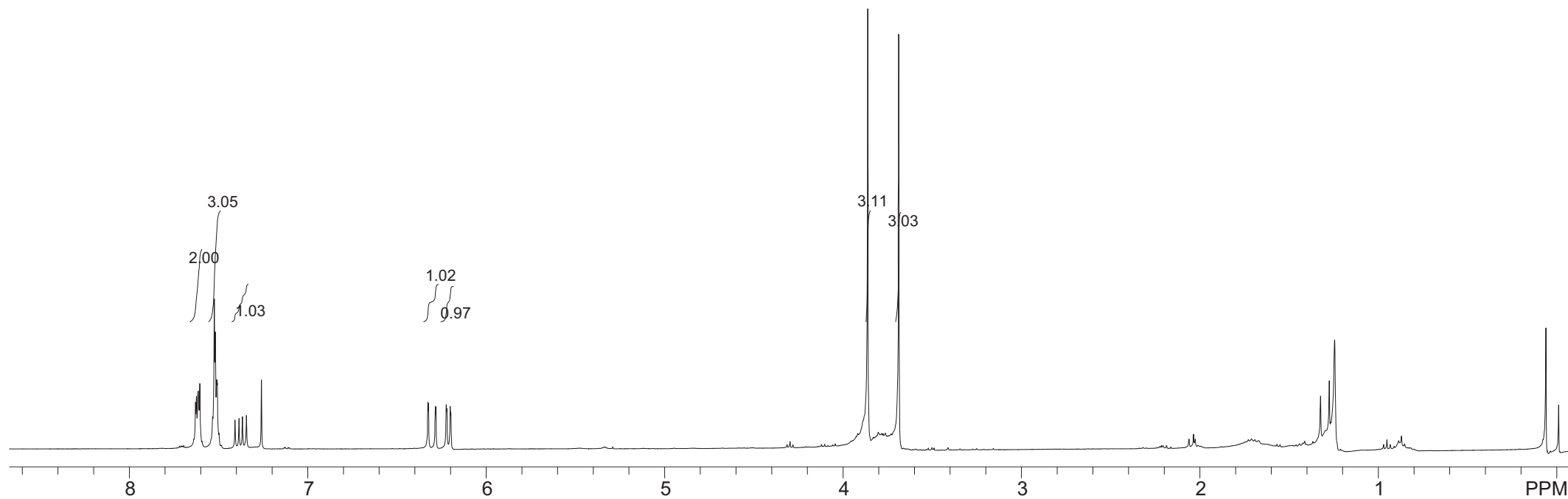


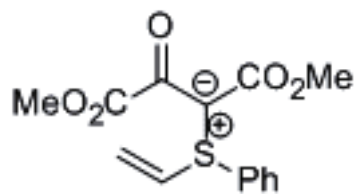




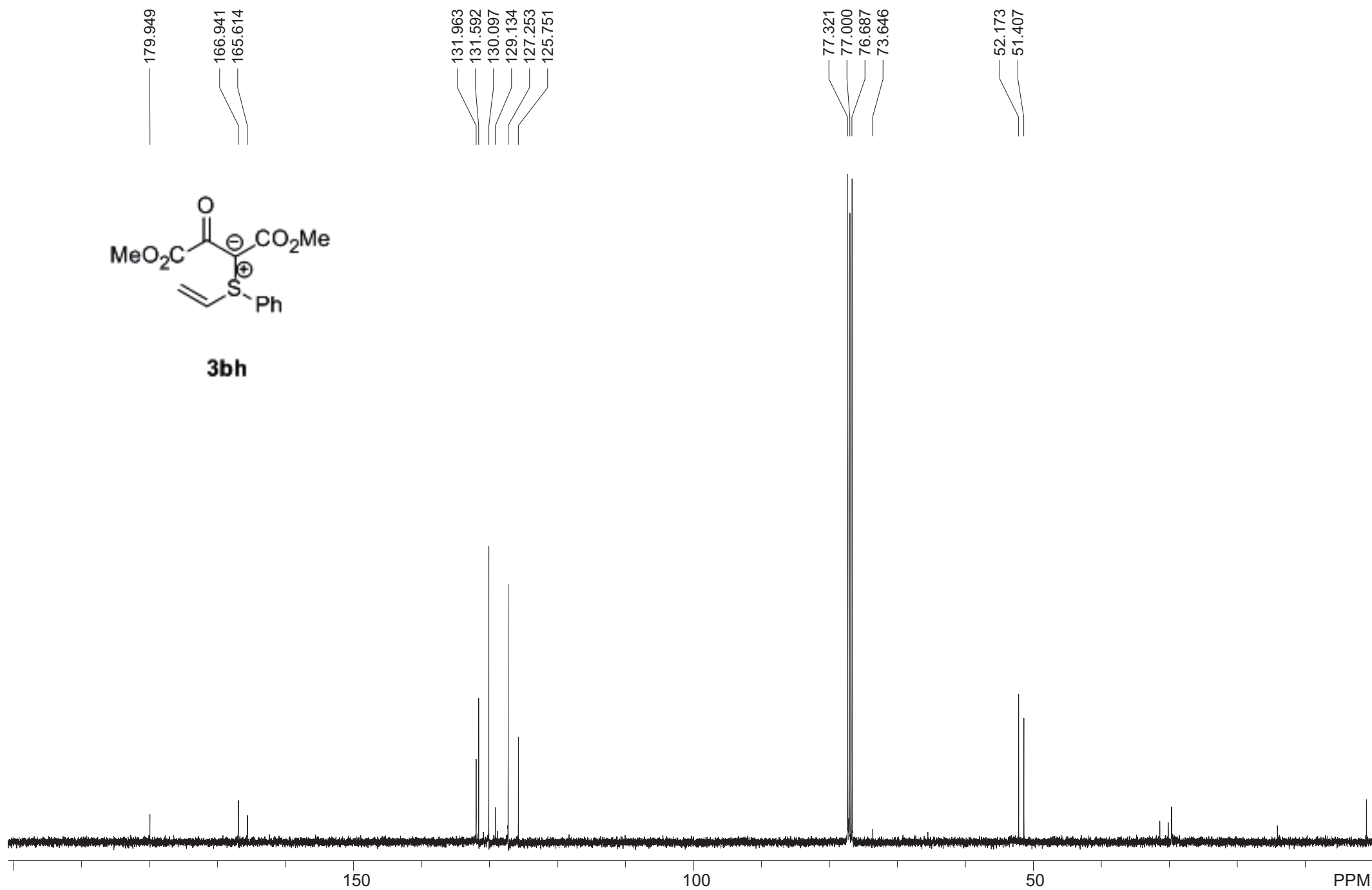


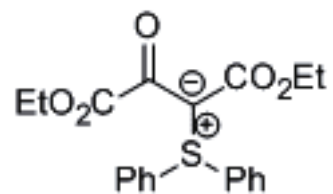
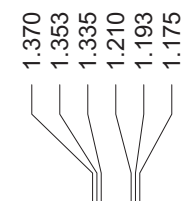
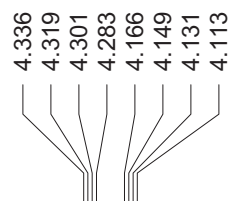
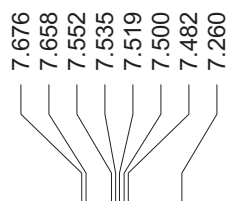
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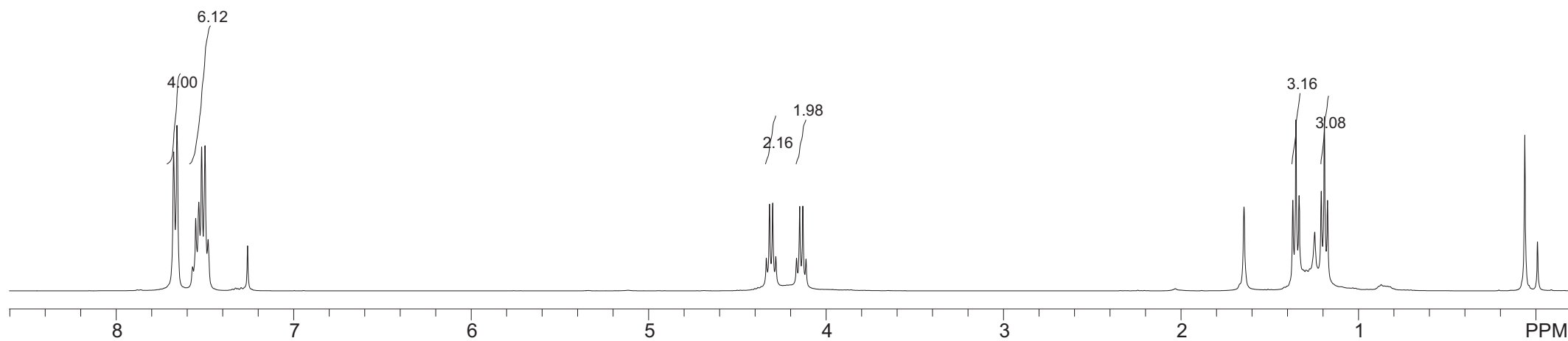


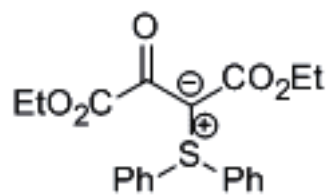
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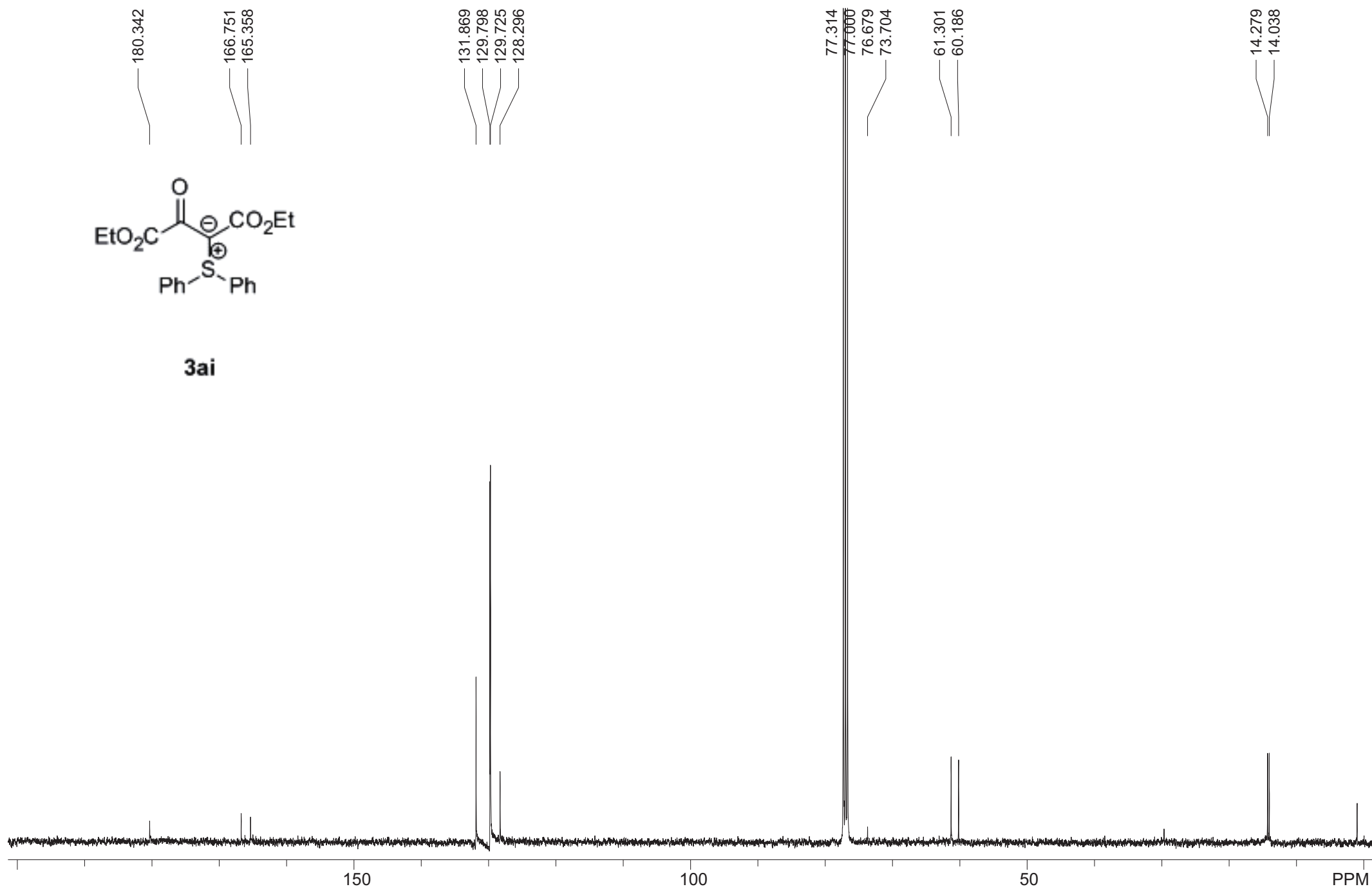


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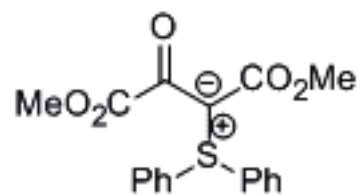


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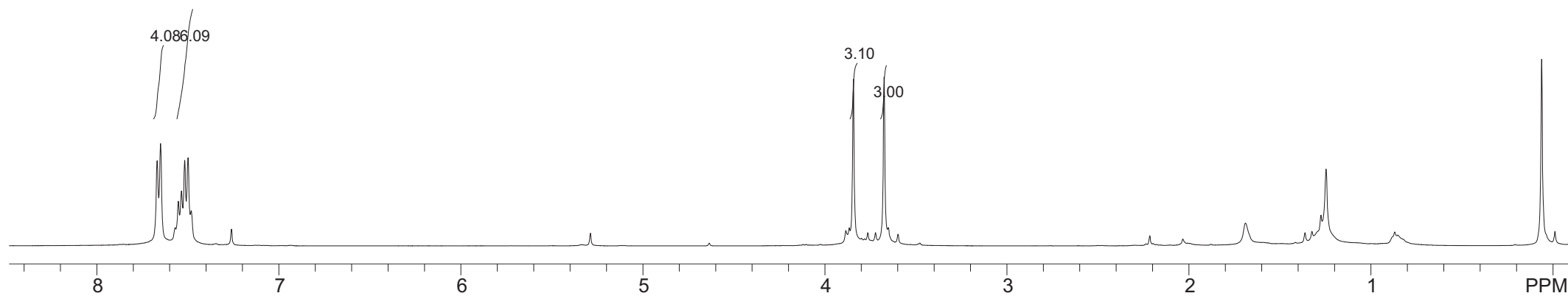


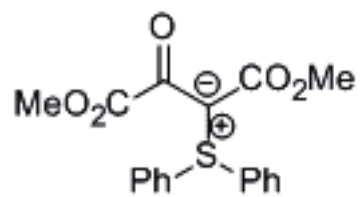
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7.499
7.481

3.844
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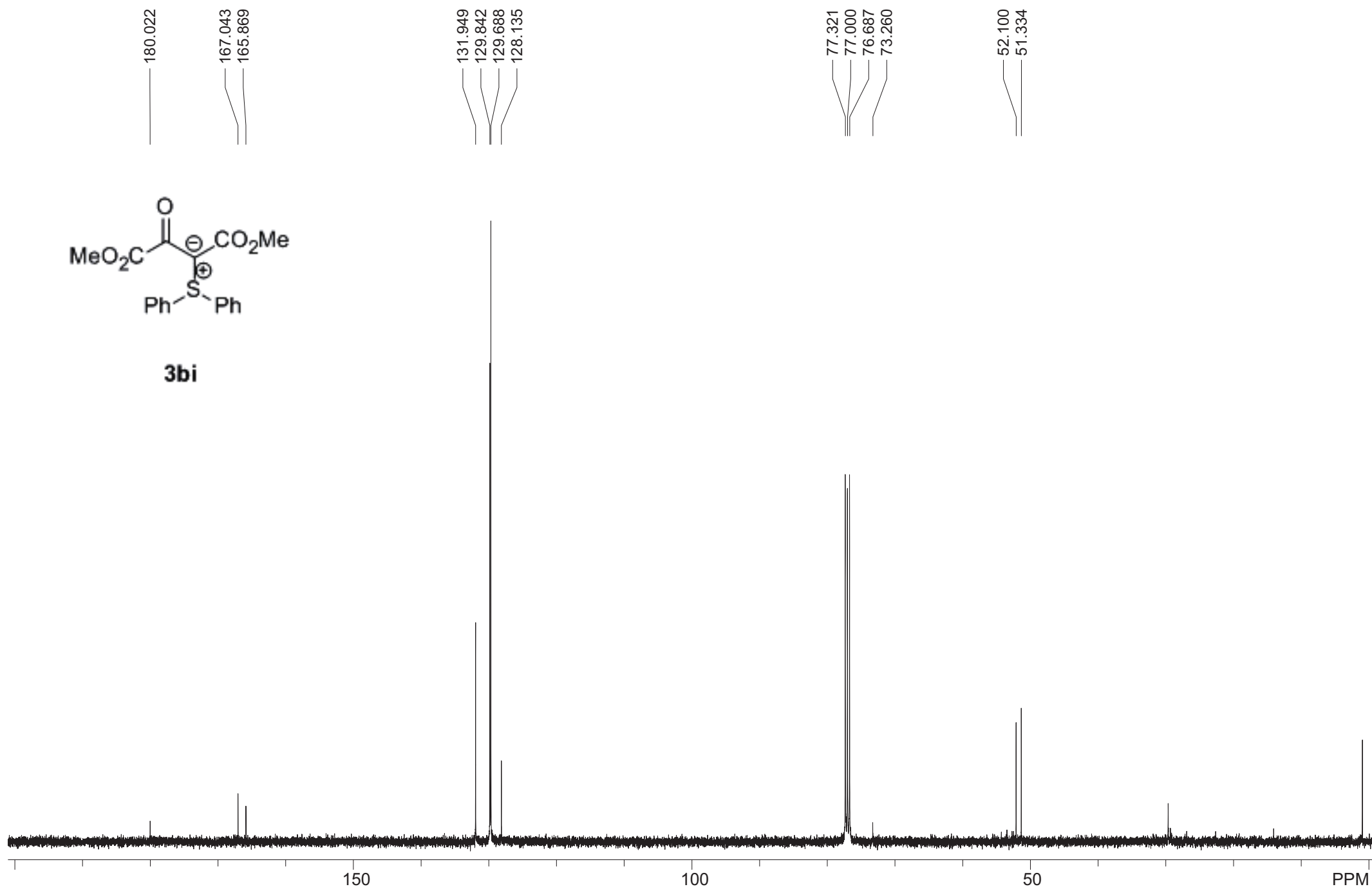


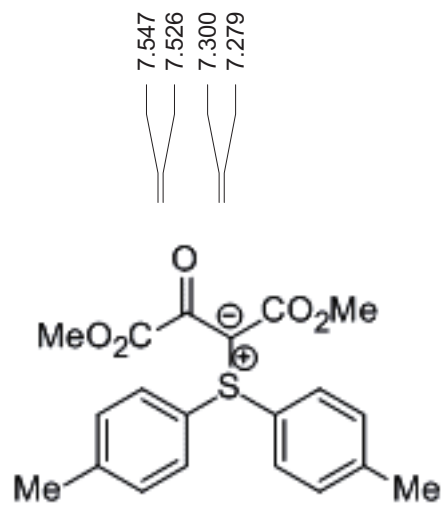
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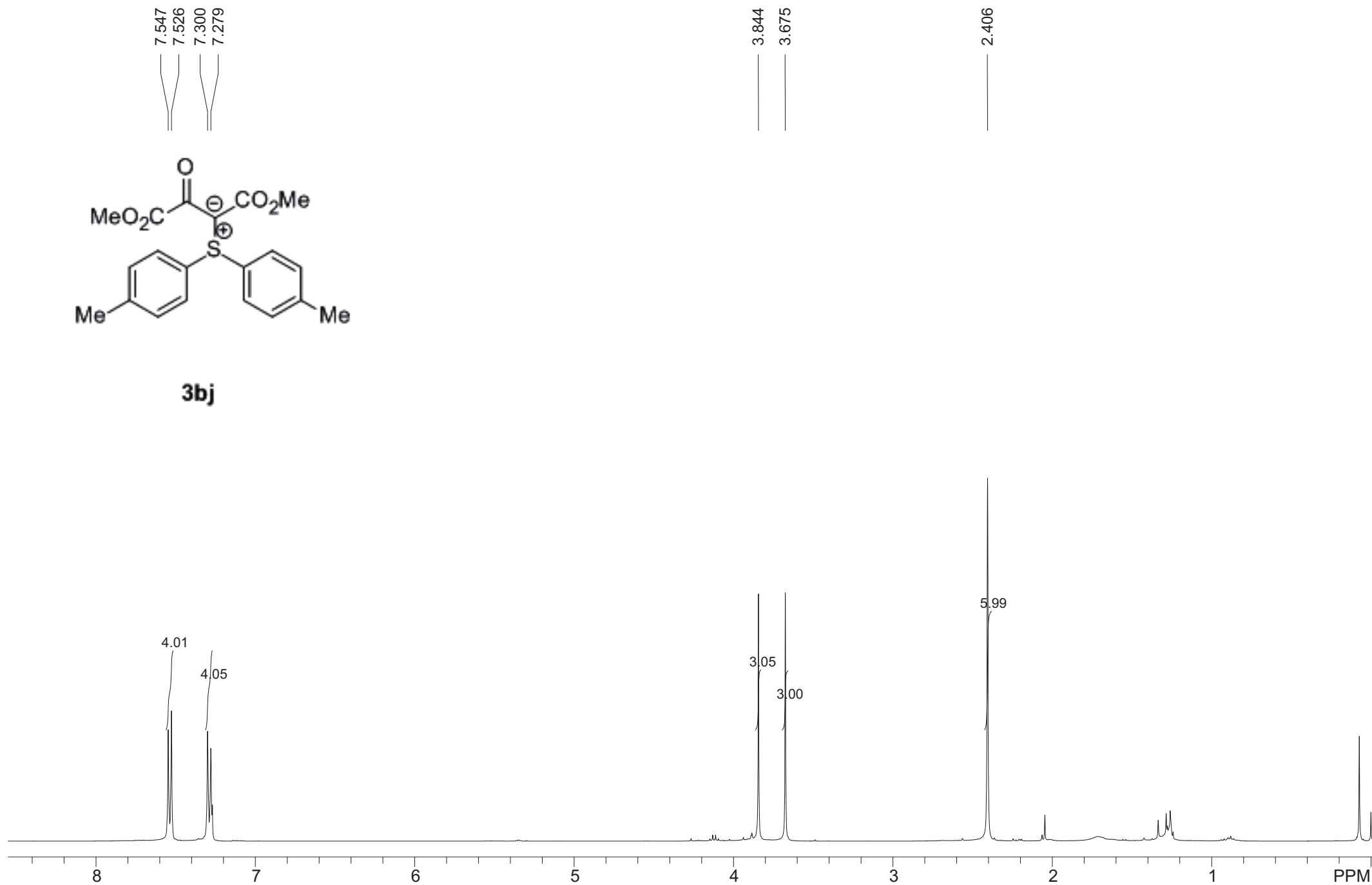


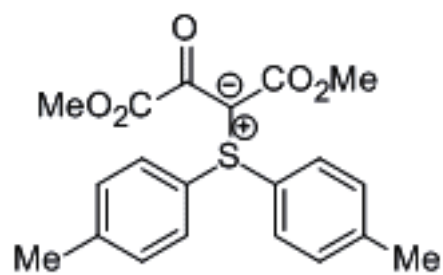
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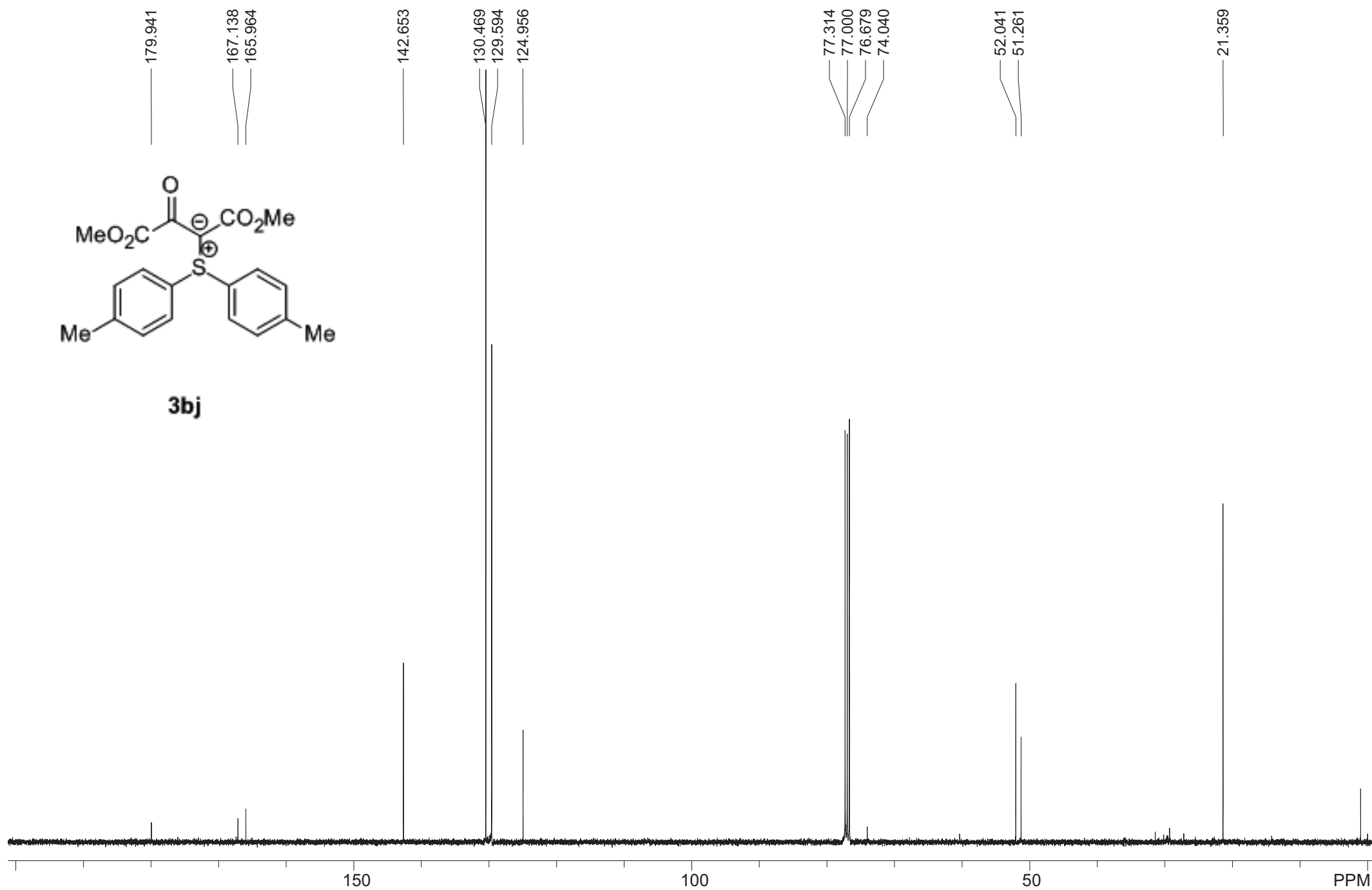


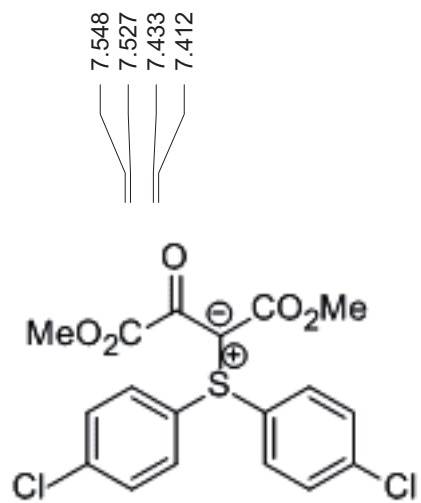
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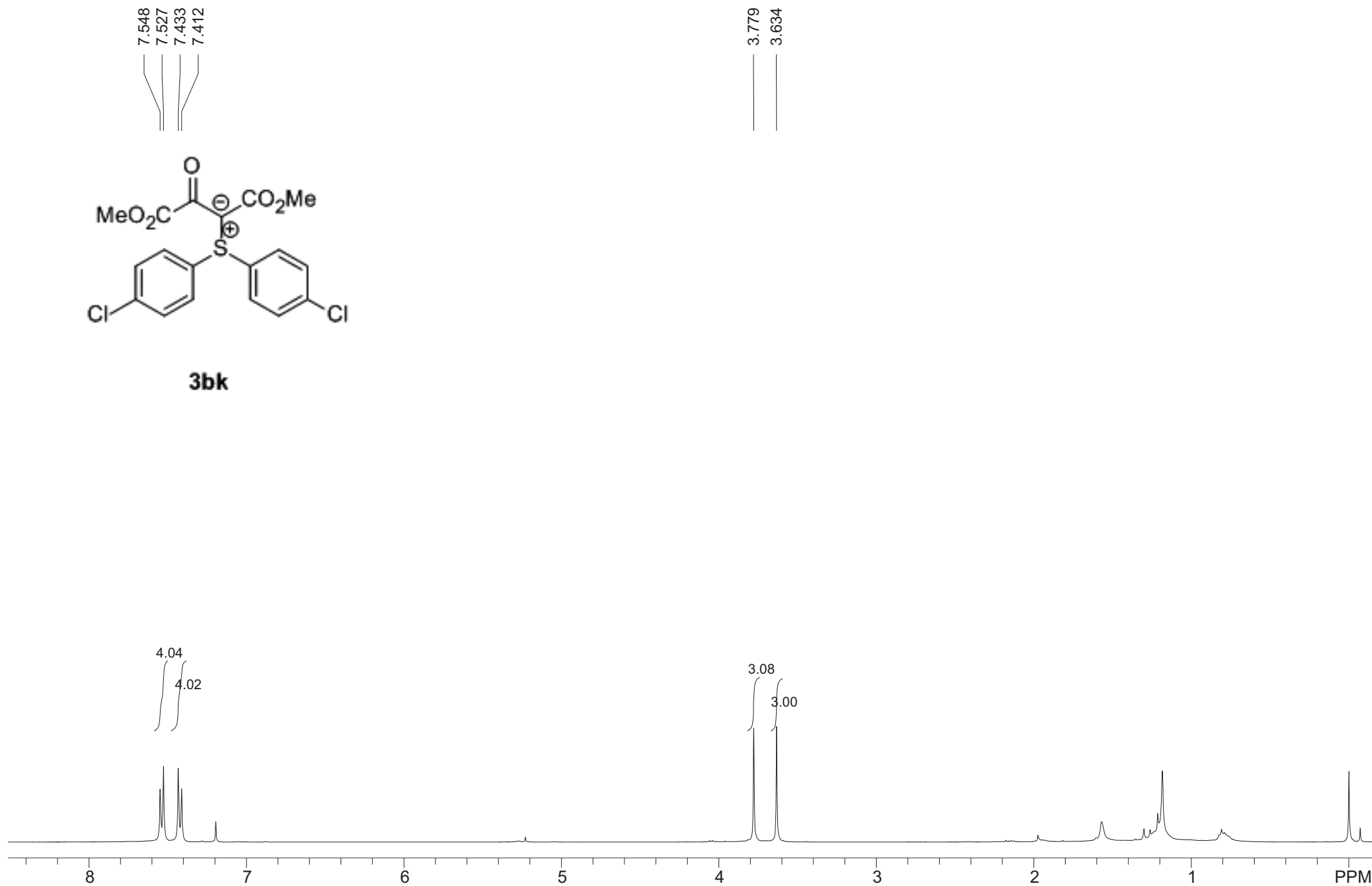


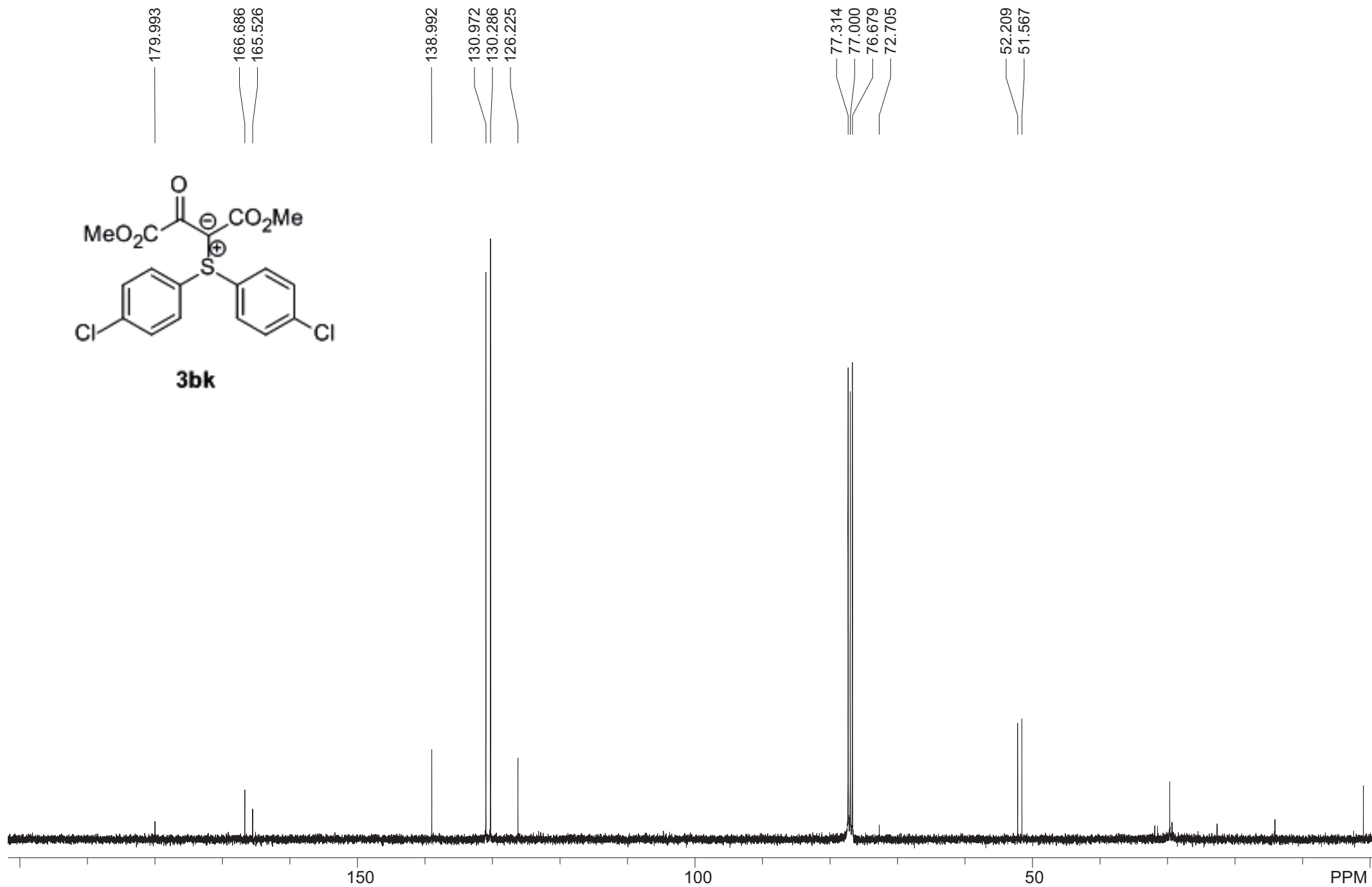
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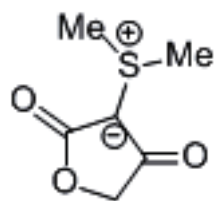




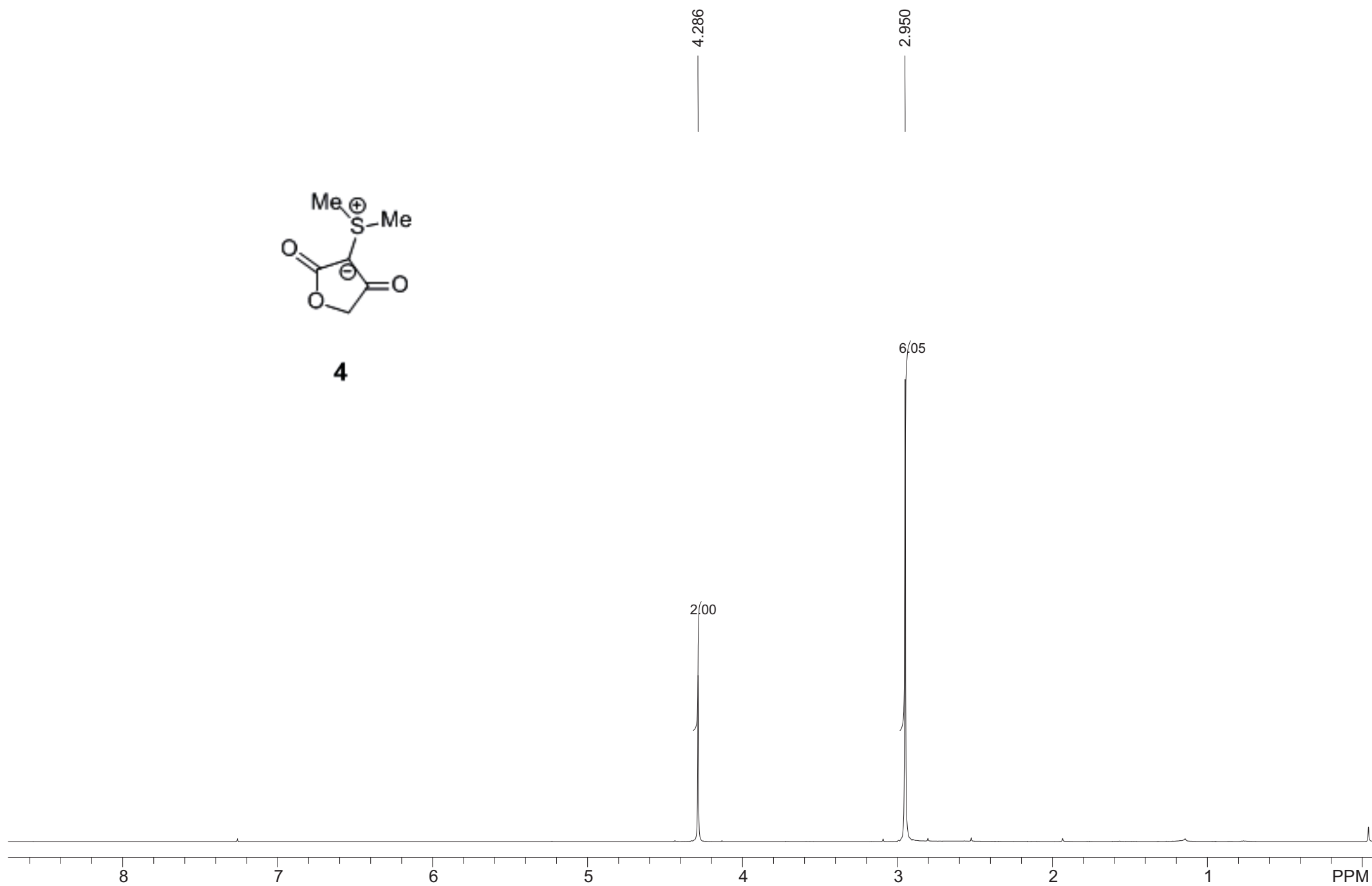
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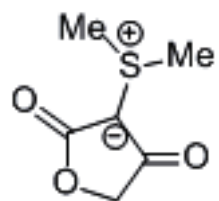




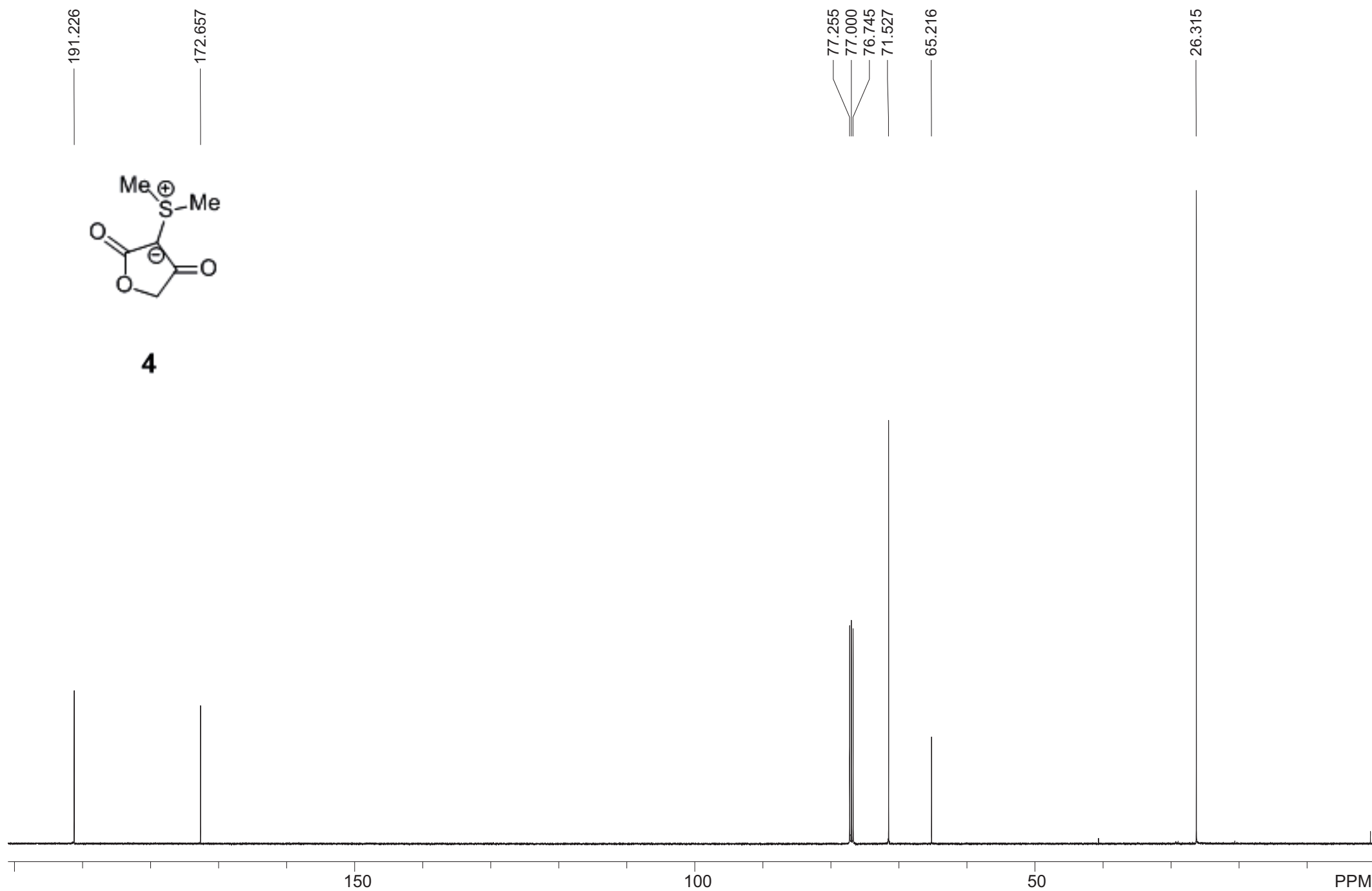


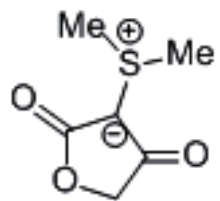
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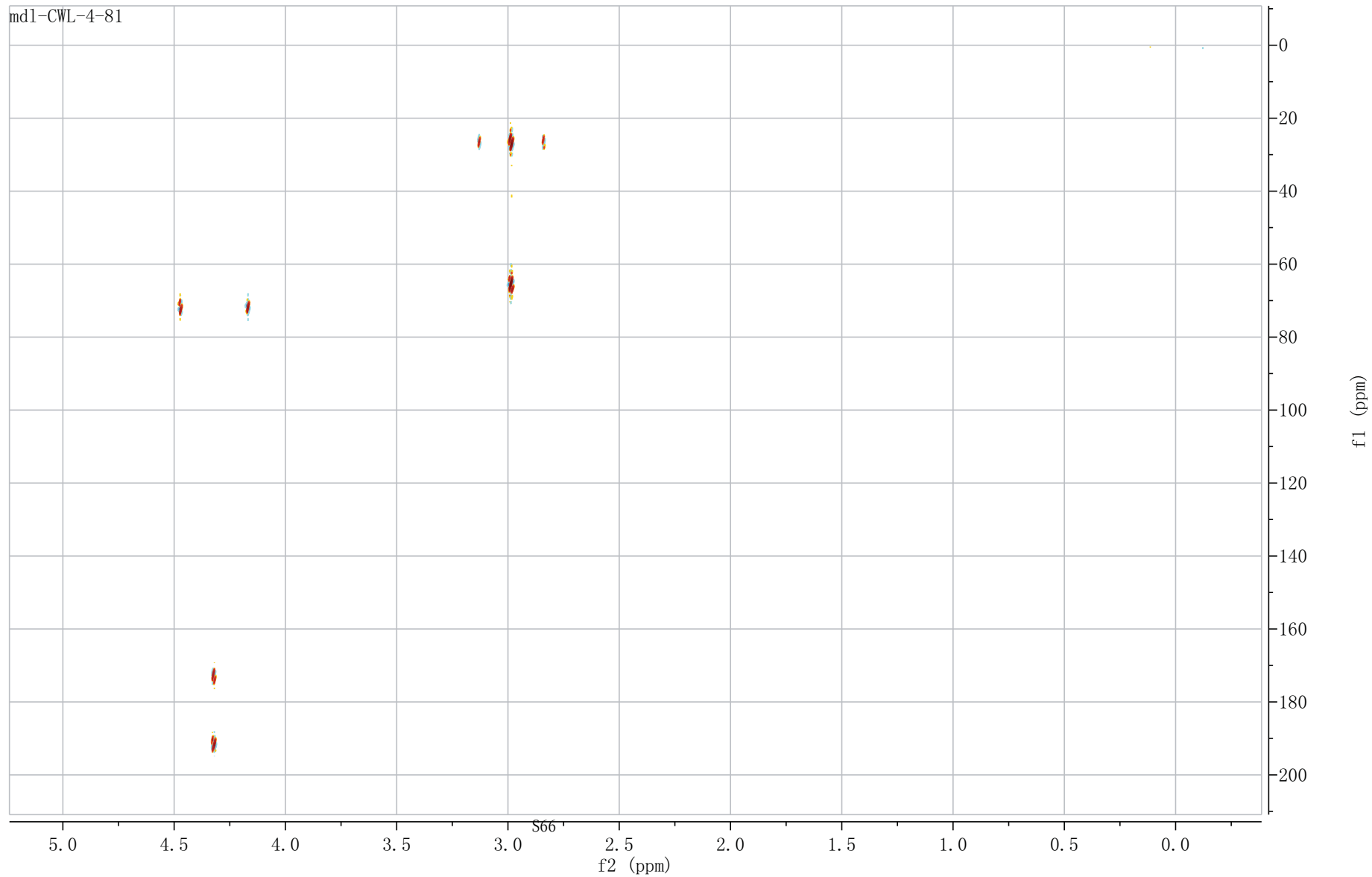


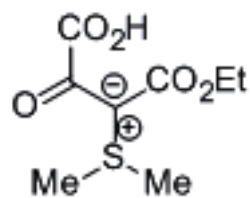
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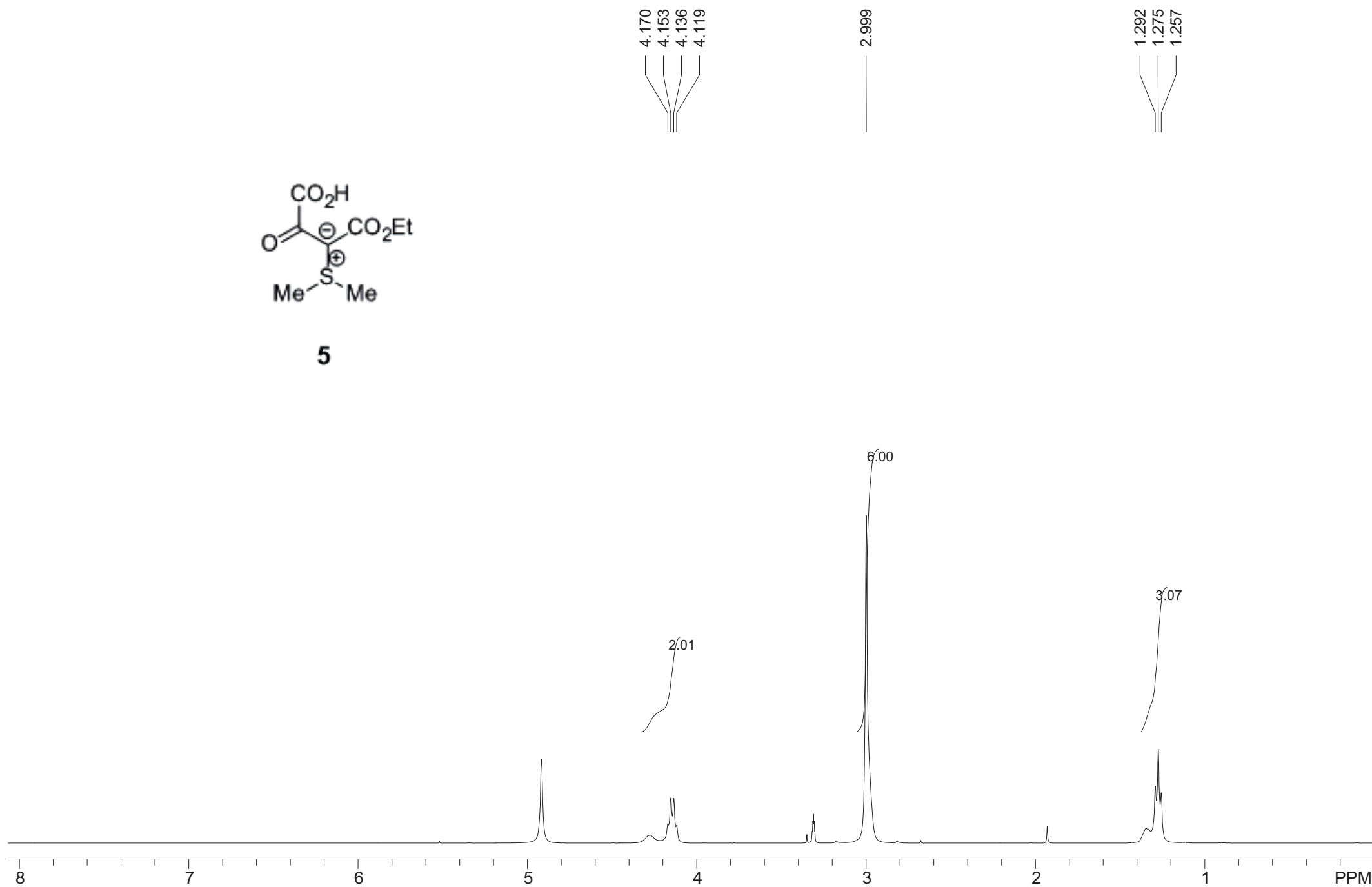


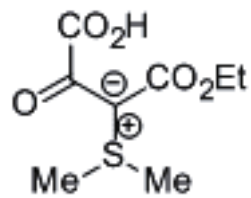
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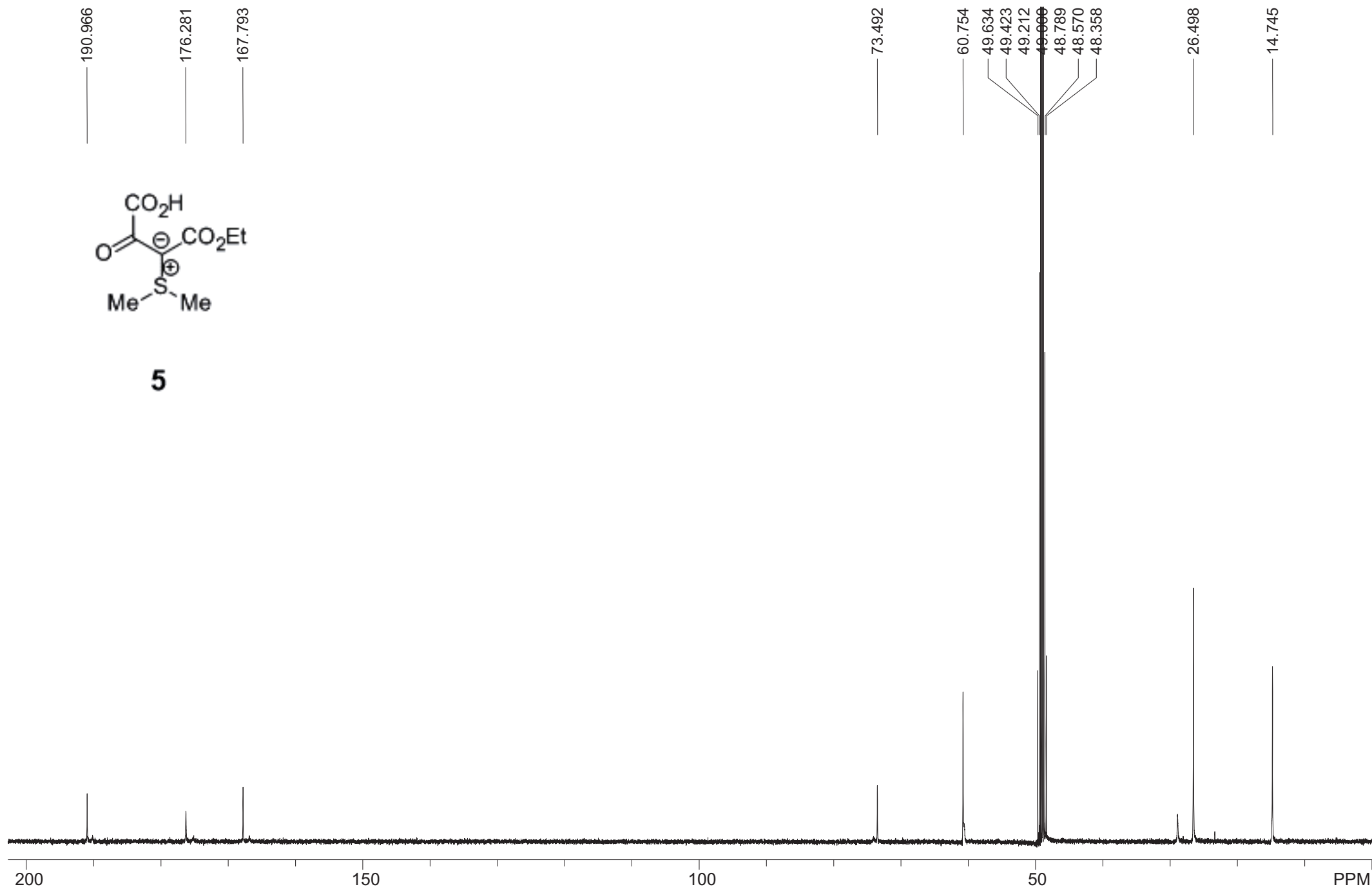


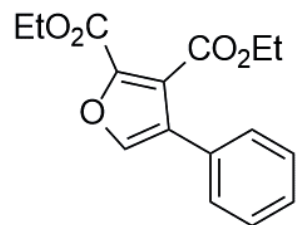
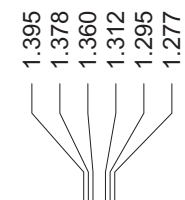
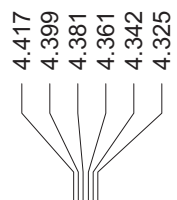
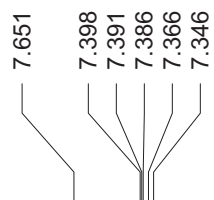
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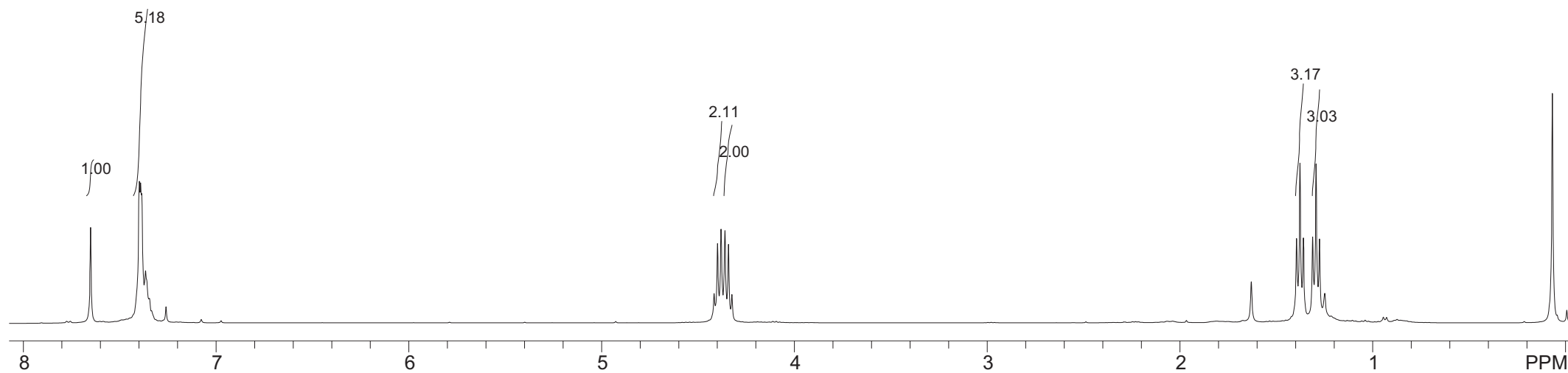


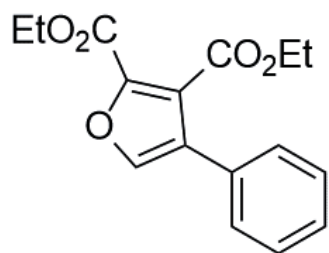
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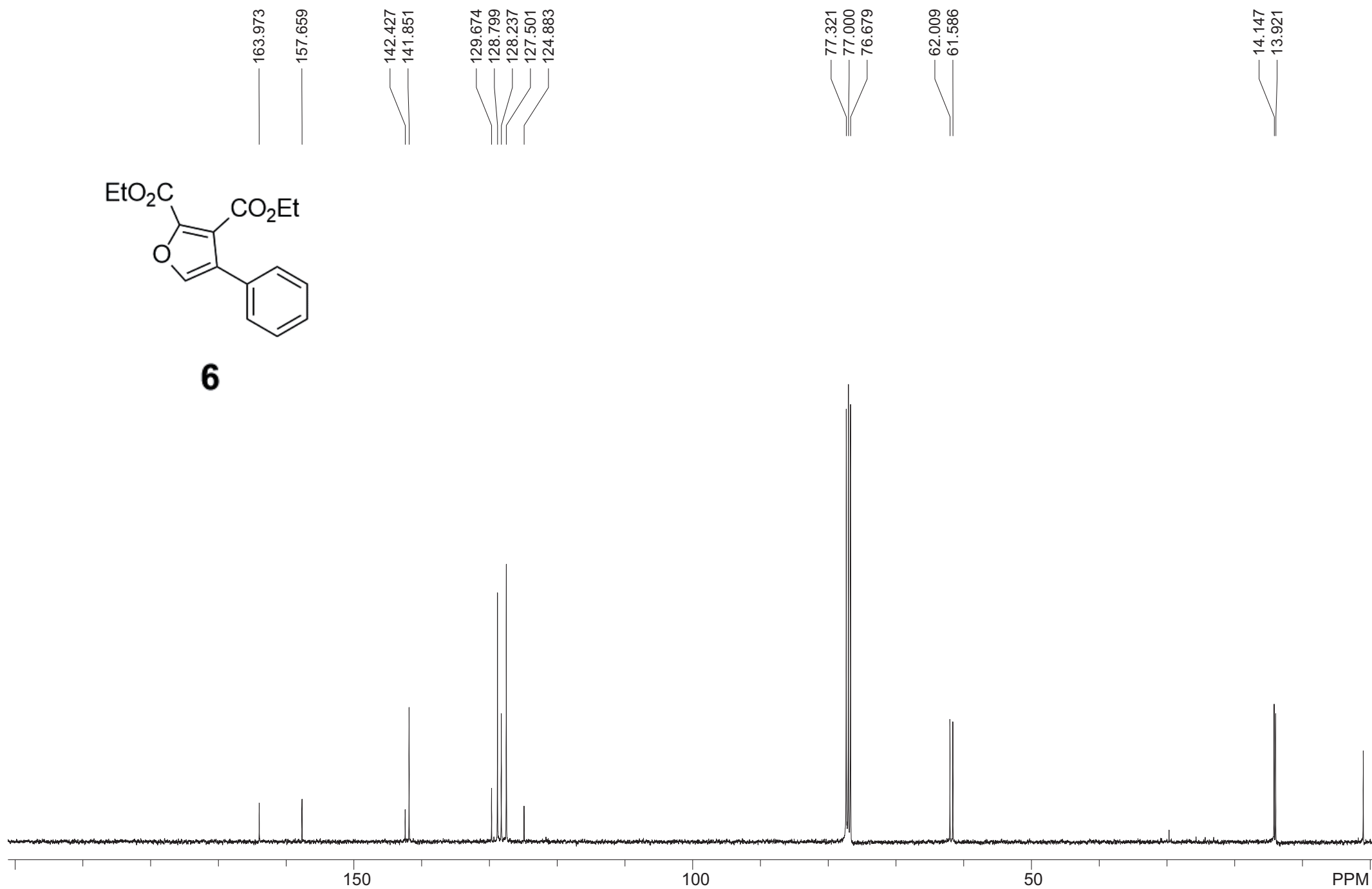


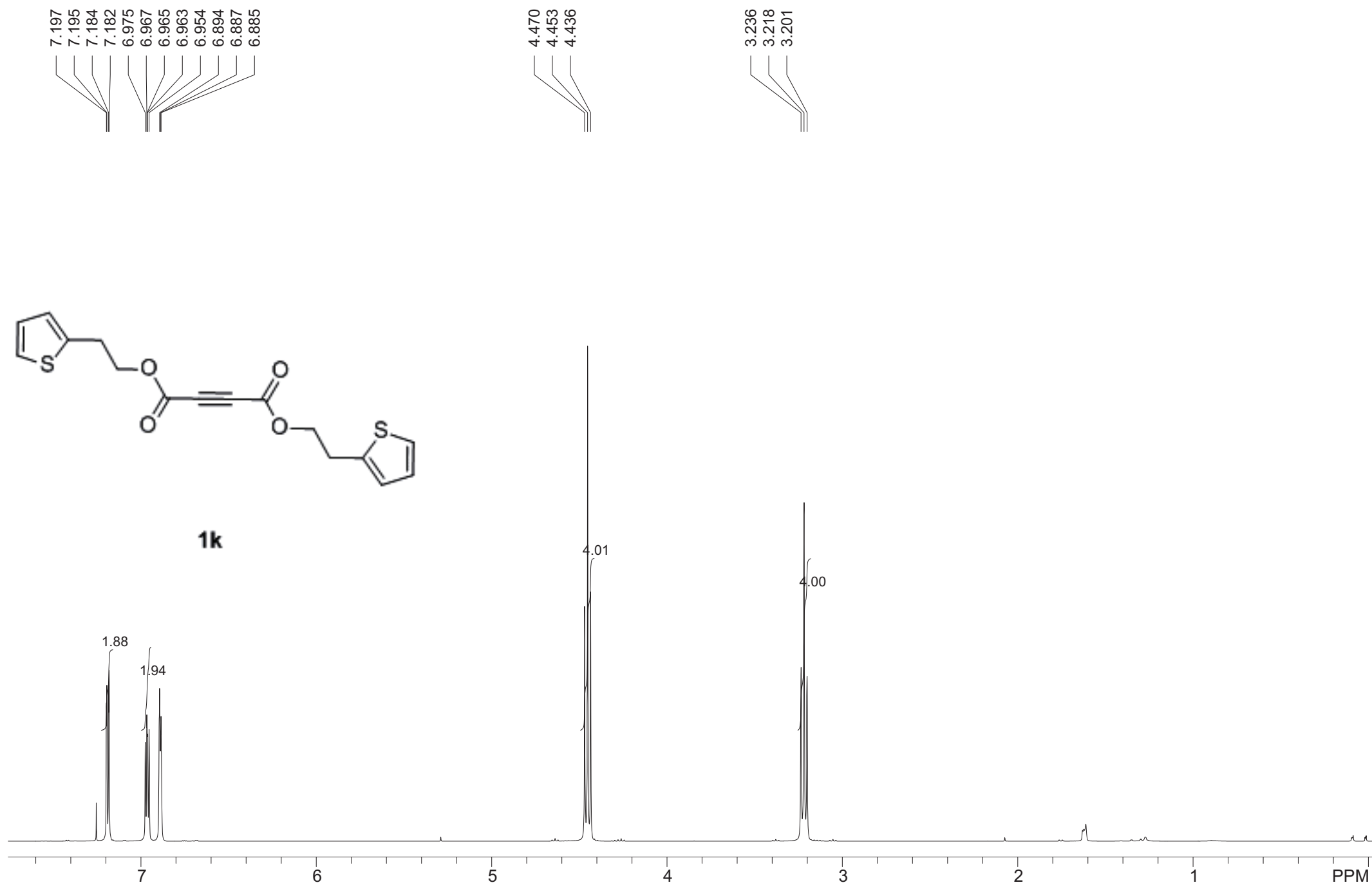
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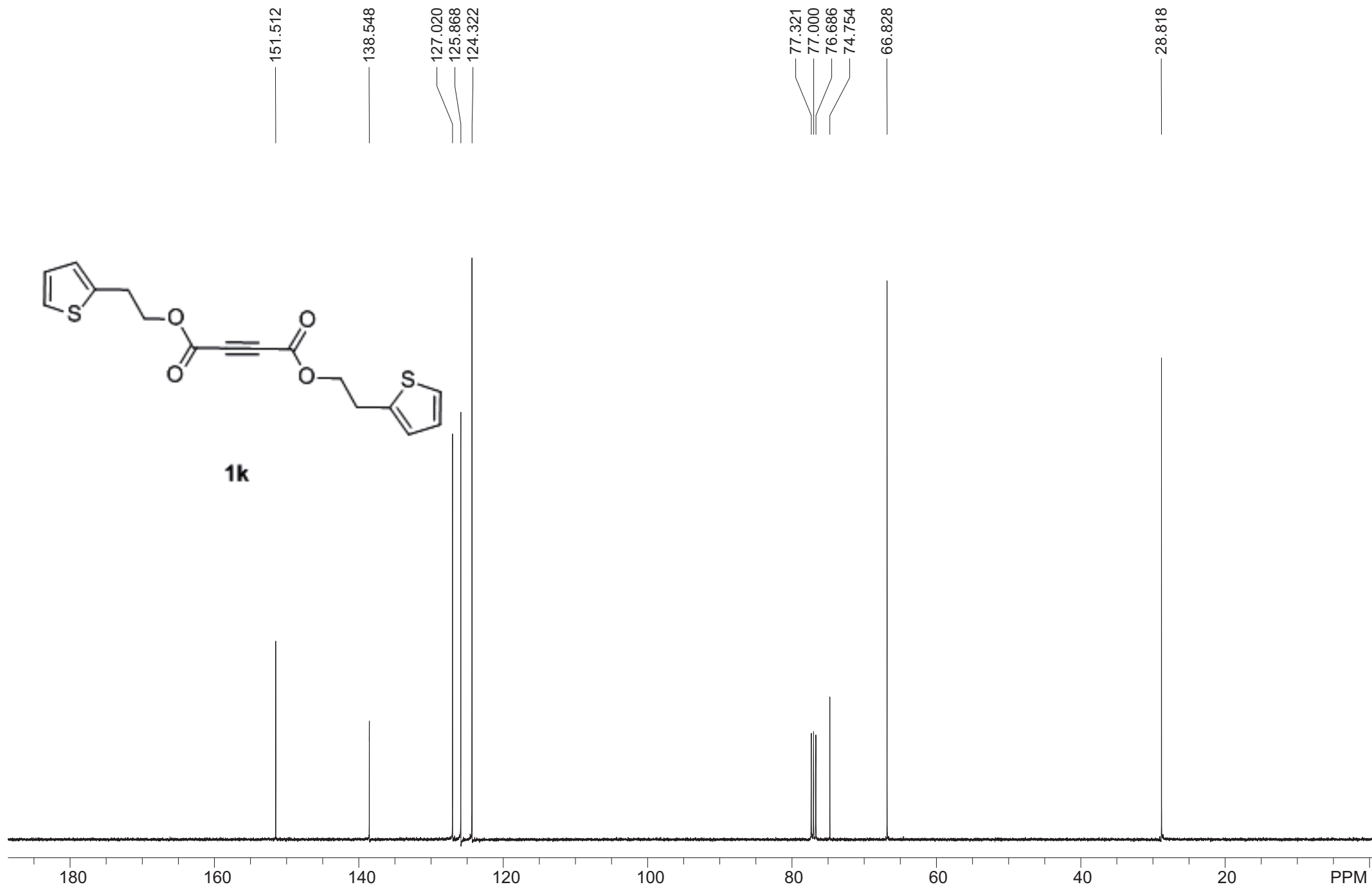


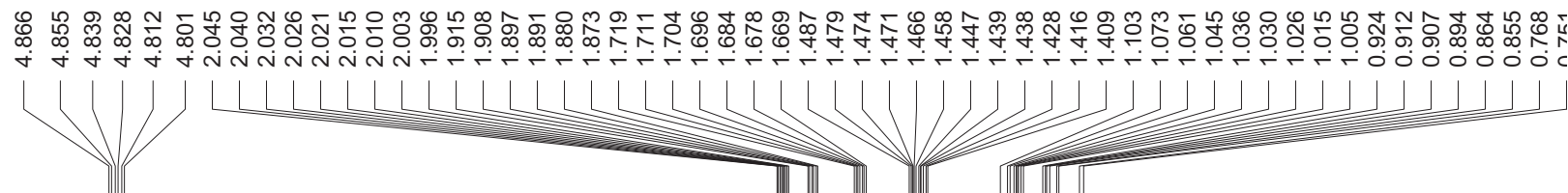
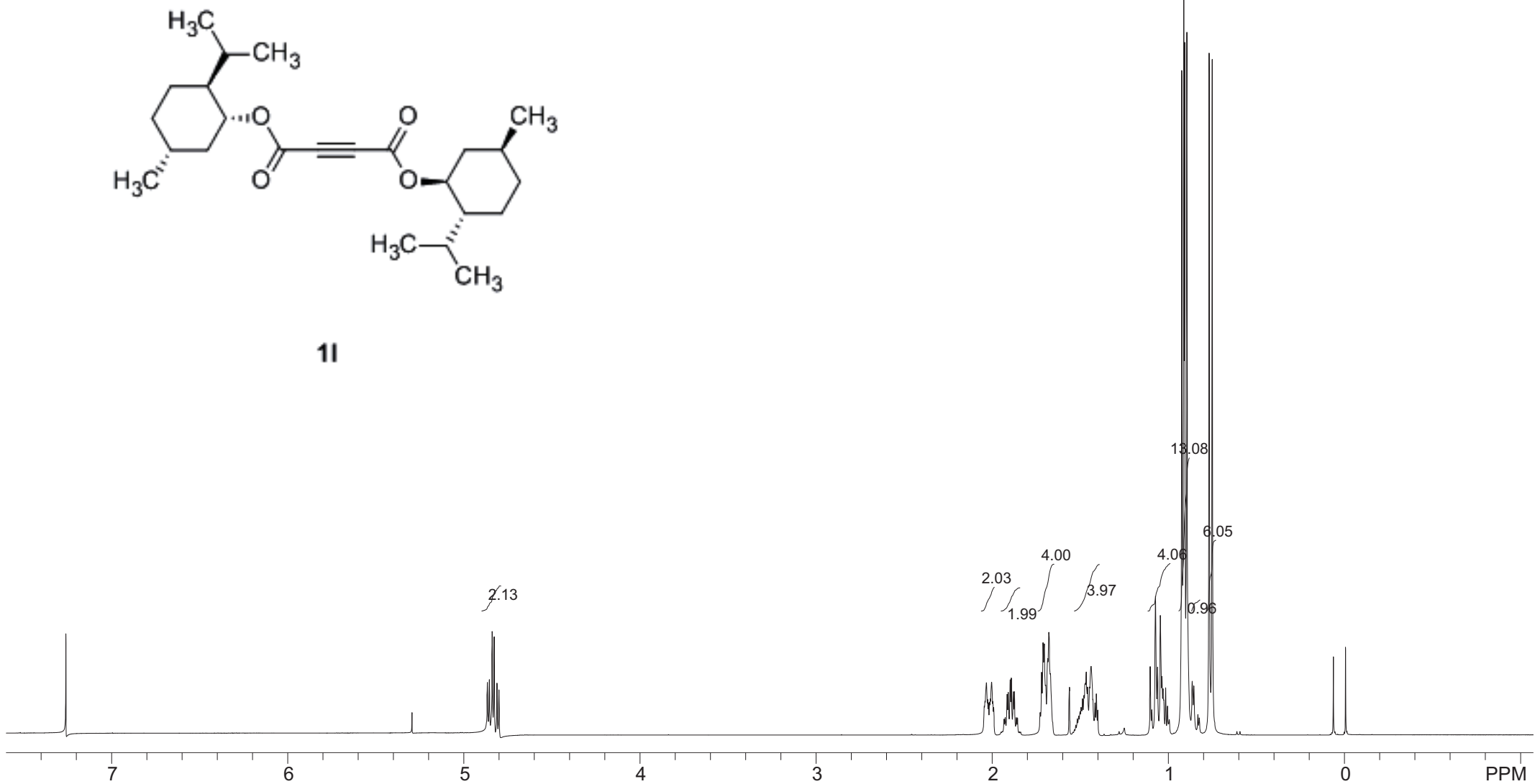


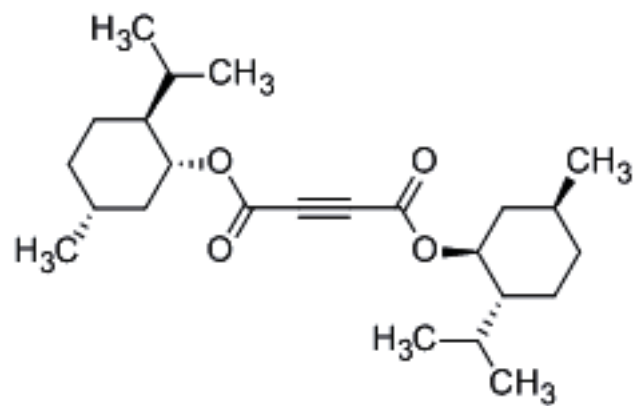
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11

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23.211

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16.058

