Highly Enantioselective δ–Protonation and Formal [3+3] Annulation Promoted by N-Heterocyclic Carbene

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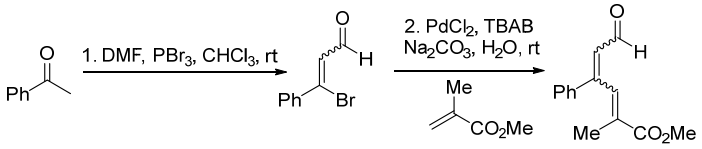
Part 1: General Information

Unless otherwise specified, all reactions were carried out under an Argon atmosphere in an oven dried sealed tube, with dry, freshly distilled solvents in anhydrous conditions. THF was distilled from Na and used directly. Reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. The silica gel (200-300 meshes) was used for column chromatography, and the distillation range of petroleum was 60-90 °C. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 600 or 400 MHz instrument in $CDCl_3$, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. The high-resolution mass spectra (HRMS) were measured on a Thermo Q-Exactive spectrometer by ESI, and mass analyzer type is Oribitrap. Data collections for crystal structure were performed at 295.13 K using Cu Kα (λ = 1.54184) radiation on a SuperNova, Dual, Cu at zero, Eos diffractometer. The determination of enantiomeric excess was performed via chiral HPLC analysis Thermo Ulti Mate 3000 HPLC, (RIGOL) L-3000 or Agilent 1260 Infinity II. Optical rotations were measured by Rudolph Research Analytical Autopol-I instrument, cell length = 1 dm, concentrations (c) are quoted in g/100 mL, sodium D line (589 nm). NHC catalysts **A**-**E** were purchased from Energy Chemical and used as received. Enamines,[1] acetophenone-derived ketamine[2] and cyclic imine[3] were prepared according to the reported literature procedures.

Part 2: Experimental Section.

1. General procedure for the preparation of enal substrates (**1a** as an example)

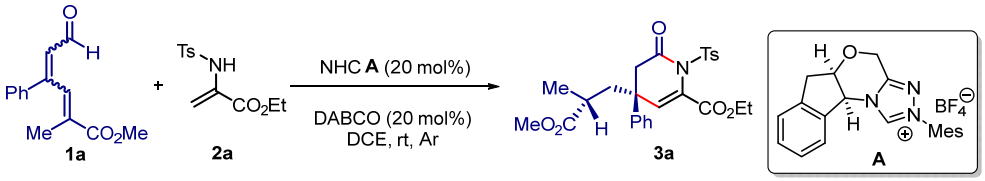


DMF (2 mL, 26 mmol) in 25 mL dry $CHCl_3$ was added PBr_3 (2.2 mL, 23 mmol) dropwise at 0 °C, and white solid precipitated during the addition process. The suspension was stirred at room temperature for further 30 min, and acetophenone (10 mmol) in 5 mL dry $CHCl_3$ was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and stirred for about 8 hours. After completely consumption of acetophenone determined by TLC, the mixture was poured into ice water, and $NaHCO_3$ were added to neutralize to PH≈6. After extraction with CH_2Cl_2, the organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced

pressure and afford the crude product of β-bromoenal. To the β-bromoenal was added methyl methacrylate (40 mmol), $PdCl_2$ (177 mg, 1 mmol), TBAB (3.2 g, 10 mmol), Na_2CO_3 (4.2 g, 40 mmol) and H_2O (50 mL). The mixture was stirred for 3 hours, and then quenched with saturated NH_4Cl solution, extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by silica gel column chromatography to afford the corresponding α,β-γ,δ-diunsaturated enal **1a** in 40% yield, and used for next reaction immediately.

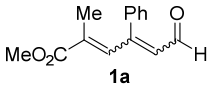
The other α,β-γ,δ-diunsaturated enals (**1b-1f, 1h-1p**) were prepared according to the standard procedure by using the corresponding β-bromoenals and olefins in 25%-50% yields.

2. General procedure for the catalytic reactions (**3a** as an example)



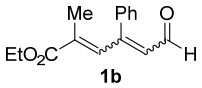
A dry 25 mL Schlenk tube with stir bar was charged with 2-aminoacrylate **2a** (27 mg, 0.1 mmol, 1.0 equiv), NHC **A** (8.4 mg, 0.02 mmol, 20 mol %), DABCO (2.2 mg, 0.02 mmol, 20 mol %). The tube was evacuated, and refilled with argon. Then enals **1a** (23 mg, 0.1 mmol, 1.0 equiv) was added and the mixture was dissolved with newly distilled solvent DCE (1.0 mL). The mixture was stirred at room temperature for 12 hours when the substrate was consumed completely (monitored by TLC). The reaction mixture was concentrated under vacuum and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford product **3a** as white solid (38 mg, 76% yield).

Part 3: Characterization of substrates and products.



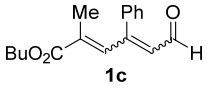
1a, Colorless oil, 40% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.80 (d, J = 8.4 Hz, 1H),7.60-7.59 (m, 1H), 7.52-7.49 (m, 2H), 7.46-7.40 (m, 3H), 6.54 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H), 1.87 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.0, 167.1, 155.4, 136.2, 135.0, 134.1, 130.8, 128.9, 127.0, 126.7, 52.3, 14.4; **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{14}H_{15}O_3^+$ 231.1016; Found

231.1010.



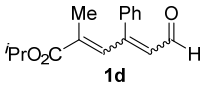
1b

1b, Colorless oil, 42% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.80 (d, J = 8.4 Hz, 1H), 7.58 (s, 1H), 7.51-7.49 (m, 2H), 7.46-7.41 (m, 3H), 6.53 (d, J = 8.0 Hz, 1H), 4.31 (d, J = 7.2 Hz, 2H), 1.86 (d, J = 1.2 Hz, 3H), 1.37 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.2, 166.7, 155.7, 136.5, 135.4, 133.9, 130.9, 129.1, 127.2, 126.8, 61.4, 14.4, 14.2; **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{15}H_{16}NaO_3^+$ 267.0992; Found 267.0995.



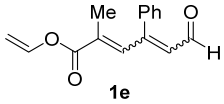
1c

1c, Colorless oil, 38% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.80 (d, J = 8.4 Hz, 1H),7.58 (s, 1H), 7.51-7.49 (m, 2H), 7.46-7.41 (m, 3H), 6.53 (d, J = 8.4 Hz, 1H), 4.26 (t, J = 6.4 Hz, 2H), 1.86 (d, J = 1.2 Hz, 3H), 1.76-1.68 (m, 2H), 1.48-1.40 (m, 2H), 0.98 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.2, 166.8, 155.7, 136.4, 135.5, 133.9, 130.9, 127.2, 126.9, 65.3, 30.6, 19.2, 14.5, 13.7; **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{17}H_{20}NaO_3^+$ 295.1305; Found 295.1308.



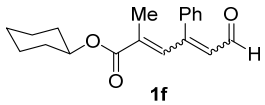
1d

1d, Colorless oil, 35% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.80 (d, J = 8.0 Hz, 1H),7.56 (s, 1H), 7.52-7.49 (m, 2H), 7.47-7.42 (m, 3H), 6.53 (d, J = 8.0 Hz, 1H), 5.19-5.12 (m, 1H), 1.86 (d, J = 1.2 Hz, 3H), 1.35 (d, J = 6.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.3, 166.3, 155.9, 136.5, 135.8, 133.5, 130.9, 129.0, 127.2, 126.8, 68.9, 21.8, 14.4; **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{16}H_{18}NaO_3^+$ 281.1148; Found 281.1152.



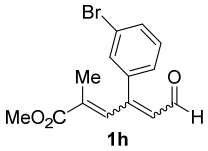
1e

1e, Colorless oil, 50% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.81 (d, J = 8.0 Hz, 1H),7.71 (s, 1H), 7.51-7.39 (m, 5H), 6.55 (d, J = 14.0 Hz, 1H), 5.04 (d, J = 14.0 Hz, 1H), 4.71 (d, J = 8.0 Hz, 1H), 1.90 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.9, 163.7, 155.2, 141.2, 136.1, 135.8, 134.1, 131.0, 129.1, 127.2, 127.0, 98.7, 14.4; **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{15}H_{14}NaO_3^+$ 265.0835; Found 265.0838.



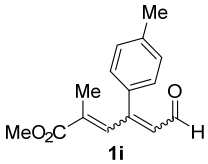
1f

1f, Colorless oil, 40% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.81 (d, J = 8.0 Hz, 1H),7.57 (s, 1H), 7.52-7.50 (m, 2H), 7.46-7.41 (m, 3H), 6.54 (d, J = 8.0 Hz, 1H), 4.97-4.91 (m, 1H), 1.95-1.90 (m, 2H), 1.86 (s, 3H), 1.76-1.75 (m, 3H), 1.60-1.51 (m, 3H), 1.49-1.39 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.3, 166.0, 155.9, 136.4, 135.9, 133.5, 130.8, 129.0, 127.1, 126.8, 73.6, 31.5, 25.3, 23.5, 14.4; **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{19}H_{22}NaO_3^+$ 321.1461; Found 321.1464.



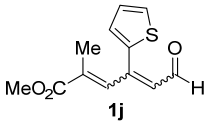
1h

1h, Colorless oil, 35% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.79 (d, J = 8.0 Hz, 1H),7.59 (d, J = 1.6 Hz, 1H), 7.54 (s, 1H), 7.43-7.40 (m, 2H), 7.32-7.29 (m, 1H), 6.50 (d, J = 8.4 Hz, 1H), 3.87 (s, 3H), 1.86 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.8, 167.0, 153.8, 138.6, 135.7, 133.7, 133.3, 130.6, 130.1, 127.8, 125.6, 123.2, 52.5, 14.6; **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{14}H_{14}BrO_3^+$ 309.0121; Found 309.0108.



1i

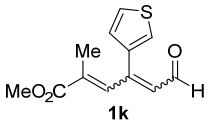
1i, Colorless oil, 40% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.78 (d, J = 8.0 Hz, 1H), 7.54 (s, 1H), 7.40 (d, J = 8.8 Hz, 1H), 7.23 (d, J = 8.8 Hz, 1H), 6.53 (d, J = 9.2 Hz, 1H), 3.87 (s, 3H), 2.40 (s, 3H), 1.86 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.2, 167.3, 155.6, 141.6, 134.9, 134.4, 133.4, 129.7, 127.1, 125.9, 52.4, 21.4, 14.5; **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{15}H_{16}NaO_3^+$ 267.0992; Found 267.0993.



1j

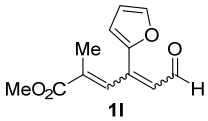
1j, Colorless oil, 54% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (d, J = 8.4 Hz, 1H),7.58(s, 1H), 7.51 (d, J = 4.8 Hz, 1H), 7.31 (d, J = 4.0 Hz, 1H), 7.11-7.09 (m, 1H), 6.47 (d, J = 8.0 Hz, 1H), 3.87 (s, 3H), 1.90 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.5, 167.1, 148.9, 140.7, 135.5, 133.0, 129.8, 128.6, 124.0, 52.5, 14.6; **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{12}H_{13}O_3S^+$

237.0580; Found 237.0574.



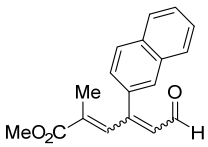
1k

1k, Colorless oil, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.76 (d, J = 8.4 Hz, 1H),7.60 (s, 1H), 7.52-7.518 (m, 1H), 7.42-7.40 (m, 1H), 7.32 (dd, J = 4.8, 0.8 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H), 1.88 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.4, 167.2, 149.8, 238.5, 134.8, 133.8, 127.8, 127.5, 125.3, 125.0, 52.5, 14.4; **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{12}H_{12}NaO_3S^+$ 259.0399; Found 259.0403.



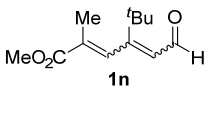
1l

1l, Colorless oil, 46% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (d, J = 8.4 Hz, 1H),7.59 (d, J = 1.2 Hz, 1H), 7.48 (s, 1H), 6.68 (d, J = 3.2 Hz, 1H), 6.57-6.51 (m, 2H), 6.47 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H), 1.89 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.7, 167.2, 150.2, 146.0, 143.2, 135.9, 131.1, 122.3, 115.3, 112.8, 52.4, 14.5; **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{12}H_{13}O_4^+$ 221.0808; Found 221.0801.



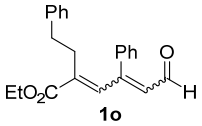
1m

1m, Colorless oil, 45% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.85 (d, J = 8.0 Hz, 1H),7.93-7.85 (m, 4H), 7.71 (s, 1H), 7.65-7.62 (m, 1H), 7.57-7.53 (m, 2H), 6.68 (d, J = 8.0 Hz, 1H), 3.90 (s, 3H), 1.89 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.7, 167.2, 150.2, 146.0, 143.2, 135.9, 131.1, 122.3, 115.3, 112.8, 52.4, 14.5; **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{18}H_{17}O_3^+$ 281.1172; Found 281.1176.



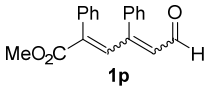
1n

1n, Colorless oil, 30% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.53 (dd, J = 8.0, 2.4 Hz, 1H),7.40 (s, 1H), 6.04 (d, J = 8.0 Hz, 1H), 3.83 (d, J = 2.8 Hz, 3H), 1.83 (s, 3H), 1.18 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.7, 167.2, 150.2, 146.0, 143.2, 135.9, 131.1, 122.3, 115.3, 112.8, 52.4, 14.5; **HRMS (ESI) m/z**: $[M+K]^+$ Calcd for $C_{12}H_{18}KO_3^+$ 249.0888; Found 249.1100



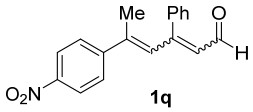
1o

1o, Colorless oil, 38% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.77 (d, J = 8.0 Hz, 1H),7.61 (s, 1H), 7.45-7.37 (m, 5H), 7.18-7.10 (m, 3H), 6.95 (d, J = 7.2 Hz, 2H), 6.44 (dd, J = 8.0, 1.2 Hz, 1H), 4.34 (q, J = 7.2 Hz, 2H), 2.68-2.64 (m, 2H), 2.55-2.51 (m, 2H), 1.40 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.9, 166.4, 155.4, 140.7, 138.8, 136.7, 134.5, 130.8, 128.9, 128.3, 127.2, 126.8, 126.1, 61.3, 34.3, 30.7, 14.2; **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{22}H_{22}NaO_3^+$ 357.1461; Found 357.1464.



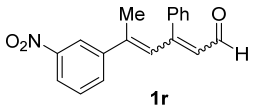
1p

1p, Colorless oil, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.79 (d, J = 8.0 Hz, 1H),7.86 (s, 1H), 7.50-7.48 (m, 2H), 7.43-7.36 (m, 4H),7.20-7.18 (m, 2H), 7.11-7.08 (m, 2H), 6.23 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.4, 166.7, 154.7, 140.0, 136.8, 125.8, 133.5, 130.7, 129.1, 128.9, 128.4, 128.1, 127.2, 126.3, 52.7; **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{19}H_{16}NaO_3^+$ 315.0992; Found 315.0997



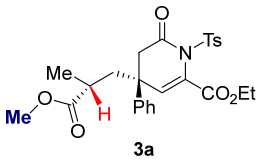
1q

1q, Colorless oil, 25% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.91 (d, J = 7.6 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.58-7.56 (m, 2H), 7.48-7.43 (m, 3H), 6.87 (s, 1H), 6.59 (dd, J = 8.0, 1.2 Hz, 1H), 2.11 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ192.4, 156.9, 147.7, 147.5, 142.0, 137.3, 130.9, 129.1, 127.3, 127.2, 126.7, 125.7, 123.9, 17.7; **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{18}H_{15}NNaO_3^+$ 316.0944; Found 316.0948.



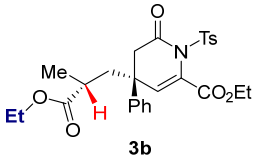
1r

1r, Colorless oil, 28% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.92 (d, J = 8.0 Hz, 1H),8.42 (s, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.63-7.56 (m, 3H), 7.48-7.45 (m, 3H), 6.86 (s, 1H), 6.59 (d, J = 8.0 Hz, 1H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.5, 157.0, 148.5, 143.0, 141.7, 137.5, 131.8, 130.8, 129.6, 129.0, 127.3, 127.2, 124.7, 123.0, 120.8, 17.8; **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{18}H_{15}NNaO_3^+$ 316.0944; Found 316.0950.



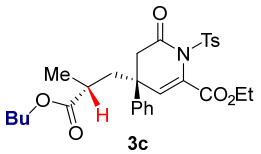
3a

3a, Prepared according to the general procedure in 0.1 mmol scale, 76% yield, 38 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.6 Hz, 2H), 7.29-7.23 (m, 4H), 7.19-7.17 (m, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.80 (s, 1H), 4.47-4.34 (m, 2H), 3.52 (s, 3H), 2.94 (d, J = 15.6 Hz, 1H), 2.67 (d, J = 16.0 Hz, 1H), 2.40-2.31 (m, 5H), 1.69 (d, J = 11.6 Hz, 1H), 1.43 (t, J = 7.6 Hz, 3H), 1.01 (d, J = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.2, 168.7, 163.0, 144.8, 141.1, 134.9, 132.3, 131.4, 129.3, 128.9, 128.87, 126.3, 62.2, 51.8, 44.9, 44.6, 42.1, 35.7, 21.6, 19.5, 13.9. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{26}H_{30}NO_7S^+$ 500.1737; Found 500.1743. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 21.0 min (major), 26.1 min (minor), 98% ee. **Optical rotation**: $[\alpha]_{25}^D$ = -3 (c = 1.0 in EtOAc)



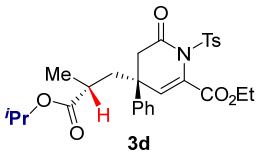
3b

3b, Prepared according to the general procedure in 0.1 mmol scale, 60% yield, 31 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1).**^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (d, J = 7.8 Hz, 2H), 7.25-7.24 (m, 3H), 7.16-7.15 (m, 2H), 7.09 (d, J = 7.8 Hz, 2H), 6.79 (s, 1H), 6.43 (d, J = 7.2 Hz, 1H), 4.43-4.34 (m, 2H), 3.93 (q, J = 7.2 Hz, 2H), 2.93 (d, J = 15.6 Hz, 1H), 2.65 (d, J = 16.2 Hz, 1H), 2.37 (s, 3H), 2.29-2.26 (m, 1H), 1.66-1.62 (m, 3H), 1.41 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H), 0.98 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 175.9, 168.7, 163.1, 144.7, 141.3, 135.0, 132.5, 131.6, 129.3, 129.1, 128.94, 128.9, 127.5, 126.5, 126.4, 62.2, 60.7, 44.8, 42.3, 35.9, 21.6, 19.6, 14.0, 13.95. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{27}H_{32}NO_7S^+$ 514.1894; Found 514.1891. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 8.9 min (major), 11.0 min (minor), 98% ee. **Optical rotation**: $[\alpha]_{25}^D$ = +21 (c = 1.0 in EtOAc)



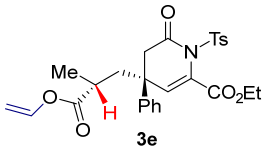
3c

3c, Prepared according to the general procedure in 0.1 mmol scale, 60% yield, 32 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 (d, J = 7.2 Hz, 2H), 7.25-7.24 (m, 3H),7.16-7.15 (m, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.78 (s, 1H), 4.41-4.35 (m, 2H), 3.91-3.84 (m, 2H), 2.93 (d, J = 16.2 Hz, 1H), 2.65 (d, J = 16.2 Hz, 1H), 2.36 (s, 3H), 2.30-2.27 (m, 1H), 1.67-1.63 (m, 2H), 1.55-1.49 (m, 2H), 1.41 (t, J = 7.2 Hz, 3H), 1.35-1.29 (m, 2H), 0.98 (d, J = 7.2 Hz, 3H), 0.92 (t, J = 7.8 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 175.9, 168.7, 163.1, 144.7, 141.3, 135.2, 132.5, 131.5, 129.3, 128.93, 128.92, 127.5, 126.4, 64.6, 62.2, 44.9, 44.8, 42.3, 35.9, 30.4, 21.6, 19.6, 19.1, 14.0, 13.6. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{29}H_{36}NO_7S^+$ 542.2207; Found 542.2210. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 7.7 min (major), 9.3 min (minor), 99% ee. **Optical rotation**: $[\alpha]_{25}^D$ = -29 (c = 1.0 in EtOAc)



3d

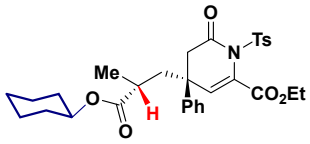
3d, Prepared according to the general procedure in 0.1 mmol scale, 55% yield, 29 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (d, J = 7.2 Hz, 2H), 7.25-7.24 (m, 3H), 7.15-7.14 (m, 2H), 7.06 (d, J = 8.4 Hz, 2H), 6.80 (s, 1H), 4.81 (hept, J = 6.0 Hz, 1H), 4.41-4.35 (m, 2H), 2.93 (d, J = 16.2 Hz, 1H), 2.64 (d, J = 16.2 Hz, 1H), 2.43-2.31 (m, 4H), 2.23-2.20 (m, 1H), 1.60 (dd, J = 15.0, 2.4 Hz, 1H), 1.41 (t, J = 7.2 Hz, 3H), 1.17 (dd, J = 14.4, 6.0 Hz, 6H), 0.96 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 175.5, 168.7, 163.1, 144.6, 141.4, 135.0, 132.6, 132.2, 129.2, 128.94, 128.90, 127.5, 126.4, 68.1, 62.2, 44.8, 42.4, 42.2, 36.0, 21.6, 19.7, 14.0. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{28}H_{34}NO_7S^+$ 528.2050; Found 528.2058. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 7.5 min (major), 8.9 min (minor), 98% ee. **Optical rotation**: $[\alpha]_{25}^D$ = -27 (c = 1.0 in EtOAc)



3e

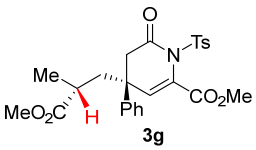
3e, Prepared according to the general procedure in 0.1 mmol scale, 33% yield, 17 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (600 MHz, $CDCl_3$)

δ 7.65 (d, J = 7.8 Hz, 2H), 7.26-7.23 (m, 3H), 7.15-7.14 (m, 2H), 7.08 (d, J = 7.8 Hz, 2H), 6.97 (dd, J = 13.8, 6.6 Hz, 1H), 6.78 (s, 1H), 4.81 (dd, J = 14.4, 1.2 Hz, 1H), 4.53 (d, J = 6.6 Hz, 1H), 4.42-4.35 (m, 2H), 2.96 (d, J = 15.6 Hz, 1H), 2.66 (d, J = 16.2 Hz, 1H), 2.43-2.36 (m, 5H), 1.73-1.68 (m, 1H), 1.41 (t, J = 6.6 Hz, 3H), 1.02 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.8, 168.6, 163.1, 144.8, 141.1, 140.9, 135.0, 132.6, 131.5, 129.3, 129.0, 128.9, 127.6, 126.4, 98.1, 62.3, 44.6, 42.2, 35.6, 29.7, 21.6, 19.3, 14.0. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{27}H_{30}NO_7S^+$ 512.1737; Found 512.1742. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 9.8 min (major), 12.1 min (minor), 99% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = -9 (c = 1.0 in EtOAc)



3f

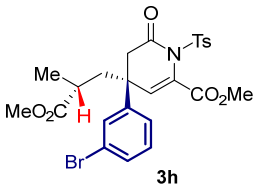
3f, Prepared according to the general procedure in 0.1 mmol scale, 55% yield, 31 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (d, J = 7.2 Hz, 2H), 7.24-7.22 (m, 3H), 7.16-7.14 (m, 2H), 7.05 (d, J = 7.8 Hz, 2H), 6.81 (s, 1H), 4.59-4.58 (m, 1H), 4.39 (q, J = 7.2 Hz, 2H), 2.93 (d, J = 15.6 Hz, 1H), 2.65 (d, J = 16.2 Hz, 1H), 2.45-2.31 (m, 4H), 2.26-2.20 (m, 1H), 1.78-1.73 (m, 2H), 1.69-1.64 (m, 2H), 1.61 (dd, J = 14.4, 2.4 Hz, 1H), 1.41 (t, J = 7.2 Hz, 3H), 1.38-1.29 (m, 5H), 0.97 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 175.4, 168.7, 163.0, 144.6, 141.4, 135.0, 132.6, 131.6, 129.2, 128.9, 128.88, 127.4, 126.4, 72.9, 62.2, 44.9, 44.7, 42.4, 36.0, 31.3, 25.3, 23.6, 21.6, 19.8, 14.0. **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{31}H_{37}NNaO_7S^+$ 590.2183; Found 590.2186. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 7.2 min (major), 8.7 min (minor), 98% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = -15 (c = 1.0 in EtOAc)



3g

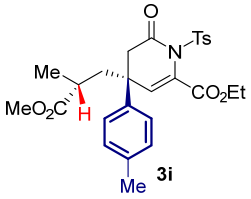
3g, Prepared according to the general procedure in 0.1 mmol scale, 75% yield, 36 mg, white soild, m. p. 59.6-61.3 ºC, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 7.8 Hz, 3H), 7.17-7.15 (m, 2H), 7.13 (d, J = 7.8 Hz, 2H), 6.79 (s, 1H), 3.92 (s, 3H), 3.50 (s, 3H), 2.92 (d, J = 15.6 Hz, 1H), 2.65 (d, J = 16.2

Hz, 1H), 2.38 (s, 3H), 2.36-2.30 (m, 2H), 1.67 (d, J = 11.4 Hz, 1H), 0.99 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 176.2, 168.7, 163.5, 144.9, 141.1, 135.0, 132.1, 131.8, 129.4, 129.0, 128.9, 127.5, 126.3, 52.8, 51.8, 45.0, 44.6, 42.3, 35.8, 21.6, 19.5. **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{25}H_{27}NNaO_7S^+$ 508.1400; Found 508.1399. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 14.6 min (major), 18.1 min (minor), 98% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = -34 (c = 1.0 in EtOAc)



3h

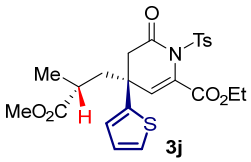
3h, Prepared according to the general procedure in 0.1 mmol scale, 43% yield, 24 mg, white soild, m. p.: 72.3-74.2 ºC, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 2H), 7.37 (dt, J = 7.2, 1.6 Hz, 1H), 7.19 (s, 3H), 7.14-7.11 (m, 4H), 6.73 (s, 1H), 3.93 (s, 3H), 3.51 (s, 3H), 2.89 (d, J = 15.6 Hz, 1H), 2.61 (d, J = 16.0 Hz, 1H), 2.40 (s, 3H), 2.34-2.30 (m, 2H), 1.67-1.65 (m, 1H), 1.02 (d, J = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.0, 168.1, 163.4, 145.2, 143.7, 134.5, 132.5, 131.1, 130.7, 130.5, 129.3, 129.2, 129.0, 125.3, 123.1, 52.9, 52.0, 44.8, 44.3, 42.1, 35.7, 21.7, 19.6. **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{25}H_{26}BrNNaO_7S^+$ 586.0506; Found 586.0509. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 15.3 min (major), 17.9 min (minor), 99% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = -15 (c = 1.0 in EtOAc).



3i

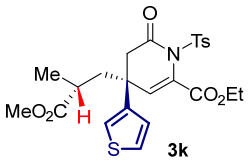
3i, Prepared according to the general procedure in 0.1 mmol scale, 56% yield, 29 mg, white soild, m. p.: 52.2-53.6 ºC, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.6 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.06-7.01 (m, 4H), 6.76 (s, 1H), 4.45-4.32 (m, 2H), 3.51 (s, 3H), 2.89 (d, J = 16.0 Hz, 1H), 2.61 (d, J = 16.0 Hz, 1H), 2.38 (s, 3H), 2.33-2.31 (m, 5H), 1.67-1.60 (m, 1H), 1.41 (t, J = 6.8 Hz, 3H), 0.99 (d, J = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.3, 168.8, 163.1, 144.7, 138.0, 137.1, 135.0, 132.2, 131.7, 129.5, 129.4, 128.8, 126.2, 62.2, 51.9, 45.0, 44.8, 41.9, 35.7, 21.6, 21.0, 19.5, 14.0. **HRMS (ESI)**

m/z: $[M+Na]^+$ Calcd for $C_{27}H_{31}NNaO_7S^+$ 536.1713; Found 536.1723. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 8.9 min (major), 11.3 min (minor), 98% ee. **Optical rotation**: $[\alpha]_{25}^D$ = -42 (c = 1.0 in EtOAc).



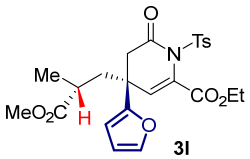
3j

3j, Prepared according to the general procedure in 0.1 mmol scale, 62% yield, 31 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, J = 7.8 Hz, 2H), 7.24-7.22 (m, 3H), 6.90 (m, 1H), 6.84 (d, J = 3.0 Hz, 1H), 6.66 (s, 1H), 4.43-4.34 (m, 2H), 3.65 (s, 3H), 2.85 (d, J = 16.2 Hz, 1H), 2.69 (d, J = 16.2 Hz, 1H), 2.43-2.34 (m, 5H), 1.68 (d, J = 13.8 Hz, 1H), 1.41 (t, J = 7.2 Hz, 3H), 1.04 (d, J = 6.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 176.2, 168.2, 162.9, 145.9, 145.1, 135.3, 132.8, 129.7, 129.2, 129.1, 127.1, 124.9, 124.8, 62.3, 52.0, 47.6, 45.3, 41.0, 36.1, 21.7, 19.4, 14.0. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{24}H_{28}NO_7S_2^+$ 506.1302; Found 506.1307. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 10.8 min (major), 12.4 min (minor), 99% ee. **Optical rotation**: $[\alpha]_{25}^D$ = -17 (c = 1.0 in EtOAc)

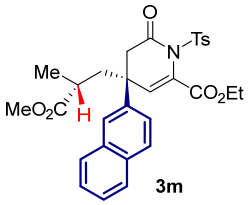


3k

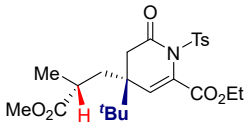
3k, Prepared according to the general procedure in 0.1 mmol scale, 70% yield, 35 mg, yellow oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.31 (dd, J = 4.8, 2.8 Hz, 1H), 6.95-6.92 (m, 2H), 6.66 (s, 1H), 4.44-4.31 (m, 2H), 3.57 (s, 3H), 2.85 (d, J = 16.0 Hz, 1H), 2.65 (d, J = 16.0 Hz, 1H), 2.40 (s, 3H), 2.36-2.30 (m, 2H), 1.64-1.58 (m, 1H), 1.40 (t, J = 7.2 Hz, 3H), 1.01 (d, J = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.2, 168.7, 163.1, 145.1, 141.9, 135.1, 132.3, 130.3, 129.5, 129.1, 127.0, 125.7, 121.5, 62.2, 51.9, 45.7, 44.2, 40.2, 35.7, 21.7, 19.5, 14.0. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{24}H_{28}NO_7S2^+$ 506.1302; Found 506.1305. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 12.1 min (major), 14.8 min (minor), 99% ee. **Optical rotation**: $[\alpha]_{25}^D$ = -12 (c = 1.0 in EtOAc)



3l, Prepared according to the general procedure in 0.1 mmol scale, 61% yield, 30 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 1H), 7.34-7.26 (m, 4H), 6.57 (s, 1H), 6.25 (dd, J = 3.2, 2.0 Hz, 1H), 6.07 (d, J = 3.2 Hz, 1H), 4.42-4.33 (m, 2H), 3.62 (s, 3H), 2.80 (d, J = 16.0 Hz, 1H), 2.66 (d, J = 16.0 Hz, 1H), 2.43 (s, 1H), 2.38-2.30 (m, 2H), 1.71 (dd, J = 18.8, 8.0 Hz, 1H), 1.40 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.0, 168.5, 163.0, 153.2, 145.3, 142.6, 135.2, 132.5, 129.8, 129.1, 127.5, 110.3, 106.9, 62.2, 52.0, 44.2, 41.6, 39.4, 36.0, 21.7, 19.1, 14.0. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{24}H_{28}NO_8S^+$ 490.1530; Found 490.1537. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 9.6 min (major), 11.5 min (minor), 97% ee. **Optical rotation**: $[\alpha]_{25}^D$ = -21 (c = 1.0 in EtOAc)

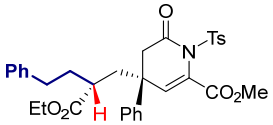


3m, Prepared according to the general procedure in 0.1 mmol scale, 72% yield, 40 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H),7.60 (d, J = 7.8 Hz, 1H), 7.53-7.46 (m, 2H), 7.39 (s, 1H), 7.31-7.23 (m, 4H), 6.89 (s, 1H), 6.43 (d, J = 7.2 Hz, 1H), 4.46-4.34 (m, 2H), 3.24 (s, 3H), 3.11 (d, J = 16.2 Hz, 1H), 2.69 (d, J = 15.6 Hz, 1H), 2.45-2.41 (m, 1H), 2.38-2.31 (m, 1H), 2.02 (s, 3H), 1.72 (dd, J = 14.4, 2.4 Hz, 1H), 1.42 (t, J = 7.2 Hz, 3H), 0.99 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 176.1, 168.5, 163.1, 144.6, 138.7, 134.4, 133.1, 132.7, 132.6, 131.8, 129.7, 128.9, 128.8, 128.3, 128.1, 127.4, 126.4, 126.38, 125.0, 124.7, 62.3, 51.6, 45.2, 43.9, 42.3, 35.6, 21.3, 19.7, 14.0. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{30}H_{32}NO_7S^+$ 550.1894; Found 550.1896. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 13.9 min (major), 17.9 min (minor), 99% ee. **Optical rotation**: $[\alpha]_{25}^D$ = -30 (c = 1.0 in EtOAc)



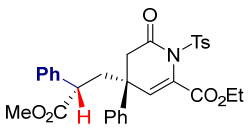
3n

3n, Prepared according to the general procedure in 0.1 mmol scale, 30% yield, 14 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). δ 8.10 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 5.89 (s, 1H), 4.41-4.32 (m, 2H), 3.64 (s, 3H), 2.53 (d, J = 17.4 Hz, 1H), 2.43 (s, 3H), 2.33 (d, J = 16.8 Hz, 1H), 2.08 (dd, J = 14.4, 7.8 Hz, 1H), 1.57-1.56 (m, 1H), 1.87 (t, J = 7.2 Hz, 3H), 1.17 (d, J = 7.2 Hz, 3H), 0.94 (s, 9H);**^{13}C NMR** (150 MHz, $CDCl_3$): δ 176.9, 170.2, 163.3, 145.3, 135.7, 132.9, 129.9, 129.1, 126.7, 62.0, 52.1, 44.5, 39.3, 38.6, 37.4, 36.5, 26.0, 21.7, 20.3. **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{24}H_{33}NO_7SNa^+$ 502.1870; Found 502.1874. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 9.1 min (major), 13.4 min (minor), 99% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = -1 (c = 1.0 in EtOAc).



3o

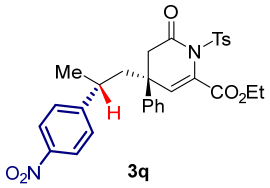
3o, Prepared according to the general procedure in 0.1 mmol scale, 52% yield, 31 mg, yellow soild, m.p.: 58.9-60.2 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.26-7.22 (m, 6H), 7.14-7.06 (m, 6H), 6.73 (s, 1H), 4.42-4.33 (m, 2H), 3.51 (s, 3H), 3.34-3.31 (m, 1H), 2.89-2.66 (m, 2H), 2.52 (d, J = 16.0 Hz, 1H), 2.37 (s, 3H), 2.14 (dd, J = 14.4, 5.2 Hz,1H), 1.40 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.4, 168.5, 163.0, 144.7, 141.1, 138.7, 125.0, 132.4, 131.3, 129.2, 129.0(2C), 128.9, 128.87, 127.6(2C), 126.3, 62.2, 52.3, 47.4, 44.5, 42.3(2C), 21.6, 14.0. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{33}H_{35}NO_7SNa^+$ 612.2026; Found 612.2018. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 15.7 min (major), 21.8 min (minor), 99% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = -41 (c = 1.0 in EtOAc)



3p

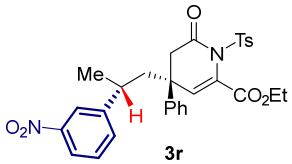
3p, Prepared according to the general procedure in 0.1 mmol scale, 73% yield, 41 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$)

δ 7.69 (d, J = 8.0 Hz, 2H), 7.26-7.19 (m, 6H), 7.14-7.09 (m, 4H), 7.03 (d, J = 7.6 Hz, 2H), 6.76 (s, 1H), 3.96-3.87 (m, 5H), 2.90 (d, J = 16.0 Hz, 1H), 2.63 (d, J = 16.0 Hz, 1H), 2.44-2.39 (m, 2H), 2.36-2.31 (m, 4H), 2.25-2.19 (m,1H), 1.83-1.7 (m, 2H), 1.54-1.43 (m, 1H), 1.19 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.1, 168.7, 163.5, 144.9, 141.0, 140.8, 134.9, 132.0, 131.9, 129.3, 129.0, 128.9, 128.4, 128.2, 127.5, 126.3, 126.0, 60.7, 52.8, 44.7, 43.2, 42.2, 41.1, 35.9, 33.1, 21.6, 14.0. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{31}H_{32}NO_7S^+$ 562.1894; Found 562.1898. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 19.7 min (major), 31.2 min (minor), 99% ee. **Optical rotation**: $[\alpha]_{25}^D$ = +5 (c = 1.0 in EtOAc)



3q

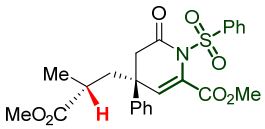
3q, Prepared according to the general procedure in 0.1 mmol scale, 70% yield, 39 mg, white soild, m.p.: 68.1-69.7 °C, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.26-7.25 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.4 Hz, 4H), 6.32 (s, 1H), 4.32-4.24 (m, 1H), 4.22-4.14 (m, 1H), 2.78-2.66 (m, 3H), 2.44-2.39 (m, 4H), 2.20 (dd, J = 14.4, 3.6 Hz, 1H), 1.27 (t, J = 7.6 Hz, 3H), 1.15 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.1, 162.7, 153.8, 146.5, 145.0, 141.2, 135.1, 131.6, 131.4, 129.4, 129.1, 128.0, 127.4, 126.0, 123.9, 62.1, 47.7, 47.0, 42.5, 36.6, 24.3, 21.6, 13.8. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{30}H_{31}N_2O_7S^+$ 563.1846; Found 563.1826. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 22.6 min (minor), 34.7 min (major), 99% ee. **Optical rotation**: $[\alpha]_{25}^D$ = +18 (c = 1.0 in EtOAc)



3r

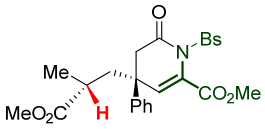
3r, Prepared according to the general procedure in 0.1 mmol scale, 53% yield, 30 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.98 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.8 Hz, 2H), 7.69 (s, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.22-7.19 (m, 3H), 7.16 (d, J = 8.4 Hz, 2H), 7.07-7.06 (m, 2H), 6.39 (s, 1H), 4.33-4.28 (m, 1H), 4.24-4.19 (m, 1H), 2.80 (d, J = 15.6 Hz, 1H), 2.73-2.67 (m, 2H), 2.39-2.35 (m, 4H),

2.17 (dd, J = 14.4, 3.6 Hz, 1H), 1.31 (t, J = 7.2 Hz, 3H), 1.15 (d, J = 6.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 169.0, 162.8, 148.3, 148.1, 145.0, 141.3, 135.2, 133.4, 131.9, 131.5, 129.6, 129.4, 129.1, 129.0, 127.4, 126.0, 122.1, 121.4, 62.1, 48.0, 46.4, 42.5, 36.4, 24.5, 21.6, 13.9; **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{30}H_{31}N_2O_7S^+$ 563.1846; Found 563.1827. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 15.5 min (major), 18.2 min (minor), 99% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = +1 (c = 1.0 in EtOAc)



3s

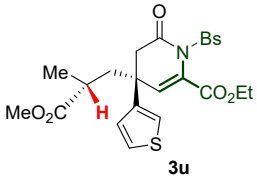
3s, Prepared according to the general procedure in 0.1 mmol scale, 76% yield, 36 mg, white solid, m.p.: 112.3-114.6 ℃, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.34 (t, J = 7.8 Hz, 2H), 7.27-7.24 (m, 3H), 7.17 (d, J = 7.8 Hz, 2H), 6.81 (s, 1H), 3.93 (s, 3H), 3.50 (s, 3H), 2.93 (d, J = 16.2 Hz, 1H), 2.66 (d, J = 16.2 Hz, 1H), 2.38-2.31 (m, 2H), 1.68 (d, J = 13.2 Hz, 1H), 1.00 (d, J = 6.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 176.2, 168.7, 163.5, 141.0, 138.1, 133.8, 132.0, 129.3, 129.0, 128.4, 127.7, 126.3, 52.9, 51.9, 45.0, 44.7, 35.8, 19.6. **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{24}H_{25}NNaO_7S^+$ 494.1244; Found 494.1245. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 15.2 min (major), 20.4 min (minor), 96% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = -41 (c = 1.0 in EtOAc)



3t

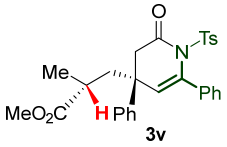
3t, Prepared according to the general procedure in 0.1 mmol scale, 42% yield, 23 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (d, J = 7.2 Hz, 2H), 7.43 (d, J = 7.8 Hz, 2H), 7.30-7.24 (m, 3H), 7.27-7.24 (m, 3H), 7.13 (d, J = 7.2 Hz, 2H), 6.84 (s, 1H), 3.92 (s, 3H), 3.49 (s, 3H), 2.96 (d, J = 16.2 Hz, 1H), 2.63 (d, J = 16.2 Hz, 1H), 2.40-2.28 (m, 2H), 1.68 (d, J = 12.0 Hz, 1H), 1.01 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 176.2, 168.7, 163.3, 141.0, 136.7, 132.7, 131.9, 131.6, 130.7, 130.5, 129.0, 127.7, 126.3, 52.9, 51.9, 44.9, 42.3, 35.8, 19.6. **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{24}H_{24}BrNNaO_7S^+$ 572.0349; Found 572.0353. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate

= 1.0 mL/min, UV = 254 nm, t_R = 13.7 min (major), 16.9 min (minor), 98% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = -18 (c = 1.0 in EtOAc)



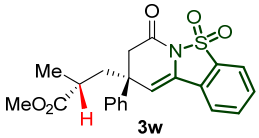
3u

3u, Prepared according to the general procedure in 0.1 mmol scale, 64% yield, 36 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.32 (dd, J = 5.2, 2.8 Hz, 1H), 6.95-6.91 (m, 2H), 6.71 (s, 1H), 4.44-4.31 (m, 2H), 3.57 (s, 3H), 2.87 (d, J = 15.6 Hz, 1H), 2.65 (d, J = 16.0 Hz, 1H), 2.37-2.30 (m, 2H), 1.67-1.60 (m, 1H), 1.40 (t, J = 6.8 Hz, 3H), 1.03 (d, J = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.2, 168.8, 162.9, 141.7, 137.0, 132.1, 131.7, 131.0, 130.9, 129.4, 137.1, 125.7, 121.6, 62.4, 52.0, 45.6, 44.3, 40.3, 35.8, 19.5, 14.0. **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{23}H_{24}BrNNaO_7S_2^+$ 592.0070; Found 592.0068. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 11.0 min (major), 13.7 min (minor), 98% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = -1 (c = 1.0 in EtOAc)



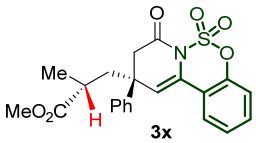
3v

3u, Prepared according to the general procedure in 0.1 mmol scale, 33% yield, 17 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.43-7.37 (m, 4H), 7.24-7.23 (m, 6H), 7.00 (d, J = 8.0 Hz, 2H), 6.03 (s, 1H), 3.48 (s, 3H), 3.03 (d, J = 16.4 Hz, 1H), 2.72 (d, J = 16.4 Hz, 1H), 2.37-2.31 (m, 5H), 1.67-1.60 (m, 1H), 0.95 (d, J = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.5, 170.5, 144.2, 142.5, 140.6, 137.6, 135.5, 129.1, 128.8, 128.4, 127.2, 126.7, 126.5, 125.8, 125.5, 51.8, 45.6, 45.4, 35.8, 21.6, 19.6. **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{29}H_{29}NNaO_5S^+$ 526.1659; Found 526.1659. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 13.9 min (minor), 18.8 min (major), 97% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = -1 (c = 1.0 in EtOAc)



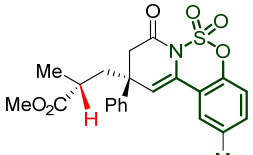
3w

3v, Prepared according to the general procedure in 0.1 mmol scale, 75% yield, 31 mg, white solid, m.p. 81.3-82.7°C, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 1H), 7.80-7.73 (m, 2H), 7.67-7.63 (m, 1H), 7.39-7.26 (m, 5H), 6.19 (s, 1H), 3.34 (s, 3H), 3.10 (d, J = 16.0 Hz, 1H), 2.87 (d, J = 16.0 Hz, 1H), 2.67-2.59 (m, 1H), 2.20-2.40 (m, 1H), 1.98 (dd, J = 14.4, 2.4 Hz, 1H), 1.14 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.5, 165.3, 142.2, 134.1, 132.6, 131.1, 129.3, 129.1, 127.6, 126.5, 125.9, 121.7, 121.6, 109.2, 51.7, 45.0, 44.2, 43.9, 36.4, 19.7. **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{22}H_{21}NNaO_5S^+$ 434.1033; Found 434.1035. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 26.5 min (major), 39.1 min (minor), 92% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = -18 (c = 1.0 in EtOAc).



3x

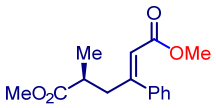
3w, Prepared according to the general procedure in 0.1 mmol scale, 89% yield, 38 mg, yellow oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.6, 1.2 Hz, 1H), 7.47 (td, J = 8.0, 1.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 3H), 7.35-7.28 (m, 3H), 7.22 (d, J = 8.0 Hz, 1H), 6.21 (s, 1H), 3.39 (s, 3H), 3.10 (d, J = 16.0 Hz, 1H), 2.87 (d, J = 16.0 Hz, 1H), 2.59 (dd, J = 14.4, 9.6 Hz, 1H), 2.47-2.37 (m, 1H), 1.95 (dd, J = 14.4, 2.4 Hz, 1H), 1.13 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.6, 166.6, 147.3, 141.4, 132.4, 131.5, 129.1, 127.7, 126.0, 120.0, 119.4, 114.9, 51.8, 45.0, 43.8, 42.3, 36.3, 19.7. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{22}H_{21}NO_6S^+$ 428.1162; Found 428.1162. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 15.7 min (minor), 18.5 min (major), 66% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = +1 (c = 1.0 in EtOAc).



3y

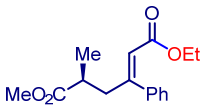
3y, Prepared according to the general procedure in 0.1 mmol scale, 96% yield, 42 mg, yellow oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 5:1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41-7.24 (m, 8H), 7.09 (d, J = 8.0 Hz, 1H), 6.17 (s, 1H), 3.40 (s, 3H), 3.09 (d, J = 16.0 Hz, 1H),

2.86 (d, J = 16.0 Hz, 1H), 2.60 (dd, J = 14.4,8.8 Hz, 1H), 2.46-2.40 (m, 4H), 1.94 (dd, J = 14.4, 2.4 Hz, 1H), 1.13 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.5, 166.7, 145.2, 141.5, 137.6, 132.5, 132.2, 129.1, 127.6, 126.0, 125.7, 119.7, 119.1, 114.6, 51.7, 44.9, 43.8, 42.2, 36.3, 21.1, 19.7. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{23}H_{24}NO_6S^+$ 442.1319; Found 442.1322. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 12.4 min (major), 14.3 min (minor), 67% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = +1 (c = 1.0 in EtOAc)



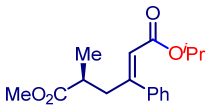
6a

6a, Prepared according to the general procedure in 0.1 mmol scale, 46% yield, 12 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.37 (m, 5H), 6.09 (s, 1H), 3.76 (s, 3H), 3.53 (dd, J = 12.0, 8.0 Hz, 1H), 3.47 (s, 3H), 3.30 (dd, 13.2, 6.8 Hz, 1H), 2.61-2.52 (m, 1H), 1.12 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.0, 166.7, 158.0, 140.6, 129.1, 128.6, 126.9, 119.1, 51.5, 51.2, 38.8, 34.0, 16.4. **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{15}H_{18}O_4Na^+$ 285.1097; Found 285.1096. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 6.3 min (major), 7.5 min (minor), 16% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = -13 (c = 1.0 in EtOAc)



6b

6b, Prepared according to the general procedure in 0.1 mmol scale, 35% yield, 10 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 5H), 6.08 (s, 1H), 4.21 (q, J = 8.0 Hz, 2H), 3.53 (dd, J = 13.2, 7.6 Hz, 1H), 3.47 (s, 3H), 3.29 (dd, 13.2, 7.6 Hz, 1H), 2.61-2.52 (m, 1H), 1.31 (t, J = 7.2 Hz, 3H), 1.12 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.1, 166.3, 157.5, 140.7, 129.0, 128.6, 126.9, 119.7, 60.0, 51.5, 38.9, 33.9, 16.4, 14.3. **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{16}H_{20}O_4Na^+$ 299.1254; Found 299.1253. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 5.03 min (major), 5.60 min (minor), 21% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = -5 (c = 1.0 in EtOAc)



6c

6c, Prepared according to the general procedure in 0.1 mmol scale, 33% yield, 10 mg, colorless oil, flash column with a petroleum ether/ethyl acetate eluent (gradient 8:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2H), 7.38-7.35 (m, 3H), 6.05 (s, 1H), 5.09 (hept, J = 6.4 Hz, 1H), 3.52 (dd, J = 13.2, 8.0 Hz, 1H), 3.47 (s, 3H), 3.28 (dd, J = 13.2, 7.2 Hz, 1H), 2.57 (sext, J = 6.8 Hz, 1H), 1.29 (q, J = 3.2 Hz, 6H), 1.12 (d, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.1, 165.8, 157.0, 140.8, 128.9, 128.5, 126.8, 120.2, 67.3, 51.4, 38.8, 33.9, 21.9, 16.4; **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{17}H_{22}O_4Na^+$ 313.1410; Found 313.1408. **HPLC**: CHIRALPAK OD-H, *n*-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, UV = 254 nm, t_R = 3.96 min (major), 4.18 min (minor), 33% ee. **Optical rotation**: $[\alpha]_{25}^{D}$ = +9 (c = 1.0 in EtOAc)

Part 4. Crystal structure of **3s**.

The product **3s** was obtained by slow diffusion in CH_2Cl_2/hexanes at room temperature, colorless crystal was observed, and absolute configuration was determined by X-Ray structure analysis. Supplementary information of the crystal is available under CCDC number 2114888, which could be accessible at free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk. Thermal ellipsoid probability is 30%.

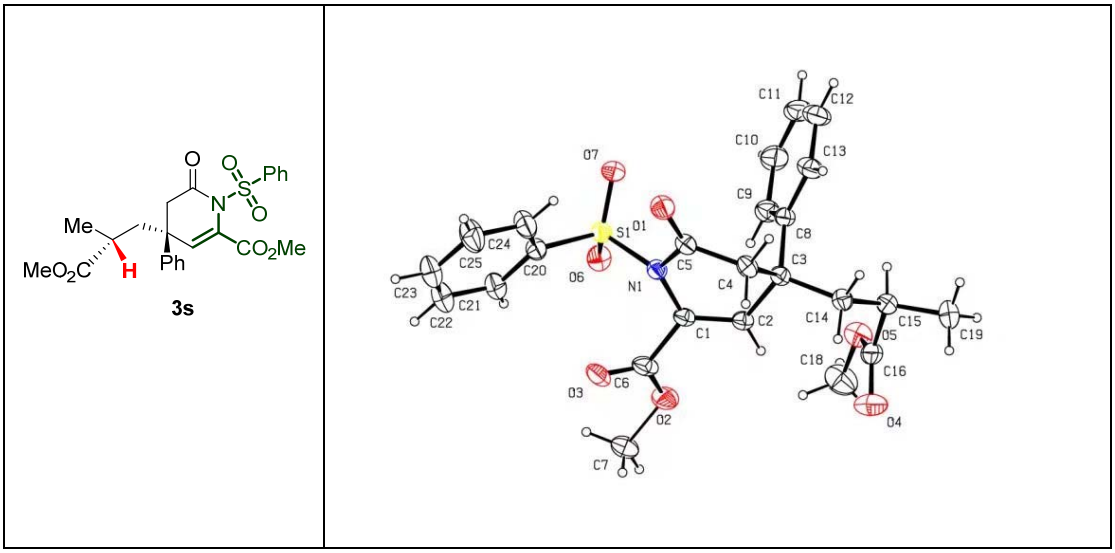


Figure S1. X-ray Crystallographic Analysis of **3s**

Table 1 Crystal data and structure refinement for 3s.

Identification code	dongmd_1208
Empirical formula	$C_{24}H_{25}NO_7S$
Formula weight	471.51
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.32517(16)
b/Å	11.40245(17)
c/Å	22.4950(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2391.89(7)
Z	4
ρ_{calc}g/cm^3	1.309
μ/mm^{-1}	1.579
F(000)	992.0
Crystal size/mm^3	0.11 × 0.05 × 0.04

Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.86 to 151.946
Index ranges	$-11 \leq h \leq 8$, $-7 \leq k \leq 13$, $-28 \leq l \leq 27$
Reflections collected	8276
Independent reflections	4194 [R_{int} = 0.0257, R_{sigma} = 0.0343]
Data/restraints/parameters	4194/0/311
Goodness-of-fit on F^2	0.892
Final R indexes [I>=2σ (I)]	R_1 = 0.0438, wR_2 = 0.1154
Final R indexes [all data]	R_1 = 0.0476, wR_2 = 0.1204
Largest diff. peak/hole / e $Å^{-3}$	0.16/-0.42
Flack parameter	0.018(11)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for dongmd_1208. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	-6991.8(8)	-5423.1(6)	-1209.2(3)	58.3(2)
O1	-7814(3)	-7628(2)	-597.0(11)	72.9(6)
O2	-3092(3)	-4325(3)	-423.7(13)	85.9(7)
O3	-3543(3)	-5694(2)	-1100.7(12)	75.8(7)
O4	-3432(3)	-4779(3)	1651.6(18)	104.8(10)
O5	-5048(3)	-3418(2)	1442.1(13)	87.9(8)
O6	-6323(3)	-4299.0(17)	-1222.1(11)	70.6(6)
O7	-8499(2)	-5502(2)	-1149.2(11)	76.9(7)
N1	-6245(2)	-6094.0(19)	-610.8(10)	51.1(5)
C1	-5139(3)	-5492(2)	-296.1(12)	49.9(6)
C2	-5190(3)	-5430(2)	293.4(12)	51.3(6)
C3	-6384(3)	-6026(2)	633.0(12)	50.6(6)
C4	-6566(3)	-7212(2)	306.1(13)	55.7(7)
C5	-6957(3)	-7039(2)	-333.9(13)	54.5(6)
C6	-3849(3)	-5158(3)	-645.7(18)	72.2(10)
C8	-7791(3)	-5333(2)	612.6(12)	53.4(6)
C9	-7854(4)	-4184(3)	417.9(16)	69.0(8)
C10	-9131(5)	-3559(4)	430(2)	88.7(12)
C11	-10350(5)	-4083(5)	630(2)	98.6(14)
C12	-10325(4)	-5225(5)	833(2)	93.2(14)
C13	-9056(4)	-5839(3)	824.1(17)	73.2(9)

C14	-5957(4)	-6299(3)	1281.9(13)	62.2(7)
C15	-5924(4)	-5259(3)	1721.7(14)	68.3(8)
C16	-4663(4)	-4476(3)	1607.0(15)	69.4(8)
C18	-3890(6)	-2608(4)	1305(3)	114.5(17)
C19	-5831(6)	-5730(5)	2358.0(16)	102.3(15)
C20	-6457(4)	-6224(3)	-1840.3(13)	62.2(7)
C21	-5451(5)	-5743(4)	-2216.1(16)	79.6(10)
C22	-5086(6)	-6343(5)	-2731.3(18)	99.9(14)
C23	-5705(6)	-7398(5)	-2858.3(19)	101.1(15)
C24	-7066(5)	-7300(4)	-1960.7(17)	87.0(11)
C25	-6687(7)	-7877(4)	-2478(2)	109.5(17)
C7	-1804(7)	-4122(8)	-783(4)	95(2)
C17	-2152(9)	-5208(10)	-1337(5)	90(3)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for dongmd_1208. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	53.0(4)	66.9(4)	54.9(3)	3.9(3)	2.7(3)	13.4(3)
O1	69.4(14)	75.1(12)	74.3(13)	-11.2(11)	4.9(12)	-21.2(12)
O2	61.1(13)	103.4(18)	93.1(17)	20.9(14)	6.2(13)	-26.7(14)
O3	59.0(12)	89.7(14)	78.6(15)	21.8(12)	26.2(12)	14.6(11)
O4	58.1(15)	113(2)	143(3)	-9(2)	-9.5(17)	5.2(15)
O5	75.9(17)	86.9(15)	101.0(19)	-4.6(14)	8.8(15)	0.7(14)
O6	84.6(16)	55.5(10)	71.6(13)	10.1(9)	0.9(12)	13.7(10)
O7	51.0(11)	109.2(17)	70.6(14)	-5.9(14)	1.3(10)	18.2(12)
N1	48.3(12)	54.4(11)	50.5(11)	4.4(9)	2.9(10)	1.2(9)
C1	40.2(12)	49.1(12)	60.4(14)	9.0(10)	4.3(11)	-0.2(11)
C2	43.7(12)	50.9(12)	59.2(14)	3.1(11)	0.6(12)	-3.1(12)
C3	46.7(13)	52.4(12)	52.7(14)	2.9(11)	5.2(11)	-0.6(11)
C4	59.7(16)	47.7(12)	59.8(15)	5.7(11)	11.9(13)	-4.8(12)
C5	51.4(14)	52.6(12)	59.4(14)	-3.2(11)	10.1(13)	-3.0(13)
C6	46.1(15)	82(2)	88(2)	41.4(19)	9.2(17)	9.9(15)
C8	44.1(13)	62.2(13)	53.9(13)	-7.1(11)	1.0(11)	-1.9(12)
C9	62.3(18)	66.8(16)	78(2)	5.4(14)	1.4(16)	10.0(15)
C10	81(3)	90(2)	95(3)	1(2)	-5(2)	28(2)
C11	59(2)	130(4)	106(3)	-32(3)	-8(2)	32(2)
C12	48.5(18)	125(4)	106(3)	-38(3)	12(2)	-8(2)
C13	52.8(16)	79(2)	88(2)	-17.3(17)	12.9(17)	-10.5(15)

C14	59.6(16)	71.5(16)	55.5(15)	9.3(13)	5.0(14)	-1.0(14)
C15	53.6(16)	95(2)	56.7(16)	-7.8(15)	2.3(14)	12.7(17)
C16	60.1(17)	87(2)	61.2(16)	-19.5(16)	-2.9(14)	4.4(17)
C18	110(4)	93(3)	141(4)	-14(3)	27(3)	-20(3)
C19	100(3)	153(4)	53.9(19)	-2(2)	12(2)	8(3)
C20	60.3(17)	72.7(16)	53.7(15)	2.2(13)	4.2(13)	9.3(15)
C21	87(2)	90(2)	61.4(17)	6.3(16)	15.4(18)	-2(2)
C22	115(4)	116(3)	69(2)	7(2)	34(2)	-1(3)
C23	123(4)	113(3)	67(2)	-12(2)	32(2)	7(3)
C24	93(3)	98(2)	70(2)	-16.9(18)	25(2)	-17(2)
C25	136(4)	106(3)	87(3)	-32(2)	34(3)	-18(3)
C7	58(3)	128(5)	99(5)	11(4)	15(3)	-39(4)
C17	52(5)	113(7)	106(7)	49(6)	31(5)	4(5)

Table 4 Bond Lengths for dongmd_1208.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O6	1.426(2)	C3	C8	1.533(4)
S1	O7	1.415(2)	C3	C14	1.544(4)
S1	N1	1.698(2)	C4	C5	1.498(4)
S1	C20	1.760(3)	C8	C9	1.383(4)
O1	C5	1.200(4)	C8	C13	1.397(4)
O2	C6	1.284(5)	C9	C10	1.388(5)
O2	C7	1.466(6)	C10	C11	1.360(7)
O3	C6	1.226(5)	C11	C12	1.380(7)
O3	C17	1.507(8)	C12	C13	1.375(6)
O4	C16	1.203(4)	C14	C15	1.544(5)
O5	C16	1.313(5)	C15	C16	1.499(5)
O5	C18	1.454(6)	C15	C19	1.531(5)
N1	C1	1.427(4)	C20	C21	1.376(5)
N1	C5	1.411(4)	C20	C24	1.379(5)
C1	C2	1.329(4)	C21	C22	1.388(6)
C1	C6	1.487(4)	C22	C23	1.364(7)
C2	C3	1.512(4)	C23	C25	1.367(7)
C3	C4	1.548(4)	C24	C25	1.383(5)

Table 5 Bond Angles for dongmd_1208.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°

O6	S1	N1	103.99(13)	O2	C6	C1	115.4(3)
O6	S1	C20	109.02(15)	O3	C6	O2	124.4(3)
O7	S1	O6	119.60(16)	O3	C6	C1	120.1(3)
O7	S1	N1	107.63(14)	C9	C8	C3	122.3(3)
O7	S1	C20	109.00(16)	C9	C8	C13	117.6(3)
N1	S1	C20	106.83(13)	C13	C8	C3	120.0(3)
C6	O2	C7	110.7(4)	C8	C9	C10	121.1(4)
C6	O3	C17	108.1(6)	C11	C10	C9	119.9(4)
C16	O5	C18	116.1(3)	C10	C11	C12	120.7(4)
C1	N1	S1	118.24(18)	C13	C12	C11	119.4(4)
C5	N1	S1	120.1(2)	C12	C13	C8	121.4(4)
C5	N1	C1	119.2(2)	C3	C14	C15	117.1(3)
N1	C1	C6	116.5(3)	C16	C15	C14	111.2(3)
C2	C1	N1	119.7(2)	C16	C15	C19	109.0(3)
C2	C1	C6	122.9(3)	C19	C15	C14	109.3(3)
C1	C2	C3	120.4(3)	O4	C16	O5	123.3(4)
C2	C3	C4	103.5(2)	O4	C16	C15	124.3(4)
C2	C3	C8	112.5(2)	O5	C16	C15	112.4(3)
C2	C3	C14	112.2(2)	C21	C20	S1	118.8(3)
C8	C3	C4	110.1(2)	C21	C20	C24	121.0(3)
C8	C3	C14	110.7(2)	C24	C20	S1	120.2(3)
C14	C3	C4	107.5(2)	C20	C21	C22	118.9(4)
C5	C4	C3	111.6(2)	C23	C22	C21	120.4(4)
O1	C5	N1	121.5(3)	C22	C23	C25	120.3(4)
O1	C5	C4	124.3(3)	C20	C24	C25	118.9(4)
N1	C5	C4	114.2(2)	C23	C25	C24	120.5(4)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for dongmd_1208.

Atom	*x*	*y*	*z*	U(eq)
H2	-4486.96	-5016.65	498.38	62
H4A	-5676.66	-7651.29	330.55	67
H4B	-7308.23	-7667.16	500.87	67
H9	-7027.29	-3823.37	276.26	83
H10	-9153.63	-2783.32	302.32	106
H11	-11208.19	-3667.62	629.53	118
H12	-11158.73	-5575.5	974.05	112
H13	-9040.36	-6608.34	961.81	88
H14A	-5012.35	-6654.59	1277.71	75

H14B	-6620.26	-6880.12	1435.24	75
H15	-6808.81	-4802.83	1678.38	82
H18A	-3441.11	-2836.33	938.9	172
H18B	-3194.6	-2624.03	1619.81	172
H18C	-4268.64	-1828.86	1266.3	172
H19A	-6656.7	-6205.41	2440.67	153
H19B	-5798.73	-5084.96	2632.02	153
H19C	-4978.45	-6194.6	2400.34	153
H21	-5023.76	-5027.51	-2126.34	96
H22	-4416.2	-6024.1	-2991.38	120
H23	-5456.88	-7792.84	-3205.06	121
H24	-7720.8	-7632.13	-1698.3	104
H25	-7104.24	-8595.9	-2568.27	131
H7A	-2077.23	-3956.7	-1185.49	142
H7B	-1208.47	-4808.68	-773.84	142
H7C	-1281.91	-3467.4	-623.84	142
H17A	-1868.51	-5641.41	-1682.95	135
H17B	-1422.76	-5275.01	-1037.17	135
H17C	-2278.1	-4397.33	-1439.69	135

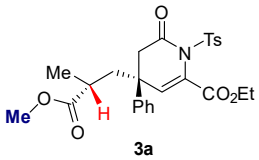
Table 7 Atomic Occupancy for dongmd_1208.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C7	0.6	H7A	0.6	H7B	0.6
H7C	0.6	C17	0.4	H17A	0.4
H17B	0.4	H17C	0.4		

Reference:

1) X.-S. Li, L.-L. Zhao, X.-K. Wang, L.-L. Cao, X.-Q. Shi, R. Zhang, J. Qi, *Org. Lett.* **2017**, *19*, 3943–3946.
2) Q. Yang, G. Shang, W. Gao, J. Deng, X. Zhang, *Angew. Chem. Int. Ed.* **2006**, *45*, 3832 –3835.
3) B. Li, J. Chen, Z. Zhang, I. D. Gridnev, W. Zhang, *Angew. Chem. Int. Ed.* **2019**, *58*, 7329 –7334.

Part 5. HPLC spectrum for all the products.



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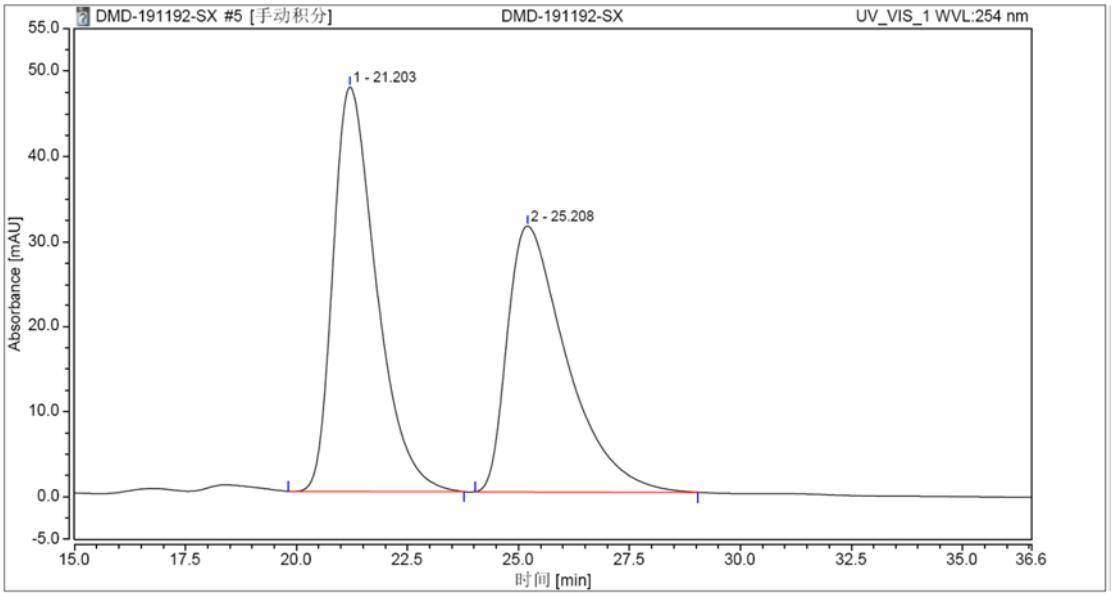
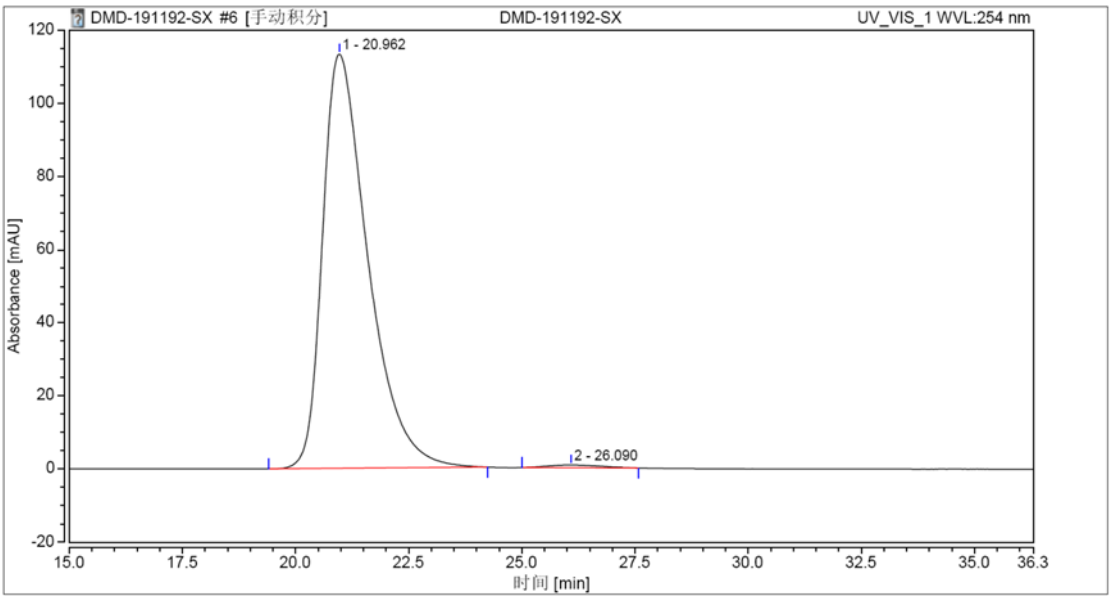
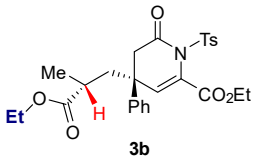


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	21.203	53.779	47.546	52.58
2	25.208	48.503	31.309	47.42
Total		**102.281**	**78.855**	100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	20.962	131.785	113.305	99.24
2	26.090	131.785	0.752	0.76
Total		**132.800**	**114.056**	100.00



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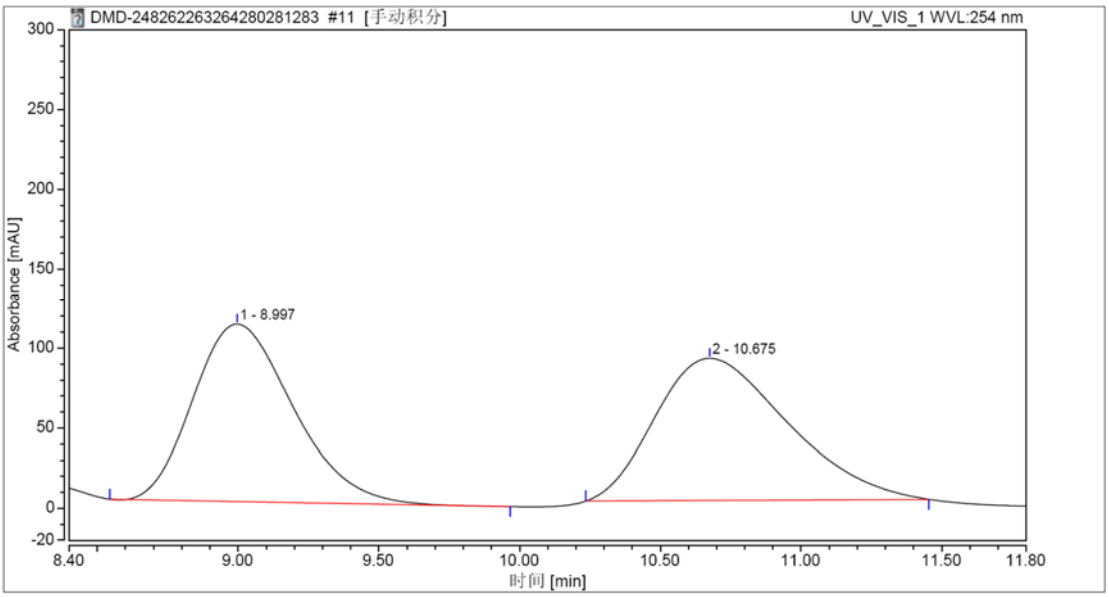
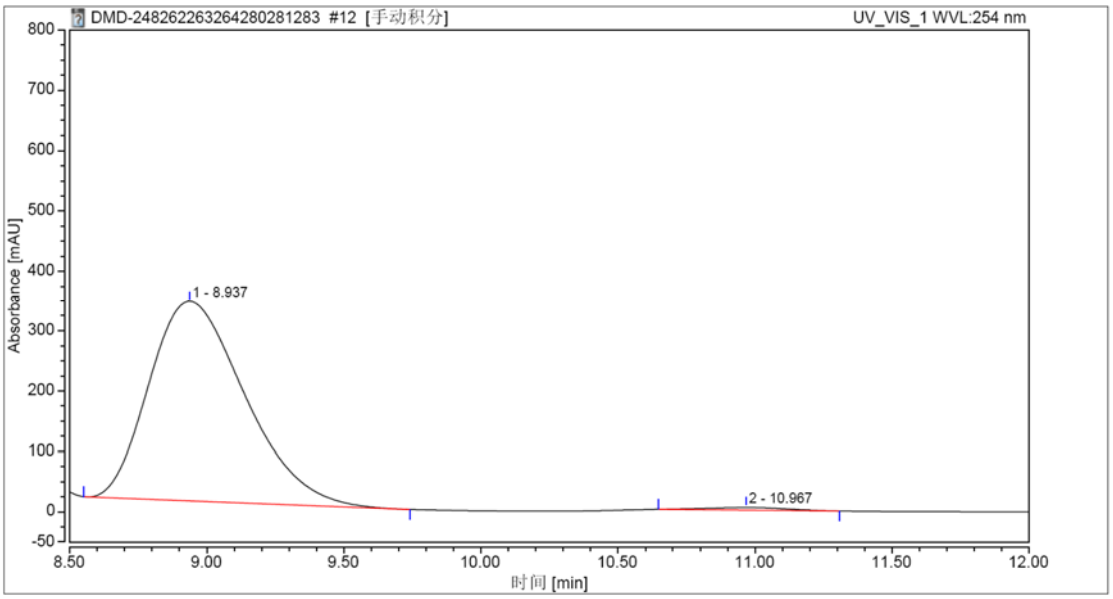
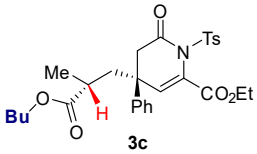


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	8.997	45.618	110.815	48.62
2	10.675	48.207	88.646	51.38
Total		**93.825**	**199.460**	100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	8.937	133.650	330.822	98.94
2	10.967	1.438	4.296	1.06
Total		**135.088**	**335.117**	100.00



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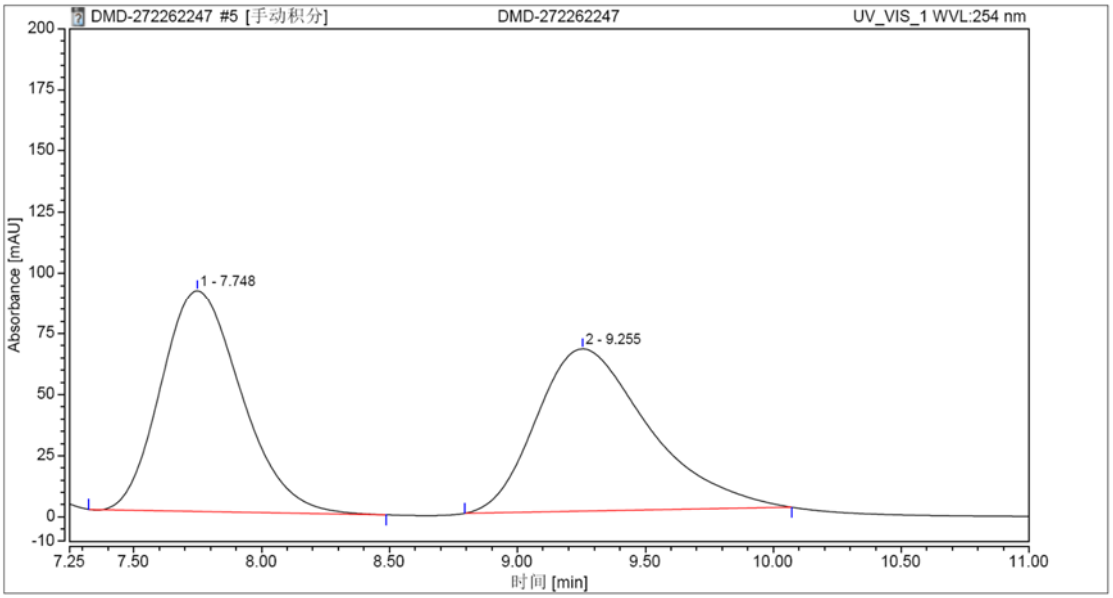
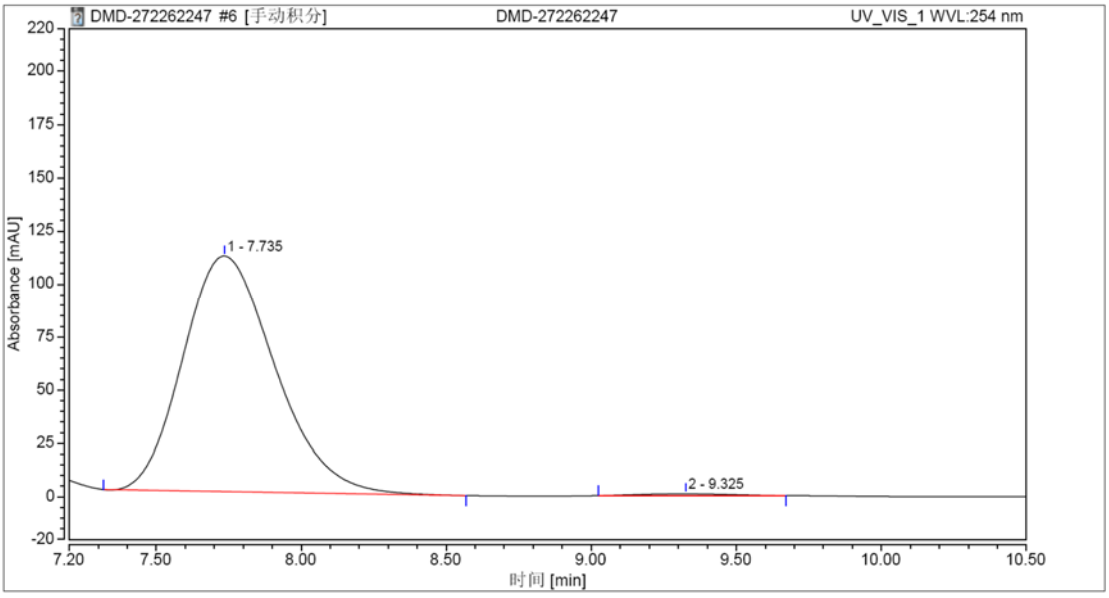
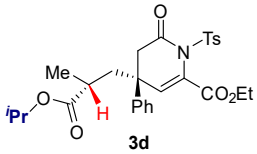


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.748	32.937	90.628	49.34
2	9.255	33.825	66.380	50.66
Total		**66.762**	**157.008**	100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.735	40.595	110.914	99.27
2	9.325	0.299	0.824	0.73
Total		**40.894**	**111.738**	100.00



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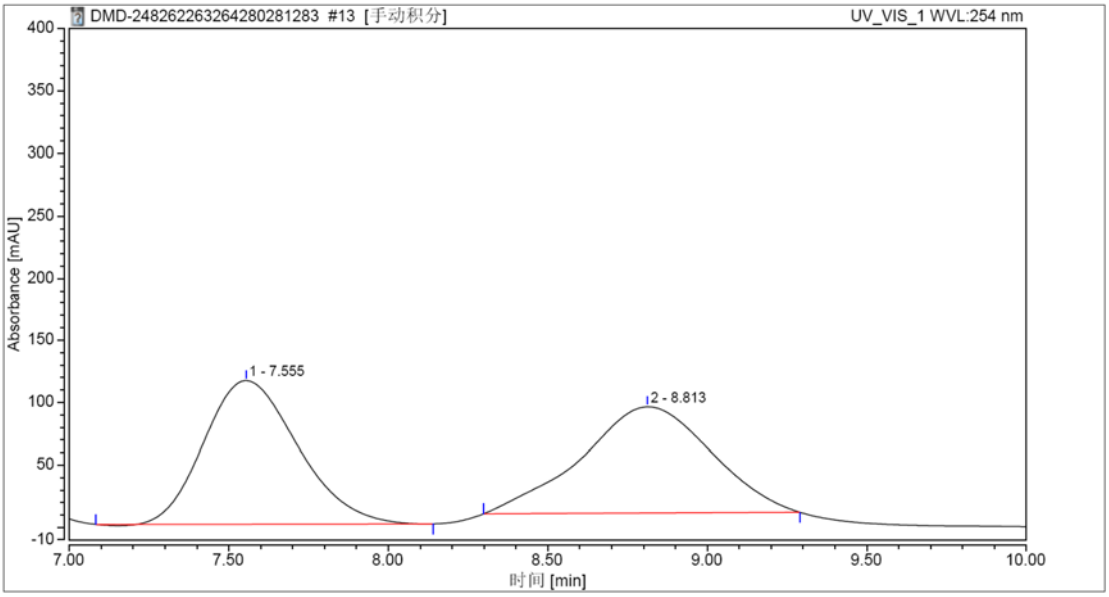
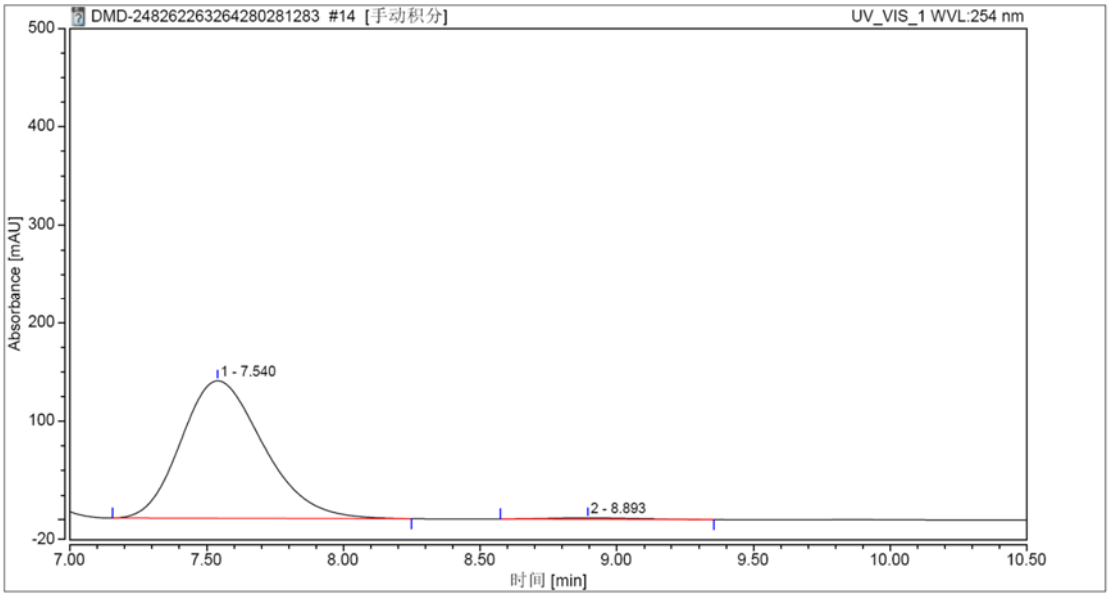
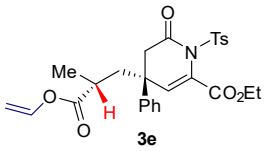


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.555	39.126	114.863	49.48
2	8.813	39.941	84.858	50.52
Total		**79.067**	**199.721**	100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.540	48.630	139.469	98.94
2	8.893	0.520	1.326	1.06
Total		**49.150**	**140.795**	100.00



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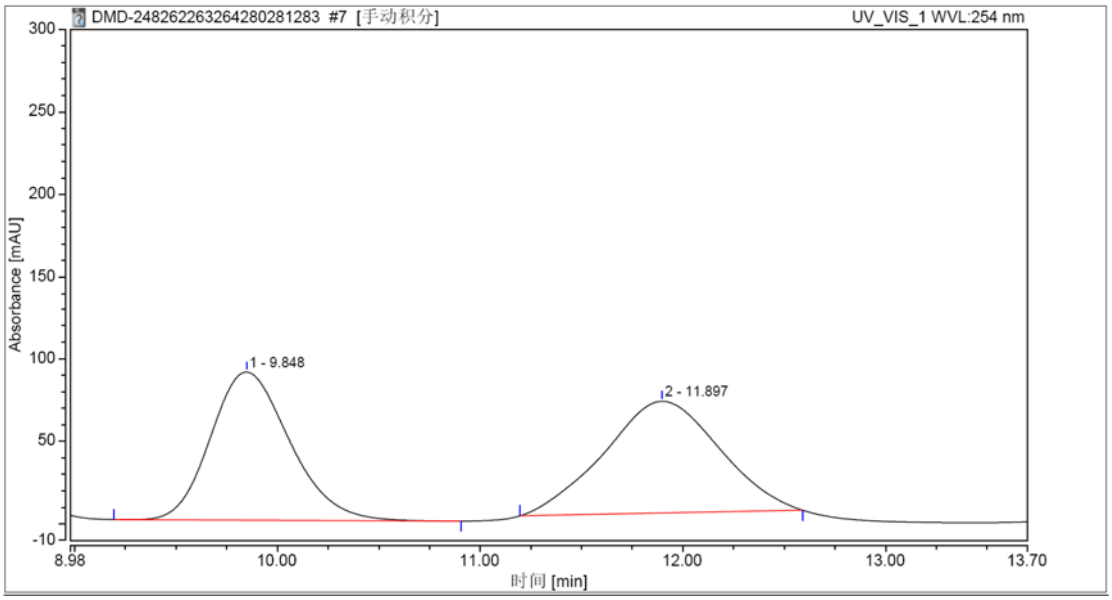
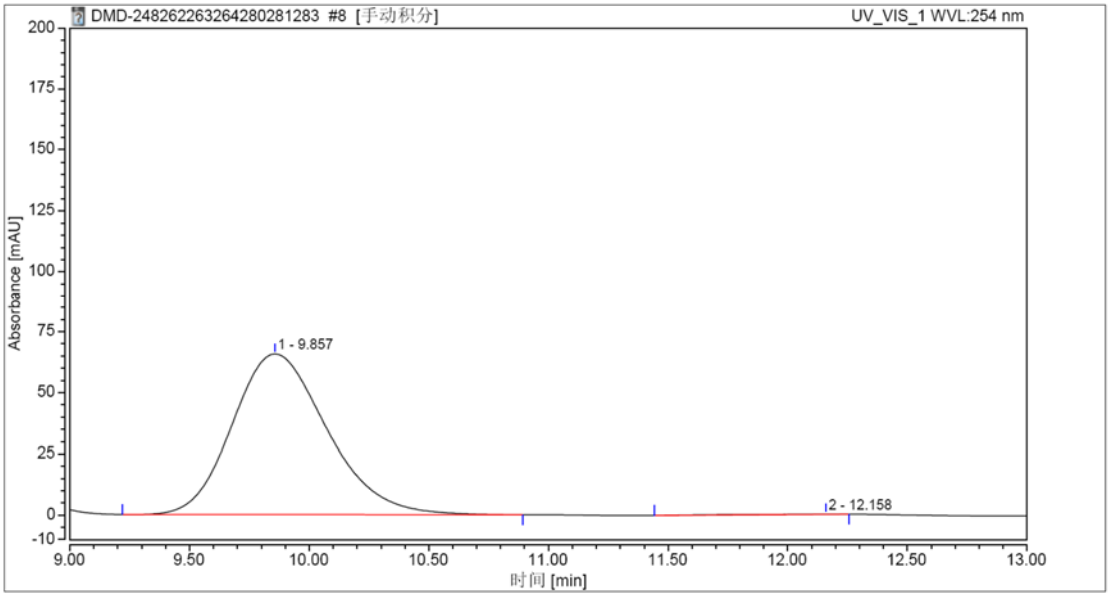
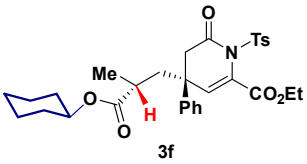


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	9.848	40.545	89.711	47.61
2	11.897	52.588	72.578	52.39
Total		**93.132**	**162.289**	100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	9.857	30.142	65.656	99.70
2	12.158	0.091	0.079	0.30
Total		**30.233**	**65.735**	100.00



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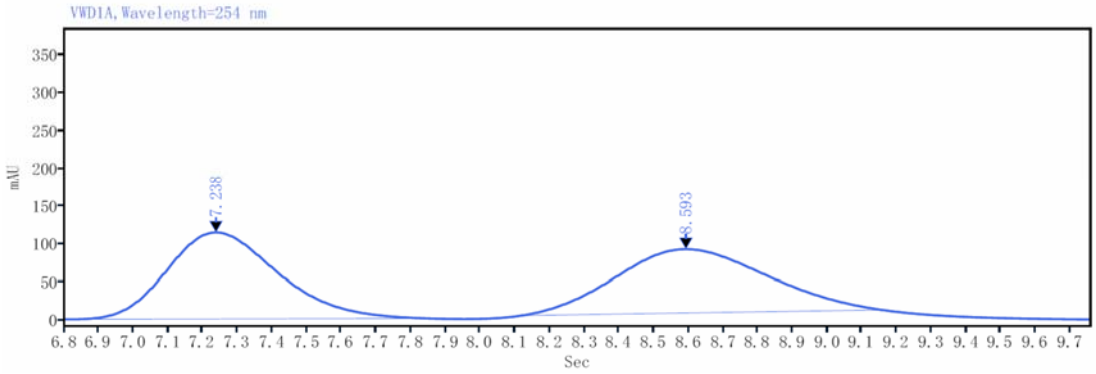
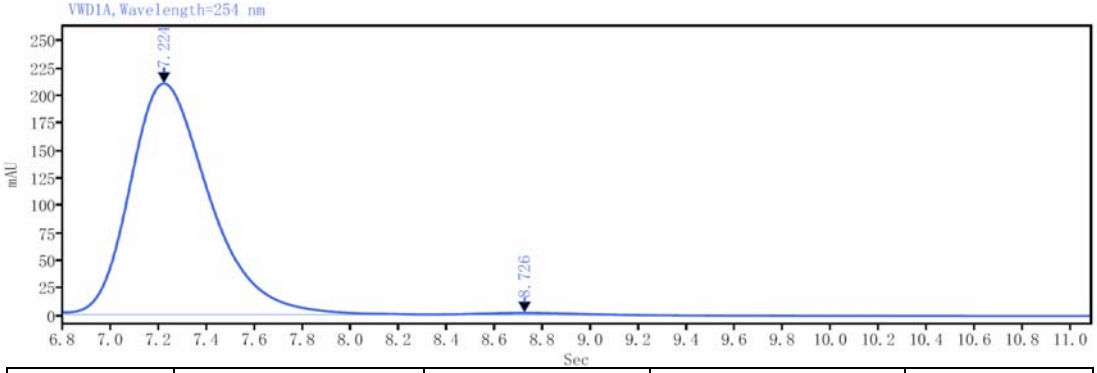
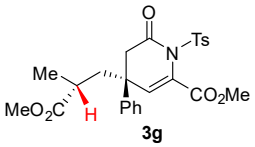


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.238	2513.14	113.44	49.87
2	8.593	2526.38	83.51	50.13
Total		5039.52		100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	7.224	4824.87	210.26	98.95
2	8.726	51.22	1.76	1.05
Total		4876.09		100.00



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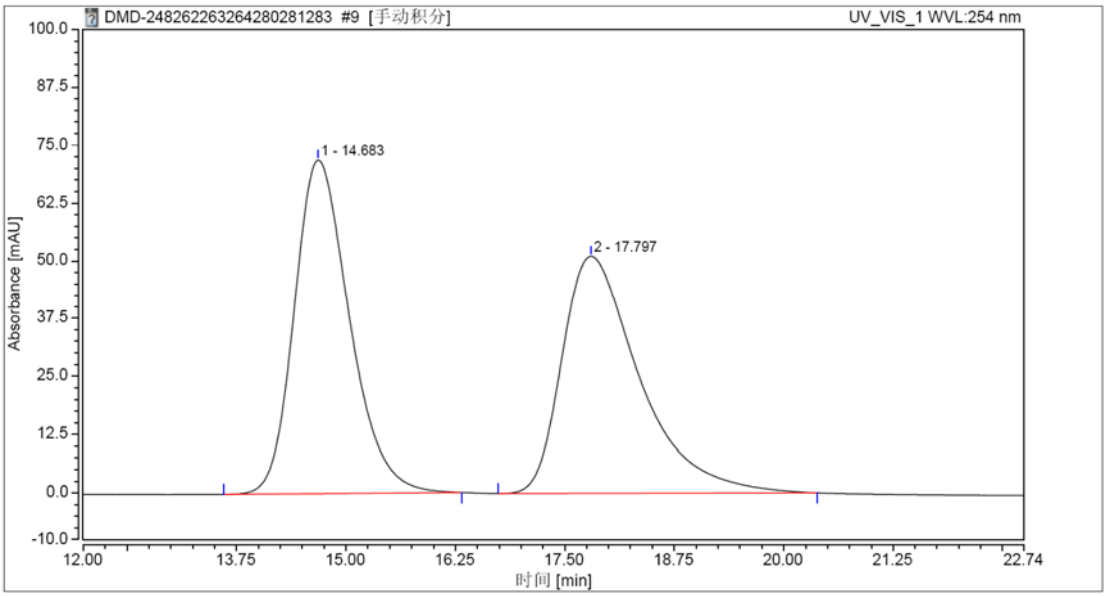
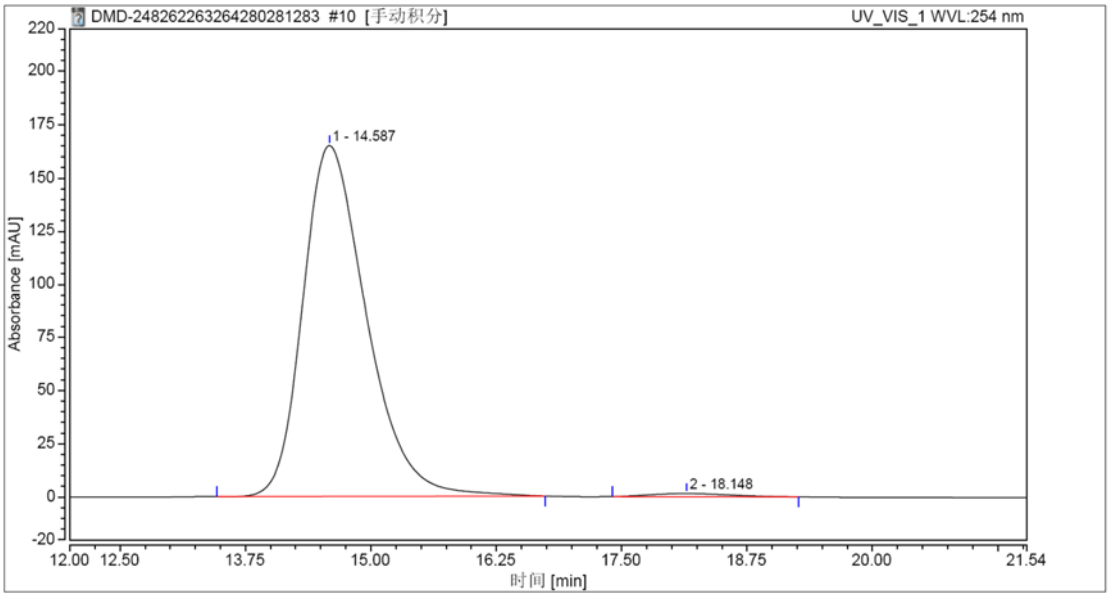
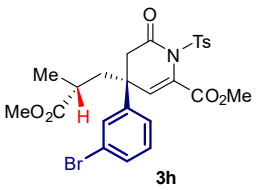


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	14.683	52.345	71.929	50.11
2	17.797	52.122	51.111	49.89
Total		**104.467**		100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	14.587	121.149	164.822	98.92
2	18.148	1.327	1.449	1.08
Total		**122.477**		100.00



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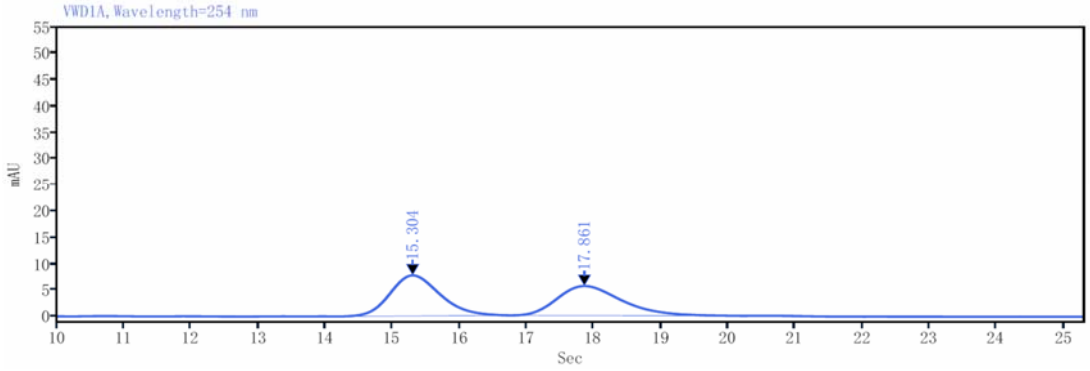
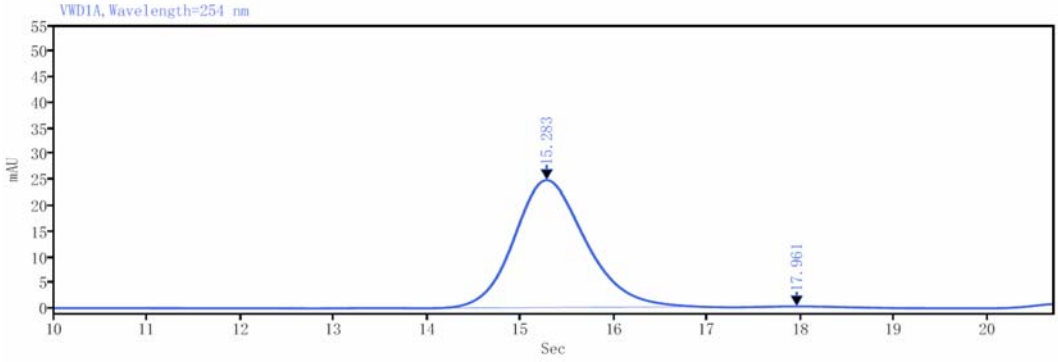
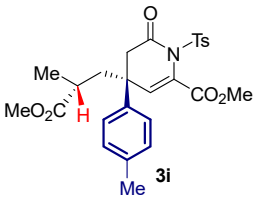


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	15.304	396.03	7.68	51.65
2	17.861	370.74	5.57	48.35
Total		766.77		100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	15.283	1323.10	24.72	99.72
2	17.961	3.66	0.11	0.28
Total		1326.75		100.00



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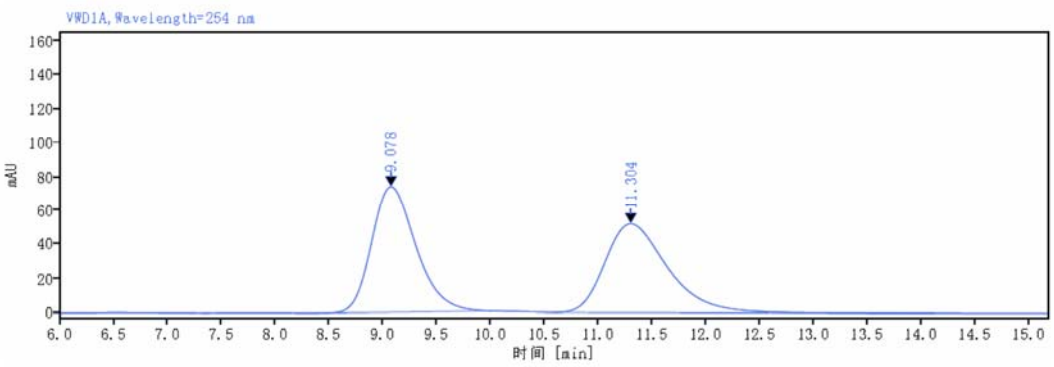
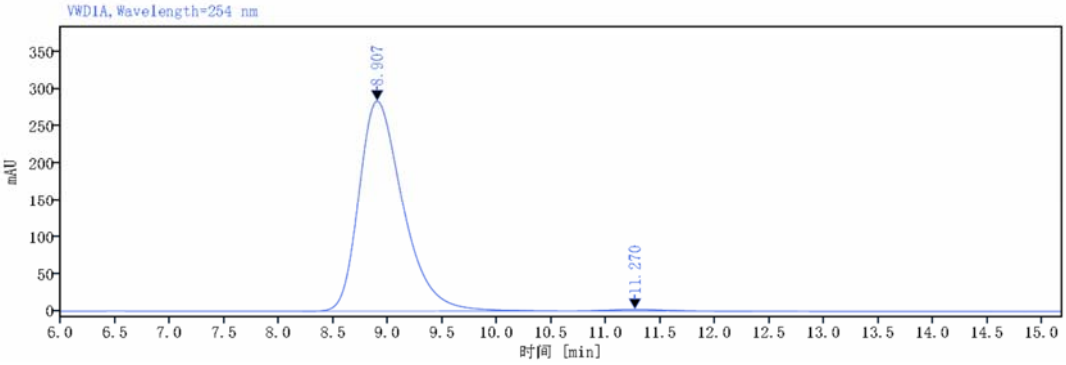
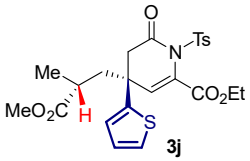


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	9.078	2095.73	73.76	50.03
2	11.304	2093.53	51.89	49.97
Total		**4189.25**		100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	8.907	7978.37	284.18	98.98
2	11.270	81.94	2.15	1.02
Total		**8060.31**		100.00



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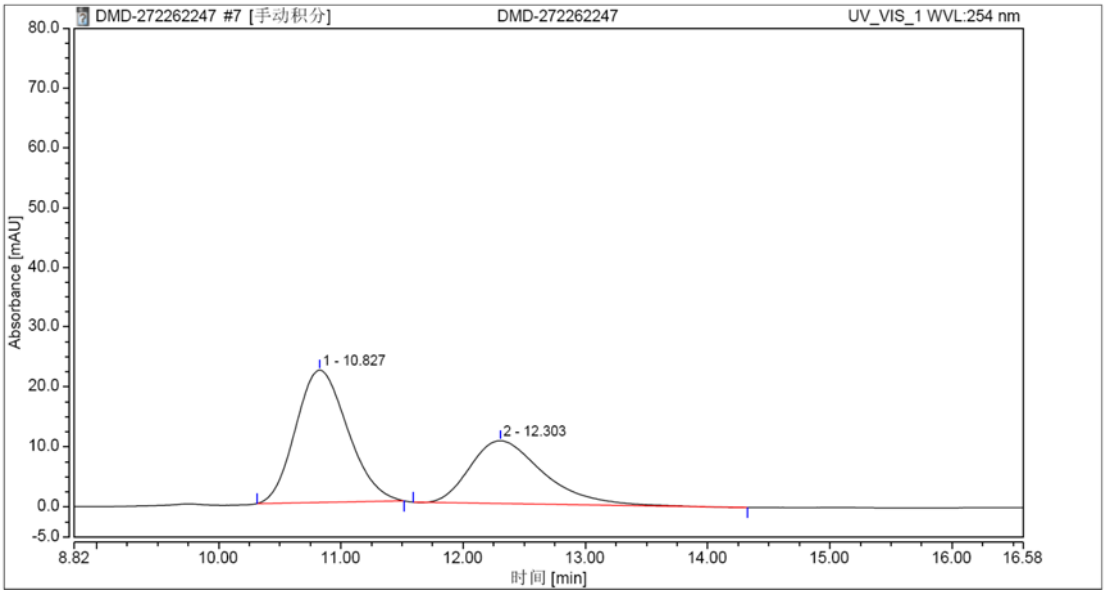
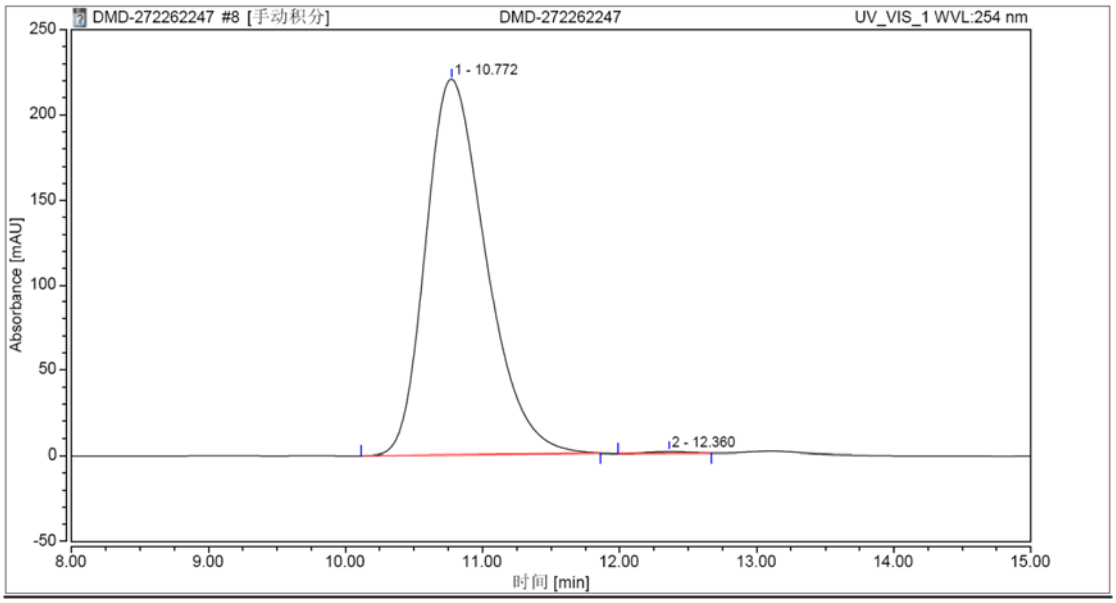
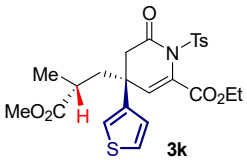


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	10.827	7.979	18.989	52.40
2	12.303	7.249	10.446	47.60
Total		**15.227**	**29.434**	100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	10.772	112.147	220.392	99.75
2	12.360	0.284	0.835	0.25
Total		**112.431**	**221.227**	100.00



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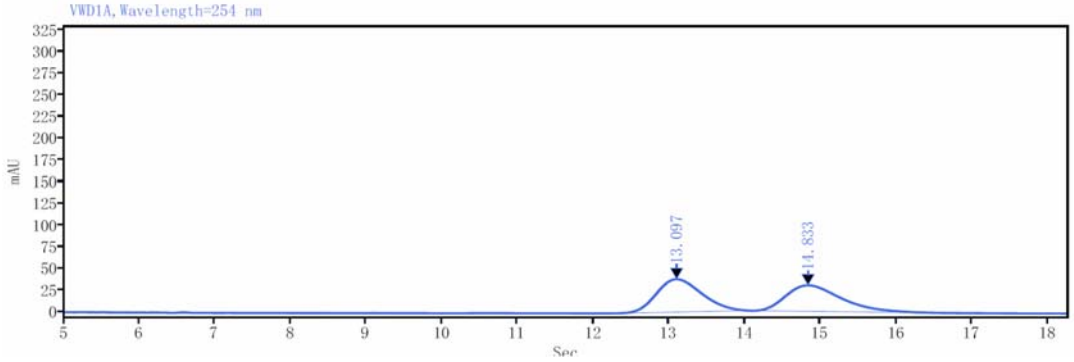
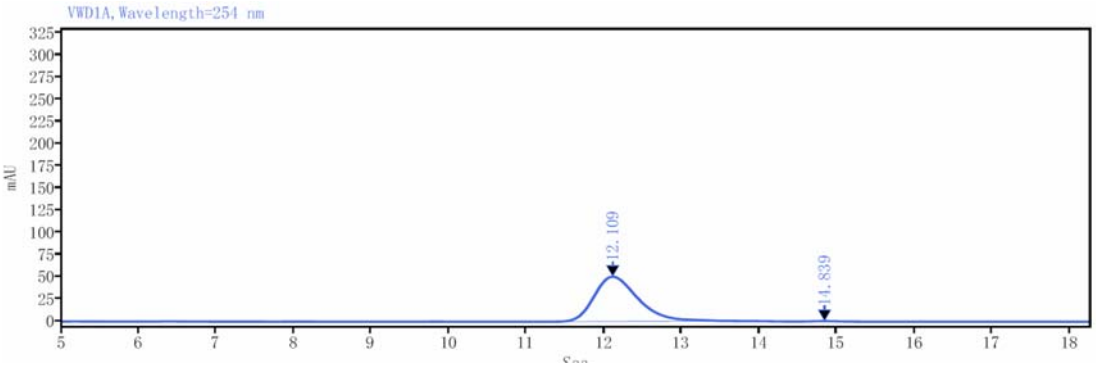
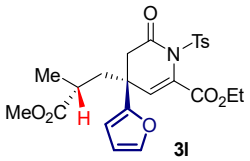


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	13.097	1574.84	38.02	50.88
2	14.833	1520.45	30.05	49.12
Total		3095.29		100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	12.109	1981.60	50.46	99.38
2	14.839	12.35	0.51	0.62
Total		1993.95		100.00



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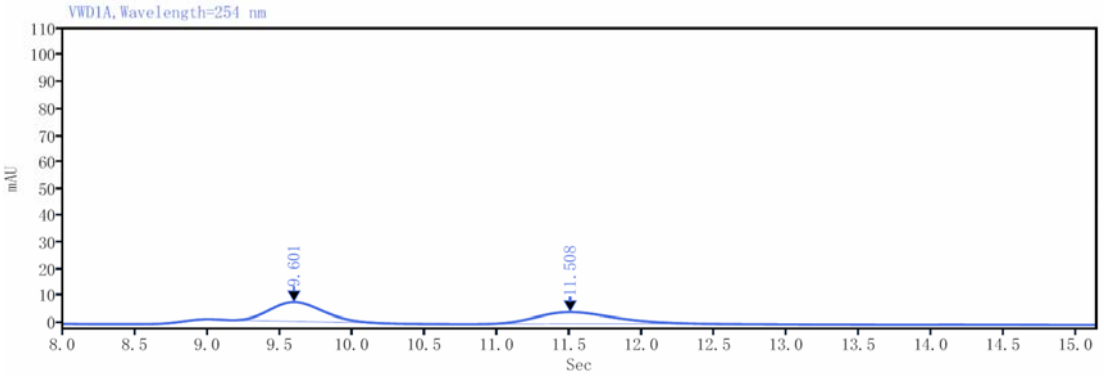
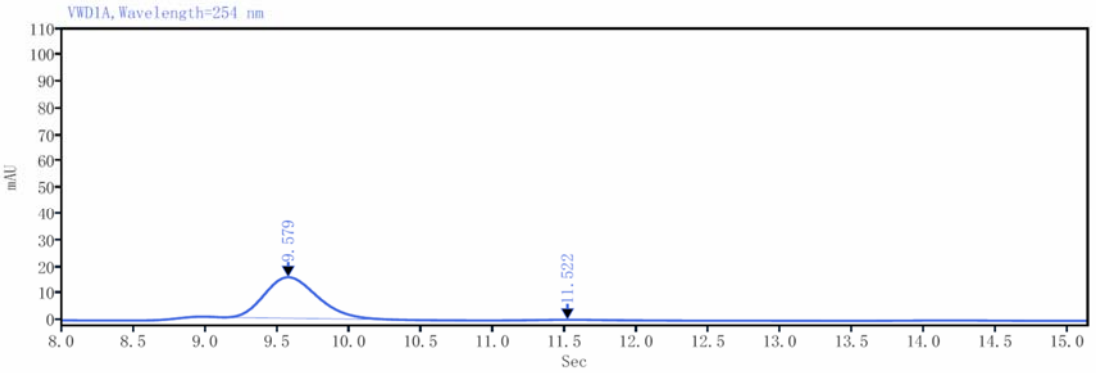
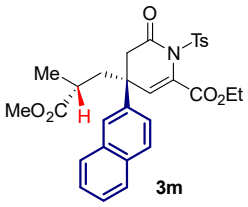


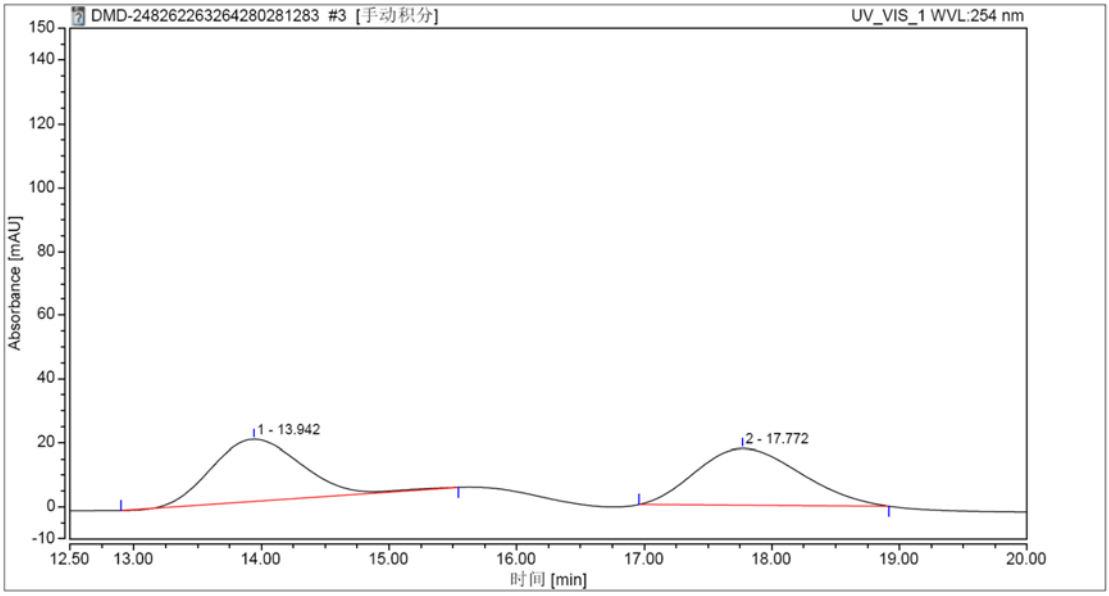
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	9.601	177.25	7.00	52.91
2	11.508	157.75	4.22	47.09
Total		335.00		100.00



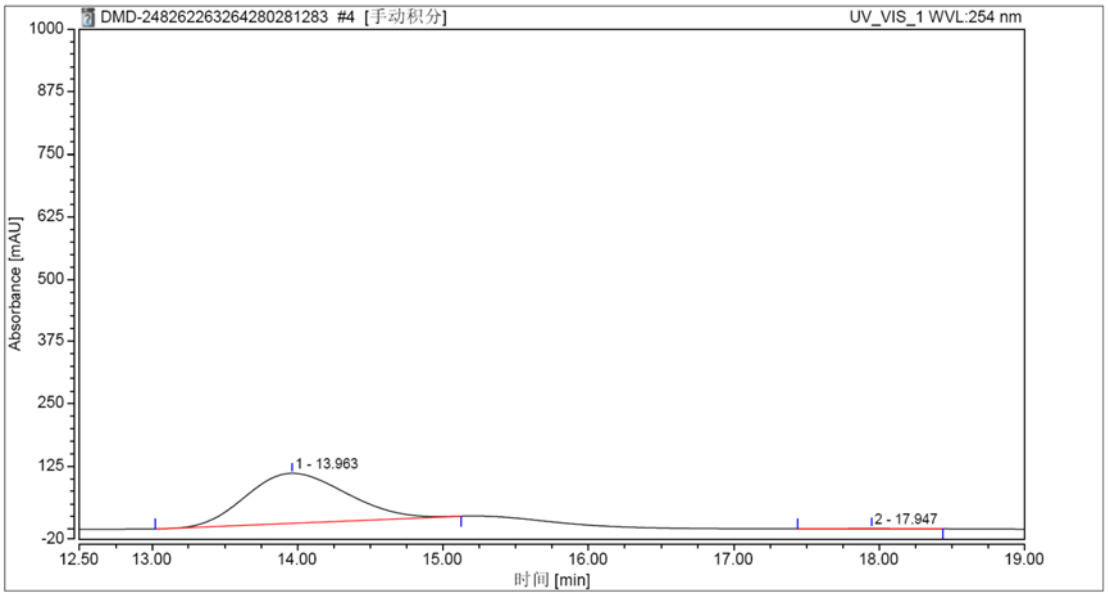
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	9.579	393.65	15.38	98.38
2	11.522	6.49	0.22	1.62
Total		400.14		100.00



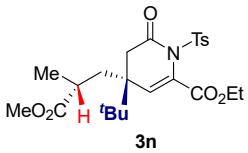
3m



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	13.942	15.709	19.340	48.28
2	17.772	16.827	17.668	51.72
Total		**32.536**	**37.008**	100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	13.963	79.183	99.650	99.67
2	17.947	0.266	0.447	0.33
Total		**79.449**	**100.098**	100.00



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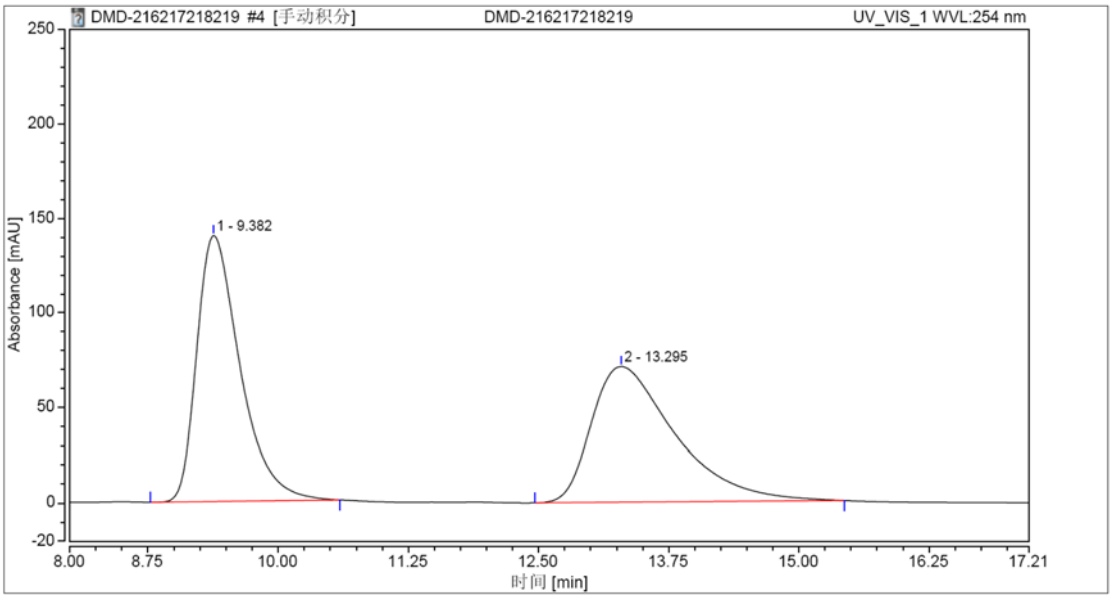
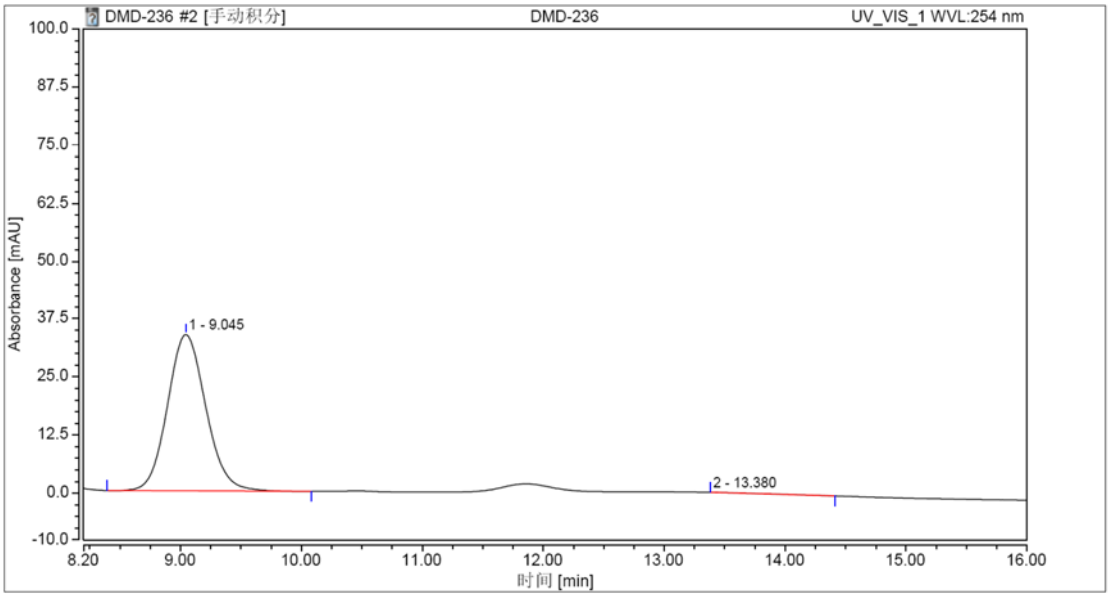
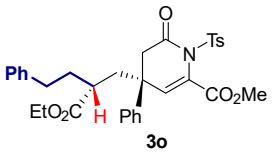


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	9.382	67.279	140.227	50.40
2	13.295	66.220	71.073	49.60
Total		**133.499**	**211.299**	100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	9.045	12.327	33.543	99.76
2	13.380	0.030	0.000	0.24
Total		**12.357**	33.543	100.00



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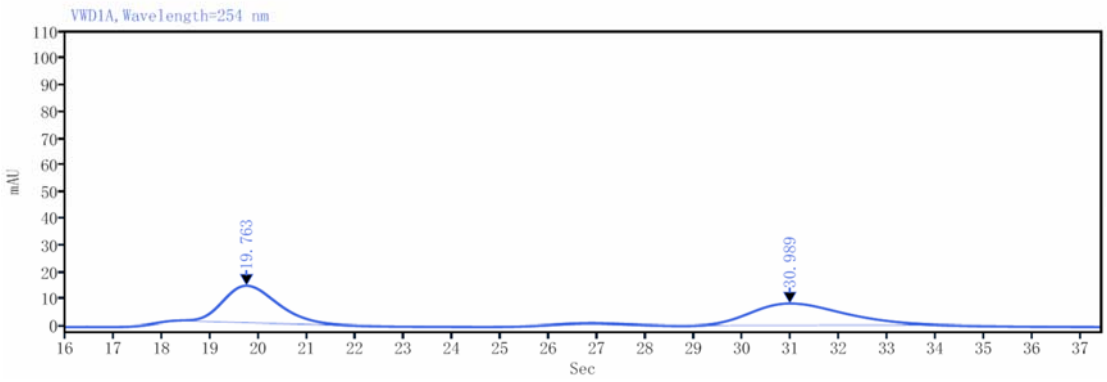
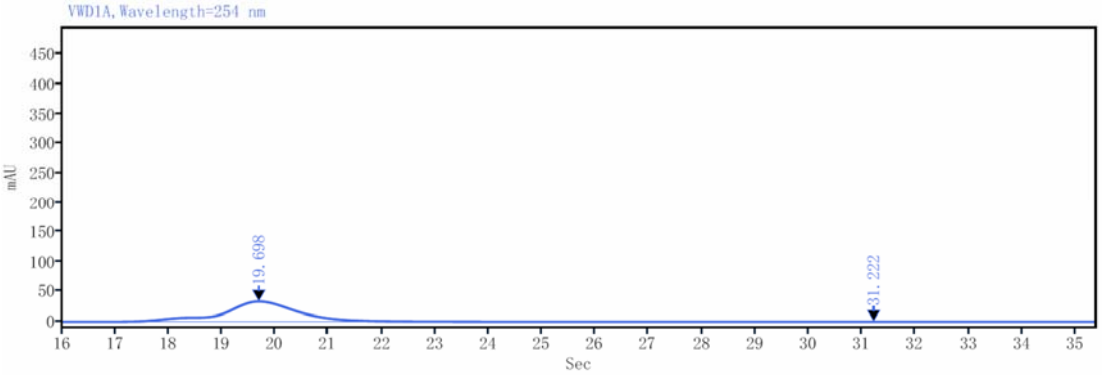
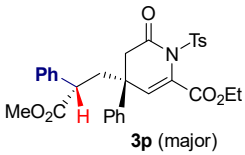


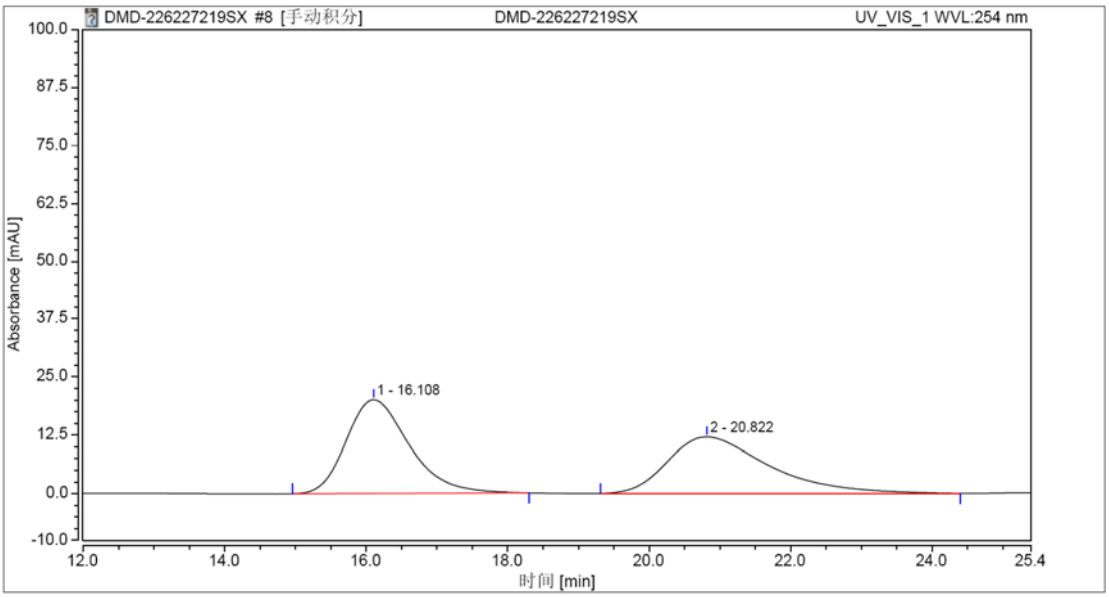
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	19.763	1076.30	13.67	50.65
2	30.989	1048.71	7.95	49.35
Total		2125.02		100.00



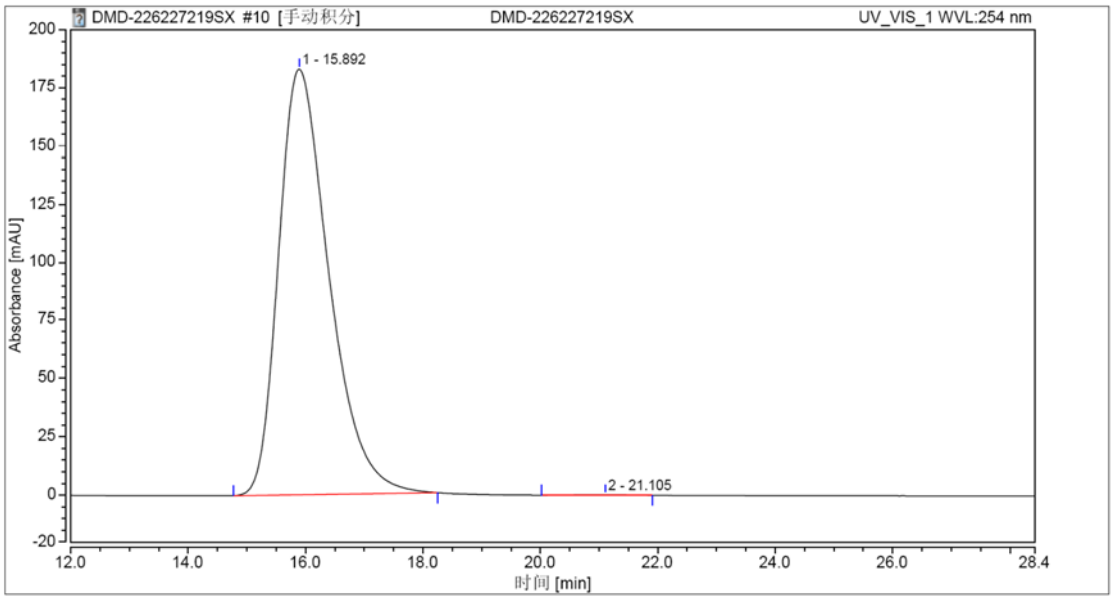
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	19.698	3230.20	33.47	99.69
2	31.222	10.04	0.09	0.31
Total		3240.24		100.00



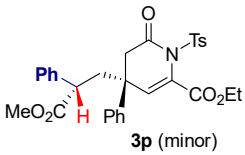
3p (major)



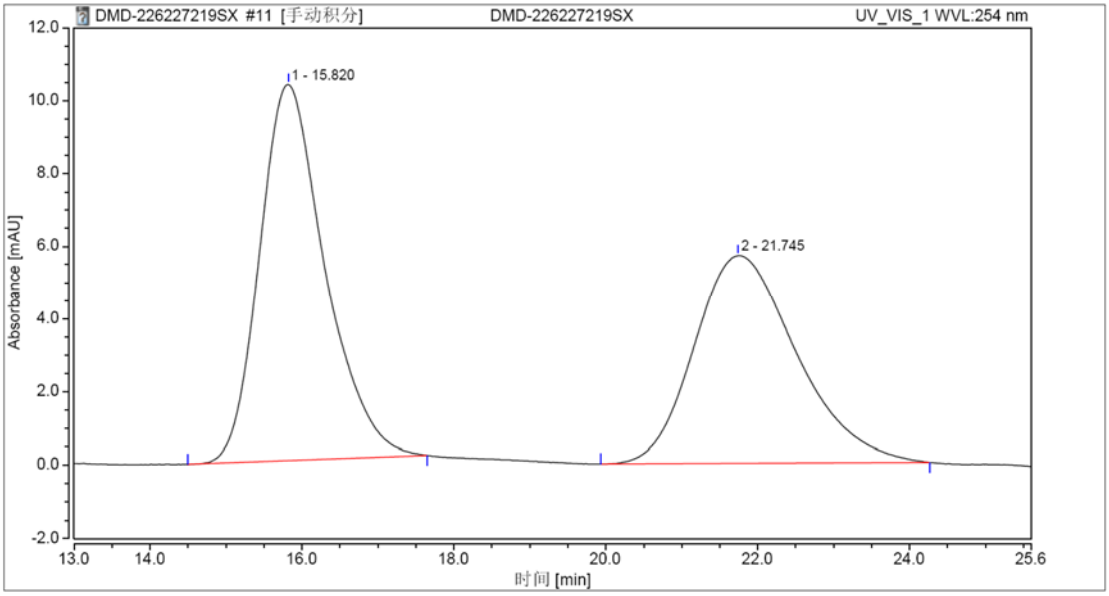
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	16.108	20.626	20.004	51.03
2	20.822	19.790	12.030	48.97
Total		**40.416**	**32.034**	100.00



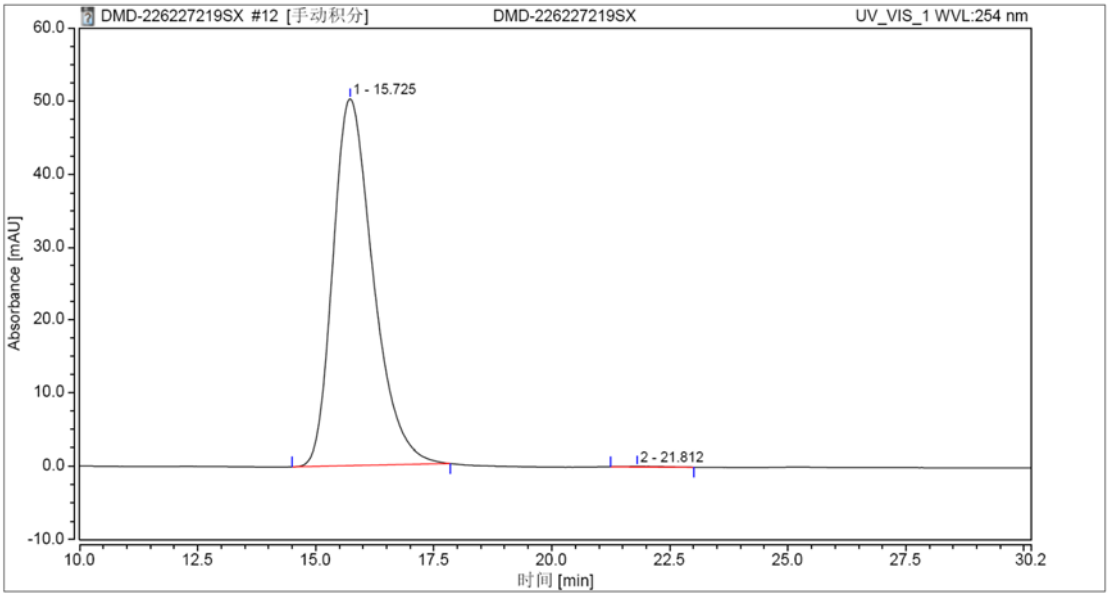
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	15.892	181.453	182.777	99.88
2	21.105	0.213	0.207	0.12
Total		**181.667**	**182.984**	100.00



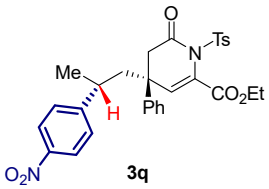
3p (minor)



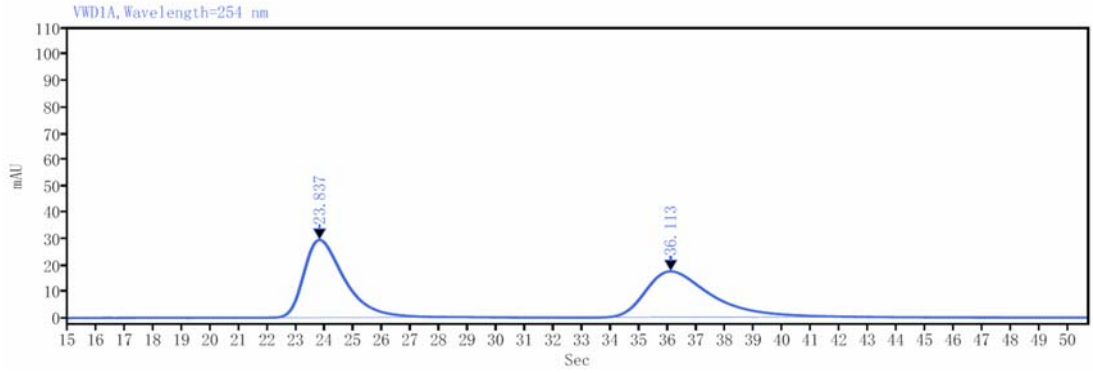
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	15.820	10.260	10.323	53.71
2	21.745	8.841	5.697	46.29
Total		**19.101**	**16.021**	100.00



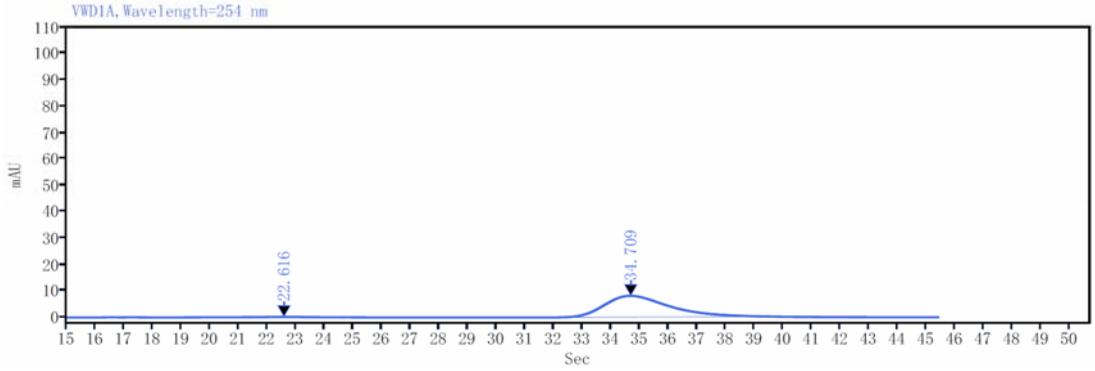
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	15.725	49.599	50.217	99.86
2	21.812	0.069	0.068	0.14
Total		**49.668**	**50.285**	100.00



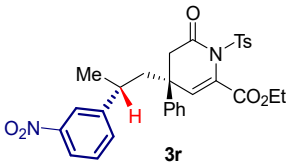
3q



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	23.837	2878.13	29.19	51.19
2	36.113	2744.40	17.22	48.81
Total		5622.54		100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	22.616	9.34	0.13	0.73
2	34.709	1269.31	8.03	99.27
Total		1278.65		100.00



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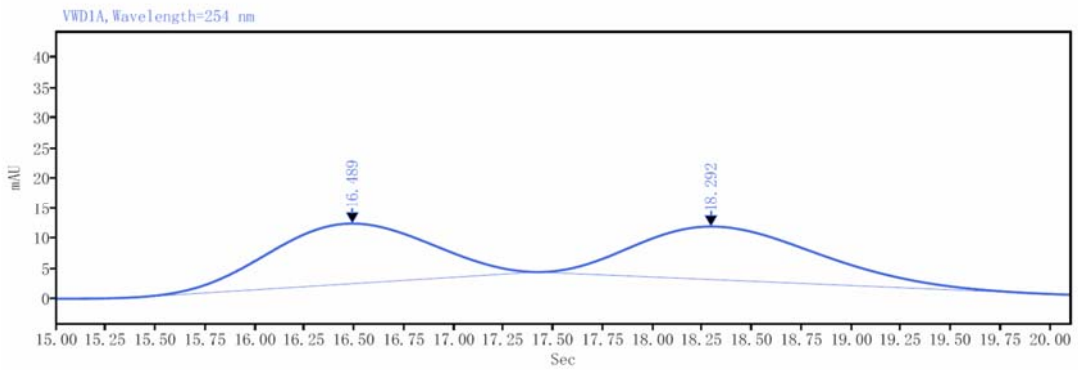
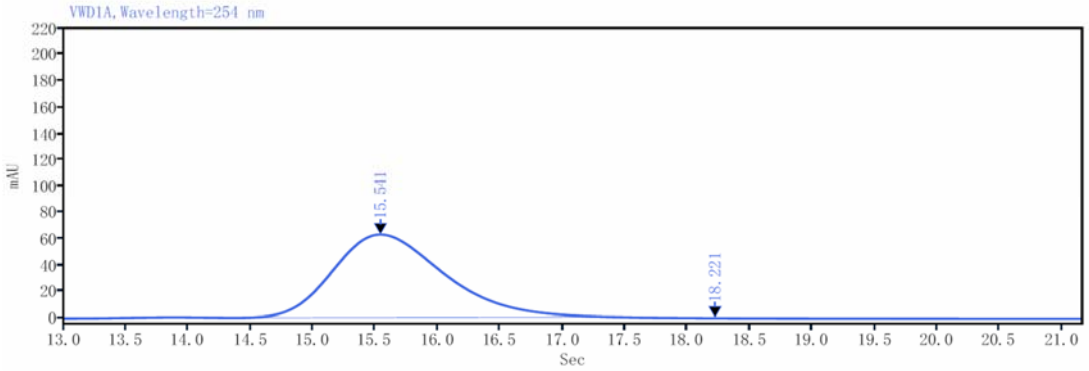
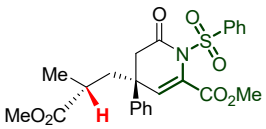


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	16.489	555.85	9.88	49.85
2	18.292	559.15	8.70	50.15
Total		1115.00		100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	15.541	3850.91	62.45	99.90
2	18.221	3.81	0.10	0.10
Total		3854.71		100.00



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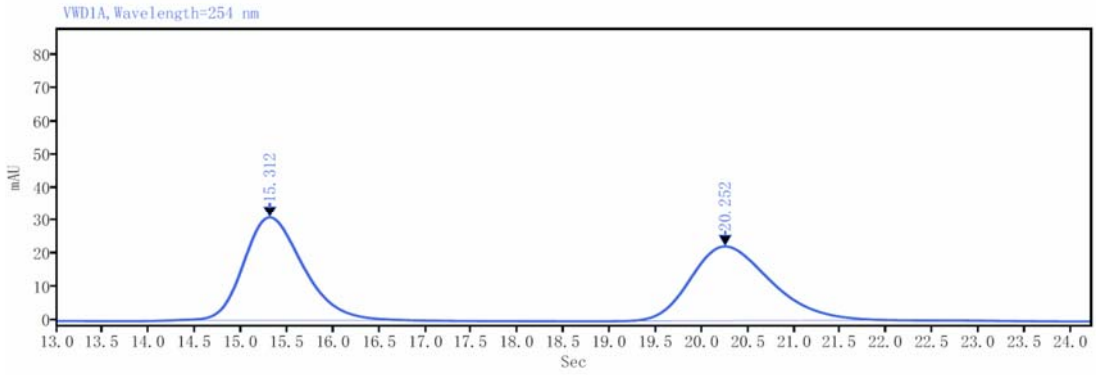
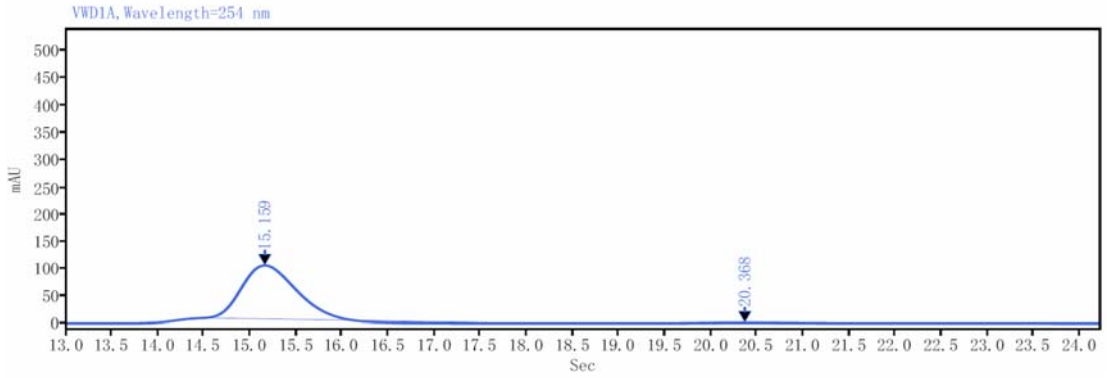
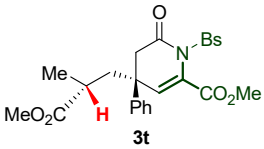


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	15.312	1391.11	30.99	50.80
2	20.252	1347.35	22.31	49.20
Total		2738.46		100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	15.159	3759.41	97.83	98.23
2	20.368	67.92	1.18	1.77
Total		3827.33		100.00



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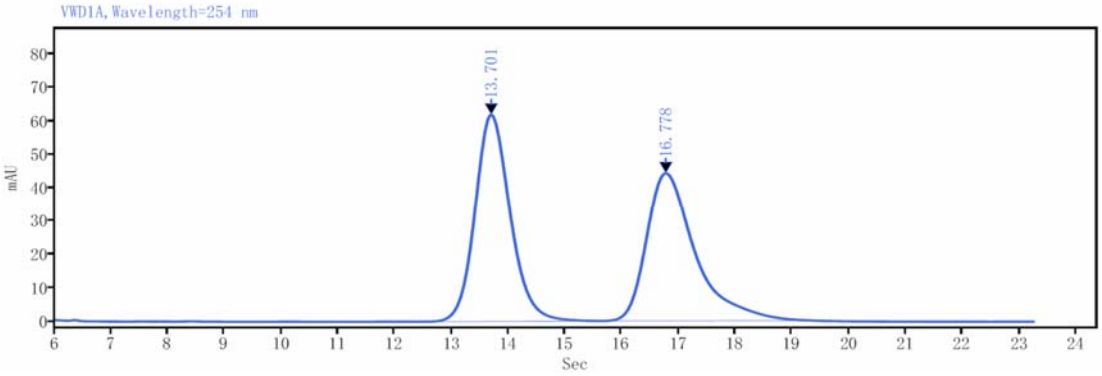
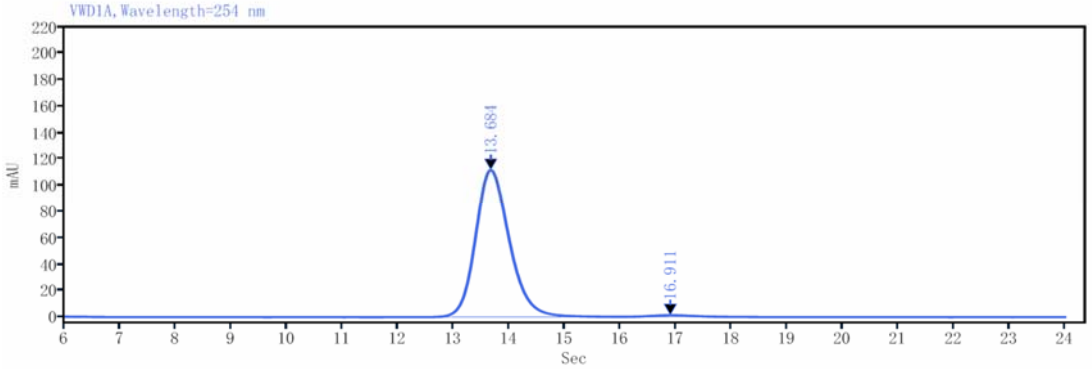
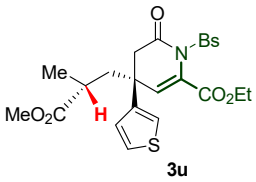


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	13.701	2663.71	61.96	50.43
2	16.778	2618.58	44.23	49.57
Total		5282.29		100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	13.684	4728.52	111.89	98.83
2	16.911	55.92	1.15	1.17
Total		4784.44		100.00



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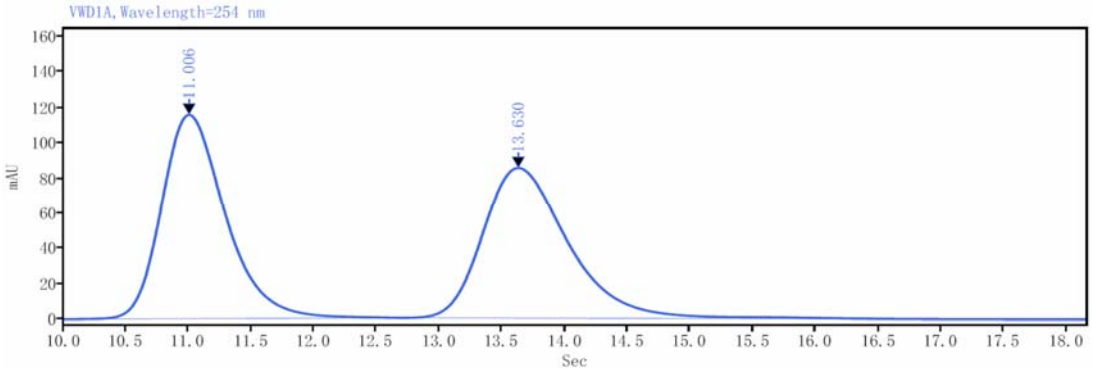
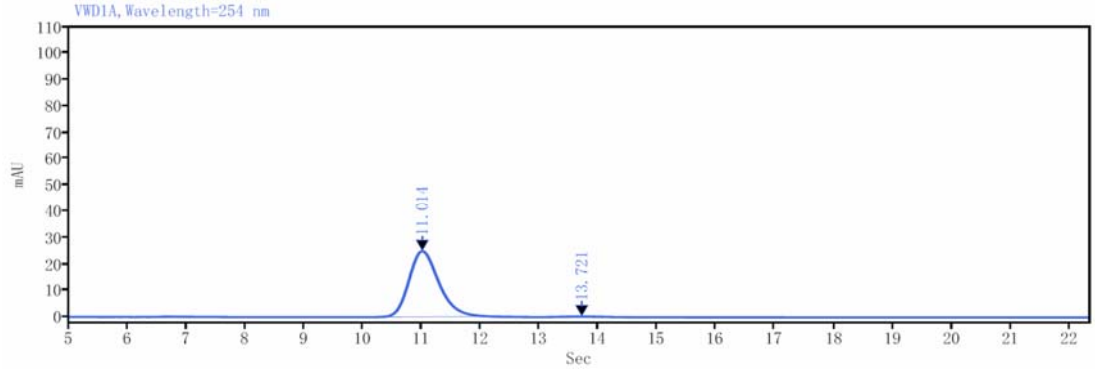
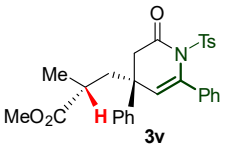


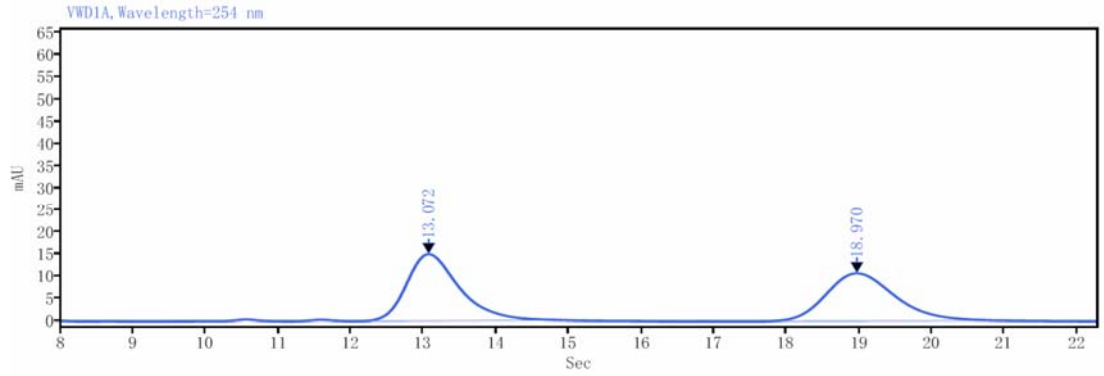
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	11.006	4089.04	115.96	50.34
2	13.630	4034.25	85.51	49.66
Total		8123.29		100.00



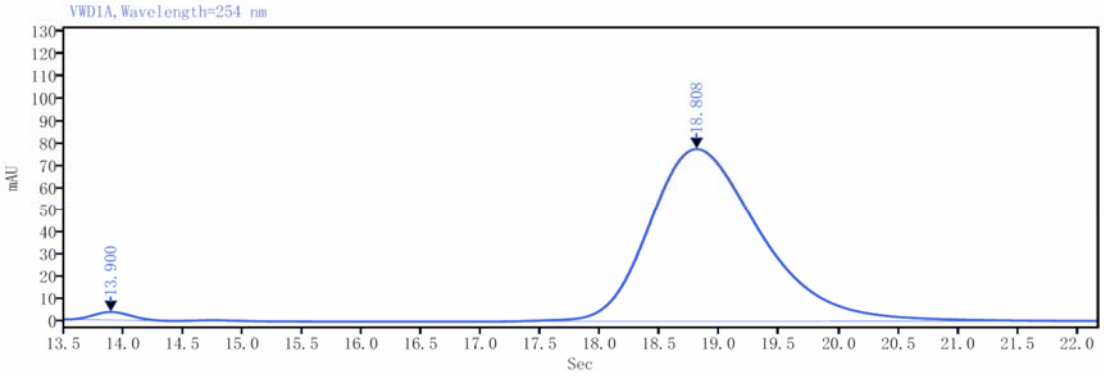
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	11.014	872.10	24.71	99.02
2	13.721	8.64	0.22	0.98
Total		8123.29		100.00



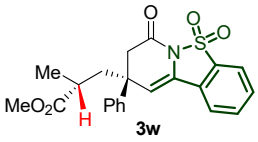
3v



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	13.072	752.32	14.98	51.80
2	18.970	700.17	10.69	48.20
Total		1452.49		100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	13.900	79.17	3.62	1.55
2	18.808	5043.86	77.72	98.45
Total		5123.03		100.00



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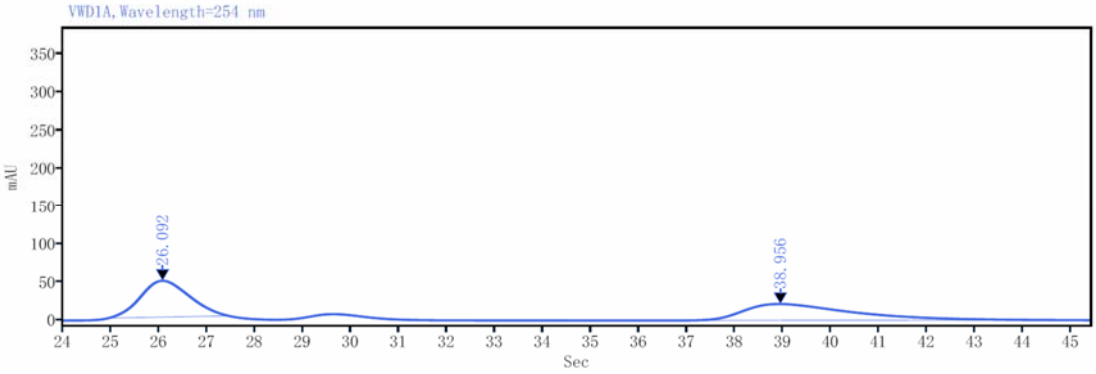
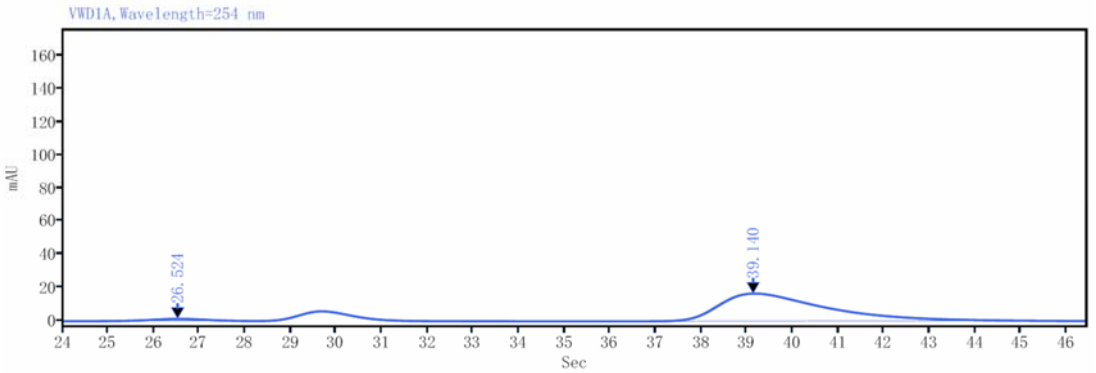
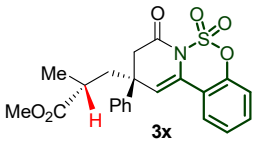
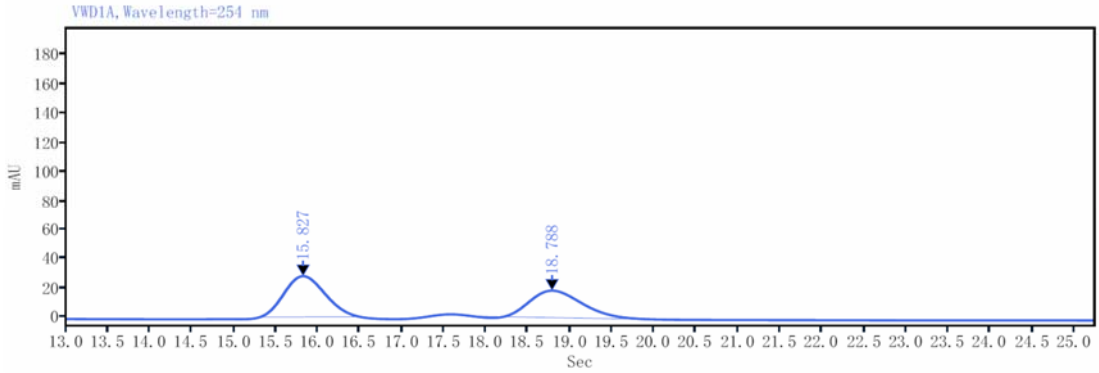


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	26.092	3373.33	47.82	50.28
2	38.956	3336.02	21.47	49.72
Total		6709.35		100.00

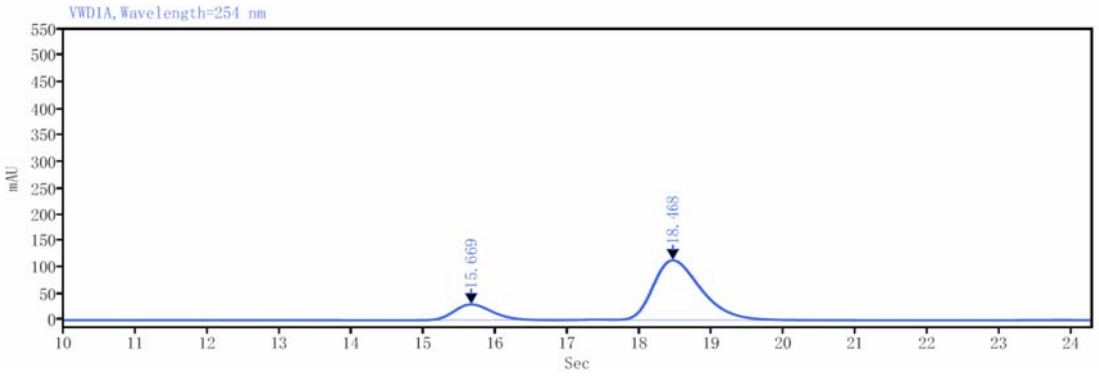


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	26.524	96.92	1.24	3.54
2	39.140	2639.48	16.47	96.46
Total		2736.40		100.00

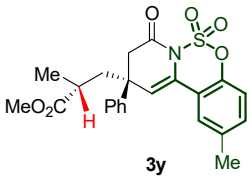




Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	15.827	934.71	27.81	54.54
2	18.788	779.20	18.38	45.46
Total		1713.91		100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	15.669	1075.22	29.66	17.06
2	18.468	5228.23	113.16	82.94
Total		6303.45		100.00



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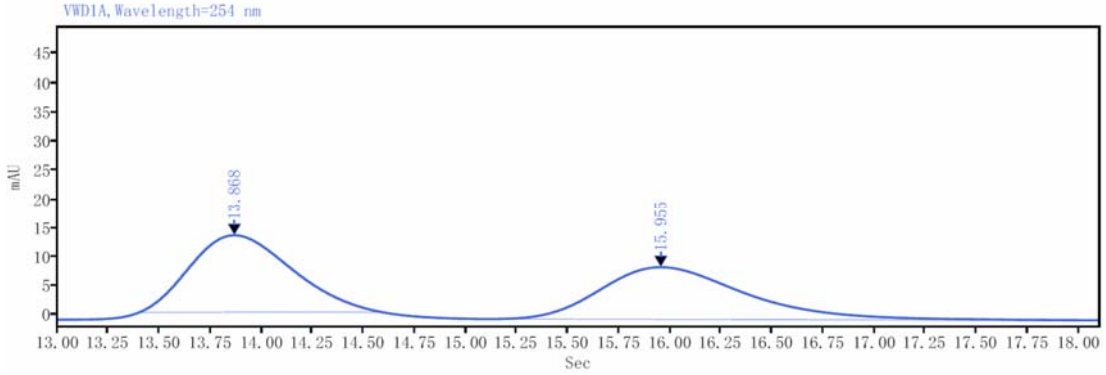
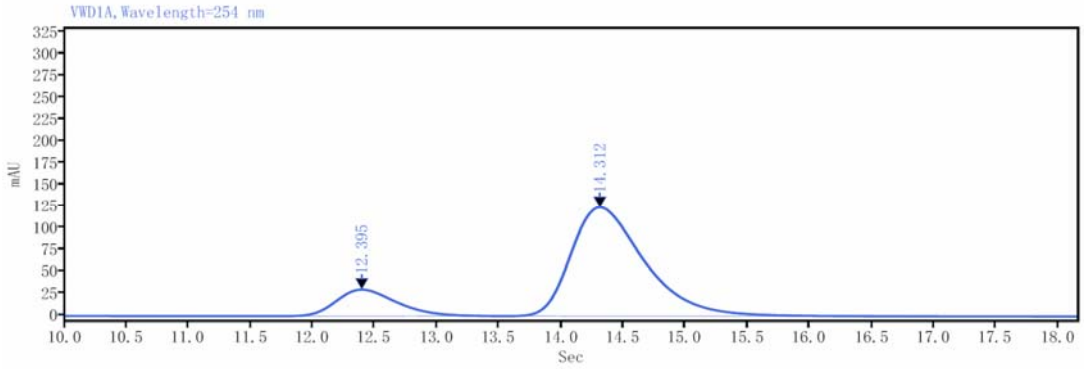
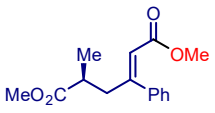


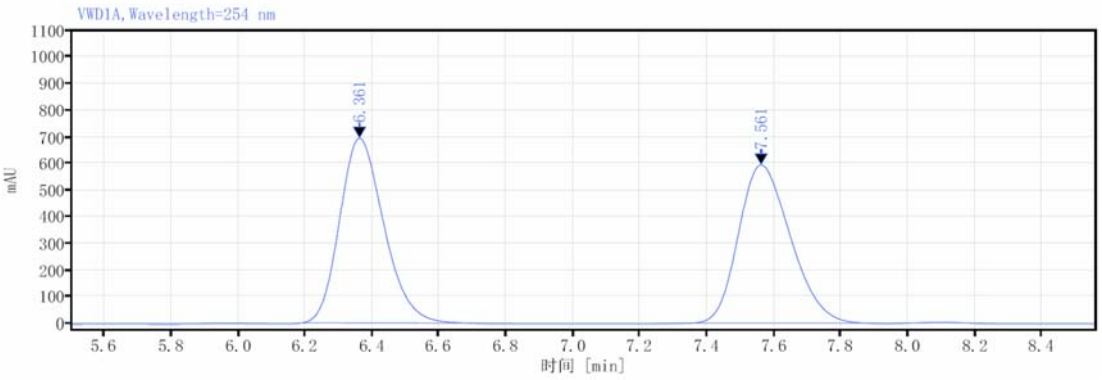
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	13.868	456.68	13.22	50.87
2	15.955	441.08	8.95	49.13
Total		897.76		100.00



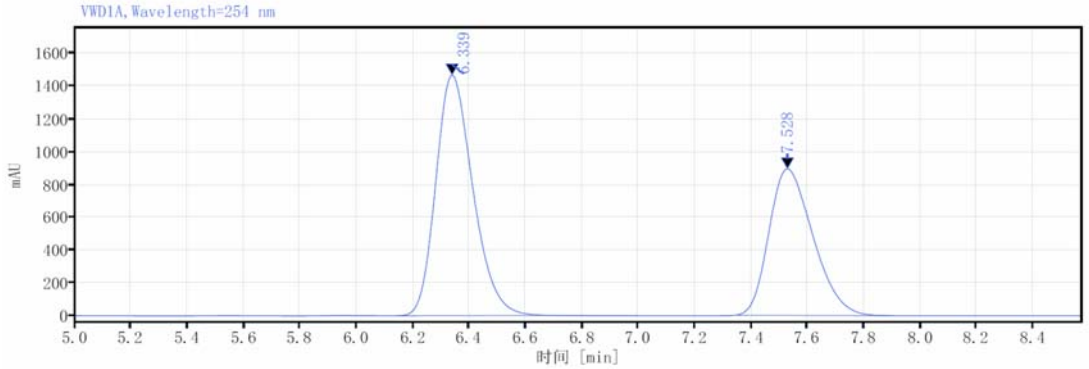
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	12.395	1021.14	30.25	16.62
2	14.312	5121.88	124.44	83.38
Total		6143.03		100.00



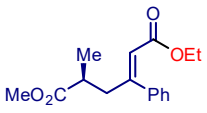
6a



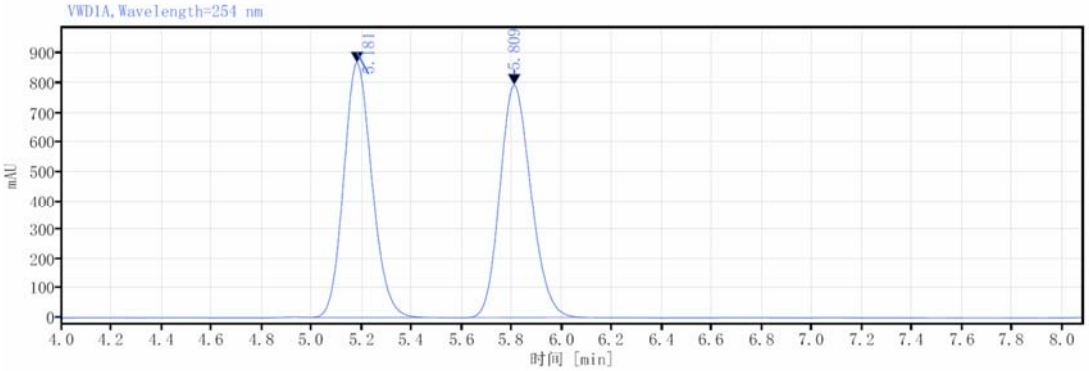
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.361	6353.01	693.84	49.87
2	7.561	6385.09	594.49	50.13
Total		12738.10		100.00



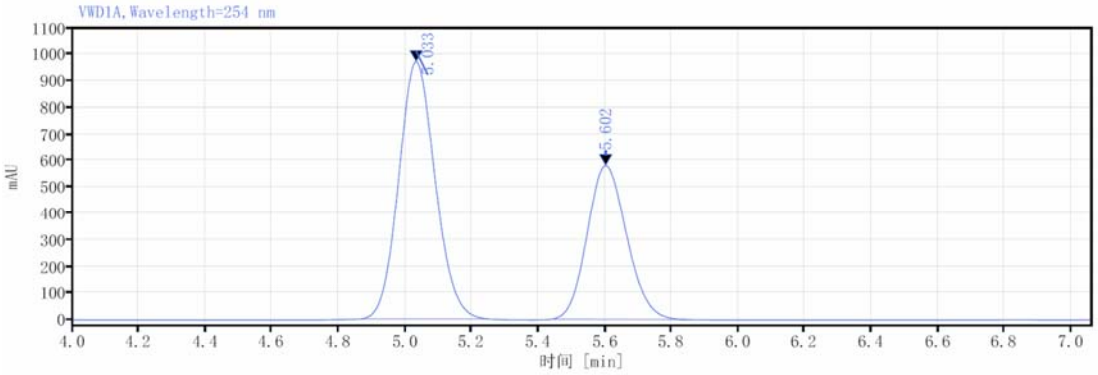
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	6.339	13463.15	1467.64	58.00
2	7.528	9748.95	899.91	42.00
Total		23212.11		100.00



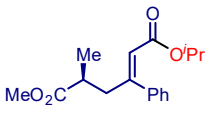
6b



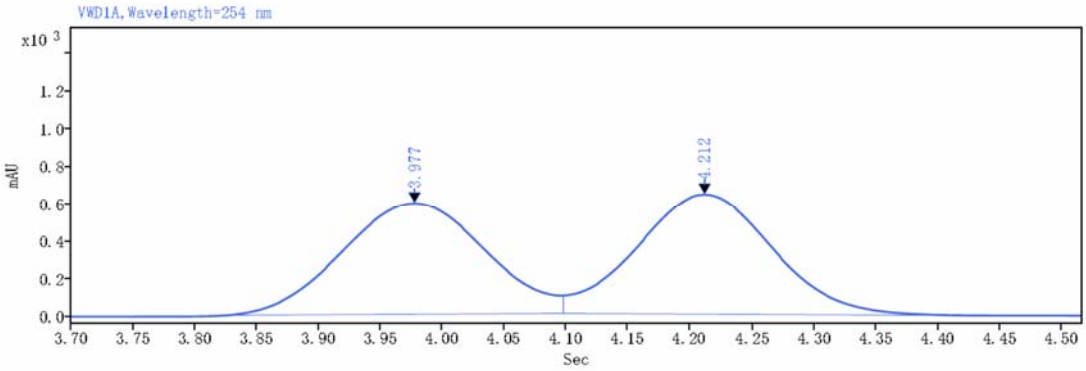
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	5.181	6821.64	866.49	49.81
2	5.809	6874.50	792.05	50.19
Total		13696.14		100.00



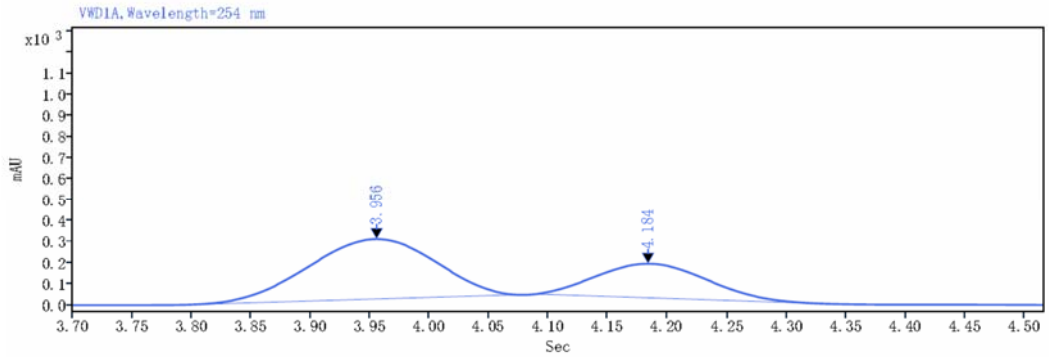
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	5.033	7357.32	968.46	60.69
2	5.602	4766.00	580.07	39.31
Total		12123.32		100.00



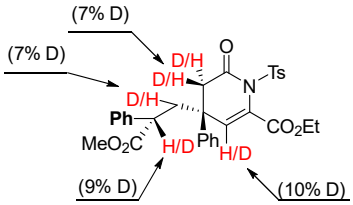
6c



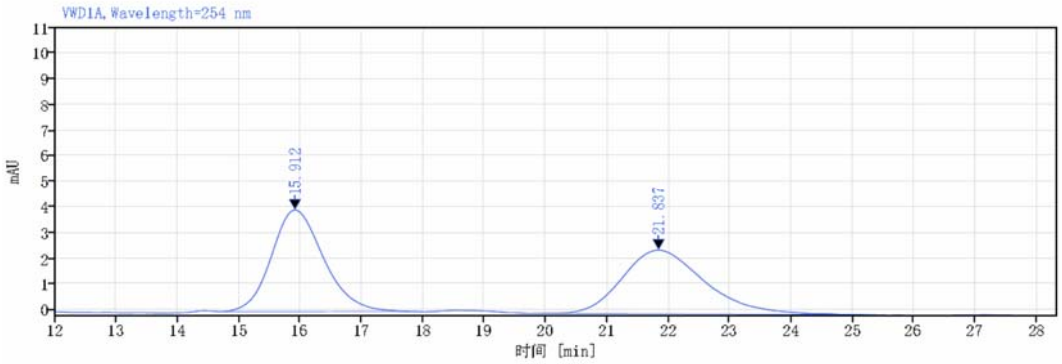
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.977	4759.20	593.52	49.37
2	4.212	4881.26	640.01	50.63
Total		9640.46		100.00



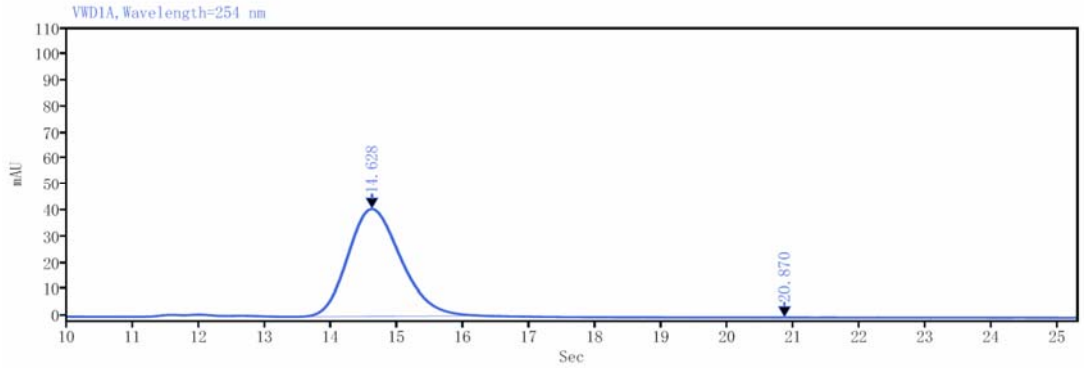
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	3.956	2088.27	282.64	66.79
2	4.184	1038.31	160.73	33.21
Total		3126.58		100.00



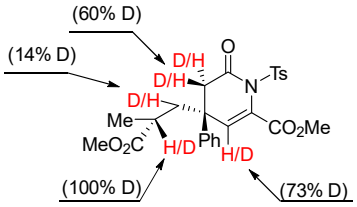
3p'



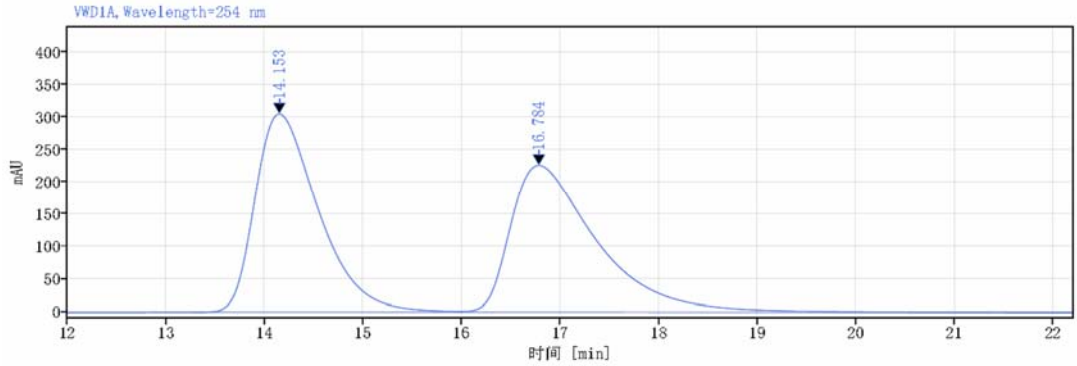
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	15.912	231.47	3.93	50.35
2	21.837	228.25	2.46	49.65
Total		459.73		100.00



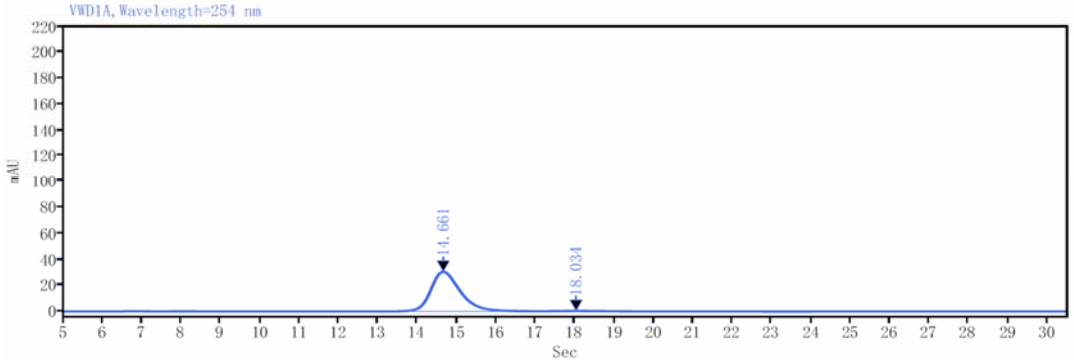
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	14.728	3184.70	58.48	99.98
2	20.751	0.53	0.02	0.02
Total		3185.23		100.00



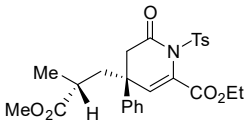
3g'



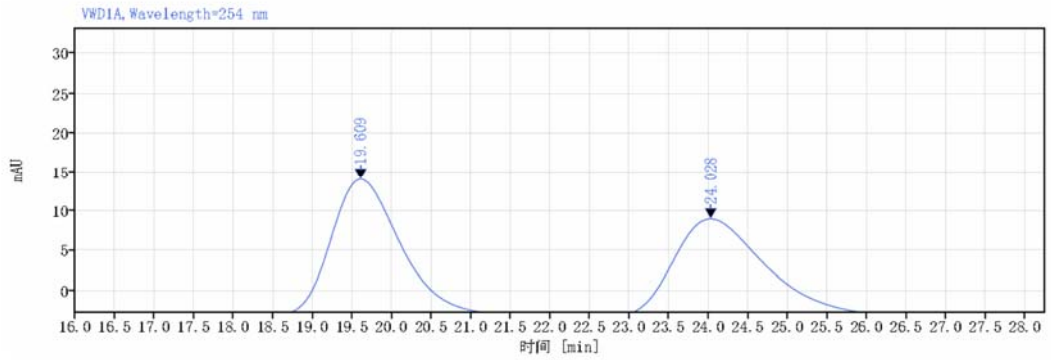
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	14.683	13649.12	305.96	49.79
2	16.784	13763.91	226.74	50.21
Total		**27413.02**		100.00



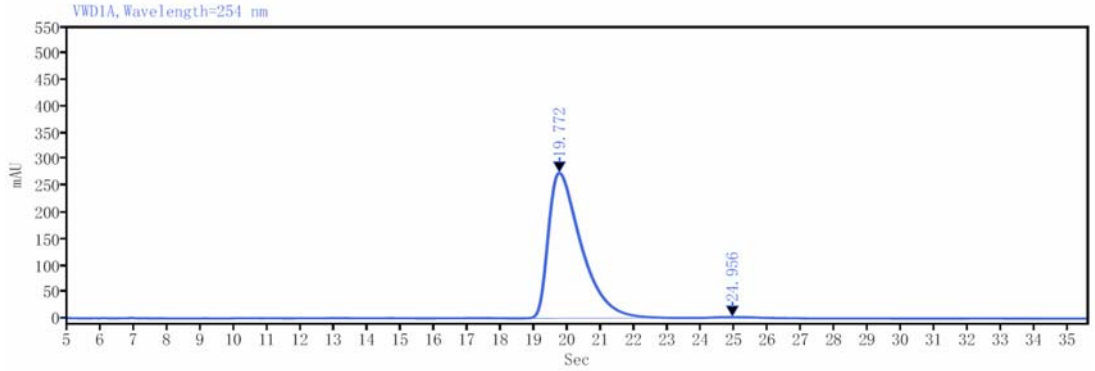
Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	14.661	1579.20	30.36	98.87
2	18.034	17.97	0.26	1.13
Total		1597.18		100.00



3a'

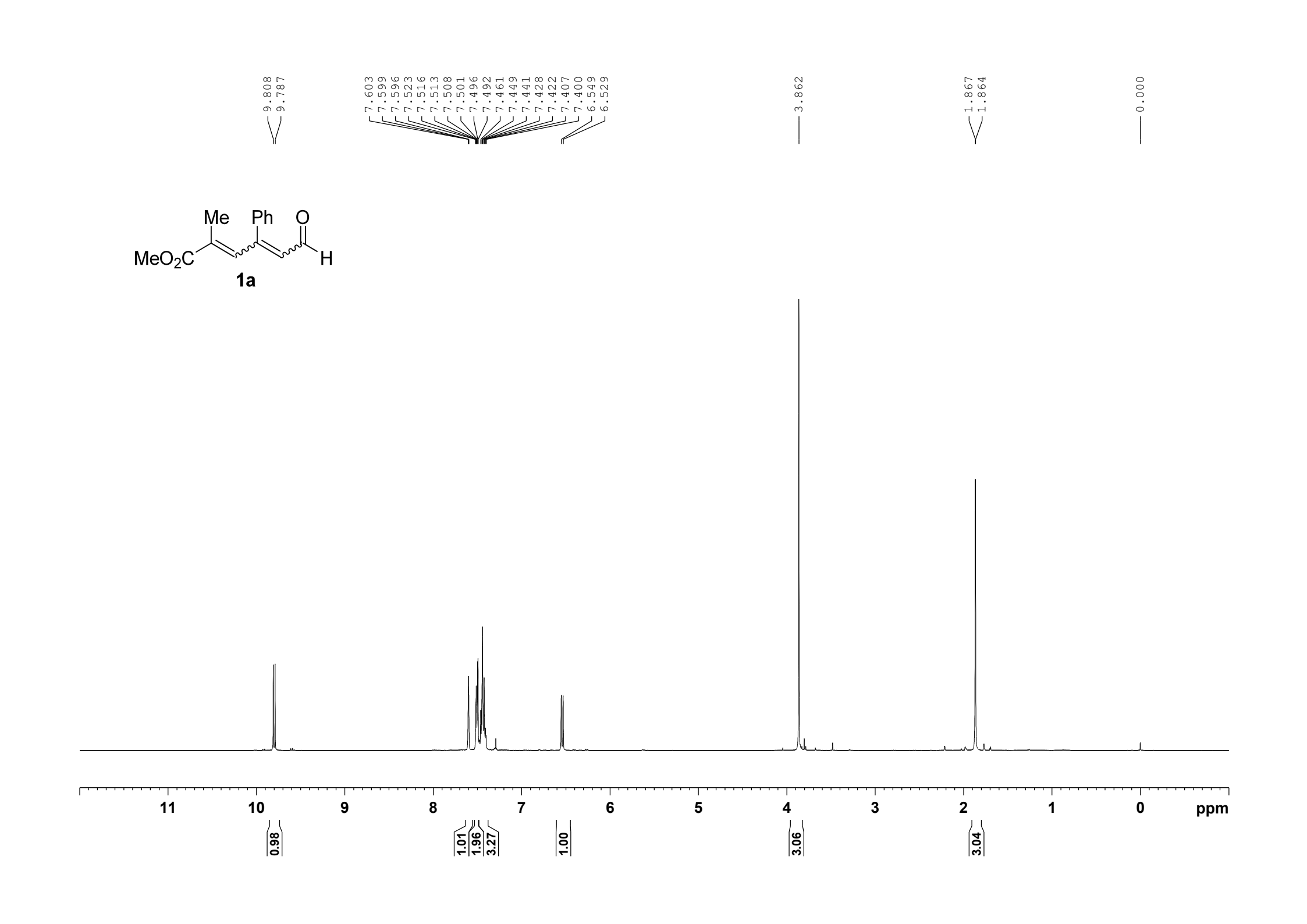


Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	19.609	1064.77	17.24	50.11
2	24.028	1060.19	12.43	49.89
Total		2124.95		100.00



Peak#	Ret. Time (min)	Area (mAU)	Height (mAU)	Area %
1	19.772	18838.86	273.82	99.01
2	24.956	188.28	2.11	0.99
Total		19027.14		100.00

Part 6: ^{1}HNMR and ^{13}CNMR spectra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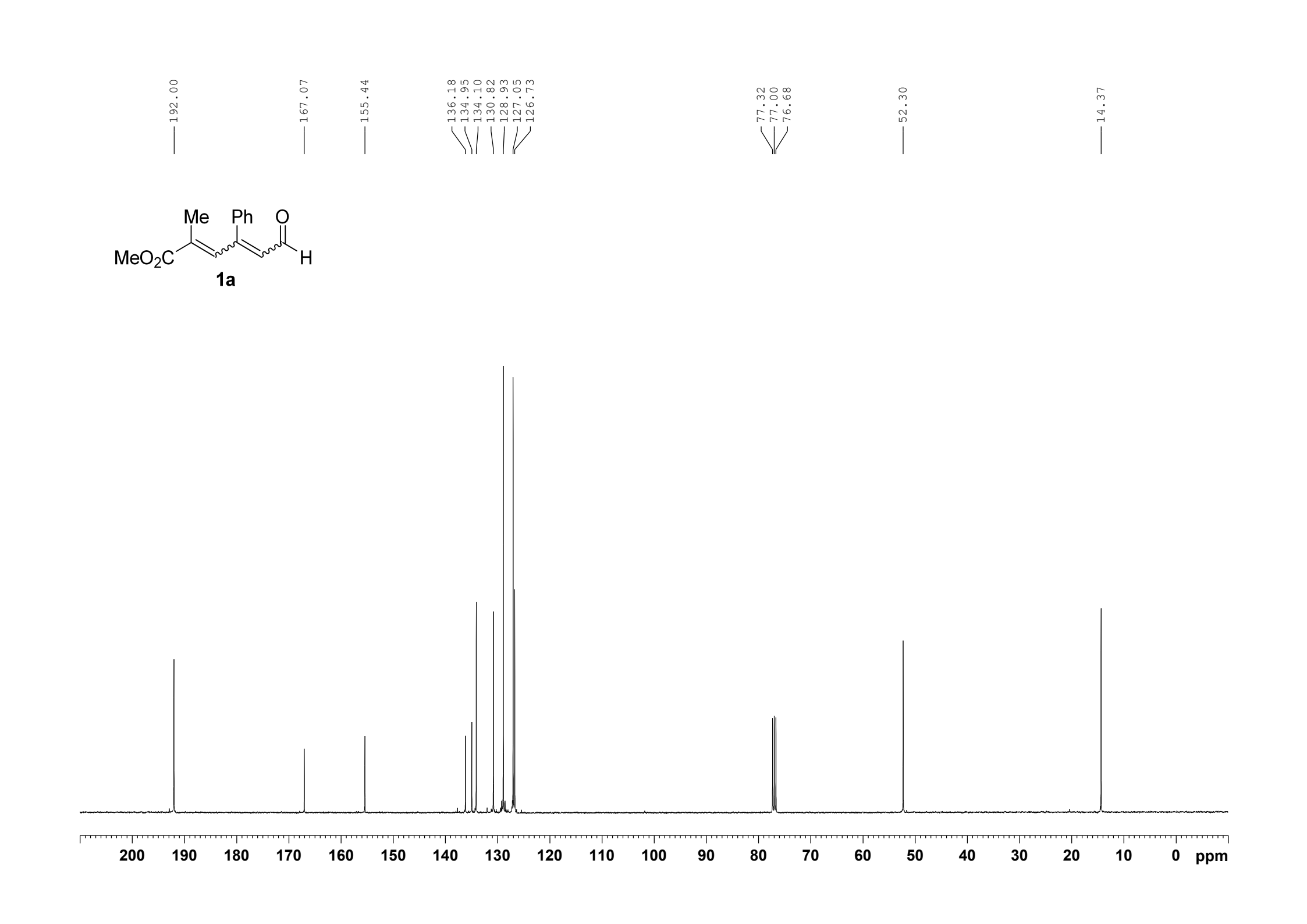
9.787
7.603
7.599
7.596
7.523
7.516
7.513
7.508
7.501
7.496
7.492
7.461
7.449
7.441
7.428
7.422
7.407
7.400
6.549
6.529
3.862
1.867
1.864
0.000
Me
Ph
O
MeO2C
H
1a
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.98
1.01
1.96
3.27
1.00
3.06
3.04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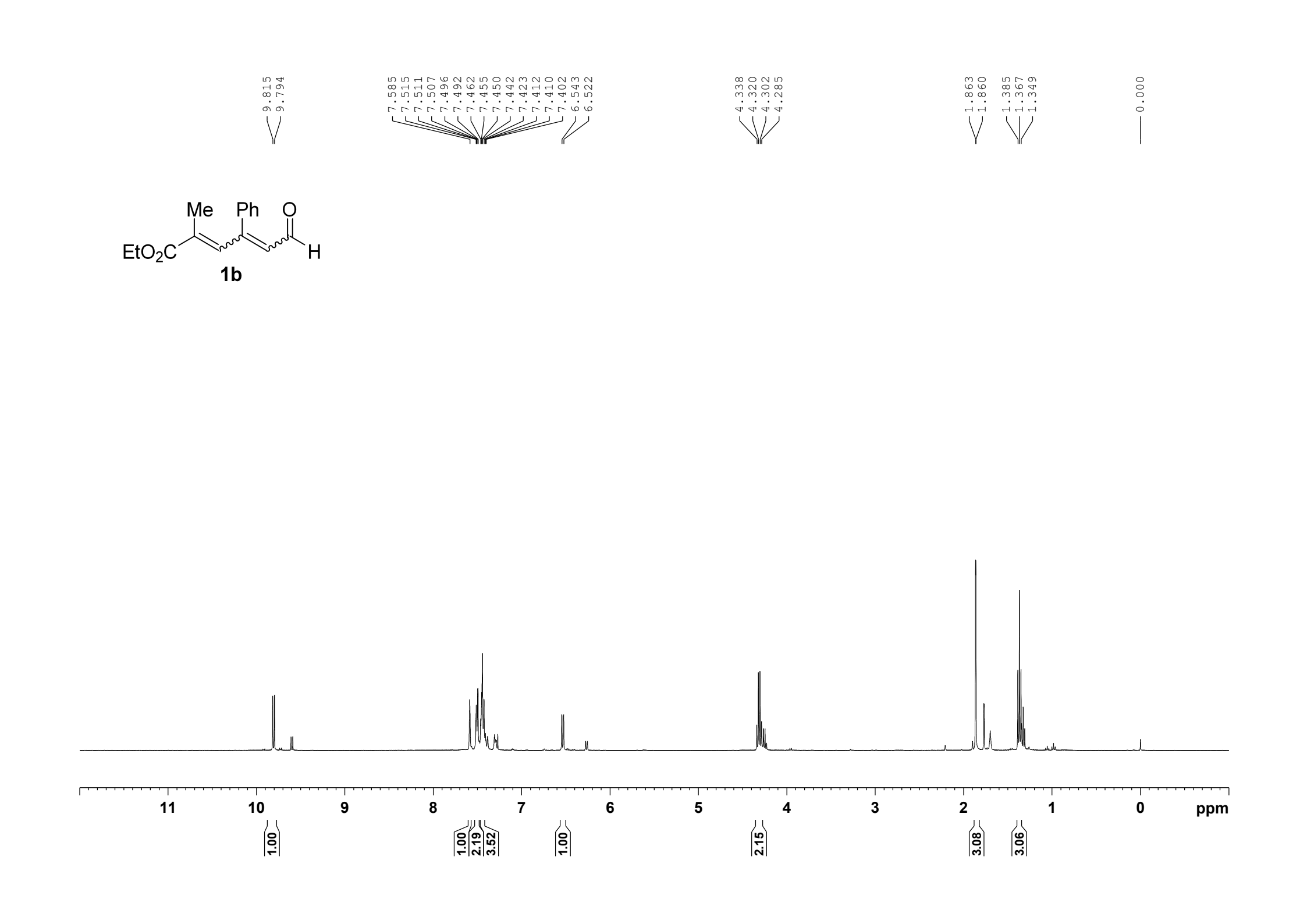
155.44
136.18
134.95
134.10
130.82
128.93
127.05
126.73
77.32
77.00
76.68
52.30
14.37
Me
Ph
O
MeO2C
H
1a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.585
7.515
7.511
7.507
7.496
7.492
7.462
7.455
7.450
7.442
7.423
7.412
7.410
7.402
6.543
6.522
4.338
4.320
4.302
4.285
1.863
1.860
1.385
1.367
1.349
0.000
Me
Ph
O
EtO2C
H
1b
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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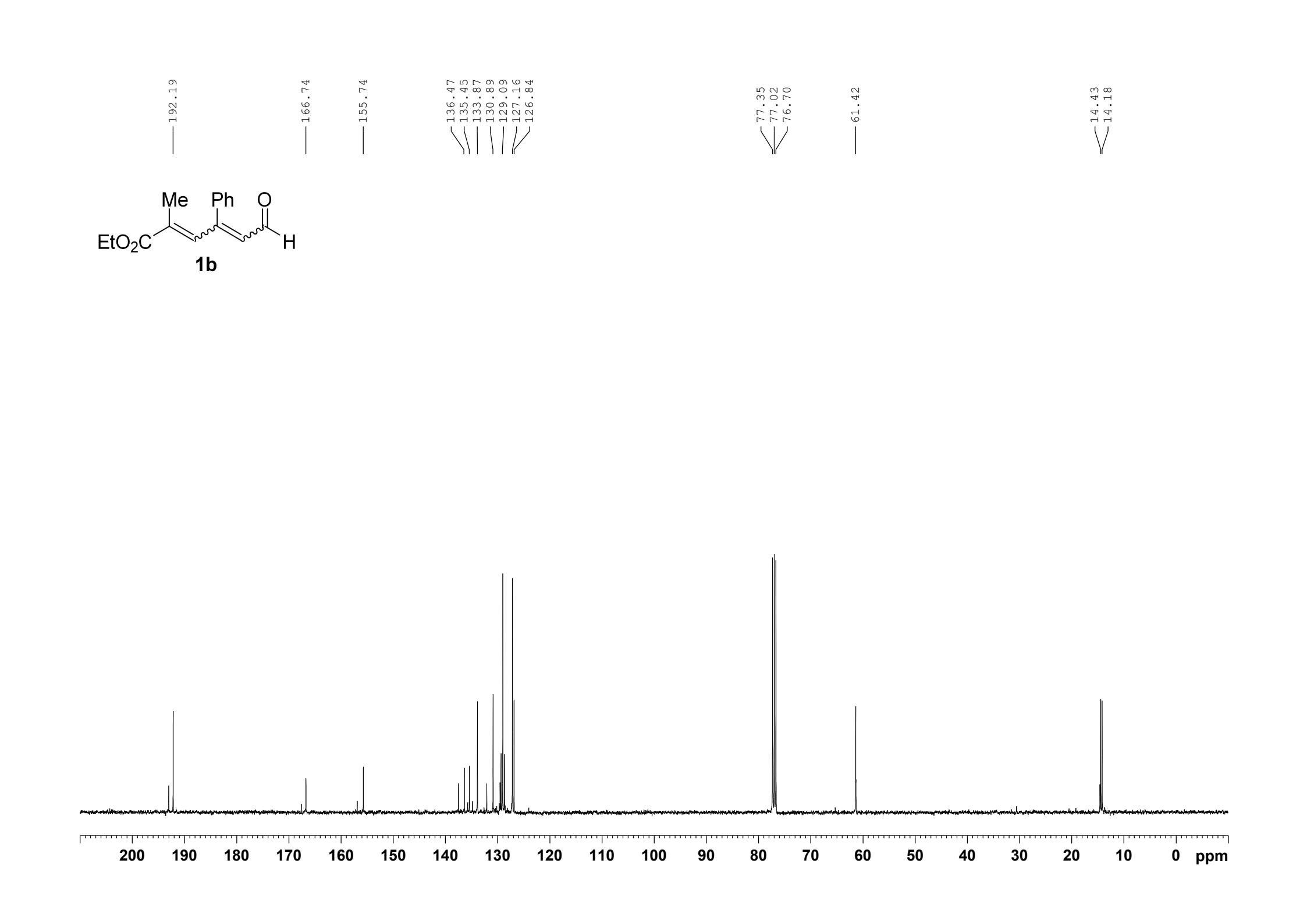
3.52
1.00
2.15
3.08
3.06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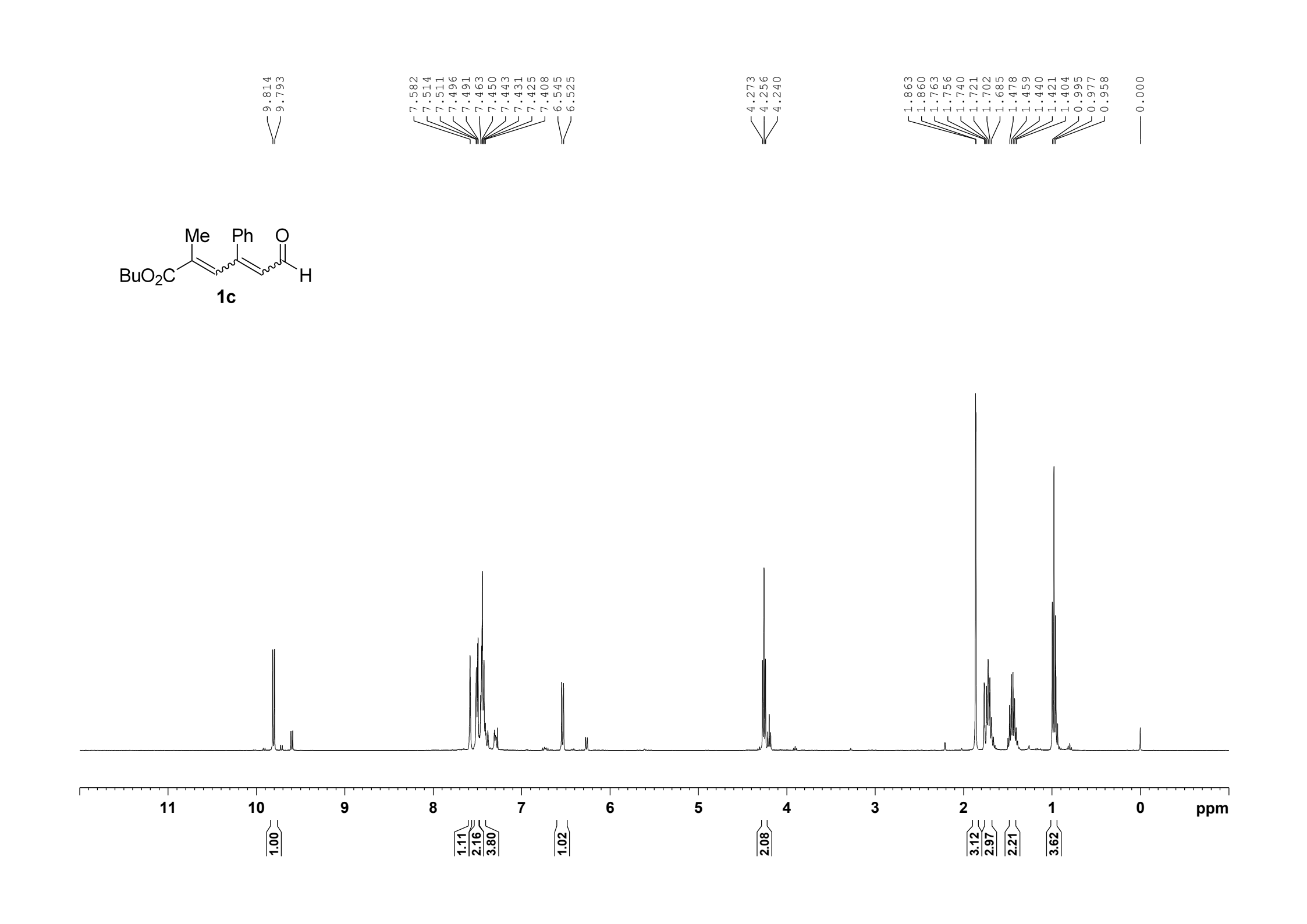
129.09
127.16
126.84
77.35
77.02
76.70
61.42
14.43
14.18
Me
Ph
O
EtO2C
H
1b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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9.793
7.582
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7.511
7.496
7.491
7.463
7.450
7.443
7.431
7.425
7.408
6.545
6.525
4.273
4.256
4.240
1.863
1.860
1.763
1.756
1.740
1.721
1.702
1.685
1.478
1.459
1.440
1.421
1.404
0.995
0.977
0.958
0.000
Me
Ph
O
BuO2C
H
1c
11
10
9
8
7
6
5
4
3
2
1
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1.11
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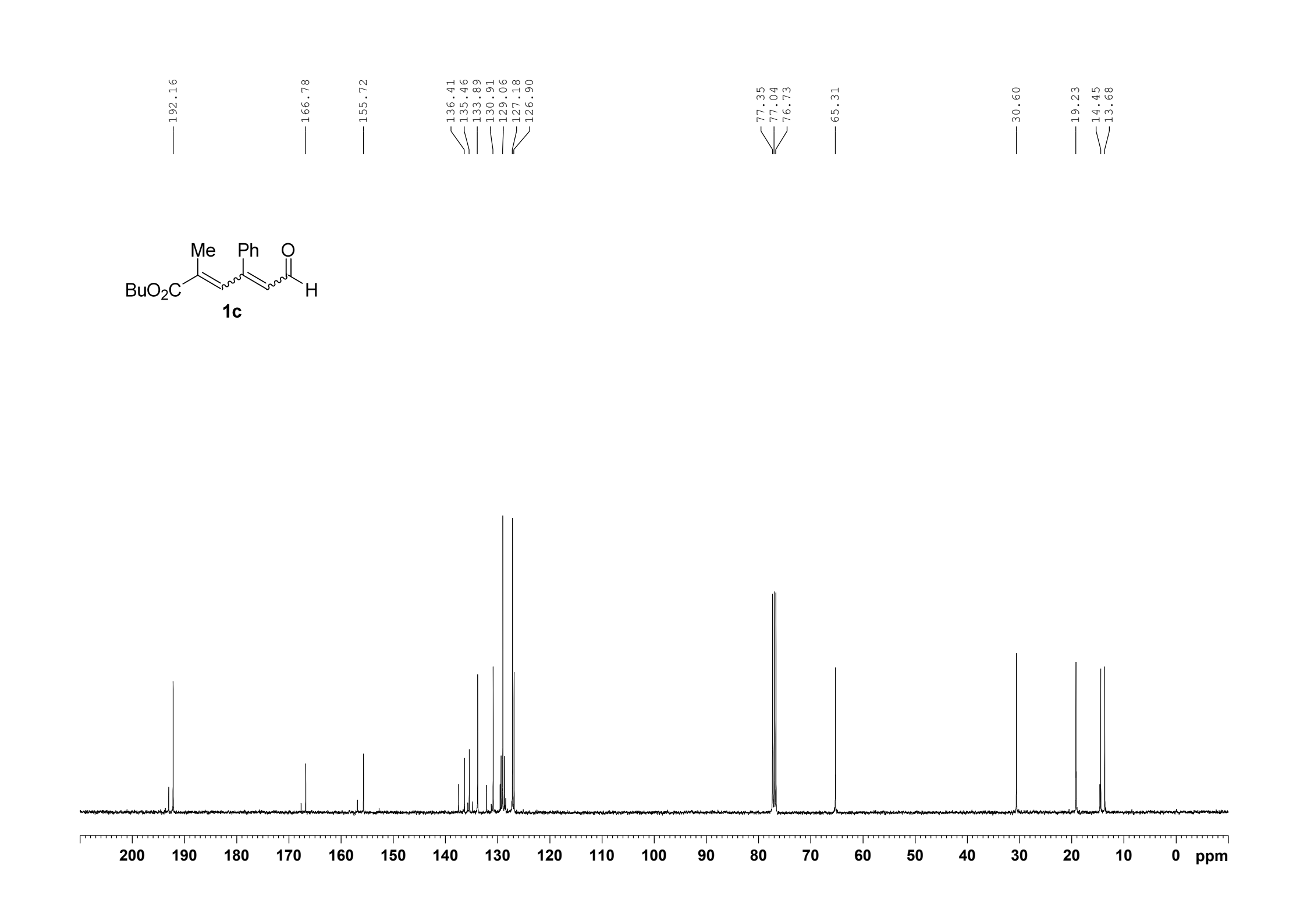
3.80
1.02
2.08
3.12
2.97
2.21
3.62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133.89
130.91
129.06
127.18
126.90
77.35
77.04
76.73
65.31
30.60
19.23
14.45
13.68
Me
Ph
O
BuO2C
H
1c
200
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180
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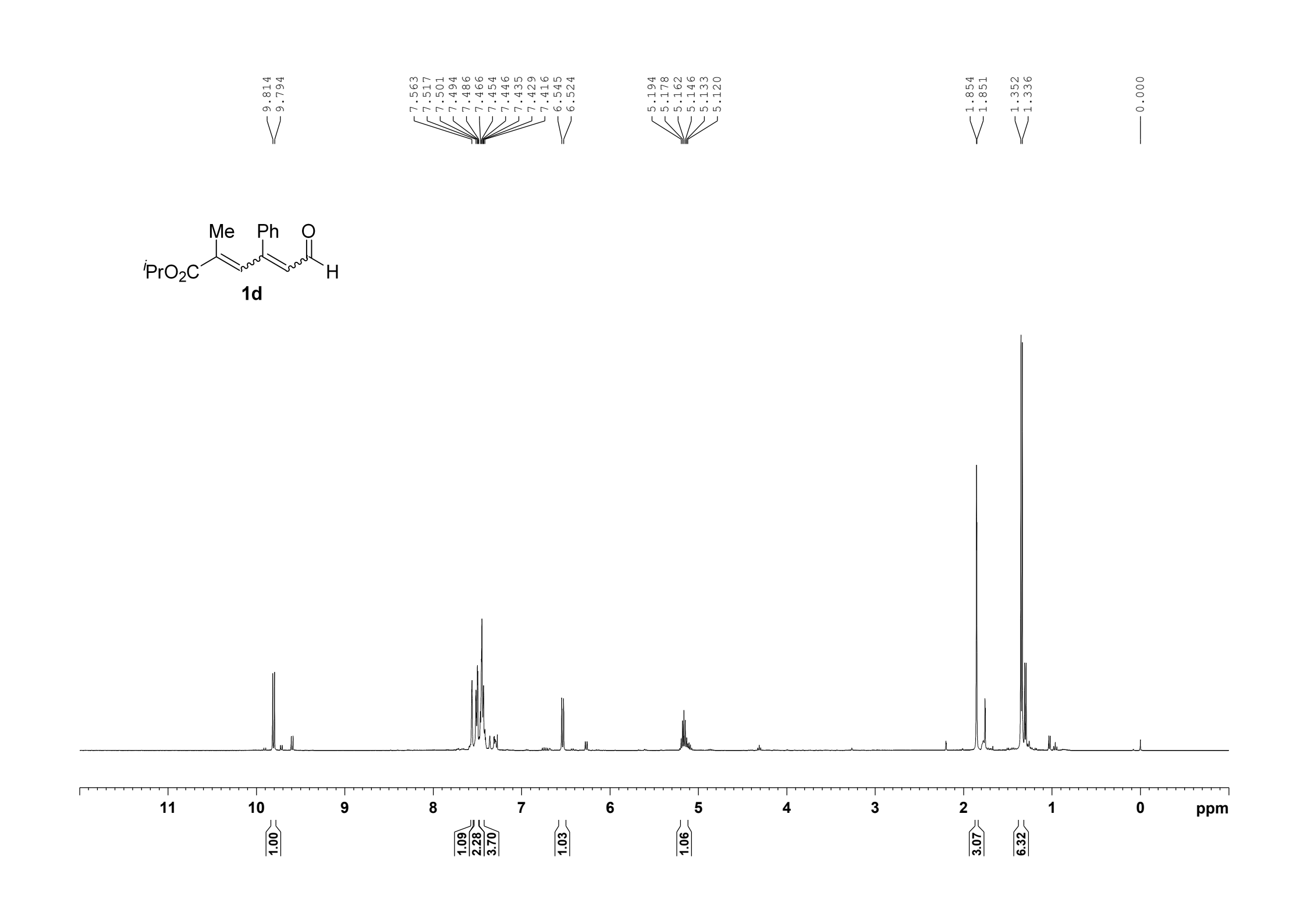
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.563
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7.501
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7.466
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7.446
7.435
7.429
7.416
6.545
6.524
5.194
5.178
5.162
5.146
5.133
5.120
1.854
1.851
1.352
1.336
0.000
Me
Ph
O
iPrO2C
H
1d
11
10
9
8
7
6
5
4
3
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1
0
ppm
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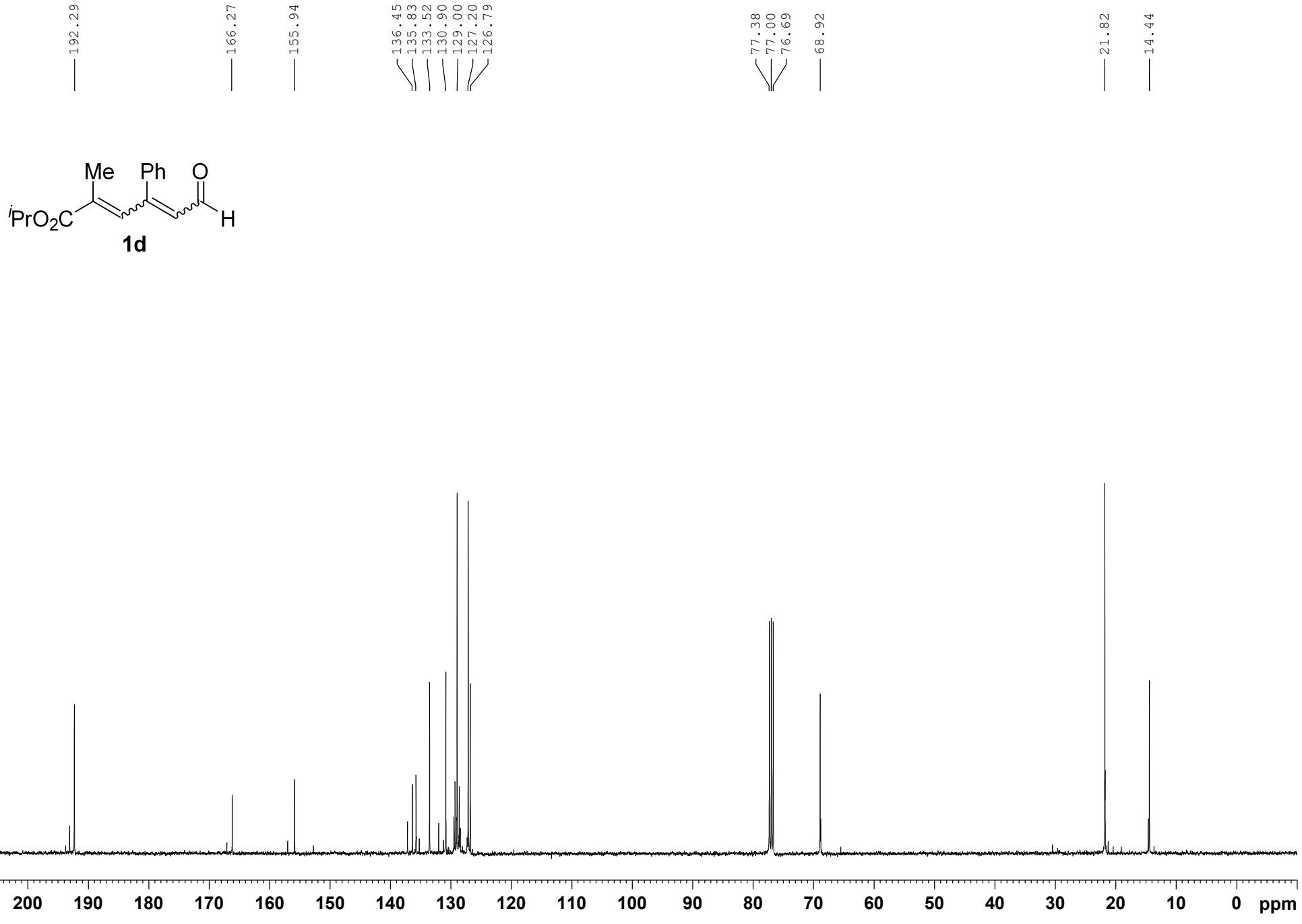
3.70
1.03
1.06
3.07
6.32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133.52
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77.38
77.00
76.69
68.92
21.82
14.44
Me
Ph
O
iPrO2C
H
1d
200
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180
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140
130
120
110
100
90
80
70
60
50
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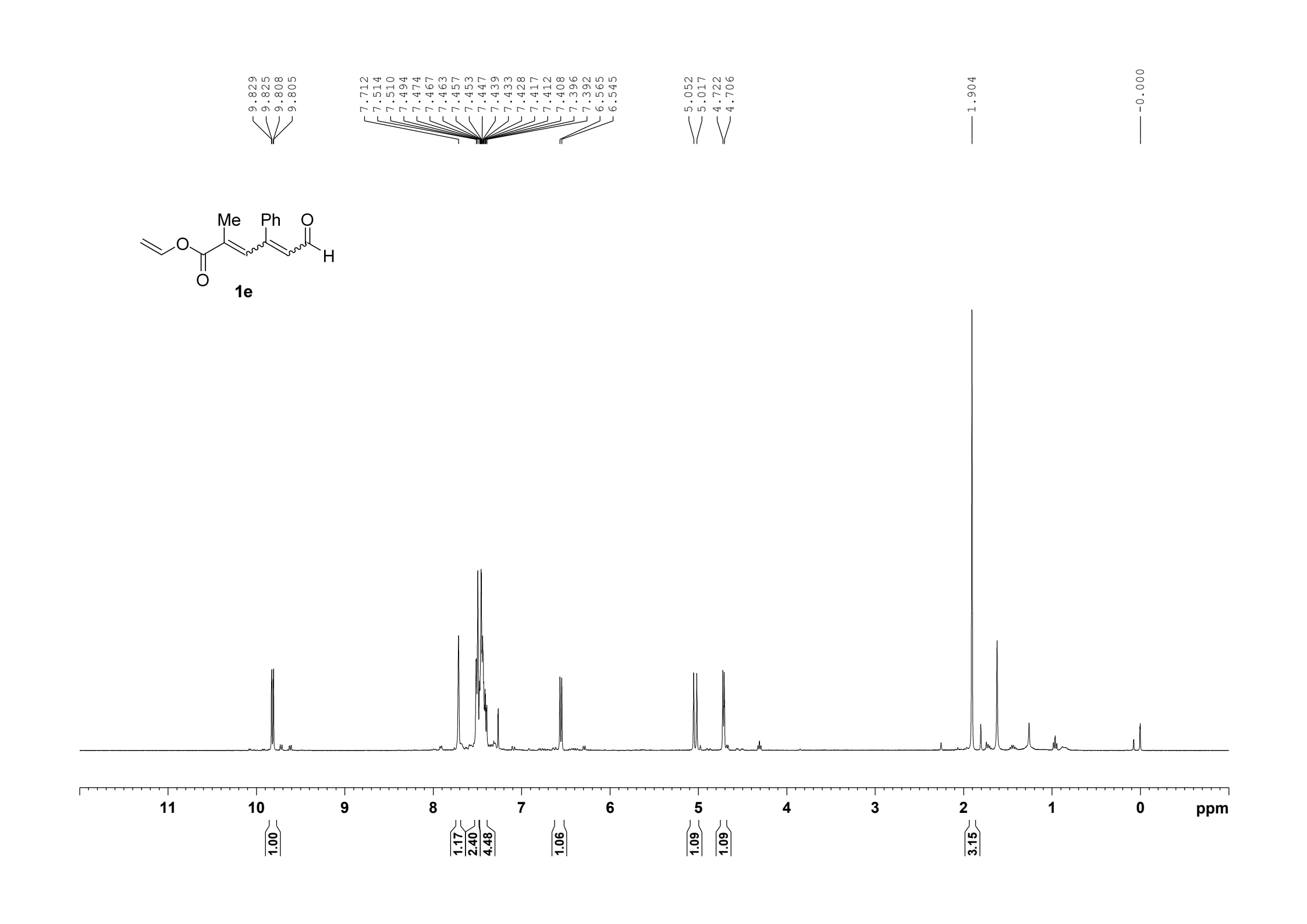
30
20
10
0
ppm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9.808
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7.712
7.514
7.510
7.494
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7.467
7.463
7.457
7.453
7.447
7.439
7.433
7.428
7.417
7.412
7.408
7.396
7.392
6.565
6.545
5.052
5.017
4.722
4.706
1.904
-0.000
Me
Ph
O
O
O
H
1e
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10
9
8
7
6
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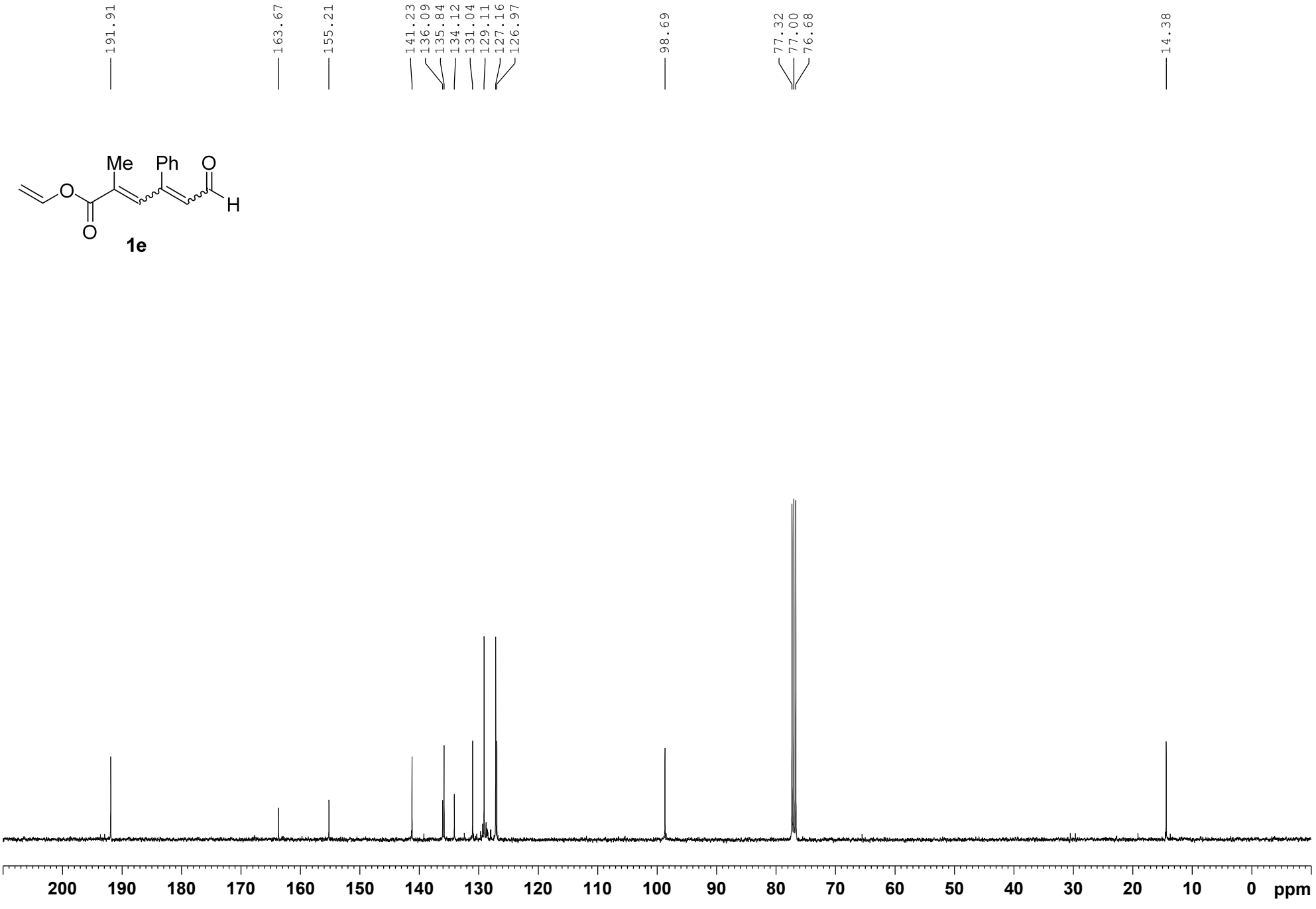
1.09
1.09
3.15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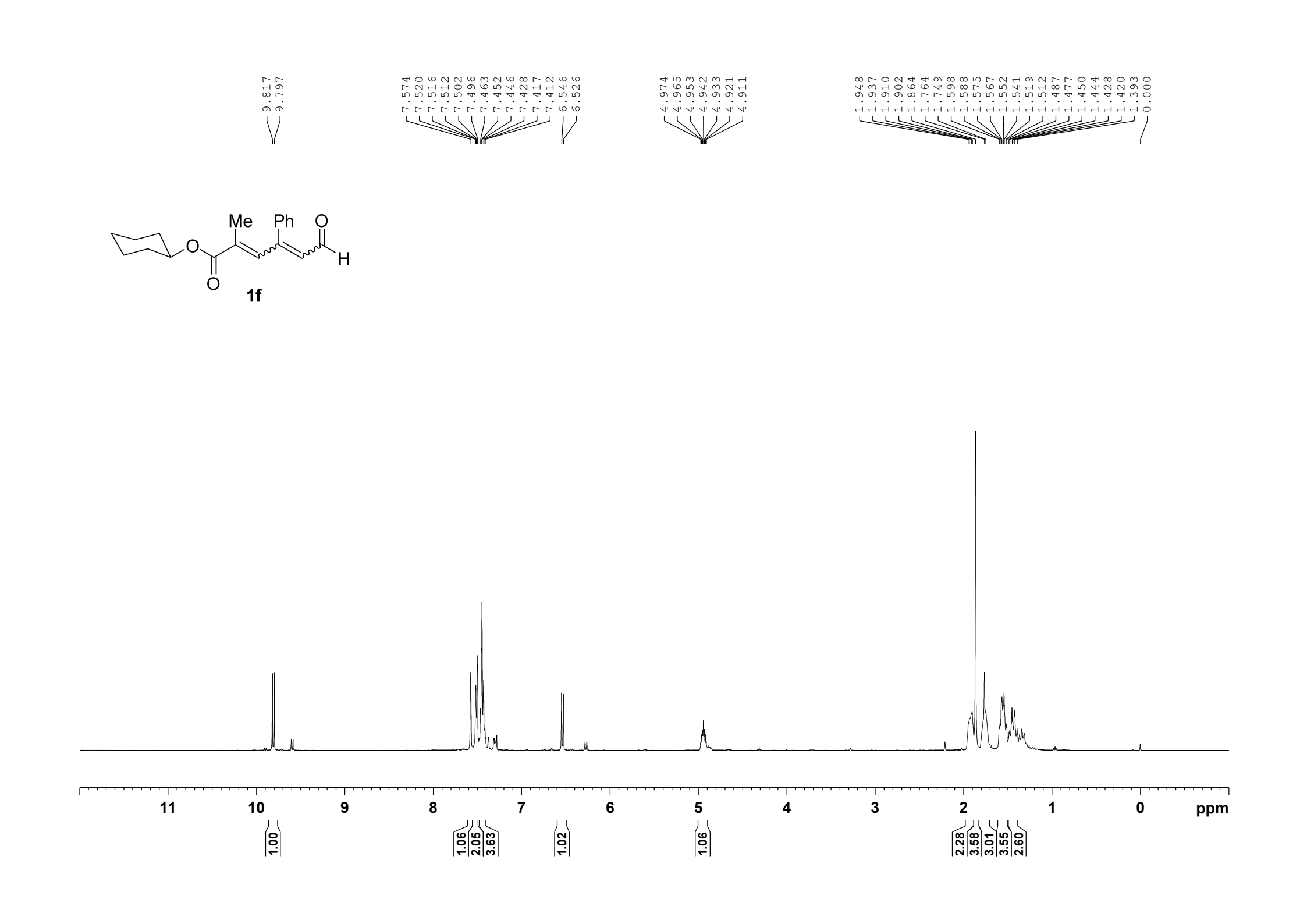
141.23
136.09
135.84
134.12
131.04
129.11
127.16
126.97
98.69
77.32
77.00
76.68
14.38
Me
Ph
O
O
O
H
1e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.502
7.496
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7.452
7.446
7.428
7.417
7.412
6.546
6.526
4.974
4.965
4.953
4.942
4.933
4.921
4.911
1.948
1.937
1.910
1.902
1.864
1.764
1.749
1.598
1.588
1.575
1.567
1.552
1.541
1.519
1.512
1.487
1.477
1.450
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1.428
1.420
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Ph
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O
O
H
1f
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10
9
8
7
6
5
4
3
2
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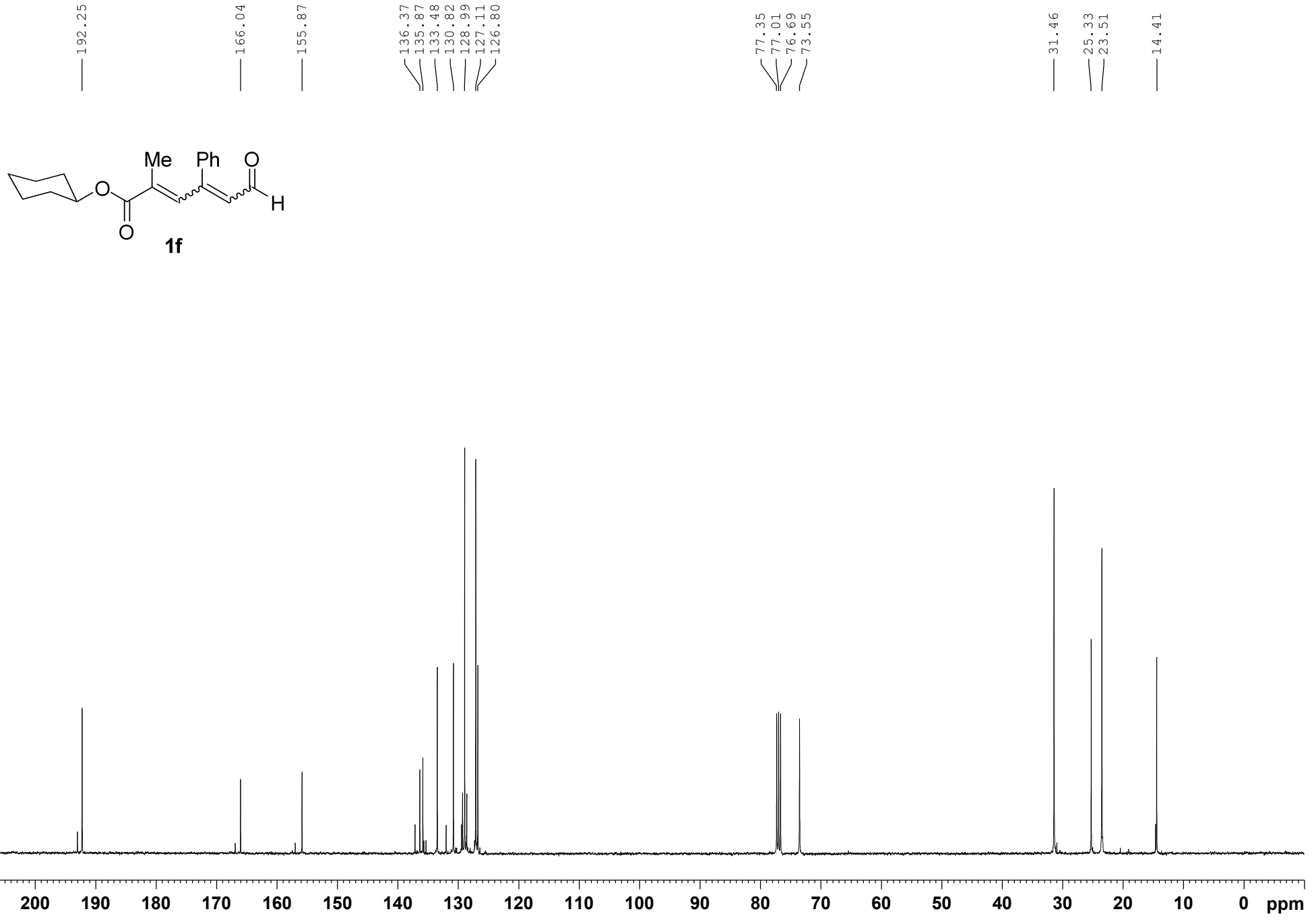
3.55
2.60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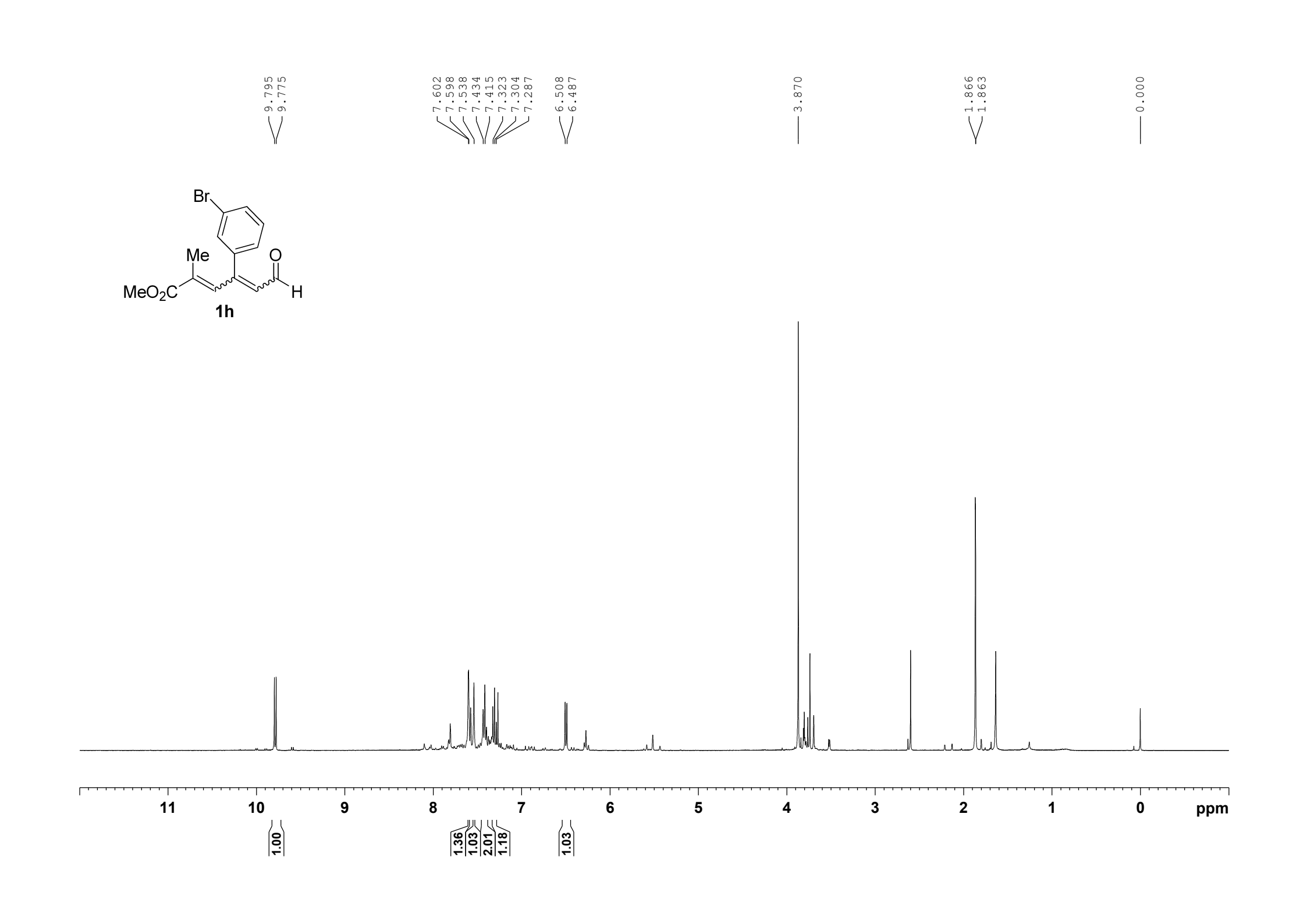
133.48
130.82
128.99
127.11
126.80
77.35
77.01
76.69
73.55
31.46
25.33
23.51
14.41
Me
Ph
O
O
O
H
1f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.602
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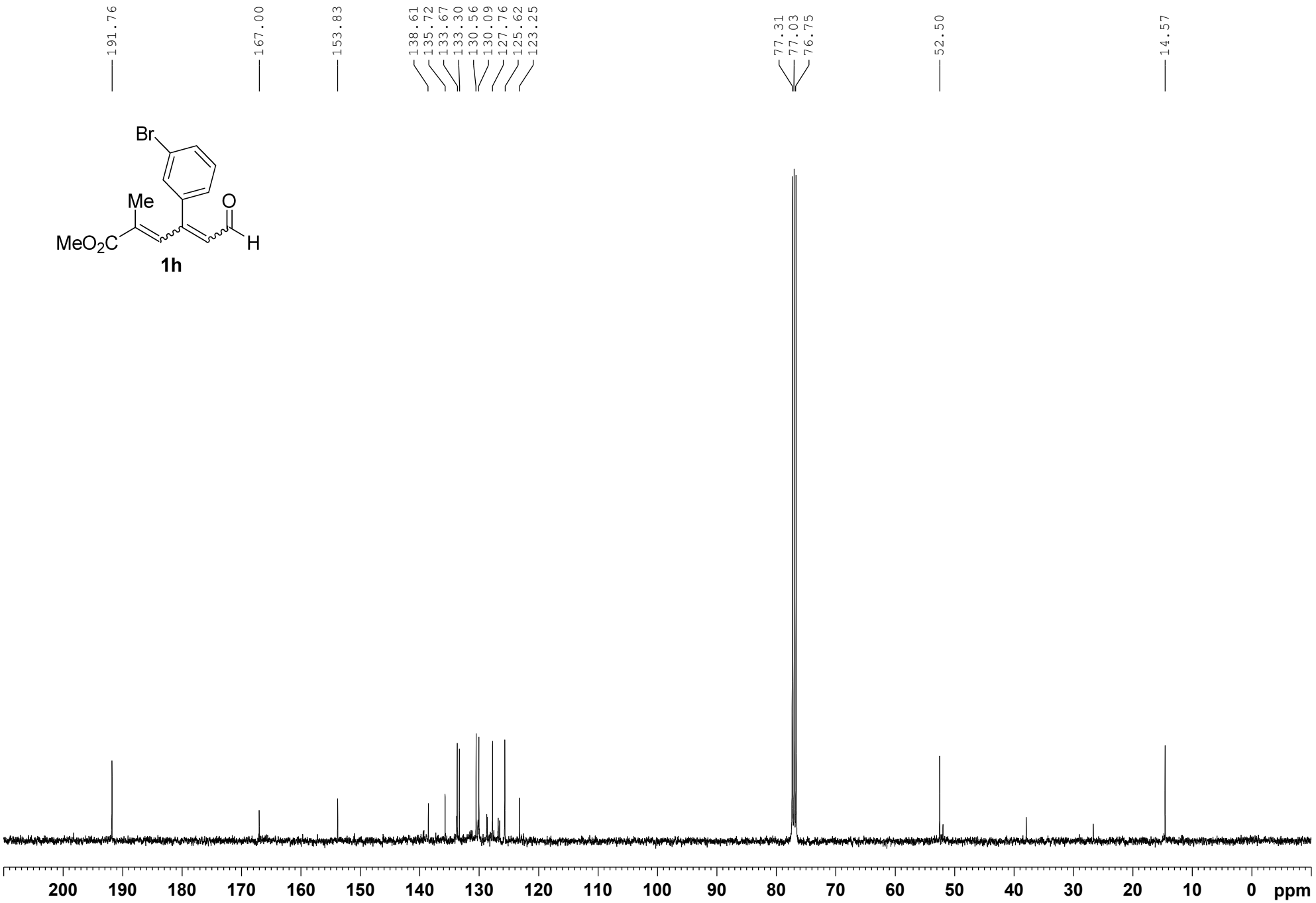
1.863
0.000
Br
Me
O
MeO2C
H
1h
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.36
1.03
2.01
1.18
1.03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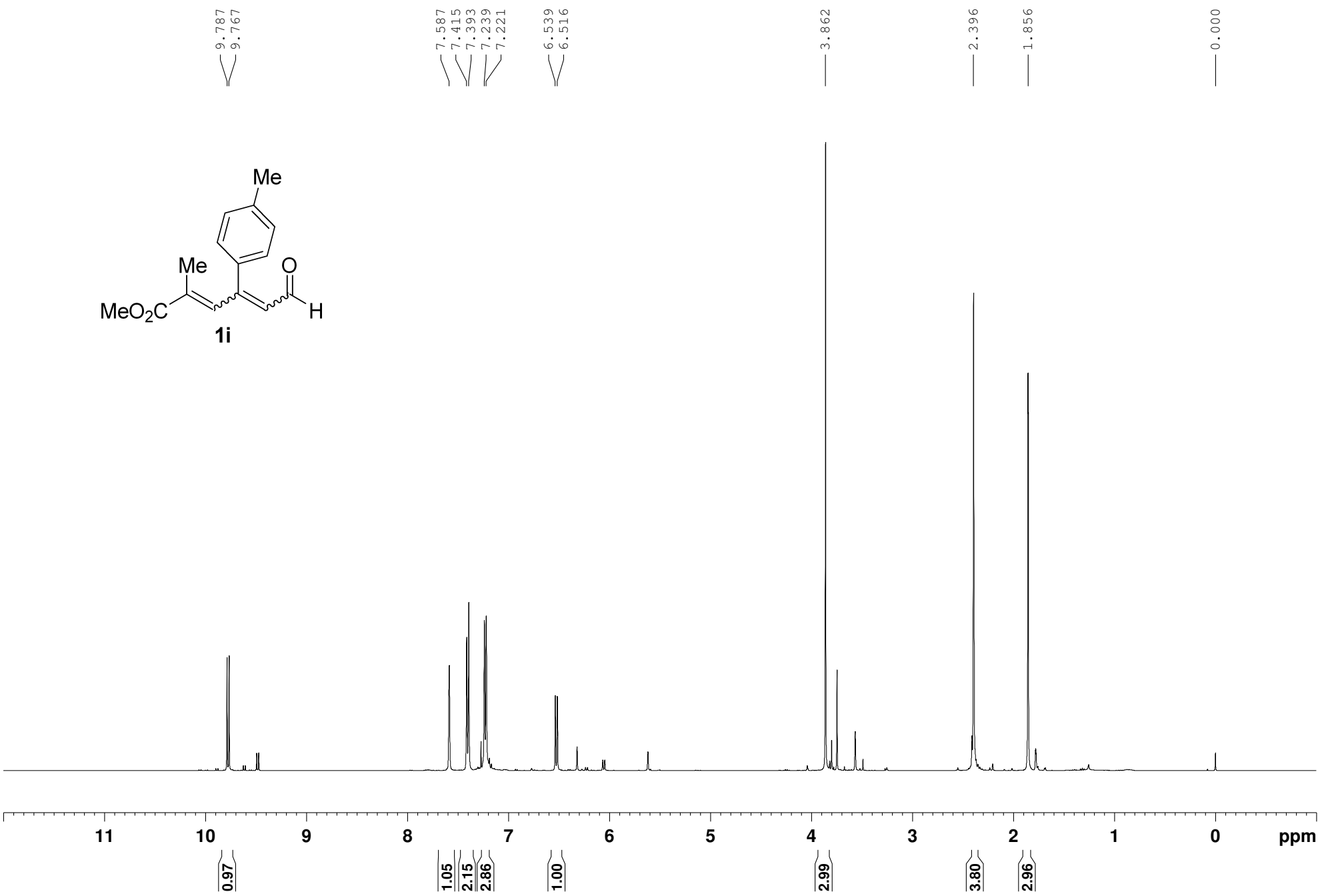
167.00
153.83
138.61
135.72
133.67
133.30
130.56
130.09
127.76
125.62
123.25
77.31
77.03
76.75
52.50
14.57
Br
Me
O
MeO2C
H
1h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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0.000
Me
Me
O
MeO2C
H
1i
11
10
9
8
7
6
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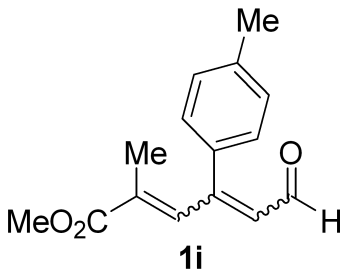
2.96



1i

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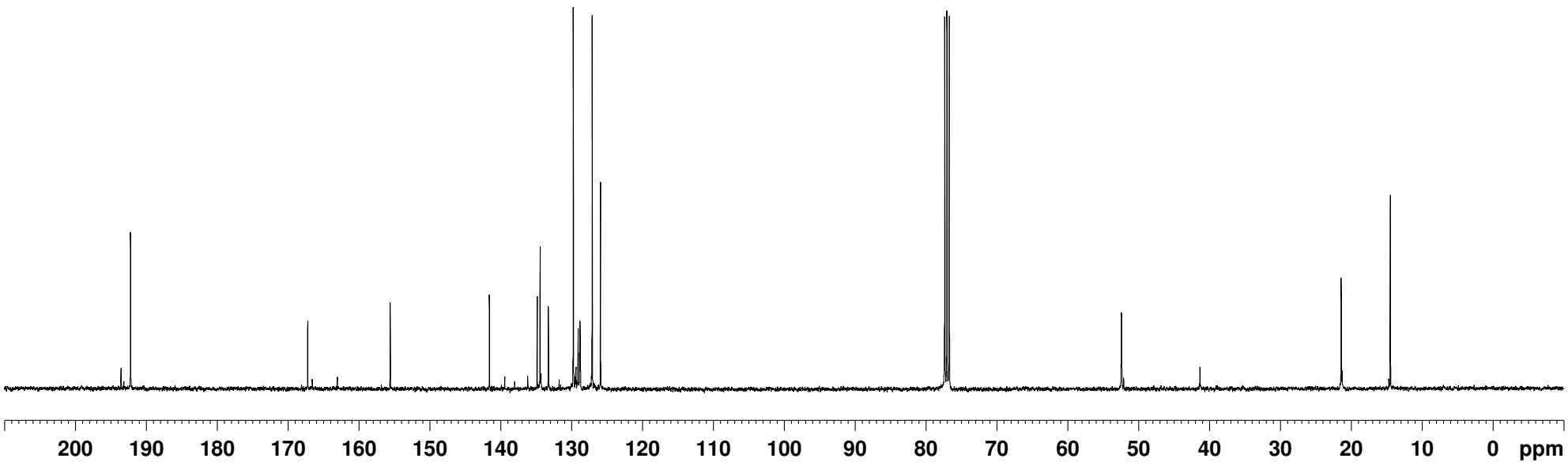

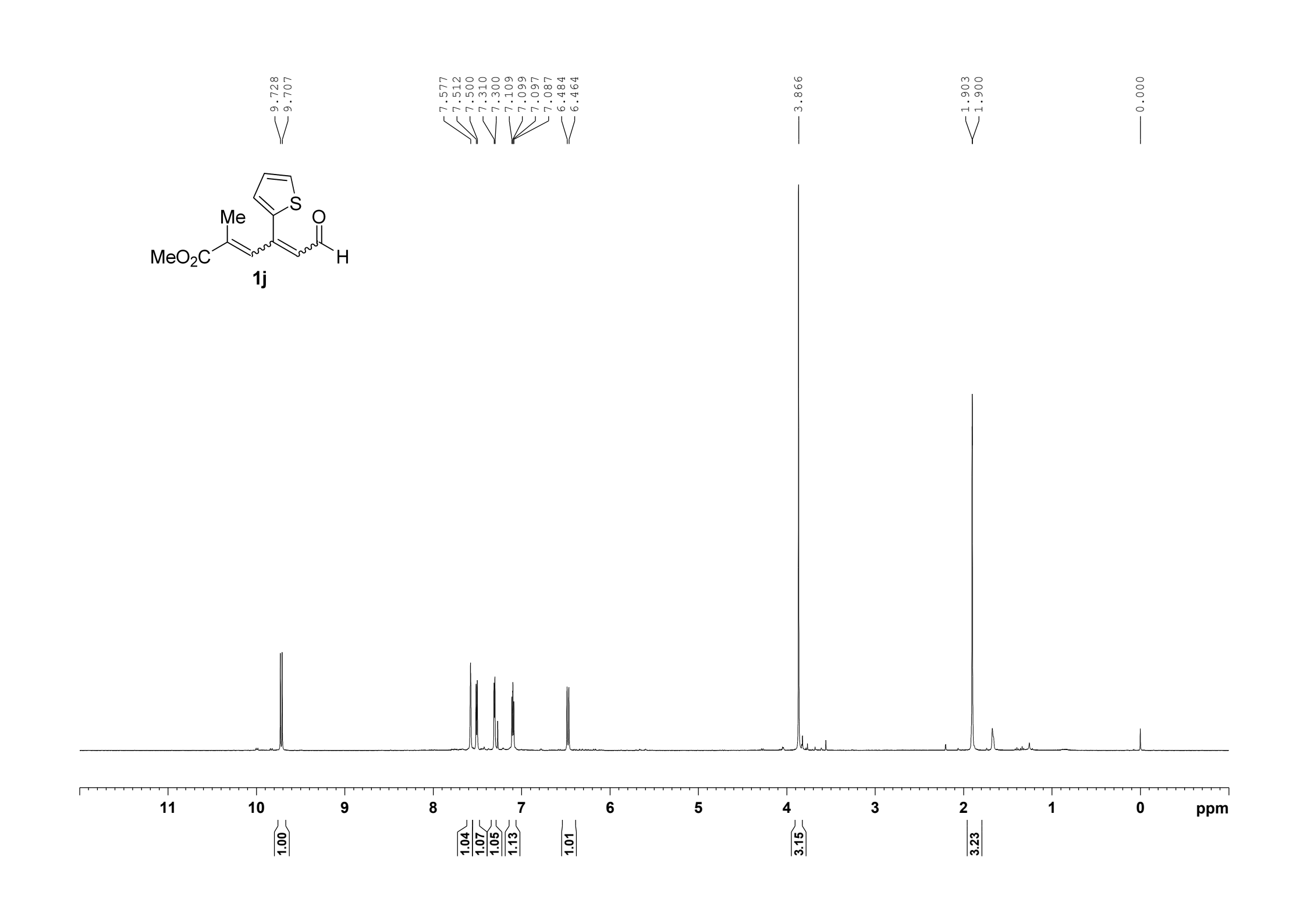
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7.087
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3.866
1.903
1.900
0.000
S
Me
O
MeO2C
H
1j
11
10
9
8
7
6
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1.05
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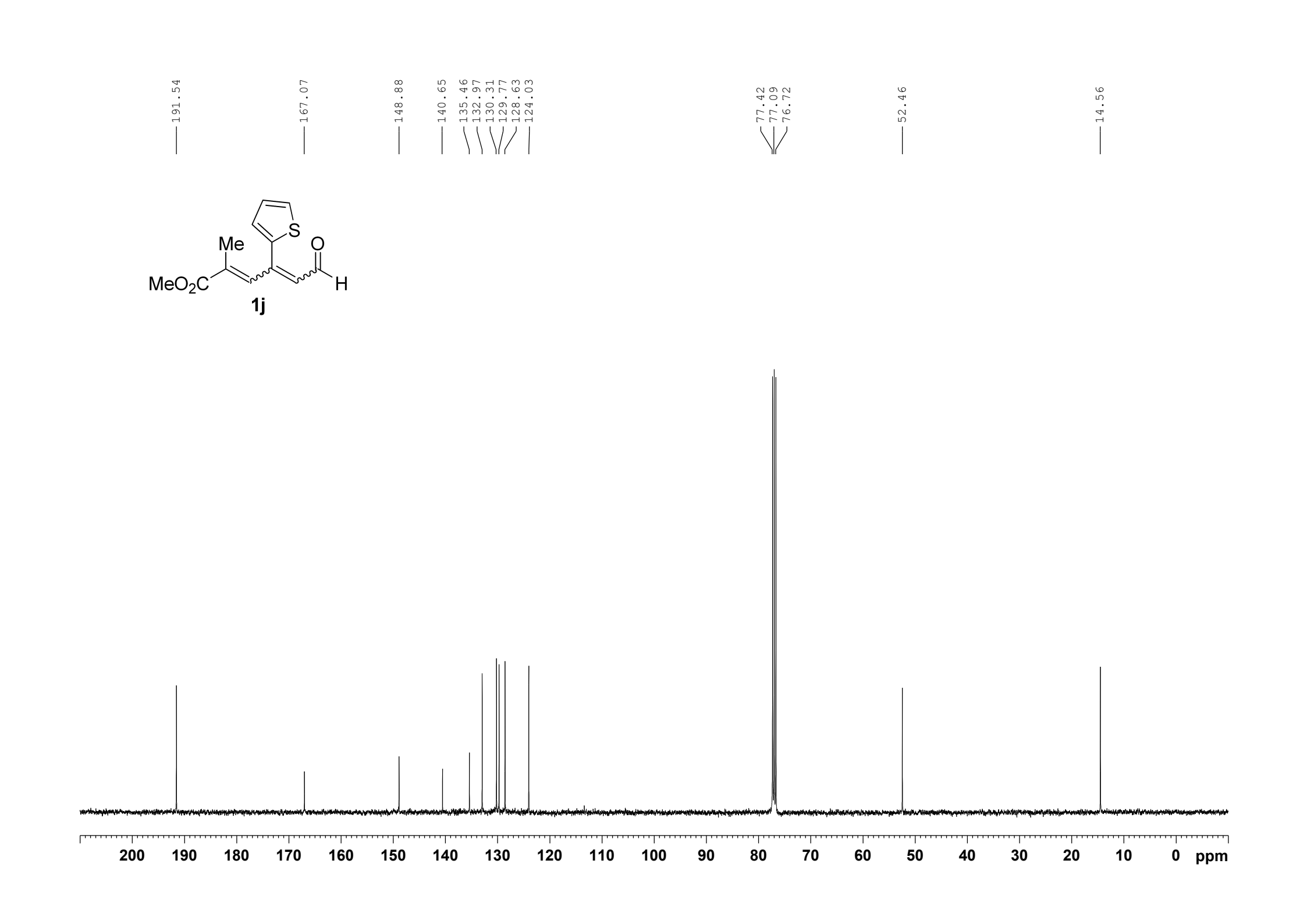
3.23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76.72
52.46
14.56
S
Me
O
MeO2C
H
1j
200
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140
130
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10
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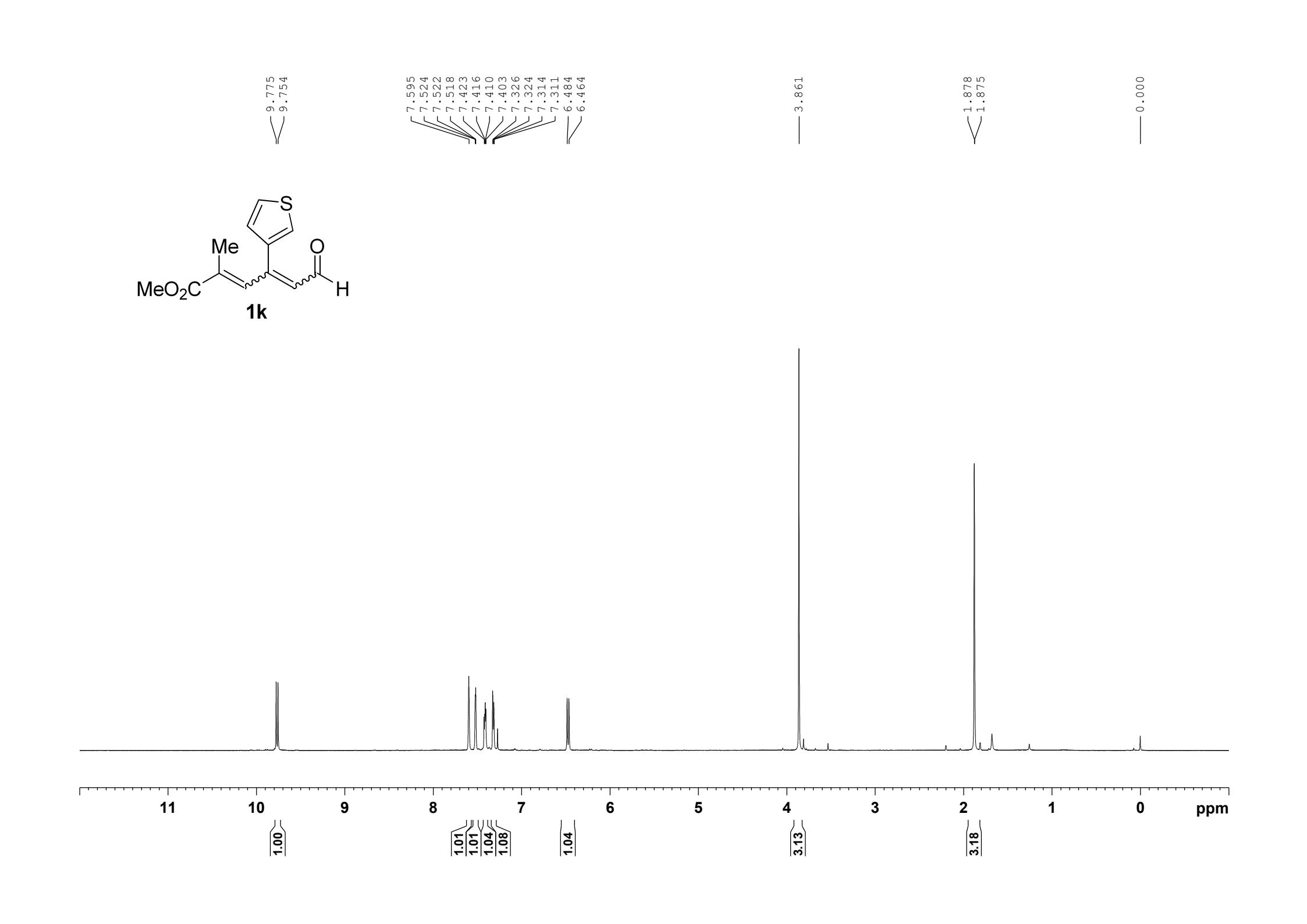
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7.324
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7.311
6.484
6.464
3.861
1.878
1.875
0.000
S
Me
O
MeO2C
H
1k
11
10
9
8
7
6
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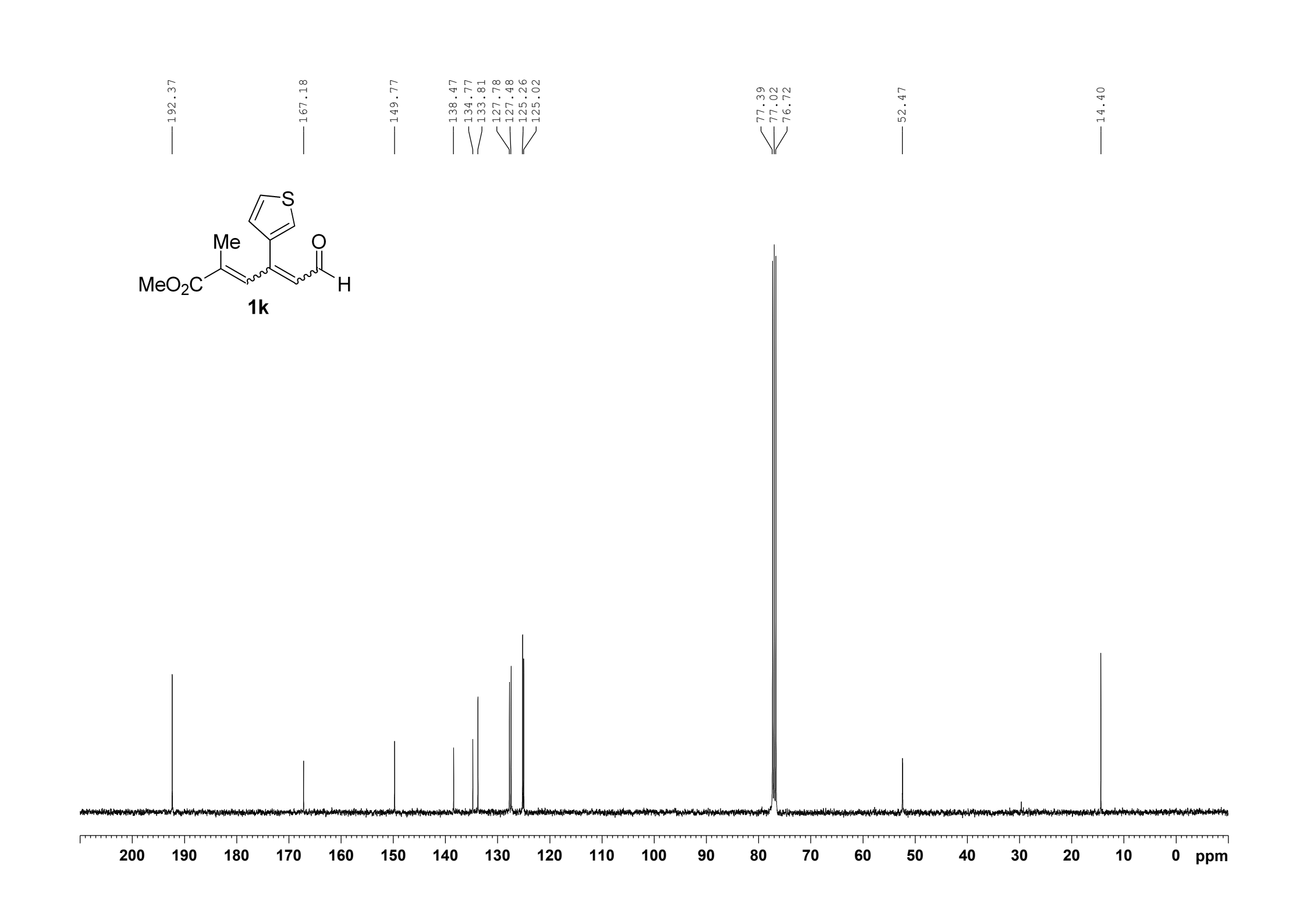
3.18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125.02
77.39
77.02
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52.47
14.40
S
Me
O
MeO2C
H
1k
200
190
180
170
160
150
140
130
120
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70
60
50
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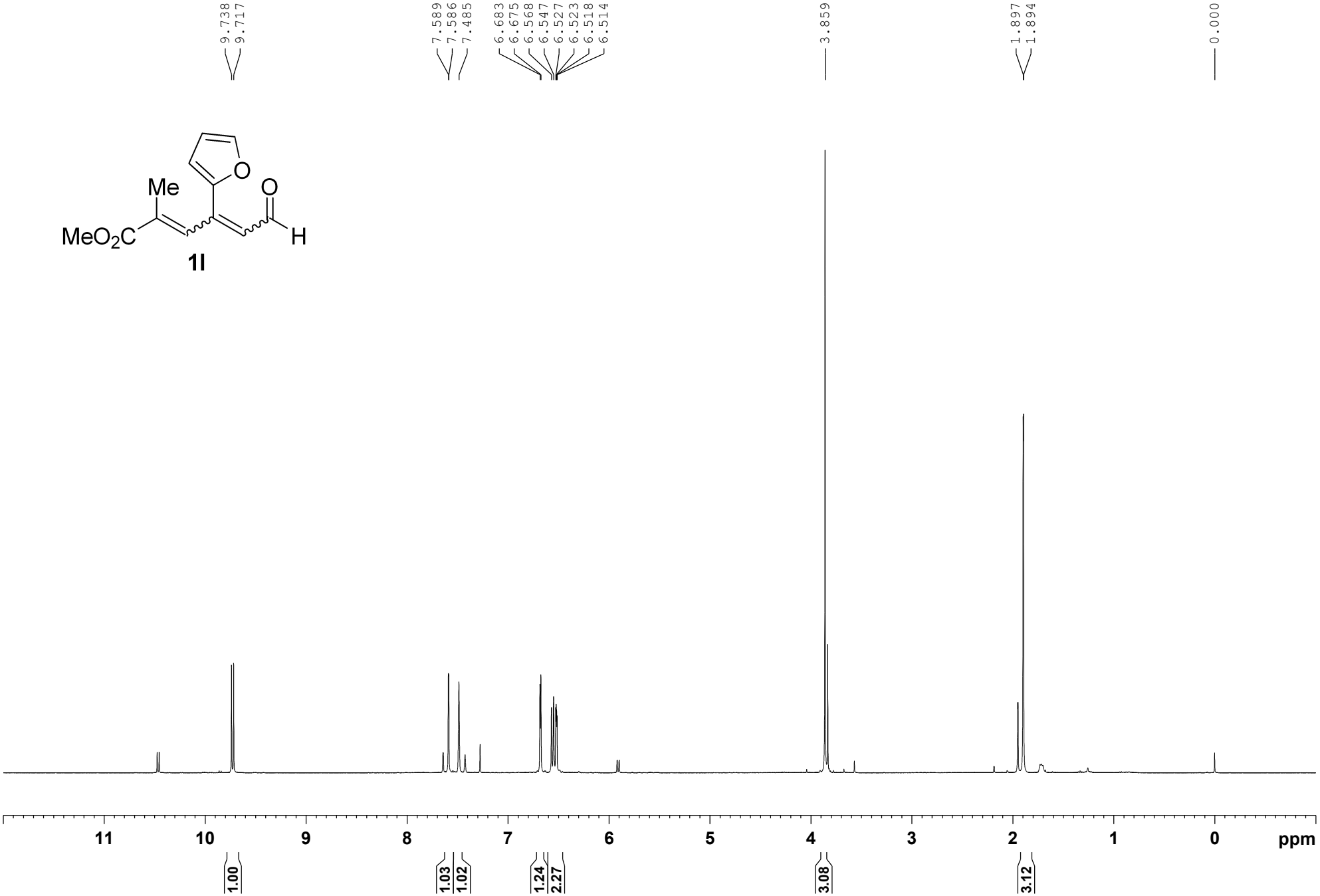
30
20
10
0
ppm

Me
O
O
MeO2C
H

1l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6.527
6.523
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6.514
3.859
1.897
1.894
0.000
11
10
9
8
7
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1.02
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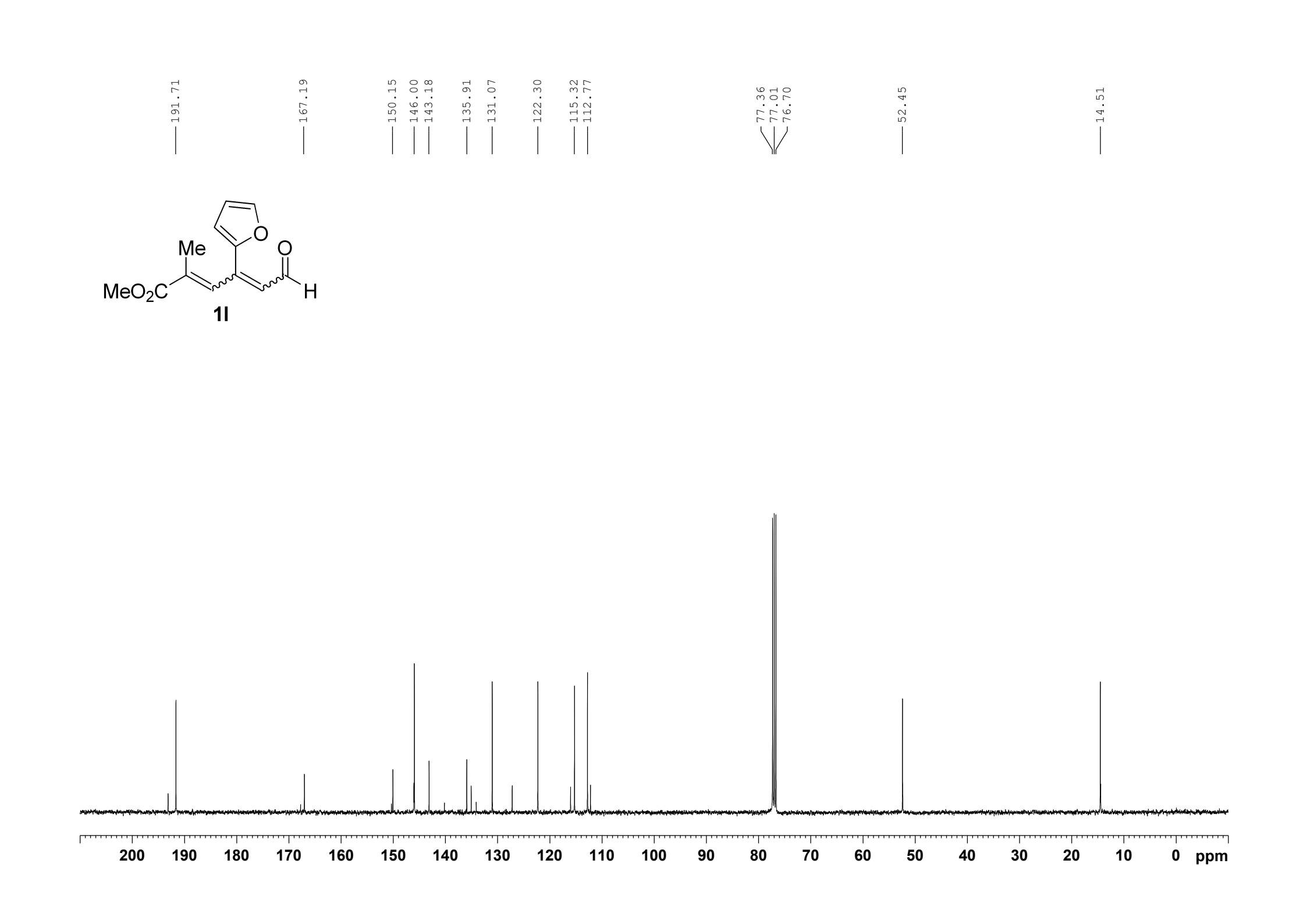
3.12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122.30
115.32
112.77
77.36
77.01
76.70
52.45
14.51
Me
O
O
MeO2C
H
1l
200
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140
130
120
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100
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20
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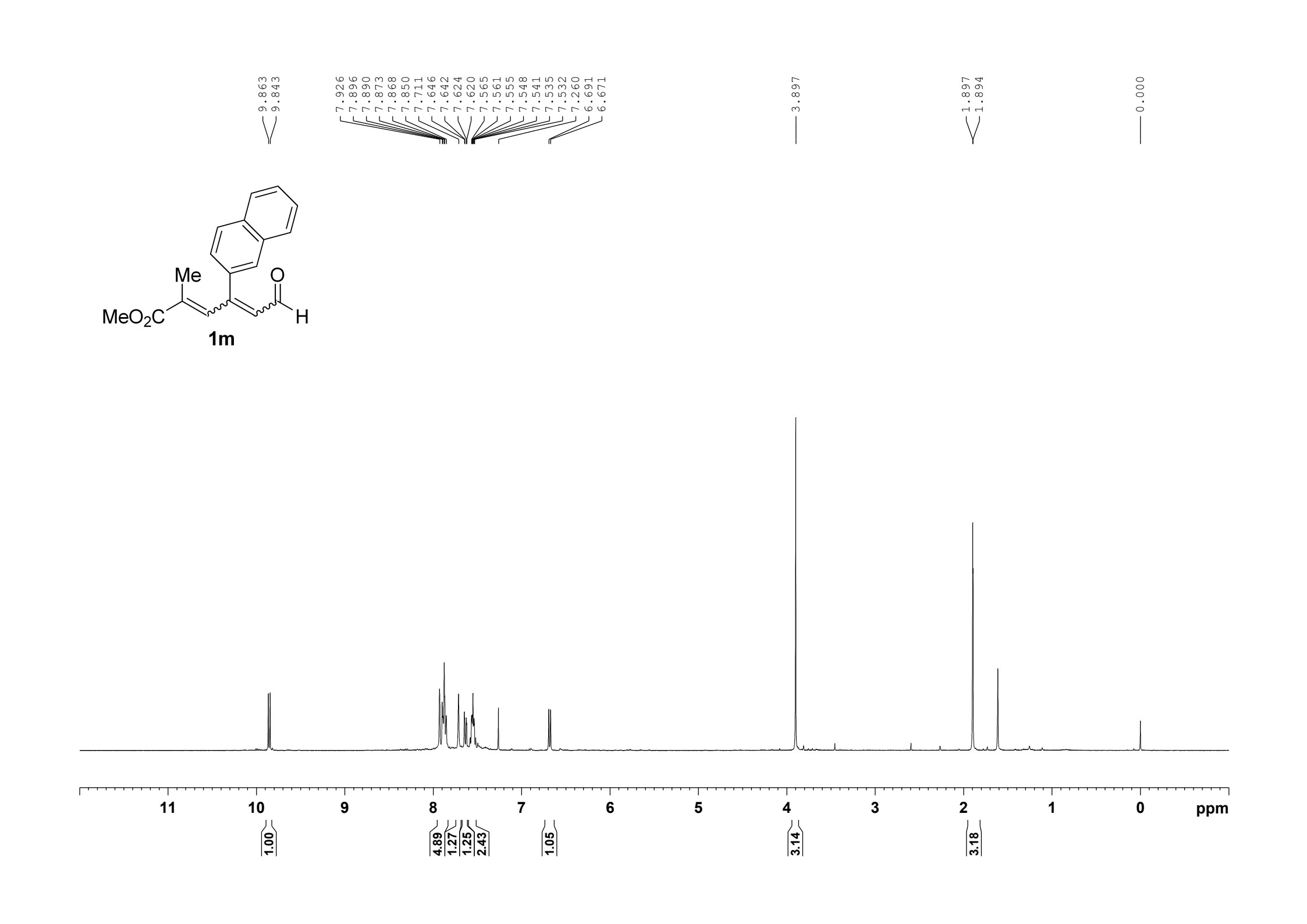
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7.850
7.711
7.646
7.642
7.624
7.620
7.565
7.561
7.555
7.548
7.541
7.535
7.532
7.260
6.691
6.671
3.897
1.897
1.894
0.000
Me
O
MeO2C
H
1m
11
10
9
8
7
6
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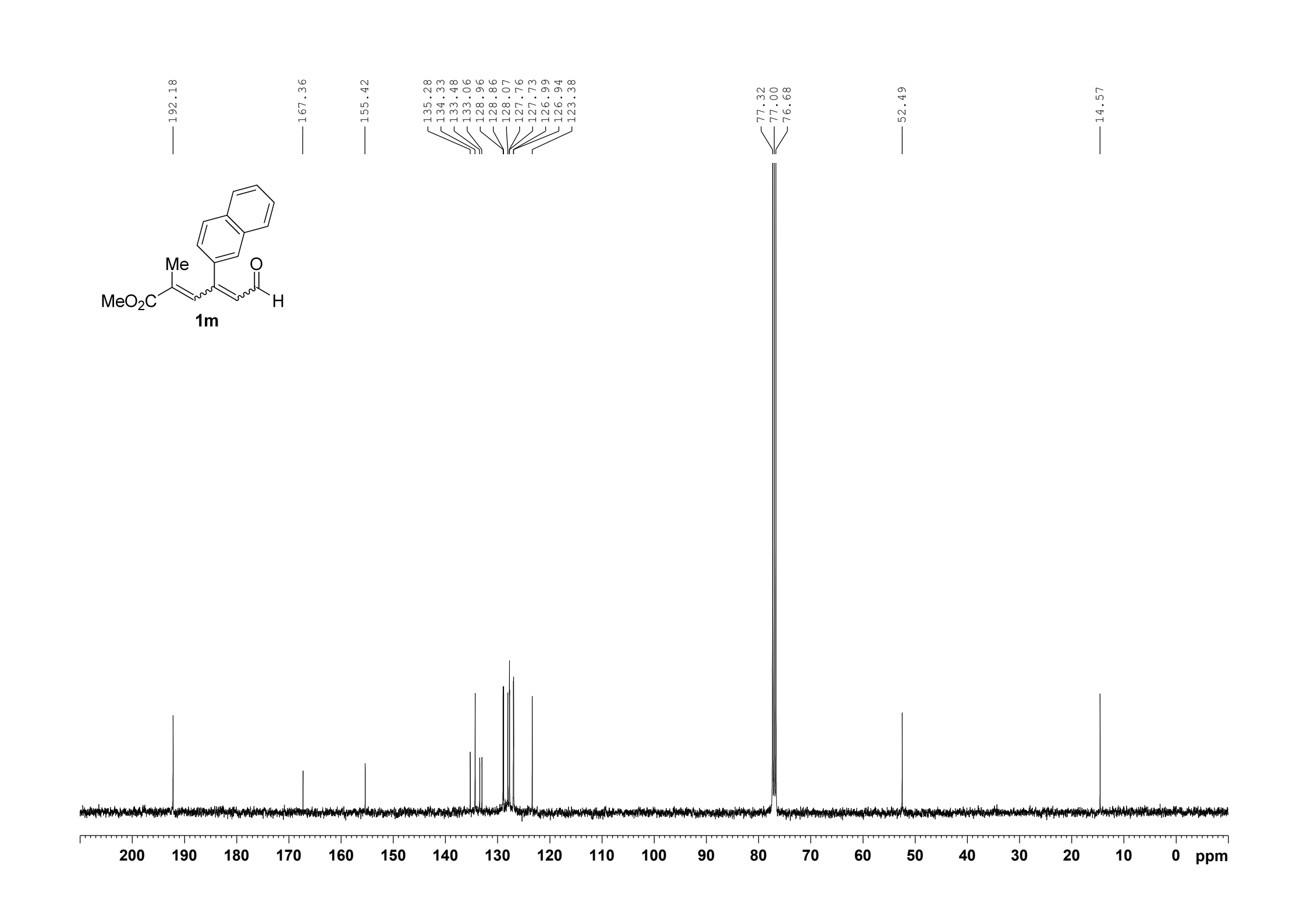
3.18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128.07
127.76
127.73
126.99
126.94
123.38
77.32
77.00
76.68
52.49
14.57
Me
O
MeO2C
H
1m
200
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180
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140
130
120
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100
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80
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60
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30
20
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0
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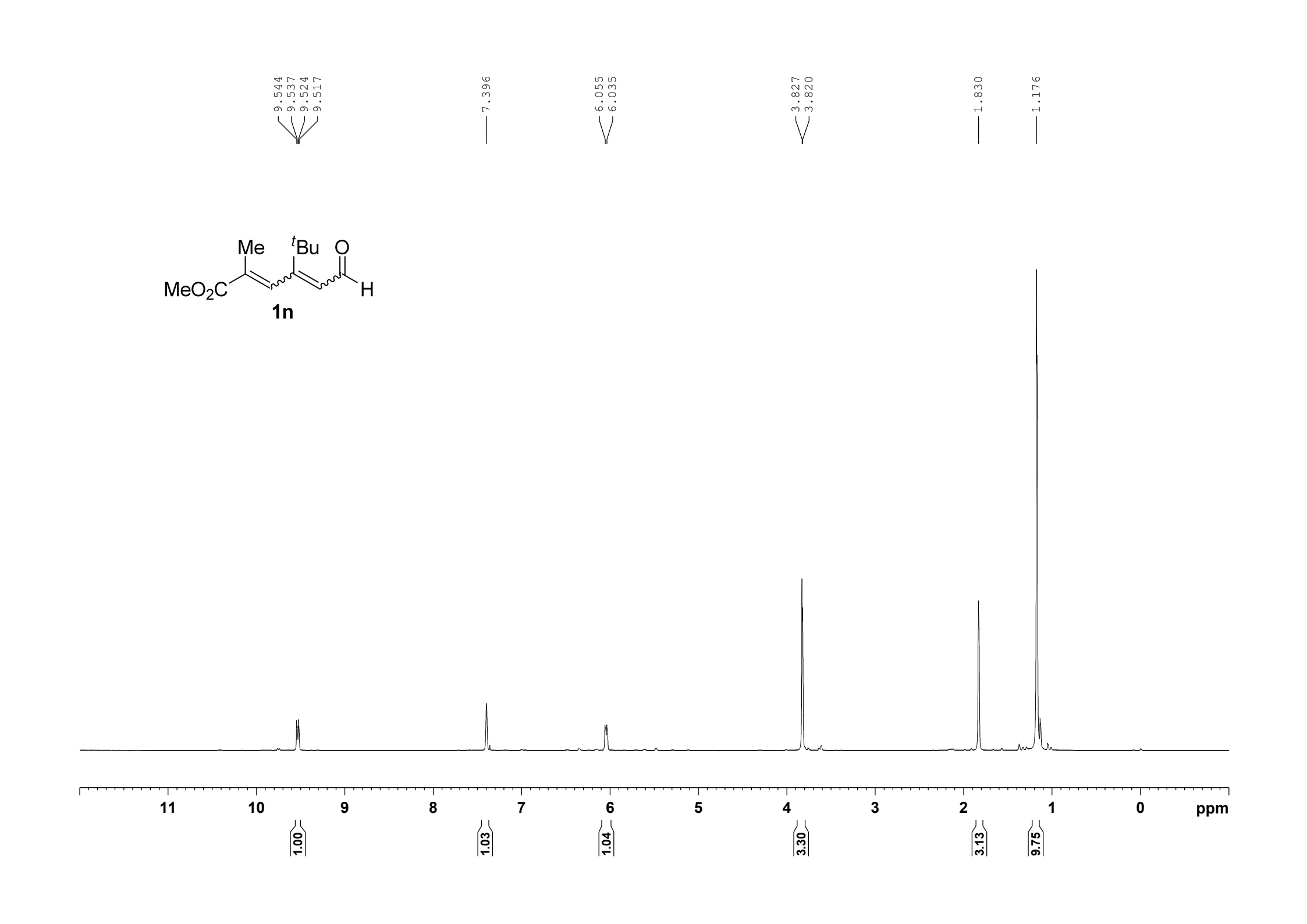
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1.176
Me
tBu
O
MeO2C
H
1n
11
10
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4
3
2
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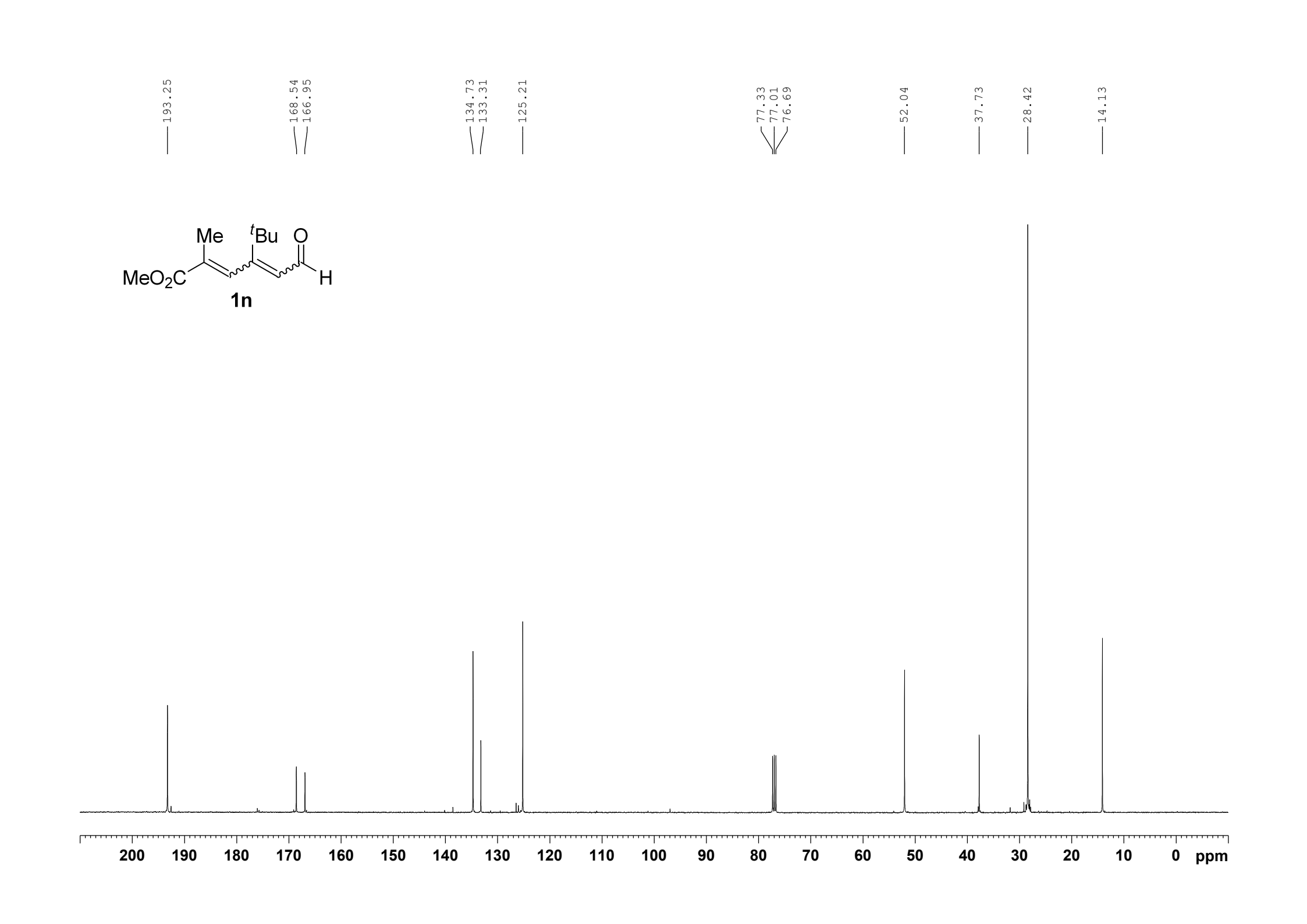
1.03
1.04
3.30
3.13
9.75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37.73
28.42
14.13
Me
tBu
O
MeO2C
H
1n
200
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180
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140
130
120
110
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50
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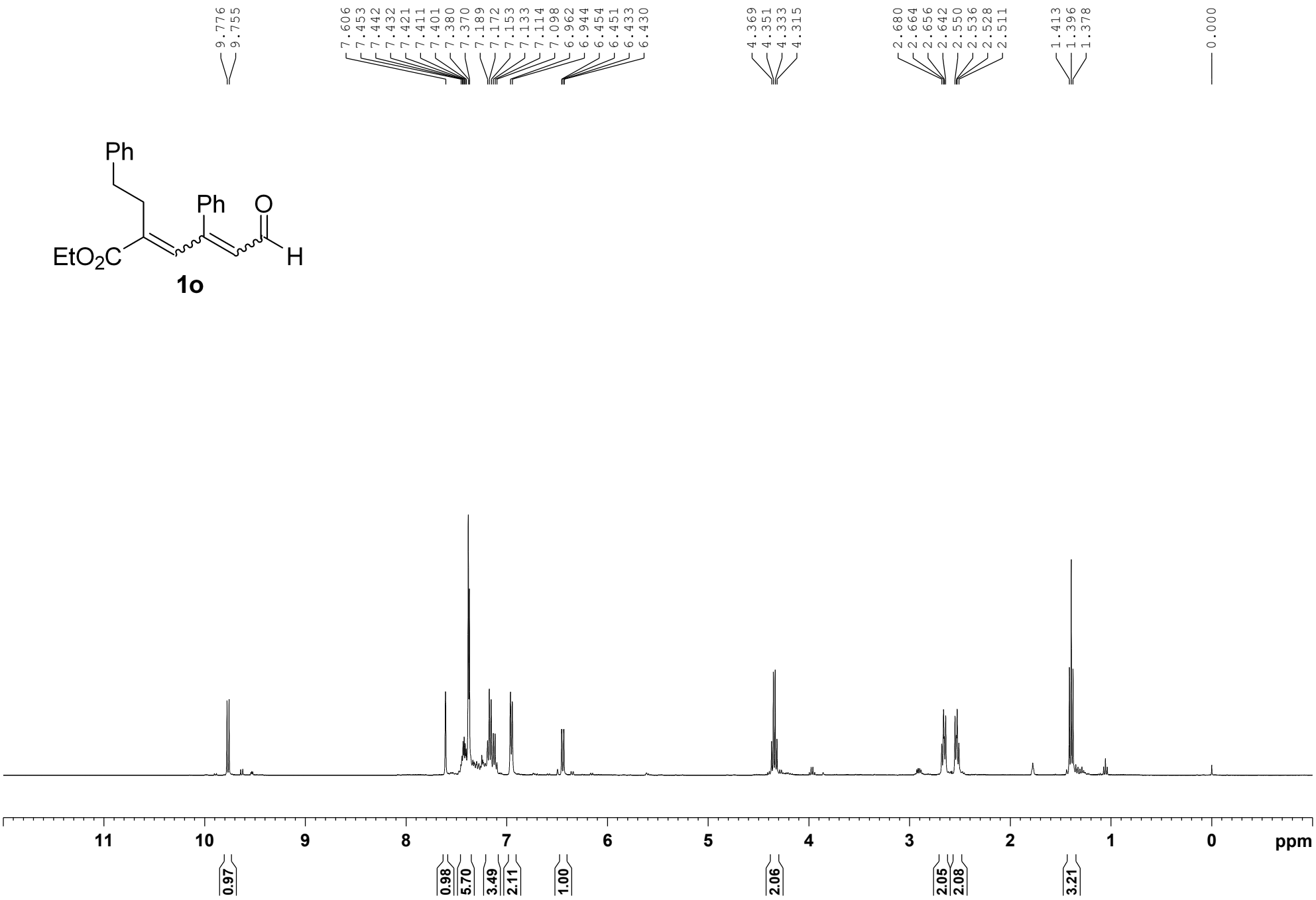
20
10
0
ppm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7.153
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7.114
7.098
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6.944
6.454
6.451
6.433
6.430
4.369
4.351
4.333
4.315
2.680
2.664
2.656
2.642
2.550
2.536
2.528
2.511
1.413
1.396
1.378
0.000
Ph
Ph
O
EtO2C
H
1o
11
10
9
8
7
6
5
4
3
2
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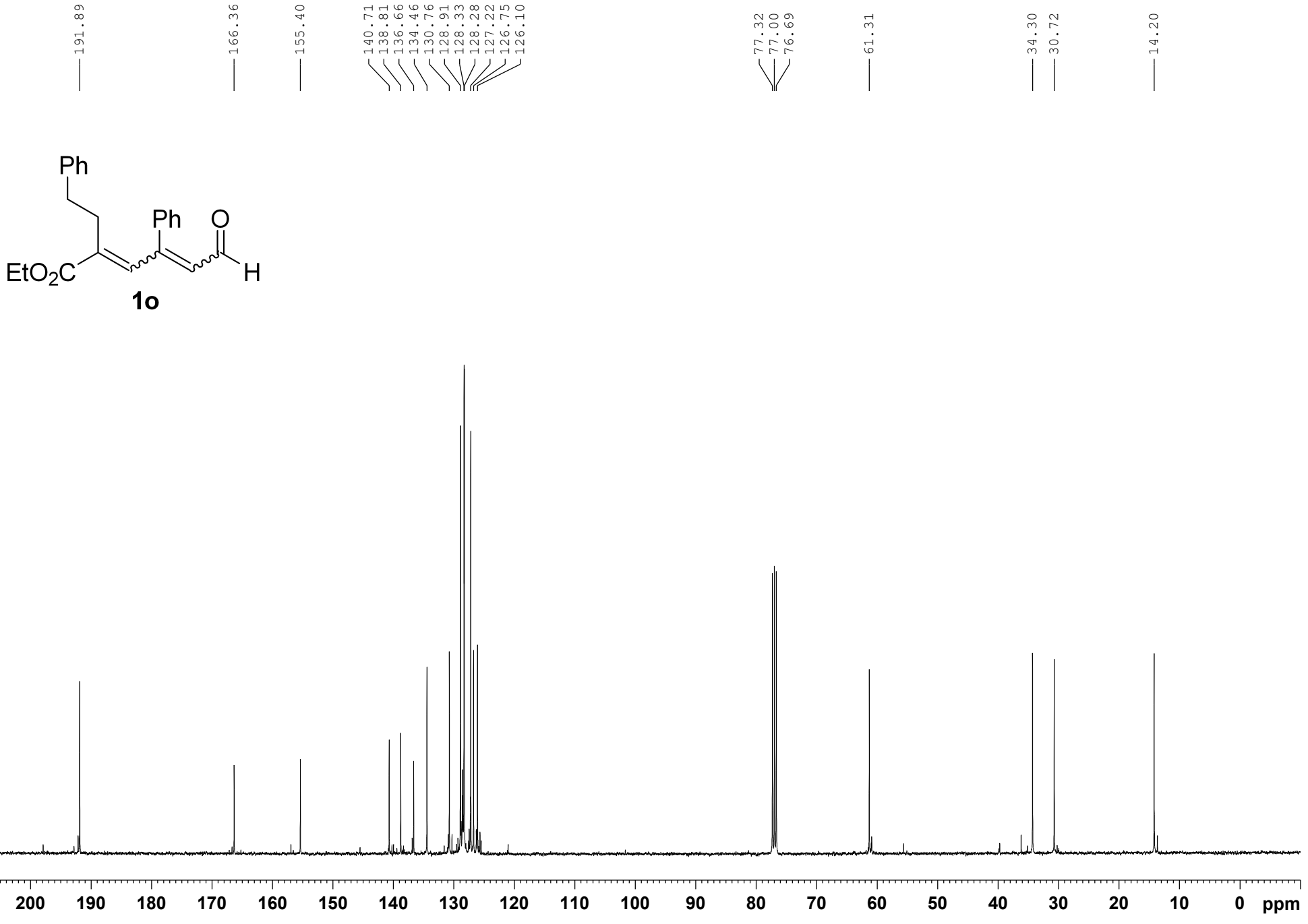
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127.22
126.75
126.10
77.32
77.00
76.69
61.31
34.30
30.72
14.20
Ph
Ph
O
EtO2C
H
1o
200
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170
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140
130
120
110
100
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20
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0
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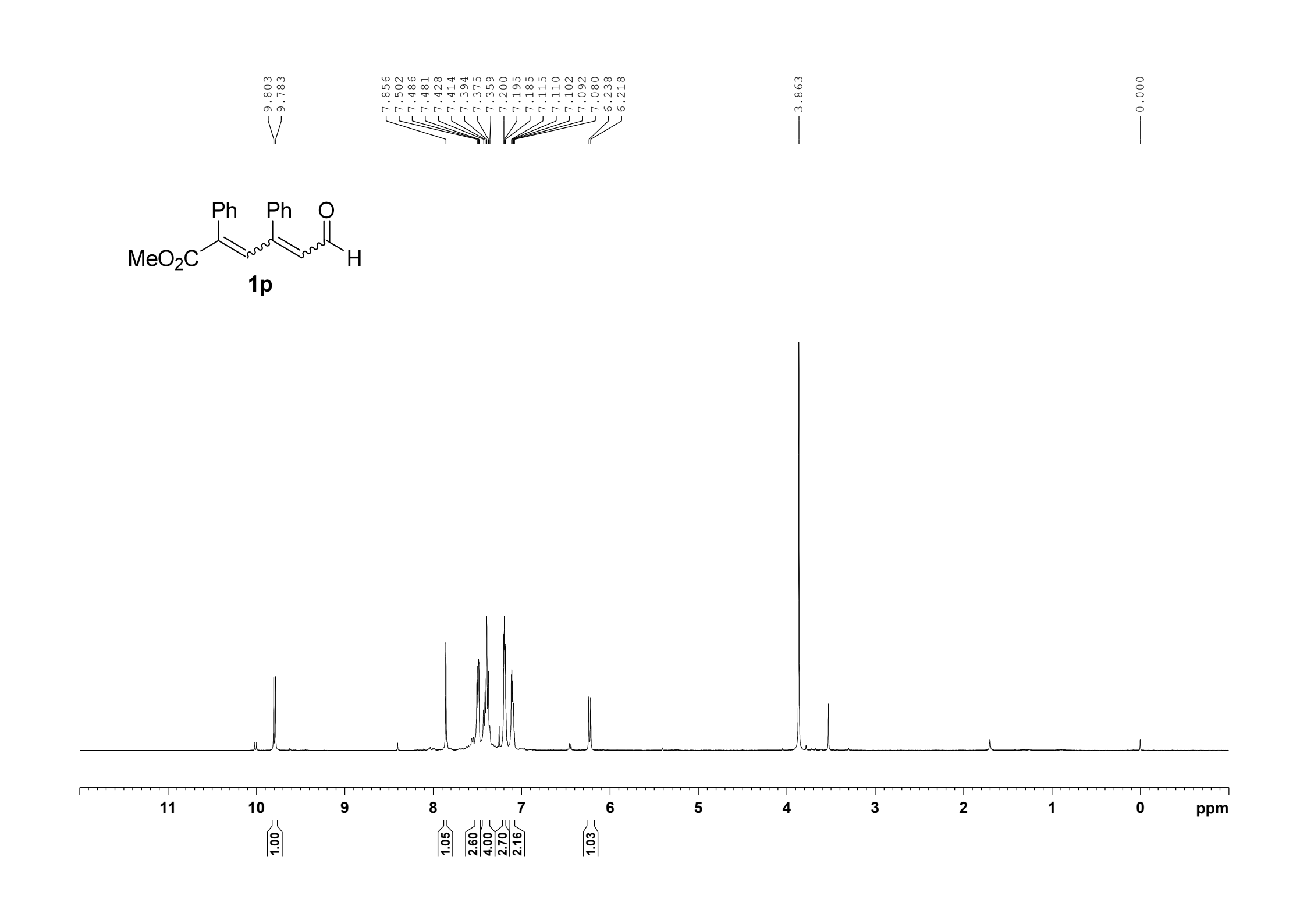
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7.185
7.115
7.110
7.102
7.092
7.080
6.238
6.218
3.863
0.000
Ph
Ph
O
MeO2C
H
1p
11
10
9
8
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2
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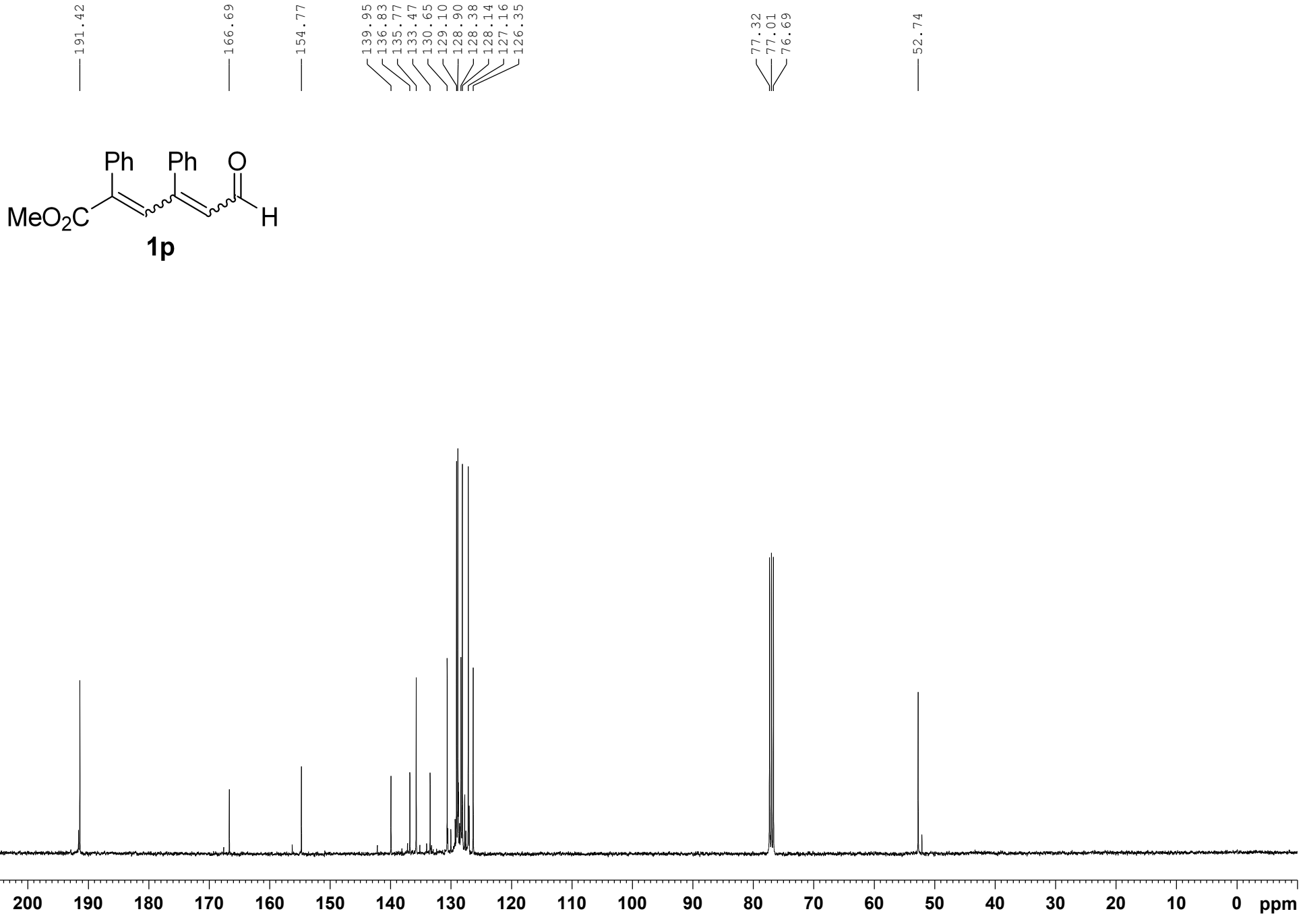
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128.38
128.14
127.16
126.35
77.32
77.01
76.69
52.74
Ph
Ph
O
MeO2C
H
1p
200
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180
170
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150
140
130
120
110
100
90
80
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60
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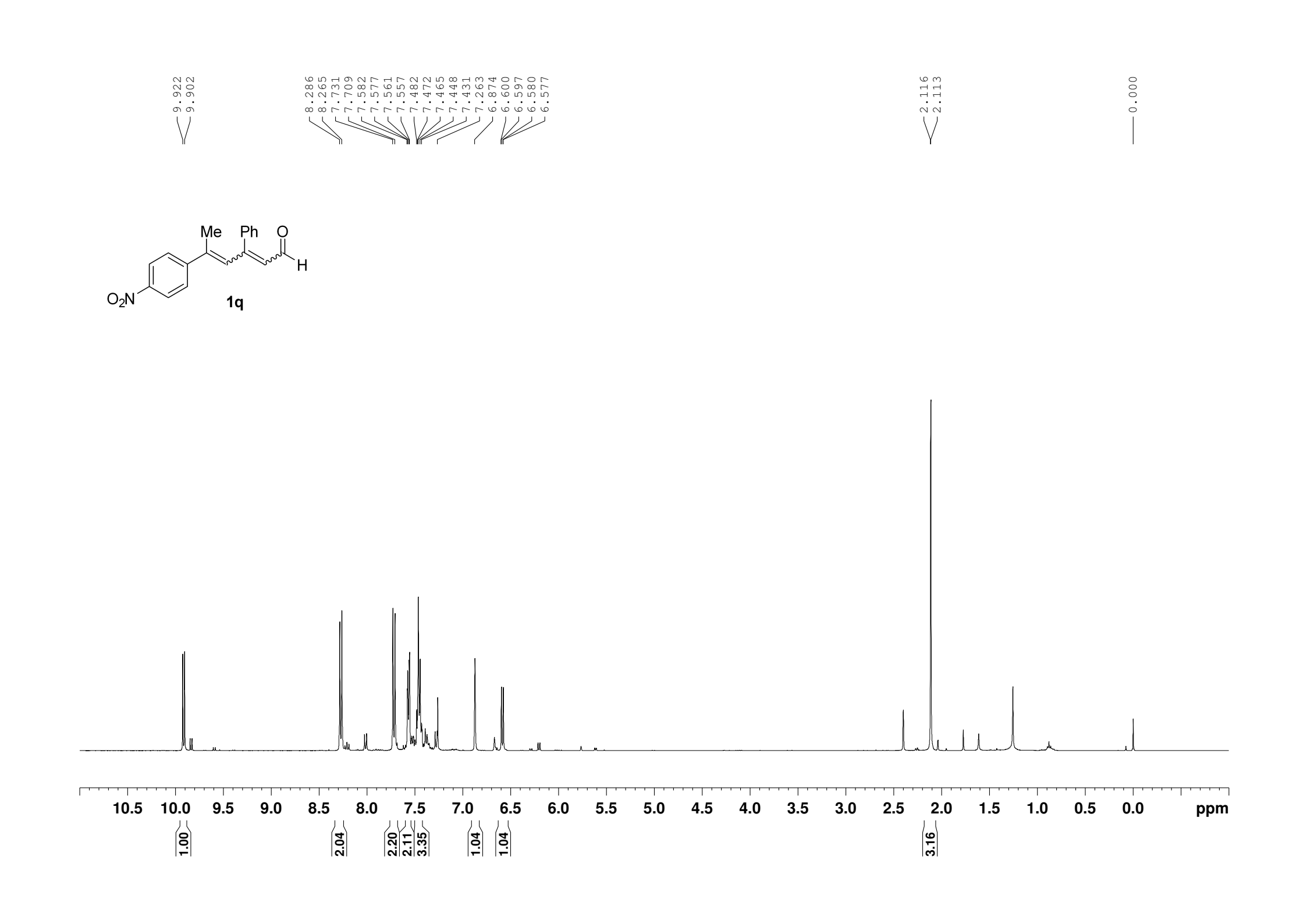
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7.448
7.431
7.263
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6.600
6.597
6.580
6.577
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2.113
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Ph
O
H
O2N
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9.0
8.5
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6.5
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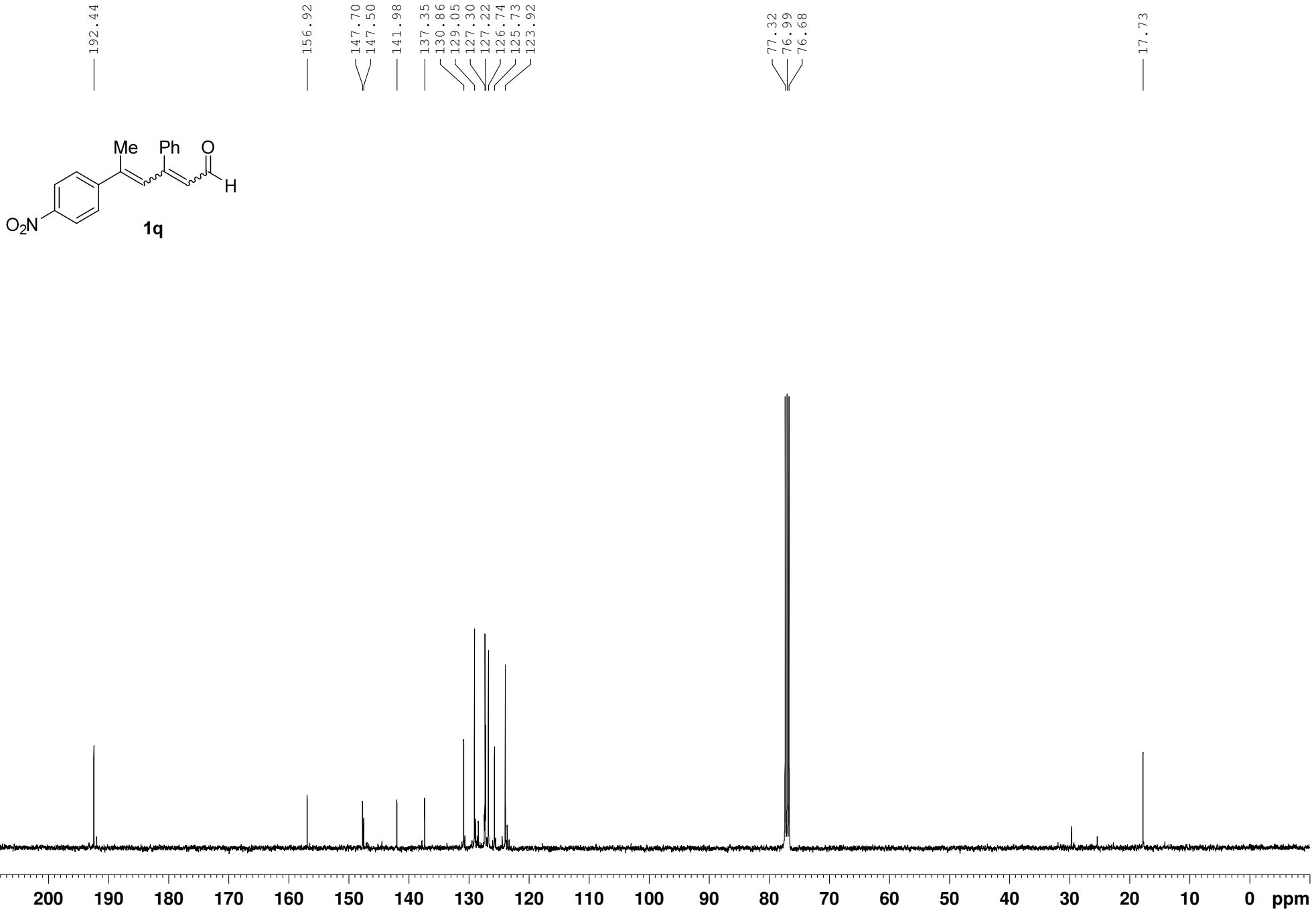
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127.22
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123.92
77.32
76.99
76.68
17.73
Me
Ph
O
H
O2N
1q
200
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140
130
120
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100
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60
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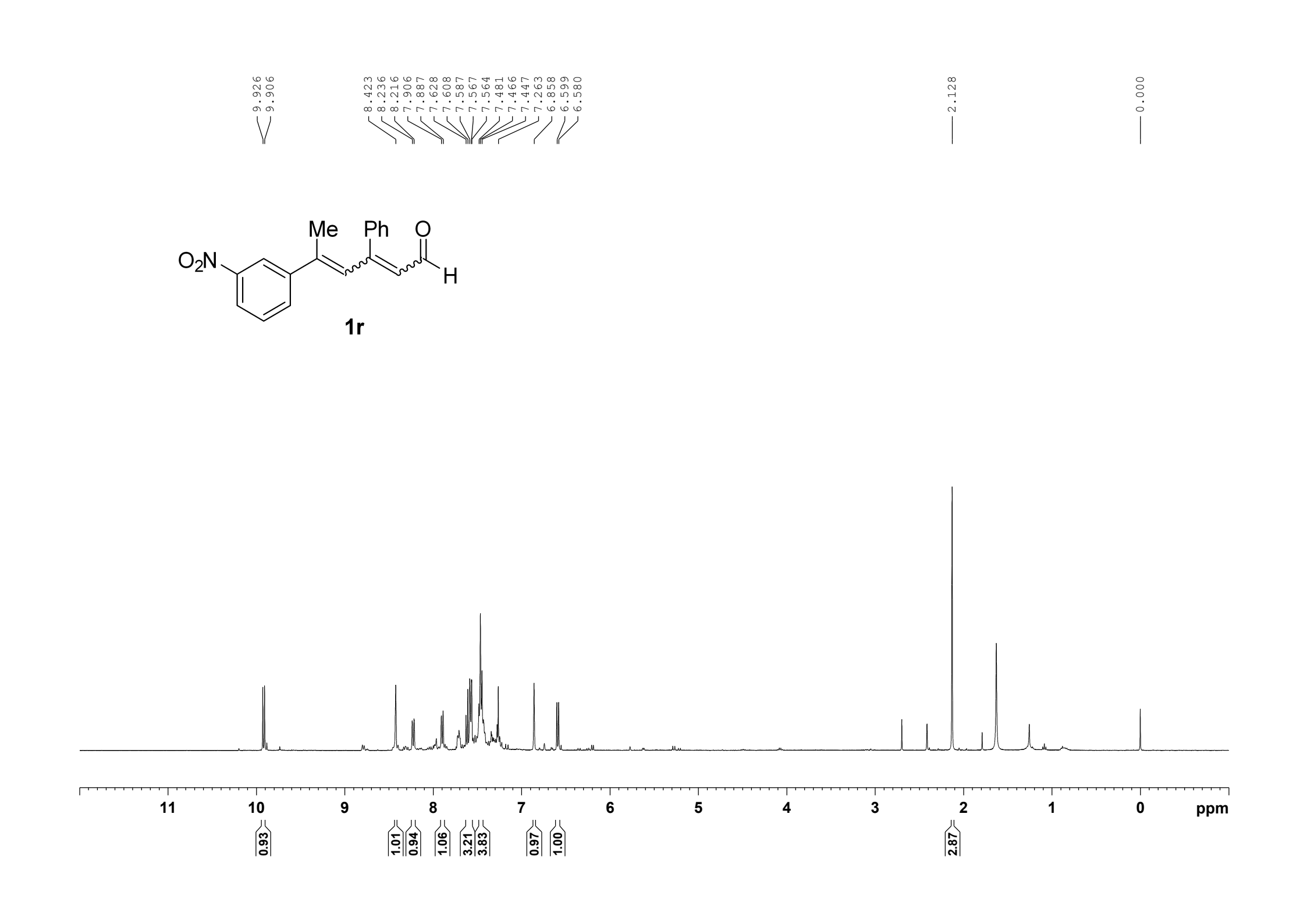
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7.466
7.447
7.263
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6.599
6.580
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Ph
O
O2N
H
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10
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7
6
5
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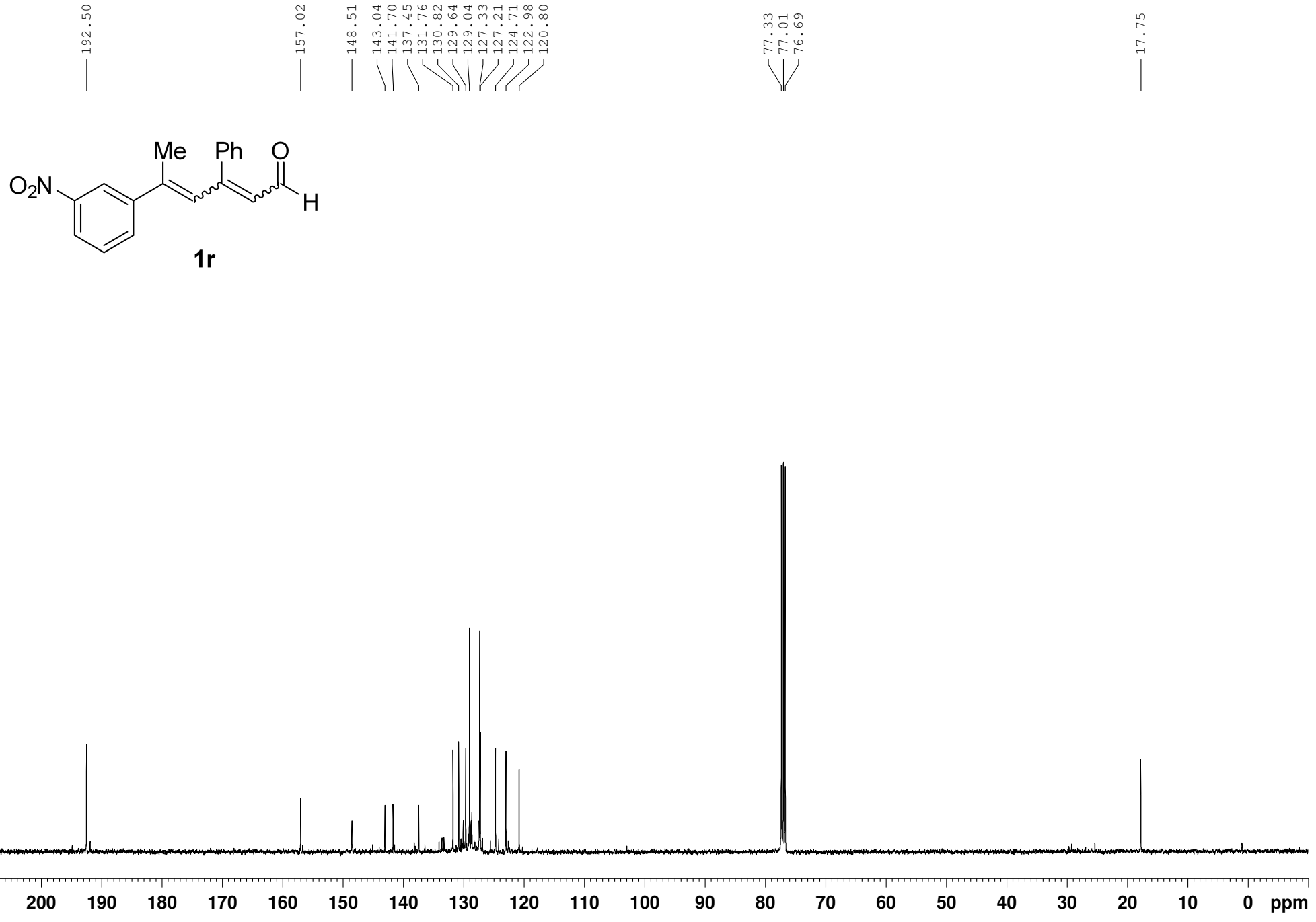
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127.21
124.71
122.98
120.80
77.33
77.01
76.69
17.75
Me
Ph
O
O2N
H
1r
200
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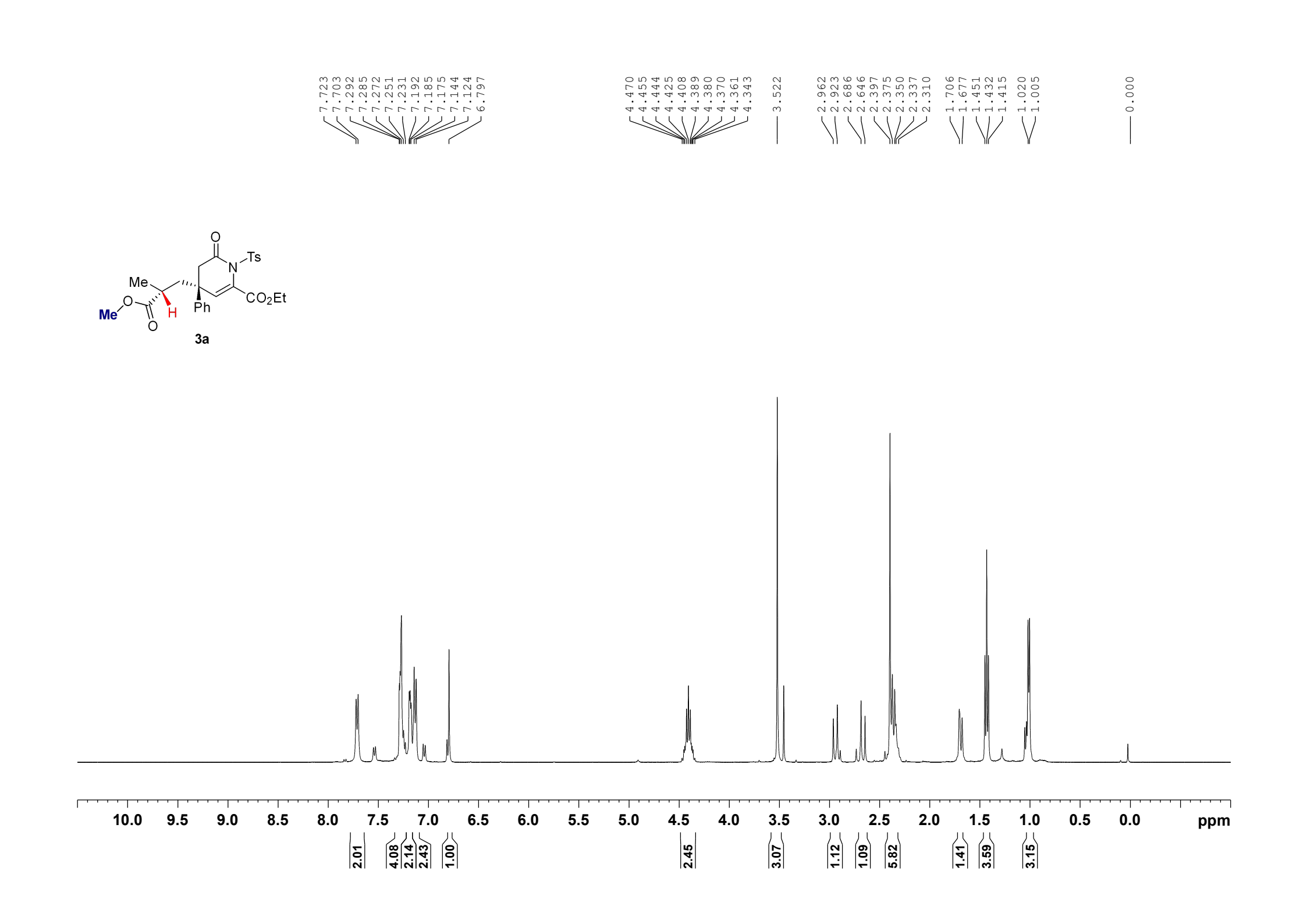
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1.005
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O
Me
O
H
Ph
N
Ts
CO2Et
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6.0
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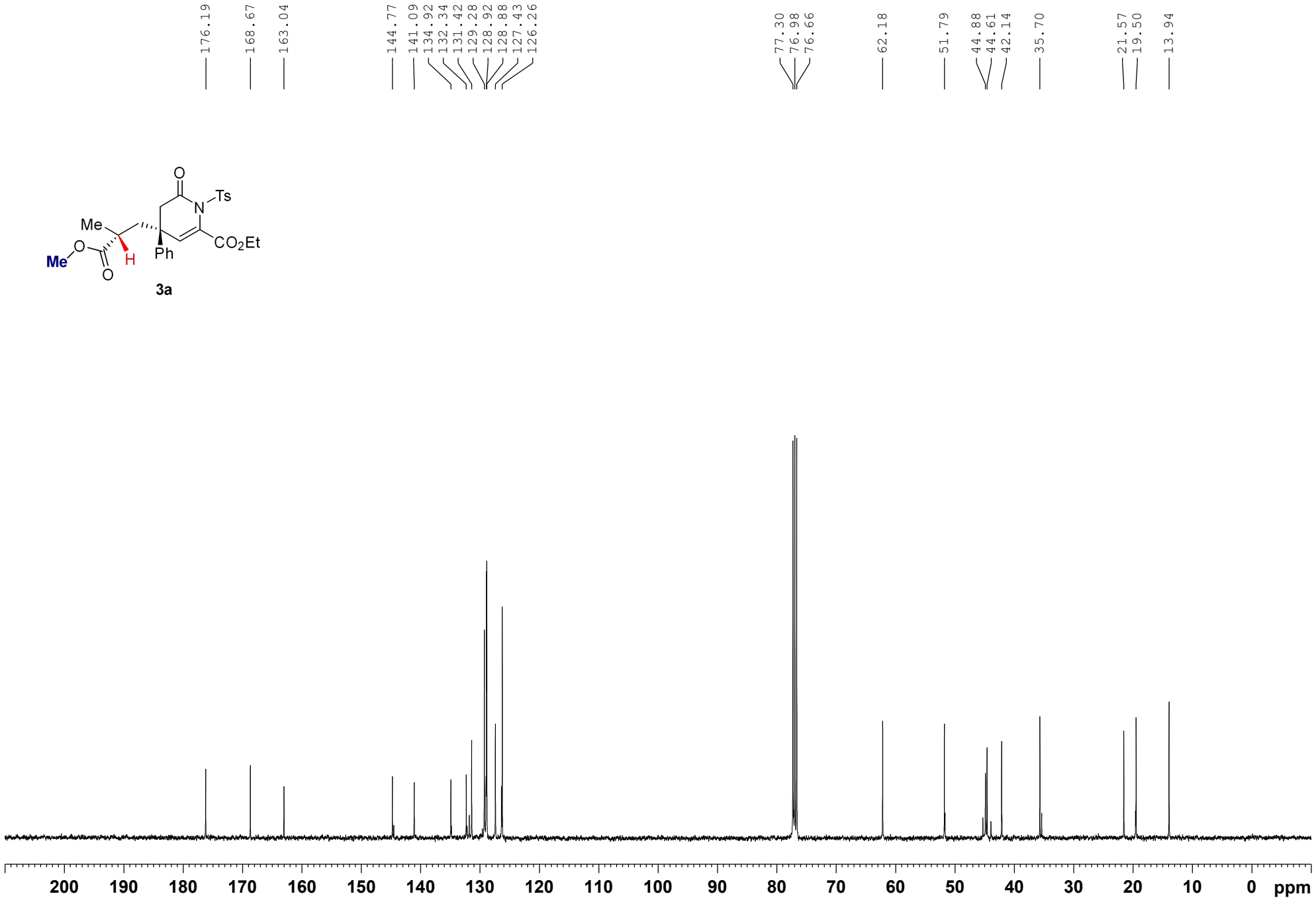
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131.42
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128.92
128.88
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77.30
76.98
76.66
62.18
51.79
44.88
44.61
42.14
35.70
21.57
19.50
13.94
O
N
Ts
Me
O
Me
H
Ph
CO2Et
O
3a
200
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140
130
120
110
100
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60
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20
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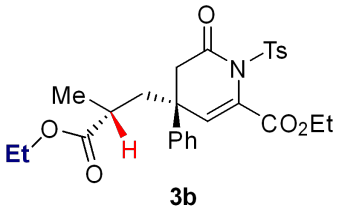
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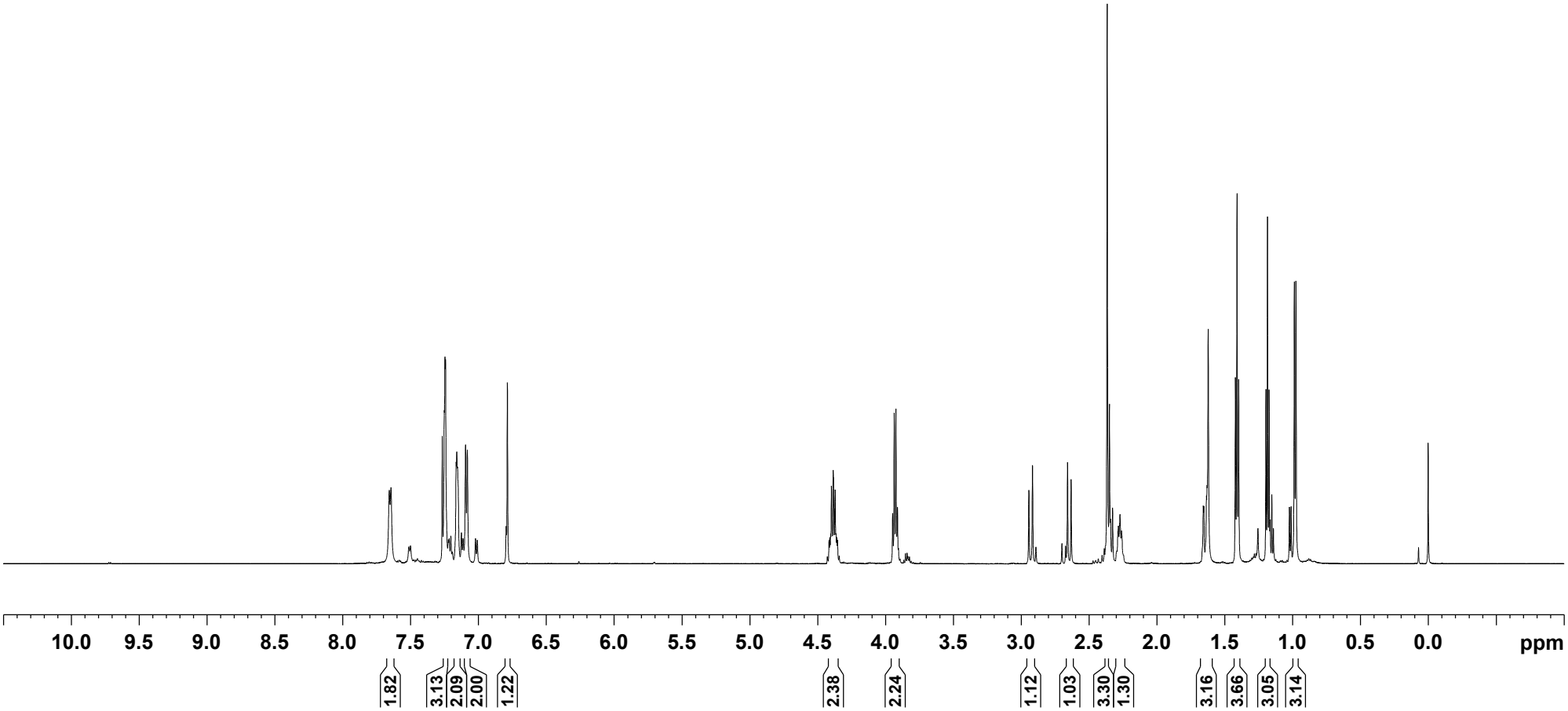
Ts
Me
O
CO2Et
Et
H
Ph
O

3b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3.922
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8.0
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7.0
6.5
6.0
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1.0
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0.0
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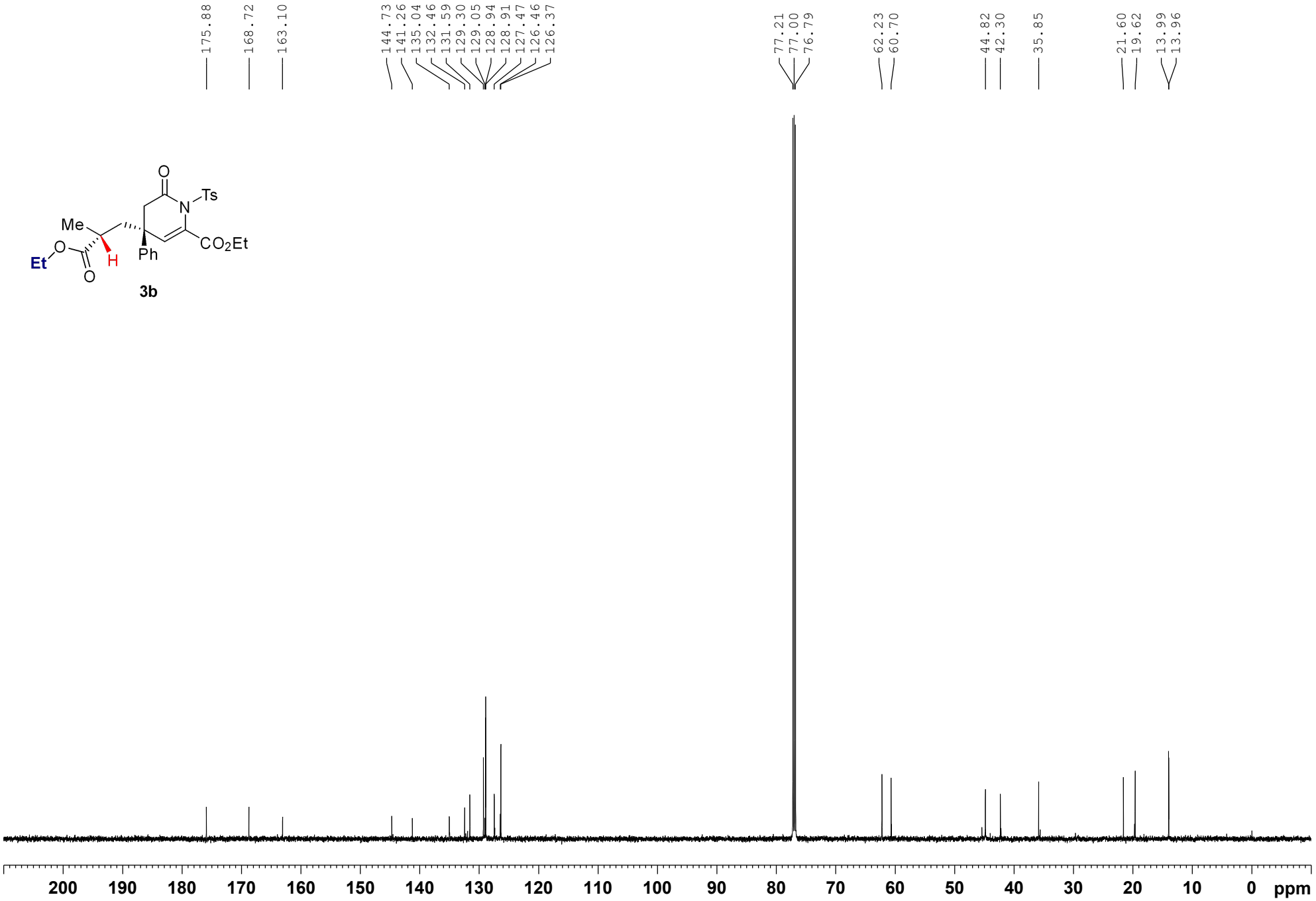
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35.85
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19.62
13.99
13.96
O
N
Ts
Me
O
Et
H
Ph
CO2Et
O
3b
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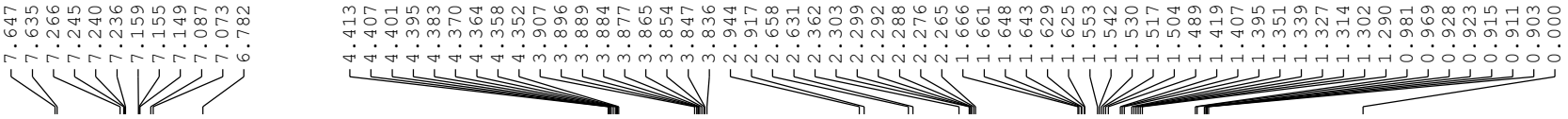
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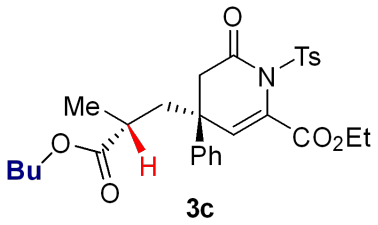
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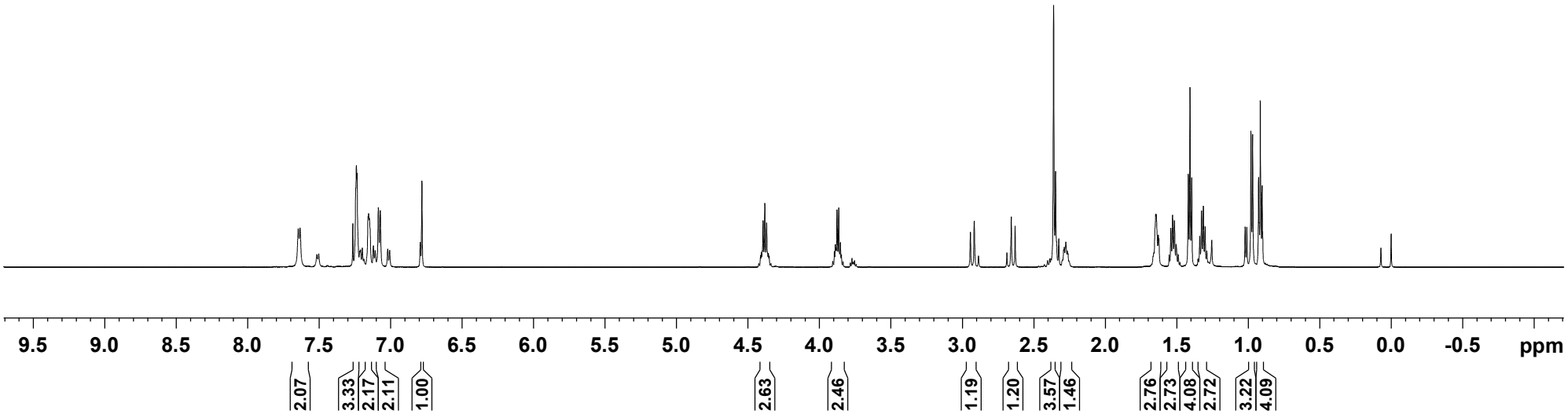
O

3c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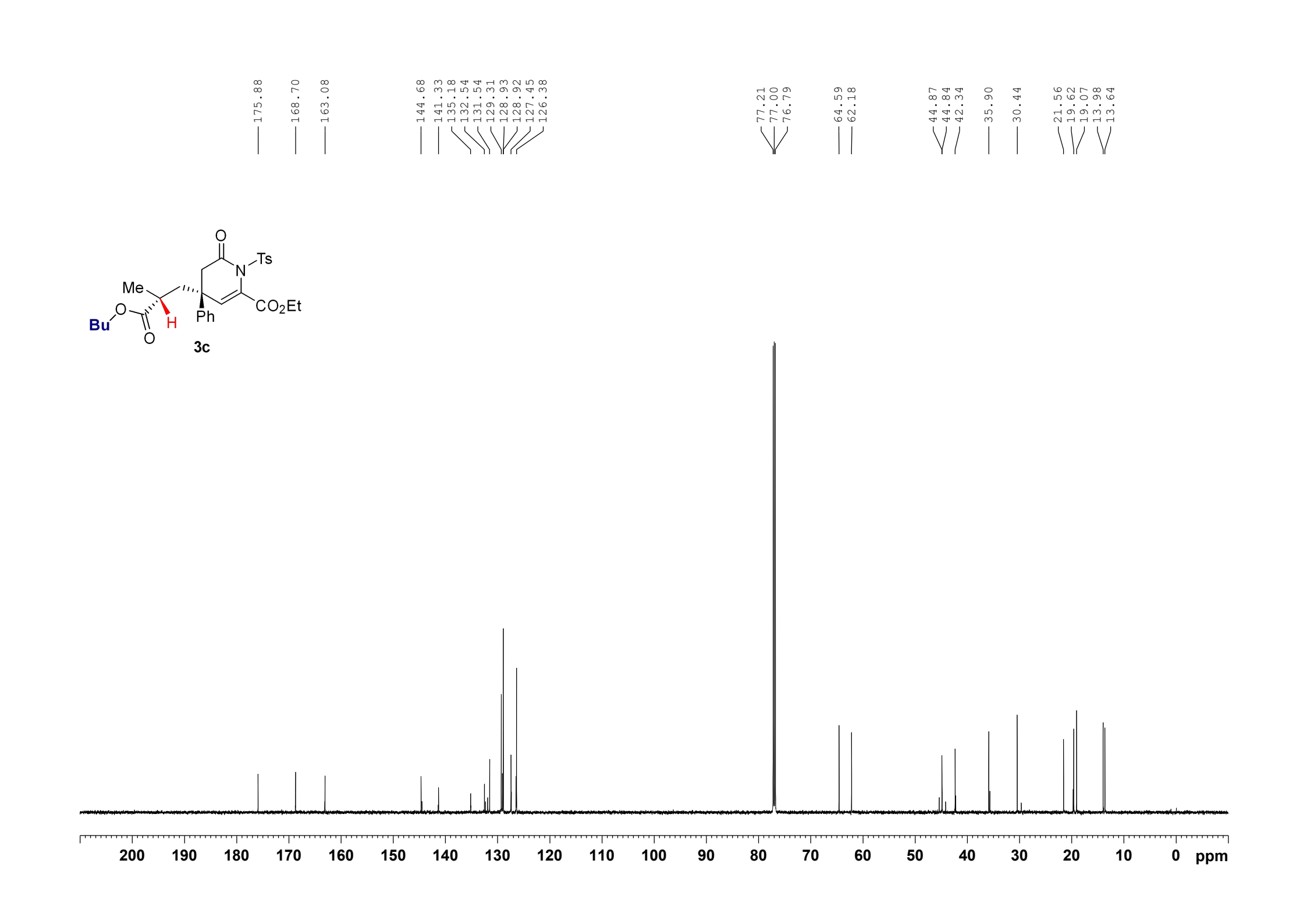
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Bu
O
H
Ph
CO2Et
3c
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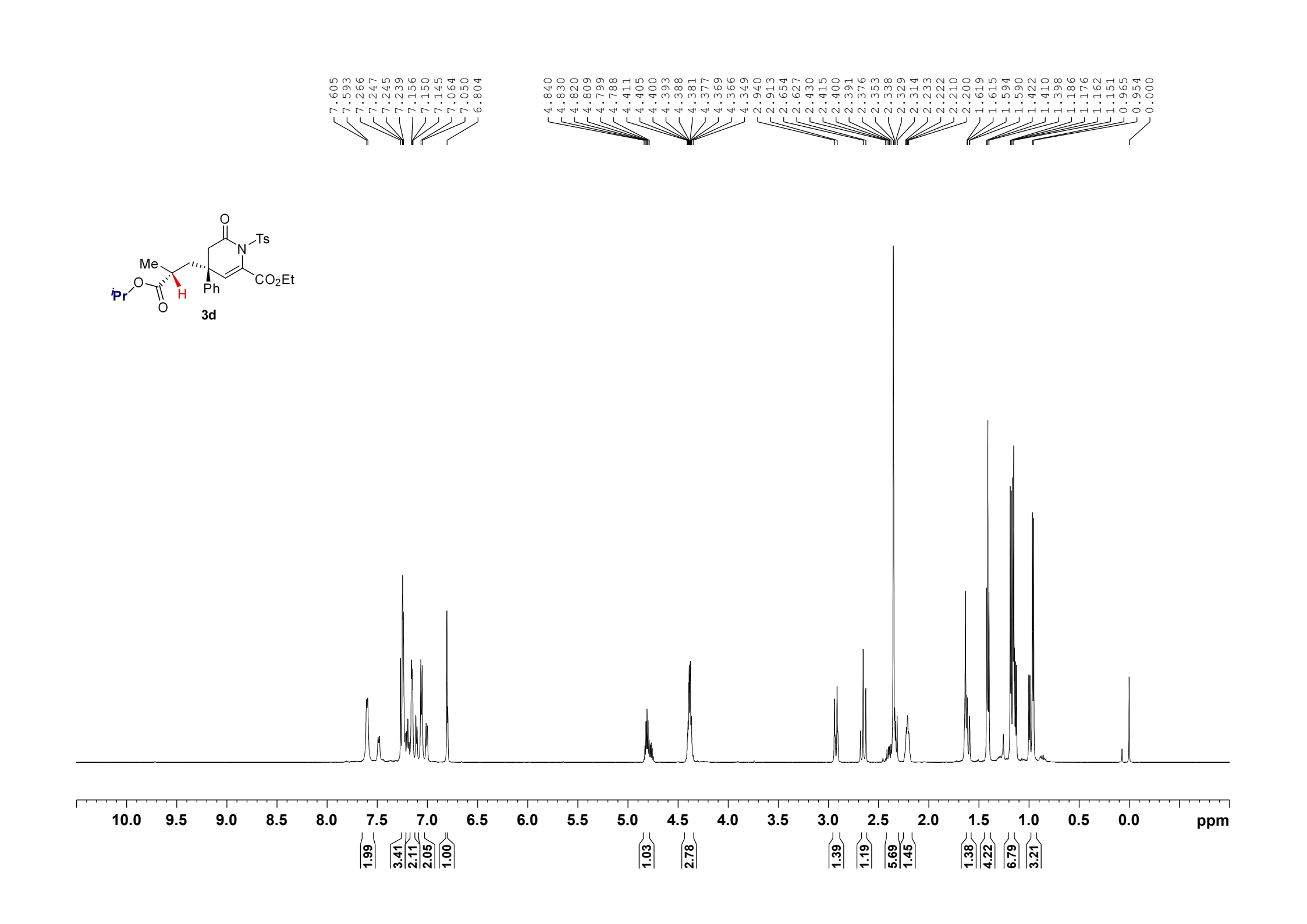
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Ts
N
Ph
CO2Et
iPr
O
H
O
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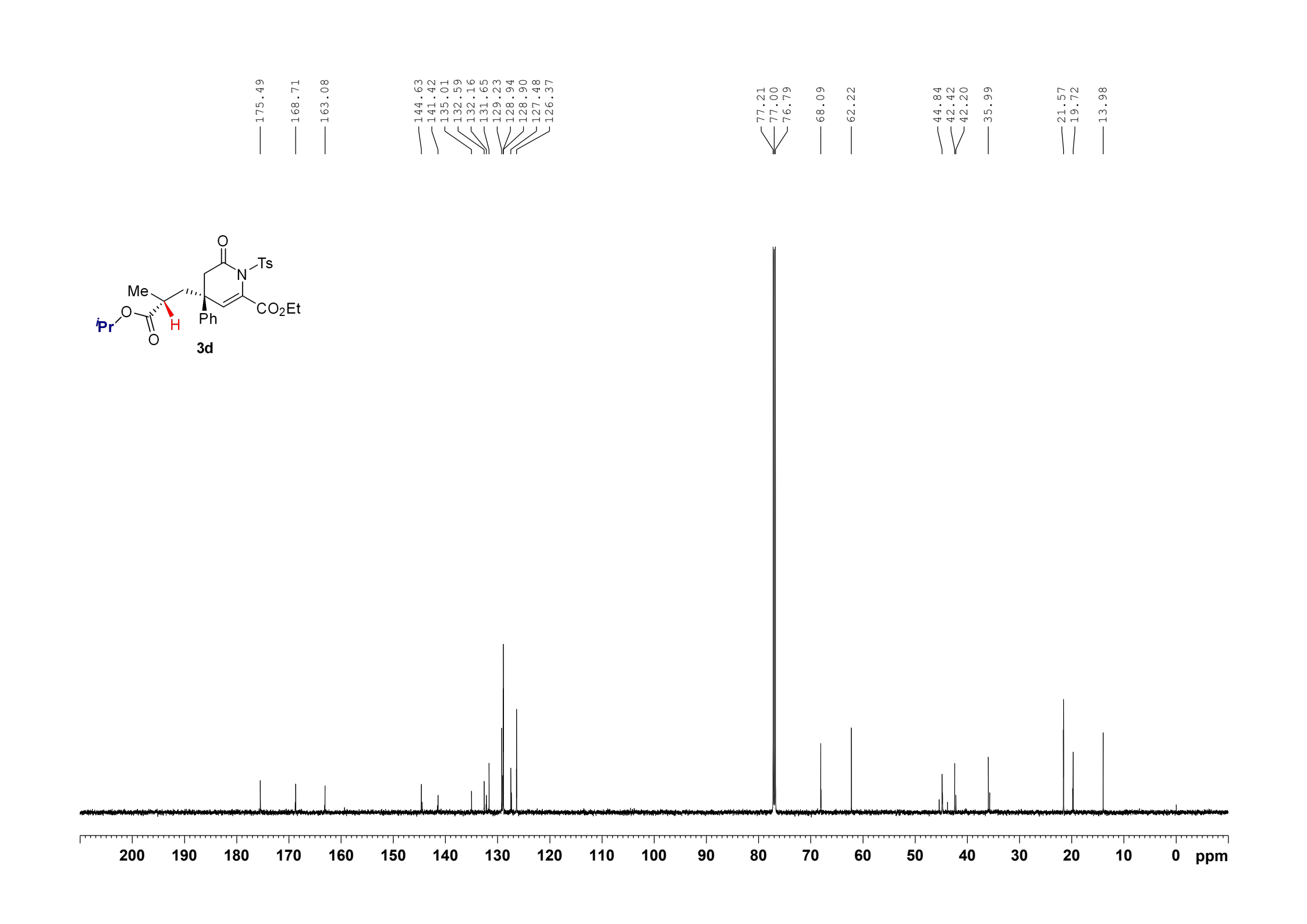
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76.79
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21.57
19.72
13.98
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N
Me
O
CO2Et
Ph
iPr
O
H
O
3d
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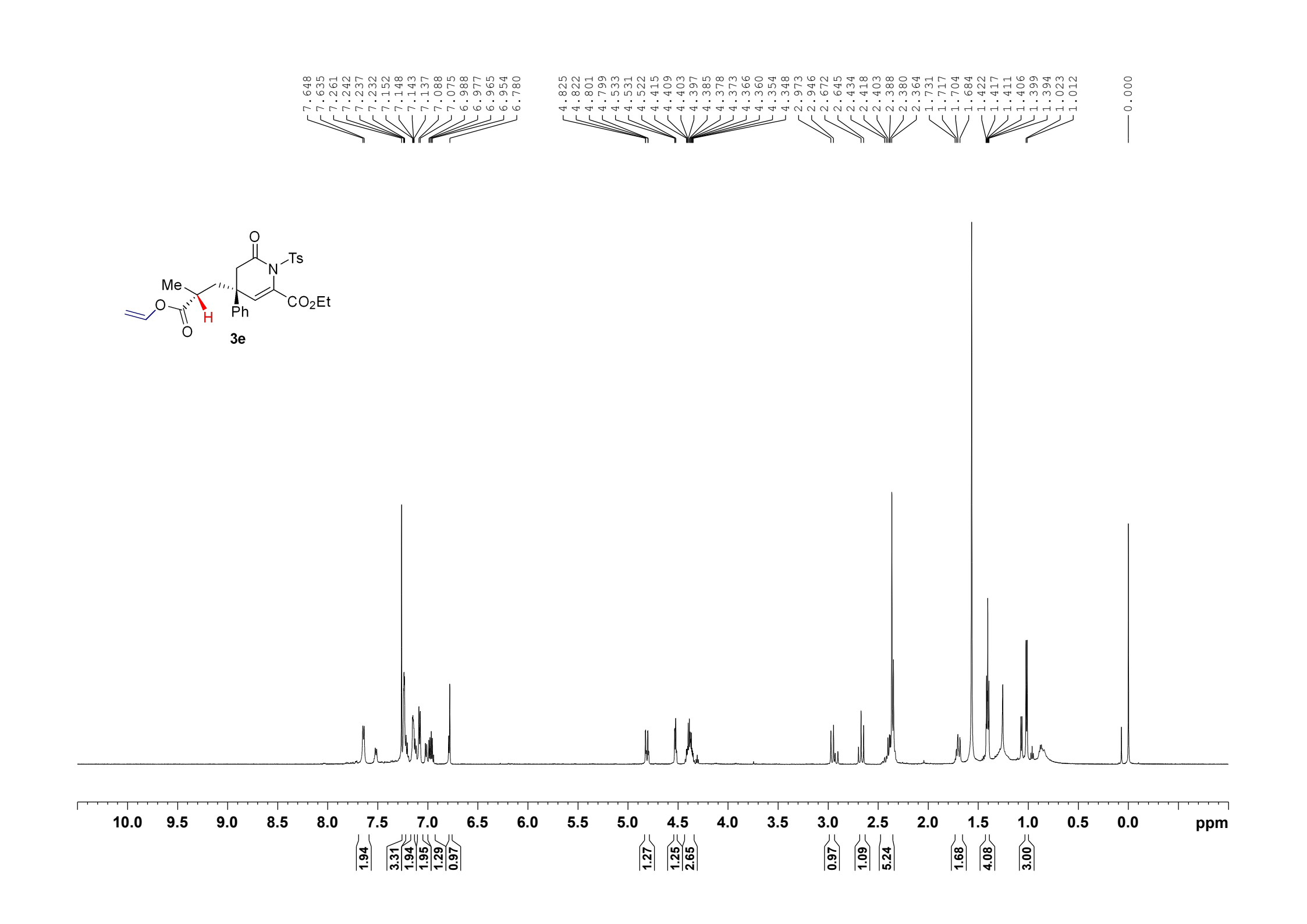
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1.422
1.417
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1.394
1.023
1.012
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O
H
O
Ph
N
Ts
CO2Et
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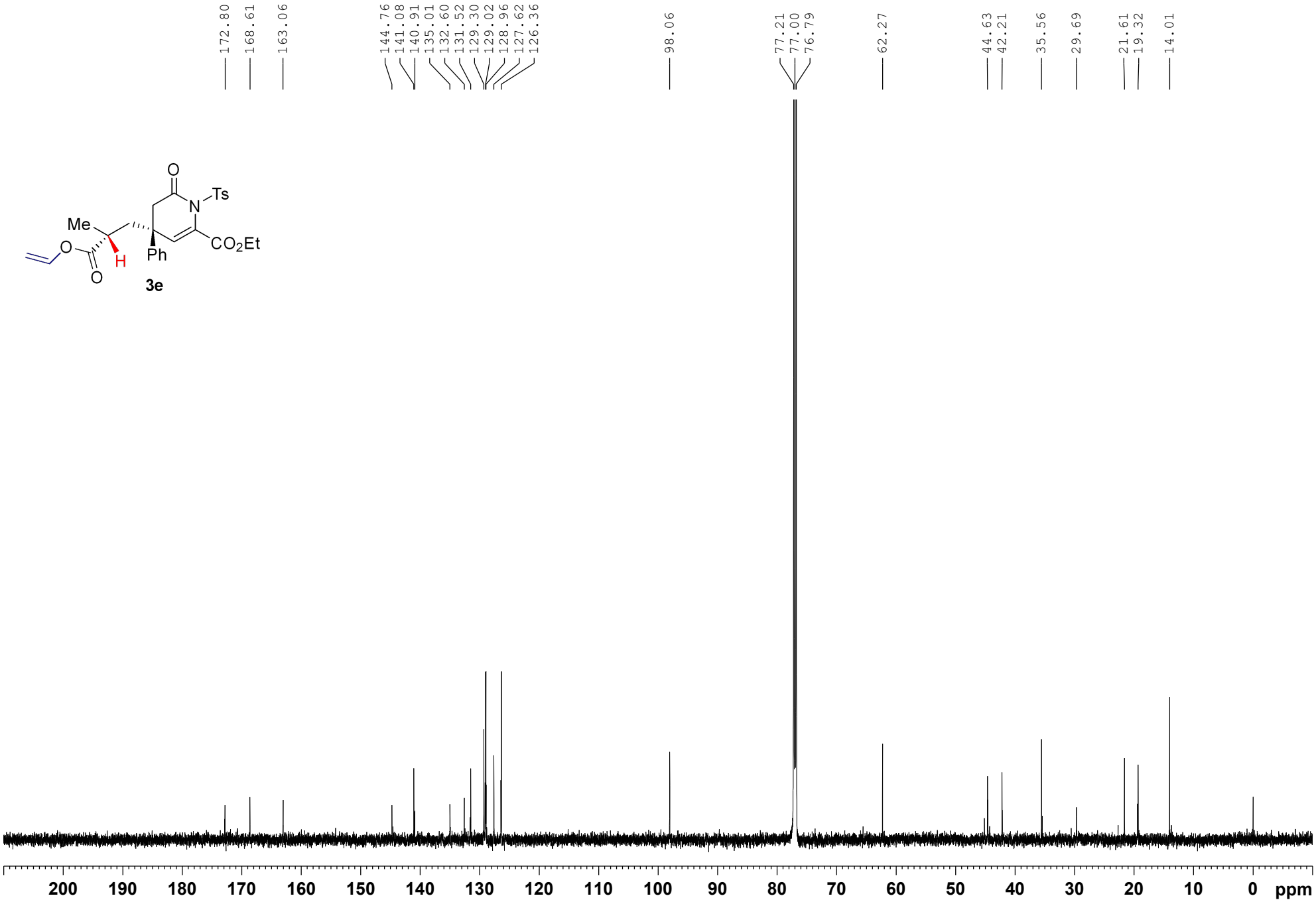
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35.56
29.69
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19.32
14.01
O
N
Ts
Me
O
H
Ph
CO2Et
O
3e
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150
140
130
120
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100
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ppm

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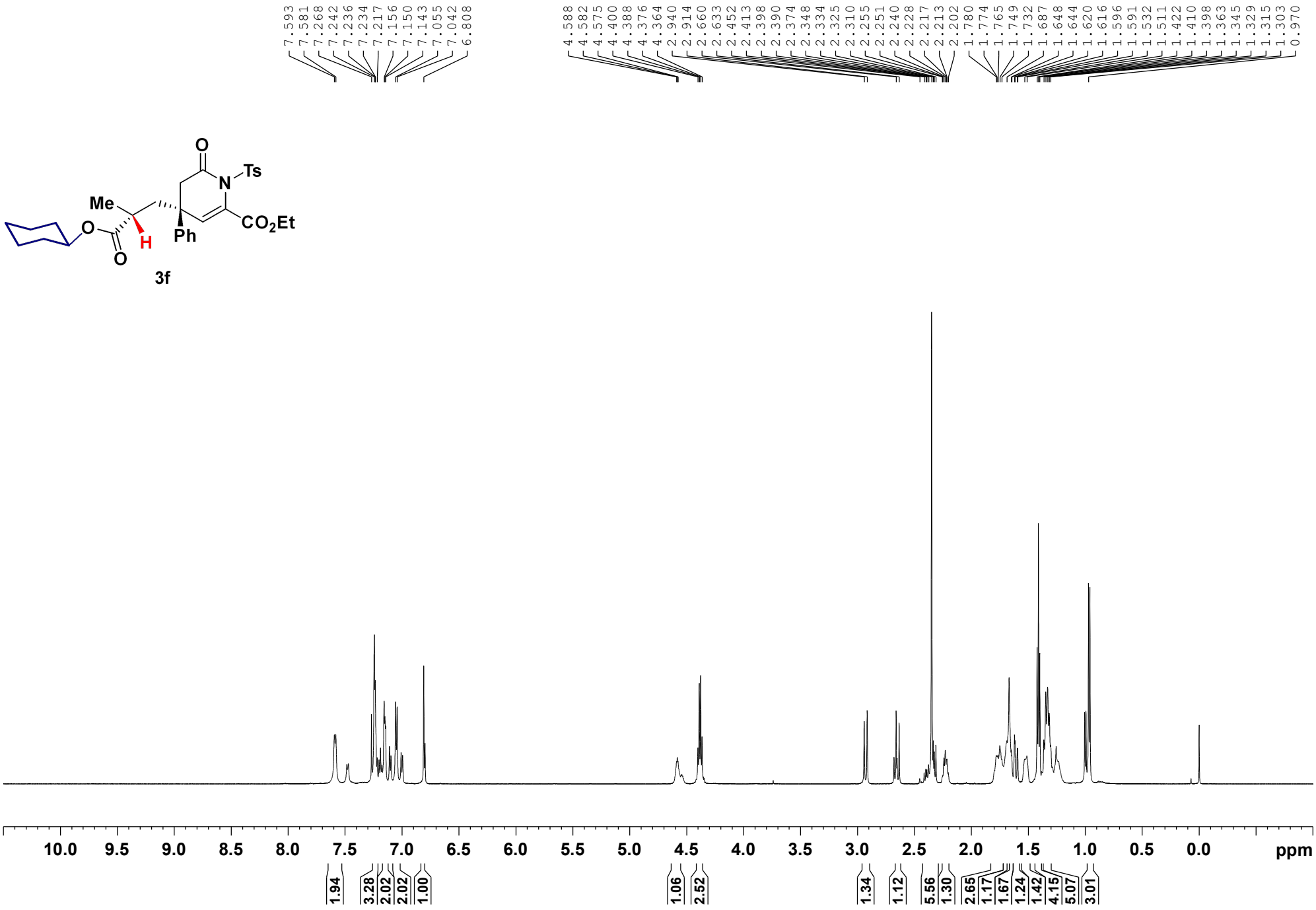
O
CO2Et
Ph
H
O

3f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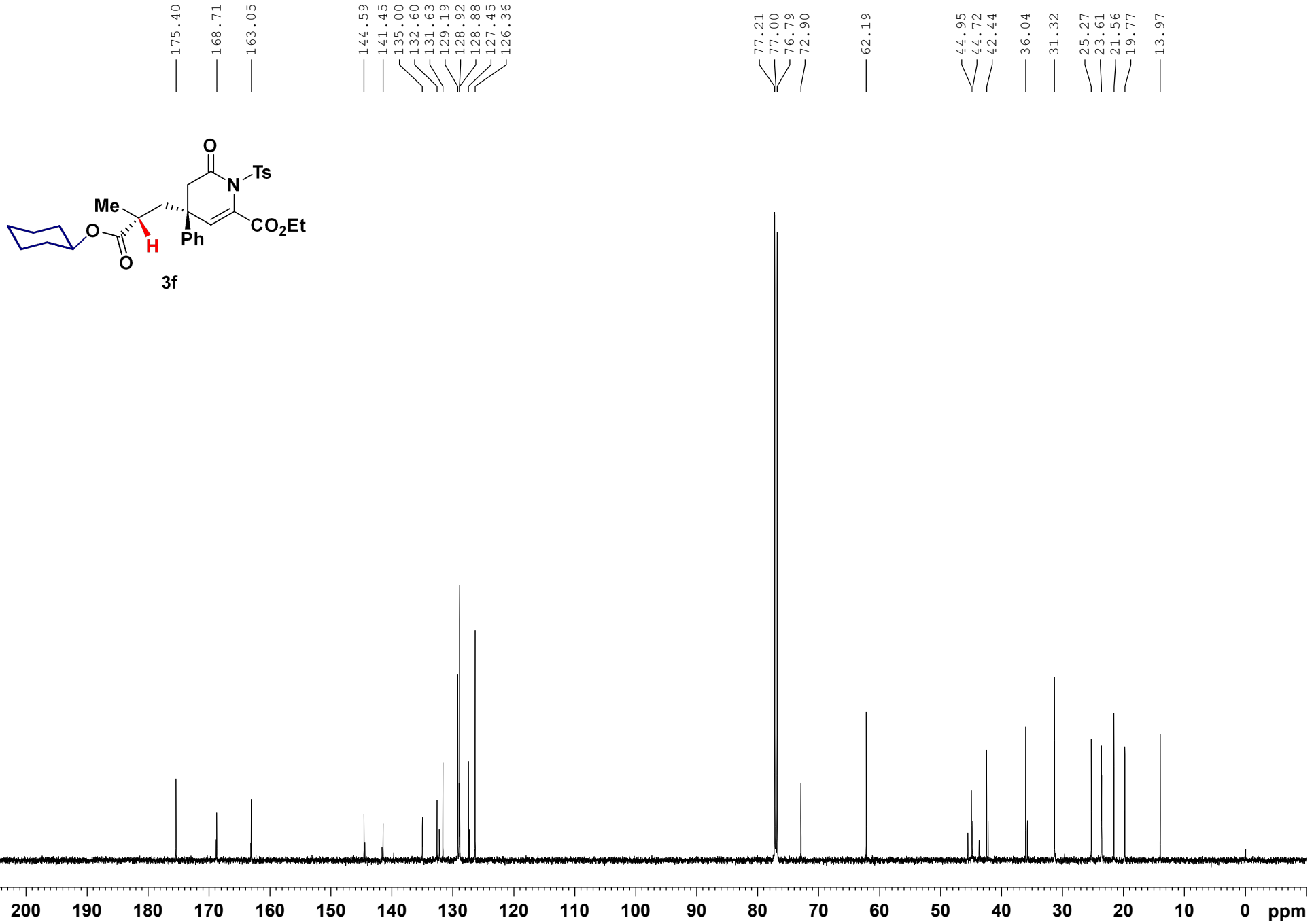
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19.77
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O
N
Ts
Me
O
H
Ph
CO2Et
O
3f
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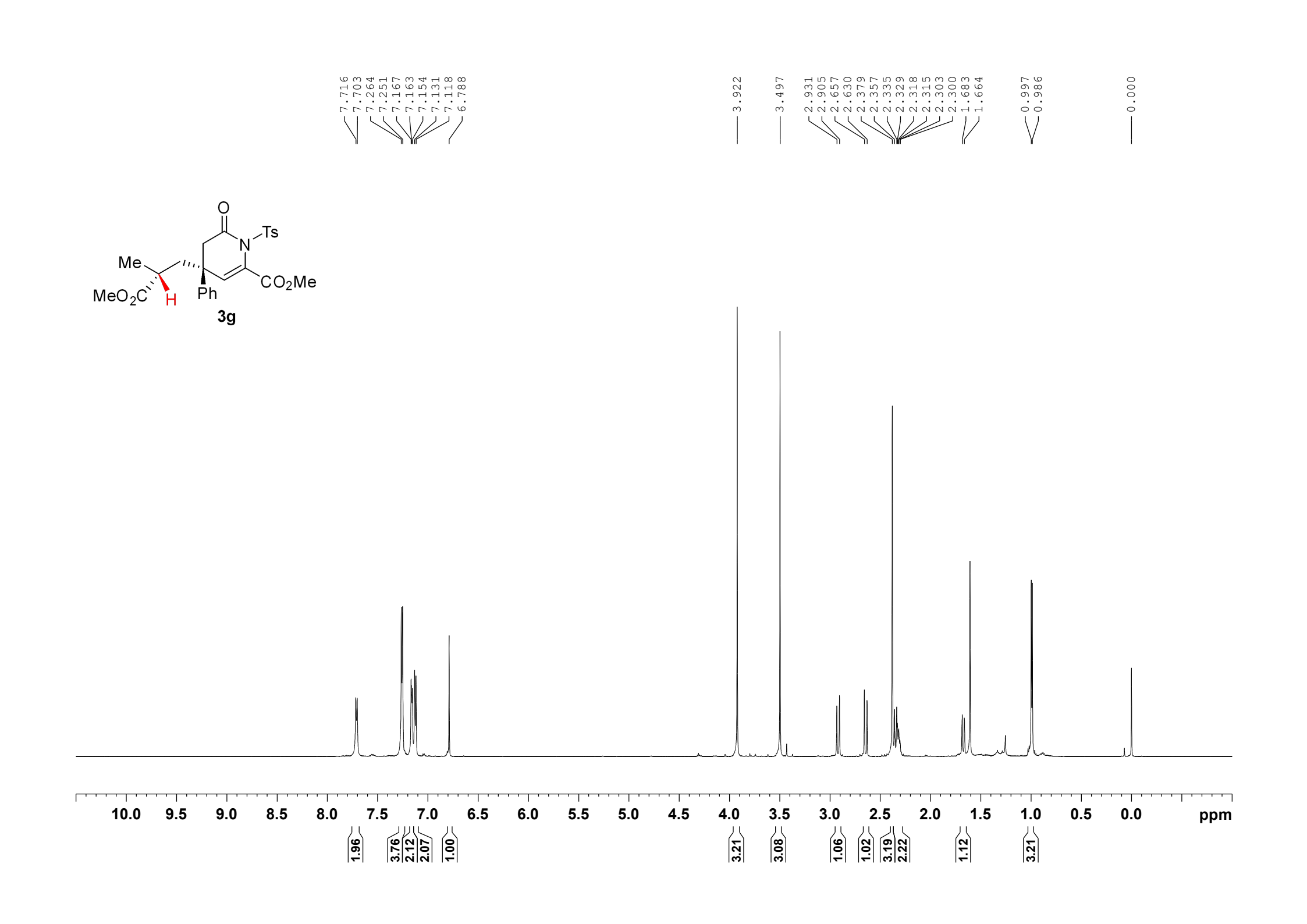
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H
Ph
CO2Me
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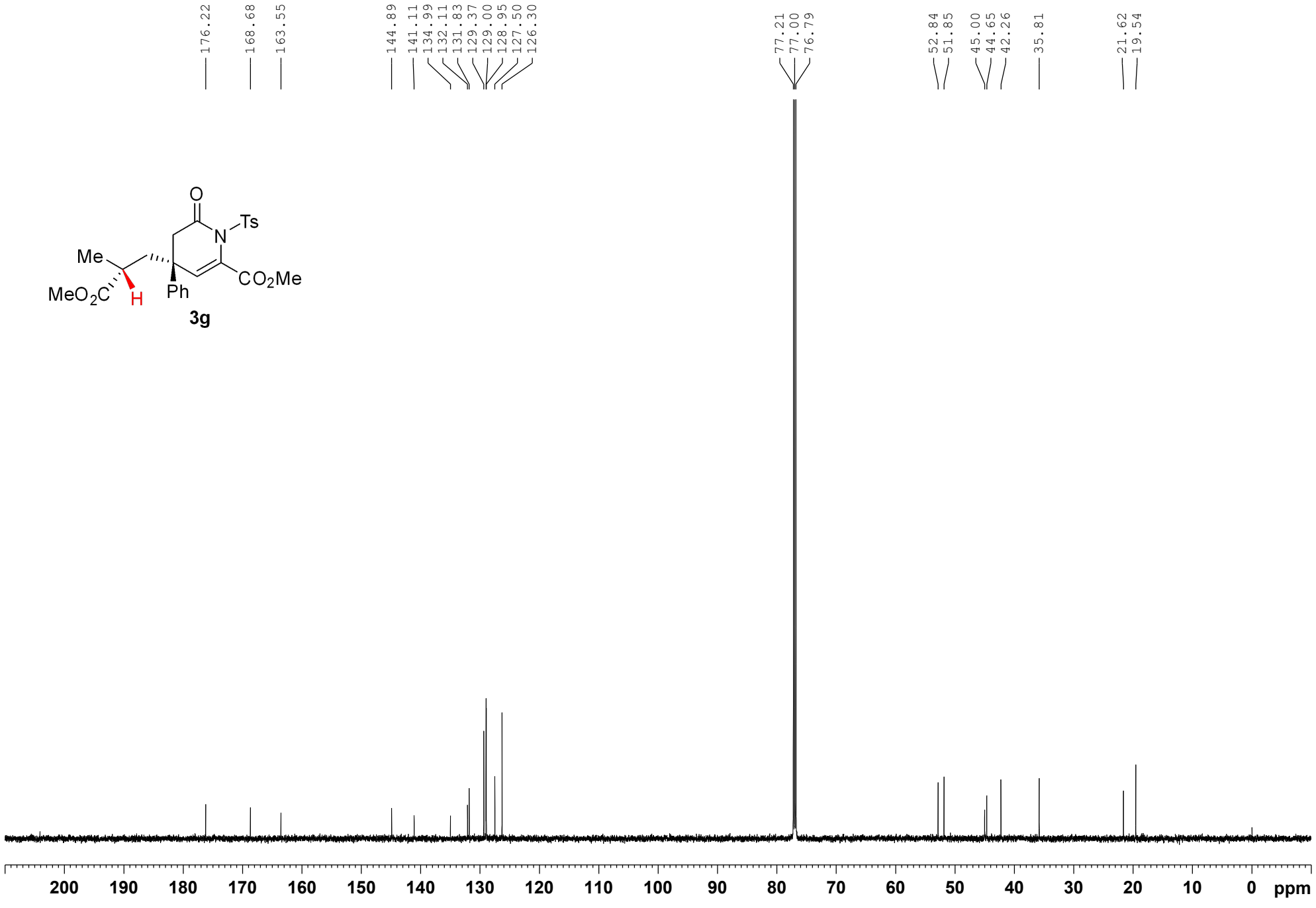
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21.62
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Me
MeO2C
H
Ph
CO2Me
3g
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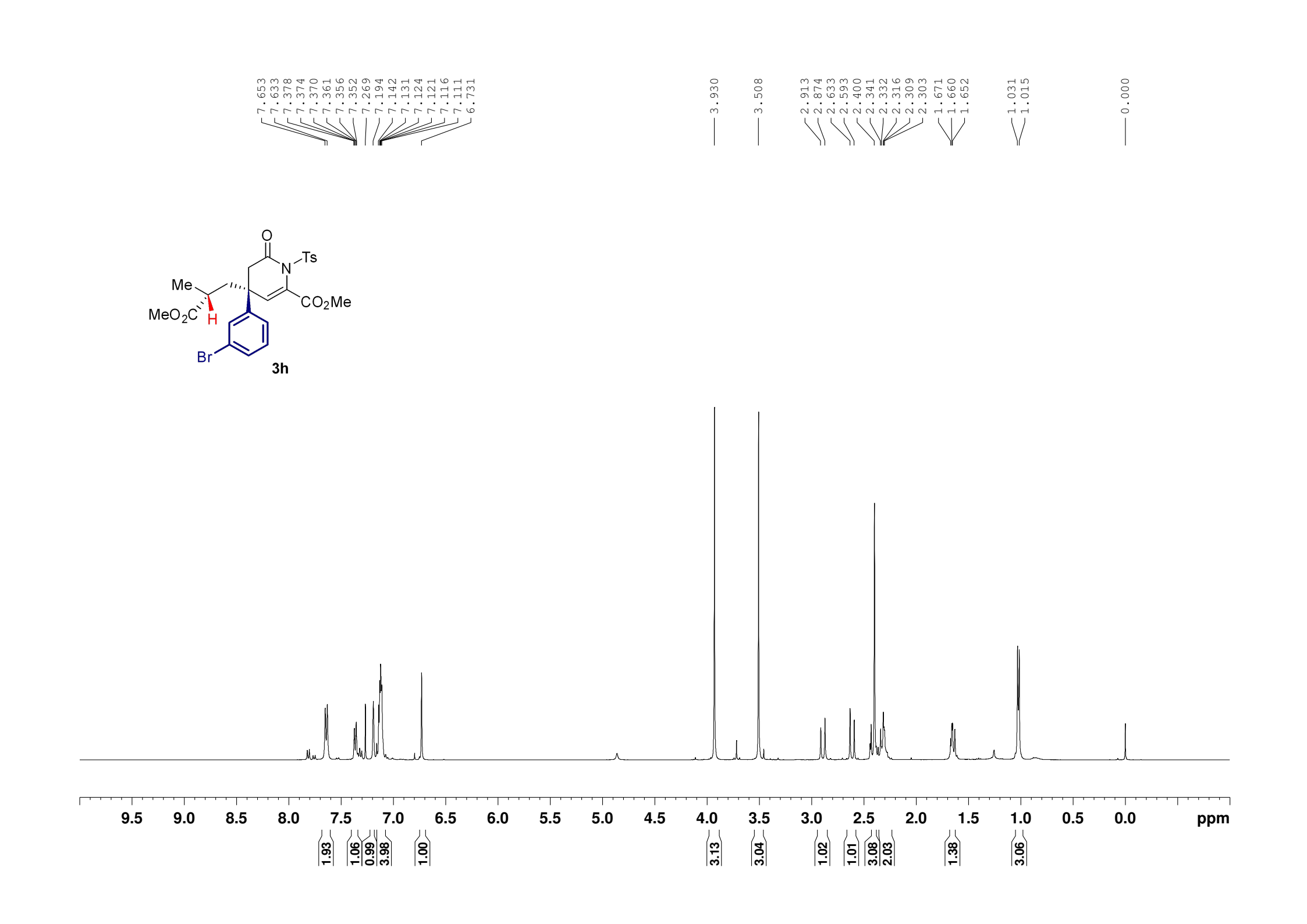
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Me
MeO2C
H
CO2Me
Br
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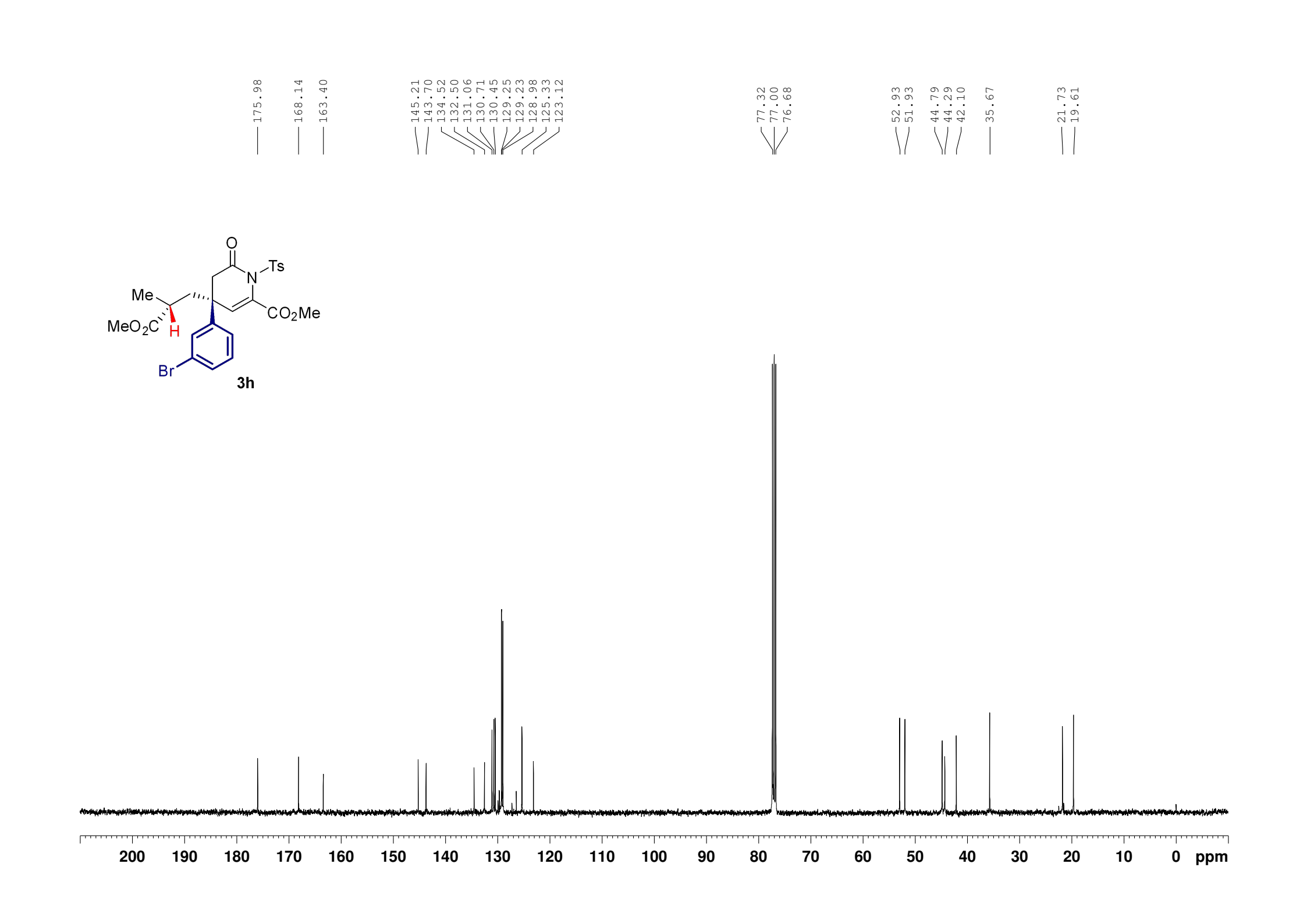
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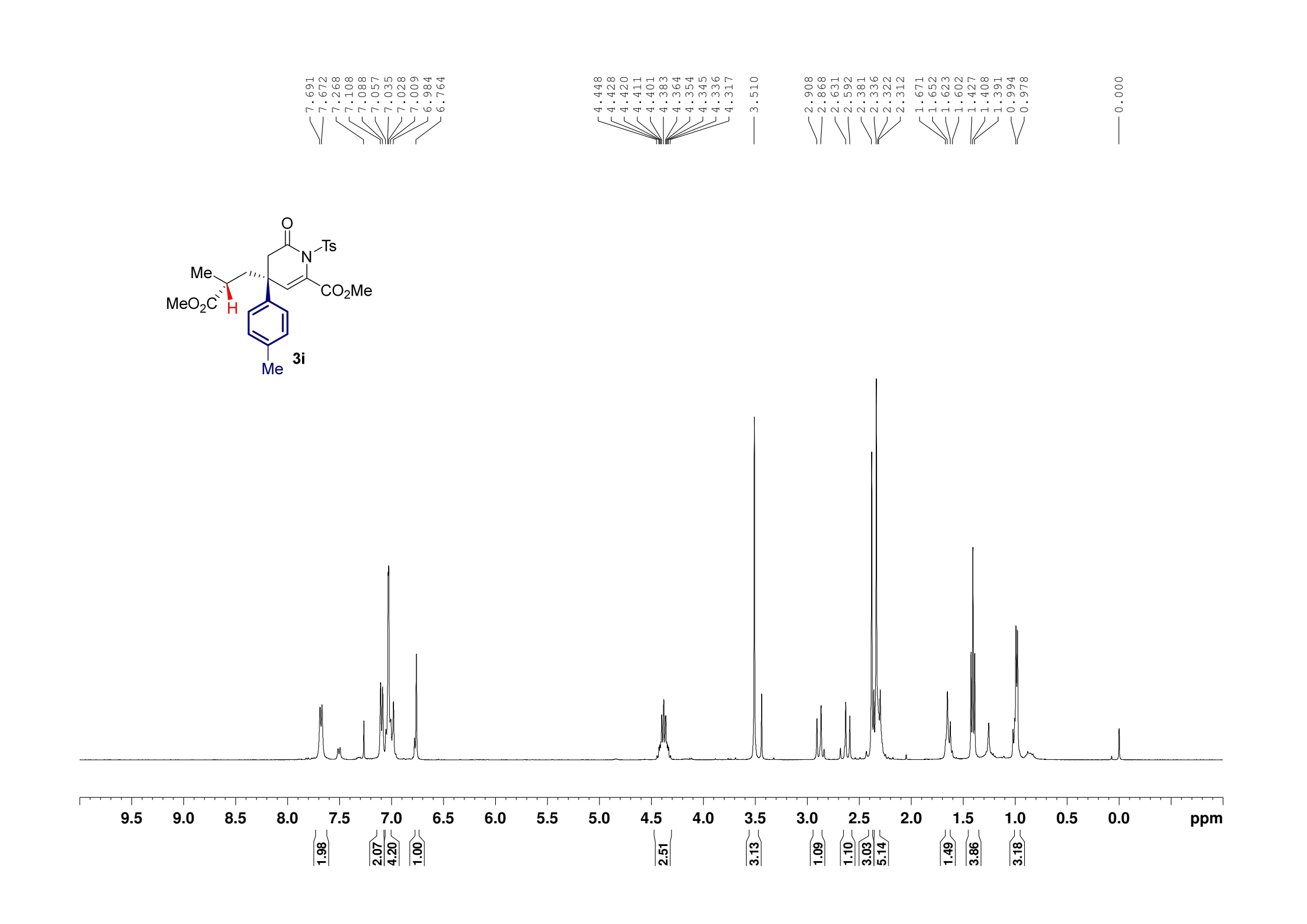
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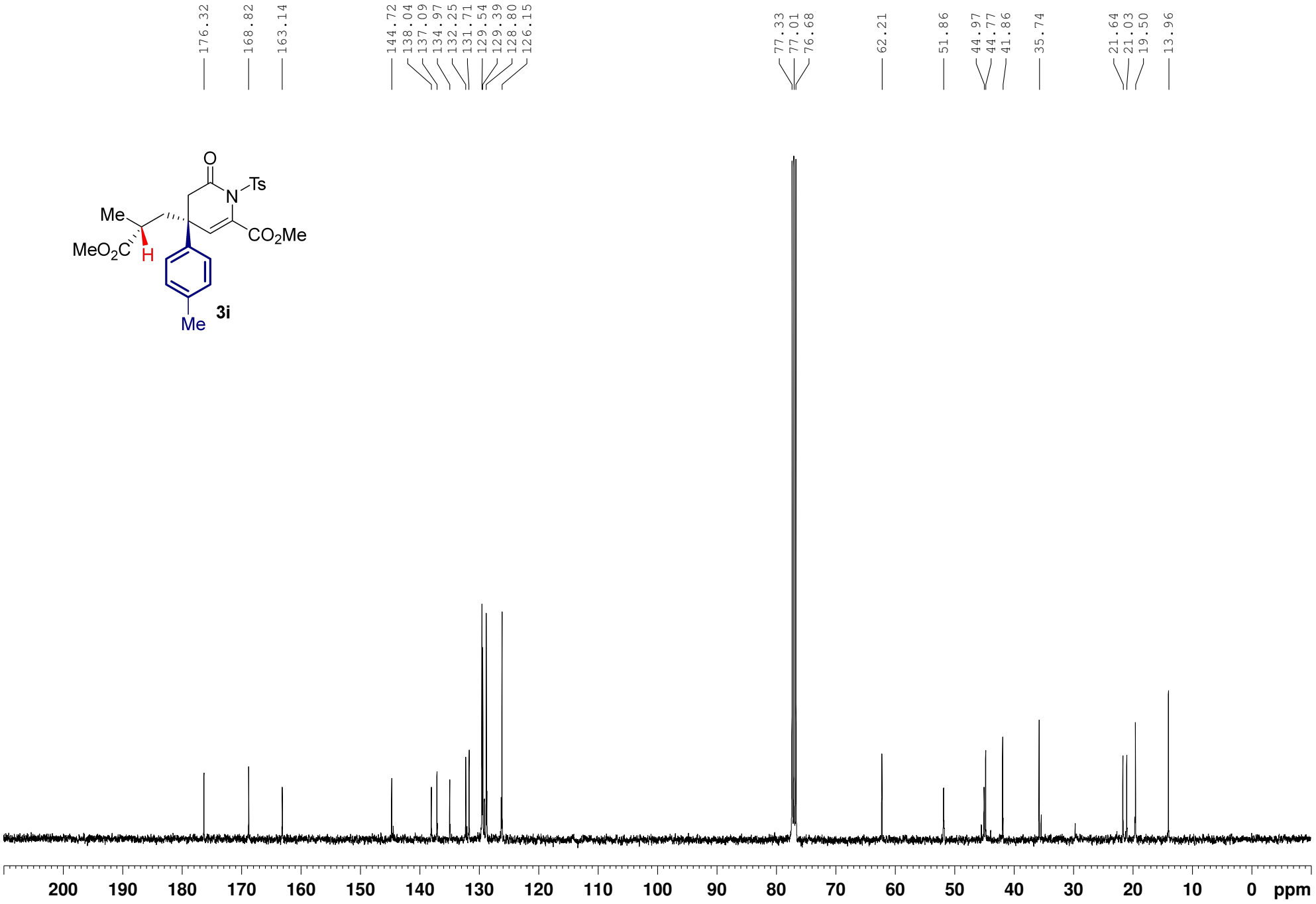
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N
Ts
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H
CO2Me
Me
3i
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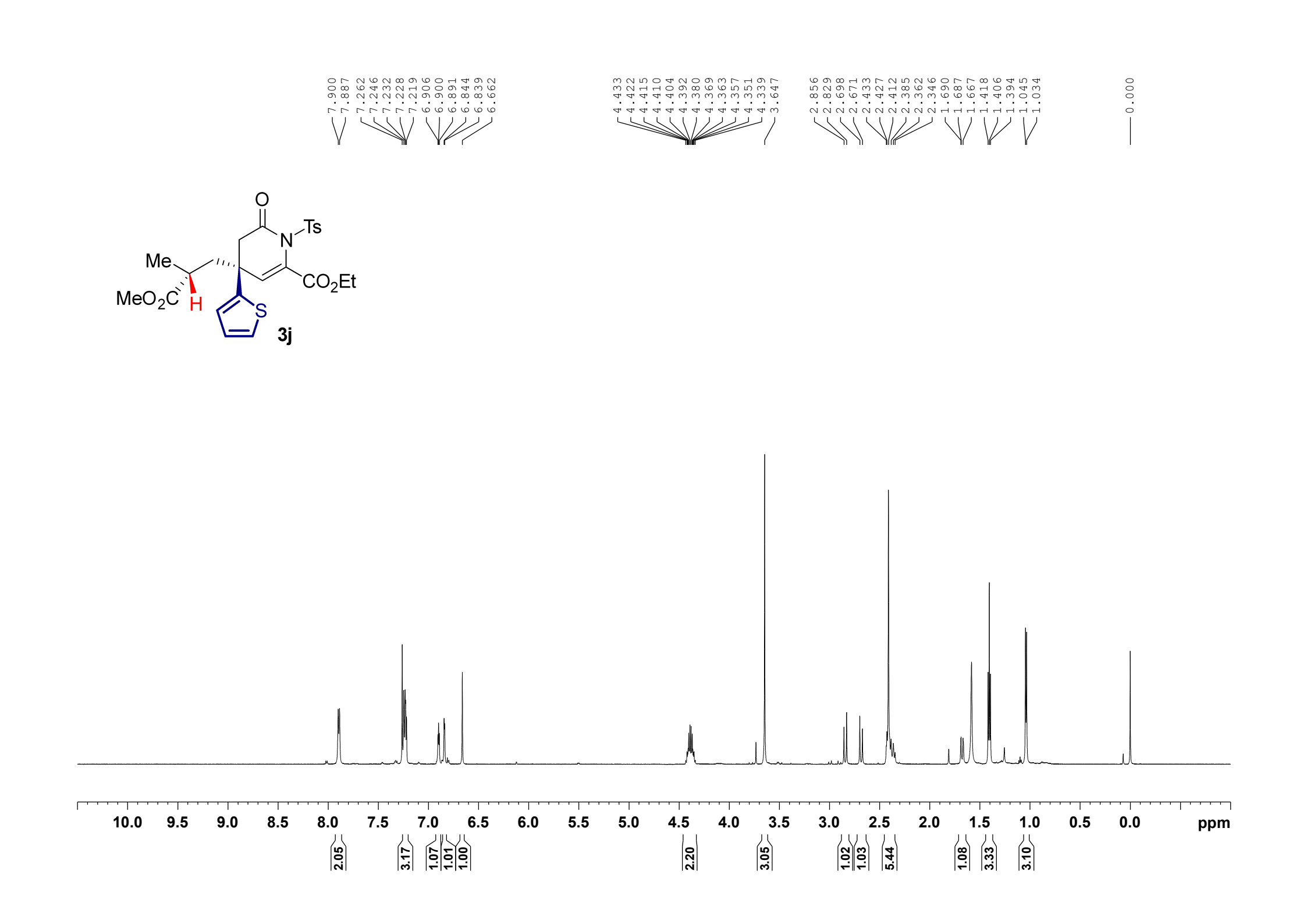
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CO2Et
MeO2C
H
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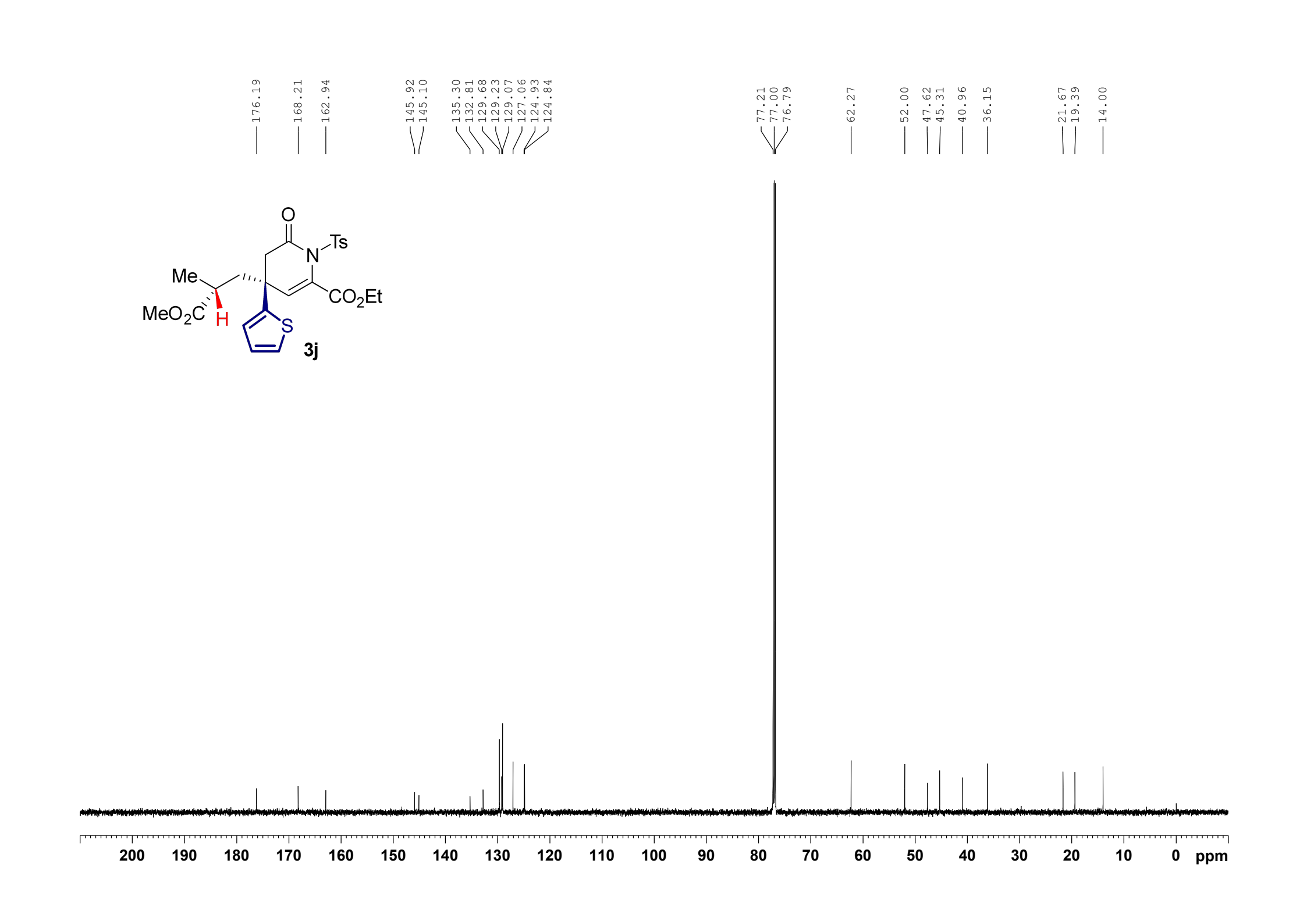
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Ts
Me
MeO2C
H
CO2Et
S
3j
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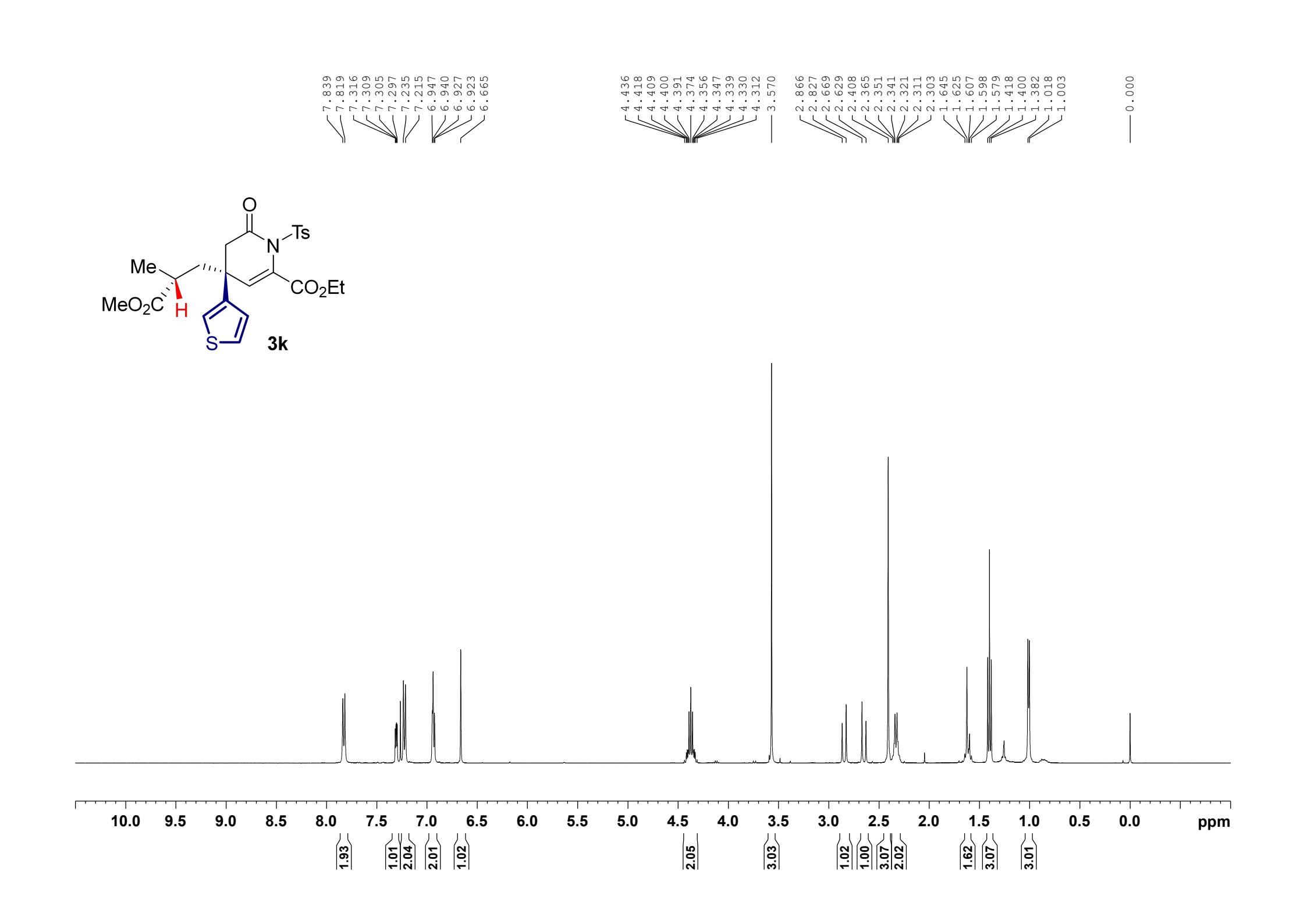
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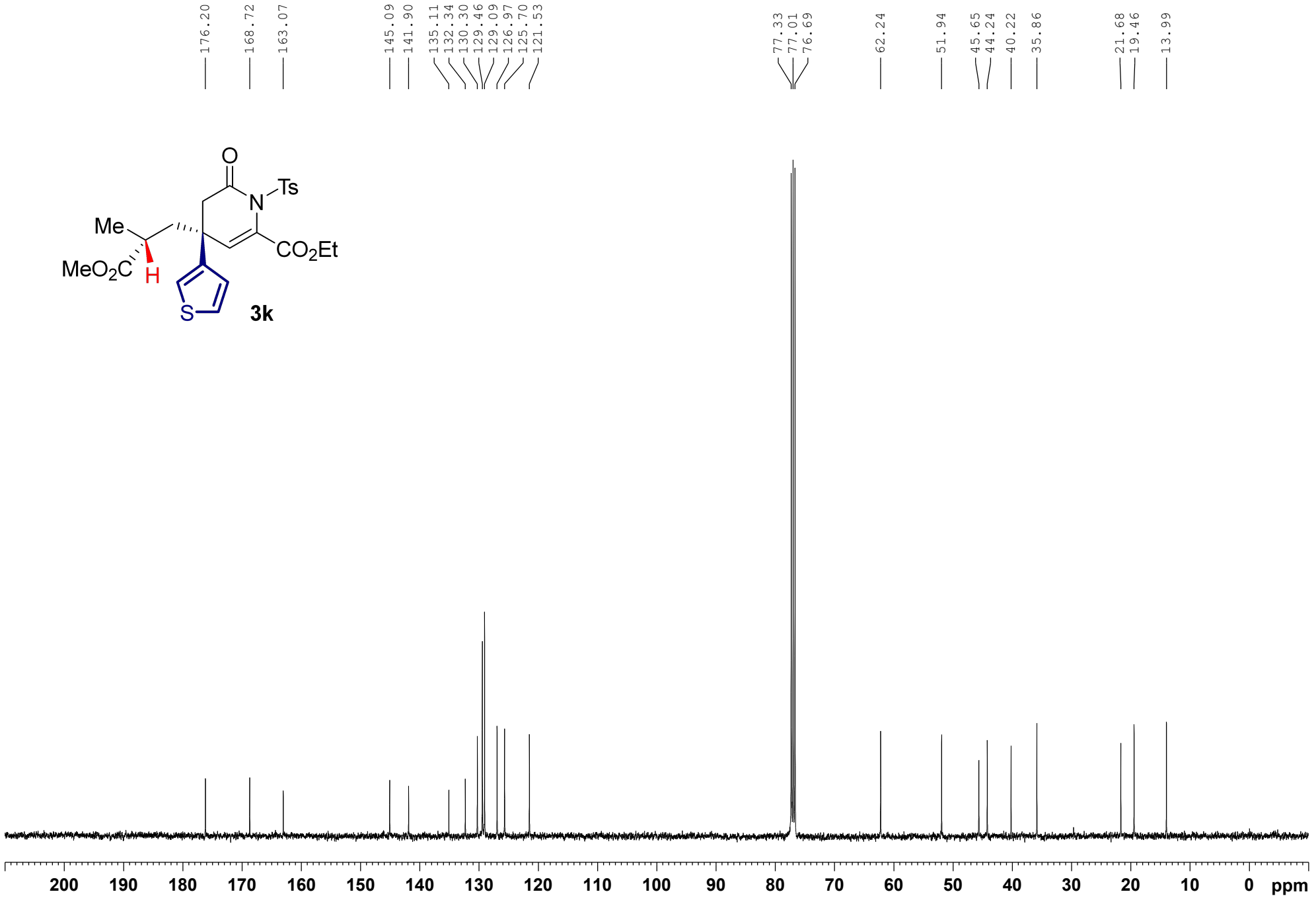
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N
Ts
Me
MeO2C
H
CO2Et
S
3k
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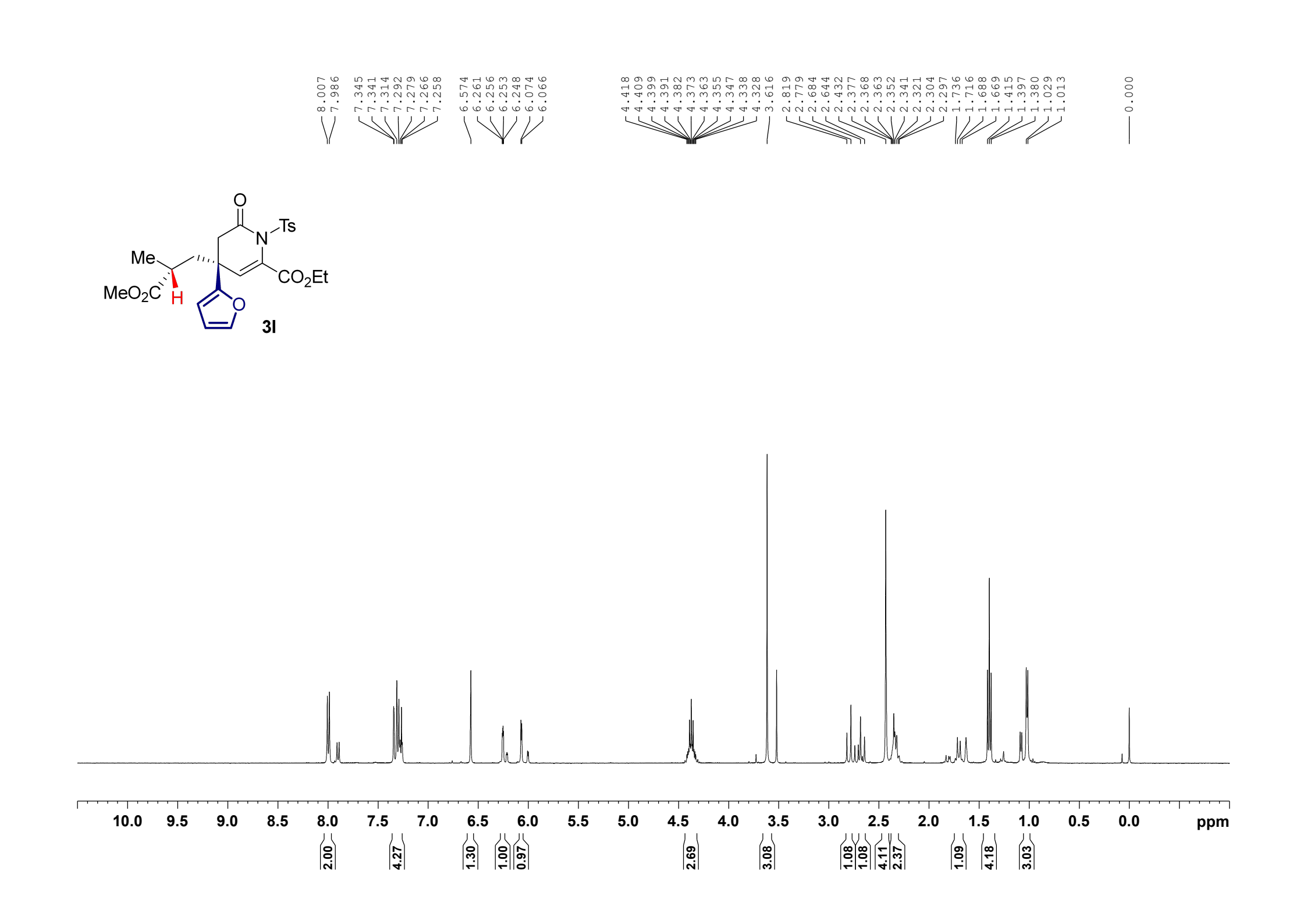
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N
Ts
Me
CO2Et
MeO2C
H
O
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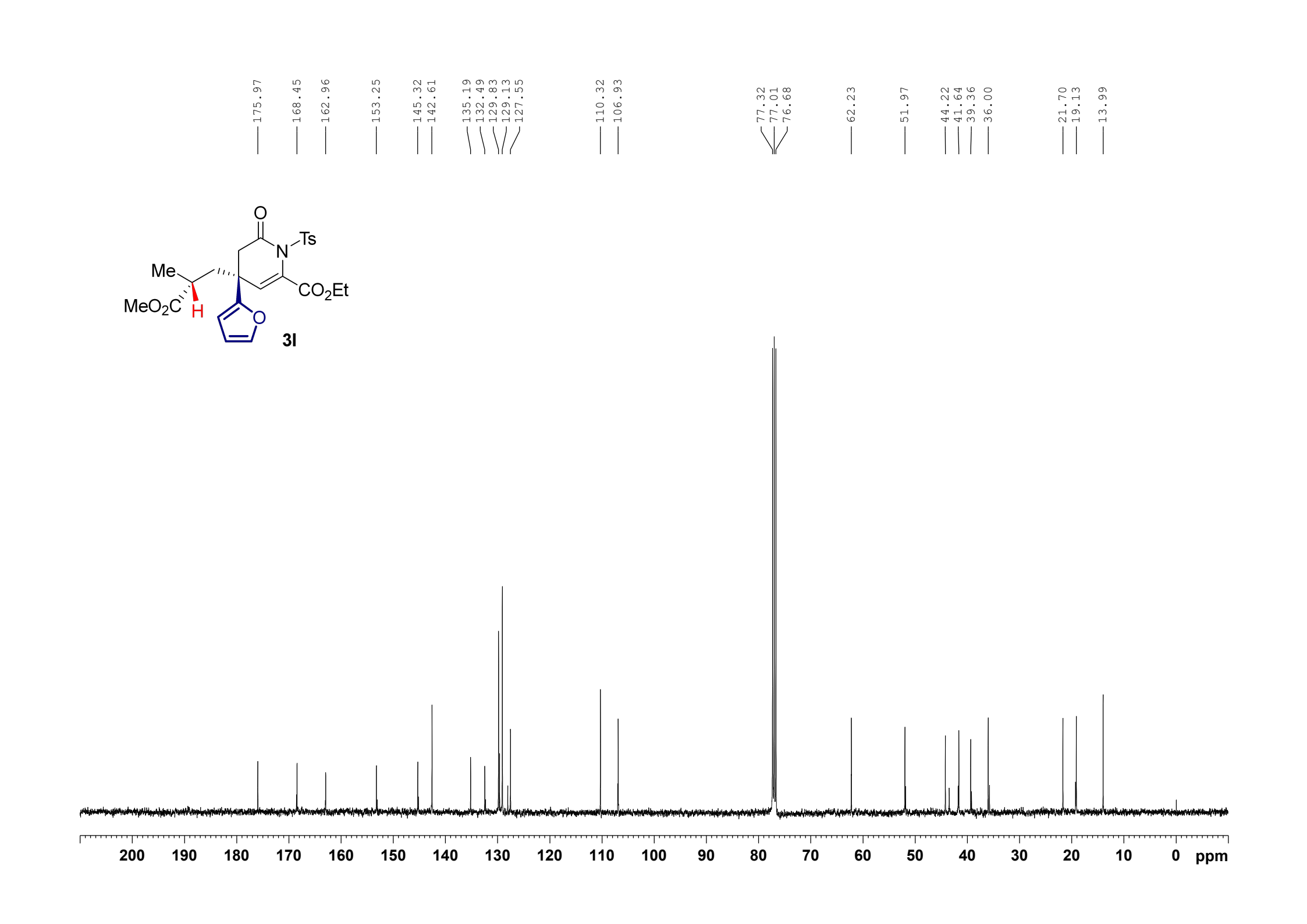
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41.64
39.36
36.00
21.70
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13.99
O
N
Ts
Me
MeO2C
H
CO2Et
O
3l
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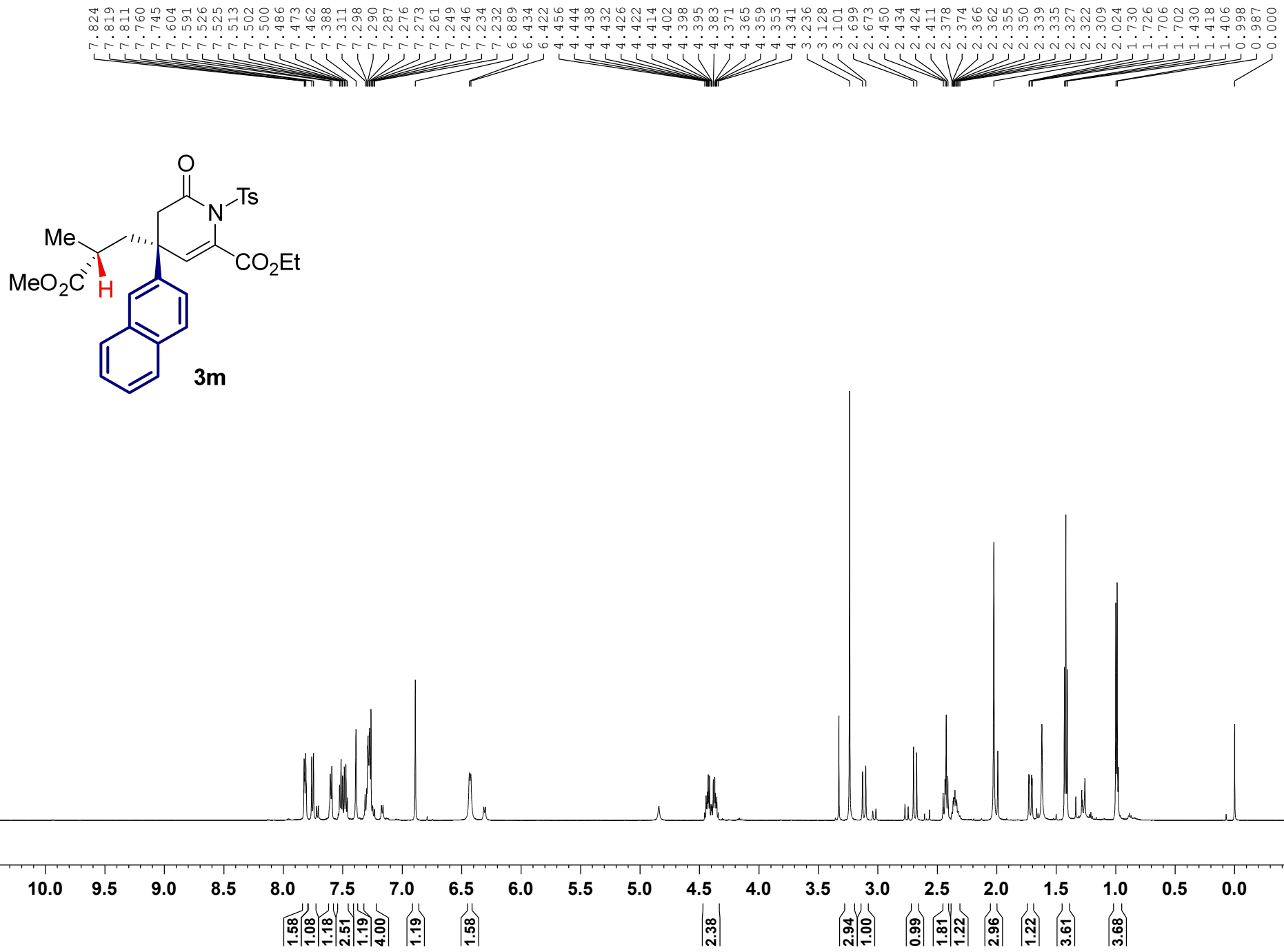
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N
Ts
Me
MeO2C
H
CO2Et
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3.5
3.0
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2.0
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0.5
0.0
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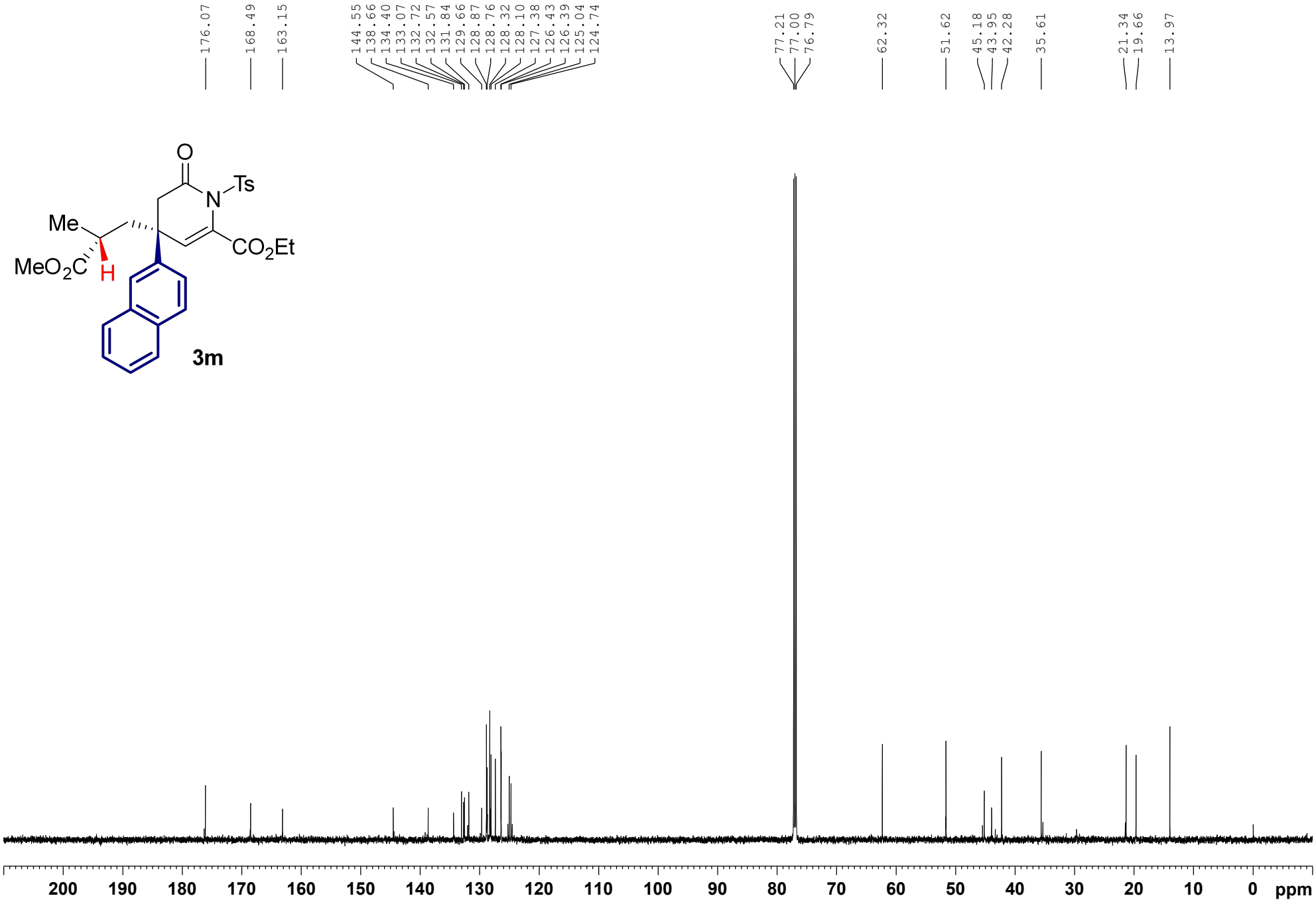
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125.04
124.74
77.21
77.00
76.79
62.32
51.62
45.18
43.95
42.28
35.61
21.34
19.66
13.97
O
Ts
N
Me
CO2Et
MeO2C
H
3m
200
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130
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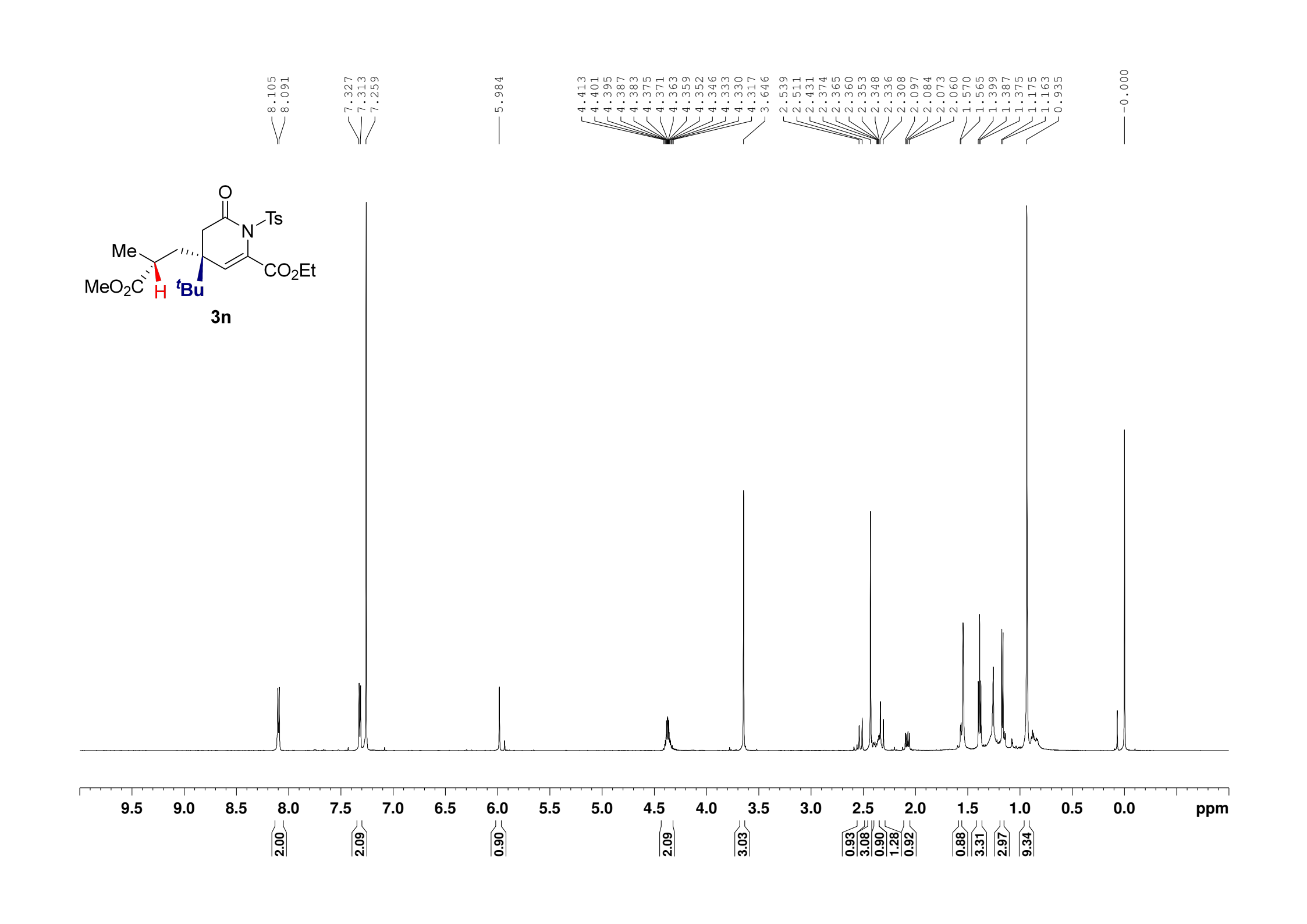
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2.374
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2.353
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2.073
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1.565
1.399
1.387
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O
N
Ts
Me
CO2Et
MeO2C
H
tBu
3n
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6.0
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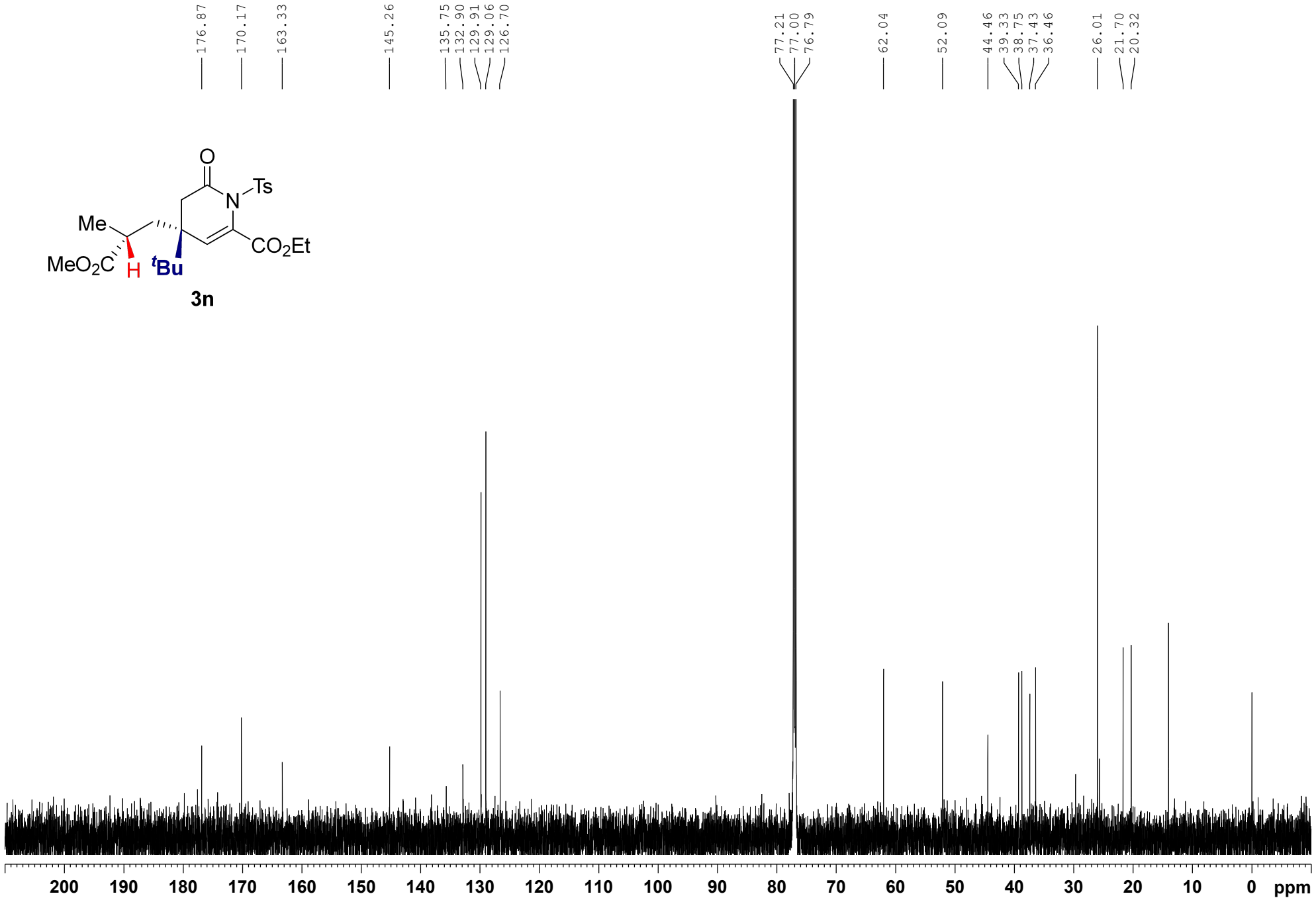
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39.33
38.75
37.43
36.46
26.01
21.70
20.32
O
Ts
N
Me
CO2Et
MeO2C
H
tBu
3n
200
190
180
170
160
150
140
130
120
110
100
90
80
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20
10
0
ppm

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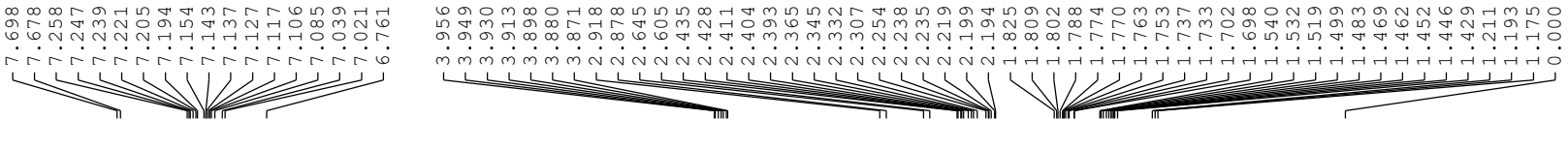
Ts
N
Ph
CO2Me
EtO2C
H
Ph

3o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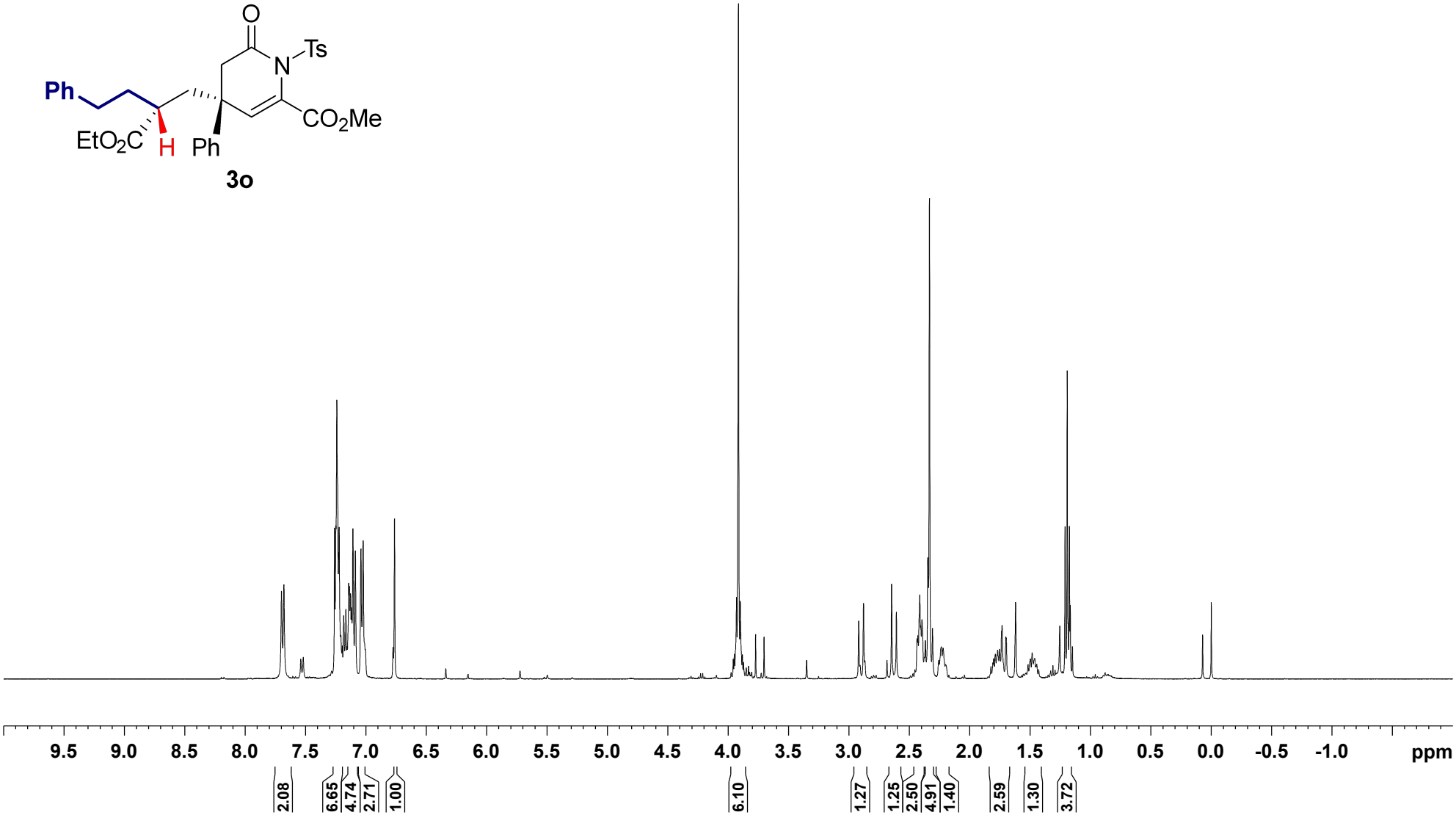
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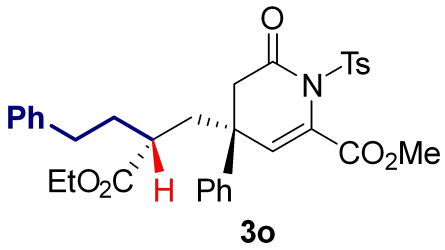

3o

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77.00
76.68
60.71
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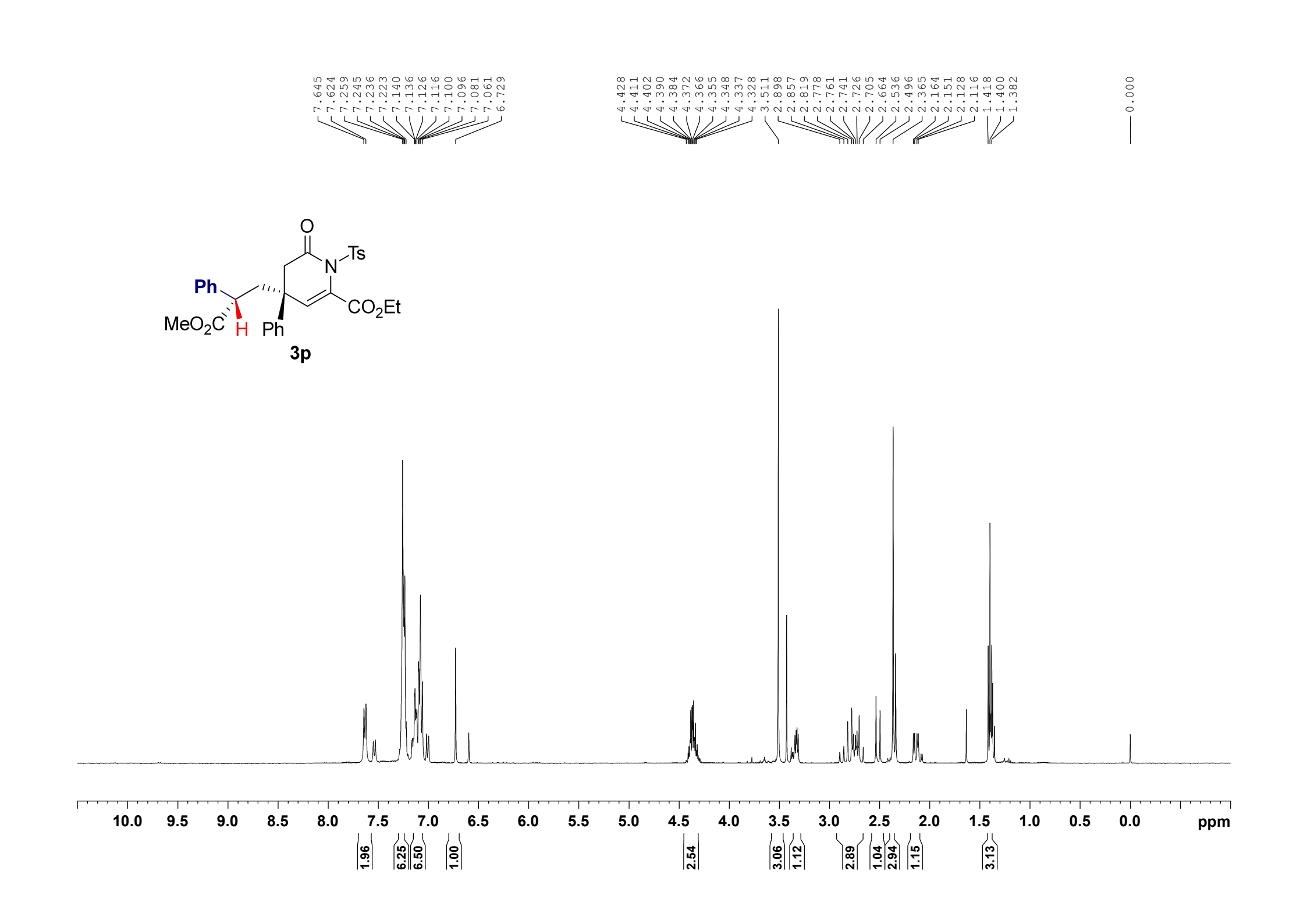
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2.151
2.128
2.116
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N
Ts
Ph
MeO2C
H
Ph
CO2Et
3p
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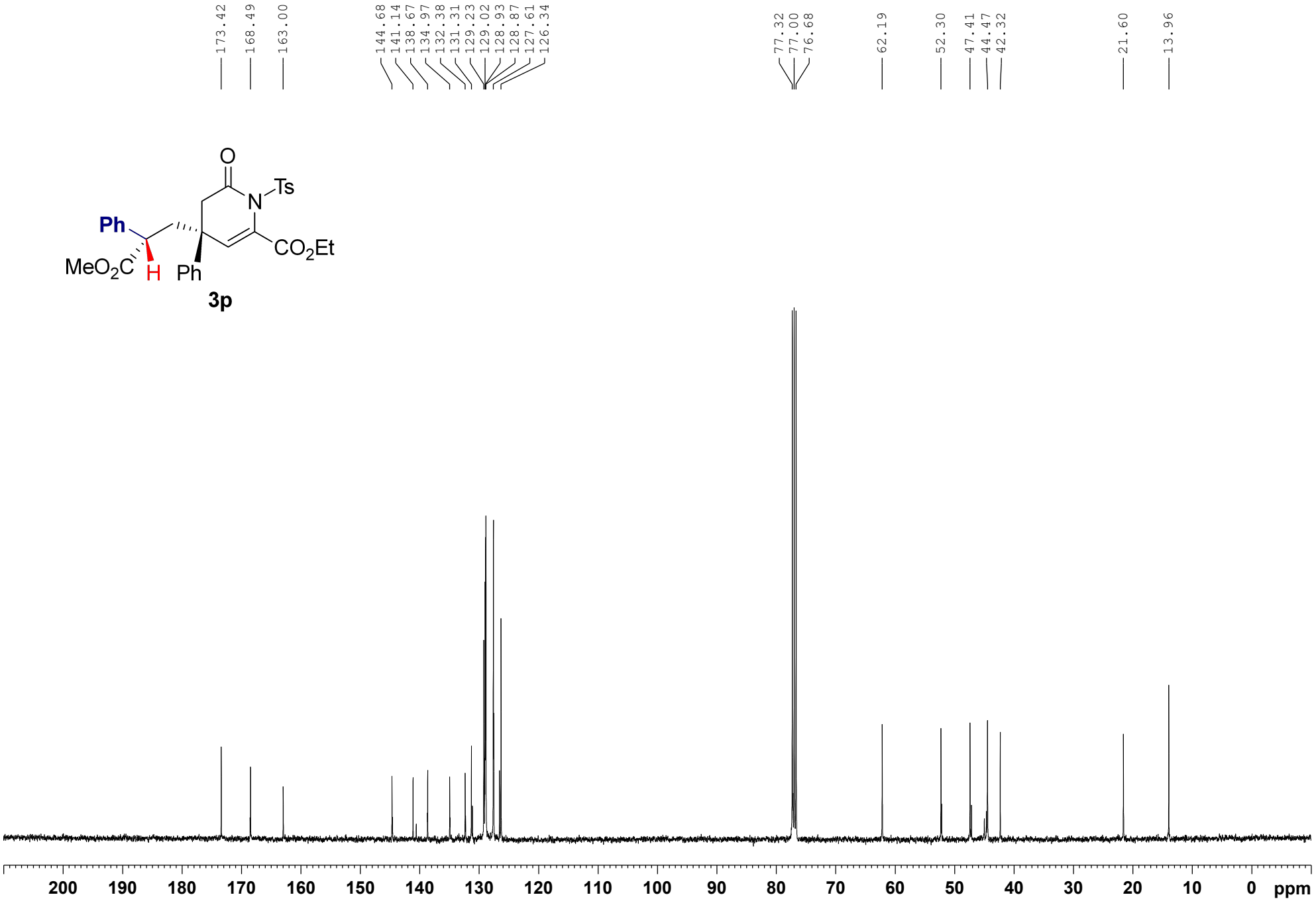
Ph
CO2Et
MeO2C
H
Ph

3p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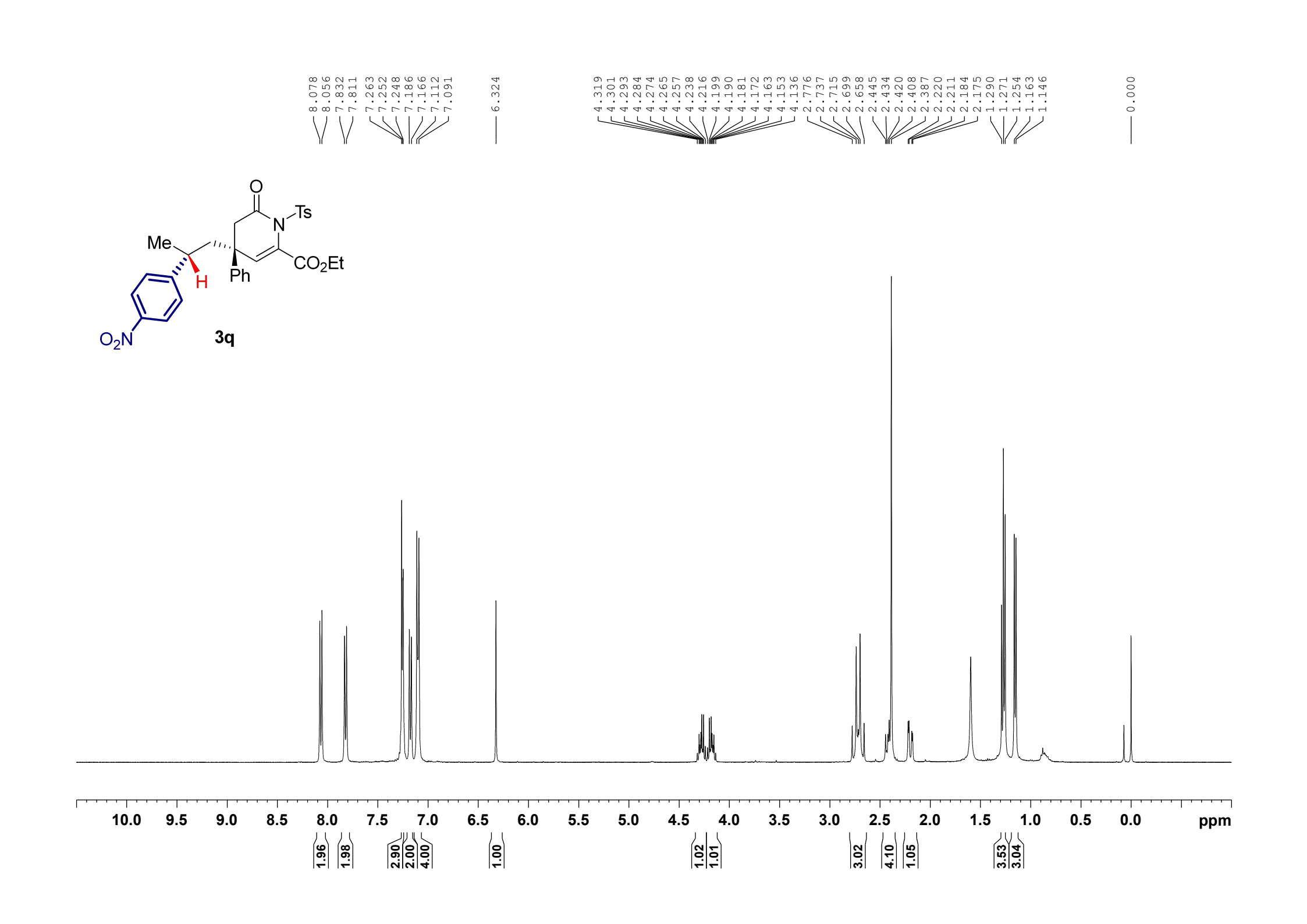
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O
N
Ts
Me
H
Ph
CO2Et
O2N
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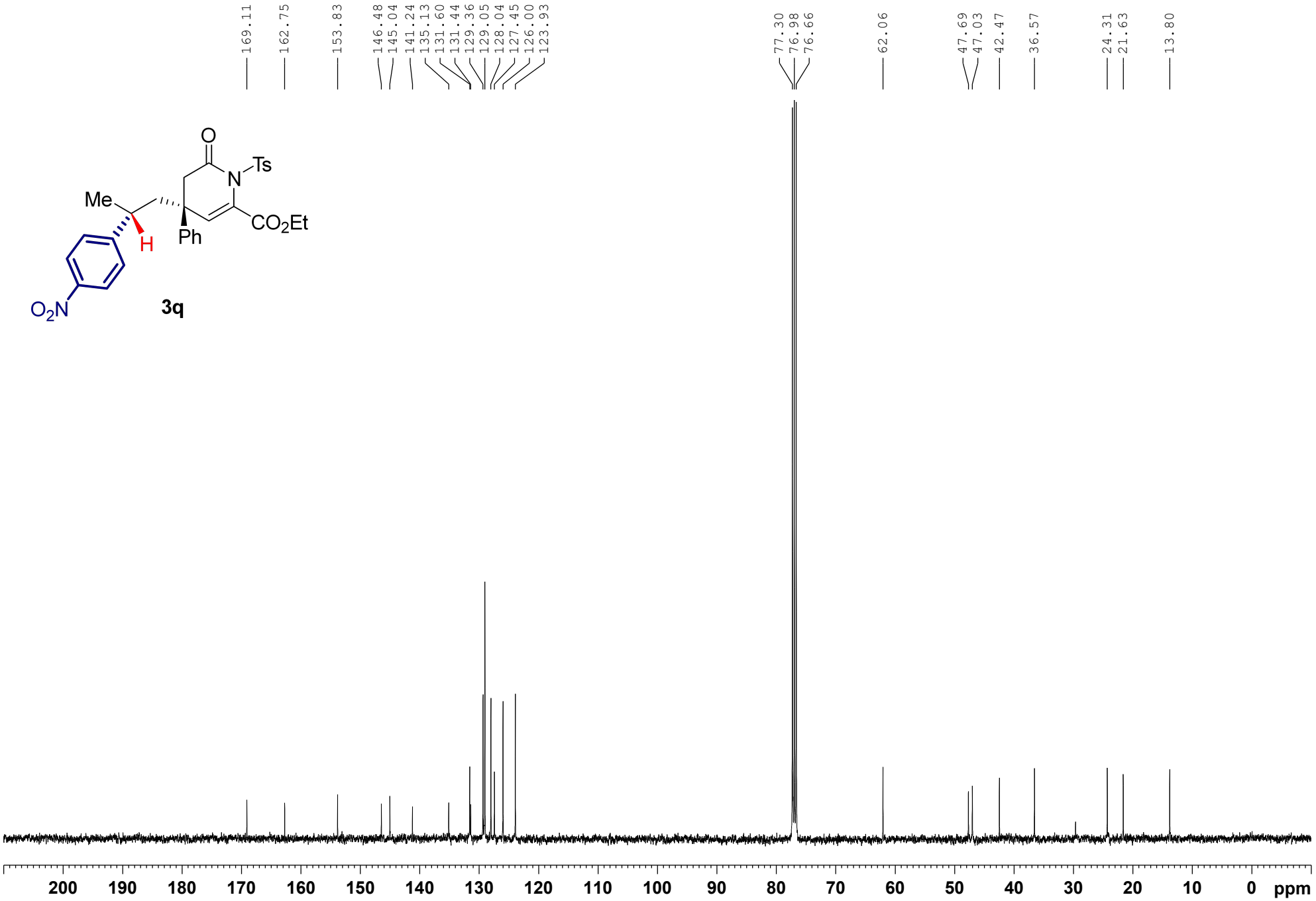
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77.30
76.98
76.66
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47.03
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36.57
24.31
21.63
13.80
O
N
Ts
Me
H
Ph
CO2Et
O2N
3q
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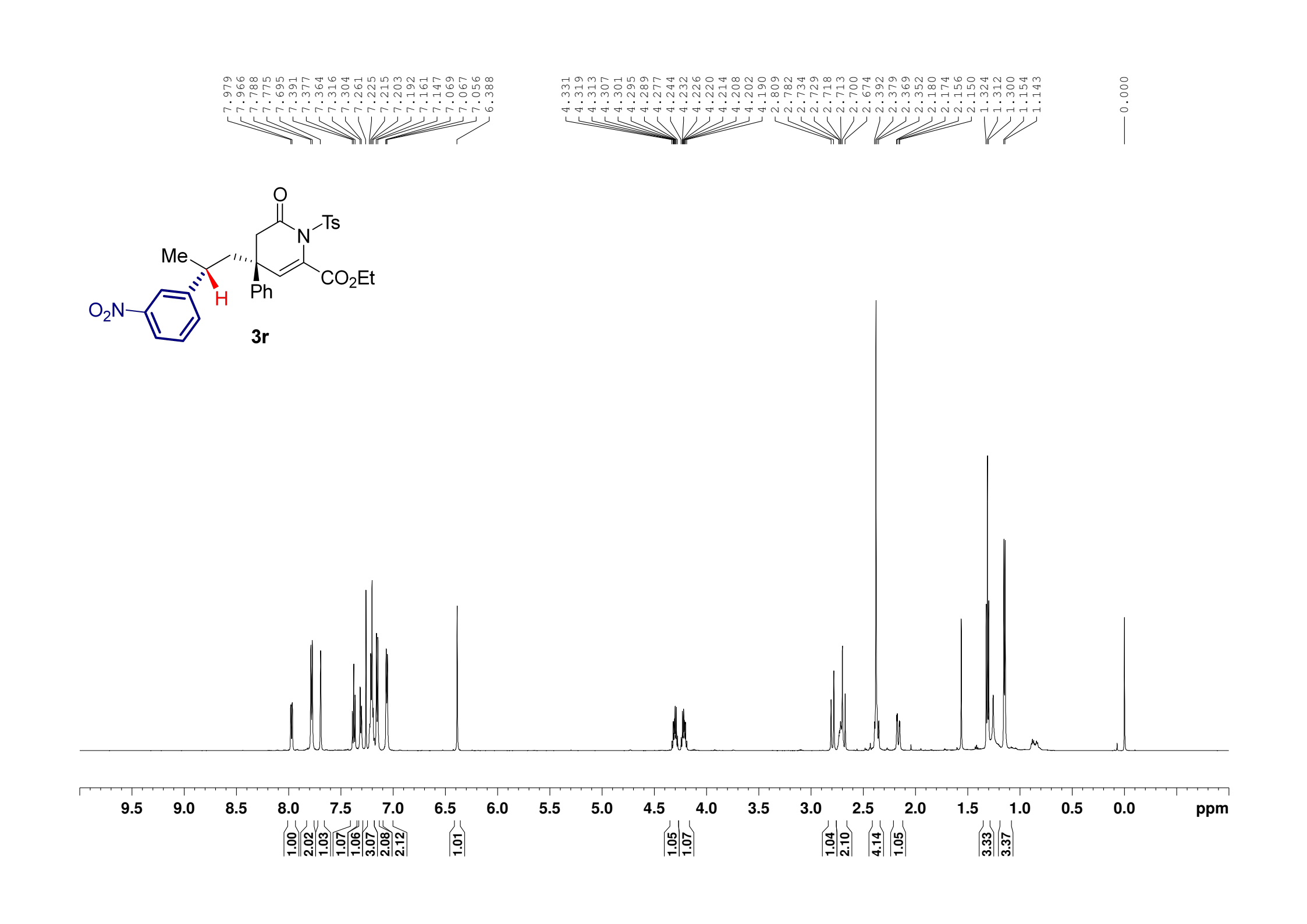
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N
Ts
Me
H
Ph
CO2Et
O2N
3r
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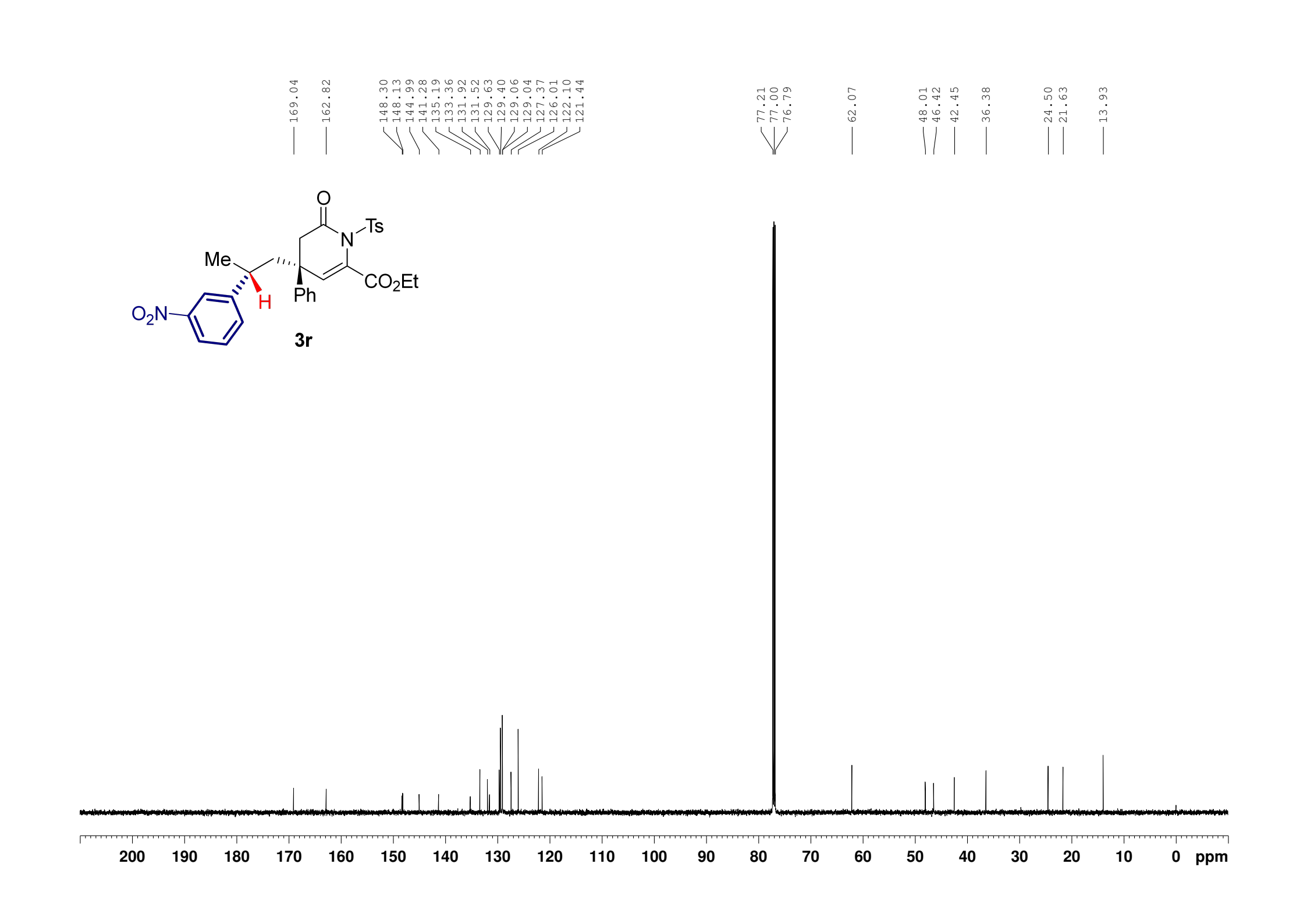
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13.93
O
N
Ts
Me
H
Ph
CO2Et
O2N
3r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
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10
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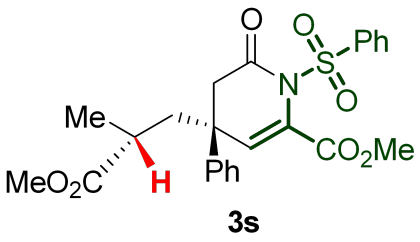
ppm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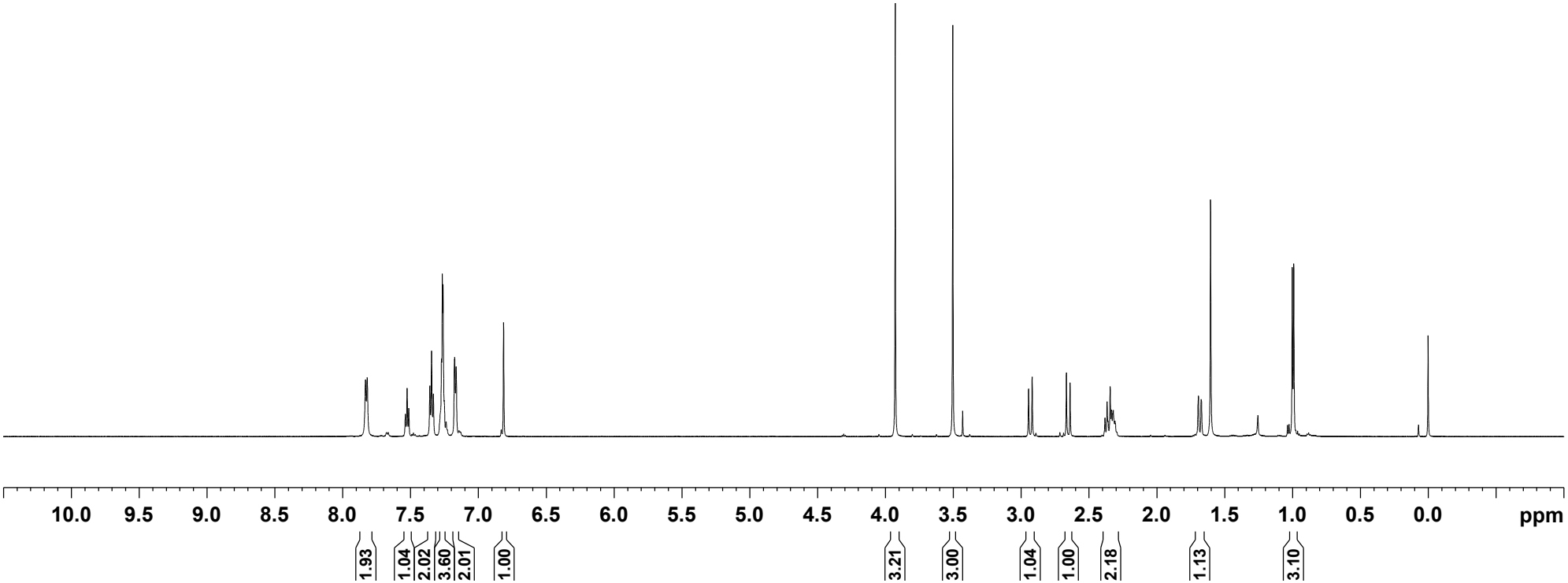
Ph
S
N
O
Me
CO2Me
Ph
MeO2C
H

3s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7.250
7.238
7.236
7.175
7.173
7.162
6.813
3.928
3.504
2.945
2.918
2.666
2.639
2.382
2.366
2.359
2.344
2.335
2.332
2.324
2.320
2.309
2.305
1.693
1.673
1.671
1.001
0.990
0.000
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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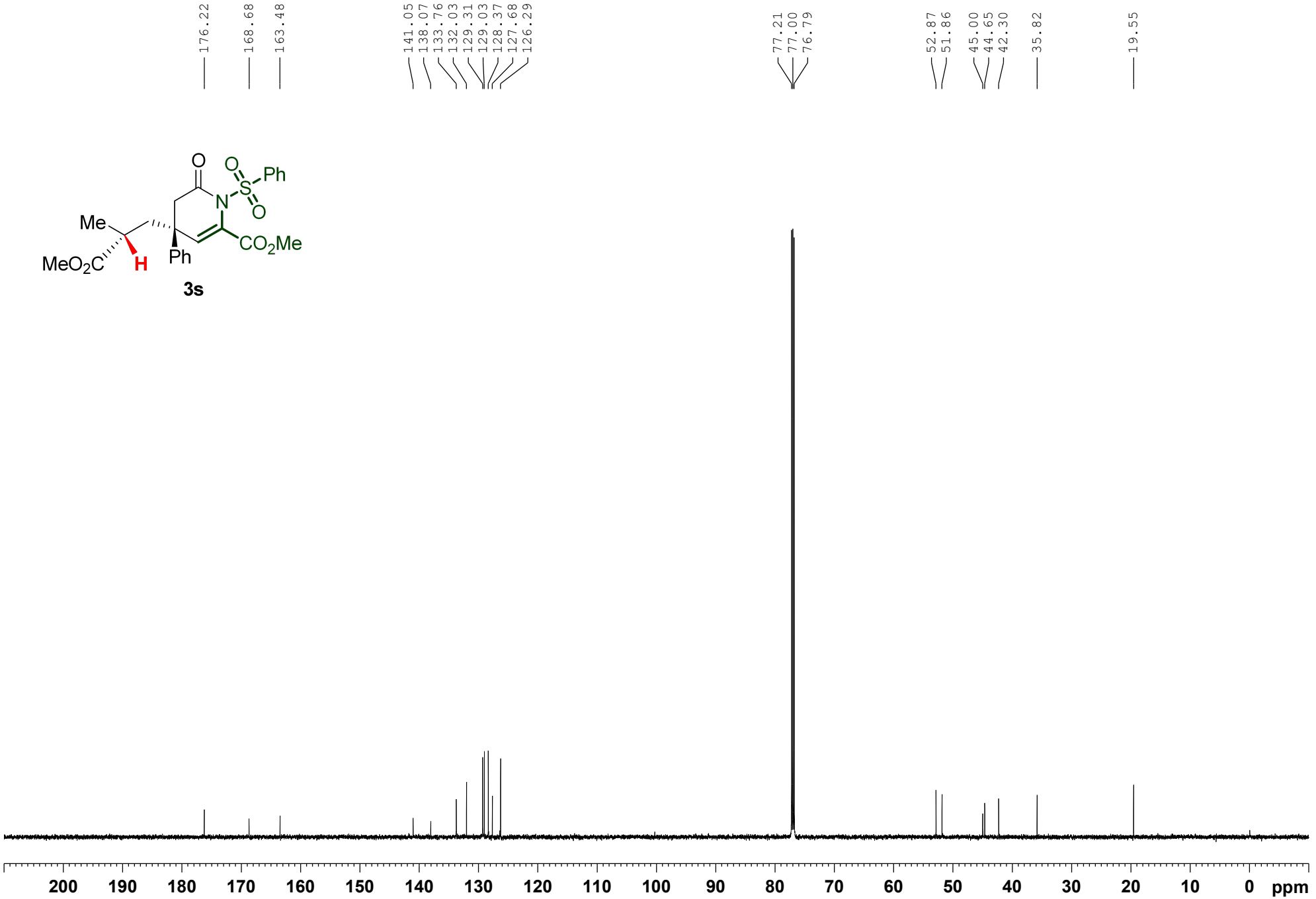
1.04
2.02
3.60
2.01
1.00
3.21
3.00
1.04
1.00
2.18
1.13
3.10

O
O
S
Ph
O
N
Me
CO2Me
MeO2C
H
Ph

3s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129.31
129.03
128.37
127.68
126.29
77.21
77.00
76.79
52.87
51.86
45.00
44.65
42.30
35.82
19.55
200
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140
130
120
110
100
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60
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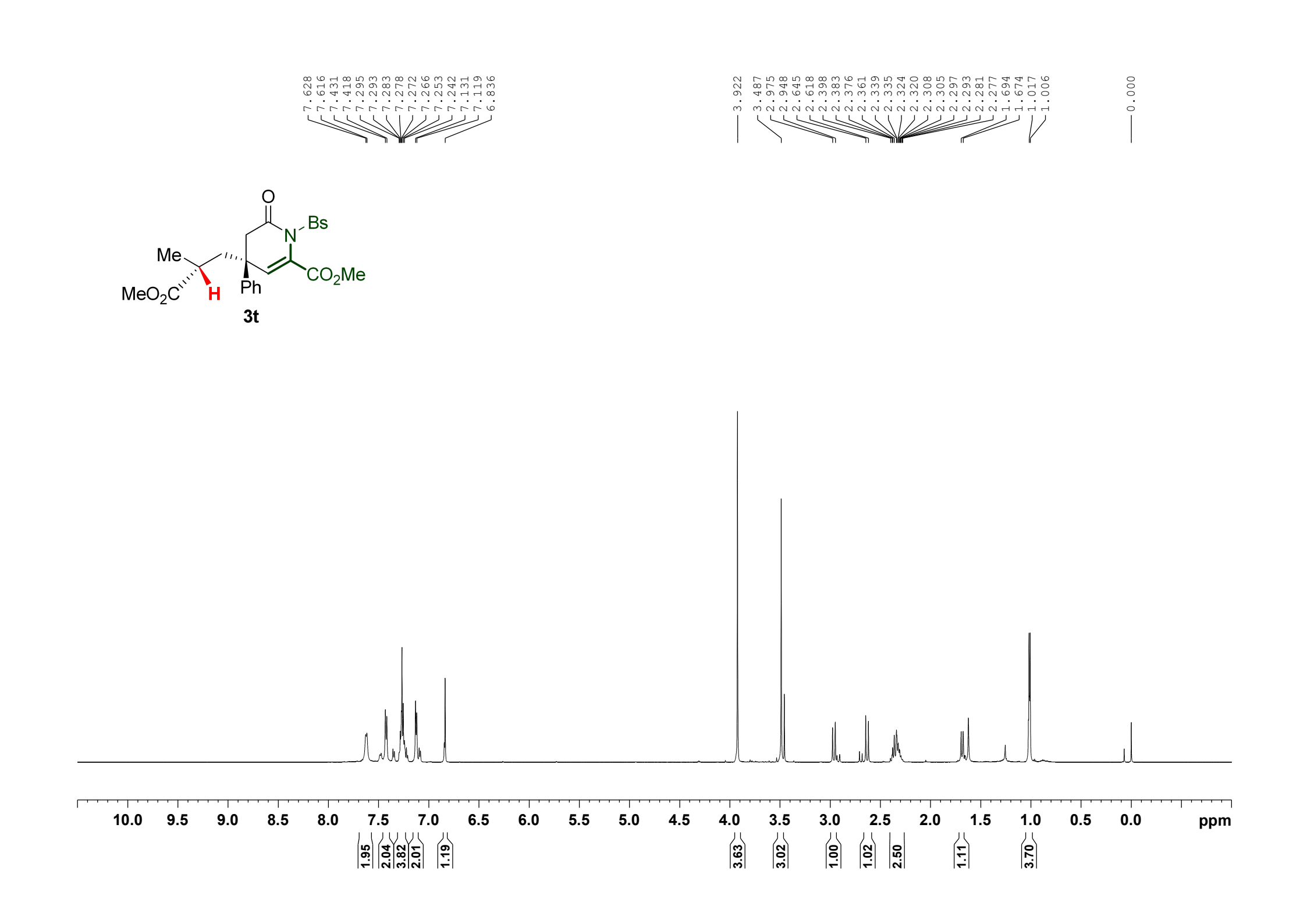
30
20
10
0
ppm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7.266
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7.242
7.131
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6.836
3.922
3.487
2.975
2.948
2.645
2.618
2.398
2.383
2.376
2.361
2.339
2.335
2.324
2.320
2.308
2.305
2.297
2.293
2.281
2.277
1.694
1.674
1.017
1.006
0.000
O
Bs
N
Me
CO2Me
Ph
MeO2C
H
3t
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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3.82
2.01
1.19
3.63
3.02
1.00
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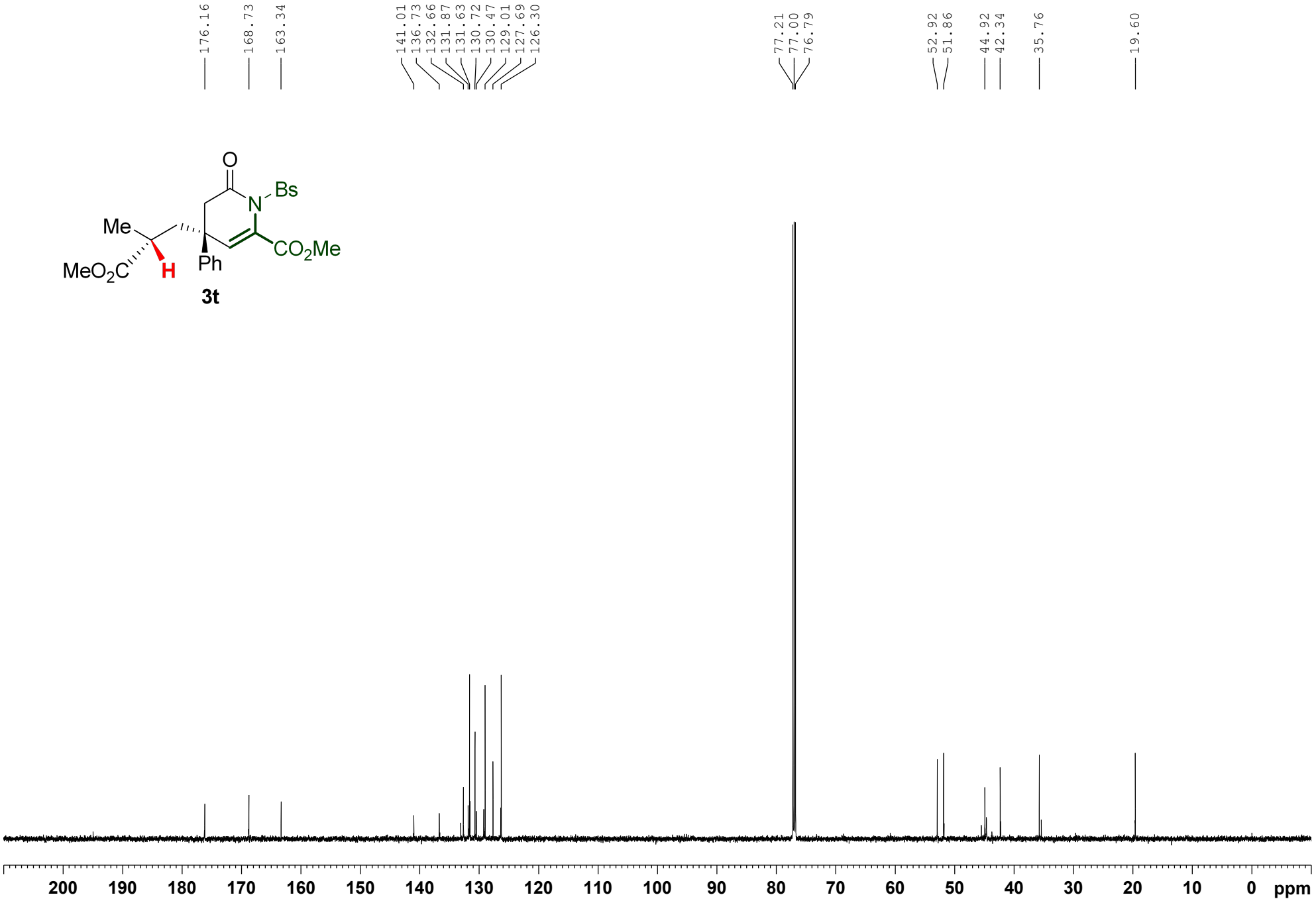
1.11
3.70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127.69
126.30
77.21
77.00
76.79
52.92
51.86
44.92
42.34
35.76
19.60
O
N
Bs
Me
CO2Me
MeO2C
H
Ph
3t
200
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140
130
120
110
100
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60
50
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20
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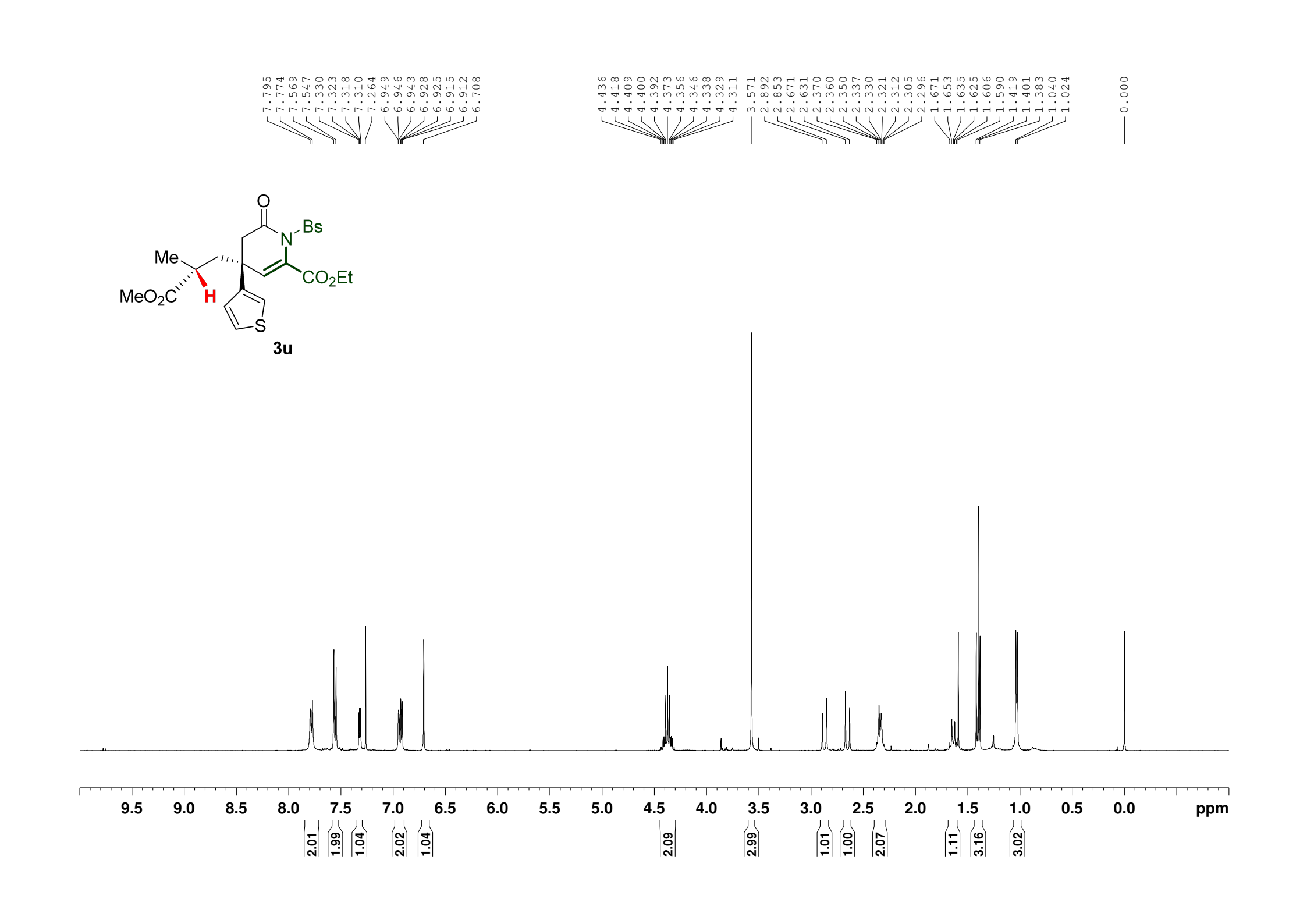
0
ppm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6.928
6.925
6.915
6.912
6.708
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4.418
4.409
4.400
4.392
4.373
4.356
4.346
4.338
4.329
4.311
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2.892
2.853
2.671
2.631
2.370
2.360
2.350
2.337
2.330
2.321
2.312
2.305
2.296
1.671
1.653
1.635
1.625
1.606
1.590
1.419
1.401
1.383
1.040
1.024
0.000
O
N
Bs
Me
CO2Et
MeO2C
H
S
3u
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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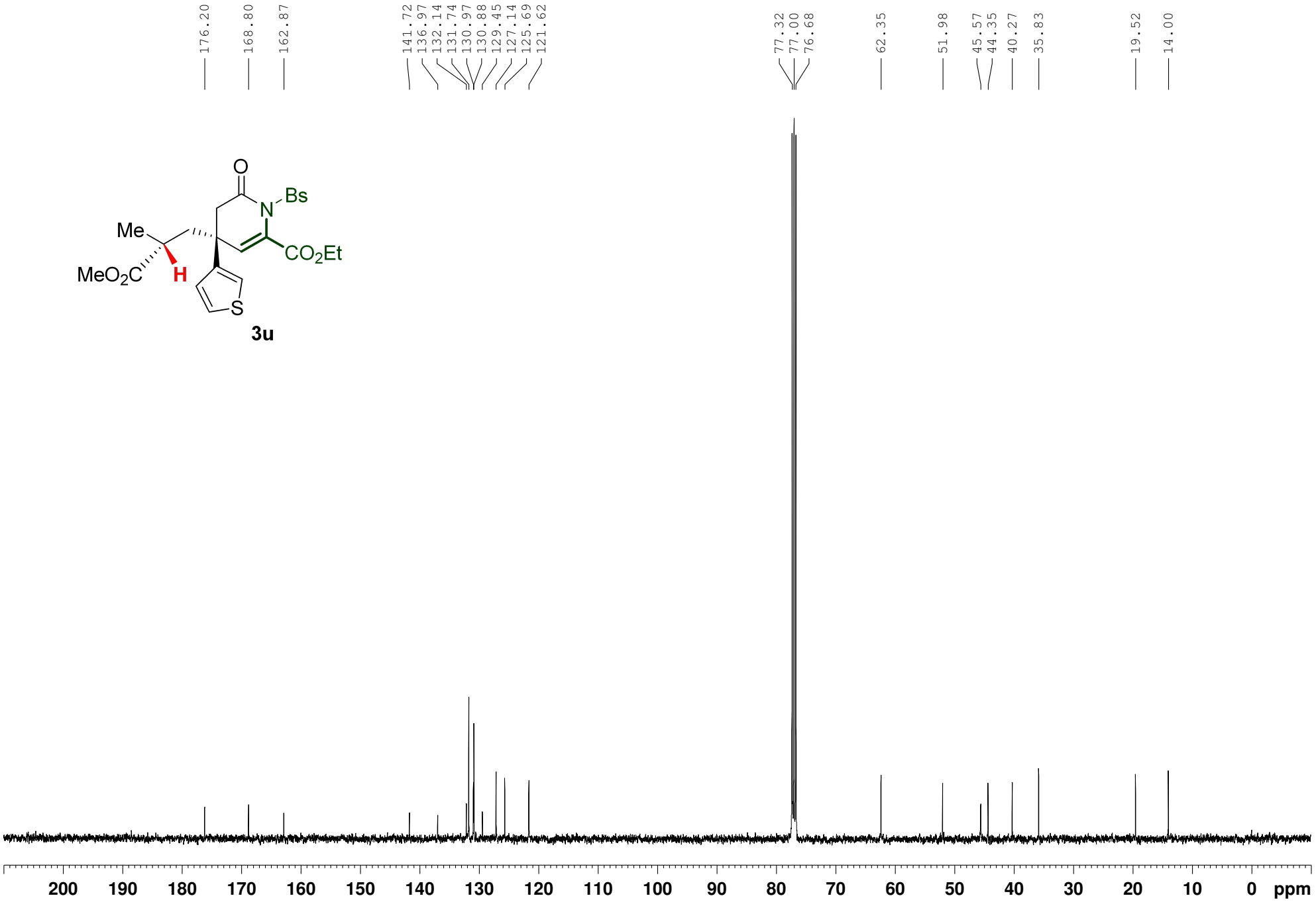
2.02
1.04
2.09
2.99
1.01
1.00
2.07
1.11
3.16
3.02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130.88
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127.14
125.69
121.62
77.32
77.00
76.68
62.35
51.98
45.57
44.35
40.27
35.83
19.52
14.00
O
N
Bs
Me
MeO2C
H
CO2Et
S
3u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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20
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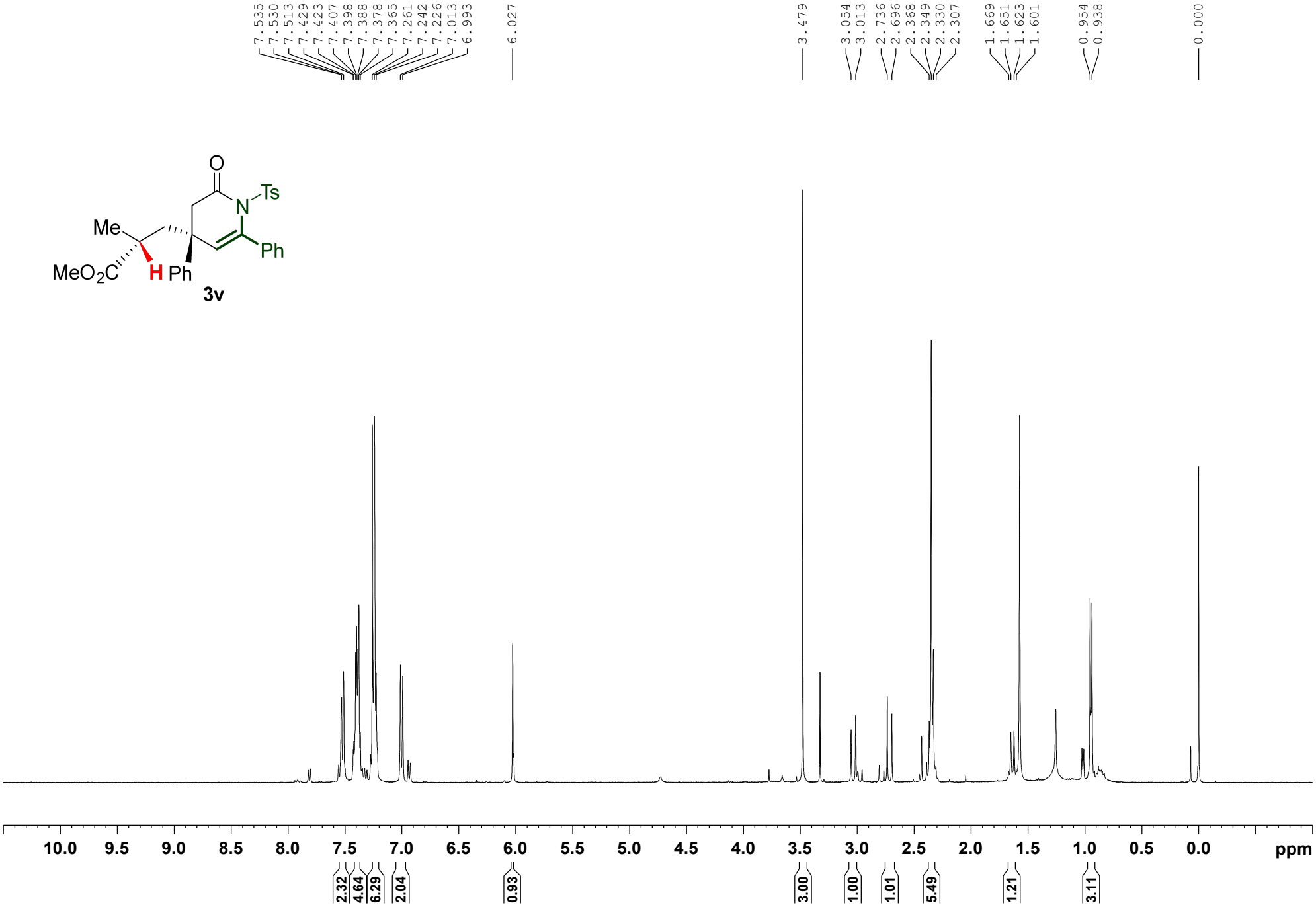
0
ppm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7.388
7.378
7.365
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7.242
7.226
7.013
6.993
6.027
3.479
3.054
3.013
2.736
2.696
2.368
2.349
2.330
2.307
1.669
1.651
1.623
1.601
0.954
0.938
0.000
O
N
Ts
Me
Ph
MeO2C
H
Ph
3v
10.0
9.5
9.0
8.5
8.0
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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1.00
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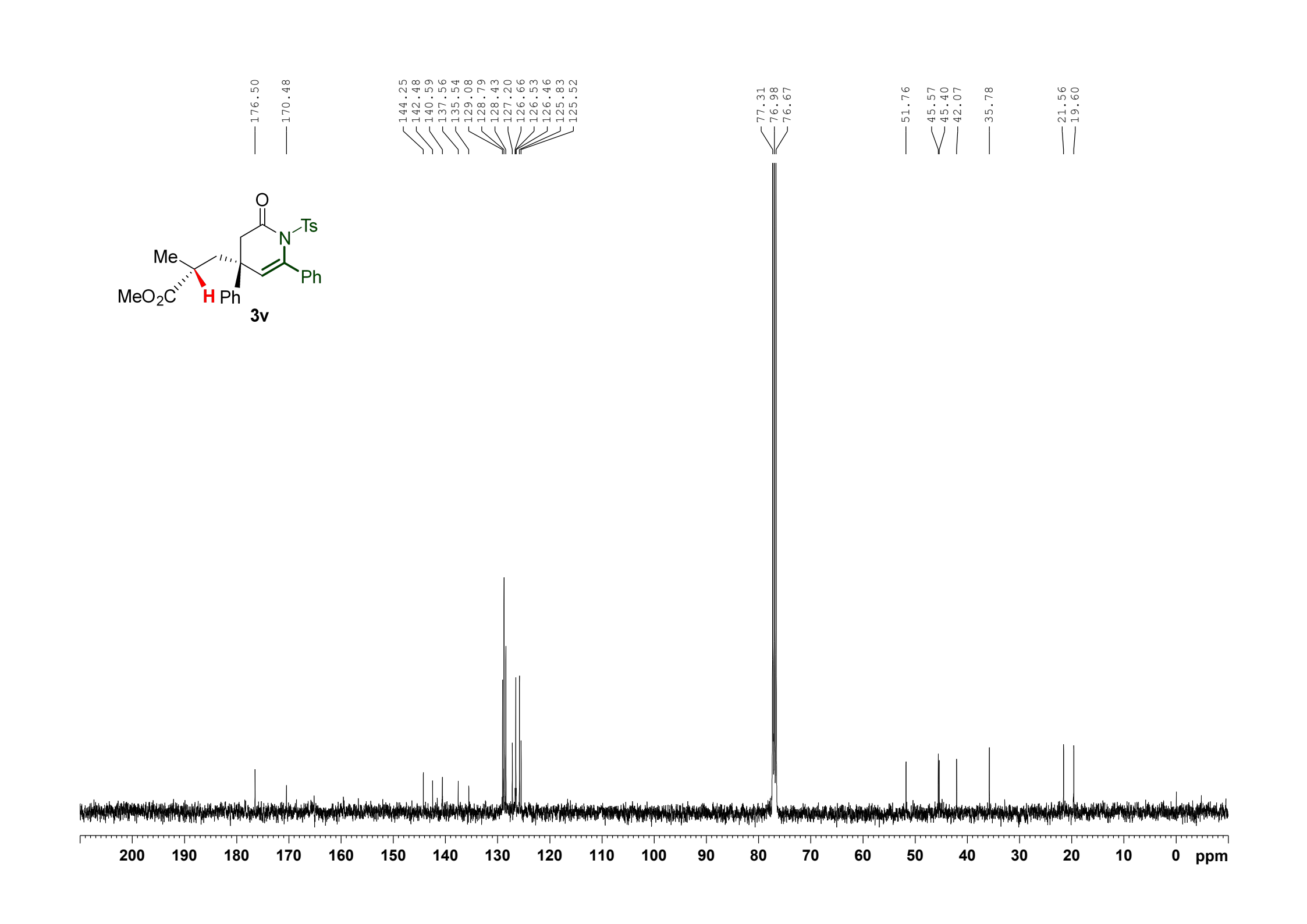
1.21
3.11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126.46
125.83
125.52
77.31
76.98
76.67
51.76
45.57
45.40
42.07
35.78
21.56
19.60
O
N
Ts
Me
Ph
MeO2C
H
Ph
3v
200
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140
130
120
110
100
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60
50
40
30
20
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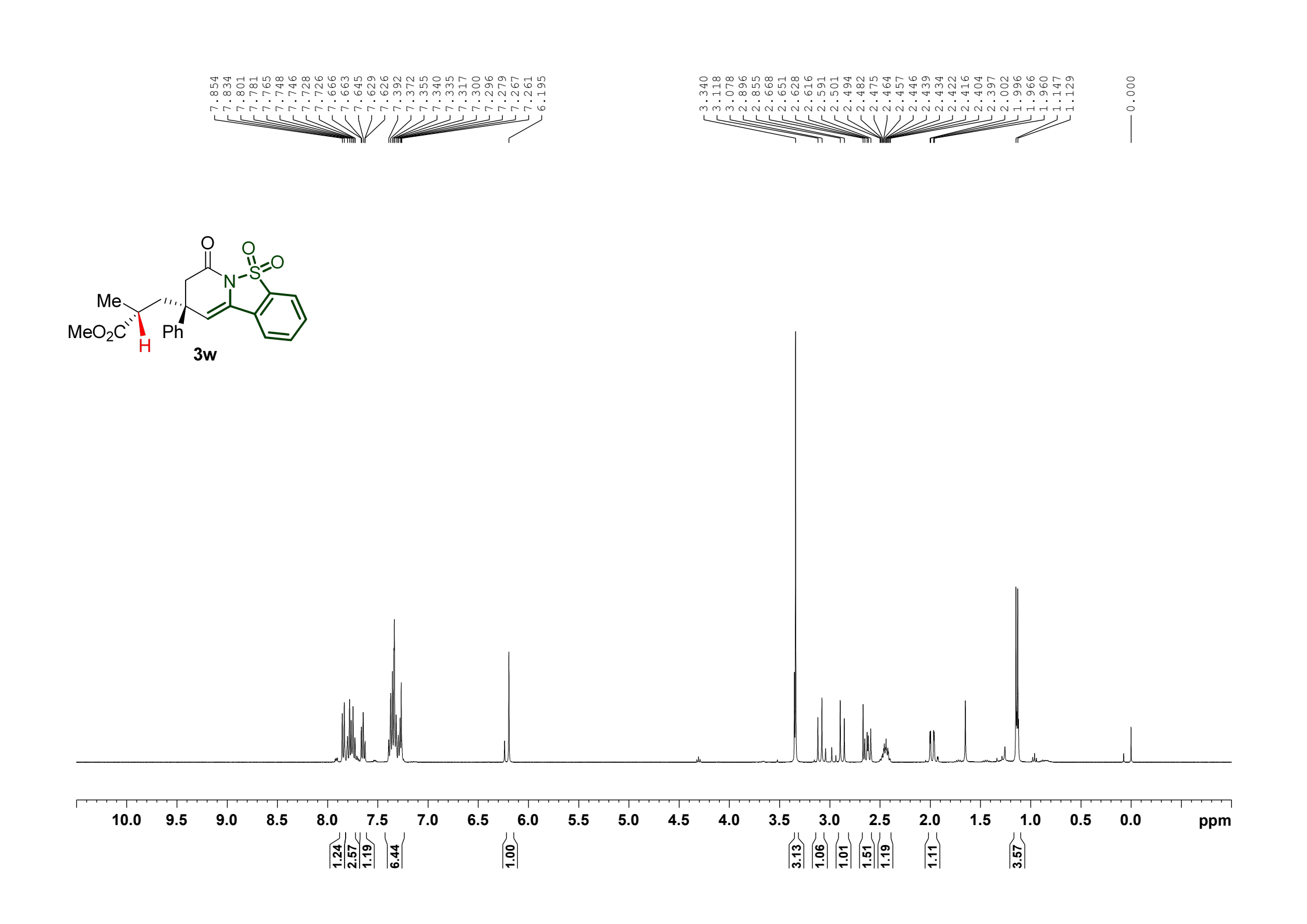
0
ppm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7.629
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7.355
7.340
7.335
7.317
7.300
7.296
7.279
7.267
7.261
6.195
3.340
3.118
3.078
2.896
2.855
2.668
2.651
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2.616
2.591
2.501
2.494
2.482
2.475
2.464
2.457
2.446
2.439
2.434
2.422
2.416
2.404
2.397
2.002
1.996
1.966
1.960
1.147
1.129
0.000
Me
MeO2C
H
Ph
O
O
S
O
N
3w
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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6.44
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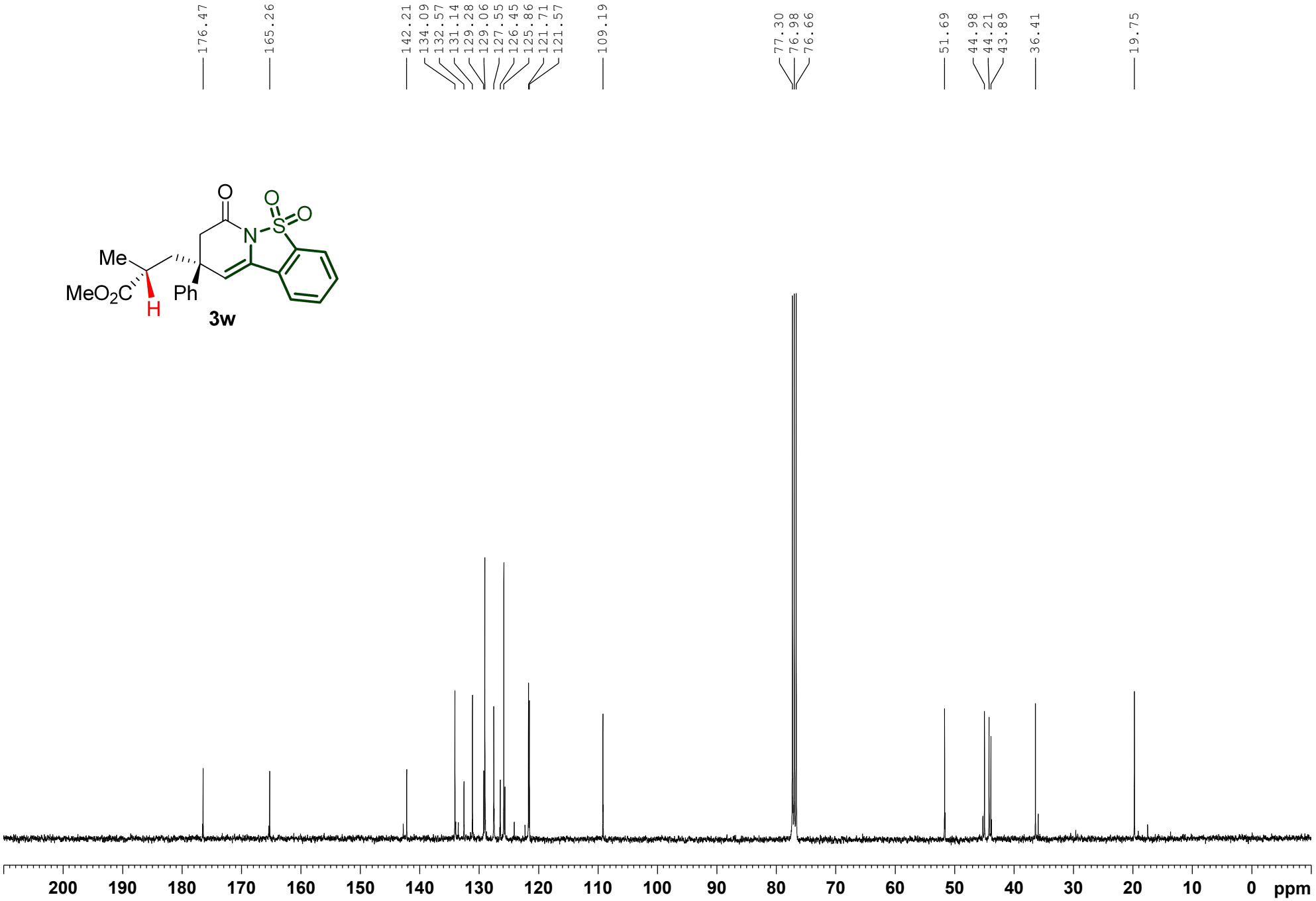
3.13
1.06
1.01
1.51
1.19
1.11
3.57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129.06
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125.86
121.71
121.57
109.19
77.30
76.98
76.66
51.69
44.98
44.21
43.89
36.41
19.75
Me
MeO2C
H
Ph
O
O
O
N
S
3w
200
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140
130
120
110
100
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80
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60
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20
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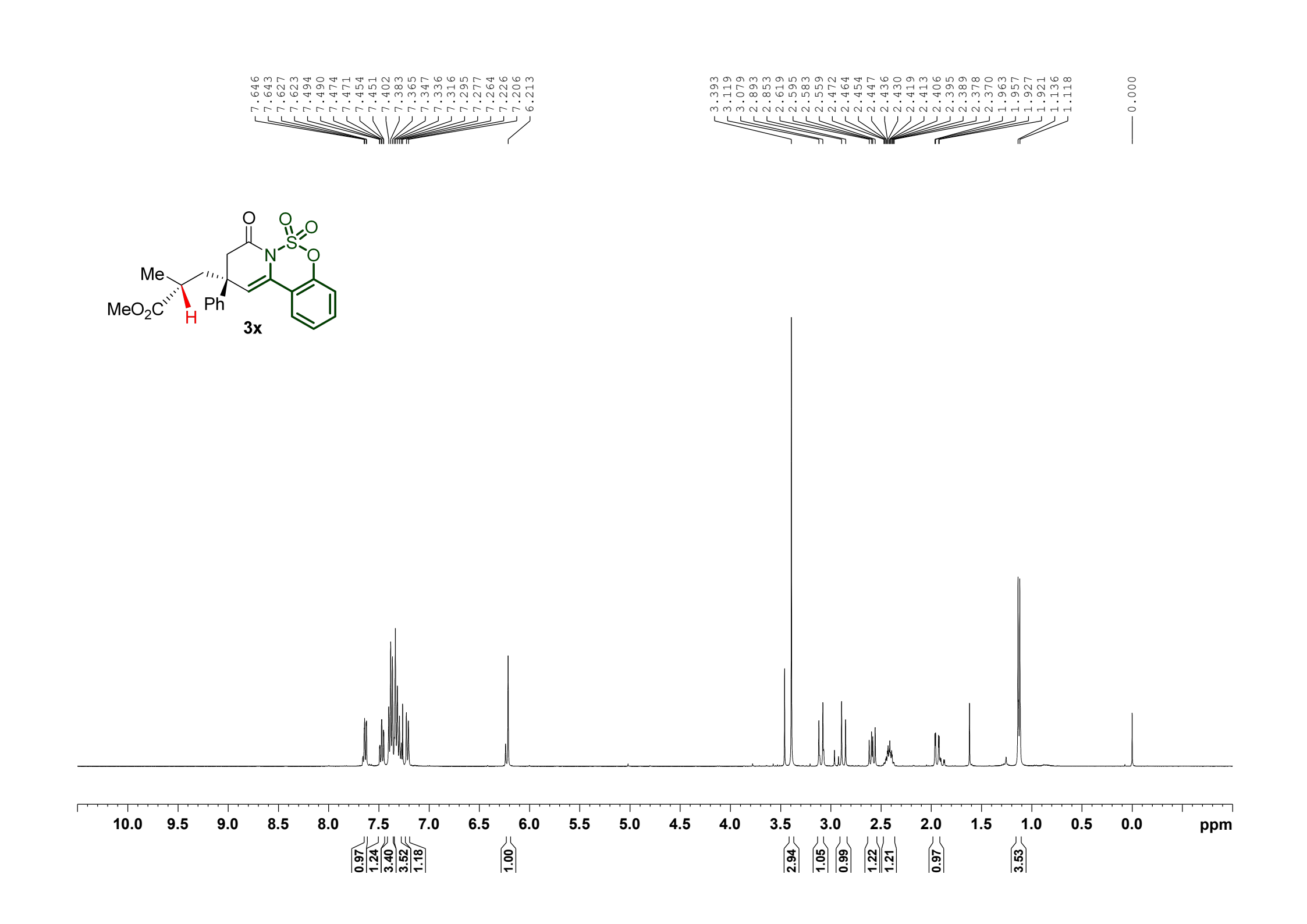
0
ppm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7.336
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7.295
7.277
7.264
7.226
7.206
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3.119
3.079
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2.853
2.619
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2.583
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2.419
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2.406
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2.370
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1.957
1.927
1.921
1.136
1.118
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Me
MeO2C
H
Ph
O
O
O
N
S
O
3x
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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0.99
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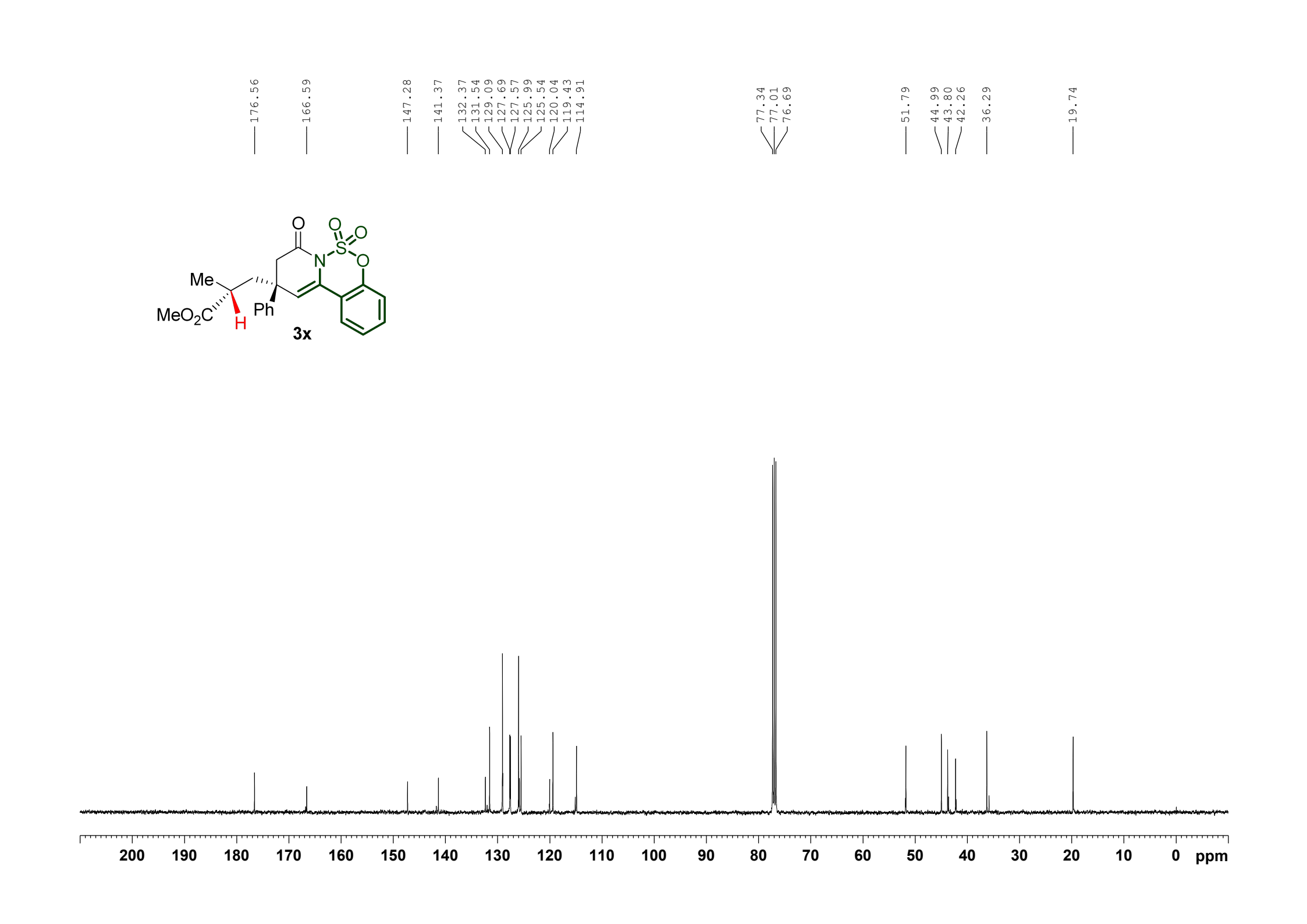
3.53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127.69
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125.99
125.54
120.04
119.43
114.91
77.34
77.01
76.69
51.79
44.99
43.80
42.26
36.29
19.74
Me
MeO2C
H
Ph
3x
200
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180
170
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150
140
130
120
110
100
90
80
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60
50
40
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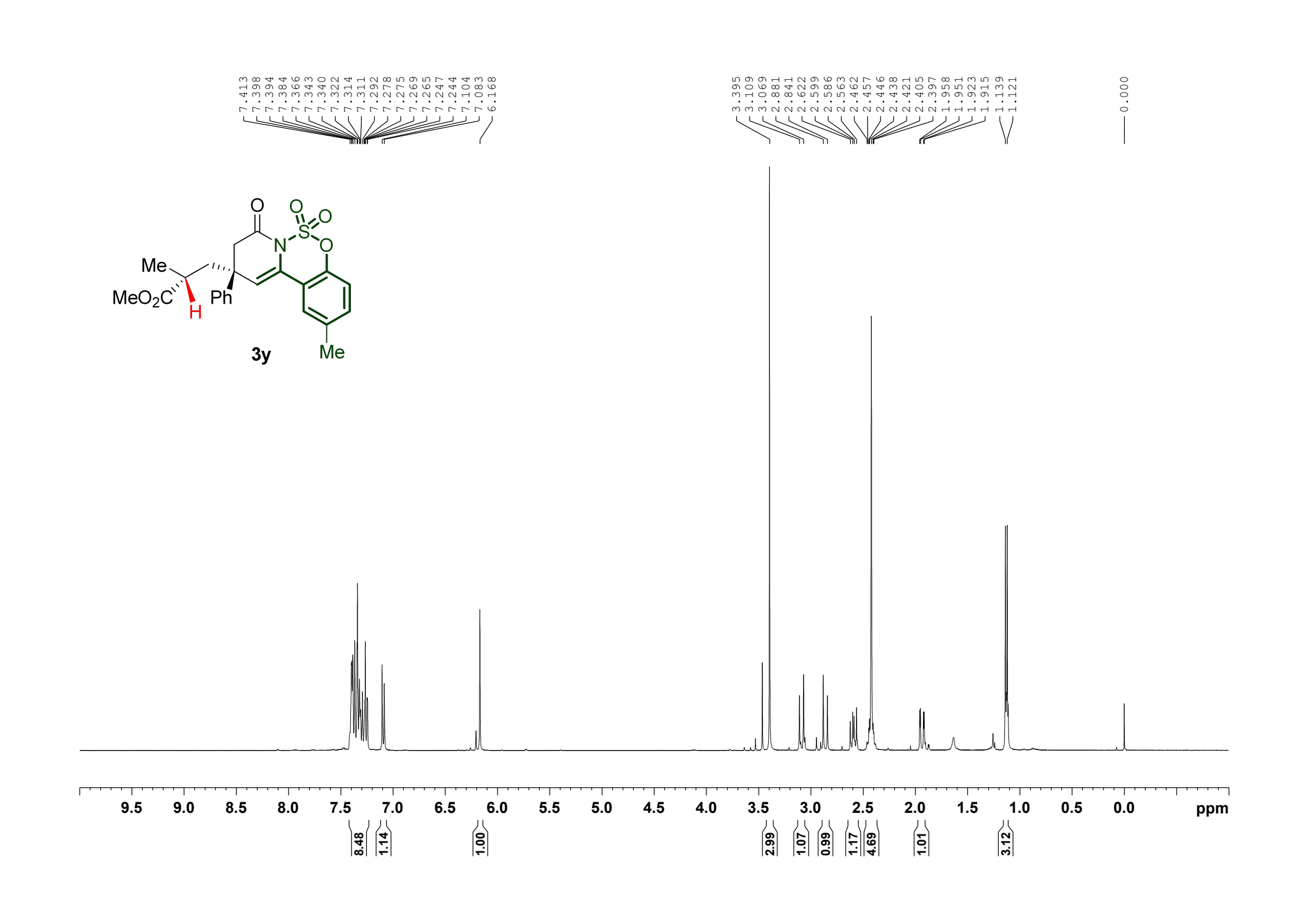
20
10
0
ppm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7.311
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7.275
7.269
7.265
7.247
7.244
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7.083
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3.069
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2.841
2.622
2.599
2.586
2.563
2.462
2.457
2.446
2.438
2.421
2.405
2.397
1.958
1.951
1.923
1.915
1.139
1.121
0.000
Me
MeO2C
H
Ph
O
O
O
S
N
O
Me
3y
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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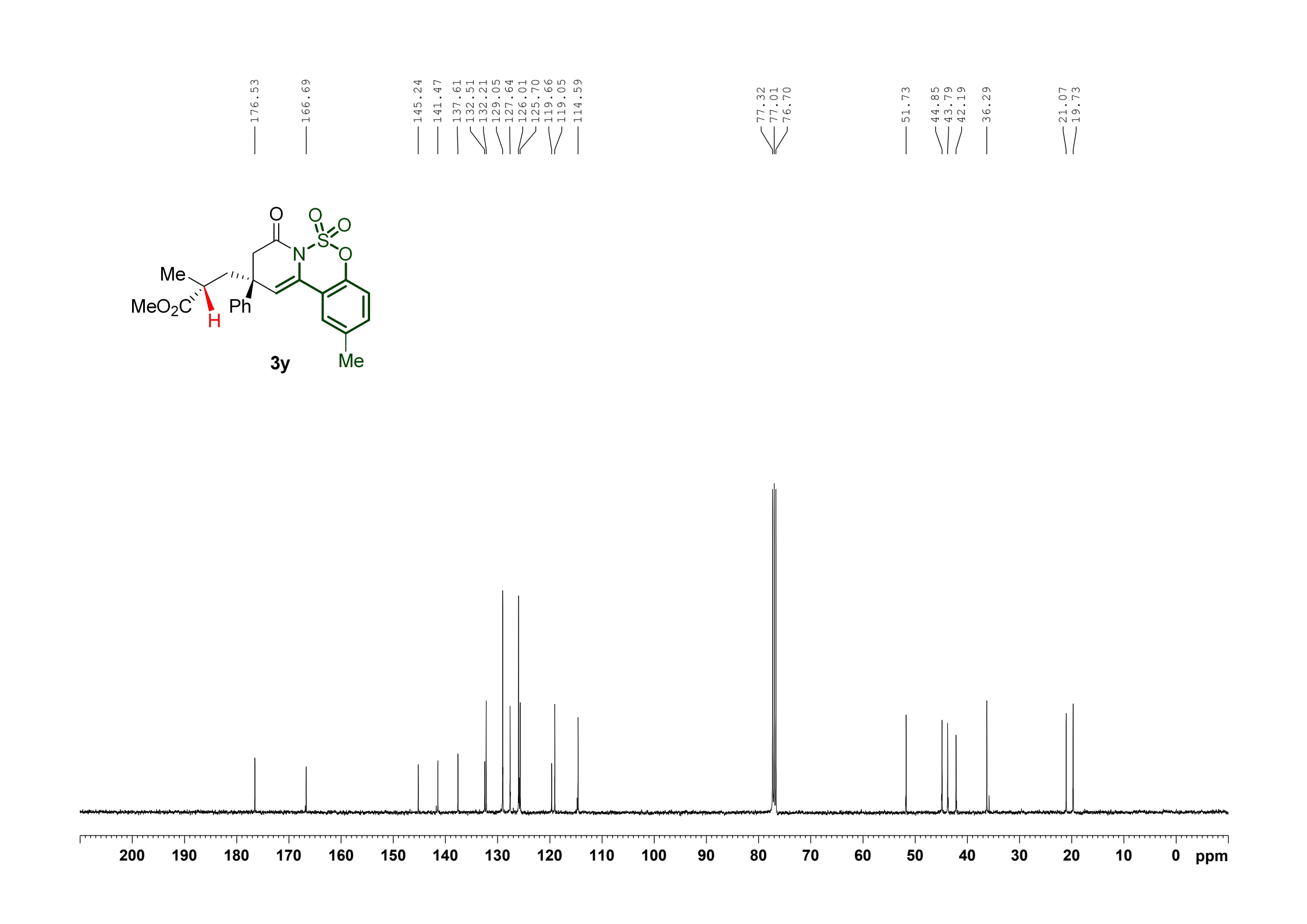
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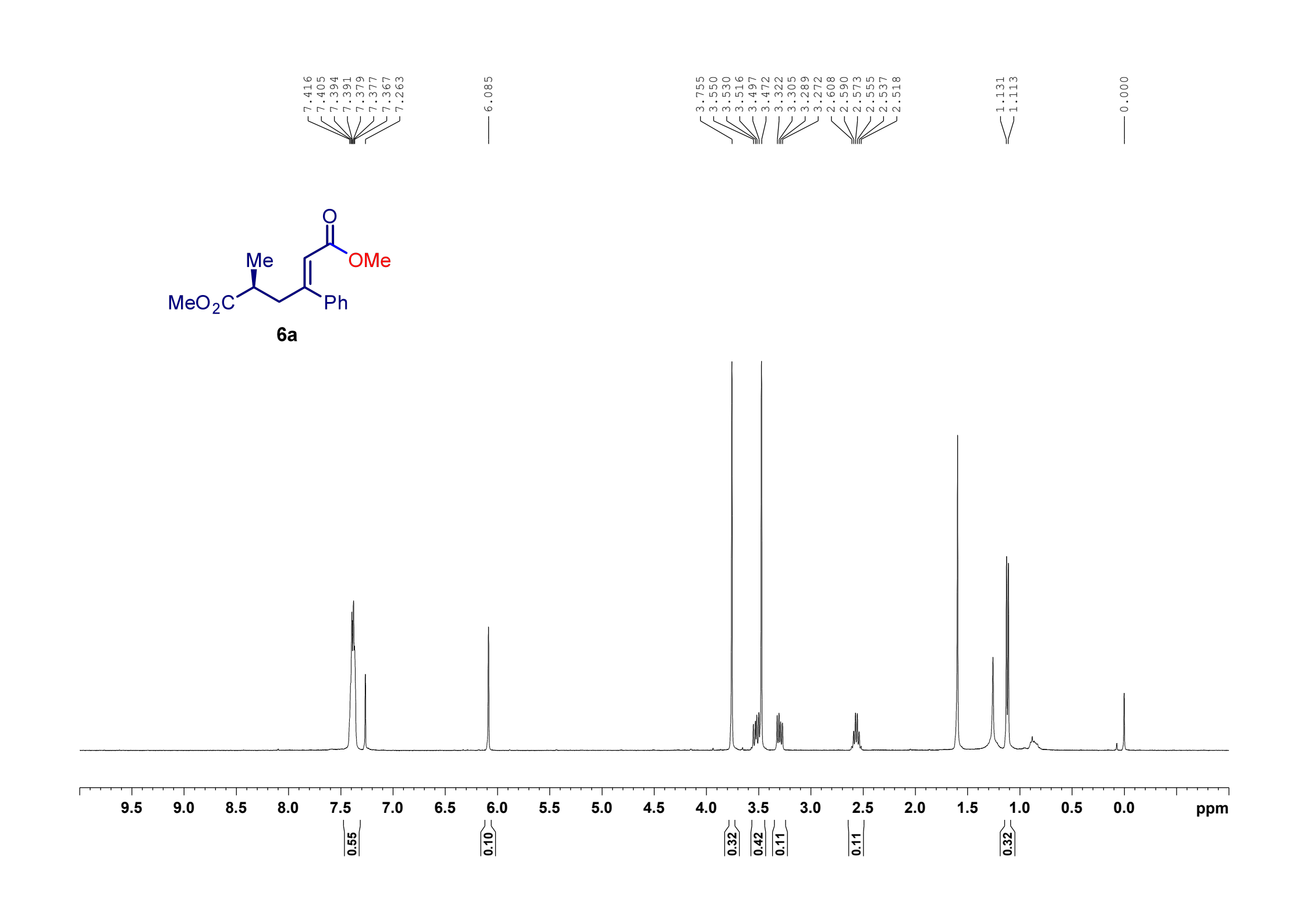
119.66
119.05
114.59
77.32
77.01
76.70
51.73
44.85
43.79
42.19
36.29
21.07
19.73
O
O
O
S
N
O
Me
MeO2C
H
Ph
Me
3y
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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3.516
3.497
3.472
3.322
3.305
3.289
3.272
2.608
2.590
2.573
2.555
2.537
2.518
1.131
1.113
0.000
O
Me
OMe
MeO2C
Ph
6a
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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ppm
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0.32
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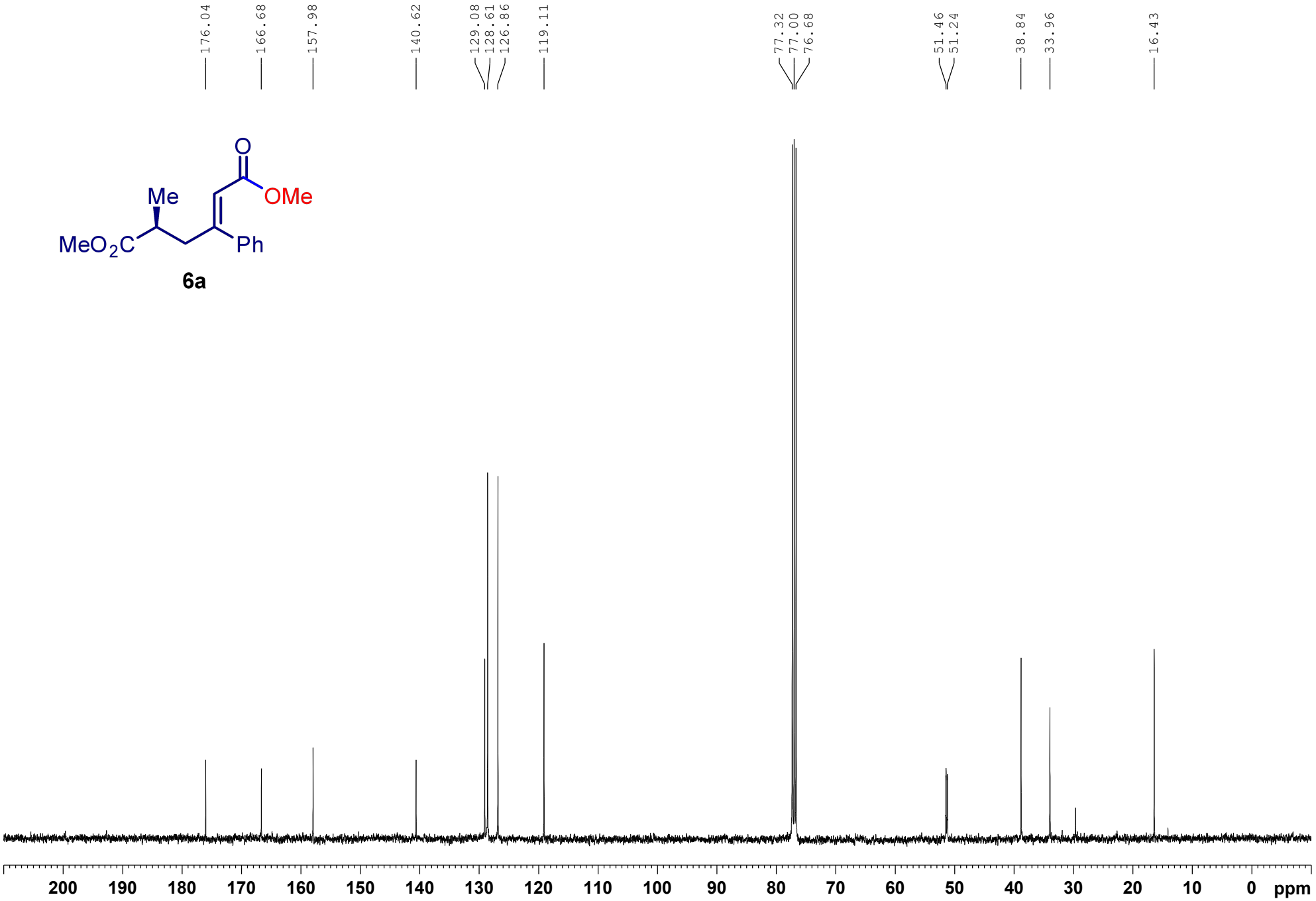
0.11
0.11
0.32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128.61
126.86
119.11
77.32
77.00
76.68
51.46
51.24
38.84
33.96
16.43
O
Me
OMe
MeO2C
Ph
6a
200
190
180
170
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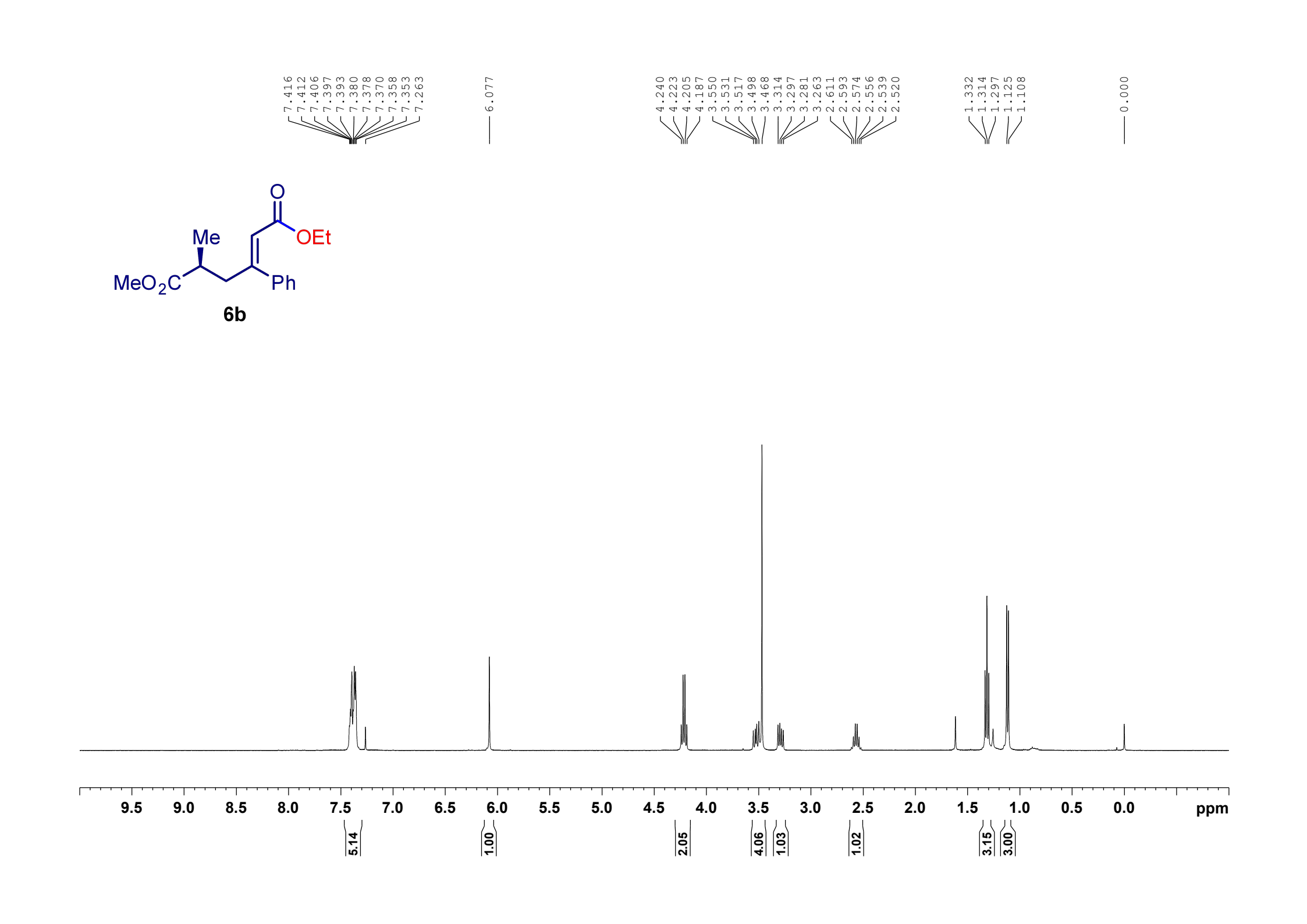
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.353
7.263
6.077
4.240
4.223
4.205
4.187
3.550
3.531
3.517
3.498
3.468
3.314
3.297
3.281
3.263
2.611
2.593
2.574
2.556
2.539
2.520
1.332
1.314
1.297
1.125
1.108
0.000
O
OEt
Me
MeO2C
Ph
6b
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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0.0
ppm
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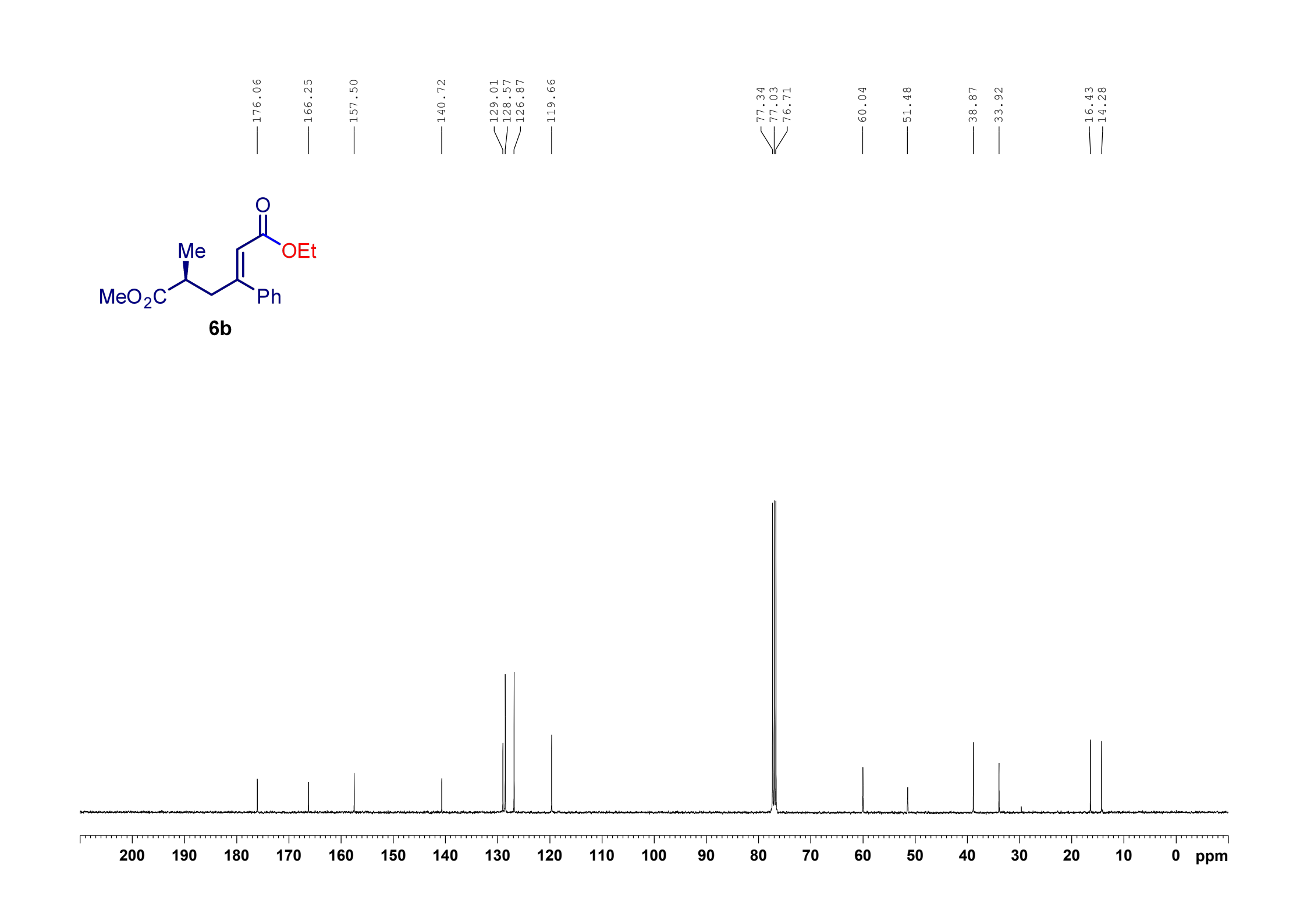
1.00
2.05
4.06
1.03
1.02
3.15
3.00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119.66
77.34
77.03
76.71
60.04
51.48
38.87
33.92
16.43
14.28
O
Me
OEt
MeO2C
Ph
6b
200
190
180
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160
150
140
130
120
110
100
90
80
70
60
50
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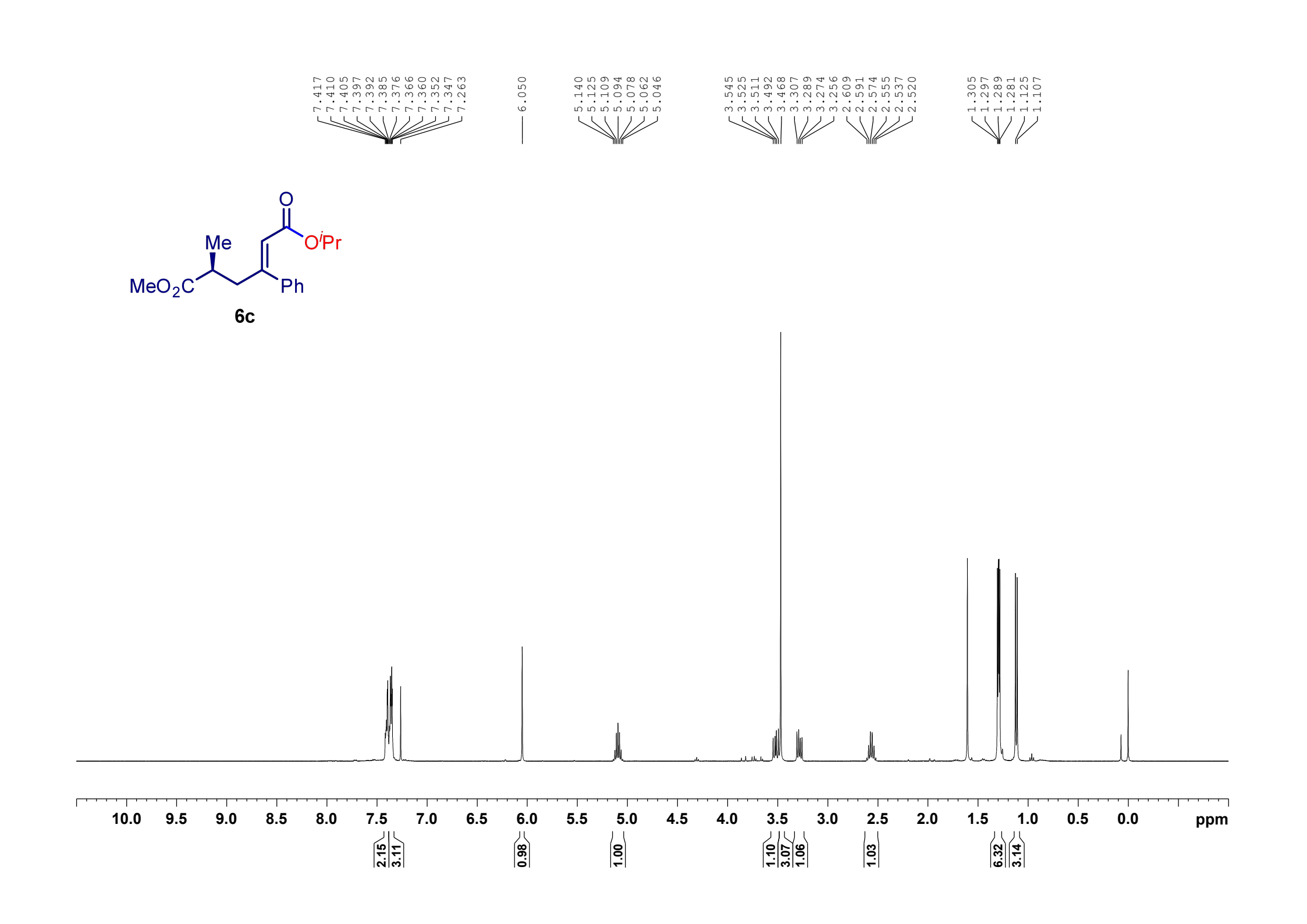
30
20
10
0
ppm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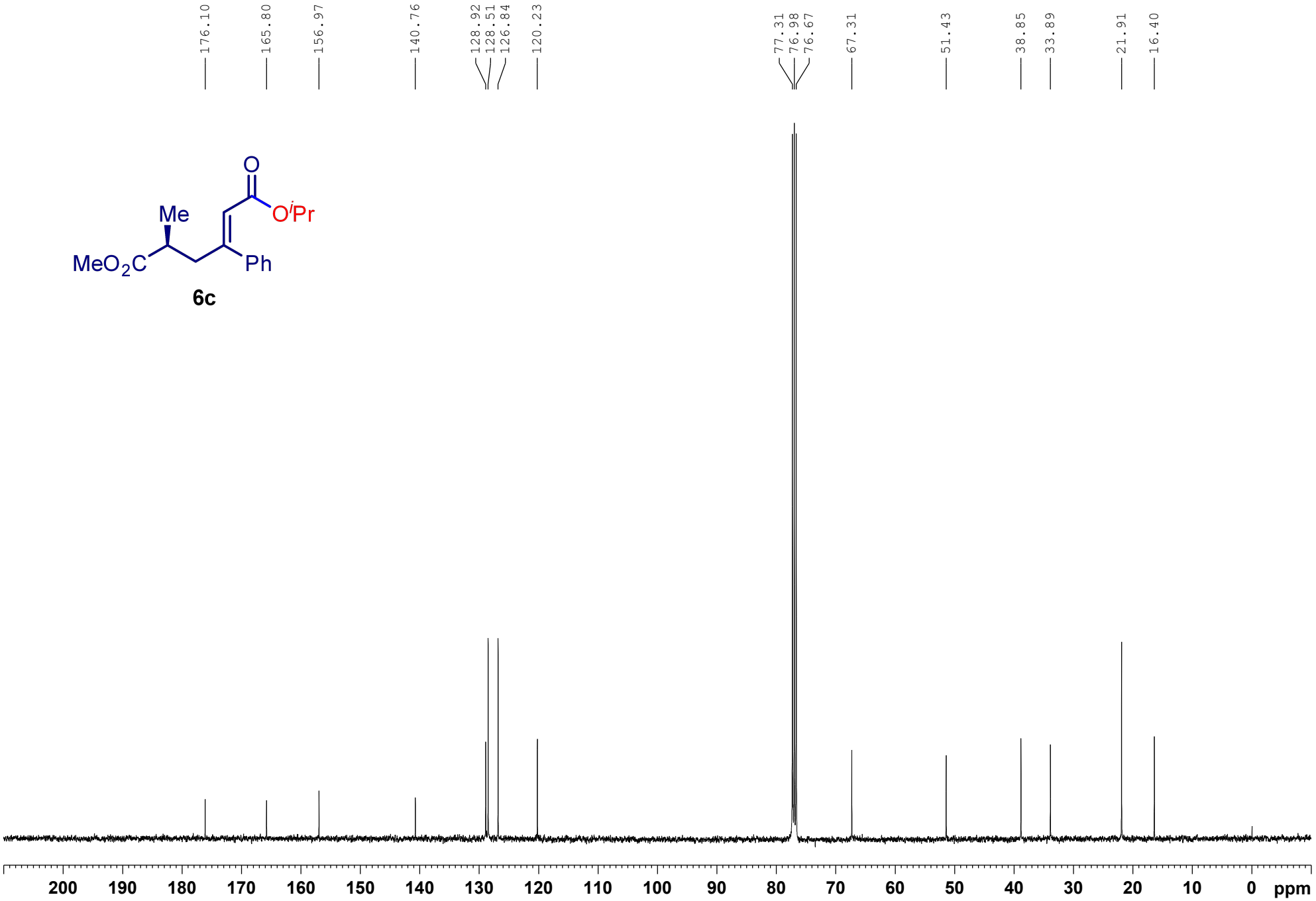
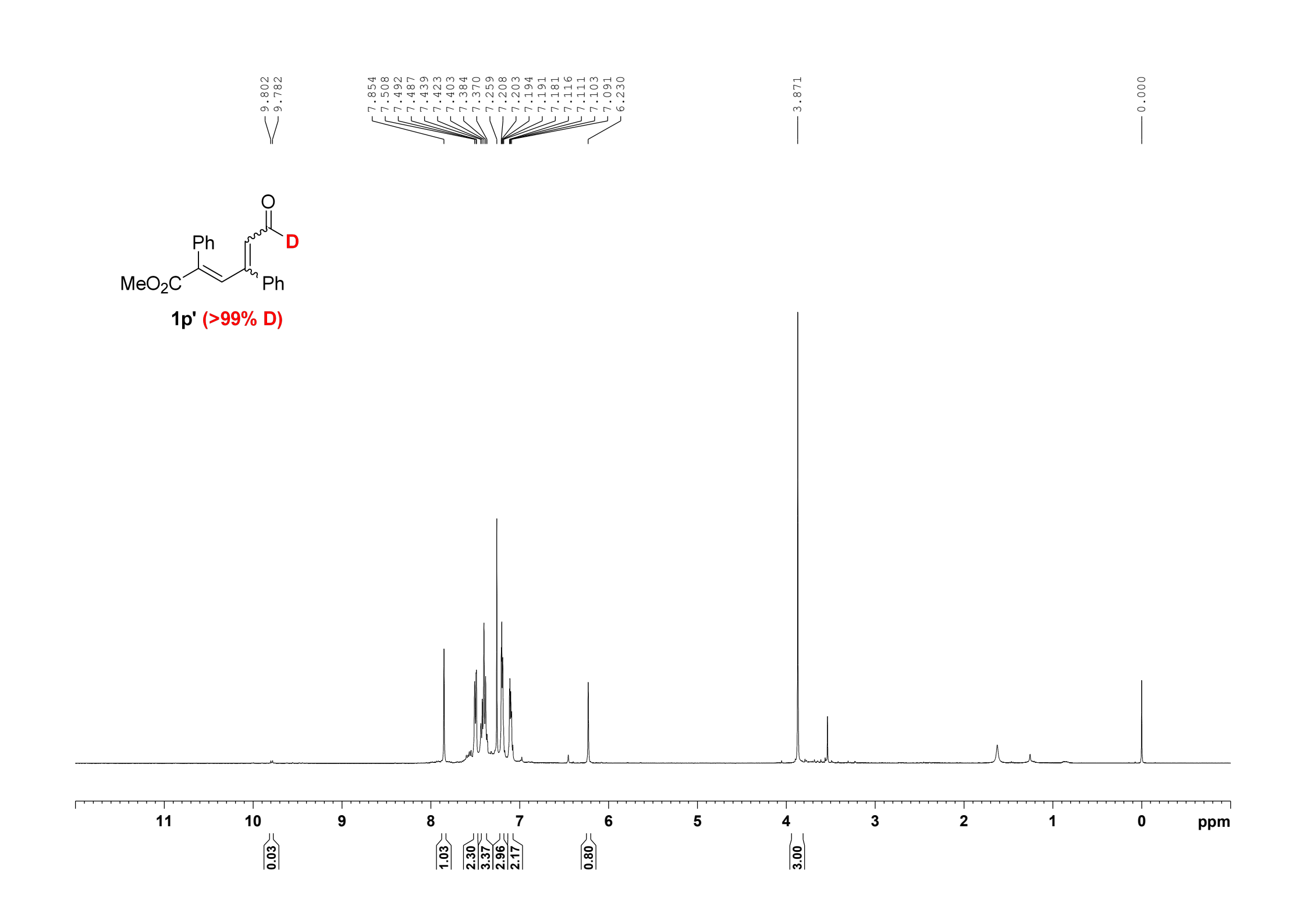
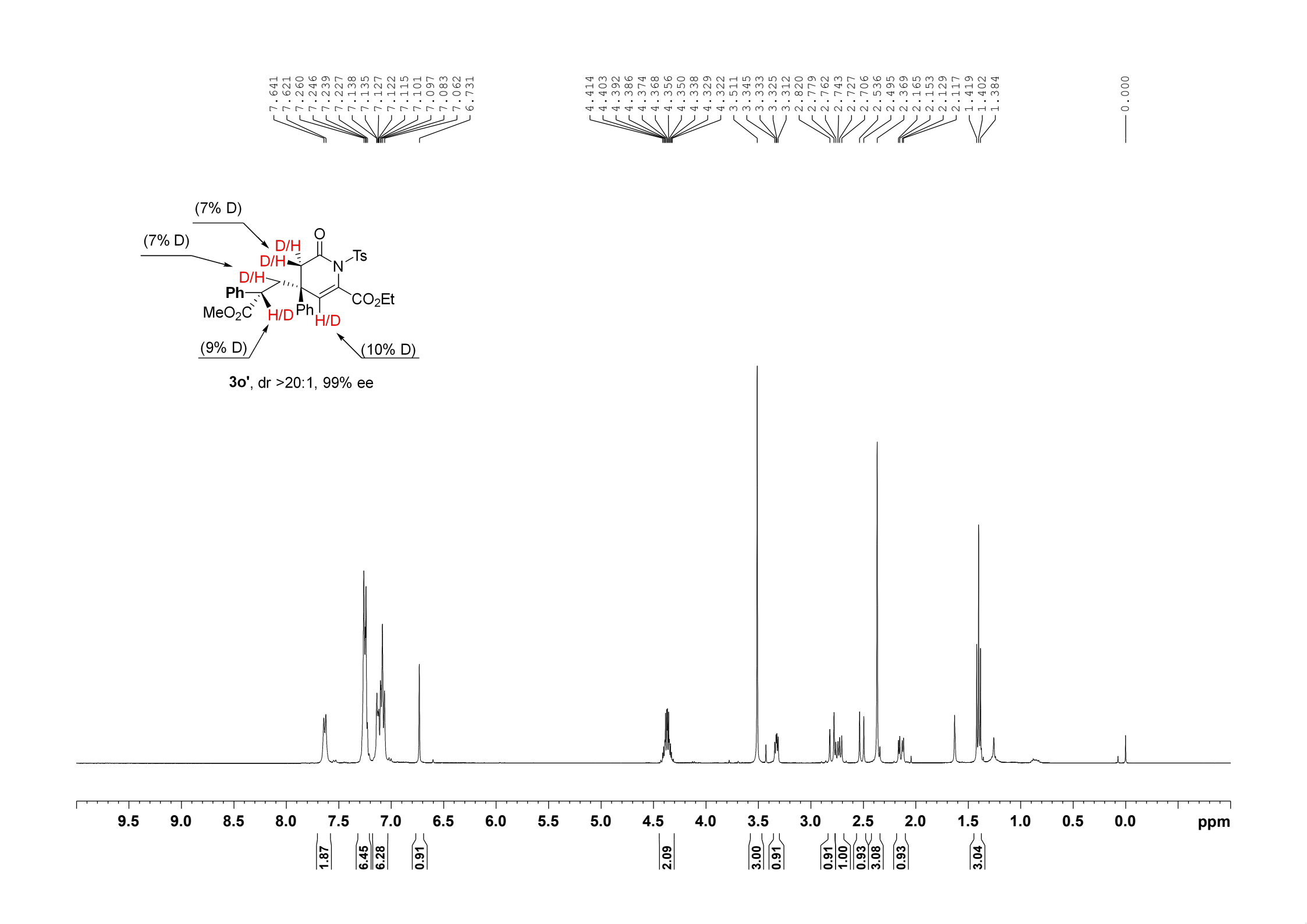
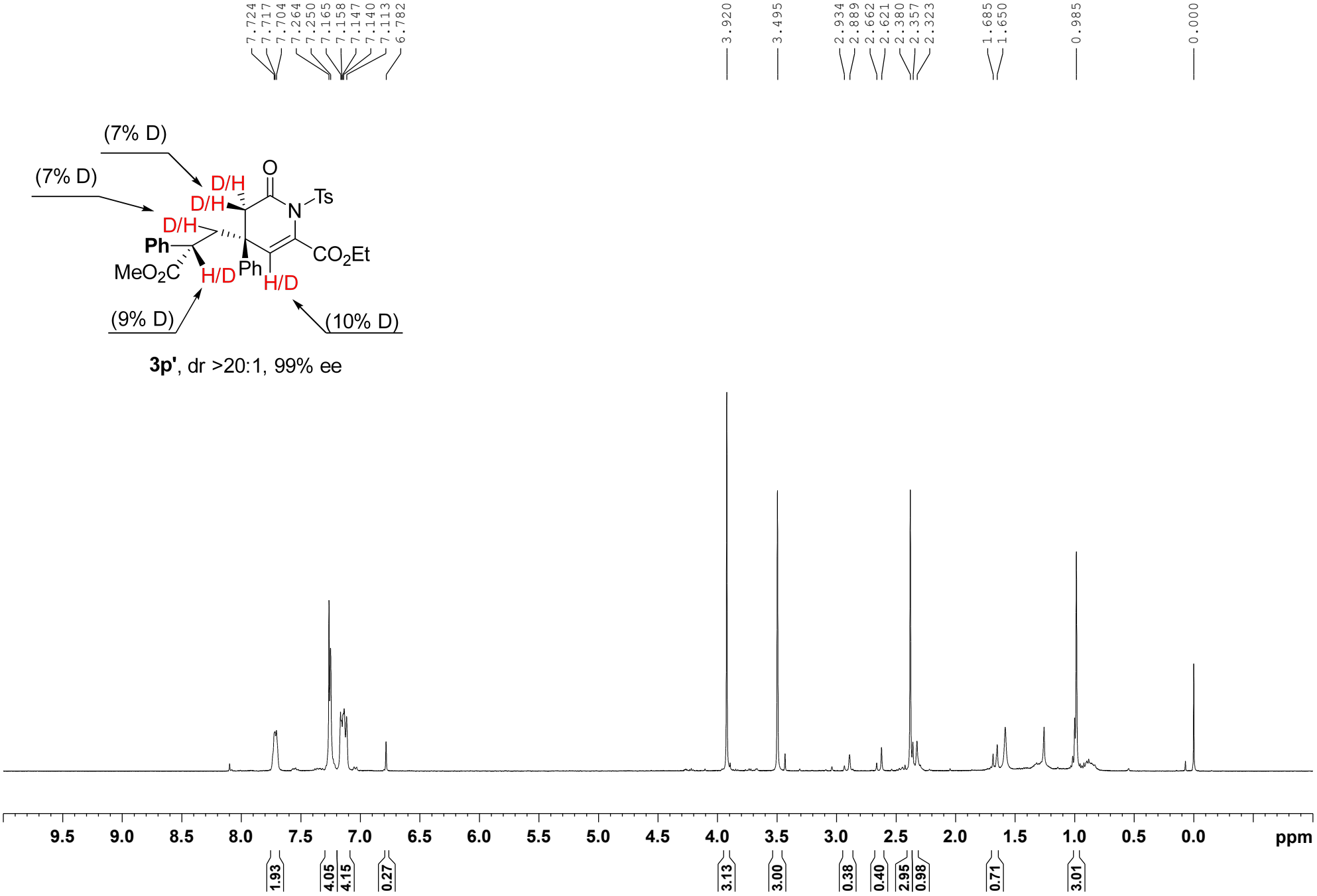
7.405
7.397
7.392
7.385
7.376
7.366
7.360
7.352
7.347
7.263
6.050
5.140
5.125
5.109
5.094
5.078
5.062
5.046
3.545
3.525
3.511
3.492
3.468
3.307
3.289
3.274
3.256
2.609
2.591
2.574
2.555
2.537
2.520
1.305
1.297
1.289
1.281
1.125
1.107
O
Me
OiPr
MeO2C
Ph
6c
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.15
3.11
0.98
1.00
1.10
3.07
1.06
1.03
6.32
3.14

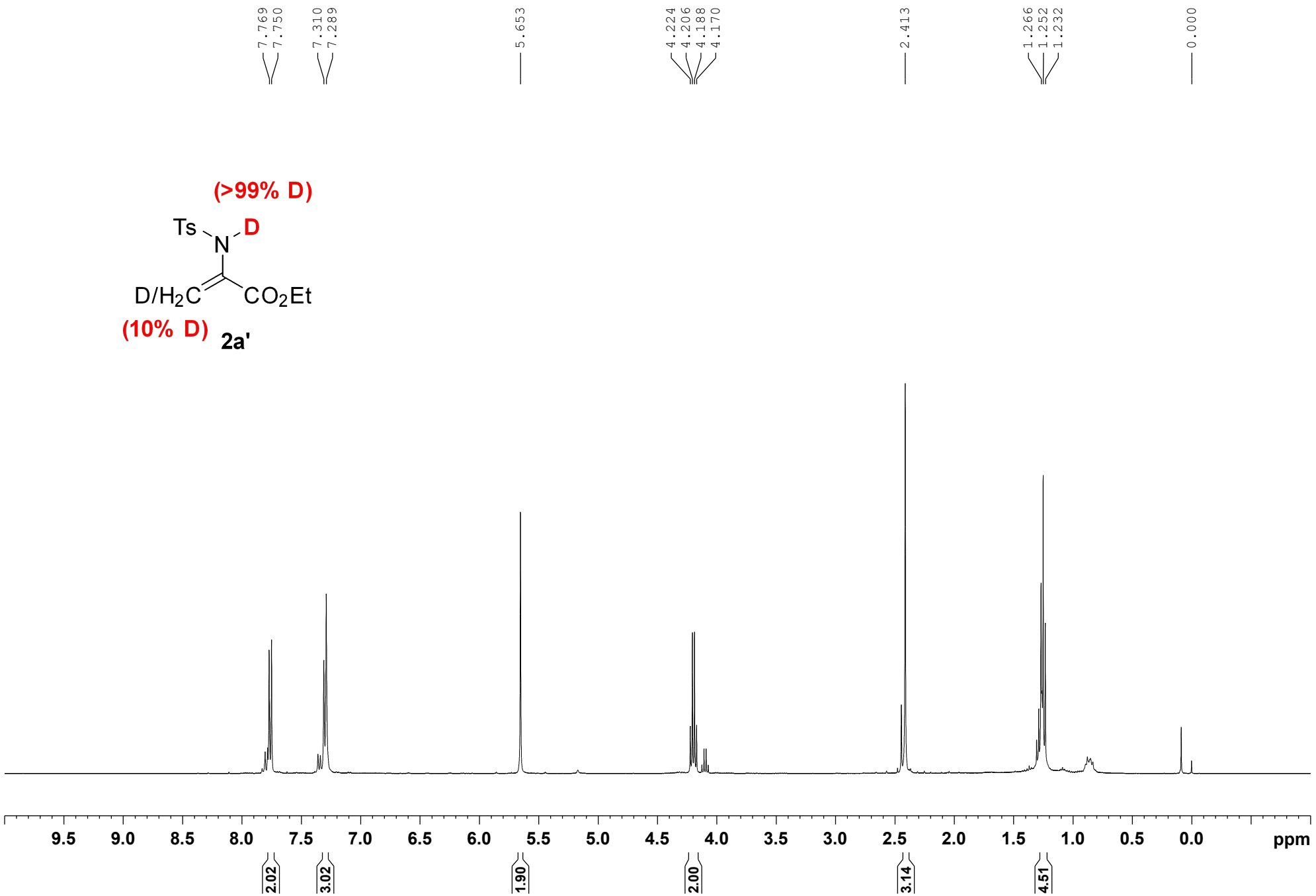

176.10
165.80
156.97
140.76
128.92
128.51
126.84
120.23
77.31
76.98
76.67
67.31
51.43
38.85
33.89
21.91
16.40
O
Me
O^{i}Pr
MeO$_2$C
Ph
6c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

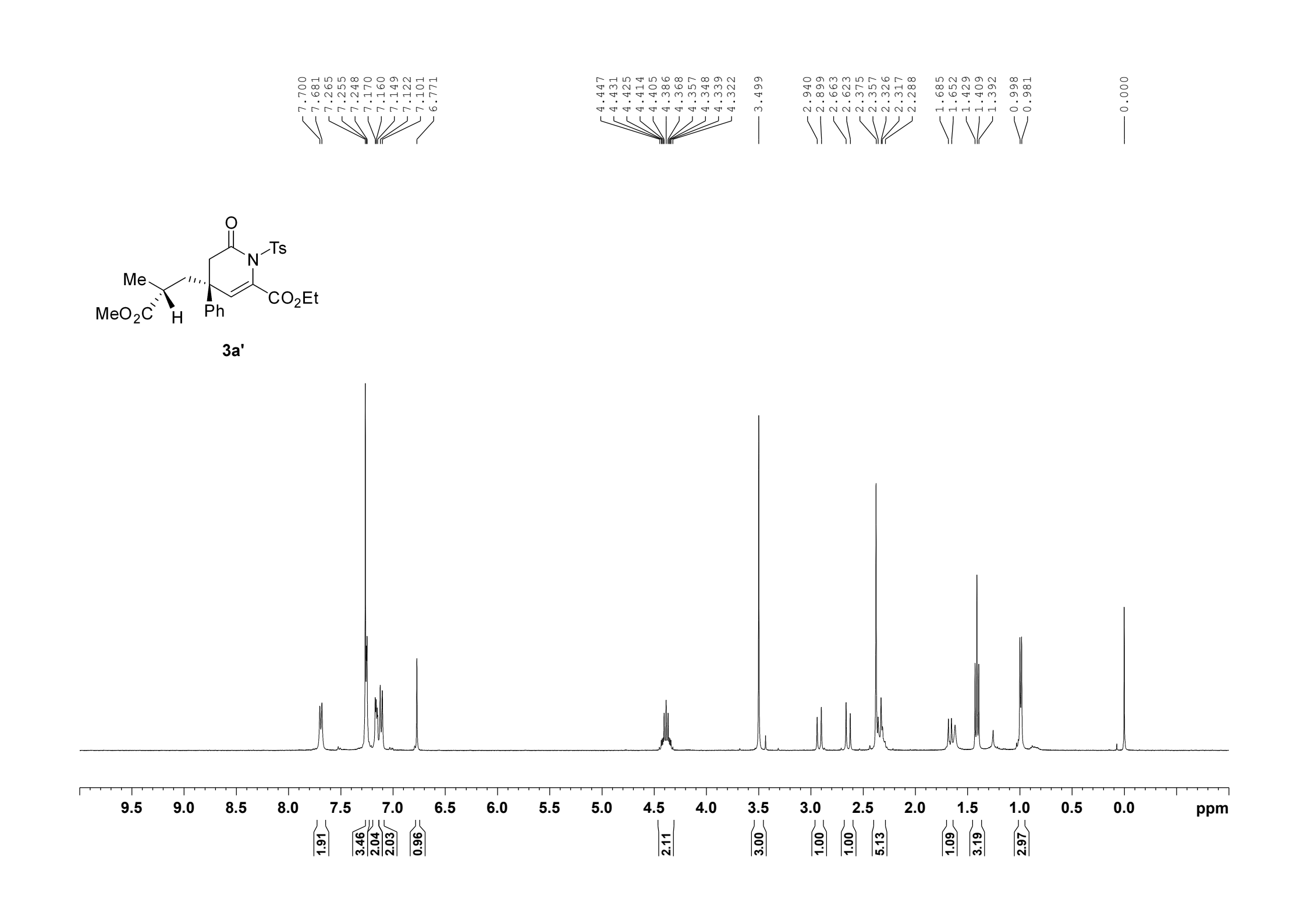

9.802
9.782
7.854
7.508
7.492
7.487
7.439
7.423
7.403
7.384
7.370
7.259
7.208
7.203
7.194
7.191
7.181
7.116
7.111
7.103
7.091
6.230
3.871
0.000
O
D
Ph
MeO2C
Ph
1p' (>99% D)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.03
1.03
2.30
3.37
2.96
2.17
0.80
3.00


7.641
7.621
7.260
7.246
7.239
7.227
7.138
7.135
7.127
7.122
7.115
7.101
7.097
7.083
7.062
6.731
4.414
4.403
4.392
4.386
4.374
4.368
4.356
4.350
4.338
4.329
4.322
3.511
3.345
3.333
3.325
3.312
2.820
2.779
2.762
2.743
2.727
2.706
2.536
2.495
2.369
2.165
2.153
2.129
2.117
1.419
1.402
1.384
0.000
(7% D)
(7% D)
D/H
D/H
D/H
Ph
MeO2C
H/D
Ph
H/D
O
N
Ts
CO2Et
(9% D)
(10% D)
3o', dr >20:1, 99% ee
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.87
6.45
6.28
0.91
2.09
3.00
0.91
0.91
1.00
0.93
3.08
0.93
3.04

3p', dr >20:1, 99% ee




7.769
7.750
7.310
7.289
5.653
4.224
4.206
4.188
4.170
2.413
1.266
1.252
1.232
0.000
(>99% D)
Ts
N
D
D/H2C
CO2Et
(10% D)
2a'
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.02
3.02
1.90
2.00
3.14
4.51


7.700
7.681
7.265
7.255
7.248
7.170
7.160
7.149
7.122
7.101
6.771
4.447
4.431
4.425
4.414
4.405
4.386
4.368
4.357
4.348
4.339
4.322
3.499
2.940
2.899
2.663
2.623
2.375
2.357
2.326
2.317
2.288
1.685
1.652
1.429
1.409
1.392
0.998
0.981
0.000
O
N
Ts
Me
MeO2C
H
Ph
CO2Et
3a'
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.91
3.46
2.04
2.03
0.96
2.11
3.00
1.00
1.00
5.13
1.09
3.19
2.97