Supporting Information

Synthesis of β-Halo α,β-unsaturated Carbonyl Systems via The Combination of Halotrimethylsilane and Tetrafluoroboric Acid

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General Information:

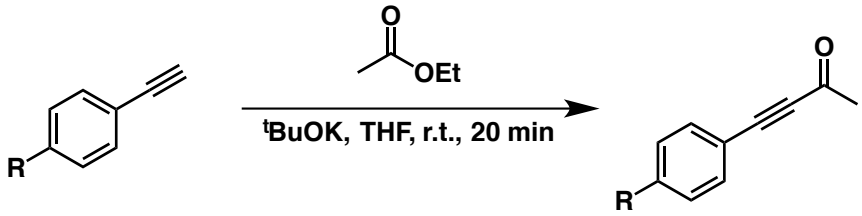
The chemicals were either used as received or purified according to the procedures outlined in *Purification of Common Laboratory Chemicals.*[1] Reactions were monitored by TLC and visualized by a dual shortwave/longwave UV lamp and stained with an ethanolic solution of potassium permanganate or vanillin. Column flash chromatography was performed using gel 60 (230−400 mesh), and analytical thin-layer chromatography (TLC) was performed using silica gel aluminum sheets. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise noted.

^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz. for ^{1}H and 100 MHz for ^{13}C. Chemical shifts (δ) are reported in parts per million relative to tetramethylsilane (TMS), and coupling constants (J) are reported in hertz. All signals are reported in ppm with the internal reference of 7.26 ppm or 77.0 ppm for chloroform. Data are presented as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, br = broad, dd = doublet of doublet, dt = doublet of triplet), coupling constant (J/Hz) and integration.

[1] Armarengo, W. L. F.; Perrin, D. D. In Purification of Laboratory Chemicals, 4th ed.; Butterworth Heinemann: Oxford, 1996

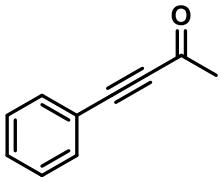
Synthesis of Ynones

General Procedure A.[2]

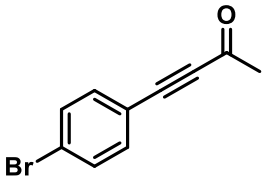


1a-c

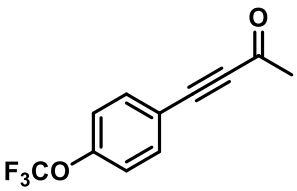
Potassium tert-butoxide (2.68 g, 23.89 mmol, 95%, 2 equiv) was dissolved in dry THF (30 mL) and the THF solution of ethyl acetate (11.34 mmol, 1 equiv) and acetylene 10 (11.34 mmol, 1 equiv) in THF (10 mL), was dropped immediately over the solution at room temperature. After stirring for 20 minutes, the reaction mixture was quenched by the addition of water (20 mL). The mixture was poured into mixture of ethyl acetate (60 mL) and ice powder (30 g). The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (n-hexane/ethyl acetate, 10:1 v/v). Fractions containing the product were combined and evaporated under reduced pressure to give the corresponding alkynones **1a-c**.



4-phenylbut-3-yn-2-one (1a): The title compound was synthesized according to the General Procedure A in 29% (474 mg) isolated yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.58 (ddd, *J* = 6.9, 3.4 e 1.7 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.41 – 7.36 (m, 2H), 2.45 (s, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 184.6, 133.0, 130.7, 128.6, 119.9, 90.3, 88.3, 32.7.



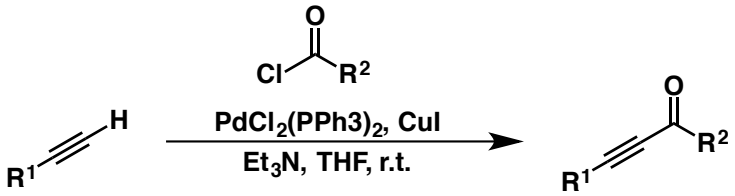
4-(4-bromophenyl)but-3-yn-2-one (1b): The title compound was synthesized according to the General Procedure A in 36% (936 mg) isolated yield as yellow solid. **NMR ^{1}H(400 MHz, $CDCl_3$)**δ 7.55 – 7.51 (m, 3H), 7.45 – 7.40 (m, 3H), 2.45 (s, 4H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 184.3, 134.3, 132.0, 125.6, 118.8, 89.0, 88.8, 32.7.



4-(4-(trifluoromethoxy)phenyl)but-3-yn-2-one (1c): The title compound was synthesized according to the General Procedure A in 39% (986 mg) as isolated yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.63 – 7.59 (m, 2H), 7.26 – 7.21 (m, 2H), 2.46 (s, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 184.3, 150.7, 134.7, 121.6, 120.9, 118.5, 88.7, 88.3, 32.7. **HRMS (ESI):** calcd. for $C_{11}H_8F_3O_2^+$ $[M+H]^+$ 229.0471, found 229.0475.

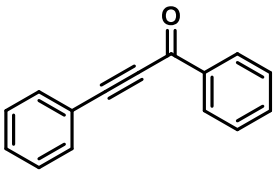
[2]B. R. Kim, H.-G. Lee, S.-B. Kang, K.-J. Jung, G. H. Sung, J.-J. Kim, S.-G. Lee and Y.-J. Yoon, *Tetrahedron*, 2013, **69**, 10331.

General Procedure B[3]

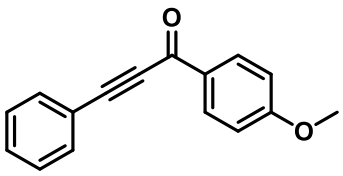


1d-w

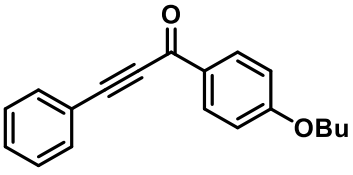
In a round-bottom flask a solution of the acetylene (1.0 equiv) in THF wasdded to a mixture of the acyl chloride (1.0 equiv), $Pd(PPh_3)_2Cl_2$ (1 mol%), copper(I) iodide (2 mol%) and triethylamine (1.1 equiv) in THF (0.5 M). The reaction mixture was stirred at room temperature. The progress of the reaction was monitored periodically by TLC. After the completion of the reaction, the solvent was removed under vacuum. The residue was then purified by flash chromatography on silica gel (n-hexane/ethyl acetate) affording ynones **1d-w**.



1,3-diphenylprop-2-yn-1-one (1d): The title compound was synthesized according to the General Procedure B in 53% (879 mg) isolated yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.26 – 8.20 (m, 2H), 7.70 (ddd, *J* = 6.8, 3.5 e 1.8 Hz, 2H), 7.66 – 7.61 (m, 1H), 7.55 – 7.51 (m, 2H), 7.49 (ddt, *J* = 8.9, 6.4 e 1.5 Hz, 1H), 7.45 – 7.40 (m, 2H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 178.0, 136.9, 134.1, 133.1, 130.8, 129.6, 128.7, 128.6, 120.2, 93.1, 86.9.



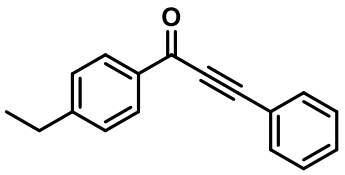
1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (1e): The title compound was synthesized according to the General Procedure B in 95% (673 mg) isolated yield as white solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.22 – 8.17 (d, *J* = 9.0 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.50 – 7.45 (m, 1H), 7.44 – 7.39 (m, 2H), 7.02 – 6.96 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 176.7, 164.5, 133.0, 132.0, 130.6, 130.4, 128.7, 120.4, 113.9, 92.3, 87.0, 55.6.



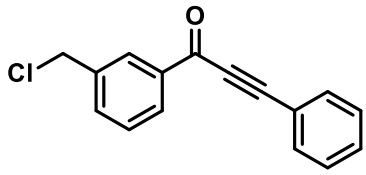
1-(4-butoxyphenyl)-3-phenylprop-2-yn-1-one (1f): The title compound was synthesized according to the General Procedure B in 51% (564 mg) isolated yield as brown solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.18 (d, *J* = 9.0 Hz, 2H), 7.67 (dd, *J* = 8.2 e 1.5 Hz, 2H), 7.50 – 7.36 (m, 3H), 6.97 (d, *J* = 9.0 Hz, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 1.86 – 1.75 (m, 2H), 1.51 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 176.6, 164.2, 132.9, 132.0, 130.5, 130.1, 128.6, 120.4, 114.3, 92.2, 87.0, 68.1, 31.1, 19.2, 13.8. **m.p.** 46-48 °C.

[3]F. Friscourt and G.-J. Boons, *Org. Letters*, 2010, **12**, 4936.

1-(4-(*tert*-butyl)phenyl)-3-phenylprop-2-yn-1-one (1g): The title compound was synthesized according to the General Procedure B in 66% (692 mg) isolated yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.8 Hz, 2H), 7.67 (dd, *J* = 8.2 e 1.5 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.49 – 7.35 (m, 3H), 1.35 (s, 9H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 177.7, 158.1, 134.6, 133.0, 130.7, 129.6, 128.7, 125.6, 120.3, 92.6, 87.1, 35.3, 31.1.

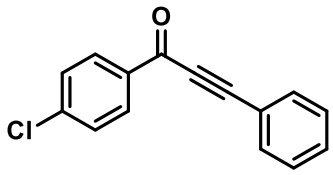


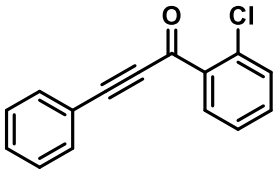
1-(4-ethylphenyl)-3-phenylprop-2-yn-1-one (1h): The title compound was synthesized according to the General Procedure B in 82% (578 mg) isolated yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.17 – 8.12 (m, 2H), 7.71 – 7.65 (m, 2H), 7.50 – 7.45 (m, 1H), 7.44 – 7.39 (m, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 177.8, 151.4, 134.9, 133.0, 130.8, 130.7, 129.8, 128.7, 128.4, 128.2, 120.3, 92.6, 87.0, 29.1, 15.2. **HRMS (ESI):** calcd. for $C_{17}H_{15}O^+$ $[M+H]^+$ 235.1117, found 235.1117. **m.p.** 46-48 °C.



1-(3-(chloromethyl)phenyl)-3-phenylprop-2-yn-1-one (1i): The title compound was synthesized according to the General Procedure B in 48% (337 mg) isolated yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.23 (td, *J* = 1.8 e 0.5 Hz, 1H), 8.21 – 8.17 (m, 1H), 7.72 – 7.65 (m, 3H), 7.56 – 7.53 (m, 1H), 7.53 – 7.47 (m, 1H), 7.46 – 7.41 (m, 2H), 4.67 (s, 2H). **NMR^{13}C (100 MHz, $CDCl_3$)** δ 177.4, 138.2, 137.4, 134.0, 133.1, 131.0, 129.6, 129.3, 129.2, 128.7, 120.0, 93.6, 86.8, 45.4. **HRMS (ESI):** calcd. for $C_{16}H_{12}ClO^+$ $[M+H]^+$ 255.0571, found 255.0576. **m.p.** 78-80 °C.

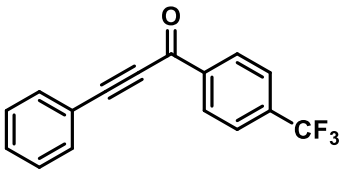
1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one (1j): The title compound was synthesized according to the General Procedure B in 95% (686 mg) isolated yield as white solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.19 – 8.12 (d, *J* = 8.8 Hz, 2H), 7.69 (ddd, *J* = 6.9, 3.4 e 1.7 Hz, 2H), 7.53 – 7.47 (m, 3H), 7.46 – 7.40 (m, 2H). **NMR^{13}C (100 MHz, $CDCl_3$)** δ 176.7, 140.7, 135.3, 133.1, 131.0, 130.9, 129.0, 128.8, 119.9, 93.6, 86.6.



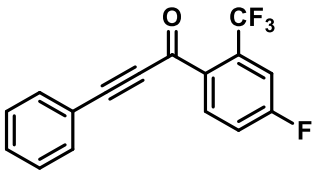


1-(2-chlorophenyl)-3-phenylprop-2-yn-1-one (1k): The title compound was synthesized according to the General Procedure B in 92% (664 mg) isolated yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.11 – 8.05 (m, 1H), 7.68 – 7.61 (m, 2H), 7.51 – 7.45

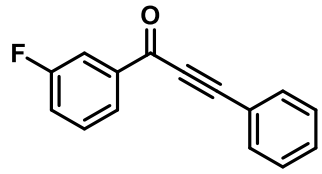
(m, 3H), 7.44 – 7.37 (m, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 176.8, 135.9, 133.6, 133.4, 133.1, 132.5, 131.6, 131.0, 128.7, 126.8, 120.0, 94.0, 88.3.



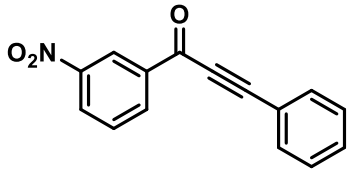
3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (1l): The title compound was synthesized according to the General Procedure B in 53% (361 mg) isolated yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.25 (dd, *J* = 8.8, 0.8 Hz, 2H), 7.71 (dd, *J* = 8.8, 0.6 Hz, 2H), 7.62 (dd, *J* = 8.3 e 1.4 Hz, 2H), 7.48 – 7.40 (m, 1H), 7.40 – 7.33 (m, 2H). **NMR^{13}C (100 MHz, $CDCl_3$)** δ 176.7, 139.4, 135.3, 133.2, 131.2, 129.8, 128.8, 125.7, 123.6, 119.7, 94.5, 86.6.



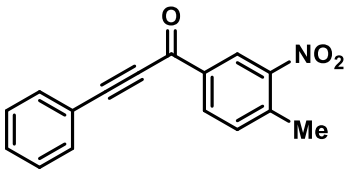
1-(4-fluoro-2-(trifluoromethyl)phenyl)-3-phenylprop-2-yn-1-one (1m): The title compound was synthesized according to the General Procedure B in 72% (842 mg) isolated yield as brown solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.20 (dd, *J* = 8.5 e 5.6 Hz, 1H), 7.63 (dd, *J* = 8.3 e 1.4 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.44 – 7.35 (m, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 175.9, 165.4, 162.9, 134.5 (d, J = 9.0 Hz, 1C), 133.1, 131.2, 128.7, 123.7, 121.0, 119.6, 118.6 (d, *J* = 21.3 Hz, 1C), 115.6 (dq, *J* = 25.4 e 5.8 Hz, 1C), 94.4, 87.8. **HRMS (ESI):** calcd. for $C_{16}H_9F_4O^+$ $[M+H]^+$ 293.0584, found 293.0585. **m.p.** 50-53 °C.



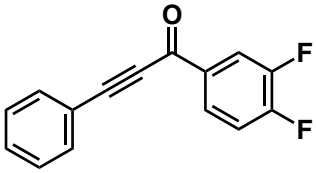
1-(3-fluorophenyl)-3-phenylprop-2-yn-1-one (1n): The title compound was synthesized according to the General Procedure B in 81% (545 mg) isolated yield asn orange solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.03 (ddd, *J* = 7.7, 1.5 e 1.1 Hz, 1H), 7.88 (ddd, *J* = 9.2, 2.5 e 1.5 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.54 – 7.47 (m, 2H), 7.47 – 7.41 (m, 2H), 7.33 (tdd, *J* = 8.2, 2.7 e 1.0 Hz, 1H). **NMR^{13}C (100 MHz, $CDCl_3$)** δ 176.6, 162.8 (d, *J* = 248.3 Hz, 1C), 139.0 (d, *J* = 6.4 Hz, 1C), 133.2, 131.0, 130.3 (d, *J* = 7.8 Hz, 1C), 128.8, 125.4 (d, *J* = 2.3 Hz, 1C), 121.1 (d, *J* = 21.6 Hz, 1C), 119.8, 115.8 (d, *J* = 22.8 Hz, 1C), 93.7, 86.6.



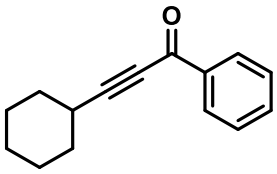
1-(3-nitrophenyl)-3-phenylprop-2-yn-1-one (1o): The title compound was synthesized according to the General Procedure B in 88% (663 mg) isolated yield as brown solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 9.05 (t, *J* = 1.8 Hz, 1H), 8.56 – 8.44 (m, 2H), 7.77 – 7.71 (m, 3H), 7.57 – 7.51 (m, 1H), 7.50 – 7.44 (m, 2H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 187.3, 148.5, 146.1, 139.3, 136.9, 134.1, 131.2, 130.0, 128.8, 127.4, 127.3, 123.4, 119.9. **HRMS (ESI):** calcd. for $C_{15}H_{10}NO_3^+$ $[M+H]^+$ 252.0655, found 252.0654. **m.p.** 132-134 °C.



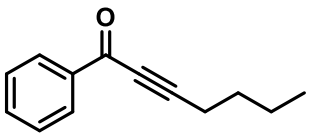
1-(4-methyl-3-nitrophenyl)-3-phenylprop-2-yn-1-one (1p): The title compound was synthesized according to the General Procedure B in 24% (256 mg) isolated yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.81 (d, *J* = 1.8 Hz, 1H), 8.31 (dd, *J* = 8.0 e 1.8 Hz, 1H), 7.72 (dd, *J* = 8.3 e 1.4 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.49 – 7.43 (m, 2H), 2.71 (s, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 175.4, 149.33, 139.6, 136.0, 133.4, 133.3, 132.7, 131.3, 128.8, 126.0, 119.5, 94.8, 86.2, 20.8. **HRMS (ESI):** calcd. for $C_{16}H_{12}NO_3^+$ $[M+H]^+$ 266.0812, found 266.0816. **m.p.** 98-100 °C.



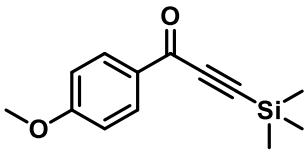
1-(3,4-difluorophenyl)-3-phenylprop-2-yn-1-one (1q): The title compound was synthesized according to the General Procedure B in 78% (190 mg) isolated yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.09 – 7.94 (m, 2H), 7.68 (ddd, *J* = 6.9, 3.4 e 1.7 Hz, 2H), 7.54 – 7.47 (m, 1H), 7.46 – 7.39 (m, 2H), 7.36 – 7.27 (m, 1H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 175.2, 154.3 (dd, *J* = 258.7 e 13.0 Hz, 1C), 150.4 (dd, *J* = 251.3 e 13.2 Hz, 1C), 134.0 (dd, *J* = 3.7 e 3.5 Hz, 1C), 133.1, 131.1, 128.8, 126.7 (dd, *J* = 7.6 e 3.2 Hz, 1C), 119.7, 118.4 (d, *J* = 18.6 Hz, 1C), 117.6 (d, *J* = 18.1 Hz, 1C), 94.0, 86.2.



3-cyclohexyl-1-phenylprop-2-yn-1-one (1r): The title compound was synthesized according to the General Procedure B in 94% (501 mg) isolated yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.17 – 8.11 (m, 2H), 7.62 – 7.55 (m, 1H), 7.50 – 7.43 (m, 2H), 2.75 – 2.64 (m, 1H), 1.92 (dd, *J* = 9.5 e 3.4 Hz, 2H), 1.83 – 1.73 (m, 2H), 1.69 – 1.53 (m, 3H), 1.40 (qd, *J* = 9.9 e 5.0 Hz, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 178.3, 137.0, 133.8, 129.5, 128.5, 100.4, 79.6, 31.7, 29.4, 25.6, 24.7.

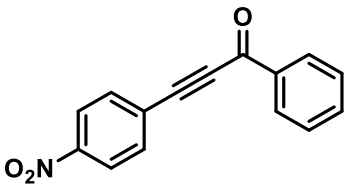


1-phenylhept-2-yn-1-one (1s): The title compound was synthesized according to the General Procedure B in 91% (422 mg) isolated yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.16 – 8.11 (m, 2H), 7.63 – 7.55 (m, 1H), 7.51 – 7.44 (m, 2H), 2.51 (dd, *J* = 9.6 e 4.6 Hz, 2H), 1.67 (dddd, *J* = 8.7, 7.1, 6.4 e 0.6 Hz, 2H), 1.57 – 1.45 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 178.2, 137.0, 133.8, 129.5, 128.5, 96.8, 79.7, 29.8, 22.1, 18.9, 13.5.

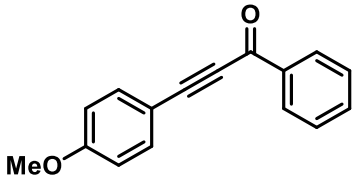


1-(4-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-one (1t): The title compound was synthesized according to the General Procedure B in 89% (414 mg) isolated yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.15 – 8.07 (m, 2H), 7.00 – 6.92 (m,

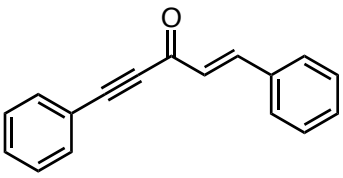
2H), 3.89 (s, 3H), 0.32 – 0.30 (s, 9H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 177.0, 165.2, 132.7, 130.6, 114.5, 101.6, 100.2, 56.2, 0.0.



3-(4-nitrophenyl)-1-phenylprop-2-yn-1-one (1u): The title compound was synthesized according to the General Procedure B in 33% (174 mg) isolated yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)**δ 8.21 (d, *J* = 9.0 Hz, 1H), 8.12 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 177.38, 148.51, 136.37, 134.69, 133.69, 129.65, 128.84, 126.78, 123.84, 89.85, 89.22. 89.22. **HRMS (ESI):** calcd. for $C_{15}H_{10}NO_3^+$ $[M+H]^+$ 252.0655, found 252.0656. **m.p.** 150-152 °C.



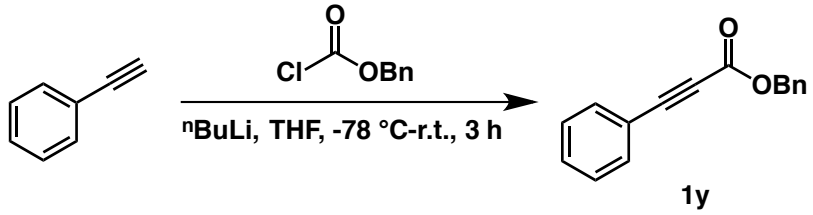
3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one (1v): The title compound was synthesized according to the General Procedure B in 66% (627 mg) isolated yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.15 (dd, *J* = 8.4 e 1.3 Hz, 2H), 7.60 – 7.52 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 178.1, 161.8, 137.1, 135.2, 133.9, 129.5, 128.6, 114.5, 111.9, 94.4, 86.9, 55.5.



(E)-1,5-diphenylpent-1-en-4-yn-3-one (1w): The title compound was synthesized according to the General Procedure B in 70% (325 mg) isolated yield as dark yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.92 (d, J = 16.1 Hz, 1H). 7.68 – 7.65 (m, 2H), 7.63 – 7.59 (m, 2H), 7.51 – 7.40 (m, 6H), 6.88 (d, J = 16.1 Hz, 1H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 178.4, 148.5, 134.2, 133.1, 131.3, 130.8, 129.2, 128.9, 128.8, 128.7, 120.3, 91.7, 86.7.

The oct-3-yn-2-one (**1x**) was synthetized according to reported literature method.[4]

Synthesis of benzyl 3-phenylpropiolate[5]



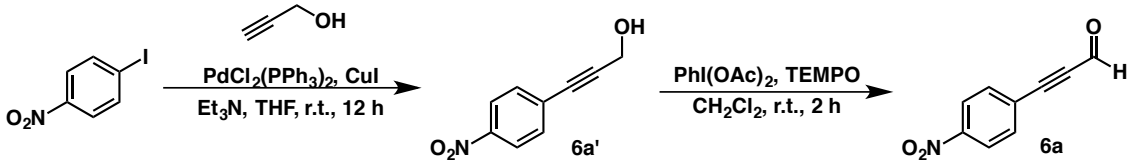
1y

[4] A. A. dos Santos, P. Castelani, B. K. Bassora, J. C. F. Junior, C. E. Costa and J. V. Comasseto, *Tetrahedron*, 2005, **61**, 9173.
[5] Y. Lee, Y. Motoyama, K. Tsuji, S.-H. Yoon, I. Mochida and H. Nagashima, *ChemCatChem*, 2012, **4**, 778.

To solution of phenylacetylene (0.549 mL, 5.00 mmol, 1.0 equiv) em dry THF (10 mL) at -78 °C was added *n*-BuLi (2.10 mL, 2.5 M in hexanes, 5.25 mmol, 1.05 equiv). The reaction mixture was stirred for 30 min at -78 °C. Phenyl chloroformate (0.785 mL, 5.50 mmol, 1.1 equiv) was added, then cooling was taken out and the reaction was allowed to reach room temperature over 2.5 h. The reaction was quenched with cold water (50 mL) and extracted with Et_2O (3 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried over sodium sulfate (Na_2SO_4) and the solvent was removed in vacuum. The residue was purified by colunm chromatography on silica gel (*n*-hexanes/ethyl acetate) to afford benzyl 3-phenylpropiolate (802 mg, 68%) as colorless oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.57 (dd, *J* = 8.3 e 1.4 Hz, 2H), 7.45 – 7.32 (m, 8H), 5.26 (s, 2H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 153.9, 134.9, 133.0, 130.7, 128.7, 128.6, 128.5, 128.4, 119.6, 86.8, 80.5, 67.7.

Synthesis of the Ynals

Synthesis of 3-(4-nitrophenyl)propiolaldehyde[6]



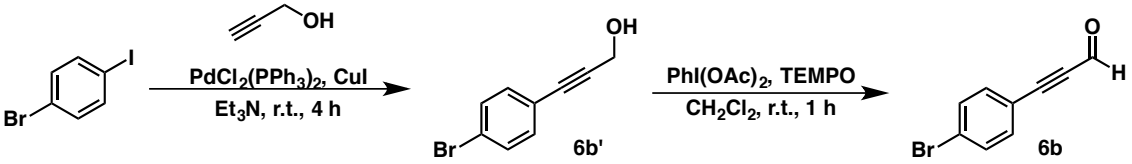
Bis(triphenylphosphine)palladium(II) dichloride (42 mg, 0.06 mmol, 1.5 mol%) wasdded to a stirred solution of propargyl alcohol (0.257 mL, 4.4 mmol, 1.1 equiv), 1-iodo-4-nitrobenzene (996 mg, 4.0 mmol, 1.0 equiv), triethylamine (0.613 mL, 4.4 mmol, 1.1 equiv), and copper(I) iodide (11 mg, 0.015 mmol, 1.5 mol%) in dry THF (12 mL). The mixture was stirred at room temperrature for 12h and then filtered through silica gel. The solvent was removed under vacum and the residue was purified by column chromatography on silica gel (n-hexane/ethyl acetate) affording the product as brown solid (678 mg, 87%). **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 8.9 Hz, 2H), 7.51 (d, *J* = 8.9 Hz, 2H), 4.47 (d, *J* = 4.8 Hz, 2H), 1.76 (t, *J* = 5.4 Hz, 1H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 147.2, 132.4, 129.4, 123.6, 92.5, 83.8, 51.5.

To the solution of TEMPO (41 mg, 0.26 mmol, 10 mol%) and the propargyl alcohol (464 mg, 2.6 mmol, 1.0 equiv) in DCM (2.6 mL) wasdded bisacetoxyiodobenzene (928 mg, 2.9 mmol, 2.0 equiv). The reaction mixture was stirred for 2 h. The solvent was removed under vacum and the residue was purified by column chromatography on silica gel (n-hexane/ethyl acetate) affording 3-(4-nitrophenyl)propiolaldehyde as red solid (314 mg, 68%). **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 9.47 (s, 1H), 8.28 (d, *J* = 8.9 Hz, 2H), 7.78 (d, *J* = 8.9 Hz, 2H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 176.1, 148.8, 133.9, 126.0, 123.9, 90.8, 90.6. **HRMS (ESI):** calcd. for $C_9H_6NO_3^+$ $[M+H]^+$ 176.0342, found 176.0312. **m.p.** 120-123 °C.

Synthesis of 3-(4-bromophenyl)propiolaldehyde[7]

[6] A. Nowak-Król, B. Koszarna, S. Y. Yoo, J. Chromiński, M. K. Węcławski, C.-H. Lee and D. T. Gryko, *J. Org. Chem.*, 2011, **76**, 2627.

[7] X. Wang, Y. Zhou, L. Qiu, R. Yao, Y. Zheng, C. Zhang, X. Bao and X. Xu, *Adv.Synth. Catal*. 2016, **358**, 1571.

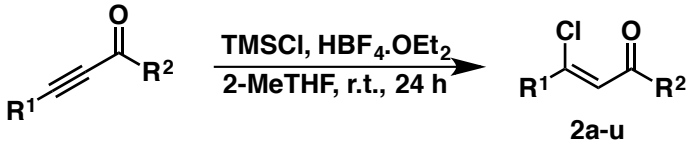


Bis(triphenylphosphine)palladium(II) dichloride (14 mg, 0.02 mmol, 1.0 mol%) wasdded to a stirred solution of propargyl alcohol (0.128 mL, 2.2 mmol, 1.1 equiv), 1-bromo-4-iodobenzene (596 mg, 4.0 mmol, 1.0 equiv) and copper(I) iodide (7.6 mg, 0.04 mmol, 2.0 mol%) in triethylamine (8 mL).The mixture was stirred at room temperrature for 12h and then filtered through silica gel. The solvent was removed under vacum and the residue was purified by column chromatography on silica gel (n-hexane/ethyl acetate) affording the product as brown solid (417.8 mg, 99%). **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 4.48 (s, 2H), 1.71 (sl, 1H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 133.27, 131.76, 122.95, 121.61, 88.46, 84.82, 51.76.

To the solution of TEMPO (16 mg, 0.1 mmol, 10 mol%) and the propargyl alcohol (211 mg, 1.0 mmol, 1.0 equiv) in DCM (1 mL) wasdded bisacetoxyiodobenzene (354 mg, 2.9 mmol, 2.0 equiv). The reaction mixture was stirred for 1 h. The solvent was removed under vacum and the residue was purified by column chromatography on silica gel (n-hexane/ethyl acetate) affording 3-(4-bromophenyl)propiolaldehyde as yellow solid (165 mg, 79%). **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 9.41 (s, 1H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 176.7, 134.7, 132.3, 126.4, 118.5, 93.7, 89.2.

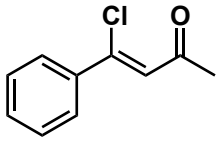
The hept-2-ynal (**6c**) was synthetized according to reported literature method.[8]

Hydrochlorination of Ynones.



2a-u

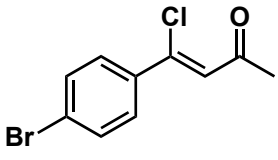
To a solution of ynone (0.15 mmol) in 2-MeTHF (0.4 mL) were added $HBF_4.OEt_2$ (82.4 μL, 0.30 mmol, 50 wt/wt%, 2 equiv or 65.9 μL, 0.24 mmol, 1.6 equiv[a]) and TMSCl (0.3 mmol, 2 equiv) at room temperature, then the mixture was monitored by TLC. After completion, the solvent was evaporated under the reduced pressure and the residue was purified by silica gel column chromatography (*n*-hexanes/EtOAc) to afford the corresponding products **2a-u**.



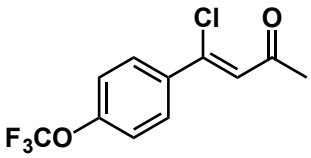
(Z)-4-chloro-4-phenylbut-3-en-2-one (2a)[a]: The title compound was isolated in 90% (24 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.70 – 7.66 (m, 2H), 7.46 – 7.39 (m, 3H), 6.78

[8] K. Frimpong, J. Wzorek, C. Lawlor, K. Spencer and T. Mitzel *J. Org. Chem.*, 2009, **74**, 5861.

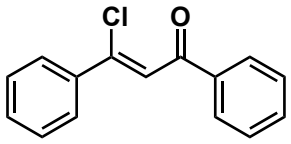
(s, 1H), 2.48 (s, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 196.7, 143.0, 137.3, 130.7, 128.7, 127.3, 124.8, 31.9. The spectroscopic data are in accordance with the literature.[9]



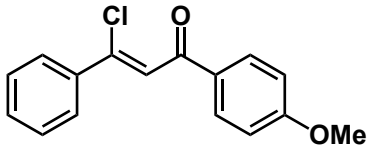
(Z)-4-(4-bromophenyl)-4-chlorobut-3-en-2-one (2b)[a]: The title compound was isolated in 82% (32 mg) yield as brown solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.47 (s, 4H), 6.68 (s, 1H), 2.40 (s, 3H). **NMR^{13}C (100 MHz, $CDCl_3$)** δ 196.4, 141.7, 136.2, 131.9, 128.8, 125.2, 125.0, 31.8. The spectroscopic data are in accordance with the literature.[9]



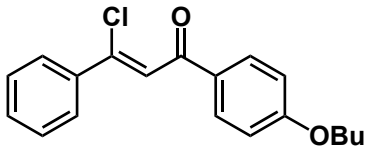
(Z)-4-chloro-4-(4-(trifluoromethoxy)phenyl)but-3-en-2-one (2c)[a]: The title compound was isolated in 66% (26 mg) yield as red oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.75 – 7.69 (m, 2H), 7.29 – 7.23 (m, 2H), 6.76 (s, 1H), 2.48 (s, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 196.3, 150.8, 141.2, 135.8, 129.0, 125.3, 120.8, 31.8. **HRMS (ESI):** calcd. for $C_{11}H_9ClF_3O_2^+$ $[M+H]^+$ 265.0238, found 265.0236.



(Z)-3-chloro-1,3-diphenylprop-2-en-1-one (2d): The title compound was isolated in 95% (34 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.03 – 7.97 (m, 2H), 7.79 – 7.73 (m, 2H), 7.63 – 7.56 (m, 1H), 7.52 – 7.46 (m, 2H), 7.46 – 7.43 (m, 3H), 7.35 (s, 1H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 189.9, 143.3, 137.8, 137.4, 133.3, 130.6, 128.8, 128.7, 127.2, 121.5. The spectroscopic data are in accordance with the literature.[9]



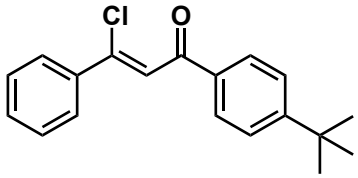
(Z)-3-chloro-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (2e): The title compound was isolated in 96% (39 mg) yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.02 – 7.96 (m, 2H), 7.77 – 7.71 (m, 2H), 7.46 – 7.40 (m, 3H), 7.27 (s, 1H), 6.99 – 6.93 (m, 2H), 3.87 (s, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 188.8, 163.9, 141.9, 137.4, 131.2, 130.4, 128.7, 127.1, 122.1, 114.0, 55.5. The spectroscopic data are in accordance with the literature.[10]



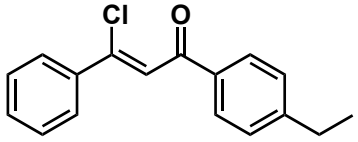
(Z)-1-(4-butoxyphenyl)-3-chloro-3-phenylprop-2-en-1-one (2f): The title compound was isolated in 92% (43 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 8.9 Hz, 2H), 7.74 (dd, *J* = 6.7 e 3.0 Hz, 2H), 7.46 –

[9] X. Zeng, Z. Lu, S. Liu, G. B. Hammond and B. Xu *J. Org. Chem.*, 2017, **82**, 13179.
[10] T. Iwai, T. Fujihara, J. Terao, Y. Tsuji J. Am. Chem. Soc., 2009, **131**, 6668.

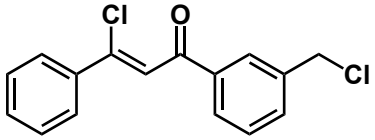
7.39 (m, 3H), 7.27 (s, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.03 (t, *J* = 6.5 Hz, 2H), 1.84 – 1.73 (m, 2H), 1.51 (dt, *J* = 14.9 e 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 188.8, 163.5, 141.7, 137.4, 131.1, 130.3, 128.6, 128.1, 127.1, 122.1, 114.4, 68.0, 31.1, 19.2, 13.8. **HRMS (ESI):** calcd. for $C_{19}H_{20}ClO_2^+$ $[M+H]^+$ 315.1146, found 315.1142.



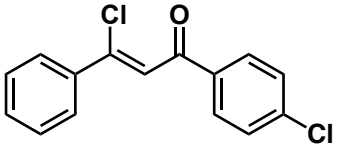
(Z)-1-(4-(*tert*-butyl)phenyl)-3-chloro-3-phenylprop-2-en-1-one (2g): The title compound was isolated in 87% (39 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.77 – 7.73 (m, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 3.5 Hz, 3H), 7.33 (s, 1H), 1.35 (s, 9H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 189.5, 157.2, 142.6, 137.4, 135.1, 130.4, 128.7, 128.7, 127.2, 125.7, 121.8, 35.2, 31.1. **HRMS (ESI):** calcd. for $C_{19}H_{20}ClO^+$ $[M+H]^+$ 299.1197, found 299.1197.



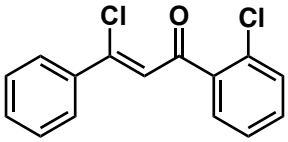
(Z)-3-chloro-1-(4-ethylphenyl)-3-phenylprop-2-en-1-one (2h): The title compound was isolated in 80% (32 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.17 – 8.12 (m, 2H), 7.71 – 7.65 (m, 2H), 7.50 – 7.45 (m, 1H), 7.44 – 7.39 (m, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 189.6, 150.5, 142.6, 137.4, 135.4, 130.4, 129.0, 128.7, 128.3, 127.2, 121.9, 29.0, 15.2. **HRMS (ESI):** calcd. for $C_{17}H_{16}ClO^+$ $[M+H]^+$ 271.0884, found 271.0881.



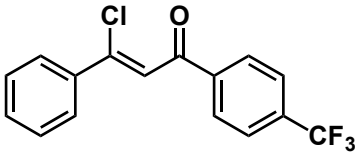
(Z)-3-chloro-1-(3-(chloromethyl)phenyl)-3-phenylprop-2-en-1-one (2i): The title compound was isolated in 85% (37 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.00 (td, *J* = 1.8 e 0.5 Hz, 1H), 7.96 – 7.92 (m, 1H), 7.78 – 7.74 (m, 2H), 7.64 – 7.60 (m, 1H), 7.49 (dd, *J* = 6.8 e 2.9 Hz, 1H), 7.48 – 7.43 (m, 3H), 7.33 (s, 1H), 4.63 (s, 2H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 189.2, 143.9, 138.3, 137.2, 133.3, 130.7, 129.2, 128.7, 128.7, 128.6, 127.2, 121.2, 45.5. **HRMS (ESI):** calcd. for $C_{16}H_{13}Cl_2O^+$ $[M+H]^+$ 291.0338, found 291.0339.



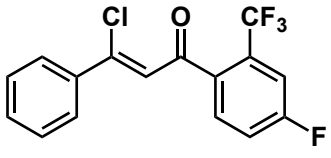
(Z)-3-chloro-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (2j): The title compound was isolated in 83% (34 mg) yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.97 – 7.90 (m, 2H), 7.79 – 7.71 (m, 2H), 7.49 – 7.42 (m, 5H), 7.29 (s, 1H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 188.7, 143.9, 139.8, 137.2, 136.1, 130.7, 130.1, 129.1, 128.8, 127.2, 121.0. The spectroscopic data are in accordance with the literature.[10]



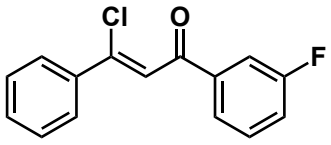
(Z)-3-chloro-1-(2-chlorophenyl)-3-phenylprop-2-en-1-one (2k): The title compound was isolated in 99% (41 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.74 (dd, *J* = 8.0 e 1.7 Hz, 2H), 7.59 (ddd, *J* = 7.5, 1.5 e 0.8 Hz, 1H), 7.46 – 7.34 (m, 6H), 7.23 (s, 1H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 190.5, 144.6, 139.6, 137.3, 132.1, 130.9, 130.3, 130.0, 128.8, 128.7, 127.4, 127.2, 123.5. The spectroscopic data are in accordance with the literature.[11]



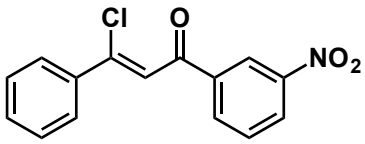
(Z)-3-chloro-3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (2l): The title compound was isolated in 79% (42 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.68 (t, *J* = 8.0 Hz, 4H), 7.44 – 7.33 (m, 3H), 7.27 (s, 1H). **NMR ^{13}C (100 MHz, CDCl3)** δ 188.7, 145.1, 140.6, 137.1, 133.2, 131.0, 129.8, 128.9, 127.3, 125.8 (q, *J* = 3.5 Hz, 1C), 120.6. The spectroscopic data are in accordance with the literature.[10]



(Z)-3-chloro-1-(4-fluoro-2-(trifluoromethyl)phenyl)-3-phenylprop-2-en-1-one (2m): The title compound was isolated in 80% (39 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.72 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.59 (dd, *J* = 8.5, 5.3 Hz, 1H), 7.51 – 7.39 (m, 4H), 7.33 (td, *J* = 8.1, 3.4 Hz, 1H), 7.08 (s, 1H). **NMR^{13}C (100 MHz, $CDCl_3$)** δ 190.5, 164.3, 161.8, 146.5, 136.8, 131.3, 130.8 (d, *J* = 8.5 Hz, 1C), 128.8, 128.1, 127.4, 123.0, 118.9 (d, *J* = 21.2 Hz, 1C), 114.7 (dq, *J* = 25.7 e 5.1 Hz, 1C). **HRMS (ESI):** calcd. for $C_{16}H_{10}ClF_4O^+$ $[M+H]^+$ 329.0351, found 329.0354.



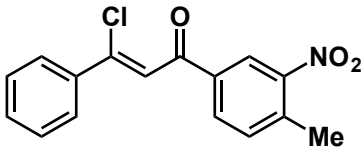
(Z)-3-chloro-1-(3-fluorophenyl)-3-phenylprop-2-en-1-one (2n): The title compound was isolated in 87% (34 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.79 – 7.74 (m, 3H), 7.70 – 7.65 (m, 1H), 7.50 – 7.42 (m, 4H), 7.31 (s, 1H), 7.31 – 7.25 (m, 1H). **NMR^{13}C (100 MHz, $CDCl_3$)** δ 188.4, 163.0 (d, *J* = 248.4 Hz, 1C), 144.4, 140.0 (d, *J* = 6.1 Hz, 1C), 137.2, 130.8, 130.4 (d, *J* = 7.7 Hz, 1C), 128.8, 127.2, 124.3 (d, *J* = 2.4 Hz, 1C), 120.8, 120.3 (d, *J* = 21.5 Hz, 1C), 115.3 (d, *J* = 22.4 Hz, 1C). **HRMS (ESI):** calcd. for $C_{15}H_{11}ClFO^+$ $[M+H]^+$ 261.0477, found 261.0482.



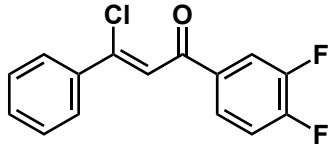
(Z)-3-chloro-1-(3-nitrophenyl)-3-phenylprop-2-en-1-one (2o): The title compound was isolated in 81% (35 mg) yield as yellow solid. **NMR ^{1}H(400 MHz, $CDCl_3$)**δ 8.78 (t, *J* = 2.0 Hz, 1H), 8.43 (ddd, *J* = 8.2, 2.3 e 1.1 Hz, 1H), 8.35 – 8.30 (m, 1H), 7.81 – 7.76 (m, 2H), 7.71 (dd, *J* = 9.6 e 6.3 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.37 (s, 1H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 187.3, 148.5, 146.1, 139.3, 136.9, 134.1,

[11] D. Wang, P. Sun, P. Jia, J. Peng, Y. Yue, C. Chen, *Synthesis*, 2017, **49**, 4309.

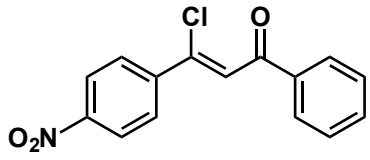
131.2, 130.0, 128.8, 127.4, 127.3, 123.3, 119.9. **HRMS (ESI):** calcd. for $C_{15}H_{11}ClNO_3^+$ $[M+H]^+$ 288.0422, found 288.0422. **m.p.** 68-70 °C.



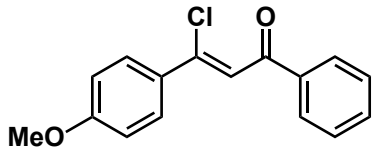
(Z)-3-chloro-1-(4-methyl-3-nitrophenyl)-3-phenylprop-2-en-1-one (2p): The title compound was isolated in 87% (40 mg) yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.53 (d, *J* = 1.8 Hz, 1H), 8.12 (dd, *J* = 8.0 e 1.8 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.53 – 7.43 (m, 4H), 7.34 (s, 1H), 2.68 (s, 3H). **NMR^{13}C (100 MHz, $CDCl_3$)** δ 187.1, 149.4, 145.5, 138.8, 136.9, 136.9, 133.5, 132.4, 131.0, 128.8, 127.3, 124.8, 120.0, 20.7. **HRMS (ESI):** calcd. for $C_{16}H_{13}ClNO_3^+$ $[M+H]^+$ 302.0578, found 302.0560. **m.p.** 117-119 °C.



(Z)-3-chloro-1-(3,4-difluorophenyl)-3-phenylprop-2-en-1-one (2q): The title compound was isolated in 90% (38 mg) yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.84 (ddd, *J* = 10.6, 7.6, 2.1 Hz, 1H), 7.80 – 7.73 (m, 3H), 7.52 – 7.41 (m, 3H), 7.32 – 7.23 (m, 2H). **NMR^{13}C (100 MHz, $CDCl_3$)** δ 187.3, 153.8 (dd, *J* = 257.6 e 12.9 Hz, 1C), 150.5 (dd, *J* = 251.5 e 12.9 Hz, 1C), 144.6, 137.0, 134.8 (t, *J* = 3.6 Hz, 1C), 130.9, 128.8, 127.2, 125.7 (dd, *J* = 7.1 e 3.3 Hz, 1C), 120.4, 117.9 (d, *J* = 18.3 Hz, 1C), 117.7 (d, *J* = 18.0 Hz, 1C). **HRMS (ESI):** calcd. for $C_{15}H_{10}ClF_2O^+$ $[M+H]^+$ 279.0383, found 279.0384. **m.p.** 37-40 °C.

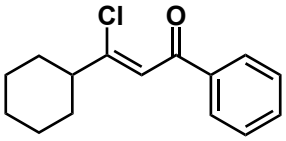


(Z)-3-chloro-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (2r): The title compound was isolated in 99% (43 mg) yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.29 (d, *J* = 8.9 Hz, 2H), 8.00 (d, *J* = 7.3 Hz, 2H), 7.92 (d, *J* = 8.9 Hz, 2H), 7.64 – 7.61 (m, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.42 (s, 1H). **NMR^{13}C (100 MHz, $CDCl_3$)** δ 189.7, 148.8, 143.1, 139.8, 137.0, 134.0, 129.0, 128.9, 128.2, 125.0, 124.0. The spectroscopic data are in accordance with the literature.[9]

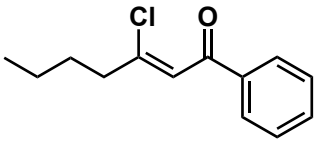


(Z)-3-chloro-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (2s): The title compound was isolated in 75% (31 mg) yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.01 – 7.97 (m, 2H), 7.73 (d, *J* = 8.9 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.51 – 7.46 (m, 2H), 7.33 (s, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H). **NMR^{13}C**

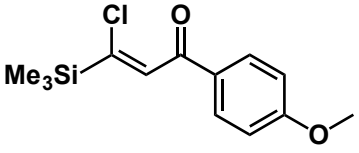
(100 MHz, $CDCl_3$) δ 189.8, 161.8, 143.9, 138.3, 133.2, 130.8, 129.0, 128.8, 128.7, 127.1, 114.1, 55.6. The spectroscopic data are in accordance with the literature.[12]



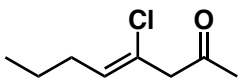
(Z)-3-chloro-3-cyclohexyl-1-phenylprop-2-en-1-one (2t): The title compound was isolated in 46% (17 mg) yield as orange oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.94 – 7.90 (m, 2H), 7.50 – 7.43 (m, 3H), 7.02 (s, 1H), 3.73 (tt, *J* = 11.4 e 3.3 Hz, 1H), 1.83 – 1.70 (m, 5H), 1.57 (dd, *J* = 11.7, 3.5 Hz, 2H), 1.44 – 1.34 (m, 2H), 1.27 – 1.17 (m, 1H). **NMR^{13}C (100 MHz, $CDCl_3$)** δ 188.7, 138.2, 133.0, 128.6, 128.3, 122.4, 42.6, 30.6, 25.6, 21.6. The spectroscopic data are in accordance with the literature.[13]



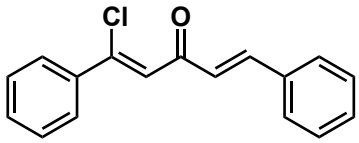
(Z)-3-chloro-1-phenylhept-2-en-1-one (2u): The title compound was isolated in 65% (22 mg) yield asn orange oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.95 – 7.89 (m, 2H), 7.59 – 7.53 (m, 1H), 7.50 – 7.44 (m, 2H), 7.12 (s, 1H), 3.03 – 2.92 (m, 2H), 1.76 – 1.60 (m, 2H), 1.49 – 1.33 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 188.6, 157.8, 138.2, 133.0, 128.7, 128.3, 123.3, 36.2, 29.9, 22.1, 13.8. The spectroscopic data are in accordance with the literature.[14]



(Z)-3-chloro-1-(4-methoxyphenyl)-3-(trimethylsilyl)prop-2-en-1-one (2v): The title compound was isolated in 98% (40 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.97 – 7.90 (m, 2H), 7.73 (s, 1H), 6.98 – 6.91 (m, 2H), 3.88 (s, 3H), 0.30 – 0.28 (m, 9H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 188.6, 164.7, 160.3, 138.5, 131.8, 131.2, 114.8, 56.4, 0.0. **HRMS (ESI):** calcd. for $C_{13}H_{18}ClO_2Si^+$ $[M+H]^+$ 269.0759, found 269.0760.



(*Z*)-4-chlorooct-4-en-2-one (2w'): The title compound was isolated in 50% (12 mg) yield as a yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 5.65 (t, *J* = 7.0 Hz, 1H), 3.40 – 3.35 (m, 2H), 2.26 – 2.16 (m, 5H), 1.51 – 1.39 (sext, *J* = 7.4 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ. 204.6, 130.9, 126.8, 53.9, 30.8, 29.0, 21.7, 13.7. **HRMS (ESI):** calcd. for $C_8H_{14}ClO^+$ $[M+H]^+$ 161.0728, found 161.0725.

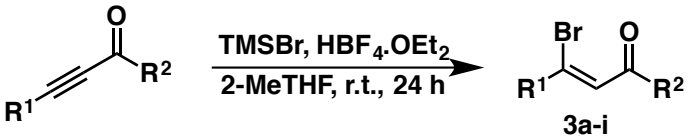


(1Z,4E)-1-chloro-1,5-diphenylpenta-1,4-dien-3-one (2x): The title compound was isolated in 89% (36 mg) yield as an orange oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.77 – 7.72

[12] P. Gandeepan, K. Parthasarathy, T.-H. Su and C.-H. Cheng, *Adv. Synth. Catal.*, 2012, **354**, 457.
[13] H. Y. Kim and K. Oh, *Org. Lett.,* 2017, **19**, 4904.
[14] J. L. Gras, B. S. Galledou, *Bull. Soc. Chim. Fr.*, 1983, **3**, 89.

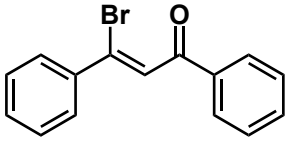
(m, 2H), 7.68 (d, *J* = 16.0, 1H), 7.62 – 7.56 (m, 2H), 7.50 – 7.36 (m, 6H), 7.04 – 7.02 (m, 2H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ.188.6, 144.1, 143.0, 137.4, 134.6, 130.7, 130.6, 129.0, 128.7, 128.5, 127.3, 127.1, 123.6. **HRMS (ESI):** calcd. for $C_{17}H_{14}ClO^+$ [M+H]+ 269.0728, found 269.0735.

Hydrobromination of Ynones.

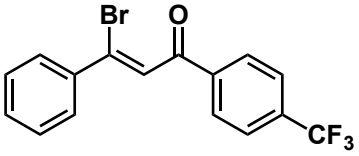


3a-i

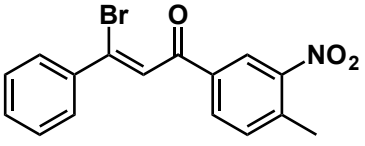
To a solution of ynone (0.15 mmol) in 2-MeTHF (0.4 mL) wasdded $HBF_4.OEt_2$ (82.4 μL, 0.30 mmol, 50 wt/wt%, 2 equiv) and TMSBr (0.3 mmol, 2 equiv) at room temperature, then the mixture was monitored by TLC. After completion, the solvent was evaporated under the reduced pressure and the residue was purified by silica gel column chromatography (*n*-hexanes/EtOAc) to afford the corresponding products **3a-i.**



(Z)-3-bromo-1,3-diphenylprop-2-en-1-one (3a): The title compound was isolated in 80% (34 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.74 – 7.68 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.52 (s, 1H), 7.43 (t, *J* = 8.9 Hz, 3H), 7.46 – 7.40 (m, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 190.5, 139.2, 137.2, 134.2, 133.5, 130.4, 128.8, 128.8, 128.6, 128.0, 125.62. The spectroscopic data are in accordance with the literature.[15]

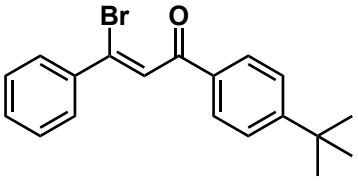


(Z)-3-bromo-3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (3b): The title compound was isolated in 83% (44 mg) yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.73 – 7.70 (m, 2H), 7.52 (s, 1H), 7.45 (dd, *J* = 5.1, 1.9 Hz, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 189.3, 140.1, 139.0, 136.1, 130.7, 130.2, 129.1, 128.7, 128.2, 128.1, 125.8, 124.6. **HRMS (ESI):** calcd. for $C_{16}H_{11}BrF_3O^+$ $[M+H]^+$ 354.9940, found 354.9942. **m.p.** 77-79 °C

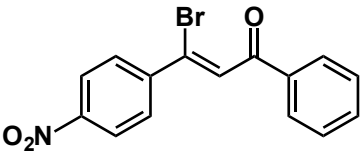


(Z)-3-bromo-1-(4-methyl-3-nitrophenyl)-3-phenylprop-2-en-1-one (3c): The title compound was isolated in 80% (42 mg) yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.55 (d, *J* = 1.9 Hz, 1H), 8.14 (dd, *J* = 8.0 e 1.8 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.52 – 7.41 (m, 5H), 2.69 (s, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 187.8, 149.4, 138.9, 138.8, 136.6, 136.4, 133.5, 132.5, 130.8, 128.7, 128.1, 124.9, 124.1, 20.7. **HRMS (ESI):** calcd. for $C_{16}H_{13}BrNO_3^+$ $[M+H]^+$ 346.0073, found 346.0072. **m.p.** 103-106 °C.

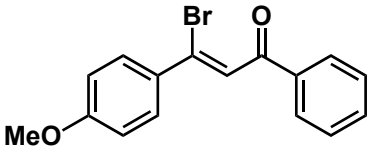
[15] E. Schraufstatter and S. Deutsch, *Zeitschrift für Naturforschung*, 1949, **4**, 276.



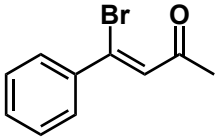
(Z)-3-bromo-1-(4-(*tert*-butyl)phenyl)-3-phenylprop-2-en-1-one (3d): The title compound was isolated in 80% (41 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.62 (dd, *J* = 6.5 e 3.0 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.42 (s, 1H), 7.37 – 7.30 (m, 3H), 1.25 (s, 9H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 190.2, 157.4, 139.3, 134.6, 133.6, 128.8, 128.8, 128.6, 128.0, 125.8, 125.6, 35.2, 31.1. **HRMS (ESI):** calcd. for $C_{19}H_{20}BrO^+$ $[M+H]^+$ 343.0692, found 343.0693.



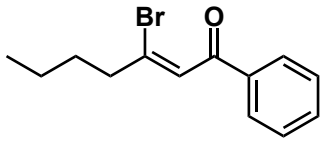
(Z)-3-bromo-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (3e): The title compound was isolated in 97% (48 mg) yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.28 (d, *J* = 9.0 Hz, 2H), 8.01 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.91 – 7.84 (m, 3H), 7.60, 7.57 – 7.49 (m, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 190.2, 144.8, 136.4, 134.0, 131.3, 130.2, 129.6, 128.9, 128.8, 123.8, 123.4. The spectroscopic data are in accordance with the literature.[9]



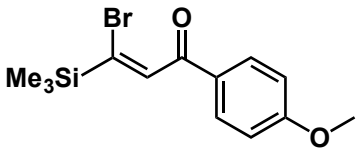
(Z)-3-bromo-3-(4-methoxyphenyl)-1-(p-tolyl)prop-2-en-1-one (3f): The title compound was isolated in 98% (48 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.00 (dd, *J* = 8.4 e 1.3 Hz, 1H), 7.68 (d, *J* = 9.1 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.52 – 7.48 (s, 3H), 6.93 (d, *J* = 9.0 Hz, 1H), 3.85 (s, 2H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 190.2, 161.4, 137.7, 134.8, 133.3, 131.5, 130.8, 129.7, 128.7, 123.4, 113.9, 55.5. **HRMS (ESI):** calcd. for $C_{16}H_{13}BrKO_2^+$ $[M+K]^+$ 354.9731, found 354.9735.



(Z)-4-bromo-4-phenylbut-3-en-2-one (3g): The title compound was isolated in 82% (28 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.42 – 7.19 (m, 5H), 6.92 (s, 1H), 2.37 (s, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 196.7, 139.4, 133.7, 130.4, 128.6, 128.2, 128.0, 31.8. The spectroscopic data are in accordance with the literature.[9]

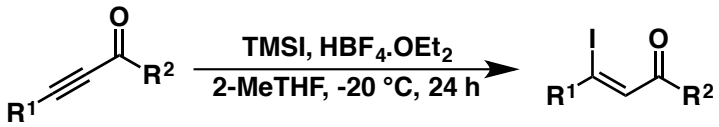


(Z)-3-bromo-1-phenylhept-2-en-1-one (3h): The title compound was isolated in 80% (32 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.92 – 7.87 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 3H), 5.76 (t, *J* = 6.9 Hz, 1H), 4.05 (s, 2H), 2.12 (q, *J* = 7.1 Hz, 2H), 1.37 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 195.6, 136.4, 133.9, 133.4, 128.7, 128.4, 118.5, 50.5, 33.6, 21.6, 13.7. **HRMS (ESI):** calcd. for $C_{13}H_{16}BrO^+$ $[M+H]^+$ 291.0178, found 291.0178.



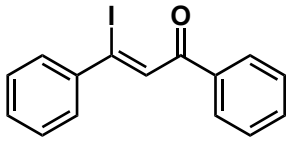
(Z)-3-bromo-1-(4-methoxyphenyl)-3-(trimethylsilyl)prop-2-en-1-one (3i): The title compound was isolated in 89% (42 mg) yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 9.0 Hz, 2H), 7.19 (s, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 3.73 (s, 3H), 0.15 (s, 9H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 193.4, 166.1, 140.3, 139.2, 133.7, 131.0, 116.1, 57.6, 0.0. **HRMS (ESI):** calcd. for $C_{13}H_{18}BrO_2Si^+$ $[M+H]^+$ 315.0254, found 315.0234. **m.p.** 69-73 °C.

Hydroiodination of Ynones.

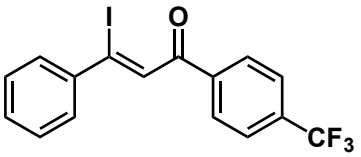


4a-e

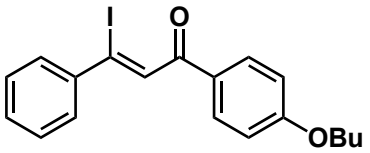
To a solution of ynone (0.15 mmol) in 2-MeTHF (0.4 mL) wasdded $HBF_4.OEt_2$ (82.4 μL, 0.30 mmol, 50 wt/wt%, 2 equiv) and TMSI (0.3 mmol, 2 equiv) at – 20 °C in the darkness, then the mixture was monitored by TLC. After completion, the solvent was evaporated under the reduced pressure and the residue was purified by silica gel column chromatography (*n*-hexanes/EtOAc) to afford the corresponding products **4a-e.**



(Z)-3-iodo-1,3-diphenylprop-2-en-1-one (4a): The title compound was isolated in 89% (45 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 7.1 Hz, 2H), 7.65 – 7.56 (m, 3H), 7.54 (s, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.39 (m, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 190.5, 143.2, 138.7, 137.0, 133.5, 131.6, 130.0, 128.8, 128.7, 128.5, 113.3. **HRMS (ESI):** calcd. for $C_{15}H_{11}IOK^+$ $[M+K]^+$ 373.2542, found 373.2171.

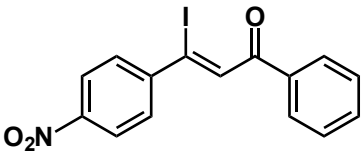


(Z)-3-iodo-3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (4b): The title compound was isolated in 96% (58 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.11 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.66 – 7.59 (m, 3H), 7.57 (s, 1H), 7.46 – 7.38 (m, 4H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 189.2, 143.1, 139.9, 138.0, 130.4, 129.1, 128.9, 128.8, 128.6, 128.2, 125.8, 115.5. **HRMS (ESI):** calcd. for $C_{16}H_{11}F_3IO^+$ $[M+H]^+$ 402.9801, found 402.9805.

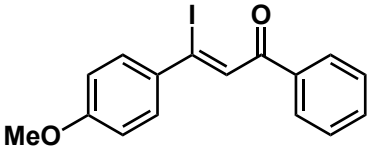


(Z)-1-(4-butoxyphenyl)-3-iodo-3-phenylprop-2-en-1-one (4c): The title compound was isolated in 93% (56 mg) yield as brown oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 9.0 Hz, 2H), 7.63 – 7.58 (m, 2H), 7.46 (s, 1H), 7.42 – 7.35 (m, 3H), 6.95 (d, J = 9.0 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 1.84 – 1.73 (m, 2H),

1.56 – 1.44 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 189.6, 163.6, 143.2, 139.0, 132.3, 131.2, 129.8, 128.7, 128.5, 114.4, 111.6, 68.0, 31.1, 19.2, 13.8. **HRMS (ESI):** calcd. for $C_{19}H_{20}IO_2^+$ $[M+H]^+$ 407.0504, found 407.0502.

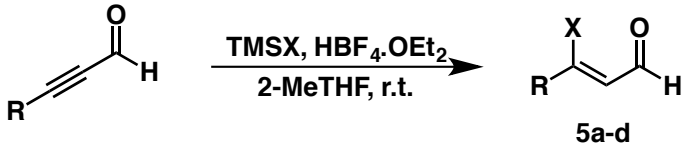


(Z)-3-iodo-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (4d): The title compound was isolated in 94% (53 mg) yield as yellow oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 9.0 Hz, 2H), 8.01 (dd, *J* = 8.4 e 1.3 Hz, 2H), 7.77 (d, *J* = 9.0 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.60 (s, 1H), 7.53 (t, *J* = 7.6 Hz, 2H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 190.4, 149.0, 148.3, 139.8, 136.3, 129.6, 129.0, 128.9, 128.8, 123.7, 108.5. **HRMS (ESI):** calcd. for $C_{15}H_{11}INO_3^+$ $[M+H]^+$ 379.9778, found 379.9742.



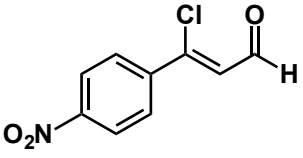
(Z)-3-iodo-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (4e): The title compound was isolated in 86% (47 mg) yield as brown oil. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 9.0 Hz, 2H), 7.51 (s, 1H), 7.52 – 7.45 (m, 3H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 190.2, 161.2, 135.6, 133.3, 130.5, 129.4, 128.7, 128.6, 127.0, 113.8, 113.8, 92.4, 55.4. **HRMS (ESI):** calcd. for $C_{16}H_{14}IO_2^+$ $[M+H]^+$ 365.0033, found 365.0009.

Hydrohalogenation of Ynals.



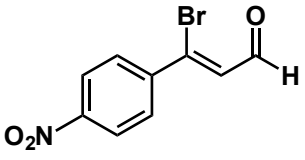
5a-d

To a solution of ynal (0.15 mmol) in 2-MeTHF (0.4 mL) were added $HBF_4.OEt_2$ (82.4 μL, 0.30 mmol, 50 wt/wt%, 2 equiv) and TMSX (X = Cl or Br, 0.30 mmol, 2 equiv) at room temperature, then the mixture was monitored by TLC. After completion, the solvent was evaporated under the reduced pressure and the residue was purified by silica gel column chromatography (*n*-hexanes/EtOAc) to afford the corresponding products **5a-e.**

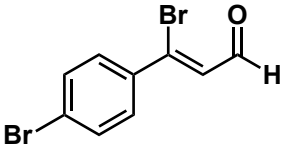


(Z)-3-chloro-3-(4-nitrophenyl)acrylaldehyde (5a): The title compound was isolated in 46% (14 mg) yield as red solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 10.25 (d, *J* = 6.6, 1H), 8.32 (d, *J* = 8.9, 2H), 7.93 (d, *J* = 8.9, 2H), 6.75 (d, *J* = 6.7, 1H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 190.6, 141.4, 133.9, 130.6, 128.2, 126.8, 124.1. The spectroscopic data are in accordance with the literature.[16]

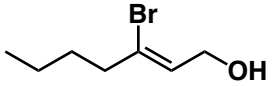
[16] R. K. Sodhi, S. Paul, J.H. Clark, *Green Chem.*, 2012, **14**, 1649.



(Z)-3-bromo-3-(4-nitrophenyl)acrylaldehyde (5b): The title compound was isolated in 81% (31 mg) yield as red solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 10.08 (d, *J* = 6.3 Hz, 1H), 8.31 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 6.4 Hz, 1H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 192.8, 149.3, 143.3, 141.1, 129.8, 129.0, 124.0. The spectroscopic data are in accordance with the literature.[17]



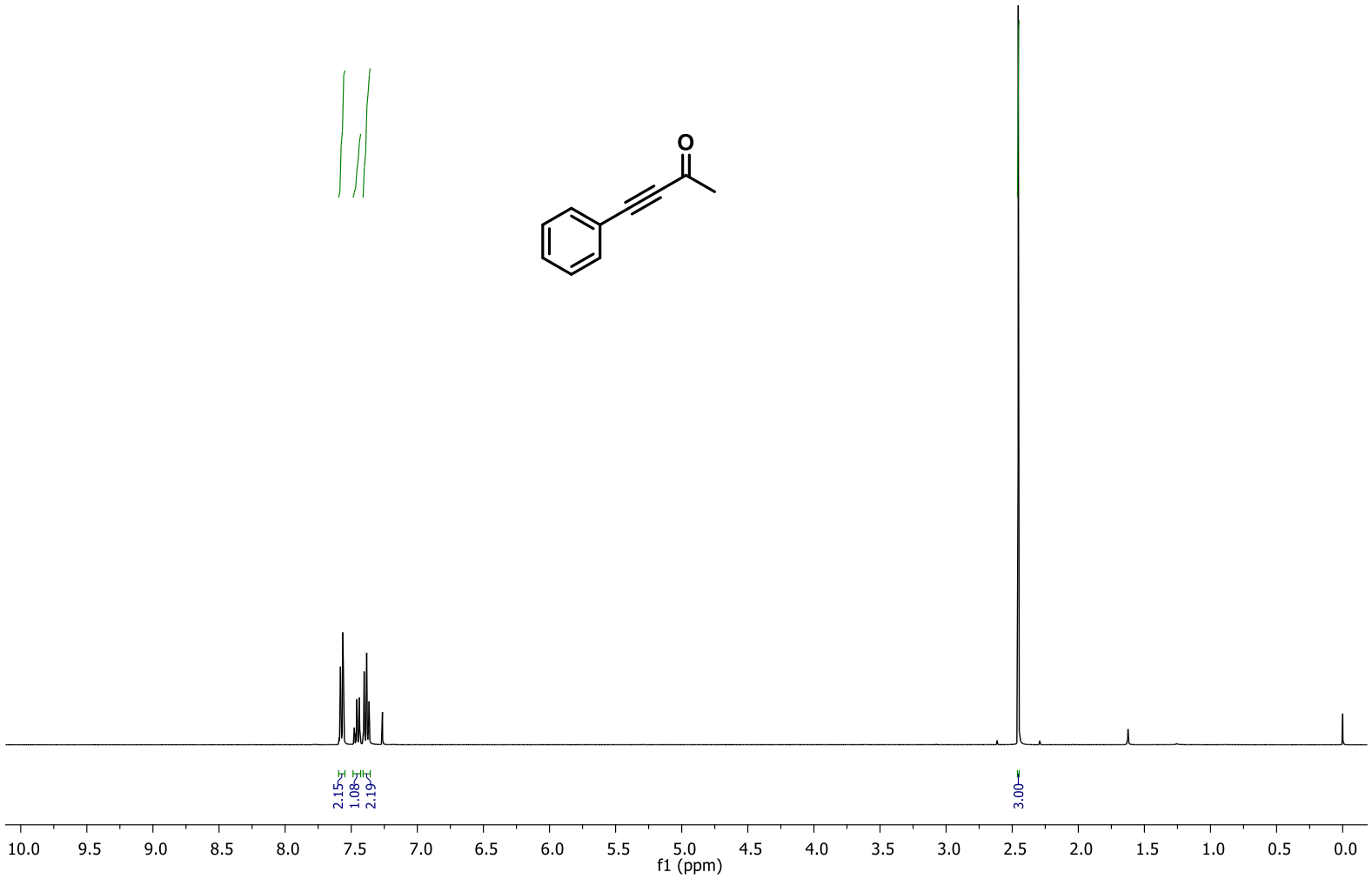
(Z)-3-bromo-3-(4-bromophenyl)acrylaldehyde (5c): The title compound was isolated in 83% (36 mg) yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 10.05 (d, *J* = 6.5 Hz, 1H), 7.60 – 7.55 (m, 4H), 6.77 (d, J = 6.5 Hz, 1H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 193.5, 143.5, 136.5, 132.2, 129.6, 127.8, 126.5. The spectroscopic data are in accordance with the literature.[18]



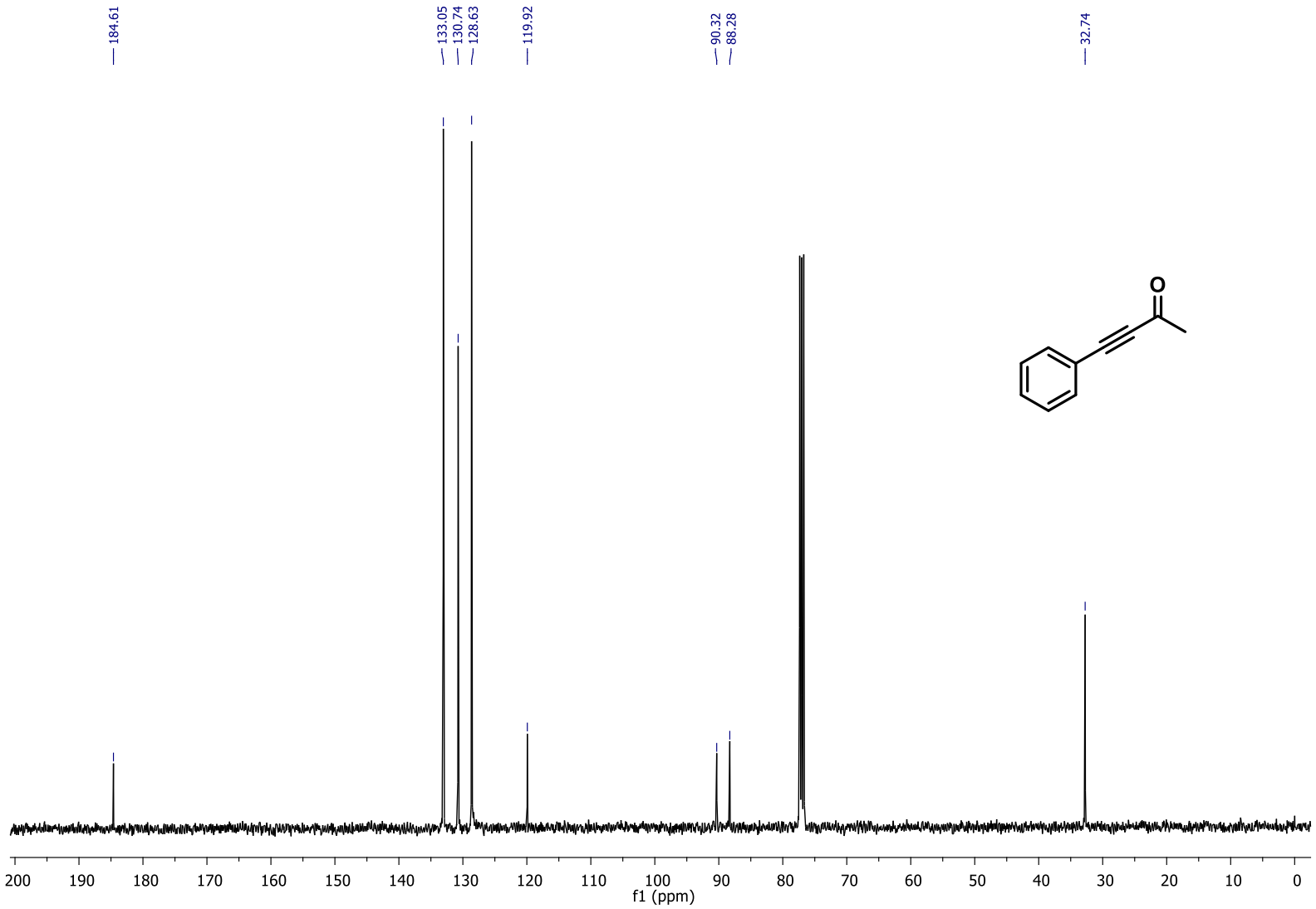
(Z)-3-bromohept-2-en-1-ol (5d): The title compound was isolated in 36% (11 mg) yield as yellow solid. **NMR ^{1}H (400 MHz, $CDCl_3$)** δ 5.93 (tt, *J* = 6.0 e 1.1 Hz, 1H), 4.26 (d, *J* = 6.1 Hz, 2H), 2.46 (td, *J* = 7.8 e 0.9 Hz, 2H), 1.55 (m, 3H), 1.33 (sext, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **NMR ^{13}C (100 MHz, $CDCl_3$)** δ 130.9, 127.4, 62.4, 41.2, 30.1, 21.6, 13.8. **HRMS (ESI):** calcd. for $C_7H_{14}BrO^+$ $[M+H]^+$ 193.0223, found 193.0220.

[17] G. Wang, X. Chen, G. Miao, W. Yao, C. Ma, *J. Org. Chem.*, 2013, **78**, 6223.
[18] T. Zhu, C. Mou, B. Li, Marie S., B.-A. Song, Y. R. Chi , *J. Am. Chem. Soc.*, 2015, **137**, 5658.

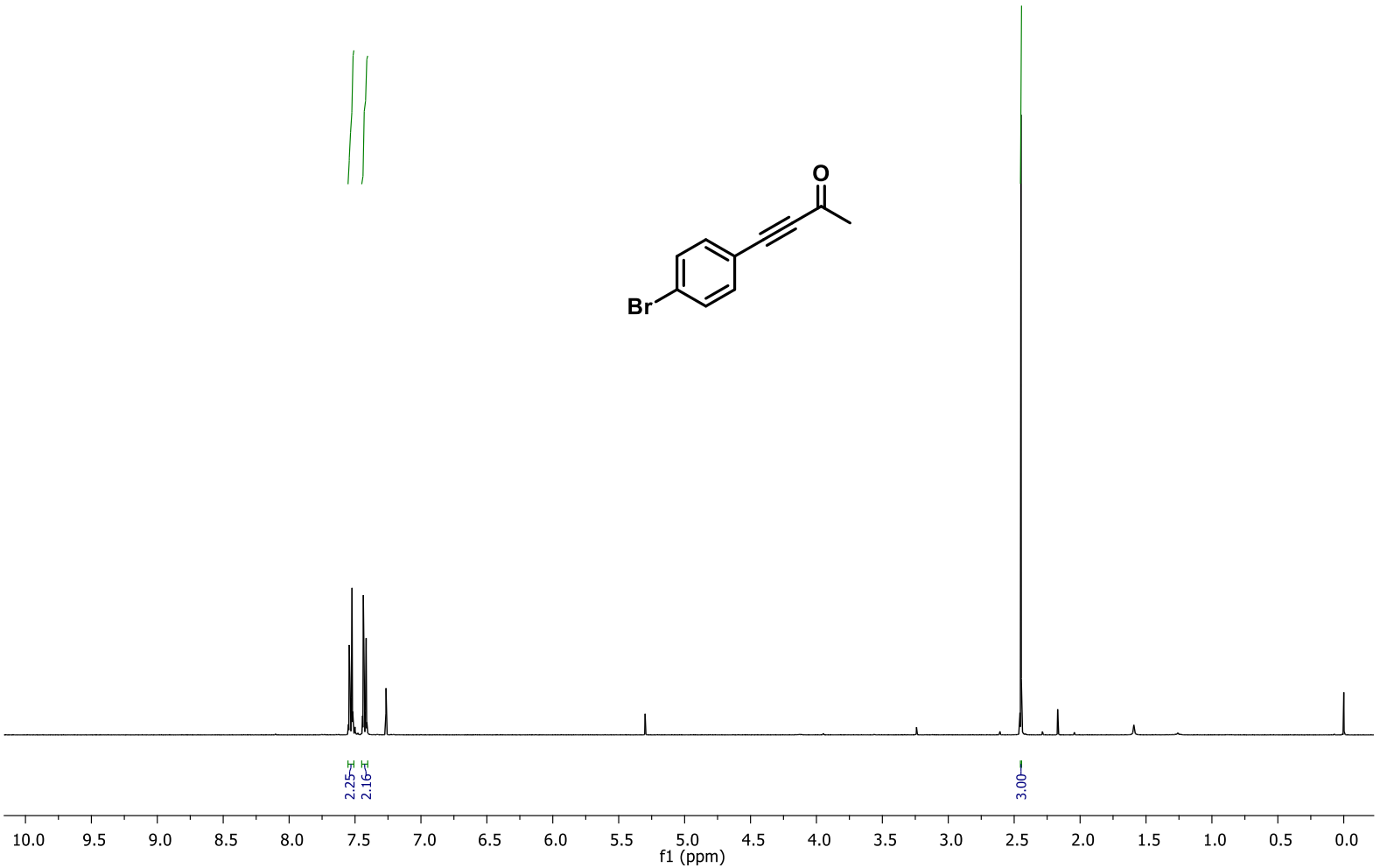
NMR Spectra



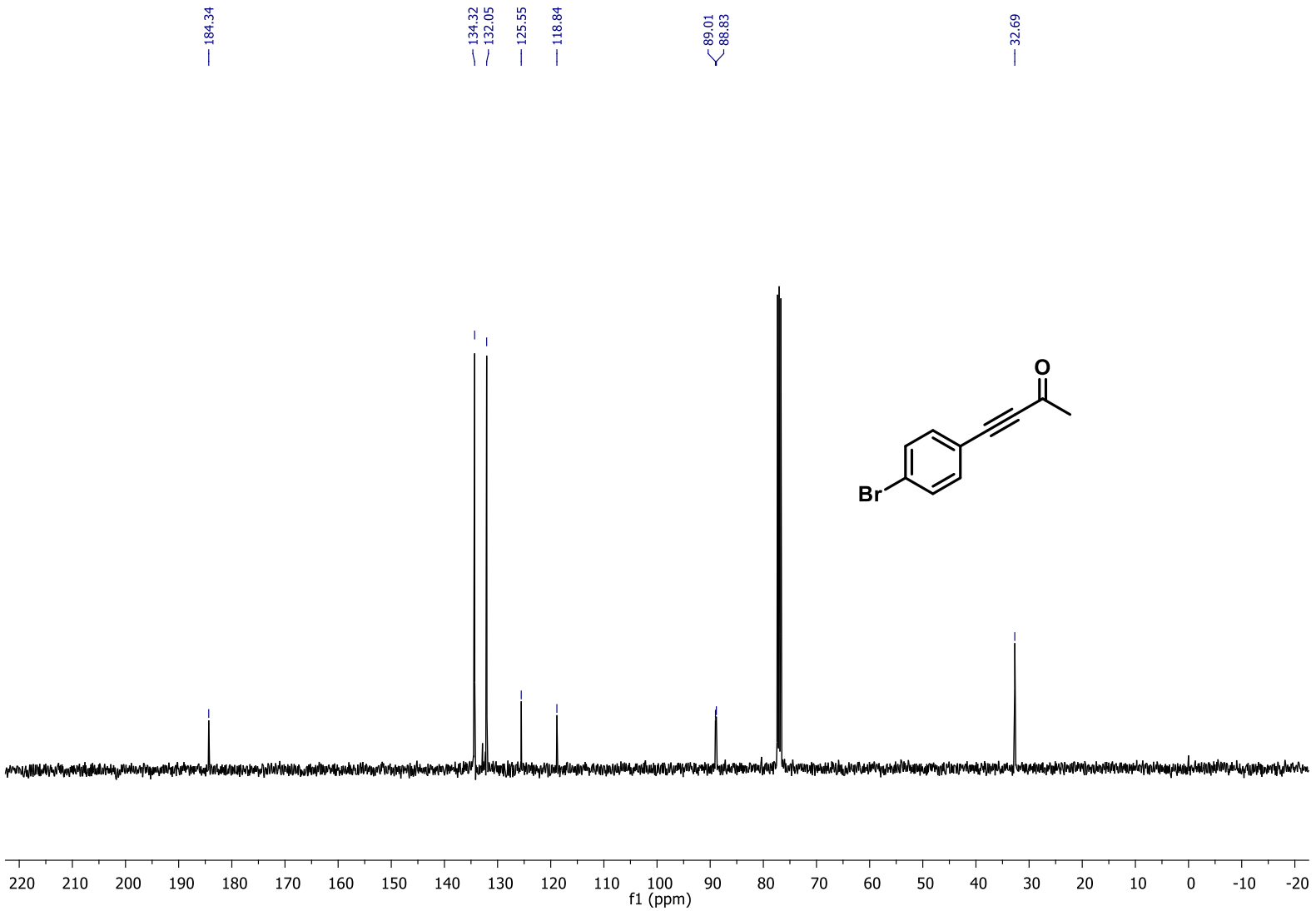
^{1}H NMR of compound **1a** (400 MHz, $CDCl_3$)



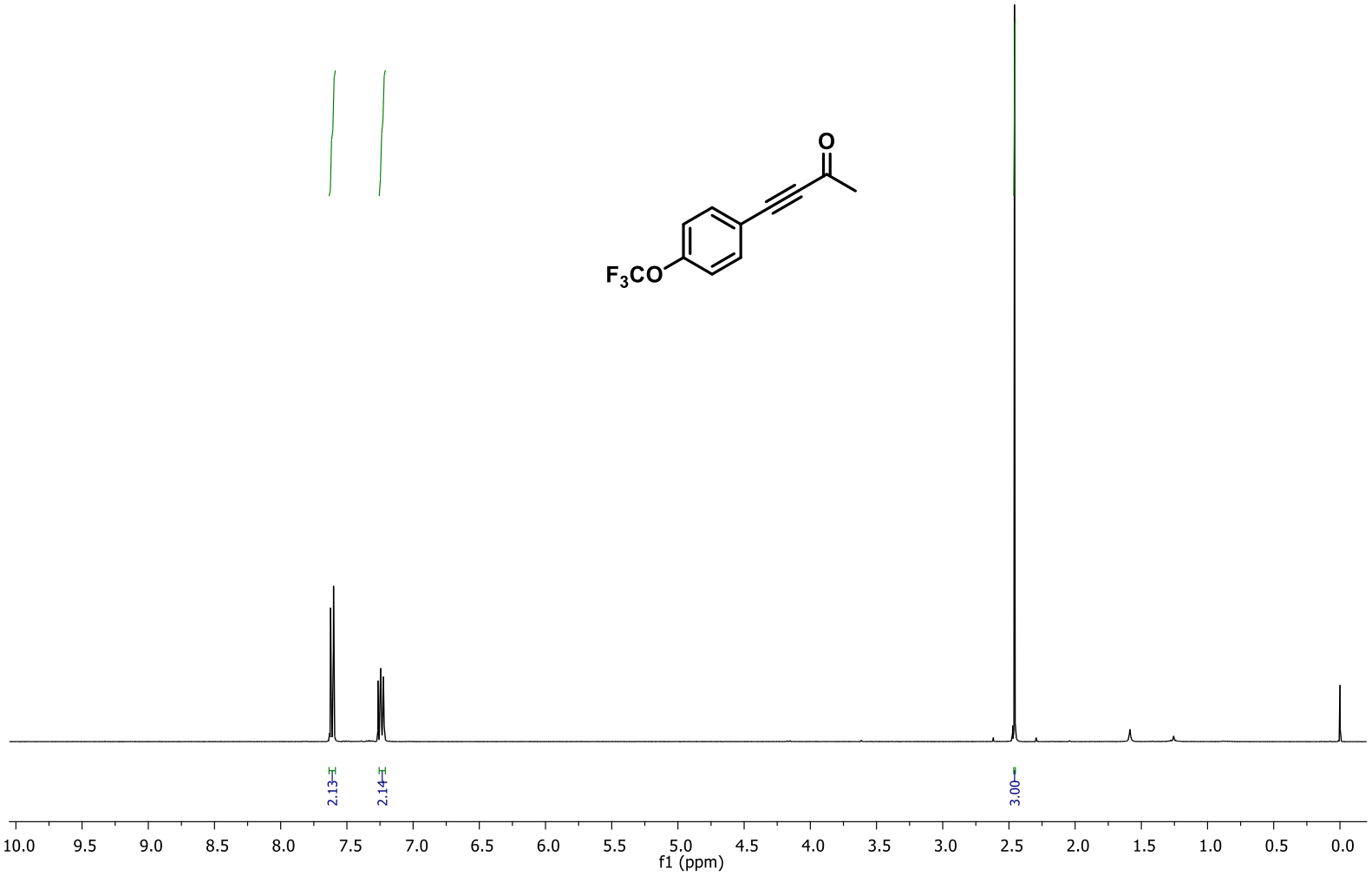
^{13}C NMR of compound **1a** (100 MHz, $CDCl_3$)



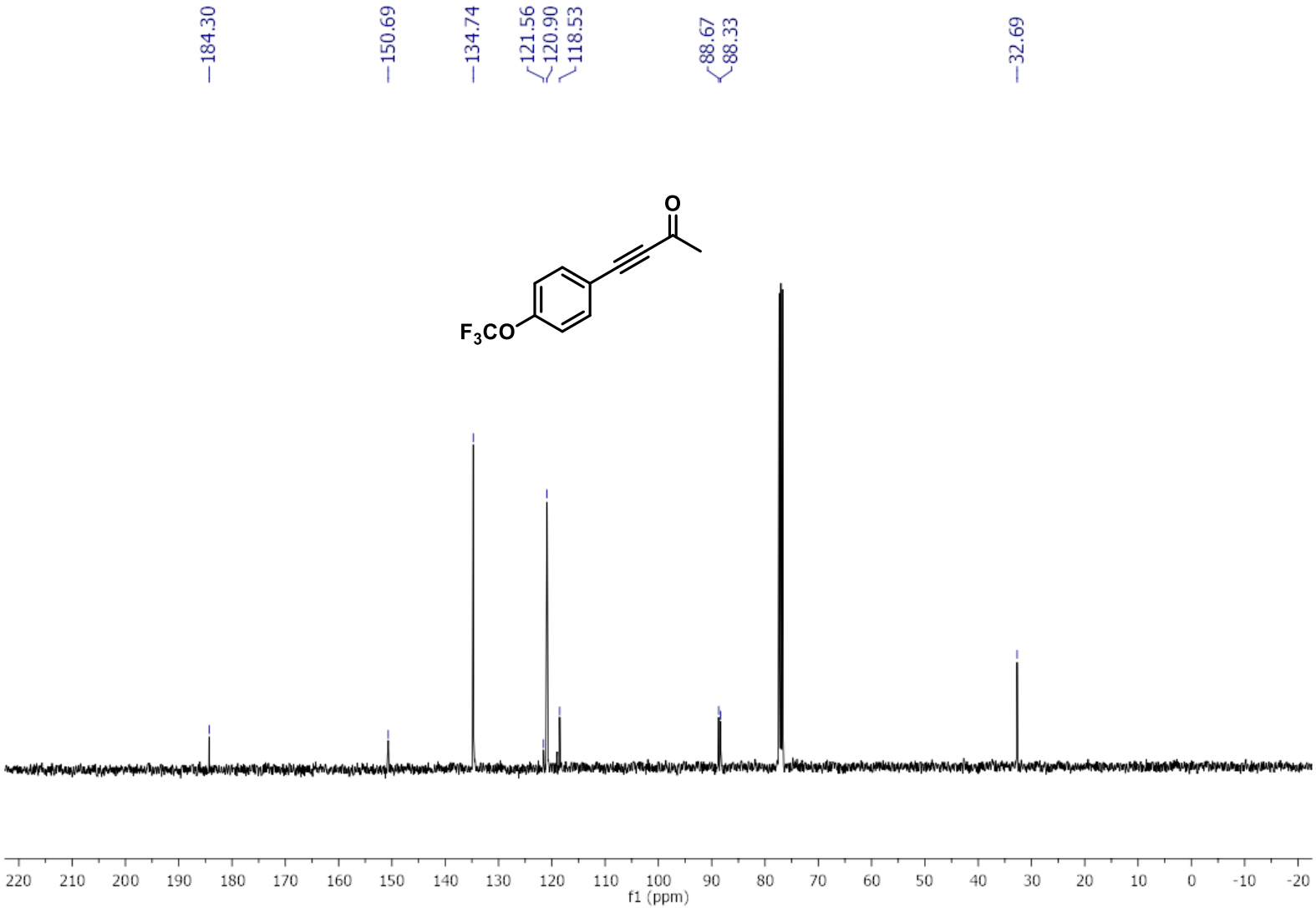
^{1}H NMR of compound **1b** (400 MHz, $CDCl_3$)



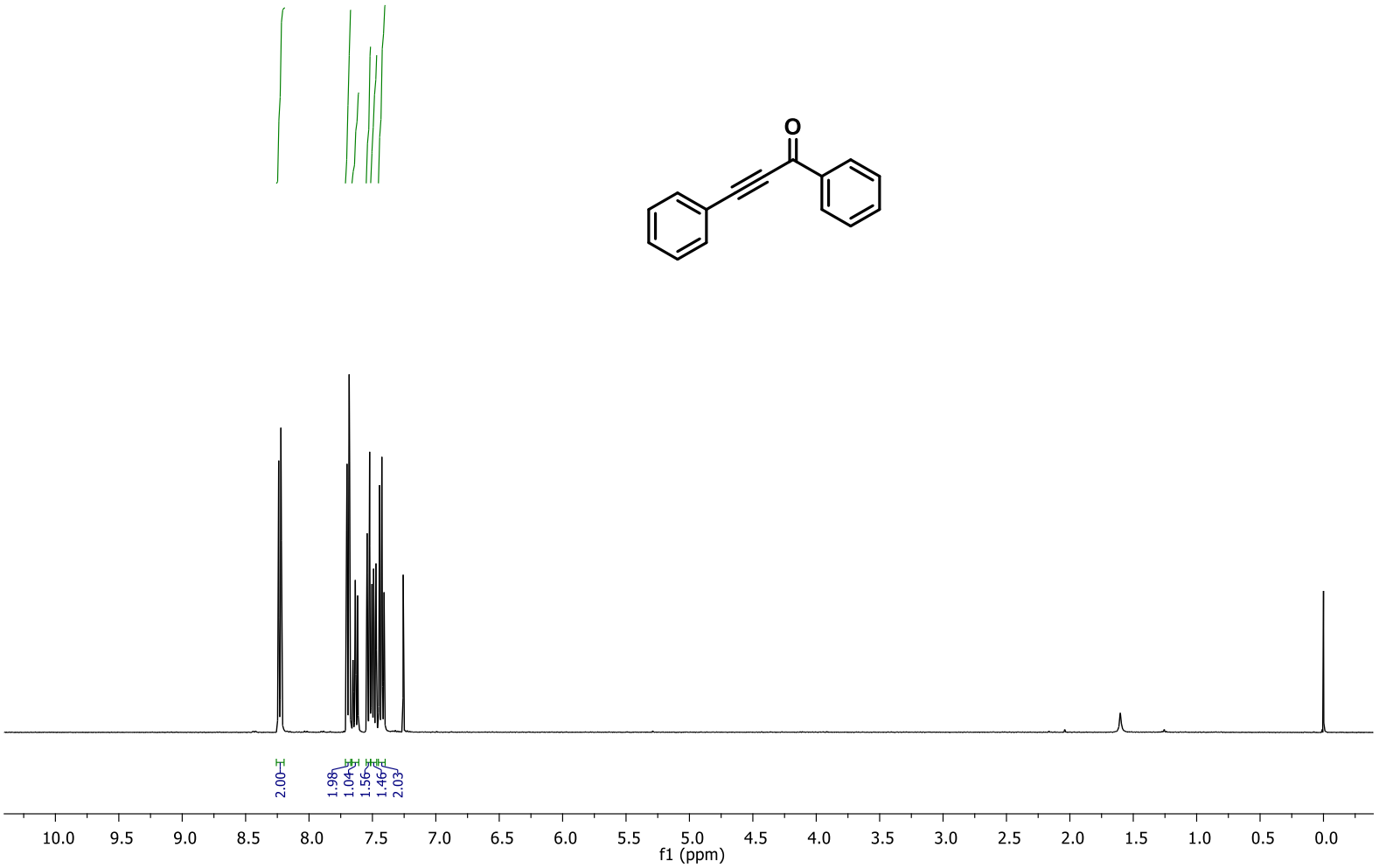
^{13}C NMR of compound **1b** (100 MHz, $CDCl_3$)



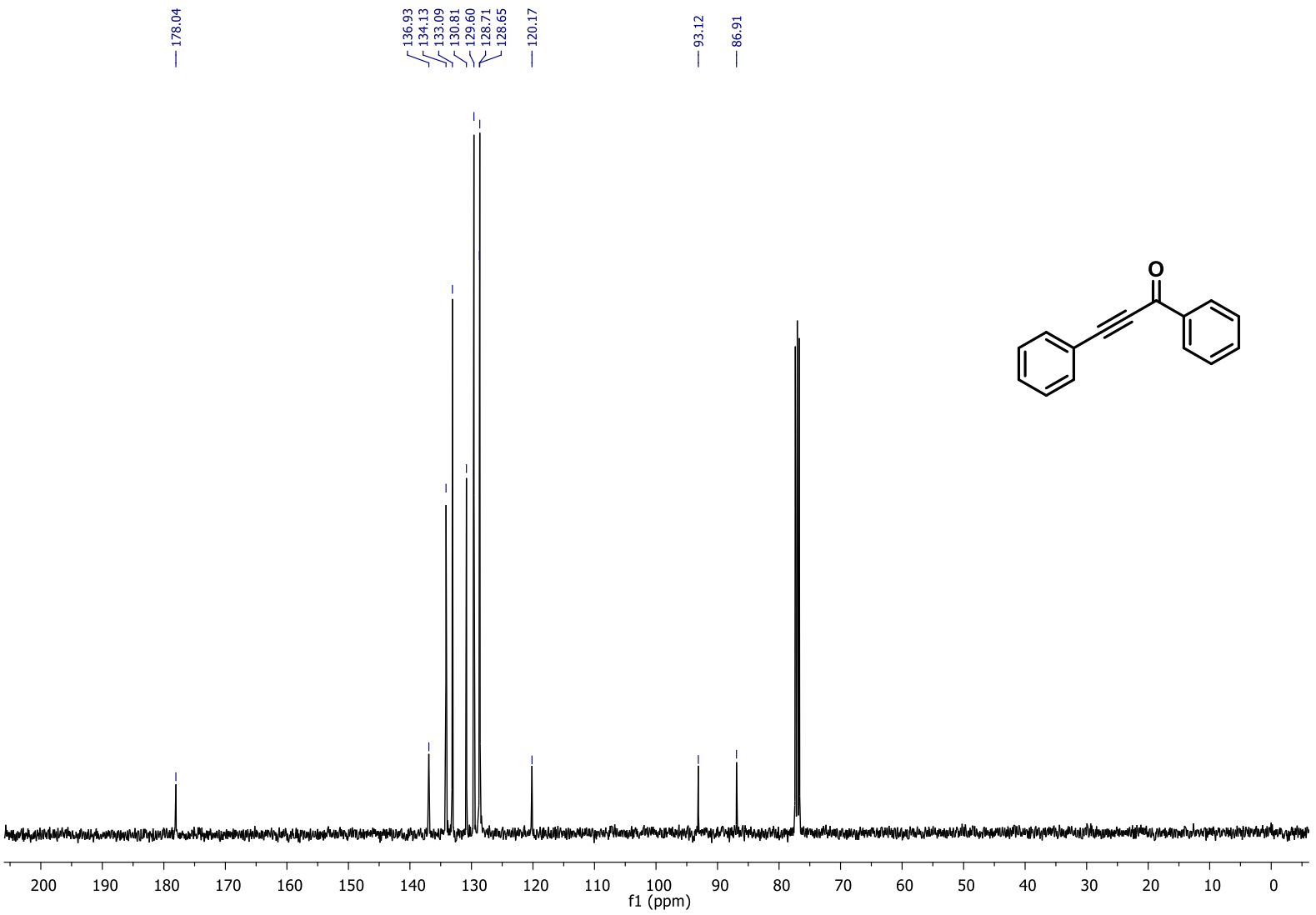
^{1}H NMR of compound **1c** (400 MHz, $CDCl_3$)



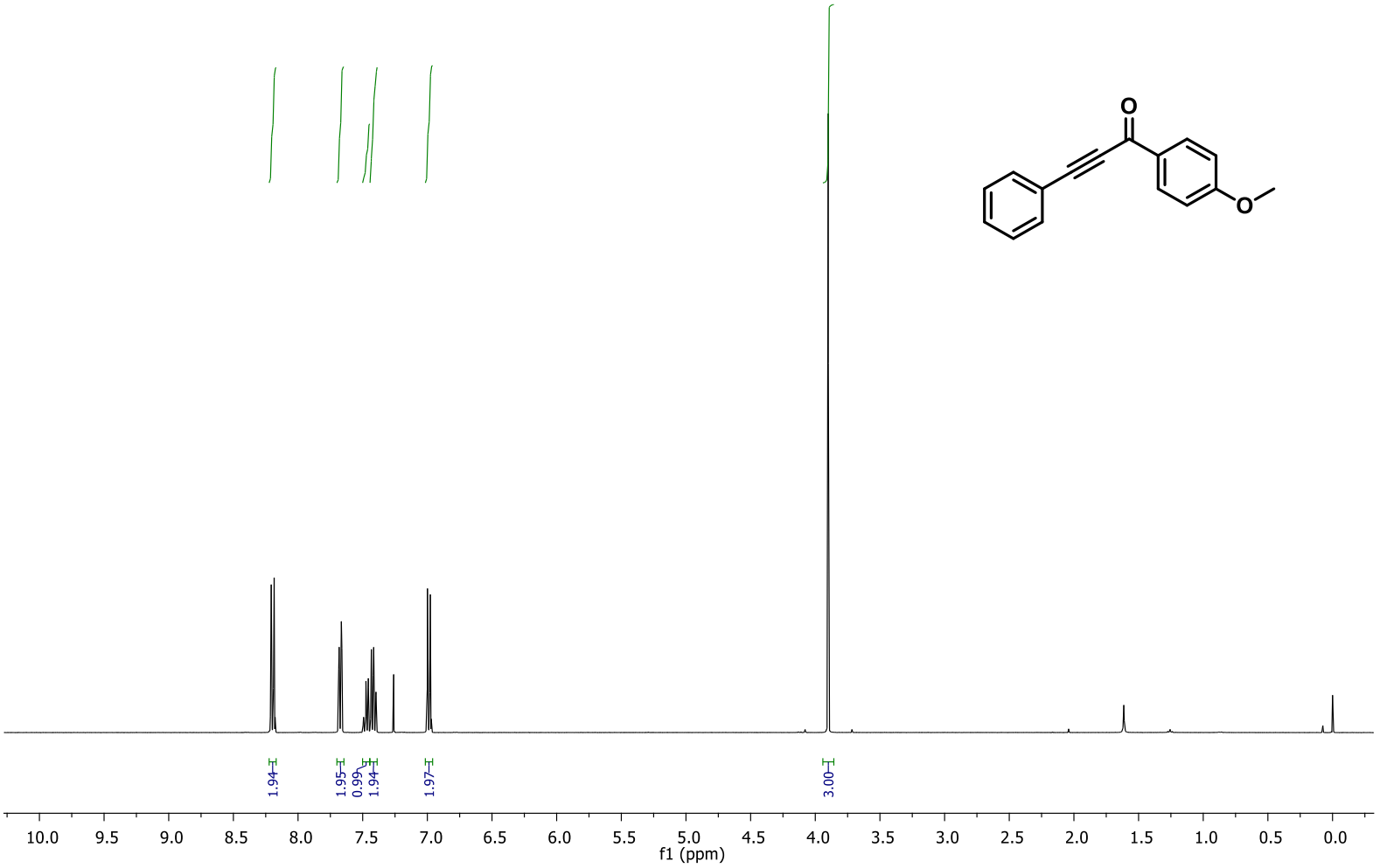
^{13}C NMR of compound **1c** (100 MHz, $CDCl_3$)



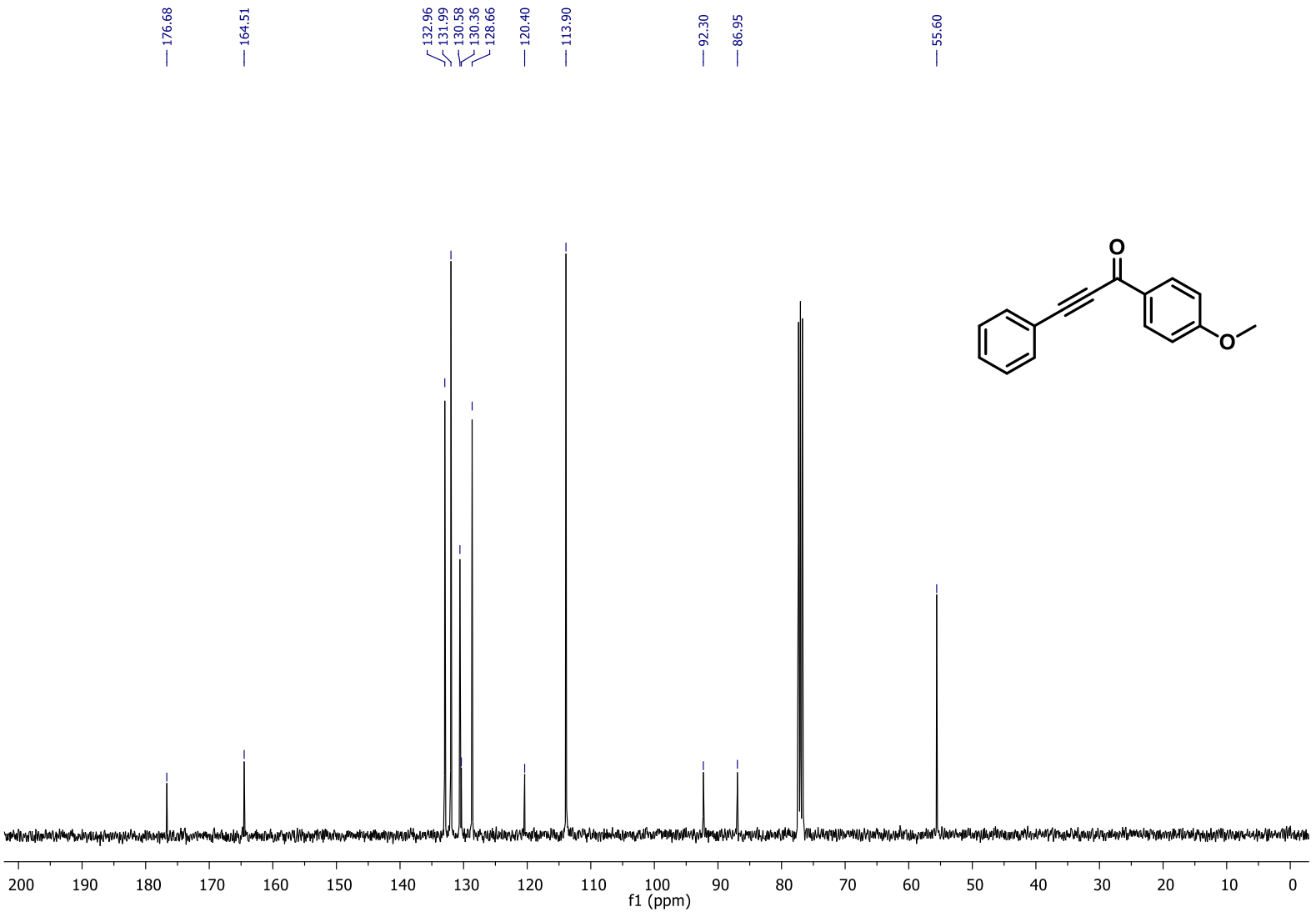
^{1}H NMR of compound **1d** (400 MHz, $CDCl_3$)



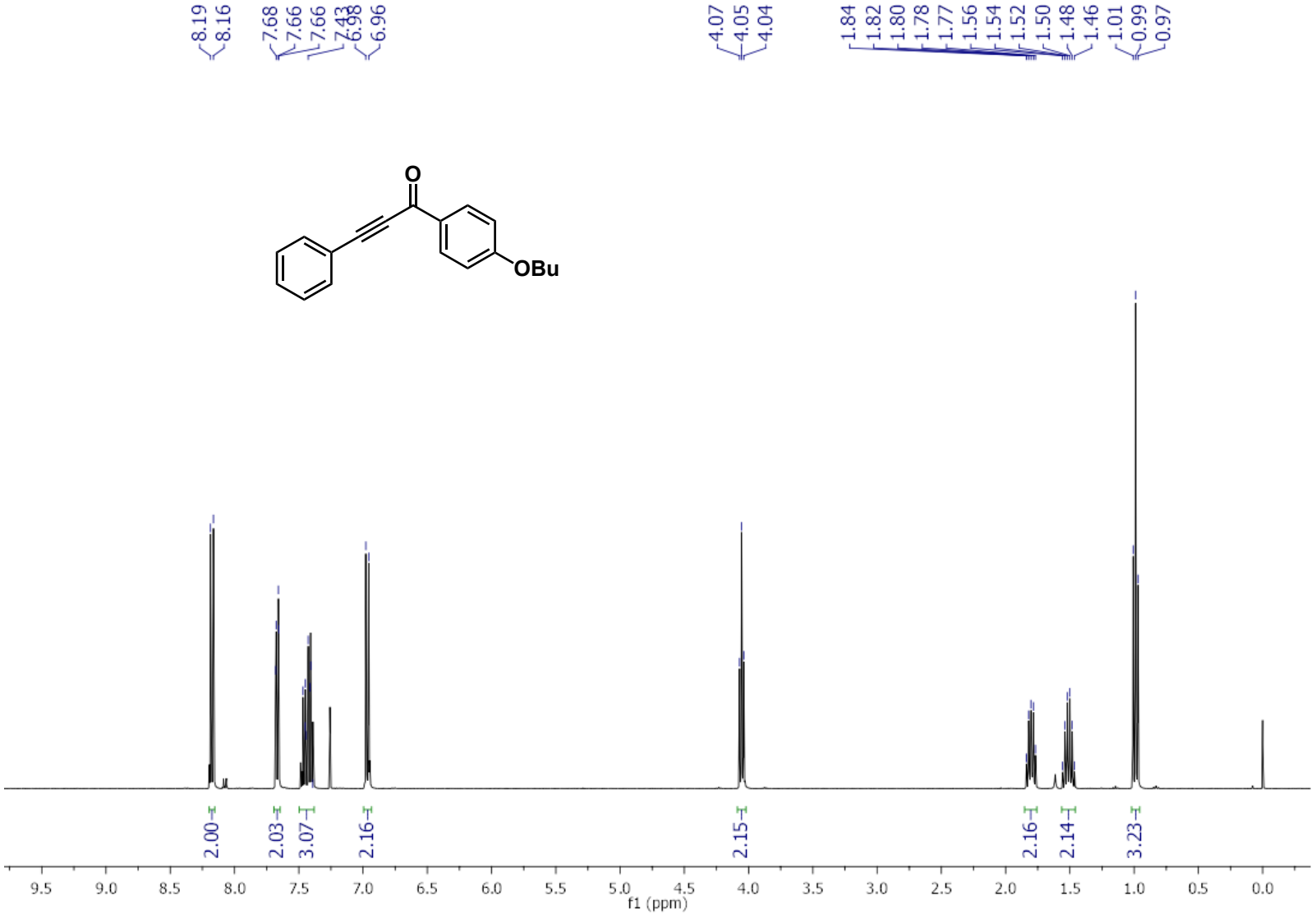
^{13}C NMR of compound **1d** (100 MHz, $CDCl_3$)



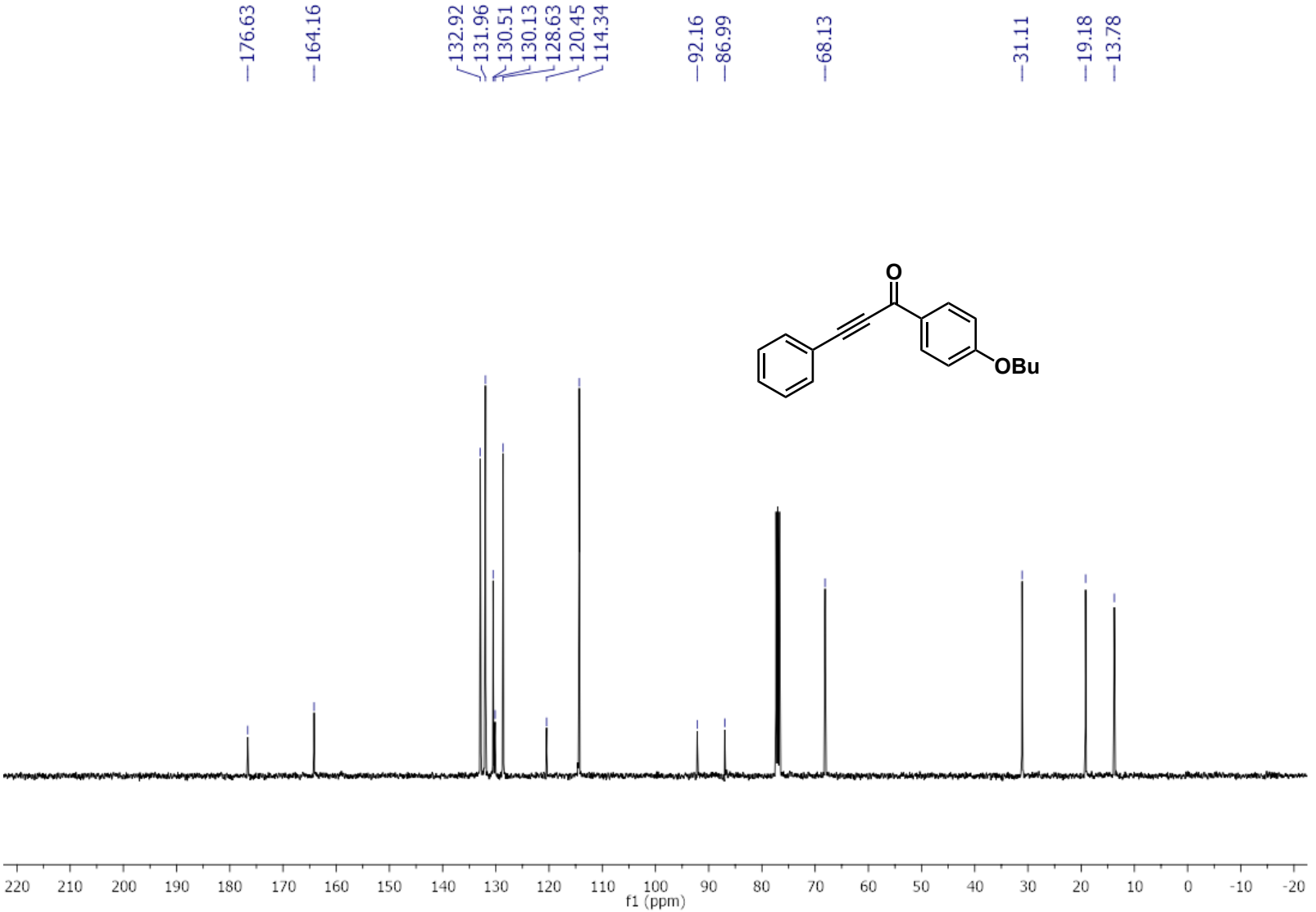
^{1}H NMR of compound **1e** (400 MHz, $CDCl_3$)



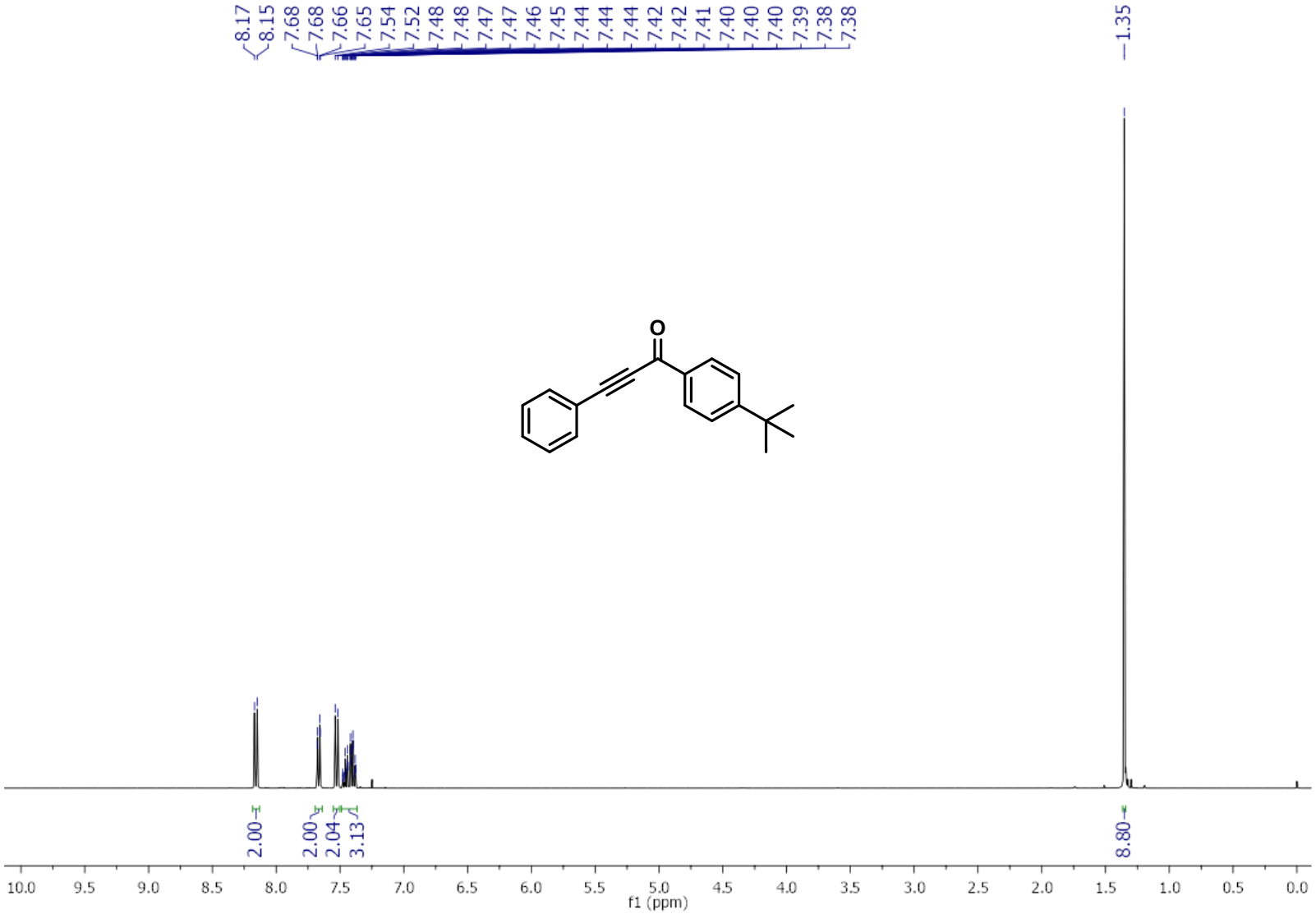
^{13}C NMR of compound **1e** (100 MHz, $CDCl_3$)



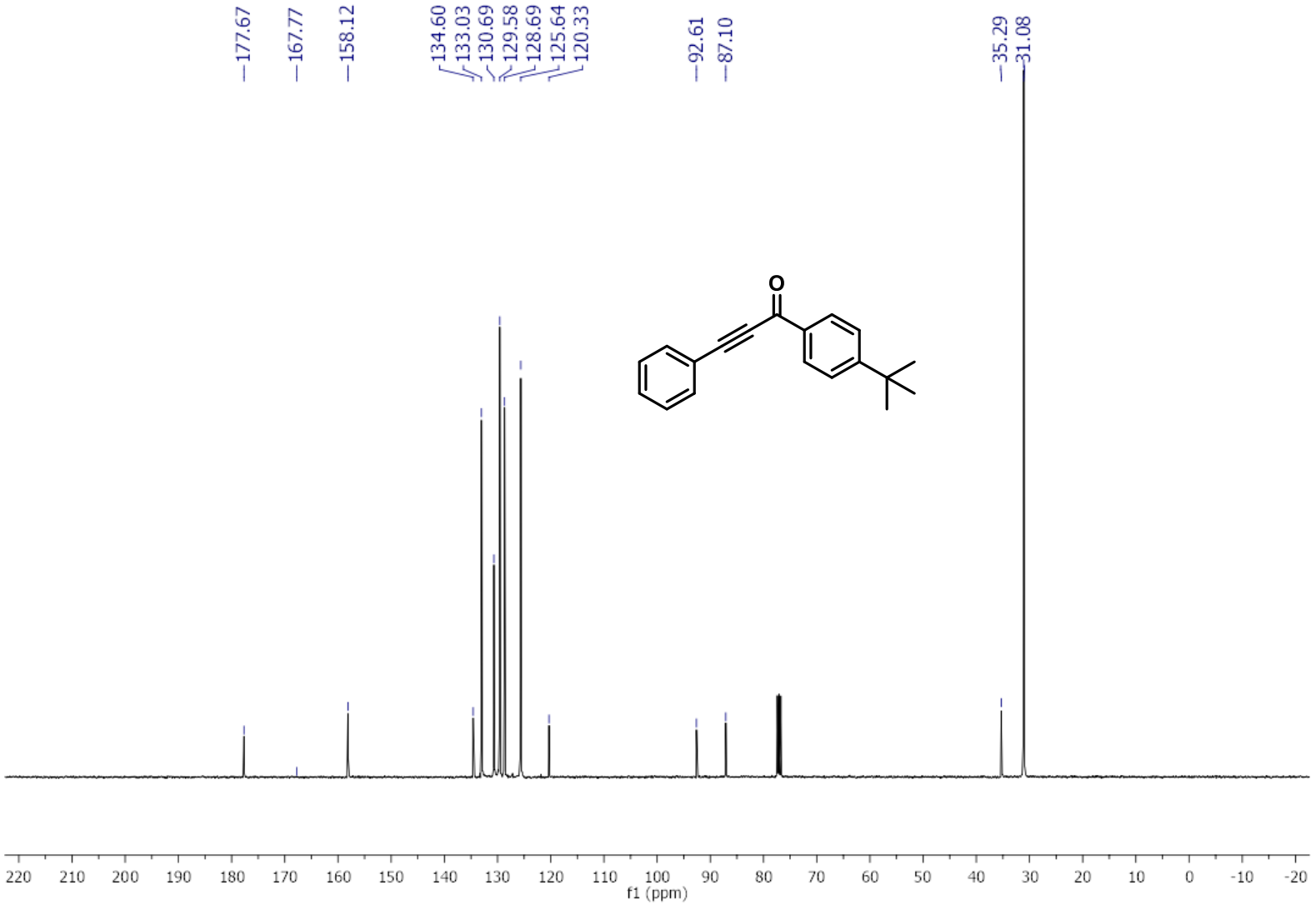
^{1}H NMR of compound **1f** (400 MHz, $CDCl_3$)



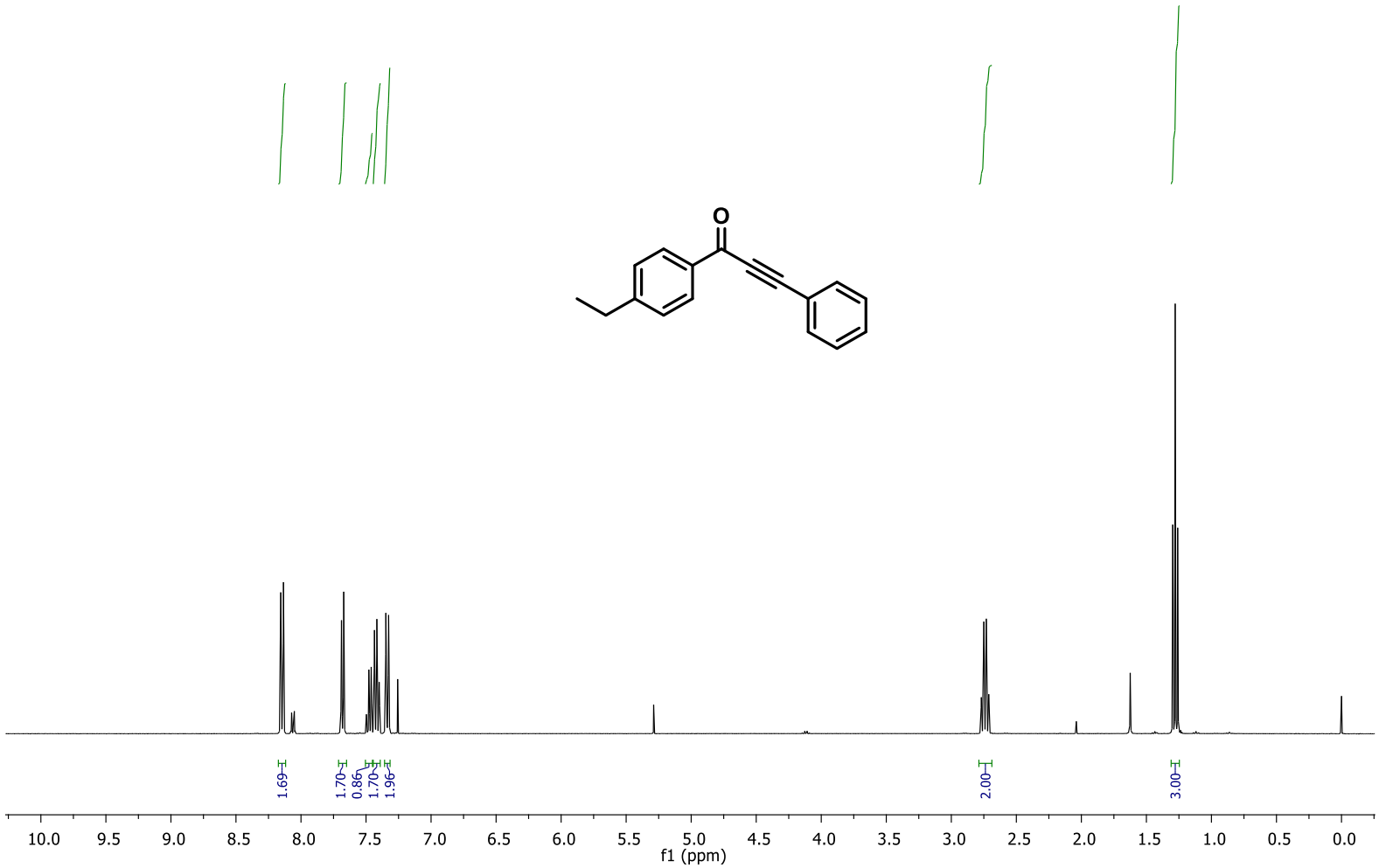
^{13}C NMR of compound **1f** (100 MHz, $CDCl_3$)



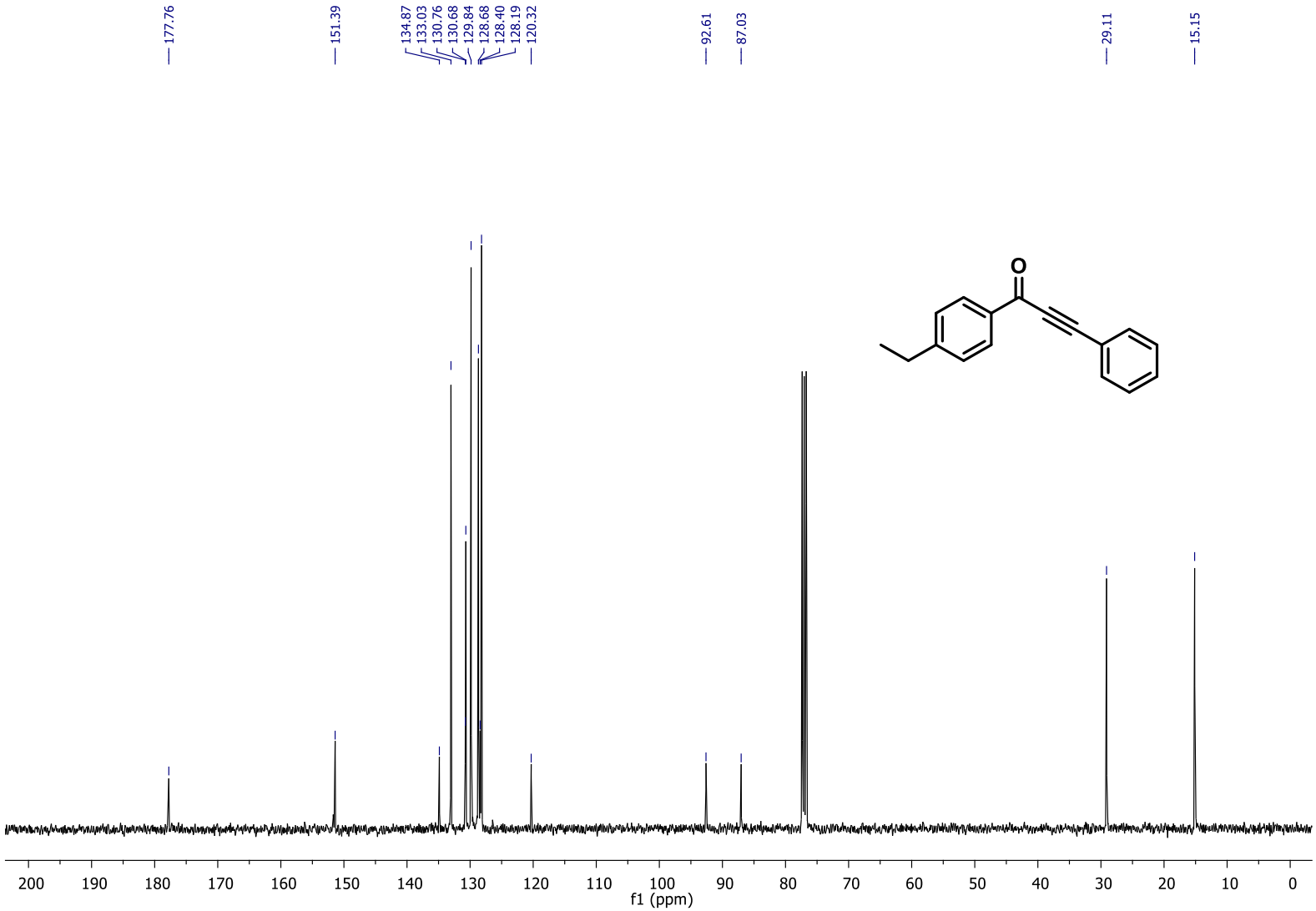
^{1}H NMR of compound **1g** (400 MHz, $CDCl_3$)



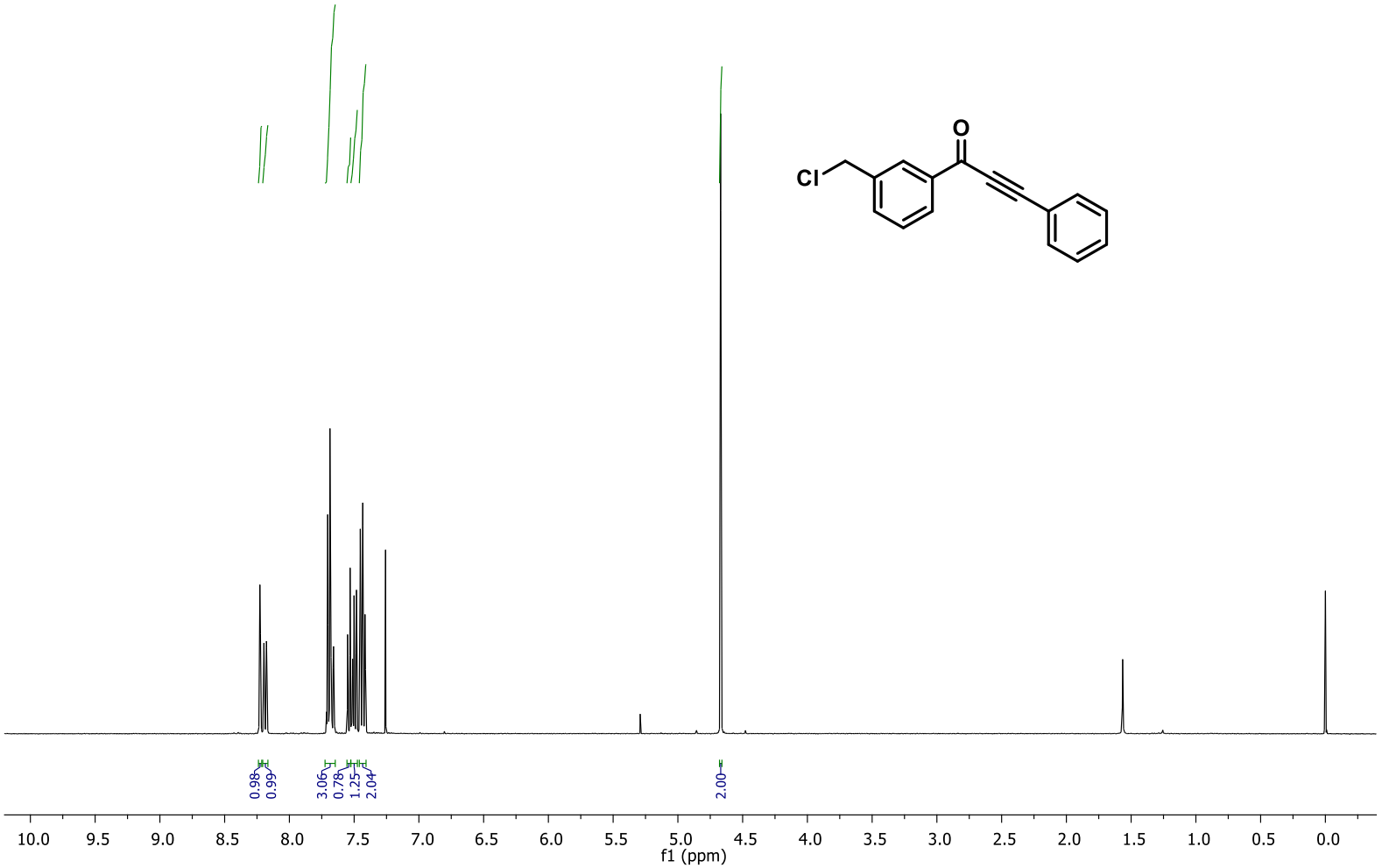
^{13}C NMR of compound **1g** (100 MHz, $CDCl_3$)



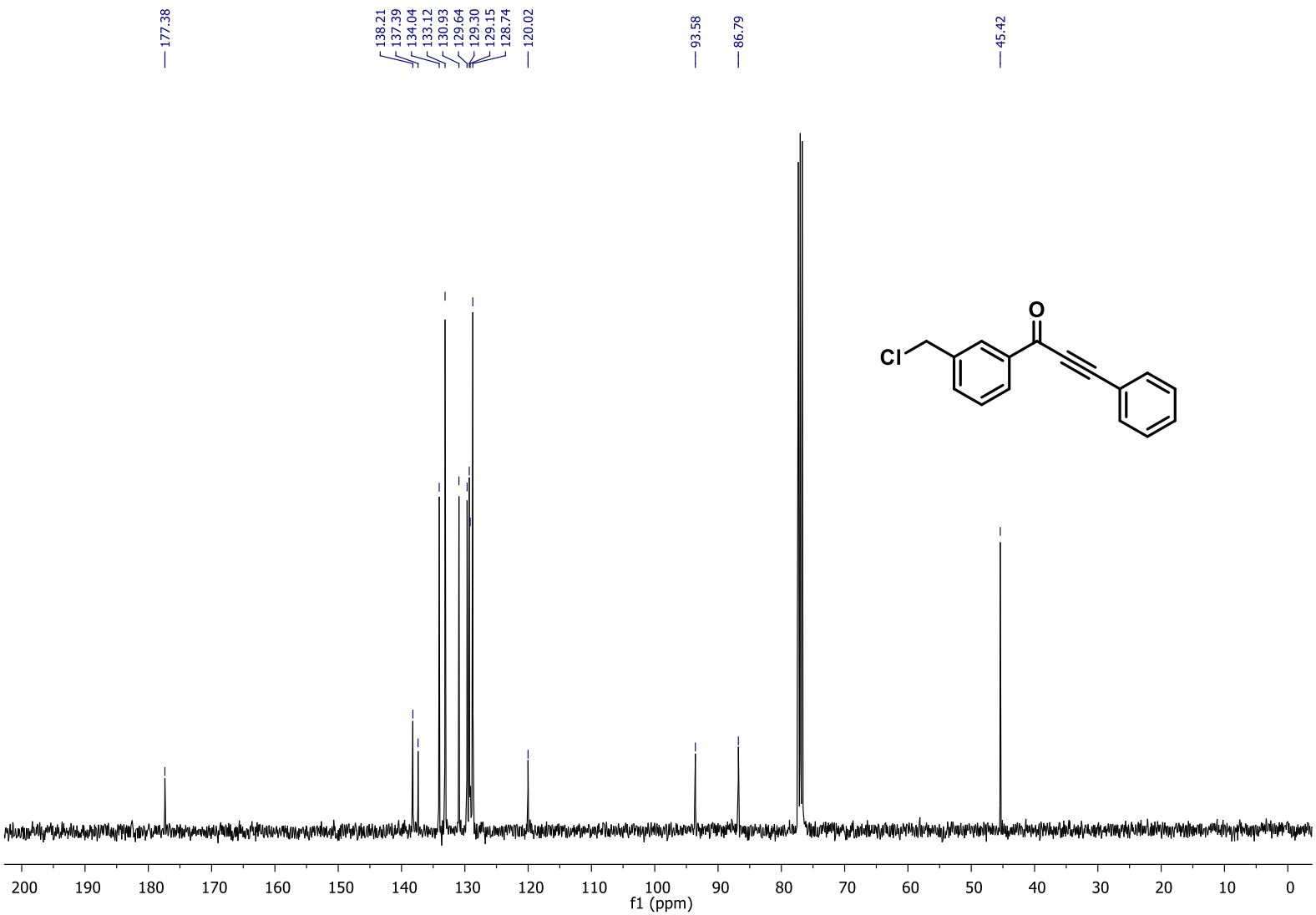
^{1}H NMR of compound **1h** (400 MHz, $CDCl_3$)



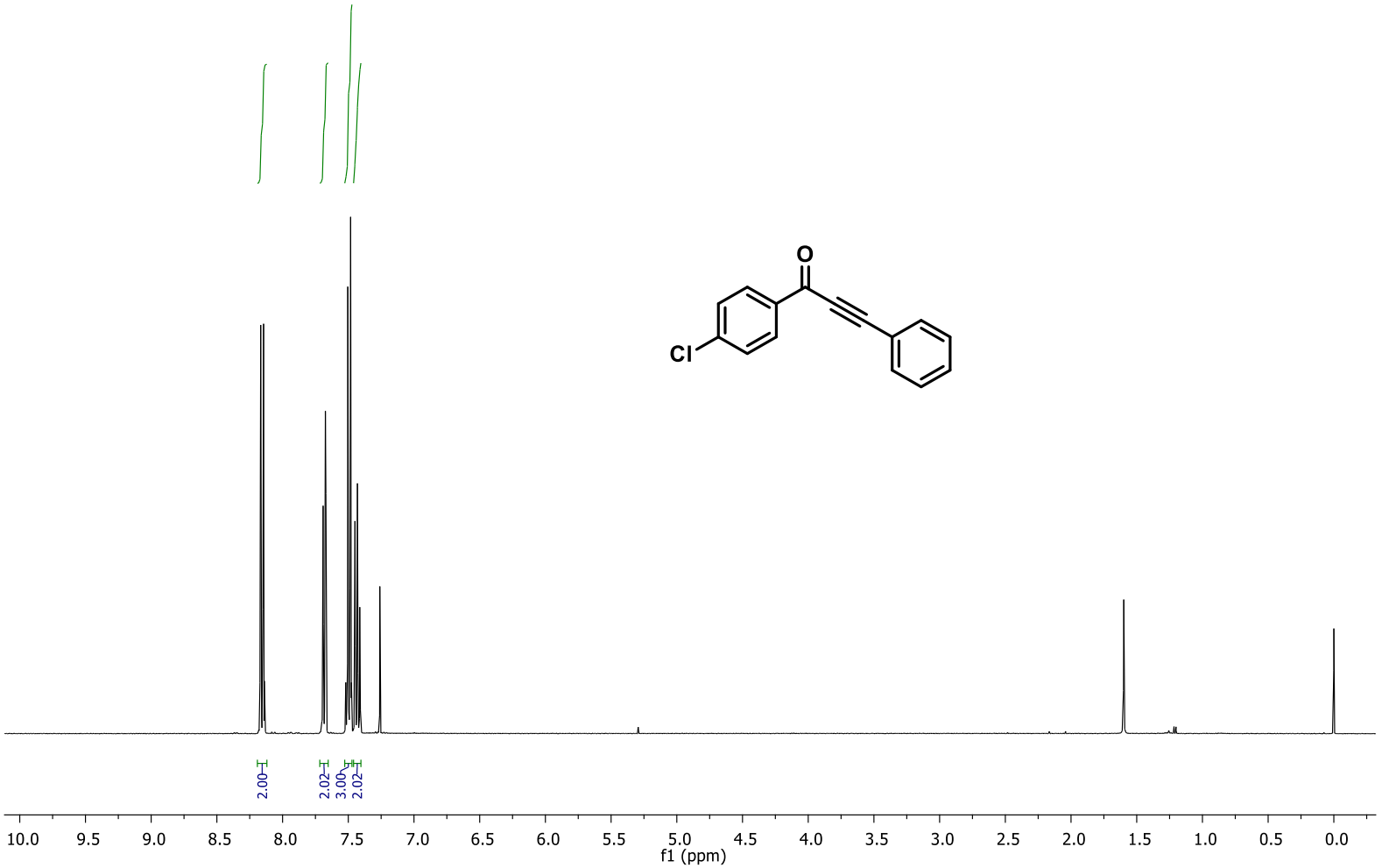
^{13}C NMR of compound **1h** (100 MHz, $CDCl_3$)



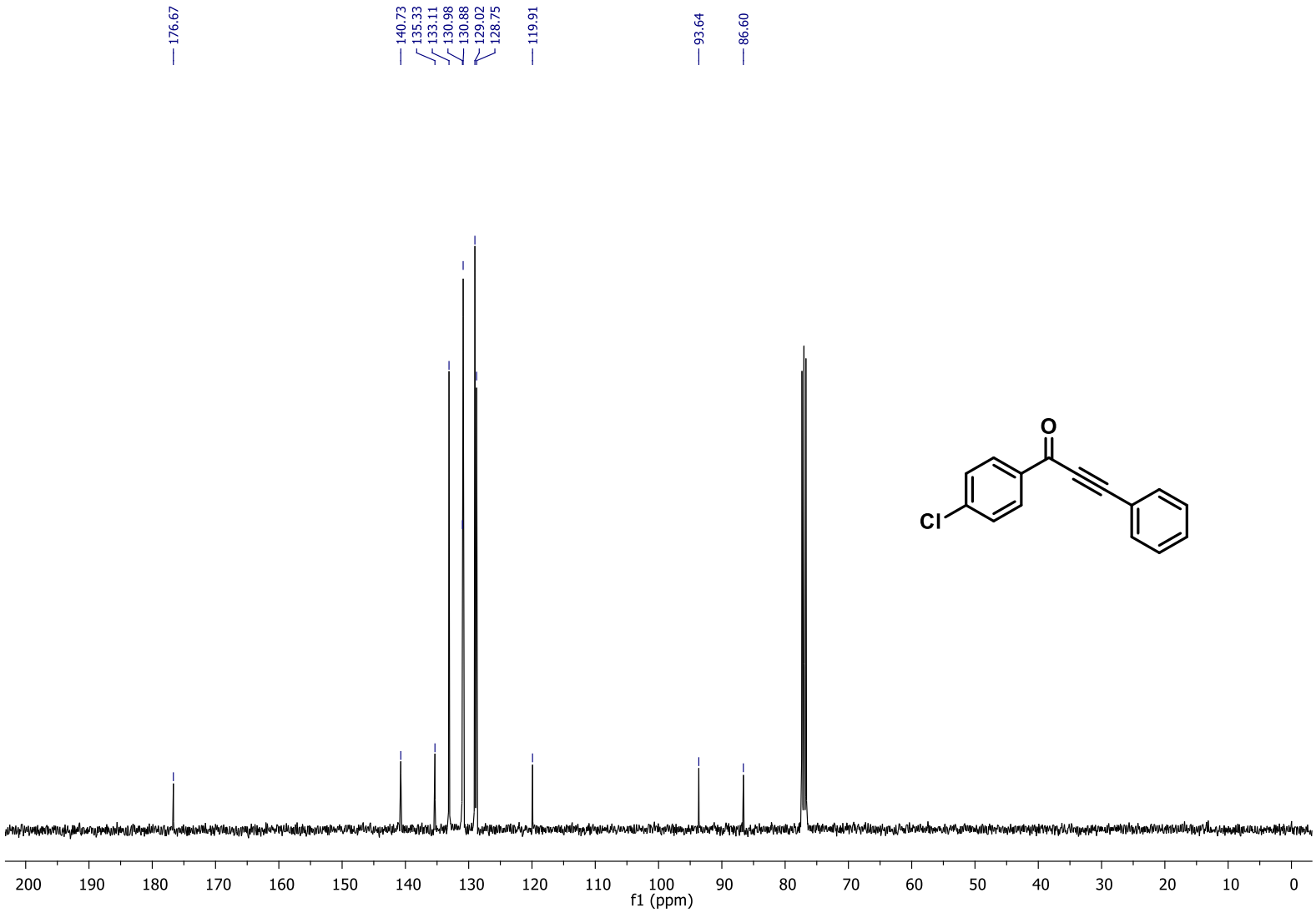
^{1}H NMR of compound **1i** (400 MHz, $CDCl_3$)



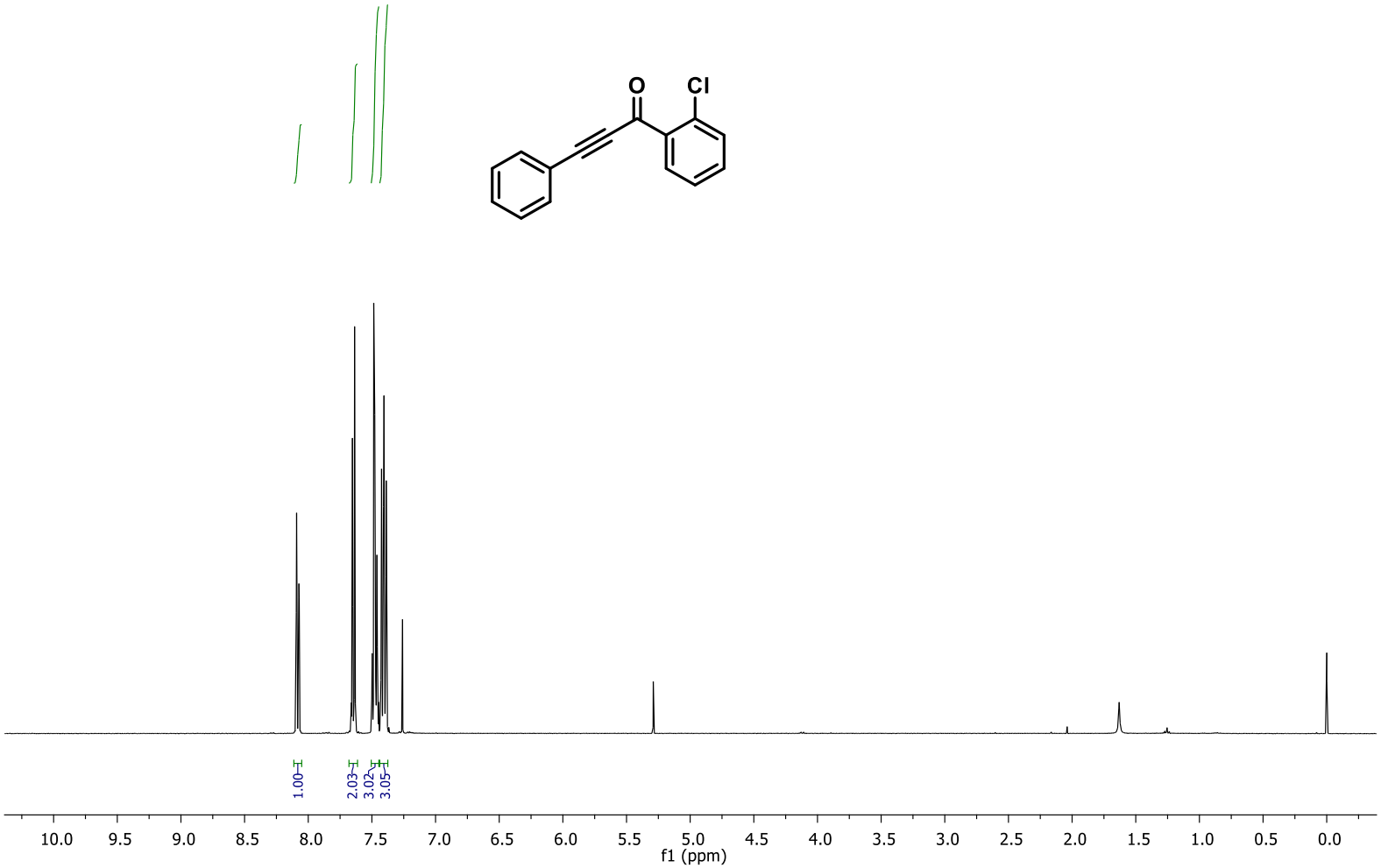
^{13}C NMR of compound **1i** (100 MHz, $CDCl_3$)



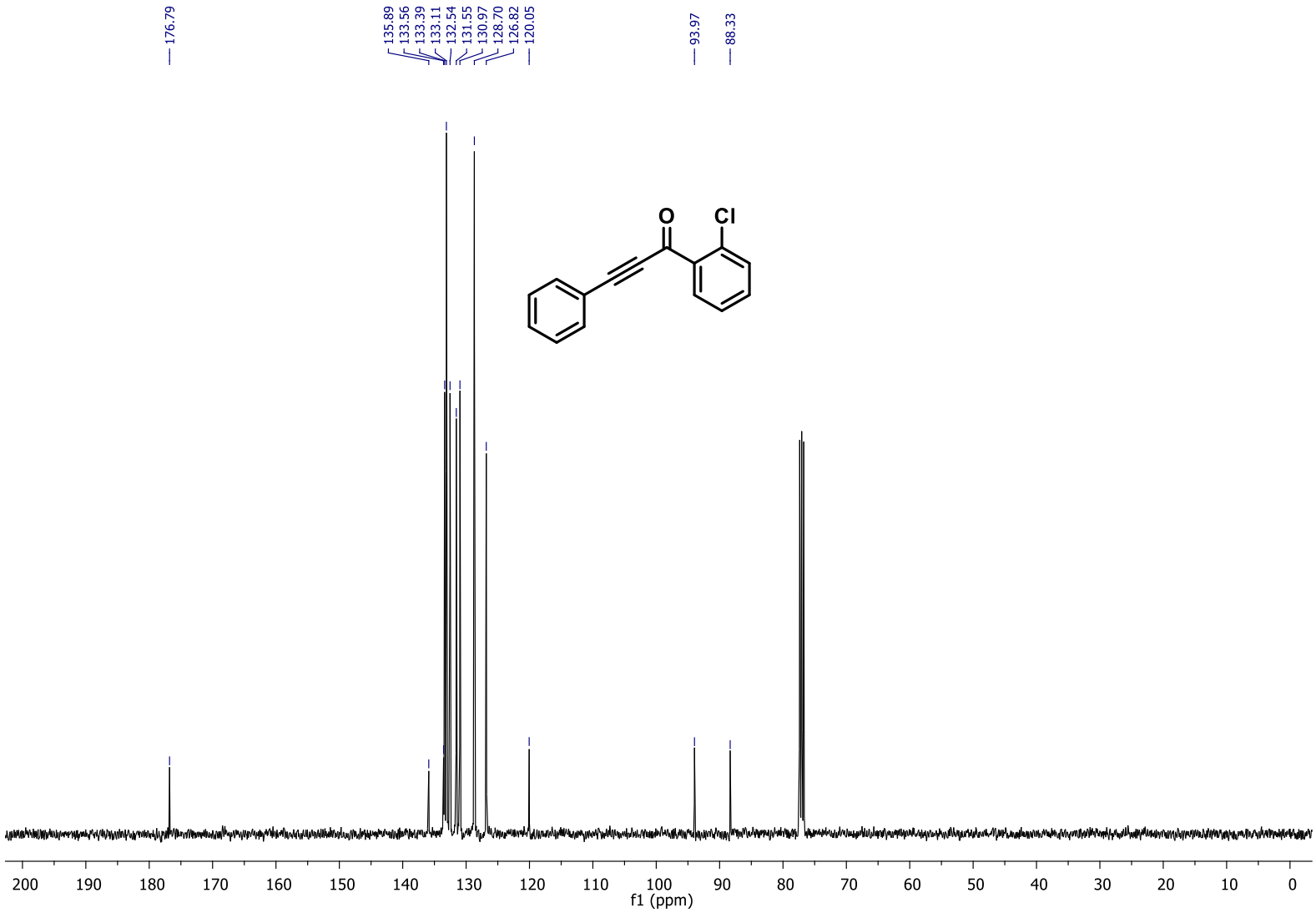
^{1}H NMR of compound **1j** (400 MHz, $CDCl_3$)



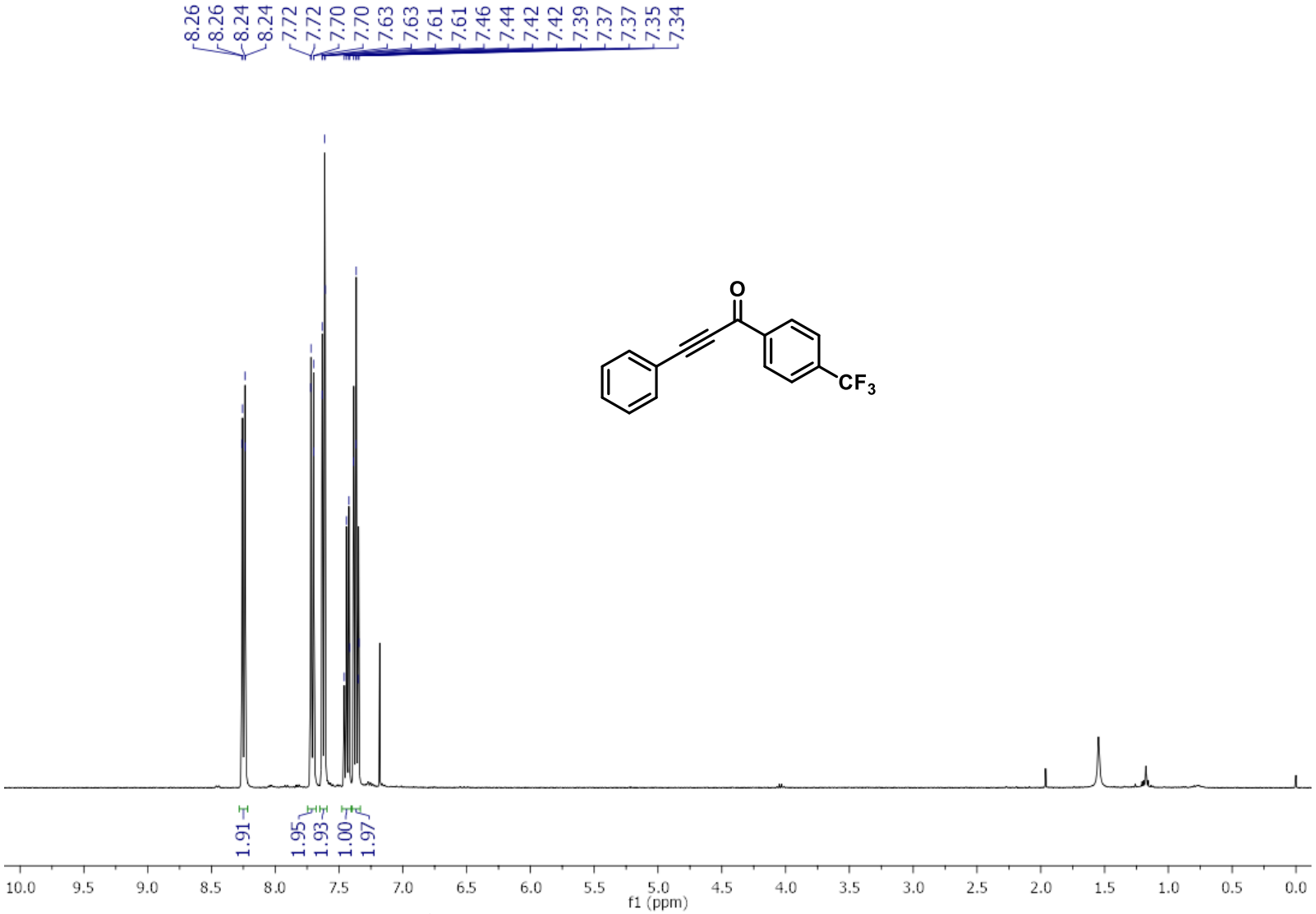
^{13}C NMR of compound **1j** (100 MHz, $CDCl_3$)



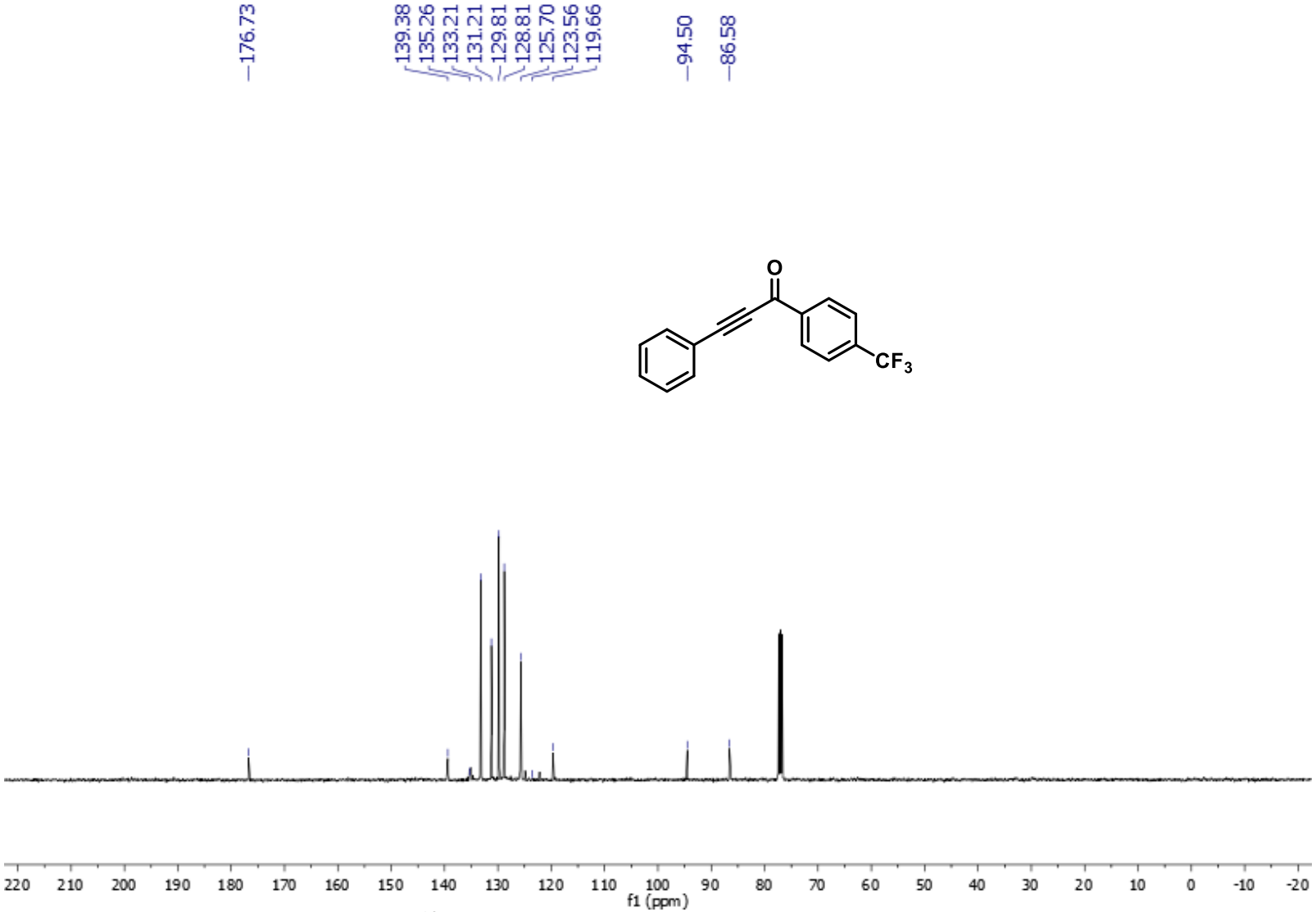
^{1}H NMR of compound **1k** (400 MHz, $CDCl_3$)



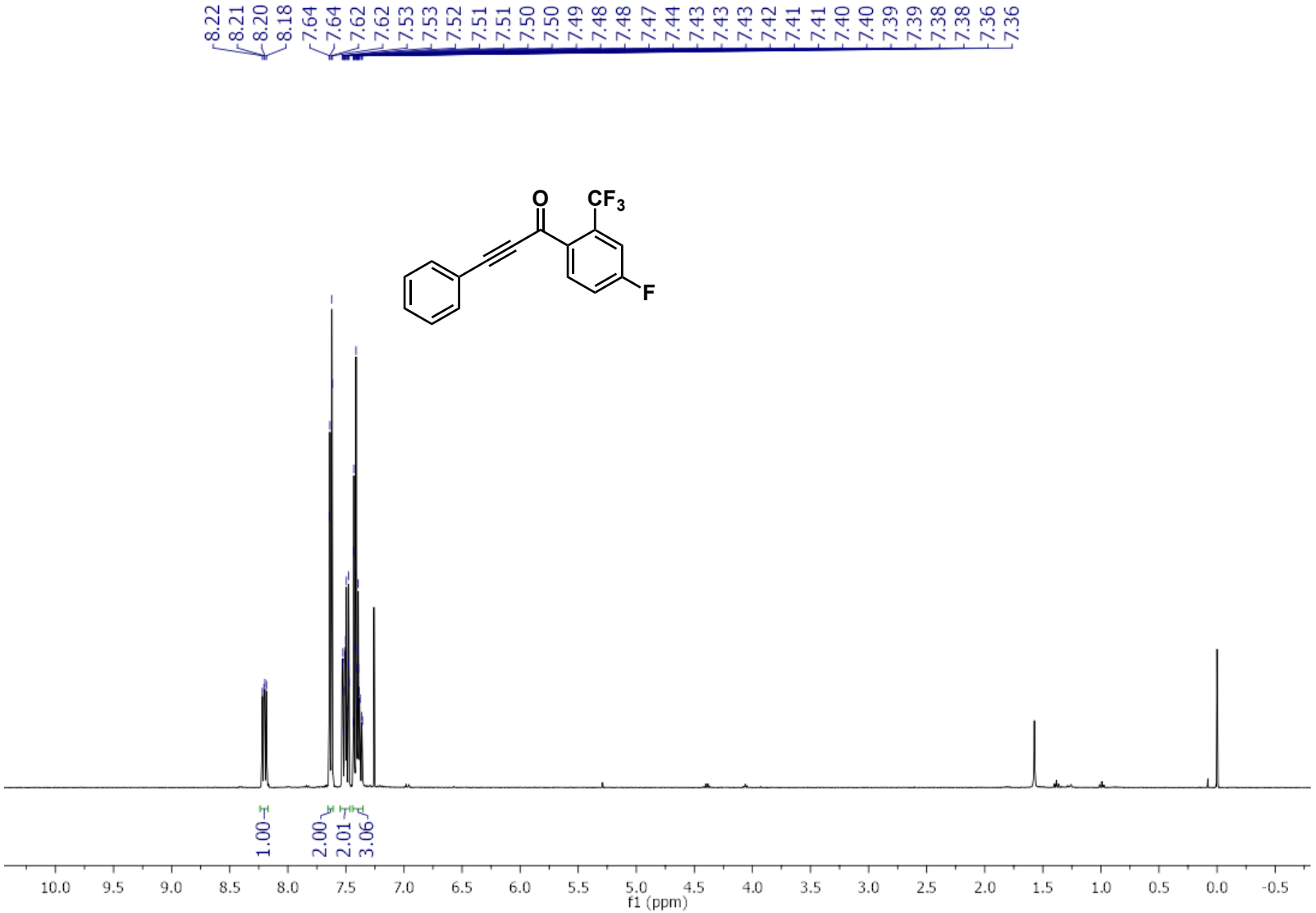
^{13}C NMR of compound **1k** (100 MHz, $CDCl_3$)



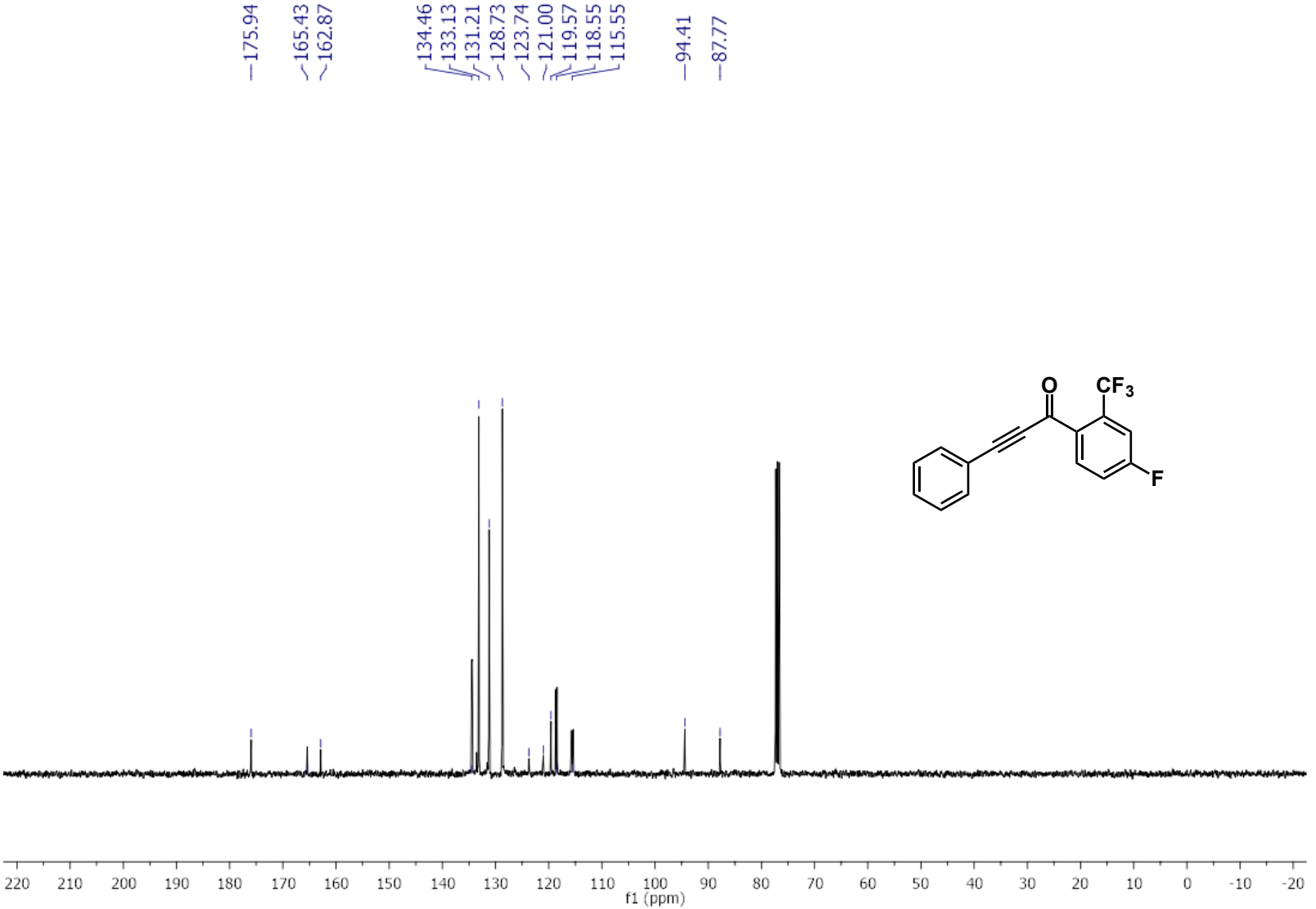
^{1}H NMR of compound **1l** (400 MHz, $CDCl_3$)



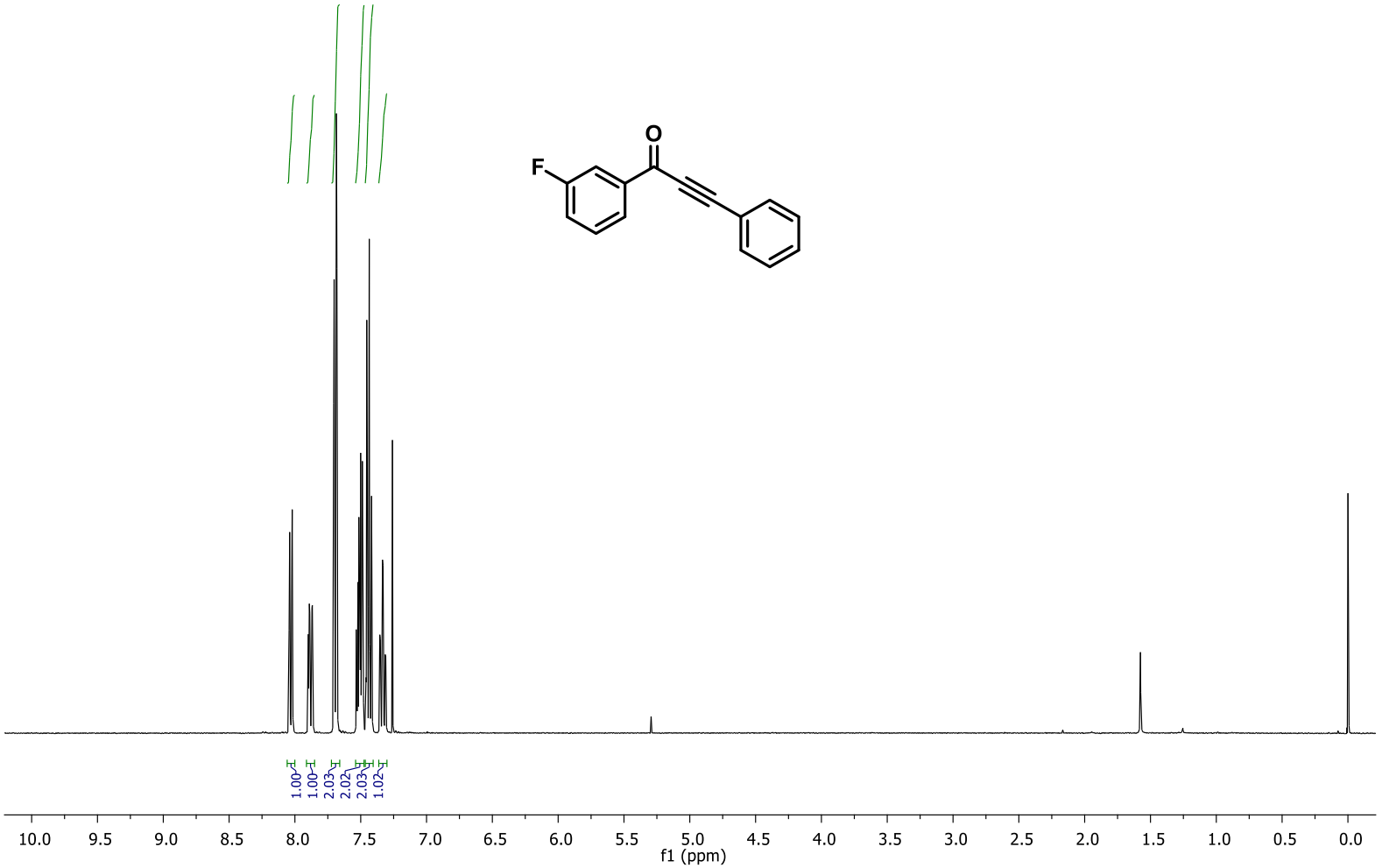
^{13}C NMR of compound **1l** (100 MHz, $CDCl_3$)



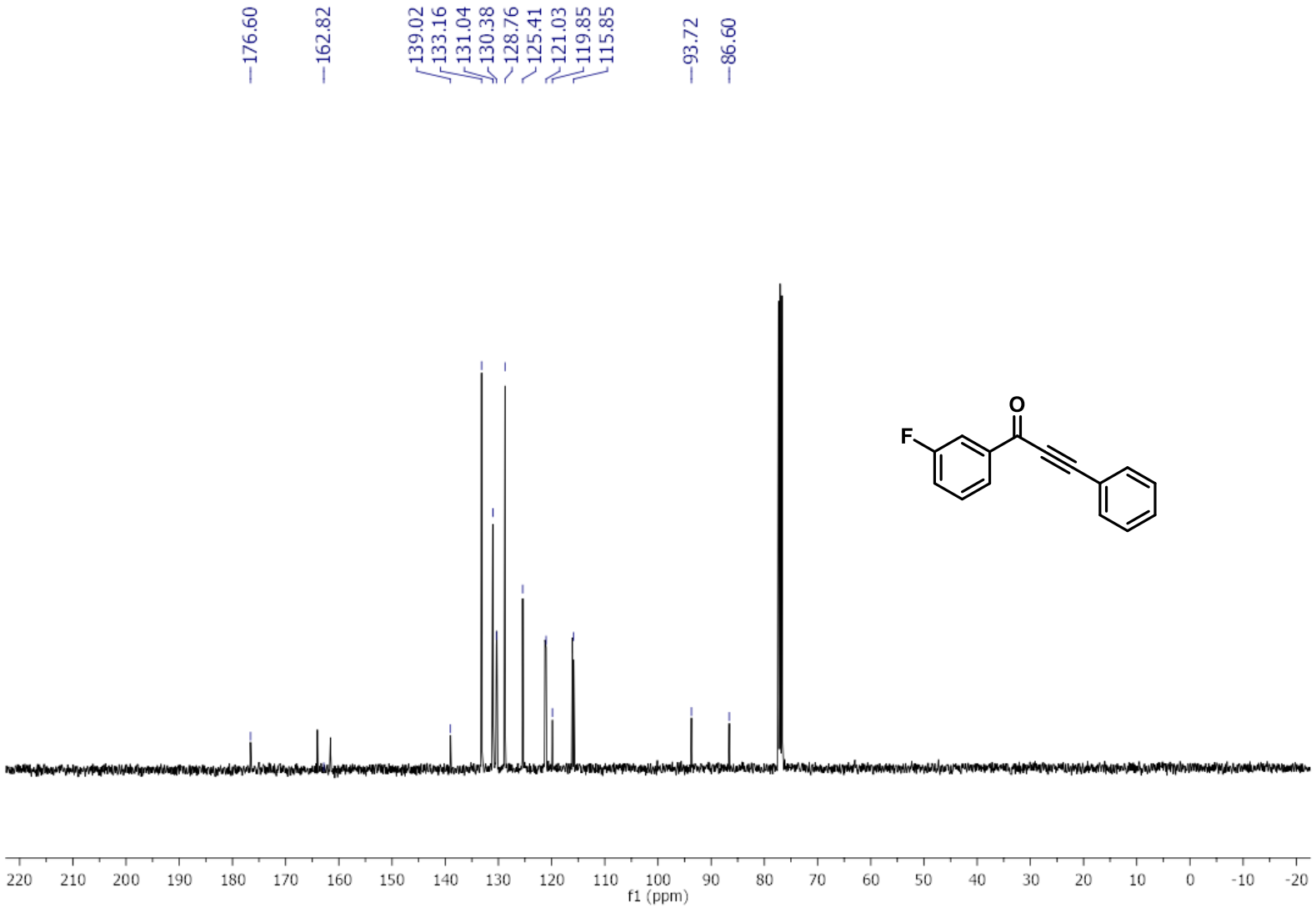
^{1}H NMR of compound **1m** (400 MHz, $CDCl_3$)



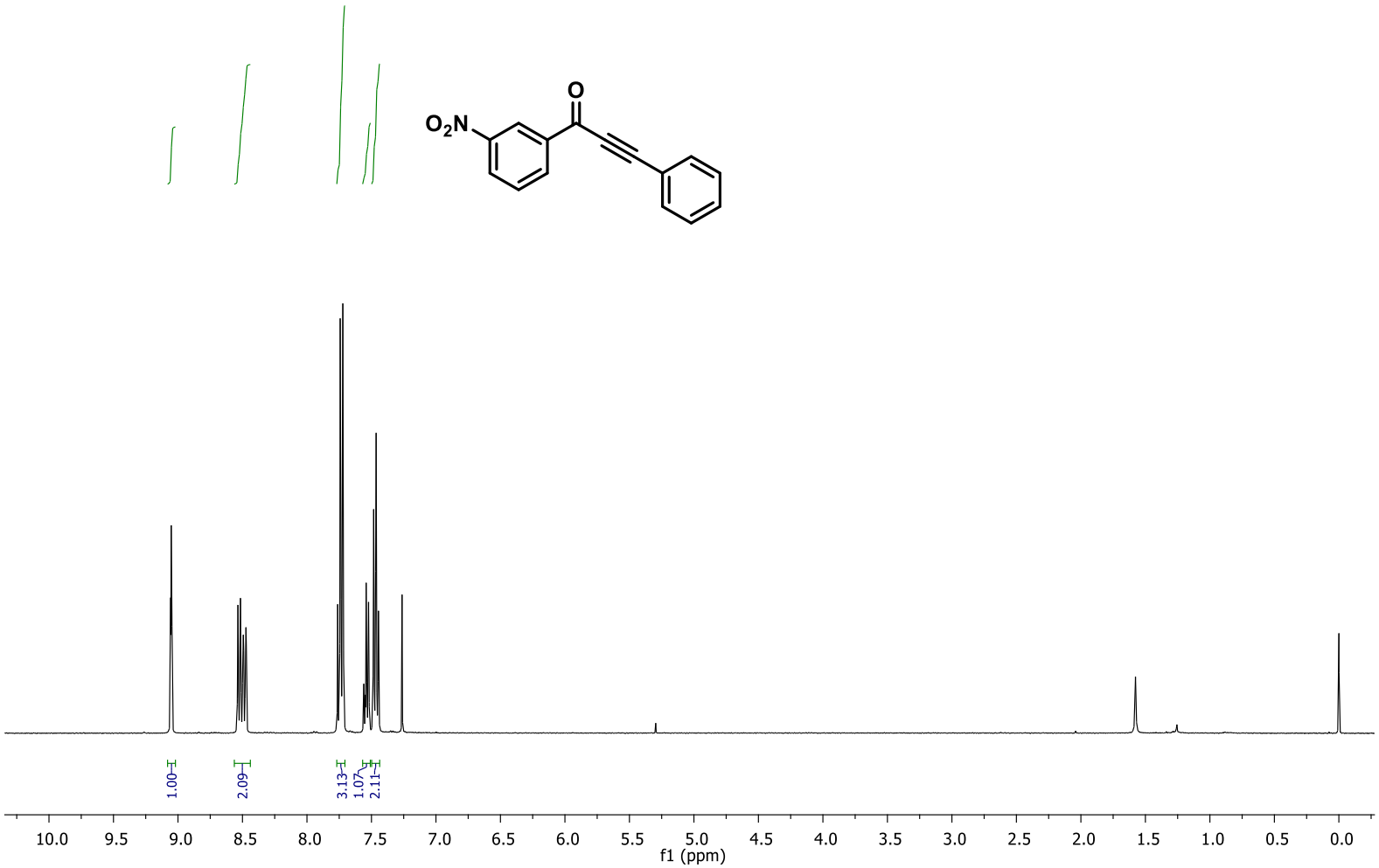
^{13}C NMR of compound **1m** (100 MHz, $CDCl_3$)



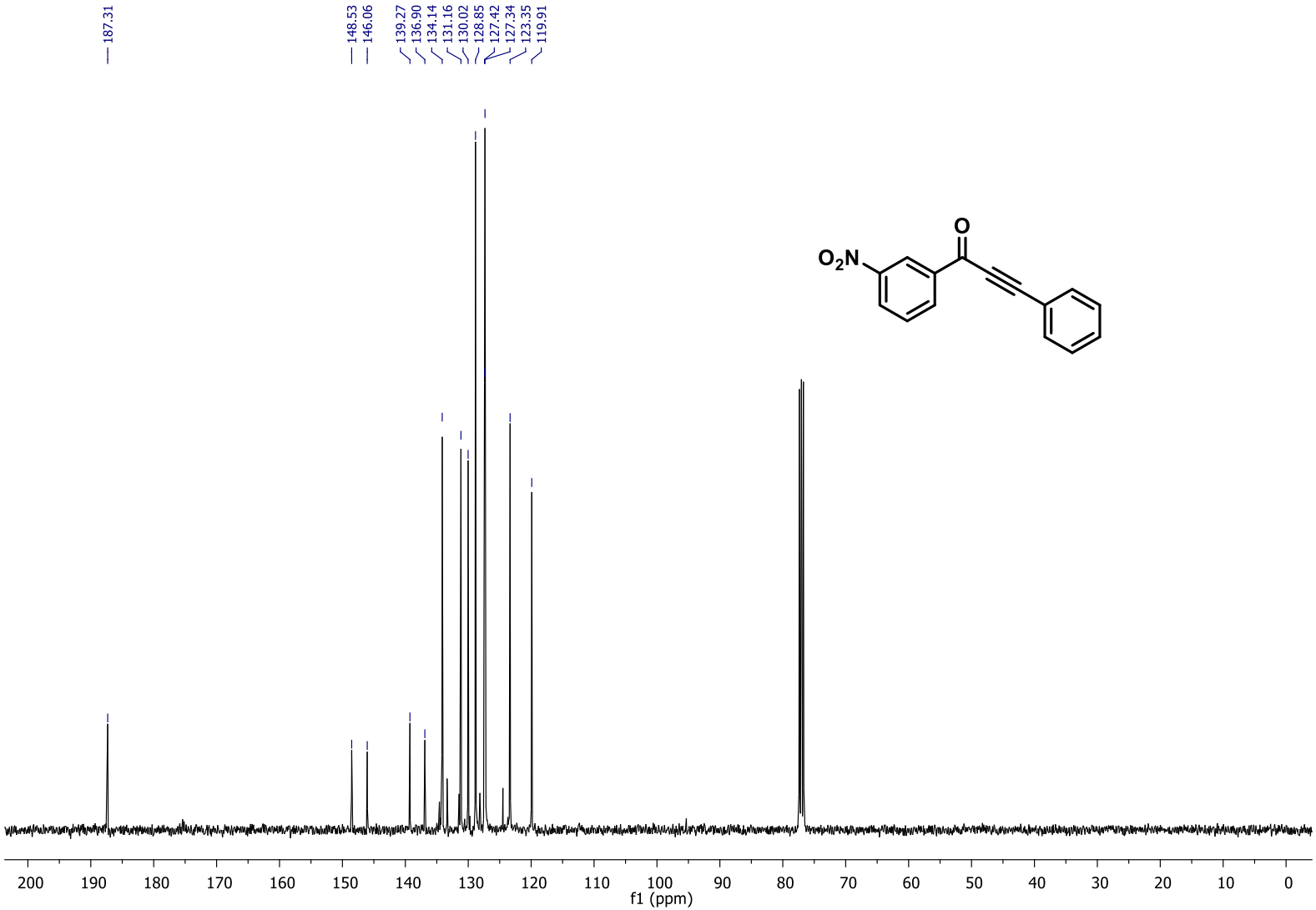
^{1}H NMR of compound **1n** (400 MHz, $CDCl_3$)



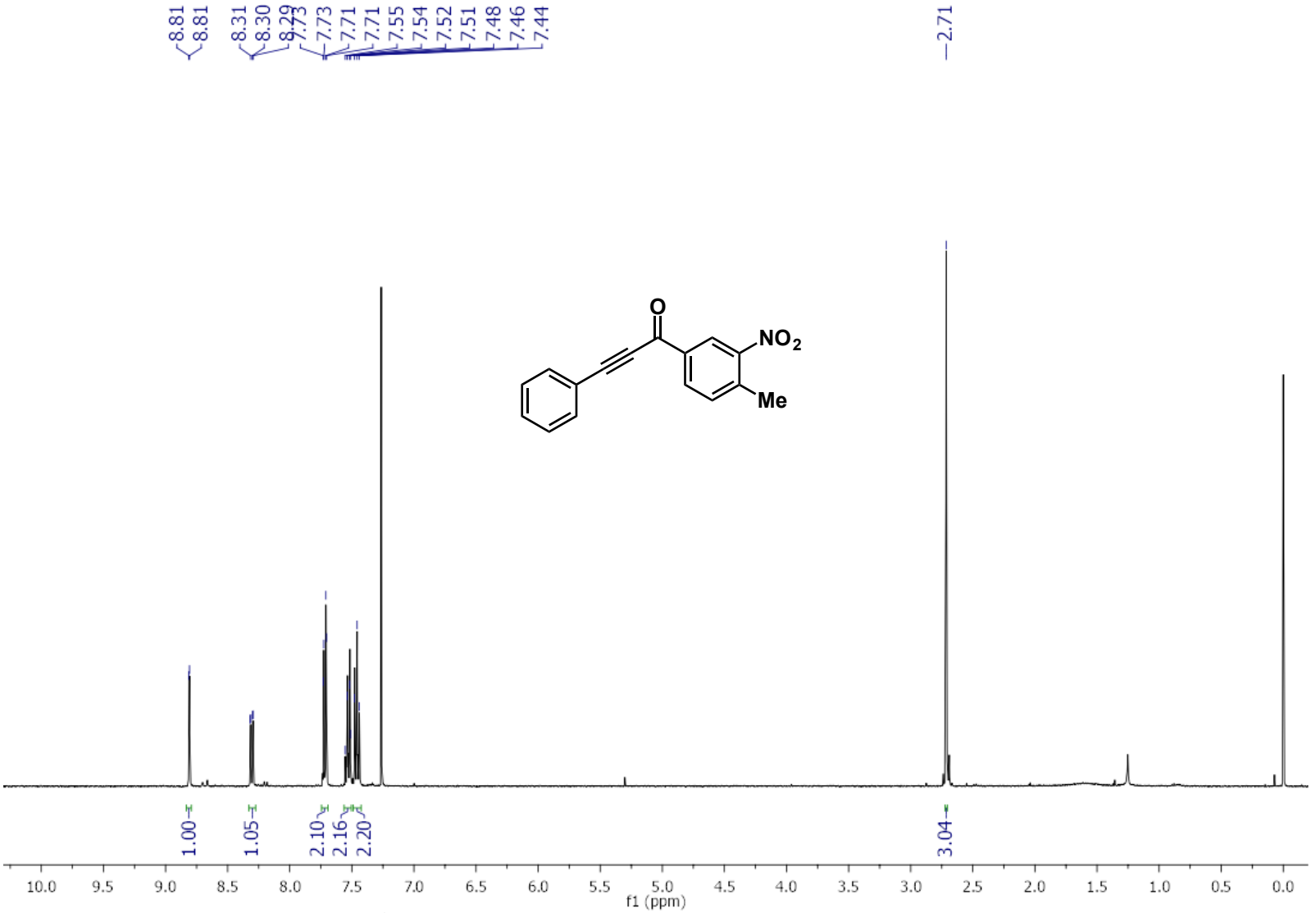
^{13}C NMR of compound **1n** (100 MHz, $CDCl_3$)



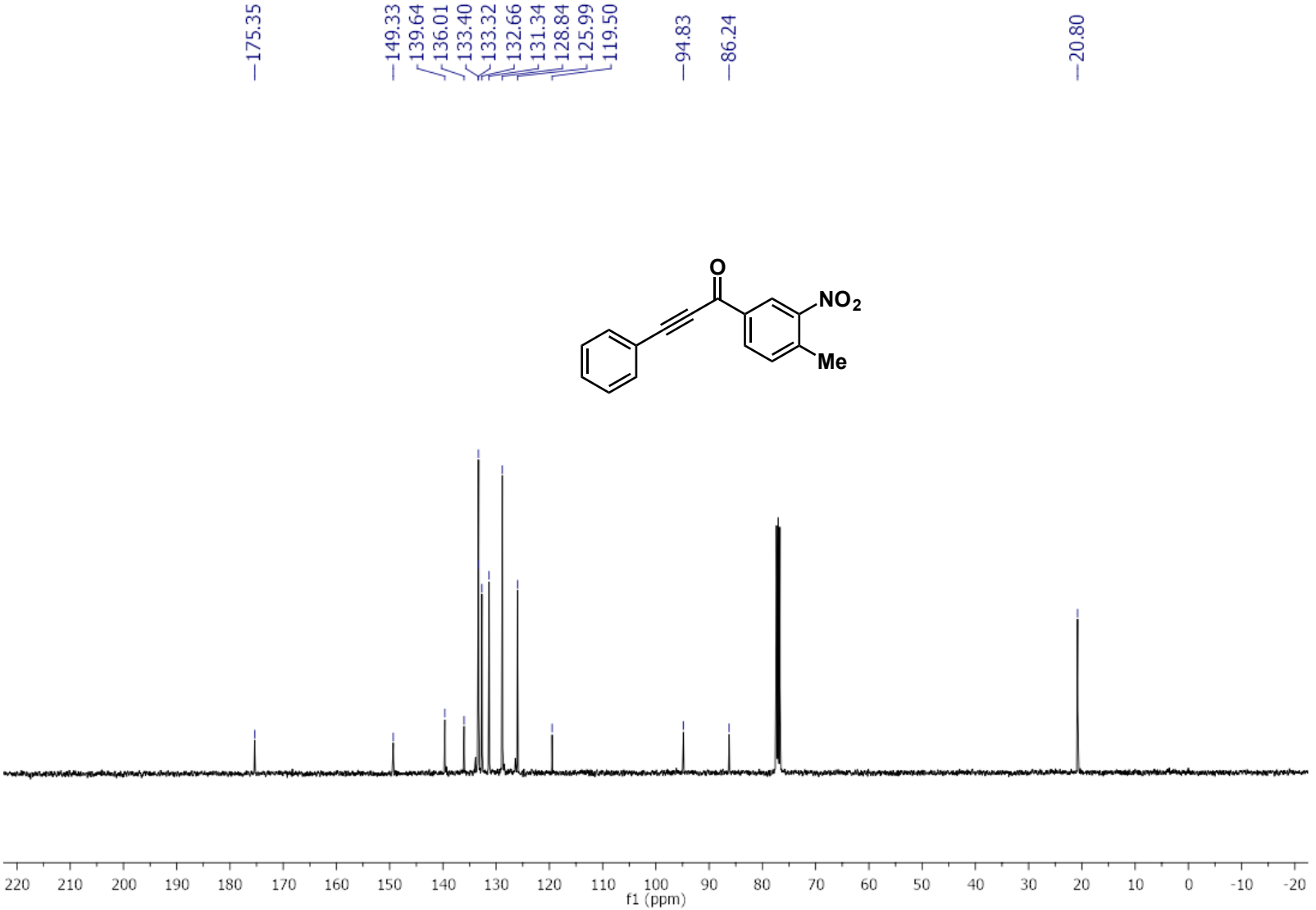
^{1}H NMR of compound **1o** (400 MHz, $CDCl_3$)



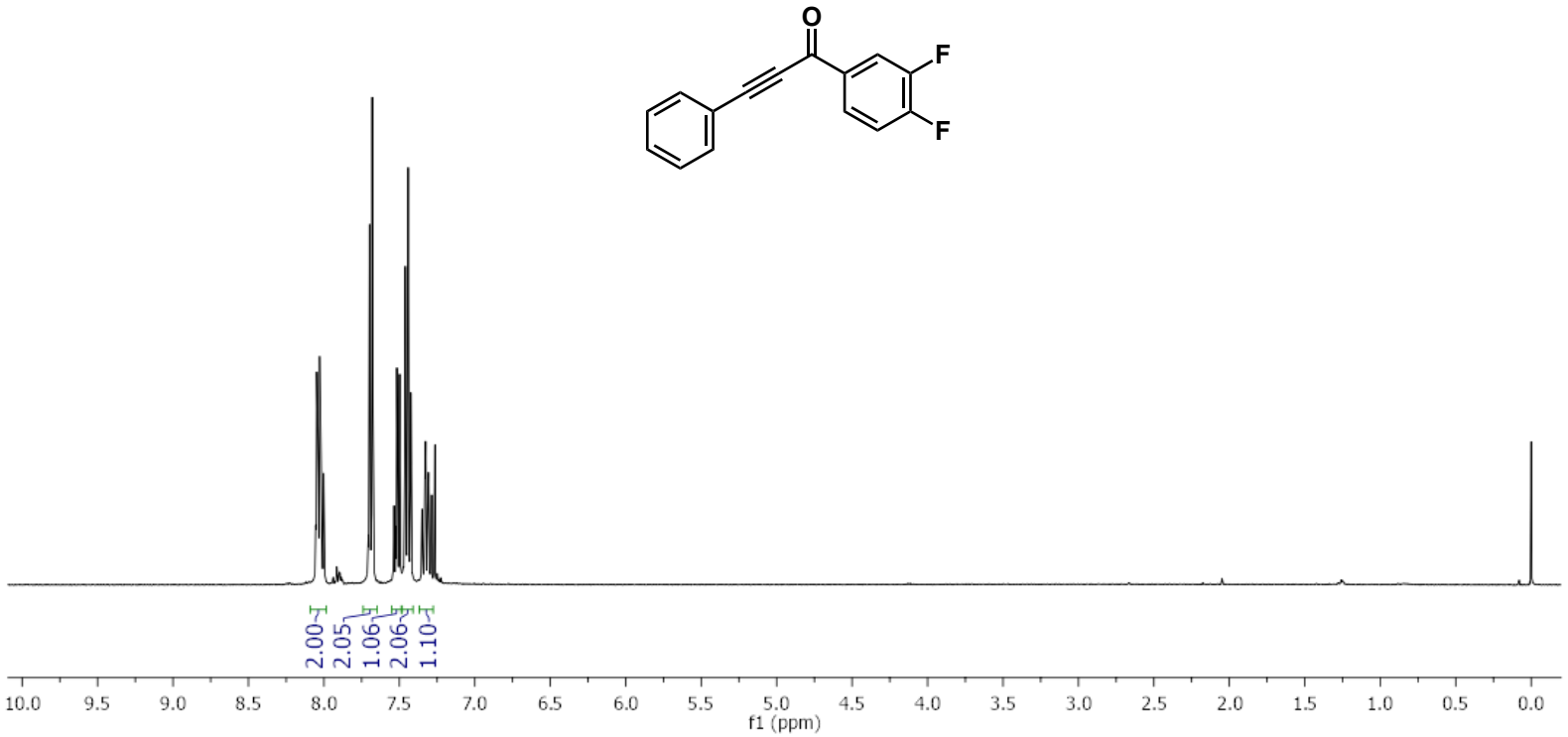
^{13}C NMR of compound **1o** (100 MHz, $CDCl_3$)



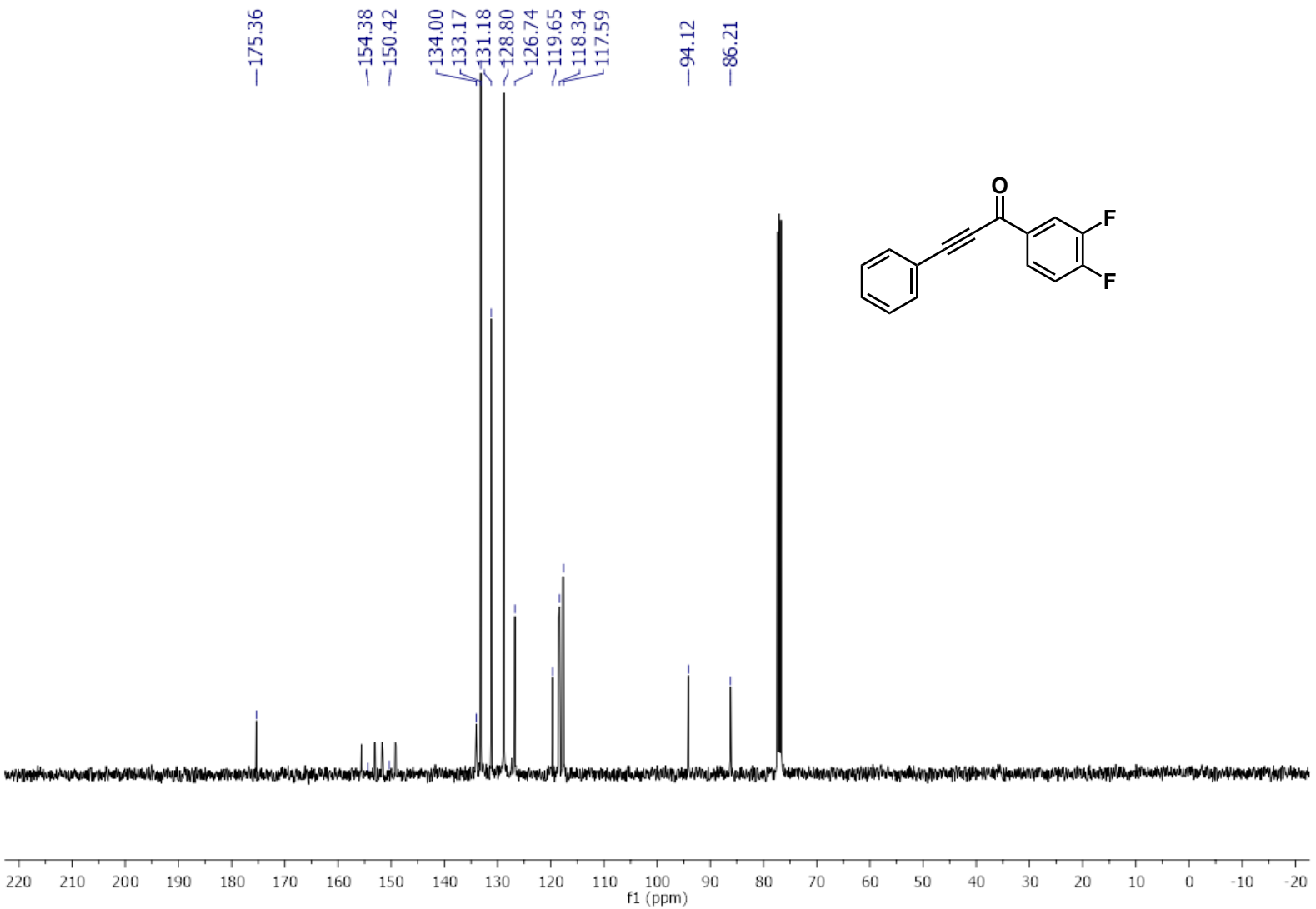
^{1}H NMR of compound **1p** (400 MHz, $CDCl_3$)



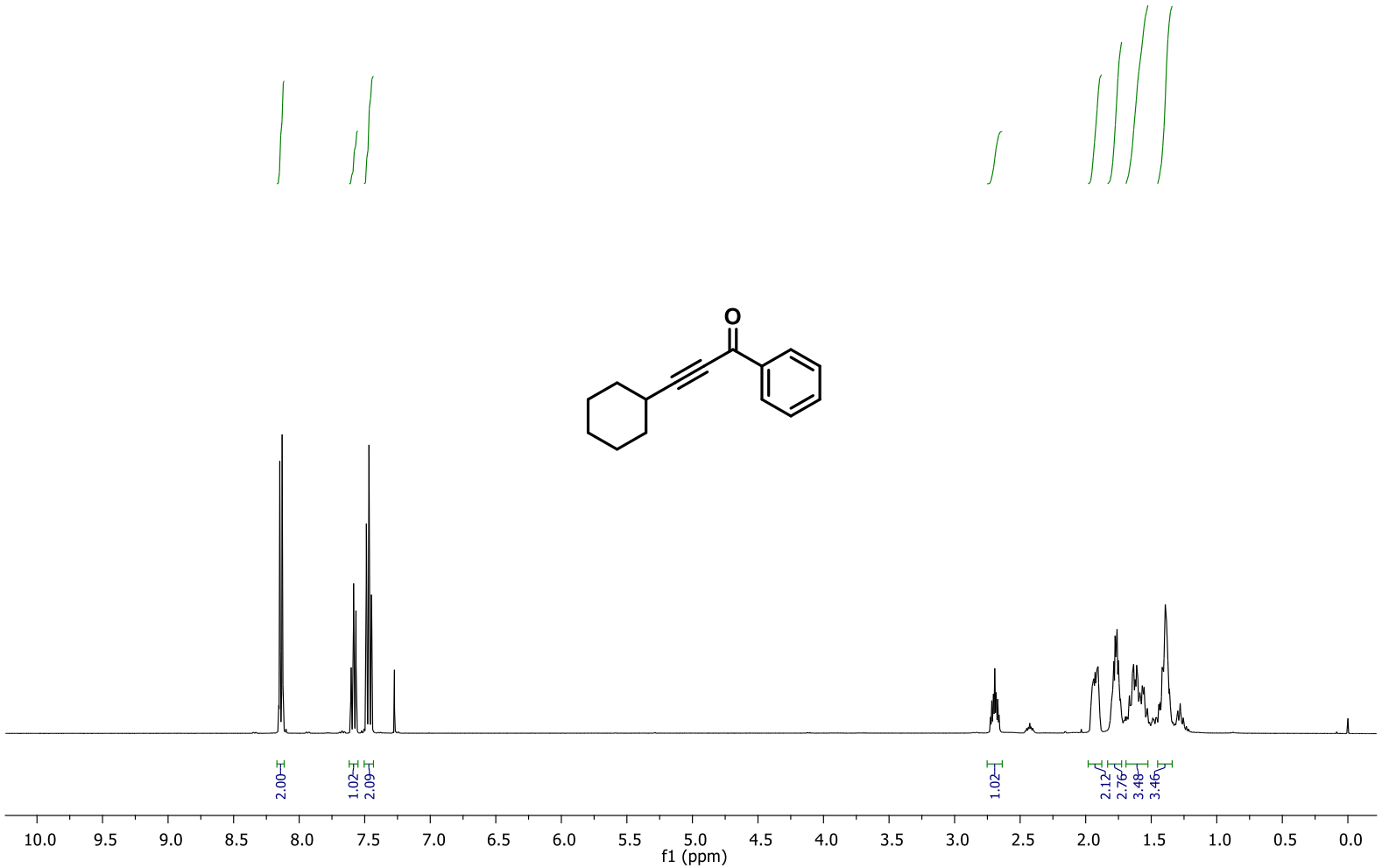
^{13}C NMR of compound **1p** (100 MHz, $CDCl_3$)



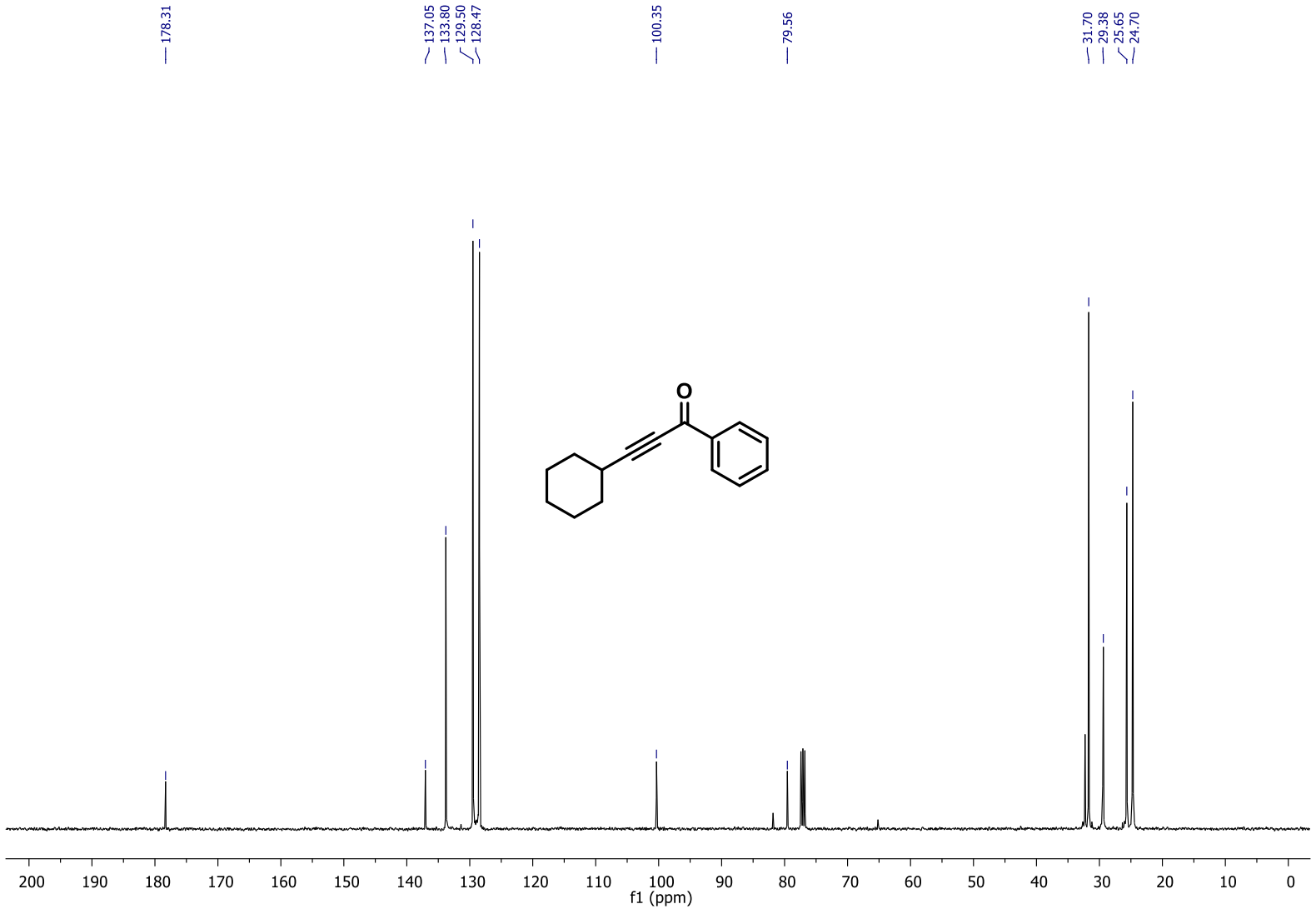
^{1}H NMR of compound **1q** (400 MHz, $CDCl_3$)



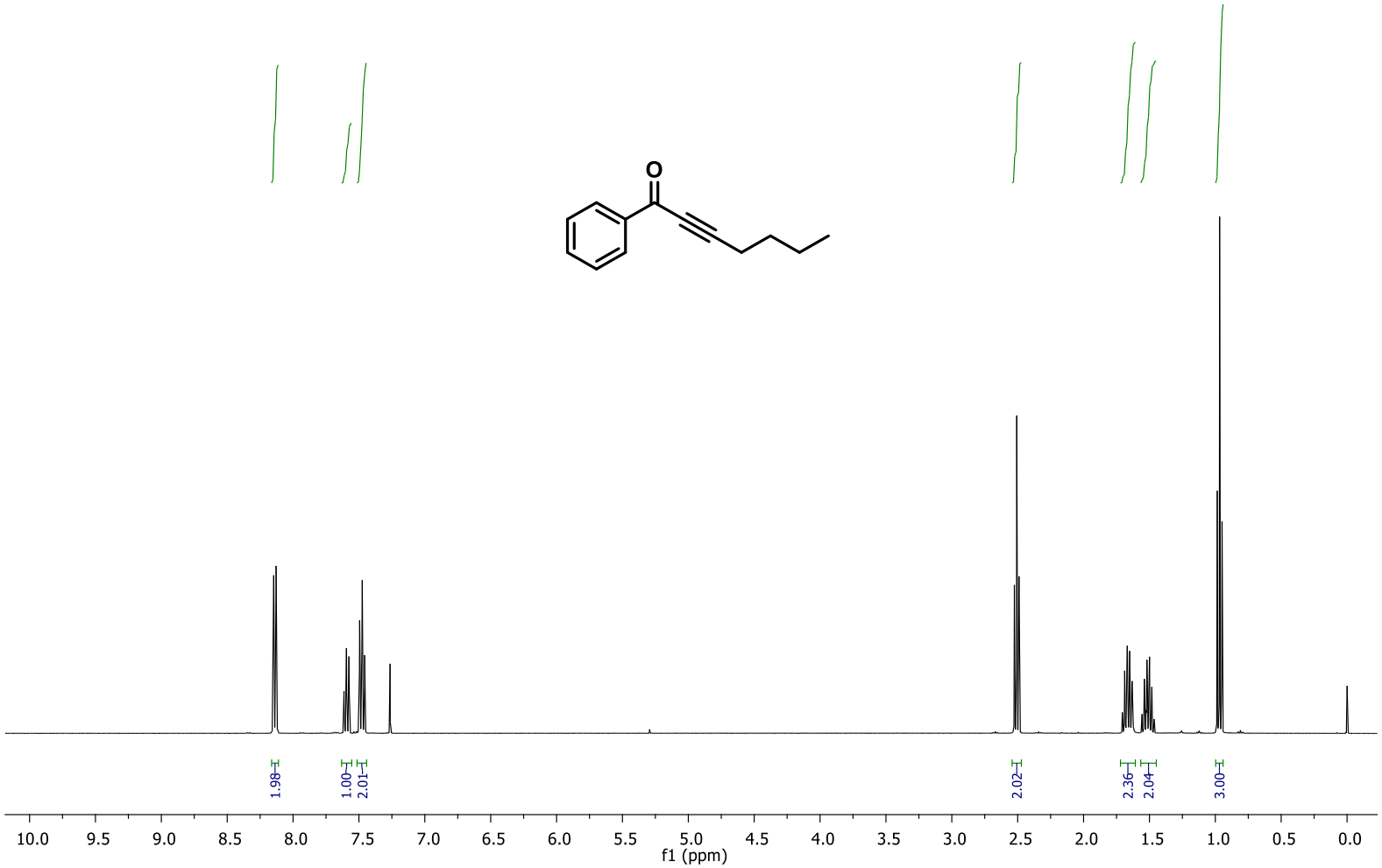
^{13}C NMR of compound **1q** (100 MHz, $CDCl_3$)



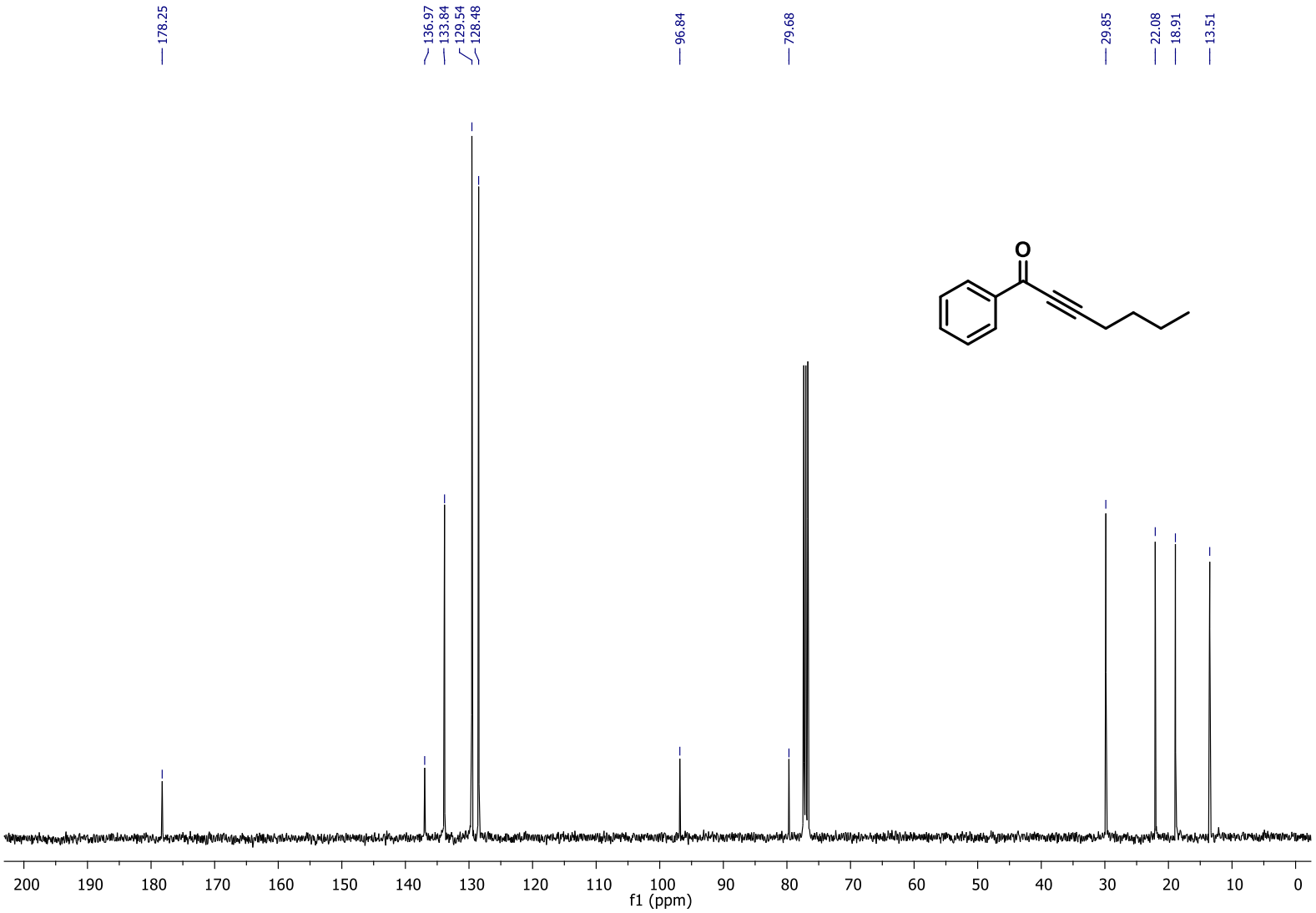
^{1}H NMR of compound **1r** (400 MHz, $CDCl_3$)



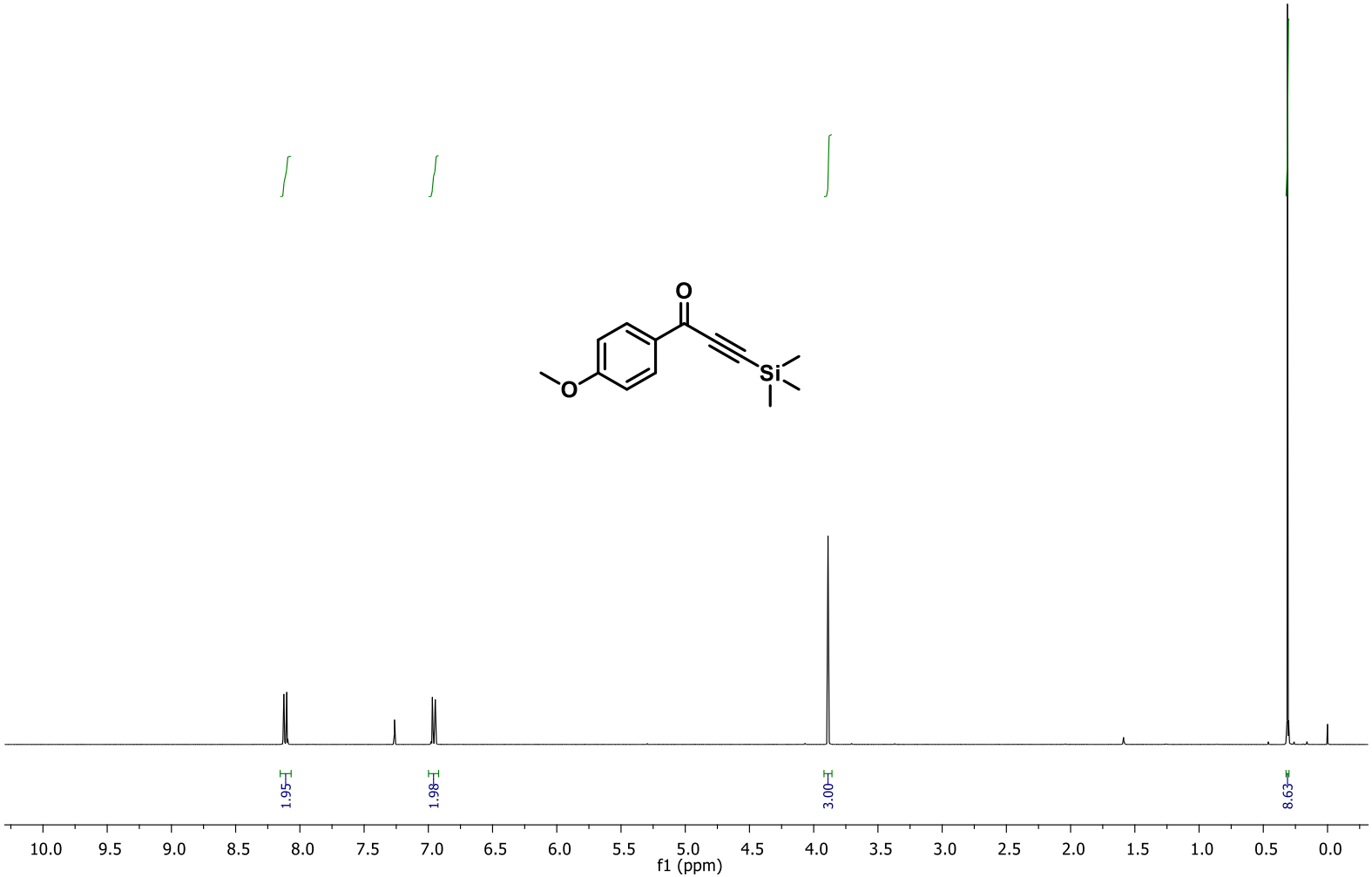
^{13}C NMR of compound **1r** (100 MHz, $CDCl_3$)



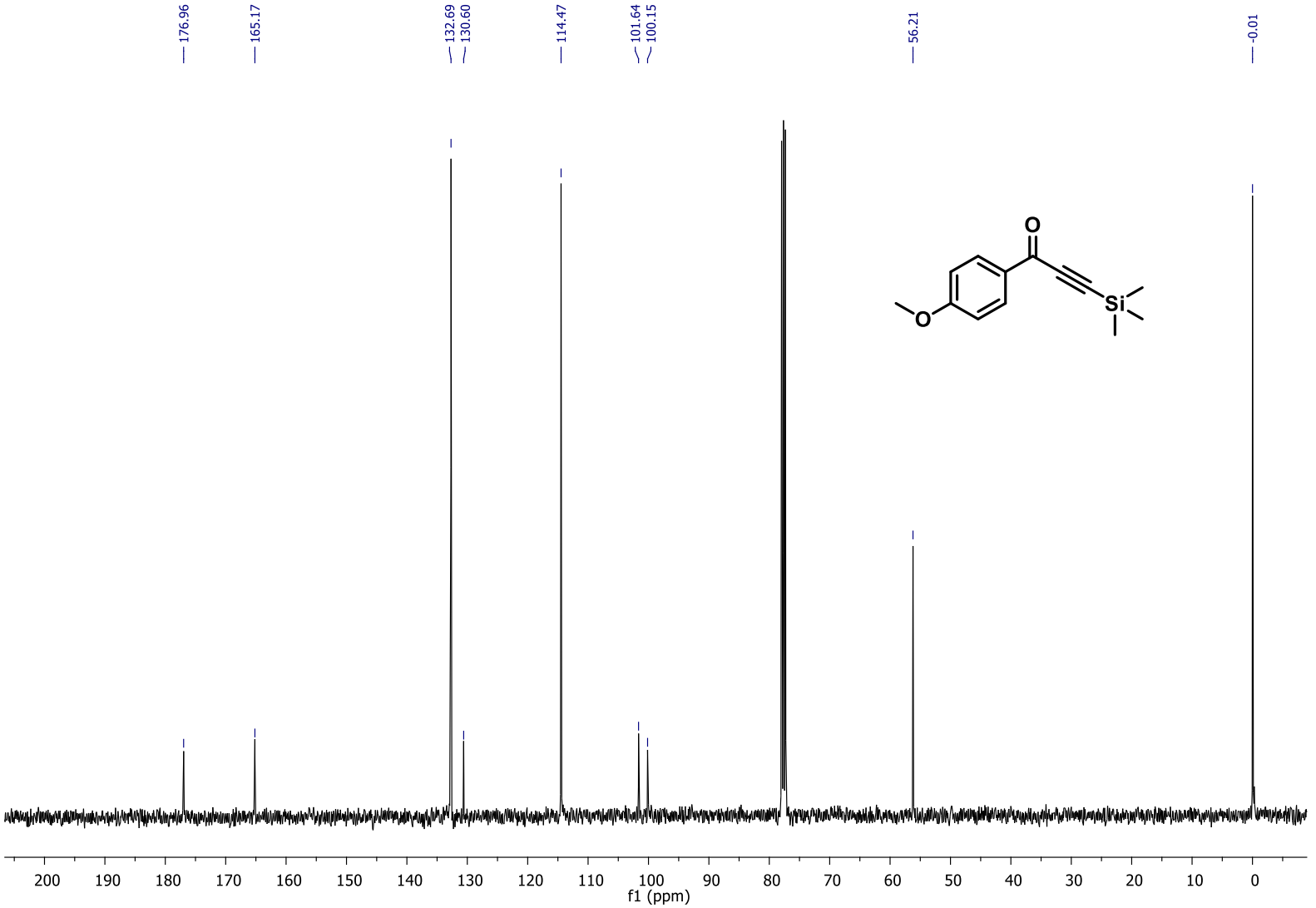
^{1}H NMR of compound **1s** (400 MHz, $CDCl_3$)



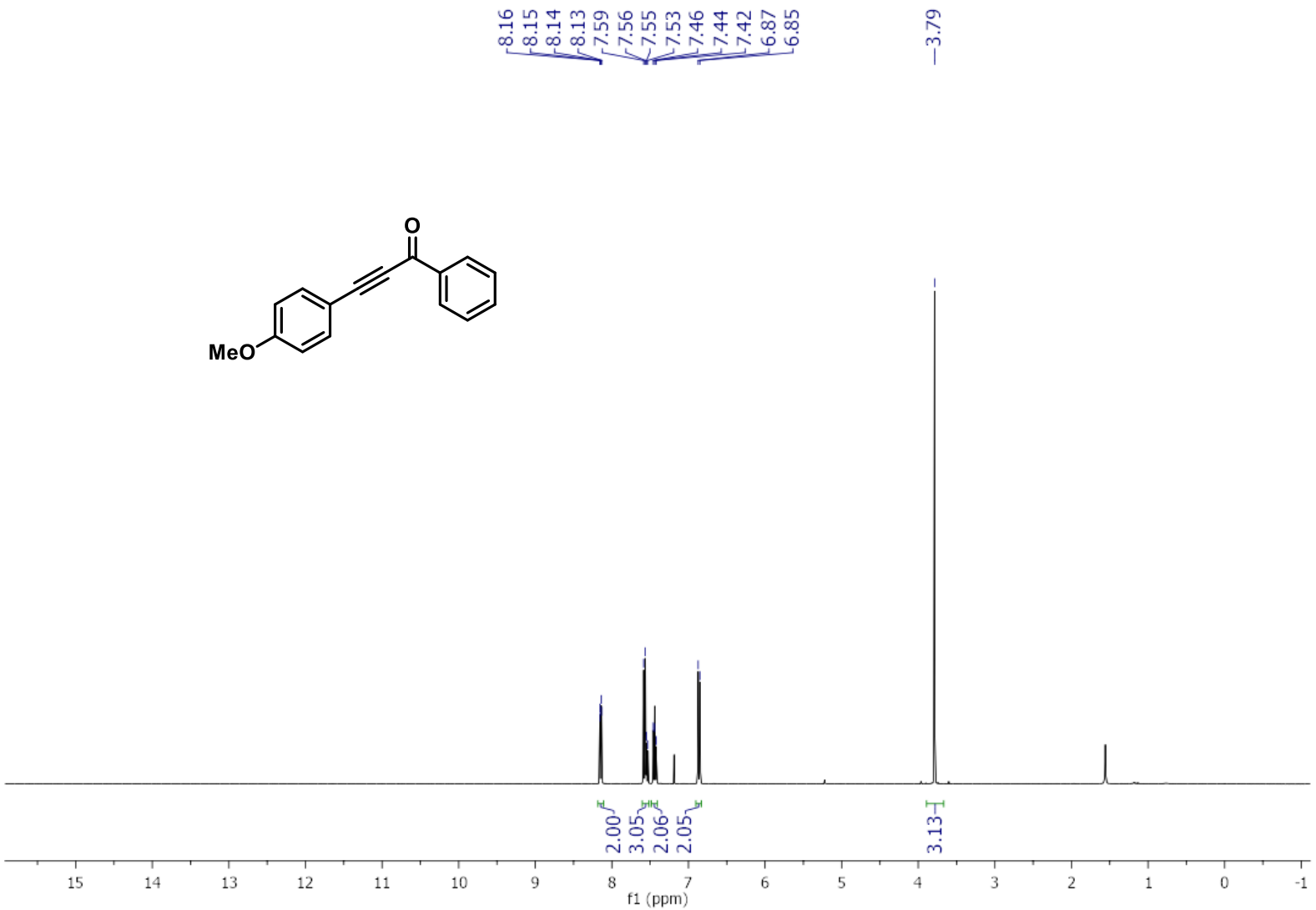
^{13}C NMR of compound **1s** (100 MHz, $CDCl_3$)



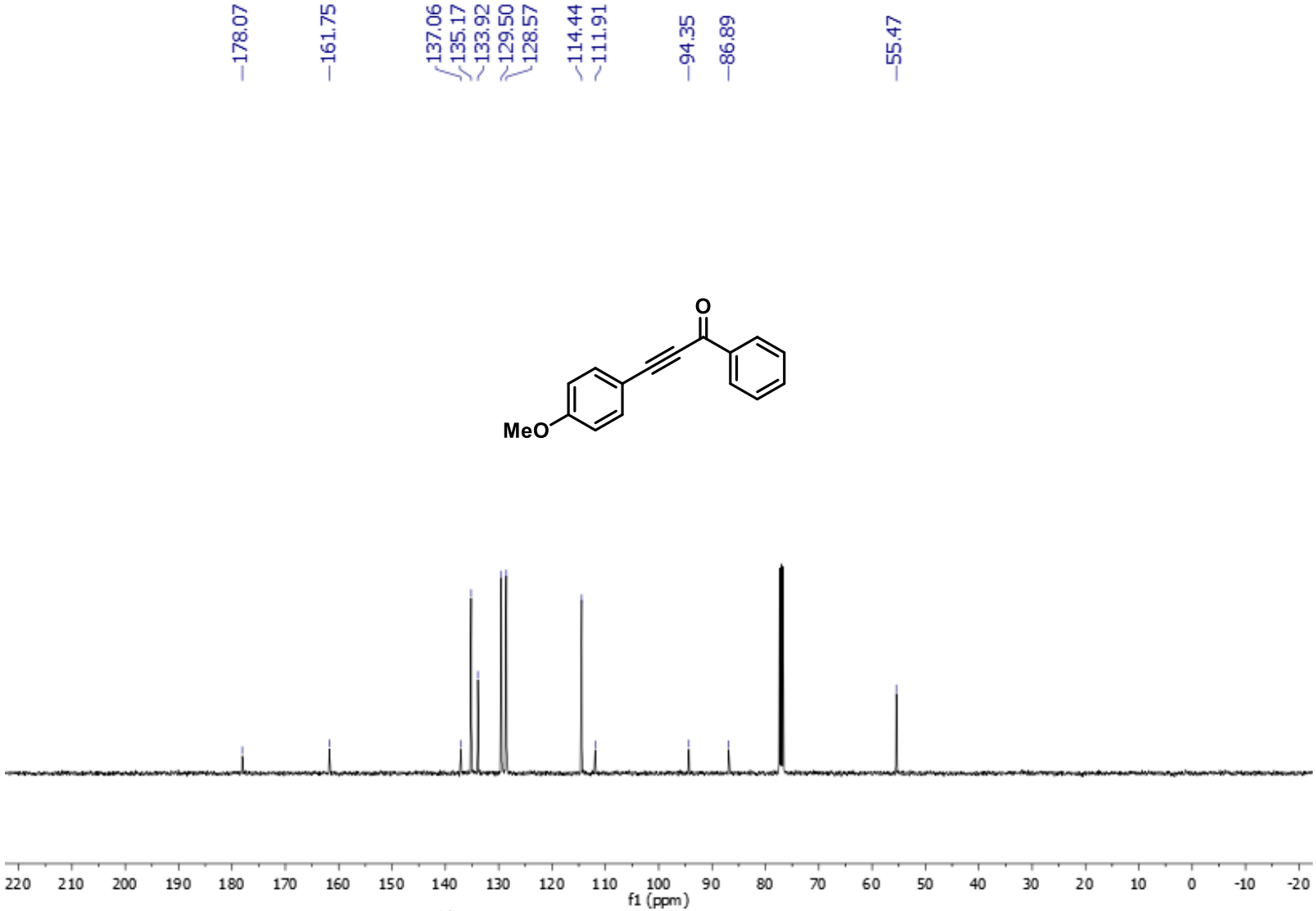
^{1}H NMR of compound **1t** (400 MHz, $CDCl_3$)



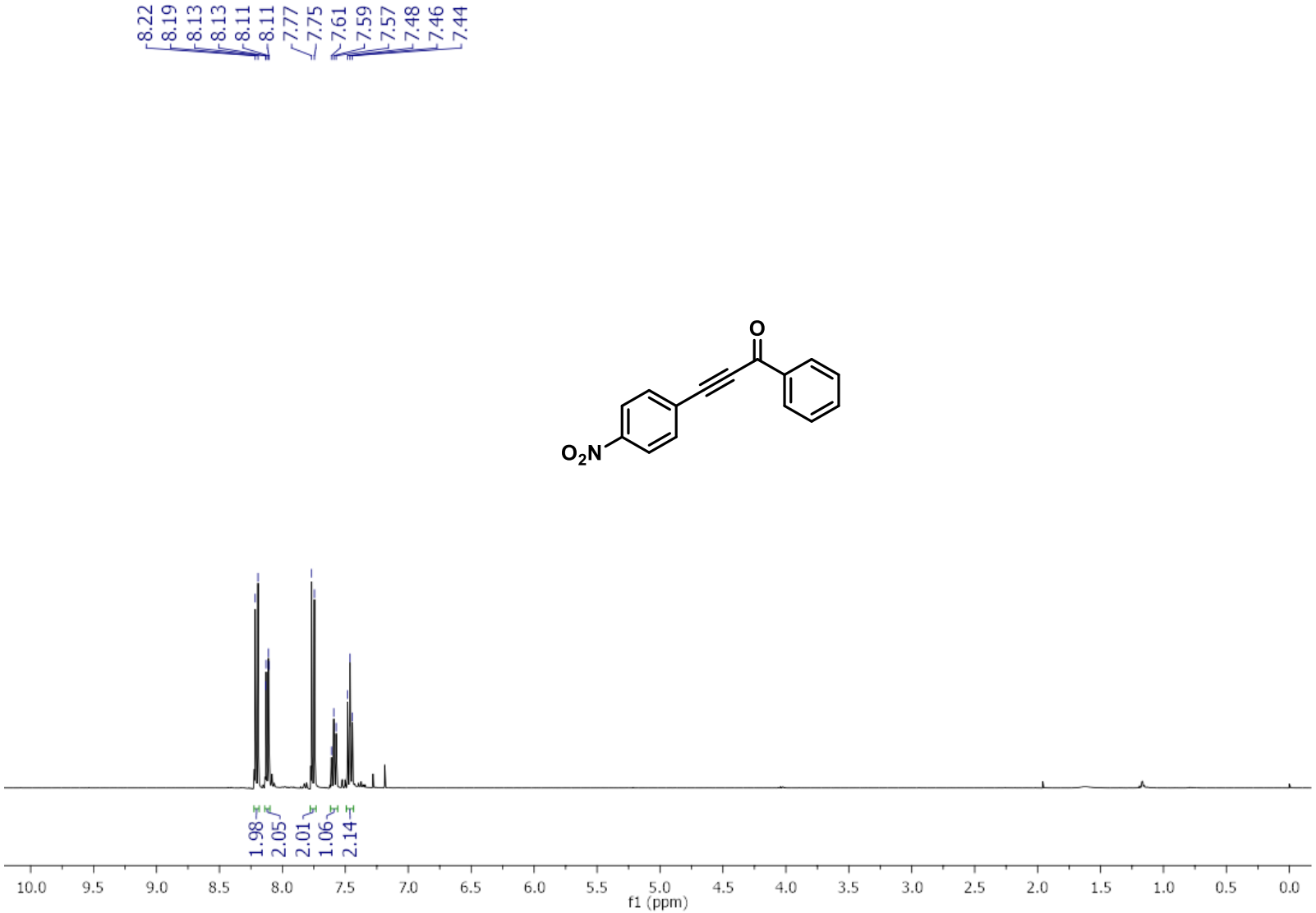
^{13}C NMR of compound **1t** (100 MHz, $CDCl_3$)



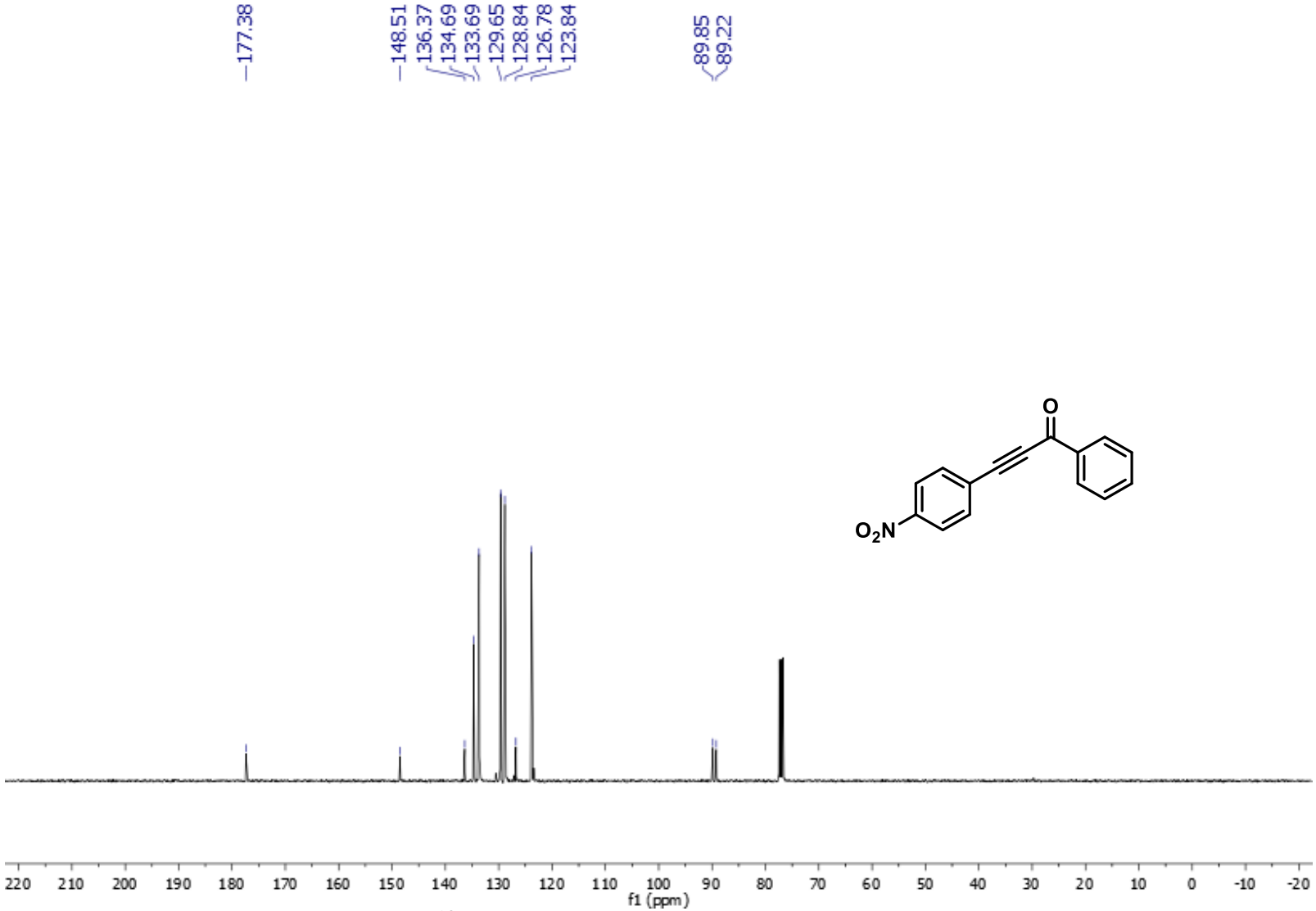
^{1}H NMR of compound **1u** (400 MHz, $CDCl_3$)



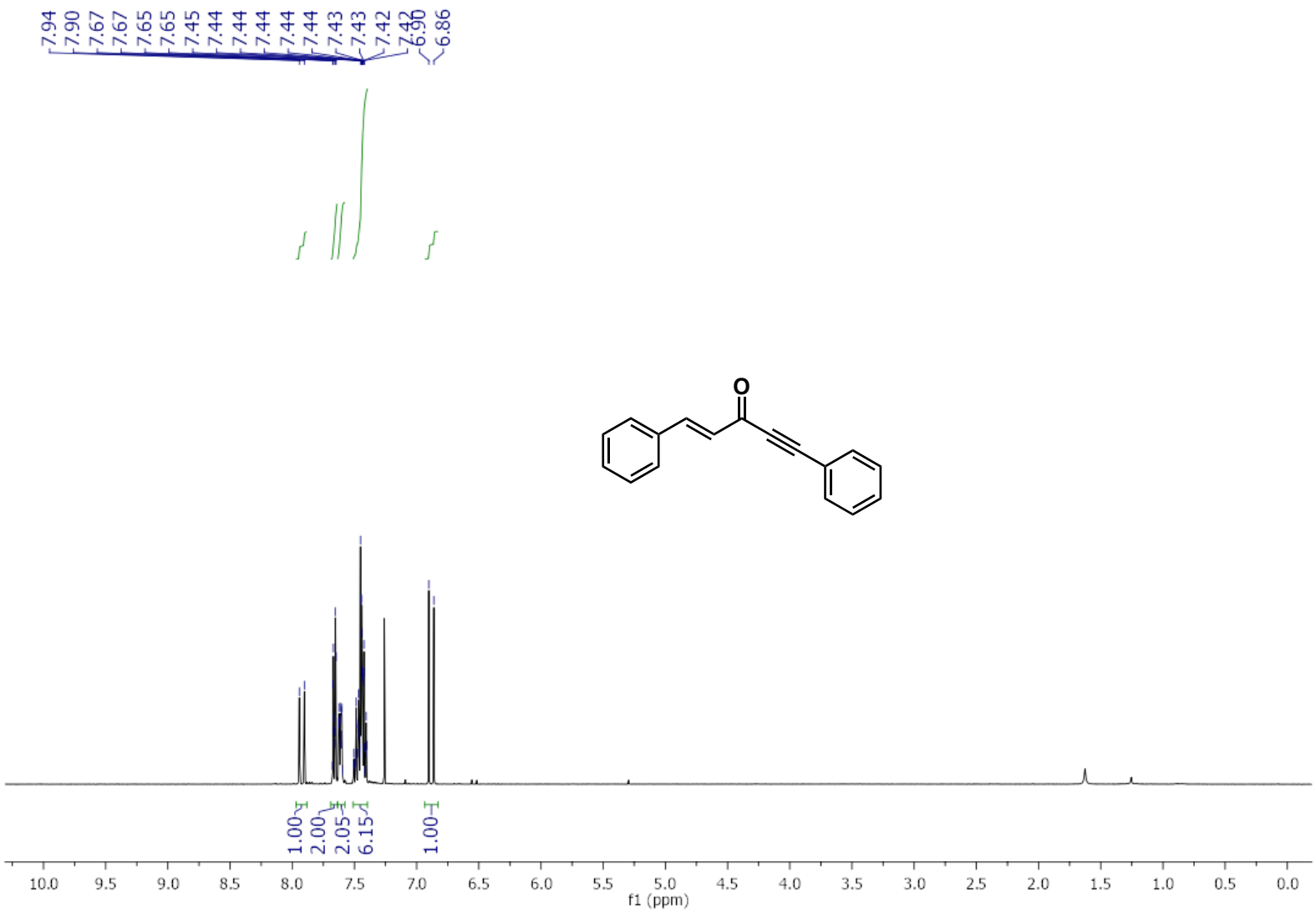
^{13}C NMR of compound **1u** (100 MHz, $CDCl_3$)



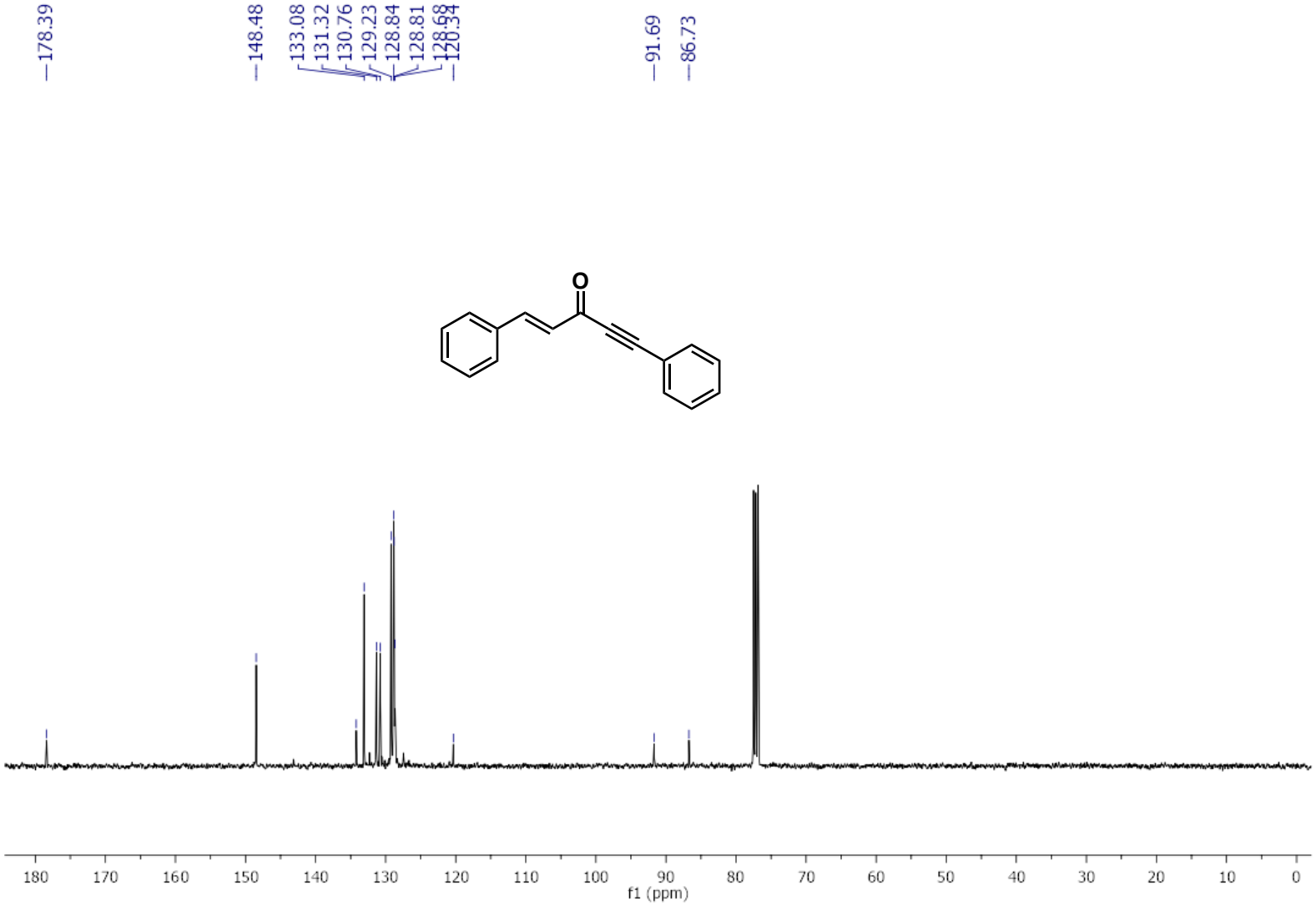
^{1}H NMR of compound **1v** (400 MHz, $CDCl_3$)



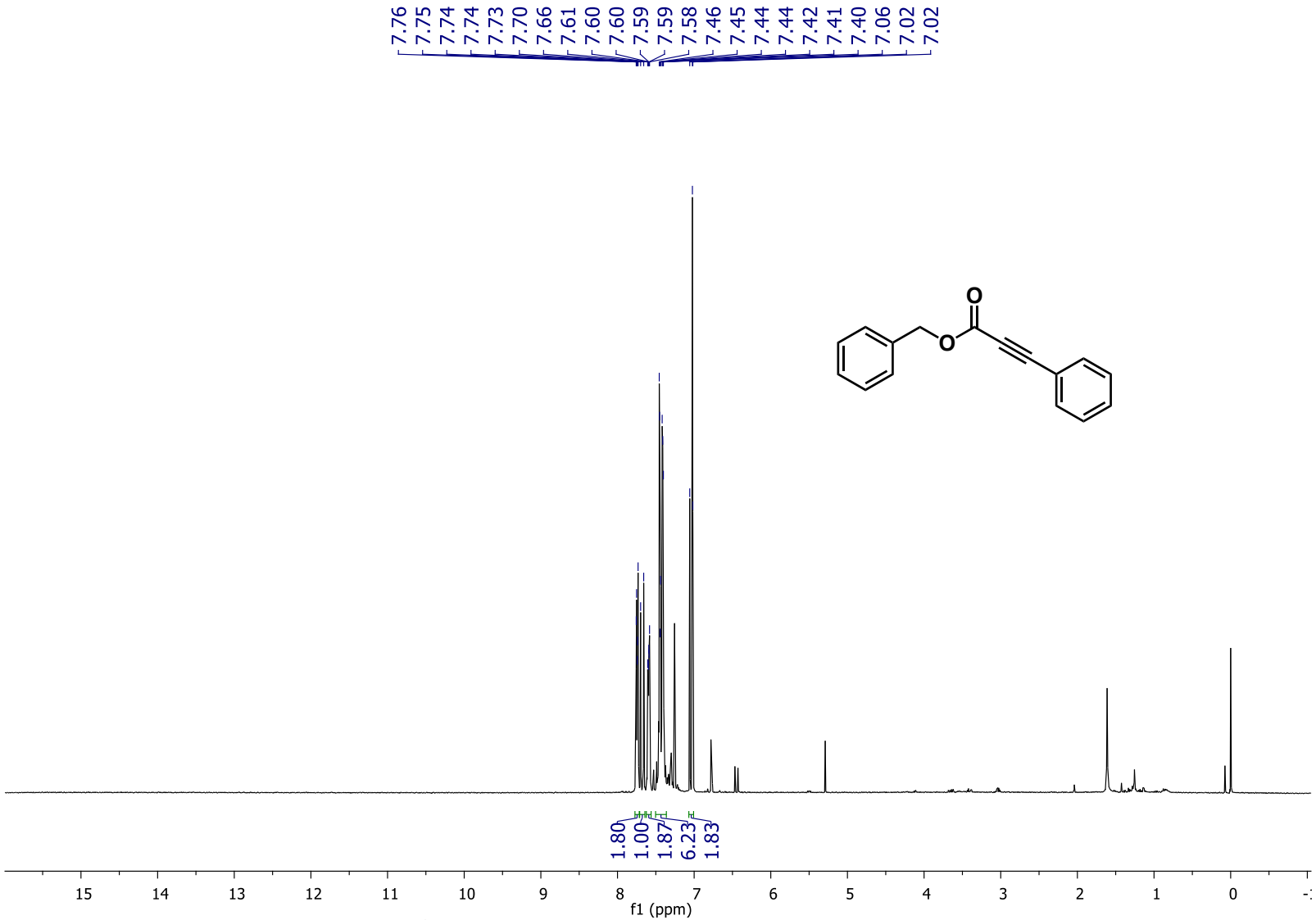
^{13}C NMR of compound **1v** (100 MHz, $CDCl_3$)



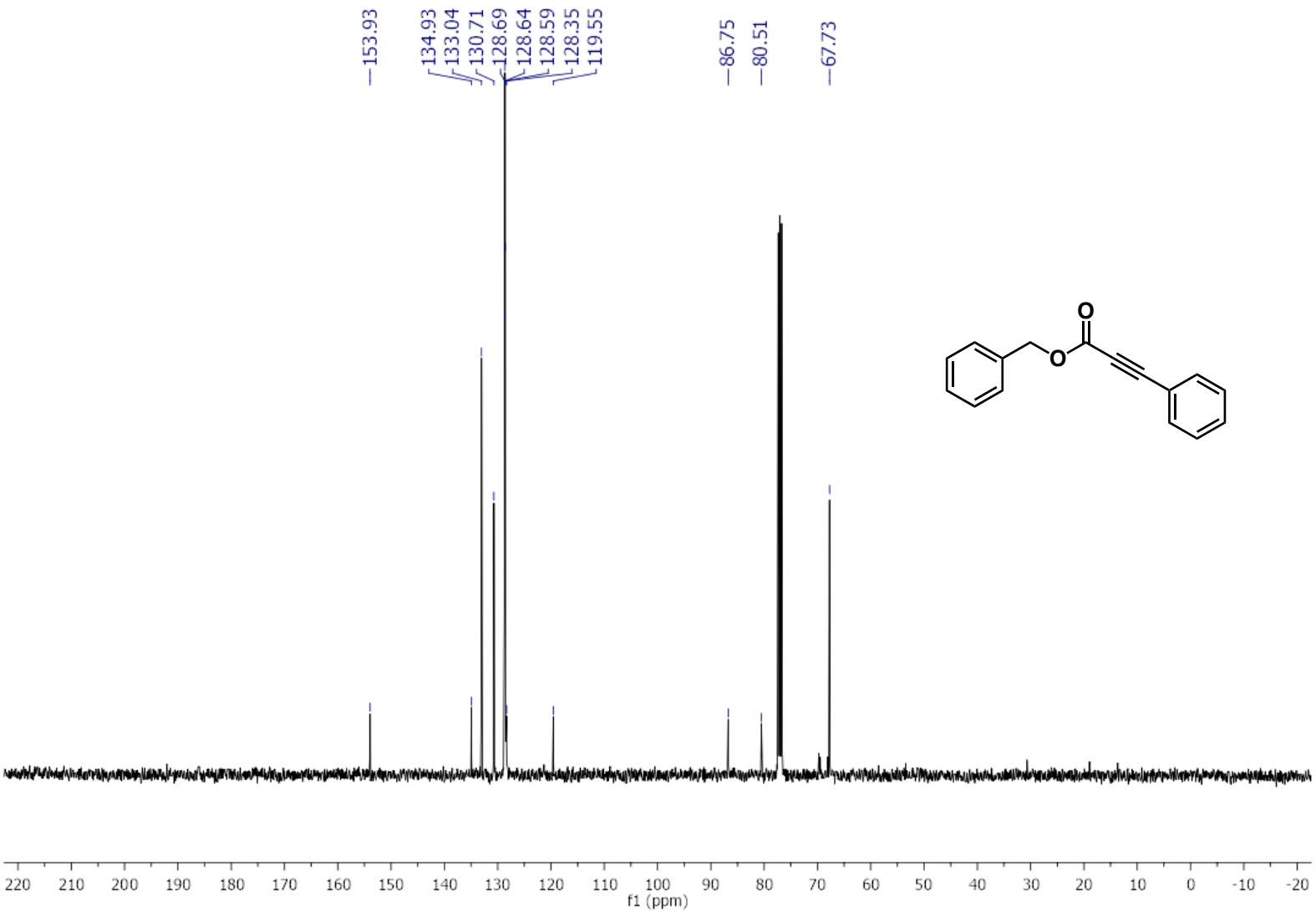
^{1}H NMR of compound **1w** (400 MHz, $CDCl_3$)



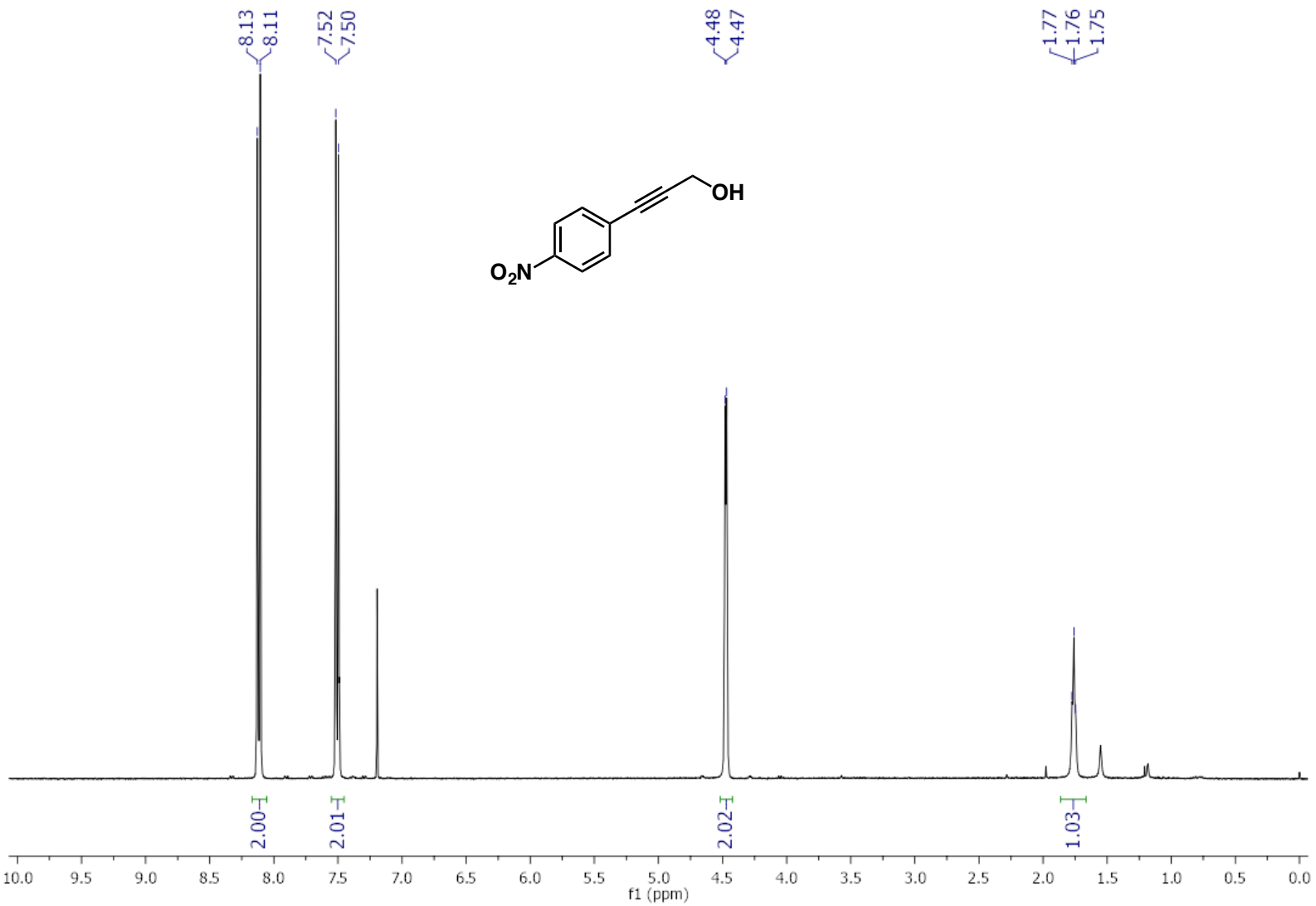
^{13}C NMR of compound **1w** (100 MHz, $CDCl_3$)



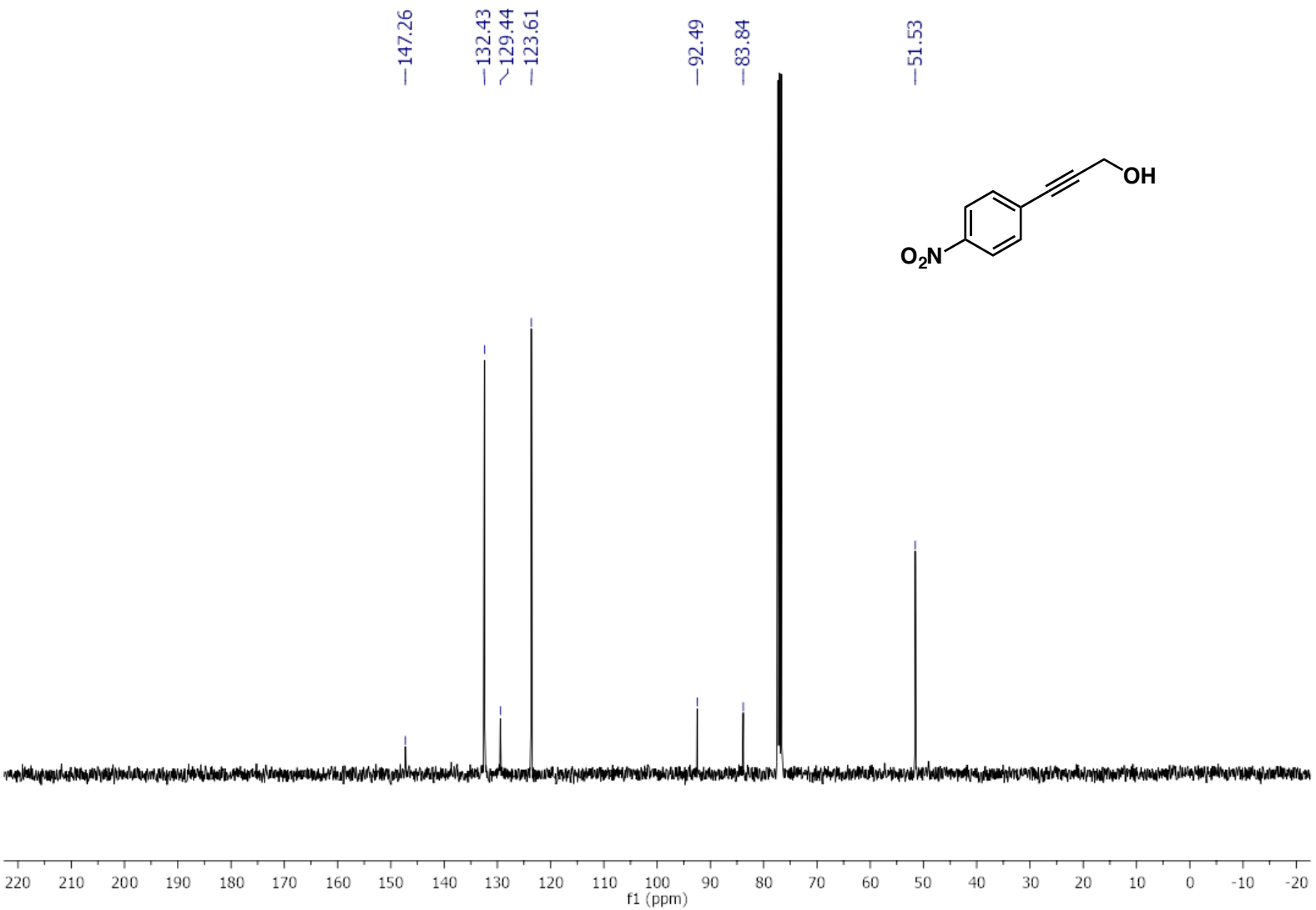
^{1}H NMR of compound **1y** (400 MHz, $CDCl_3$)



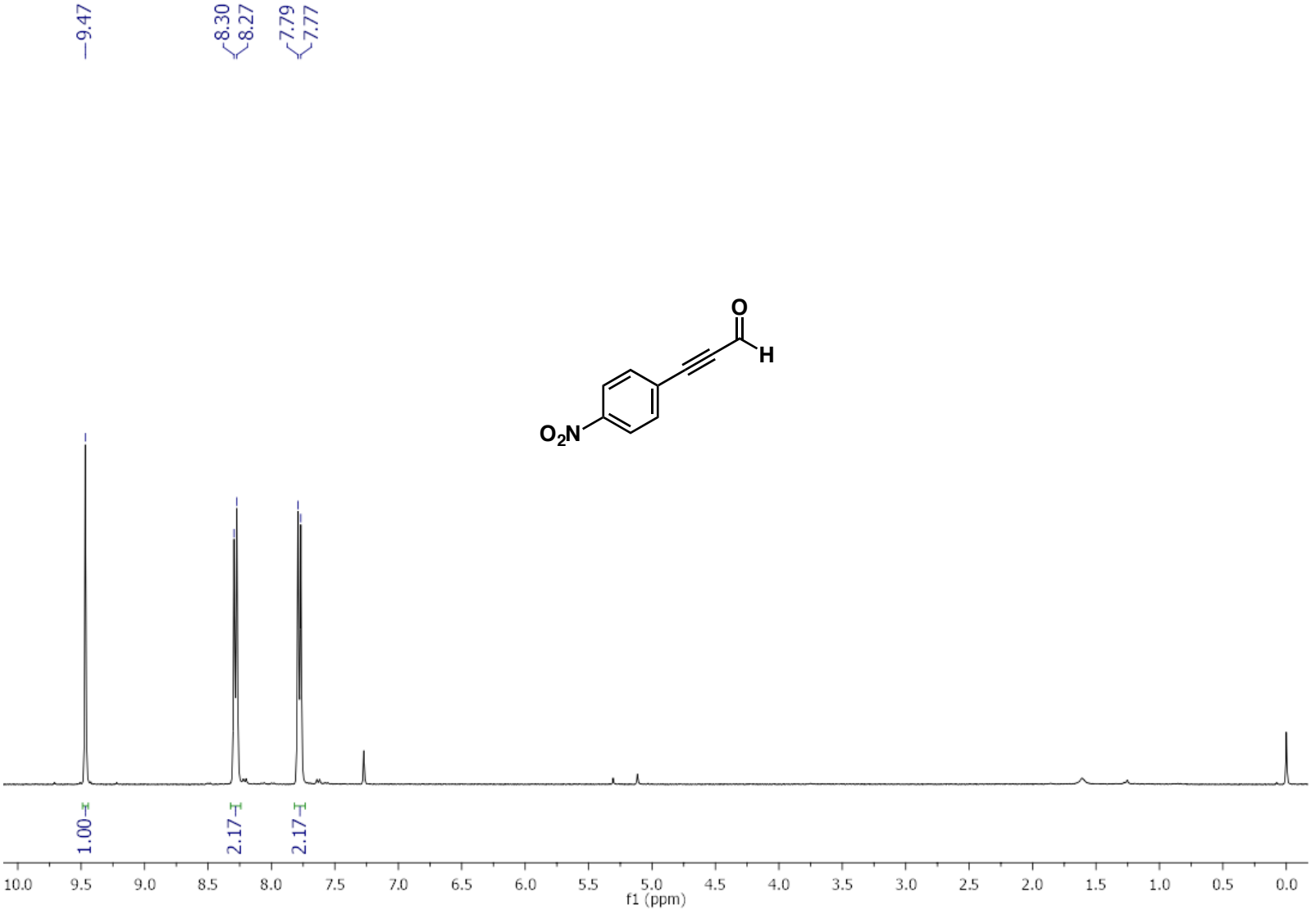
^{13}C NMR of compound **1y** (100 MHz, $CDCl_3$)



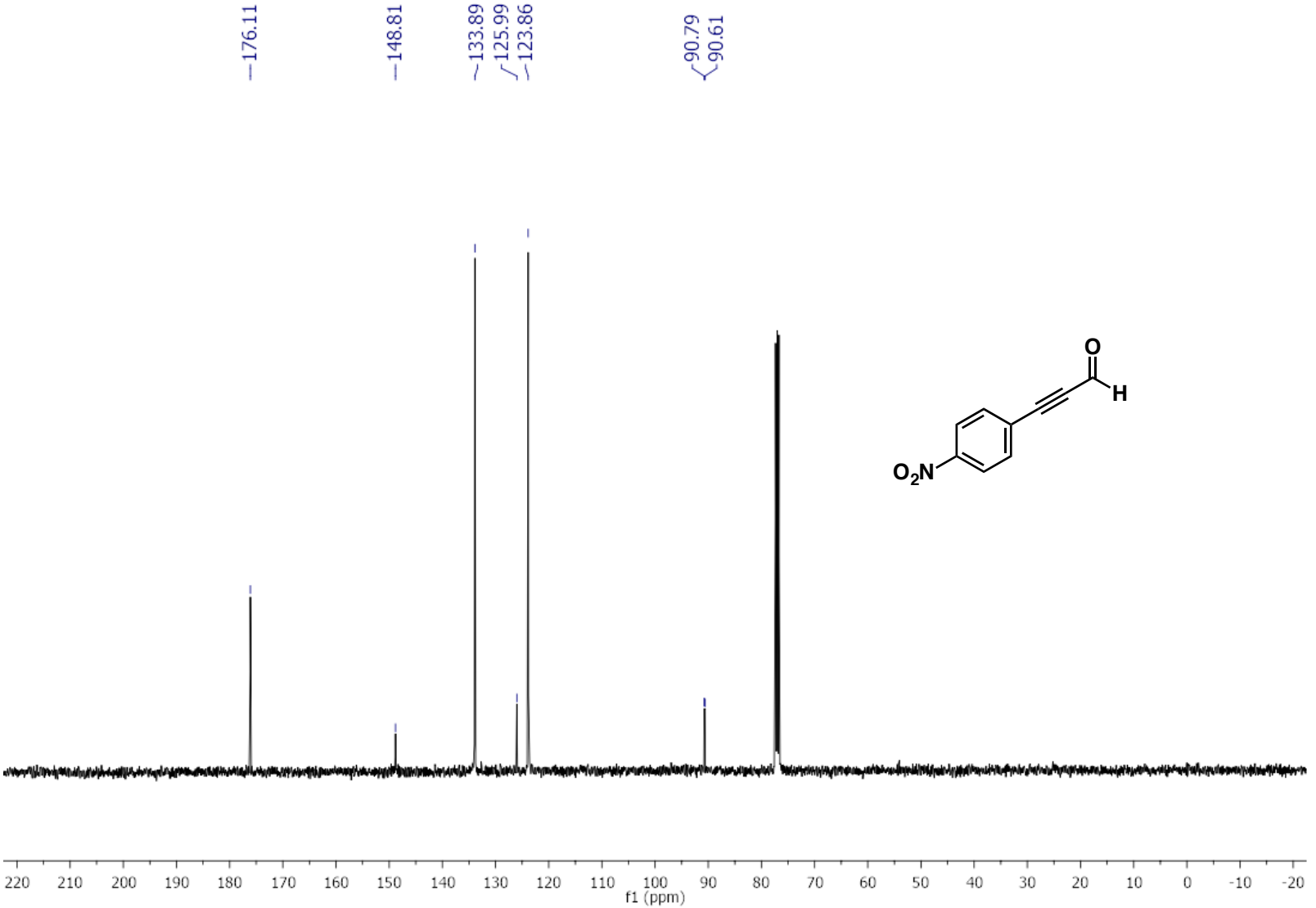
^{1}H NMR of compound **6a'** (400 MHz, $CDCl_3$)



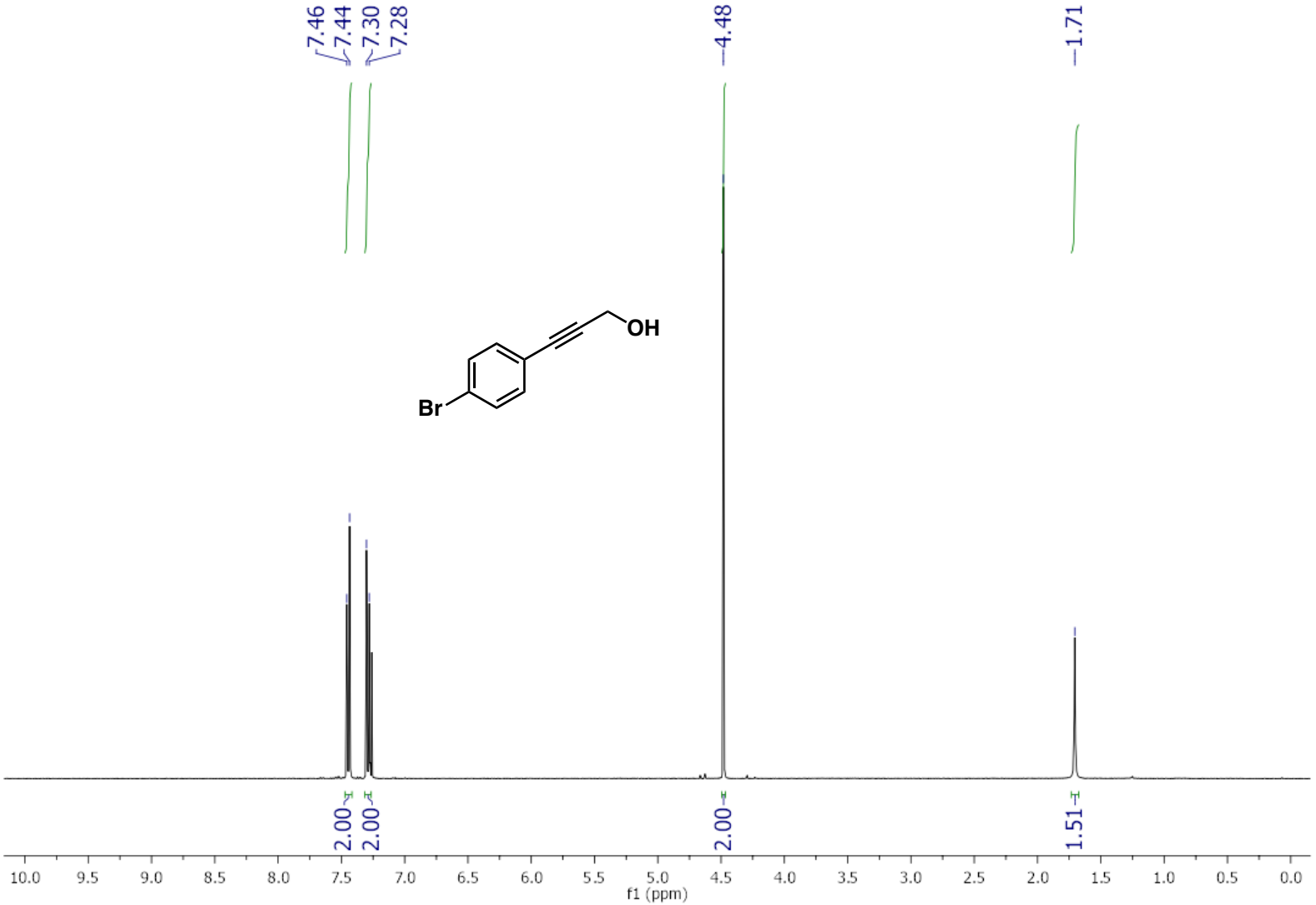
^{13}C NMR of compound **6a'** (100 MHz, $CDCl_3$)



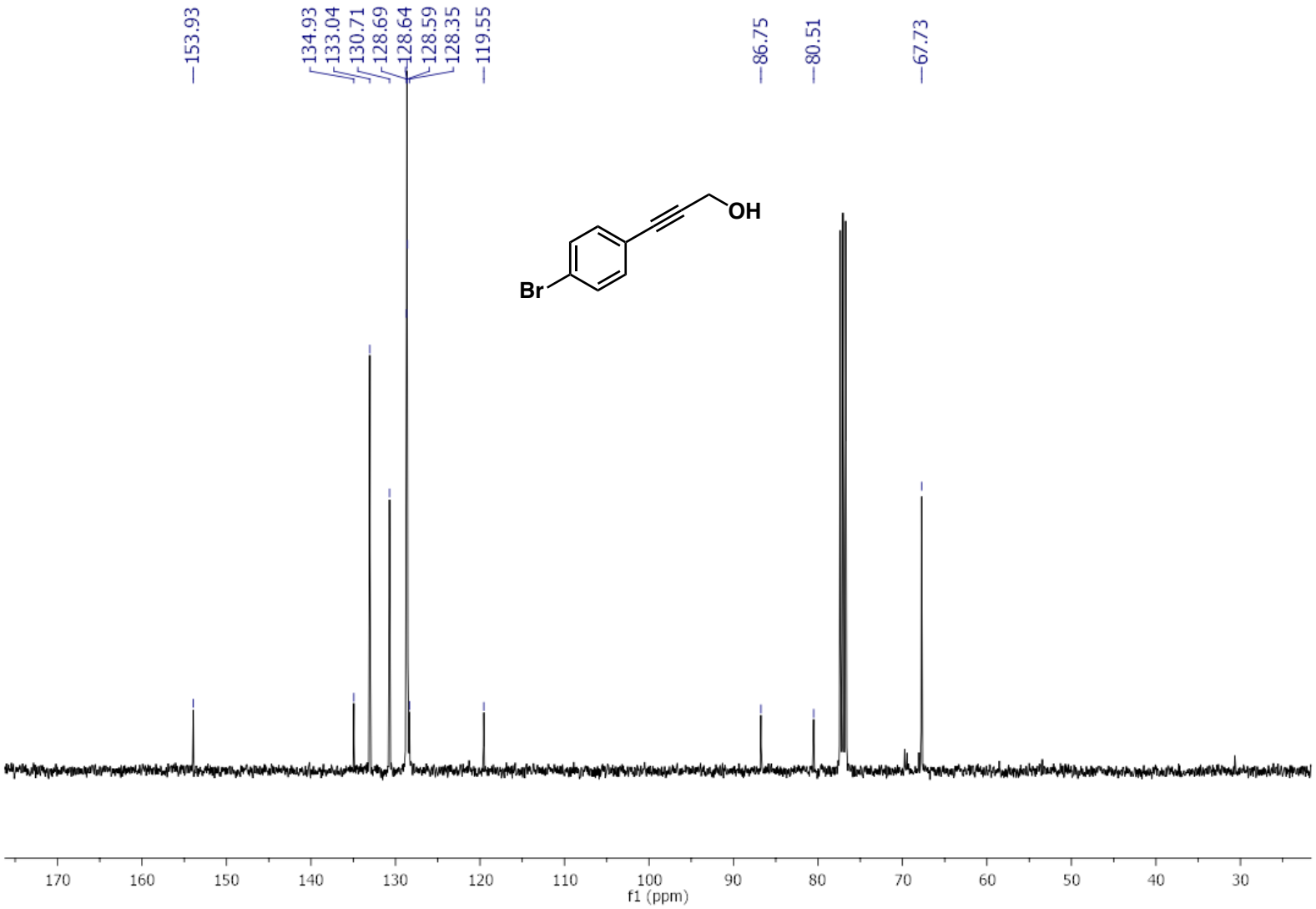
^{1}H NMR of compound **6a** (400 MHz, $CDCl_3$)



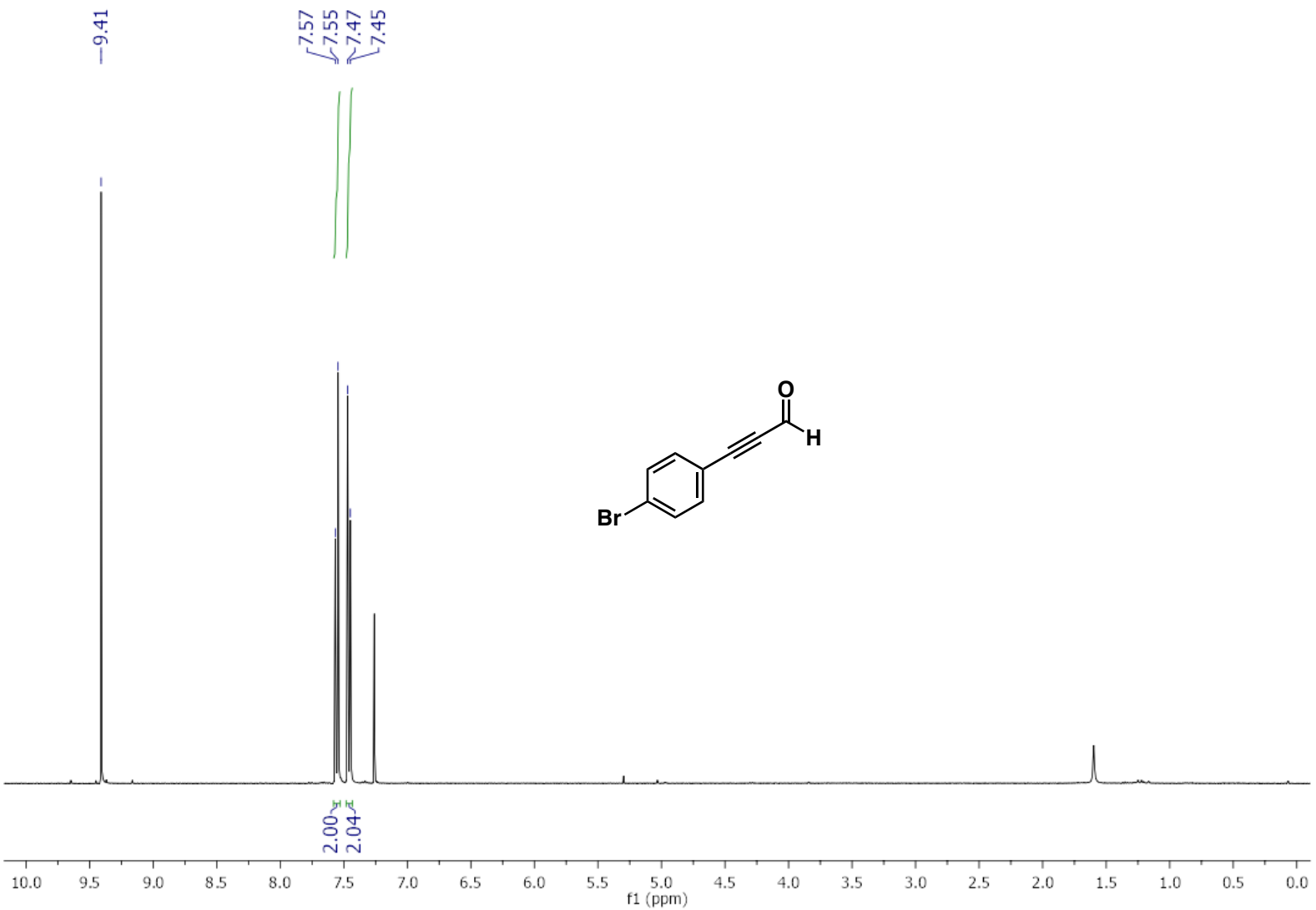
^{13}C NMR of compound **6a** (100 MHz, $CDCl_3$)



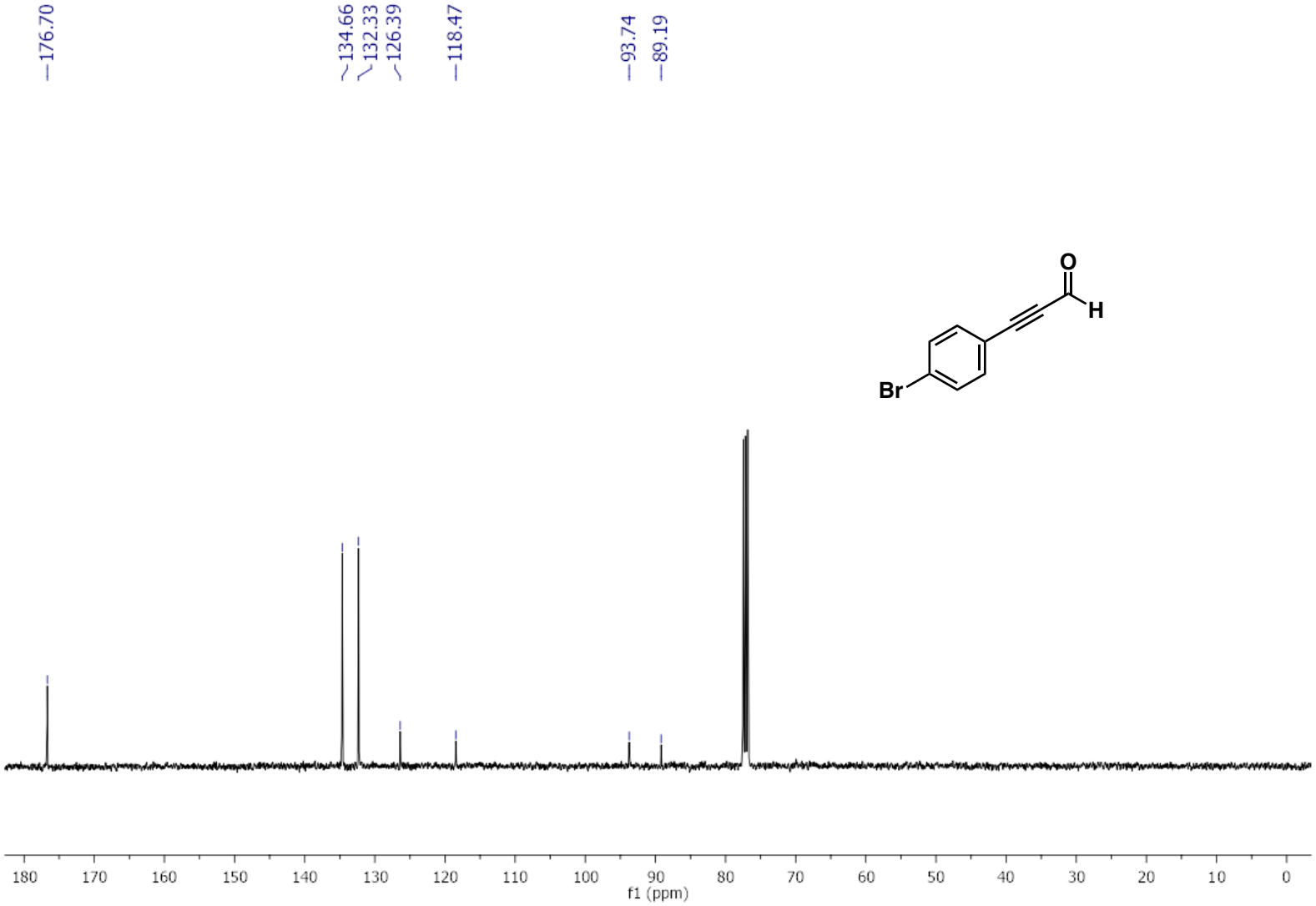
^{1}H NMR of compound **6b'** (400 MHz, $CDCl_3$)



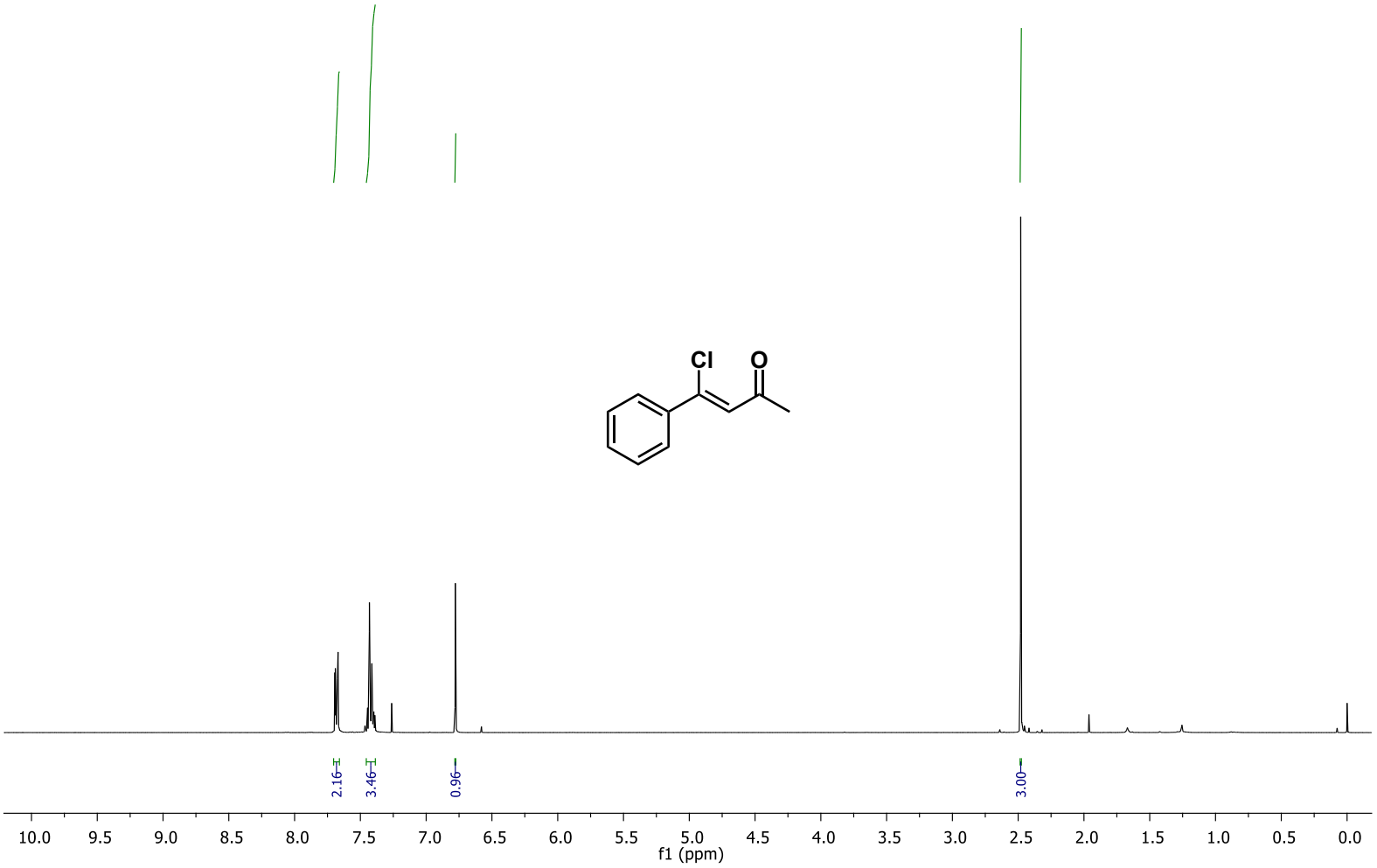
^{13}C NMR of compound **6b'** (100 MHz, $CDCl_3$)



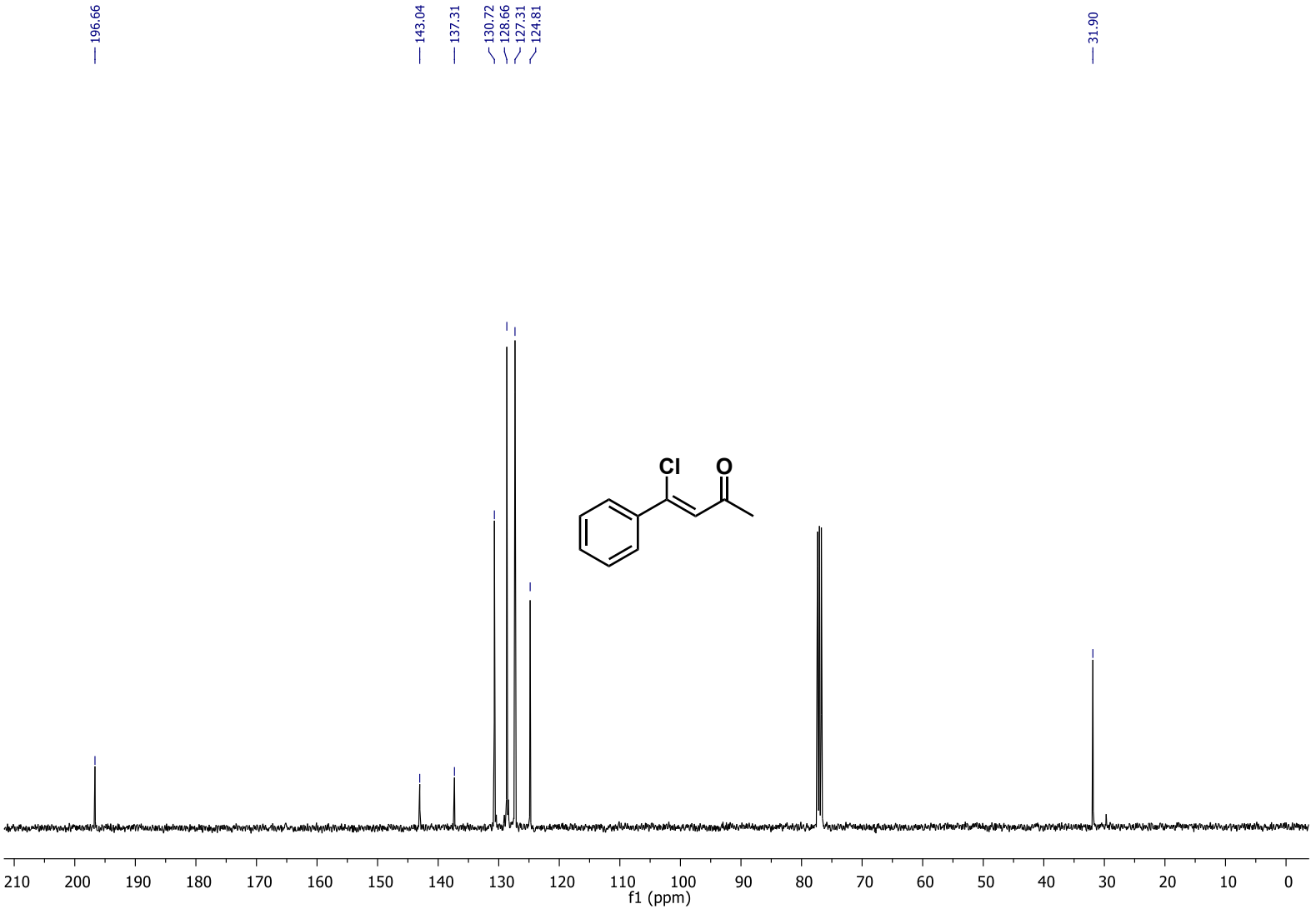
^{1}H NMR of compound **6b** (400 MHz, $CDCl_3$)



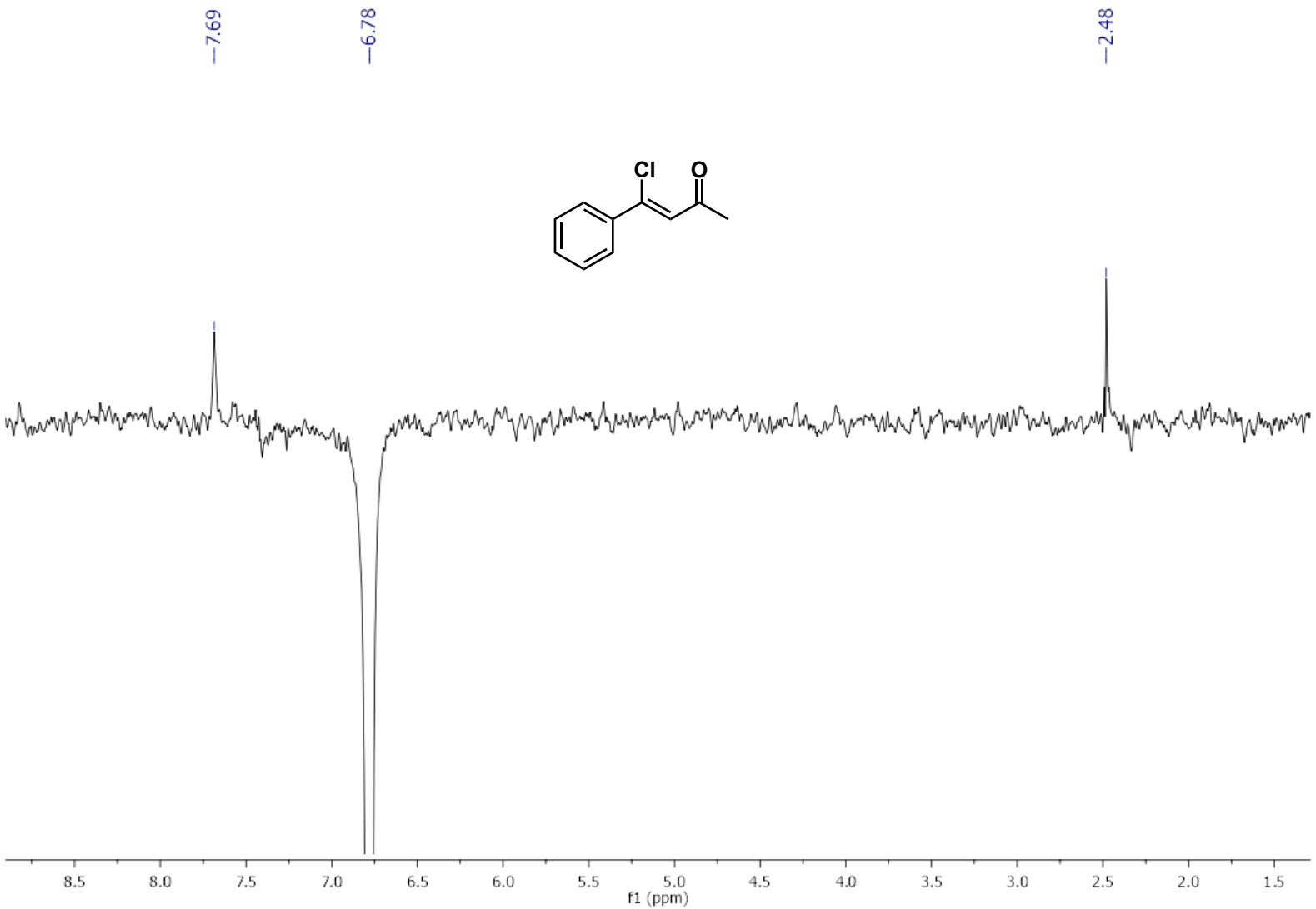
^{13}C NMR of compound **6b** (100 MHz, $CDCl_3$)



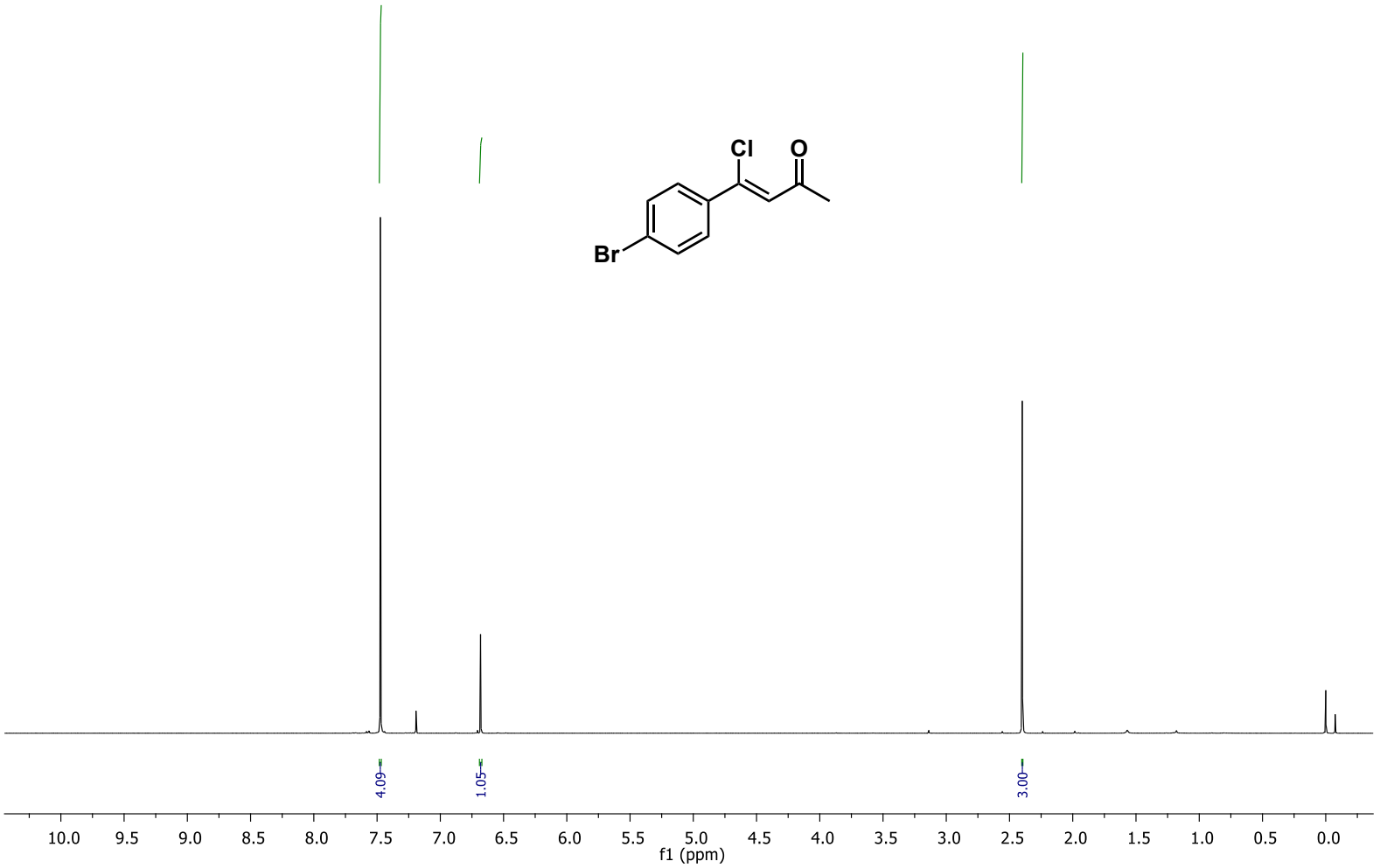
^{1}H NMR of compound **2a** (400 MHz, $CDCl_3$)



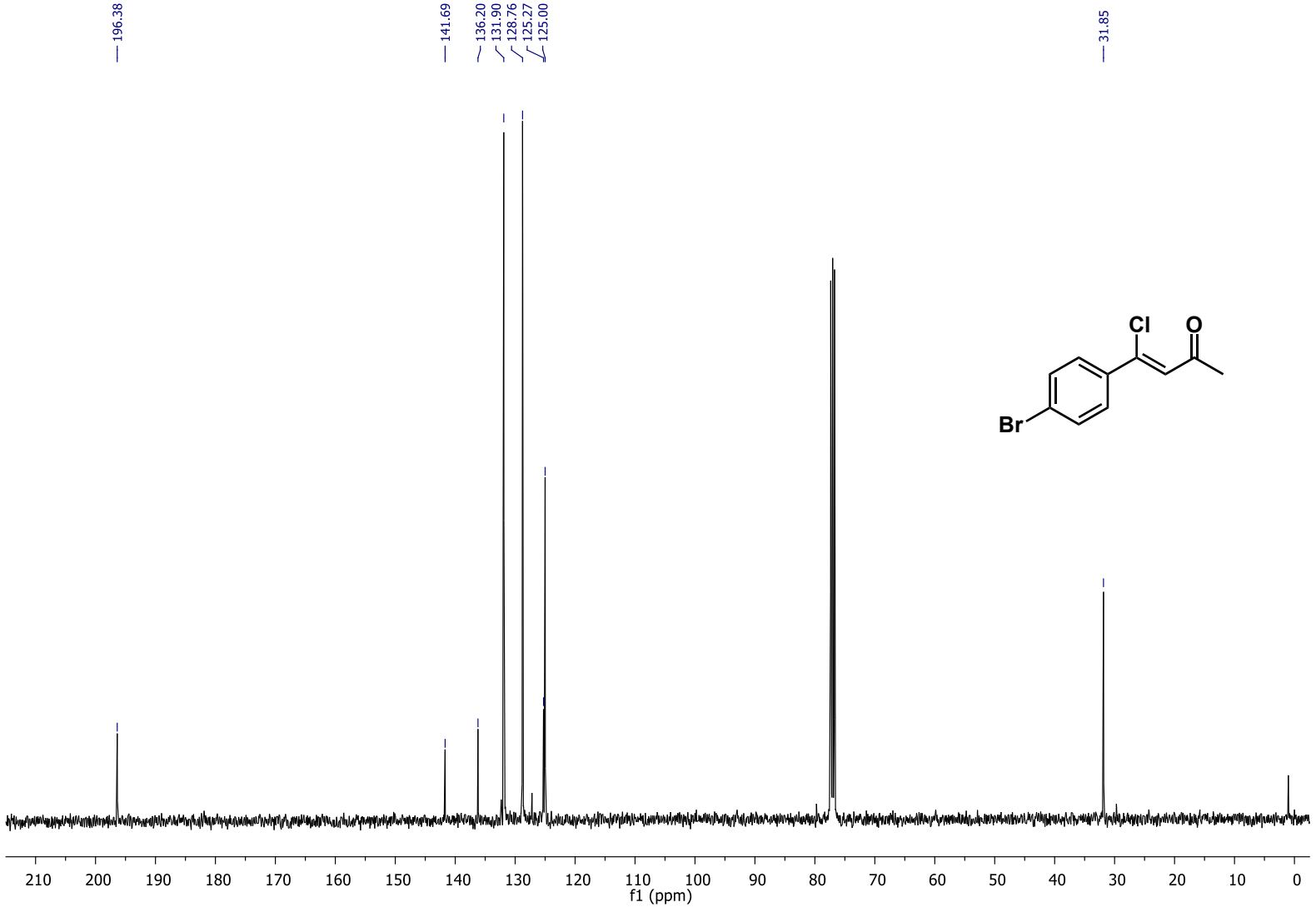
^{13}C NMR of compound **2a** (100 MHz, $CDCl_3$)



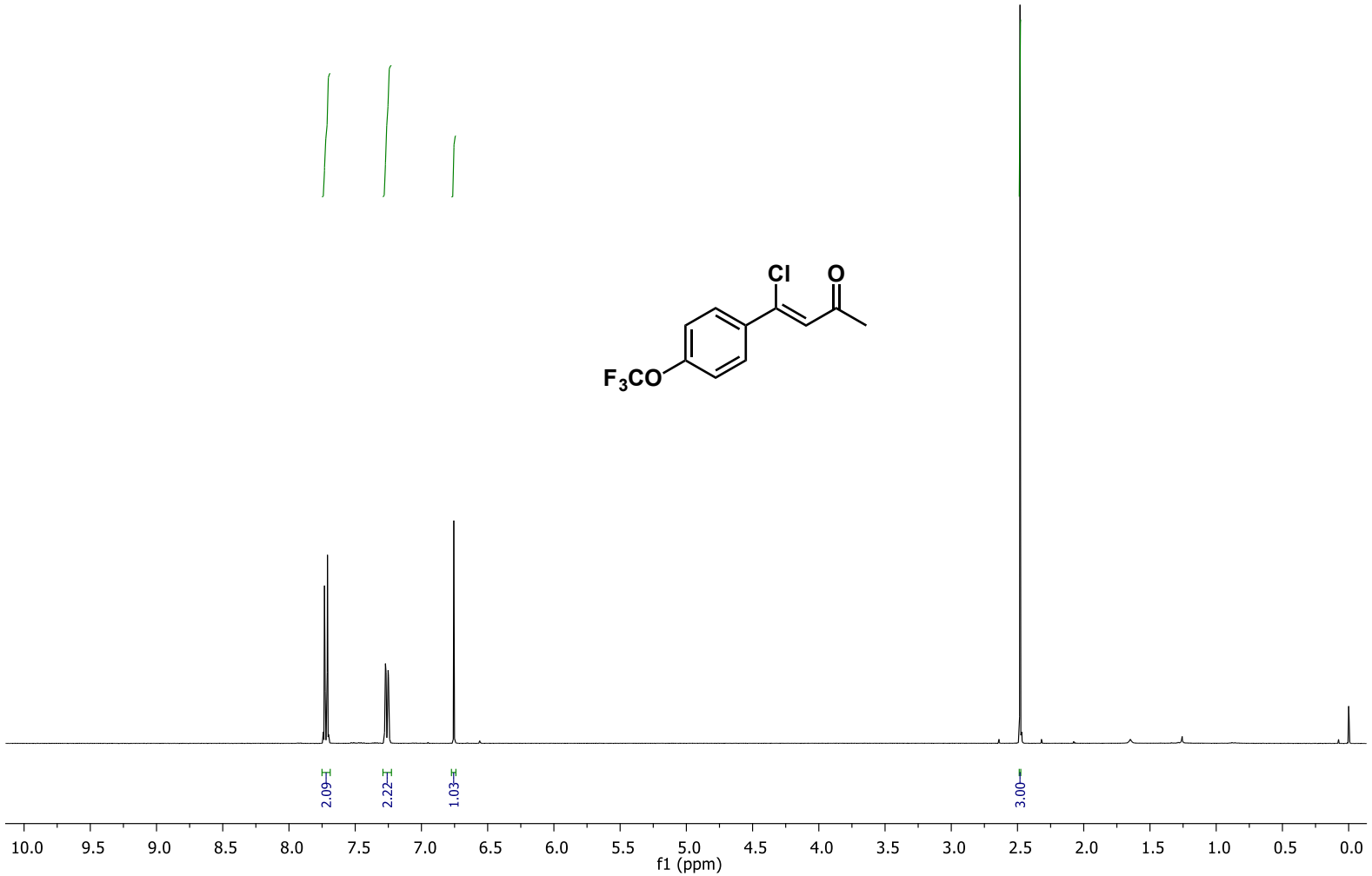
^{1}H NOE NMR of compound **2a** (600 MHz, $CDCl_3$)



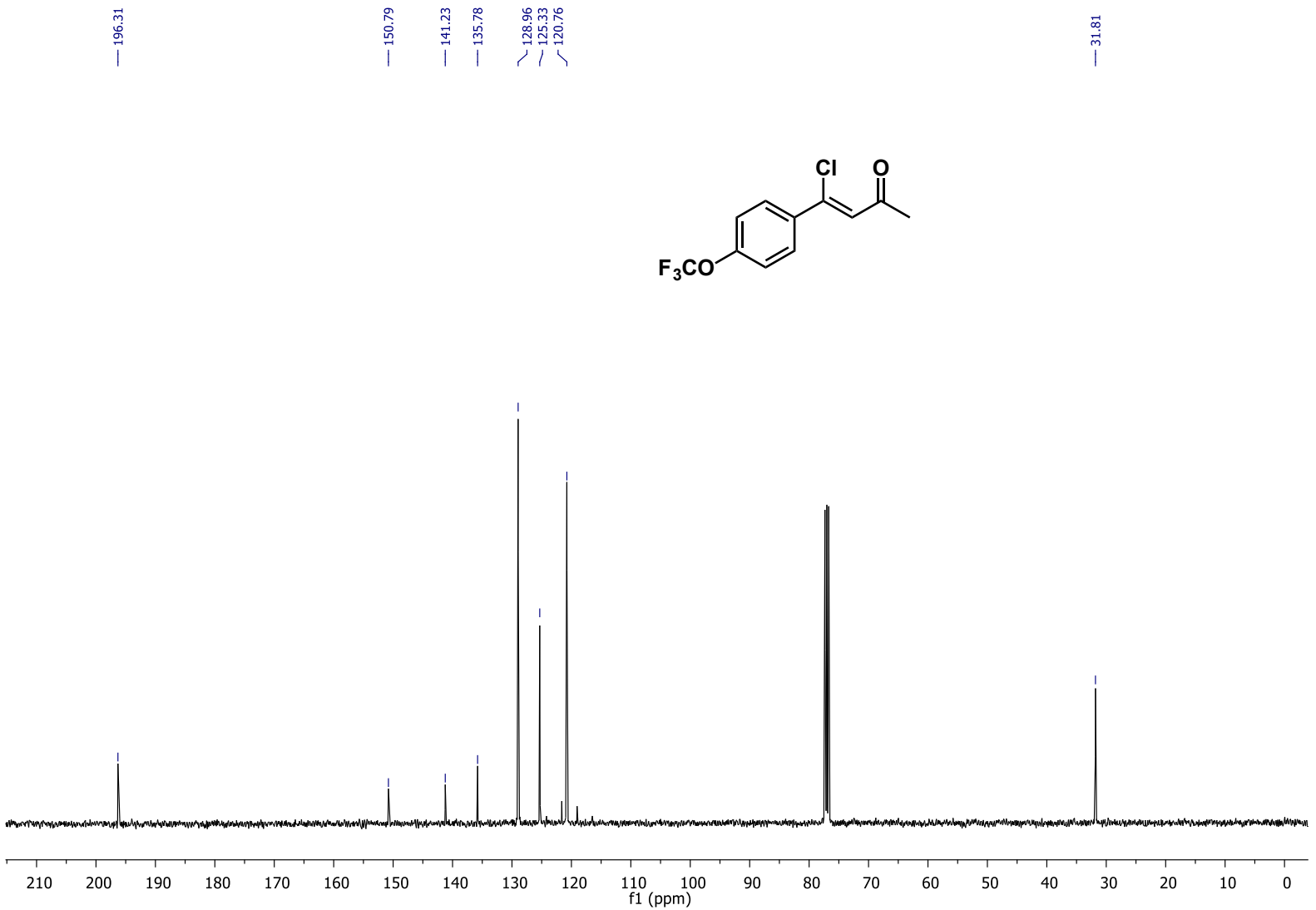
^{1}H NMR of compound **2b** (400 MHz, $CDCl_3$)



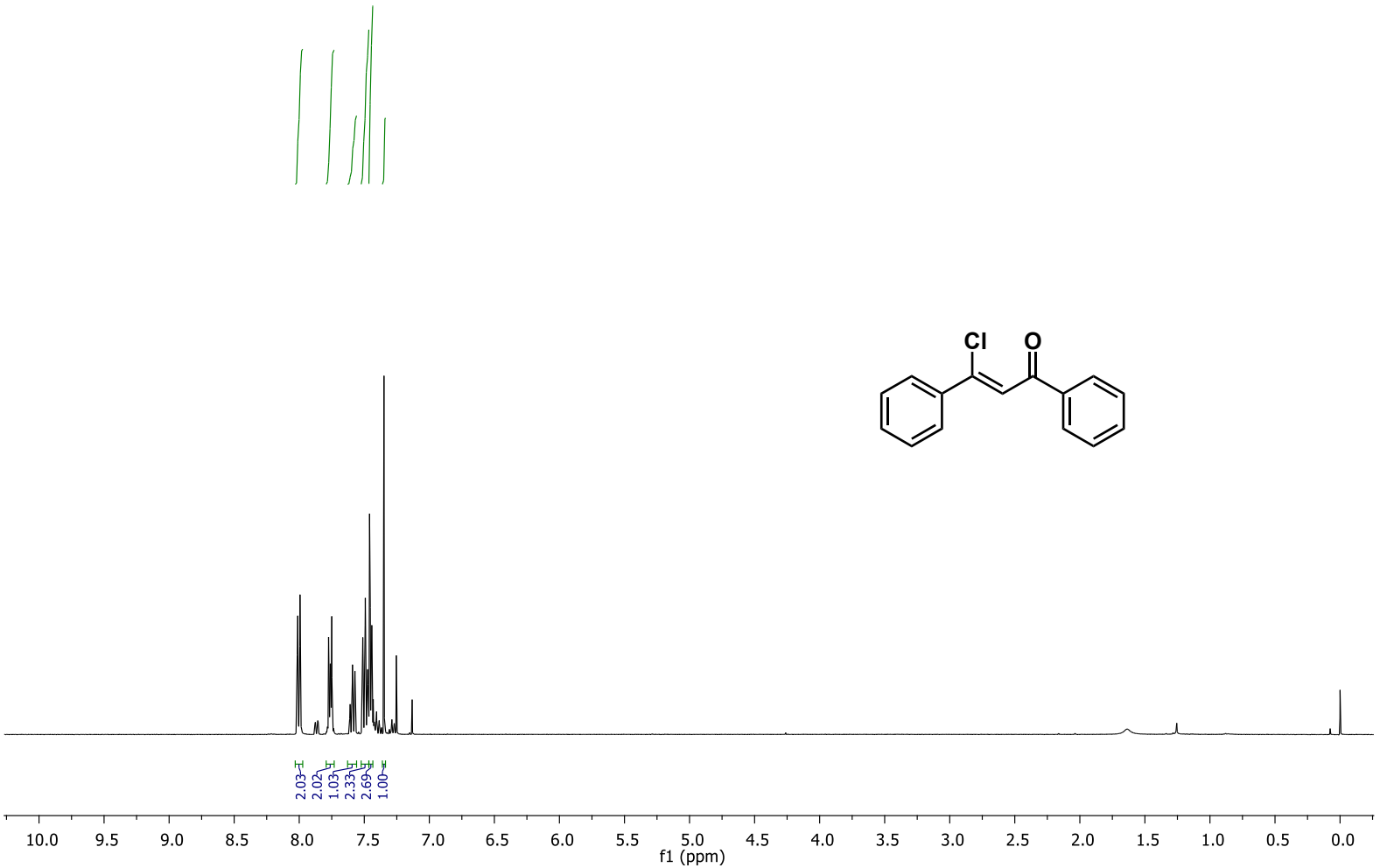
^{13}C NMR of compound **2b** (100 MHz, $CDCl_3$)



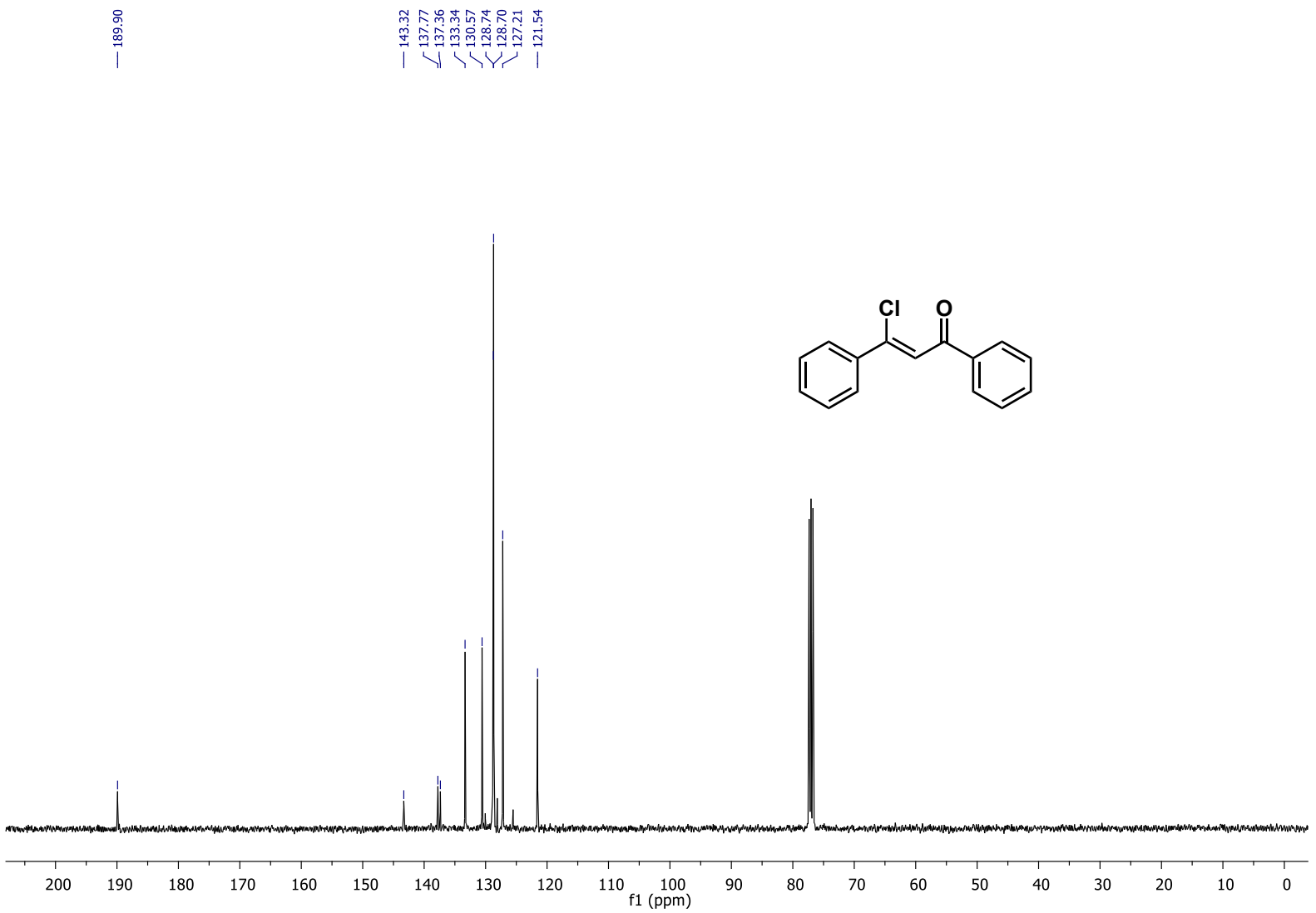
^{1}H NMR of compound **2c** (400 MHz, $CDCl_3$)



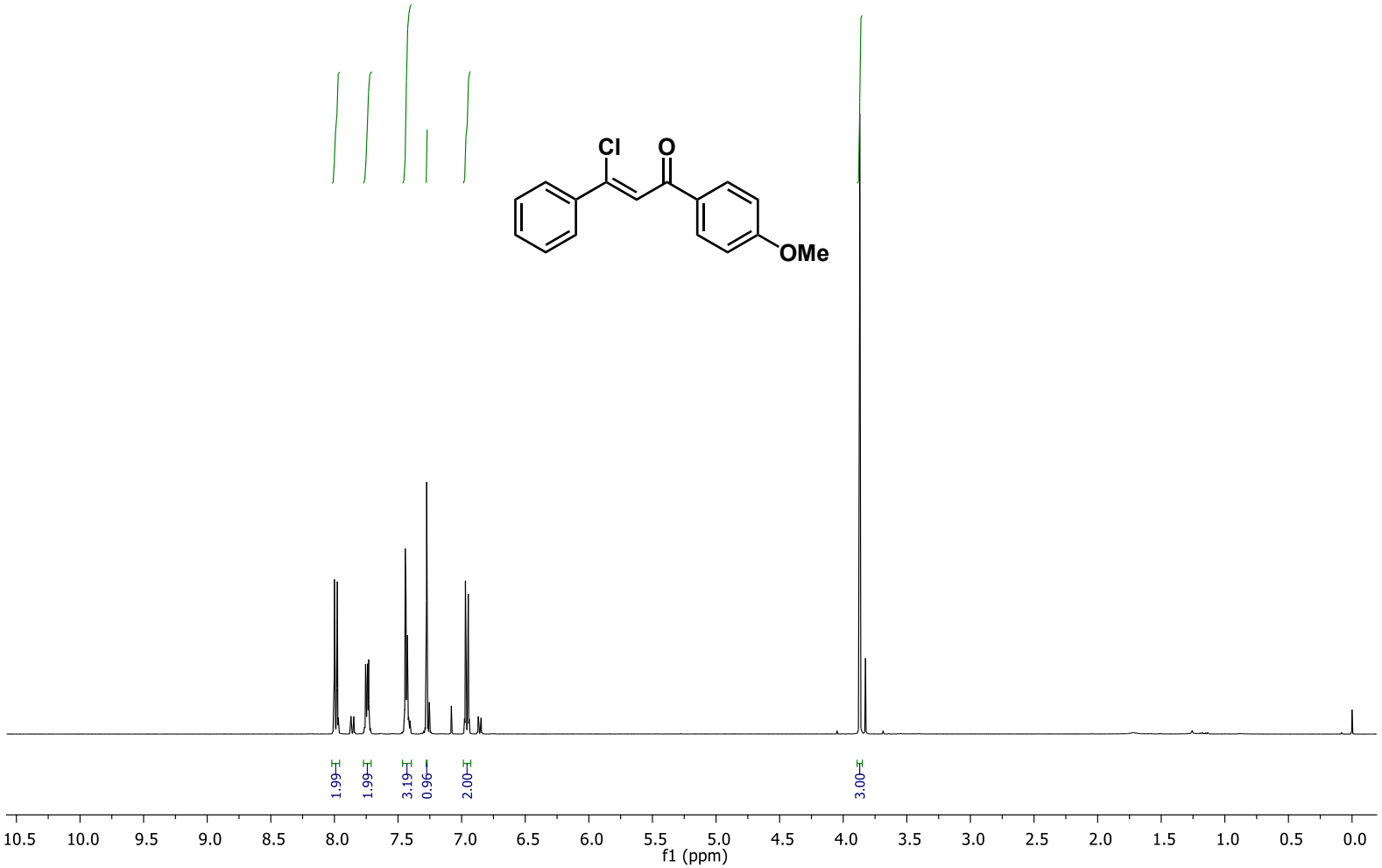
^{13}C NMR of compound **2c** (100 MHz, $CDCl_3$)



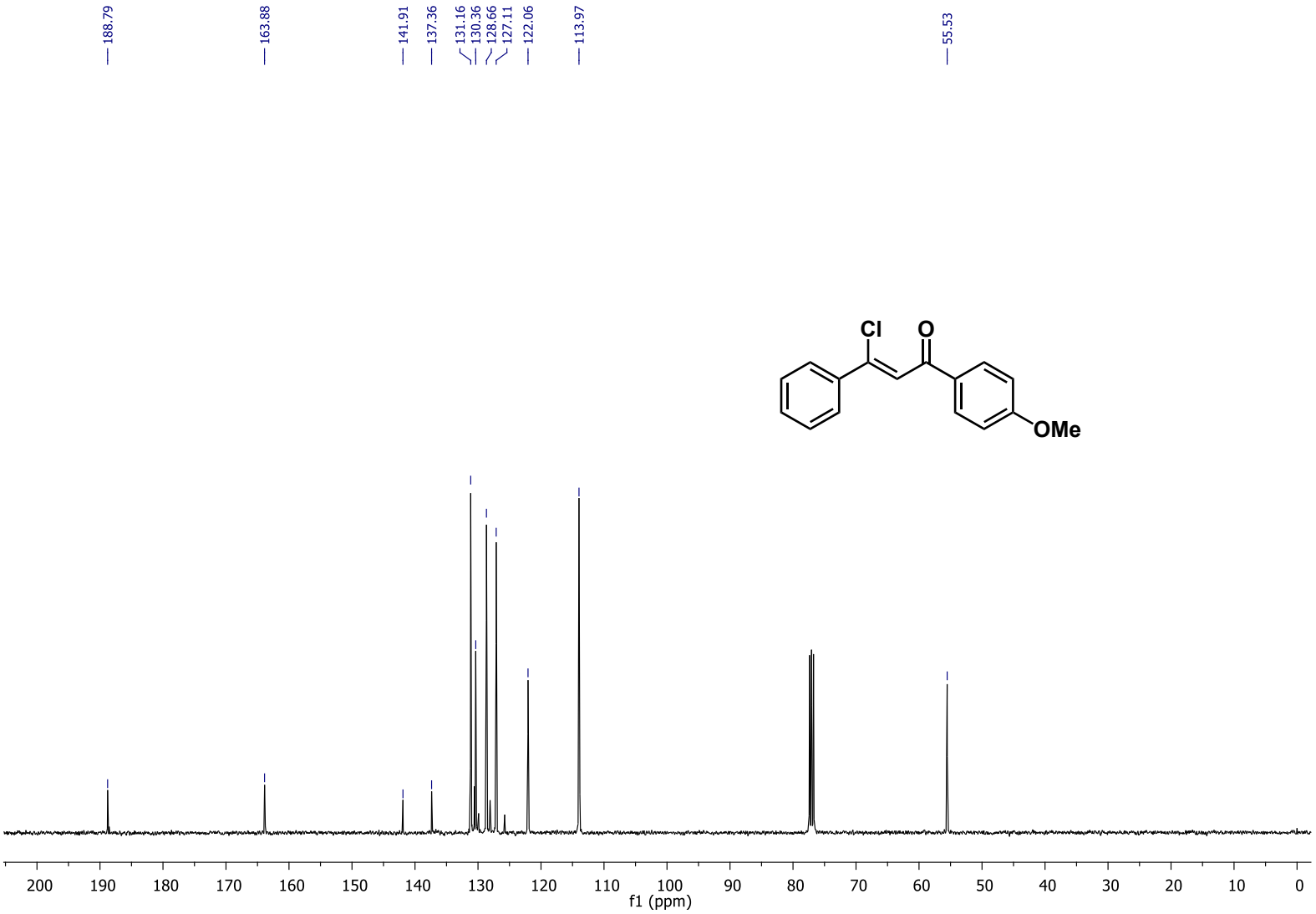
^{1}H NMR of compound **2d** (400 MHz, $CDCl_3$)



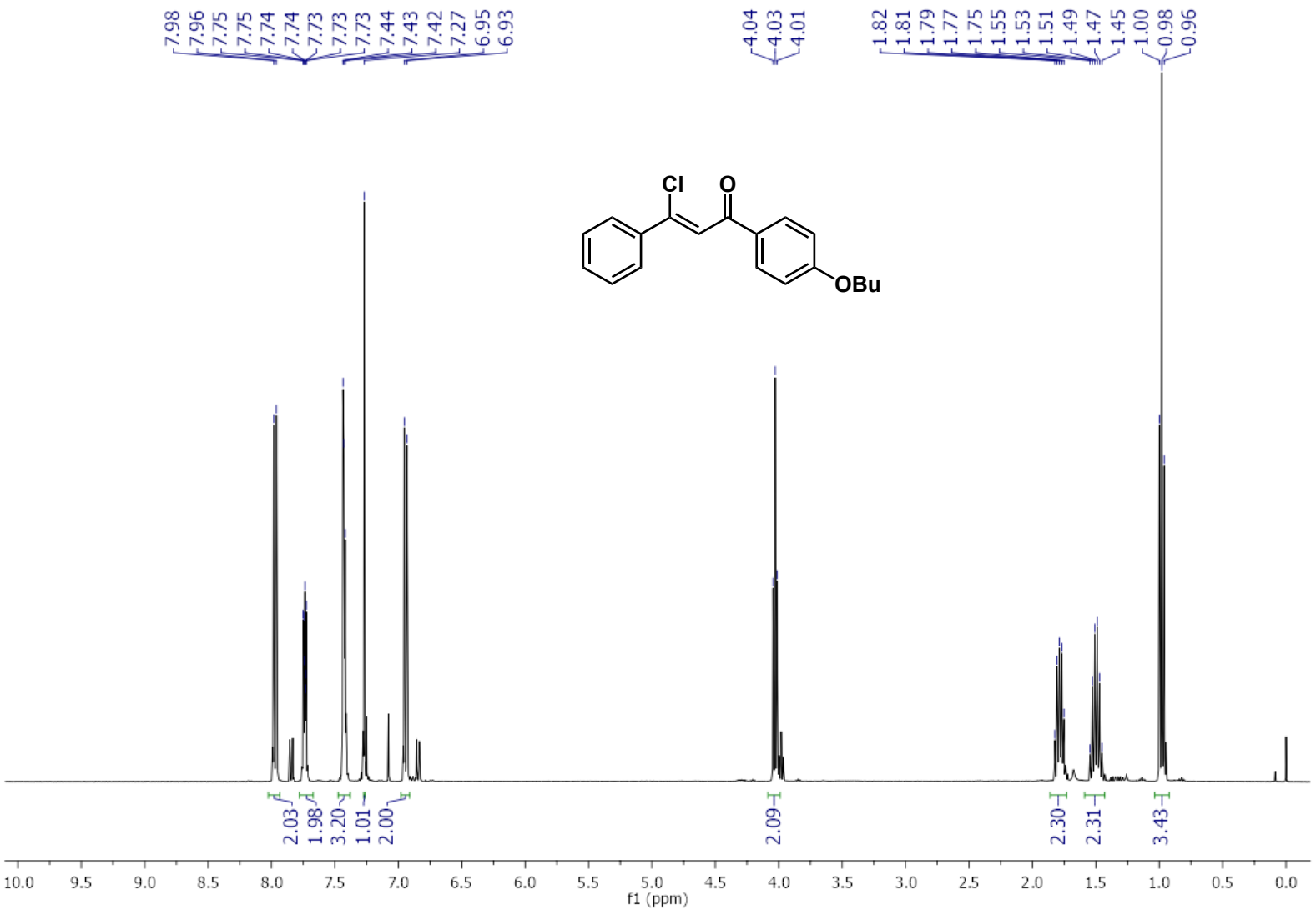
^{13}C NMR of compound **2d** (100 MHz, $CDCl_3$)



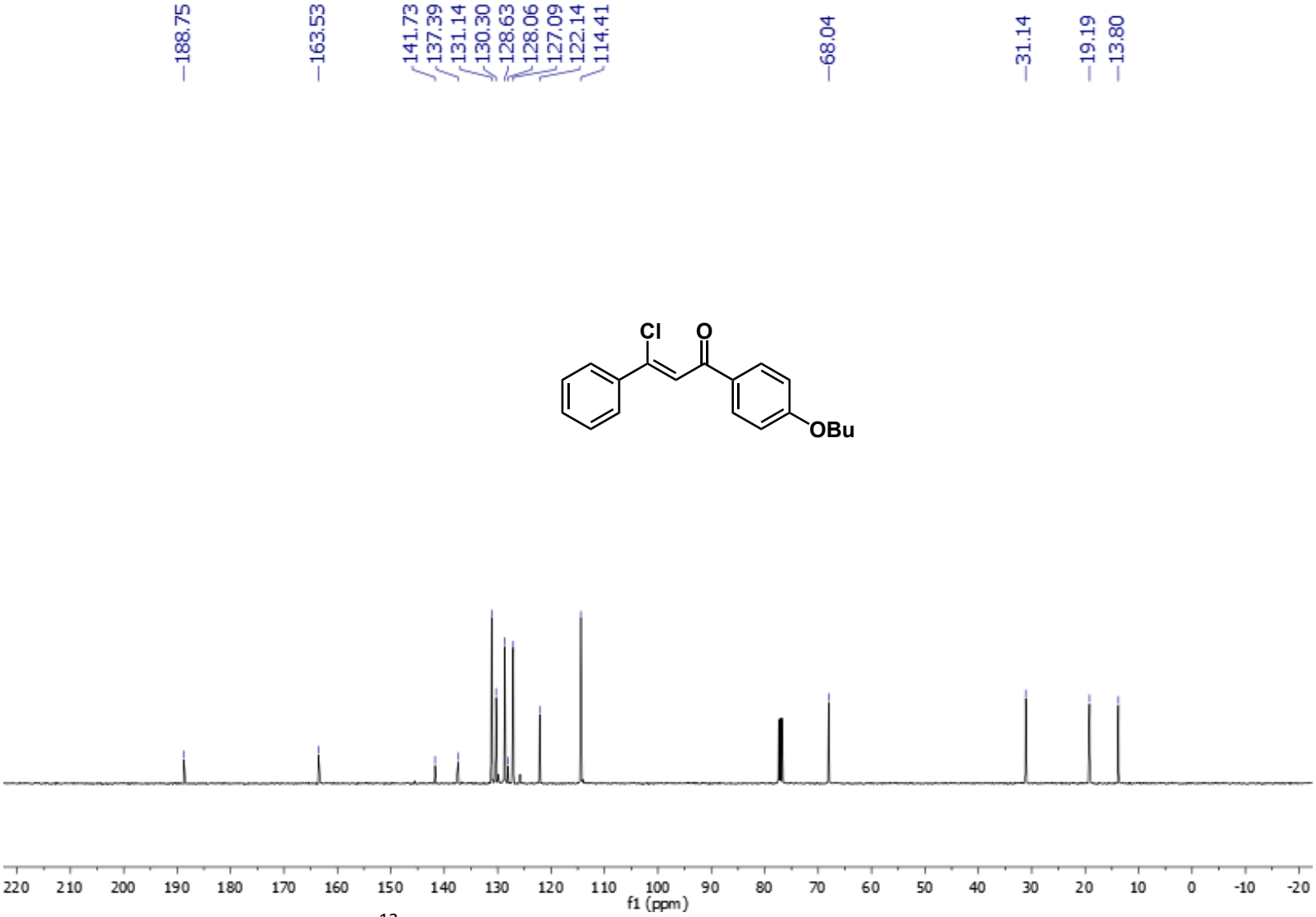
^{1}H NMR of compound **2e** (400 MHz, $CDCl_3$)



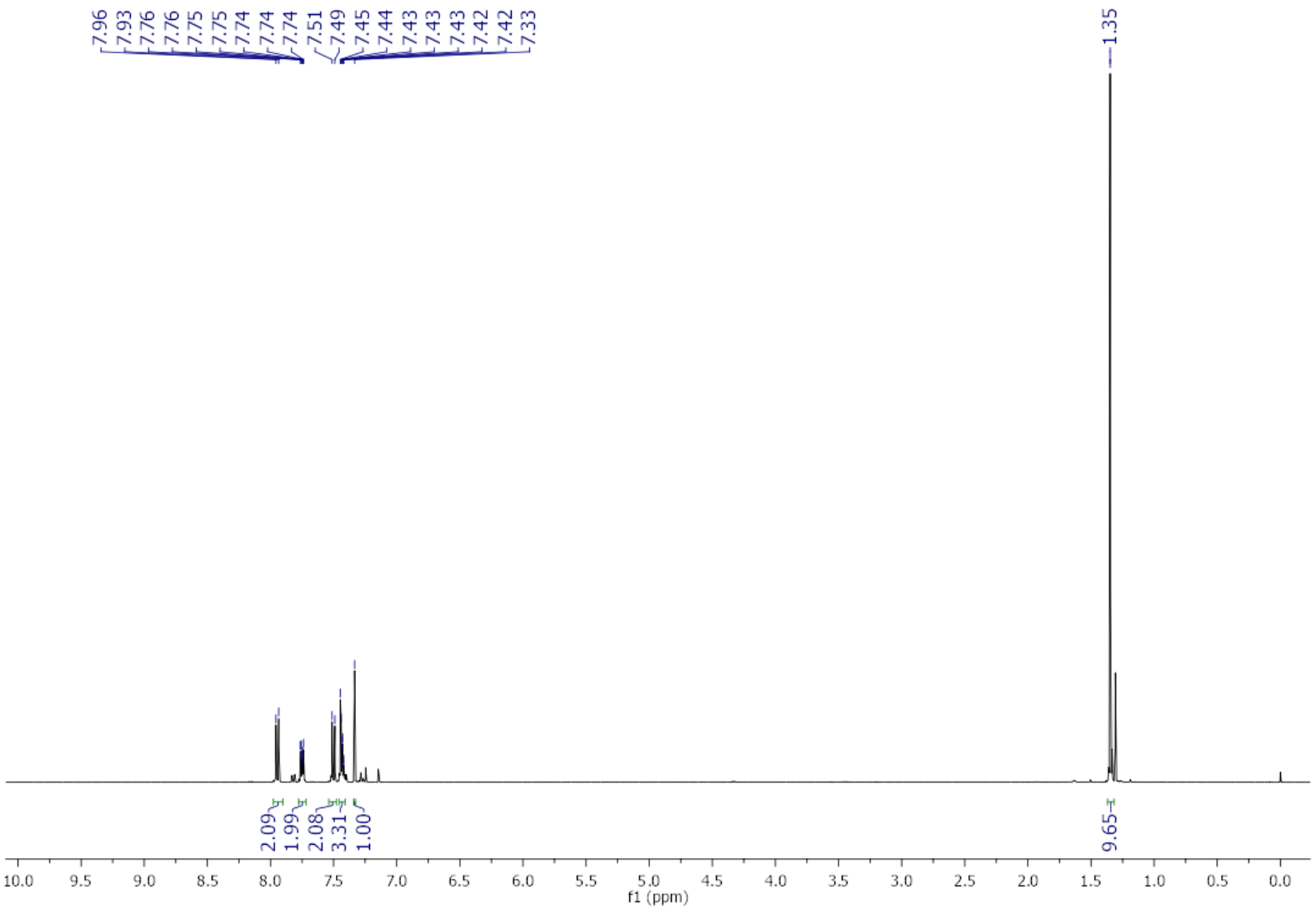
^{13}C NMR of compound **2**e (100 MHz, $CDCl_3$)



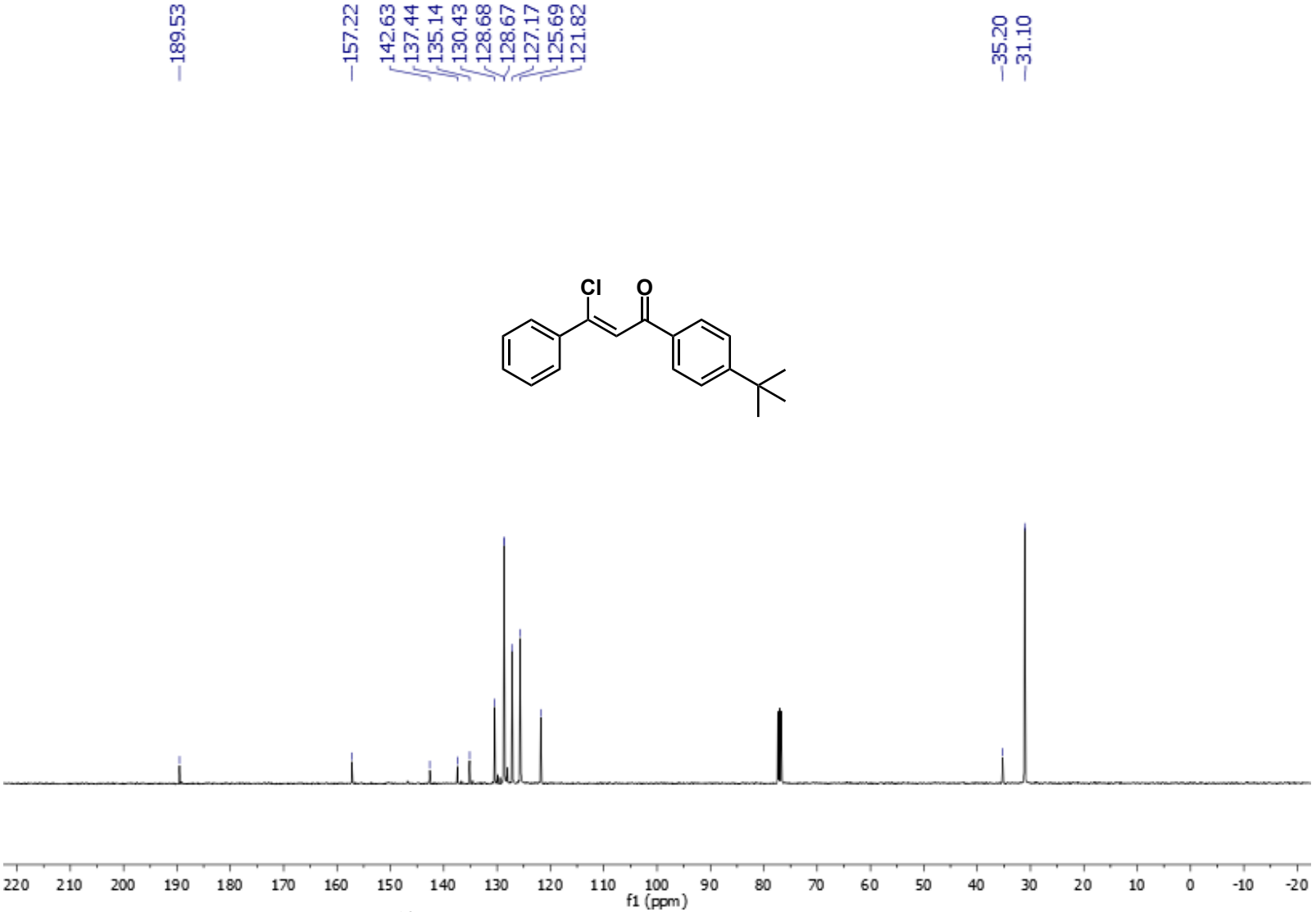
^{1}H NMR of compound **2f** (400 MHz, $CDCl_3$)



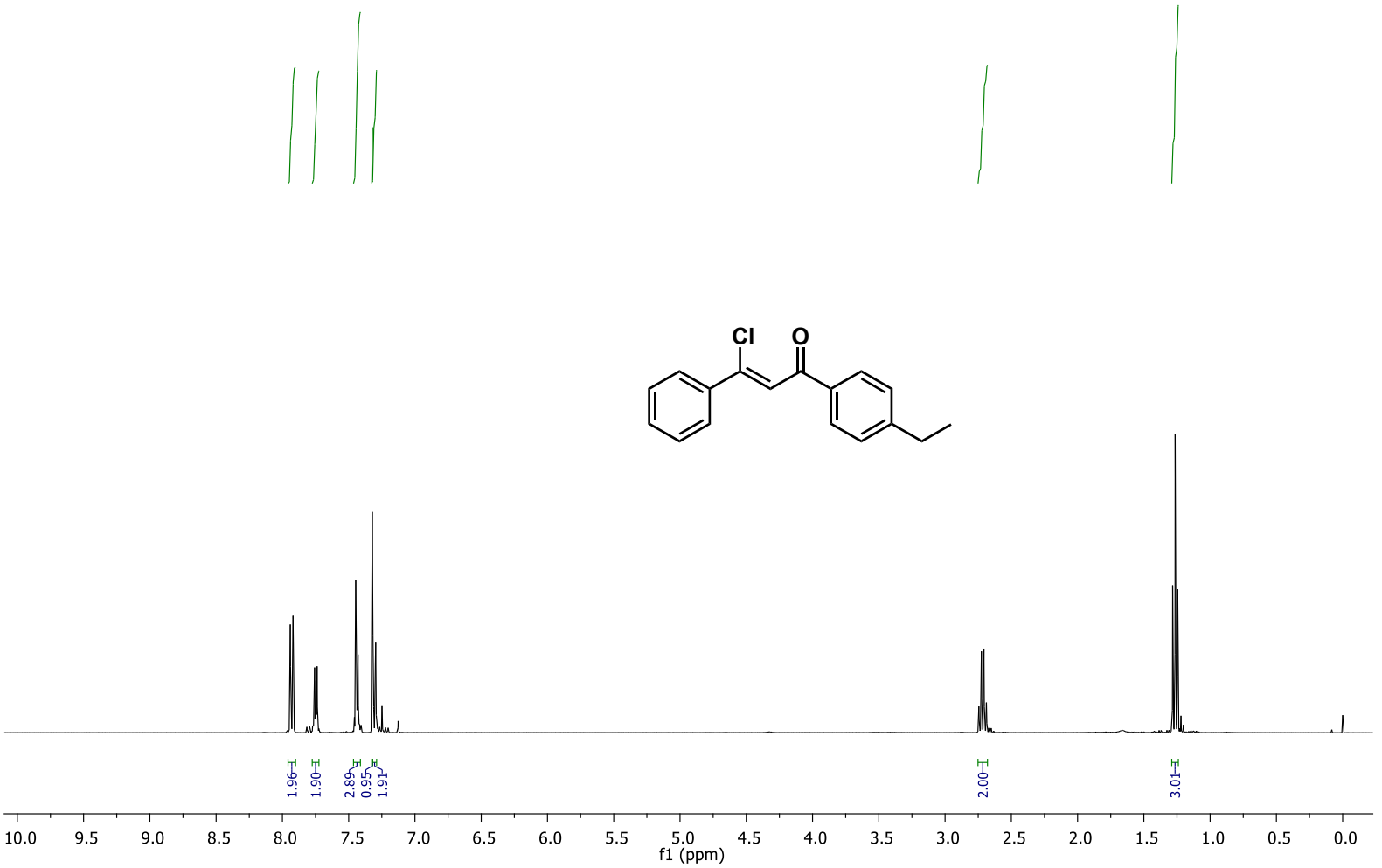
^{13}C NMR of compound **2f** (100 MHz, $CDCl_3$)



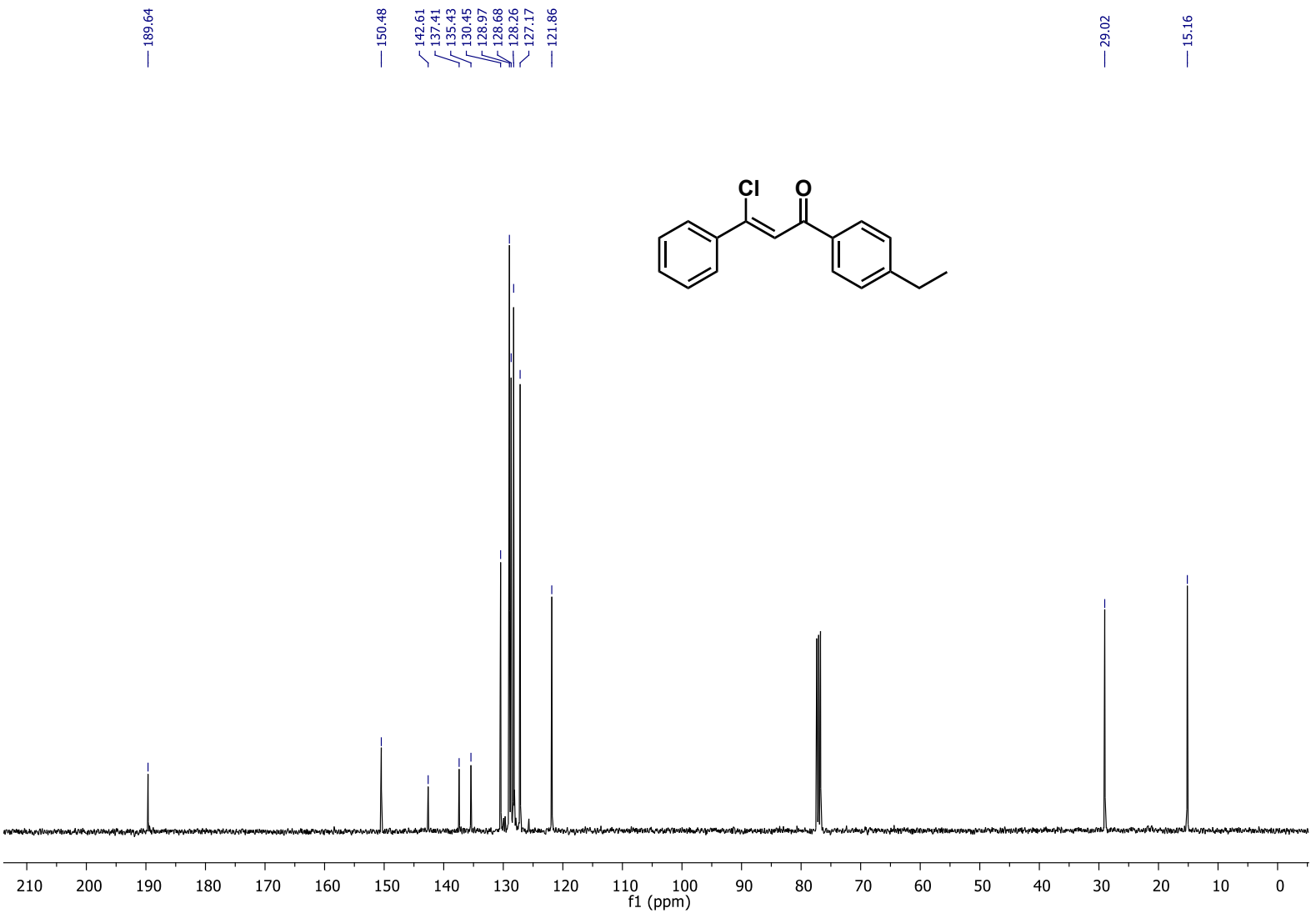
^{1}H NMR of compound **2g** (400 MHz, $CDCl_3$)



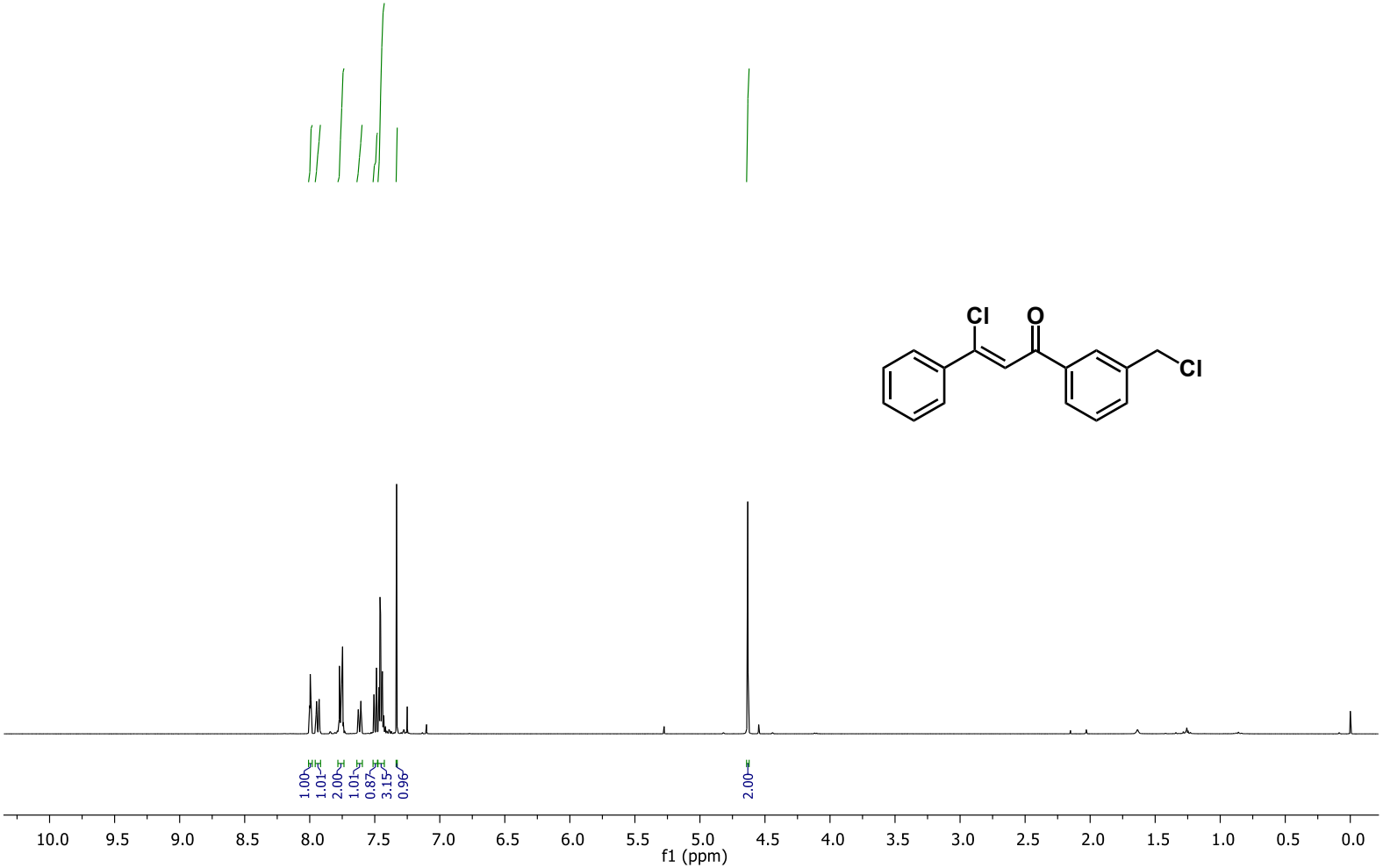
^{13}C NMR of compound **2g** (100 MHz, $CDCl_3$)



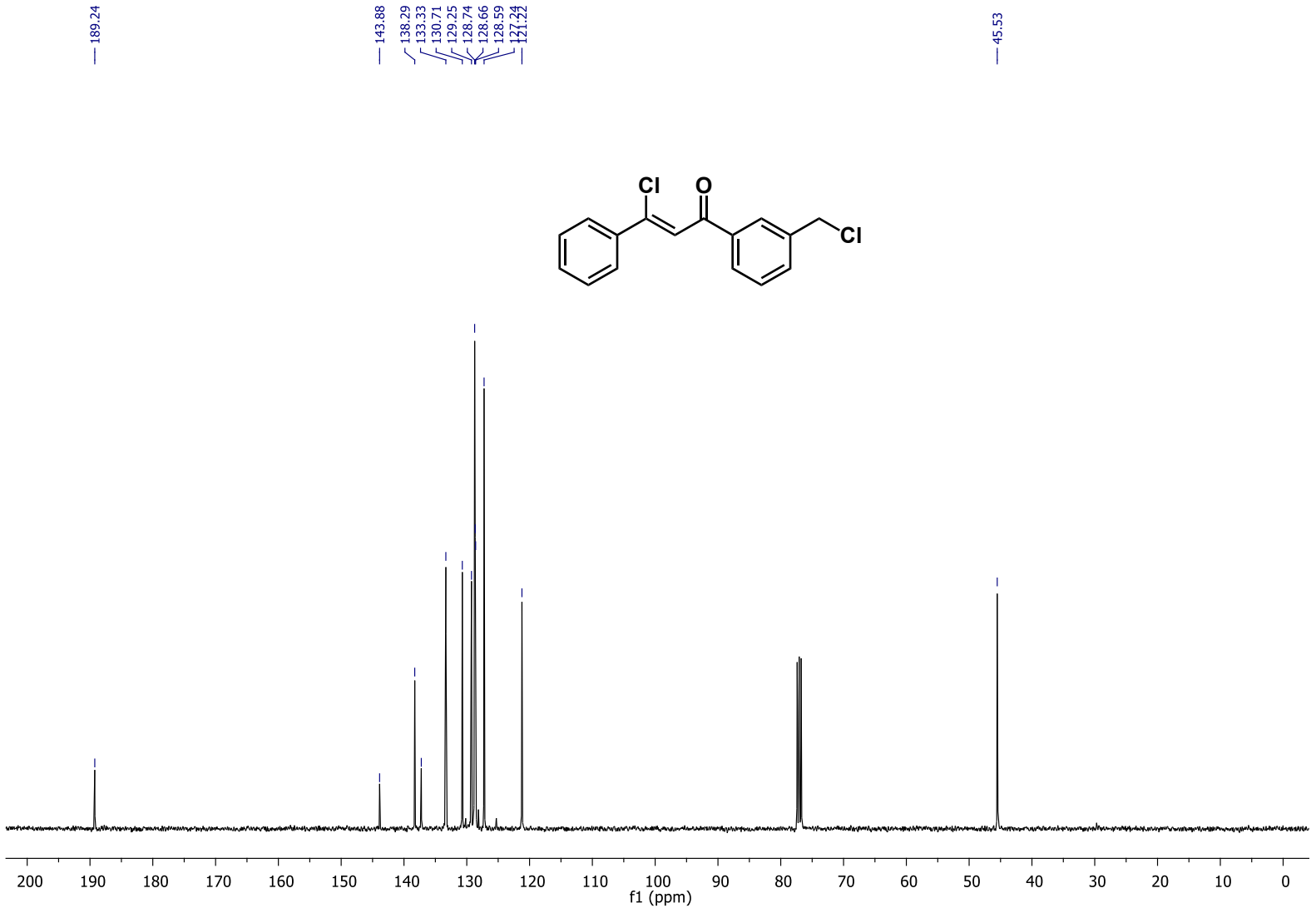
^{1}H NMR of compound **2h** (400 MHz, $CDCl_3$)



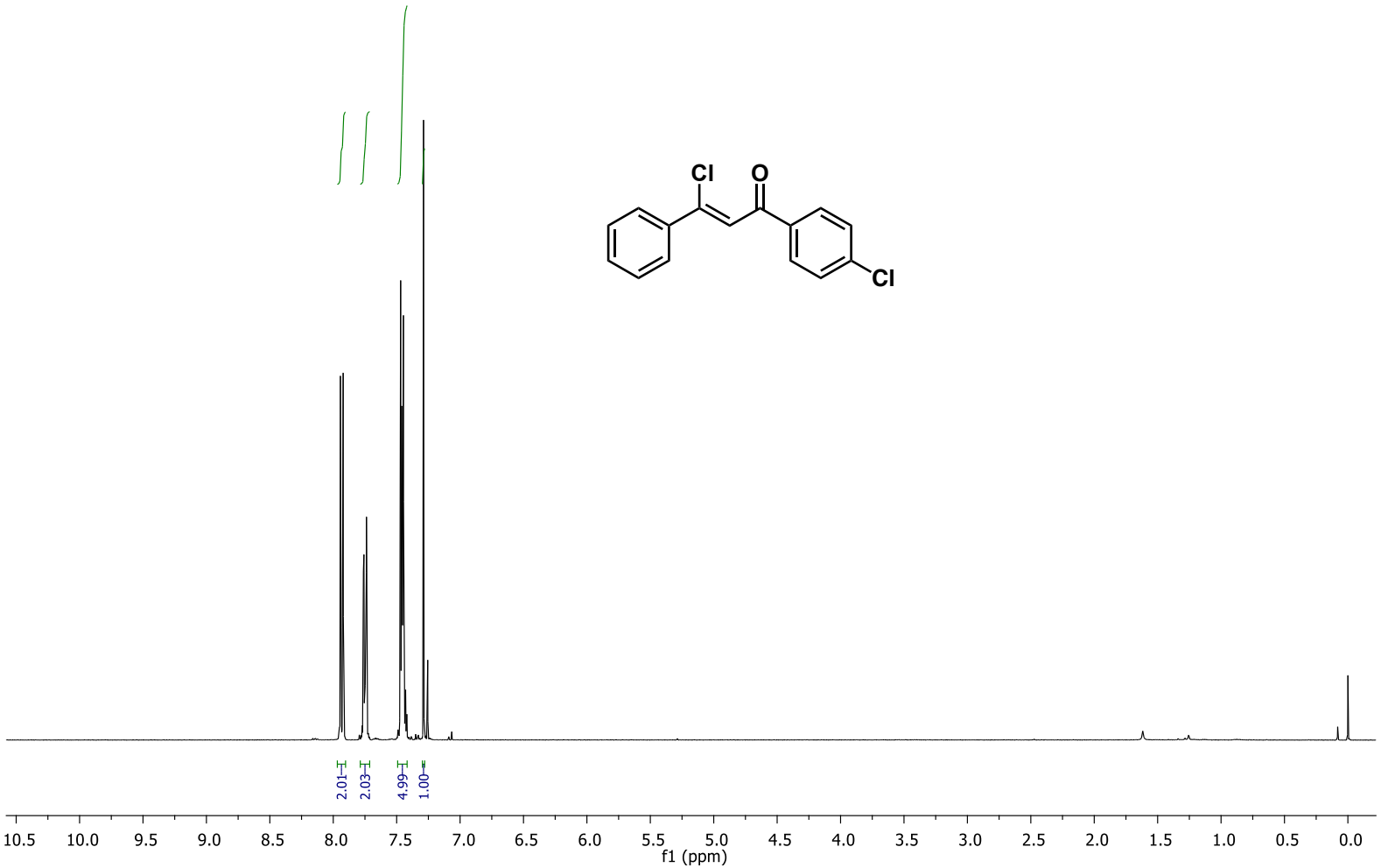
^{13}C NMR of compound **2h** (100 MHz, $CDCl_3$)



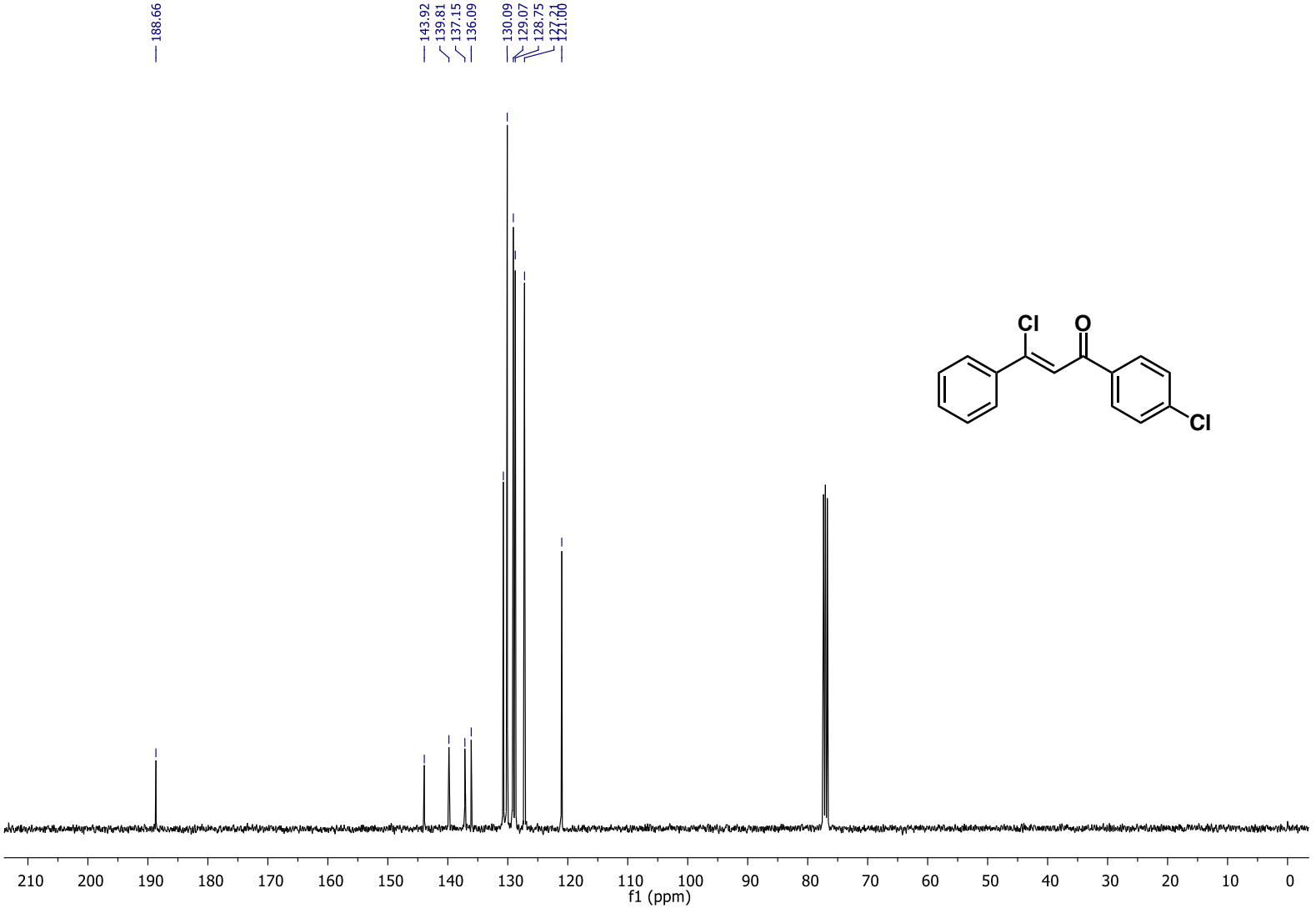
^{1}H NMR of compound **2i** (400 MHz, $CDCl_3$)



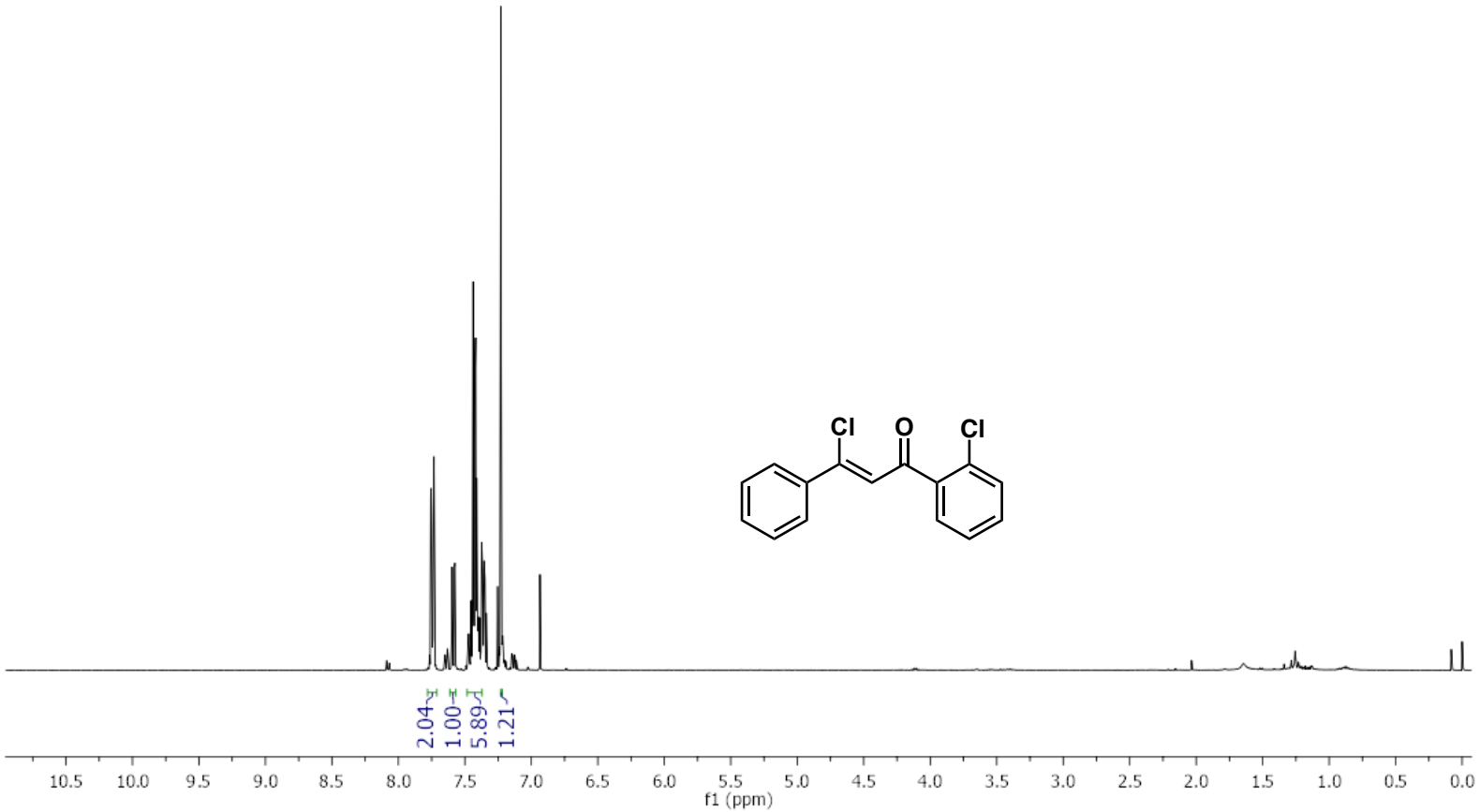
^{13}C NMR of compound **2i** (100 MHz, $CDCl_3$)



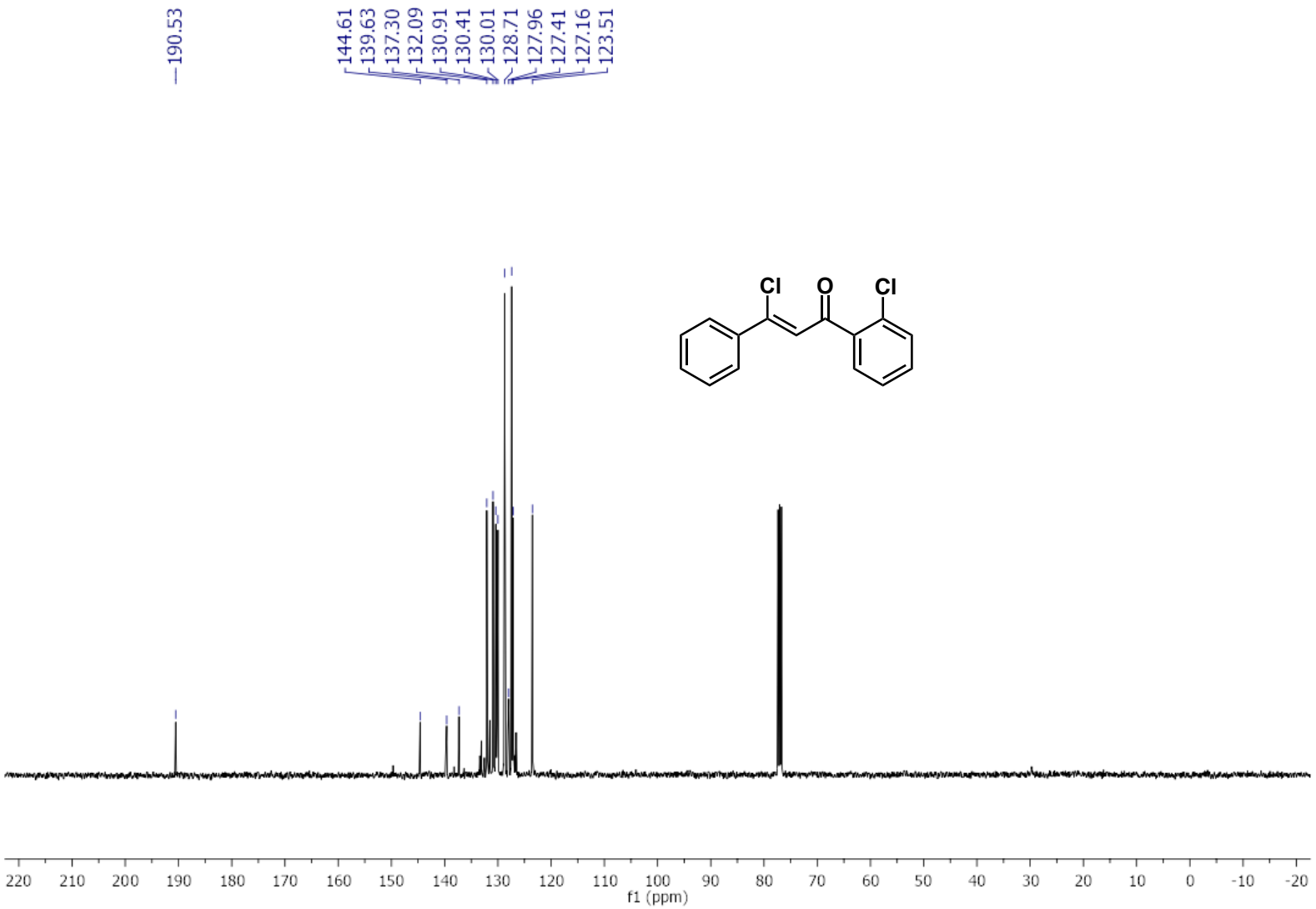
^{1}H NMR of compound **2j** (400 MHz, $CDCl_3$)



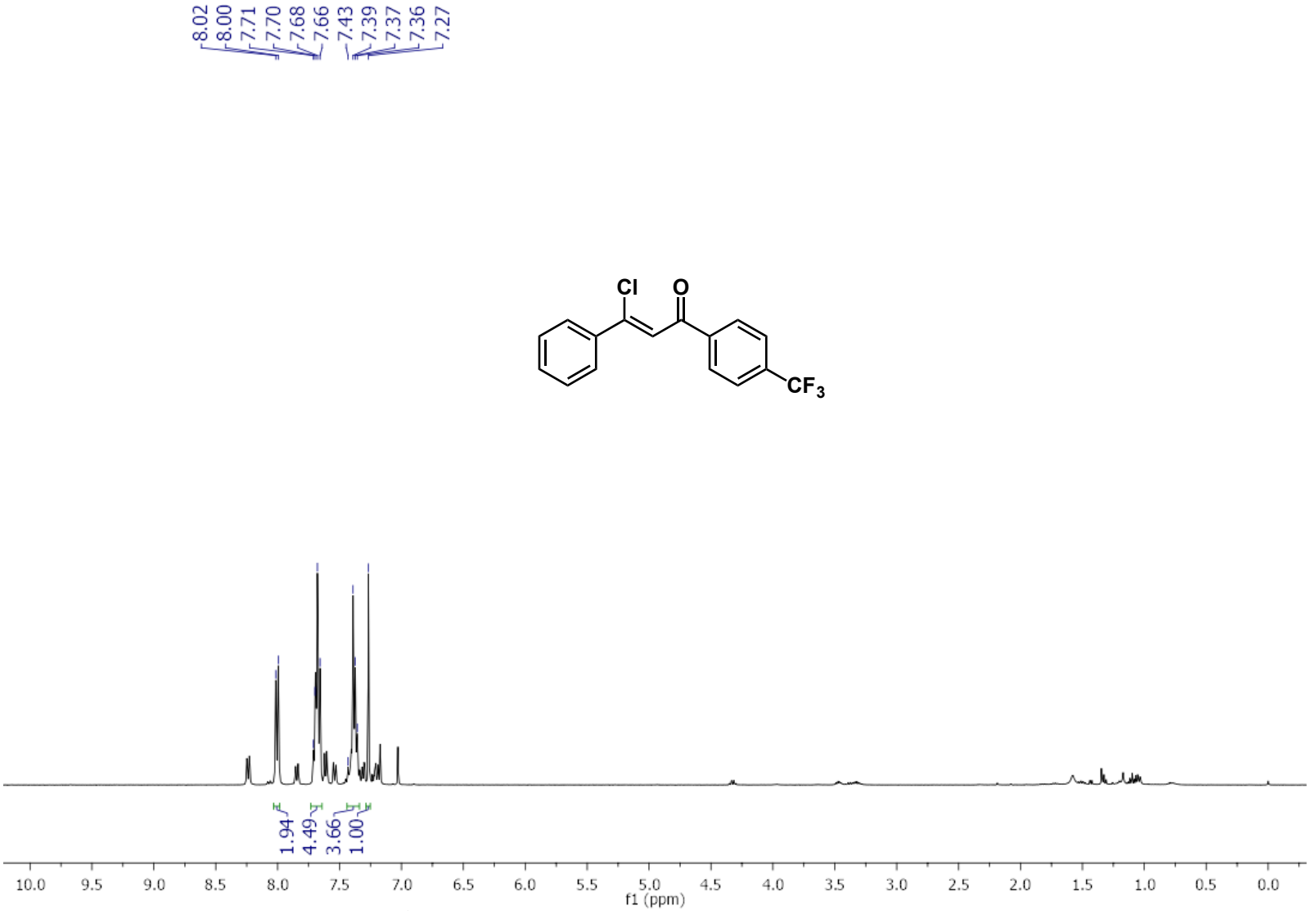
^{13}C NMR of compound **2j** (100 MHz, $CDCl_3$)



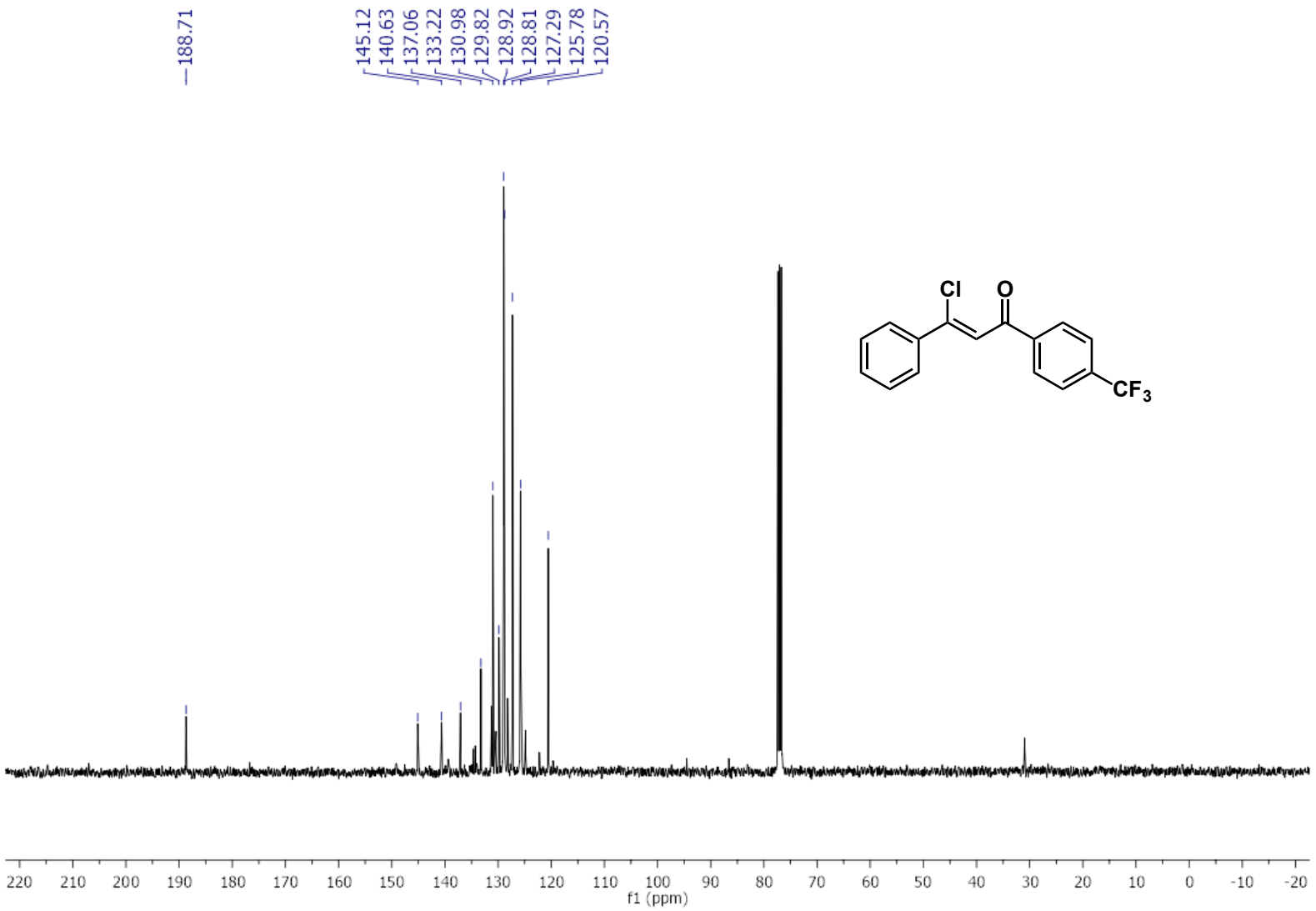
^{1}H NMR of compound **2k** (400 MHz, $CDCl_3$)



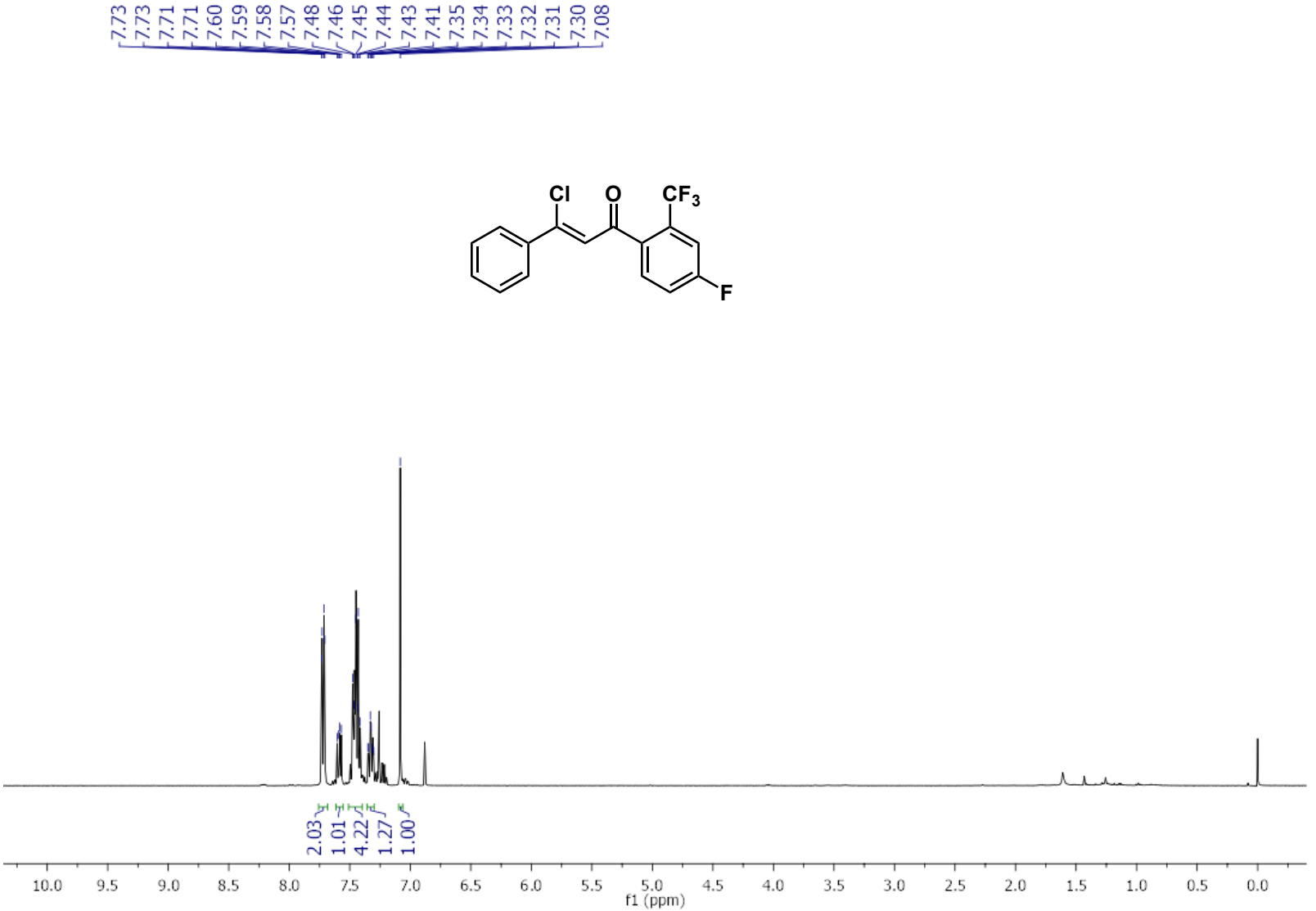
^{13}C NMR of compound **2k** (100 MHz, $CDCl_3$)



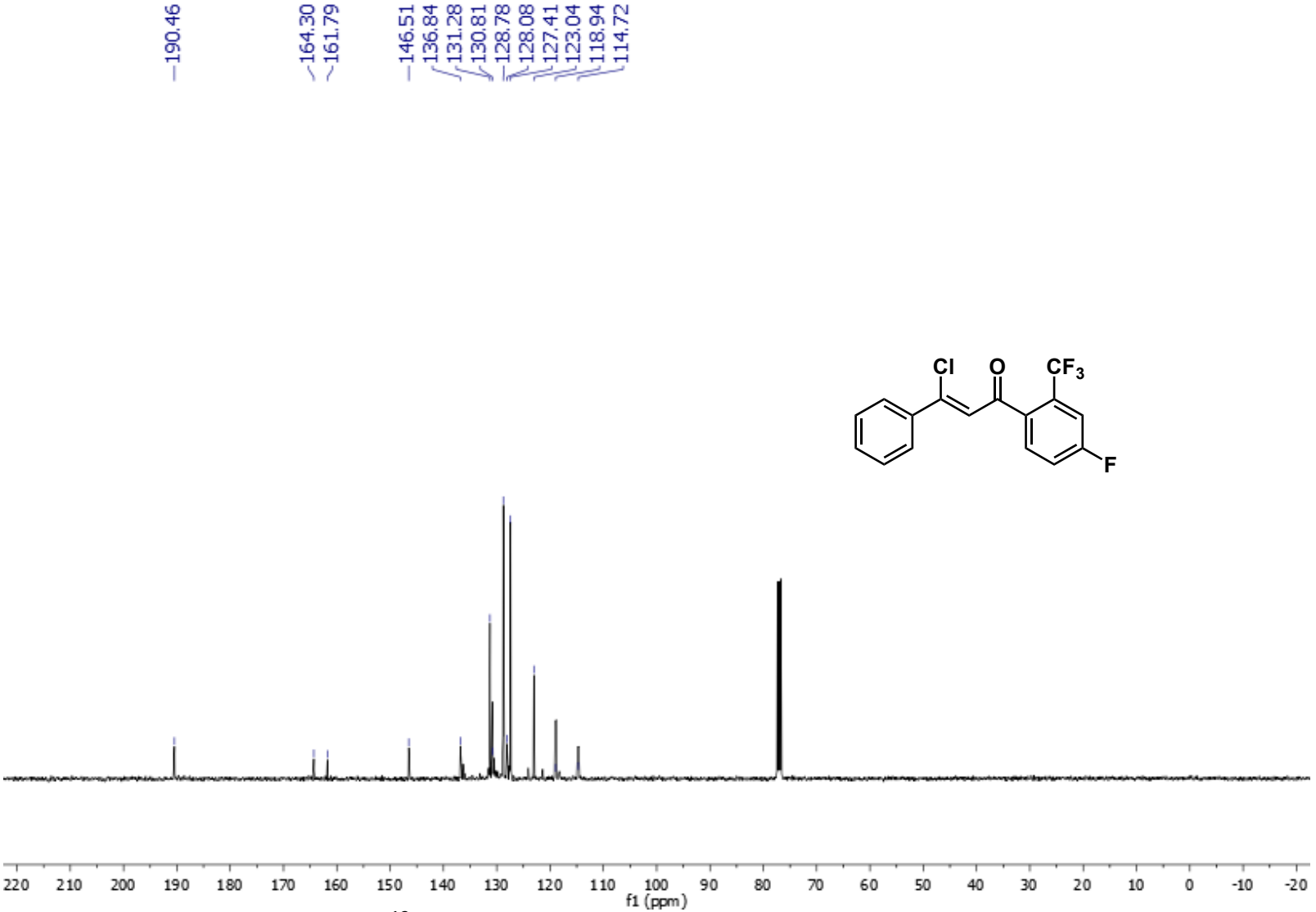
^{1}H NMR of compound **2l** (400 MHz, $CDCl_3$)



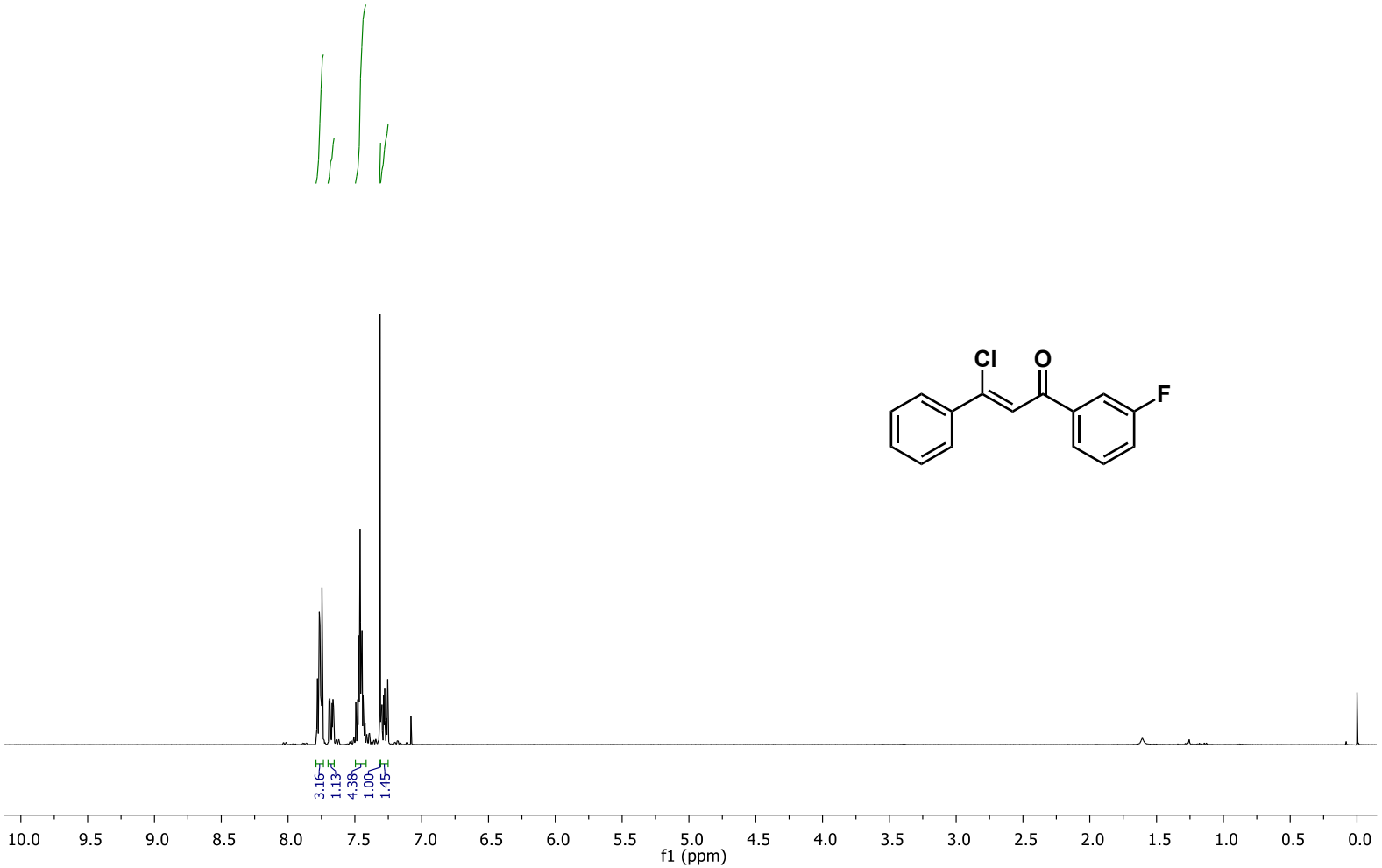
^{13}C NMR of compound **2l** (100 MHz, $CDCl_3$)



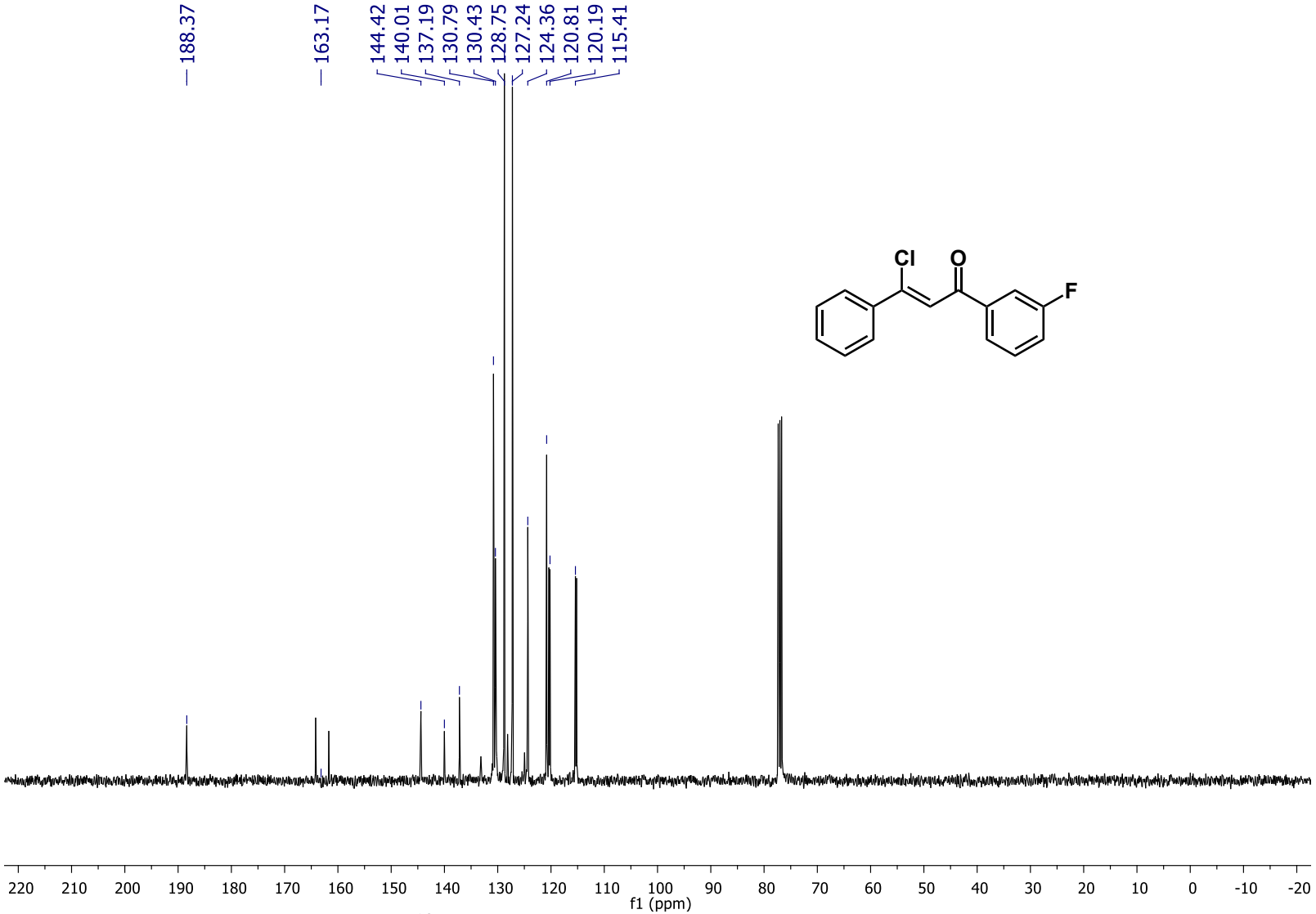
^{1}H NMR of compound **2m** (400 MHz, $CDCl_3$)



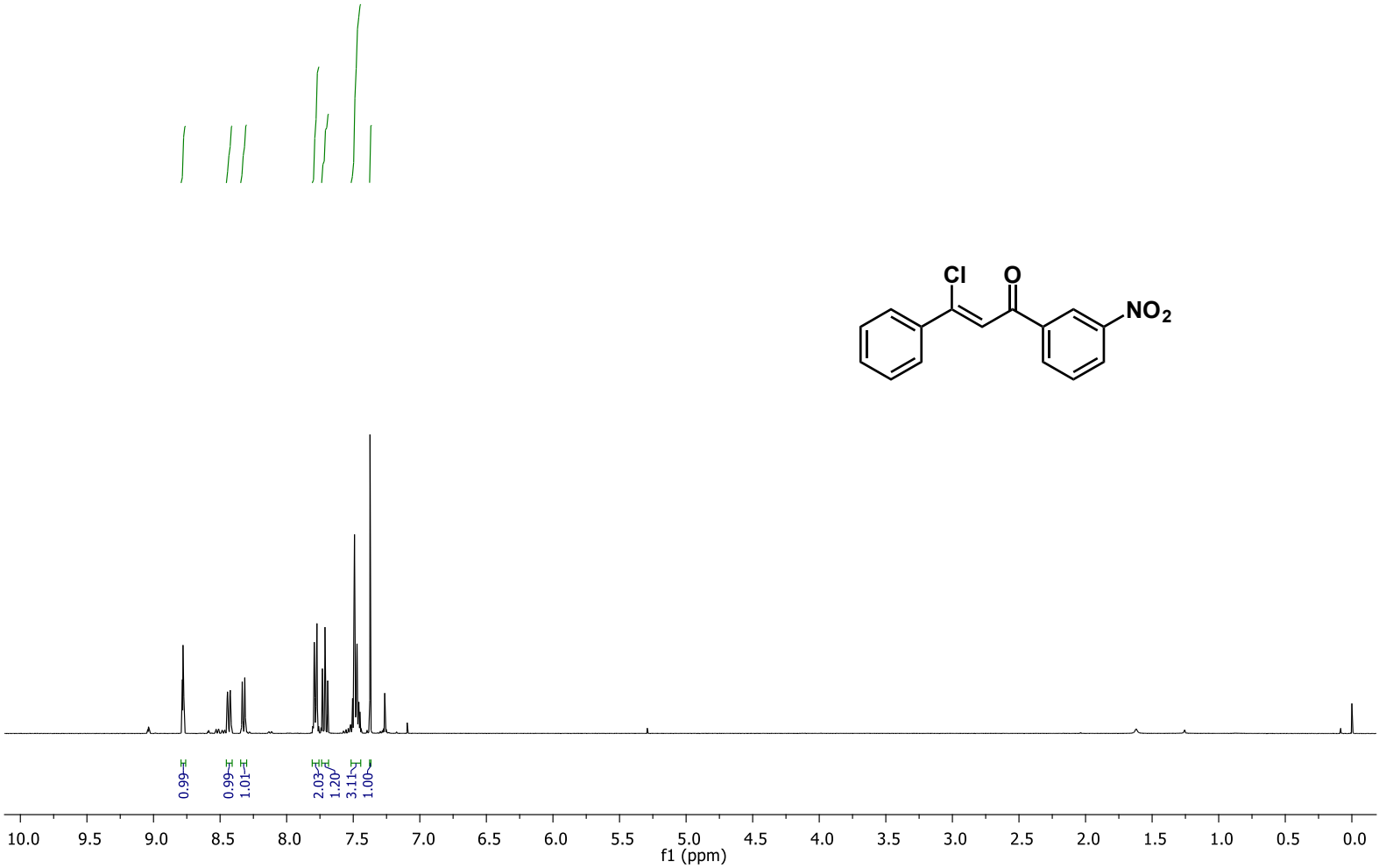
^{13}C NMR of compound **2m** (100 MHz, $CDCl_3$)



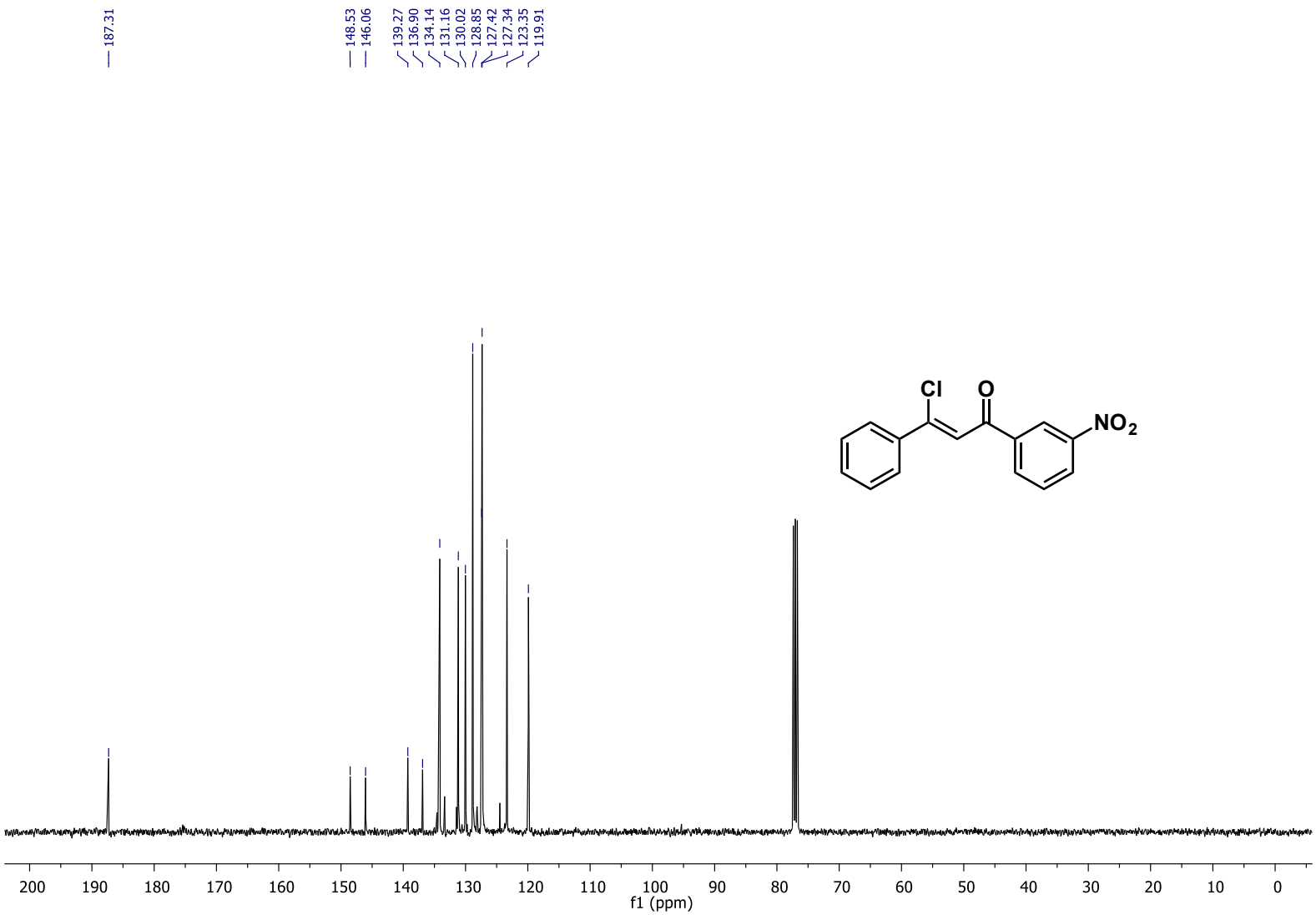
^{1}H NMR of compound **2n** (400 MHz, $CDCl_3$)



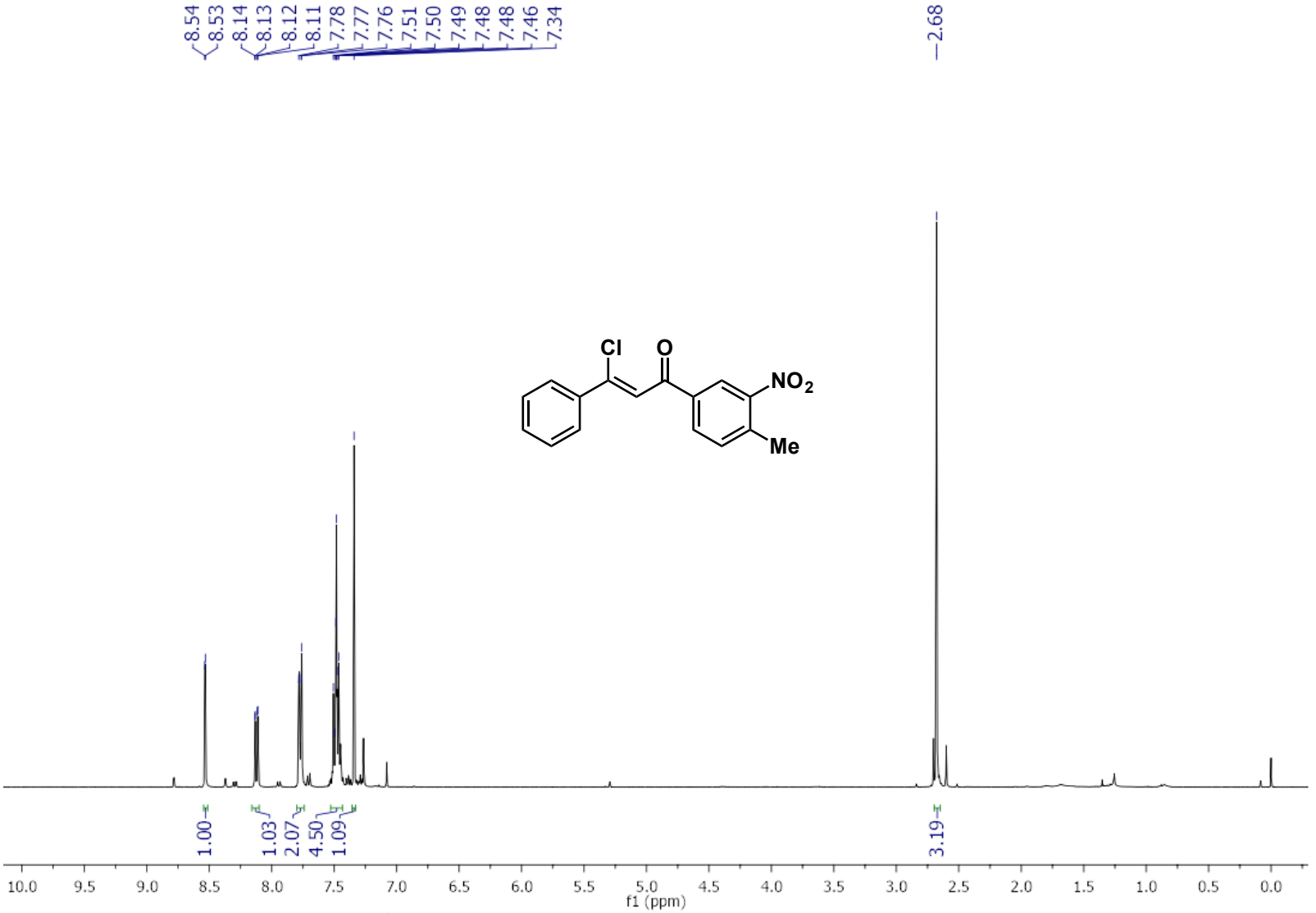
^{13}C NMR of compound **2n** (100 MHz, $CDCl_3$)



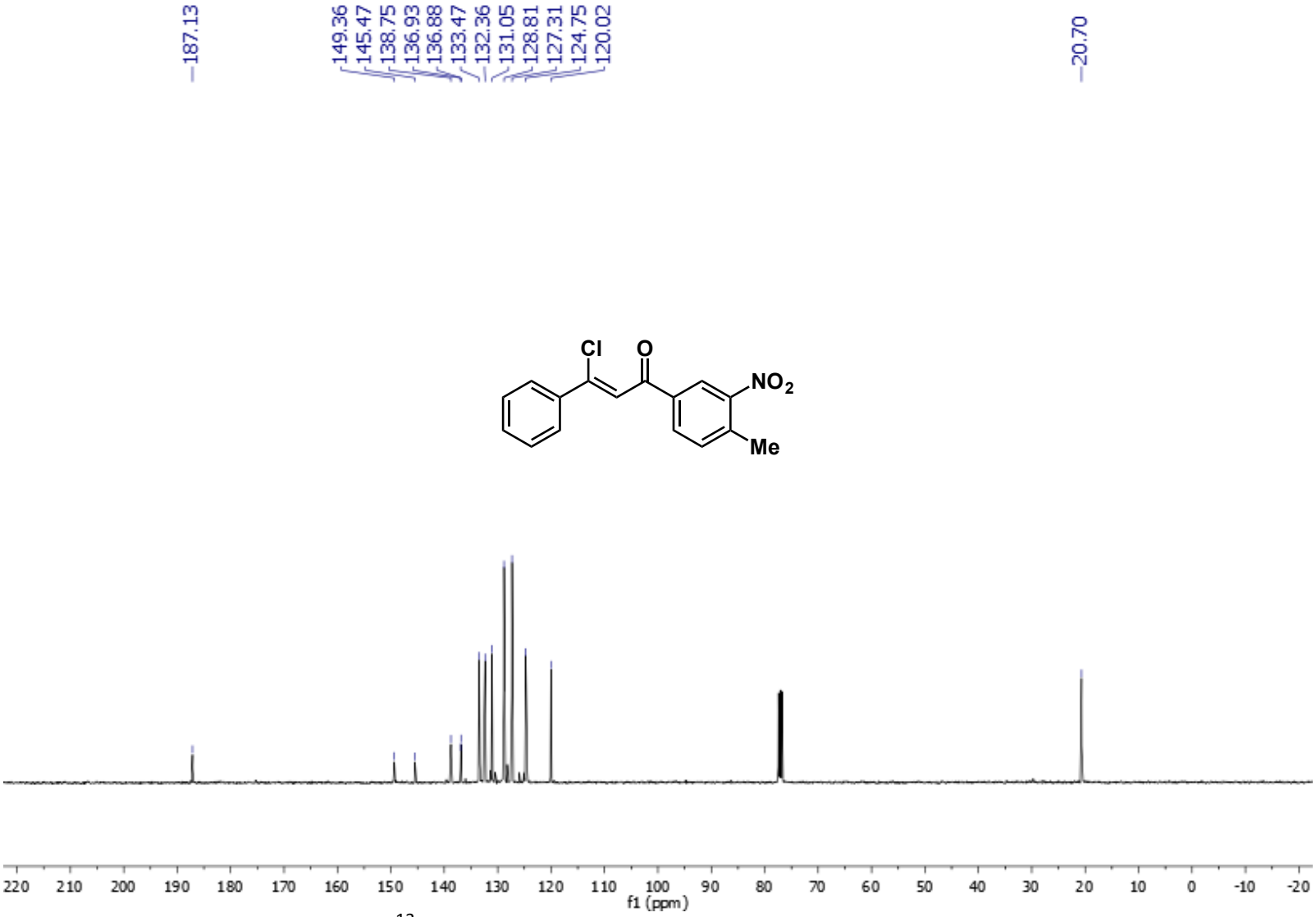
^{1}H NMR of compound **2o** (400 MHz, $CDCl_3$)



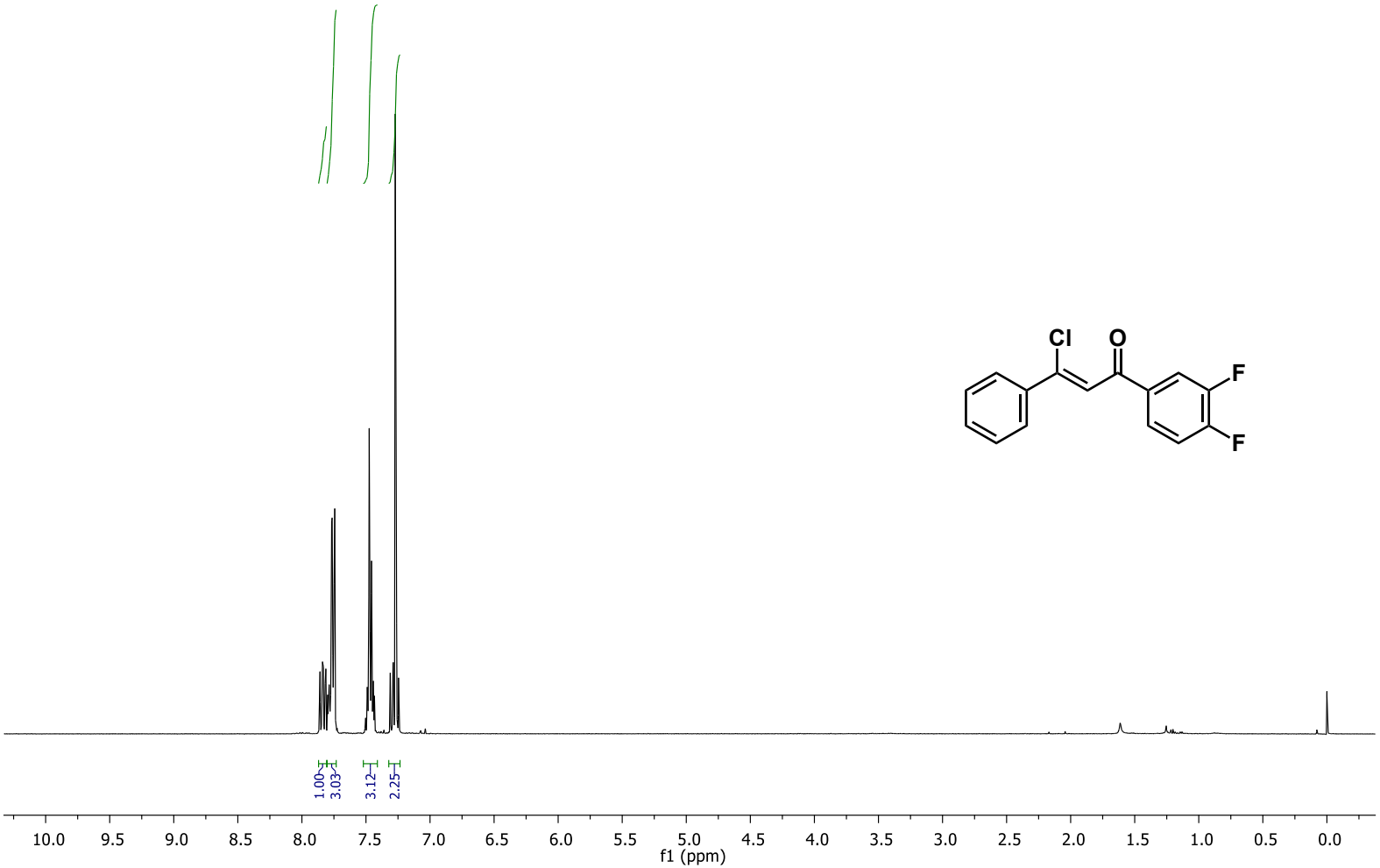
^{13}C NMR of compound **2o** (100 MHz, $CDCl_3$)



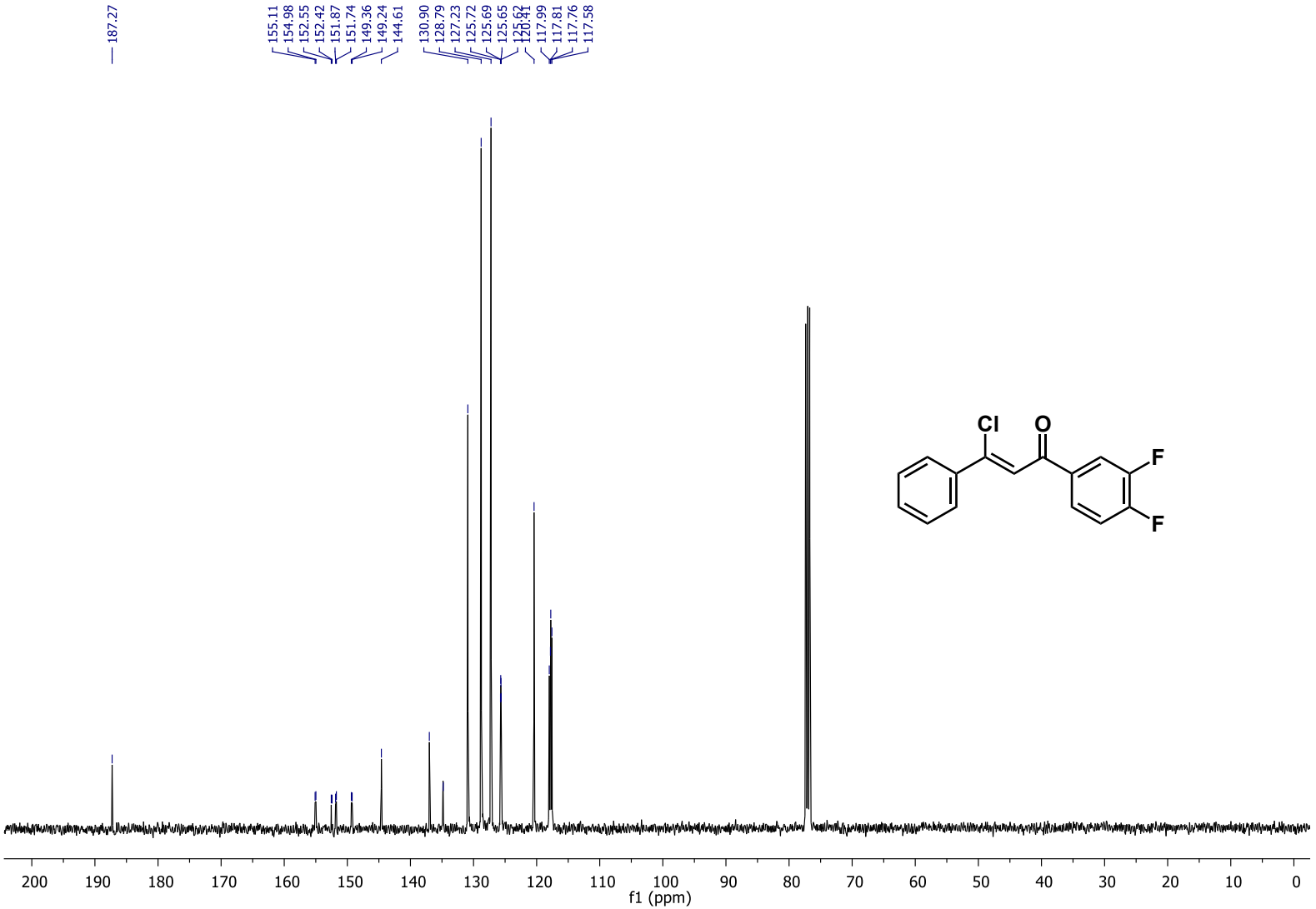
^{1}H NMR of compound **2p** (400 MHz, $CDCl_3$)



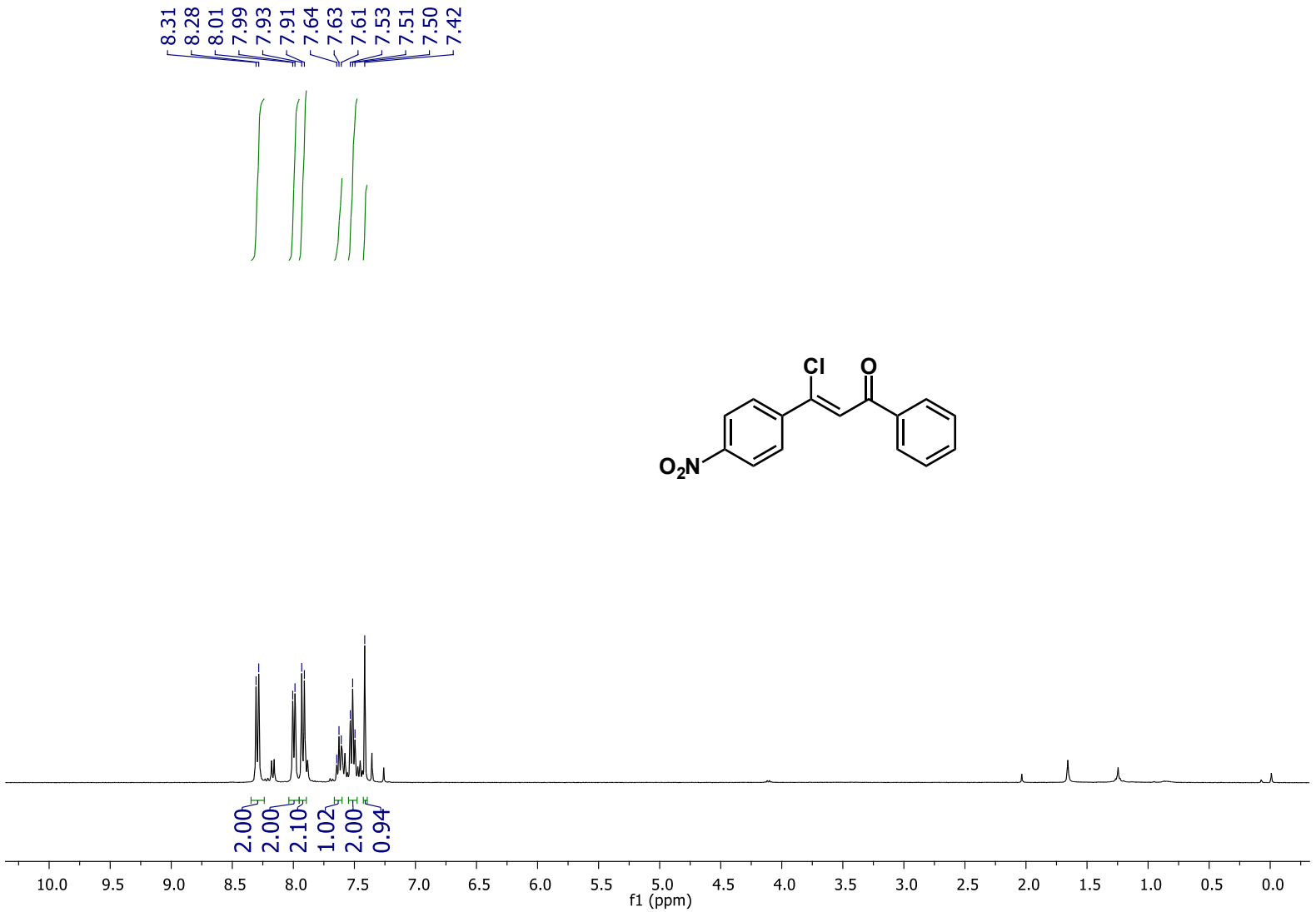
^{13}C NMR of compound **2p** (100 MHz, $CDCl_3$)



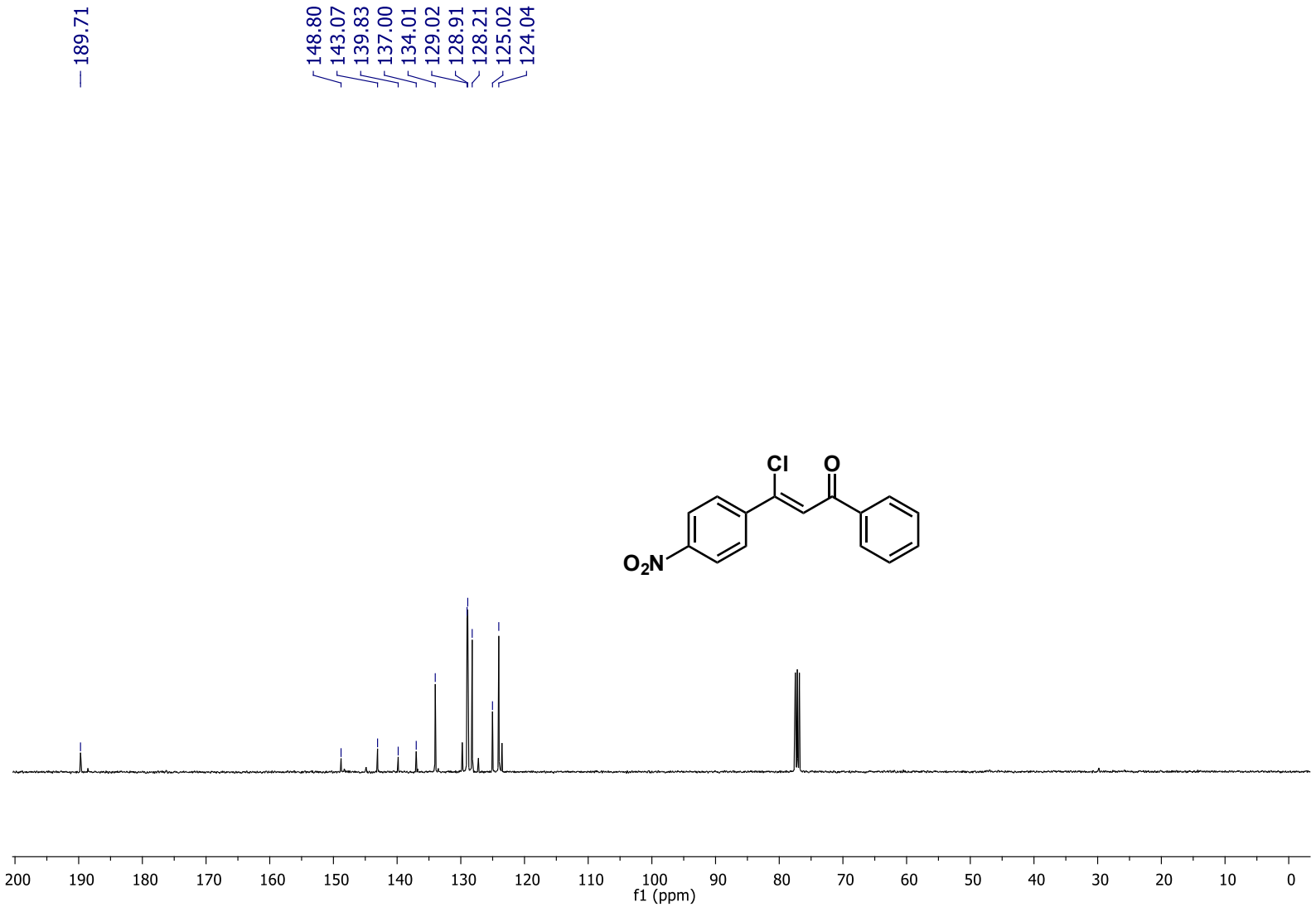
^{1}H NMR of compound **2q** (400 MHz, $CDCl_3$)



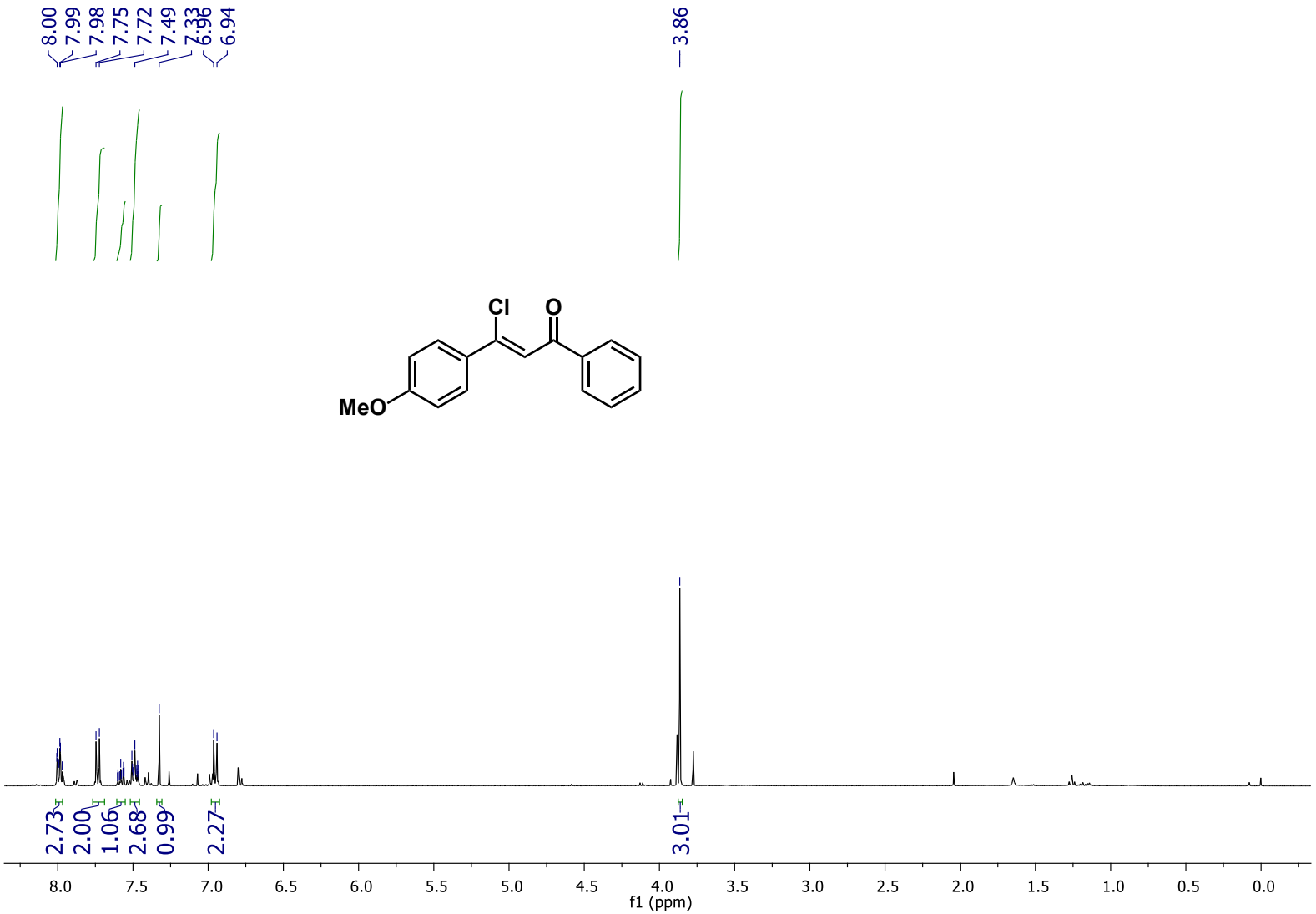
^{13}C NMR of compound **2q** (100 MHz, $CDCl_3$)



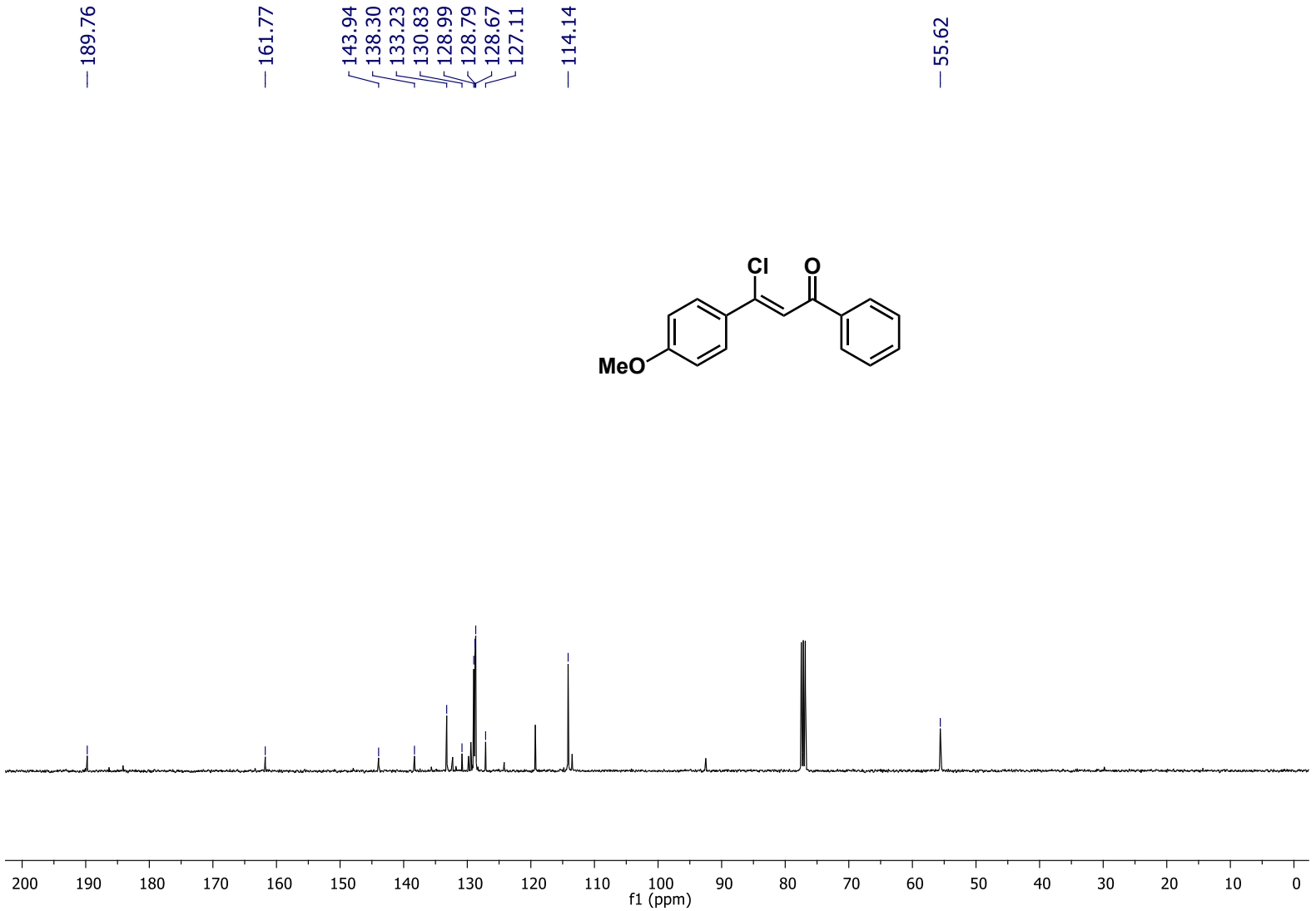
^{1}H NMR of compound **2r** (400 MHz, $CDCl_3$)



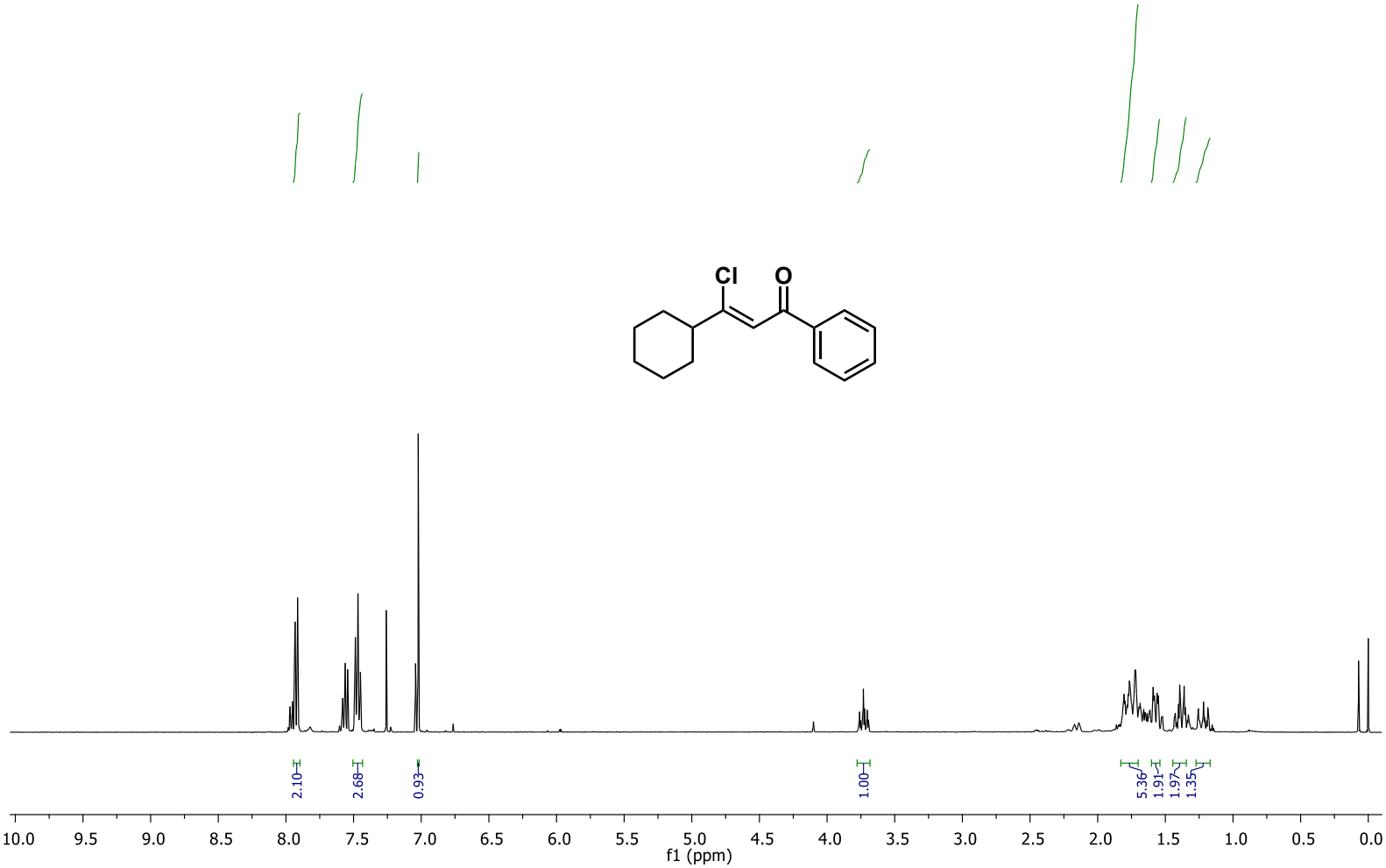
^{13}C NMR of compound **2r** (100 MHz, $CDCl_3$)



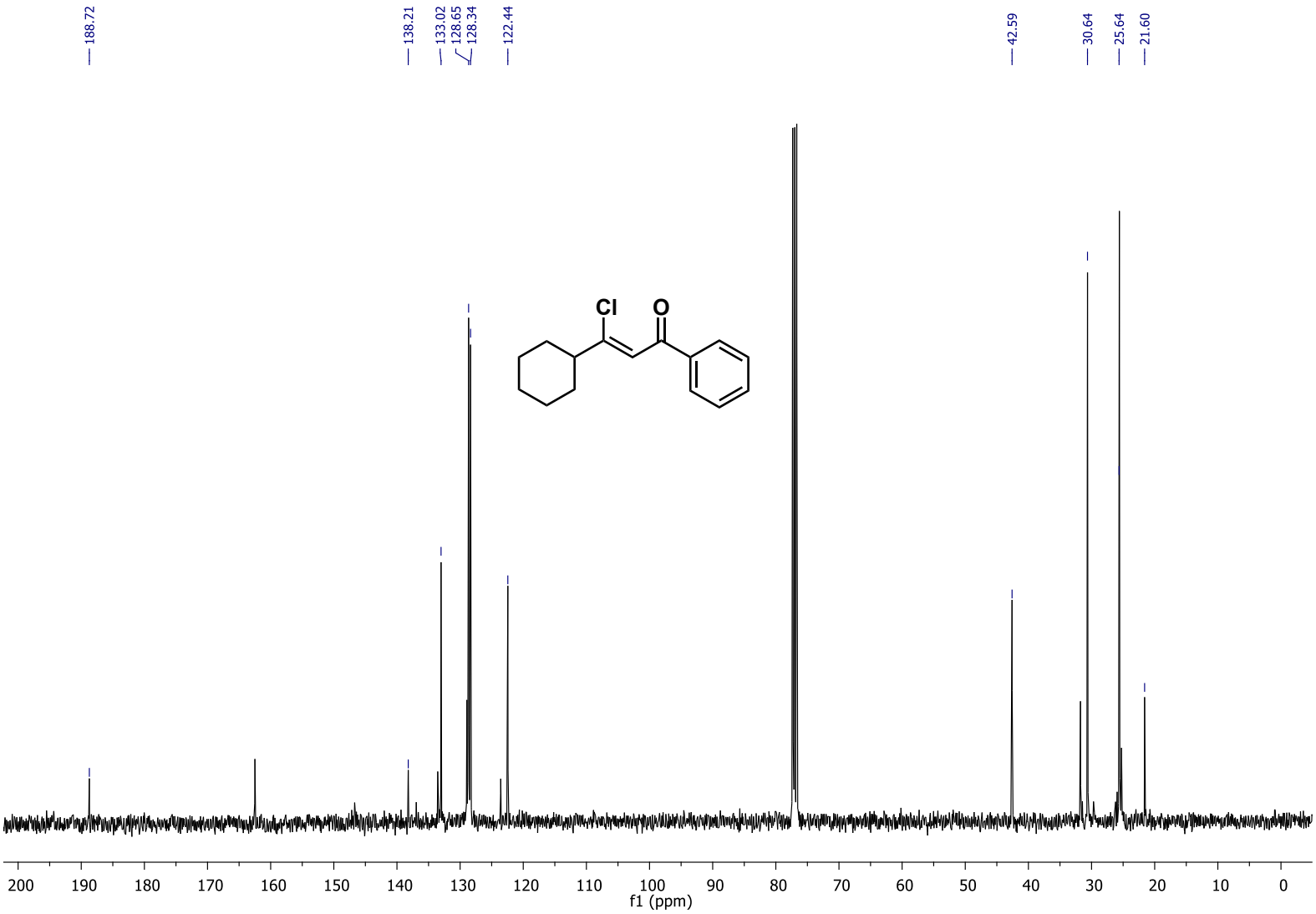
^{1}H NMR of compound **2s** (400 MHz, $CDCl_3$)



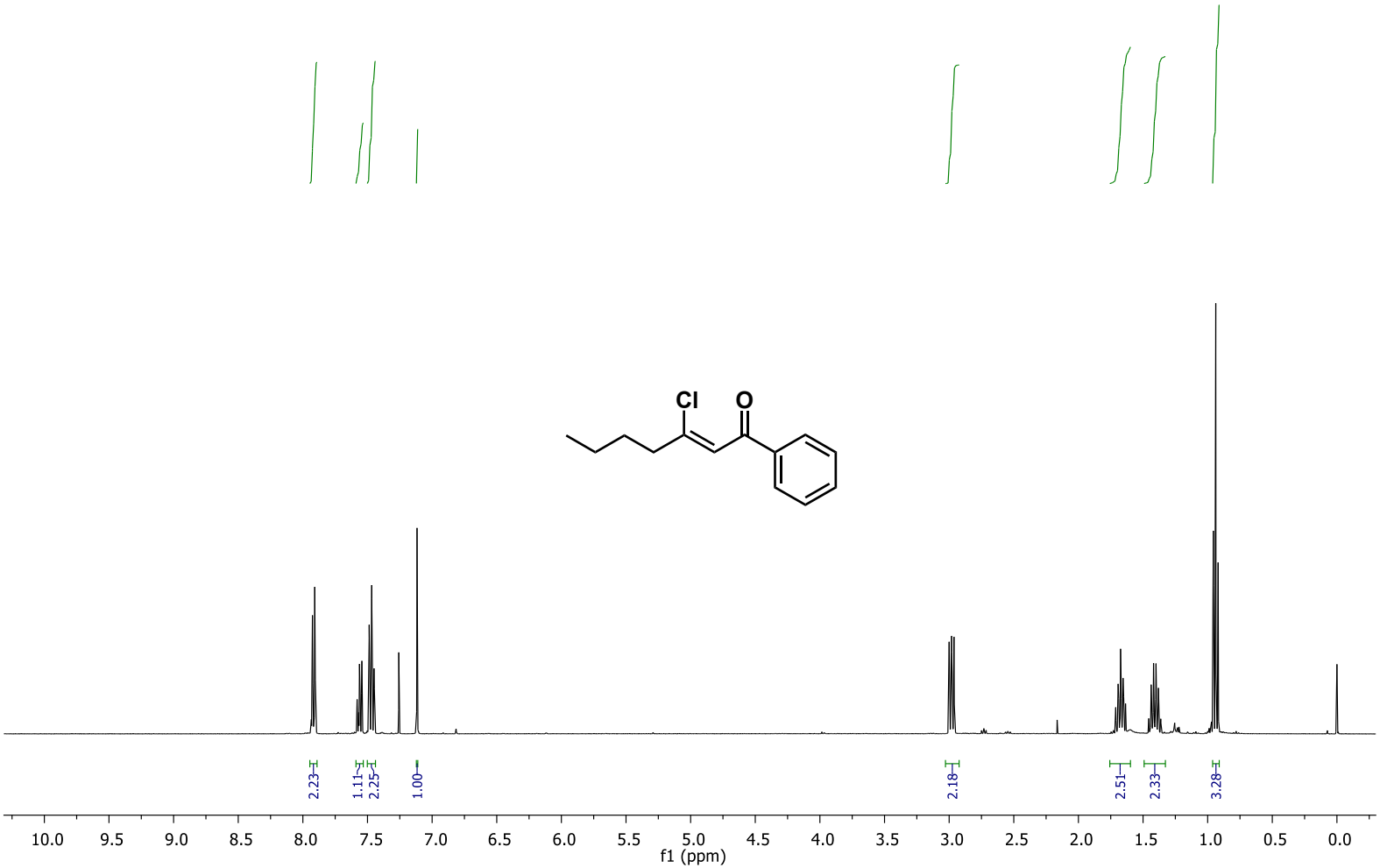
^{13}C NMR of compound **2s** (100 MHz, $CDCl_3$)



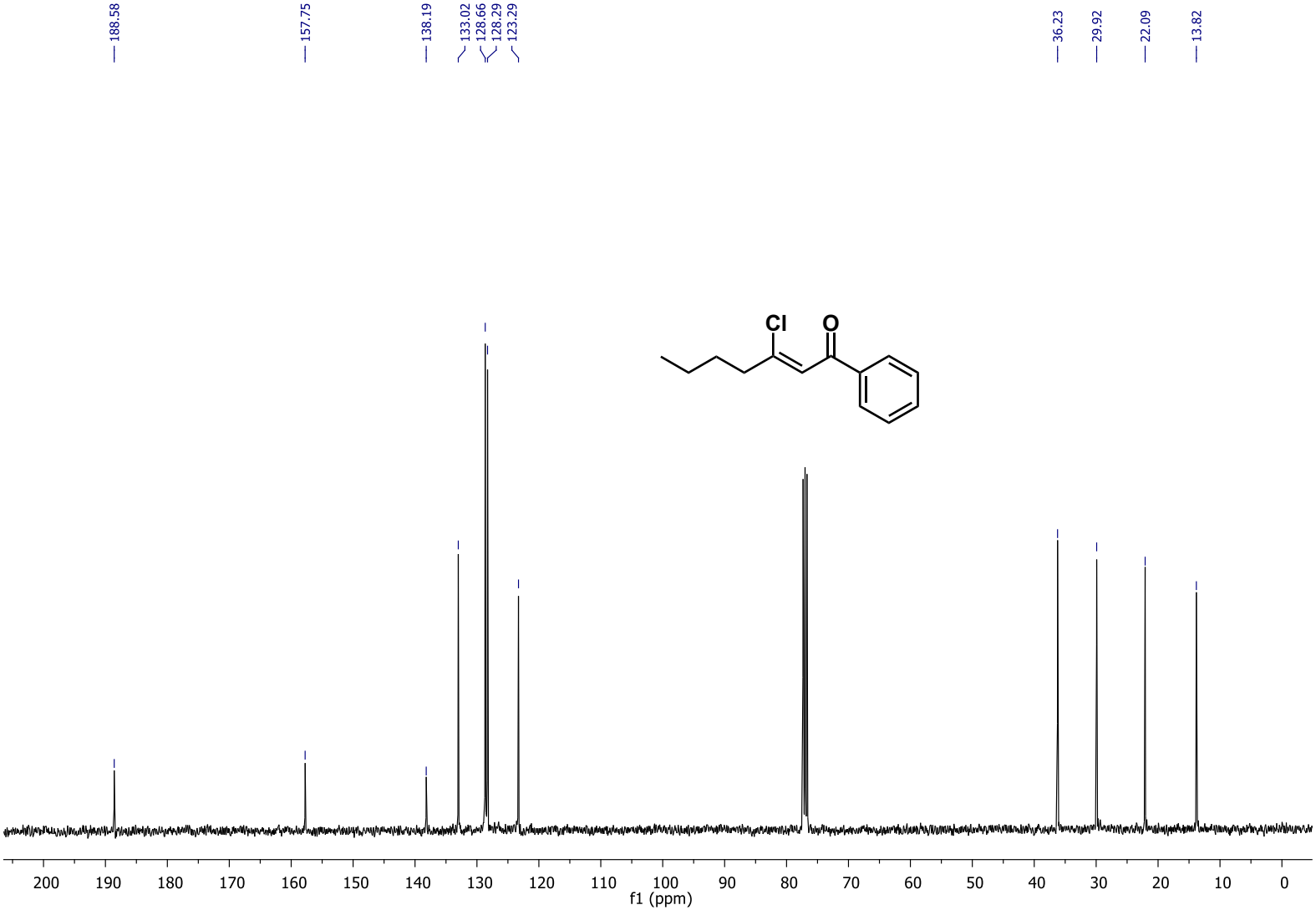
^{1}H NMR of compound **2t** (400 MHz, $CDCl_3$)



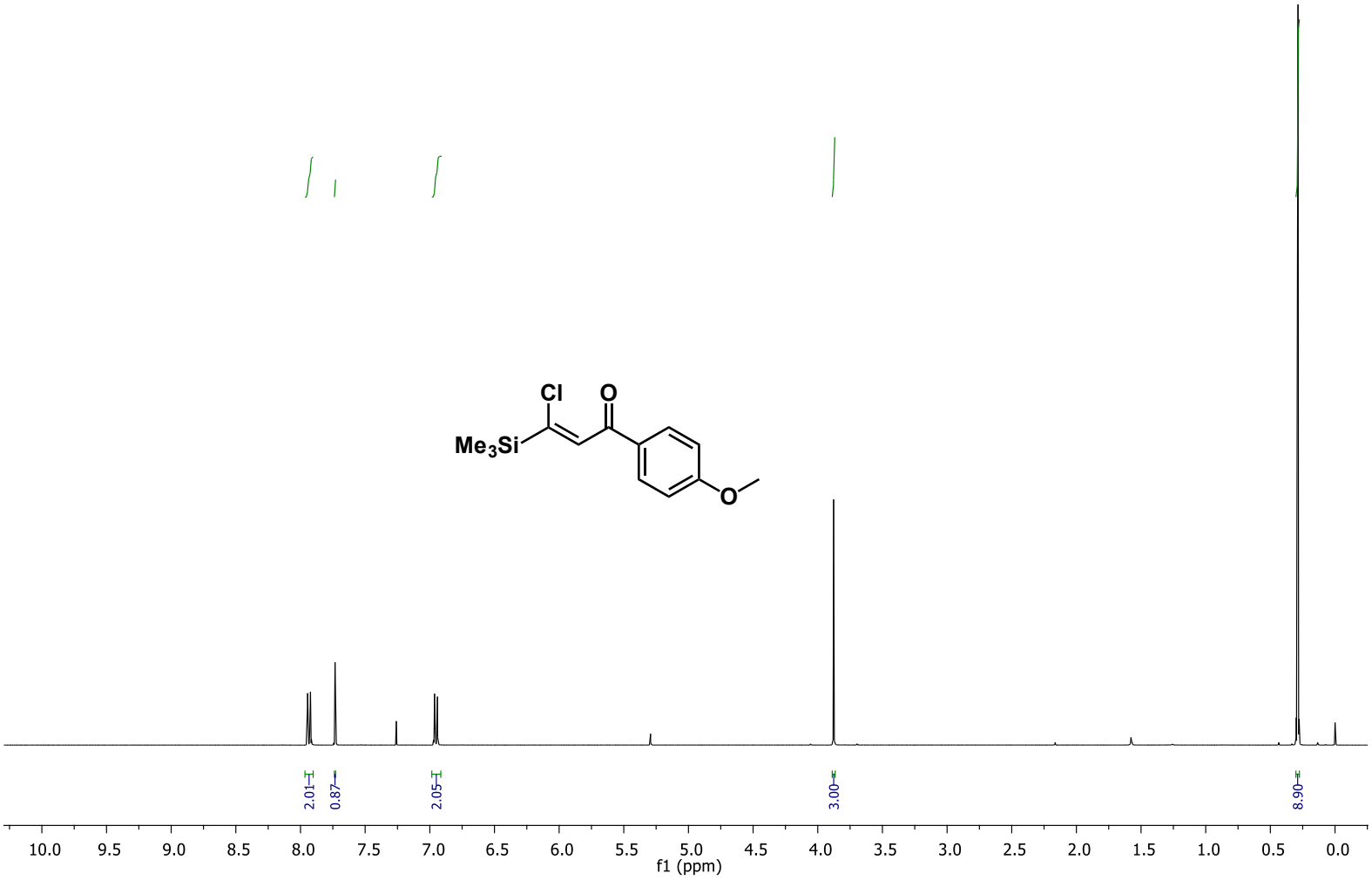
^{13}C NMR of compound **2t** (100 MHz, $CDCl_3$)



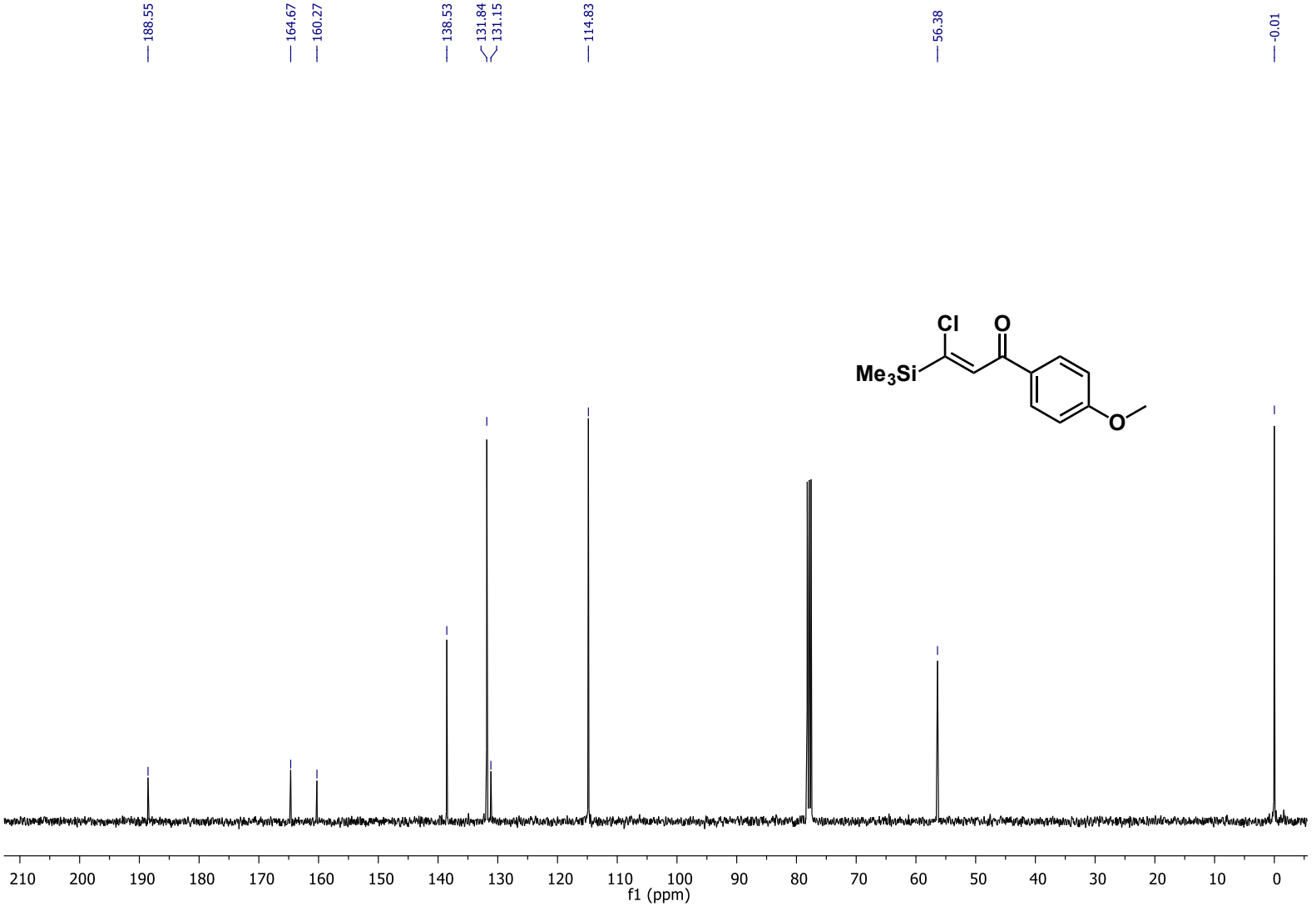
^{1}H NMR of compound **2u** (400 MHz, $CDCl_3$)



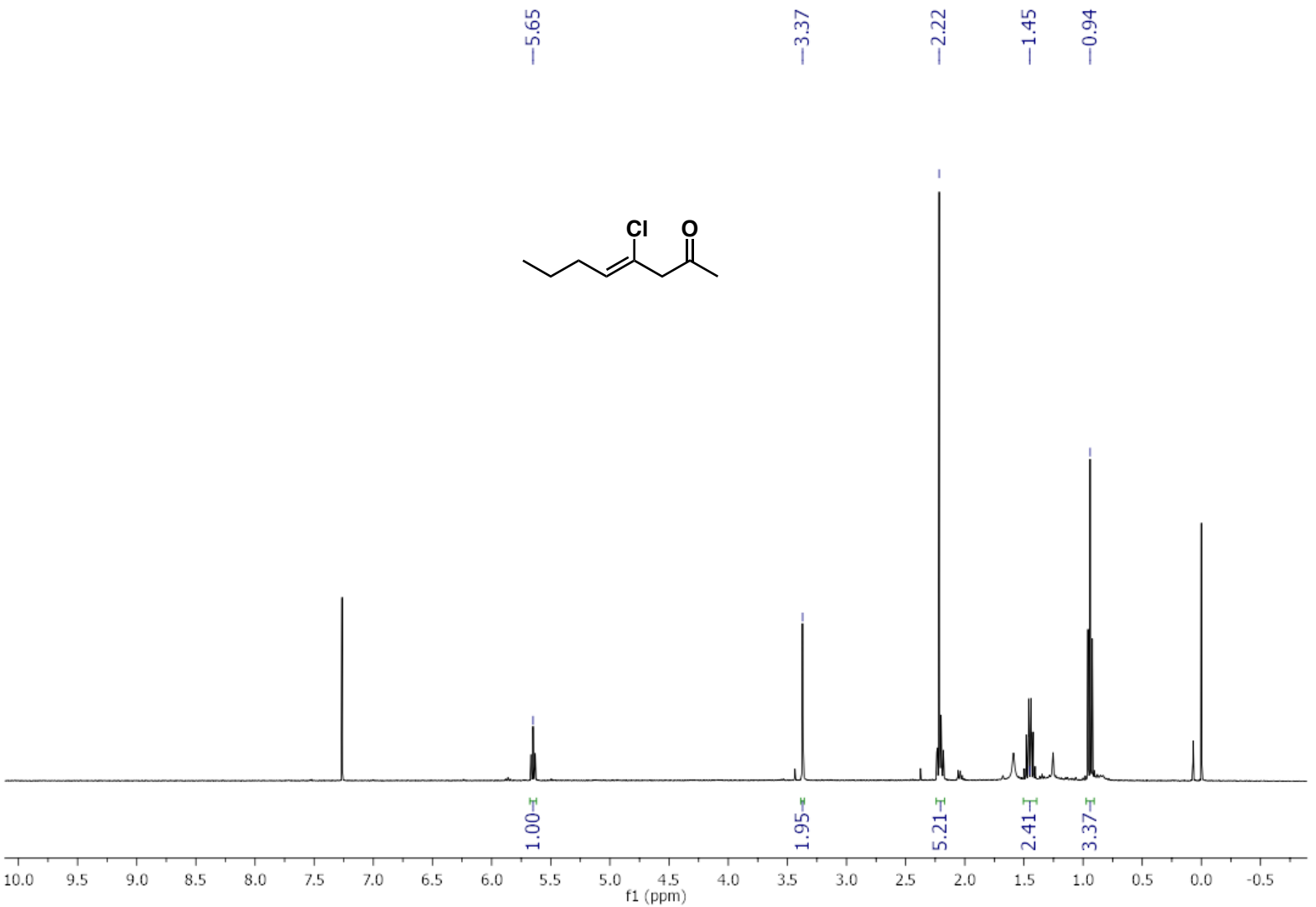
^{13}C NMR of compound **2u** (100 MHz, $CDCl_3$)



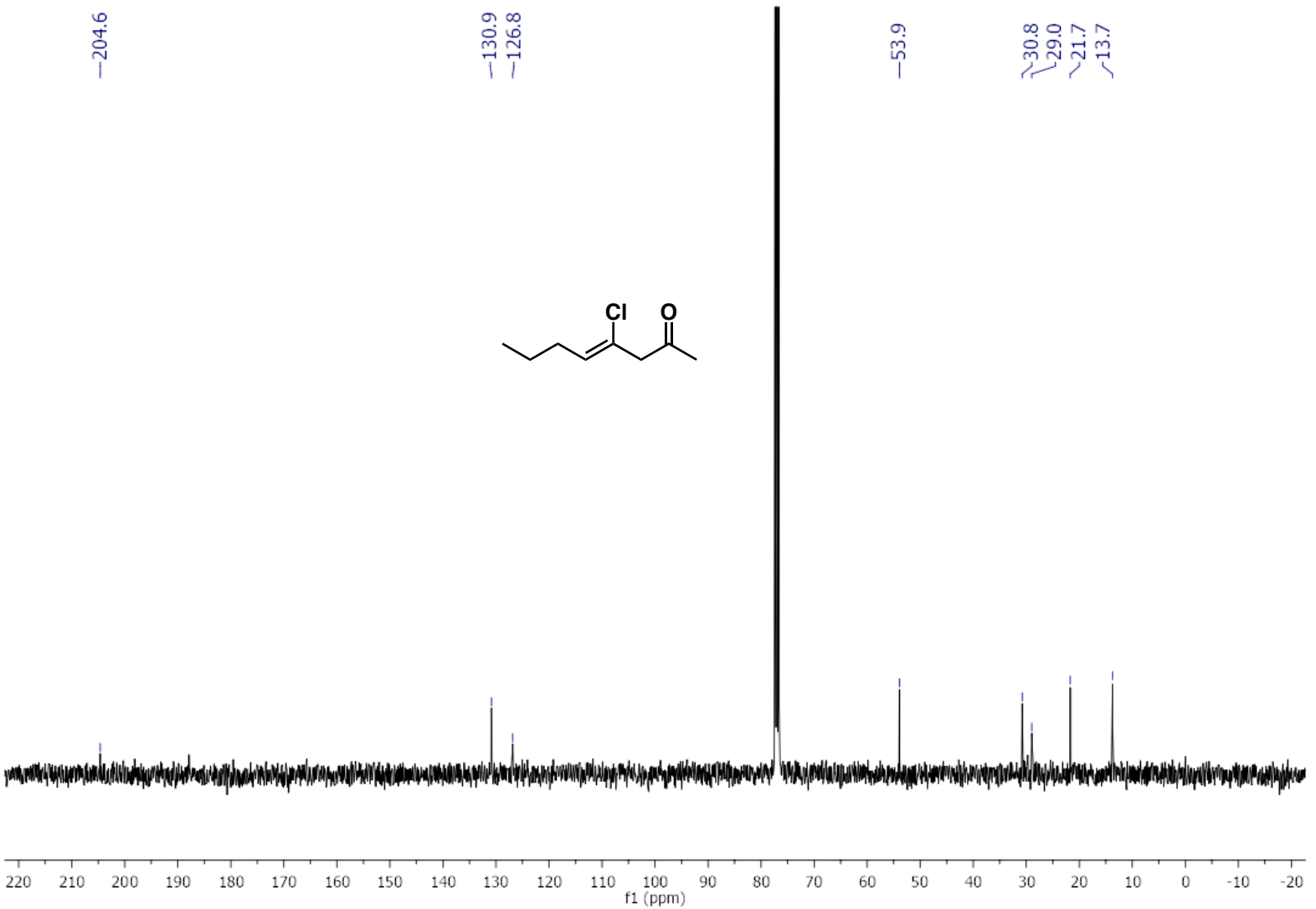
^{1}H NMR of compound **2v** (400 MHz, $CDCl_3$)



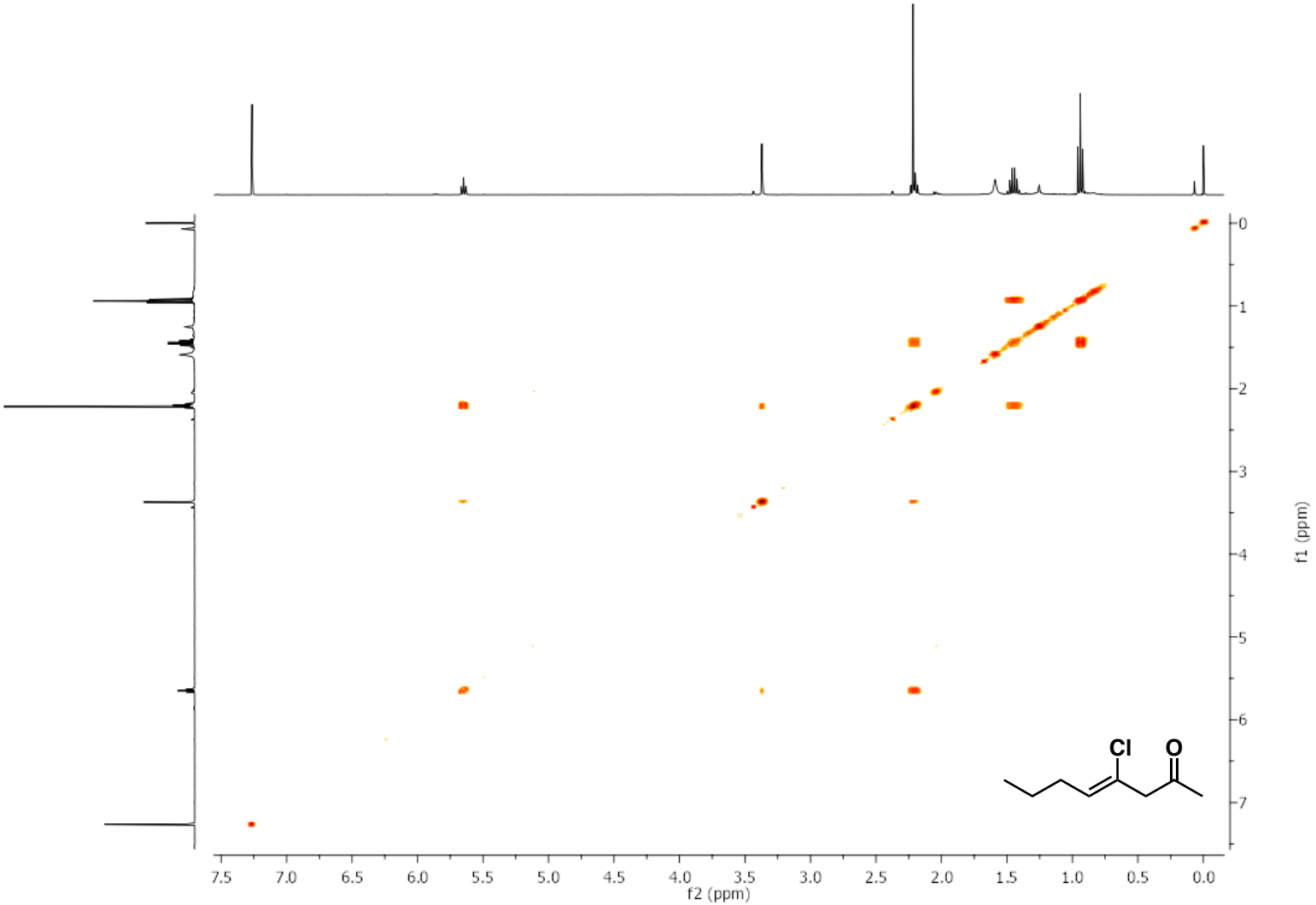
^{13}C NMR of compound **2v** (100 MHz, $CDCl_3$)



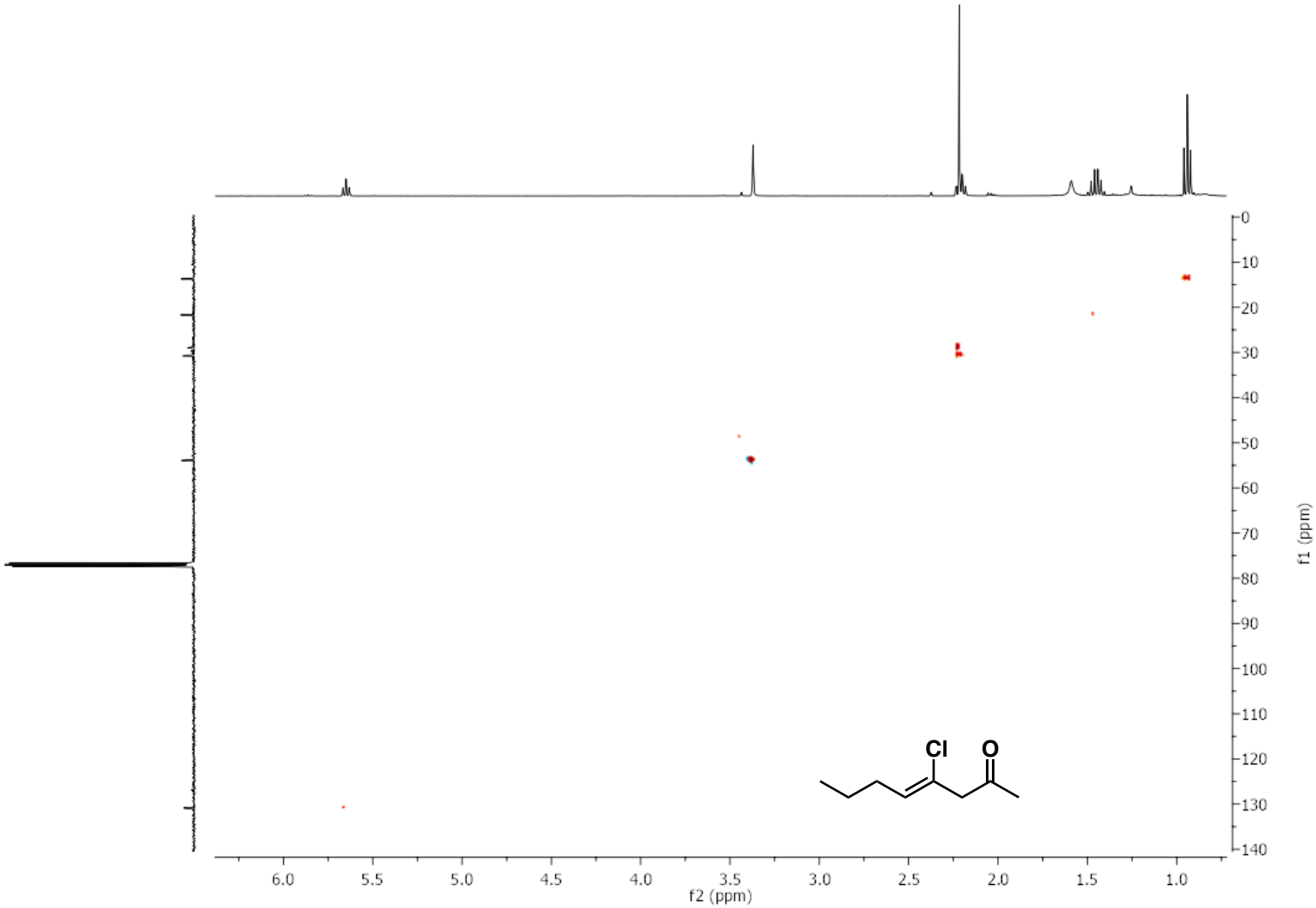
^{1}H NMR of compound **2w'** (400 MHz, $CDCl_3$)



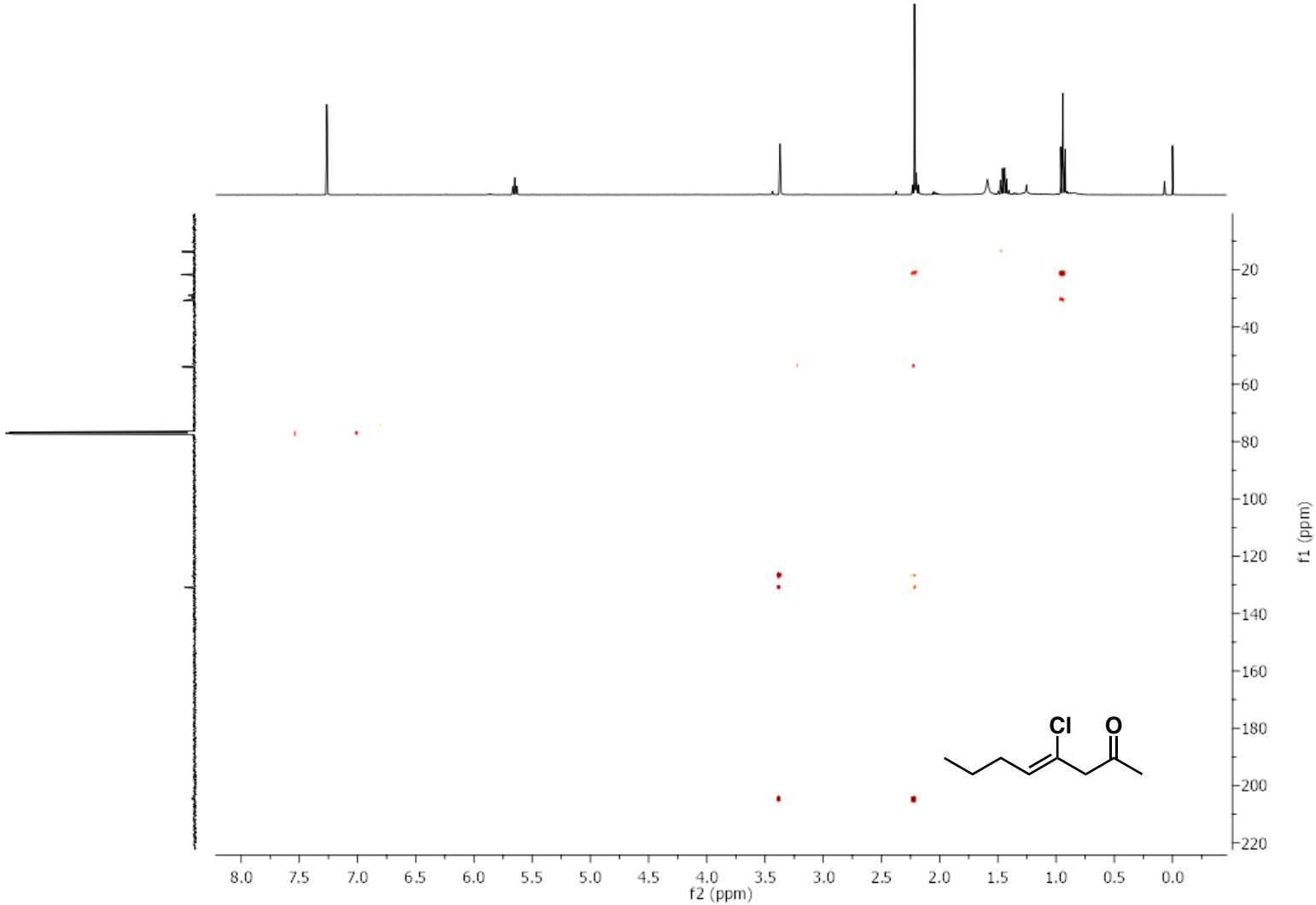
^{13}C NMR of compound **2w'** (100 MHz, $CDCl_3$)



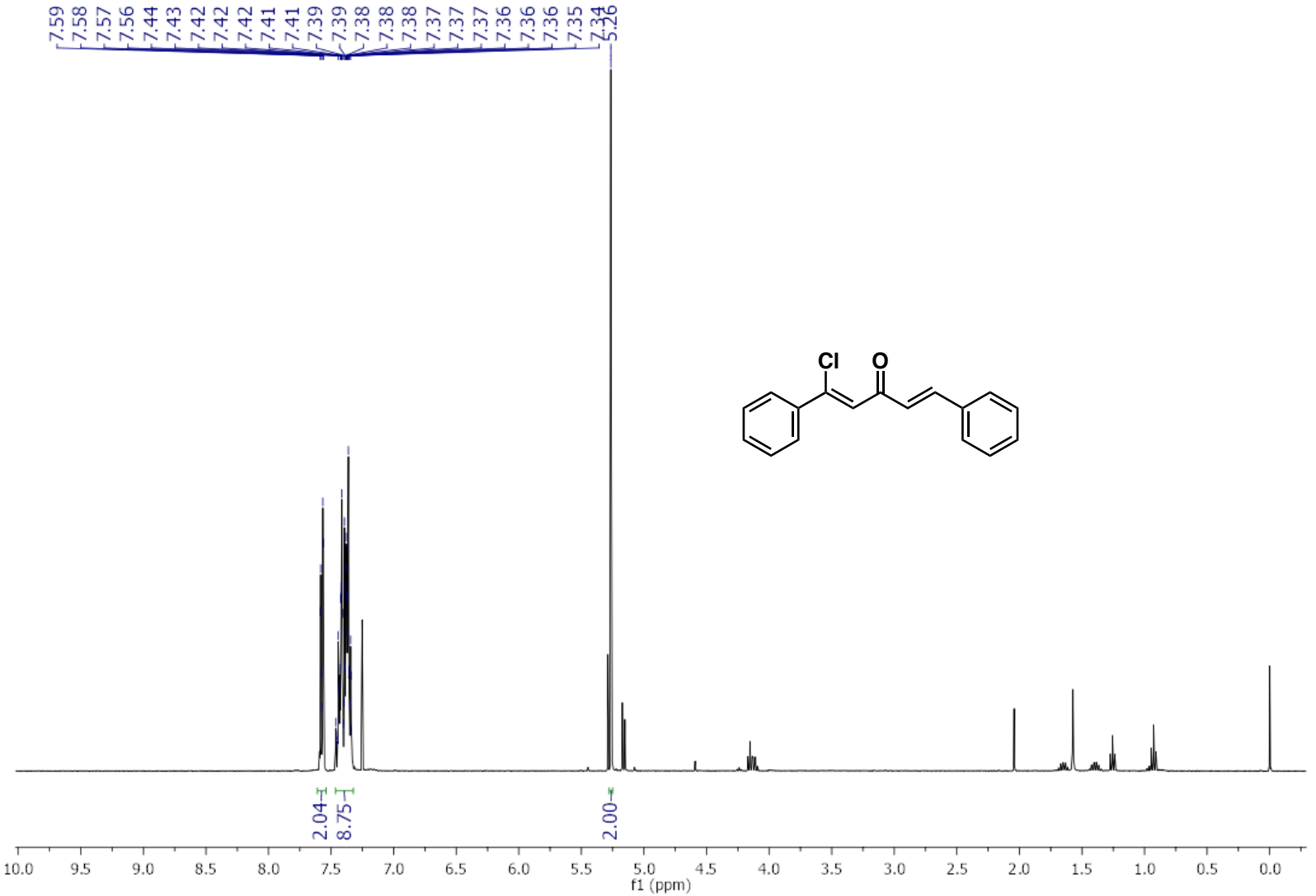
^{1}H COSY of compound **2w'** (400 MHz, $CDCl_3$)



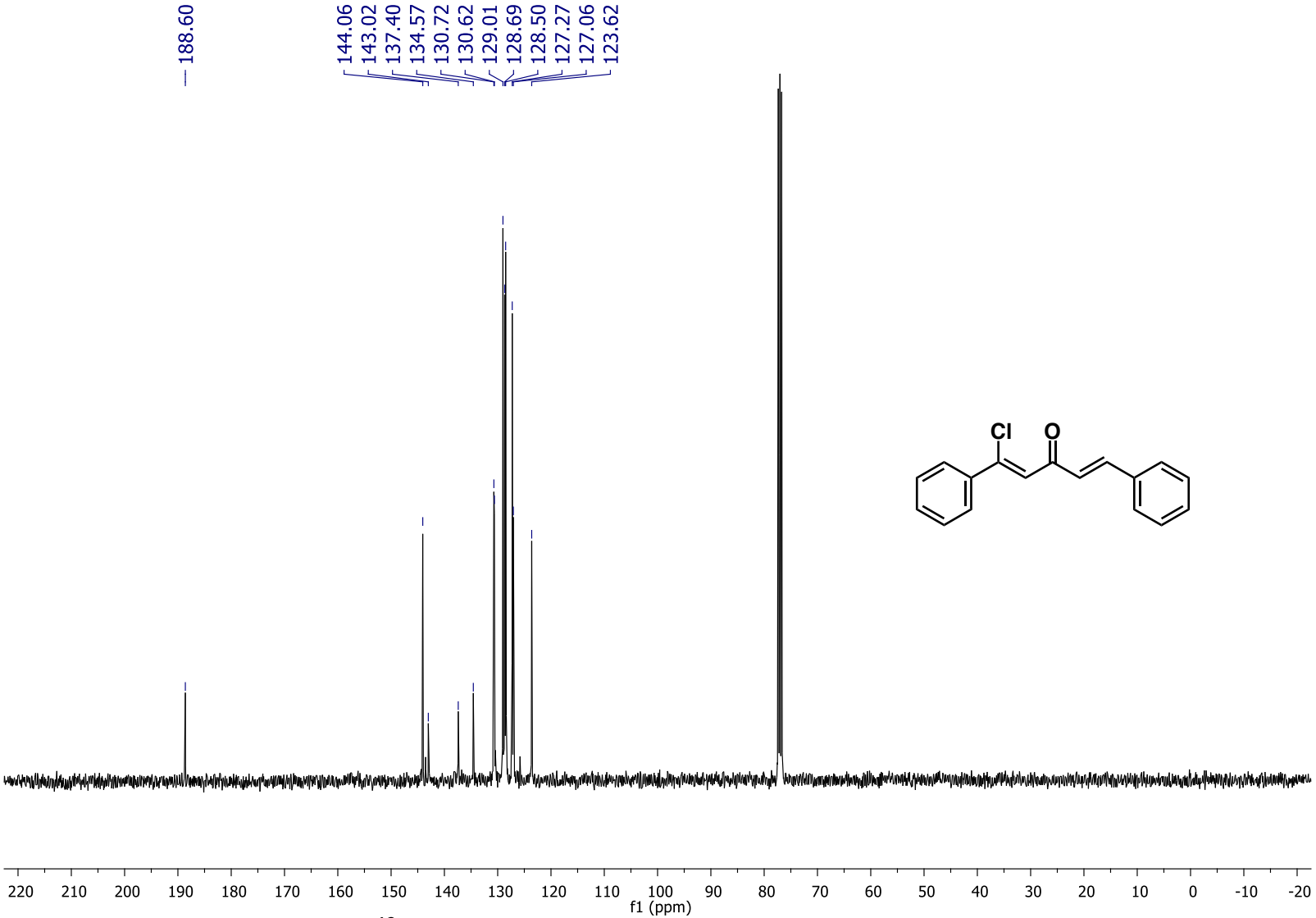
HSQC of compound **2w'** (100 MHz, $CDCl_3$)



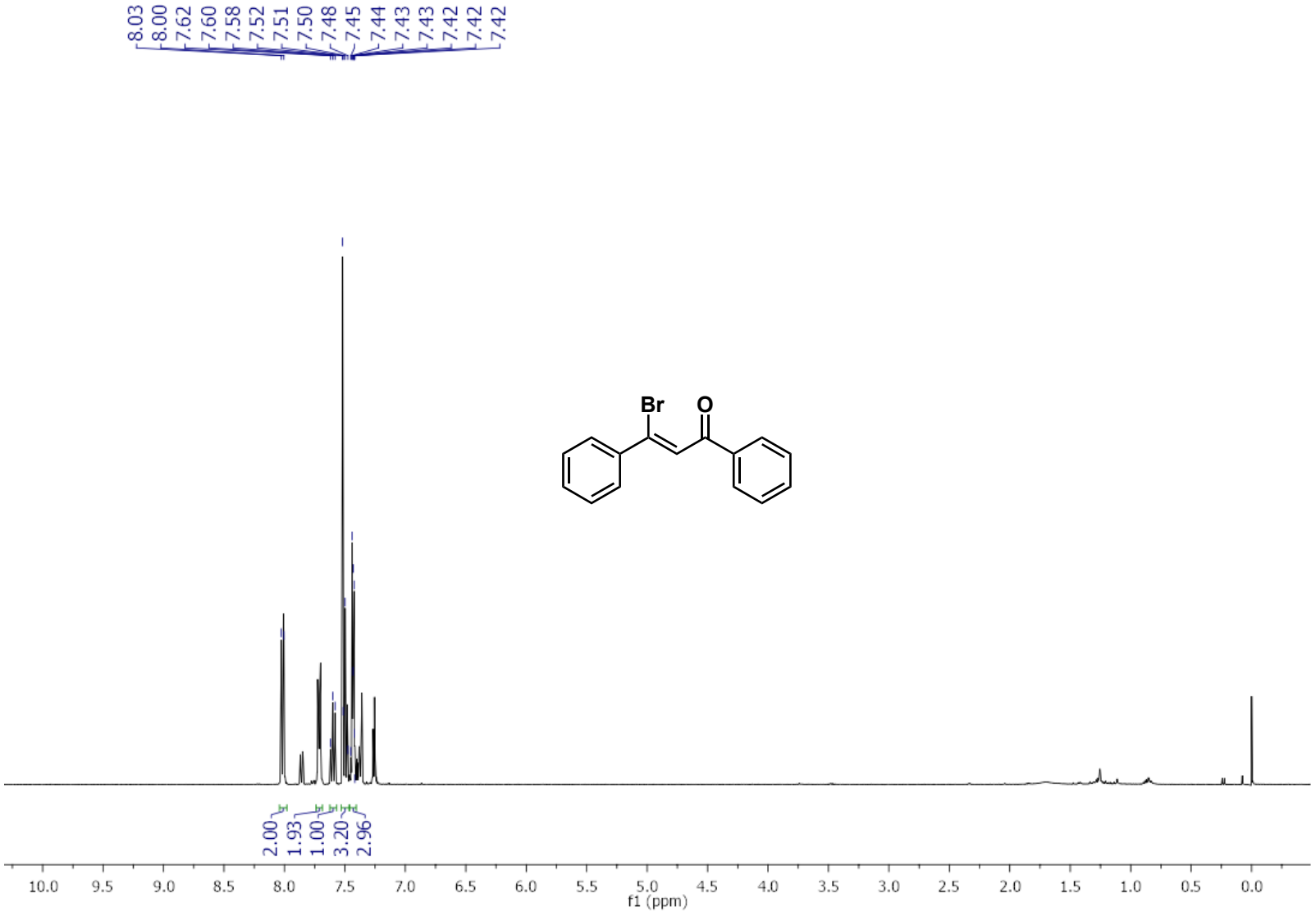
HMBC experiment of compound **2w'** (100 MHz, $CDCl_3$)



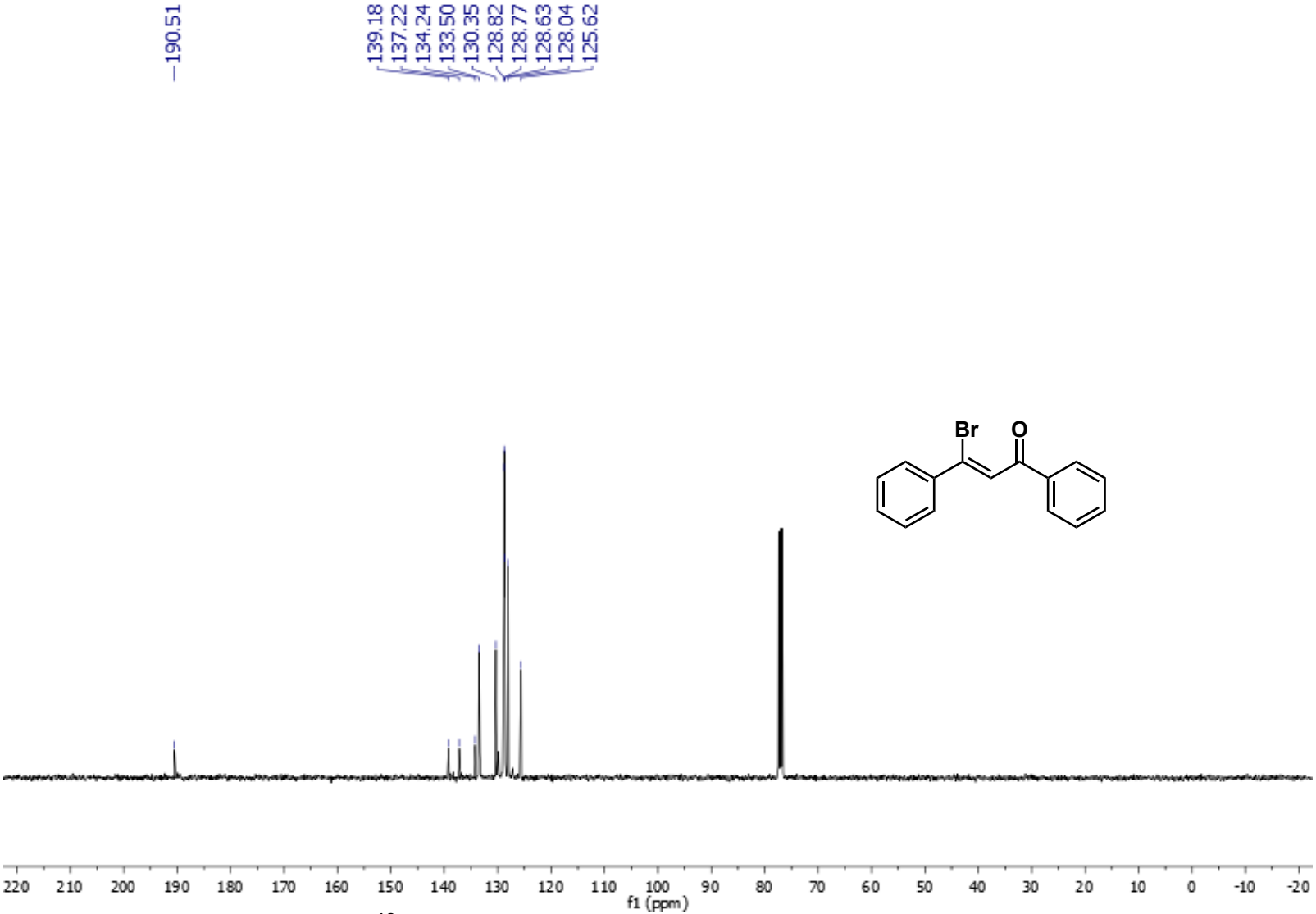
^{1}H NMR of compound **2x** (400 MHz, $CDCl_3$)



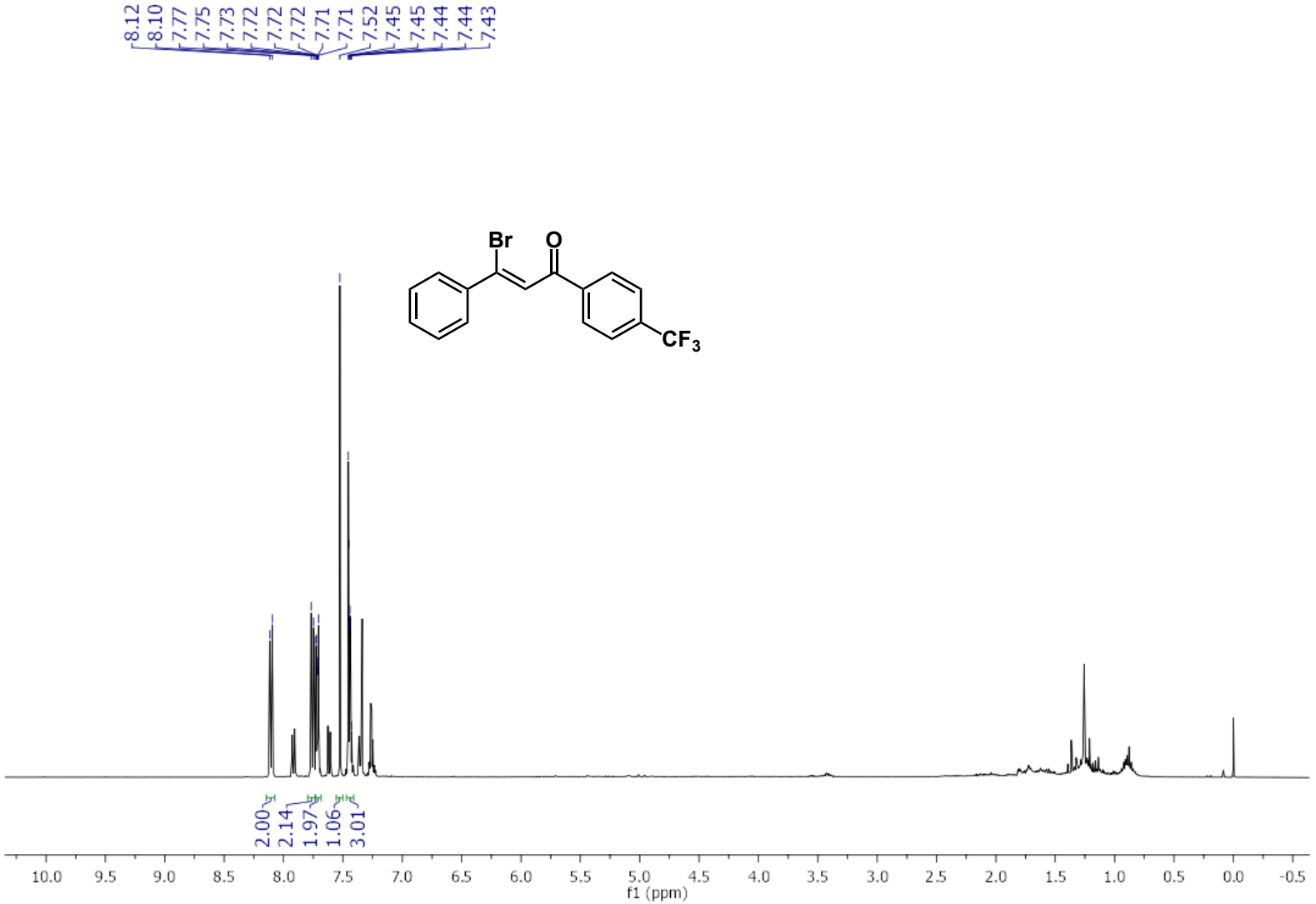
^{13}C NMR of compound **2x** (100 MHz, $CDCl_3$)



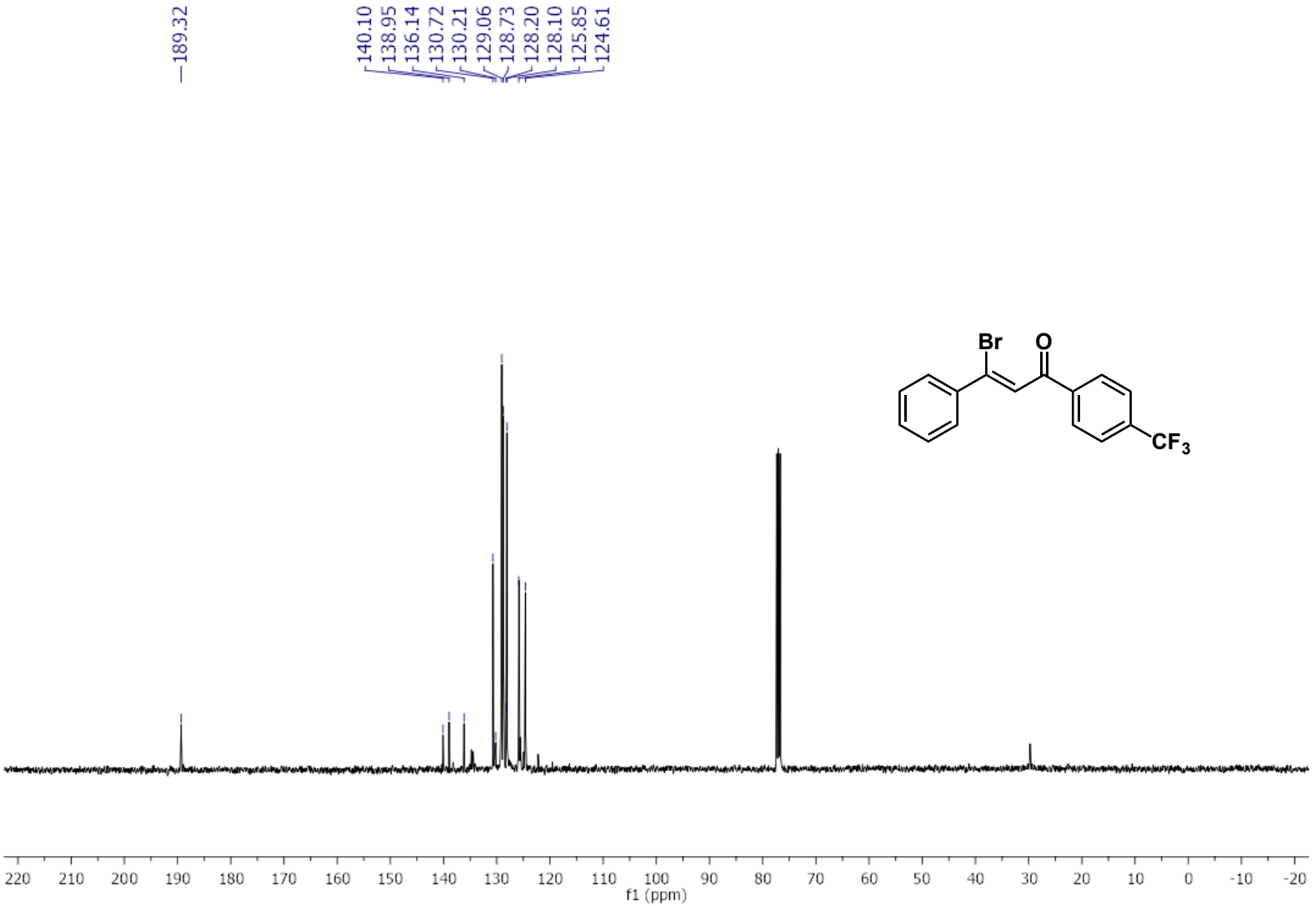
^{1}H NMR of compound **3a** (400 MHz, $CDCl_3$)



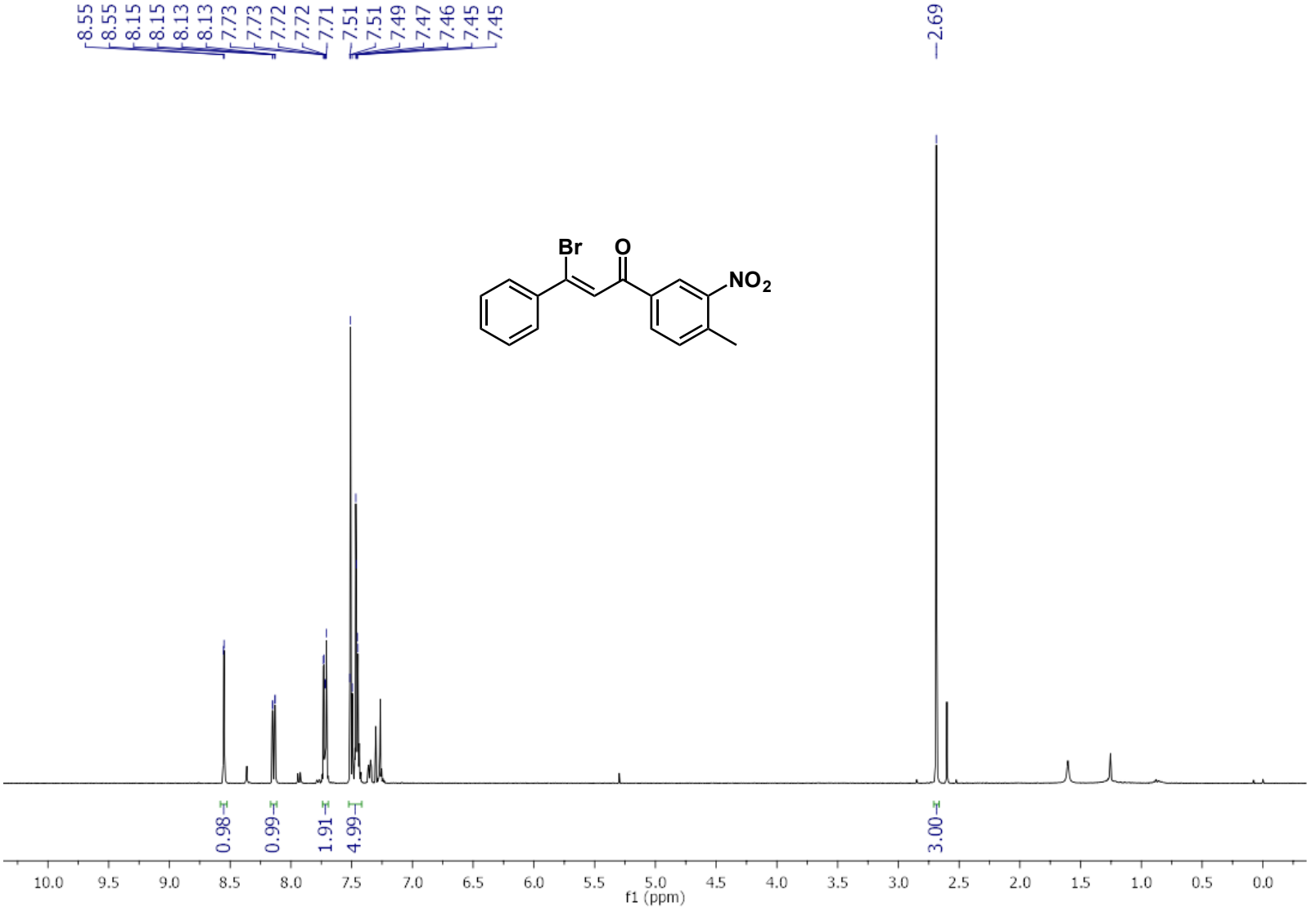
^{13}C NMR of compound **3a** (100 MHz, $CDCl_3$)



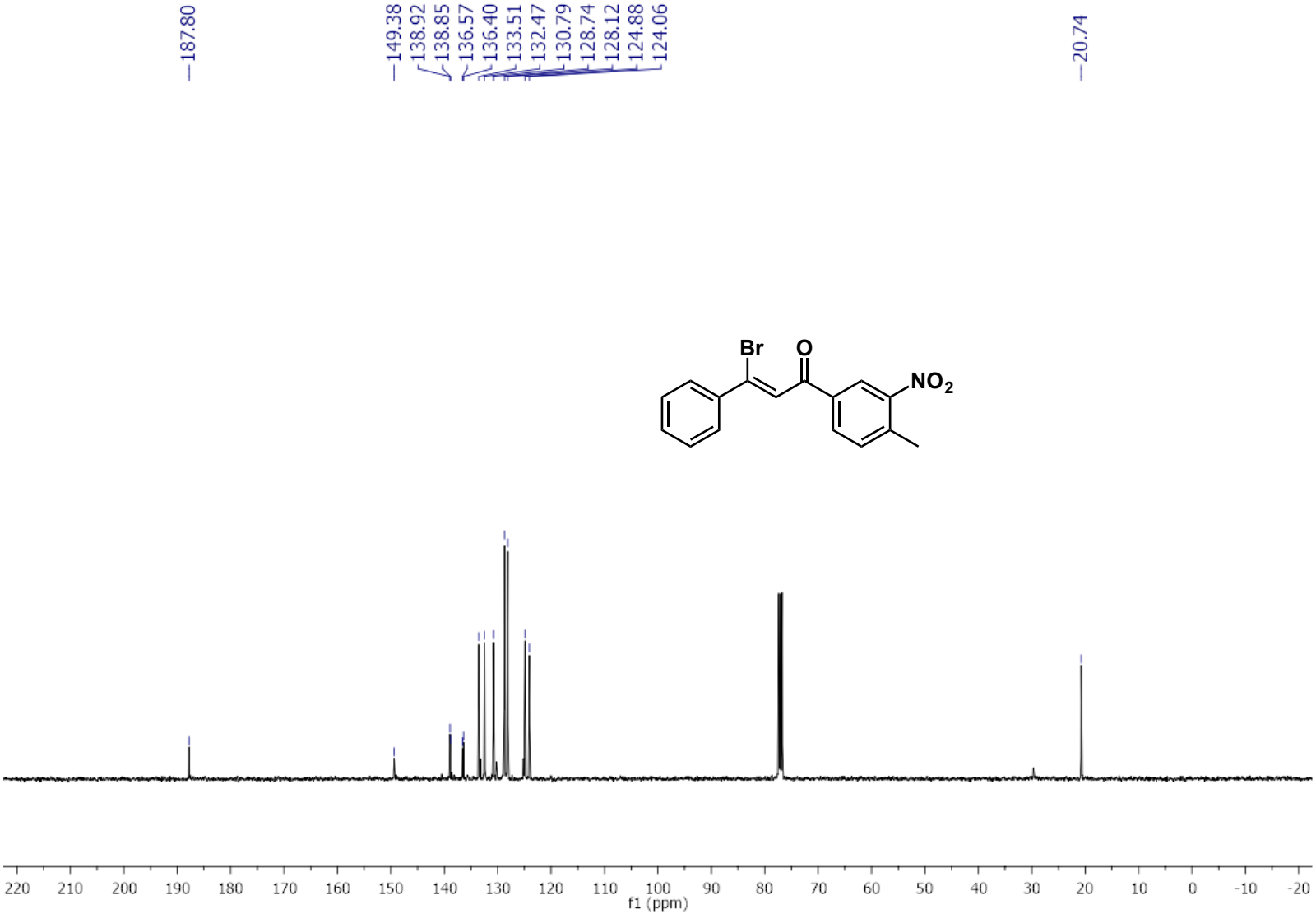
^{1}H NMR of compound **3b** (400 MHz, $CDCl_3$)



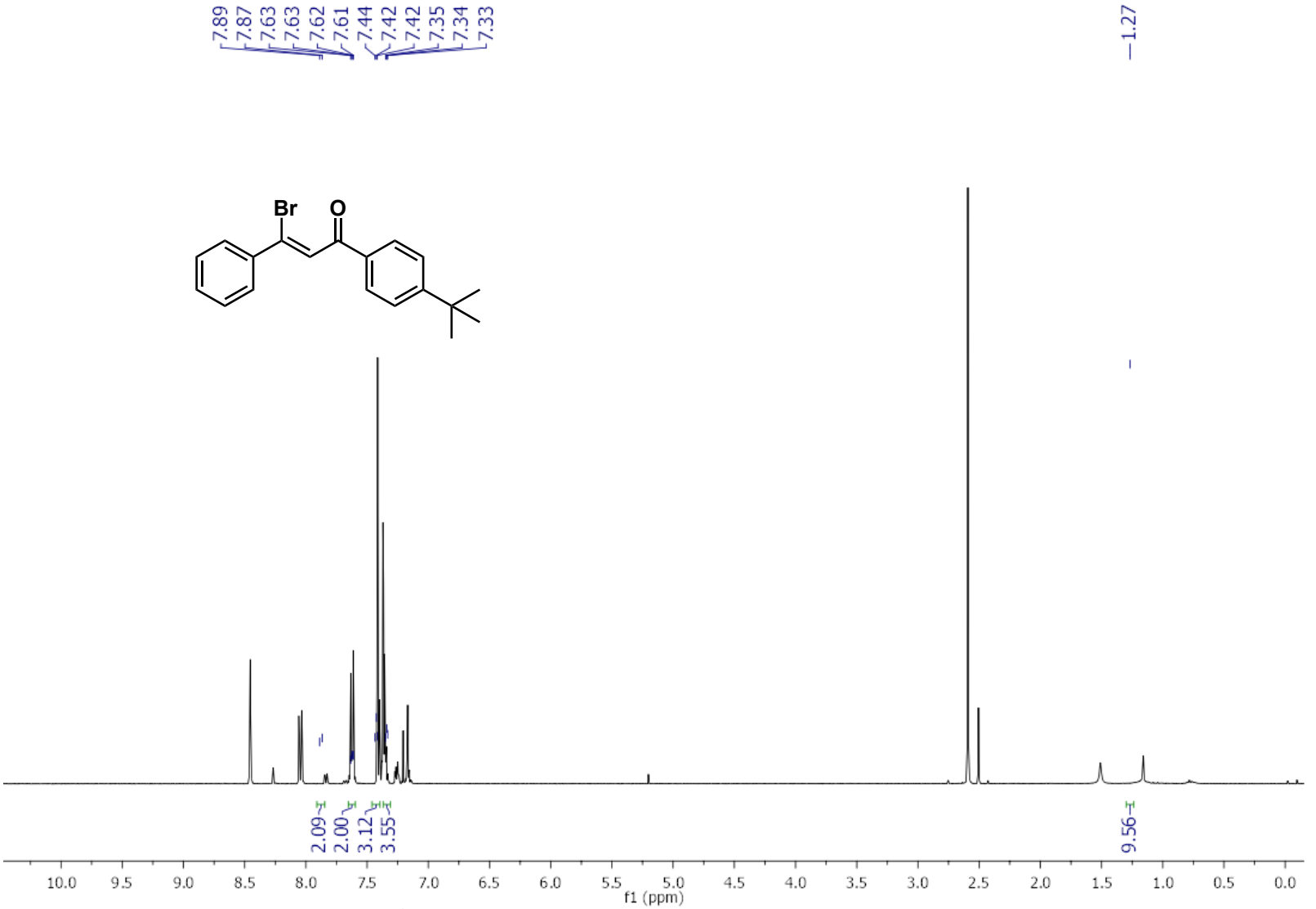
^{13}C NMR of compound **3b** (100 MHz, $CDCl_3$)



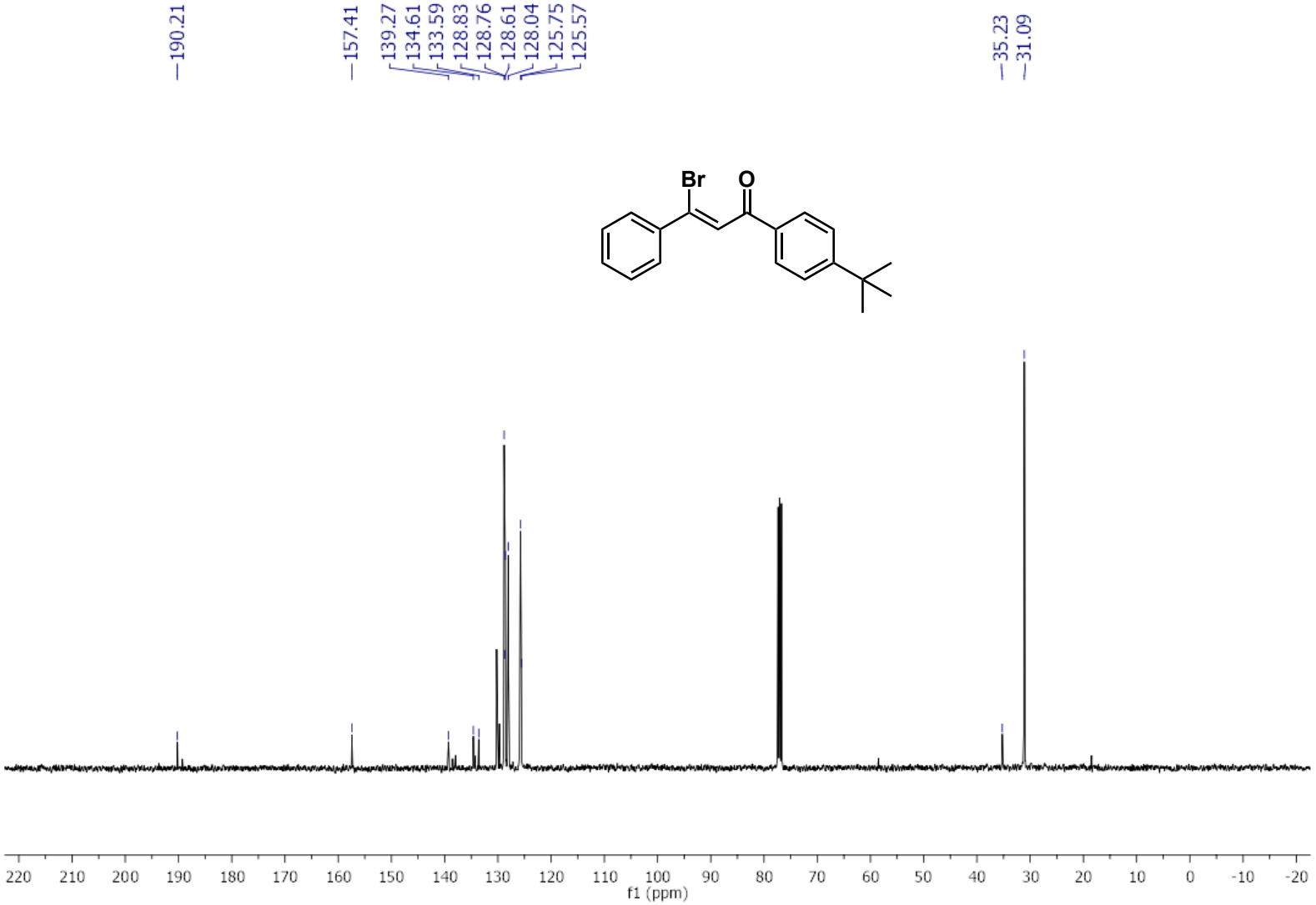
^{1}H NMR of compound **3c** (400 MHz, $CDCl_3$)



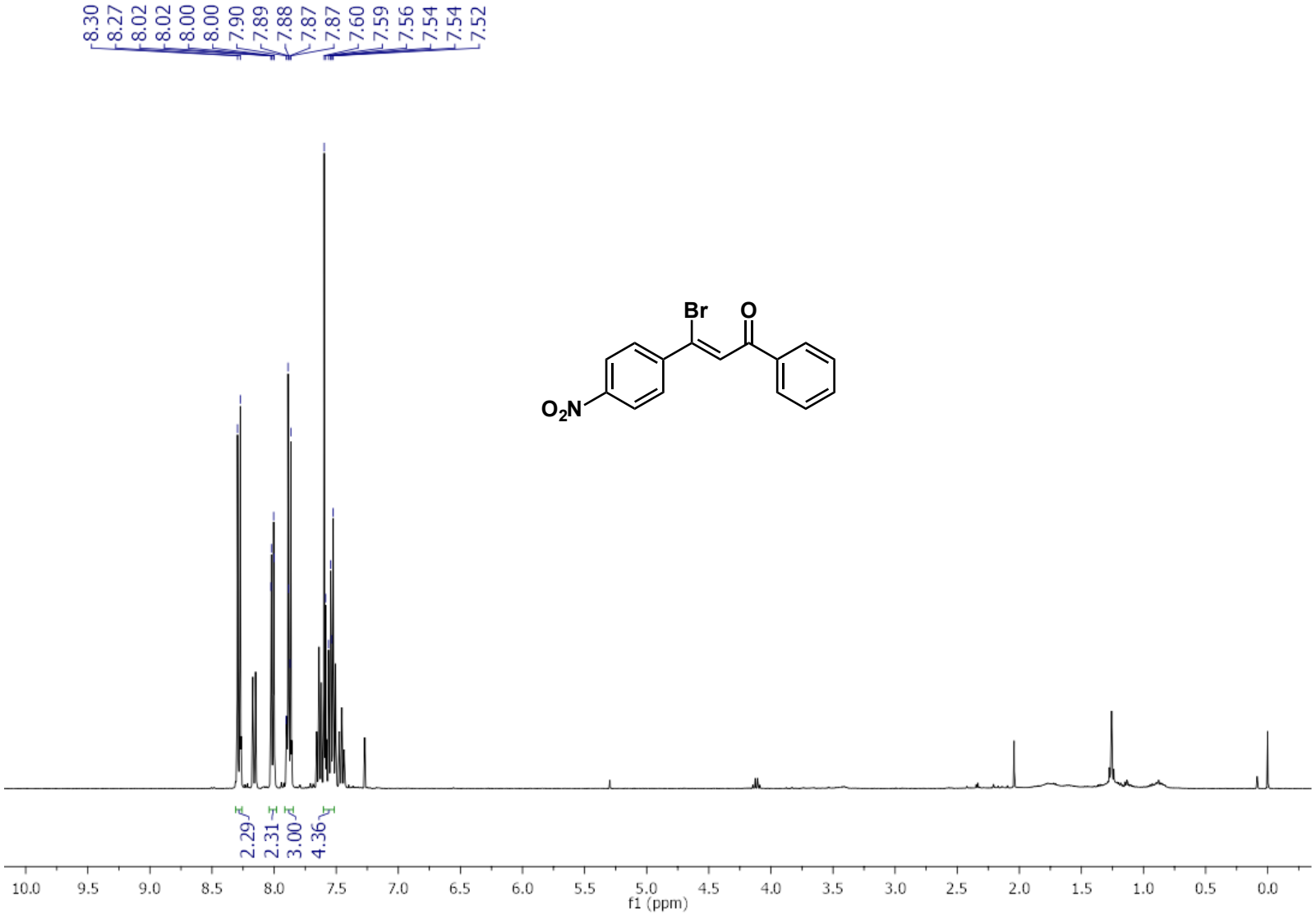
^{13}C NMR of compound **3c** (100 MHz, $CDCl_3$)



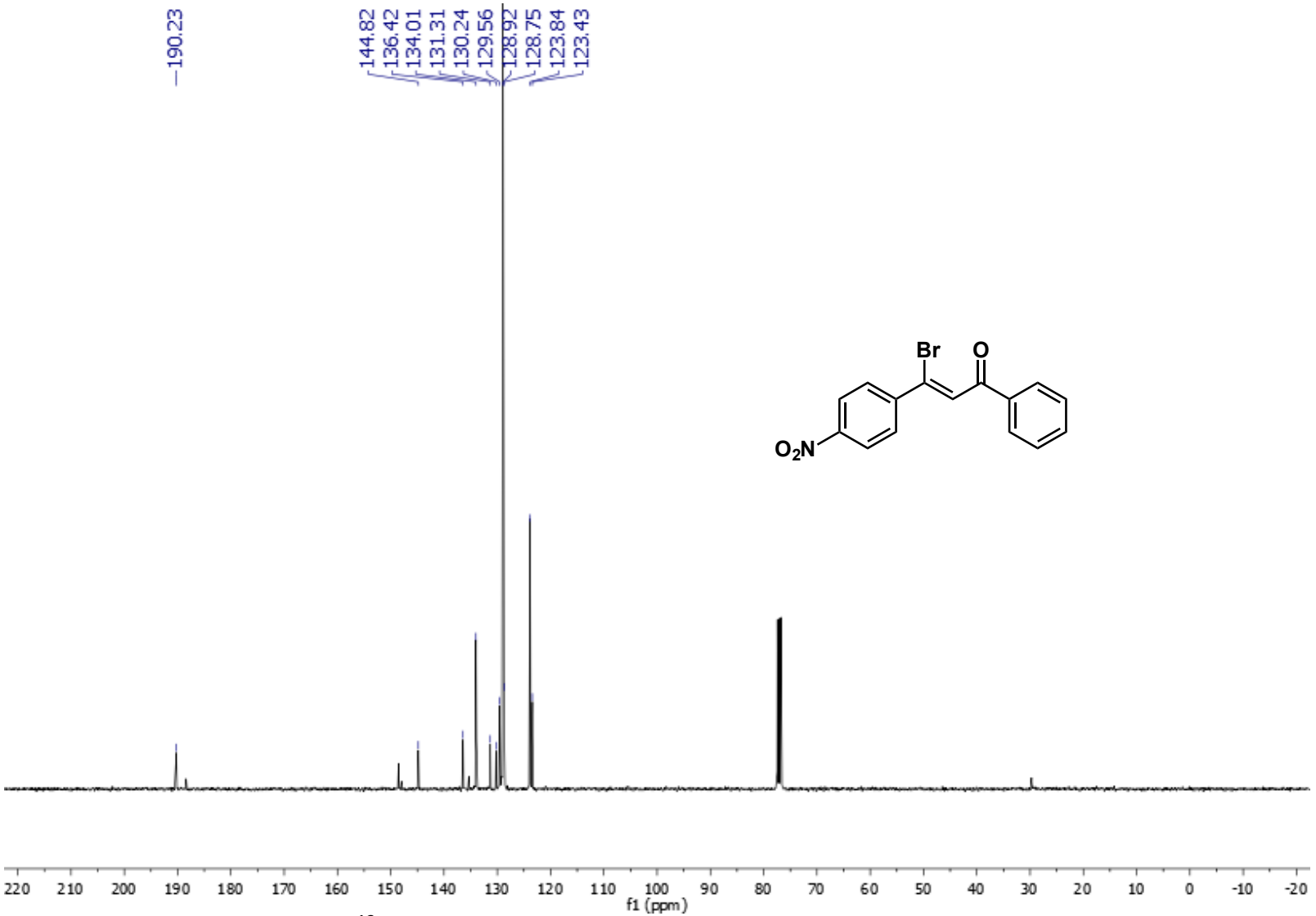
^{1}H NMR of compound **3d** (400 MHz, $CDCl_3$)



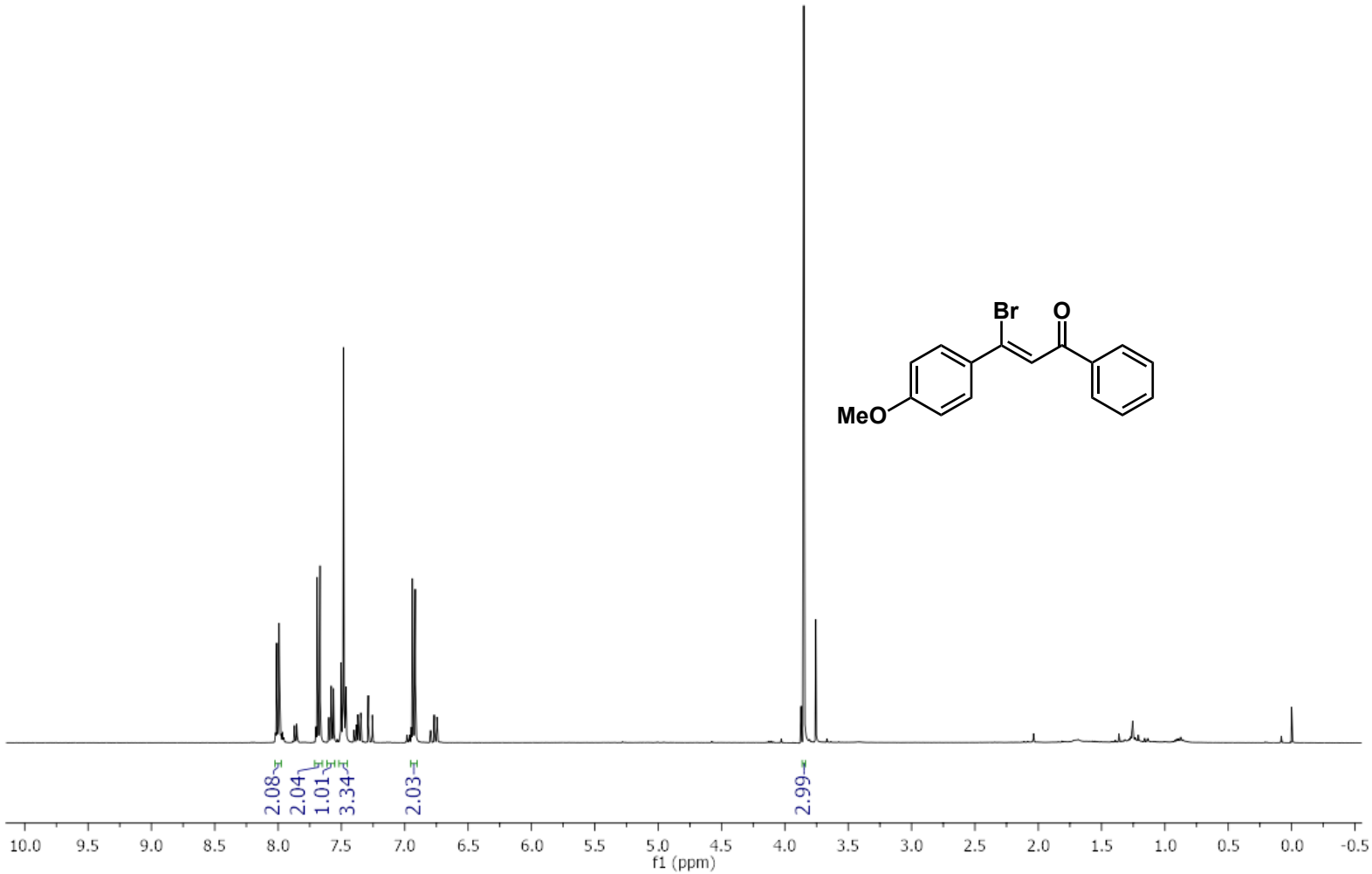
^{13}C NMR of compound **3d** (100 MHz, $CDCl_3$)



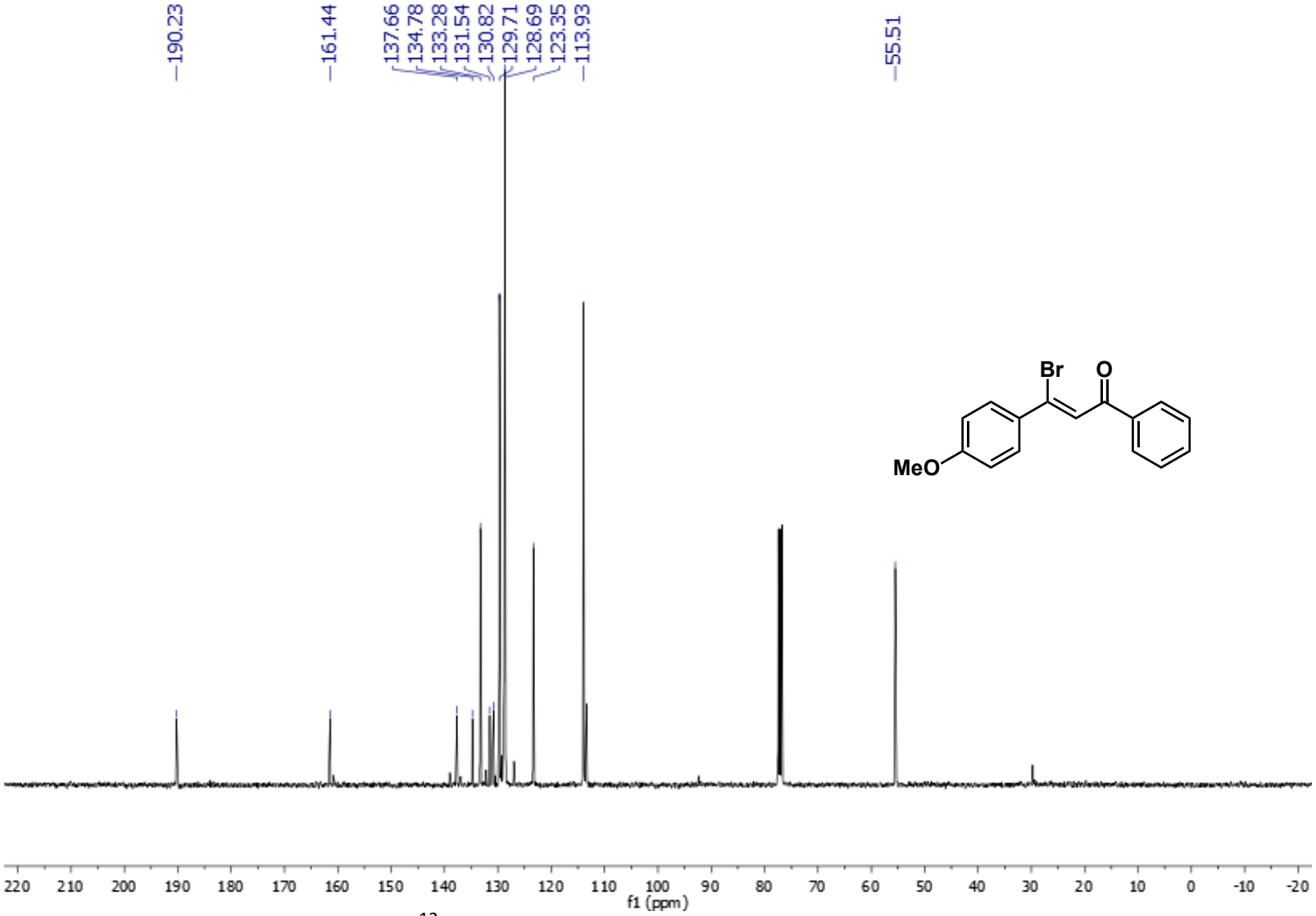
^{1}H NMR of compound **3e** (400 MHz, $CDCl_3$)



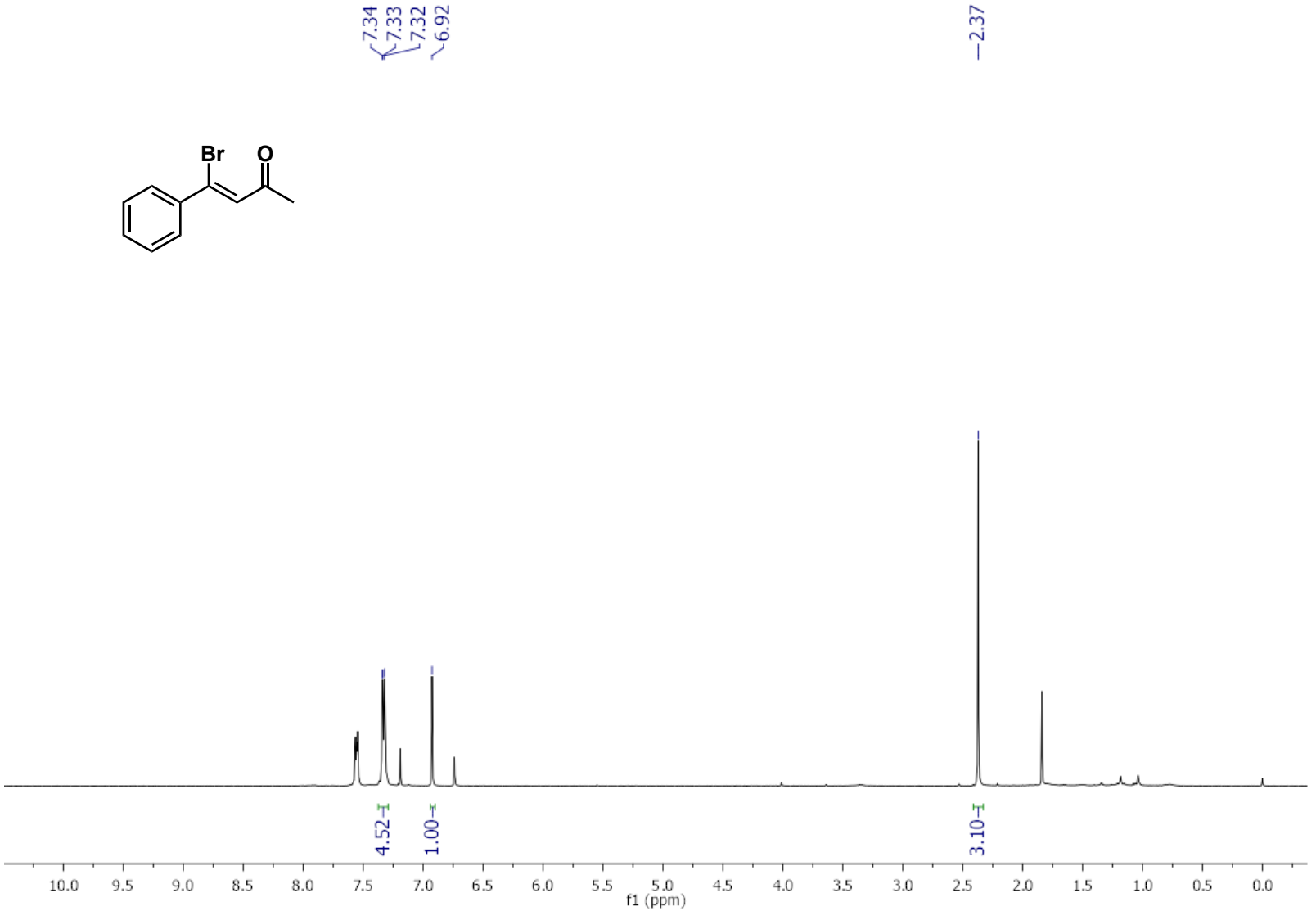
^{13}C NMR of compound **3e** (100 MHz, $CDCl_3$)



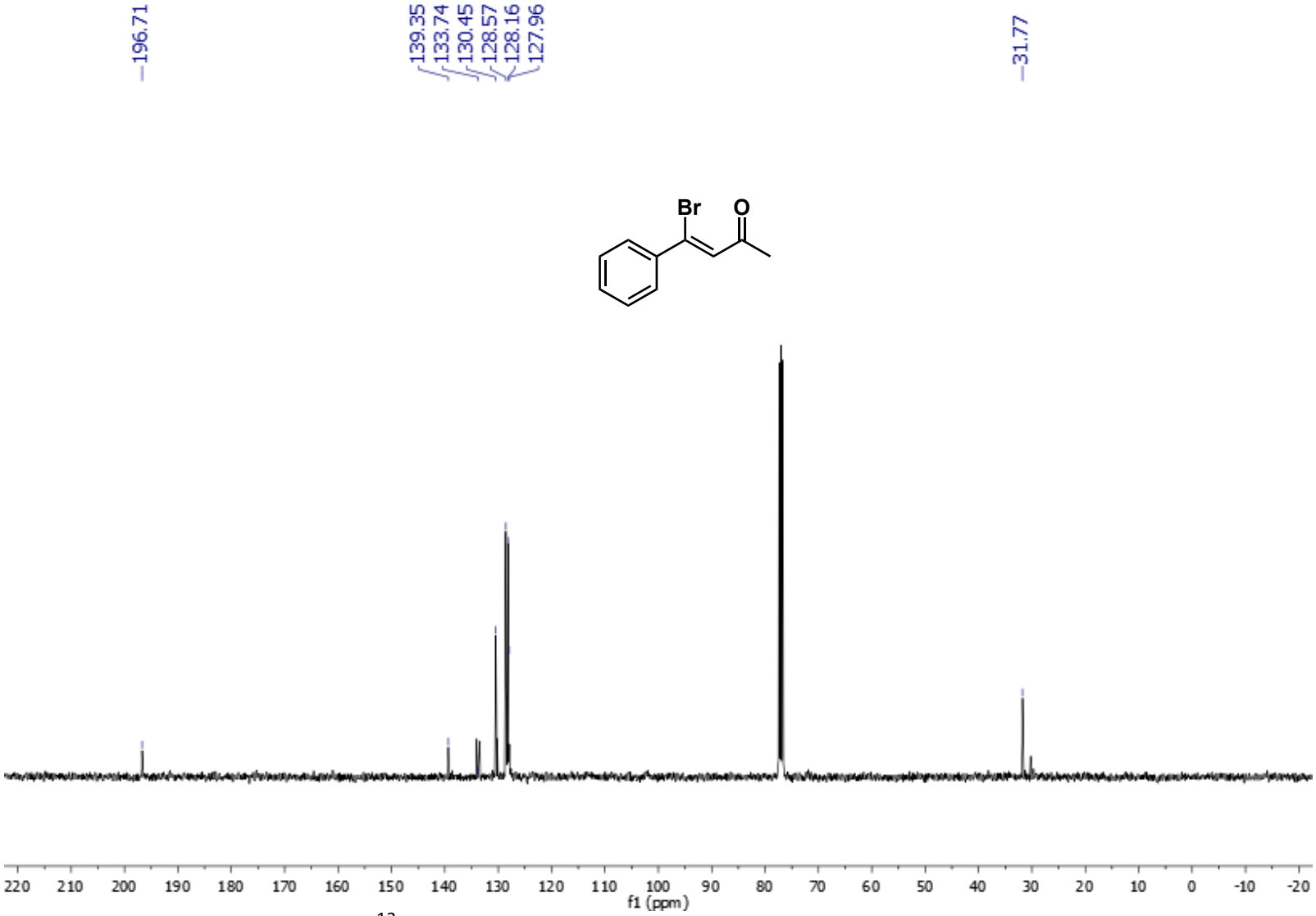
^{1}H NMR of compound **3f** (400 MHz, $CDCl_3$)



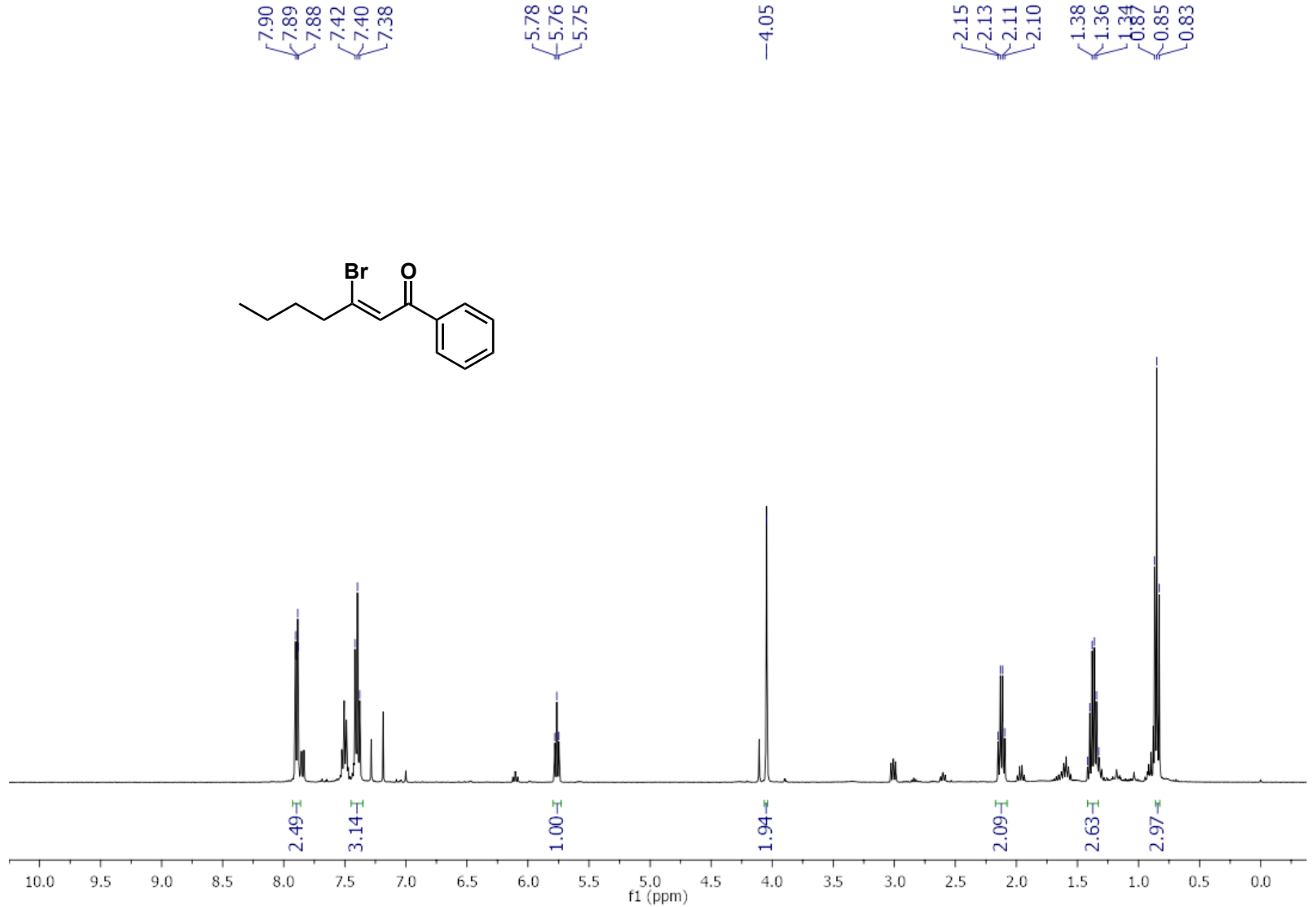
^{13}C NMR of compound **3f** (100 MHz, $CDCl_3$)



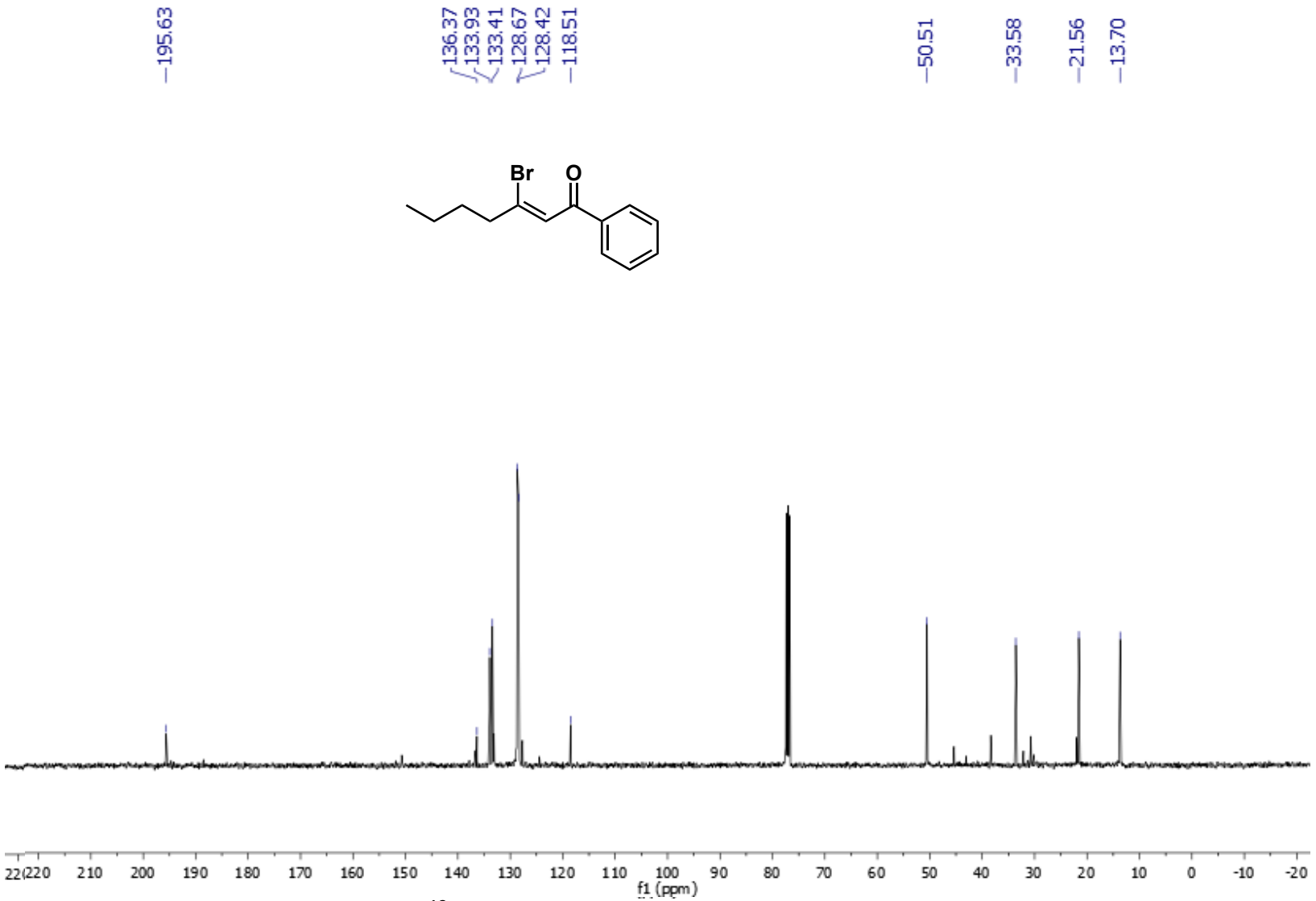
^{1}H NMR of compound **3g** (400 MHz, $CDCl_3$)



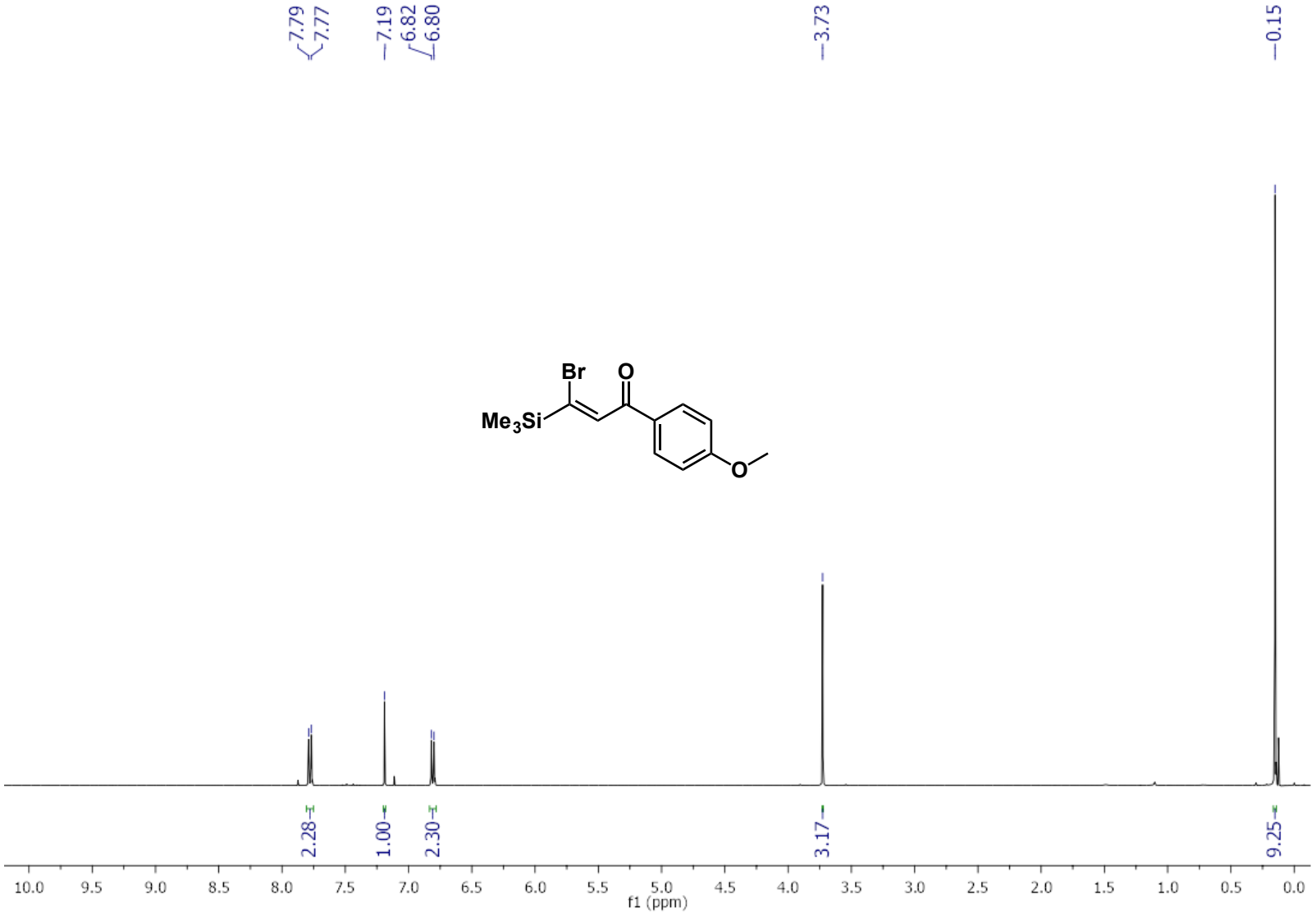
^{13}C NMR of compound **3g** (100 MHz, $CDCl_3$)



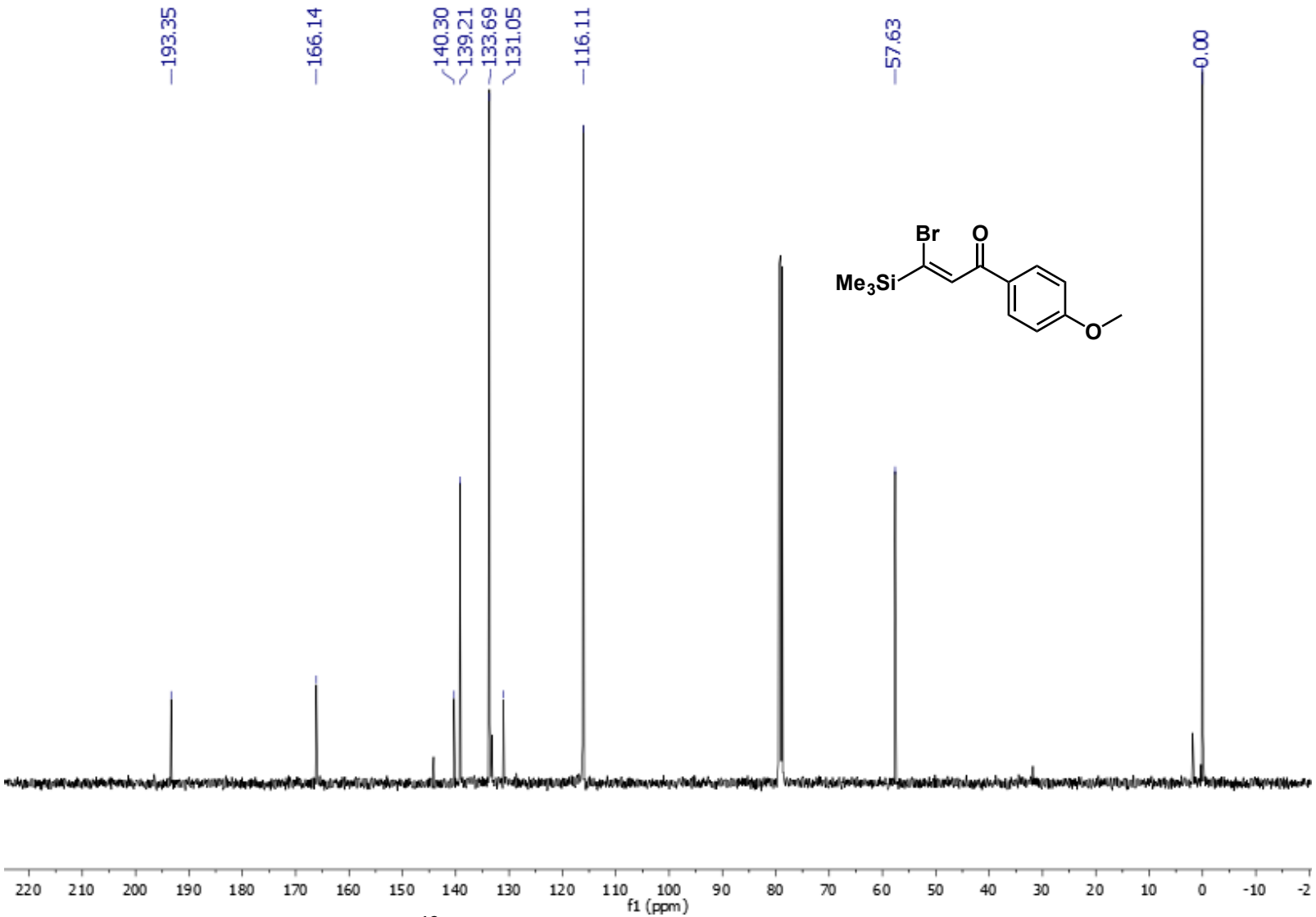
^{1}H NMR of compound **3h** (400 MHz, $CDCl_3$)



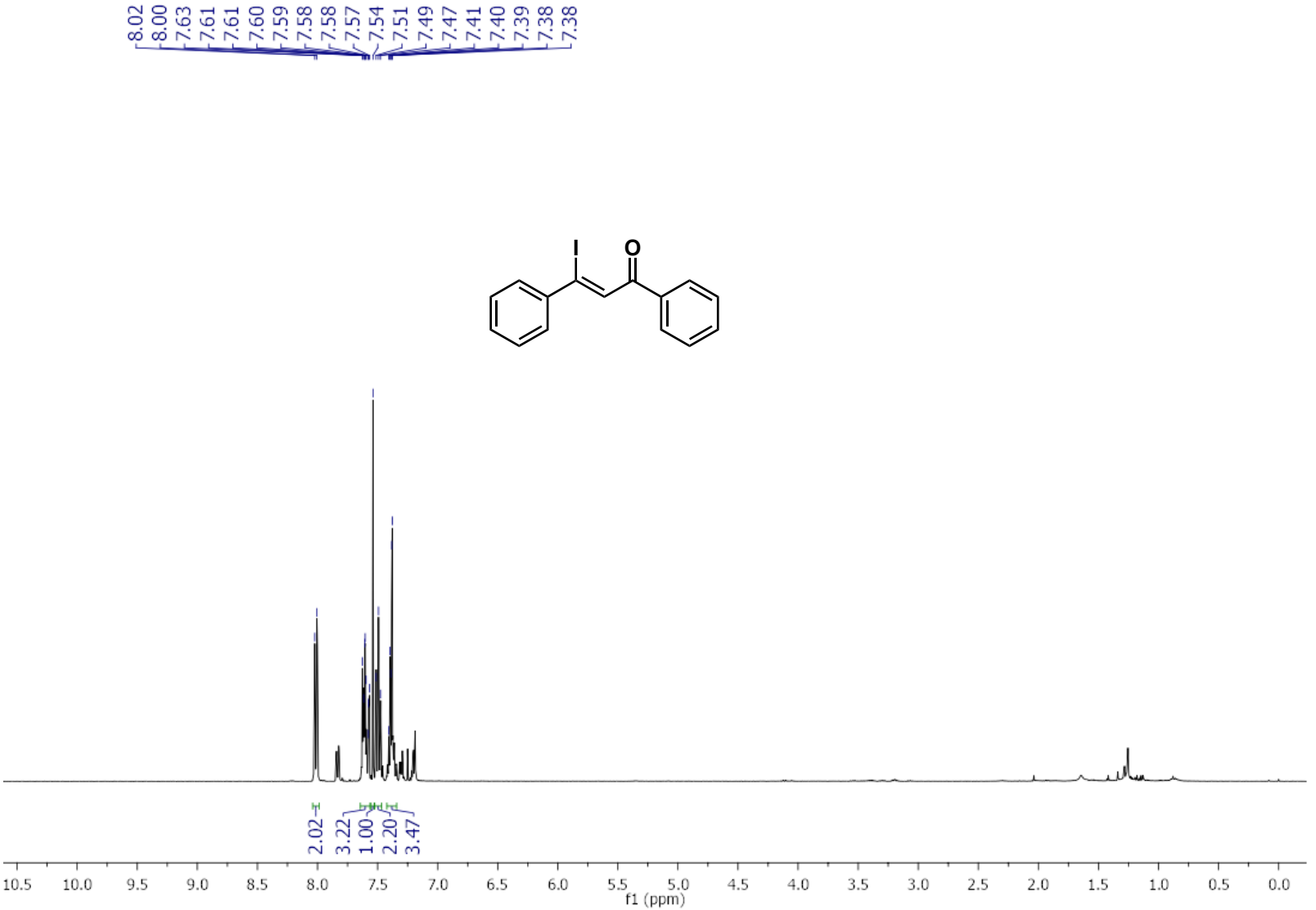
^{13}C NMR of compound **3h** (100 MHz, $CDCl_3$)



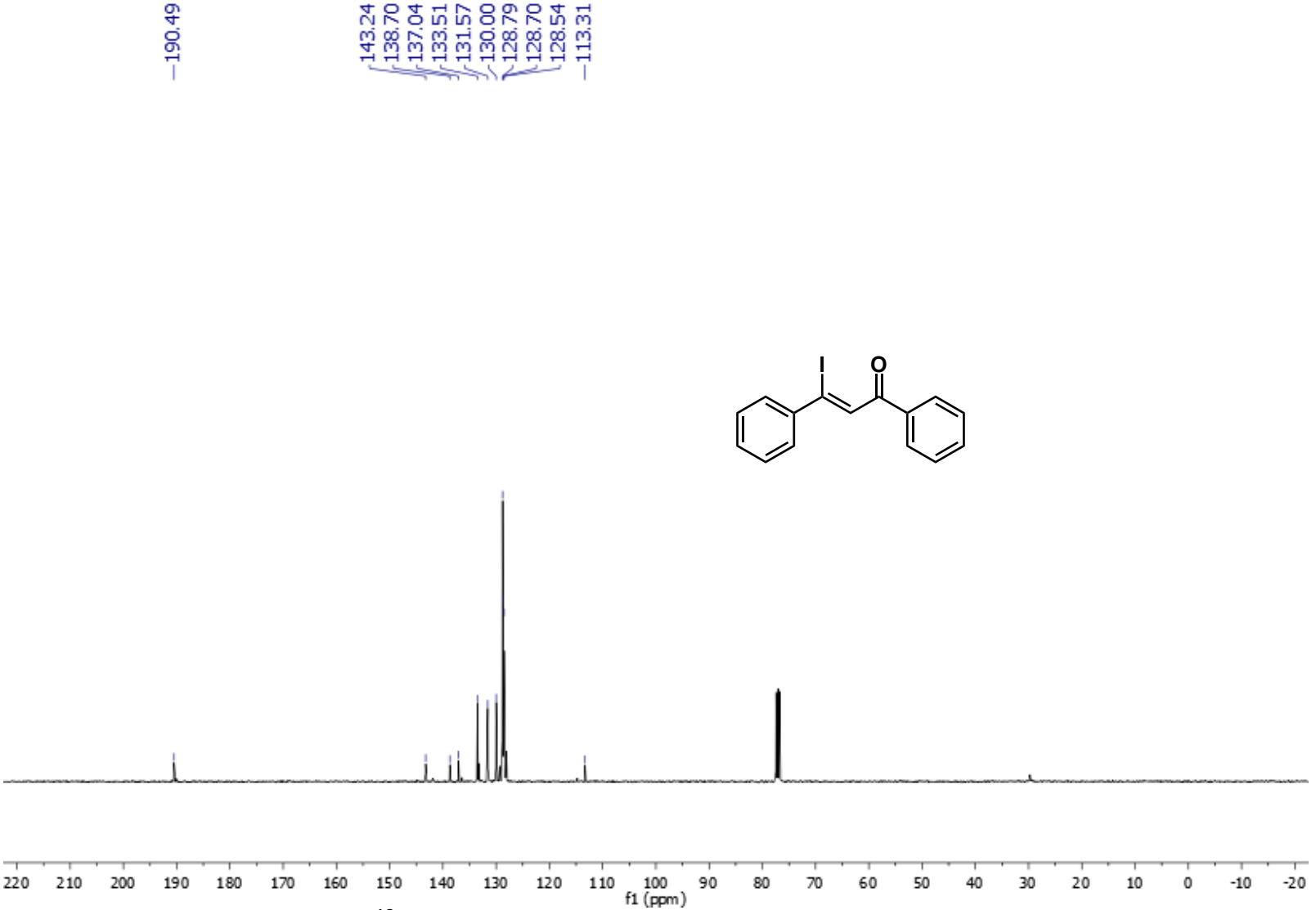
^{1}H NMR of compound **3i** (400 MHz, $CDCl_3$)



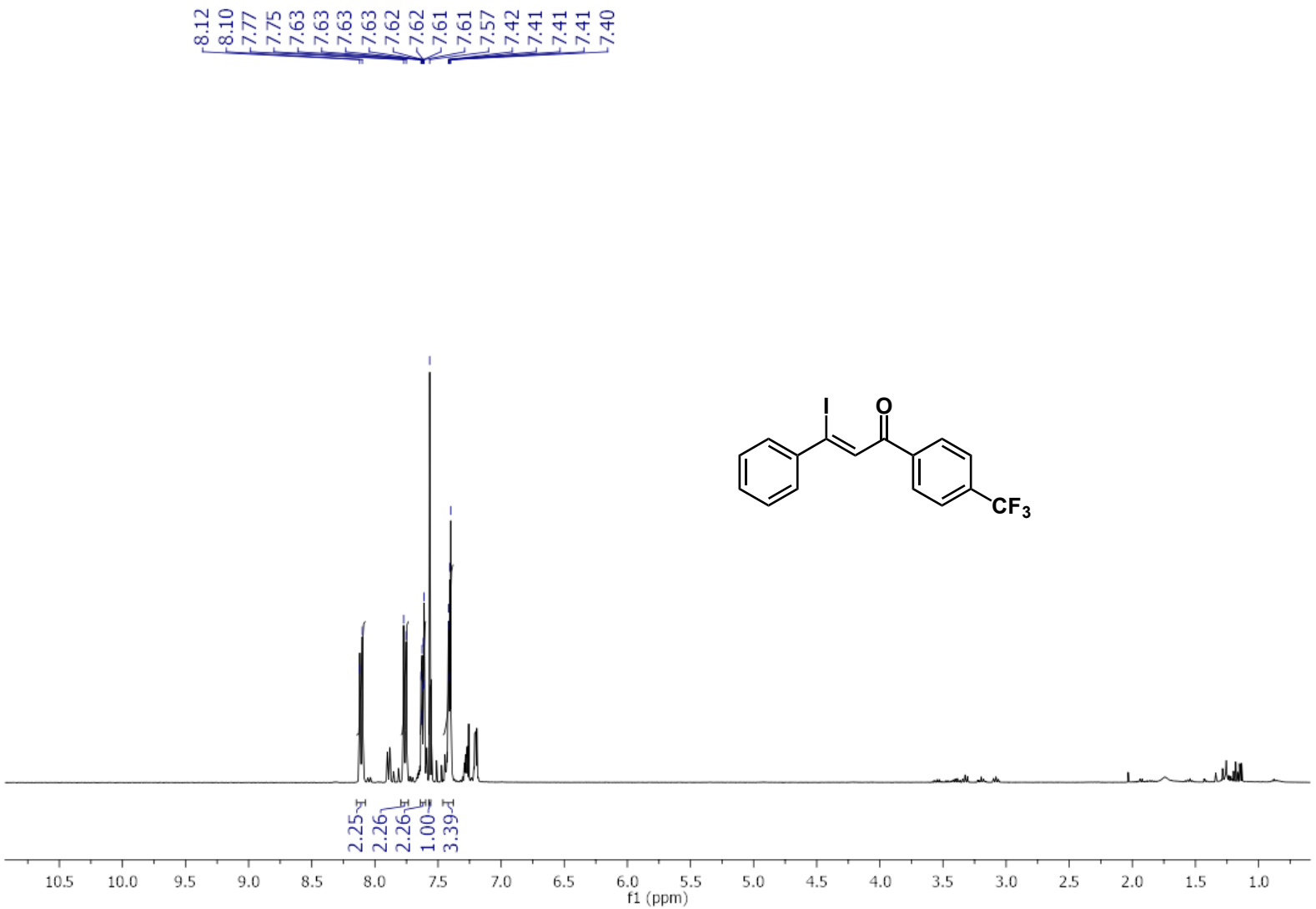
^{13}C NMR of compound **3i** (100 MHz, $CDCl_3$)



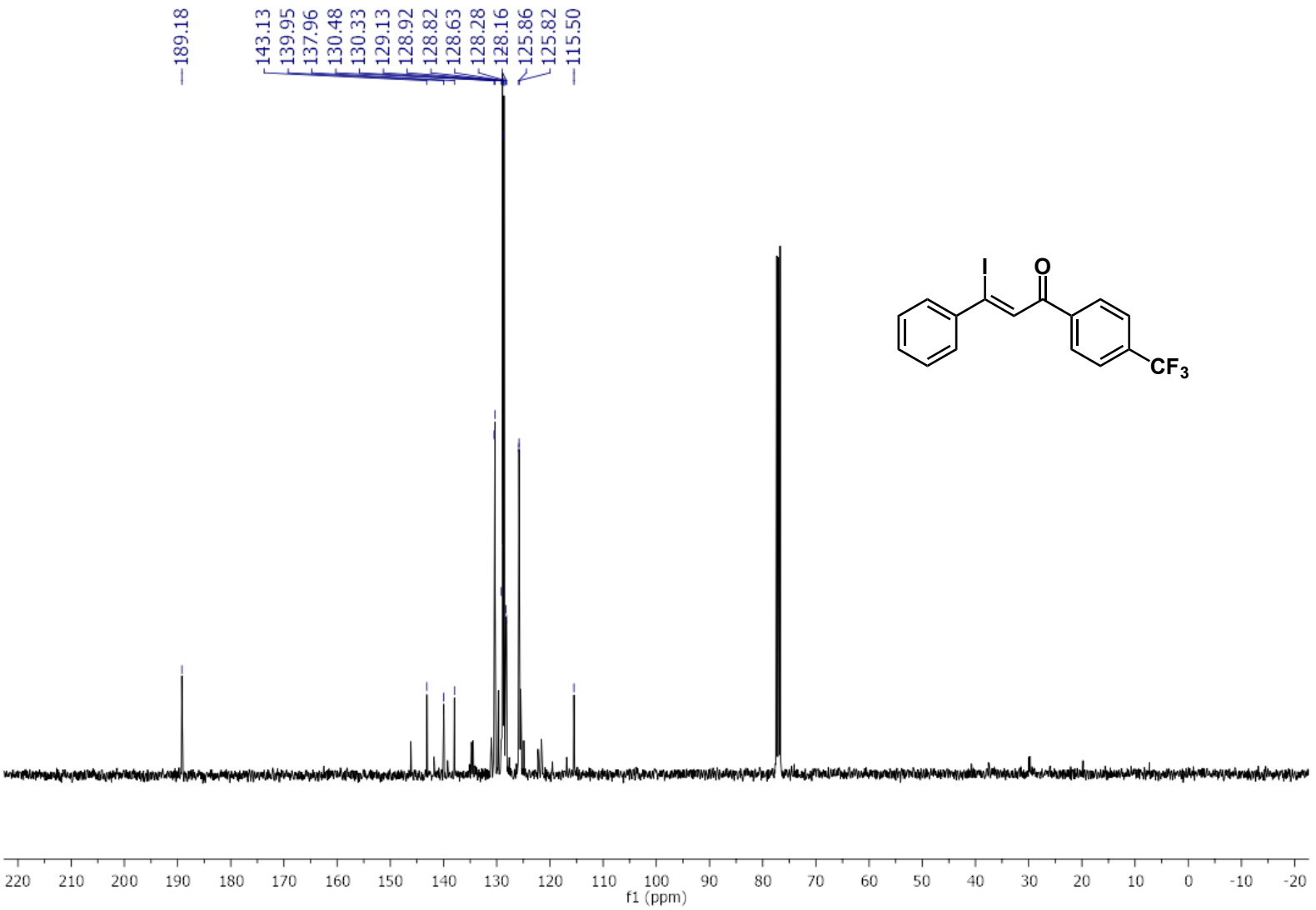
^{1}H NMR of compound **4a** (400 MHz, $CDCl_3$)



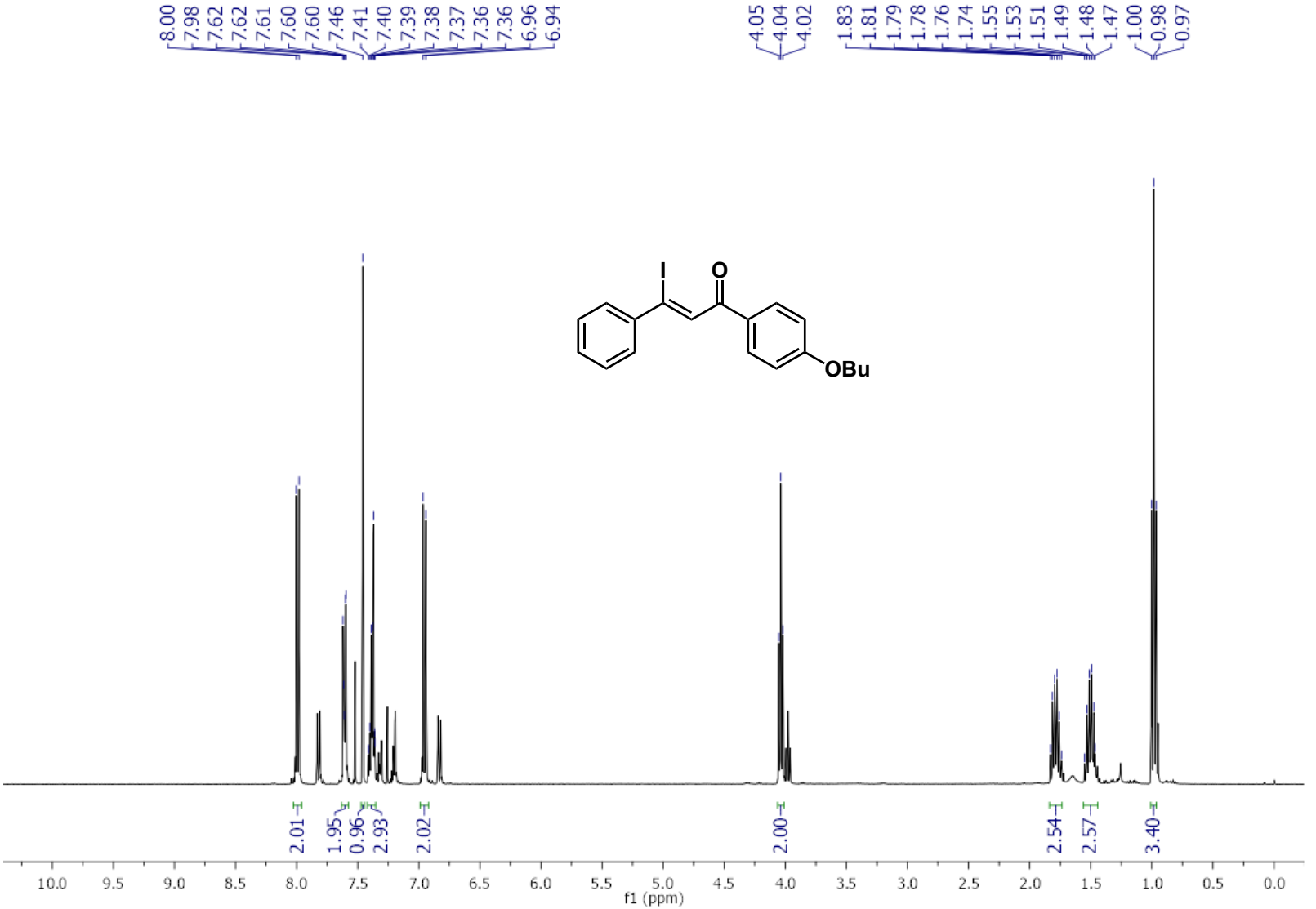
^{13}C NMR of compound **4a** (100 MHz, $CDCl_3$)



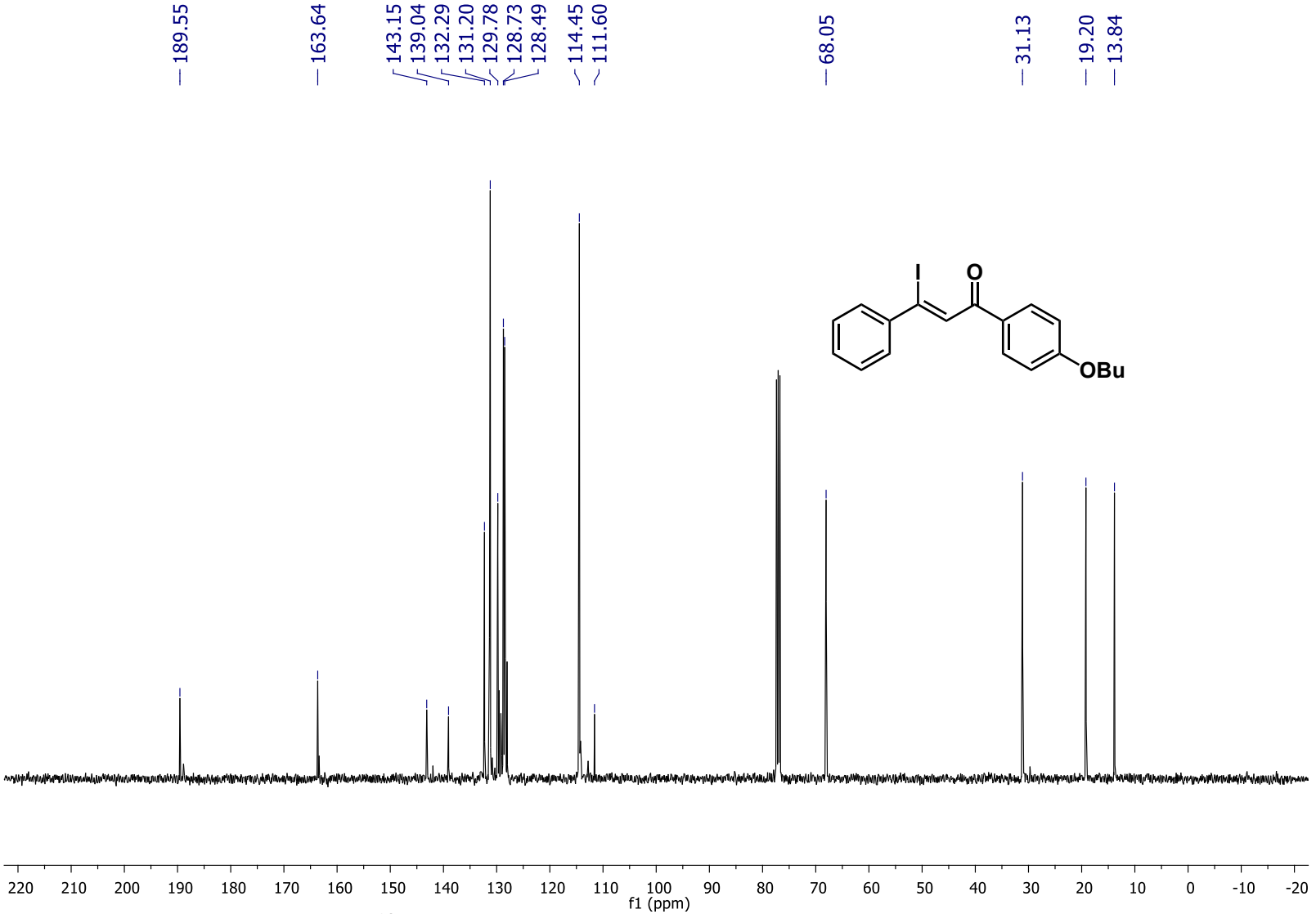
^{1}H NMR of compound **4b** (400 MHz, $CDCl_3$)



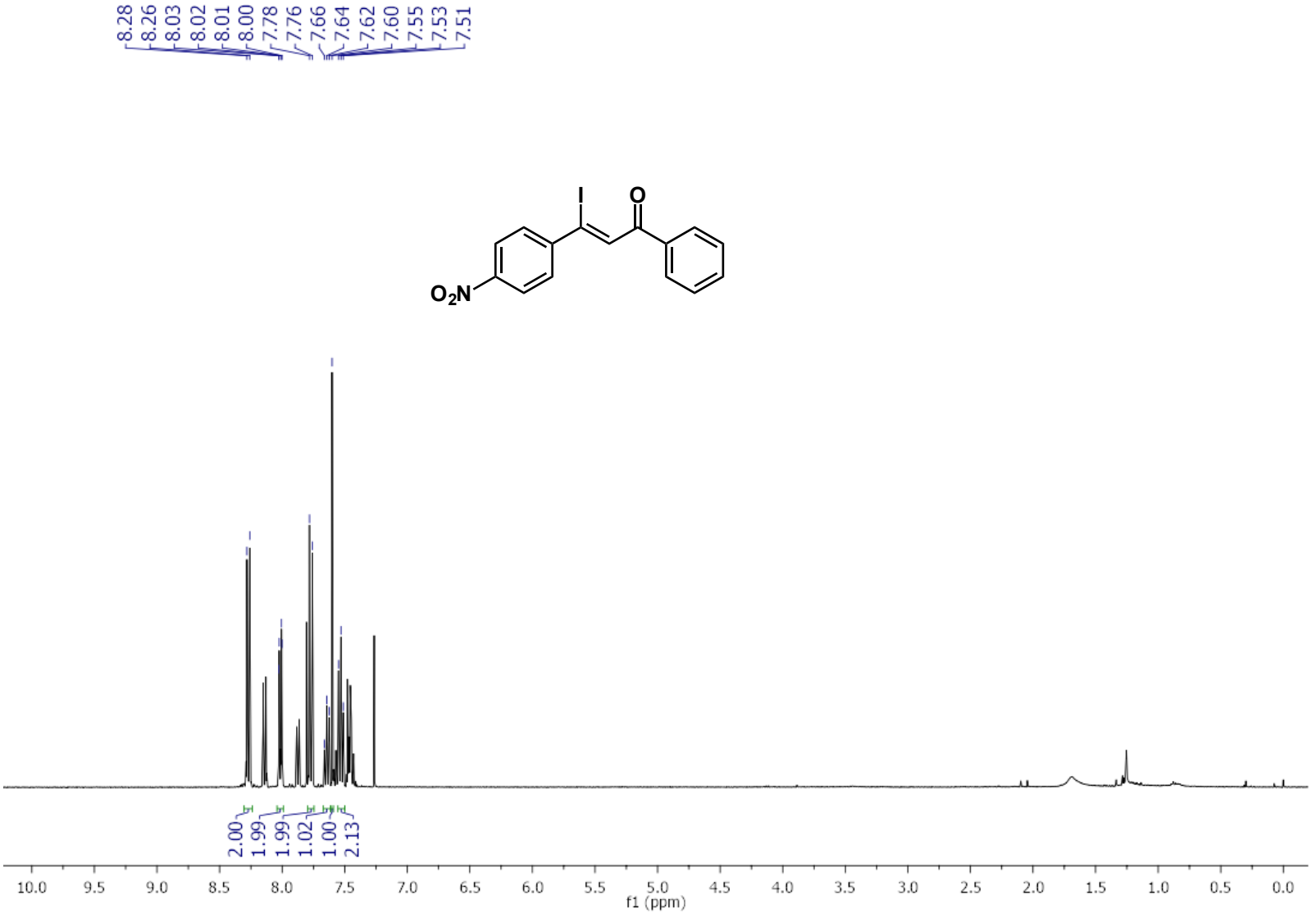
^{13}C NMR of compound **4b** (100 MHz, $CDCl_3$)



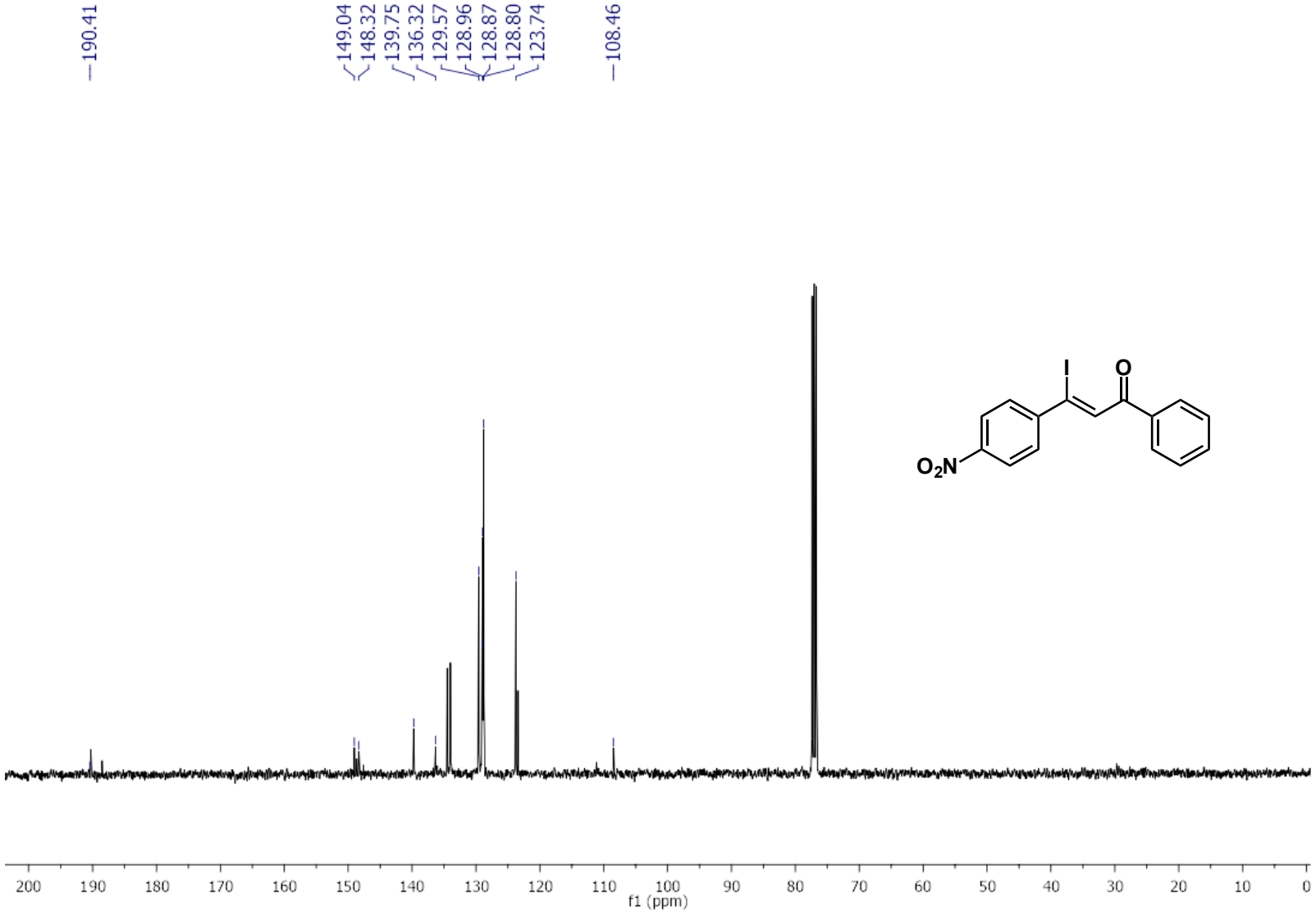
^{1}H NMR of compound **4c** (400 MHz, $CDCl_3$)



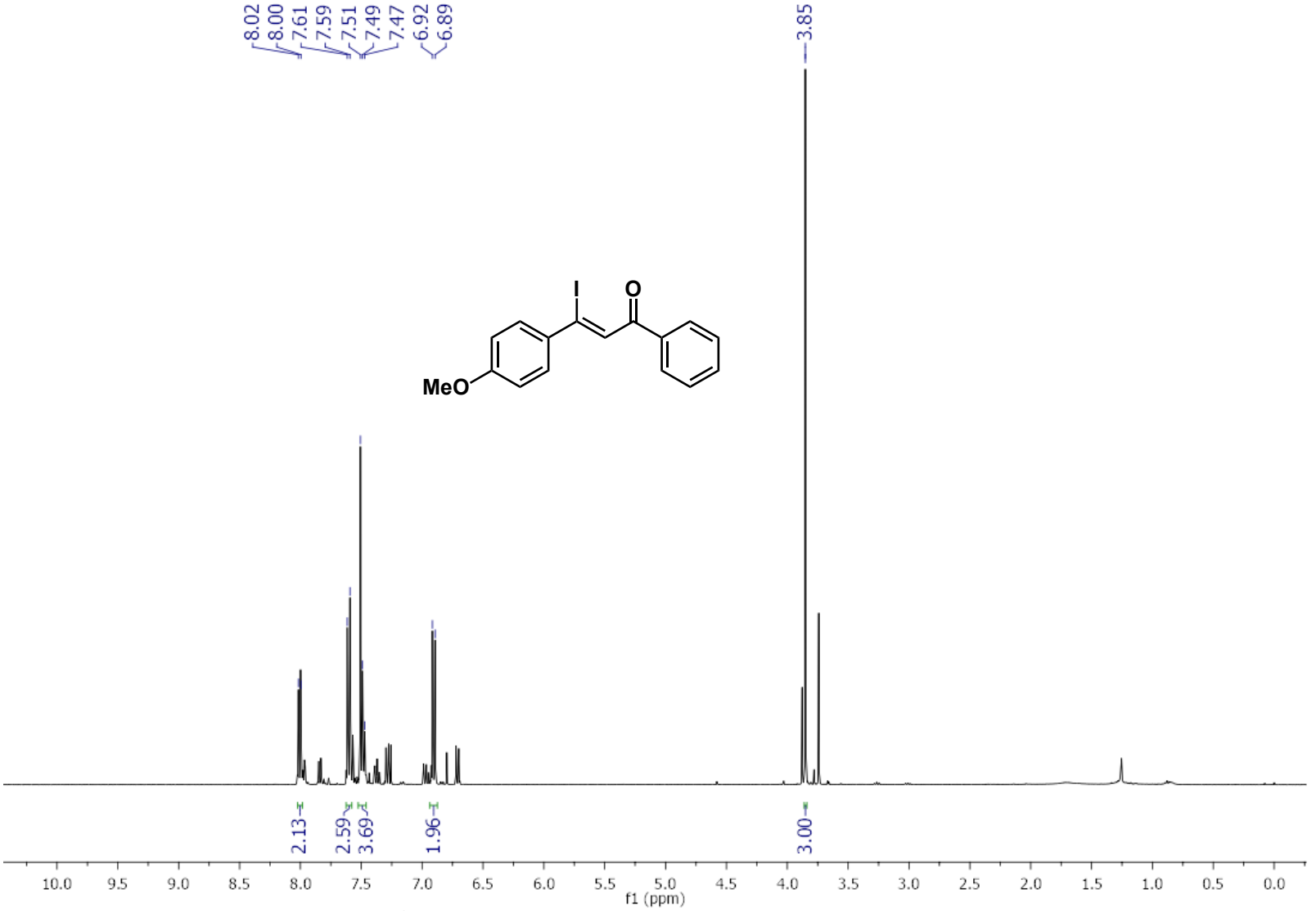
^{13}C NMR of compound **4c** (100 MHz, $CDCl_3$)



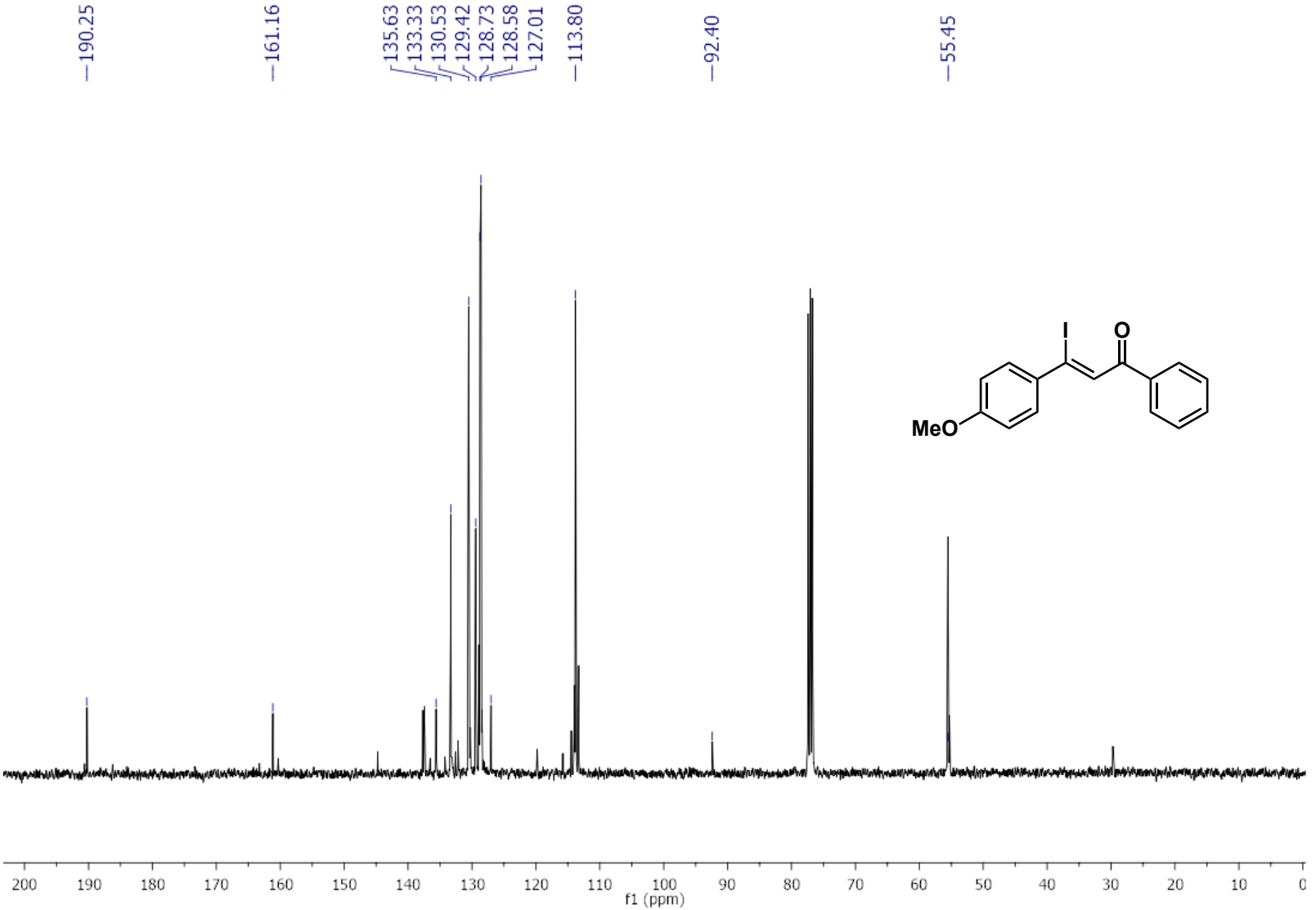
^{1}H NMR of compound **4d** (400 MHz, $CDCl_3$)



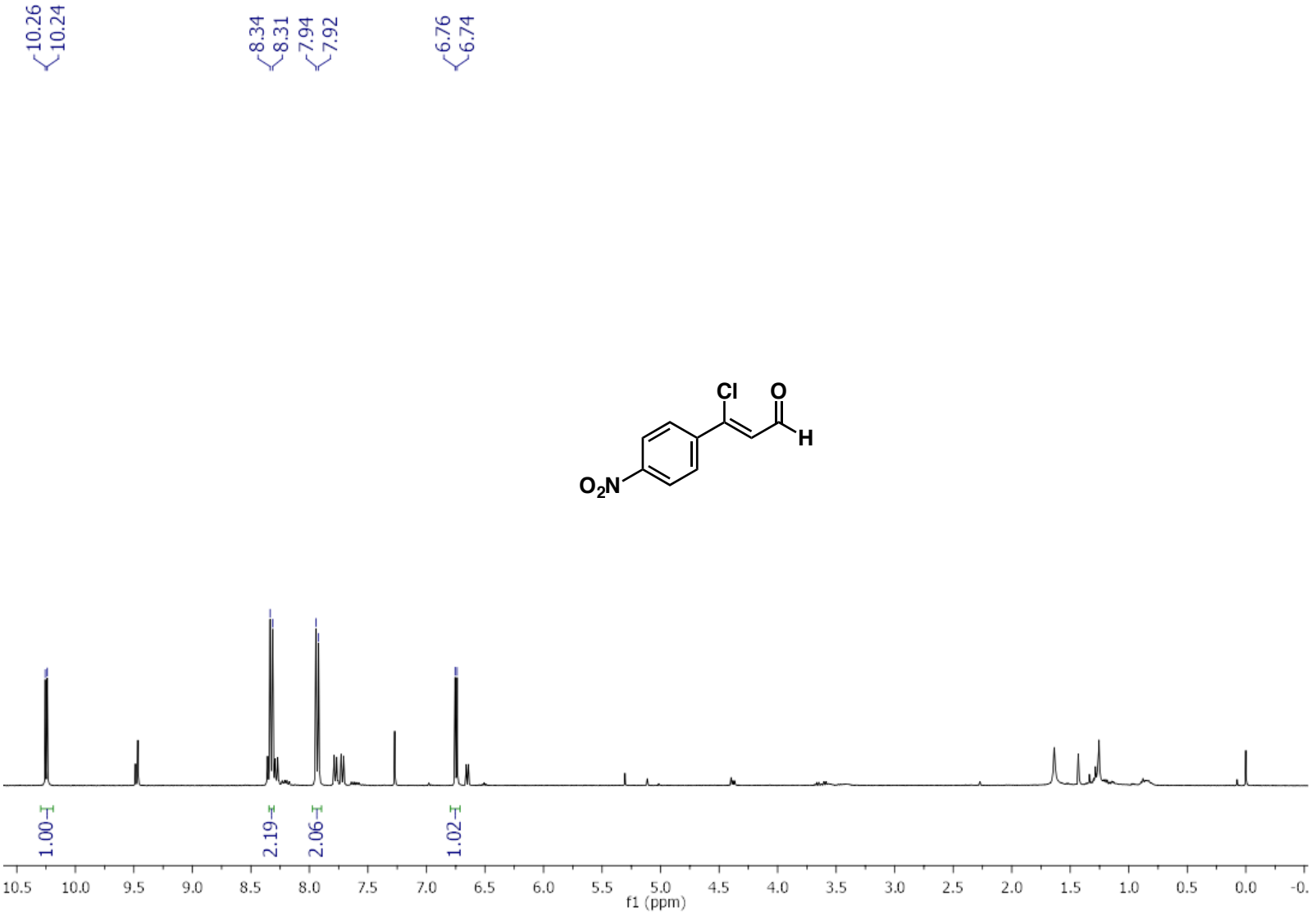
^{13}C NMR of compound **4d** (100 MHz, $CDCl_3$)



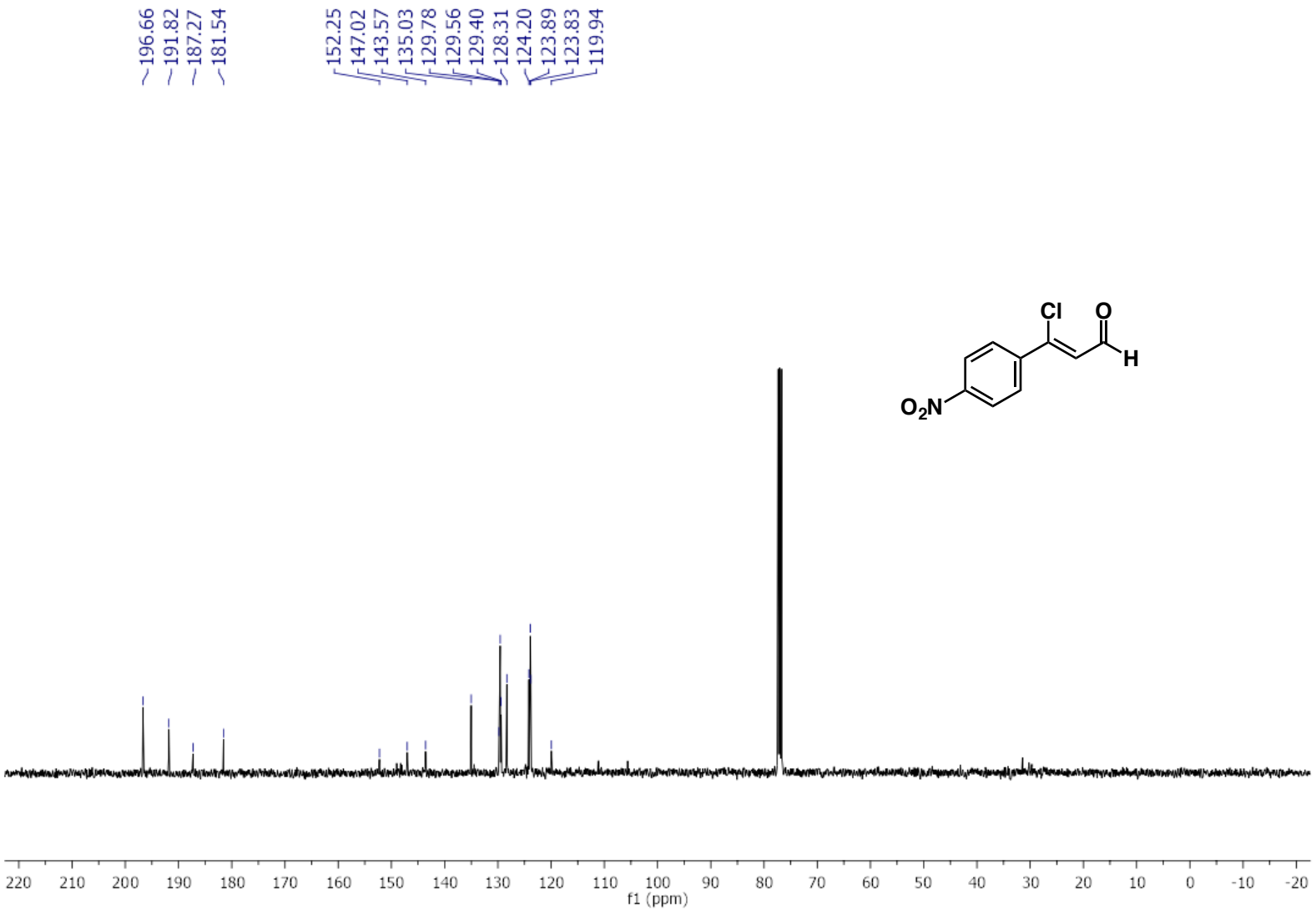
^{1}H NMR of compound **4e** (400 MHz, $CDCl_3$)



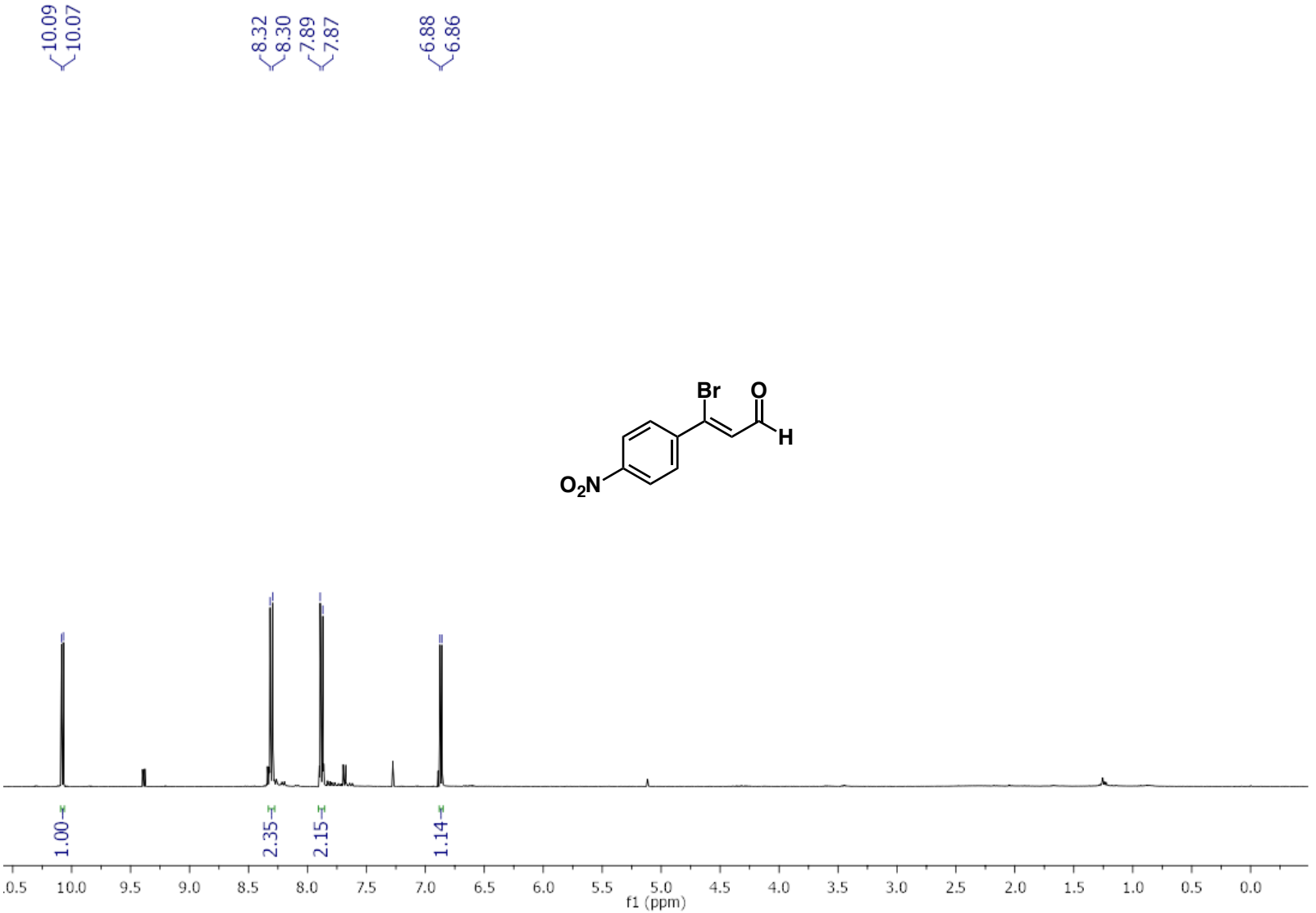
^{13}C NMR of compound **4e** (100 MHz, $CDCl_3$)



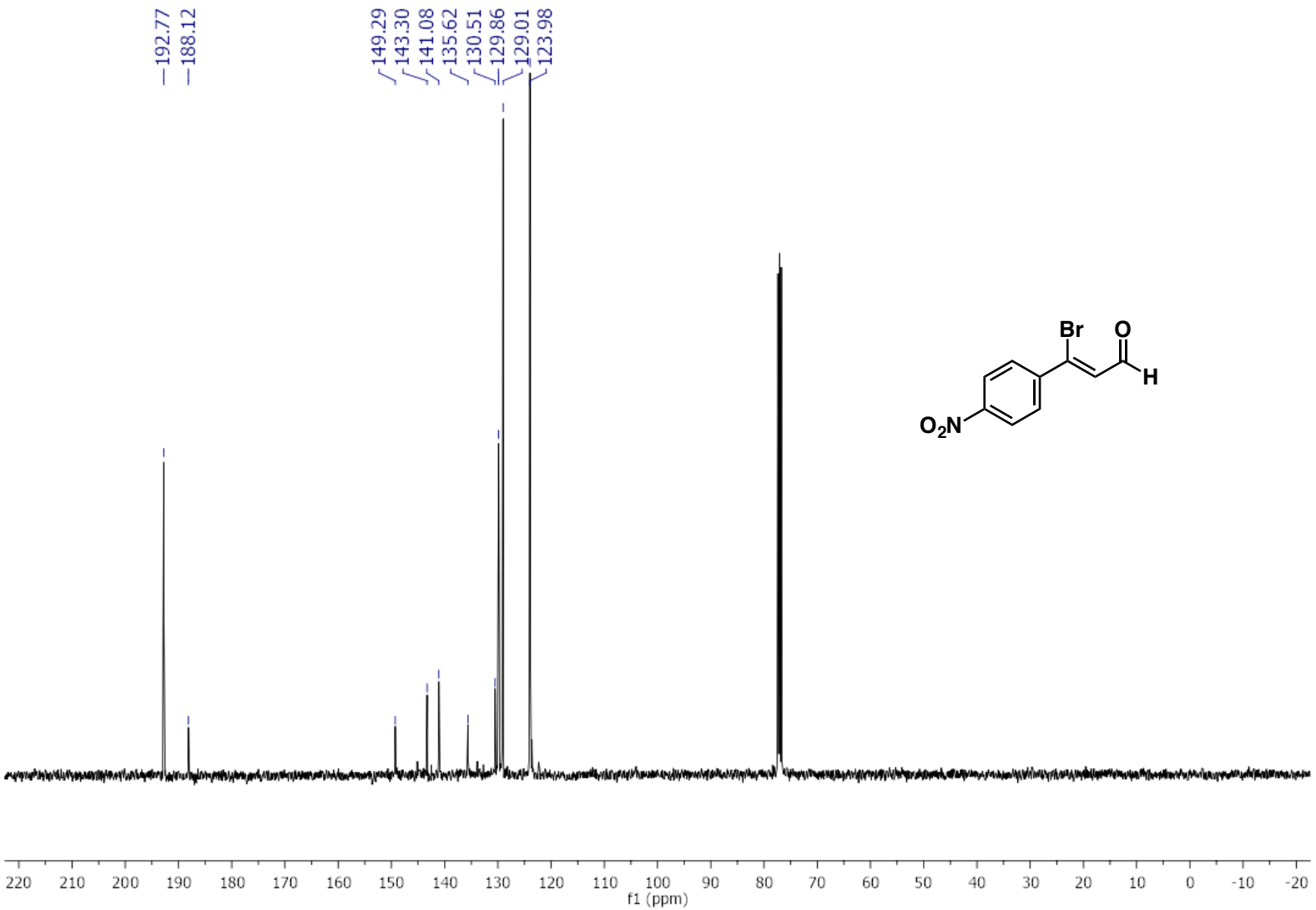
^{1}H NMR of compound **5a** (400 MHz, $CDCl_3$)



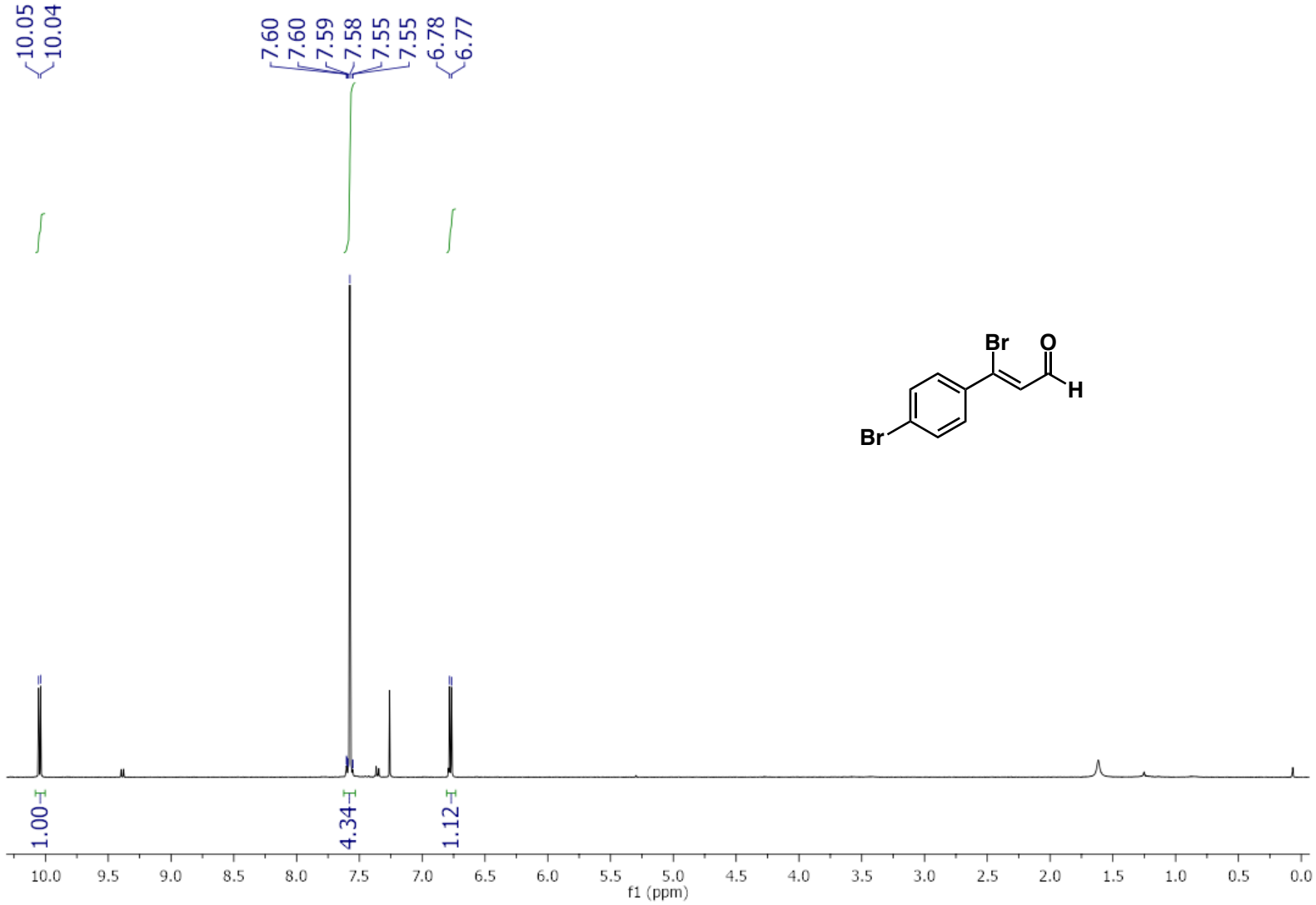
^{13}C NMR of compound **5a** (100 MHz, $CDCl_3$)



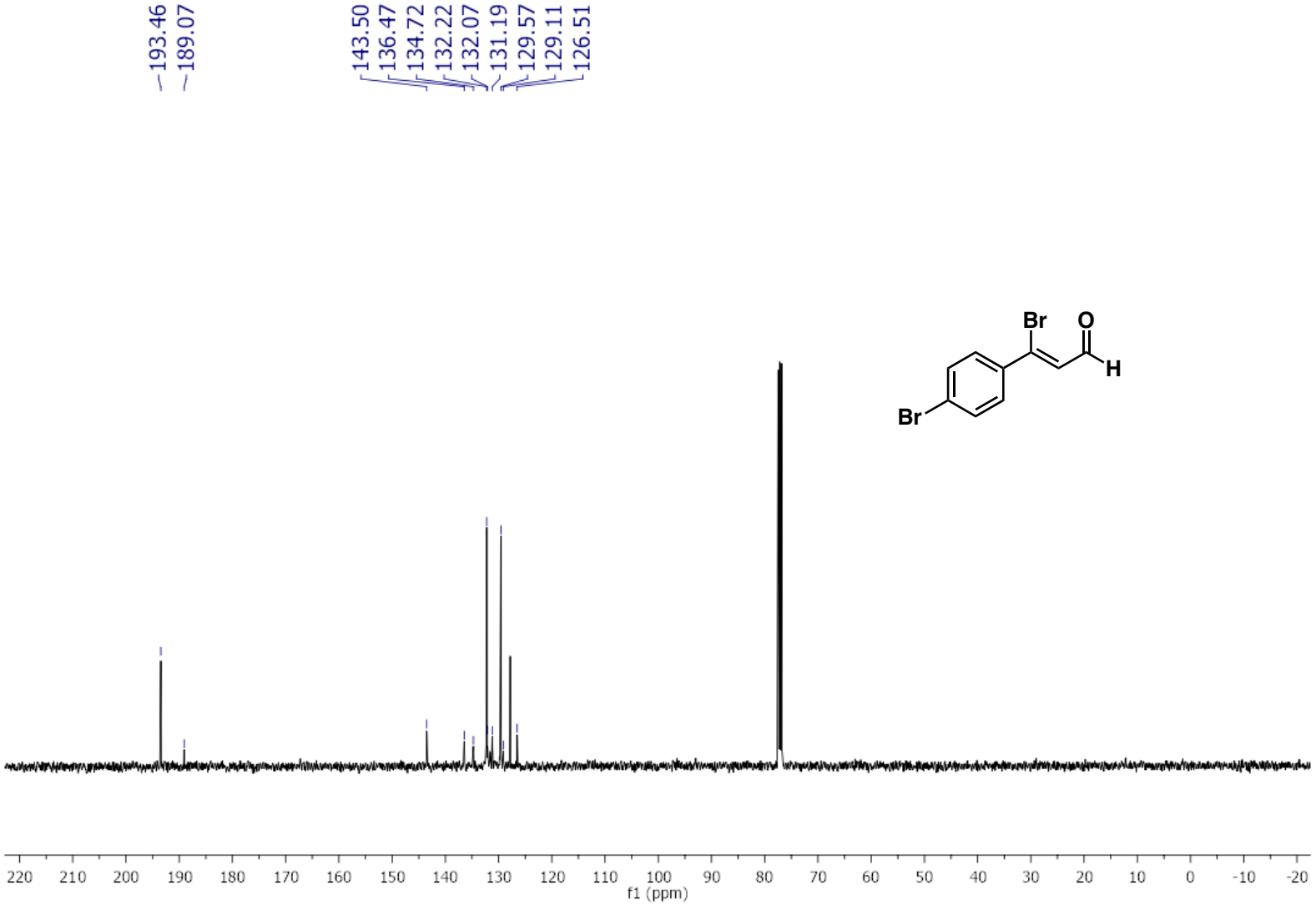
^{1}H NMR of compound **5b** (400 MHz, $CDCl_3$)



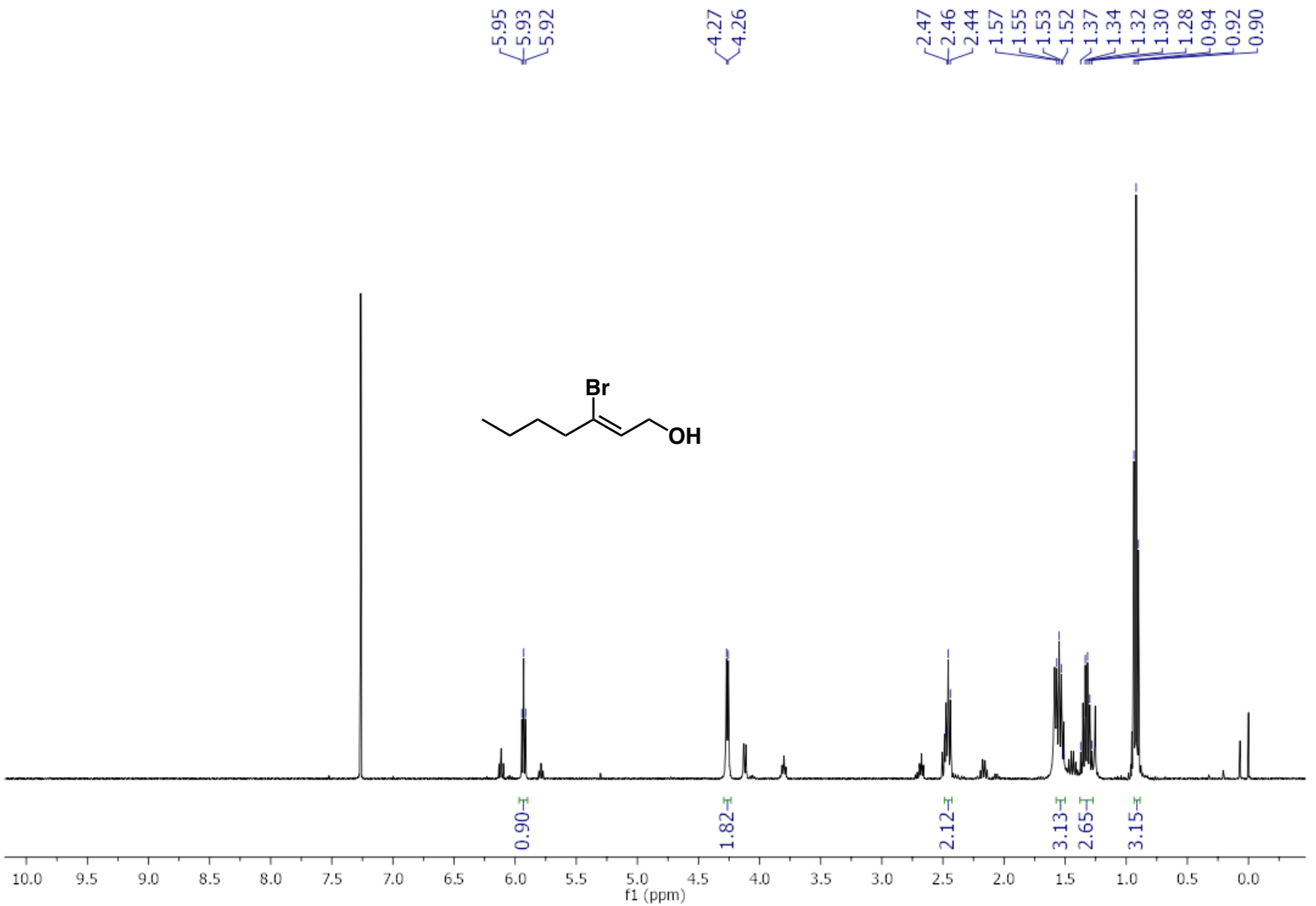
^{13}C NMR of compound **5b** (100 MHz, $CDCl_3$)



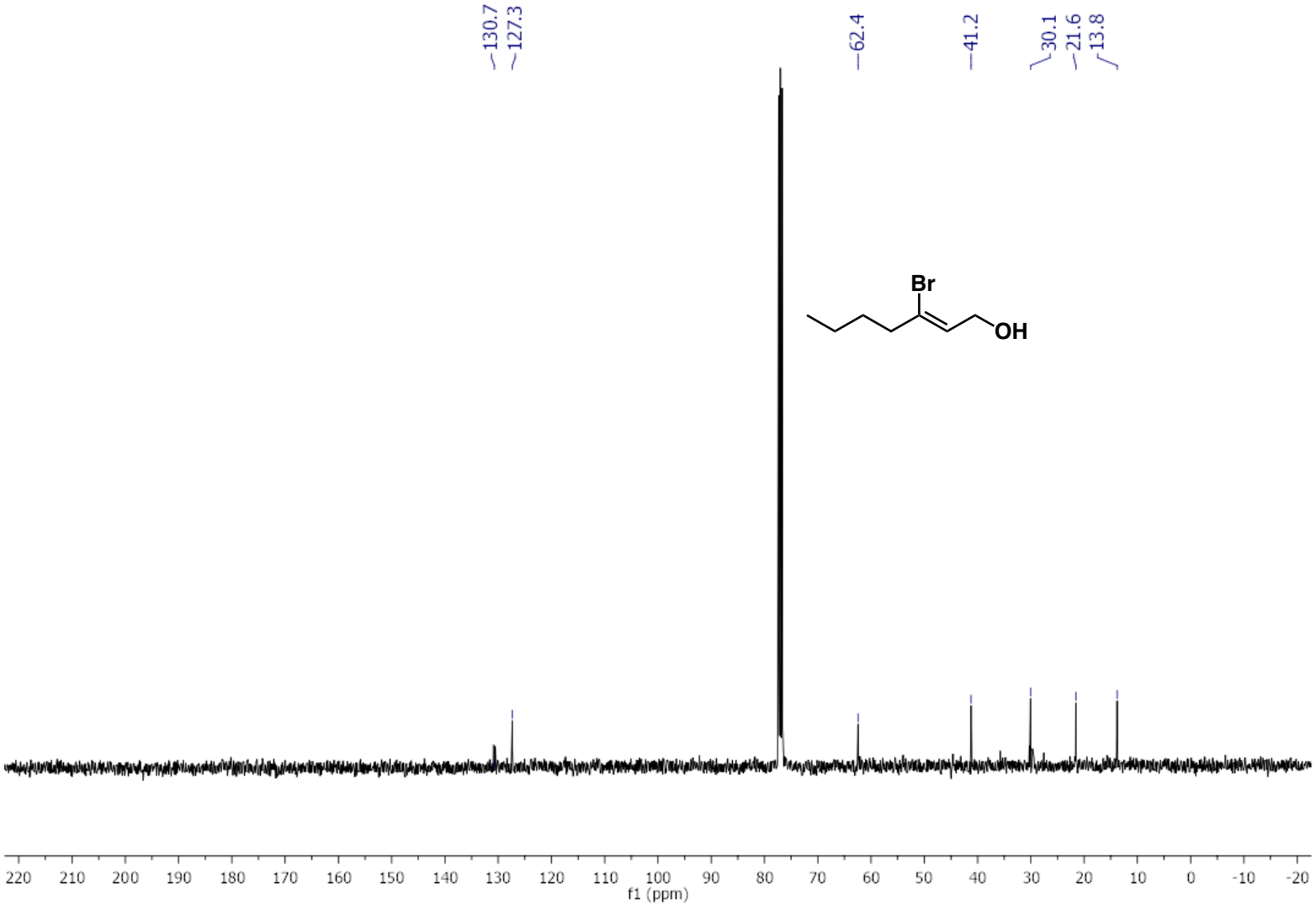
^{1}H NMR of compound **5c** (400 MHz, $CDCl_3$)



^{13}C NMR of compound **5c** (100 MHz, $CDCl_3$)



^{1}H NMR of compound **5d** (400 MHz, $CDCl_3$)



^{13}C NMR of compound **5d** (100 MHz, $CDCl_3$)