Ligand-Controlled Regiodivergent Hydroformylation of Ynamides: A Stereospecific and Regioselective Access to 2- and 3-Aminoacroleins

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Supporting information

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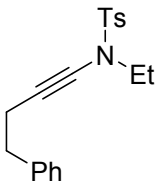
1. General information

All reagents, chemicals, ligands (except BiPhePhos) and dry solvents were purchased from commercial sources and used without purification. (Acetylacetonato)dicarbonylrhodium(I) was purchased from Sigma-Aldrich Co. BiPhePhos was prepared as reported previously by Buchwald *et al.*.[1] All experiments were performed under argon atmosphere except where otherwise noted. All hydroformylation reactions were performed in a high pressure reactor from Parr Instrument Company using gases supplied by Air Liquide. Reactions were monitored by TLC (Thin Layer silica gel Chromatography) using Merck silica gel 60 F_{254} on aluminium sheets. TLC plates were visualized under UV light and revealed with acidic *p*-anisaldehyde stain or $KMnO_4$ stain. Crude products were purified by flash column chromatography on Merck silica gel Si 60 (40-63 µm) or by using CombiFlashRf (Teledyne Isco). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker (500 MHz/125 MHz and 400 MHz/100 MHz) spectrometer. Conditions are specified for each spectrum (temperature 25 °C unless specified). Chemical shifts are reported in parts per million (ppm) relative to residual solvent and coupling constants (*J*) are reported in hertz (Hz). Signals are described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), ddt (doublet of doublet of triplets), br s (broad singlet), br d (broad doublet), br q (broad quadruplet) and br dd (broad doublet of doublets). Deutered solvents were purchased from Eurisotop®. HRMS were obtained on an Agilent Technologie 6520 Accurate-Mass Q.Tof LC/MC apparatus using electrospray ionization mode and time-of flight analyzer (ESI-TOF).

2. Experimental procedures

2.1. General procedures for the synthesis of ynamides 1a-n

Under argon in an oven-dried flask, carbamate or sullfonamide (1 equiv.), $CuSO_4.5H_2O$ (0.2 equiv.), 1,10-phenanthroline or (1*R*,2*R*)-*N*,*N*'-dimethyl-1,2-cyclohexanediamine (0.4 equiv.) and K_3PO_4 (2 equiv.) was added to a solution of alkynyl bromide (1.1 - 1.5 equiv.) in anhydrous toluene (0.8 to 1.0 M). The flask was backfilled 3 times with argon and stirred at 70 °C except **1f** (110 °C) for 16 h except for **1f**, **1g**, **1n** (72 h). The mixture was diluted with chloroform, filtered through celite pad, washed with methylene chloride and concentrated under vacuum. The crude product was purified by flash column chromatography using a heptane / ethyl acetate mixture as eluant.

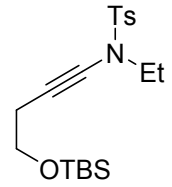


***N*-ethyl-4-methyl-*N*-(4-phenylbut-1-yn-1-yl)benzene-1-sulfonamide (1a)**

Synthesized following the general procedure **2.1** using *N*-ethyl-4-methylbenzene-1-sulfonamide (900 mg, 4.52 mmol), (4-bromobut-3-yn-1-yl)benzene, 1,10-phenanthroline as ligand, and heptane/EtOAc (85:15) as chromatography eluent. Entitled product **1a** was obtained in 85 % yield (1.25 g) as pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 1.11 (t, *J*=7.2 Hz, 3H), 2.44 (s, 3H), 2.58 (t, *J*=7.3 Hz, 2H), 2.81 (t, *J*=7.3 Hz, 2H), 3.30 (q, *J*=7.2 Hz, 2H), 7.18 – 7.22 (m, 3H), 7.28 – 7.30 (m, 4H), 7.70 (d, *J*=8.0 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 13.2, 20.8, 21.8, 35.4, 46.7, 69.7, 73.6, 126.4, 127.7, 128.5, 128.6, 129.7, 135.0, 140.7, 144.3; **HRMS (ESI)** : calculated for: $C_{19}H_{22}NO_2S$ $[M + H]^+$: 328,1366, found 328.1359.

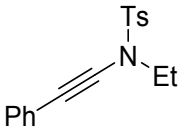
[1] Cuny, G. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2066.



***N*-{4-[(*tert*-butyldimethylsilyl)oxy]but-1-yn-1-yl}-*N*-ethyl-4-methylbenzene-1-sulfonamide (1b)**

Synthesized following the general procedure **2.1** using *N*-ethyl-4-methylbenzene-1-sulfonamide (199 mg, 1.00 mmol), [(4-bromobut-3-yn-1-yl)oxy](tert-butyl)dimethylsilane, 1,10-phenanthroline as ligand, and heptane/EtOAc (90:10) as chromatography eluent. Entitled product **1b** was obtained in 78 % yield (299 mg) as colorless oil.

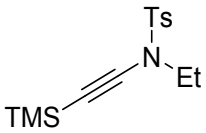
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 0.05 (s, 6H), 0.88 (s, 9H), 1.18 (t, *J*=7.2 Hz, 3H), 2.44 (s, 3H), 2.48 (t, *J*=7.2 Hz, 2H), 3.34 (q, *J*=7.2 Hz, 2H), 3.67 (t, *J*=7.2 Hz, 2H), 7.31 – 7.34 (m, 2H), 7.76 – 7.79 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = -5.3, 13.2, 18.3, 21.6, 22.9, 25.9, 46.5, 62.2, 67.4, 73.7, 127.6, 129.6, 134.8, 144.3; **HRMS (ESI)** : calculated for: $C_{19}H_{31}NO_3SSi$ [M + H]$^+$: 382,1867, found 382.1873.



***N*-ethyl-4-methyl-*N*-(2-phenylethynyl)benzene-1-sulfonamide (1c)[2]**

Synthesized following the general procedure **2.1** using *N*-ethyl-4-methylbenzene-1-sulfonamide (200 mg, 1.00 mmol), (2-bromoethynyl)benzene, (1*R*,2*R*)-*N*,*N*'-dimethyl-1,2-cyclohexanediamine as ligand, and heptane/EtOAc (90:10) as chromatography eluent. Entitled product **1c** was obtained in 90 % yield (269 mg) as colorless oil.

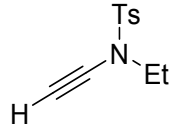
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 1.28 (t, *J*=7.2 Hz, 3H), 2.45 (s, 3H), 3.49 (q, *J*=7.2 Hz, 2H), 7.27 – 7.31 (m, 3H), 7.35 – 7.38 (m, 4H), 7.83 – 7.85 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 13.4, 21.8, 46.9, 70.9, 82.2, 123.0, 127.8, 127.9, 128.4, 129.9, 131.5, 134.8, 144.7.



***N*-ethyl-4-methyl-*N*-[2-(trimethylsilyl)ethynyl]benzene-1-sulfonamide (1d)**

Synthesized following the general procedure **2.1** using *N*-ethyl-4-methylbenzene-1-sulfonamide (400 mg, 2.01 mmol), (2-bromoethynyl)trimethylsilane, (1*R*,*2R*)-*N*,*N*'-dimethyl-1,2-cyclohexanediamine as ligand, and heptane/EtOAc (90:10) as chromatography eluent. Entitled product **1d** was obtained in 29 % yield (174 mg) as colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 0.16 (s, 9H), 1.20 (t, *J*=7.2 Hz, 3H), 2.45 (s, 3H), 3.38 (q, *J*=7.2 Hz, 2H), 7.32 – 7.35 (m, 2H), 7.78 – 7.80 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 0.3, 13.2, 21.8, 46.6, 73.5, 94.9, 127.9, 129.7, 134.9, 144.7 ; **HRMS (ESI)** : calculated for: $C_{14}H_{22}NO_2SSi$ [M + H]$^+$: 296,1135, found 296.1136.



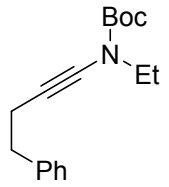
***N*-ethyl-*N*-ethynyl-4-methylbenzene-1-sulfonamide (1e)[2]**

Synthesized following the general procedure **2.1** using *N*-ethyl-4-methylbenzene-1-sulfonamide (400 mg, 2.01 mmol), (2-bromoethynyl)tris(propan-2-yl)silane and 1,10-phenanthroline as ligand. Entitled product **1e** was

[2] Tu, Y.; Zheng, X.; Wang, H.; Zhao, J. *Org. Lett.* **2018**, *20*, 280.

obtained after a deprotection procedure using TBAF (1.0 M in THF) at -5 °C and a purification by flash column chromatography using heptane/EtOAc (90:10) as eluent, to give a yellow oil in 70 % yield (138 mg).

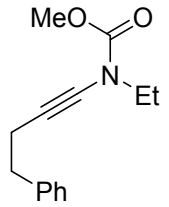
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 1.20 (t, *J*=7.2 Hz, 3H), 2.44 (s, 3H), 2.73 (s, 1H), 3.38 (q, *J*=7.2 Hz, 2H), 7.32 – 7.36 (m, 2H), 7.78 – 7.81 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 13.1, 21.7, 46.5, 59.3, 75.8, 127.7, 129.9, 134.9, 144.8.



***tert*-butyl *N*-ethyl-*N*-(4-phenylbut-1-yn-1-yl)carbamate (1f)**

Synthesized following the general procedure **2.1** using *tert*-butyl *N*-ethylcarbamate (127 mg, 0.88 mmol), (4-bromobut-3-yn-1-yl)benzene, 1,10-phenanthroline as ligand, reaction time 72 h, heating 110 °C, and heptane/EtOAc (98:2) as chromatography eluent. Entitled product **1f** was obtained in 29 % yield (70 mg) as colorless oil.

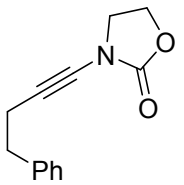
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 1.16 (t, *J*=7.2 Hz, 3H), 1.48 (s, 9H), 2.60 (t, *J*=7.5 Hz, 2H), 2.84 (t, *J*=7.5 Hz, 2H), 3.39 (q, *J*=7.2 Hz, 2H), 7.18 – 7.31 (m, 6H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ = 13.0, 20.8, 26.9, 28.1, 35.3, 35.6, 44.3, 68.5, 74.9, 81.8, 82.6, 125.8, 126.2, 128.3, 128.5, 141.0, 142.0, 153.2, 154.5, 175.5; **HRMS (ESI):** calculated for: $C_{17}H_{23}NNaO_2$ $[M+Na]^+$: 296,1621, found 296.1622.



methyl *N*-ethyl-*N*-(4-phenylbut-1-yn-1-yl)carbamate (1g)

Synthesized following the general procedure **2.1** using methyl *N*-ethylcarbamate (206 mg, 2.00 mmol), (4-bromobut-3-yn-1-yl)benzene, 1,10-phenanthroline as ligand, reaction time 72 h, and heptane/EtOAc (95:5 to 90:10) as chromatography eluent. Entitled product **1h** was obtained in 46 % yield (213 mg) as colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 1.16 (t, *J*=7.2 Hz, 3H), 2.61 (td, *J*=7.4, 0.6 Hz, 2H), 2.85 (t, *J*=7.4 Hz, 2H), 3.45 (q, *J*=7.2 Hz, 2H), 3.78 (s, 3H), 7.19 – 7.31 (m, 6H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ = 12.9, 20.7, 35.5, 45.1, 53.7, 69.2, 74.2, 126.2, 128.3, 128.5, 140.8, 156.0**; HRMS (ESI):** calculated for: $C_{14}H_{18}NO_2$ $[M + H]^+$: 232,1332, found 232.1327.

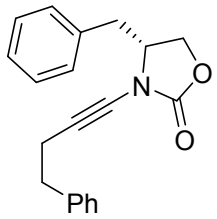


3-(4-phenylbut-1-yn-1-yl)-1,3-oxazolidin-2-one (1h)[3]

Synthesized following the general procedure **2.1** using 2-oxazolidone (131 mg, 1.50 mmol), (4-bromobut-3-yn-1-yl)benzene, (1*R*,2*R*)-*N*,*N*'-dimethyl-1,2-cyclohexanediamine as ligand, and heptane/EtOAc (70:30) as chromatography eluent. Entitled product **1h** was obtained in 78 % yield (253 mg) as colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.58 – 2.62 (m, 2H), 2.85 (t, *J*=7.6 Hz, 2H), 3.81 – 3.85 (m, 2H), 4.38 – 4.42 (m, 2H), 7.21 – 7.23 (m, 3H), 7.28 – 7.32 (m, 2H).

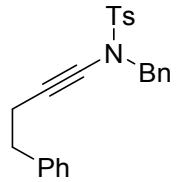
[3] Jouvin, K.; Couty, F.; Evano, G. *Org. Lett.* **2010**, *12*, 3272.



(4*R*)-4-benzyl-3-(4-phenylbut-1-yn-1-yl)-1,3-oxazolidin-2-one (1i)[4]

Synthesized following the general procedure **2.1** using (*R*)-4-benzyl-2-oxazolidinone (354 mg, 2.00 mmol), (4-bromobut-3-yn-1-yl)benzene, (1*R*,2*R*)-*N*,*N*'-dimethyl-1,2-cyclohexanediamine as ligand, and heptane/EtOAc (80:20) as chromatography eluent. Entitled product **1i** was obtained in 73 % yield (443 mg) as pale yellow oil.

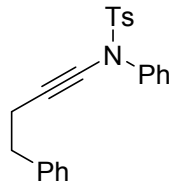
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.68 (t, *J*=7.4 Hz, 2H), 2.80 (dd, *J*=13.9, 8.3 Hz, 1H), 2.88 (t, *J*=7.4 Hz, 2H), 3.07 (dd, *J*=13.9, 3.9 Hz, 1H), 4.07 (dd, *J*=8.4, 5.9 Hz, 1H), 4.10 – 4.17 (m, 1H), 4.27 (t, *J*=8.1 Hz, 1H), 7.13 – 7.15 (m, 2H), 7.18 – 7.22 (m, 1H), 7.24 – 7.26 (m, 2H), 7.28 – 7.35 (m, 5H); $[\propto]_D^{18}$ = -116.0 (*c* 2.00, DMF).



***N*-benzyl-4-methyl-*N*-(4-phenylbut-1-yn-1-yl)benzenesulfonamide (1j)**[5]

Synthesized following the general procedure **2.1** using *N*-benzyl-4-methylbenzene-1-sulfonamide (200 mg, 0.77 mmol), (4-bromobut-3-yn-1-yl)benzene, (1*R*,2*R*)-*N*,*N*'-dimethyl-1,2-cyclohexanediamine as ligand, and heptane/EtOAc (85:15) as chromatography eluent. Entitled product **1i** was obtained in 86 % yield (256 mg) as colorless oil.

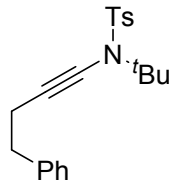
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 2.44 (s, 3H), 2.48 (t, *J*=7.3 Hz, 2H), 2.69 (t, *J*=7.3 Hz, 2H), 4.40 (s, 2H), 7.08–7.10 (m, 1.7 Hz, 2H), 7.18 – 7.21 (m, 3H), 7.23 – 7.26 (m, 3H), 7.27 – 7.29 (m, 4H), 7.64 – 7.66 (m, 2H).



4-methyl-*N*-phenyl-*N*-(4-phenylbut-1-yn-1-yl)benzenesulfonamide (1k)[6]

Synthesized following the general procedure **2.1** using 4-methyl-*N*-phenylbenzene-1-sulfonamide (150 mg, 0.61 mmol), (4-bromobut-3-yn-1-yl)benzene, (1*R*,2*R*)-*N*,*N*'-dimethyl-1,2-cyclohexanediamine as ligand, and heptane/EtOAc (90:10) as chromatography eluent. Entitled product **1k** was obtained in 90 % yield (206 mg) as colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.43 (s, 3H), 2.61 (t, *J*=7.3 Hz, 2H), 2.82 (t, *J*=7.3 Hz, 2H), 7.13 – 7.17 (m, 4H), 7.21 – 7.27 (m, 8H), 7.45 – 7.48 (m, 2H).



***N*-(tert-butyl)-4-methyl-*N*-(4-phenylbut-1-yn-1-yl)benzenesulfonamide (1l)**[5]

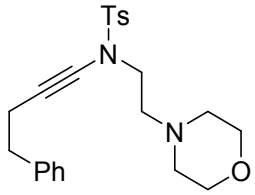
[4] Takimoto, M.; Gholap, S. S.; Hou, Z. *Chem. Eur. J.*, **2015**, *21*, 15218.

[5] Harkat, H.; Borghèse, S.; De Nigris, M.; Kiselev, S.; Bénéteau, V.; Pale, P. *Adv. Synth. Catal.* **2014**, *356*, 3842.

[6] Xu, W.; Wang, G.; Sun, N.; Liu, Y. *Org. Lett.* **2017**, *19*, 3307.

Synthesized following the general procedure **2.1** using 4-methyl-*N*-phenylbenzene-1-sulfonamide (200 mg, 0.88 mmol), (4-bromobut-3-yn-1-yl)benzene, (1*R*,2*R*)-*N*,*N*'-dimethyl-1,2-cyclohexanediamine as ligand, and heptane/EtOAc (90:10) as chromatography eluent. Entitled product **1l** was obtained in 74 % yield (232 mg) as colorless oil.

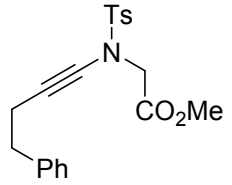
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 1.34 (m, 9H), 2.42 (s, 3H), 2.61 (t, *J*=7.3 Hz, 2H), 2.81 (t, *J*=7.4 Hz, 2H), 7.18 – 7.21 (m, 3H), 7.25 – 7.30 (m, 4H), 7.73 – 7.76 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 21.7, 29.3, 30.0, 35.4, 63.4, 71.2, 74.0, 126.3, 127.7, 128.5, 128.6, 129.4, 138.0, 140.9, 143.8.



4-methyl-*N*-(2-morpholinoethyl)-*N*-(4-phenylbut-1-yn-1-yl)benzenesulfonamide (1m)

Synthesized following the general procedure **2.1** using 4-methyl-*N*-[2-(morpholin-4-yl)ethyl]benzene-1-sulfonamide (142 mg, 0.50 mmol), (4-bromobut-3-yn-1-yl)benzene, (1*R*,2*R*)-*N*,*N*'-dimethyl-1,2-cyclohexanediamine as ligand, and heptane/EtOAc (40:60) as chromatography eluent. Entitled product **1m** was obtained in 87 % yield (180 mg) as colorless oil.

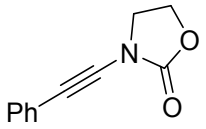
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.38 – 2.40 (m, 4H), 2.44 (s, 3H), 2.49 (t, *J*=6.9 Hz, 2H), 2.58 (t, *J*=7.2 Hz, 2H), 2.79 (t, *J*=7.3 Hz, 2H), 3.36 (t, *J*=6.9 Hz, 2H), 3.62 – 3.64 (m, 4H), 7.16 – 7.23 (m, 3H), 7.25 – 7.30 (m, 4H), 7.71 – 7.74 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 20.6, 21.8, 35.3, 48.7, 53.7, 56.1, 67.0, 69.6, 74.0, 126.4, 127.8, 128.5, 128.6, 129.7, 135.0, 140.7, 144.4.**; HRMS (ESI):** calculated for: $C_{23}H_{29}N_2O_3S$ $[M + H]^+$: 413,1893, found 413.1897.



methyl *N*-(4-phenylbut-1-yn-1-yl)-N-tosylglycinate (1n)

Synthesized following the general procedure **2.1** using methyl 2-[(4-methylphenyl)sulfonamido]acetate (50 mg, mmol), (4-bromobut-3-yn-1-yl)benzene, (1*R*,2*R*)-*N*,*N*'-dimethyl-1,2-cyclohexanediamine as ligand, and heptane/EtOAc (80:20) as chromatography eluent. Entitled product **1n** was obtained in 50 % yield (38 mg) as colorless oil.

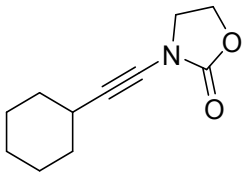
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.43 (s, 3H), 2.52 (t, *J*=7.3 Hz, 2H), 2.76 (t, *J*=7.4 Hz, 2H), 3.65 (s, 3H), 4.14 (s, 2H), 7.15 – 7.21 (m, 3H), 7.24 – 7.29 (m, 4H), 7.69 – 7.71 (m, 2H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 20.7, 21.8, 35.2, 52.4, 52.5, 69.5, 73.8, 76.8, 126.3, 128.1, 128.4, 128.6, 129.6, 134.7, 140.6, 144.7, 167.8**; HRMS (ESI):** calculated for $C_{20}H_{22}NO_4S$ $[M + H]^+$: 372,1264, found 372.1260.



3-(phenylethynyl)oxazolidin-2-one (1o)[7]

Synthesized following the general procedure **2.1** using oxazolidinone (1.70 g, 19.52 mmol), (bromoethynyl)benzene, 1,10-phenanthroline as ligand, and heptane/EtOAc (80:20) as chromatography eluent. Entitled product **1o** was obtained in 70 % yield (2.79 g) as white solid.

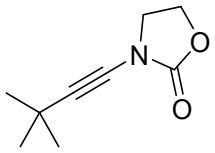
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.46-7.42 (m, 2H), 7.32-7.29 (m, 3H), 4.51-4.47 (m, 2H), 4.03-3.99 (m, 2H).



3-(cyclohexylethynyl)oxazolidin-2-one (1p)[8]

Synthesized following the general procedure **2.1** using oxazolidinone (1.16 g, 13.33 mmol), (bromoethynyl)cyclohexane, 1,10-phenanthroline as ligand and heptane/EtOAc (80:20) as chromatography eluent. Entitled product **1p** was obtained in 73 % yield (1.88 g) as colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = δ 4.35 (dd, *J* = 8.8 Hz and 8.0 Hz, 2H), 3.80 (dd, *J* = 8.8 Hz and 8.0 Hz, 2H), 2.45-2.37 (m, 1H), 1.76-1.71 (m, 2H), 1.66-1.57 (m, 2H), 1.49-1.12 (m, 6H).



3-(3,3-dimethylbut-1-yn-1-yl)oxazolidin-2-one (1q)[8]

Synthesized following an adapted version of Evano's synthesis of ynamides starting from dibromo-olefines.[9]

In a pressure tube, oxazolidinone (749 mg, 8.6 mmol), 1,1-dibromo-3,3-dimethylbut-1-ene (3.12 g, 12.9 mmol), Cs_2CO_3 (11.29 g, 34.4 mmol), and copper(I) iodide (204 mg, 1.075 mmol). The tube was then evacuated under high vacuum and backfilled with argon. Dry and degassed DMF (16 mL) and *N*,*N*'- dimethylethylenediamine (161 µL, 1.6 mmol) were added, and the tube was then sealed. The suspension was heated at 70°C for 48h. The resulting dark suspension was cooled down and the crude reaction mixture was diluted with water, extracted with diethyl ether and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by flash chromatography over silica gel using heptane/EtOAc (80:20) as eluent. Entitled product **1q** was obtained in 33 % yield (560 mg) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 4.37 (dd, *J* = 8.8 Hz and 7.2 Hz, 2H), 3.83 (dd, *J* = 8.8 and 7.2 Hz, 2H), 1.22 (s, 9H).

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[7] Hamada, T.; Ye, X.; Stahl, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 833.

[8] Jouvin, K., ; Couty, F. ; Evano, E. *Org. Lett.* **2010**, *121*, 43272.

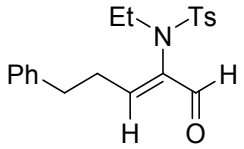
[9] Jouvin, K. ; Coste, A. ; Bayle, A. ; Legrand, F. ; Karthikeyan, G.; Tadiparthi, K.; Evano, G. *Organomet.* **2012**, *31,* 7933.

2.2. General procedures for the hydroformylation reaction of ynamides

BiPhePhos: In a dry Schlenk glassware under argon were introduced $Rh(CO)_2(acac)$ (2 mol%) and anhydrous degassed Toluene (1 mL). Biphephos (8 mol%) was added and CO evolution was observed. Subsequent addition of ynamide was performed. The mixture was transferred via a syringe in a dry stainless autoclave under argon. The glassware was rinsed with anhydrous degassed toluene (3 × 3 mL) to reach a final concentration of 0.03 M. The autoclave was purged with CO before setting the pressure at 10 bars: 1/5: H_2/CO. The autoclave was then heated at 70 °C for 16 h. After cooling and degassing, the reaction was concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel.

Xantphos: In a dry Schlenk glassware under argon were introduced $Rh(CO)_2(acac)$ (2 mol%) and anhydrous degassed Toluene (1 mL). Xantphos (8 mol%) was added and CO evolution was observed. Subsequent addition of ynamide was performed. The mixture was transferred via a syringe in a dry stainless autoclave under argon. The glassware was rinsed with anhydrous degassed toluene (3 × 3 mL) to reach a final concentration of 0.03 M. The autoclave was purged with H_2/CO (1:1) before setting the pressure at 5 bar. The autoclave was then heated at 70 °C for 16 h. After cooling and degassing, the reaction was concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel.

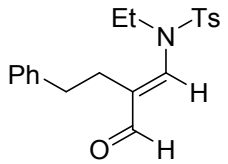
All the aldehyde overall yields are reported in the manuscript.



(*Z*)-*N*-ethyl-4-methyl-*N*-(1-oxo-5-phenylpent-2-en-2-yl)benzenesulfonamide (2a)
Synthesized following the general procedure **2.2**, using *N*-ethyl-4-methyl-*N*-(4-phenylbut-1-yn-1-yl)benzene-1-sulfonamide **1a** (100 mg, 0.31 mmol), BiPhePhos as ligand, and pentane/CH_2Cl_2/Et_2O (50:47:3) as chromatography eluent. Entitled product **2a** (43 mg, 53%) was obtained as colorless oil.

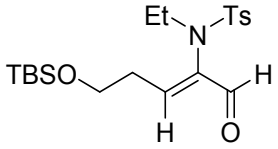
Scale-up : In a dry Schlenk glassware under argon were introduced 6.2 mg of $Rh(CO)_2(acac)$ (2 mol%, 0.024 mmol) and anhydrous degassed toluene (10 mL). 77 mg of BiPhePhos (8 mol%, 0.098 mmol) were added and CO evolution was observed. Subsequent addition of ynamide **1a** (400 mg, 1.22 mmol) was performed. The mixture was transferred via a syringe in a dry stainless autoclave under argon. The glassware was rinsed with anhydrous degassed toluene (3 × 10 mL) to reach a final concentration of 0.03 M. The autoclave was purged with CO before setting the pressure at 10 bars: 1/5: H_2/CO. The autoclave was heated at 70 °C (internal temperature) overnight. After cooling and degassing, the reaction was concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel (eluent pentane/CH_2Cl_2/Et_2O: 50:47:3) to afford **2a** (214 mg, 49%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J*=7.2 Hz, 3H), 2.43 (s, 3H), 2.94 (bs, 4H), 3.24 (bs, 1H), 3.56 (bs, 1H), 6.96 (m, 1H), 7.22-7.36 (m, 7H), 7.70 (m, 2H), 9.25 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 14.1, 21.7, 31.5, 34.1, 43.4, 126.5, 127.8, 128.6, 128.7, 129.5, 136.8, 138.6, 140.4, 143.6, 159.8, 189.6; **HRMS (ESI):** calculated for $C_{20}H_{24}NO_3S$ $[M + H]^+$: 358.1471, found 358.1471.



(*E*)-*N*-ethyl-*N*-(2-formyl-4-phenylbut-1-en-1-yl)-4-methylbenzenesulfonamide (3a)
Synthesized following the general procedure **2.2**, using *N*-ethyl-4-methyl-*N*-(4-phenylbut-1-yn-1-yl)benzene-1-sulfonamide **1a** (100 mg, 0.31 mmol), Xantphos as ligand, and pentane/CH_2Cl_2/Et_2O (50:47:3) as chromatography eluent. Entitled product **3a** (75 mg, 69%) was obtained as colorless oil.

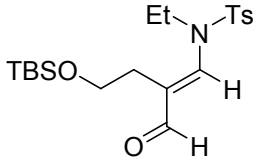
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (t, *J*=7.2 Hz, 3H), 2.47 (s, 3H), 2.59 (m, 4H), 3.48 (q, *J*=7.2 Hz, 2H), 7.05-7.19 (m, 5H), 7.37 (m, 2H), 7.46 (s, 1H), 7.69 (m, 2H), 9.28 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 14.7, 21.8, 25.7, 35.6, 41.8, 123.0, 126.3, 127.4, 128.4, 128.5, 130.4, 135.5, 141.1, 145.2, 146.8, 193.3; **HRMS (ESI):** calculated for $C_{20}H_{24}NO_3S$ $[M + H]^+$: 358.1471, found 358.1476.



(*Z*)-*N*-(5-((tert-butyldimethylsilyl)oxy)-1-oxopent-2-en-2-yl)-*N*-ethyl-4-methylbenzenesulfonamide (2b)

Synthesized following the general procedure **2.2**, using *N*-{4-[(*tert*-butyldimethylsilyl)oxy]but-1-yn-1-yl}-*N*-ethyl-4-methylbenzene-1-sulfonamide **1b** (100 mg, 0.26 mmol), BiPhePhos as ligand, and CH_2Cl_2/EtOAc (99:1) as chromatography eluent. Entitled product **2b** (50 mg, 46%) was obtained as colorless oil.

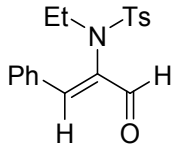
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 0.07 (s, 6H), 0.90 (s, 9H), 1.04 (t, *J*=7.2 Hz, 3H), 2.41 (s, 3H), 2.81 (d, *J*=6.5 Hz, 2H), 3.26 (broad s, 1H), 3.58 (broad s, 1H), 3.83 (t, *J*=5.9 Hz, 2H), 7.13 (t, *J*=7.2 Hz, 1H), 7.25 – 7.28 (m, 2H), 7.66 – 7.69 (m, 2H), 9.28 (s, 1H).; **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = -5.2, 14.3, 18.4, 21.7, 26.0, 33.4, 43.5, 61.1, 127.8, 129.5, 136.9, 139.1, 143.6, 158.9, 189.7**; HRMS (ESI):** calculated for $C_{14}H_{20}NO_4S$ $[M – TBS + 2H]^+$: 298.1108, found 298.1107.



(*E*)-*N*-(4-((tert-butyldimethylsilyl)oxy)-2-formylbut-1-en-1-yl)-*N*-ethyl-4-methylbenzenesulfonamide (3b)

Synthesized following the general procedure **2.2**, using *N*-ethyl-4-methyl-*N*-(4-phenylbut-1-yn-1-yl)benzene-1-sulfonamide **1b** (100 mg, 0.26), Xantphos as ligand, and CH_2Cl_2/EtOAc (99:1) as chromatography eluent. Entitled product **3b** (57 mg, 54%) was obtained as colorless oil.

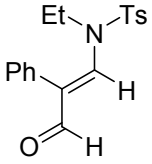
^{1}H NMR (500 MHz, Chloroform-*d*) δ = -0.15 (s, 6H), 0.72 (s, 9H), 1.17 (t, *J*=7.1 Hz, 3H), 2.45 (s, 3H), 2.54 (t, *J*=5.9 Hz, 2H), 3.59 (t, *J*=5.9 Hz, 2H), 3.93 (q, *J*=7.1 Hz, 2H), 7.34 – 7.36 (m, 2H), 7.60 (s, 1H), 7.73 – 7.76 (m, 2H), 9.25 (s, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ = -5.5, 14.8, 18.3, 21.7, 26.0, 26.7, 41.7, 61.9, 119.3, 127.5, 130.3, 135.5, 145.1, 148.4, 193.6**; HRMS (ESI):** calculated for $C_{20}H_{34}NO_4SSi$ $[M + H]^+$: 412.1972, found 412.1971.



(*Z*)-*N*-ethyl-4-methyl-*N*-(3-oxo-1-phenylprop-1-en-2-yl)benzenesulfonamide (2c)

Synthesized following the general procedure **2.2**, using *N*-ethyl-4-methyl-*N*-(2-phenylethynyl)benzene-1-sulfonamide **1c** (100 mg, 0.33 mmol), BiPhePhos as ligand, and CH_2Cl_2/EtOAc (97.5:2.5) as chromatography eluent. Entitled product **2c** (43 mg, 39%) was obtained as colorless oil.

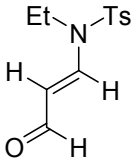
^{1}H NMR ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 1.01 (t, *J*=7.3 Hz, 3H), 2.43 (s, 3H), 3.54 (s, 2H), 7.28 – 7.31 (m, 2H), 7.41 – 7.48 (m, 4H), 7.73 – 7.76 (m, 2H), 7.94 – 7.96 (m, 2H), 9.43 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 13.8, 21.7, 43.7, 128.2, 129.0, 129.5, 131.5, 132.1, 132.3, 135.5, 136.8, 143.8, 152.0, 190.8.**; HRMS (ESI):** calculated for $C_{18}H_{20}NO_3S$ $[M + H]^+$: 330.1158, found 330.1154.



(E)-N-ethyl-4-methyl-N-(3-oxo-2-phenylprop-1-en-1-yl)benzenesulfonamide (3c)

Synthesized following the general procedure **2.2**, using *N*-ethyl-4-methyl-*N*-(2-phenylethynyl)benzene-1-sulfonamide **1c** (100 mg, 0.33 mmol), Xantphos as ligand, and CH_2Cl_2/EtOAc (97.5:2.5) as chromatography eluent. Entitled product **3c** (87 mg, 79%) was obtained as amorphous white solid.

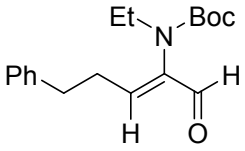
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 0.64 (t, *J*=7.0 Hz, 3H), 2.47 (s, 3H), 3.25 (q, *J*=7.0 Hz, 2H), 7.05 – 7.07 (m, 2H), 7.30 – 7.33 (m, 3H), 7.39 (d, *J*=8.0 Hz, 2H), 7.75 – 7.78 (m, 3H), 9.48 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 13.6, 21.8, 41.9, 124.4, 127.4, 128.3, 128.4, 130.3, 130.4, 131.9, 135.5, 145.3, 146.1, 191.8.**; HRMS (ESI):** calculated for $C_{18}H_{20}NO_3S$ $[M + H]^+$: 330.1158, found 330.1157.



(*E*)-*N*-ethyl-4-methyl-*N*-(3-oxoprop-1-en-1-yl)benzenesulfonamide (3e)

Synthesized following the general procedure **2.2**, using *N*-ethyl-*N*-ethynyl-4-methylbenzene-1-sulfonamide **1e** (72 mg, 0.32 mmol), Xantphos as ligand, and heptane/EtOAc (75:25) as chromatography eluent. Entitled product **3e** (44 mg, 54%) was obtained as amorphous white solid.

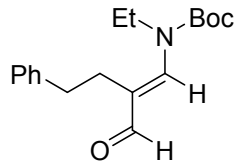
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 1.14 (t, *J*=7.1 Hz, 3H), 2.46 (s, 3H), 3.51 (d, *J*=7.1 Hz, 2H), 5.48 (dd, *J*=14.0, 7.8 Hz, 1H), 7.36 – 7.38 (m, 2H), 7.71 – 7.73 (m, 2H), 7.89 (d, *J*=14.1, 1H), 9.41 (d, *J*=7.8 Hz, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 12.2, 21.8, 41.5, 110.2, 127.4, 130.5, 135.1, 145.5, 149.2, 191.2**; HRMS (ESI):** calculated for $C_{12}H_{16}NO_3S$ $[M + H]^+$: 254.0845, found 254.0843.



***tert*-butyl (*Z*)-ethyl(1-oxo-5-phenylpent-2-en-2-yl)carbamate (2f)**

Synthesized following the general procedure **2.2**, using *tert*-butyl *N*-ethyl-*N*-(4-phenylbut-1-yn-1-yl)carbamate **1f** (35 mg, 0.13 mmol), BiPhePhos as ligand, and CH_2Cl_2/EtOAc (99:1 to 90:10) as chromatography eluent. Entitled product **2f** (16 mg, 41%) was obtained as amorphous white solid.

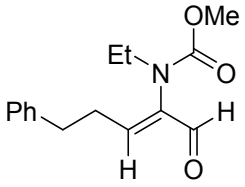
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 0.99 (t, *J*=7.2 Hz, 3H), 1.36 – 1.49 (m, 9H), 2.57 – 2.69 (m, 2H), 2.83 (t, *J*=7.2 Hz, 2H), 3.24 – 3.43 (m, 2H), 5.30 (s, 1H), 6.51 – 6.66 (dt, *J*=45.1, 7.2 Hz, 1H), 7.19 – 7.23 (m, 3H), 7.30 – 7.34 (m, 2H), 9.32 – 9.34 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 13.5, 14.2, 28.3, 28.5, 30.1, 30.6, 34.0, 34.2, 42.8, 43.6, 80.4, 126.5, 126.6, 128.5, 128.5, 128.8, 140.3, 150.4, 152.2, 154.2, 190.0, 190.2; **HRMS (ESI):** calculated for $C_{18}H_{25}NNaO_3$ $[M+Na]^+$: 326.1732, found 326.1716.



***tert*-butyl (*E*)-ethyl(2-formyl-4-phenylbut-1-en-1-yl)carbamate (3f)**

Synthesized following the general procedure **2.2**, using *tert*-butyl *N*-ethyl-*N*-(4-phenylbut-1-yn-1-yl)carbamate **1f** (52 mg, 0.19 mmol), Xantphos as ligand, and CH_2Cl_2/EtOAc (99:1 to 90:10) as chromatography eluent. Entitled product **3f** (35 mg, 61%) was obtained as colorless oil.

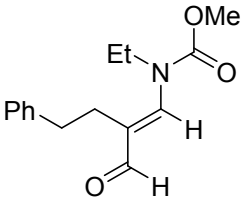
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 1.18 (t, *J*=7.0 Hz, 3H), 1.54 (s, 9H), 2.61 – 2.72 (m, 4H), 3.69 (q, *J*=7.1 Hz, 2H), 7.17 – 7.21 (m, 3H), 7.25 – 7.30 (m, 2H), 7.56 (s, 1H), 9.24 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 14.5, 26.0, 28.2, 35.7, 41.0, 83.5, 122.3, 126.3, 128.5, 128.6, 141.6, 148.8, 152.7, 194.2**; HRMS (ESI):** calculated for $C_{18}H_{25}NNaO_3$ $[M+Na]^+$: 326.1732, found 326.1719.



methyl (*Z*)-ethyl(1-oxo-5-phenylpent-2-en-2-yl)carbamate (2g)

Synthesized following the general procedure **2.2**, using methyl *N*-ethyl-*N*-(4-phenylbut-1-yn-1-yl)carbamate **1g** (83 mg, 0.36 mmol), BiPhePhos as ligand, and CH_2Cl_2/EtOAc (99:1 to 90:10) as chromatography eluent. Entitled product **2g** (43 mg, 46%) was obtained as thick yellow oil.

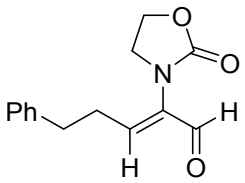
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 0.98 – 1.03 (m, 3H),2.61 – 2.67 (m, 2H), 2.81 – 2.87 (m, 2H), 3.33 – 3.41 (m, 2H), 3.60 –3.75 (m, 3H), 6.58 – 6.71 (m, 1H), 7.17 – 7.25 (m, 3H), 7.29 – 7.33 (m, 2H), 9.33 – 9.35 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 13.4, 14.1, 30.3, 30.5, 34.1, 43.4, 43.6, 53.0, 53.1, 126.7, 128.5, 128.5, 128.8, 151.6, 152.8, 189.8, 189.9**; HRMS (ESI):** calculated for $C_{15}H_{20}NO_3$ $[M+H]^+$: 262.1438, found 262.1429.



methyl (*E*)-ethyl(2-formyl-4-phenylbut-1-en-1-yl)carbamate (3g)

Synthesized following the general procedure **2.2**, using methyl *N*-ethyl-*N*-(4-phenylbut-1-yn-1-yl)carbamate **1g** (100 mg, 0.43 mmol), Xantphos as ligand, and CH_2Cl_2/EtOAc (99:1 to 90:10) as chromatography eluent. Entitled product **3g** (86 mg, 76%) was obtained as amorphous white solid.

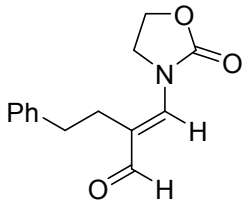
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 1.20 (t, *J*=7.1 Hz, 3H), 2.63 – 2.73 (m, 4H), 3.73 (q, *J*=7.1 Hz, 2H), 3.88 (s, 3H), 7.18 – 7.22 (m, 3H), 7.27 – 7.31 (m, 2H), 7.54 (s, 1H), 9.28 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 14.4, 26.0, 35.6, 41.3, 54.4, 123.6, 126.4, 128.5, 141.4, 148.3, 154.6, 194.0**; HRMS (ESI):** calculated for $C_{15}H_{20}NO_3$ $[M+H]^+$: 262.1438, found 262.1433.



(*Z*)-2-(2-oxooxazolidin-3-yl)-5-phenylpent-2-enal (2h)

Synthesized following the general procedure **2.2**, using 3-(4-phenylbut-1-yn-1-yl)-1,3-oxazolidin-2-one **1h** (100 mg, 0.46 mmol), BiPhePhos as ligand, and CH_2Cl_2/EtOAc (92.5:7.5) as chromatography eluent. Entitled product **2h** (54 mg, 47%) was obtained as colorless oil.

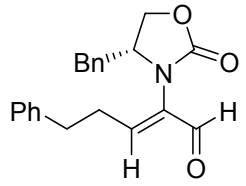
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.74 (qd, *J*=7.3, 0.9 Hz, 2H), 2.89 (t, *J*=7.3 Hz, 2H), 3.57 – 3.61 (m, 2H), 4.38 – 4.42 (m, 2H), 6.74 (t, *J*=7.4 Hz, 1H), 7.19 – 7.24 (m, 3H), 7.28 – 7.33 (m, 2H), 9.34 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 30.8, 34.0, 45.2, 63.1, 126.7, 128.6, 128.8, 140.4, 153.7, 189.1**; HRMS (ESI):** calculated for $C_{14}H_{16}NO_3$ $[M+H]^+$: 246.1125, found 246.1116.



(*E*)-2-((2-oxooxazolidin-3-yl)methylene)-4-phenylbutanal (3h)

Synthesized following the general procedure **2.2**, using 3-(4-phenylbut-1-yn-1-yl)-1,3-oxazolidin-2-one **1h** (100 mg, 0.46 mmol), Xantphos as ligand, and CH_2Cl_2/EtOAc (92.5:7.5) as chromatography eluent. Entitled product **3h** (73 mg, 64%) was obtained as amorphous white solid.

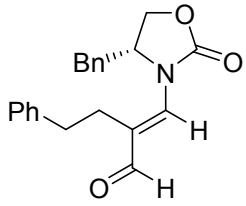
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.62 – 2.66 (m, 2H), 2.71 – 2.75 (m, 2H), 3.61 – 3.65 (m, 2H), 4.25 – 4.29 (m, 2H), 7.12 – 7.15 (m, 2H), 7.19 – 7.24 (m, 1H), 7.26 – 7.30 (m, 2H), 9.23 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 25.2, 35.5, 43.6, 62.7, 123.0, 126.5, 128.6, 128.8, 141.1, 143.9, 155.4, 193.2**; HRMS (ESI):** calculated for $C_{14}H_{16}NO_3$ $[M+H]^+$: 246.1125, found 246.1117.



(*S,Z*)-2-(4-benzyl-2-oxooxazolidin-3-yl)-5-phenylpent-2-enal (2i)

Synthesized following the general procedure **2.2**, using (4*S*)-4-benzyl-3-(4-phenylbut-1-yn-1-yl)-1,3-oxazolidin-2-one **1i** (100 mg, 0.33 mmol), BiPhePhos as ligand, and heptane/EtOAc (80:20) as chromatography eluent. Entitled product **2i** (47 mg, 43%) was obtained as amorphous beige solid.

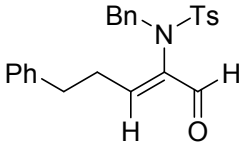
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 2.45 (dd, *J*=13.5, 9.5 Hz, 1H), 2.61 – 2.71 (m, 2H), 2.80 – 2.88 (m, 2H), 2.91 – 2.98 (m, 1H), 4.08 (dd, *J*=8.7, 6.9 Hz, 1H), 4.36 (t, *J*=8.5 Hz, 1H), 4.67 – 4.73 (m, 1H), 6.73 – 6.75 (m, 1H), 7.02 – 7.05 (m, 2H), 7.19 – 7.33 (m, 8H), 9.30 (s, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ = 31.2, 34.0, 39.7, 56.5, 68.4, 126.7, 127.4, 128.6, 128.8, 128.9, 129.0, 13 5.3, 136.1, 140.3, 155.0, 155.8, 189.4**; HRMS (ESI):** calculated for $C_{21}H_{22}NO_3$ $[M+H]^+$: 336.1594, found 336.1592; $[\propto]_D^{18}$ = – 116.0 (*c* 1.00, DMF).



(*S,E*)-2-((4-benzyl-2-oxooxazolidin-3-yl)methylene)-4-phenylbutanal (3i)

Synthesized following the general procedure **2.2**, using (4*S*)-4-benzyl-3-(4-phenylbut-1-yn-1-yl)-1,3-oxazolidin-2-one **1i** (100 mg, 0.33 mmol), Xantphos as ligand, and heptane/EtOAc (80:20) as chromatography eluent. Entitled product **3i** (83 mg, 76%) was obtained as amorphous off white solid.

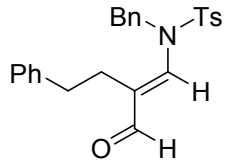
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.33 – 2.41 (m, 1H), 2.57 – 2.66 (m, 2H), 2.92 – 2.99 (m, 2H), 3.16 (ddd, *J*=13.5, 6.5, 5.6 Hz, 1H), 3.77 – 3.81 (m, 1H) ,3.95 – 4.01 (m, 1H), 4.08 (dd, *J*=8.8, 1.7 Hz, 1H), 7.03 – 7.05 (m, 2H), 7.13 – 7.16 (m, 2H), 7.18 – 7.22 (m, 1H), 7.24 – 7.34 (m, 6H), 7.40 (s, 1H)., 9.44 (d, *J*=1.1 Hz, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 25.9, 35.0, 37.6, 54.9, 66.4, 123.1, 126.7, 127.9, 128.8, 129.0, 129.2, 129.3, 134.1, 141.0, 143.1, 154.9, 193.3**; HRMS (ESI):** calculated for $C_{21}H_{22}NO_3$ $[M+H]^+$: 336.1594, found 336.1586; $[\propto]_D^{18}$ = – 60.0 (*c* 1.00, DMF).



(*Z*)-*N*-benzyl-4-methyl-*N*-(1-oxo-5-phenylpent-2-en-2-yl)benzenesulfonamide (2j)

Synthesized following the general procedure **2.2**, using *N*-benzyl-4-methyl-*N*-(4-phenylbut-1-yn-1-yl)benzenesulfonamide **1j** (41 mg, 0.11 mmol), BiPhePhos as ligand, and pentane/Et_2O (80:20 to 75/25) as chromatography eluent. Entitled product **2j** (21 mg, 47%) was obtained as amorphous off white solid.

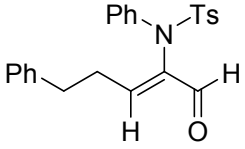
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.34 – 2.43 (m, 5H), 2.58 – 2.62 (s, 2H), 4.23 (broad s, 1H), 4.87 (bs, 1H), 6.70 (t, *J*=7.3 Hz, 1H), 7.02 – 7.04 (m, 2H), 7.17 – 7.30 (m, 10H), 7.69 – 7.72 (m, 2H), 9.08 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 21.7, 31.3, 33.7, 52.0, 126.4, 127.8, 128.3, 128.5, 128.6, 128.7, 129.6, 129.7, 135.7, 136.9, 137.9, 140.3, 143.8, 161.1, 189.6**; HRMS (ESI):** calculated for $C_{25}H_{25}NNaO_3S$ $[M+Na]^+$: 442.1453, found 442.1443.



(*E*)-*N*-benzyl-*N*-(2-formyl-4-phenylbut-1-en-1-yl)-4-methylbenzenesulfonamide (3j)

Synthesized following the general procedure **2.2**, using *N*-benzyl-4-methyl-*N*-(4-phenylbut-1-yn-1-yl)benzenesulfonamide **1j** (100 mg, 0.26 mmol), Xantphos as ligand, and pentane/Et_2O (80:20 to 75/25) as chromatography eluent. Entitled product **3j** (75 mg, 70%) was obtained as colorless oil.

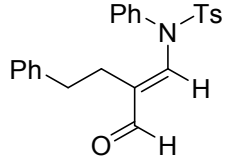
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.33 – 2.37 (m, 2H), 2.43 – 2.55 (m, 5H), 4.57 (s, 2H), 6.94 – 6.96 (m, 2H), 7.07 – 7.10 (m, 2H), 7.13 – 7.18 (m, 3H), 7.26 – 7.34 (m, 3H), 7.38 (d, *J*=8.1 Hz, 2H), 7.65 (s, 1H), 7.68 – 7.71 (m, 2H), 9.34 (s, 1H); **^{13}C NMR** ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 21.8, 25.4, 35.3, 50.0, 123.9, 125.9, 126.2, 127.5, 127.8, 128.4, 128.6, 129.0, 130.3, 135.2, 135.5, 141.2, 145.3, 147.4, 193.4**; HRMS (ESI):** calculated for $C_{25}H_{26}NO_3S$ $[M+H]^+$: 420.1628, found 420.1624.



(*Z*)-4-methyl-*N*-(1-oxo-5-phenylpent-2-en-2-yl)-*N*-phenylbenzenesulfonamide (2k)

Synthesized following the general procedure **2.2**, using 4-methyl-*N*-phenyl-*N*-(4-phenylbut-1-yn-1-yl)benzenesulfonamide **1k** (90 mg, 0.24 mmol), BiPhePhos as ligand, and heptane/EtOAc (90:10 to 80:20) as chromatography eluent. Entitled product **2k** (44 mg, 45%) was obtained as amorphous yellowish solid.

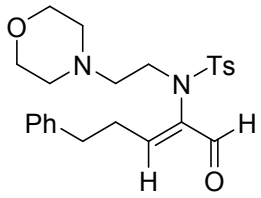
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 2.39 (s, 3H), 2.78 (t, *J*=7.6 Hz, 2H), 2.94 (q, *J*=7.4 Hz, 2H), 6.89 (t, *J*=7.4 Hz, 1H), 7.15 – 7.17 (m, 2H), 7.19 – 7.25 (m, 8H), 7.28 – 7.31 (m, 2H), 7.65 – 7.66 (m, 2H), 9.44 (s, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ = 21.7, 30.9, 33.8, 126.6, 127.0, 127.5, 128.5, 128.6, 128.8, 129.3, 129.3, 136.5, 139.8, 140.2, 142.1, 143.9, 157.6, 190.2**; HRMS (ESI):** calculated for $C_{24}H_{23}NNaO_3S$ $[M+Na]^+$: 428.1296, found 428.1298.



(*E*)-*N*-(2-formyl-4-phenylbut-1-en-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (3k)

Synthesized following the general procedure **2.2**, using 4-methyl-*N*-phenyl-*N*-(4-phenylbut-1-yn-1-yl)benzenesulfonamide **1k** (90 mg, 0.24 mmol), Xantphos as ligand, and heptane/EtOAc (90:10 to 80:20) as chromatography eluent. Entitled product **3k** (70 mg, 72%) was obtained as amorphous white solid.

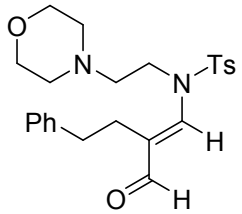
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 1.68 – 1.71 (m, 2H), 2.19 – 2.22 (m, 2H), 2.45 (s, 3H), 6.74 – 6.76 (m, 2H), 6.99 – 7.01 (m, 2H), 7.07 – 7.10 (m, 1H), 7.12 – 7.15 (m, 2H), 7.30 (d, *J*=8.0 Hz, 2H), 7.34 – 7.34 (m, 2H), 7.42 – 7.46 (m, 1H), 7.51 – 7.52 (m, 2H), 7.74 (s, 1H), 9.32 (s, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ = 21.9, 24.8, 34.1, 124.7, 125.9, 128.1, 128.2, 128.4, 129.6, 130.0, 130.1, 130.2, 134.0, 136.7, 141.4, 145.5, 147.8, 193.2**; HRMS (ESI):** calculated for $C_{24}H_{24}NO_3S$ $[M+H]^+$: 406.1471, found 406.1463.



(*Z*)-4-methyl-*N*-(2-morpholinoethyl)-*N*-(1-oxo-5-phenylpent-2-en-2-yl)benzenesulfonamide (2m)

Synthesized following the general procedure **2.2**, using 4-methyl-*N*-(2-morpholinoethyl)-*N*-(4-phenylbut-1-yn-1-yl)benzenesulfonamide **1m** (100 mg, 0.24 mmol), BiPhePhos as ligand, and CH_2Cl_2/EtOAc (80:20) as chromatography eluent. Entitled product **2m** (31 mg, 29%) was obtained as yellowish oil.

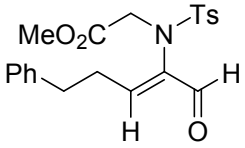
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.18 – 2.26 (m, 5H), 2.37 – 2.41 (m, 4H), 2.85 (broad s, 4H), 3.36 (broad s, 1H),3.54 –3.57 (m, 5H), 6.84 – 6.87 (m, 1H), 7.18 – 7.24 (m, 3H), 7.28 – 7.33 (m, 3H), 7.65 – 7.68 (m, 2H), 9.20 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 21.7, 31.3, 34.2, 45.1, 53.4, 57.4, 66.9, 126.6, 127.8, 128.6, 128.8, 129.6, 136.6, 138.8, 140.5, 143.9, 156.6, 189.4**; HRMS (ESI):** calculated for $C_{24}H_{31}N_2O_4S$ $[M+H]^+$: 443.1999, found 443.1989.



(*E*)-*N*-(2-formyl-4-phenylbut-1-en-1-yl)-4-methyl-*N*-(2-morpholinoethyl)benzenesulfonamide (3m)

Synthesized following the general procedure **2.2**, using 4-methyl-*N*-(2-morpholinoethyl)-*N*-(4-phenylbut-1-yn-1-yl)benzenesulfonamide **1m** (93 mg, 0.23 mmol), Xantphos as ligand, and CH_2Cl_2/EtOAc (80:20) as chromatography eluent. Entitled product **3m** (73 mg, 73%) was obtained as yellowish oil.

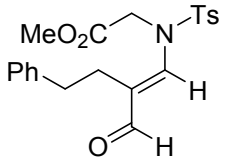
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.35 – 2.38 (m, 4H), 2.46 – 2.49 (m, 5H), 2.58 – 2.65 (m, 4H), 3.52 – 3.56 (m, 2H), 3.61 –3.63 (m, 4H), 7.09 – 7.18 (m, 5H), 7.37 – 7.40 (m, 3H), 7.69 – 7.71 (m, 2H), 9.27 (s, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ = 21.8, 25.2, 35.5, 44.6, 53.8, 56.6, 66.9, 126.3, 127.4, 128.4, 128.6, 130.4, 135.1, 141.0, 145.4, 147.1, 193.3**; HRMS (ESI):** calculated for $C_{24}H_{31}N_2O_4S$ $[M+H]^+$: 443.1999, found 443.1993.



methyl (*Z*)-*N*-(1-oxo-5-phenylpent-2-en-2-yl)-*N*-tosylglycinate (2n)

Synthesized following the general procedure **2.2**, using methyl *N*-(4-phenylbut-1-yn-1-yl)-*N*-tosylglycinate **1n** (70 mg, 0.19 mmol), BiPhePhos as ligand, and CH_2Cl_2/EtOAc (98:2 to 97:3) as chromatography eluent. Entitled product **2n** (37 mg, 49%) was obtained as thick colorless oil.

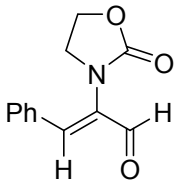
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.41 (s, 3H), 2.88 (t, *J*=7.6 Hz, 2H), 3.10 (large s, 2H), 3.70 (s, 3H), 4.15 (broad s, 3H), 6.93 (t, *J*=7.3 Hz, 1H), 7.21 – 7.25 (m, 2H), 7.27 – 7.34 (m, 5H), 7.62 – 7.64 (m, 2H), 9.15 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 21.8, 29.9, 31.7, 33.9, 52.4, 126.5, 127.8, 128.7, 129.7, 136.1, 140.6, 144.3, 160.8, 169.3, 189.4**; HRMS (ESI):** calculated for $C_{21}H_{24}NO_5S$ $[M+H]^+$: 402.1370, found 402.1365.



methyl (*E*)-*N*-(2-formyl-4-phenylbut-1-en-1-yl)-*N*-tosylglycinate (3n)

Synthesized following the general procedure **2.2**, using methyl *N*-(4-phenylbut-1-yn-1-yl)-*N*-tosylglycinate **1n** (70 mg, 0.19 mmol), BiPhePhos as ligand, and CH_2Cl_2/EtOAc (98:2 to 97:3) as chromatography eluent. Entitled product **3n** (39 mg, 51%) was obtained as thick yellowish oil.

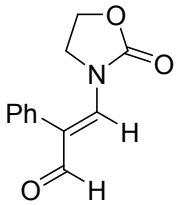
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 2.37 – 2.41 (m, 2H), 2.47 (s, 3H), 2.58 –2.62 (m, 2H), 3.62 (s, 3H), 4.16 (s, 2H), 7.05 – 7.08 (m, 2H), 7.12 – 7.16 (m, 1H), 7.17 – 7.21 (m, 2H), 7.36 – 7.38 (m, 2H), 7.45 (s, 1H), 7.71 – 7.73 (m, 2H), 9.26 (s, 1H); **^{13}C NMR** (101 MHz, Chlo roform-*d*) δ = 21.8, 25.5, 35.2, 47.7, 52.9, 123.7, 126.4, 127.8, 128.5, 128.6, 130.3, 134.8, 140.9, 145.6, 146.9, 167.7, 193.1**; HRMS (ESI):** calculated for $C_{21}H_{24}NO_5S$ $[M+H]^+$: 402.1370, found 402.1363.



(*Z*)-2-(2-oxooxazolidin-3-yl)-3-phenylacrylaldehyde (2o)

Synthesized following the general procedure **2.2**, **3-(phenylethynyl)oxazolidin-2-one 1o** (88 mg, 0.47 mmol), Xantphos as ligand, and pentane/CH_2Cl_2/Et_2O (35:50:15) as chromatography eluent. Entitled product **2o** (23 mg, 23%) was obtained as colorless oil.

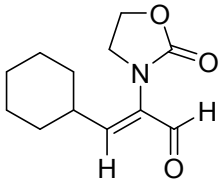
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 3.78 (m, 2H), 4.55 (m, 2H), 7.41 (s, 1H), 7.44 – 7.49 (m, 3H), 7.62 – 7.67 (m, 2H), 9.54 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 45.2, 63.3, 129.3, 130.4, 131.8, 132.2, 134.8, 148.2, 157.5, 189.1; **HRMS (ESI):** calculated for $C_{12}H_{11}KNO_3$ $[M+K]^+$: 256.0376, found 256.0371.



(*E*)-3-(2-oxooxazolidin-3-yl)-2-phenylacrylaldehyde (3o)

Synthesized following the general procedure **2.2**, **3-(phenylethynyl)oxazolidin-2-one 1o** (70 mg, 0.37 mmol), Xantphos as ligand, and pentane/CH_2Cl_2/Et_2O (35:50:15) as chromatography eluent. Entitled product **3o** (33 mg, 41%) was obtained as colorless oil.

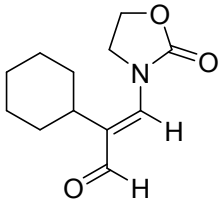
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 3.29 (m, 2H), 4.29 (m, 2H), 7.15 – 7.20 (m, 2H) 7.36 – 7.41 (m, 3H), 7.66 (s, 1H), 9.55 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 44.6, 63.1, 125.5, 128.2, 128.7, 130.9, 131.2, 143.1, 155.6, 191.5; **HRMS (ESI):** calculated for $C_{12}H_{11}KNO_3$ $[M+K]^+$: 256.0376, found 256.0374.



(*Z*)-3-cyclohexyl-2-(2-oxooxazolidin-3-yl)acrylaldehyde (2p)

Synthesized following the general procedure **2.2**, **3-(cyclohexylethynyl)oxazolidin-2-one 1p** (120 mg, 0.62 mmol), BiPhePhos as ligand, and pentane/CH_2Cl_2/Et_2O (40:50:10) as chromatography eluent. Entitled product **2p** (65 mg, 47%) was obtained as amorphous white solid.

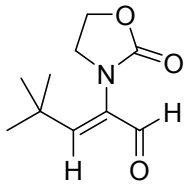
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 1.16 – 1.38 (m, 5H), 1.66 – 1.81 (m, 5H), 2.54 (qt, *J* = 10.7, 3.3 Hz, 1H), 3.79 (m, 2H), 4.47 (m, 2H), 6.59 (d, *J* = 10.2 Hz, 1H), 9.32 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 25.2 (2*C), 25.7, 31.5 (2*C), 38.0, 46.0, 62.9, 135.5, 156.9, 160.5, 189.3; **HRMS (ESI):** calculated for $C_{12}H_{17}NNaO_3$ $[M+Na]^+$: 246.1106, found 246.1101.



(*E*)-2-cyclohexyl-3-(2-oxooxazolidin-3-yl)acrylaldehyde (3p)

Synthesized following the general procedure **2.2**, **3-(cyclohexylethynyl)oxazolidin-2-one 1p** (120 mg, 0.62 mmol), Xantphos as ligand, and pentane/CH_2Cl_2/Et_2O (40:50:10) as chromatography eluent. Entitled product **3p** (41 mg, 29%) was obtained as thick yellowish oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 1.12 – 1.35 (m, 3H), 1.46 (m, 2H), 1.66 (m, 1H), 1.81 (m, 2H), 2.09 (qd, *J* = 12.6, 3.4 Hz, 2H), 2.48 – 2.57 (m, 1H), 4.21 (m, 2H), 4.53 (m, 2H), 7.23 (s, 1H), 9.27 (d, *J* = 2.2 Hz, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 25.7, 27.1 (2*C), 30.3 (2*C), 37.1, 44.7, 62.7, 129.3, 143.5, 155.9, 193.9; **HRMS (ESI):** calculated for $C_{12}H_{17}NNaO_3$ $[M+Na]^+$: 246.1106, found 246.1106.



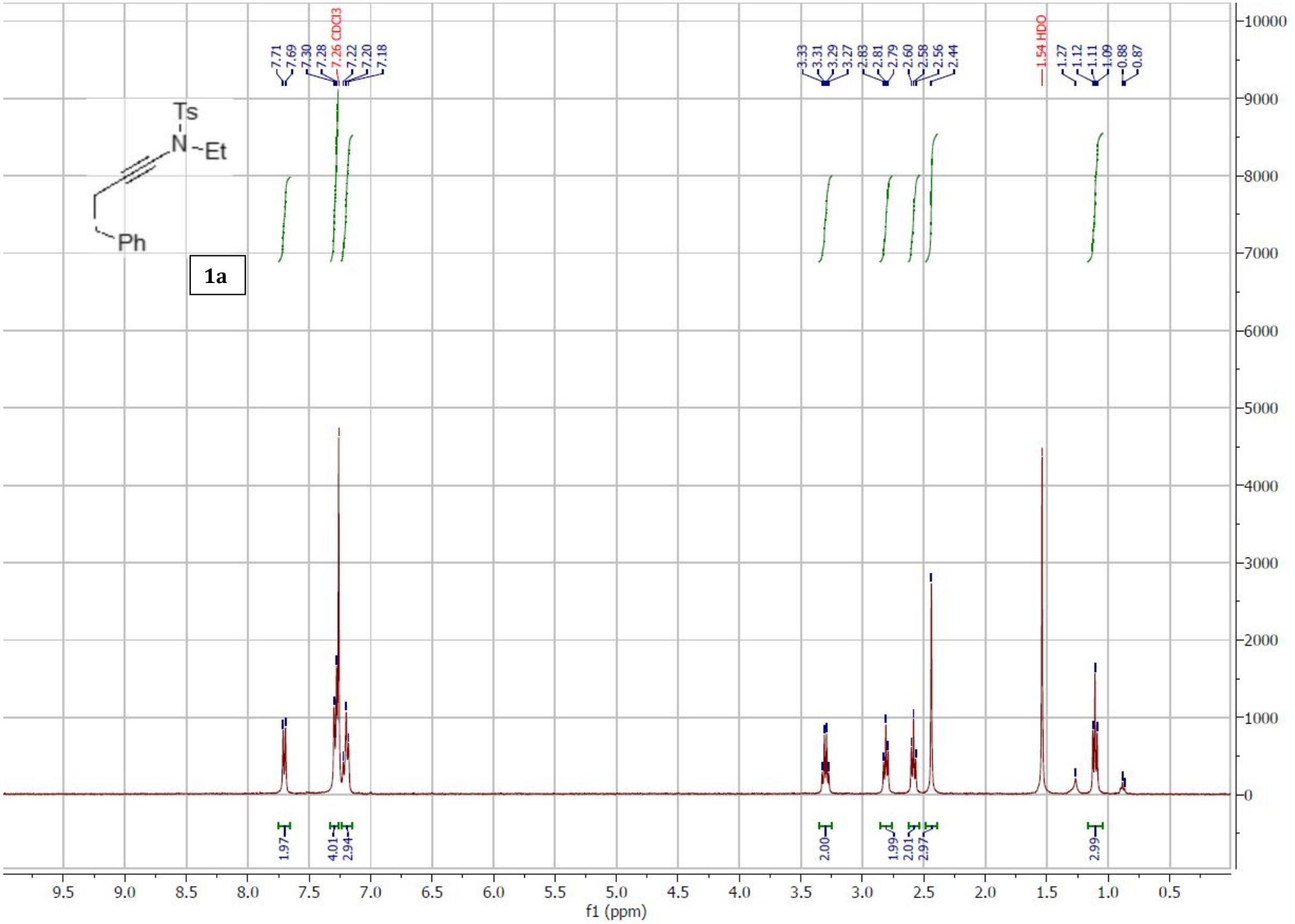
(*Z*)-4,4-dimethyl-2-(2-oxooxazolidin-3-yl)pent-2-enal (2q)

Synthesized following the general procedure **2.2**, **3-(3,3-dimethylbut-1-yn-1-yl)oxazolidin-2-one 1q** (78 mg, 0.47 mmol), Xantphos as ligand, and pentane/CH_2Cl_2/Et_2O (35:50:15) as chromatography eluent. Entitled product **2q** (56 mg, 61%) was obtained as amorphous white solid.

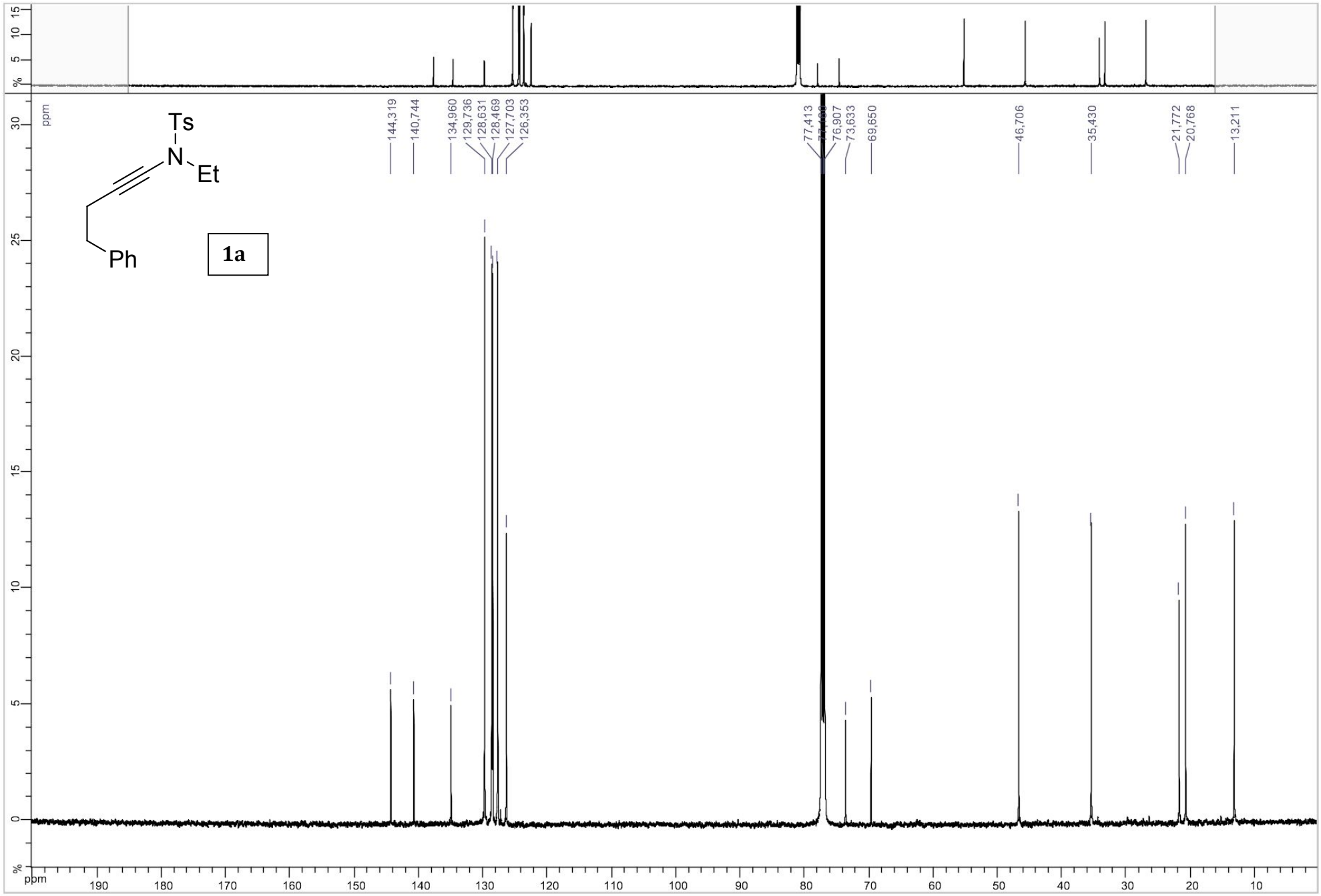
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 1.23 (s, 9H), 3.32 – 4.06 (bm, 2H), 4.43 (m, 2H), 6.72 (s, 1H), 9.28 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 29.1 (3*C), 35.5, 46.7, 62.9, 135.2, 157.6, 166.0, 190.1; **HRMS (ESI):** calculated for $C_{10}H_{15}KNO_3$ $[M+K]^+$: 236.0689, found 236.0633.

3. ^{1}H & ^{13}C NMR spectra

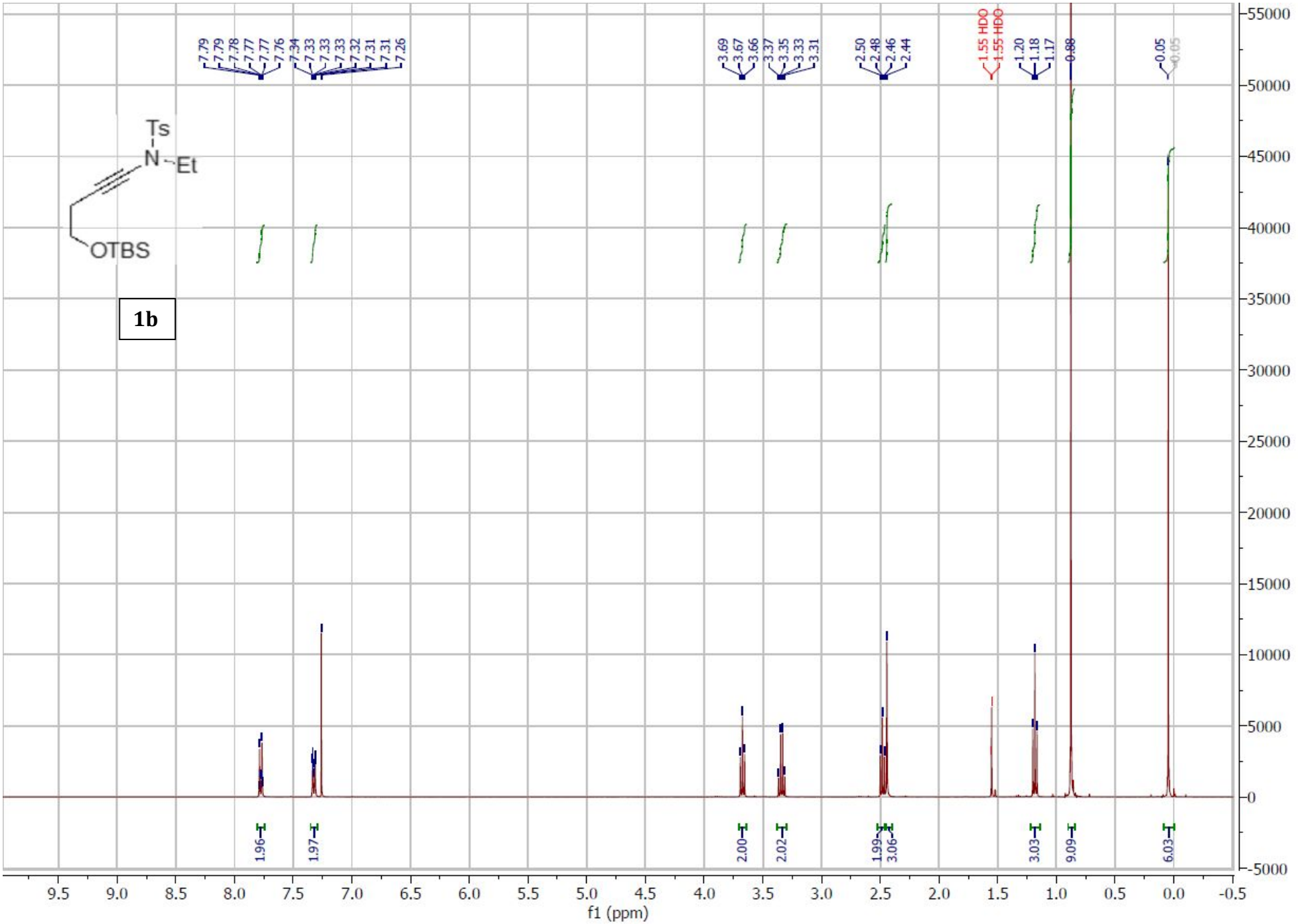
^{1}H NMR of compound **1a** (400 MHz, $CDCl_3$):



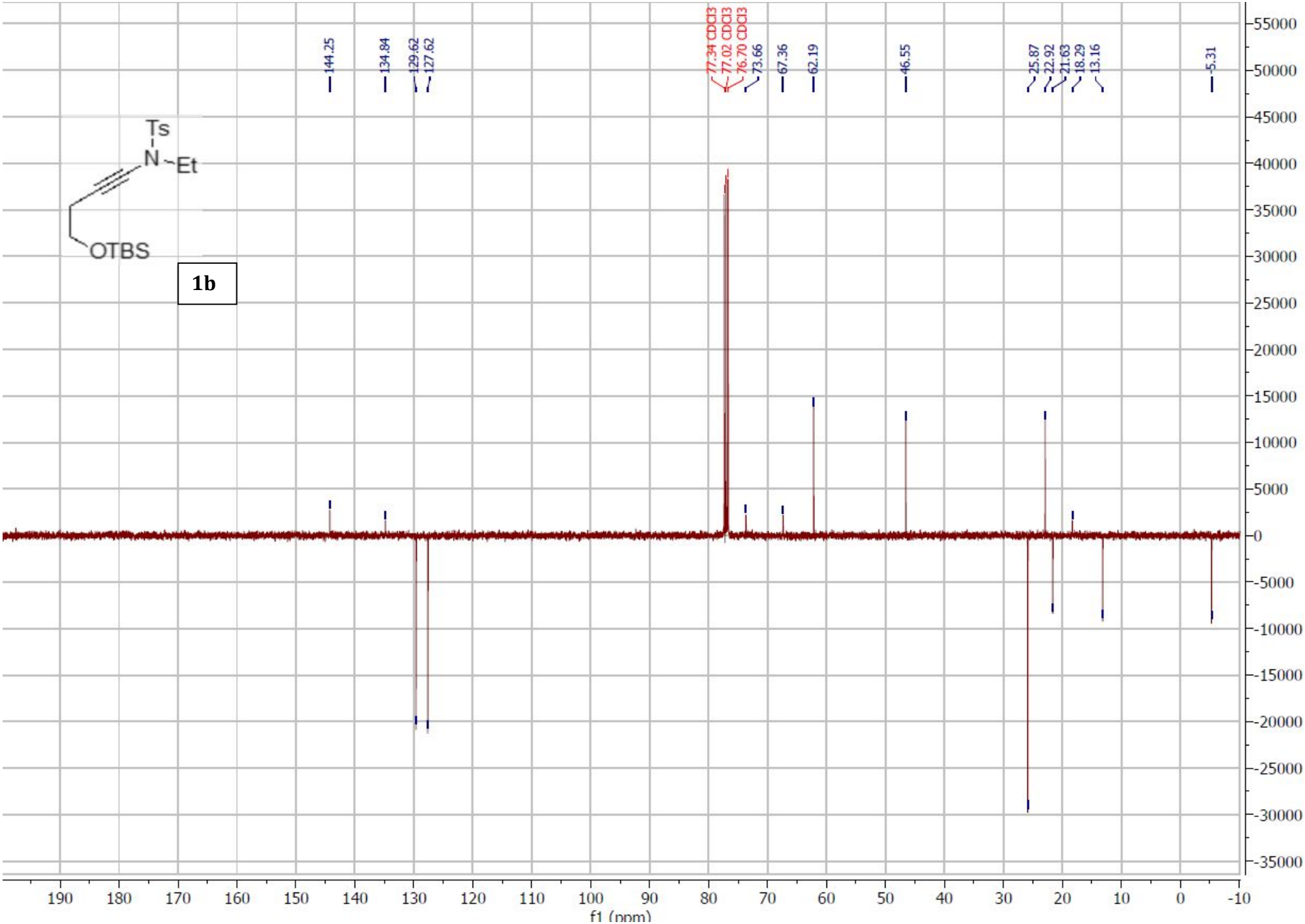
^{13}C NMR of compound **1a** (101 MHz, $CDCl_3$):



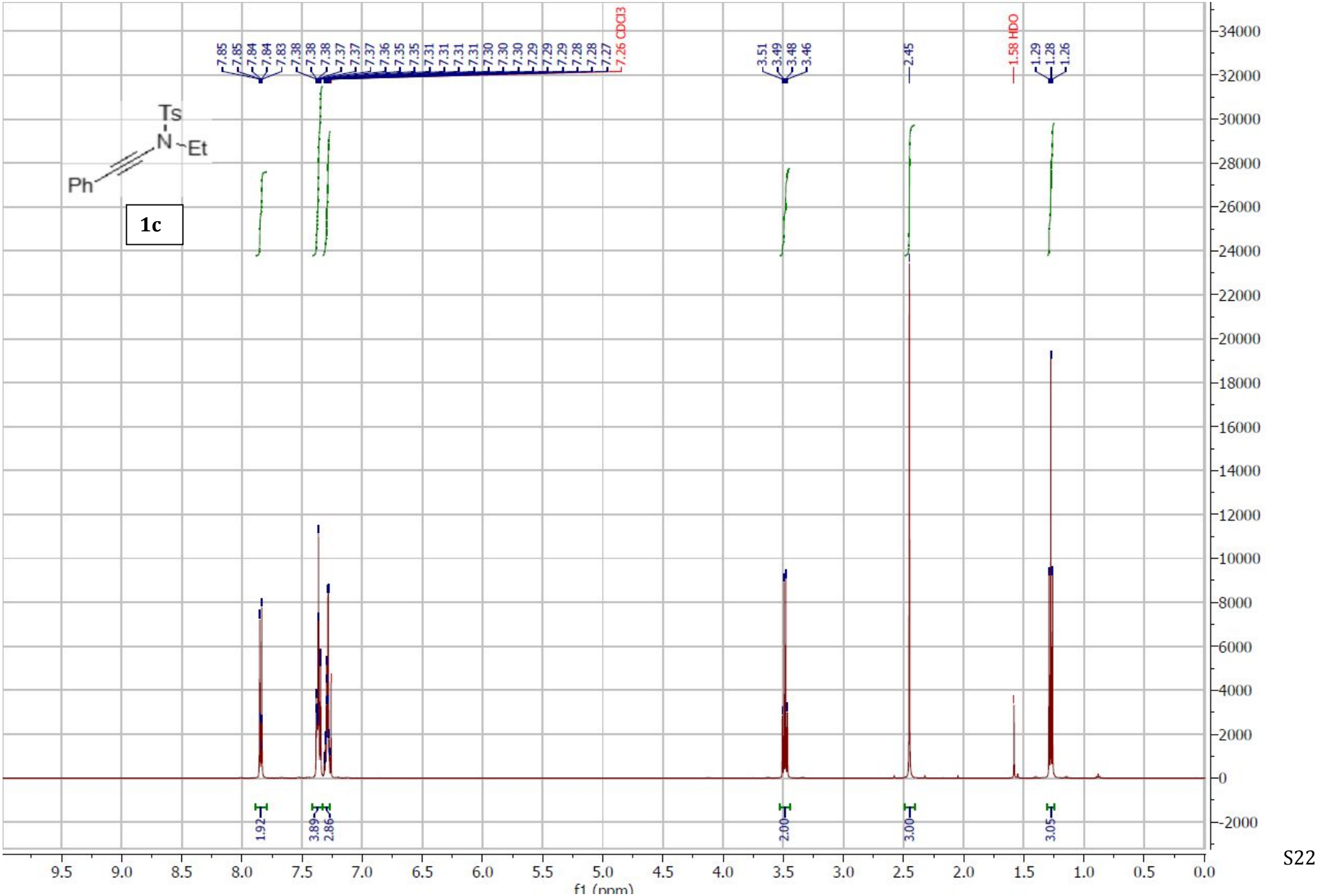
^{1}H NMR of compound **1b** (400 MHz, $CDCl_3$):



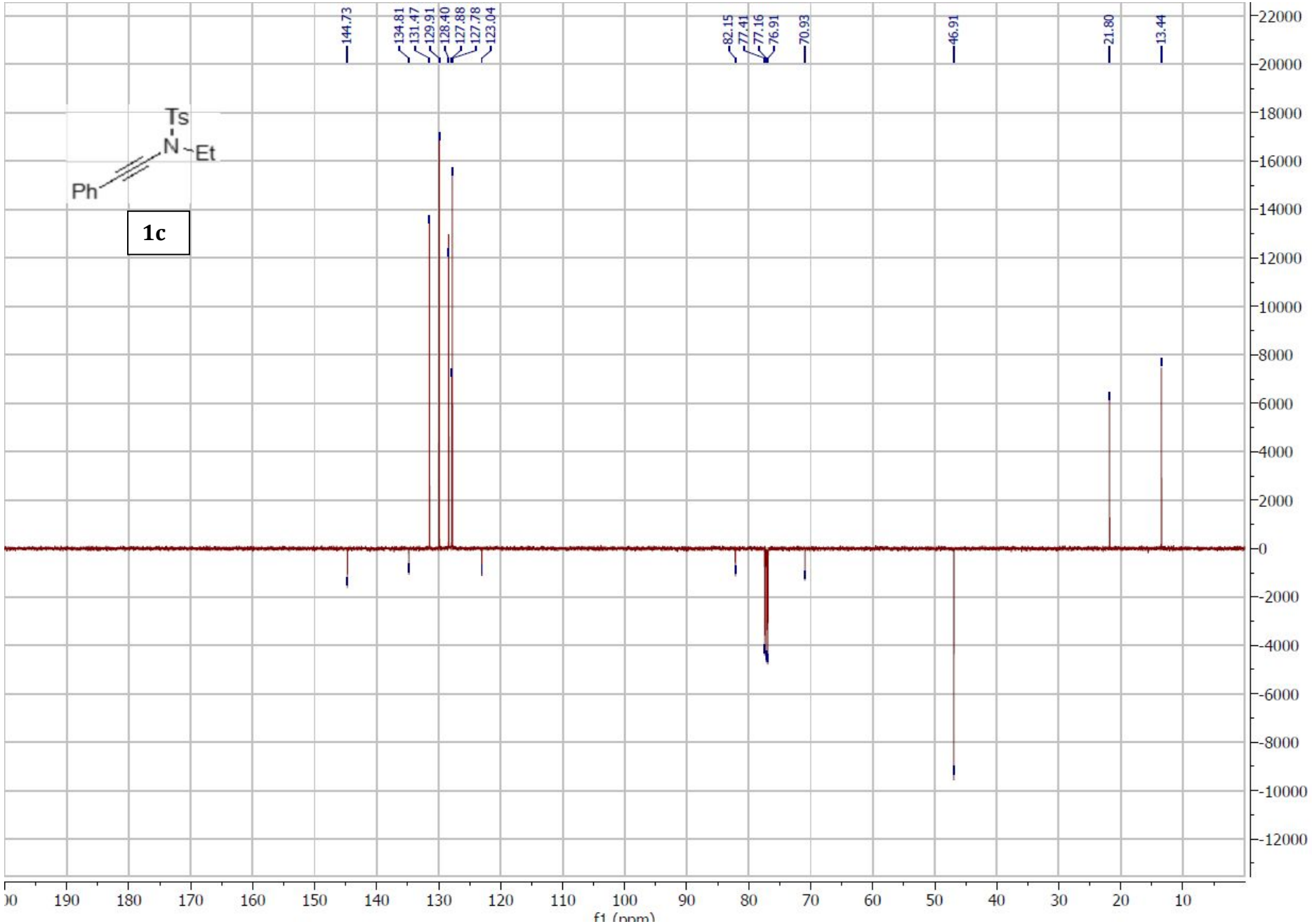
^{13}C NMR of compound **1b** (101 MHz, $CDCl_3$):



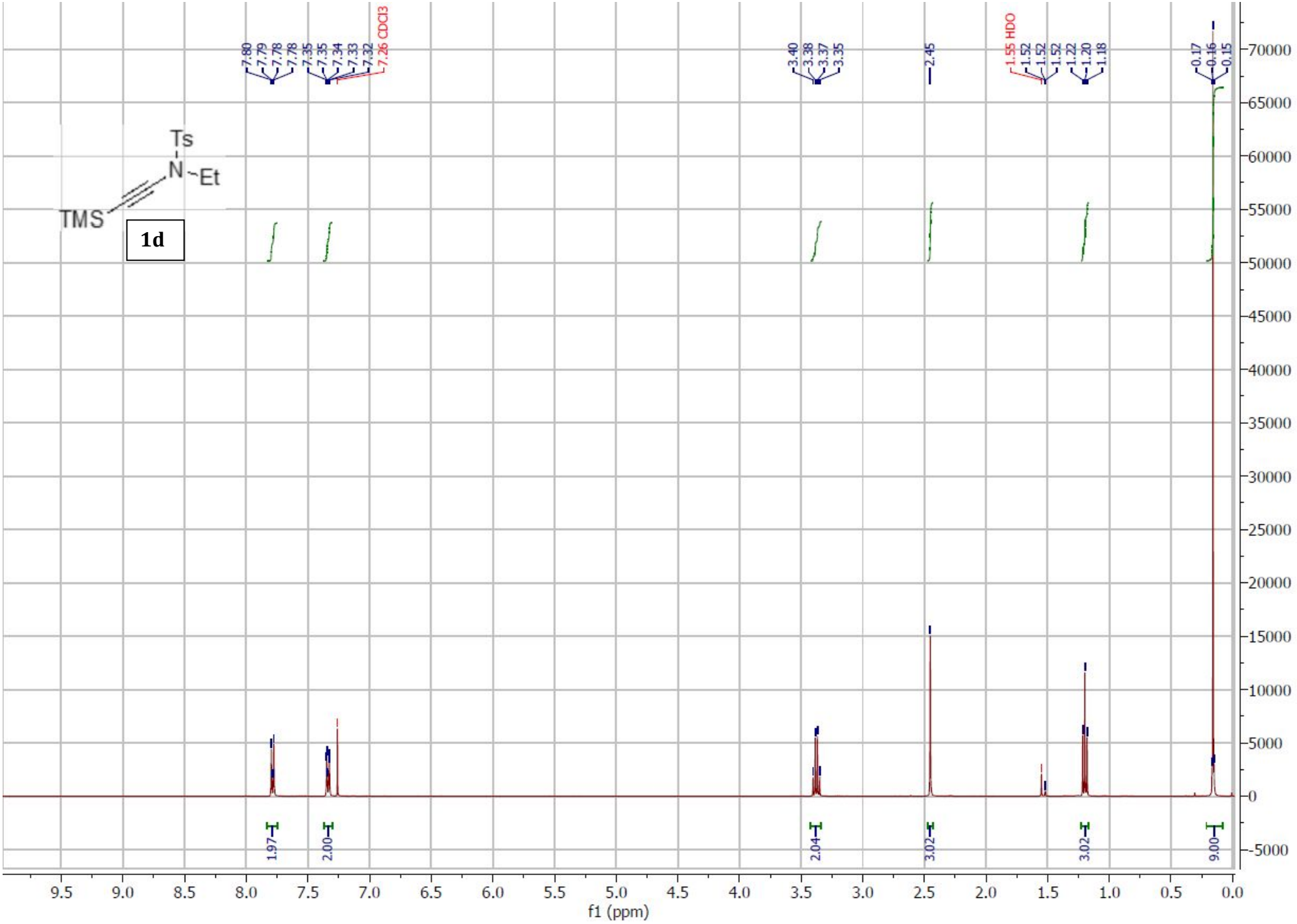
^{1}H NMR of compound **1c** (500 MHz, $CDCl_3$):



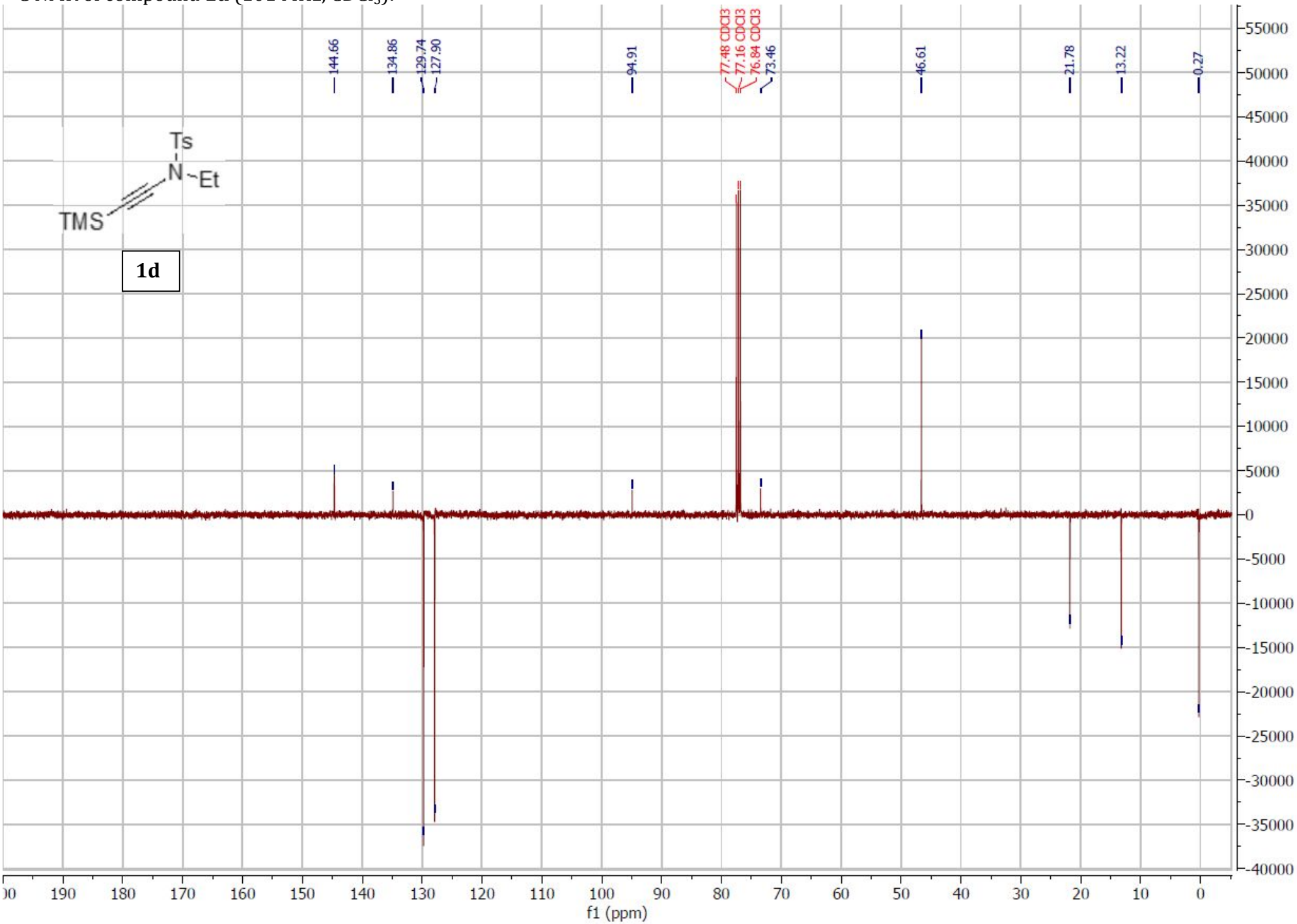
^{13}C NMR of compound **1c** (126 MHz, $CDCl_3$):



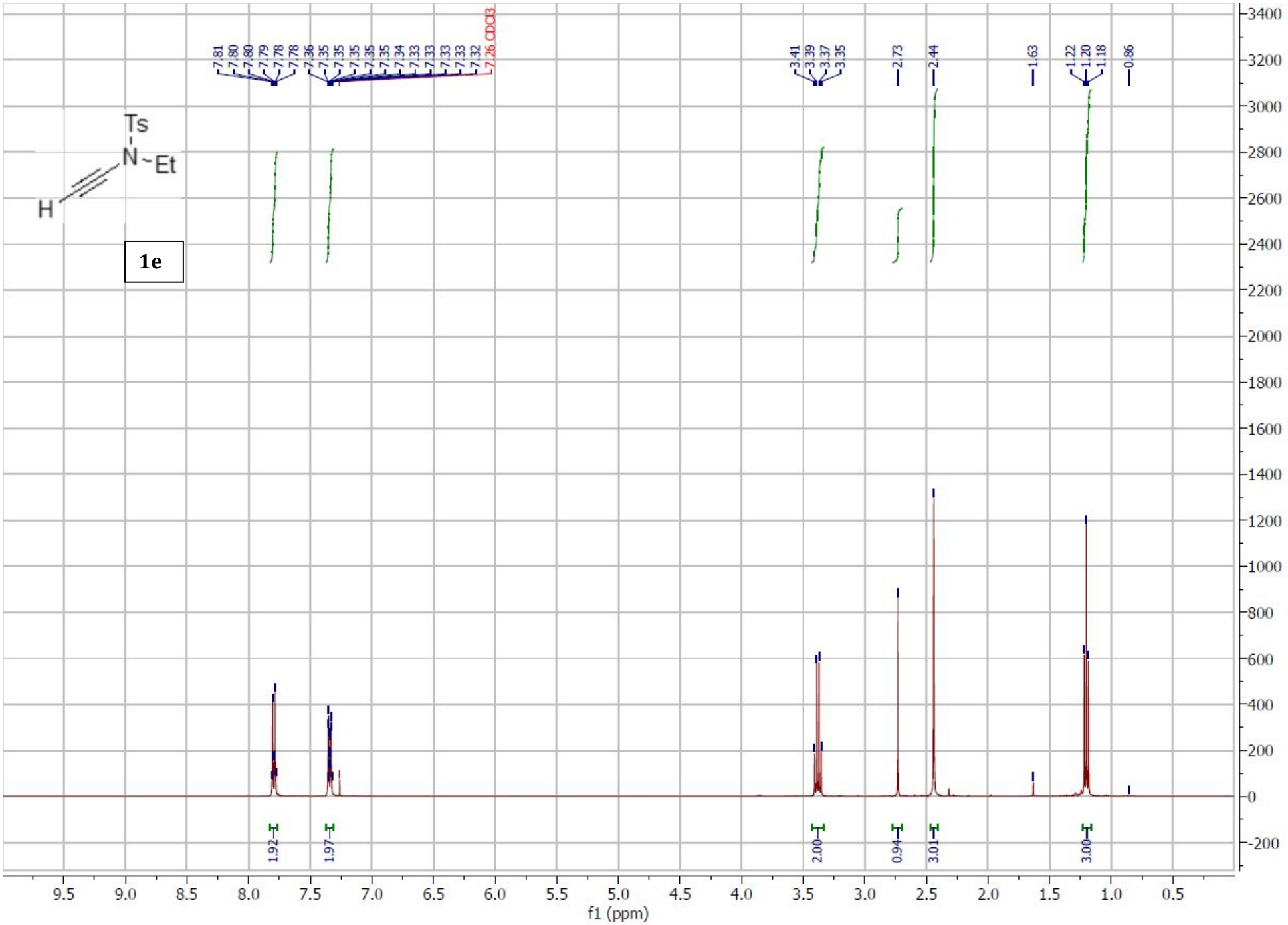
^{1}H NMR of compound **1d** (400 MHz, $CDCl_3$):



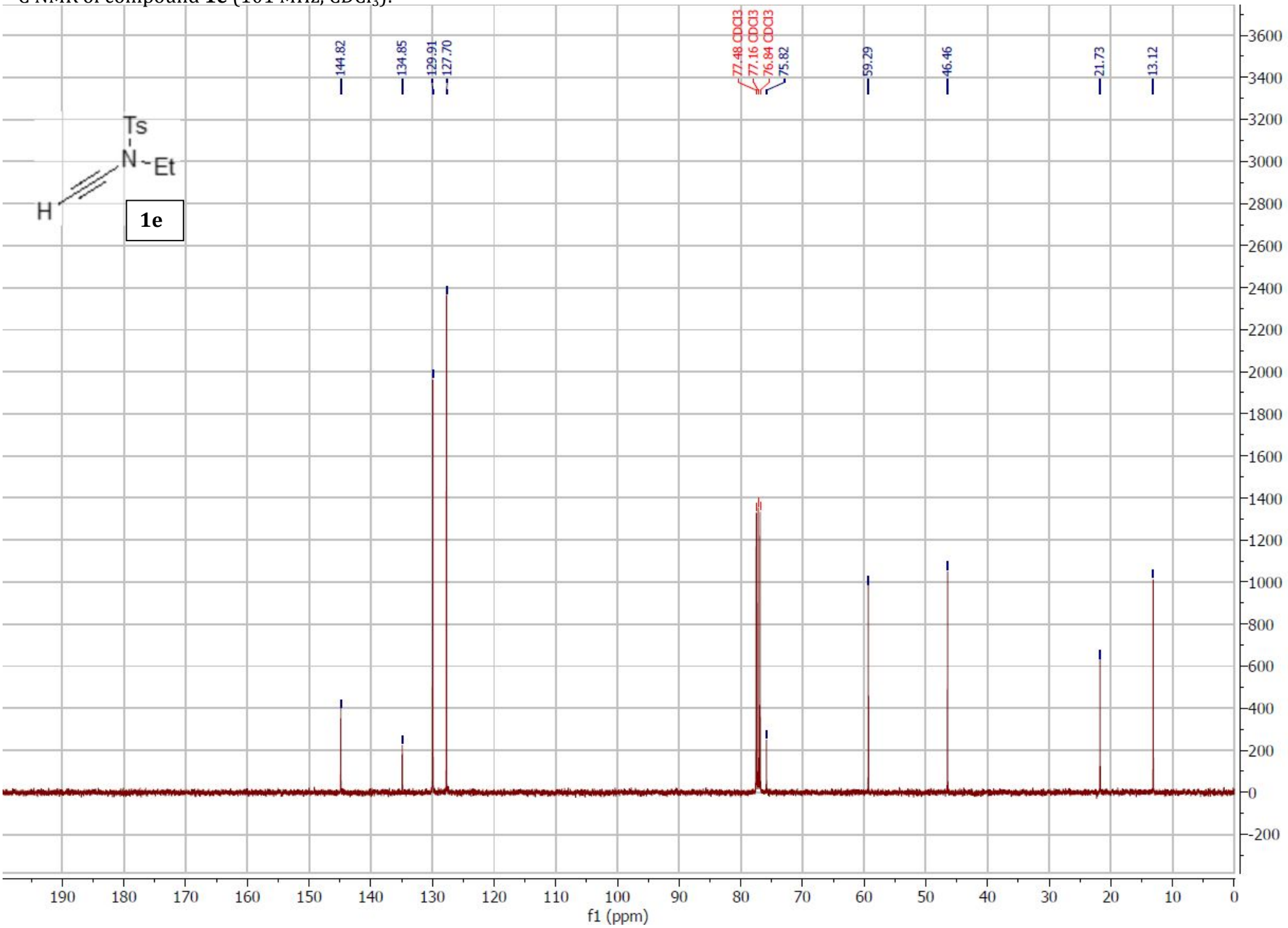
^{13}C NMR of compound **1d** (101 MHz, $CDCl_3$):



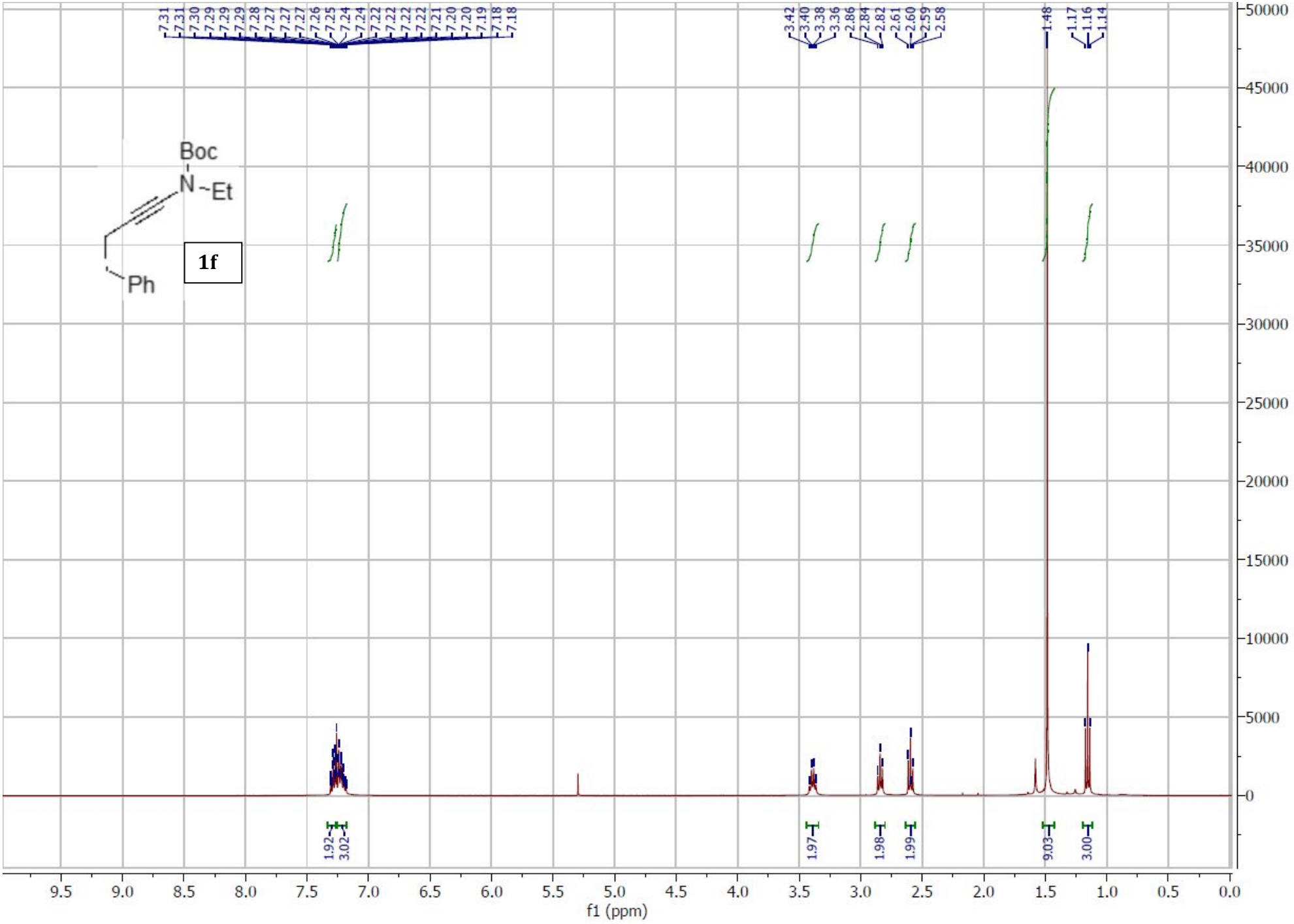
^{1}H NMR of compound **1e** (400 MHz, $CDCl_3$):



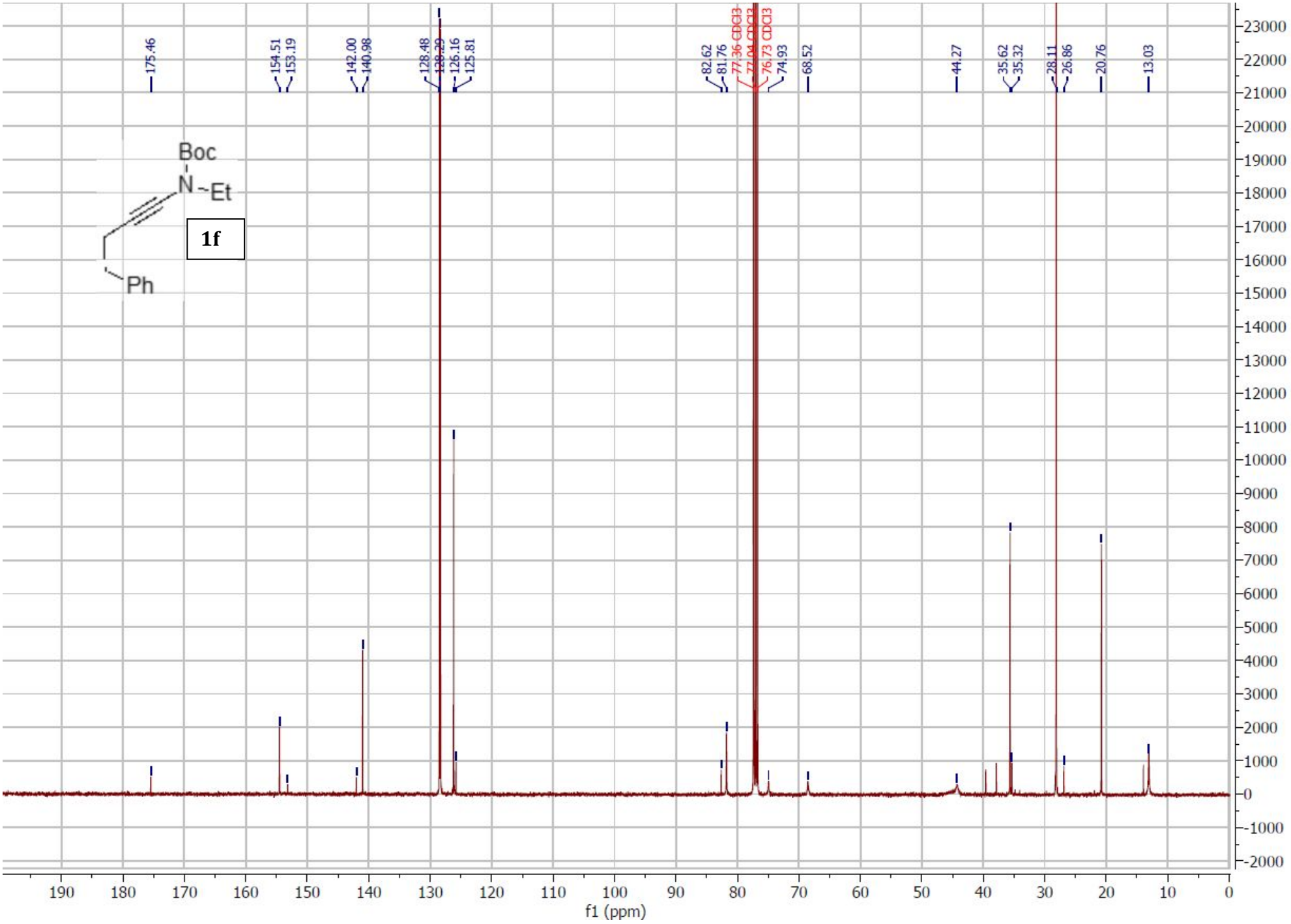
^{13}C NMR of compound **1e** (101 MHz, $CDCl_3$):



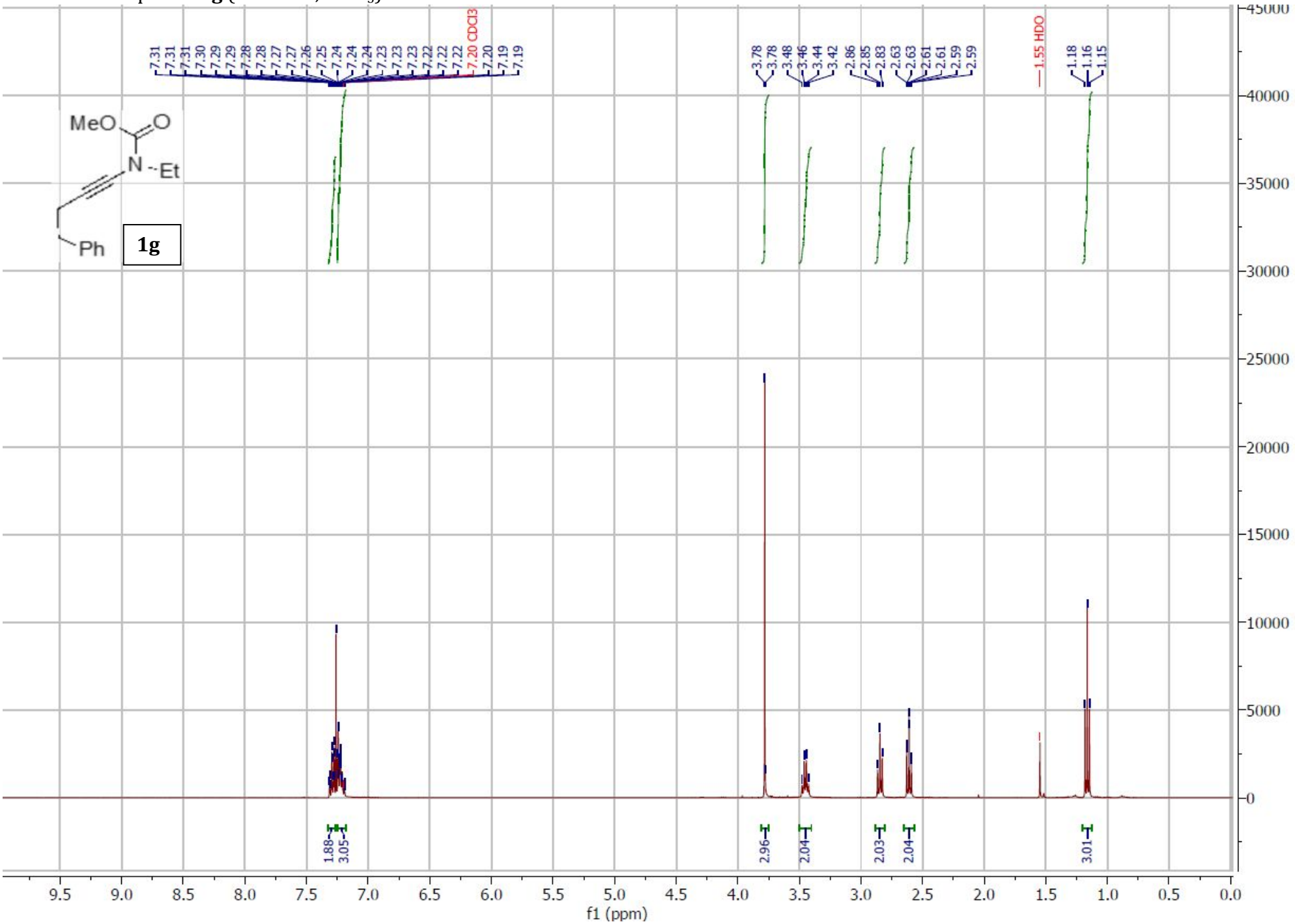
^{1}H NMR of compound **1f** (400 MHz, $CDCl_3$):



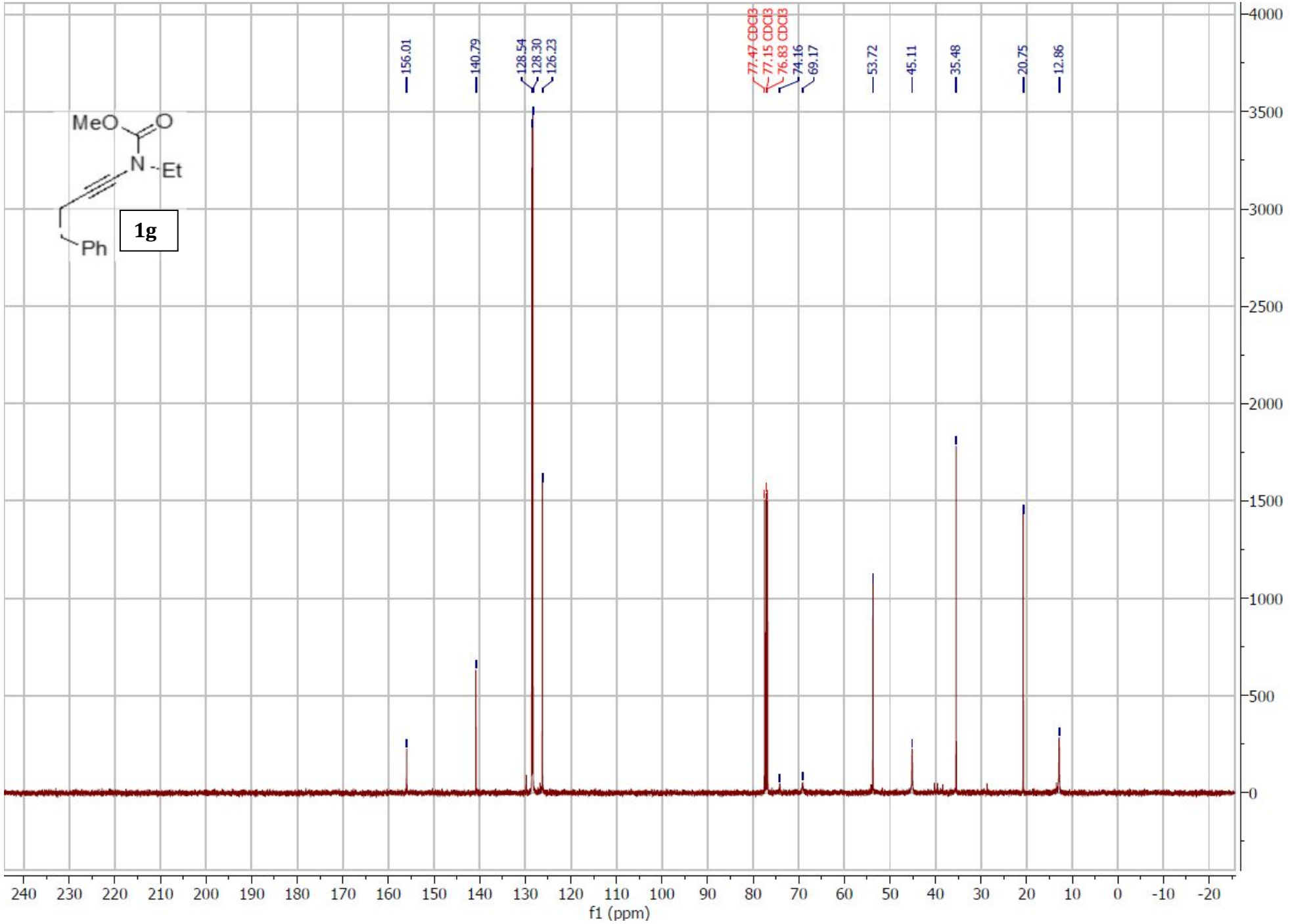
^{13}C NMR of compound **1f** (126 MHz, $CDCl_3$):



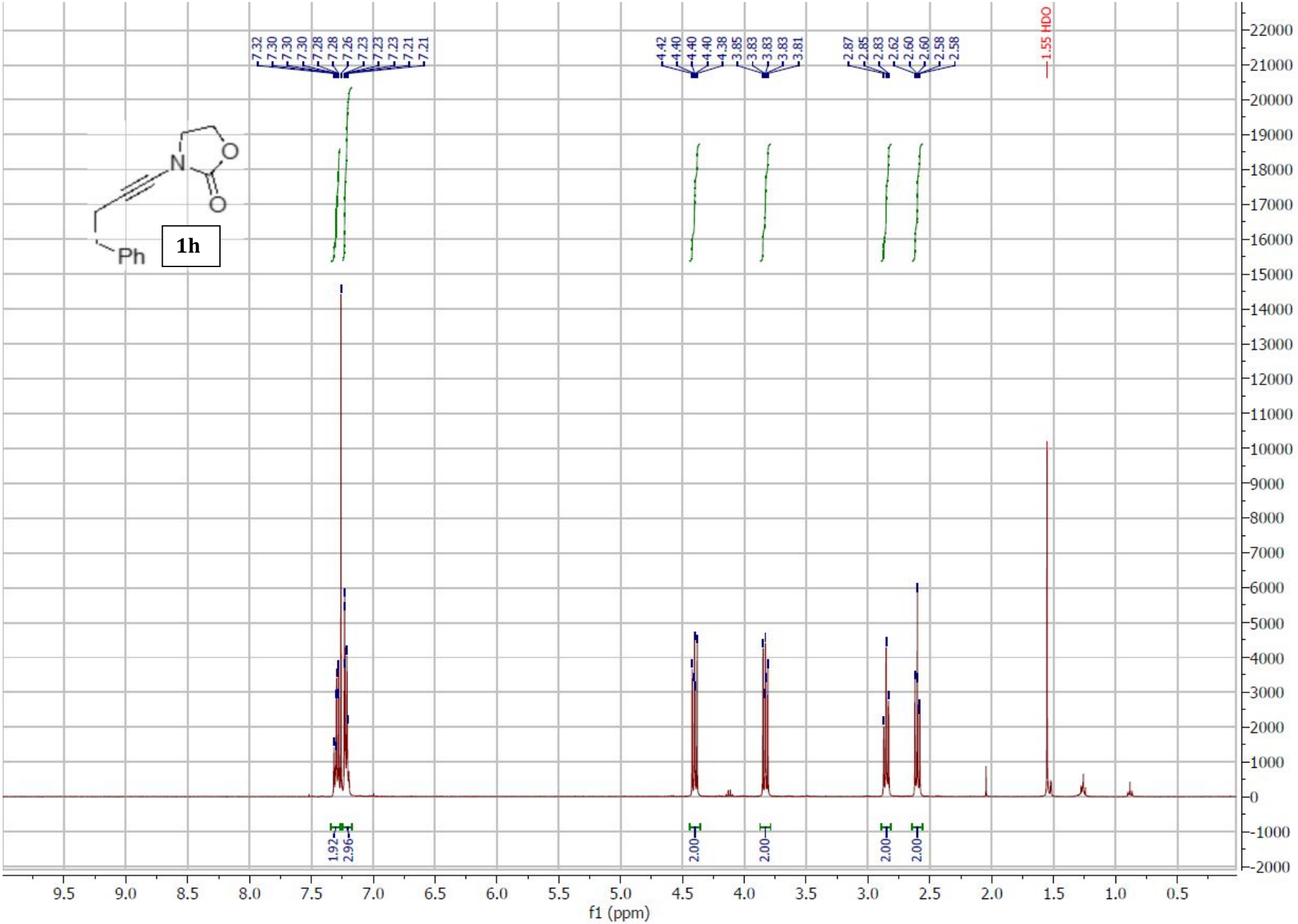
^{1}H NMR of compound **1g** (400 MHz, $CDCl_3$):



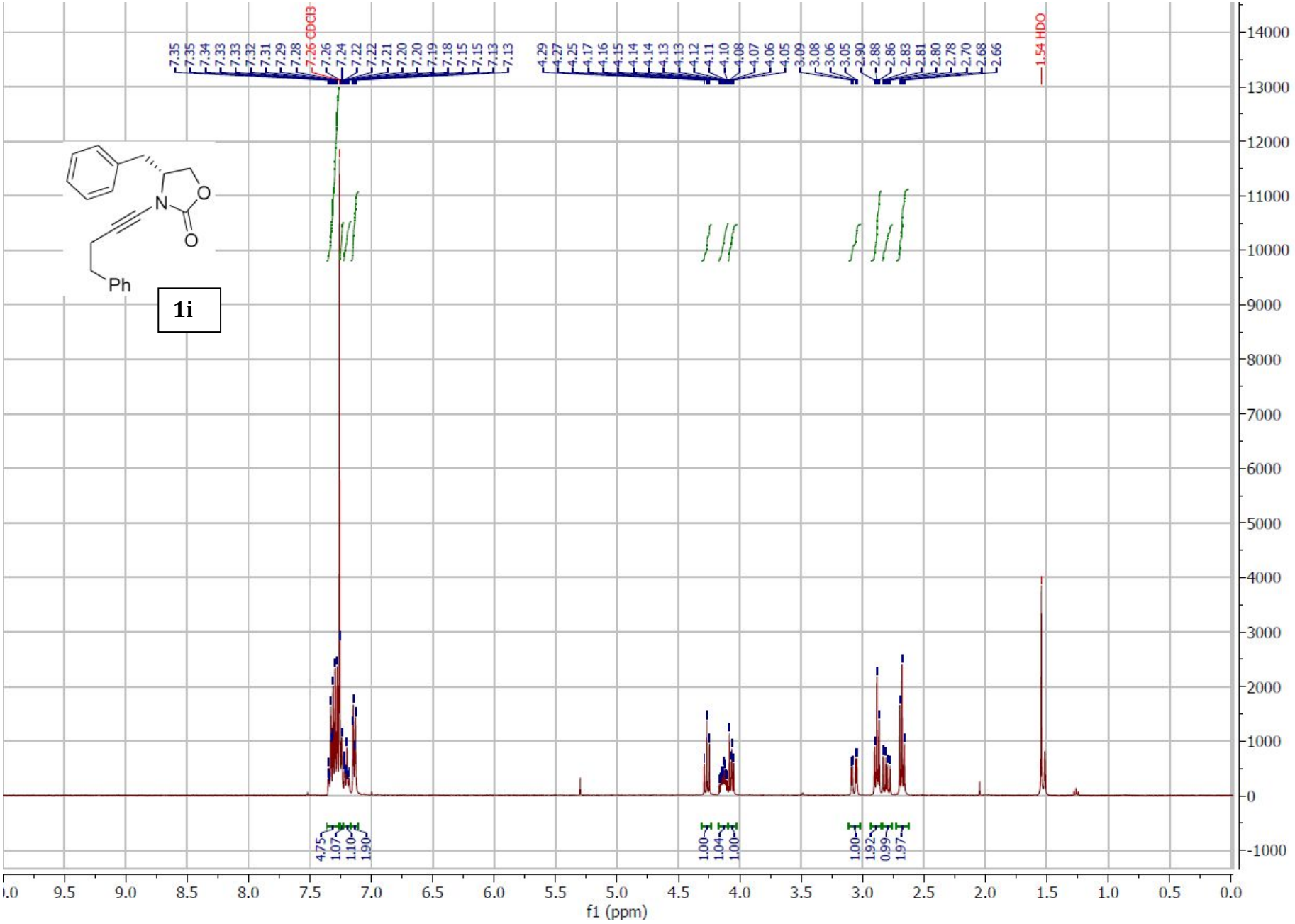
^{13}C NMR of compound **1g** (126 MHz, $CDCl_3$):



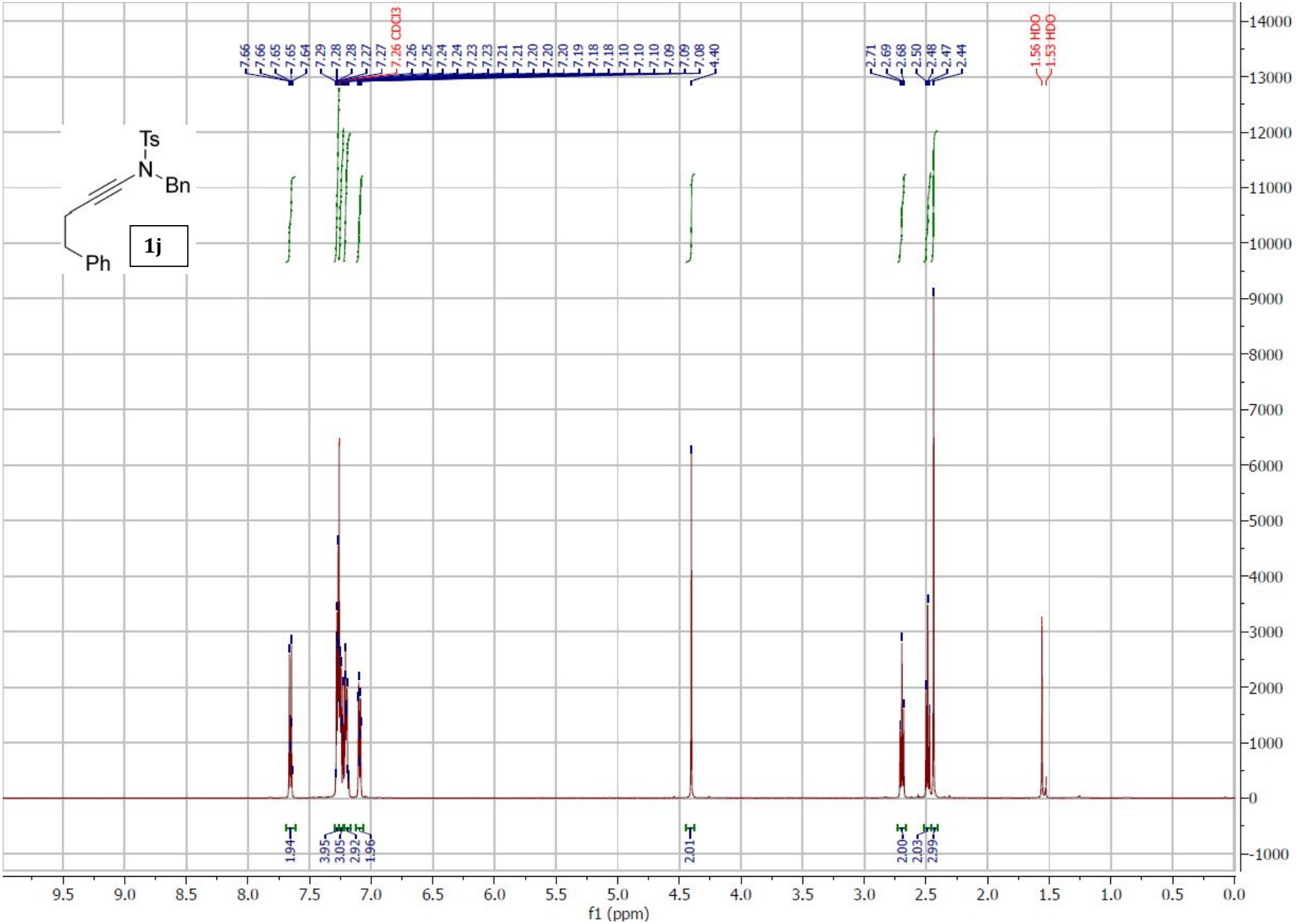
^{1}H NMR of compound **1h** (400 MHz, $CDCl_3$):



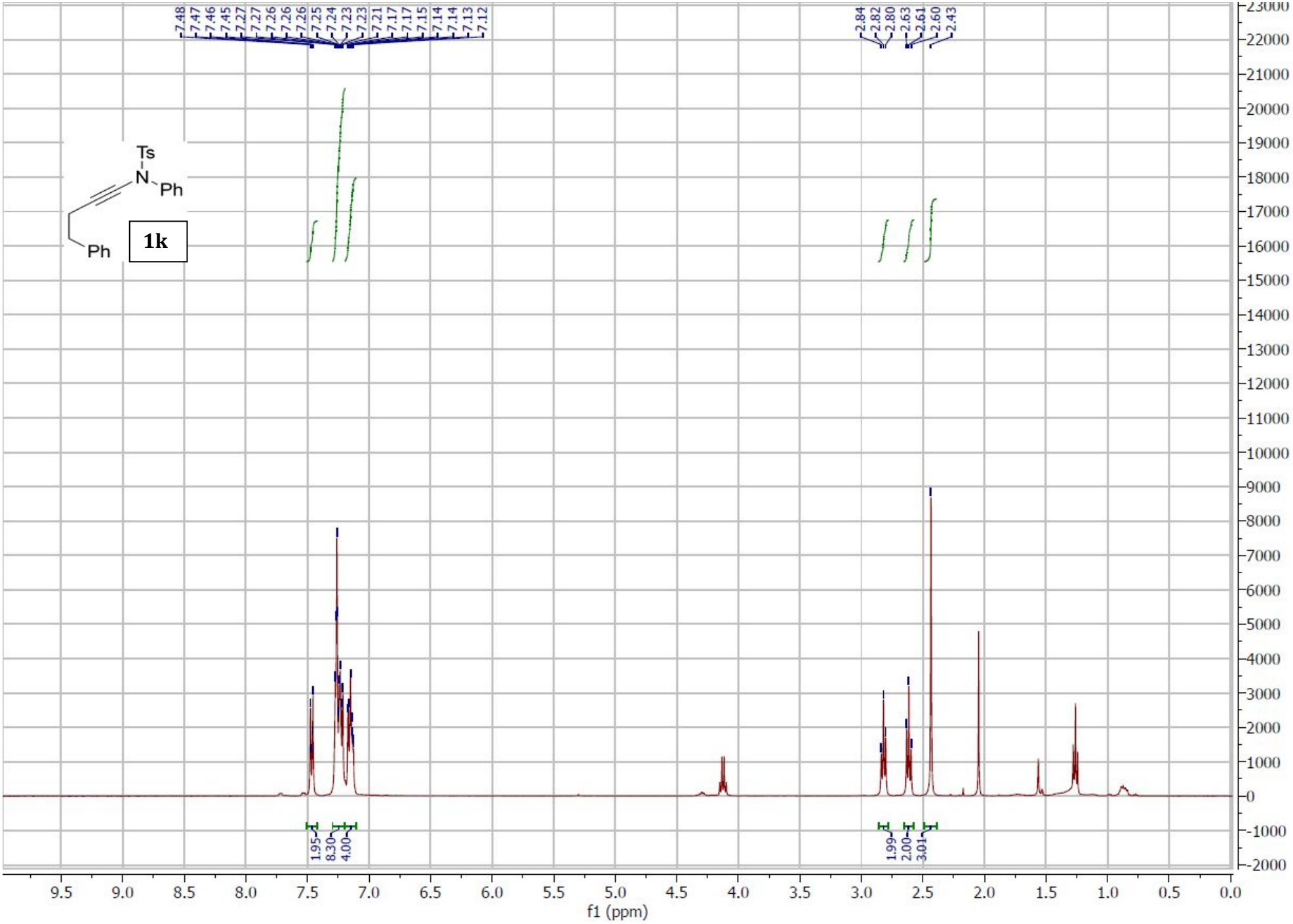
^{1}H NMR of compound **1i** (400 MHz, $CDCl_3$):



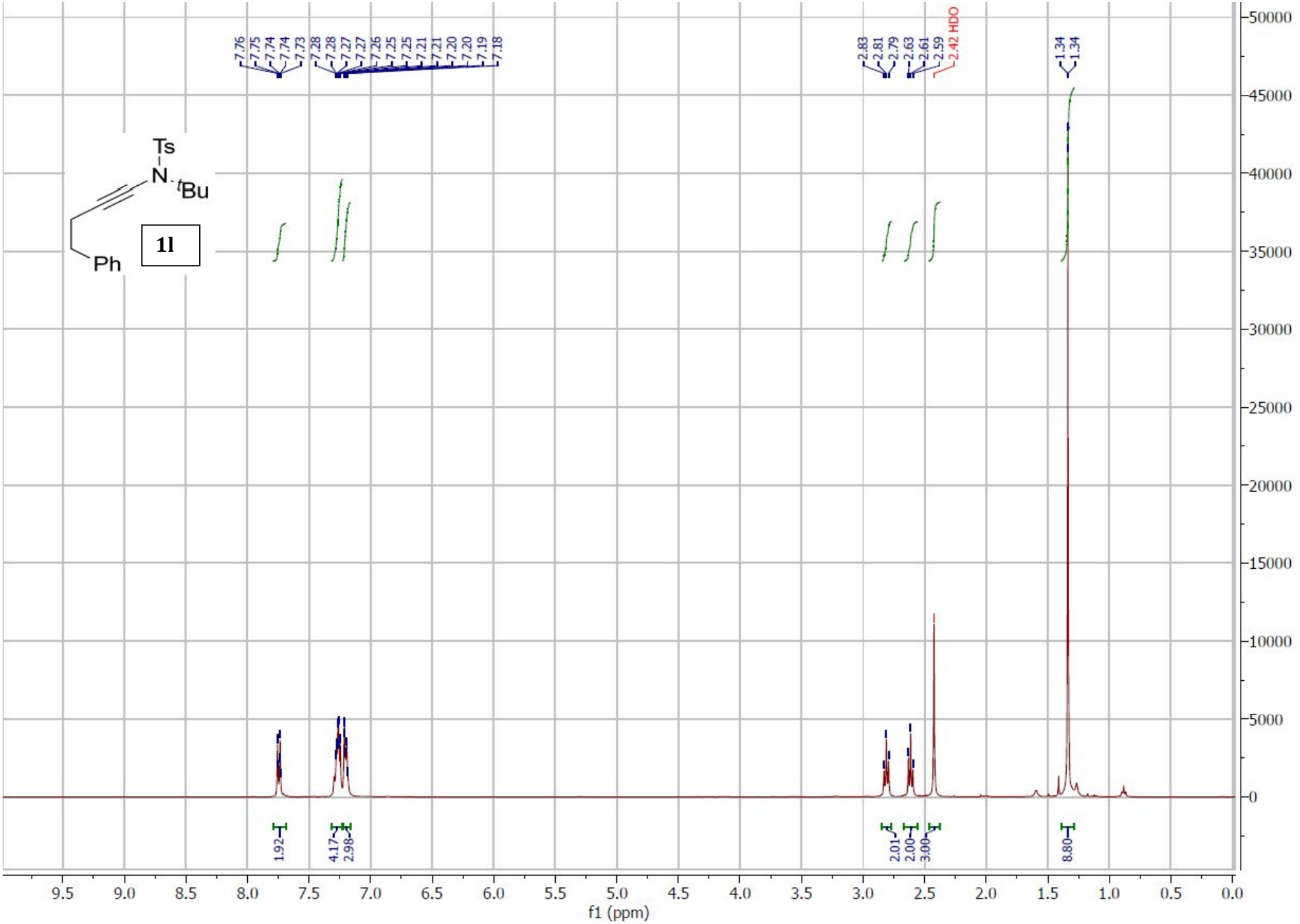
^{1}H NMR of compound **1j** (500 MHz, $CDCl_3$):



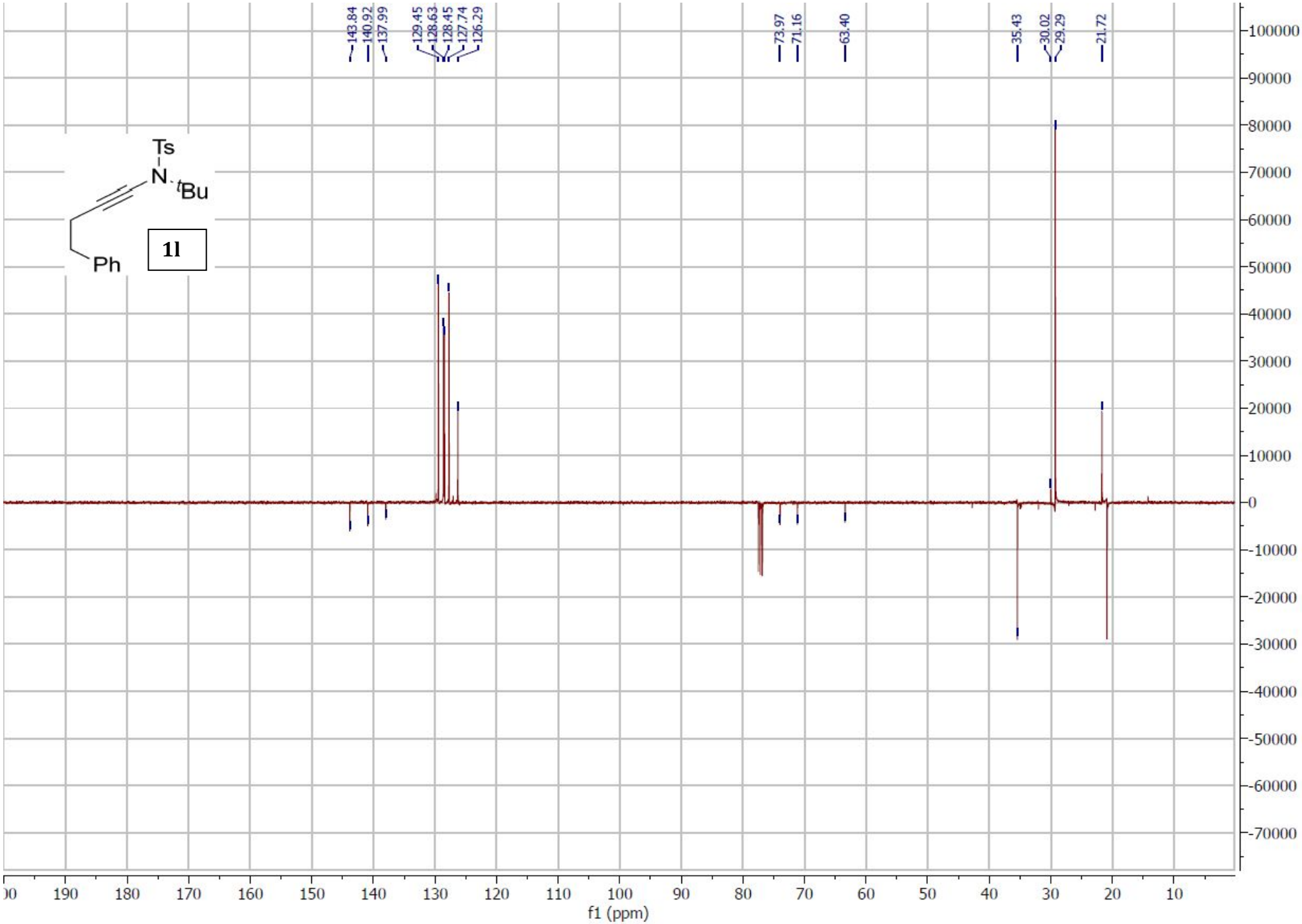
^{1}H NMR of compound **1k** (400 MHz, $CDCl_3$):



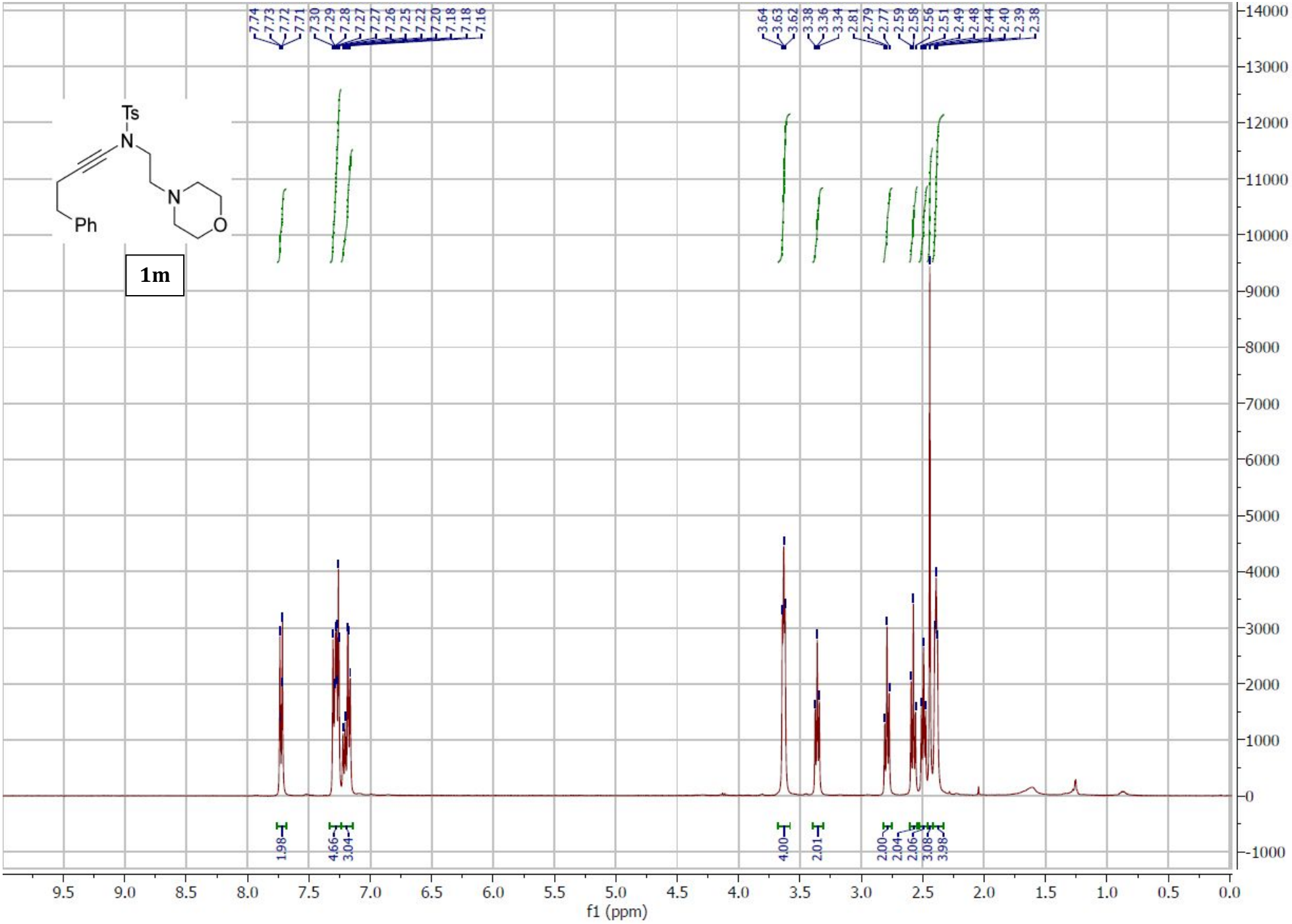
^{1}H NMR of compound **1l** (400 MHz, $CDCl_3$):



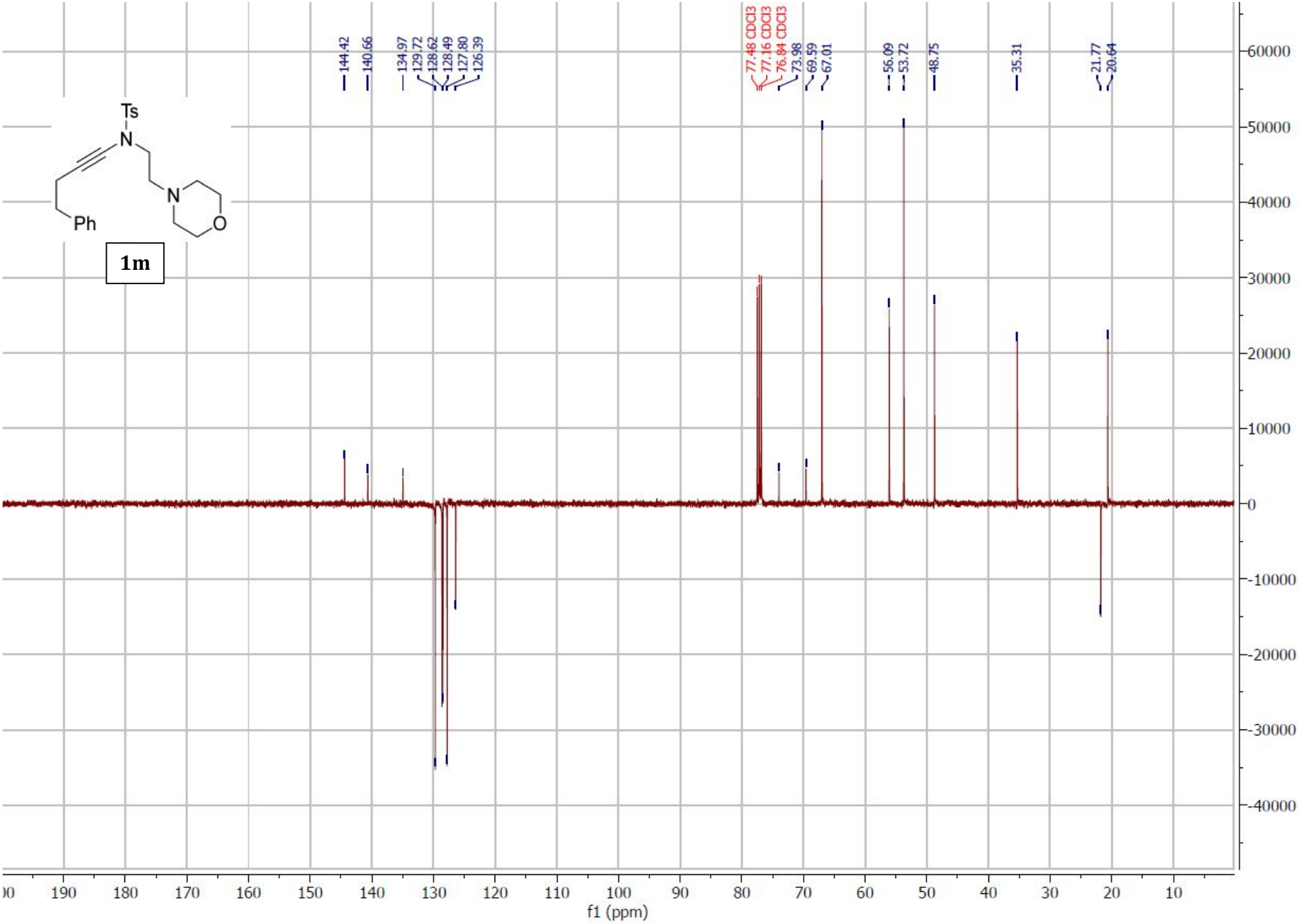
^{13}C NMR of compound **1l** (101 MHz, $CDCl_3$):



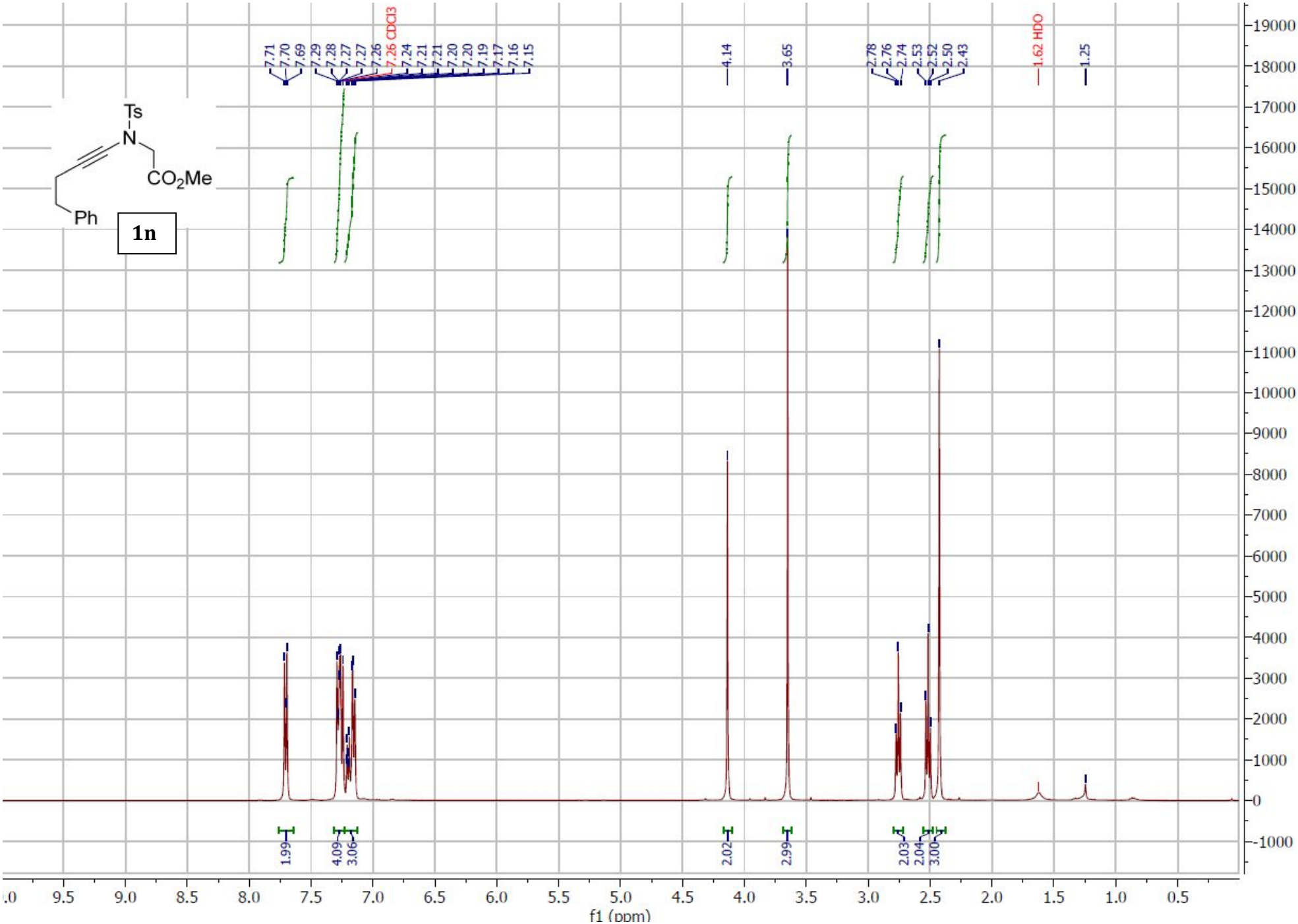
^{1}H NMR of compound **1m** (400 MHz, $CDCl_3$):



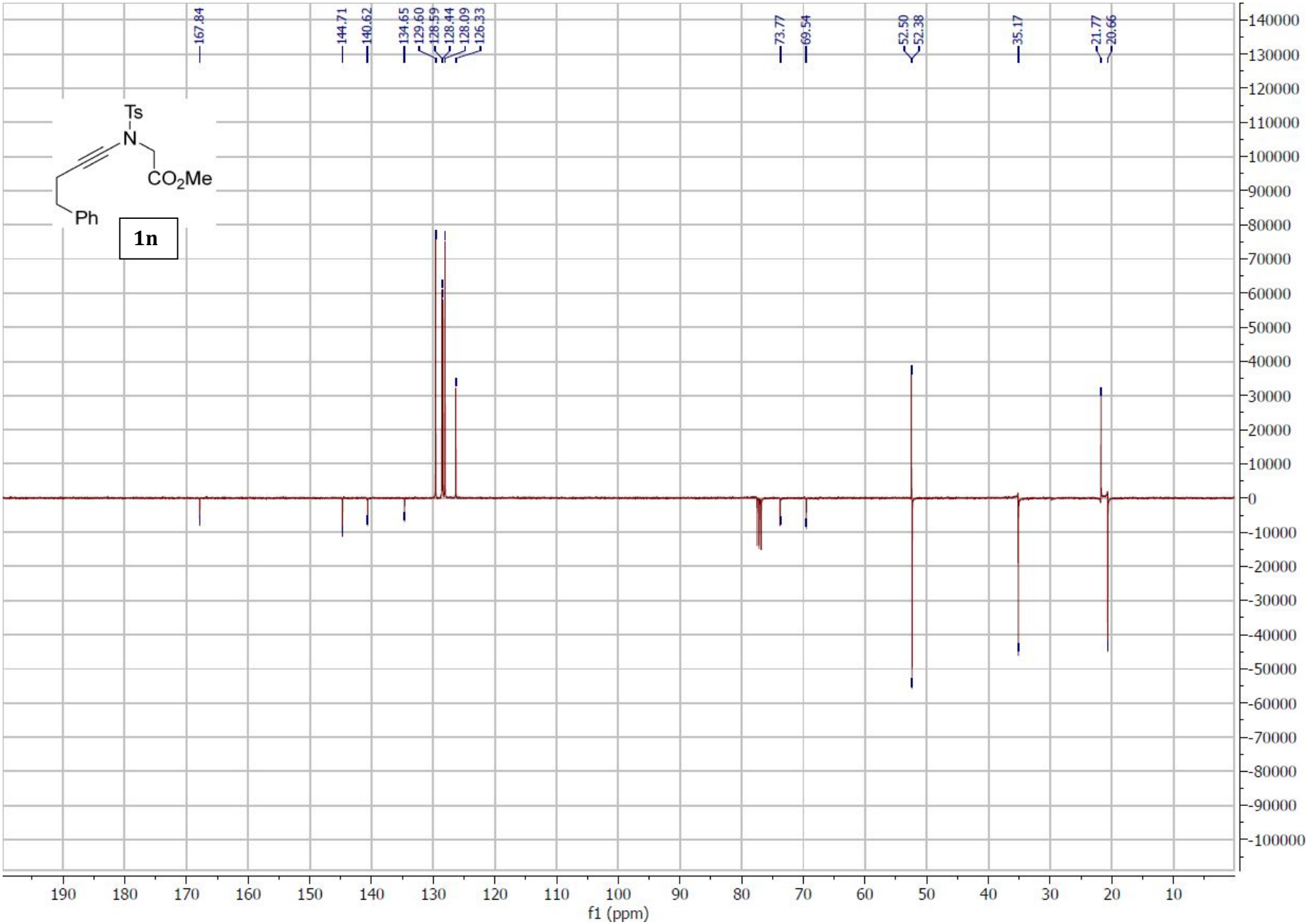
^{13}C NMR of compound **1m** (101 MHz, $CDCl_3$):



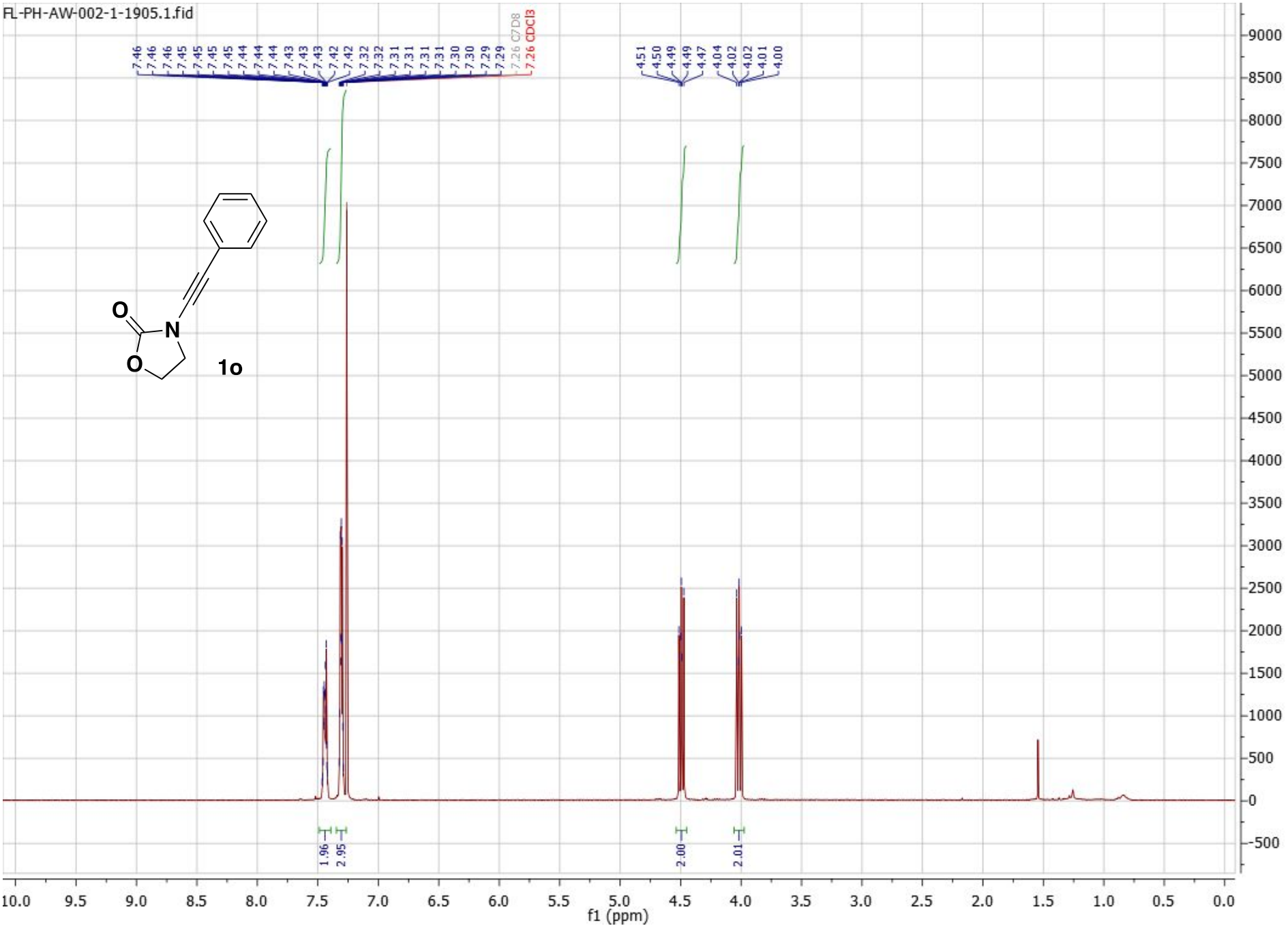
^{1}H NMR of compound **1n** (400 MHz, $CDCl_3$):



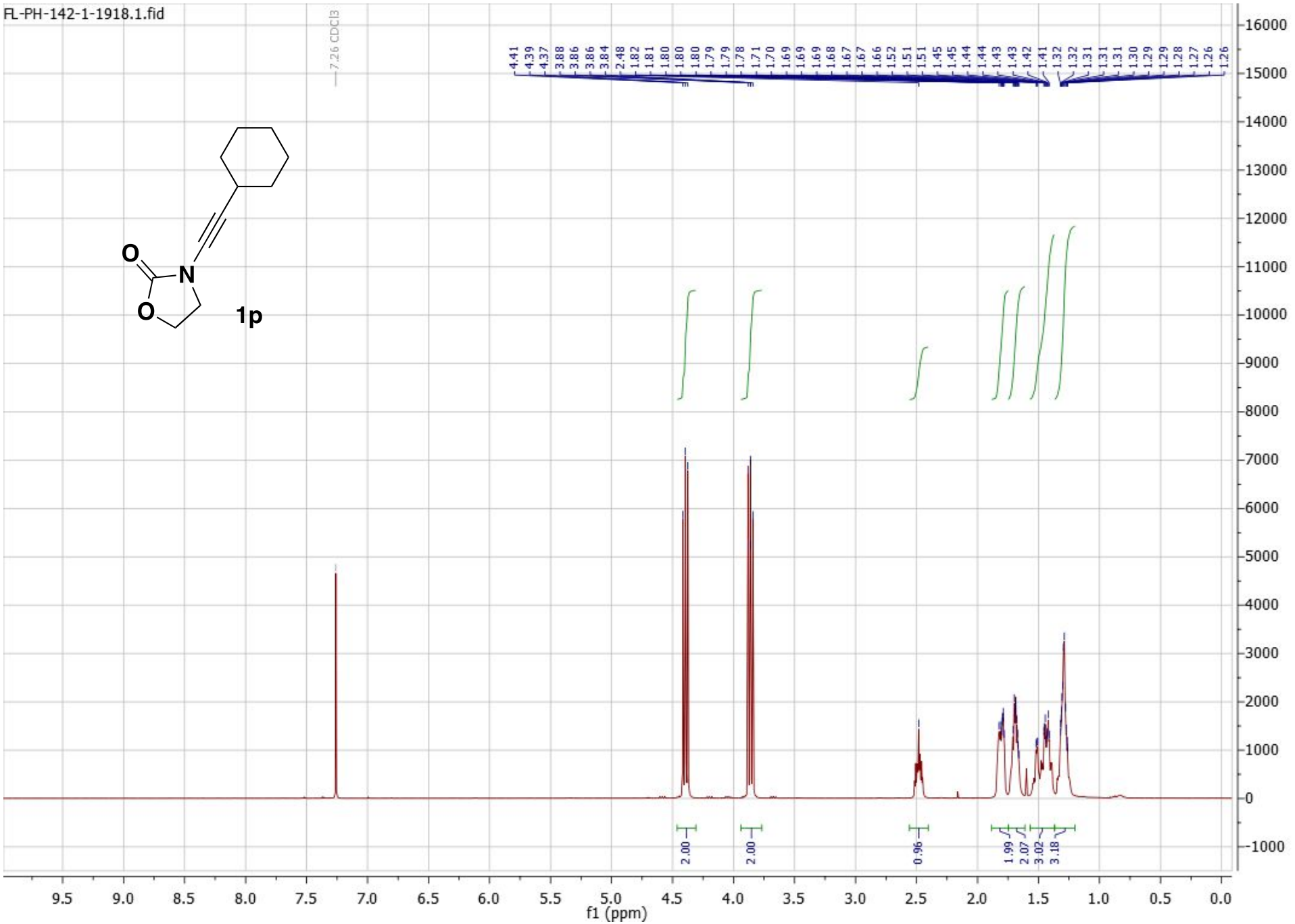
^{13}C NMR of compound **1n** (101 MHz, $CDCl_3$):



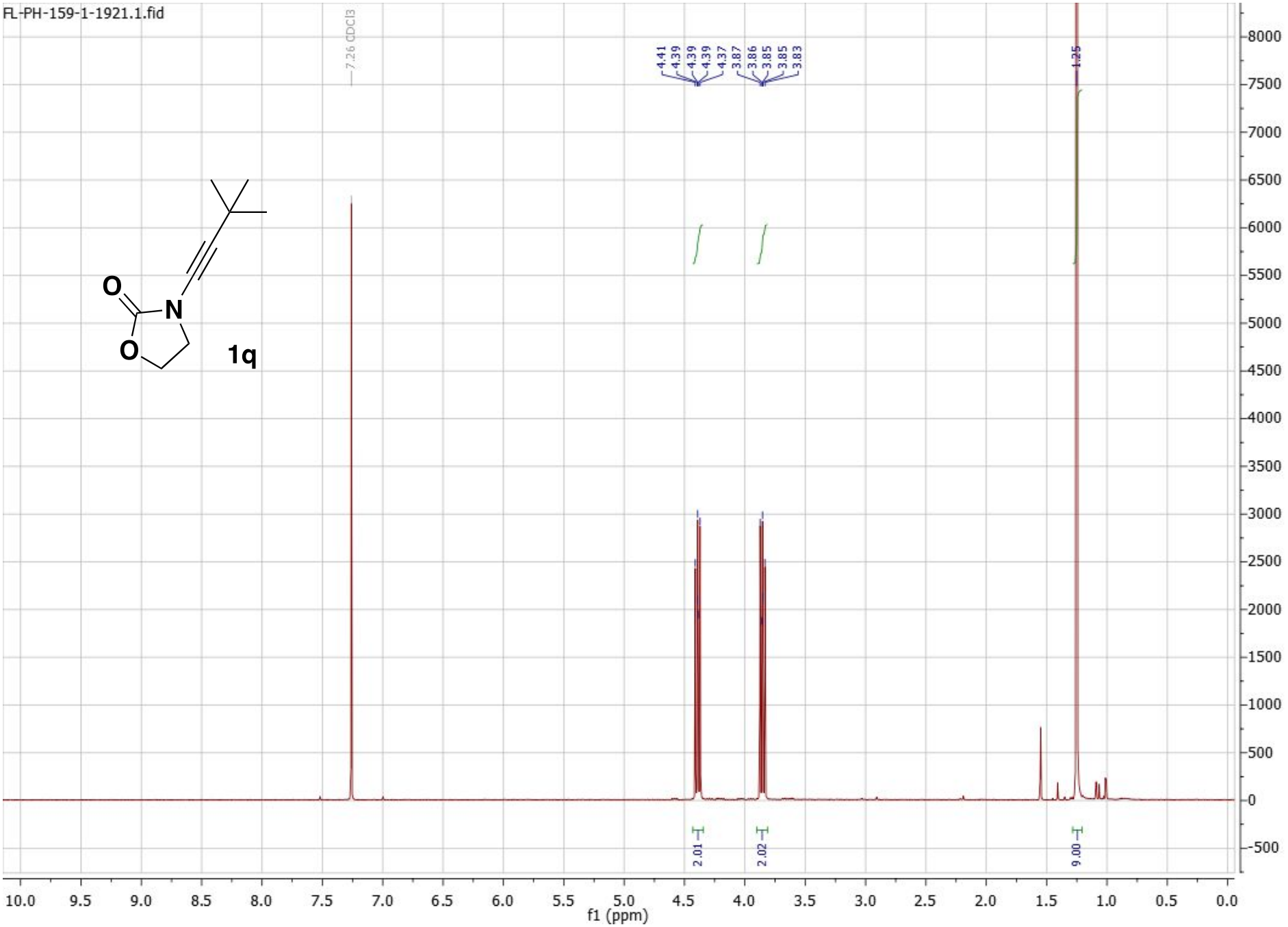
^{1}H NMR of compound **1o** (400 MHz, $CDCl_3$):



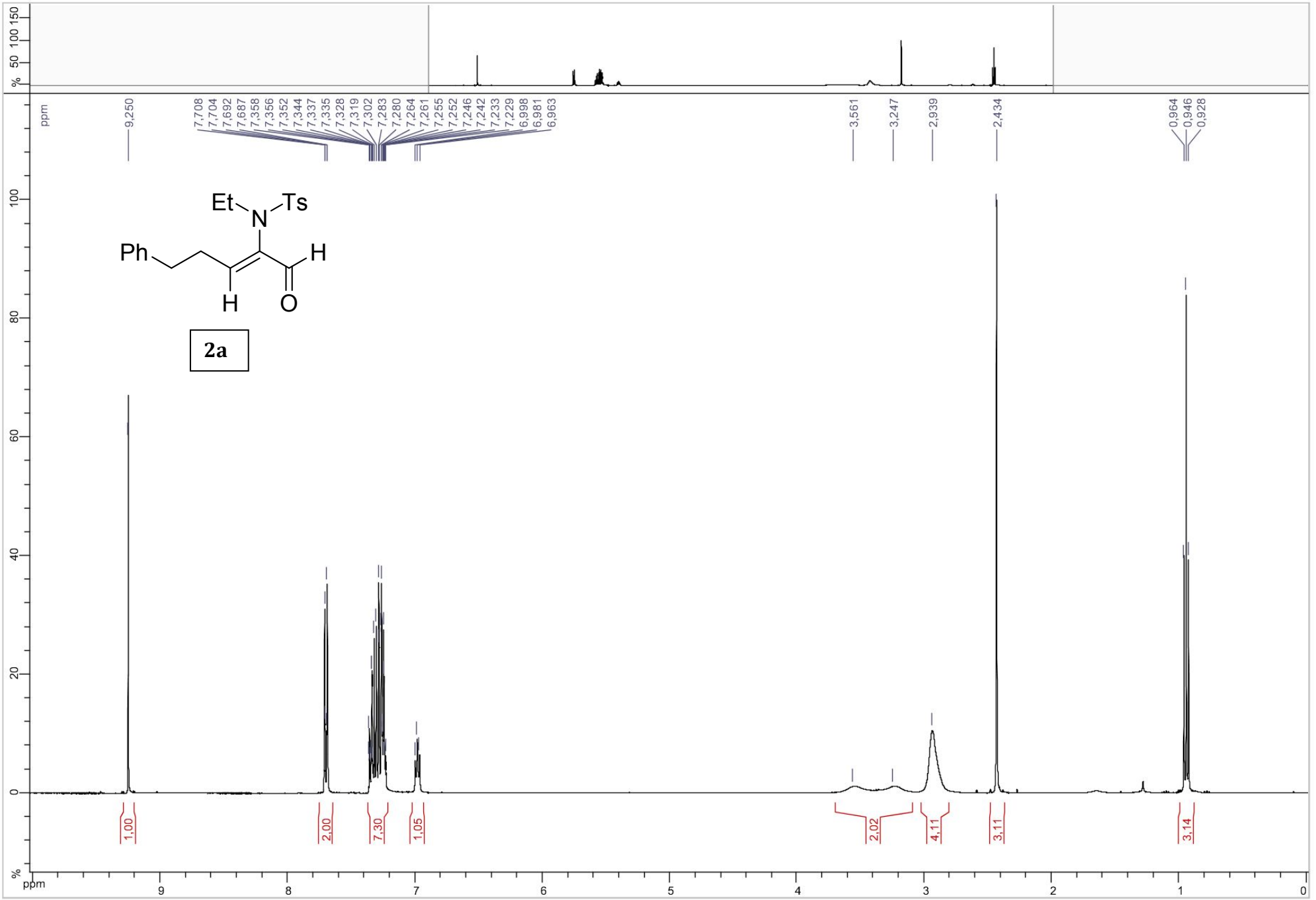
^{1}H NMR of compound **1p** (400 MHz, $CDCl_3$):



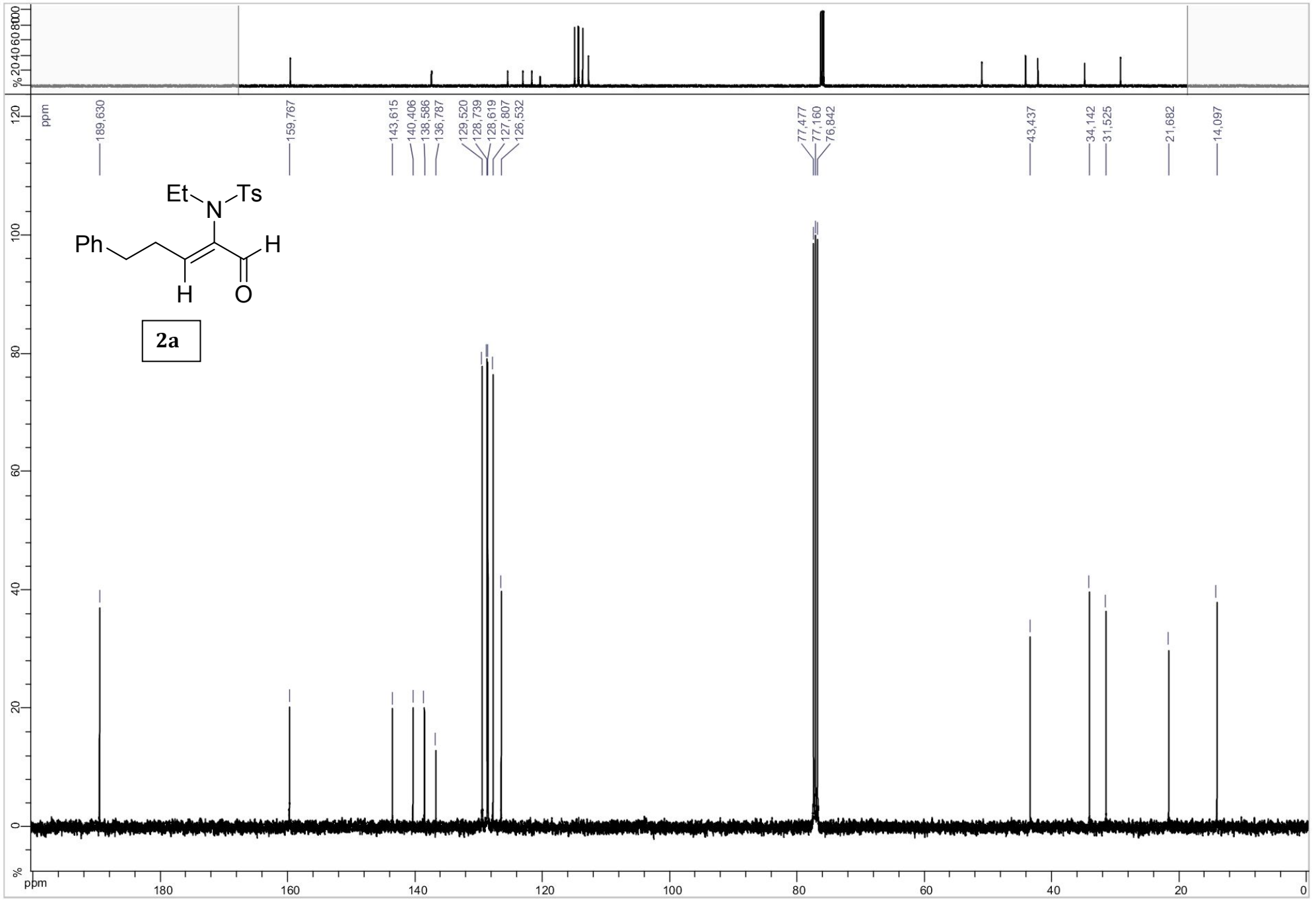
^{1}H NMR of compound **1q** (400 MHz, $CDCl_3$):



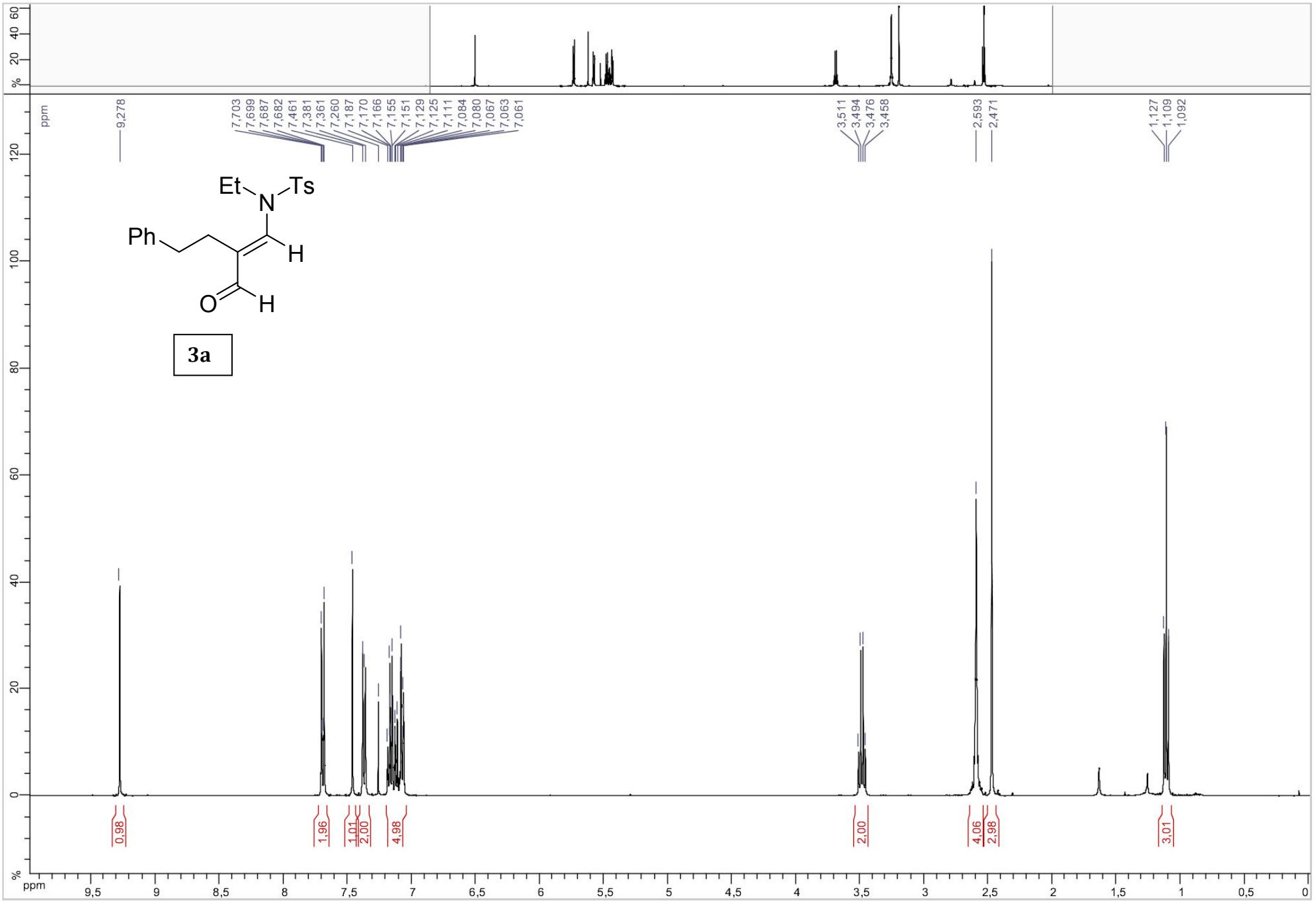
^{1}H NMR of compound **2a** (400 MHz, $CDCl_3$):



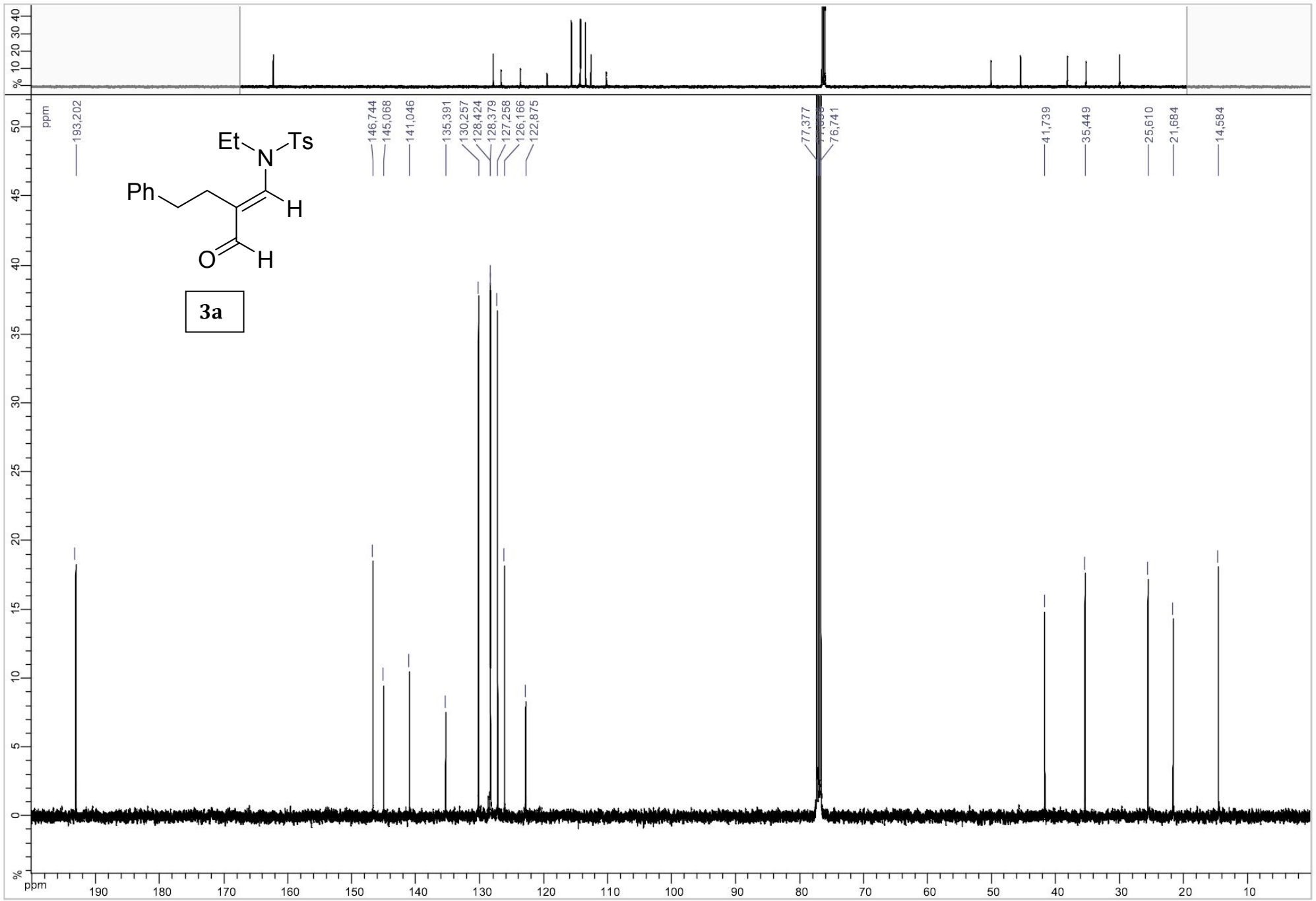
^{13}C NMR of compound **2a** (101 MHz, $CDCl_3$):



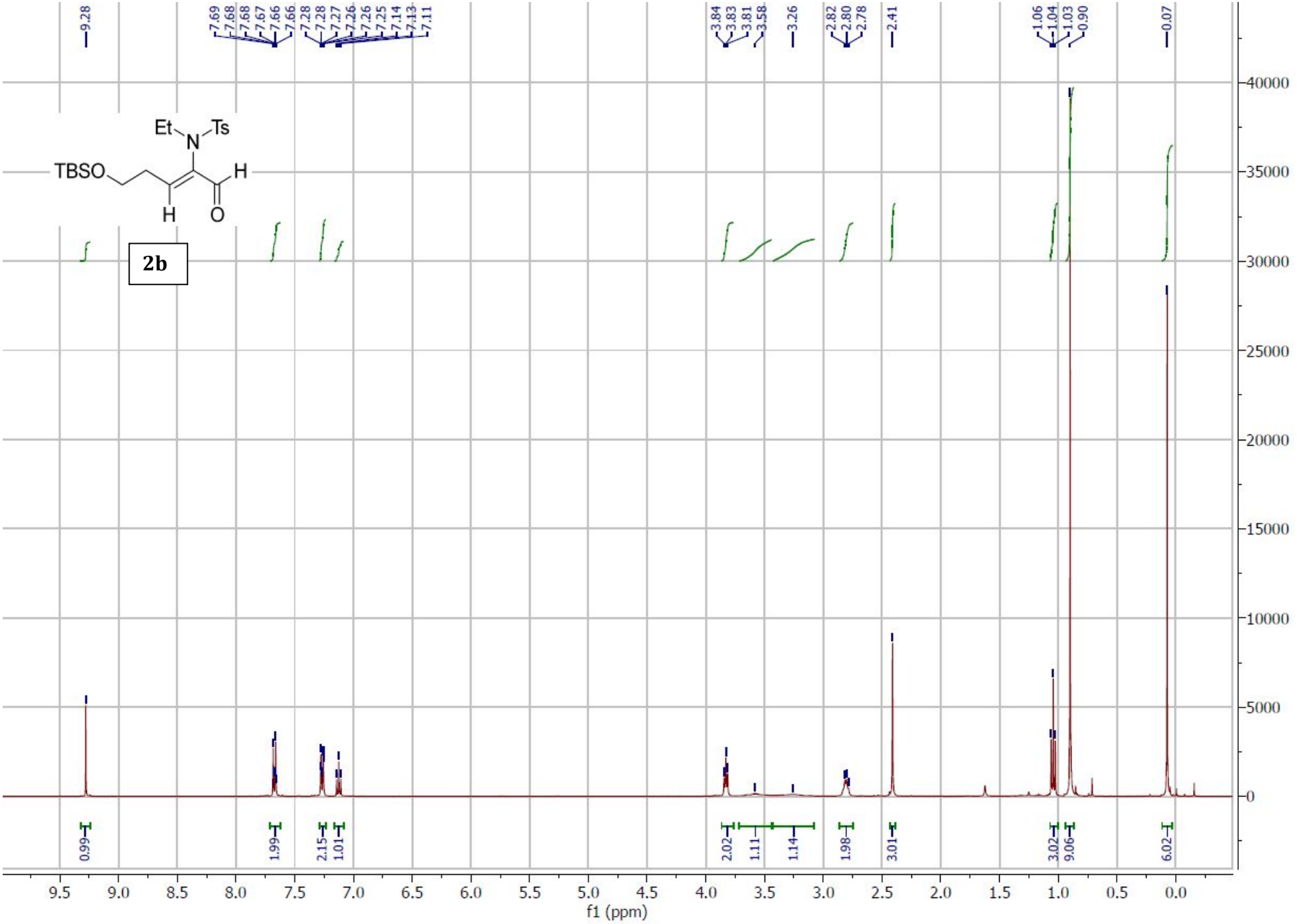
^{1}H NMR of compound **3a** (400 MHz, $CDCl_3$):



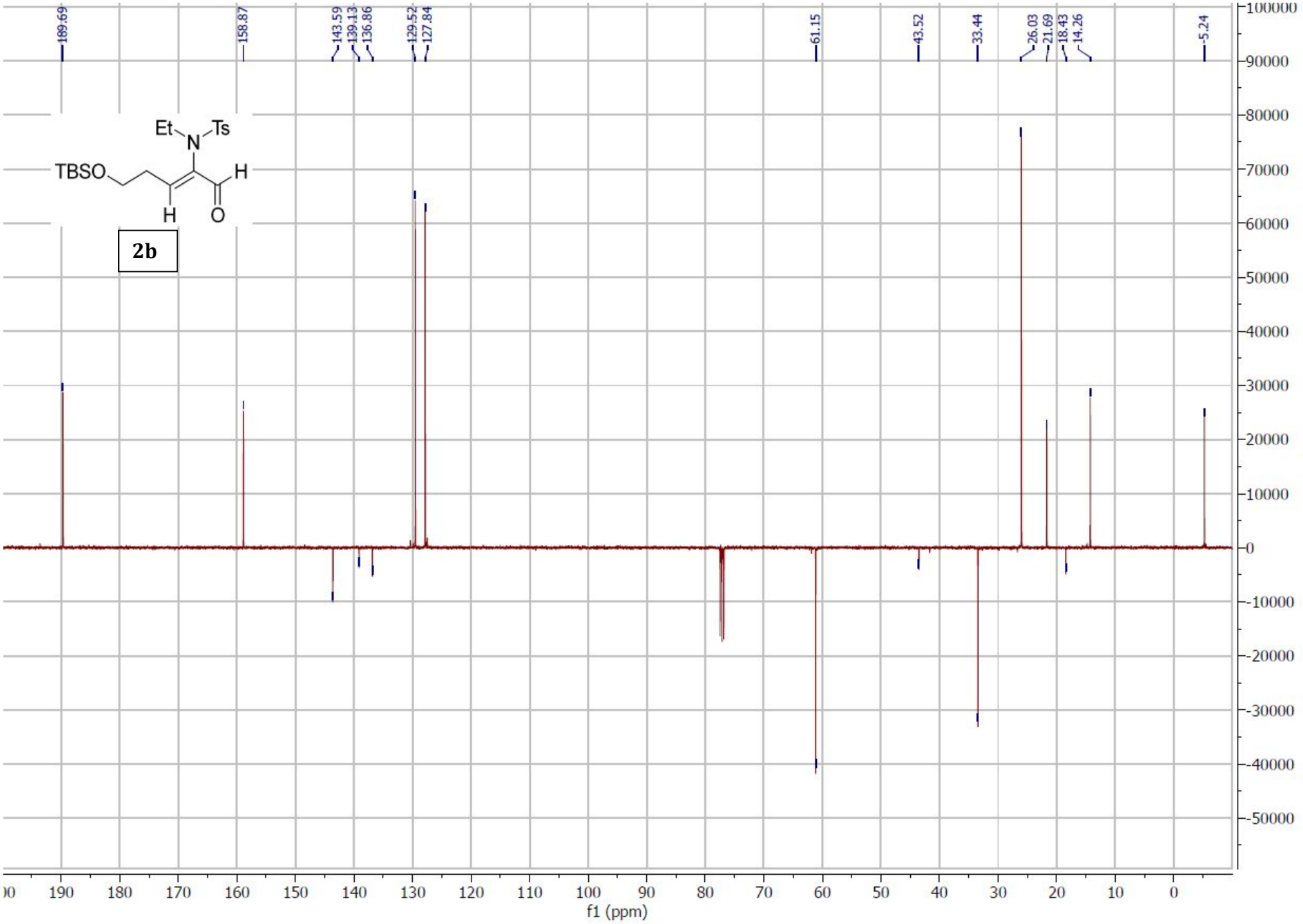
^{13}C NMR of compound **3a** (101 MHz, $CDCl_3$):



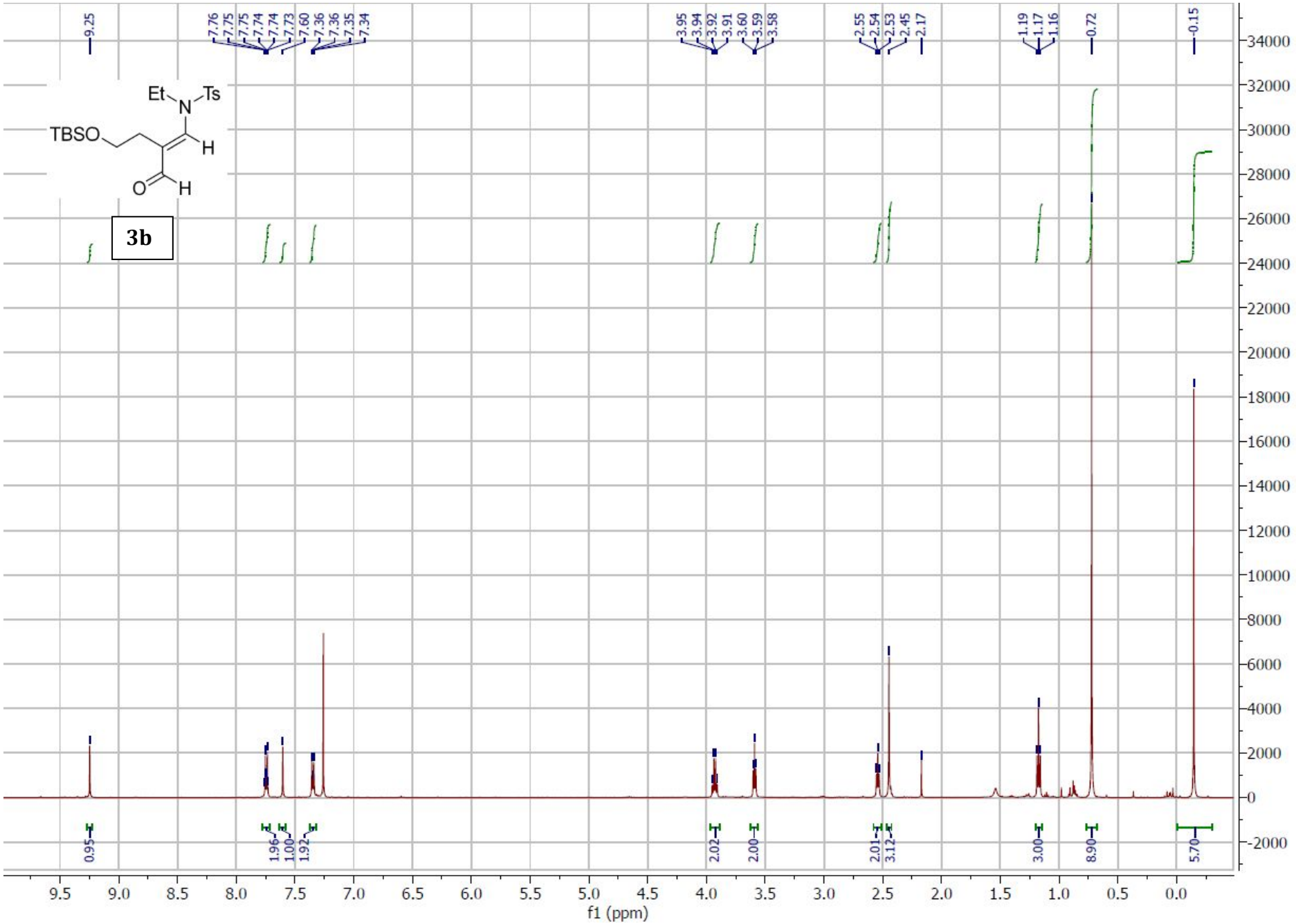
^{1}H NMR of compound **2b** (400 MHz, $CDCl_3$):



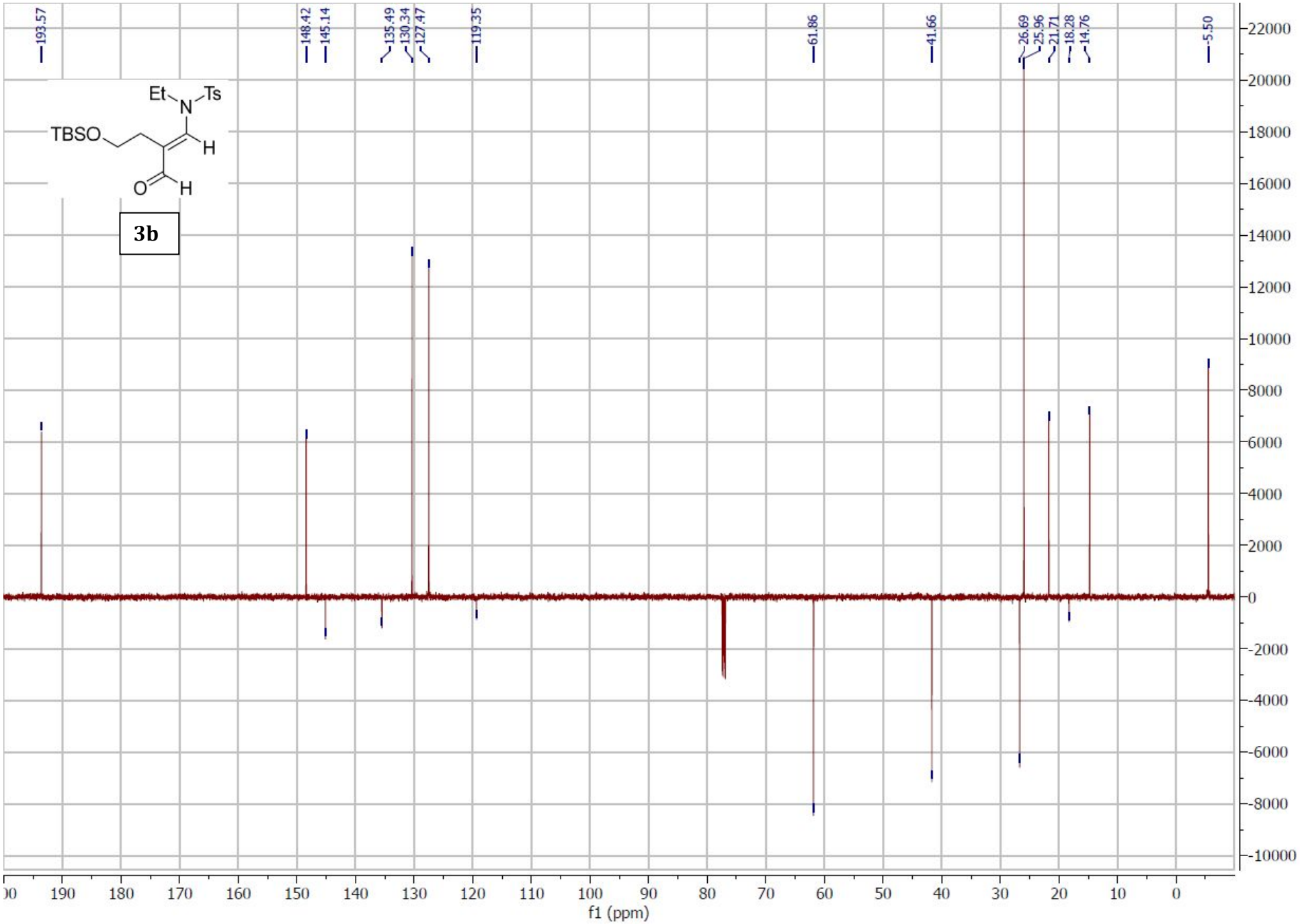
^{13}C NMR of compound **2b** (101 MHz, $CDCl_3$):



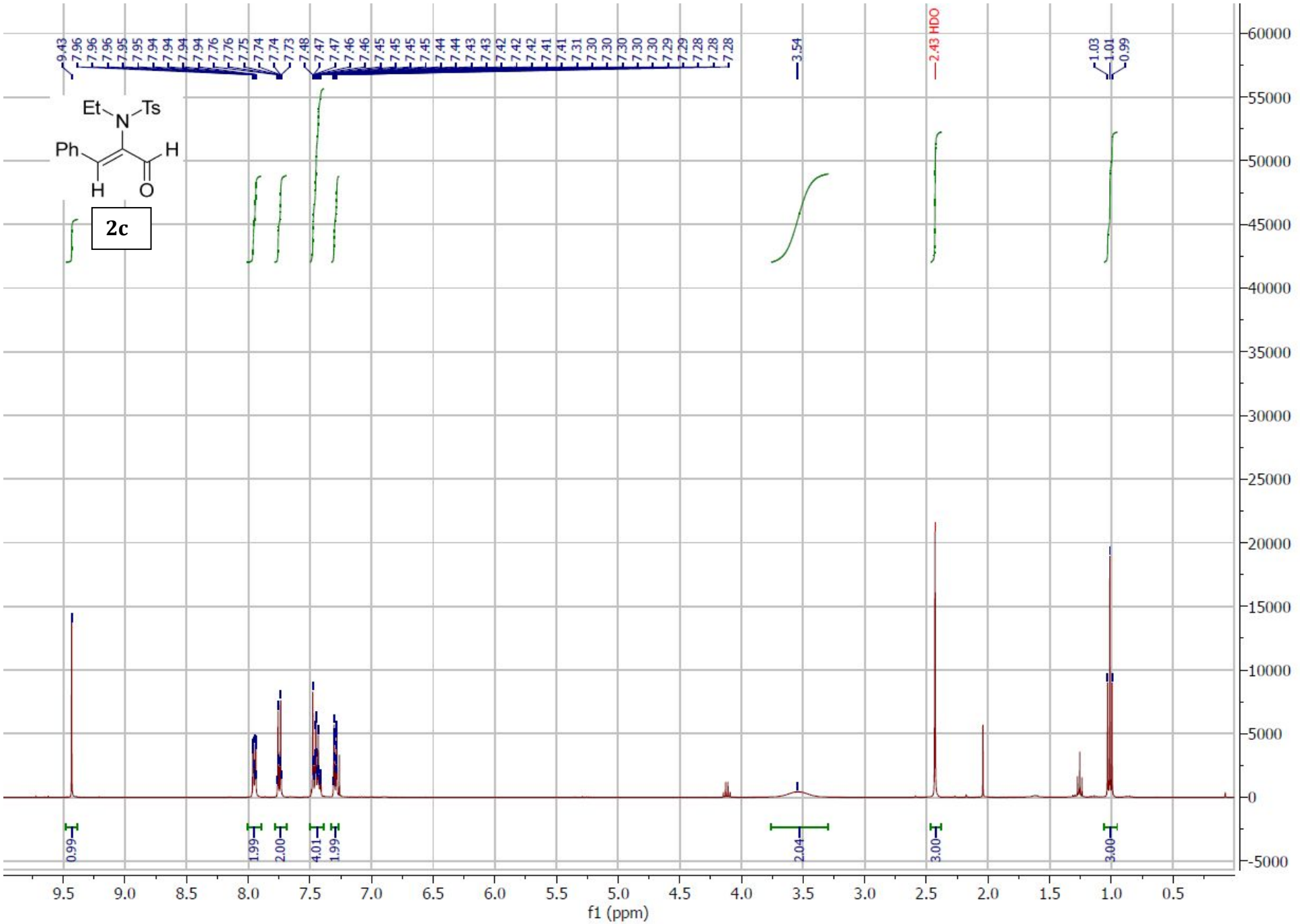
^{1}H NMR of compound **3b** (500 MHz, $CDCl_3$):



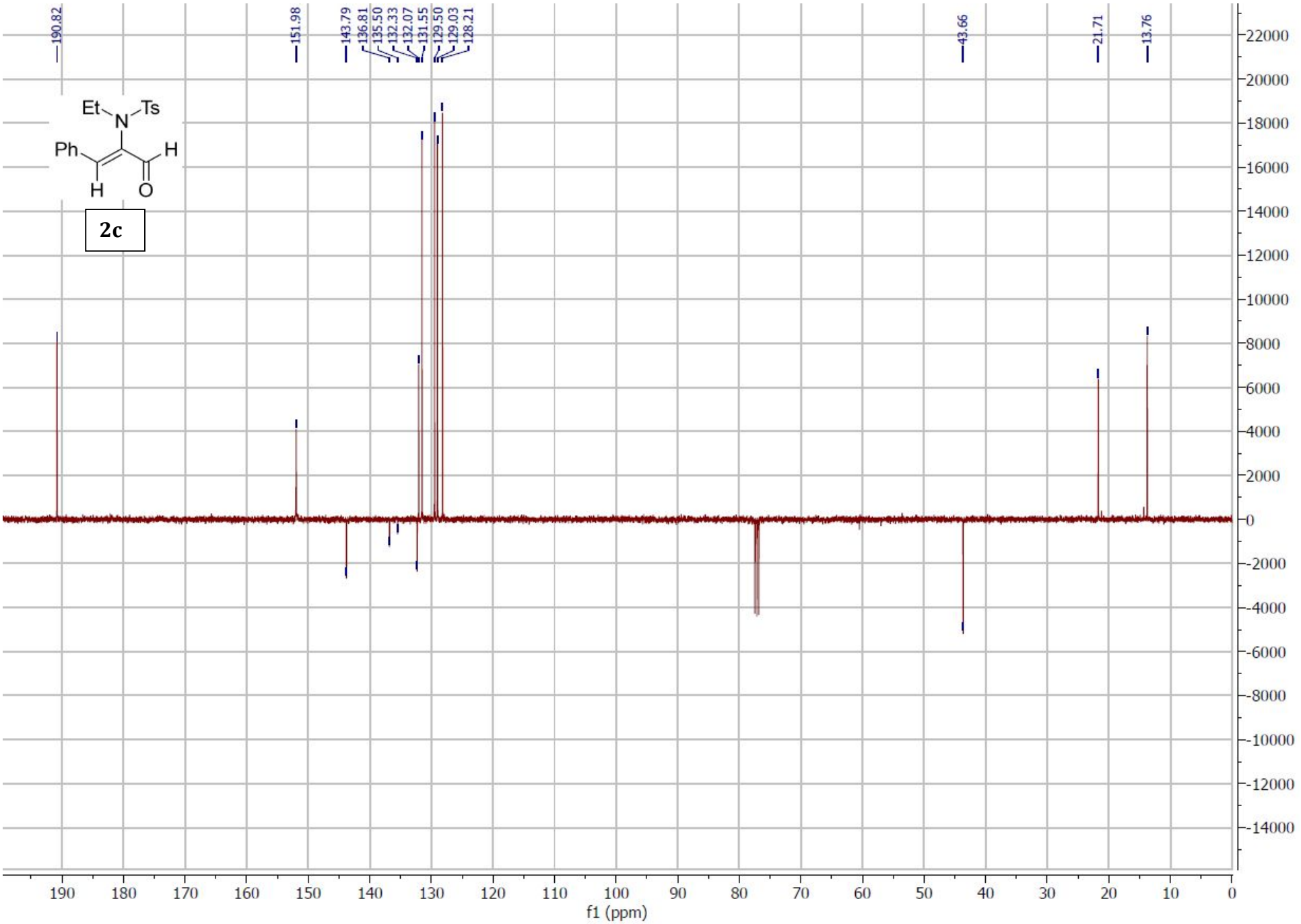
^{13}C NMR of compound **3b** (126 MHz, $CDCl_3$):



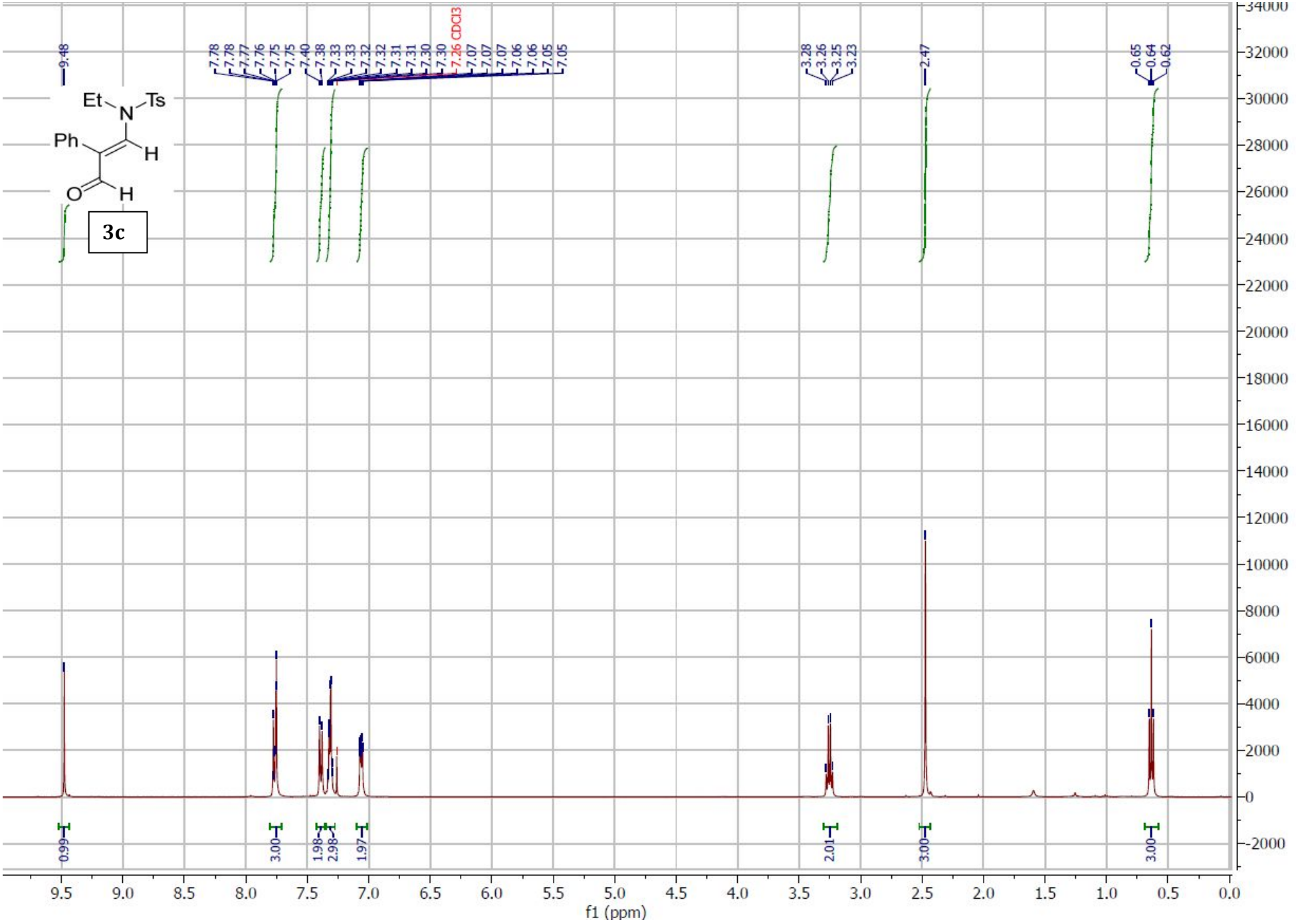
^{1}H NMR of compound **2c** (400 MHz, $CDCl_3$):



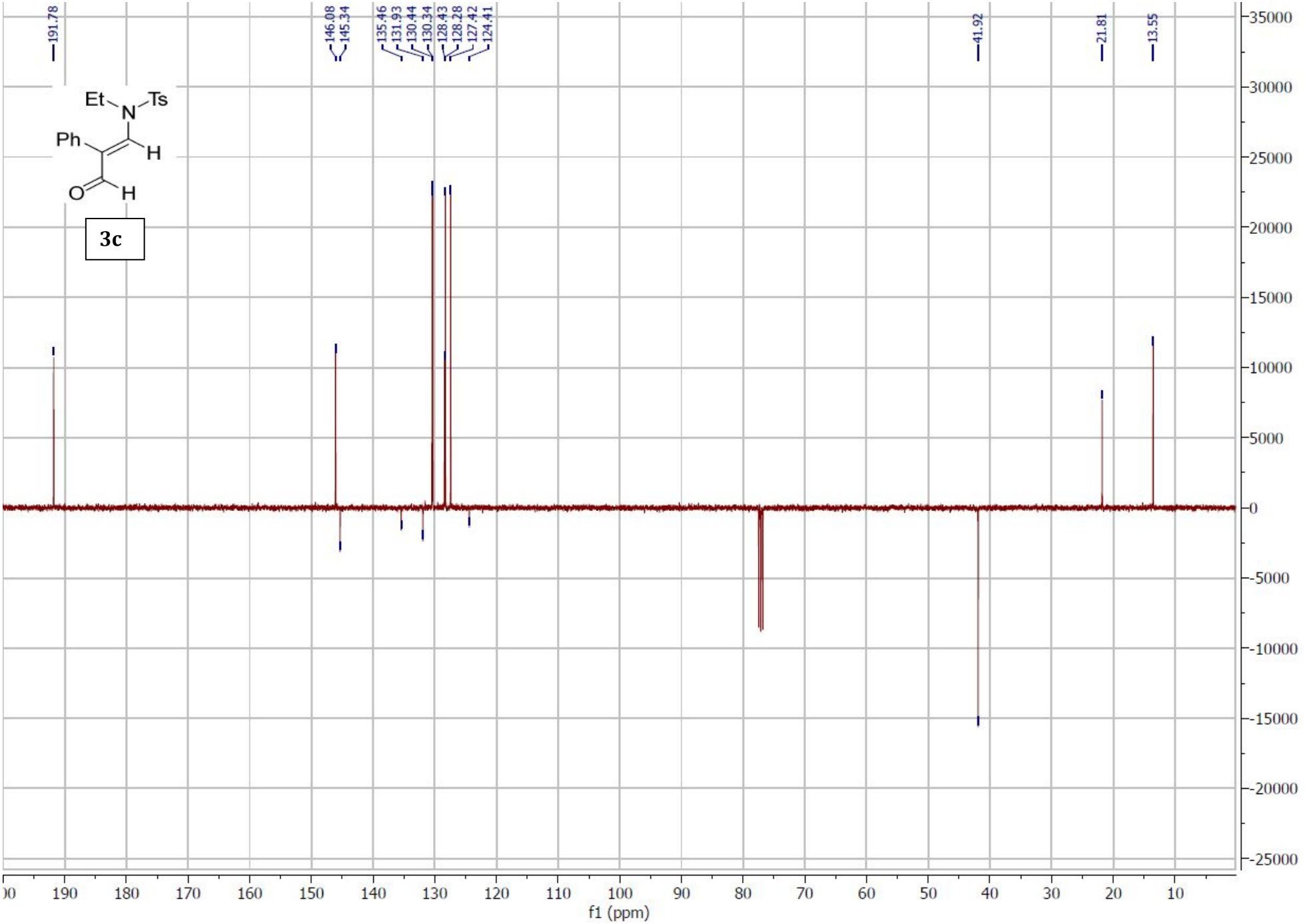
^{13}C NMR of compound **2c** (101 MHz, $CDCl_3$):



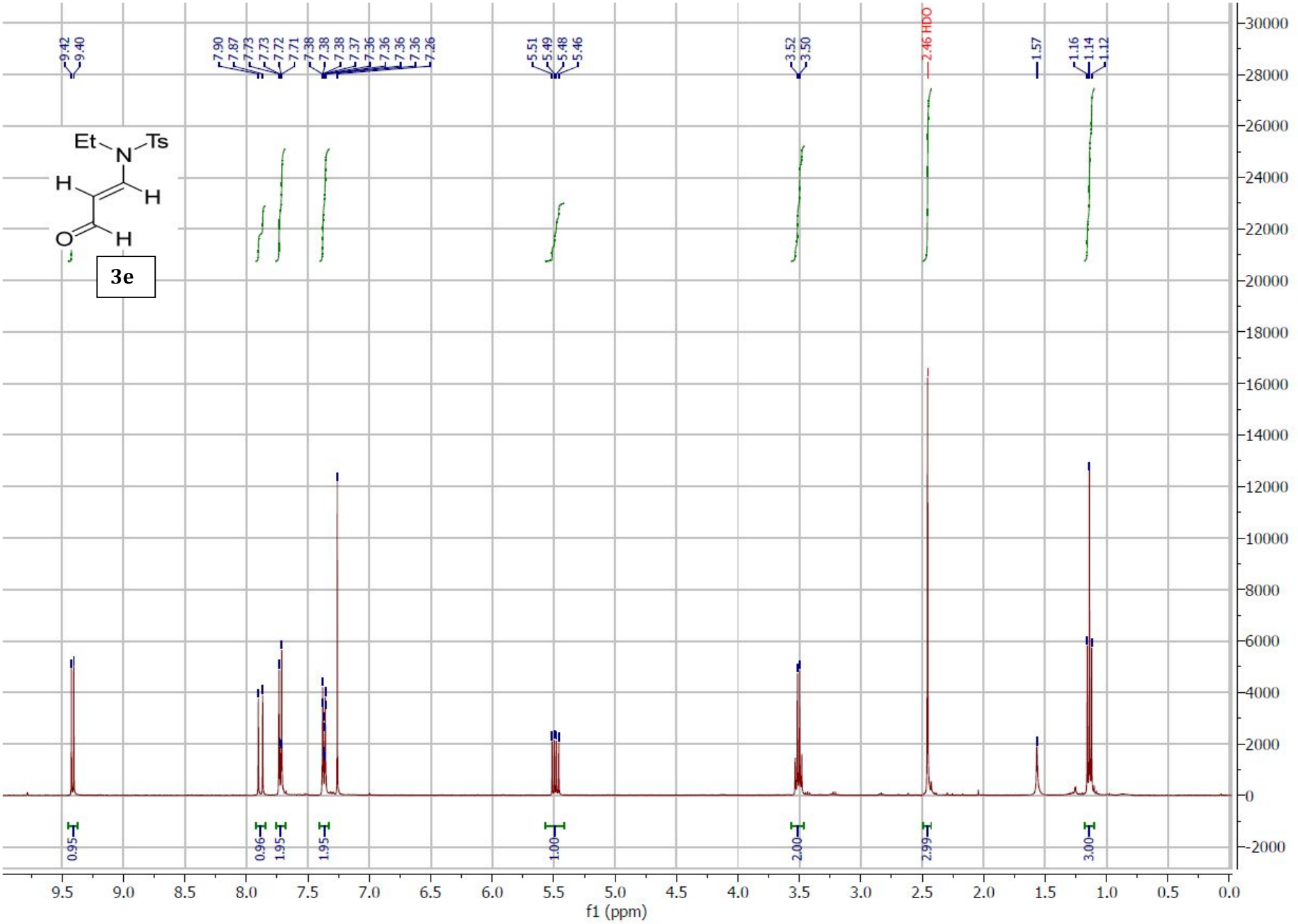
^{1}H NMR of compound **3c** (400 MHz, $CDCl_3$):



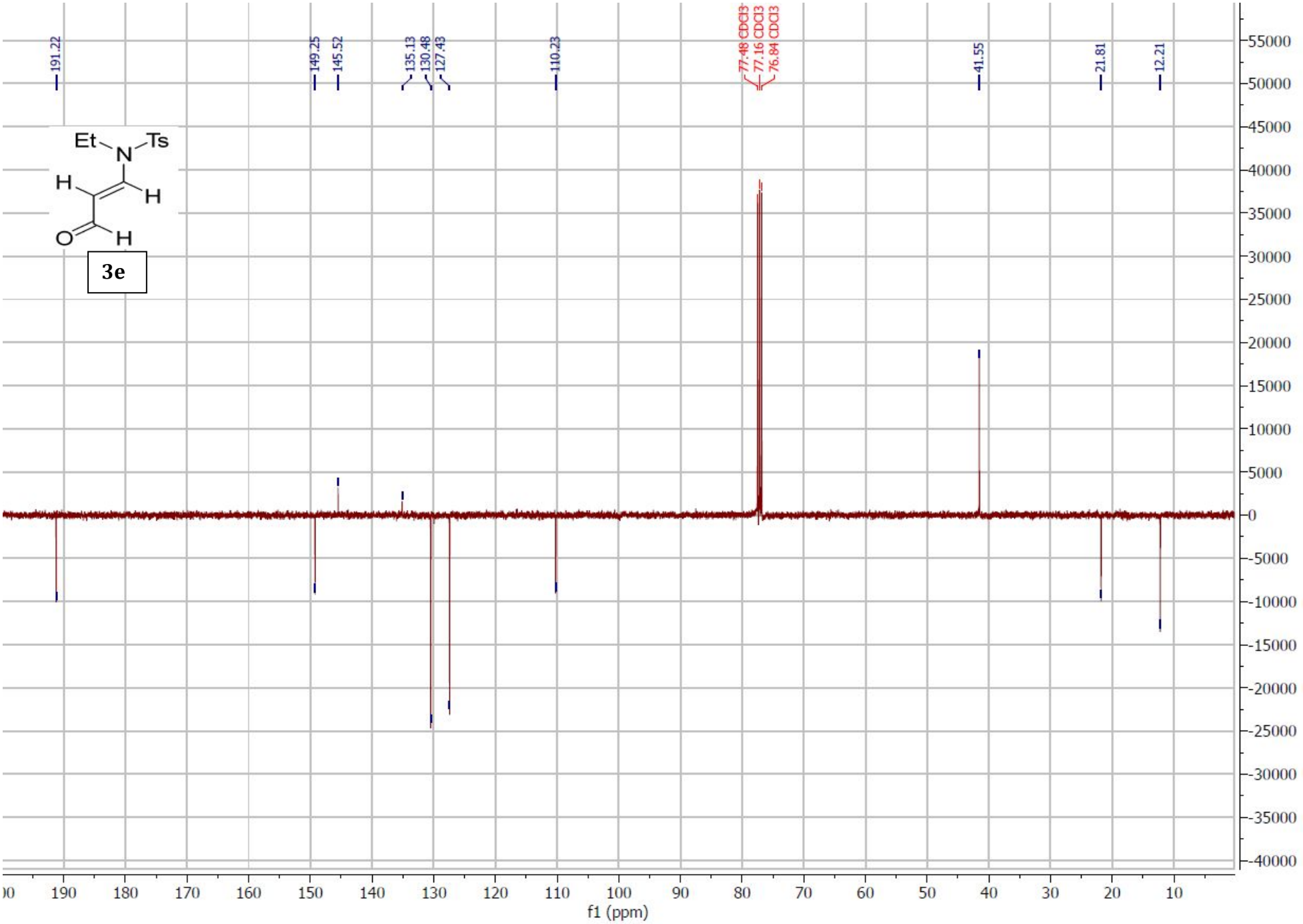
^{13}C NMR of compound **3c** (101 MHz, $CDCl_3$):



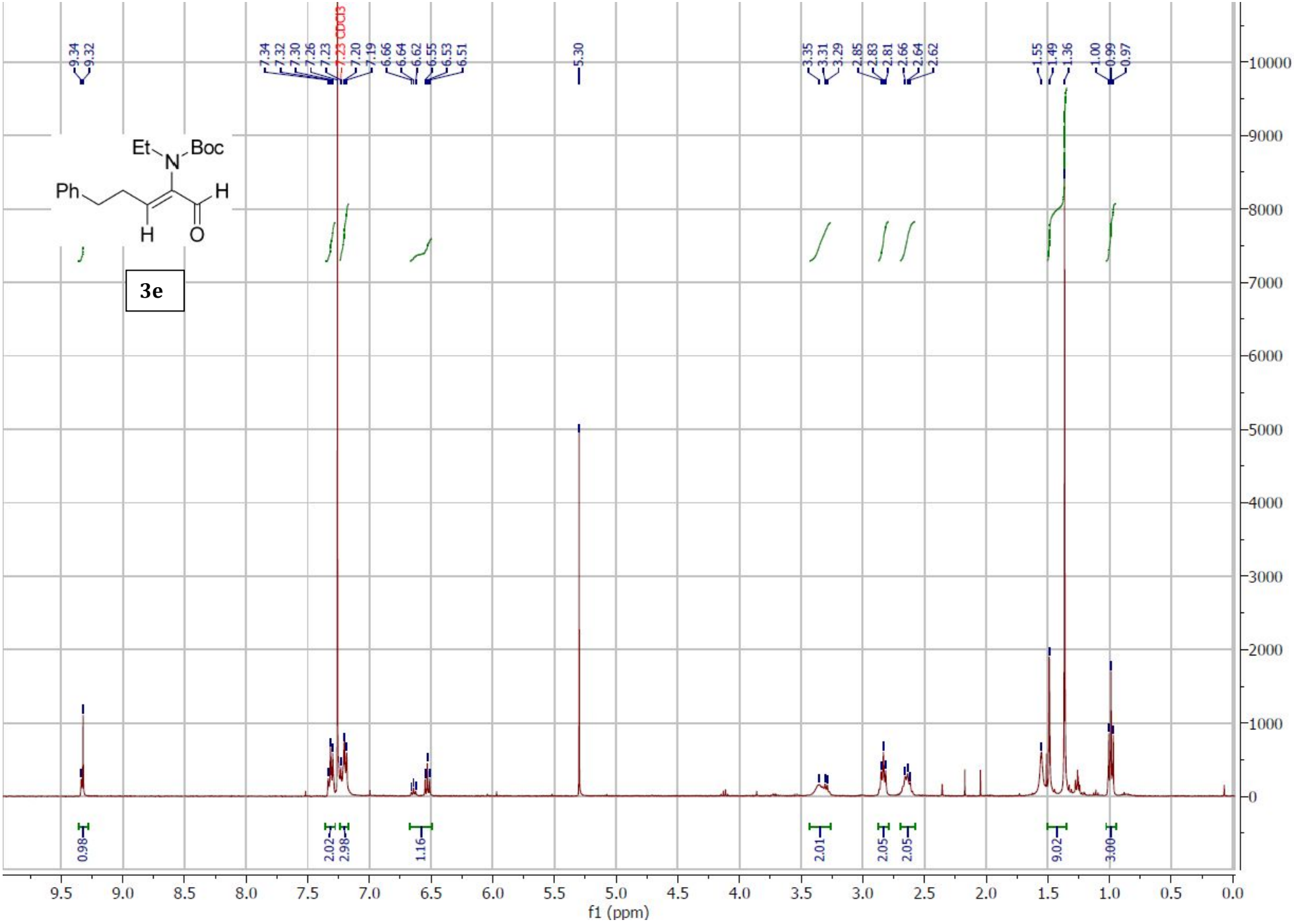
^{1}H NMR of compound **3e** (400 MHz, $CDCl_3$):



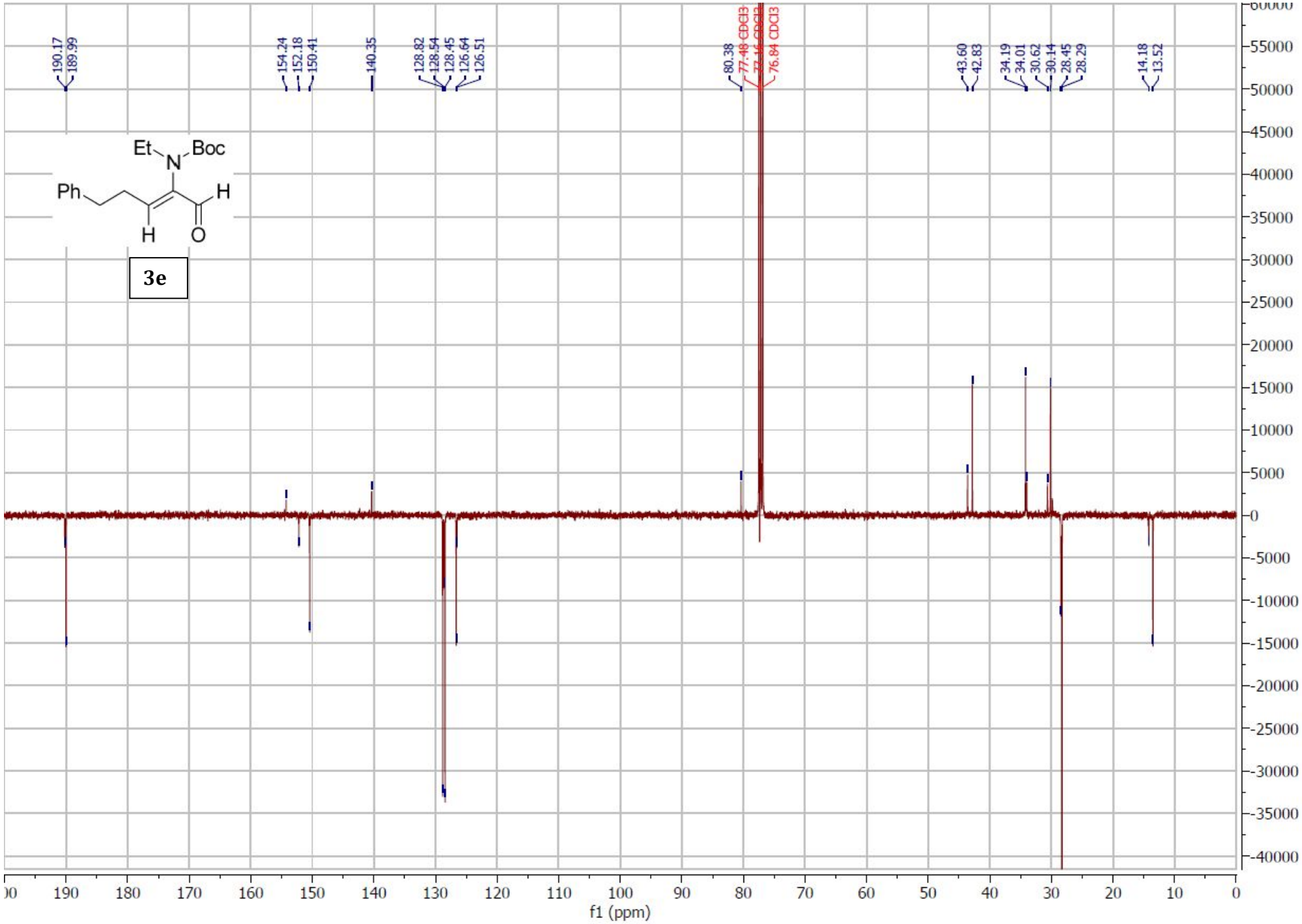
^{13}C NMR of compound **3e** (101 MHz, $CDCl_3$):



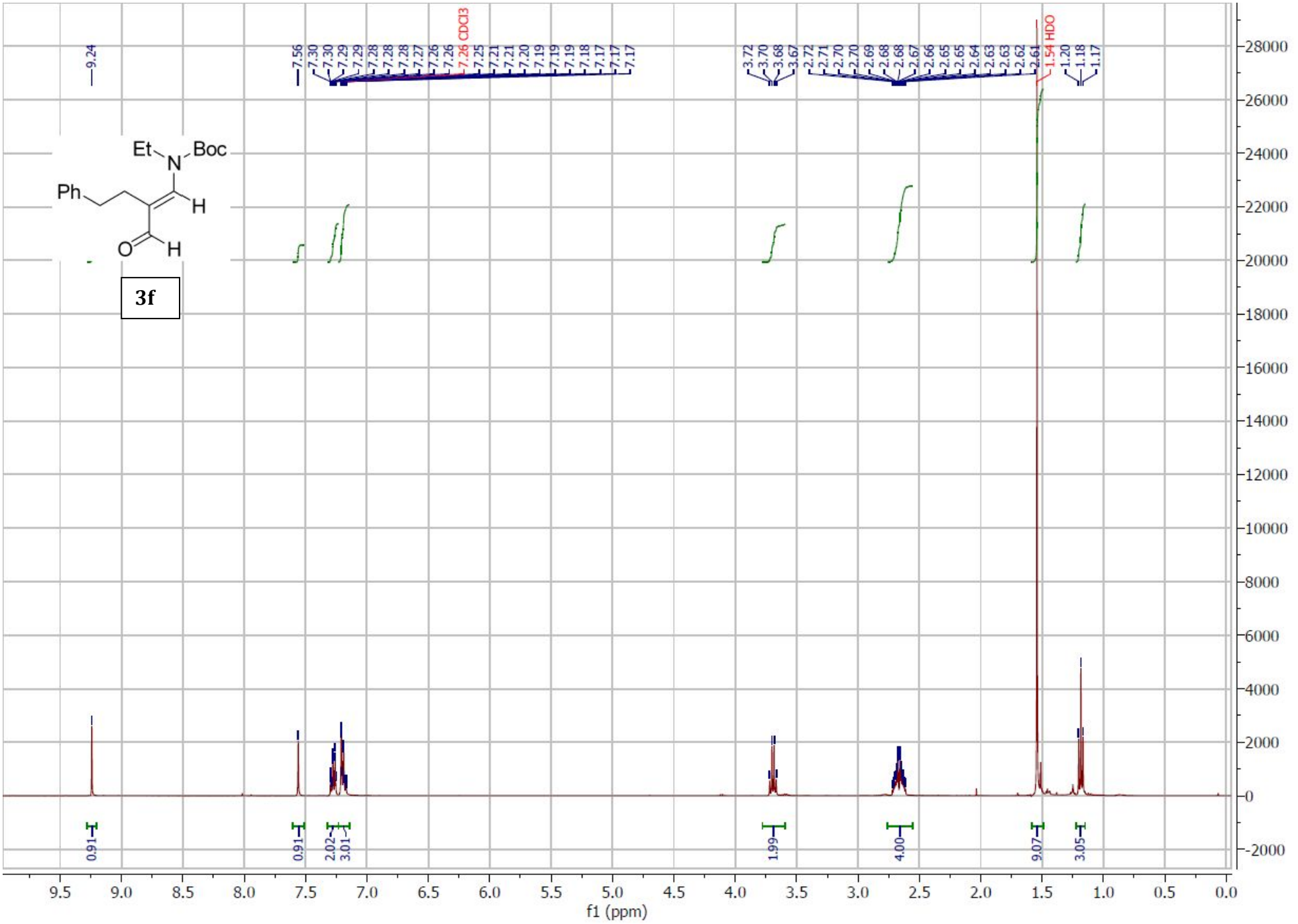
^{1}H NMR of compound **2f** (400 MHz, $CDCl_3$):



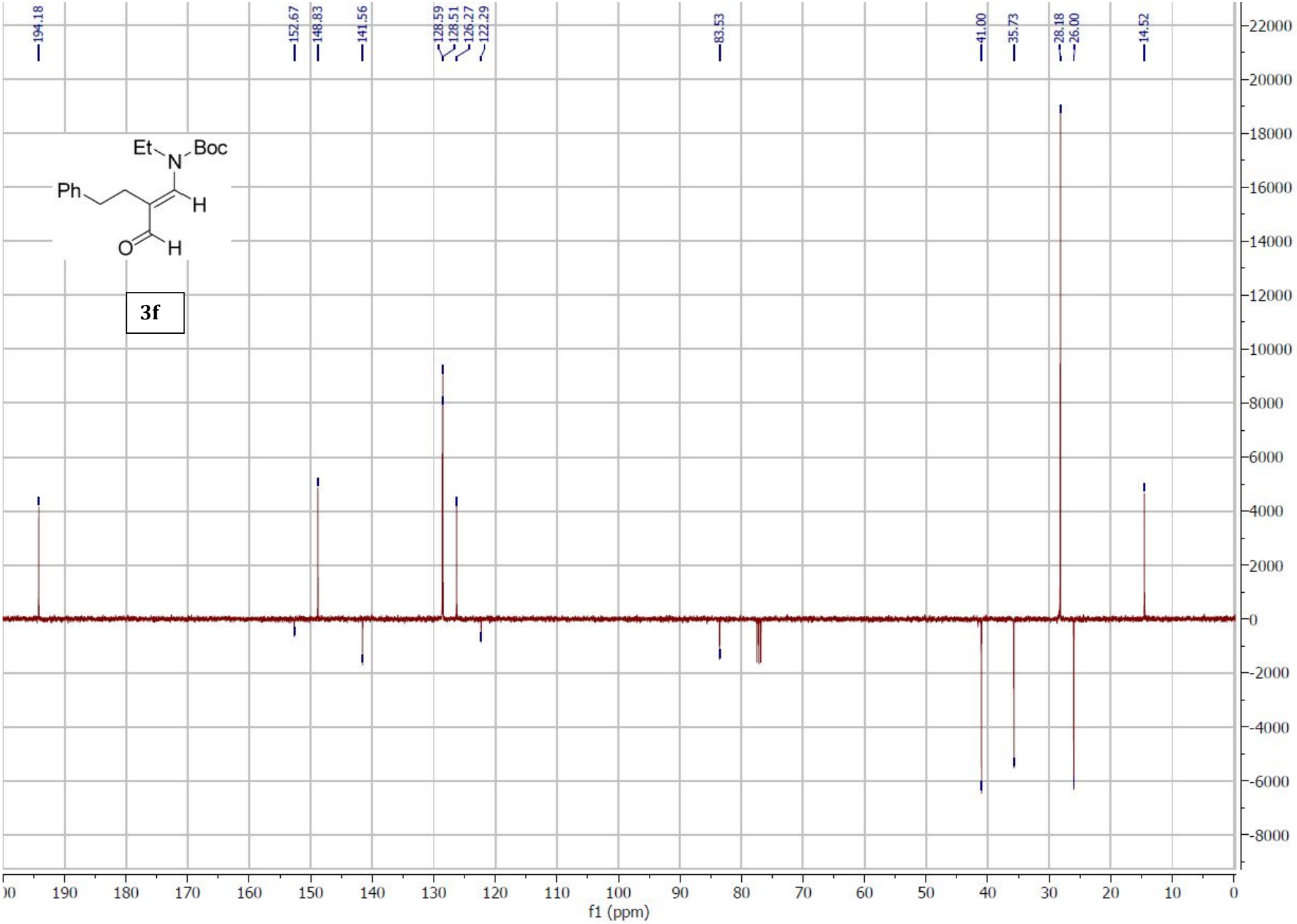
^{13}C NMR of compound **2f** (101 MHz, $CDCl_3$):



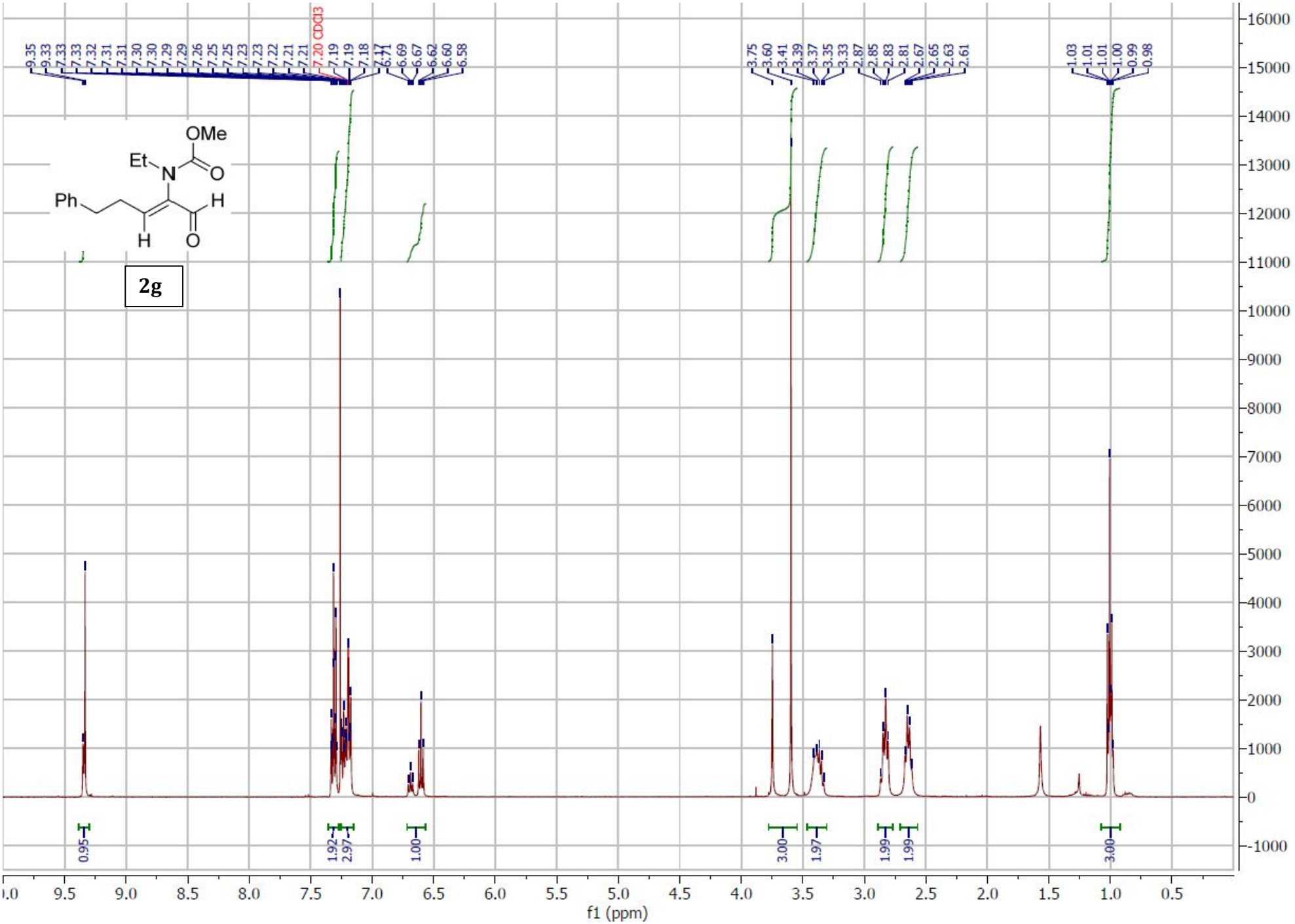
^{1}H NMR of compound **3f** (400 MHz, $CDCl_3$):



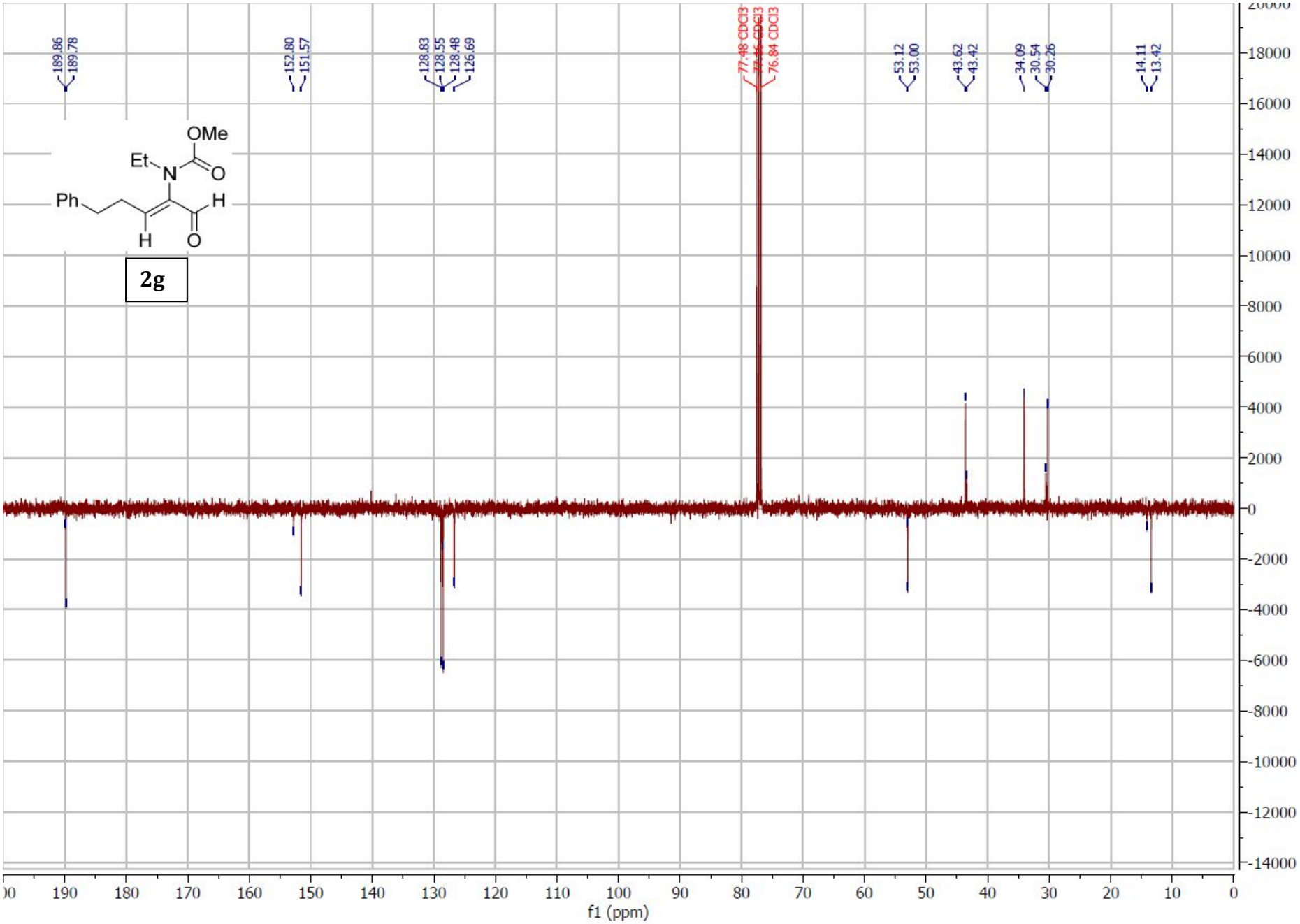
^{13}C NMR of compound **3f** (101 MHz, $CDCl_3$):



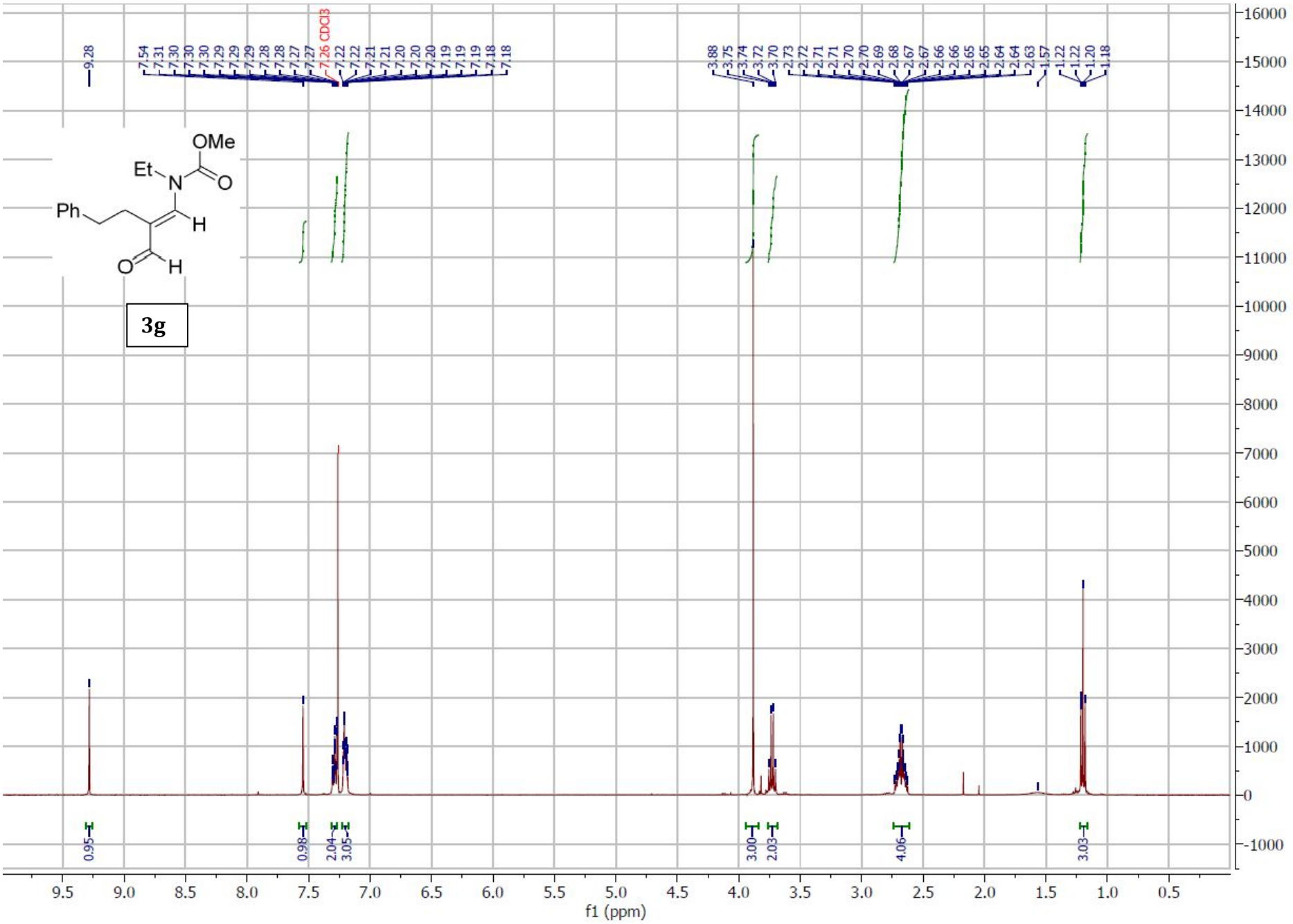
^{1}H NMR of compound **2g** (400 MHz, $CDCl_3$):



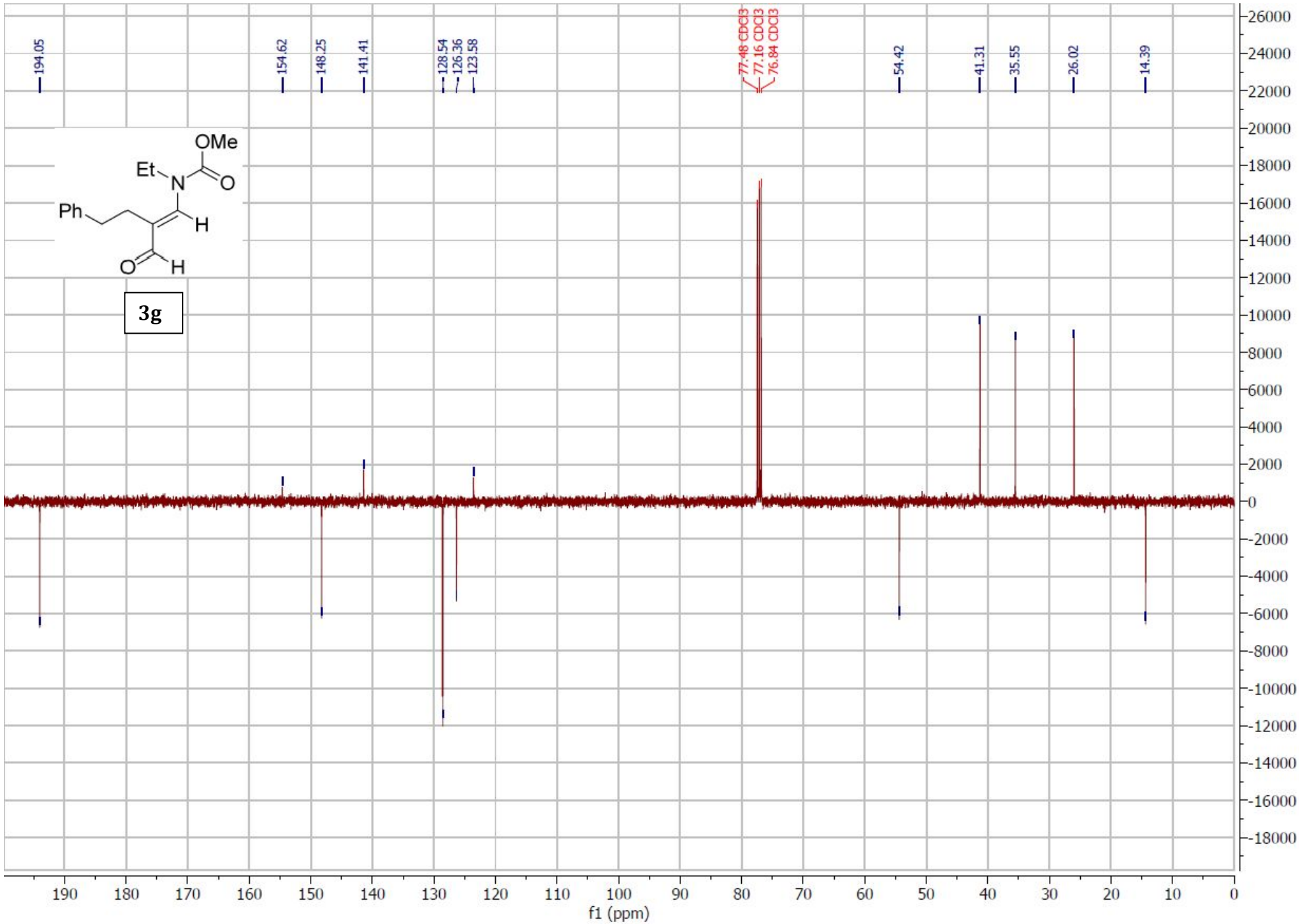
^{13}C NMR of compound **2g** (101 MHz, $CDCl_3$):



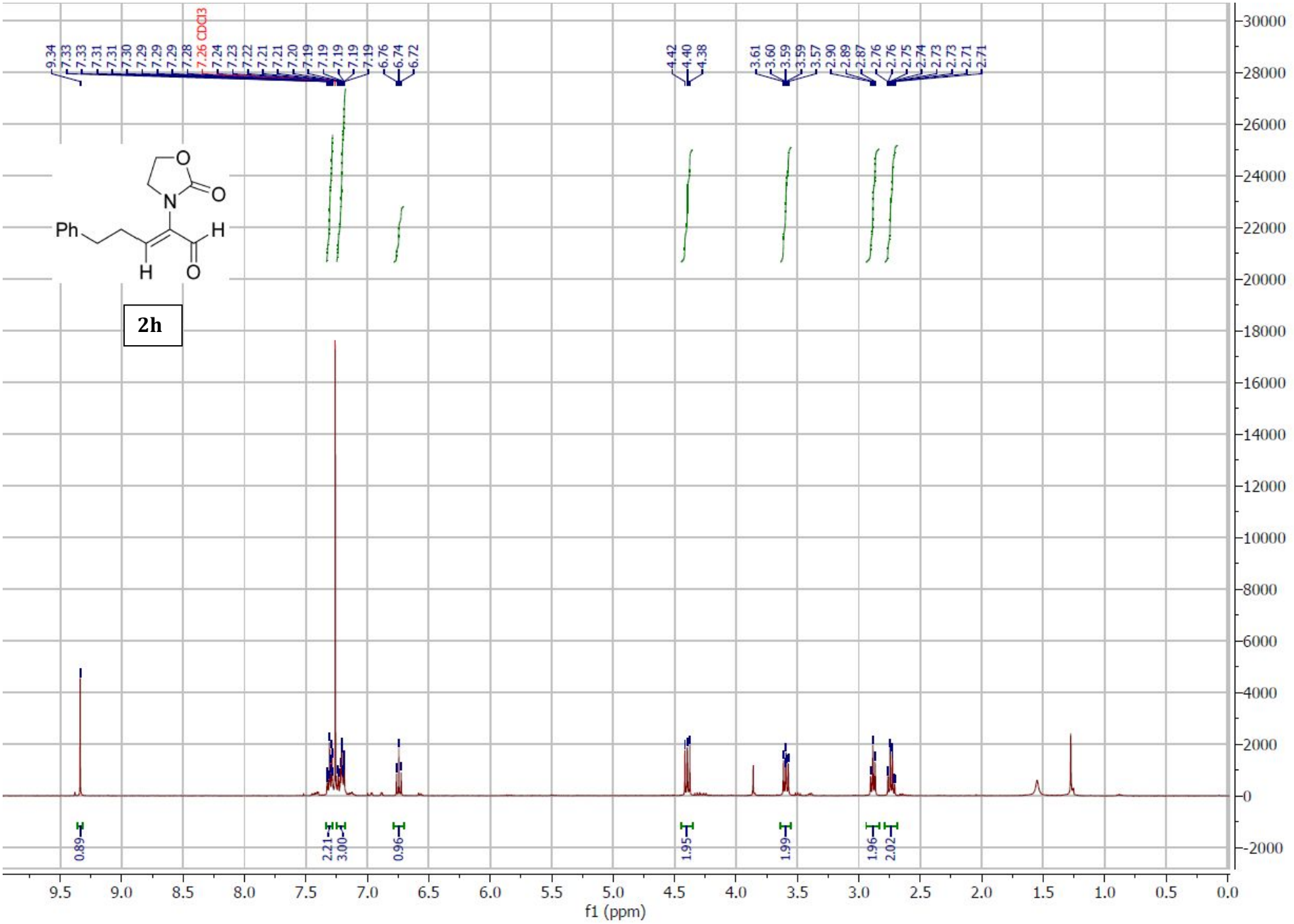
^{1}H NMR of compound **3g** (400 MHz, $CDCl_3$):



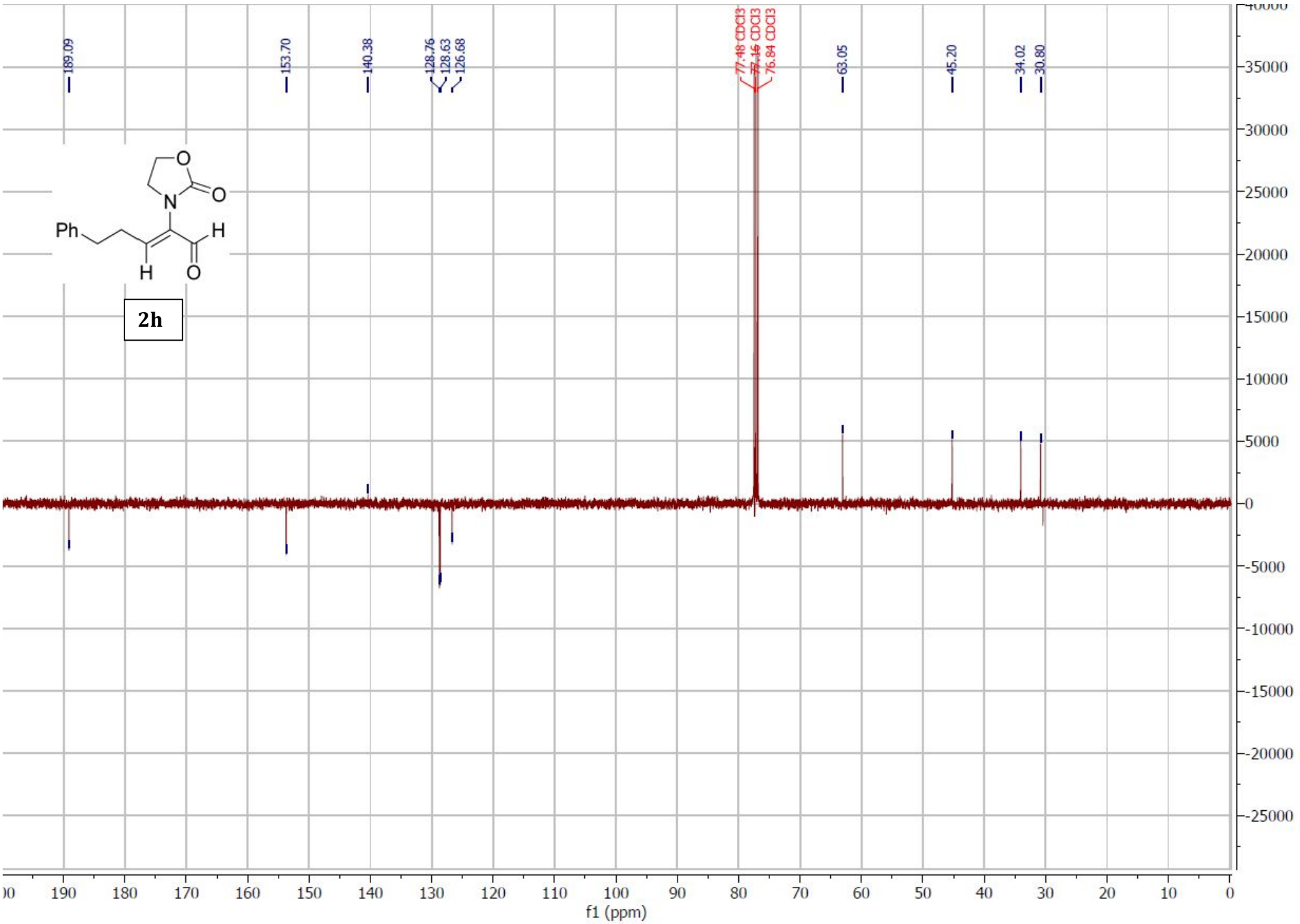
^{13}C NMR of compound **3g** (101 MHz, $CDCl_3$):



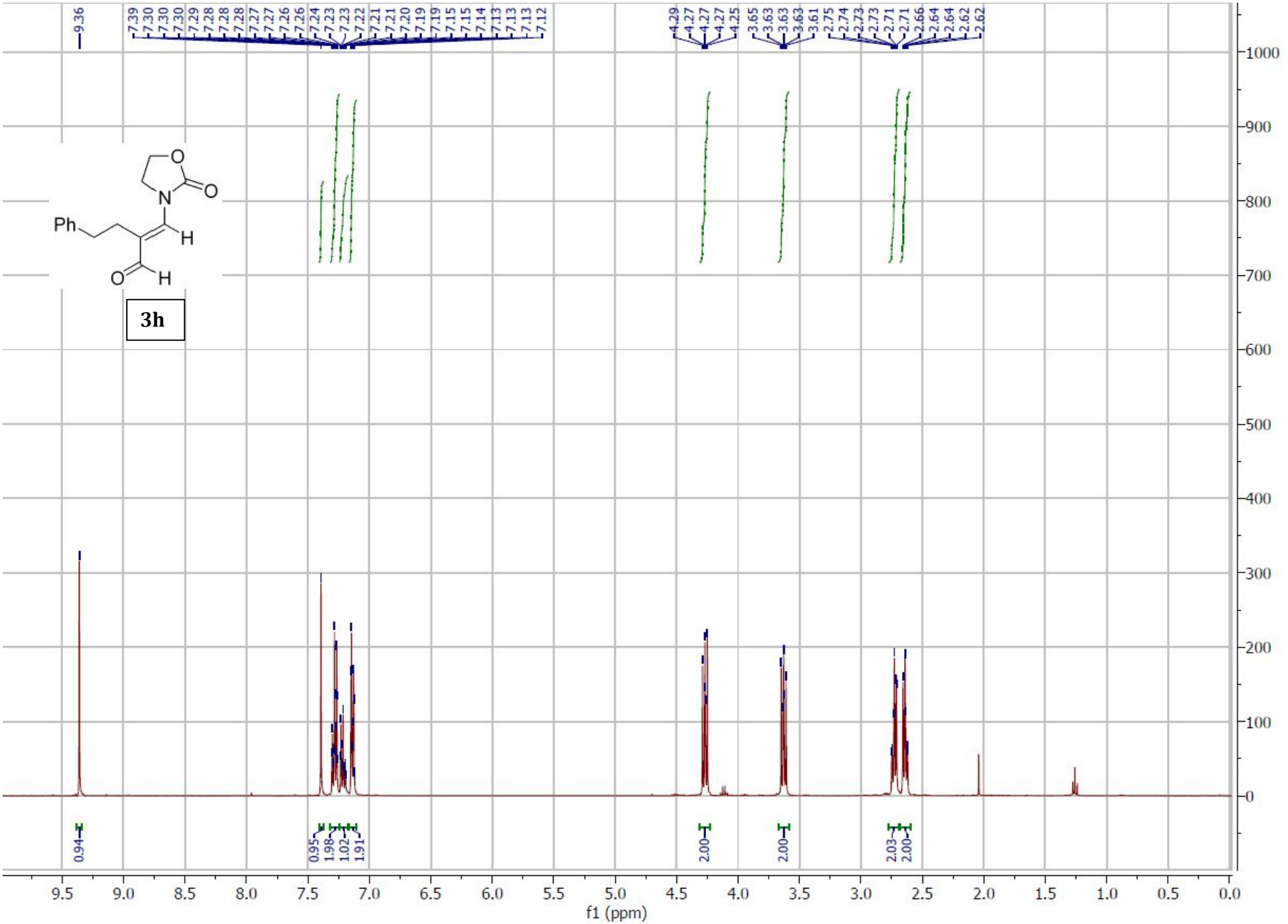
^{1}H NMR of compound **2h** (400 MHz, $CDCl_3$):



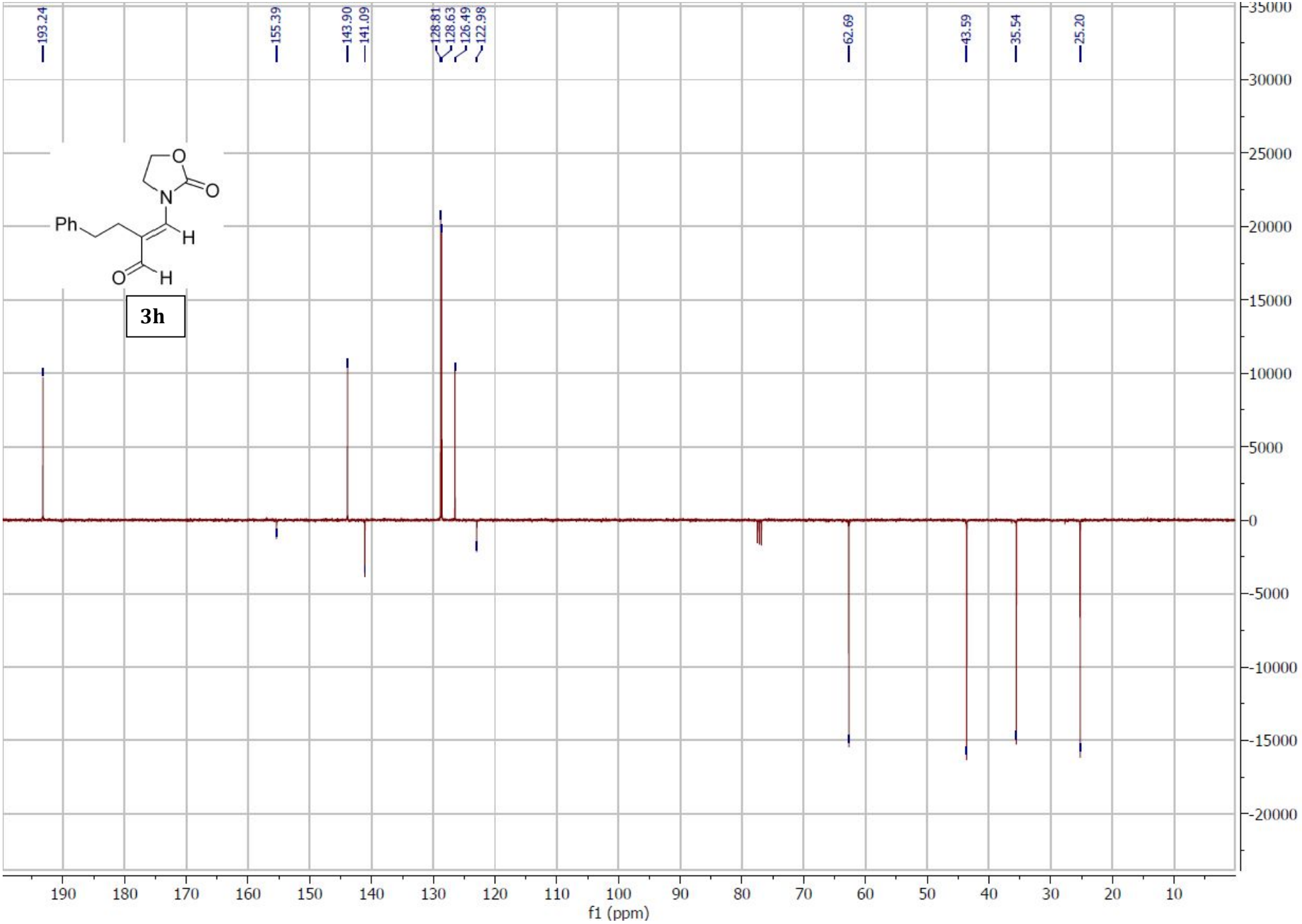
^{13}C NMR of compound **2h** (101 MHz, $CDCl_3$):



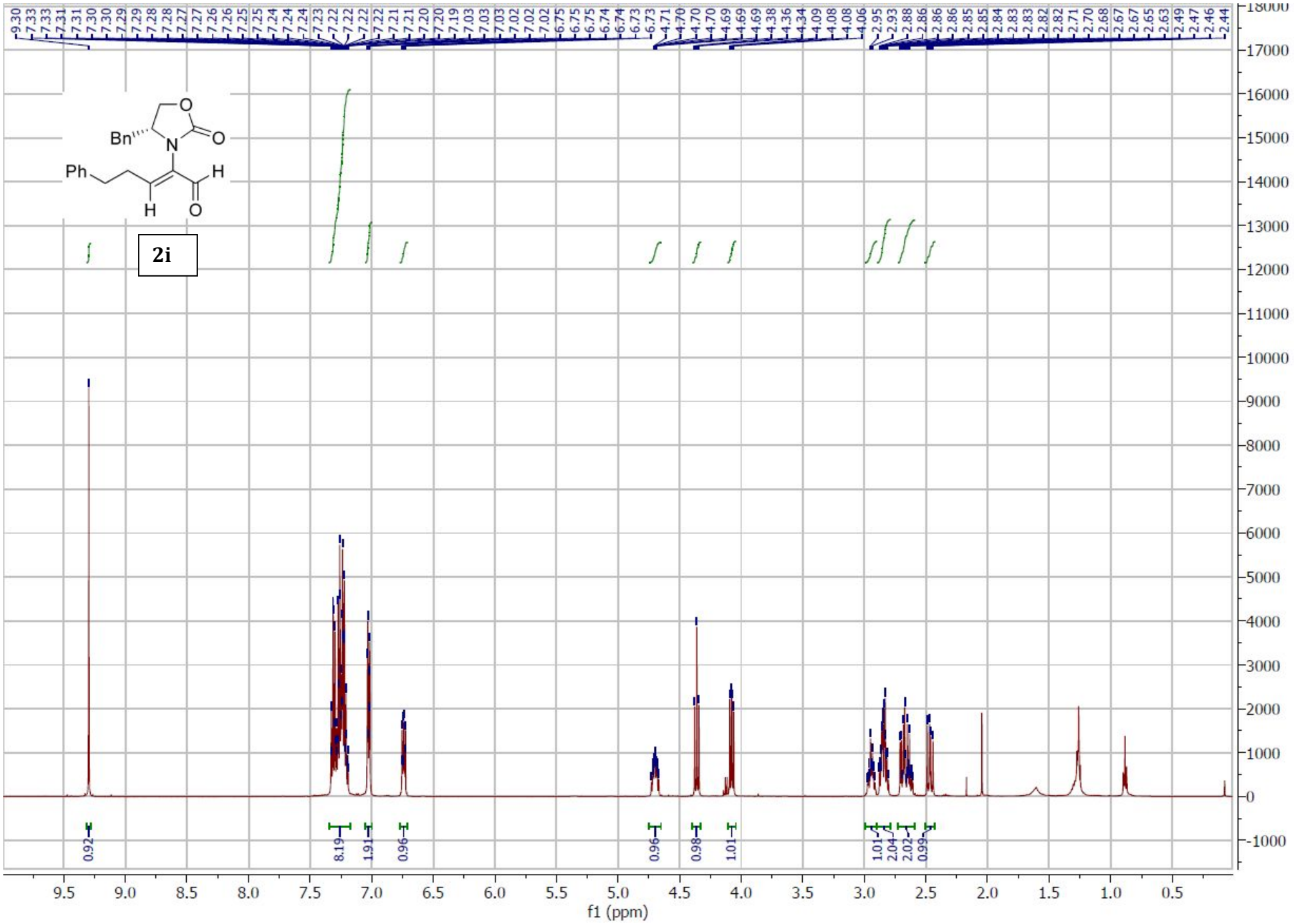
^{1}H NMR of compound **3h** (400 MHz, $CDCl_3$):



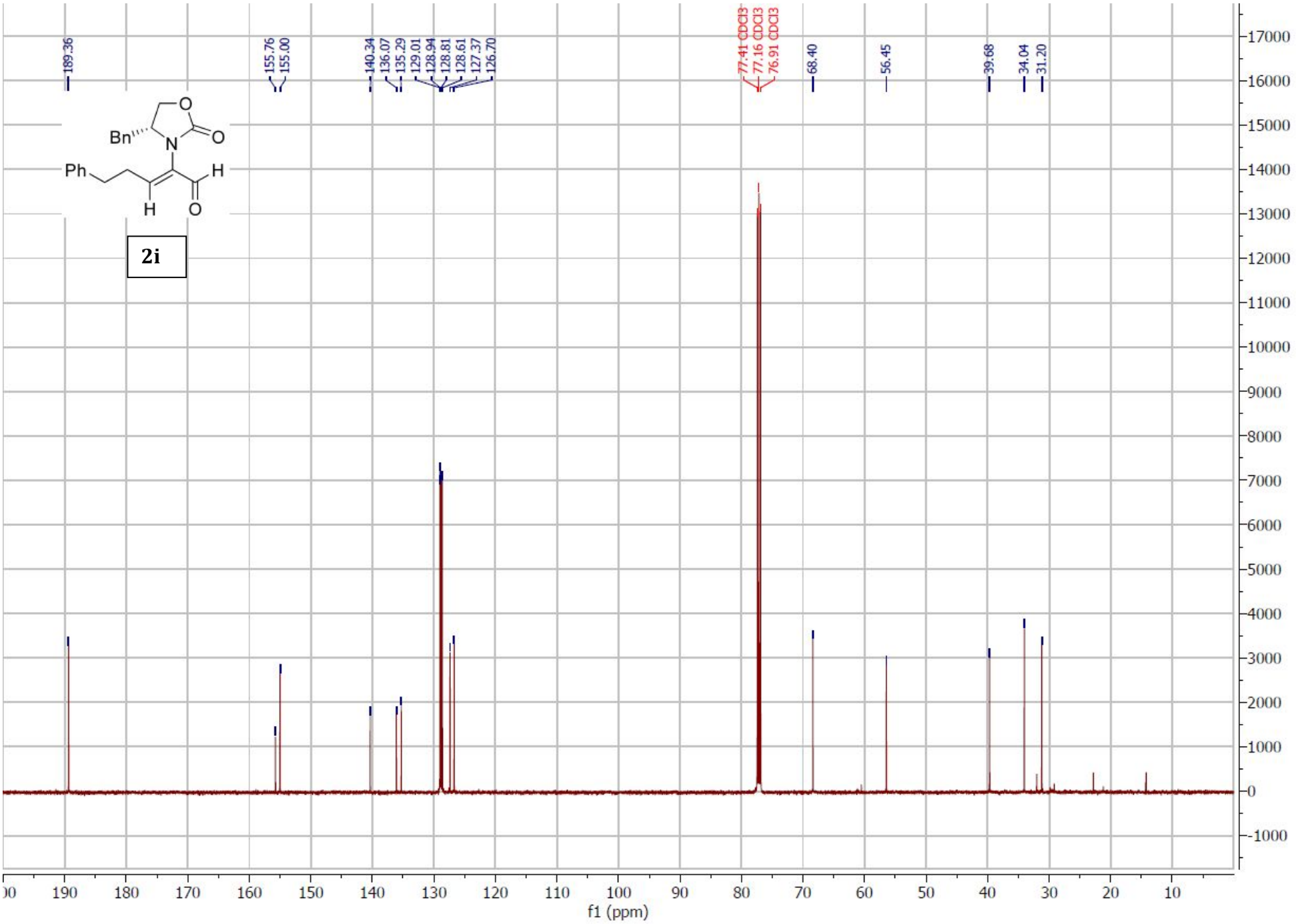
^{13}C NMR of compound 3**h** (101 MHz, $CDCl_3$):



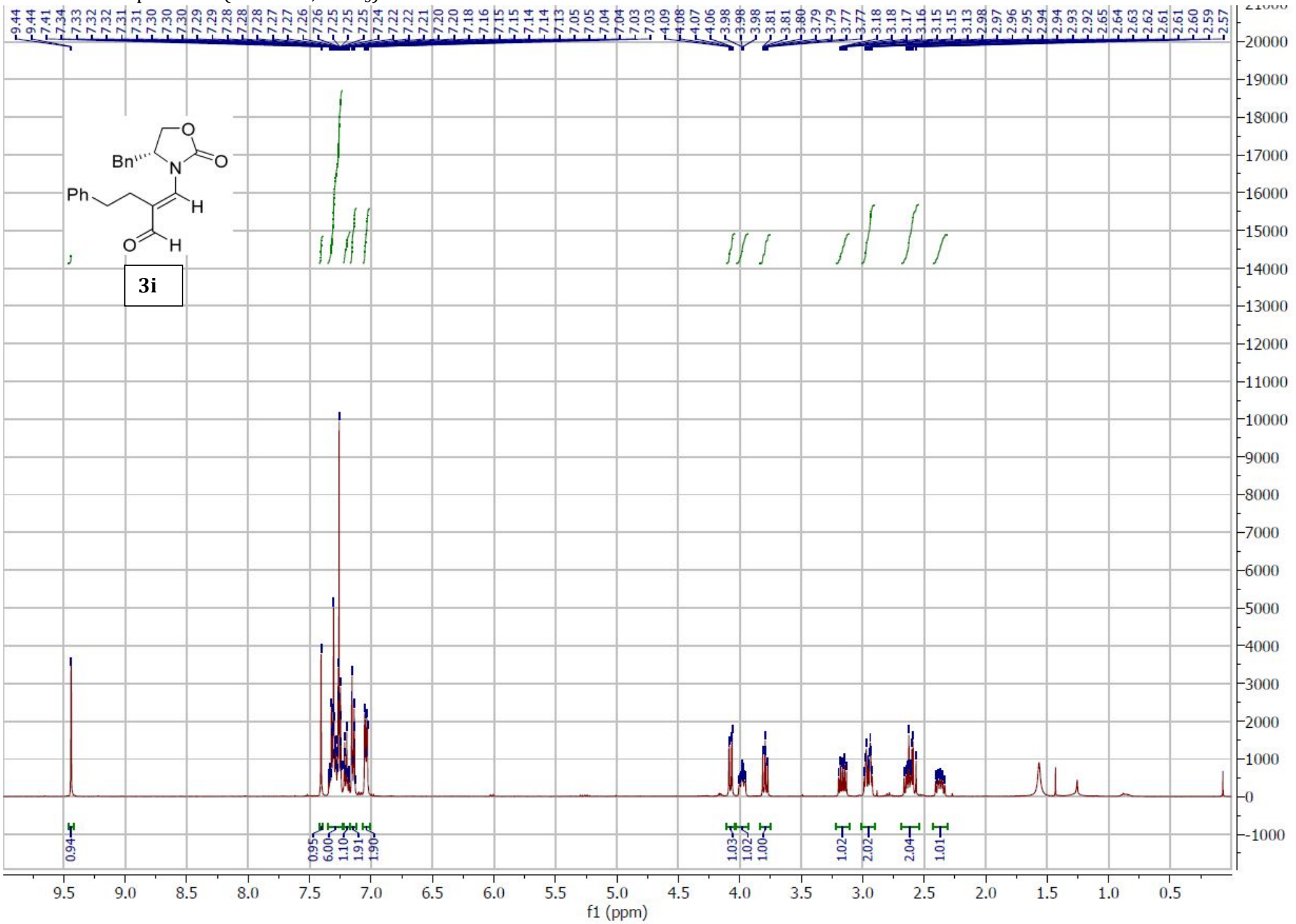
^{1}H NMR of compound **2i** (500 MHz, $CDCl_3$):



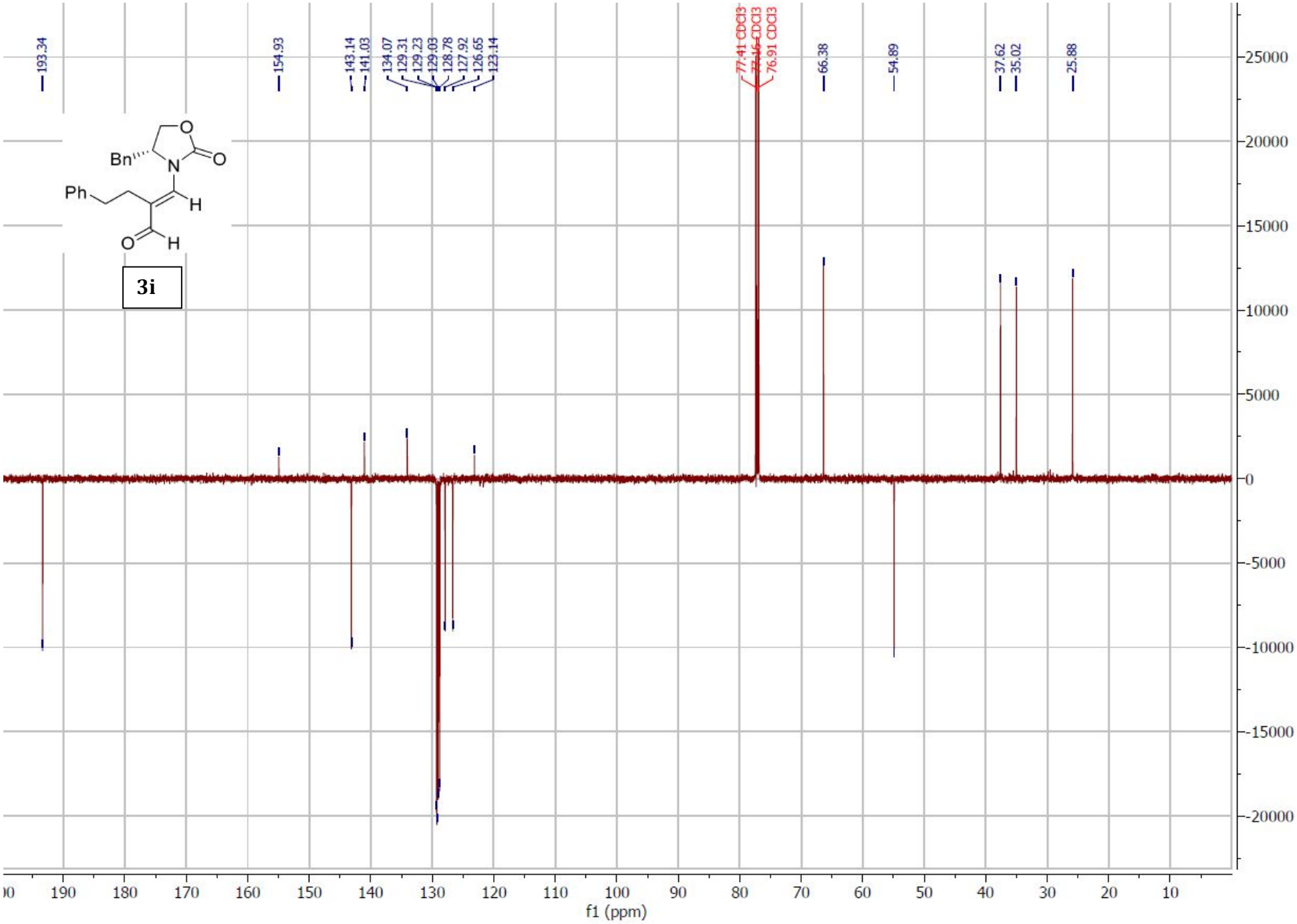
^{13}C NMR of compound **2i** (126 MHz, $CDCl_3$):



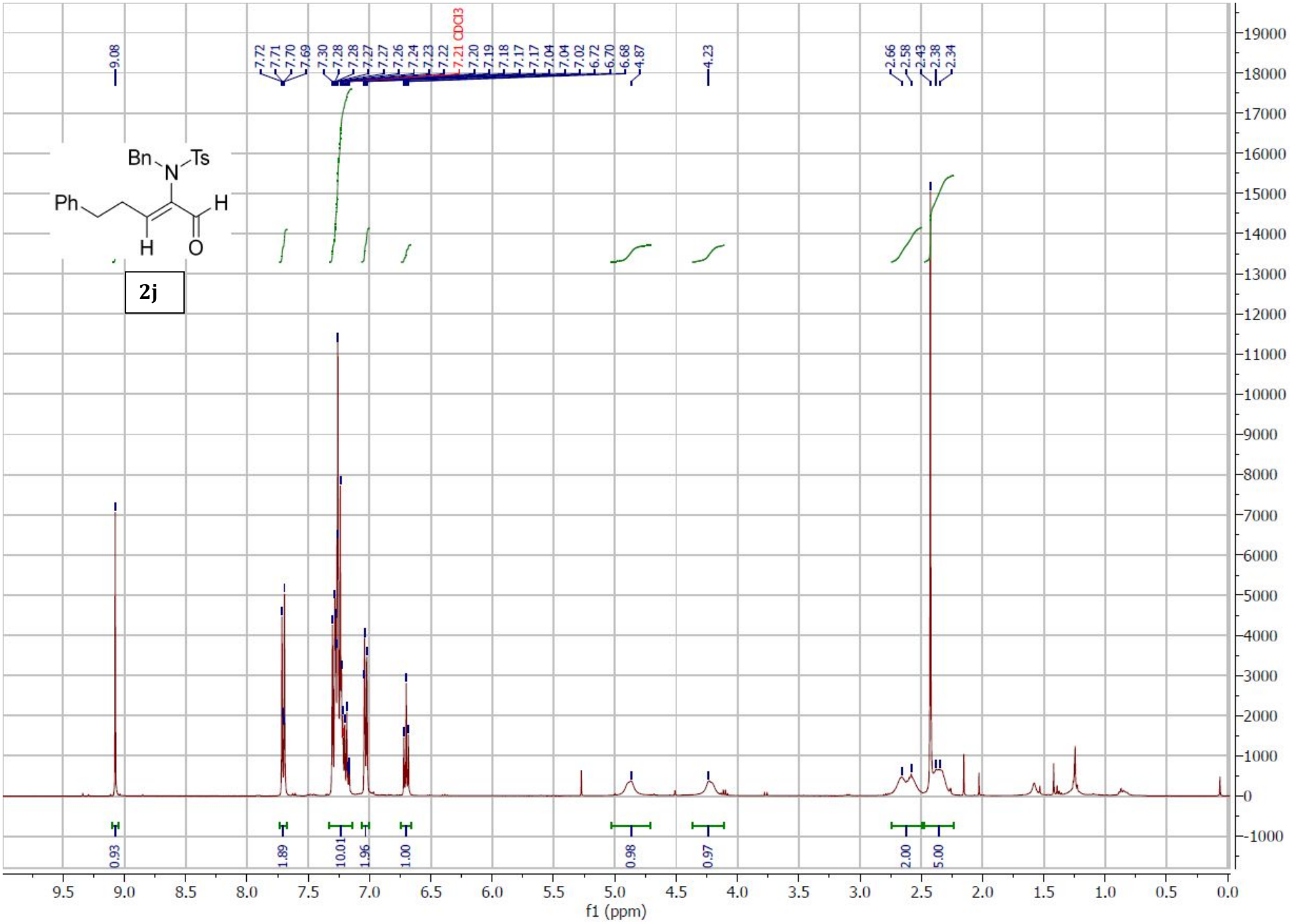
^{1}H NMR of compound **3i** (500 MHz, $CDCl_3$):



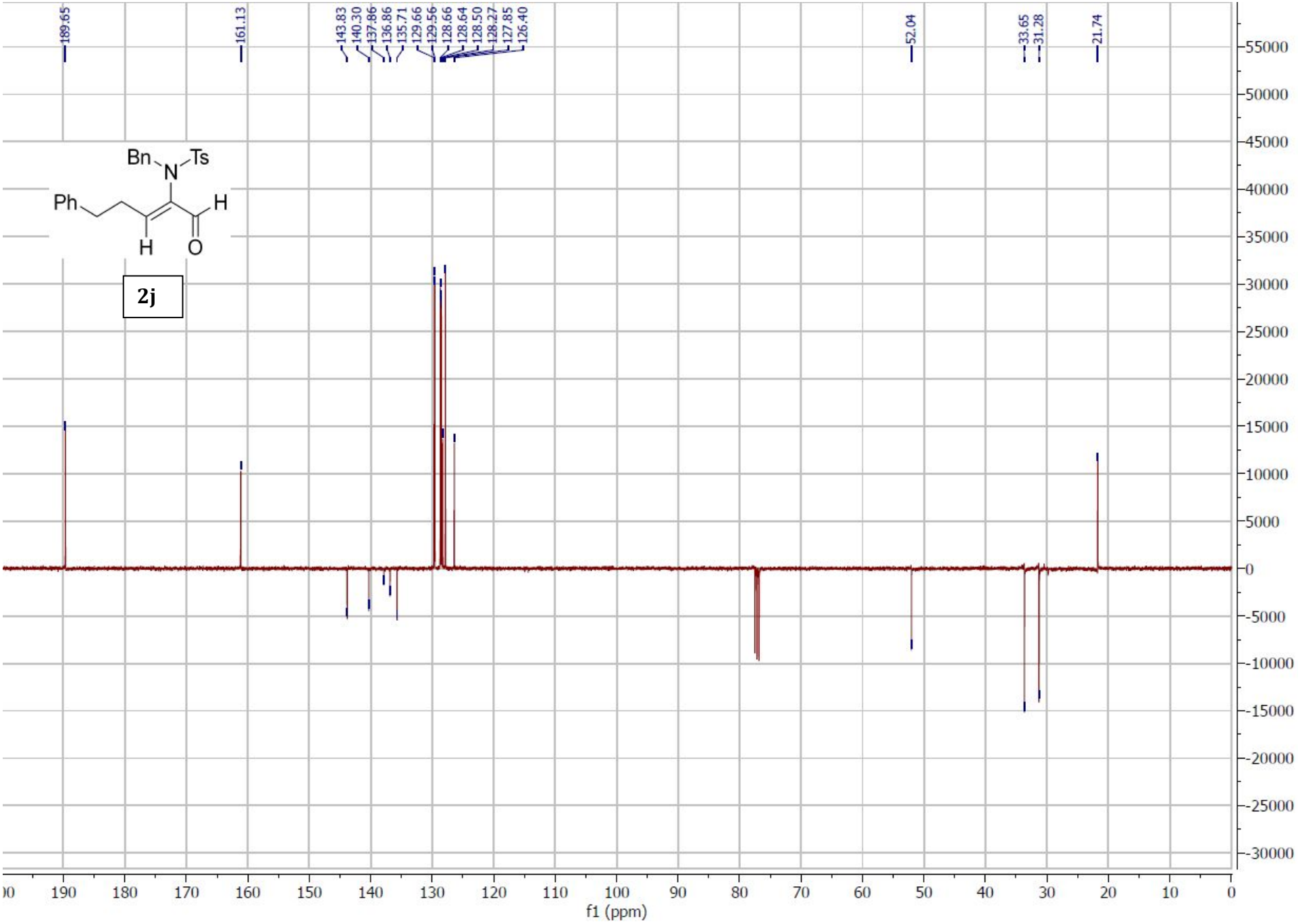
^{13}C NMR of compound **3i** (126 MHz, $CDCl_3$):



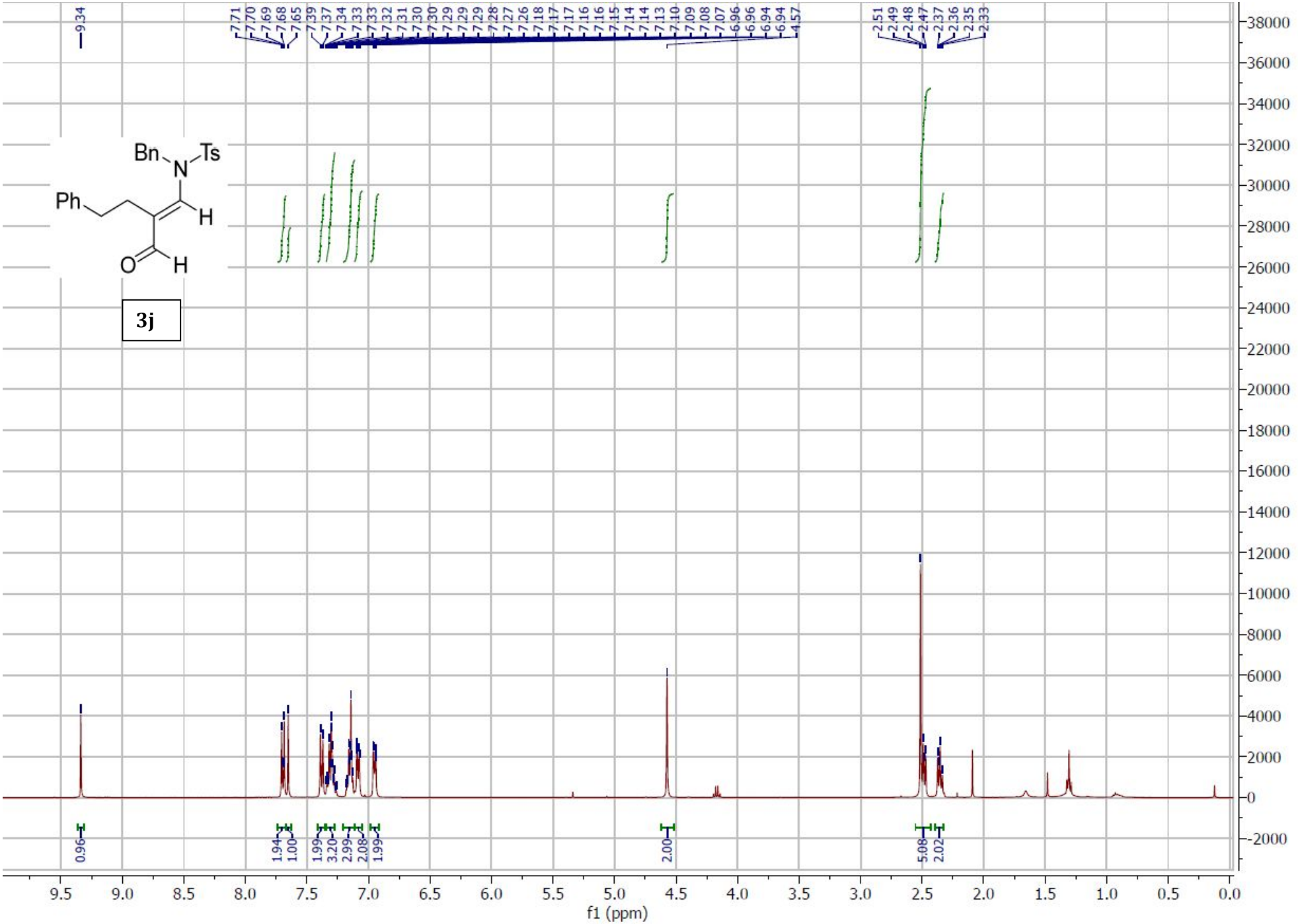
^{1}H NMR of compound **2j** (400 MHz, $CDCl_3$):



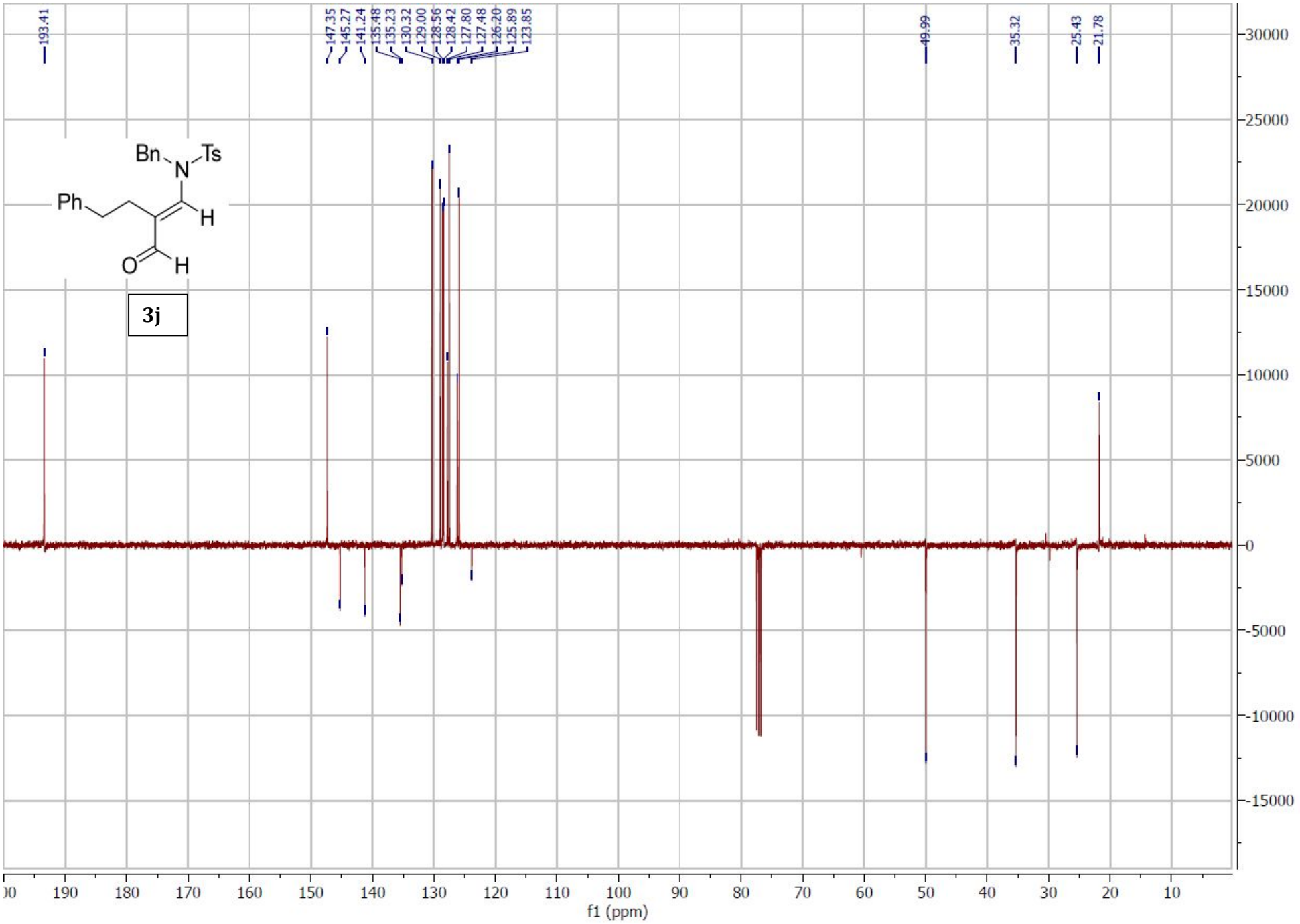
^{13}C NMR of compound **2j** (101 MHz, $CDCl_3$):



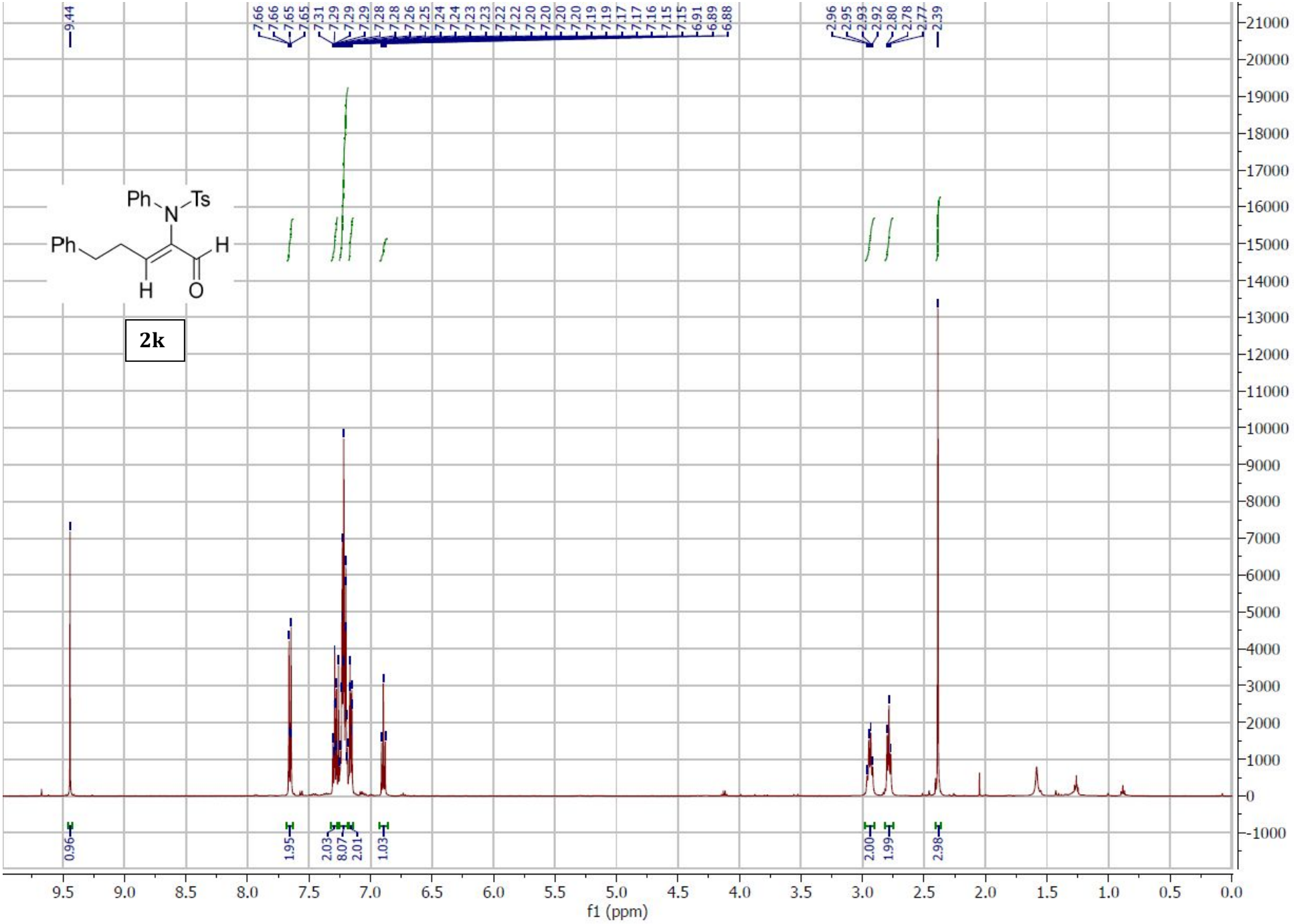
^{1}H NMR of compound **3j** (400 MHz, $CDCl_3$):



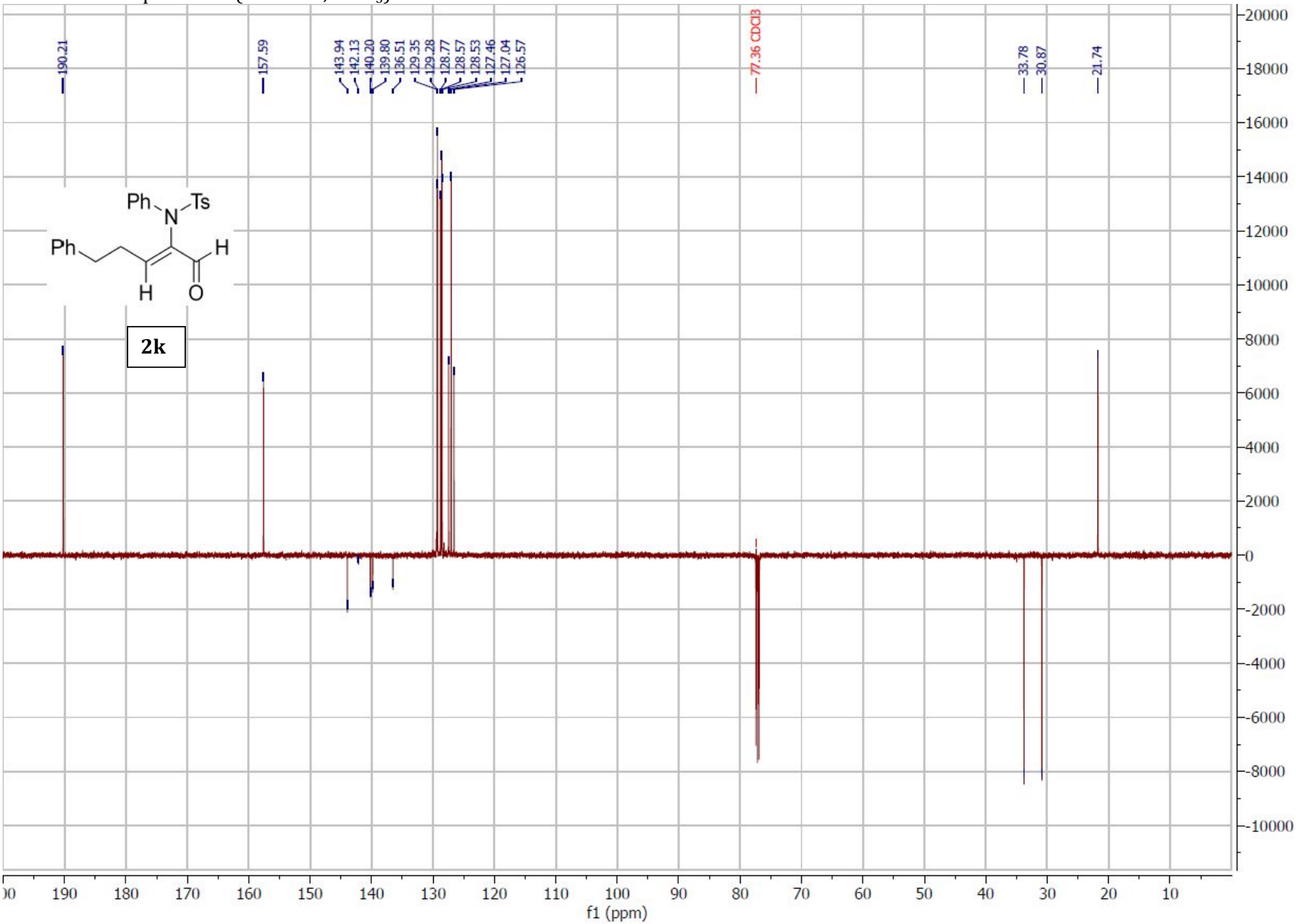
^{13}C NMR of compound **3j** (101 MHz, $CDCl_3$):



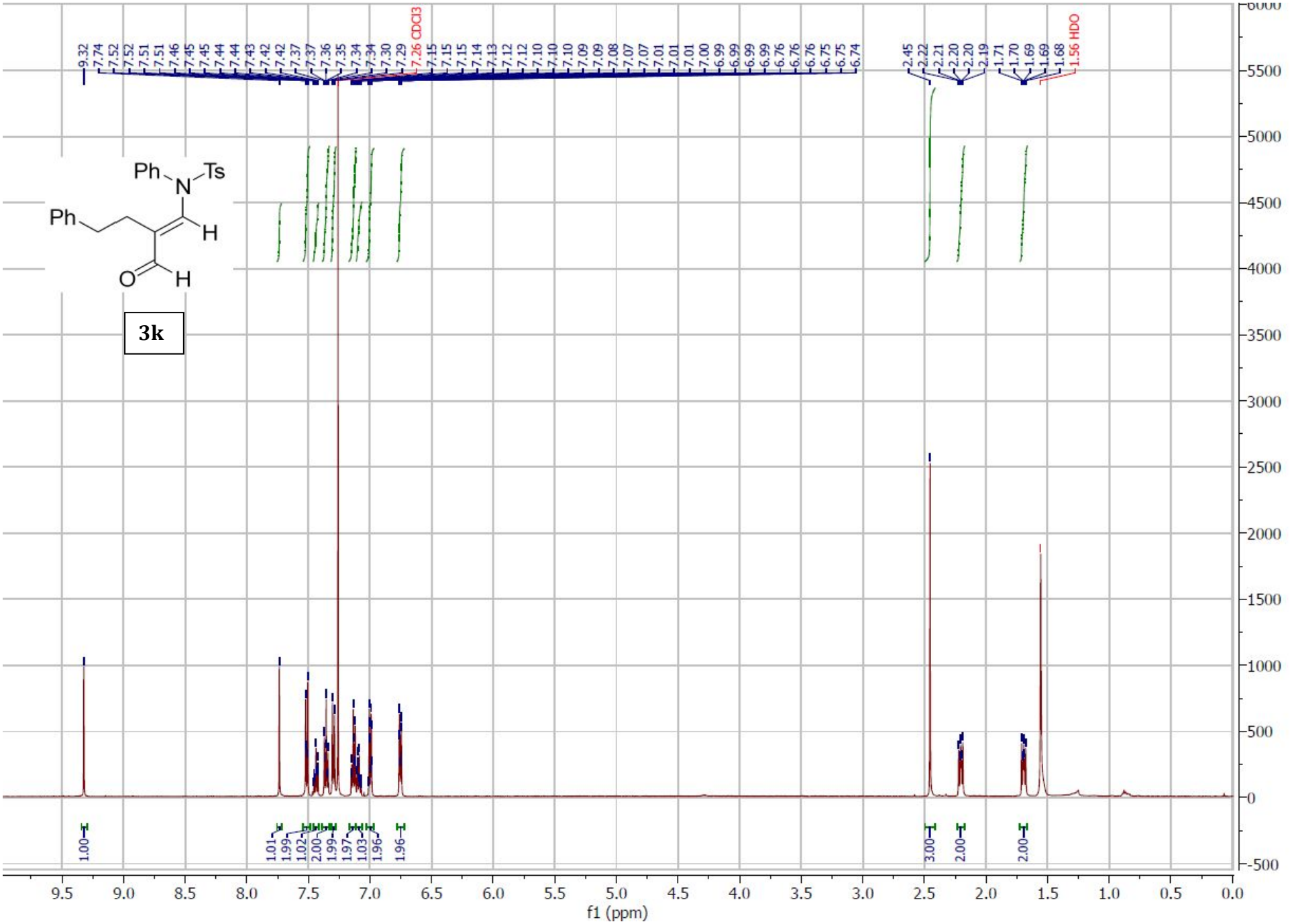
^{1}H NMR of compound **2k** (500 MHz, $CDCl_3$):



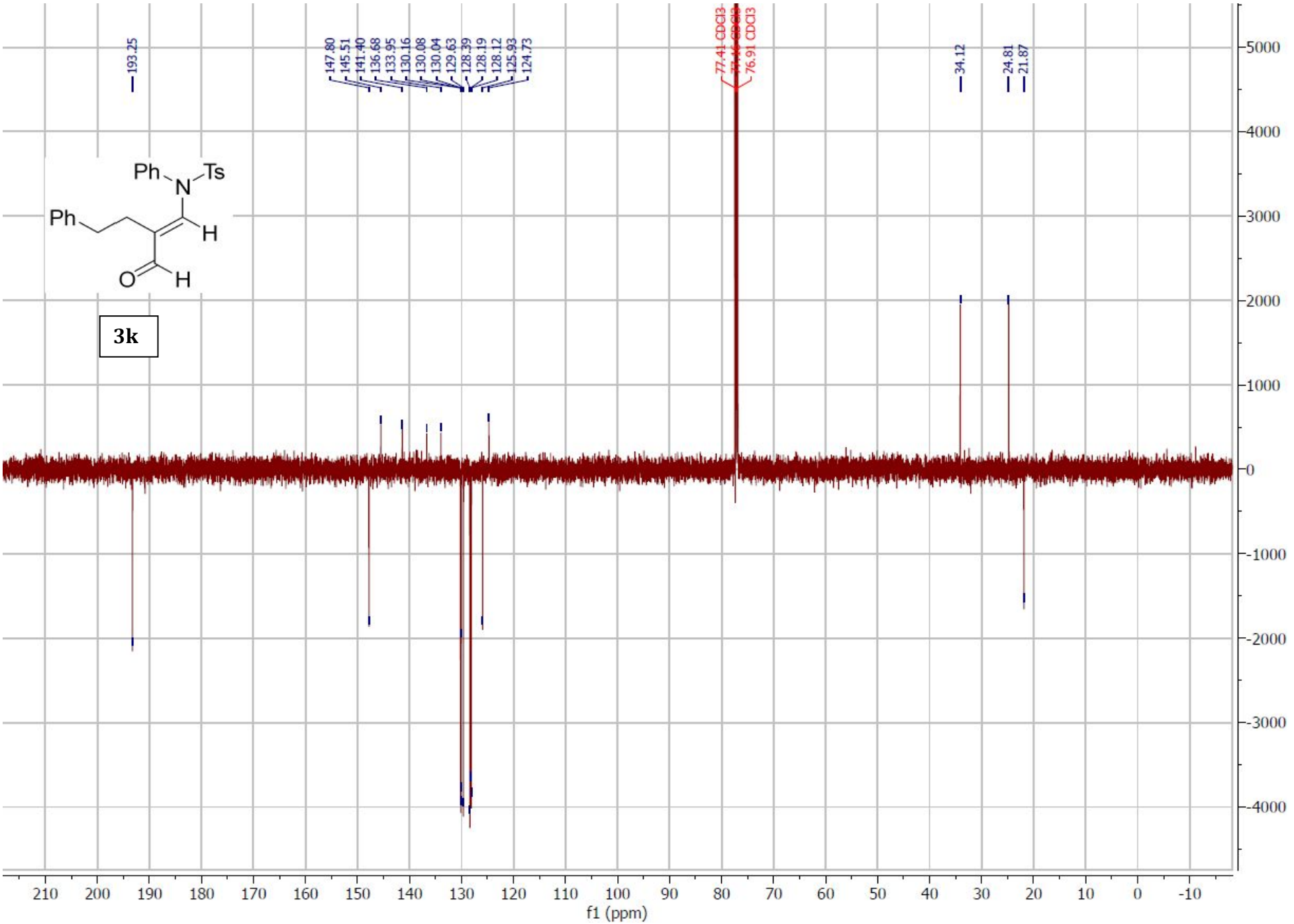
^{13}C NMR of compound **2k** (126 MHz, $CDCl_3$):



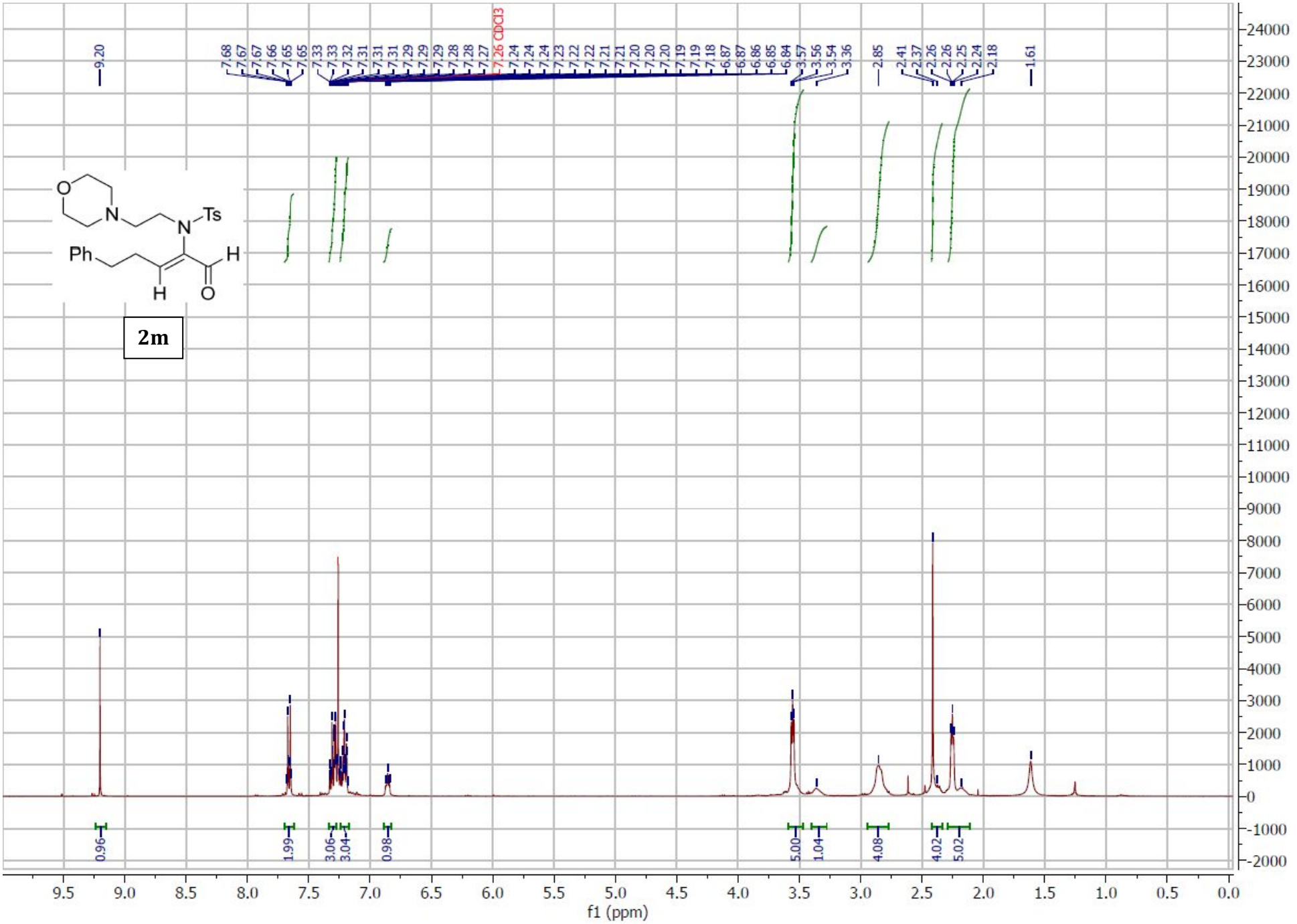
^{1}H NMR of compound **3k** (500 MHz, $CDCl_3$):



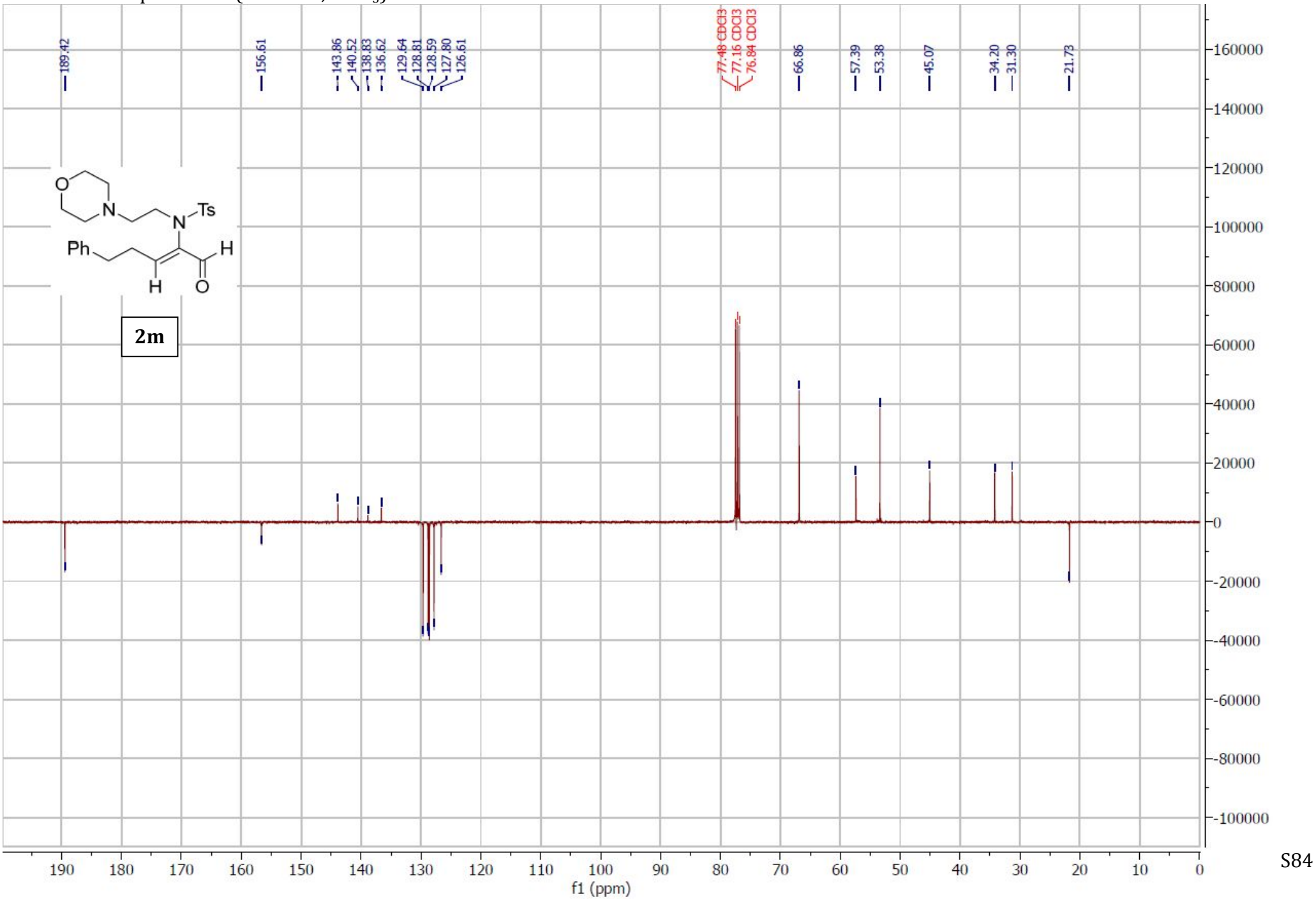
^{13}C NMR of compound **3k** (126 MHz, $CDCl_3$):



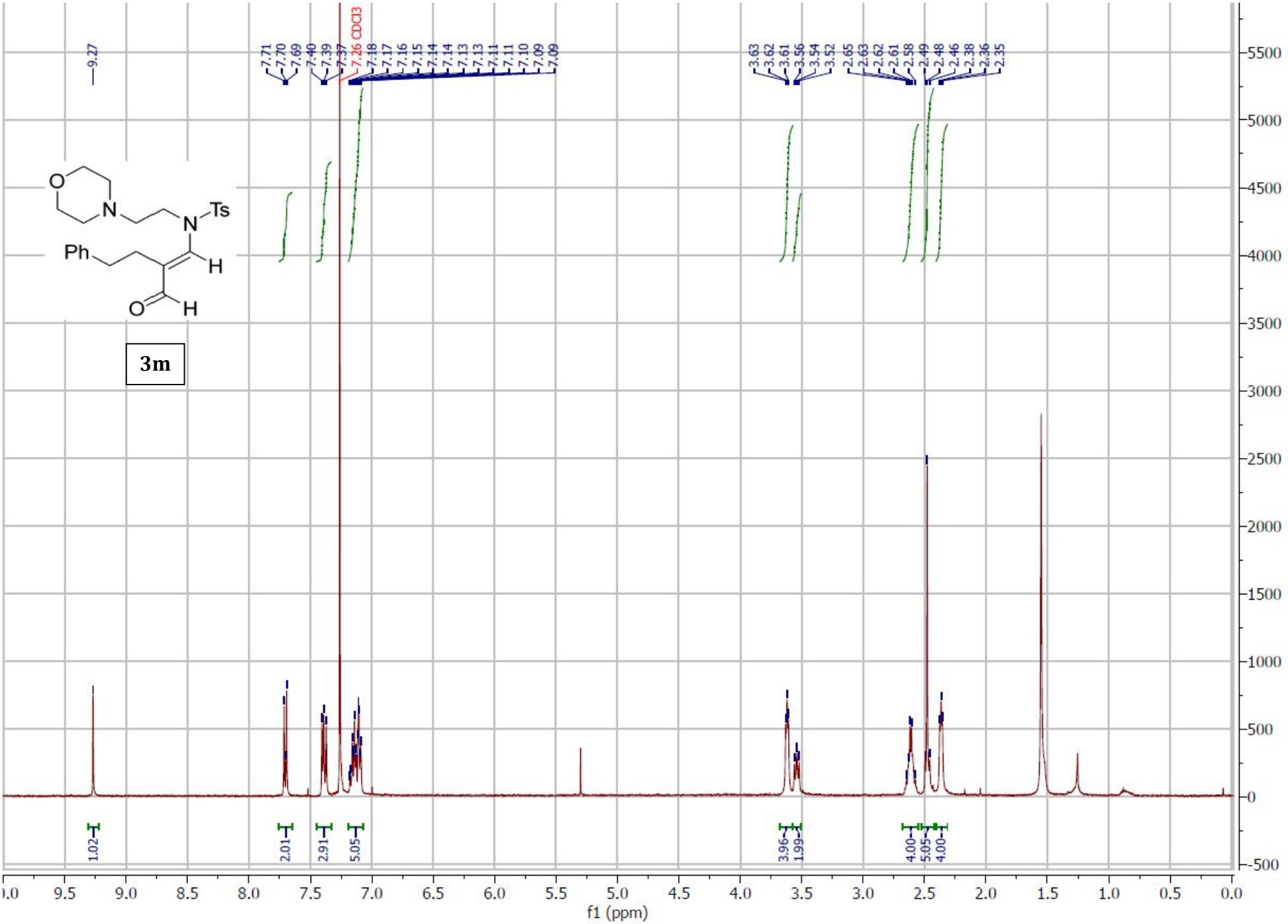
^{1}H NMR of compound **2m** (400 MHz, $CDCl_3$):



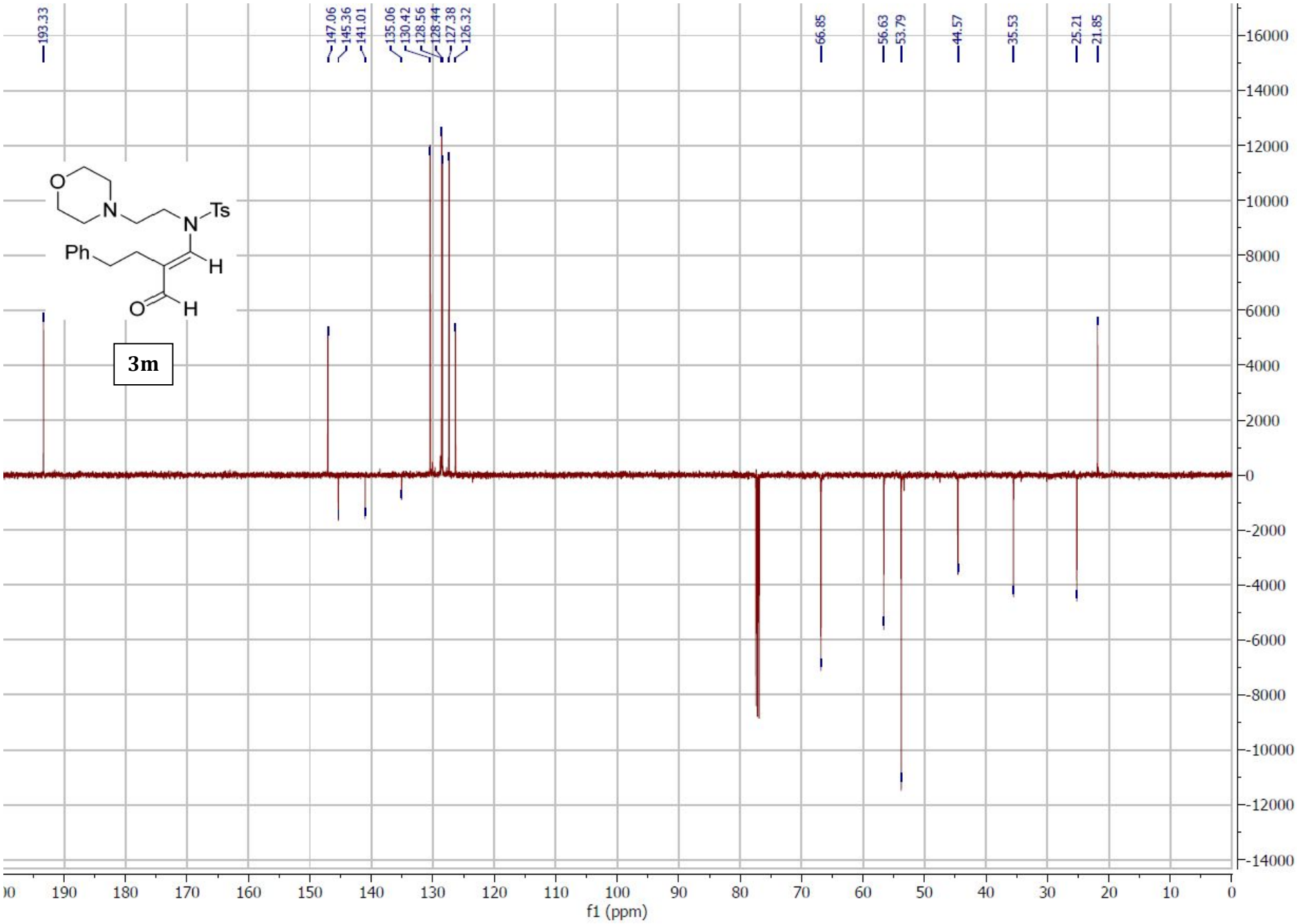
^{13}C NMR of compound **2m** (101 MHz, $CDCl_3$):



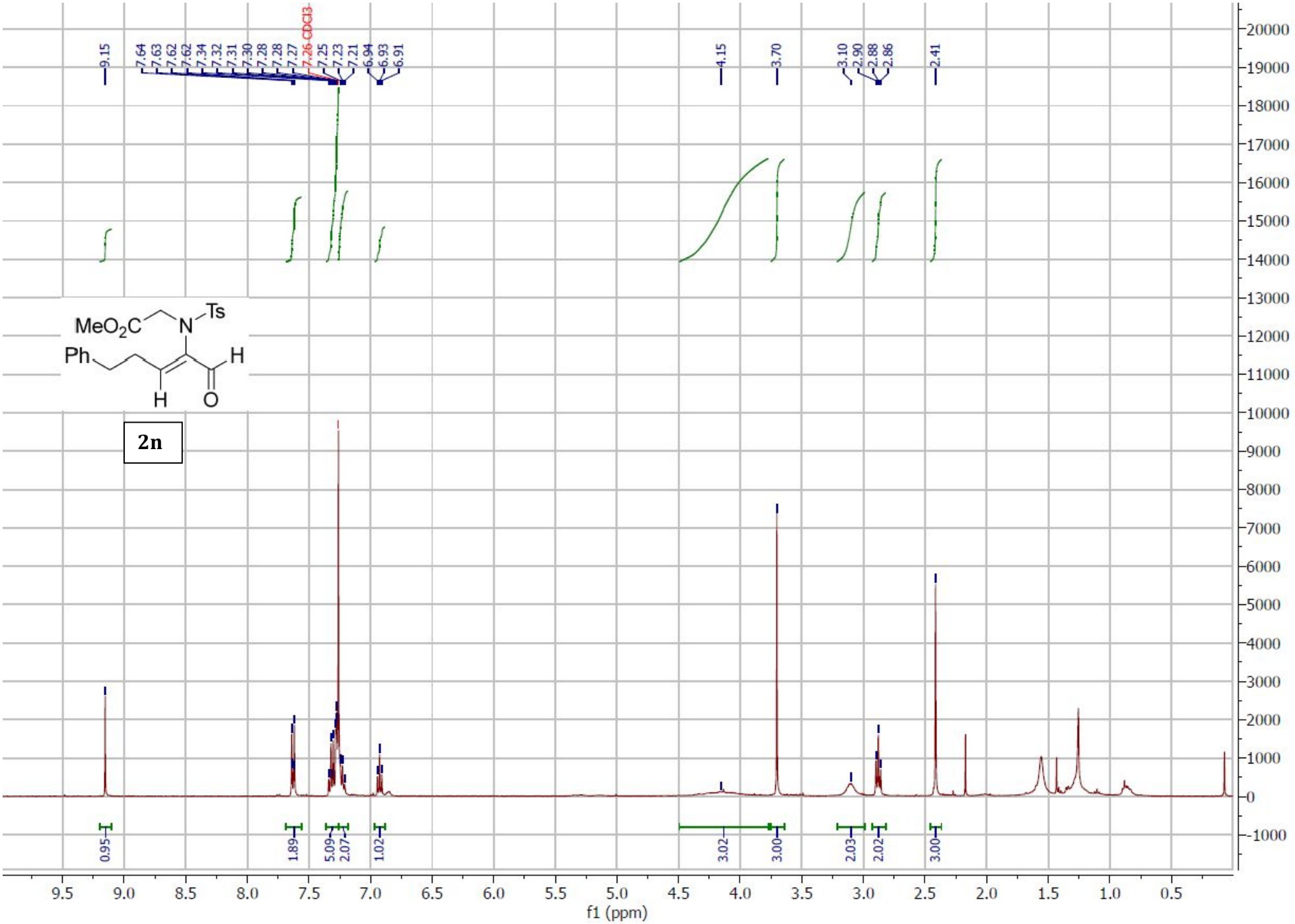
^{1}H NMR of compound **3m** (400 MHz, $CDCl_3$):



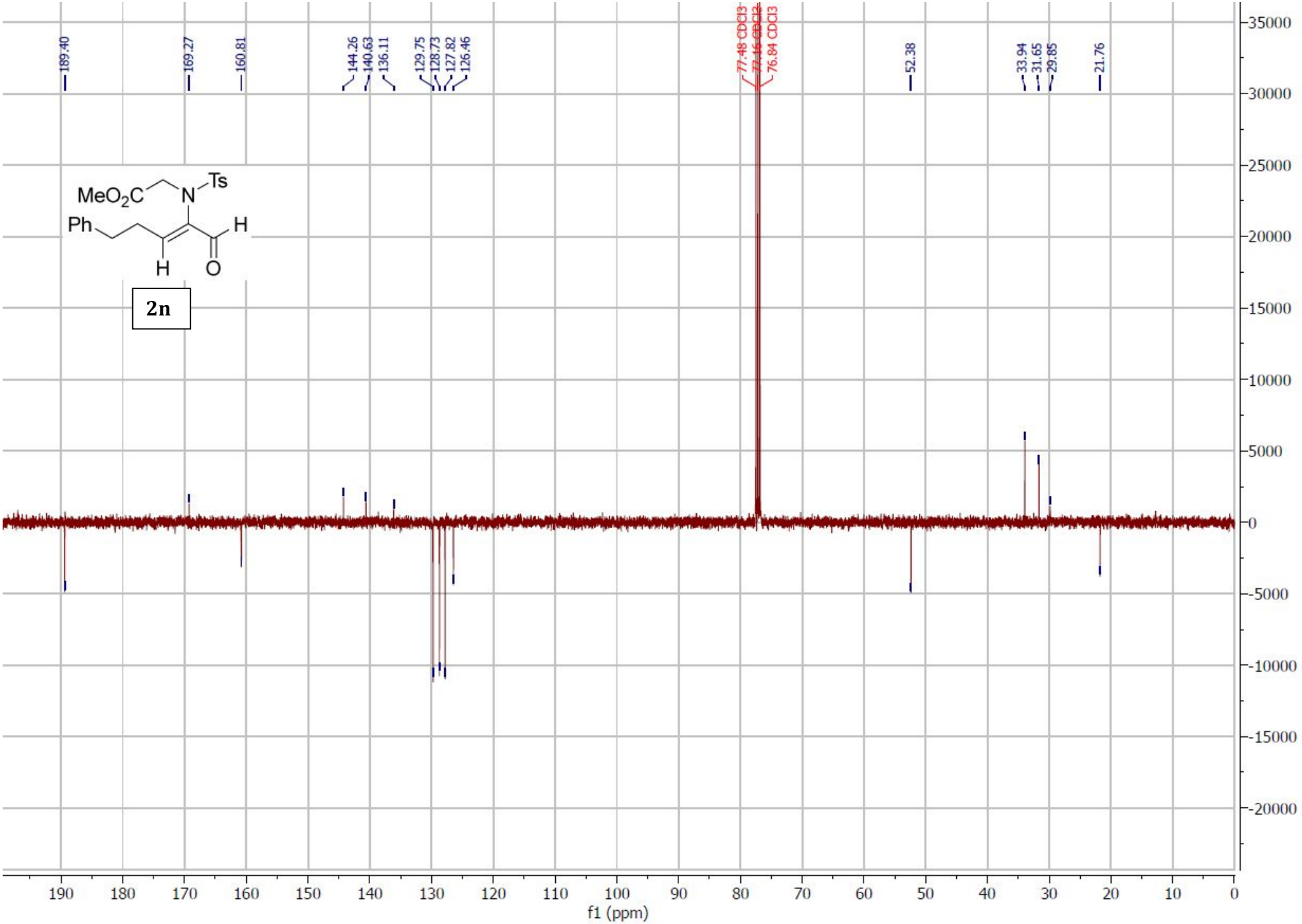
^{13}C NMR of compound **3m** (101 MHz, $CDCl_3$):



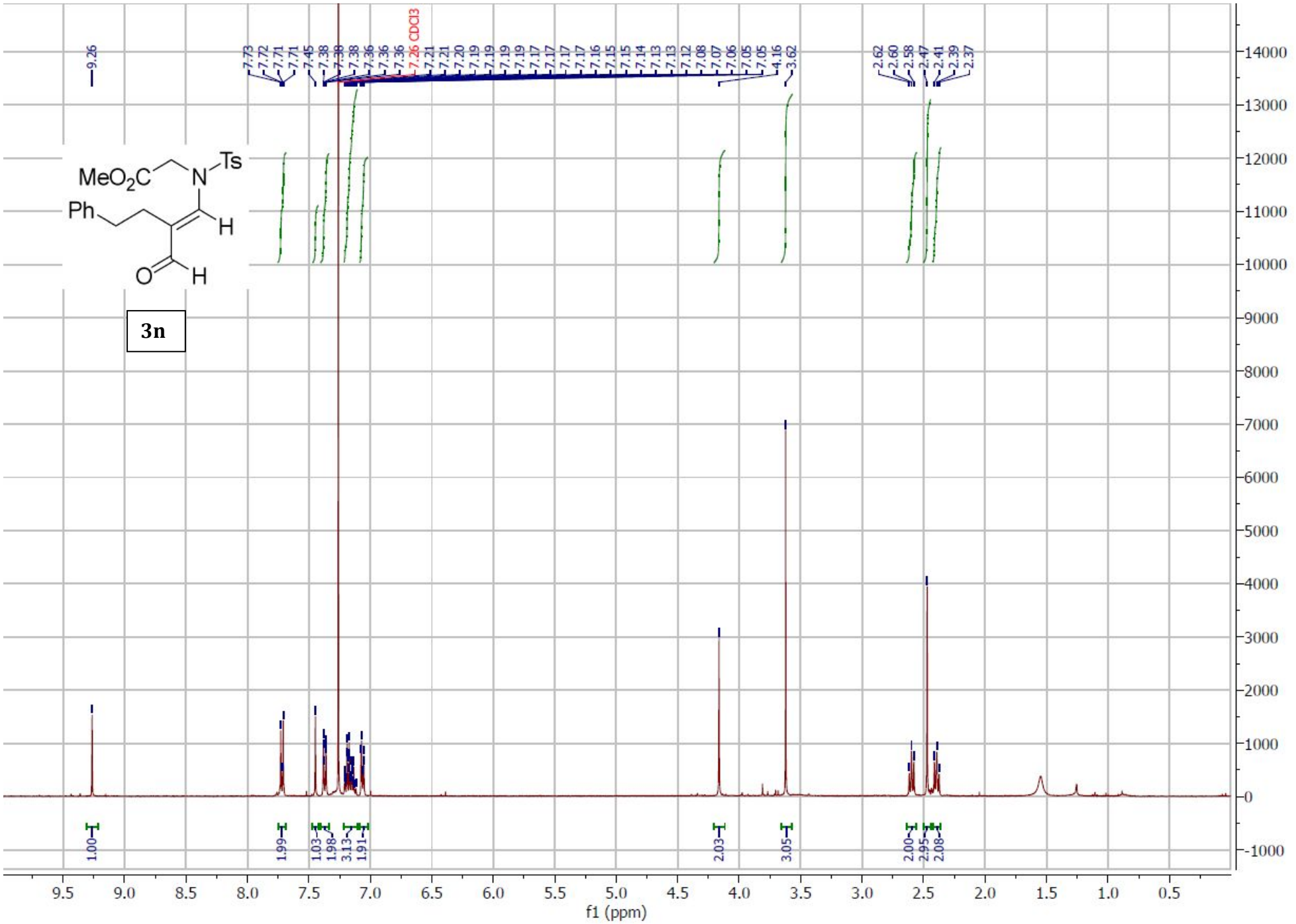
^{1}H NMR of compound **2n** (400 MHz, $CDCl_3$):



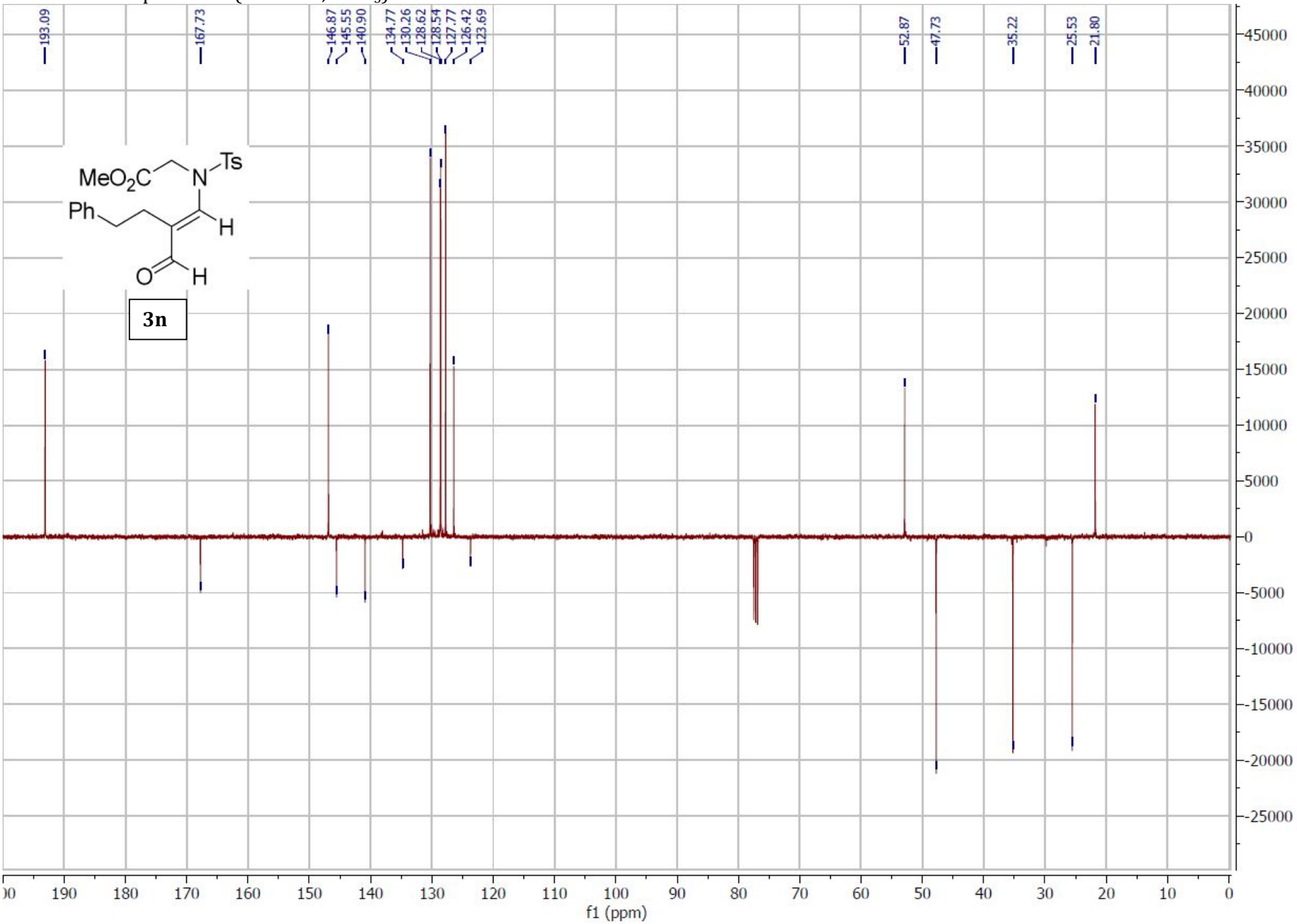
^{13}C NMR of compound **2n** (101 MHz, $CDCl_3$):



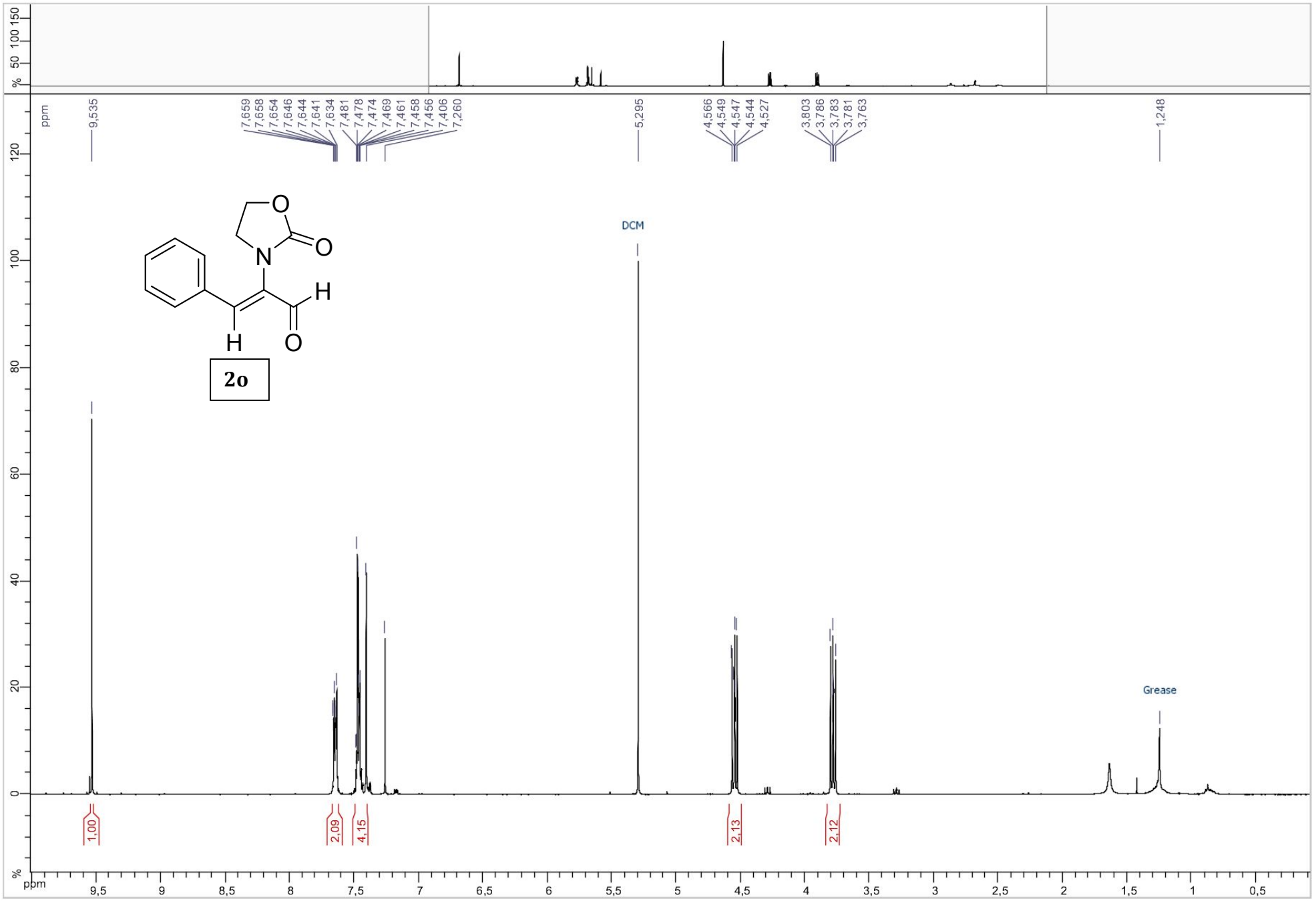
^{1}H NMR of compound **3n** (400 MHz, $CDCl_3$):



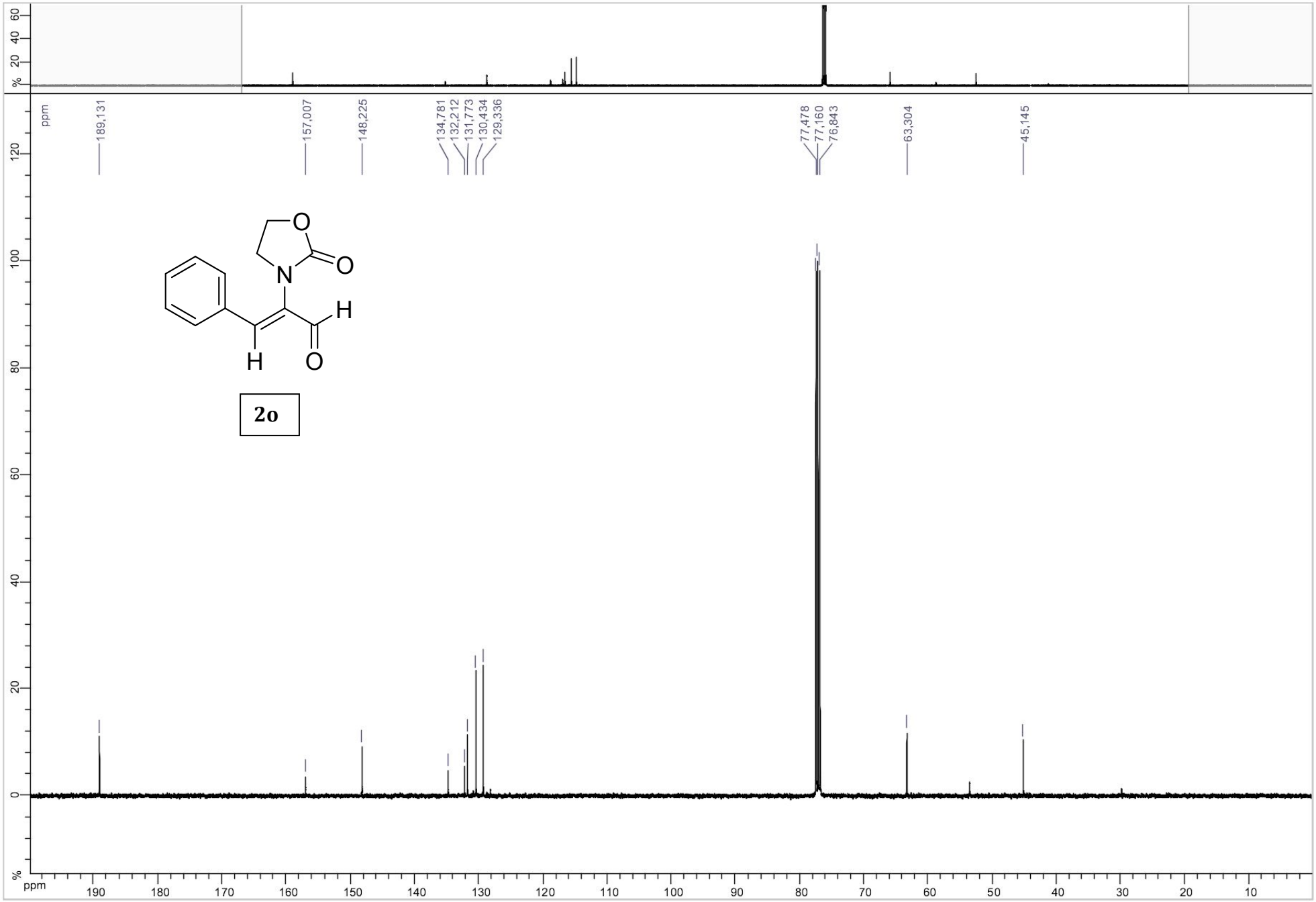
^{13}C NMR of compound **3n** (101 MHz, $CDCl_3$):



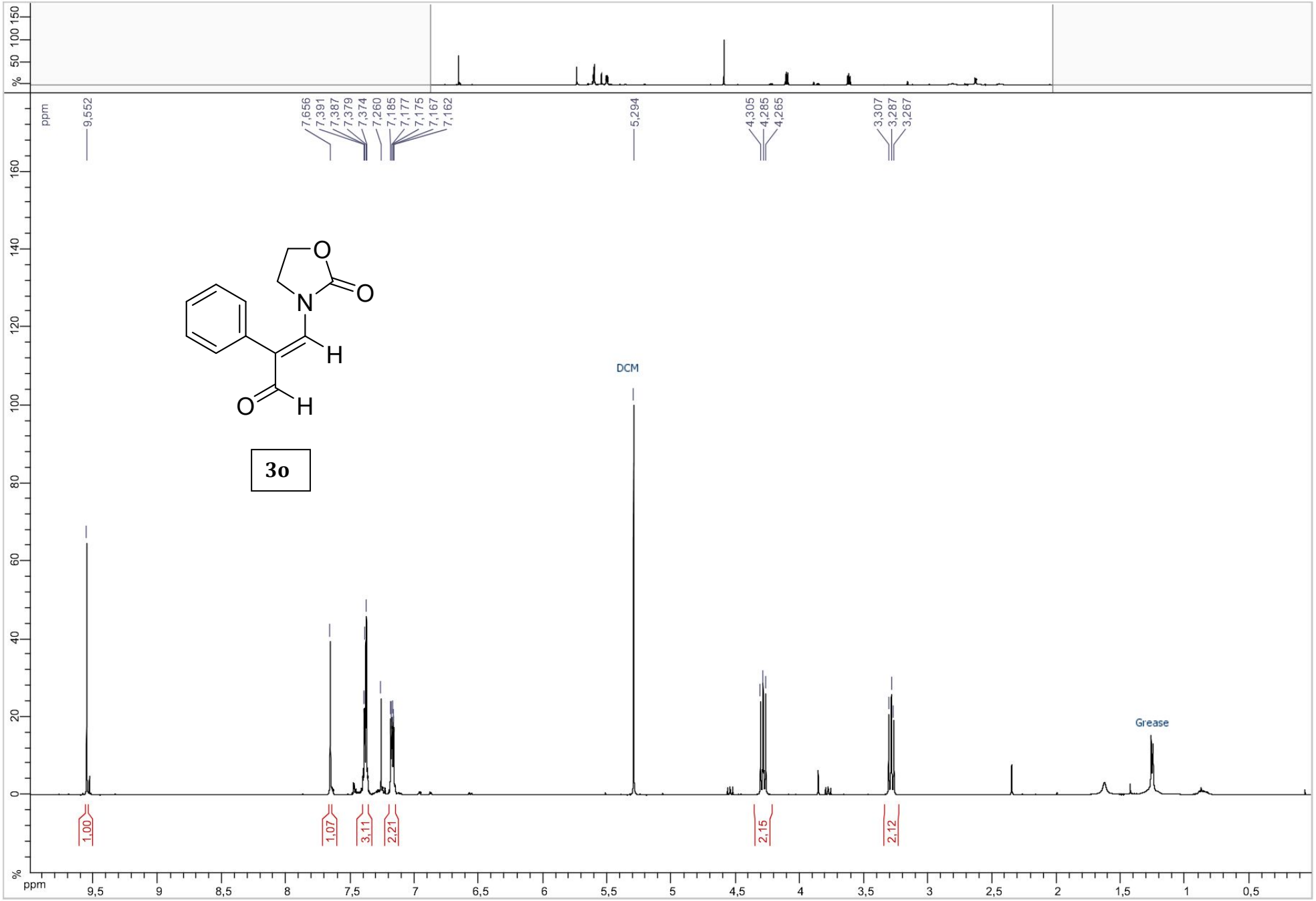
^{1}H NMR of compound **2o** (400 MHz, $CDCl_3$):



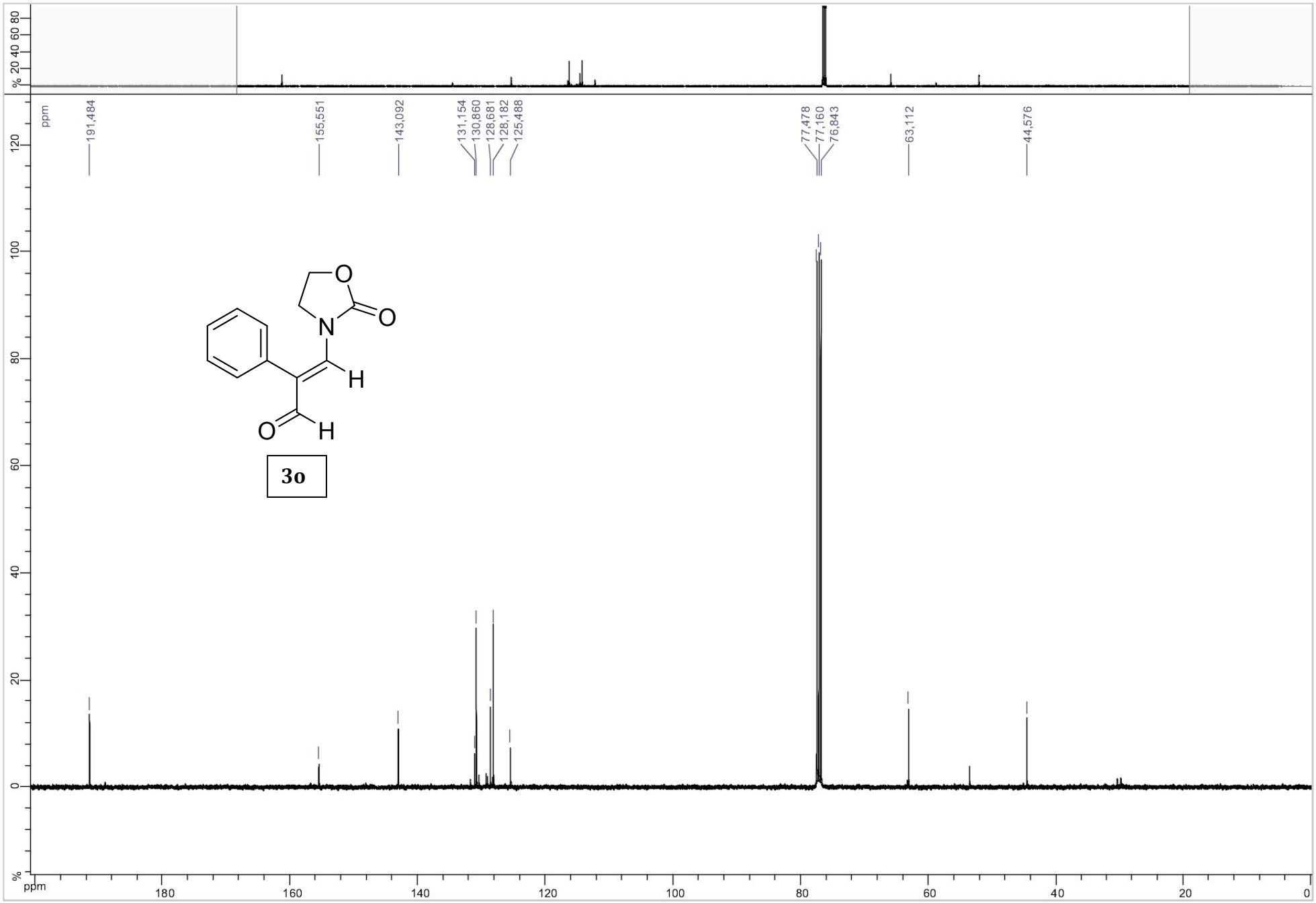
^{13}C NMR of compound **2o** (101 MHz, $CDCl_3$):



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

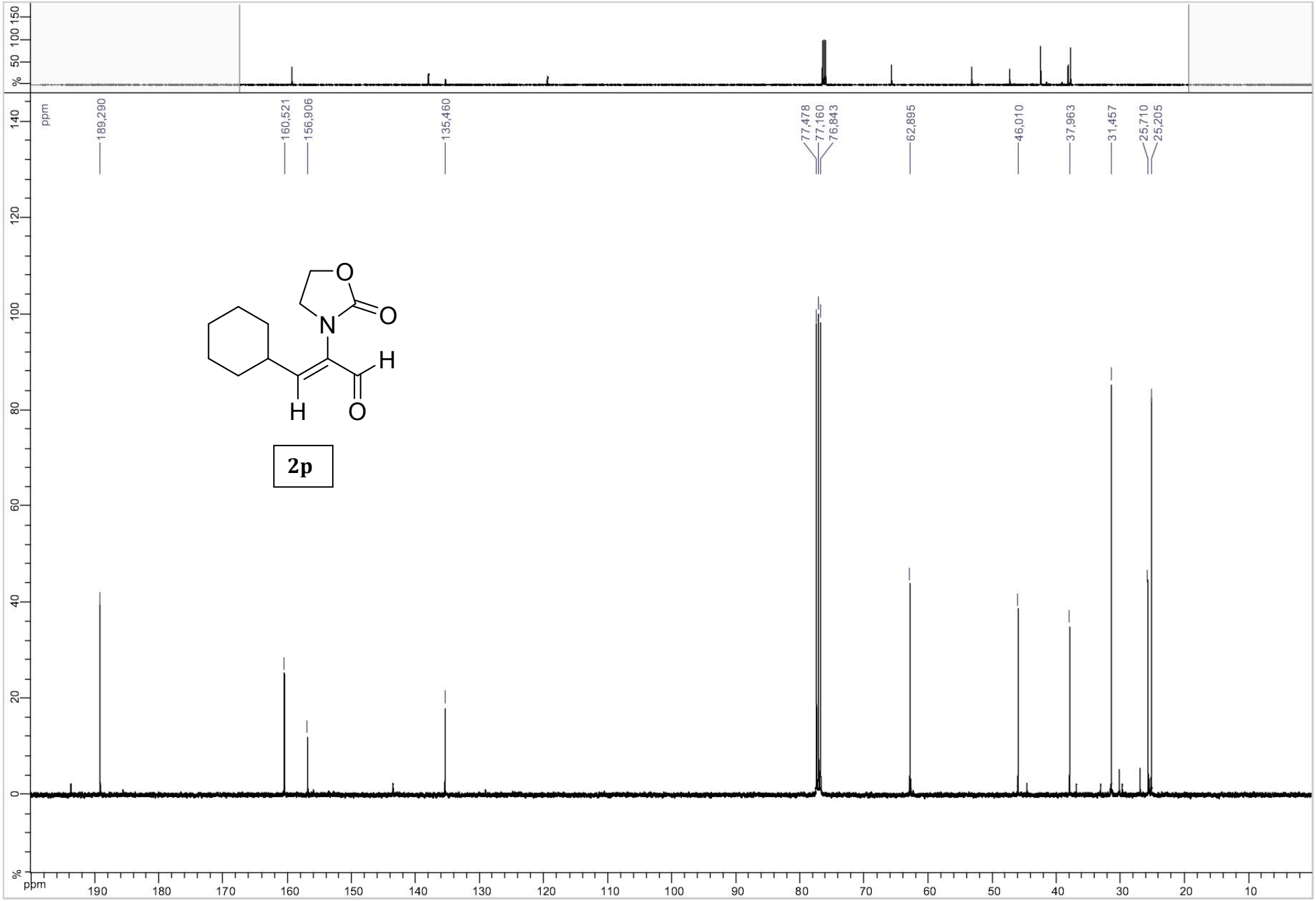


^{13}C NMR of compound **3o** (101 MHz, $CDCl_3$):

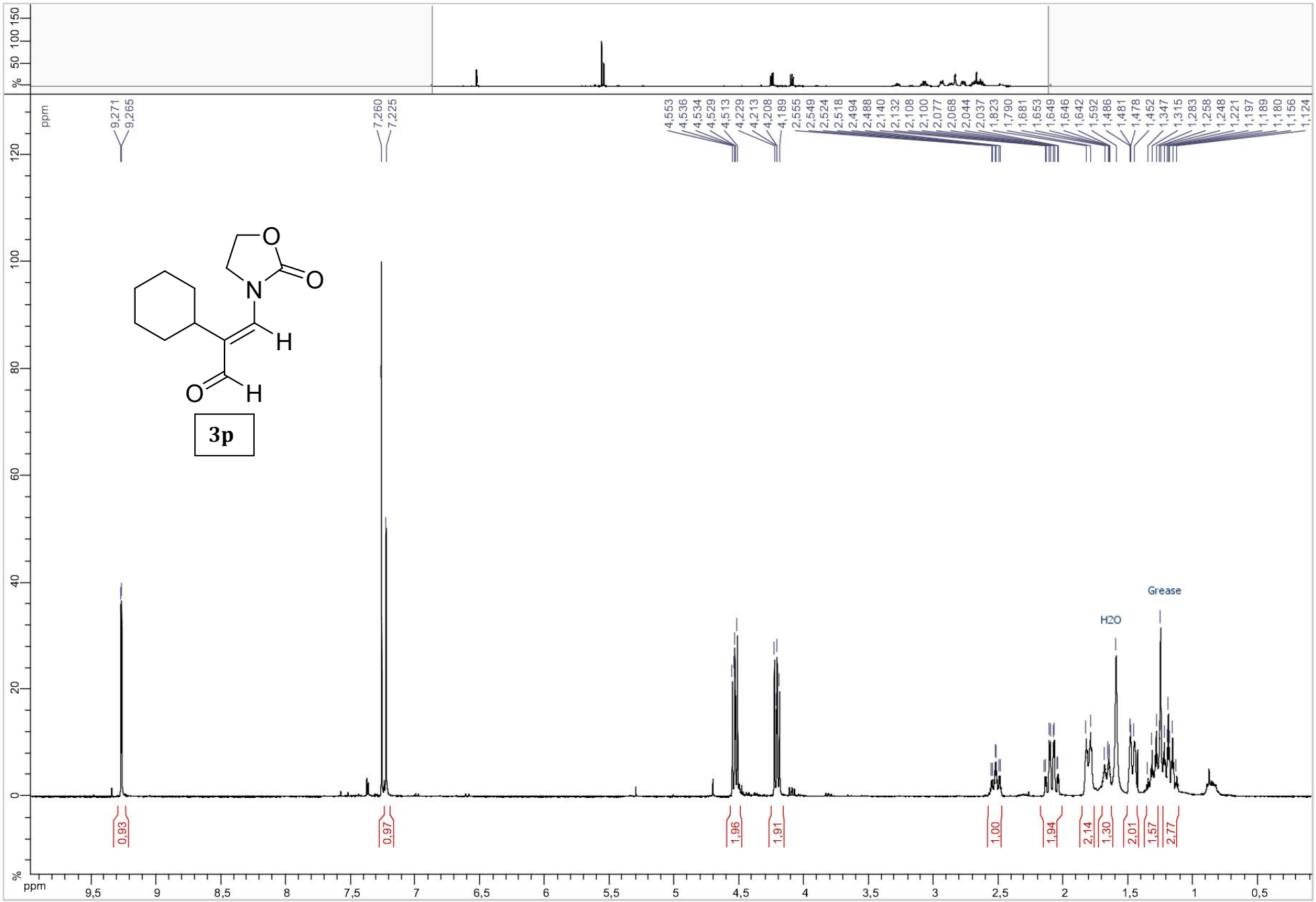


^{1}H NMR of compound **2p** (400 MHz, $CDCl_3$):

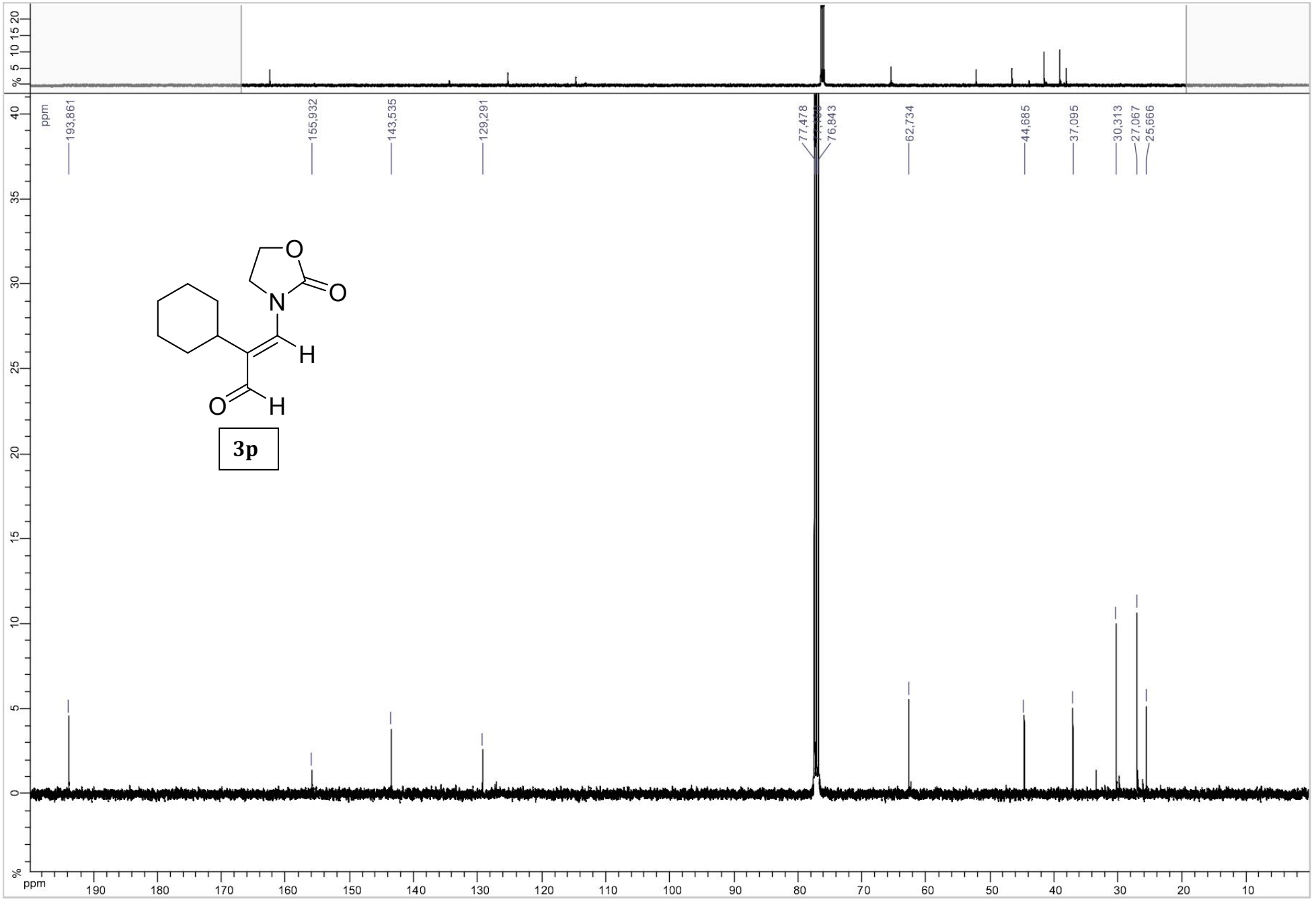
^{13}C NMR of compound **2p** (101 MHz, $CDCl_3$):



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

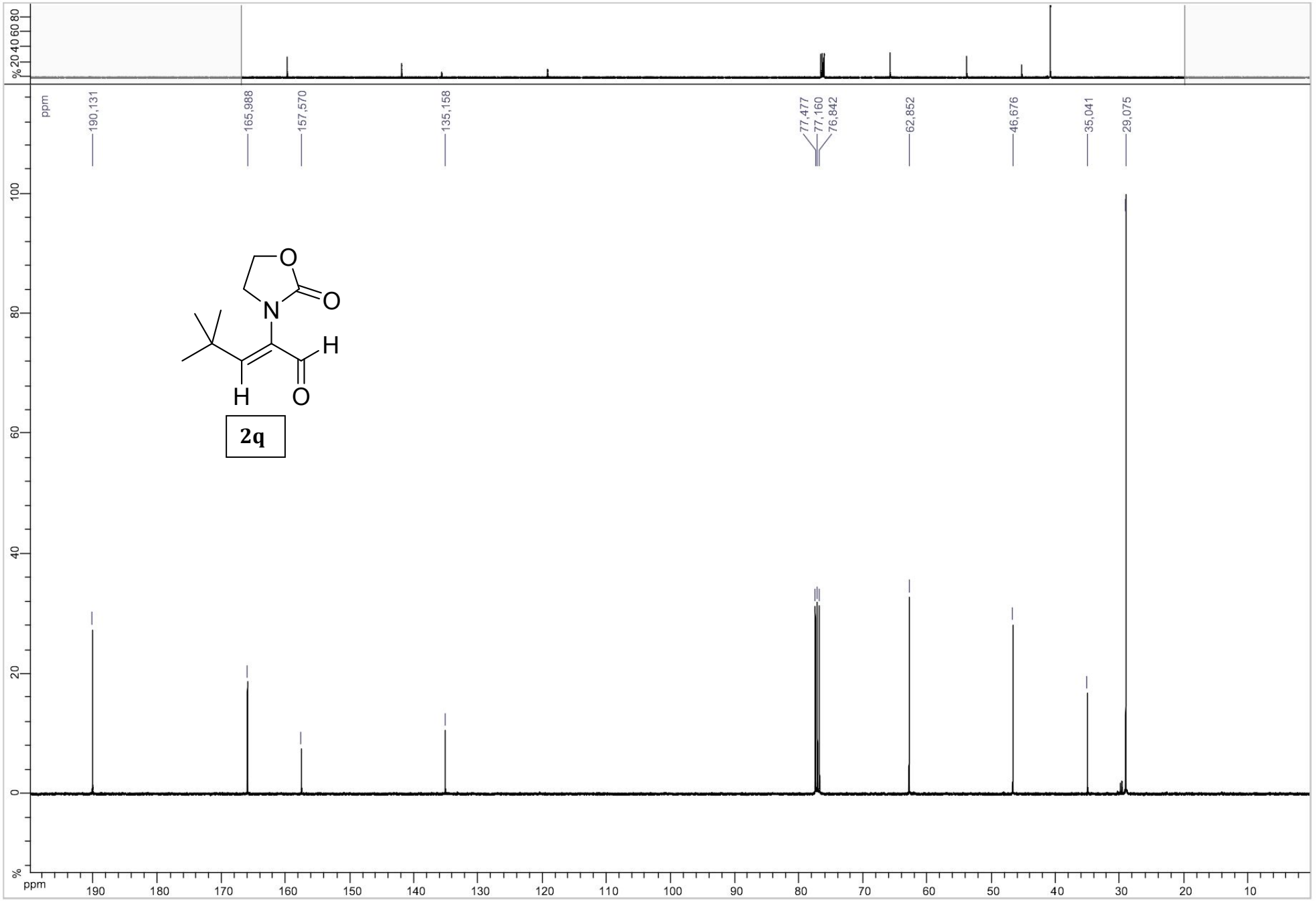


^{13}C NMR of compound **3p** (101 MHz, $CDCl_3$):



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

^{13}C NMR of compound **2q** (101 MHz, $CDCl_3$):



NOESY of compound **2q** (400 MHz, $CDCl_3$):