Supporting Information for

N-Methoxy-N-methylcyanoformamide, a Highly Reactive Reagent for the Formation of β-Keto-Weinreb Amides and Unsymmetrical Ketones.

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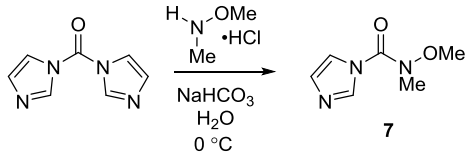
General Experimental Procedures

Unless otherwise specified, proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded at 18 °C in base-filtered $CDCl_3$ on a Varian spectrometer operating at 400 or 500 MHz for proton and 100 or 125 MHz for carbon nuclei. For ^{1}H NMR spectra, signals arising from the residual protio-forms of the solvent were used as the internal standards. ^{1}H NMR data are recorded as follows: chemical shift (d) [multiplicity, coupling constant(s) *J* (Hz), relative integral] where multiplicity is defined as: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; b = broad or combinations of the above. The signal due to residual $CHCl_3$ appearing at δ_H 7.26 and the central resonance of the $CDCl_3$ "triplet" appearing at δ_C 77.0 were used to reference ^{1}H and ^{13}C NMR spectra, respectively. Low-resolution ESI mass spectra were recorded on a single quadrupole liquid chromatograph-mass spectrometer, while high-resolution measurements were conducted on a time-of-flight instrument. Low- and high-resolution EI mass spectra were recorded on a magnetic-sector machine. Melting points were measured on an automated melting point system and are uncorrected. Analytical thin layer chromatography (TLC) was performed on aluminum-backed 0.2 mm thick silica gel 60 F_{254} plates. Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable dip followed by heating. These dips included phosphomolybdic acid : ceric sulfate : sulfuric acid (conc.) : water (37.5 g : 7.5 g : 37.5 g : 720 mL) or potassium permanganate : potassium carbonate : 5% sodium hydroxide aqueous solution : water (3 g : 20 g: 5 mL : 300 mL). Flash chromatographic separations were carried out following protocols defined by Still *et al*.[1] with silica gel 60 (40-63 mm) as the stationary phase and using the AR- or HPLC-grade solvents indicated. Tetrahydrofuran (THF), methanol and dichloromethane (DCM) were dried using a Glass Contour solvent purification system that is based upon a technology originally described by Grubbs *et al*.[1] Where necessary, reactions were performed under a nitrogen atmosphere.

Specific Experimental Procedures and Product Characterization

N-Methoxy-N-methylcarbamoyl imidazole ***7****.*

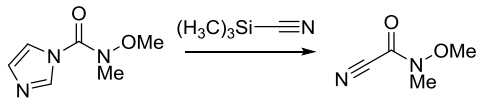


A magnetically stirred solution of *N*,*O*-dimethylhydroxylamine hydrochloride (20.0 g, 205 mmol), ice (100 g) and $NaHCO_3$ (100 mL of a saturated aqueous solution) in water (100 mL) in a 1L conical flask was maintained at 0 °C (ice/water) then treated, portionwise over a period of 2 minutes, with *N*,*N*′-carbonyldiimidazole (43.2 g, 267 mmol). The resultant mixture was maintained at 0 °C for 0.33 h then extracted with DCM (4 × 50 mL). The combined organic phases were washed with brine (25 mL) then dried (Na_2SO_4), filtered, and concentrated *in vacuo* to give compound **7** (29.6 g, 93%) as a pale yellow oil which was then held under high vacuum (1 mmHg, 18 ºC) for 5 h and used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.56 (t, *J* = 1.4 Hz, 1H), 7.05 (s, 1H), 3.68 (s, 3H), 3.38 (s, 3H).

Spectra were consistent with those previously reported.[2]

*N-Methoxy-N-methylcyanoformamide **4**. Preparation at 0 - 18 °C / 18 hours*



This reaction should be carried out in a well maintained and fully functioning fume-hood, wearing appropriate personal protective equipment. Magnetically stirred *N*-methoxy-*N*-methylcarbamoylimidazole **7** (15.5 g, 100 mmol) at 0 °C (ice/water bath) was treated dropwise via a pressure equalising dropping addition funnel, under an atmosphere of nitrogen, with trimethylsilyl cyanide (13.1 mL, 105 mmol **CAUTION!**). The cold bath was removed and replaced with an empty glass evaporating dish and the reaction stirred for 18 h. The solution was then poured onto a mixture of aqueous sodium bicarbonate (50 mL satd. solution) and ice (50 g), stirred for 0.10 h and then extracted with DCM (5 × 20 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4) and concentrated by rotary evaporation (415 mmHg, water bath at 35 °C) and then the residue was dissolved in ether (20 mL) and loaded onto a pad of silica (55 g, pre-wetted with ether), in a sintered vacuum funnel (60 mm I.D.) and washed through with ether (~400 mL, monitored by TLC analysis). The ethereal solution was then concentrated by rotary evaporation (415 mmHg, water bath at 35 °C), then held at 10 mmHg at 18 °C for 0.5 h to afford *N*-methoxy-*N*-methylcyanoformamide **4** as a pale yellow, clear, free flowing oil (10.6 g, 93%) and can be used without further purification to undertake the described transformations. A portion of the product (4.36 g) was distilled by short-path (b.p. 81-84 °C, 19 mmHg) to afford **4** (3.61 g, 83%) as a colorless oil (m.p. 8-11 °C). Distillation typically leads to approximately 5% impurity of the symmetrical urea, 1,3-dimethoxy-1,3-dimethylurea.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.89 (s, 3H), 3.28 (s, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.1, 110.0, 63.2, 32.3.
^{1}H NMR (C_6D_6, 400 MHz) δ 2.92 (s, 3H), 2.38 (s, 3H).
^{13}C NMR (C_6D_6, 100 MHz) δ 144.3, 110.9, 62.4, 31.4.
MS (EI): *m/z* (%) 114 ($M^{+\bullet}$, 47%), 99 (9), 88 (18), 84 (68), 83 (19), 71 (19), 60 (77), 57 (31), 54 (100).
HRMS (EI) *m/z* $M^{+\bullet}$ calcd for $[C_4H_6N_2O_2]^{+\bullet}$: 114.0424; found, 114.0430.
IR (KBr) ν_{max} 2946, 2238 1687, 1460, 1395, 1199, 987, 710 cm^{-1}.

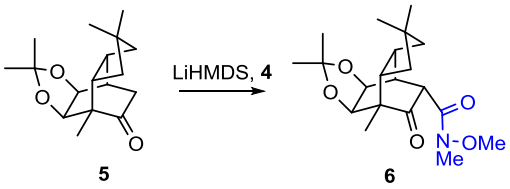
*N-Methoxy-N-methylcyanoformamide **4**. Preparation at 100 °C / 10 minutes*

This reaction should be carried out in a well maintained and fully functioning fume-hood, wearing appropriate personal protective equipment. Magnetically stirred *N*-methoxy-*N*-methyl carbamoyl imidazole **7** (15.5 g, 100 mmol) in a two necked round-bottomed flask (free from any scratches or imperfections) at 0 °C (ice/water bath) fitted with dry ice / acetone condenser, was treated dropwise via a pressure equalising dropping addition funnel, under an atmosphere of nitrogen, with trimethylsilyl cyanide (13.2 mL, 105 mmol **CAUTION!**). The cold bath was removed and replaced with an oil bath and heated to 100 °C and maintained, with stirring at this temperature for 0.2 h. The mixture was cooled to 0 °C and the reaction worked up as above for the preparation at room temperature (10.5 g, 92%).

*N-Methoxy-N-methyl cyanoformamide **4**. Preparation from N-methoxy-N-methylcarbamoyl chloride **2**.*

Following a procedure analogous to that used by Weber[3] for isobutyl cyanoformate: A magnetically stirred solution of *N*-methoxy-*N*-methylcarbamoyl chloride[4] (9.40 g, 76.1 mmol) in DCM (40 mL) at 0 °C (ice/water bath) under an atmosphere of nitrogen was treated with potassium cyanide (5.45 g, 84.0 mmol, **CAUTION!**) portion-wise over 1 minute followed by 18-crown-6 (100 mg). The reaction was warmed to 18 °C over 48 h and then the mixture was vacuum filtered through a 1 cm pad of sand and concentrated by distillation at atmospheric pressure. The crude oil was then distilled through a 10 cm vigreux (b.p. 81-84 °C, 19 mmHg) to afford **4** (4.77 g, 55%) as a colorless oil.

*β-Keto-Weinreb amide **6***



5 **6**

A magnetically stirred solution of ketone **5**[5] (200 mg, 0.72 mmol) in dry THF (5 mL) was cooled to −78 °C then treated dropwise with LiHMDS [generated from *n*-butyllithium (675 μL of a 1.6 M solution in hexanes, 1.08 mmol) and hexamethyldisilazane (233 μL, 1.11 mmol) in THF (10 mL)] . The resulting mixture was maintained at this temperature for 0.5 h then warmed to to 0 °C for 0.08 h then recooled to −78 °C and treated with **4** (106 mg, 0.94 mmol). After 0.5 h at −78 °C the mixture was treated with $NaHCO_3$ (5 mL of a saturated aqueous solution) and extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (1 × 5 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica, 4:1 to 1:1 v/v hexane/ethyl acetate) to afford, after concentration of the appropriate fractions compound **6** (205 mg, 78%) as a colorless oil.

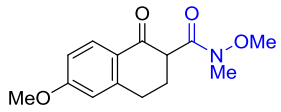
^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.81 (dd, *J* = 7.9, 3.7 Hz, 1H), 4.06 (d, *J* = 7.9 Hz, 1H), 3.84 (m, 1H), 3.72 (s, 3H), 3.18 (s, 3H), 2.98 (dddd, *J* = 11.8, 10.2, 8.5, 2.9 Hz, 1H), 2.63 (td, *J* = 11.8, 7.9 Hz, 1H), 2.54 (ddd, *J* = 6.2, 2.2, 2.2 Hz, 1H), 1.60 (ddd, *J* = 12.6, 8.5, 2.2 Hz, 1H), 1.52 (s, 3H), 1.46 (ddd, *J* = 12.6, 7.9, 2.1 Hz, 1H), 1.35 (s, 3H), 1.27 – 1.16 (m, 1H), 1.05 (s, 3H), 1.04 (s, 3H), 0.96 (s, 3H), 0.70 (dd, *J* = 12.6 Hz, 1H)
^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.3, 170.0, 109.6, 76.8, 73.3, 61.3, 53.0, 48.1, 43.6, 42.5, 38.1 (2C), 37.5, 31.7, 30.9, 28.6, 27.0, 25.5, 24.0, 15.2.
MS (EI): *m/z* (%) 365 ($M^{+\bullet}$, 3), 350 (22), 279 (100), 219 (60), 218 (55), 217 (45), 161 (38).
HRMS (EI) *m/z* $M^{+\bullet}$ calcd for $[C_{20}H_{31}NO_5]^{+\bullet}$: 365.2197; found, 365.2194;
IR (KBr) ν_{max} 2942, 1733, 1660, 1382, 1208. 1065, 1001, 886.

*General procedure for enolisation with LiHMDS and addition of **4**:*

A magnetically stirred solution of the appropriate ketone or ester (1.0 mmol) in dry THF (5 mL) was cooled to −78 °C then treated with LiHMDS (1.10 mL of a 1 M solution in THF, 1.10 mmol). The resultant mixture was maintained at this temperature for 1 h then treated with cyanoformamide **4** (125 mg, 1.10 mmol). After 15 minutes at −78 °C the reaction was treated with $NaHCO_3$ (5 mL of a saturated aqueous solution) and extracted with Et_2O (3 × 5 mL). The combined organic phases were

washed with brine (1 × 5 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica) to afford, after concentration of the appropriate fractions, the required Weinreb amide.

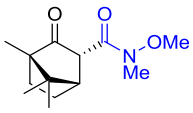
β-Keto-Weinreb amide ***9a***



Compound **9a** was prepared from 6-methoxy-1-tetralone according to the general procedure. Purified by flash chromatography (silica, 1:1 hexane/EtOAc) to afford **9a** (227 mg, 86%) as a white solid, mp. 95 – 100 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, *J* = 8.7 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.70 (d, *J* = 2.6 Hz, 1H), 4.06 (dd, *J* = 11.4, 3.0 Hz, 1H), 3.86 (s, 3H), 3.74 (s, 3H), 3.29 (s, 3H), 3.06 – 2.97 (m, 2H), 2.51 (m, 1H), 2.24 (m, 1H).
^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.1, 171.4, 163.8, 146.4, 130.1, 125.8, 113.3, 112.5, 61.4, 55.4, 50.9, 32.0, 28.7, 26.2.
MS (+LRESI) *m/z* (%) 264 (30) $[M+H]^+$, 286 (100) $[M+Na]^+$
HRMS (+ESI) *m/z* $[M+Na]^+$ calcd for $[C_{14}H_{17}NNaO_4]^+$: 286.1050; found, 286.1048;
IR (KBr) ν_{max} 1667, 1643, 1596, 1423, 1356, 1251, 1237, 987, 814 cm^{-1}.

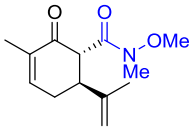
β-Keto-Weinreb amide ***9b***



Compound **9b** was prepared from (1*R*)-(+)-camphor according to the general procedure. Purified by flash chromatography (silica, 3:1 hexane/EtOAc) to afford **9b** (208 mg, 87%, *dr* 95:5) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.70 (s, 3H), 3.60 (d, *J* = 3.0 Hz, 1H), 3.18 (s, 3H), 2.38 (dd, *J* = 4.4, 4.4 Hz, 1H), 1.84 – 1.75 (complex m, 1H), 1.69 – 1.55 (complex m, 3H), 1.00 (s, 3H), 0.93 (s, 3H), 0.89 (s, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz) δ 213.1, 170.7, 61.5, 58.4, 53.7, 47.0, 46.0, 32.0, 29.4, 22.2, 19.6, 18.9, 9.6.
MS (+LRESI) *m/z* (%) 262 (100) $[M+Na]^+$, 501 (30) $[2M+Na]^+$
HRMS (+ESI) *m/z* $[M+Na]^+$ calcd for $[C_{13}H_{21}NNaO_3]^+$: 262.1414; found, 262.1411;
IR (KBr) ν_{max} 2963m 1750, 1656, 1447, 1379, 1176, 1102, 730 cm^{-1}.
$[\alpha]_D$ = + 76.7 (*c* 0.6, $CDCl_3$)

β-Keto-Weinreb amide ***9c***



Compound **9c** was prepared from (*S*)-(+)-carvone according to the general procedure. Purified by flash chromatography (silica, 1:1 hexane/EtOAc) to afford **9c** (197 mg, 83%, *dr* >99:1) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (m, 1H), 4.81 (m, 2H), 4.10 (d, J = 12.9 Hz, 1H), 3.72 (s, 3H), 3.32-3.20 (complex m, 4H), 2.51 (dt, J = 18.6, 5.4 Hz, 1H), 2.34 (m, 1H), 1.80 (dt, J = 2.6, 1.3 Hz, 3H), 1.76 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 170.8, 145.4, 144.6, 135.1, 112.0, 61.4, 54.0, 44.9, 32.0, 31.1, 20.4, 15.8.

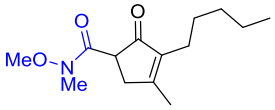
MS (EI) *m/z* (%) = 237 ($M^{+\bullet}$, 3), 177 (60), 149 (100).

HRMS (EI) *m/z* $M^{+\bullet}$ calcd for $C_{13}H_{19}NO_3$: 237.1365. Found: 237.1354.

IR (KBr) ν_{max} 2973, 2923, 1673, 1650, 1380 cm^{-1}.

[α]$_D$ = + 88.9 (*c* 1.0, $CHCl_3$).

β-Keto-Weinreb amide ***9d***



Compound **9d** was prepared from dihydrojasmone according to the general procedure. Purified by flash chromatography (silica, 1:1 hexane/EtOAc) to afford **9d** (208 mg, 82%) as a pale yellow oil.

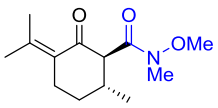
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (m, 1H), 3.75 (s, 3H), 3.12 (s, 3H), 2.75 (d, J = 18.1 Hz, 1H), 2.53 (dd, J = 18.1, 7.0 Hz, 1H), 2.05 (m, 2H), 1.98 (s, 3H), 1.26(m, 2H), 1.16 (m, 4H), 0.75 (t, J = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 170.7, 170.4, 139.0, 139.0, 61.8, 47.5, 32.1, 31.6, 27.8, 23.2, 22.4, 17.1, 13.9.

MS (EI): *m/z* (%) = 253 ($M^{+\bullet}$, 42), 193 (100), 149 (100).

HRMS (EI) *m/z* $M^{+\bullet}$ calcd for $C_{14}H_{23}NO_3$: 253.1672. Found: 253.1671.

IR (KBr) ν_{max} 2951, 2930, 2856, 1700, 1659, 1640, 1383 cm^{-1}.

β-Keto-Weinreb amide ***9e***



Compound **9e** was prepared from (*R*)-(+)-pulegone according to double the scale of the general procedure. Purified by flash chromatography (silica, 4:1 hexane/EtOAc) to afford **9e** (42 mg, 93%, *dr* 95:5) as a colorless oil.

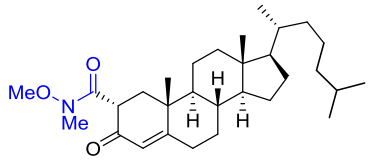
^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.70 (s, 3H), 3.52 (d, *J* = 10.5 Hz, 1H), 3.27 (s, 3H), 2.72 (dt, *J* = 15.6, 4.1 Hz, 1H), 2.48 – 2.38 (m, 1H), 2.33 (m, 1H), 1.99 (d, *J* = 1.4 Hz, 3H), 1.94 (ddt, *J* = 13.2, 4.6, 3.5 Hz, 1H), 1.80 (s, 3H), 1.42 (qd, *J* = 12.6, 4.6 Hz, 1H), 0.99 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.6, 171.5, 144.0, 130.9, 61.5, 61.3, 33.9, 31.9, 31.7, 28.3, 23.1, 22.3, 20.8.

IR (KBr) ν_{max} 2929, 1651, 1444, 1380, 1290, 1170, 974, 765 cm^{-1}.

[α]$_D$ = − 16.38 (*c* 1.7, $CDCl_3$)

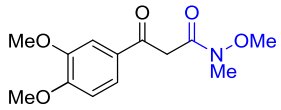
β-Keto-Weinreb amide ***9f***



Compound **9f** was prepared from (+)-4-cholesten-3-one according to the general procedure. Purified by flash chromatography (silica, 1:10 hexane/EtOAc) to afford **9f** (400 mg, 85%, *dr* 97:3) as a white solid, mp. 147 – 149 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.74 (d, *J* = 1.2 Hz, 1H), 4.00 (dd, *J* = 13.6, 2.8 Hz, 1H), 3.69 (s, 3H), 3.26 (s, 3H), 2.36 (m, 1H), 2.27 (ddd, *J* = 14.6, 4.5, 2.5 Hz, 1H), 2.16 (dd, *J* = 13.9, 13.9 Hz, 1H), 2.06 – 1.96 (complex m, 2H), 1.89 – 1.76 (complex m, 2H), 1.63 – 1.43 (complex m, 4H), 1.43 – 1.19 (complex m, 5H), 1.22 (s, 3H), 1.18 – 0.94 (m, 10H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.69 (s, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.9, 171.4, 171.2, 123.1, 61.4, 55.9, 55.7, 53.9, 45.9, 42.3, 39.5, 39.4, 38.7, 38.5, 36.1, 35.7, 35.5, 32.7, 32.0, 31.9, 28.1, 28.0, 24.1, 23.7, 22.8, 22.5, 20.8, 18.6, 17.7, 11.9.
MS (+LRESI) *m/z* (%) 472 (100) $[M+H]^+$, 494 (50) $[M+Na]^+$.
HRMS (+ESI) *m/z* $[M+Na]^+$ calcd for $[C_{30}H_{49}NNaO_3]^+$: 494.3605; found, 494.3604.
IR (KBr) ν_{max} 2934, 2866, 1668, 1651, 1451, 1384, 1173, 966 cm^{-1}.
[α]$_D$ = + 94.5 (*c* 1.0, $CDCl_3$)

β-Keto-Weinreb amide ***9g***

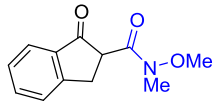


Compound **9g** was prepared from 3′,4′-dimethoxyacetophenone according to double the scale of the general procedure. Purified by flash chromatography (silica, 5:1 hexane/EtOAc) to afford **9g** (356 mg, 67%) as an 87:13 mixture of keto and enol tautomers as a cream solid, mp. 60 – 65 ºC.

^{1}H NMR ($CDCl_3$, 500 MHz) *Keto tautomer* δ 7.60 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.09 (s, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 3.68 (s, 3H), 3.24 (s, 3H).
^{1}H NMR ($CDCl_3$, 500 MHz) *Enol tautomer* δ 7.42 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.36 (d, *J* = 2.1 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.00 (s, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.76 (s, 3H), 3.27 (s, 3H).

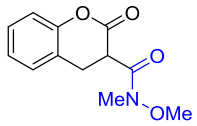
^{13}C NMR ($CDCl_3$, 125 MHz) *87:13 Mixture of keto and enol tautomers* δ 191.8, 172.8, 171.4, 168.6, 153.6, 151.3, 149.0, 148.7, 129.5, 123.3, 119.3, 110.6, 110.3, 110.0, 109.0, 83.0, 61.2, 60.2, 55.9, 55.9, 55.8, 44.0, 32.1.
MS (+LRESI) *m/z* (%) 290 (100) $[M+Na]^+$.
HRMS (+ESI) *m/z* $[M+Na]^+$ calcd for $[C_{13}H_{17}NNaO_5]^+$: 290.0933; found, 290.0999.
IR (KBr) ν_{max} 2972, 1667, 1634, 1584, 1512, 1417, 1321, 1268, 1152, 1025, 1008, 884, 796 cm^{-1}.

β-Keto-Weinreb amide ***9h***



Compound **9h** was prepared from 1-indanone according to the general procedure. Purified by flash chromatography (silica, 2:1 hexane/EtOAc) to afford **9h** (182 mg, 83%) as a pale yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 4.29 (m, 1H), 3.83 (s, 3H), 3.45 (m, 1H), 3.33 (m, 1H), 3.27 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 170.2, 154.1, 135.5, 135.0, 127.4, 126.4, 124.2, 61.6, 50.1, 32.2, 30.6.
MS (EI): *m/z* (%) = 219 ($M^{+\bullet}$, 33), 159 (100), 131 (80).
HRMS (EI) *m/z* $M^{+\bullet}$ calcd for $C_{12}H_{13}NO_3$: 219.0890. Found: 219.0895.
IR (KBr) ν_{max} 2973, 2935, 1713, 1649 cm^{-1}.

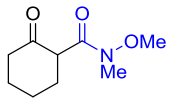
β-Carbonyl-Weinreb amide **9i**



Compound **9i** was prepared from 3,4-dihydrocoumarin according to the general procedure. Purified by flash chromatography (silica, 2:1 hexane/EtOAc) to afford **9i** (204 mg, 87%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.19 (complex m, 2H), 7.10 (m, 1H), 7.04 (m, 1H), 4.18 (dd, J = 12.9, 6.3 Hz, 1H), 3.72 (s, 3H), 3.27 (s, 3H), 3.49 (dd, J = 16.1, 12.9 Hz, 1H), 2.96 (dd, J = 16.1, 6.3 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 165.6, 151.2, 128.3, 128.0, 124.6, 121.7, 116.5, 61.5, 42.2, 32.1, 26.7.
MS (EI): *m/z* (%) = 235 ($M^{+\bullet}$, 20), 175 (39), 147 (100).
HRMS (EI) *m/z* $M^{+\bullet}$ calcd for $C_{12}H_{13}NO_4$: 235.0839. Found: 235.0846.
IR (KBr) ν_{max} 2976, 2943, 1760, 1659, 1138 cm^{-1}.

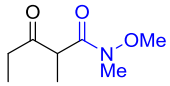
β-Keto-Weinreb amide ***9j***



Compound **9j** was prepared from cyclohexanone according to the general procedure. Purified by flash chromatography (silica, 4:1 hexane/EtOAc) to afford **9j** (140 mg, 76%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (m, 1H), 3.64 (s, 3H), 3.23 (s, 3H), 2.53 (m, 1H), 2.37 (m, 1H), 2.24-1.92 (complex m, 4H), 1.88-1.62 (complex m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 170.8, 61.2, 53.7, 41.9, 32.0, 29.7, 27.2, 23.7.
MS (EI): *m/z* (%) = 185 ($M^{+\bullet}$, 20), 125 (100).
HRMS (EI) *m/z* $M^{+\bullet}$ calcd for $C_9H_{15}NO_3$: 185.1046. Found: 185.1055.
IR (KBr) ν_{max} 2939, 2865, 1711, 1653, 1385 cm^{-1}.

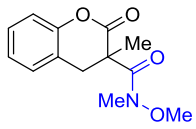
β-Keto-Weinreb amide ***9k***



Compound **9k** was prepared according to the general procedure. Purified by flash chromatography (silica, 4:1 hexane/EtOAc) to afford **9k** (130 mg, 77%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (m, 1H), 3.66 (s, 3H), 3.20 (s, 3H), 2.50 (m, 2H), 1.33 (d, J = 7.2 Hz, 3H), 1.05 (t, J = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 171.9, 61.1, 49.8, 33.6, 32.4, 13.1, 7.5.
MS (EI): *m/z* (%) = 173 ($M^{+\bullet}$, 3), 113 (42).
HRMS (EI) *m/z* $M^{+\bullet}$ calcd for $C_8H_{15}NO_3$: 173.1046. Found: 173.1048.
IR (KBr) ν_{max} 2980, 2941, 1719, 1661, 1460, 1381 cm^{-1}.

β-Keto-Weinreb amide ***9l***



A magnetically stirred solution of 3-methylchroman-2-one (168 mg, 1.0 mmol) in dry THF (5 mL) was cooled to 0 °C then treated with LiHMDS (1.1 mL of a 1 M solution in THF, 1.1 mmol). The resulting mixture was maintained at this temperature for 0.5 h then cooled to −78 °C and treated with cyanoformamide 4 (125 mg, 1.1 mmol). After 0.1 h at −78 °C the mixture was warmed to −40 °C and maintained at this temperature for 0.5 h before being treated with $NaHCO_3$ (5 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with brine (1 × 5 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica, 4:1 v/v hexane/ethyl acetate)

to afford, after concentration of the appropriate fractions compound 9l (230 mg, 92%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (m, 1H), 7.18 (m, 1H), 7.08 (m, 1H), 7.03 (m, 1H), 3.64 (s, 3H), 3.56 (d, J = 15.6 Hz, 1H), 3.12 (s, 3H), 2.78 (d, J = 15.6 Hz, 1H), 1.56 (m, 3H).

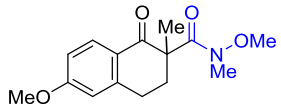
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 168.9, 151.1, 128.4, 128.2, 124.5, 121.4, 116.2, 60.4, 47.9, 35.0, 33.0, 21.6.

MS (EI): *m/z* (%) = 249 ($M^{+\bullet}$, 20), 234 (39), 161 (100).

HRMS (EI) *m/z* $M^{+\bullet}$ calcd for $C_{13}H_{15}NO_4$: 249.1001. Found: 249.1003.

IR (KBr) ν_{max} 2985, 2939, 1759, 1655, 1457, 1231 cm^{-1}.

β-Keto-Weinreb amide ***9m***



A magnetically stirred solution of 6-methoxy-2-methyl-1-tetralone (190 mg, 1.00 mmol) in dry ether (3 mL) was cooled to −78 °C then treated dropwise with lithium diisopropylamide (1.29 mL, 1.05 mmol, 0.81 M solution in ether [generated from *n*-butyllithium (7.00 mL of a 1.5 M solution in hexanes) and diisopropylamine (1.60 mL, 11.5 mmol) in ether (4.3 mL)]. The resulting mixture was maintained at this temperature for 1 h then warmed to 0 °C for 0.25 h then recooled to −78 °C and treated with **4** (125 mg, 1.10 mmol) followed by hexamethylphosphoramide (HMPA) (179 µL, 1.00 mmol) After 0.5 h at −78 °C the mixture was treated with $NaHCO_3$ (5 mL of a saturated aqueous solution) and extracted with DCM (3 × 10 mL). The combined organic phases were washed with lithium chloride (10 mL, 5% w/v), brine (1 × 5 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica, 4:1 v/v hexane/ethyl acetate) to afford, after concentration of the appropriate fractions compound **9m** (174 mg, 63%) as white crystals, m.p. 89 – 92 ºC. The reaction was carried out in duplicate with 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (250 µL) in place of HMPA to afford **9m** (173 mg, 63%) as white crystals, m.p. 89 – 92 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, J = 8.7 Hz, 1H), 6.79 (dd, J = 8.7, 2.5 Hz, 1H), 6.64 (d, J = 2.5 Hz, 1H), 3.81 (s, 3H), 3.29 (s, 3H), 3.12 (s, 3H), 2.96 (ddd, J = 16.6, 11.6, 4.8 Hz, 1H), 2.81 (ddd, J = 16.6, 4.6, 4.6 Hz, 1H), 2.54 (ddd, J = 13.0, 11.6, 4.8 Hz, 1H), 1.81 (dt, J = 13.0, 4.6 Hz, 1H), 1.41 (s, 3H).

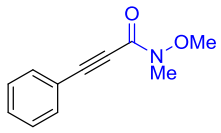
^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.3, 174.3, 163.3, 144.8, 129.8, 125.1, 113.3, 112.2, 59.0, 55.3, 52.7, 32.7, 31.9, 25.7, 20.1.

MS (EI): *m/z* (%) 277 ($M^{+\bullet}$, 8), 217 (9), 189 (30), 161 (100), 91 (10).

HRMS (EI) *m/z* $M^{+\bullet}$ calcd for $[C_{15}H_{19}NO_4]^{+\bullet}$: 277.1309; found, 277.1316;

IR (KBr) ν_{max} 1653, 1598, 1457, 1374, 1346, 1262, 1230, 1093, 999, 858 cm^{-1}.

*Weinreb amide **10a** – Prepared from lithium phenyl acetylide*

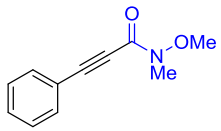


A magnetically stirred solution of phenyl acetylene (102 mg, 1.0 mmol) in dry THF (5 mL) was cooled to −78 °C then treated with LiHMDS (1.1 mL of a 1M solution in THF, 1.1 mmol). The resulting mixture was maintained at this temperature for 20 minutes then treated with cyanoformamide 4 (125 mg, 1.1 mmol). The resulting mixture was maintained at −78 °C for 15 minutes then treated with $NaHCO_3$ (5 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with brine (1 × 5 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica, 4:1 v/v hexane/ethyl acetate) to afford, after concentration of the appropriate fractions compound **10a** (174 mg, 92%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.1 Hz, 2H), 7.43 (m, 1H), 7.37 (m, 2H), 3.84 (s, 3H), 3.29 (br m, 3H).

All spectra were consistent with those previously reported.[6]

*Weinreb amide **10a** – Prepared from magnesium phenyl acetylide*

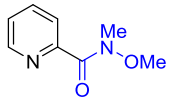


A magnetically stirred solution of phenyl acetylene (102 mg, 1.0 mmol) in dry THF (5 mL) was cooled to 0 °C then treated with MeMgBr (0.33 mL of a 3M solution in Et_2O, 1.1 mmol). The resulting mixture was maintained at this temperature for 1 h then treated with cyanoformamide 4 (125 mg, 1.1 mmol). After 0.25 h at 0 °C the reaction was treated with $NaHCO_3$ (5 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with brine (1 × 5 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica, 4:1 v/v hexane/ethyl acetate) to afford, after concentration of the appropriate fractions compound **10a** (144 mg, 76%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.1 Hz, 2H), 7.43 (m, 1H), 7.37 (m, 2H), 3.84 (s, 3H), 3.29 (br m, 3H).

All spectra were consistent with those previously reported.[6]

Weinreb amide ***10b***

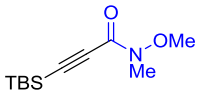


A magnetically stirred solution of 2-bromopyridine (158 mg, 1.0 mmol) in dry THF (5 mL) was cooled to −78 °C then treated with *n*-butyllithium (0.8 mL of a 1.45 M solution in hexanes, 1.1 mmol). The resulting solution was stirred at −78 °C for 1 hour then treated with cyanoformamide 4 (125 mg, 1.1 mmol) and warmed to 0 °C over 20 minutes. The reaction was treated with $NaHCO_3$ (5 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with brine (1 × 5 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica, 1:1 v/v hexane/ethyl acetate) to afford, after concentration of the appropriate fractions compound **10b** (125 mg, 75%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 4.8 Hz, 1H), 7.78 (td, J = 7.7, 1.7 Hz, 1H), 7.66 (broad s, 1H), 7.35 (dd, J = 7.7, 4.8 Hz, 1H), 3.75 (s, 3H), 3.40 (s, 3H).

All spectra were consistent with those previously reported.[7]

Weinreb amide ***10c***



A magnetically stirred solution of tert-butyl(ethynyl)dimethylsilane (228 mg, 2.0 mmol) in dry THF (8 mL) was cooled to −78 °C then treated with *n*-Butyl lithium (1.0 mL of a 2.05 M solution in hexanes, 2.05 mmol). The resulting mixture was maintained at this temperature for 0.25 h then treated with cyanoformamide 4 (228 mg, 2.0 mmol). The resulting mixture was maintained at −78 °C for 0.1 h then treated with $NaHCO_3$ (5 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 5 mL). The combined organic phases were washed with brine (1 × 5 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica, 4:1 v/v hexane/ethyl acetate) to afford, after concentration of the appropriate fractions compound **10c** (399 mg, 88%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.77 (s, 3H), 3.23 (s, 3H), 0.98 (s, 9H), 0.19 (s, 6H).

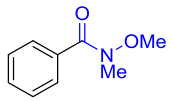
^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.7, 109.9, 95.8, 62.0, 32.2, 25.9 (3C), 16.4, -5.3 (2C).

MS (+LRESI) *m/z* (%) 228 (100) $[M+H]^+$.

HRMS (+ESI) *m/z* $[M+Na]^+$ calcd for $[C_{11}H_{21}NNaO_2Si]^+$: 250.1234; found, 250.1236.

IR (KBr) ν_{max} 2955, 2932, 1647, 1472, 1463, 1410, 1381, 1252, 1118, 1007, 940, 842, 828, 779, 724 cm^{-1}.

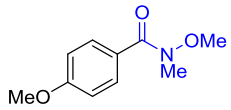
*Weinreb amide **10d***



A magnetically stirred solution of cyanoformamide 4 (125 mg, 1.1 mmol) in dry THF (5 mL) at 0 °C was treated, dropwise, with a solution of phenylmagnesium bromide (1.0 mL of a 1M solution in THF, 1.0 mmol). The resulting mixture was maintained at this temperature for 15 minutes then treated with $NaHCO_3$ (5 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with brine (1 × 5 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica, 4:1 v/v hexane/ethyl acetate) to afford, after concentration of the appropriate fractions compound **10d** (152 mg, 92%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (m, 2H), 7.41 (m, 3H), 3.55 (s, 3H), 3.36 (s, 3H).
All spectra were consistent with those previously reported.[8]

*Weinreb amide **10e***

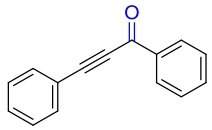


A magnetically stirred solution of 4-bromoanisole (0.126 mL, 1.0 mmol), magnesium turnings (26 mg, 1.0 mmol) and a crystal of iodine in dry THF (5 mL) was heated at 50 °C for 30 minutes. The resulting suspension was cooled to 0 °C and treated with cyanoformamide 4 (125 mg, 1.1 mmol). After 15 minutes at this temperature the mixture was treated with $NaHCO_3$ (5 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with brine (1 × 5 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica, 4:1 v/v hexane/ethyl acetate) to afford, after concentration of the appropriate fractions compound **10e** (171 mg, 88%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 3.56 (s, 3H), 3.35 (s, 3H).

All spectra were consistent with those previously reported.[88]

*Ketone **10f***



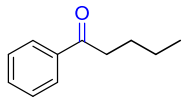
A magnetically stirred solution of phenyl acetylene (102 mg, 1.0 mmol) in dry THF (5 mL) was cooled to −78 °C then treated with LiHMDS (1.1 mL of a 1M solution in THF, 1.1 mmol). The

resulting mixture was maintained at this temperature for 0.33 h then treated with cyanoformamide 4 (125 mg, 1.1 mmol). The resulting mixture was maintained at −78 °C for 15 minutes then warmed to 0 °C and treated with PhMgBr (1.5 mL of a 1M solution in THF, 1.5 mmol). The resulting mixture was maintained at this temperature for 30 minutes then treated with $NaHCO_3$ (5 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with brine (1 × 5 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica, 4:1 v/v hexane/ethyl acetate) to afford, after concentration of the appropriate fractions compound **10f** (184 mg, 89%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (m, 2H), 7.70 (m, 2H), 7.64 (m, 1H), 7.56 – 7.47 (complex m, 3H), 7.43 (m, 2H).

All spectra were consistent with those previously reported.[9]

*Ketone **10g***

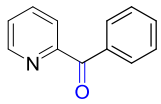


A magnetically stirred solution of cyanoformamide 4 (125 mg, 1.1 mmol) in dry THF (5 mL) at 0 °C was treated, dropwise, with a solution of phenylmagnesium bromide (1.0 mL of a 1M solution in THF, 1.0 mmol). The resulting mixture was maintained at this temperature for 0.25 h then cooled to −78 °C and treated with *n*-butyllithium (1 mL of a 1.5 M solution in hexanes, 1.5 mmol). The reaction was maintained at this temperature for 20 minutes then treated with $NaHCO_3$ (5 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with brine (1 × 5 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica, 4:1 v/v hexane/ethyl acetate) to afford, after concentration of the appropriate fractions compound **10g** (140 mg, 86%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (m, 2H), 7.55 (m, 1H), 7.46 (m, 2H), 2.97 (dd, J = 7.4 Hz, 2H), 1.73 (m, 2H), 1.42 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H).

All spectra were consistent with those previously reported.[10]

*Ketone **10h***



A magnetically stirred solution of 2-bromopyridine (158 mg, 1.0 mmol) in dry THF (5 mL) was cooled to −78 °C then treated with *n*-butyllithium (0.8 mL of a 1.45 M solution in hexanes, 1.1 mmol). The resulting solution was stirred at −78 °C for 1 h then treated with cyanoformamide 4 (125 mg, 1.1 mmol) and warmed to 0 °C over 0.33 h then treated with PhMgBr (1.5 mL of a 1M solution in THF, 1.5 mmol). The reaction was maintained at this temperature for 20 minutes then treated with $NaHCO_3$

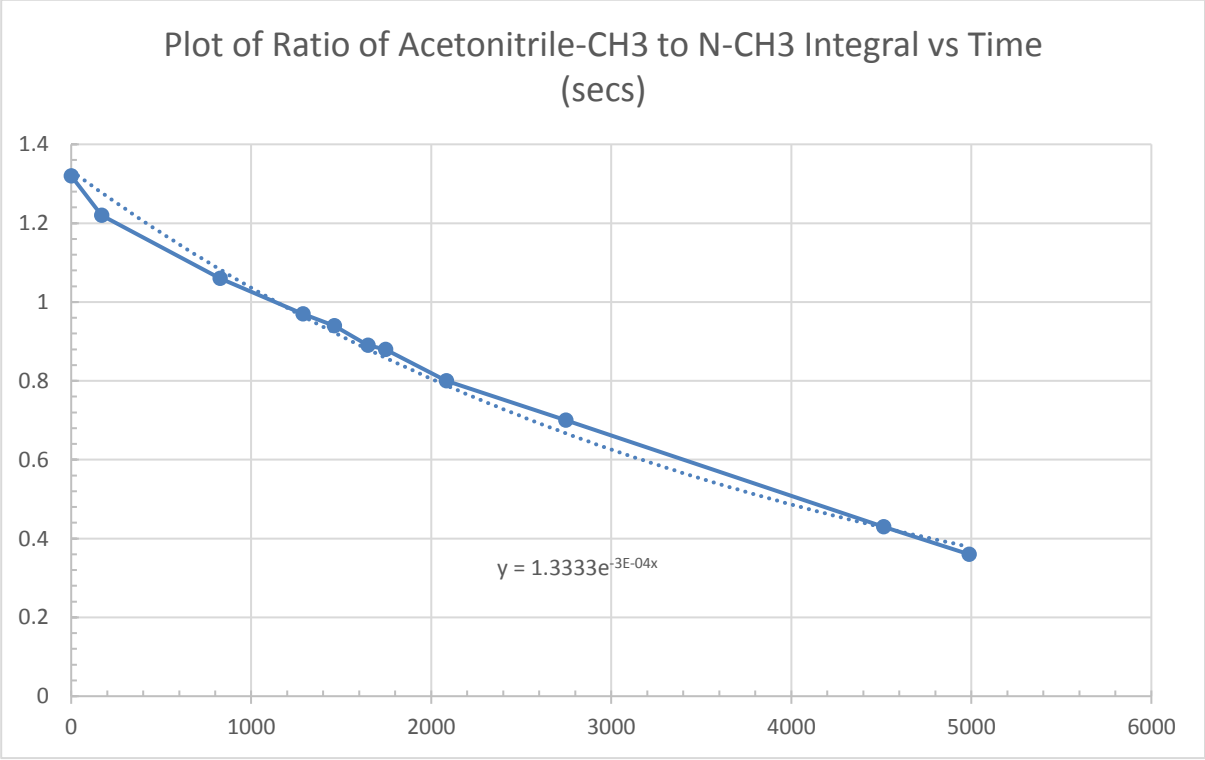
(5 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with brine (1 × 5 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica, 4:1 v/v hexane/ethyl acetate) to afford, after concentration of the appropriate fractions compound **10h** (159 mg, 86%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (dt, J = 4.8, 1.3 Hz, 1H), 8.06 (m, 3H), 7.91 (td, J = 7.7, 1.7 Hz, 1H), 7.60 (m, 1H), 7.49 (m, 3H).

All spectra were consistent with those previously reported.[11]

Half-life determination experiment.

An NMR tube was charged with cyanoformamide **4** (5 µL), acetonitrile (2 µL) and D_2O (0.5 mL) and shaken vigorously for 30 seconds. The ^{1}H NMR spectrum was recorded at regular intervals and the ratio of the N$\underline{CH_3}$ to $\underline{CH_3}$CN integral was recorded. The $t_{1/2}$ was calculated to be 2344 minutes (39 h).



References

[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem*., **1978**, *43*, 2923.
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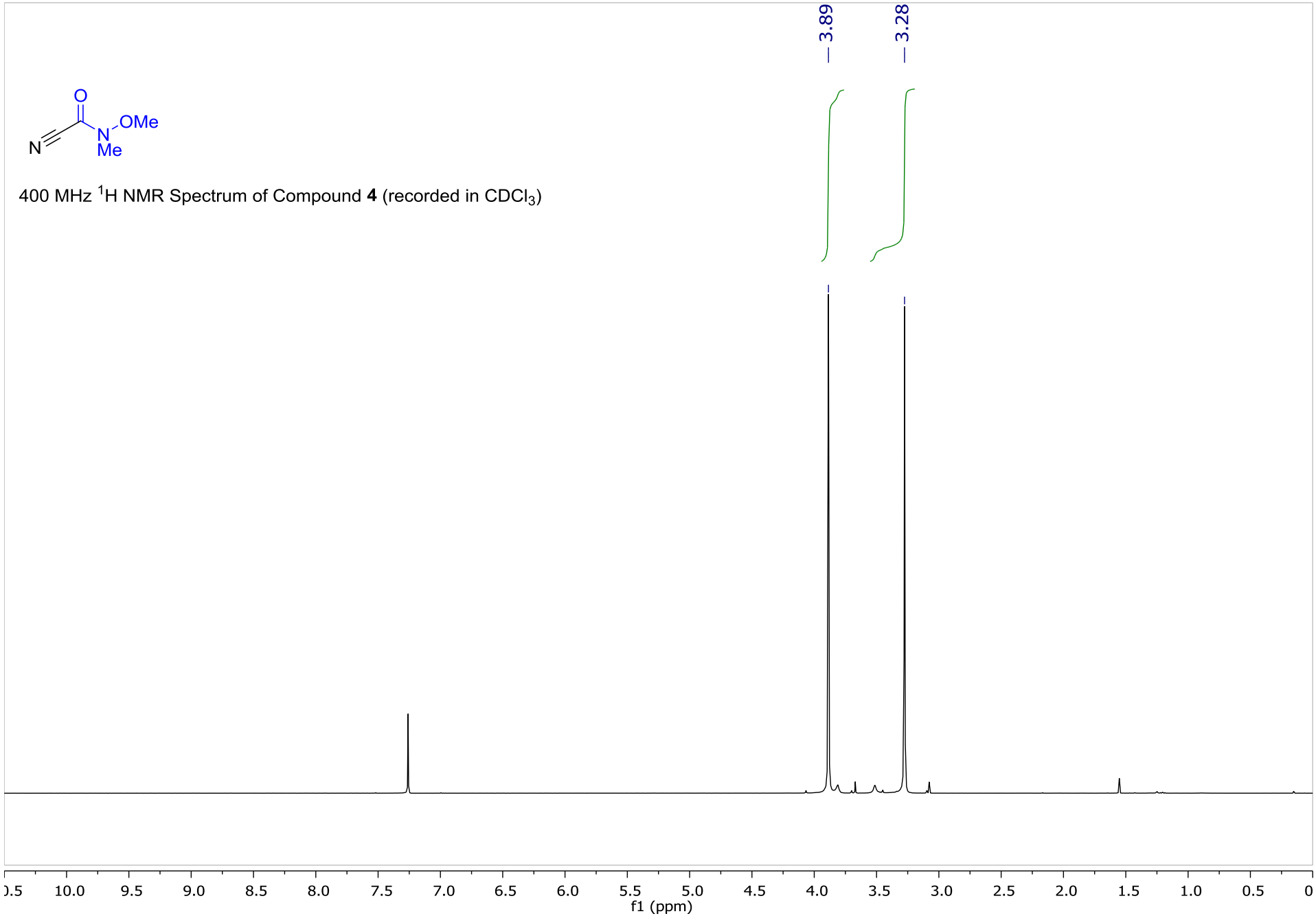
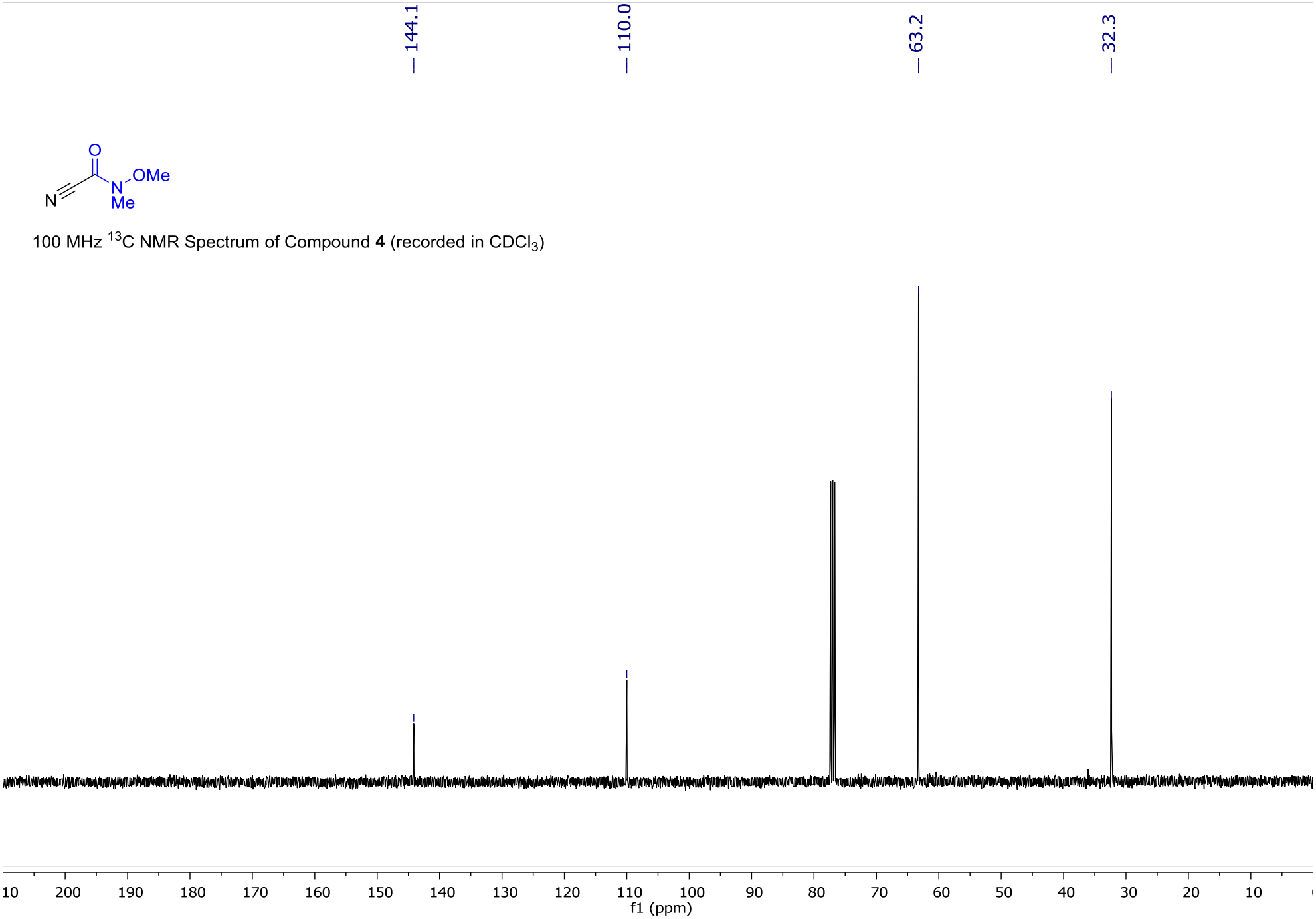
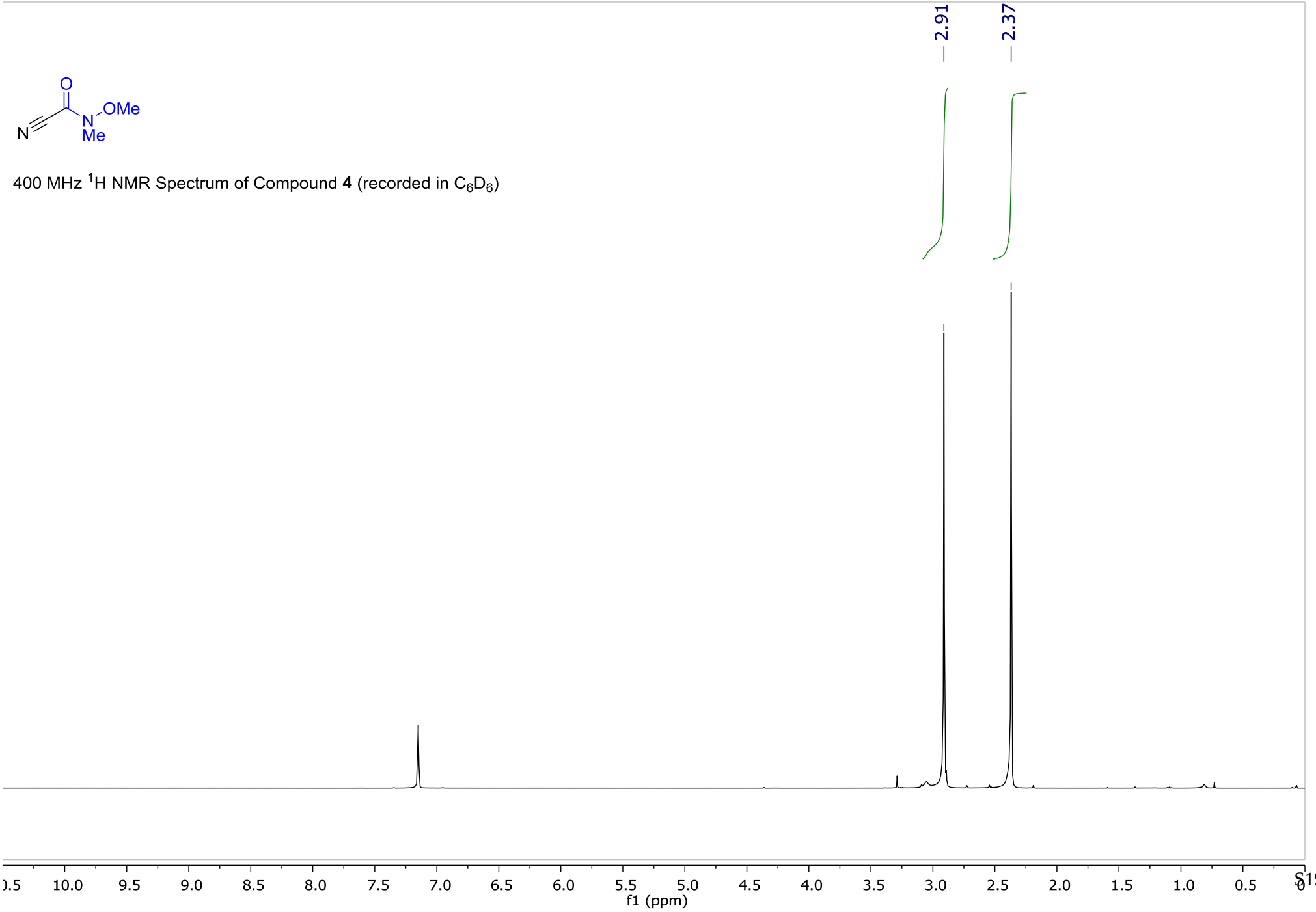
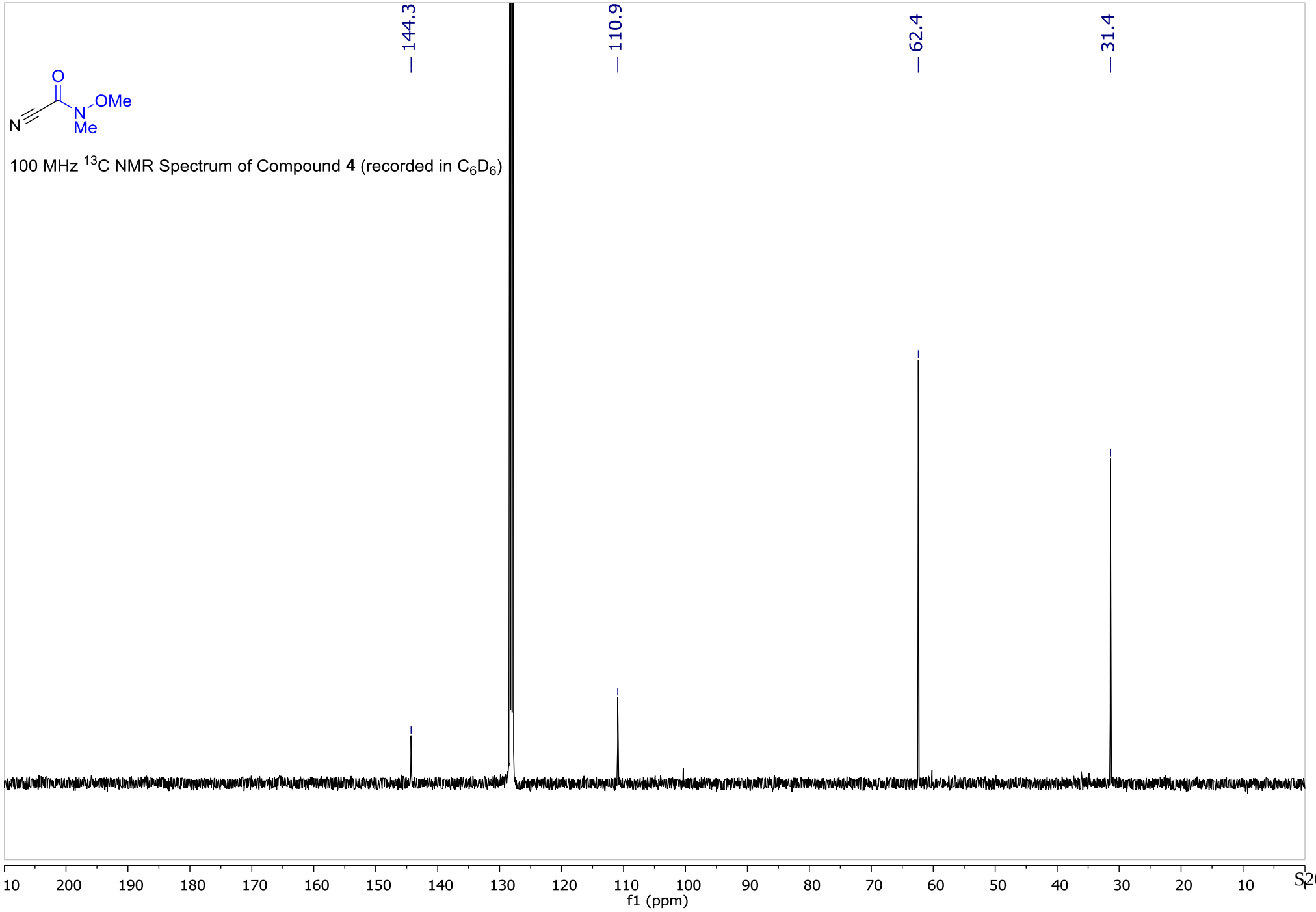


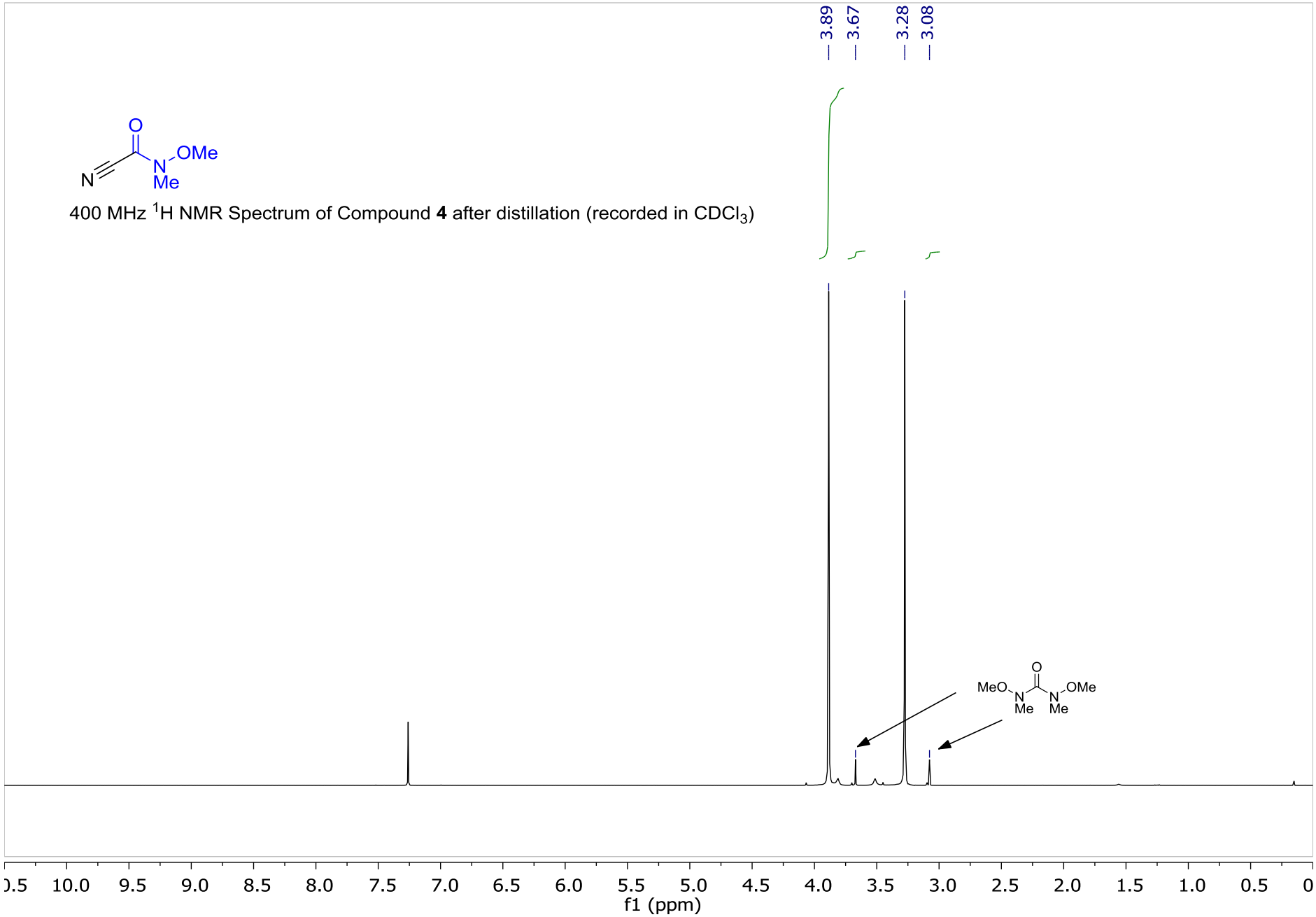
400 MHz ^{1}H NMR Spectrum of Compound **4** (recorded in $CDCl_3$)


144.1
110.0
63.2
32.3
O
N
OMe
N
Me
100 MHz ^{13}C NMR Spectrum of Compound **4** (recorded in $CDCl_3$)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

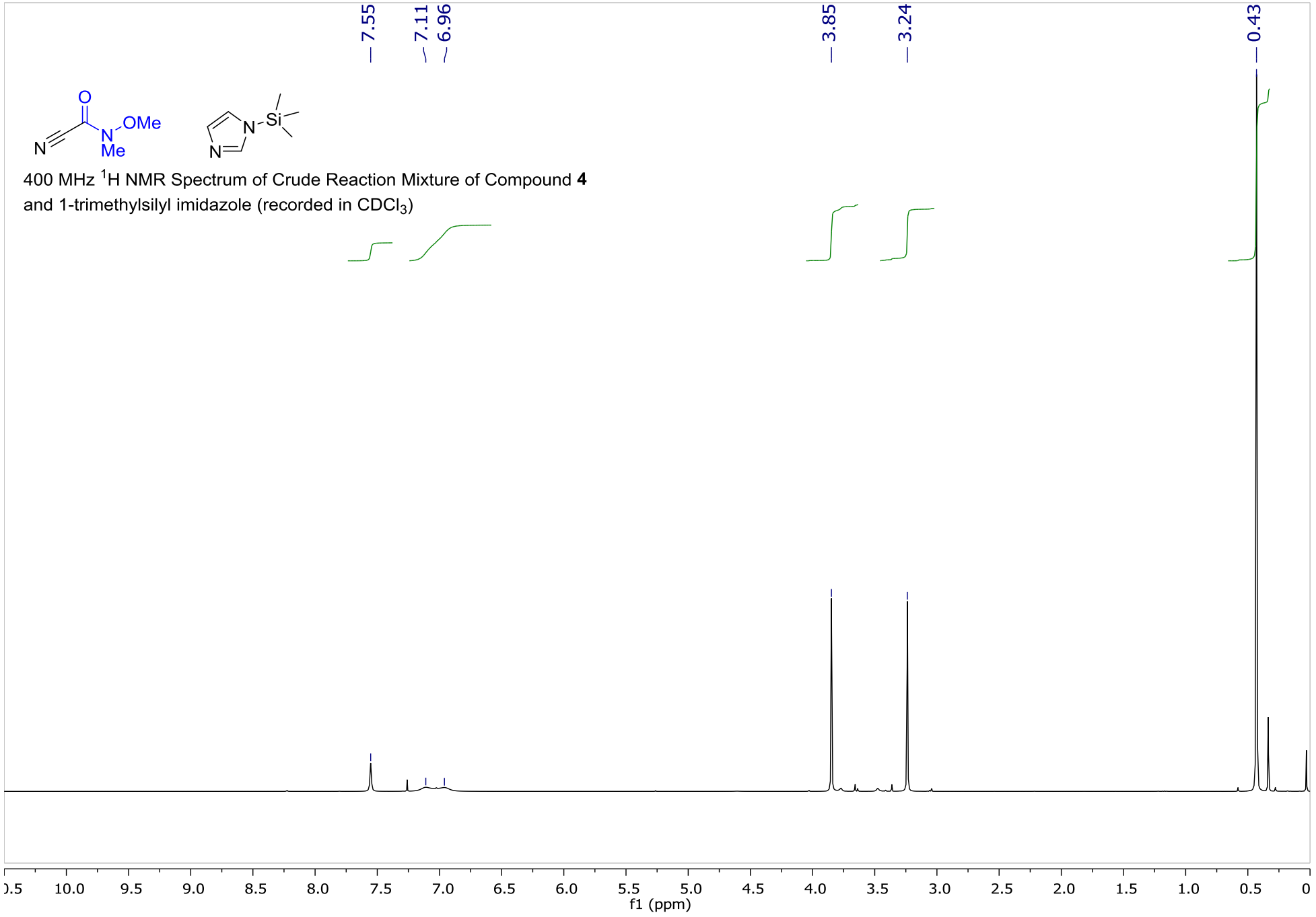


400 MHz ^{1}H NMR Spectrum of Compound **4** (recorded in C_6D_6)

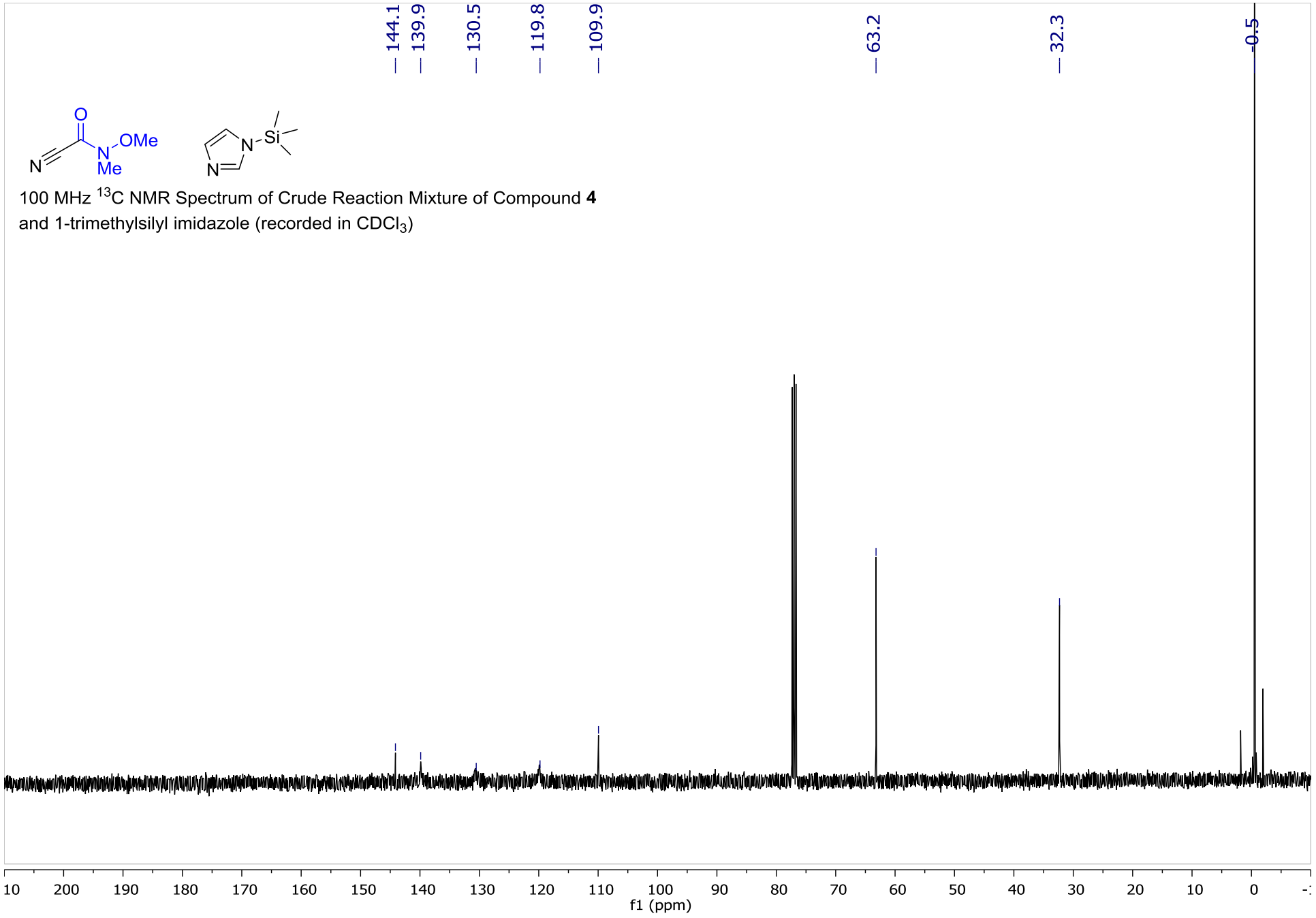

144.3
110.9
62.4
31.4
O
N
OMe
N
Me
100 MHz ^{13}C NMR Spectrum of Compound **4** (recorded in C_6D_6)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



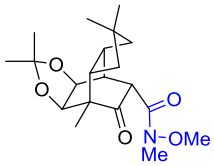
400 MHz ^{1}H NMR Spectrum of Compound **4** after distillation (recorded in $CDCl_3$)



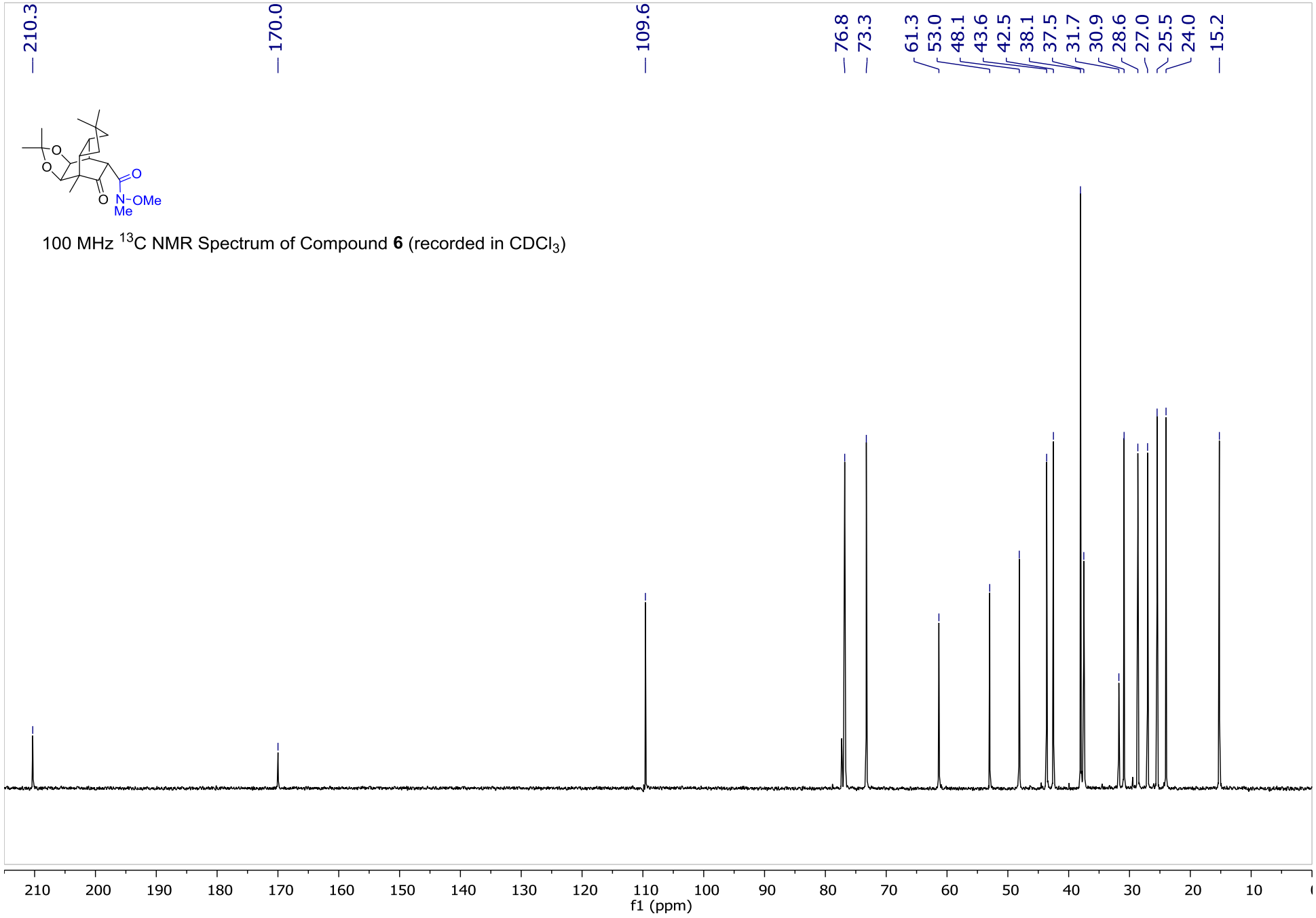
400 MHz ^{1}H NMR Spectrum of Crude Reaction Mixture of Compound **4** and 1-trimethylsilyl imidazole (recorded in $CDCl_3$)

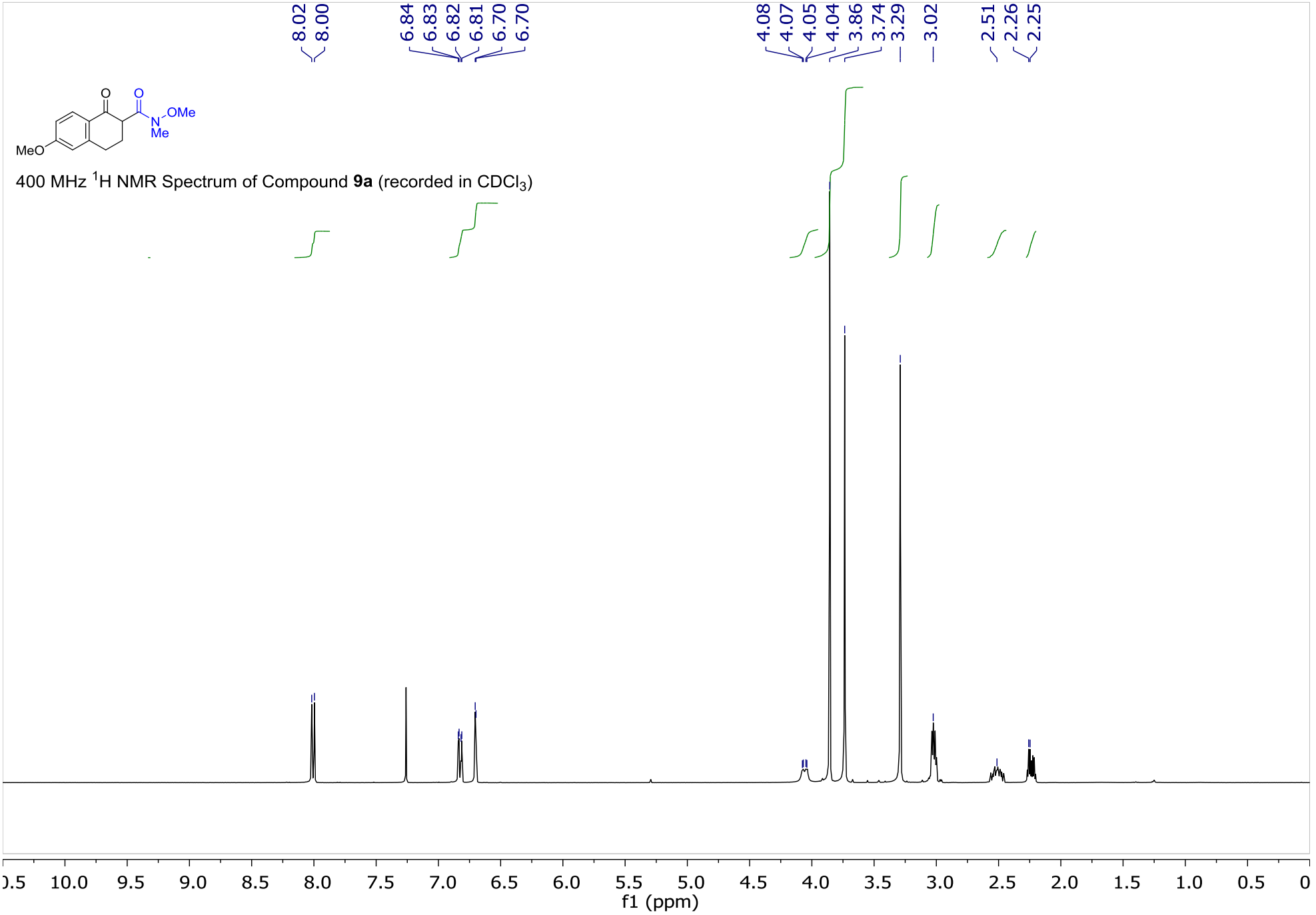


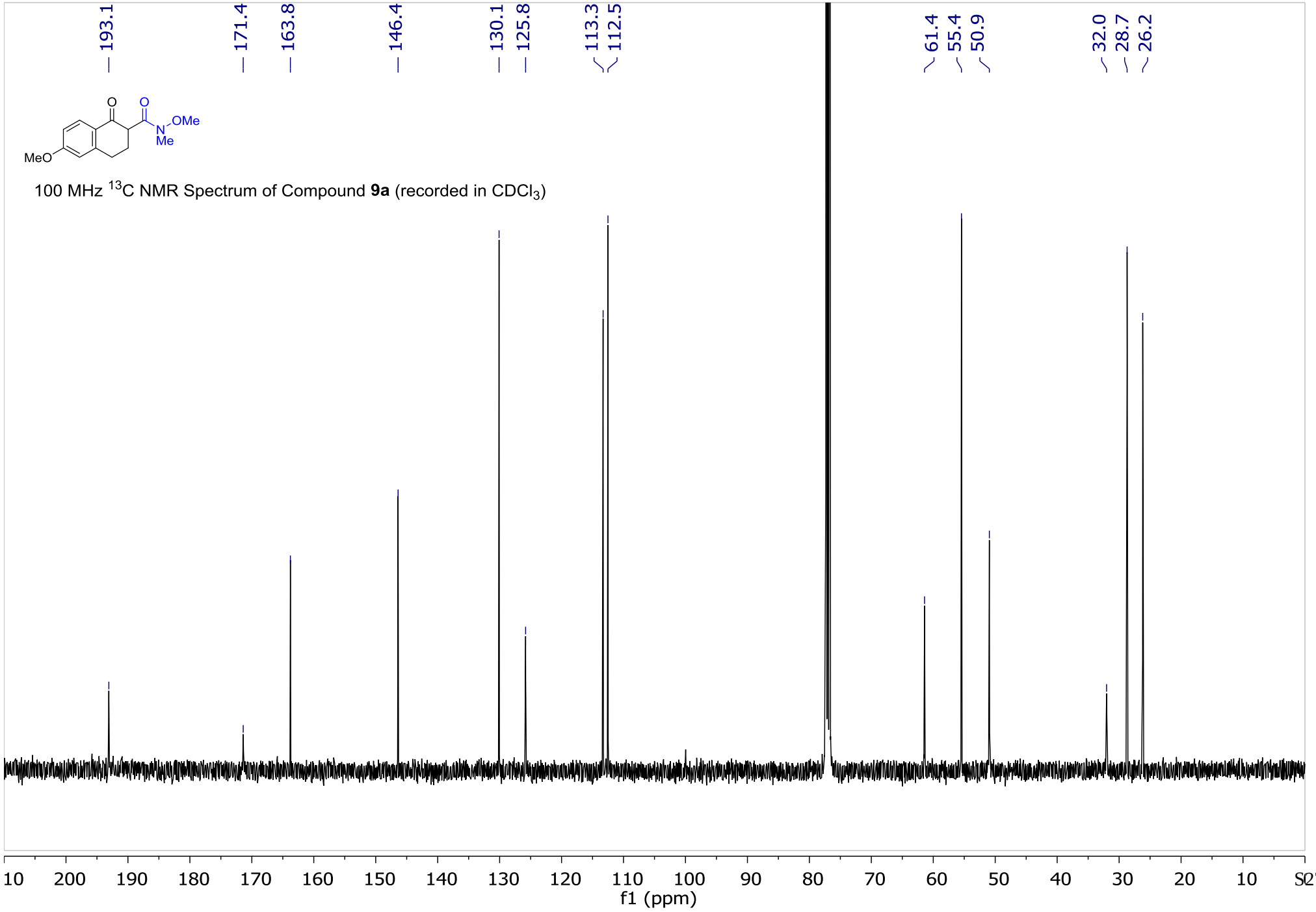
100 MHz ^{13}C NMR Spectrum of Crude Reaction Mixture of Compound **4** and 1-trimethylsilyl imidazole (recorded in $CDCl_3$)

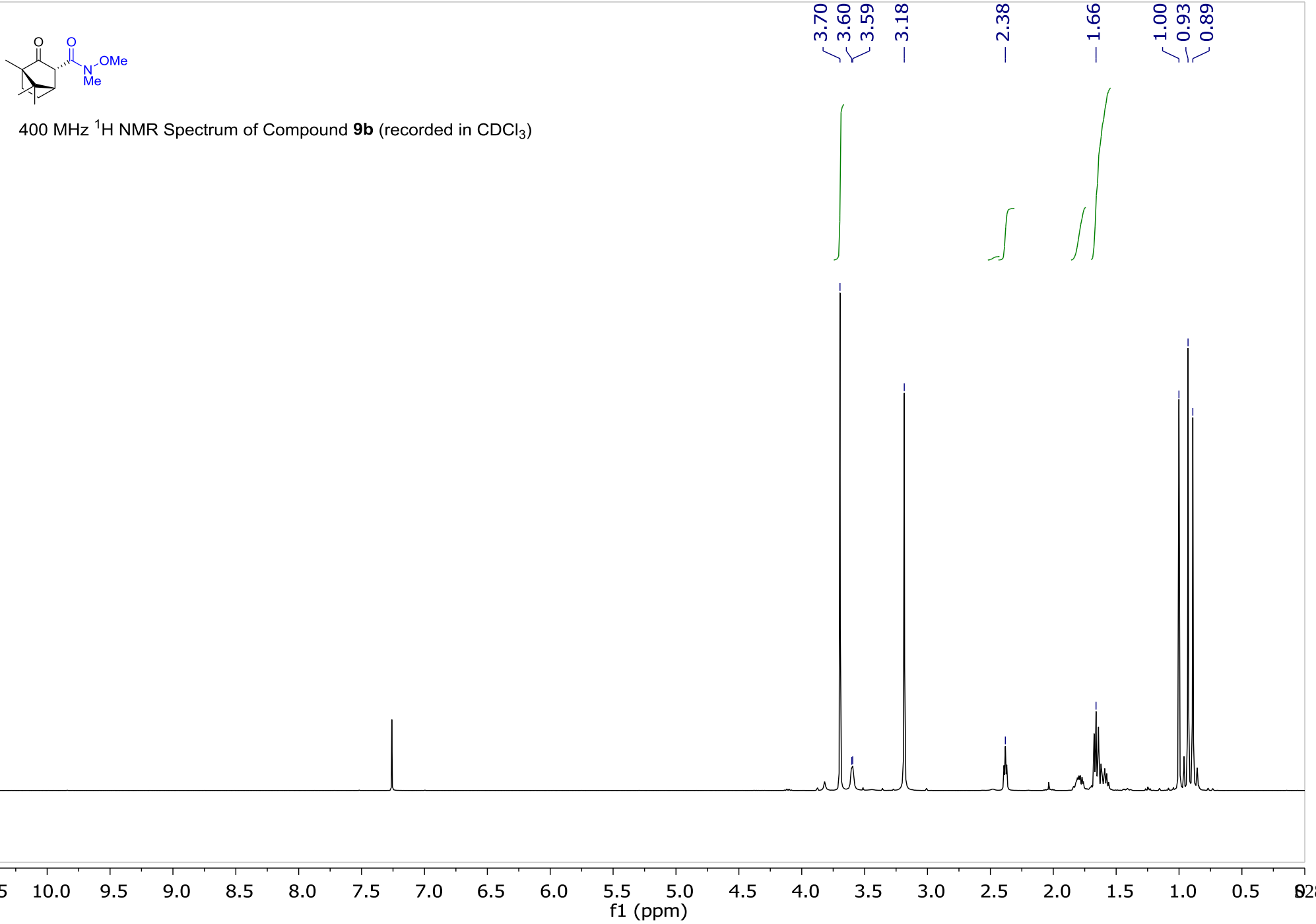


400 MHz ^{1}H NMR Spectrum of Compound **6** (recorded in $CDCl_3$)

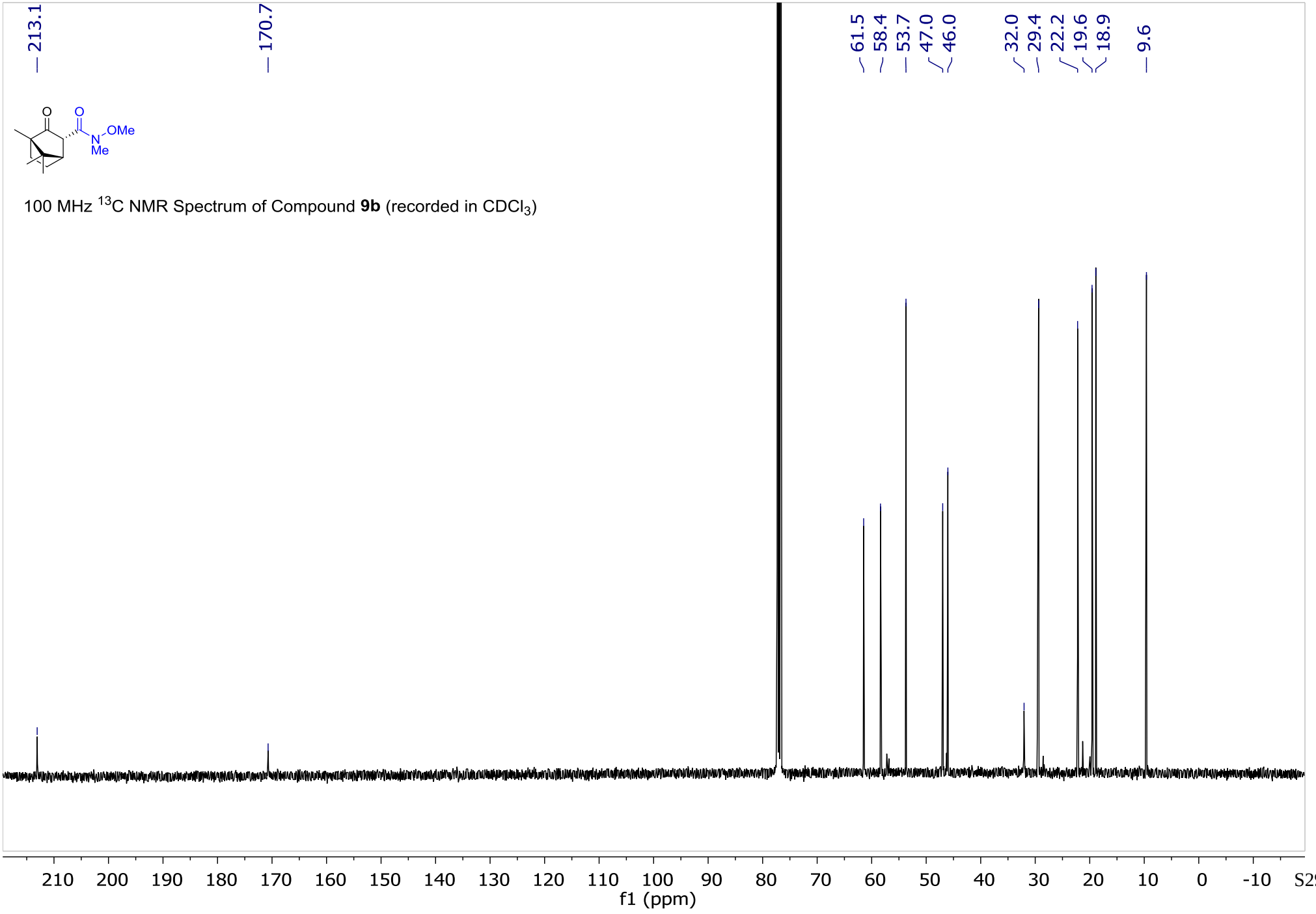

210.3
170.0
109.6
76.8
73.3
61.3
53.0
48.1
43.6
42.5
38.1
37.5
31.7
30.9
28.6
27.0
25.5
24.0
15.2
O
O
O
N-OMe
Me
100 MHz ^{13}C NMR Spectrum of Compound **6** (recorded in $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

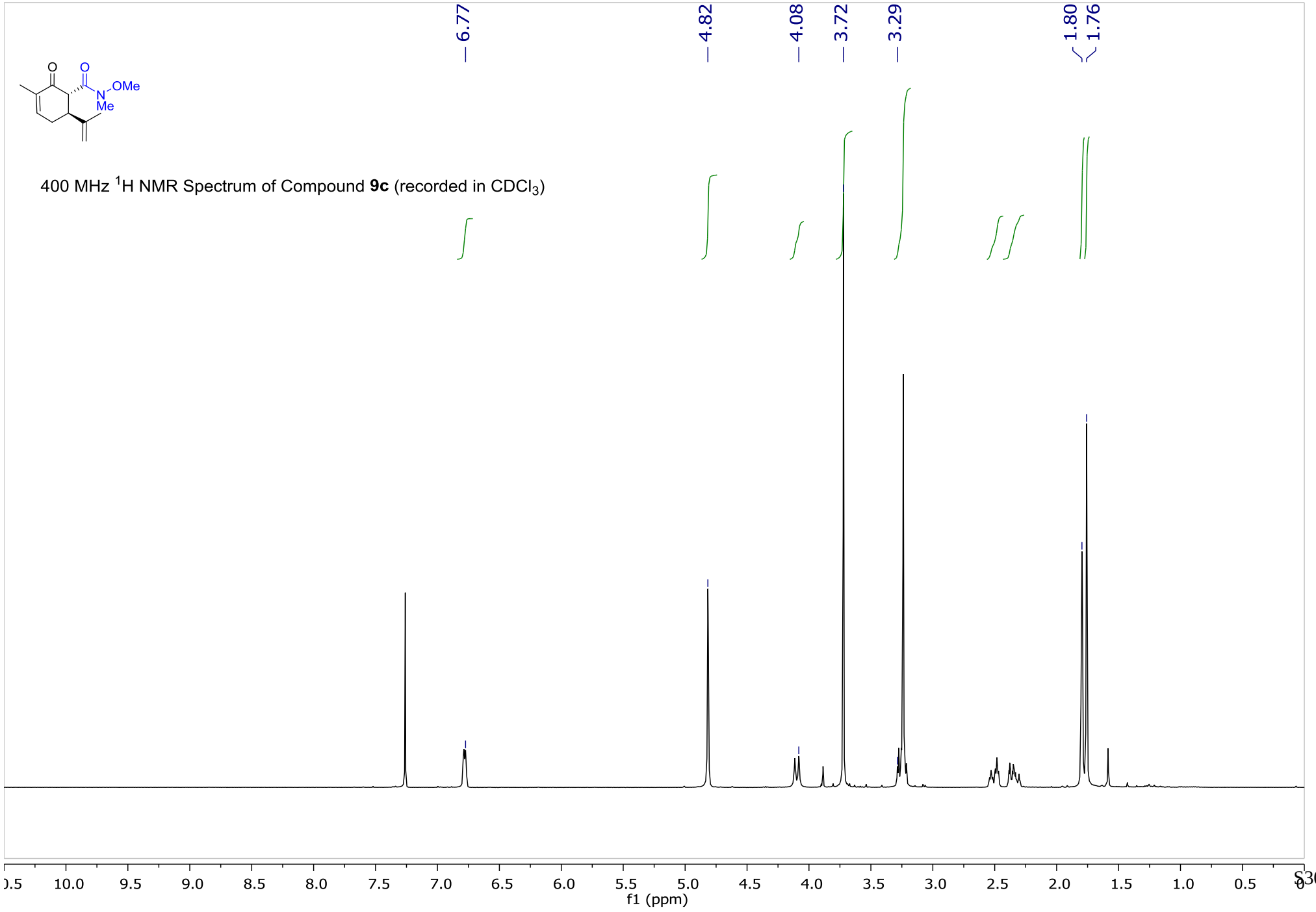

8.02
8.00
6.84
6.83
6.82
6.81
6.70
6.70
4.08
4.07
4.05
4.04
3.86
3.74
3.29
3.02
2.51
2.26
2.25
O
O
N
OMe
Me
MeO
400 MHz ^{1}H NMR Spectrum of Compound **9a** (recorded in $CDCl_3$)
f1 (ppm)


193.1
171.4
163.8
146.4
130.1
125.8
113.3
112.5
61.4
55.4
50.9
32.0
28.7
26.2
O
O
N
OMe
Me
MeO
100 MHz ^{13}C NMR Spectrum of Compound **9a** (recorded in $CDCl_3$)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

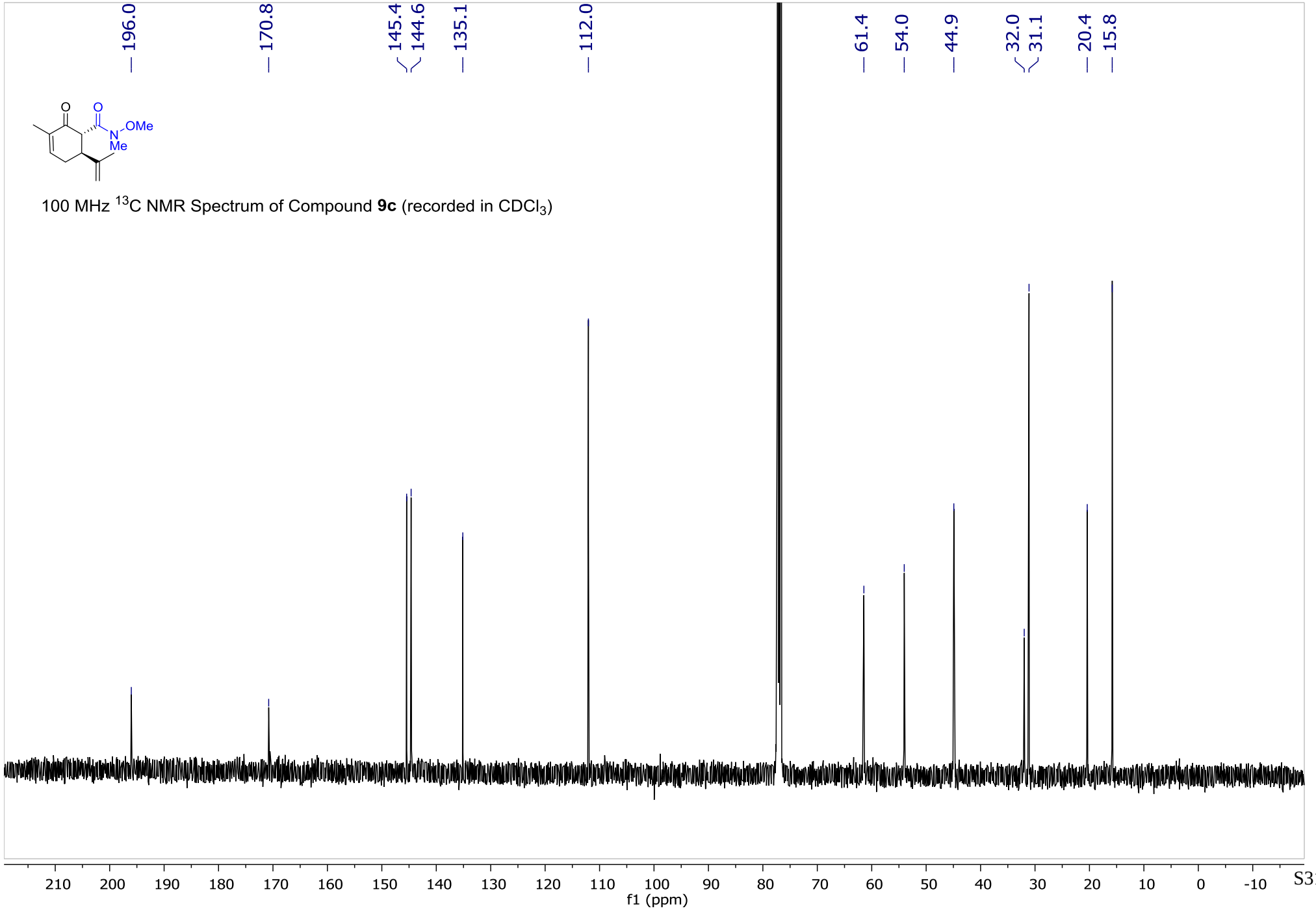


400 MHz ^{1}H NMR Spectrum of Compound **9b** (recorded in $CDCl_3$)

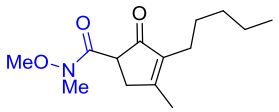

213.1
170.7
61.5
58.4
53.7
47.0
46.0
32.0
29.4
22.2
19.6
18.9
9.6
O
O
N
OMe
Me
100 MHz 13C NMR Spectrum of Compound 9b (recorded in CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



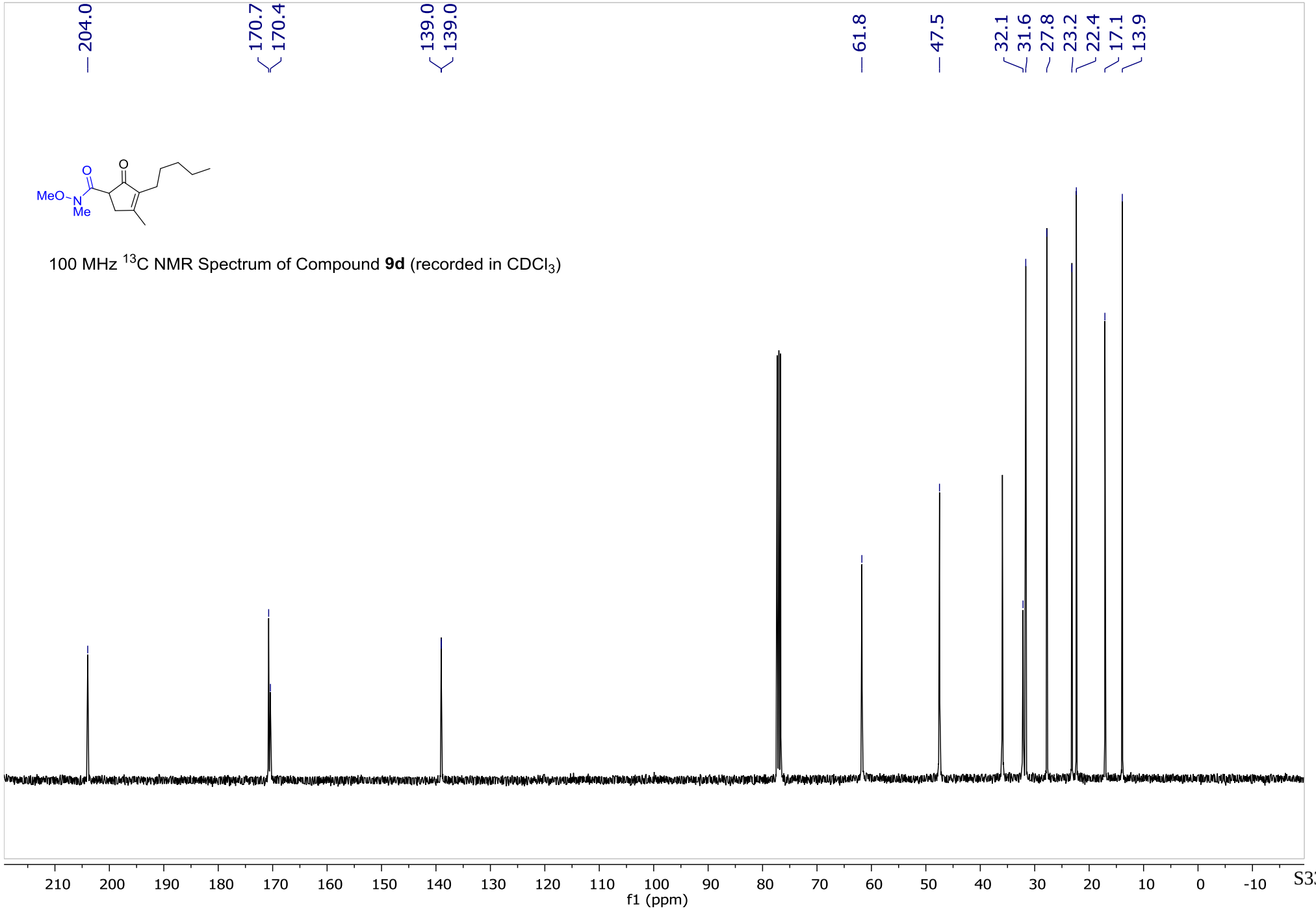
400 MHz ^{1}H NMR Spectrum of Compound **9c** (recorded in $CDCl_3$)

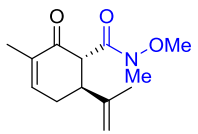


100 MHz ^{13}C NMR Spectrum of Compound **9c** (recorded in $CDCl_3$)

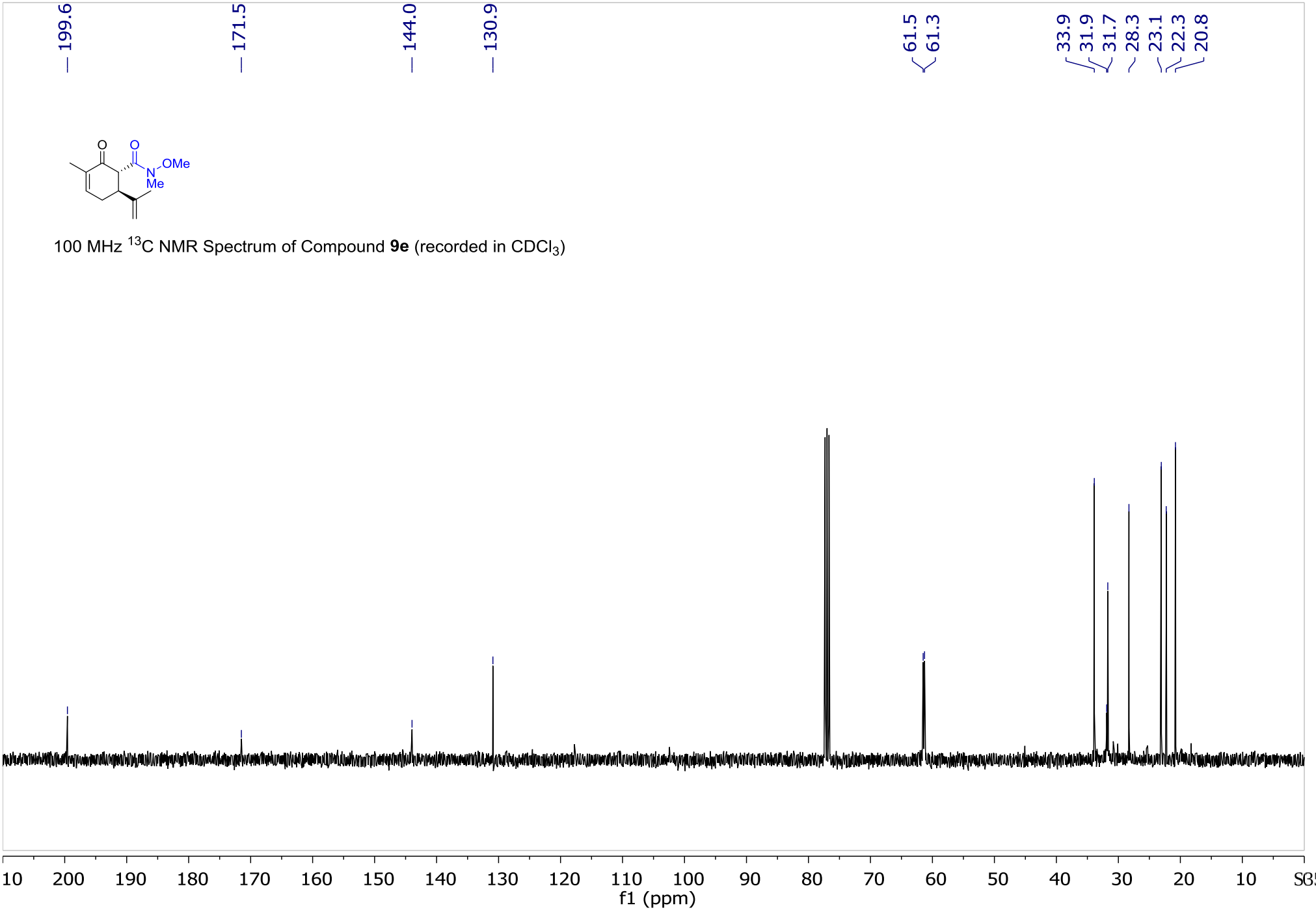


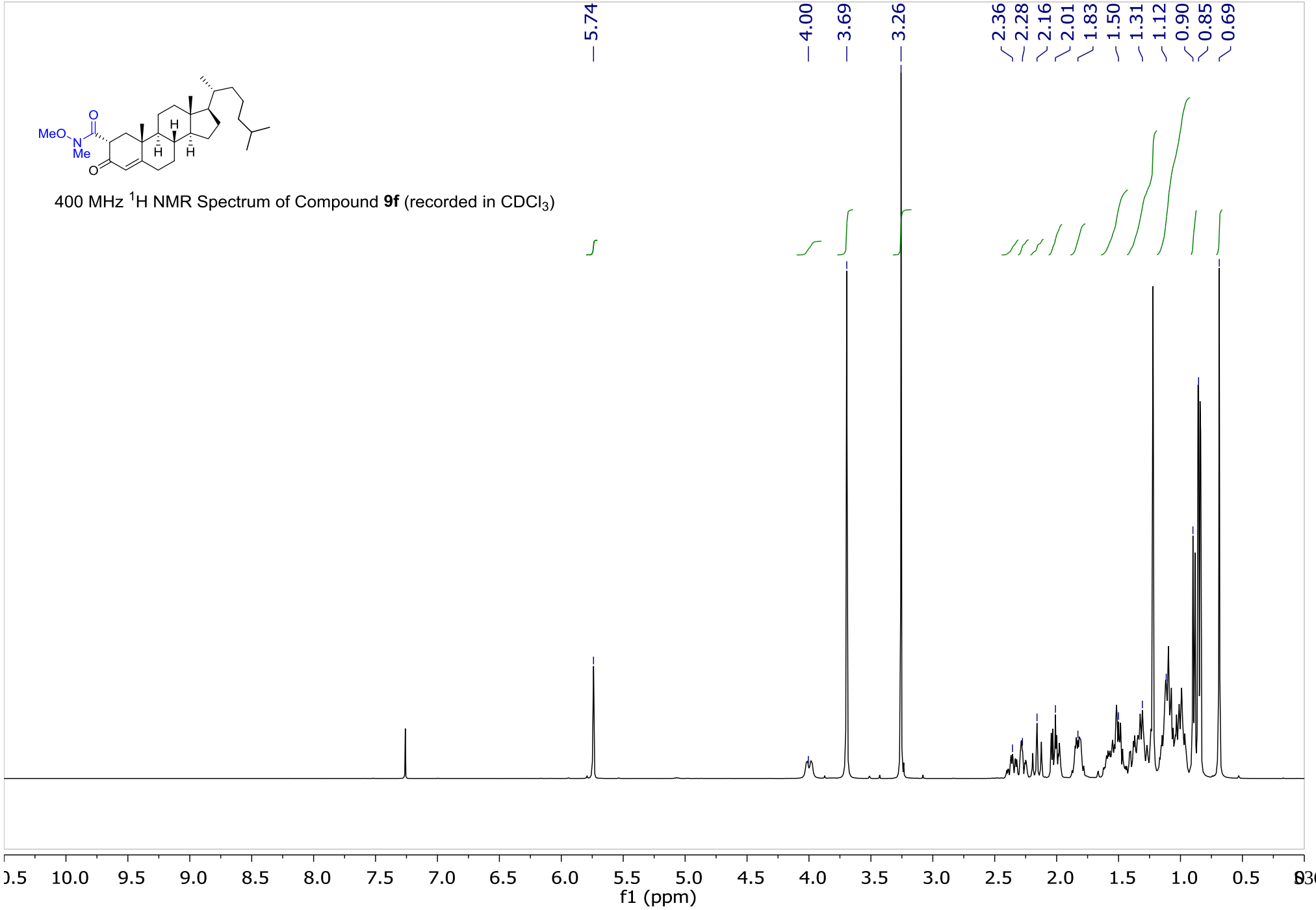
400 MHz ^{1}H NMR Spectrum of Compound **9d** (recorded in $CDCl_3$)

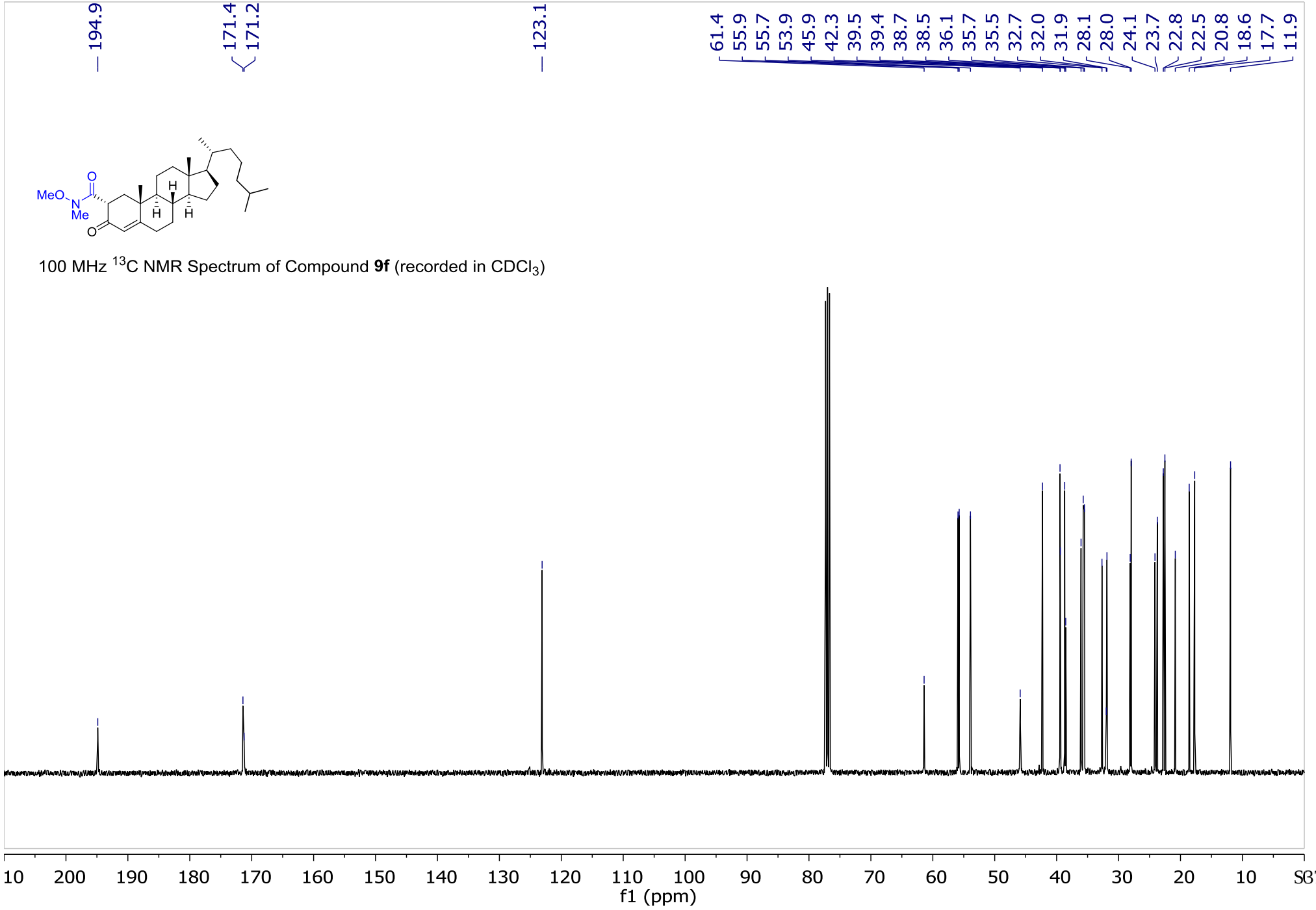

204.0
170.7
170.4
139.0
139.0
61.8
47.5
32.1
31.6
27.8
23.2
22.4
17.1
13.9
O
O
MeO
N
Me
100 MHz 13C NMR Spectrum of Compound 9d (recorded in CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

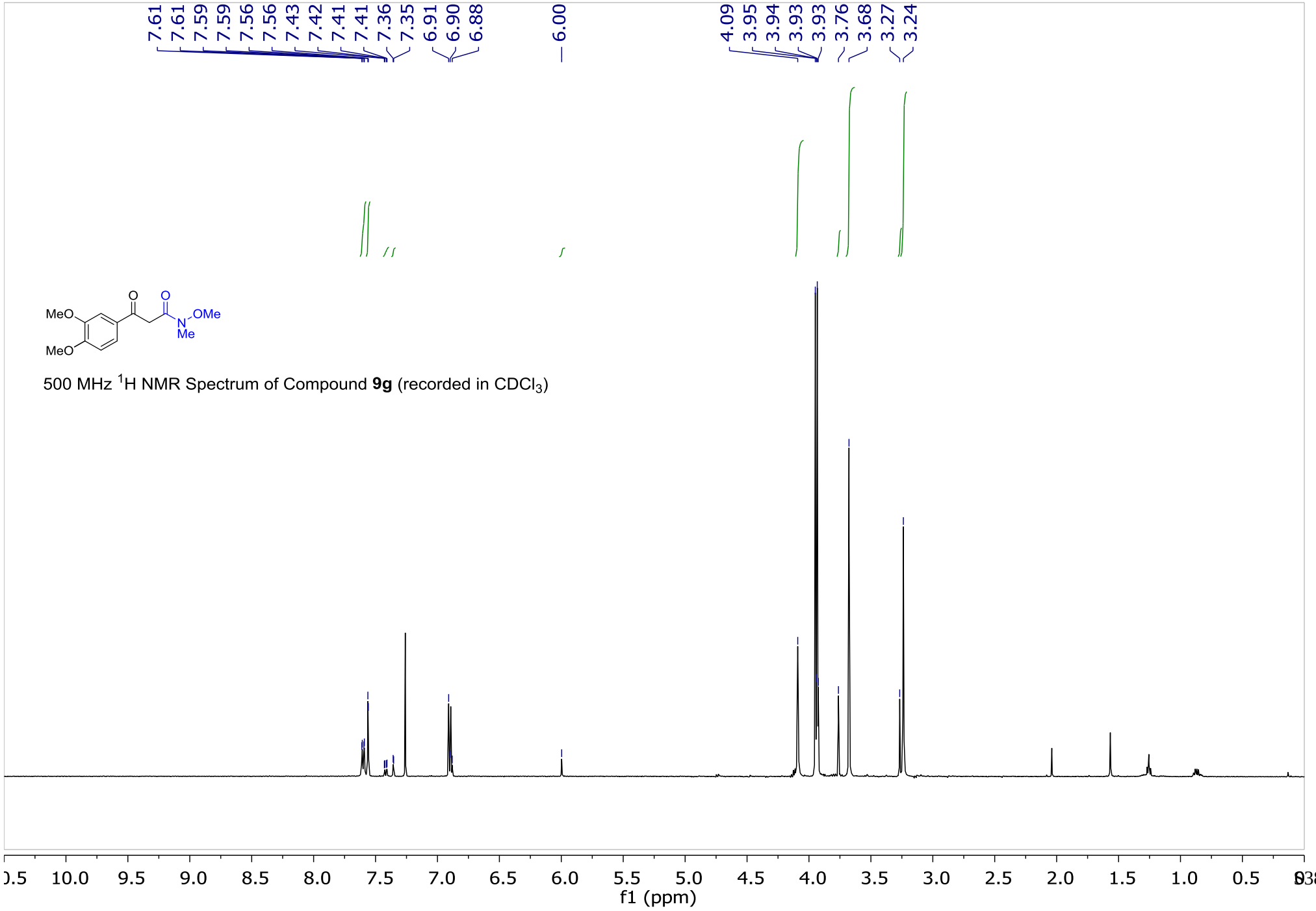


500 MHz ^{1}H NMR Spectrum of Compound **9e** (recorded in $CDCl_3$)

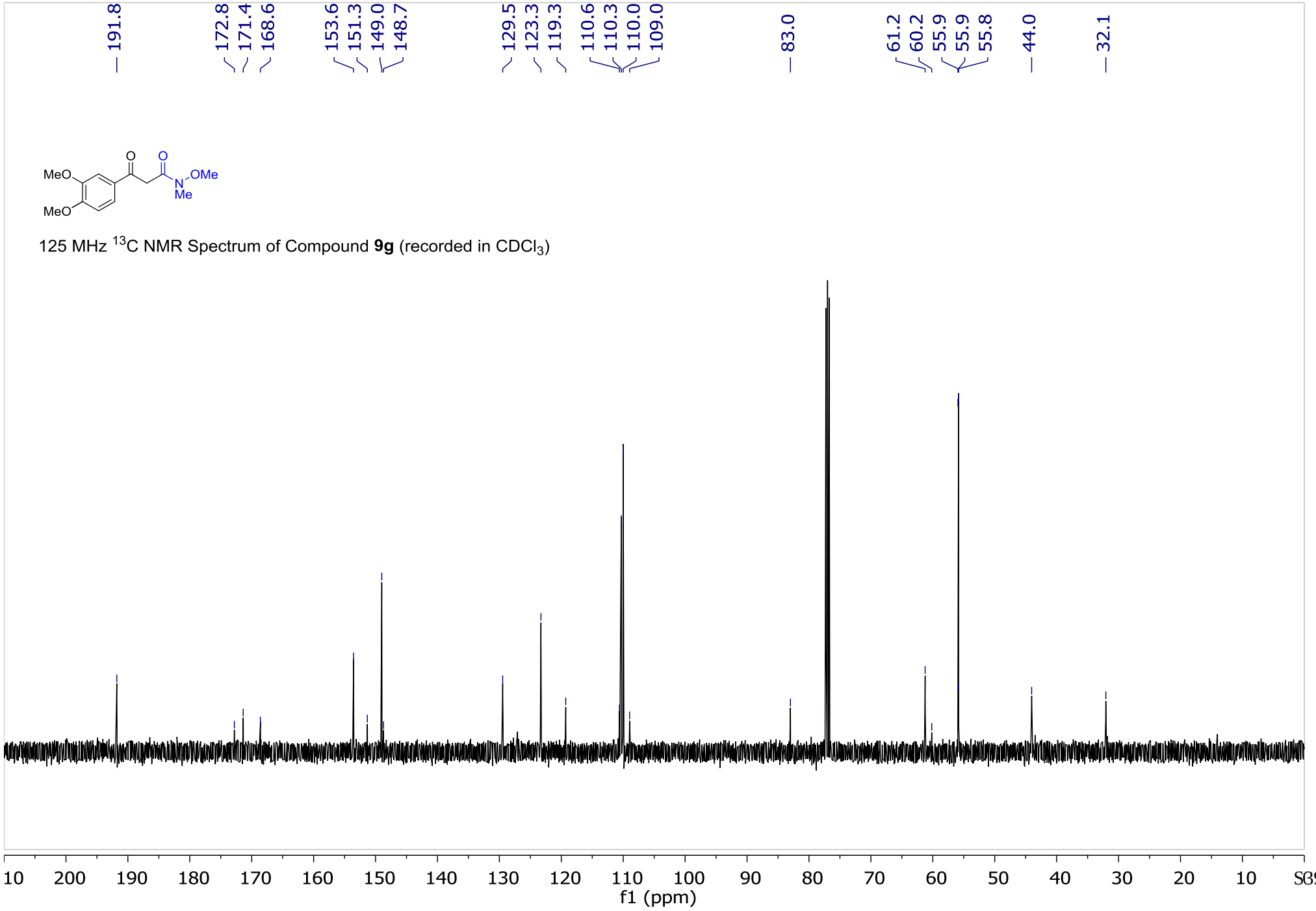

199.6
171.5
144.0
130.9
61.5
61.3
33.9
31.9
31.7
28.3
23.1
22.3
20.8
O
O
N
OMe
Me
100 MHz ^{13}C NMR Spectrum of Compound **9e** (recorded in $CDCl_3$)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


5.74
4.00
3.69
3.26
2.36
2.28
2.16
2.01
1.83
1.50
1.31
1.12
0.90
0.85
0.69
MeO
N
Me
O
O
H
H
H
400 MHz ^{1}H NMR Spectrum of Compound **9f** (recorded in $CDCl_3$)
f1 (ppm)

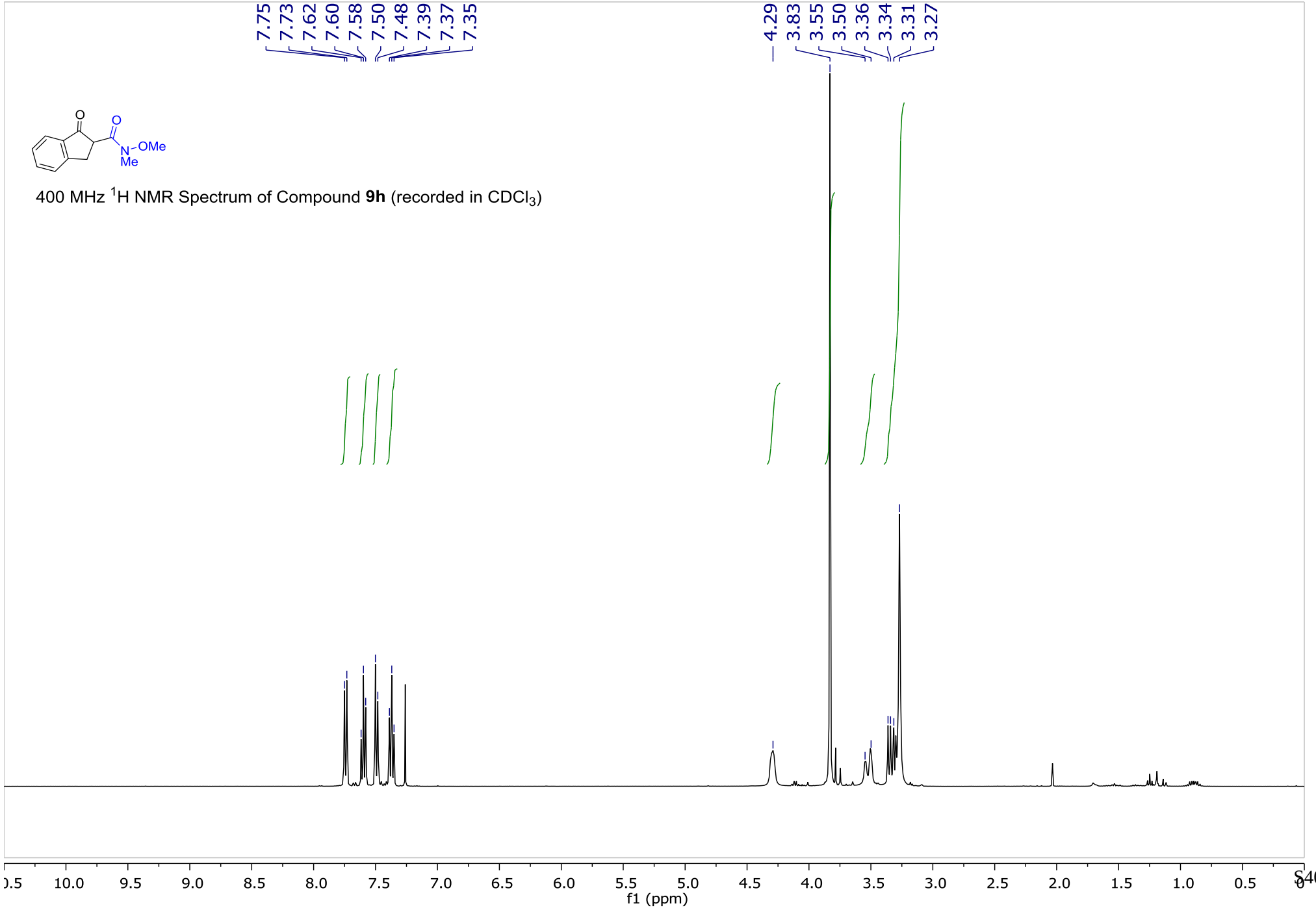

194.9
171.4
171.2
123.1
61.4
55.9
55.7
53.9
45.9
42.3
39.5
39.4
38.7
38.5
36.1
35.7
35.5
32.7
32.0
31.9
28.1
28.0
24.1
23.7
22.8
22.5
20.8
18.6
17.7
11.9
MeO
N
Me
O
O
H
H
H
100 MHz ^{13}C NMR Spectrum of Compound **9f** (recorded in $CDCl_3$)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

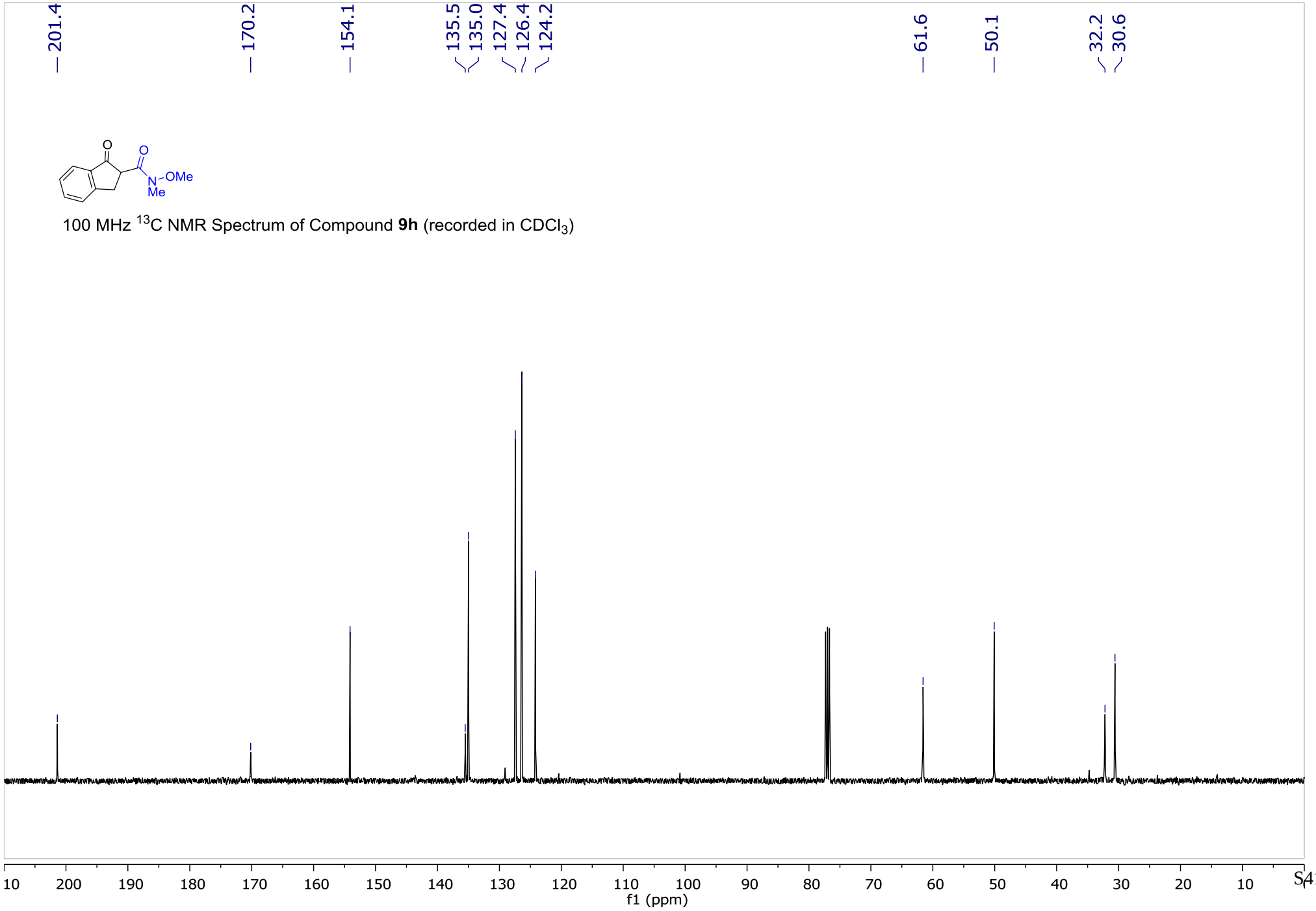


500 MHz ^{1}H NMR Spectrum of Compound **9g** (recorded in $CDCl_3$)

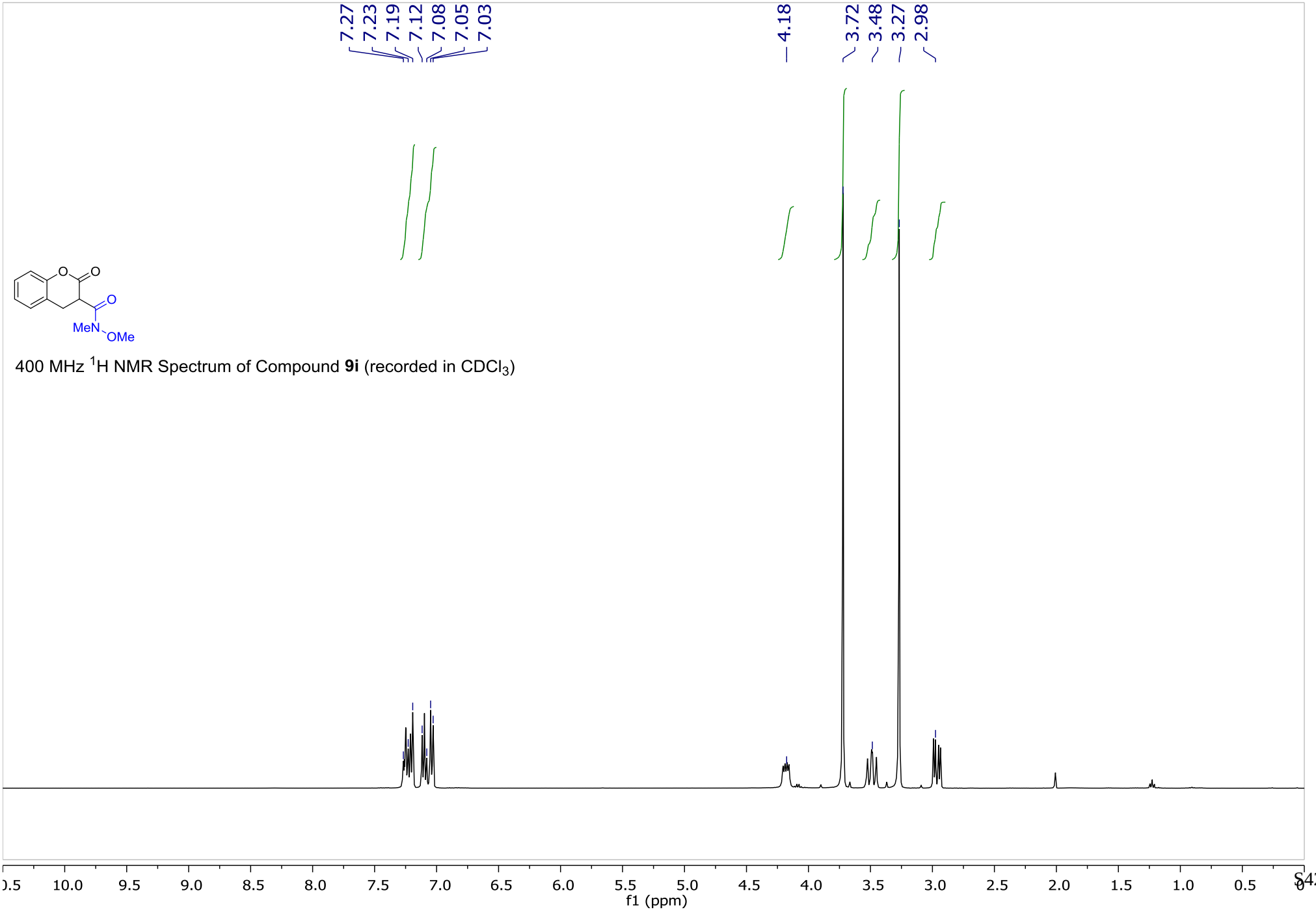


125 MHz ^{13}C NMR Spectrum of Compound **9g** (recorded in $CDCl_3$)

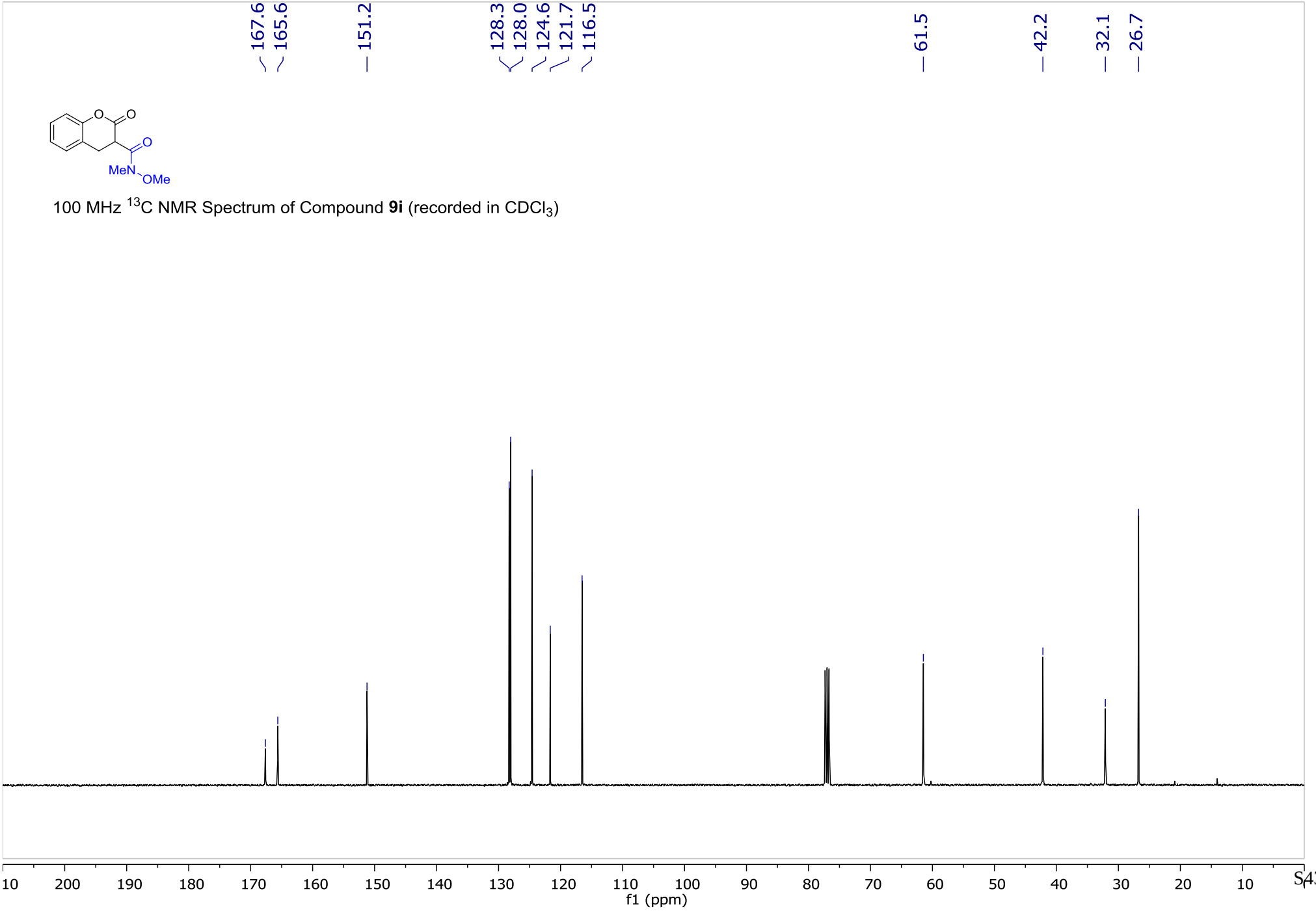

7.75
7.73
7.62
7.60
7.58
7.50
7.48
7.39
7.37
7.35
4.29
3.83
3.55
3.50
3.36
3.34
3.31
3.27
O
O
N
OMe
Me
400 MHz ^{1}H NMR Spectrum of Compound **9h** (recorded in $CDCl_3$)
f1 (ppm)



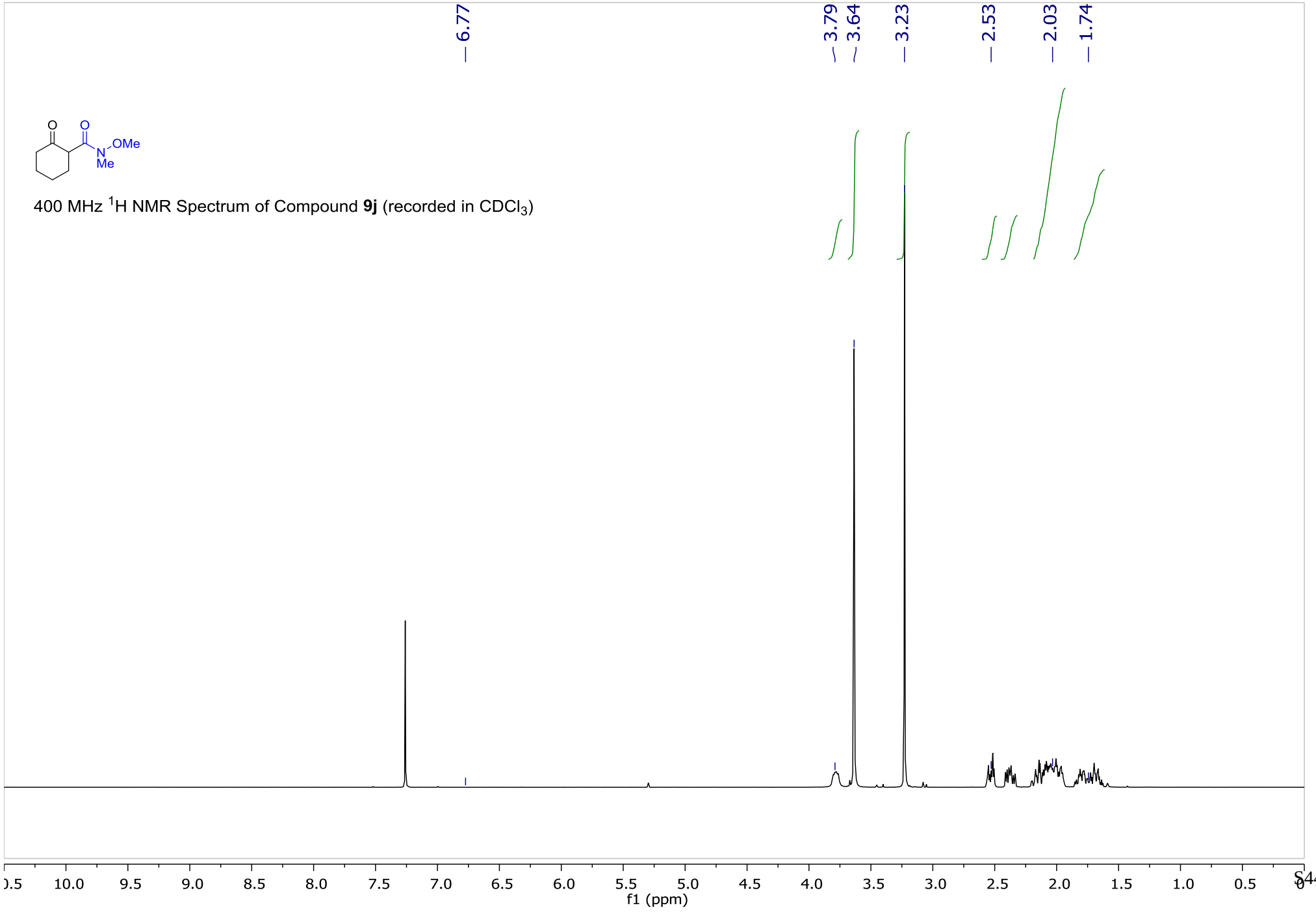
100 MHz ^{13}C NMR Spectrum of Compound **9h** (recorded in $CDCl_3$)

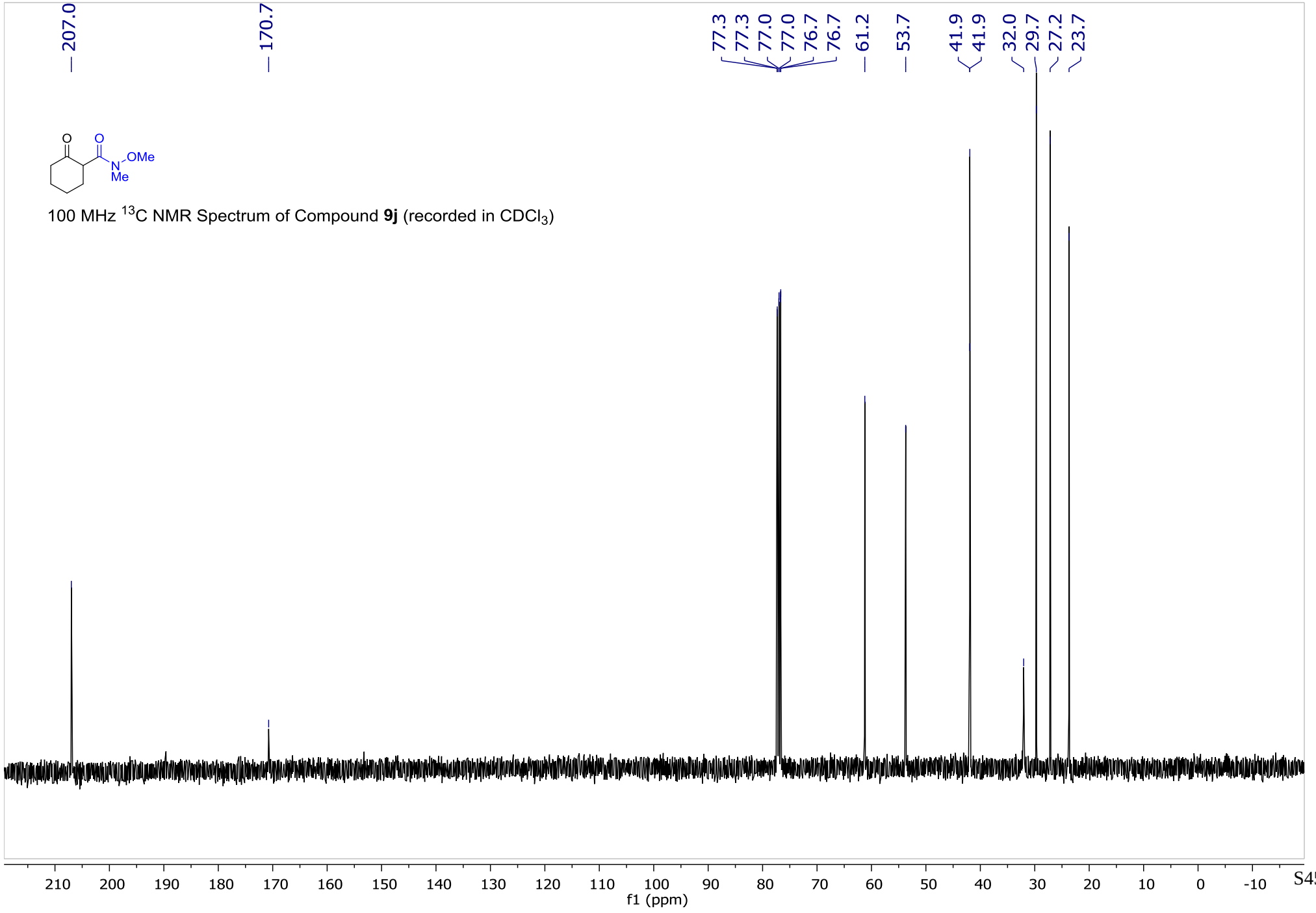


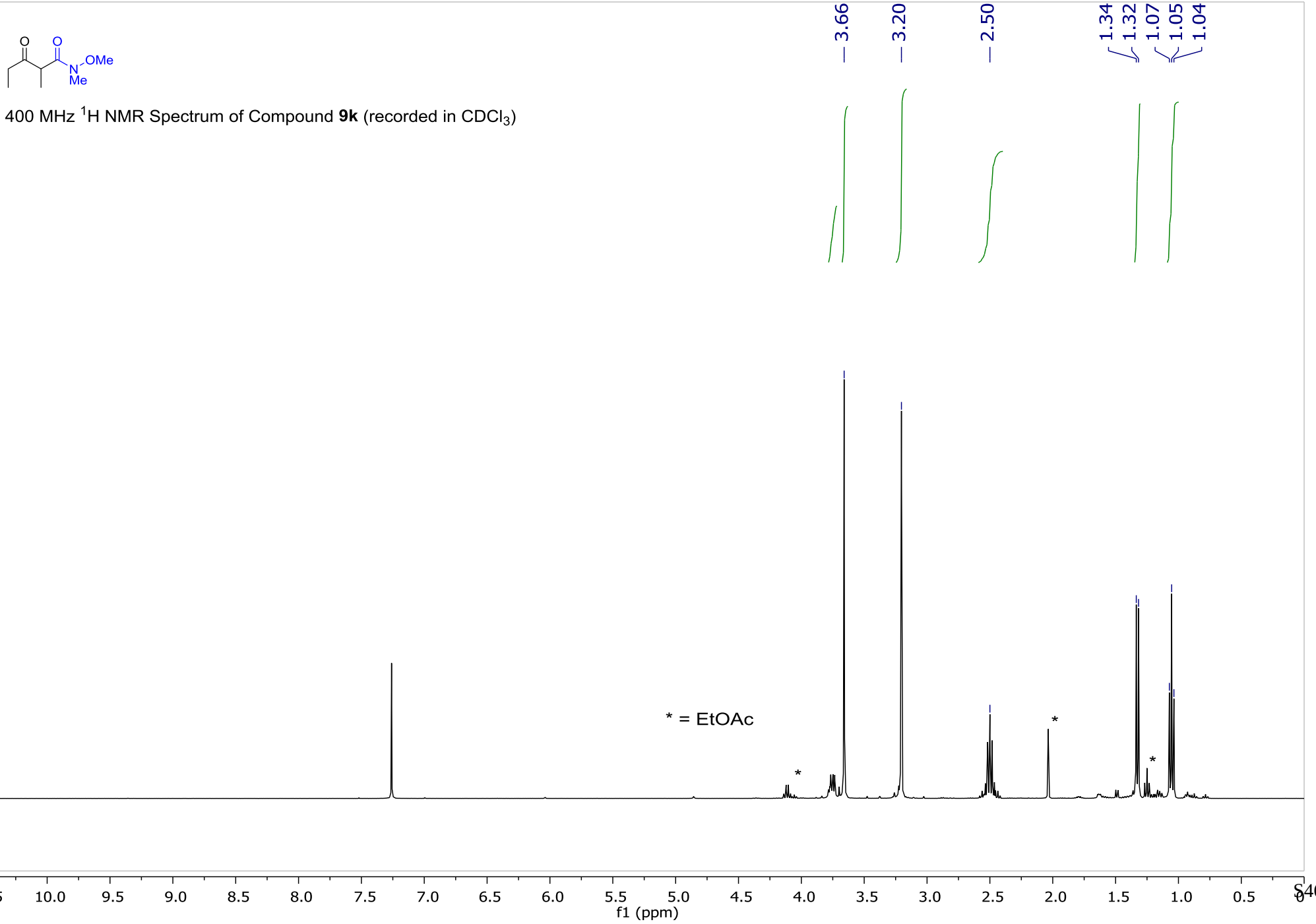
400 MHz ^{1}H NMR Spectrum of Compound **9i** (recorded in $CDCl_3$)



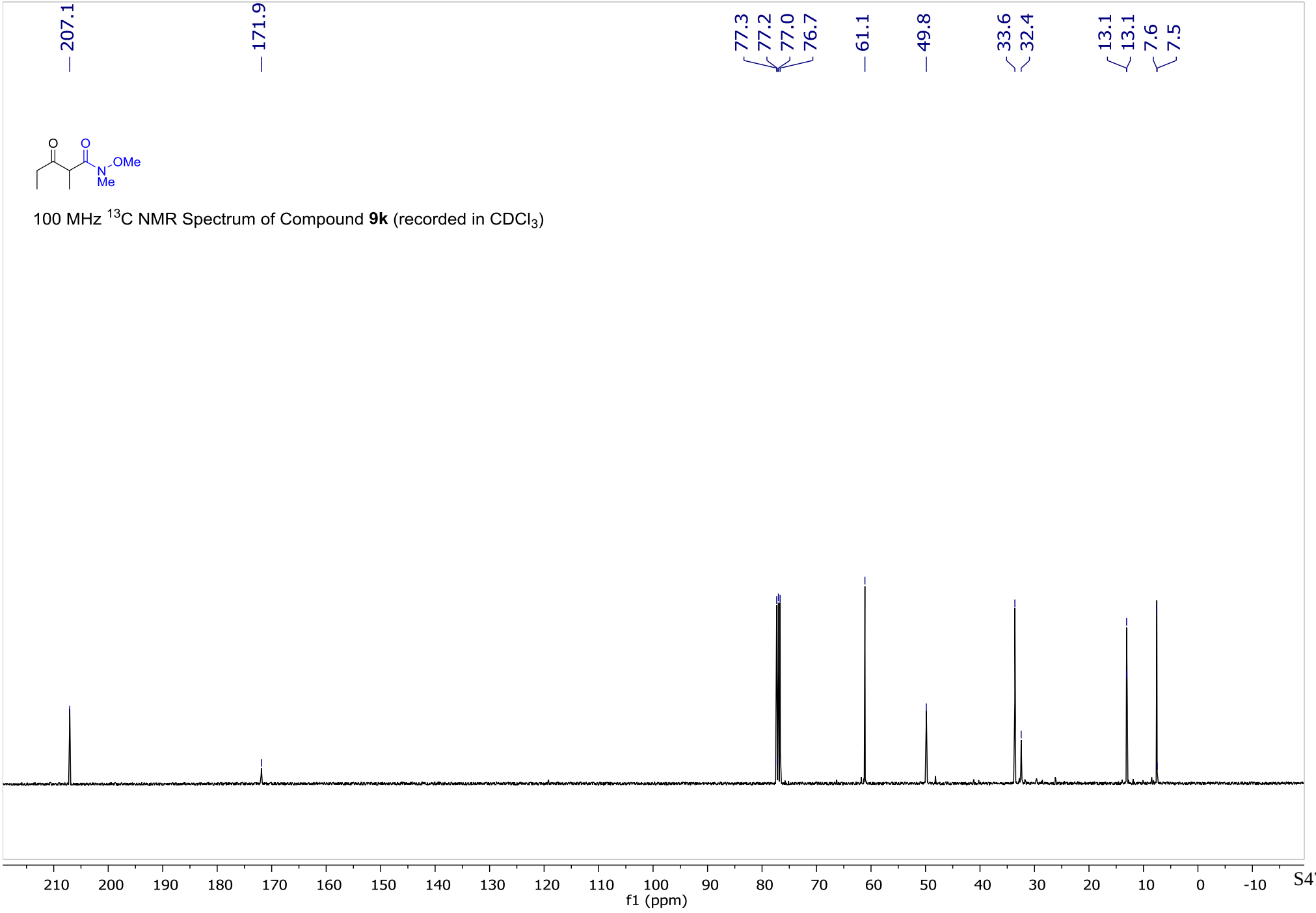
100 MHz ^{13}C NMR Spectrum of Compound **9i** (recorded in $CDCl_3$)


6.77
3.79
3.64
3.23
2.53
2.03
1.74
O
O
N
OMe
Me
400 MHz ^{1}H NMR Spectrum of Compound **9j** (recorded in $CDCl_3$)
f1 (ppm)

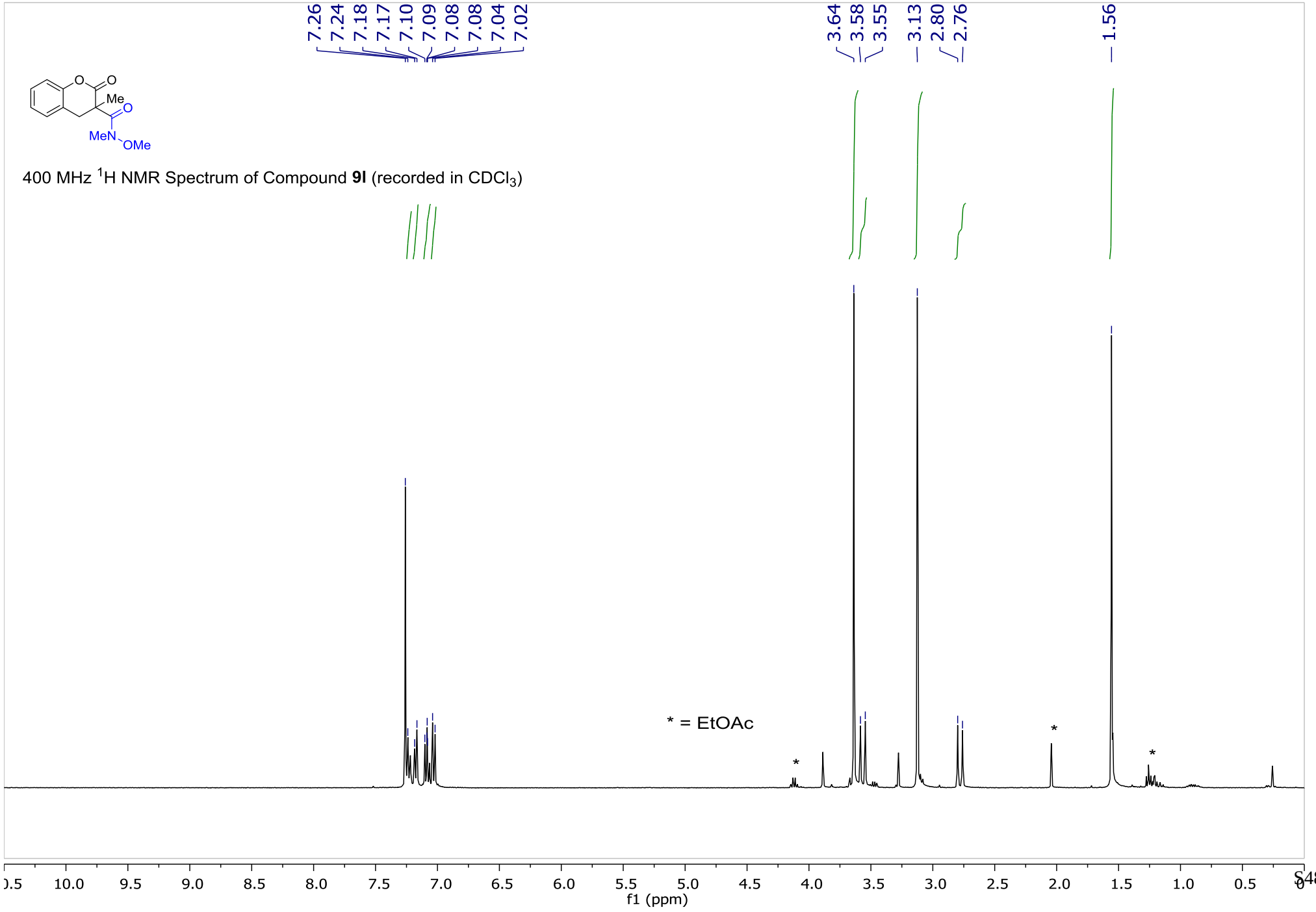

207.0
170.7
77.3
77.3
77.0
77.0
76.7
76.7
61.2
53.7
41.9
41.9
32.0
29.7
27.2
23.7
O
O
N
OMe
Me
100 MHz ^{13}C NMR Spectrum of Compound **9j** (recorded in $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

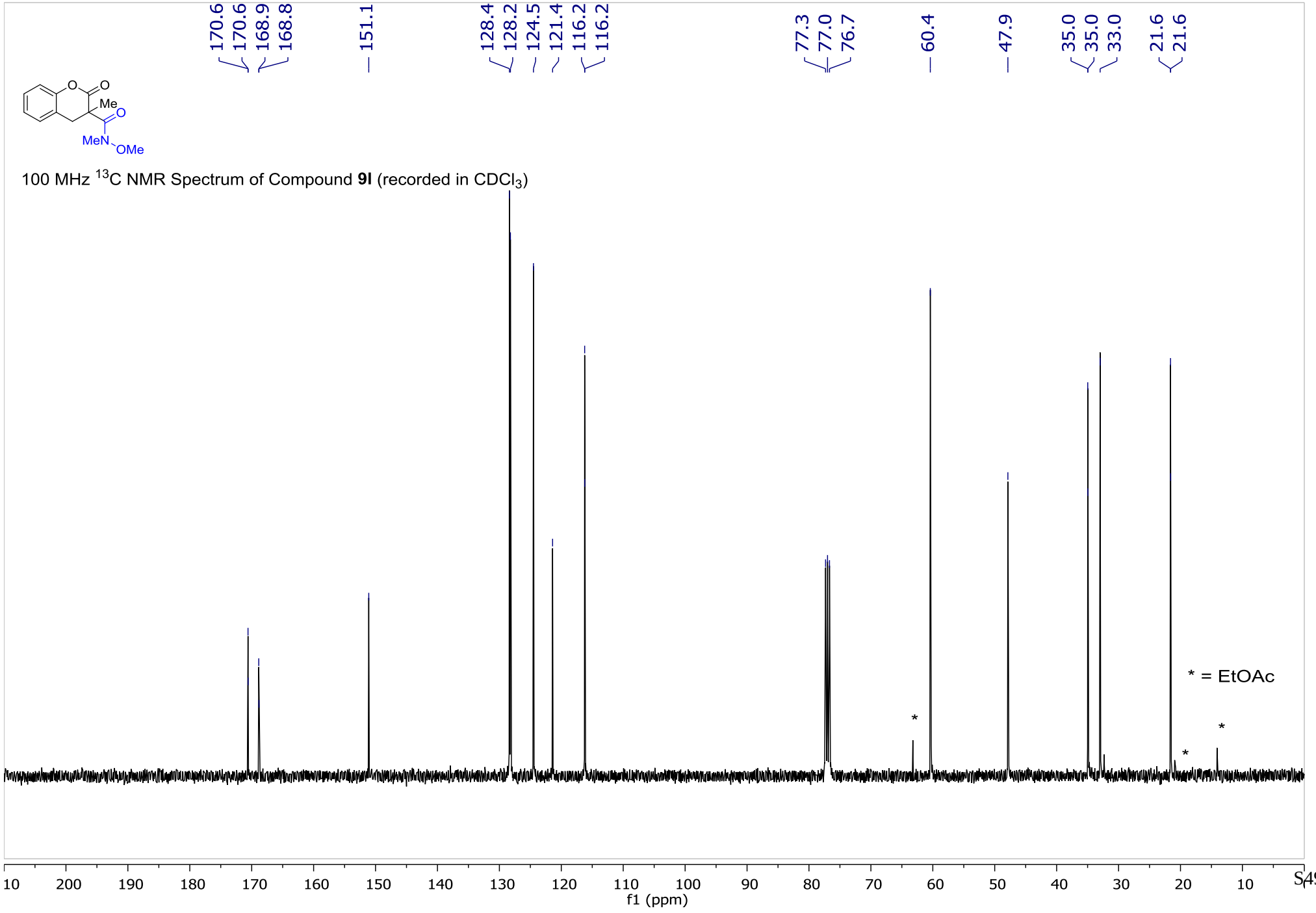


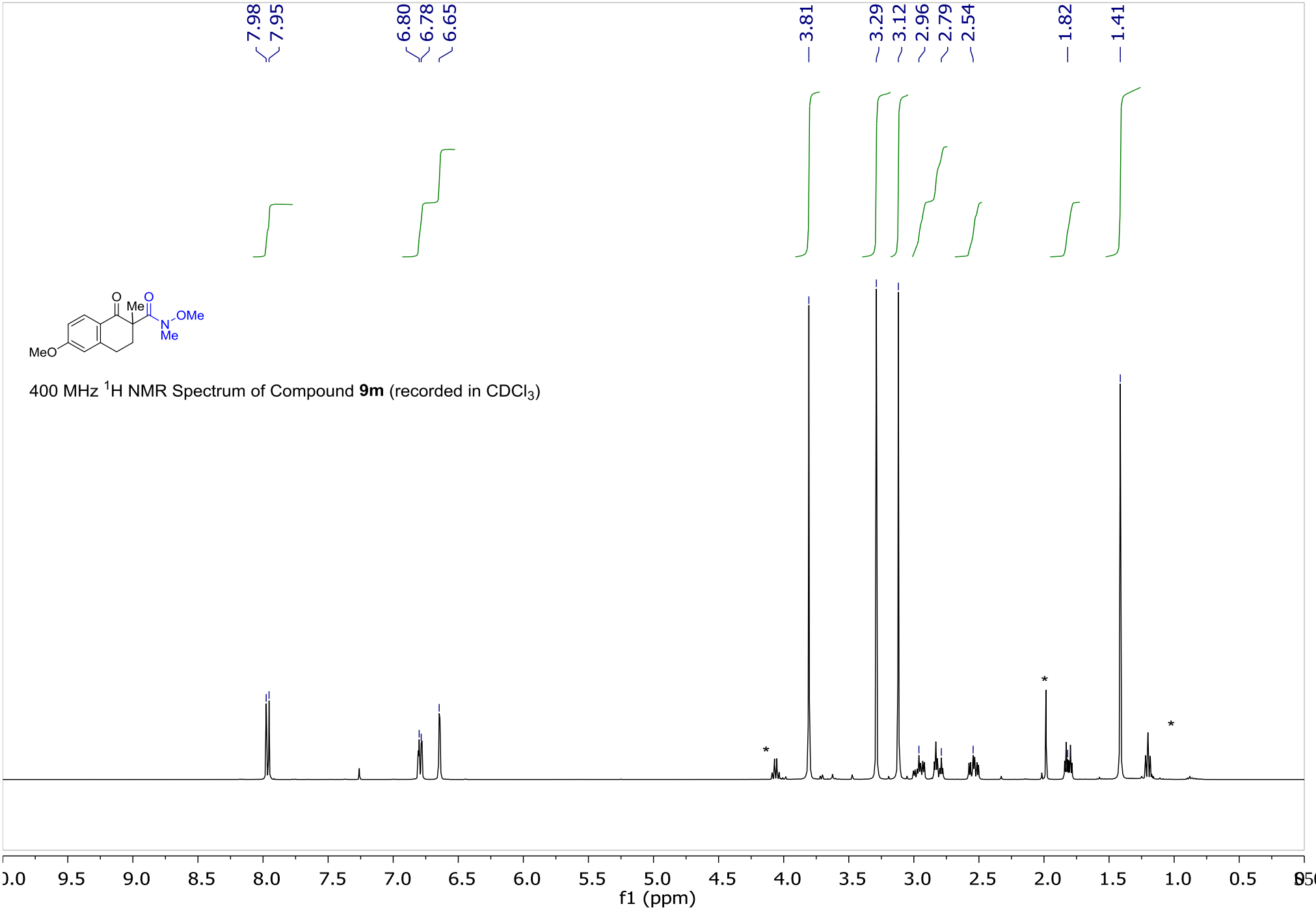
400 MHz ^{1}H NMR Spectrum of Compound **9k** (recorded in $CDCl_3$)

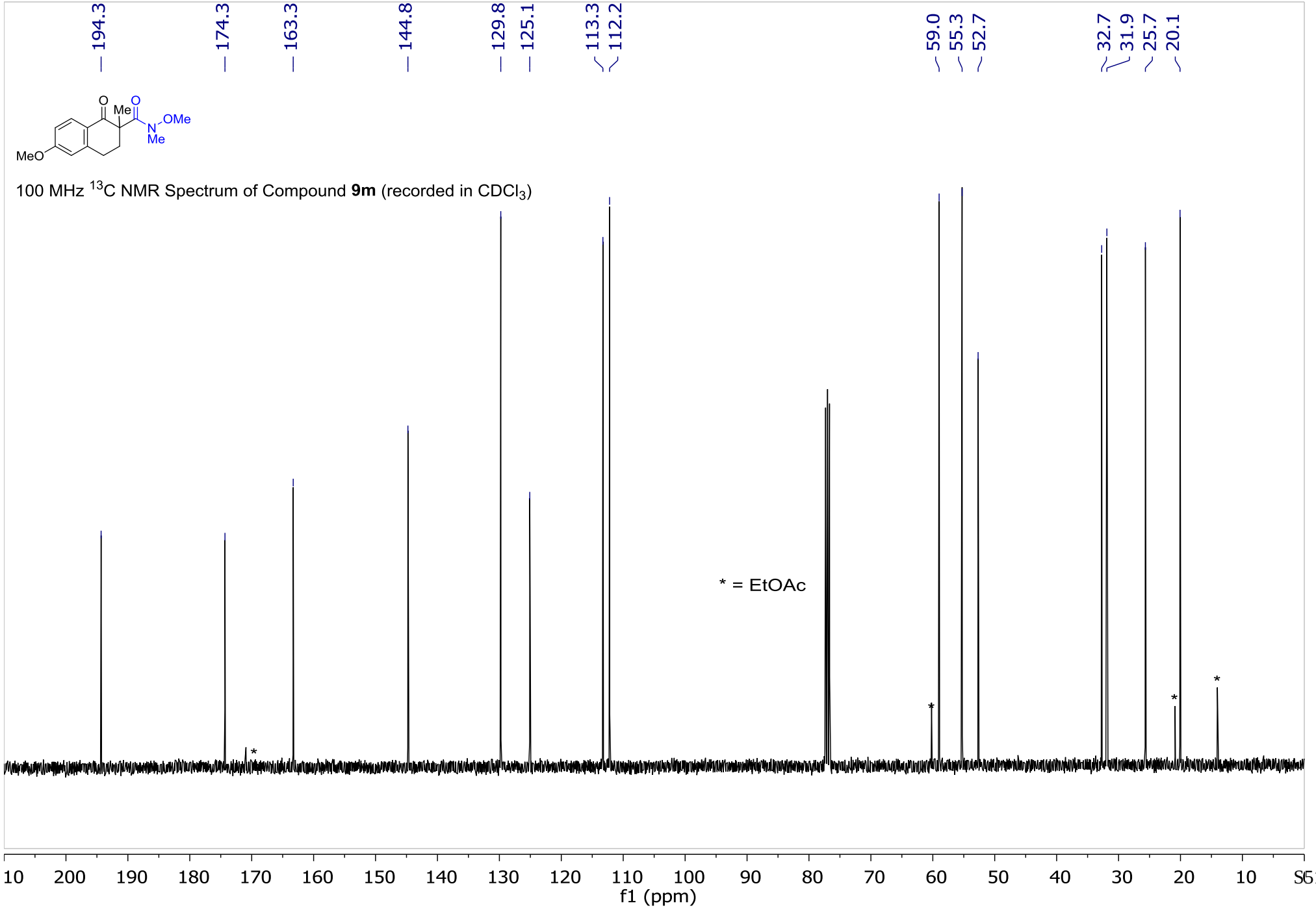


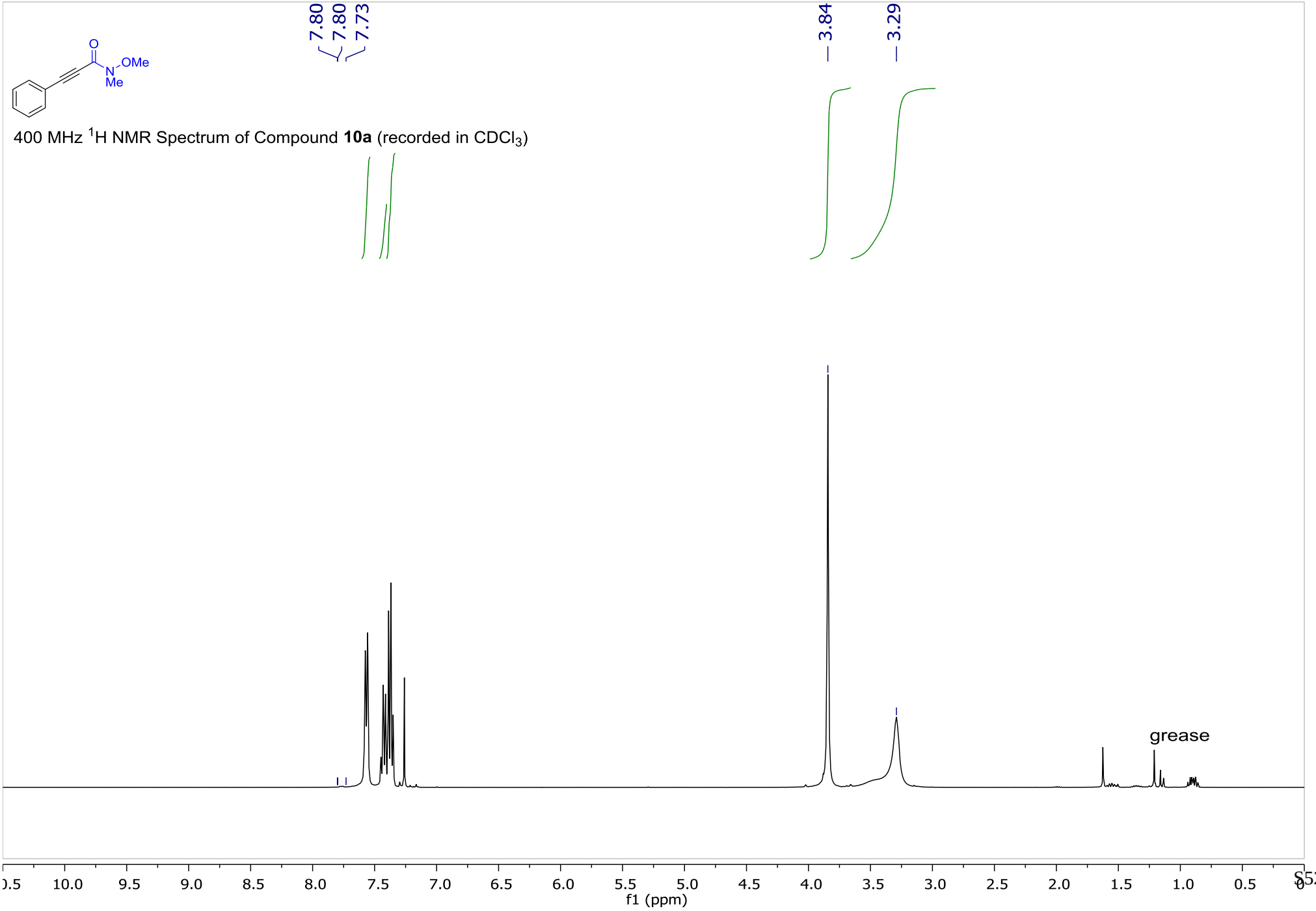
100 MHz ^{13}C NMR Spectrum of Compound **9k** (recorded in $CDCl_3$)


7.26
7.24
7.18
7.17
7.10
7.09
7.08
7.08
7.04
7.02
3.64
3.58
3.55
3.13
2.80
2.76
1.56
O
O
Me
O
MeN
OMe
400 MHz ^{1}H NMR Spectrum of Compound **9l** (recorded in $CDCl_3$)
* = EtOAc
*
*
*
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

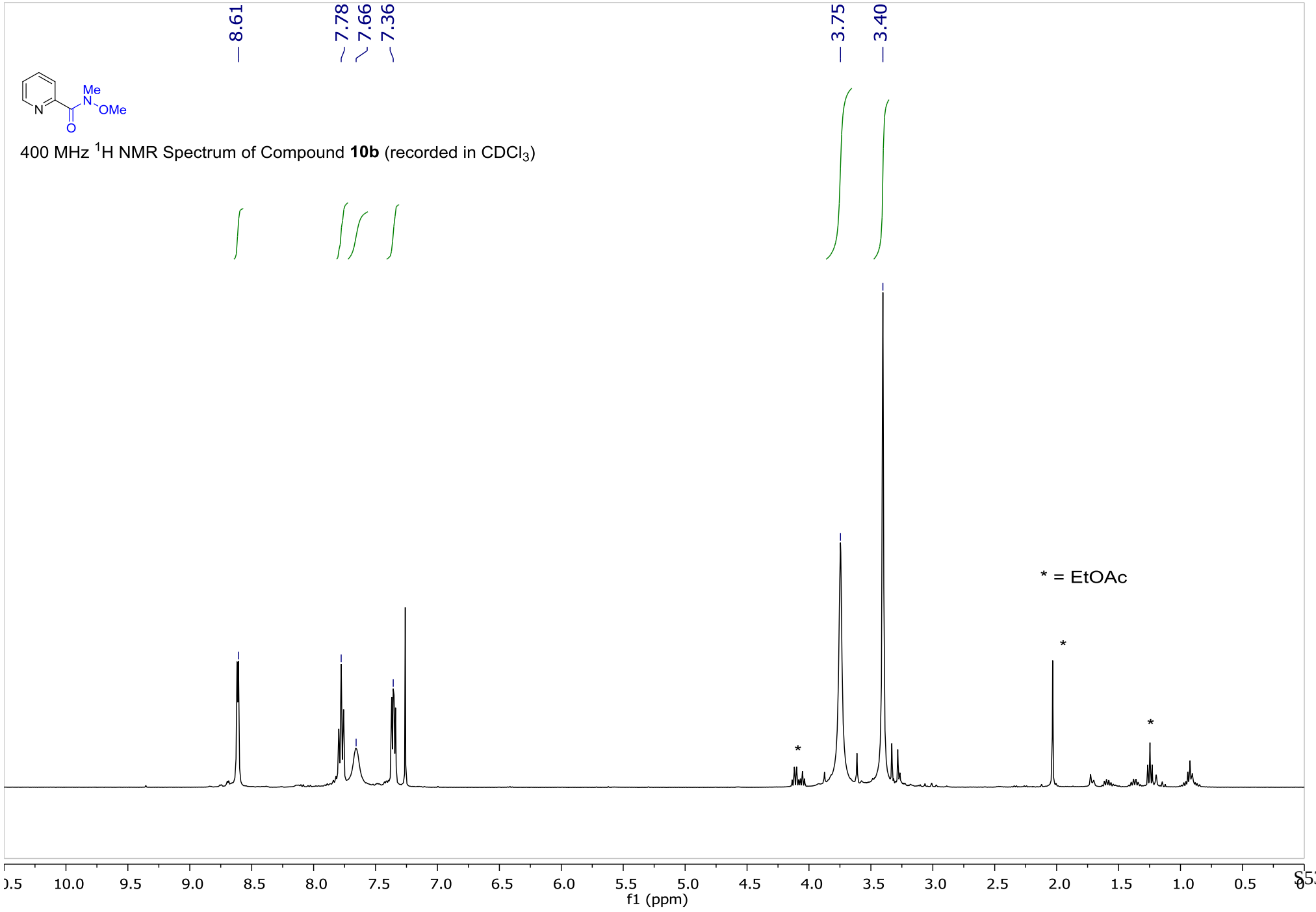

170.6
170.6
168.9
168.8
151.1
128.4
128.2
124.5
121.4
116.2
116.2
77.3
77.0
76.7
60.4
47.9
35.0
35.0
33.0
21.6
21.6
O
O
Me
O
MeN
OMe
100 MHz ^{13}C NMR Spectrum of Compound **9l** (recorded in $CDCl_3$)
* = EtOAc
*
*
*
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

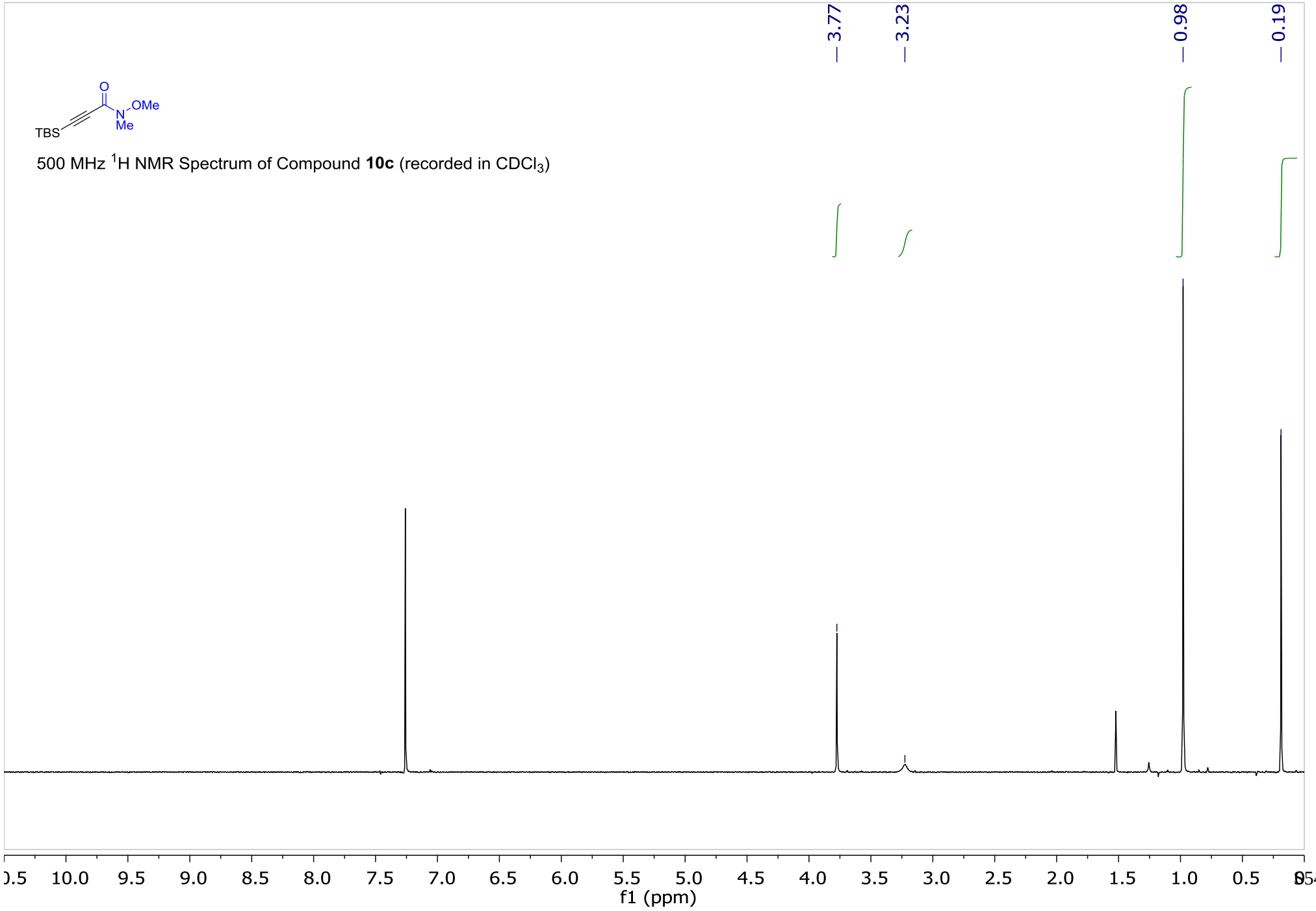

7.98
7.95
6.80
6.78
6.65
3.81
3.29
3.12
2.96
2.79
2.54
1.82
1.41
O
Me
O
N
OMe
Me
MeO
400 MHz ^{1}H NMR Spectrum of Compound **9m** (recorded in $CDCl_3$)
*
*
*
f1 (ppm)

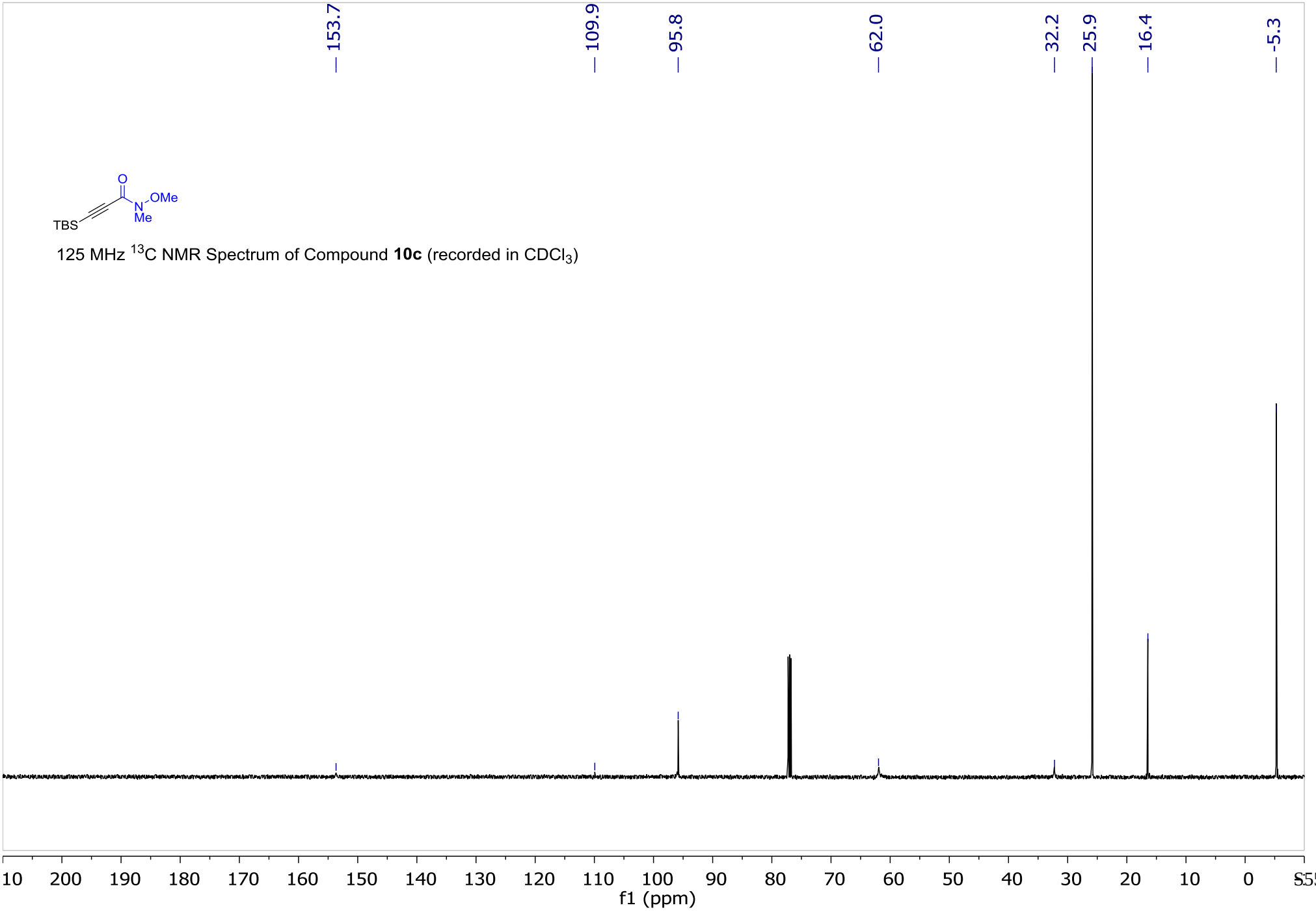

194.3
174.3
163.3
144.8
129.8
125.1
113.3
112.2
59.0
55.3
52.7
32.7
31.9
25.7
20.1
O
Me
O
N
OMe
Me
MeO
100 MHz 13C NMR Spectrum of Compound 9m (recorded in CDCl3)
* = EtOAc
*
*
*
*
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

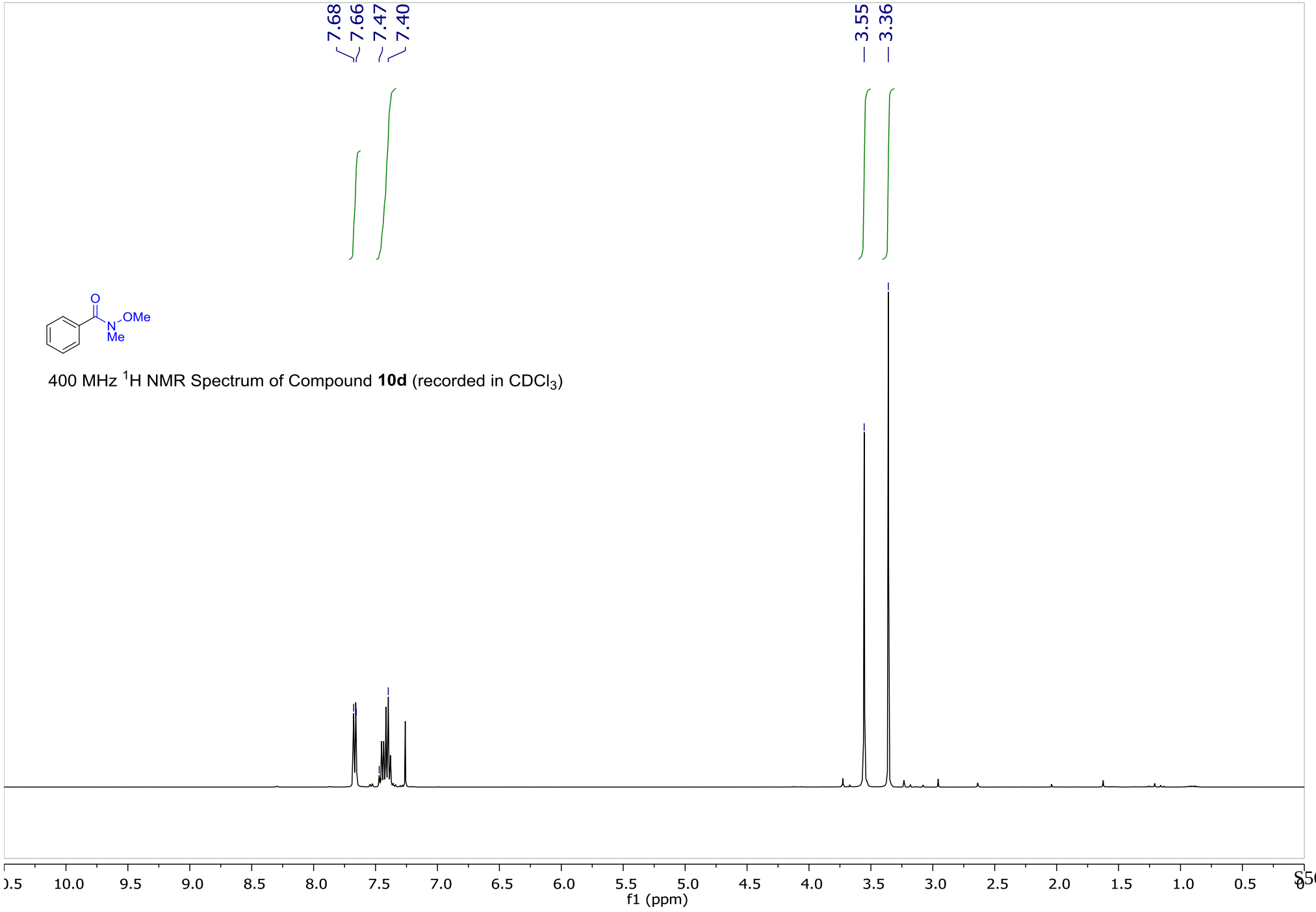


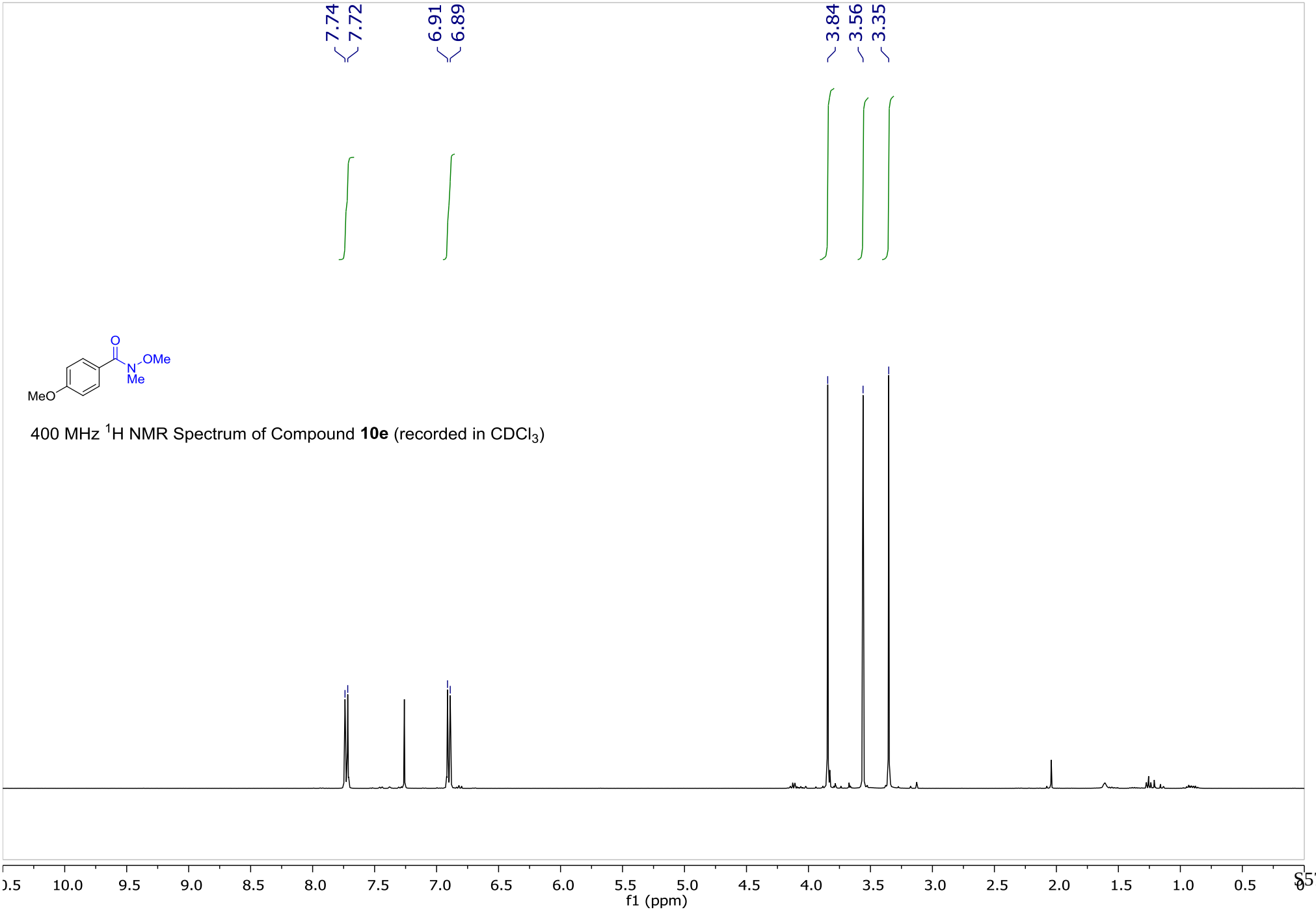
400 MHz ^{1}H NMR Spectrum of Compound **10a** (recorded in $CDCl_3$)

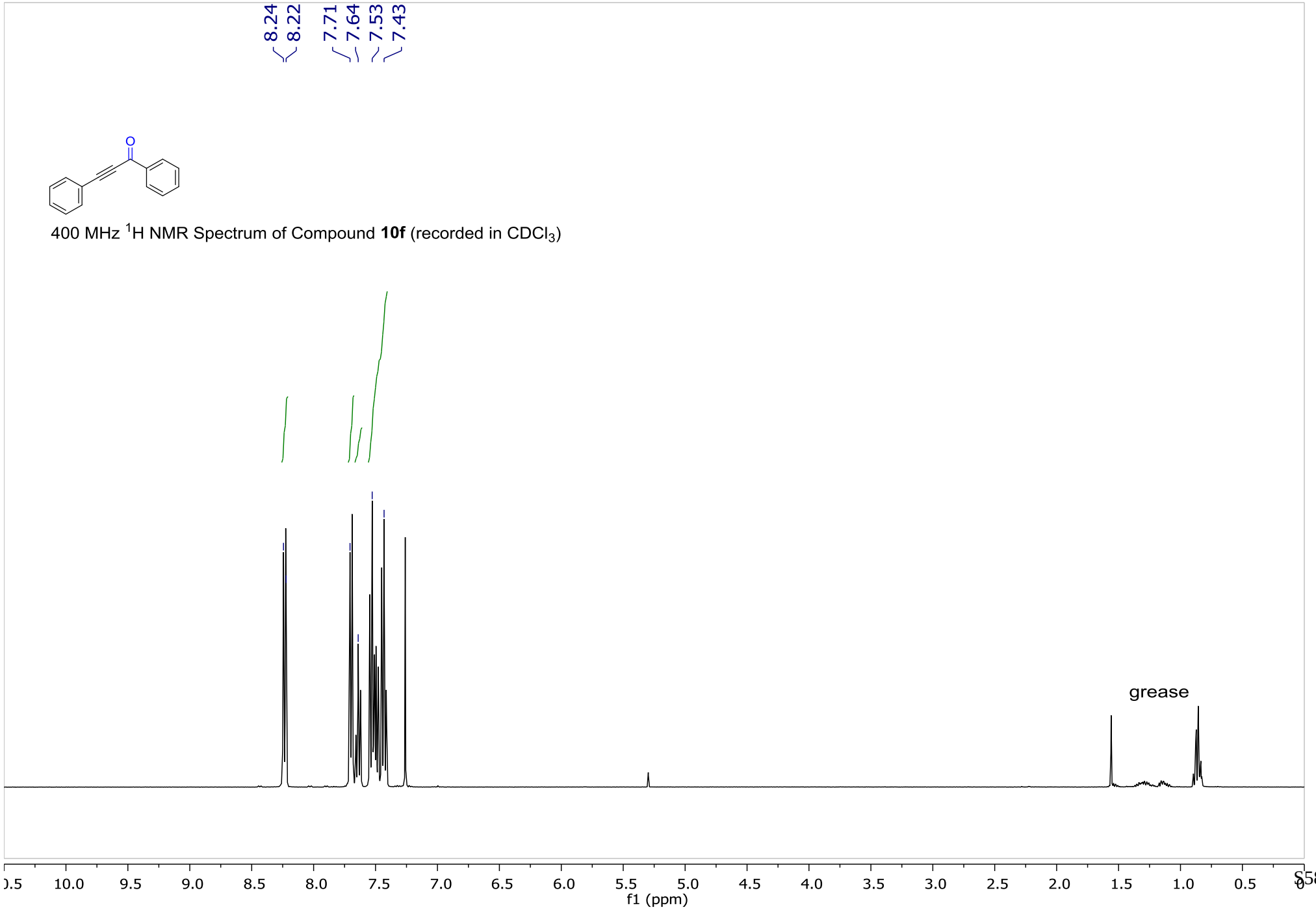

8.61
7.78
7.66
7.36
3.75
3.40
Me
N
OMe
O
N
400 MHz ^{1}H NMR Spectrum of Compound **10b** (recorded in $CDCl_3$)
* = EtOAc
*
*
*
f1 (ppm)


3.77
3.23
0.98
0.19
O
N
OMe
Me
TBS
500 MHz ^{1}H NMR Spectrum of Compound **10c** (recorded in $CDCl_3$)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

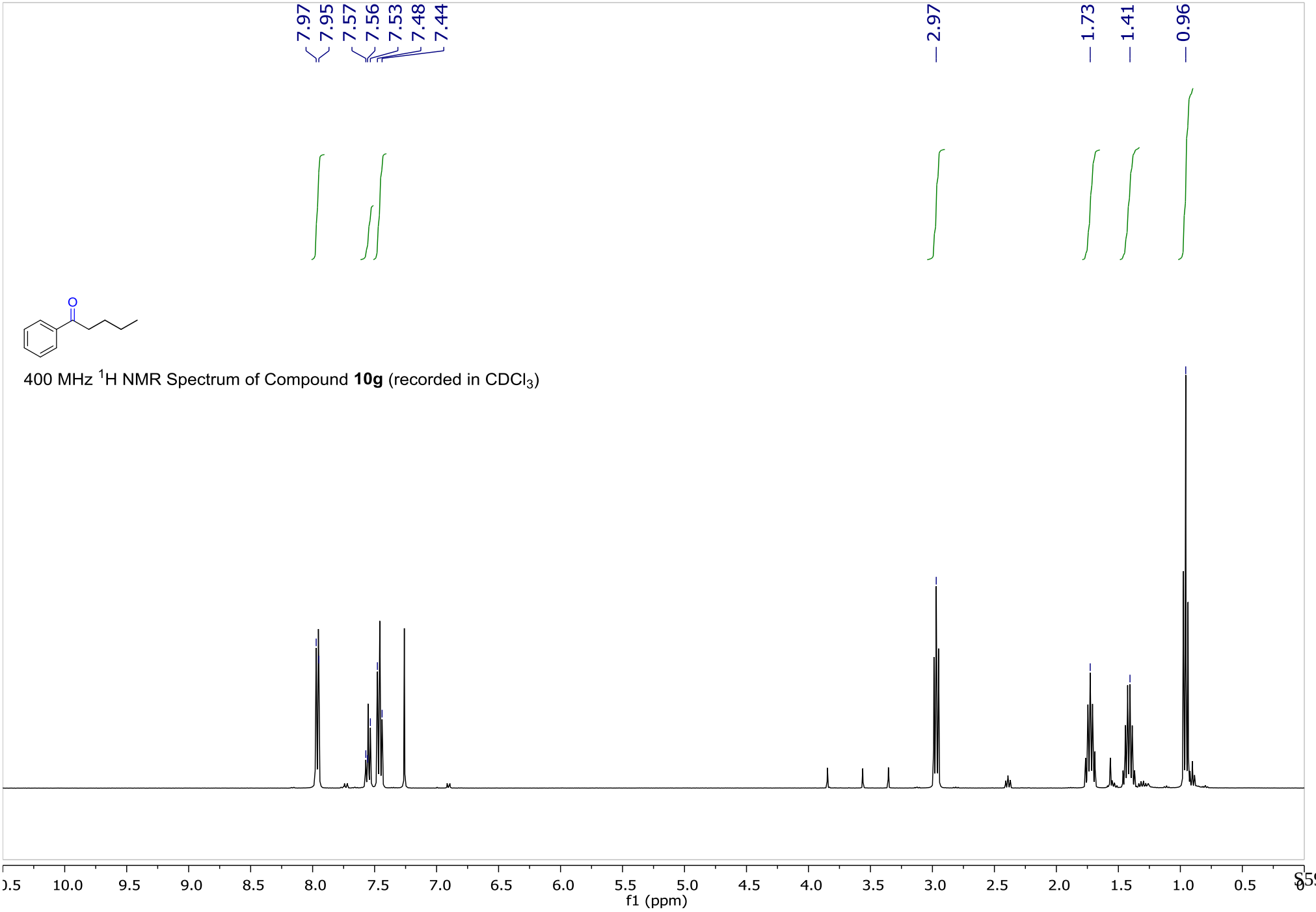

153.7
109.9
95.8
62.0
32.2
25.9
16.4
-5.3
O
N
OMe
Me
TBS
125 MHz ^{13}C NMR Spectrum of Compound **10c** (recorded in $CDCl_3$)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

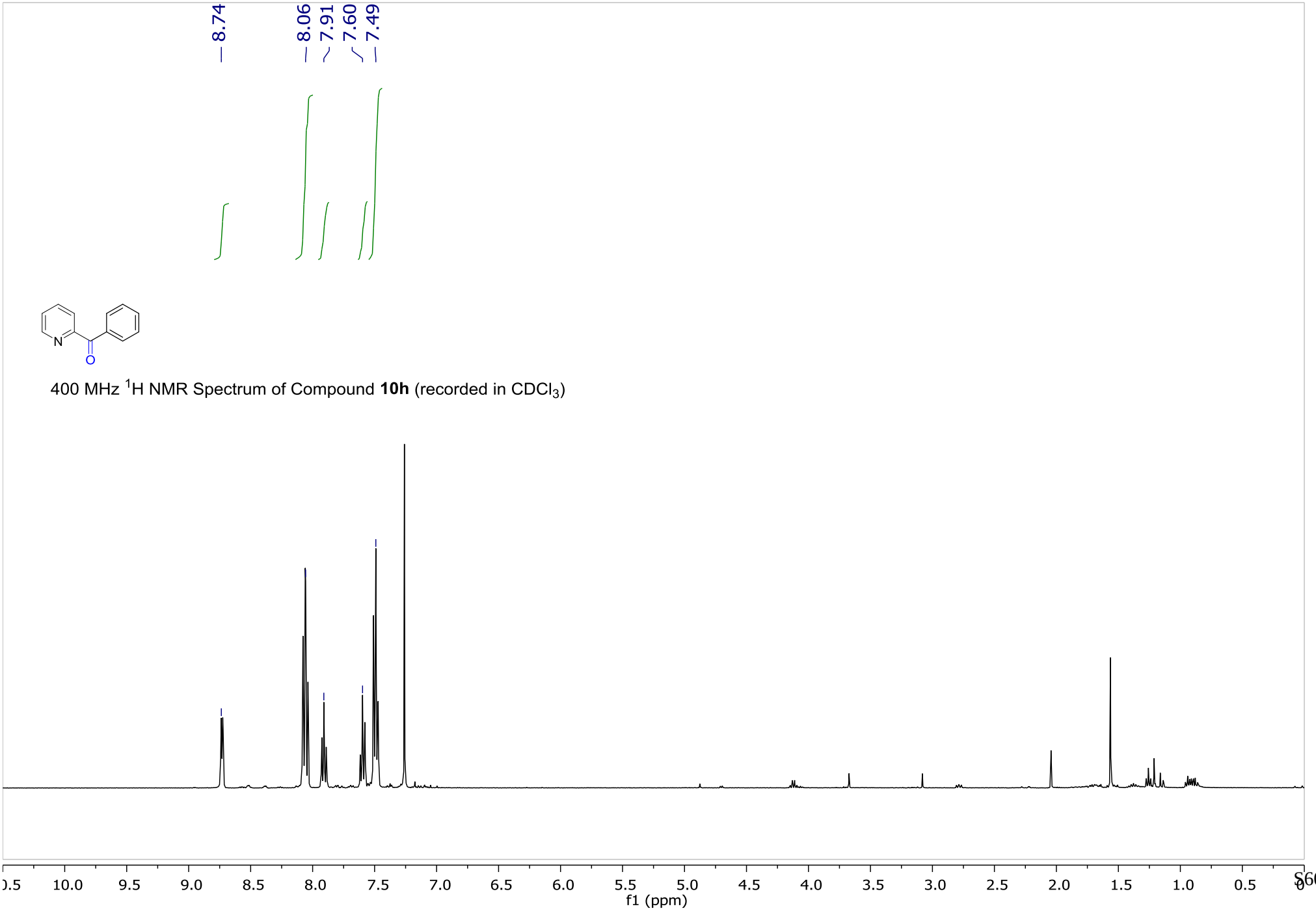

7.68
7.66
7.47
7.40
3.55
3.36
O
N
OMe
Me
400 MHz ^{1}H NMR Spectrum of Compound **10d** (recorded in $CDCl_3$)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


7.74
7.72
6.91
6.89
3.84
3.56
3.35
O
N
OMe
Me
MeO
400 MHz ^{1}H NMR Spectrum of Compound **10e** (recorded in $CDCl_3$)
f1 (ppm)



400 MHz ^{1}H NMR Spectrum of Compound **10f** (recorded in $CDCl_3$)


7.97
7.95
7.57
7.56
7.53
7.48
7.44
2.97
1.73
1.41
0.96
O
400 MHz ^{1}H NMR Spectrum of Compound **10g** (recorded in $CDCl_3$)
f1 (ppm)



400 MHz ^{1}H NMR Spectrum of Compound **10h** (recorded in $CDCl_3$)