Supporting Information

Palladium and Lewis Acid-Catalyzed Intramolecular Aminocyanation of Alkenes: Scope, Mechanism, and Diastereoselective Alkene Difunctionalizations

Zhongda Pan,[†] Shengyang Wang,[†] Jason T. Brethorst, and Christopher J. Douglas*

Department of Chemistry, University of Minnesota - Twin Cities, 207 Pleasant St. SE, Minneapolis, MN 55455

1. General details

Unless otherwise noted, all reactions were carried out using oven-dried glassware under a nitrogen atmosphere. Dichloromethane (CH_2Cl_2) and toluene were distilled from CaH_2 prior to use. Tetrahydrofuran (THF) was distilled from Na/benzophenone prior to use. *m*-Xylene and toluene were further degassed by bubbling a stream of argon through the liquid in a Strauss flask and then stored in a nitrogen-filled glove box. Acetonitrile (CH_3CN), benzene, methanol (MeOH), anhydrous *N*,*N*-dimethylformamide (DMF) and anhydrous diethyl ether (Et_2O) were purchased from Sigma-Aldrich and Alfa Aesar, and used without further purification. Unless otherwise noted, all chemicals were purchased from commercial sources and used as received. All transition-metal complexes, except for CpPd(1-phenylallyl), were purchased from Sigma-Aldrich or Strem and used as received. CpPd(1-phenylallyl) was synthesized following a known procedure.[1] Triphenylborane (BPh_3) was purchased from Strem and recrystallized from anhydrous heptanes under nitrogen.[2] Tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] was purchased from Strem and used as received.

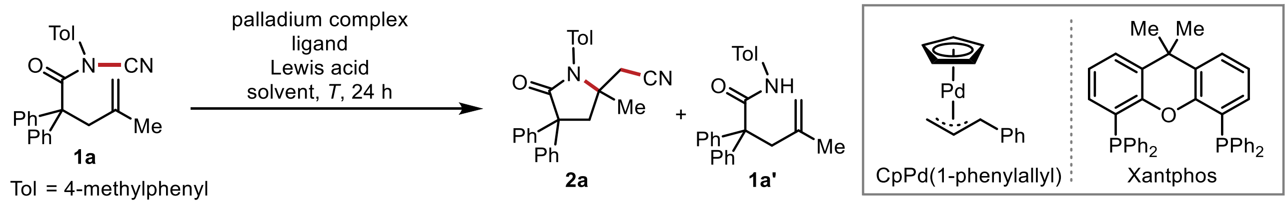
Analytical thin-layer chromatography (TLC) and preparative thin-layer chromatography were carried out using 250 μm and 1000 μm silica plates (SiliCycle), respectively. Eluted plates were visualized first with a UV lamp (254 nm) and then stained with potassium permanganate, iodine, or bromocresol green. Flash column chromatography was performed using 230–400 mesh (particle size 40–63 μm) silica gel purchased from SiliCycle.

^{1}H NMR (400 and 500 MHz), ^{13}C NMR (75 and 125 MHz), and ^{19}F NMR (375 and 470 MHz) spectra were obtained on Varian Inova and Bruker Avance instruments. ^{1}H NMR spectra data were reported as δ values in ppm relative to TMS (δ 0.00) or chloroform (7.26) if collected in $CDCl_3$, or dimethyl sulfoxide (δ 2.50) if collected in DMSO-d_6. ^{13}C NMR spectra data were reported as δ values in ppm relative to chloroform (δ 77.00) if collected in $CDCl_3$ or dimethyl sulfoxide (δ 39.50) if collected in DMSO-d_6. ^{19}F NMR spectra data were reported as δ values in ppm using instrument standard. ^{1}H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); dq (doublet of quartets); app (apparent); br (broad). Raw NMR data files or processed NMR data files, referred to as ".mnova files" in the tables below, are available from the corresponding author upon request. Infrared (IR) spectra were obtained on a MIDAC FT-IR spectrometer. A thin-film of sample was prepared by evaporating solvent (CH_2Cl_2 or $CDCl_3$) on NaCl plates. High-resolution mass spectra (HRMS) in electrospray ionization (ESI) experiments were performed on a Bruker BioTOF II (Time-of-flight) instrument using PEG-300, PEG-400 or PPG-400 as an internal standard.

2. Optimization of aminocyanation conditions

A general procedure: In a nitrogen-filled glove box, a one-dram vial was charged with a magnetic stirring bar, substrate **1a** (38.1 mg, 0.1 mmol), BPh_3 (9.7 mg, 0.04 mmol), Xantphos (5.8 mg, 0.01 mmol), and a solution of CpPd(1-phenylallyl) in toluene (0.02 M, 0.5 mL, 0.01 mmol). The reaction mixture was sealed with a PTFE lined cap, removed from the glove box, and heated in an aluminum heating block for 24 h. The resulting mixture was allowed to cool to room temperature and a stock solution of *p*-methoxyacetophenone (0.1 M in toluene, 0.3 mL, 0.03 mmol) was added as the internal NMR-standard. The resulting mixture was concentrated in vacuo and the yield of **2a** was determined by ^{1}H NMR analysis. The isolated yield was obtained by concentrating the crude mixture onto Celite, followed by flash column chromatography.

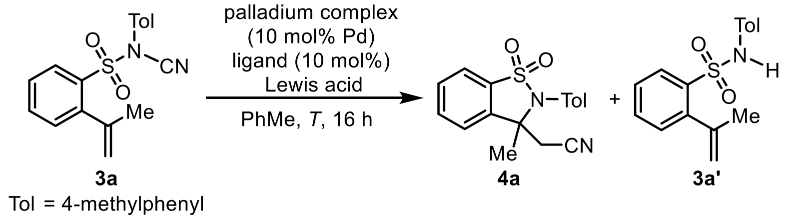
Table S1. Optimization of aminocyanation of *N*-acyl cyanamide **1a**



Entry	Palladium[a]	Ligand[b]	Lewis acid (equiv.)	Solvent	T (°C)	Yield of **2a** (%)[c]
1	CpPd(1-phenylallyl)	Xantphos	BPh_3 (0.5)	PhMe	90	87[d]
2	$Pd(OAc)_2$	Xantphos	BPh_3 (0.5)	PhMe	90	67
3	$Pd(TFA)_2$	Xantphos	BPh_3 (0.5)	PhMe	90	17
4	$[Pd(allyl)Cl]_2$	Xantphos	BPh_3 (0.4)	PhMe	100	0[e]
5	Pd_2dba_3	Xantphos	BPh_3 (0.5)	PhMe	90	69
6	$Pd(PPh_3)_4$	–	BPh_3 (0.5)	PhMe	90	81
7	CpPd(1-phenylallyl)	Xantphos[f]	$B(C_6F_5)_3$ (0.5)	PhMe	100	0[e]
8	CpPd(1-phenylallyl)	Xantphos[f]	$AlMe_2Cl$ (0.5)	PhMe	100	0[e]
9	CpPd(1-phenylallyl)	Xantphos[f]	$AlCl_3$ (0.5)	PhMe	100	0[e]
10	CpPd(1-phenylallyl)	Xantphos[f]	$ZnCl_2$ (0.5)	PhMe	100	0[g]
11	CpPd(1-phenylallyl)	Xantphos[f]	$Zn(OTf)_2$ (0.5)	PhMe	100	0[g]
12	CpPd(1-phenylallyl)	dppe	BPh_3 (0.4)	PhMe	80	0[e]
13	CpPd(1-phenylallyl)	dppp	BPh_3 (0.4)	PhMe	80	23
14	CpPd(1-phenylallyl)	dppb	BPh_3 (0.4)	PhMe	80	49
15	CpPd(1-phenylallyl)	DPEphos	BPh_3 (0.4)	PhMe	80	72
16	CpPd(1-phenylallyl)	Xantphos	BPh_3 (0.4)	PhMe	80	93
17	CpPd(1-phenylallyl)	Nixantphos	BPh_3 (0.4)	PhMe	80	81
18	CpPd(1-phenylallyl)	DBFphos	BPh_3 (0.4)	PhMe	80	0[e]
19	CpPd(1-phenylallyl)	Xantphos[f]	BPh_3 (0.4)	THF	80	26
20	CpPd(1-phenylallyl)	Xantphos[f]	BPh_3 (0.4)	$PhCF_3$	80	0[g]
21	CpPd(1-phenylallyl)	Xantphos[f]	BPh_3 (0.4)	dioxane	80	20
22	CpPd(1-phenylallyl)	Xantphos[f]	BPh_3 (0.4)	1,2-DCE	80	0[e]
23	CpPd(1-phenylallyl)	Xantphos[f]	BPh_3 (0.4)	DMF	80	0[g]
24	CpPd(1-phenylallyl)	Xantphos[f]	BPh_3 (0.4)	cyclohexane	80	85
25	CpPd(1-phenylallyl)	Xantphos	–	PhMe	80	< 20[h]
26	–	–	BPh_3 (0.5)	PhMe	100	0[e]
27	–	–	$B(C_6F_5)_3$ (0.5)	PhMe	80	0[e]
28	–	–	$AlCl_3$ (0.5)	PhMe	80	0[h]
29	CpPd(1-phenylallyl)	Xantphos	BPh_3 (0.4)	PhMe	80	89
30	CpPd(1-phenylallyl)	Xantphos	BEt_3 (0.4)	PhMe	80	99

[a]10mol% palladium complex. [b]10 mol% ligand. [c]Determined by ^{1}H NMR analysis using *p*-methoxyacetophenone as the internal standard. [d]Isolated yiled after column chromatography. [e]Only **1a** and **1a'** detected by NMR spectroscopy. [f]15mol% Xantphos. [g]Unconsumed **1a**. [h]Complex reaction mixture.

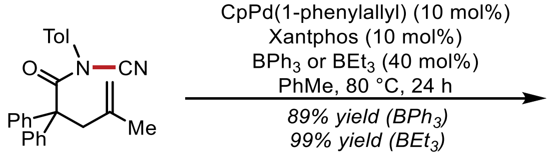
Table S2. Optimization of aminocyanation of *N*-sulfonyl cyanamide **3a**



Entry	Palladium	Ligand	Lewis acid (equiv.)	T (°C)	Yield of **4a** (%)[a]
1	–	–	$B(C_6F_5)_3$ (1.0)	100	0[b]
2	–	–	BF_3•OEt_2 (1.0)	100	0[b]
3	–	–	BPh_3 (0.4)	100	0[b]
4	$Pd(OAc)_2$	Xantphos	BPh_3 (0.4)	100	69
5	$Pd(PPh_3)_4$	Xantphos	BPh_3 (0.4)	100	32
6	$Pd(TFA)_2$	Xantphos	BPh_3 (0.4)	100	63
7	Pd_2dba_3	Xantphos	BPh_3 (0.4)	100	85
8	Pd_2dba_3	Xantphos	BPh_3 (0.4)	90	95
9	Pd_2dba_3	Xantphos	BPh_3 (0.4)	80	99[c]
10	Pd_2dba_3	Xantphos	BPh_3 (0.4)	70	78
11	Pd_2dba_3	Xantphos	–	100	0[b]

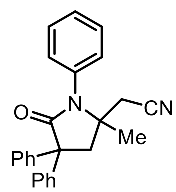
[a]Determined by ^{1}H NMR analysis using DMSO-d_6 as the solvent and *p*-methoxyacetophenone as the internal standard. [b]Unconsumed starting material. [c]Isolated yield after column chromatography.

3. Results of aminocyanation reactions



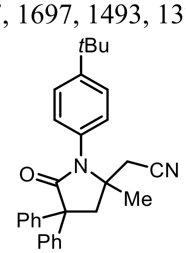
1a **2a**

Aminocyanation of 1a as a representative example: In a nitrogen-filled glove box, a one-dram vial was charged with a magnetic stirring bar, cyanamide **1a** (76.2 mg, 0.2 mmol), BPh_3 or BEt_3 (BPh_3: 19.4 mg, 0.08 mmol; BEt_3: 1.0 M in Hex, 80 µL, 0.08 mmol), Xantphos (11.6 mg, 0.02 mmol), and a solution of CpPd(1-phenylallyl) in toluene (0.02 M, 1.0 mL, 0.02 mmol). The reaction mixture was sealed with a PTFE lined cap, removed from the glove box, and heated at 80 °C in an aluminum heating block for 24 h. The resulting mixture was allowed to cool to room temperature, diluted with CH_2Cl_2 (5 mL), and concentrated onto Celite. The crude product was purified by gradient flash column chromatography (1:9 → 15:85 EtOAc/Hex) to afford **2a** as a pale yellow foam (0.198 mmol, 99% yield with BEt_3). R_f = 0.32 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, J = 7.7 Hz, 2H), 7.46 (d, J = 7.7 Hz, 2H), 7.35 (dt, J = 13.2, 7.6 Hz, 4H), 7.29 – 7.22 (m, 4H), 7.03 (d, J = 7.8 Hz, 2H), 3.33 (d, J = 13.7 Hz, 1H), 3.00 (d, J = 13.7 Hz, 1H), 2.42 (d, J = 16.6 Hz, 1H), 2.37 (s, 3H), 2.33 (d, J = 16.5 Hz, 1H), 1.33 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.9, 142.9, 142.8, 138.9, 132.2, 130.3, 129.2, 128.8, 128.5, 127.7, 127.6, 127.2, 127.0, 116.8, 59.8, 56.9, 46.7, 29.3, 26.5, 21.1; **HRMS** (ESI) calcd for $[C_{26}H_{24}N_2O + Na]^+$ 403.1781, found 403.1786; **IR** (thin film) 2247, 1697, 1513, 1373.



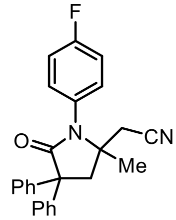
2b

Prepared from **1b** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (40 mol%) in toluene at 80 °C for 24 h. **2b** was purified by gradient flash column chromatography (1:9 → 15:85 EtOAc/Hex) as an off-white foam (0.192 mmol, 96% yield). R_f = 0.24 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.50 – 7.31 (m, 9H), 7.28 (td, J = 7.7, 7.1, 1.7 Hz, 2H), 7.20 – 7.14 (m, 2H), 3.36 (d, J = 13.8 Hz, 1H), 3.03 (d, J = 13.7 Hz, 1H), 2.44 (d, J = 16.5 Hz, 1H), 2.36 (d, J = 16.6 Hz, 1H), 1.36 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.0, 142.9, 142.7, 135.0, 129.7, 129.5, 128.9, 128.8, 128.6, 127.7, 127.6, 127.3, 127.1, 116.8, 59.9, 56.9, 46.8, 29.4, 26.6; **HRMS** (ESI) calcd for $[C_{25}H_{22}N_2O + Na]^+$ 389.1624, found 389.1625; **IR** (thin film) 2247, 1697, 1493, 1371.



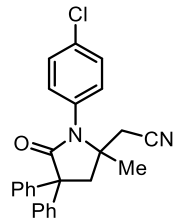
2c

Prepared from **1c** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (40 mol%) in toluene at 80 °C for 24 h. **2c** was purified by gradient flash column chromatography (1:9 → 1:4 EtOAc/Hex) as a pale yellow foam (0.186 mmol, 93% yield). R_f = 0.51 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.1 Hz, 2H), 7.46 (ddd, J = 8.3, 3.8, 1.3 Hz, 4H), 7.39 – 7.23 (m, 6H), 7.08 (d, J = 7.1 Hz, 2H), 3.34 (d, J = 1.2 Hz, 1H), 3.02 (d, J = 1.1 Hz, 1H), 2.43 (d, J = 1.1 Hz, 1H), 2.36 (d, J = 16.5 Hz, 1H), 1.36 (d, J = 1.2 Hz, 3H), 1.33 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.0, 151.9, 143.0, 142.7, 132.1, 128.9, 128.8, 128.5, 127.7, 127.6, 127.3, 127.0, 126.7, 116.9, 59.9, 56.9, 46.7, 34.7, 31.2, 29.3, 26.6; **HRMS** (ESI) calcd for $[C_{29}H_{30}N_2O + Na]^+$ 445.2250, found 445.2244; **IR** (thin film) 2247, 1696, 1510, 1372.



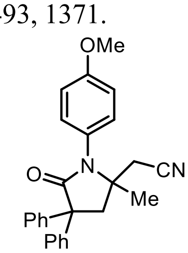
2d

Prepared from **1d** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (40 mol%) in toluene at 80 °C for 24 h. **2d** was purified by flash column chromatography (1:9 → 1:4 EtOAc/Hex) as a pale yellow foam (0.180 mmol, 90% yield). R_f = 0.29 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, J = 7.7 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.36 (dt, J = 10.6, 7.6 Hz, 4H), 7.28 (t, J = 7.1 Hz, 2H), 7.15 (d, J = 6.6 Hz, 4H), 3.34 (d, J = 13.7 Hz, 1H), 3.03 (d, J = 13.7 Hz, 1H), 2.43 (d, J = 16.6 Hz, 1H), 2.35 (d, J = 16.6 Hz, 1H), 1.34 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.2, 162.6 (d, $^1J_{F\text{–}C}$ = 249.2 Hz), 142.7, 142.6, 131.4 (d, $^3J_{F\text{–}C}$ = 8.7 Hz), 130.9 (d, $^4J_{F\text{–}C}$ = 3.2 Hz), 128.9, 128.6, 127.7, 127.6, 127.4, 127.2, 116.8 (d, $^2J_{F\text{–}C}$ = 22.8 Hz), 116.6, 59.9, 56.9, 46.7, 29.4, 26.5; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –111.9; **HRMS** (ESI) calcd for $[C_{25}H_{21}FN_2O + Na]^+$ 407.1530, found 407.1536; **IR** (thin film) 2247, 1698, 1509, 1374, 1221.



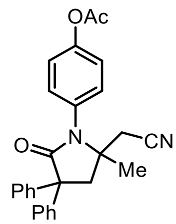
2e

Prepared from **1e** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BPh_3 (60 mol%) in toluene at 80 °C for 24 h. **2e** was purified by flash column chromatography (1:9 → 15:85 EtOAc/Hex) as an off-white foam (0.172 mmol, 86% yield). R_f = 0.32 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 – 7.41 (m, 6H), 7.36 (dt, J = 10.3, 7.6 Hz, 4H), 7.30 – 7.26 (m, 2H), 7.12 (d, J = 8.5 Hz, 2H), 3.34 (d, J = 13.7 Hz, 1H), 3.02 (d, J = 13.7 Hz, 1H), 2.42 (d, J = 16.6 Hz, 1H), 2.34 (d, J = 16.5 Hz, 1H), 1.33 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.0, 142.6, 142.5, 135.0, 133.6, 130.8, 130.0, 128.9, 128.6, 127.6, 127.5, 127.4, 127.2, 116.6, 59.9, 56.9, 46.7, 29.4, 26.6; **HRMS** (ESI) calcd for $[C_{25}H_{21}ClN_2O + Na]^+$ 423.1235, found 423.1236; **IR** (thin film) 2247, 1698, 1493, 1371.



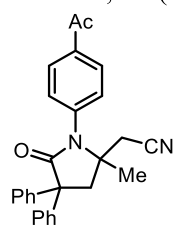
2f

Prepared from **1f** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (40 mol%) in toluene at 80 °C for 24 h. **2f** was purified by flash column chromatography (1:3 EtOAc/Hex) as a pale yellow oil (0.190 mmol, 95% yield). R_f = 0.32 (3:7 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.35 (dt, J = 12.5, 7.6 Hz, 4H), 7.30 – 7.24 (m, 2H), 7.08 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 3.33 (d, J = 13.7 Hz, 1H), 3.00 (d, J = 13.7 Hz, 1H), 2.42 (d, J = 16.6 Hz, 1H), 2.34 (d, J = 16.6 Hz, 1H), 1.33 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.1, 159.7, 143.0, 142.8, 130.6, 128.8, 128.5, 127.7, 127.6, 127.4, 127.2, 127.0, 116.9, 114.9, 59.8, 56.8, 55.5, 46.6, 29.3, 26.5; **HRMS** (ESI) calcd for $[C_{26}H_{24}N_2O_2 + Na]^+$ 419.1730, found 419.1736; **IR** (thin film) 2247, 1696, 1512, 1375, 1251.



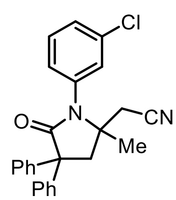
2g

Prepared from **1g** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (40 mol%) in toluene at 80 °C for 24 h. **2g** was purified by flash column chromatography (1:3 → 45:55 EtOAc/Hex) as an off-white foam (0.180 mmol, 90% yield). R_f = 0.59 (1:1 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, J = 7.7 Hz, 2H), 7.45 (d, J = 7.8 Hz, 2H), 7.39 – 7.32 (m, 4H), 7.30 – 7.26 (m, 2H), 7.23 – 7.15 (m, 4H), 3.36 (d, J = 13.8 Hz, 1H), 3.03 (d, J = 13.7 Hz, 1H), 2.45 (d, J = 16.5 Hz, 1H), 2.37 (d, J = 16.6 Hz, 1H), 2.31 (s, 3H), 1.34 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.1, 169.0, 150.8, 142.7, 142.6, 132.4, 130.6, 128.8, 128.6, 127.7, 127.6, 127.3, 127.1, 122.9, 116.7, 60.0, 57.0, 46.7, 29.4, 26.6, 21.1; **HRMS** (ESI) calcd for $[C_{27}H_{24}N_2O_3 + Na]^+$ 447.1679, found 447.1682; **IR** (thin film) 2247, 1755, 1698, 1507, 1371, 1196.



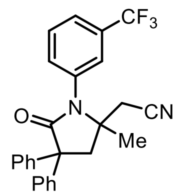
2h

Prepared from **1h** on a 0.2 mmol scale with CpPd(1-phenylallyl) (15 mol%), Xantphos (15 mol%), and BEt_3 (100 mol%) in toluene at 70 °C for 30 h. **2h** was purified by flash column chromatography (1:4 → 3:7 EtOAc/Hex) as a pale yellow foam (0.134 mmol, 67% yield). R_f = 0.36 (4:6 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.37 (dt, J = 11.6, 7.7 Hz, 4H), 7.29 (t, J = 7.6 Hz, 4H), 3.38 (d, J = 13.8 Hz, 1H), 3.06 (d, J = 13.7 Hz, 1H), 2.62 (s, 3H), 2.46 (d, J = 16.6 Hz, 1H), 2.38 (d, J = 16.6 Hz, 1H), 1.38 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.0, 175.0, 142.5, 142.4, 139.6, 137.1, 129.7, 129.6, 128.9, 128.7, 127.6, 127.5, 127.4, 127.2, 116.5, 60.2, 57.0, 46.9, 29.5, 26.8, 26.7; **HRMS** (ESI) calcd for $[C_{27}H_{24}N_2O_2 + Na]^+$ 431.1730, found 431.1733; **IR** (thin film) 2247, 1687, 1600, 1367, 1266.



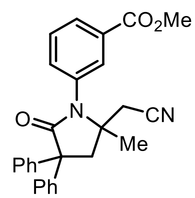
2i

Prepared from **1i** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (80 mol%) in toluene at 70 °C for 24 h. **2i** was purified by flash column chromatography (1:9 → 15:85 EtOAc/Hex) as a white foam (0.152 mmol, 76% yield). R_f = 0.31 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, J = 7.7 Hz, 2H), 7.46 – 7.32 (m, 8H), 7.31 – 7.26 (m, 2H), 7.17 (t, J = 1.3 Hz, 1H), 7.12 – 7.07 (m, 1H), 3.36 (d, J = 13.7 Hz, 1H), 3.03 (d, J = 13.7 Hz, 1H), 2.44 (d, J = 16.6 Hz, 1H), 2.36 (d, J = 16.6 Hz, 1H), 1.36 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.0, 142.6, 142.4, 136.3, 135.2, 130.7, 129.7, 129.3, 128.9, 128.6, 127.9, 127.6, 127.5, 127.4, 127.2, 116.5, 60.0, 56.9, 46.8, 29.4, 26.6; **HRMS** (ESI) calcd for $[C_{25}H_{21}ClN_2O + Na]^+$ 423.1235, found 423.1234; **IR** (thin film) 2248, 1699, 1478, 1368.



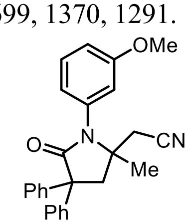
2j

Prepared from **1j** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 70 °C for 24 h. **2j** was purified by flash column chromatography (1:9 → 1:4 EtOAc/Hex) as a pale yellow foam (0.172 mmol, 86% yield). R_f = 0.29 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, J = 7.9 Hz, 1H), 7.61 (t, J = 7.9 Hz, 1H), 7.49 (d, J = 7.9 Hz, 2H), 7.47 – 7.33 (m, 8H), 7.29 (dd, J = 8.8, 7.2 Hz, 2H), 3.37 (d, J = 13.8 Hz, 1H), 3.05 (d, J = 13.7 Hz, 1H), 2.43 (d, J = 16.6 Hz, 1H), 2.36 (d, J = 16.6 Hz, 1H), 1.37 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.1, 142.5, 142.4, 135.8, 133.2, 132.2 (q, $^2J_{F\text{–}C}$ = 33.0 Hz), 130.4, 128.9, 128.7, 127.6, 127.51, 127.46, 127.3, 126.2 (q, $^3J_{F\text{–}C}$ = 3.7 Hz), 125.8 (q, $^3J_{F\text{–}C}$ = 3.8 Hz), 122.4 (q, $^1J_{F\text{–}C}$ = 270.9 Hz), 116.4, 60.1, 57.0, 46.8, 29.5, 26.7; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –62.6; **HRMS** (ESI) calcd for $[C_{26}H_{21}F_3N_2O + Na]^+$ 457.1498, found 457.1502; **IR** (thin film) 2249, 1700, 1328, 1129.



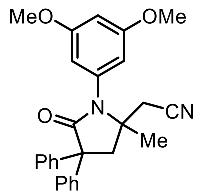
2k

Prepared from **1k** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 70 °C for 24 h. **2k** was purified by flash column chromatography (15:85 → 3:7 EtOAc/Hex) as a pale yellow foam (0.184 mmol, 92% yield). R_f = 0.39 (3:7 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (dt, J = 7.9, 1.4 Hz, 1H), 7.81 (t, J = 1.9 Hz, 1H), 7.56 (t, J = 7.9 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.47 – 7.42 (m, 2H), 7.42 – 7.33 (m, 5H), 7.32 – 7.26 (m, 2H), 3.92 (s, 3H), 3.38 (d, J = 13.8 Hz, 1H), 3.04 (d, J = 13.7 Hz, 1H), 2.45 (d, J = 16.5 Hz, 1H), 2.39 (d, J = 16.5 Hz, 1H), 1.39 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.0, 165.9, 142.7, 142.4, 135.4, 134.2, 131.9, 130.3, 130.0, 129.9, 128.9, 128.6, 127.6, 127.5, 127.4, 127.1, 116.5, 60.0, 56.9, 52.4, 46.9, 29.4, 26.7; **HRMS** (ESI) calcd for $[C_{27}H_{24}N_2O_3 + Na]^+$ 447.1679, found 447.1683; **IR** (thin film) 2250, 1723, 1699, 1370, 1291.



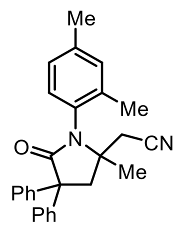
2l

Prepared from **1l** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (40 mol%) in toluene at 80 °C for 24 h. **2l** was purified by flash column chromatography (15:85 → 1:4 EtOAc/Hex) as a yellow oil (0.168 mmol, 84% yield). R_f = 0.19 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.46 (d, J = 7.6 Hz, 2H), 7.38 – 7.32 (m, 5H), 7.31 – 7.22 (m, 2H), 6.95 (dd, J = 8.4, 2.5 Hz, 1H), 6.74 (dd, J = 7.7, 1.8 Hz, 1H), 6.71 (d, J = 2.3 Hz, 1H), 3.81 (s, 3H), 3.35 (d, J = 13.7 Hz, 1H), 3.01 (d, J = 13.7 Hz, 1H), 2.45 (d, J = 16.6 Hz, 1H), 2.35 (d, J = 16.6 Hz, 1H), 1.34 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.8, 160.4, 142.8, 142.7, 136.1, 130.3, 128.8, 128.5, 127.7, 127.6, 127.3, 127.1, 121.5, 116.8, 115.6, 114.2, 59.9, 56.9, 55.4, 46.7, 29.4, 26.6; **HRMS** (ESI) calcd for $[C_{26}H_{24}N_2O_2 + Na]^+$ 419.1730, found 419.1732; **IR** (thin film) 2248, 1697, 1491, 1372, 1287, 1267.



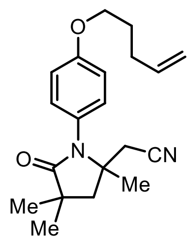
2m

Prepared from **1m** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (40 mol%) in toluene at 70 °C for 30 h. **2m** was purified by flash column chromatography (1:4 → 1:3 EtOAc/Hex) as a pale yellow foam (0.174 mmol, 87% yield). R_f = 0.36 (3:7 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, J = 7.4 Hz, 2H), 7.46 (d, J = 7.5 Hz, 2H), 7.35 (dt, J = 9.7, 7.6 Hz, 4H), 7.30 – 7.24 (m, 2H), 6.50 (t, J = 2.3 Hz, 1H), 6.30 (d, J = 2.1 Hz, 2H), 3.79 (s, 6H), 3.35 (d, J = 13.7 Hz, 1H), 3.01 (d, J = 13.7 Hz, 1H), 2.49 (d, J = 16.6 Hz, 1H), 2.36 (d, J = 16.6 Hz, 1H), 1.34 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.6, 161.3, 142.8, 142.7, 136.6, 128.8, 128.6, 127.7, 127.6, 127.3, 127.1, 116.9, 107.8, 100.6, 59.9, 56.9, 55.5, 46.8, 29.4, 26.6; **HRMS** (ESI) calcd for $[C_{27}H_{26}N_2O_3 + Na]^+$ 449.1836, found 449.1837; **IR** (thin film) 2248, 1698, 1206, 1157.



2n

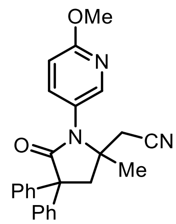
Prepared from **1n** on a 0.2 mmol scale with CpPd(1-phenylallyl) (15 mol%), Xantphos (15 mol%), and BEt_3 (100 mol%) in toluene at 70 °C for 48 h. **2n** was purified by flash column chromatography twice (first: 1:9 EtOAc/Hex; second: CH_2Cl_2) as a colorless oil (0.086 mmol, 43% yield). R_f = 0.49 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.42 – 7.33 (m, 4H), 7.31 – 7.26 (m, 2H), 6.97 (s, 1H), 6.95 (d, J = 1.1 Hz, 2H), 3.29 (d, J = 13.9 Hz, 1H), 3.05 (d, J = 13.9 Hz, 1H), 2.54 (d, J = 16.7 Hz, 1H), 2.49 (d, J = 16.7 Hz, 1H), 2.28 (s, 3H), 2.11 (s, 3H), 1.41 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.8, 143.3, 143.3, 142.8, 133.0, 130.9, 129.8, 128.7, 128.4, 128.0, 127.9, 127.4, 127.2, 126.5, 120.7, 116.4, 81.1, 58.6, 48.7, 30.2, 26.9, 20.9, 18.4; **HRMS** (ESI) calcd for $[C_{27}H_{26}N_2O + Na]^+$ 417.1937, found 417.1941; **IR** (thin film) 2253, 1698, 1494, 1125.



2o

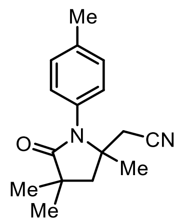
Prepared from **1o** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (40 mol%) in toluene at 80 °C for 24 h. **2o** was purified by flash column chromatography (1:4 → 2:3 EtOAc/Hex) as a colorless oil (0.168 mmol, 84% yield).* R_f = 0.31 (2:3 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 – 7.04 (m, 2H), 6.97 – 6.91 (m, 2H), 5.85 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.07 (dq, J = 17.1, 1.7 Hz, 1H), 5.01 (dq, J = 10.2, 1.4 Hz, 1H), 3.97 (t, J = 6.4 Hz, 2H), 2.48 (s, 2H), 2.32 (d, J = 13.7 Hz, 1H), 2.28 – 2.20 (m, 2H), 2.11 (d, J = 13.7 Hz, 1H), 1.94 – 1.84 (m, 2H), 1.43 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.6, 159.1, 137.6, 130.6, 127.3, 117.1, 115.33, 115.27, 67.3, 59.6, 46.5, 39.6, 30.8, 30.0, 28.3, 28.2, 27.8, 27.0; **HRMS** (ESI) calcd for $[C_{20}H_{26}N_2O_2 + Na]^+$ 349.1886, found 349.1881; **IR** (thin film) 2248, 1691, 1511, 1394, 1249.

* Note: Product contained a small amount of impurity (ca. 5%) presumably resulting from olefin isomerization.



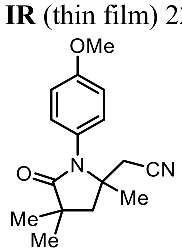
2p

Prepared from **1p** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (80 mol%) in toluene at 80 °C for 24 h. **2p** was purified by flash column chromatography (15:85 → 3:7 EtOAc/Hex) as a pale yellow oil (0.192 mmol, 96% yield). R_f = 0.35 (3:7 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, J = 2.6 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.45 – 7.43 (m, 2H), 7.41 (dd, J = 8.7, 2.7 Hz, 1H), 7.36 (ddd, J = 11.2, 8.6, 7.0 Hz, 4H), 7.31 – 7.25 (m, 2H), 6.83 (d, J = 8.7 Hz, 1H), 3.95 (s, 3H), 3.34 (d, J = 13.7 Hz, 1H), 3.03 (d, J = 13.7 Hz, 1H), 2.41 (d, J = 16.6 Hz, 1H), 2.33 (d, J = 16.6 Hz, 1H), 1.33 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.5, 163.9, 147.3, 142.5, 142.5, 139.9, 128.9, 128.6, 127.6, 127.5, 127.4, 127.2, 125.1, 116.5, 111.9, 59.8, 56.9, 53.8, 46.6, 29.3, 26.4; **HRMS** (ESI) calcd for $[C_{25}H_{23}N_3O_2 + Na]^+$ 420.1682, found 420.1690; **IR** (thin film) 2248, 1698, 1494, 1385, 1285.



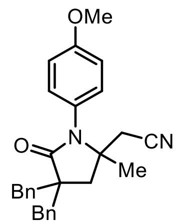
2q

Prepared from **1q** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (40 mol%) in toluene at 80 °C for 24 h. **2q** was purified by flash column chromatography (1:4 → 1:1 EtOAc/Hex) as pale yellow oil (0.186 mmol, 93% yield). R_f = 0.43 (1:1 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 2H), 7.09 – 7.04 (m, 2H), 2.49 (d, J = 1.5 Hz, 2H), 2.38 (s, 3H), 2.34 (d, J = 13.7 Hz, 1H), 2.12 (d, J = 13.7 Hz, 1H), 1.44 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.5, 138.7, 132.4, 130.3, 129.4, 117.1, 59.6, 46.7, 39.7, 30.9, 28.3, 27.8, 27.1, 21.1; **HRMS** (ESI) calcd for $[C_{16}H_{20}N_2O + Na]^+$ 279.1468, found 279.1467; **IR** (thin film) 2248, 1694, 1514, 1393.



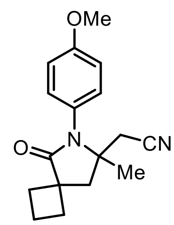
2r

Prepared from **1r** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (40 mol%) in toluene at 80 °C for 24 h. 2r was purified by flash column chromatography (30:70:0 → 30:70:0.5 EtOAc/Hex/MeOH) as a thick tan oil (0.176 mmol, 88% yield). R_f = 0.25 (1:1 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.10 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H), 2.48 (app s, 2H), 2.32 (d, J = 13.7 Hz, 1H), 2.11 (d, J = 13.7 Hz, 1H), 1.43 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.6, 159.6, 130.7, 127.5, 117.1, 114.8, 59.6, 55.4, 46.5, 39.6, 30.8, 28.2, 27.8, 27.0; **HRMS** (ESI) calcd for $[C_{16}H_{20}N_2O_2 + Na]^+$ 295.1417, found 295.1413; **IR** (thin film) 2247, 1693, 1513, 1394, 1251.



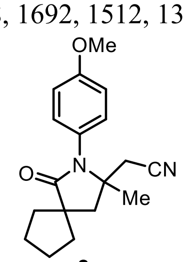
2s

Prepared from **1s** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (80 mol%) in toluene at 70 °C for 48 h. **2s** was purified by flash column chromatography (1:9 → 3:7 EtOAc/Hex) as a pale yellow oil (0.164 mmol, 82% yield). R_f = 0.32 (3:7 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.26 (m, 10H), 6.89 – 6.82 (m, 2H), 6.58 – 6.51 (m, 2H), 3.77 (s, 3H), 3.49 (d, *J* = 13.0 Hz, 2H), 2.64 (d, *J* = 11.6 Hz, 1H), 2.61 (d, *J* = 11.6Hz, 1H), 2.31 (d, *J* = 14.5 Hz, 1H), 2.12 (d, *J* = 14.5 Hz, 1H), 1.56 (d, *J* = 16.0 Hz, 1H), 0.43 (d, *J* = 16.1 Hz, 1H), 0.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.7, 159.6, 137.9, 137.5, 130.91, 130.89, 130.5, 128.6, 128.3, 127.4, 127.2, 127.1, 117.0, 114.7, 58.9, 55.4, 51.9, 44.9, 44.8, 36.2, 29.2, 25.9; **HRMS** (ESI) calcd for $[C_{28}H_{28}N_2O_2 + Na]^+$ 447.2043, found 447.2036; **IR** (thin film) 2250, 1689, 1512, 1249.



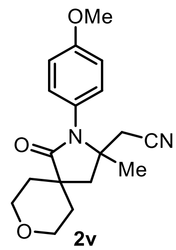
2t

Prepared from **1t** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 70 °C for 24 h. **2t** was purified by flash column chromatography (30:70:0.5 → 30:70:1 EtOAc/Hex/MeOH) as a pale yellow oil (0.186 mmol, 93% yield). R_f = 0.19 (30:70:0.5 EtOAc/Hex/MeOH); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.08 – 7.02 (m, 2H), 6.98 – 6.92 (m, 2H), 3.82 (s, 3H), 2.70 – 2.57 (m, 2H), 2.51 (d, *J* = 13.4 Hz, 1H), 2.48 (d, *J* = 16.7 Hz, 1H), 2.43 (d, *J* = 16.7 Hz, 1H), 2.33 (d, *J* = 13.4 Hz, 1H), 2.21 – 2.12 (m, 1H), 2.12 – 1.97 (m, 3H), 1.37 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.5, 159.5, 130.6, 127.5, 116.8, 114.8, 60.5, 55.4, 46.4, 44.6, 32.3, 31.6, 29.6, 26.8, 16.5; **HRMS** (ESI) calcd for $[C_{17}H_{20}N_2O_2 + Na]^+$ 307.1417, found 307.1415; **IR** (thin film) 2248, 1692, 1512, 1386, 1250.



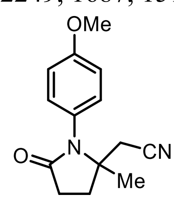
2u

Prepared from **1u** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (100 mol%) in toluene at 80 °C for 36 h. **2u** was purified by flash column chromatography (20:80:1 → 20:80:2 EtOAc/Hex/MeOH) as a pale yellow oil (0.192 mmol, 96% yield). R_f = 0.16 (20:80:1 EtOAc/Hex/MeOH); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 – 7.04 (m, 2H), 6.98 – 6.92 (m, 2H), 3.82 (s, 3H), 2.52 (d, *J* = 16.5 Hz, 1H), 2.48 (d, *J* = 16.5 Hz, 1H), 2.34 (d, *J* = 13.4 Hz, 1H), 2.25 – 2.10 (m, 3H), 1.94 – 1.83 (m, 2H), 1.77 – 1.68 (m, 4H), 1.43 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.8, 159.5, 130.7, 127.6, 117.0, 114.8, 60.1, 55.4, 49.7, 47.1, 39.7, 39.2, 30.3, 27.5, 25.54, 25.46; **HRMS** (ESI) calcd for $[C_{18}H_{22}N_2O_2 + Na]^+$ 321.1573, found 321.1570; **IR** (thin film) 2246, 1691, 1513, 1387, 1250.



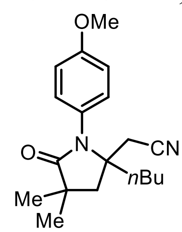
2v

Prepared from **1v** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 80 °C for 24 h. **2v** was purified by flash column chromatography (40:60:0 → 50:50:2 EtOAc/Hex/MeOH) as a colorless oil (0.170 mmol, 85% yield). R_f = 0.21 (50:50:1 EtOAc/Hex/MeOH); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.14 – 7.06 (m, 2H), 7.00 – 6.92 (m, 2H), 4.05 (ddt, J = 13.8, 11.7, 4.1 Hz, 2H), 3.83 (s, 3H), 3.58 (dddd, J = 16.4, 11.6, 10.6, 2.7 Hz, 2H), 2.52 (d, J = 16.8 Hz, 1H), 2.47 (d, J = 16.8 Hz, 1H), 2.37 (d, J = 13.9 Hz, 1H), 2.26 (d, J = 14.0 Hz, 1H), 2.24 – 2.13 (m, 2H), 1.63 (ddt, J = 13.6, 4.5, 2.4 Hz, 1H), 1.52 (ddt, J = 13.5, 4.5, 2.4 Hz, 1H), 1.44 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.8, 159.7, 130.7, 127.1, 117.1, 114.9, 64.1, 63.9, 60.1, 55.5, 43.3, 41.4, 35.4, 35.0, 30.9, 28.9; **HRMS** (ESI) calcd for $[C_{18}H_{22}N_2O_3 + Na]^+$ 337.1523, found 337.1521; **IR** (thin film) 2249, 1687, 1513, 1384, 1251.



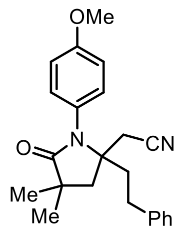
2w

Prepared from **1w** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BPh_3 (40 mol%) in *m*-xylene at 120 °C for 24 h. **2w** was purified by flash column chromatography (25:75:0 → 40:60:0 → 60:40:5 EtOAc/Hex/MeOH) as a pale yellow oil (0.066 mmol, 33% yield). R_f = 0.45 (5:95 MeOH/CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 – 7.07 (m, 2H), 6.99 – 6.93 (m, 2H), 3.82 (s, 3H), 2.74 (ddd, J = 16.9, 9.9, 6.6 Hz, 1H), 2.63 (ddd, J = 17.5, 9.9, 6.3 Hz, 1H), 2.53 (d, J = 16.8 Hz, 1H), 2.48 (d, J = 16.8 Hz, 1H), 2.40 (ddd, J = 13.3, 9.9, 6.3 Hz, 1H), 2.18 (ddd, J = 13.3, 9.9, 6.6 Hz, 1H), 1.40 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.7, 159.8, 130.6, 127.1, 116.8, 115.0, 62.5, 55.5, 31.7, 29.4, 29.2, 26.7; **HRMS** (ESI) calcd for $[C_{14}H_{16}N_2O_2 + Na]^+$ 267.1104, found 267.1105; **IR** (thin film) 2244, 1693, 1513, 1387, 1251.



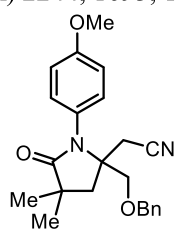
2x

Prepared from **1x** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 80 °C for 24 h. **2x** was purified by flash column chromatography (20:80:0 → 30:70:1 EtOAc/Hex/MeOH) as a pale yellow oil (0.180 mmol, 90% yield). R_f = 0.16 (3:7 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 7.06 (m, 2H), 7.00 – 6.92 (m, 2H), 3.82 (s, 3H), 2.52 (d, J = 16.8 Hz, 1H), 2.42 (d, J = 16.8 Hz, 1H), 2.21 (d, J = 14.1 Hz, 1H), 2.14 (d, J = 14.1 Hz, 1H), 1.71 – 1.60 (m, 1H), 1.53 (ddd, J = 13.9, 11.6, 3.1 Hz, 1H), 1.41 (s, 3H), 1.33 (s, 3H), 1.45 – 1.22 (m, 4H), 0.93 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.0, 159.5, 130.5, 127.7, 117.5, 114.8, 62.8, 55.4, 42.8, 39.3, 39.3, 29.7, 27.7, 27.5, 26.4, 22.7, 13.9; **HRMS** (ESI) calcd for $[C_{19}H_{26}N_2O_2 + Na]^+$ 337.1886, found 337.1892; **IR** (thin film) 2246, 1694, 1513, 1395, 1252.



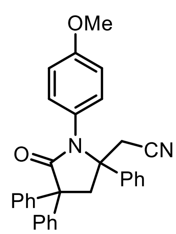
2y

Prepared from **1y** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (100 mol%) in toluene at 70 °C for 36 h. **2y** was purified by flash column chromatography (20:80:0 → 30:70:1 EtOAc/Hex/MeOH) as a pale yellow oil (0.160 mmol, 80% yield). R_f = 0.14 (3:7 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 7.19 – 7.10 (m, 4H), 7.00 – 6.89 (m, 2H), 3.81 (s, 3H), 2.74 (td, J = 12.6, 12.2, 4.3 Hz, 1H), 2.66 – 2.55 (m, 2H), 2.50 (d, J = 16.9 Hz, 1H), 2.34 (d, J = 14.2 Hz, 1H), 2.24 (d, J = 14.1 Hz, 1H), 1.98 (ddd, J = 14.1, 12.2, 5.6 Hz, 1H), 1.89 (ddd, J = 14.1, 12.1, 4.3 Hz, 1H), 1.45 (s, 3H), 1.39 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.0, 159.6, 139.9, 130.5, 128.8, 128.1, 127.5, 126.5, 117.3, 114.9, 62.6, 55.4, 42.9, 41.4, 39.3, 30.6, 29.8, 27.61, 27.57; **HRMS** (ESI) calcd for $[C_{23}H_{26}N_2O_2 + Na]^+$ 385.1886, found 385.1888; **IR** (thin film) 2244, 1693, 1512, 1395, 1252.



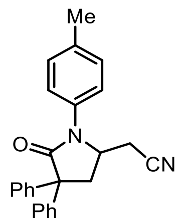
2z

Prepared from **1z** on a 0.2 mmol scale with CpPd(1-phenylallyl) (20 mol%), Xantphos (20 mol%), and BEt_3 (100 mol%) in toluene at 90 °C for 24 h. **2z** was purified by preparative thin-layer chromatography (30:70:3 EtOAc/Hex/MeOH) as a thick colorless oil (0.074 mmol, 37% yield). R_f = 0.29 (3:7 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 7.15 – 7.05 (m, 2H), 6.96 – 6.86 (m, 2H), 4.53 (s, 2H), 3.81 (s, 3H), 3.36 (d, J = 9.2 Hz, 1H), 3.30 (d, J = 9.3 Hz, 1H), 2.59 (d, J = 16.9 Hz, 1H), 2.42 (d, J = 16.9 Hz, 1H), 2.36 (d, J = 13.9 Hz, 1H), 2.13 (d, J = 14.0 Hz, 1H), 1.39 (s, 3H), 1.31 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.6, 159.6, 136.8, 130.7, 128.6, 128.1, 127.9, 127.5, 116.9, 114.8, 73.5, 73.1, 62.4, 55.5, 42.2, 39.4, 27.8, 27.1, 26.8; **HRMS** (ESI) calcd for $[C_{23}H_{26}N_2O_3 + Na]^+$ 401.1836, found 401.1829; **IR** (thin film) 2253, 1692, 1512, 1396, 1251.



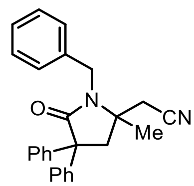
2aa

Prepared from **1aa** on a 0.2 mmol scale with CpPd(1-phenylallyl) (15 mol%), Xantphos (15 mol%), and BEt_3 (100 mol%) in toluene at 80 °C for 36 h. **2aa** was purified by flash column chromatography (15:85 → 3:7 EtOAc/Hex) as a thick pale yellow oil (0.170 mmol, 85% yield). R_f = 0.42 (3:7 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.38 (dd, J = 8.6, 7.0 Hz, 2H), 7.35 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 7.24 – 7.16 (m, 8H), 7.07 – 6.96 (m, 2H), 6.83 – 6.70 (m, 2H), 3.74 (s, 3H), 3.51 (d, J = 14.1 Hz, 1H), 3.46 (d, J = 14.1 Hz, 1H), 3.19 (d, J = 16.9 Hz, 1H), 2.83 (d, J = 16.9 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.5, 158.6, 144.0, 141.0, 140.7, 128.8, 128.53 (two overlapped peaks), 128.46, 128.2 (two overlapped peaks), 127.8, 127.7, 127.2, 127.0, 126.5, 116.8, 114.3, 65.6, 56.9, 55.3, 49.1, 27.3; **HRMS** (ESI) calcd for $[C_{31}H_{26}N_2O_2 + Na]^+$ 481.1886, found 481.1895; **IR** (thin film) 2250, 1694, 1511, 1361, 1252.



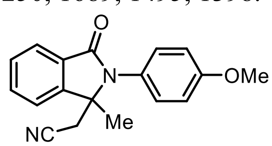
2ab

Prepared from **1ab** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 70 °C for 48 h. **2ab** was purified by flash column chromatography (12:88:0 → 20:80:1 EtOAc/Hex/MeOH) as a colorless oil (0.094 mmol, 47% yield). R_f = 0.32 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.39 – 7.26 (m, 8H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.26 (dddd, *J* = 11.4, 9.0, 6.8, 3.3 Hz, 1H), 3.22 (dd, *J* = 13.1, 5.9 Hz, 1H), 2.83 (dd, *J* = 13.0, 8.3 Hz, 1H), 2.66 (dd, *J* = 17.0, 3.3 Hz, 1H), 2.47 (dd, *J* = 16.9, 7.4 Hz, 1H), 2.36 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.4, 142.7, 141.1, 137.3, 133.3, 130.1, 128.7, 128.5, 127.9, 127.6, 127.4, 127.2, 124.9, 115.9, 57.8, 52.4, 40.1, 22.3, 21.1; **HRMS** (ESI) calcd for $[C_{25}H_{22}N_2O + Na]^+$ 389.1624, found 389.1623; **IR** (thin film) 2251, 1699, 1514, 1385, 1298.



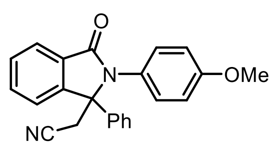
2ac

Prepared from **1ac** on a 0.2 mmol scale with CpPd(1-phenylallyl) (15 mol%), Xantphos (15 mol%), and BPh_3 (50 mol%) in *m*-xylene at 120 °C for 24 h. **2ac** was purified by flash column chromatography (1:9 → 1:4 EtOAc/Hex) as a thick pale yellow oil (0.058 mmol, 29% yield). R_f = 0.35 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.41 – 7.18 (m, 13H), 4.85 (d, *J* = 15.3 Hz, 1H), 4.39 (d, *J* = 15.3 Hz, 1H), 3.19 (d, *J* = 13.8 Hz, 1H), 2.84 – 2.71 (m, 1H), 2.11 (d, *J* = 16.7 Hz, 1H), 1.96 (d, *J* = 16.6 Hz, 1H), 1.39 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.0, 143.3, 142.2, 137.6, 128.90, 128.88, 128.4, 127.9, 127.8, 127.6, 127.5, 127.4, 126.9, 116.8, 59.0, 56.6, 47.1, 43.6, 28.8, 25.7; **HRMS** (ESI) calcd for $[C_{26}H_{24}N_2O + Na]^+$ 403.1781, found 403.1782; **IR** (thin film) 2250, 1689, 1495, 1398.



2ad

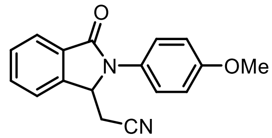
Prepared from **1ad** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 80 °C for 24 h. **2ad** was purified by flash column chromatography (0.6:100 → 1:100 MeOH/CH_2Cl_2) as a pale yellow foam (0.198 mmol, 99% yield). R_f = 0.29 (2:100 MeOH/CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.72 – 7.62 (m, 2H), 7.57 (td, *J* = 7.3, 1.2 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.06 – 7.00 (m, 2H), 3.85 (s, 3H), 2.90 (d, *J* = 16.6 Hz, 1H), 2.70 (d, *J* = 16.7 Hz, 1H), 1.67 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.6, 159.9, 147.1, 132.7, 130.9, 130.8, 129.4, 126.6, 124.6, 121.2, 115.9, 115.2, 63.7, 55.5, 28.5, 24.8; **HRMS** (ESI) calcd for $[C_{18}H_{16}N_2O_2 + Na]^+$ 315.1104, found 315.1101; **IR** (thin film) 2247, 1697, 1513, 1377, 1249.



2ae

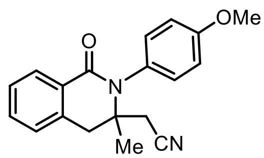
Prepared from **1ae** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 80 °C for 24 h. **2ae** was purified by flash column chromatography (1:100 MeOH/CH_2Cl_2) as a yellow foam (0.198 mmol, 99% yield). R_f = 0.33 (2:100 MeOH/CH_2Cl_2); **^{1}H NMR** (400

MHz, $CDCl_3$) δ 8.14 – 7.95 (m, 1H), 7.71 – 7.54 (m, 2H), 7.41 – 7.28 (m, 4H), 7.11 – 7.03 (m, 2H), 6.83 – 6.71 (m, 4H), 3.76 (s, 3H), 3.49 (d, *J* = 16.4 Hz, 1H), 3.20 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 159.3, 147.6, 137.7, 133.1, 131.4, 129.61, 129.60, 129.1, 129.0, 127.0, 126.7, 124.6, 122.5, 115.6, 114.6, 68.8, 55.4, 25.8; **HRMS** (ESI) calcd for $[C_{23}H_{18}N_2O_2 + Na]^+$ 377.1260, found 377.1269; **IR** (thin film) 2252, 1698, 1513, 1366, 1250.



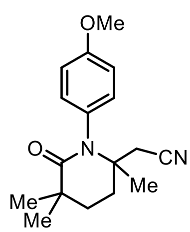
2af

Prepared from **1af** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 70 °C for 24 h. **2af** was purified by flash column chromatography (1:4 → 1:1 EtOAc/Hex) as a pale yellow foam (0.118 mmol, 59% yield). R_f = 0.36 (1:4 → 1:1 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.61 (td, *J* = 7.4, 1.3 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.06 – 6.98 (m, 2H), 5.24 (dd, *J* = 7.4, 3.4 Hz, 1H), 3.85 (s, 3H), 3.00 (dd, *J* = 16.8, 3.5 Hz, 1H), 2.67 (dd, *J* = 16.8, 7.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 158.4, 141.7, 132.6, 132.0, 129.8, 128.2, 126.2, 124.6, 122.3, 115.4, 114.9, 57.2, 55.5, 22.0; **HRMS** (ESI) calcd for $[C_{17}H_{14}N_2O_2 + Na]^+$ 301.0947, found 301.0942; **IR** (thin film) 2250, 1695, 1514, 1249.



2ag

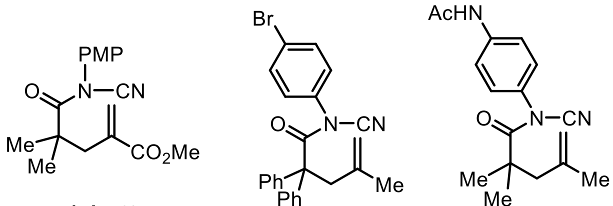
Prepared from **1ag** on a 0.2 mmol scale with CpPd(1-phenylallyl) (15 mol%), Xantphos (15 mol%), and BEt_3 (100 mol%) in toluene at 80 °C for 24 h. **2ag** was purified by preparative thin-layer chromatography (2:100 $MeOH/CH_2Cl_2$) as an yellow foam (0.188 mmol, 94% yield). R_f = 0.48 (2:100 $MeOH/CH_2Cl_2$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.53 (td, *J* = 7.5, 1.4 Hz, 1H), 7.41 (td, *J* = 7.6, 1.2 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.14 – 7.08 (m, 2H), 7.00 – 6.92 (m, 2H), 3.84 (s, 3H), 3.40 (d, *J* = 15.9 Hz, 1H), 3.28 (d, *J* = 15.9 Hz, 1H), 2.69 (d, *J* = 16.6 Hz, 1H), 2.62 (dd, *J* = 16.5, 0.9 Hz, 1H), 1.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.8, 159.4, 134.7, 132.8, 131.1, 130.44, 130.37, 128.9, 128.3, 127.8, 127.6, 116.6, 115.0, 114.6, 58.6, 55.5, 40.3, 28.5, 26.2; **HRMS** (ESI) calcd for $[C_{19}H_{18}N_2O_2 + Na]^+$ 329.1260, found 329.1262; **IR** (thin film) 2247, 1656, 1511, 1372, 1250.



2ah

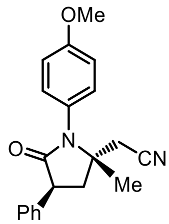
Prepared from **1ah** on a 0.2 mmol scale with CpPd(1-phenylallyl) (20 mol%), Xantphos (20 mol%), and BEt_3 (100 mol%) in toluene at 70 °C for 48 h. **2ah** was purified by preparative thin-layer chromatography (40:60:4 EtOAc/Hex/MeOH) as a pale yellow oil (0.098 mmol, 49% yield). R_f = 0.48 (40:60:4 EtOAc/Hex/MeOH); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 6.85 (m, 4H), 3.81 (s, 3H), 2.54 (d, *J* = 16.7 Hz, 1H), 2.44 (d, *J* = 16.7 Hz, 1H), 2.37 (ddd, *J* = 13.8, 9.7, 4.0 Hz, 1H), 2.06 – 1.81 (m, 3H), 1.39 (s, 3H), 1.34 (s, 3H), 1.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.4, 159.0, 131.2 (br), 130.7, 117.1, 114.5, 59.2, 55.4, 38.4, 31.6, 31.5, 30.5, 27.9, 27.7, 27.5; **HRMS** (ESI) calcd for $[C_{17}H_{22}N_2O_2 + Na]^+$ 309.1573, found 309.1565; **IR** (thin film) 2241, 1645, 1511, 1390, 1249.

unsuccessful substrates



1ai, 0% **1aj,** 0% **1ak,** 0%

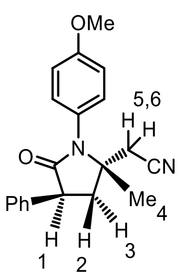
The aminocyanation reactions of these substrates resulted in unconsumed starting material. No desired product was detected in the crude reaction mixture.

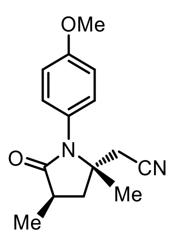


(±)-2al

Prepared from **1al** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (100 mol%) in toluene at 80 °C for 24 h. **2al** was purified by flash column chromatography (1:4:0 → 3:7:0.1 EtOAc/Hex/MeOH) as a pale yellow oil (0.096 mmol, 48% yield). R_f = 0.14 (3:7 EtOAc/Hex); > 20:1 d.r. based on ^{1}H NMR spectroscopy. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 – 7.21 (m, 5H), 7.16 – 7.09 (m, 2H), 7.00 – 6.91 (m, 2H), 4.13 (app t, J = 9.7 Hz, 1H), 3.82 (s, 3H), 2.91 (dd, J = 13.7, 9.6 Hz, 1H), 2.61 (d, J = 16.8 Hz, 1H), 2.53 (d, J = 16.7 Hz, 1H), 2.26 (dd, J = 13.7, 9.8 Hz, 1H), 1.42 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.5, 159.7, 138.9, 130.7, 128.8, 128.0, 127.3, 127.2, 117.0, 114.9, 60.8, 55.4, 46.3, 41.5, 28.5, 28.1; **HRMS** (ESI) calcd for $[C_{20}H_{20}N_2O_2 + Na]^+$ 343.1417, found 343.1416; **IR** (thin film) 2244, 1695, 1512, 1387, 1251.

Assignment of stereochemistry of **(±)-2al** by nOe NMR experiments
Conclusion: **H1** and **H4** are *anti*; Ph group and **H4** are *syn*.

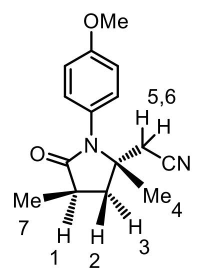
Assigned Structure	Key ^{1}H NMR Signals	Irradiation	Key nOe Results	Associate File
 **(±)-2al** *> 20:1 d.r.*	**H1:** 4.13 (app t, J = 9.7 Hz, 1H) **H2:** 2.26 (dd, J = 13.7, 9.8 Hz, 1H) **H3:** 2.91 (dd, J = 13.7, 9.6 Hz, 1H) **H4:** 1.42 (s, 3H) **H5,6:** 2.61 (d, J = 16.8 Hz, 1H), 2.53 (d, J = 16.7 Hz, 1H)	**H4**	nOe observed: **H2, H5,6** nOe not observed: **H1**	2al-nOe-exp1.mnova
		H1	nOe observed: **H3, H5,6** nOe not observed: **H4**	2al-nOe-exp2.mnova

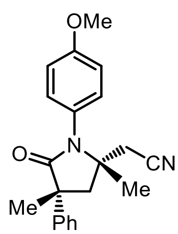


(±)-2am

Prepared from **1am** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 80 °C for 24 h. **2am** was purified by flash column chromatography (4:6:0 → 5:5:0.15 EtOAc/Hex/MeOH) as a pale yellow oil (0.118 mmol, 59% yield). R_f = 0.21 (1:1 EtOAc/Hex); 9:1 d.r. based on ^{1}H NMR spectroscopy. *Major diastereomer:* ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.10 – 7.02 (m, 2H), 6.99 – 6.92 (m, 2H), 3.82 (s, 3H), 2.98 – 2.83 (m, 1H), 2.66 (dd, *J* = 13.4, 9.1 Hz, 1H), 2.54 (d, *J* = 16.7 Hz, 1H), 2.47 (d, *J* = 16.5 Hz, 1H), 1.78 (dd, *J* = 13.4, 9.8 Hz, 1H), 1.38 (s, 3H), 1.32 (d, *J* = 7.1 Hz, 3H); *Major diastereomer:* ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 177.2, 159.6, 130.6, 127.4, 117.1, 114.9, 60.7, 55.4, 40.9, 35.0, 28.3, 28.1, 16.7; **HRMS** (ESI) calcd for $[C_{15}H_{18}N_2O_2 + Na]^+$ 281.1260, found 281.1267; **IR** (thin film) 2244, 1694, 1513, 1390, 1251.

Assignment of stereochemistry of **(±)-2am** (major diastereomer) by nOe NMR experiments
Conclusion: **H4** and **H7** are *syn*.

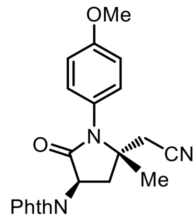
Assigned Structure	**Key ^{1}H NMR Signals**	**Irradiation**	**Key nOe Results**	**Associate File**
 **(±)-2am** *9:1 d.r.* *major diastereomer*	**H1:** 2.98 – 2.83 (m, 1H) **H2:** 1.78 (dd, *J* = 13.4, 9.8 Hz, 1H) **H3:** 2.66 (dd, *J* = 13.4, 9.1 Hz, 1H) **H4:** 1.38 (s, 3H) **H5,6:** 2.54 (d, *J* = 16.7 Hz, 1H), 2.47 (d, *J* = 16.5 Hz, 1H) **H7:** 1.32 (d, *J* = 7.1 Hz, 3H)	**H2**	nOe observed: **H3, H4, H7** nOe not observed: **H1, H5,6**	2am-nOe-exp1.mnova



(±)-2an

Prepared from **1an** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 80 °C for 24 h. **2an** was purified by flash column chromatography (1:4 → 3:7 EtOAc/Hex) to yield a mixture of diastereomers as an off-white solid (0.146 mmol, 73% yield). R_f = 0.25 (2:3 EtOAc/Hex); 19:1 d.r. based on ^{1}H NMR spectroscopy. The major and minor diastereomers could be separated as a saturated solution in 1:1 isopropanol:hexanes via HPLC using an Agilent Eclipse XDB-CN column, with an injection volume of 50 µL, flow rate of 5 mL/min., and eluting with an isocratic 15:85 isopropanol:hexanes solvent system. R_t major diastereomer = 6.93 min; R_t minor diastereomer = 9.36 min. *Major diastereomer:* ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.40 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.33 – 7.25 (m, 1H), 7.07 – 7.00 (m, 2H), 7.00 – 6.93 (m, 2H), 3.83 (s, 3H), 3.07 (d, *J* = 13.7 Hz, 1H), 2.31 (app t, *J* = 15.5 Hz, 2H), 2.18 (d, *J* = 16.4 Hz, 1H), 1.64 (s, 3H), 1.45 (s, 3H); *Major diastereomer:* ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 177.0, 159.7, 144.0, 130.7, 129.2, 127.4, 127.2, 125.9, 116.9, 114.9, 59.8, 55.5, 48.5, 47.4, 28.4, 28.2, 27.3; *Major diastereomer*: ^{1}**H-NMR** (500 MHz; CD_3CN): δ 7.54-7.53 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.31-7.29 (m, 1H), 7.16-7.14 (m, 2H), 7.03-7.02 (m, 2H), 3.83 (s, 3H), 2.80 (d, *J* = 13.8 Hz, 1H), 2.51 (d, *J* = 16.9 Hz, 1H), 2.40 (d, *J* = 13.8 Hz, 1H), 2.33 (d, *J* = 16.9 Hz, 1H), 1.62 (s, 3H), 1.41 (s, 3H).; *Minor diastereomer*: ^{1}**H-NMR** (500 MHz; CD_3CN): δ 7.49-7.48 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.17-7.15 (m, 1H), 7.04-7.02 (m, 1H), 3.83 (s, 1H), 2.70 (d, *J* = 13.7 Hz, 1H), 2.62 (d, *J* = 16.9 Hz, 1H), 2.59 (d, *J* = 17.1 Hz, 1H), 2.51 (d, *J* = 13.7 Hz, 1H), 1.60 (s, 1H), 1.11 (s, 1H).

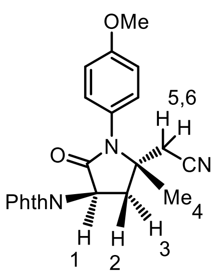
HRMS (ESI) calcd for $[C_{21}H_{22}N_2O_2 + Na]^+$ 357.1573, found 357.1595; **IR** (thin film) 2235, 1688, 1513, 1452, 1388, 1250.

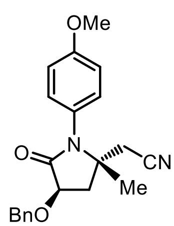


(±)-2ao

Prepared from **1ao** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 80 °C for 24 h. **2ao** was purified by flash column chromatography (4:6:0 → 5:5:0.2 EtOAc/Hex/MeOH) as a pale yellow foam (0.286 mmol, 77% yield). R_f = 0.22 (1:1 EtOAc/Hex); > 20:1 d.r. based on ^{1}H NMR spectroscopy. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 5.5, 3.0 Hz, 2H), 7.74 (dd, J = 5.5, 3.1 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.03 – 6.95 (m, 2H), 5.34 (dd, J = 10.3, 9.3 Hz, 1H), 3.83 (s, 3H), 2.85 (dd, J = 13.7, 10.3 Hz, 1H), 2.70 (d, J = 16.8 Hz, 1H), 2.61 (d, J = 16.8 Hz, 1H), 2.51 (dd, J = 13.7, 9.3 Hz, 1H), 1.49 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 167.3, 159.9, 134.3, 131.8, 130.5, 126.8, 123.5, 116.8, 115.0, 60.6, 55.5, 48.3, 36.8, 29.7, 27.3; **HRMS** (ESI) calcd for $[C_{22}H_{19}N_3O_4 + Na]^+$ 412.1268, found 412.1277; **IR** (thin film) 2252, 1776, 1714, 1512, 1390, 1251.

Assignment of stereochemistry of **(±)-2ao** by nOe NMR experiments
Conclusion: **H1** and **H4** are *anti*; NPhth group and **H4** are *syn*.

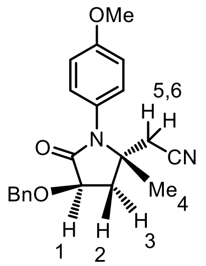
Assigned Structure	Key ^{1}H NMR Signals	Irradiation	Key nOe Results	Associate File
 **(±)-2ao** *> 20:1 d.r.*	**H1:** 5.34 (dd, J = 10.3, 9.3 Hz, 1H) **H2:** 2.51 (dd, J = 13.7, 9.3 Hz, 1H) **H3:** 2.85 (dd, J = 13.7, 10.3 Hz, 1H) **H4:** 1.49 (s, 3H) **H5,6:** 2.70 (d, J = 16.8 Hz, 1H), 2.61 (d, J = 16.8 Hz, 1H)	**H1**	nOe observed: **H2, H3, H5,6** nOe not observed: **H4**	2ao-nOe-exp1.mnova
		H4	nOe observed: **H2, H5,6** nOe not observed: **H1**	2ao-nOe-exp2.mnova

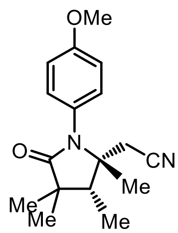


(±)-2ap

Prepared from **1ap** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 70 °C for 24 h. **2ap** was purified by flash column chromatography (2:8:0 → 3:7:0.15 EtOAc/Hex/MeOH) as a yellow oil (0.148 mmol, 74% yield). R_f = 0.10 (3:7 EtOAc/Hex); 3.2:1 d.r. based on ^{1}H NMR spectroscopy. *Major diastereomer:* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 5H), 7.14 – 7.07 (m, 2H), 7.00 – 6.93 (m, 2H), 5.07 (d, J = 11.7 Hz, 1H), 4.77 (d, J = 11.7 Hz, 1H), 4.43 (dd, J = 8.2, 5.6 Hz, 1H), 3.81 (s, 3H), 2.63 (dd, J = 14.0, 8.3 Hz, 1H), 2.46 (app s, 2H), 2.17 (dd, J = 13.9, 5.6 Hz, 1H), 1.42 (s, 3H); *Major diastereomer:* **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 159.8, 137.6, 130.4, 128.4, 128.0, 127.8, 126.6, 116.8, 115.0, 74.2, 72.5, 60.9, 55.4, 39.6, 29.3, 27.7; **HRMS** (ESI) calcd for $[C_{21}H_{22}N_2O_3 + Na]^+$ 373.1523, found 373.1536; **IR** (thin film) 2247, 1702, 1512, 1388, 1251.

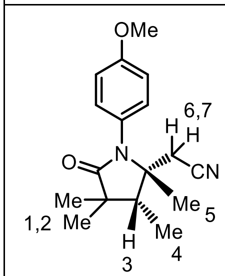
Assignment of stereochemistry of **(±)-2ap** (major diastereomer) by nOe NMR experiments
Conclusion: **H1** and **H4** are *anti*; OBn group and **H4** are *syn*.

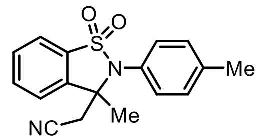
Assigned Structure	Key ^{1}H NMR Signals	Irradiation	Key nOe Results	Associate File
 **(±)-2ap** *3.2:1 d.r.* *major diastereomer*	**H1:** 4.43 (dd, J = 8.2, 5.6 Hz, 1H) **H2:** 2.17 (dd, J = 13.9, 5.6 Hz, 1H) **H3:** 2.63 (dd, J = 14.0, 8.3 Hz, 1H) **H4:** 1.42 (s, 3H) **H5,6:** 2.46 (app s, 2H)	**H1**	nOe observed: **H3, H5,6** nOe not observed: **H4**	2ap-nOe-exp1.mnova


(±)-2aq

Prepared from **1aq** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 80 °C for 24 h. **2aq** was purified by flash column chromatography (30:70:0 → 30:70:0.5 EtOAc/Hex/MeOH) as a pale yellow oil (0.184mmol, 92% yield). R_f = 0.27 (1:1 EtOAc/Hex); 4.4:1 d.r. based on ^{1}H NMR spectroscopy. *Major diastereomer:* ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.08 – 7.02 (m, 2H), 6.99 – 6.93 (m, 2H), 3.82 (s, 3H), 2.54 (app s, 2H), 2.20 (q, J = 7.4 Hz, 1H), 1.44 (s, 3H), 1.25 (d, J = 8.0 Hz, 3H), 1.24 (s, 3H), 1.22 (s, 3H); *Major diastereomer:* ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 179.8, 159.6, 130.9, 127.5, 117.3, 114.8, 62.9, 55.4, 49.1, 42.2, 27.9, 26.6, 24.4, 21.2, 9.6; **HRMS** (ESI) calcd for $[C_{17}H_{22}N_2O_2 + Na]^+$ 309.1573, found 309.1578; **IR** (thin film) 2245, 1694, 1513, 1398, 1250.

Assignment of stereochemistry of **(±)-2aq** (major diastereomer) by nOe NMR experiments
Conclusion: **H3** and **H5** are *syn*; **H5** and **H4** are *anti*.

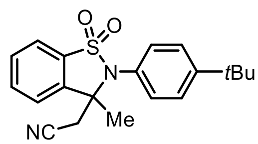
Assigned Structure	Key ^{1}H NMR Signals	Irradiation	Key nOe Results	Associate File
 **(±)-2aq** *4.4:1 d.r.* *major diastereomer*	**H1,2:** 1.24 (s, 3H), 1.22 (s, 3H) **H3:** 2.20 (q, J = 7.4 Hz, 1H) **H4:** 1.25 (d, J = 8.0 Hz, 3H) **H5:** 1.44 (s, 3H) **H6,7:** 2.54 (app s, 2H)	**H3**	nOe observed: **H5, H4** nOe not observed: **H6,7**	2aq-nOe-exp1.mnova
		H5	nOe observed: **H3, H6,**7 nOe not observed: **H4**	2aq-nOe-exp2.mnova



4a

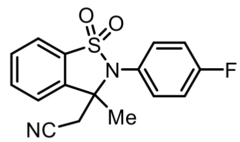
Prepared from **3a** on a 0.2 mmol scale with Pd_2dba_3 (5 mol%), Xantphos (10 mol%), and BPh_3 (40 mol%) in toluene at 80 °C for 16 h. **4a** was purified by flash column chromatography (15:85:1 EtOAc/Hex/MeOH → 3:100 MeOH/CH_2Cl_2) as an amorphous pale yellow solid (0.198 mmol, 99% yield). R_f = 0.50 (1:1 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$)* δ 7.98 – 7.87 (m, 1H), 7.79 – 7.70 (m, 2H), 7.67 (ddd, J = 7.7, 5.9, 2.6 Hz, 1H), 7.39 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 2.91 (d, J = 16.7 Hz, 1H), 2.85 (d, J = 16.7 Hz, 1H), 2.43 (s, 3H), 1.72 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.8, 139.0, 134.3, 133.4, 132.8, 130.7, 130.3, 127.0, 123.3, 121.9, 116.0, 63.4, 29.2, 25.2, 21.3; **HRMS** (ESI) calcd for $[C_{17}H_{16}N_2O_2S + Na]^+$ 335.0825, found 335.0831; **IR** (thin film) 2254, 1508, 1180.

*Note: Sulfonamides **4a–4k** were only partially soluble in $CDCl_3$. For consistency, the corresponding ^{1}H and ^{13}C NMR spectra were still collected in $CDCl_3$.



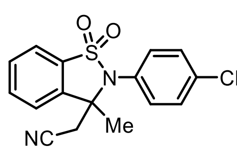
4b

Prepared from **3b** on a 0.2 mmol scale with Pd_2dba_3 (5 mol%), Xantphos (10 mol%), and BPh_3 (40 mol%) in toluene at 80 °C for 16 h. **4b** was purified by flash column chromatography (15:85:1 EtOAc/Hex/MeOH → 3:100 MeOH/CH_2Cl_2) as an amorphous pale yellow solid (0.186 mmol, 93% yield). R_f = 0.57 (1:1 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.8 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.65 (ddd, J = 8.3, 5.0, 3.4 Hz, 1H), 7.53 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 2.92 (d, J = 16.7 Hz, 1H), 2.84 (d, J = 16.7 Hz, 1H), 1.71 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.5, 139.0, 134.1, 133.3, 132.5, 130.2, 127.0, 126.8, 123.3, 121.7, 116.0, 63.6, 34.8, 31.2, 29.1, 25.2; **HRMS** (ESI) calcd for $[C_{20}H_{22}N_2O_2S + Na]^+$ 377.1294, found 377.1296; **IR** (thin film) 2253, 1511, 1297, 1178, 1151.



4c

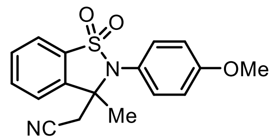
Prepared from **3c** on a 0.2 mmol scale with Pd_2dba_3 (5 mol%), Xantphos (10 mol%), and BPh_3 (40 mol%) in toluene at 80 °C for 16 h. **4c** was purified by flash column chromatography (15:85:1 EtOAc/Hex/MeOH → 3:100 MeOH/CH_2Cl_2) as an amorphous pale yellow solid (0.188 mmol, 94% yield). R_f = 0.46 (1:1 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.7 Hz, 1H), 7.82 – 7.63 (m, 3H), 7.52 (dd, J = 8.7, 4.9 Hz, 2H), 7.32 – 7.20 (m, 2H), 2.90 (d, J = 16.7 Hz, 1H), 2.84 (d, J = 16.8 Hz, 1H), 1.71 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.7 (d, $^1J_{F-C}$ = 251.7 Hz), 138.7, 135.0 (d, $^3J_{F-C}$ = 9.1 Hz), 134.0, 133.6, 130.4, 125.7 (d, $^4J_{F-C}$ = 3.3 Hz), 123.3, 121.9, 117.2 (d, $^2J_{F-C}$ = 22.7 Hz), 115.7, 63.6, 29.3, 25.3; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –109.3; **HRMS** (ESI) calcd for $[C_{16}H_{13}FN_2O_2S + Na]^+$ 339.0574, found 339.0579; **IR** (thin film) 2253, 1505, 1302, 1291, 1178, 1152.



4d

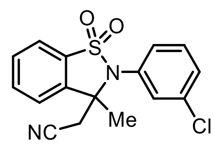
Prepared from **3d** on a 0.2 mmol scale with Pd_2dba_3 (5 mol%), Xantphos (10 mol%), and BPh_3 (40 mol%) in toluene at 80 °C for 16 h. **4d** was purified by flash column chromatography (15:85:1 EtOAc/Hex/MeOH → 3:100 MeOH/CH_2Cl_2) as an amorphous pale yellow solid (0.186 mmol, 93% yield). R_f = 0.49 (1:1

EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (dt, J = 7.7, 0.9 Hz, 1H), 7.77 (td, J = 7.6, 1.2 Hz, 1H), 7.73 – 7.64 (m, 2H), 7.54 – 7.50 (m, 2H), 7.47 (dt, J = 8.9, 2.1 Hz, 2H), 2.90 (d, J = 16.7 Hz, 1H), 2.83 (d, J = 16.8 Hz, 1H), 1.71 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.7, 136.9, 134.3, 134.0, 133.6, 130.5, 130.4, 128.5, 123.3, 121.9, 115.7, 63.7, 29.3, 25.3; **HRMS** (ESI) calcd for $[C_{16}H_{13}ClN_2O_2S + Na]^+$ 355.0278, found 355.0281; **IR** (thin film) 2253, 1490, 1302, 1177.



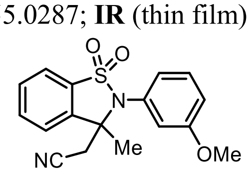
4e

Prepared from **3e** on a 0.2 mmol scale with Pd_2dba_3 (5 mol%), Xantphos (10 mol%), and BPh_3 (40 mol%) in toluene at 80 °C for 16 h. **4e** was purified by flash column chromatography (15:85:1 EtOAc/Hex/MeOH → 3:100 MeOH/CH_2Cl_2) as an amorphous white solid (0.178 mmol, 89% yield). R_f = 0.32 (1:1 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, J = 7.8 Hz, 1H), 7.78 – 7.61 (m, 3H), 7.43 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.3 Hz, 2H), 3.86 (s, 3H), 2.90 (d, J = 16.8 Hz, 1H), 2.83 (d, J = 16.7 Hz, 1H), 1.70 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.0, 139.0, 134.3, 134.2, 133.4, 130.3, 123.3, 121.9, 121.6, 116.0, 115.3, 63.5, 55.6, 29.2, 25.2; **HRMS** (ESI) calcd for $[C_{17}H_{16}N_2O_3S + Na]^+$ 351.0774, found 351.0763; **IR** (thin film) 2253, 1507, 1265, 1177.



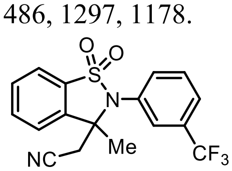
4f

Prepared from **3f** on a 0.2 mmol scale with Pd_2dba_3 (5 mol%), Xantphos (10 mol%), and BPh_3 (40 mol%) in toluene at 80 °C for 16 h. **4f** was purified by flash column chromatography (15:85:1 EtOAc/Hex/MeOH → 3:100 MeOH/CH_2Cl_2) as a tan foam (0.190 mmol, 95% yield). R_f = 0.43 (1:1 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.7 Hz, 1H), 7.77 (dd, J = 7.4, 1.1 Hz, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.69 (td, J = 7.5, 1.2 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.49 (t, J = 7.8 Hz, 1H), 7.45 (dt, J = 7.8, 1.6 Hz, 1H), 2.91 (d, J = 16.7 Hz, 1H), 2.86 (d, J = 16.7 Hz, 1H), 1.74 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.7, 135.6, 133.9, 133.6, 133.1, 131.33, 131.30, 130.9, 130.8, 130.5, 123.3, 121.9, 115.6, 63.8, 29.4, 25.3; **HRMS** (ESI) calcd for $[C_{16}H_{13}ClN_2O_2S + Na]^+$ 355.0278, found 355.0287; **IR** (thin film) 2254, 1588, 1471, 1180.



4g

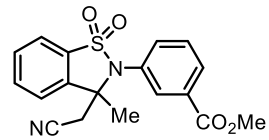
Prepared from **3g** on a 0.2 mmol scale with Pd_2dba_3 (5 mol%), Xantphos (10 mol%), and BPh_3 (40 mol%) in toluene at 80 °C for 16 h. **4g** was purified by flash column chromatography (15:85:1 EtOAc/Hex/MeOH → 3:100 MeOH/CH_2Cl_2) as an amorphous pale yellow solid (0.180 mmol, 90% yield). R_f = 0.46 (1:1 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.7 Hz, 1H), 7.79 – 7.69 (m, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 8.1 Hz, 1H), 7.16 – 7.02 (m, 3H), 3.84 (s, 3H), 2.94 (d, J = 16.8 Hz, 1H), 2.85 (d, J = 16.8 Hz, 1H), 1.72 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.6, 138.9, 134.2, 133.4, 130.9, 130.5, 130.3, 124.9, 123.3, 121.7, 118.6, 116.1, 115.9, 63.7, 55.5, 29.2, 25.3; **HRMS** (ESI) calcd for $[C_{17}H_{16}N_2O_3S + Na]^+$ 351.0774, found 351.0782; **IR** (thin film) 2253, 1600, 1486, 1297, 1178.



4h

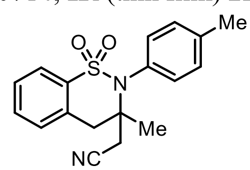
Prepared from **3h** on a 0.2 mmol scale with Pd_2dba_3 (5 mol%), Xantphos (10 mol%), and BPh_3 (40 mol%) in toluene at 80 °C for 16 h. **4h** was purified by flash column chromatography (15:85:1 EtOAc/Hex/MeOH →

3:100 MeOH/CH_2Cl_2) as an amorphous pale yellow solid (0.184 mmol, 92% yield). R_f = 0.47 (1:1 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.7 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.80 – 7.63 (m, 6H), 2.91 (d, J = 16.8 Hz, 1H), 2.85 (d, J = 16.8 Hz, 1H), 1.73 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.6, 136.5, 133.80, 133.75, 132.7 (q, $^2J_{F-C}$ = 33.2 Hz), 131.0, 130.8, 130.6, 129.9 (q, $^3J_{F-C}$ = 3.8 Hz), 127.3 (q, $^3J_{F-C}$ = 3.6 Hz), 123.3, 123.2 (q, $^1J_{F-C}$ = 271.1 Hz), 121.9, 115.5, 63.9, 29.4, 25.3; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –62.6; **HRMS** (ESI) calcd for $[C_{17}H_{13}F_3N_2O_2S + Na]^+$ 389.0542, found 389.0549; **IR** (thin film) 2255, 1332, 1179, 1151.



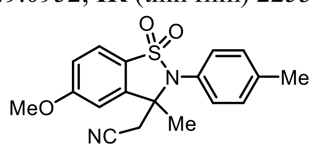
4i

Prepared from **3i** on a 0.2 mmol scale with Pd_2dba_3 (5 mol%), Xantphos (10 mol%), and BPh_3 (40 mol%) in toluene at 80 °C for 16 h. **4i** was purified by flash column chromatography (15:85:1 EtOAc/Hex/MeOH → 3:100 MeOH/CH_2Cl_2) as pale yellow foam (0.178 mmol, 89% yield). R_f = 0.24 (1:1 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.24 (dt, J = 7.8, 1.4 Hz, 1H), 8.16 (t, J = 1.9 Hz, 1H), 7.95 (dt, J = 7.8, 0.9 Hz, 1H), 7.81 – 7.73 (m, 3H), 7.70 (ddd, J = 7.6, 6.9, 1.5 Hz, 1H), 7.64 (t, J = 7.9 Hz, 1H), 3.95 (s, 3H), 2.92 (d, J = 17.0 Hz, 1H), 2.88 (d, J = 17.0 Hz, 1H), 1.76 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.7, 138.8, 137.5, 134.1, 134.0, 133.6, 132.4, 131.5, 130.5, 130.4, 130.2, 123.4, 121.9, 115.7, 63.7, 52.5, 29.5, 25.2; **HRMS** (ESI) calcd for $[C_{18}H_{16}N_2O_4S + Na]^+$ 379.0723, found 379.0714; **IR** (thin film) 2255, 1724, 1296, 1180.



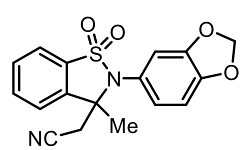
4j

Prepared from **3j** on a 0.2 mmol scale with Pd_2dba_3 (5 mol%), Xantphos (10 mol%), and BPh_3 (40 mol%) in toluene at 80 °C for 24 h. **4j** was purified by preparative thin-layer chromatography (35:65 EtOAc/Hex) as a yellow foam (0.116 mmol, 58% yield). R_f = 0.37 (3:7 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (dd, J = 7.6, 1.2 Hz, 1H), 7.59 (td, J = 7.6, 1.4 Hz, 1H), 7.48 (td, J = 7.7, 1.2 Hz, 1H), 7.43 (dd, J = 7.5, 1.1 Hz, 1H), 7.21 – 6.85 (br m 4H), 3.61 (d, J = 15.2 Hz, 1H), 3.53 (d, J = 15.2 Hz, 1H), 2.76 (d, J = 16.5 Hz, 1H), 2.71 (d, J = 16.5 Hz, 1H), 2.36 (s, 3H), 1.37 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.7, 139.5, 133.0, 132.7, 131.8 (br), 131.3, 130.2, 129.2, 127.8, 122.3, 116.5, 60.7, 39.0, 30.5, 26.3, 21.1; **HRMS** (ESI) calcd for $[C_{18}H_{18}N_2O_2S + Na]^+$ 349.0981, found 349.0952; **IR** (thin film) 2253, 1508, 1325, 1174.



4k

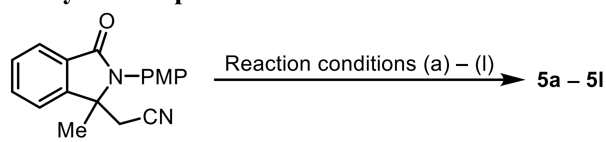
Prepared from **3k** on a 0.2 mmol scale with Pd_2dba_3 (5 mol%), Xantphos (10 mol%), and BPh_3 (40 mol%) in toluene at 80 °C for 24 h. **4k** was purified by flash column chromatography (1:4 → 1:1 EtOAc/Hex) as an pale yellow foam (0.152 mmol, 76% yield). R_f = 0.18 (3:7 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, J = 8.5 Hz, 1H), 7.38 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 3.92 (s, 3H), 2.88 (d, J = 16.7 Hz, 1H), 2.82 (d, J = 16.7 Hz, 1H), 2.42 (s, 3H), 1.69 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.6, 141.4, 140.6, 132.9, 130.6, 127.1, 126.1, 123.3, 116.6, 116.1, 108.0, 63.2, 56.0, 29.2, 25.2, 21.2; **HRMS** (ESI) calcd for $[C_{18}H_{18}N_2O_3S + Na]^+$ 365.0930, found 365.0938; **IR** (thin film) 2254, 1597, 1293, 1172.



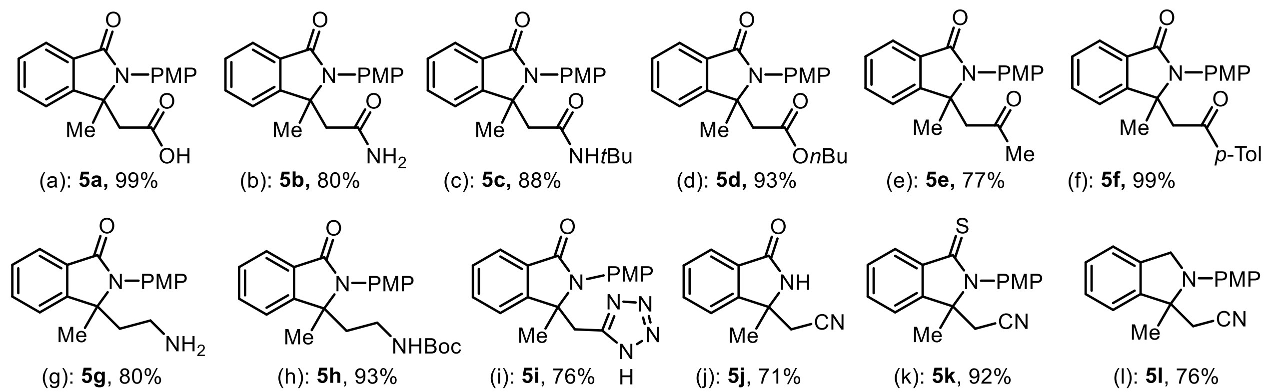
4m

Prepared from **3e** on a 0.2 mmol scale with Pd_2dba_3 (5 mol%), Xantphos (10 mol%), and BPh_3 (40 mol%) in toluene at 80 °C for 16 h. **4e** was purified by flash column chromatography (15:85:1 EtOAc/Hex/MeOH → 2:100 MeOH/CH_2Cl_2) as an amorphous white solid (0.178 mmol, 89% yield). R_f = 0.46 (1:1 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 1H), 7.78 – 7.70 (m, 2H), 7.67 (ddd, J = 7.7, 6.7, 1.8 Hz, 1H), 7.01 (dd, J = 8.2, 2.1 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 6.93 (d, J = 8.2 Hz, 1H), 6.07 (d, J = 1.1 Hz, 2H), 2.93 (d, J = 16.6 Hz, 1H), 2.84 (d, J = 16.6 Hz, 1H), 1.73 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.5, 148.7, 138.9, 134.1, 133.5, 130.4, 127.3, 123.4, 122.7, 121.9, 115.9, 113.3, 109.0, 102.2, 63.6, 29.2, 25.2; **HRMS** (ESI) calcd for $[C_{17}H_{14}N_2O_4S + Na]^+$ 365.0566, found 365.0557; **IR** (thin film) 2139, 1482, 1295, 1177.

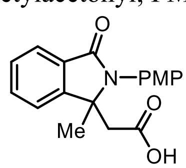
4. Transformations of aminocyanation products 2ad and 2af



2ad

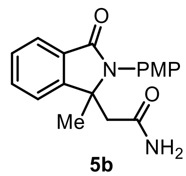


Reaction conditions: (a) KOH, EtOH/H_2O, 90 °C, 40 h; (b) KOH, MeOH/H_2O, 90 °C, 2 h; (c) H_2SO_4 (1.2 equiv), *t*BuOH, 80 °C, 12 h; (d) TsOH·H_2O (2 equiv), *n*BuOH, 120 °C, 20 h; (e) Ni(acac)$_2$ (10 mol%), $AlMe_3$ (3 equiv), benzene, 50 °C, 5 h; (f) Pd(OAc)$_2$ (10 mol%), *p*-tolylboronic acid (2 equiv), 2,2′-bipyridyl (20 mol%), CF_3CO_2H (10 equiv), THF/H_2O, 90 °C, 28 h; (g) $NaBH_4$ (4 equiv), $CoCl_2 \cdot 6H_2O$ (1.5 equiv), MeOH, 0 °C, 2 h; (h) (Boc)$_2$O (2.5 equiv), $NaBH_4$ (4 equiv), $CoCl_2 \cdot 6H_2O$ (1.5 equiv), MeOH, 0 °C, 3 h; (i) $TMSN_3$ (3 equiv), *n*Bu_2Sn(O) (0.5 equiv), PhMe, 100 °C, 48 h; (j) cerium (IV) ammonium nitrate (6 equiv), CH_3CN/H_2O, rt, 2 h; (k) Lawesson's reagent (1 equiv), PhMe, 100 °C, 2.5 h; (l) Tf_2O (1.2 equiv), CH_2Cl_2, 0 °C to rt, 30 min, then Hantzsch ester (3 equiv), rt, 4 h. acac = acetylacetonyl; PMP = 4-methoxyphenyl.



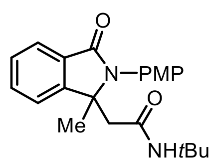
5a

Synthesis of 5a: In a one-dram reaction vial, **2ad** (58.5 mg, 0.2 mmol) was heated with KOH (224 mg, 4 mmol) in EtOH (0.6 mL) and H_2O (0.6 mL) at 90 °C for 40 h. The reaction was cooled to room temperature, acidified with 1 M HCl (10 mL), and extracted with EtOAc (15 mL × 3). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. Analytically pure **5a** was obtained as a pale brown powder without further purification (0.2 mmol, quant. yield). R_f = 0.35 (5:95 MeOH/CH_2Cl_2); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.08 (br s, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.26 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.9 Hz, 2H), 3.81 (s, 3H), 3.01 (d, J = 15.9 Hz, 1H), 2.62 (d, J = 15.9 Hz, 1H), 1.48 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 170.3, 167.2, 158.8, 149.3, 131.8, 131.2, 130.9, 128.03, 128.00, 122.8, 122.1, 114.4, 64.3, 55.3, 41.0, 26.3; **HRMS** (ESI) calcd for $[C_{18}H_{17}NO_4 + Na]^+$ 334.1050, found 334.1058; **IR** (thin film) 1712, 1651, 1513, 1246, 1185.



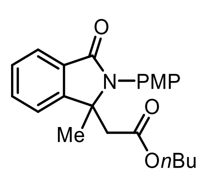
5b

Synthesis of 5b: In a one-dram reaction vial, **2ad** (58.5 mg, 0.2 mmol) was heated with KOH (224 mg, 4 mmol) in MeOH (1.0 mL) and H_2O (1.0 mL) at 90 °C for 2 h. The reaction was cooled to room temperature, acidified with 1 M HCl (10 mL), and extracted with EtOAc (15 mL × 3). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting mixture was purified by flash column chromatography (4:96 → 5:95 MeOH/CH_2Cl_2) to give **5b** as a white foam (0.160 mmol, 80% yield). R_f = 0.24 (2:100 MeOH/CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, J = 7.5 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.48 (td, J = 7.1, 1.7 Hz, 1H), 7.16 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 5.64 (s, 1H), 5.42 (s, 1H), 3.82 (s, 3H), 2.74 (d, J = 14.6 Hz, 1H), 2.54 (d, J = 14.6 Hz, 1H), 1.63 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.8, 168.1, 159.4, 148.9, 132.2, 131.0, 130.9, 128.6, 127.5, 124.1, 122.0, 114.8, 65.3, 55.4, 44.1, 25.8; **HRMS** (ESI) calcd for $[C_{18}H_{18}N_2O_3 + Na]^+$ 333.1210, found 333.1214; **IR** (thin film) 3327, 3191, 1670, 1615, 1513, 1387, 1248.



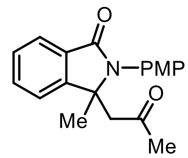
5c

Synthesis of 5c: To a one-dram reaction vial was added **2ad** (58.5 mg, 0.2 mmol), *tert*-butyl alcohol (0.40 mL), and conc. H_2SO_4 (3 drops via glass pipiet, ca. 60 mg, 0.6 mmol). The reaction was heated at 80 °C for 24 h. The reaction was cooled to room temperature, diluted with CH_2Cl_2 (3 mL), and washed with saturated aqueous $NaHCO_3$ (5 mL). The aqueous phase was extracted with CH_2Cl_2 (3 mL × 3). The combined organic extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting mixture was purified by flash column chromatography (1:1 EtOAc/Hex) to afford **5c** as a white foam (0.176 mmol, 88% yield). R_f = 0.16 (1:1 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (dd, J = 7.5, 0.9 Hz, 1H), 7.63 (dd, J = 7.4, 1.1 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.37 – 7.31 (m, 2H), 7.04 – 6.97 (m, 2H), 4.77 (s, 1H), 3.85 (s, 3H), 2.70 (d, J = 14.3 Hz, 1H), 2.56 (d, J = 14.4 Hz, 1H), 1.59 (s, 3H), 1.06 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.4, 159.4, 149.0, 132.1, 131.6, 131.0, 128.7, 127.8, 124.9, 124.5, 121.7, 114.8, 65.7, 55.5, 51.1, 46.4, 28.3, 26.1; **HRMS** (ESI) calcd for $[C_{22}H_{26}N_2O_3 + Na]^+$ 389.1836, found 389.1845; **IR** (thin film) 3330, 1680, 1656, 1512, 1391, 1247.



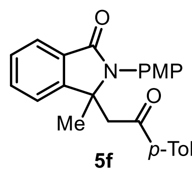
5d

Synthesis of 5d: 2ad (0.2 mmol) was heated with TsOH·H_2O (76.1 mg, 0.4 mmol) and *n*BuOH (0.2 mL, 2.2 mmol) in a HPLC vial at 120 °C for 20 h. The reaction mixture was cooled to room temperature, concentrated onto Celite, and purified by flash column chromatography (1.5:100 MeOH/CH_2Cl_2) to afford **5d** as a colorless oil (0.186 mmol, 93% yield). R_f = 0.31 (2:100 MeOH/CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dt, J = 7.5, 1.0 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.52 – 7.47 (m, 2H), 7.33 – 7.27 (m, 2H), 7.05 – 6.95 (m, 2H), 3.85 (s, 3H), 3.82 (t, J = 6.7 Hz, 2H), 2.86 (d, J = 15.0 Hz, 1H), 2.79 (d, J = 15.0 Hz, 1H), 1.60 (s, 3H), 1.37 – 1.24 (m, 2H), 1.20 – 1.08 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 168.1, 159.4, 148.6, 131.8, 131.4, 131.0, 128.4, 127.8, 124.0, 121.6, 114.8, 64.8, 64.5, 55.4, 42.5, 30.2, 26.5, 18.9, 13.5; **HRMS** (ESI) calcd for $[C_{22}H_{25}NO_4 + Na]^+$ 390.1676, found 390.1679; **IR** (thin film) 1730, 1696, 1513, 1377, 1248.



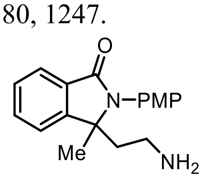
5e

Synthesis of 5e:[3] Under N_2, $AlMe_3$ (2 M Hex, 0.6 mL, 1.2 mmol) was added dropwise to a solution of **2ad** (117 mg, 0.4 mmol) and $Ni(acac)_2$ (10.4 mmol, 0.04 mmol) in benzene (0.4 mL) at room temperature. The reaction was heated at 50 °C for 5 h and was allowed to cool to room temperature and stir overnight. The reaction was cooled to 0 °C and quenched by careful addition of water (2 mL), which was then taken up to 1 M HCl (10 mL) and extracted with EtOAc (20 mL × 3). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting mixture was purified by flash column chromatography (1.5:100 MeOH/CH_2Cl_2) to give **5e** as pale yellow oil (0.308 mmol, 77% yield). R_f = 0.27 (2:100 MeOH/CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 1H), 7.58 (td, *J* = 7.4, 1.1 Hz, 1H), 7.54 (d, *J* = 7.1 Hz, 1H), 7.49 (td, *J* = 7.4, 1.2 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.03 – 6.96 (m, 2H), 3.85 (s, 3H), 3.00 (d, *J* = 16.5 Hz, 1H), 2.80 (d, *J* = 16.6 Hz, 1H), 1.89 (s, 3H), 1.64 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.4, 168.0, 159.4, 148.9, 131.9, 131.4, 130.8, 128.3, 127.9, 124.1, 121.6, 114.7, 64.9, 55.4, 50.0, 31.4, 26.3; **HRMS** (ESI) calcd for $[C_{19}H_{19}NO_3 + Na]^+$ 332.1257, found 332.1262; **IR** (thin film) 1689, 1613, 1513, 1379, 1247.



5f

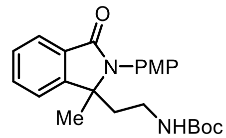
Synthesis of 5f:[4] To a one-dram reaction vial was added **2ad** (58.5 mg, 0.2 mmol), *p*-tolylboronic acid (54.4 mg, 0.4 mmol), 2,2′-bipyridyl (6.2 mg, 0.04 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), CF_3CO_2H (150 µL, 2.0 mmol), THF (0.5 mL), and H_2O (0.1 mL). The reaction vessel was briefly purged with N_2 for ca. 1 min and then heated at 90 °C for 28 h. The reaction was cooled to room temperature, diluted with EtOAc (20 mL), and washed with 1 M HCl (5 mL). The aqueous phase was extracted with EtOAc (10 mL × 2). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting mixture was purified by flash column chromatography (1.5:100 MeOH/CH_2Cl_2) to give **5f** as an off-white powder (0.201 mmol, quant. yield). R_f = 0.28 (2:100 MeOH/CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (dt, *J* = 6.3, 1.5 Hz, 1H), 7.70 – 7.56 (m, 2H), 7.52 – 7.38 (m, 3H), 7.23 – 7.09 (m, 4H), 7.03 – 6.86 (m, 2H), 3.81 (s, 3H), 3.50 (d, *J* = 16.8 Hz, 1H), 3.31 (d, *J* = 16.8 Hz, 1H), 2.36 (s, 3H), 1.73 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.5, 168.3, 159.4, 149.3, 144.0, 134.7, 131.7, 131.5, 130.9, 129.2, 128.1, 128.0, 127.9, 124.0, 121.7, 114.8, 65.1, 55.4, 44.5, 26.5, 21.5; **HRMS** (ESI) calcd for $[C_{25}H_{23}NO_3 + Na]^+$ 408.1570, found 408.1562; **IR** (thin film) 1687, 1606, 1513, 1380, 1247.



5g

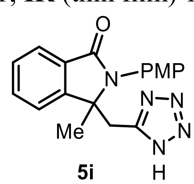
Synthesis of 5g: To a solution of **2ad** (58.5 mg, 0.2 mmol) and $CoCl_2{\cdot}6H_2O$ (71.4 mg, 0.3 mmol) in MeOH (1.5 mL) was added $NaBH_4$ (30.3 mg, 0.8 mmol) in one portion at 0 °C. The resulting mixture was stirred at 0 °C for 2 h and quenched with saturated aqueous NH_4Cl (ca. 2 mL), which was then taken up to 1 N NaOH (10 mL) and extracted with EtOAc (15 mL × 3). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting mixture was purified by flash column chromatography (5:95:0.5 → 7:93:0.1 MeOH/CH_2Cl_2/Et_3N) to give **5g** as a tan oil (0.160 mmol, 80% yield). R_f = 0.26 (5:95:0.5 MeOH/CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.59 (td, *J* = 7.5, 1.2 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.22 – 7.16 (m, 2H), 7.03 – 6.96 (m, 2H), 3.82 (s, 3H), 2.86 (br s, 2H), 2.62 (ddd, *J* = 12.0, 10.4, 4.8 Hz, 1H), 2.27 – 1.98 (m, 3H), 1.48 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ

168.3, 159.3, 149.2, 132.2, 131.1, 130.2, 128.3, 127.9, 124.2, 121.2, 114.9, 66.4, 55.4, 40.1, 36.7, 26.6; **HRMS** (ESI) calcd for $[C_{18}H_{20}N_2O_2 + Na]^+$ 319.1417, found 319.1417; **IR** (thin film) 3367, 1683, 1513, 1380, 1248.



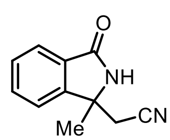
5h

Synthesis of 5h: To a solution of **2ad** (58.5 mg, 0.2 mmol), Boc_2O (109 mg, 0.5 mmol), and $CoCl_2{\cdot}6H_2O$ (71.4 mg, 0.3 mmol) in MeOH (1.5 mL) was added $NaBH_4$ (30.3 mg, 0.8 mmol) in one portion at 0 °C. The resulting mixture was stirred at 0 °C for 3 h and quenched with saturated aqueous NH_4Cl (ca. 2 mL), which was then taken up to 1 N NaOH (10 mL) and extracted with EtOAc (15 mL × 3). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting mixture was purified by flash column chromatography (0.6:100 → 1:100 MeOH/CH_2Cl_2) to give **5h** as a white foam (0.186 mmol, 93% yield). R_f = 0.15 (1:100 MeOH/CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.53 – 7.41 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.02 – 6.93 (m, 2H), 4.28 (br s, 1H), 3.84 (s, 3H), 3.02 – 2.95 (br m 1H), 2.73 – 2.60 (br m 1H), 2.23 – 2.13 (br m 1H), 2.05 – 1.97 (br m 1H), 1.49 (s, 3H), 1.39 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.3, 159.2, 155.6, 149.0, 132.3, 131.1, 130.3, 128.3, 128.0, 124.4, 121.3, 114.8, 66.2, 55.4, 37.8, 36.0, 28.3, 26.7; **HRMS** (ESI) calcd for $[C_{23}H_{28}N_2O_4 + Na]^+$ 419.1941, found 419.1961; **IR** (thin film) 1683, 1513, 1382, 1249, 1173.



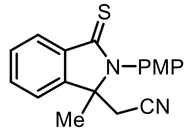
5i

Synthesis of 5i:[5] $TMSN_3$ (81 µL, 0.6 mmol) was added to a mixture of **2ad** (58.5 mg, 0.2 mmol) and *n*$Bu_2Sn(O)$ (24.9 mg, 0.1 mmol) in toluene (1.0 mL) at room temperature in a one-dram reaction vial. The resulting mixture was heated at 100 °C for 48 h. Upon cooling to room temperature, the reaction mixture was co-concentrated with MeOH (2 mL × 3 cycles). The residue was concentrated onto Celite and purified by flash column chromatography (3:100 → 5:100 MeOH/CH_2Cl_2) to give **5i** as an off-white solid (0.146 mmol, 73% yield). R_f = 0.20 (5:95 MeOH/CH_2Cl_2); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.65 – 7.53 (m, 3H), 7.53 – 7.47 (m, 2H), 7.43 (td, *J* = 7.2, 1.4 Hz, 1H), 7.13 – 7.03 (m, 2H), 3.82 (s, 3H), 3.55 (d, *J* = 15.2 Hz, 1H), 3.32 (d, *J* = 15.2 Hz, 1H), 1.63 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 166.9, 158.9, 152.5 (br), 147.9, 132.0, 131.5, 130.7, 128.4, 127.8, 122.9, 122.3, 114.4, 65.5, 55.3, 31.6, 25.5; **LRMS** (ESI) calcd for $[C_{18}H_{17}N_5O_2 - H]^-$ 334.1, found 334.1; **IR** (thin film) 1654, 1514.



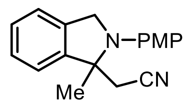
5j

Synthesis of 5j: Cerium (IV) ammonium nitrate (658 mg, 1.2 mmol) was added in one portion to a solution of **2ad** (58.5 mg, 0.2 mmol) in CH_3CN (1.6 mL) and H_2O (0.6 mL) at room temperature in a one-dram reaction vial. The resulting mixture was stirred for 2 h and diluted with water (10 mL), which was then extracted with EtOAc (15 mL × 3). Without further treatment,[6] the combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting mixture was purified by flash column chromatography (2:100 → 4:100 MeOH/CH_2Cl_2) to give **5j** as a pale yellow oil (0.142 mmol, 71% yield). R_f = 0.14 (2:100 MeOH/CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (br s, 1H), 7.87 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.65 (td, *J* = 7.5, 1.2 Hz, 1H), 7.61 – 7.49 (m, 2H), 2.91 (d, *J* = 16.6 Hz, 1H), 2.84 (d, *J* = 16.6 Hz, 1H), 1.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 148.9, 132.8, 130.7, 129.4, 124.3, 121.2, 116.3, 58.9, 30.2, 25.2; **HRMS** (ESI) calcd for $[C_{11}H_{10}N_2O + Na]^+$ 209.0685, found 209.0683; **IR** (thin film) 2251, 1699, 1470.



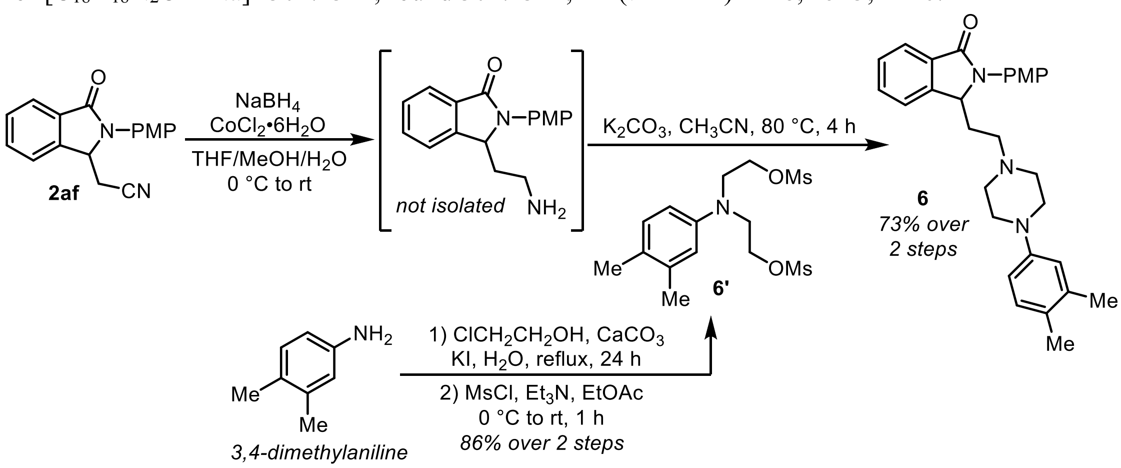
5k

Synthesis of 5k: 2ad (58.5 mg, 0.2 mmol) was heated with Lawesson's reagent (80.8 mg, 0.2 mmol) in toluene (0.8 mL) at 100 °C for 2.5 h in a one-dram reaction vial. The reaction mixture was cooled to room temperature, concentrated onto Celite, and purified by flash column chromatography (0:100 → 0.6:100 MeOH/CH_2Cl_2) to afford **5k** as a bright yellow foam (0.184 mmol, 92% yield). R_f = 0.58 (1:100 MeOH/CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (dt, J = 7.7, 1.0 Hz, 1H), 7.70 (td, J = 7.5, 1.2 Hz, 1H), 7.65 – 7.55 (m, 2H), 7.25 – 7.19 (m, 2H), 7.13 – 7.06 (m, 2H), 3.87 (s, 3H), 2.95 (d, J = 16.6 Hz, 1H), 2.75 (d, J = 16.6 Hz, 1H), 1.72 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.8, 160.2, 145.0, 137.4, 132.6, 130.6, 129.8, 128.7, 126.5, 120.9, 115.5, 115.4, 55.5, 28.0, 24.0; **HRMS** (ESI) calcd for $[C_{18}H_{16}N_2OS+ Na]^+$ 331.0876, found 331.0883; **IR** (thin film) 2252, 1609, 1512, 1388, 1318, 1251.



5l

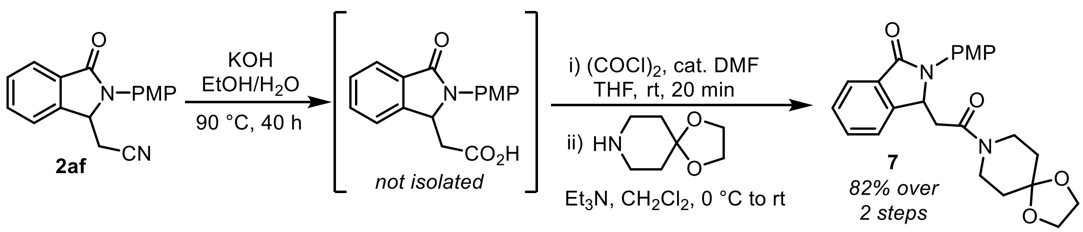
Synthesis of 5l:[7] Tf_2O (40.4 μL, 0.24 mmol) was added dropwise to a solution of **2ad** (58.5 mg, 0.2 mmol) in CH_2Cl_2 (2.0 mL) at 0 °C under N_2. The reaction was stirred for 5 min at 0 °C, then it was allowed to warm to room temperature and stir for additional 30 min, whereupon Hantzsch ester (152 mg, 0.6 mmol) was added in one portion. The resulting mixture was stirred at room temperature for 4 h, then it was directly concentrated onto Celite and purified by flash column chromatography (CH_2Cl_2) to afford **5l** as a colorless oil (0.152 mmol, 76% yield). **5l** appeared to be unstable upon extended exposure to air (> 5 h), but it can still be handled and characterized without special precautions. R_f = 0.56 (CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 4H), 7.02 – 6.95 (m, 2H), 6.95 – 6.90 (m, 2H), 4.76 (d, J = 13.0 Hz, 1H), 4.60 (d, J = 13.1 Hz, 1H), 3.80 (s, 3H), 2.95 (d, J = 16.7 Hz, 1H), 2.90 (d, J = 16.7 Hz, 1H), 1.80 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4, 144.6, 138.3, 136.7, 128.3, 127.7, 122.5, 121.7, 118.8, 117.5, 114.9, 67.1, 55.7, 55.1, 27.8, 26.2; **HRMS** (ESI) calcd for $[C_{18}H_{18}N_2O + Na]^+$ 301.1311, found 301.1314; **IR** (thin film) 2248, 1513, 1246.



Synthesis of dimesylate 6':[8] A suspension of 3,4-dimethylaniline (606 mg, 5 mmol), 2-chloroethanol (1.7 mL, 25 mmol), $CaCO_3$ (1300 mg, 13 mmol), and KI (83 mg, 0.5 mmol) in water (5 mL) was heated to reflux (oil bath temperature 110 °C) for 24 h. The reaction mixture was cooled to room temperature, diluted with EtOAc (50 mL) and water (10 mL), filtered through a pad of Celite, and separated. The organic phase was washed with water (10 mL) and brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting diol product was used for next step without further purification. Next, the above obtained diol (5 mmol theoretical) was dissolved in EtOAc (15 mL) and cooled to 0 °C. Et_3N (2.8 mL, 20 mmol), followed by a solution of MsCl (1718 mg, 15 mmol) in EtOAc (5 mL) was added dropwise at 0 °C. The resulting mixture was allowed to warm to room temperature and stir for 1 h. Upon completion, the reaction was diluted with

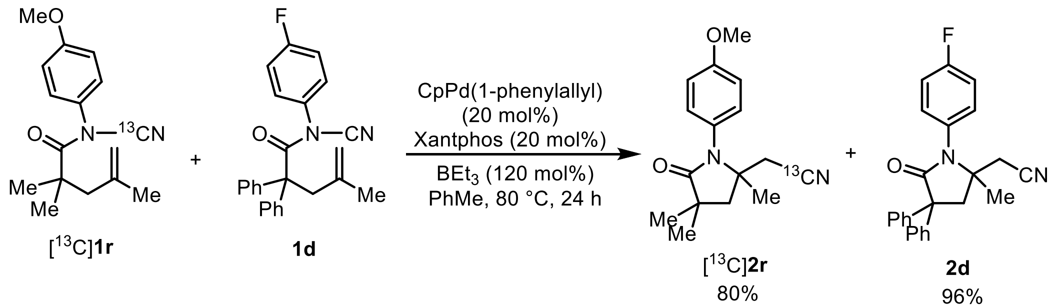
Et_2O (30 mL), filtered through a pad of Celite, washed with 1 M HCl (20 mL), and separated. The organic phase was washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting mixture was purified by flash column chromatography (2:3 → 3:2 EtOAc/Hex) to afford dimesylate **6'** as a pale yellow oil (4.3 mmol, 86% yield over 2 steps). R_f = 0.44 (2:100 MeOH/CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.3 Hz, 1H), 6.55 (d, *J* = 2.8 Hz, 1H), 6.49 (dd, *J* = 8.3, 2.9 Hz, 1H), 4.34 (t, *J* = 5.9 Hz, 4H), 3.72 (t, *J* = 5.9 Hz, 4H), 2.97 (s, 6H), 2.23 (s, 3H), 2.17 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.3, 137.9, 130.7, 126.6, 114.7, 110.6, 66.7, 51.0, 37.4, 20.3, 18.5.

Synthesis of piperazine 6: To a solution of **2af** (167 mg, 0.6 mmol) and $CoCl_2·6H_2O$ (214 mg, 0.9 mmol) in THF/MeOH/H_2O (4.0, 0.5, 2.0 mL, respectively) was added $NaBH_4$ (182 mg, 4.8 mmol) in one portion at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with saturated aqueous NH_4Cl (ca. 5 mL), which was then taken up to 1 N NaOH (20 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting amine product was used for next step without further purification. Next, the above obtained amine (0.6 mmol theoretical) was heated with dimesylate **6'** (146 mg, 0.4 mmol)[9] and K_2CO_3 (220 mg, 1.6 mmol) in CH_3CN (2 mL) at 80 °C for 4 h. The reaction was cooled to room temperature, diluted with EtOAc (30 mL), washed with water (5 mL), and separated. The organic phase was washed with brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting mixture was purified by flash column chromatography (4:6:0 → 5:5:0.15 EtOAc/Hex/MeOH) to afford **6** as a pale yellow oil (0.29 mmol, 73% yield over 2 steps based on **6'**). R_f = 0.30 (5:5:0.1 EtOAc/Hex/MeOH); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (dt, *J* = 7.6, 1.1 Hz, 1H), 7.59 (td, *J* = 7.5, 1.2 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.03 – 6.92 (m, 3H), 6.69 (d, *J* = 2.6 Hz, 1H), 6.62 (dd, *J* = 8.2, 2.7 Hz, 1H), 5.30 (dd, *J* = 6.0, 2.7 Hz, 1H), 3.84 (s, 3H), 3.06 – 2.98 (m, 4H), 2.41 – 2.34 (m, 4H), 2.20 (s, 3H), 2.19 – 1.96 (m, 7H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.1, 157.4, 149.4, 144.6, 137.0, 132.4, 131.8, 130.1, 129.8, 128.3, 128.0, 125.4, 124.1, 122.1, 118.0, 114.4, 113.7, 59.6, 55.5, 53.2, 52.4, 49.5, 28.2, 20.1, 18.7; **HRMS** (ESI) calcd for $[C_{29}H_{33}N_3O_2 + H]^+$ 456.2646, found 456.2652; **IR** (thin film)1690, 1513, 1389, 1248.



Synthesis of amide 7: 2af (111 mg, 0.4 mmol) was heated with KOH (448 mg, 8 mmol) in EtOH (1 mL) and H_2O (1 mL) at 90 °C for 40 h. The reaction was cooled to room temperature, acidified with 1 M HCl (15 mL), and extracted with EtOAc (20 mL × 3). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting carboxylic acid product was used for next step without further purification. Next, to a suspension of the above obtained carboxylic acid (0.4 mmol theoretical) in THF (1 mL) was added one drop of DMF via glass pipet, followed by addition of $(COCl)_2$ (2.5 M solution in CH_2Cl_2, 0.32 mL, 0.8 mmol) at room temperature. The reaction mixture was stirred for 20 min, whereupon gas evolution ceased. The mixture was concentrated in vacuo at room temperature to afford the crude acid chloride, which was redissolved in THF (2 mL) and cooled to 0 °C. To this solution was added Et_3N (112 µL, 0.6 mmol), followed by a solution of 1,4-dioxa-8-azaspiro[4.5]decane (86 mg, 0.6 mmol) in CH_2Cl_2 (0.5 mL) at 0 °C. The reaction was allowed to warm to room temperature and stir overnight. Upon completion, the reaction was diluted with EtOAc (30 mL), washed with 0.5 M HCl (10 mL), and separated. The organic phase was washed with brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting mixture was purified by flash column chromatography (3:2 → 7:3 EtOAc/Hex) to afford amide **7** as a pale yellow oil (0.33 mmol, 82% yield over 2 steps based on **2af**). R_f = 0.36 (7:3 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.3 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.56 (td, *J* = 7.4, 1.3 Hz, 1H), 7.54 – 7.48 (m, 3H), 7.04 – 6.87 (m, 2H), 5.79 (dd, *J* = 9.3, 3.7 Hz, 1H), 4.00 – 3.90 (m, 4H), 3.83 (s, 4H), 3.79 – 3.73(m, 1H), 3.72 – 3.66 (m, 1H), 3.36 – 3.26 (m, 2H), 2.88 (dd, *J* = 15.9, 3.7 Hz, 1H), 2.43 (dd, *J* = 16.0, 9.4 Hz, 1H), 1.71 – 1.62 (m, 2H), 1.50 (t, *J* = 5.8 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.9, 166.7, 157.4, 145.3, 132.1, 131.8, 129.4, 128.6, 125.1, 123.9, 123.2, 114.5, 106.5, 64.4, 58.3, 55.4, 43.5, 39.9, 36.3, 35.3, 34.7; **HRMS** (ESI) calcd for $[C_{24}H_{26}N_2O_5 + Na]^+$ 445.1734, found 445.1749; **IR** (thin film) 1694, 1633, 1514, 1361, 1248.

5. Double cross-over experiment

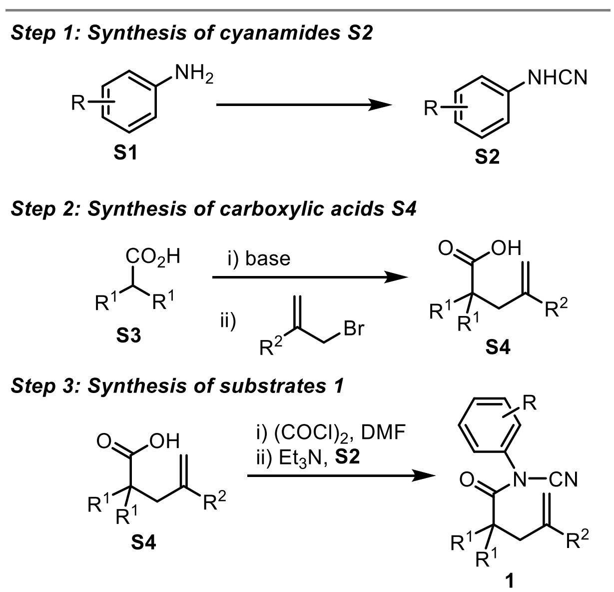


[^{13}C]**1r** was prepared in the same manner as **1r**, from cyanamide [^{13}C]**S2g** and carboxylic acid **S4b**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 2H), 6.98 – 6.90 (m, 2H), 4.99 – 4.89 (m, 1H), 4.87 (app s, 1H), 3.82 (s, 3H), 2.75 (s, 2H), 1.81 (s, 3H), 1.50 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.2 (d, $^2J_{C\text{–}C}$ = 4.5 Hz), 159.9, 141.4, 128.8, 127.7, 114.9, 114.8, 111.1 (^{13}CN), 55.5, 46.9, 44.9, 26.2, 23.9.

Double cross-over experiment: In a nitrogen-filled glove box, a one-dram vial was charged with a magnetic stirring bar, [^{13}C]**1r** (27.3 mg, 0.1 mmol), **1d** (38.4 mg, 0.1 mmol), BEt_3 (1.0 M in Hex, 120 µL, 0.12 mmol), Xantphos (11.6 mg, 0.02 mmol), and a solution of CpPd(1-phenylallyl) in toluene (0.02 M, 1.0 mL, 0.02 mmol). The reaction mixture was sealed with a PTFE lined cap, removed from the glove box, and heated at 80 °C in an aluminum heating block for 24 h. The resulting mixture was allowed to cool to room temperature, concentrated onto Celite, and purified by flash column chromatography (1:4 → 1:1 EtOAc/Hex) to give an inseparable mixture of [^{13}C]**2r** and **2d**. The yields were determined by integration of ^{1}H NMR spectrum of product mixture. **2d** showed no detectable enrichment in ^{13}C by analysis of the ^{1}H and ^{13}C NMR spectra, or the HRMS data for the mixture.

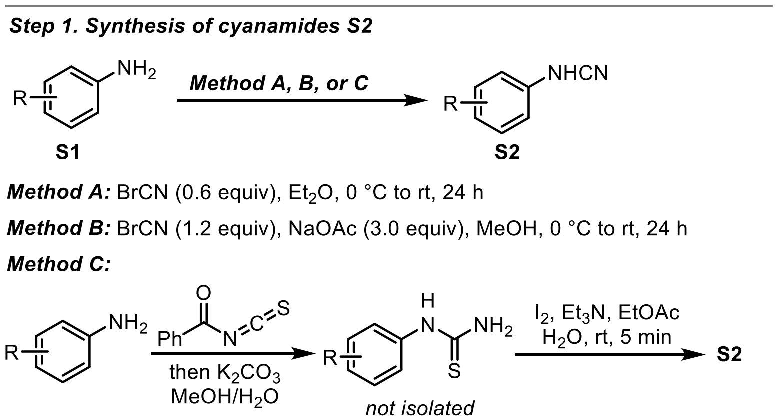
6. Synthesis of substrates: *N*-acyl cyanamides

All *N*-acyl cyanamide substrates **1** are synthesized in 3 steps. Step 1 synthesizes aryl cyanamides **S2** from the corresponding anilines **S1**. Step 2 synthesizes carboxylic acids **S4**. Step 3 synthesizes substrates **1** by coupling cyanamides **S2** with acids **S4**.



6.1 Synthesis of cyanamides S2 (Step 1)

CAUTION! *Cyanogen bromide (BrCN) is highly toxic and hydrolyzes readily to release hydrogen cyanide. The related preparation must be carried out in a well-ventilated fume hood. Excess BrCN should be destroyed with aqueous NaOH solution and the resulting aqueous solution should be disposed of properly.*



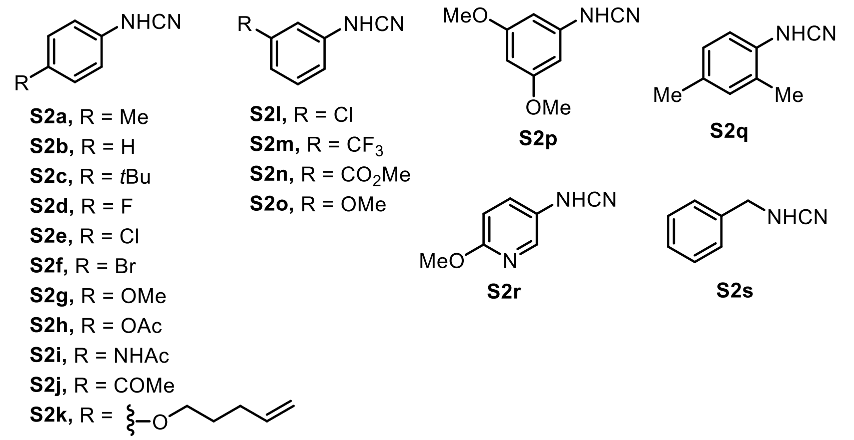
Method A: A solution of BrCN (1271 mg, 12 mmol) in Et_2O (10 mL) was slowly added to aniline **S1** (20 mmol) in Et_2O (20 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stir for 24 h. Upon completion, the mixture was diluted with Et_2O (40 mL) and filtered through a pad of Celite. The filtrate was washed with 1 M HCl (10 mL), saturated aqueous $NaHCO_3$ (10 mL), and brine (10 mL), and were dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography or precipitated from Et_2O/Hex or CH_2Cl_2/Hex at 0 °C.

Method B: A solution of BrCN (2542 mg, 24 mmol) in MeOH (30 mL) was slowly added to a mixture of aniline (20 mmol) and NaOAc (60 mmol) in MeOH (30 mL) at 0 °C. The reaction mixture was stirred for 1 h, then was allowed to warm to room temperature and stir overnight. Upon completion, the reaction was neutralized with saturated aqueous $NaHCO_3$ (20 mL) and concentrated to a small volume. The residue was taken up to water (50 mL) and extracted with CH_2Cl_2 (30 mL × 3). The combined organic extracts were washed with brine (20 mL), dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography.

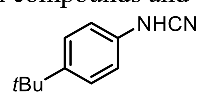
Method C: To a solution of aniline **S1** (10 mmol) in THF (15 mL) was added benzoyl isothiocyanate (1.48 mL, 11 mmol) in THF (10 mL) at room temperature. The resulting solution was stirred for 2–3 h. Upon completion, the reaction was concentrated, and the residue was suspended in MeOH (30 mL) and treated with a solution of K_2CO_3 (30 mmol) in H_2O (10 mL). The reaction was stirred overnight and concentrated, which was then taken up to water (100 mL). The resulting thiourea product was precipitated and collected by filtration, and was used without further purification. Next, to a suspension of the above obtained thiourea (10 mmol theoretical) in EtOAc (30 mL) was added H_2O (2 mL) and Et_3N (2.8 mL, 20 mmol), followed by addition of I_2 (2792 mg, 11 mol) in 6–7 batches at room temperature. Upon complete addition of I_2, the reaction was stirred for additional 5 min and quenched by addition of saturated aqueous $NaHSO_3$ (2 mL). The resulting mixture was diluted with EtOAc (50 mL) and filtered through a pad of Celite. The filtrate was washed with H_2O (10 mL) and brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography.

Method D: A solution of BrCN (2542 mg, 8 mmol) in toluene (4 mL) was slowly added to a mixture of aniline (4 mmol) and $NaHCO_3$ (14 mmol) in toluene (4 mL) at room temperature. The reaction mixture was stirred for overnight. Upon completion, the reaction was neutralized with saturated aqueous $NaHCO_3$ (5 mL) and taken up to water (20 mL). The crude product was collected by filtration and dissolved in DCM followed by water wash. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to afford solid product.

Synthesized cyanamides S2

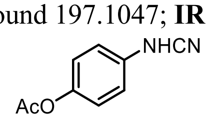


S2a, **S2b**, **S2d–S2g**, **S2o**, and **S2s** were known compounds and were prepared following reported procedures.[10]



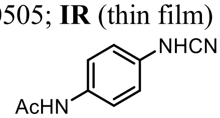
S2c

Prepared from 4-(*tert*-butyl)aniline on a 20.0 mmol scale using method A. **S2c** was purified by flash column chromatography (2:100 MeOH/CH_2Cl_2) as an off-white solid (9.36 mmol, 94% yield). R_f = 0.44 (5:95 MeOH/CH_2Cl_2); mp 86–88 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.00 – 6.90 (m, 2H), 6.10 (br s, 1H), 1.30 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 146.8, 134.4, 126.6, 115.1, 111.3, 34.3, 31.3; **HRMS** (ESI) calcd for $[C_{11}H_{14}N_2 + Na]^+$ 197.1049, found 197.1047; **IR** (thin film) 3159, 2227, 1517, 1253.



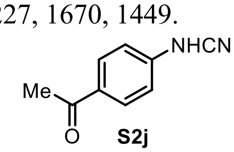
S2h

Prepared from 4-aminophenyl acetate[11] on a 9.7 mmol scale using method B. **S2h** was purified by precipitation (CH_2Cl_2/Hex) as an off-white solid (8.2 mmol, 85% yield). R_f = 0.54 (1:1 EtOAc/Hex); mp 95–97 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 8.8, 1.1 Hz, 2H), 6.97 – 6.90 (m, 2H), 2.31 (d, *J* = 1.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.2, 146.3, 135.1, 122.8, 116.3, 111.0, 21.1; **HRMS** (ESI) calcd for $[C_9H_8N_2O_2 + Na]^+$ 199.0478, found 199.0505; **IR** (thin film) 3183, 2237, 1757, 1510, 1221, 1195.



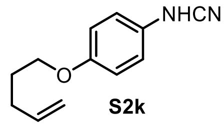
S2i

Prepared from *N*-(4-aminophenyl)acetamide on a 10 mmol scale using method B. **S2i** was purified by precipitation (MeOH/H_2O) as a tacky white solid. R_f = 0.48 (1:9 MeOH/CH_2Cl_2); **^{1}H NMR** (500 MHz, DMSO-d_6) δ 9.88 (s, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 2.01 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 167.9, 134.4, 133.7, 120.5, 115.2, 112.5, 23.8; **HRMS** (ESI) calcd for $[C_9H_9N_3O + Na]^+$ 198.0638, found 198.0649; **IR** (thin film) 2227, 1670, 1449.



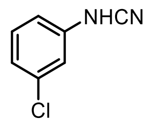
S2j

Prepared from 1-(4-aminophenyl)ethan-1-one on a 10.0 mmol scale using method C. **S2j** was purified by flash column chromatography (2:100 MeOH/CH_2Cl_2) as a pale yellow solid (6.2 mmol, 62% yield). R_f = 0.45 (5:95 MeOH/CH_2Cl_2); mp 110–112 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.73 (s, 1H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 2.51 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 196.2, 143.2, 131.5, 130.5, 114.7, 111.2, 26.4; **HRMS** (ESI) calcd for $[C_9H_8N_2O - H]^-$ 159.0564, found 159.0526; **IR** (thin film) 3188, 2229, 1740, 1272.



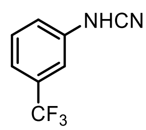
S2k

Prepared from 4-(pent-4-en-1-yloxy)aniline[12] on a 7.3 mmol scale using method B. **S2k** was purified by flash column chromatography (1:100 → 2:100 $MeOH/CH_2Cl_2$) as an oily purple solid (4.96 mmol, 68% yield). R_f = 0.28 (1:100 $MeOH/CH_2Cl_2$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.97 – 6.91 (m, 2H), 6.90 – 6.85 (m, 2H), 6.11 (br s, 1H), 5.85 (ddt, J = 16.8, 10.1, 6.6 Hz, 1H), 5.06 (dt, J = 17.1, 1.5 Hz, 1H), 5.00 (dt, J = 10.2, 1.5 Hz, 1H), 3.93 (t, J = 6.6 Hz, 2H), 2.30 – 2.17 (m, 2H), 1.94 – 1.81 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.6, 137.7, 130.0, 116.8, 115.7, 115.2, 111.8, 67.6, 30.0, 28.3. **HRMS** (ESI) calcd for $[C_{12}H_{14}N_2O + Na]^+$ 225.0998, found 225.0998; **IR** (thin film) 2218, 1640, 1510, 1233.



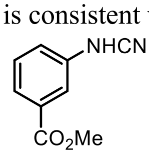
S2l

Prepared from 3-chloroaniline on a 15.0 mmol scale using method C. **S2l** was purified by flash column chromatography (2:100 $MeOH/CH_2Cl_2$) as a pale yellow solid (10.51 mmol, 71% yield). R_f = 0.48 (5:95 $MeOH/CH_2Cl_2$); mp 68–70 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 1H), 7.07 (dd, J = 8.0, 1.8 Hz, 1H), 7.04 (t, J = 2.2 Hz, 1H), 6.92 (dd, J = 8.2, 2.3 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.3, 135.5, 130.8, 123.9, 115.7, 113.6, 110.7; **HRMS** (ESI) calcd for $[C_7H_5ClN_2 - H]^-$ 151.0068, found 151.0060; **IR** (thin film) 3396, 2237, 1600.



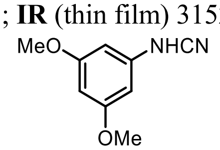
S2m

Prepared from 3-(trifluoromethyl)aniline on a 20.0 mmol scale using method C. **S2m** was purified by flash column chromatography (2:100 $MeOH/CH_2Cl_2$) as a pale yellow solid (16.8 mmol, 84% yield). R_f = 0.46 (5:95 $MeOH/CH_2Cl_2$); mp 85–87 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (t, J = 7.9 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 7.23 (dd, J = 8.2, 2.3 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.9, 132.3 (q, $^2J_{F-C}$ = 32.8 Hz), 130.5, 123.4 (q, $^1J_{F-C}$ = 270.8 Hz), 120.5 (q, $^3J_{F-C}$ = 3.8 Hz), 118.6, 112.3 (q, $^3J_{F-C}$ = 3.9 Hz), 110.7; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –63.0; **LRMS** (ESI) calcd for $[C_8H_5F_3O_2 - H]^-$ 185.0, found 185.1; **IR** (thin film) 3110, 2242, 1331. The NMR data is consistent with a literature report.[13]



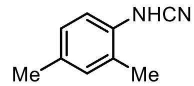
S2n

Prepared from methyl 3-aminobenzoate on a 15.0 mmol scale using method C. **S2n** was purified by flash column chromatography (1:100 → 2:100 $MeOH/CH_2Cl_2$) as a pale yellow solid (13.5 mmol, 90% yield). R_f = 0.46 (5:95 $MeOH/CH_2Cl_2$); mp 88–91 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.7, 1.3 Hz, 1H), 7.71 (app s, 1H), 7.44 (t, J = 7.9 Hz, 1H), 7.28 (dd, J = 8.1, 2.6 Hz, 1H), 3.94 (d, J = 1.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.6, 137.8, 131.5, 130.0, 124.6, 119.6, 116.4, 110.8, 52.6; **HRMS** (ESI) calcd for $[C_9H_8N_2O_2 + Na]^+$ 199.0478, found 199.0478; **IR** (thin film) 3152, 2227, 1594, 1251.



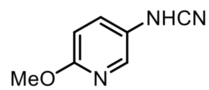
S2p

Prepared from 3,5-dimethoxyaniline on a 10.0 mmol scale using method B. **S2p** was purified by flash column chromatography (3:100 $MeOH/CH_2Cl_2$) as a white solid (5.2 mmol, 52% yield). R_f = 0.44 (5:95 $MeOH/CH_2Cl_2$); mp 138–140 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 (s, 1H), 6.19 (d, J = 2.1 Hz, 1H), 6.16 (d, J = 2.1 Hz, 2H), 3.78 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.9, 138.8, 110.4, 95.8, 94.0, 55.5; **HRMS** (ESI) calcd for $[C_9H_{10}N_2O_2 - H]^-$ 177.0670, found 177.0689. **IR** (thin film) 2946, 2242, 1114, 1028.



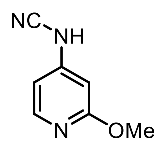
S2q

Prepared from 2,4-dimethylaniline on a 10.0 mmol scale using method A. **S2q** was purified by precipitation (Et_2O/Hex) as an off-white solid (8.4 mmol, 84% yield). R_f = 0.46 (5:95 $MeOH/CH_2Cl_2$); mp 102–104 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.08 (d, J = 8.1 Hz, 1H), 7.03 (d, J = 8.3 Hz, 1H), 6.96 (app s, 1H), 6.06 (br s, 1H), 2.28 (s, 3H), 2.20 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 133.3, 132.9, 131.6, 127.9, 124.1, 115.6, 111.9, 20.6, 16.9; **HRMS** (ESI) calcd for $[C_9H_{10}N_2 + Na]^+$ 169.0736, found 169.0740; **IR** (thin film) 3184, 2220, 1514.



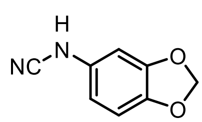
S2r

Prepared from 6-methoxypyridin-3-amine on a 10.0 mmol scale using method C. **S2r** was purified by flash column chromatography (3:97 → 5:95 $MeOH/CH_2Cl_2$) as a brick red solid (6.75 mmol, 68% yield). R_f = 0.44 (5:95 $MeOH/CH_2Cl_2$); mp 105–107 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.11 (br s, 1H), 7.84 (dd, J = 3.0, 0.7 Hz, 1H), 7.36 (dd, J = 8.8, 3.0 Hz, 1H), 6.84 (dd, J = 8.8, 0.7 Hz, 1H), 3.80 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 159.6, 133.0, 129.6, 127.3, 112.1, 111.3, 53.3; **HRMS** (ESI) calcd for $[C_7H_7N_3O + H]^+$ 150.0662, found 150.0654; **IR** (thin film) 3054, 2210, 1495.



S2t

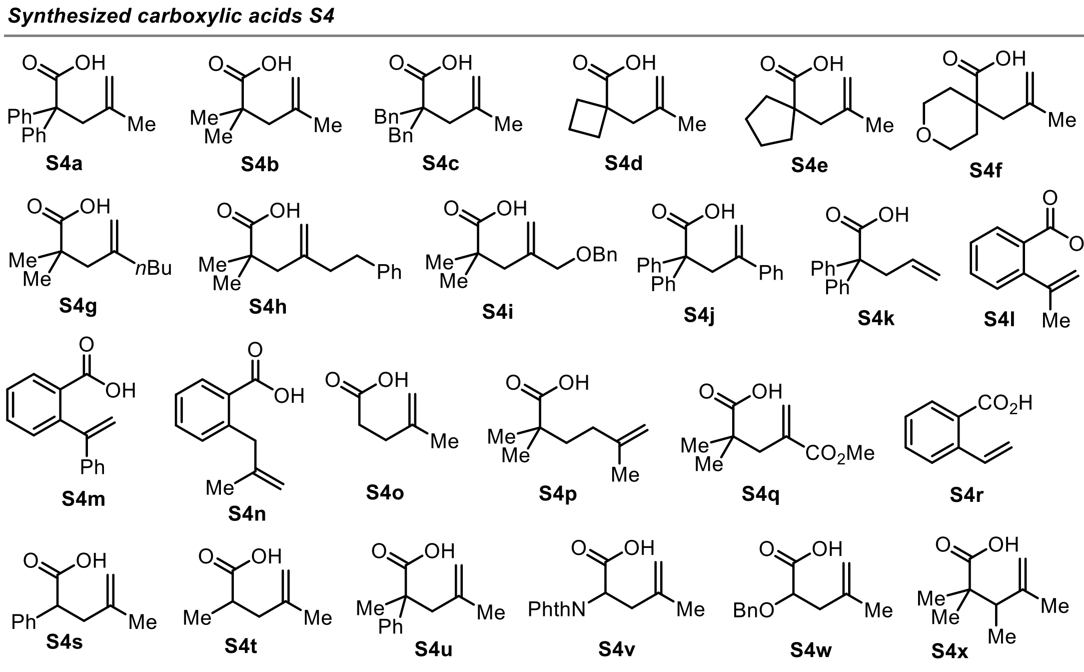
Prepared from 6-methoxypyridin-4-amine on a 4.0 mmol scale using method C. **S2t** was purified by flash column chromatography (4:100 → 5:100 $MeOH/CH_2Cl_2$) as a white solid (2.76 mmol, 69% yield). R_f= 0.44 (5:100 $MeOH/CH_2Cl_2$); mp 171–174 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.47 (s, 1H), 7.88 (d, J = 5.7 Hz, 1H), 6.53 (d, J = 5.1 Hz, 1H), 6.21 (d, J = 1.7 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 163.5, 156.9, 144.4, 114.1, 107.2, 94.6, 54.9; **HRMS** (ESI) calcd for $[C_7H_7N_3O + Na]^+$ 172.0481, found 172.0510; **IR** (thin film) 2138, 1631, 1595, 1494.



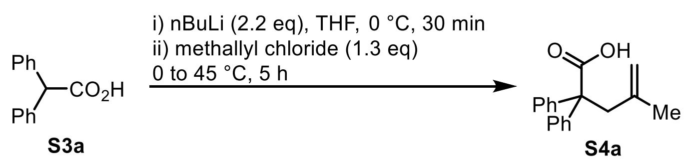
S2u

Prepared from benzo[d][1,3]dioxol-5-amine on a 4.0 mmol scale using method D. **S2u** was collected as a white solid (0.13 mmol, 33% yield).). R_f = 0.51 (5:100 $MeOH/CH_2Cl_2$); mp 83–85 °C;**^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.75 (d, J = 8.4 Hz, 1H), 6.57 (s, 1H), 6.45 (d, J = 8.2 Hz, 1H), 5.97 (s, 2H), 5.61 (br s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.7, 144.2, 131.6, 111.6, 108.7, 108.0, 101.6, 98.1; **HRMS** (ESI) calcd for $[C_8H_6N_2O_2 + Na]^+$ 185.0321, found 185.0304; **IR** (thin film) 2222, 1637, 1485, 1199.

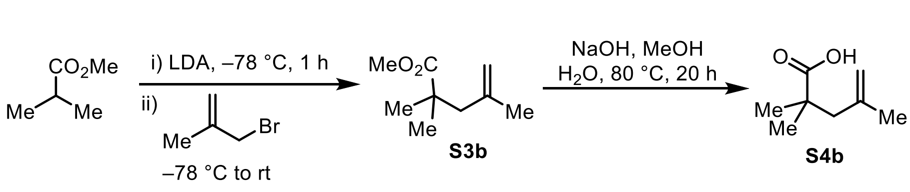
6.2 Synthesis of carboxylic acids S4 (Step 2)



S4j–S4o, S4r, and **S4s** were known compounds and were prepared following known procedures.[14]

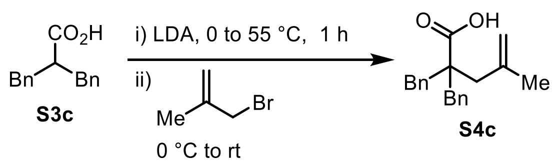


Synthesis of S4a: To a solution of diphenylacetic acid **S3a** (10.610g, 50 mmol) in THF (100 mL) was slowly added *n*BuLi (2.5 M Hex, 44 mL, 110 mmol) at 0 °C. The mixture was stirred at 0 °C for 30 min, followed by slow addition of methally chloride (7.04 mL, 65 mmol). The reaction was heated to 45 °C for 5 hours, which was then cooled in an ice bath, acidified with 2 N HCl to pH < 2, and separated. The aqueous phase was extracted with Et_2O (30 mL × 3). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over anhydrous $MgSO_4$, and concentrated to a small volume, whereupon acid **S4a** began to precipitate. Cold hexanes (ca. 80 mL) was added to allow further precipitation of **S4a**, which was collected by vacuum filtration as a white crystalline solid (8.65g, 32.5 mmol, 65% yield). R_f = 0.32 (1:4 EA/Hex); mp 117–118 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 4H), 7.31 – 7.21 (m, 6H), 4.71 (t, J = 1.7 Hz, 1H), 4.55 (app s, 1H), 3.18 (s, 2H), 1.33 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.1, 142.6, 141.8, 129.0, 127.8, 126.9, 115.6, 60.1, 45.6, 24.3; **IR** (thin film) 3059, 1699, 1495, 1215. The NMR data is consistent with a literature report.[15]

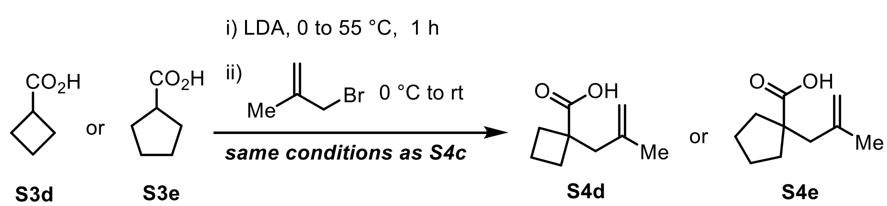


Synthesis of S3b: To a solution of *i*Pr_2NH (3.36 mL, 24 mmol) in THF (15 mL) was dropwise added *n*BuLi (2.5 M Hex, 9.2 mL, 23 mmol) at –78 °C. The resulting solution was stirred at –78 °C for 40 min, then a solution of methyl isobutyrate (2043 mg, 20 mmol) in THF (10 mL) was dropwise added. The reaction mixture was stirred at –78 °C for additional 1 h, followed by slow addition of methallyl bromide (2.62 mL, 26 mmol) at the same temperature. The resulting mixture was allowed to warm to room temperature and stir overnight, which was then quenched with saturated aqueous NH_4Cl (10 mL) and extracted with Et_2O (20 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The resulting mixture was purified by flash column chromatography (2:98 → 1:9 Et_2O/Hex) to give ester **S3b** as a colorless oil (2340 mg, 15 mmol, 75% yield). R_f = 0.44 (5:95 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.81 – 4.74 (m, 1H), 4.62 – 4.60 (m, 1H), 3.64 (s, 3H), 2.28 (s, 2H), 1.62 (s, 3H), 1.16 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.3, 142.4, 114.1, 51.6, 48.5, 42.0, 25.5, 23.4; **IR** (thin film) 1734, 1643, 1199, 1131.

Synthesis of S4b: A mixture of **S3b** (1562 mg, 10 mmol), NaOH (800 mg, 20 mmol), MeOH (10 mL), and H_2O (10 mL) was heated at 80 °C for 20 h. The reaction was cooled to 0 °C, acidified with 2 N HCl to pH ≤ 2, and extracted with Et_2O (20 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to give **S4b** as a bright yellow oil (1390 mg, 9.8 mmol, 98% crude yield). **S4b** was co-concentrated with benzene (5 mL × 3 cycles) and was used without further purification. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.84 – 4.82 (m, 1H), 4.71 – 4.69 (m, 1H), 2.34 (s, 2H), 1.71 (s, 3H), 1.21 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 185.2, 142.2, 114.4, 48.2, 42.0, 25.3, 23.6. The NMR data is consistent with a known report.[16]



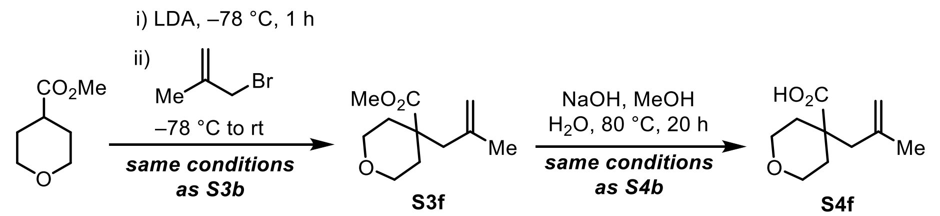
Synthesis of S4c: To a solution of *i*Pr_2NH (1.05 mL, 7.5 mmol) in THF (6 mL) was dropwise added *n*BuLi (2.5 M Hex, 2.9 mL, 7.2 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min, then a solution of 2-benzyl-3-phenylpropanoic acid **S3c**[17] (721 mg, 3.0 mmol) in THF (3 mL) was slowly added. The reaction mixture was heated at 55 °C for 1 h, then was cooled back to 0 °C and added methallyl bromide (0.43 mL, 4.2 mmol). The reaction was allowed to warm to room temperature and stir overnight, then it was acidified with 2 N HCl to pH ≤ 2 and extracted with Et_2O (20 mL × 3). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated. The resulting mixture was purified by flash column chromatography (1:4 → 3:7 Et_2O/Hex) to give acid **S4c** as a pale yellow oil (795 mg, 2.7 mmol, 90% yield). R_f = 0.39 (3:7 Et_2O/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.16 (m, 10H), 5.02 (app s, 1H), 4.87 (app s, 1H), 3.10 (d, J = 14.0 Hz, 2H), 3.05 (d, J = 14.0 Hz, 2H), 2.26 (s, 2H), 1.73 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 182.6, 142.1, 137.1, 130.4, 128.0, 126.6, 113.1, 50.5, 41.1, 40.9, 25.1; **HRMS** (ESI) calcd for $[C_{20}H_{22}O_2 - H]^-$ 293.1547, found 293.1536; **IR** (thin film) 1700, 1454, 1265.



S4d and **S4e** were synthesized in the manner as **S4c**.

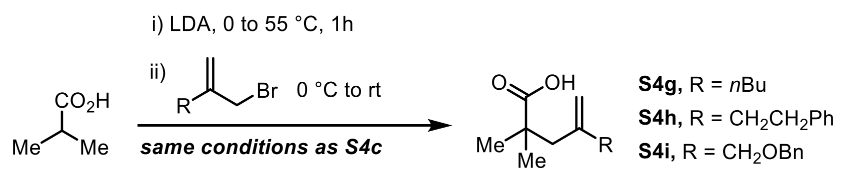
S4d was synthesized from cyclobutanecarboxylic acid **S3d** on a 5 mmol scale. **S4d** was purified by flash column chromatography (1:9 → 15:85 EtOAc/Hex) as a colorless oil (648 mg, 4.2 mmol, 84% yield). R_f = 0.52 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.76 (app s, 1H), 4.60 (app s, 1H), 2.56 (s, 2H), 2.55 – 2.47 (m, 2H), 2.06 – 1.98 (m, 2H), 1.98 – 1.90 (m, 2H), 1.69 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.7, 142.3, 112.1, 47.0, 45.4, 30.5, 23.3, 15.8; **LRMS** (ESI) calcd for $[C_9H_{14}O_2 - H]^-$ 153.1, found 153.1; **IR** (thin film) 3076, 1698, 1650, 1256, 1225.

S4e was synthesized from cyclopentanecarboxylic acid **S3e** on a 15 mmol scale. **S4e** was purified by flash column chromatography (1:4 → 1:3 Et_2O/Hex) as a pale yellow oil (1796 mg, 10.68 mmol, 71% yield). R_f = 0.32 (3:7 Et_2O/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.78 – 4.77 (m, 1H), 4.67 (d, J = 1.1 Hz, 1H), 2.42 (s, 2H), 2.19 – 2.11 (m, 2H), 1.70 (s, 3H), 1.68 – 1.50 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 184.6, 142.8, 113.2, 53.3, 46.4, 36.2, 24.8, 23.3; **HRMS** (ESI) calcd for $[C_{10}H_{16}O_2 - H]^-$ 167.1078, found 167.1049; **IR** (thin film) 3075, 1697, 1650, 1453, 1223.



S3f was synthesized in the same manner as **S3b**, starting from methyl tetrahydro-2*H*-pyran-4-carboxylate on a 7.3 mmol scale. **S3f** was purified by flash column chromatography (1:9 → 15:85 Et_2O/Hex) as a pale yellow oil (1230 mg, 6.2 mmol, 85% yield). R_f = 0.42 (1:9 Et_2O/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.84 – 4.83 (m, 1H), 4.66 (dd, *J* = 2.1, 1.0 Hz, 1H), 3.82 (dt, *J* = 11.9, 3.8 Hz, 2H), 3.71 (s, 3H), 3.45 (td, *J* = 11.6, 2.3 Hz, 2H), 2.31 (s, 2H), 2.09 (dd, *J* = 13.9, 2.7 Hz, 2H), 1.67 (s, 3H), 1.55 (ddd, *J* = 13.8, 11.2, 4.4 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.0, 140.9, 114.9, 65.3, 51.6, 48.7, 45.0, 34.6, 23.7; **HRMS** (ESI) calcd for $[C_{11}H_{18}O_3 + Na]^+$ 221.1148, found 221.1168; **IR** (thin film) 1730, 1647, 1194, 1134.

S4f was synthesized in the same manner as **S4b**, from the hydrolysis of **S3f** on a 10.0 mmol scale. **S4f** was obtained as a white solid (1784 mg, 9.7 mmol, 97% crude yield) and was used without further purification. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.88 – 4.83 (m, 1H), 4.72 (app s, 1H), 3.86 (dt, *J* = 12.0, 3.8 Hz, 2H), 3.53 (td, *J* = 11.7, 2.3 Hz, 2H), 2.35 (s, 2H), 2.09 (dd, *J* = 13.9, 2.6 Hz, 2H), 1.73 (s, 3H), 1.59 (ddd, *J* = 13.8, 11.2, 4.5 Hz, 2H).

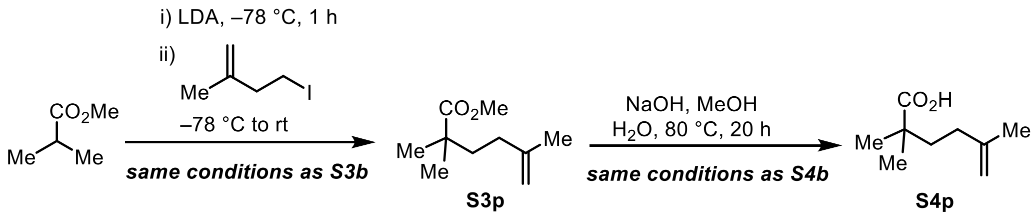


S4g–S4i were synthesized in the same manner as **S4c** by quenching the dianion of isobutyric acid with the corresponding substituted allyl bromide.

S4g was synthesized from isobutyric acid on a 8.0 mmol scale, using 2-(bromomethyl)hex-1-ene[18] as the quenching electrophile. **S4g** was purified by flash column chromatography (5:95 → 1:9 EtOAc/Hex) as a colorless oil (1066 mg, 5.78 mmol, 72% yield). R_f = 0.60 (1:4 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.84 (q, *J* = 1.5 Hz, 1H), 4.73 (app s, 1H), 2.33 (s, 2H), 1.97 (t, *J* = 7.3 Hz, 2H), 1.45 – 1.35 (m, 2H), 1.34 – 1.23 (m, 2H), 1.21 (s, 6H), 0.89 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.9, 146.3, 112.9, 46.2, 42.2, 36.7, 30.1, 25.4, 22.4, 13.9; **LRMS** (ESI) calcd for $[C_{11}H_{20}O_2 - H]^-$ 183.1, found 183.2; **IR** (thin film) 3053, 1699, 1640, 1474.

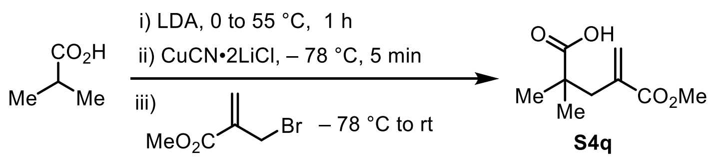
S4h was synthesized from isobutyric acid on a 6.0 mmol scale, using 2(3-(bromomethyl)but-3-en-1-yl)benzene[19] as the quenching electrophile. **S4h** was purified by flash column chromatography (5:95 → 1:9 EtOAc/Hex) as a pale yellow oil (981 mg, 4.22 mmol, 70% yield). R_f = 0.41 (15:85 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.20 – 7.12 (m, 3H), 4.88 (q, *J* = 1.5 Hz, 1H), 4.78 (app s, 1H), 2.79 – 2.69 (m, 2H), 2.37 (s, 2H), 2.33 – 2.22 (m, 2H), 1.22 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 184.8, 145.5, 142.0, 128.3, 128.3, 125.7, 113.8, 46.1, 42.2, 38.9, 34.6, 25.4; **HRMS** (ESI) calcd for $[C_{15}H_{20}O_2 - H]^-$ 231.1391, found 231.1375; **IR** (thin film) 3064, 1697, 1641, 1474, 1219.

S4i was synthesized from isobutyric acid on a 8.0 mmol scale, using 2(((2-(bromomethyl)allyl)oxy)methyl)benzene[20] as the quenching electrophile (performed at –78 °C instead of 0 °C). Unfortunately, several attempts to purify **S4i** by flash column chromatography were unsuccessful. **S4i** was thus taken to the next step without further treatment.

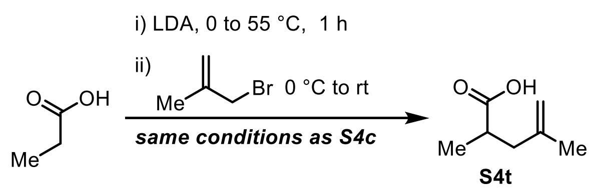


S3p was synthesized in the same manner as **S3b**, starting from methyl isobutyrate on a 20 mmol scale and using 4-iodo-2-methylbut-1-ene[21] as the quenching electrophile. **S3p** was purified by flash column chromatography (5:95 Et_2O/Hex) as a colorless oil (2348 mg, 13.8 mmol, 69% yield). R_f = 0.48 (5:95 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.69 (app s, 1H), 4.67 (app s, 1H), 3.67 (s, 3H), 1.96 – 1.88 (m, 2H), 1.72 (s, 3H), 1.68 – 1.63 (m, 2H), 1.19 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.3, 145.7, 109.7, 51.6, 42.1, 38.8, 33.1, 25.1, 22.6; **IR** (thin film) 1734, 1650, 1194, 1133.

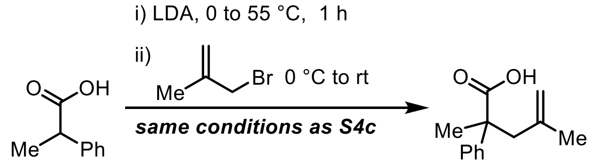
S4p was synthesized in the same manner as **S4b**, from the hydrolysis of **S3p** on a 13.8 mmol scale. **S4p** was obtained as a pale yellow oil (2051 mg, 13.1 mmol, 95% crude yield), and was used without further purification. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.71 – 4.69 (m, 1H), 4.69 – 4.68 (m, 1H), 2.05 – 1.93 (m, 2H), 1.74 (s, 3H), 1.72 – 1.64 (m, 2H), 1.22 (s, 6H).



Synthesis of S4q: To a solution of *i*Pr_2NH (1.9 mL, 13.5 mmol) in THF (10 mL) was dropwise added *n*BuLi (2.5 M Hex, 5.2 mL, 13.0 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min, followed by addition of isobutyric acid (475 mg, 5.4 mmol) in THF (5 mL). The reaction was heated at 55 °C for 1 h, which was then cooled back to –78 °C and was added CuCN•2LiCl (1 M THF solution, 6.4 mL, 6.4 mmol). The resulting mixture was stirred at –78 °C for 5 min, whereupon methyl 2-(bromomethyl)acrylate[22] (1353 mg, 7.56 mmol) was added. The reaction was allowed to warm to room temperature and stir overnight, then it was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with Et_2O (20 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The resulting mixture was purified by flash column chromatography (2:100 → 5:100 MeOH/CH_2Cl_2) to give **S4q** as a pale yellow oil (376 mg, 2.02 mmol, 37% yield). R_f = 0.54 (5:95 MeOH/CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.26 (d, J = 1.5 Hz, 1H), 5.61 (d, J = 1.3 Hz, 1H), 3.73 (s, 3H), 2.66 (d, J = 1.0 Hz, 2H), 1.19 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.6, 167.9, 137.0, 128.3, 51.9, 42.8, 40.7, 24.6; **IR** (thin film) 1705, 1701, 1440, 1299, 1199, 1168.

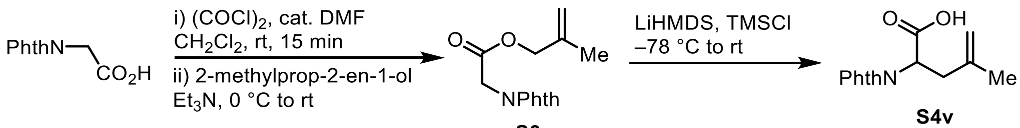


S4t was synthesized in the same manner as **S4c** by quenching the dianion of propionic acid with methallyl bromide. **S4t** obtained as a pale yellow oil, which was sufficiently pure without column chromatography purification (95% yield). R_f = 0.35 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.80 (app s, 1H), 4.74 (d, J = 1.0 Hz, 1H), 2.67 (sextet, J = 7.1 Hz, 1H), 2.45 (ddd, J = 14.2, 7.1, 1.2 Hz, 1H), 2.10 (ddd, J = 14.1, 7.8, 1.1 Hz, 1H), 1.72 (s, 3H), 1.17 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.9, 142.5, 112.5, 41.5, 37.6, 22.1, 16.5. The NMR data is consistent with a literature report.[23]



S4u

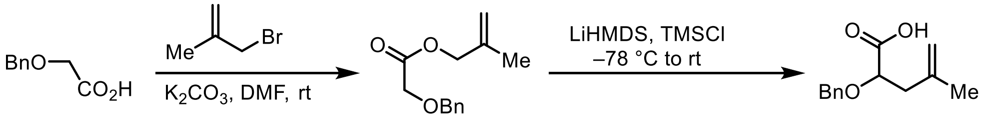
S4u was synthesized in the same manner as **S4c** by quenching the dianion of 2-phenylpropanoic acid[24] with methallyl bromide. **S4u** was purified by flash column chromatography (1:9 EtOAc/Hex) as a pale yellow oil (68% yield). R_f = 0.35 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 2H), 7.33 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.29 – 7.22 (m, 1H), 4.85 – 4.79 (m, 1H), 4.66 (d, *J* = 1.2 Hz, 1H), 2.94 (d, *J* = 13.5 Hz, 1H), 2.65 (d, *J* = 13.5 Hz, 1H), 1.57 (s, 3H), 1.47 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 182.4, 142.9, 141.9, 128.4, 127.1, 126.2, 115.4, 49.2, 46.8, 23.8, 21.7; **LRMS** (ESI) calcd for $[(C_{13}H_{15}O_2)_2 + Na]^-$ 429.2, found 429.2. **IR** (thin film) 2941, 1690, 1449, 1408, 1375, 1320, 1274.



S3v **S4v**

Synthesis of S3v: To a solution of *N*-phthaloylglycine (2462 mg, 12 mmol) in CH_2Cl_2 (20 mL) was added 4 drops of DMF via glass pipet, followed by addition of $(COCl)_2$ (2.5 M solution in CH_2Cl_2, 4.4 mL, 11 mmol) at room temperature. The reaction mixture was stirred for 15 min, whereupon gas evolution ceased, and it was cooled to 0 °C. To this solution was added Et_3N (3.34 mL, 24 mmol), followed by a solution of 2-methylprop-2-en-1-ol (721 mg, 10 mmol) in CH_2Cl_2 (6 mL) at 0 °C. The reaction was allowed to warm to room temperature and stir for 1.5 h. The reaction was diluted with CH_2Cl_2 (30 mL), washed with 1 M HCl (20 mL), and separated. The organic phase was washed with brine (20 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting mixture was purified by flash column chromatography (1:4 EtOAc/Hex) to afford **S3v** as a white foam (2182 mg, 8.4 mmol, 84% yield). R_f = 0.36 (1:4 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.98 (t, *J* = 1.2 Hz, 1H), 4.95 (dd, *J* = 1.6, 0.8 Hz, 1H), 4.59 (s, 2H), 4.49 (s, 2H), 1.75 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 167.0, 139.0, 134.2, 132.0, 123.6, 113.7, 69.0, 38.8, 19.4; **HRMS** (ESI) calcd for $[C_{14}H_{13}NO_4 + Na]^+$ 282.0737, found 282.0744; **IR** (thin film) 1752, 1724, 1416, 1193.

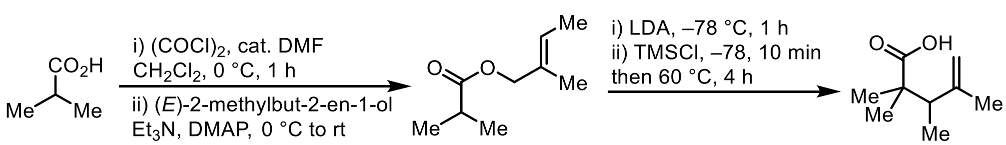
Synthesis of S4v: To a solution of hexamethyldisilazane (2.2 mL, 10.4 mmol) in THF (4 mL) was dropwise added *n*BuLi (2.5 M Hex, 3.8 mL, 9.6 mmol) at 0 °C. The resulting LiHMDS solution was allowed to warm to room temperature and stirred for 20 min, which was then dropwise added to a solution of **S3v** (2074 mg, 8 mmol) and TMSCl (1.32 mL, 10.4 mmol) in THF (12 mL) at –78 °C. The reaction was stirred at –78 °C for 10 min and was allowed to warm to room temperature and stir overnight. 1 M HCl (20 mL) was added and the resulting mixture was stirred at room temperature for 30 min and extracted with EtOAc (20 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The resulting mixture was purified by flash column chromatography (1:100:1 → 2:100:0.5 MeOH/CH_2Cl_2/AcOH) to give **S4v** as a yellow foam (520 mg, 2.0 mmol, 25% yield). R_f = 0.44 (2:100:0.1 MeOH/CH_2Cl_2/AcOH); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.14 (dd, *J* = 12.2, 4.2 Hz, 1H), 4.70 (t, *J* = 1.7 Hz, 1H), 4.66 (d, *J* = 1.9 Hz, 1H), 3.13 (dd, *J* = 14.4, 12.1 Hz, 1H), 2.83 (dd, *J* = 14.4, 4.1 Hz, 1H), 1.75 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.8, 167.4, 140.4, 134.2, 131.6, 123.6, 114.5, 50.1, 36.7, 21.4; **LRMS** (ESI) calcd for $[C_{14}H_{13}NO_4 – H]^-$ 258.1, found 258.2; **IR** (thin film) 1775, 1714, 1391.



S3w **S4w**

Synthesis of S3w: 2-(benzyloxy)acetic acid[25] (2493 mg, 15 mmol) was stirred with methallyl bromide (2228 mg, 16.5 mmol) and K_2CO_3 (3105 mg, 22.5 mmol) in DMF (30 mL) at room temperature for 24 h. The reaction was taken up to water (150 mL) and extracted with Et_2O (30 mL × 3). The combined organic extracts were washed with 2 M LiCl (10 mL × 2) and brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated. The resulting mixture was purified by flash column chromatography (5:95 EtOAc/Hex) to give **S3w** as a colorless oil (2766 mg, 12.6 mmol, 84% yield). R_f = 0.32 (5:95 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 5H), 4.99 (t, *J* = 1.2 Hz, 1H), 4.96 – 4.92 (m, 1H), 4.65 (s, 2H), 4.59 (s, 2H), 4.14 (s, 2H), 1.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 139.4, 137.0, 128.4, 128.00, 127.97, 113.4, 73.3, 67.9, 67.1, 19.4; **HRMS** (ESI) calcd for $[C_{13}H_{16}O_3 + Na]^+$ 243.0992, found 243.0996; **IR** (thin film) 1758, 1454, 1193, 1129.

Synthesis of S4w: To a solution of hexamethyldisilazane (2.9 mL, 14 mmol) in THF (5 mL) was dropwise added *n*BuLi (2.5 M Hex, 5.2 mL, 13 mmol) at 0 °C. The resulting LiHMDS solution was allowed to warm to room temperature and stirred for 20 min, which was then dropwise added to a solution of **S3w** (2203 mg, 10 mmol) and TMSCl (1.9 mL, 15 mmol) in THF (25 mL) at –78 °C. The reaction was stirred at –78 °C for 40 min and was allowed to warm to room temperature and stir for additional 2 h. 1 M NaOH (10 mL) was added and the resulting mixture was stirred at room temperature for 30 min, which was then diluted with water (50 mL), washed with Et_2O (10 mL × 2), and separated. The aqueous phase was acidified with concentrated HCl to pH < 2 and extracted with Et_2O (30 mL × 3). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated. The resulting mixture was purified by flash column chromatography (3:100 MeOH/CH_2Cl_2) to give **S4w** as a tan oil (1734 mg, 7.87 mmol, 79% yield). R_f = 0.42 (5:95 MeOH/CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.85 (br s, 1H), 7.43 – 7.26 (m, 5H), 4.87 (t, *J* = 1.7 Hz, 1H), 4.83 (app s, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.14 (t, *J* = 6.4 Hz, 1H), 2.54 (dd, *J* = 6.5, 1.0 Hz, 2H), 1.74 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.8, 140.6, 136.9, 128.4, 128.04, 128.02, 114.0, 76.6, 72.6, 40.8, 22.5; **HRMS** (ESI) calcd for $[C_{13}H_{16}O_3 + Na]^+$ 243.0992, found 243.1000; **IR** (thin film) 1717, 1455, 1207, 1107.



S3x S4x

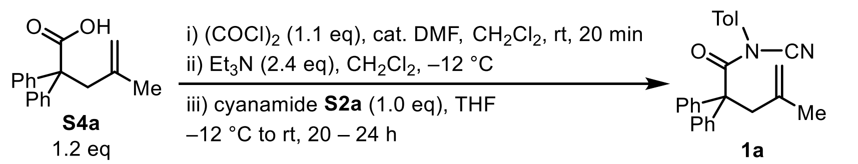
Synthesis of S3x: To a solution of isobutyric acid (1489 mg, 16.9 mmol) in CH_2Cl_2 (13 mL) was added 6 drops of DMF via glass pipet, followed by addition of $(COCl)_2$ (2 M solution in CH_2Cl_2, 7.8 mL, 15.6 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, whereupon a solution of (*E*)-2-methylbut-2-en-1-ol[26] (1119 mg, 13 mmol) in CH_2Cl_2 (10 mL) was added, followed by addition of Et_3N (4.5 mL, 33 mmol) and DMAP (159 mg, 1.3 mmol). The reaction was allowed to warm to room temperature and stir overnight. The reaction was diluted with CH_2Cl_2 (40 mL), washed with 1 M HCl (30 mL), followed by saturated aqueous $NaHCO_3$ (20 mL) and brine, and separated. The organic phase was washed with brine (20 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford **S3x** as a colorless oil (1137 mg, 7.3 mmol, 56% crude yield). **S3x** was used for next step without further purification. R_f = 0.76 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.58 – 5.51 (m, 1H), 4.46 (d, *J* = 0.9 Hz, 2H), 2.57 (hept, *J* = 7.2 Hz, 1H), 1.68 – 1.59 (m, 6H), 1.19 (d, *J* = 0.7 Hz, 3H), 1.17 (d, *J* = 0.7 Hz, 3H); **IR** (thin film) 1737, 1471, 1191, 1155.

Synthesis of S4x: To a solution of *i*Pr_2NH (1.47 mL, 10.5 mmol) in THF (10 mL) was dropwise added *n*BuLi (2.5 M Hex, 4 mL, 10 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min then it was cooled to –78 °C and was added a solution of **S3x** (781 mg, 5 mmol) in THF (5 mL). The reaction was stirred at –78 °C for additional 1 h, followed by addition of TMSCl (1.27 mL, 10 mmol) at the same temperature. The resulting mixture was stirred at –78 °C for 10 min, then it was allowed to warm to room temperature over 30 min and heated at 60 °C for 4 h. The reaction was cooled to room temperature, stirred with 2 M HCl (15 mL) for 1 h, and extracted with Et_2O (20 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, and concentrated. Unfortunately, attempts to purify **S4x** by flash column chromatography were unsuccessful. **S4x** was thus taken to the next step without further treatment. R_f = 0.44

(15:85 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.86 (t, J = 1.7 Hz, 1H), 4.77 – 4.74 (m, 1H), 2.60 (q, J = 7.2 Hz, 1H), 1.73 (s, 3H), 1.17 (s, 3H), 1.16 (s, 3H), 1.06 (d, J = 7.2 Hz, 3H); **LRMS** (ESI) calcd for $[C_9H_{16}O_2 - H]^-$ 155.1, found 155.2; **IR** (thin film) 1699, 1461, 1255.

6.3 Synthesis of substrates 1 (Step 3)

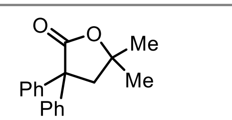
Step 3: synthesis of substrates 1, standard conditions



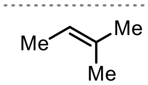
Modified conditions:

2-methyl-2-butene (8–10 eq) *was added at step i) under otherwise identical conditions.*

Synthesis of substrate 1a as a representative example, standard conditions: To a suspension of acid **S4a** (1598 mg, 6.0 mmol) in CH_2Cl_2 (5.0 mL) was added DMF (3 drops via glass pipet), followed by dropwise addition of $(COCl)_2$ (2.0 M in CH_2Cl_2, 2.8 mL, 5.5 mmol) at room temperature. The mixture was stirred for 15–20 minutes, whereupon gas evolution ceased and all acid dissolved. The reaction flask was cooled to –12 °C in an ethylene glycol/dry ice bath and a solution of Et_3N (1.67 mL, 12.0 mmol) in CH_2Cl_2 (4.0 mL) was dropwise added. Thereafter, a solution of *N*-(*p*-tolyl)cyanamide **S2a** (661 mg, 5.0 mmol) in CH_2Cl_2/THF (3.0 and 1.0 mL, respectively) was slowly added at the same temperature. The resulting mixture was allowed to warm up to room temperature and stir for 20 h. Et_2O (30 mL) was added to allow precipitation of triethylamine hydrochloride, which was filtrated through a short Celite column. Without further treatment,[27] the filtrate was concentrated in vacuo and the resulting oily residue was purified by flash column chromatography to afford substrate **1a** as a white powder (1.79 mmol, 36% yield). R_f = 0.49 (1:9 EtOAc/Hex); mp 108–110 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (dt, J = 6.2, 1.3 Hz, 4H), 7.40 (dd, J = 8.6, 6.8 Hz, 4H), 7.36 – 7.30 (m, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.10 – 7.03 (m, 2H), 4.77 (app s, 1H), 4.48 (app s, 1H), 3.42 (s, 2H), 2.35 (s, 3H), 1.42 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.0, 141.0, 139.4, 139.2, 133.7, 130.2, 128.8, 128.3, 127.6, 125.9, 116.5, 109.3, 62.1, 47.1, 24.5, 21.1; **HRMS** (ESI) calcd for $[C_{26}H_{24}N_2O + Na]^+$ 403.1781, found 403.1778; **IR** (thin film) 2230, 1725, 1508, 1203.

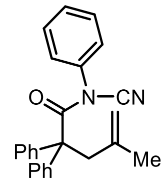


5,5-dimethyl-3,3-diphenyldihydrofuran-2(3H)-one



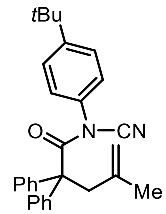
2-methyl-2-butene

Modified conditions: In step i), 5,5-dimethyl-3,3-diphenyldihydrofuran-2(3*H*)-one was formed as a by-product. This compound frequently coeluted with product **1** during column chromatography. It was found that the addition of 2-methyl-2-butene (8–10 equivalents) at step i) significantly reduced the amount of this by-product in the crude reaction mixture. Under such conditions, most substrates were readily purified after one column chromatography and were obtained as thick oil or tacky solid. Some substrates were further precipitated from CH_2Cl_2/Hex or CH_2Cl_2/pentane and were converted to crystalline solid.



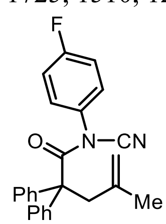
1b

Prepared from acid **S4a** and cyanamide **S2b** on a 5.0 mmol scale under standard conditions. **1b** was purified by flash column chromatography (2:3 → 1:1 CH_2Cl_2/Hex) as a white powder (1.96 mmol, 39% yield). R_f = 0.53 (15:85 EtOAc/Hex); mp 101–103 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 4H), 7.44 – 7.31 (m, 9H), 7.20 (d, *J* = 7.6 Hz, 2H), 4.78 (app s, 1H), 4.49 (app s, 1H), 3.43 (s, 2H), 1.43 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.9, 141.0, 139.1, 136.3, 129.6, 129.1, 128.8, 128.4, 127.7, 126.1, 116.6, 109.2, 62.2, 47.1, 24.5; **HRMS** (ESI) calcd for $[C_{25}H_{22}N_2O + Na]^+$ 389.1624, found 389.1622; **IR** (thin film) 2231, 1725, 1491, 1204.



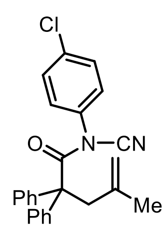
1c

Prepared from acid **S4a** and cyanamide **S2c** on a 5.0 mmol scale under standard conditions. **1c** was purified by flash column chromatography (3:7 → 2:3 CH_2Cl_2/Hex) as a white solid (2.28 mmol, 46% yield). R_f = 0.68 (1:1 CH_2Cl_2/Hex); mp 118–121 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 4H), 7.44 – 7.38 (m, 6H), 7.36 – 7.30 (m, 2H), 7.12 (dd, *J* = 8.6, 1.0 Hz, 2H), 4.78 (d, *J* = 1.6 Hz, 1H), 4.49 (app s, 1H), 3.43 (s, 2H), 1.42 (s, 3H), 1.30 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.1, 152.4, 141.1, 139.2, 133.6, 128.8, 128.3, 127.6, 126.6, 125.5, 116.6, 109.3, 62.2, 47.1, 34.7, 31.2, 24.5; **HRMS** (ESI) calcd for $[C_{29}H_{30}N_2O + Na]^+$ 445.2250, found 445.2256; **IR** (thin film) 2231, 1725, 1510, 1205.



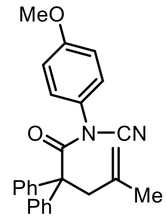
1d

Prepared from acid **S4a** and cyanamide **S2d** on a 5.0 mmol scale under standard conditions. **1d** was purified by flash column chromatography (3:7 → 1:1 CH_2Cl_2/Hex), and further precipitated (CH_2Cl_2/pentane, 1:40 v/v) as a white powder (2.21 mmol, 44% yield). R_f = 0.48 (1:1 CH_2Cl_2/Hex); mp 110–112 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 4H), 7.41 (dd, *J* = 8.5, 6.9 Hz, 4H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.20 – 7.14 (m, 2H), 7.10 (t, *J* = 8.5 Hz, 2H), 4.78 (app s, 1H), 4.49 (app s, 1H), 3.42 (s, 2H), 1.42 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.0, 162.4 (d, $^1J_{F\text{–}C}$ = 250.1 Hz), 141.0, 139.0, 132.2 (d, $^4J_{F\text{–}C}$ = 3.2 Hz), 128.7, 128.4, 128.2 (d, $^3J_{F\text{–}C}$ = 9.0 Hz), 127.8, 116.7 (d, $^2J_{F\text{–}C}$ = 23.3 Hz), 116.58, 109.0, 62.2, 47.1, 24.5; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –111.0; **HRMS** (ESI) calcd for $[C_{25}H_{21}FN_2O + Na]^+$ 407.1530, found 407.1530; **IR** (thin film) 2233, 1727, 1506, 1202.



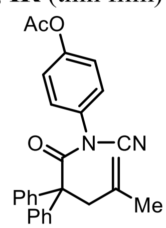
1e

Prepared from acid **S4a** and cyanamide **S2e** on a 5.0 mmol scale under standard conditions. **1e** was purified by flash column chromatography (35:65 → 2:3 CH_2Cl_2/Hex), and further precipitated (CH_2Cl_2/Hex, 1:40 v/v) as a white powder (2.30 mmol, 46% yield). R_f = 0.38 (1:1 CH_2Cl_2/Hex); mp 116–118 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 4H), 7.44 – 7.36 (m, 6H), 7.36 – 7.30 (m, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 4.78 (app s, 1H), 4.48 (app s, 1H), 3.42 (s, 2H), 1.41 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.8, 141.0, 138.9, 135.1, 134.7, 129.8, 128.7, 128.4, 127.8, 127.4, 116.6, 108.8, 62.2, 47.1, 24.5; **HRMS** (ESI) calcd for $[C_{25}H_{21}ClN_2O + Na]^+$ 423.1235, found 423.1242; **IR** (thin film) 2232, 1727, 1488, 1191.



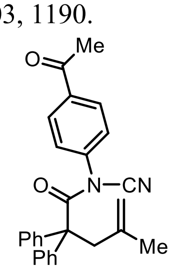
1f

Prepared from acid **S4a** and cyanamide **S2g** on a 5.0 mmol scale under standard conditions. **1f** was purified by flash column chromatography (3:7 → 1:1 CH_2Cl_2/Hex) as a white solid (2.37 mmol, 47% yield). R_f = 0.42 (1:1 CH_2Cl_2/Hex); mp 90–92 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 4H), 7.40 (t, *J* = 7.7 Hz, 4H), 7.37 (t, *J* = 7.1 Hz, 2H), 7.10 – 7.06 (m, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.77 (d, *J* = 1.4 Hz, 1H), 4.48 (app s, 1H), 3.79 (s, 3H), 3.42 (s, 2H), 1.42 (d, *J* = 1.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.2, 159.9, 141.1, 139.2, 128.9, 128.8, 128.3, 127.6, 127.5, 116.5, 114.8, 109.4, 62.1, 55.5, 47.1, 24.5; **HRMS** (ESI) calcd for $[C_{26}H_{24}N_2O_2 + Na]^+$ 419.1730, found 419.1736; **IR** (thin film) 2230, 1725, 1508, 1249.



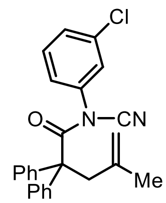
1g

Prepared from acid **S4a** and cyanamide **S2h** on a 5.0 mmol scale under standard conditions. **1g** was purified by flash column chromatography (1:1 CH_2Cl_2/Hex → 15:85 EtOAc/Hex), and further precipitated (CH_2Cl_2/Hex, 1:40 v/v) as a white powder (1.34 mmol, 27% yield). R_f = 0.35 (1:4 EtOAc/Hex); mp 120–121 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 4H), 7.40 (t, *J* = 7.3 Hz, 4H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.23 – 7.19 (m, 2H), 7.18 – 7.12 (m, 2H), 4.78 (d, *J* = 1.5 Hz, 1H), 4.48 (app s, 1H), 3.42 (s, 2H), 2.29 (d, *J* = 0.9 Hz, 3H), 1.42 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.8, 168.8, 150.7, 141.0, 139.0, 133.5, 128.7, 128.4, 127.7, 127.2, 122.8, 116.6, 109.0, 62.2, 47.1, 24.5, 21.1; **HRMS** (ESI) calcd for $[C_{27}H_{24}N_2O_3 + Na]^+$ 447.1679, found 447.1676; **IR** (thin film) 2232, 1765, 1726, 1503, 1190.



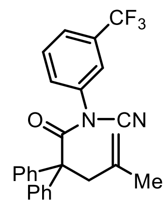
1h

Prepared from acid **S4a** and cyanamide **S2j** on a 4.0 mmol scale under standard conditions. **1h** was purified by flash column chromatography (1:9 acetone/Hex) as a thick yellow oil (1.04 mmol, 26% yield). R_f = 0.37 (1:4 acetone/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.53 (m, *J* = 7.5 Hz, 4H), 7.42 (t, *J* = 8.5 Hz, 4H), 7.35 (td, *J* = 8.5, 1.6 Hz, 4H), 4.79 (t, *J* = 1.8 Hz, 1H), 4.49 (app s, 1H), 3.43 (s, 2H), 2.60 (s, 3H), 1.41 (d, *J* = 1.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.5, 172.6, 140.9, 140.1, 138.8, 137.1, 129.6, 128.7, 128.5, 127.8, 126.0, 116.7, 108.6, 62.4, 47.1, 26.7, 24.5; **HRMS** (ESI) calcd for $[C_{27}H_{24}N_2O_2 + Na]^+$ 431.1730, found 431.1721; **IR** (thin film) 2232, 1728, 1688, 1600, 1178.



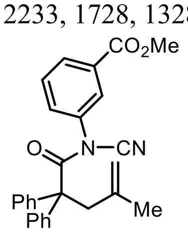
1i

Prepared from acid **S4a** and cyanamide **S2l** on a 5.0 mmol scale under standard conditions. **1i** was purified by flash column chromatography (3:7 → 4:6 CH_2Cl_2/Hex), and further precipitated (CH_2Cl_2/Hex, 1:40 v/v) as a white powder (2.27 mmol, 45% yield). R_f = 0.44 (1:9 EtOAc/Hex); mp 114–116 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, J = 7.7 Hz, 4H), 7.42 (t, J = 7.7 Hz, 4H), 7.38 – 7.32 (m, 4H), 7.22 (d, J = 2.1 Hz, 1H), 7.11 (dd, J = 6.1, 2.7 Hz, 1H), 4.79 (app s, 1H), 4.48 (app s, 1H), 3.42 (s, 2H), 1.41 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.7, 140.9, 138.9, 137.2, 135.1, 130.5, 129.4, 128.7, 128.5, 127.8, 126.5, 124.3, 116.7, 108.7, 62.3, 47.1, 24.5; **HRMS** (ESI) calcd for $[C_{25}H_{21}ClN_2O + Na]^+$ 423.1235, found 423.1238; **IR** (thin film) 2232, 1729, 1589, 1190.



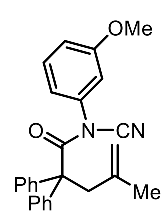
1j

Prepared from acid **S4a** and cyanamide **S2m** on a 5.0 mmol scale under standard conditions. **1j** was purified by flash column chromatography (3:7 → 4:6 CH_2Cl_2/Hex) as a white solid (2.31 mmol, 46% yield). R_f = 0.57 (1:1 CH_2Cl_2/Hex); mp 111–112 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, J = 7.8 Hz, 1H), 7.59 – 7.50 (m, 5H), 7.48 (app s, 1H), 7.45 – 7.38 (m, 5H), 7.38 – 7.32 (m, 2H), 4.80 (app s, 1H), 4.50 (app s, 1H), 3.44 (s, 2H), 1.42 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.8, 140.9, 138.8, 136.8, 132.2 (q, $^2J_{F\text{–}C}$ = 33.5 Hz), 130.3, 129.4, 128.7, 128.5, 127.9, 126.0 (q, $^3J_{F\text{–}C}$ = 3.7 Hz), 123.3 (q, $^3J_{F\text{–}C}$ = 3.8 Hz), 123.1 (q, $^1J_{F\text{–}C}$ = 271.0 Hz), 116.7, 108.6, 62.3, 47.1, 24.5; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –62.7; **HRMS** (ESI) calcd for $[C_{26}H_{21}F_3N_2O + Na]^+$ 457.1498, found 457.1501; **IR** (thin film) 2233, 1728, 1328, 1177.



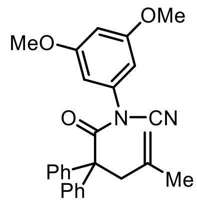
1k

Prepared from acid **S4a** and cyanamide **S2n** on a 5.0 mmol scale under standard conditions. **1k** was purified by flash column chromatography (3:7 → 6:4 CH_2Cl_2/Hex) as a tacky white solid (3.07 mmol, 61% yield). R_f = 0.32 (1:1 CH_2Cl_2/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (dd, J = 7.8, 1.4 Hz, 1H), 7.90 (d, J = 1.8 Hz, 1H), 7.54 (dt, J = 8.2, 1.3 Hz, 4H), 7.50 (td, J = 7.9, 1.0 Hz, 1H), 7.42 (dd, J = 8.2, 6.8 Hz, 4H), 7.39 – 7.32 (m, 3H), 4.79 (app s, 1H), 4.50 (app s, 1H), 3.93 (s, 3H), 3.43 (s, 2H), 1.42 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.8, 165.5, 141.0, 138.9, 136.5, 131.9, 130.5, 130.2, 129.7, 128.8, 128.5, 127.8, 127.3, 116.7, 108.8, 62.3, 52.5, 47.1, 24.5; **HRMS** (ESI) calcd for $[C_{27}H_{24}N_2O_3 + Na]^+$ 447.1679, found 447.1684; **IR** (thin film) 2233, 1727, 1289.



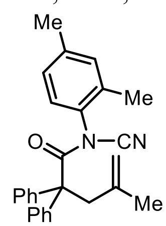
1l

Prepared from acid **S4a** and cyanamide **S2o** on a 5.0 mmol scale under standard conditions. **1l** was purified by flash column chromatography (5:95 → 1:9 EtOAc/Hex) as a white solid (1.84 mmol, 37% yield). R_f = 0.42 (15:85 EtOAc/Hex); mp 80–83 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 4H), 7.40 (t, *J* = 7.7 Hz, 4H), 7.36 – 7.27 (m, 3H), 6.90 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.78 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.70 (t, *J* = 2.3 Hz, 1H), 4.78 (app s, 1H), 4.49 (app s, 1H), 3.76 (s, 3H), 3.42 (s, 2H), 1.42 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.9, 160.3, 141.0, 139.1, 137.2, 130.2, 128.8, 128.3, 127.6, 118.2, 116.5, 114.7, 112.1, 109.1, 62.2, 55.5, 47.1, 24.5; **HRMS** (ESI) calcd for $[C_{26}H_{24}N_2O_2 + Na]^+$ 419.1730, found 419.1725; **IR** (thin film) 2231, 1727, 1606, 1490, 1204.



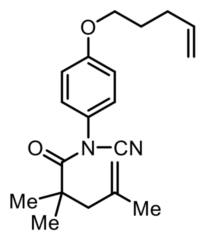
1m

Prepared from acid **S4a** and cyanamide **S2p** on a 4.5 mmol scale under standard conditions. **1m** was purified by flash column chromatography twice (8:92 → 12:88 acetone/Hex) as a thick colorless oil (1.96 mmol, 44% yield). R_f = 0.23 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 4H), 7.40 (t, *J* = 7.6 Hz, 4H), 7.36 – 7.30 (m, 2H), 6.44 (t, *J* = 2.3 Hz, 1H), 6.30 (d, *J* = 2.3 Hz, 2H), 4.77 (app s, 1H), 4.47 (app s, 1H), 3.75 (s, 6H), 3.41 (s, 2H), 1.41 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.8, 161.2, 141.1, 139.1, 137.7, 128.8, 128.4, 127.7, 116.6, 109.1, 104.6, 101.1, 62.3, 55.5, 47.2, 24.5; **HRMS** (ESI) calcd for $[C_{27}H_{26}N_2O_3 + Na]^+$ 449.1836, found 449.1828; **IR** (thin film) 2231, 1728, 1206, 1158.



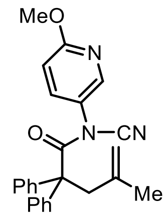
1n

Prepared from acid **S4a** and cyanamide **S2q** on a 5.0 mmol scale under standard conditions. **1n** was purified by flash column chromatography (3:7 → 1:1 CH_2Cl_2/Hex), and further precipitated (pentane) as a white powder (0.46 mmol, 9% yield). R_f = 0.44 (1:9 EtOAc/Hex); mp 108–110 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 – 7.30 (m, 10H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 1H), 4.69 (app s, 1H), 4.40 (app s, 1H), 3.41 (app s, 1H), 3.35 (app s, 1H), 2.30 (s, 3H), 1.87 (s, 3H), 1.31 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.8, 141.0, 140.0, 135.5, 132.6, 132.2, 129.4, 128.9, 128.4, 128.3, 128.0, 127.8, 127.0, 116.7, 108.9, 62.5, 47.8, 24.5, 21.1, 16.8; **HRMS** (ESI) calcd for $[C_{27}H_{26}N_2O + Na]^+$ 417.1937, found 417.1944; **IR** (thin film) 2230, 1721, 1499, 1209.



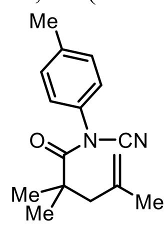
1o

Prepared from acid **S4b** and cyanamide **S2k** on a 3.0 mmol scale under standard conditions. **1o** was purified by flash column chromatography (4:96 → 8:92 EtOAc/Hex) as a colorless oil (2.07 mmol, 69% yield). R_f = 0.49 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 2H), 6.93 (d, *J* = 9.1 Hz, 2H), 5.84 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.06 (dt, *J* = 17.1, 1.5 Hz, 1H), 5.01 (d, *J* = 10.1 Hz, 1H), 4.94 (app s, 1H), 4.86 (app s, 1H), 3.97 (t, *J* = 6.5 Hz, 2H), 2.75 (s, 2H), 2.26 – 2.21 (app q, 2H), 1.89 (p, *J* = 6.8 Hz, 2H), 1.81 (s, 3H), 1.49 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.2, 159.4, 141.4, 137.5, 128.6, 127.7, 115.4 (two overlapped peaks), 114.8, 111.1, 67.4, 46.9, 44.8, 30.0, 28.2, 26.2, 23.9; **HRMS** (ESI) calcd for $[C_{20}H_{26}N_2O_2 + Na]^+$ 349.1886, found 349.1870; **IR** (thin film) 2227, 1508, 1249, 1190.



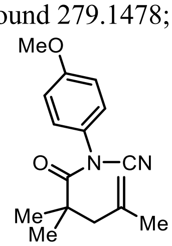
1p

Prepared from acid **S4a** and cyanamide **S2r** on a 4.0 mmol scale under modified conditions. **1p** was purified by flash column chromatography (1:9 → 15:85 EtOAc/Hex) as a tacky white solid (3.22 mmol, 81% yield). R_f = 0.62 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, J = 2.7 Hz, 1H), 7.51 (dd, J = 8.5, 1.3 Hz, 4H), 7.40 (dd, J = 8.6, 6.8 Hz, 4H), 7.37 – 7.31 (m, 3H), 6.76 (d, J = 8.9 Hz, 1H), 4.79 (t, J = 1.7 Hz, 1H), 4.53 – 4.46 (m, 1H), 3.93 (s, 3H), 3.43 (s, 2H), 1.42 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.2, 164.0, 144.7, 140.9, 139.0, 136.6, 128.7, 128.4, 127.8, 127.0, 116.6, 111.7, 108.9, 62.1, 54.0, 46.9, 24.4; **HRMS** (ESI) calcd for $[C_{25}H_{23}N_3O_2 + Na]^+$ 420.1682, found 420.1694; **IR** (thin film) 2233, 1728, 1492, 1388, 1202.



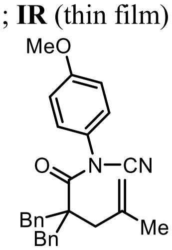
1q

Prepared from acid **S4b** and cyanamide **S2a** on a 5.0 mmol scale under standard conditions. **1q** was purified by flash column chromatography (2:98 → 5:95 EtOAc/Hex) as a pale yellow oil (4.39 mmol, 88% yield). R_f = 0.53 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 7.18 – 7.11 (m, 2H), 4.94 (d, J = 1.6 Hz, 1H), 4.87 (t, J = 1.0 Hz, 1H), 2.75 (s, 2H), 2.37 (s, 3H), 1.81 (s, 3H), 1.50 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.0, 141.4, 139.3, 133.6, 130.2, 126.1, 114.8, 111.0, 46.9, 44.9, 26.1, 23.8, 21.1; **HRMS** (ESI) calcd for $[C_{16}H_{20}N_2O + Na]^+$ 279.1468, found 279.1478; **IR** (thin film) 2228, 1725, 1509, 1190.



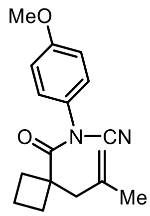
1r

Prepared from acid **S4b** and cyanamide **S2g** on a 5.0 mmol scale under standard conditions. **1r** was purified by flash column chromatography (3:7 → 1:1 CH_2Cl_2/Hex) as a colorless oil (3.61 mmol, 72% yield). R_f = 0.36 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 – 7.17 (m, 2H), 6.95 (d, J = 8.8 Hz, 2H), 4.94 (d, J = 4.5 Hz, 1H), 4.87 (app s, 1H), 3.82 (s, 3H), 2.75 (s, 2H), 1.81 (s, 3H), 1.50 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.2, 159.9, 141.4, 128.8, 127.7, 114.9, 114.8, 111.1, 55.5, 46.9, 44.8, 26.2, 23.8; **HRMS** (ESI) calcd for $[C_{16}H_{20}N_2O_2 + Na]^+$ 295.1417, found 295.1411; **IR** (thin film) 2228, 1724, 1509, 1250, 1189.



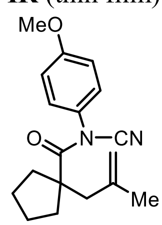
1s

Prepared from acid **S4c** and cyanamide **S2g** on a 4.0 mmol scale under standard conditions. **1s** was purified by flash column chromatography twice (first: 3:7 → 1:1 CH_2Cl_2/Hex; second: 3:97 → 1:9 EtOAc/Hex) as a thick colorless oil (1.28 mmol, 32% yield). R_f = 0.56 (1:1 CH_2Cl_2/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 10H), 6.87 (app s, 4H), 5.09 (app s, 1H), 4.91 (app s, 1H), 3.79 (s, 3H), 3.36 (d, J = 14.7 Hz, 2H), 3.32 (d, J = 14.8 Hz, 2H), 2.74 (s, 2H), 1.85 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.9, 159.9, 141.9, 136.5, 130.5, 128.8, 128.4, 127.7, 127.1, 114.8, 112.5, 110.7, 55.5, 52.6, 41.1, 40.2, 25.1; **HRMS** (ESI) calcd for $[C_{28}H_{28}N_2O_2 + Na]^+$ 447.2043, found 447.2050; **IR** (thin film) 2228, 1723, 1508, 1250, 1181.



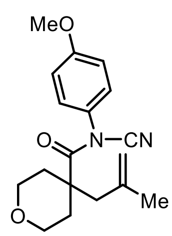
1t

Prepared from acid **S4d** and cyanamide **S2g** on a 4.0 mmol scale under modified conditions. **1t** was purified by flash column chromatography (5:95 → 1:9 EtOAc/Hex) as a colorless oil (3.51 mmol, 88% yield). R_f = 0.36 (1:9 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (dt, J = 9.1, 2.2 Hz, 2H), 6.94 (dt, J = 9.1, 2.2 Hz, 2H), 4.90 – 4.88 (m, 1H), 4.87 (t, J = 1.7 Hz, 1H), 3.82 (s, 3H), 2.96 (s, 2H), 2.84 – 2.73 (m, 2H), 2.32 – 2.21 (m, 2H), 2.12 – 1.99 (m, 1H), 1.96 – 1.83 (m, 1H), 1.75 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.6, 159.8, 142.1, 127.9, 127.4, 114.8, 114.3, 110.4, 55.5, 49.4, 45.1, 31.4, 23.0, 15.2; **HRMS** (ESI) calcd for $[C_{17}H_{20}N_2O_2 + Na]^+$ 307.1417, found 307.1430; **IR** (thin film) 2230, 1728, 1509, 1251, 1188.



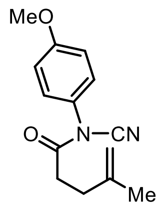
1u

Prepared from acid **S4e** and cyanamide **S2g** on a 4.0 mmol scale under modified conditions. **1u** was purified by flash column chromatography (5:95 → 15:85 EtOAc/Hex) as a pale yellow oil (3.27 mmol, 82% yield). R_f = 0.39 (1:9 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (dt, J = 9.0, 2.1 Hz, 2H), 6.94 (dt, J = 9.0, 2.1 Hz, 2H), 4.93 – 4.92 (m, 1H), 4.91 (t, J = 1.6 Hz, 1H), 3.82 (s, 3H), 2.82 (d, J = 1.1 Hz, 2H), 2.48 (dddd, J = 13.5, 6.8, 3.7, 1.6 Hz, 2H), 1.87 (dddd, J = 13.2, 7.6, 5.2, 1.8 Hz, 2H), 1.79 (s, 3H), 1.76 – 1.64 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 159.8, 142.2, 128.7, 127.6, 114.8, 114.4, 111.0, 55.7, 55.5, 46.1, 37.1, 25.1, 23.5; **HRMS** (ESI) calcd for $[C_{18}H_{22}N_2O_2 + Na]^+$ 321.1573, found 321.1575; **IR** (thin film) 2228, 1724, 1509, 1250, 1184.



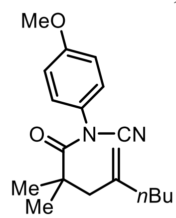
1v

Prepared from acid **S4f** and cyanamide **S2g** on a 4.0 mmol scale under modified conditions. **1v** was purified by flash column chromatography twice (1:9 → 1:4 EtOAc/Hex) as a thick pale yellow oil (2.05 mmol, 51% yield). R_f = 0.34 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (dt, J = 9.0, 2.1 Hz, 2H), 6.97 (dt, J = 8.9, 2.4 Hz, 2H), 4.98 – 4.97 (m, 1H), 4.97 – 4.96 (m, 1H), 3.89 (dt, J = 12.2, 4.0 Hz, 2H), 3.83 (s, 3H), 3.59 (ddd, J = 12.5, 10.5, 2.4 Hz, 2H), 2.81 (s, 2H), 2.54 – 2.48 (m, 2H), 1.89 – 1.77 (m, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.2, 160.1, 140.3, 128.4, 127.8, 115.8, 115.0, 110.8, 64.8, 55.6, 47.3, 46.1, 34.8, 23.9; **HRMS** (ESI) calcd for $[C_{18}H_{22}N_2O_3 + Na]^+$ 337.1523, found 337.1518; **IR** (thin film) 2227, 1723, 1509, 1250, 1185, 1114.



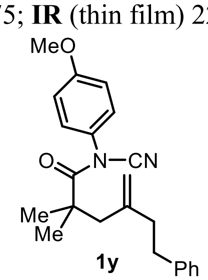
1w

Prepared from acid **S4o** and cyanamide **S2g** on a 3.0 mmol scale under standard conditions. **1w**was purified by flash column chromatography (1:9 → 1:4 EtOAc/Hex) as a pale yellow oil (1.79 mmol, 60% yield). R_f = 0.21 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 6.96 (dd, *J* = 9.0, 0.8 Hz, 2H), 4.81 (app s, 1H), 4.74 (app s, 1H), 3.83 (s, 3H), 2.87 (br app s, 2H), 2.45 (t, *J* = 7.6 Hz, 2H), 1.77 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.7, 160.0, 143.0, 127.3, 127.0, 115.0, 111.3, 110.0, 55.6, 32.7, 32.0, 22.4; **HRMS** (ESI) calcd for $[C_{14}H_{16}N_2O_2 + Na]^+$ 267.1104, found 267.1106; **IR** (thin film) 2233, 1735, 1509, 1251.



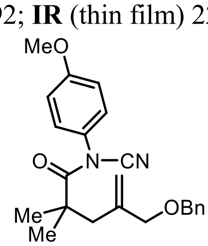
1x

Prepared from acid **S4g** and cyanamide **S2g** on a 4.0 mmol scale under modified conditions. **1x** was purified by flash column chromatography (2:3 → 3:2 CH_2Cl_2/Hex) as a colorless oil (2.72 mmol, 68% yield). R_f = 0.44 (1:1 CH_2Cl_2/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (dt, *J* = 9.0, 2.0 Hz, 2H), 6.95 (dt, *J* = 9.0, 2.4 Hz, 2H), 4.94 (d, *J* = 1.5 Hz, 1H), 4.87 (d, *J* = 1.4 Hz, 1H), 3.82 (s, 3H), 2.74 (s, 2H), 2.08 – 2.02 (m, 2H), 1.52 – 1.42 (m, 8H), 1.39 – 1.28 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.2, 159.9, 145.6, 128.8, 127.7, 114.9, 113.0, 111.1, 55.5, 45.1, 45.0, 36.9, 30.1, 26.2, 22.4, 14.0; **HRMS** (ESI) calcd for $[C_{19}H_{26}N_2O_2 + Na]^+$ 337.1886, found 337.1875; **IR** (thin film) 2230, 1724, 1509.



1y

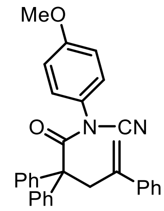
Prepared from acid **S4h** and cyanamide **S2g** on a 3.5 mmol scale under modified conditions. **1y** was purified by flash column chromatography (5:95 → 1:9 EtOAc/Hex) as a pale yellow oil (2.55 mmol, 73% yield). R_f = 0.32 (1:9 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.23 – 7.17 (m, 3H), 7.10 – 7.05 (m, 2H), 6.91 – 6.85 (m, 2H), 5.00 (d, *J* = 1.4 Hz, 1H), 4.93 (app s, 1H), 3.80 (s, 3H), 2.87 – 2.75 (m, 4H), 2.36 (dd, *J* = 8.9, 7.4 Hz, 2H), 1.50 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.2, 159.9, 144.8, 141.6, 128.7, 128.37, 128.35, 127.7, 125.9, 114.8, 113.7, 111.1, 55.5, 45.5, 45.0, 38.9, 34.4, 26.2; **HRMS** (ESI) calcd for $[C_{23}H_{26}N_2O_2 + Na]^+$ 385.1886, found 385.1892; **IR** (thin film) 2227, 1724, 1508, 1250, 1183.



1z

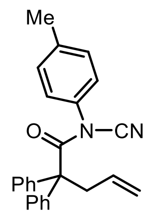
Prepared from acid **S4i** and cyanamide **S2g** on a 3.4 mmol scale under modified conditions. **1z** was purified by flash column chromatography (5:95 → 15:85 EtOAc/Hex) as a colorless oil (1.72 mmol, 51% yield). R_f = 0.42

(15:85 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 7.30 – 7.27 (m, 1H), 7.18 – 7.13 (m, 2H), 6.93 – 6.88 (m, 2H), 5.25 (d, *J* = 1.5 Hz, 1H), 5.12 (d, *J* = 1.3 Hz, 1H), 4.50 (s, 2H), 3.98 (s, 2H), 3.81 (s, 3H), 2.83 (d, *J* = 1.1 Hz, 2H), 1.50 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.2, 159.9, 142.2, 138.0, 128.8, 128.4, 127.8, 127.8, 127.6, 116.3, 114.8, 111.1, 73.1, 71.8, 55.5, 44.7, 42.2, 26.1; **HRMS** (ESI) calcd for $[C_{23}H_{26}N_2O_3 + Na]^+$ 401.1836, found 401.1833; **IR** (thin film) 2230, 1723, 1509, 1250, 1182.



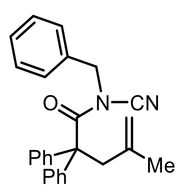
1aa

Prepared from acid **S4j** and cyanamide **S2g** on a 4.0 mmol scale under modified conditions. **1aa** was purified by flash column chromatography twice (first: 1:4 → 1:1 CH_2Cl_2/Hex; second: 8:92 → 1:4 Et_2O/Hex) as a white foam (2.46 mmol, 61% yield). R_f = 0.24 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 4H), 7.35 – 7.16 (m, 11H), 6.83 – 6.78 (m, 2H), 6.73 – 6.68 (m, 2H), 5.18 (d, *J* = 1.4 Hz, 1H), 4.70 (d, *J* = 1.3 Hz, 1H), 3.93 (s, 2H), 3.76 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.6, 159.8, 143.9, 142.3, 139.4, 129.3, 128.7, 128.1, 128.0, 127.6, 127.4, 127.2, 126.7, 120.1, 114.6, 109.5, 62.0, 55.5, 44.1; **HRMS** (ESI) calcd for $[C_{31}H_{26}N_2O_2 + Na]^+$ 481.1886, found 481.1894; **IR** (thin film) 2230, 1725, 1508, 1249, 1202.



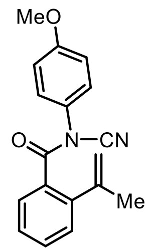
1ab

Prepared from acid **S4k** and cyanamide **S2a** on a 5.0 mmol scale under standard conditions. **1ab** was purified by flash column chromatography (3:7 → 1:1 CH_2Cl_2/Hex), and further precipitated (CH_2Cl_2/Hex, 1:40 v/v) as a white powder (2.58 mmol, 52% yield). R_f = 0.54 (15:85 EtOAc/Hex); mp 99–100 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 – 7.39 (m, 8H), 7.39 – 7.31 (m, 2H), 7.24 – 7.18 (m, 2H), 7.12 – 7.05 (m, 2H), 5.65 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.05 (ddd, *J* = 17.1, 3.4, 1.5 Hz, 1H), 5.01 – 4.98 (m, 1H), 3.36 (d, *J* = 7.0 Hz, 2H), 2.36 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.0, 139.4, 138.9, 133.6, 133.2, 130.2, 128.8, 128.5, 127.8, 126.0, 119.2, 109.2, 62.1, 44.8, 21.1; **HRMS** (ESI) calcd for $[C_{25}H_{22}N_2O + Na]^+$ 389.1624, found 389.1626; **IR** (thin film) 2231, 1725, 1508, 1206.



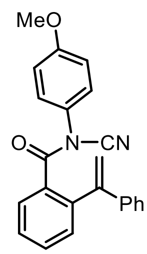
1ac

Prepared from acid **S4a** and cyanamide **S2s** on a 5.0 mmol scale under standard conditions. **1ac** was purified by flash column chromatography (3:7 → 1:1 CH_2Cl_2/Hex) as a colorless oil (3.98 mmol, 80% yield). R_f = 0.55 (15:85 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 13H), 7.18 (dd, *J* = 7.4, 1.8 Hz, 2H), 4.72 (s, 2H), 4.63 (d, *J* = 1.9 Hz, 1H), 4.30 (app s, 1H), 3.30 (s, 2H), 1.31 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.8, 140.9, 138.9, 133.8, 128.9, 128.70, 128.65, 128.6, 128.2, 127.5, 116.4, 109.9, 62.0, 52.7, 47.1, 24.4; **HRMS** (ESI) calcd for $[C_{26}H_{24}N_2O + Na]^+$ 403.1781, found 403.1781; **IR** (thin film) 2231, 1710, 1496, 1193.



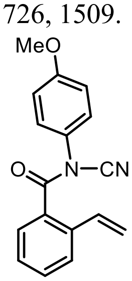
1ad

Prepared from acid **S4l** and cyanamide **S2g** on a 5.0 mmol scale under modified conditions. **1ad** was purified by flash column chromatography (2:3 → 3:2 CH_2Cl_2/Hex) as an oily solid (2.68 mmol, 54% yield). R_f = 0.20 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.42 – 7.37 (m, 2H), 7.28 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 5.34 (app s, 1H), 5.13 (app s, 1H), 3.83 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.0, 159.8, 143.2, 141.7, 131.4, 130.7, 128.1, 127.6, 127.5, 127.4, 126.8, 117.2, 114.8, 110.0, 55.6, 23.2; **HRMS** (ESI) calcd for $[C_{18}H_{16}N_2O_2 + Na]^+$ 315.1104, found 315.1116; **IR** (thin film) 2235, 1723, 1509, 1250.



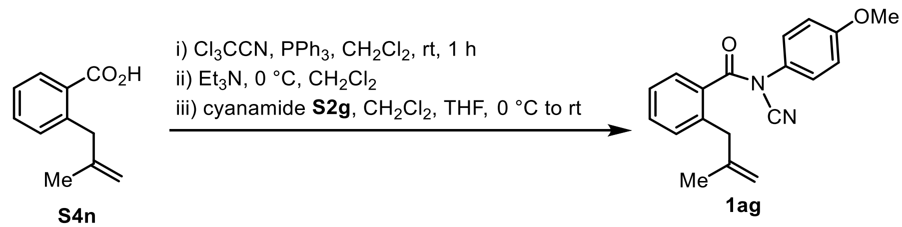
1ae

Prepared from acid **S4m** and cyanamide **S2g** on a 4.8 mmol scale under modified conditions. **1ae** was purified by flash column chromatography (1:9 → 1:4 EtOAc/Hex), and further precipitated (CH_2Cl_2/pentane, 1:40 v/v) as a white powder (3.02 mmol, 63% yield). R_f = 0.43 (1:4 EtOAc/Hex); mp 103–105 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (dd, J = 7.6, 1.3 Hz, 1H), 7.58 (td, J = 7.6, 1.4 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.39 – 7.30 (m, 5H), 6.82 (dt, J = 9.1, 2.1 Hz, 2H), 6.78 (dt, J = 9.2, 2.1 Hz, 2H), 5.74 (app s, 1H), 5.49 (app s, 1H), 3.78 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.5, 159.7, 147.6, 141.2, 140.3, 131.9, 131.5, 131.2, 128.5, 128.3, 127.95, 127.89, 127.8, 127.0, 126.8, 117.4, 114.6, 110.0, 55.5; **HRMS** (ESI) calcd for $[C_{23}H_{18}N_2O_2 + Na]^+$ 377.1260, found 377.1268; **IR** (thin film) 2253, 1726, 1509.

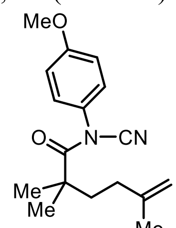


1af

Prepared from acid **S4r** and cyanamide **S2a** on a 3.2 mmol scale under modified conditions. **1af** was purified by flash column chromatography (5:95 → 1:4 EtOAc/Hex) as a waxy solid (1.33 mmol, 41% yield). R_f = 0.37 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 1H), 7.51 – 7.47 (m, 2H), 7.36 (td, J = 7.6, 1.2 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.00 – 6.88 (m, 3H), 5.79 (d, J = 17.4 Hz, 1H), 5.48 (d, J = 11.0 Hz, 1H), 3.82 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.1, 159.9, 136.5, 132.9, 131.7, 130.2, 127.7, 127.6, 127.4, 127.0, 126.7, 118.8, 114.9, 109.6, 55.6; **HRMS** (ESI) calcd for $[C_{17}H_{14}N_2O_2 + Na]^+$ 301.0947, found 301.0947; **IR** (thin film) 2238, 1719, 1509, 1251.

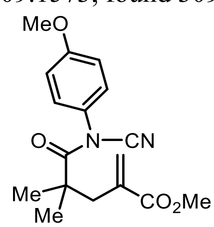


Synthesis of 1ag following a different procedure:[28] To a solution of acid **S4n** (1057 mg, 6.0 mmol) and Cl_3CCN (1733 mg, 12.0 mmol) in CH_2Cl_2 (6.0 mL) was added PPh_3 (3147 mg, 12 mmol) in CH_2Cl_2 (6.0 mL) at room temperature. The resulting mixture was stirred for 1 h and cooled to 0 °C, whereupon a solution of Et_3N (1.0 mL, 7.5 mmol) in CH_2Cl_2 (3.0 mL) was added, followed by cyanamide **S2g** (741 mg, 5.0 mmol) in CH_2Cl_2–THF (4 mL, 3:1 v/v). The resulting mixture was allowed to warm to room temperature and stir overnight, which was then diluted with Et_2O (30 mL), filtered through a short Celite column, concentrated, and purified by flash column chromatography (1:9 → 15:85 EtOAc/Hex) to afford **1ag** as an oily yellow solid (4.57 mmol, 91% yield). R_f = 0.42 (15:85 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 1H), 7.47 (td, J = 7.6, 1.4 Hz, 1H), 7.36 – 7.29 (m, 4H), 6.97 (d, J = 8.9 Hz, 2H), 4.93 (app s, 1H), 4.70 (app s, 1H), 3.84 (s, 3H), 3.53 (s, 2H), 1.73 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.0, 159.9, 144.3, 138.7, 131.7, 131.6, 131.3, 127.7, 127.4, 127.0, 126.4, 114.9, 113.1, 110.0, 55.6, 41.4, 22.4; **HRMS** (ESI) calcd for $[C_{19}H_{18}N_2O_2 + Na]^+$ 329.1260, found 329.1269; **IR** (thin film) 2236, 1721, 1509, 1252.



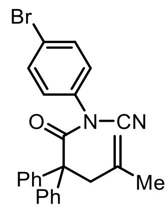
1ah

Prepared from acid **S4p** and cyanamide **S2g** on a 4.0 mmol scale under modified conditions. **1ah** was purified by flash column chromatography (5:95 → 15:85 EtOAc/Hex) as a colorless oil (3.29 mmol, 82% yield). R_f = 0.51 (1:1 CH_2Cl_2/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (dt, J = 9.2, 2.4 Hz 2H), 6.95 (dt, J = 8.9, 2.1 Hz 2H), 4.77 (m, 1H), 4.76 (app s, 1H), 3.82 (s, 3H), 2.07 (app s, 4H), 1.80 (s, 3H), 1.49 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.1, 159.9, 144.7, 128.7, 127.7, 114.9, 110.8, 110.7, 55.5, 44.9, 37.6, 33.1, 25.2, 22.5; **HRMS** (ESI) calcd for $[C_{17}H_{22}N_2O_2 + Na]^+$ 309.1573, found 309.1569; **IR** (thin film) 2228, 1725, 1509, 1250.



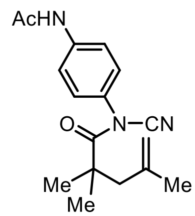
1ai

Prepared from acid **S4q** and cyanamide **S2a** on a 2.6 mmol scale under modified conditions. **1ai** was purified by flash column chromatography (3:2 CH_2Cl_2/Hex → CH_2Cl_2) as a colorless oil (1.57 mmol, 61% yield). R_f = 0.61 (CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 6.97 – 6.93 (m, 2H), 6.31 (d, J = 1.3 Hz, 1H), 5.70 (d, J = 1.2 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 3.03 (d, J = 1.0 Hz, 2H), 1.46 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.5, 167.4, 159.9, 136.3, 129.1, 129.0, 127.9, 114.8, 111.3, 55.5, 52.1, 44.8, 40.9, 25.5; **HRMS** (ESI) calcd for $[C_{17}H_{20}N_2O_4 + Na]^+$ 339.1315, found 339.1318; **IR** (thin film) 2230, 1721, 1509, 1250.



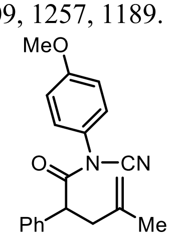
1aj

Prepared from acid **S4a** and cyanamide **S2f** on a 5.0 mmol scale under standard conditions. **1aj** was purified by flash column chromatography (3:7 → 1:1 CH_2Cl_2/Hex) as a white solid (1.77 mmol, 35% yield). R_f = 0.33 (1:1 CH_2Cl_2/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.47 (m, 6H), 7.41 (t, J = 7.6 Hz, 4H), 7.37 – 7.30 (m, 2H), 7.08 (d, J = 8.6 Hz, 2H), 4.78 (d, J = 1.2 Hz, 1H), 4.48 (app s, 1H), 3.42 (s, 2H), 1.41 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.7, 141.0, 138.9, 135.3, 132.8, 128.7, 128.4, 127.8, 127.7, 123.1, 116.6, 108.7, 62.3, 47.1, 24.5; **HRMS** (ESI) calcd for $[C_{25}H_{21}BrN_2O + Na]^+$ 467.0729, found 467.0729; **IR** (thin film) 2232, 1727, 1486, 1189.



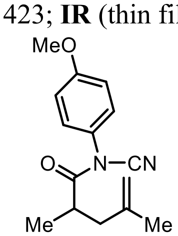
1ak

Prepared from acid **S4b** and cyanamide **S2i** on a 5.0 mmol scale under standard conditions. **1ak** was purified by flash column chromatography twice (first: 1:20 MeOH/CH_2Cl_2; second: Et_2O) as a pale yellow oil (3.31 mmol, 66% yield). R_f = 0.47 (5:95 MeOH/CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (br s, 1H), 7.58 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 4.95 (app s, 1H), 4.86 (app s, 1H), 2.75 (s, 2H), 2.15 (s, 3H), 1.81 (s, 3H), 1.50 (d, J = 1.4 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.2, 168.6, 141.3, 138.8, 131.5, 127.0, 120.5, 114.9, 110.8, 46.9, 45.0, 26.1, 24.5, 23.9; **HRMS** (ESI) calcd for $[C_{17}H_{21}N_3O_2 + Na]^+$ 322.1526, found 322.1526; **IR** (thin film) 2229, 1725, 1676, 1509, 1257, 1189.



1al

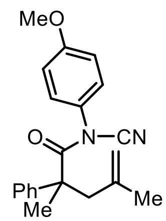
Prepared from acid **S4s** and cyanamide **S2g** on a 4.0 mmol scale under modified conditions. **1al** was purified by flash column chromatography (5:95 → 15:85 EtOAc/Hex) as a pale yellow oil (2.42 mmol, 61% yield). R_f = 0.31 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 5H), 7.11 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 9.2 Hz, 2H), 4.83 (app s, 1H), 4.74 (app s, 1H), 4.51 (br m, 1H), 3.81 (s, 3H), 2.94 (dd, J = 14.7, 9.2 Hz, 1H), 2.50 – 2.34 (br m, 1H), 1.75 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.3 (br), 160.1 (br), 142.0, 136.7, 129.0, 128.1, 128.0, 127.5 (br), 127.1, 114.8, 112.7, 110.0 (br), 55.6, 48.6 (br), 42.0, 22.8; **HRMS** (ESI) calcd for $[C_{20}H_{20}N_2O_2 + Na]^+$ 343.1417, found 343.1423; **IR** (thin film) 2233, 1734, 1508, 1251.



1am

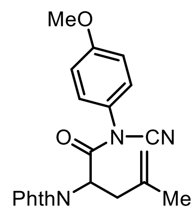
Prepared from acid **S4t** and cyanamide **S2g** on a 3.0 mmol scale under modified conditions. **1al** was purified by flash column chromatography (1:9 EtOAc/Hex) as a pale yellow oil (1.47 mmol, 49% yield). R_f = 0.56 (3:7

EtOAc/Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 6.99 – 6.88 (m, 2H), 4.88 – 4.82 (m, 1H), 4.77 (app s, 1H), 3.82 (s, 3H), 3.35 (br app s, 1H), 2.55 (dd, J = 14.0, 7.6 Hz, 1H), 2.17 (dd, J = 14.0, 6.9 Hz, 1H), 1.77 (s, 3H), 1.28 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.5, 160.0, 141.9, 127.3, 127.1, 114.9, 113.2, 110.1, 55.5, 41.8, 36.6 (br), 22.3, 17.0; **HRMS** (ESI) calcd for $[C_{15}H_{18}N_2O_2 + Na]^+$ 281.1260, found 281.1266; **IR** (thin film) 2231, 1736, 1509, 1251, 1180.



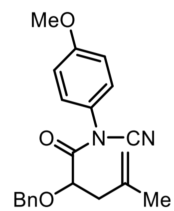
1an

Prepared from acid **S4u** and cyanamide **S2g** on a 2.0 mmol scale under modified conditions. **1an** was purified by flash column chromatography (1:9 EtOAc/Hex) as an off-white tacky solid (0.72 mmol, 36% yield). R_f = 0.42 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.39 – 7.31 (m, 3H), 7.16 – 7.10 (m, 2H), 6.96 – 6.87 (m, 2H), 4.95 (t, J = 1.8 Hz, 1H), 4.80 (dd, J = 2.1, 1.0 Hz, 1H), 3.81 (s, 3H), 3.19 (d, J = 14.0 Hz, 1H), 2.79 (d, J = 13.7 Hz, 1H), 1.80 (s, 3H), 1.48 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.3, 159.9, 141.6, 141.0, 129.0, 128.6, 127.8, 127.5, 126.4, 116.6, 114.8, 109.5, 100.0, 55.6, 52.2, 46.3, 24.1; **HRMS** (ESI) calcd for $[C_{21}H_{22}N_2O_2 + Na]^+$ 357.1573, found 357.1578; **IR** (thin film) 2229, 1719, 1507, 1245, 1220.



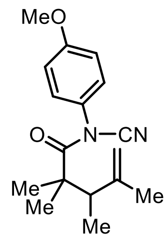
1ao

Prepared from acid **S4v** and cyanamide **S2g** on a 1.67 mmol scale under modified conditions. **1ao** was purified by flash column chromatography (3:7 EtOAc/Hex) as a white foam (0.56 mmol, 33% yield). R_f = 0.38 (3:7 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 5.5, 3.1 Hz, 2H), 7.76 (dd, J = 5.5, 3.0 Hz, 2H), 7.33 – 7.19 (m, 2H), 6.97 – 6.86 (m, 2H), 5.42 (dd, J = 11.0, 4.3 Hz, 1H), 4.74 (app s, 1H), 4.66 (app s, 1H), 3.80 (s, 3H), 3.05 (dd, J = 14.0, 11.0 Hz, 1H), 2.84 (dd, J = 14.1, 4.3 Hz, 1H), 1.80 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 166.8, 160.2, 139.9, 134.5, 131.3, 127.2, 127.1, 123.8, 115.6, 115.0, 108.9, 55.6, 50.6, 37.4, 21.6; **HRMS** (ESI) calcd for $[C_{22}H_{19}N_3O_4 + Na]^+$ 412.1268, found 412.1273; **IR** (thin film) 2233, 1777, 1717, 1508, 1384, 1251.



1ap

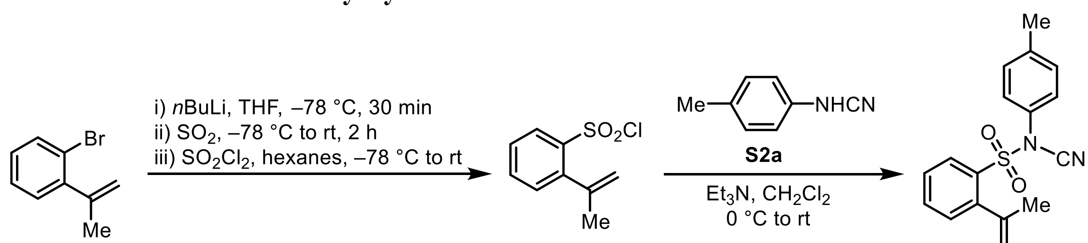
Prepared from acid **S4w** and cyanamide **S2g** on a 5.0 mmol scale under modified conditions. **1ap** was purified by flash column chromatography (15:85 EtOAc/Hex) as a pale yellow oil (4.63 mmol, 93% yield). R_f = 0.23 (1:9 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 5H), 7.16 – 7.08 (m, 2H), 6.96 – 6.86 (m, 2H), 4.92 (app s, 1H), 4.88 (app s, 1H), 4.68 (d, J = 11.5 Hz, 1H), 4.66 (br t, 1H), 4.60 (d, J = 11.5 Hz, 1H), 3.81 (s, 3H), 2.65 (d, J = 6.7 Hz, 2H), 1.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 160.0, 140.0, 136.5, 128.5, 128.3, 128.2, 127.2, 126.8, 114.9, 114.7, 109.3, 72.9, 55.5, 40.6, 22.5 (one peak overlapped by $CDCl_3$); **HRMS** (ESI) calcd for $[C_{21}H_{22}N_2O_3 + Na]^+$ 373.1523, found 373.1538; **IR** (thin film) 2232, 1745, 1509, 1251, 1183.



1aq

Prepared from acid **S4x** and cyanamide **S2g** on a 4.0 mmol scale under modified conditions. **1aq** was purified by flash column chromatography (3:97 → 1:9 EtOAc/Hex) as a colorless oil (2.93 mmol, 73% yield). R_f = 0.35 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 – 7.10 (m, 2H), 6.99 – 6.91 (m, 2H), 5.05 – 5.01 (m, 1H), 4.96 (t, J = 1.6 Hz, 1H), 3.82 (s, 3H), 3.36 (q, J = 7.1 Hz, 1H), 1.80 (s, 3H), 1.48 (s, 3H), 1.40 (s, 3H), 1.14 (d, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.4, 159.9, 146.1, 129.0, 127.8, 114.8, 114.4, 111.2, 55.5, 48.6, 45.0, 23.1, 22.2, 21.5, 14.7; **HRMS** (ESI) calcd for $[C_{17}H_{22}N_2O_2 + Na]^+$ 309.1573, found 309.1568; **IR** (thin film) 2227, 1723, 1509, 1250, 1179.

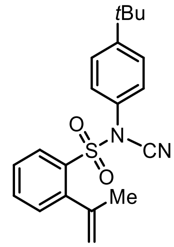
7. Synthesis of substrates: *N*-sulfonyl cyanamides



Synthesis of substrate 3a as a representative example: To a solution of 1-bromo-2-(prop-1-en-2-yl)benzene[29] (8672 mg, 44 mmol) in THF (40 mL) was dropwise added *n*BuLi (2.5 M Hex, 16 mL, 40 mmol) at –78 °C. The reaction was stirred at –78 °C for 30 min, whereupon a stock solution of SO_2 (ca. 2.3 M THF, 34.8 mL, 80 mmol)[30] was dropwise added. The reaction was allowed to warm to room temperature and stirred for additional 2 h. The reaction was concentrated to dryness to afford the lithium sulfinate as a white solid, which was triturated with pentane (20 mL × 2) to remove the residual 1-bromo-2-(prop-1-en-2-yl)benzene, followed by suspended in hexanes (150 mL) and cooled to –78 °C. To this suspension was slowly added SO_2Cl_2 (2.92 mL, 36 mmol) in hexanes (40 mL). The resulting mixture was vigorously stirred at –78 °C for 20 min, which was then allowed to warm to room temperature and stir for additional 30 min. The reaction was quenched with saturated aqueous $NaHCO_3$ (20 mL), diluted with H_2O (20 mL), and extracted with Et_2O (30 mL × 3). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, and concentrated. The resulting mixture was purified by flash column chromatography (5:95 EtOAc/Hex) to afford sulfonyl chloride **S5a** as a pale yellow oil (6684 mg, 30.8 mmol, 86% yield over 2 steps based on SO_2Cl_2). R_f = 0.59 (1:9 EtOAc/Hex). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 8.2, 1.3 Hz, 1H), 7.68 (td, J = 7.6, 1.3 Hz, 1H), 7.50 (ddd, J = 8.7, 7.6, 1.4 Hz, 1H), 7.35 (dd, J = 7.6, 1.4 Hz, 1H), 5.38 (t, J = 1.5 Hz, 1H), 5.08 (t, J = 1.2 Hz, 1H), 2.17 (t, J = 1.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.0, 142.3, 141.9, 135.0, 131.5, 128.8, 127.9, 117.6, 25.1.

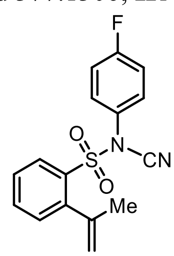
Next, the above obtained sulfonyl chloride **S5a** (520 mg, 2.4 mmol) was dissolved in CH_2Cl_2 (2.0 mL) and added to a solution of cyanamide **S2a** (2.0 mmol) and Et_3N (0.42 mL, 3.0 mmol) in CH_2Cl_2 (4.0 mL) at 0 °C. The reaction was allowed to warm to room temperature and stir for 4–6 h until TLC indicated the complete consumption of staring material. The mixture was then diluted with CH_2Cl_2 (30 mL), washed with 1 M HCl (10 mL), and separated. The organic phase was washed with brine (10 mL), dried over $MgSO_4$, and concentrated. The resulting mixture was purified by flash column chromatography (Hex → 1:9 EtOAc/Hex) to afford substrate **3a** as a pale yellow oil (1.72 mmol, 86% yield). R_f = 0.51 (1:4 EtOAc/Hex). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (dd, J = 8.1, 1.3 Hz, 1H), 7.64 (td, J = 7.6, 1.3 Hz, 1H), 7.40 (ddd, J = 8.5, 7.5, 1.4 Hz, 1H), 7.33 (dd, J = 7.6, 1.4 Hz, 1H), 7.14 (d, J = 8.3 Hz, 2H), 7.09 – 7.03 (m, 2H), 5.30 (t, J = 1.5 Hz, 1H), 4.76

(t, J = 1.1 Hz, 1H), 2.34 (s, 3H), 2.10 (t, J = 1.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.2, 143.0, 140.2, 134.8, 134.0, 131.6, 131.4, 130.9, 130.4, 127.6, 126.1, 117.2, 108.1, 25.4, 21.1; **HRMS** (ESI) calcd for $[C_{17}H_{16}N_2O_2S + Na]^+$ 335.0825, found 335.0818; **IR** (thin film) 2236, 1505, 1380, 1181.



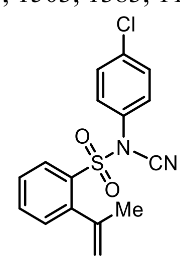
3b

Prepared from sulfonyl chloride **S5a** and cyanamide **S2c** on a 2.0 mmol scale. **3b** was purified by flash column chromatography (2:98 → 1:9 EtOAc/Hex) as a white solid (1.70 mmol, 85% yield). R_f = 0.55 (1:4 EtOAc/Hex). mp 84–86 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (dd, J = 8.1, 1.3 Hz, 1H), 7.65 (d, J = 1.4 Hz, 1H), 7.43 (d, J = 1.3 Hz, 1H), 7.35 (d, J = 8.8 Hz, 2H), 7.31 (dd, J = 7.6, 1.3 Hz, 1H), 7.09 (d, J = 8.7 Hz, 2H), 5.24 (app s, 1H), 4.64 (app s, 1H), 2.07 (s, 3H), 1.28 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.3, 145.2, 143.0, 134.8, 134.1, 131.5, 131.4, 130.8, 127.7, 126.8, 125.8, 117.0, 108.2, 34.8, 31.1, 25.4; **HRMS** (ESI) calcd for $[C_{20}H_{22}N_2O_2S + Na]^+$ 377.1294, found 377.1306; **IR** (thin film) 2233, 1504, 1381, 1182.



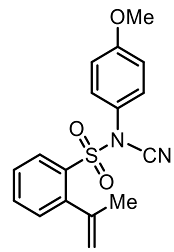
3c

Prepared from sulfonyl chloride **S5a** and cyanamide **S2d** on a 2.0 mmol scale. **3c** was purified by flash column chromatography (Hex → 1:9 EtOAc/Hex) as a yellow oil (1.68 mmol, 84% yield). R_f = 0.53 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (dd, J = 8.1, 1.3 Hz, 1H), 7.66 (td, J = 7.5, 1.3 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.34 (dd, J = 7.7, 1.4 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.05 (dd, J = 9.1, 7.9 Hz, 2H), 5.30 (app s, 1H), 4.74 (app s, 1H), 2.11 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.0 (d, $^1J_{F–C}$ = 251.7 Hz), 145.3, 143.1, 135.1, 133.7, 131.6, 131.0, 130.1 (d, $^4J_{F–C}$ =3.2 Hz), 128.6 (d, $^3J_{F–C}$ = 9.1 Hz), 127.8, 117.2, 117.0 (d, $^2J_{F–C}$ = 23.3 Hz), 107.9, 25.5; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –109.4; **HRMS** (ESI) calcd for $[C_{16}H_{13}FN_2O_2S + Na]^+$ 339.0574, found 339.0565; **IR** (thin film) 2237, 1503, 1383, 1181.



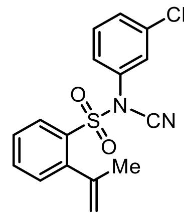
3d

Prepared from sulfonyl chloride **S5a** and cyanamide **S2e** on a 2.0 mmol scale. **3d** was purified by flash column chromatography (5:95 → 1:9 EtOAc/Hex) as a white solid (1.78 mmol, 89% yield). R_f = 0.49 (1:4 EtOAc/Hex); mp 68–70 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 8.1, 1.3 Hz, 1H), 7.66 (td, J = 7.5, 1.3 Hz, 1H), 7.43 (ddd, J = 8.6, 7.6, 1.4 Hz, 1H), 7.36 – 7.32 (m, 3H), 7.16 (dt, J = 8.8, 2.2 Hz, 2H), 5.31 (app s, 1H), 4.75 (app s, 1H), 2.11 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.2, 143.0, 135.8, 135.2, 133.7, 132.8, 131.6, 131.0, 130.1, 127.8, 127.2, 117.3, 107.6, 25.4; **HRMS** (ESI) calcd for $[C_{16}H_{13}ClN_2O_2S + Na]^+$ 355.0278, found 355.0275; **IR** (thin film) 2253, 2239, 1486, 1184.



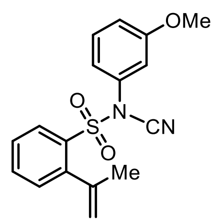
3e

Prepared from sulfonyl chloride **S5a** and cyanamide **S2g** on a 2.0 mmol scale. **3e** was purified by flash column chromatography (1:9 → 1:4 EtOAc/Hex) as a colorless oil (1.78 mmol, 89% yield). R_f = 0.30 (1:4 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 8.1, 1.3 Hz, 1H), 7.64 (td, J = 7.6, 1.3 Hz, 1H), 7.39 (ddd, J = 8.0, 7.5, 1.4 Hz, 1H), 7.34 (dd, J = 7.7, 1.3 Hz, 1H), 7.12 – 7.03 (m, 2H), 6.87 – 6.77 (m, 2H), 5.31 (t, J = 1.5 Hz, 1H), 4.78 (t, J = 1.1 Hz, 1H), 3.79 (s, 3H), 2.11 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.7, 145.2, 143.1, 134.8, 133.9, 131.4, 131.0, 128.3, 127.6, 126.5, 117.1, 114.9, 108.2, 55.6, 25.5; **HRMS** (ESI) calcd for $[C_{17}H_{16}N_2O_3S + Na]^+$ 351.0774, found 351.0781; **IR** (thin film) 2253, 1507, 1383, 1265, 1182.



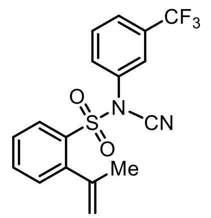
3f

Prepared from sulfonyl chloride **S5a** and cyanamide **S2l** on a 2.0 mmol scale. **3f** was purified by flash column chromatography (1:9 → 1:4 EtOAc/Hex) as a white solid (1.62 mmol, 81% yield). mp 58–61 °C; R_f = 0.43 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.2, 1.3 Hz, 1H), 7.67 (td, J = 7.5, 1.3 Hz, 1H), 7.45 (ddd, J = 8.7, 7.5, 1.4 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.30 (t, J = 8.0 Hz, 1H), 7.26 (dd, J = 3.9, 1.8 Hz, 1H), 7.13 (ddd, J = 8.0, 2.2, 1.1 Hz, 1H), 5.30 (app s, 1H), 4.73 (app s, 1H), 2.11 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.3, 143.0, 135.4, 135.3, 135.2, 133.7, 131.6, 131.0, 130.7, 129.8, 127.8, 125.7, 123.5, 117.3, 107.4, 25.4; **HRMS** (ESI) calcd for $[C_{16}H_{13}ClN_2O_2S + Na]^+$ 355.0278, found 355.0284; **IR** (thin film) 2230, 1589, 1383, 1182.



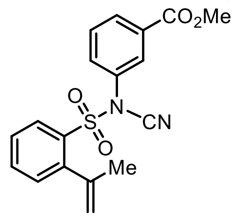
3g

Prepared from sulfonyl chloride **S5a** and cyanamide **S2o** on a 2.0 mmol scale. **3g** was purified by flash column chromatography (8:92 → 1:9 EtOAc/Hex) as a yellow solid (1.43 mmol, 71% yield). R_f = 0.38 (1:4 EtOAc/Hex); mp 85–87 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (dd, J = 8.2, 1.3 Hz, 1H), 7.64 (td, J = 7.6, 1.3 Hz, 1H), 7.42 (ddd, J = 8.1, 7.4, 1.4 Hz, 1H), 7.33 (dd, J = 7.7, 1.3 Hz, 1H), 7.23 (t, J = 8.5 Hz, 1H), 6.89 (ddd, J = 8.5, 2.3, 1.1 Hz, 1H), 6.79 – 6.72 (m, 2H), 5.32 (app s, 1H), 4.77 (app s, 1H), 3.74 (s, 3H), 2.11 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.4, 145.2, 142.9, 135.2, 134.9, 134.1, 131.5, 131.0, 130.4, 127.7, 117.6, 117.3, 115.6, 111.3, 107.8, 55.5, 25.4; **HRMS** (ESI) calcd for $[C_{17}H_{16}N_2O_3S + Na]^+$ 351.0774, found 351.0785; **IR** (thin film) 2253, 2234, 1606, 1183.



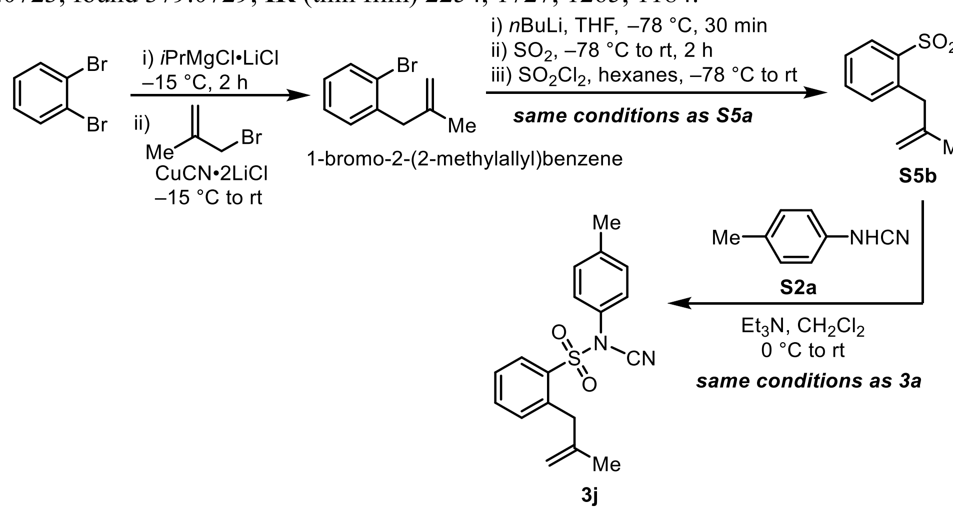
3h

Prepared from sulfonyl chloride **S5a** and cyanamide **S2m** on a 2.0 mmol scale. **3h** was purified by flash column chromatography (5:95 → 1:9 EtOAc/Hex) as a thick pale yellow oil (1.62 mmol, 81% yield). R_f = 0.49 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (dd, J = 8.2, 1.3 Hz, 1H), 7.68 (td, J = 7.6, 1.3 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.9 Hz, 1H), 7.49 – 7.42 (m, 3H), 7.35 (dd, J = 7.6, 1.3 Hz, 1H), 5.27 (app s, 1H), 4.67 (app s, 1H), 2.10 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.3, 143.0, 135.4, 135.0, 133.5, 132.5 (q, $^2J_{F\text{–}C}$ = 33.5 Hz), 131.7, 131.0, 130.6, 128.7, 127.9, 126.2 (q, $^3J_{F\text{–}C}$ = 3.7 Hz), 122.9 (q, $^1J_{F\text{–}C}$ = 271.0 Hz), 122.5 (q, $^3J_{F\text{–}C}$ = 3.9 Hz), 117.2, 107.3, 25.4; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –63.0; **HRMS** (ESI) calcd for $[C_{17}H_{13}F_3N_2O_2S + Na]^+$ 389.0542, found 389.0539; **IR** (thin film) 2253, 1386, 1328, 1183, 1139.



3i

Prepared from sulfonyl chloride **S5a** and cyanamide **S2n** on a 2.0 mmol scale. **3e** was purified by flash column chromatography (1:9 → 1:4 EtOAc/Hex) as a pale yellow oil (1.69 mmol, 85% yield). R_f = 0.31 (1:4 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 1H), 7.92 – 7.85 (m, 2H), 7.67 (td, J = 7.6, 1.3 Hz, 1H), 7.51 – 7.40 (m, 3H), 7.35 (dd, J = 7.6, 1.3 Hz, 1H), 5.30 (app s, 1H), 4.75 (app s, 1H), 3.91 (s, 3H), 2.11 (d, J = 0.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.2, 145.2, 143.0, 135.2, 134.7, 133.8, 132.1, 131.6, 131.0, 130.5, 130.0, 129.8, 127.8, 126.6, 117.4, 107.6, 52.6, 25.4; **HRMS** (ESI) calcd for $[C_{18}H_{16}N_2O_4S + Na]^+$ 379.0723, found 379.0729; **IR** (thin film) 2254, 1727, 1265, 1184.

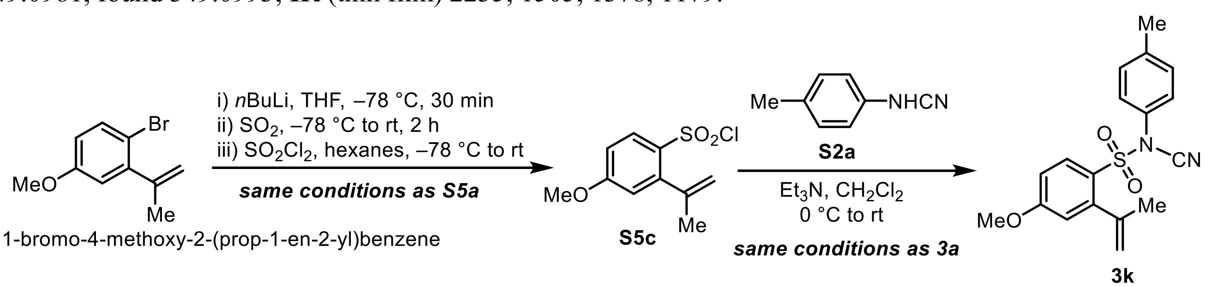


3j

Synthesis of 1-bromo-2-(2-methylallyl)benzene: To a solution of *i*PrMgCl·LiCl (0.77 M in THF, 14.3 mL, 11 mmol) was slowly added 1,2-dibromobenzene (1.23 mL, 10 mmol) at –15 °C. The resulting solution was stirred at –15 °C for 2 h, whereupon methallyl bromide (1.21 mL, 12 mmol) and CuCN·2LiCl (1.0 M in THF, 1.0 mL, 1.0 mmol) were sequentially added. The reaction was allowed to warm to room temperature and stir overnight, which was then quenched with saturated aqueous NH_4Cl (10 mL) and extracted with Et_2O (20 mL × 3). The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated to afford 1-bromo-2-(2-methylallyl)benzene as a pale yellow oil (1972 mg, 9.3 mmol, 93% crude yield), which was taken to the next step without further purification. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.07 (ddd, *J* = 7.9, 6.7, 2.3 Hz, 1H), 4.86 (app s, 1H), 4.59 (app s, 1H), 3.46 (s, 2H), 1.76 (s, 3H). The NMR data is consistent with a literature report.[31]

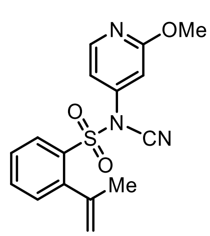
Synthesis of sulfonyl chloride S5b: Sulfonyl chloride **S5b** was prepared in the same manner as **S5a**, starting from 1-bromo-2-(2-methylallyl)benzene on a 2.5 mmol scale. **S5b** was purified by flash column chromatography (1:9 Et_2O/Hex) as a colorless oil (1.9 mmol, 76% yield). R_f = 0.63 (1:9 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.66 (td, *J* = 7.6, 1.4 Hz, 1H), 7.50 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.45 (td, *J* = 7.8, 1.4 Hz, 1H), 4.98 (t, *J* = 1.5 Hz, 1H), 4.68 – 4.57 (m, 1H), 3.89 (s, 2H), 1.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 142.9, 139.5, 135.0, 132.5, 128.9, 127.1, 114.1, 40.1, 22.5.

Synthesis of substrate 3j: 3j was prepared in the same manner as **3a**, starting from sulfonyl chloride **S5b** and cyanamide **S2a** on a 2.0 mmol scale. **3j** was purified by flash column chromatography (1:9 → 1:4 EtOAc/Hex) as a colorless oil (1.17 mmol, 83% yield). R_f = 0.30 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.62 (td, *J* = 7.5, 1.4 Hz, 1H), 7.45 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.35 (td, *J* = 7.7, 1.3 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.10 – 7.04 (m, 2H), 4.90 (app s, 1H), 4.48 (d, *J* = 0.7 Hz, 1H), 3.63 (s, 2H), 2.35 (s, 3H), 1.73 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.7, 140.6, 140.5, 134.9, 134.4, 132.6, 131.55, 131.53, 130.4, 127.1, 126.4, 113.6, 108.4, 40.7, 22.6, 21.1; **HRMS** (ESI) calcd for $[C_{18}H_{18}N_2O_2S + Na]^+$ 349.0981, found 349.0993; **IR** (thin film) 2235, 1505, 1378, 1179.



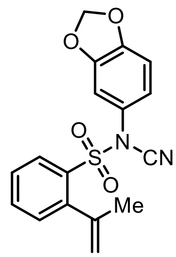
Synthesis of sulfonyl chloride S5c: Sulfonyl chloride **S5c** was prepared in the same manner as **S5a**, starting from 1-bromo-4-methoxy-2-(prop-1-en-2-yl)benzene[32] on a 7.2 mmol scale. **S5c** was purified by flash column chromatography (1:9 EtOAc/Hex) as an oily yellow solid (4.8 mmol, 67% yield). R_f = 0.38 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 9.1 Hz, 1H), 6.93 (dd, *J* = 9.1, 2.7 Hz, 1H), 6.78 (d, *J* = 2.7 Hz, 1H), 5.39 – 5.32 (m, 1H), 5.13 – 5.02 (m, 1H), 3.91 (s, 3H), 2.16 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.4, 146.6, 142.4, 133.8, 131.7, 117.2, 116.4, 112.8, 55.9, 25.0.

Synthesis of substrate 3k: 3k was prepared in the same manner as **3a**, starting from sulfonyl chloride **S5c** and cyanamide **S2a** on a 2.0 mmol scale. **3k** was purified by flash column chromatography (1:9 → 1:4 EtOAc/Hex) as a white solid (1.74 mmol, 87% yield). R_f = 0.30 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.0 Hz, 1H), 7.17 – 7.13 (m, 2H), 7.11 – 7.05 (m, 2H), 6.84 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.77 (d, *J* = 2.7 Hz, 1H), 5.27 (app s, 1H), 4.76 (app s, 1H), 3.89 (s, 3H), 2.34 (s, 3H), 2.10 (d, *J* = 0.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.2, 147.7, 143.1, 140.0, 133.7, 131.8, 130.4, 126.1, 125.3, 116.8, 116.5, 112.7, 108.4, 55.8, 25.3, 21.1; **HRMS** (ESI) calcd for $[C_{18}H_{18}N_2O_3S + Na]^+$ 365.0930, found 365.0941; **IR** (thin film) 2235, 1590, 1369, 1242, 1176.



3l

Prepared from sulfonyl chloride **S5a** and cyanamide **S2t** on a 1.0 mmol scale. **3l** was purified by flash column chromatography (15:85 → 20:80 EtOAc/Hex) as a yellow gel (0.54 mmol, 54 % yield). R_f = 0.18 (1:4 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, J = 5.8 Hz, 1H), 8.06 (dd, J = 8.1, 1.3 Hz, 1H), 7.67 (td, J = 7.5, 1.2 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.33 (dd, J = 7.7, 1.4 Hz, 1H), 6.84 (dd, J = 5.8, 2.1 Hz, 1H), 6.67 (d, J = 2.1 Hz, 1H), 5.40 (s, 1H), 4.81 (s, 1H), 3.90 (s, 3H), 2.14 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.3, 148.7, 145.2, 144.1, 142.4, 135.5, 134.0, 131.7, 131.2, 127.9, 118.2, 108.9, 105.9, 102.6, 54.0, 25.2. **HRMS** (ESI) calcd for $[C_{16}H_{15}N_3O_3S + Na]^+$ 352.0726, found 352.0749; **IR** (thin film) 2230, 1594, 1481, 1381.

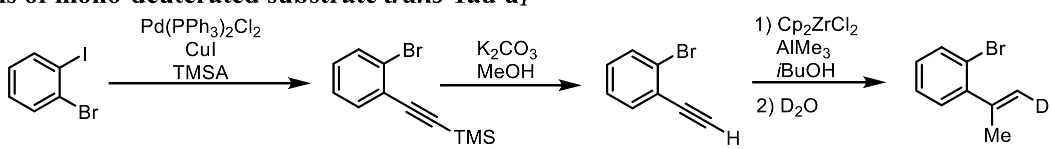


3m

Prepared from sulfonyl chloride **S5a** and cyanamide **S2u** on a 1.0 mmol scale. **3m** was purified by flash column chromatography (1:4 EtOAc/Hex) as a yellow gel (0.65 mmol, 65% yield). R_f = 0.45 (1:4 EtOAc/Hex); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 8.2, 1.3 Hz, 1H), 7.65 (td, J = 7.5, 1.3 Hz, 1H), 7.42 (td, J = 7.8, 1.4 Hz, 1H), 7.35 (dd, J = 7.6, 1.4 Hz, 1H), 6.71 (d, J = 8.3 Hz, 1H), 6.68 (d, J = 2.2 Hz, 1H), 6.61 (dd, J = 8.3, 2.2 Hz, 1H), 6.02 (s, 2H), 5.34 (s, 1H), 4.82 (s, 1H), 2.12 (s, 3H).. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.0, 148.5, 145.3, 143.2, 135.0, 133.9, 131.5, 131.1, 127.7, 127.6, 121.0, 117.3, 108.5, 108.1, 108.0, 102.3, 77.3, 77.0, 76.7, 25.5. **HRMS** (ESI) calcd for $[C_{17}H_{14}N_2O_4S + Na]^+$ 365.0566, found 365.0574; **IR** (thin film) 2229, 1607, 1505, 1482, 1180.

8. Study towards the stereochemistry of alkene addition step

Synthesis of mono-deuterated substrate *trans*-1ad-*d*$_1$

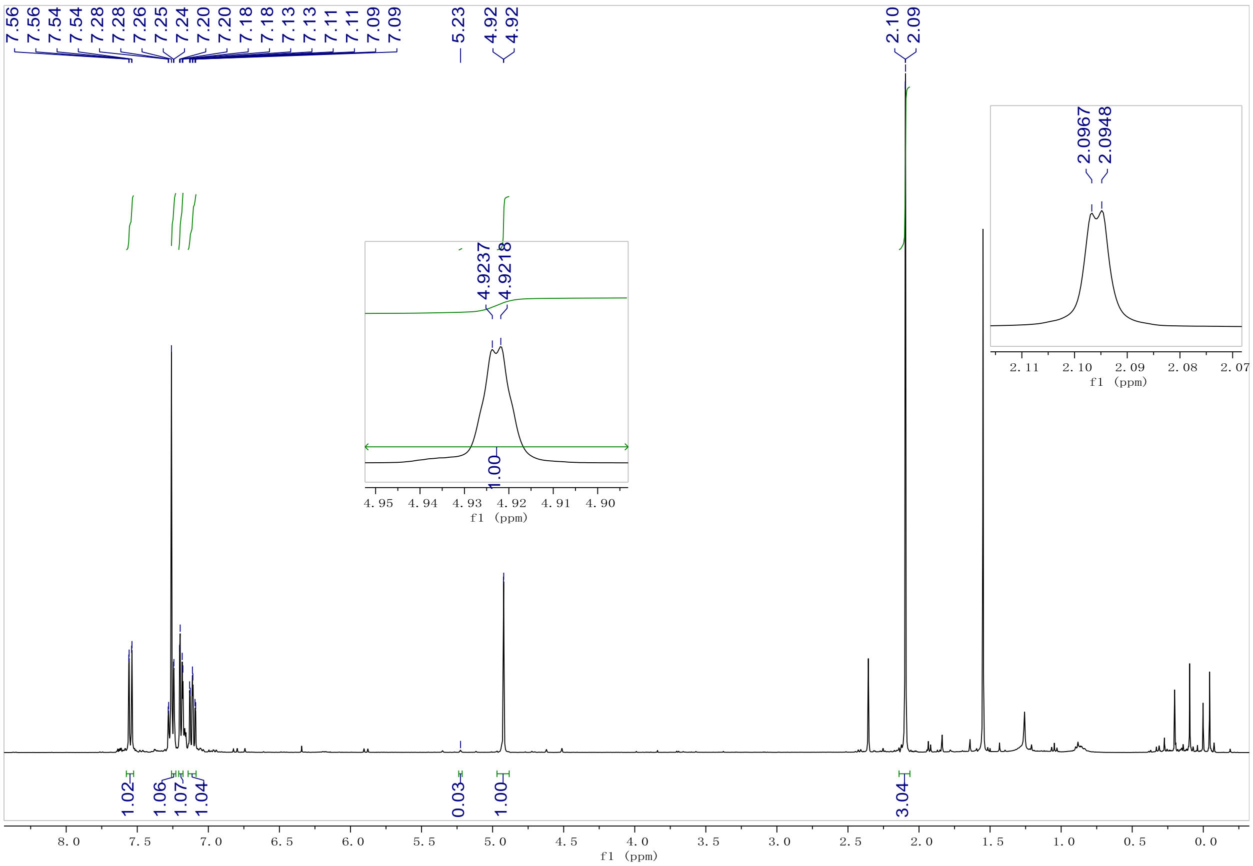


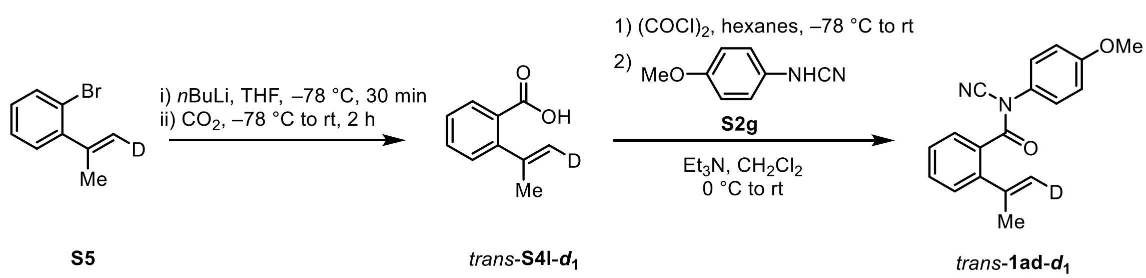
S5

The precursor of **S5** (2-bromo-1-ethynylbenzene) was prepared from 2-bromoiodobenzene in 2 steps based on the reported procedures.[33]

(*E*)-1-bromo-2-(prop-1-en-2-yl-1-d)benzene (S5): The preparation of **S5** was performed according to a literature reference.[34] To a flame dried, N_2 purged, 25 mL round bottomed flask, bis(cyclopentadienyl)zirconium dichloride (73 mg, 0.25 mmol, 5.0 mol %) and Me_3Al (3.75 mL, 7.5 mmol, 1.5 equiv, 2.0 M solution in toluene) were added at 0 °C. Then isobutanol (0.05 mL, 0.5 mmol, 10 mol %) was added at the same temperature, while a white fume can be observed over the reaction mixture in the flask. After 10 minutes, 2-bromo-1-ethynylbenzene (905 mg, 5.0 mmol, 1 equiv.) was added. The mixture was stirred at room temperature overnight. D_2O (10 mL) was dropwise added to the mixture at 0 °C (*Caution!* Gas evolution, reaction vessel must be vented.) The aqueous phase was extracted with petroleum ether and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuum. The crude product **S5** (815 mg) with 97% D-labeling was obtained as a dark orange oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 8.0, 1.0 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.19 (dd, J = 7.6, 1.8 Hz, 1H), 7.11 (td, J = 7.9, 1.9 Hz, 1H), 5.23 – 5.22 (m, 0.03H), 4.92 (s, 1H), 2.10 (d, J = 0.8 Hz, 3H).

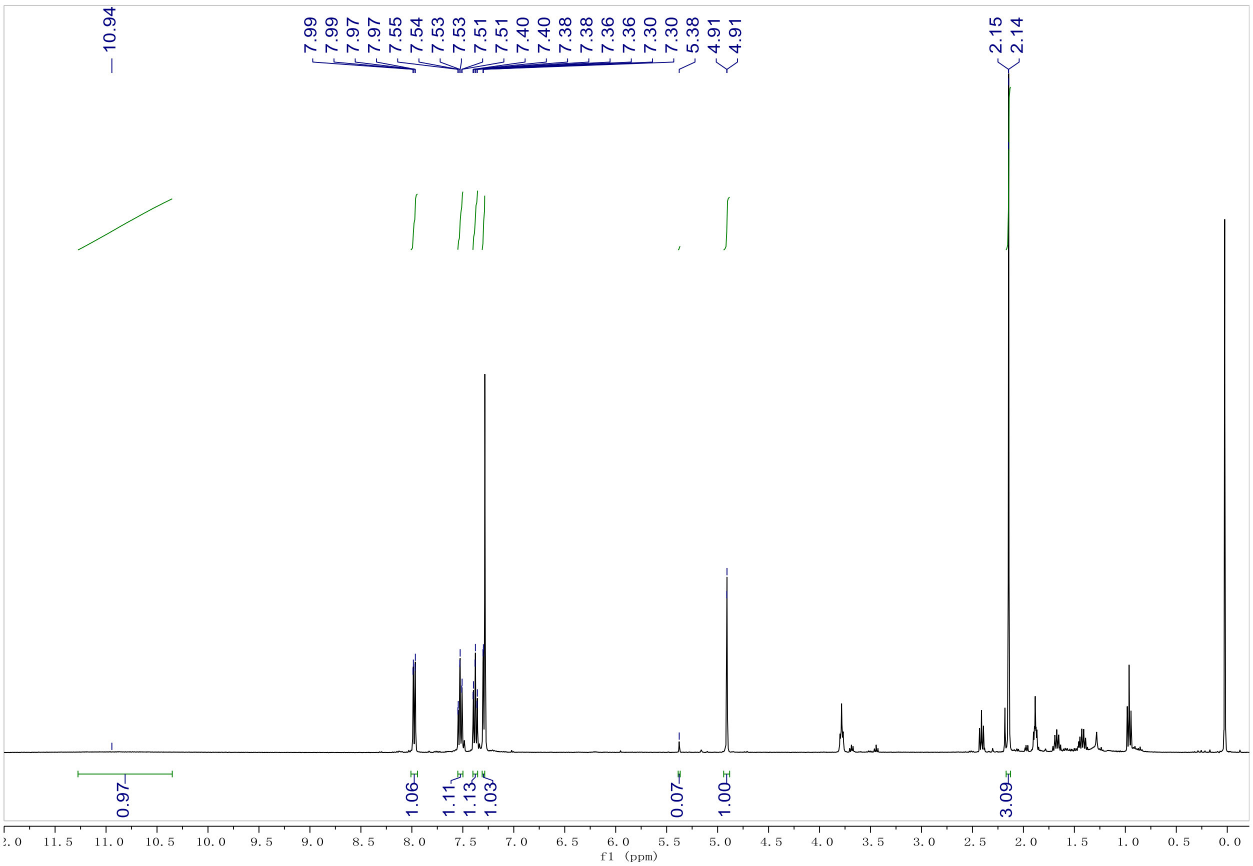
Figure S1. The 1H-NMR spectrum of crude S5



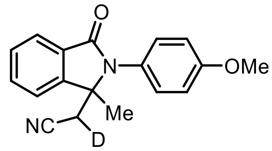


***trans*-S4l-*d*1:** To a solution of **S5** (815mg, crude mass) in anhydrous THF (4 mL), nBuLi (1.5 mL, 2.5 M solution in hexanes) was added dropwise at -78 °C. After 30 minutes, CO_2 gas was bubbled into the flask for 10 minutes (CO_2 gas was introduced by warming dry ice and passing the vapor through an anhydrous $CaSO_4$ column prior to entering the reaction vessel). The resulting mixture was allowed to warm up to room temperature and stir overnight. The reaction was quenched with sat. $NaHCO_3$ solution (5 mL). The aqueous layer was extracted with diethyl ether (10 mL). The aqueous portion was then acidified with 1M HCl until pH=1 (as indicated by pH paper). The resulting milky-white aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated in vacuo to afford the crude *trans*-**S4l-*d*1** as a pale-yellow solid (495 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.94 (s, 1H), 7.98 (dd, J = 7.7, 1.4 Hz, 1H), 7.53 (td, J = 7.5, 1.4 Hz, 1H), 7.38 (td, J = 7.7, 1.4 Hz, 1H), 7.30 – 7.26 (m, 1H), 5.38 (s, 0.07H), 4.91 (d, J = 0.9 Hz, 1H), 2.14 (d, J = 0.9 Hz, 3H).

Figure S2. The ^{1}H-NMR spectrum of crude *trans*-S4l-d_1



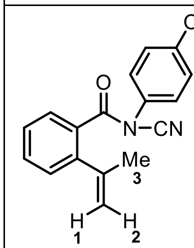
***trans*-1ad-d_1**: The preparation of *trans*-**1ad-d_1** was performed based on standard conditions (See 6.3 synthesis of substrate **1ad**) with modifications. To a suspension of acid ***trans*-S4l-d_1** (495 mg, crude mass) in CH_2Cl_2 (3 mL) was added DMF (1 drop via glass pipet) and isoamylene (6.3 mL, 60 mmol), followed by dropwise addition of $(COCl)_2$ (2.0 M in CH_2Cl_2, 1.5 mL, 3.0 mmol) at room temperature. The mixture was stirred for 30 minutes, whereupon gas evolution ceased and all ***trans*-S4l-d_1** dissolved. The reaction flask was cooled to –12 °C in an ethylene glycol/dry ice bath and a solution of Et_3N (0.82 mL, 6.0 mmol) in CH_2Cl_2 (2.0 mL) was added dropwise. Thereafter, a solution of cyanamide **S2g** (445 mg, 3.0 mmol) in CH_2Cl_2/THF (1.5 and 0.5 mL, respectively) was slowly added at the same temperature. The resulting mixture was allowed to warm up to room temperature and stir for 20 h. Et_2O (20 mL) was added to precipitate triethylamine hydrochloride, which was filtrated through a short Celite® column. Without further treatment, the filtrate was concentrated in vacuo and the resulting oily residue was purified by flash column chromatography to afford ***trans*-1ad-d_1** as a sticky white wax (2.0 mmol, 67 % yield). R_f = 0.20 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2H), 7.43 – 7.36 (m, 2H), 7.28 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 5.34 (app s, 0.01H), 5.13 (app s, 1H), 3.83 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.1, 159.9, 143.1, 141.8, 131.5, 130.7, 128.2, 127.6, 127.52, 127.46, 126.9, 116.9 (t, J = 24.4 Hz), 114.9, 110.1, 55.6, 23.2; **HRMS** (ESI) calcd for $[C_{18}H_{15}DN_2O_2 + Na]^+$ 316.1104, found 316.1116; **IR** (thin film) 2230, 1712, 1607, 1506, 1244.

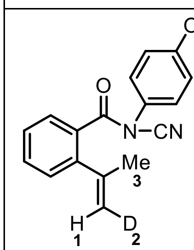


2ad-*d*₁

Prepared from ***trans*-1ad-*d*₁** on a 0.2 mmol scale with CpPd(1-phenylallyl) (10 mol%), Xantphos (10 mol%), and BEt_3 (60 mol%) in toluene at 80 °C for 24 h. **2ad-*d*₁** was purified by flash column chromatography (0.6:100 → 1:100 MeOH/CH_2Cl_2) as a pale yellow foam (0.19 mmol, 95% yield). R_f = 0.29 (2:100 MeOH/CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.22 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 3.85 (s, 3H), 2.88 (s, 1H), 1.67 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.7, 160.0, 147.1, 132.7, 131.0, 130.9, 129.5, 126.7, 124.7, 121.3, 116.0, 115.3, 63.7, 55.6, 28.4 (t, *J* = 20.5 Hz), 24.9; **HRMS** (ESI) calcd for $[C_{18}H_{15}DN_2O_2 + Na]^+$ 316.1167, found 316.1151; **IR** (thin film) 2246, 1691, 1609, 1511, 1370, 1246.

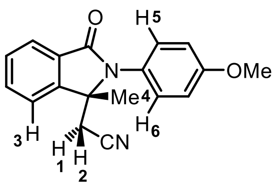
Assignment of stereochemistry of *trans*-1ad-*d*₁ by nOe NMR experiments

Assigned Structure	Key ^{1}H NMR Signals	Irradiation	Key nOe Results	Associate File
 **1ad**	**H1:** 5.15 (s, 1H) **H2:** 5.35 (s, 1H) **H3:** 2.23 (s, 3H)	**H1**	nOe observed: **H2** nOe not observed: **H3**	1ad-nOe-exp1.mnova
		H3	Strong nOe: **H2** Weak nOe: **H1**	1ad-nOe-exp2.mnova

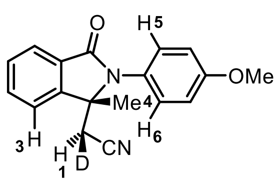
Assigned Structure	Key ^{1}H NMR Signals	Irradiation	Key nOe Results	Associate File
 ***trans*-1ad-*d*₁**	**H1:**5.14 (s, 1H) **H3:**2.23 (s, 3H)	**H1**	nOe not observed: **H3**	1ad-D-nOe-exp1.mnova

Conclusion: The proton and methyl group are *trans*.

Assignment of stereochemistry of (±)-2ad by nOe NMR experiments

Assigned Structure	Key ^{1}H NMR Signals	Irradiation	Key nOe Results	Associate File
 (±)-2ad	**H1:** 2.89 (d, J = 16.7 Hz, 1H) **H2:** 2.70 (d, J = 16.7 Hz, 1H) **H3:** 7.66 – 7.63 (m, 1H) **H4:** 1.68 (s, 3H) **H5,6:** 7.22 (d, J = 8.9 Hz, 2H)	**H1**	nOe observed: **H2, H3, H4, H5,6**	2ad-nOe-exp1.mnova
		H2	nOe observed: **H1, H4, H5,6** nOe not observed: **H3**	2ad-nOe-exp2.mnova

Assignment of stereochemistry of (±)-2ad-*d₁* by nOe NMR experiments

Assigned Structure	Key ^{1}H NMR Signals	Irradiation	Key nOe Results	Associate File
 (±)-2ad-d_1-I	**H1:** 2.88 (s, 1H) **H3:** 7.66 – 7.63 (m, 1H) **H4:** 1.68 (s, 3H) **H5,6:** 7.22 (d, J = 8.9 Hz, 2H)	**H1**	nOe observed: **H3, H4, H5,6**	2ad-D-nOe-exp1.mnova

9. Computation of ^{1}H-NMR chemical shifts of 2ad

The protocol of computational prediction was provided by Hoye et al.[35] The studied molecule (**2ad**) was initially subjected to a Monte Carlo conformational search using MacroModel (version 11.0, MMFF forcefield) and Maestro (version 10.4.017), implemented in the Schrödinger software suite. Then each geometry of **2ad** was optimized at the M062X/6-31+G(d,p) level of theory with CPCM(chloroform) solvation model. The nature of each optimized geometry was verified by frequency calculation (298K, at the same level of theory). The relative free energies obtained from the frequency calculation were used to determine the Boltzmann weighting factors for each conformer. NMR calculation was performed for each conformer at the b3lyp/6-311+G(2d,p) level of theory. We used the scaling parameters for this protocol [b3lyp/6-311+G(2d,p)//M06-2X/6-31+G(d,p)] created by Tantillo et al.[36] The Boltzmann weighting factors were applied to the computed NMR shielding tensors for each nucleus of each individual conformer.

Table S3. Electronic Energies and Boltzmann Factor of 2ad Conformers 1-7

Conformer	***Energy (a.u.)***	***Energy (kcal/mol)***	***Relative Energy (kcal/mol)***	***Boltzmann Factor***	***Equilibrium Mole Fraction***
2ad-conf-1	-954.920767	-599221.749	0.837097528	0.243064839	0.071029052
2ad-conf-2	-954.920985	-599221.8858	0.70030048	0.306271354	0.089499428
2ad-conf-3	-954.91905	-599220.6715	1.914531152	0.039362362	0.011502574
2ad-conf-4	-954.919157	-599220.7387	1.847387647	0.04409124	0.012884459
2ad-conf-5	-954.921925	-599222.4756	0.110441653	0.8297664	0.242476539
2ad-conf-6	-954.922062	-599222.5616	0.024472866	0.959491986	0.280385294
2ad-conf-7	-954.922101	-599222.5861	0	1	0.292222654

Figure S3. The label number of the atoms in 2ad

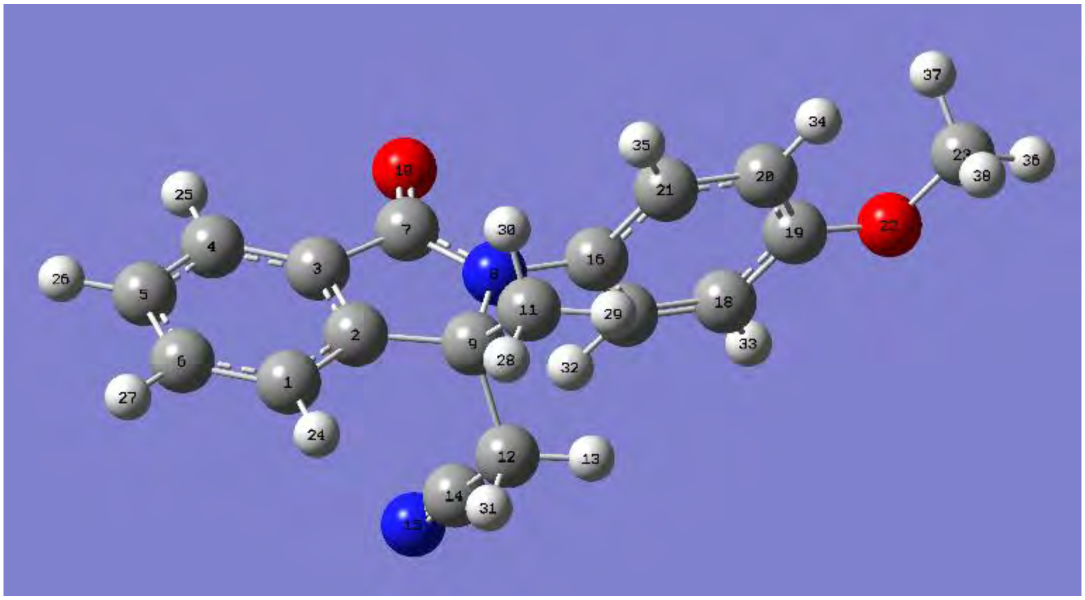


Table S4. Predicted and experimental chemical shifts in ^{1}H-NMR of 2ad

Gaussian atom numbers	Predicted chemical shift (ppm)	Experimental Chemical Shift (ppm)	$\delta_{Exp\text{-}comp}$ (ppm)
13	2.60	2.70	0.10
24	7.49	7.64	0.15
25	7.77	7.97	0.20
26	7.44	7.58	0.14
27	7.54	7.68	0.14
28	1.79		
29	1.69	1.68	0.09*
30	1.30		
31	2.82	2.89	0.07
32	7.32	7.22	-0.10
33	6.93	7.03	0.10
34	6.93	7.03	0.10
35	7.22	7.22	0.00
36	3.91		
37	3.65	3.86	0.12*
38	3.65		

* For methyl protons, $\delta_{Exp\text{-}comp} = \delta_{Exp} - \overline{\delta_{comp}}$

Cartesian Coordinates
2ad-Conformer 1

C	3.737329	0.579261	0.279851	C	-3.28445	-0.25394	1.42171
C	2.463073	0.034384	0.160862	C	-1.90394	-0.37062	1.389717
C	2.297299	-1.31028	-0.1492	O	-5.35086	-0.00506	0.361395
C	3.376156	-2.15922	-0.36279	C	-6.12599	0.122259	-0.81871
C	4.65559	-1.61645	-0.25519	H	3.891698	1.62496	0.531858
C	4.830163	-0.2643	0.063973	H	3.215609	-3.20709	-0.60054
C	0.844815	-1.62392	-0.17997	H	5.526453	-2.24521	-0.41445
N	0.199055	-0.44851	0.13218	H	5.835772	0.13748	0.148806
C	1.108507	0.694388	0.336138	H	1.679719	2.117278	1.862605
O	0.310465	-2.6945	-0.42094	H	-0.05747	1.754698	1.830717
C	0.941824	1.322889	1.719484	H	1.09262	0.564011	2.491259
C	0.827263	1.728933	-0.78467	H	-0.21321	2.067118	-0.7143
H	0.970864	1.260107	-1.76392	H	-1.41166	-0.19456	-1.96416
C	1.69505	2.905647	-0.69811	H	-3.86756	0.010217	-1.93437
N	2.384317	3.830472	-0.61598	H	-3.83048	-0.28228	2.359566
C	-1.22148	-0.33323	0.168427	H	-1.34495	-0.50359	2.311786
C	-1.94182	-0.19927	-1.01487	H	-7.16253	0.185884	-0.49112
C	-3.33246	-0.08765	-0.99715	H	-5.85858	1.031697	-1.36818
C	-4.00491	-0.11003	0.228025	H	-5.99897	-0.7512	-1.46773

2ad-Conformer 2

C	3.712518	0.566566	0.463941	C	-4.00121	-0.07511	-0.23807
C	2.44949	0.028563	0.239676	C	-3.39392	-0.2251	1.011575
C	2.302273	-1.31697	-0.07611	C	-2.00602	-0.35162	1.08749
C	3.389874	-2.17339	-0.1927	O	-5.33839	0.055659	-0.42559
C	4.659024	-1.63752	0.020398	C	-6.17415	0.027779	0.719098
C	4.814323	-0.28466	0.346307	H	3.851462	1.612785	0.722673
C	0.855765	-1.62257	-0.2273	H	3.243536	-3.22165	-0.43784
N	0.193198	-0.44208	0.023576	H	5.536294	-2.27226	-0.06086
C	1.088972	0.69716	0.296729	H	5.811627	0.111662	0.514374
O	0.336562	-2.69166	-0.50527	H	1.538269	2.124595	1.859492
C	0.810244	1.33374	1.658186	H	-0.19233	1.771457	1.682316
C	0.908835	1.727349	-0.84858	H	0.890731	0.57773	2.443239
H	1.131096	1.253104	-1.81038	H	-0.13168	2.072251	-0.86753
C	1.773788	2.899297	-0.69457	H	-1.23208	-0.17967	-2.21202
N	2.45992	3.82001	-0.5581	H	-3.71462	0.046951	-2.36151
C	-1.2245	-0.31898	-0.06288	H	-3.9781	-0.25456	1.923694
C	-1.84188	-0.17978	-1.31185	H	-1.52888	-0.48819	2.053972
C	-3.21895	-0.0582	-1.4014	H	-7.19202	0.143508	0.349899

H	-6.08227	-0.92667	1.24908	H	-5.9351	0.852041	1.400253

2ad-Conformer 3

C	3.842344	1.095638	0.222044	C	-3.14087	-0.31647	1.073531
C	2.654309	0.37692	0.158159	C	-1.74942	-0.31281	1.18239
C	2.67003	-1.00004	-0.01891	O	-5.06868	-0.48792	-0.40278
C	3.855071	-1.71537	-0.14152	C	-5.92357	-0.3178	0.71451
C	5.050082	-1.00023	-0.08131	H	3.852218	2.173879	0.365102
C	5.040903	0.388837	0.098214	H	3.838185	-2.79301	-0.27864
C	1.269062	-1.49603	-0.048	H	5.99855	-1.52093	-0.17291
N	0.471752	-0.39238	0.157381	H	5.983736	0.92633	0.143612
C	1.224649	0.871555	0.269632	H	1.596529	2.474191	1.67185
O	0.881574	-2.64107	-0.21725	H	-0.07367	1.879564	1.693721
C	0.973271	1.577298	1.603216	H	1.228133	0.908521	2.428936
C	0.917299	1.80829	-0.92655	H	0.983484	1.246644	-1.86426
H	1.670547	2.603164	-0.95901	H	-0.91811	-0.73838	-2.08004
C	-0.39615	2.460683	-0.85064	H	-3.40647	-0.76236	-2.28566
N	-1.41089	3.011561	-0.78623	H	-3.74141	-0.20588	1.968586
C	-0.9494	-0.44337	0.053011	H	-1.28612	-0.21378	2.159839
C	-1.54649	-0.61548	-1.20131	H	-6.93918	-0.34942	0.322751
C	-2.92544	-0.63259	-1.32121	H	-5.78597	-1.12586	1.441634
C	-3.72944	-0.47132	-0.18413	H	-5.74713	0.648574	1.199818

2ad-Conformer 4

C	3.858588	1.069385	-0.00633	C	-3.03082	-0.20844	1.468331
C	2.662098	0.364319	0.051061	C	-1.6453	-0.2234	1.466007
C	2.649736	-1.01864	-0.07061	O	-5.08983	-0.36437	0.376607
C	3.814594	-1.75377	-0.25384	C	-5.84876	-0.54066	-0.80719
C	5.01794	-1.05266	-0.31465	H	3.890092	2.152251	0.091508
C	5.036781	0.342513	-0.1926	H	3.776595	-2.83575	-0.3446
C	1.245369	-1.49681	0.027089	H	5.951242	-1.58925	-0.45647
N	0.478191	-0.37489	0.247551	H	5.985678	0.868868	-0.24205
C	1.250866	0.881852	0.252901	H	1.746969	2.531924	1.557854
O	0.835059	-2.64267	-0.06631	H	0.077434	1.961584	1.732595
C	1.11079	1.641581	1.573083	H	1.422247	1.00207	2.402566
C	0.860709	1.776854	-0.95093	H	0.848003	1.179613	-1.86864
H	1.616605	2.560572	-1.07182	H	-1.10469	-0.77241	-1.83979
C	-0.43684	2.447152	-0.79697	H	-3.56935	-0.77016	-1.85815
N	-1.43877	3.010781	-0.67119	H	-3.59093	-0.06068	2.38642
C	-0.94699	-0.40712	0.2683	H	-1.0965	-0.09908	2.395029
C	-1.6516	-0.61056	-0.91407	H	-6.89324	-0.47061	-0.50701
C	-3.04575	-0.61072	-0.92303	H	-5.62339	0.243801	-1.53813
C	-3.73709	-0.39647	0.272745	H	-5.66045	-1.52416	-1.25203

2ad-Conformer 5

C	3.747511	-0.79175	-0.77006	C	-3.23326	0.691065	-1.37368
C	2.517382	-0.22118	-0.46688	C	-1.84819	0.7413	-1.36641
C	2.442322	0.941221	0.288972	O	-5.27802	0.222734	-0.34541
C	3.577081	1.58115	0.771505	C	-6.02299	-0.2097	0.780458
C	4.814707	1.013252	0.472722	H	3.826116	-1.7024	-1.35958
C	4.896306	-0.15933	-0.2887	H	3.490655	2.488597	1.362514
C	1.01249	1.31488	0.456757	H	5.726199	1.480346	0.833348
N	0.291547	0.361898	-0.22984	H	5.871193	-0.58513	-0.50817
C	1.125382	-0.68857	-0.83967	H	1.626397	-1.50805	-2.7775
O	0.549204	2.26691	1.06246	H	-0.08839	-1.08643	-2.59881
C	0.931866	-0.77656	-2.35454	H	1.129873	0.196704	-2.81025
C	0.79958	-2.06567	-0.21309	H	1.444588	-2.83384	-0.65203
H	-0.24121	-2.33308	-0.4298	H	-1.26737	-0.41525	1.772396
C	0.987334	-2.06813	1.240123	H	-3.73078	-0.50585	1.787065
N	1.133019	-2.04609	2.386873	H	-3.8039	1.011556	-2.23983
C	-1.13354	0.324986	-0.23736	H	-1.31133	1.118287	-2.23233
C	-1.82435	-0.11634	0.887929	H	-7.07069	-0.13694	0.492502
C	-3.21891	-0.16315	0.895537	H	-5.78371	-1.24829	1.034676
C	-3.92478	0.235491	-0.24304	H	-5.83468	0.434002	1.64673

2ad-Conformer 6

C	3.705682	-0.68375	-0.98915	C	-3.10046	-0.36983	1.265533
C	2.487364	-0.16654	-0.56617	C	-1.72311	-0.27467	1.150939
C	2.43819	0.968025	0.233033	O	-5.25834	-0.08805	0.415567
C	3.588005	1.633068	0.640241	C	-6.13413	0.344353	-0.61132
C	4.813937	1.120241	0.21879	H	3.764146	-1.57277	-1.61302
C	4.869534	-0.02504	-0.5853	H	3.522068	2.518136	1.266742
C	1.015939	1.284643	0.532086	H	5.736647	1.609329	0.516236
N	0.271304	0.332601	-0.12985	H	5.835846	-0.40835	-0.90022
C	1.084877	-0.67086	-0.83833	H	1.446099	-1.41854	-2.83559
O	0.573604	2.196673	1.210693	H	-0.25947	-1.05728	-2.50177
C	0.768183	-0.72195	-2.33404	H	0.898281	0.269841	-2.7739
C	0.856763	-2.07533	-0.22909	H	1.483955	-2.80932	-0.74549
H	-0.19034	-2.37105	-0.36296	H	-1.522	1.110334	-1.94275
C	1.171645	-2.11209	1.201557	H	-3.97257	0.927213	-1.77213
N	1.417518	-2.11607	2.331275	H	-3.56432	-0.76453	2.164222
C	-1.14709	0.243789	-0.01567	H	-1.08118	-0.58897	1.970038
C	-1.96806	0.677908	-1.05149	H	-7.142	0.149928	-0.24764
C	-3.35704	0.580283	-0.95058	H	-6.01412	1.416134	-0.80443
C	-3.92382	0.051547	0.212112	H	-5.96337	-0.2177	-1.53635

2ad-Conformer 7

C	3.707261	0.597209	1.036411	C	-3.35559	-0.66402	0.896205
C	2.486688	0.119987	0.574804	C	-1.96611	-0.76409	0.984994
C	2.43173	-0.95656	-0.30075	O	-5.26289	0.122813	-0.39648
C	3.578059	-1.60085	-0.74899	C	-6.13473	-0.42139	0.579447
C	4.806344	-1.12757	-0.28955	H	3.76981	1.440582	1.720414
C	4.86763	-0.04107	0.591963	H	3.507991	-2.44003	-1.43532
C	1.008005	-1.24114	-0.6247	H	5.726455	-1.60198	-0.61723
N	0.269218	-0.32642	0.093712	H	5.835611	0.31219	0.935643
C	1.087264	0.615493	0.876898	H	1.439614	1.212882	2.925967
O	0.560503	-2.10471	-1.36098	H	-0.26555	0.885074	2.555925
C	0.761886	0.558406	2.370384	H	0.884632	-0.4636	2.737166
C	0.874598	2.063434	0.373019	H	1.505084	2.750928	0.946287
H	-0.17057	2.357967	0.523472	H	-1.09116	0.792289	-1.90191
C	1.198158	2.204706	-1.04913	H	-3.57594	0.976142	-2.07307
N	1.450531	2.292686	-2.17399	H	-3.96795	-1.09138	1.681422
C	-1.14958	-0.2286	-0.00608	H	-1.51552	-1.27725	1.830033
C	-1.73009	0.398644	-1.11534	H	-7.14437	-0.20172	0.235641
C	-3.10821	0.498653	-1.21757	H	-6.00298	-1.50591	0.662345
C	-3.92723	-0.02792	-0.2091	H	-5.97085	0.045178	1.557279

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(9) It was difficult to separate product **6** from the residual dimesylate **6'** during column chromatography. Thus **6'** was tentatively used as the limiting reactant.

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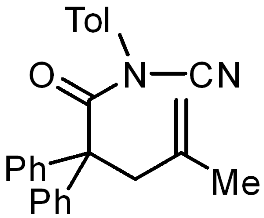
11. Spectra for new compounds



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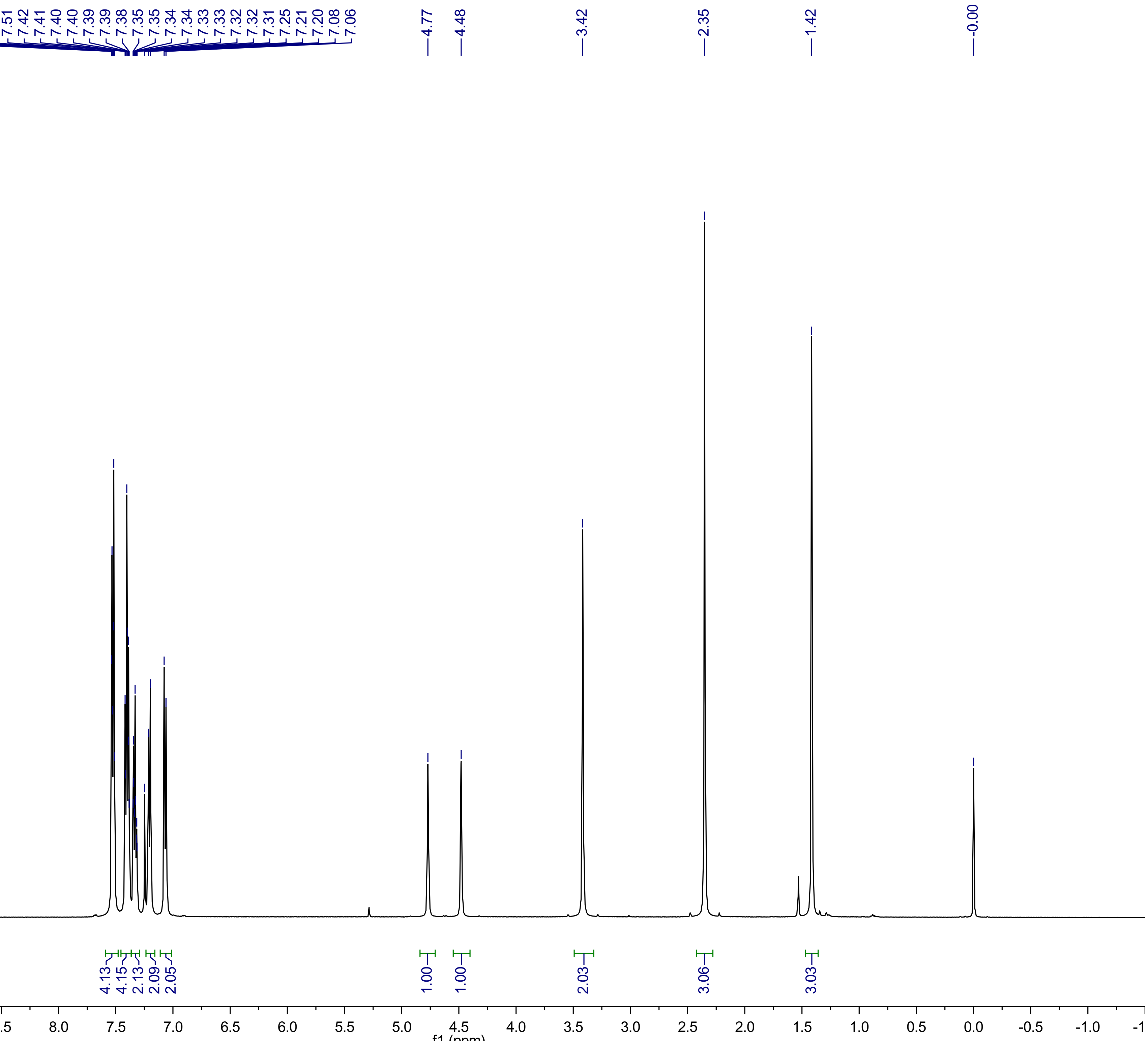
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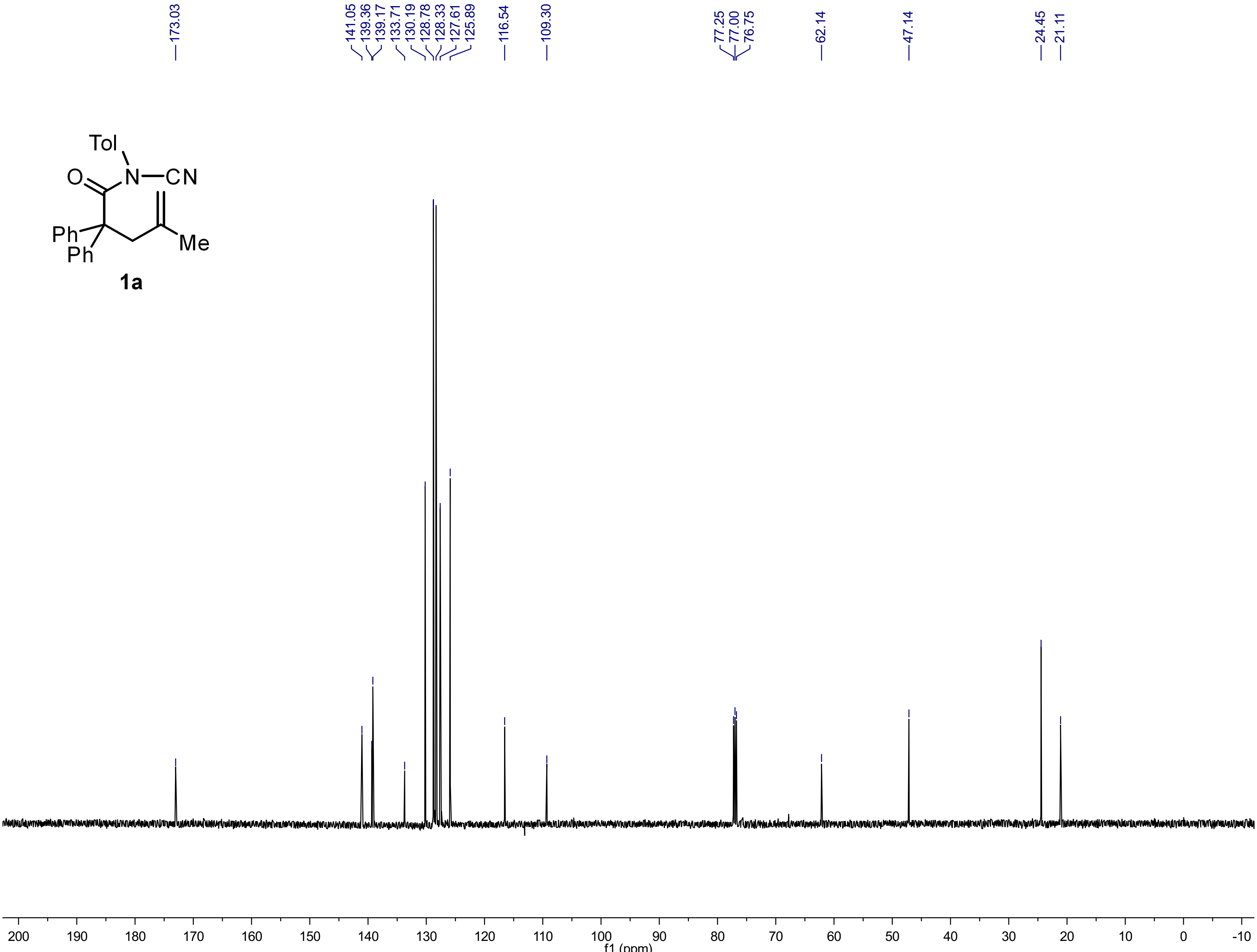
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47.14
24.45
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Ph
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1a
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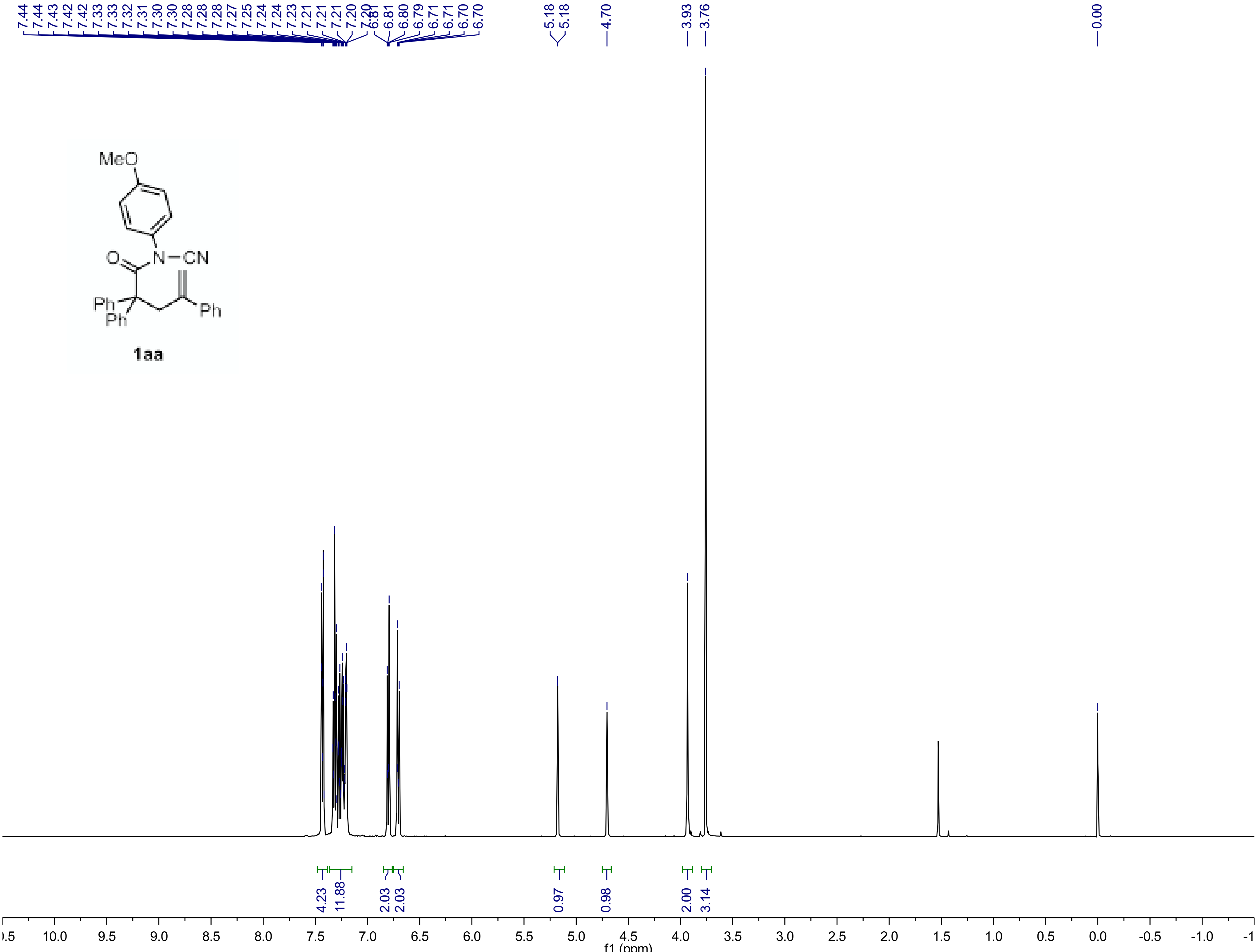
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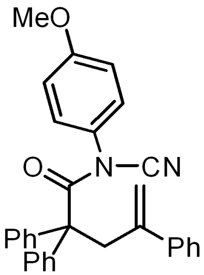
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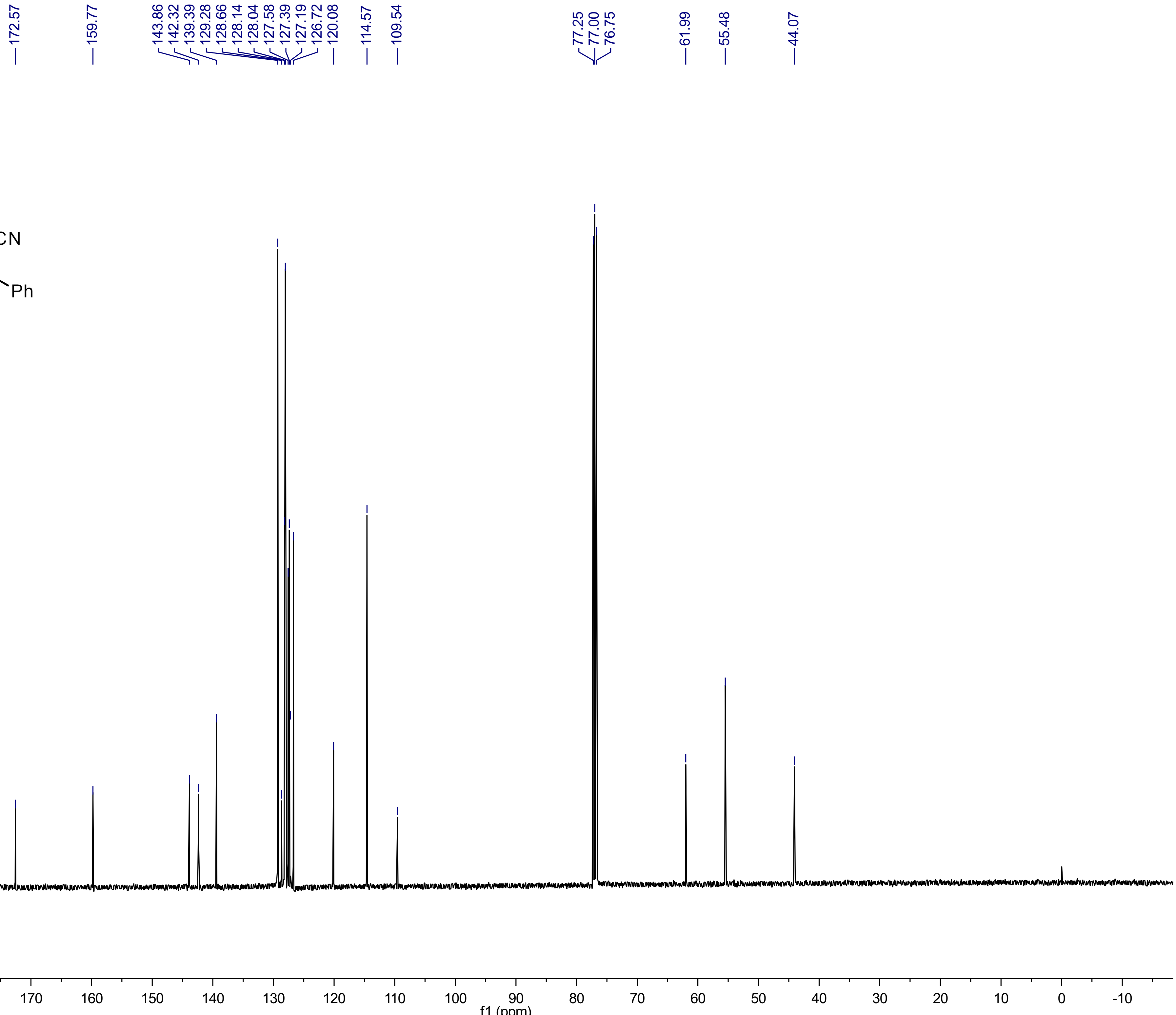
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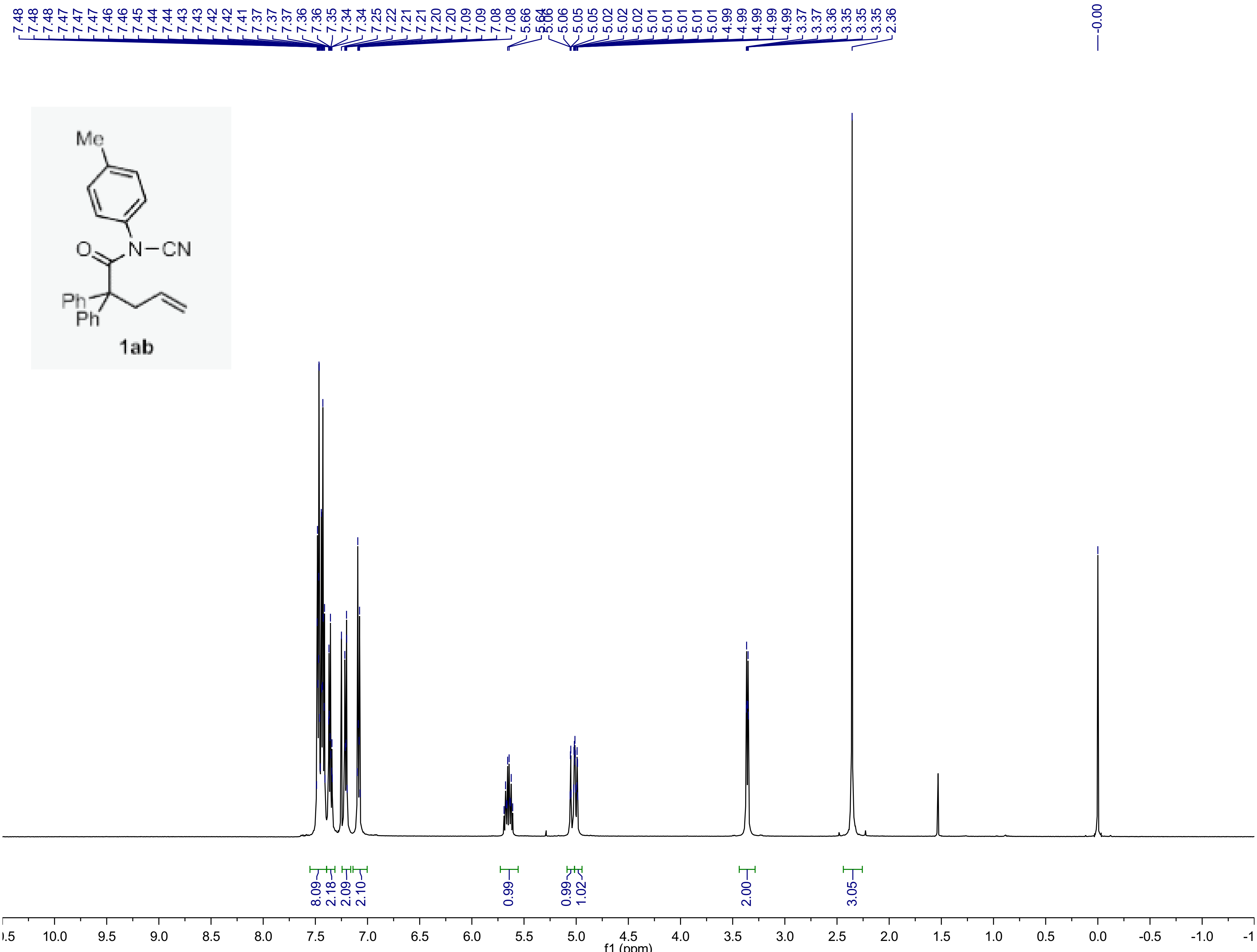
f1 (ppm)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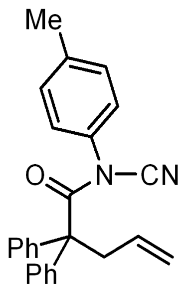
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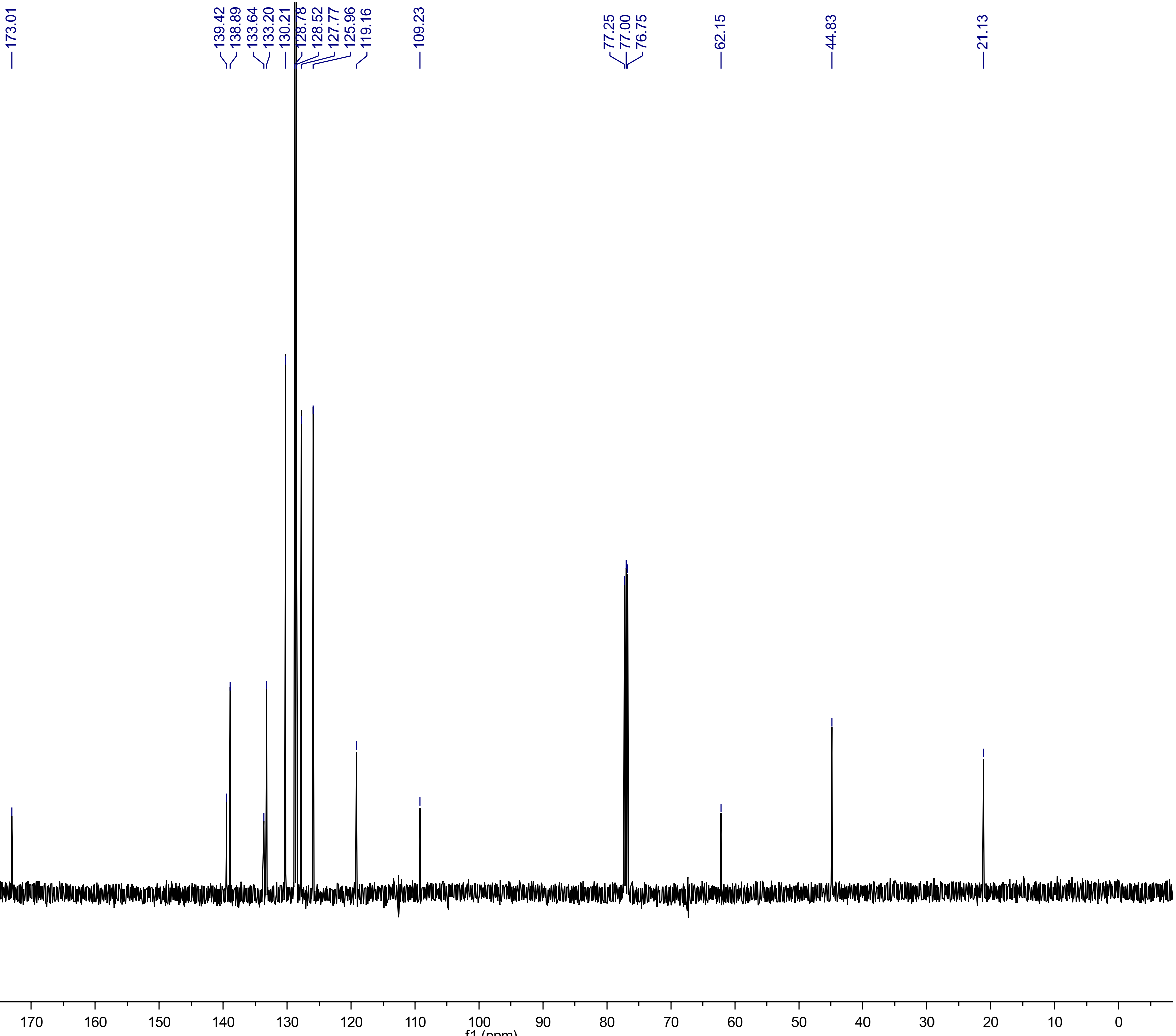
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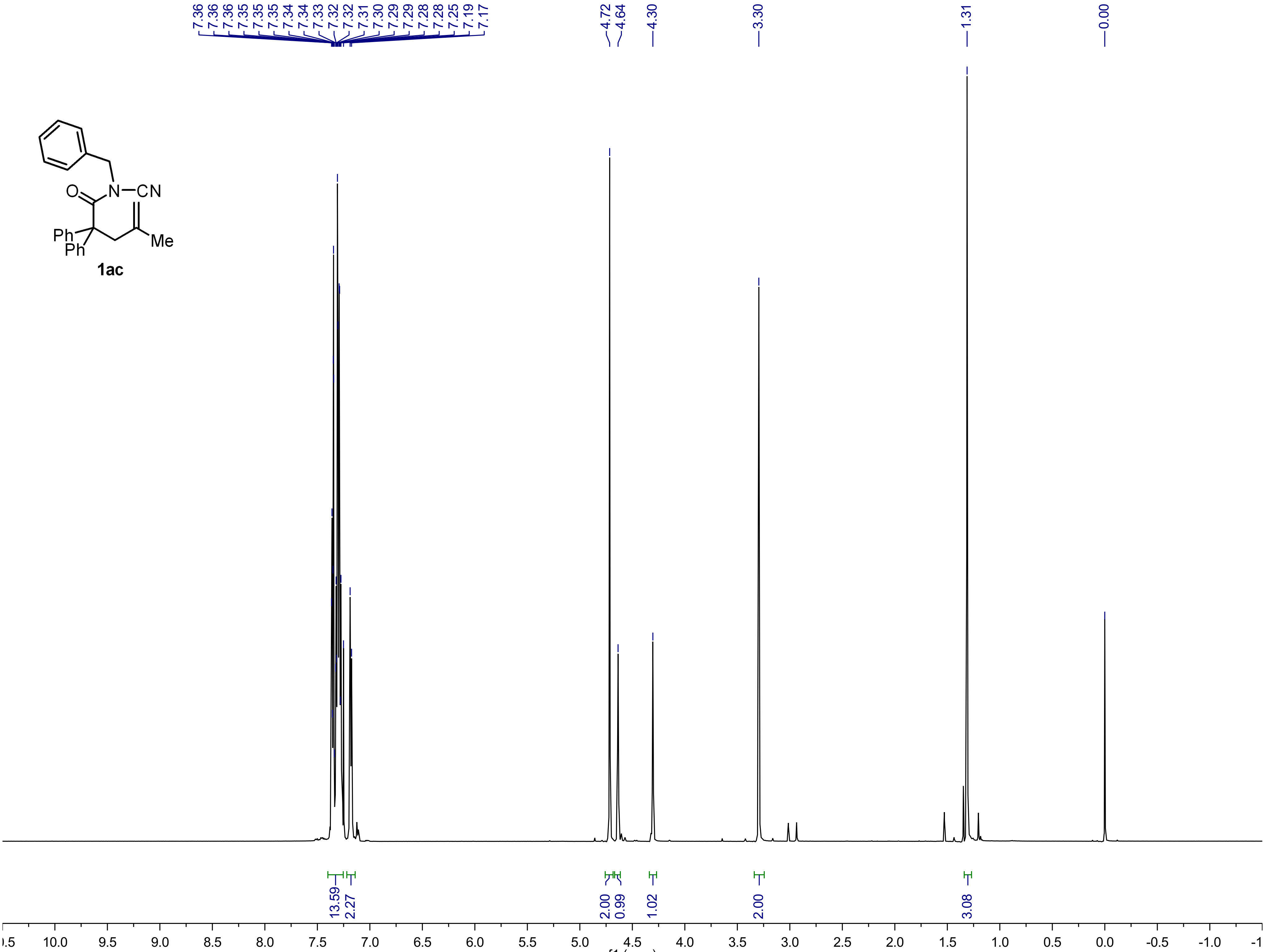
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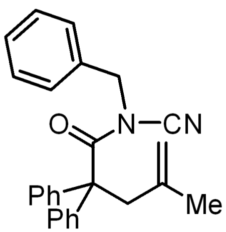

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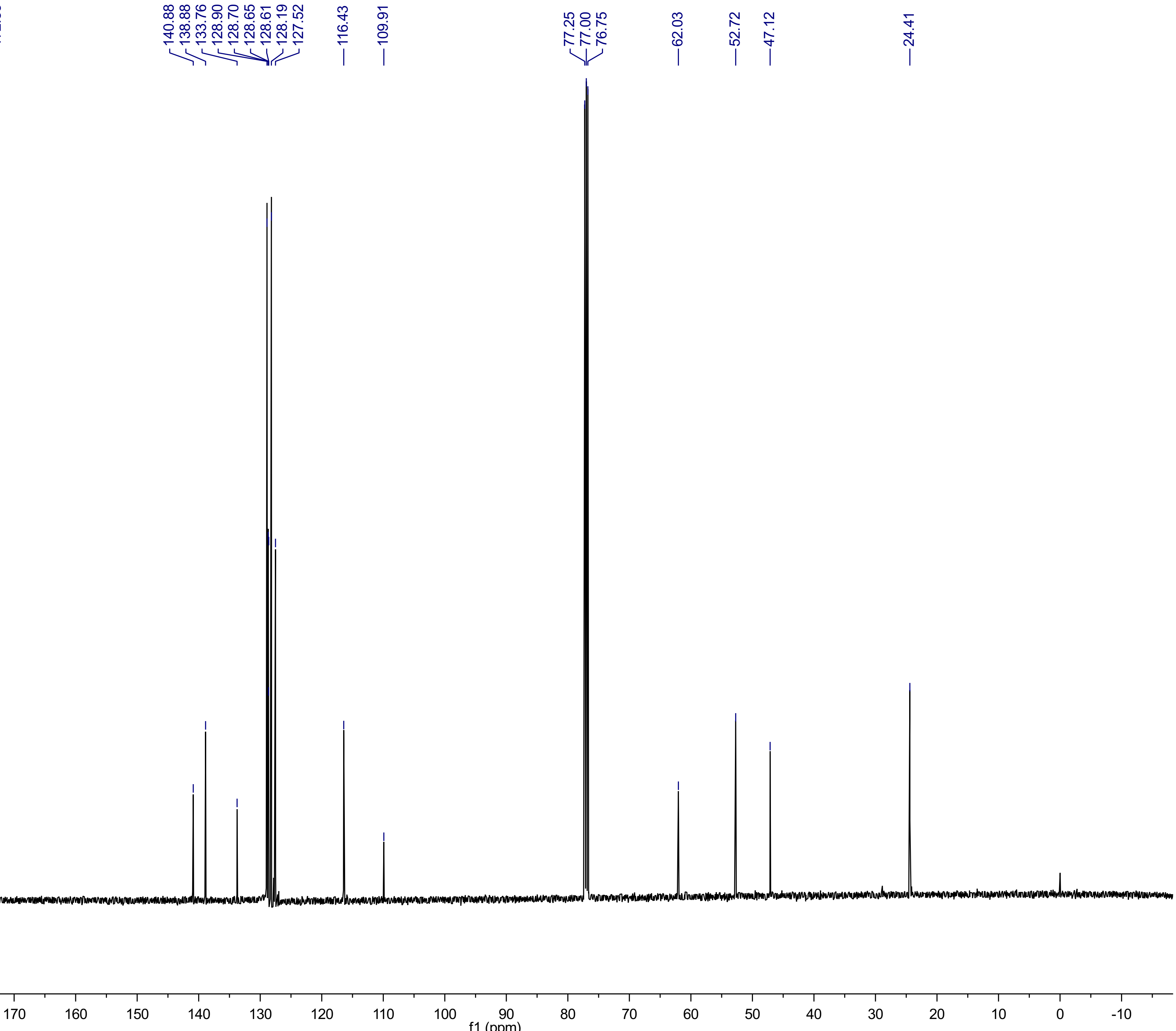
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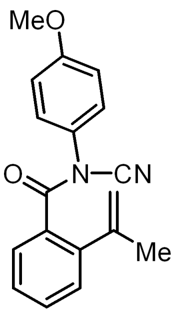

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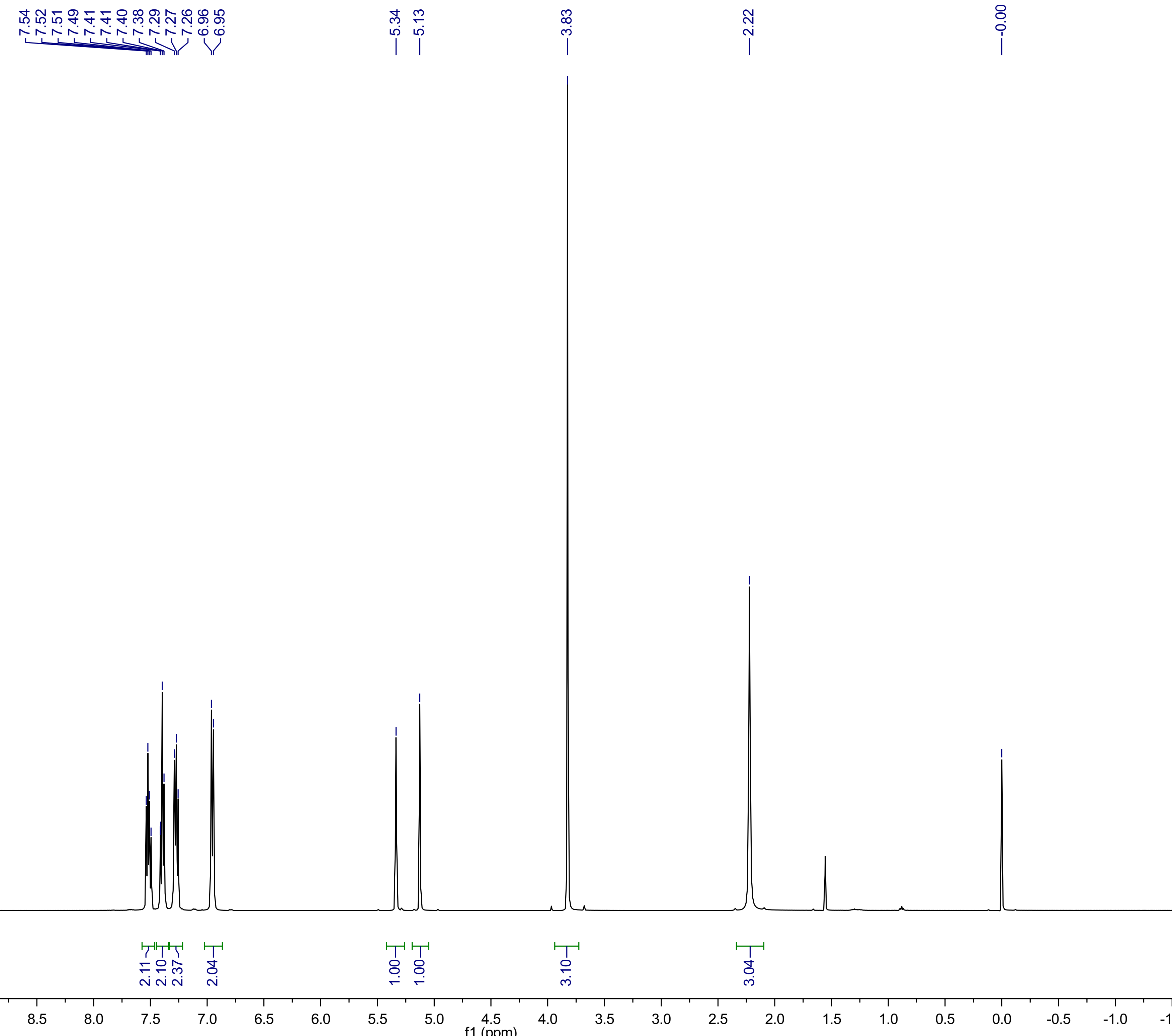
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6.95
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5.13
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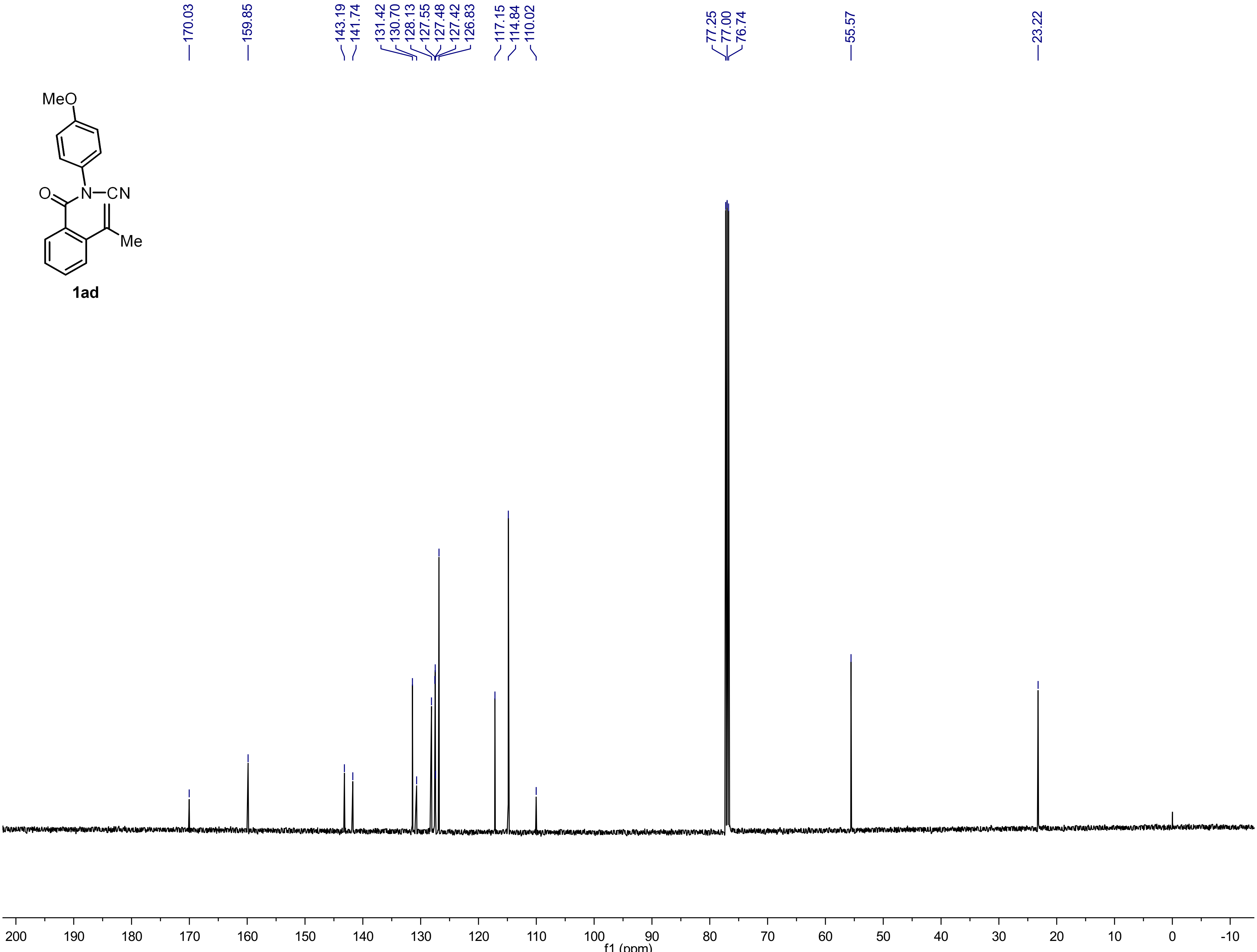
2.10
2.37
2.04
1.00
1.00
3.10
3.04
f1 (ppm)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114.84
110.02
77.25
77.00
76.74
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N
CN
Me
1ad
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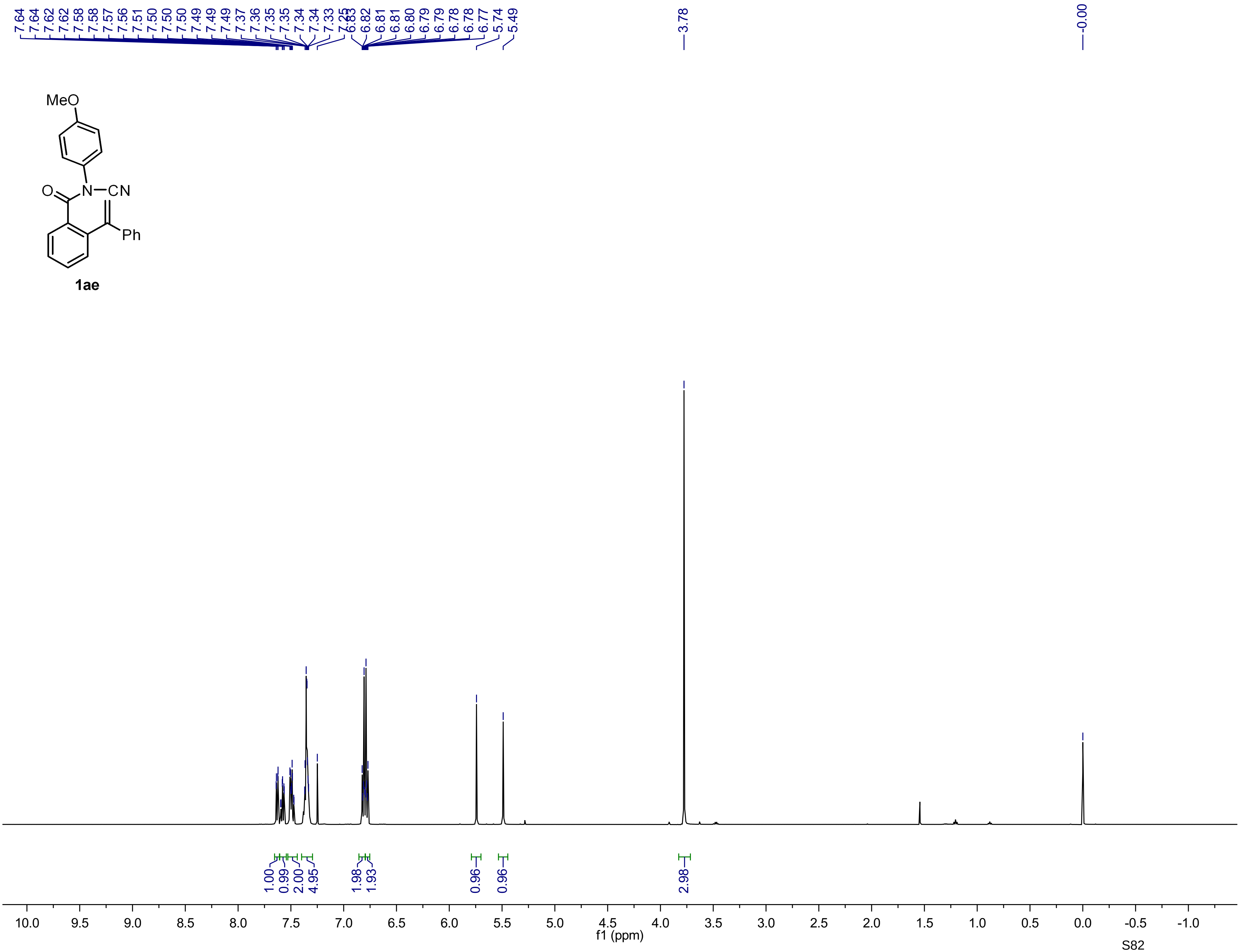
f1 (ppm)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7.49
7.49
7.49
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.25
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6.82
6.81
6.81
6.80
6.79
6.79
6.78
6.78
6.77
5.74
5.49
3.78
-0.00
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O
N
CN
Ph
1ae
1.00
0.99
2.00
4.95
1.98
1.93
0.96
0.96
2.98
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
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2.0
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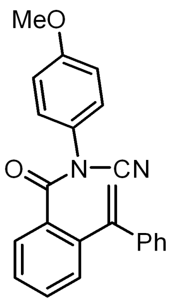
f1 (ppm)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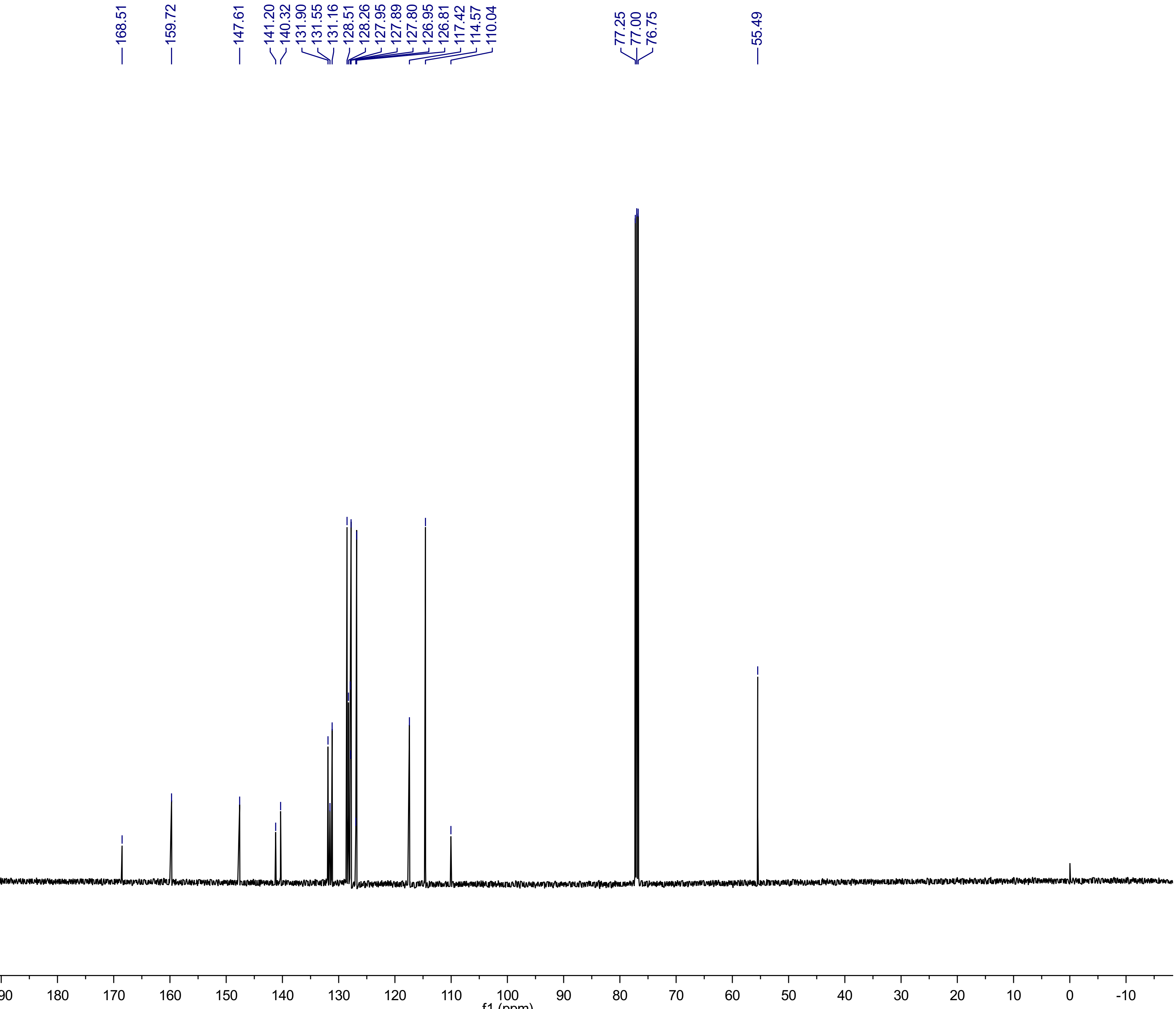
Ph

1ae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127.80
126.95
126.81
117.42
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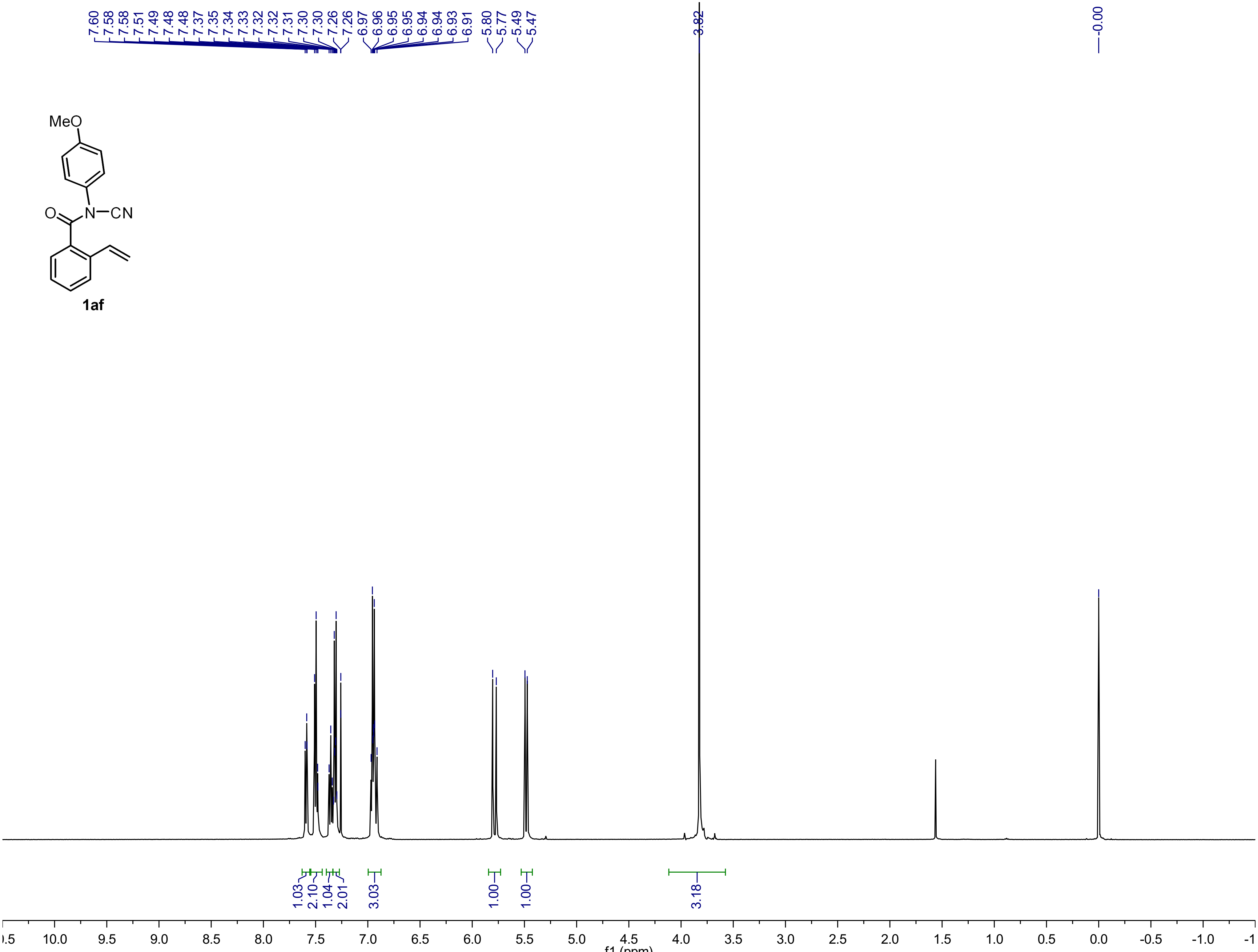
76.75
55.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.32
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7.30
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7.26
6.97
6.96
6.95
6.95
6.94
6.94
6.93
6.91
5.80
5.77
5.49
5.47
3.82
-0.00
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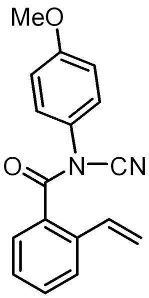
2.10
1.04
2.01
3.03
1.00
1.00
3.18
f1 (ppm)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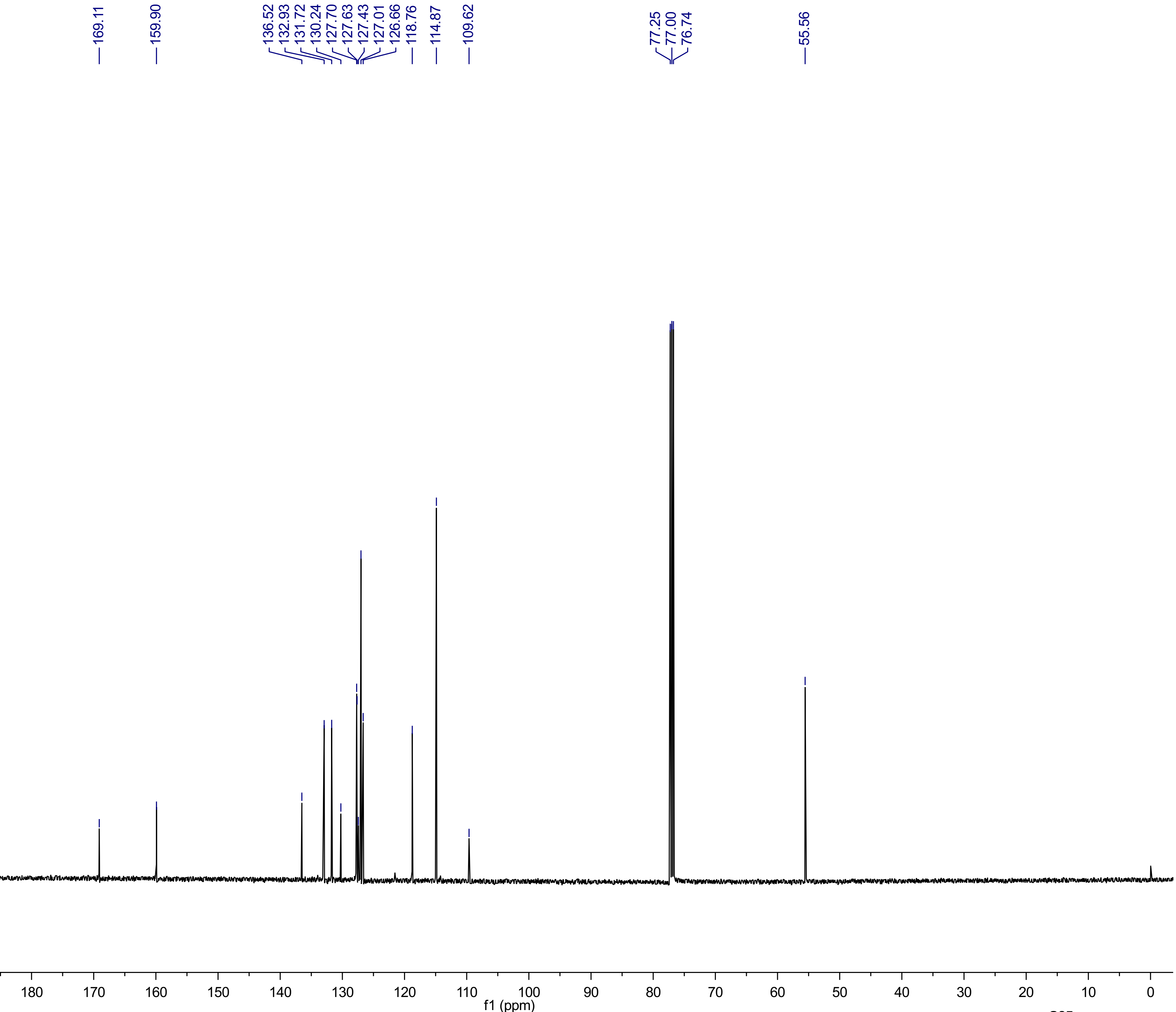
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114.87
109.62
77.25
77.00
76.74
55.56
200
190
180
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10
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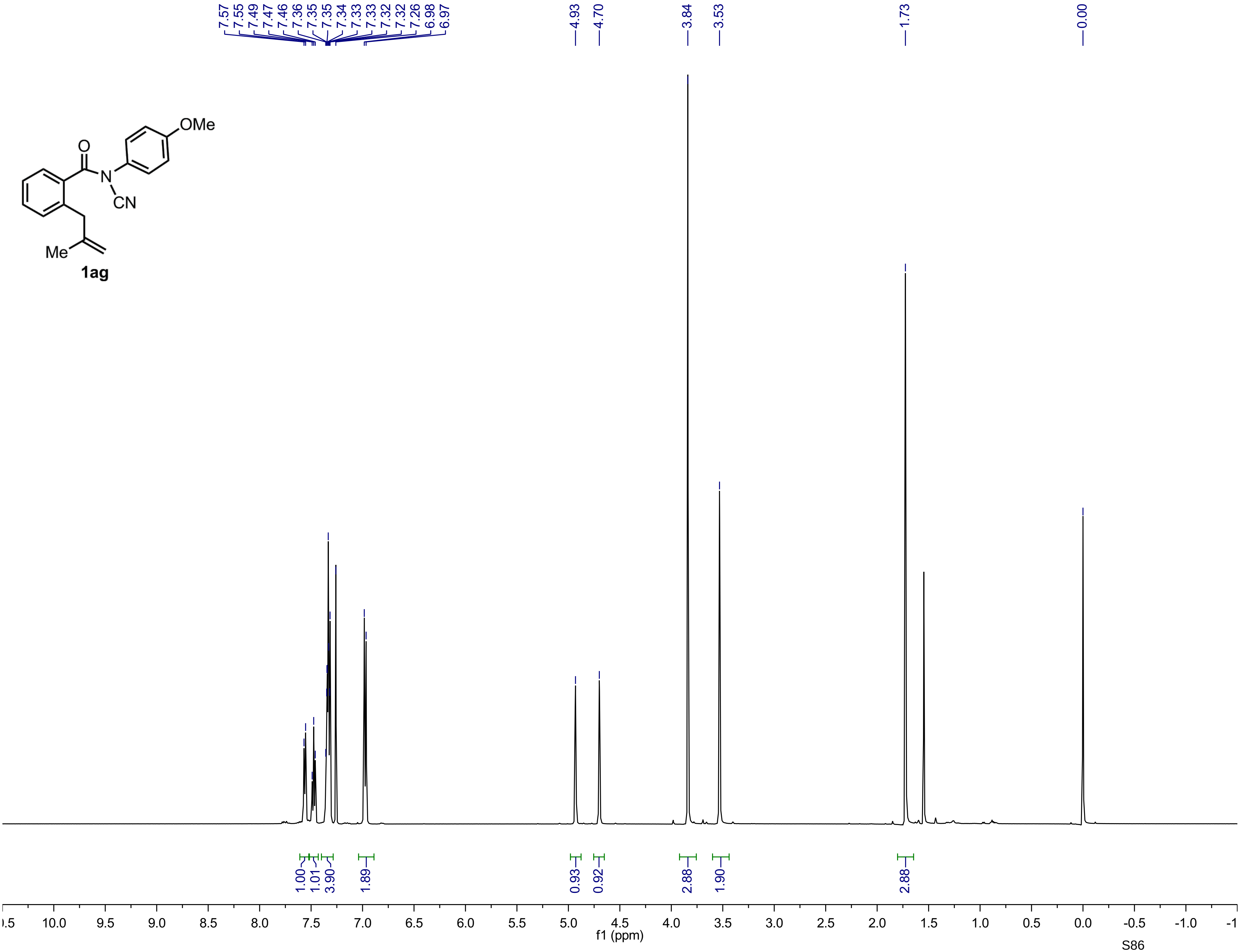
f1 (ppm)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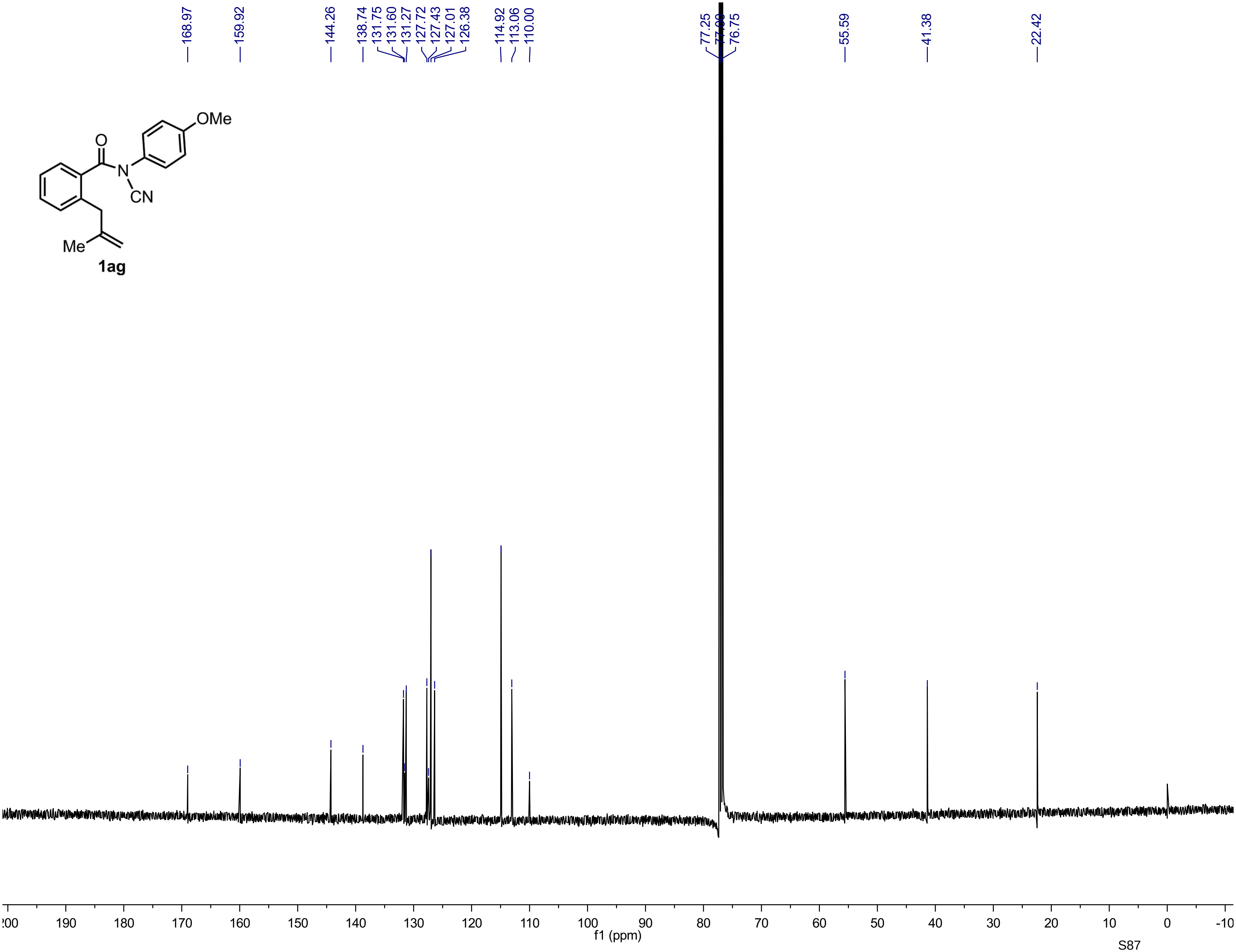
4.93
4.70
3.84
3.53
1.73
0.00
OMe
O
N
CN
Me
1ag
1.00 1.01 3.90 1.89
0.93 0.92
2.88 1.90
2.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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131.75
131.60
131.27
127.72
127.43
127.01
126.38
114.92
113.06
110.00
77.25
77.00
76.75
55.59
41.38
22.42
200
190
180
170
160
150
140
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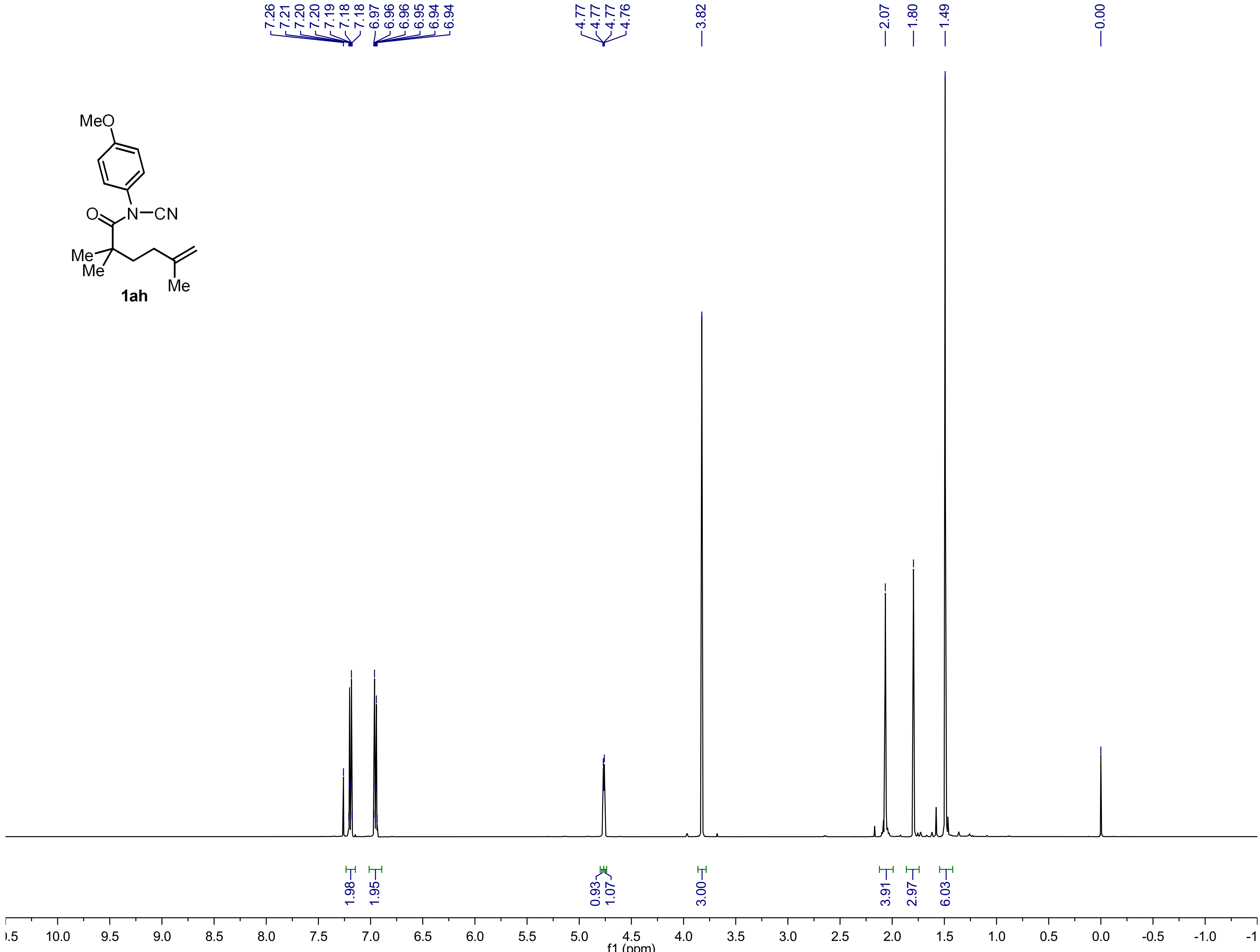
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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6.94
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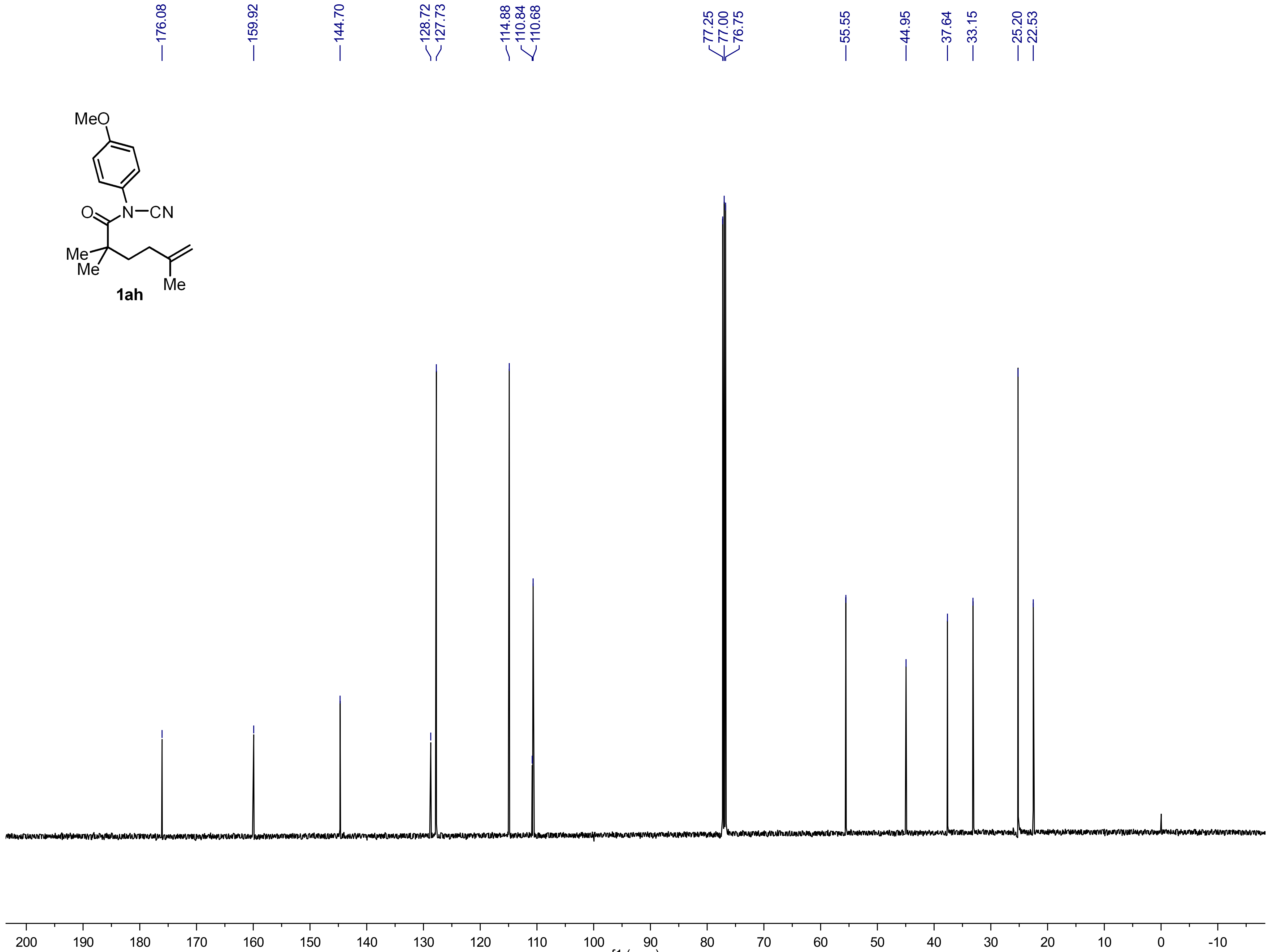
4.77
4.77
4.76
3.82
2.07
1.80
1.49
0.00
MeO
O
N
CN
Me
Me
Me
1ah
1.98
1.95
0.93
1.07
3.00
3.91
2.97
6.03
f1 (ppm)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77.25
77.00
76.75
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44.95
37.64
33.15
25.20
22.53
MeO
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CN
Me
Me
Me
1ah
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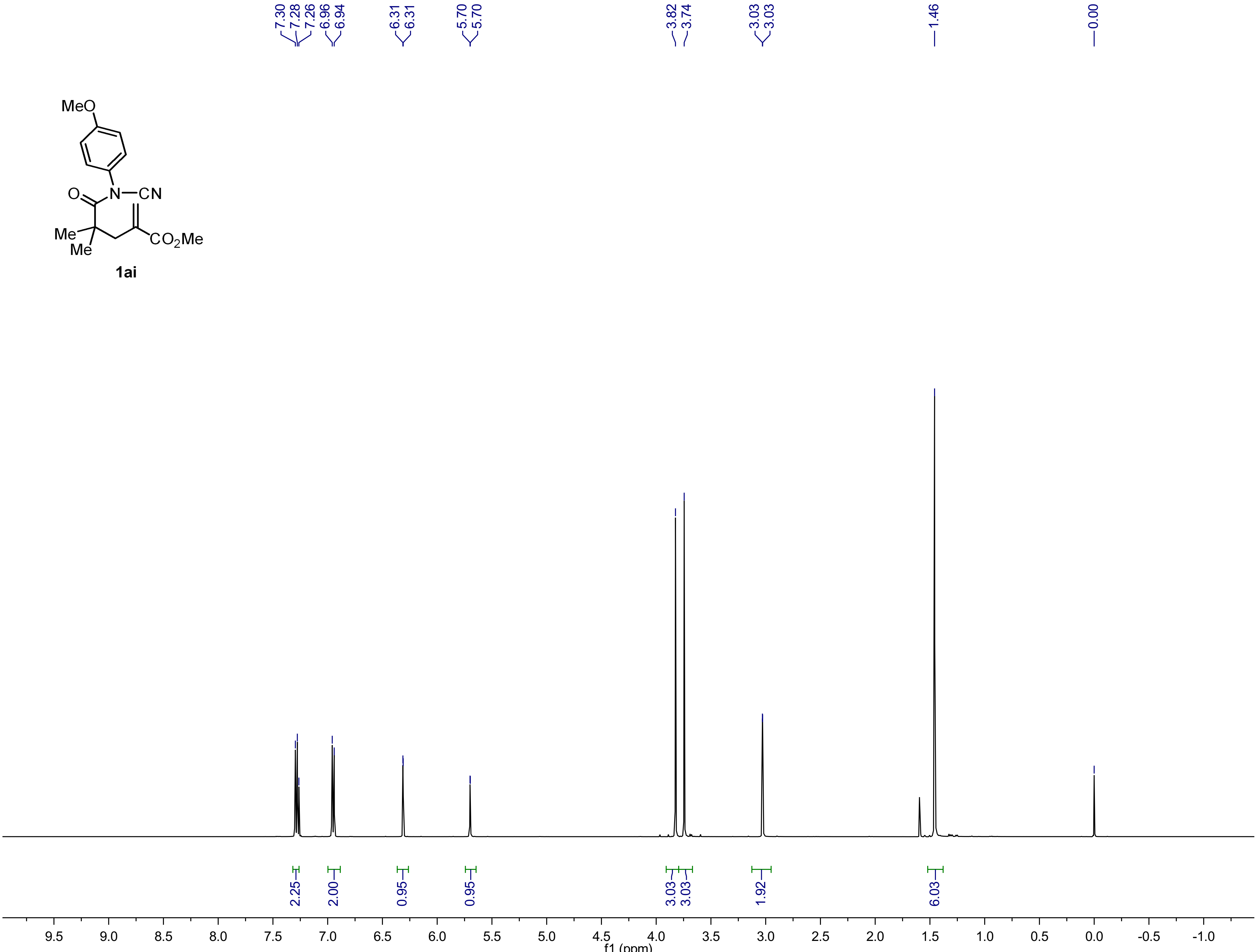
f1 (ppm)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6.94
6.31
6.31
5.70
5.70
3.82
3.74
3.03
3.03
1.46
0.00
MeO
O
N
CN
Me
Me
CO_2Me
1ai
2.25
2.00
0.95
0.95
3.03
3.03
1.92
6.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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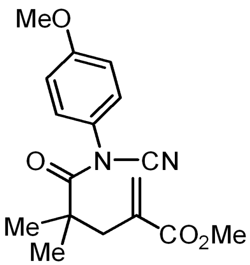
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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Me
CO2Me
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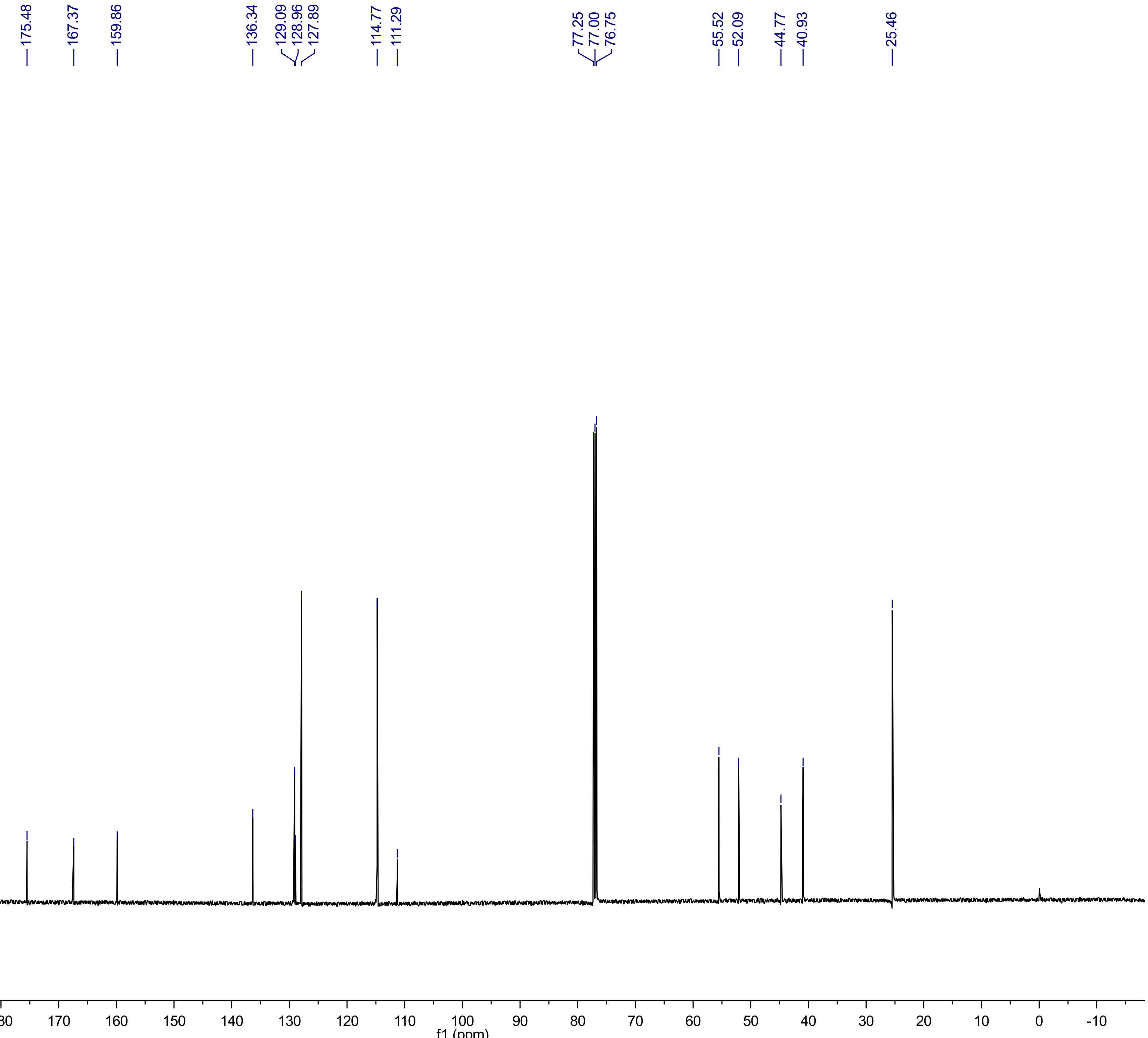
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77.25
77.00
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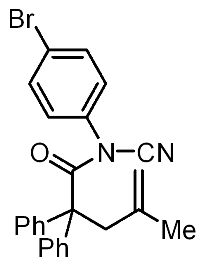
52.09
44.77
40.93
25.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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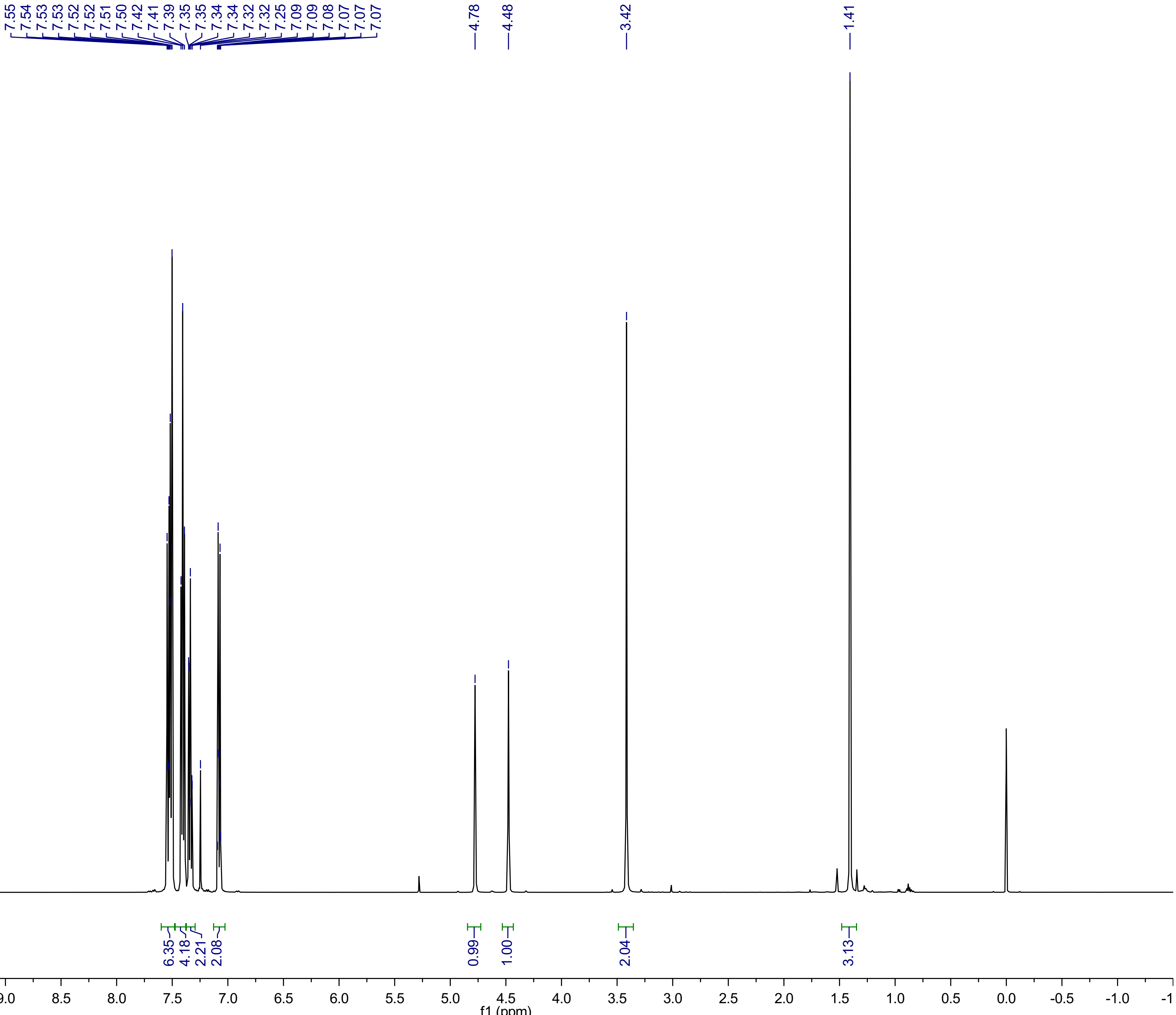
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4.78
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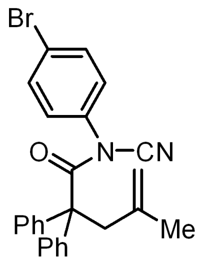
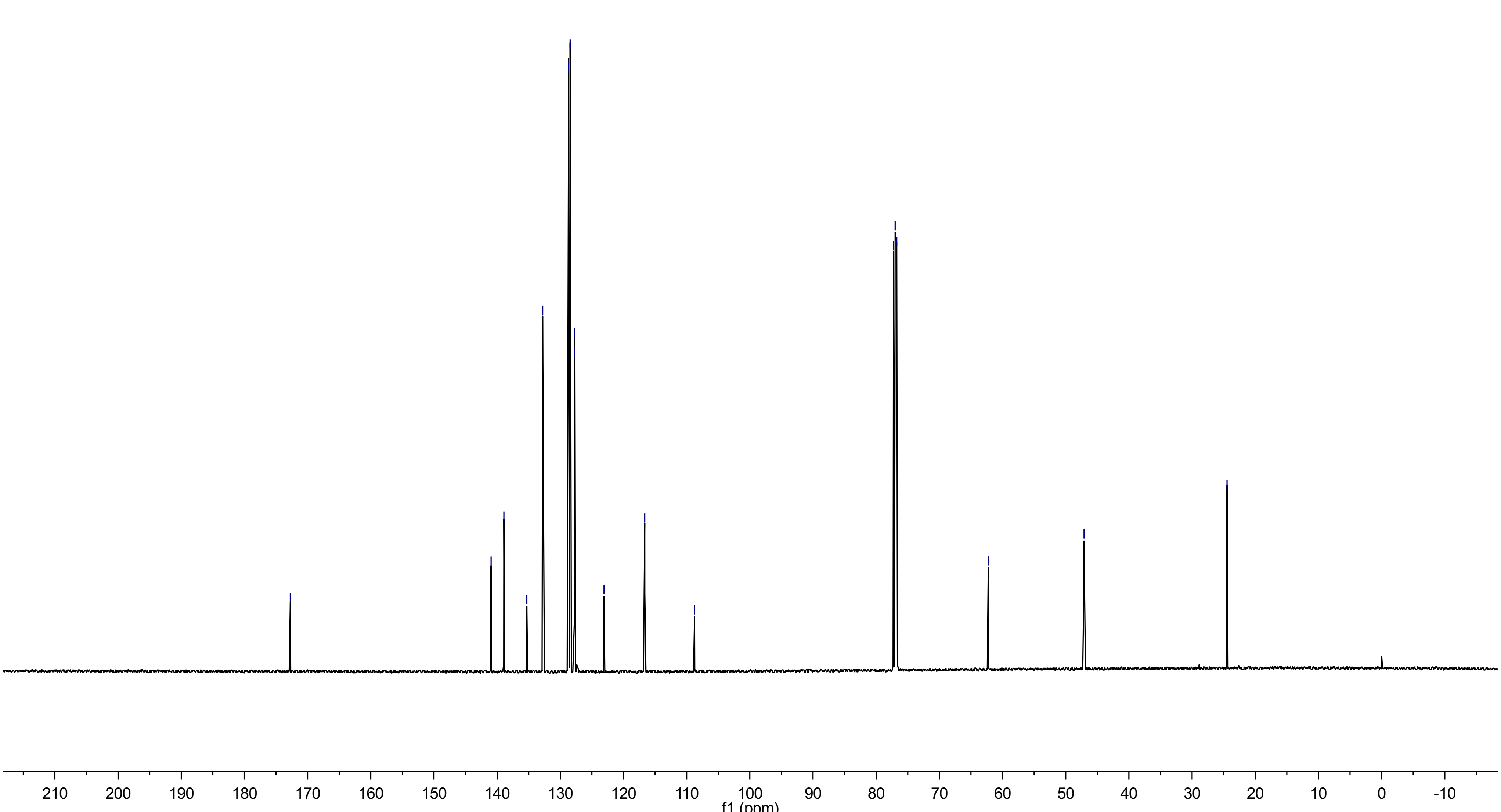
3.42
1.41
6.35
4.18
2.21
2.08
0.99
1.00
2.04
3.13
f1 (ppm)


Br
O
N
CN
Ph
Ph
Me

1aj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127.78
127.70
123.08
116.63
108.75
77.25
77.00
76.75
62.26
47.10
24.47
210
200
190
180
170
160
150
140
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120
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100
90
80
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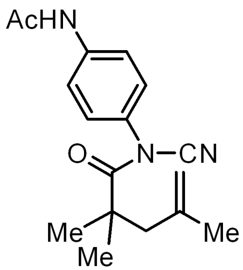
50
40
30
20
10
0
-10
f1 (ppm)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Me
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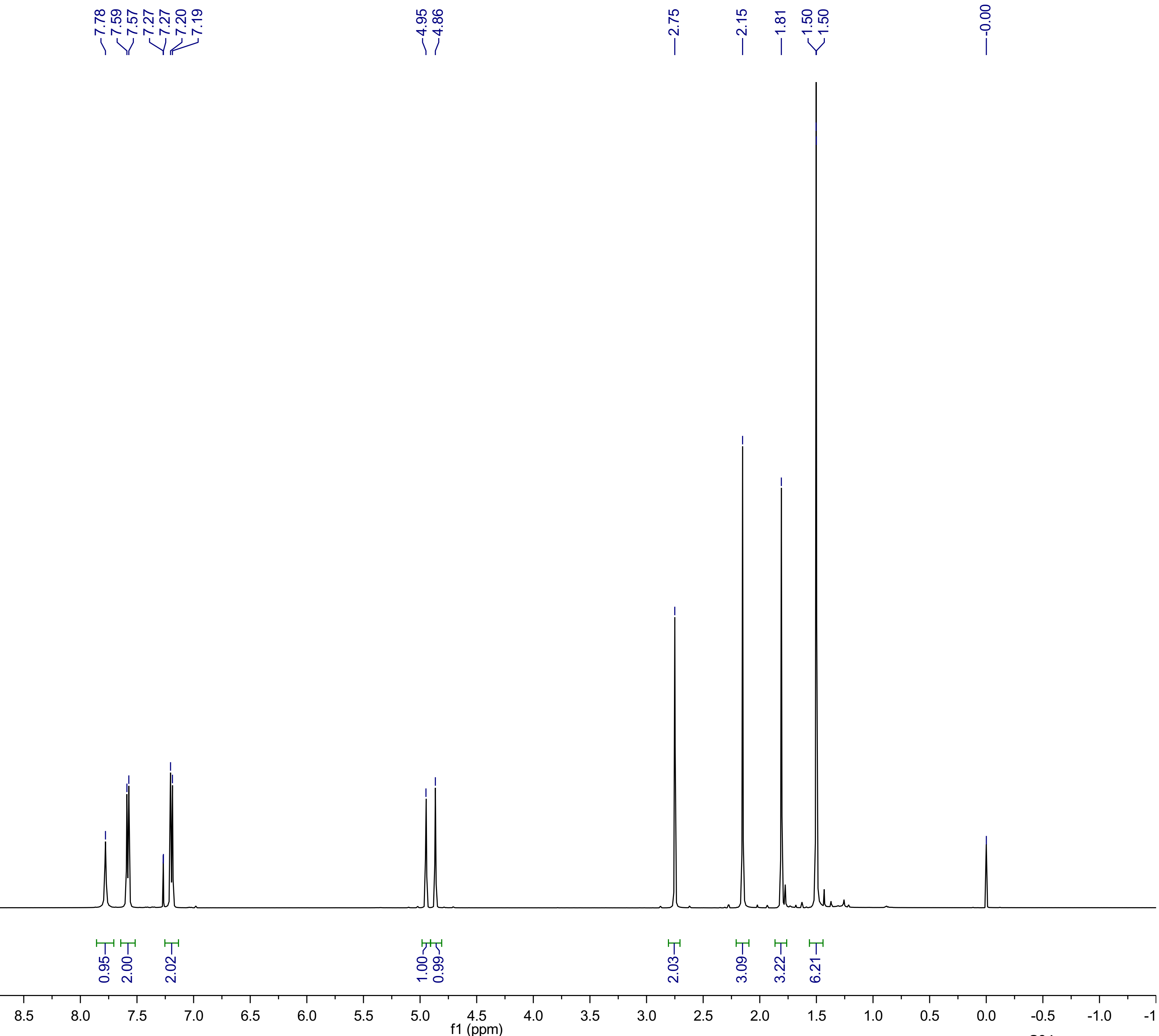
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2.15
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1.50
1.50
-0.00
0.95
2.00
2.02
1.00
0.99
2.03
3.09
3.22
6.21
10.0
9.5
9.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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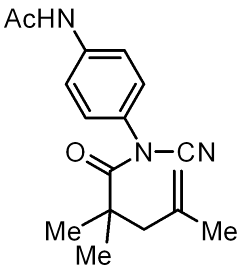
f1 (ppm)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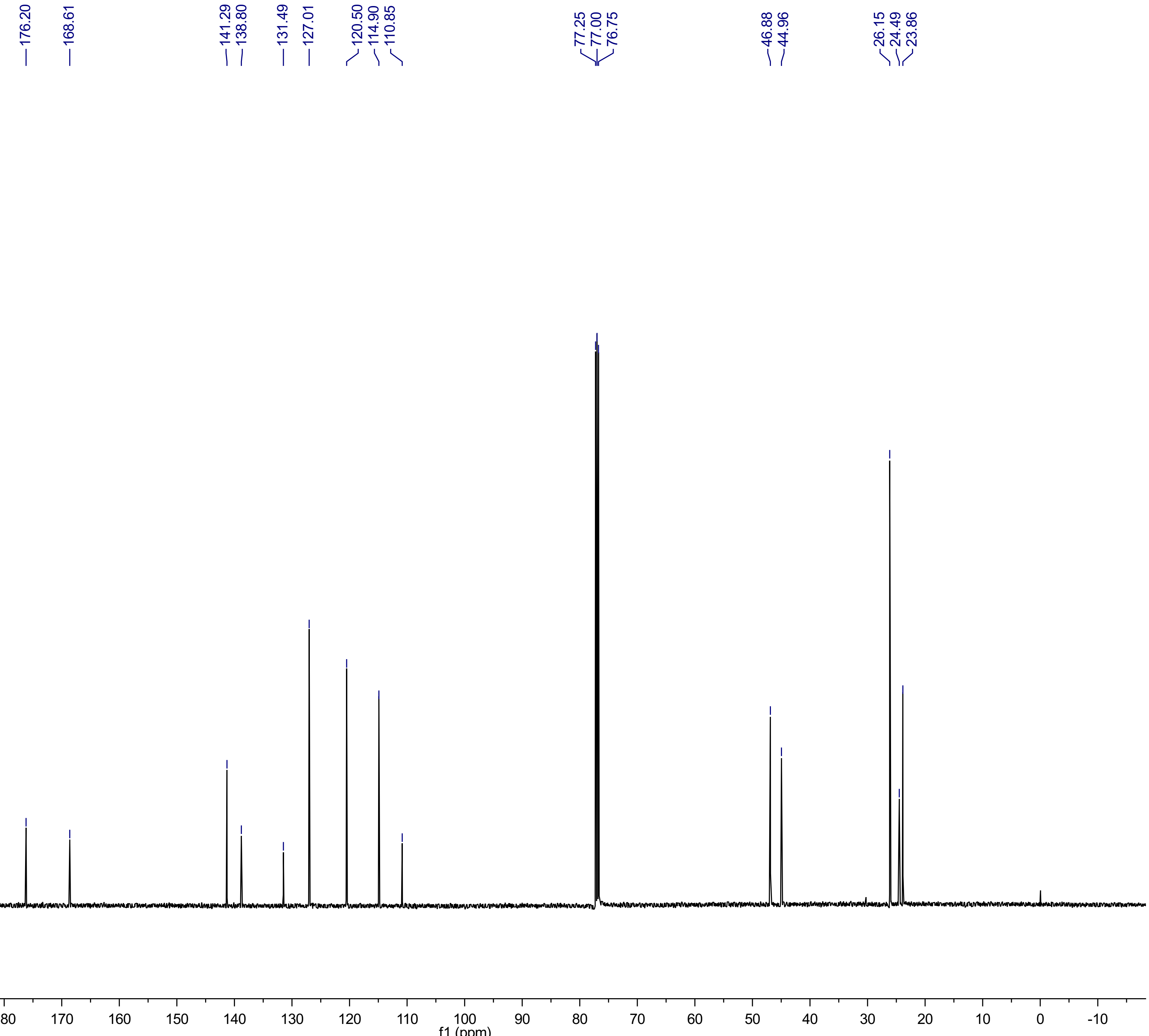
CN
Me
Me
Me

1ak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24.49
23.86
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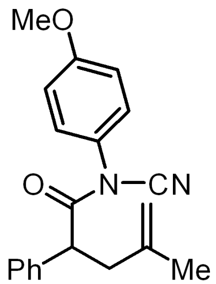
f1 (ppm)



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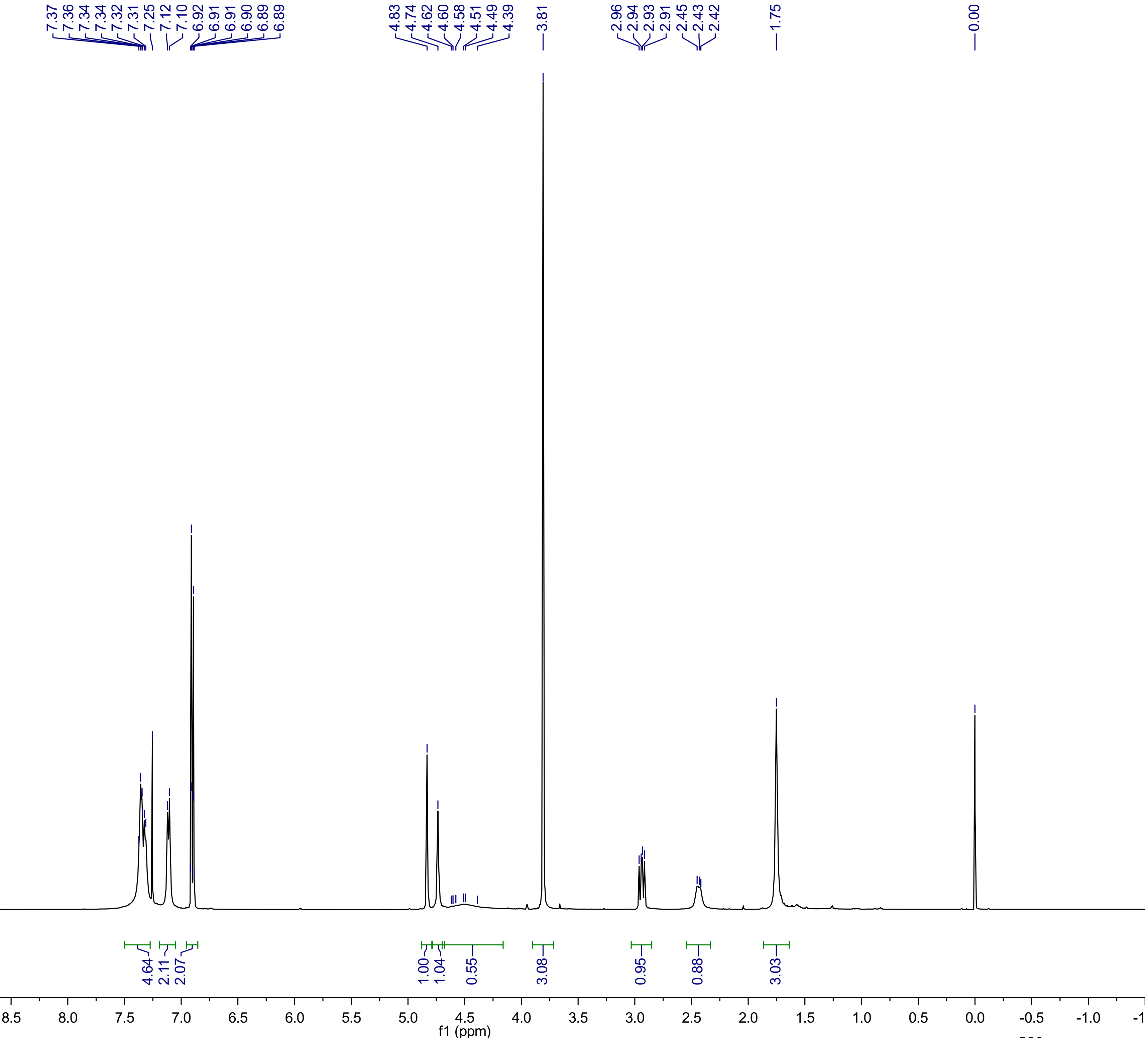

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7.12
7.10
6.92
6.91
6.91
6.90
6.89
6.89
4.83
4.74
4.62
4.60
4.58
4.51
4.49
4.39
3.81
2.96
2.94
2.93
2.91
2.45
2.43
2.42
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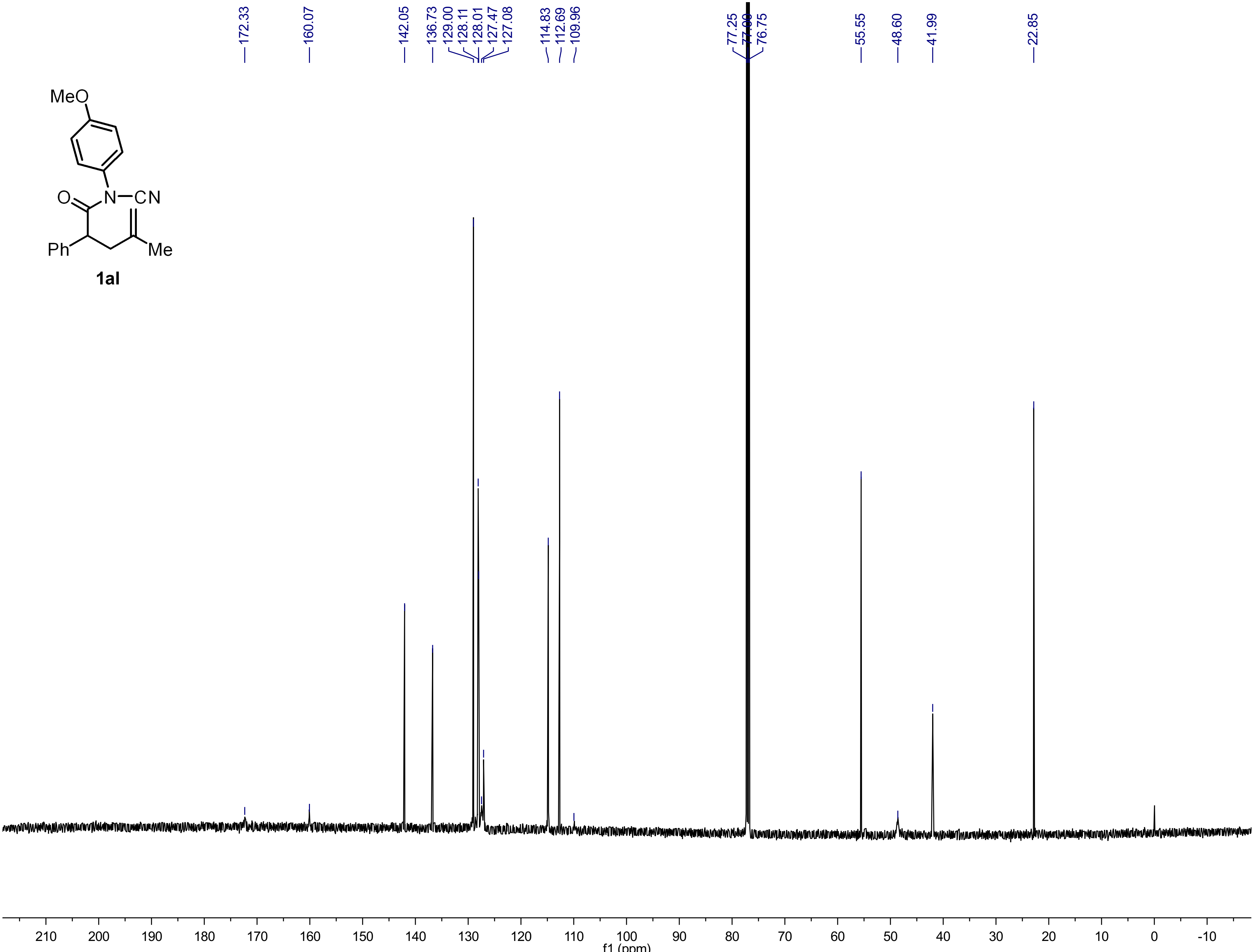
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N
CN
Ph
Me
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128.11
128.01
127.47
127.08
114.83
112.69
109.96
77.25
77.00
76.75
55.55
48.60
41.99
22.85
210
200
190
180
170
160
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100
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60
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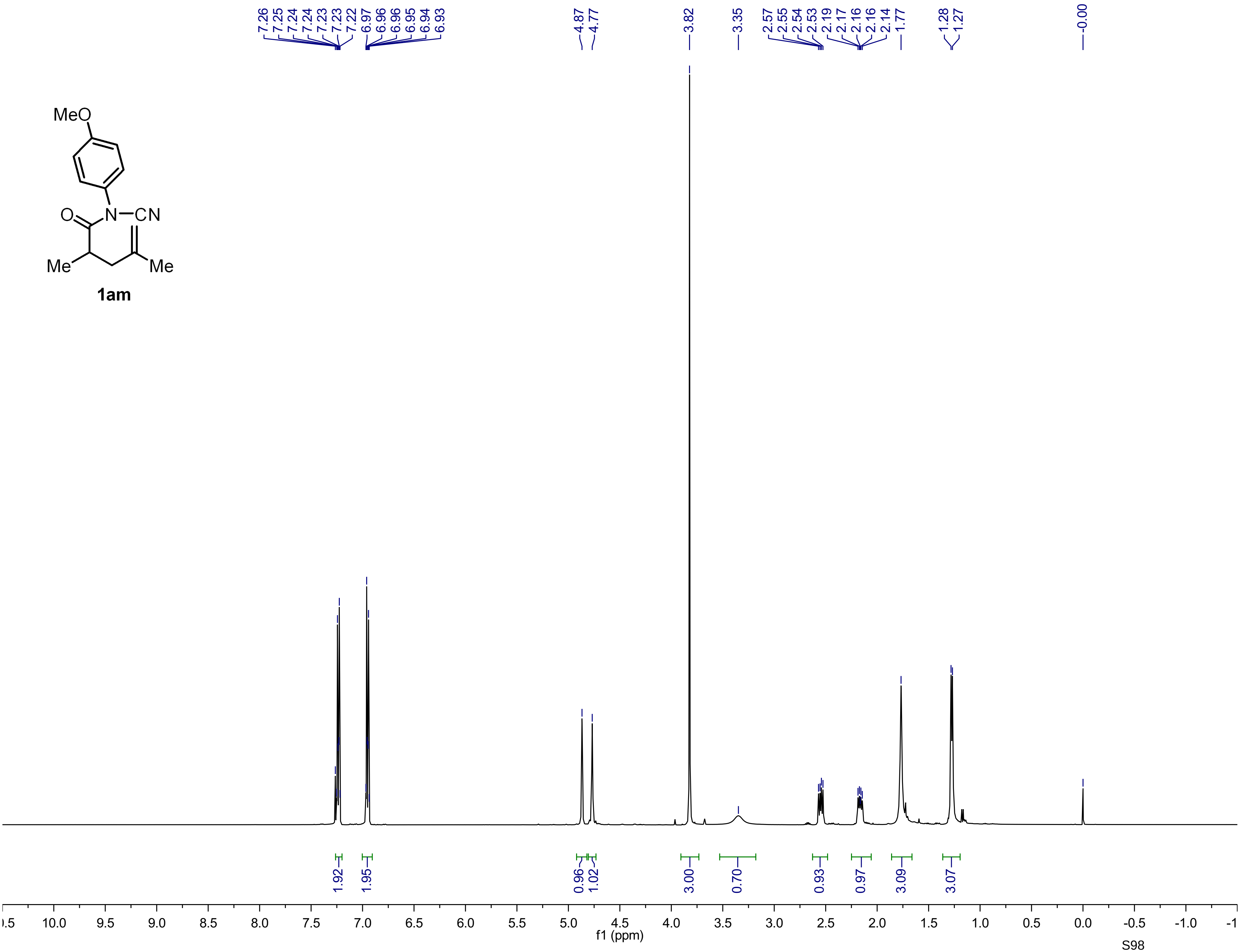
-10
f1 (ppm)

1al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6.96
6.95
6.94
6.93
4.87
4.77
3.82
3.35
2.57
2.55
2.54
2.53
2.19
2.17
2.16
2.16
2.14
1.77
1.28
1.27
-0.00
MeO
O
N
CN
Me
Me
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1.95
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1.02
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0.70
0.93
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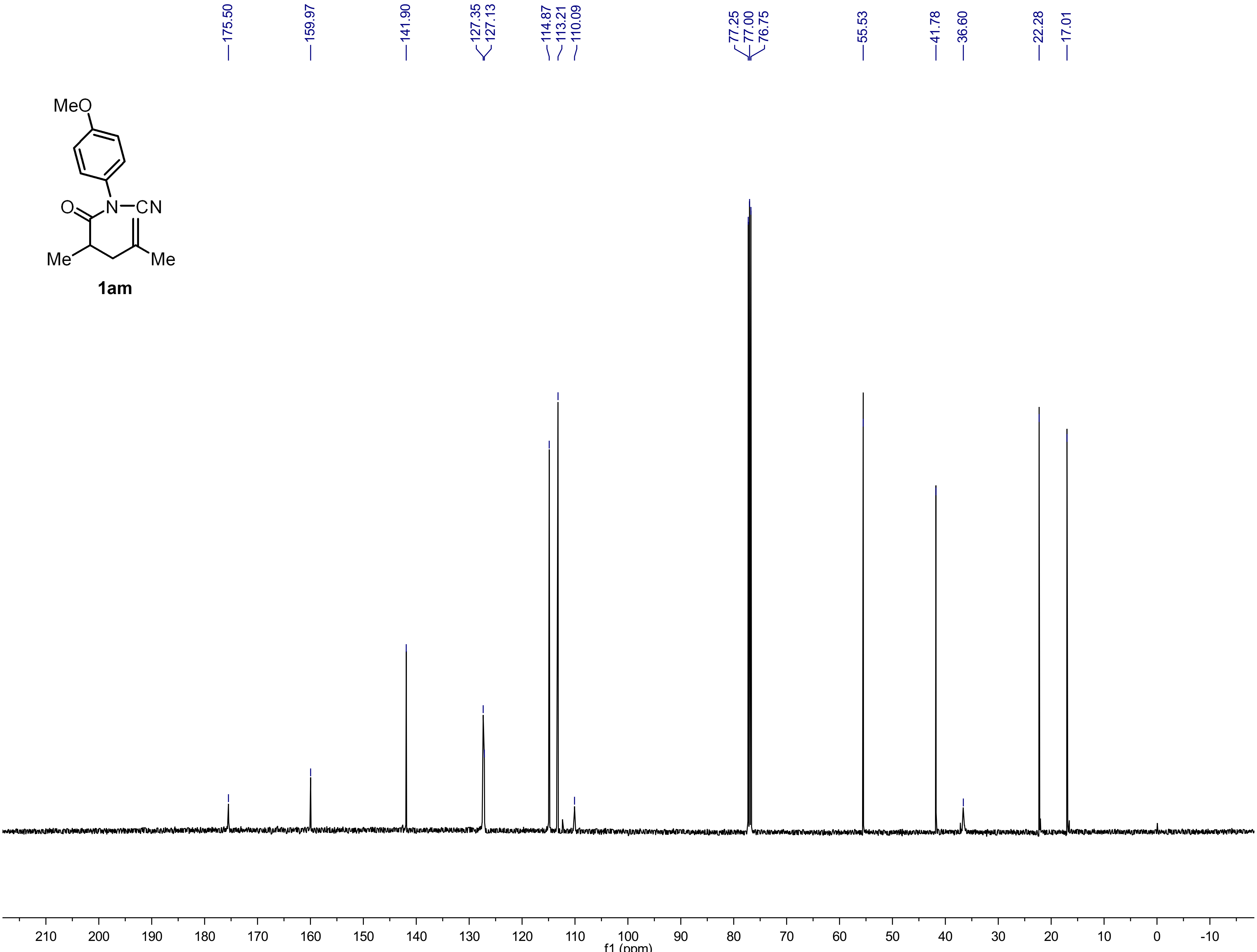
3.09
3.07
f1 (ppm)
1am



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127.13
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110.09
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76.75
55.53
41.78
36.60
22.28
17.01
MeO
O
N
CN
Me
Me
1am
210
200
190
180
170
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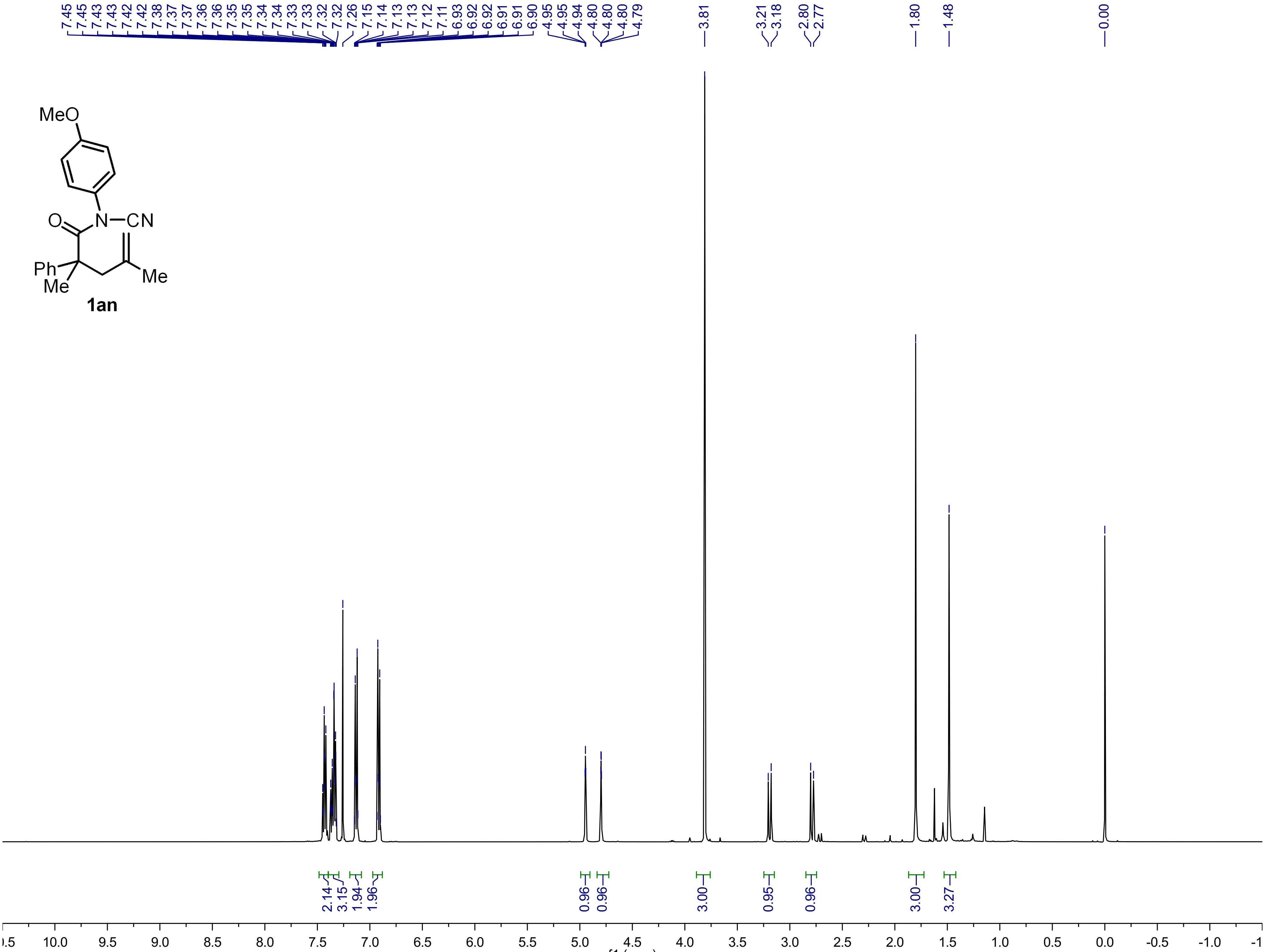
0
-10
f1 (ppm)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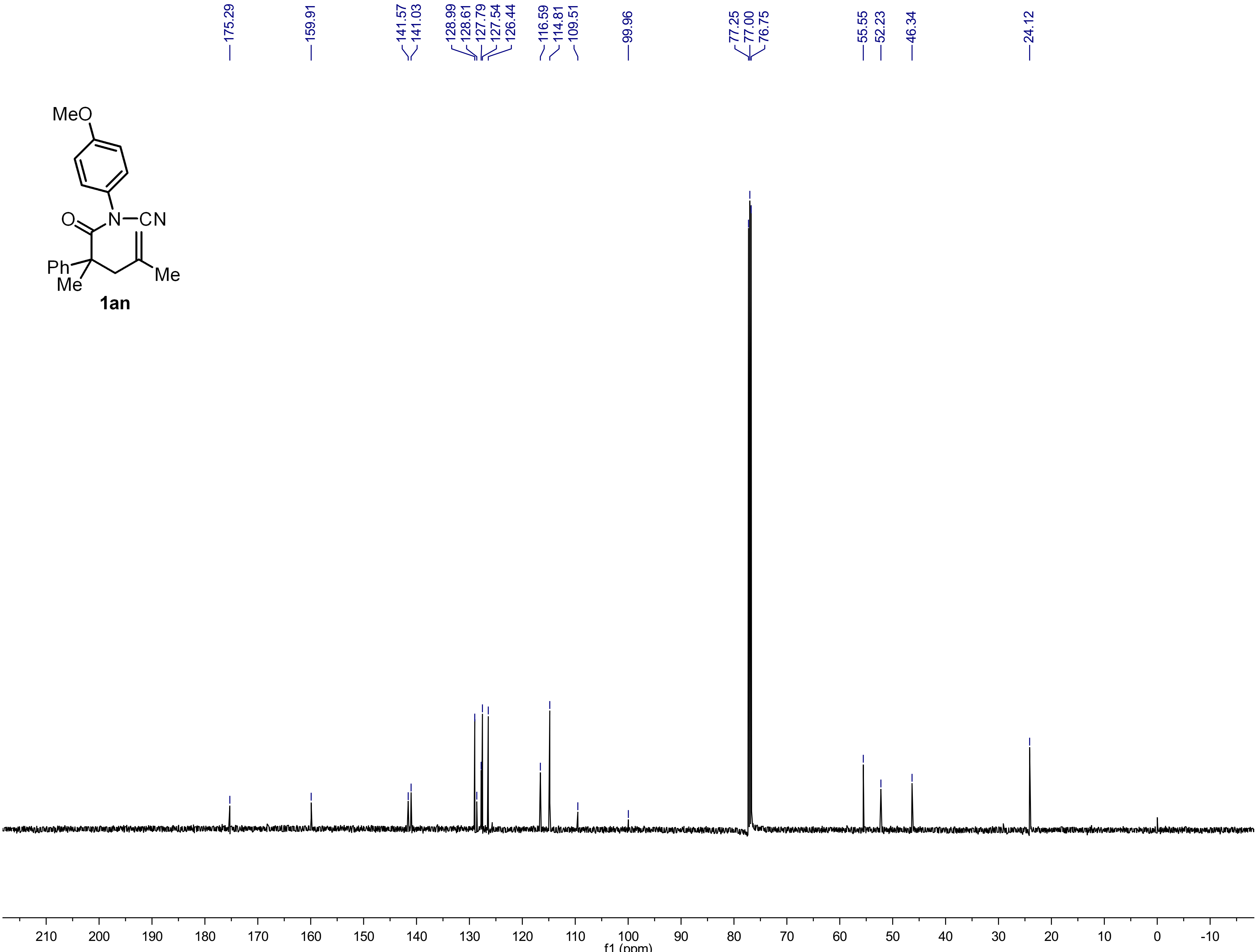
3.81
3.21 3.18
2.80 2.77
1.80
1.48
0.00
MeO
O
N
CN
Ph
Me
Me
1an
2.14 3.15 1.94 1.96 0.96 0.96 3.00 0.95 0.96 3.00 3.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


MeO
O
N
CN
Ph
Me
Me
1an
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127.79
127.54
126.44
116.59
114.81
109.51
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77.25
77.00
76.75
55.55
52.23
46.34
24.12
210
200
190
180
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100
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40
30
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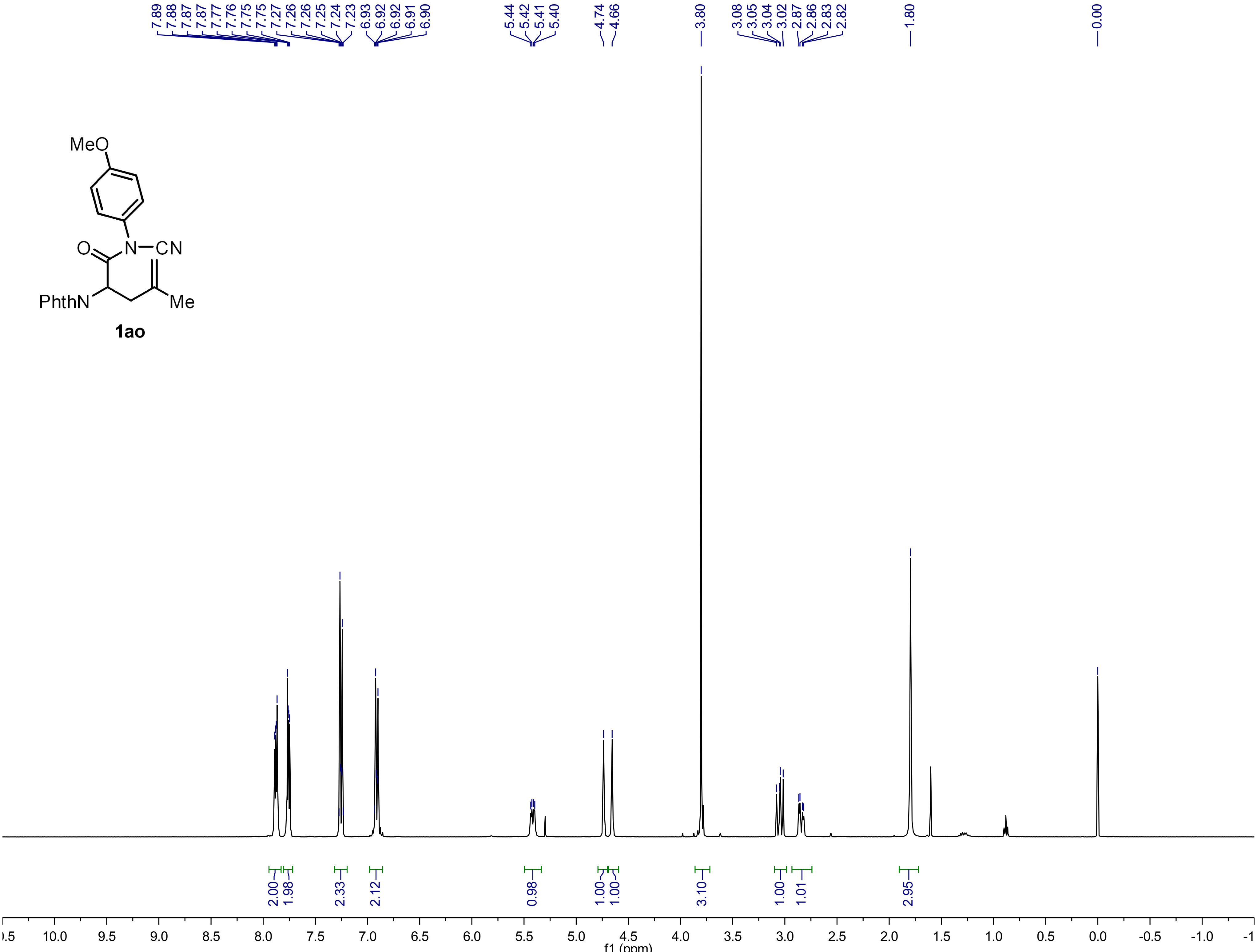
10
0
-10
f1 (ppm)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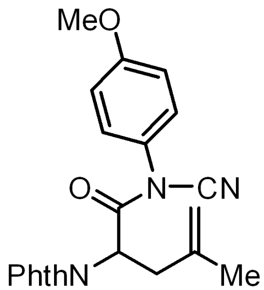
5.44 5.42 5.41 5.40
4.74 4.66
3.80
3.08 3.05 3.04 3.02 2.87 2.86 2.83 2.82
1.80
0.00
MeO
O
N
CN
PhthN
Me
1ao
2.00 1.98 2.33 2.12 0.98 1.00 1.00 3.10 1.00 1.01 2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


MeO
O
N
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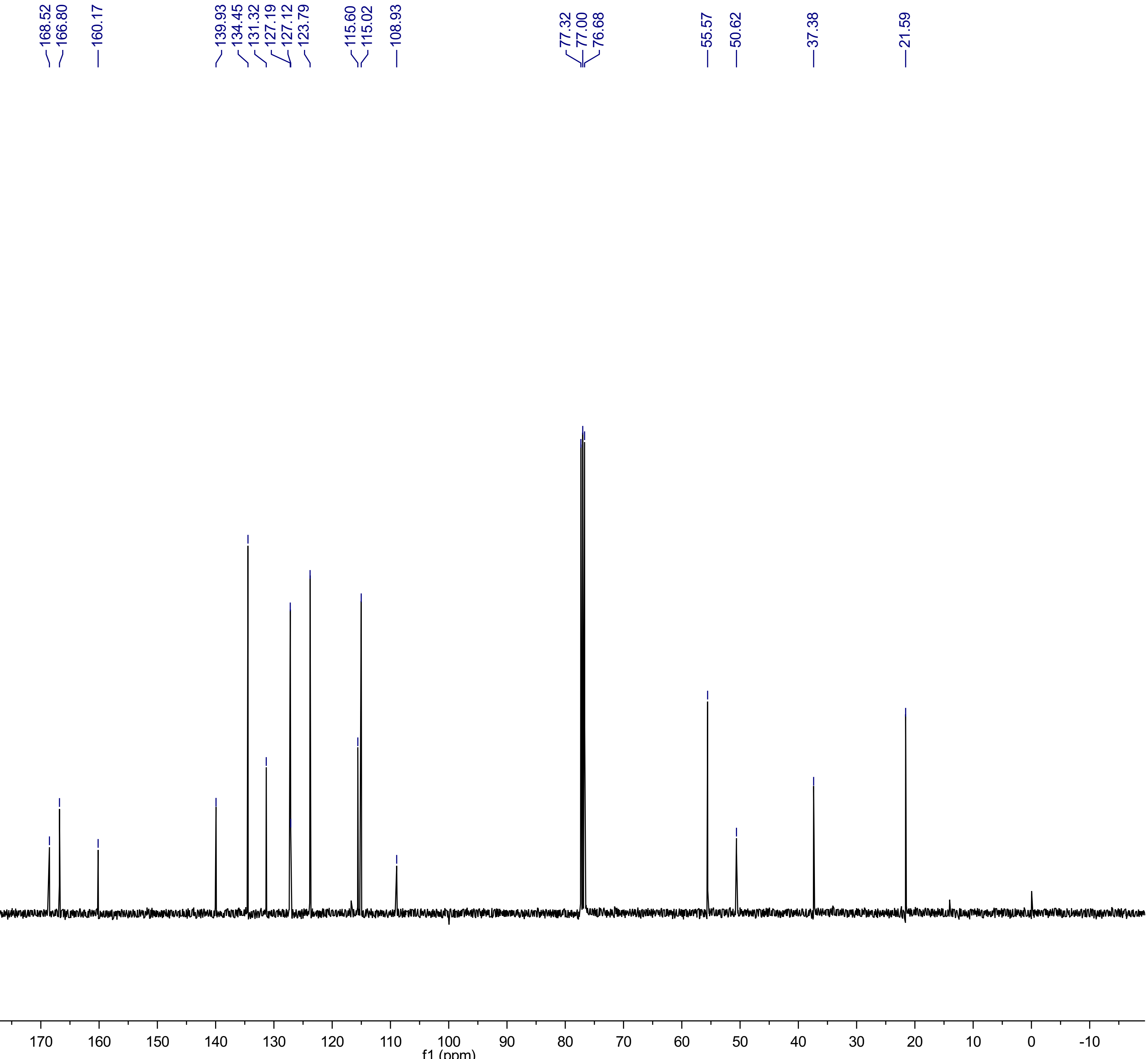
PhthN
Me

1ao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115.02
108.93
77.32
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37.38
21.59
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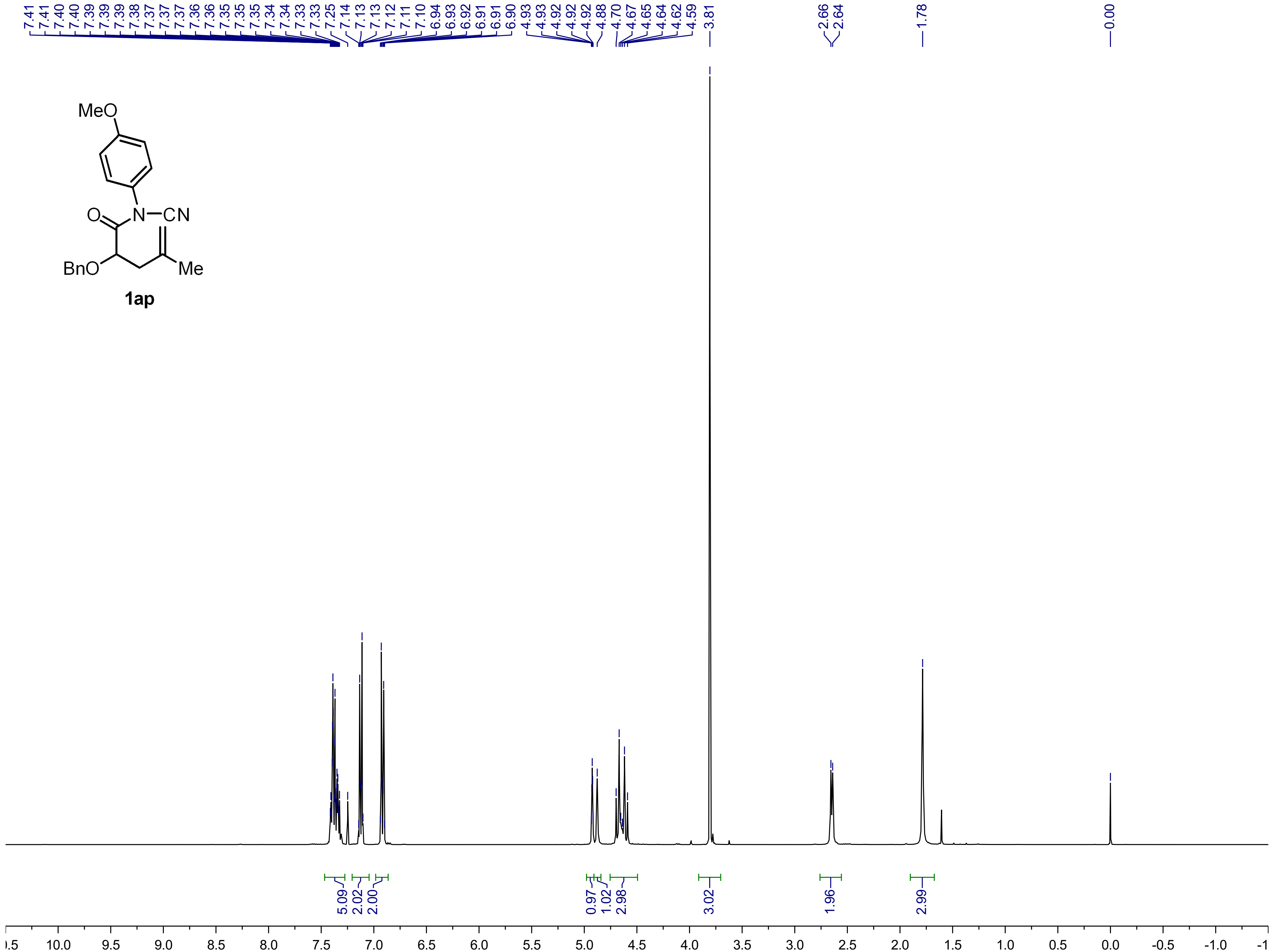
f1 (ppm)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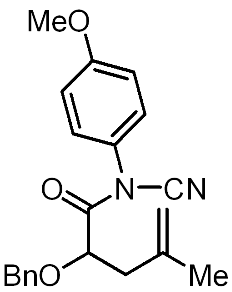
2.66 2.64
1.78
0.00
MeO
O
N
CN
BnO
Me
1ap
5.09 2.02 2.00 0.97 1.02 2.98 3.02 1.96 2.99
f1 (ppm)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CN
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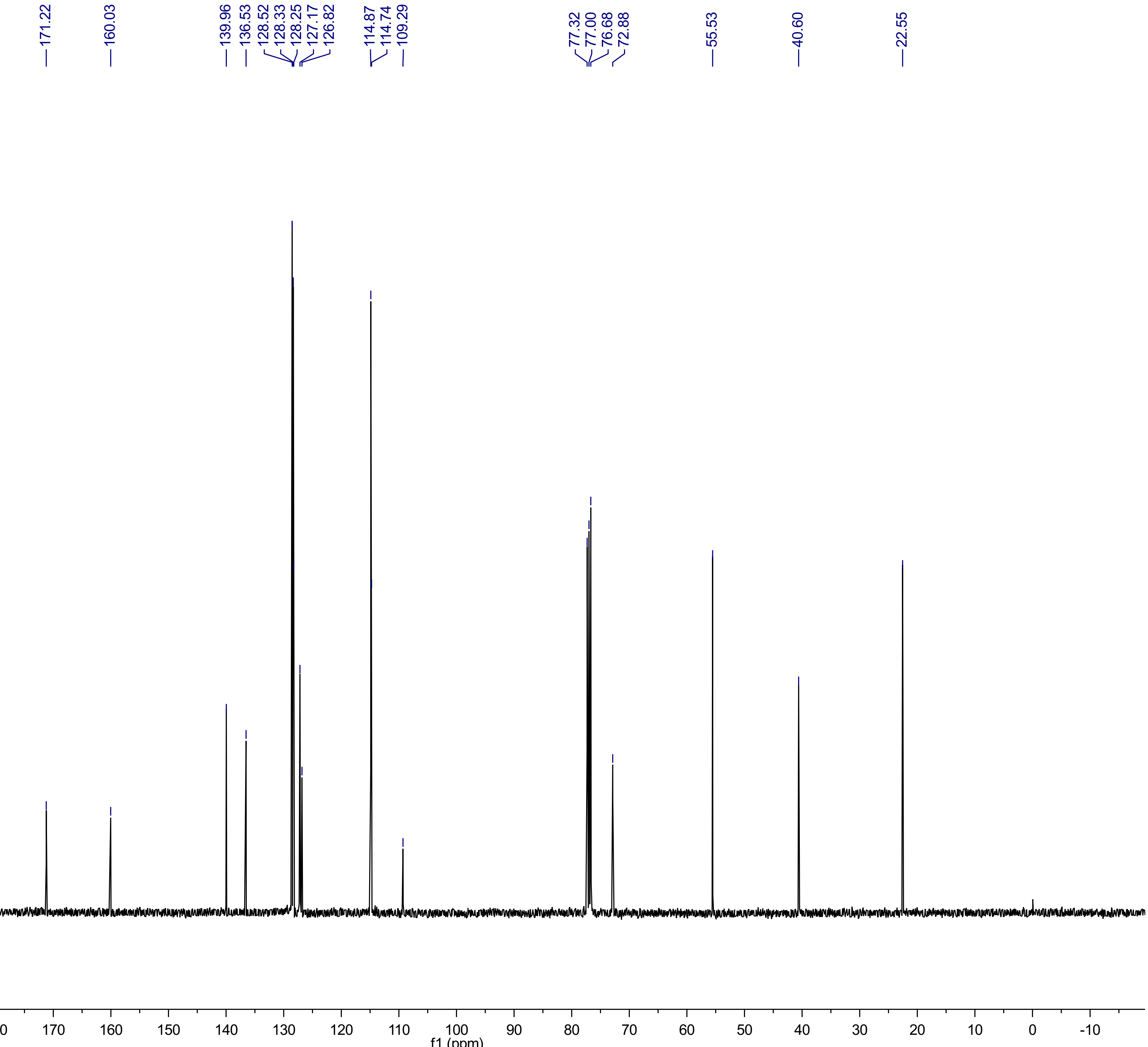
1ap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77.32
77.00
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40.60
22.55
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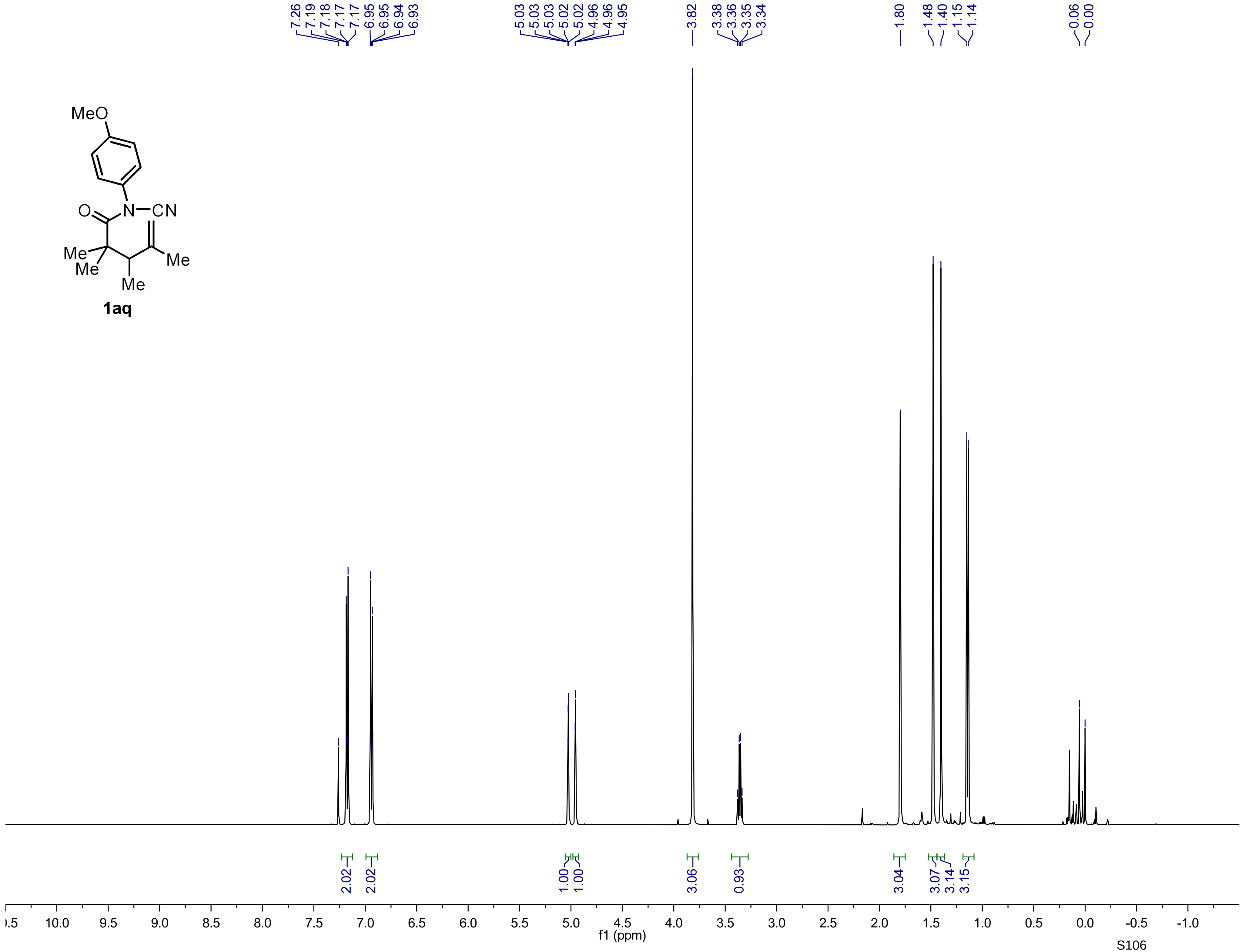
f1 (ppm)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6.94
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5.03
5.03
5.02
5.02
4.96
4.96
4.95
3.82
3.38
3.36
3.35
3.34
1.80
1.48
1.40
1.15
1.14
0.06
0.00
MeO
O
N
CN
Me
Me
Me
Me
2.02
2.02
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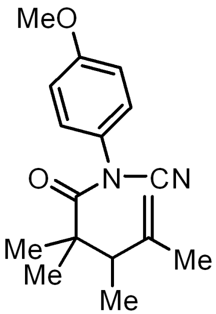
1.00
3.06
0.93
3.04
3.07
3.14
3.15
f1 (ppm)

1aq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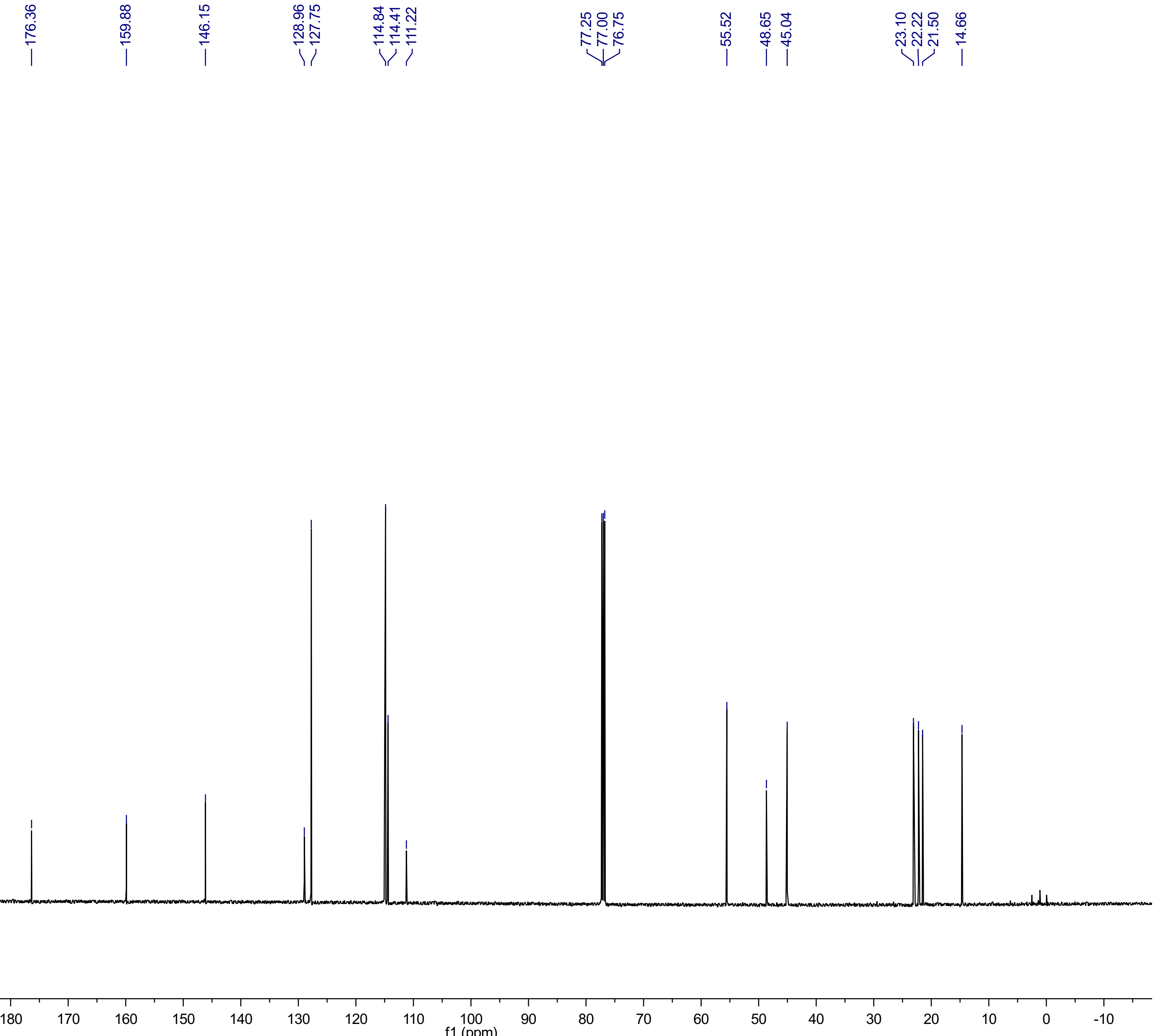
CN
Me
Me
Me
Me

1aq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55.52
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22.22
21.50
14.66
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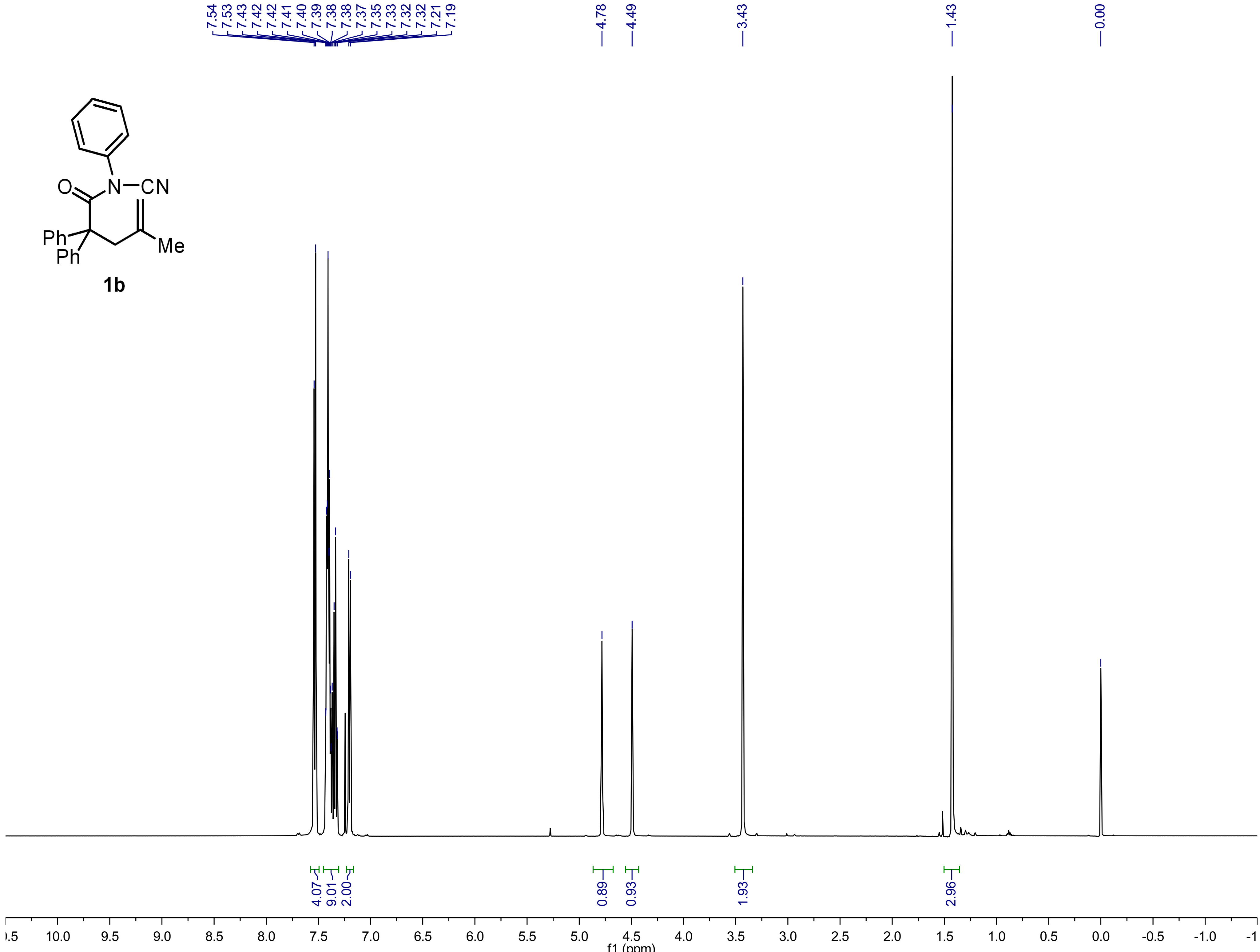
f1 (ppm)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7.33
7.32
7.32
7.21
7.19
4.78
4.49
3.43
1.43
0.00
O
N
CN
Ph
Ph
Me
1b
4.07
9.01
2.00
0.89
0.93
1.93
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
1.5
1.0
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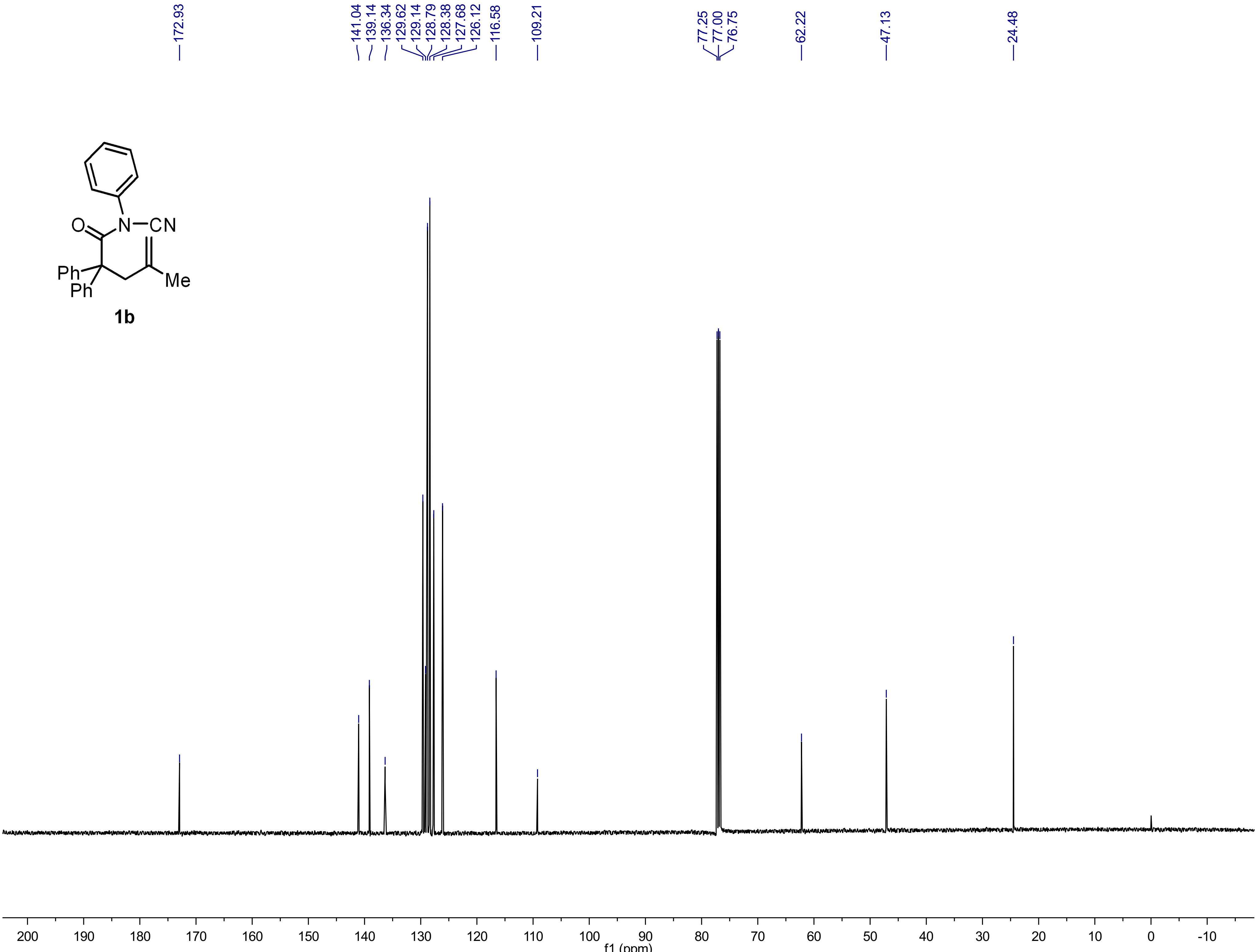
0.0
-0.5
-1.0
f1 (ppm)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CN
Ph
Ph
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1b
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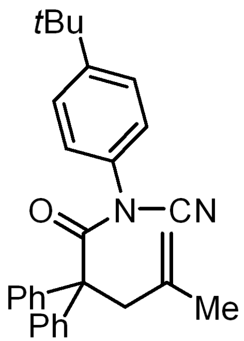
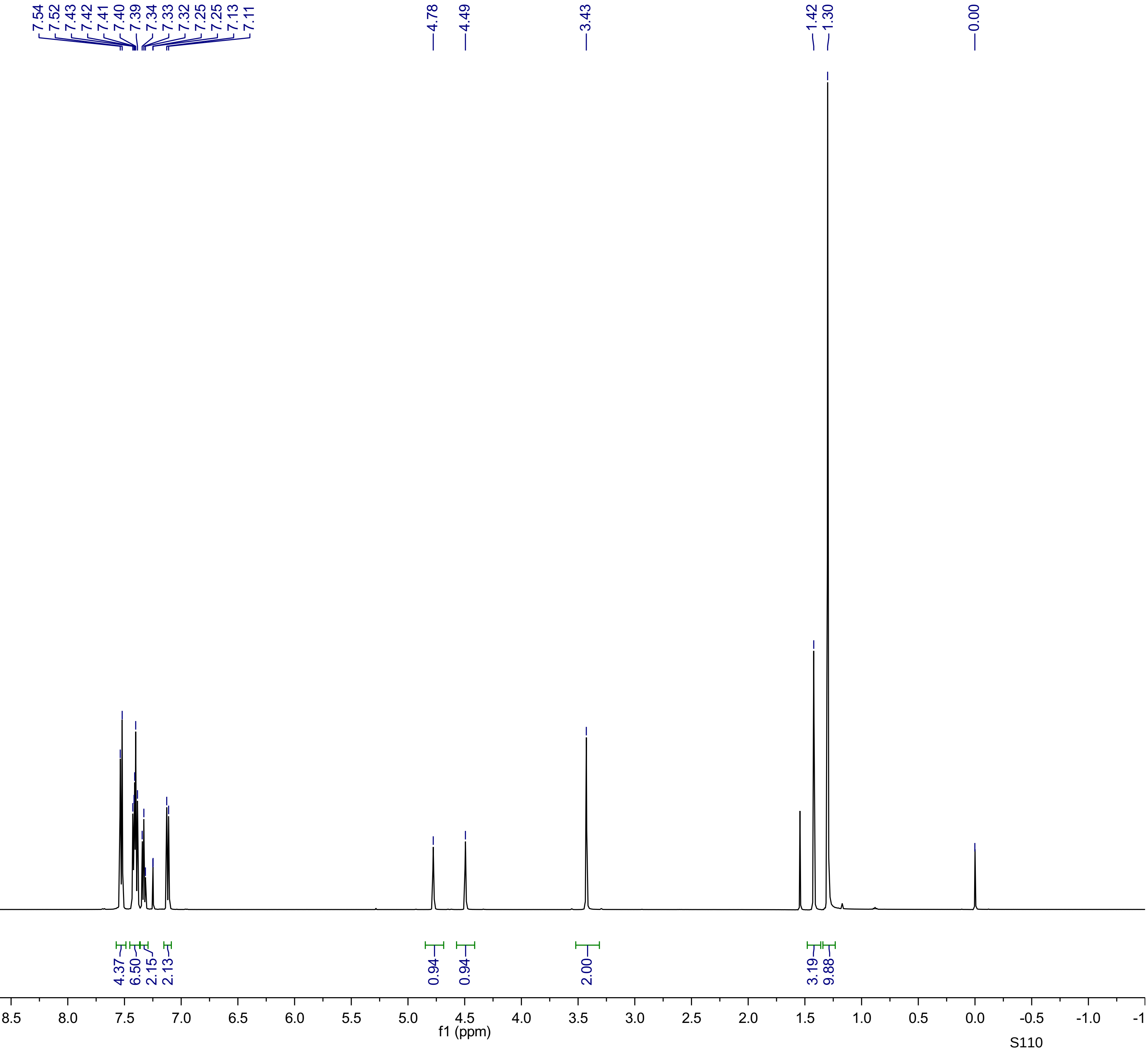
136.34
129.62
129.14
128.79
128.38
127.68
126.12
116.58
109.21
77.25
77.00
76.75
62.22
47.13
24.48
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



1c



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7.52
7.43
7.42
7.41
7.40
7.39
7.34
7.33
7.32
7.25
7.25
7.13
7.11
4.78
4.49
3.43
1.42
1.30
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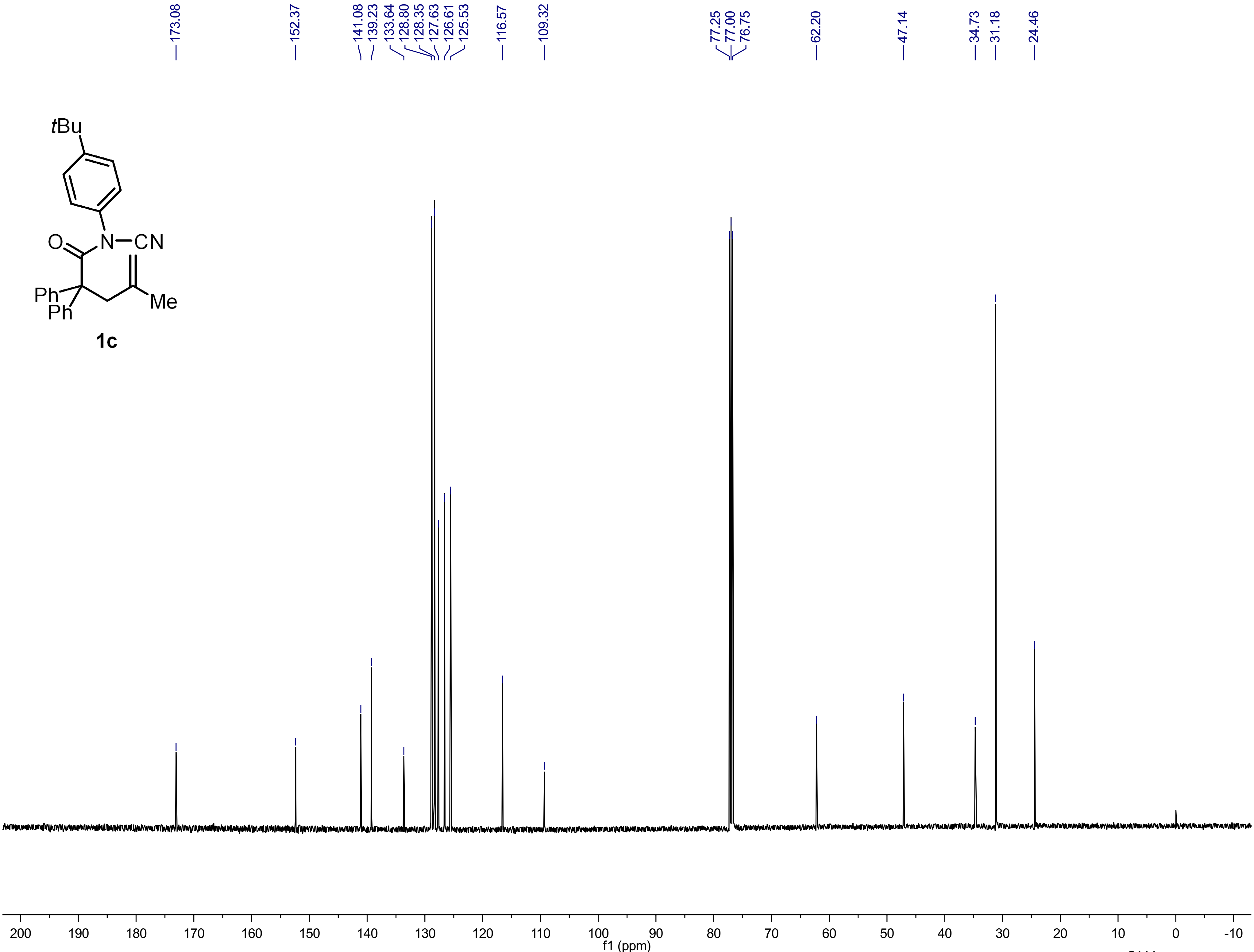
4.37
6.50
2.15
2.13
0.94
0.94
2.00
3.19
9.88
f1 (ppm)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141.08
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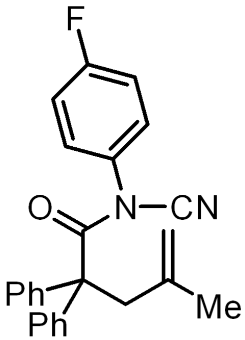
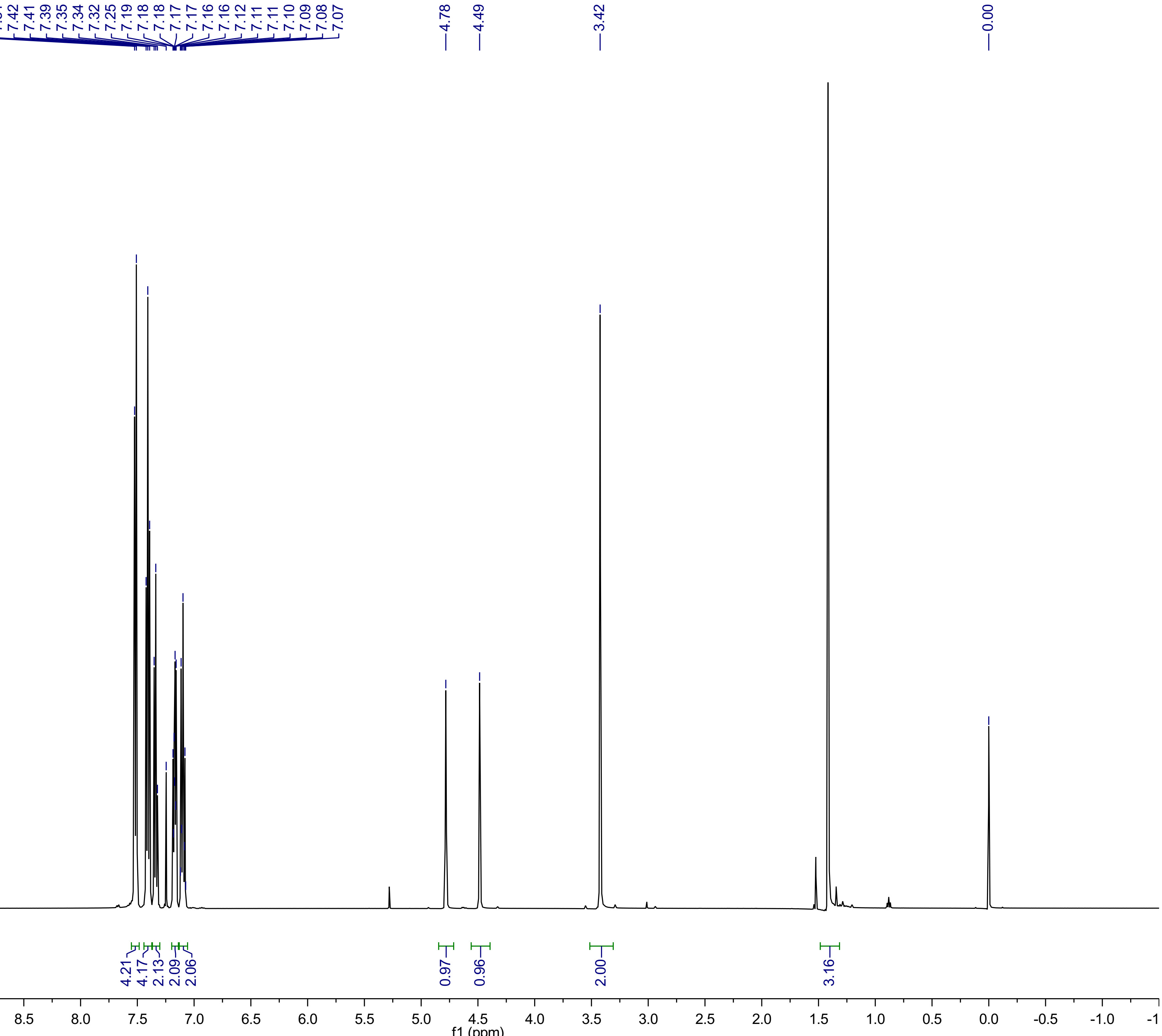
128.80
128.35
127.63
126.61
125.53
116.57
109.32
77.25
77.00
76.75
62.20
47.14
34.73
31.18
24.46
tBu
O
N
CN
Ph
Ph
Me
1c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


F
O
N
CN
Ph
Ph
Me

1d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7.51
7.42
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7.35
7.34
7.32
7.25
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.12
7.11
7.11
7.10
7.09
7.08
7.07
4.78
4.49
3.42
0.00
4.21
4.17
2.13
2.09
2.06
0.97
0.96
2.00
3.16
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
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2.5
2.0
1.5
1.0
0.5
0.0
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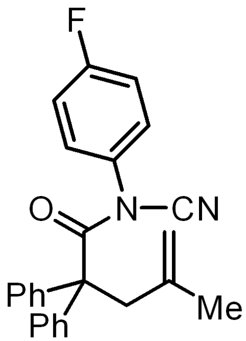
-1.0
f1 (ppm)



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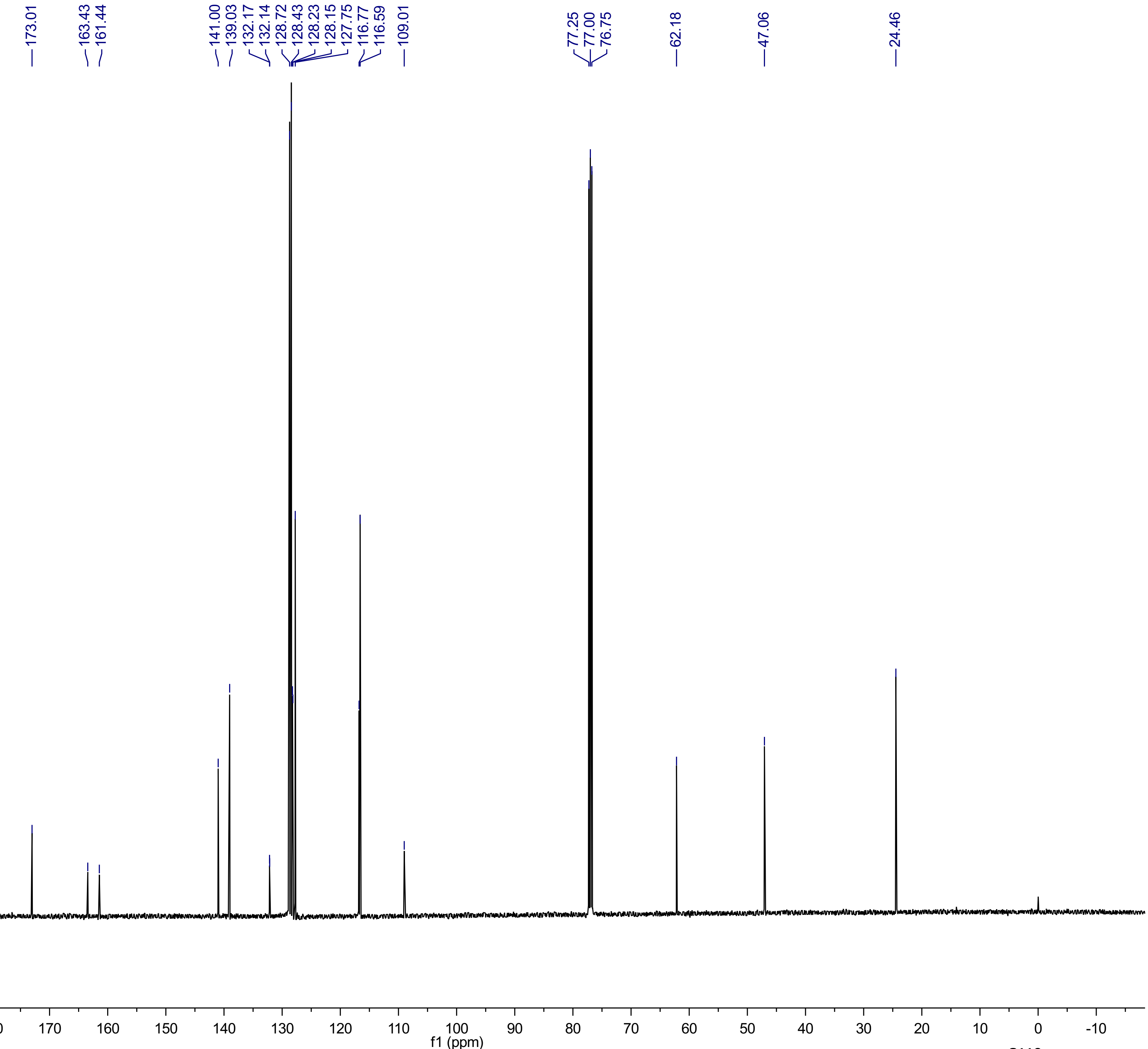

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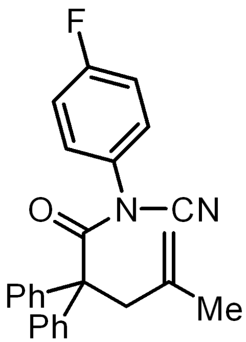
132.17
132.14
128.72
128.43
128.23
128.15
127.75
116.77
116.59
109.01
77.25
77.00
76.75
62.18
47.06
24.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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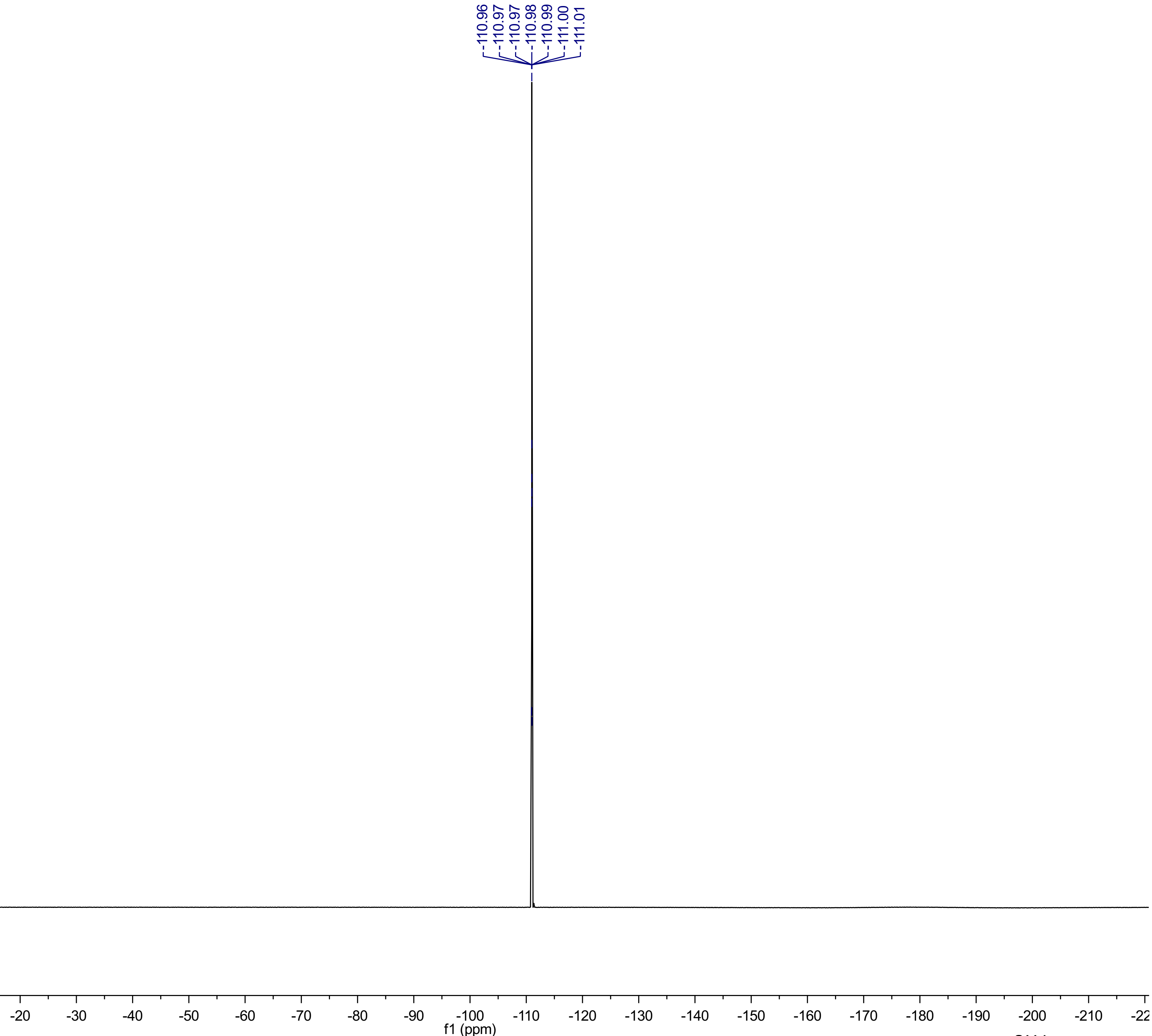
-110.96
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-111.01
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
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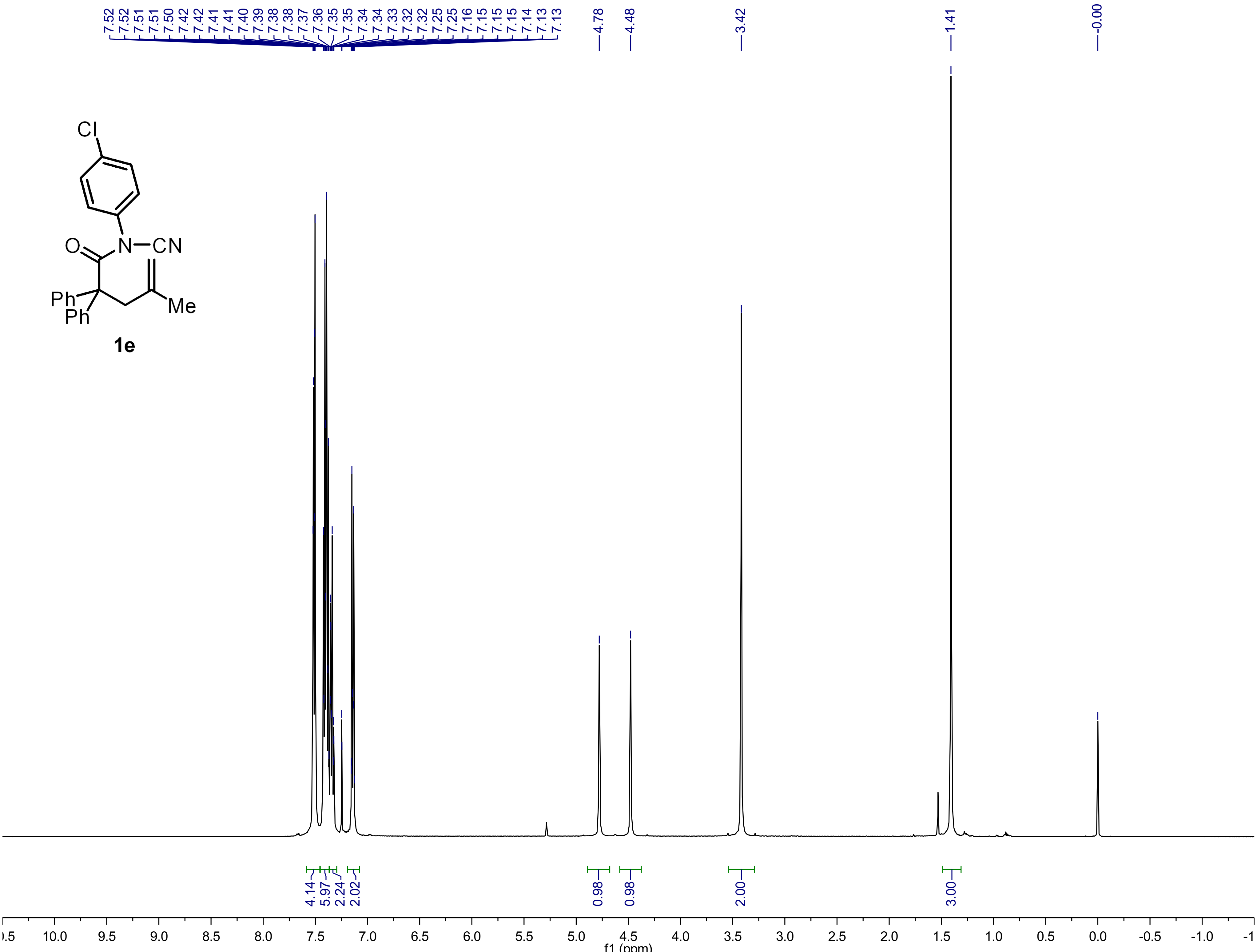
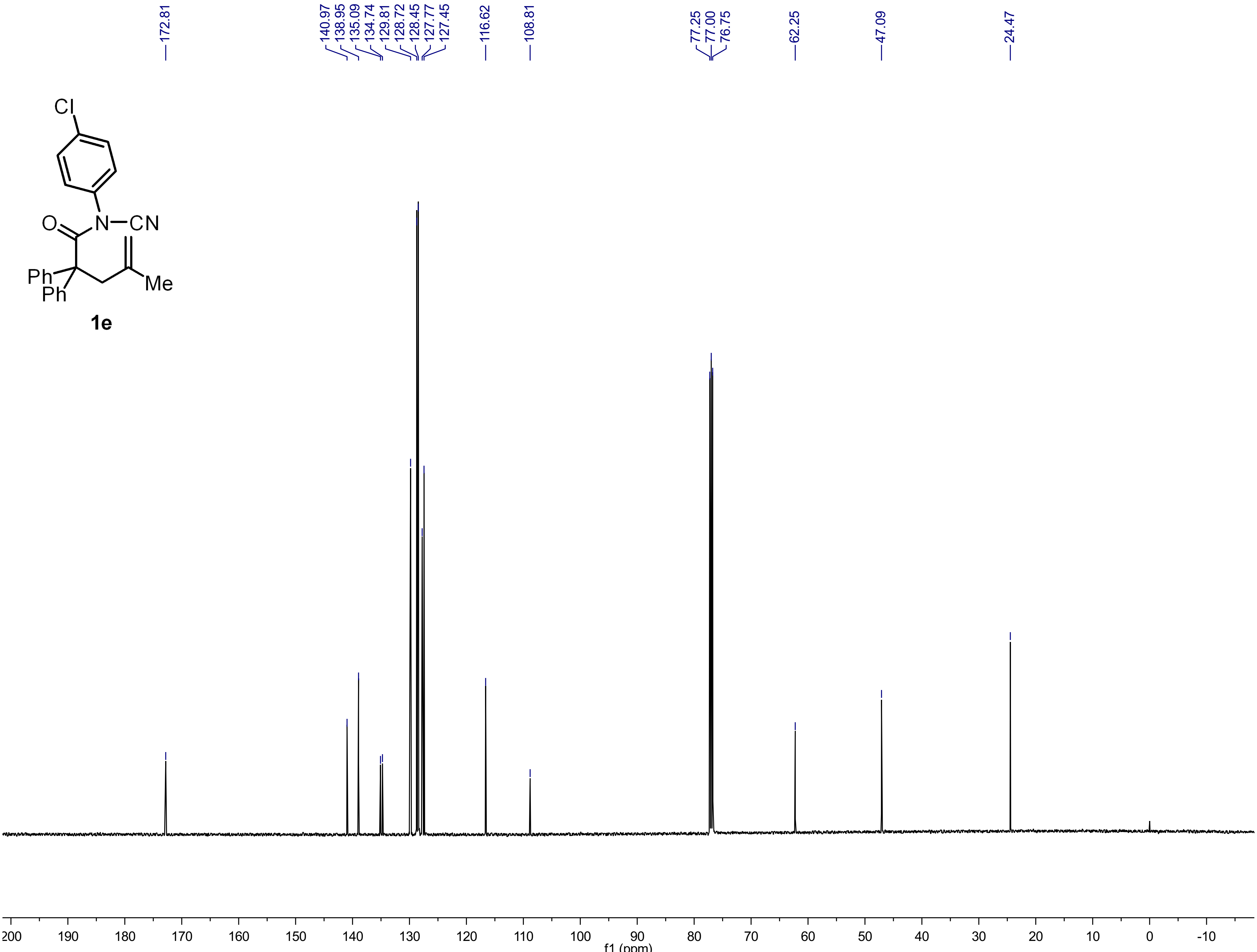
-130
-140
-150
-160
-170
-180
-190
-200
-210
-22
f1 (ppm)



7.52 7.52 7.51 7.51 7.50 7.42 7.42 7.41 7.41 7.40 7.39 7.38 7.38 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.32 7.25 7.25 7.16 7.15 7.15 7.15 7.14 7.13 7.13
4.78
4.48
3.42
1.41
0.00
Cl
O
N
CN
Ph
Ph
Me
4.14
5.97
2.24
2.02
0.98
0.98
2.00
3.00
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 -0.5 -1.0
f1 (ppm)

1e



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116.62
108.81
77.25
77.00
76.75
62.25
47.09
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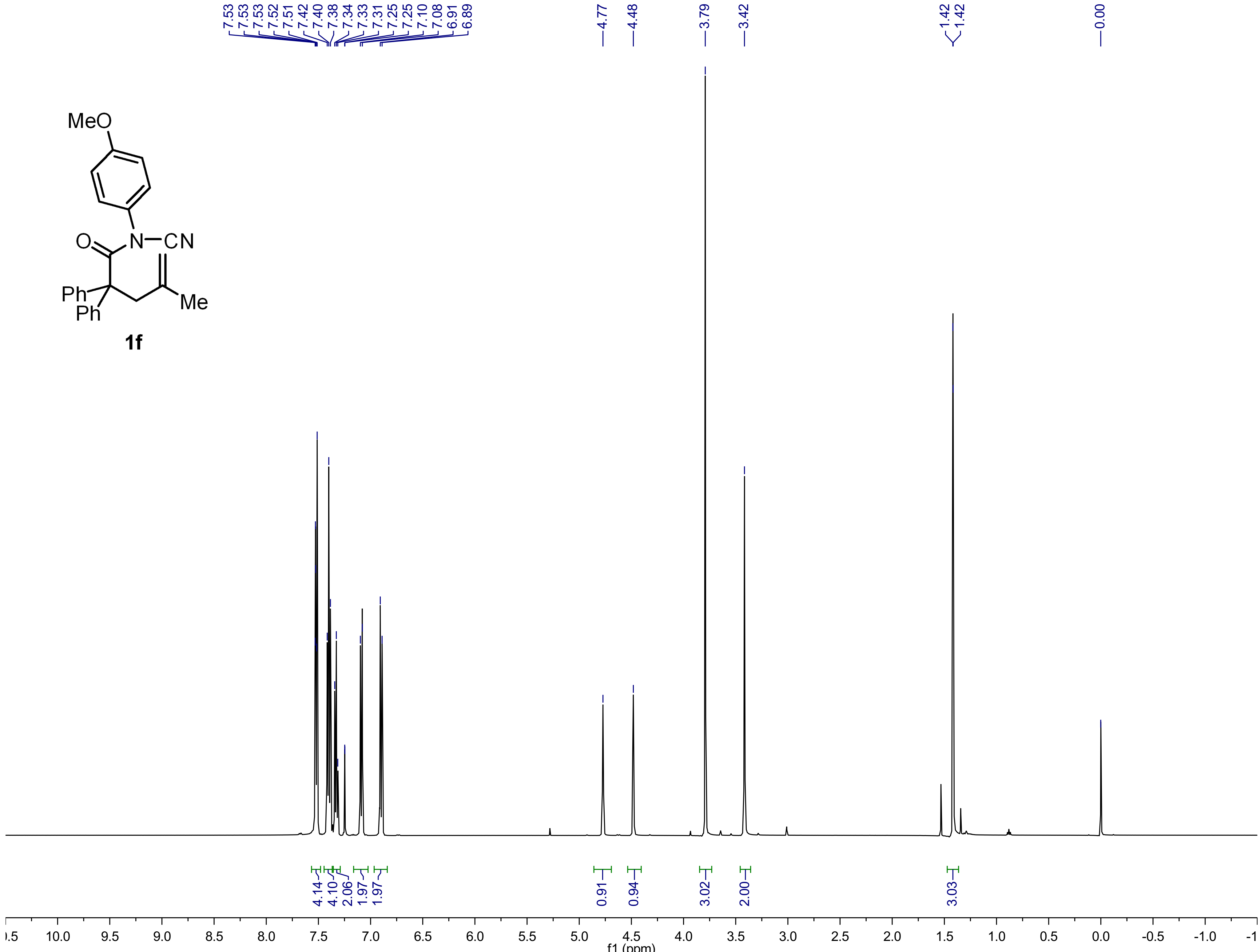
Cl
O
N
CN
Ph
Ph
Me
1e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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7.31
7.25
7.25
7.10
7.08
6.91
6.89
4.77
4.48
3.79
3.42
1.42
1.42
0.00
MeO
O
N
CN
Ph
Ph
Me
1f
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1.97
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2.00
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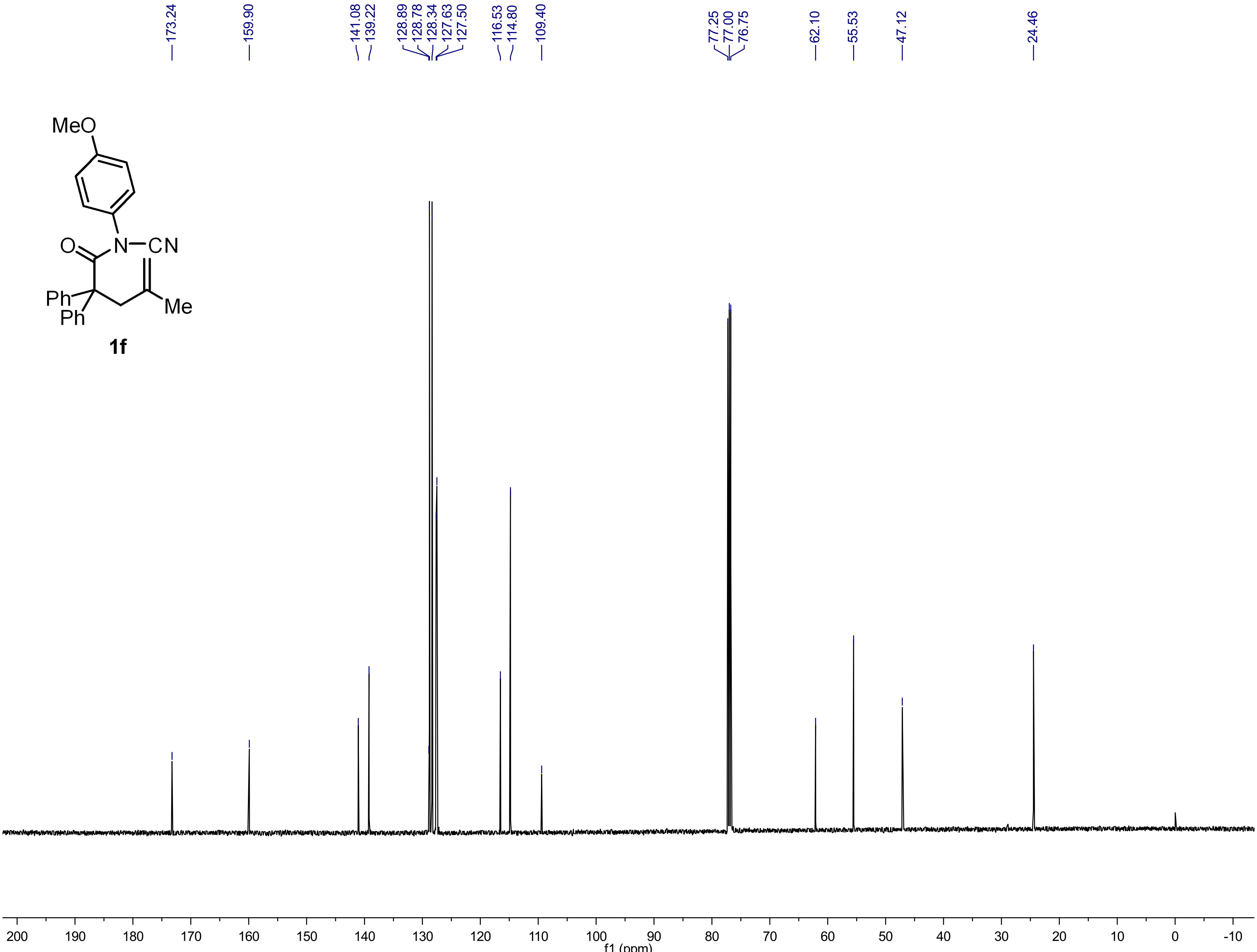
f1 (ppm)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109.40
77.25
77.00
76.75
62.10
55.53
47.12
24.46
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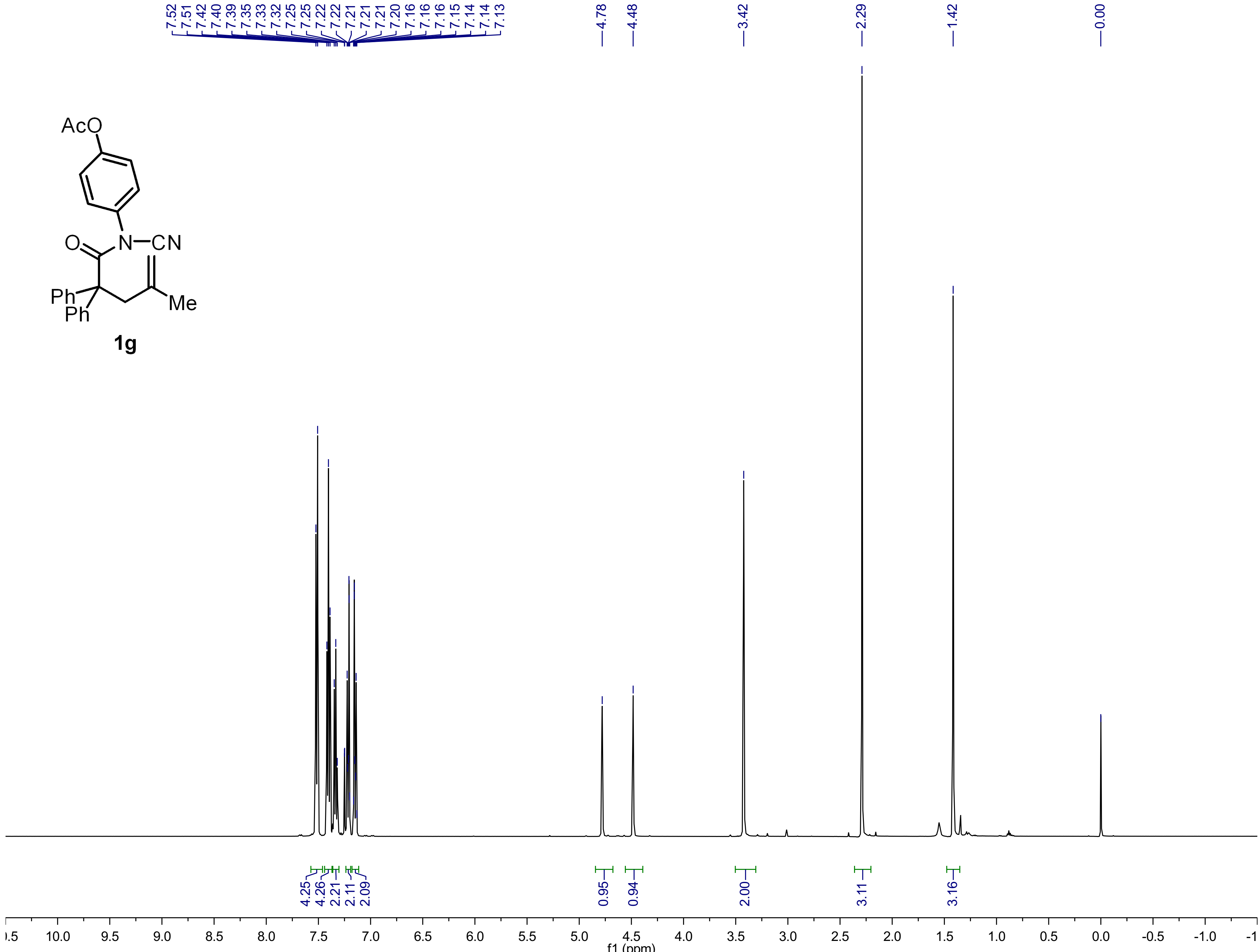
O
N
CN
Ph
Ph
Me
1f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.32
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7.25
7.22
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7.21
7.21
7.21
7.20
7.16
7.16
7.16
7.15
7.14
7.14
7.13
4.78
4.48
3.42
2.29
1.42
0.00
AcO
O
N
CN
Ph
Ph
Me
1g
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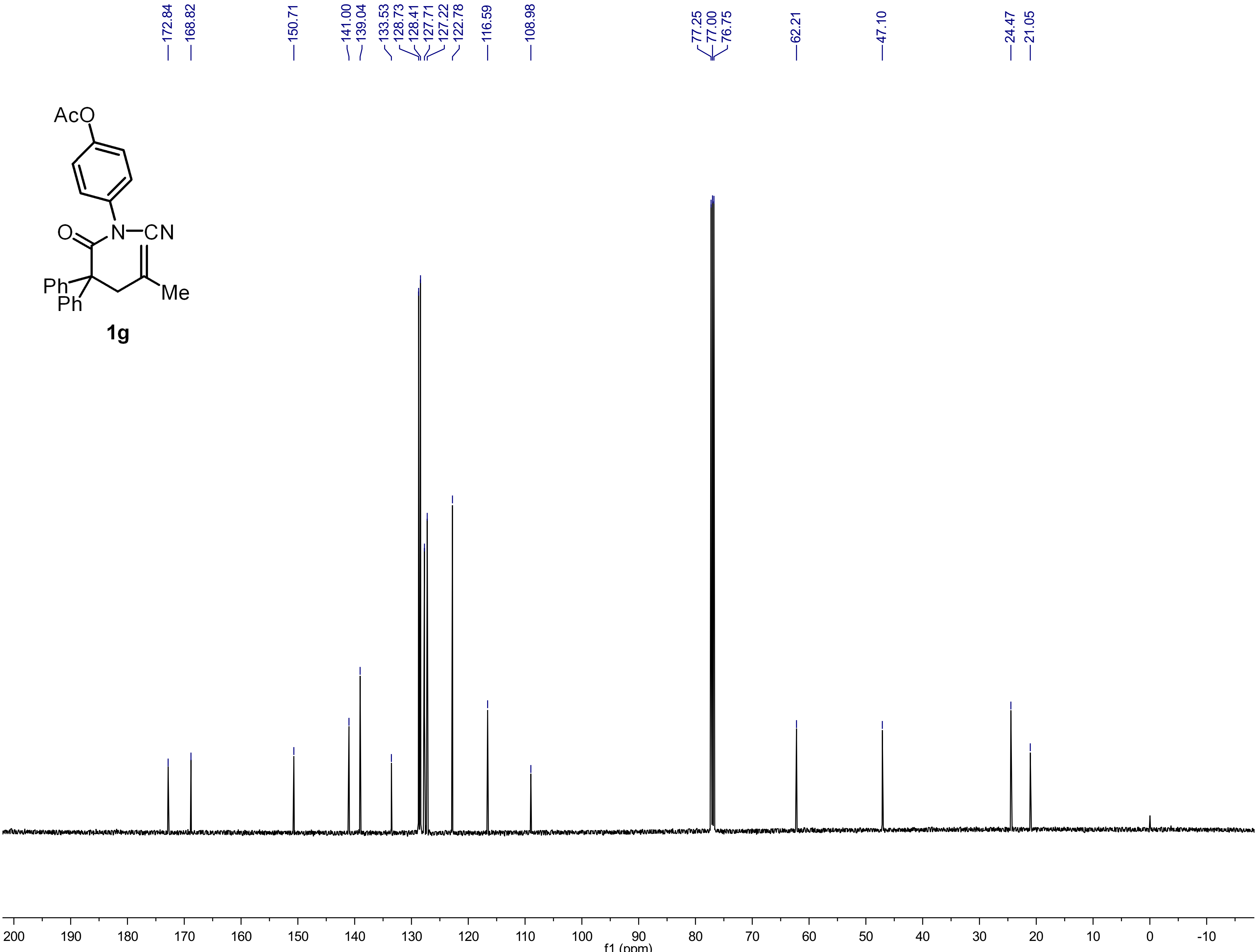
0.94
2.00
3.11
3.16
f1 (ppm)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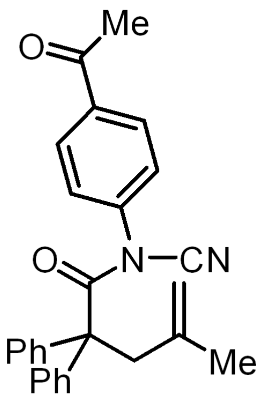
127.22
122.78
116.59
108.98
77.25
77.00
76.75
62.21
47.10
24.47
21.05
AcO
O
N
CN
Ph
Ph
Me
1g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



Me
O
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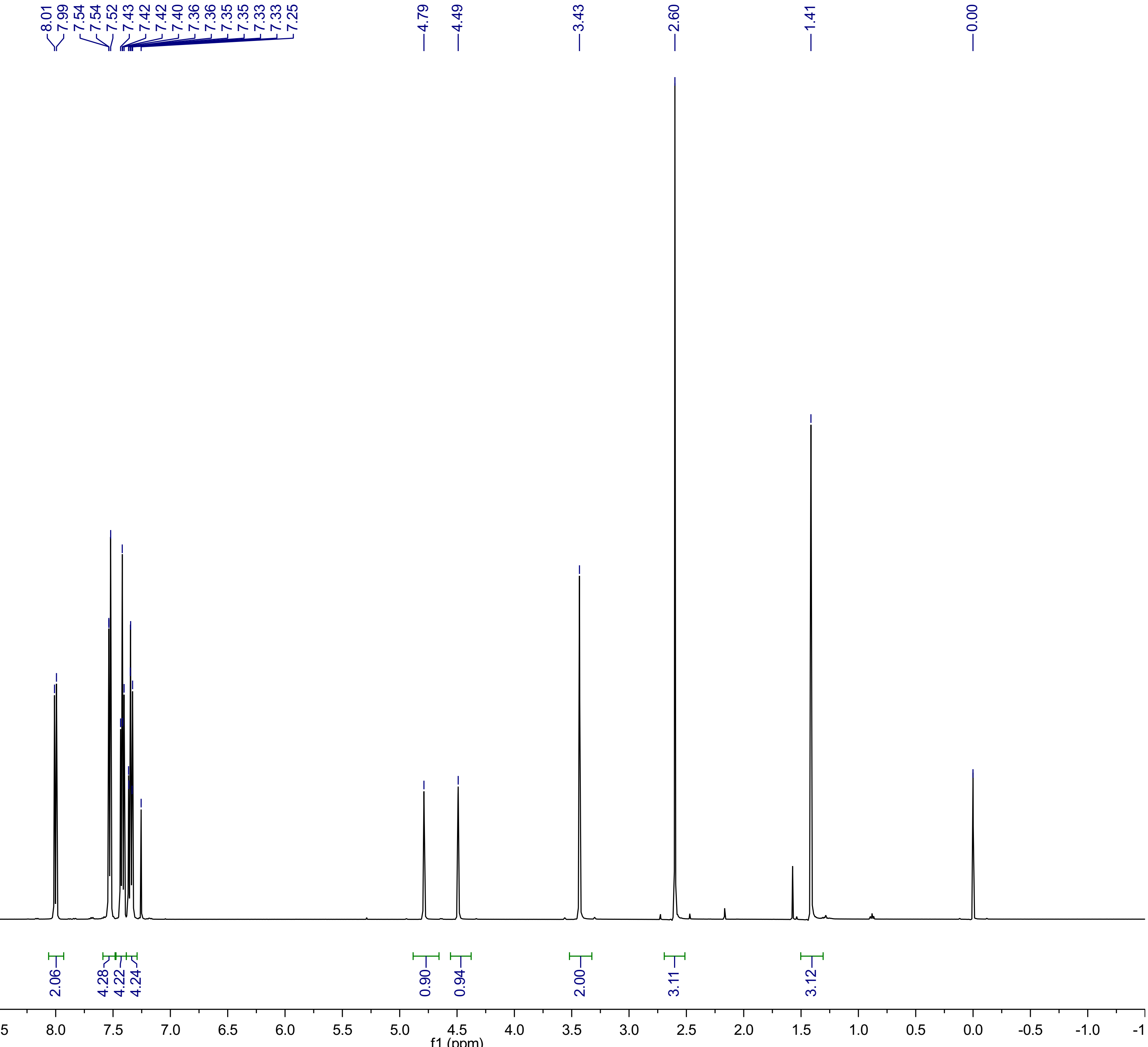
CN
O
Ph
Ph
Me

1h



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7.33
7.33
7.25
4.79
4.49
3.43
2.60
1.41
0.00
2.06
4.28
4.22
4.24
0.90
0.94
2.00
3.11
3.12
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
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2.0
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1.0
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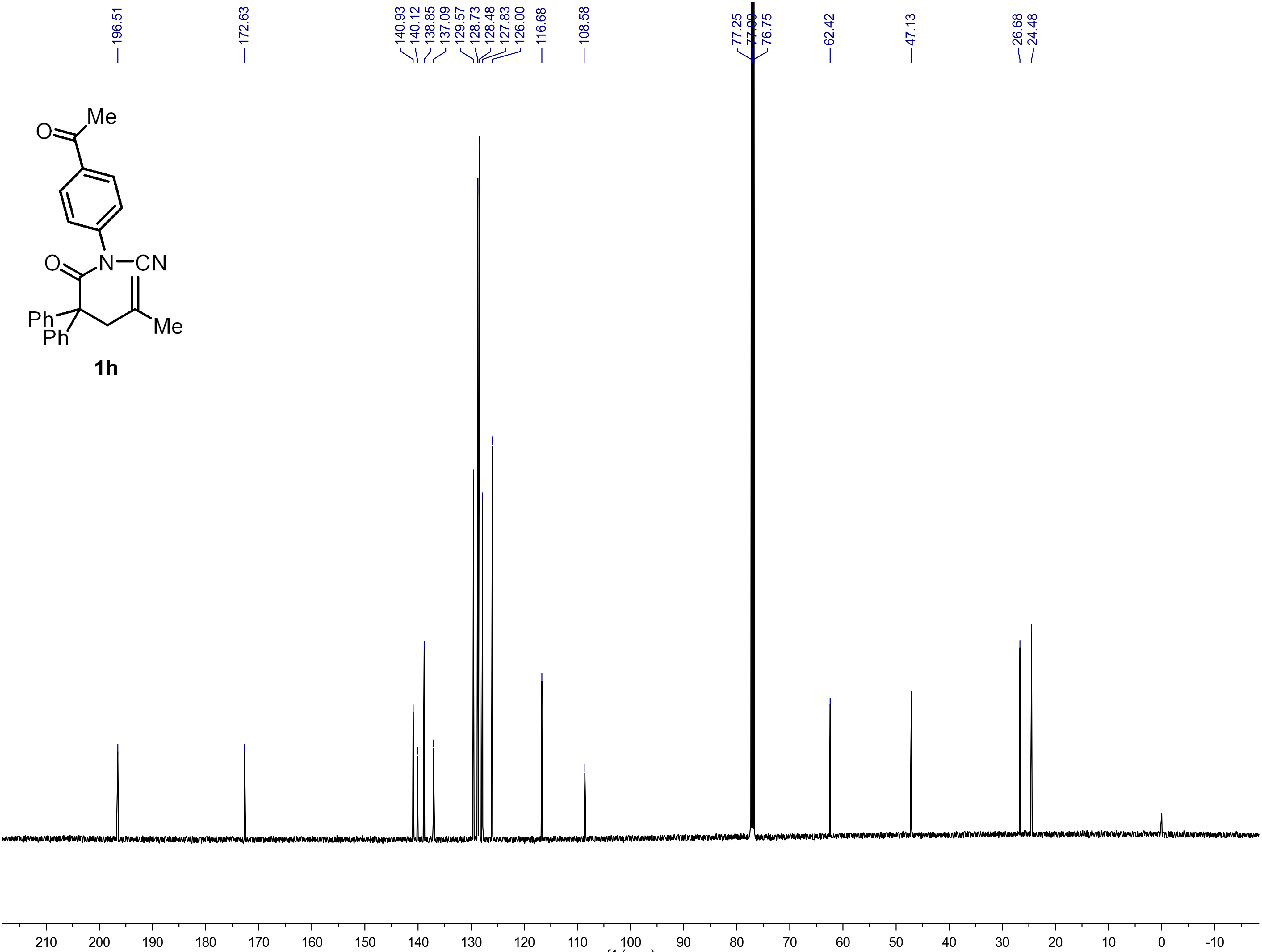
f1 (ppm)



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108.58
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77.00
76.75
62.42
47.13
26.68
24.48
Me
O
O
N
CN
Ph
Ph
Me
1h
210
200
190
180
170
160
150
140
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120
110
100
90
80
70
60
50
40
30
20
10
0
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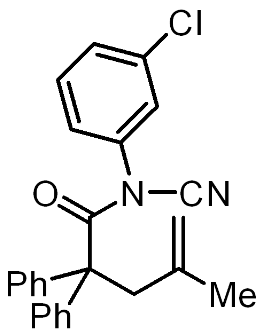
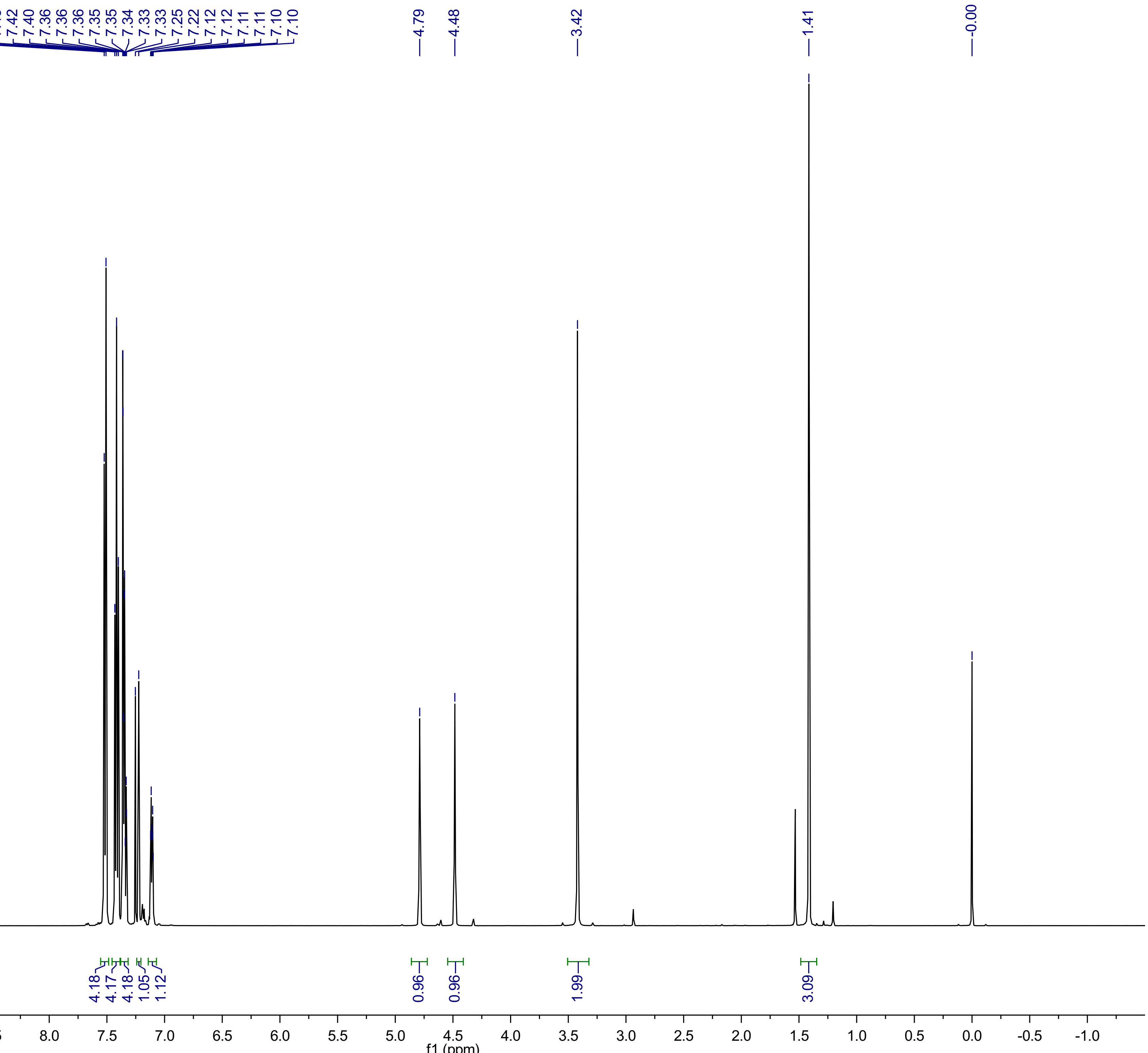
f1 (ppm)



1i



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7.43
7.42
7.40
7.36
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7.36
7.35
7.35
7.34
7.33
7.33
7.25
7.22
7.12
7.12
7.11
7.11
7.10
7.10
4.79
4.48
3.42
1.41
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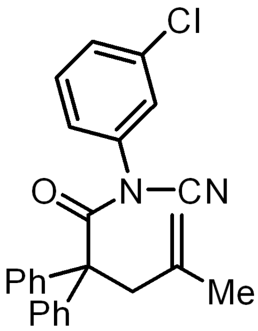
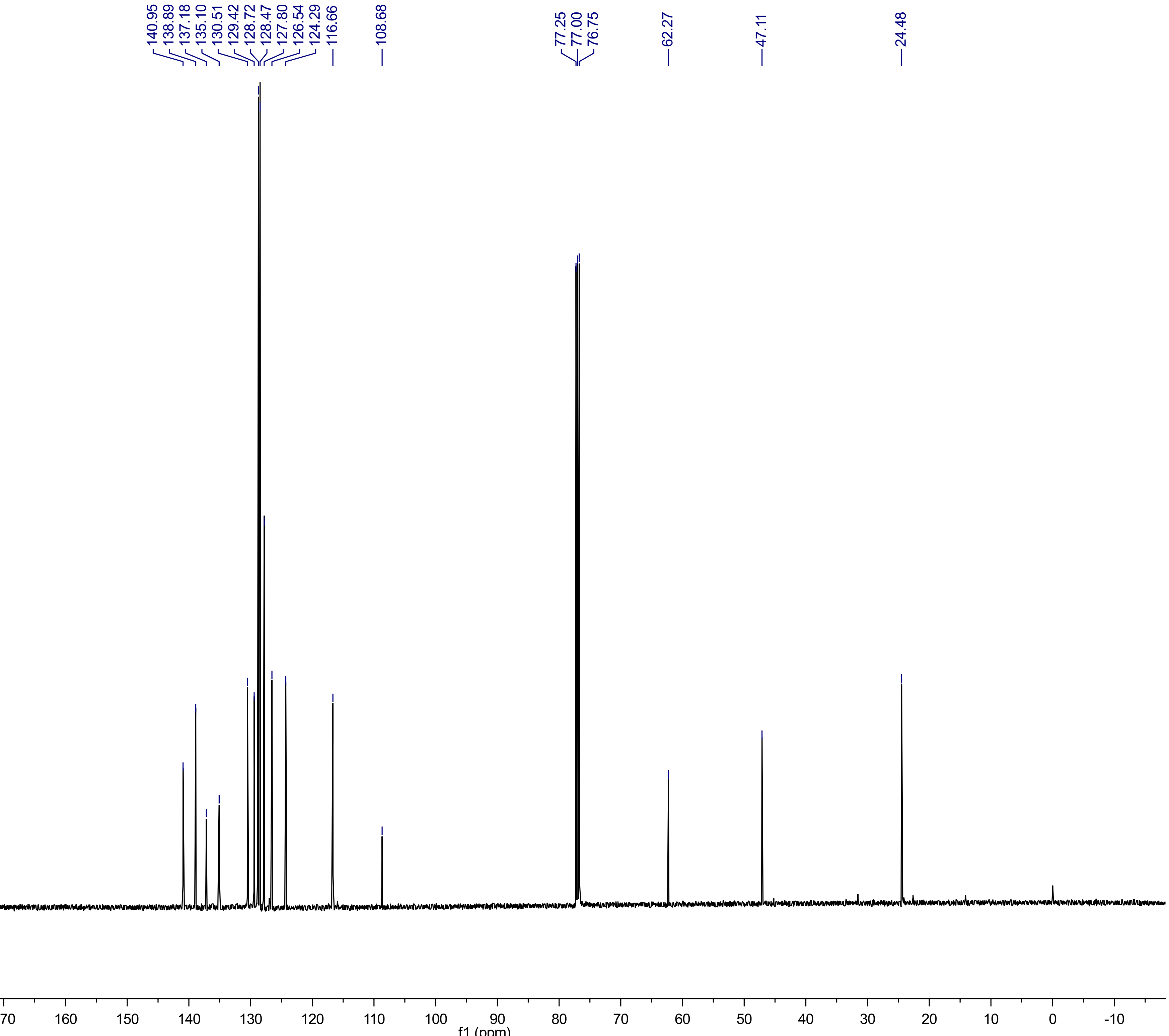
4.17
4.18
1.05
1.12
0.96
0.96
1.99
3.09
f1 (ppm)


Cl
O
N
CN
Ph
Ph
Me

1i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127.80
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124.29
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108.68
77.25
77.00
76.75
62.27
47.11
24.48
200
190
180
170
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150
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110
100
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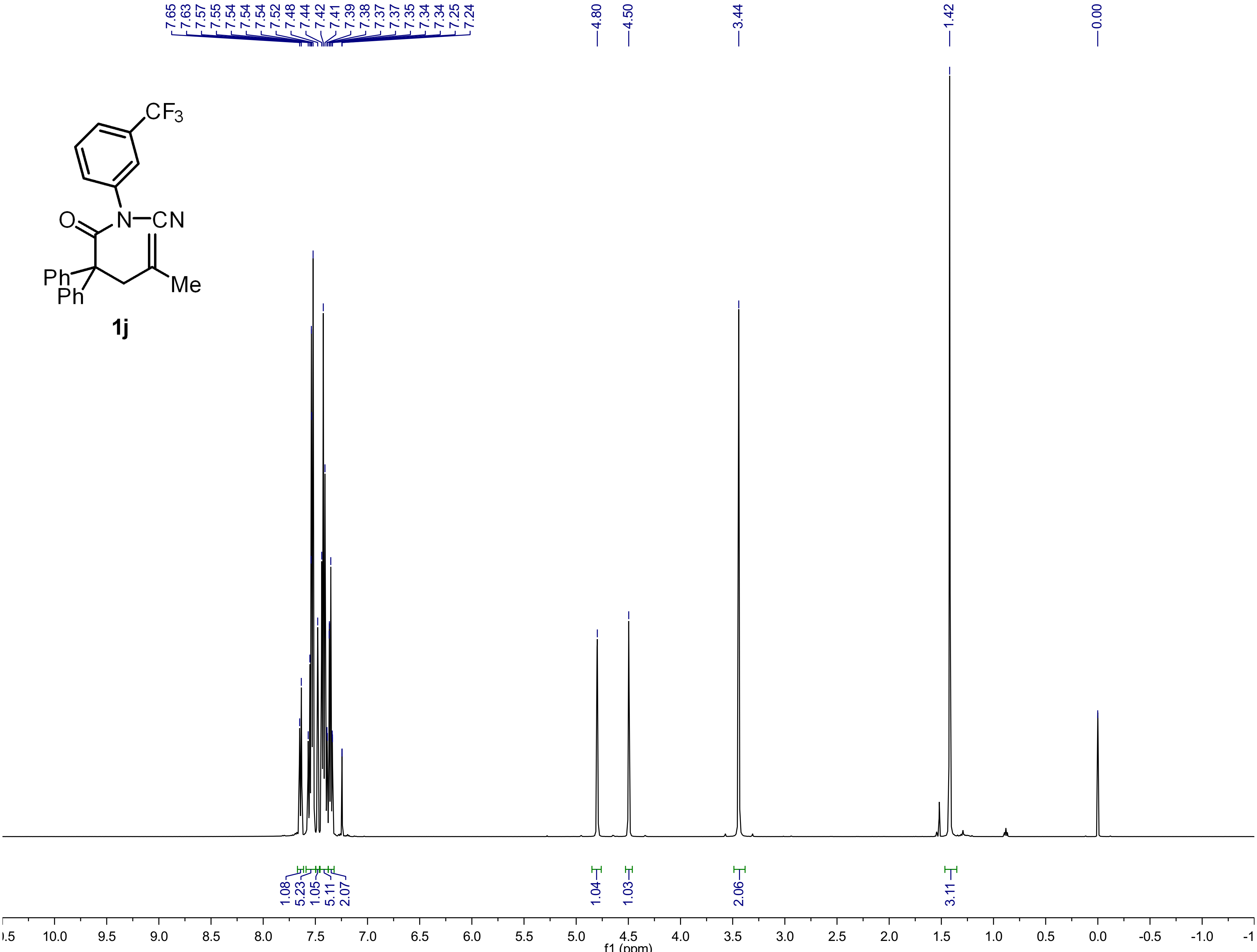
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.55
7.54
7.54
7.54
7.52
7.48
7.44
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7.39
7.38
7.37
7.37
7.35
7.34
7.34
7.25
7.24
4.80
4.50
3.44
1.42
0.00
CF3
O
N
CN
Ph
Ph
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1j
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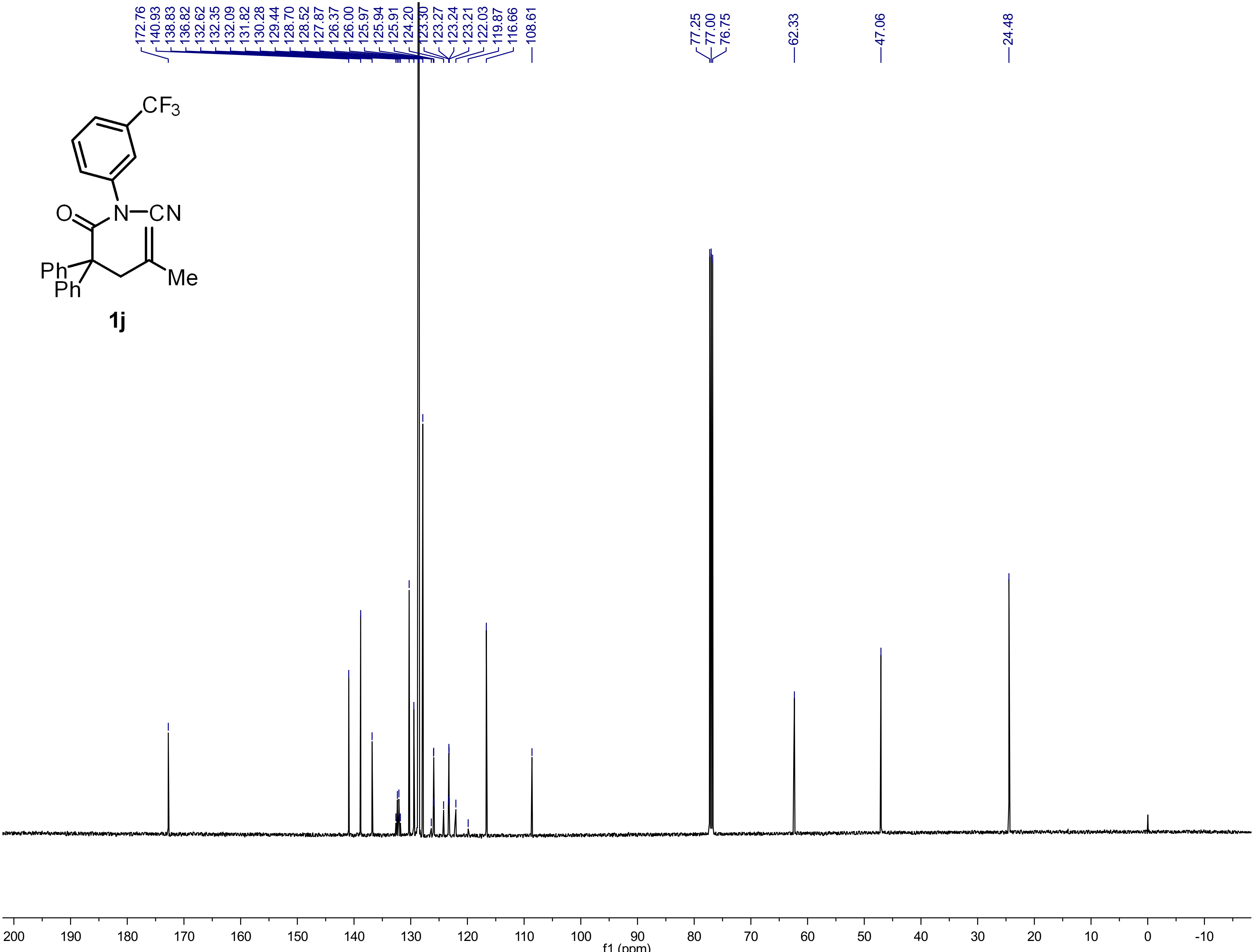
5.23
1.05
5.11
2.07
1.04
1.03
2.06
3.11
f1 (ppm)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127.87
126.37
126.00
125.97
125.94
125.91
124.20
123.30
123.27
123.24
123.21
122.03
119.87
116.66
108.61
77.25
77.00
76.75
62.33
47.06
24.48
CF3
O
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CN
Ph
Ph
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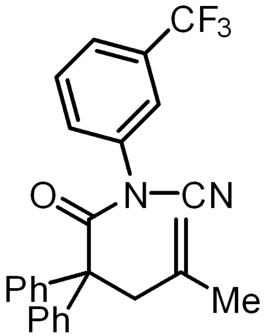
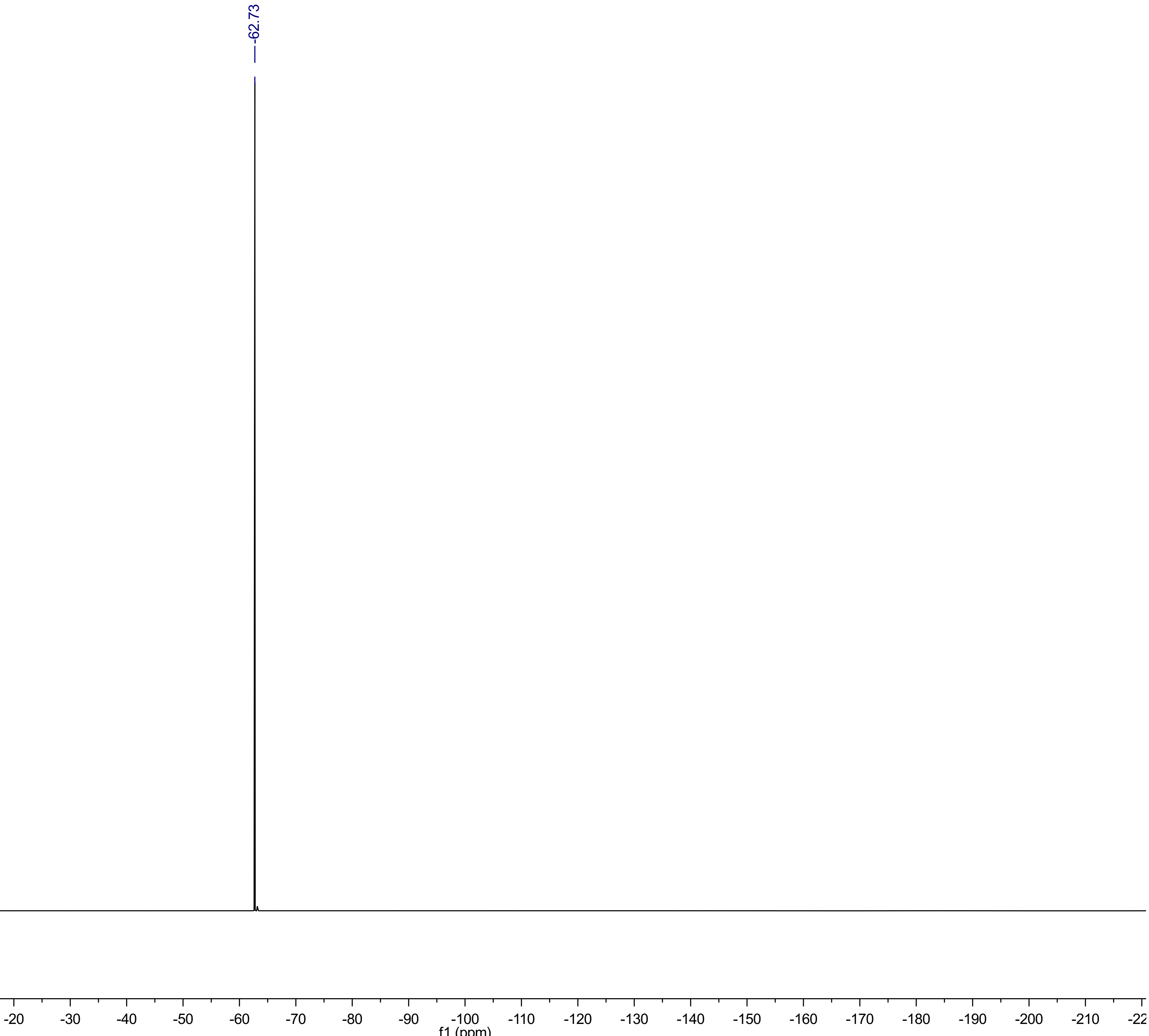
1j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



CF3
O
N
CN
Ph
Ph
Me

1j



-62.73
20
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-10
-20
-30
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-50
-60
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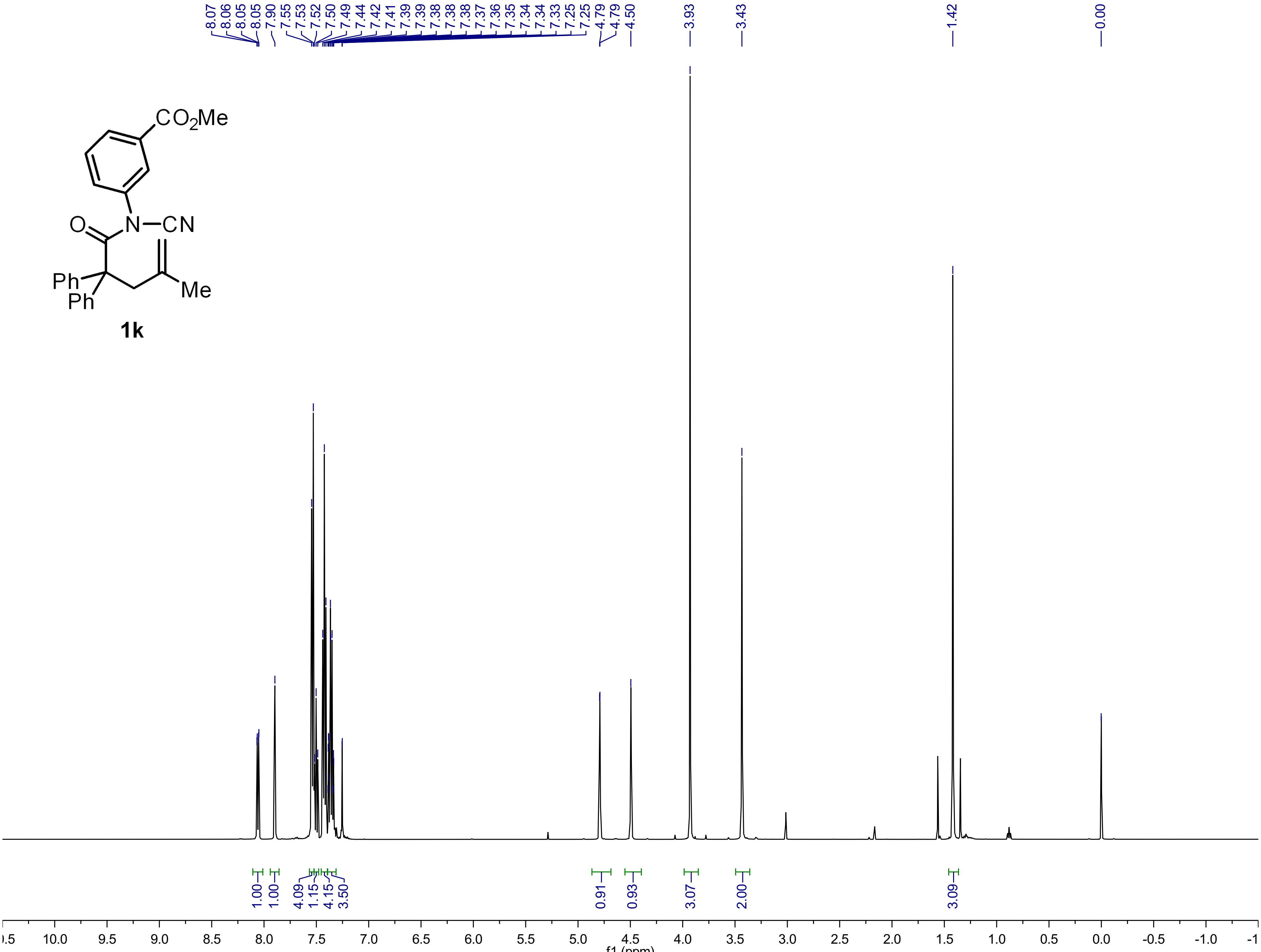
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-22
f1 (ppm)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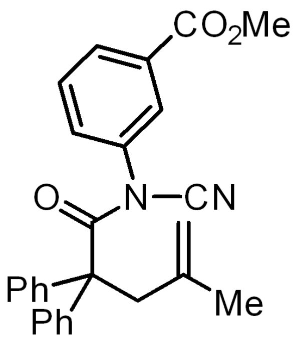
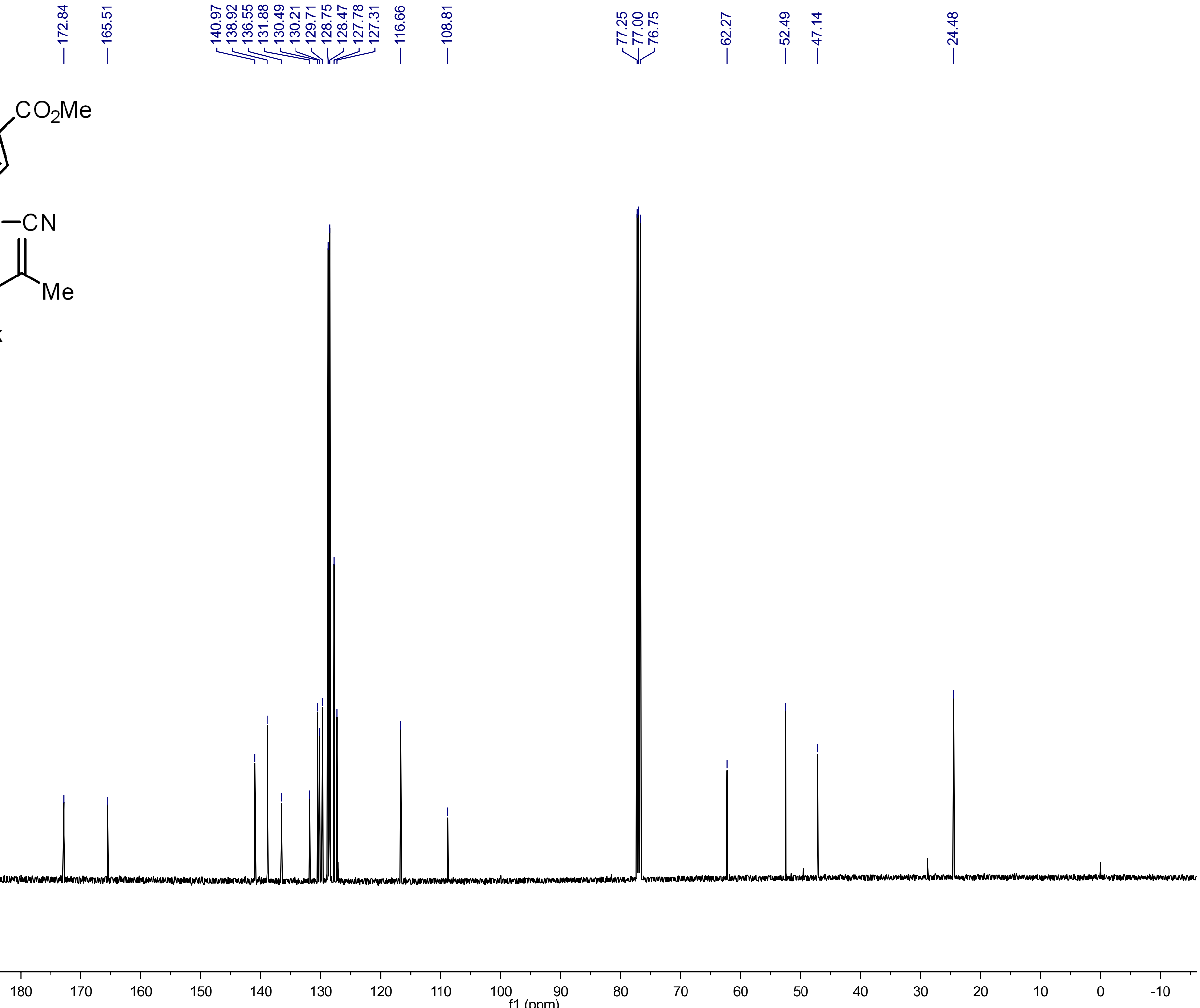
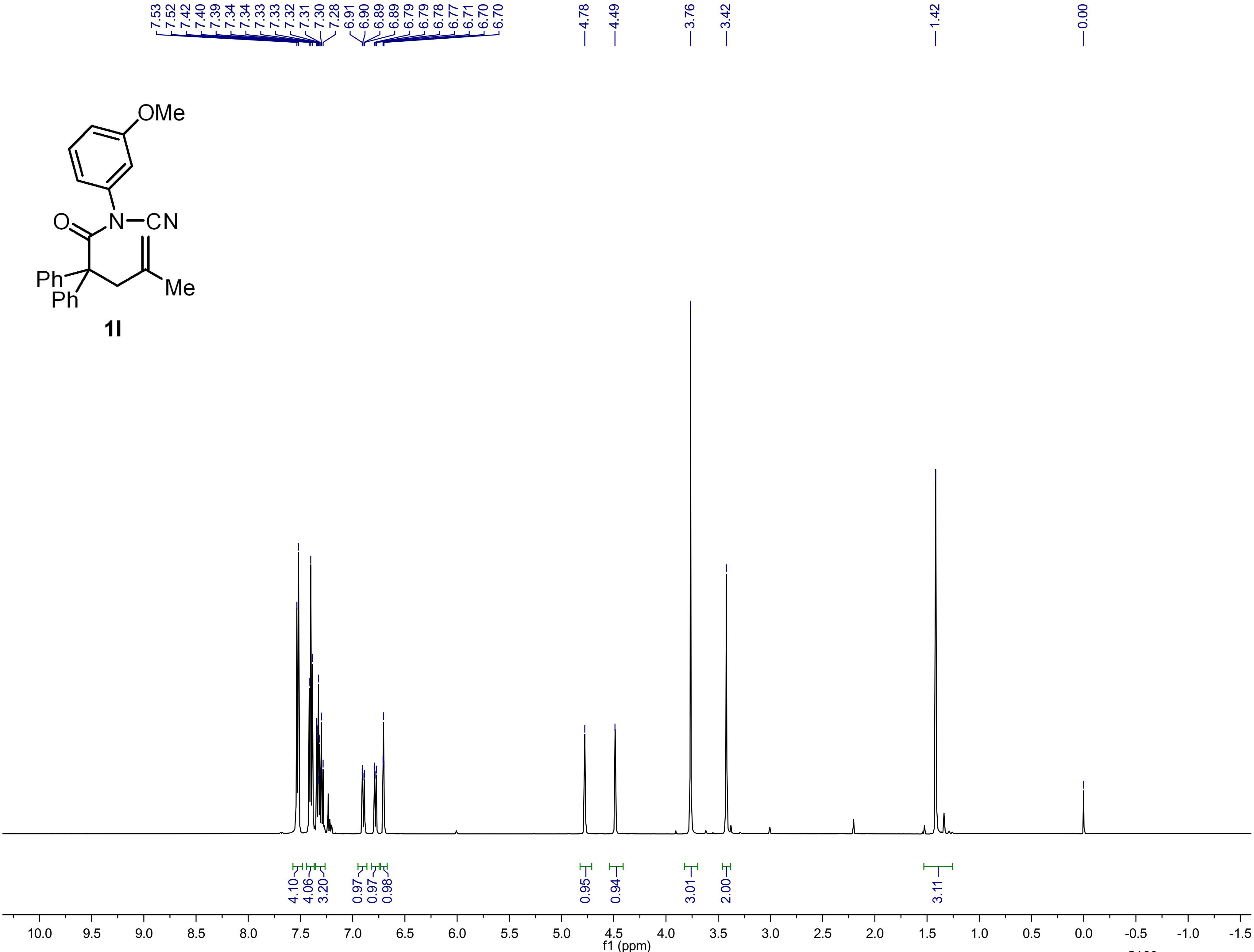
3.93
3.43
1.42
0.00
CO_2Me
O
N
CN
Ph
Ph
Me
1k
1.00 1.00 4.09 1.15 4.15 3.50
0.91
0.93
3.07
2.00
3.09
f1 (ppm)

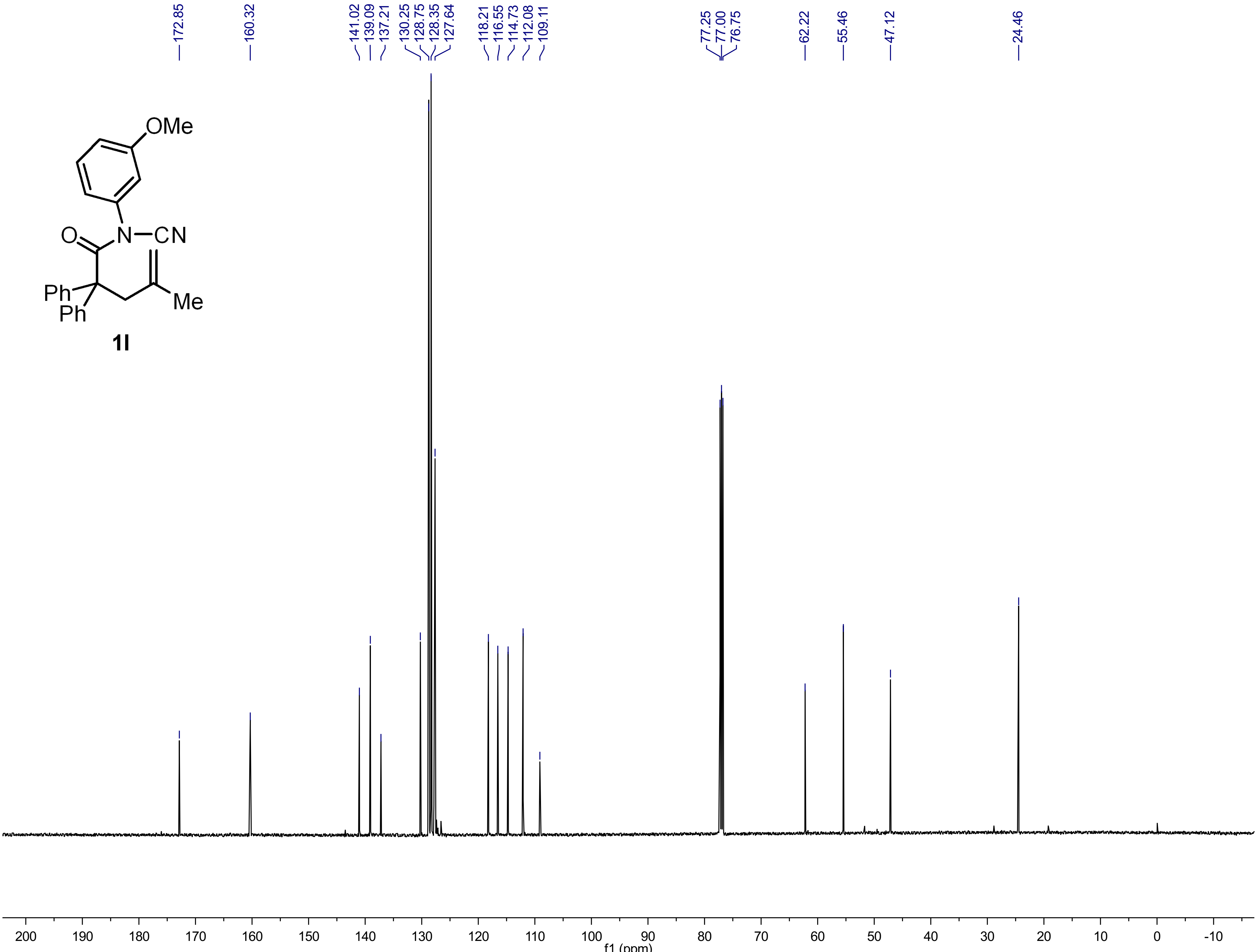


1k


172.84
165.51
140.97
138.92
136.55
131.88
130.49
130.21
129.71
128.75
128.47
127.78
127.31
116.66
108.81
77.25
77.00
76.75
62.27
52.49
47.14
24.48
f1 (ppm)



OMe
N
CN
O
Ph
Ph
Me
1l
7.53 7.52 7.42 7.40 7.39 7.34 7.34 7.33 7.33 7.32 7.31 7.30 7.28 6.91 6.90 6.89 6.89 6.79 6.79 6.78 6.77 6.71 6.70 6.70
4.78
4.49
3.76
3.42
1.42
0.00
4.10 4.06 3.20 0.97 0.97 0.98 0.95 0.94 3.01 2.00 3.11
f1 (ppm)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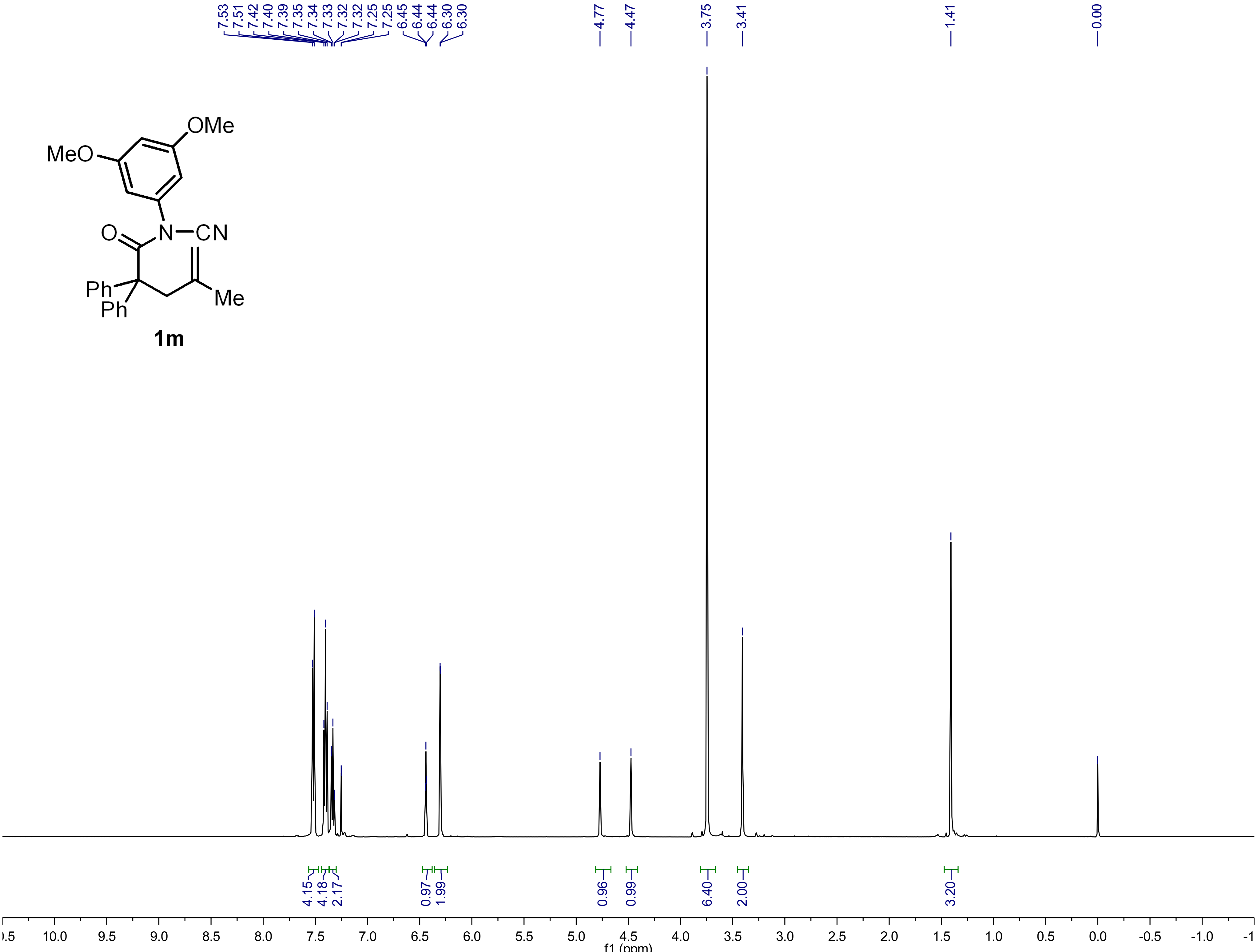
139.09
137.21
130.25
128.75
128.35
127.64
118.21
116.55
114.73
112.08
109.11
77.25
77.00
76.75
62.22
55.46
47.12
24.46
OMe
O
N
CN
Ph
Ph
Me
1l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


1m
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7.51
7.42
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7.39
7.35
7.34
7.33
7.32
7.32
7.25
7.25
6.45
6.44
6.44
6.30
6.30
4.77
4.47
3.75
3.41
1.41
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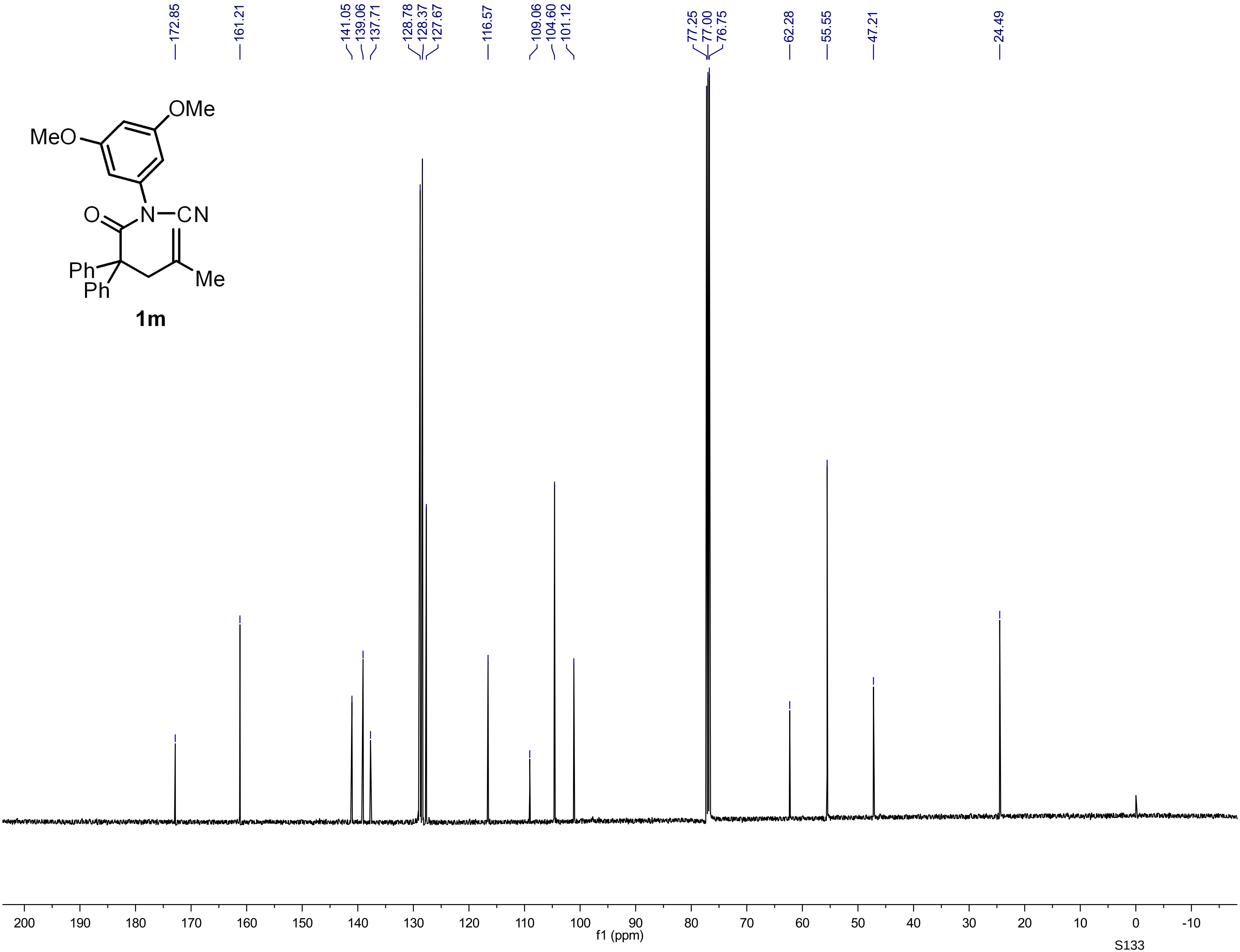
4.18
2.17
0.97
1.99
0.96
0.99
6.40
2.00
3.20
f1 (ppm)



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161.21
141.05
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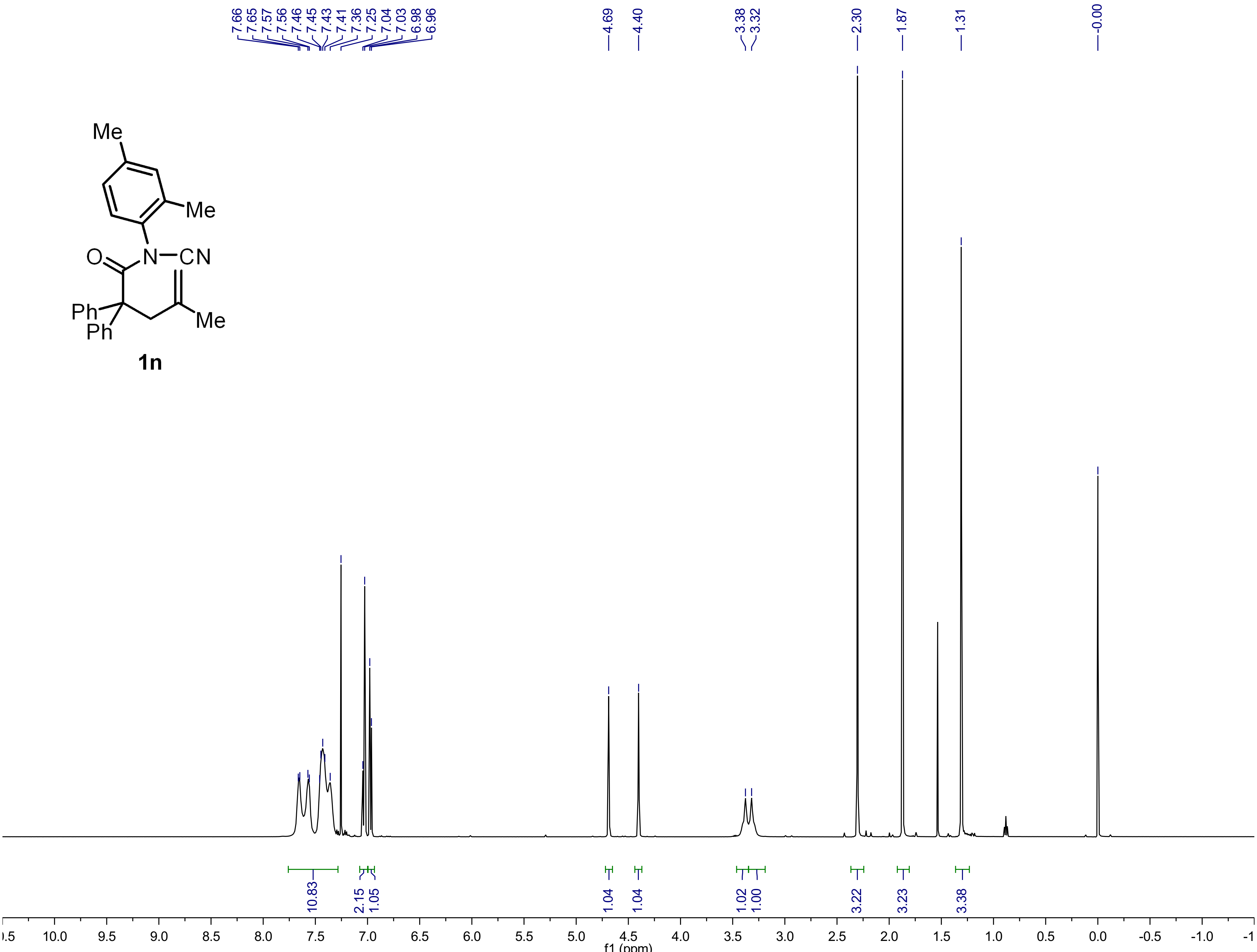
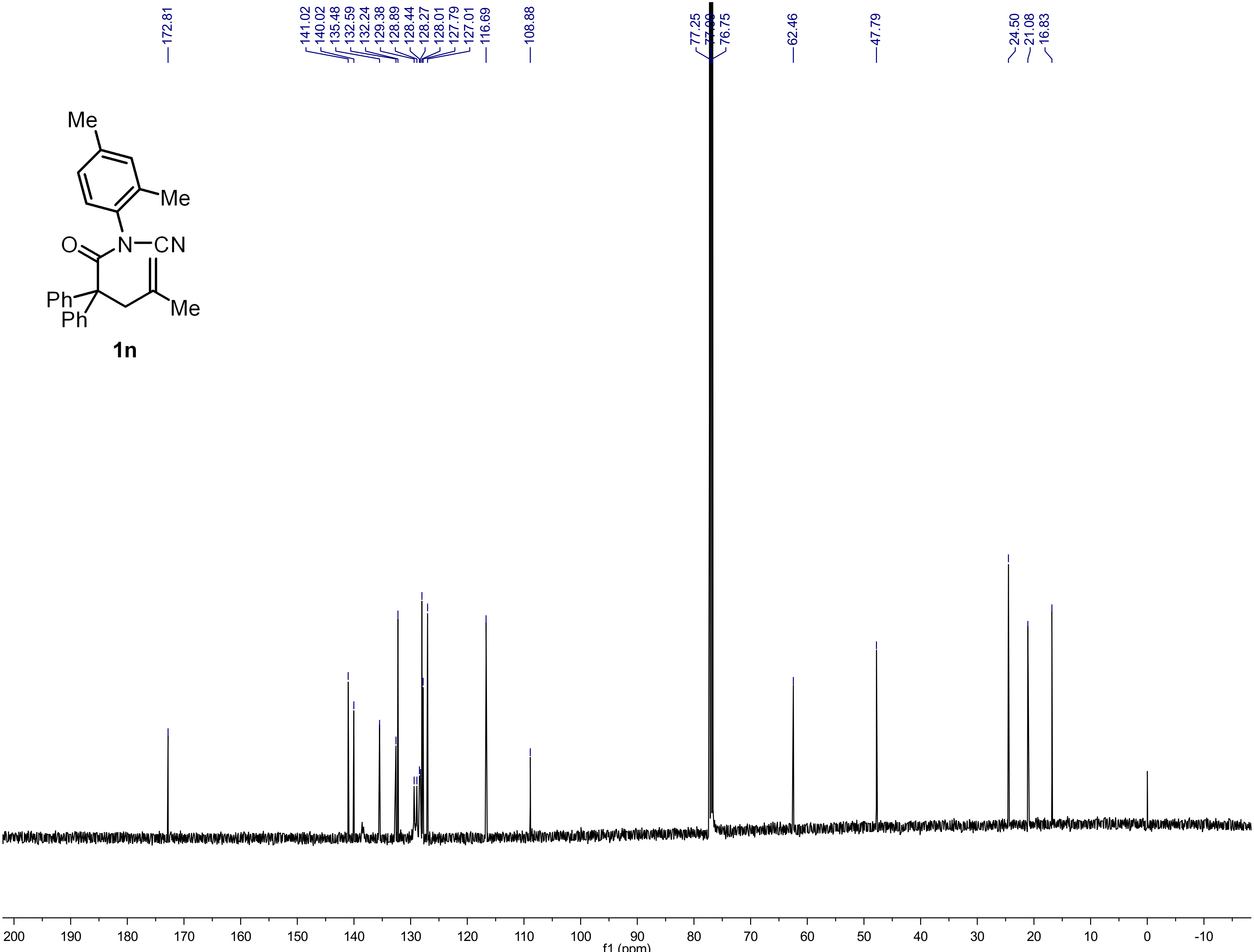
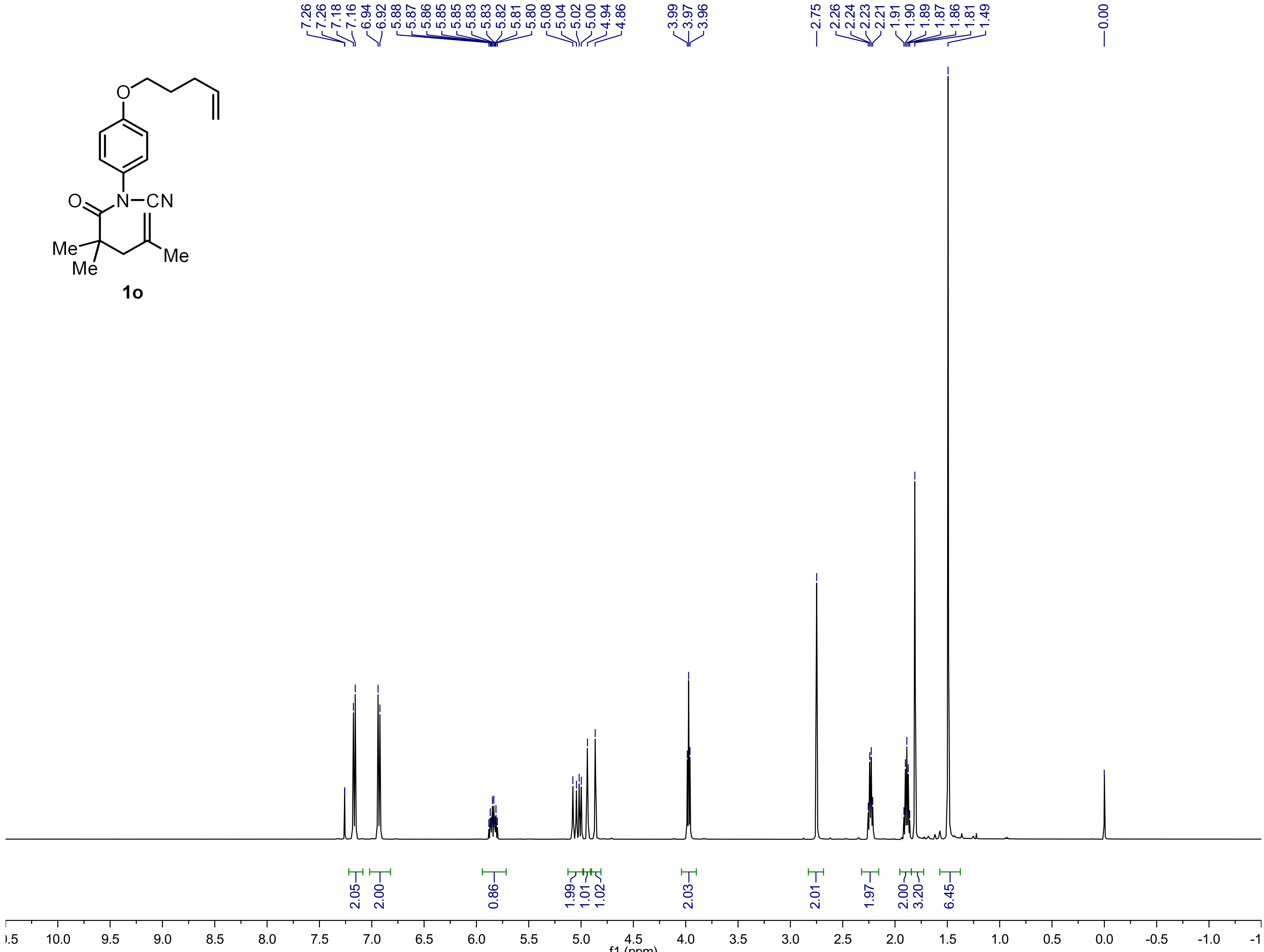
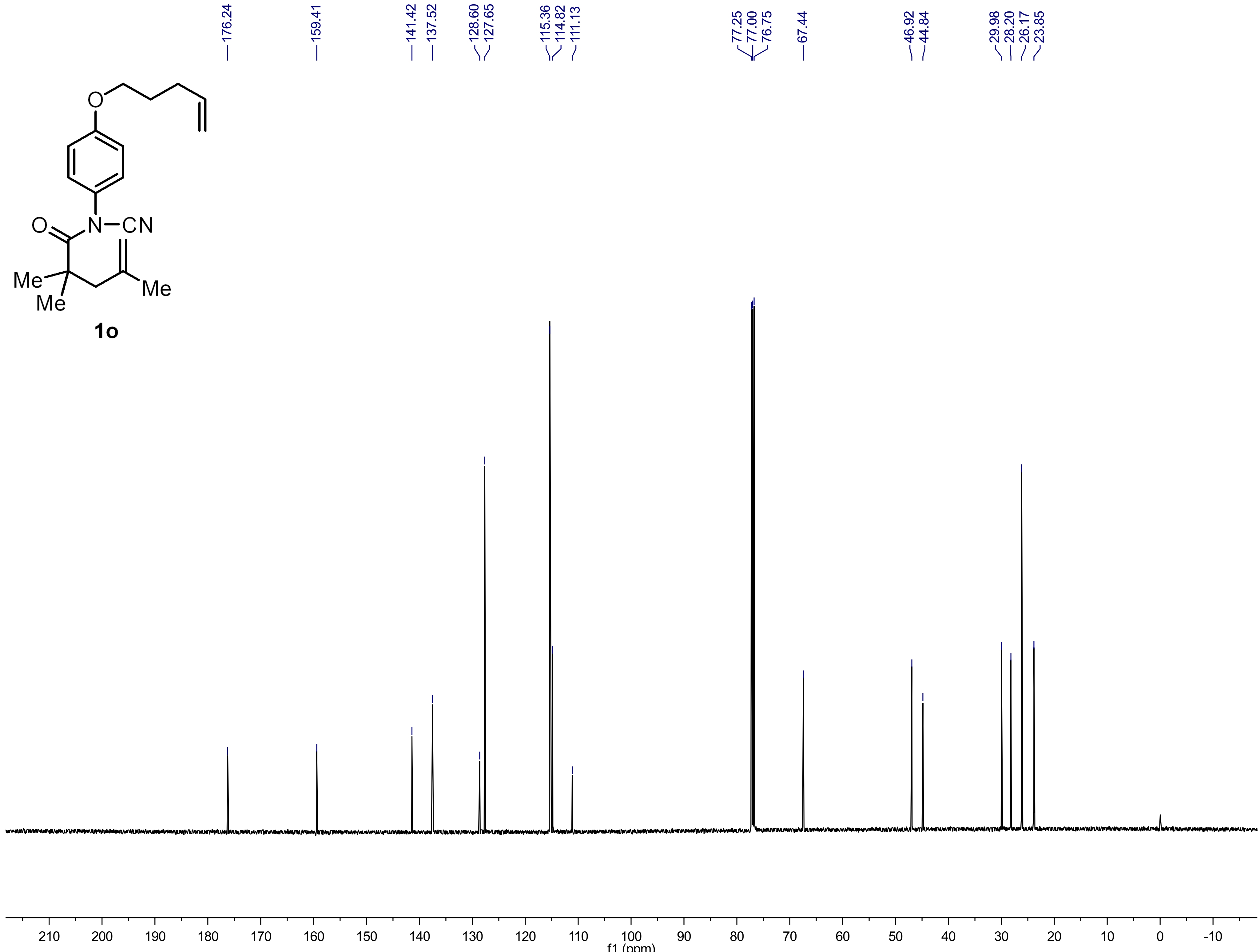
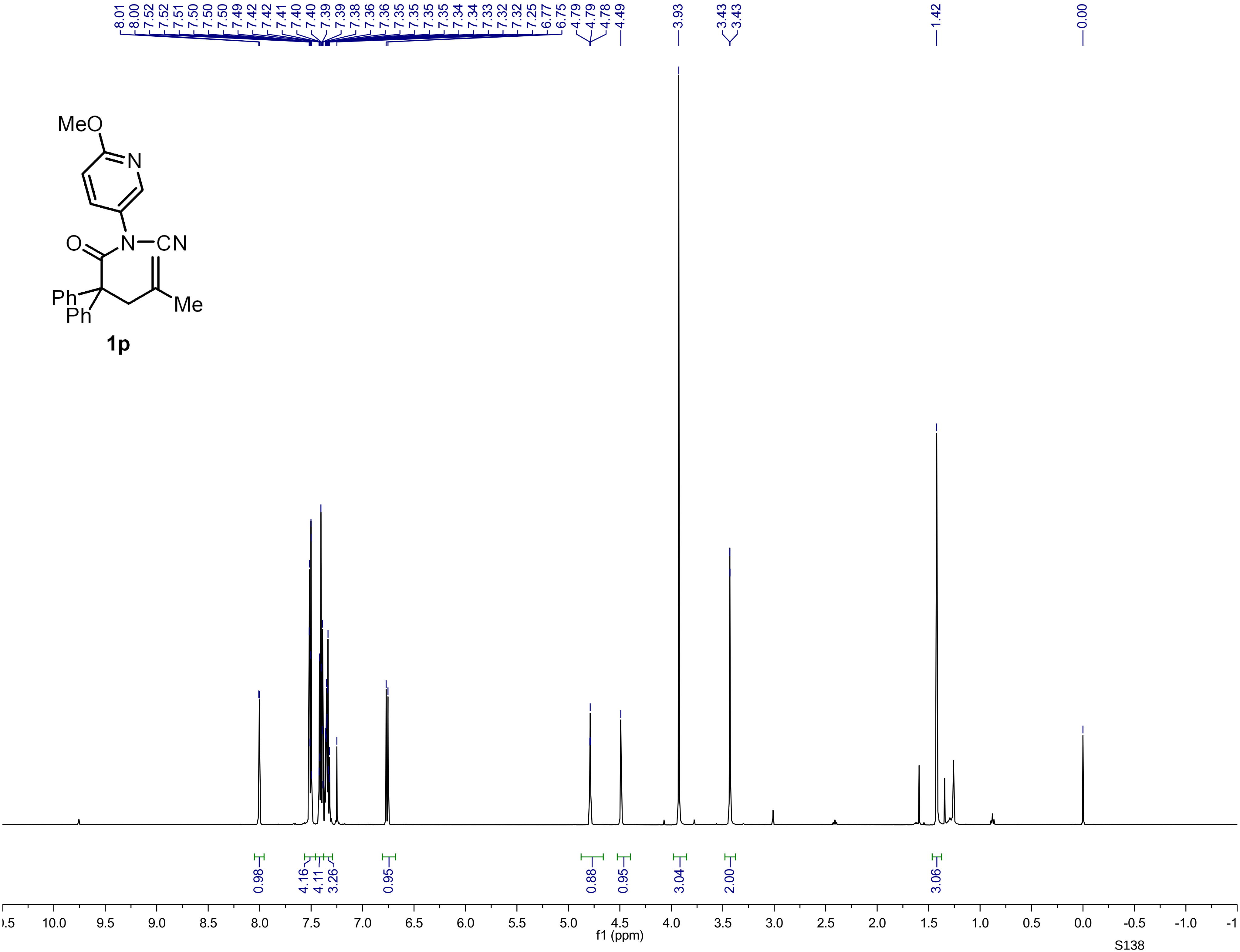
128.78
128.37
127.67
116.57
109.06
104.60
101.12
77.25
77.00
76.75
62.28
55.55
47.21
24.49
OMe
MeO
O
N
CN
Ph
Ph
Me
1m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.66 7.65 7.57 7.56 7.46 7.45 7.43 7.41 7.36 7.25 7.04 7.03 6.98 6.96
4.69
4.40
3.38 3.32
2.30
1.87
1.31
-0.00
Me
Me
O
N
CN
Ph
Ph
Me
1n
10.83
2.15
1.05
1.04
1.04
1.02
1.00
3.22
3.23
3.38
f1 (ppm)

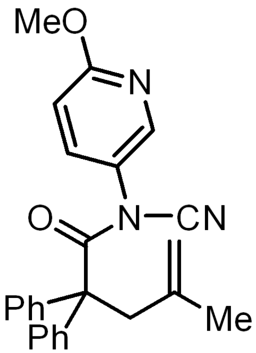

172.81
141.02
140.02
135.48
132.59
132.24
129.38
128.89
128.44
128.27
128.01
127.79
127.01
116.69
108.88
77.25
76.75
62.46
47.79
24.50
21.08
16.83
Me
Me
O
N
CN
Ph
Ph
Me
1n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.26
7.26
7.18
7.16
6.94
6.92
5.88
5.87
5.86
5.85
5.85
5.83
5.83
5.82
5.81
5.80
5.08
5.04
5.02
5.00
4.94
4.86
3.99
3.97
3.96
2.75
2.26
2.24
2.23
2.21
1.91
1.90
1.89
1.87
1.86
1.81
1.49
0.00
O
O
N
CN
Me
Me
Me
1o
2.05
2.00
0.86
1.99
1.01
1.02
2.03
2.01
1.97
2.00
3.20
6.45
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
-0.5
-1.0
f1 (ppm)


176.24
159.41
141.42
137.52
128.60
127.65
115.36
114.82
111.13
77.25
77.00
76.75
67.44
46.92
44.84
29.98
28.20
26.17
23.85
O
N
CN
O
Me
Me
Me
1o
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)



MeO
N
O
N
CN
Ph
Ph
Me
1p
8.01
8.00
7.52
7.52
7.51
7.50
7.50
7.50
7.49
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.36
7.36
7.35
7.35
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.25
6.77
6.75
4.79
4.79
4.78
4.49
3.93
3.43
3.43
1.42
0.00
0.98
4.16
4.11
3.26
0.95
0.88
0.95
3.04
2.00
3.06
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
-0.5
-1.0
f1 (ppm)



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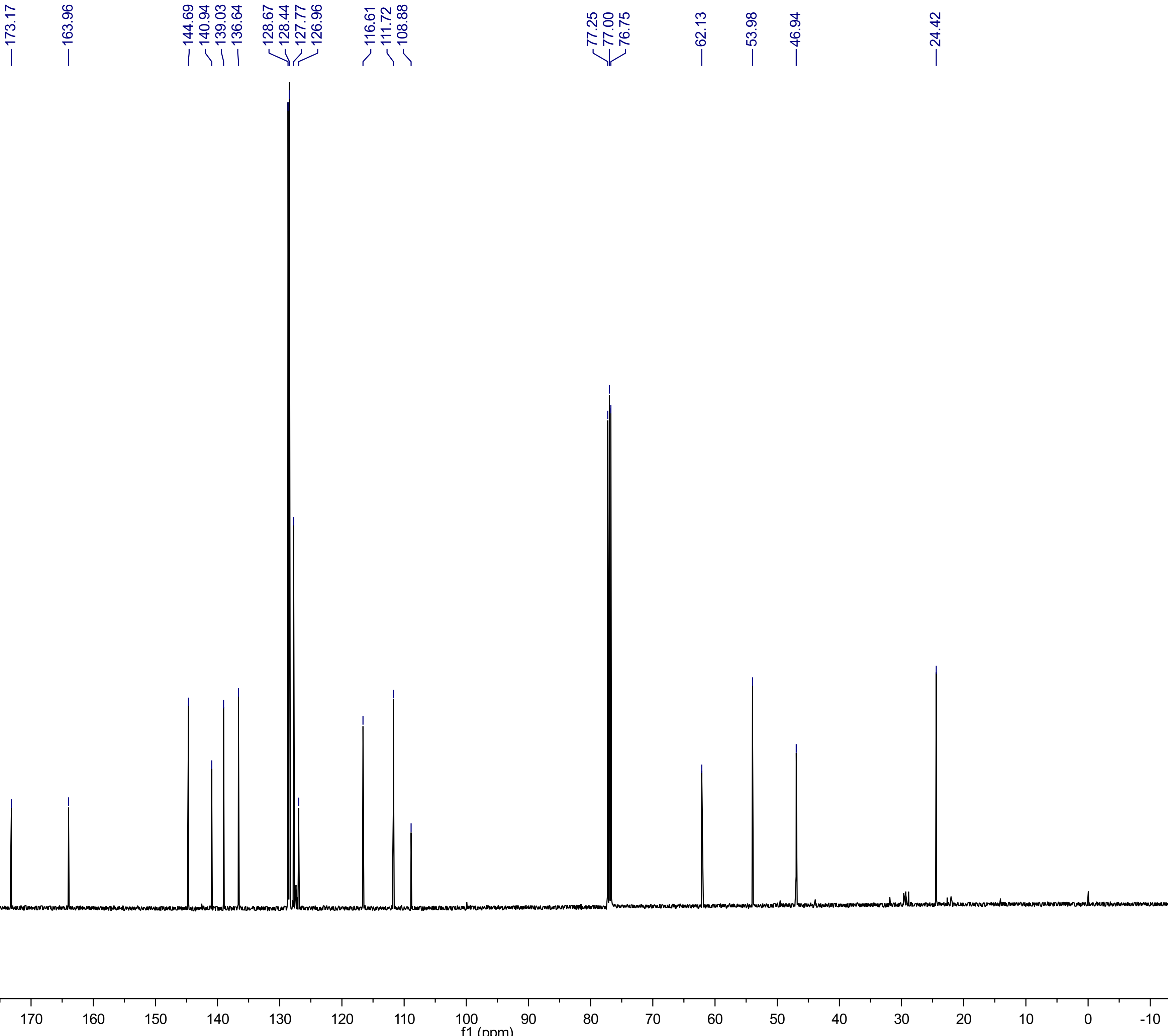
173.17
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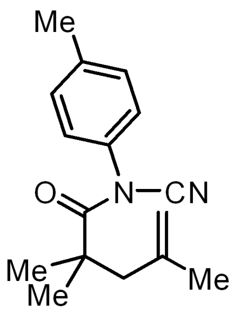
140.94
139.03
136.64
128.67
128.44
127.77
126.96
116.61
111.72
108.88
77.25
77.00
76.75
62.13
53.98
46.94
24.42
f1 (ppm)



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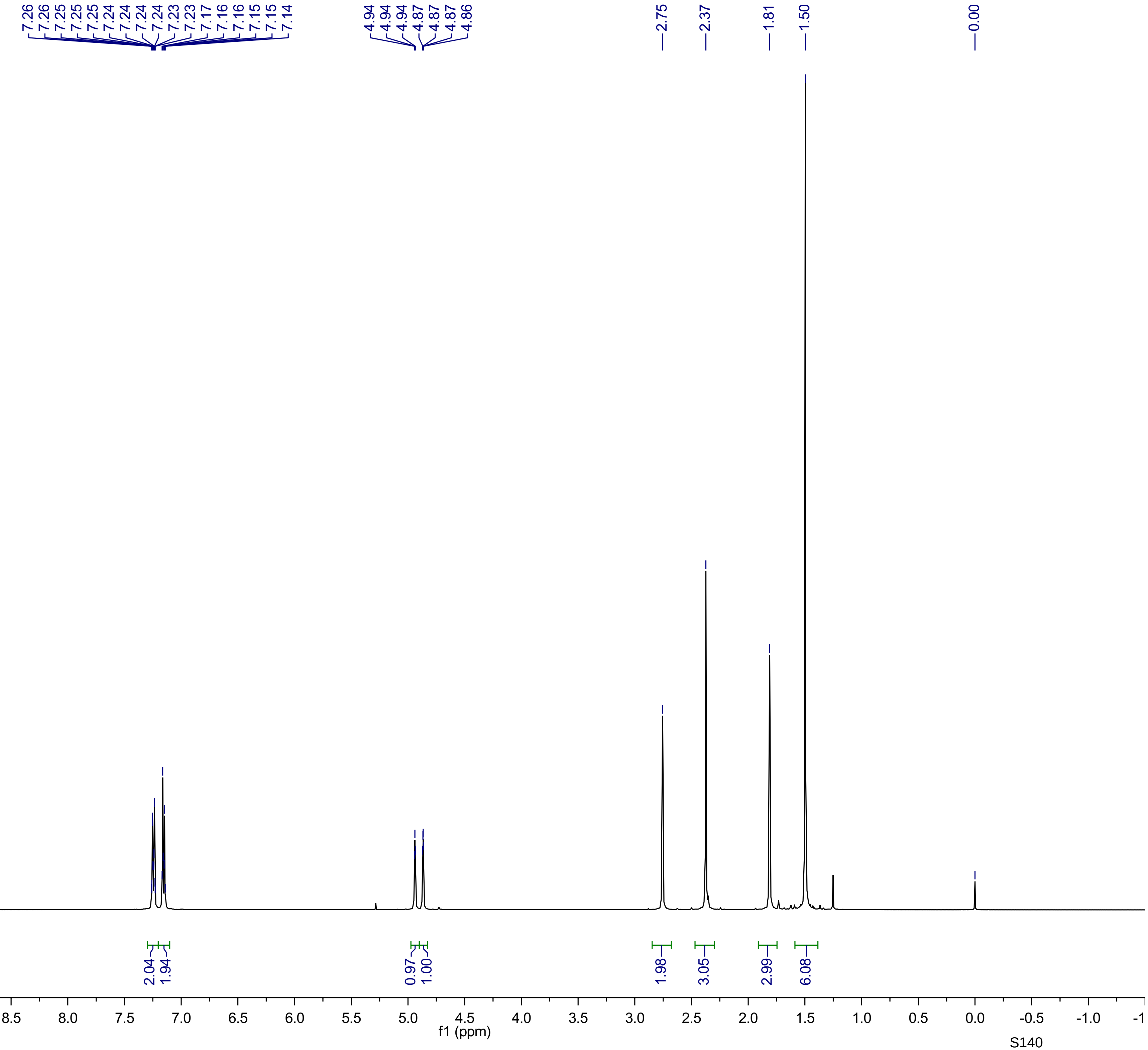
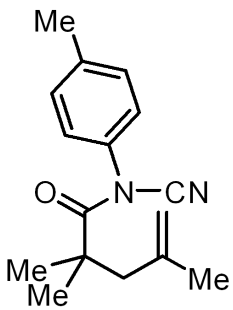
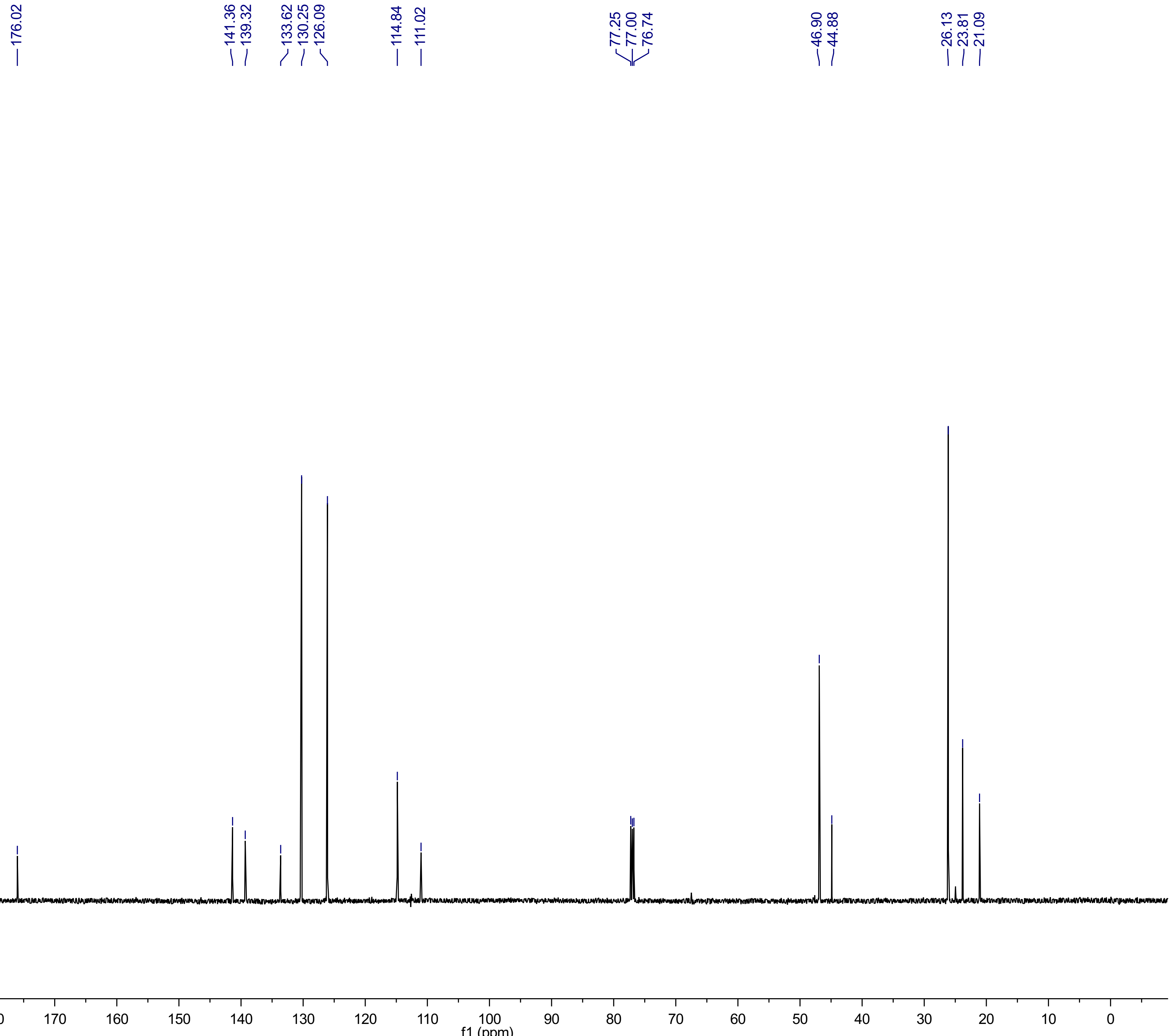
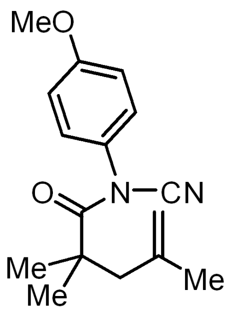


7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.24
7.24
7.23
7.23
7.17
7.16
7.16
7.15
7.15
7.14
4.94
4.94
4.94
4.87
4.87
4.87
4.86
2.75
2.37
1.81
1.50
0.00
2.04
1.94
0.97
1.00
1.98
3.05
2.99
6.08
f1 (ppm)

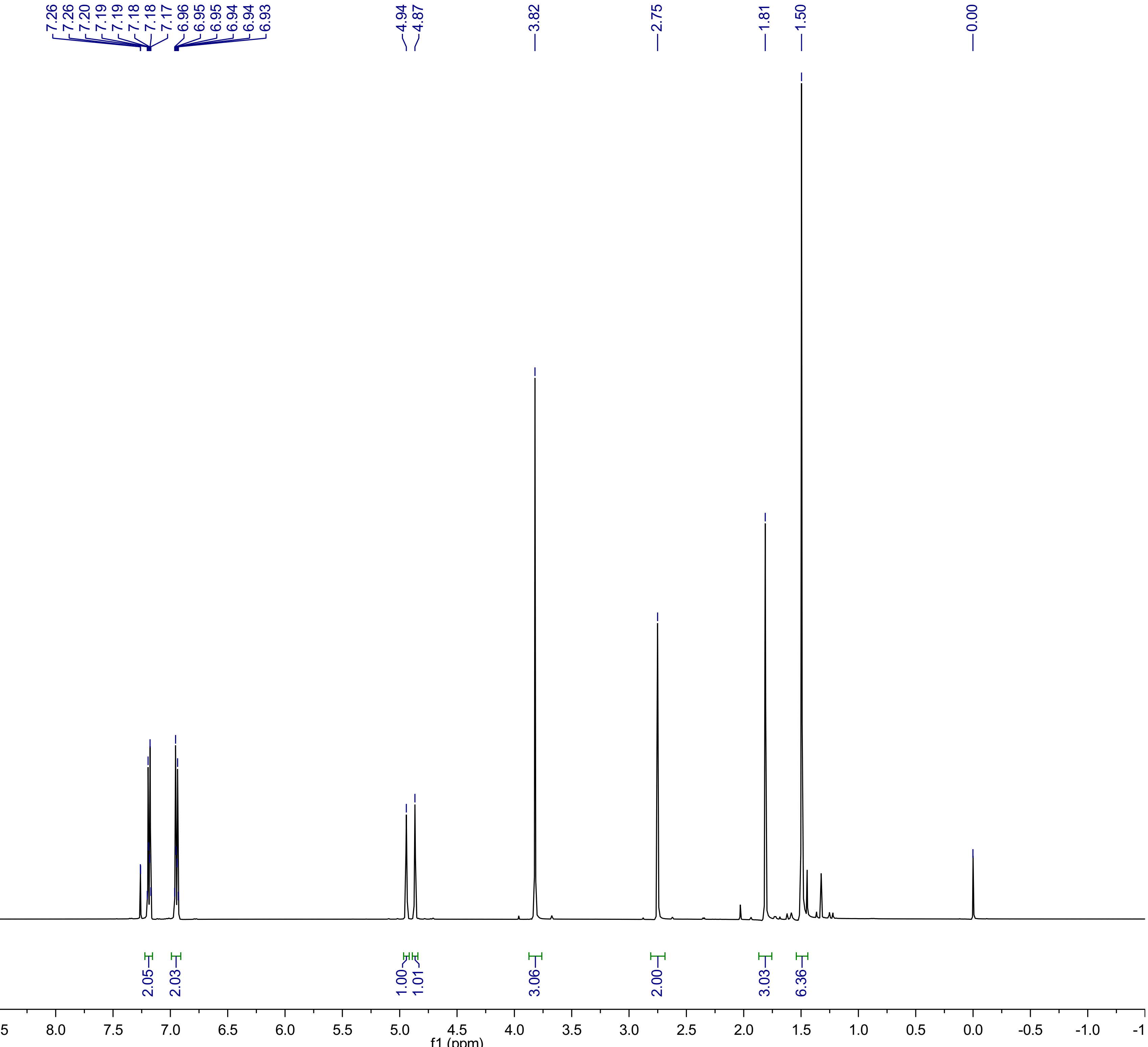

Me
O
N
CN
Me
Me
Me

1q

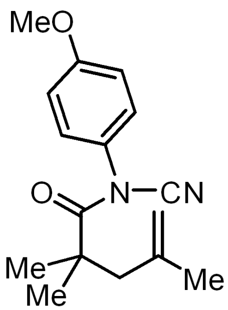

176.02
141.36
139.32
133.62
130.25
126.09
114.84
111.02
77.25
77.00
76.74
46.90
44.88
26.13
23.81
21.09
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



1r

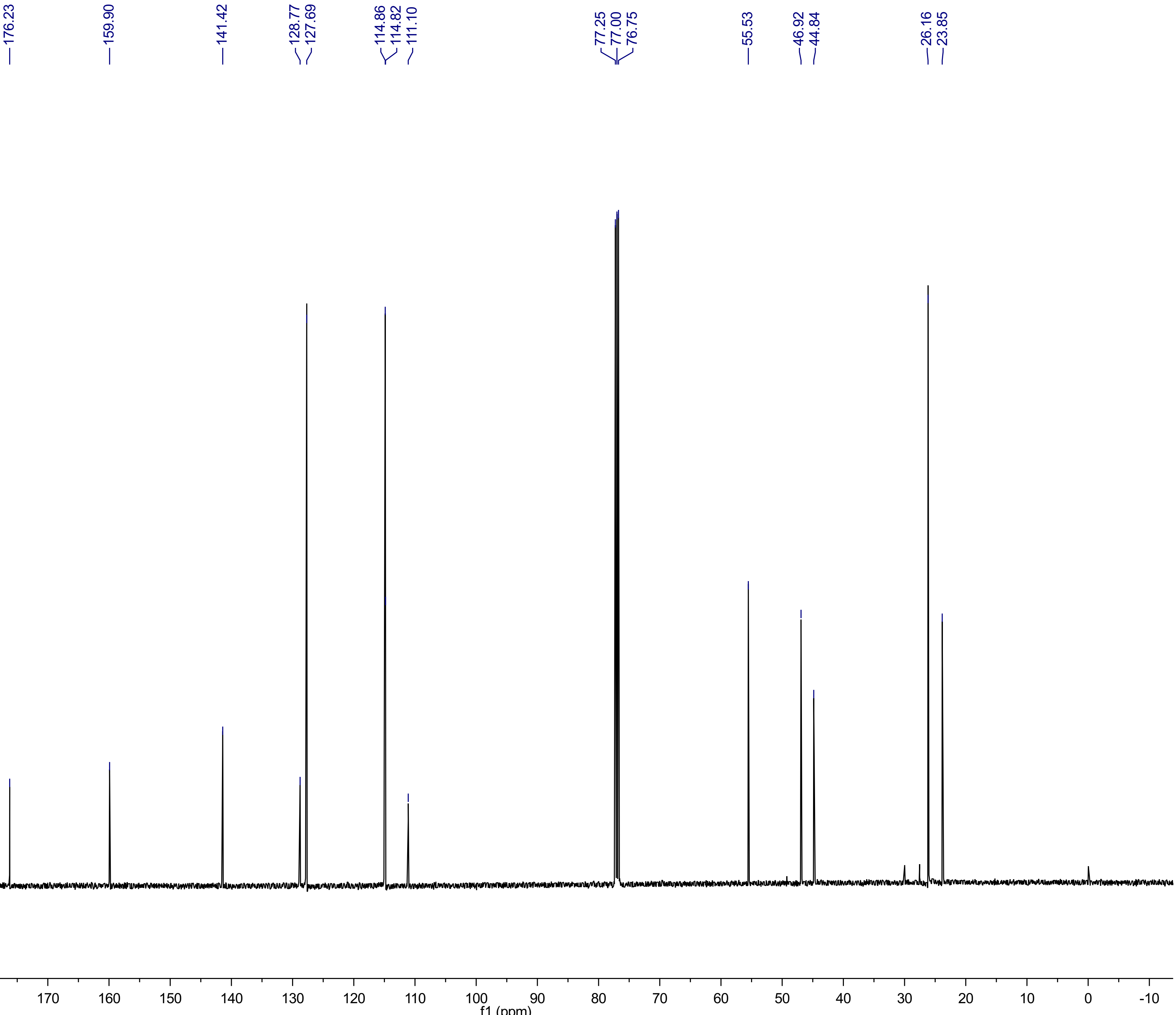


7.26 7.26 7.20 7.19 7.19 7.18 7.18 7.17 6.96 6.95 6.95 6.94 6.94 6.93
4.94 4.87
3.82
2.75
1.81
1.50
0.00
2.05 2.03 1.00 1.01 3.06 2.00 3.03 6.36
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)



MeO
O
N
CN
Me
Me
Me

1r



176.23
159.90
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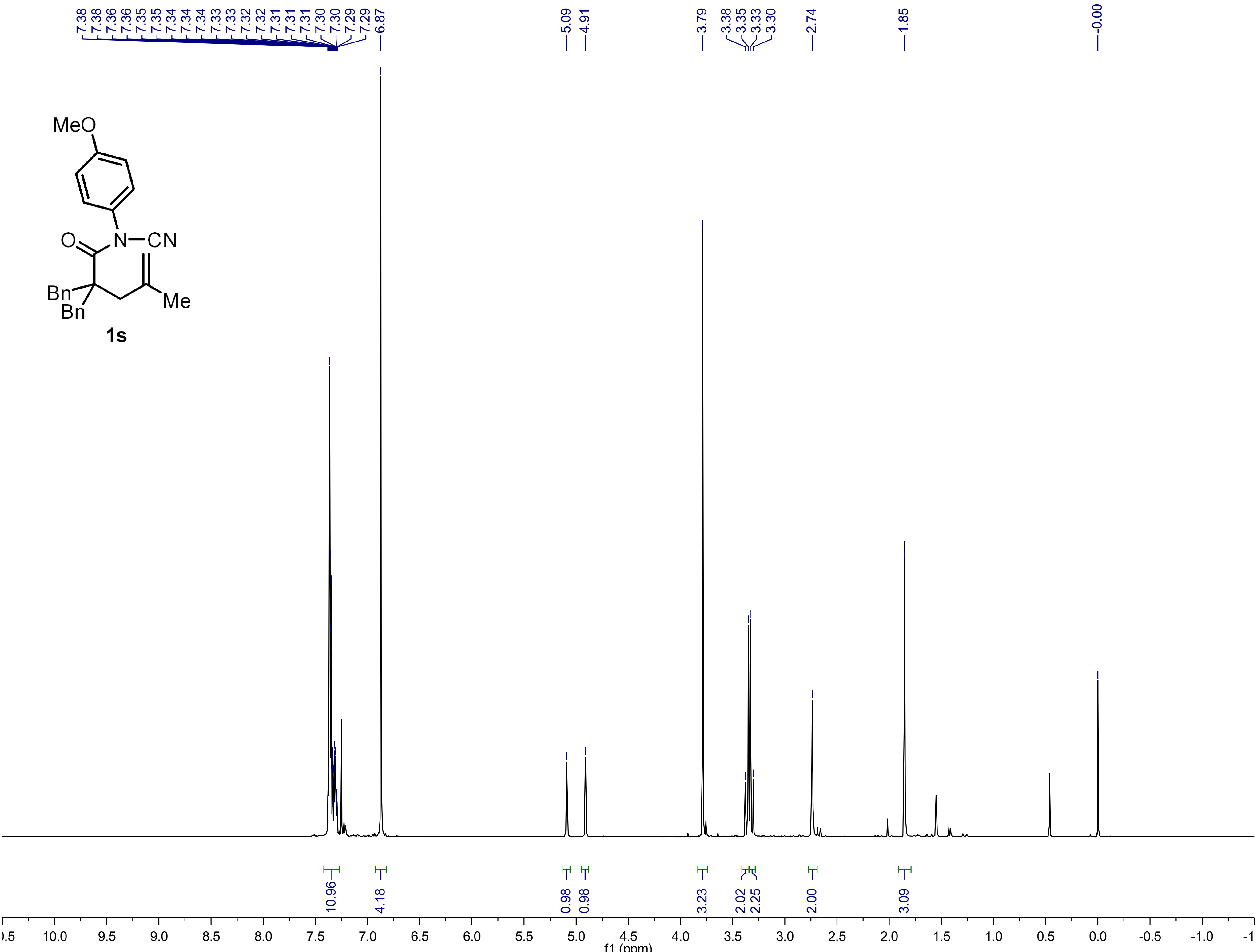
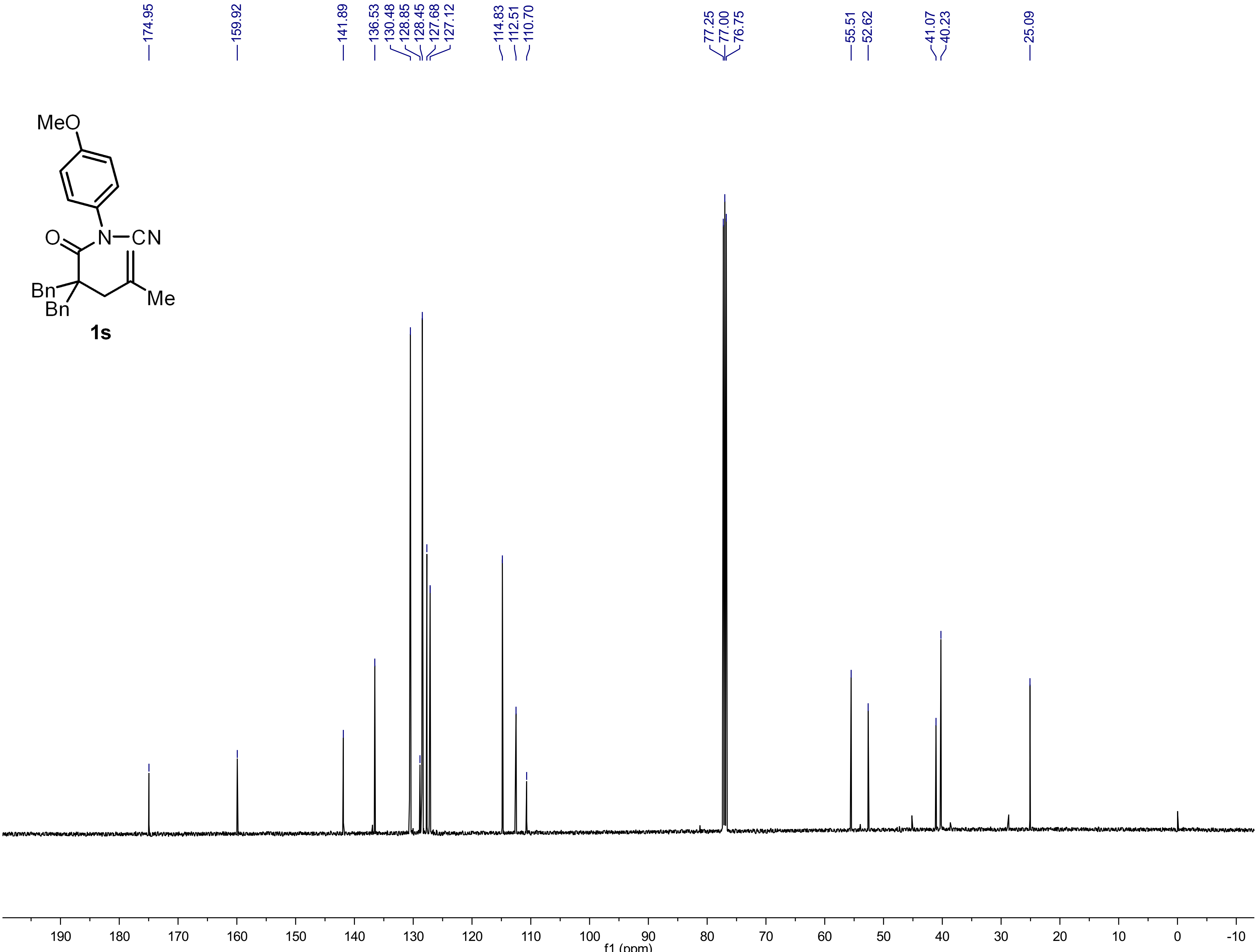
128.77
127.69
114.86
114.82
111.10
77.25
77.00
76.75
55.53
46.92
44.84
26.16
23.85
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.38 7.38 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.29 6.87
5.09 4.91
3.79 3.38 3.35 3.33 3.30 2.74
1.85
-0.00
MeO
O
N
CN
Bn
Bn
Me
1s
10.96 4.18 0.98 0.98 3.23 2.02 2.25 2.00 3.09
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 -0.5 -1.0 -1
f1 (ppm)



1s
174.95
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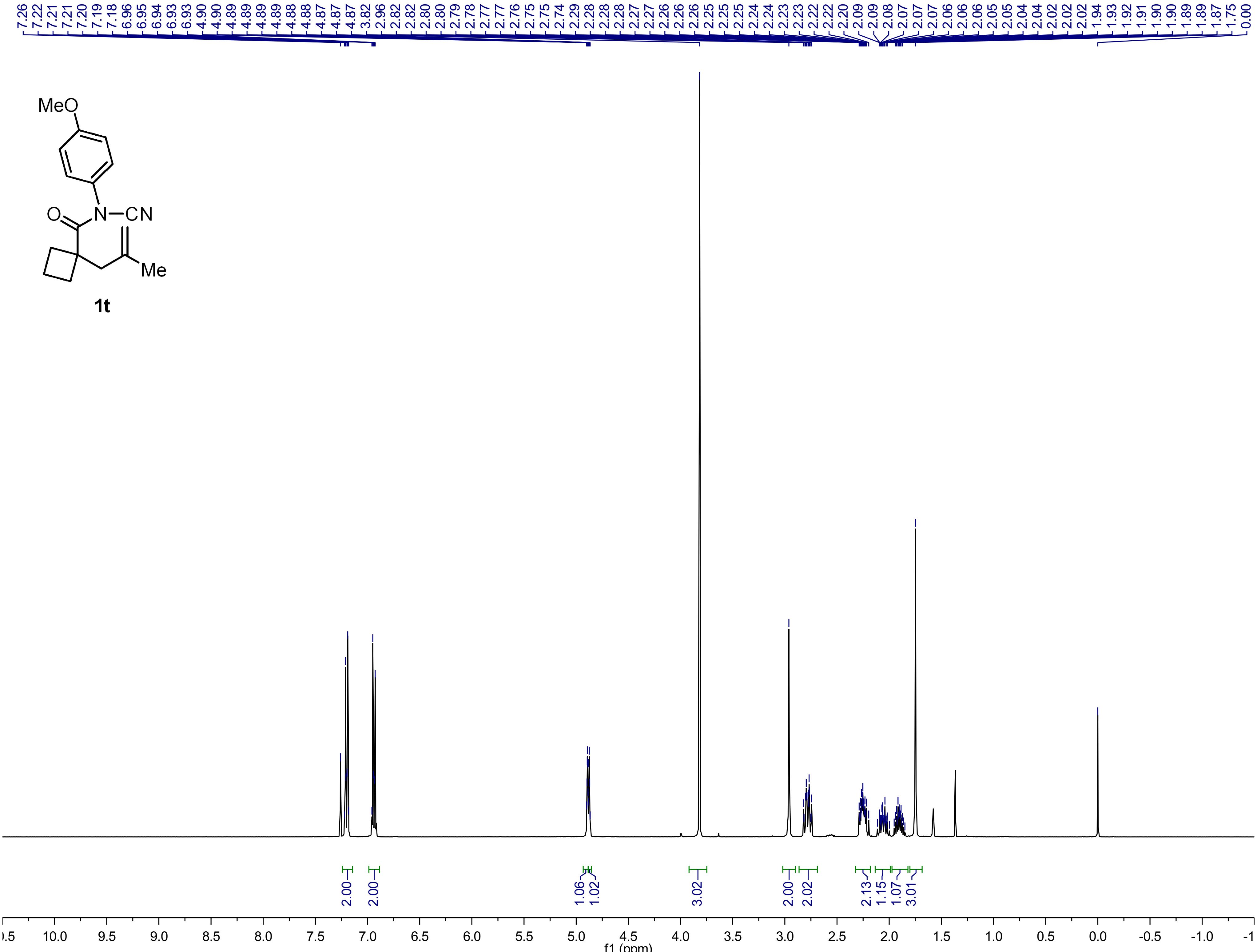
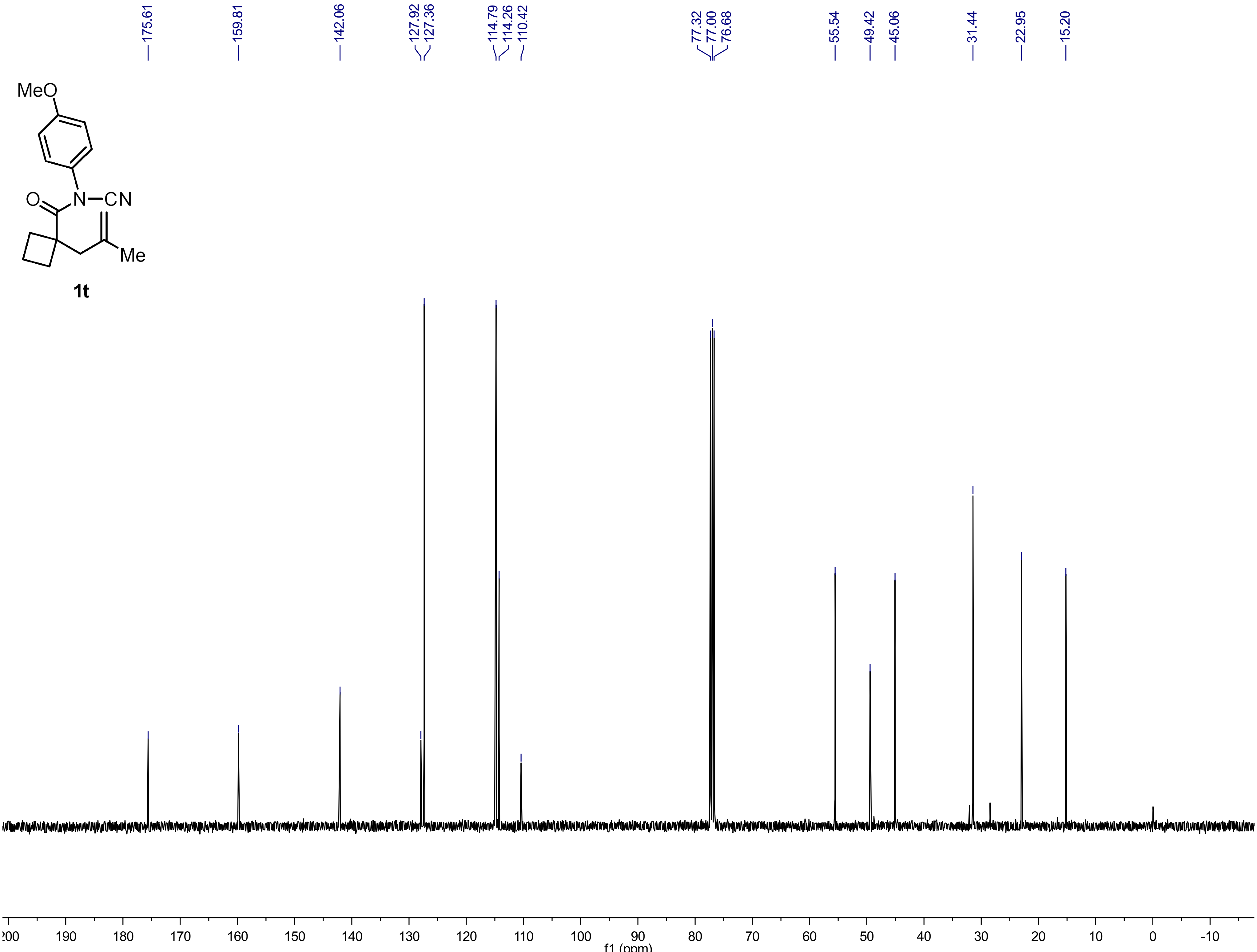
136.53
130.48
128.85
128.45
127.68
127.12
114.83
112.51
110.70
77.25
77.00
76.75
55.51
52.62
41.07
40.23
25.09
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



7.26 7.22 7.21 7.21 7.20 7.19 7.18 6.96 6.95 6.94 6.93 6.93 4.90 4.90 4.89 4.89 4.89 4.88 4.88 4.87 4.87 4.87 3.82 2.96 2.82 2.82 2.80 2.80 2.79 2.78 2.77 2.77 2.76 2.75 2.75 2.74 2.29 2.28 2.28 2.28 2.27 2.27 2.26 2.26 2.26 2.25 2.25 2.25 2.24 2.24 2.23 2.23 2.22 2.22 2.20 2.09 2.09 2.08 2.07 2.07 2.07 2.06 2.06 2.05 2.05 2.04 2.04 2.02 2.02 2.02 1.94 1.93 1.92 1.91 1.90 1.90 1.89 1.89 1.87 1.75 0.00
MeO
O
N
CN
Me
1t
2.00 2.00 1.06 1.02 3.02 2.00 2.02 2.13 1.15 1.07 3.01
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 -0.5 -1.0
f1 (ppm)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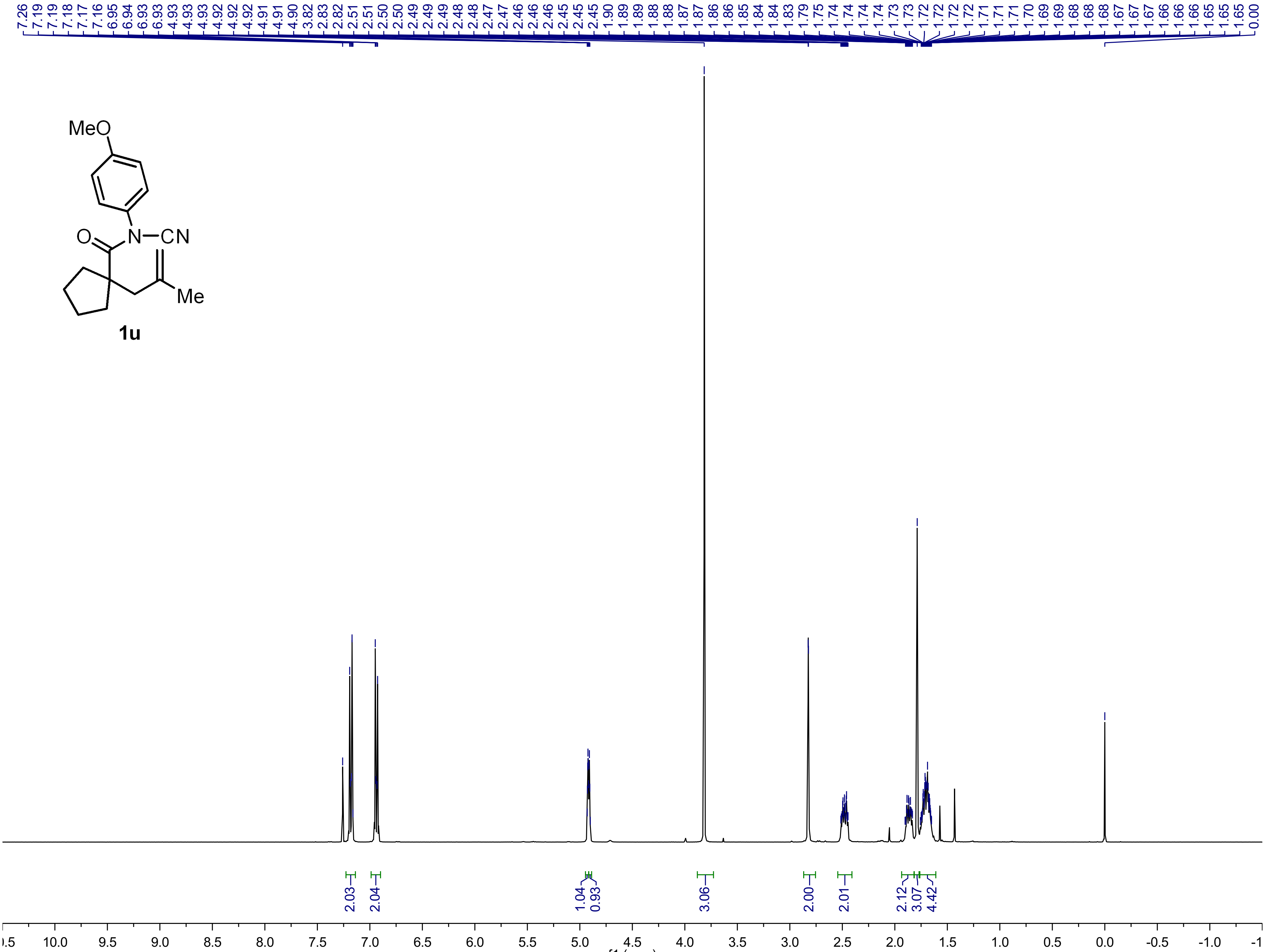
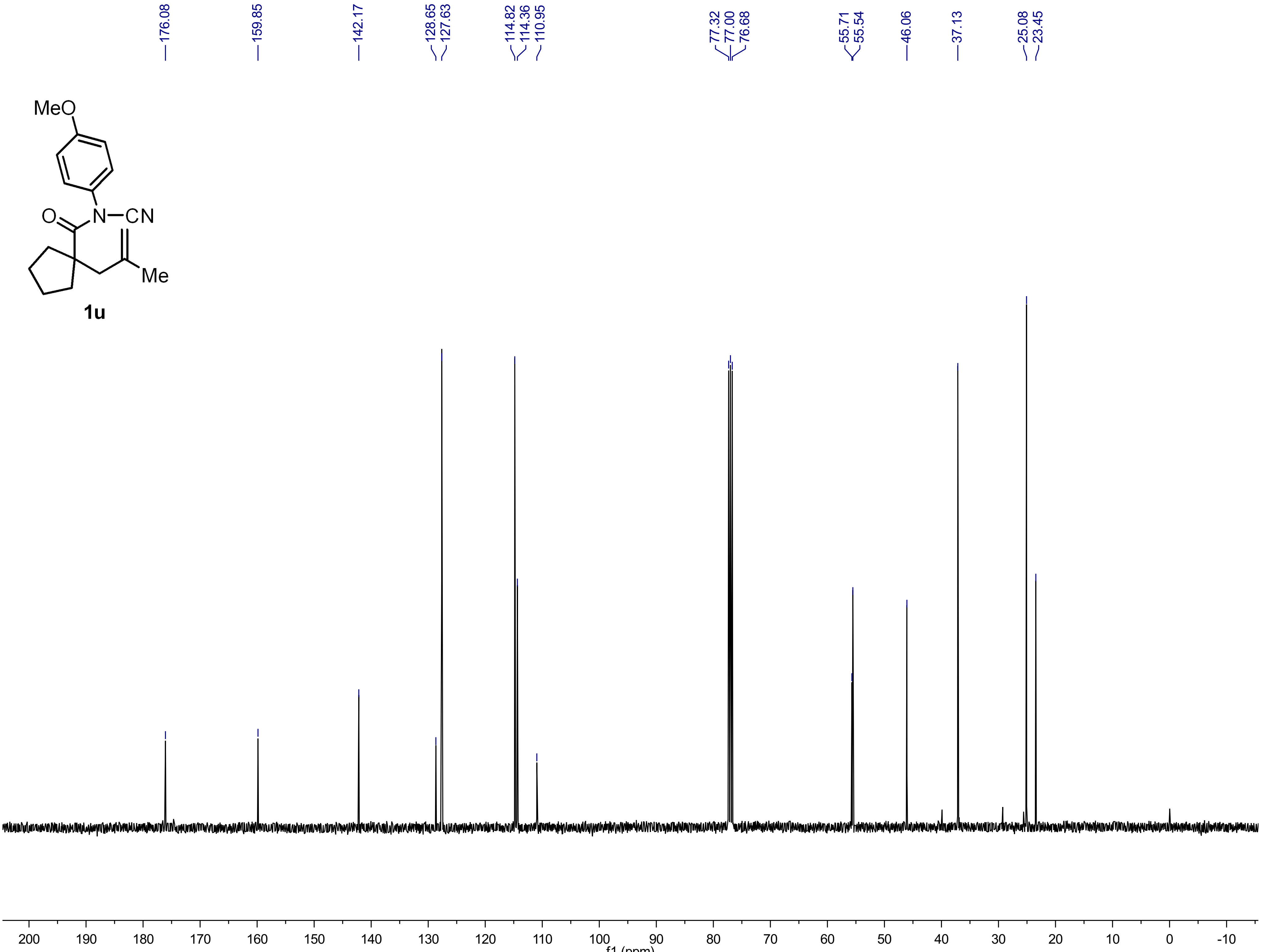
127.92
127.36
114.79
114.26
110.42
77.32
77.00
76.68
55.54
49.42
45.06
31.44
22.95
15.20
MeO
O
N
CN
Me
1t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



1u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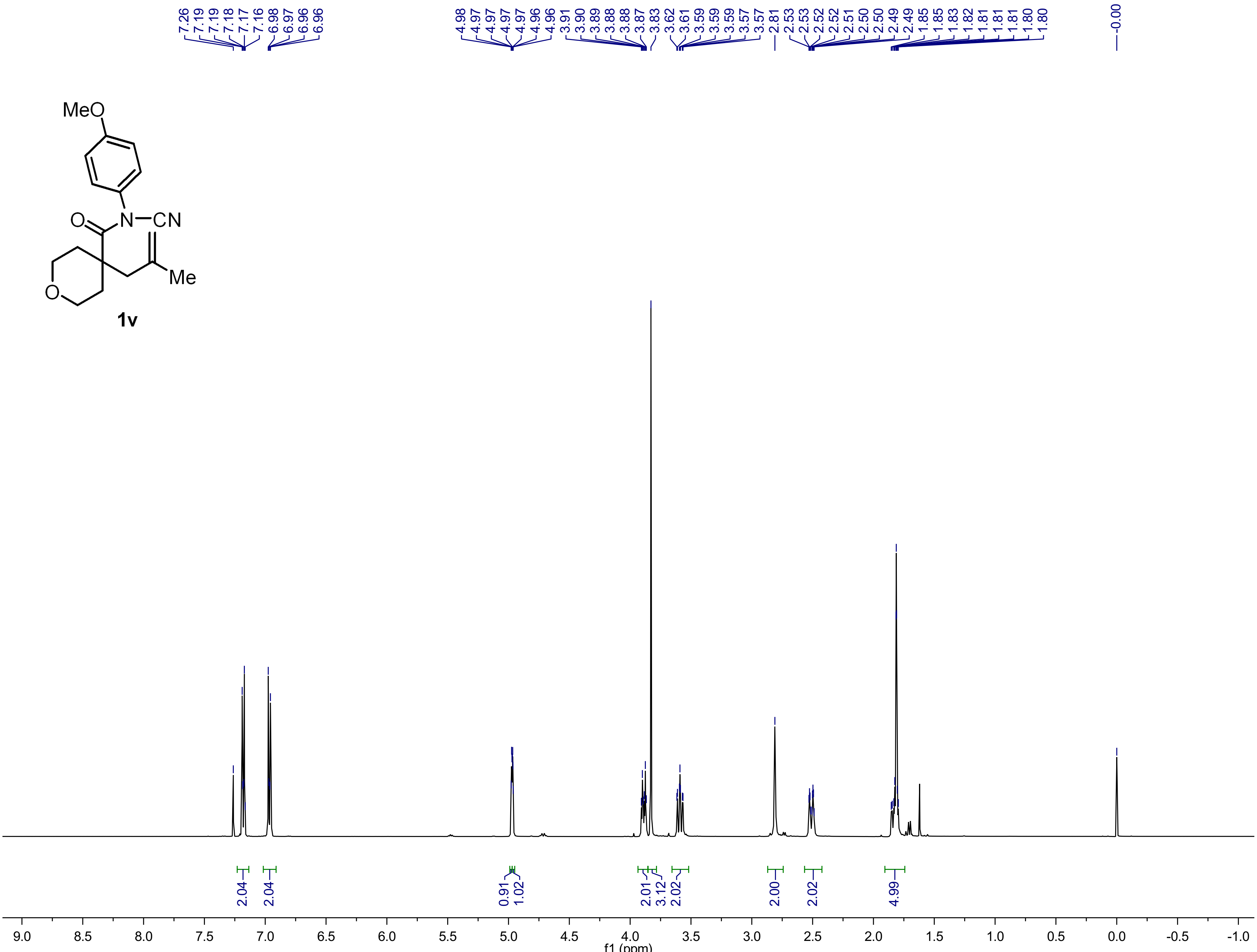
127.63
114.82
114.36
110.95
77.32
77.00
76.68
55.71
55.54
46.06
37.13
25.08
23.45
MeO
O
N
CN
Me
1u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



MeO
O
N
CN
O
Me
1v
7.26
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7.19
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7.17
7.16
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6.97
6.96
6.96
4.98
4.97
4.97
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4.96
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3.88
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3.87
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3.59
3.57
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2.53
2.53
2.52
2.52
2.51
2.50
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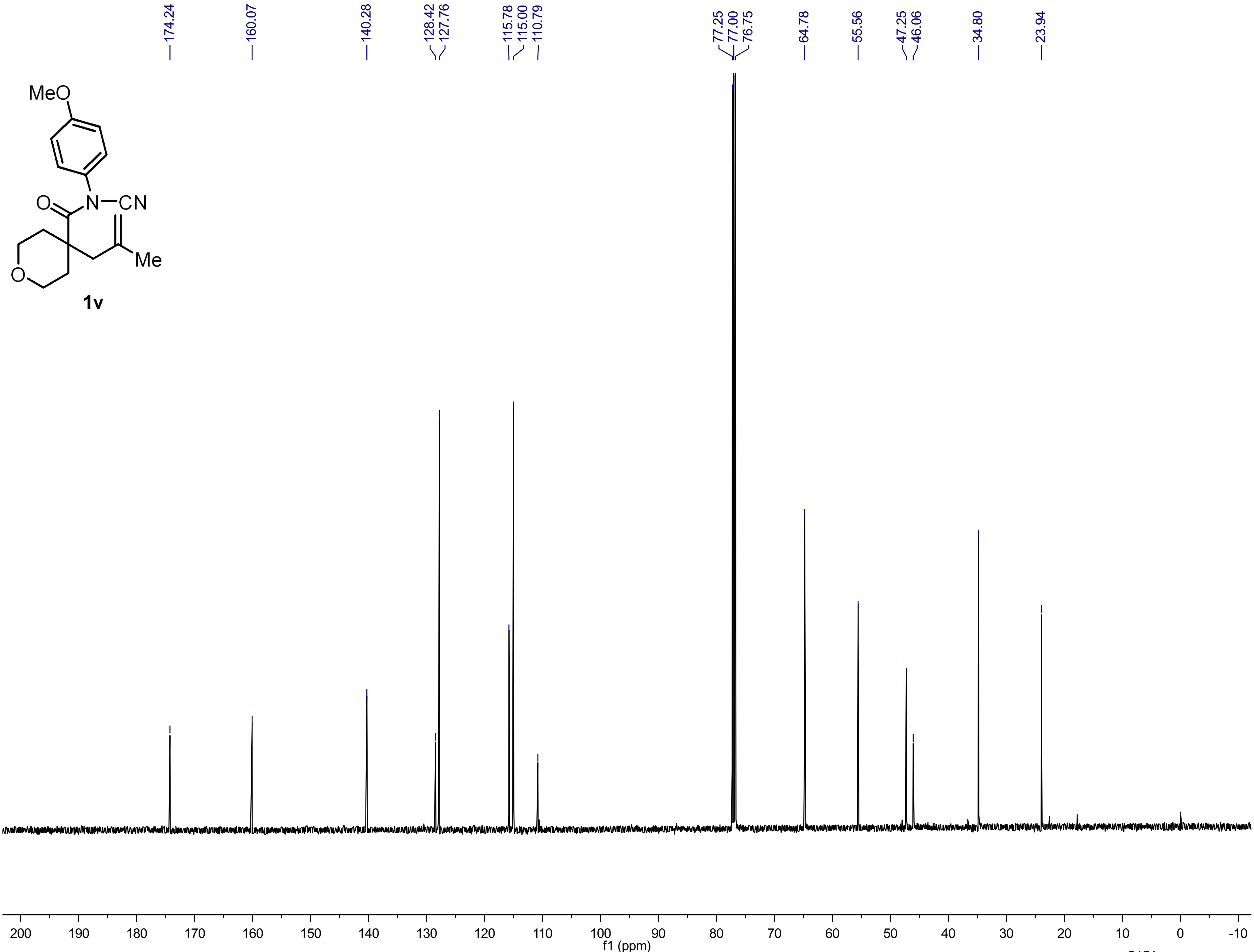
2.49
2.49
1.85
1.85
1.83
1.82
1.81
1.81
1.81
1.81
1.80
1.80
-0.00
2.04
2.04
0.91
1.02
2.01
3.12
2.02
2.00
2.02
4.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



174.24
160.07
140.28
128.42
127.76
115.78
115.00
110.79
77.25
77.00
76.75
64.78
55.56
47.25
46.06
34.80
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N
CN
Me
O
1v
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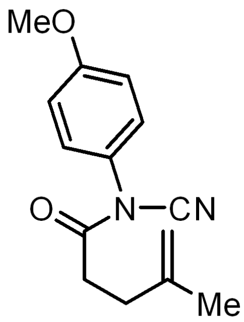
f1 (ppm)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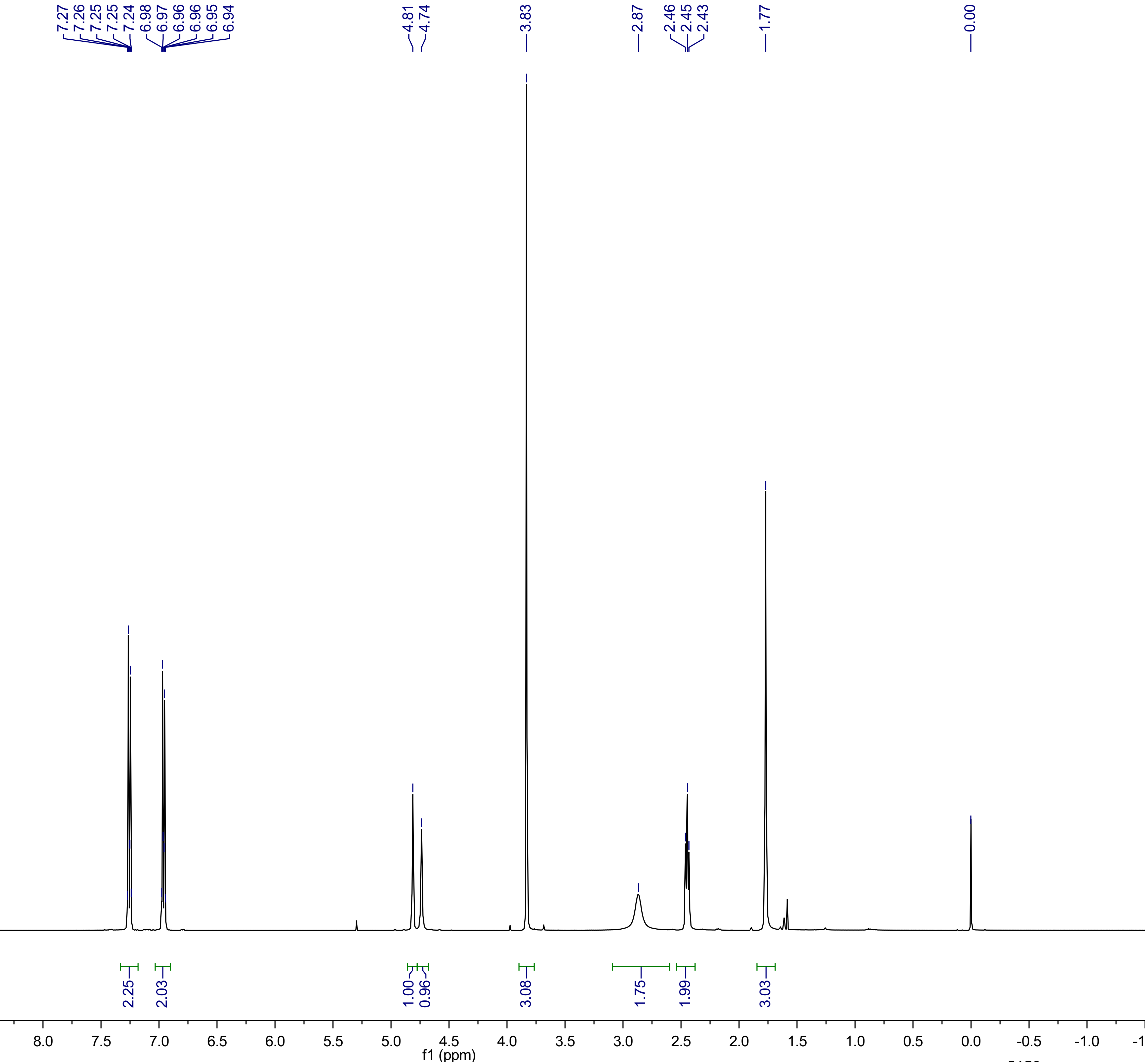
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4.74
3.83
2.87
2.46
2.45
2.43
1.77
0.00
2.25
2.03
1.00
0.96
3.08
1.75
1.99
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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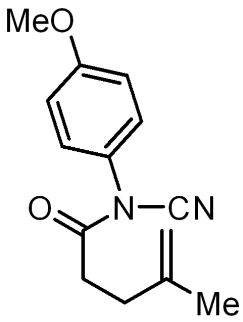
f1 (ppm)



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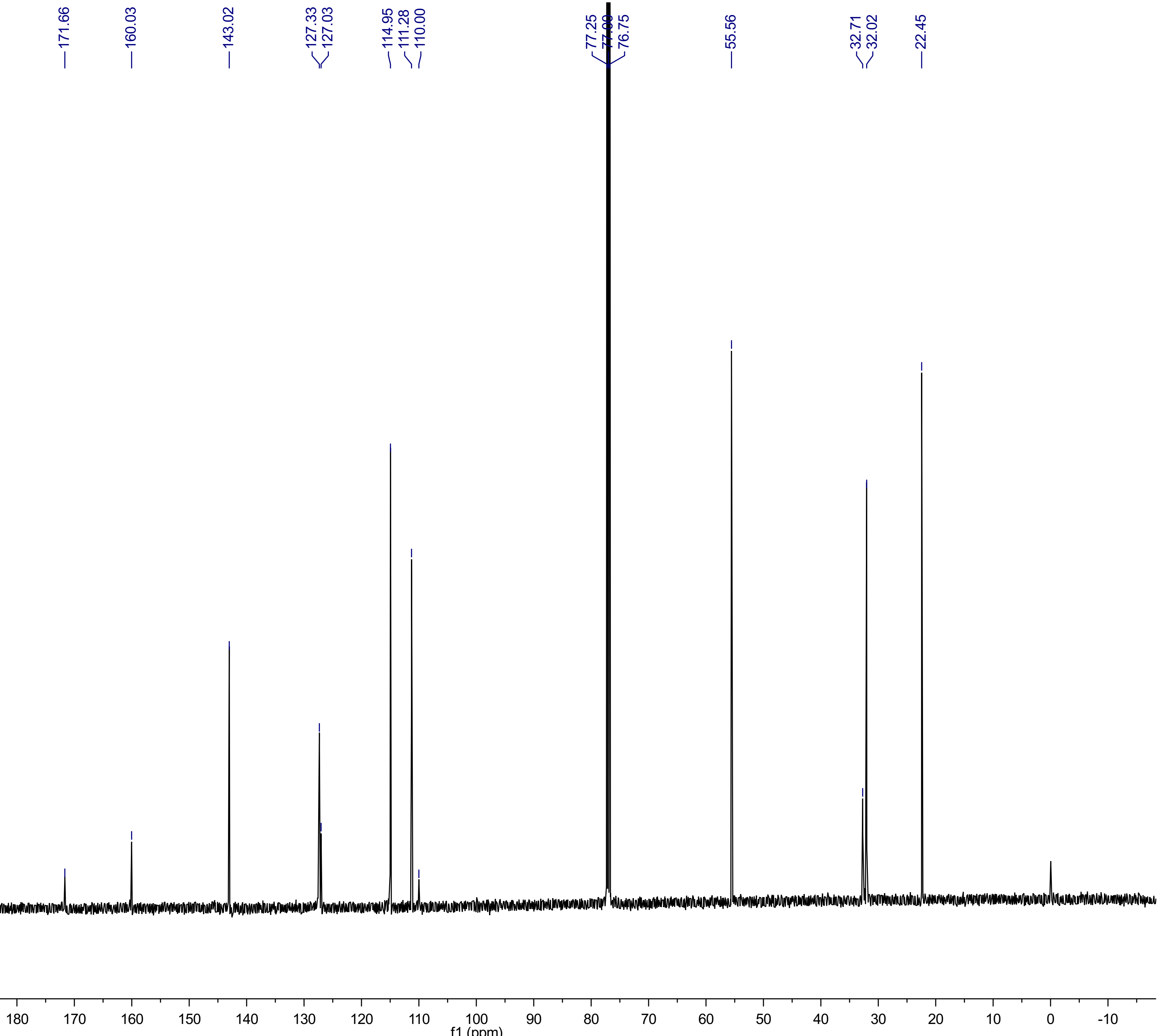
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32.71
32.02
22.45
210
200
190
180
170
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100
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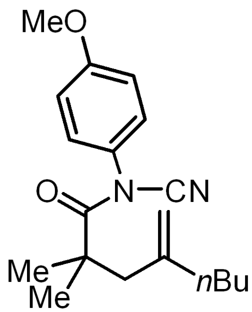
0
-10
f1 (ppm)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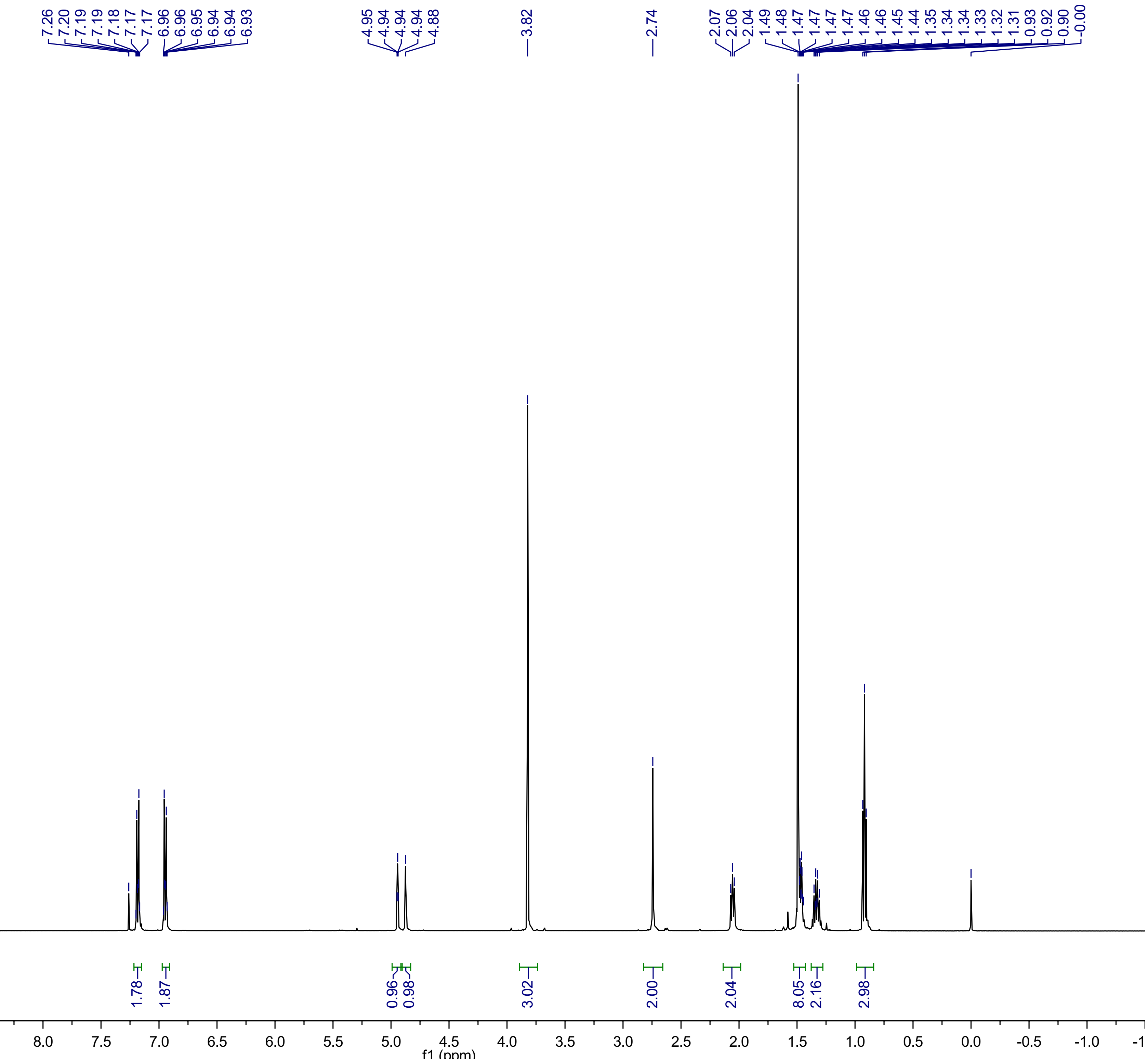
O
Me
Me
nBu

1x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4.95
4.94
4.94
4.94
4.88
3.82
2.74
2.07
2.06
2.04
1.49
1.48
1.47
1.47
1.47
1.47
1.46
1.46
1.45
1.44
1.35
1.34
1.34
1.33
1.32
1.31
0.93
0.92
0.90
-0.00
1.78
1.87
0.96
0.98
3.02
2.00
2.04
8.05
2.16
2.98
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
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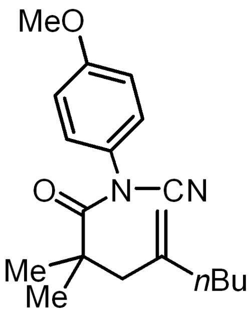
f1 (ppm)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CN
Me
Me
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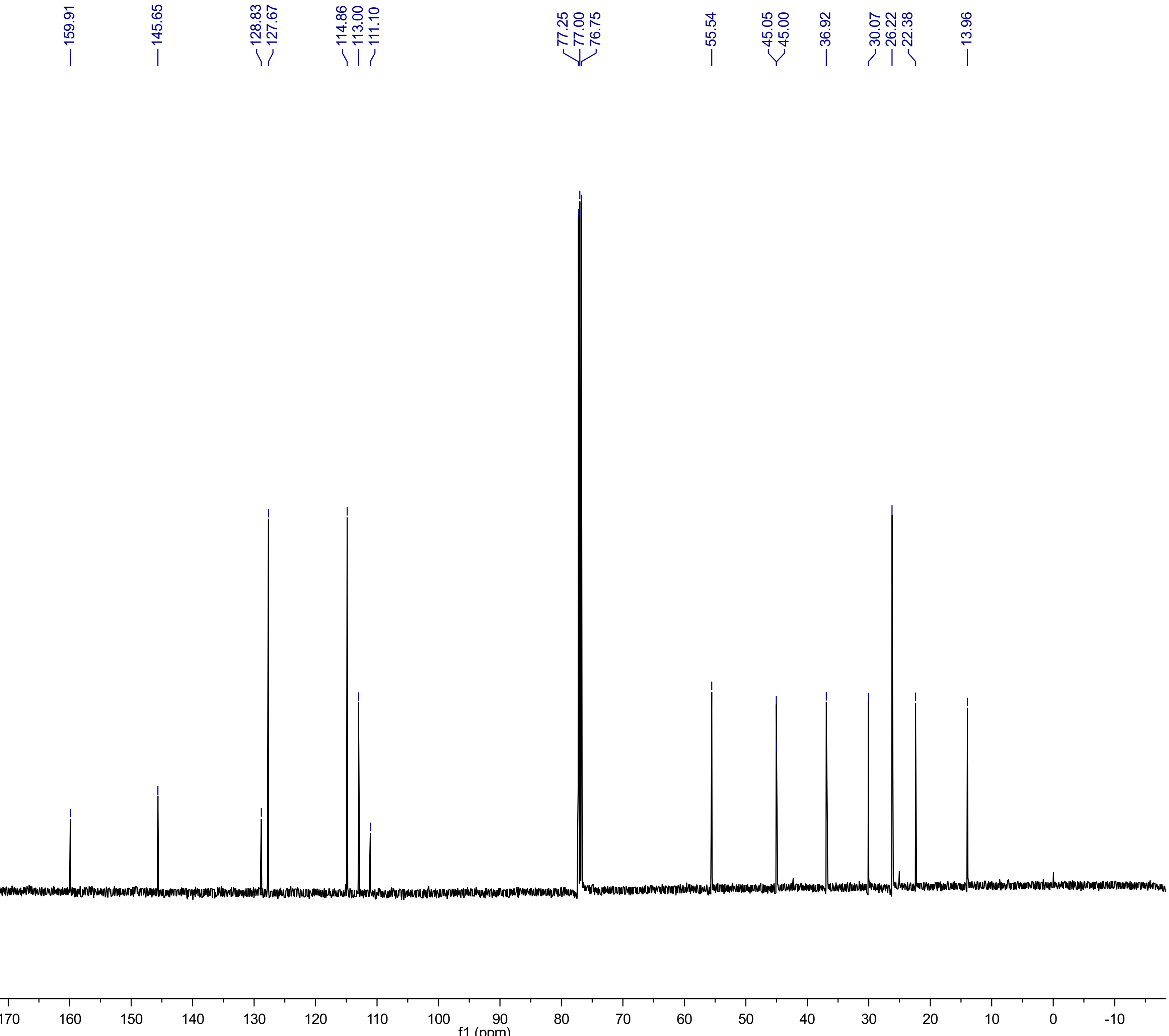
1x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55.54
45.05
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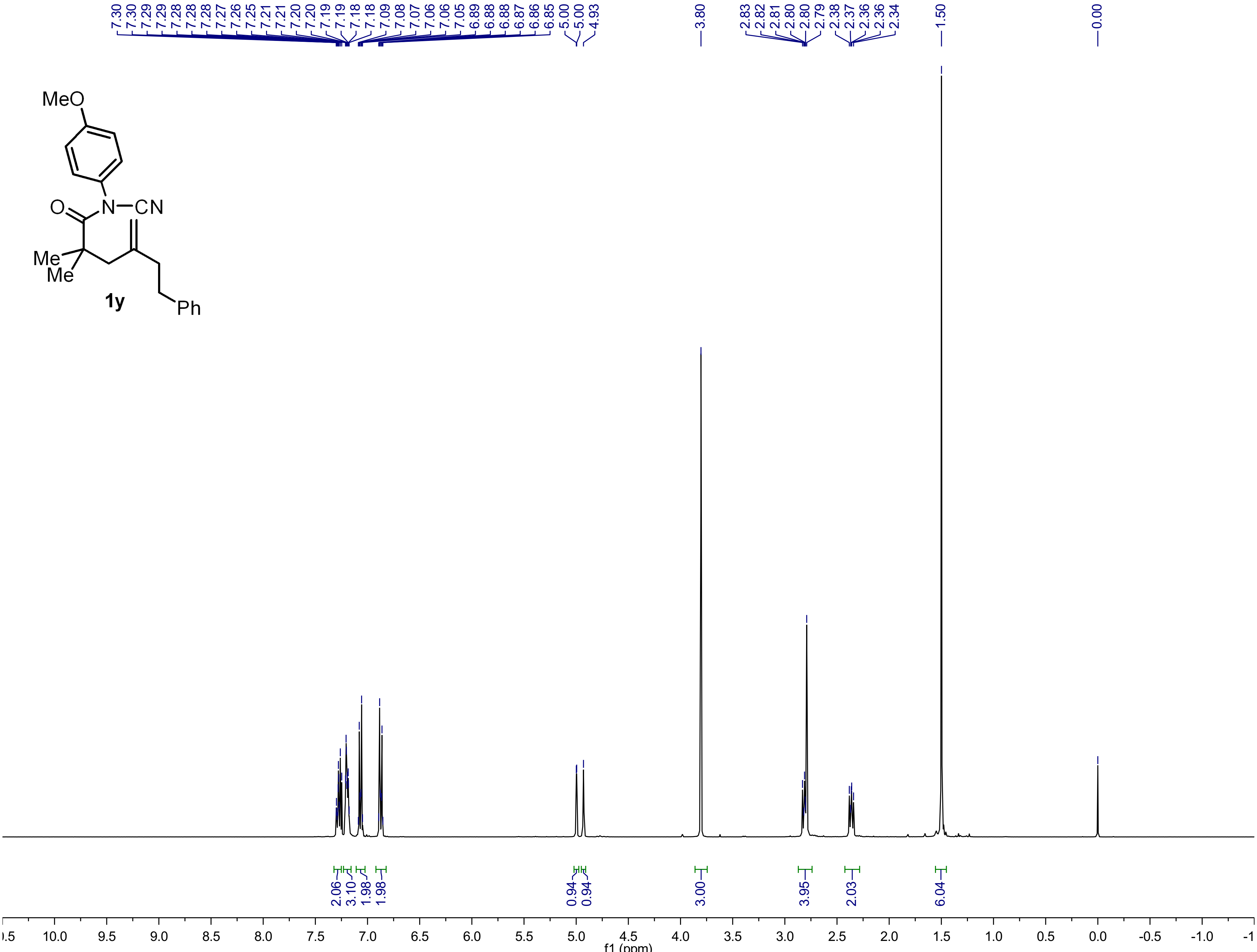
26.22
22.38
13.96
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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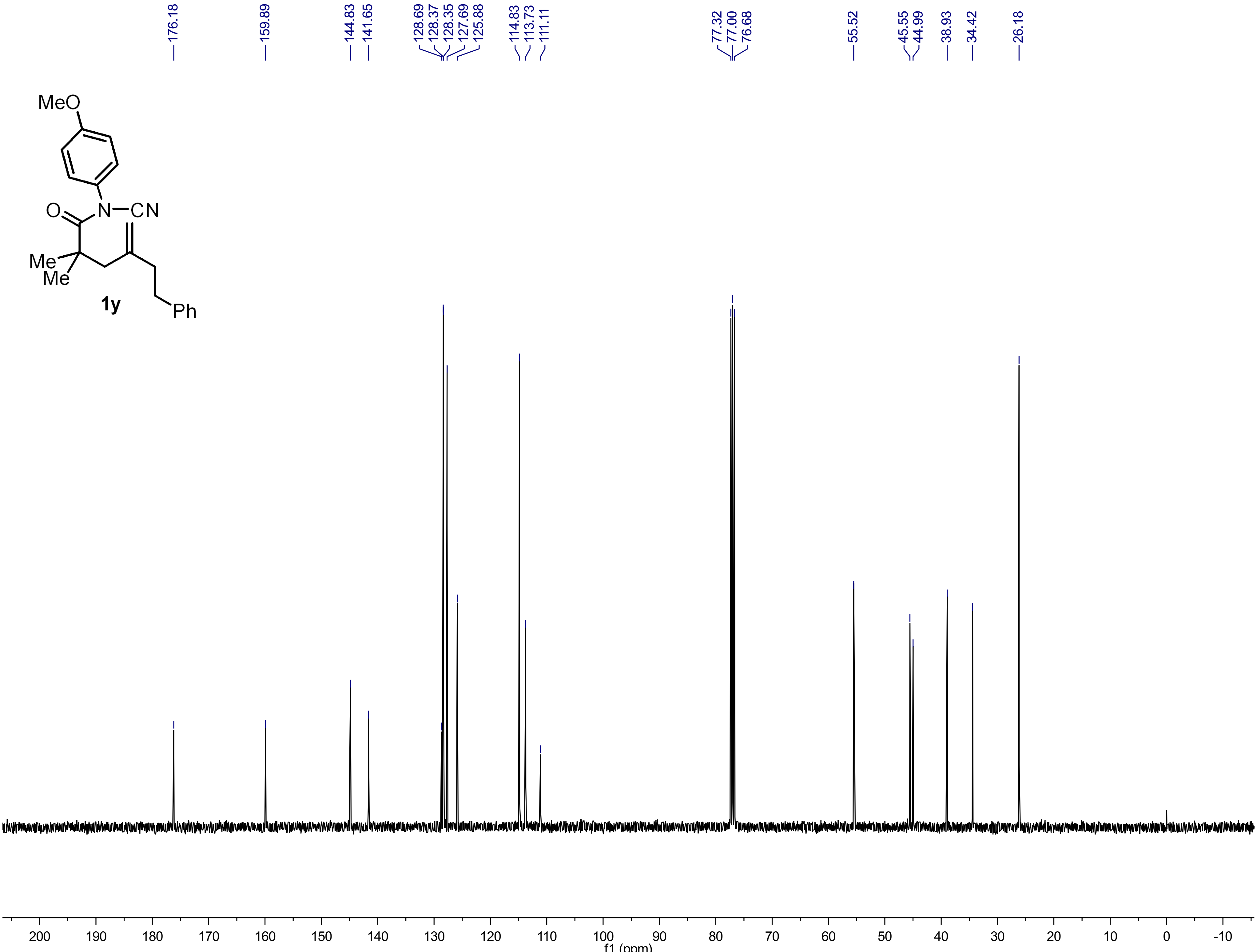
3.80
2.83 2.82 2.81 2.80 2.80 2.79 2.38 2.37 2.36 2.36 2.34
1.50
0.00
MeO
O
N
CN
Me
Me
1y
Ph
2.06 3.10 1.98 1.98
0.94 0.94
3.00
3.95
2.03
6.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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127.69
125.88
114.83
113.73
111.11
77.32
77.00
76.68
55.52
45.55
44.99
38.93
34.42
26.18
MeO
O
N
CN
Me
Me
1y
Ph
200
190
180
170
160
150
140
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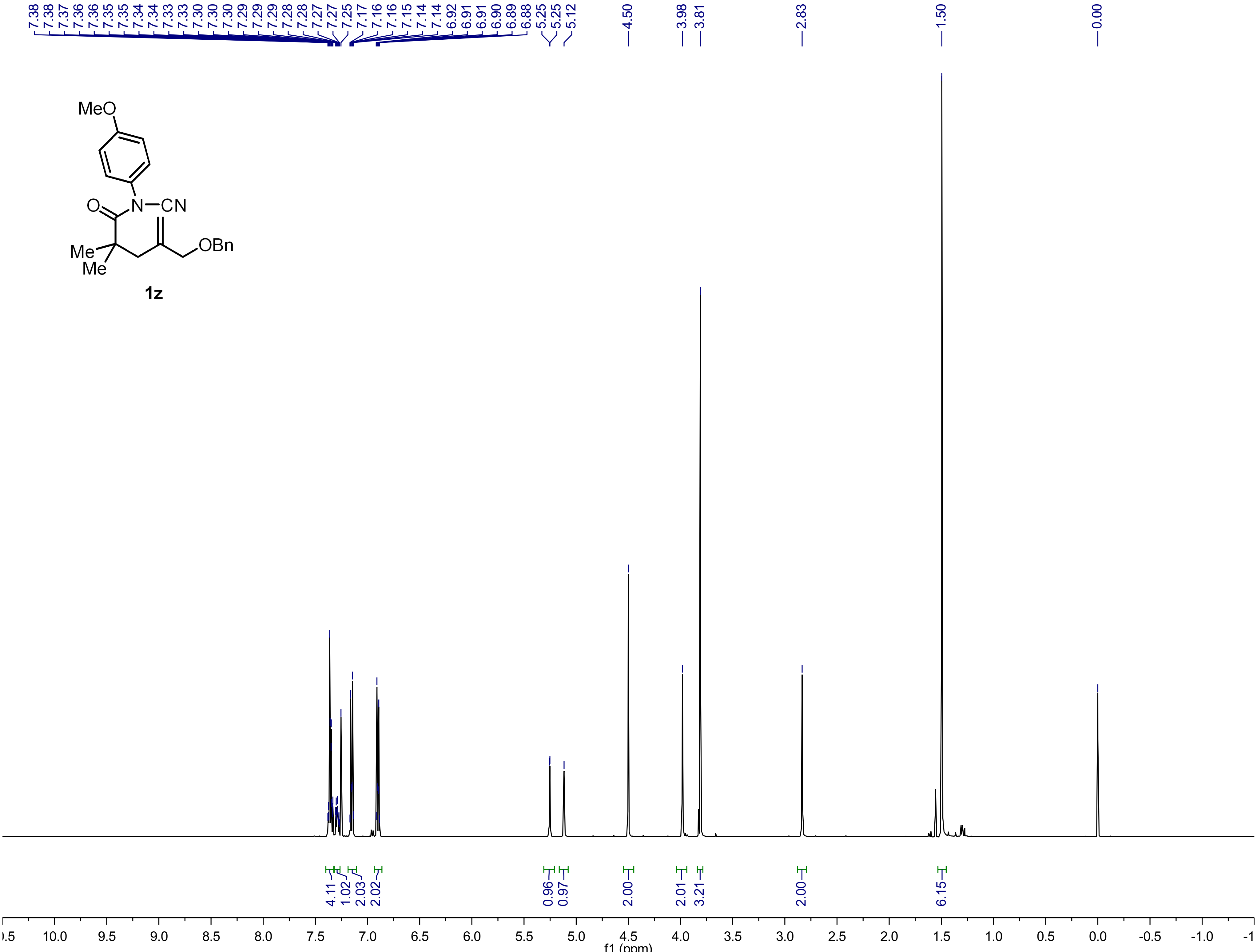
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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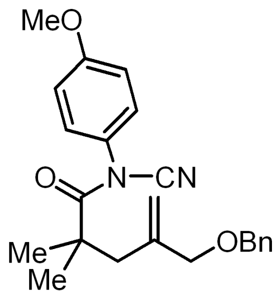
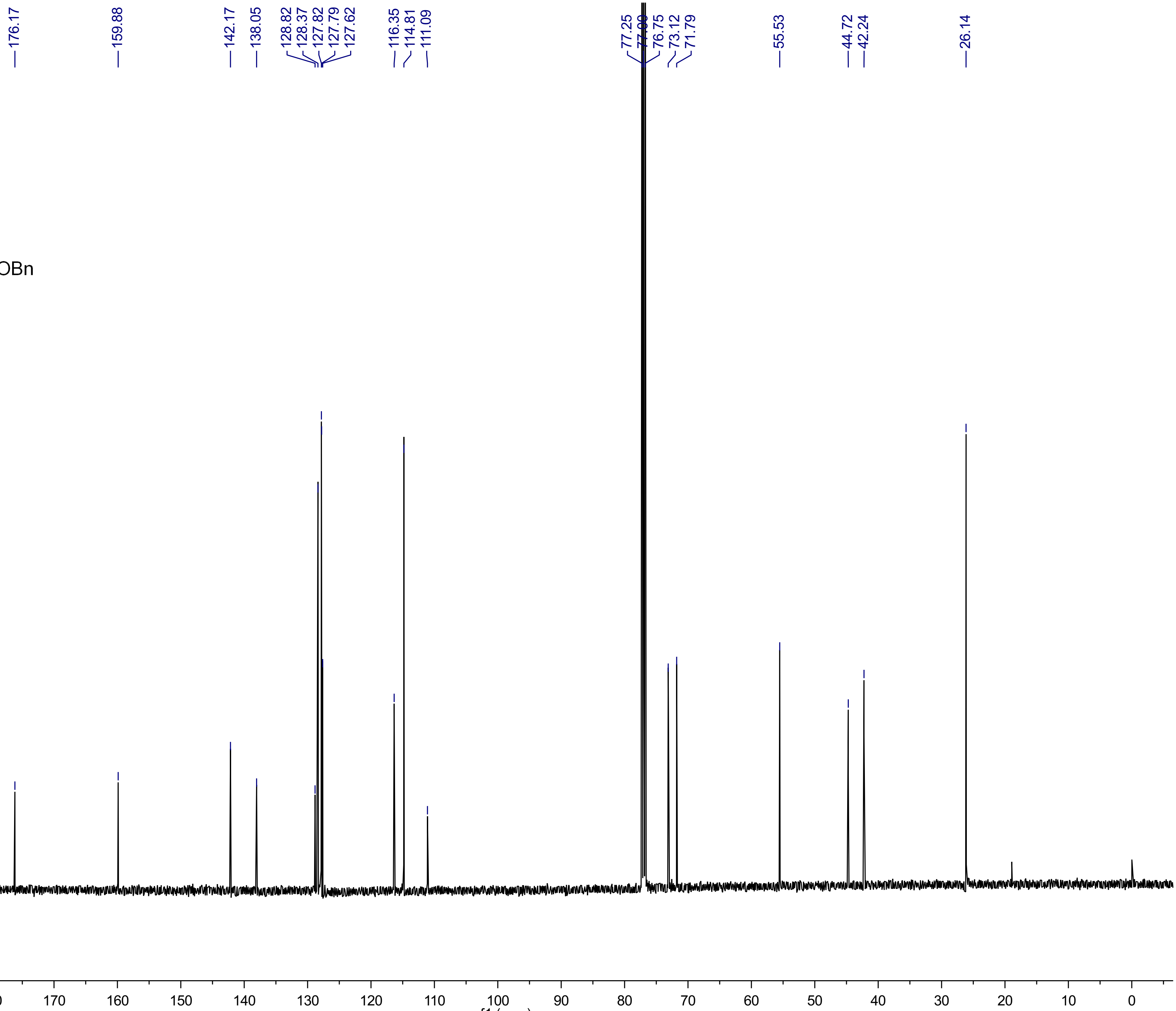
MeO
N
CN
O
Me
Me
OBn
1z
4.11 1.02 2.03 2.02 0.96 0.97 2.00 2.01 3.21 2.00 6.15
f1 (ppm)


MeO
N
CN
O
Me
Me
OBn

1z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114.81
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77.00
76.75
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55.53
44.72
42.24
26.14
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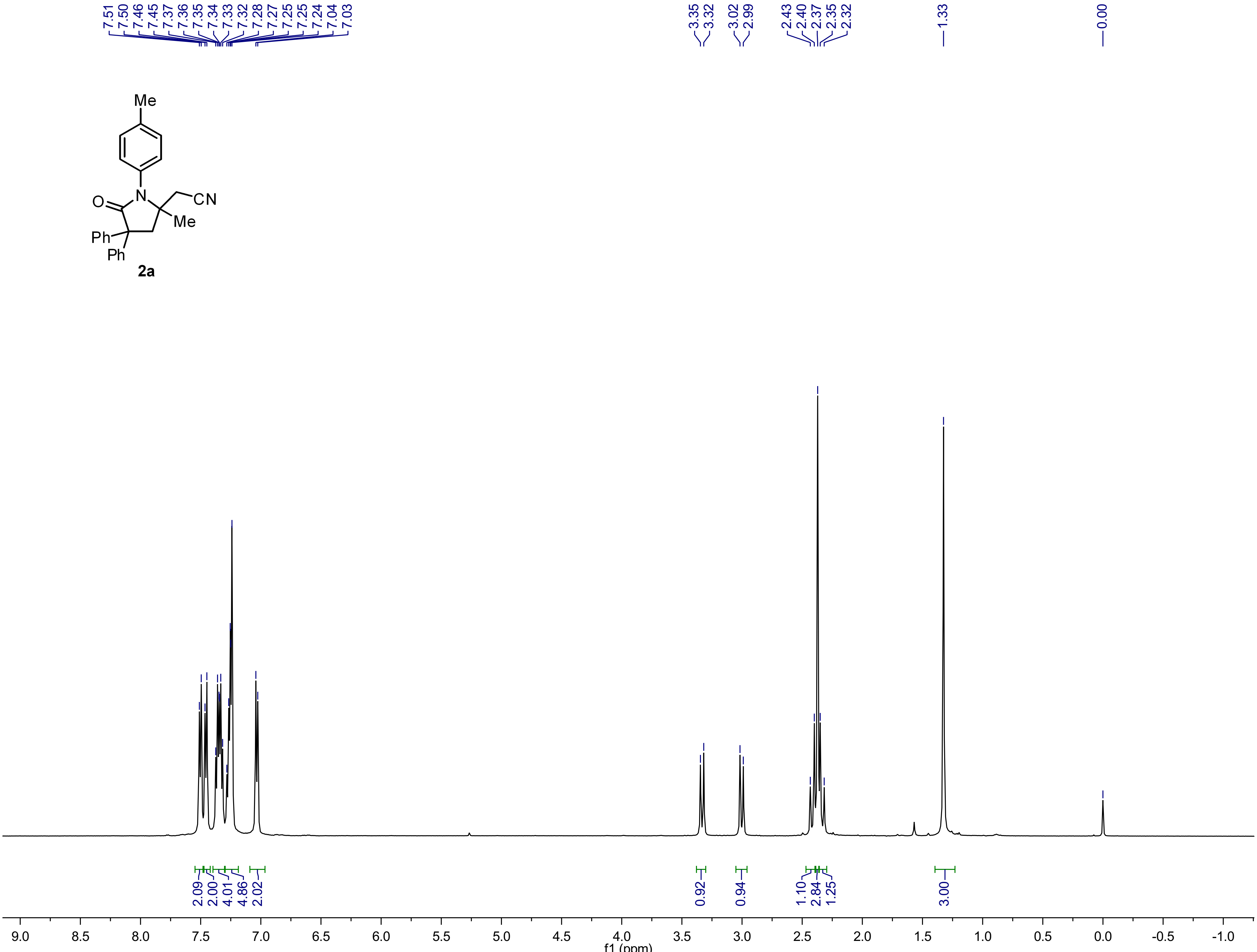
f1 (ppm)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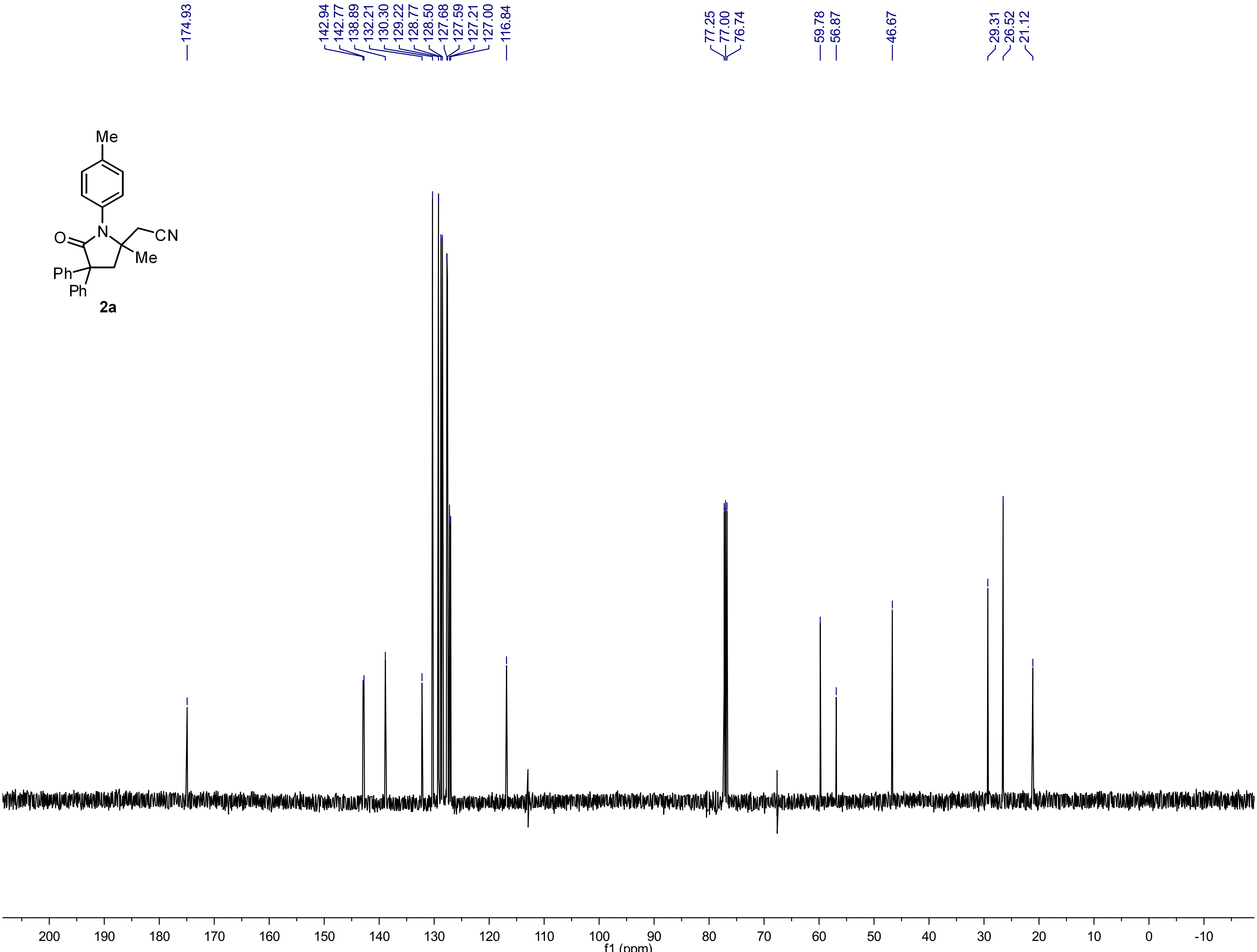
3.35 3.32 3.02 2.99
2.43 2.40 2.37 2.35 2.32
1.33
0.00
Me
O
N
CN
Me
Ph
Ph
2a
2.09 2.00 4.01 4.86 2.02
0.92
0.94
1.10 2.84 1.25
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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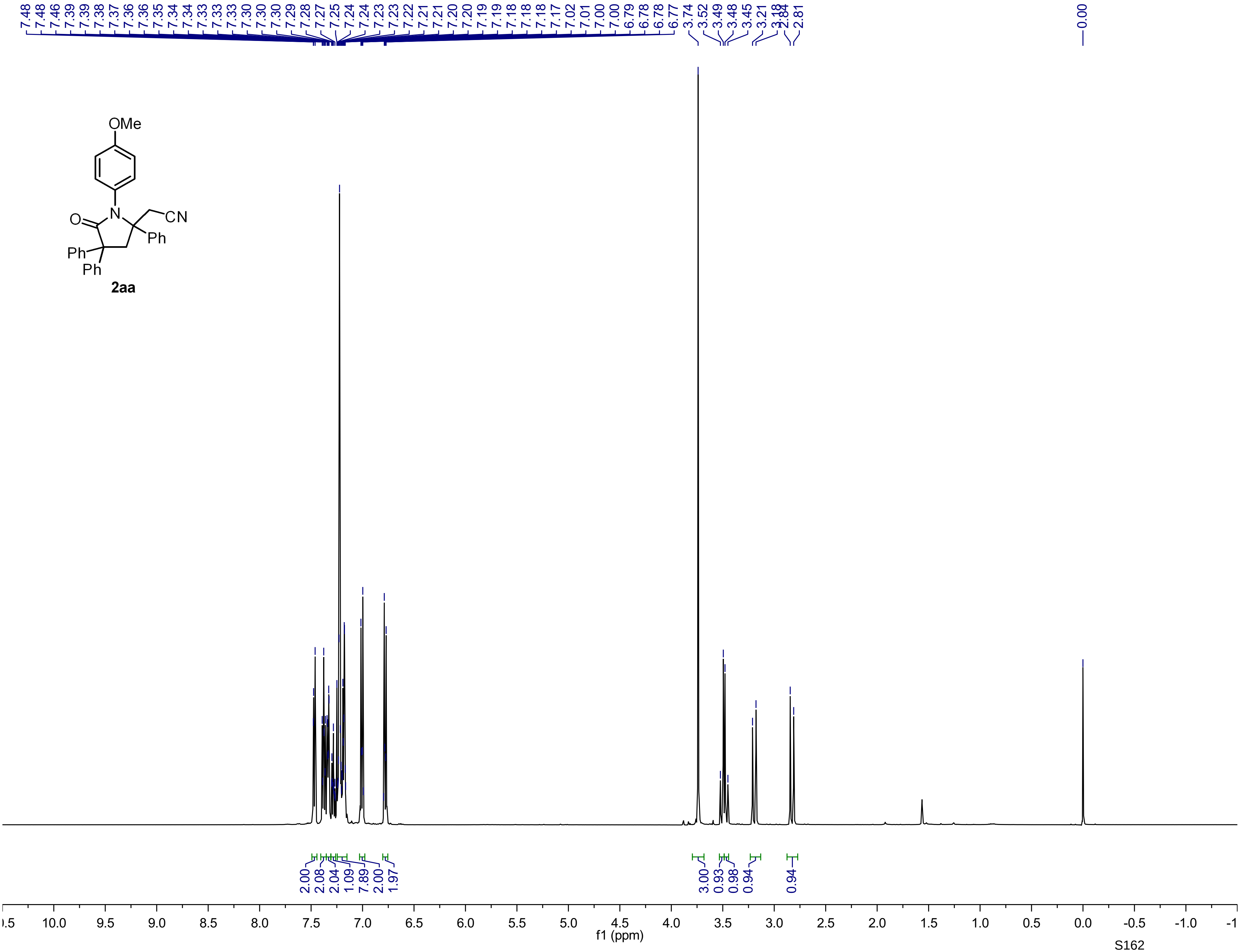
127.68
127.59
127.21
127.00
116.84
77.25
77.00
76.74
59.78
56.87
46.67
29.31
26.52
21.12
Me
O
N
CN
Me
Ph
Ph
2a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.27
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7.23
7.23
7.22
7.21
7.21
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7.19
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7.18
7.18
7.18
7.17
7.02
7.01
7.00
7.00
6.79
6.78
6.78
6.77
3.74
3.52
3.49
3.48
3.45
3.21
3.18
2.84
2.81
0.00
OMe
O
N
CN
Ph
Ph
Ph
2.00
2.08
2.04
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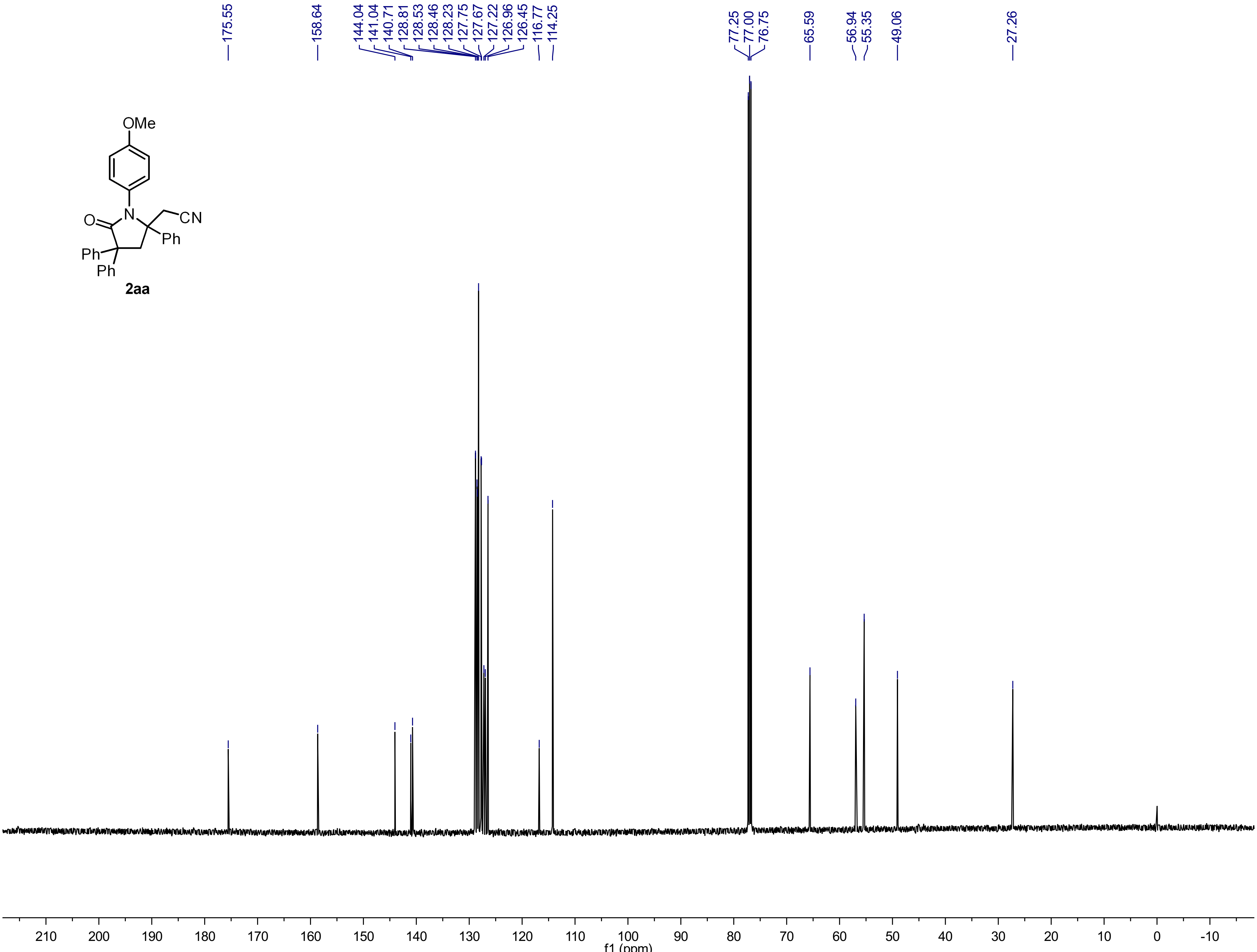
2.00
1.97
3.00
0.93
0.98
0.94
0.94
f1 (ppm)

2aa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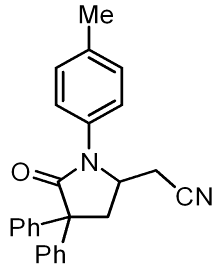
128.23
127.75
127.67
127.22
126.96
126.45
116.77
114.25
77.25
77.00
76.75
65.59
56.94
55.35
49.06
27.26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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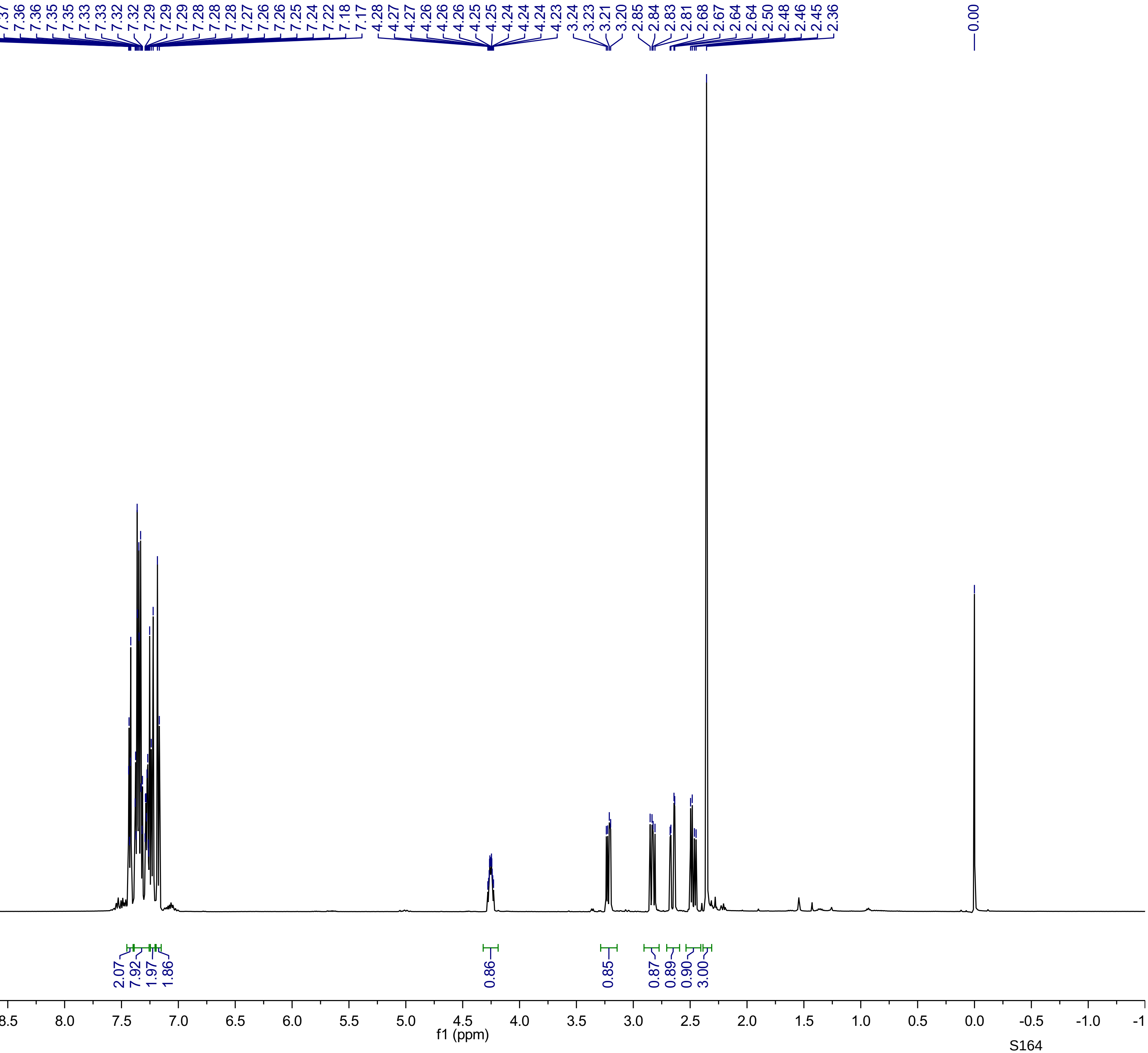
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7.29
7.28
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7.26
7.26
7.25
7.24
7.22
7.18
7.17
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4.27
4.26
4.26
4.26
4.25
4.25
4.24
4.24
4.24
4.23
3.24
3.23
3.21
3.20
2.85
2.84
2.83
2.81
2.68
2.67
2.64
2.64
2.50
2.48
2.46
2.45
2.36
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0.86
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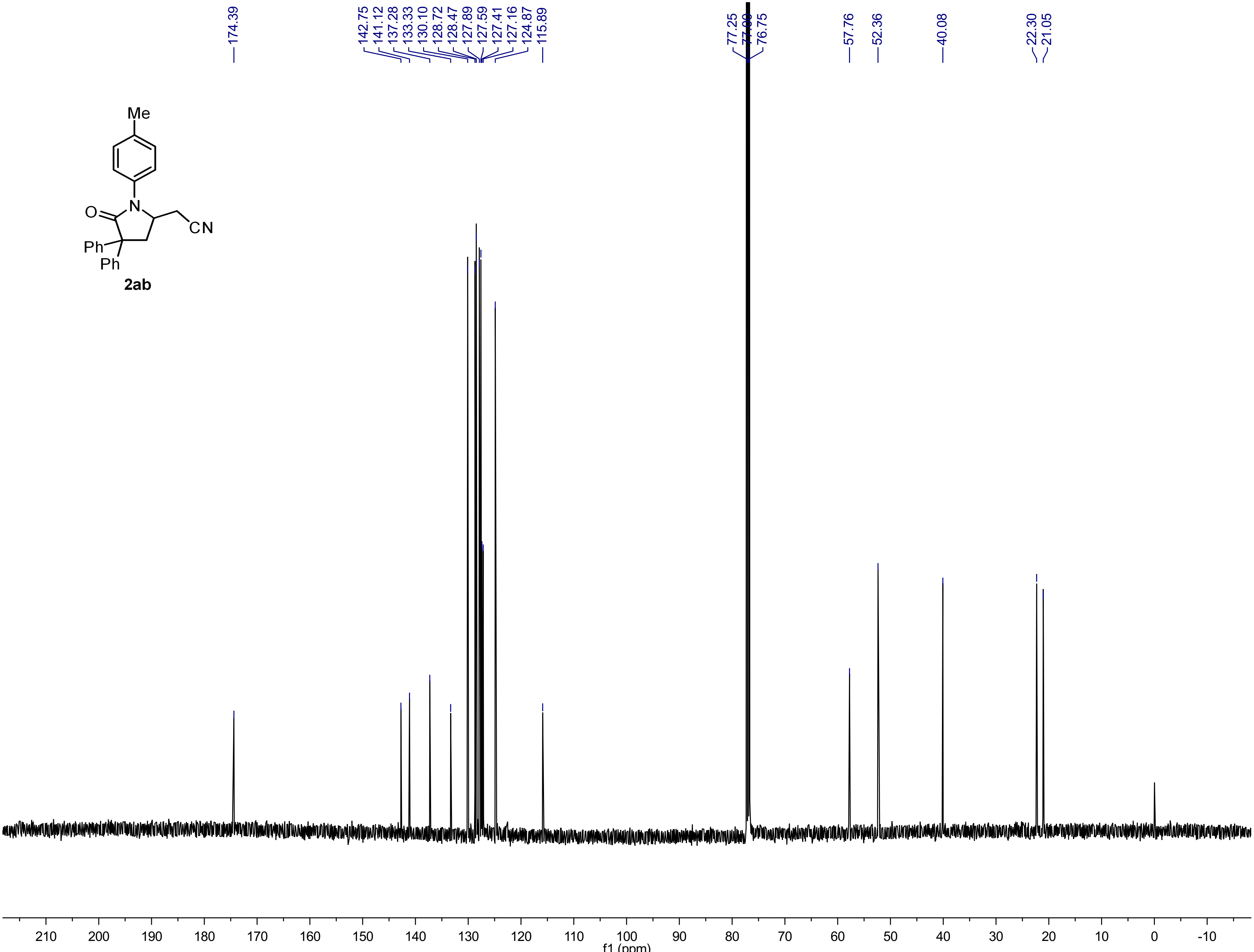
3.00
f1 (ppm)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124.87
115.89
77.25
77.00
76.75
57.76
52.36
40.08
22.30
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Me
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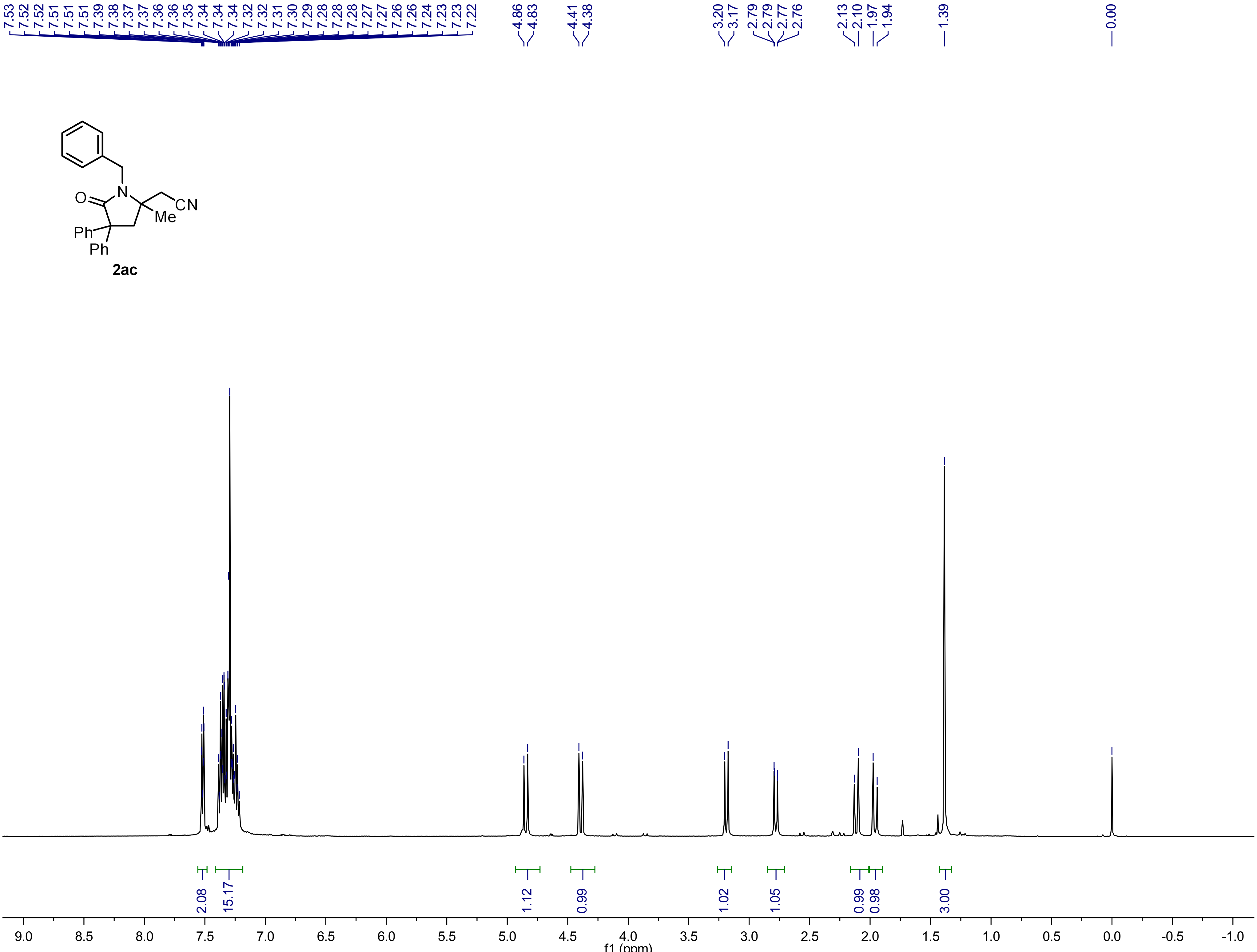
N
CN
Ph
Ph
2ab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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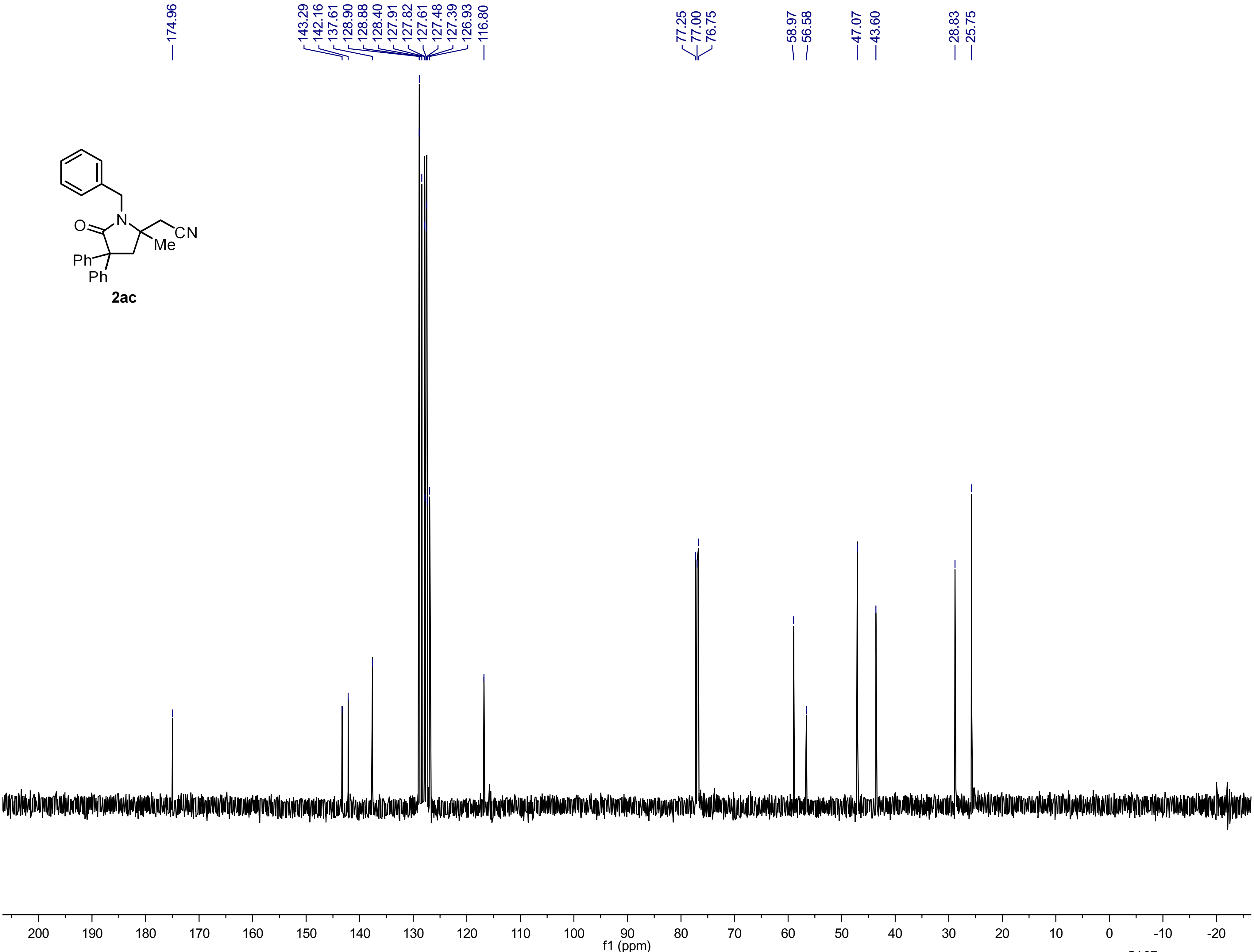
4.86 4.83
4.41 4.38
3.20 3.17
2.79 2.79 2.77 2.76
2.13 2.10 1.97 1.94
1.39
0.00
O
N
CN
Me
Ph
Ph
2ac
2.08 15.17 1.12 0.99 1.02 1.05 0.99 0.98 3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



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127.48
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77.00
76.75
58.97
56.58
47.07
43.60
28.83
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Me
Ph
Ph
2ac
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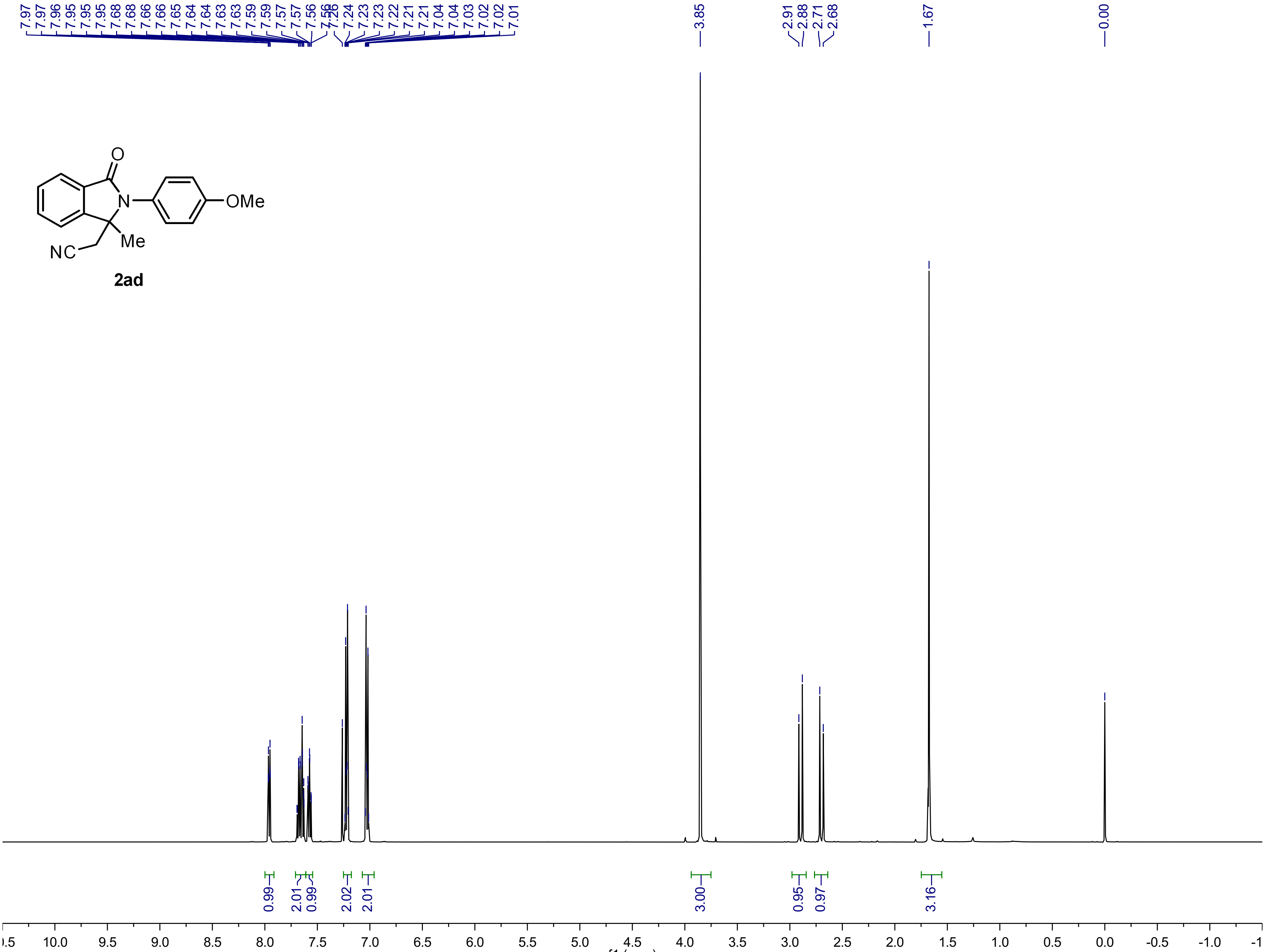
f1 (ppm)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7.23
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7.04
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7.02
7.02
7.01
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2.88
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OMe
Me
NC
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0.99
2.02
2.01
3.00
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9.0
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4.5
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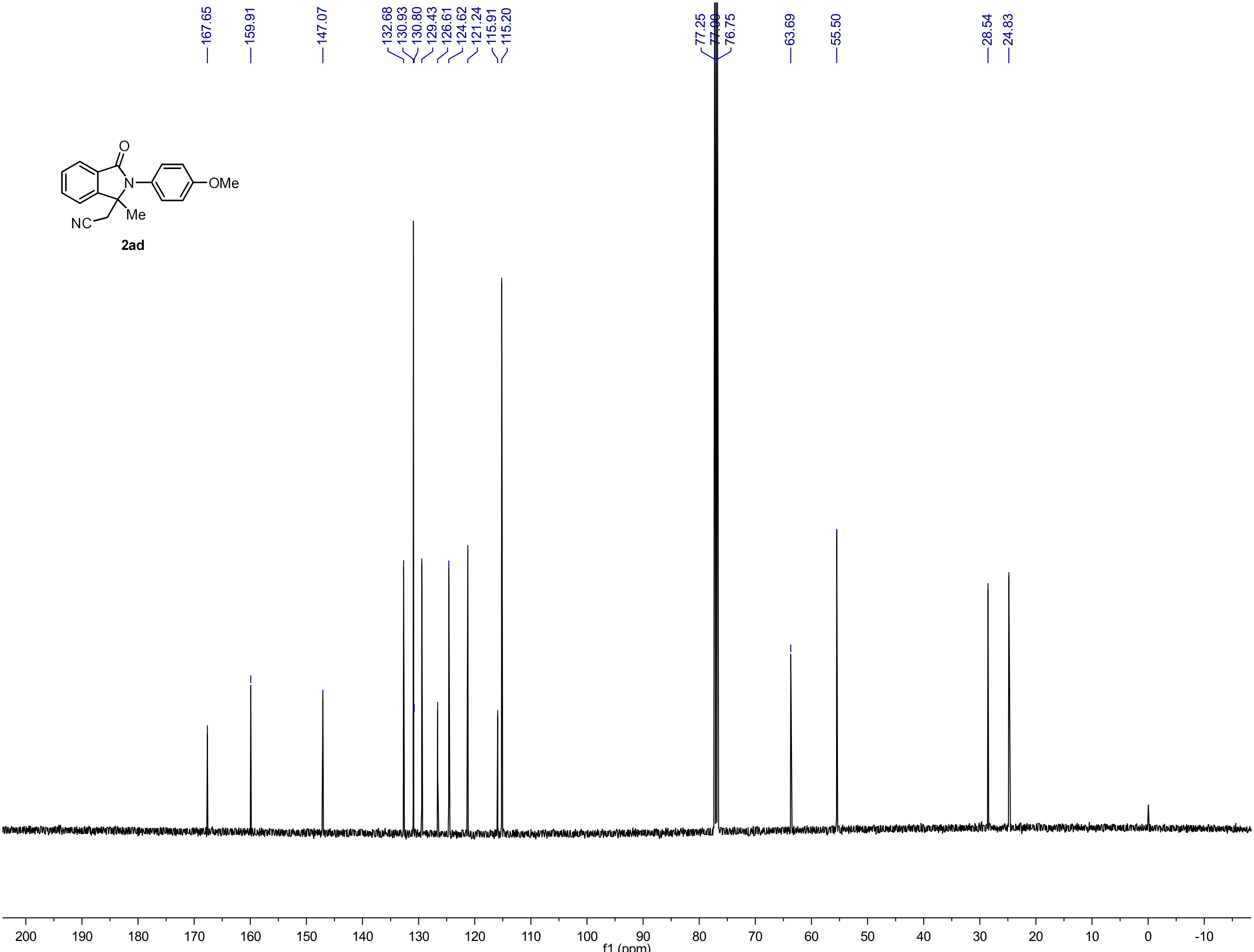
f1 (ppm)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121.24
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77.25
77.00
76.75
63.69
55.50
28.54
24.83
O
N
OMe
NC
Me
2ad
200
190
180
170
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100
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80
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40
30
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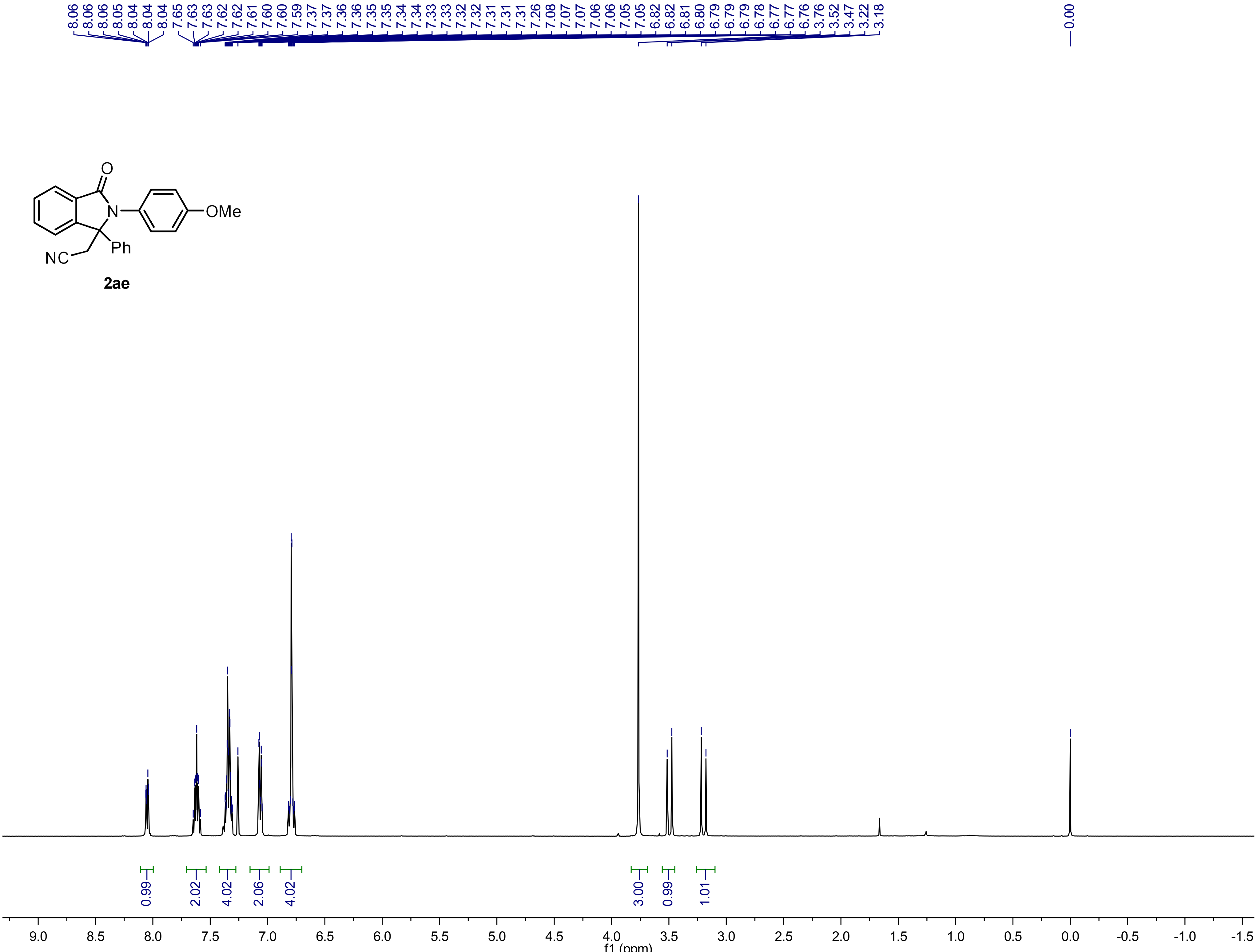
-10
f1 (ppm)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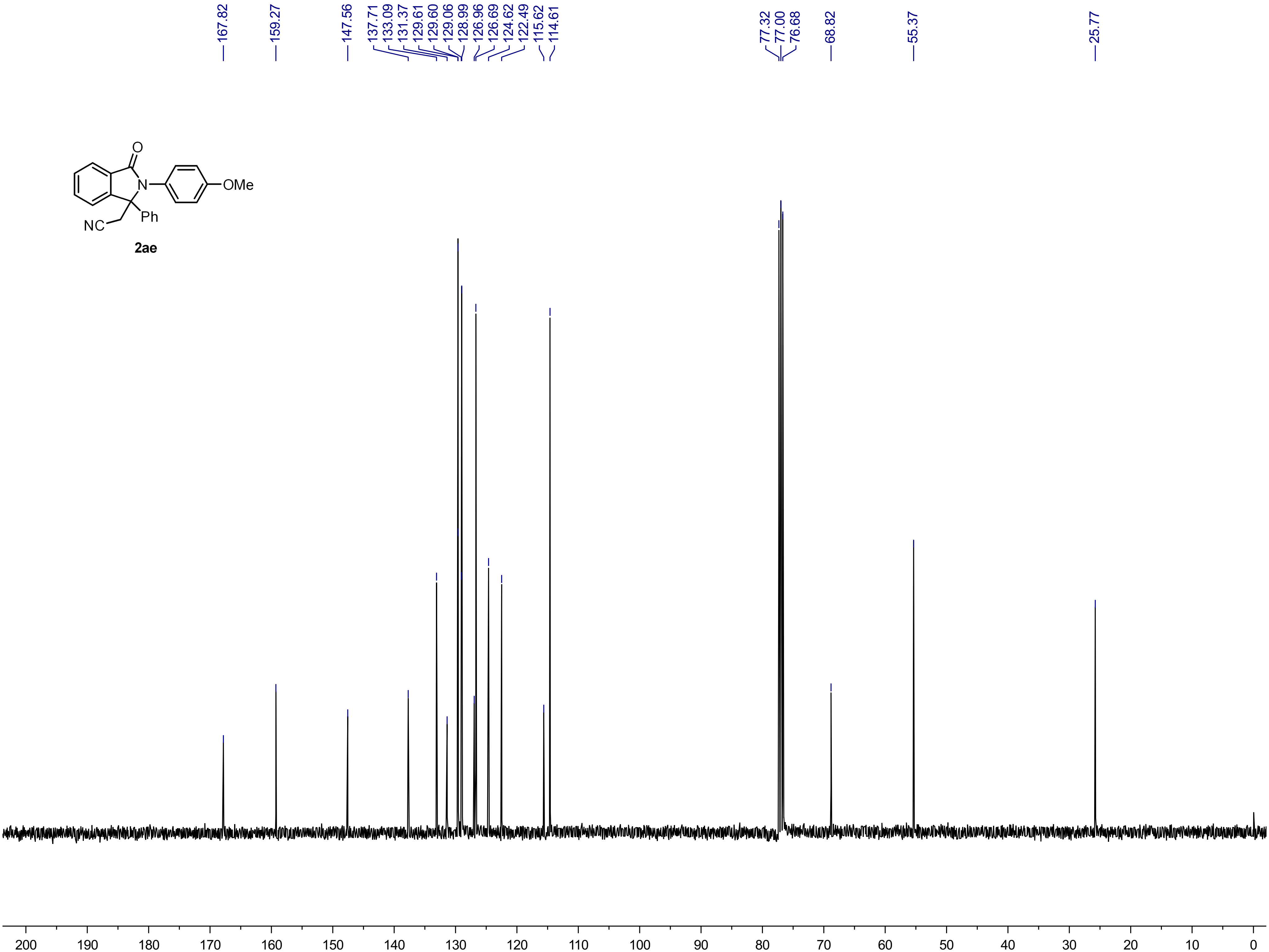
0.00
O
N
OMe
Ph
NC
2ae
0.99
2.02
4.02
2.06
4.02
3.00
0.99
1.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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76.68
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N
OMe
Ph
NC
2ae
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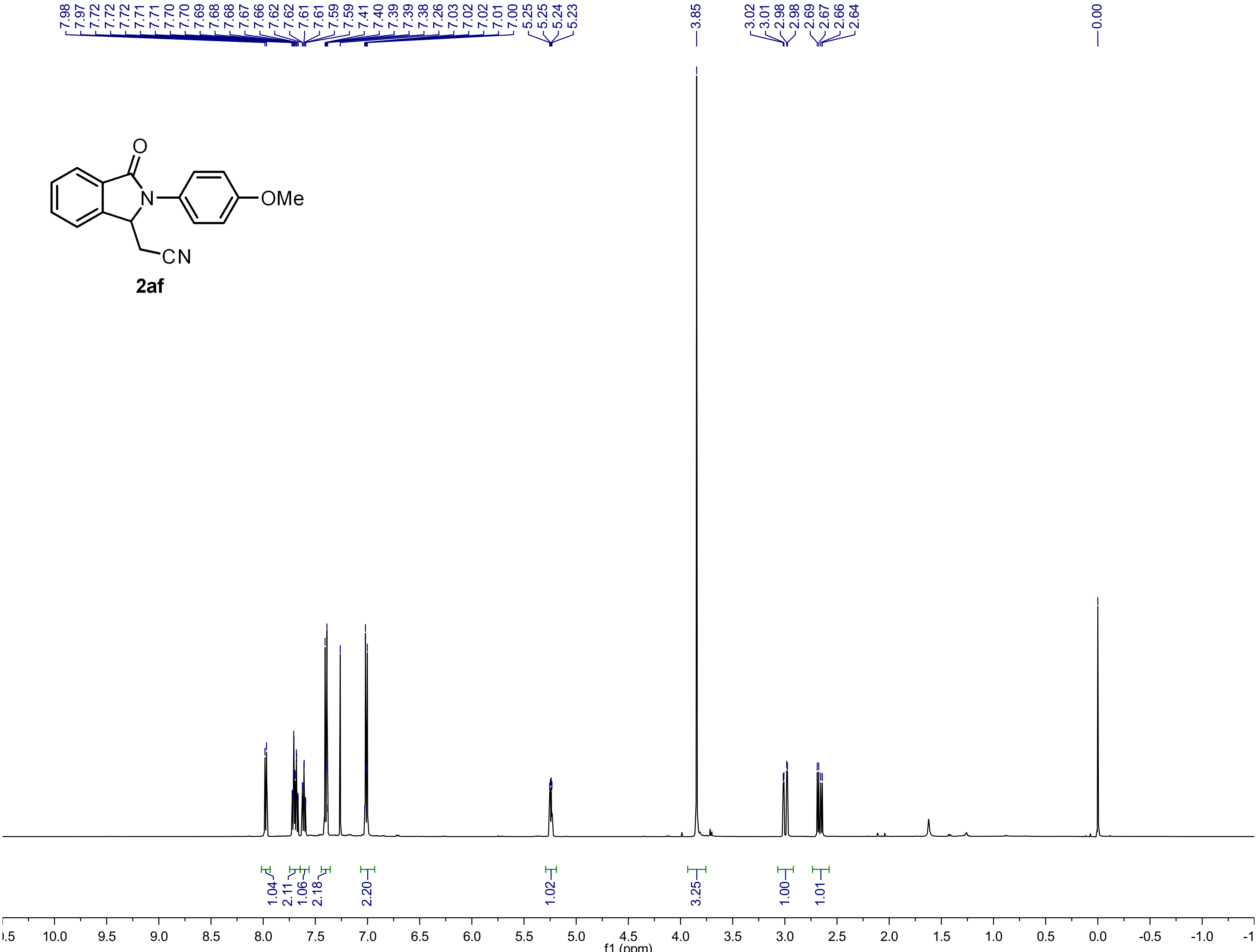
f1 (ppm)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N
OMe
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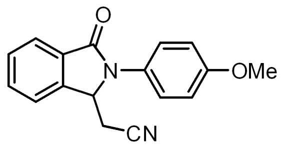
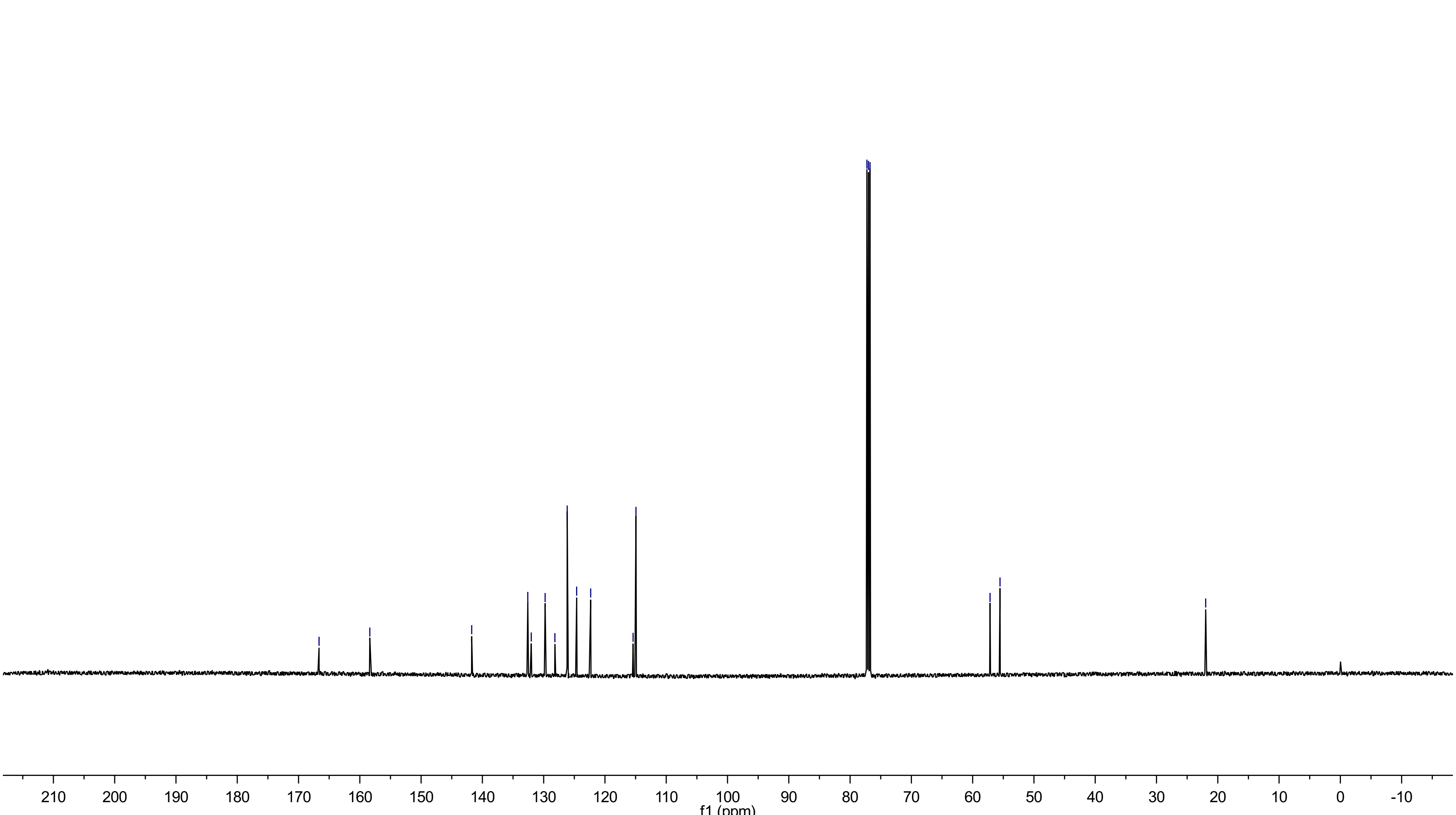
-1.0
f1 (ppm)



2af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132.03
129.76
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122.33
115.41
114.94
77.25
77.00
76.75
57.16
55.54
21.97
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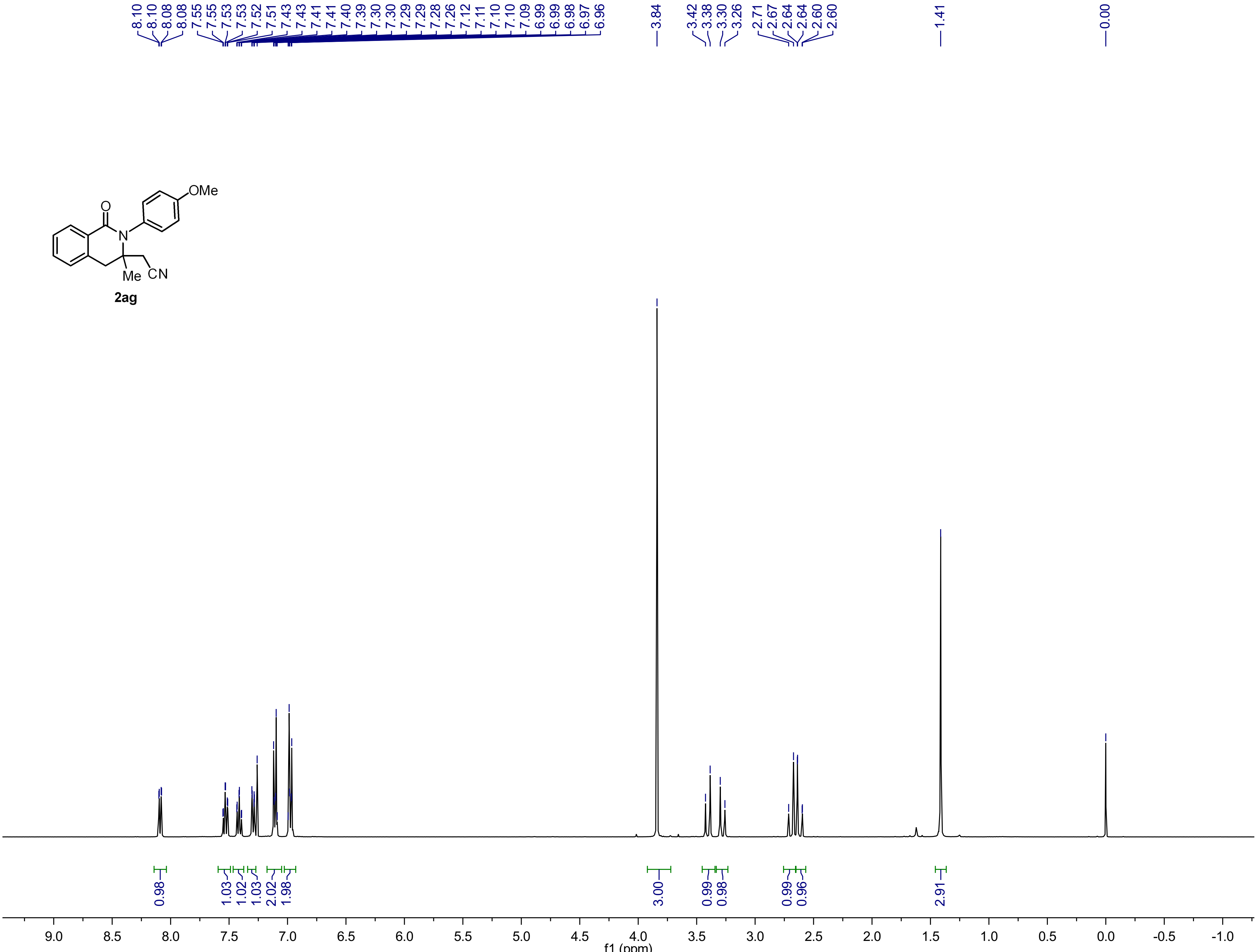
f1 (ppm)



8.10
8.10
8.08
8.08
7.55
7.55
7.53
7.53
7.52
7.51
7.43
7.43
7.41
7.41
7.40
7.39
7.30
7.29
7.29
7.28
7.26
7.12
7.11
7.10
7.09
6.99
6.99
6.98
6.97
6.96
3.84
3.42
3.38
3.30
3.26
2.71
2.67
2.64
2.64
2.60
2.60
1.41
0.00
OMe
O
N
Me
CN
2ag
0.98
1.03
1.02
1.03
2.02
1.98
3.00
0.99
0.98
0.99
0.96
2.91
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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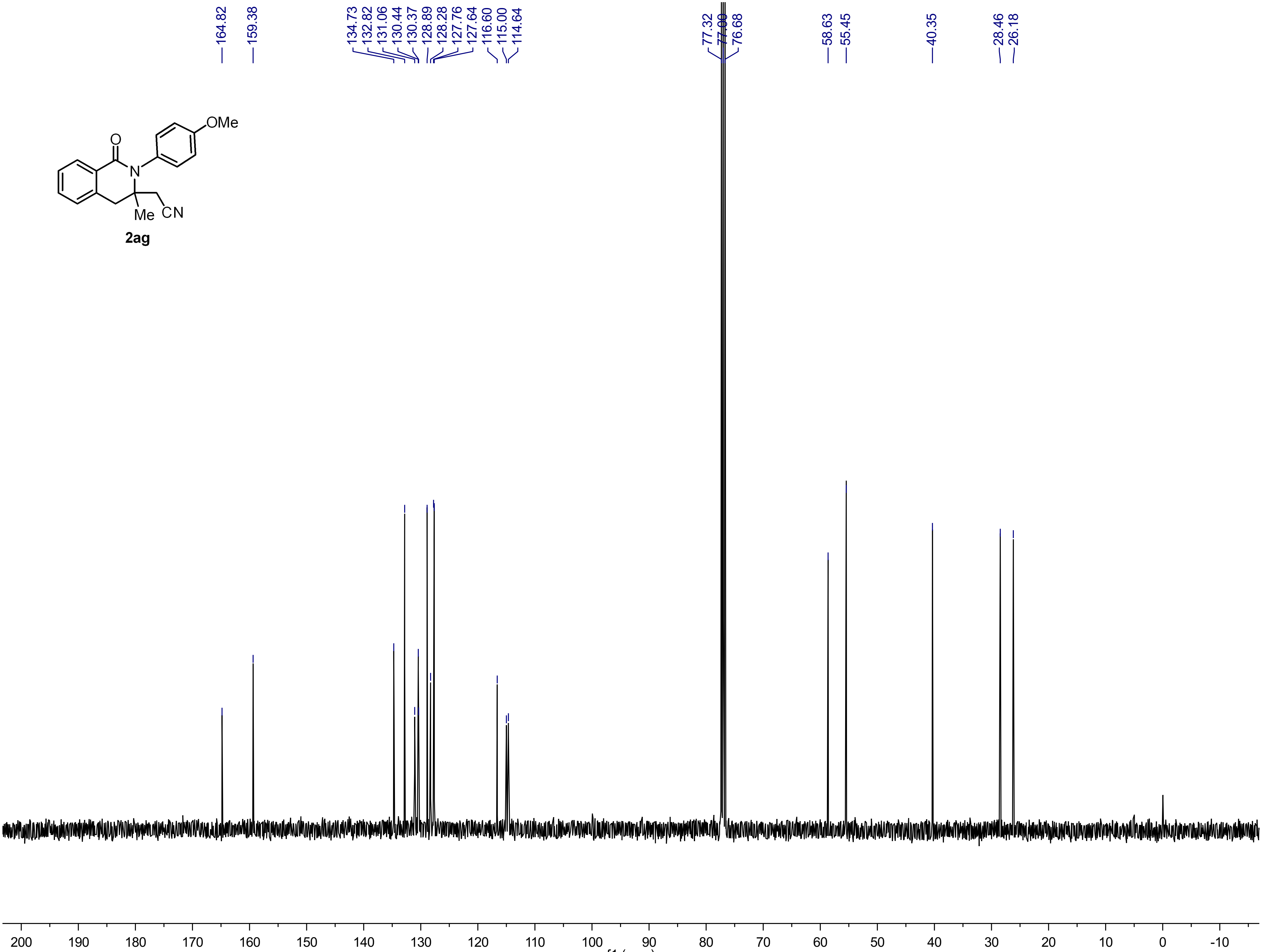
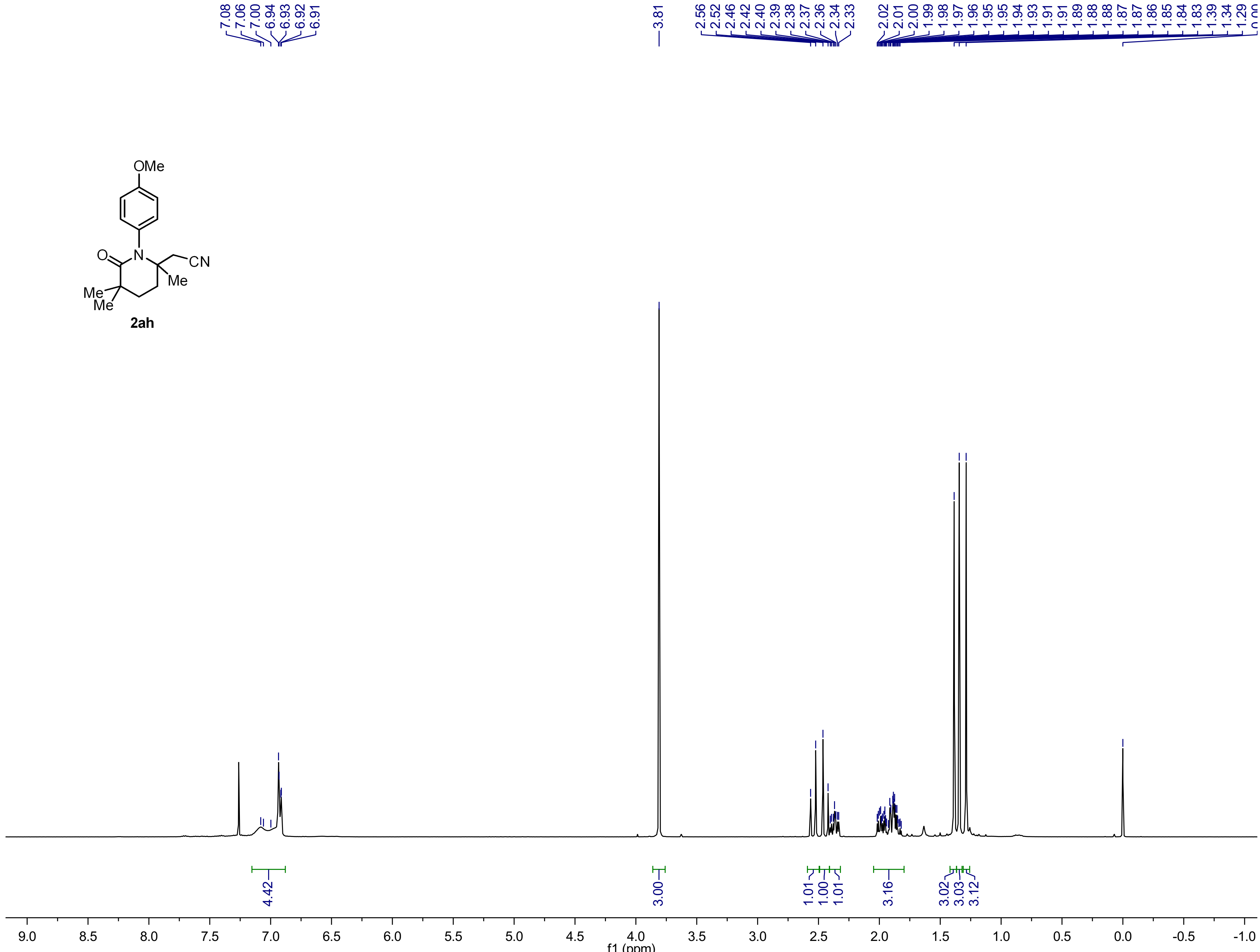
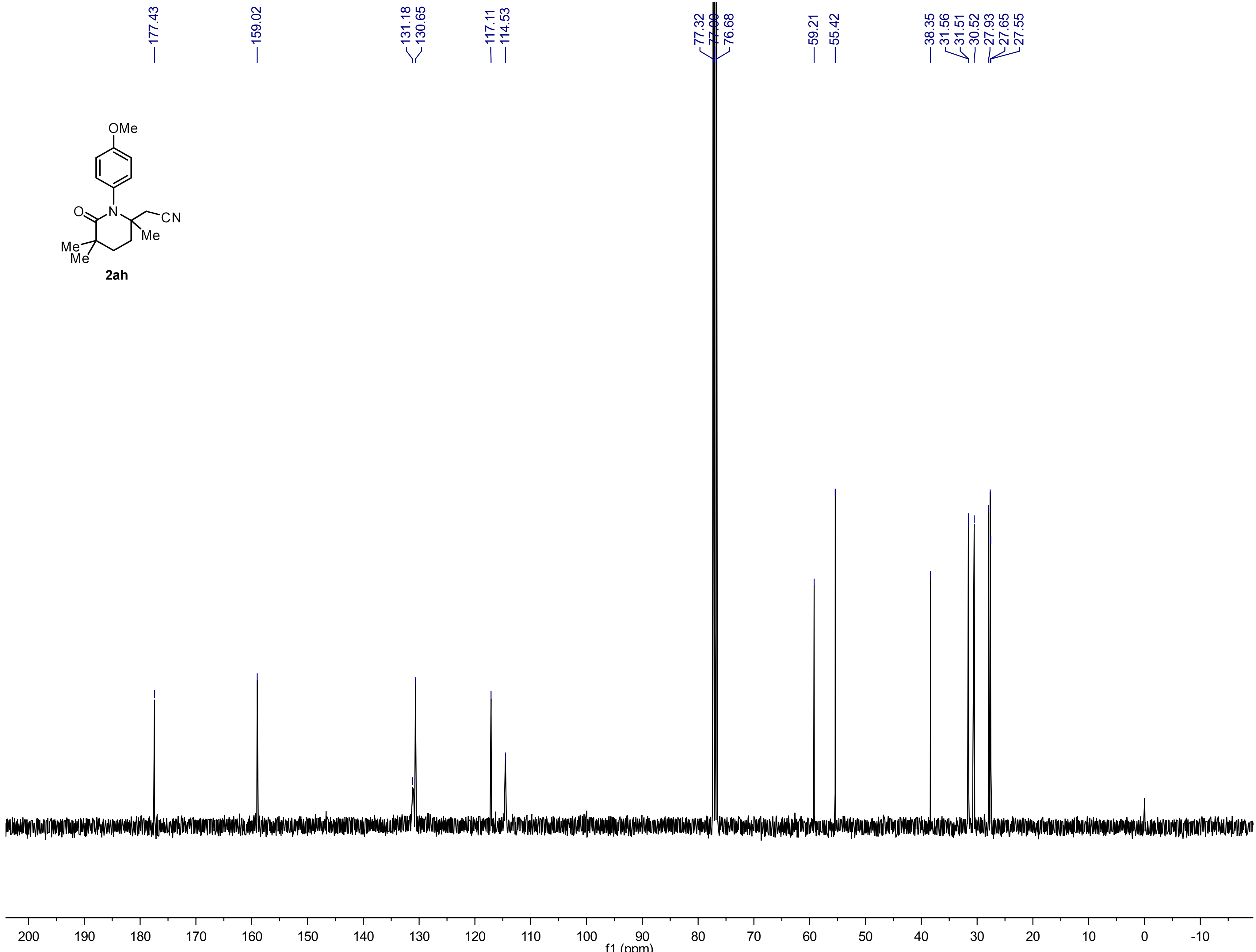
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



164.82
159.38
134.73
132.82
131.06
130.44
130.37
128.89
128.28
127.76
127.64
116.60
115.00
114.64
77.32
77.00
76.68
58.63
55.45
40.35
28.46
26.18
OMe
O
N
Me
CN
2ag
f1 (ppm)


OMe
O
N
CN
Me
Me
Me
2ah
f1 (ppm)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159.02
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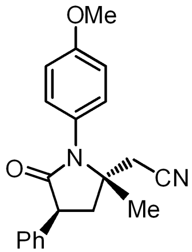
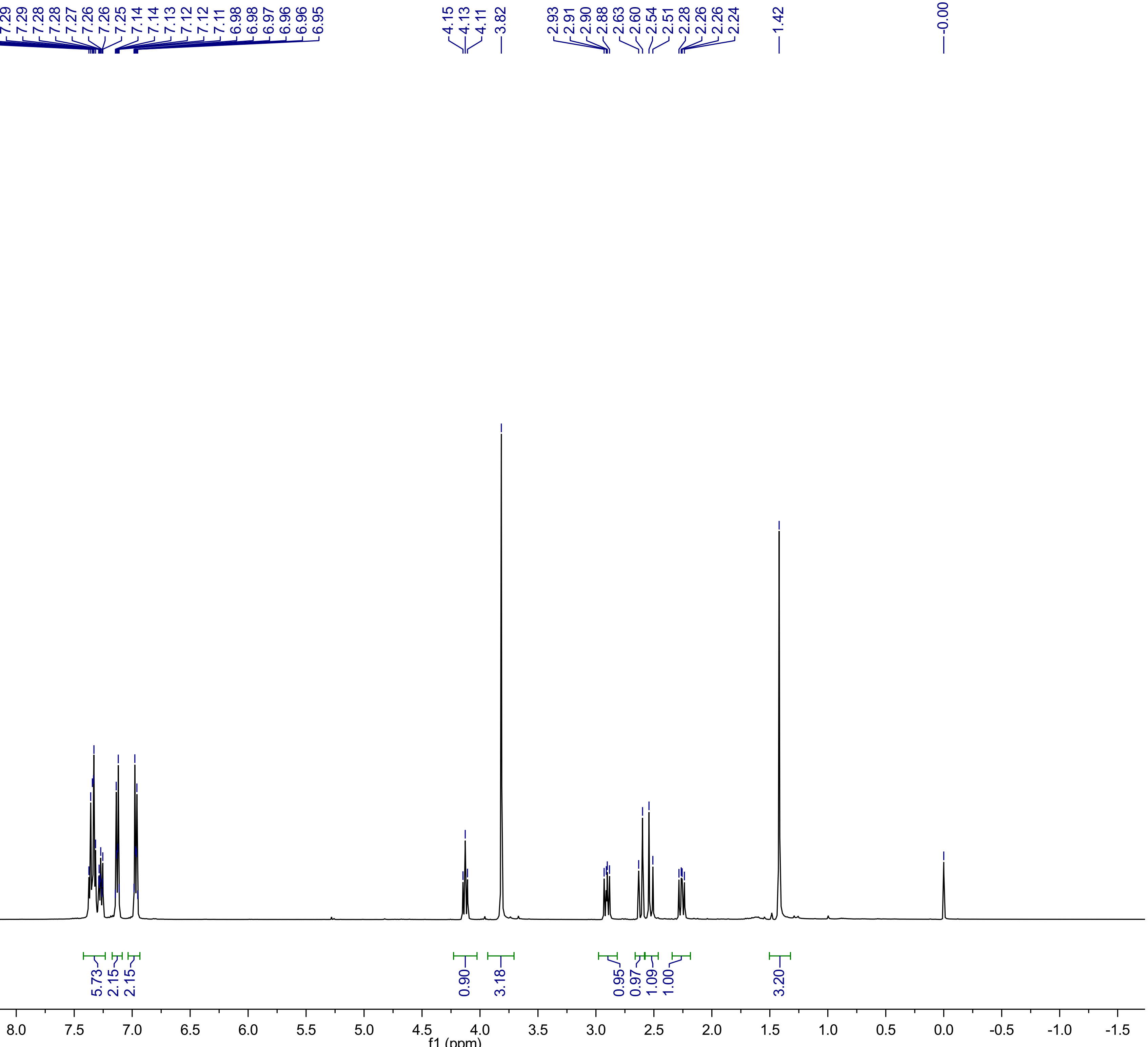
130.65
117.11
114.53
77.32
77.00
76.68
59.21
55.42
38.35
31.56
31.51
30.52
27.93
27.65
27.55
OMe
O
N
CN
Me
Me
Me
2ah
f1 (ppm)


OMe
O
N
CN
Me
Ph

(±)-2al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7.36
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7.33
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7.32
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.14
7.14
7.13
7.12
7.12
7.11
6.98
6.98
6.97
6.96
6.96
6.95
4.15
4.13
4.11
3.82
2.93
2.91
2.90
2.88
2.63
2.60
2.54
2.51
2.28
2.26
2.26
2.24
1.42
-0.00
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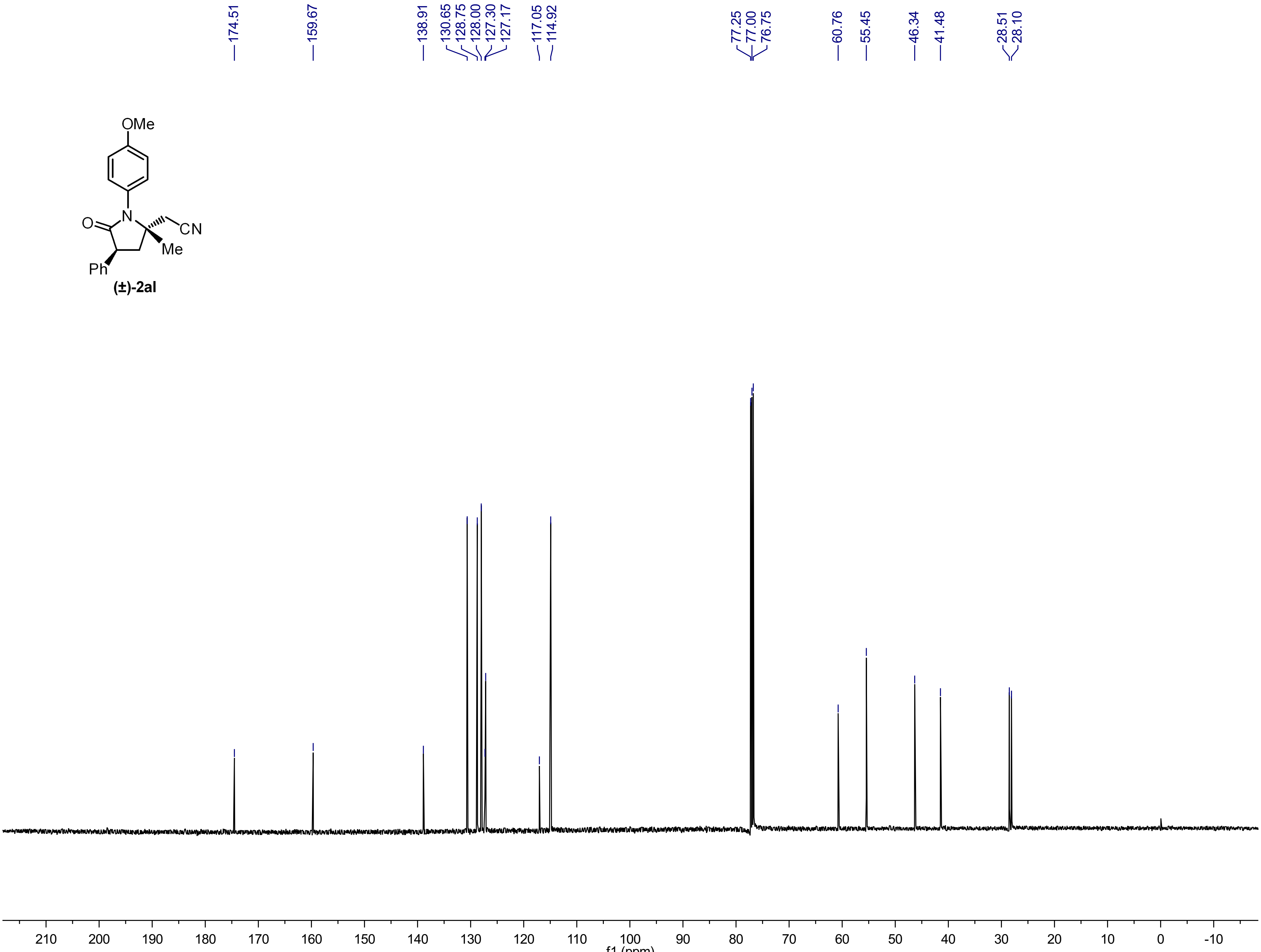
2.15
0.90
3.18
0.95
0.97
1.09
1.00
3.20
f1 (ppm)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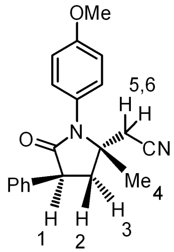
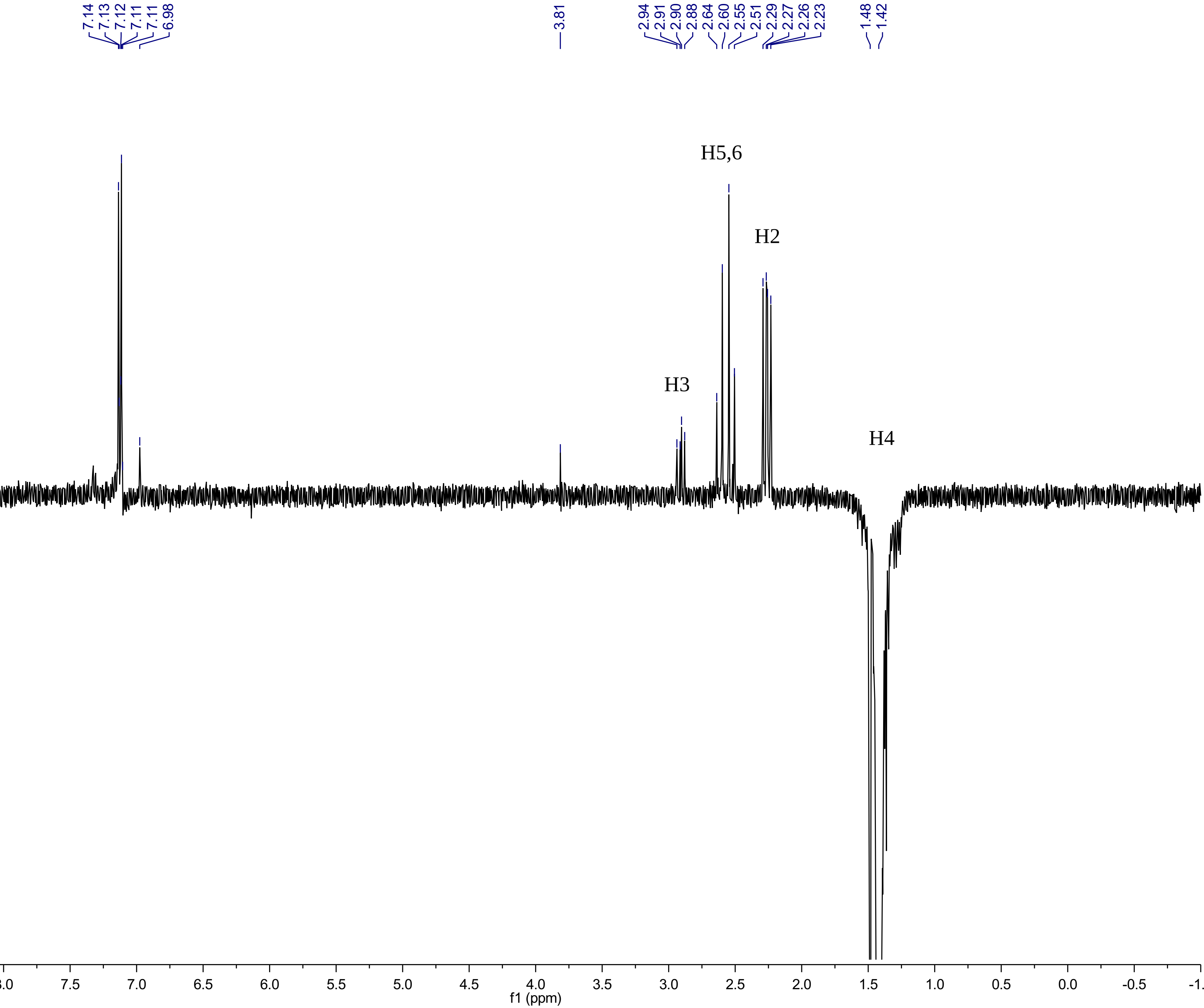
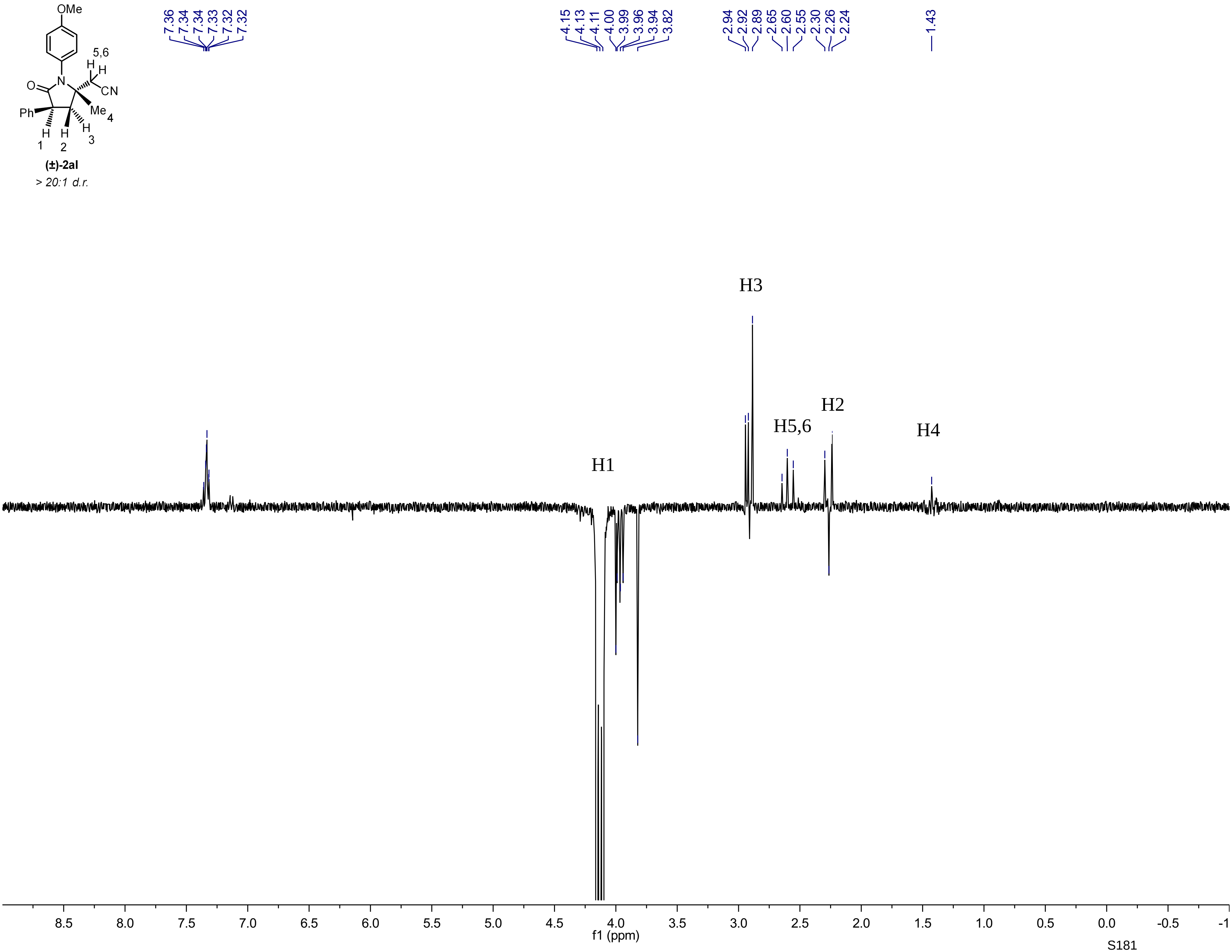
128.00
127.30
127.17
117.05
114.92
77.25
77.00
76.75
60.76
55.45
46.34
41.48
28.51
28.10
OMe
O
N
CN
Me
Ph
(±)-2al
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OMe
5,6
H
H
CN
O
N
Ph
Me
4
H
H
H
1
2
3

(±)-2al

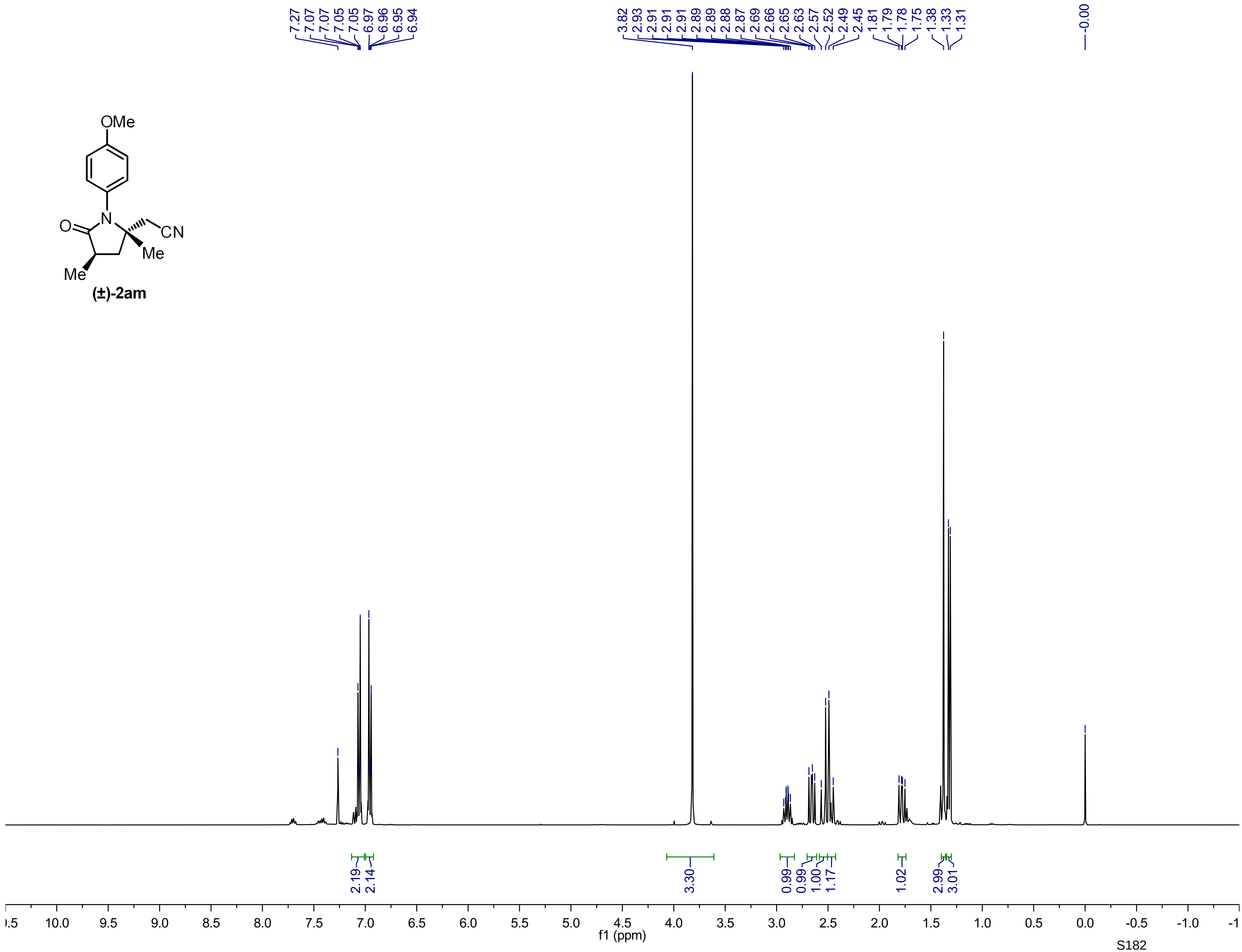
> 20:1 d.r.

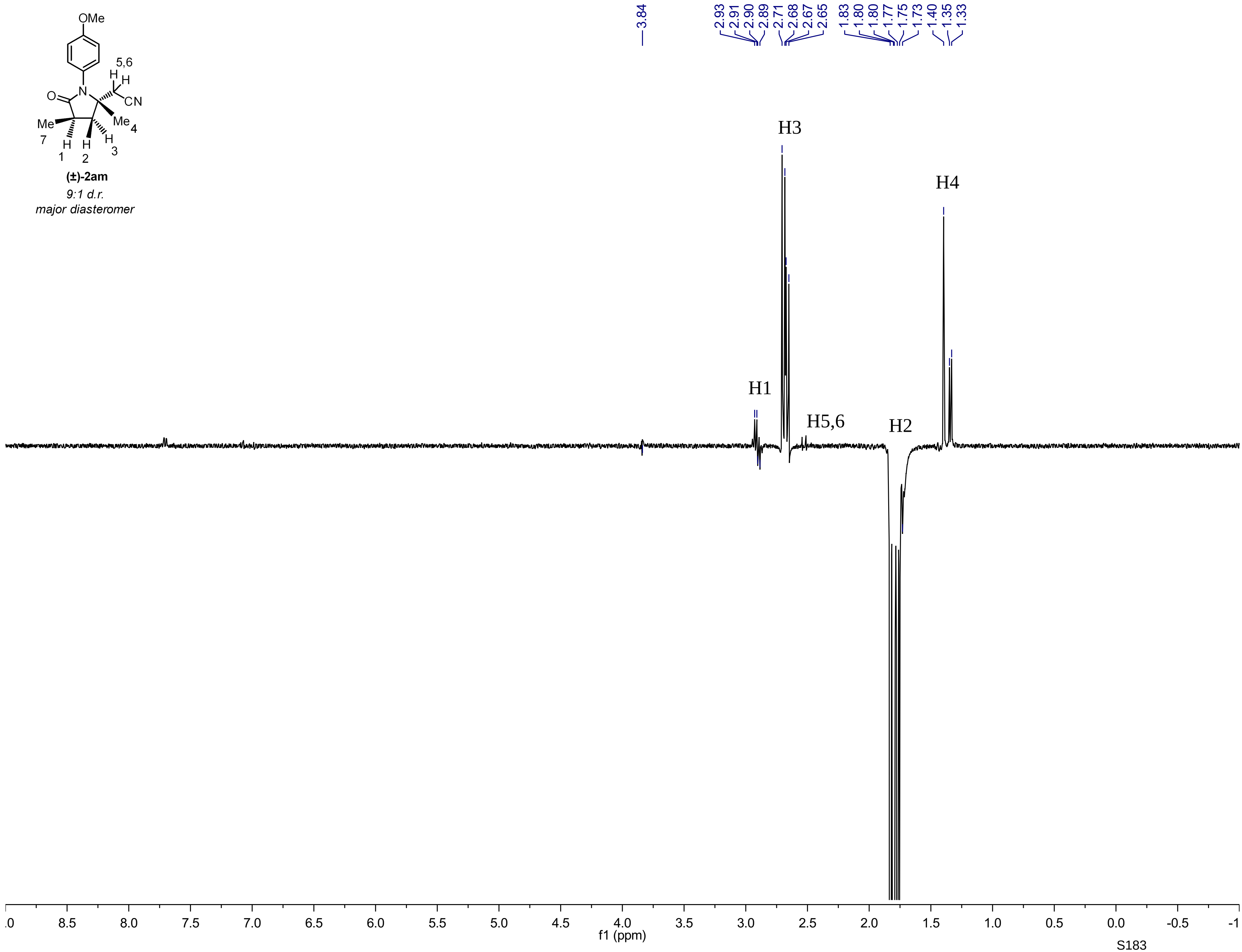

7.14
7.13
7.12
7.11
7.11
6.98
3.81
2.94
2.91
2.90
2.88
2.64
2.60
2.55
2.51
2.29
2.27
2.26
2.23
1.48
1.42
H5,6
H2
H3
H4
f1 (ppm)


OMe
5,6
H
H
O
N
CN
Ph
Me
4
H
H
H
1
2
3
7.36
7.34
7.34
7.33
7.32
7.32
4.15
4.13
4.11
4.00
3.99
3.96
3.94
3.82
2.94
2.92
2.89
2.65
2.60
2.55
2.30
2.26
2.24
1.43
H3
H2
H5,6
H4
H1
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
-0.5
-1
f1 (ppm)

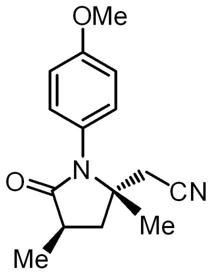
(±)-2al

> 20:1 d.r.

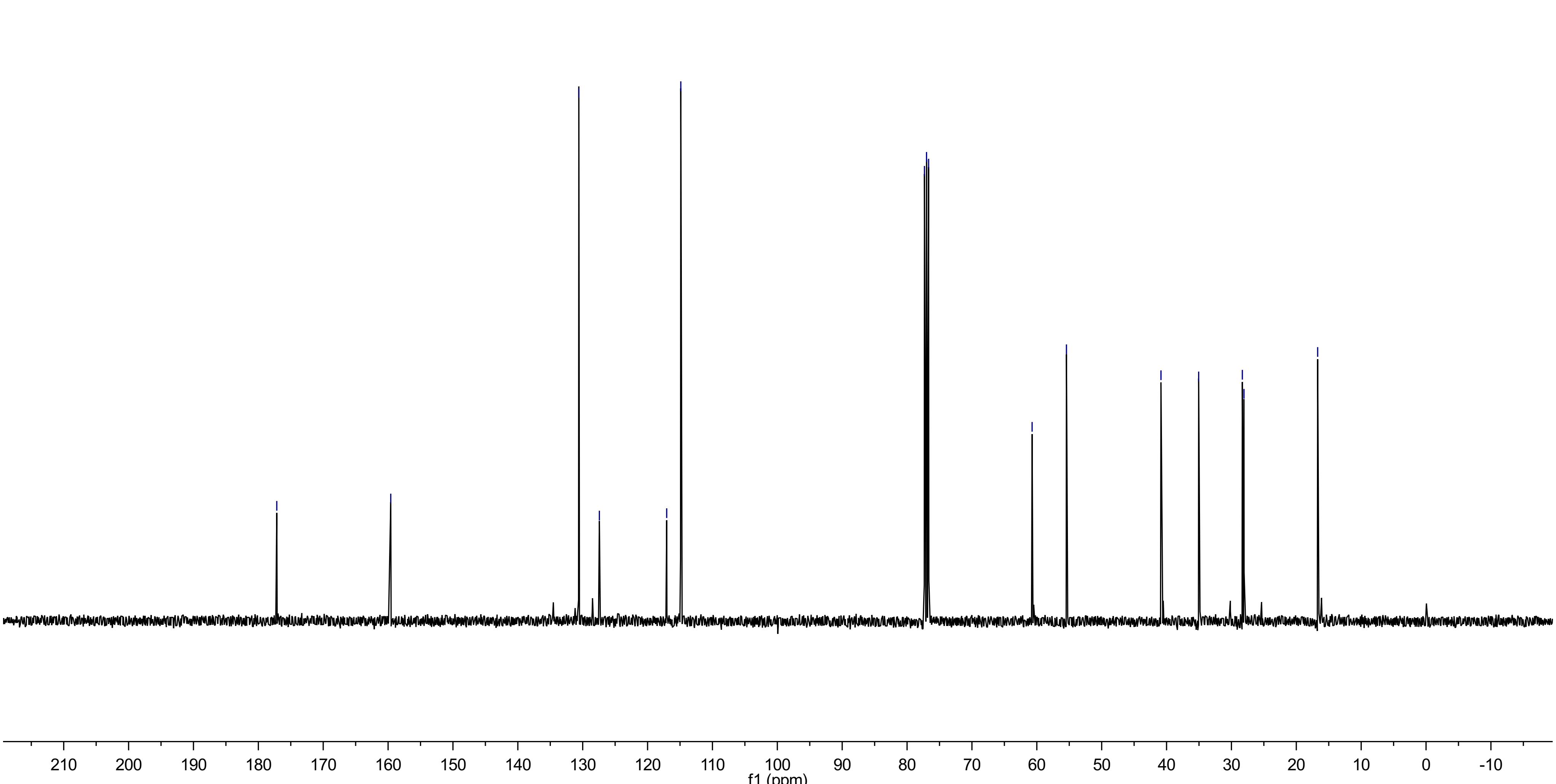

7.27
7.07
7.07
7.05
7.05
6.97
6.96
6.95
6.94
3.82
2.93
2.91
2.91
2.91
2.89
2.89
2.88
2.87
2.69
2.66
2.65
2.63
2.57
2.52
2.49
2.45
1.81
1.79
1.78
1.75
1.38
1.33
1.31
-0.00
OMe
N
O
CN
Me
Me
(±)-2am
2.19
2.14
3.30
0.99
0.99
1.00
1.17
1.02
2.99
3.01
f1 (ppm)



OMe
5,6
H
H
CN
O
N
Me
4
Me
7
H
1
H
2
H
3
(±)-2am
9:1 d.r.
major diasteromer
3.84
2.93
2.91
2.90
2.89
2.71
2.68
2.67
2.65
1.83
1.80
1.80
1.77
1.75
1.73
1.40
1.35
1.33
H3
H4
H1
H5,6
H2
f1 (ppm)


OMe
O
N
CN
Me
Me

(±)-2am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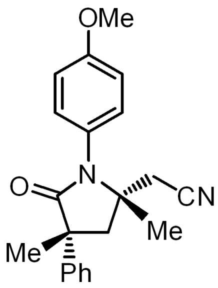
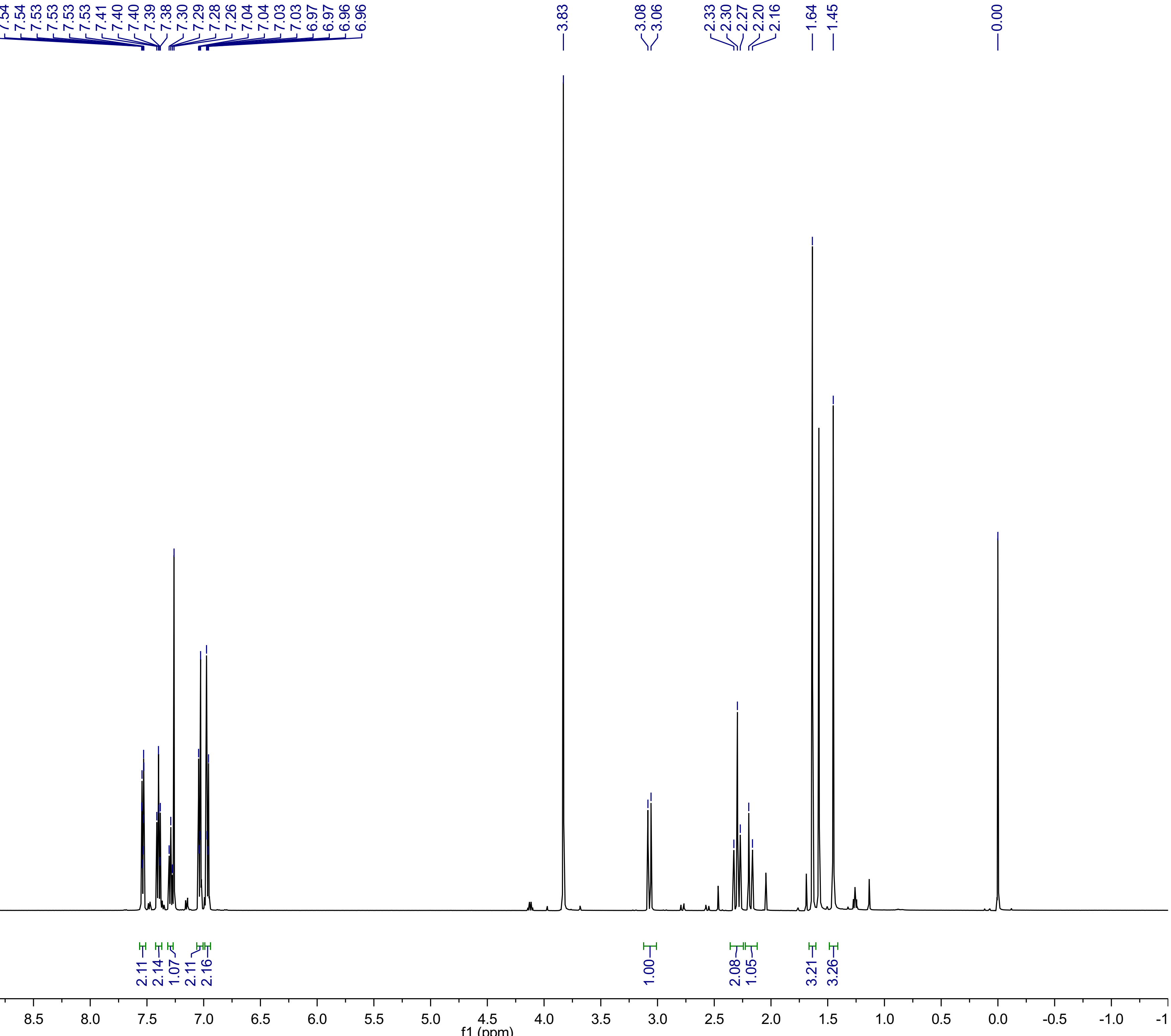
77.00
76.68
60.72
55.43
40.86
35.05
28.32
28.07
16.71
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



OMe
O
N
CN
Me
Me
Ph

(±)-2an



7.55
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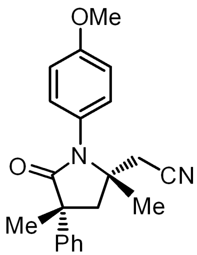
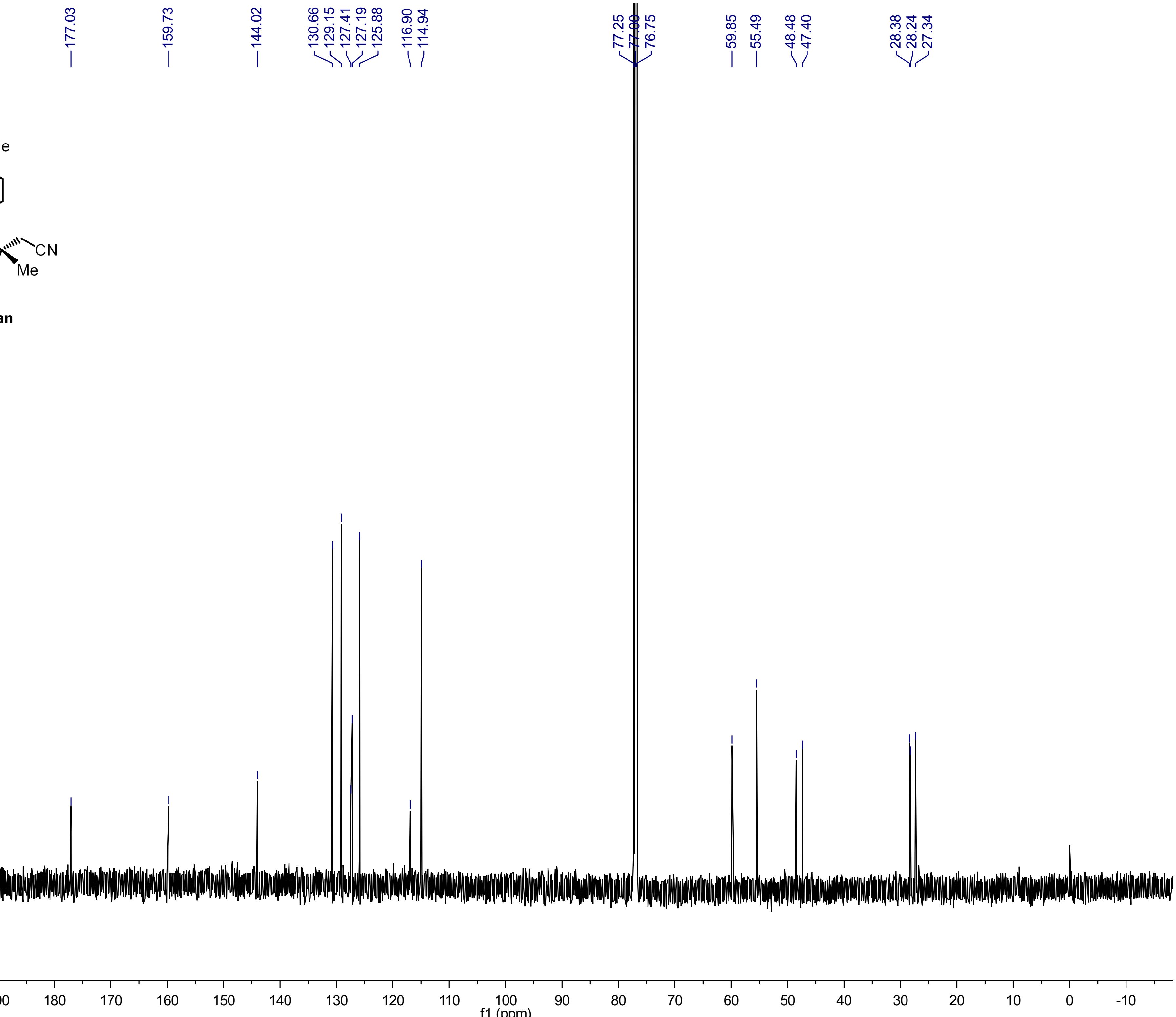
7.54
7.53
7.53
7.53
7.53
7.41
7.40
7.40
7.39
7.38
7.30
7.29
7.28
7.26
7.04
7.04
7.03
7.03
6.97
6.97
6.96
6.96
3.83
3.08
3.06
2.33
2.30
2.27
2.20
2.16
1.64
1.45
0.00
2.11
2.14
1.07
2.11
2.16
1.00
2.08
1.05
3.21
3.26
f1 (ppm)


OMe
O
N
CN
Me
Me
Ph
(±)-2an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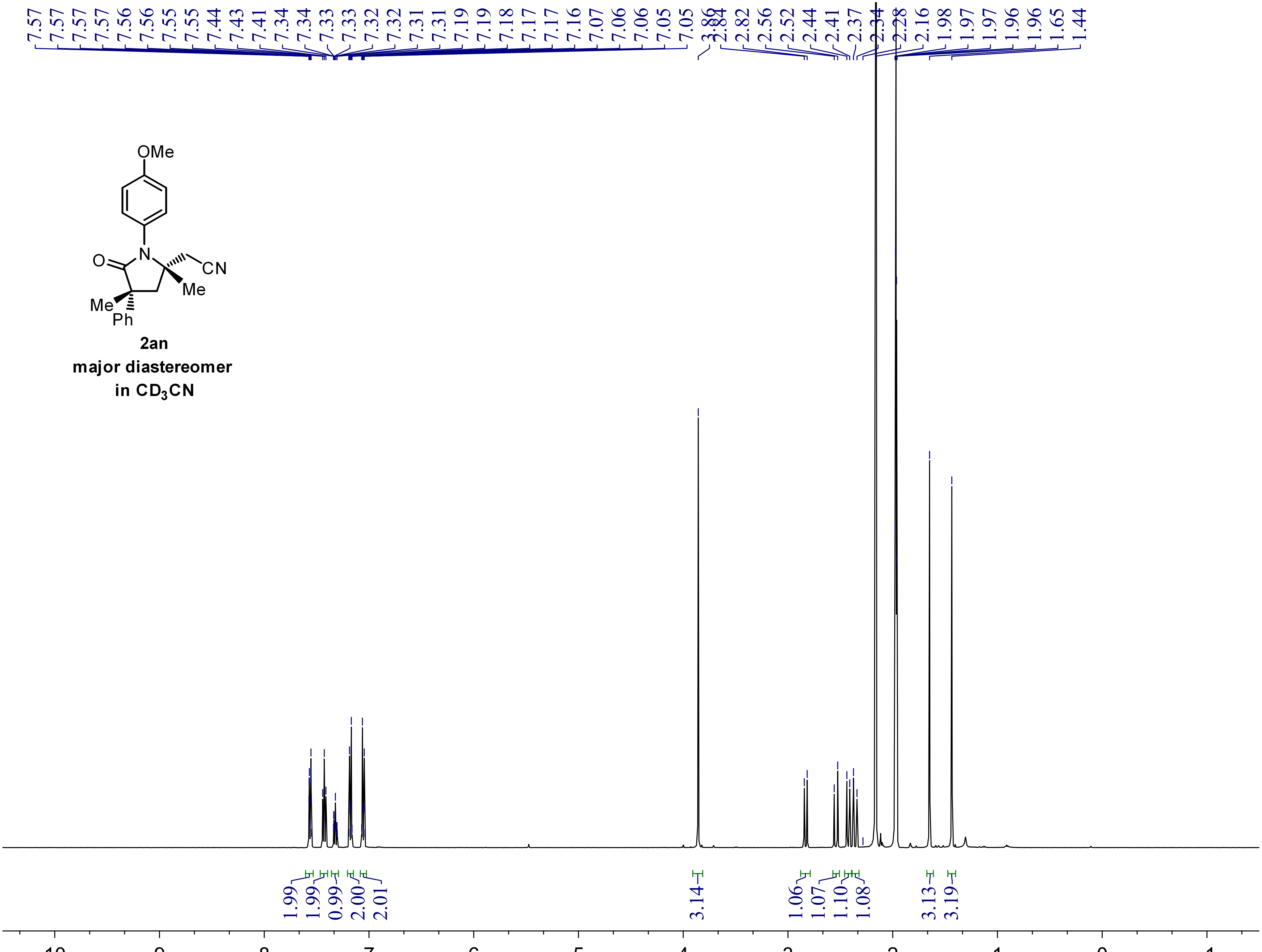
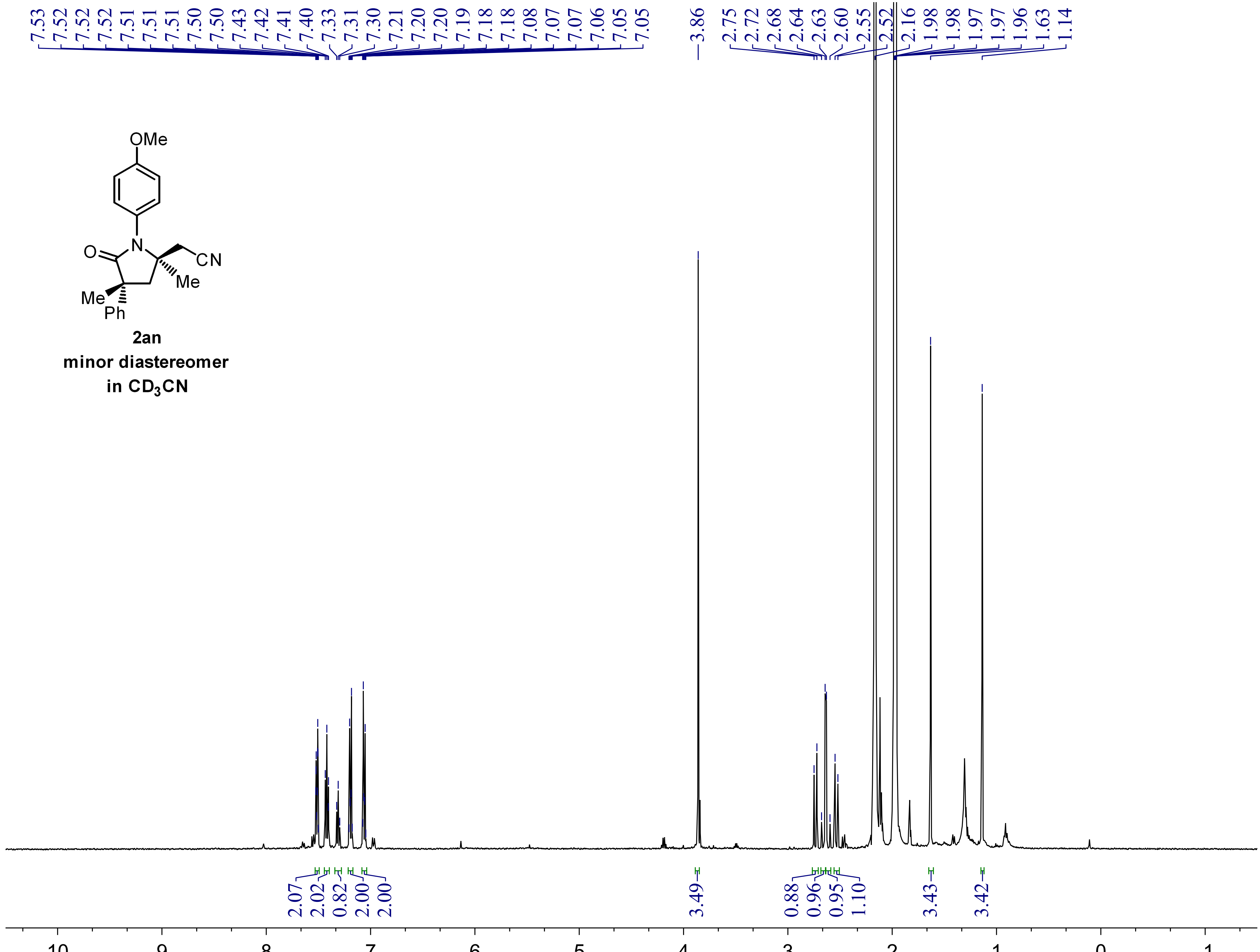
125.88
116.90
114.94
77.25
77.00
76.75
59.85
55.49
48.48
47.40
28.38
28.24
27.34
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



7.57
7.57
7.57
7.57
7.56
7.56
7.55
7.55
7.44
7.43
7.41
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.19
7.19
7.18
7.17
7.17
7.16
7.07
7.06
7.06
7.05
7.05
3.86
2.84
2.82
2.56
2.52
2.44
2.41
2.37
2.34
2.28
2.16
1.98
1.97
1.97
1.96
1.96
1.65
1.44
OMe
O
N
CN
Me
Me
Ph
2an
major diastereomer
in CD3CN
1.99
1.99
0.99
2.00
2.01
3.14
1.06
1.07
1.10
1.08
3.13
3.19
10
9
8
7
6
5
4
3
2
1
0
-1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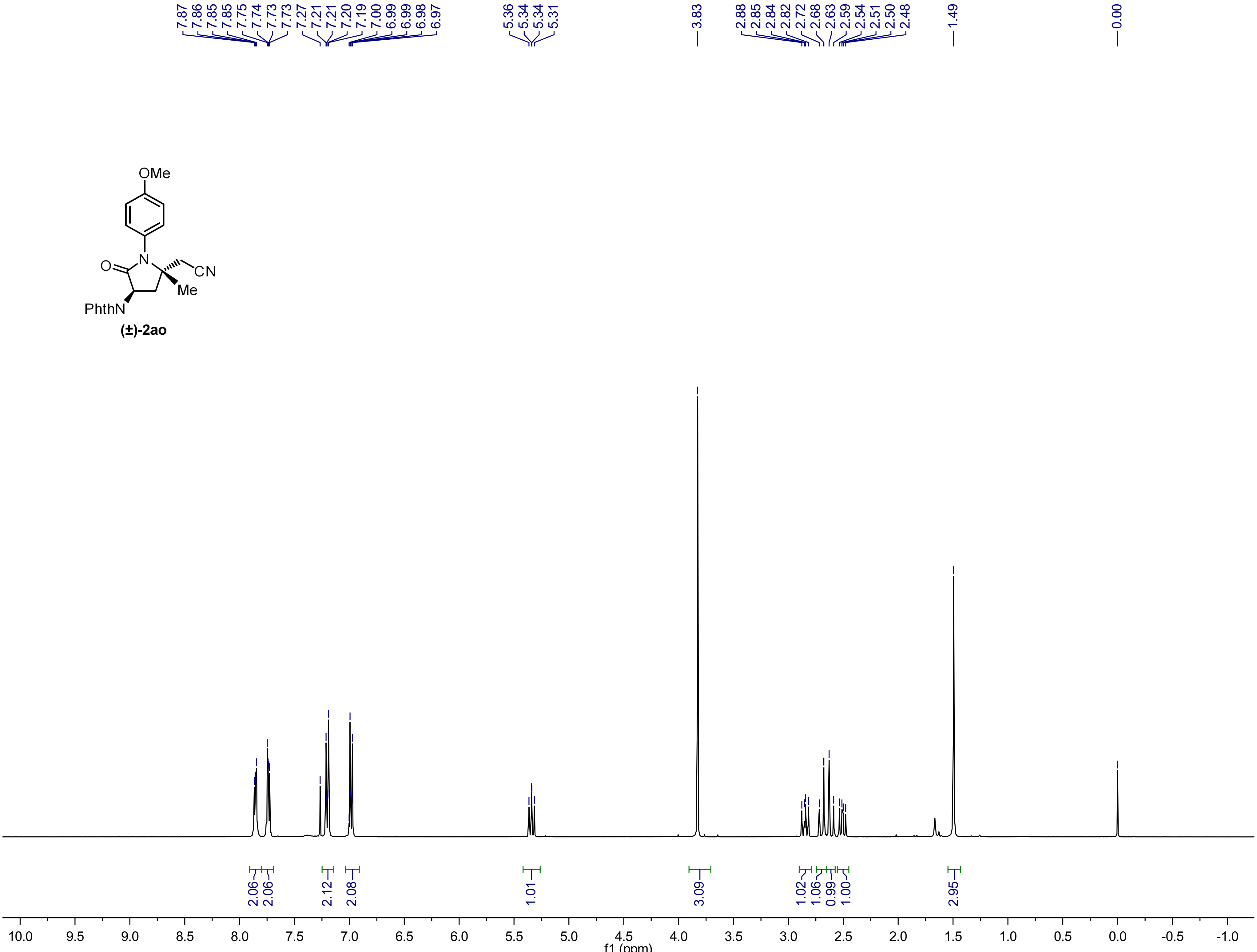
3.86
2.75 2.72 2.68 2.64 2.63 2.60 2.55 2.52 2.16 1.98 1.98 1.97 1.97 1.96 1.63 1.14
OMe
O
N
CN
Me
Me
Ph
2an
minor diastereomer
in CD_3CN
2.07 2.02 0.82 2.00 2.00
3.49
0.88 0.96 0.95 1.10
3.43
3.42
10 9 8 7 6 5 4 3 2 1 0 -1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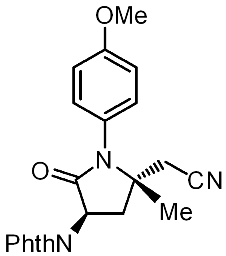
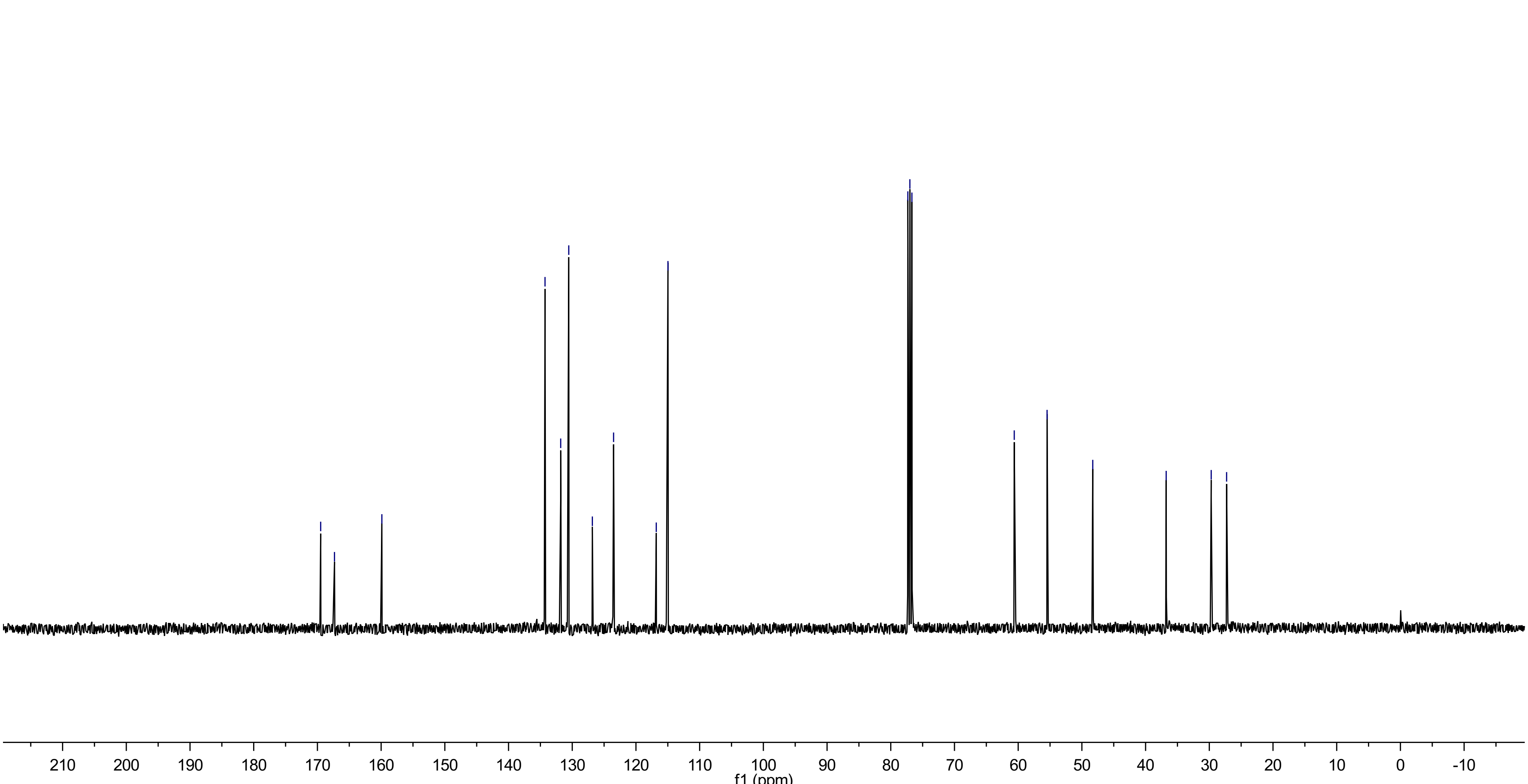
5.36 5.34 5.34 5.31
3.83
2.88 2.85 2.84 2.82 2.72 2.68 2.63 2.59 2.54 2.51 2.50 2.48
1.49
0.00
OMe
O
N
CN
Me
PhthN
(±)-2ao
2.06 2.06 2.12 2.08 1.01 3.09 1.02 1.06 0.99 1.00 2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


OMe
N
O
CN
Me
PhthN

(±)-2ao


169.49
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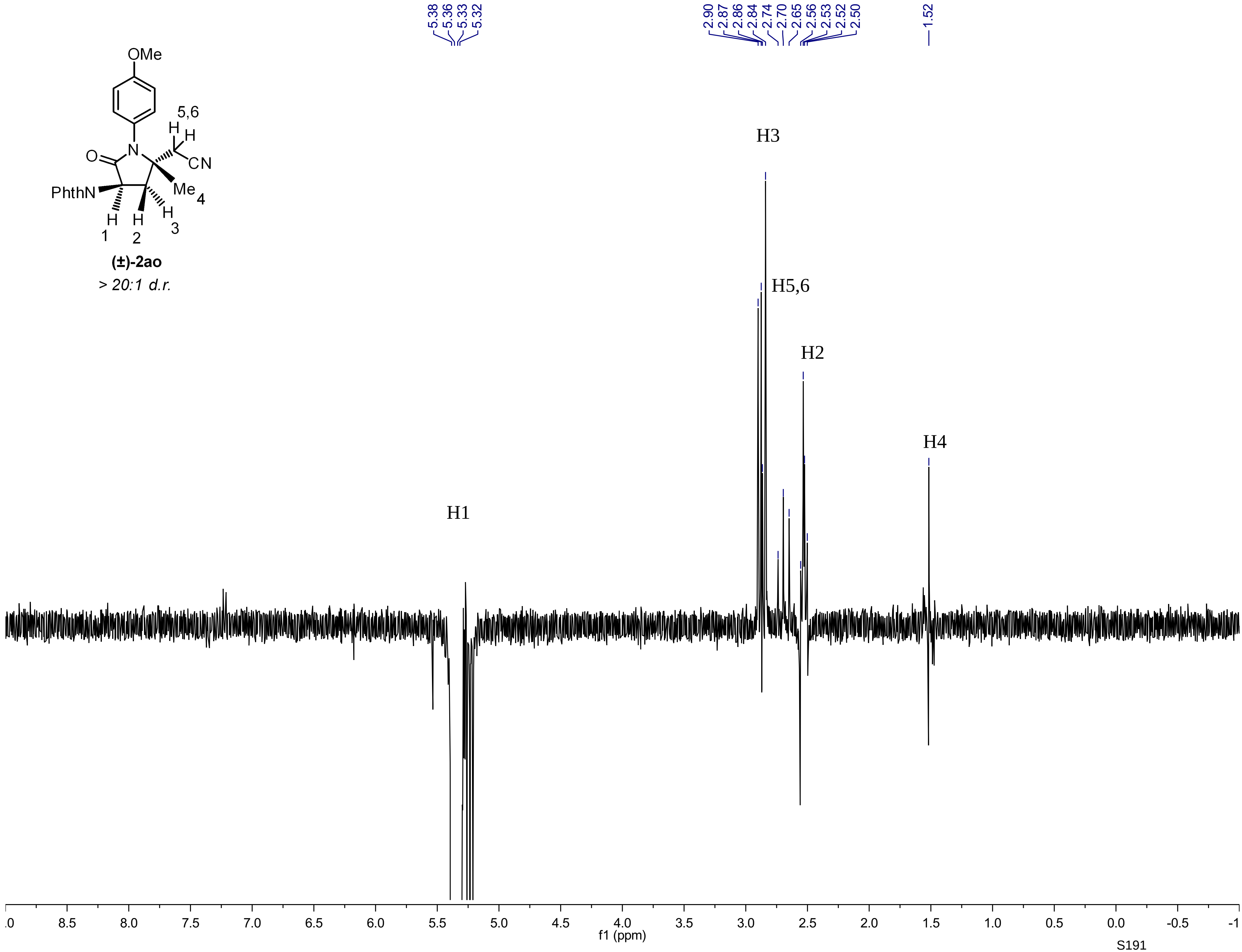
134.27
131.81
130.55
126.84
123.51
116.81
114.97
77.32
77.00
76.68
60.62
55.46
48.29
36.77
29.70
27.28
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


5.38
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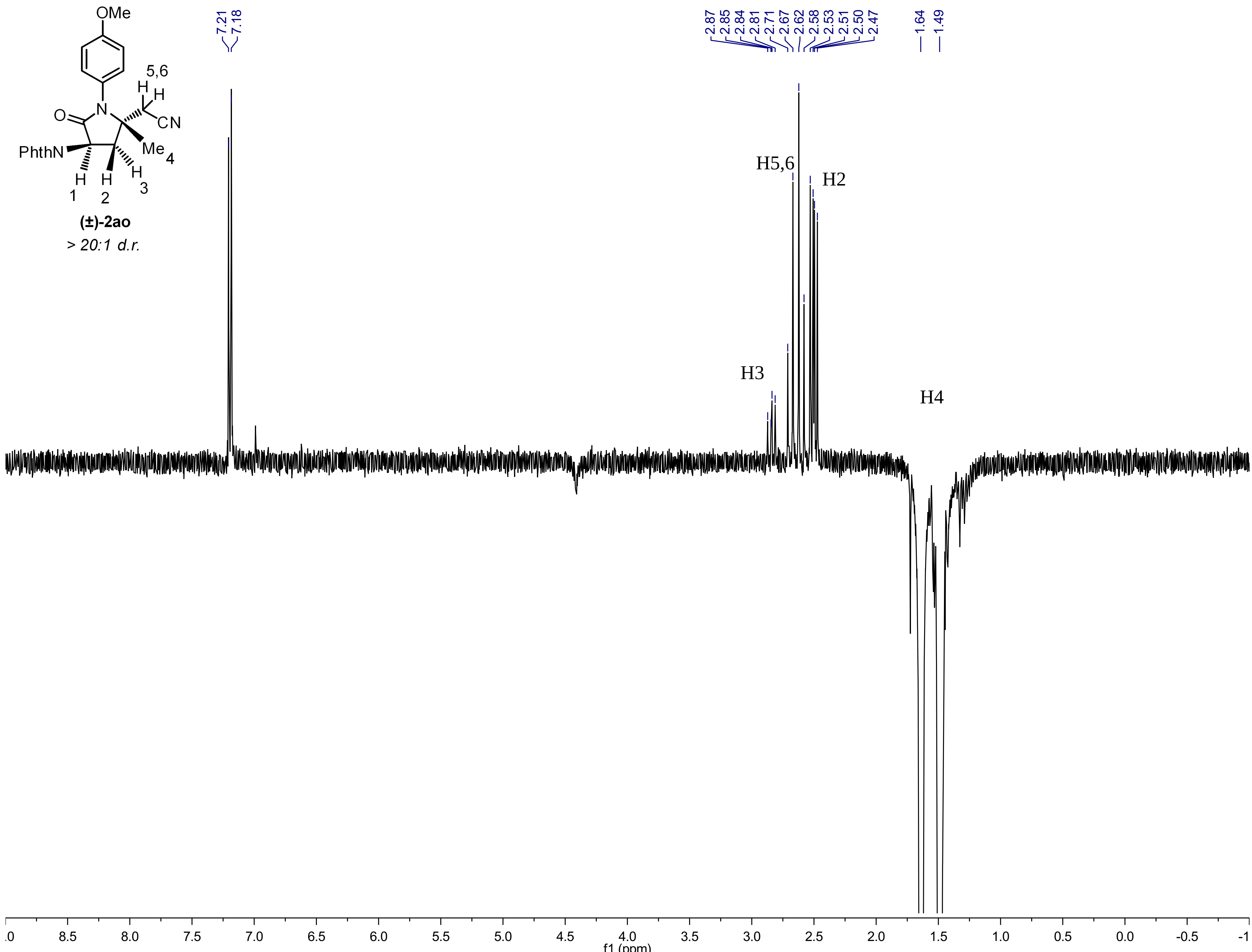
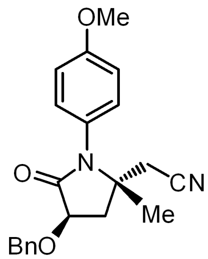
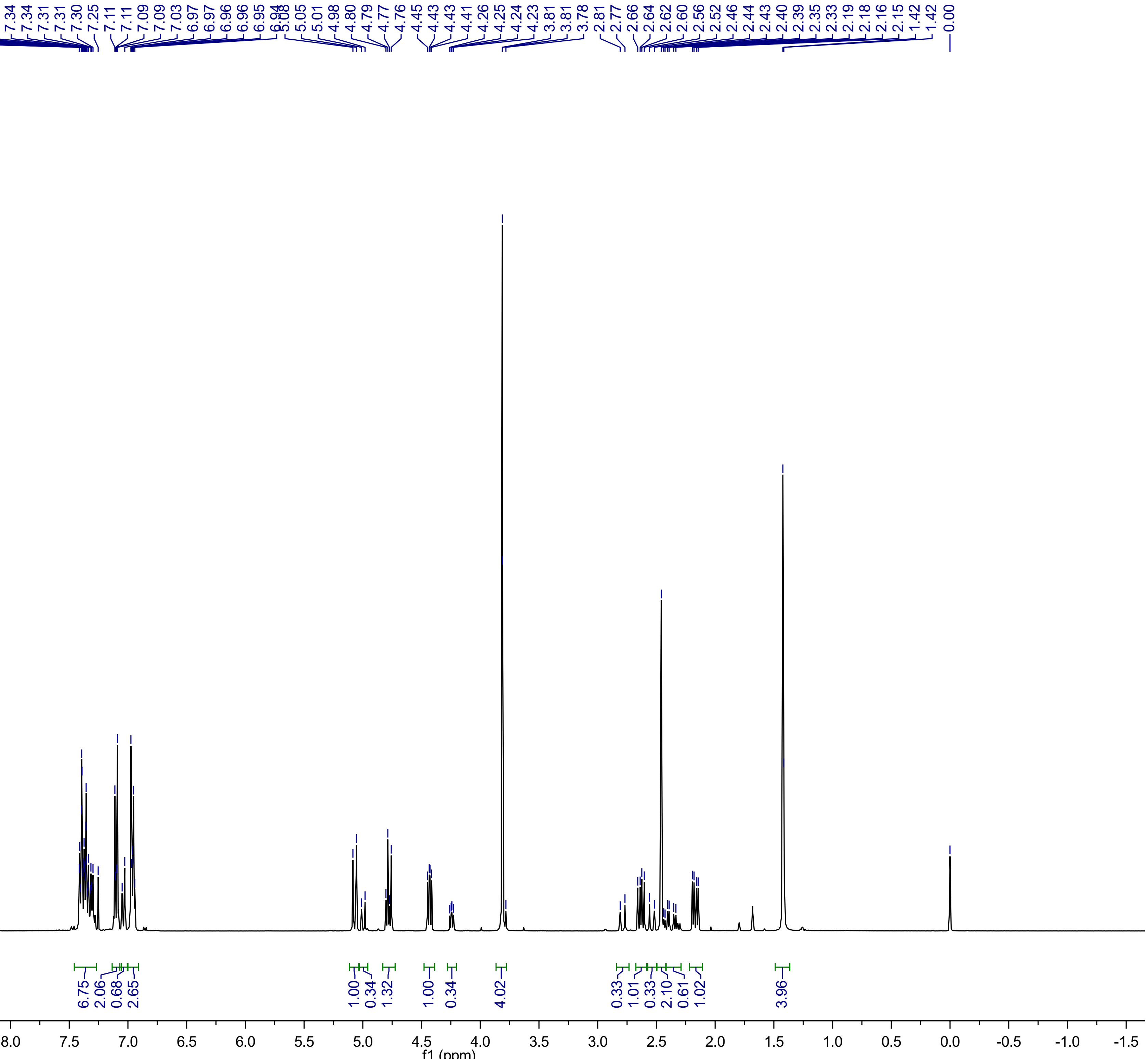
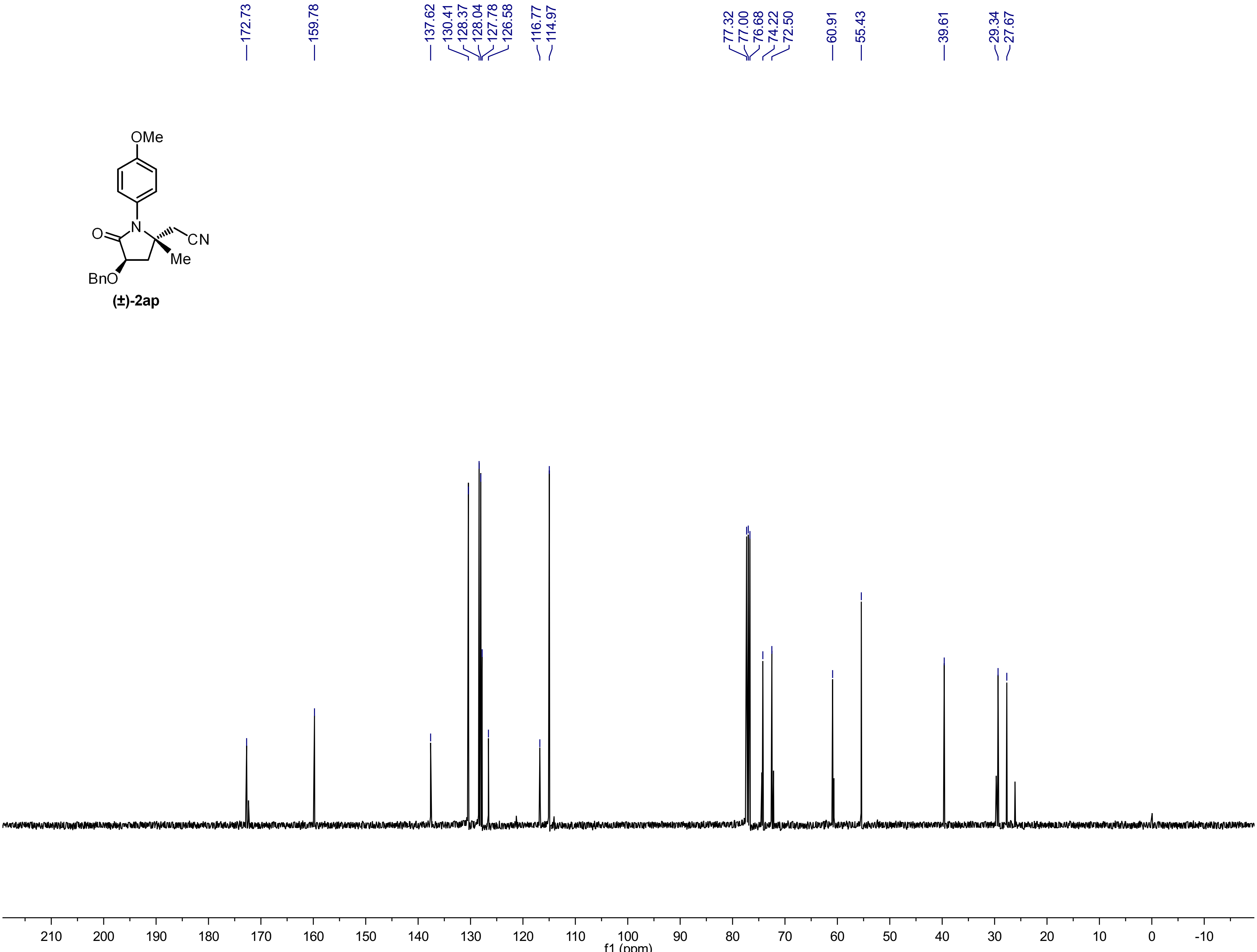
5.33
5.32
2.90
2.87
2.86
2.84
2.74
2.70
2.65
2.56
2.53
2.52
2.50
1.52
OMe
5,6
H
H
O
N
CN
PhthN
Me
4
H
H
H
1
2
3
(±)-2ao
> 20:1 d.r.
H3
H5,6
H2
H4
H1
f1 (ppm)


OMe
5,6
H
H
O
N
CN
PhthN
Me
4
H
H
H
3
1
2
(±)-2ao
> 20:1 d.r.
7.21
7.18
2.87
2.85
2.84
2.81
2.71
2.67
2.62
2.58
2.53
2.51
2.50
2.47
1.64
1.49
H5,6
H2
H3
H4
f1 (ppm)

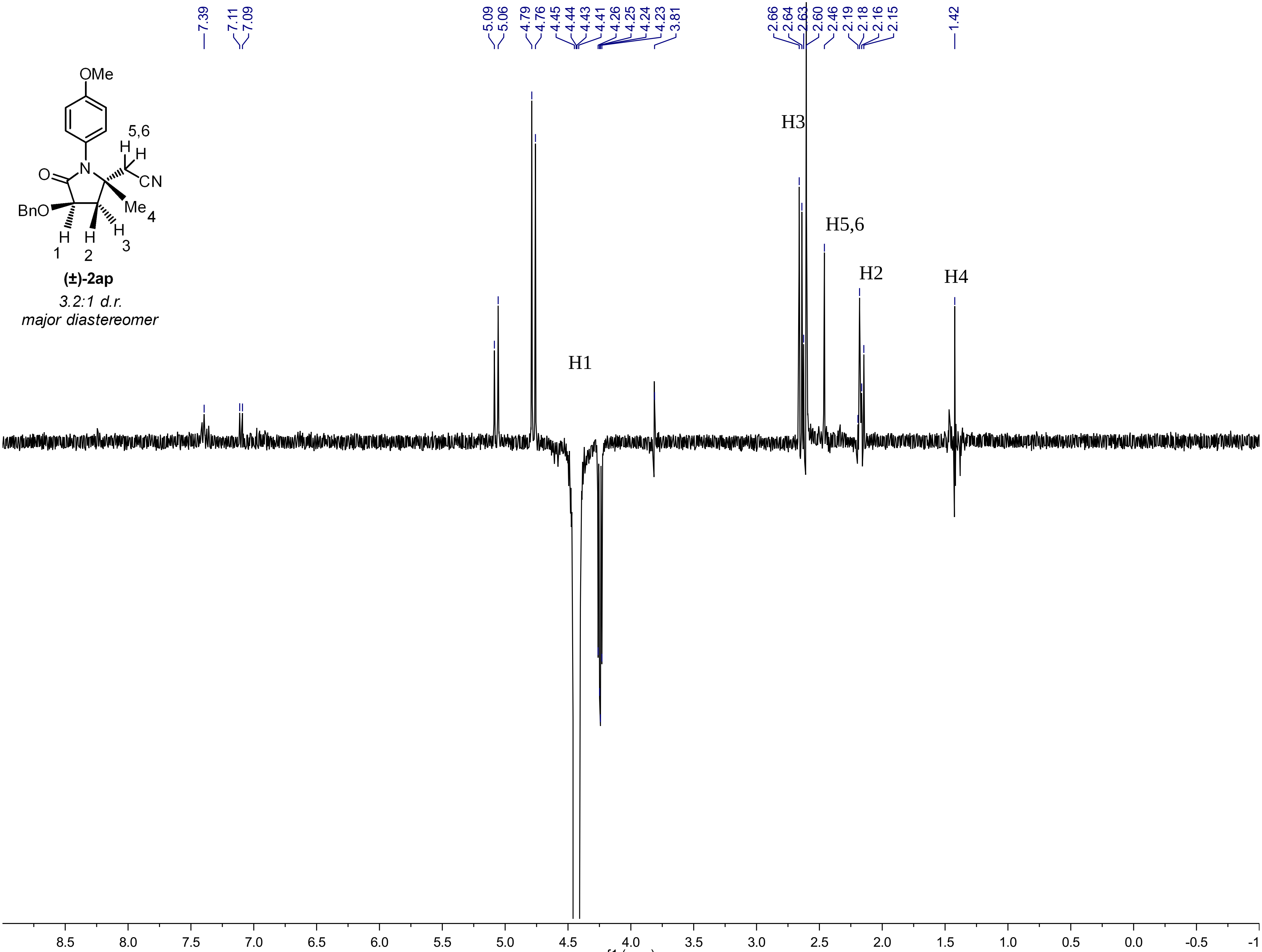


(±)-2ap




172.73
159.78
137.62
130.41
128.37
128.04
127.78
126.58
116.77
114.97
77.32
77.00
76.68
74.22
72.50
60.91
55.43
39.61
29.34
27.67
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)
OMe
O
N
CN
Me
BnO

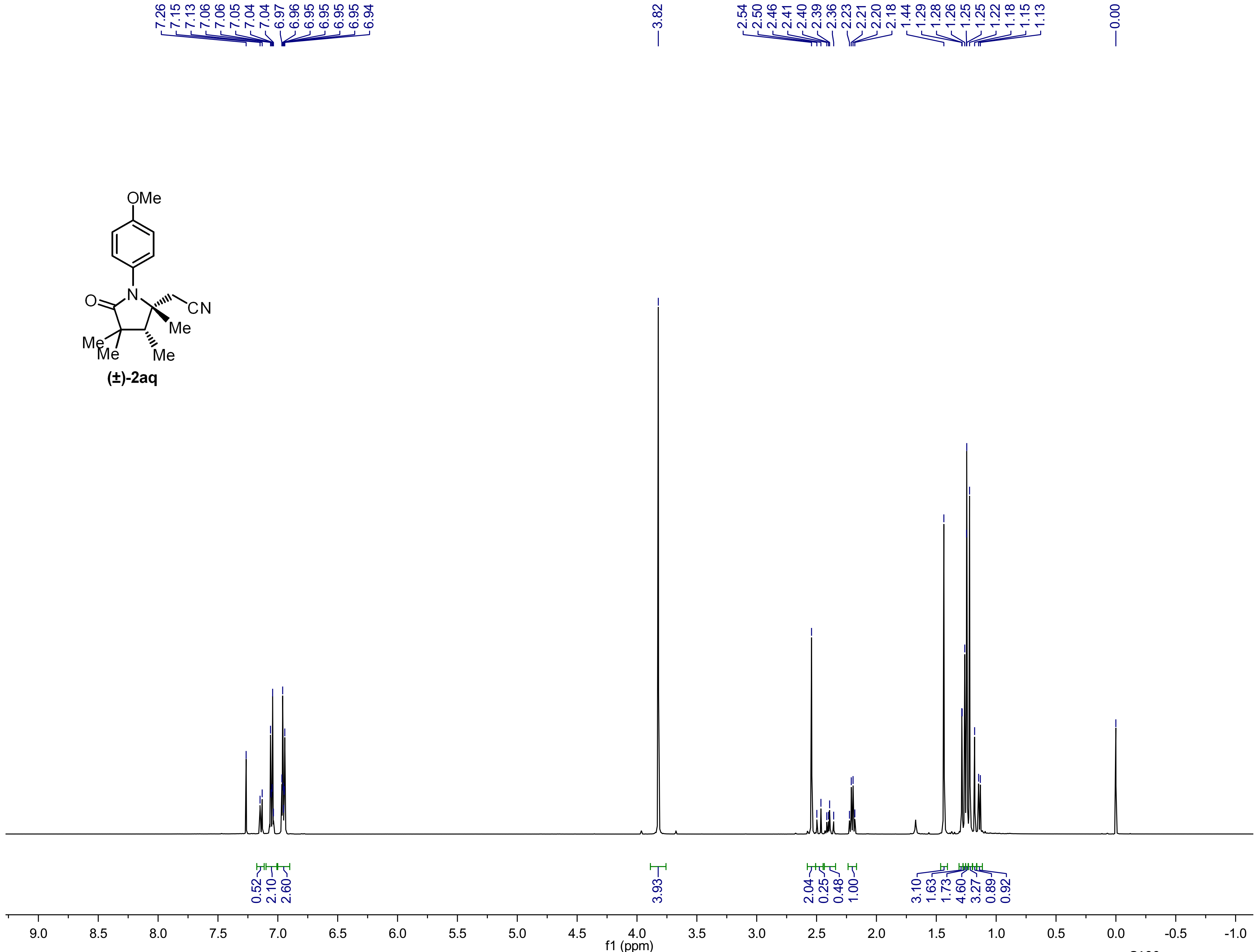
(±)-2ap



(±)-2ap

3.2:1 d.r.

major diastereomer


7.26
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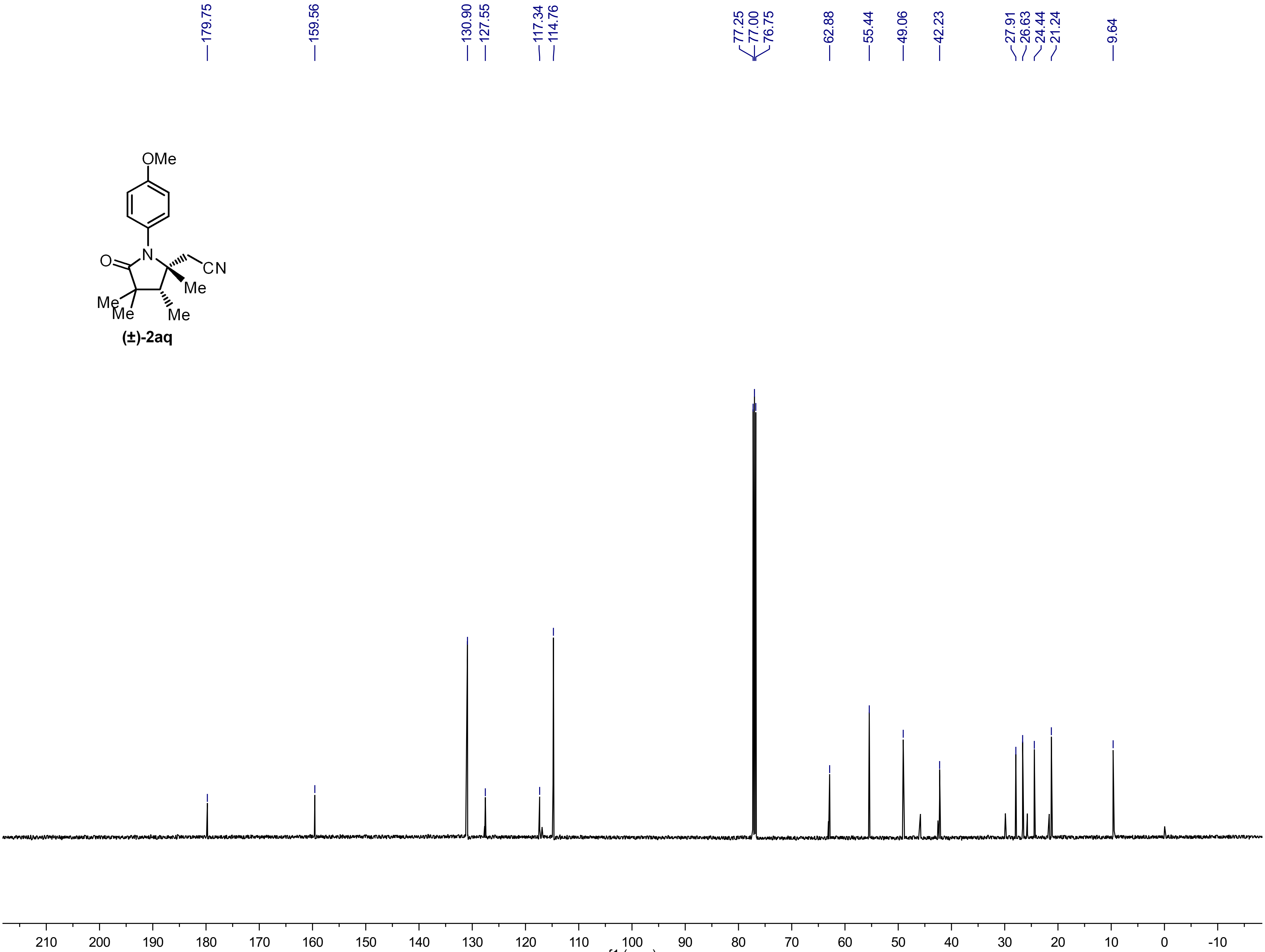
7.06
7.05
7.04
7.04
6.97
6.96
6.95
6.95
6.95
6.95
6.94
3.82
2.54
2.50
2.46
2.41
2.40
2.39
2.36
2.23
2.21
2.20
2.18
1.44
1.29
1.28
1.26
1.25
1.25
1.22
1.18
1.15
1.13
0.00
OMe
O
N
CN
Me
Me
Me
Me
(±)-2aq
0.52
2.10
2.60
3.93
2.04
0.25
0.48
1.00
3.10
1.63
1.73
4.60
3.27
0.89
0.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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127.55
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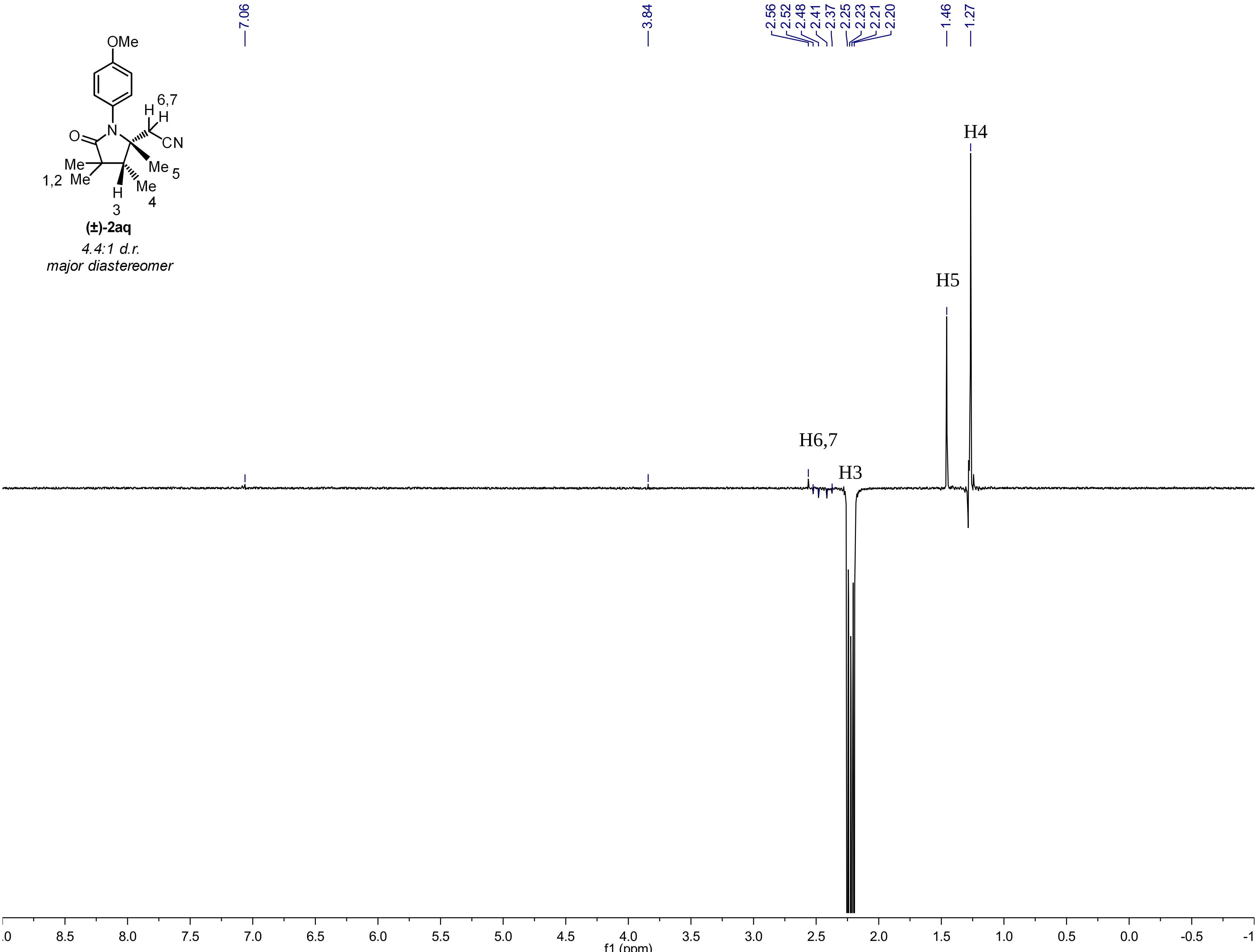
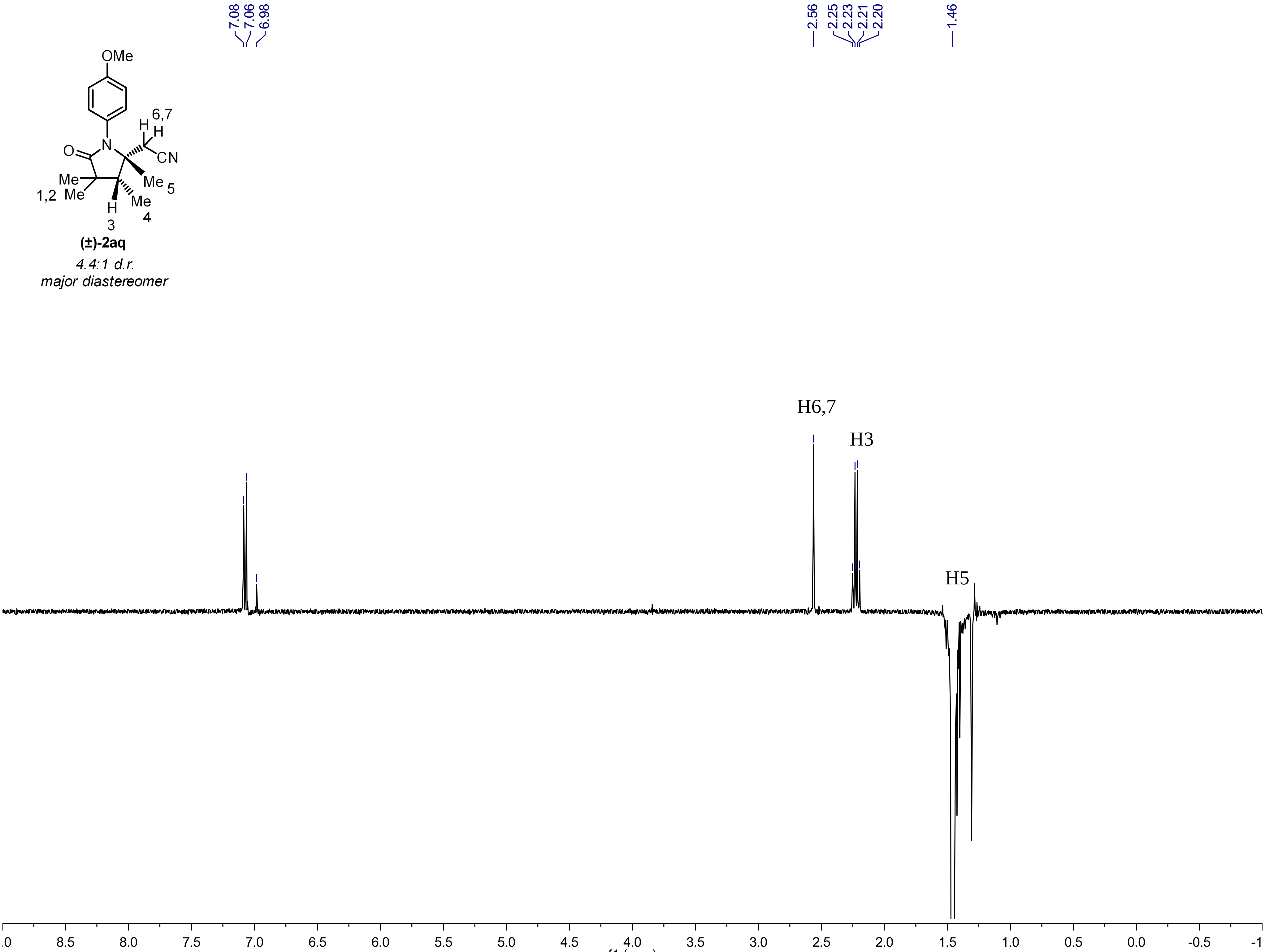
77.00
76.75
62.88
55.44
49.06
42.23
27.91
26.63
24.44
21.24
9.64
OMe
O
N
CN
Me
Me
Me
Me
(±)-2aq
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



OMe
6,7
H
H
O
N
CN
Me
1,2
Me
Me
5
H
Me
3
4
(±)-2aq
4.4:1 d.r.
major diastereomer
7.06
3.84
2.56
2.52
2.48
2.41
2.37
2.25
2.23
2.21
2.20
1.46
1.27
H4
H5
H6,7
H3
.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
-0.5
-1
f1 (ppm)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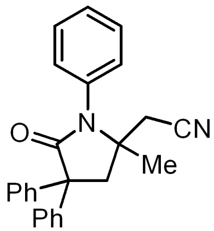
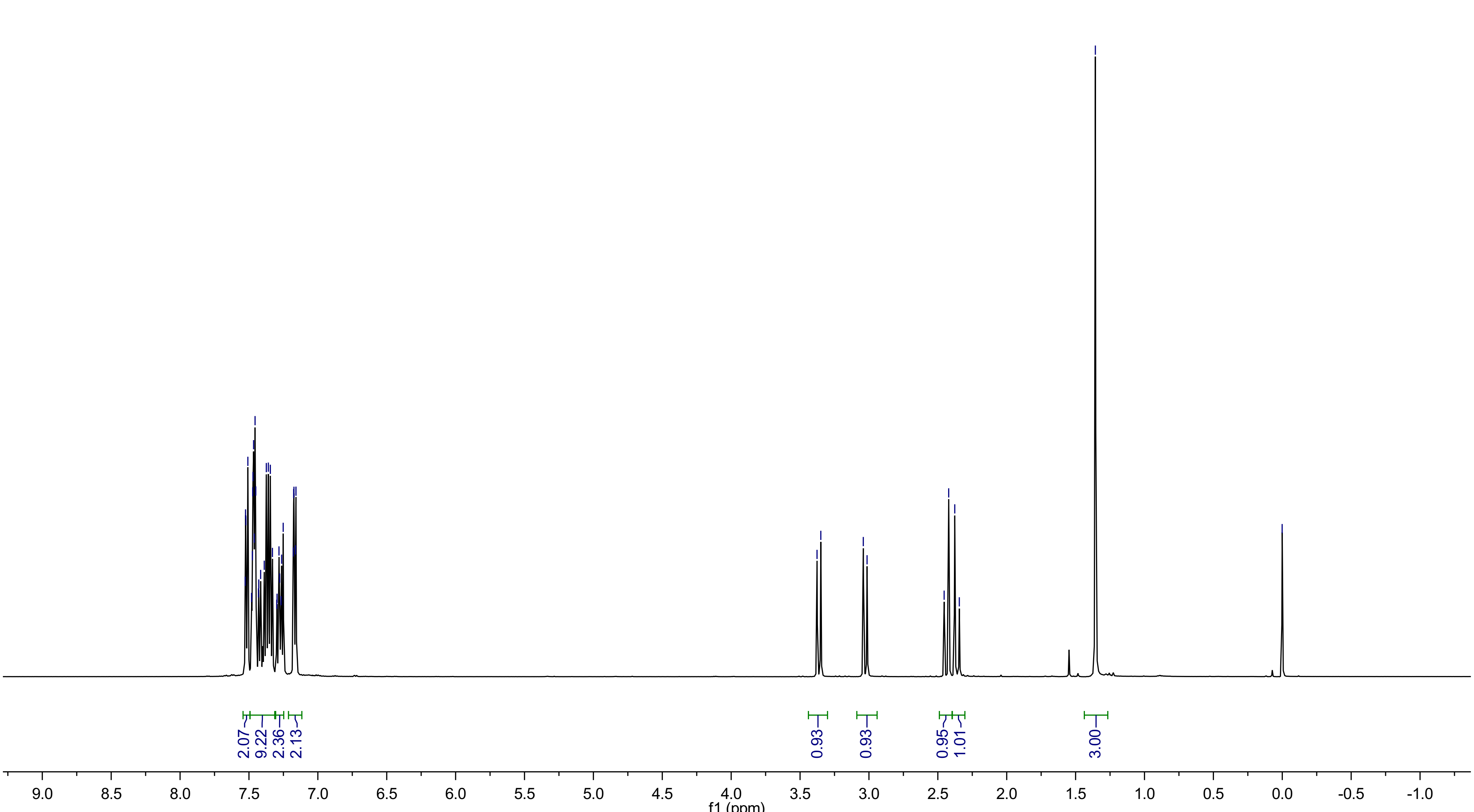
2.23
2.21
2.20
1.46
OMe
6,7
H
H
O
N
CN
Me
Me
1,2
Me
5
H
Me
3
4
(±)-2aq
4.4:1 d.r.
major diastereomer
H6,7
H3
H5
f1 (ppm)



O
N
CN
Me
Ph
Ph

2b



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7.43
7.43
7.42
7.39
7.37
7.36
7.34
7.33
7.30
7.30
7.28
7.28
7.27
7.26
7.25
7.18
7.18
7.17
7.16
7.16
3.38
3.35
3.04
3.01
2.45
2.42
2.38
2.34
1.36
0.00
2.07
9.22
2.36
2.13
0.93
0.93
0.95
1.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
1.5
1.0
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0.0
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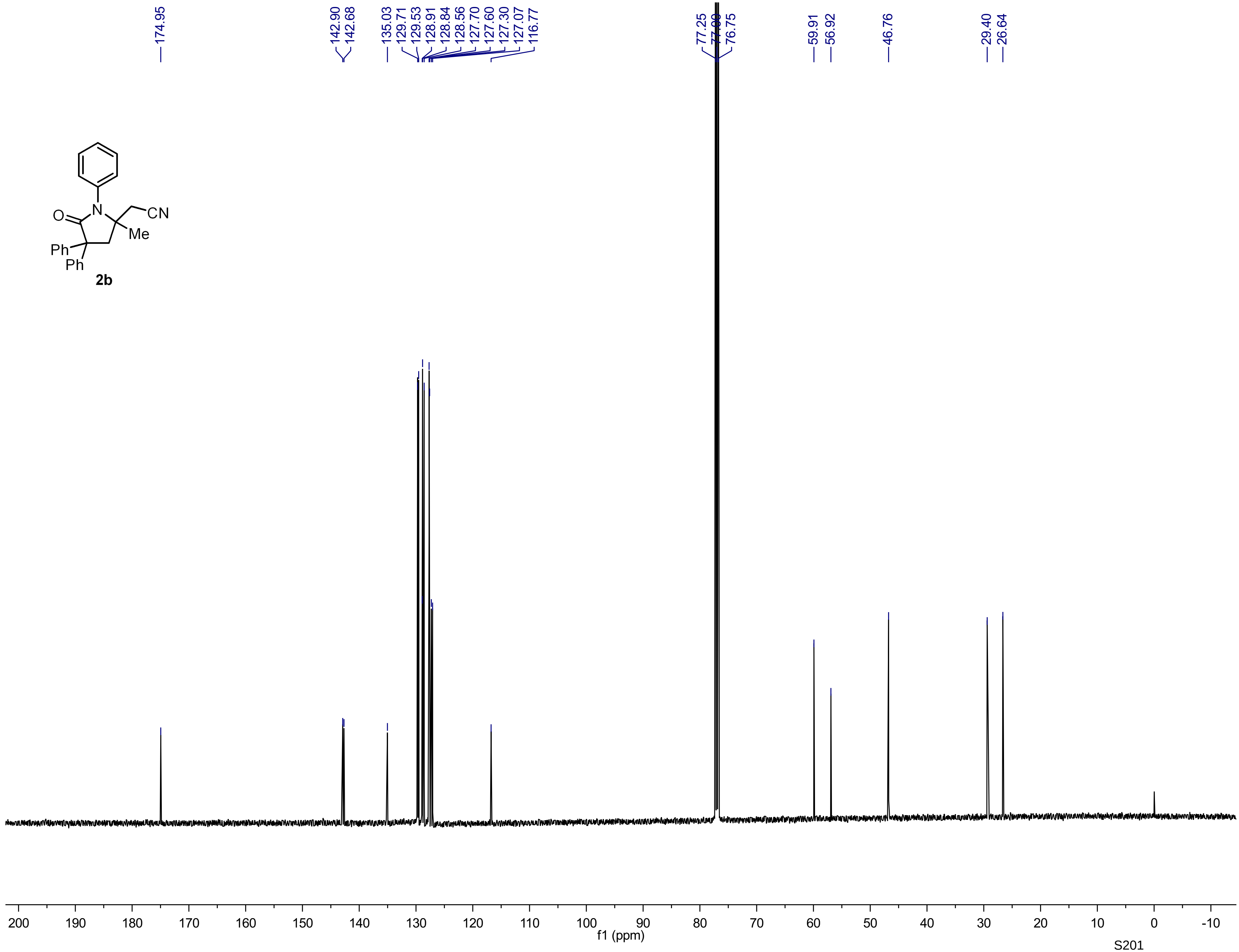
-1.0
f1 (ppm)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127.70
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127.30
127.07
116.77
77.25
77.00
76.75
59.91
56.92
46.76
29.40
26.64
O
N
CN
Me
Ph
Ph
2b
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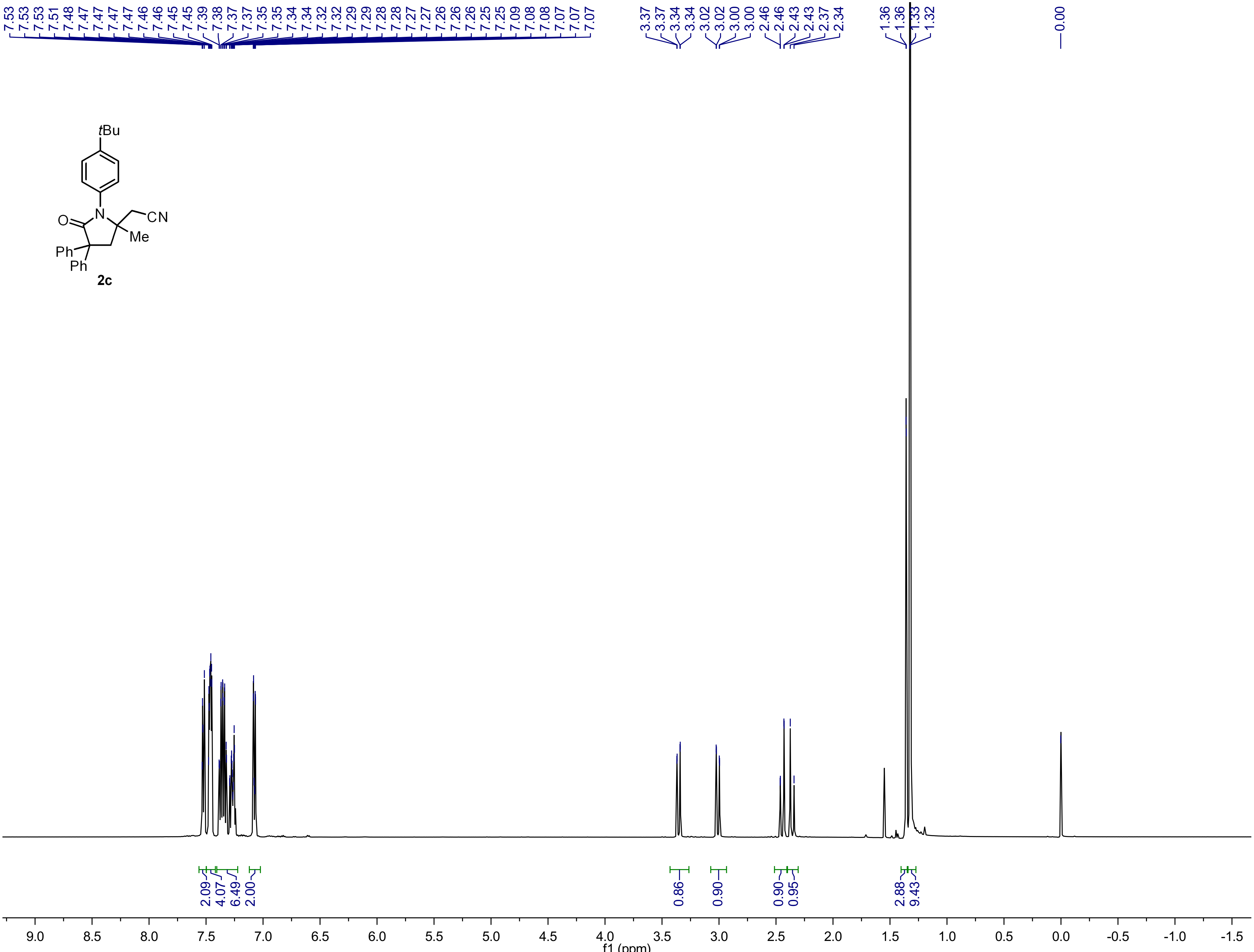
f1 (ppm)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7.34
7.32
7.32
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.09
7.08
7.08
7.07
7.07
7.07
3.37
3.37
3.34
3.34
3.02
3.02
3.00
3.00
2.46
2.46
2.43
2.43
2.37
2.34
1.36
1.36
1.33
1.32
0.00
tBu
O
N
CN
Me
Ph
Ph
2c
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6.49
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0.95
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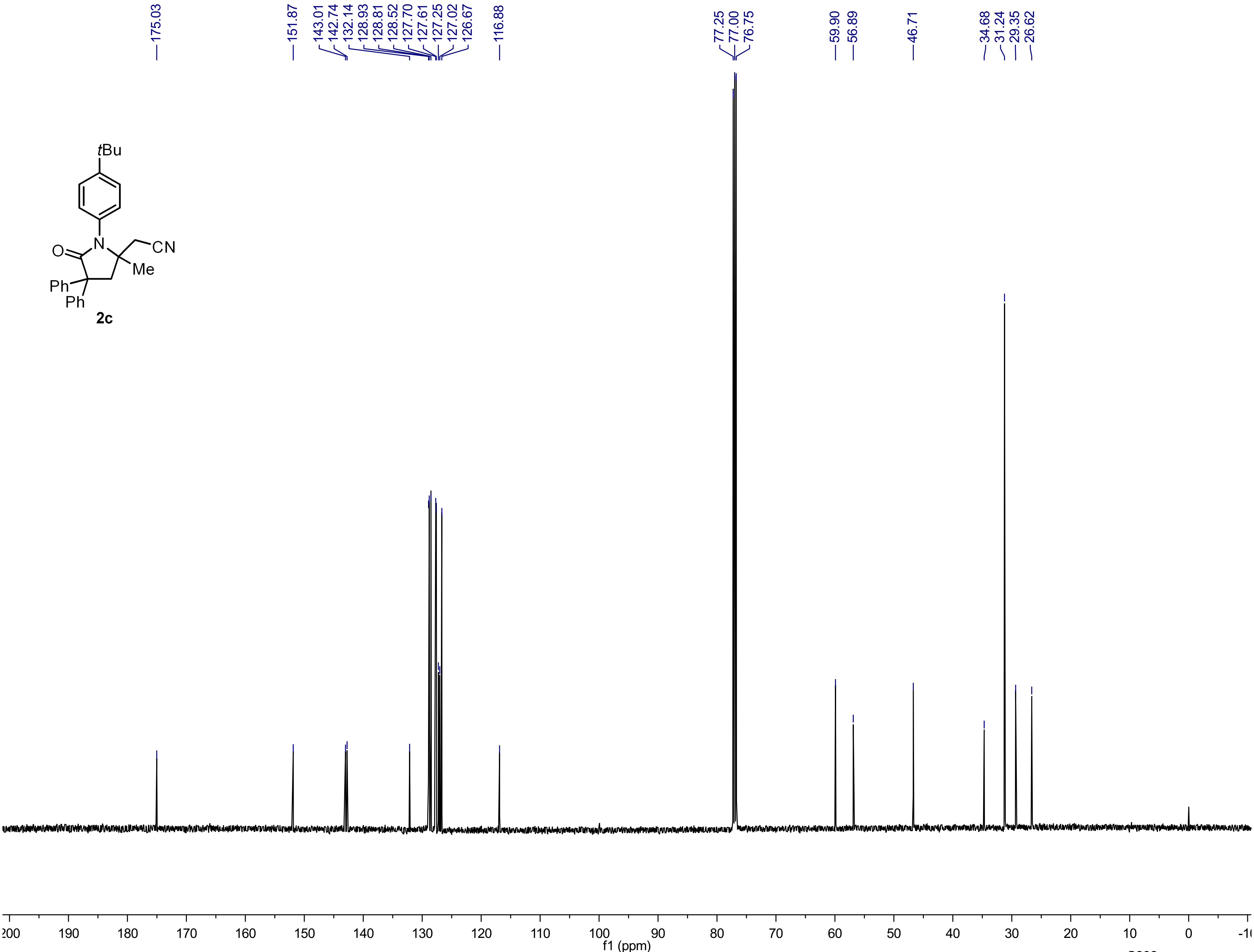
9.43
f1 (ppm)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151.87
143.01
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132.14
128.93
128.81
128.52
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127.61
127.25
127.02
126.67
116.88
77.25
77.00
76.75
59.90
56.89
46.71
34.68
31.24
29.35
26.62
tBu
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N
CN
Me
Ph
Ph
2c
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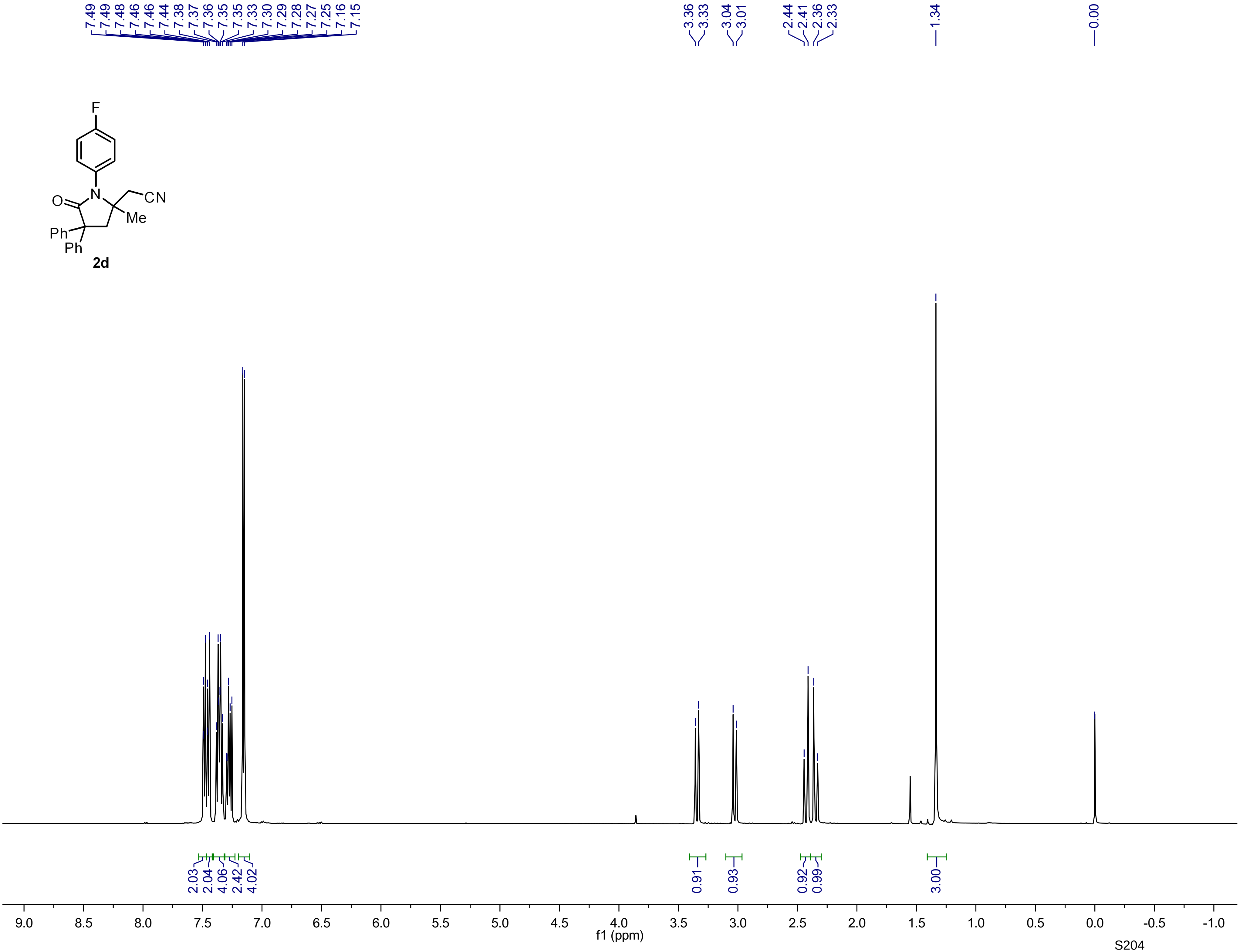
f1 (ppm)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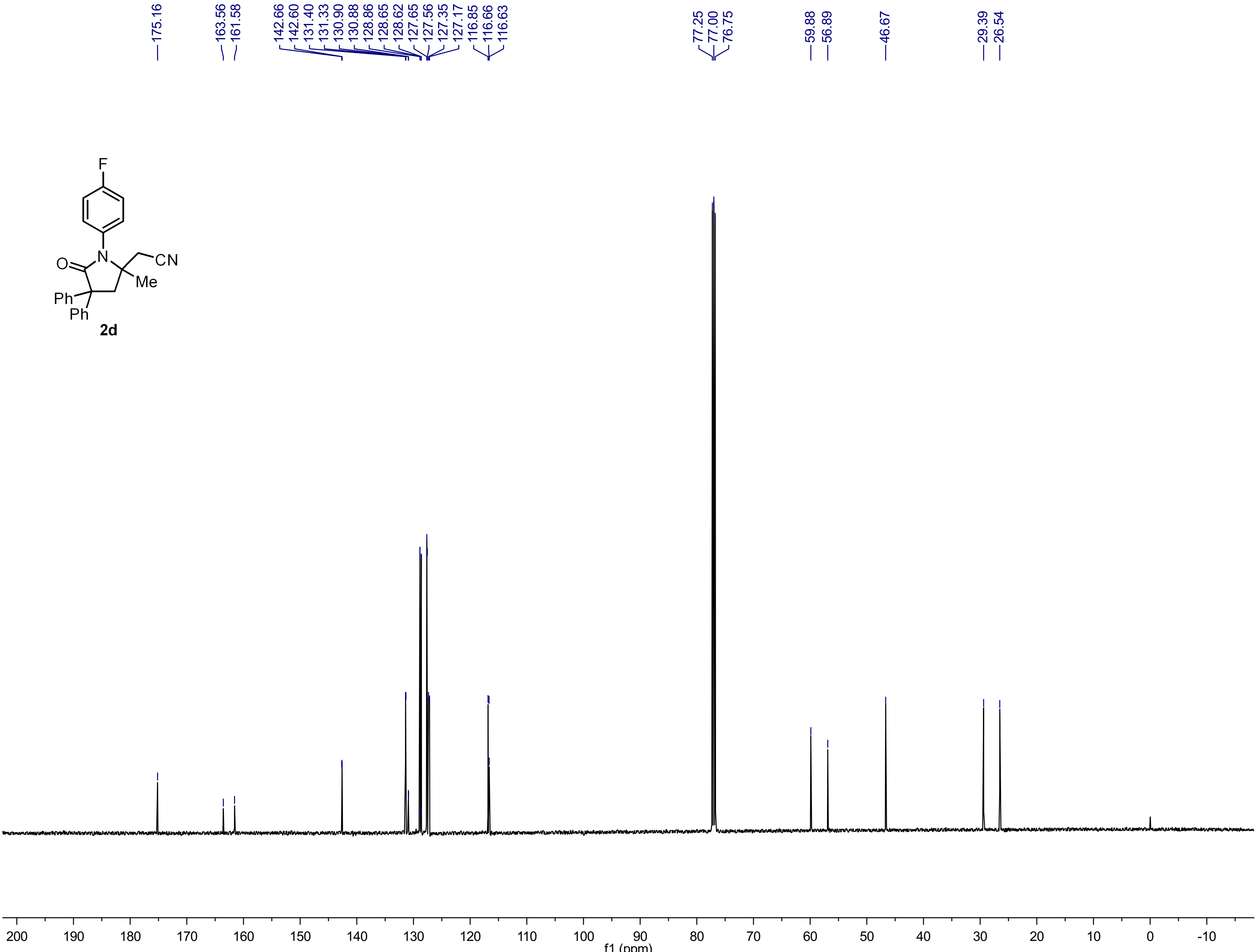
3.36 3.33 3.04 3.01
2.44 2.41 2.36 2.33
1.34
0.00
F
O
N
CN
Me
Ph
Ph
2d
2.03 2.04 4.06 2.42 4.02
0.91
0.93
0.92 0.99
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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142.60
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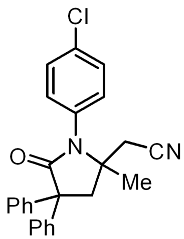
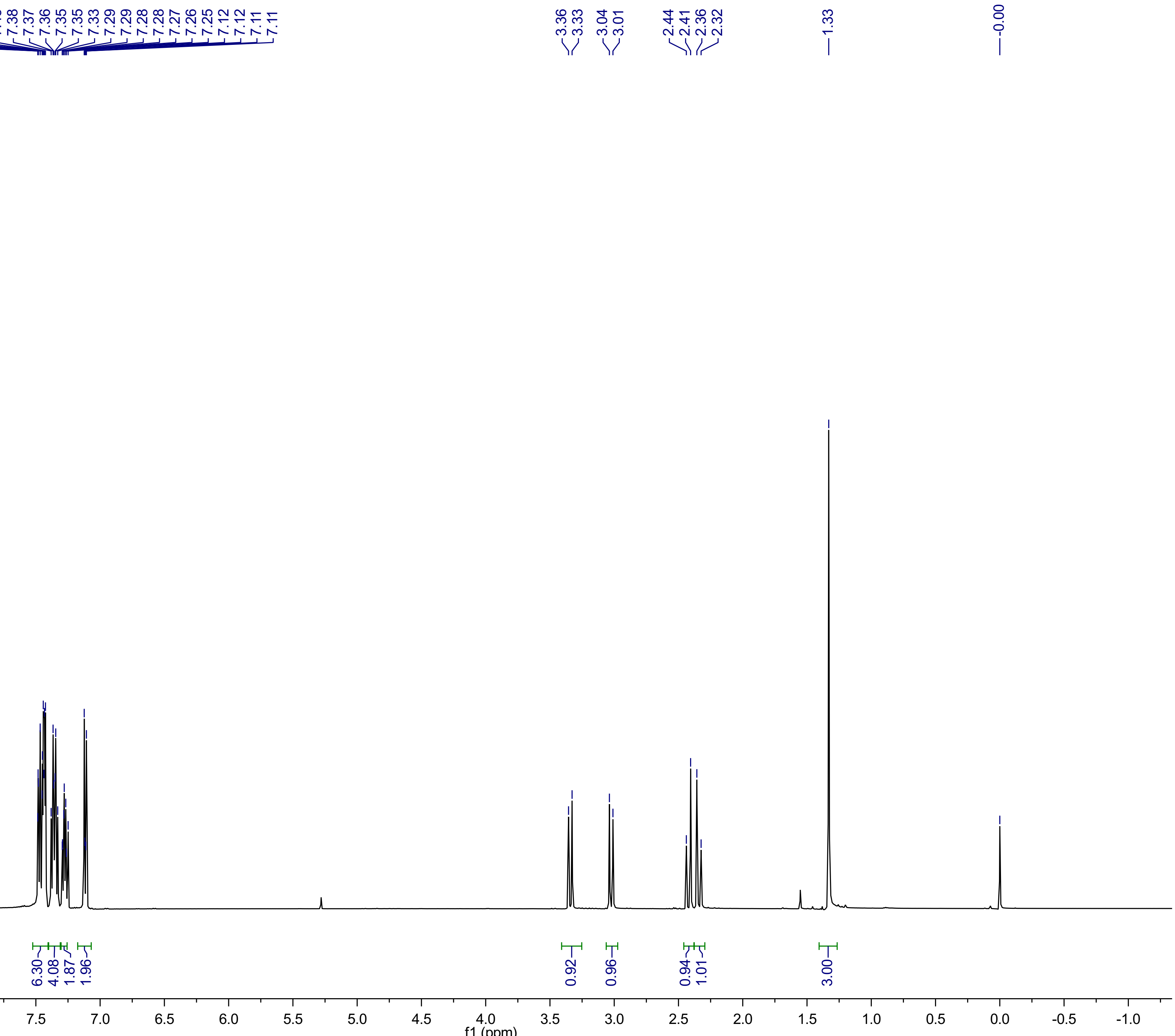
130.90
130.88
128.86
128.65
128.62
127.65
127.56
127.35
127.17
116.85
116.66
116.63
77.25
77.00
76.75
59.88
56.89
46.67
29.39
26.54
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
F
O
N
CN
Me
Ph
Ph

2d


Cl
O
N
CN
Me
Ph
Ph

2e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7.44
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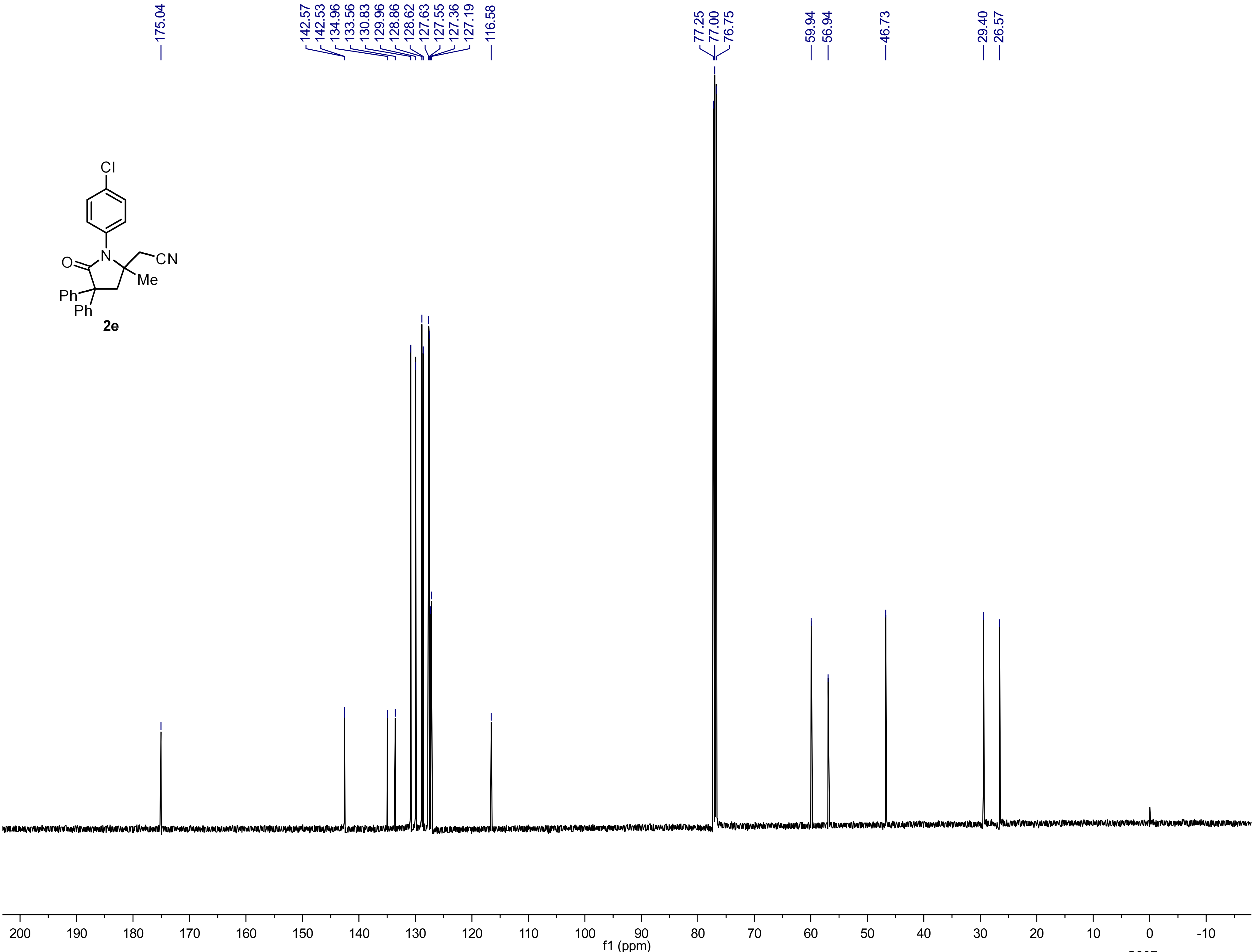
7.36
7.35
7.35
7.33
7.29
7.28
7.28
7.27
7.26
7.25
7.12
7.12
7.11
7.11
3.36
3.33
3.04
3.01
2.44
2.41
2.36
2.32
1.33
-0.00
6.30
4.08
1.87
1.96
0.92
0.96
0.94
1.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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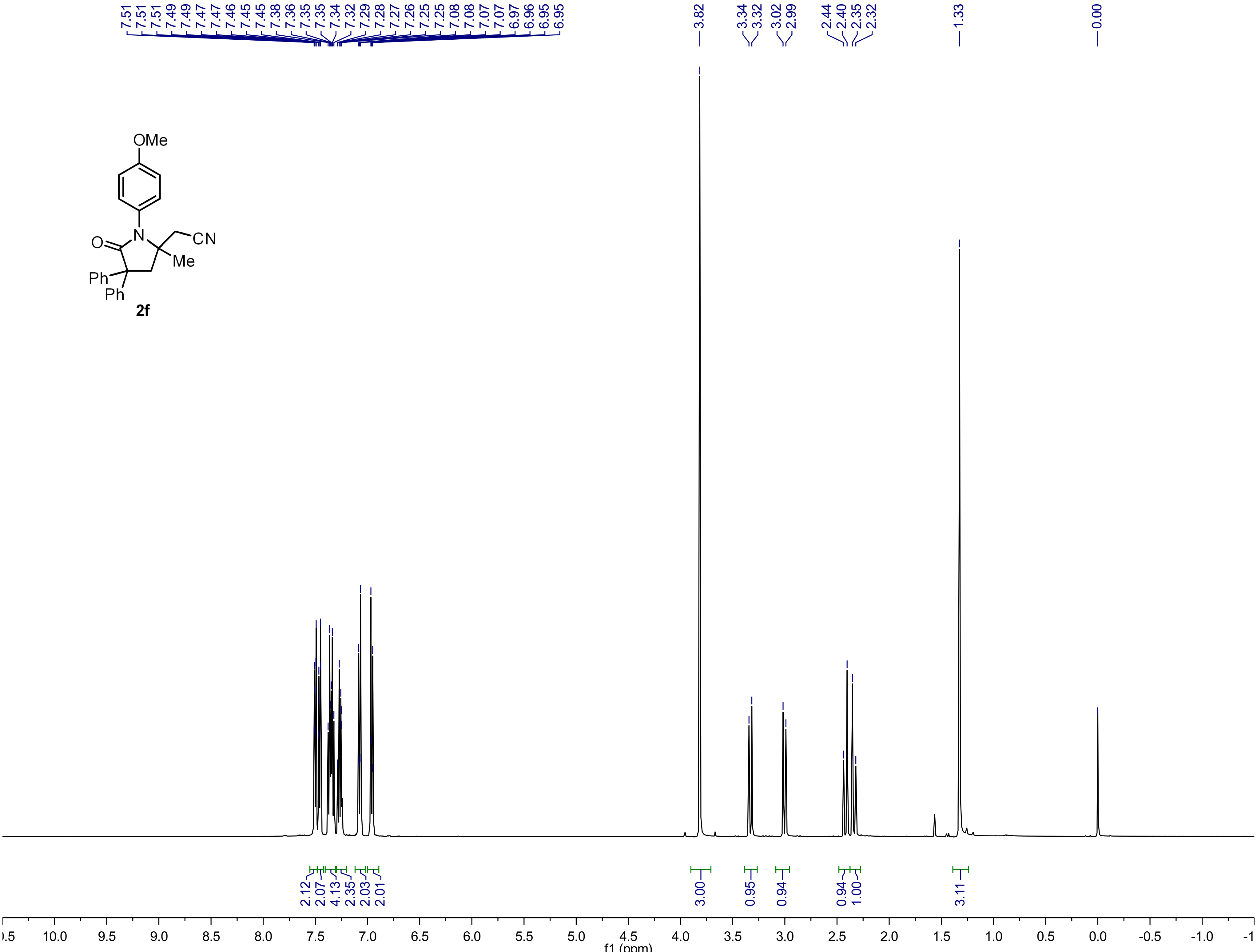
128.62
127.63
127.55
127.36
127.19
116.58
77.25
77.00
76.75
59.94
56.94
46.73
29.40
26.57
Cl
O
N
CN
Me
Ph
Ph
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.46
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7.38
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7.35
7.35
7.34
7.32
7.29
7.28
7.27
7.26
7.25
7.25
7.08
7.08
7.07
7.07
6.97
6.96
6.95
6.95
3.82
3.34
3.32
3.02
2.99
2.44
2.40
2.35
2.32
1.33
0.00
OMe
N
O
CN
Me
Ph
Ph
2f
2.12
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2.03
2.01
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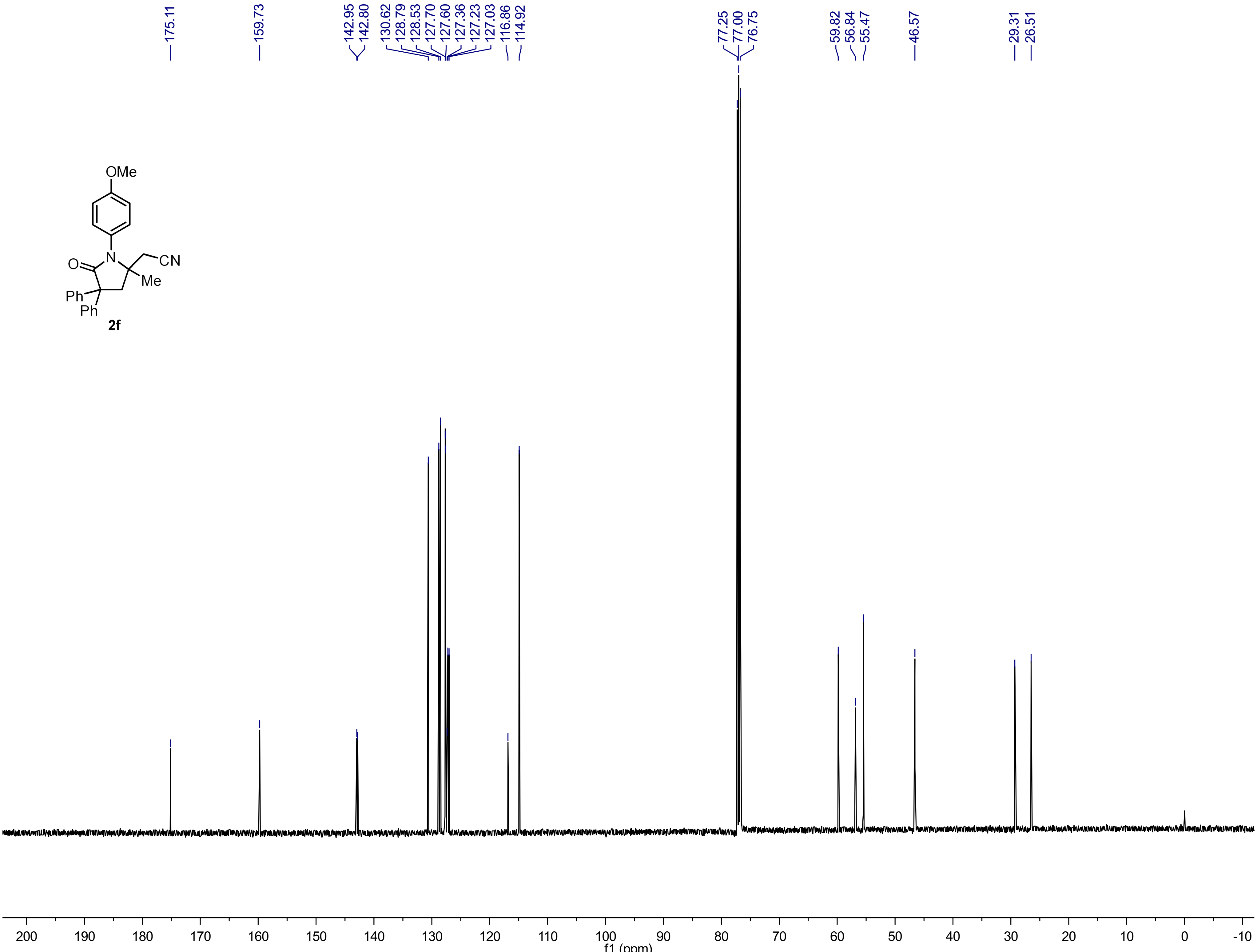
0.94
1.00
3.11
f1 (ppm)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127.70
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116.86
114.92
77.25
77.00
76.75
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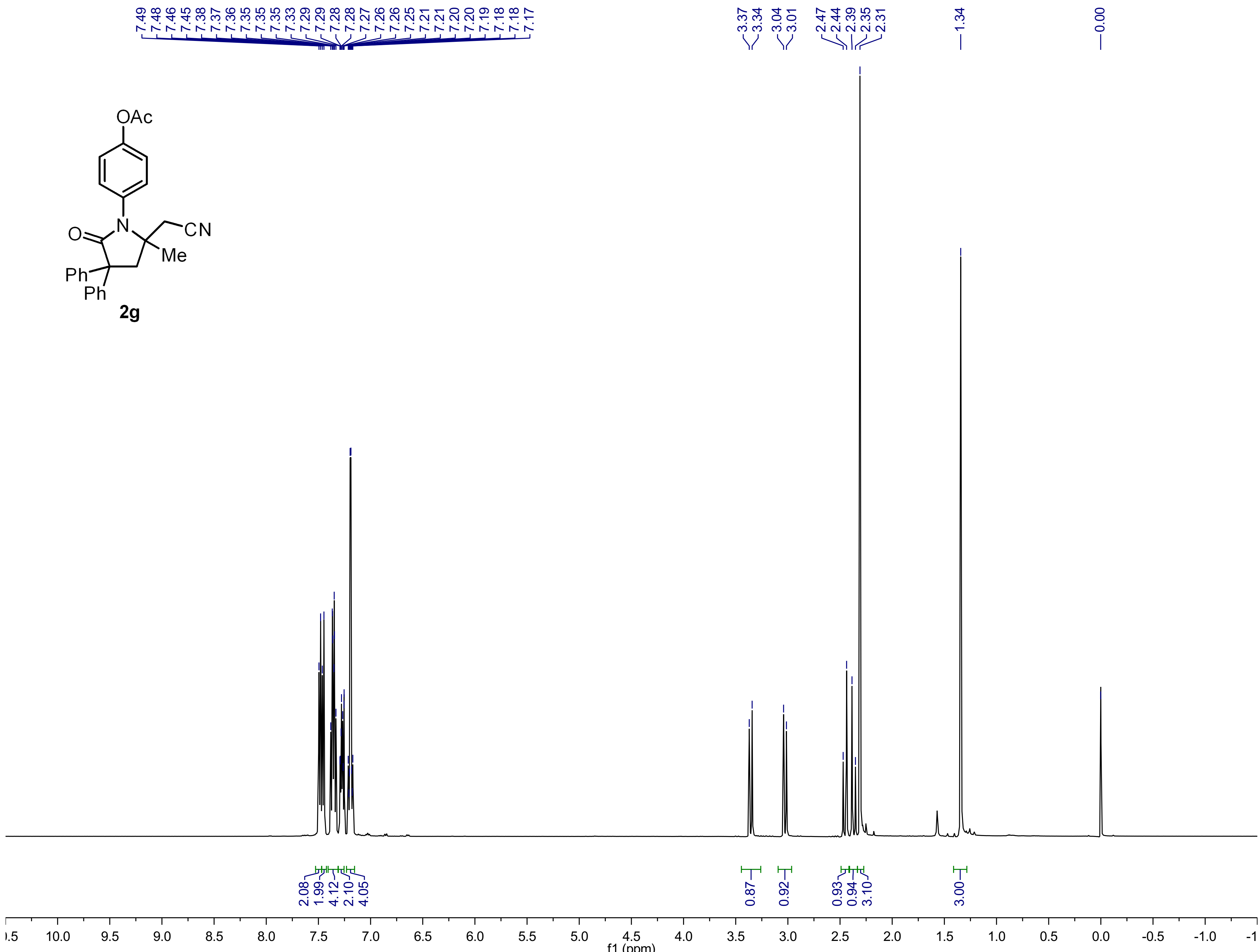
46.57
29.31
26.51
OMe
N
CN
O
Me
Ph
Ph
2f
f1 (ppm)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7.28
7.28
7.27
7.26
7.26
7.25
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.17
3.37
3.34
3.04
3.01
2.47
2.44
2.39
2.35
2.31
1.34
0.00
OAc
O
N
CN
Me
Ph
Ph
2g
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4.05
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3.10
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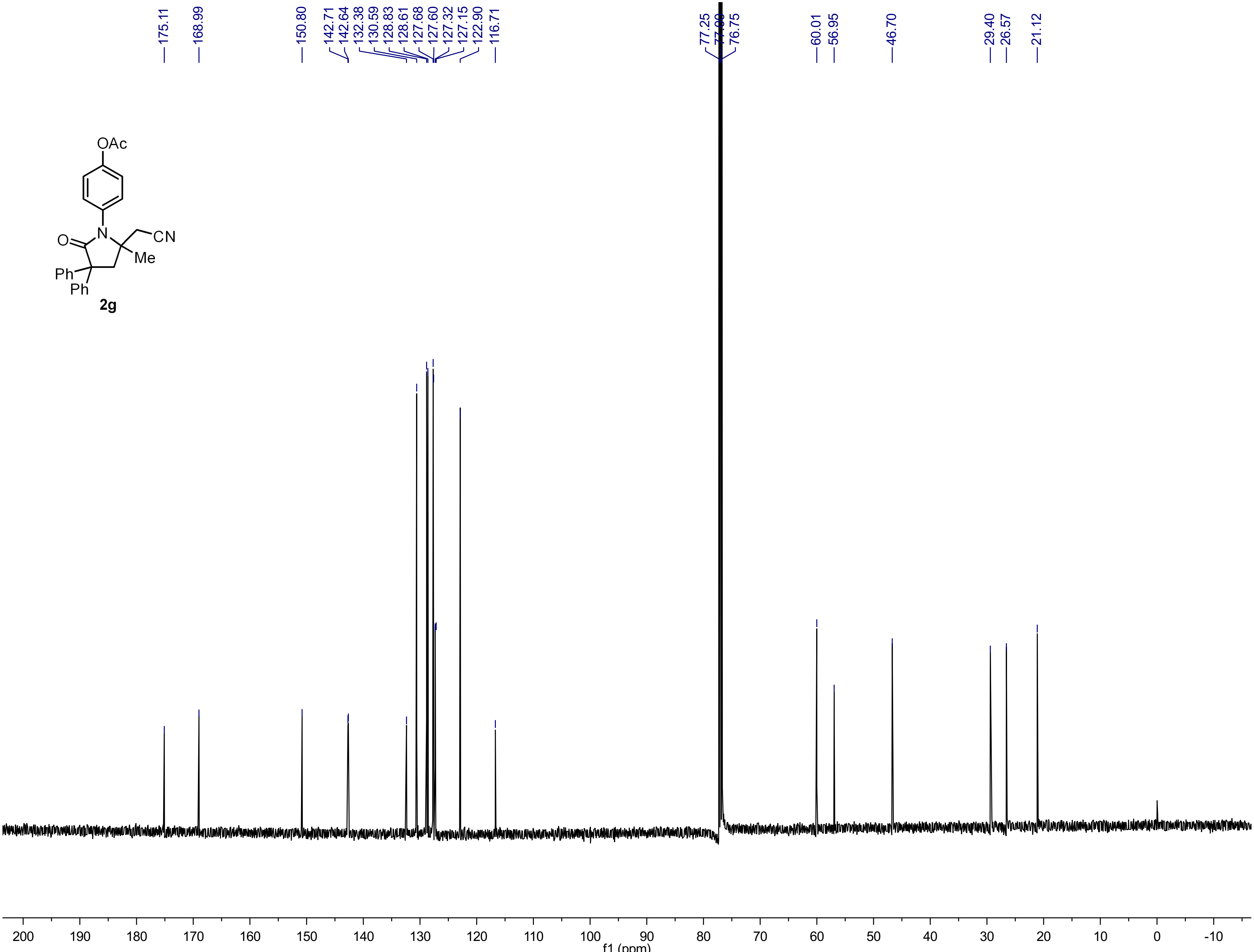

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127.60
127.32
127.15
122.90
116.71
77.25
76.75
60.01
56.95
46.70
29.40
26.57
21.12
OAc
N
O
CN
Me
Ph
Ph
2g
200
190
180
170
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140
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100
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80
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40
30
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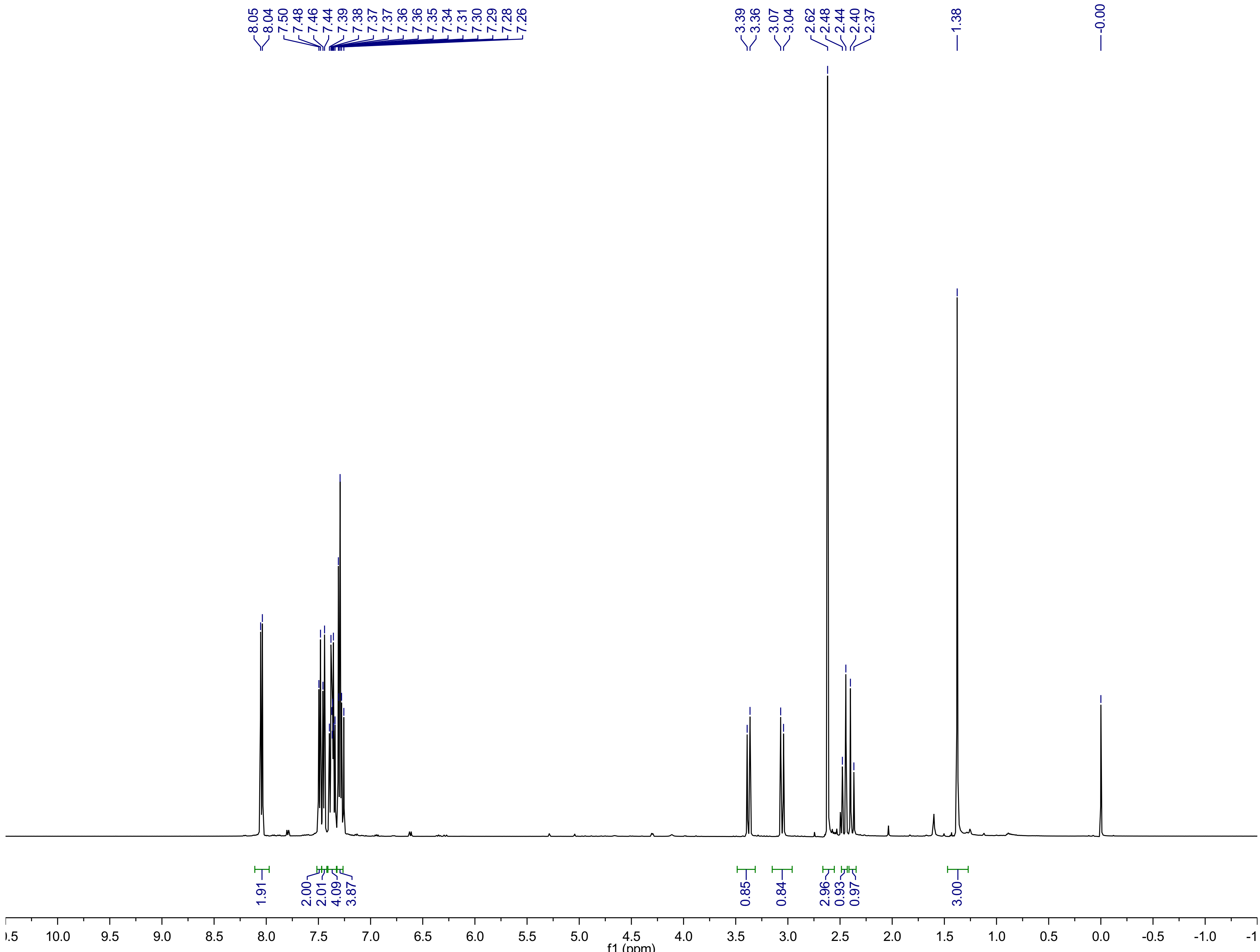
0
-10
f1 (ppm)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7.37
7.36
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7.35
7.34
7.31
7.30
7.29
7.28
7.26
3.39
3.36
3.07
3.04
2.62
2.48
2.44
2.40
2.37
1.38
-0.00
1.91
2.00
2.01
4.09
3.87
0.85
0.84
2.96
0.93
0.97
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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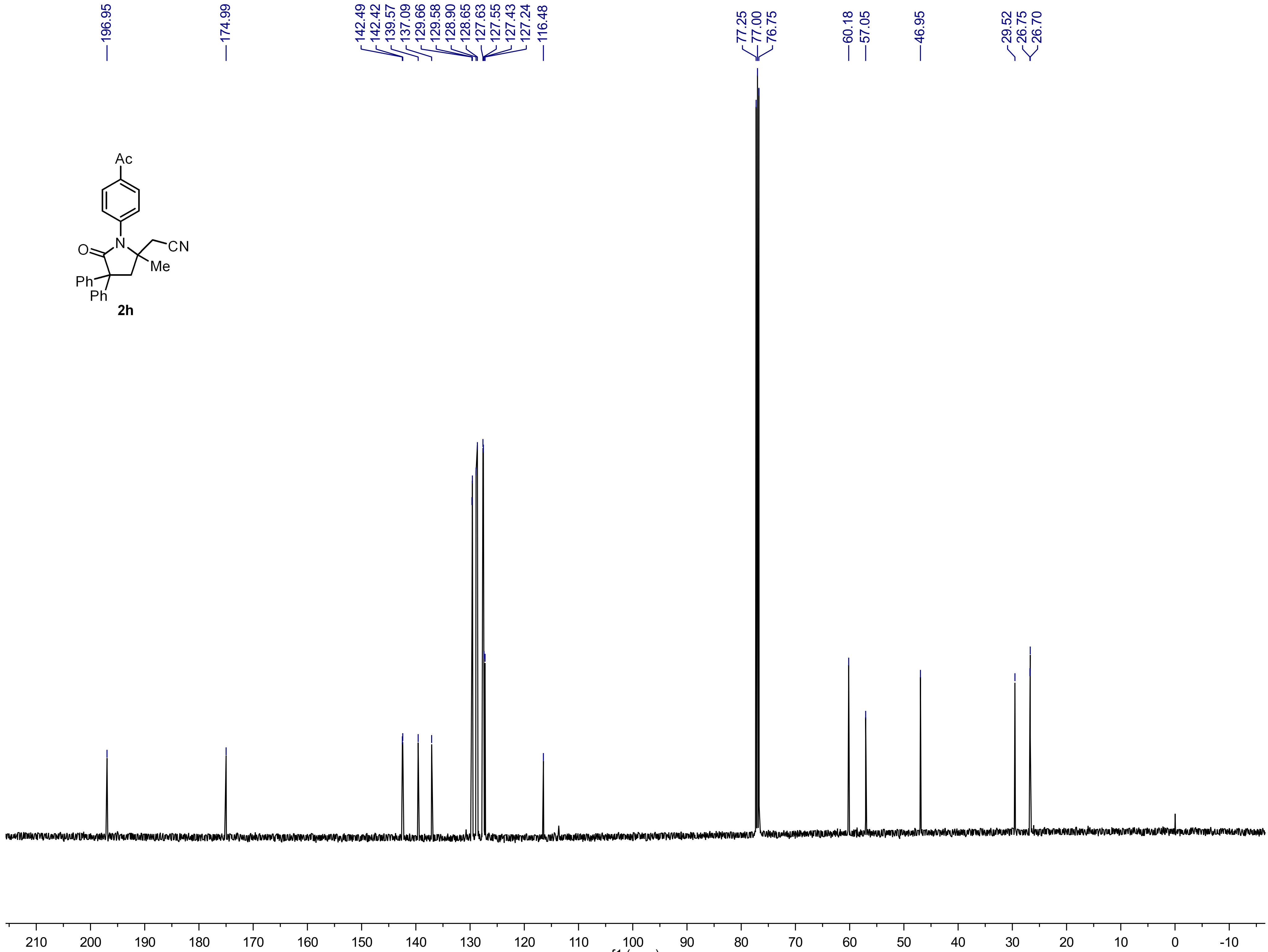
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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127.43
127.24
116.48
77.25
77.00
76.75
60.18
57.05
46.95
29.52
26.75
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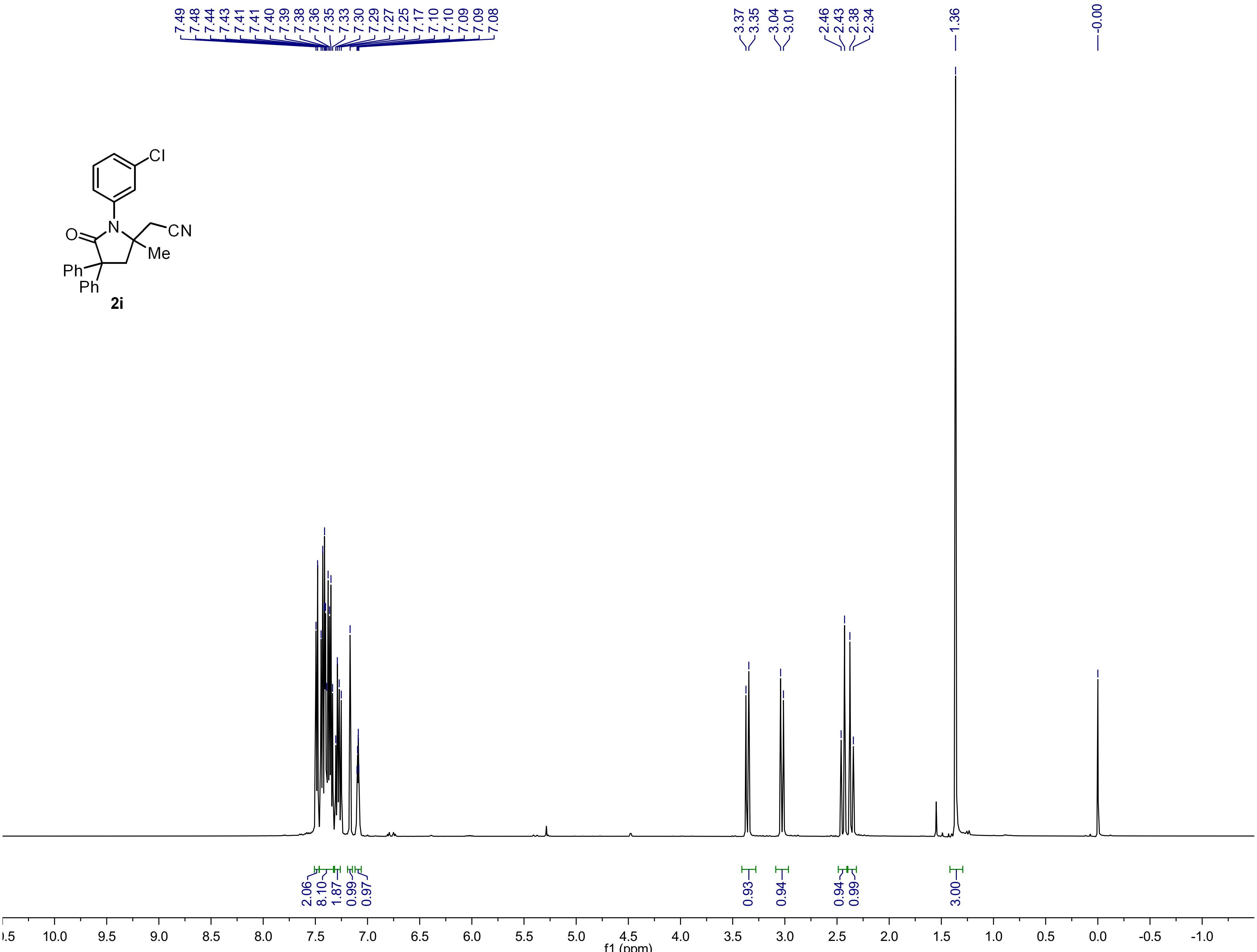
O
CN
Me
Ph
Ph
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.29
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7.10
7.10
7.09
7.09
7.08
3.37
3.35
3.04
3.01
2.46
2.43
2.38
2.34
1.36
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Cl
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CN
Me
Ph
Ph
2i
2.06
8.10
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0.93
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3.00
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9.0
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6.5
6.0
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5.0
4.5
4.0
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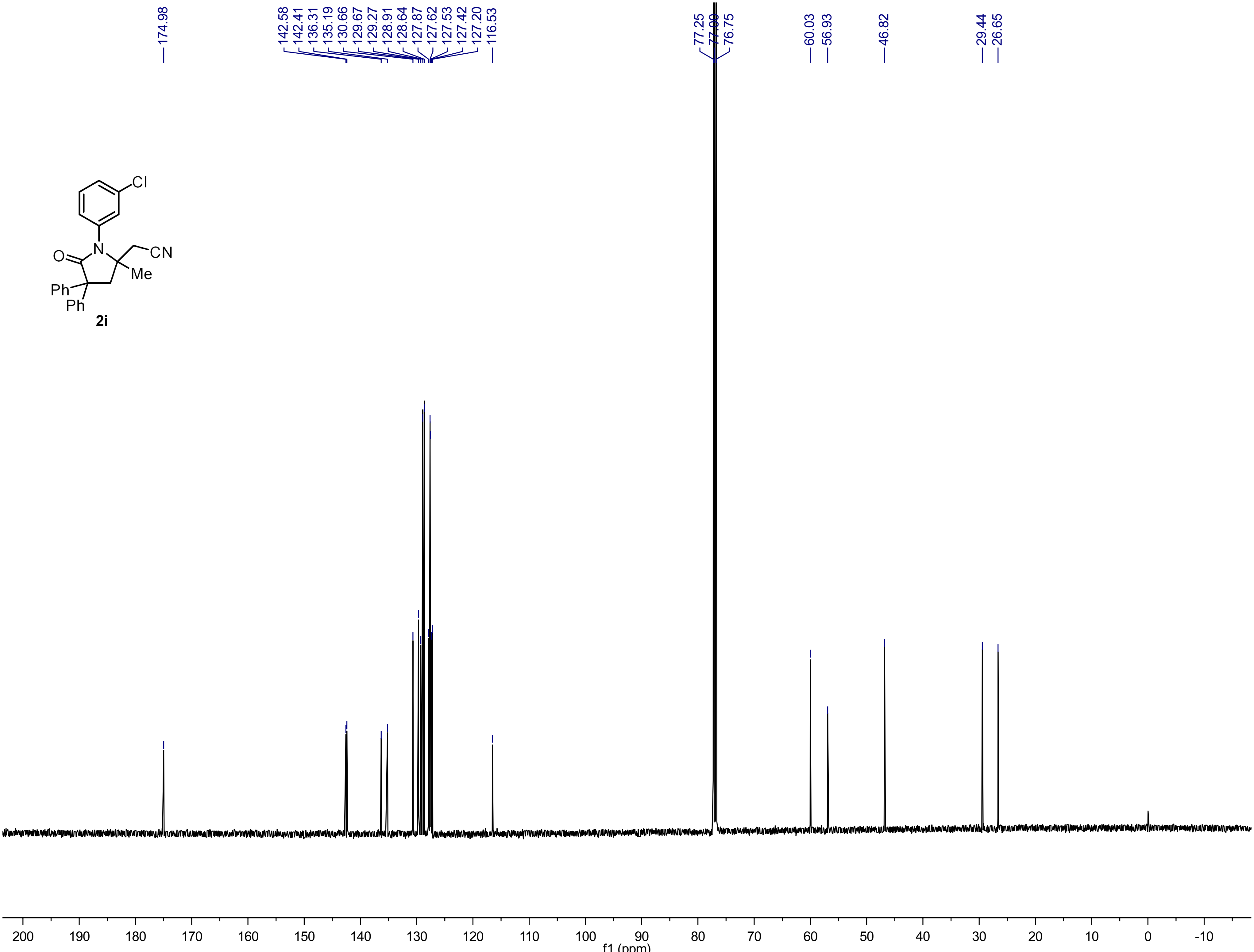
f1 (ppm)



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127.53
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127.20
116.53
77.25
77.00
76.75
60.03
56.93
46.82
29.44
26.65
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CN
Me
Ph
Ph
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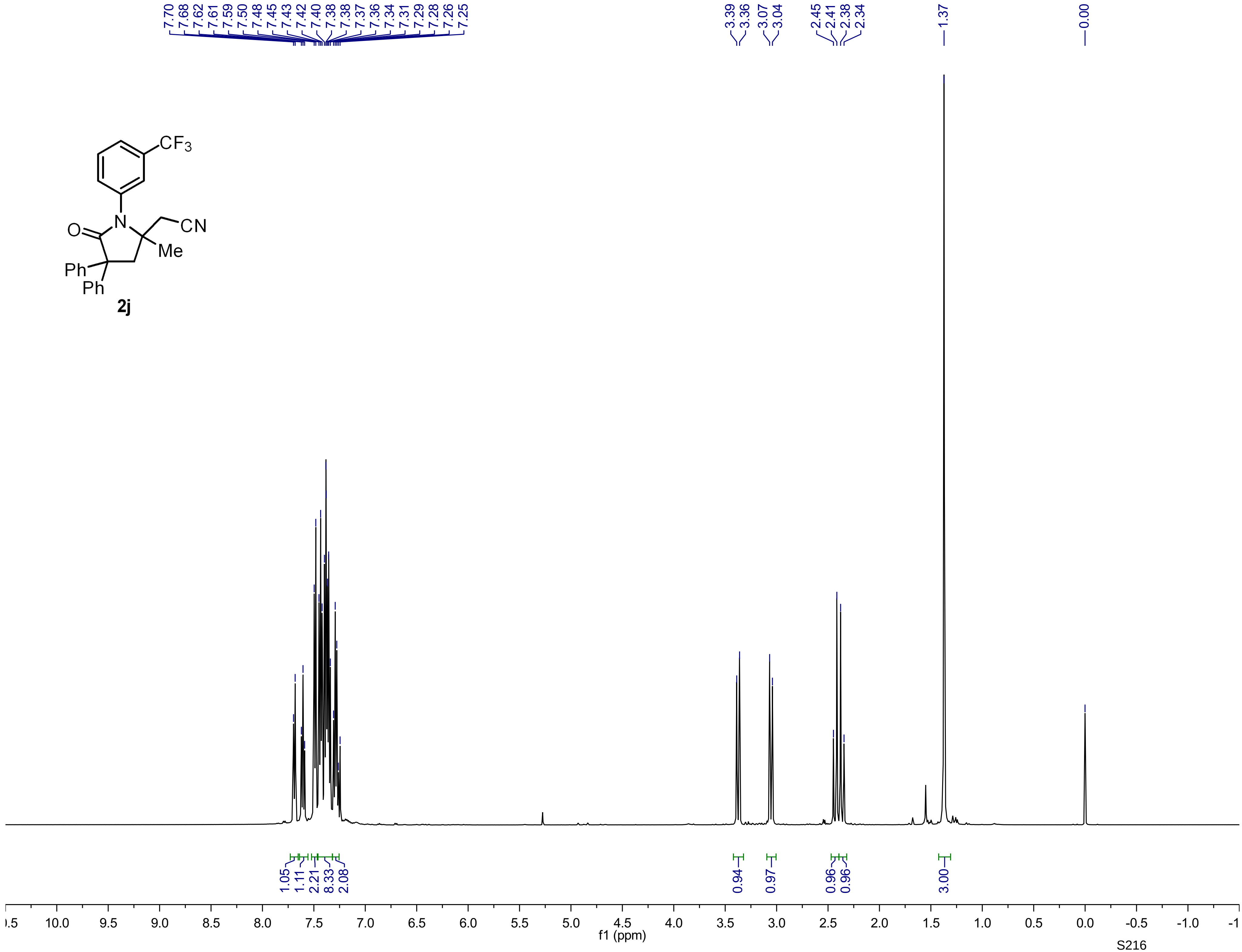
f1 (ppm)



CF3
O
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CN
Me
Ph
Ph
2j
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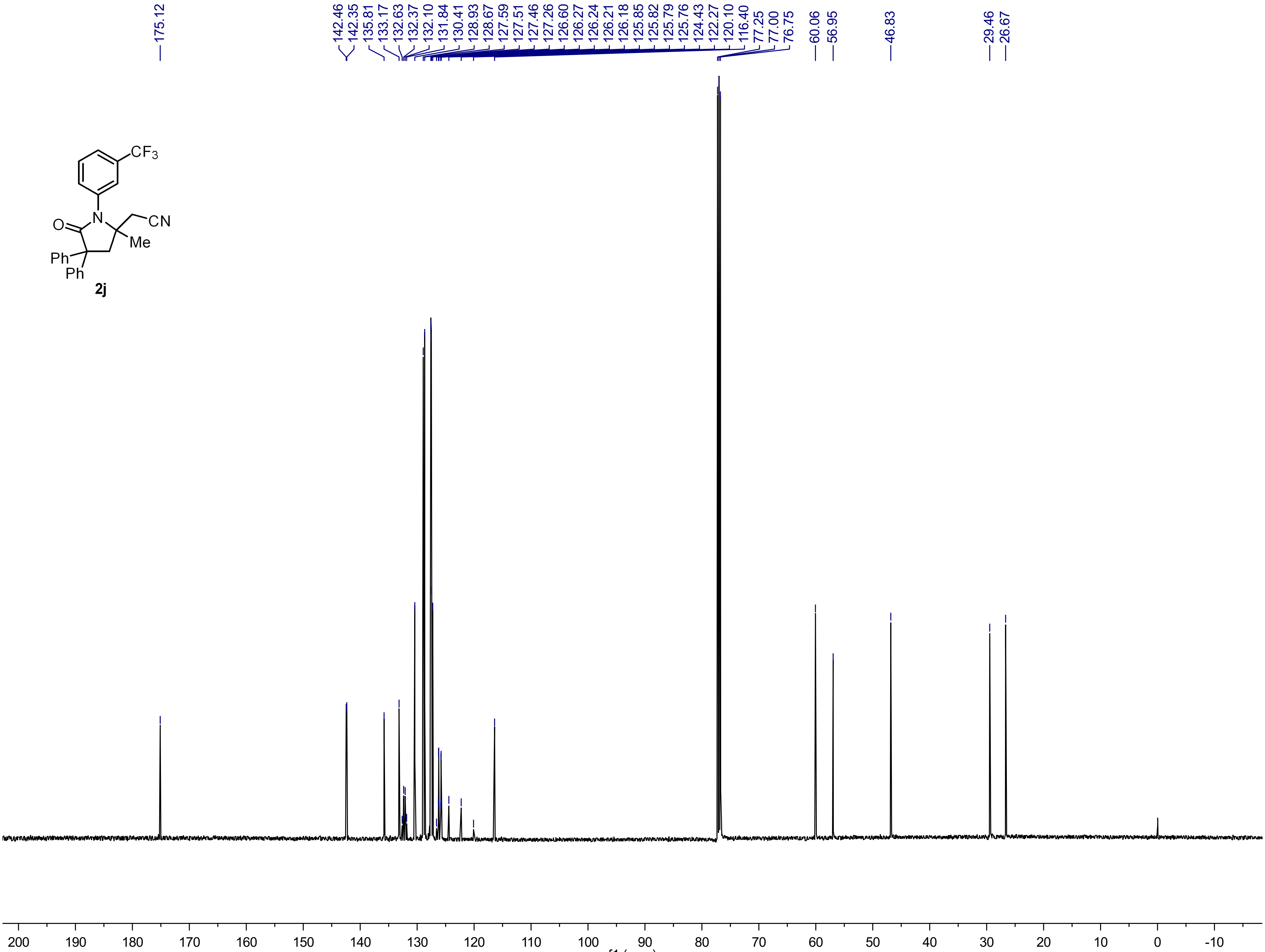
3.39 3.36 3.07 3.04
2.45 2.41 2.38 2.34
1.37
0.00
1.05 1.11 2.21 8.33 2.08
0.94
0.97
0.96 0.96
3.00
f1 (ppm)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126.18
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122.27
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77.00
76.75
60.06
56.95
46.83
29.46
26.67
CF3
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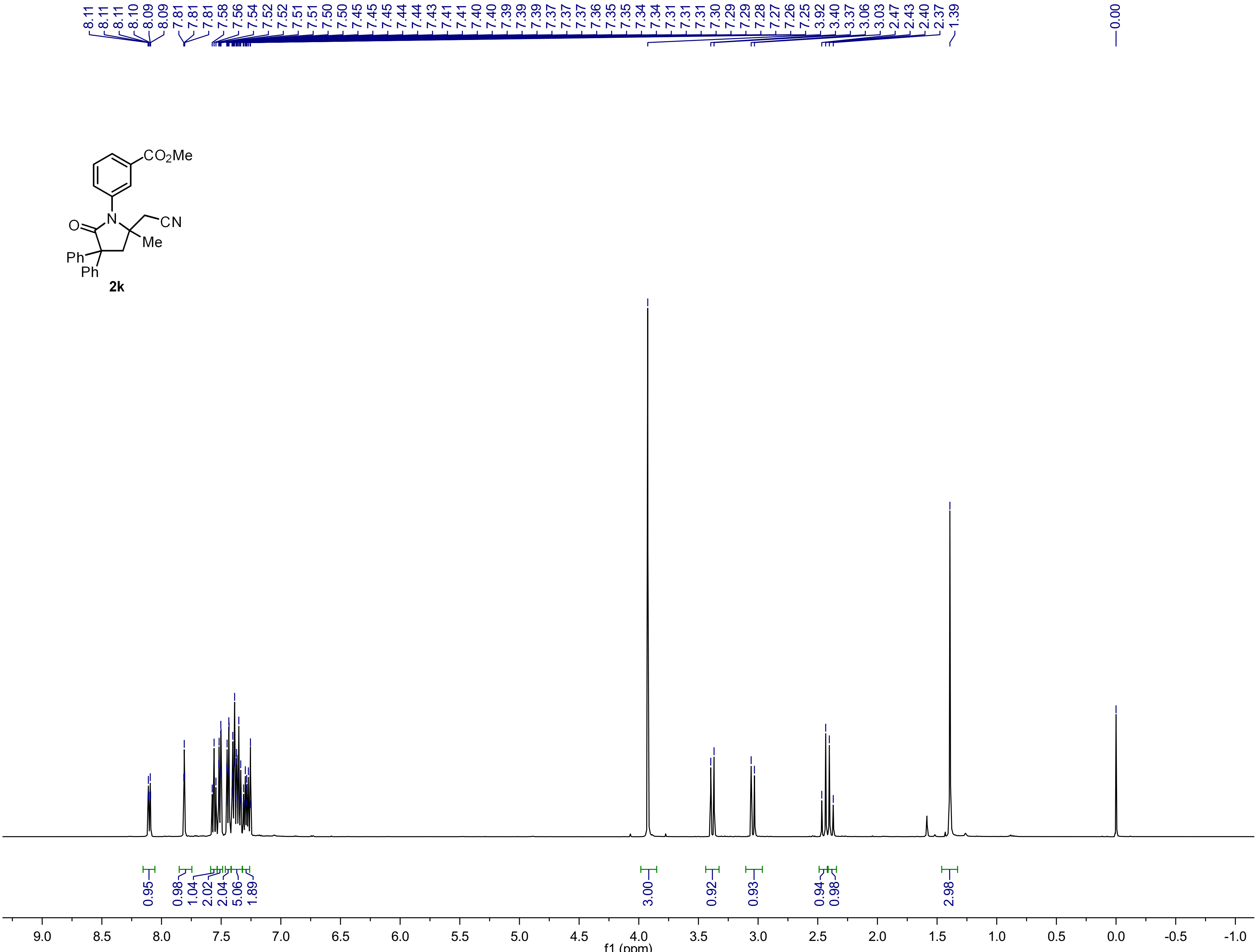
N
CN
Me
Ph
Ph
2j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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CO_2Me
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CN
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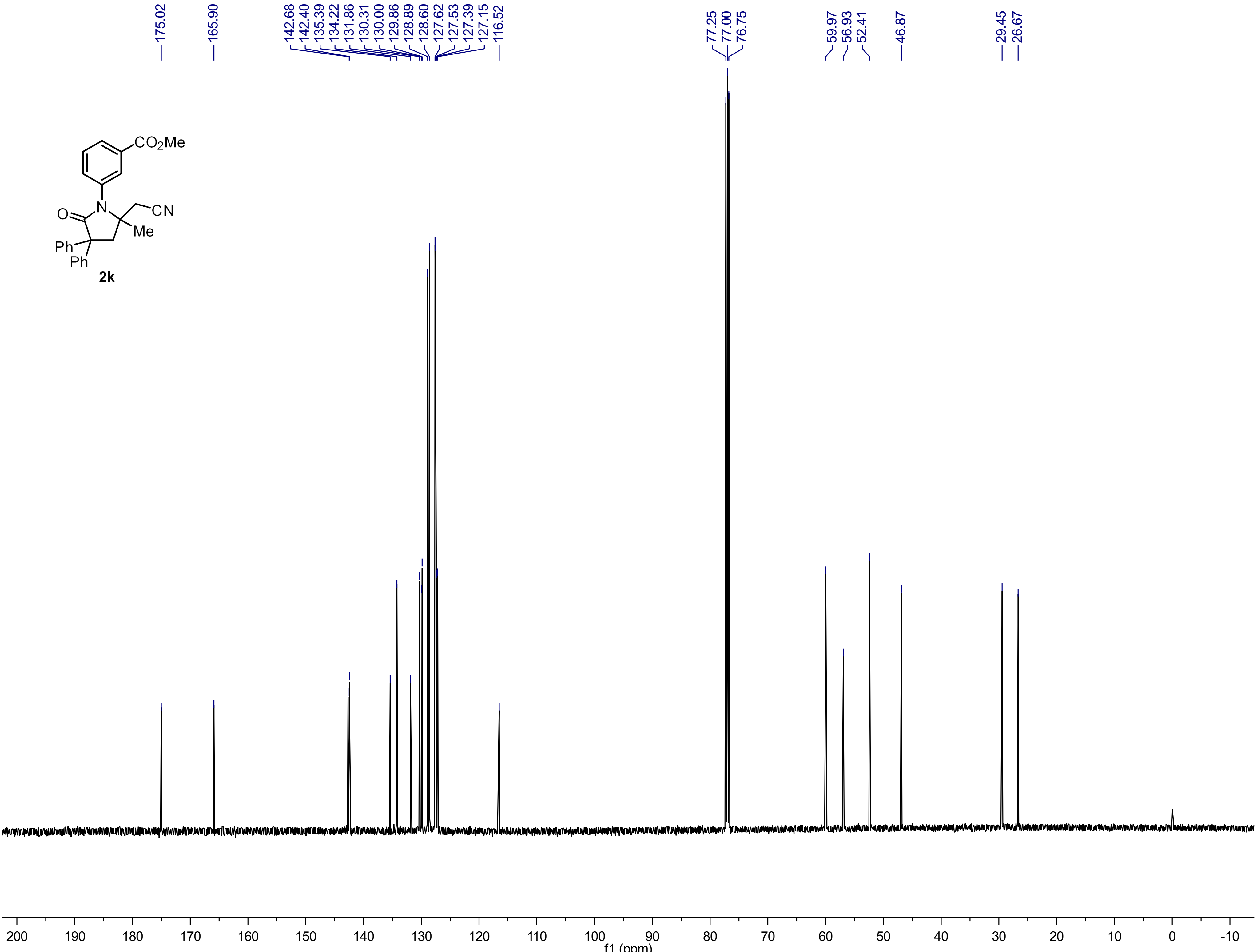
f1 (ppm)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127.62
127.53
127.39
127.15
116.52
77.25
77.00
76.75
59.97
56.93
52.41
46.87
29.45
26.67
CO_2Me
N
CN
O
Me
Ph
Ph
2k
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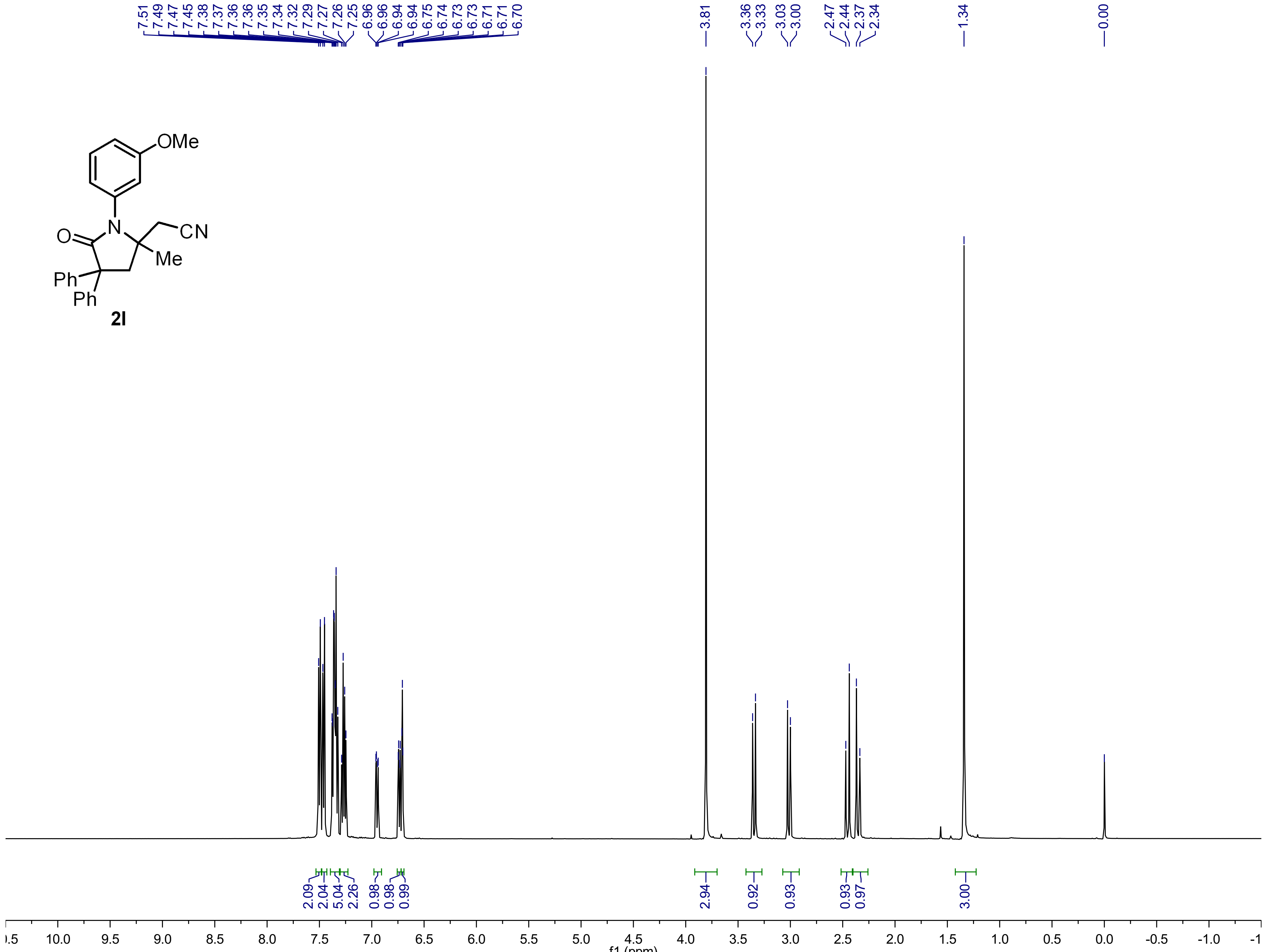
f1 (ppm)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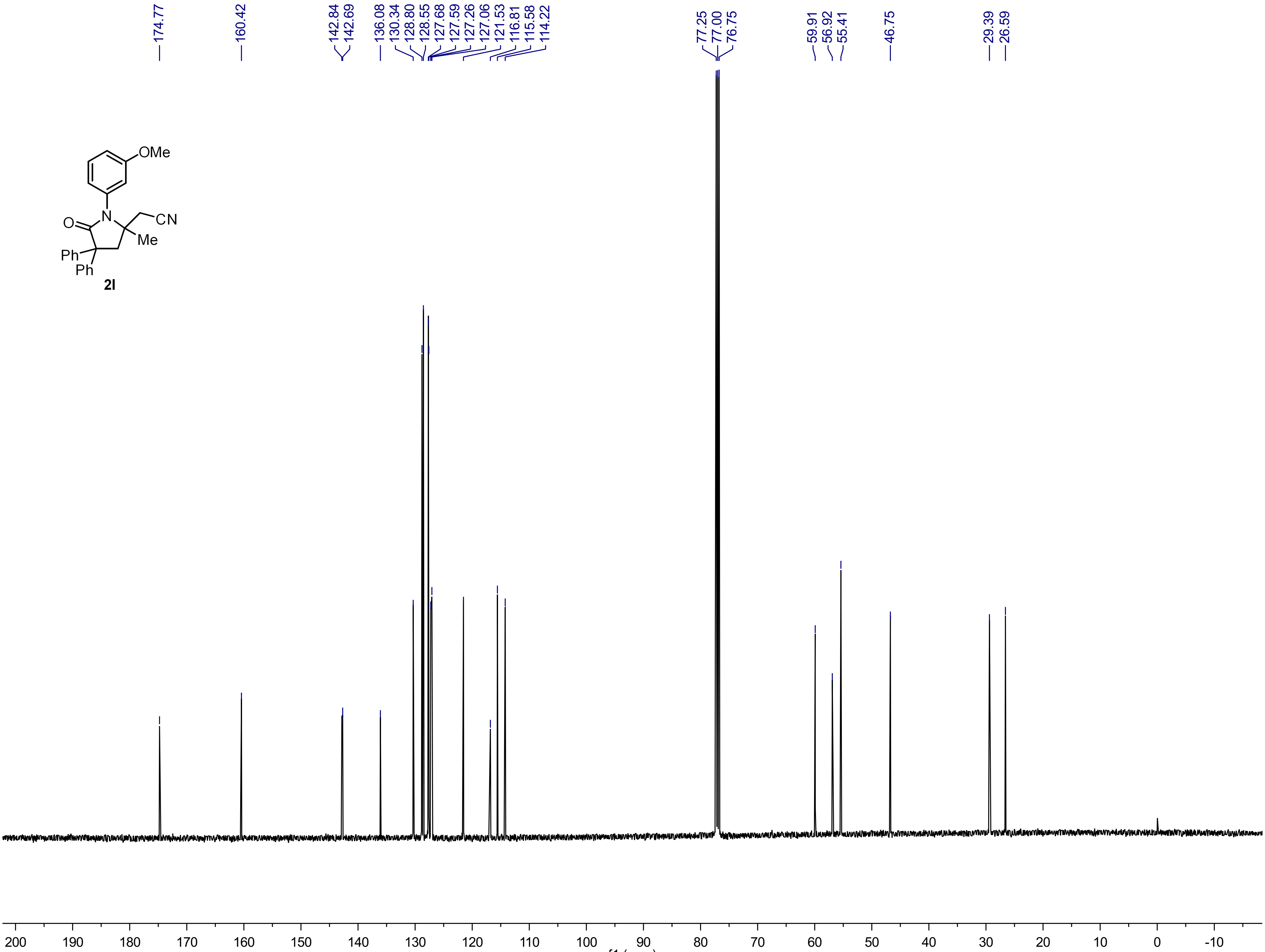
3.81
3.36 3.33 3.03 3.00
2.47 2.44 2.37 2.34
1.34
0.00
OMe
O
N
CN
Me
Ph
Ph
2l
2.09 2.04 5.04 2.26 0.98 0.98 0.99
2.94
0.92
0.93
0.93 0.97
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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127.26
127.06
121.53
116.81
115.58
114.22
77.25
77.00
76.75
59.91
56.92
55.41
46.75
29.39
26.59
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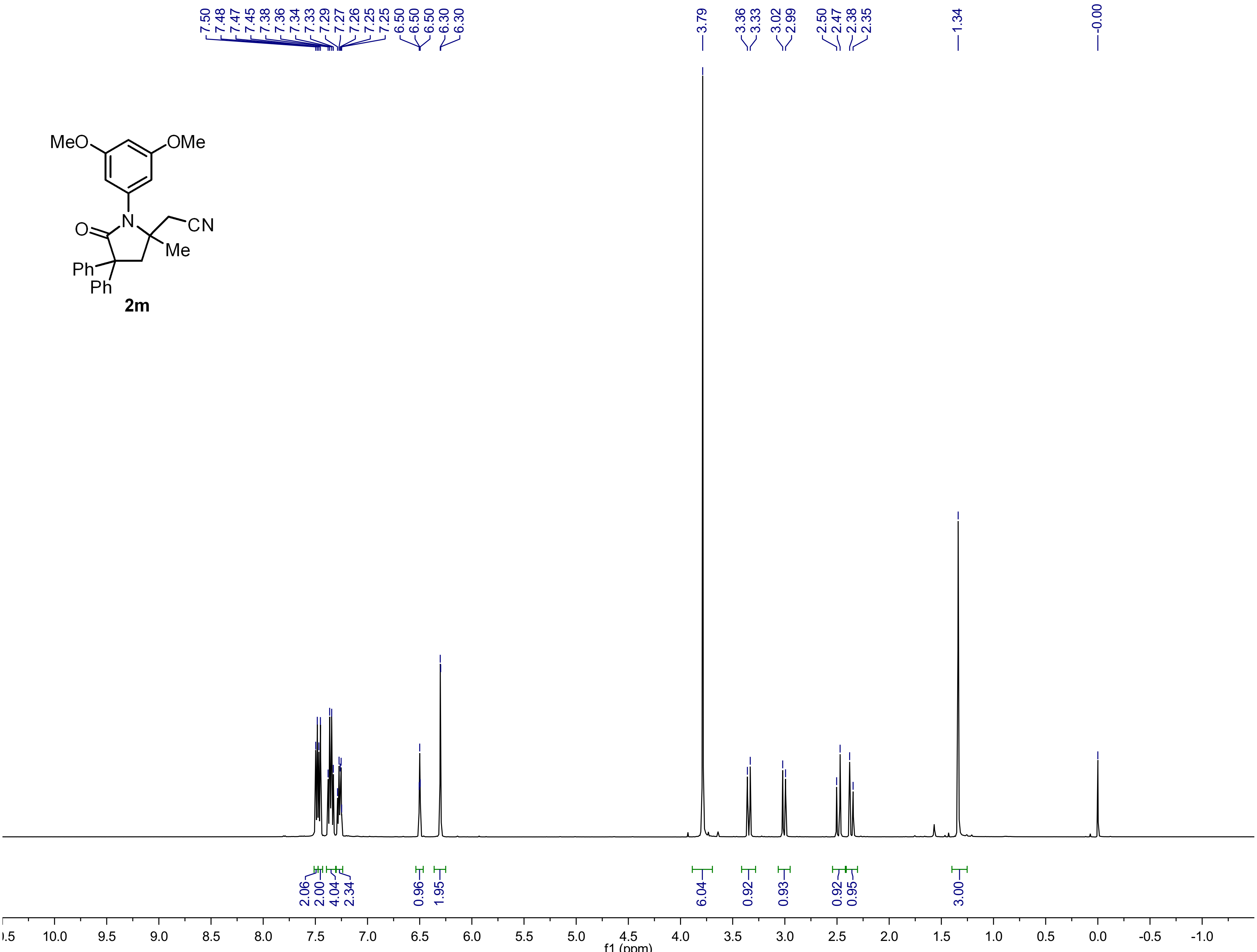
N
CN
Me
Ph
Ph
2l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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6.50
6.50
6.50
6.30
6.30
3.79
3.36
3.33
3.02
2.99
2.50
2.47
2.38
2.35
1.34
-0.00
MeO
OMe
N
O
CN
Me
Ph
Ph
2m
2.06
2.00
4.04
2.34
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1.95
6.04
0.92
0.93
0.92
0.95
3.00
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
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2.0
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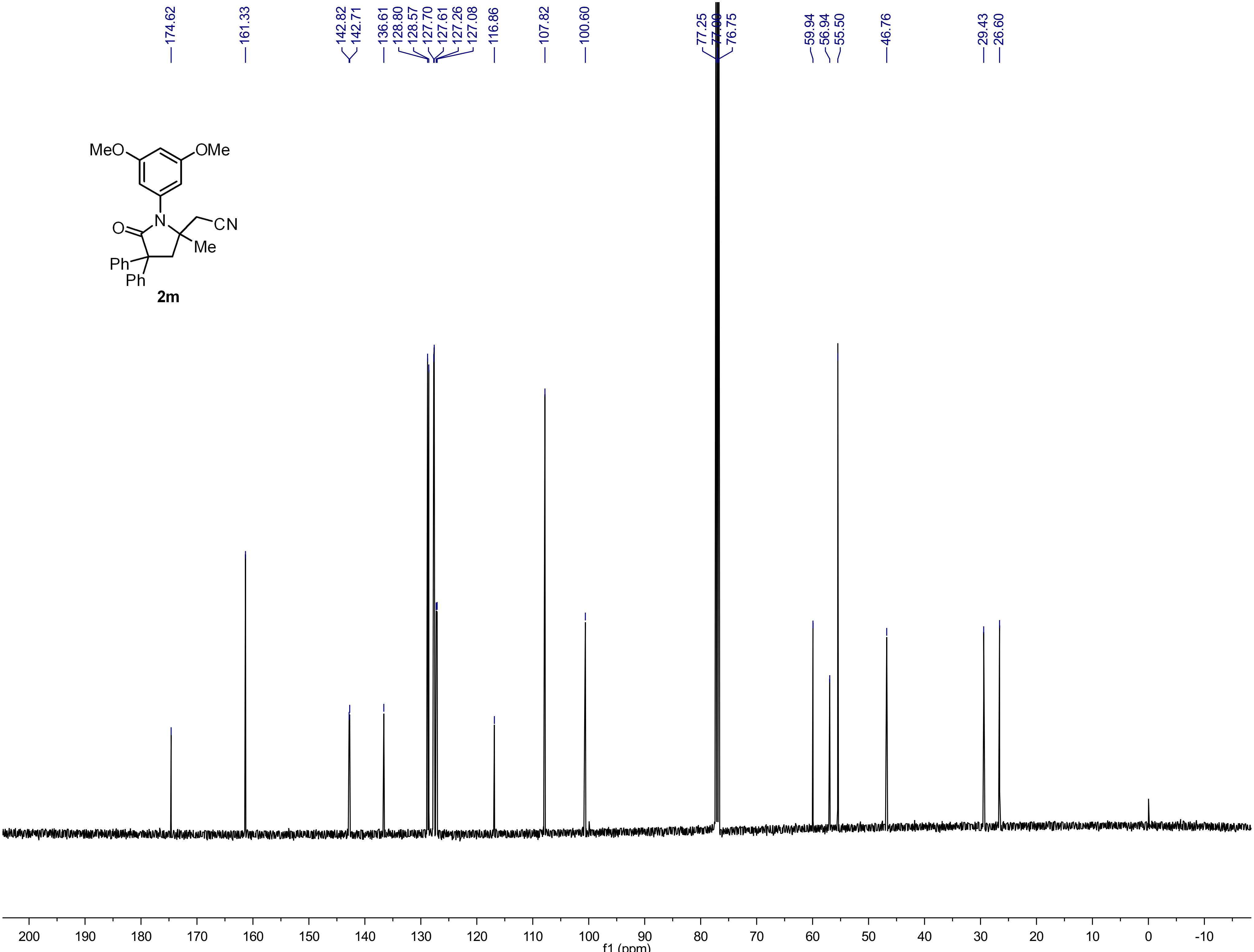
-0.5
-1.0
f1 (ppm)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127.26
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107.82
100.60
77.25
77.00
76.75
59.94
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29.43
26.60
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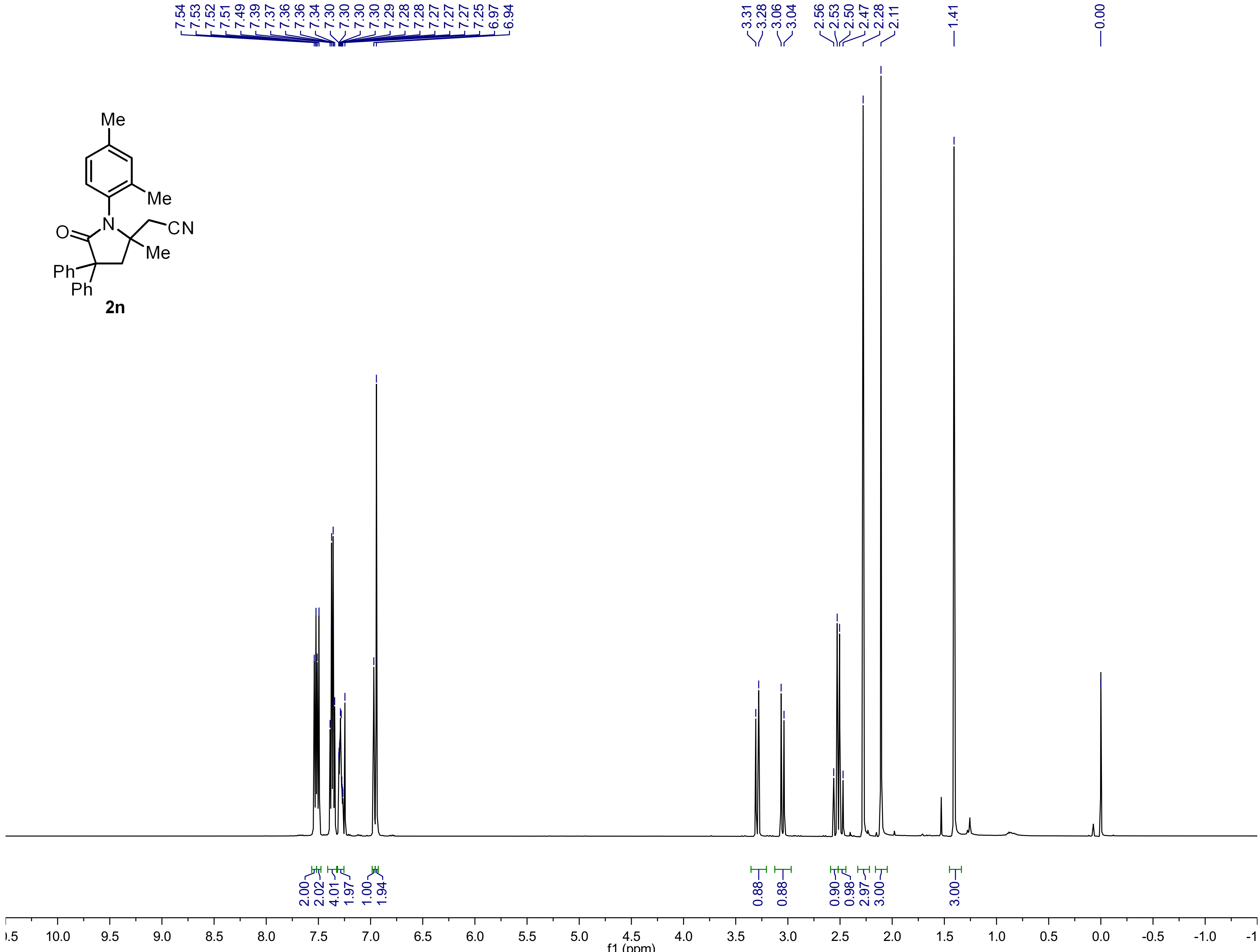
OMe
N
O
CN
Me
Ph
Ph
2m
f1 (ppm)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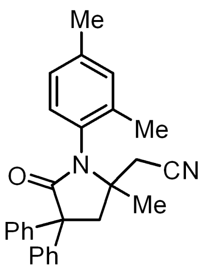
3.31 3.28 3.06 3.04 2.56 2.53 2.50 2.47 2.28 2.11 1.41 0.00
Me
Me
O
N
CN
Me
Ph
Ph
2n
2.00 2.02 4.01 1.97 1.00 1.94 0.88 0.88 0.90 0.98 2.97 3.00 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



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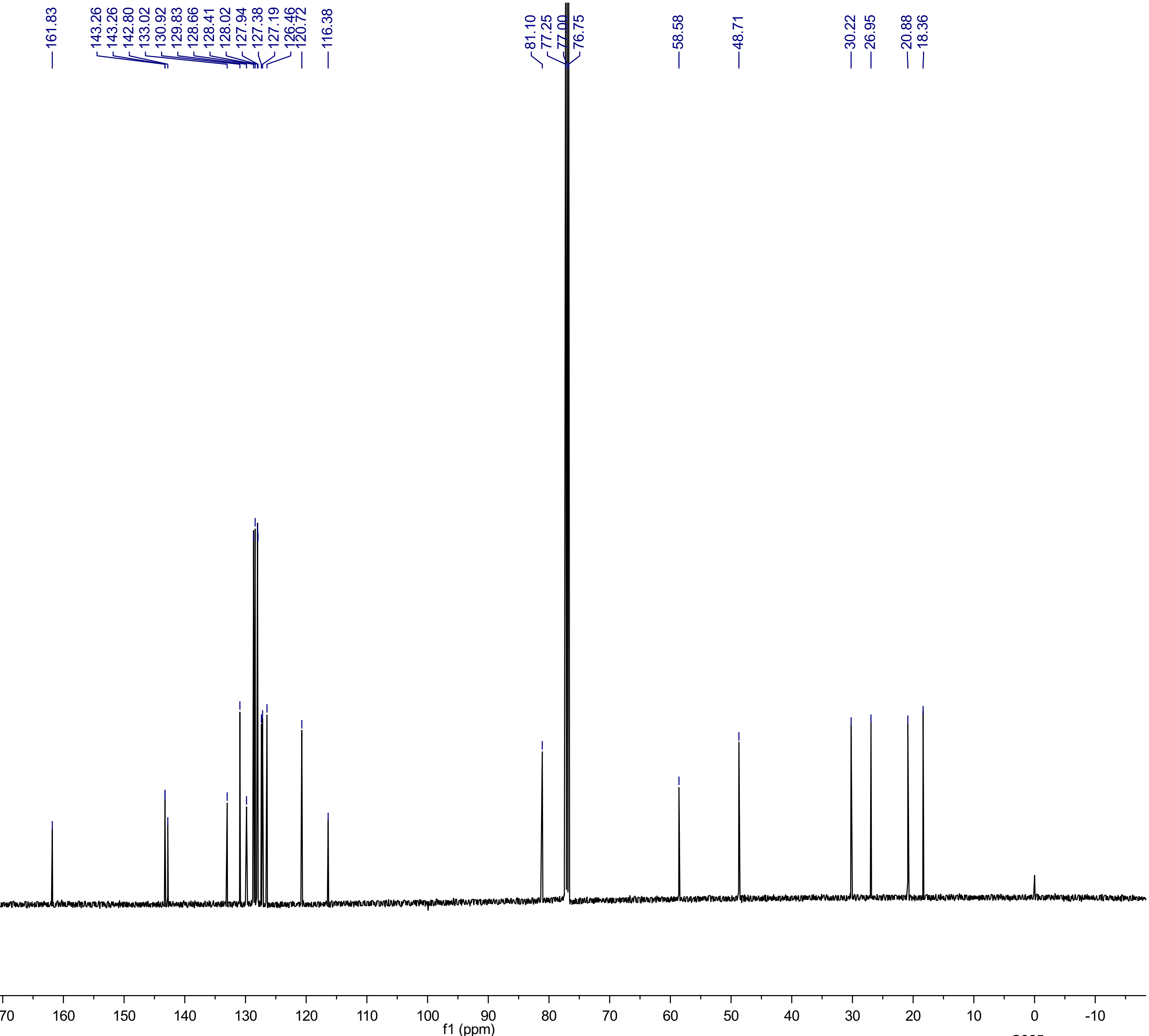

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129.83
128.66
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128.02
127.94
127.38
127.19
126.46
120.72
116.38
81.10
77.25
77.00
76.75
58.58
48.71
30.22
26.95
20.88
18.36
200
190
180
170
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100
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80
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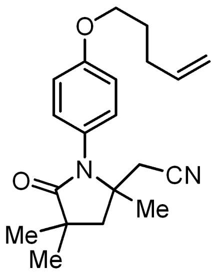
40
30
20
10
0
-10
f1 (ppm)



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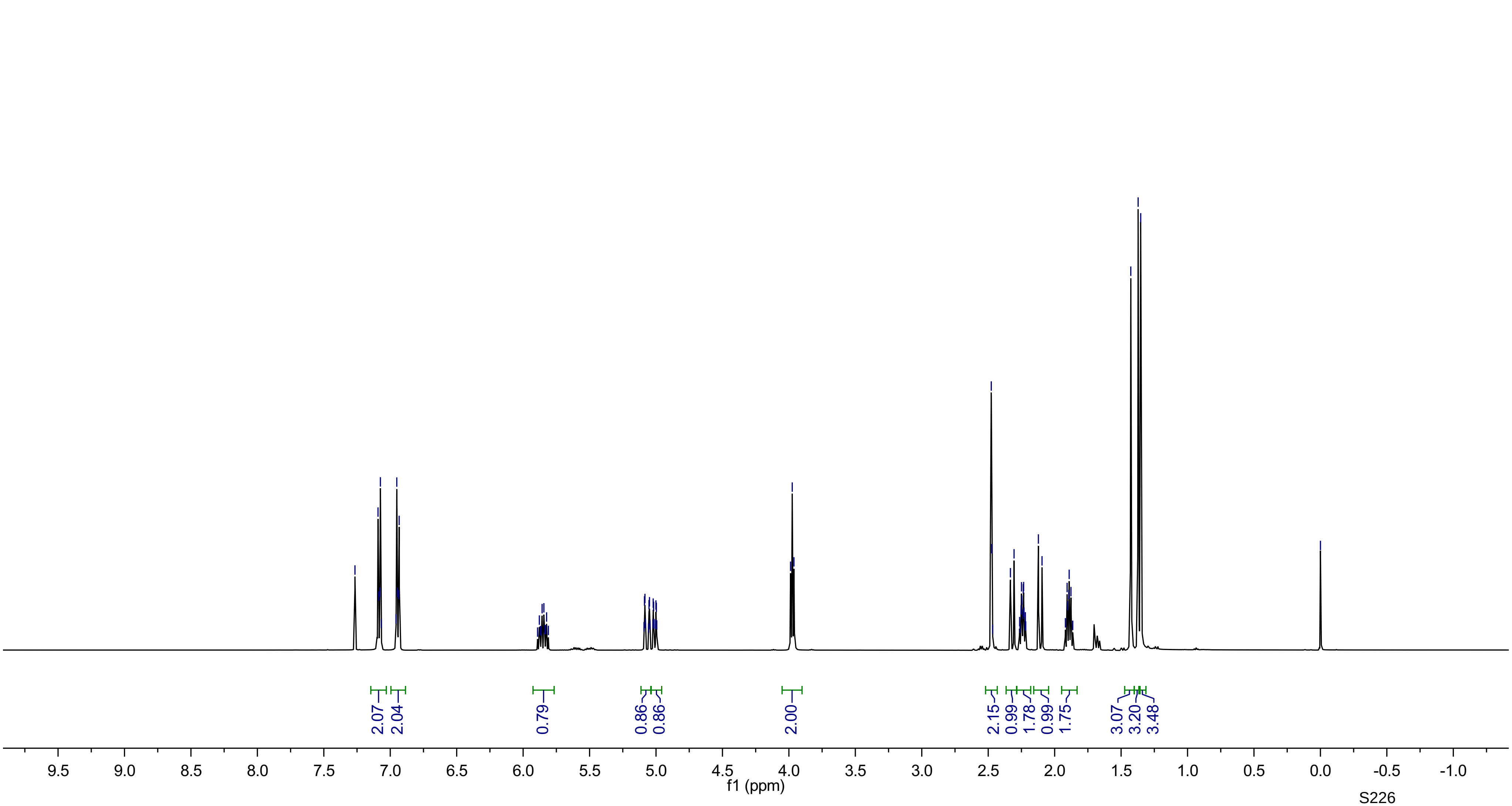
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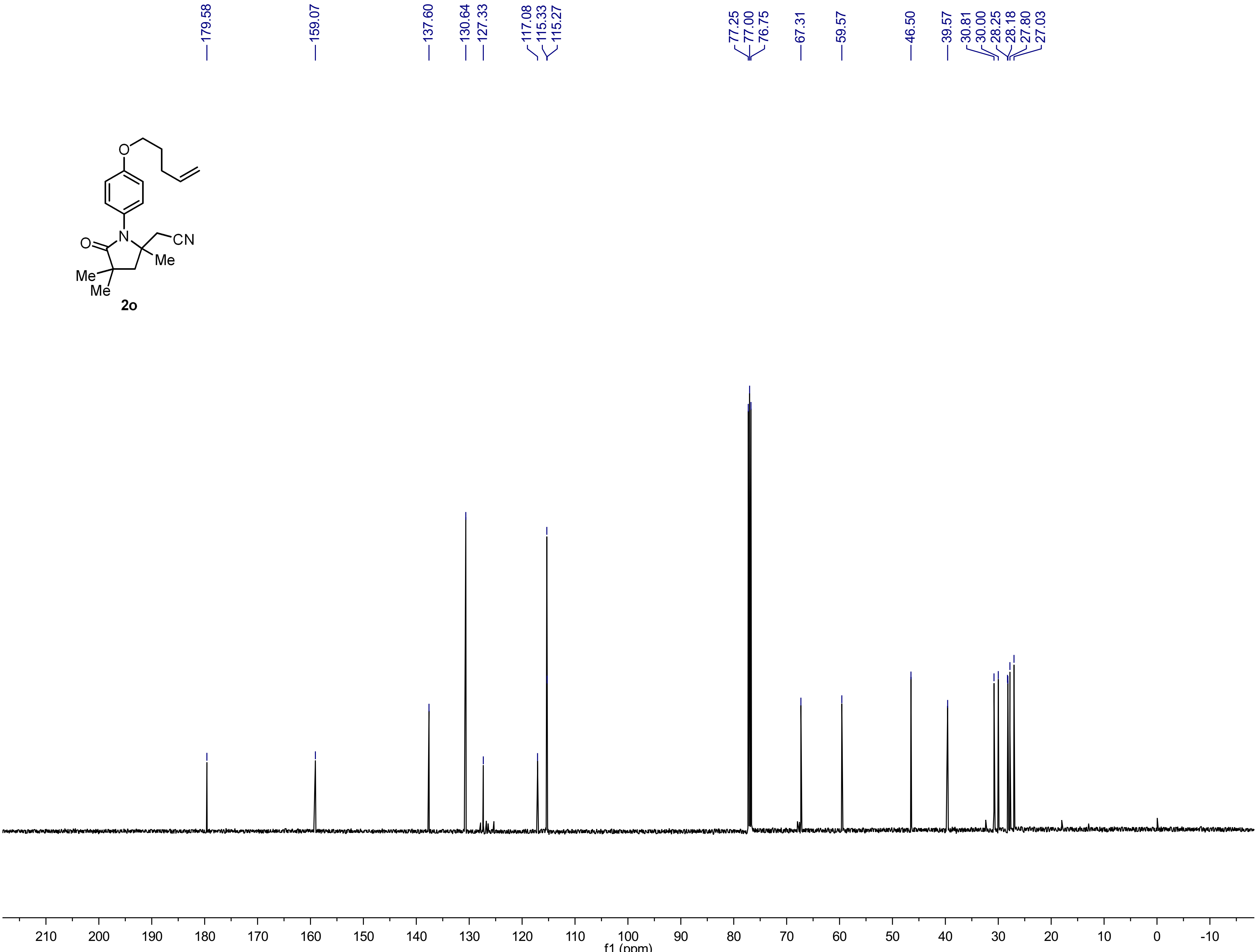
2.07 2.04 0.79 0.86 0.86 2.00 2.15 0.99 1.78 0.99 1.75 3.07 3.20 3.48
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


2o
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117.08
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115.27
77.25
77.00
76.75
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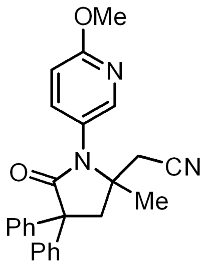
59.57
46.50
39.57
30.81
30.00
28.25
28.18
27.80
27.03
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OMe
N
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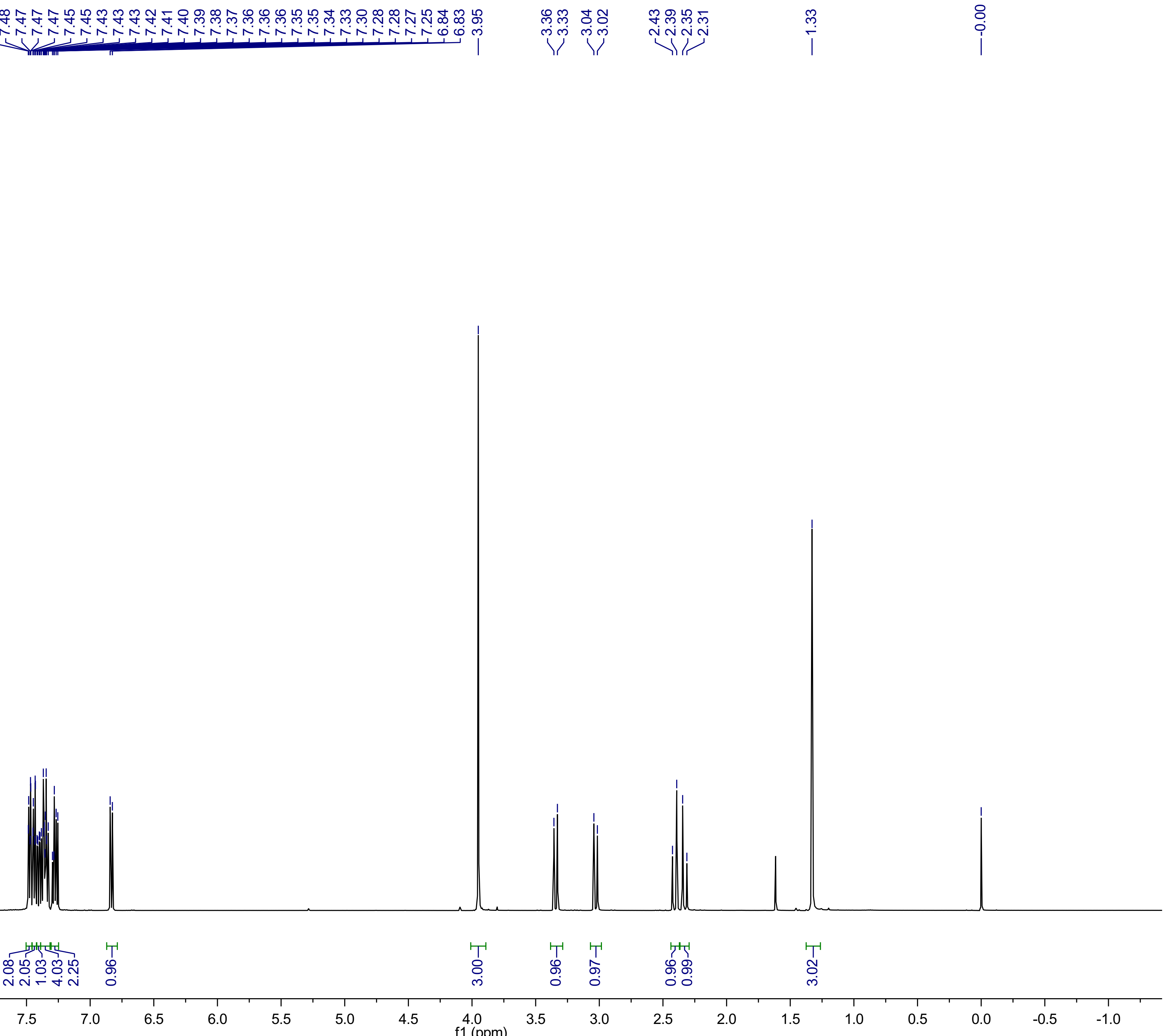
N
CN
Me
Ph
Ph

2p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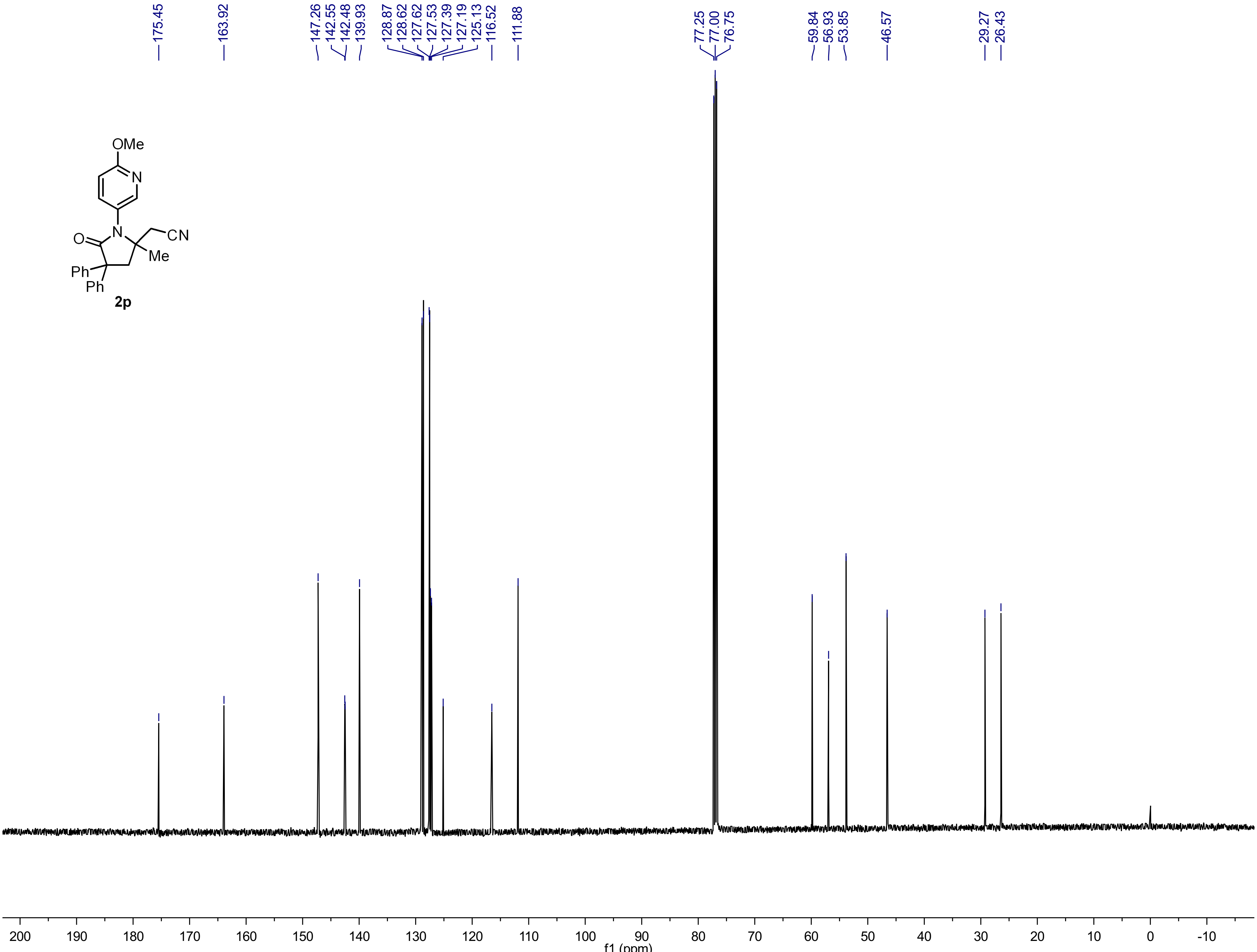
7.43
7.43
7.43
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.36
7.36
7.35
7.35
7.34
7.33
7.30
7.28
7.28
7.27
7.25
6.84
6.83
3.95
3.36
3.33
3.04
3.02
2.43
2.39
2.35
2.31
1.33
-0.00
0.99
2.08
2.05
1.03
4.03
2.25
0.96
3.00
0.96
0.97
0.96
0.99
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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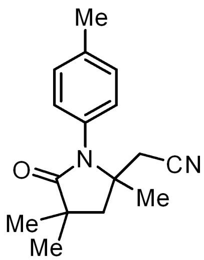
127.19
125.13
116.52
111.88
77.25
77.00
76.75
59.84
56.93
53.85
46.57
29.27
26.43
OMe
N
O
N
CN
Me
Ph
Ph
2p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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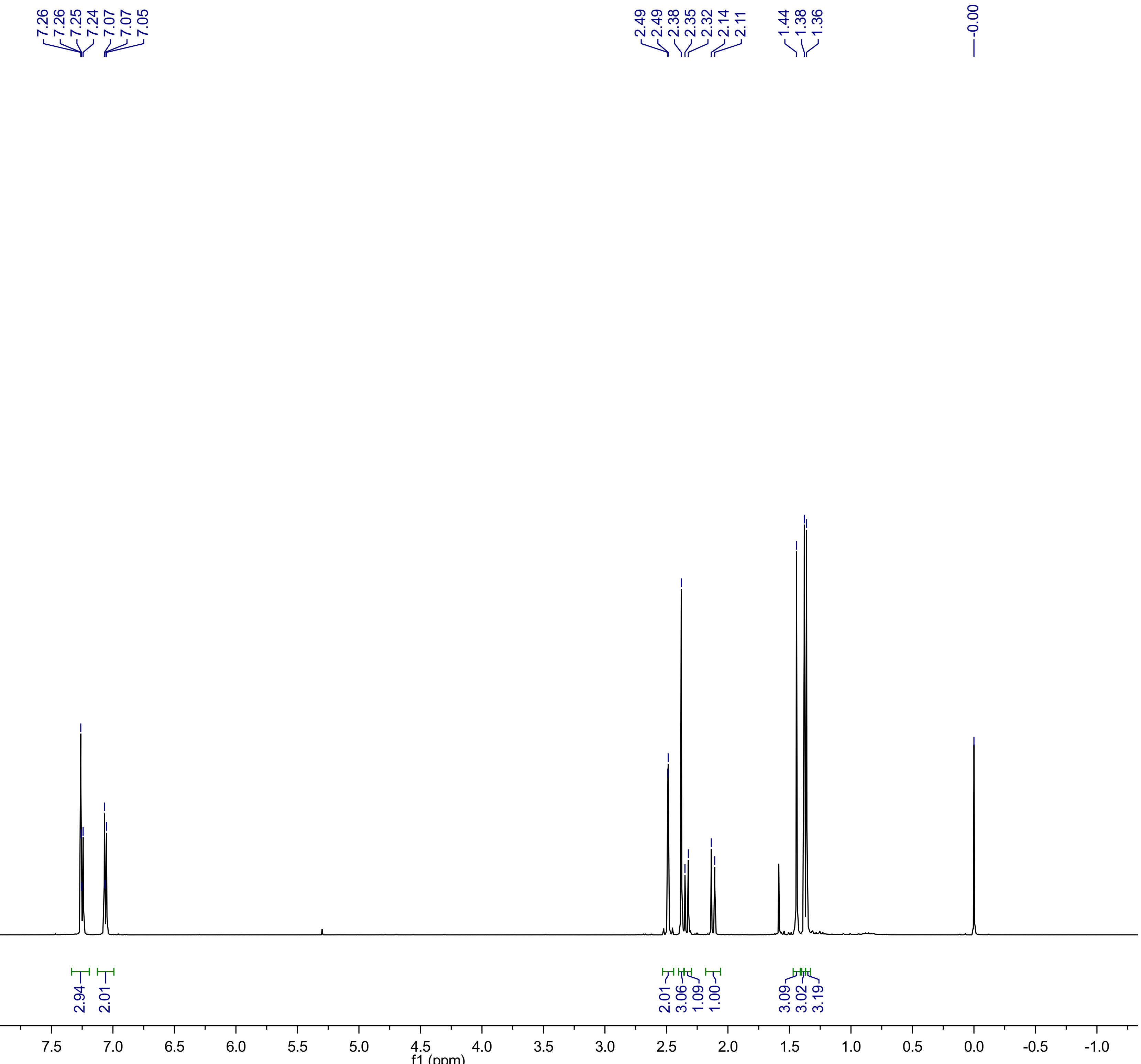

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7.24
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7.07
7.05
2.49
2.49
2.38
2.35
2.32
2.14
2.11
1.44
1.38
1.36
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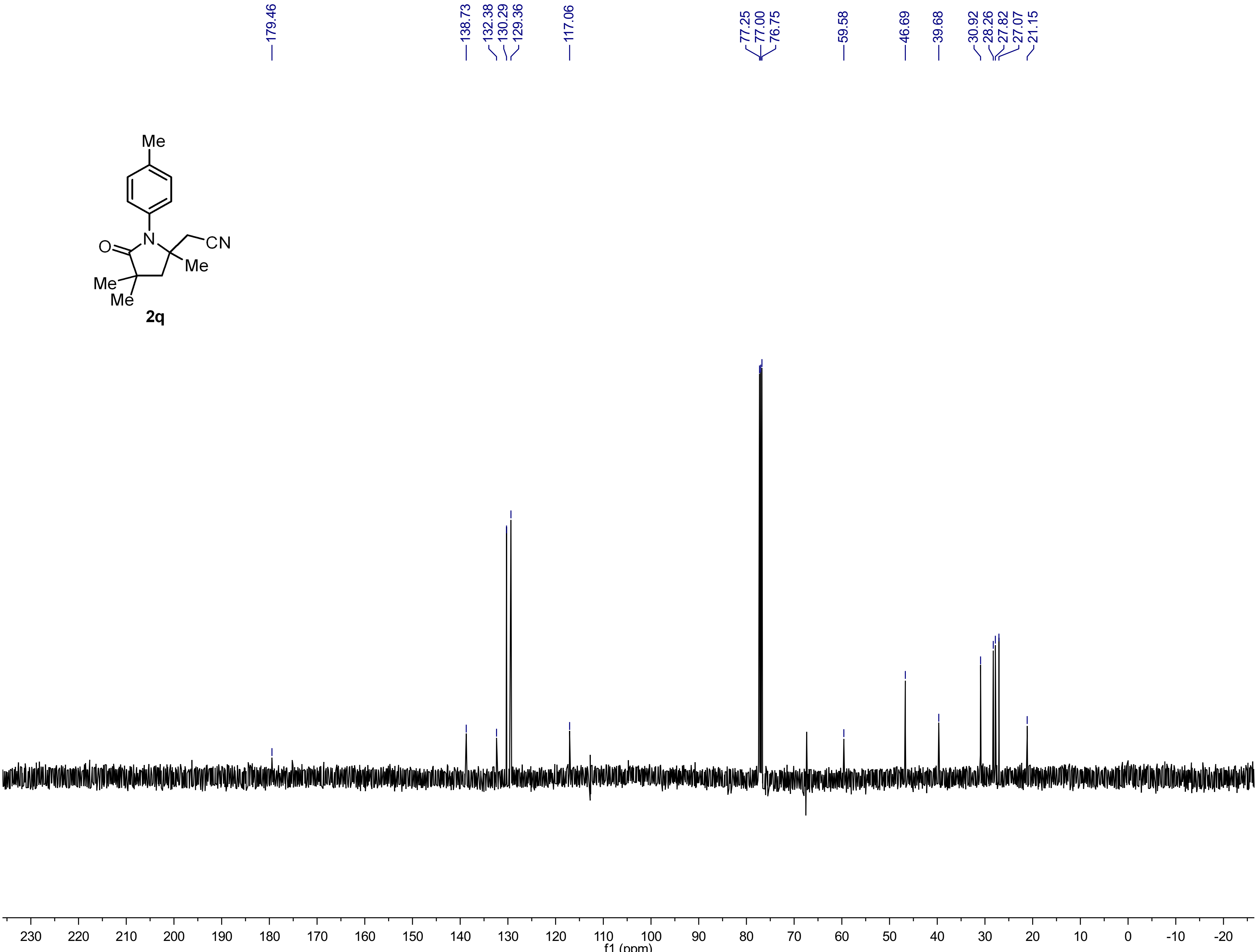
2.01
2.01
3.06
1.09
1.00
3.09
3.02
3.19
f1 (ppm)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77.00
76.75
59.58
46.69
39.68
30.92
28.26
27.82
27.07
21.15
Me
O
N
CN
Me
Me
Me
2q
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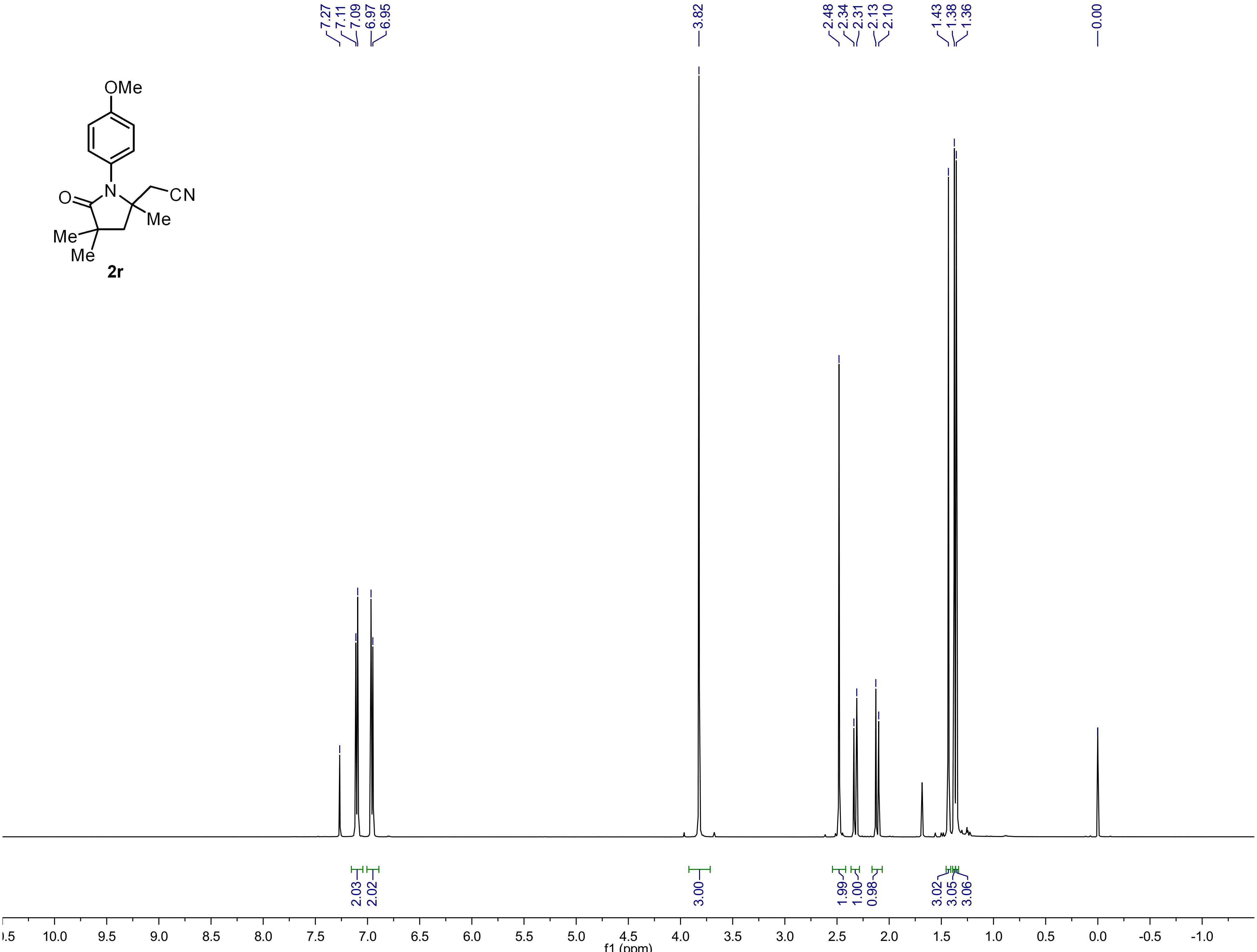
f1 (ppm)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3.82
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2.34
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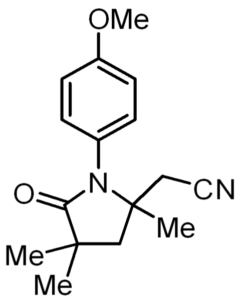
2.13
2.10
1.43
1.38
1.36
0.00
OMe
O
N
CN
Me
Me
Me
2r
2.03
2.02
3.00
1.99
1.00
0.98
3.02
3.05
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



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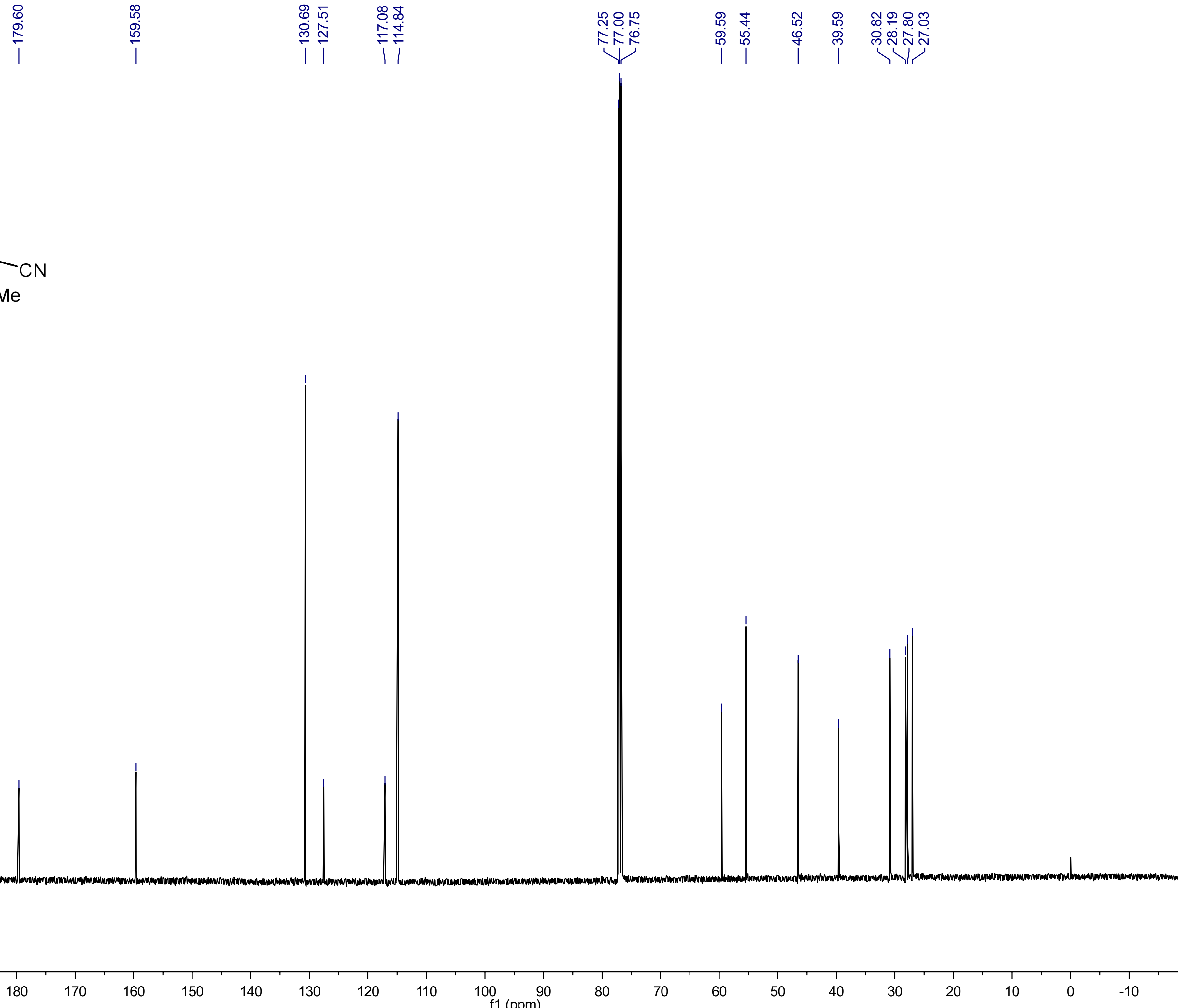

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76.75
59.59
55.44
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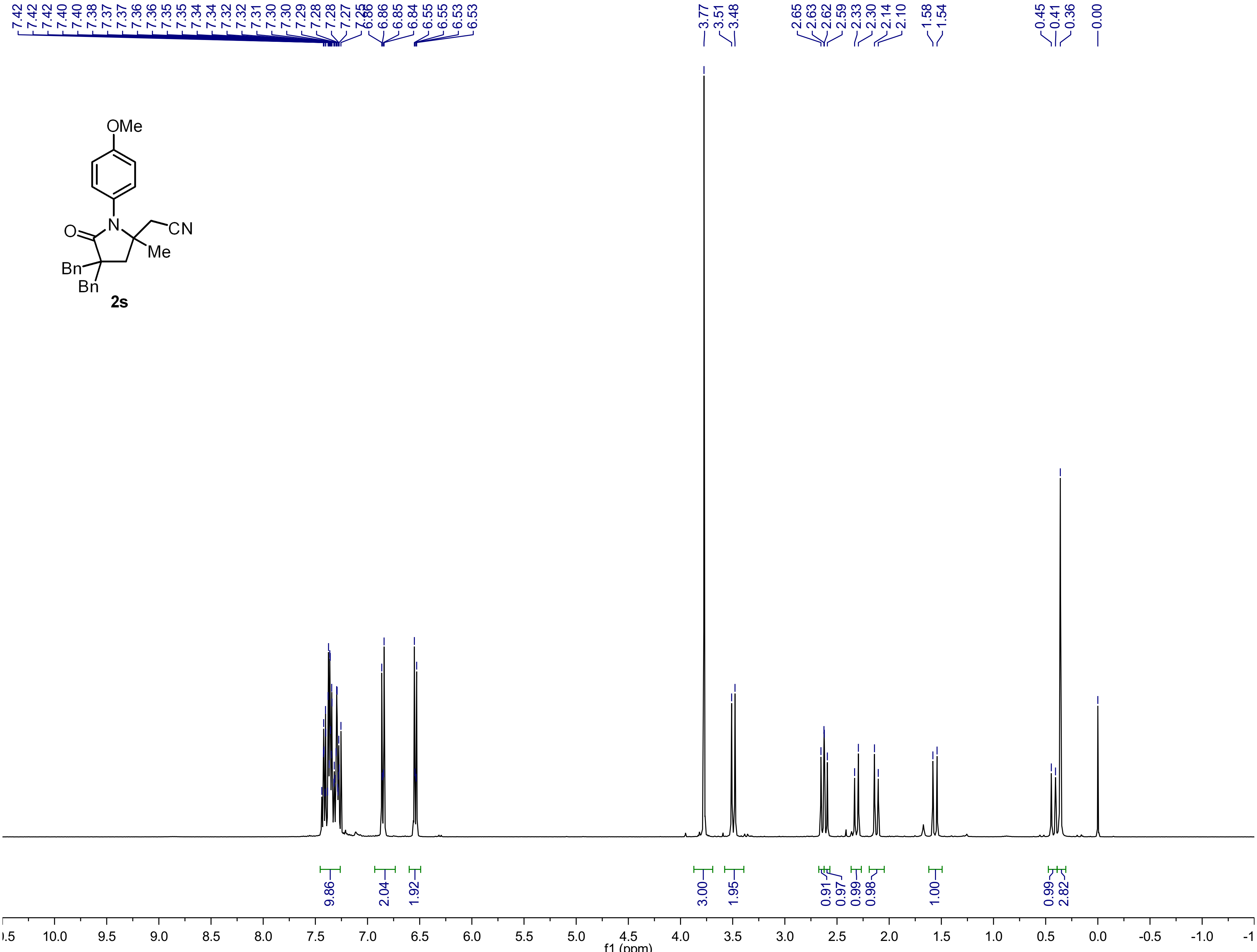
28.19
27.80
27.03
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.30
7.29
7.28
7.28
7.27
7.25
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6.86
6.85
6.84
6.55
6.55
6.53
6.53
3.77
3.51
3.48
2.65
2.63
2.62
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2.33
2.30
2.14
2.10
1.58
1.54
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0.36
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OMe
N
O
CN
Me
Bn
Bn
2s
9.86
2.04
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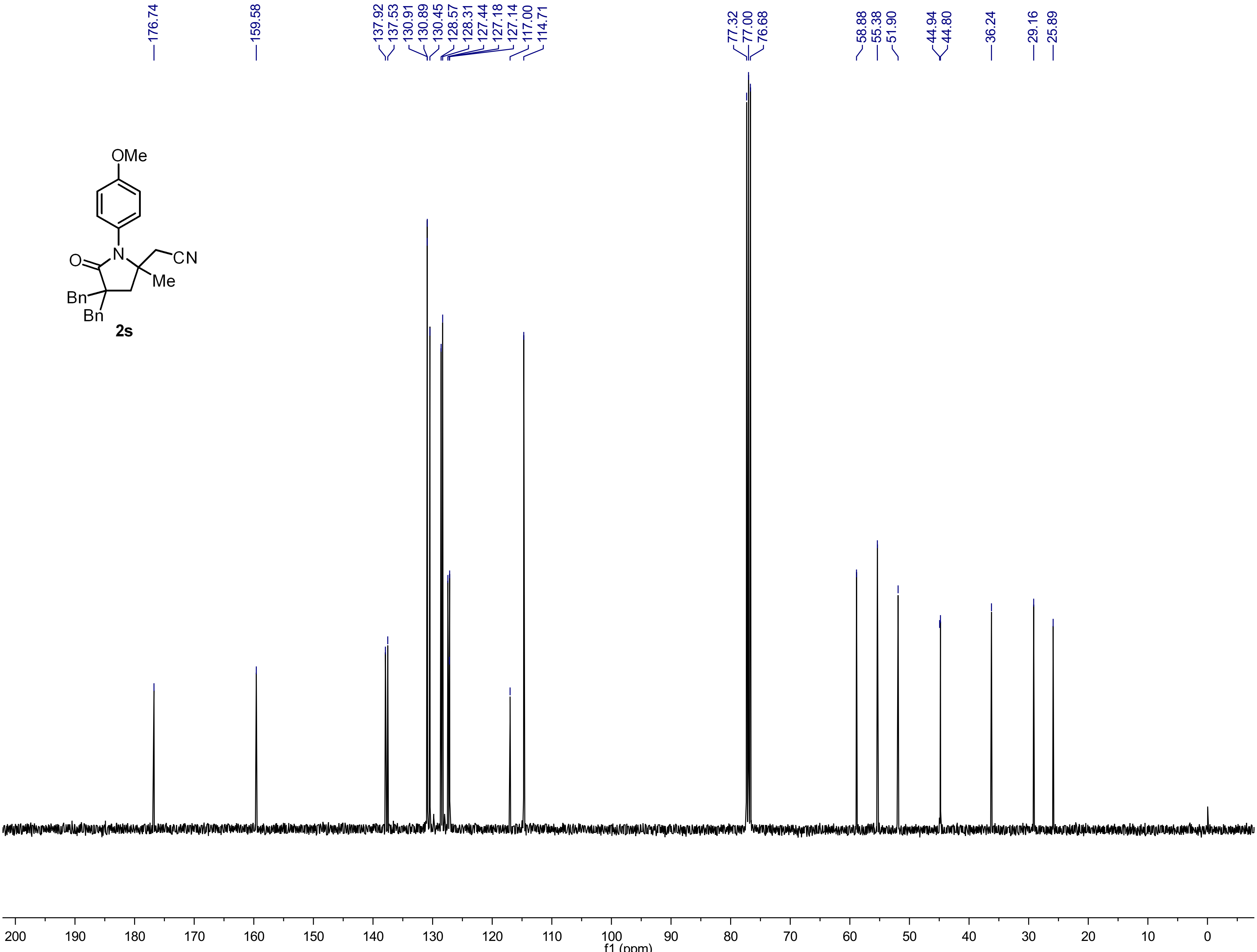
1.00
0.99
2.82
f1 (ppm)



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77.00
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58.88
55.38
51.90
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OMe
O
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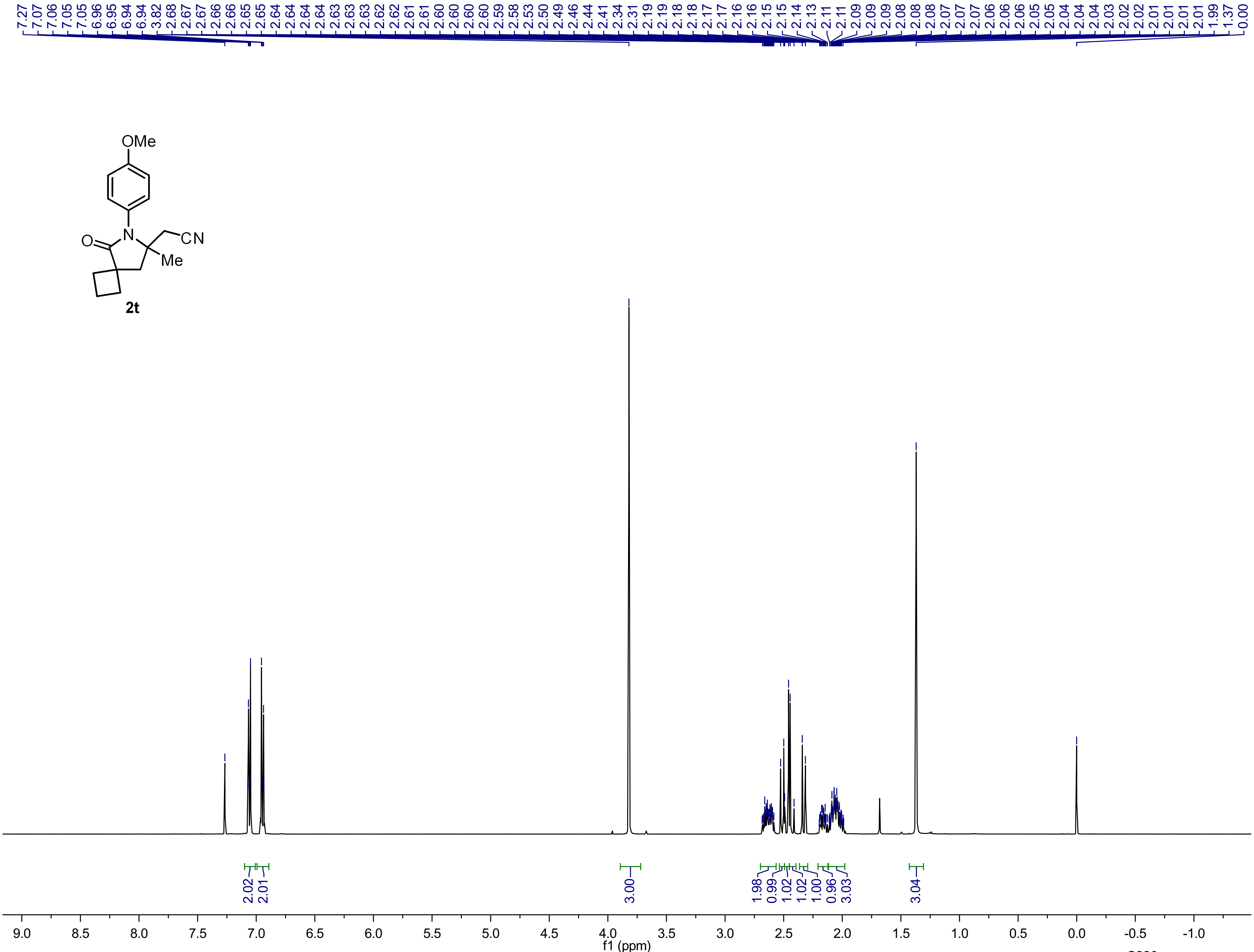
CN
Me
Bn
Bn
2s
f1 (ppm)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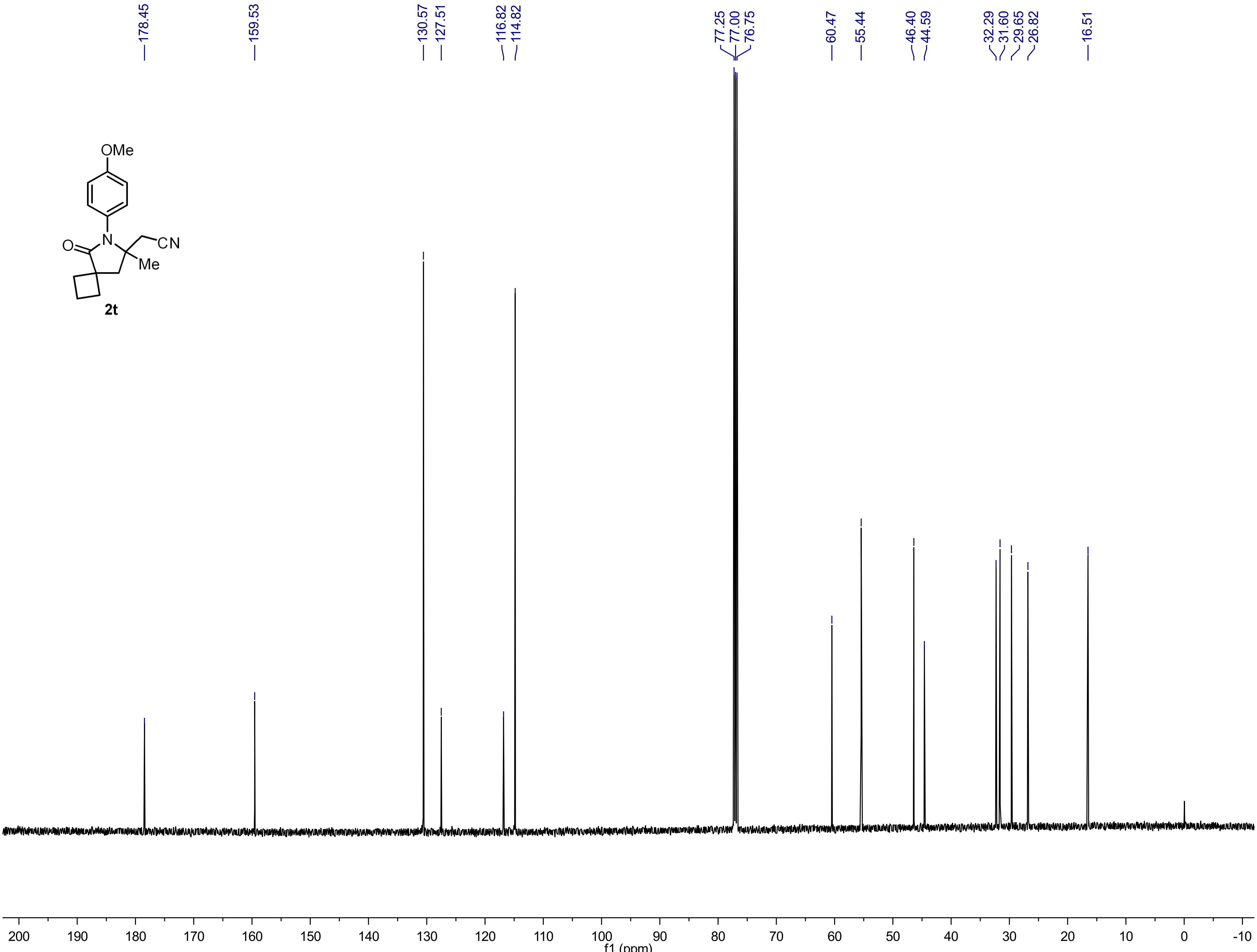
OMe
O
N
CN
Me
2t
2.02
2.01
3.00
1.98
0.99
1.02
1.02
1.00
0.96
3.03
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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44.59
32.29
31.60
29.65
26.82
16.51
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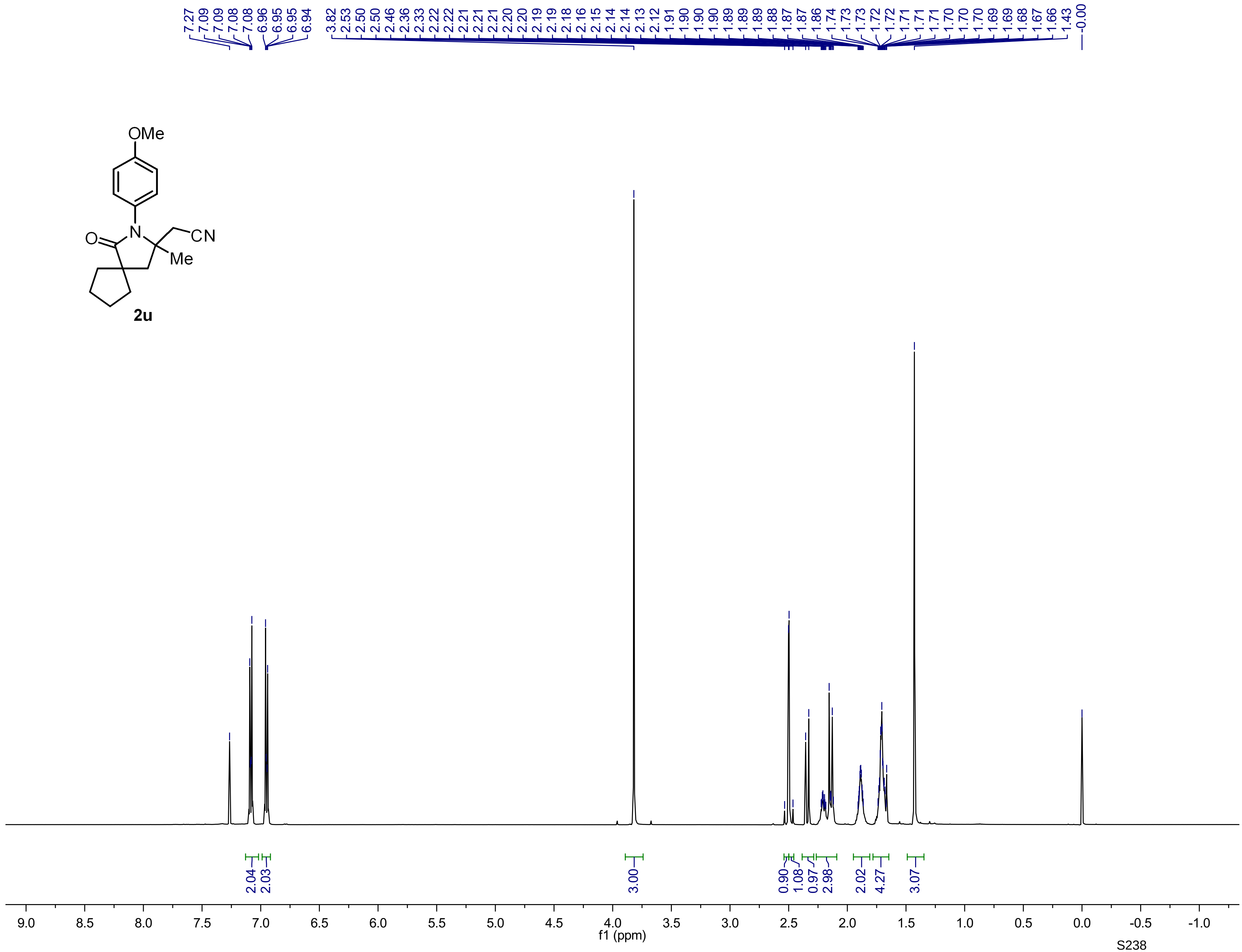
N
O
CN
Me
2t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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2.36
2.33
2.22
2.22
2.21
2.21
2.21
2.20
2.19
2.19
2.18
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2.15
2.14
2.14
2.13
2.12
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1.90
1.90
1.90
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1.68
1.67
1.66
1.43
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O
N
CN
Me
2u
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2.03
3.00
0.90
1.08
0.97
2.98
2.02
4.27
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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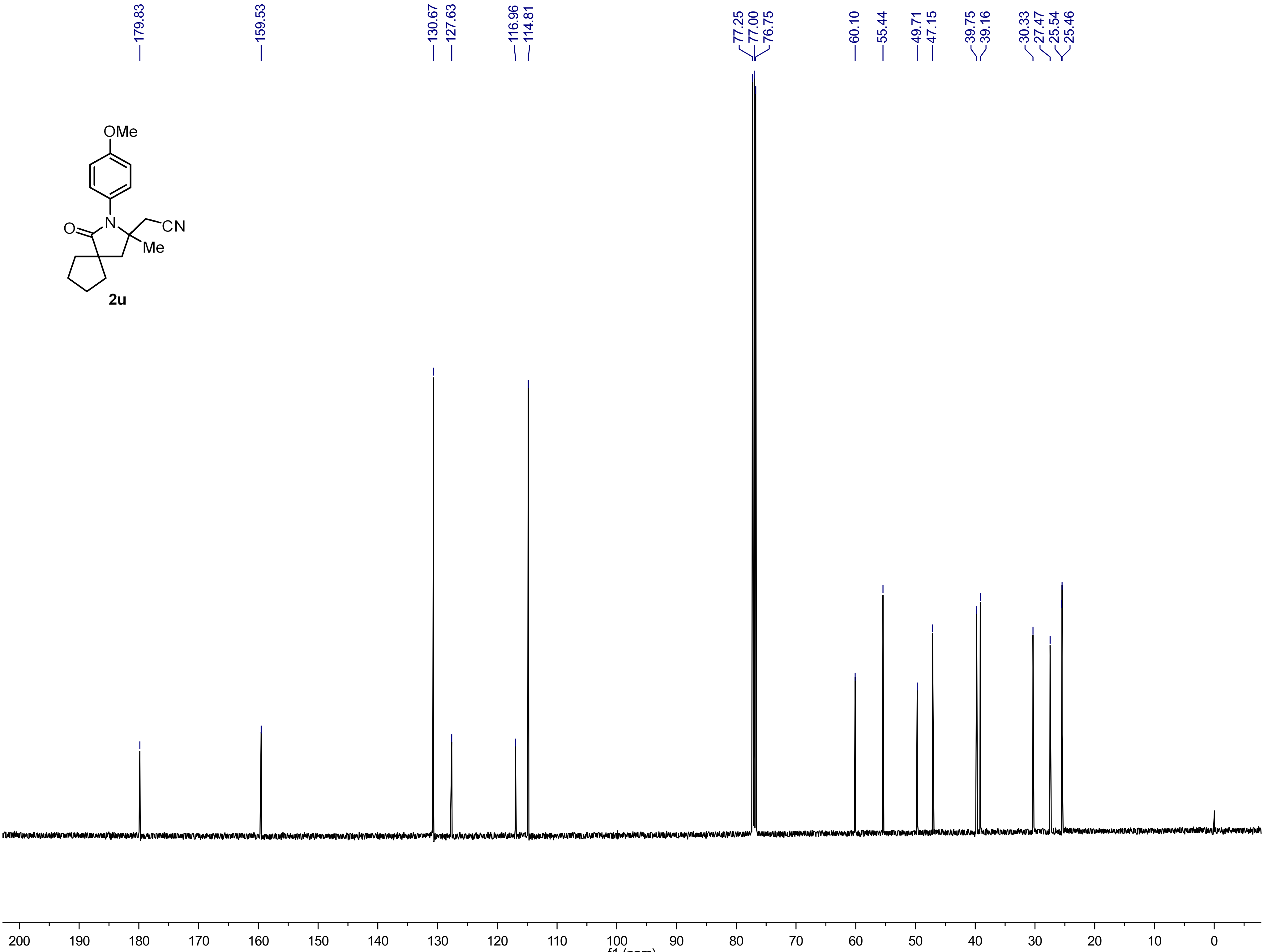
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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49.71
47.15
39.75
39.16
30.33
27.47
25.54
25.46
OMe
O
N
CN
Me
2u
200
190
180
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110
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90
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70
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50
40
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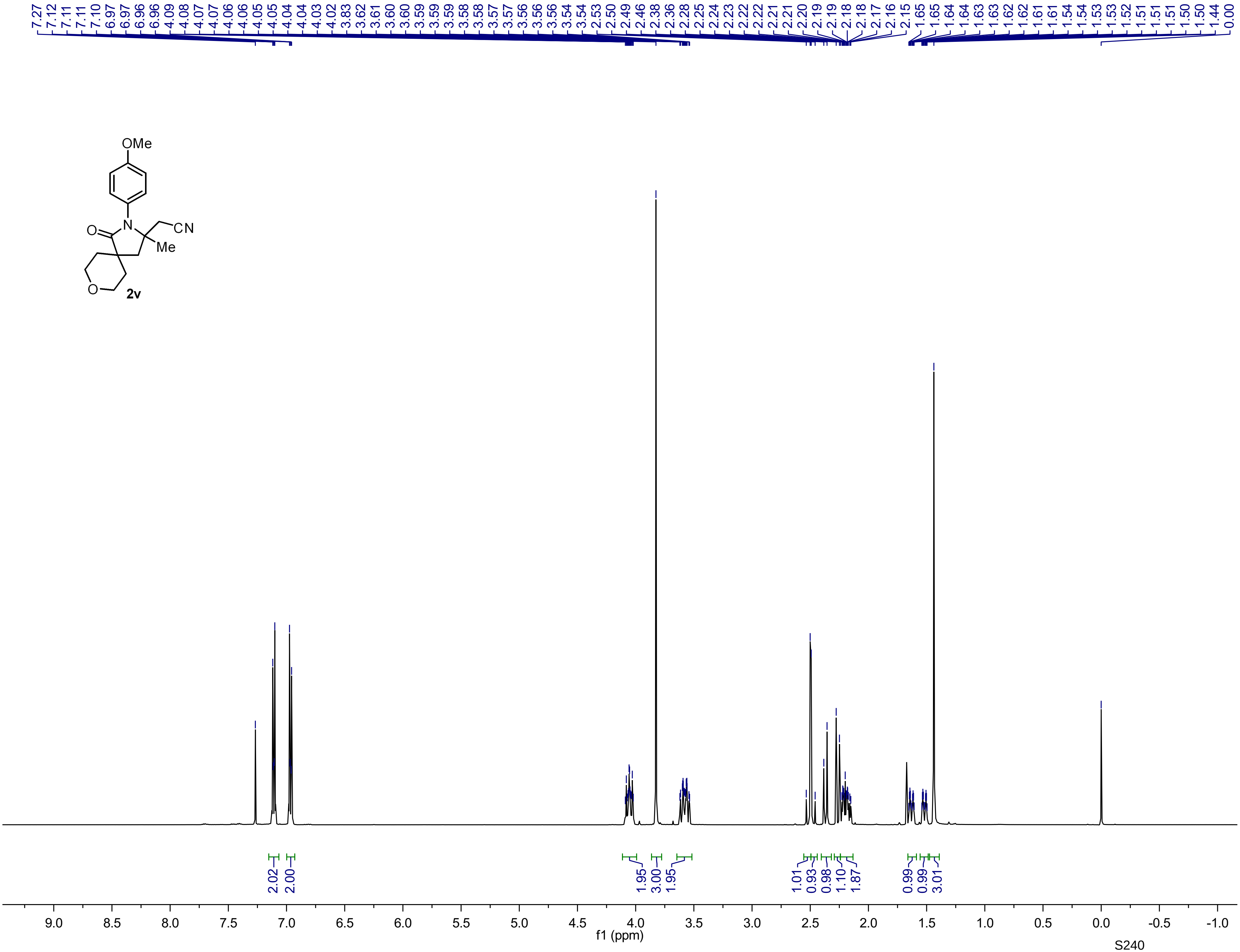
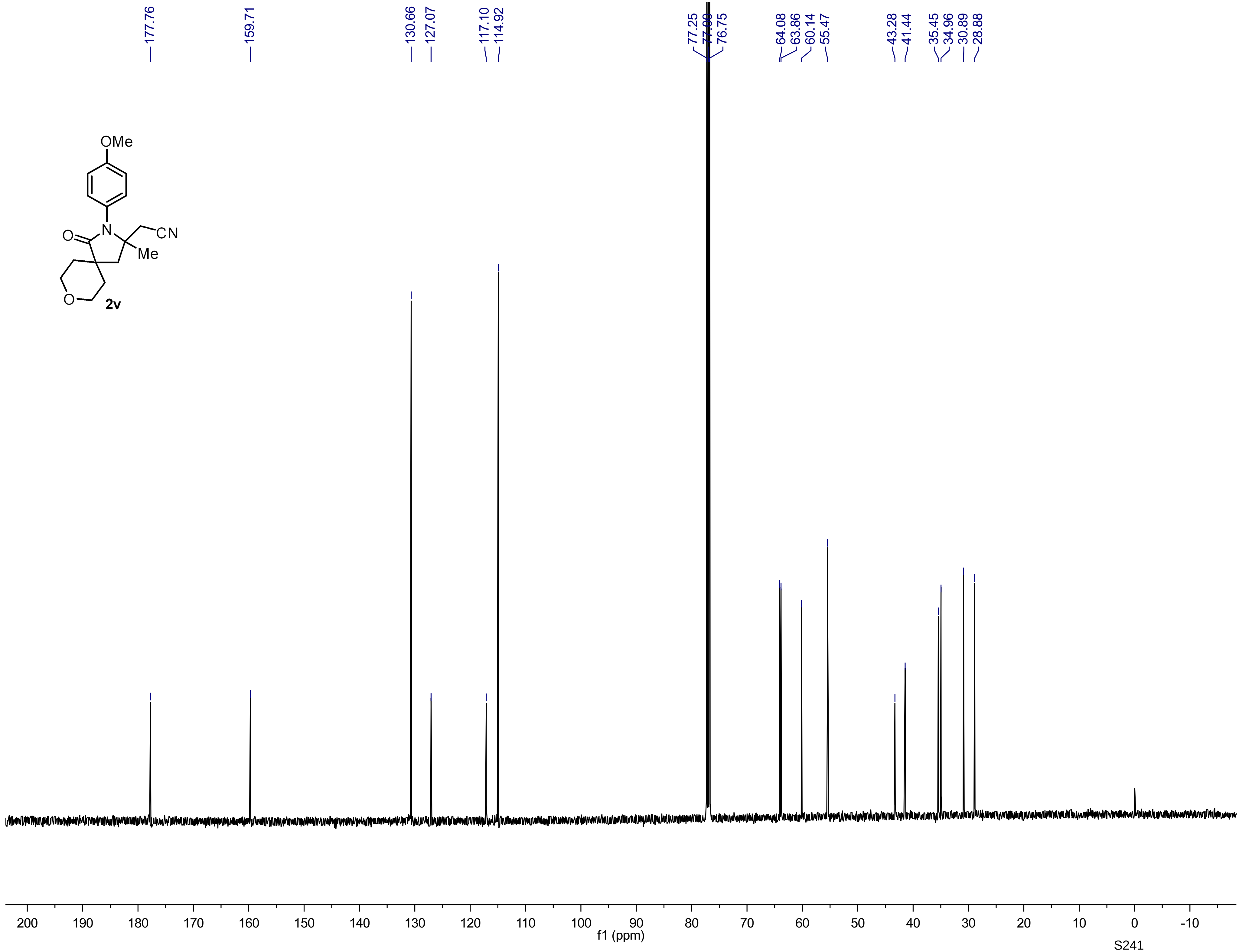
10
0
f1 (ppm)

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64.08
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55.47
43.28
41.44
35.45
34.96
30.89
28.88
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N
CN
Me
O
2v
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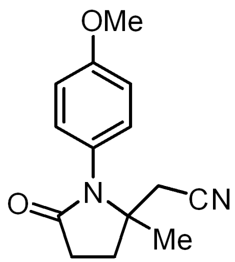
f1 (ppm)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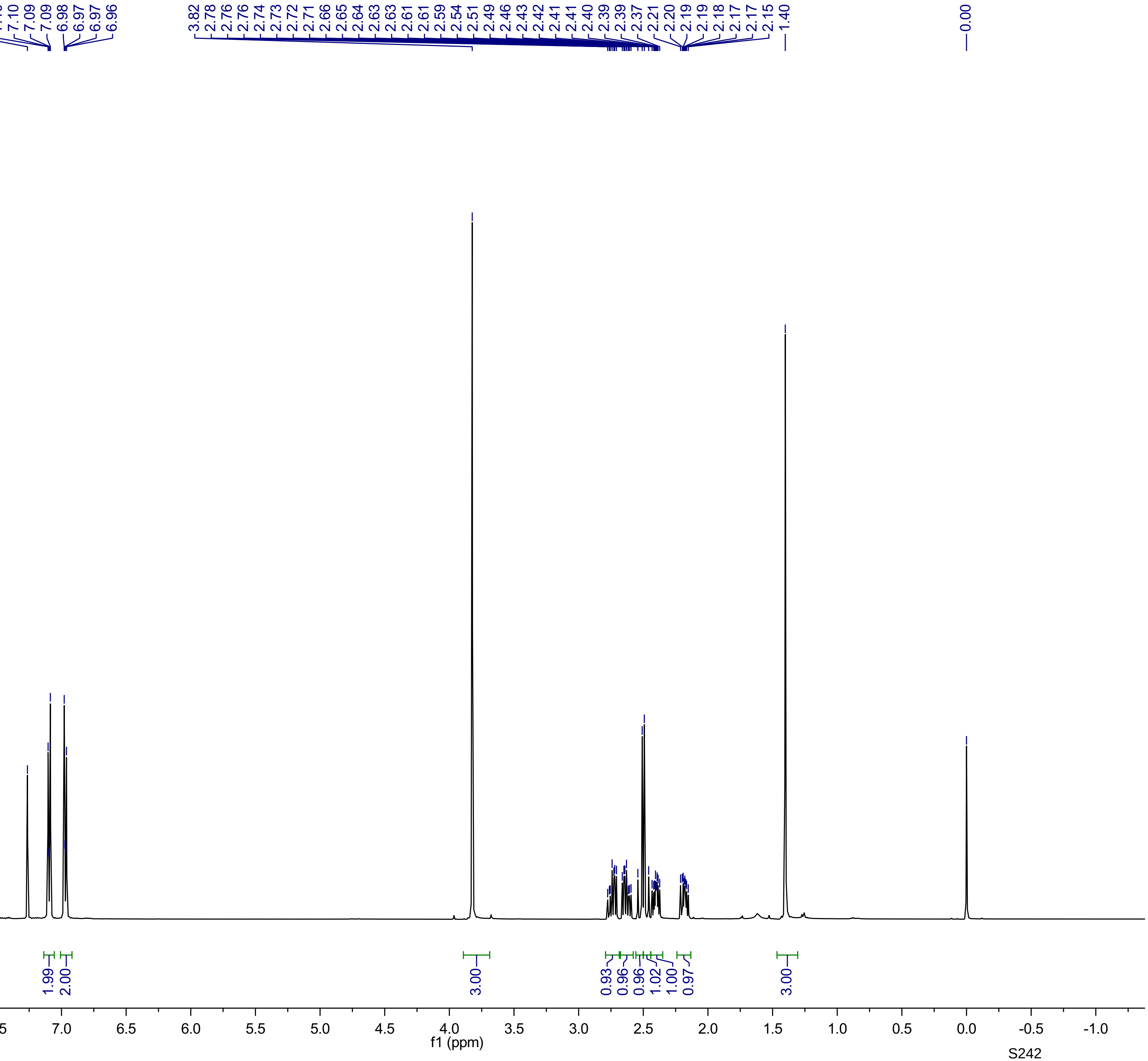
N
CN
Me

2w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2.78
2.76
2.76
2.74
2.73
2.72
2.71
2.66
2.65
2.64
2.63
2.63
2.61
2.61
2.59
2.54
2.51
2.49
2.46
2.43
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2.41
2.41
2.40
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2.39
2.37
2.21
2.20
2.19
2.19
2.18
2.17
2.17
2.15
1.40
0.00
1.99
2.00
3.00
0.93
0.96
0.96
1.02
1.00
0.97
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
1.5
1.0
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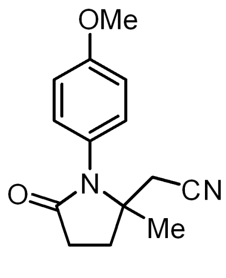
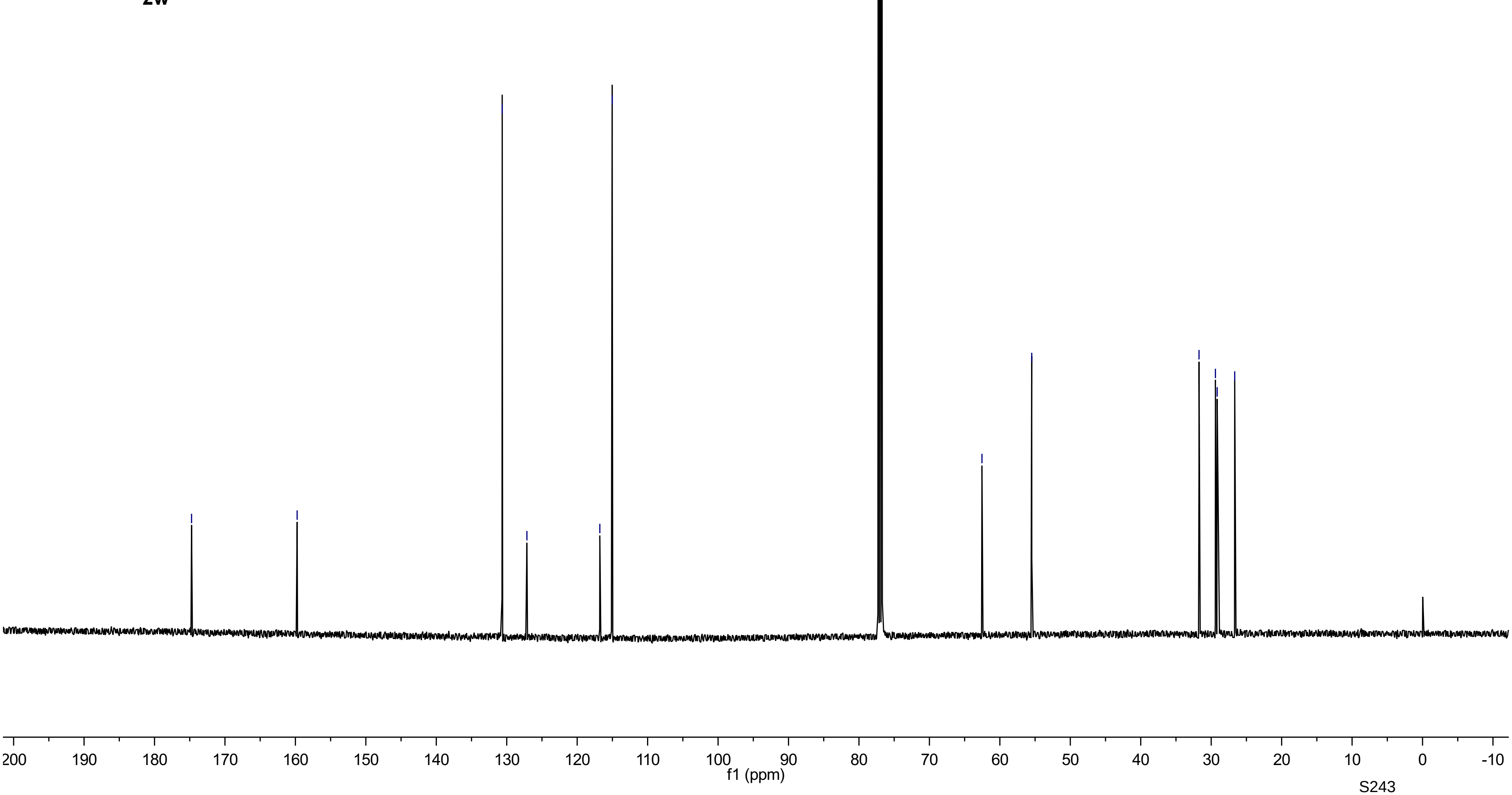
-1.0
f1 (ppm)



2w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115.04
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77.00
76.75
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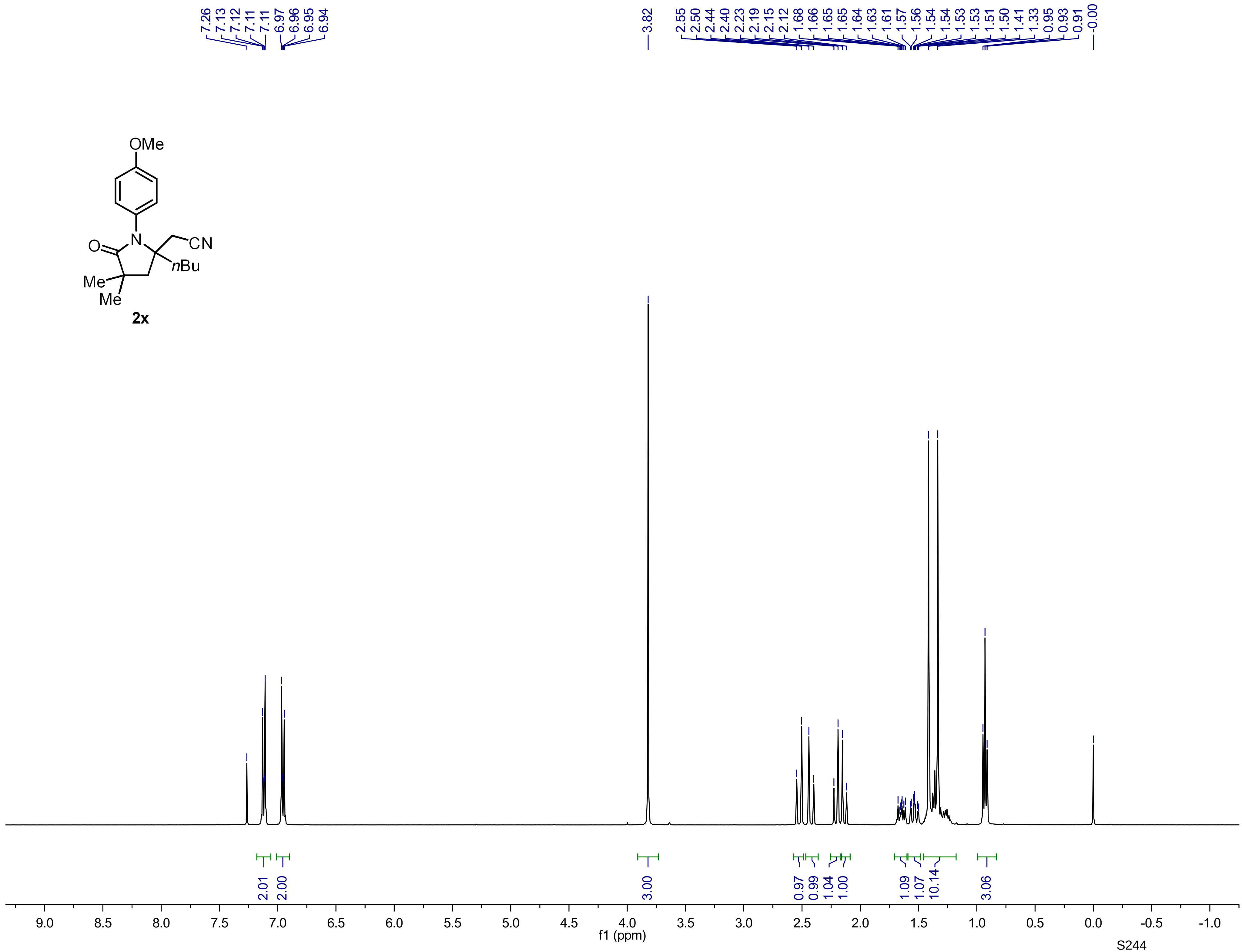
29.40
29.15
26.66
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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O
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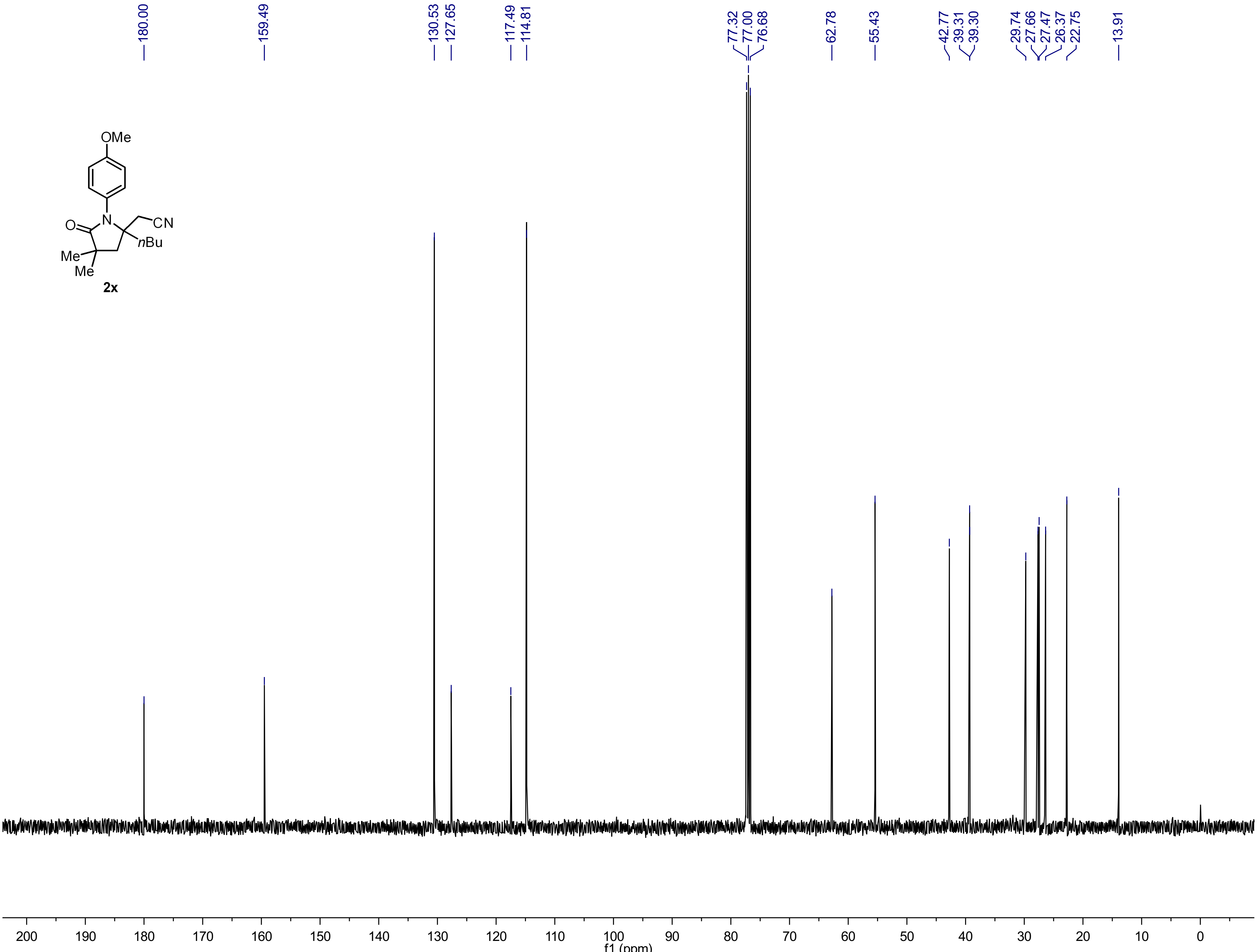
CN
nBu
Me
Me
2x
f1 (ppm)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77.00
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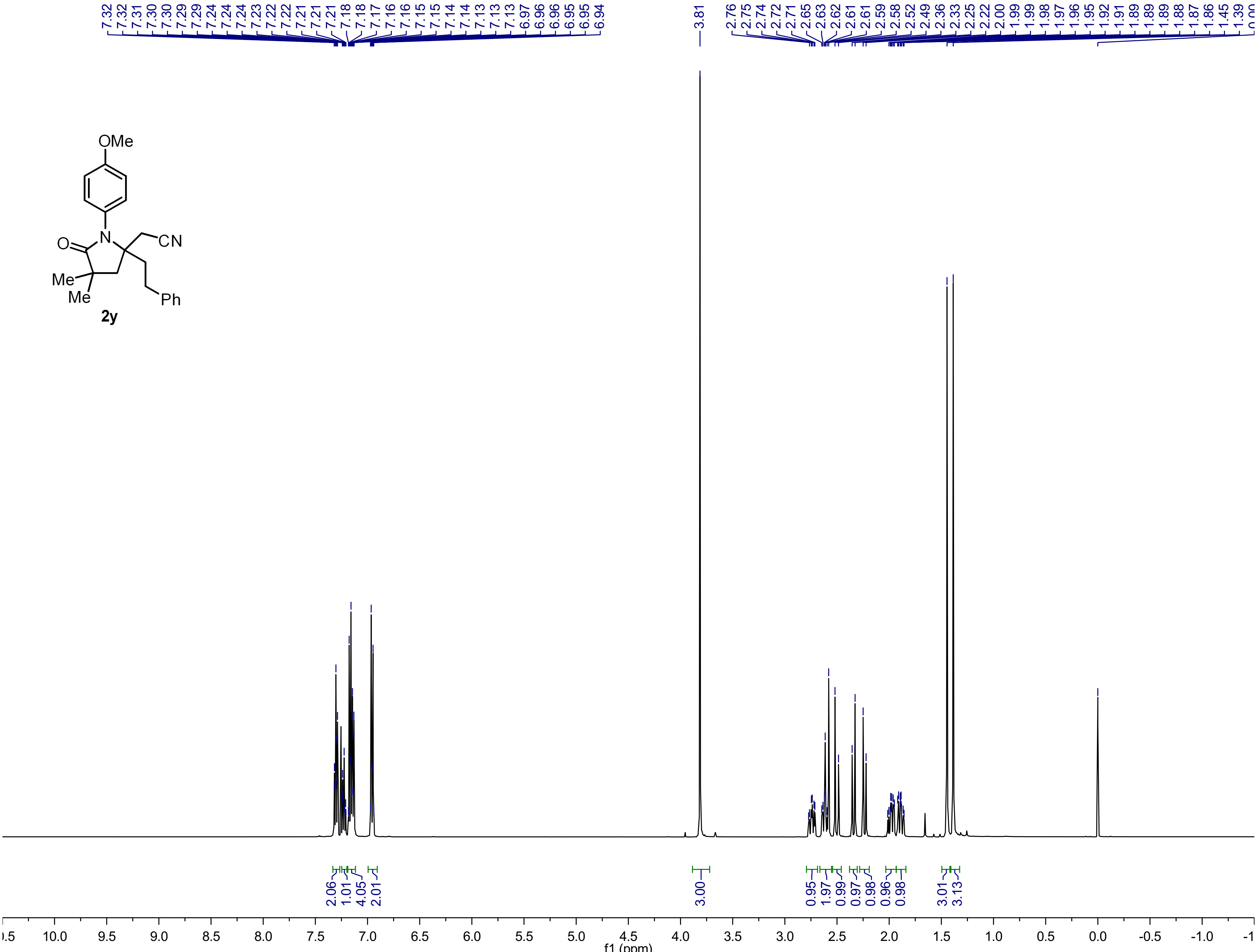
62.78
55.43
42.77
39.31
39.30
29.74
27.66
27.47
26.37
22.75
13.91
OMe
O
N
CN
nBu
Me
Me
2x
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OMe
O
N
CN
Me
Me
Ph
2y
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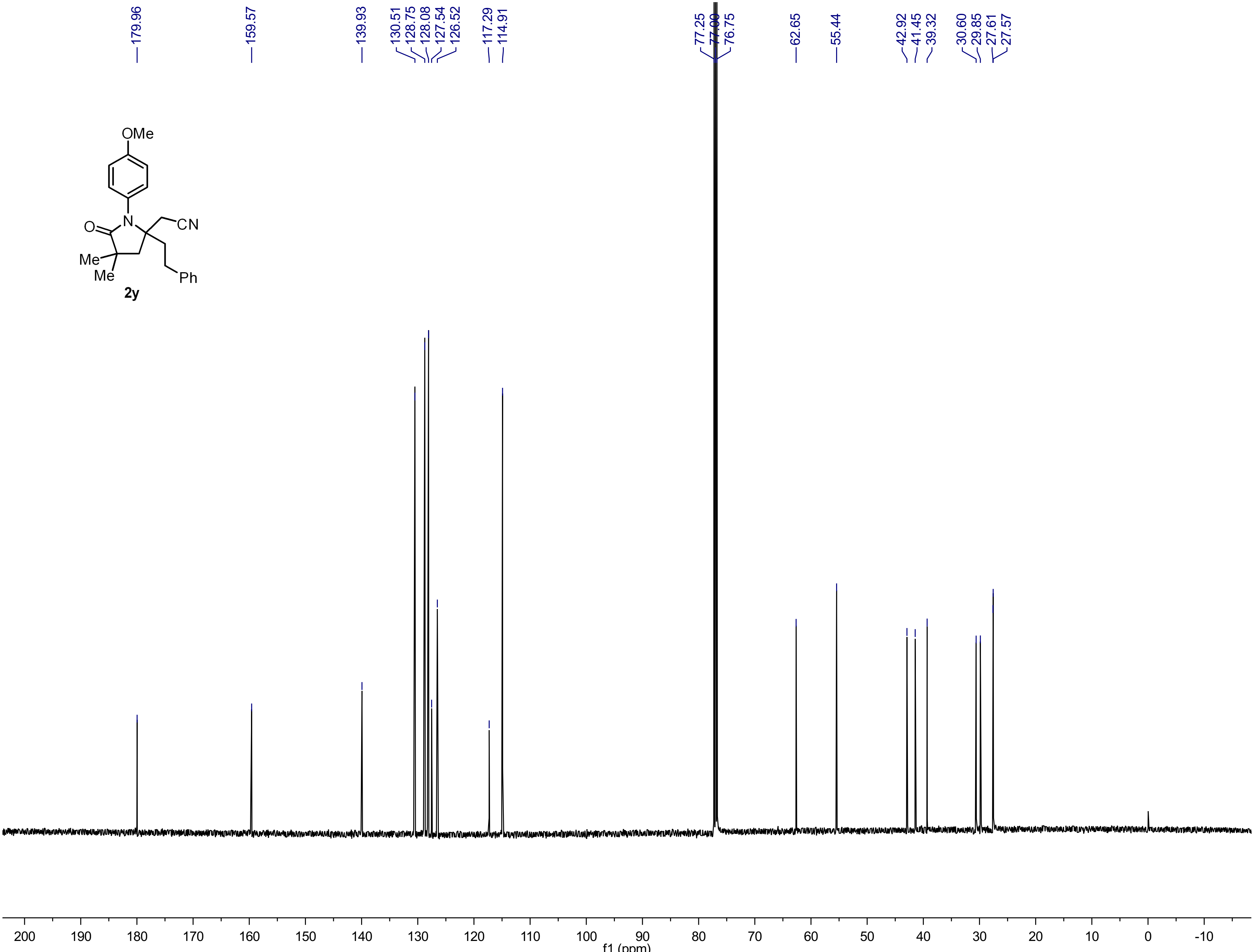
3.81
2.76 2.75 2.74 2.72 2.71 2.65 2.63 2.62 2.61 2.61 2.59 2.58 2.52 2.49 2.36 2.33 2.25 2.22 2.00 1.99 1.99 1.98 1.97 1.96 1.95 1.92 1.91 1.89 1.89 1.88 1.87 1.86 1.45 1.39
2.06 1.01 4.05 2.01
3.00
0.95 1.97 0.99 0.97 0.98 0.96 0.98
3.01 3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



OMe
O
N
CN
Me
Me
Ph
2y
179.96
159.57
139.93
130.51
128.75
128.08
127.54
126.52
117.29
114.91
77.25
77.00
76.75
62.65
55.44
42.92
41.45
39.32
30.60
29.85
27.61
27.57
200
190
180
170
160
150
140
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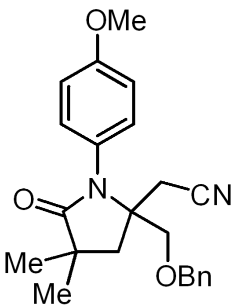
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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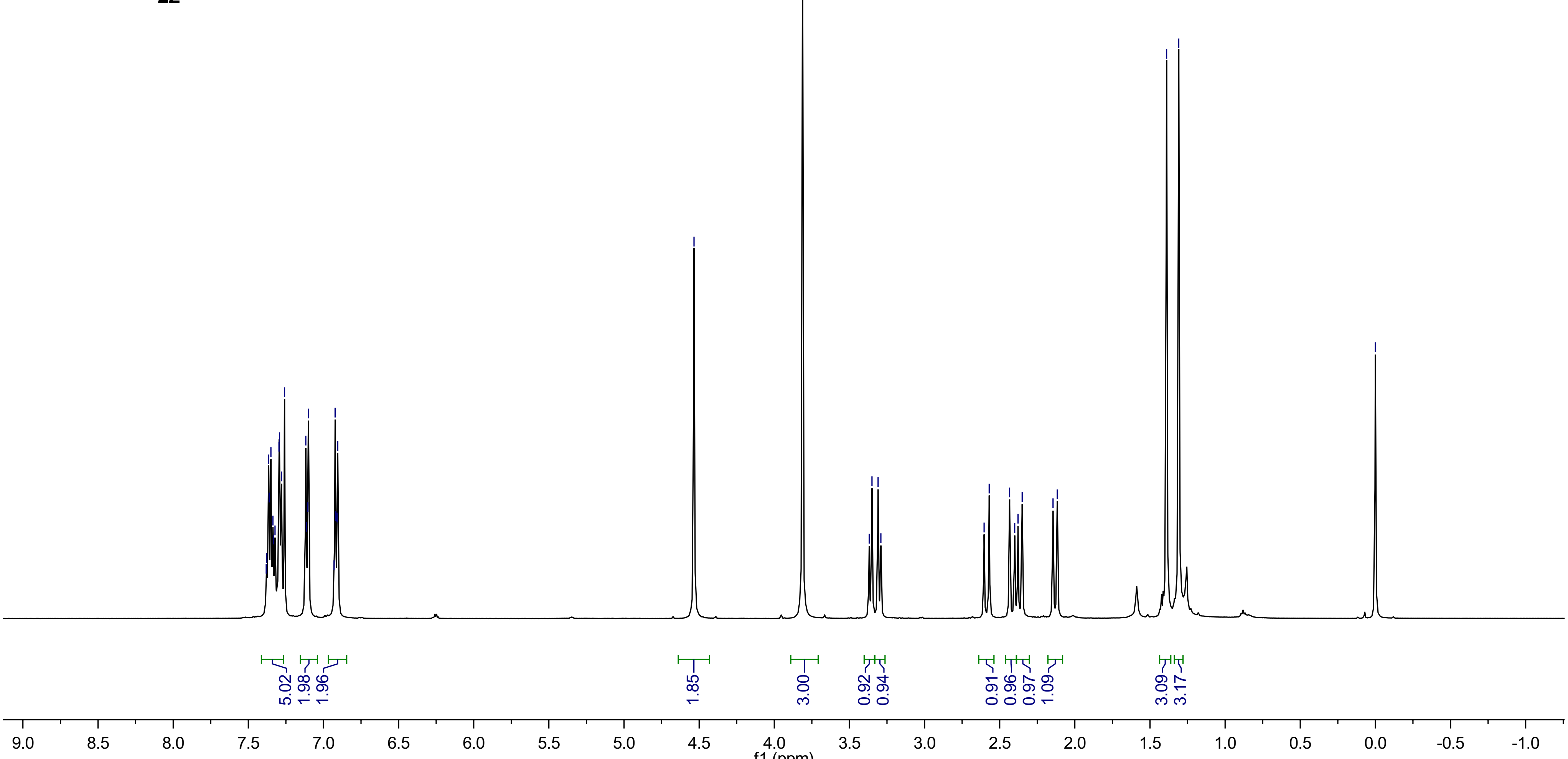
N
O
CN
Me
Me
OBn

2z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7.32
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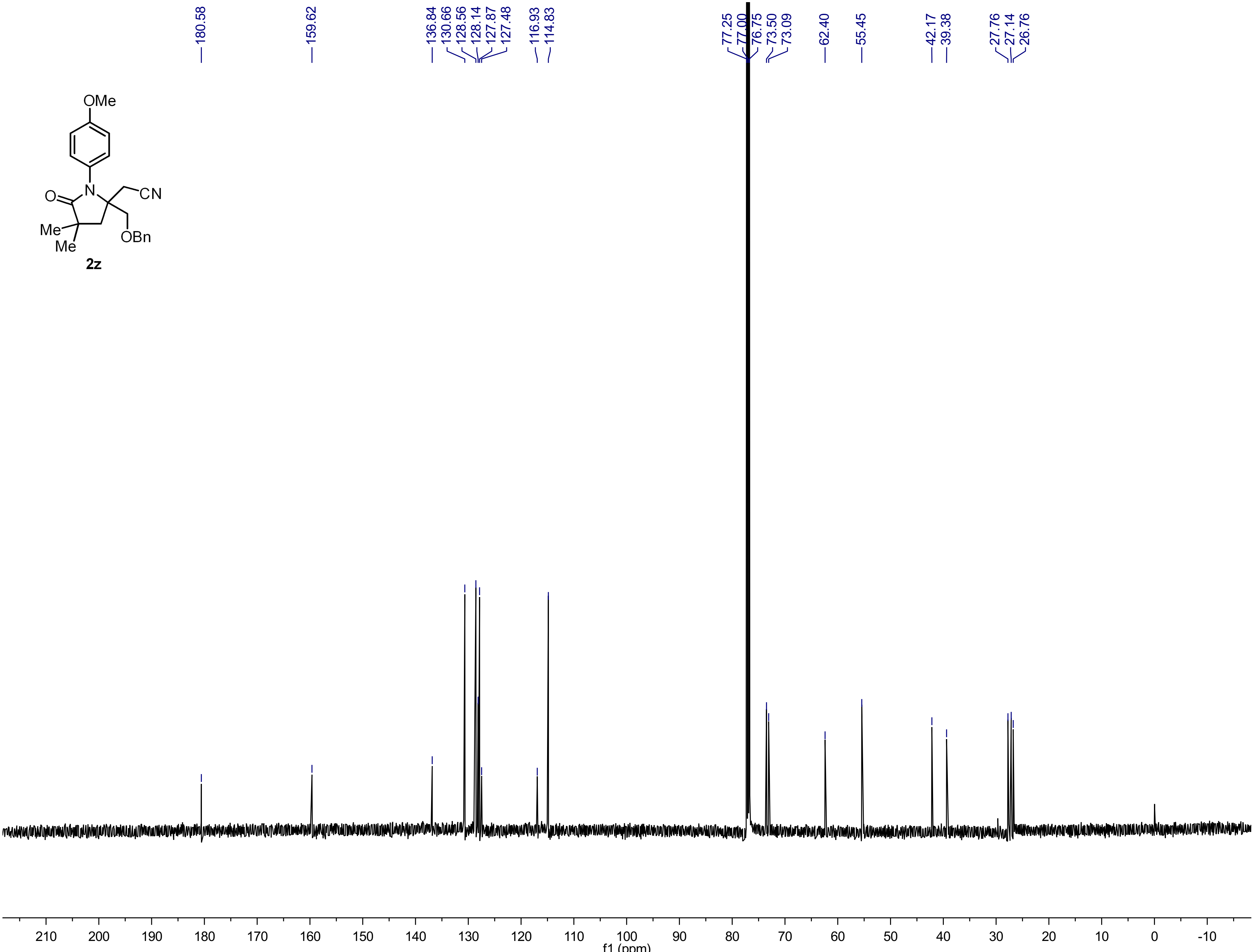
7.28
7.26
7.12
7.11
7.10
7.10
6.93
6.92
6.92
6.91
6.90
4.53
3.81
3.37
3.35
3.31
3.29
2.60
2.57
2.43
2.40
2.38
2.35
2.15
2.12
1.39
1.31
0.00
5.02
1.98
1.96
1.85
3.00
0.92
0.94
0.91
0.96
0.97
1.09
3.09
3.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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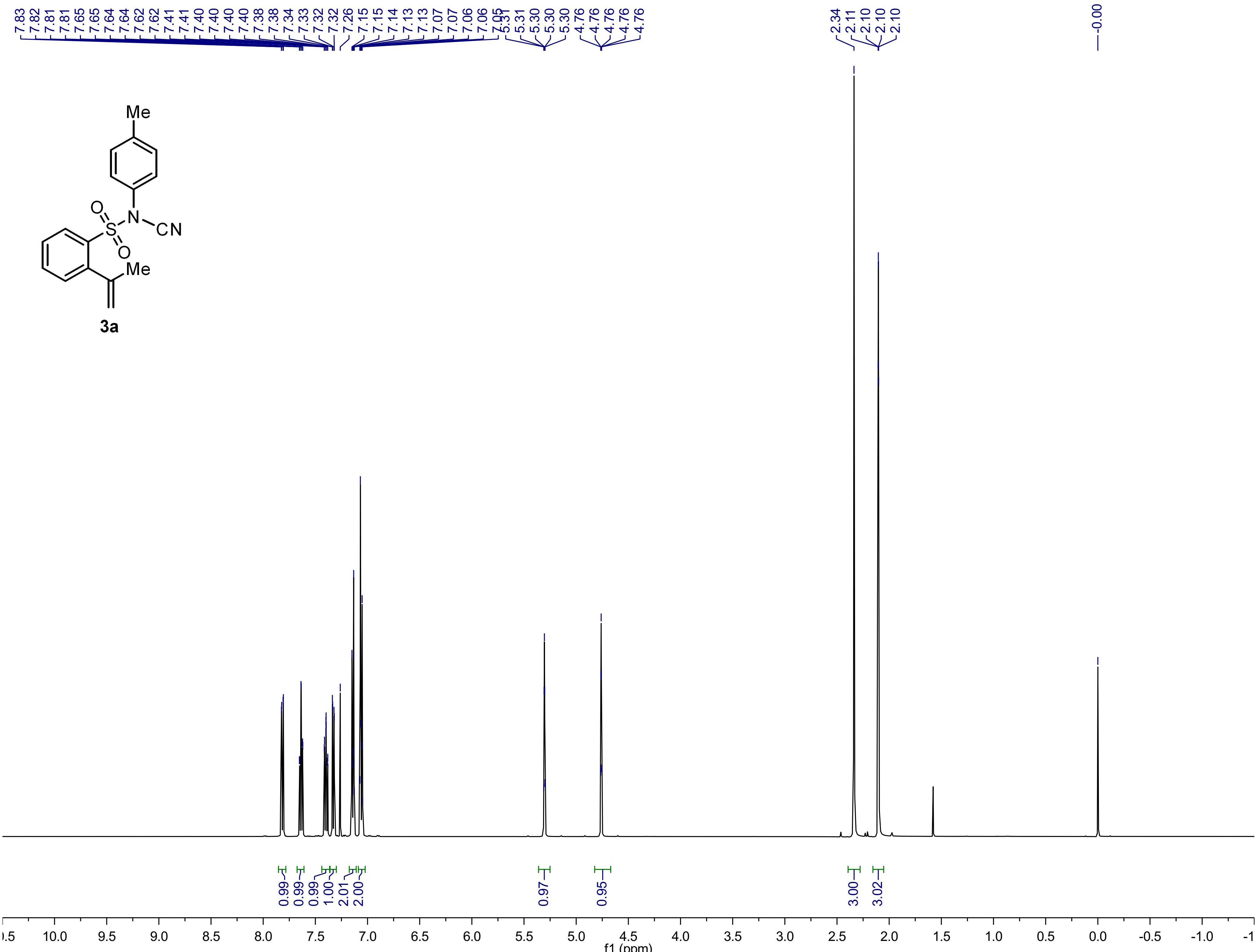
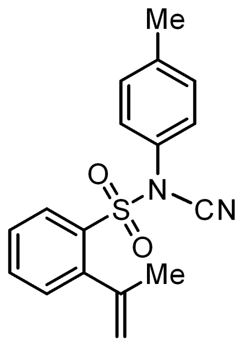
128.14
127.87
127.48
116.93
114.83
77.25
77.00
76.75
73.50
73.09
62.40
55.45
42.17
39.38
27.76
27.14
26.76
OMe
O
N
CN
Me
Me
OBn
2z
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

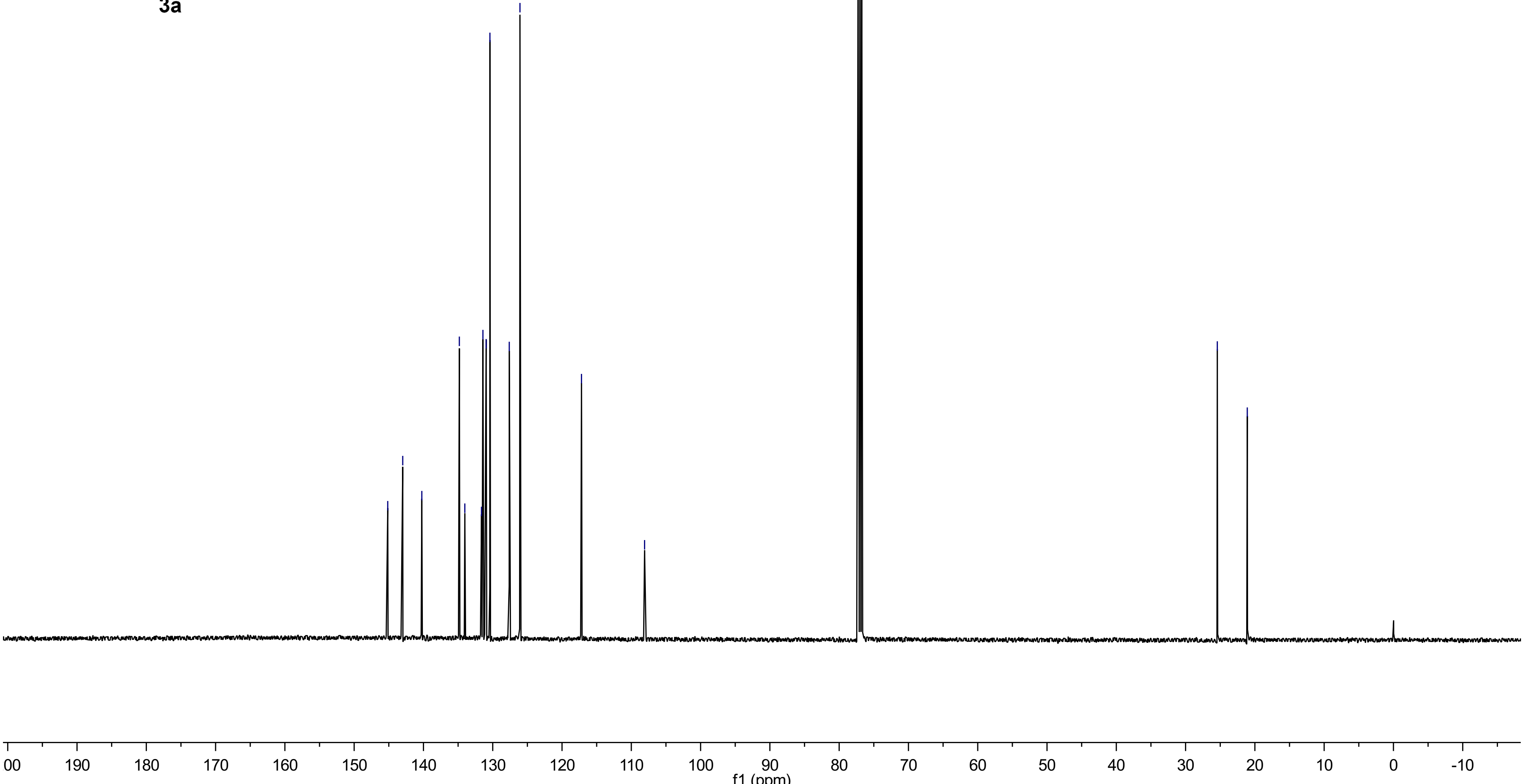


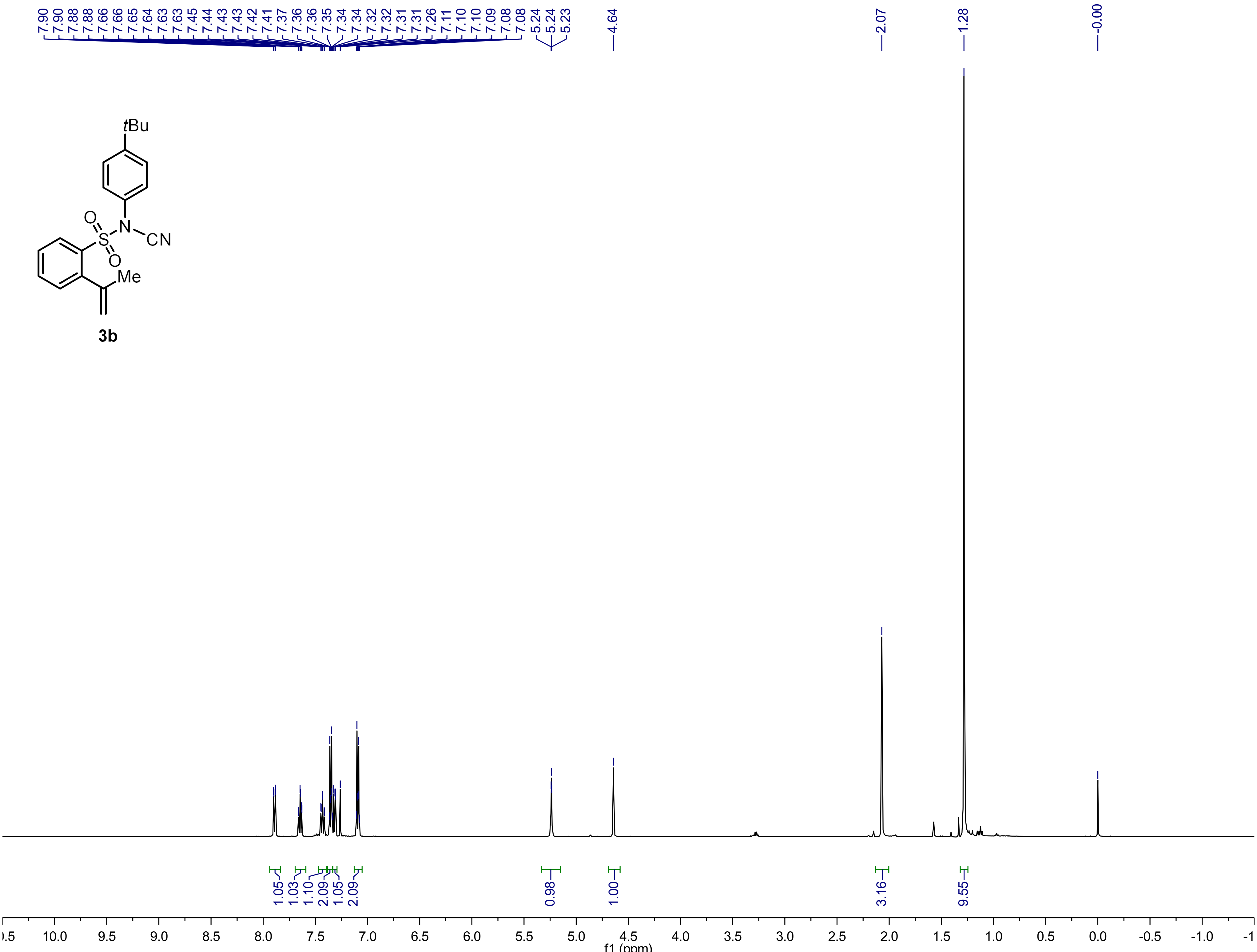
7.83
7.82
7.81
7.81
7.65
7.65
7.64
7.64
7.62
7.62
7.41
7.41
7.40
7.40
7.40
7.38
7.38
7.34
7.33
7.32
7.32
7.26
7.15
7.15
7.14
7.13
7.13
7.07
7.07
7.06
7.06
7.05
5.31
5.31
5.30
5.30
5.30
4.76
4.76
4.76
4.76
4.76
2.34
2.11
2.10
2.10
2.10
-0.00
0.99
0.99
0.99
1.00
2.01
2.00
0.97
0.95
3.00
3.02
10.0
9.5
9.0
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
-0.5
-1.0
f1 (ppm)

3a



3a


145.15
142.99
140.24
134.82
134.03
131.62
131.42
130.95
130.41
127.61
126.07
117.19
108.08
77.25
77.00
76.75
25.42
21.10
f1 (ppm)



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7.90
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7.88
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7.66
7.65
7.64
7.63
7.63
7.45
7.44
7.43
7.43
7.42
7.41
7.37
7.36
7.36
7.35
7.34
7.34
7.32
7.32
7.31
7.31
7.26
7.11
7.10
7.09
7.08
7.08
5.24
5.24
5.23
4.64
2.07
1.28
-0.00
tBu
O
S
O
N
CN
Me
3b
1.05
1.03
1.10
2.09
1.05
2.09
0.98
1.00
3.16
9.55
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
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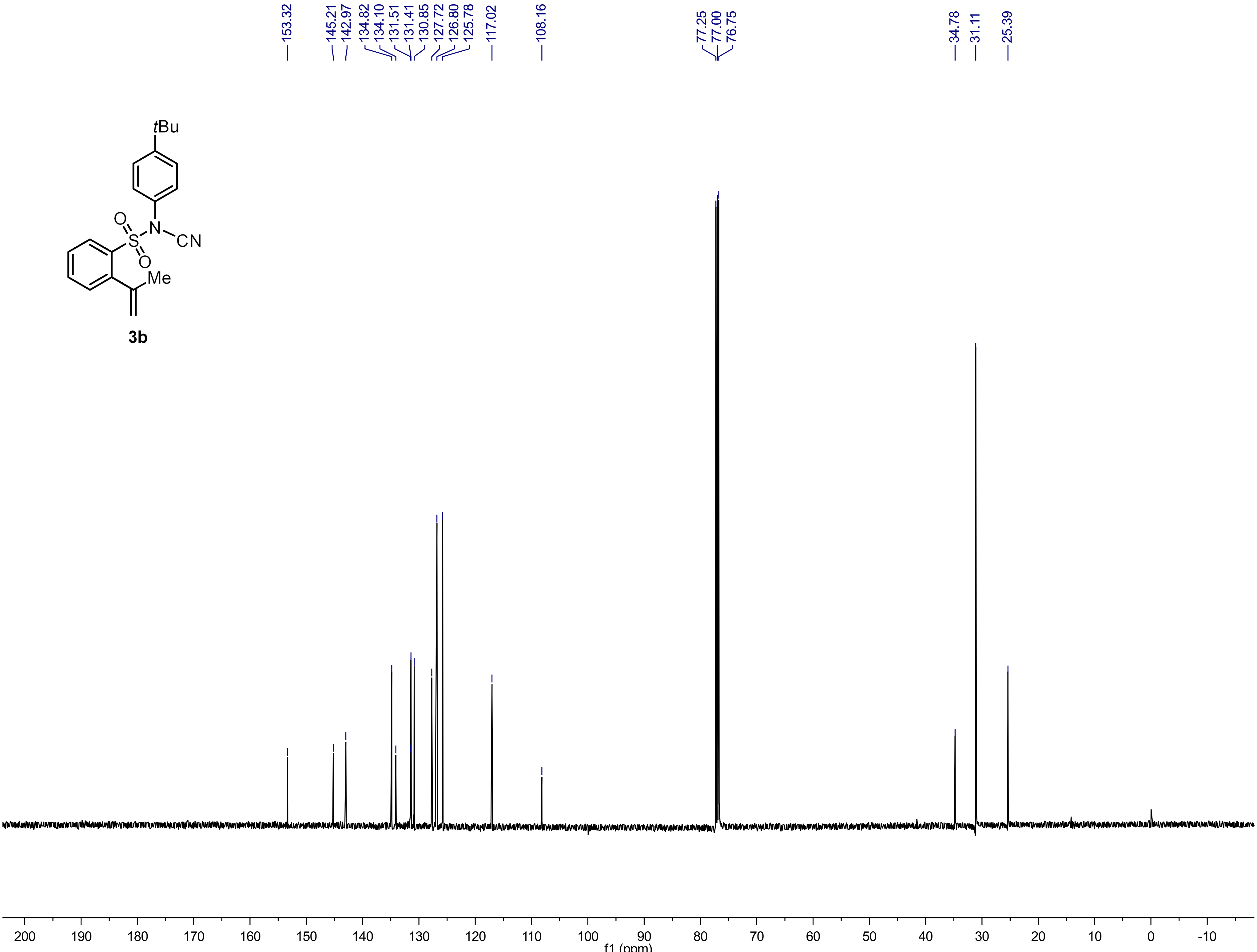
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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134.10
131.51
131.41
130.85
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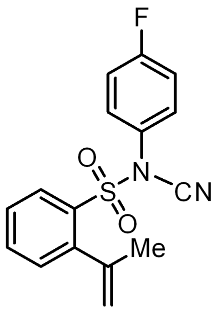
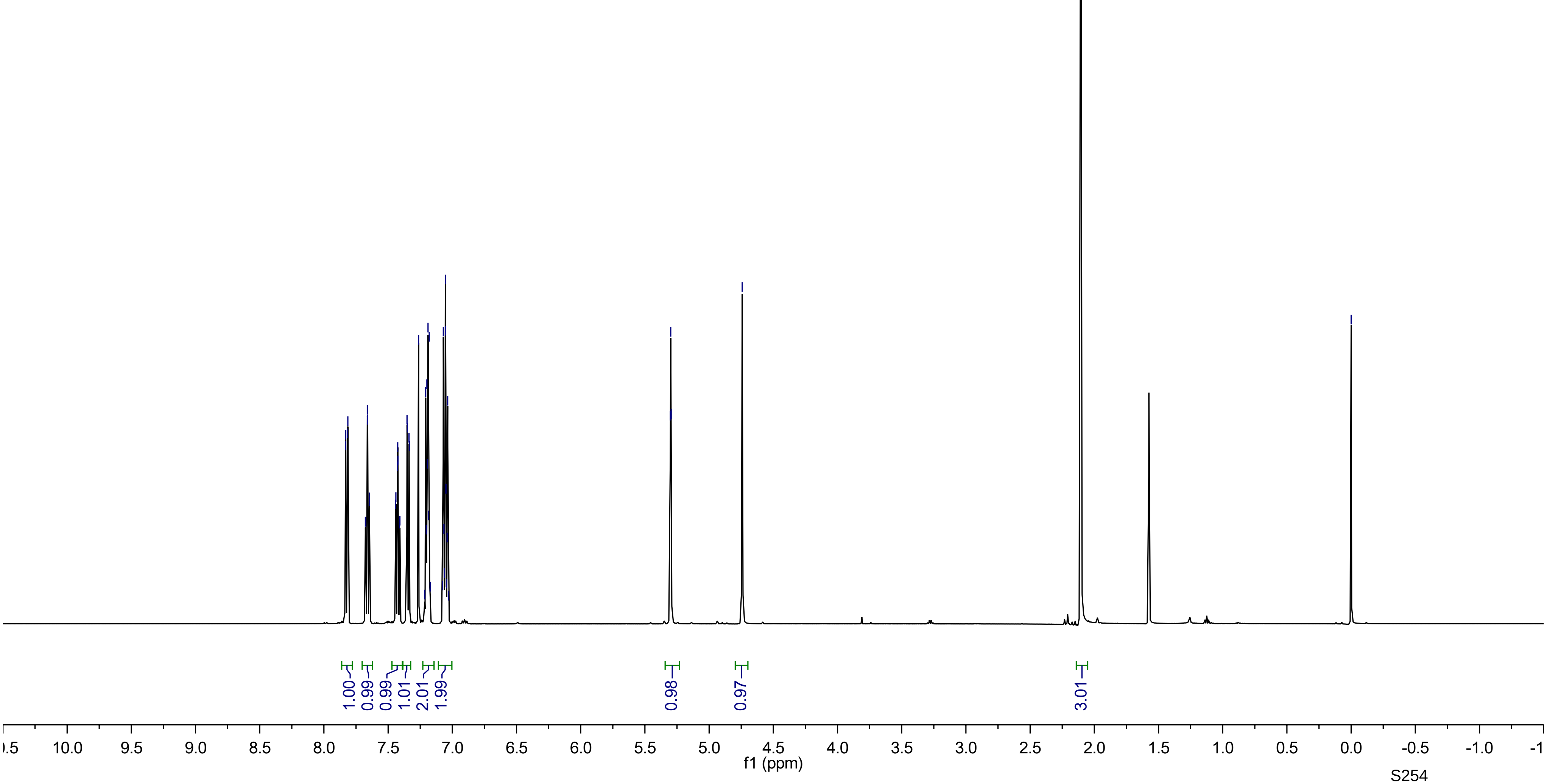
126.80
125.78
117.02
108.16
77.25
77.00
76.75
34.78
31.11
25.39
tBu
O
S
N
CN
O
Me
3b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3c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7.67
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7.66
7.65
7.64
7.44
7.44
7.43
7.43
7.42
7.41
7.41
7.35
7.35
7.34
7.33
7.26
7.21
7.20
7.19
7.19
7.18
7.18
7.07
7.07
7.05
7.05
7.05
7.04
5.30
5.30
5.30
4.74
2.11
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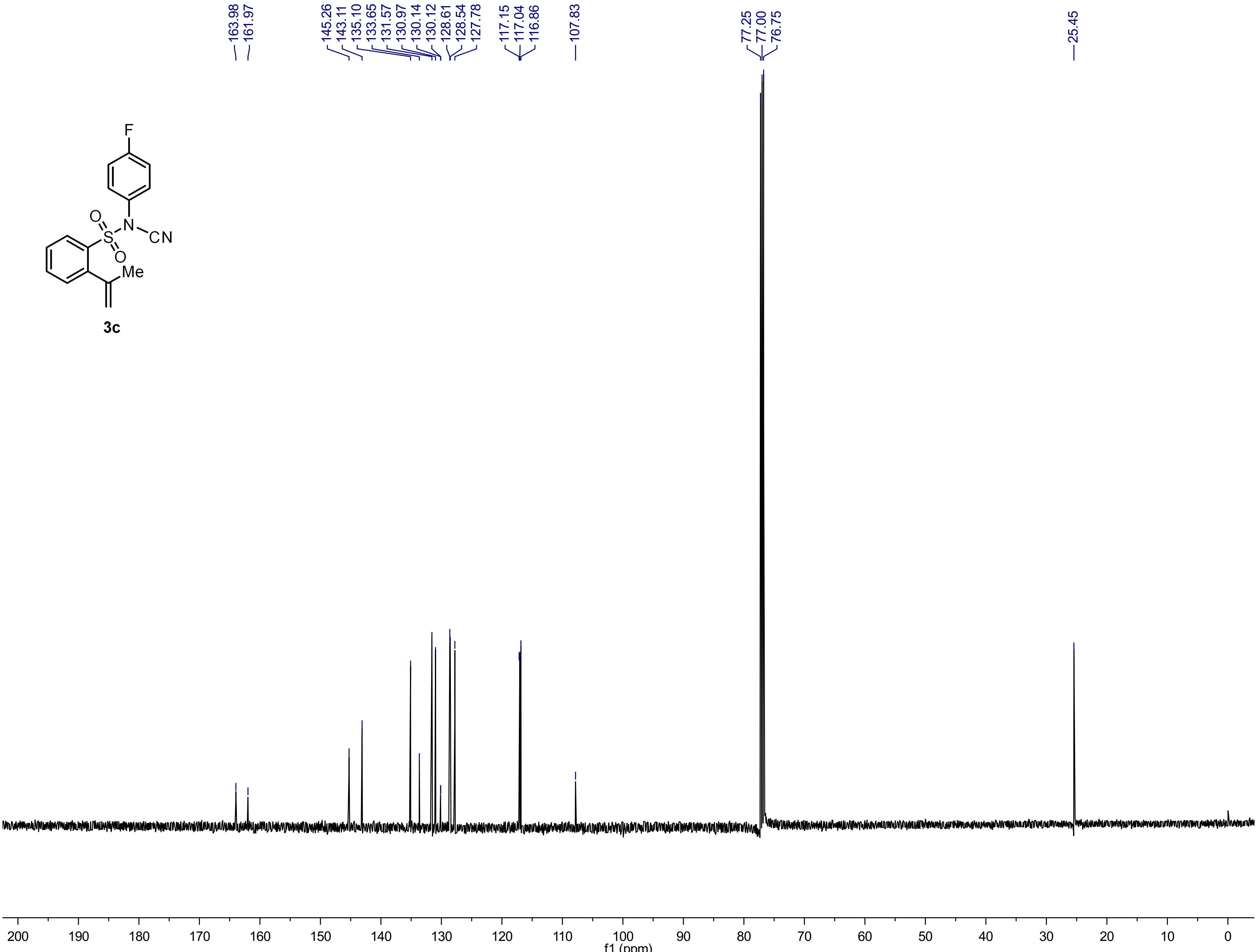
1.00
0.99
0.99
1.01
2.01
1.99
0.98
0.97
3.01
f1 (ppm)



163.98
161.97
145.26
143.11
135.10
133.65
131.57
130.97
130.14
130.12
128.61
128.54
127.78
117.15
117.04
116.86
107.83
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77.00
76.75
25.45
3c
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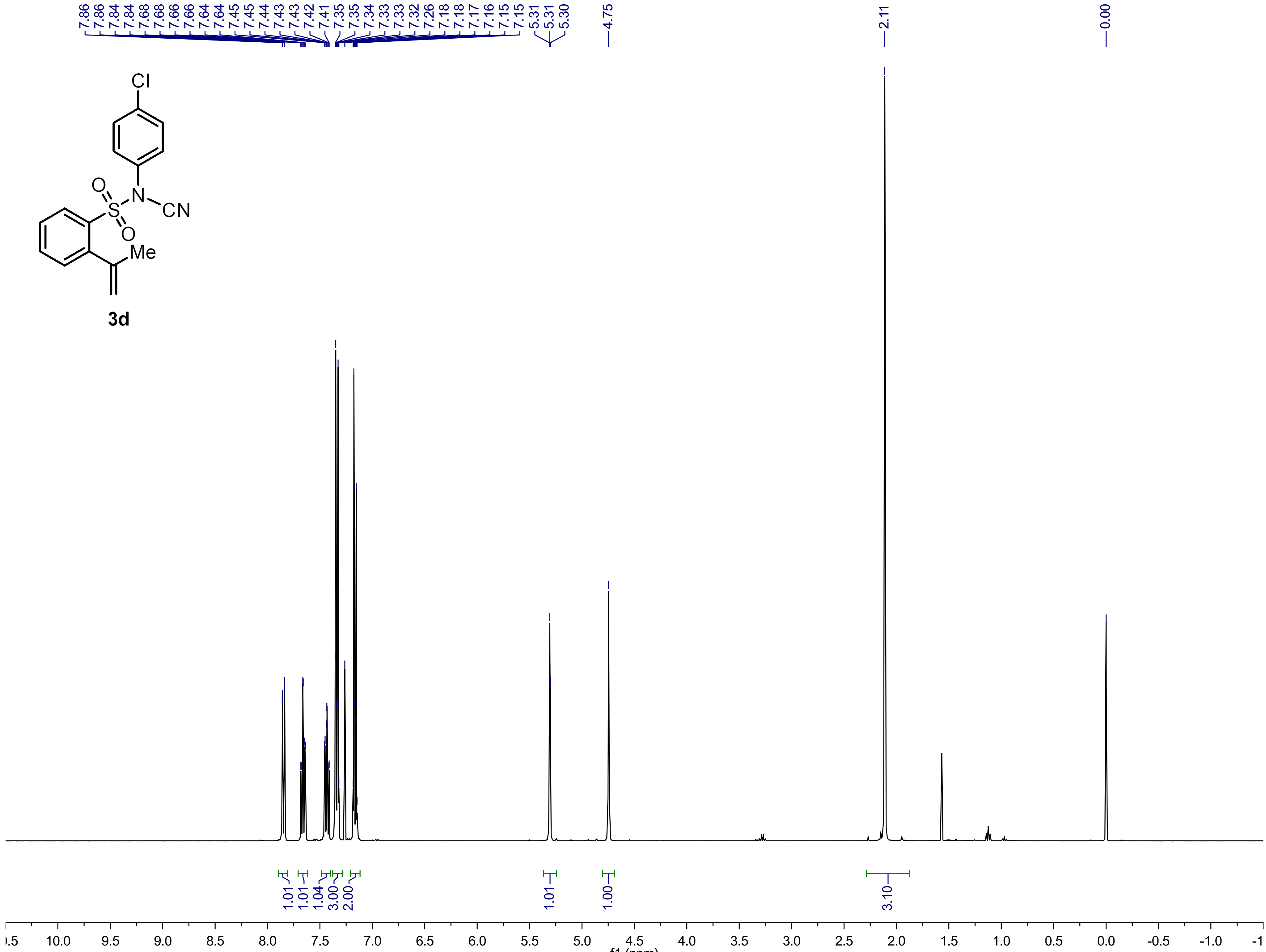
f1 (ppm)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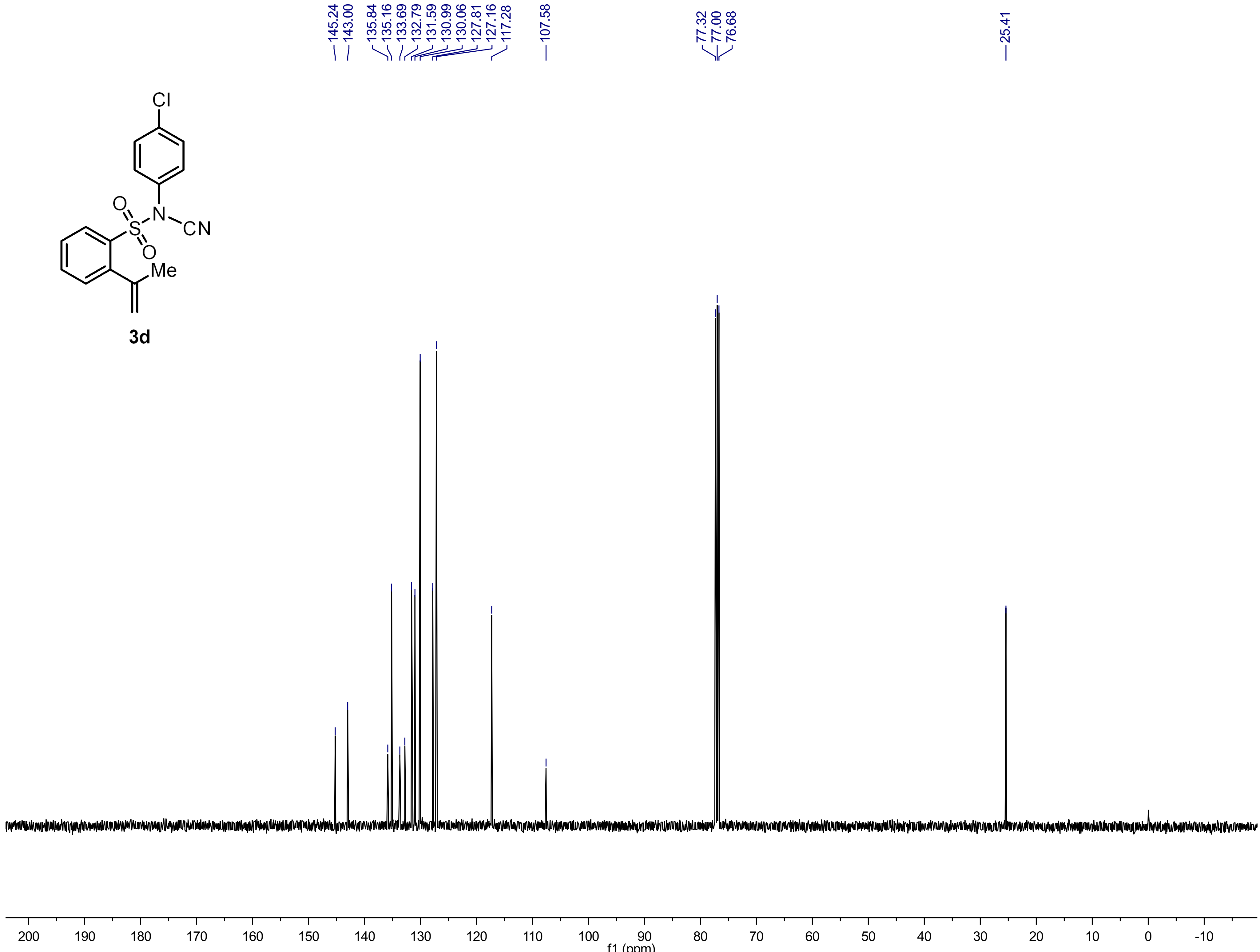
4.75
2.11
0.00
Cl
O
S
N
CN
O
Me
3d
1.01
1.01
1.04
3.00
2.00
1.01
1.00
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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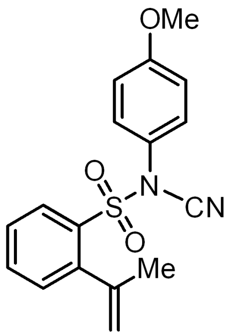
127.81
127.16
117.28
107.58
77.32
77.00
76.68
25.41
Cl
O
S
N
CN
O
Me
3d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OMe
O
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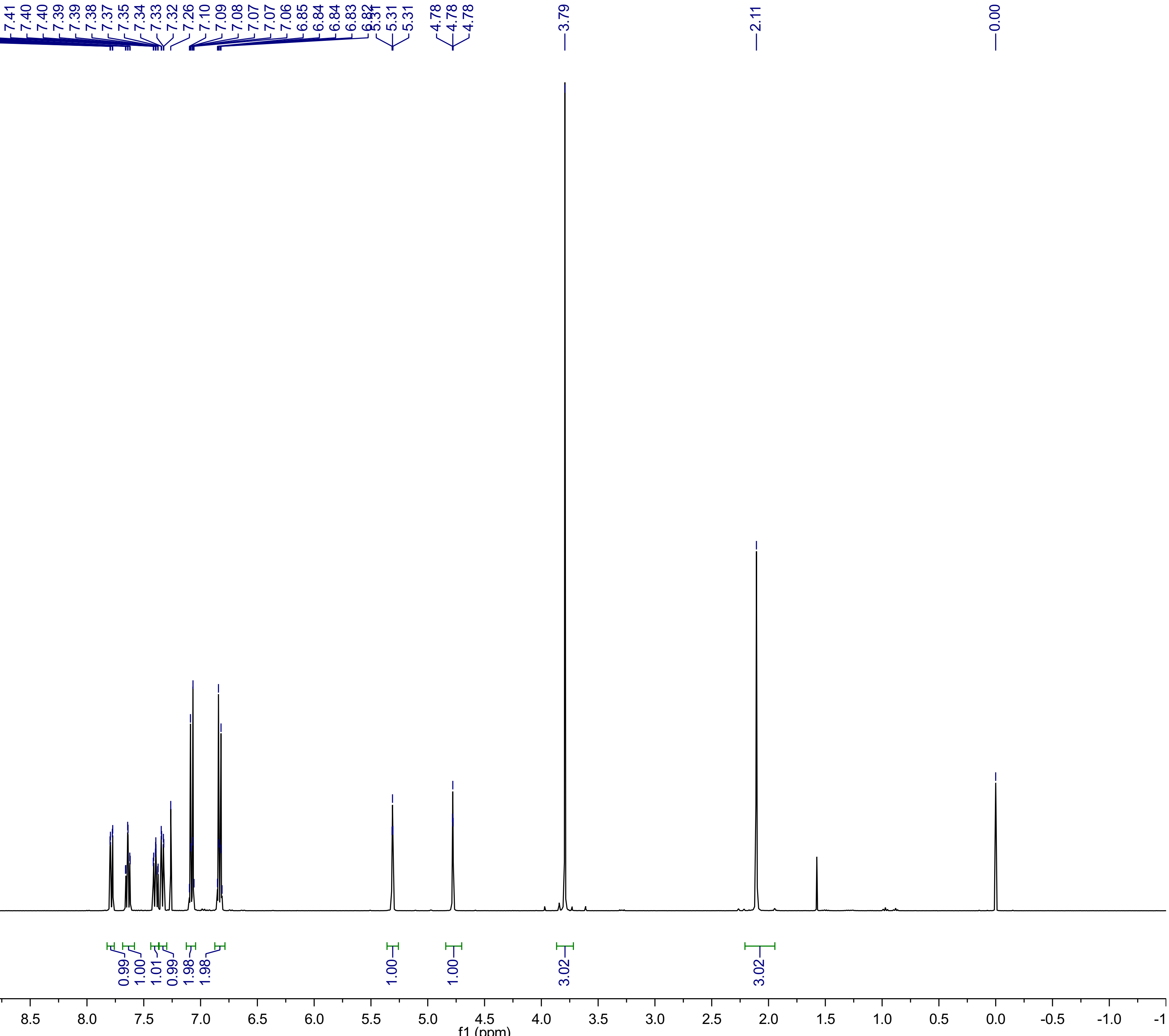
N
CN
O
Me

3e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7.62
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7.40
7.40
7.39
7.39
7.38
7.37
7.35
7.34
7.33
7.33
7.32
7.26
7.10
7.09
7.08
7.07
7.07
7.06
6.85
6.84
6.84
6.83
6.82
5.31
5.31
5.31
4.78
4.78
4.78
3.79
2.11
0.00
0.99
1.00
1.01
0.99
1.98
1.98
1.00
1.00
3.02
3.02
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
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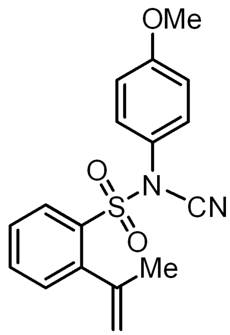
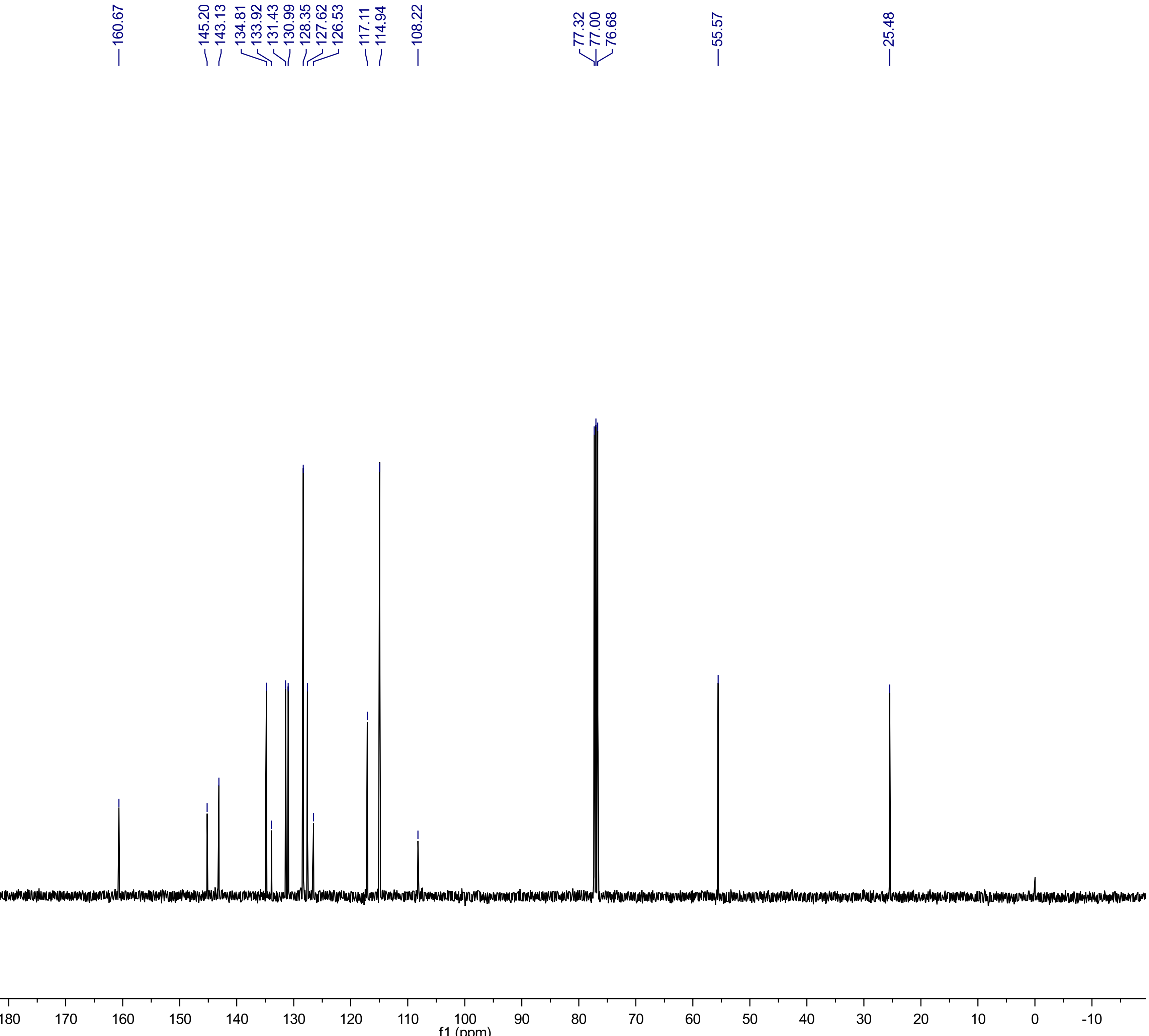
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



3e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126.53
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108.22
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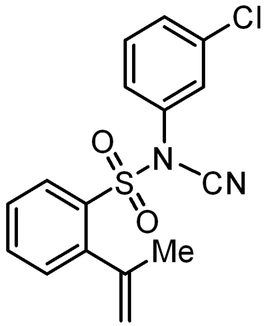
77.00
76.68
55.57
25.48
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
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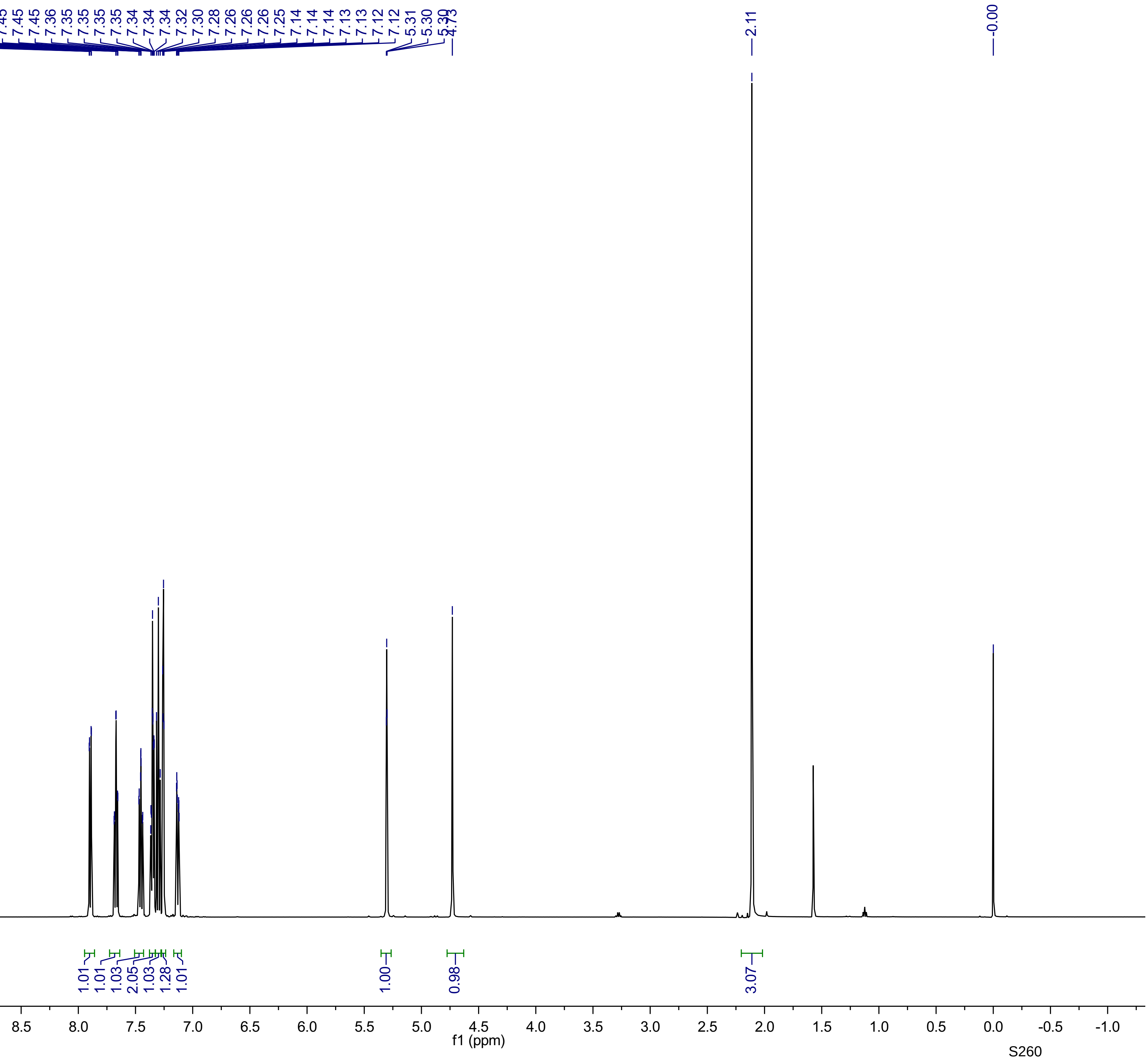
N
CN
O
Me

3f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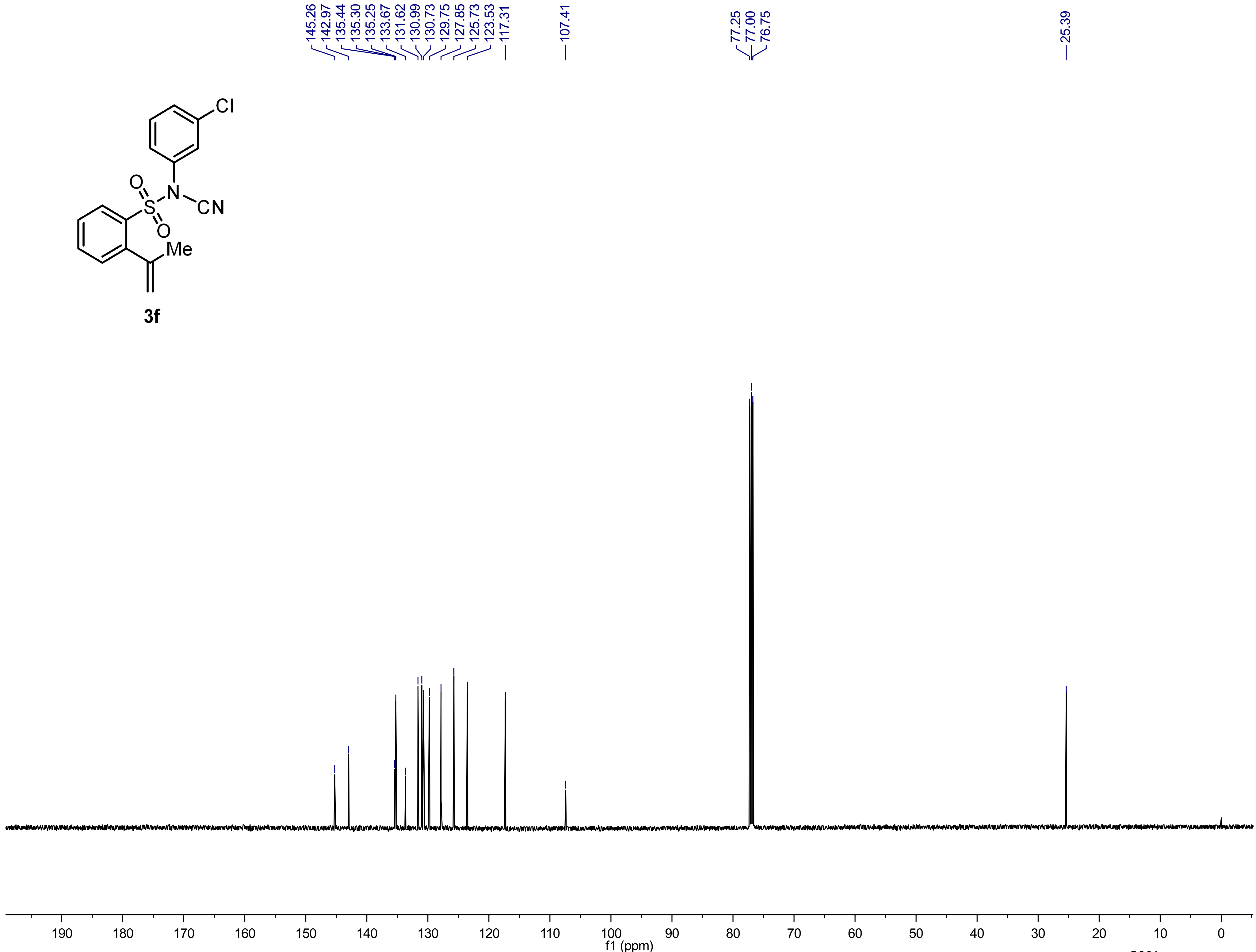
7.26
7.26
7.25
7.14
7.14
7.14
7.13
7.13
7.12
7.12
5.31
5.30
5.30
4.73
2.11
-0.00
1.01
1.01
1.03
2.05
1.03
1.28
1.01
1.00
0.98
3.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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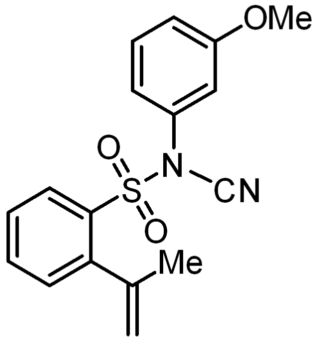
129.75
127.85
125.73
123.53
117.31
107.41
77.25
77.00
76.75
25.39
Cl
O
S
N
CN
O
Me
3f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
O
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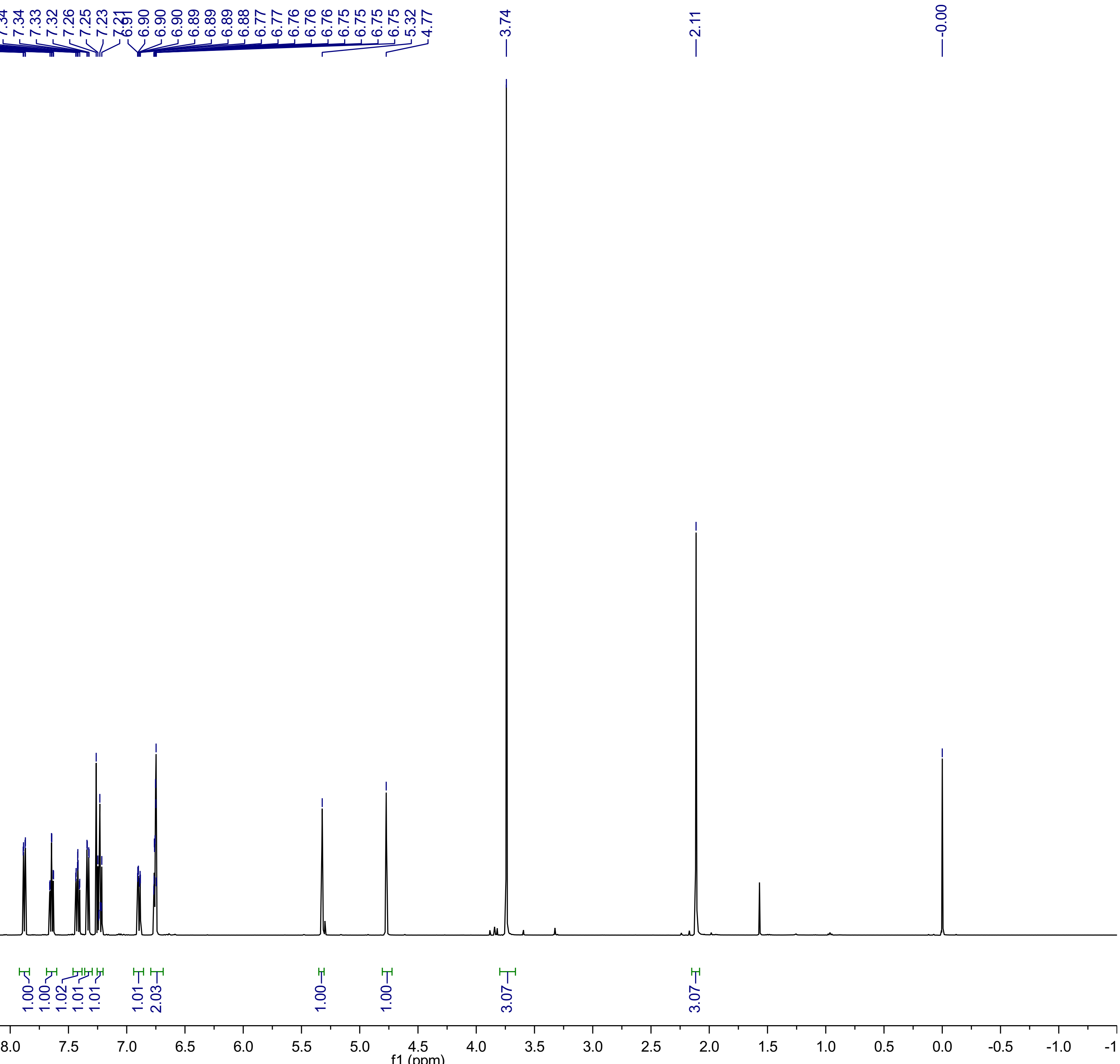
N
CN
O
Me

3g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7.42
7.42
7.40
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7.34
7.33
7.32
7.26
7.25
7.23
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6.90
6.90
6.90
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6.89
6.88
6.77
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6.76
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6.76
6.75
6.75
6.75
6.75
5.32
4.77
3.74
2.11
-0.00
1.00
1.00
1.02
1.01
1.01
1.01
2.03
1.00
1.00
3.07
3.07
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9.0
8.5
8.0
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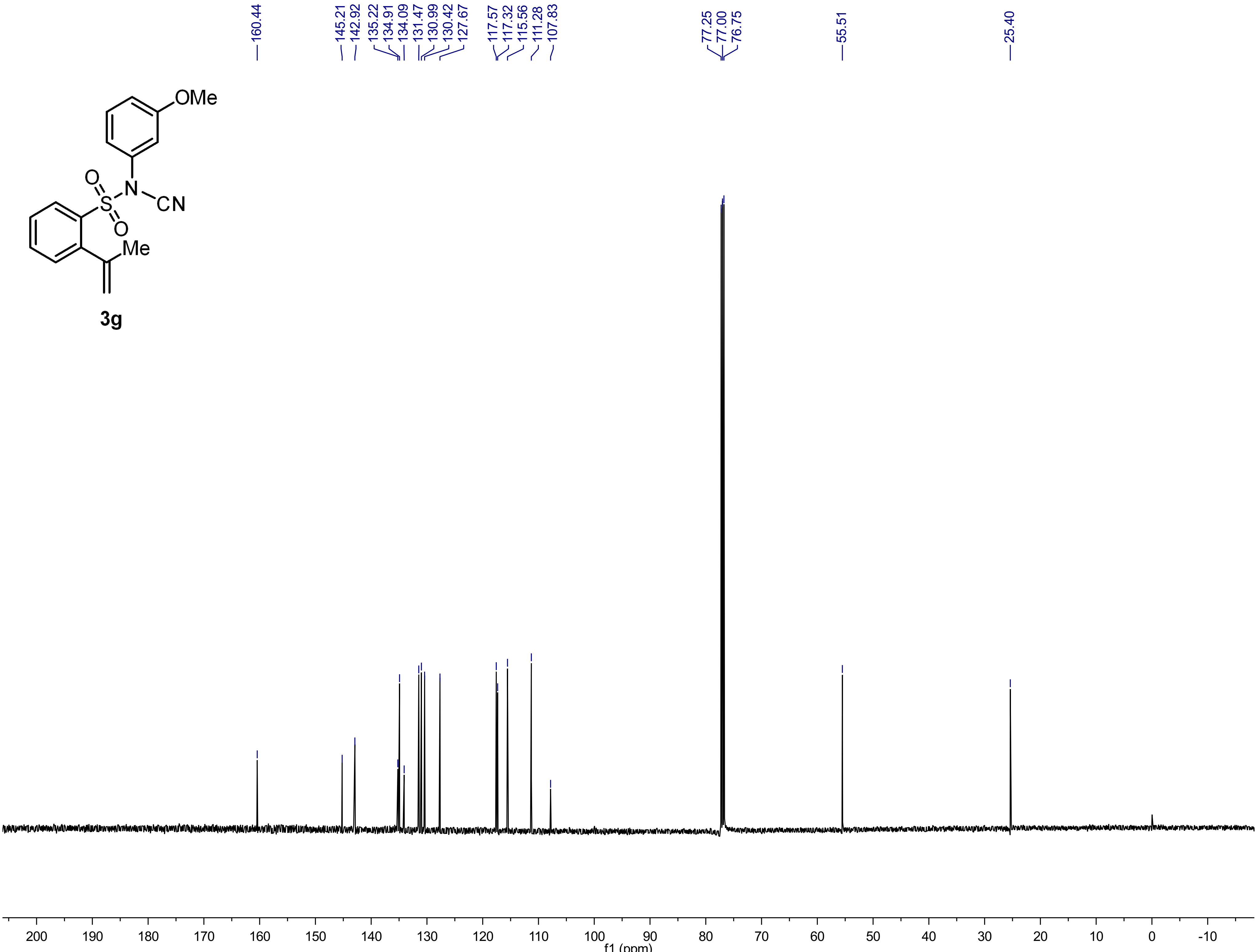
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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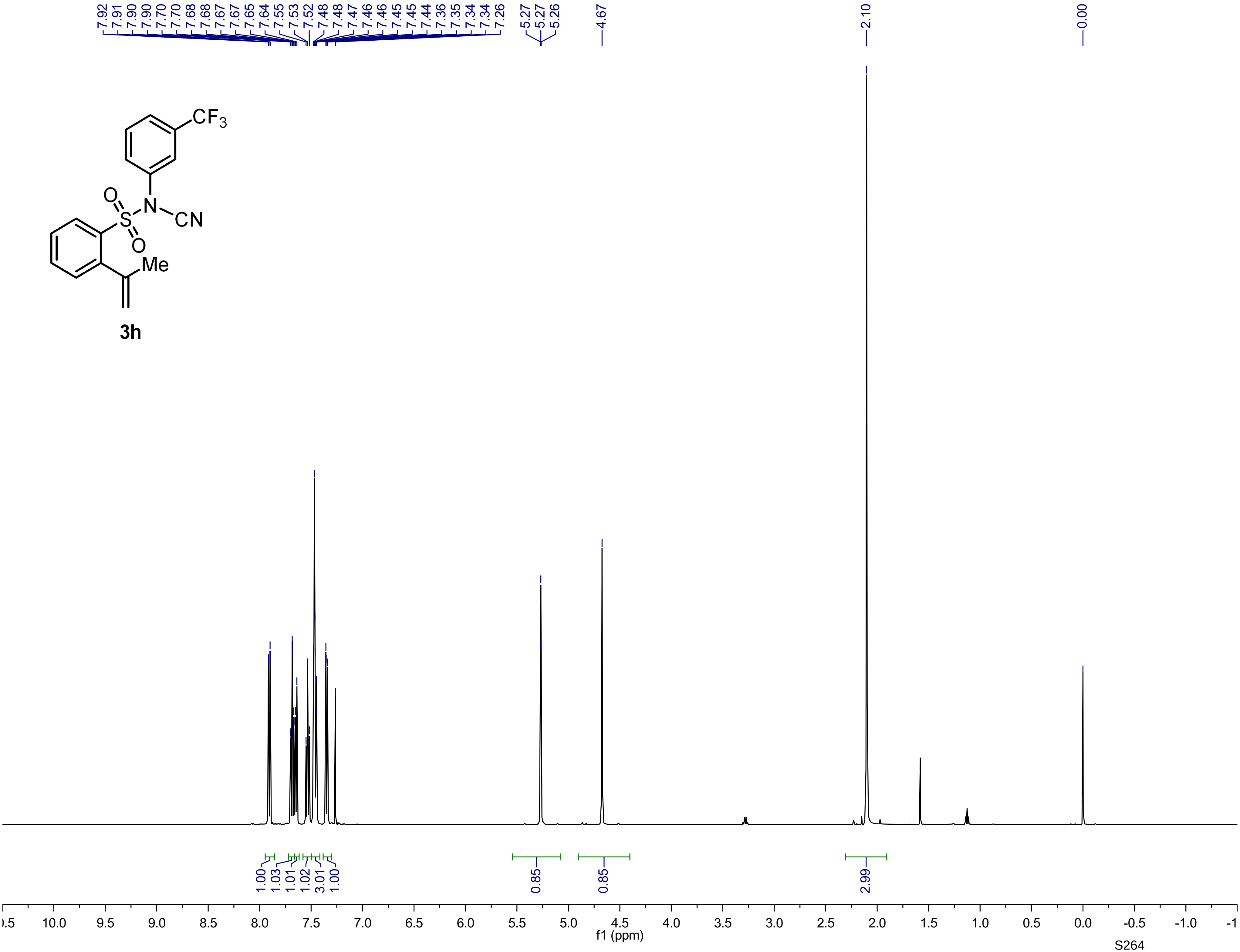
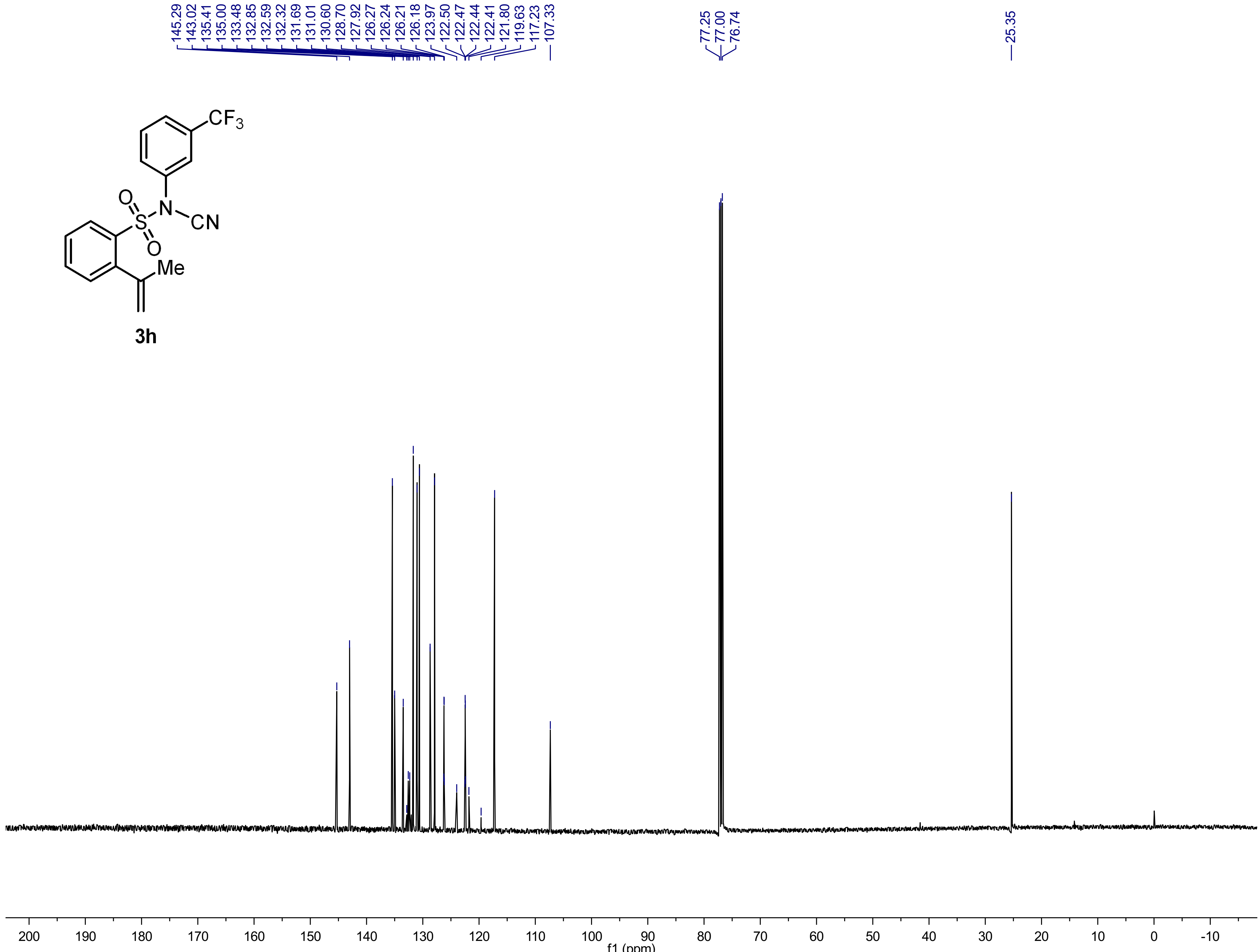
142.92
135.22
134.91
134.09
131.47
130.99
130.42
127.67
117.57
117.32
115.56
111.28
107.83
77.25
77.00
76.75
55.51
25.40
OMe
O
S
N
CN
O
Me
f1 (ppm)

3g


CF3
O
S
N
CN
O
Me
7.92
7.91
7.90
7.90
7.70
7.70
7.68
7.68
7.67
7.67
7.65
7.64
7.55
7.53
7.52
7.48
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.36
7.35
7.34
7.34
7.26
5.27
5.27
5.26
4.67
2.10
0.00
1.00
1.03
1.01
1.02
3.01
1.00
0.85
0.85
2.99
f1 (ppm)

3h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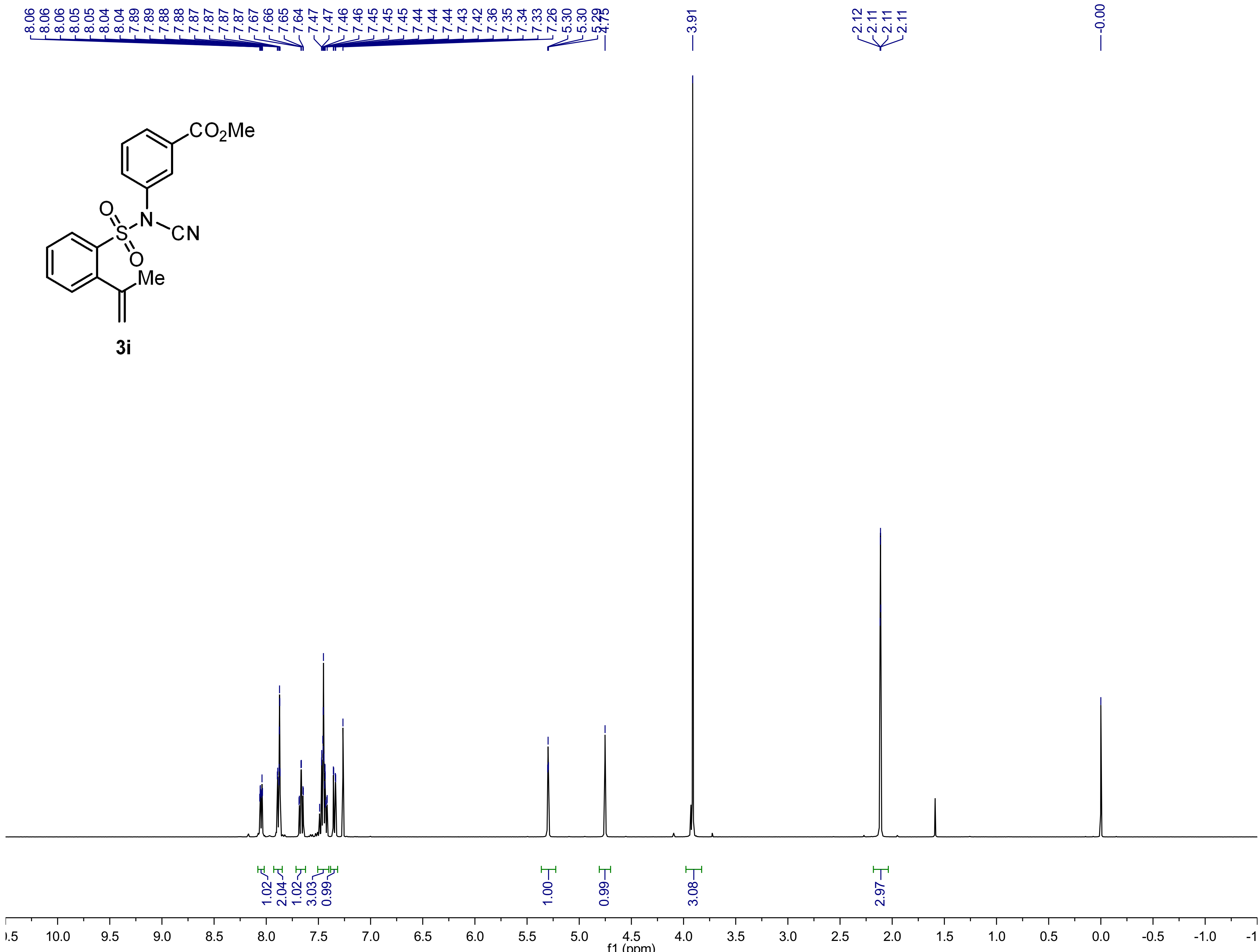
143.02
135.41
135.00
133.48
132.85
132.59
132.32
131.69
131.01
130.60
128.70
127.92
126.27
126.24
126.21
126.18
123.97
122.50
122.47
122.44
122.41
121.80
119.63
117.23
107.33
77.25
77.00
76.74
25.35
CF3
O
S
N
CN
O
Me
3h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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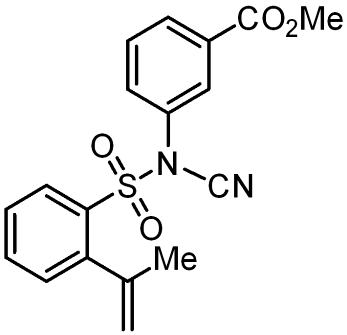
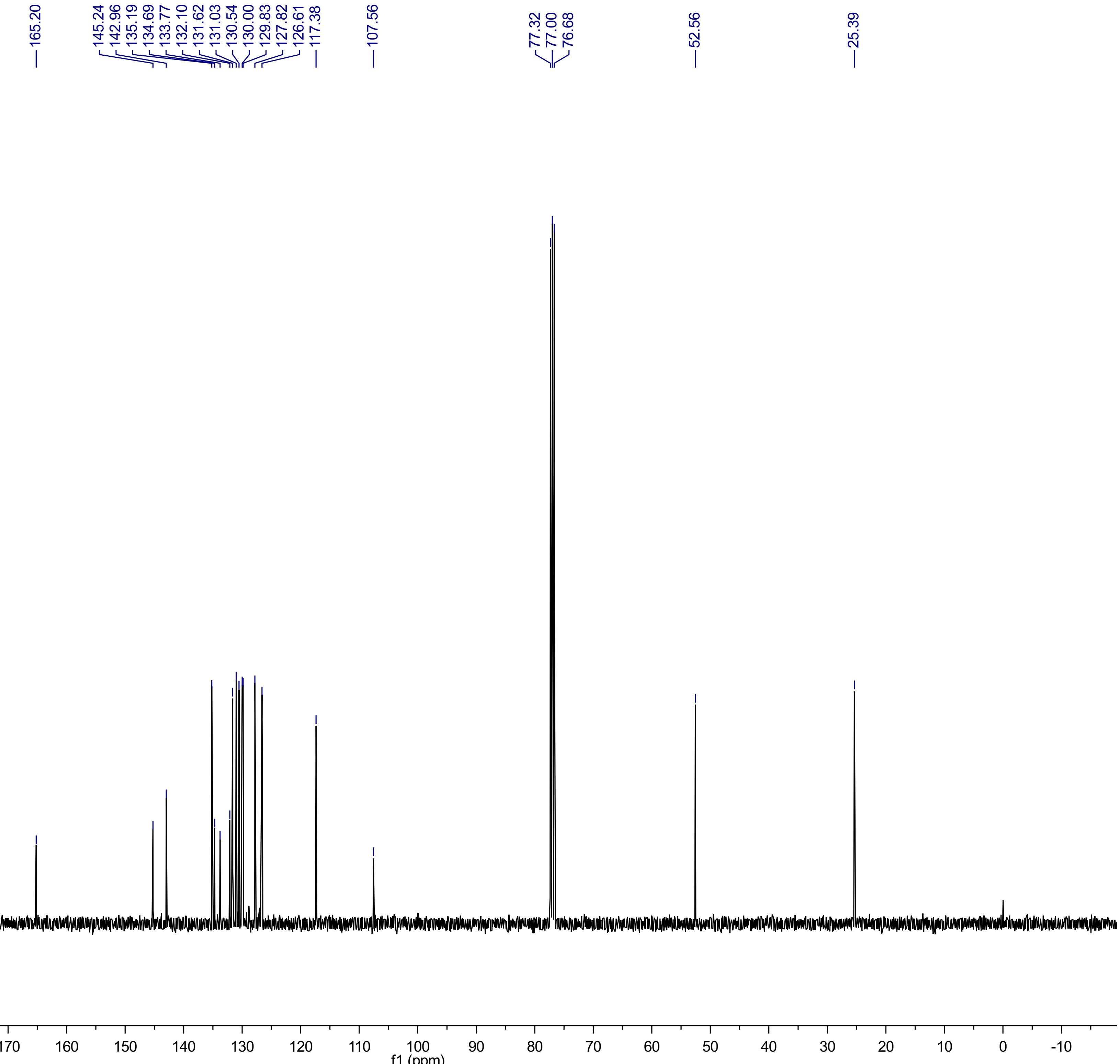
3.91
2.12 2.11 2.11 2.11
-0.00
CO2Me
O
S
N
CN
O
Me
3i
1.02 2.04 1.02 3.03 0.99
1.00
0.99
3.08
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



3i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135.19
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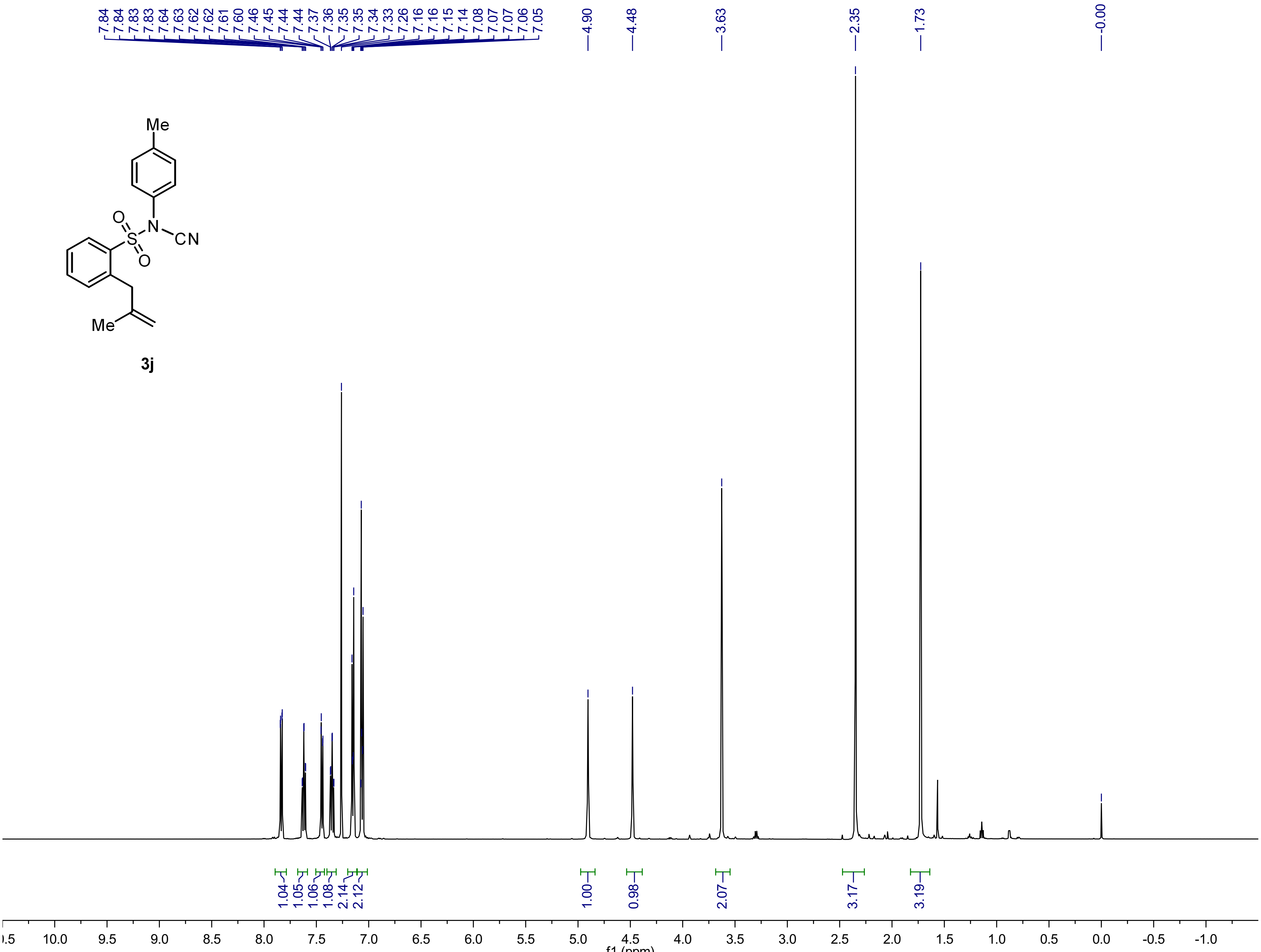
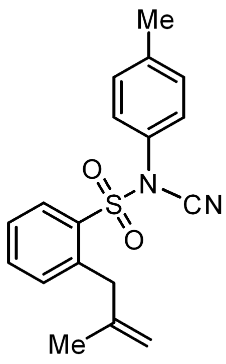
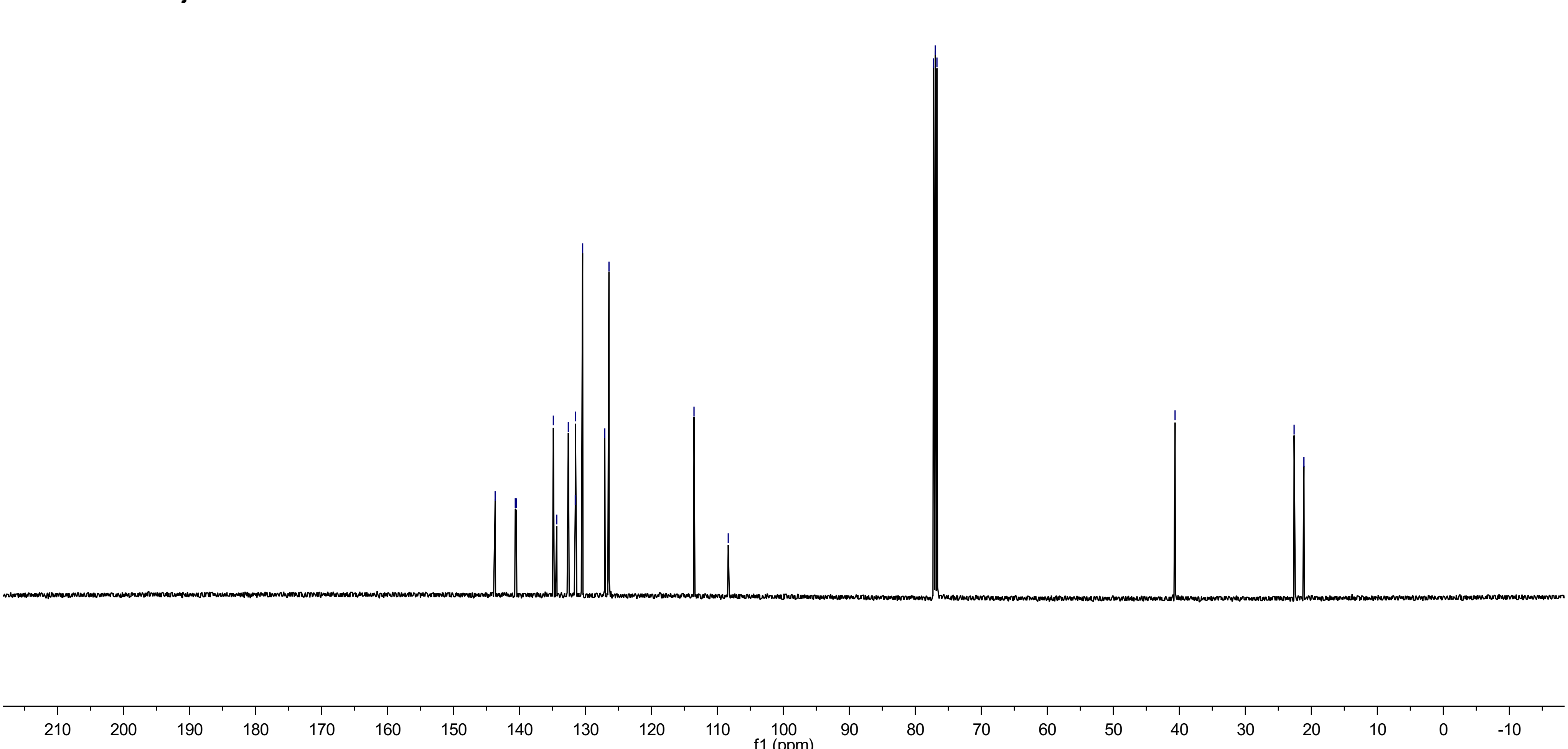
133.77
132.10
131.62
131.03
130.54
130.00
129.83
127.82
126.61
117.38
107.56
77.32
77.00
76.68
52.56
25.39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



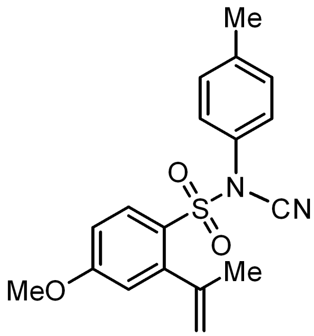
7.84 7.84 7.83 7.83 7.64 7.63 7.62 7.62 7.61 7.60 7.46 7.45 7.44 7.44 7.37 7.36 7.35 7.35 7.34 7.33 7.26 7.16 7.16 7.15 7.14 7.08 7.07 7.07 7.06 7.05
4.90
4.48
3.63
2.35
1.73
-0.00
Me
O
S
N
CN
O
Me
3j
1.04
1.05
1.06
1.08
2.14
2.12
1.00
0.98
2.07
3.17
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



3j

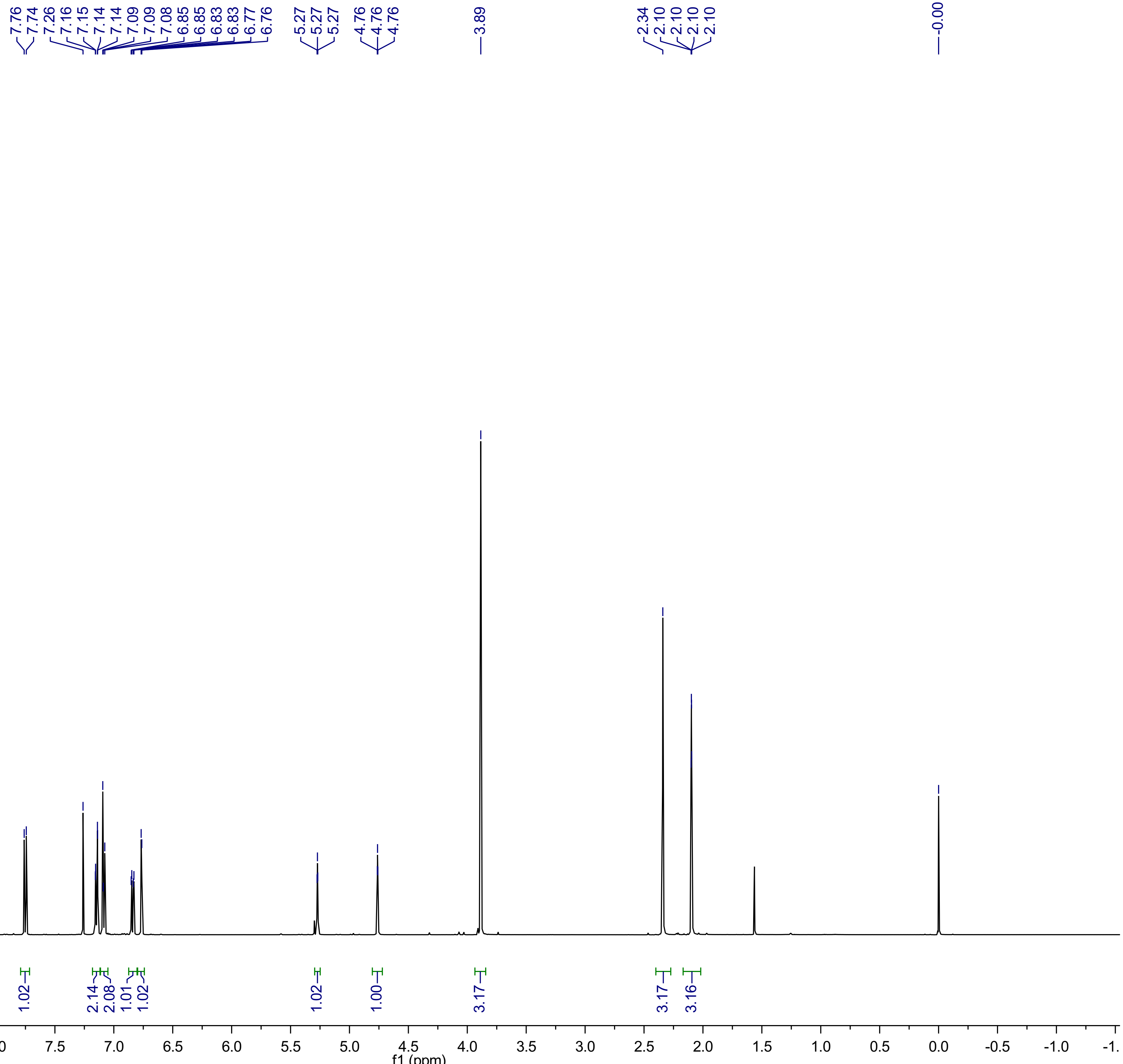


143.68
140.63
140.50
134.87
134.35
132.60
131.55
131.53
130.43
127.08
126.44
113.55
108.37
77.25
77.00
76.75
40.67
22.63
21.14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

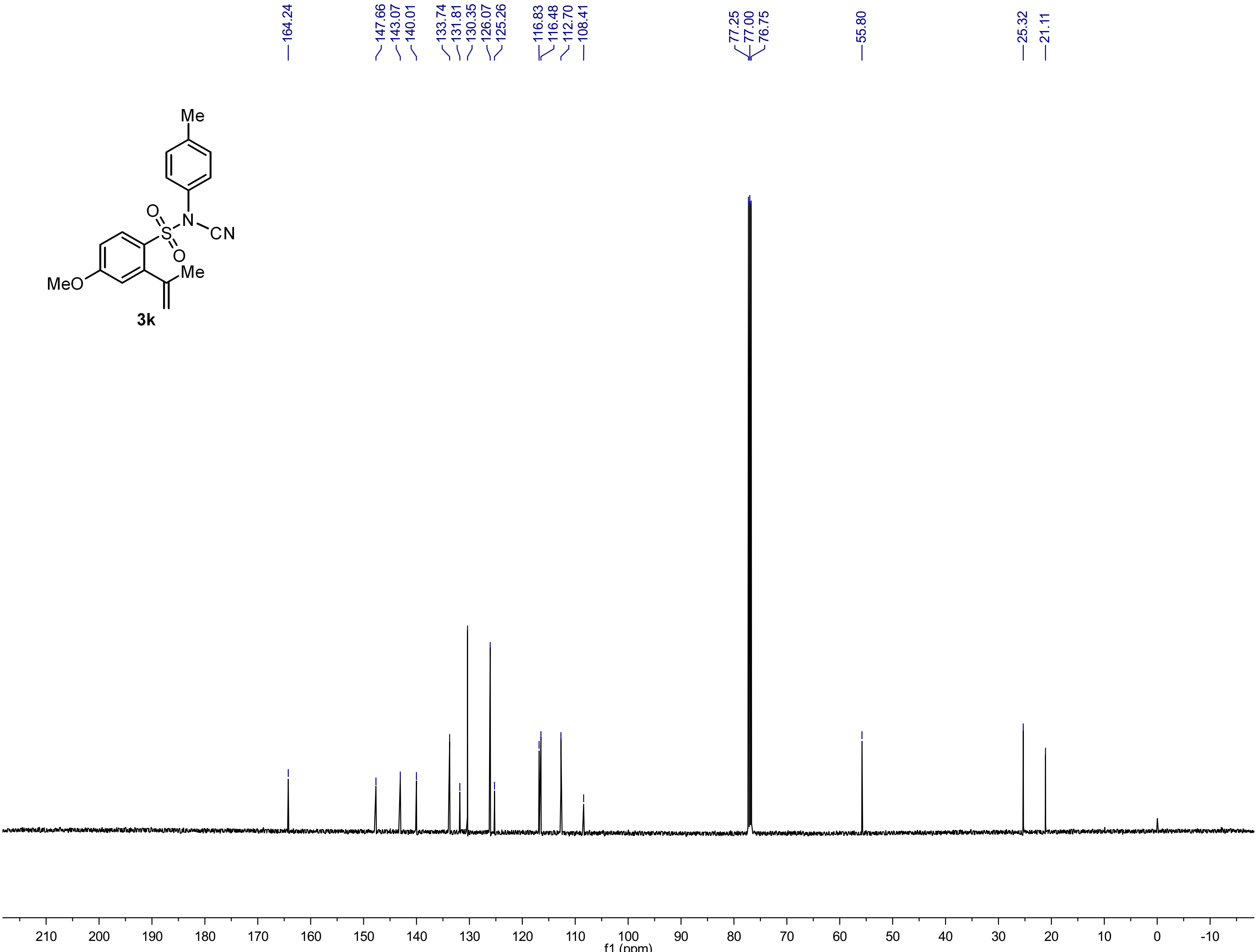


Me
O
S
N
CN
O
MeO
Me

3k



7.76
7.74
7.26
7.16
7.15
7.14
7.14
7.09
7.09
7.08
6.85
6.85
6.83
6.83
6.77
6.76
5.27
5.27
5.27
4.76
4.76
4.76
3.89
2.34
2.10
2.10
2.10
2.10
-0.00
1.02
2.14
2.08
1.01
1.02
1.02
1.00
3.17
3.17
3.16
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 -0.5 -1.0 -1.
f1 (ppm)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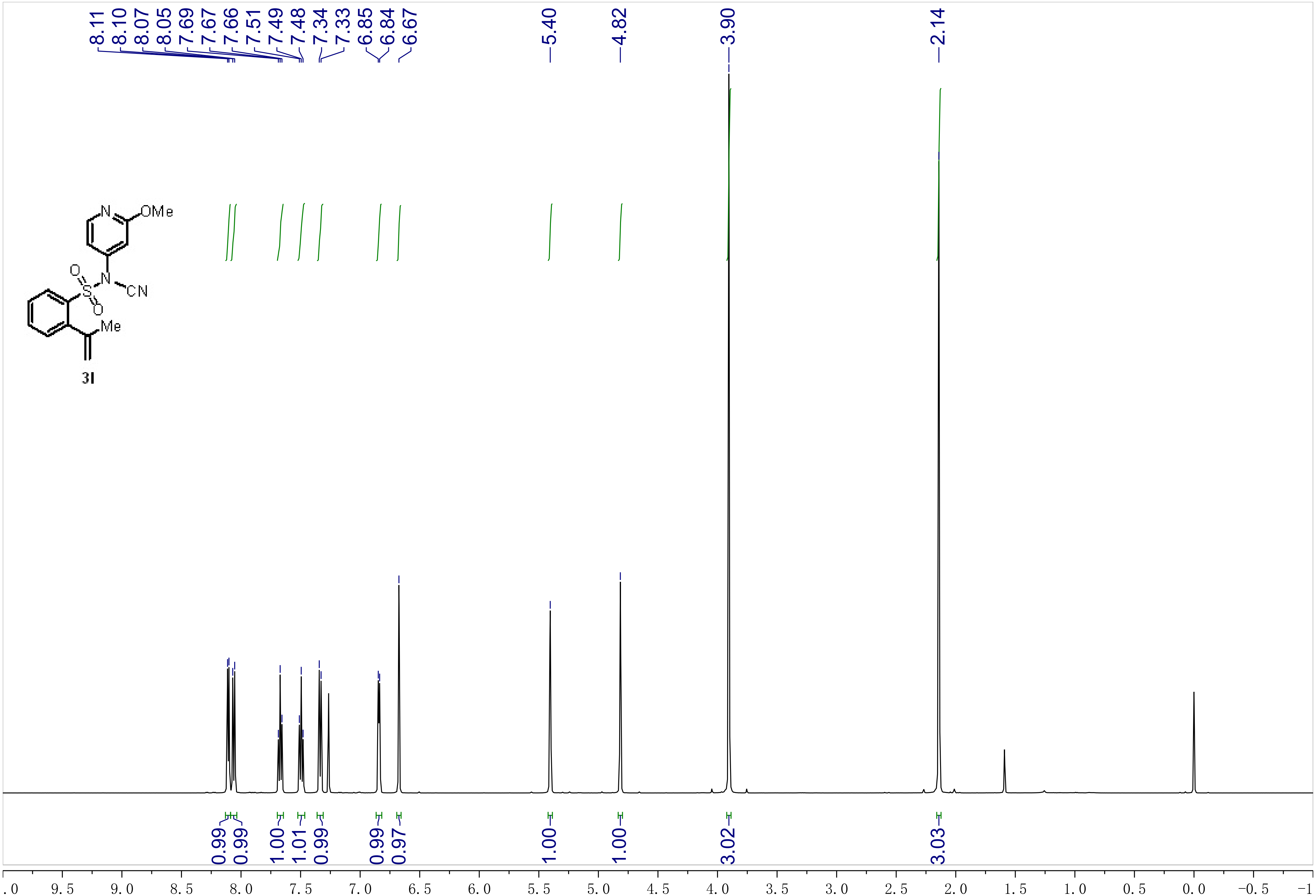
130.35
126.07
125.26
116.83
116.48
112.70
108.41
77.25
77.00
76.75
55.80
25.32
21.11
Me
O
S
N
CN
O
Me
MeO
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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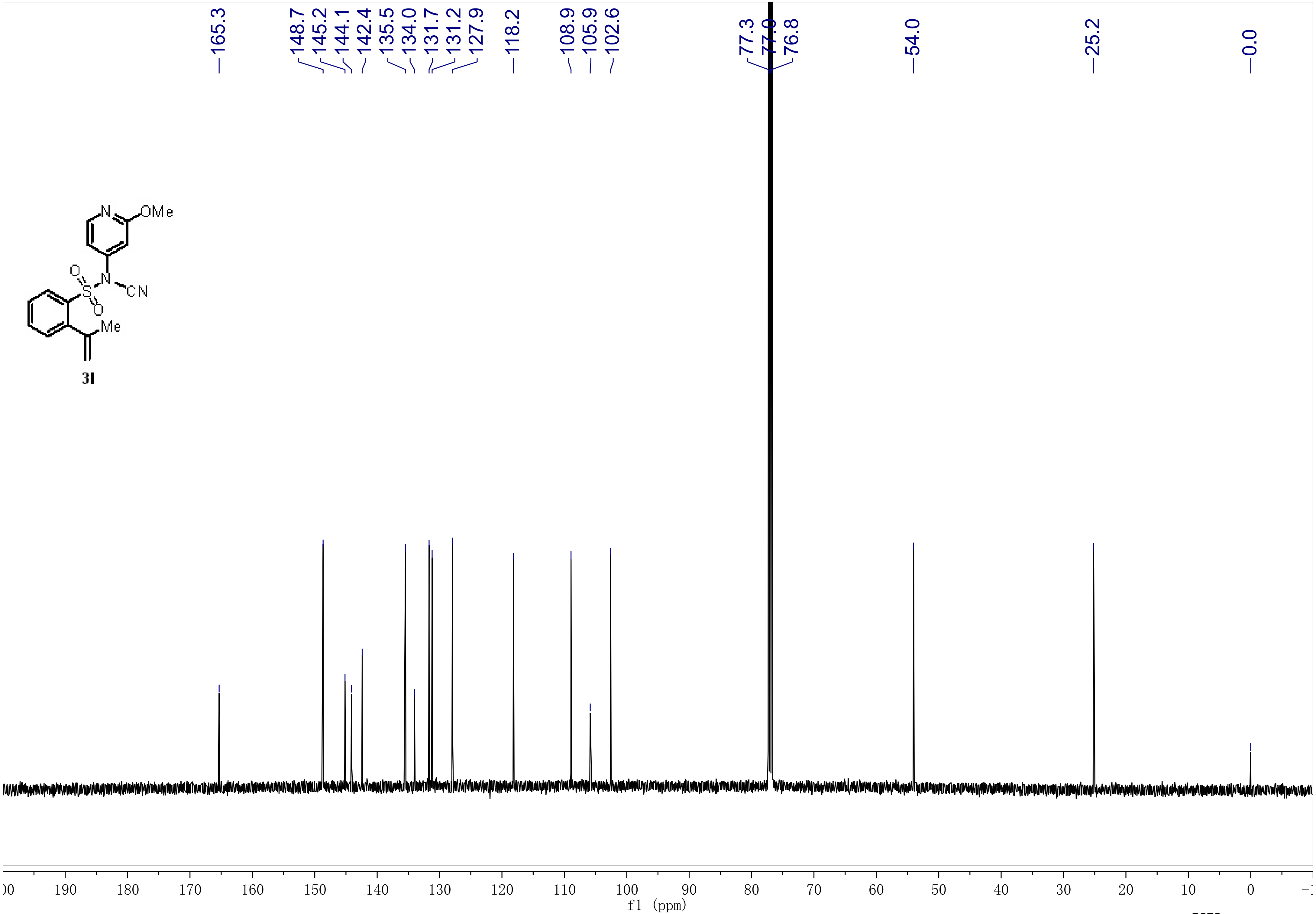
8.10
8.07
8.05
7.69
7.67
7.66
7.51
7.49
7.48
7.34
7.33
6.85
6.84
6.67
5.40
4.82
3.90
2.14
N
OMe
O
S
O
N
CN
Me
0.99
0.99
1.00
1.01
0.99
0.99
0.97
1.00
1.00
3.02
3.03
f1 (ppm)

3l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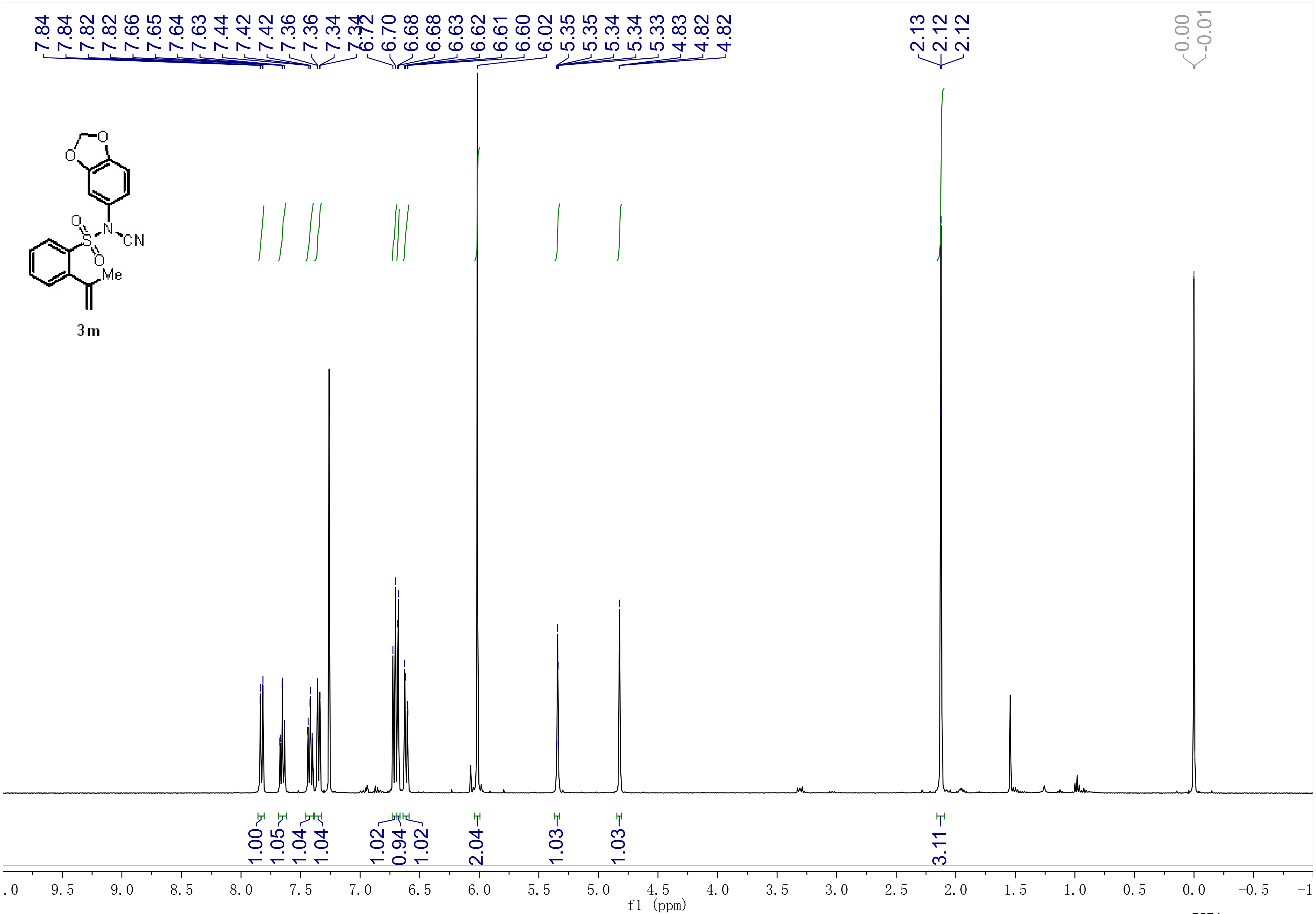
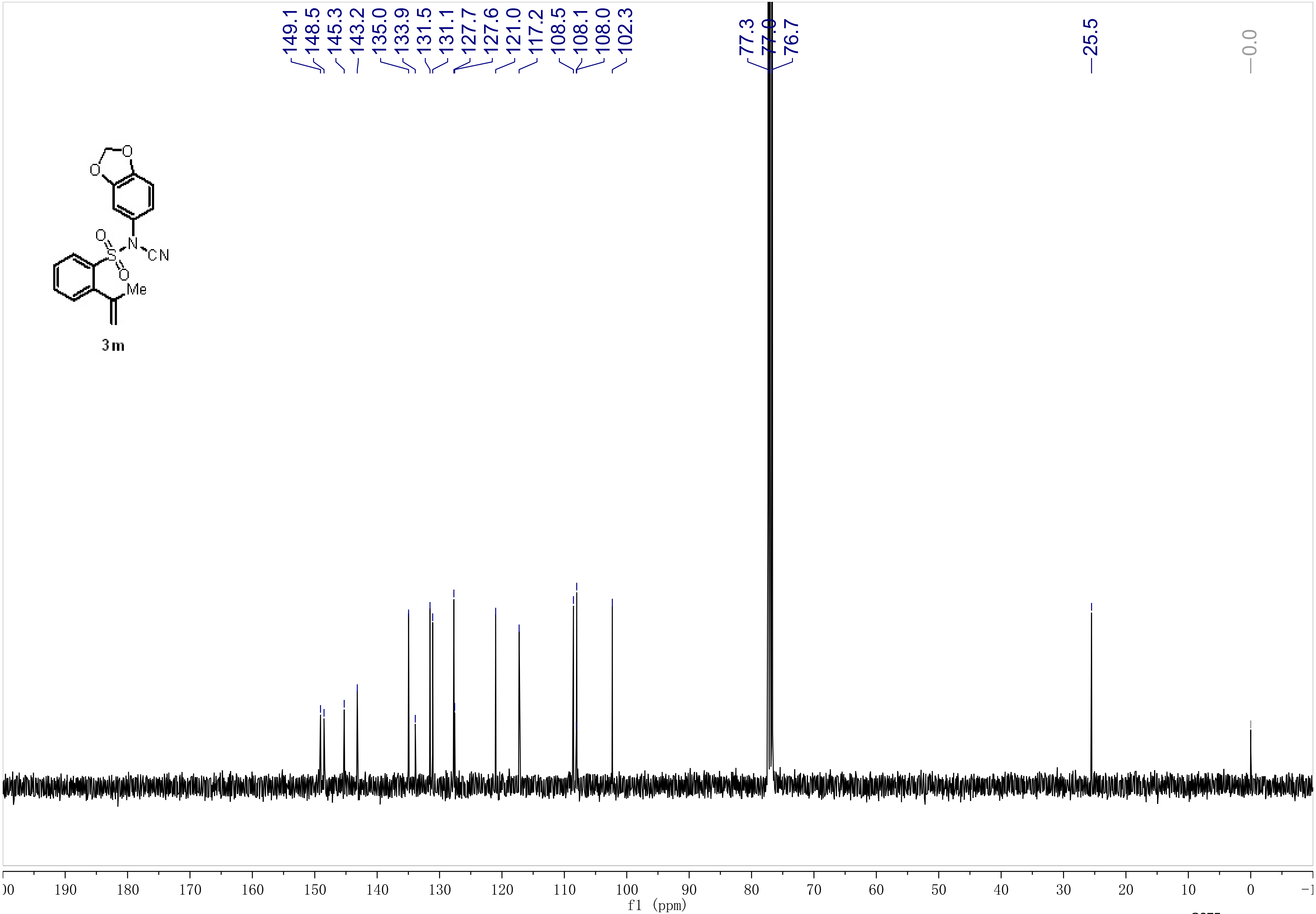
148.7
145.2
144.1
142.4
135.5
134.0
131.7
131.2
127.9
118.2
108.9
105.9
102.6
77.3
77.0
76.8
54.0
25.2
0.0
N
OMe
O
S
O
N
CN
Me
3l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.84 7.84 7.82 7.82 7.66 7.65 7.64 7.63 7.44 7.42 7.42 7.36 7.36 7.34 7.34 6.72 6.70 6.68 6.68 6.63 6.62 6.61 6.60 6.02 5.35 5.35 5.34 5.34 5.33 4.83 4.82 4.82
2.13 2.12 2.12
0.00 -0.01
O
O
O
O
S
N
CN
Me
3m
1.00 1.05 1.04 1.04 1.02 0.94 1.02 2.04 1.03 1.03 3.11
.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 -0.5 -1
f1 (ppm)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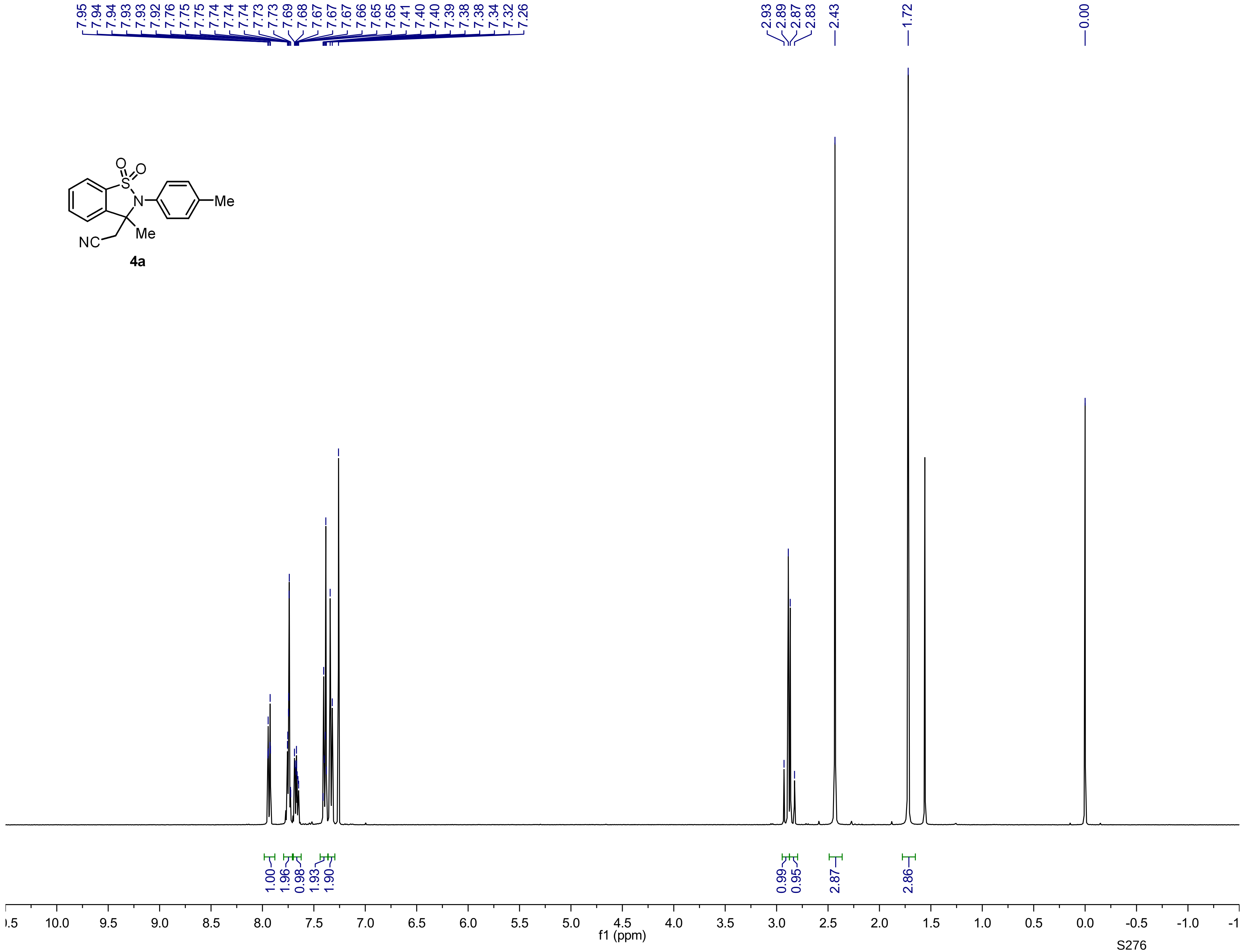
148.5
145.3
143.2
135.0
133.9
131.5
131.1
127.7
127.6
121.0
117.2
108.5
108.1
108.0
102.3
77.3
77.0
76.7
25.5
0.0
O
O
O
S
O
N
CN
Me
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.94
7.94
7.93
7.93
7.92
7.76
7.75
7.75
7.74
7.74
7.74
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7.73
7.69
7.68
7.67
7.67
7.67
7.66
7.65
7.65
7.41
7.40
7.40
7.39
7.38
7.38
7.34
7.32
7.26
2.93
2.89
2.87
2.83
2.43
1.72
0.00
Me
NC
Me
4a
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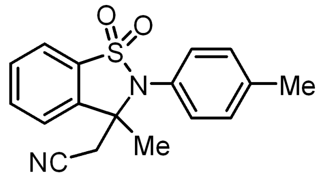
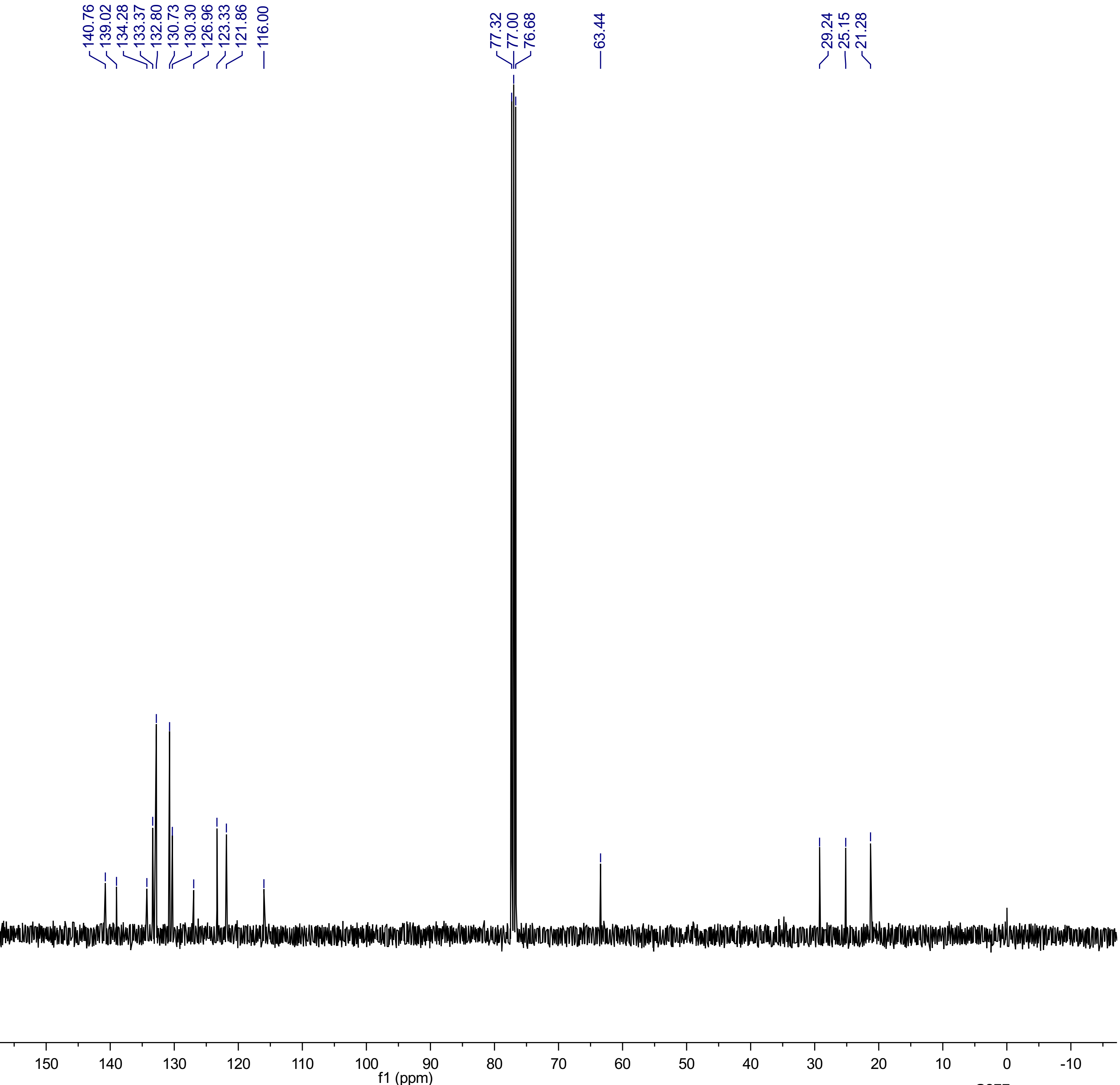
1.96
0.98
1.93
1.90
0.99
0.95
2.87
2.86
f1 (ppm)



Me
Me
NC

4a



140.76
139.02
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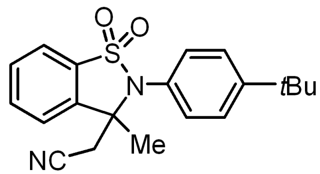
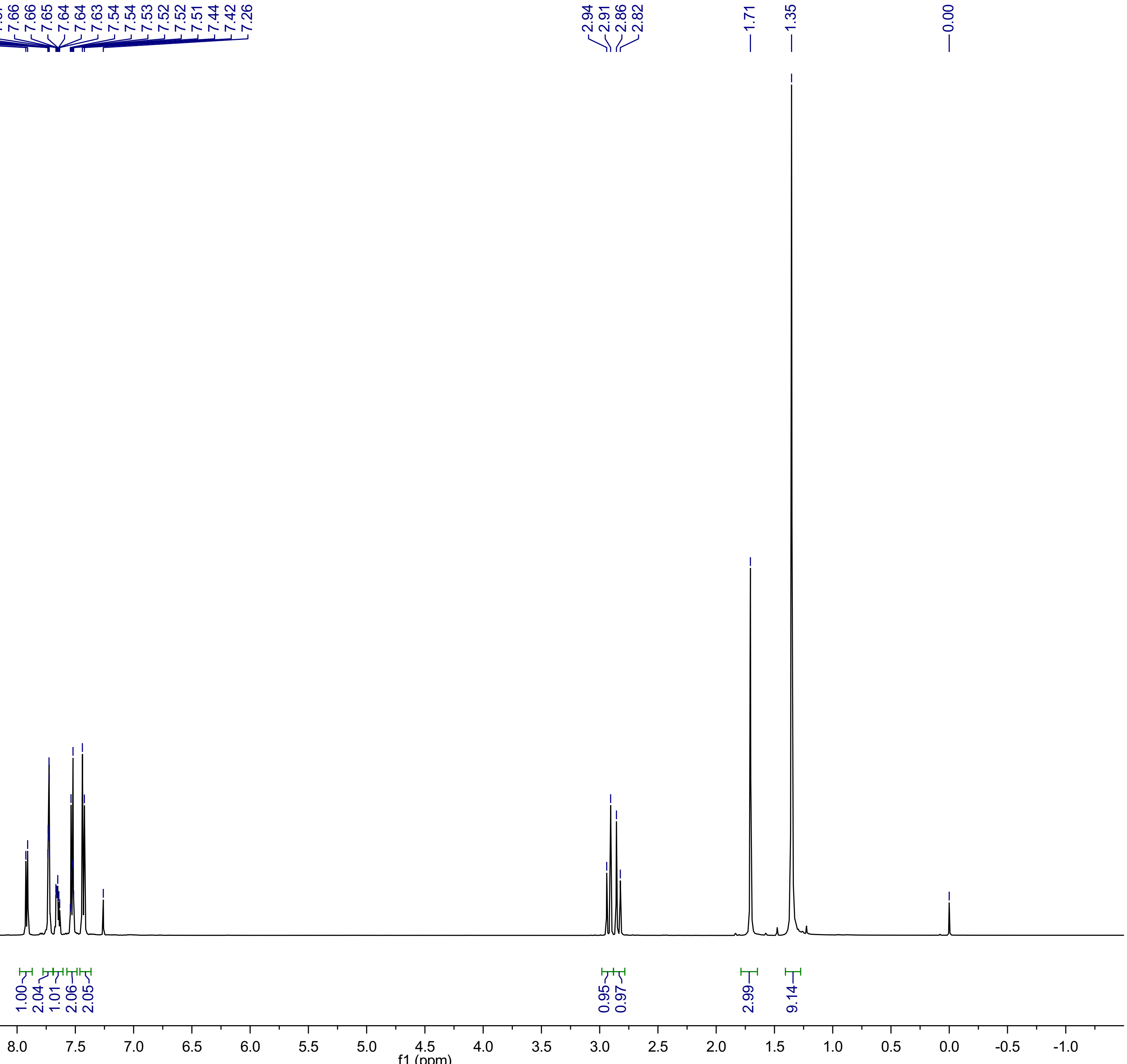
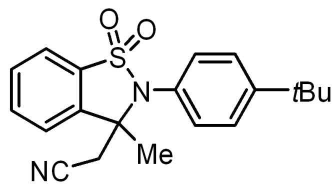
132.80
130.73
130.30
126.96
123.33
121.86
116.00
77.32
77.00
76.68
63.44
29.24
25.15
21.28
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



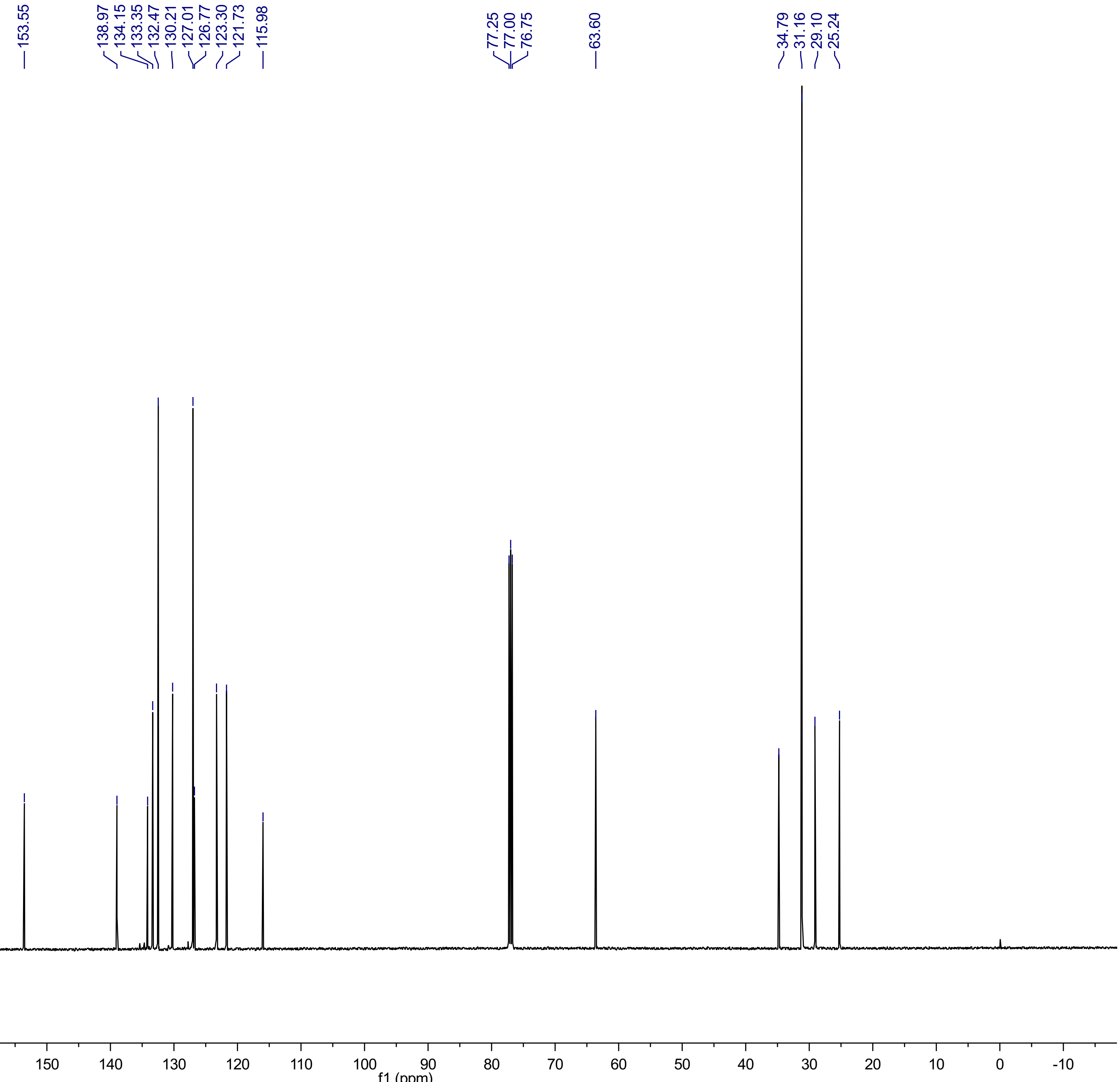
4b



7.92
7.91
7.74
7.73
7.73
7.73
7.72
7.67
7.66
7.66
7.65
7.64
7.64
7.63
7.54
7.54
7.53
7.52
7.52
7.51
7.44
7.42
7.26
2.94
2.91
2.86
2.82
1.71
1.35
0.00
1.00
2.04
1.01
2.06
2.05
0.95
0.97
2.99
9.14
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
-0.5
-1.0
f1 (ppm)



4b



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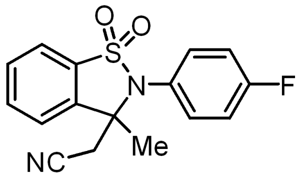
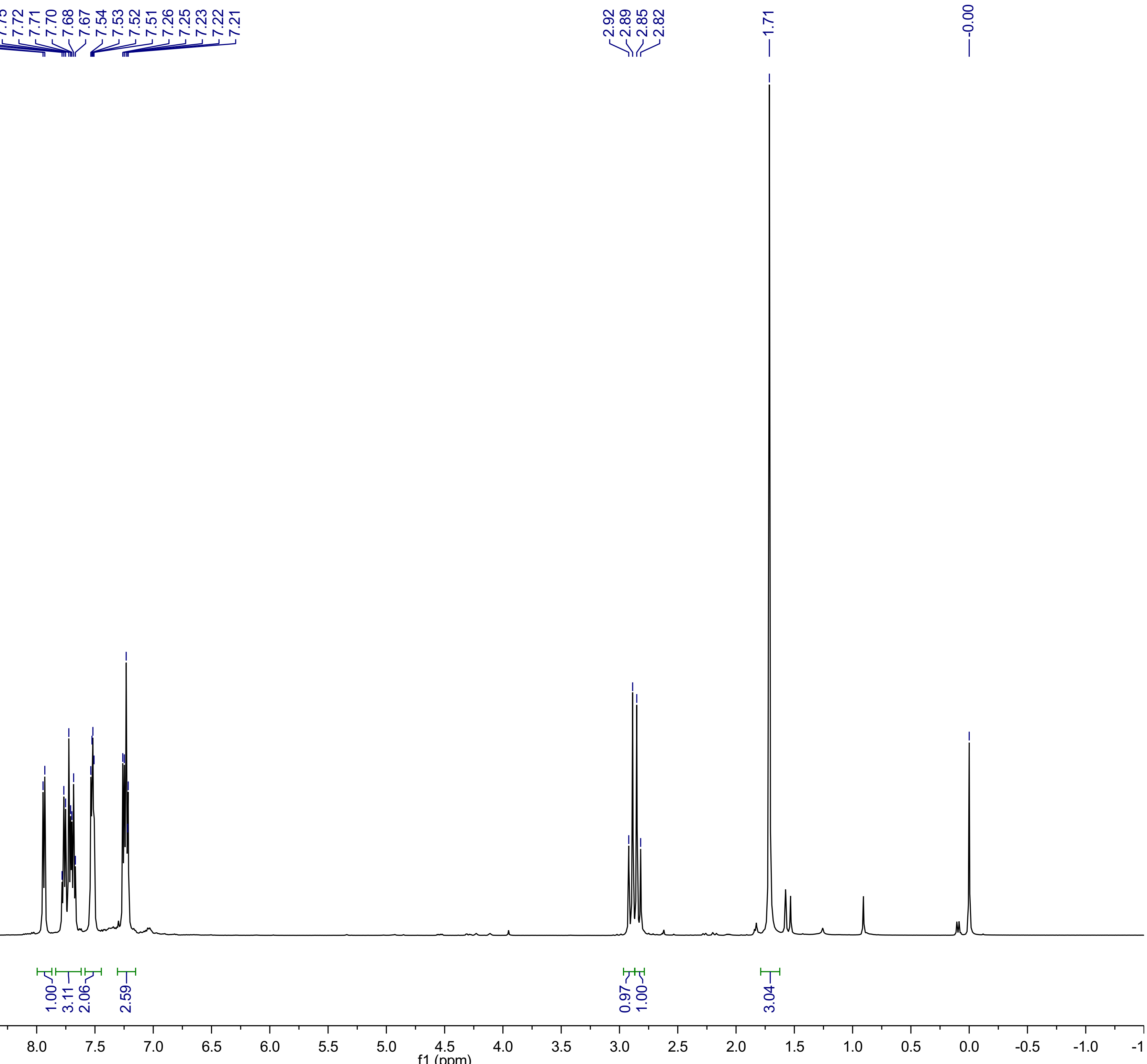
138.97
134.15
133.35
132.47
130.21
127.01
126.77
123.30
121.73
115.98
77.25
77.00
76.75
63.60
34.79
31.16
29.10
25.24
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



4c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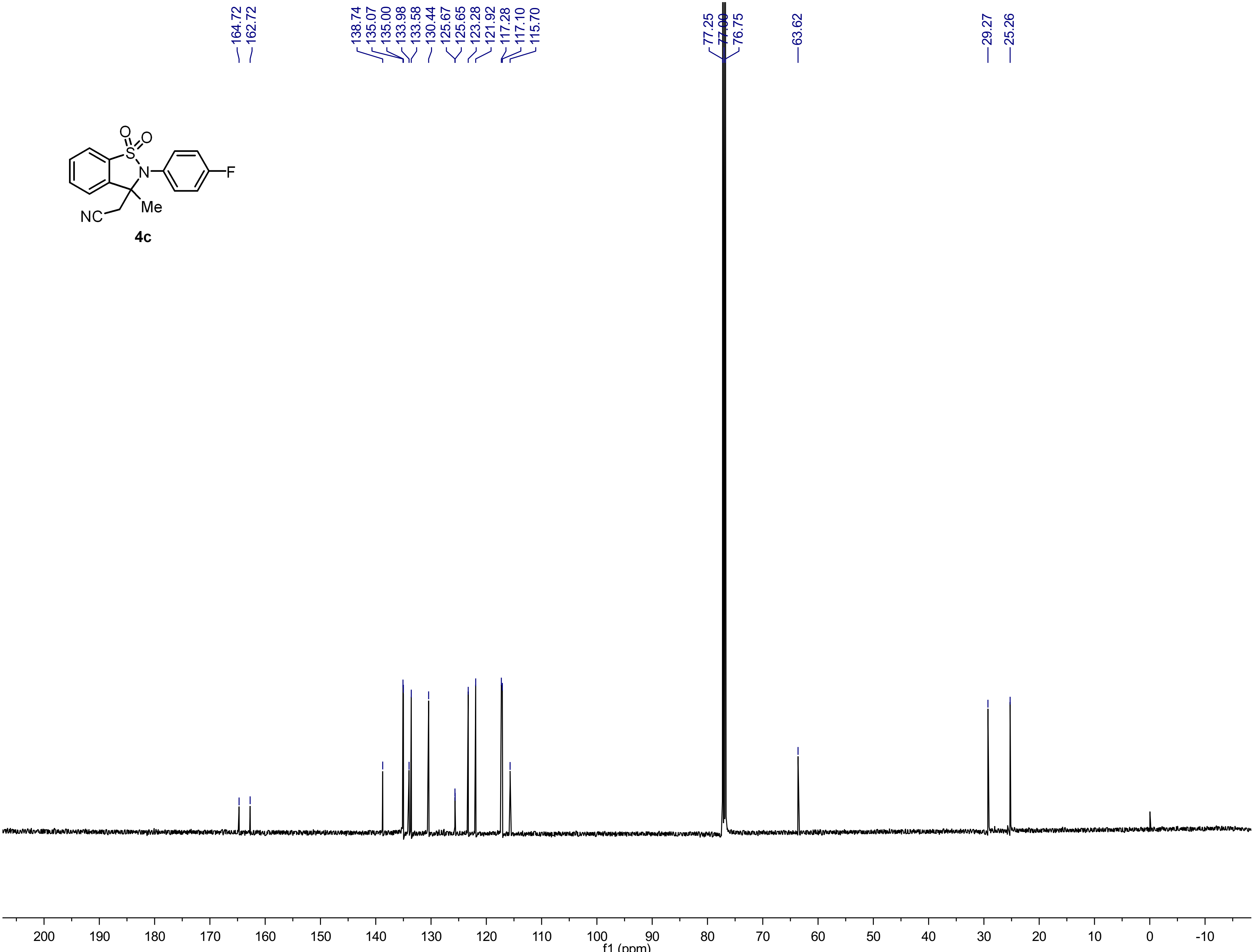
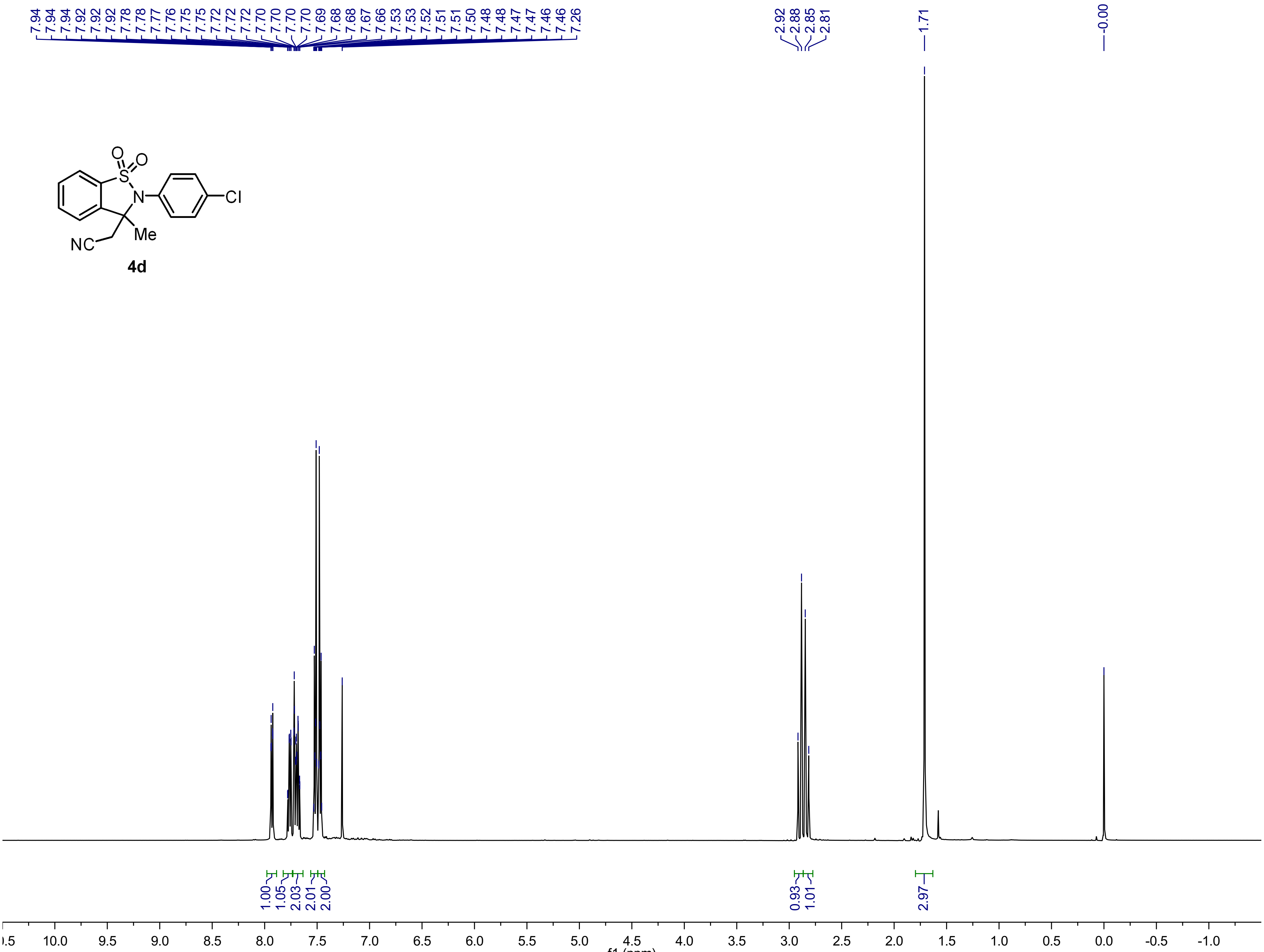
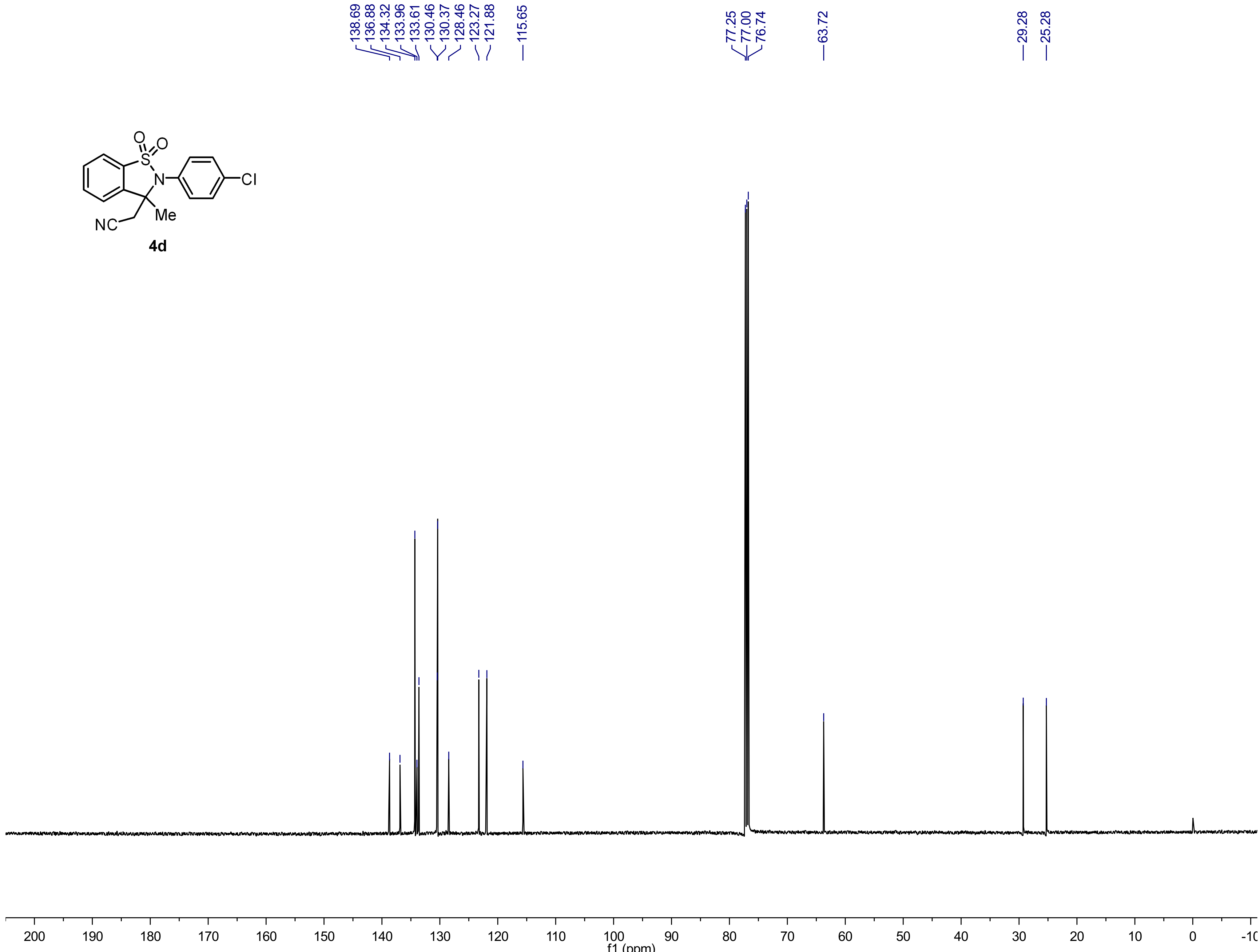
7.77
7.75
7.72
7.71
7.70
7.68
7.67
7.54
7.53
7.52
7.51
7.26
7.25
7.23
7.22
7.21
2.92
2.89
2.85
2.82
1.71
-0.00
1.00
3.11
2.06
2.59
0.97
1.00
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


164.72
162.72
138.74
135.07
135.00
133.98
133.58
130.44
125.67
125.65
123.28
121.92
117.28
117.10
115.70
77.25
77.00
76.75
63.62
29.27
25.26
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
O
O
S
N
F
Me
NC

4c


7.94 7.94 7.94 7.92 7.92 7.92 7.78 7.78 7.77 7.76 7.75 7.75 7.72 7.72 7.72 7.70 7.70 7.70 7.70 7.69 7.68 7.68 7.67 7.66 7.53 7.53 7.52 7.51 7.51 7.50 7.48 7.48 7.47 7.47 7.46 7.46 7.26
2.92 2.88 2.85 2.81
1.71
-0.00
O
O
S
N
Cl
Me
NC
4d
1.00 1.05 2.03 2.01 2.00
0.93 1.01
2.97
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 -0.5 -1.0
f1 (ppm)



138.69
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134.32
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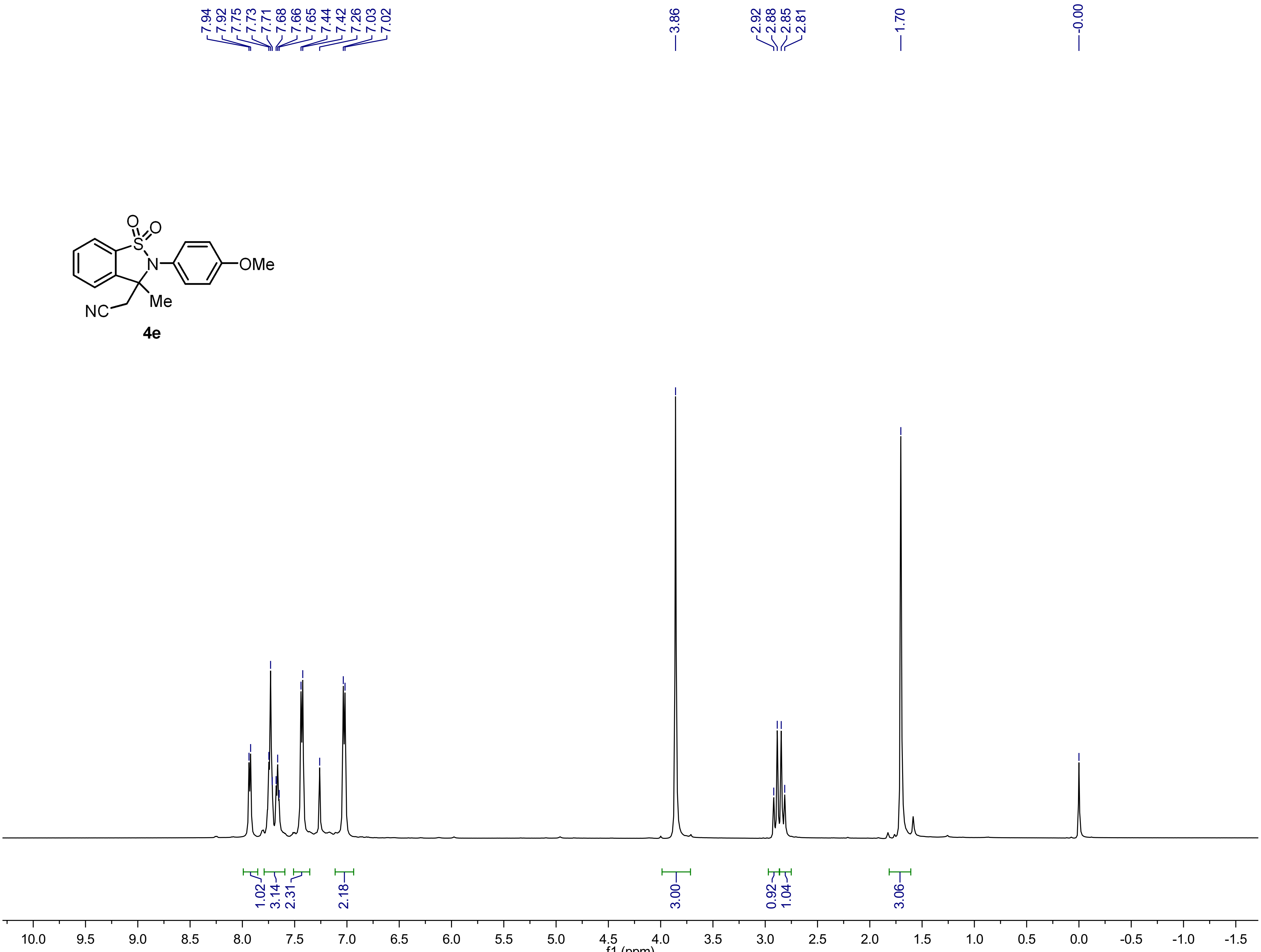
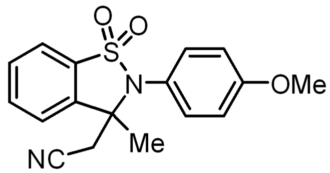
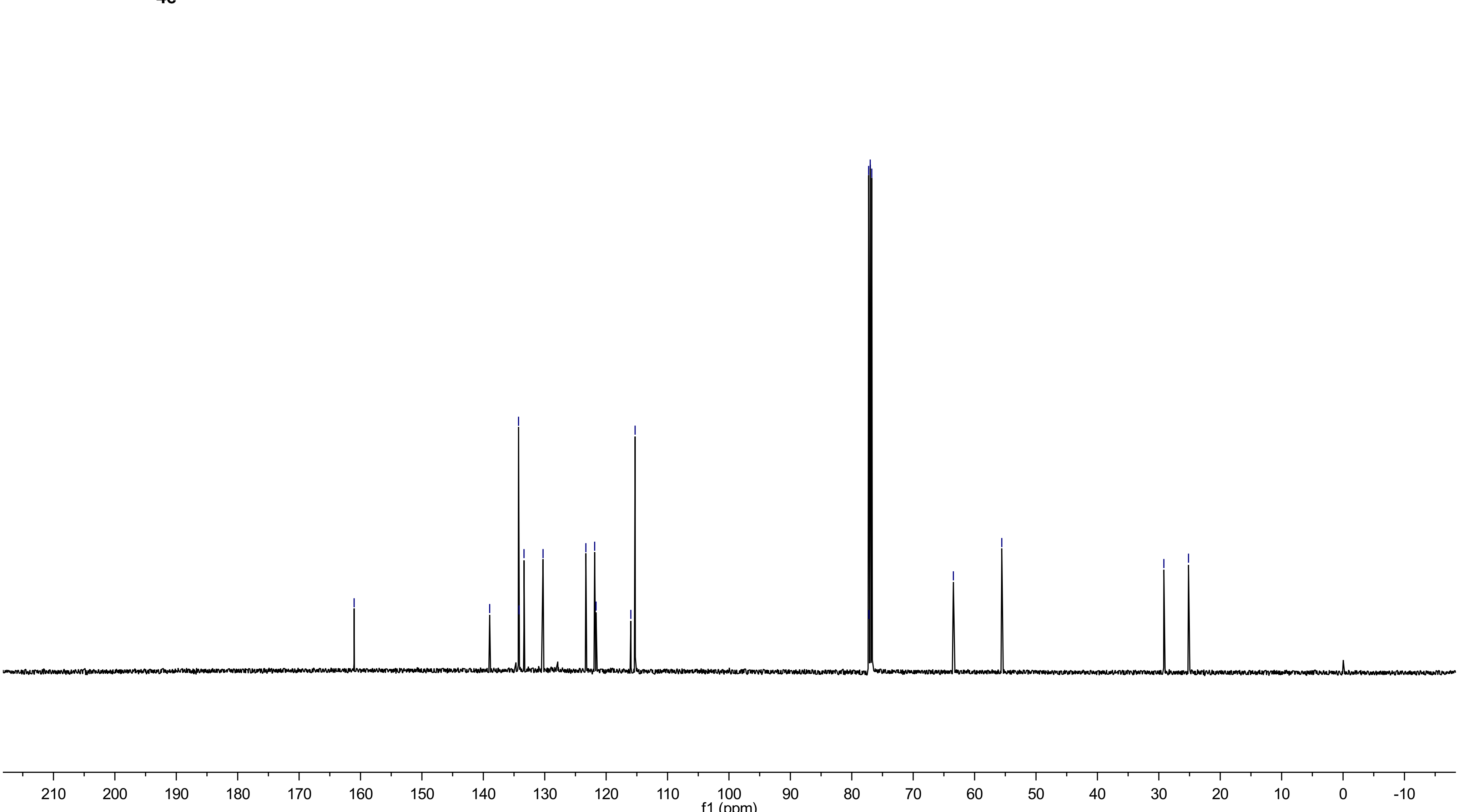
133.61
130.46
130.37
128.46
123.27
121.88
115.65
77.25
77.00
76.74
63.72
29.28
25.28
O
O
S
N
Cl
Me
NC
4d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.94 7.92 7.75 7.73 7.71 7.68 7.66 7.65 7.44 7.42 7.26 7.03 7.02
3.86
2.92 2.88 2.85 2.81
1.70
-0.00
OMe
Me
NC
4e
1.02 3.14 2.31 2.18 3.00 0.92 1.04 3.06
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 -0.5 -1.0 -1.5
f1 (ppm)


O
O
S
N
OMe
Me
NC

4e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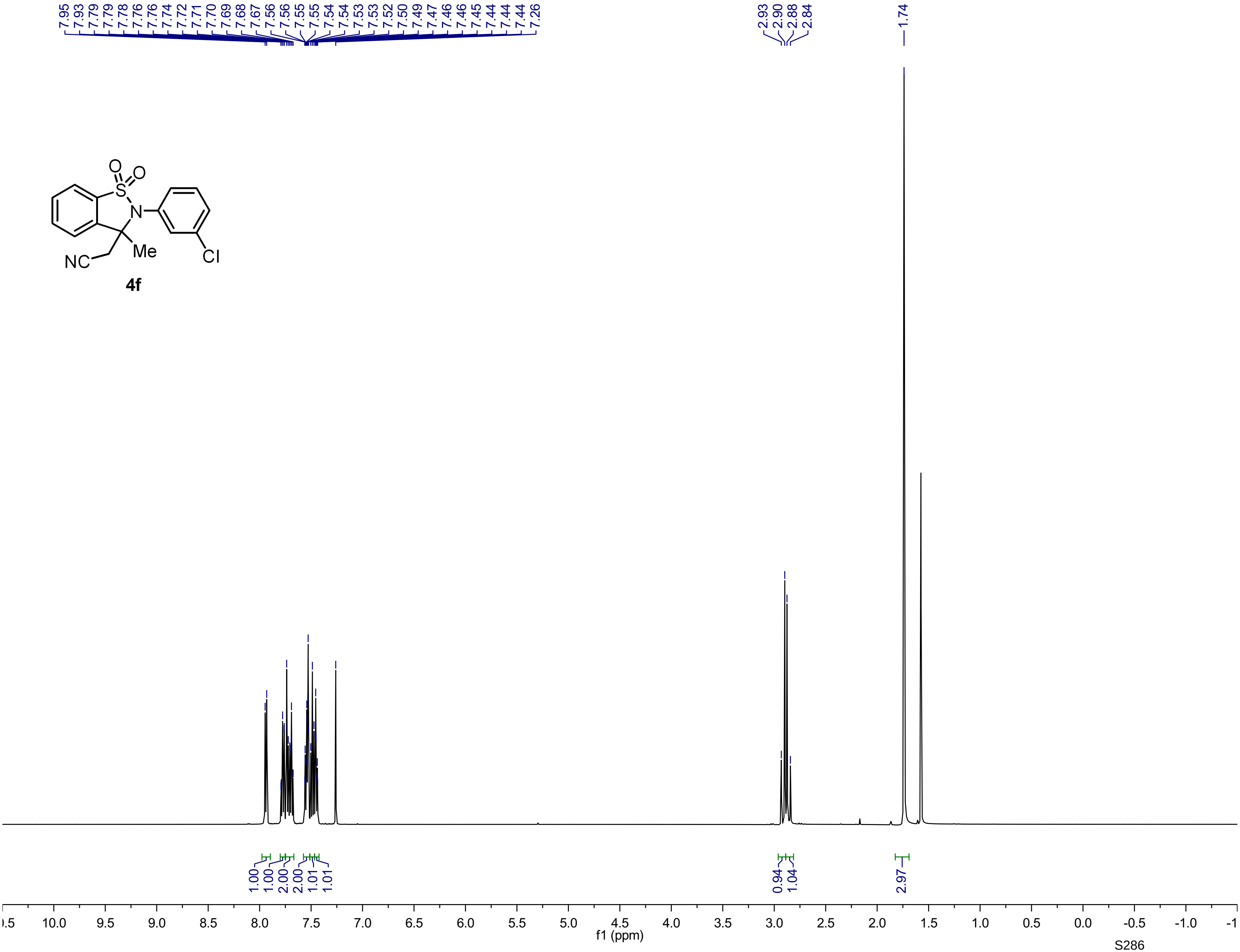
130.28
123.30
121.87
121.65
115.98
115.28
77.25
77.20
77.00
76.75
63.46
55.57
29.18
25.17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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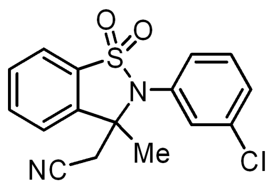
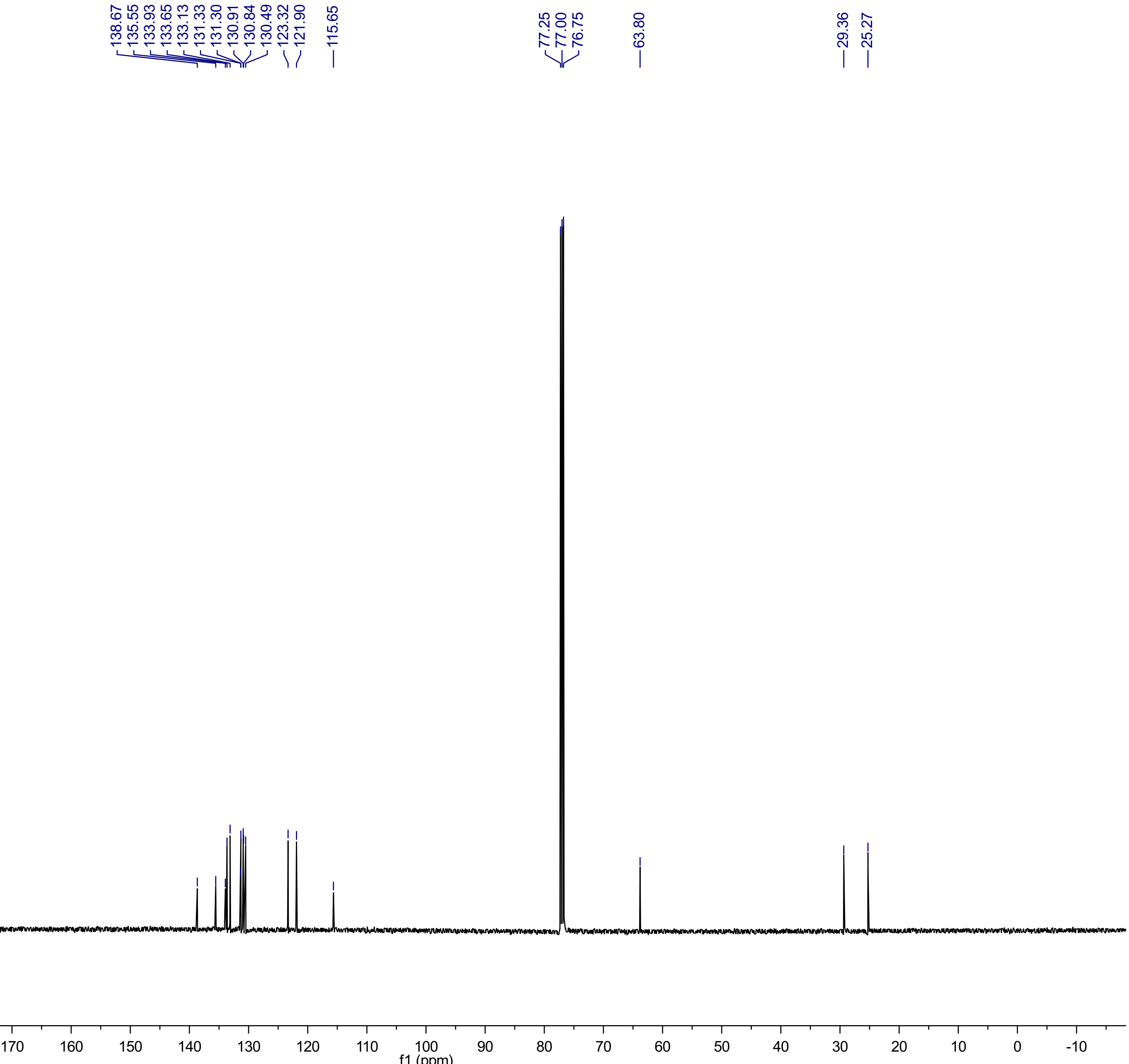
2.93 2.90 2.88 2.84
1.74
O O S N Me NC Cl
4f
1.00 1.00 2.00 2.00 1.01 1.01
0.94 1.04
2.97
f1 (ppm)



4f


138.67
135.55
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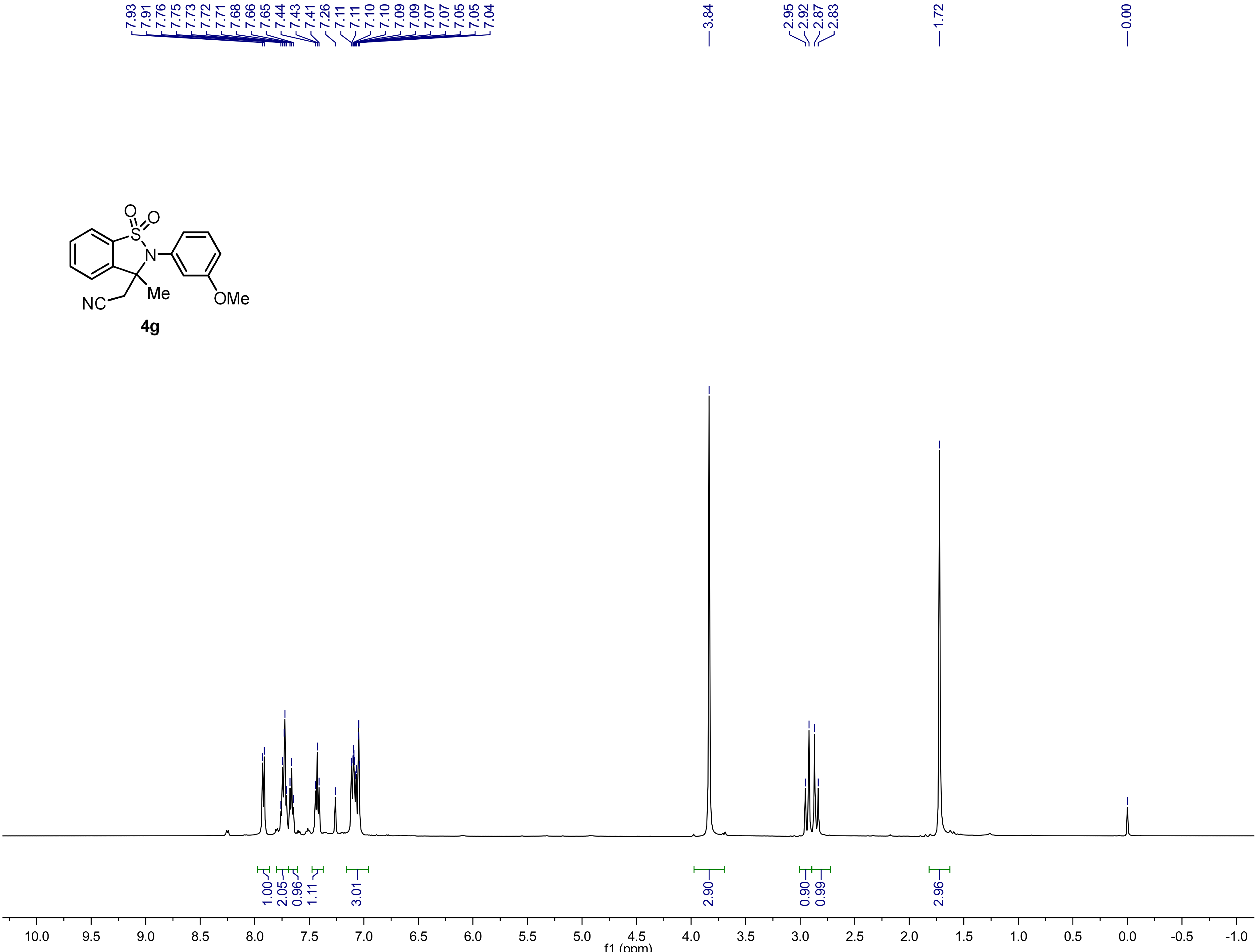
131.33
131.30
130.91
130.84
130.49
123.32
121.90
115.65
77.25
77.00
76.75
63.80
29.36
25.27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



7.93
7.91
7.76
7.75
7.73
7.72
7.71
7.68
7.66
7.65
7.44
7.43
7.41
7.26
7.11
7.11
7.10
7.10
7.09
7.09
7.07
7.07
7.05
7.05
7.04
3.84
2.95
2.92
2.87
2.83
1.72
0.00
O
O
S
N
NC
Me
OMe
4g
1.00
2.05
0.96
1.11
3.01
2.90
0.90
0.99
2.96
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
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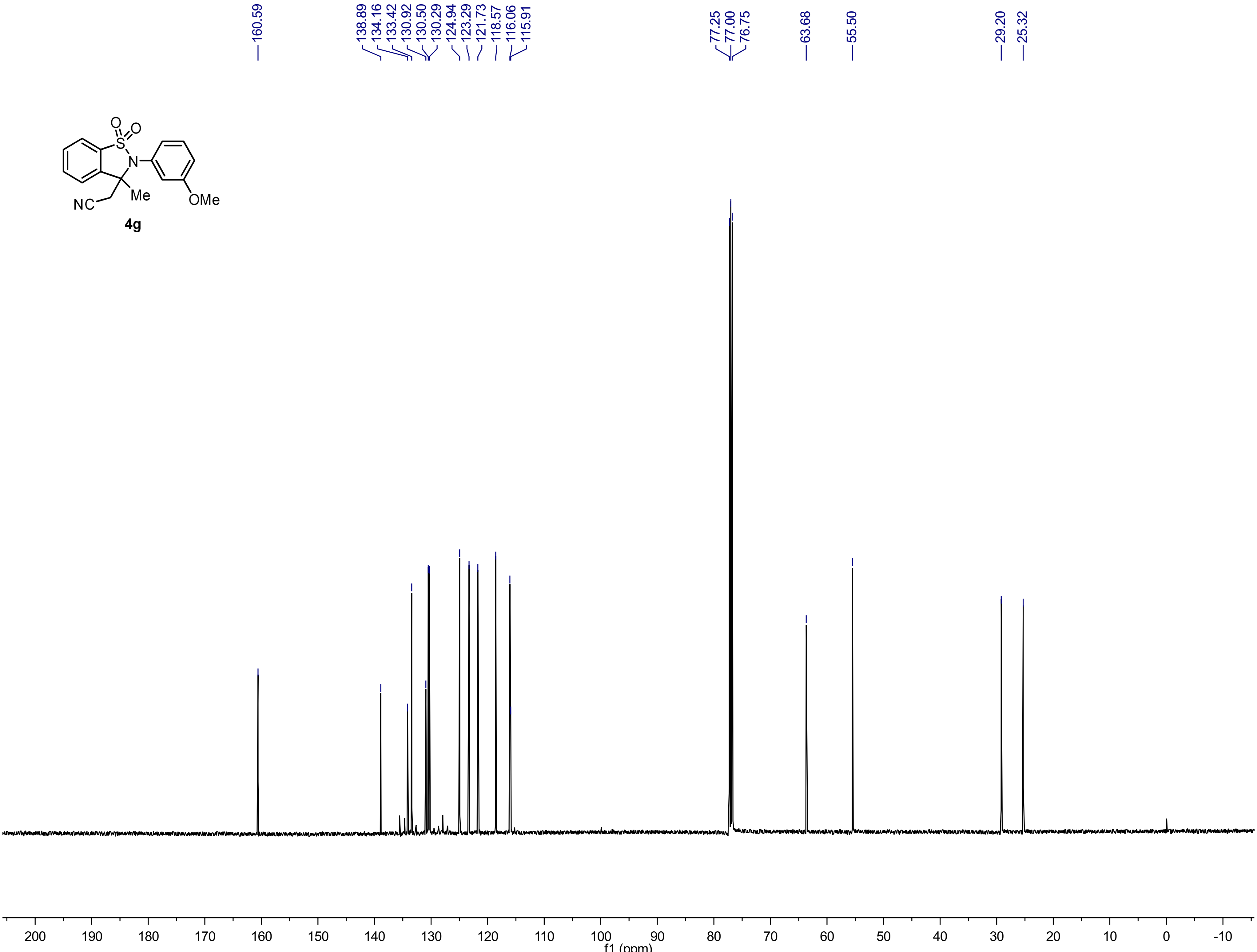
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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138.89
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133.42
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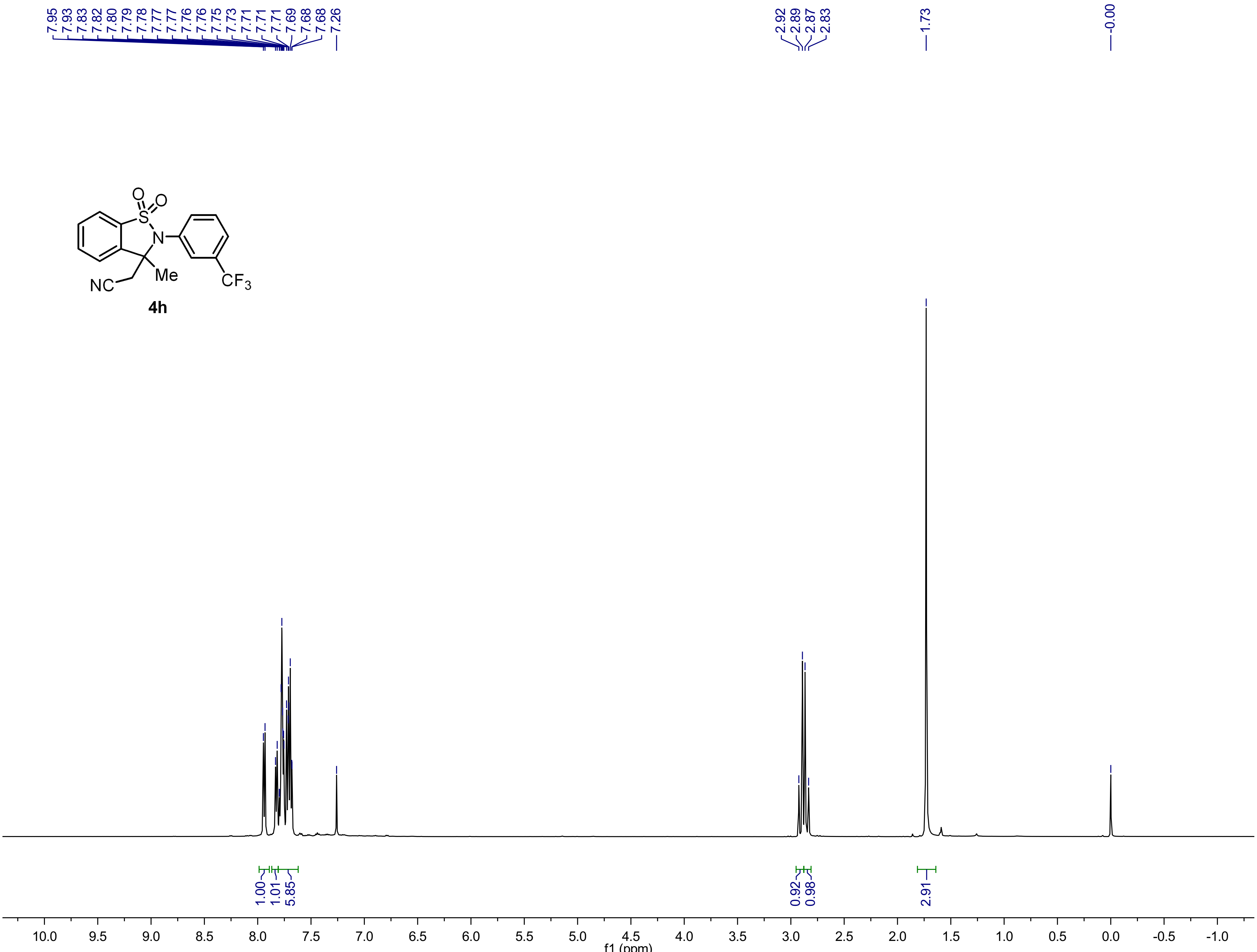
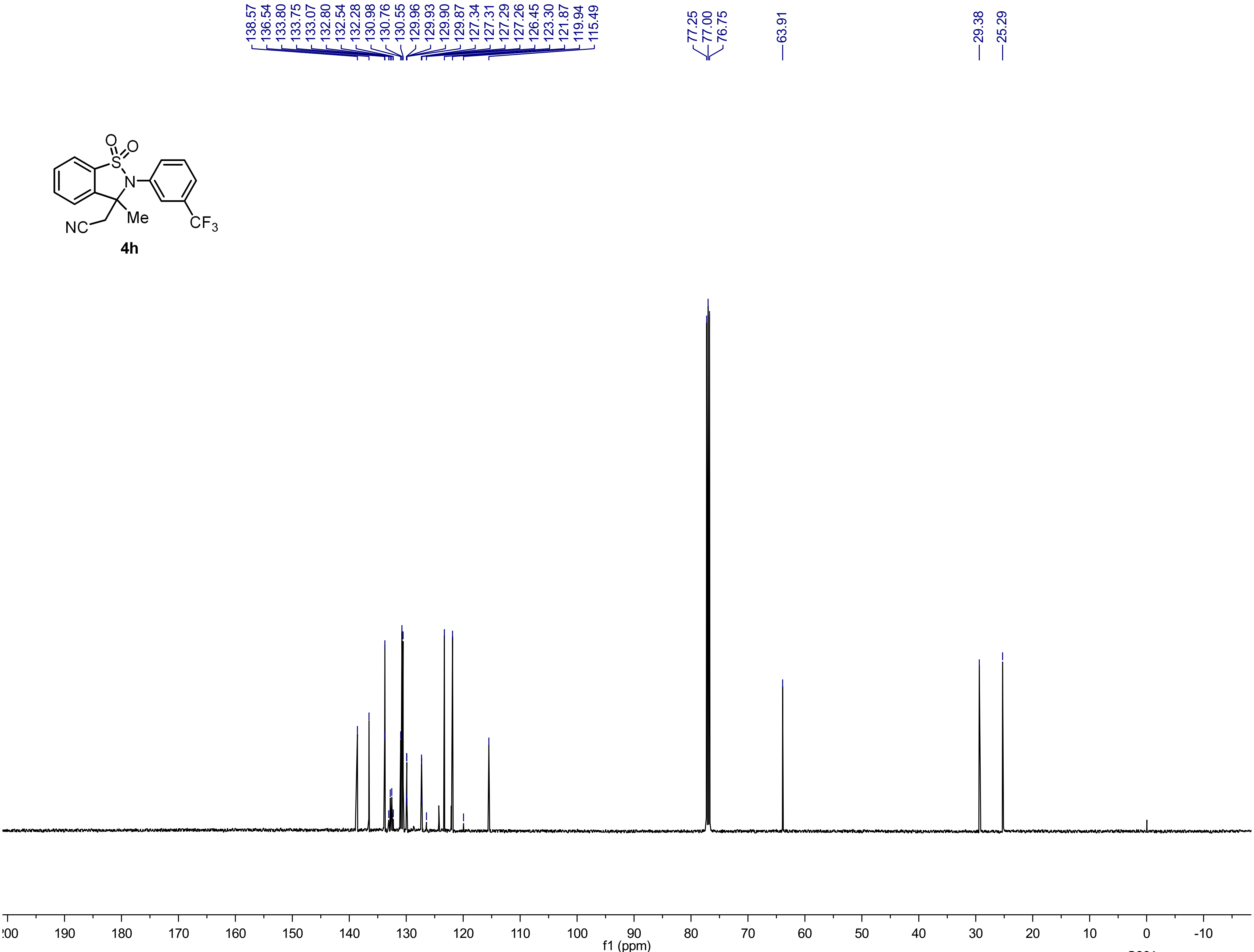
130.50
130.29
124.94
123.29
121.73
118.57
116.06
115.91
77.25
77.00
76.75
63.68
55.50
29.20
25.32
NC
Me
OMe
N
S
O
O
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

4g

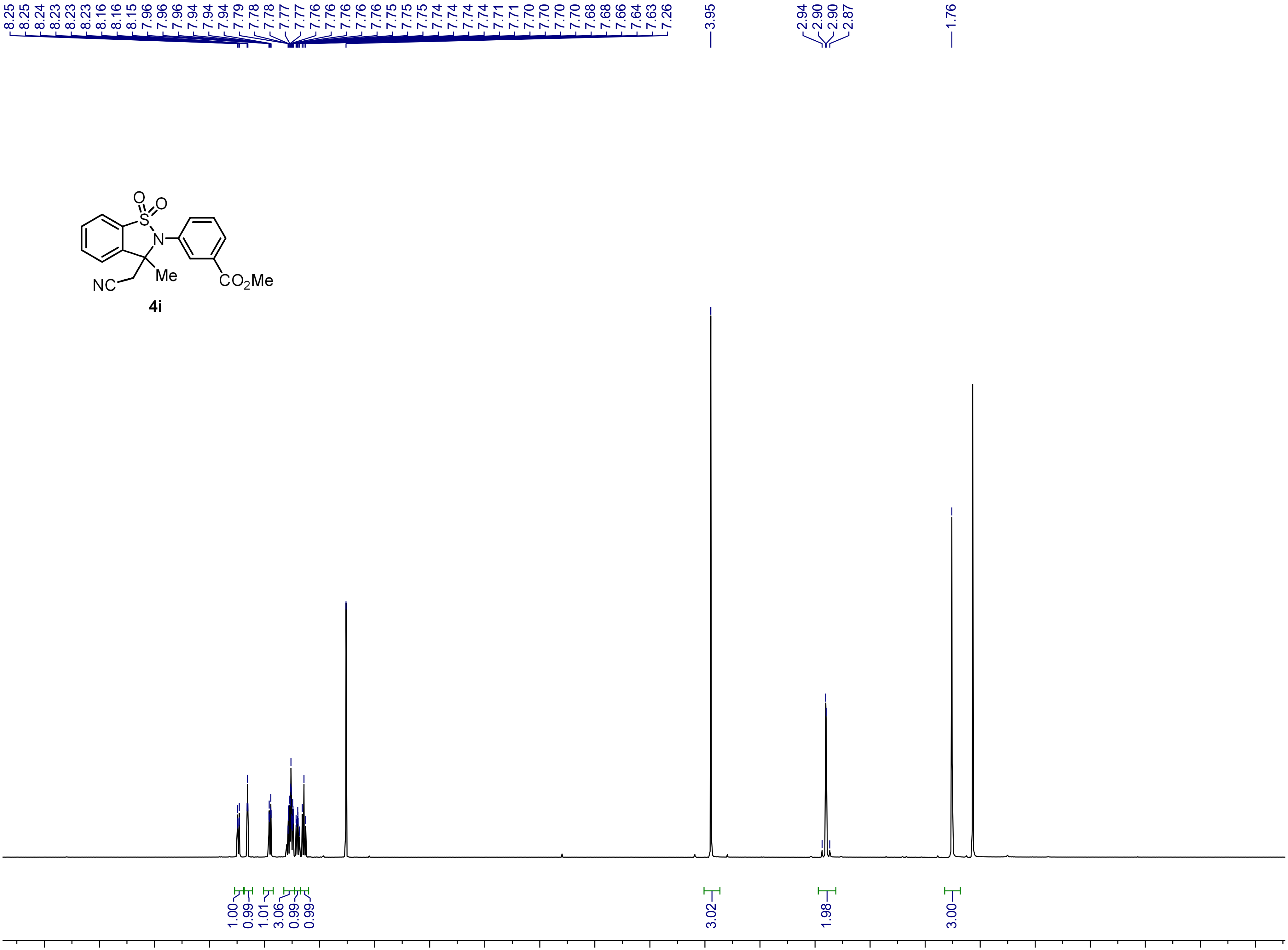


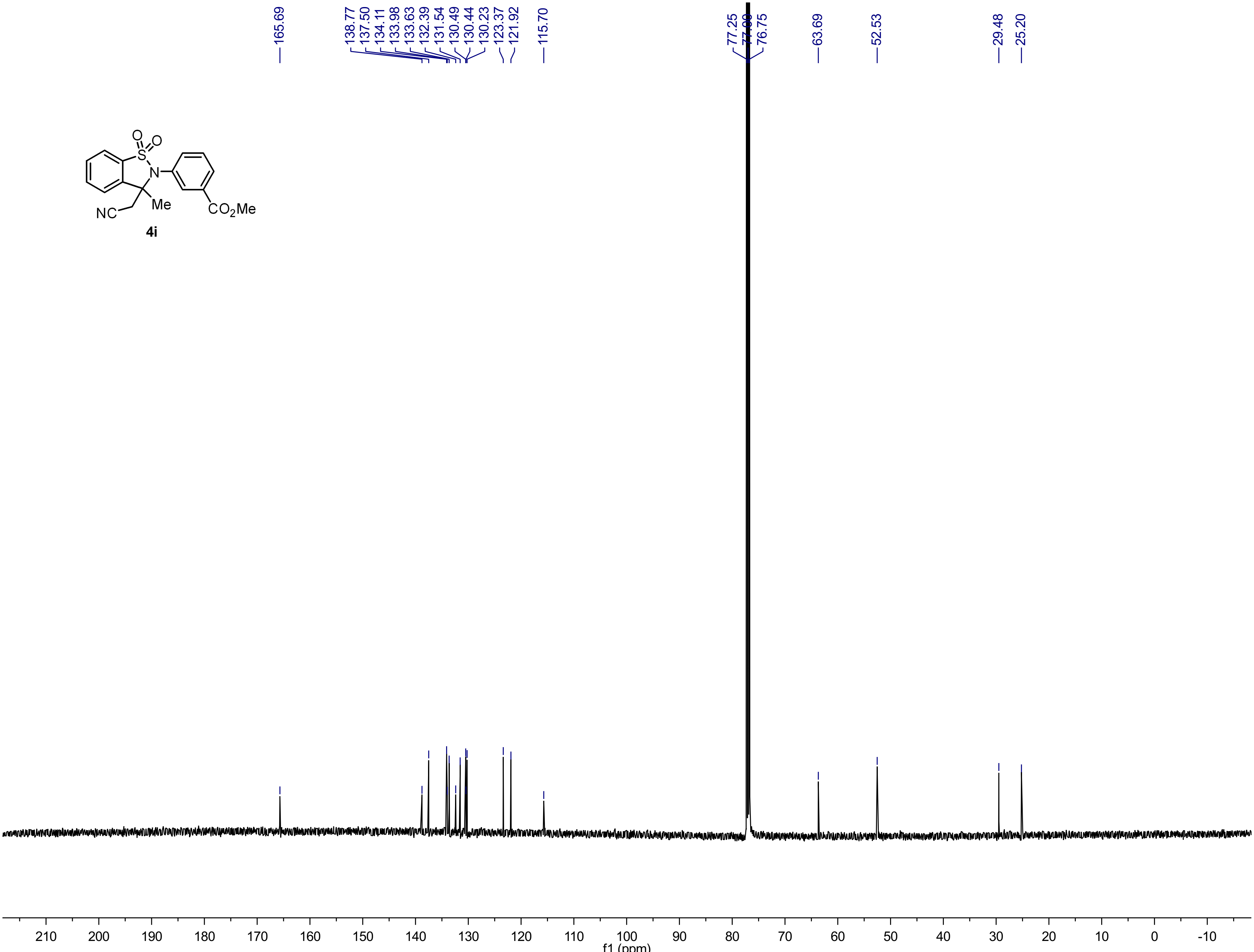
7.95
7.93
7.83
7.82
7.80
7.79
7.78
7.77
7.77
7.76
7.76
7.75
7.73
7.71
7.71
7.71
7.69
7.68
7.68
7.26
2.92
2.89
2.87
2.83
1.73
-0.00
1.00
1.01
5.85
0.92
0.98
2.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
O
O
S
N
NC
Me
CF_3

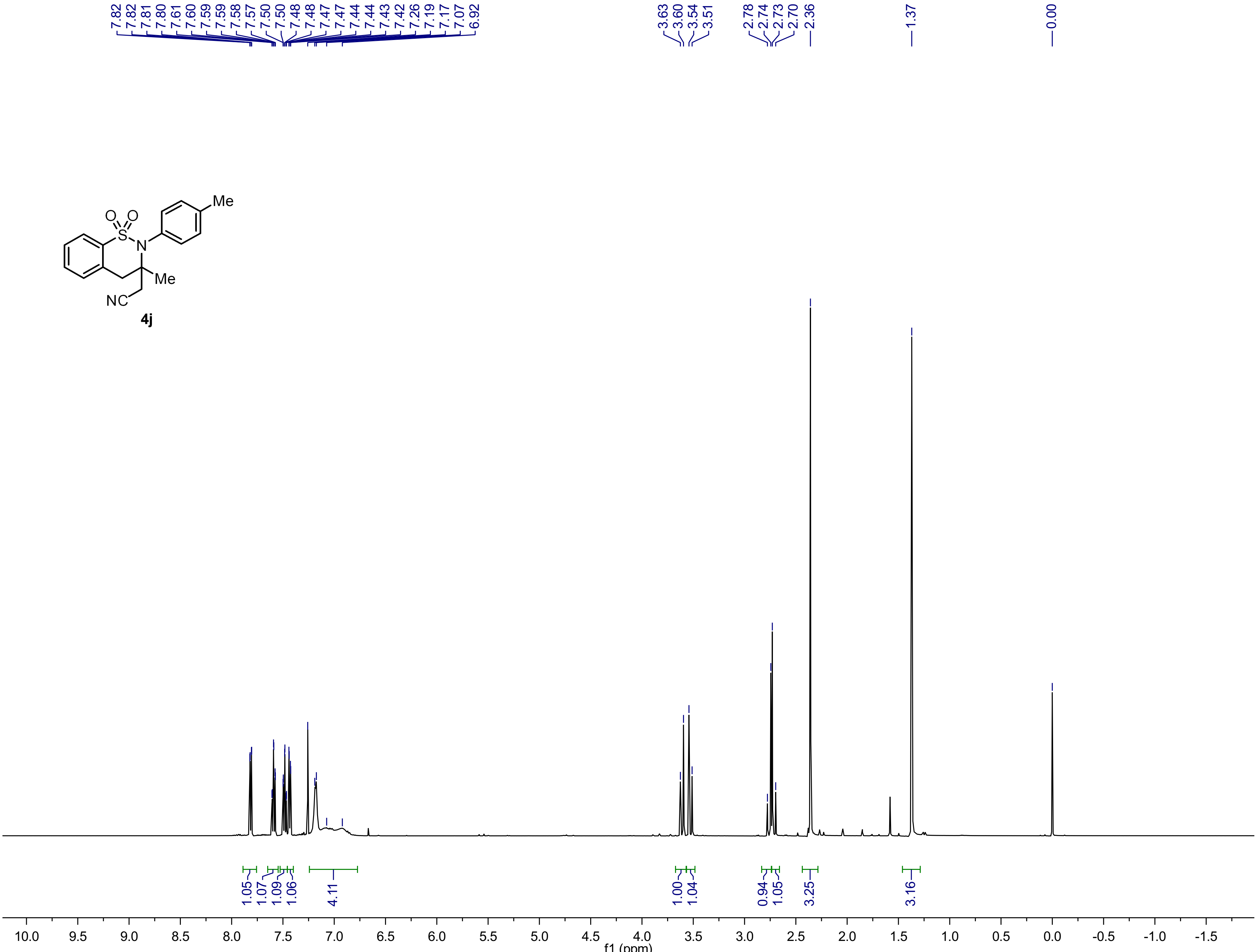
4h

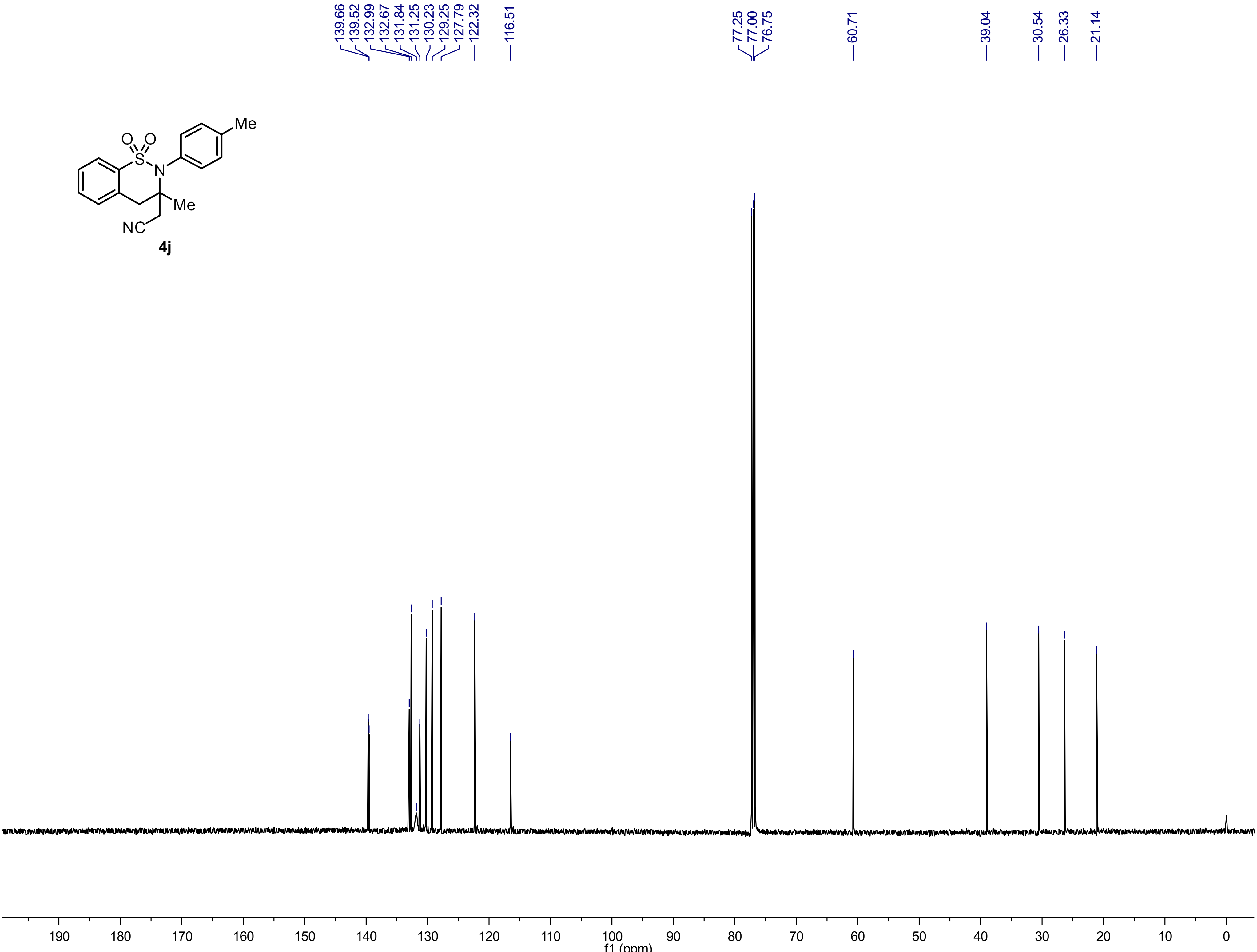

O
O
S
N
Me
NC
CF3
138.57
136.54
133.80
133.75
133.07
132.80
132.54
132.28
130.98
130.76
130.55
129.96
129.93
129.90
129.87
127.34
127.31
127.29
127.26
126.45
123.30
121.87
119.94
115.49
77.25
77.00
76.75
63.91
29.38
25.29
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

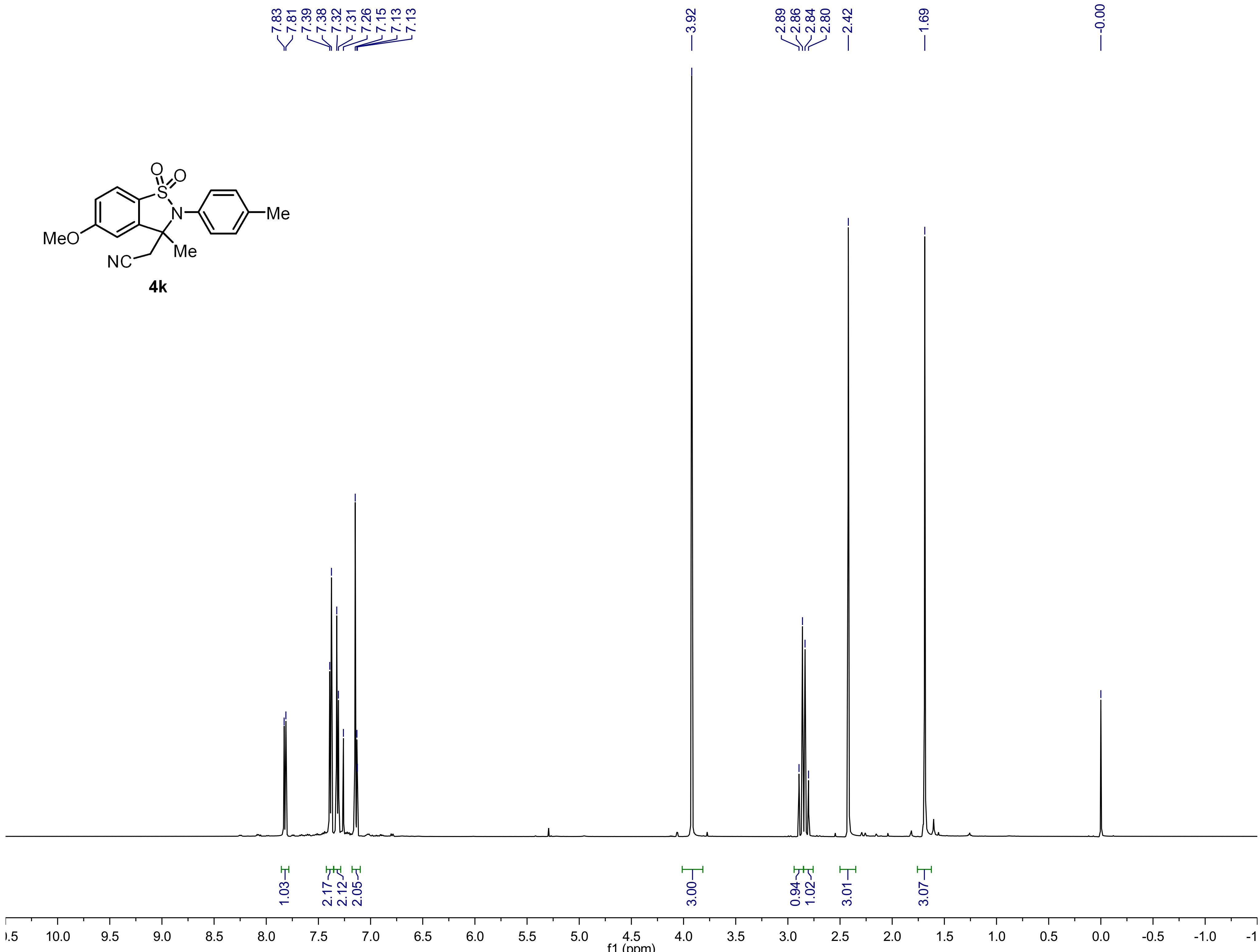
4h

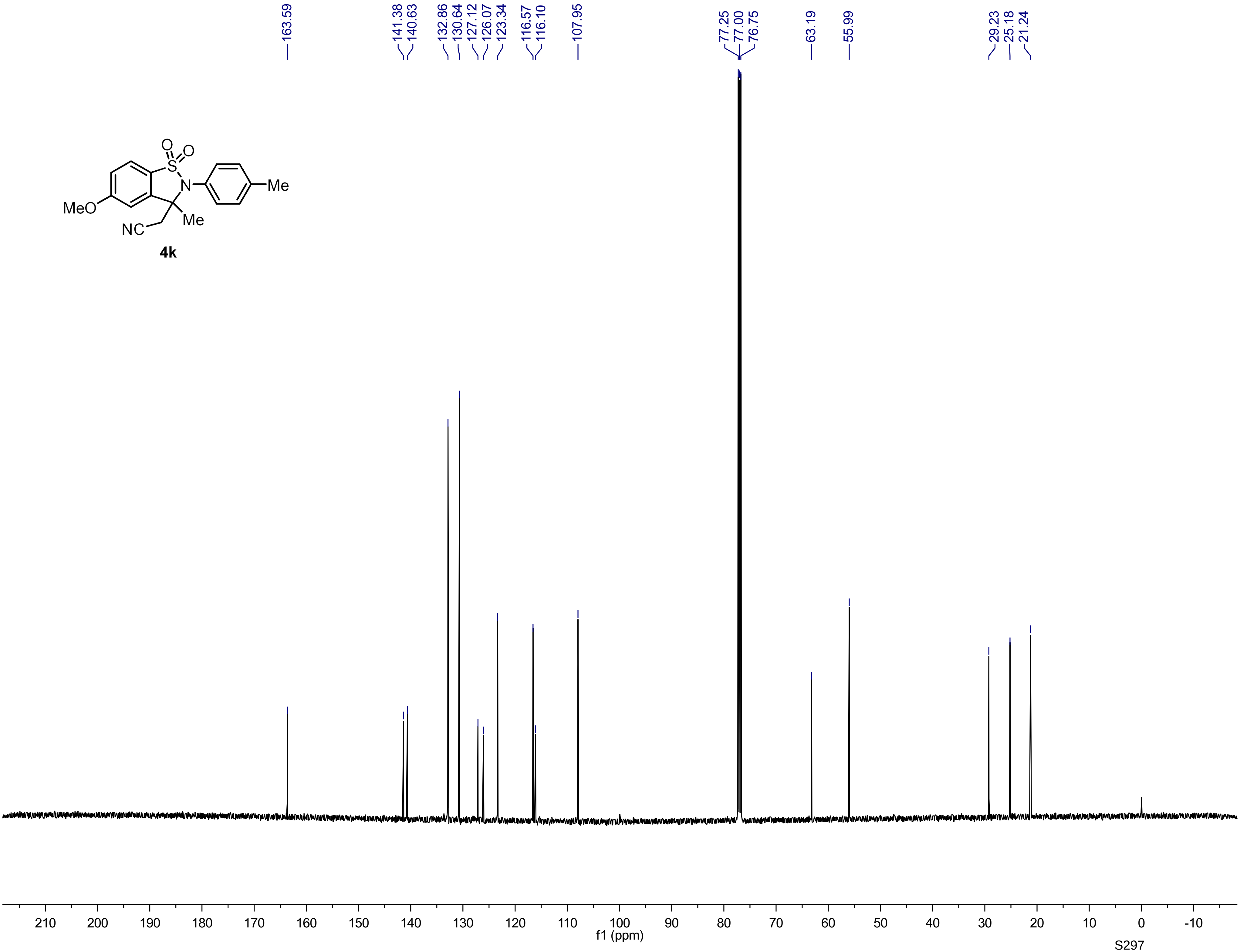

8.25 8.25 8.24 8.23 8.23 8.23 8.16 8.16 8.15 7.96 7.96 7.96 7.94 7.94 7.94 7.79 7.78 7.78 7.77 7.77 7.76 7.76 7.76 7.76 7.75 7.75 7.75 7.74 7.74 7.74 7.71 7.71 7.70 7.70 7.70 7.68 7.68 7.66 7.64 7.63 7.26
3.95
2.94 2.90 2.90 2.87
1.76
O
O
S
N
NC
Me
CO2Me
4i
1.00
0.99
1.01
3.06
0.99
0.99
3.02
1.98
3.00
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 -0.5 -1.0
f1 (ppm)


165.69
138.77
137.50
134.11
133.98
133.63
132.39
131.54
130.49
130.44
130.23
123.37
121.92
115.70
77.25
77.00
76.75
63.69
52.53
29.48
25.20
NC
Me
CO2Me
4i
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)


O
O
S
N
Me
Me
NC
4j
7.82
7.82
7.81
7.80
7.61
7.60
7.59
7.59
7.58
7.57
7.50
7.50
7.48
7.48
7.47
7.47
7.44
7.44
7.43
7.42
7.26
7.19
7.17
7.07
6.92
3.63
3.60
3.54
3.51
2.78
2.74
2.73
2.70
2.36
1.37
0.00
1.05
1.07
1.09
1.06
4.11
1.00
1.04
0.94
1.05
3.25
3.16
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
-0.5
-1.0
-1.5
f1 (ppm)


139.66
139.52
132.99
132.67
131.84
131.25
130.23
129.25
127.79
122.32
116.51
77.25
77.00
76.75
60.71
39.04
30.54
26.33
21.14
4j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.83
7.81
7.39
7.38
7.32
7.31
7.26
7.15
7.13
7.13
3.92
2.89
2.86
2.84
2.80
2.42
1.69
-0.00
MeO
NC
Me
Me
O
O
S
N
4k
1.03
2.17
2.12
2.05
3.00
0.94
1.02
3.01
3.07
f1 (ppm)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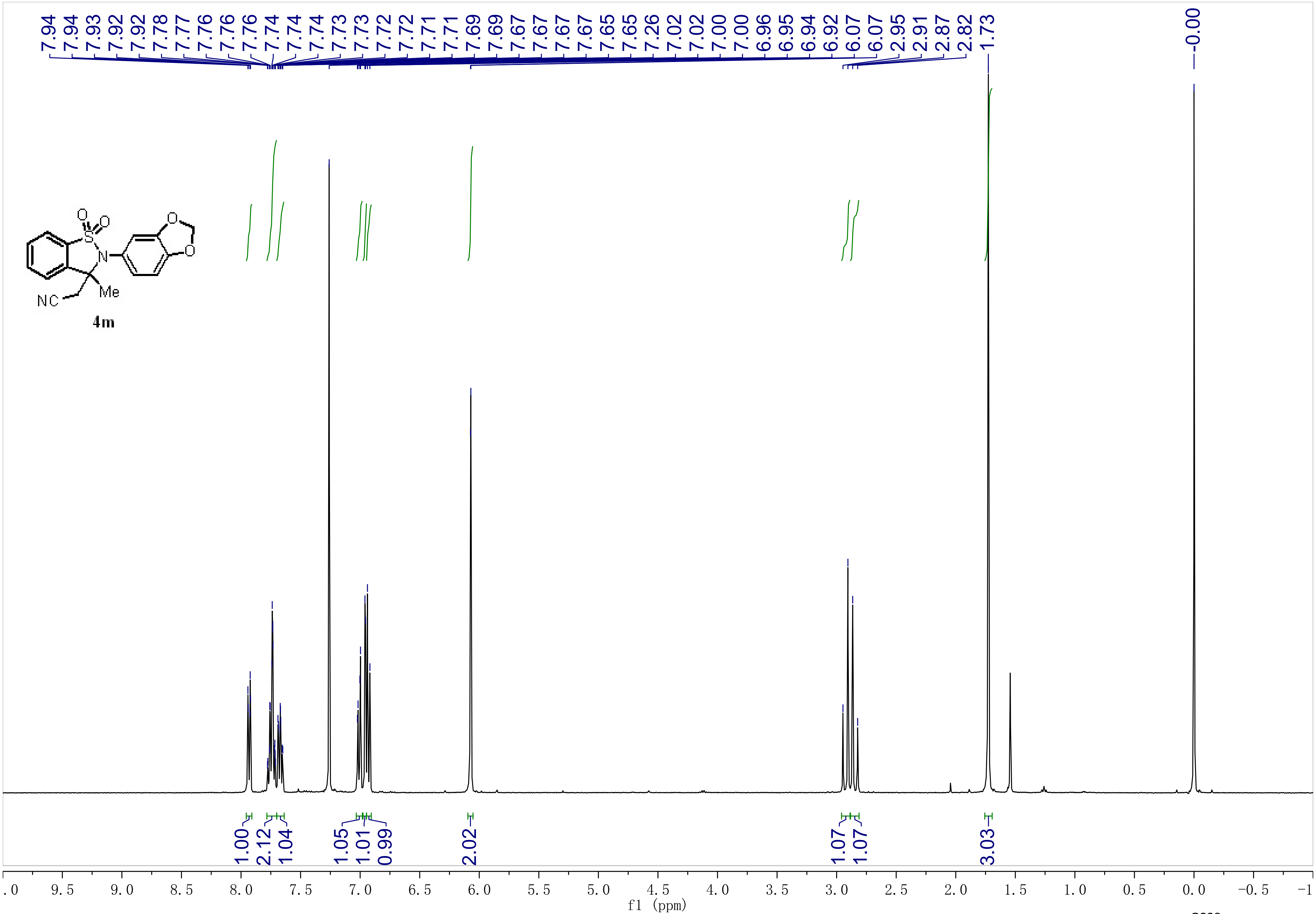
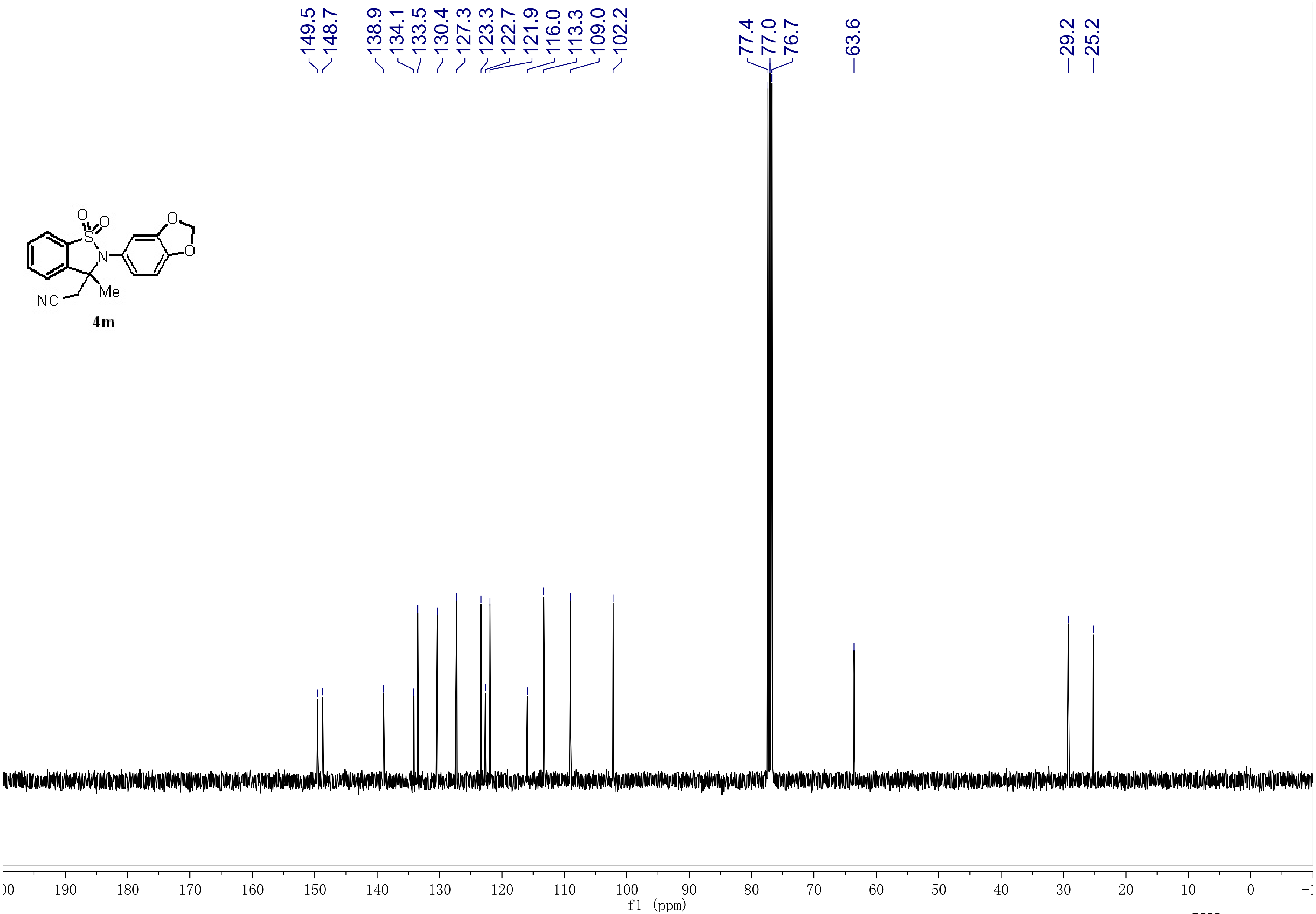
132.86
130.64
127.12
126.07
123.34
116.57
116.10
107.95
77.25
77.00
76.75
63.19
55.99
29.23
25.18
21.24
MeO
NC
Me
N
S
O
O
Me
4k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.94 7.94 7.93 7.92 7.92 7.78 7.77 7.76 7.76 7.76 7.74 7.74 7.74 7.73 7.73 7.72 7.72 7.71 7.71 7.69 7.69 7.67 7.67 7.67 7.67 7.65 7.65 7.26 7.02 7.02 7.00 7.00 6.96 6.95 6.94 6.92 6.07 6.07 2.95 2.91 2.87 2.82 1.73
-0.00
1.00 2.12 1.04 1.05 1.01 0.99 2.02 1.07 1.07 3.03
NC
Me
4m
f1 (ppm)


4m
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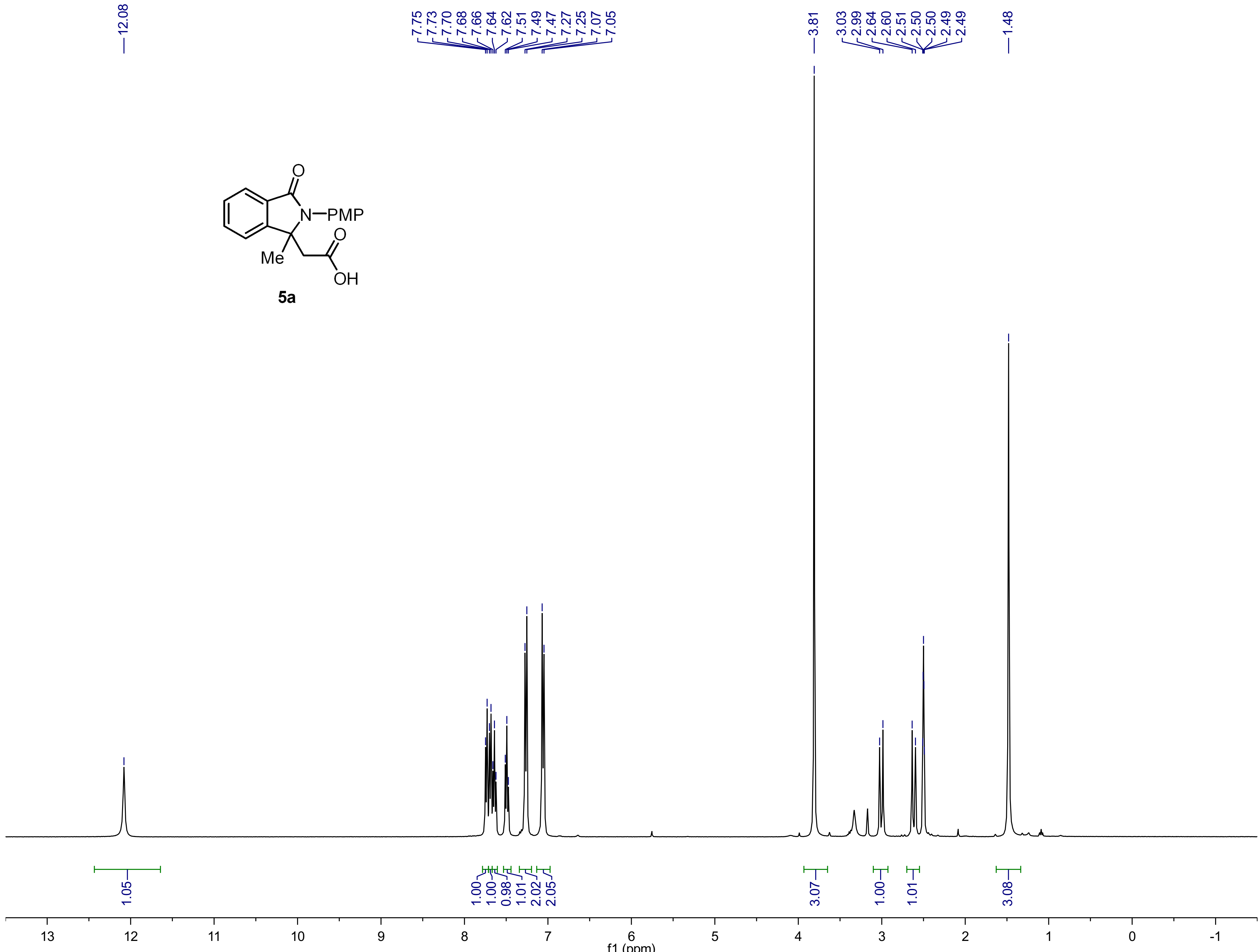
148.7
138.9
134.1
133.5
130.4
127.3
123.3
122.7
121.9
116.0
113.3
109.0
102.2
77.4
77.0
76.7
63.6
29.2
25.2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.08
7.75
7.73
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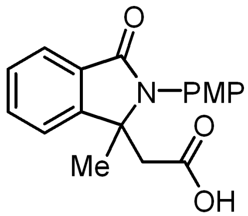
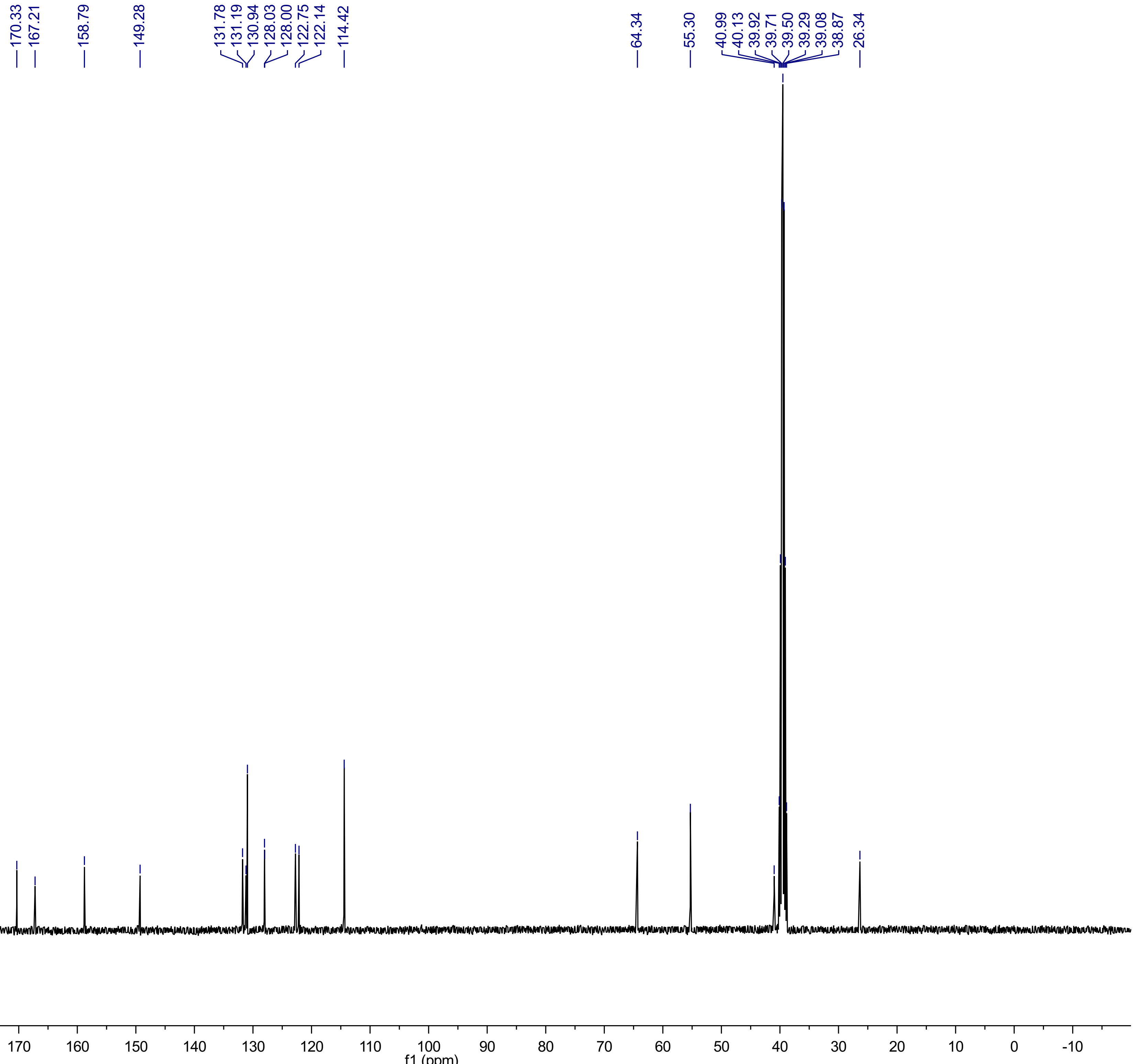
7.68
7.66
7.64
7.62
7.51
7.49
7.47
7.27
7.25
7.07
7.05
3.81
3.03
2.99
2.64
2.60
2.51
2.50
2.50
2.49
2.49
1.48
N—PMP
Me
OH
O
5a
1.05
1.00
1.00
0.98
1.01
2.02
2.05
3.07
1.00
1.01
3.08
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


O
N—PMP
Me
O
OH

5a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131.19
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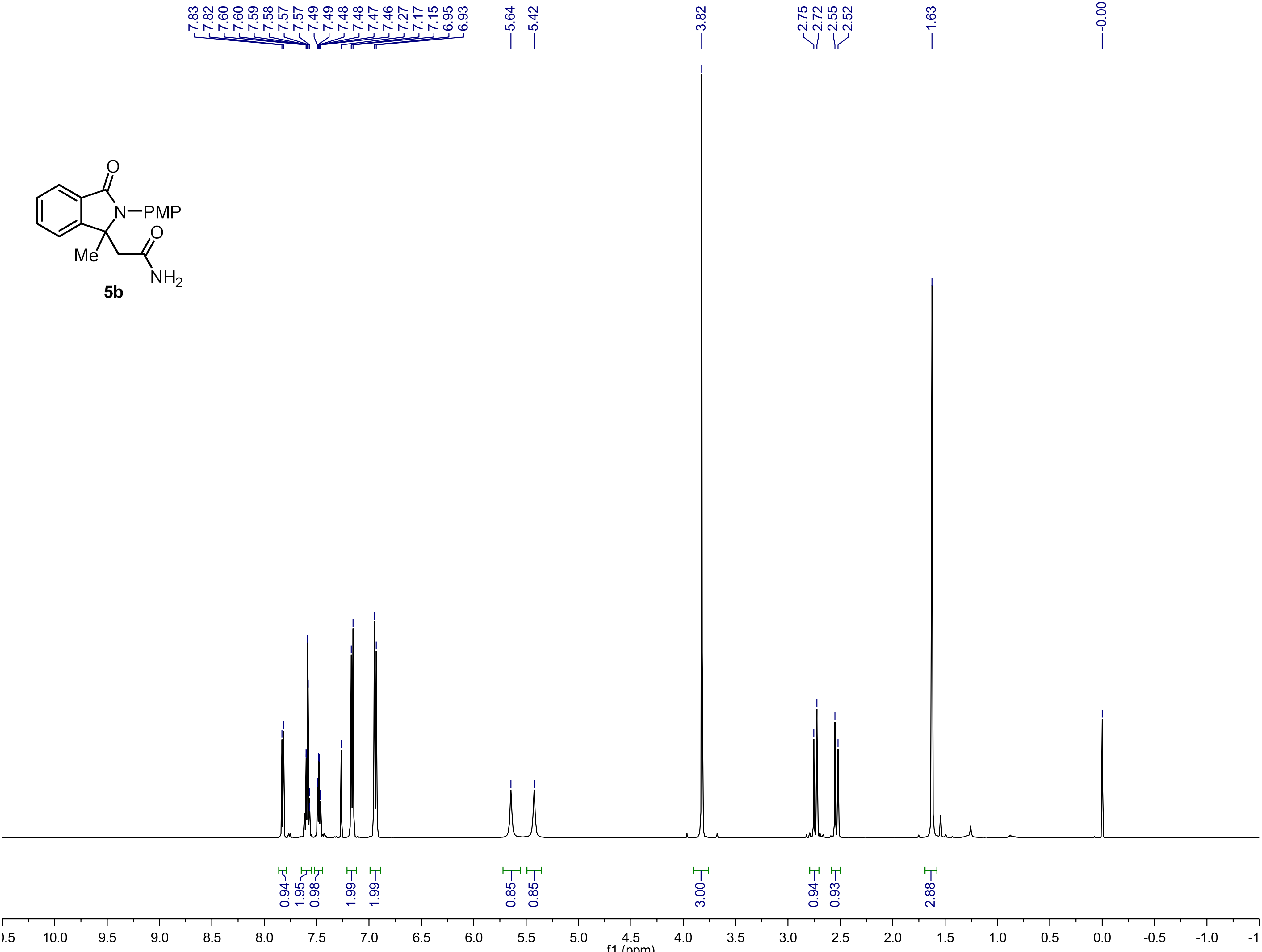
128.03
128.00
122.75
122.14
114.42
64.34
55.30
40.99
40.13
39.92
39.71
39.50
39.29
39.08
38.87
26.34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
N—PMP
O
Me
NH2
5b
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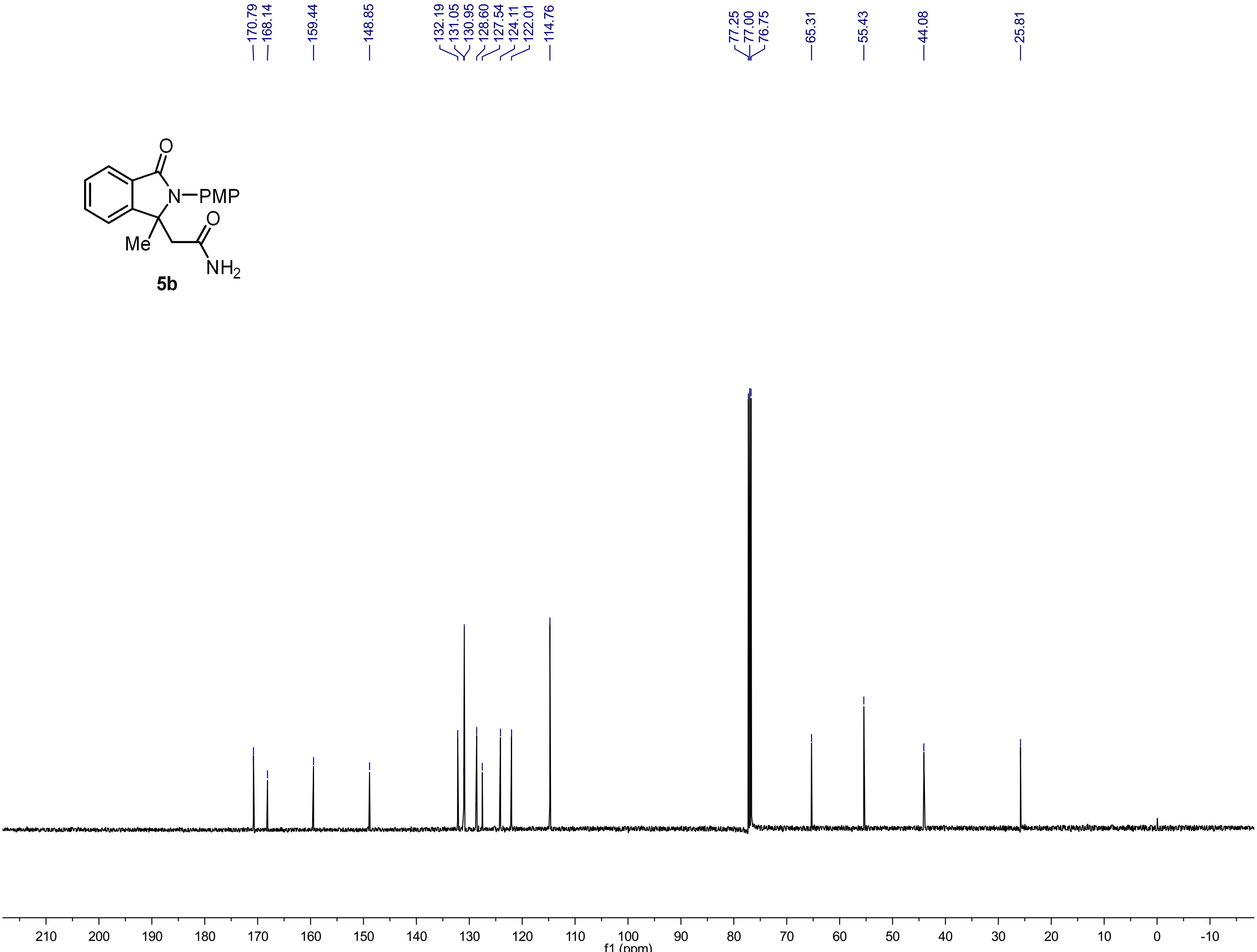
7.60
7.59
7.58
7.57
7.57
7.49
7.49
7.48
7.48
7.47
7.46
7.27
7.17
7.15
6.95
6.93
5.64
5.42
3.82
2.75
2.72
2.55
2.52
1.63
-0.00
0.94
1.95
0.98
1.99
1.99
0.85
0.85
3.00
0.94
0.93
2.88
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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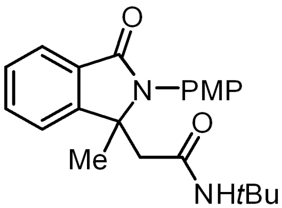
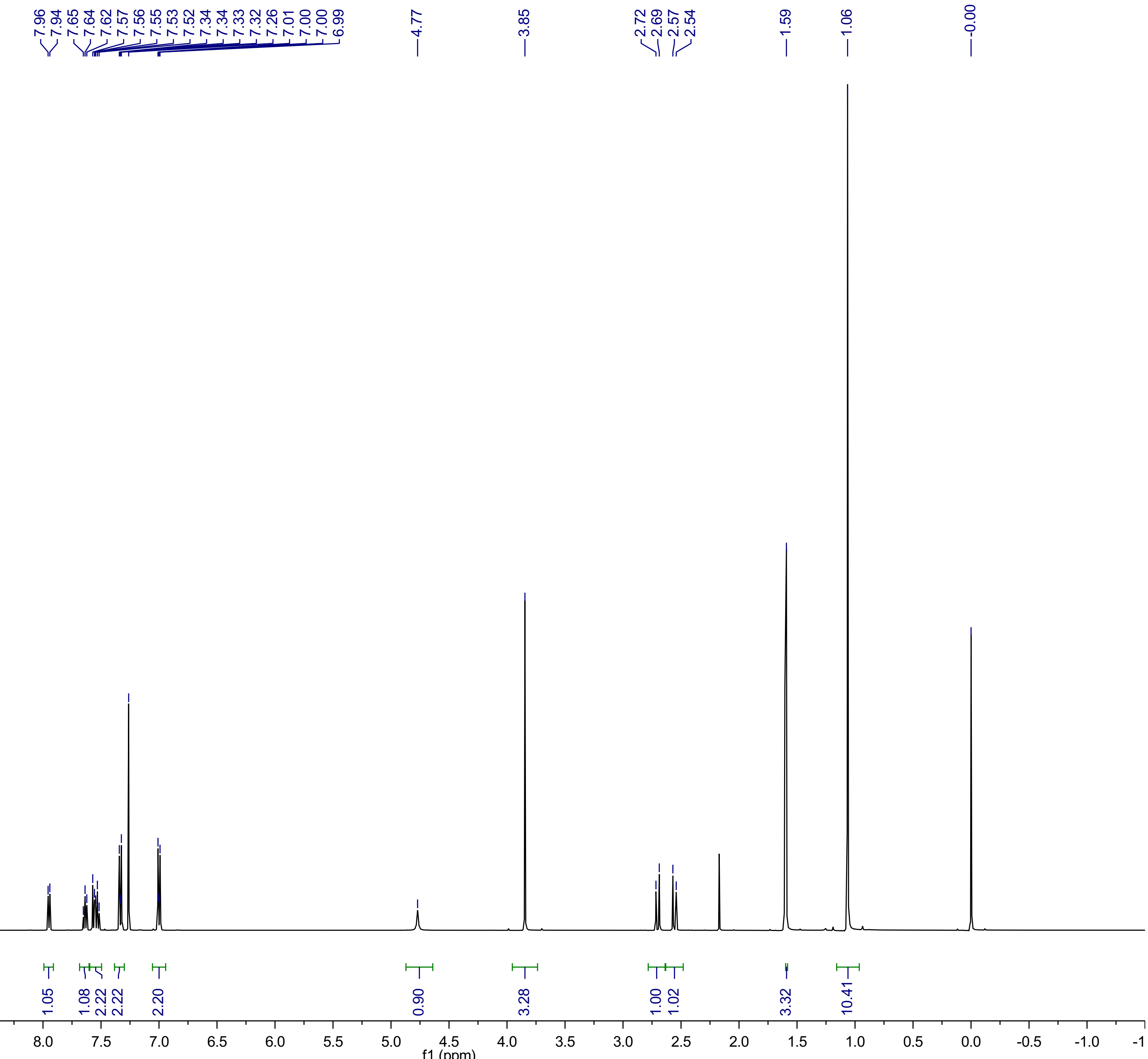
128.60
127.54
124.11
122.01
114.76
77.25
77.00
76.75
65.31
55.43
44.08
25.81
O
N
PMP
O
Me
NH2
5b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
N
PMP
O
Me
NHtBu

5c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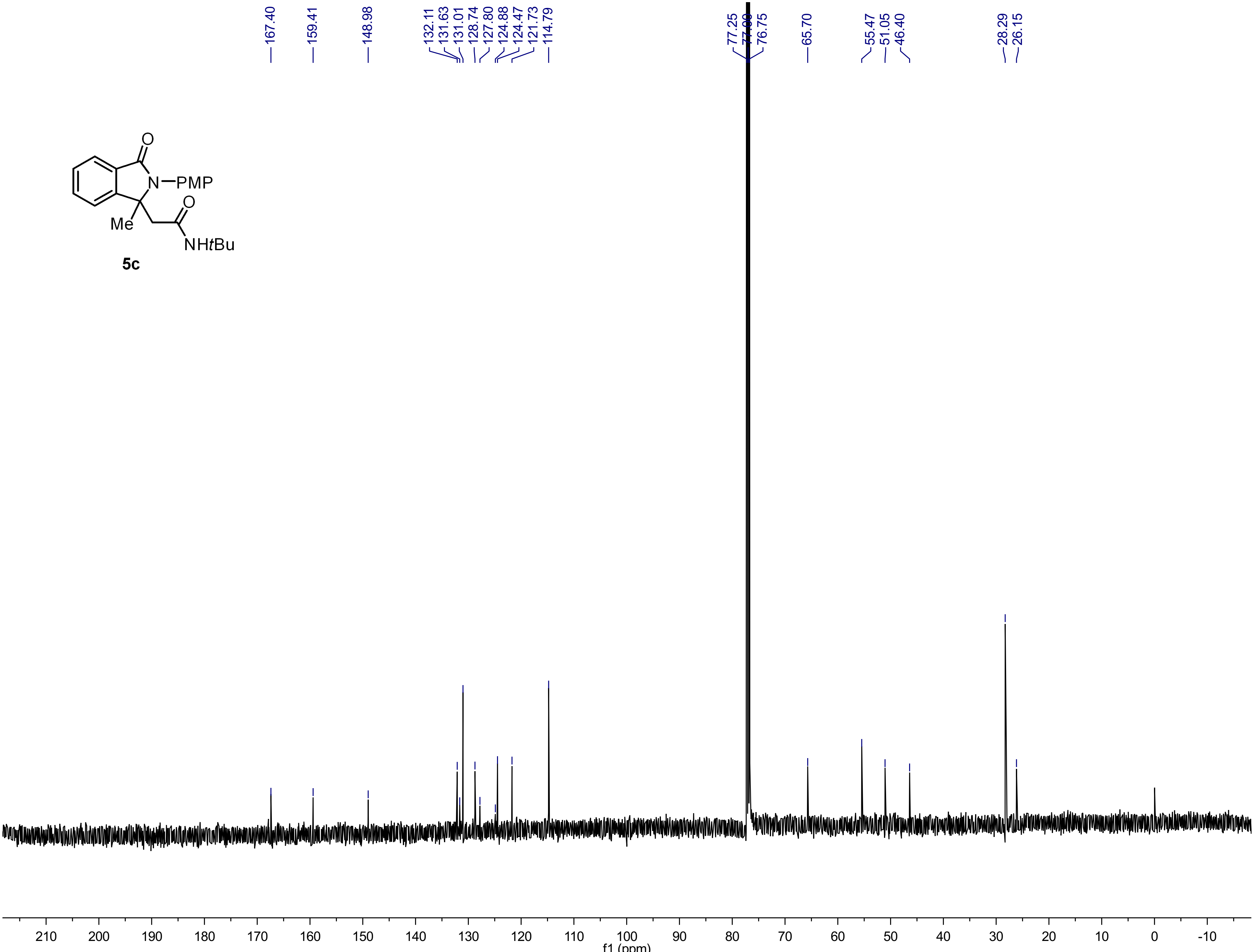
7.94
7.65
7.64
7.62
7.57
7.56
7.55
7.53
7.52
7.34
7.34
7.33
7.32
7.26
7.01
7.00
7.00
6.99
4.77
3.85
2.72
2.69
2.57
2.54
1.59
1.06
-0.00
1.05
1.08
2.22
2.22
2.20
0.90
3.28
1.00
1.02
3.32
10.41
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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131.01
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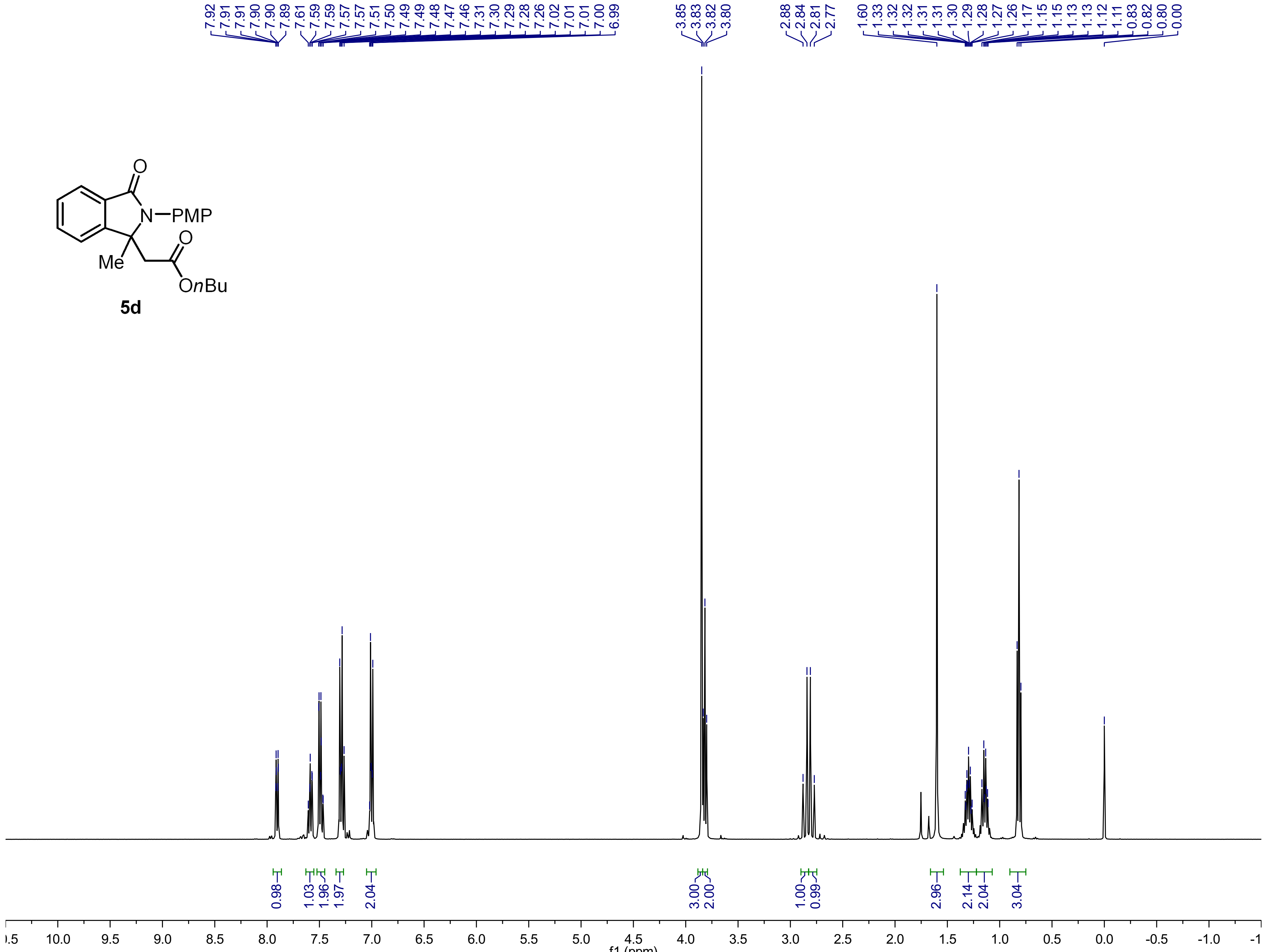
127.80
124.88
124.47
121.73
114.79
77.25
77.00
76.75
65.70
55.47
51.05
46.40
28.29
26.15
O
N
PMP
O
Me
NH*t*Bu
5c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.57
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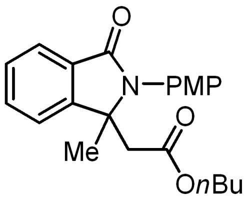
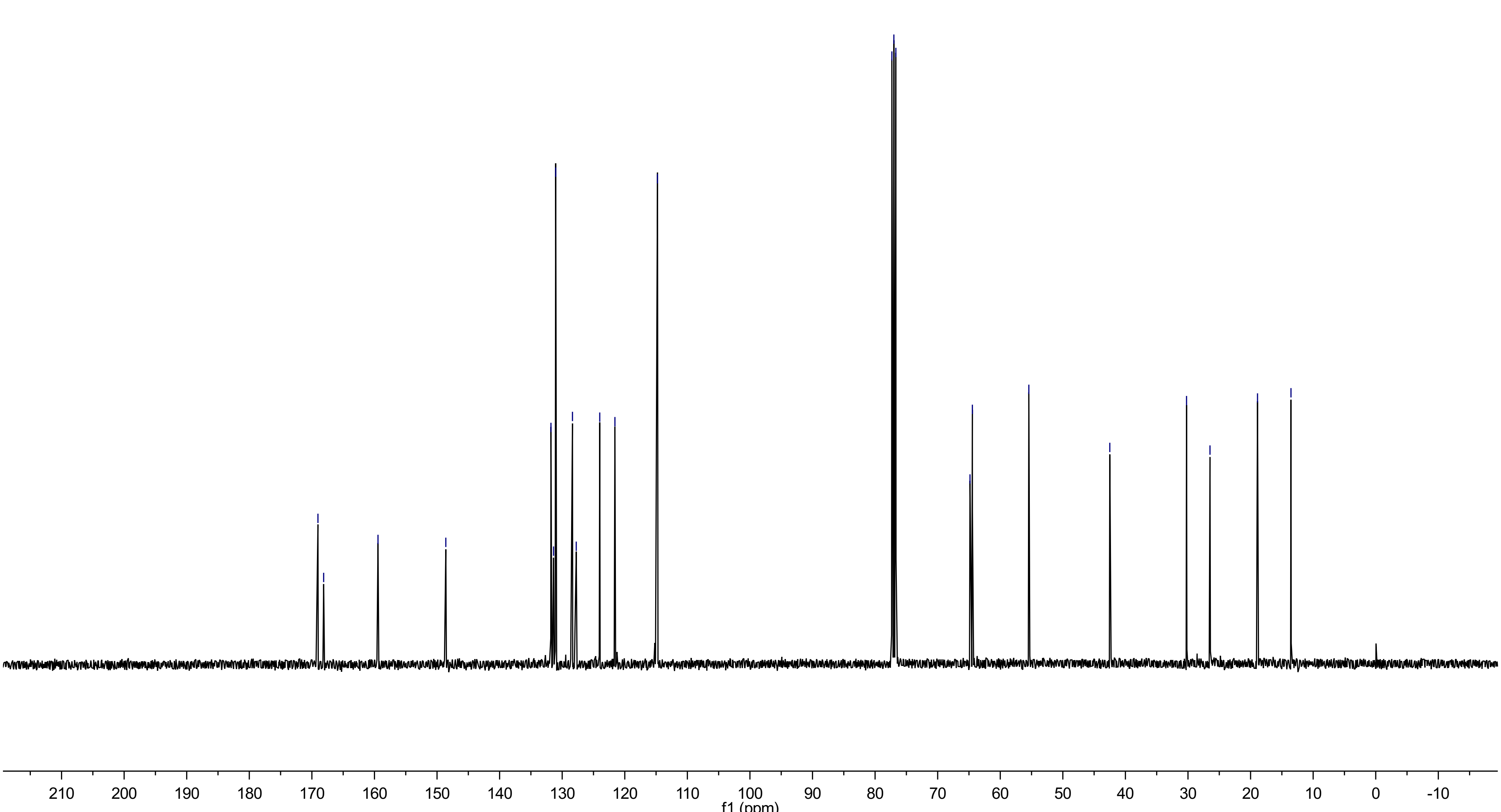
7.50
7.49
7.49
7.48
7.47
7.46
7.31
7.30
7.29
7.28
7.26
7.02
7.01
7.01
7.00
6.99
3.85
3.83
3.82
3.80
2.88
2.84
2.81
2.77
1.60
1.33
1.32
1.32
1.31
1.31
1.30
1.29
1.28
1.27
1.26
1.17
1.15
1.15
1.13
1.13
1.12
1.11
0.83
0.82
0.80
0.00
N—PMP
Me
OnBu
5d
0.98
1.03
1.96
1.97
2.04
3.00
2.00
1.00
0.99
2.96
2.14
2.04
3.04
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
-0.5
-1.0
f1 (ppm)


O
N—PMP
O
Me
OnBu

5d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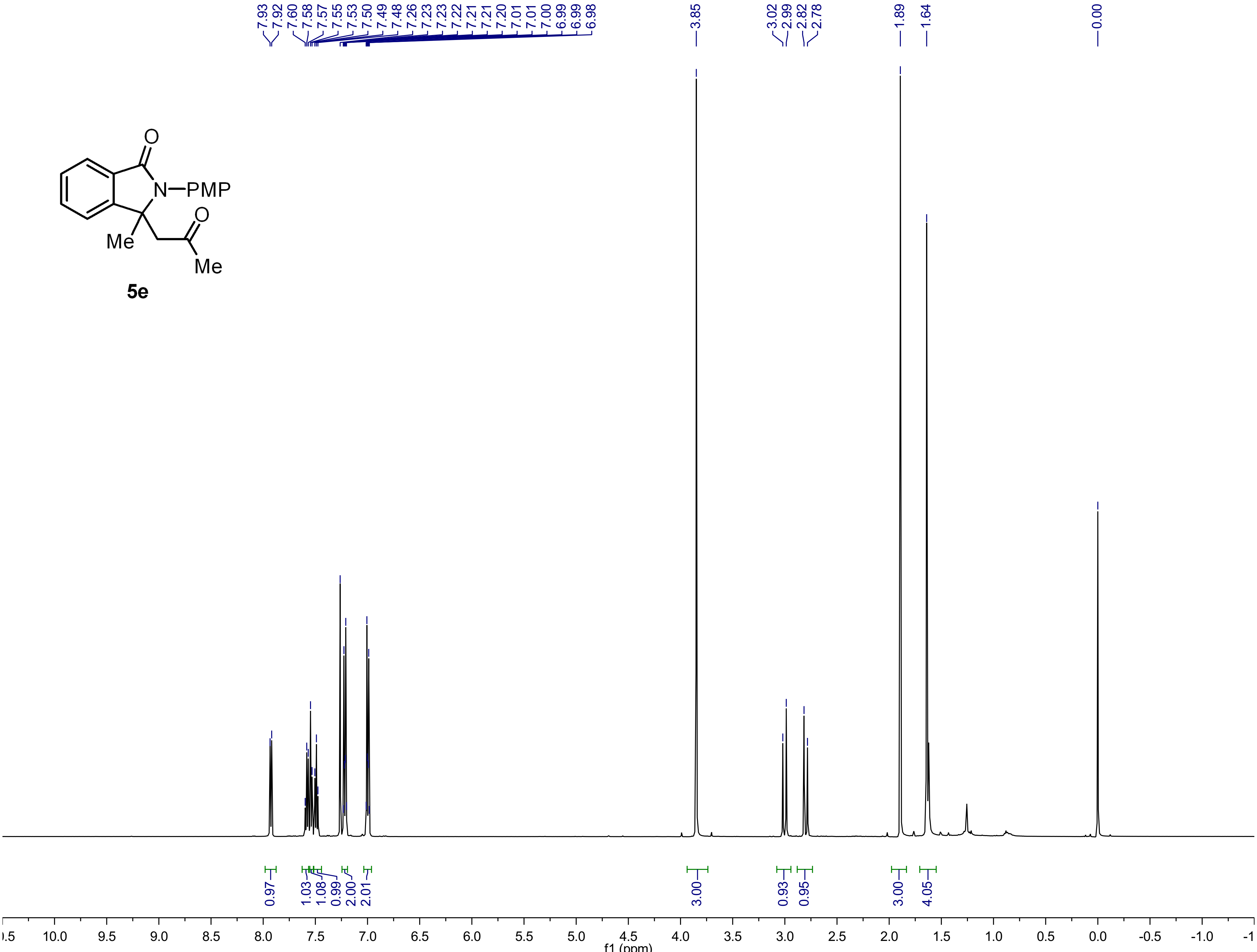
131.38
131.04
128.36
127.75
124.00
121.57
114.77
77.32
77.00
76.68
64.84
64.46
55.43
42.49
30.23
26.48
18.89
13.54
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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3.85
3.02 2.99 2.82 2.78
1.89 1.64
0.00
O
N—PMP
O
Me
Me
5e
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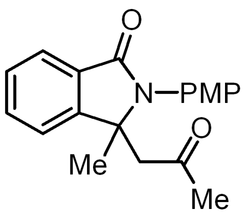
f1 (ppm)



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N—PMP
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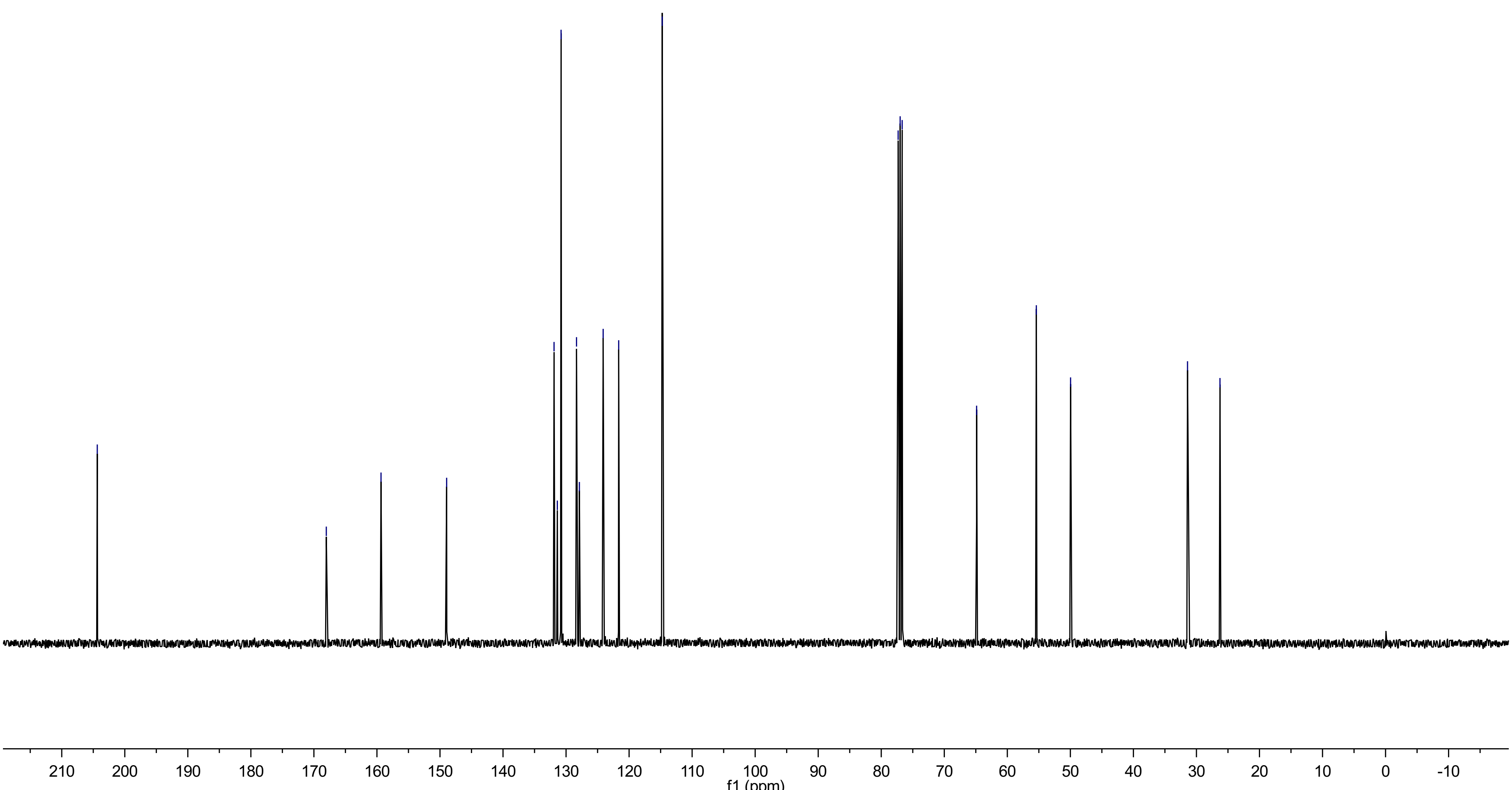
Me

5e



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121.65
114.75
77.32
77.00
76.68
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49.97
31.41
26.27
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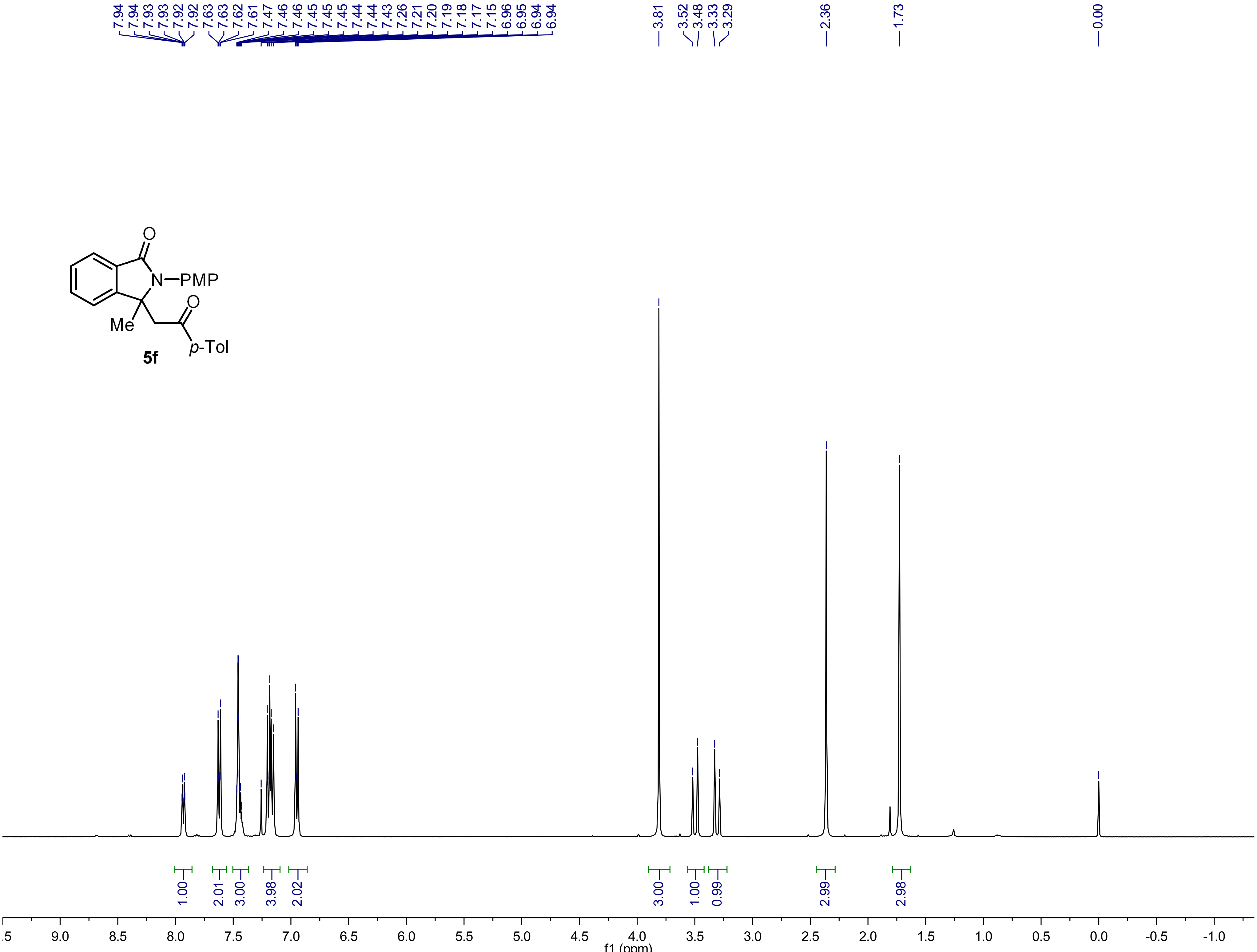
f1 (ppm)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7.46
7.45
7.45
7.45
7.44
7.44
7.43
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7.18
7.17
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6.95
6.94
6.94
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3.52
3.48
3.33
3.29
2.36
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2.02
3.00
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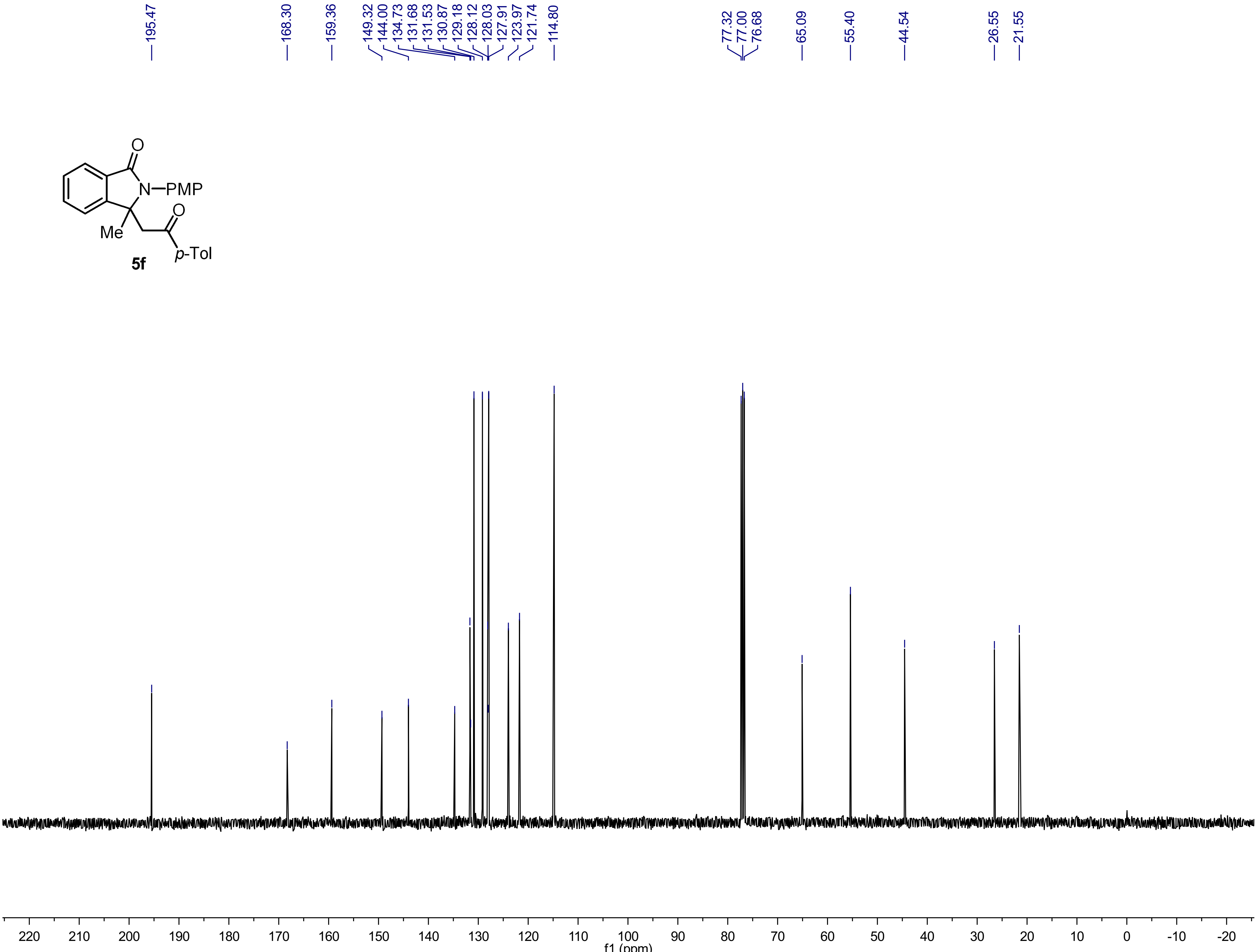
2.98
f1 (ppm)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114.80
77.32
77.00
76.68
65.09
55.40
44.54
26.55
21.55
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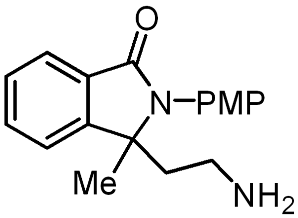
N−PMP
O
Me
p-Tol
5f
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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NH2
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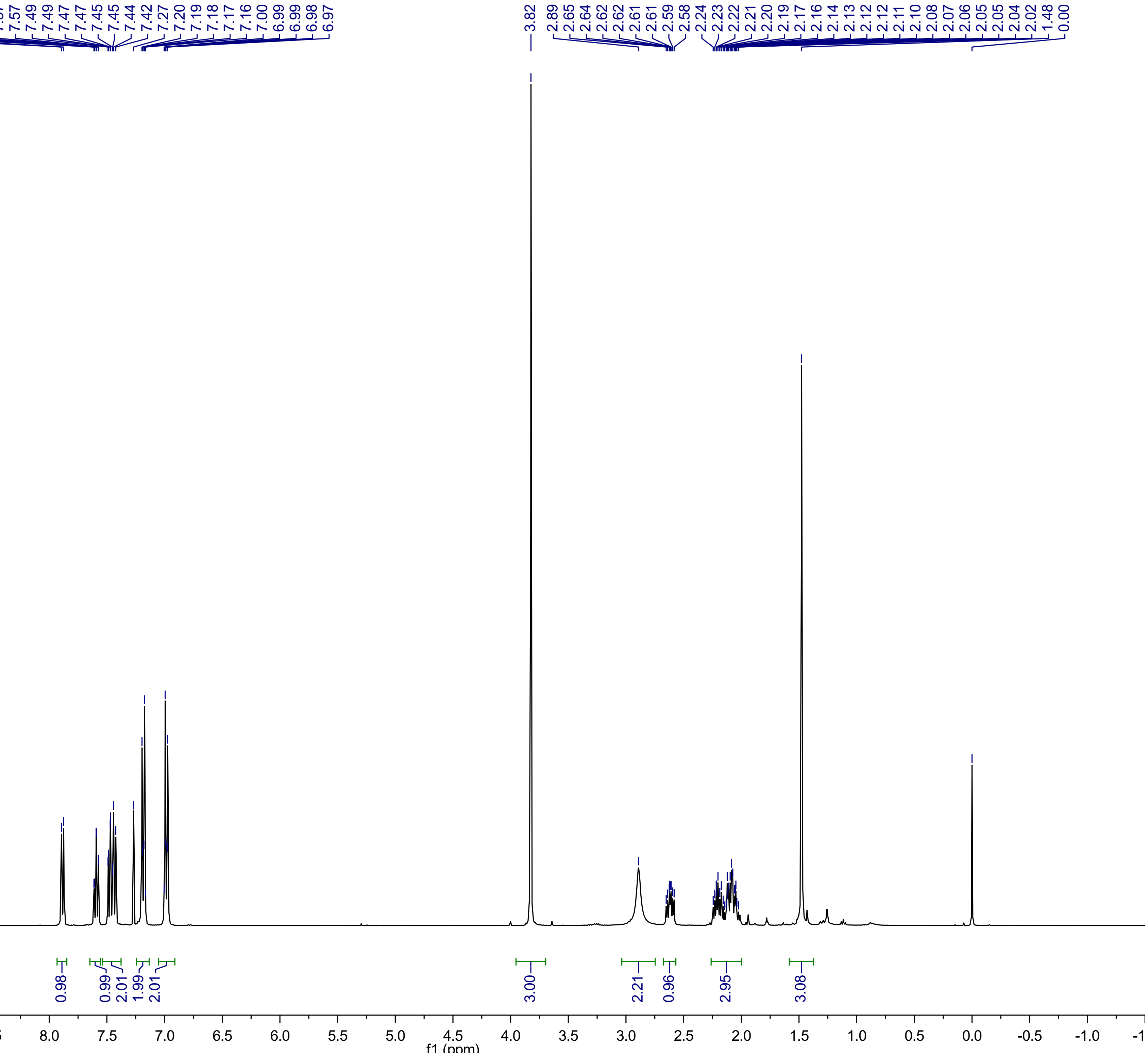
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7.27
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7.16
7.00
6.99
6.99
6.98
6.97
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2.89
2.65
2.64
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2.62
2.61
2.61
2.59
2.58
2.24
2.23
2.22
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2.20
2.19
2.17
2.16
2.14
2.13
2.12
2.12
2.11
2.10
2.08
2.07
2.06
2.05
2.05
2.04
2.02
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0.98
0.99
2.01
1.99
2.01
3.00
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2.95
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9.0
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6.0
5.5
5.0
4.5
4.0
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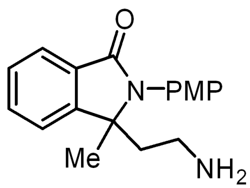
f1 (ppm)



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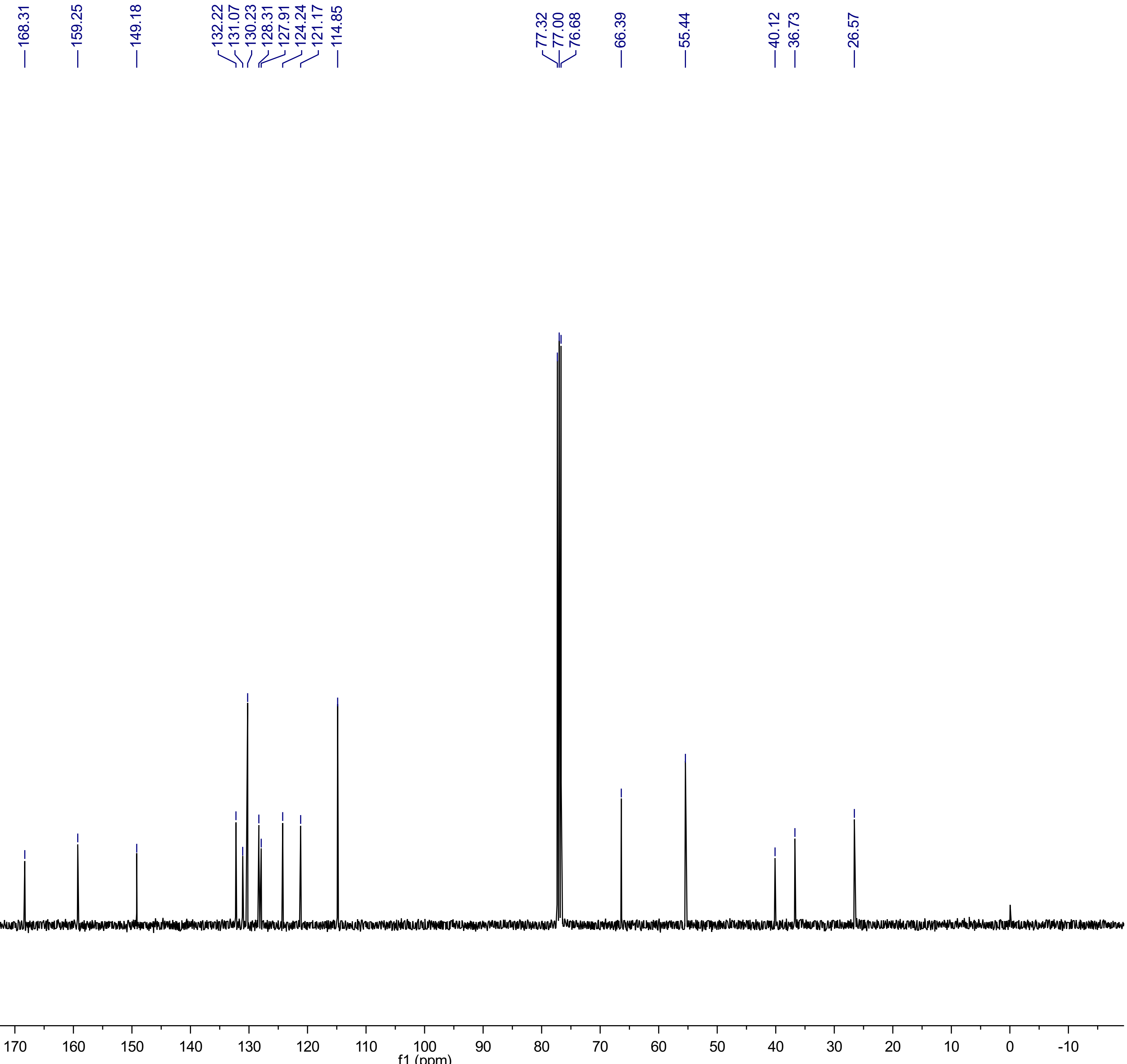

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128.31
127.91
124.24
121.17
114.85
77.32
77.00
76.68
66.39
55.44
40.12
36.73
26.57
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200
190
180
170
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100
90
80
70
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50
40
30
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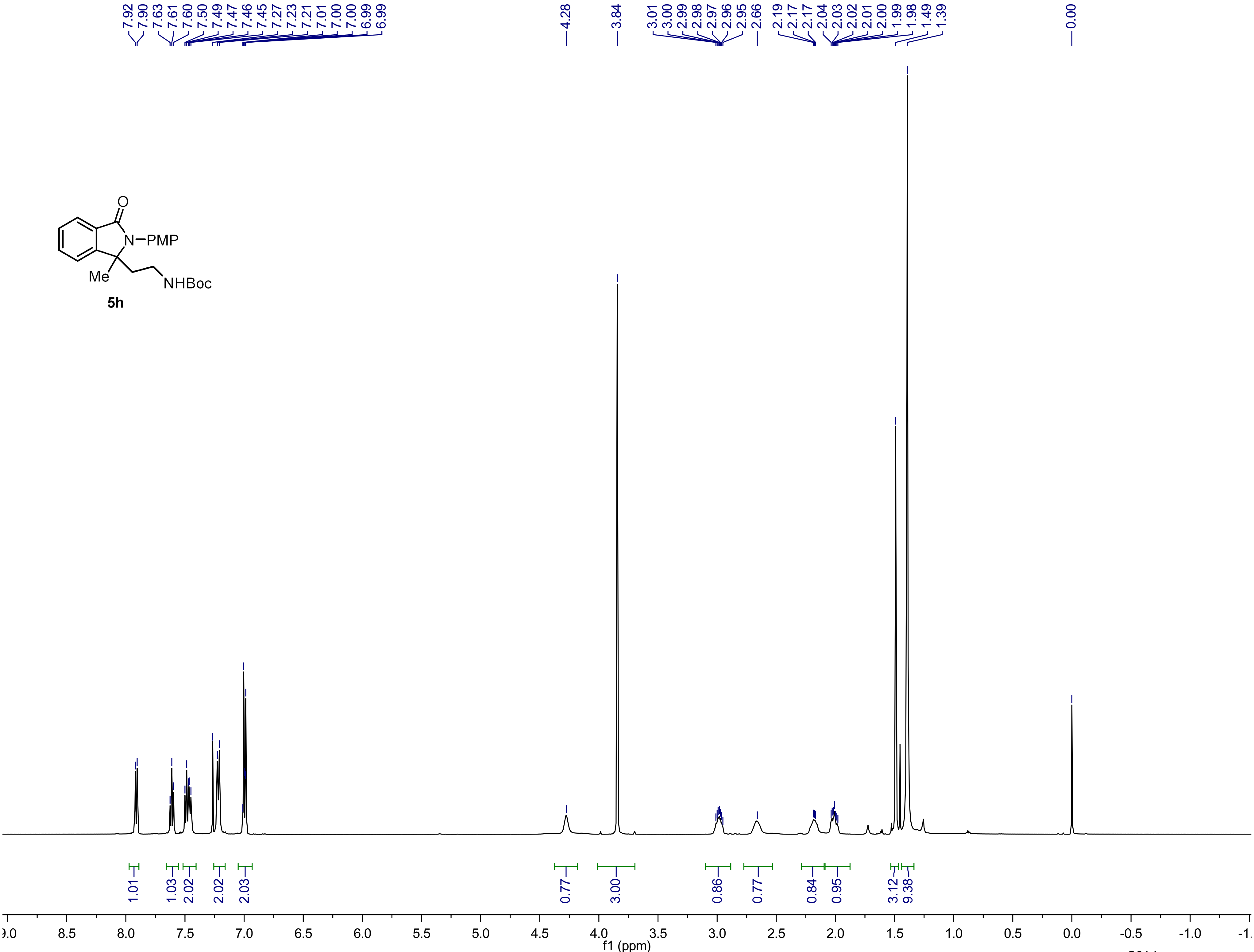
10
0
-10
f1 (ppm)



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7.47
7.46
7.45
7.27
7.23
7.21
7.01
7.00
7.00
6.99
6.99
4.28
3.84
3.01
3.00
2.99
2.98
2.97
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2.95
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2.19
2.17
2.17
2.04
2.03
2.02
2.01
2.00
1.99
1.98
1.49
1.39
0.00
O
N
PMP
Me
NHBoc
5h
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1.03
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2.02
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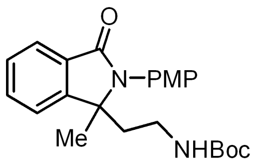
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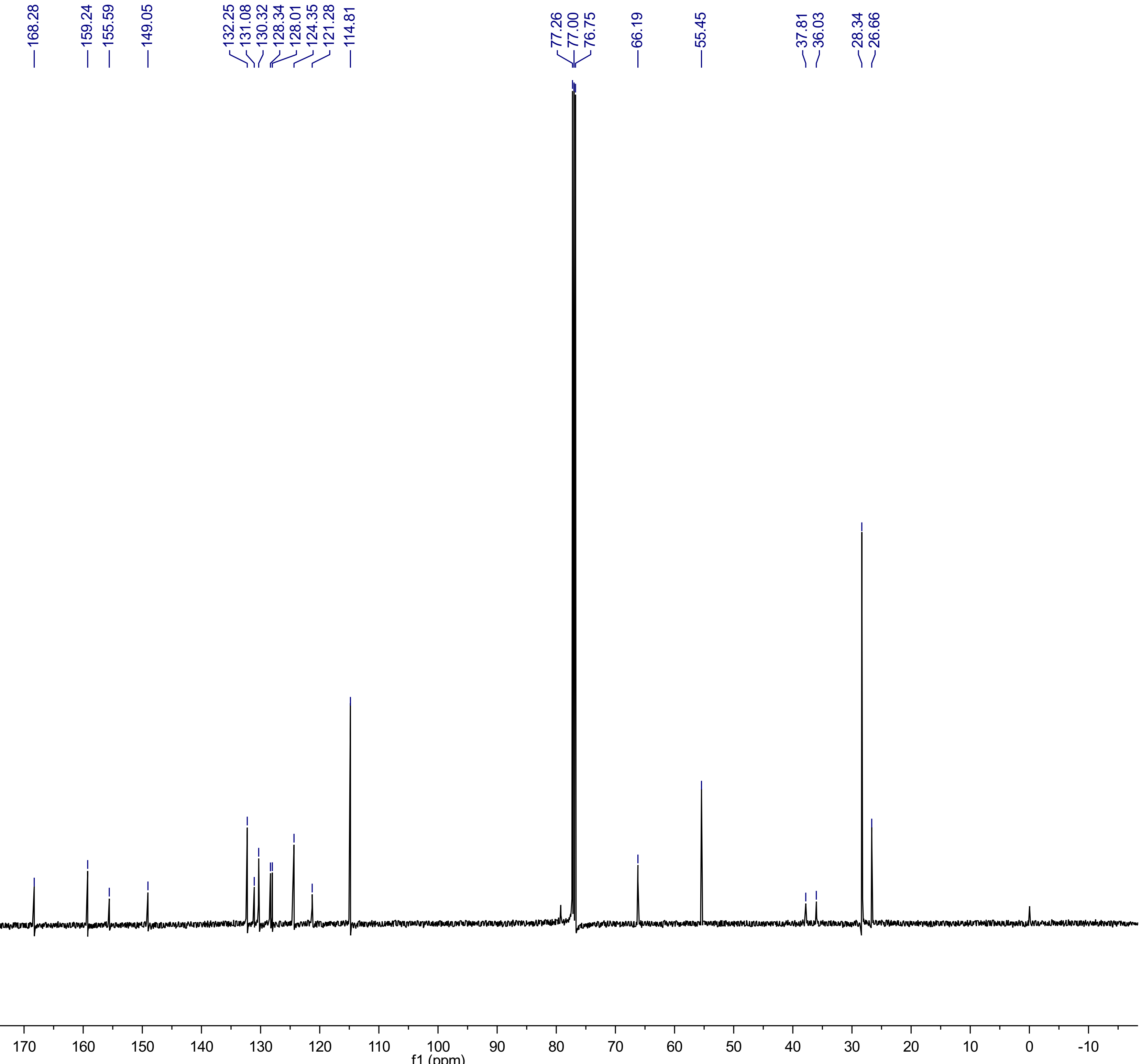

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128.01
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114.81
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76.75
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36.03
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26.66
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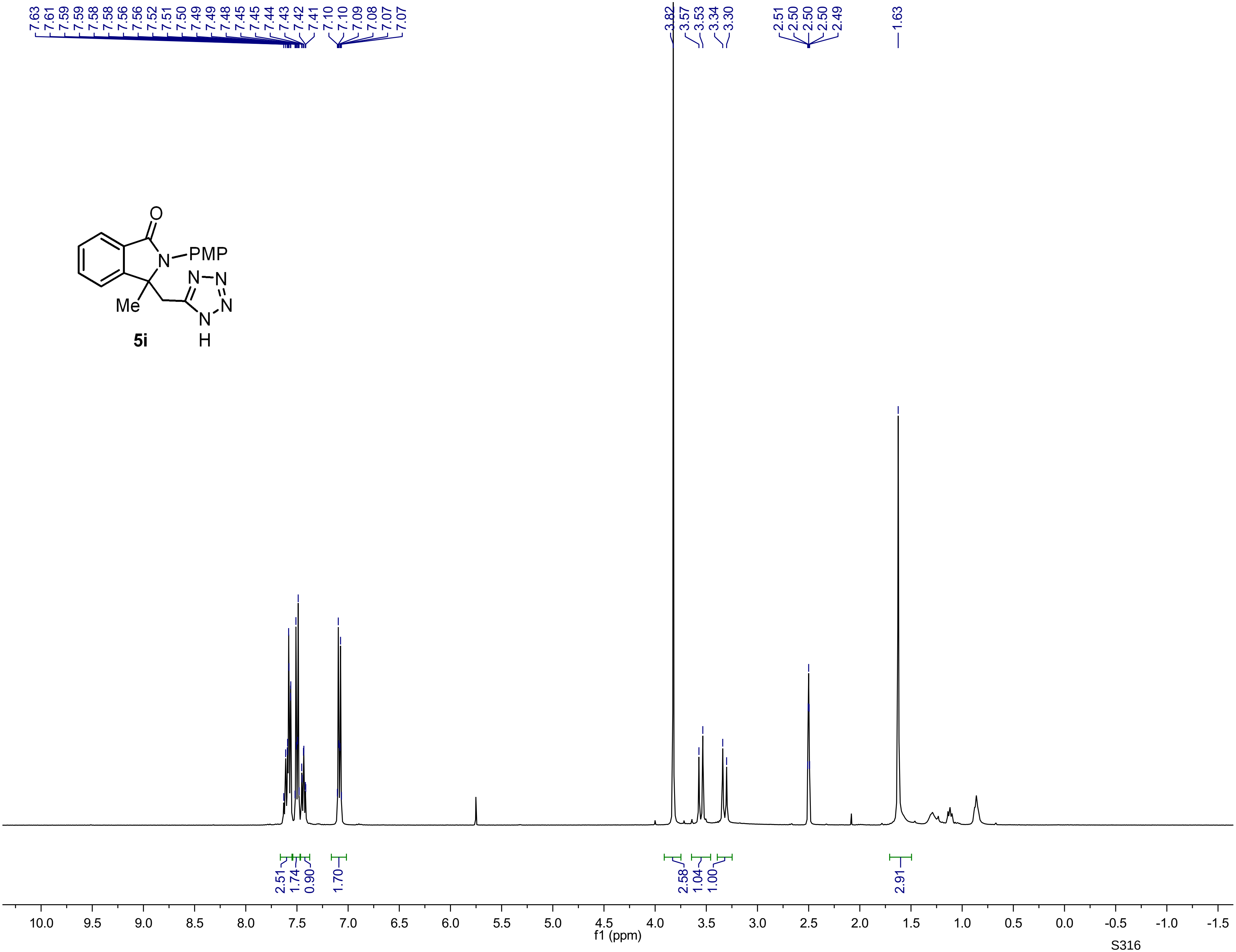
f1 (ppm)


PMP
Me
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7.48
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7.45
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7.43
7.42
7.41
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7.10
7.09
7.08
7.07
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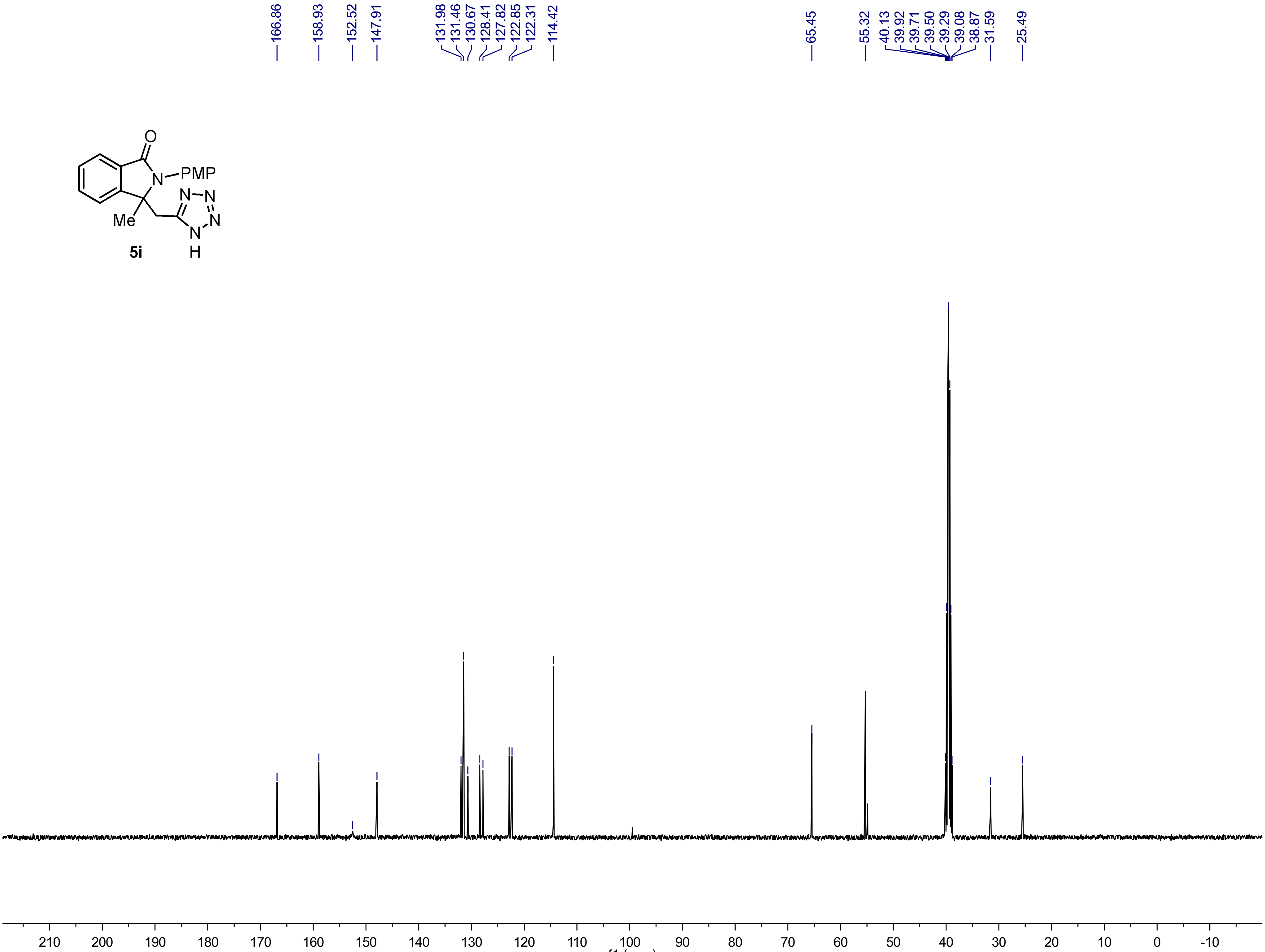
3.57
3.53
3.34
3.30
2.51
2.50
2.50
2.50
2.49
1.63
2.51
1.74
0.90
1.70
2.58
1.04
1.00
2.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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114.42
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39.71
39.50
39.29
39.08
38.87
31.59
25.49
O
N
PMP
N
N
N
N
H
Me
5i
210
200
190
180
170
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140
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100
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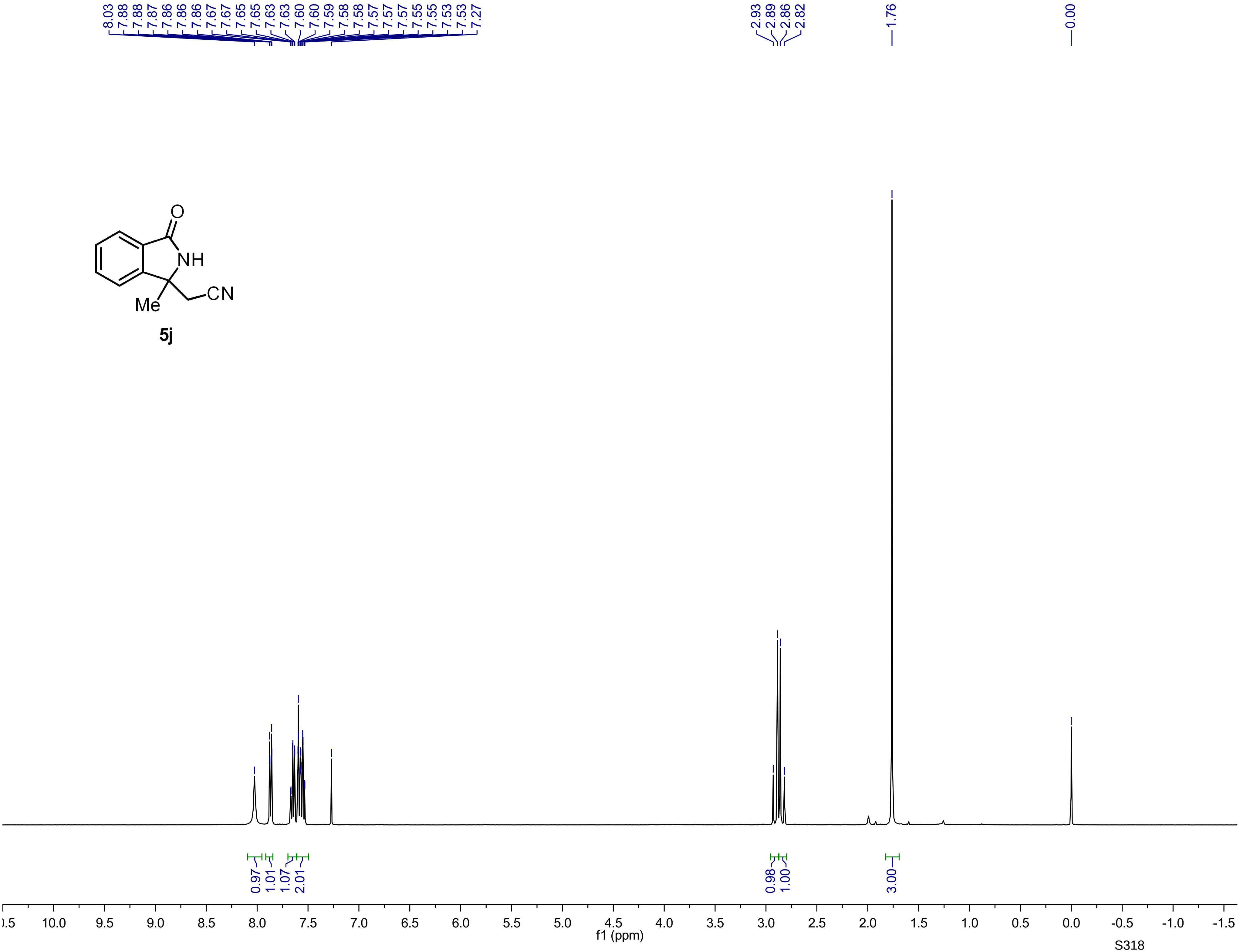
0
-10
f1 (ppm)



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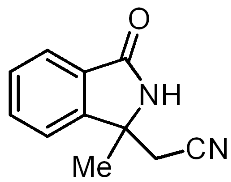

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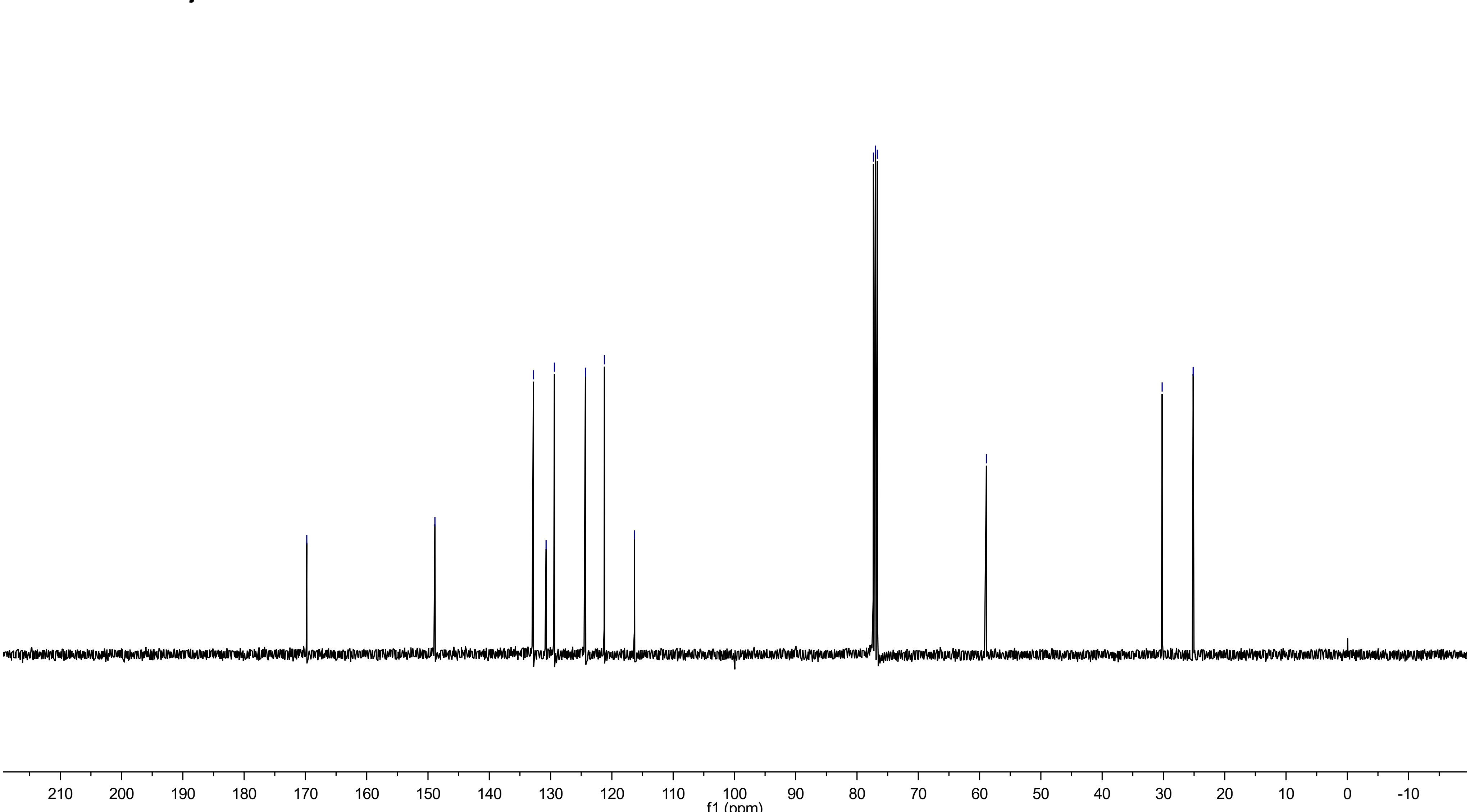

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116.31
77.32
77.00
76.68
58.89
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25.15
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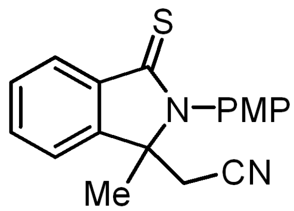
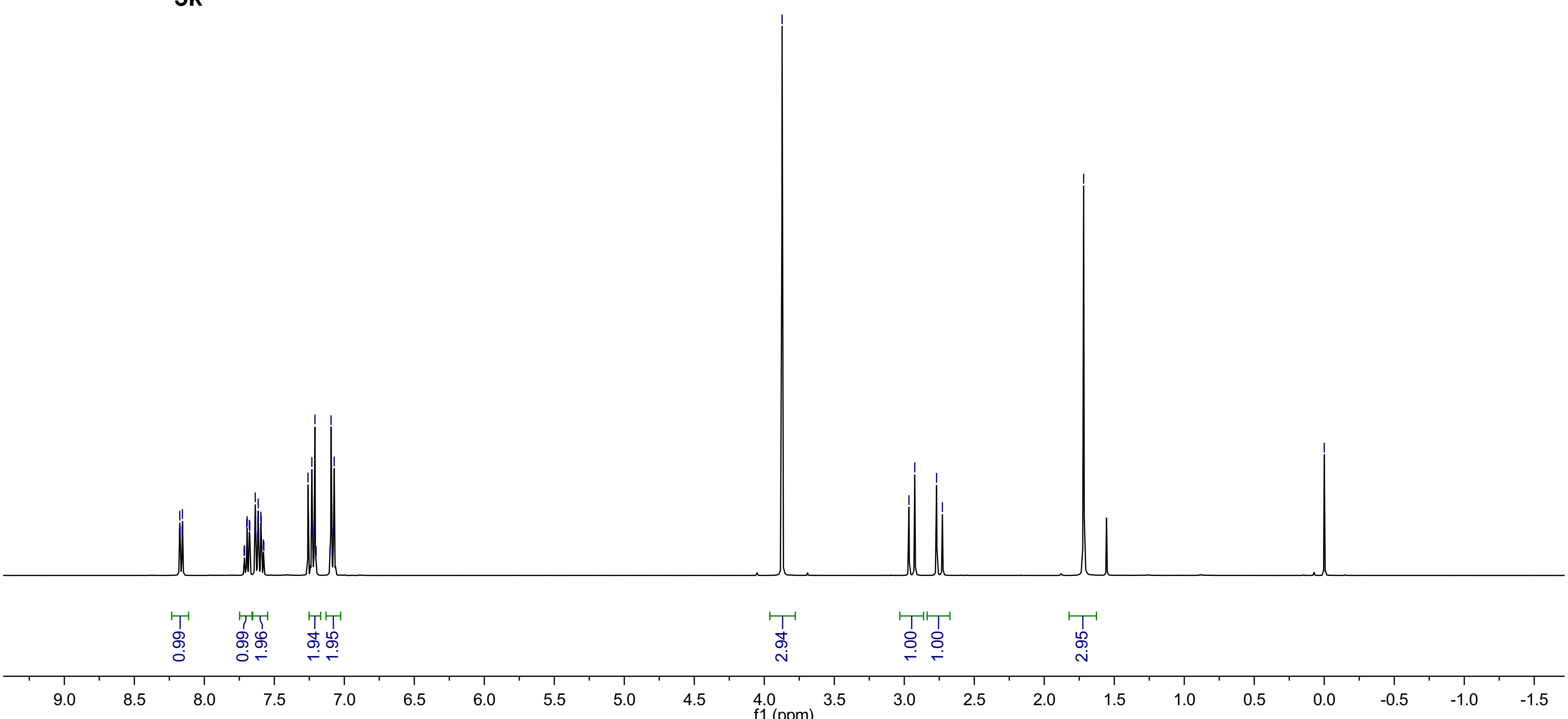
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


S
N–PMP
CN
Me

5k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7.63
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7.62
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7.59
7.58
7.57
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7.23
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7.22
7.21
7.20
7.10
7.09
7.09
7.08
7.07
3.87
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2.93
2.77
2.73
1.72
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0.99
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1.94
1.95
2.94
1.00
1.00
2.95
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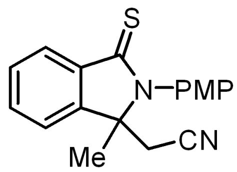

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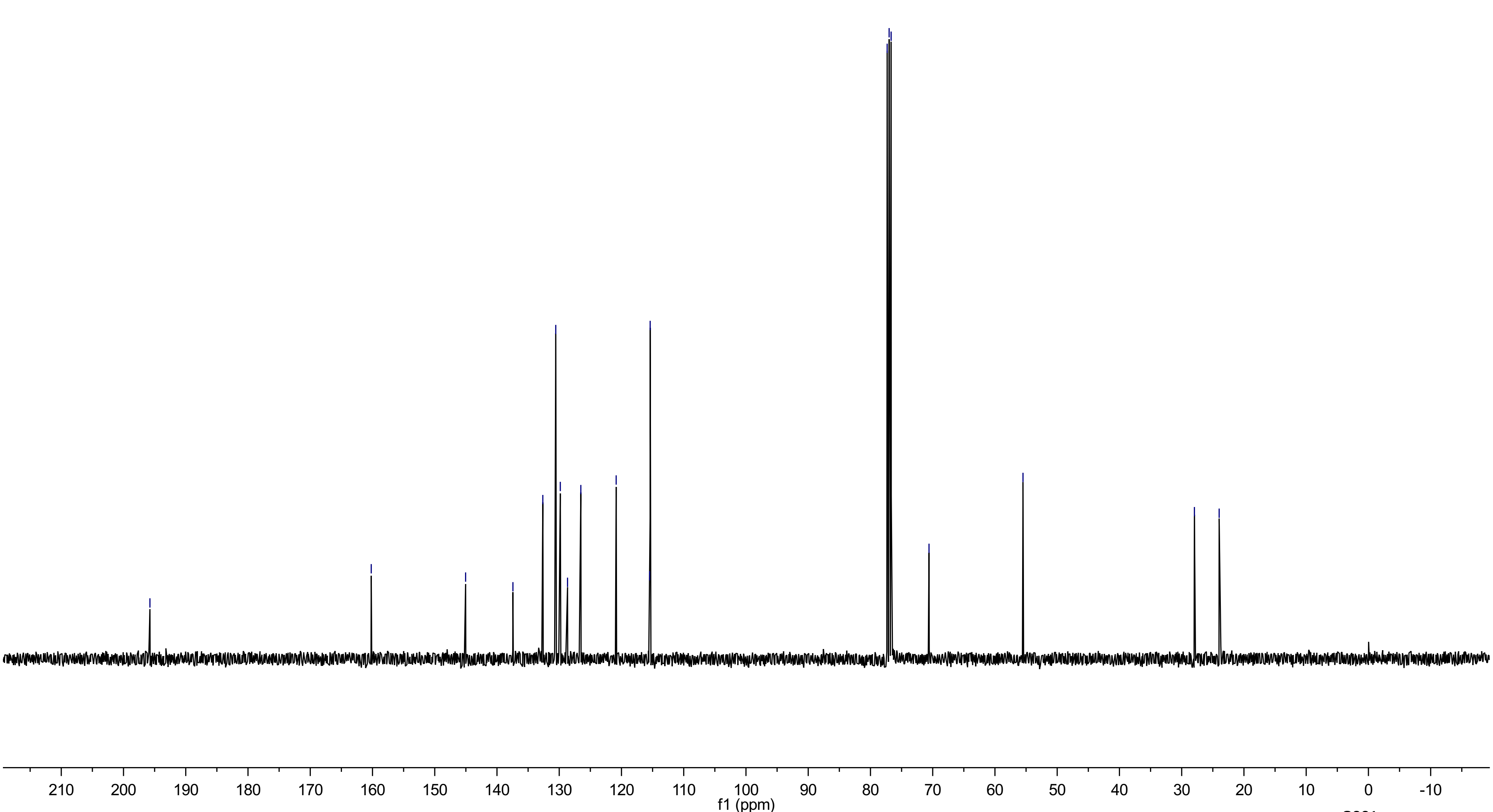

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77.32
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55.49
27.96
23.98
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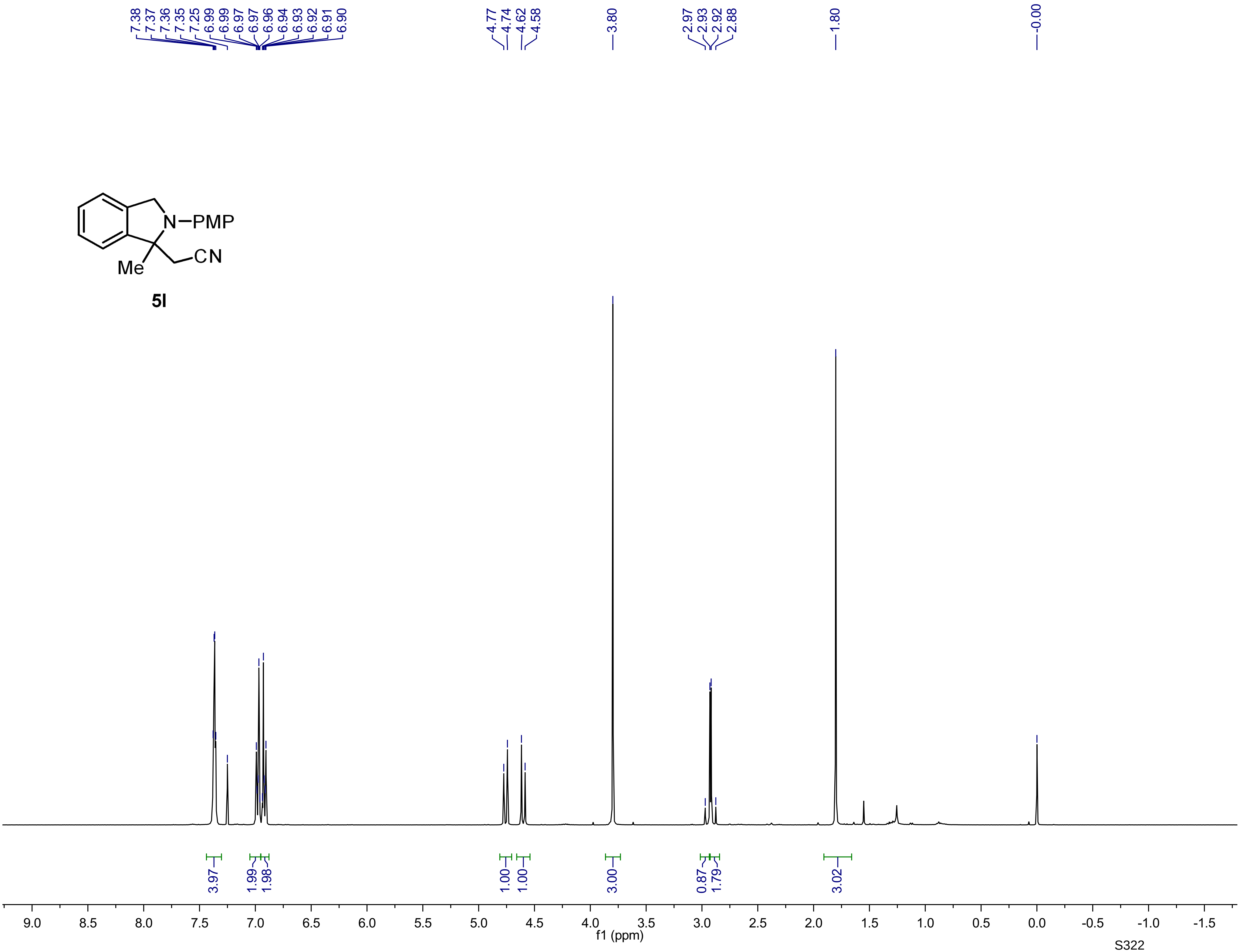
f1 (ppm)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6.90
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Me
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1.00
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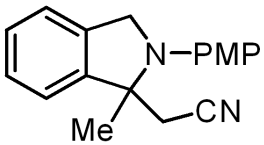
N
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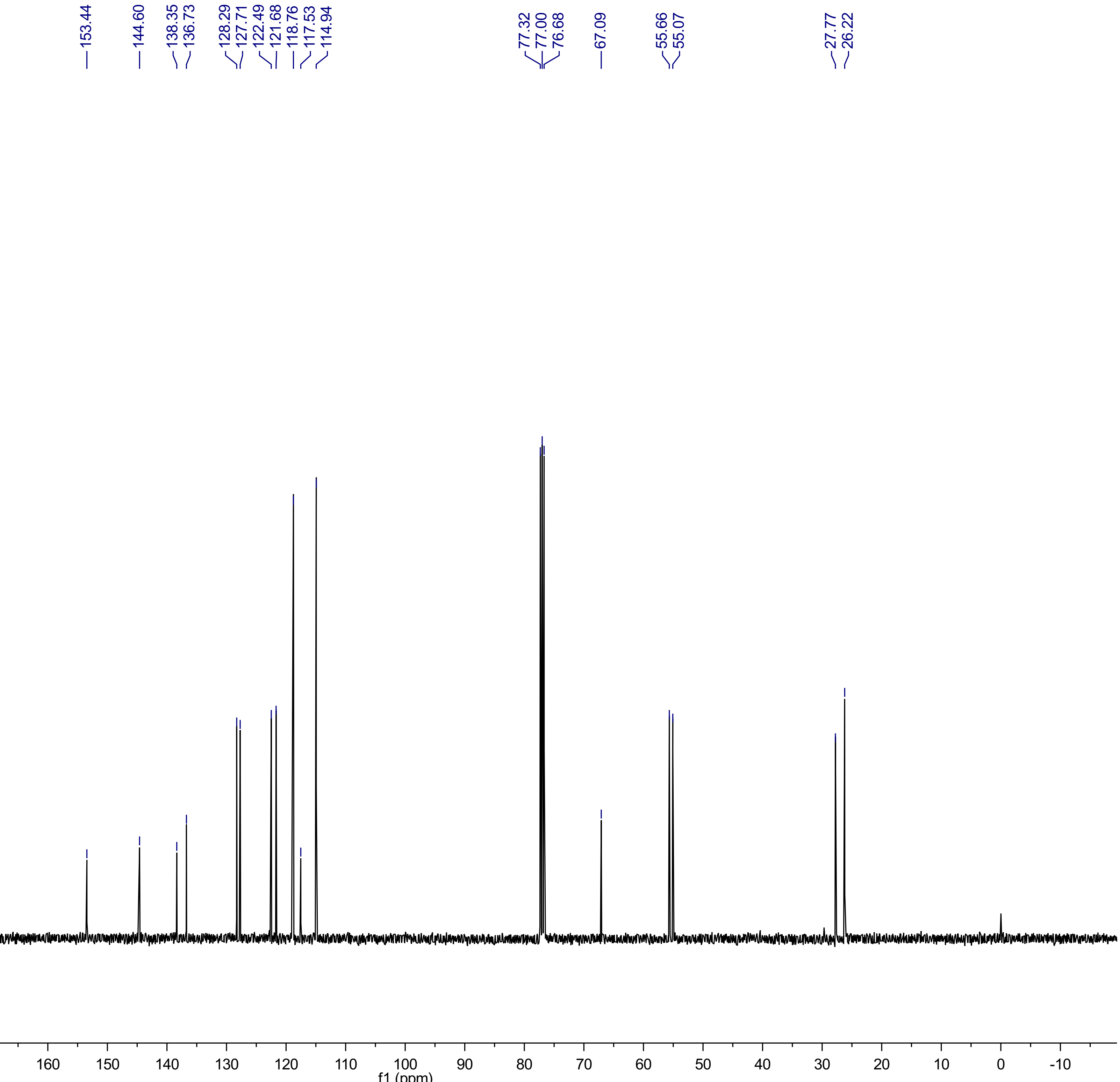
CN

5l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77.00
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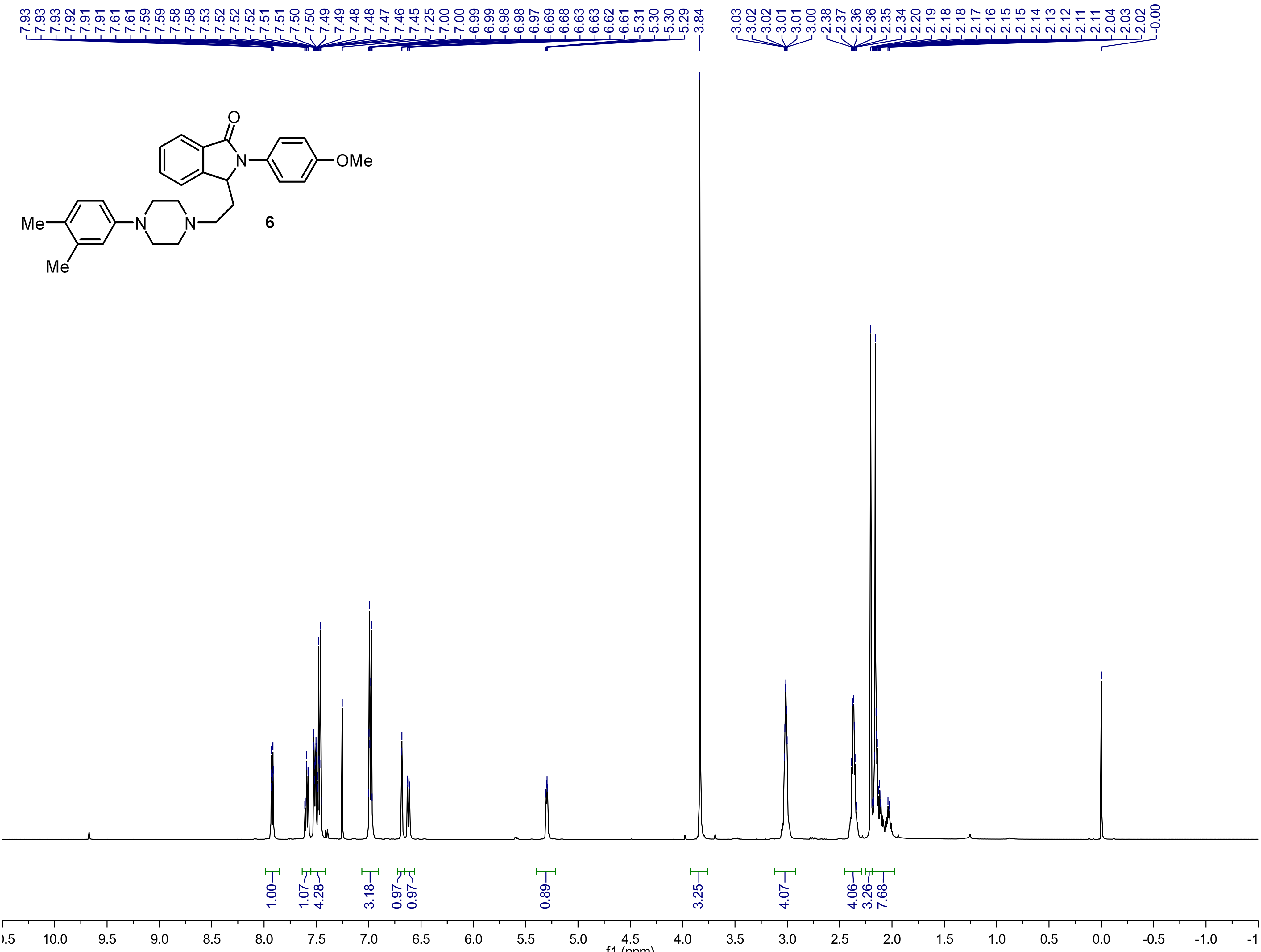
26.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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6.98
6.97
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6.63
6.62
6.61
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5.30
5.30
5.29
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3.03
3.02
3.02
3.01
3.01
3.00
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2.12
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2.04
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2.02
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O
N
OMe
Me
N
N
Me
6
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0.97
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3.26
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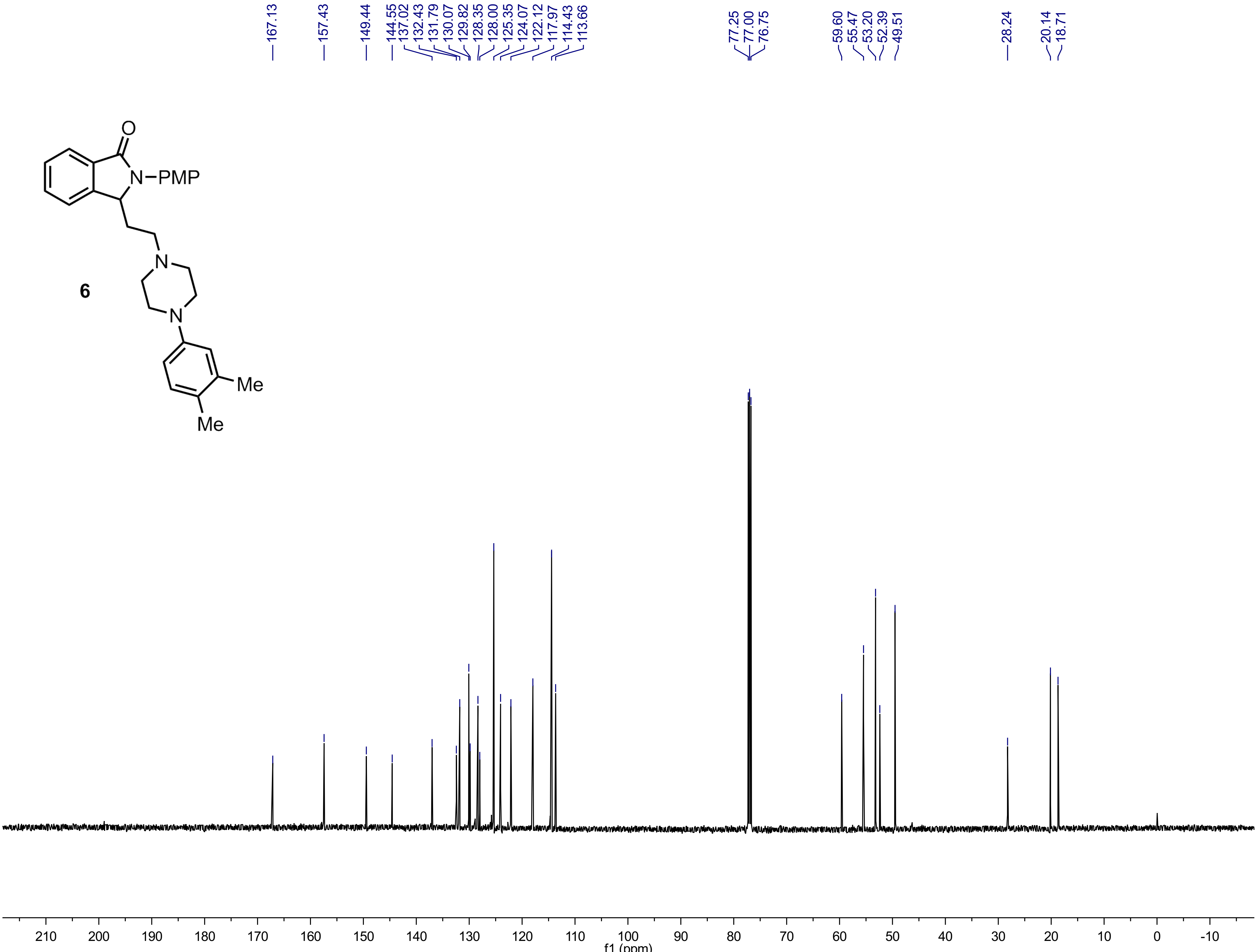
f1 (ppm)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117.97
114.43
113.66
77.25
77.00
76.75
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28.24
20.14
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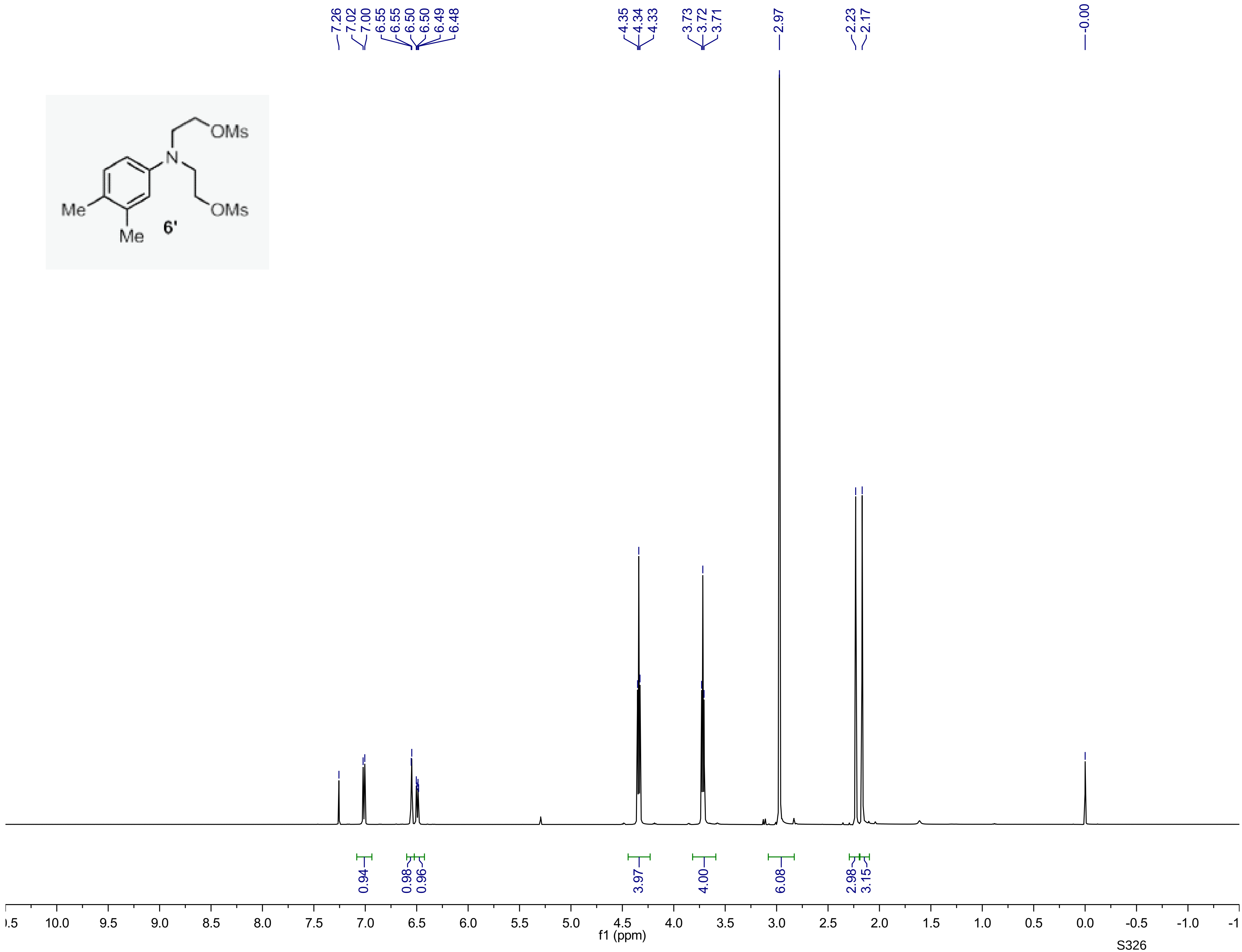
N–PMP
6
Me
Me
f1 (ppm)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3.73
3.72
3.71
2.97
2.23
2.17
-0.00
OMs
N
OMs
Me
Me
6'
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0.98
0.96
3.97
4.00
6.08
2.98
3.15
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.5
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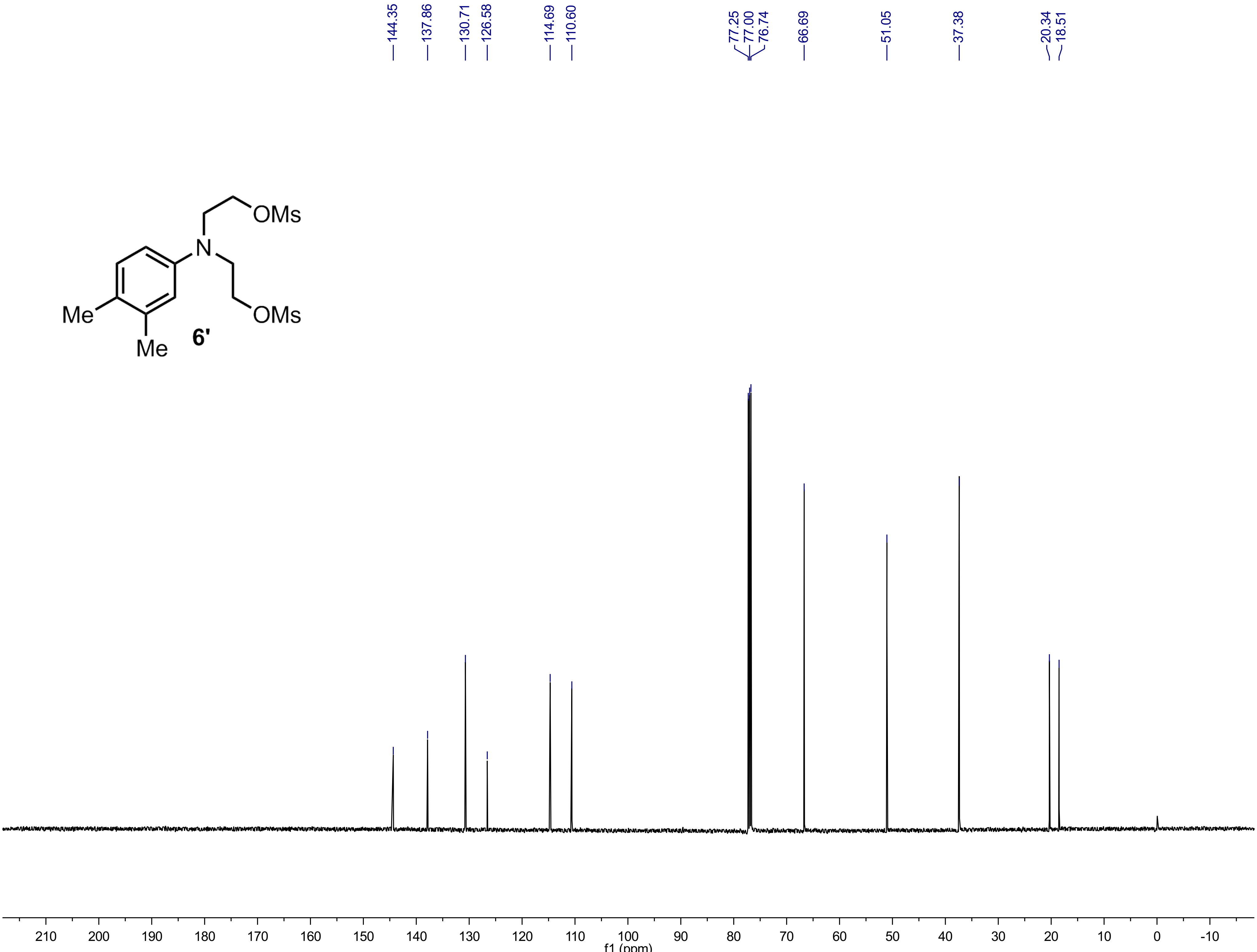
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)



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114.69
110.60
77.25
77.00
76.74
66.69
51.05
37.38
20.34
18.51
OMs
N
Me
OMs
Me
6'
210
200
190
180
170
160
150
140
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120
110
100
90
80
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60
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40
30
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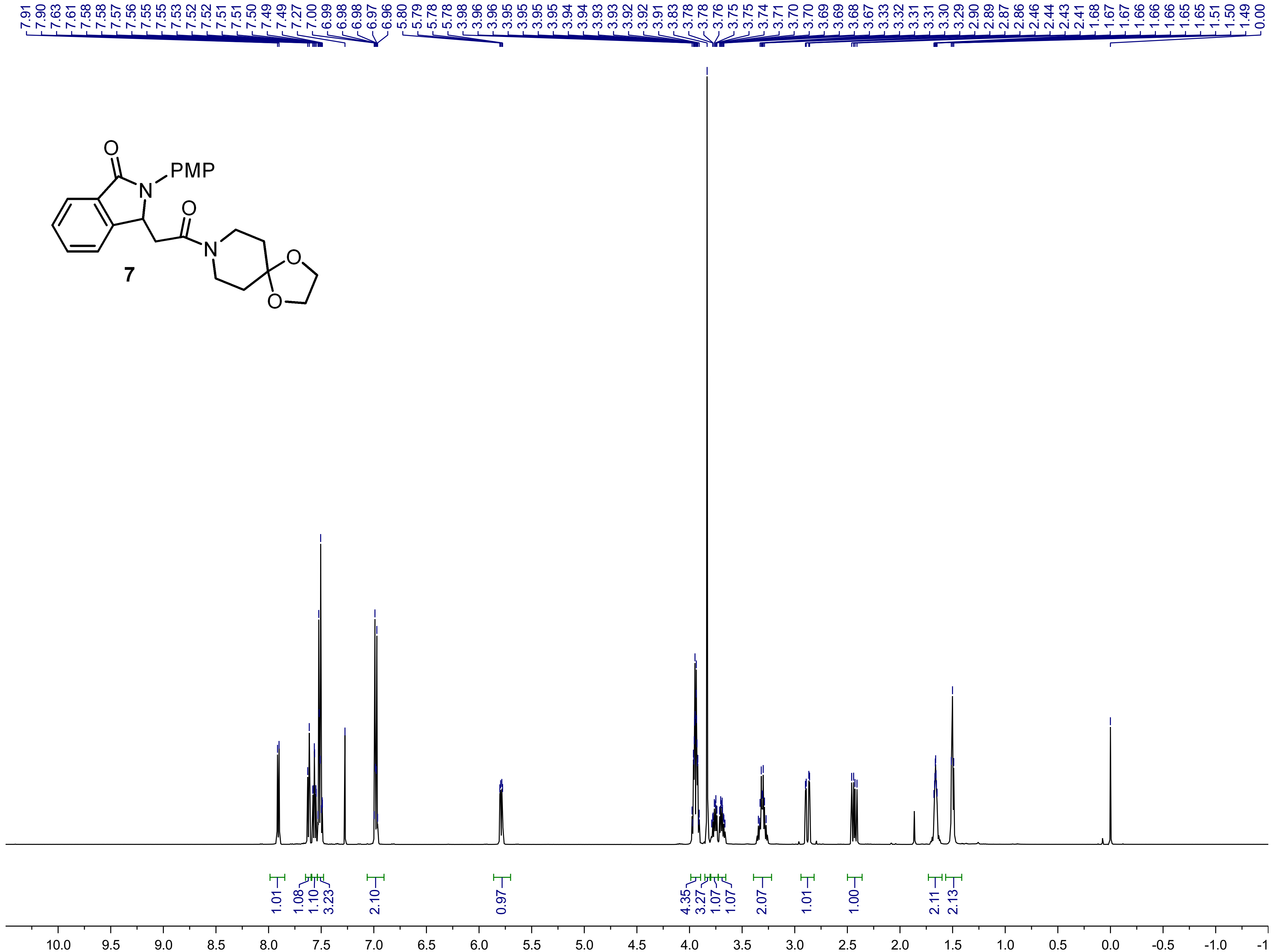
0
-10
f1 (ppm)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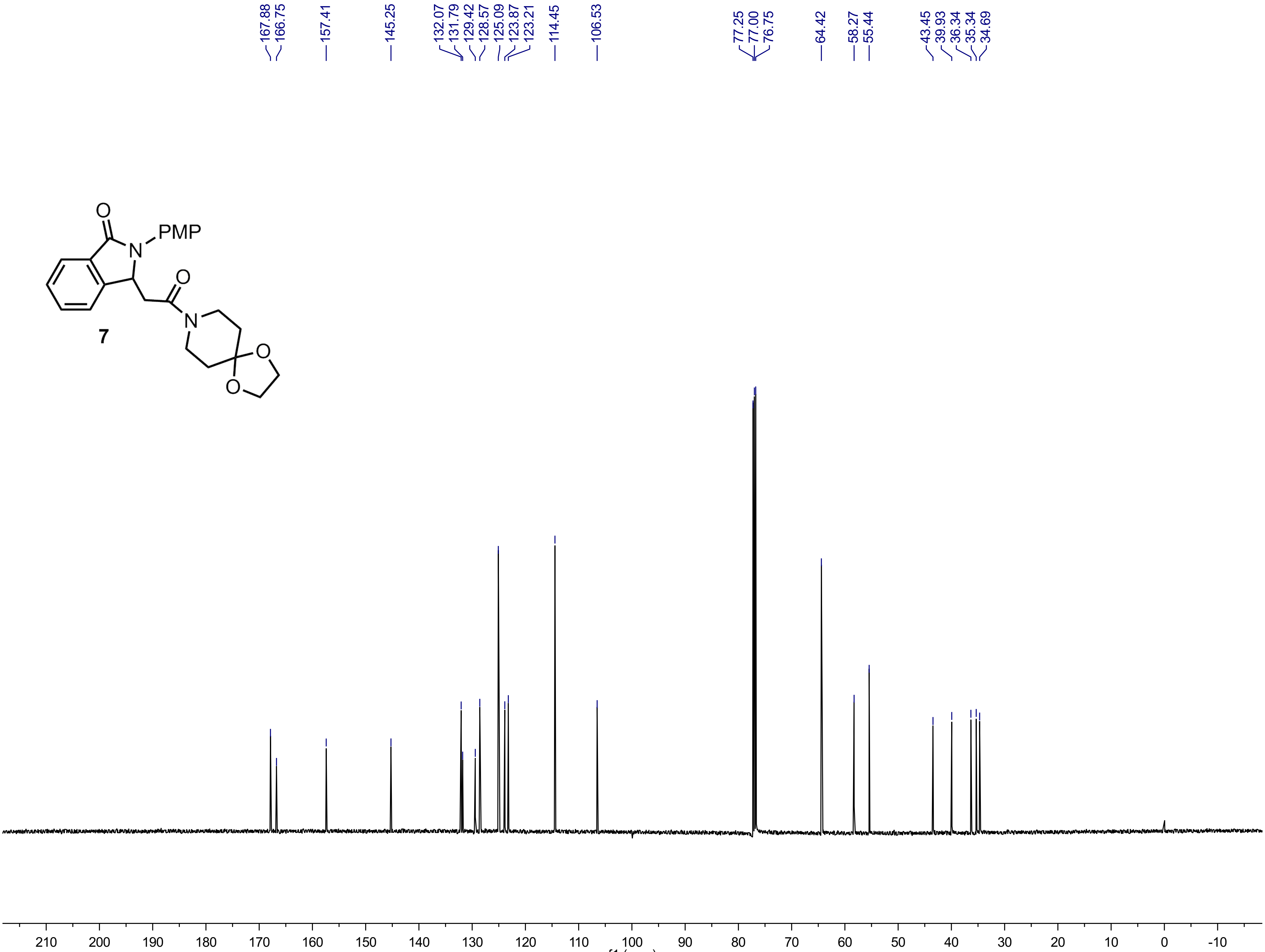
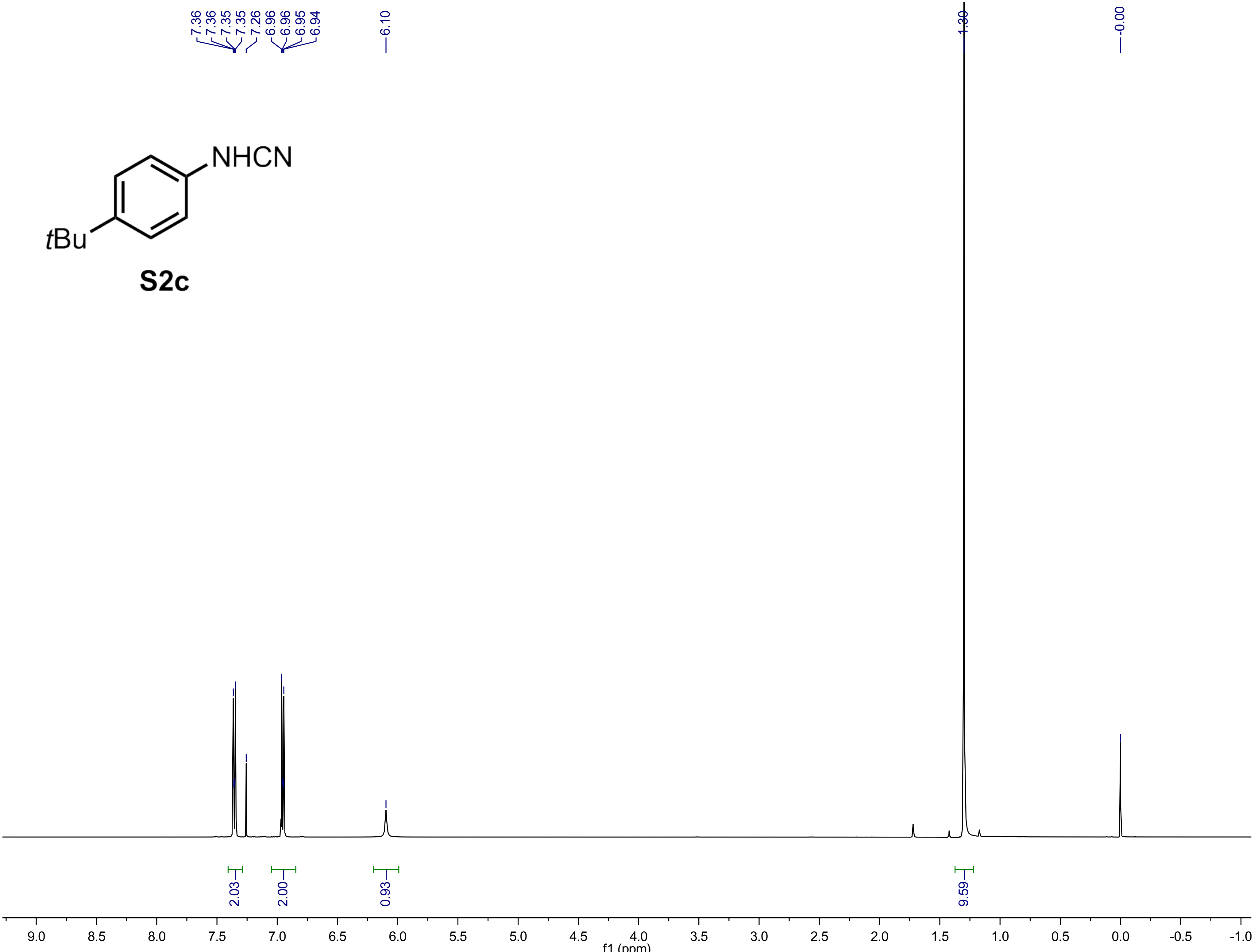
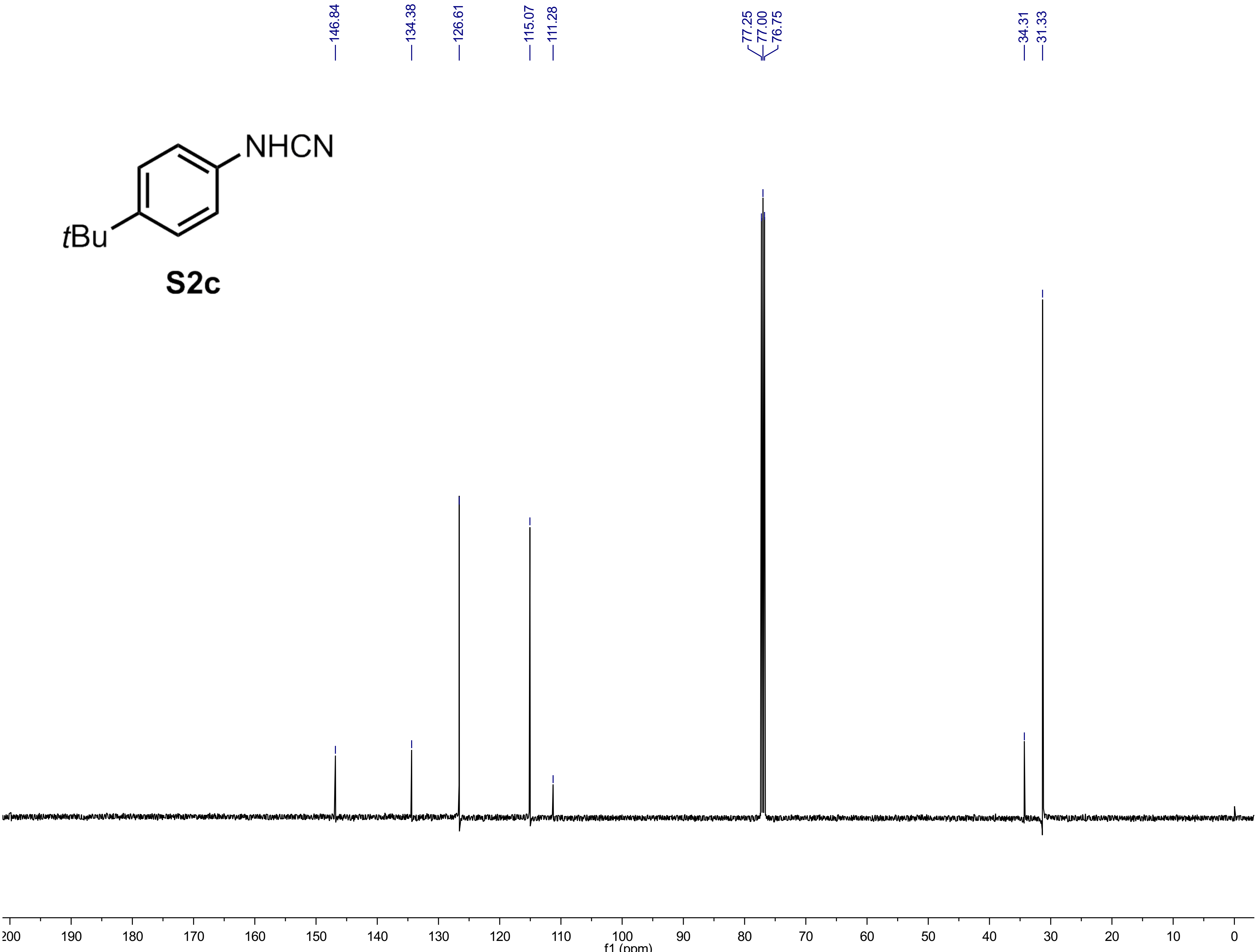
PMP
7
1.01 1.08 1.10 3.23 2.10 0.97 4.35 3.27 1.07 1.07 2.07 1.01 1.00 2.11 2.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)

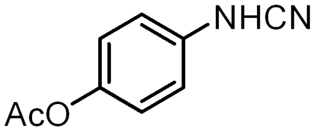

167.88
166.75
157.41
145.25
132.07
131.79
129.42
128.57
125.09
123.87
123.21
114.45
106.53
77.25
77.00
76.75
64.42
58.27
55.44
43.45
39.93
36.34
35.34
34.69
O
PMP
N
O
N
O
O
7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



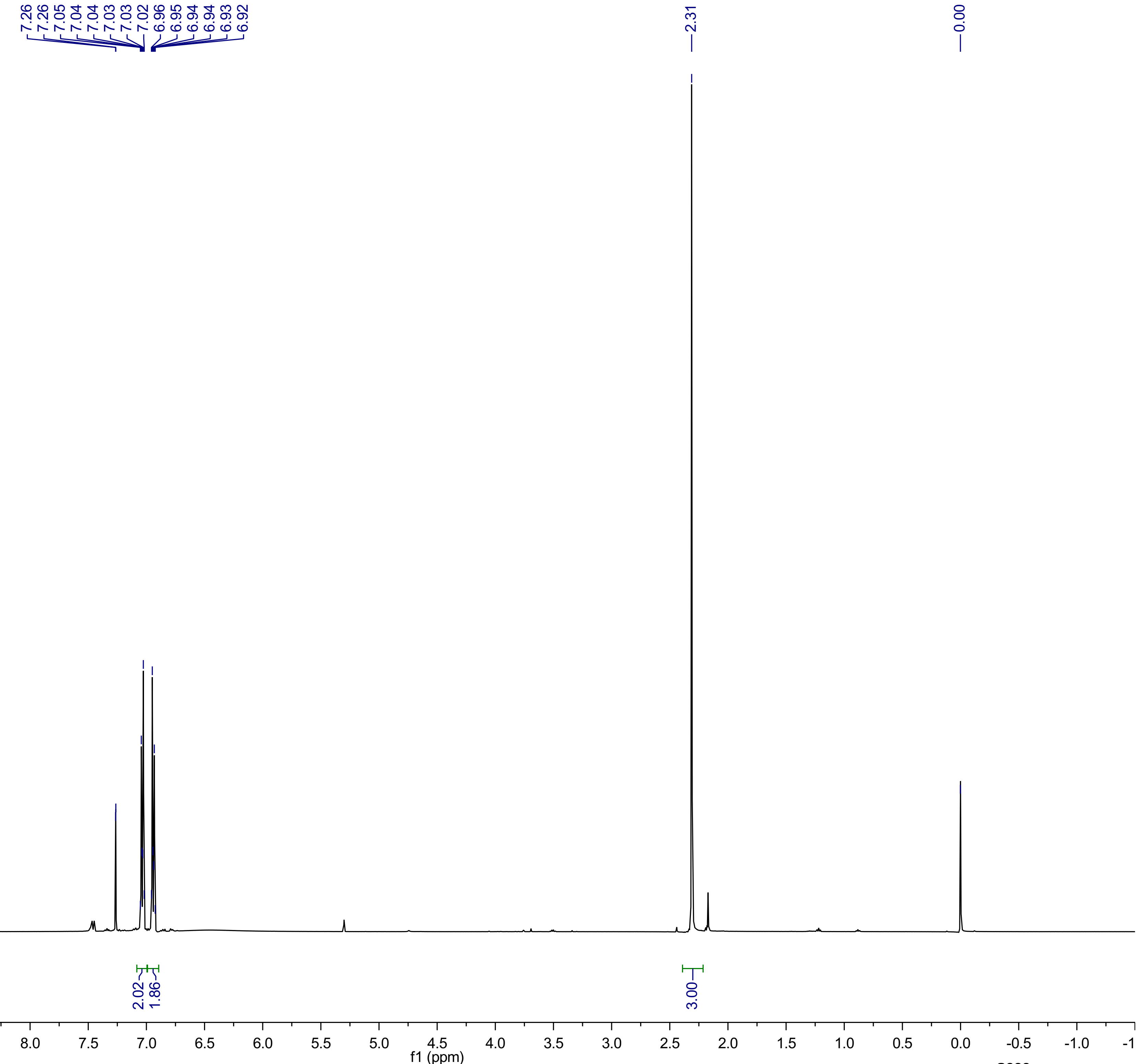
NHCN
tBu
S2c
7.36
7.36
7.35
7.35
7.26
6.96
6.96
6.95
6.94
6.10
1.30
-0.00
2.03
2.00
0.93
9.59
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



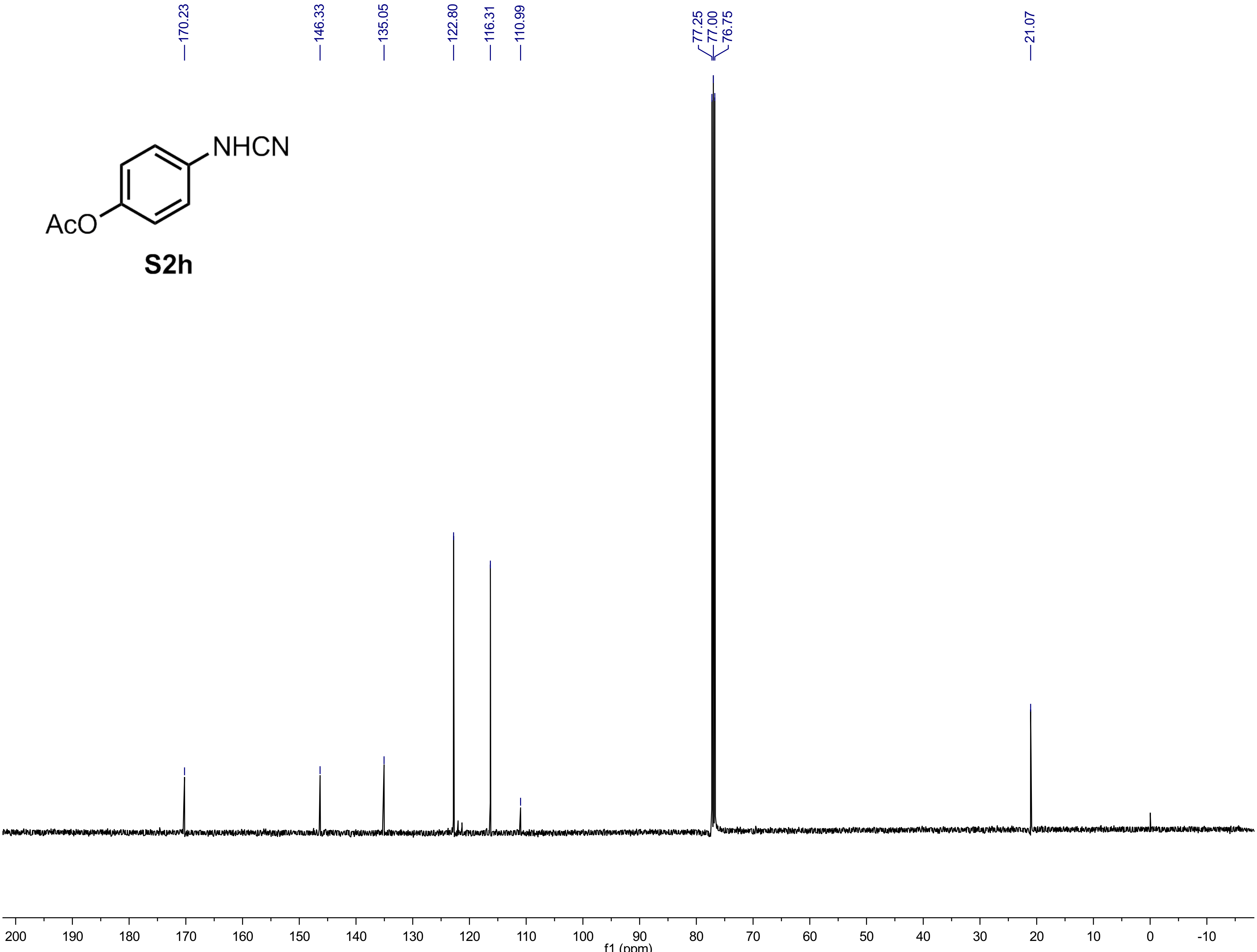
146.84
134.38
126.61
115.07
111.28
77.25
77.00
76.75
34.31
31.33
NHCN
tBu
S2c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

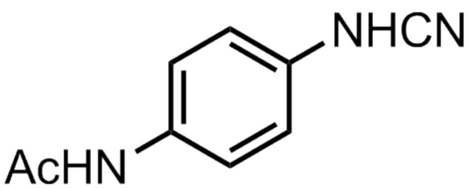


S2h

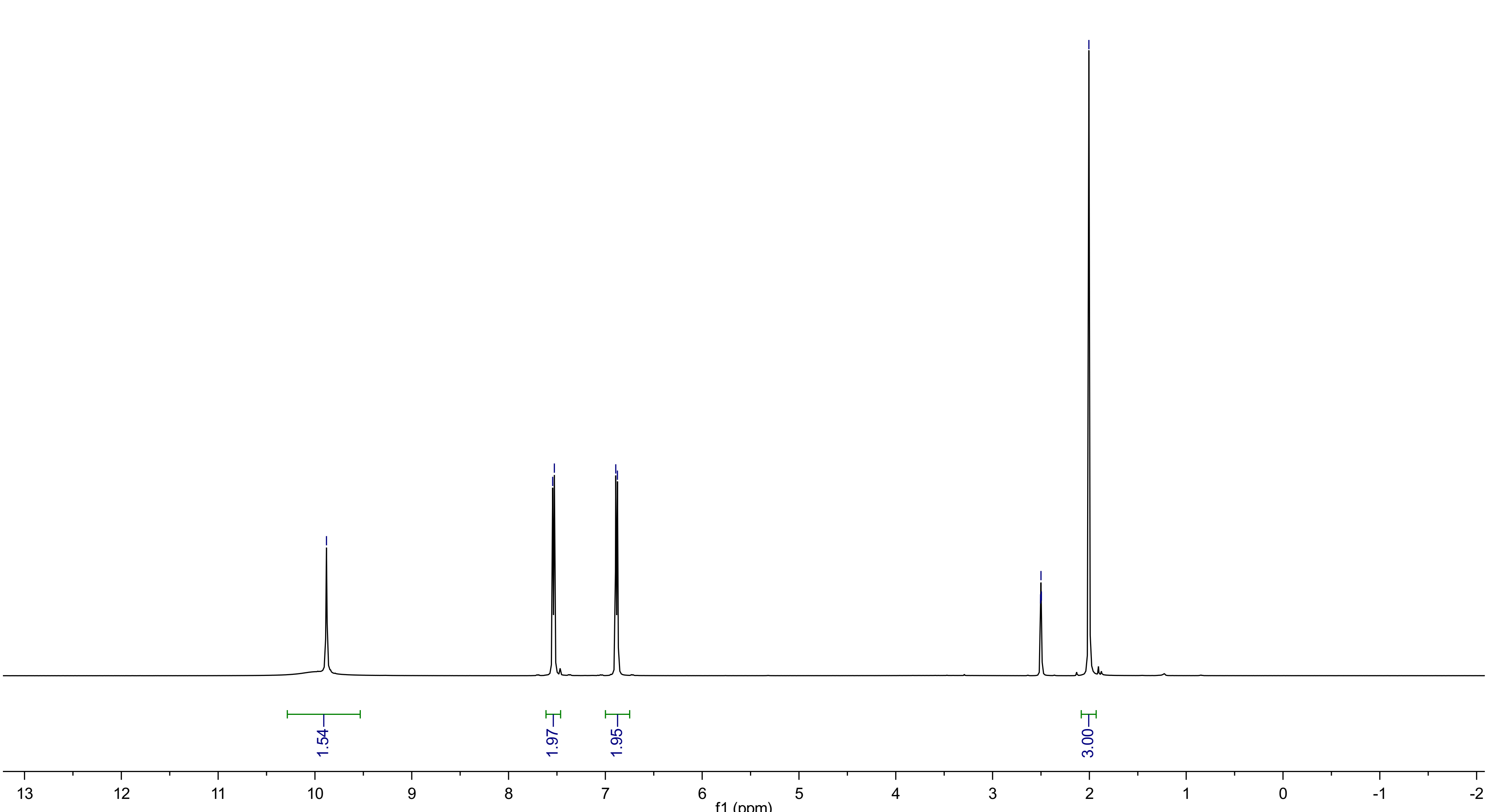


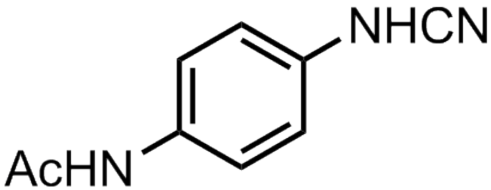
7.26
7.26
7.05
7.04
7.04
7.03
7.03
7.02
6.96
6.95
6.94
6.94
6.93
6.92
2.31
0.00
2.02
1.86
3.00
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1
f1 (ppm)


170.23
146.33
135.05
122.80
116.31
110.99
77.25
77.00
76.75
21.07
NHCN
AcO
S2h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

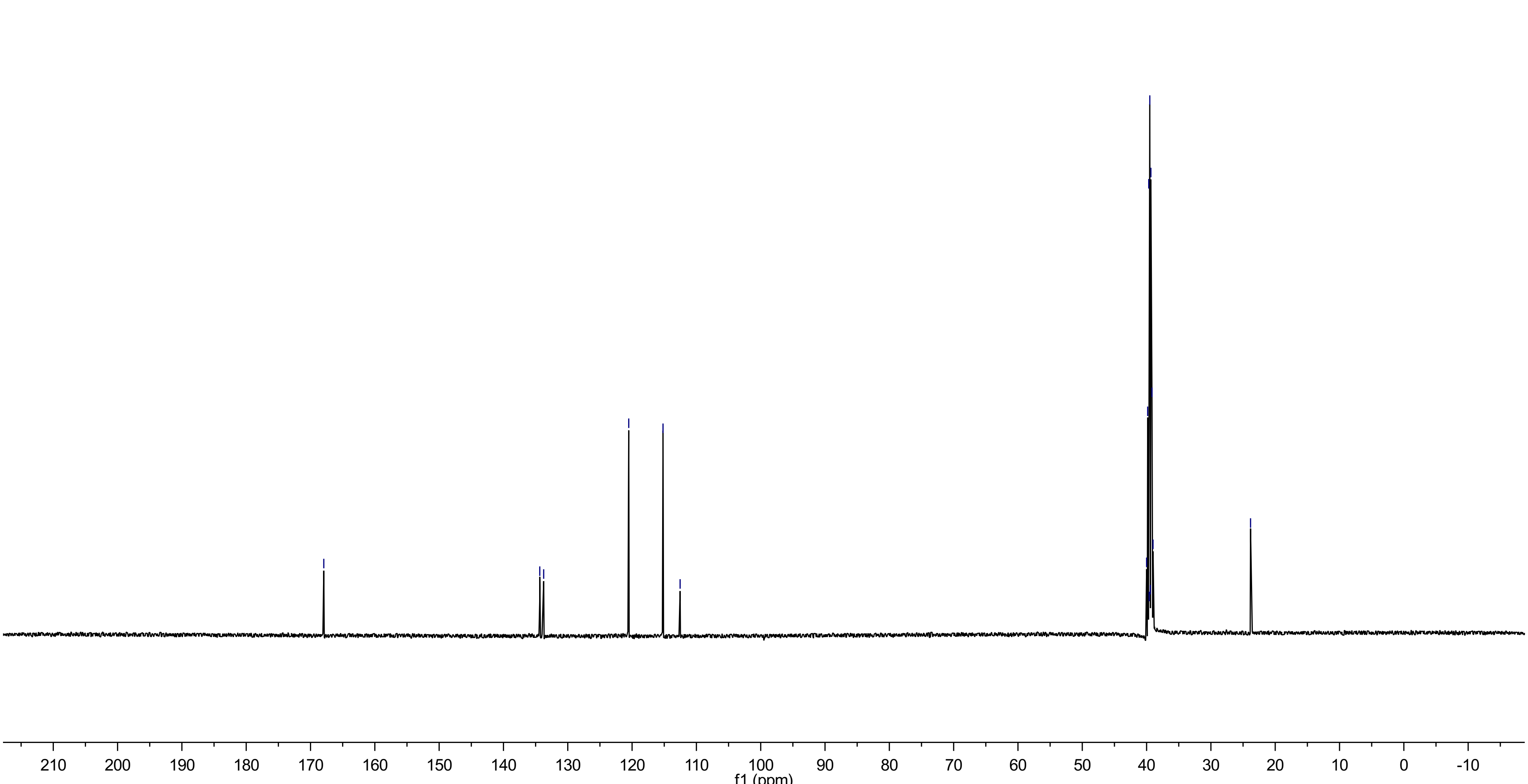

NHCN
AcHN

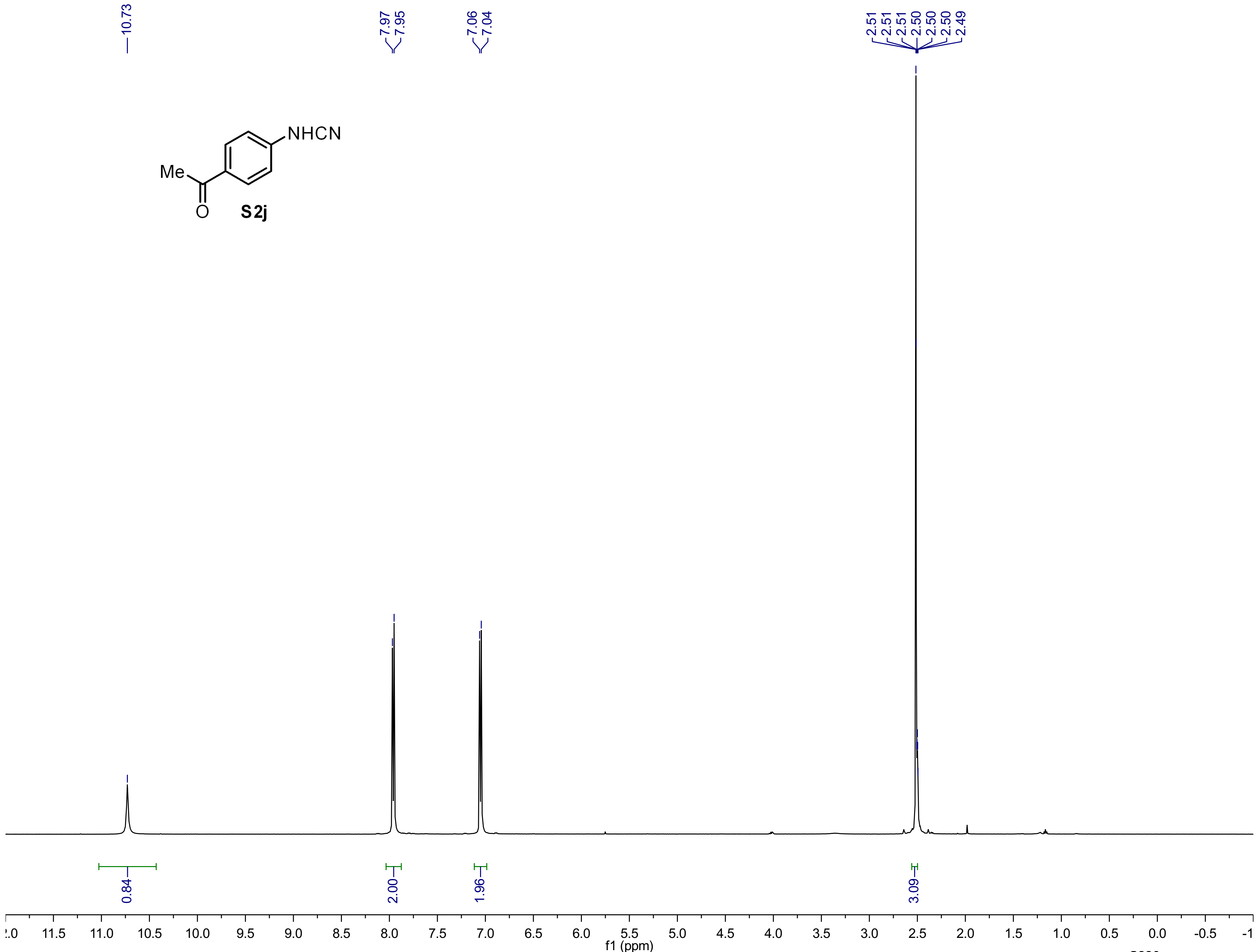
S2i

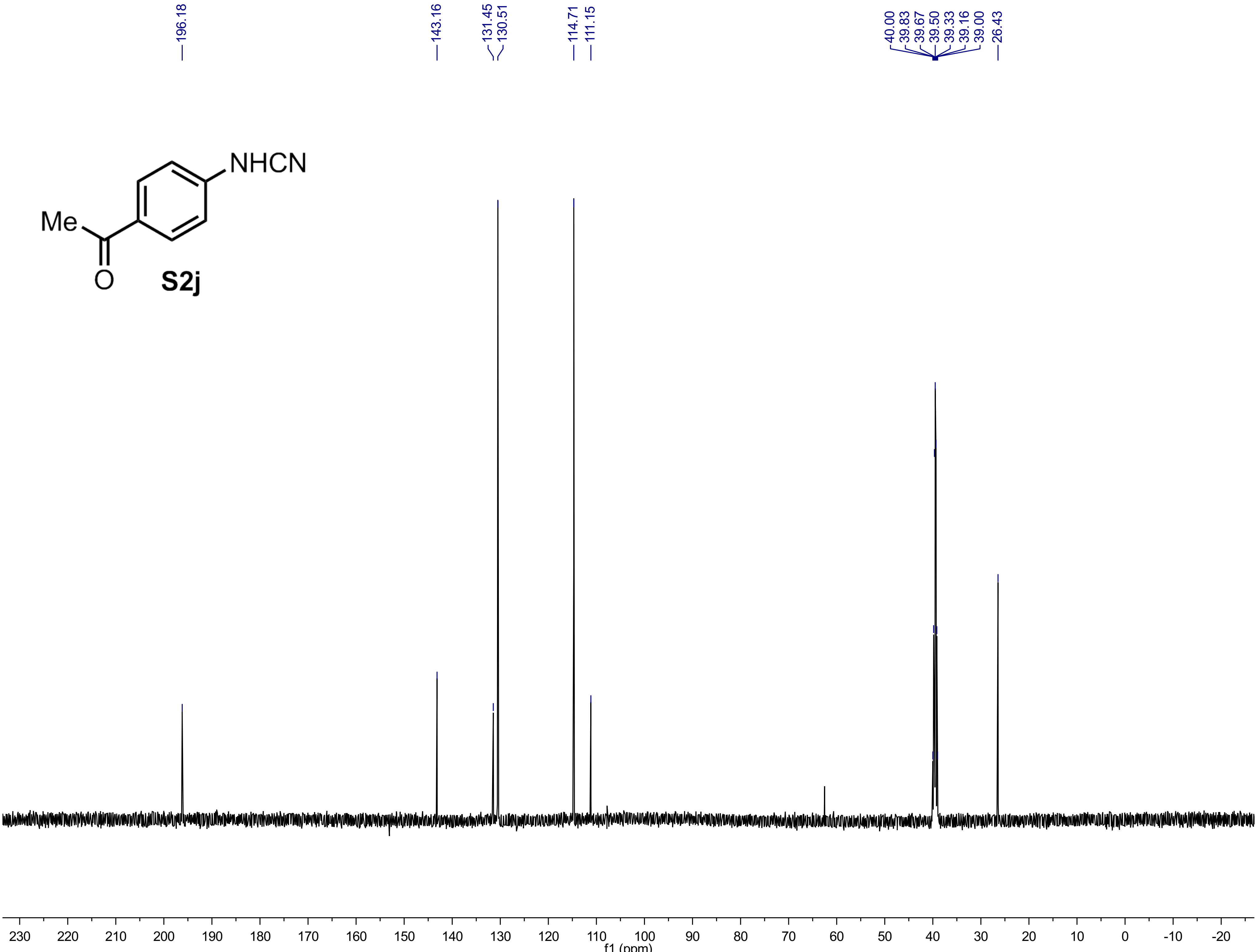

9.88
7.54
7.53
6.89
6.88
2.50
2.50
2.50
2.01
1.54
1.97
1.95
3.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

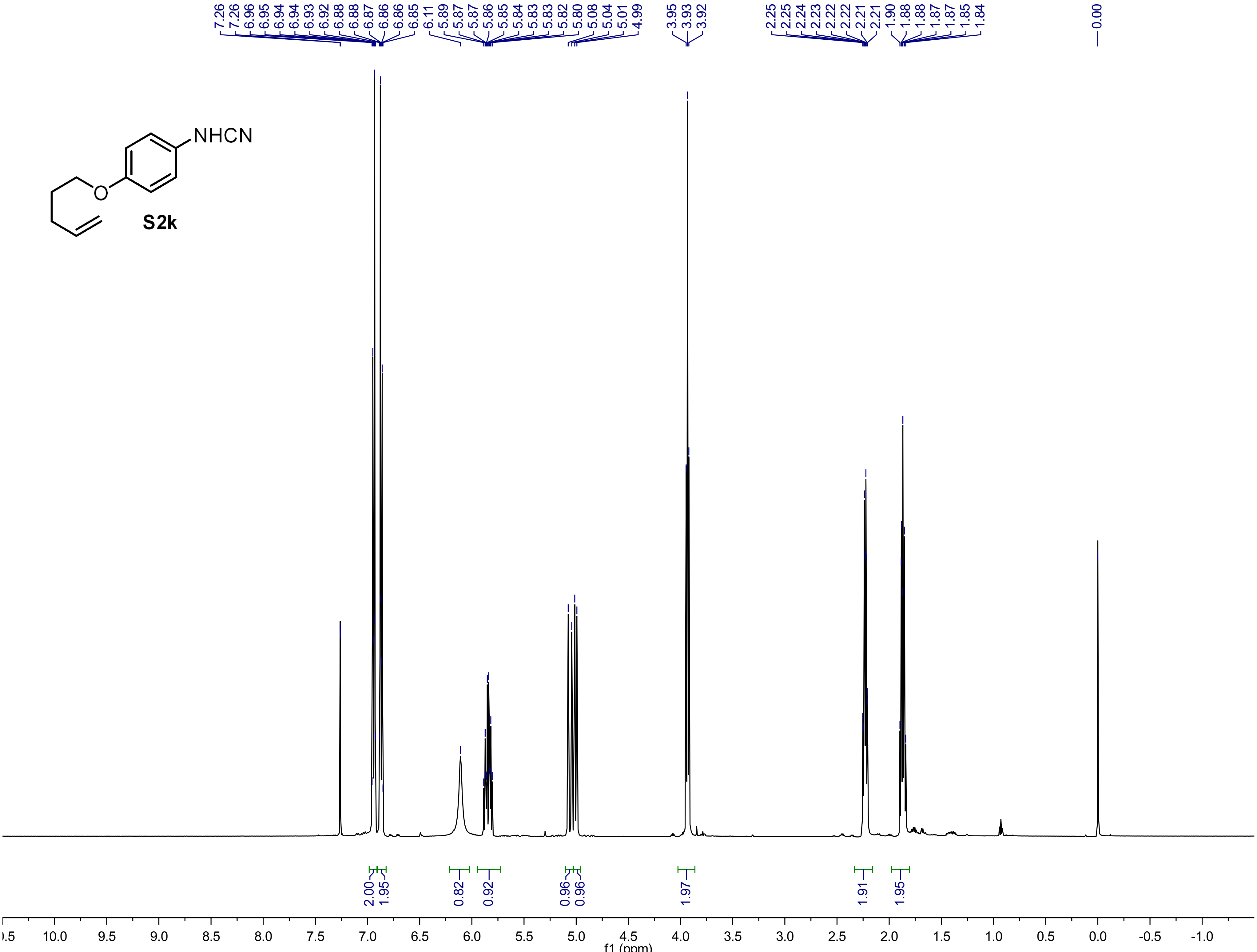

NHCN
AcHN

S2i

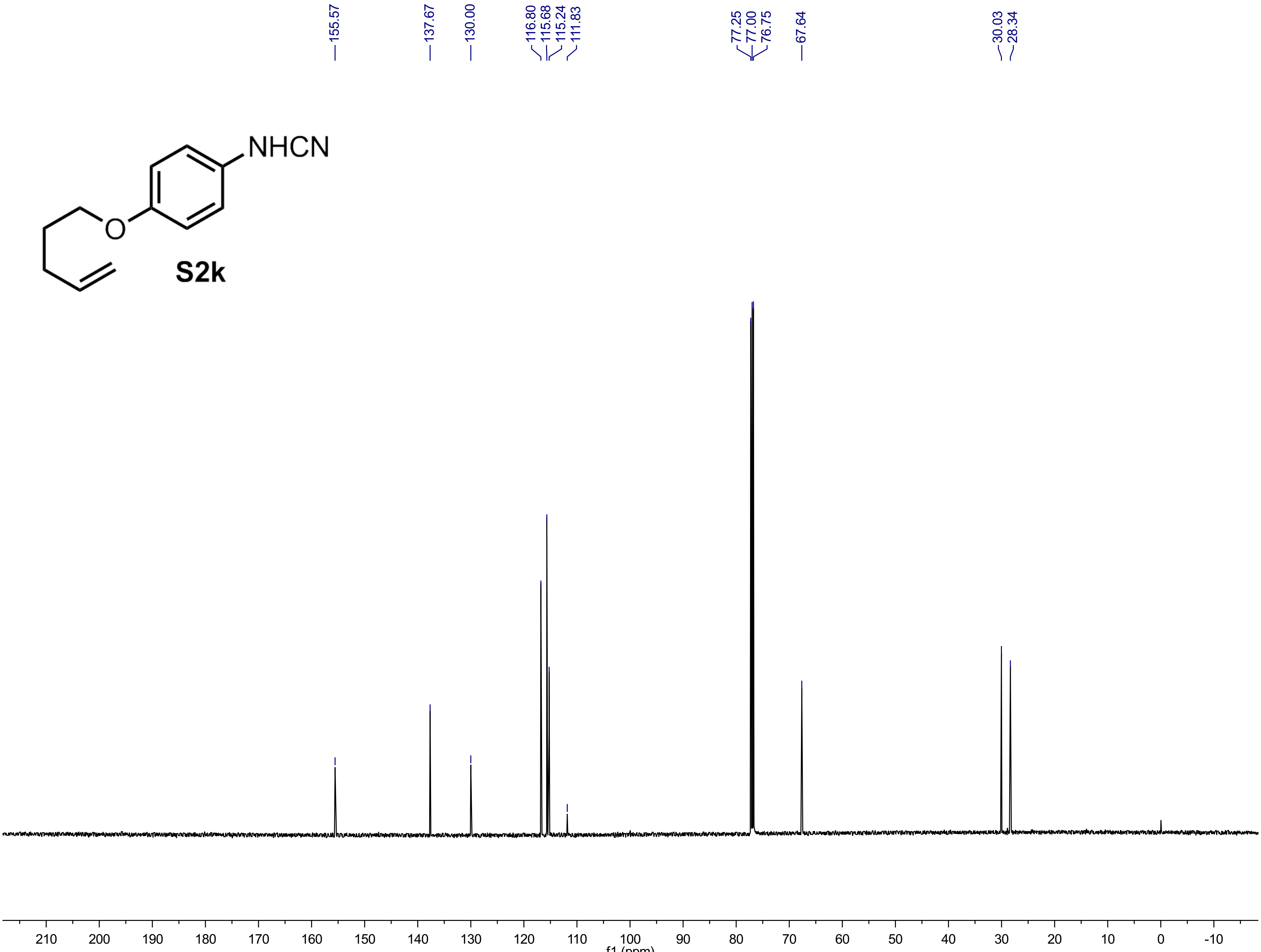

167.94
134.35
133.75
120.52
115.19
112.53
40.00
39.83
39.67
39.60
39.50
39.43
39.33
39.17
39.00
23.84
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

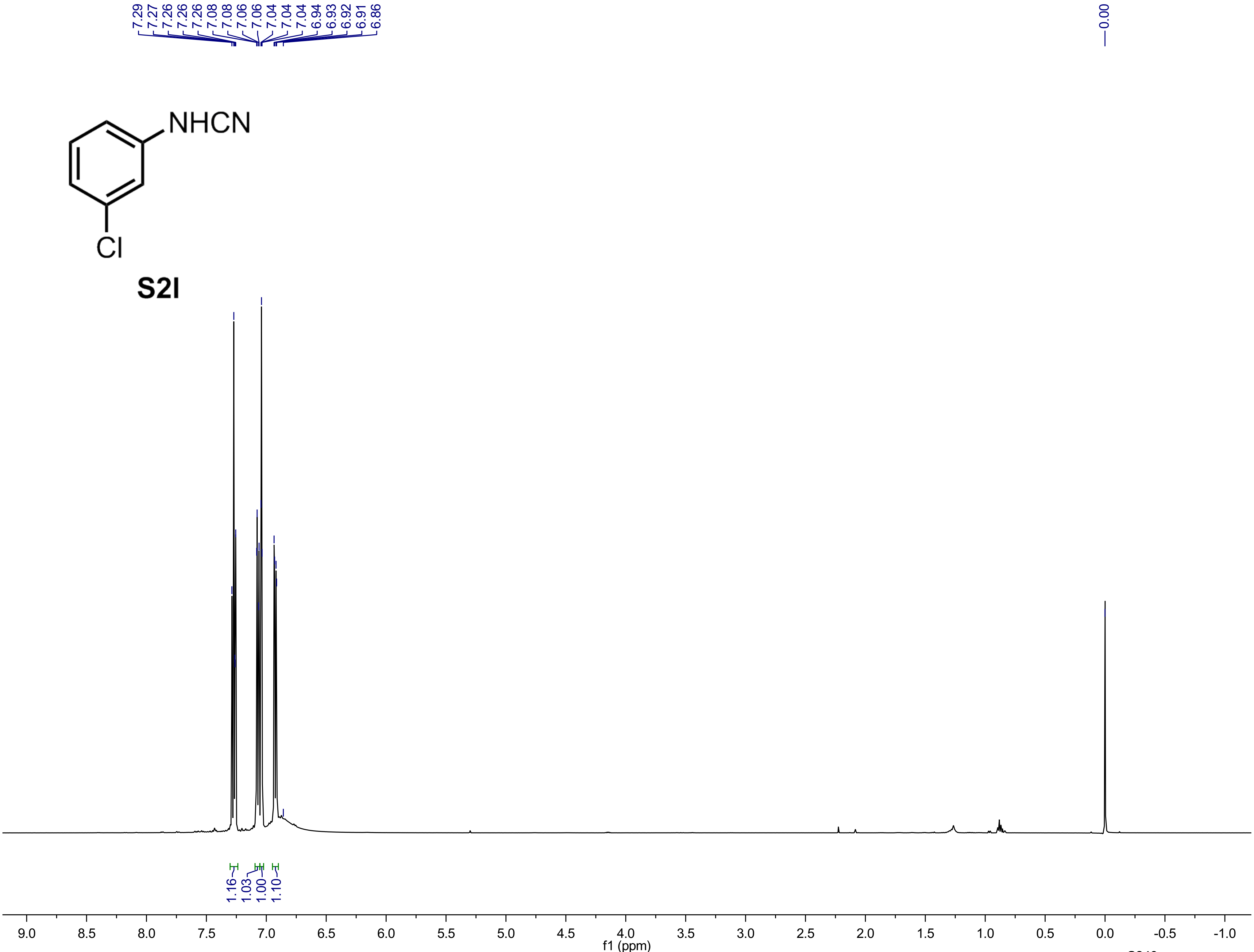

10.73
7.97
7.95
7.06
7.04
2.51
2.51
2.51
2.50
2.50
2.50
2.49
NHCN
Me
O
S 2j
0.84
2.00
1.96
3.09
f1 (ppm)


196.18
143.16
131.45
130.51
114.71
111.15
40.00
39.83
39.67
39.50
39.33
39.16
39.00
26.43
NHCN
Me
O
S2j
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

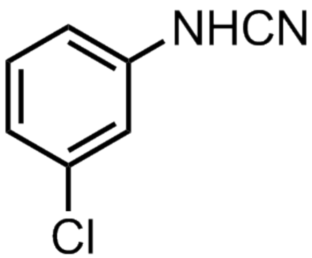


7.26 7.26 6.96 6.95 6.94 6.94 6.93 6.92 6.88 6.88 6.87 6.86 6.86 6.85 6.11 5.89 5.87 5.87 5.86 5.85 5.84 5.83 5.83 5.82 5.80 5.08 5.04 5.01 4.99 3.95 3.93 3.92 2.25 2.25 2.24 2.23 2.22 2.22 2.21 2.21 1.90 1.88 1.88 1.87 1.87 1.85 1.84 0.00
NHCN
O
S2k
2.00 1.95 0.82 0.92 0.96 0.96 1.97 1.91 1.95
10.5 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 -0.5 -1.0
f1 (ppm)

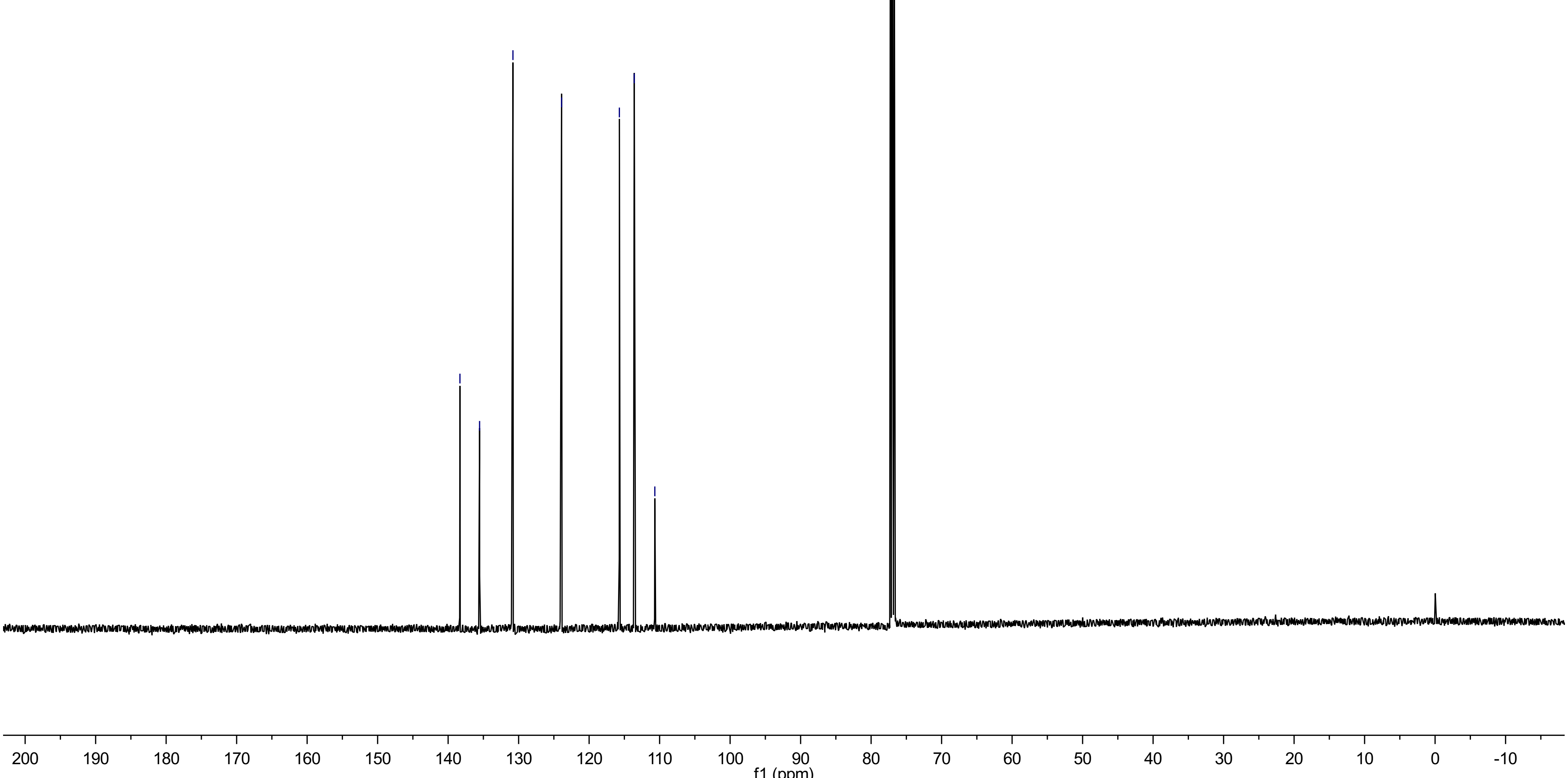

155.57
137.67
130.00
116.80
115.68
115.24
111.83
77.25
77.00
76.75
67.64
30.03
28.34
NHCN
O
S2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

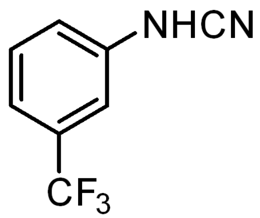

7.29
7.27
7.26
7.26
7.26
7.08
7.08
7.06
7.06
7.04
7.04
7.04
6.94
6.93
6.92
6.91
6.86
0.00
NHCN
Cl
1.16
1.03
1.00
1.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

S2I

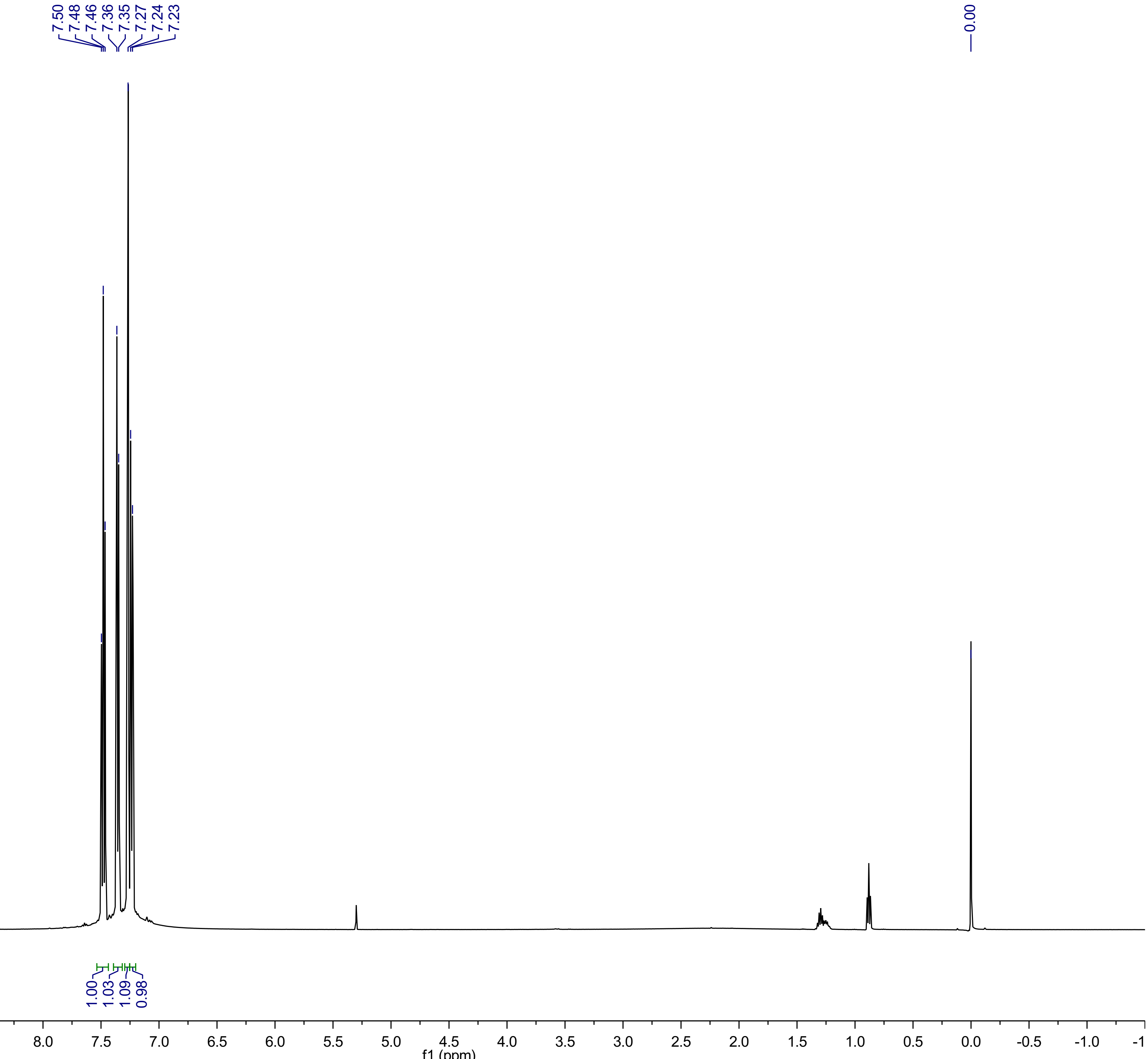


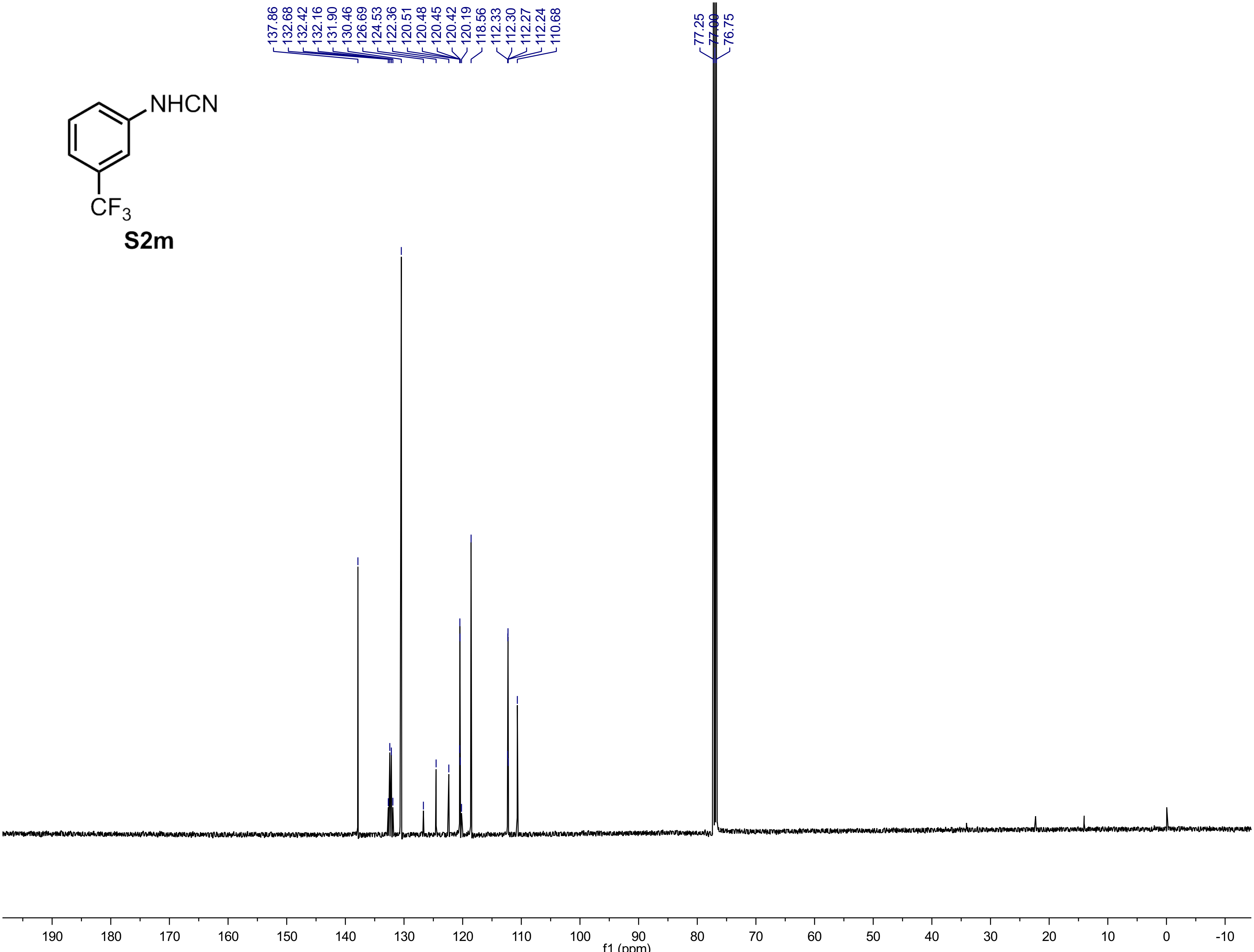
S2l


138.32
135.54
130.81
123.91
115.71
113.60
110.68
77.25
77.00
76.75
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

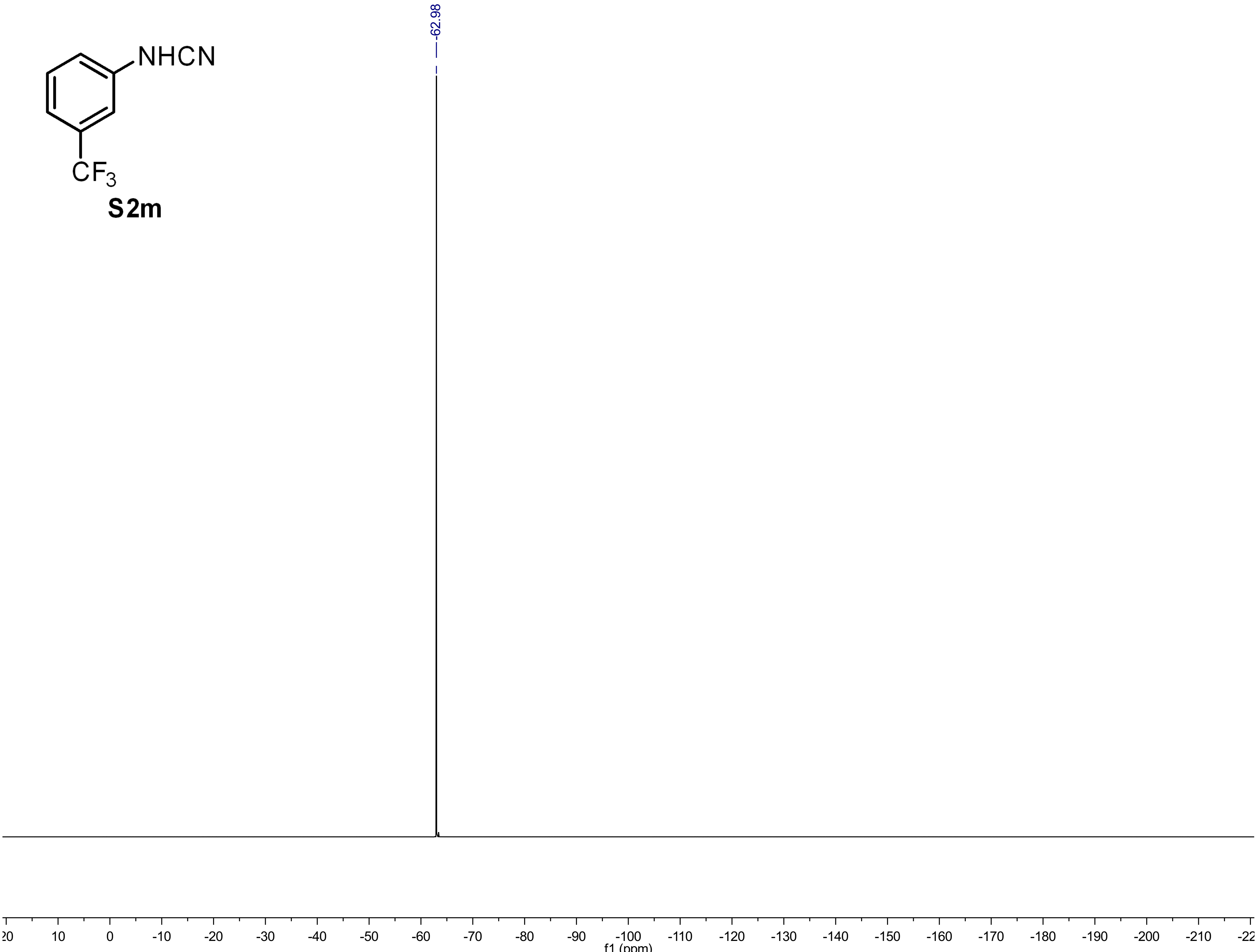


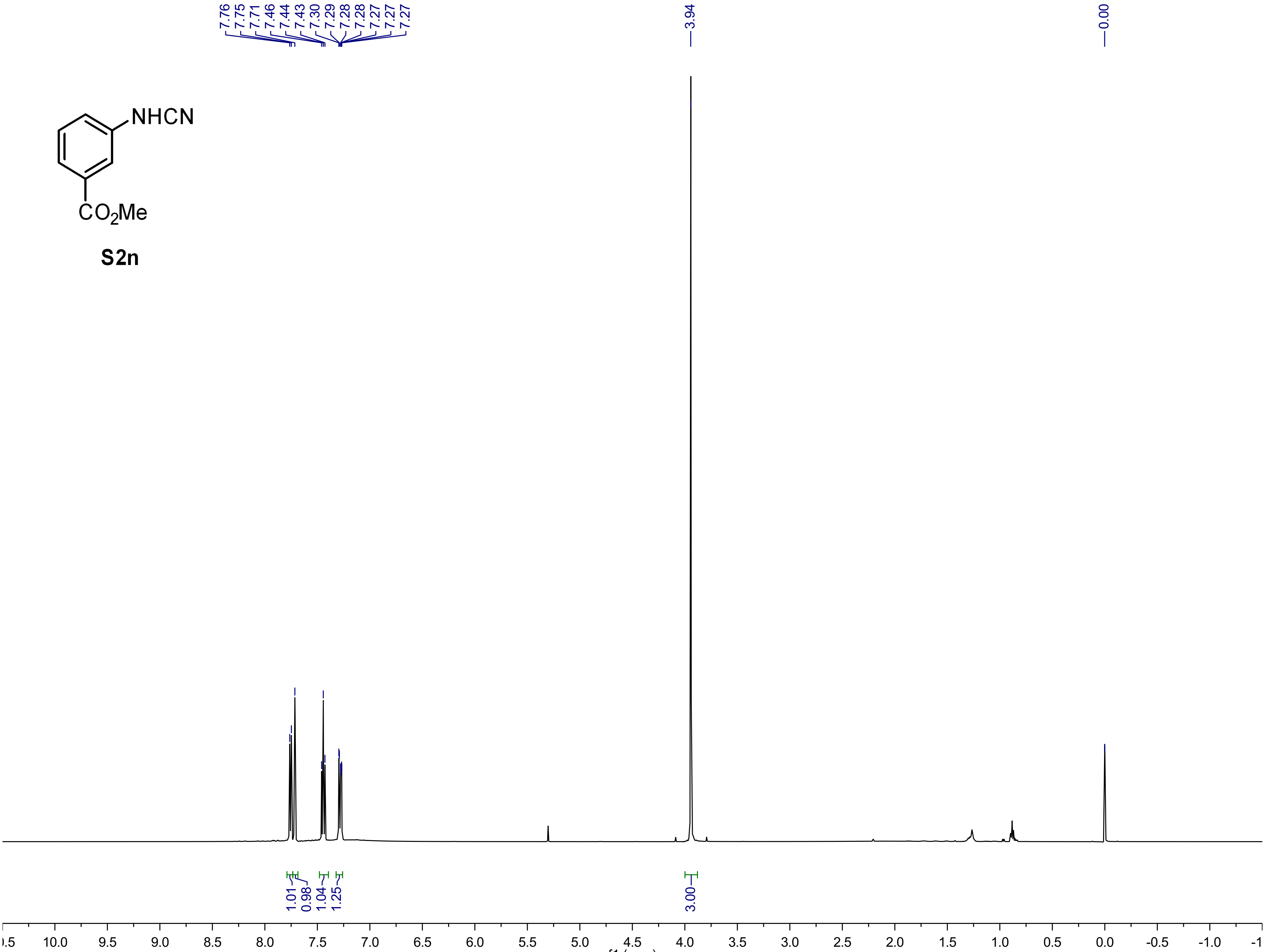
S2m



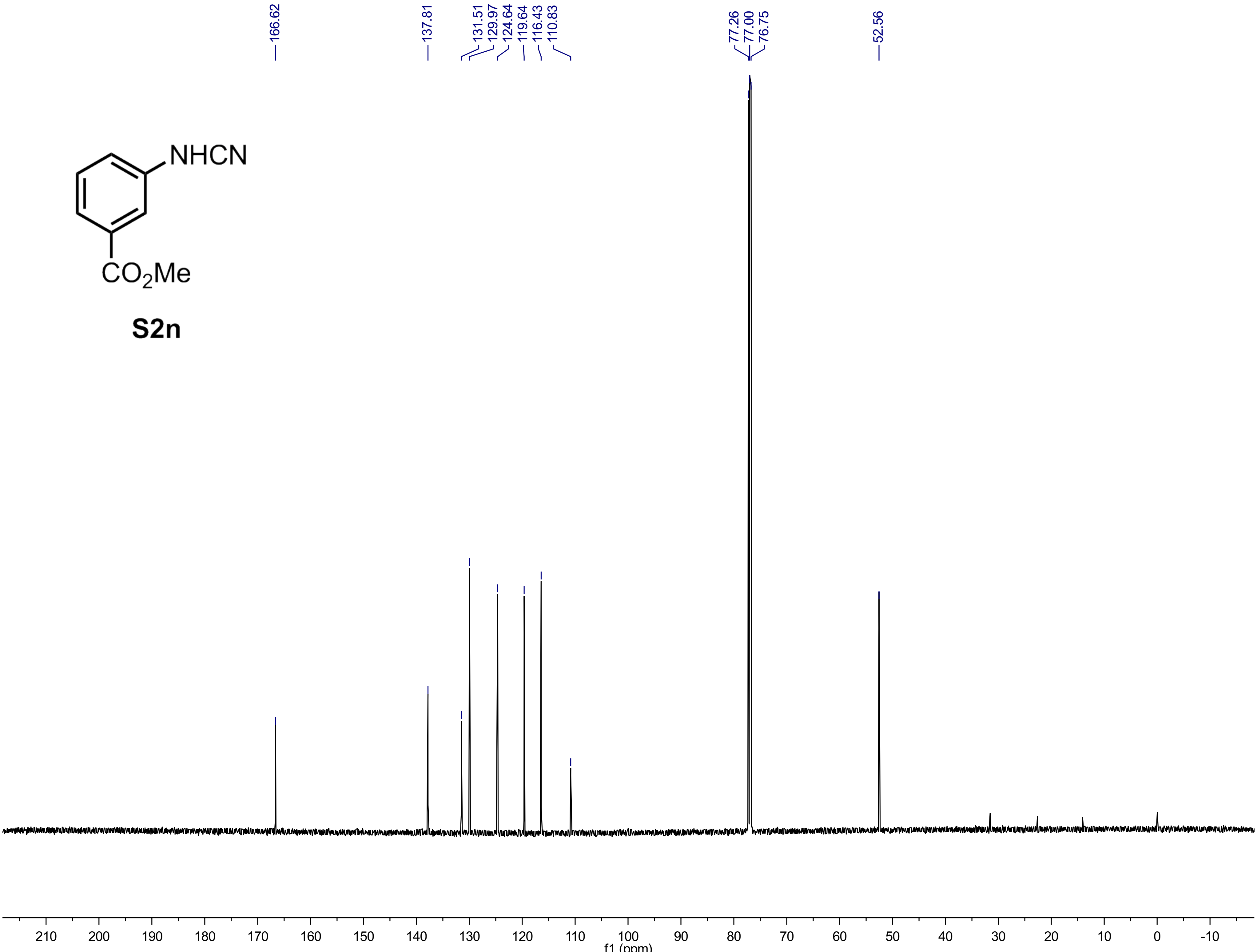


137.86
132.68
132.42
132.16
131.90
130.46
126.69
124.53
122.36
120.51
120.48
120.45
120.42
120.19
118.56
112.33
112.30
112.27
112.24
110.68
77.25
77.00
76.75
NHCN
CF3
S2m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

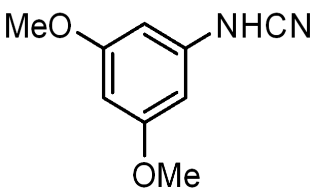

NHCN
CF3
S2m
-62.98
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220



NHCN
CO2Me
S2n
7.76
7.75
7.71
7.46
7.44
7.43
7.30
7.29
7.28
7.28
7.27
7.27
7.27
3.94
0.00
1.01
0.98
1.04
1.25
3.00
f1 (ppm)

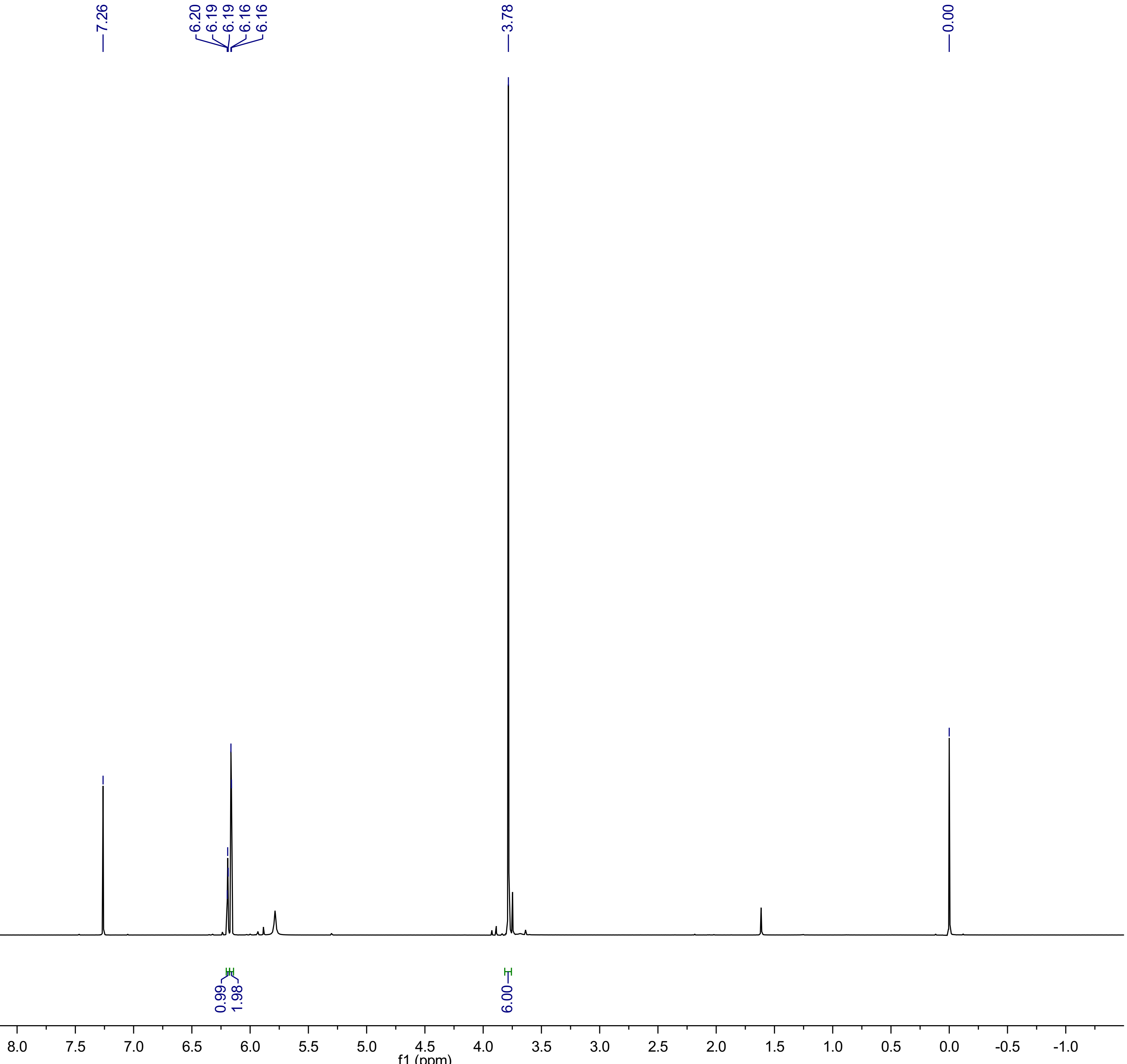


166.62
137.81
131.51
129.97
124.64
119.64
116.43
110.83
77.26
77.00
76.75
52.56
NHCN
CO2Me
S2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

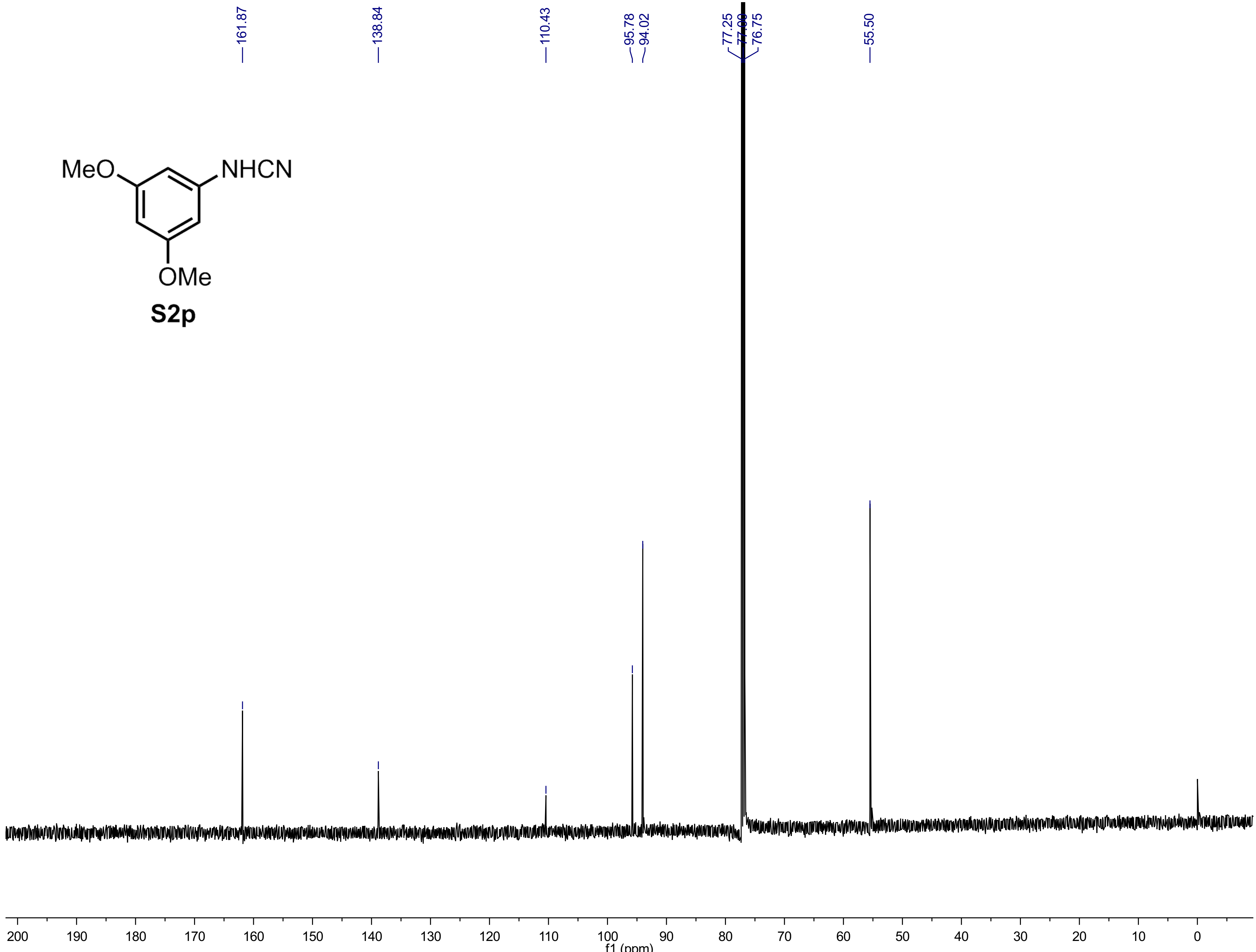


MeO
NHCN
OMe

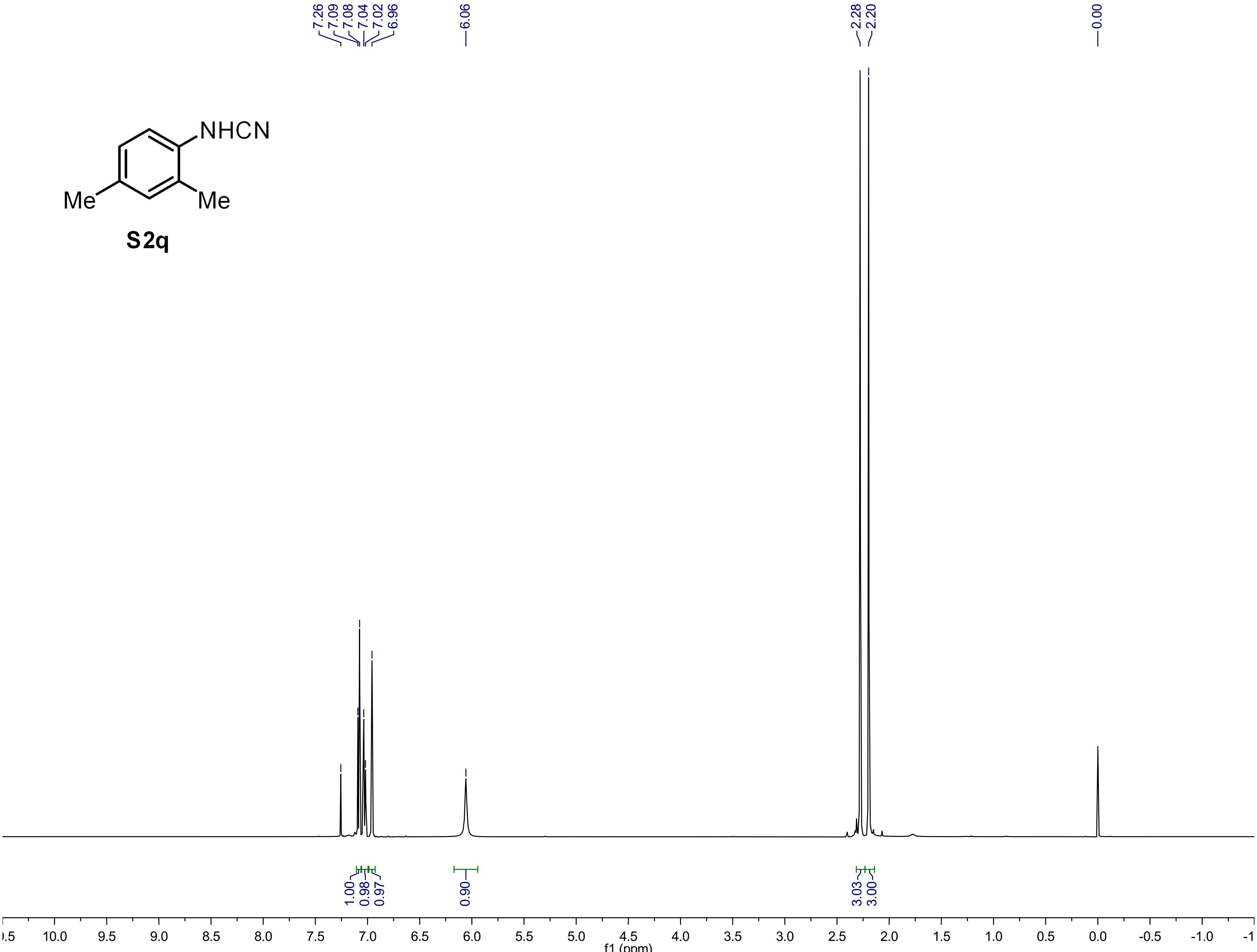
S2p

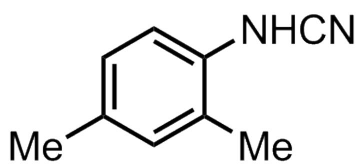


7.26
6.20
6.19
6.19
6.16
6.16
3.78
0.00
0.99
1.98
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

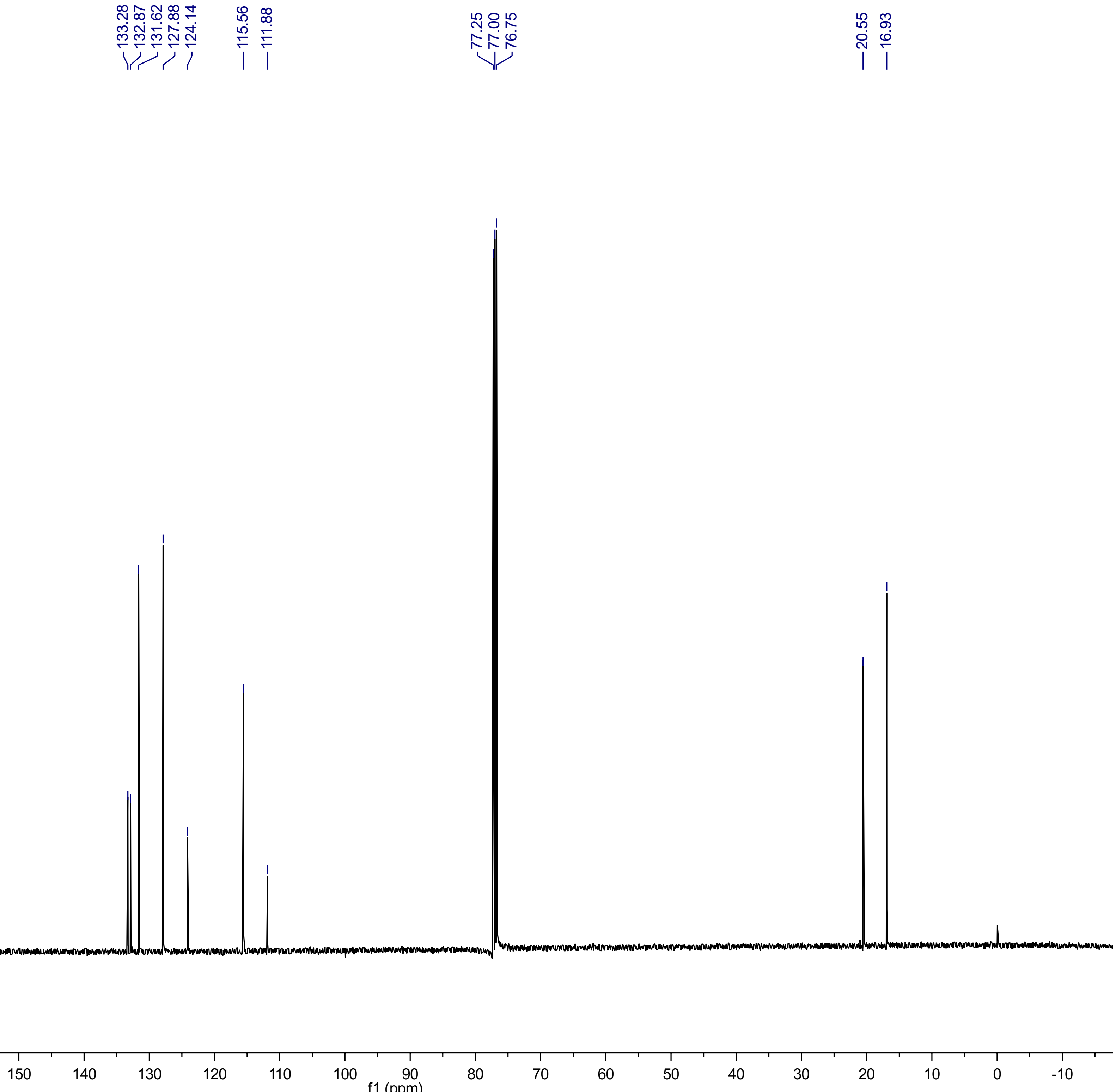


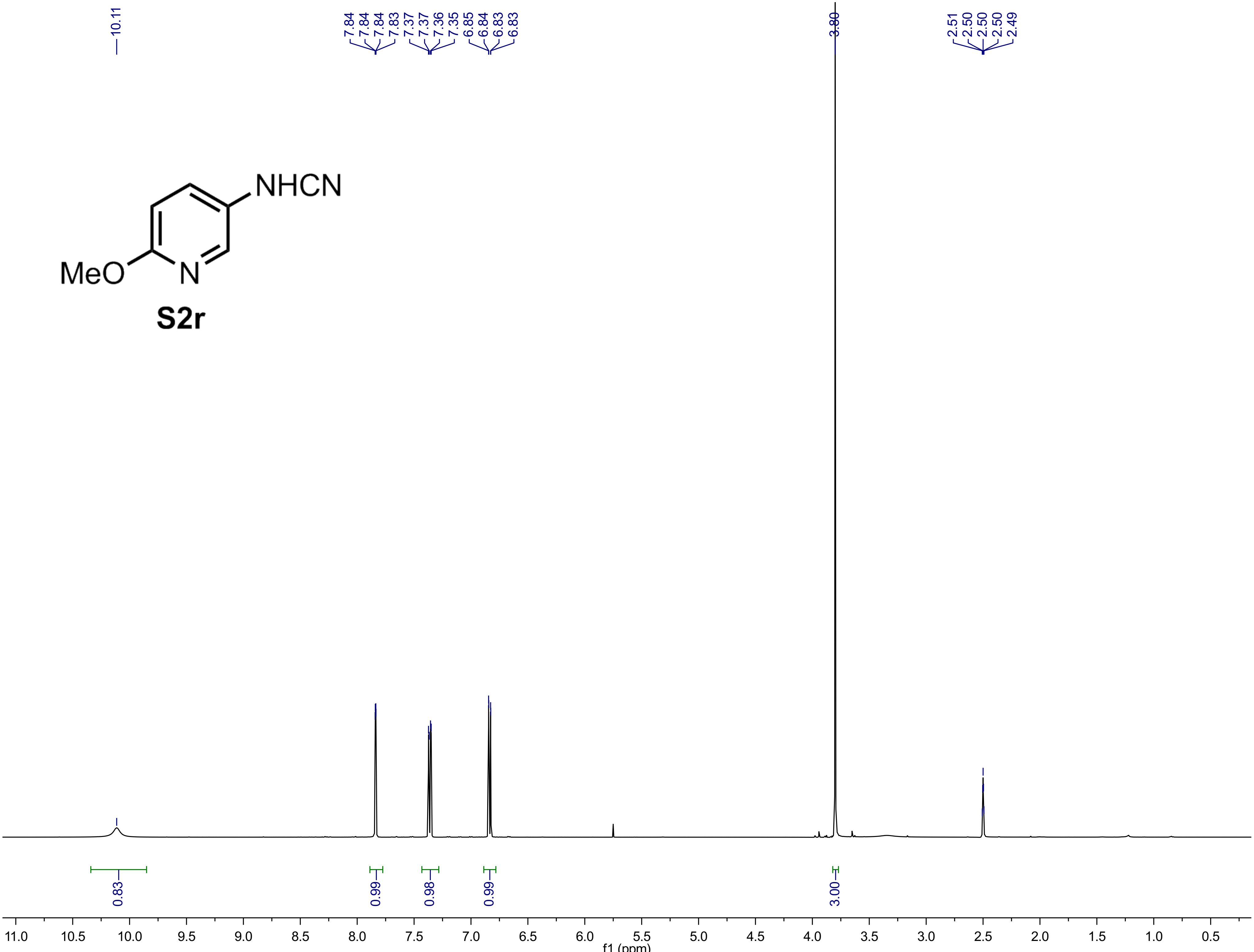
161.87
138.84
110.43
95.78
94.02
77.25
77.00
76.75
55.50
MeO
NHCN
OMe
S2p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

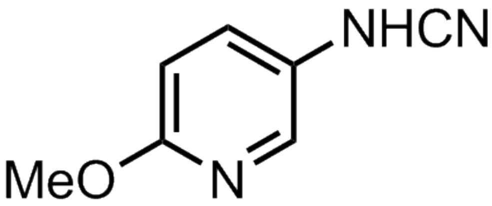

NHCN
Me
Me
S2q
7.26
7.09
7.08
7.04
7.02
6.96
6.06
2.28
2.20
0.00
1.00
0.98
0.97
0.90
3.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



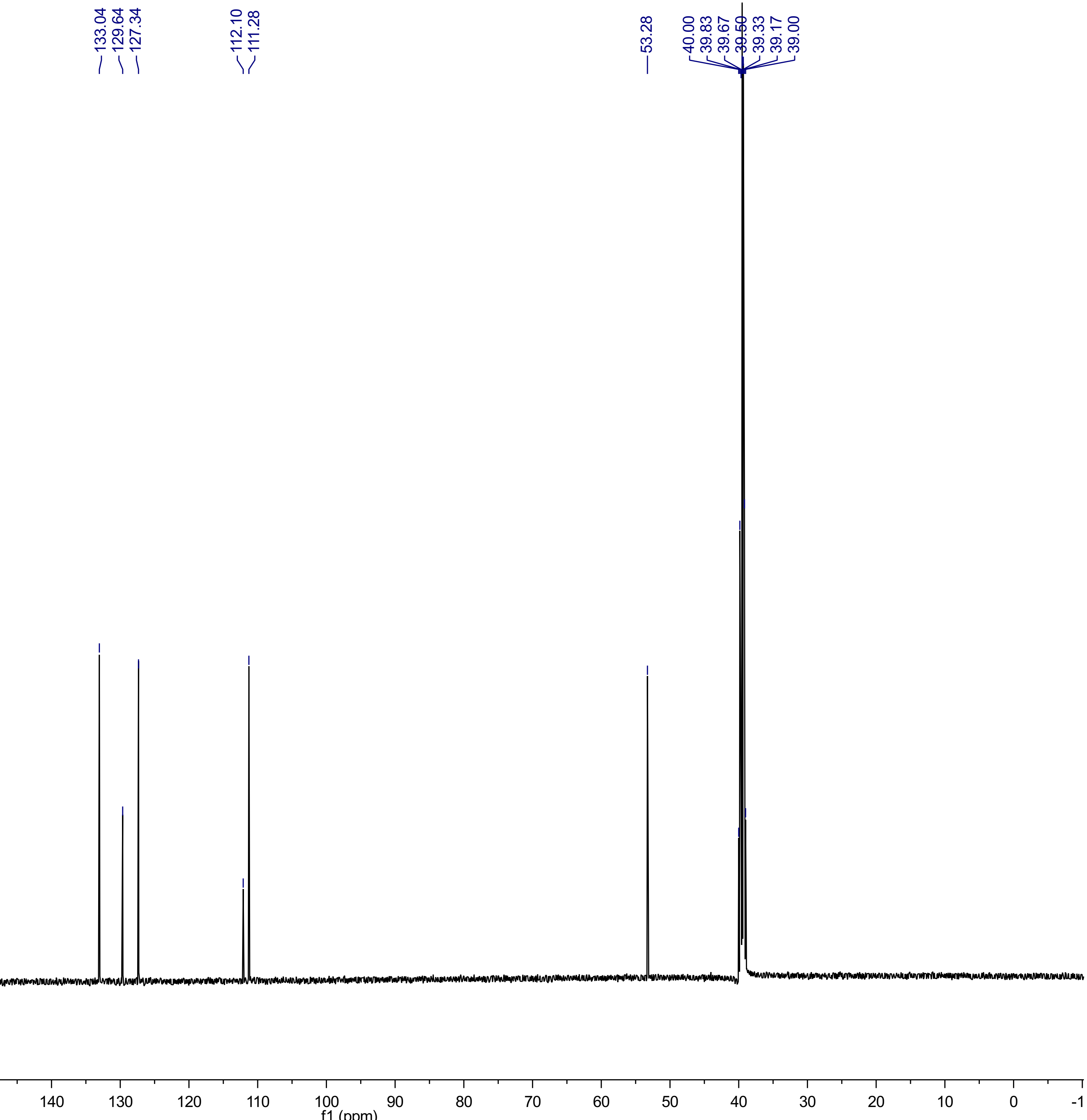
S2q

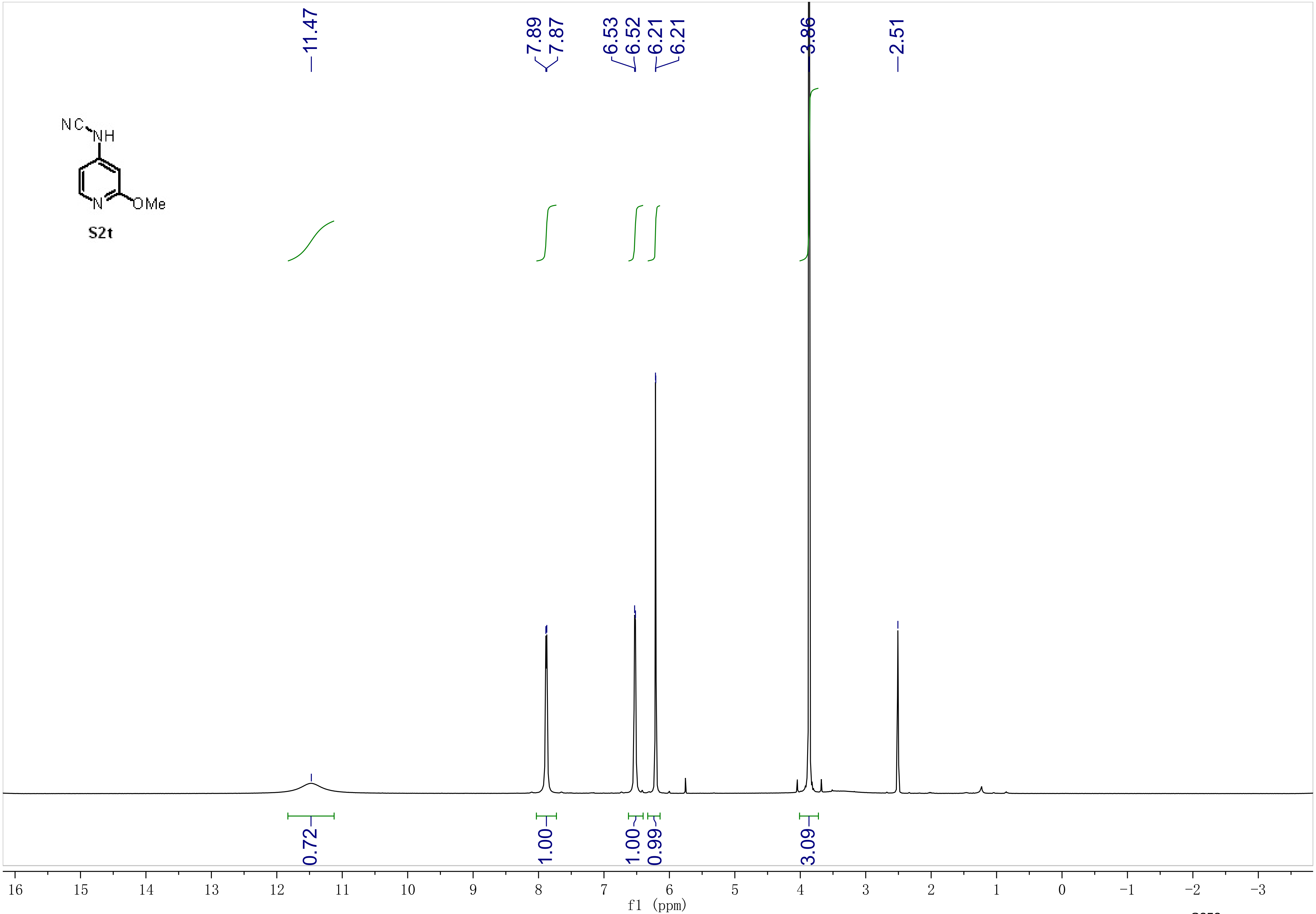

133.28
132.87
131.62
127.88
124.14
115.56
111.88
77.25
77.00
76.75
20.55
16.93
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

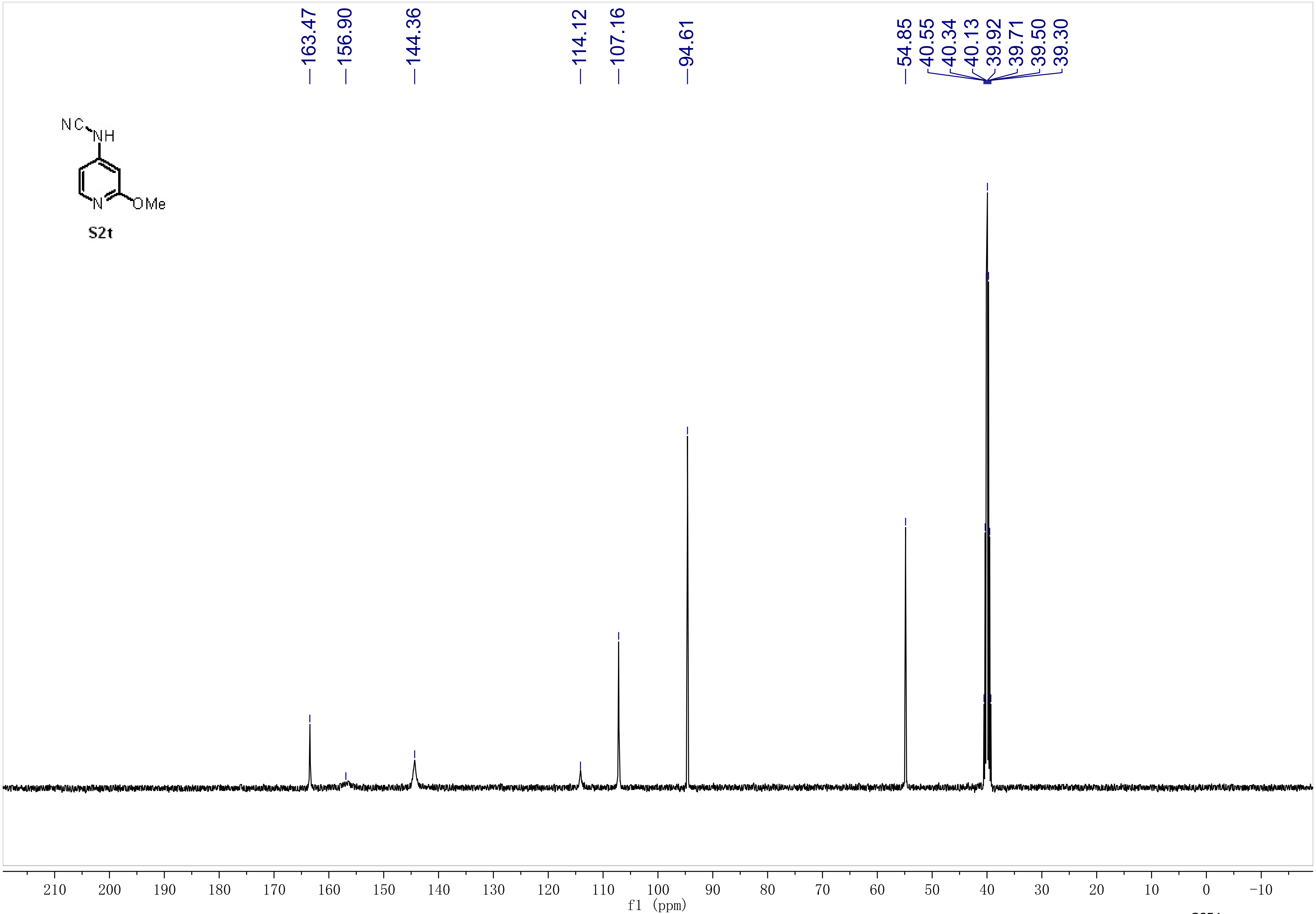

10.11
7.84
7.84
7.84
7.83
7.37
7.37
7.36
7.35
6.85
6.84
6.83
6.83
3.80
2.51
2.50
2.50
2.50
2.49
NHCN
MeO
N
S2r
0.83
0.99
0.98
0.99
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

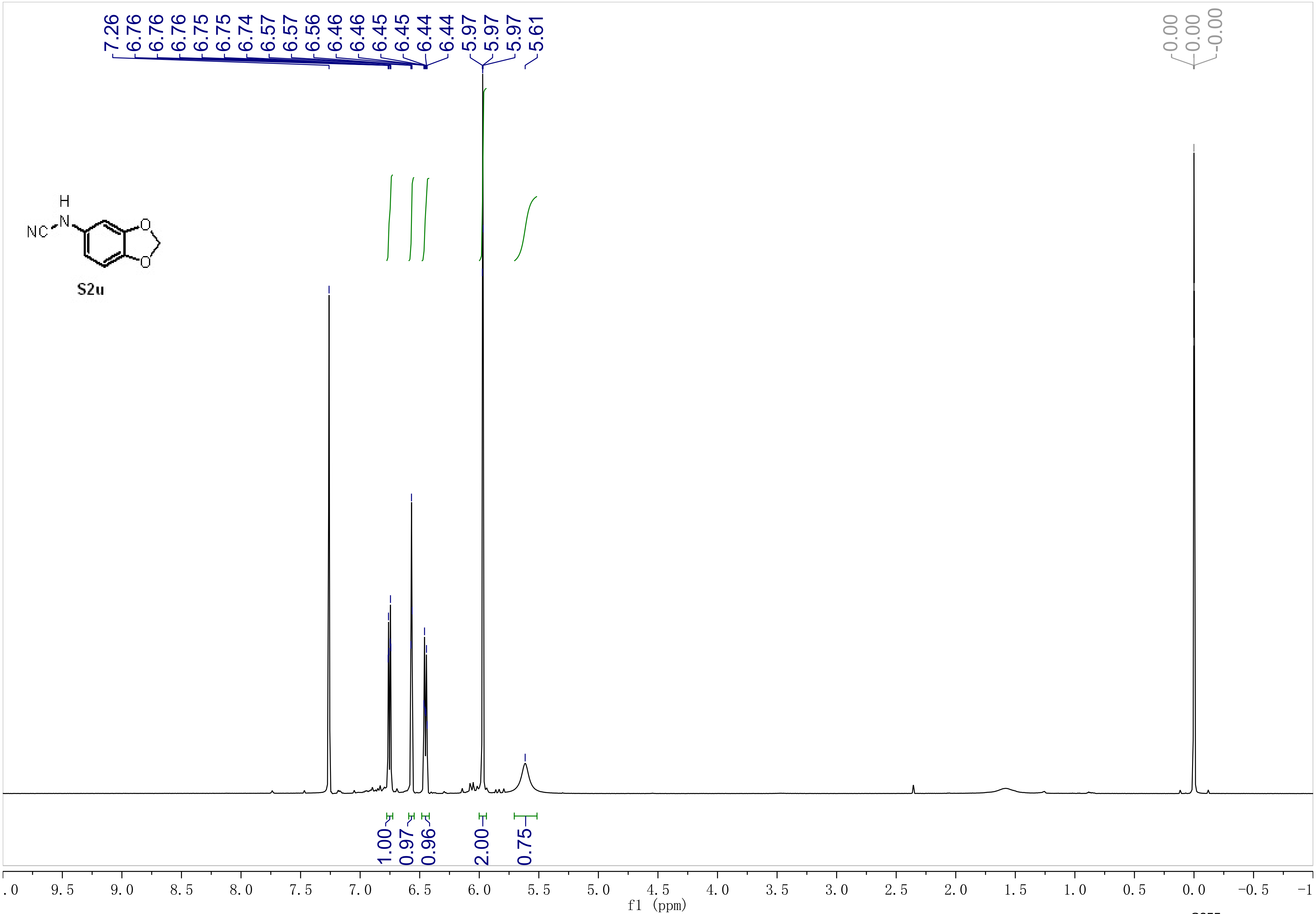

NHCN
MeO
N

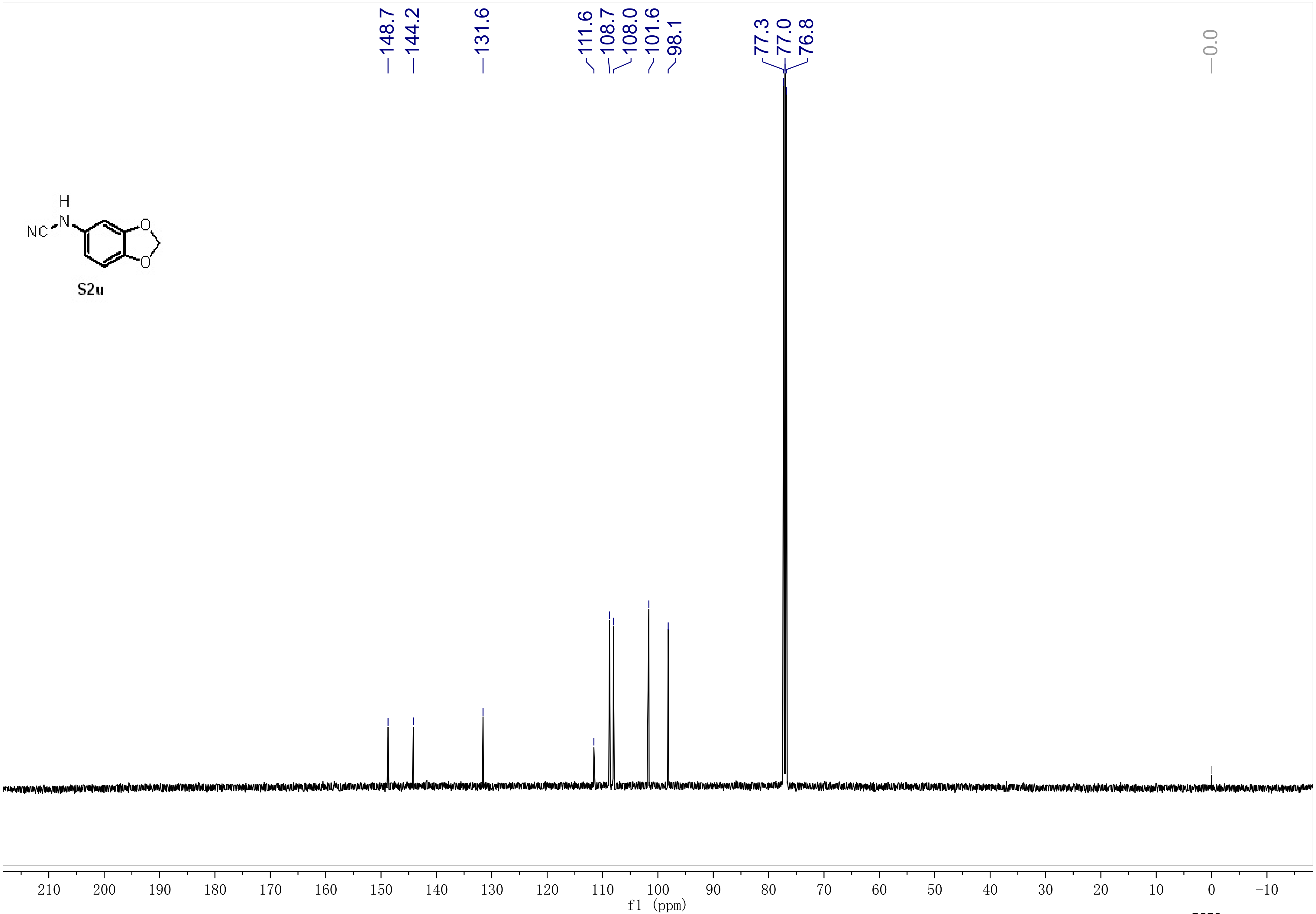
S2r

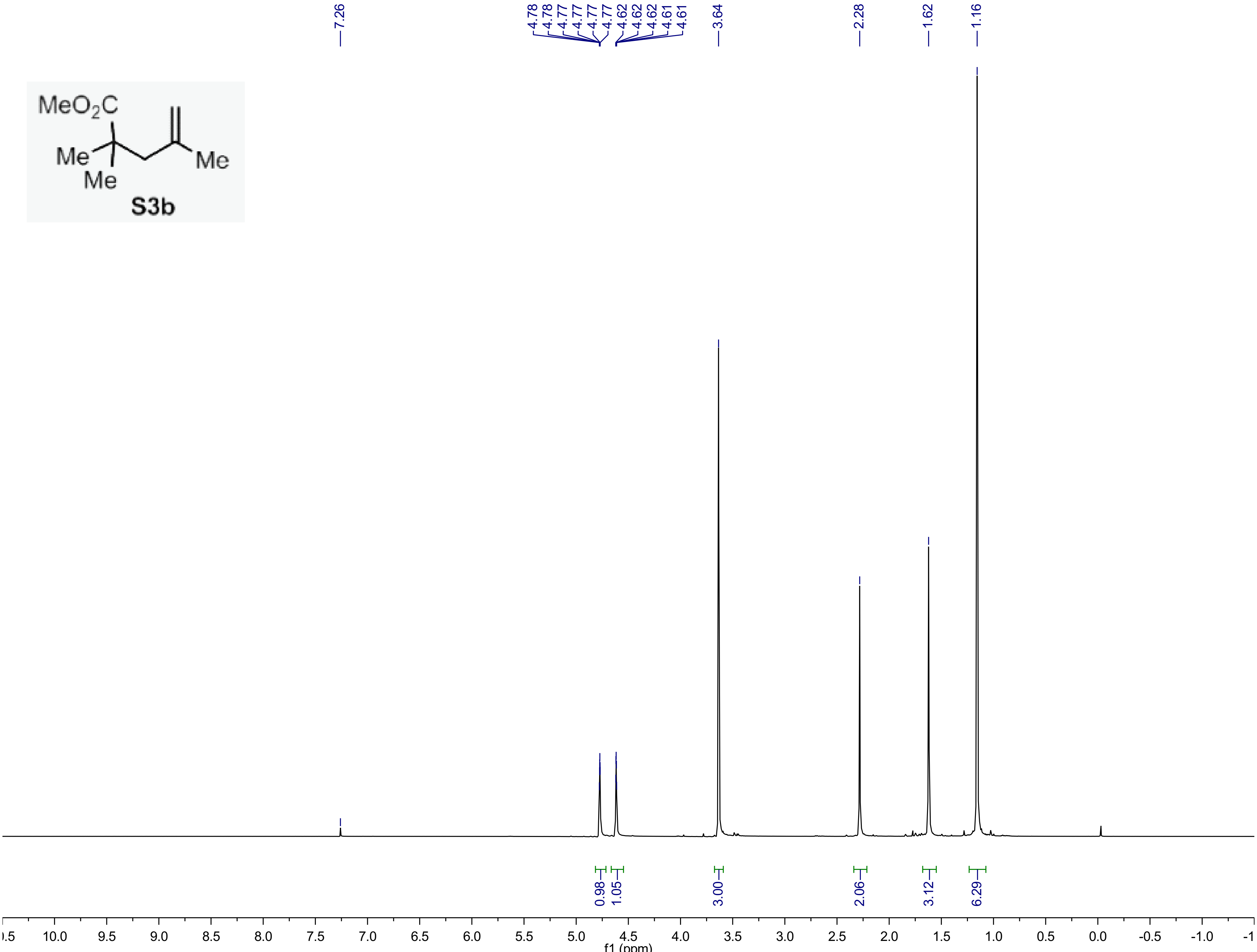

159.63
133.04
129.64
127.34
112.10
111.28
53.28
40.00
39.83
39.67
39.50
39.33
39.17
39.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

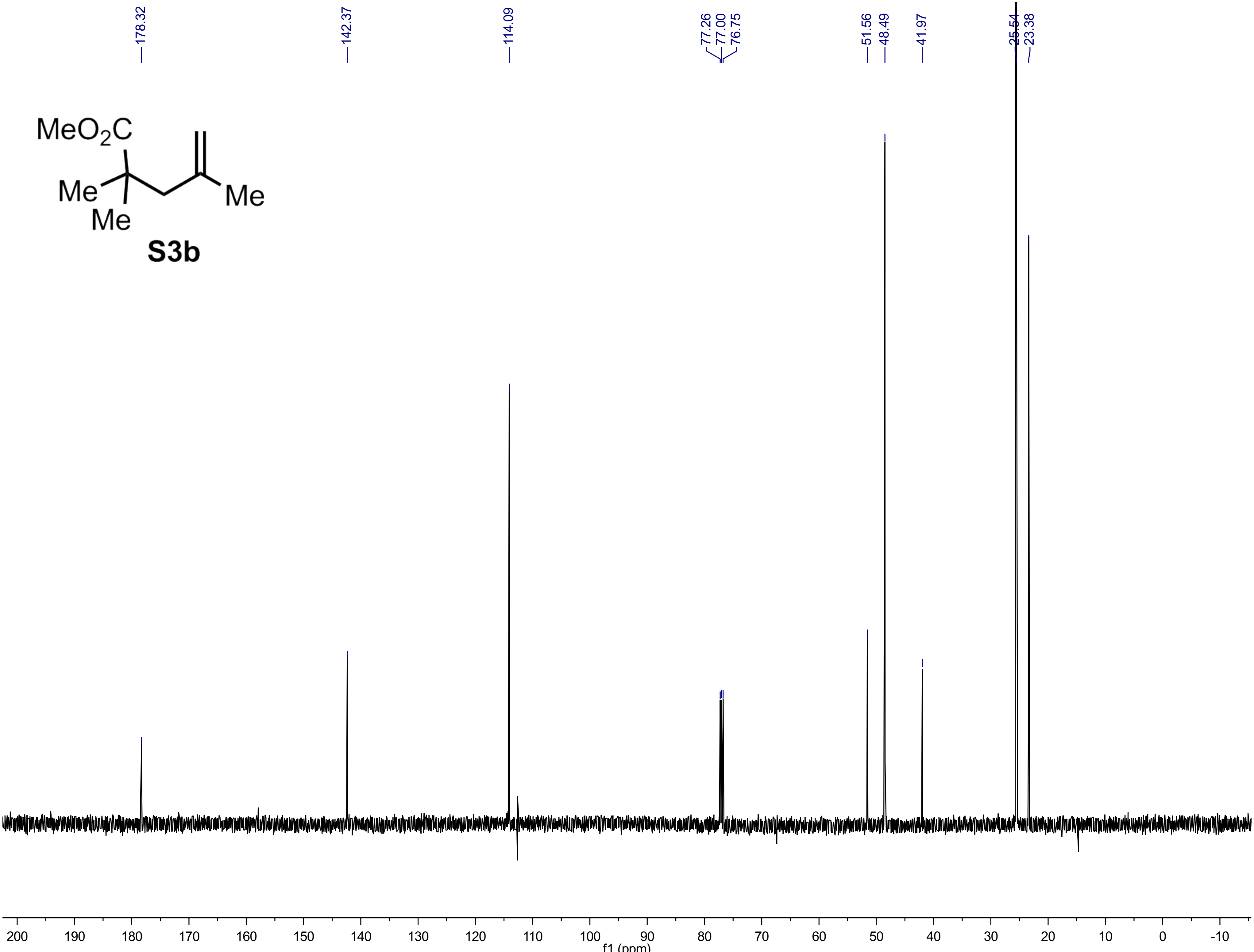

NC
NH
N
OMe
S2t
11.47
7.89
7.87
6.53
6.52
6.21
6.21
3.86
2.51
0.72
1.00
1.00
0.99
3.09
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)


163.47
156.90
144.36
114.12
107.16
94.61
54.85
40.55
40.34
40.13
39.92
39.71
39.50
39.30
NC
NH
N
OMe
S2t
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)

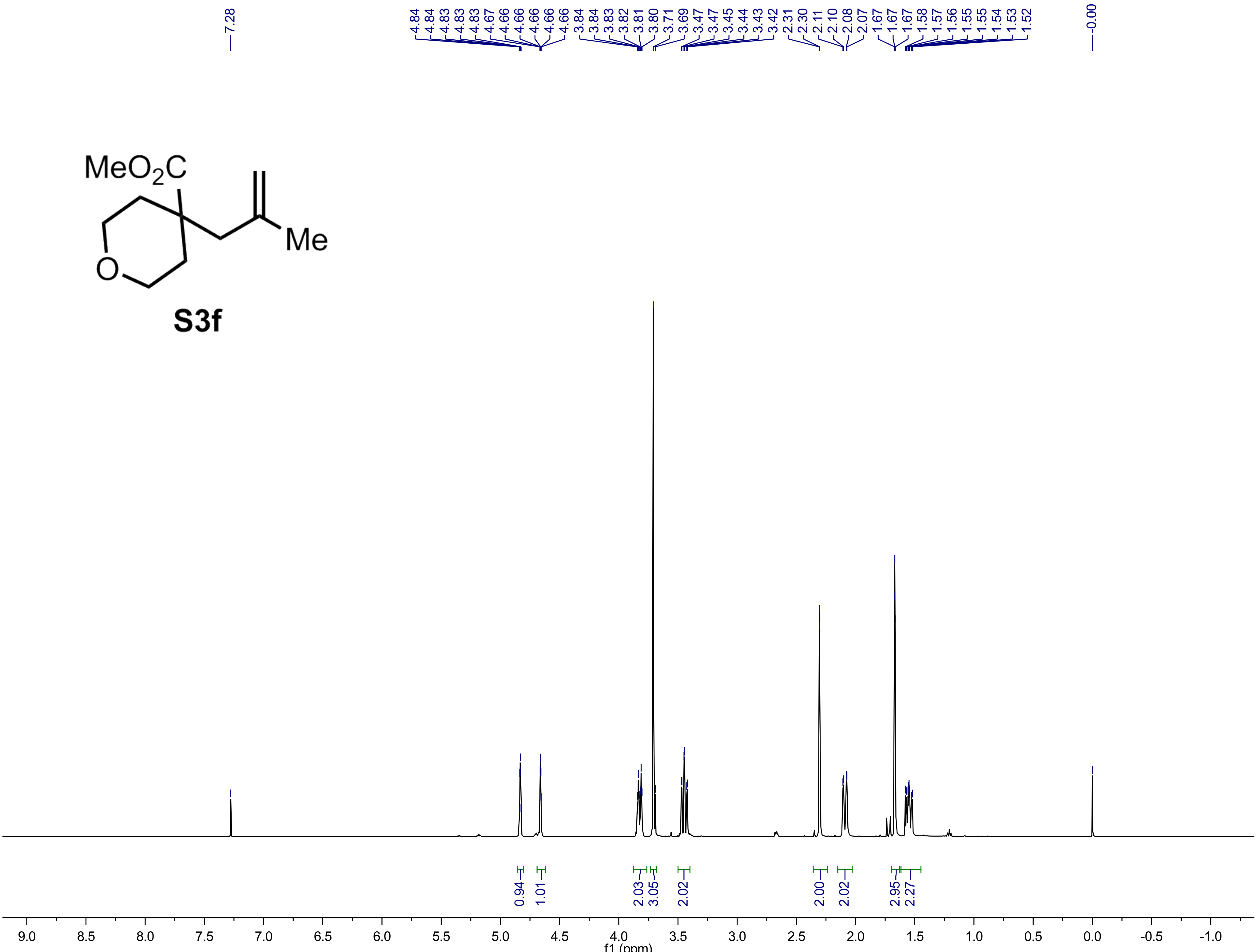

7.26
6.76
6.76
6.76
6.75
6.75
6.74
6.57
6.57
6.56
6.46
6.46
6.45
6.45
6.44
6.44
5.97
5.97
5.97
5.61
0.00
0.00
-0.00
H
N
NC
O
O
S2u
1.00
0.97
0.96
2.00
0.75
f1 (ppm)

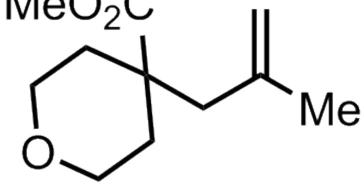

148.7
144.2
131.6
111.6
108.7
108.0
101.6
98.1
77.3
77.0
76.8
0.0
H
N
NC
O
O
S2u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26
4.78
4.78
4.77
4.77
4.77
4.77
4.62
4.62
4.62
4.61
4.61
3.64
2.28
1.62
1.16
MeO2C
Me
Me
Me
S3b
0.98
1.05
3.00
2.06
3.12
6.29
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 -0.5 -1.0
f1 (ppm)

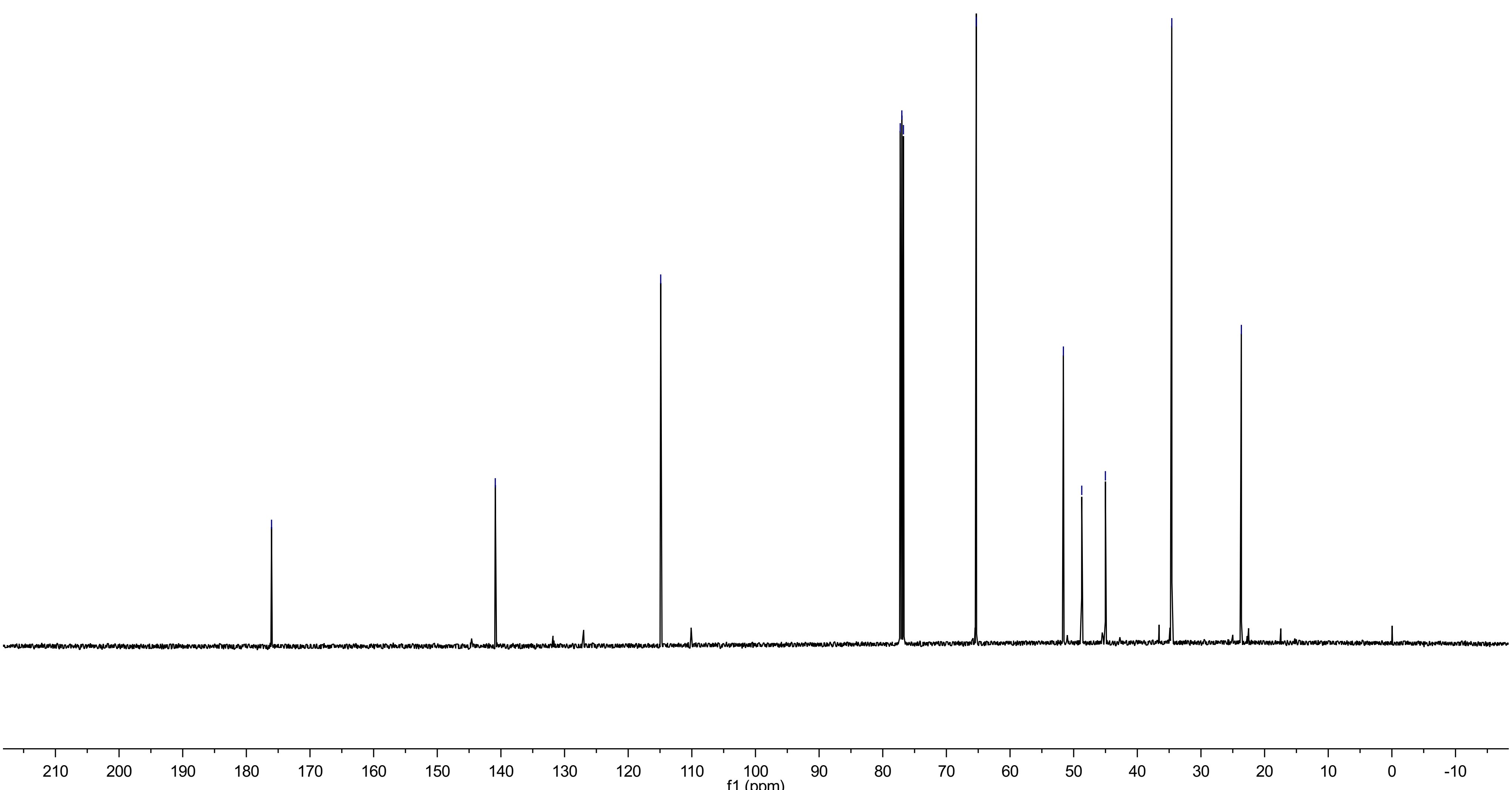


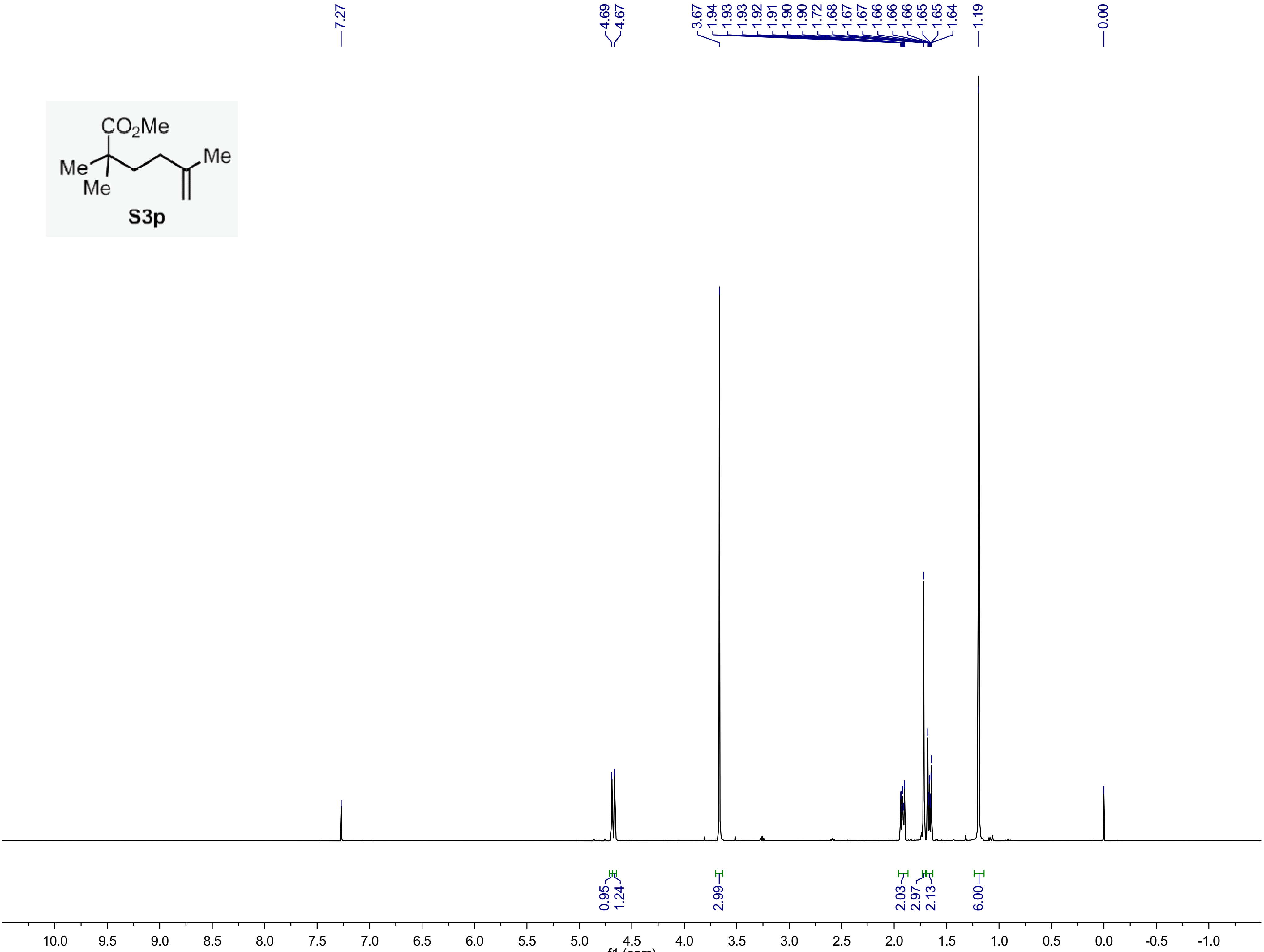
178.32
142.37
114.09
77.26
77.00
76.75
51.56
48.49
41.97
25.54
23.38
MeO2C
Me
Me
Me
S3b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

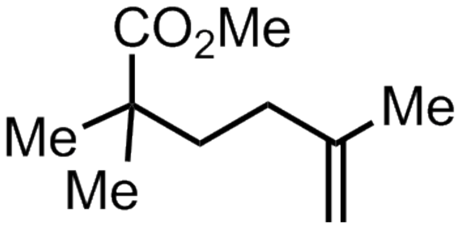

MeO2C
Me
O
S3f
7.28
4.84
4.84
4.83
4.83
4.83
4.67
4.66
4.66
4.66
4.66
4.66
3.84
3.84
3.83
3.82
3.81
3.80
3.71
3.69
3.47
3.47
3.45
3.44
3.43
3.42
2.31
2.30
2.11
2.10
2.08
2.07
1.67
1.67
1.67
1.58
1.57
1.56
1.55
1.55
1.54
1.53
1.52
-0.00
0.94
1.01
2.03
3.05
2.02
2.00
2.02
2.95
2.27
f1 (ppm)


MeO2C
Me
O

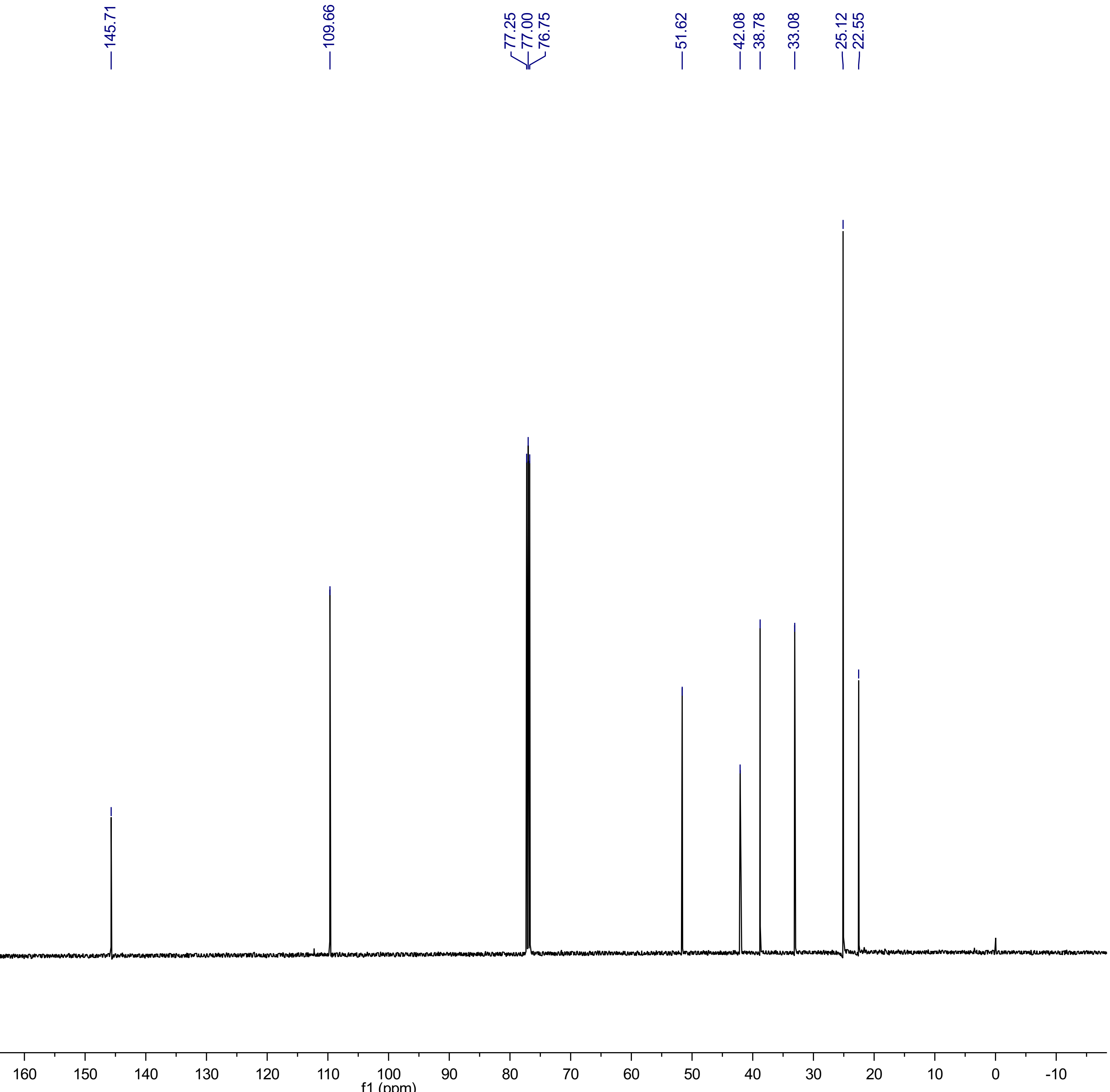
S3f

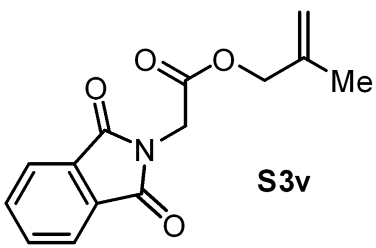

176.04
140.89
114.89
77.25
77.00
76.75
65.30
51.62
48.73
45.02
34.58
23.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CO2Me
Me
Me
Me
S3p
7.27
4.69
4.67
3.67
1.94
1.93
1.93
1.92
1.91
1.90
1.90
1.72
1.68
1.67
1.67
1.66
1.66
1.66
1.65
1.65
1.64
1.19
0.00
0.95
1.24
2.99
2.03
2.97
2.13
6.00
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 -0.5 -1.0
f1 (ppm)

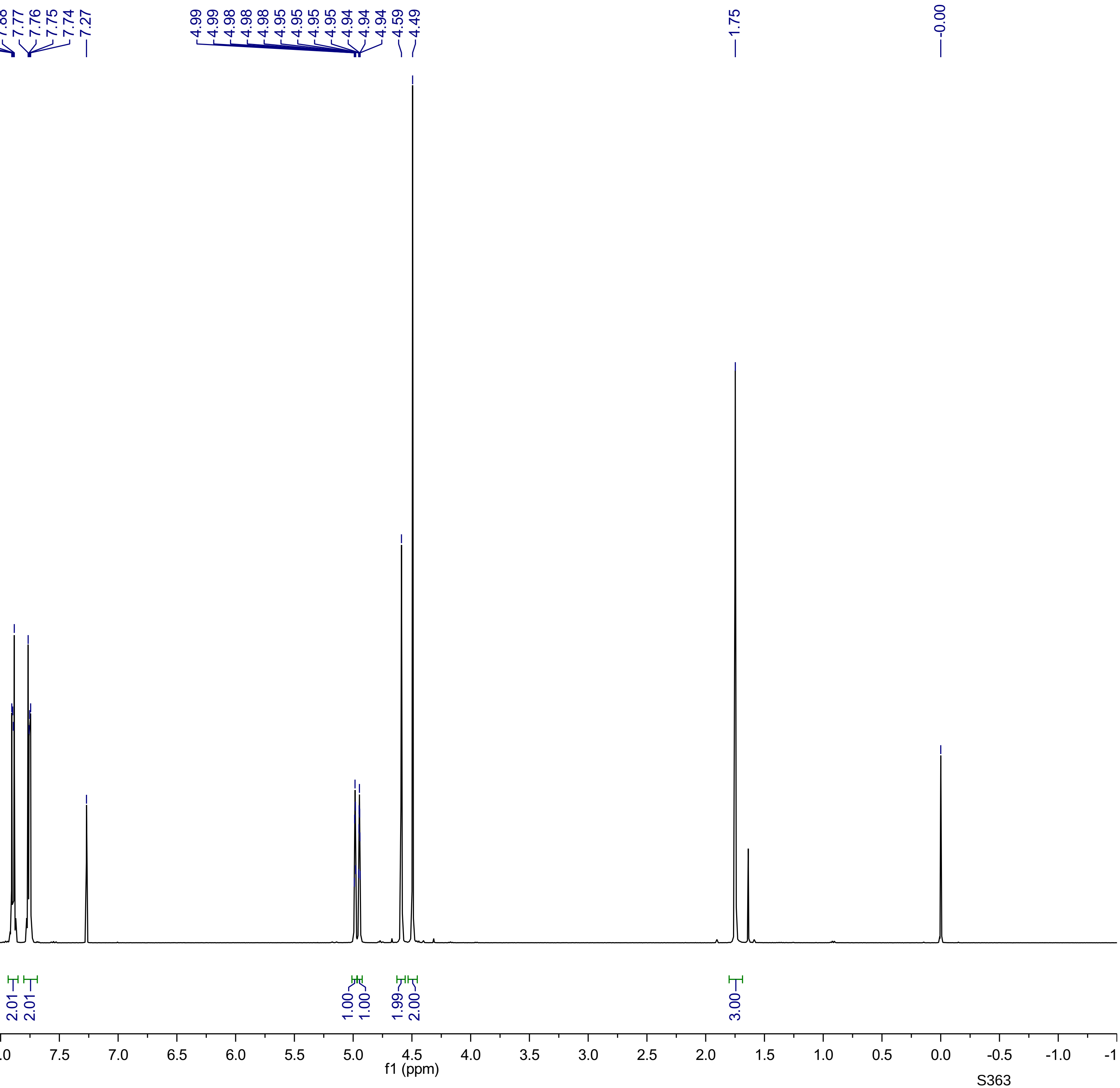


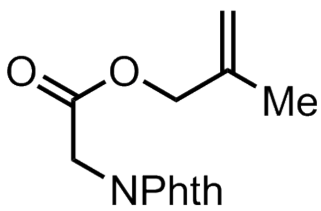
S3p


178.27
145.71
109.66
77.25
77.00
76.75
51.62
42.08
38.78
33.08
25.12
22.55
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)

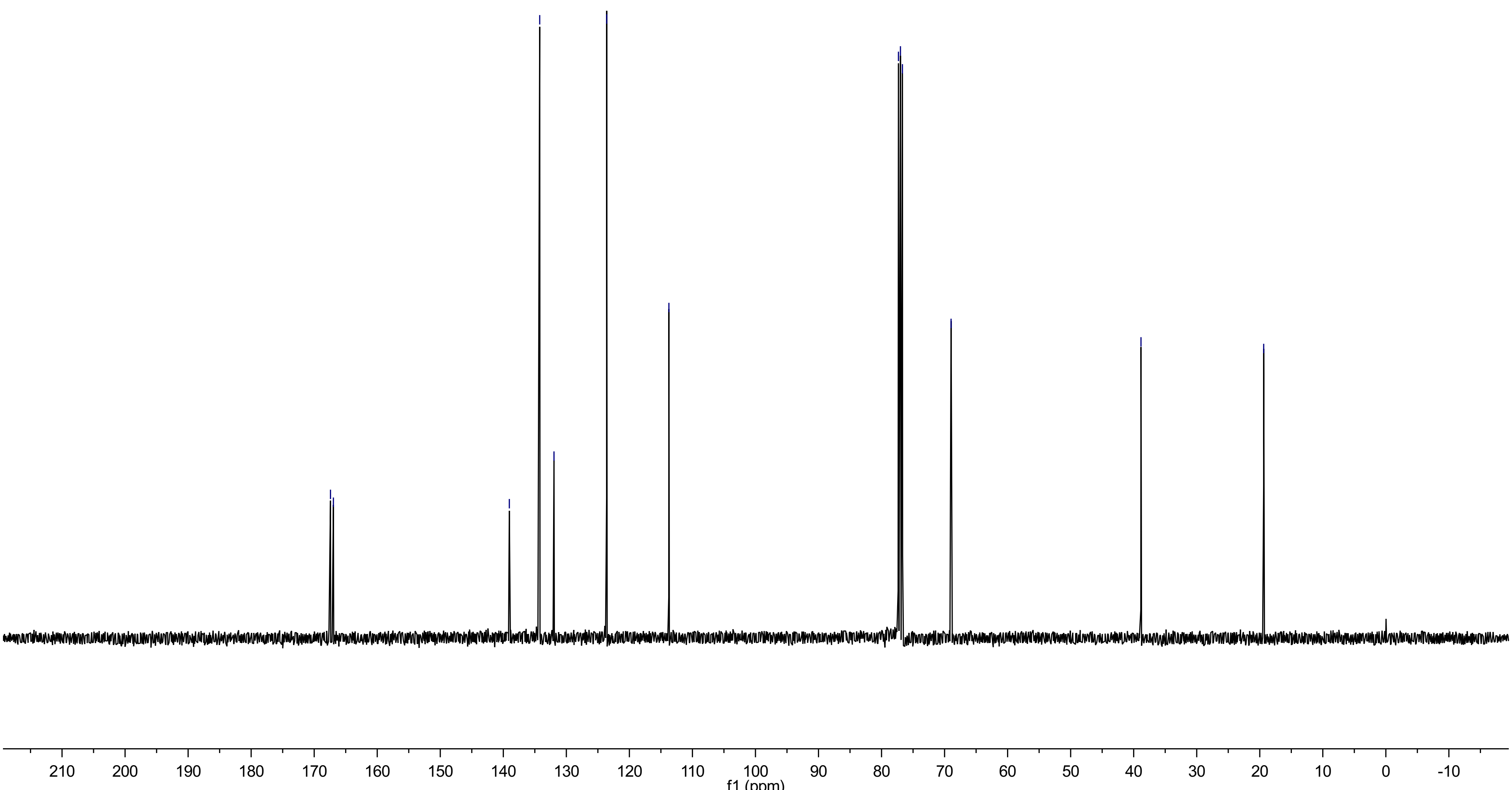


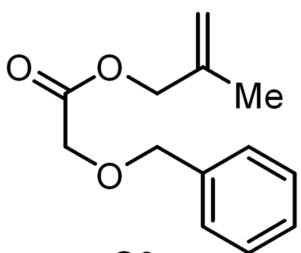
S3v


7.90
7.90
7.89
7.88
7.77
7.76
7.75
7.74
7.27
4.99
4.99
4.98
4.98
4.98
4.95
4.95
4.95
4.94
4.94
4.94
4.59
4.49
1.75
-0.00
2.01
2.01
1.00
1.00
1.99
2.00
3.00
f1 (ppm)

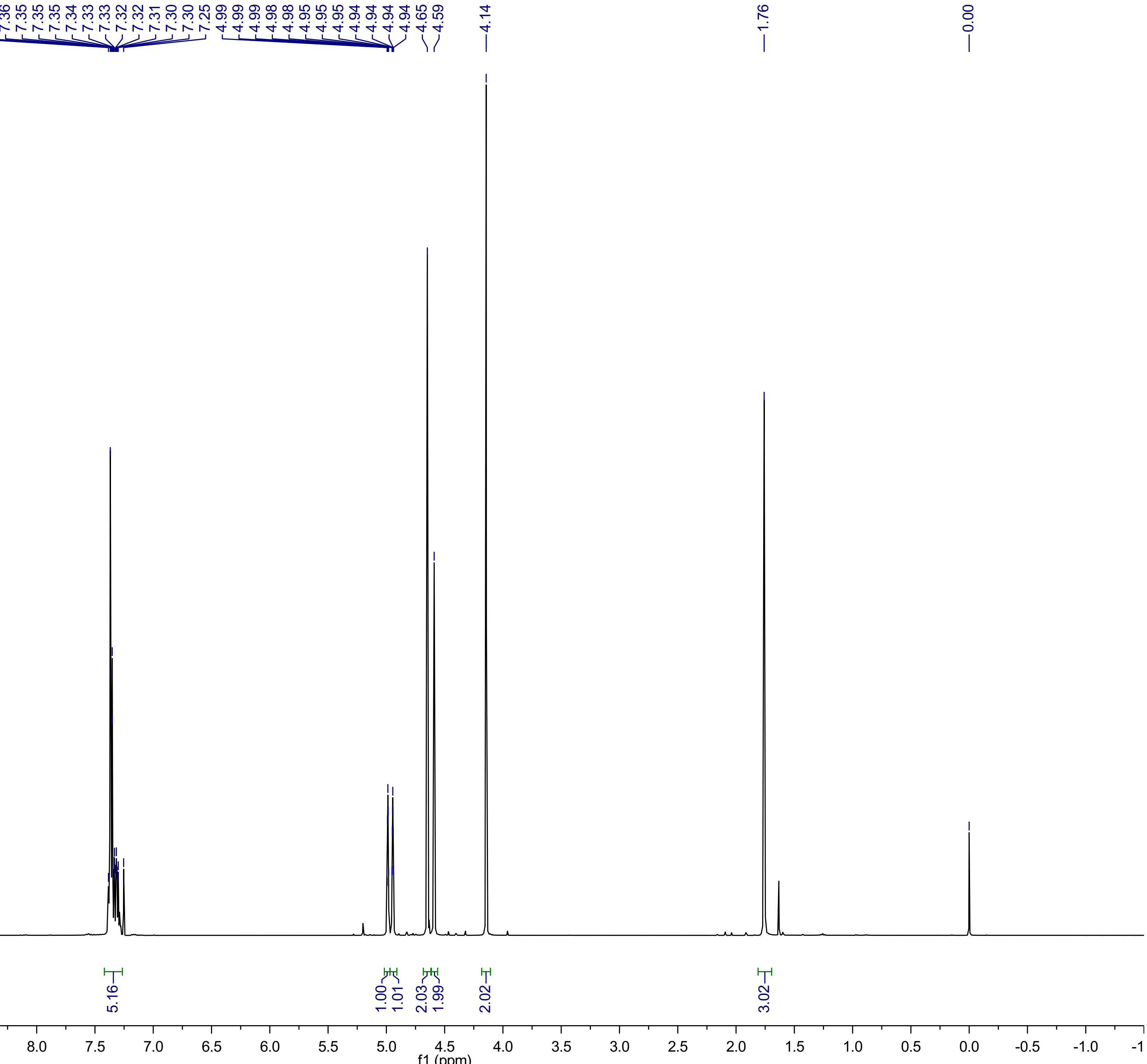

O
O
Me
NPhth

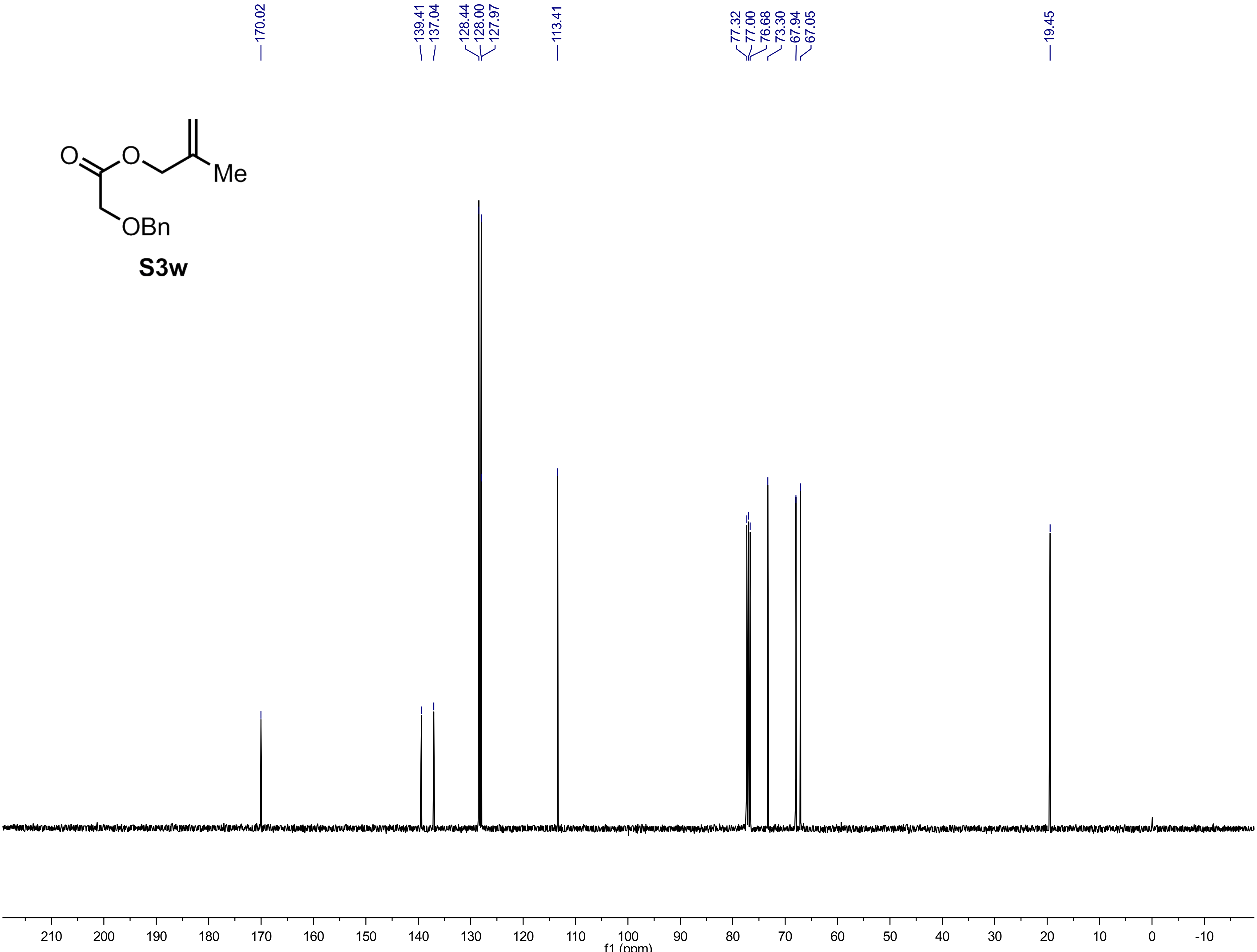
S3v

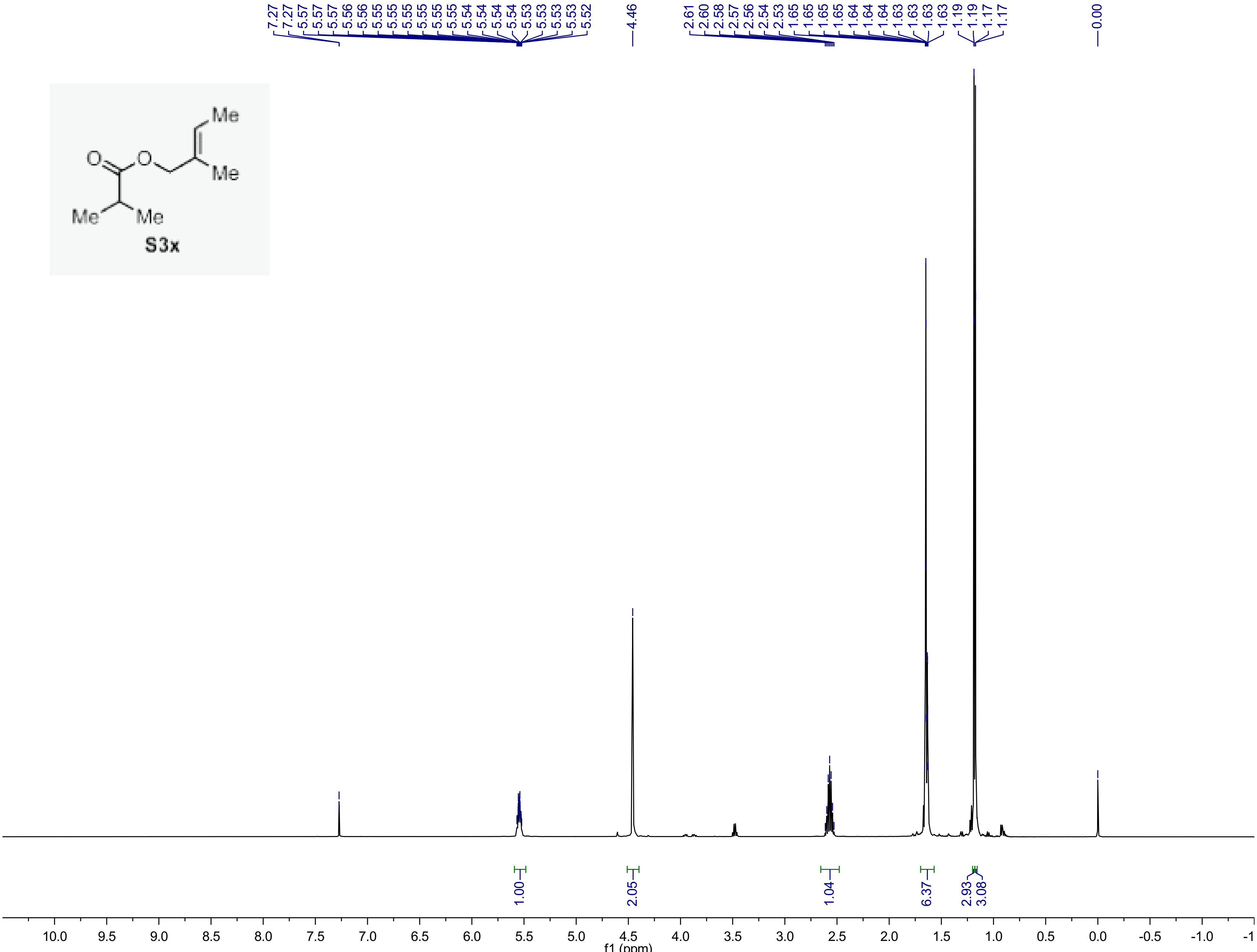

167.42
166.95
139.04
134.23
131.96
123.60
113.73
77.32
77.00
76.68
68.97
38.84
19.38
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



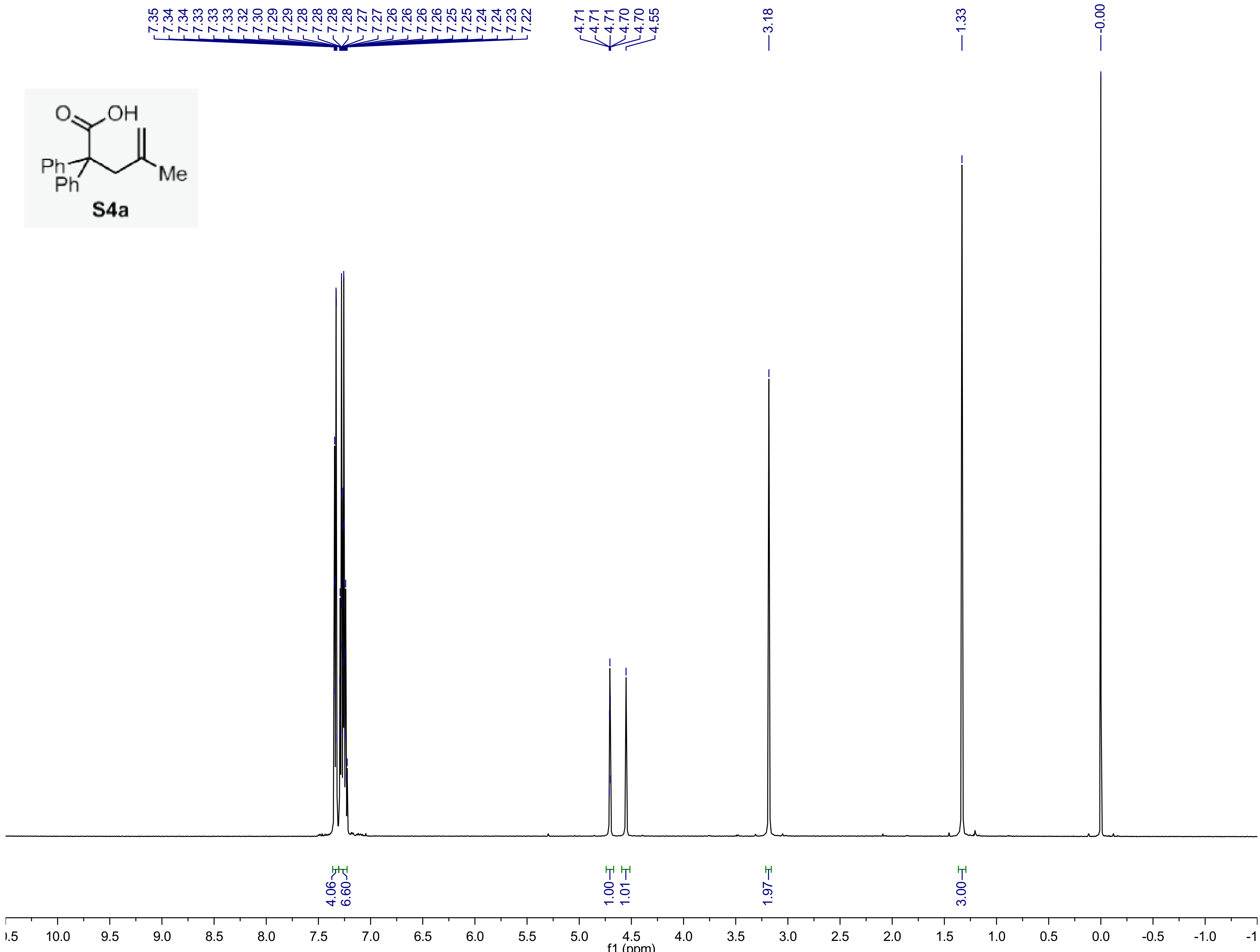
S3w


7.38
7.37
7.36
7.35
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.25
4.99
4.99
4.99
4.98
4.98
4.95
4.95
4.95
4.94
4.94
4.94
4.94
4.65
4.59
4.14
1.76
0.00
5.16
1.00
1.01
2.03
1.99
2.02
3.02
f1 (ppm)


O
O
Me
OBn
S3w
170.02
139.41
137.04
128.44
128.00
127.97
113.41
77.32
77.00
76.68
73.30
67.94
67.05
19.45
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)



Me
O
O
Me
Me
Me
S3x
7.27
7.27
5.57
5.57
5.57
5.56
5.56
5.55
5.55
5.55
5.55
5.55
5.55
5.54
5.54
5.54
5.54
5.53
5.53
5.53
5.53
5.52
4.46
2.61
2.60
2.58
2.57
2.56
2.54
2.53
1.65
1.65
1.65
1.64
1.64
1.64
1.63
1.63
1.63
1.63
1.19
1.19
1.17
1.17
0.00
1.00
2.05
1.04
6.37
2.93
3.08
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
-0.5
-1.0
-1
f1 (ppm)


7.35
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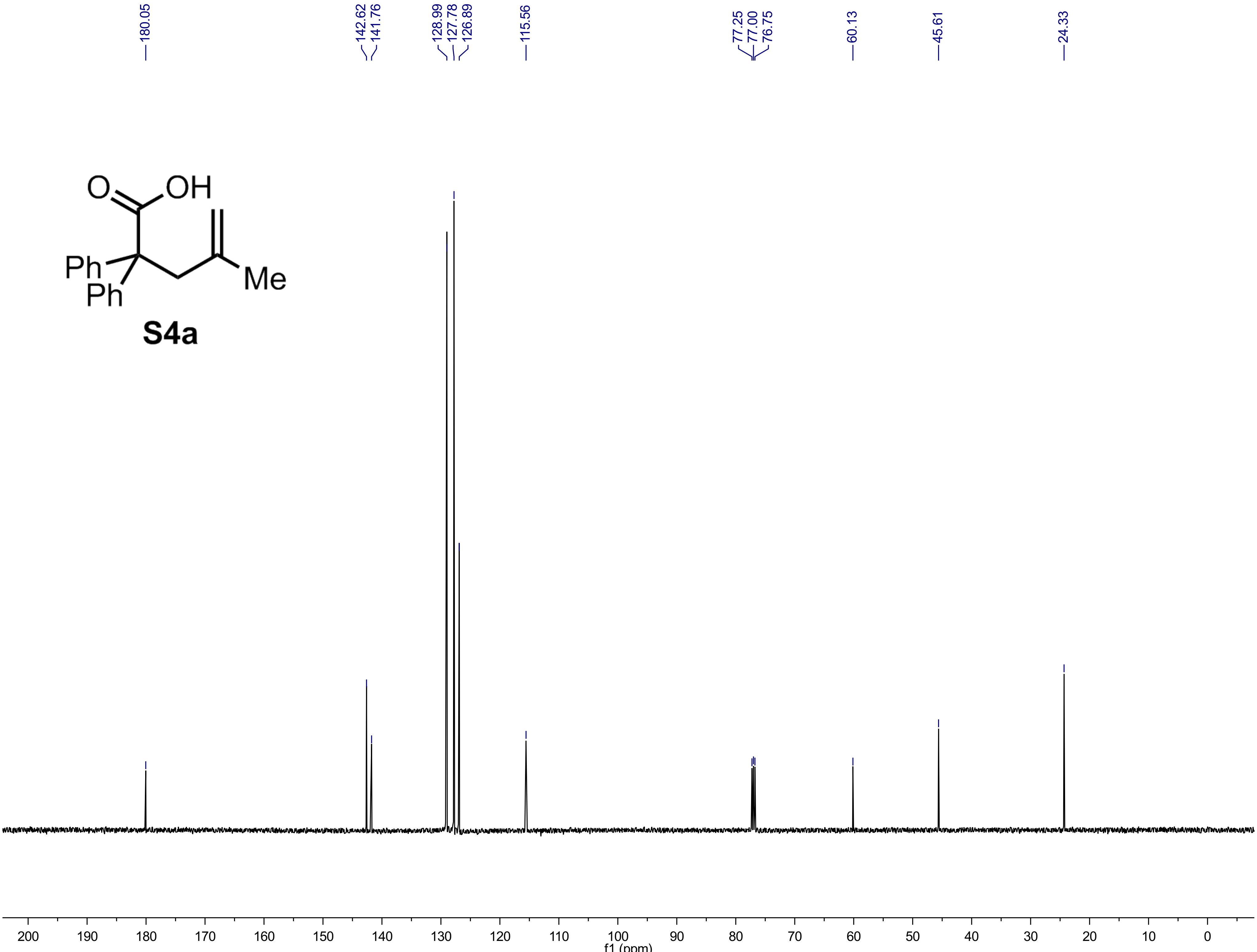
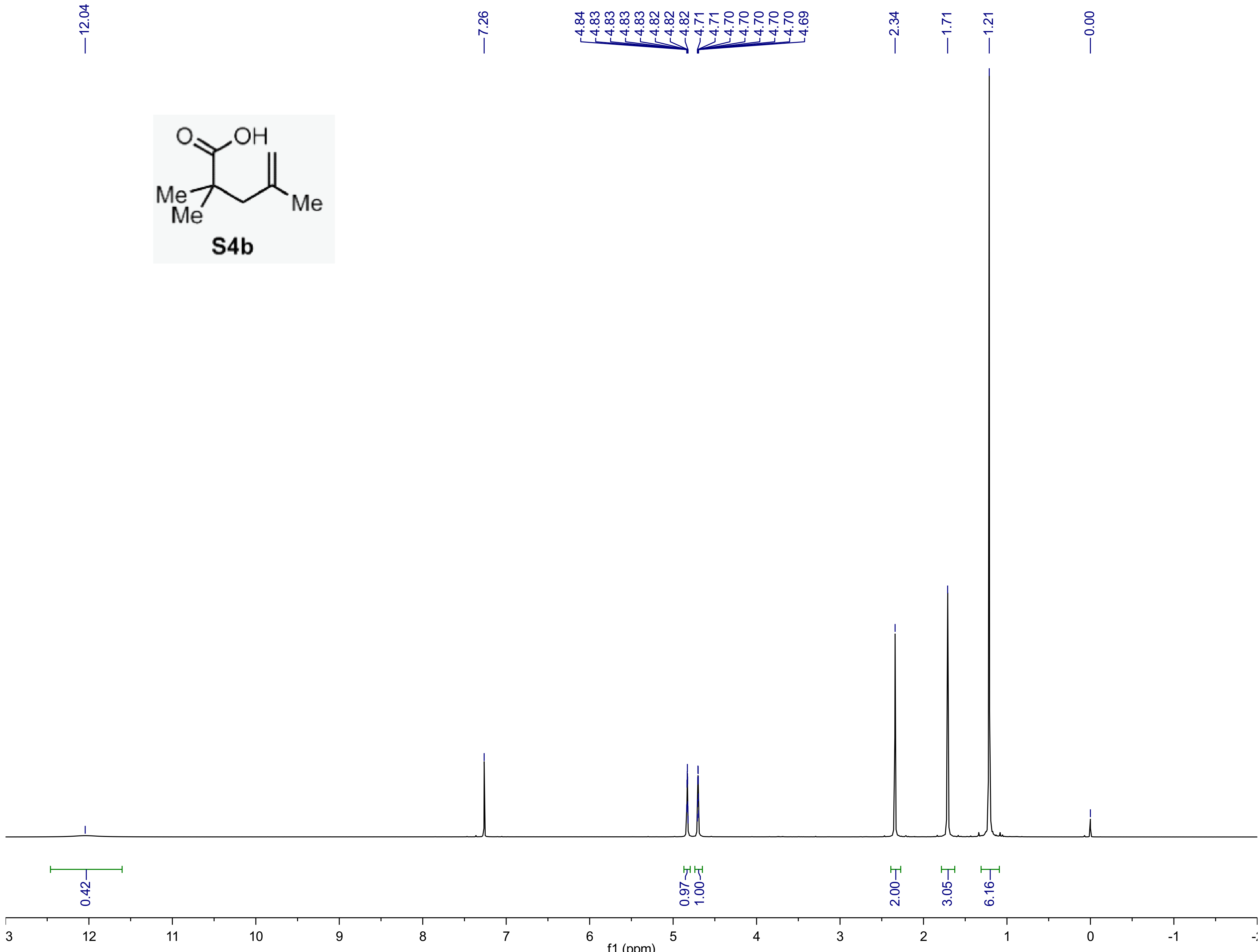
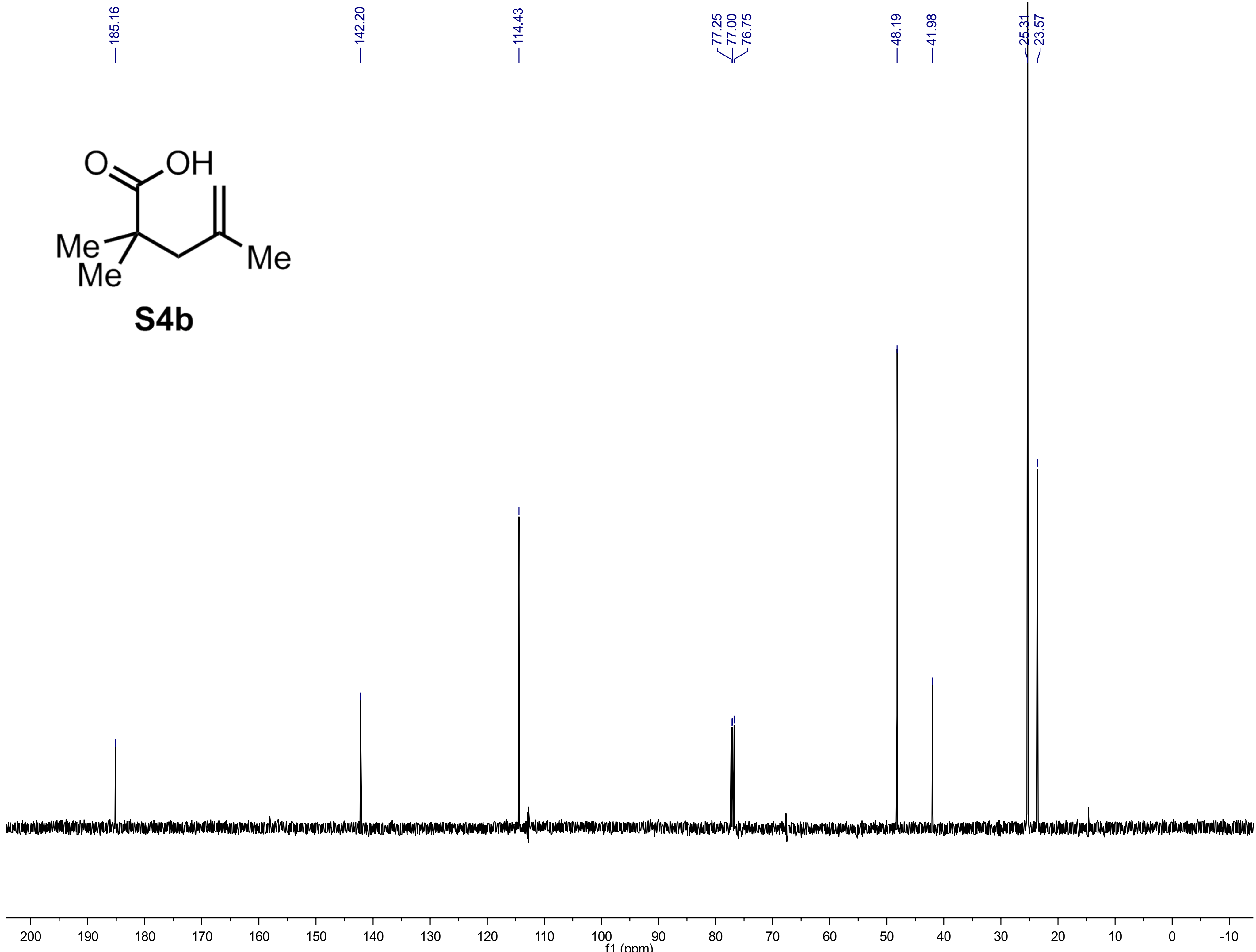
7.34
7.33
7.33
7.33
7.32
7.30
7.29
7.29
7.28
7.28
7.28
7.28
7.27
7.26
7.26
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.22
4.71
4.71
4.71
4.70
4.70
4.55
3.18
1.33
-0.00
O
OH
Ph
Ph
Me
S4a
4.06
6.60
1.00
1.01
1.97
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

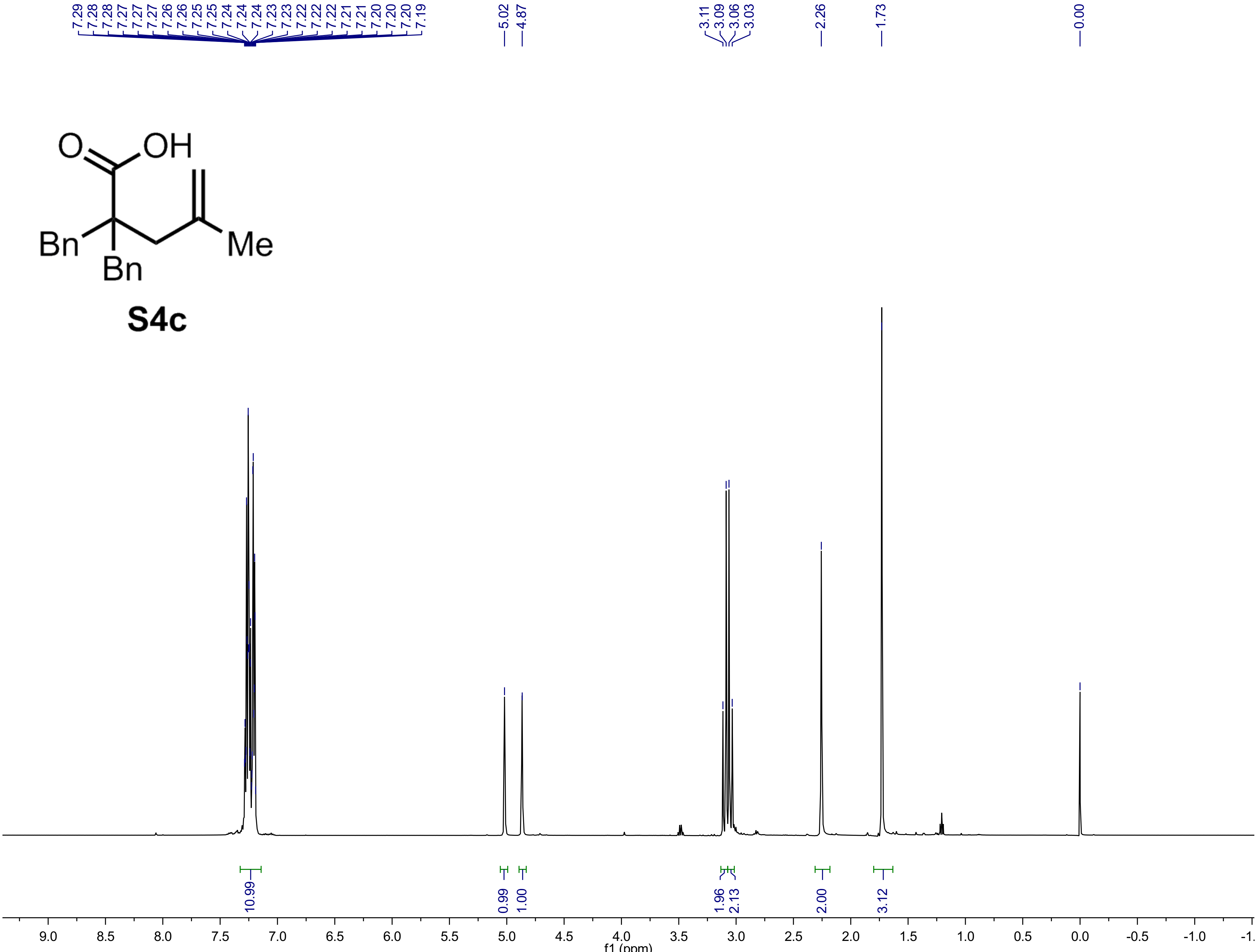

S4a
180.05
142.62
141.76
128.99
127.78
126.89
115.56
77.25
77.00
76.75
60.13
45.61
24.33
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

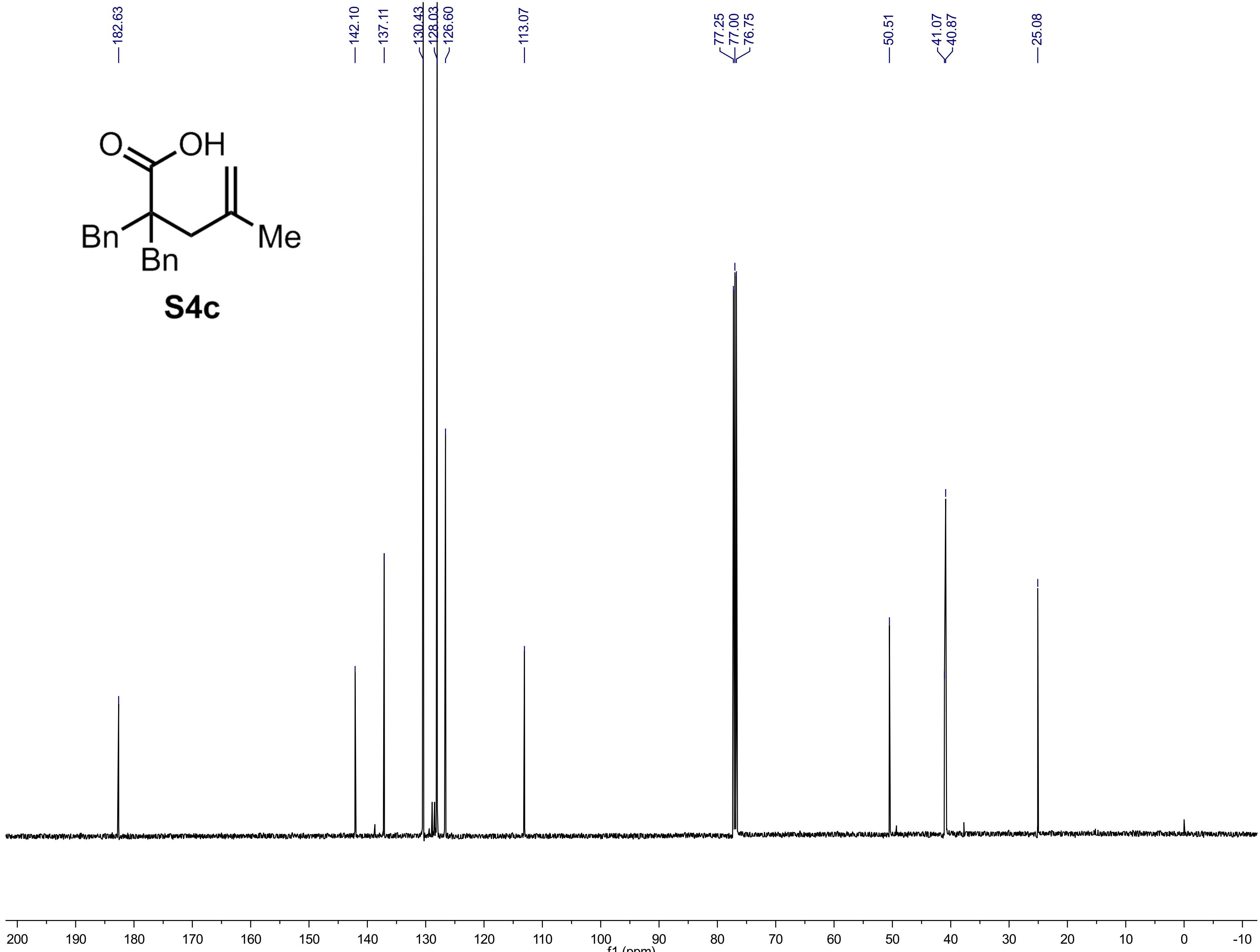


12.04
7.26
4.84
4.83
4.83
4.83
4.83
4.82
4.82
4.82
4.71
4.71
4.70
4.70
4.70
4.70
4.70
4.69
2.34
1.71
1.21
0.00
O
OH
Me
Me
Me
S4b
0.42
0.97
1.00
2.00
3.05
6.16
f1 (ppm)

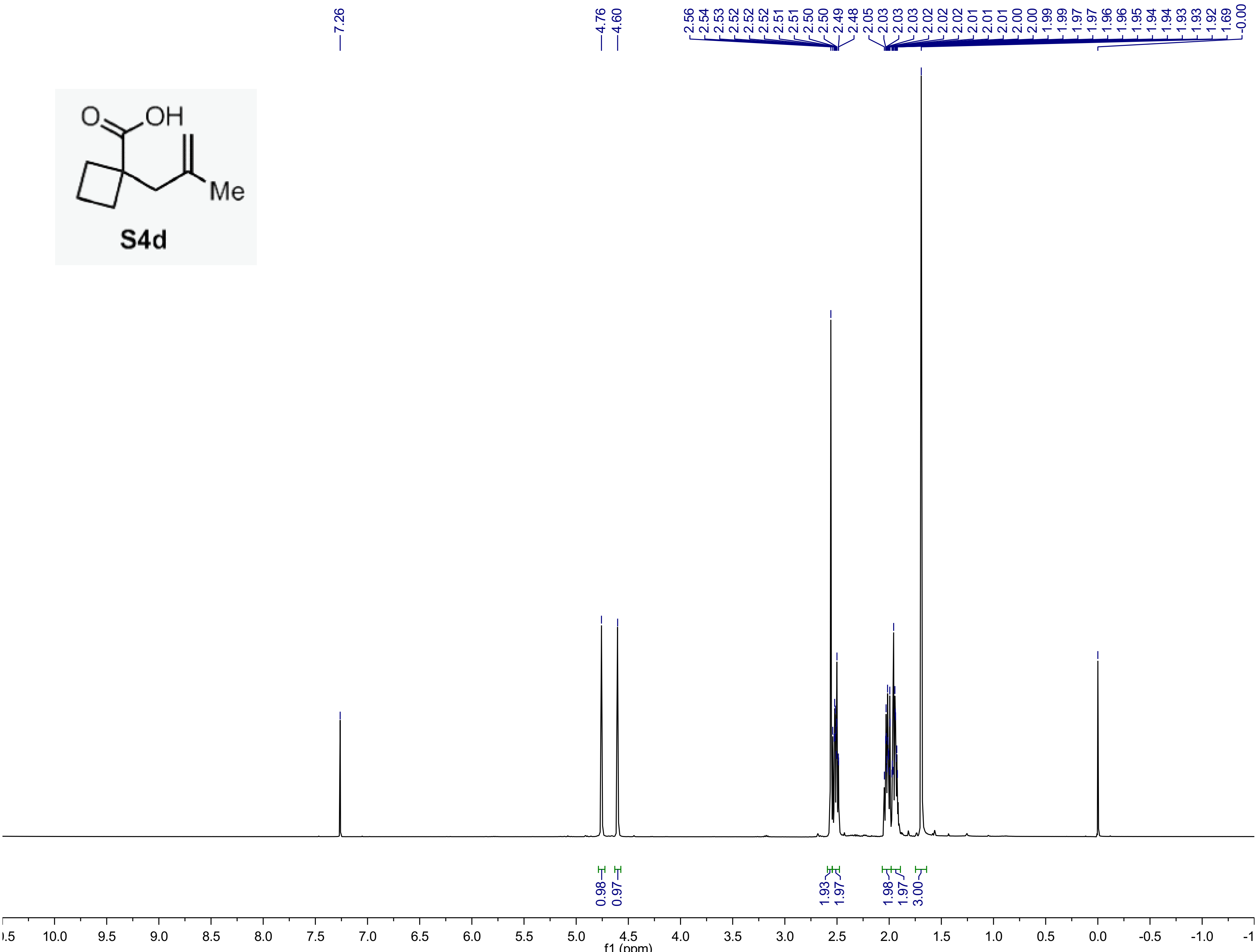

185.16
142.20
114.43
77.25
77.00
76.75
48.19
41.98
25.31
23.57
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
O
OH
Me
Me
Me

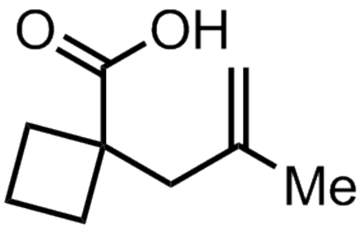
S4b


7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.24
7.23
7.23
7.22
7.22
7.22
7.21
7.21
7.20
7.20
7.20
7.19
5.02
4.87
3.11
3.09
3.06
3.03
2.26
1.73
0.00
O
OH
Bn
Bn
Me
S4c
10.99
0.99
1.00
1.96
2.13
2.00
3.12
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
-0.5
-1.0
f1 (ppm)

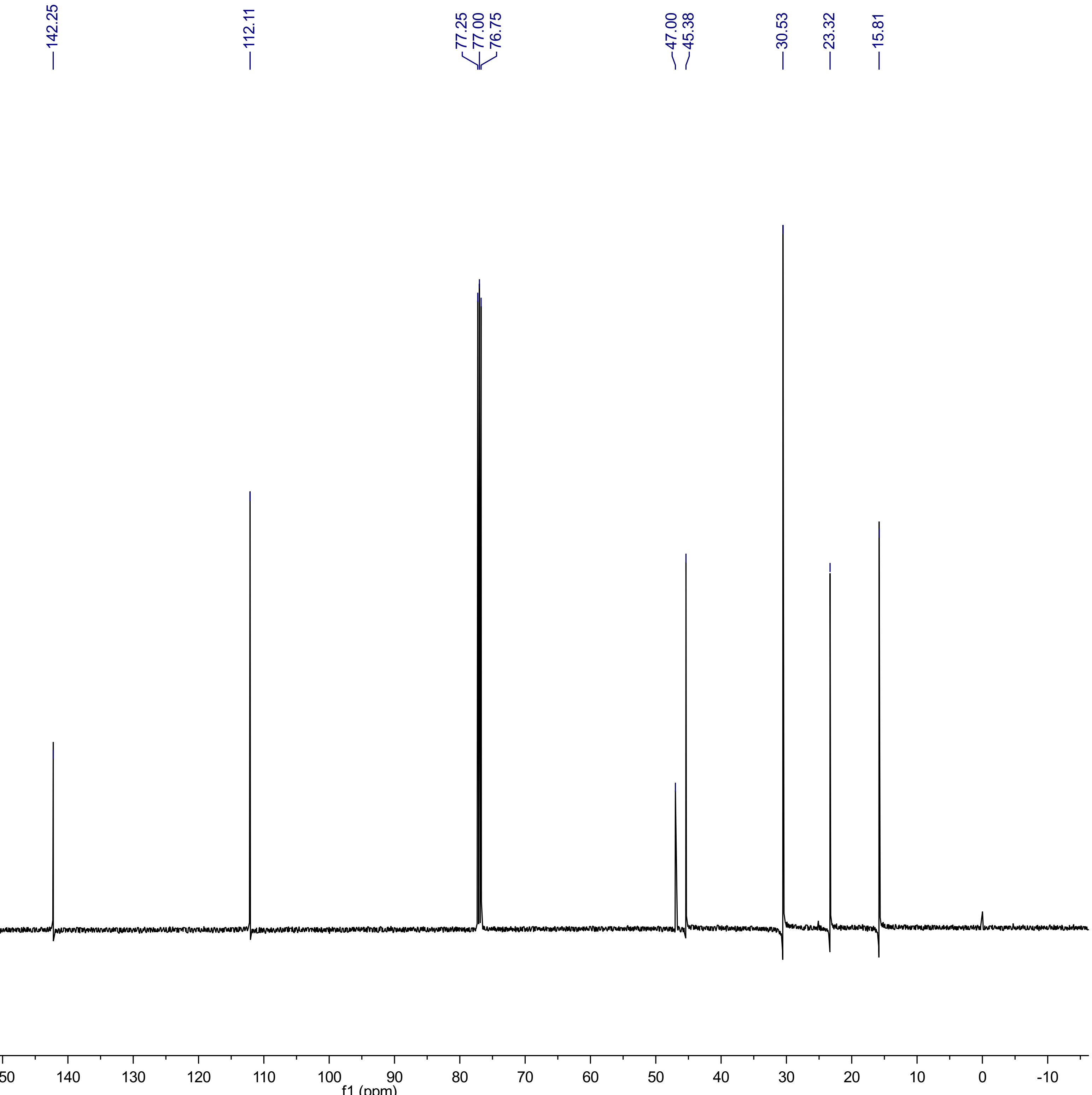


182.63
142.10
137.11
130.43
128.03
126.60
113.07
77.25
77.00
76.75
50.51
41.07
40.87
25.08
O
OH
Bn
Bn
Me
S4c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

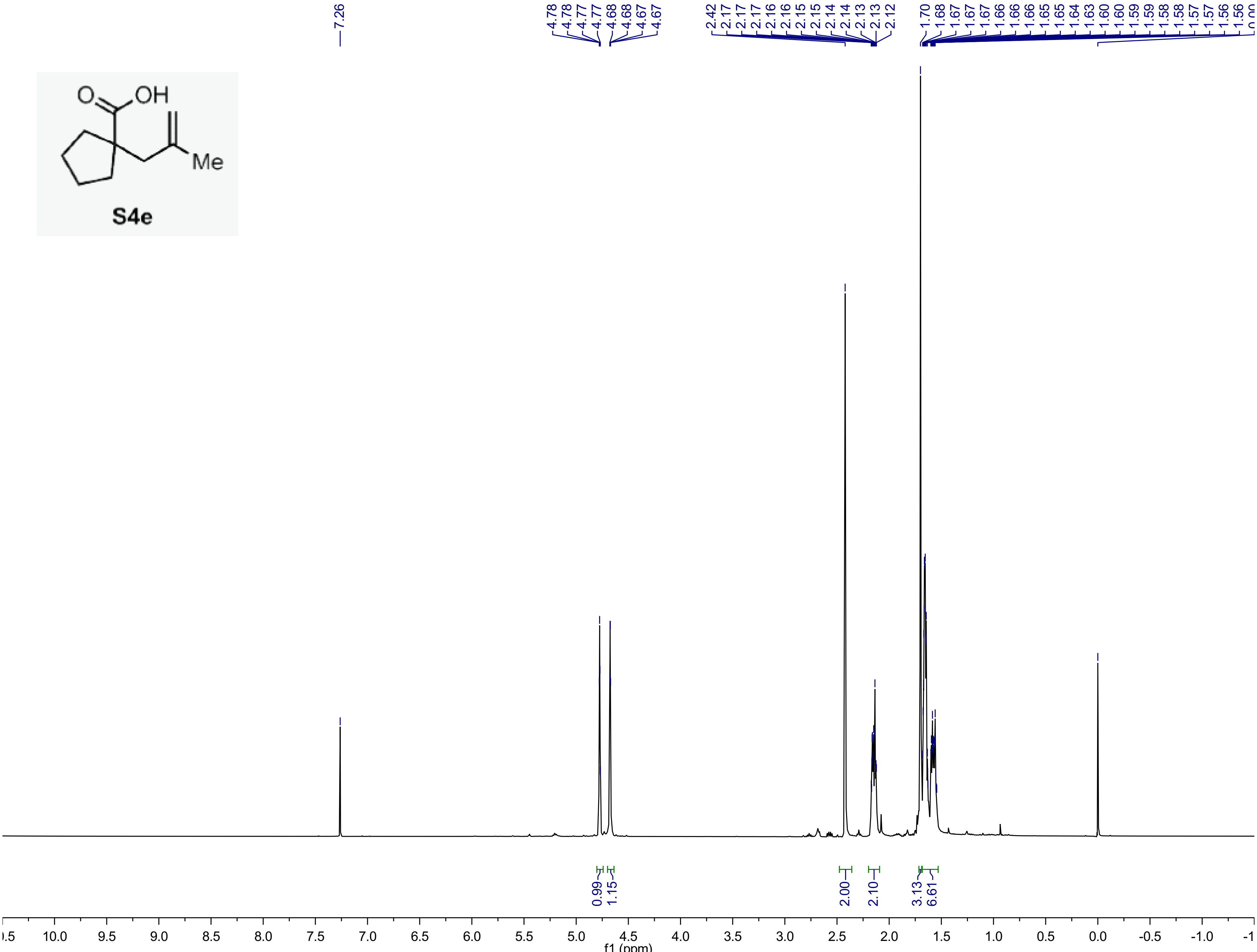

O
OH
Me
S4d
7.26
4.76
4.60
2.56
2.54
2.53
2.52
2.52
2.52
2.51
2.51
2.50
2.50
2.49
2.48
2.05
2.03
2.03
2.03
2.02
2.02
2.02
2.01
2.01
2.01
2.00
2.00
1.99
1.99
1.97
1.96
1.96
1.95
1.94
1.94
1.93
1.93
1.92
1.69
-0.00
0.98
0.97
1.93
1.97
1.98
1.97
3.00
f1 (ppm)



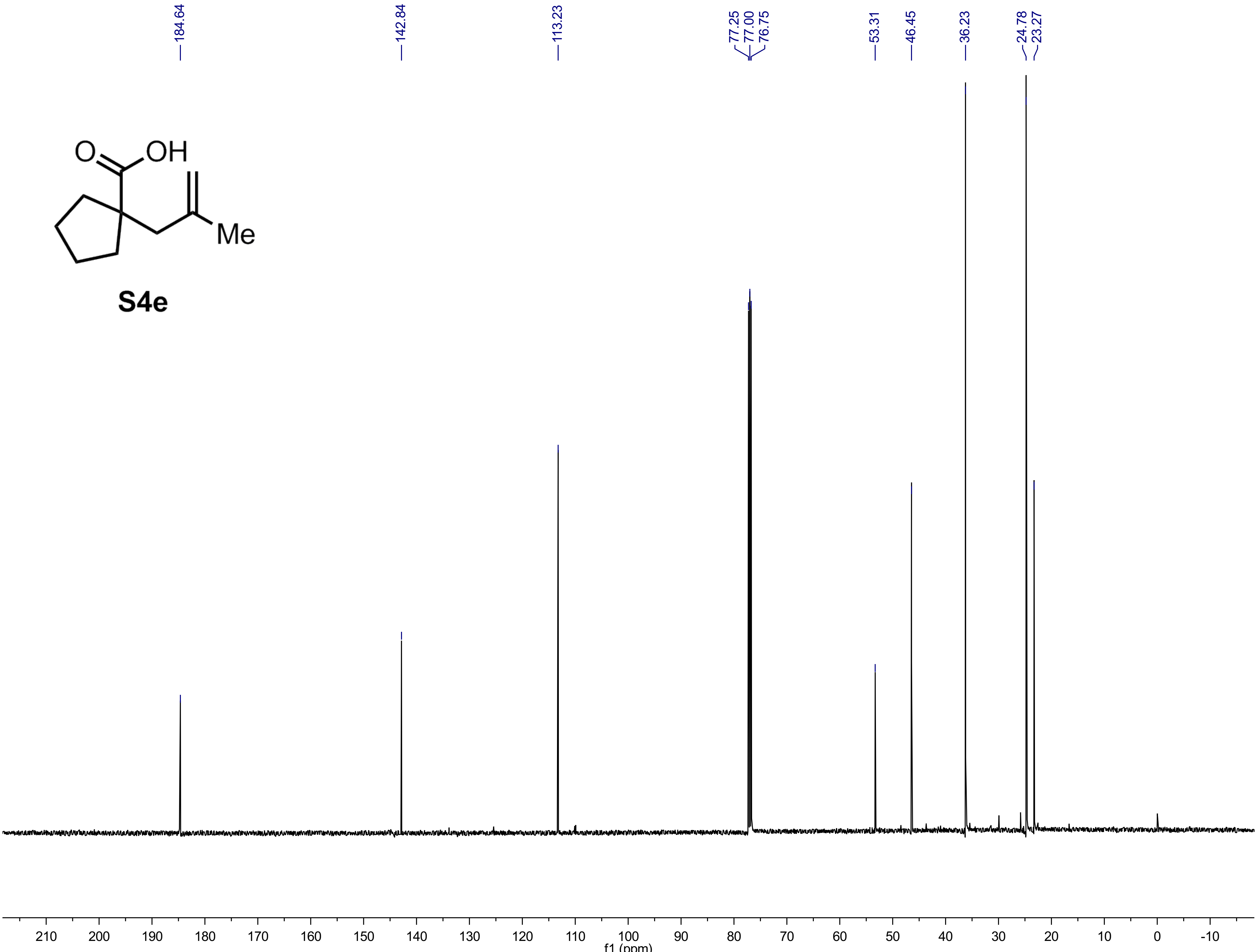
S4d



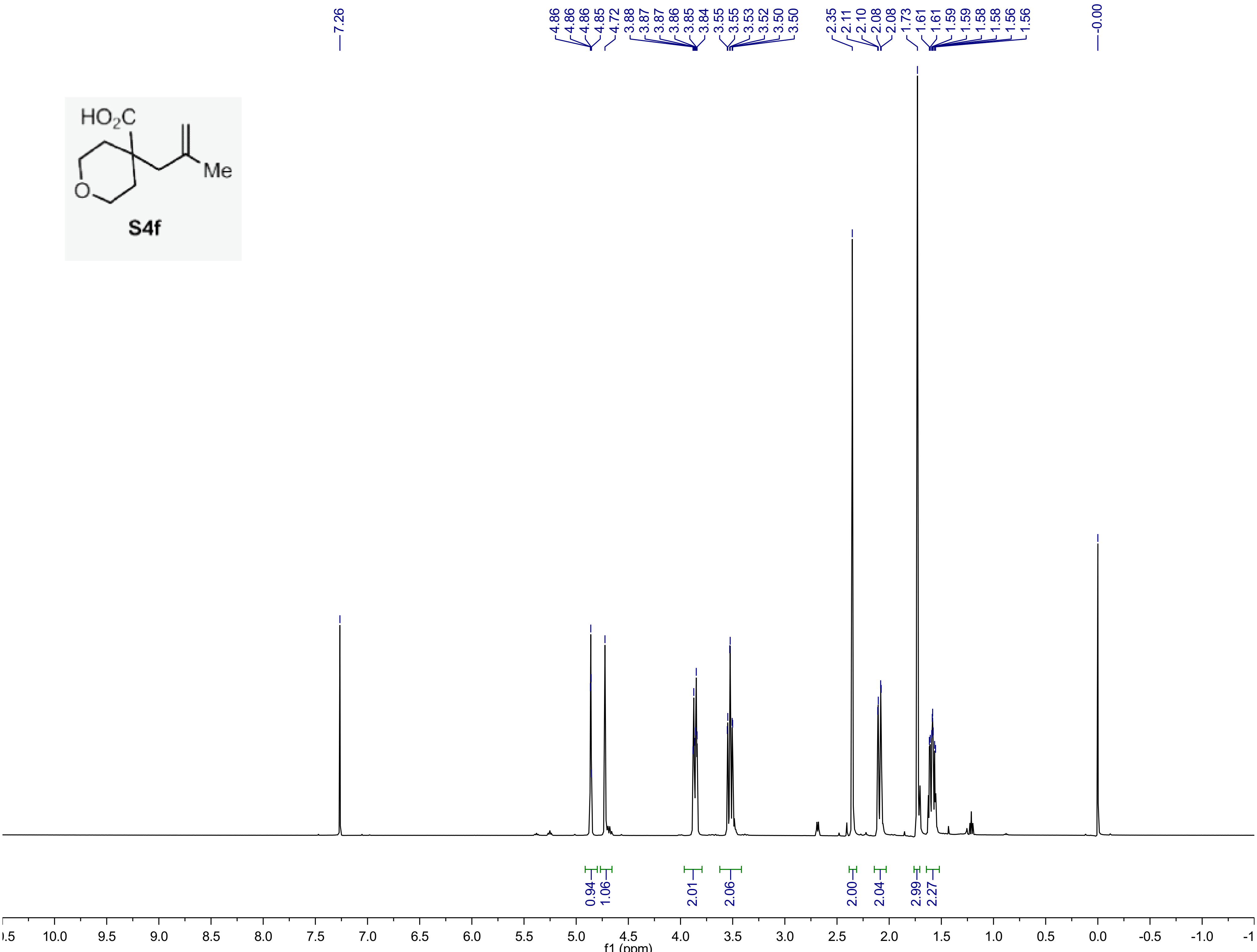
183.70
142.25
112.11
77.25
77.00
76.75
47.00
45.38
30.53
23.32
15.81
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



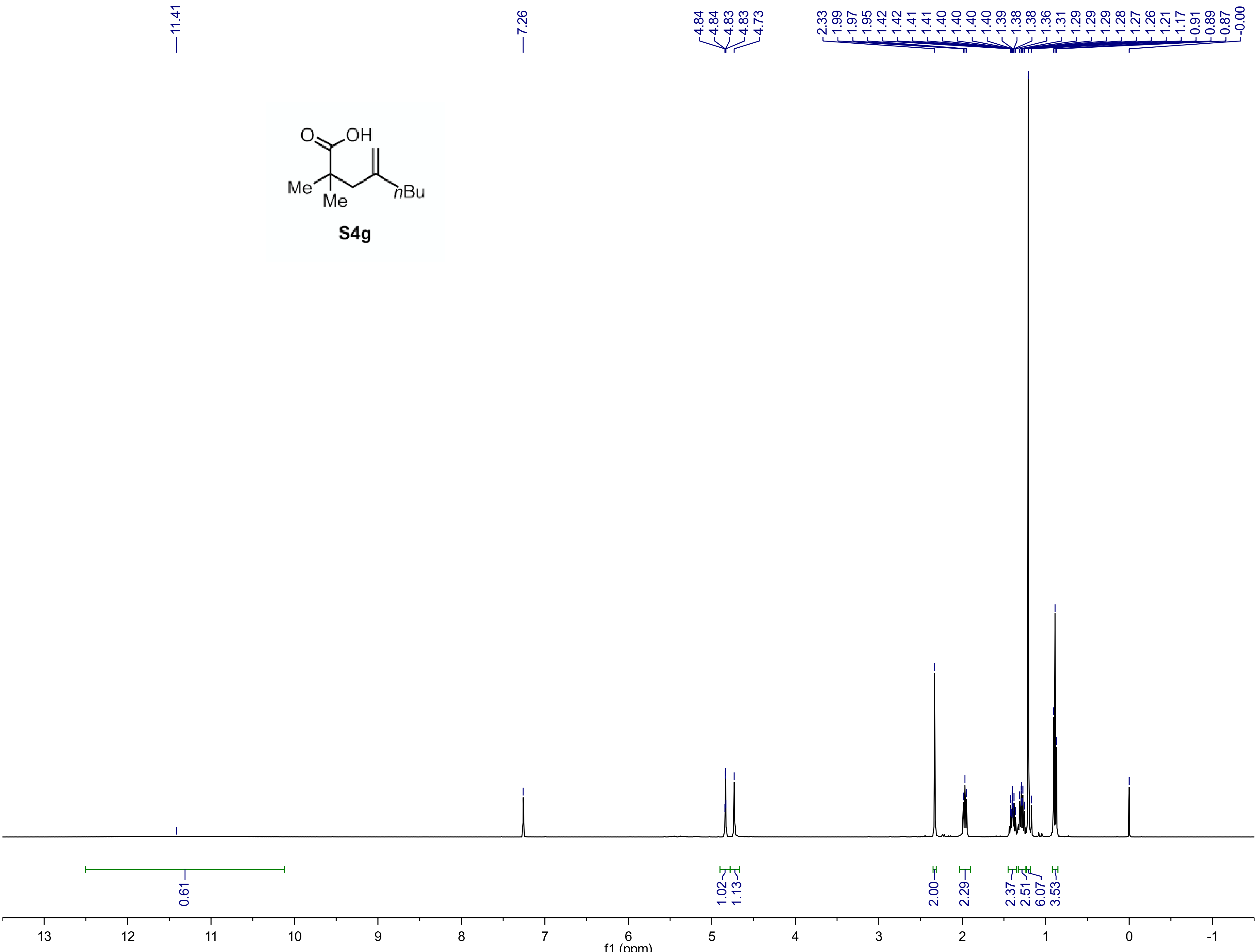
7.26
4.78 4.78 4.77 4.77 4.68 4.68 4.67 4.67
2.42 2.17 2.17 2.17 2.16 2.16 2.15 2.15 2.14 2.14 2.13 2.13 2.12
1.70 1.68 1.67 1.67 1.67 1.66 1.66 1.66 1.65 1.65 1.64 1.63 1.60 1.60 1.59 1.59 1.58 1.58 1.57 1.57 1.56 1.56
O OH
Me
S4e
0.99 1.15 2.00 2.10 3.13 6.61
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

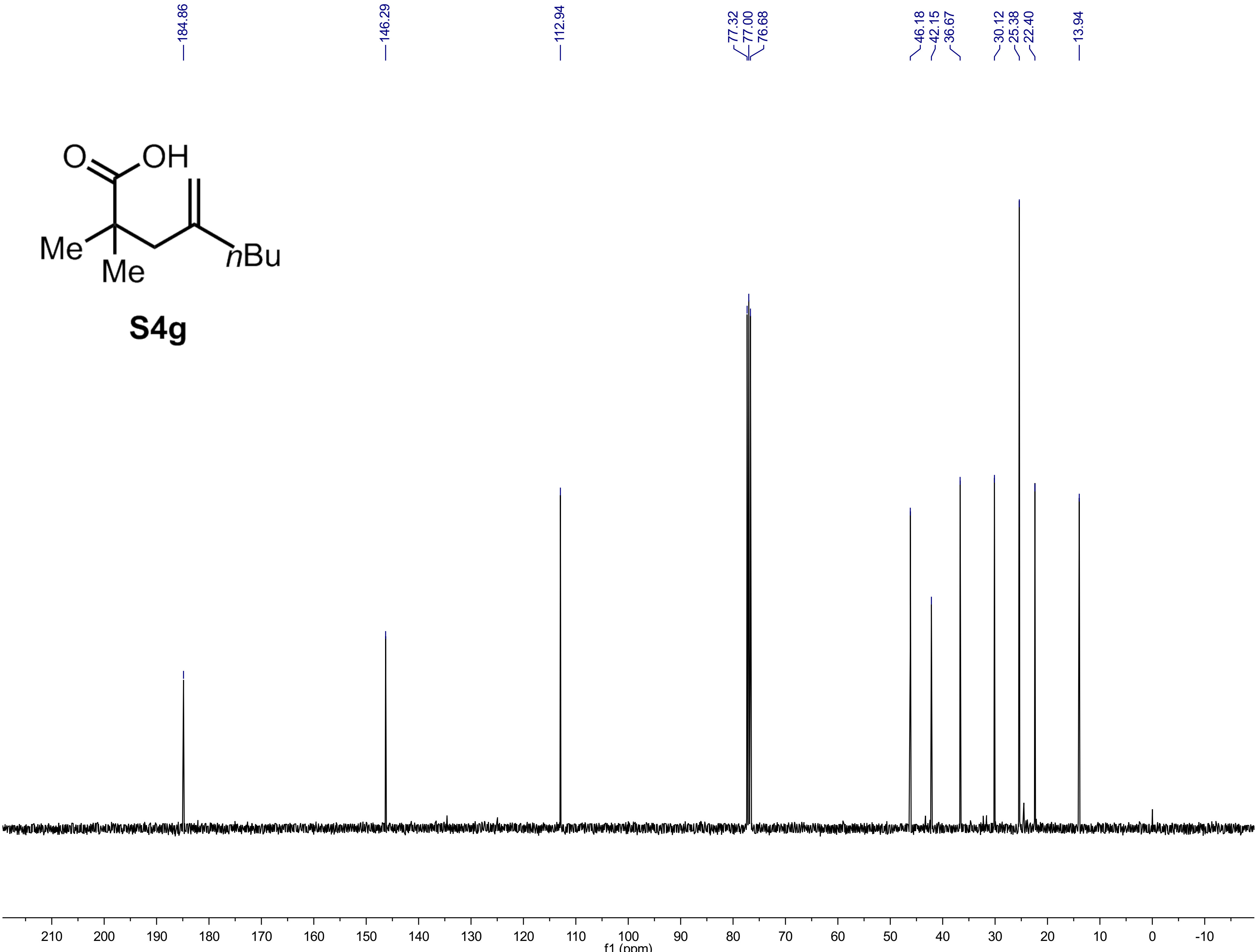

O
OH
Me
184.64
142.84
113.23
77.25
77.00
76.75
53.31
46.45
36.23
24.78
23.27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

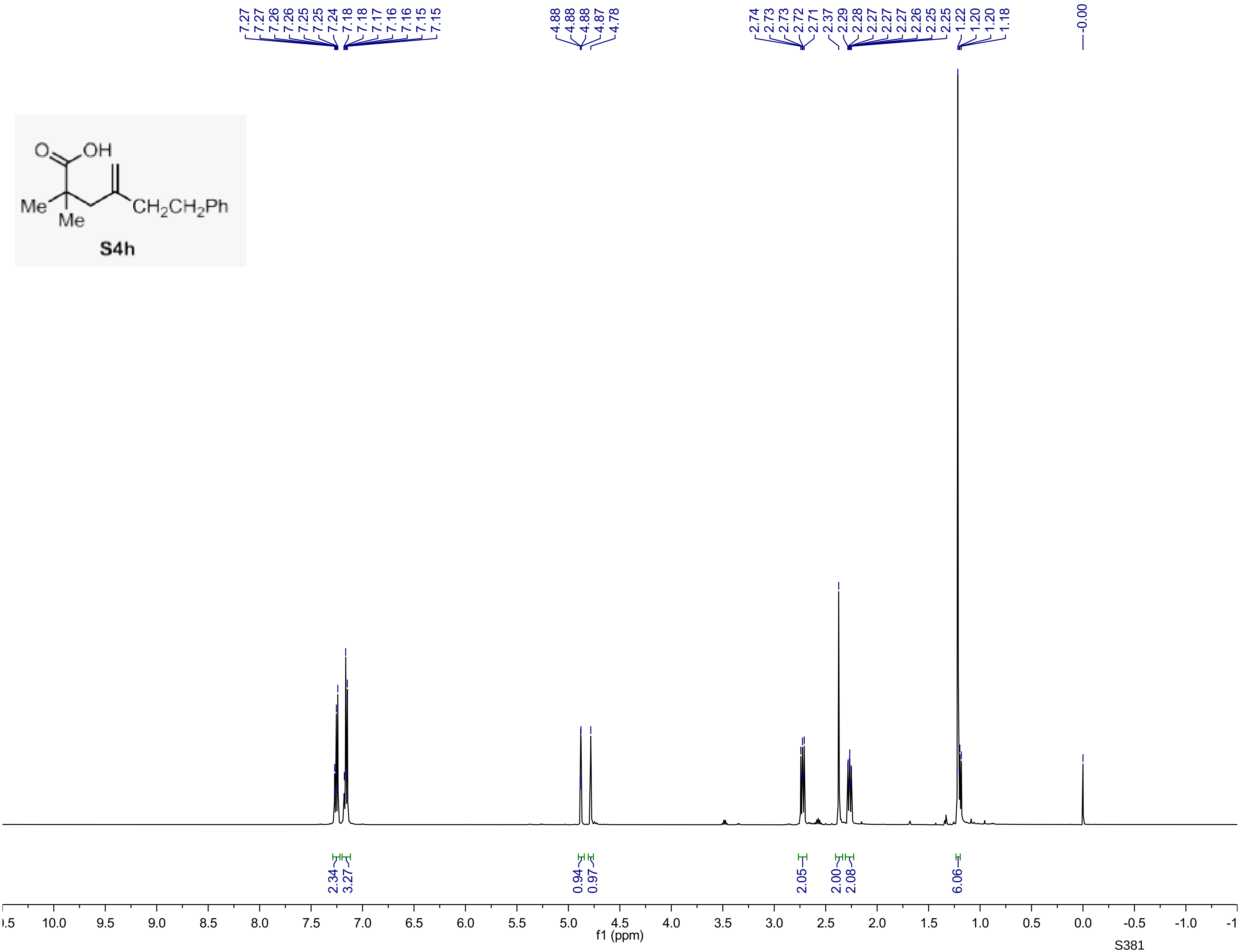
S4e



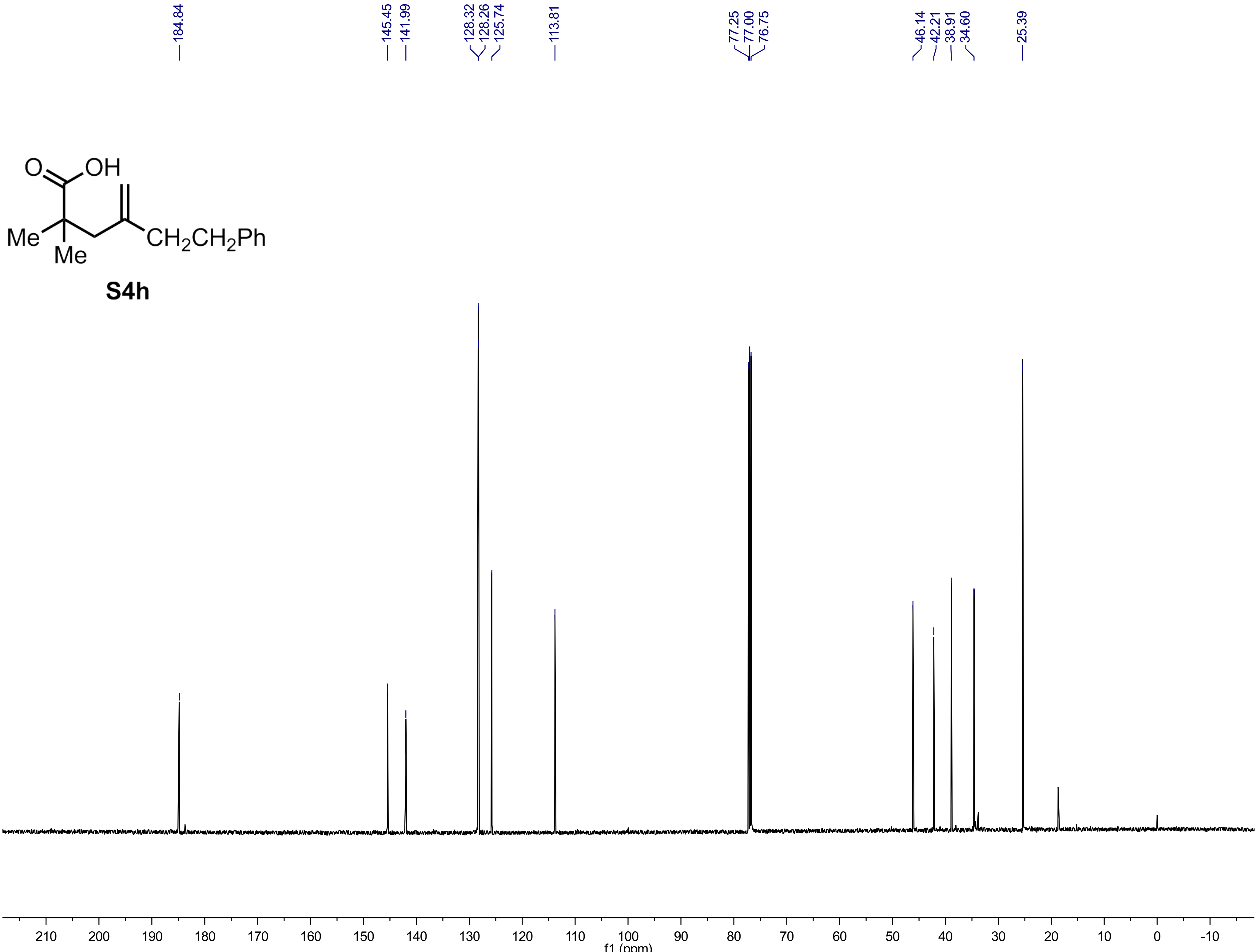
HO2C
Me
O
S4f
7.26
4.86
4.86
4.86
4.85
4.72
3.88
3.87
3.87
3.86
3.85
3.84
3.55
3.55
3.53
3.52
3.50
3.50
2.35
2.11
2.10
2.08
2.08
1.73
1.61
1.61
1.59
1.59
1.58
1.58
1.56
1.56
0.00
0.94
1.06
2.01
2.06
2.00
2.04
2.99
2.27
f1 (ppm)


11.41
7.26
4.84
4.84
4.83
4.83
4.73
2.33
1.99
1.97
1.95
1.42
1.42
1.41
1.41
1.40
1.40
1.40
1.40
1.39
1.38
1.38
1.36
1.31
1.29
1.29
1.29
1.28
1.27
1.26
1.21
1.17
0.91
0.89
0.87
-0.00
O
OH
Me
Me
nBu
S4g
0.61
1.02
1.13
2.00
2.29
2.37
2.51
6.07
3.53
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

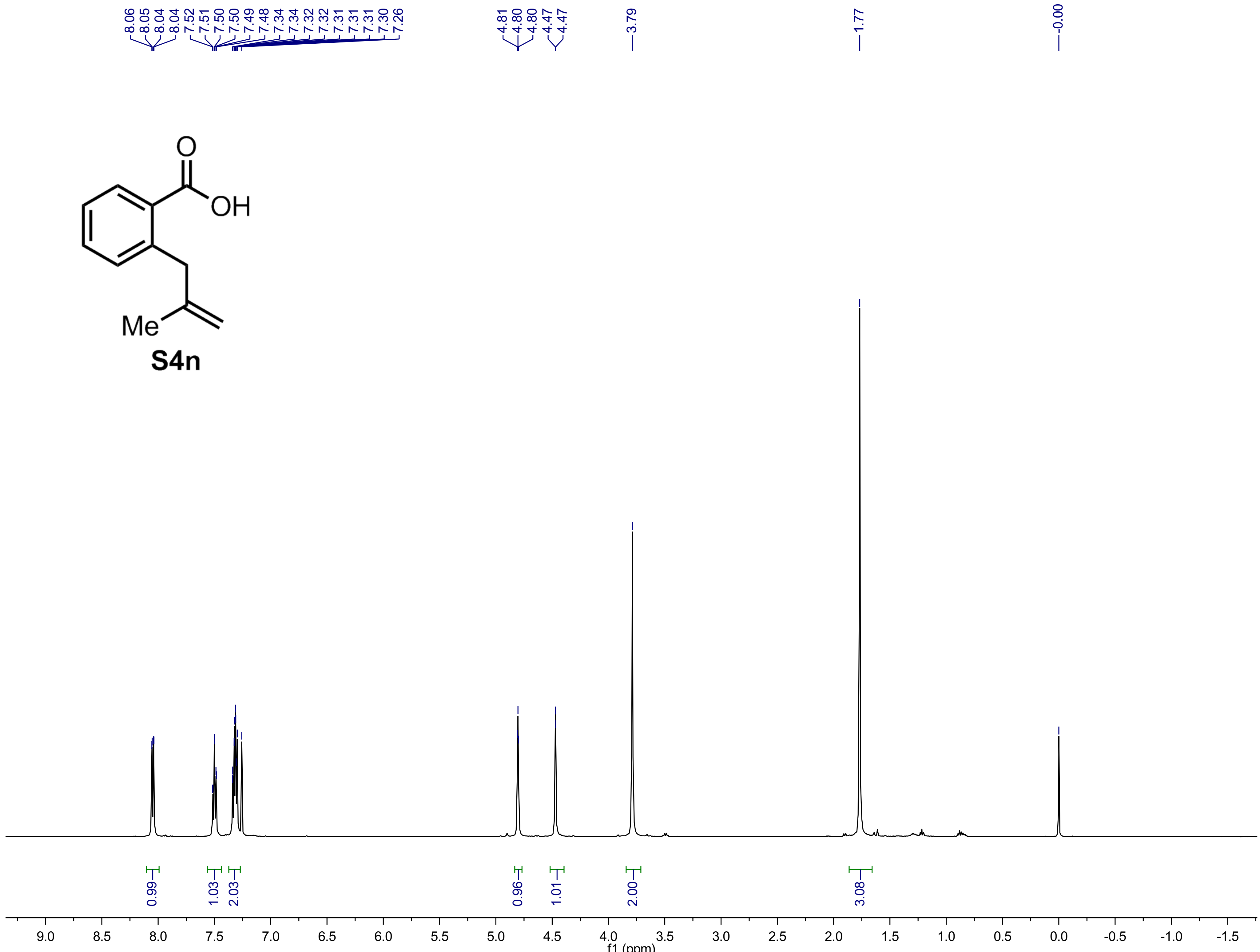

O
OH
Me
Me
nBu
S4g
184.86
146.29
112.94
77.32
77.00
76.68
46.18
42.15
36.67
30.12
25.38
22.40
13.94
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



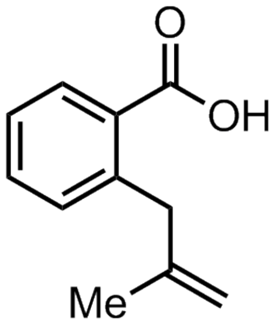
S4h
f1 (ppm)



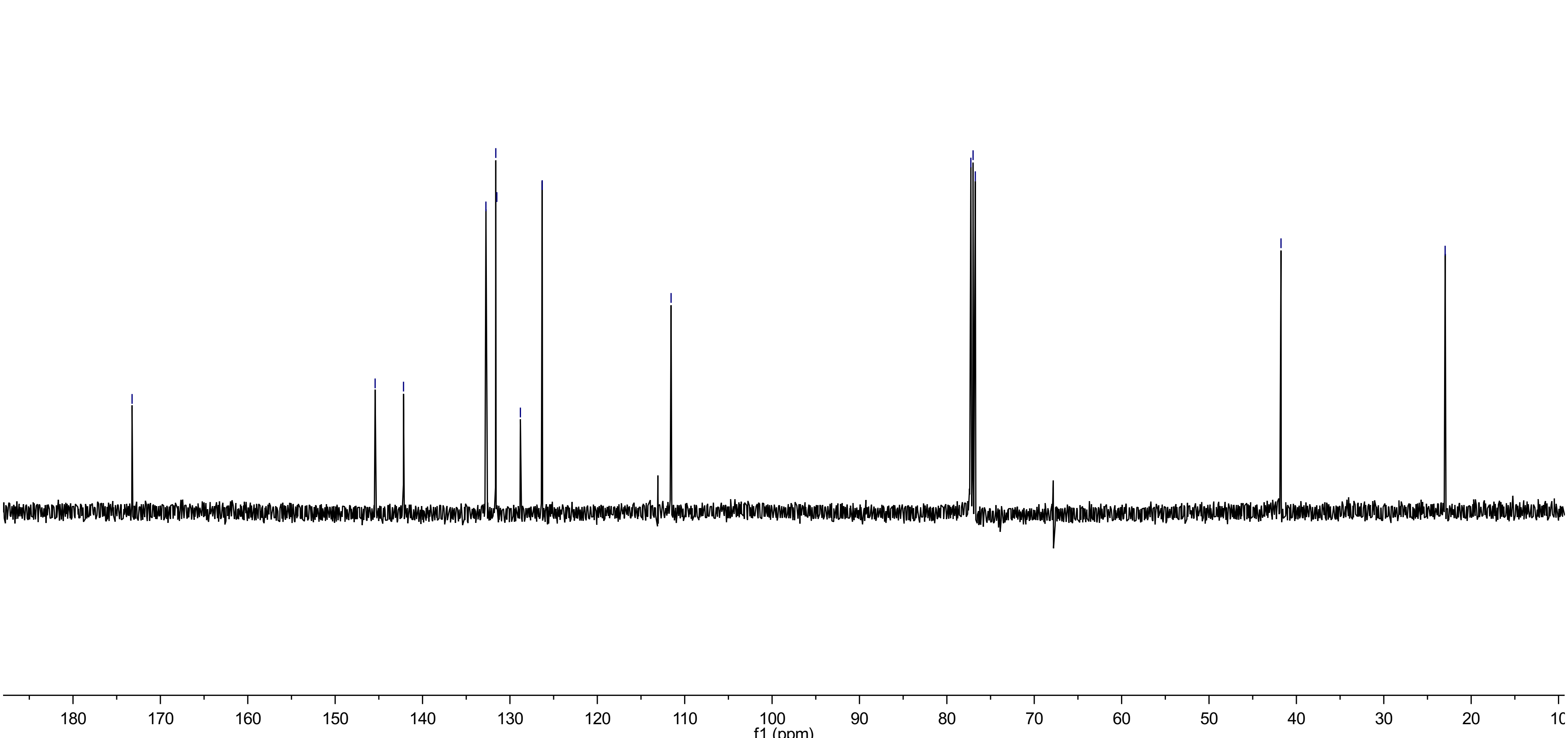
184.84
145.45
141.99
128.32
128.26
125.74
113.81
77.25
77.00
76.75
46.14
42.21
38.91
34.60
25.39
OH
O
Me
Me
CH2CH2Ph
S4h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

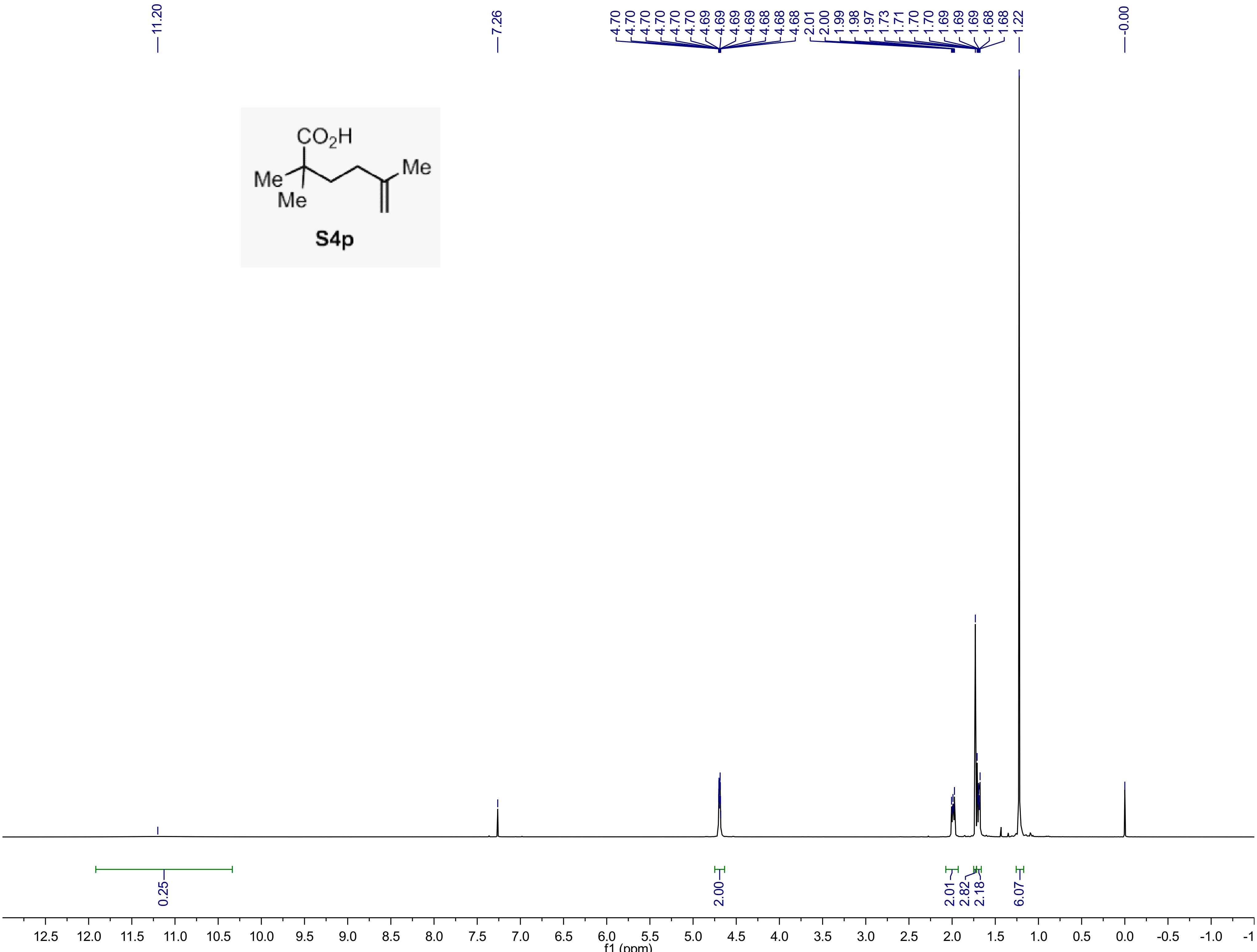


8.06
8.05
8.04
8.04
7.52
7.51
7.50
7.50
7.49
7.48
7.34
7.34
7.32
7.32
7.31
7.31
7.31
7.30
7.26
4.81
4.80
4.80
4.47
4.47
3.79
1.77
-0.00
OH
Me
S4n
0.99
1.03
2.03
0.96
1.01
2.00
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

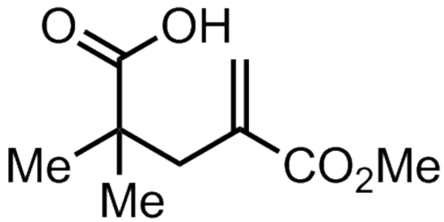


S4n

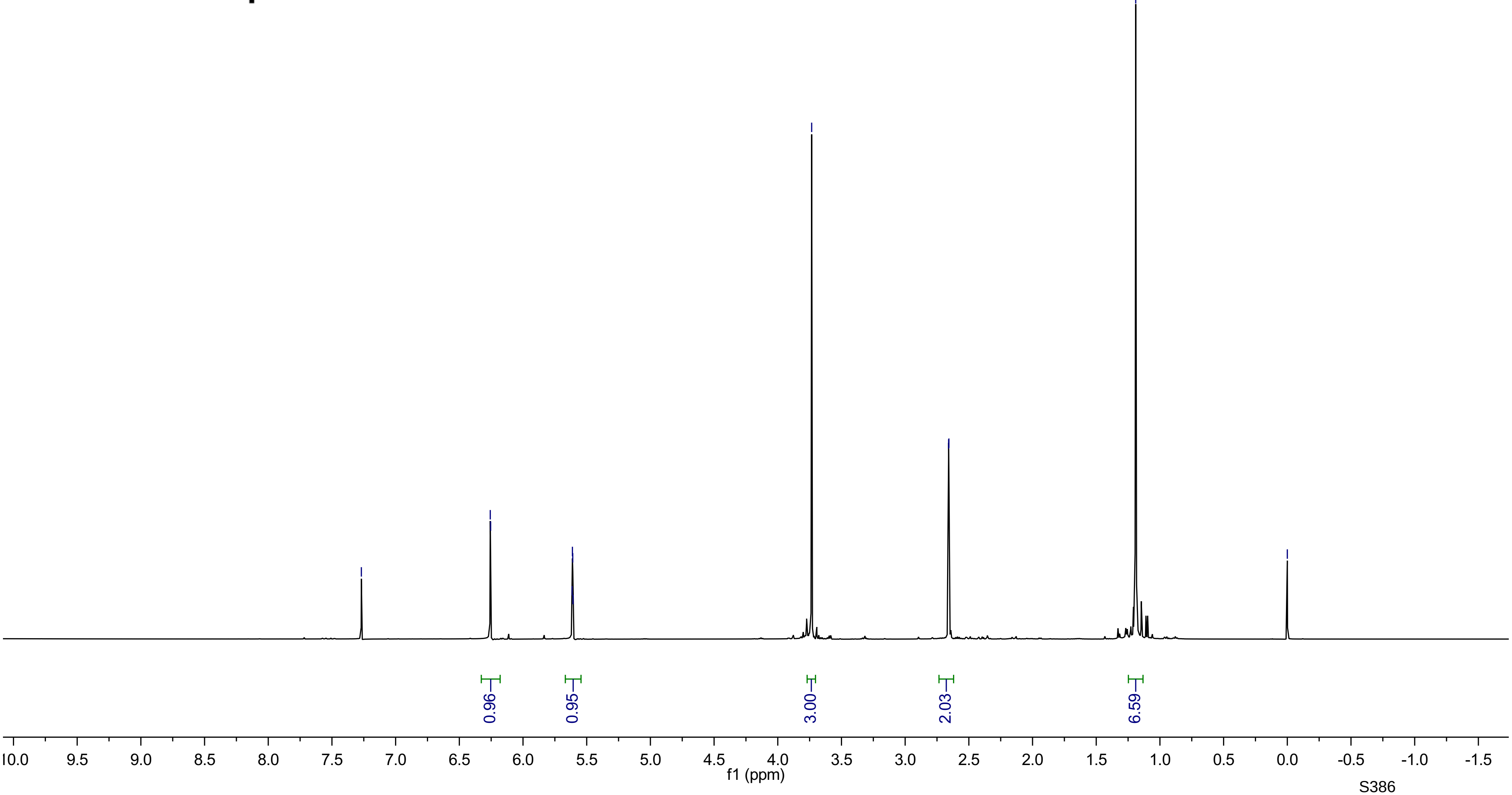

173.24
145.42
142.18
132.75
131.62
131.50
128.80
126.31
111.56
77.25
77.00
76.75
41.76
22.98
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

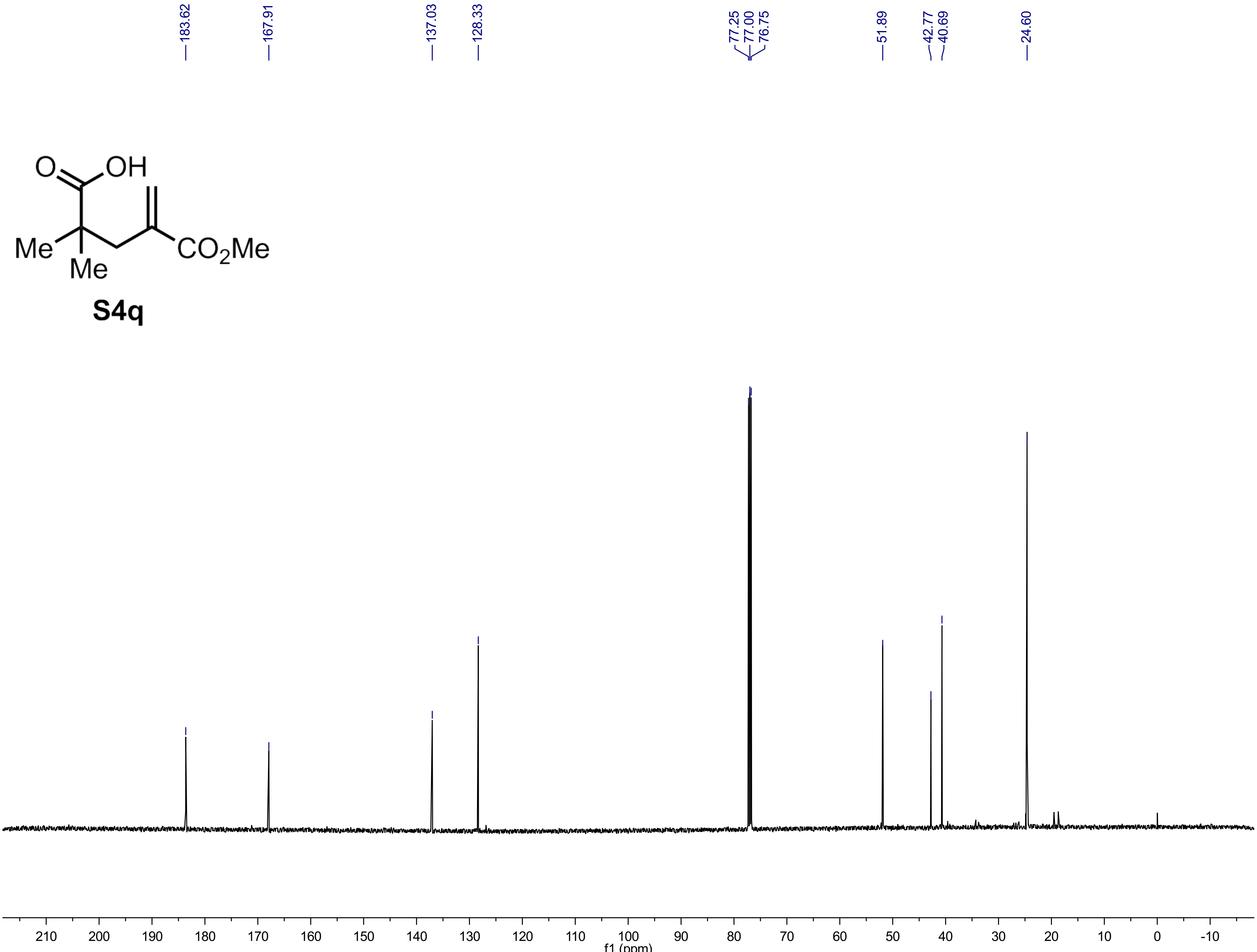


11.20
7.26
4.70
4.70
4.70
4.70
4.70
4.70
4.69
4.69
4.69
4.69
4.68
4.68
4.68
2.01
2.00
1.99
1.98
1.97
1.73
1.71
1.70
1.70
1.69
1.69
1.69
1.68
1.68
1.22
-0.00
CO2H
Me
Me
Me
S4p
0.25
2.00
2.01
2.82
2.18
6.07
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1
f1 (ppm)


O
OH
Me
Me
CO2Me

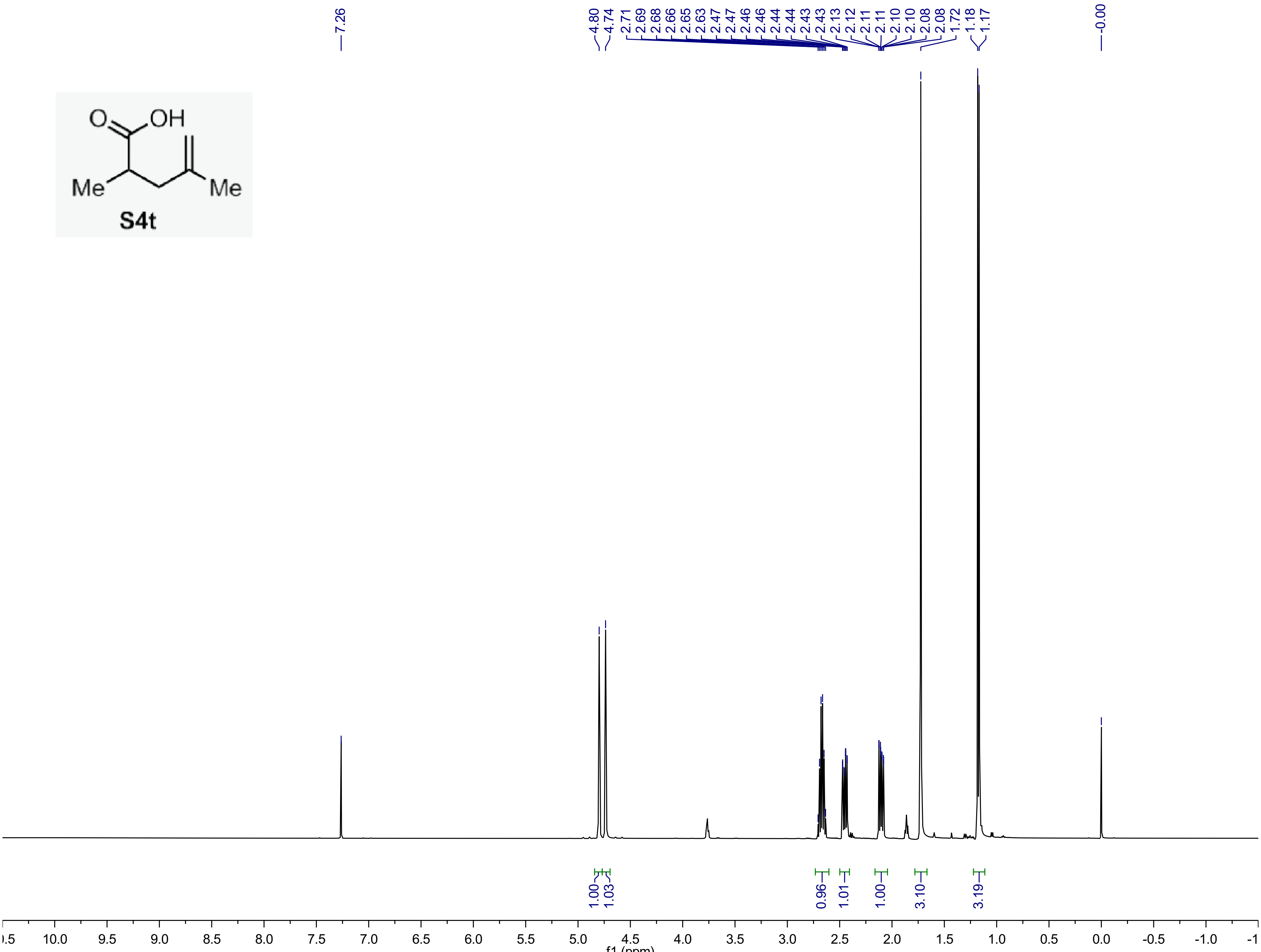
S4q


7.27
6.26
6.25
5.61
5.61
5.61
5.61
3.73
2.66
2.66
1.19
-0.00
0.96
0.95
3.00
2.03
6.59
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 -0.5 -1.0 -1.5
f1 (ppm)

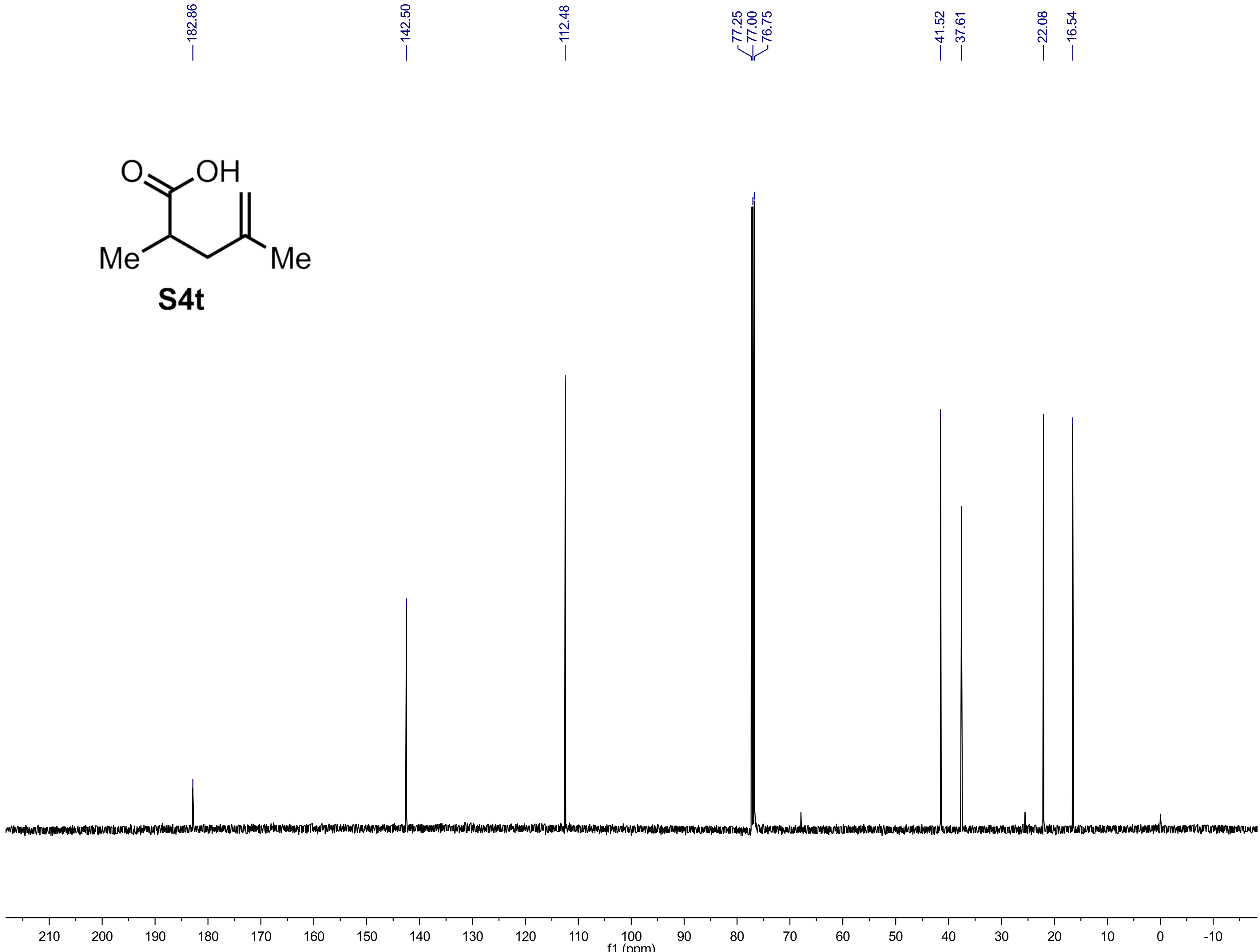


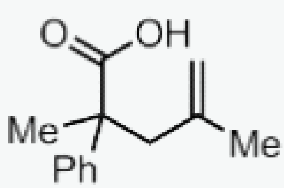
183.62
167.91
137.03
128.33
77.25
77.00
76.75
51.89
42.77
40.69
24.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
O
OH
Me
Me
CO_2Me

S4q

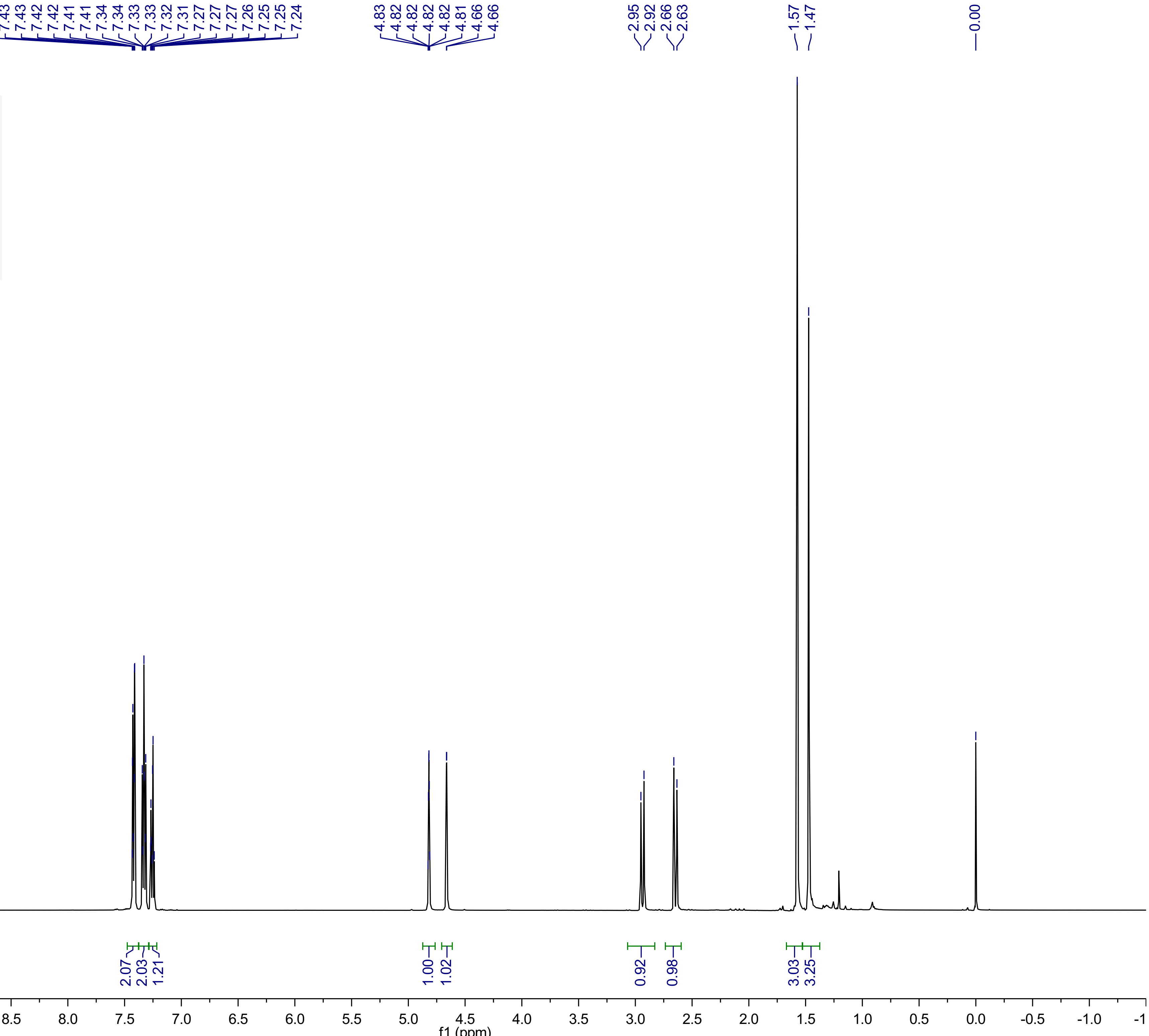


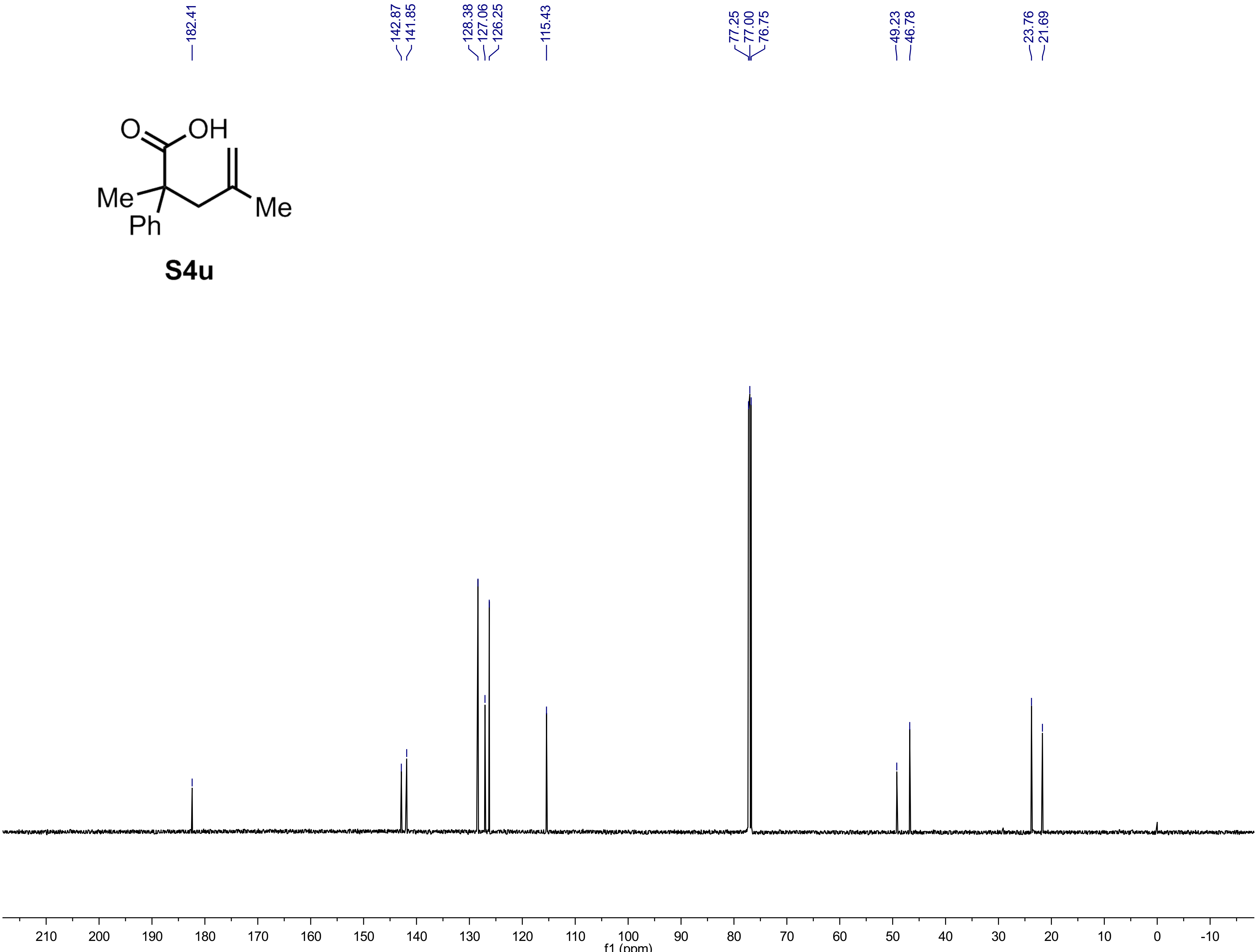
7.26
4.80
4.74
2.71
2.69
2.68
2.66
2.65
2.63
2.47
2.47
2.46
2.46
2.44
2.44
2.43
2.43
2.13
2.12
2.11
2.11
2.10
2.10
2.08
2.08
1.72
1.18
1.17
-0.00
O
OH
Me
Me
S4t
1.00
1.03
0.96
1.01
1.00
3.10
3.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

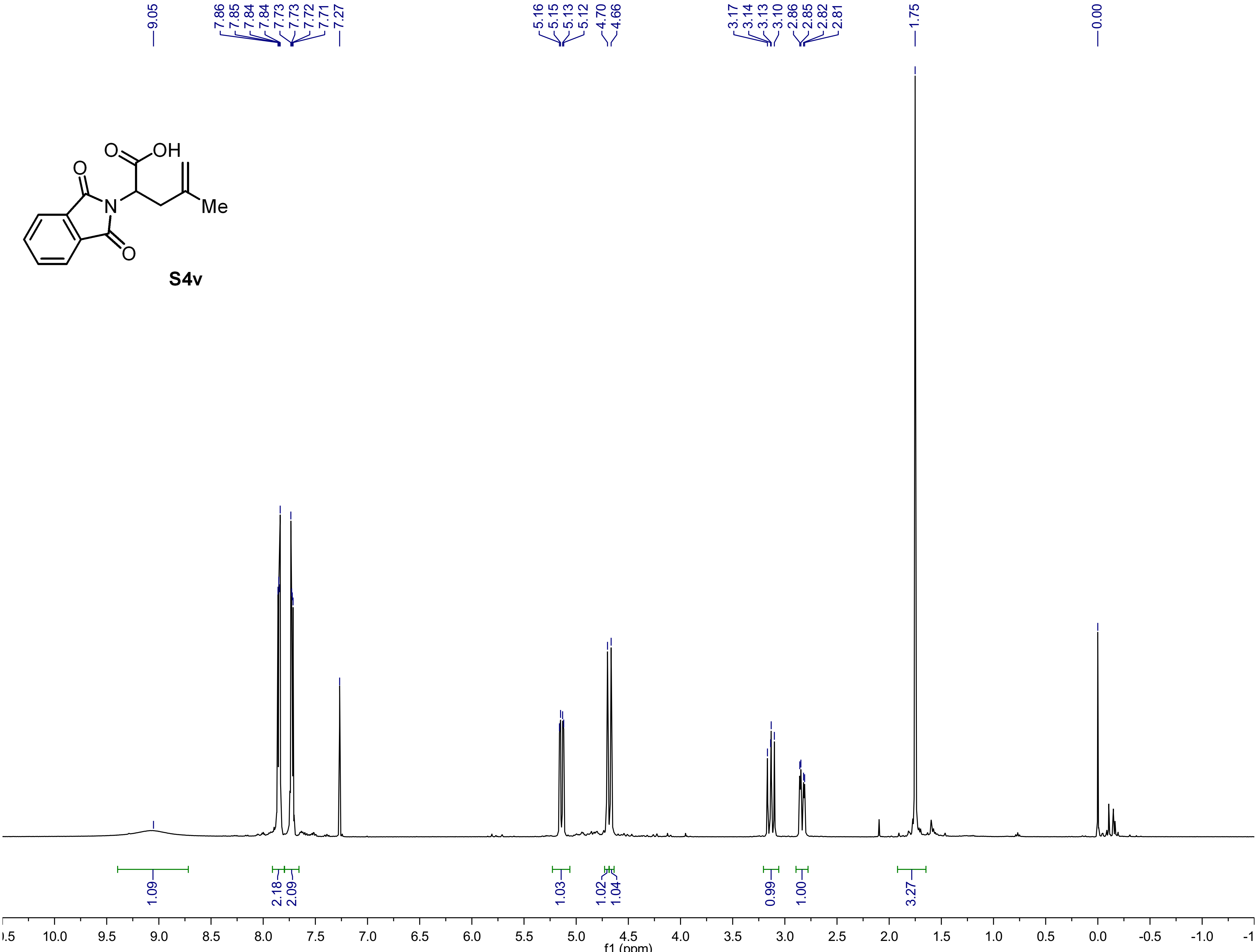

182.86
142.50
112.48
77.25
77.00
76.75
41.52
37.61
22.08
16.54
O
OH
Me
Me
S4t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

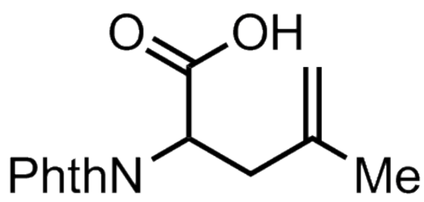

O
OH
Me
Ph
Me

S4u

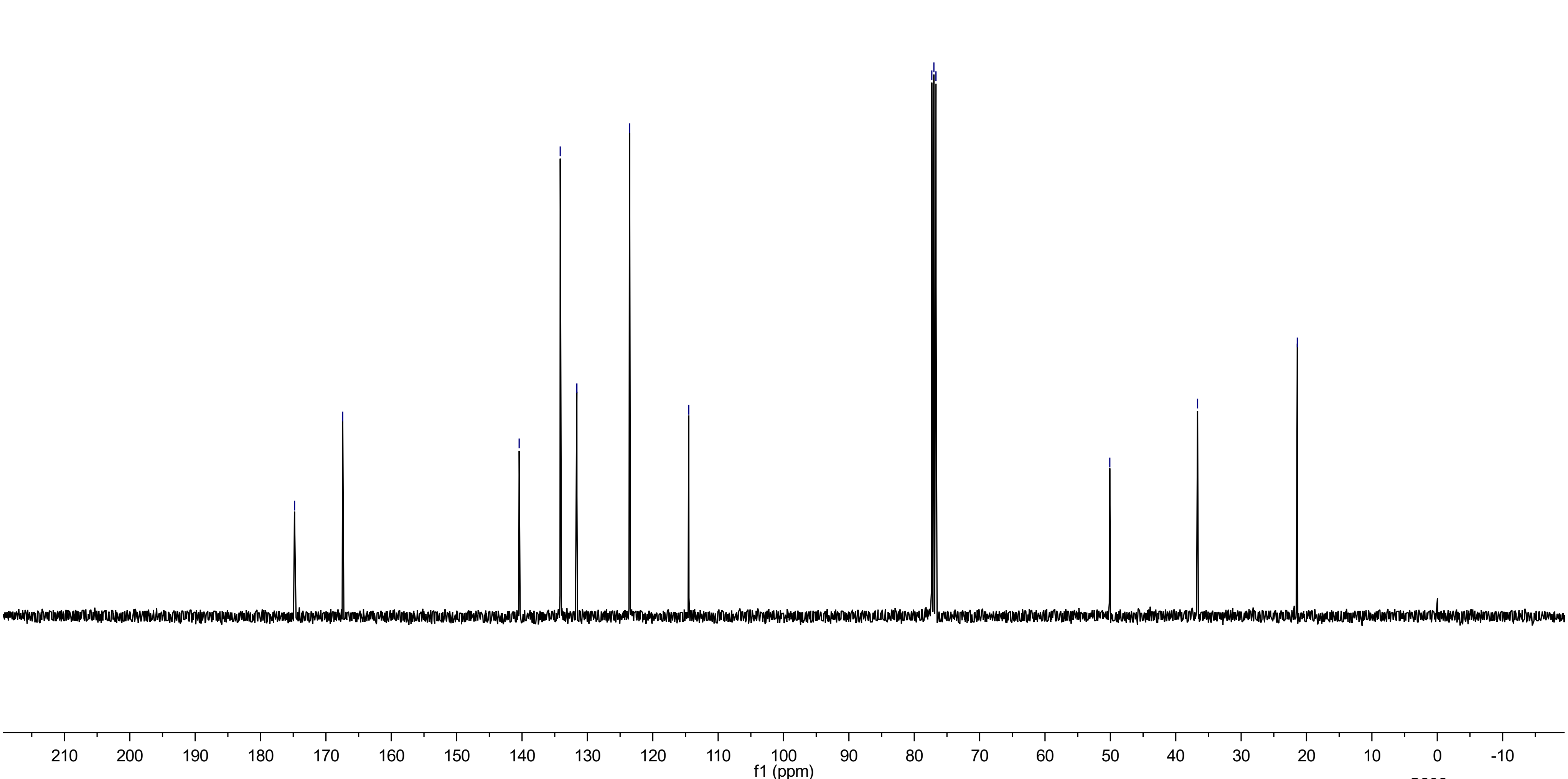

7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.34
7.33
7.33
7.32
7.31
7.27
7.27
7.27
7.26
7.25
7.25
7.24
4.83
4.82
4.82
4.82
4.82
4.81
4.66
4.66
2.95
2.92
2.66
2.63
1.57
1.47
0.00
2.07
2.03
1.21
1.00
1.02
0.92
0.98
3.03
3.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

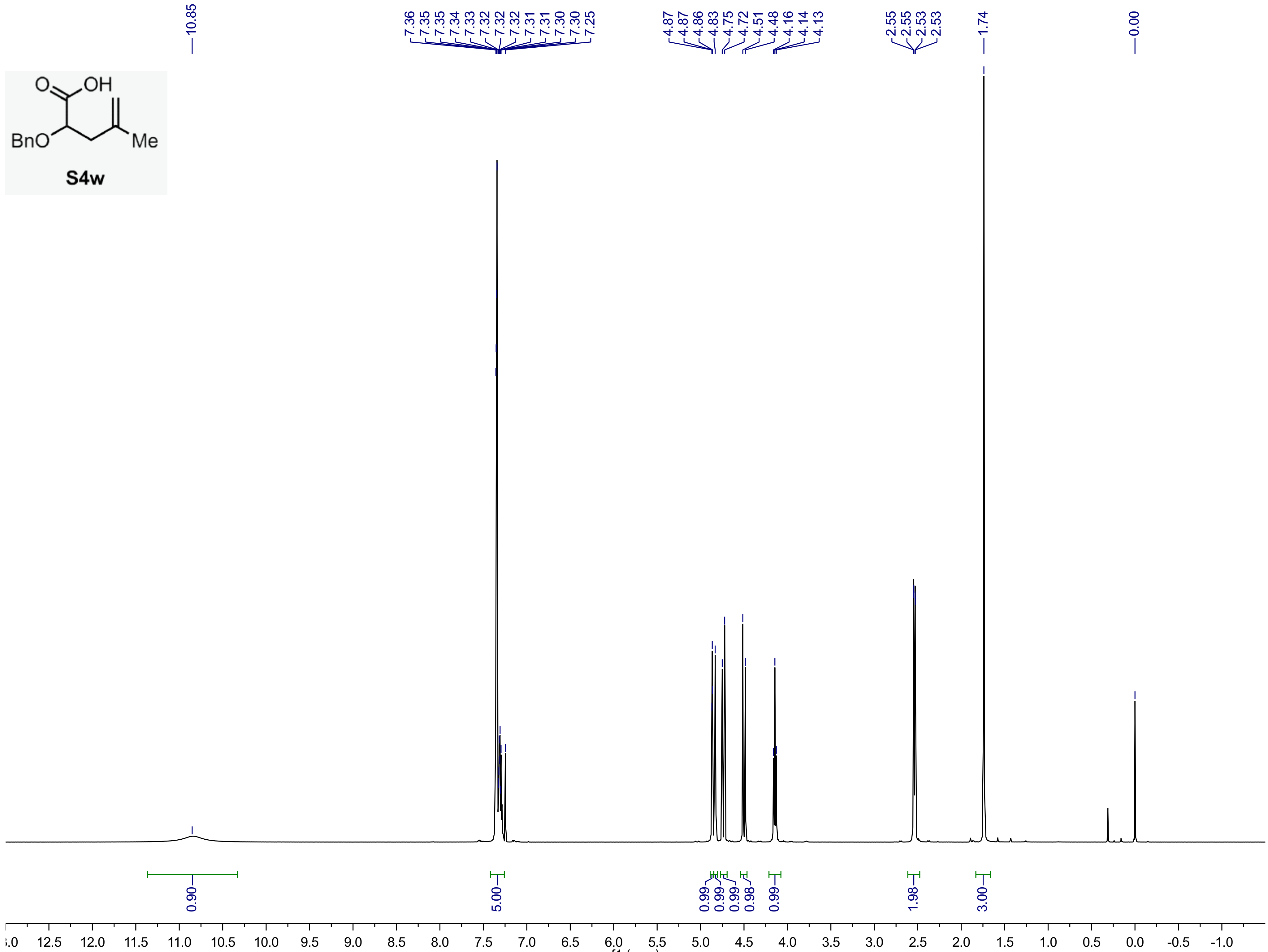

182.41
142.87
141.85
128.38
127.06
126.25
115.43
77.25
77.00
76.75
49.23
46.78
23.76
21.69
O
OH
Me
Ph
Me
S4u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

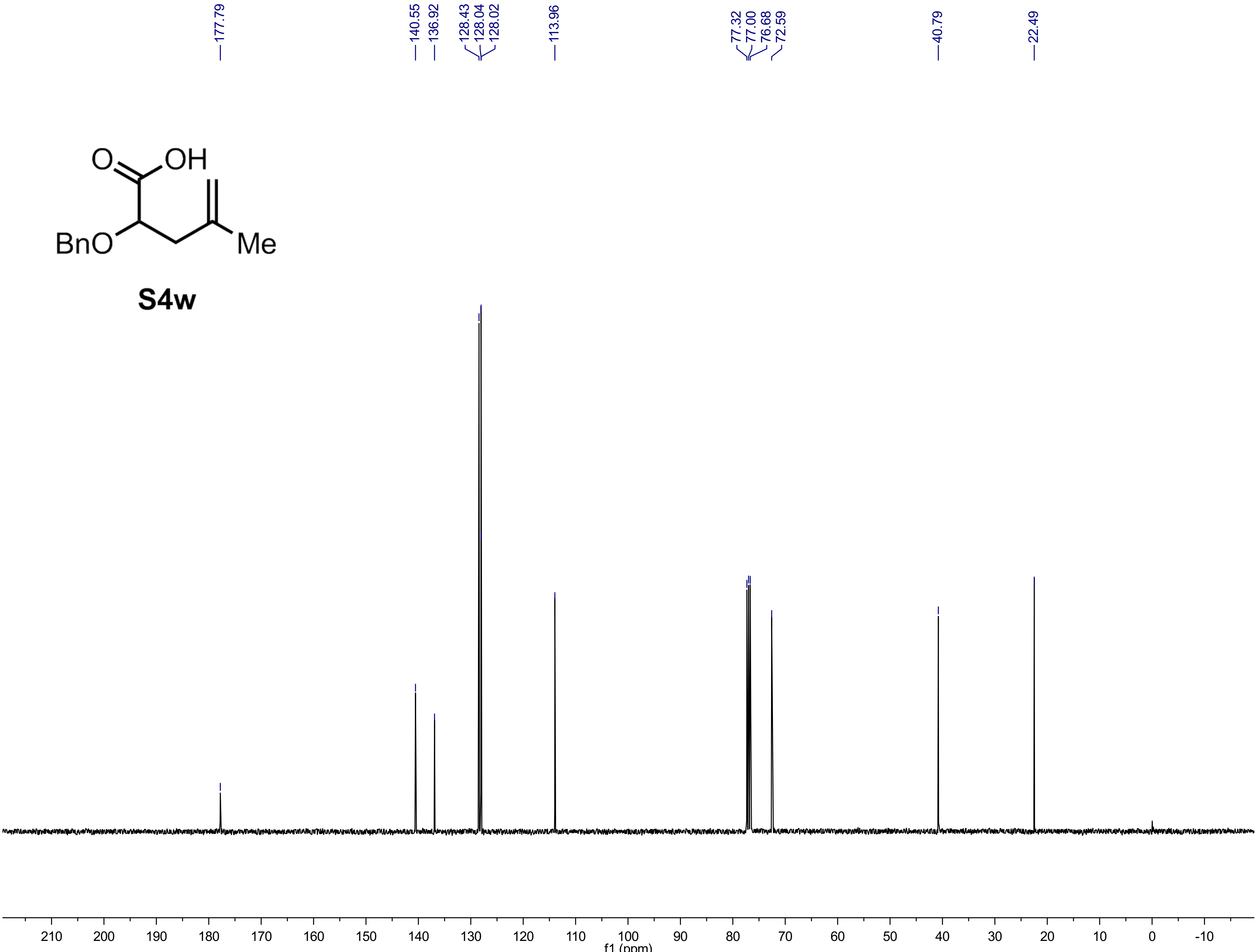

9.05
7.86
7.85
7.84
7.84
7.73
7.73
7.72
7.71
7.27
5.16
5.15
5.13
5.12
4.70
4.66
3.17
3.14
3.13
3.10
2.86
2.85
2.82
2.81
1.75
0.00
O
OH
O
N
Me
O
S4v
1.09
2.18
2.09
1.03
1.02
1.04
0.99
1.00
3.27
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

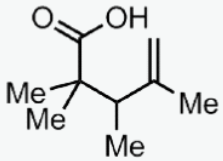


S4v

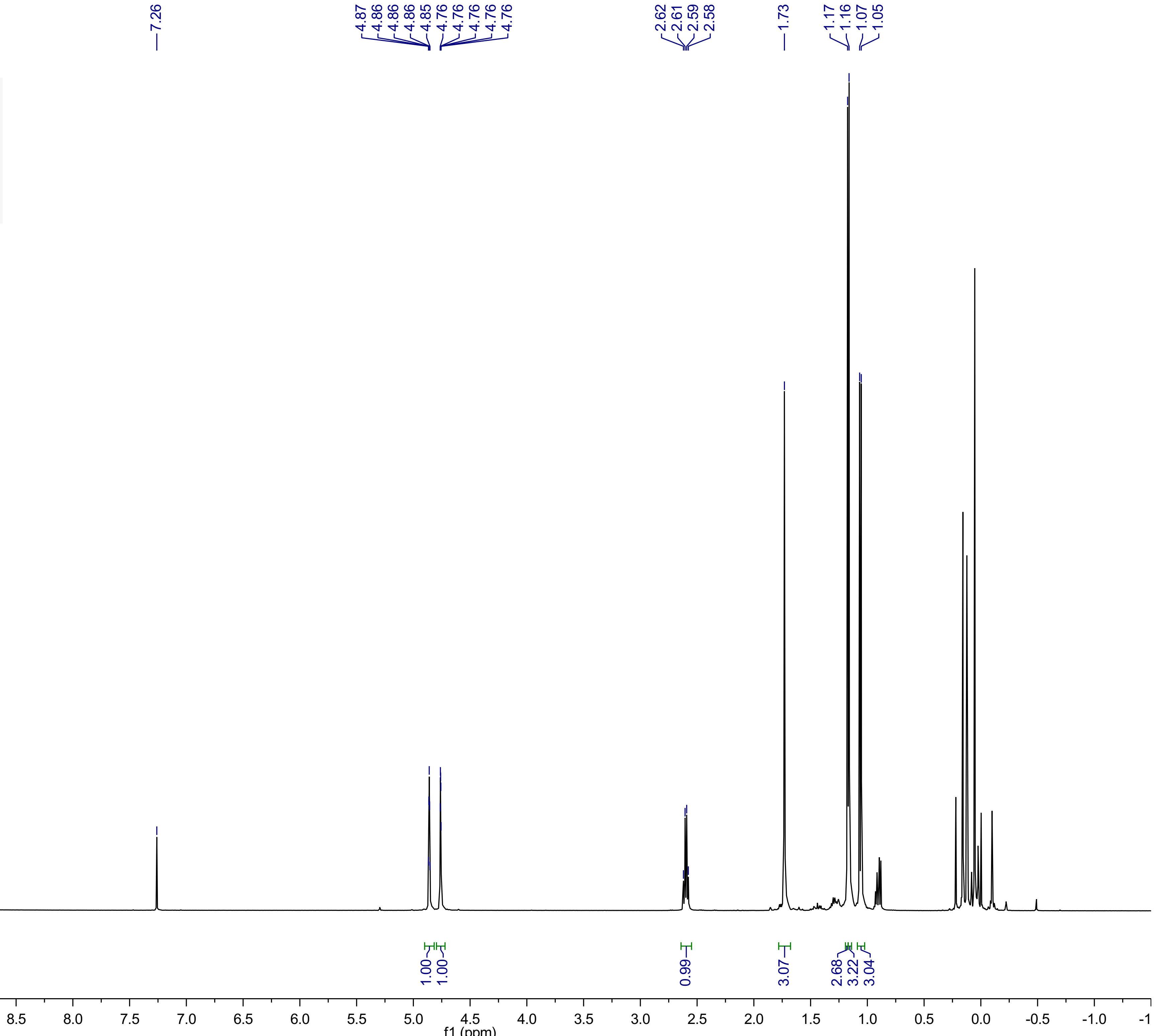

174.80
167.43
140.44
134.16
131.61
123.55
114.50
77.32
77.00
76.68
50.09
36.67
21.41
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

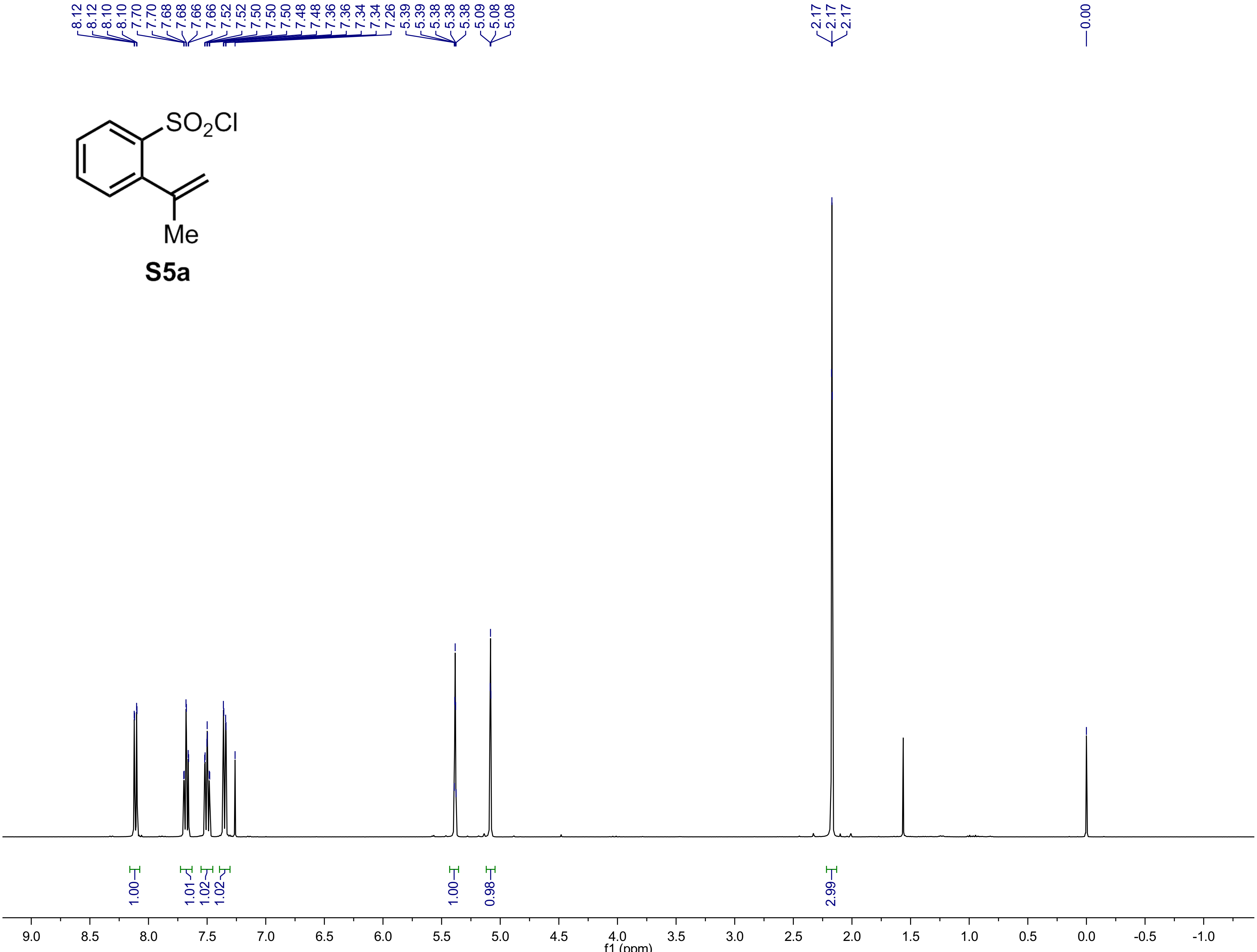

10.85
7.36 7.35 7.35 7.34 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.25
4.87 4.87 4.86 4.83 4.75 4.72 4.51 4.48 4.16 4.14 4.13
2.55 2.55 2.53 2.53
1.74
0.00
OH
O
BnO
Me
S4w
0.90
5.00
0.99 0.99 0.99 0.98
0.99
1.98
3.00
f1 (ppm)

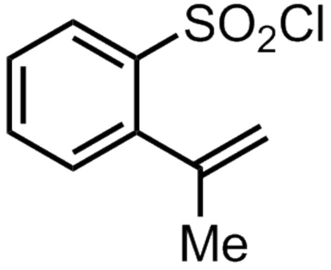

177.79
140.55
136.92
128.43
128.04
128.02
113.96
77.32
77.00
76.68
72.59
40.79
22.49
O
OH
BnO
Me
S4w
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
OH
Me
Me
Me
Me

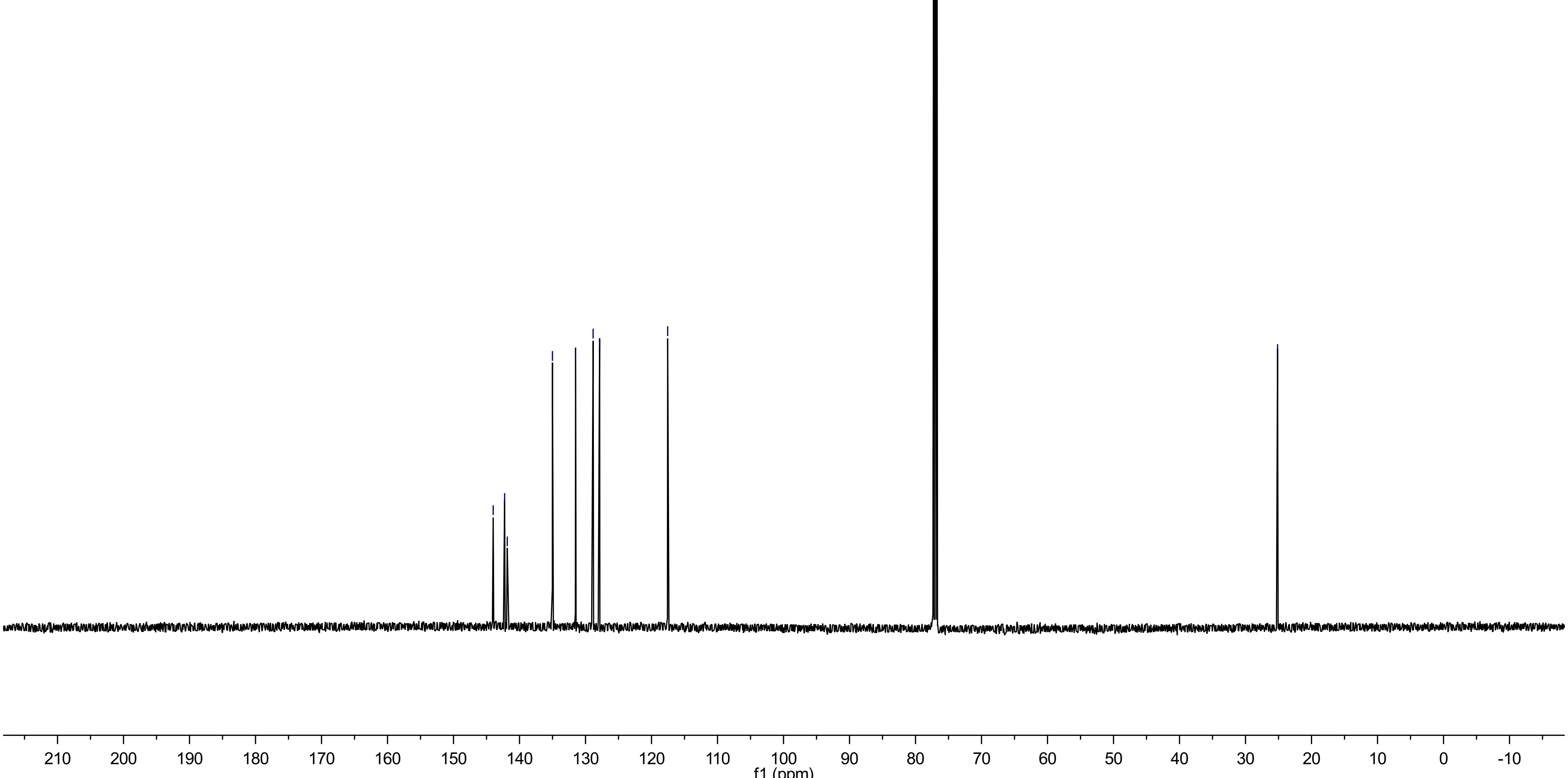
S4x

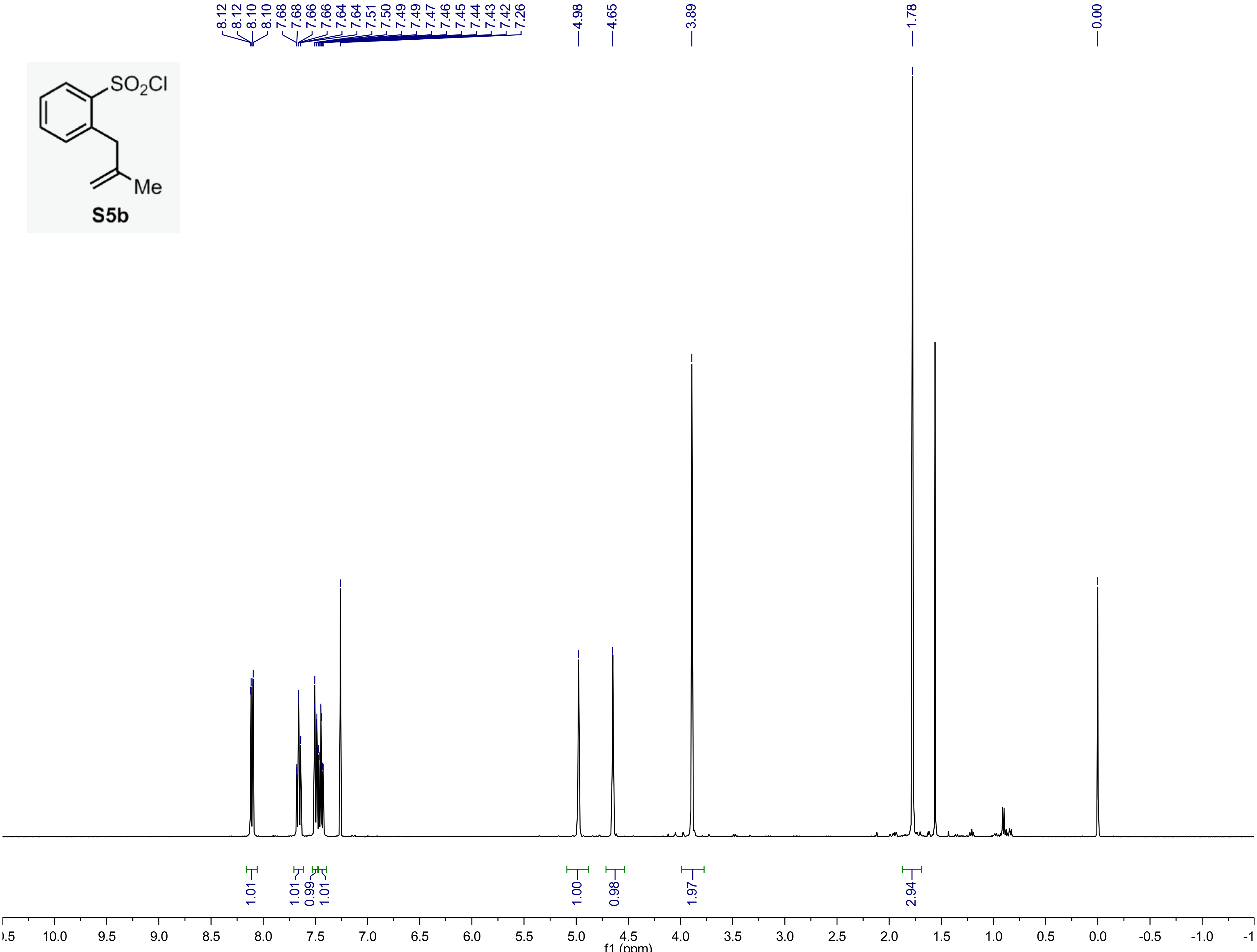

7.26
4.87
4.86
4.86
4.86
4.85
4.76
4.76
4.76
4.76
4.76
2.62
2.61
2.59
2.58
1.73
1.17
1.16
1.07
1.05
1.00
1.00
0.99
3.07
2.68
3.22
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


SO2Cl
Me
S5a
8.12 8.12 8.10 8.10 7.70 7.70 7.68 7.68 7.66 7.66 7.52 7.52 7.50 7.50 7.50 7.48 7.48 7.36 7.36 7.34 7.34 7.26 5.39 5.39 5.38 5.38 5.38 5.09 5.08 5.08
2.17 2.17 2.17
0.00
1.00 1.01 1.02 1.02 1.00 0.98 2.99
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 -0.5 -1.0
f1 (ppm)

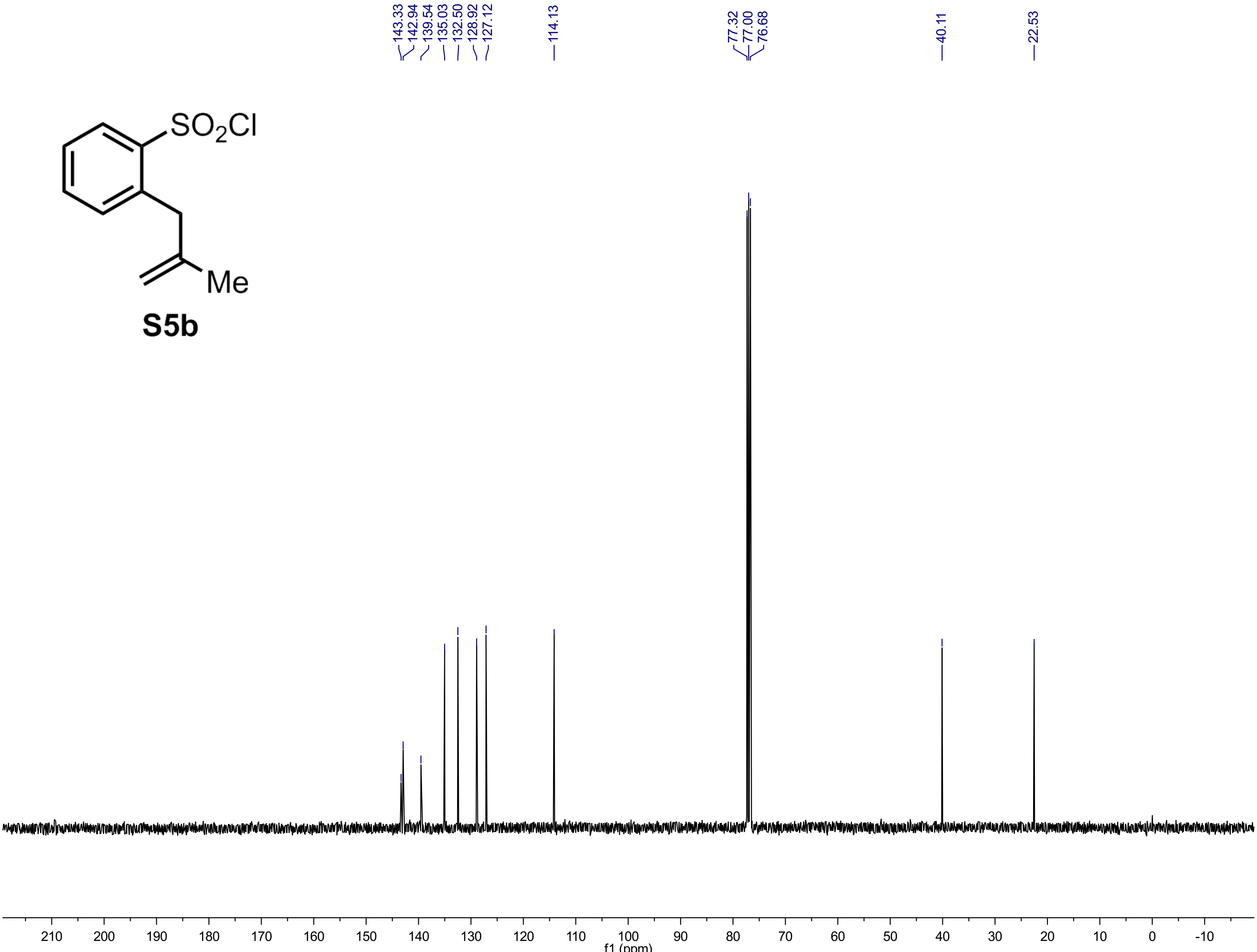

SO2Cl
Me

S5a

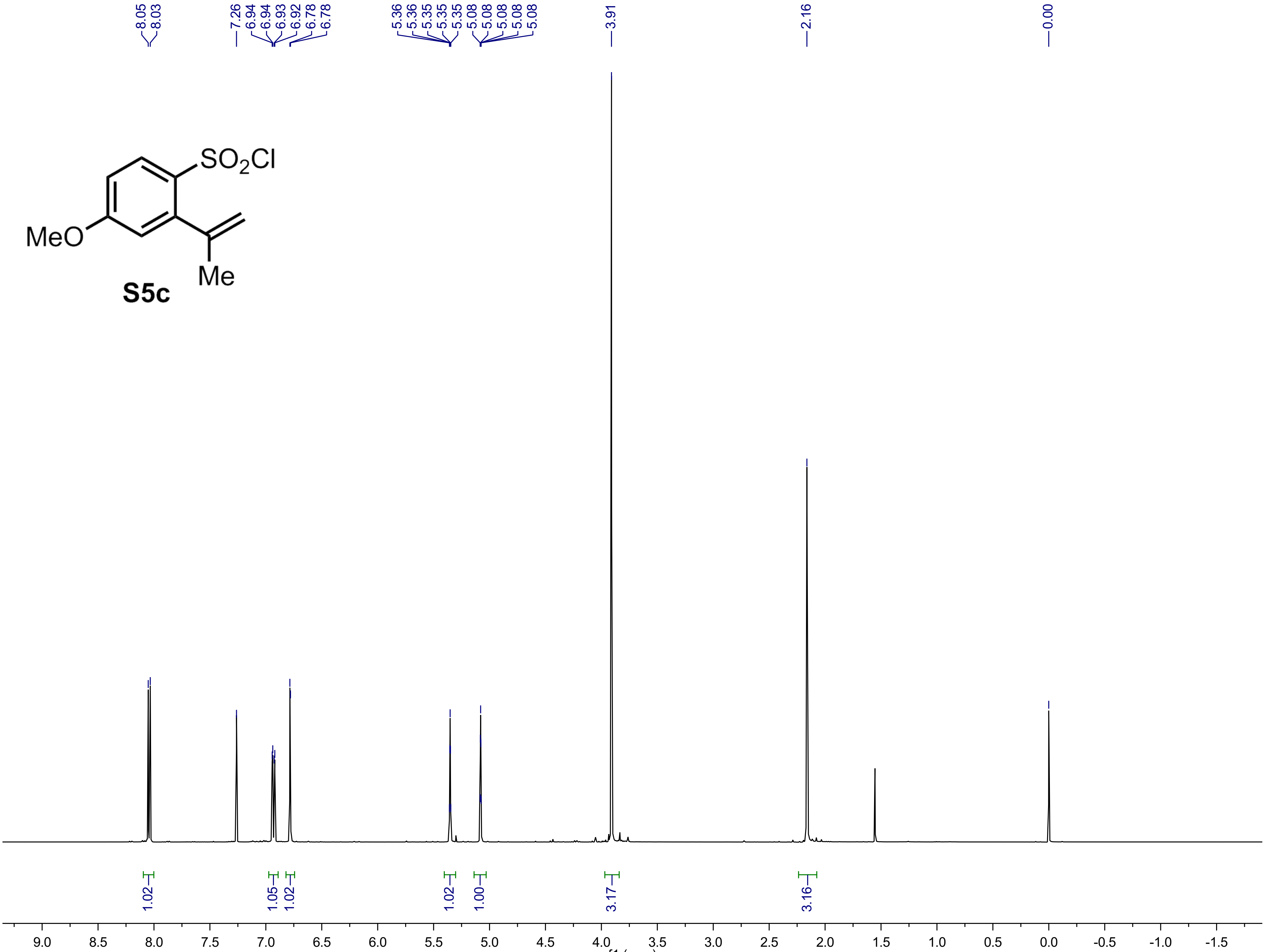

143.99
142.26
141.86
135.01
131.50
128.85
127.86
117.55
77.25
77.00
76.75
25.14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



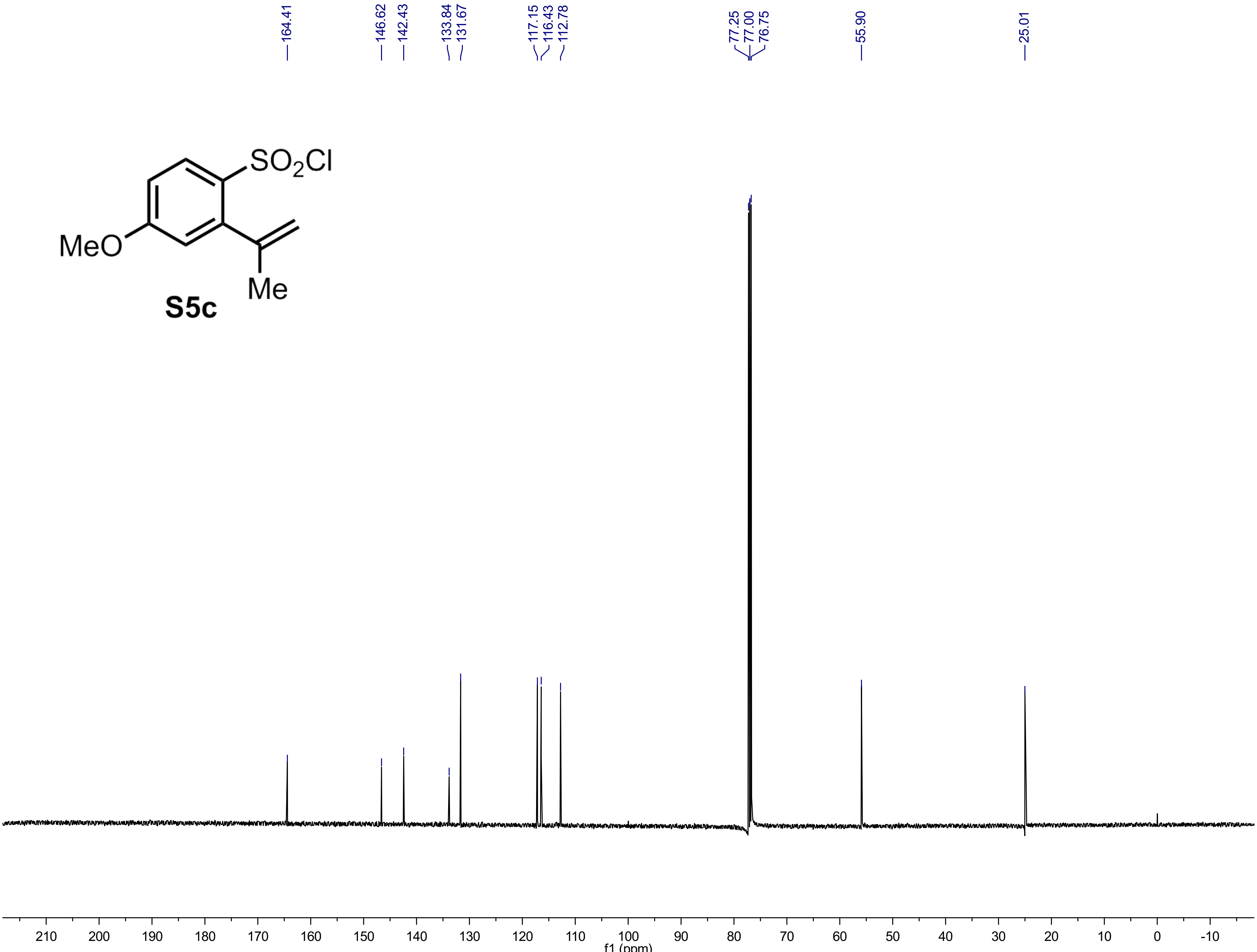
8.12
8.12
8.10
8.10
7.68
7.68
7.66
7.66
7.64
7.64
7.51
7.50
7.49
7.49
7.47
7.46
7.45
7.44
7.43
7.42
7.26
4.98
4.65
3.89
1.78
0.00
SO2Cl
Me
S5b
1.01
1.01
0.99
1.01
1.00
0.98
1.97
2.94
f1 (ppm)



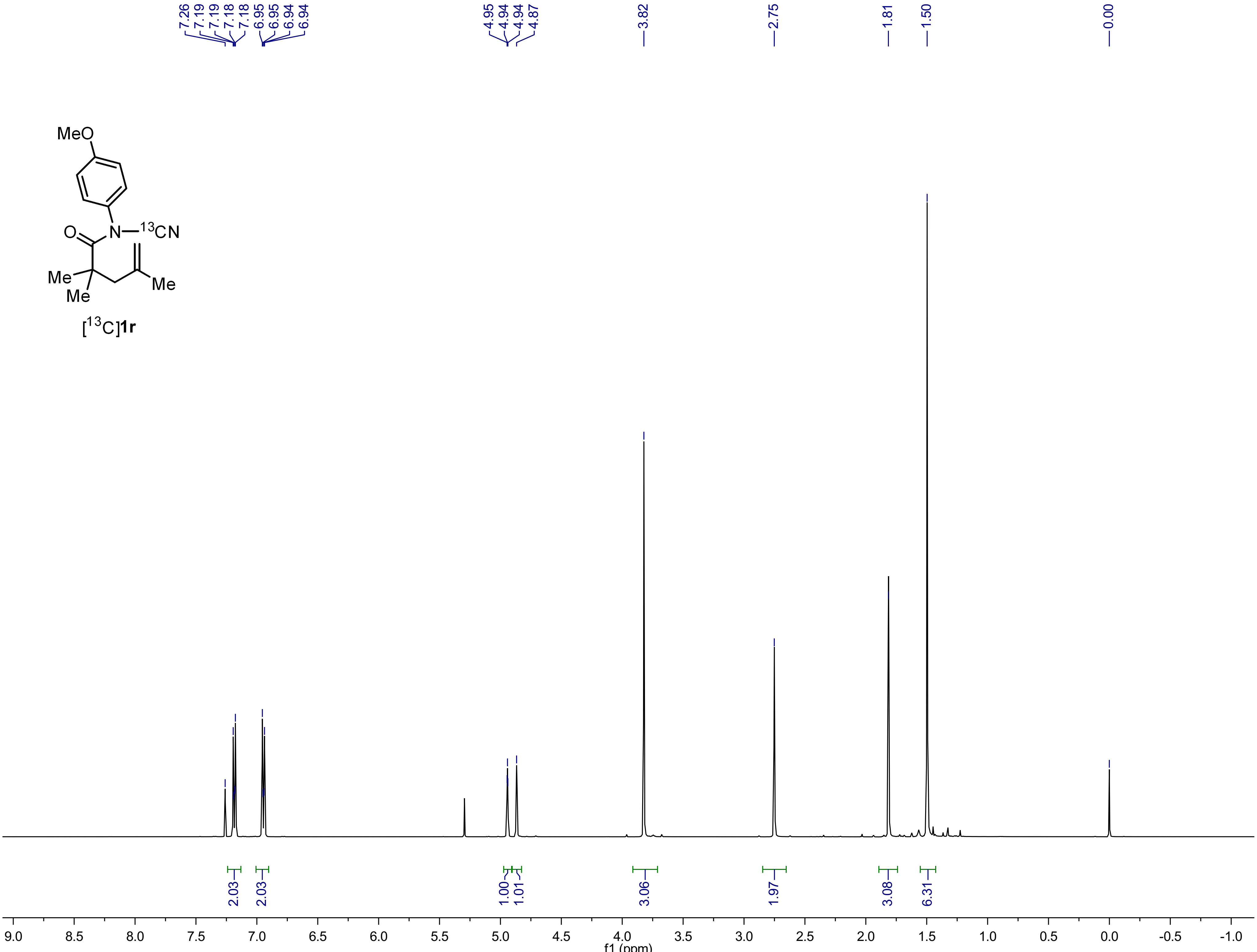
SO2Cl
Me
S5b
143.33
142.94
139.54
135.03
132.50
128.92
127.12
114.13
77.32
77.00
76.68
40.11
22.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



8.05
8.03
7.26
6.94
6.94
6.93
6.92
6.78
6.78
5.36
5.36
5.35
5.35
5.35
5.08
5.08
5.08
5.08
5.08
3.91
2.16
0.00
SO2Cl
MeO
Me
S5c
1.02
1.05
1.02
1.02
1.00
3.17
3.16
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 -0.5 -1.0 -1.5
f1 (ppm)

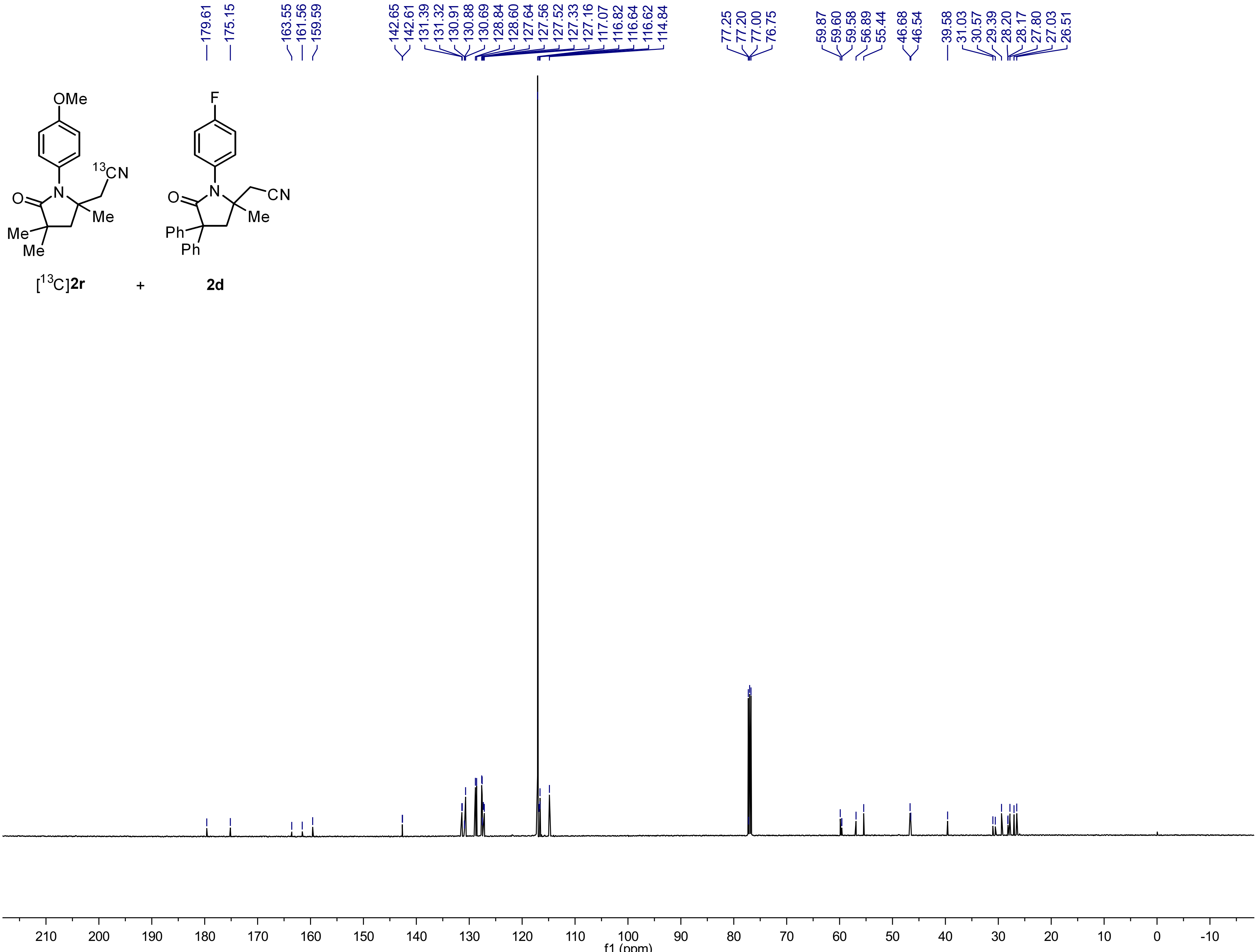


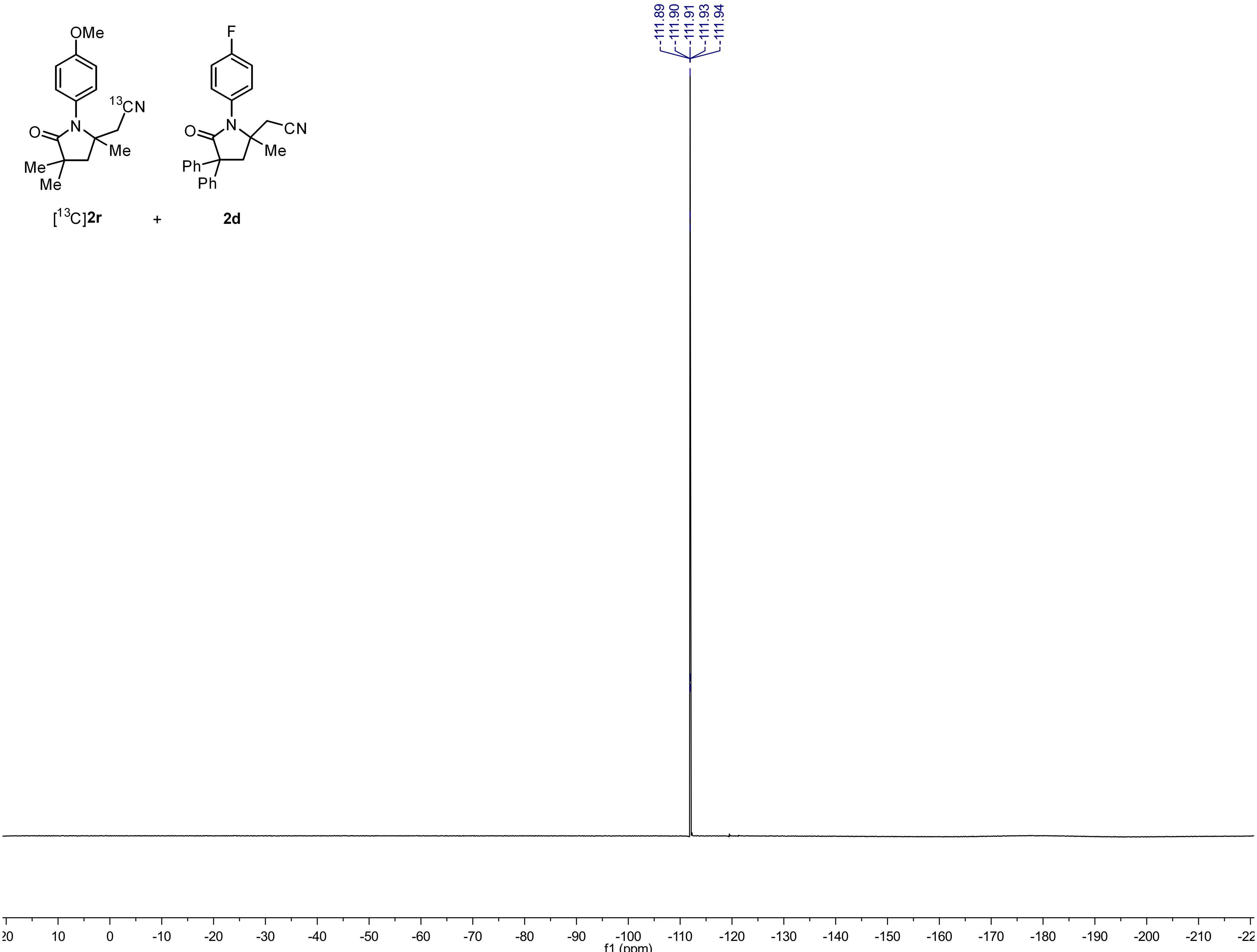
164.41
146.62
142.43
133.84
131.67
117.15
116.43
112.78
77.25
77.00
76.75
55.90
25.01
SO2Cl
MeO
Me
S5c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

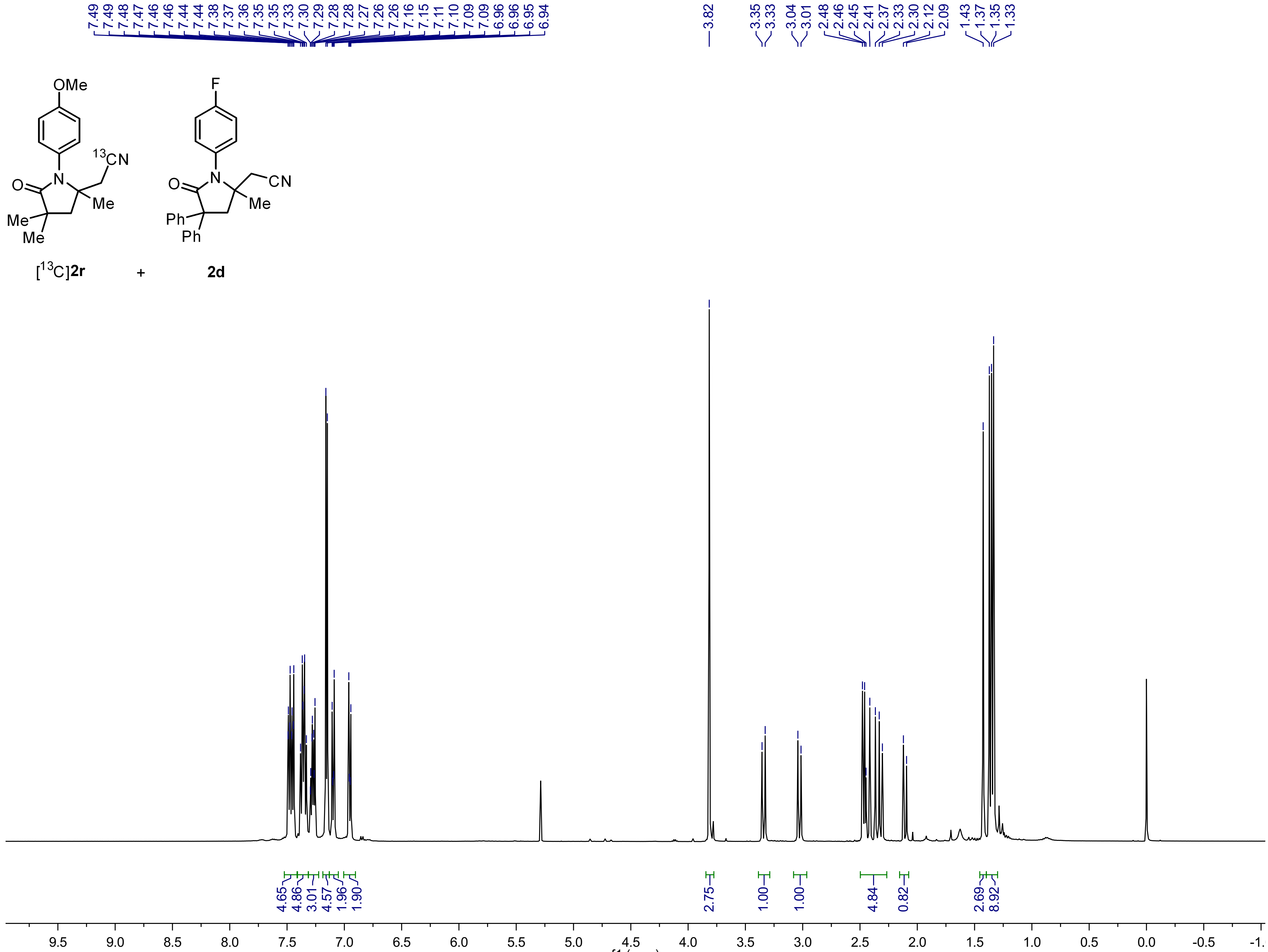


7.26
7.19
7.19
7.18
7.18
6.95
6.95
6.94
6.94
4.95
4.94
4.94
4.87
3.82
2.75
1.81
1.50
0.00
MeO
O
N
^{13}CN
Me
Me
Me
2.03
2.03
1.00
1.01
3.06
1.97
3.08
6.31
f1 (ppm)

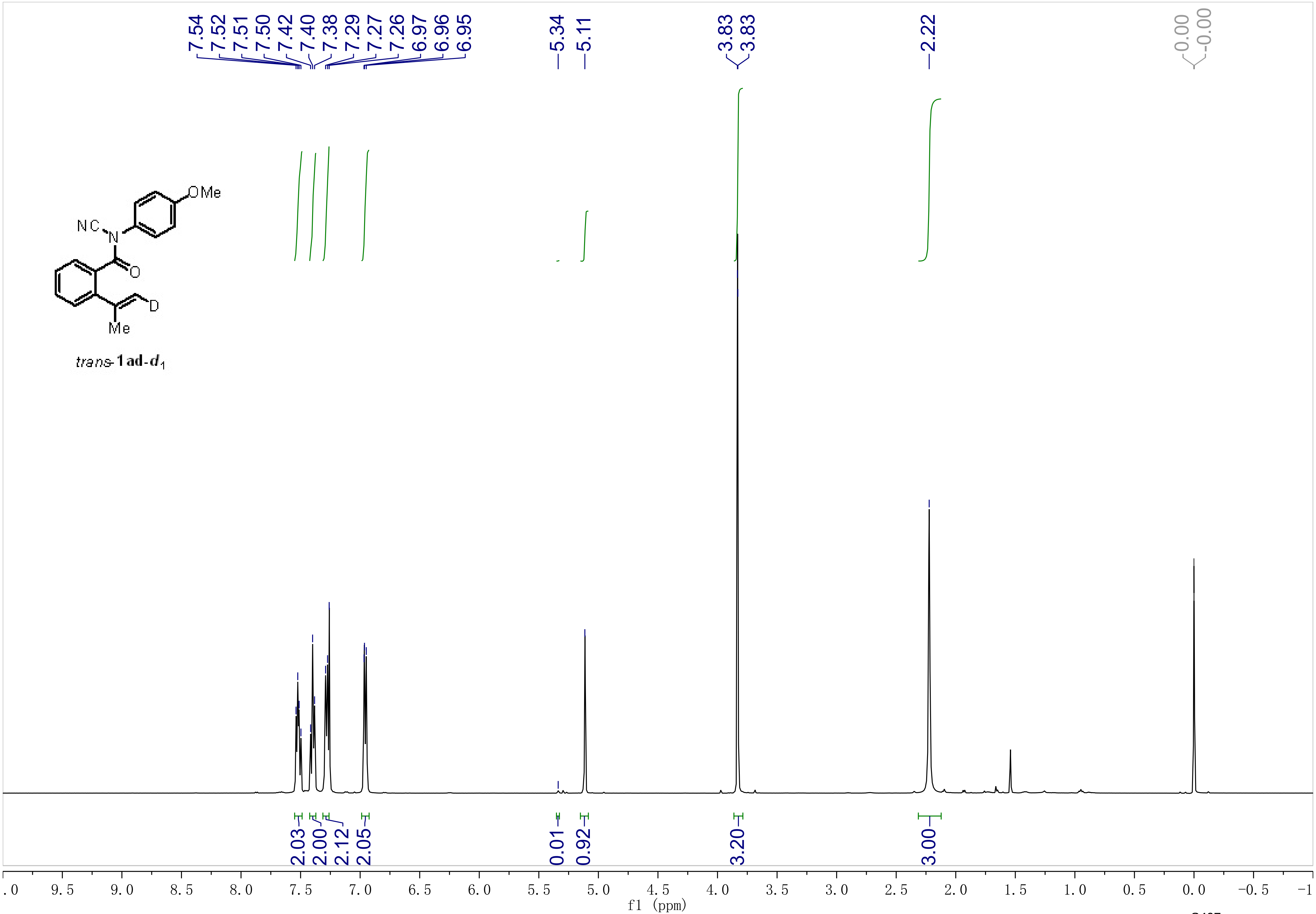
[^{13}C]**1r**


179.61
175.15
163.55
161.56
159.59
142.65
142.61
131.39
131.32
130.91
130.88
130.69
128.84
128.60
127.64
127.56
127.52
127.33
127.16
117.07
116.82
116.64
116.62
114.84
77.25
77.20
77.00
76.75
59.87
59.60
59.58
56.89
55.44
46.68
46.54
39.58
31.03
30.57
29.39
28.20
28.17
27.80
27.03
26.51
OMe
13CN
O
N
Me
Me
Me
F
O
N
CN
Me
Ph
Ph
[13C]2r
+
2d
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)


OMe
^{13}CN
O
N
Me
Me
Me
F
CN
Ph
Ph
[^{13}C]**2r** + **2d**
-111.89
-111.90
-111.91
-111.93
-111.94
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

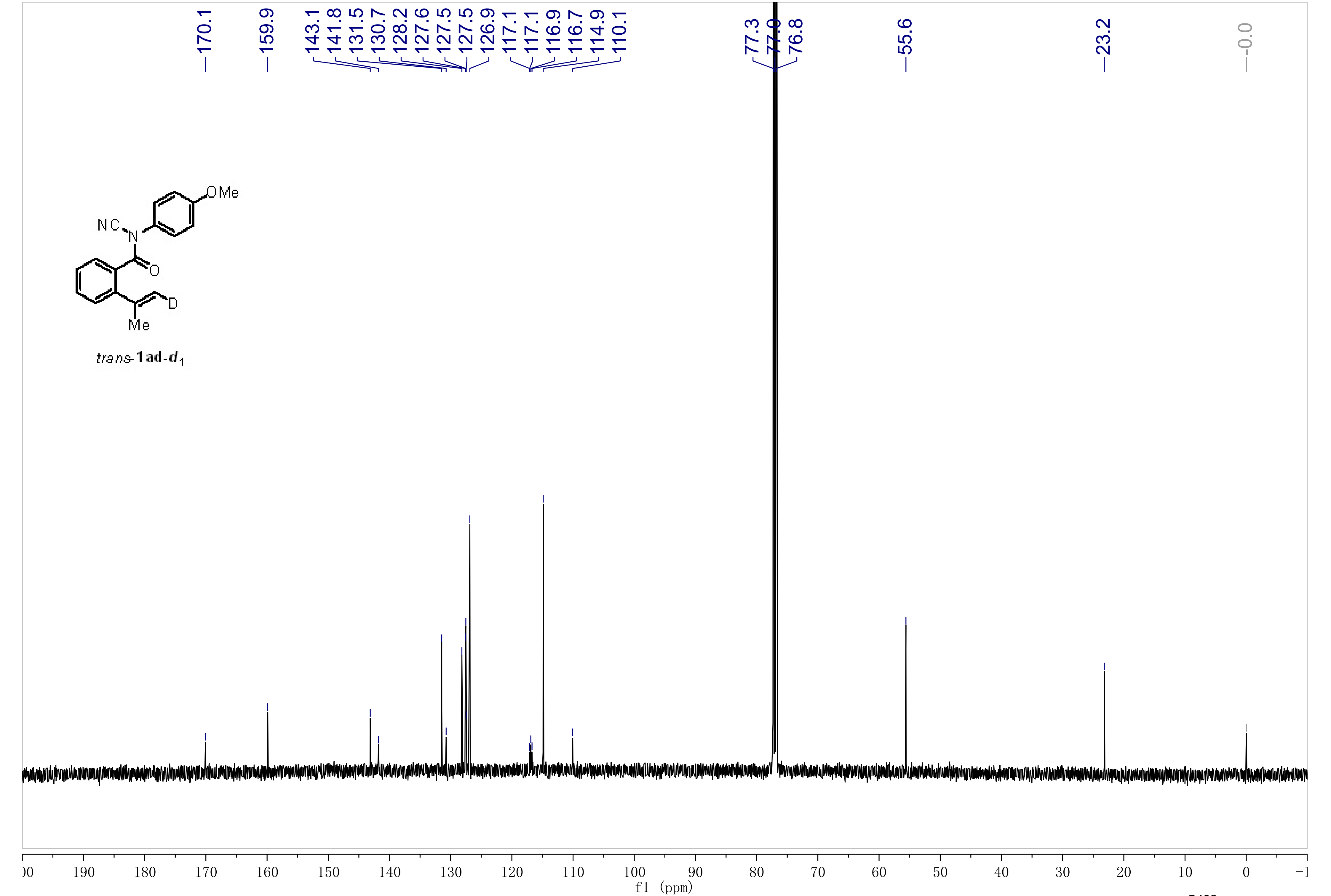


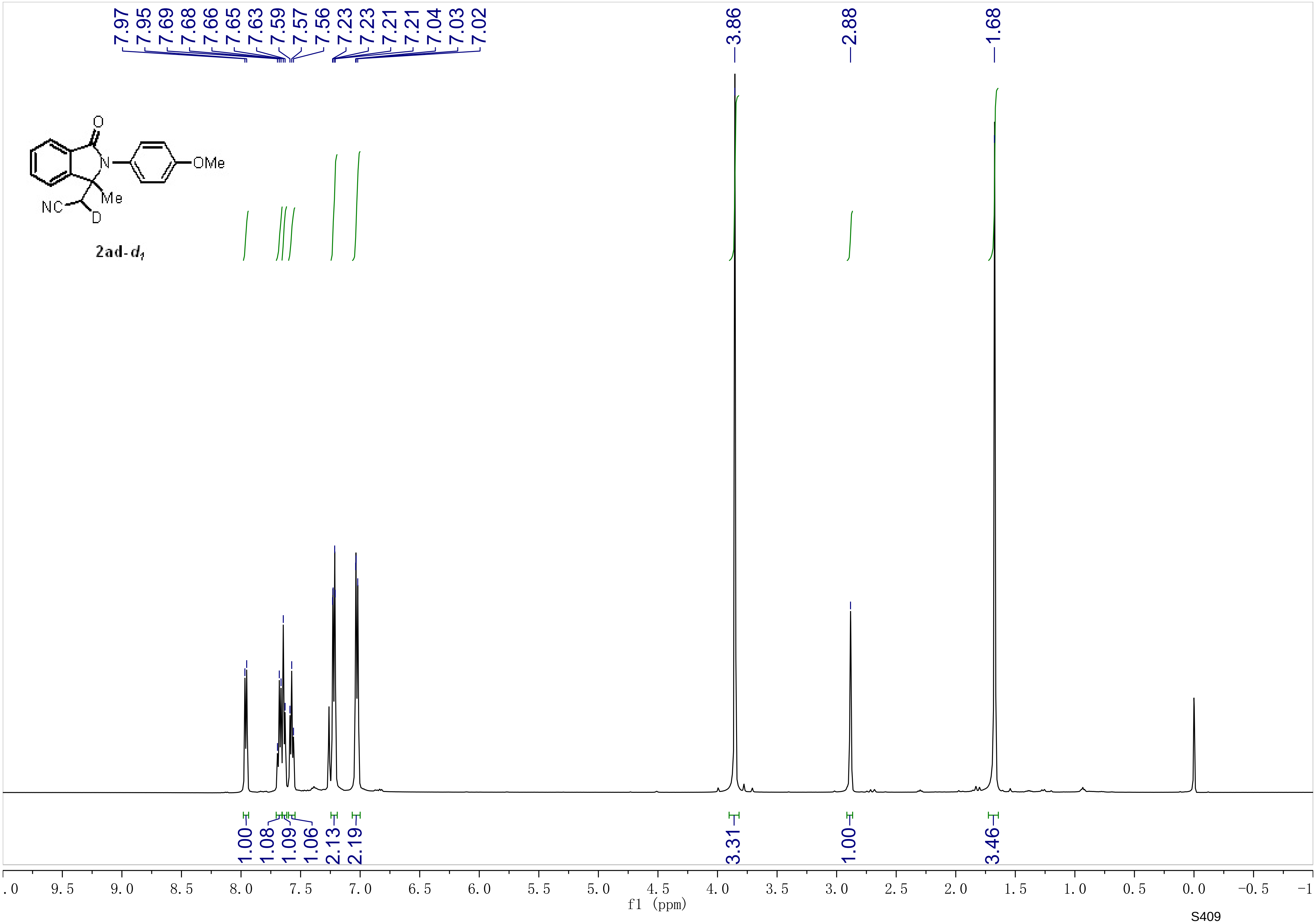
7.49 7.49 7.48 7.47 7.46 7.46 7.44 7.44 7.38 7.37 7.36 7.35 7.35 7.33 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.16 7.15 7.11 7.10 7.09 6.96 6.96 6.95 6.94
3.82
3.35 3.33 3.04 3.01 2.48 2.46 2.45 2.41 2.37 2.33 2.30 2.12 2.09
1.43 1.37 1.35 1.33
OMe
F
13CN
CN
O
N
Me
Ph
[13C]2r
+
2d
4.65 4.86 3.01 4.57 1.96 1.90
2.75
1.00
1.00
4.84
0.82
2.69 8.92
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 -0.5
f1 (ppm)

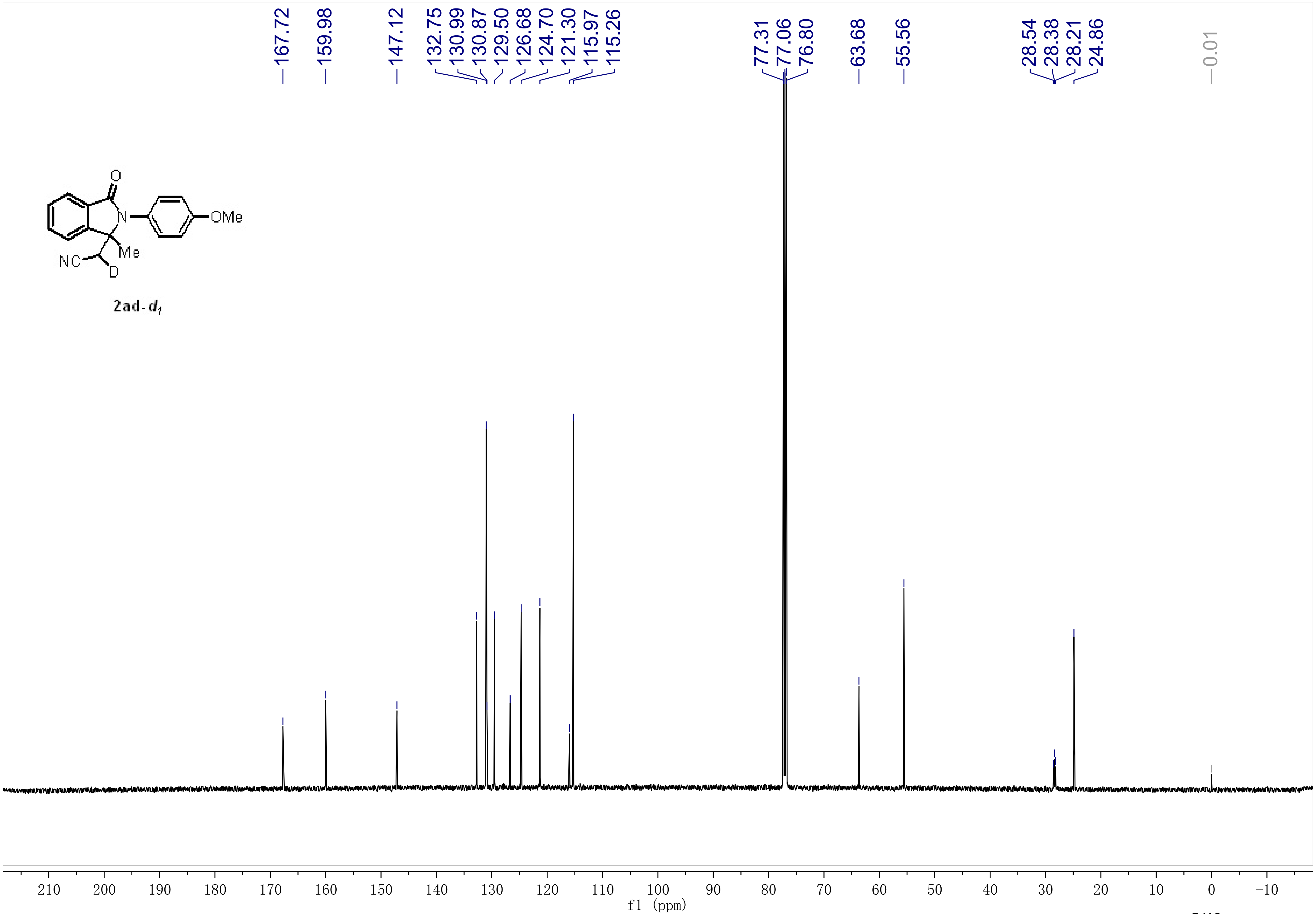


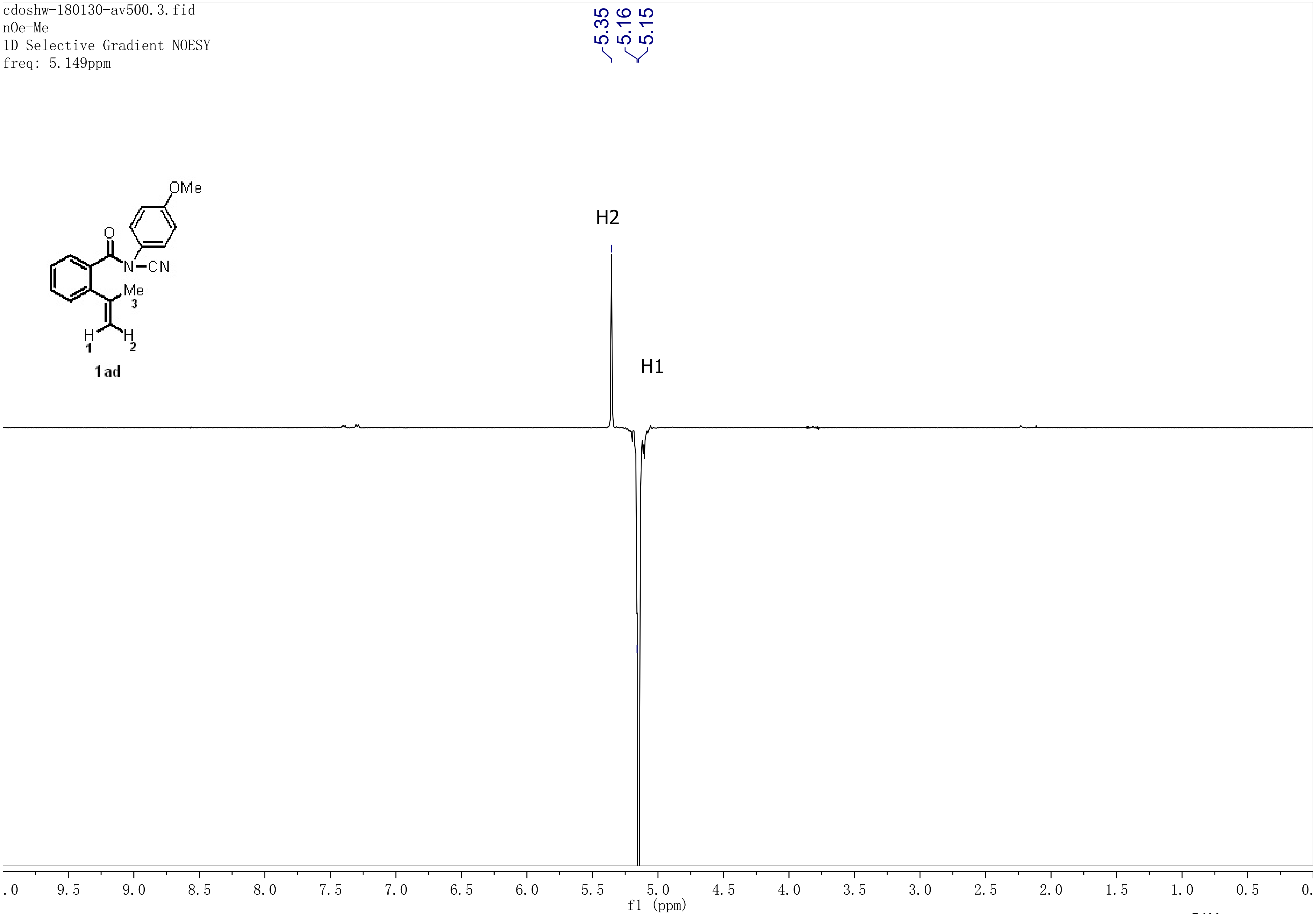
7.54
7.52
7.51
7.50
7.42
7.40
7.38
7.29
7.27
7.26
6.97
6.96
6.95
5.34
5.11
3.83
3.83
2.22
0.00
-0.00
2.03
2.00
2.12
2.05
0.01
0.92
3.20
3.00
NC
N
OMe
O
D
Me
f1 (ppm)

trans-**1ad**-d_1

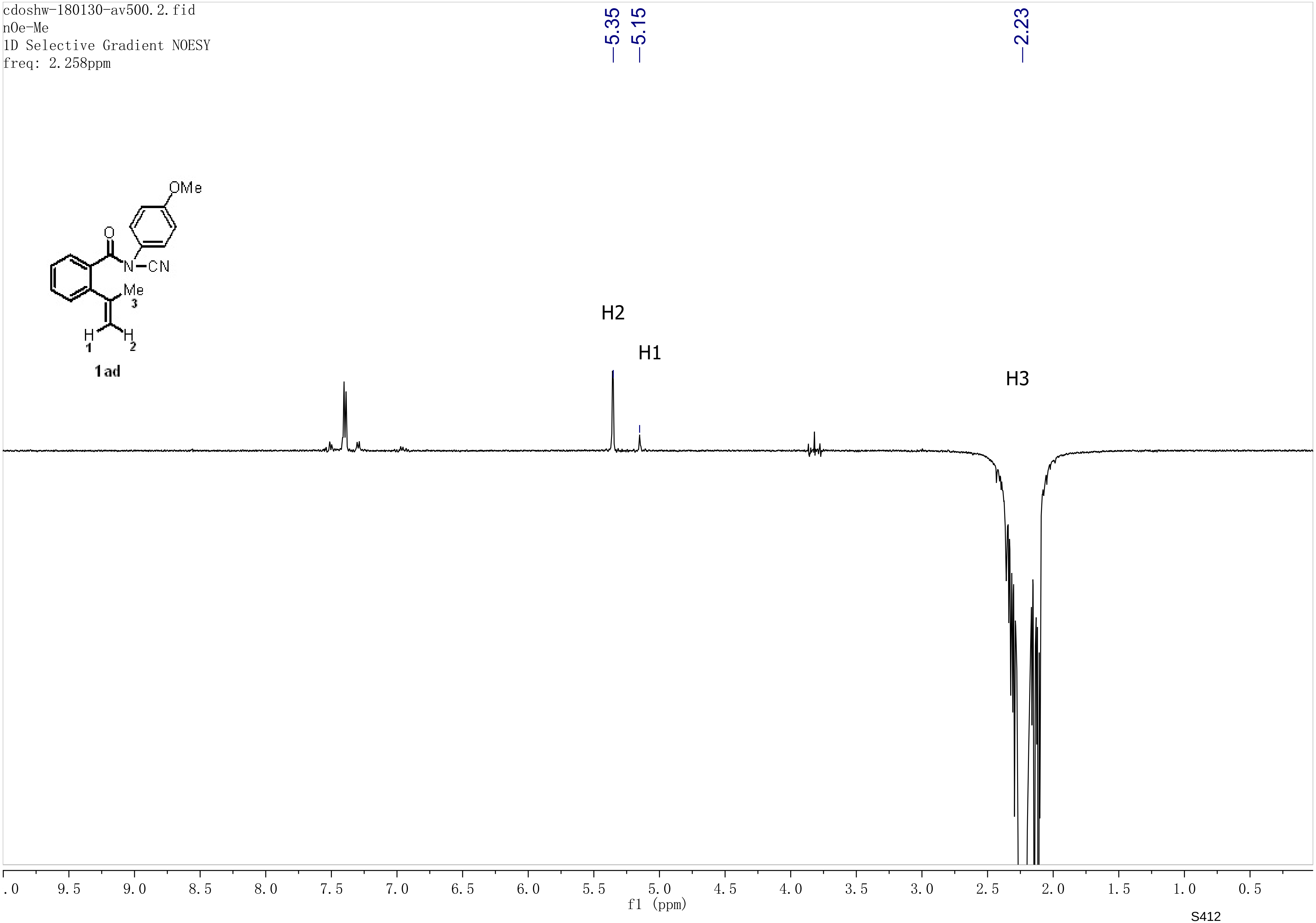

170.1
159.9
143.1
141.8
131.5
130.7
128.2
127.6
127.5
127.5
126.9
117.1
117.1
116.9
116.7
114.9
110.1
77.3
77.0
76.8
55.6
23.2
0.0
NC
N
OMe
O
D
Me
trans-**1ad**-d_1
f1 (ppm)

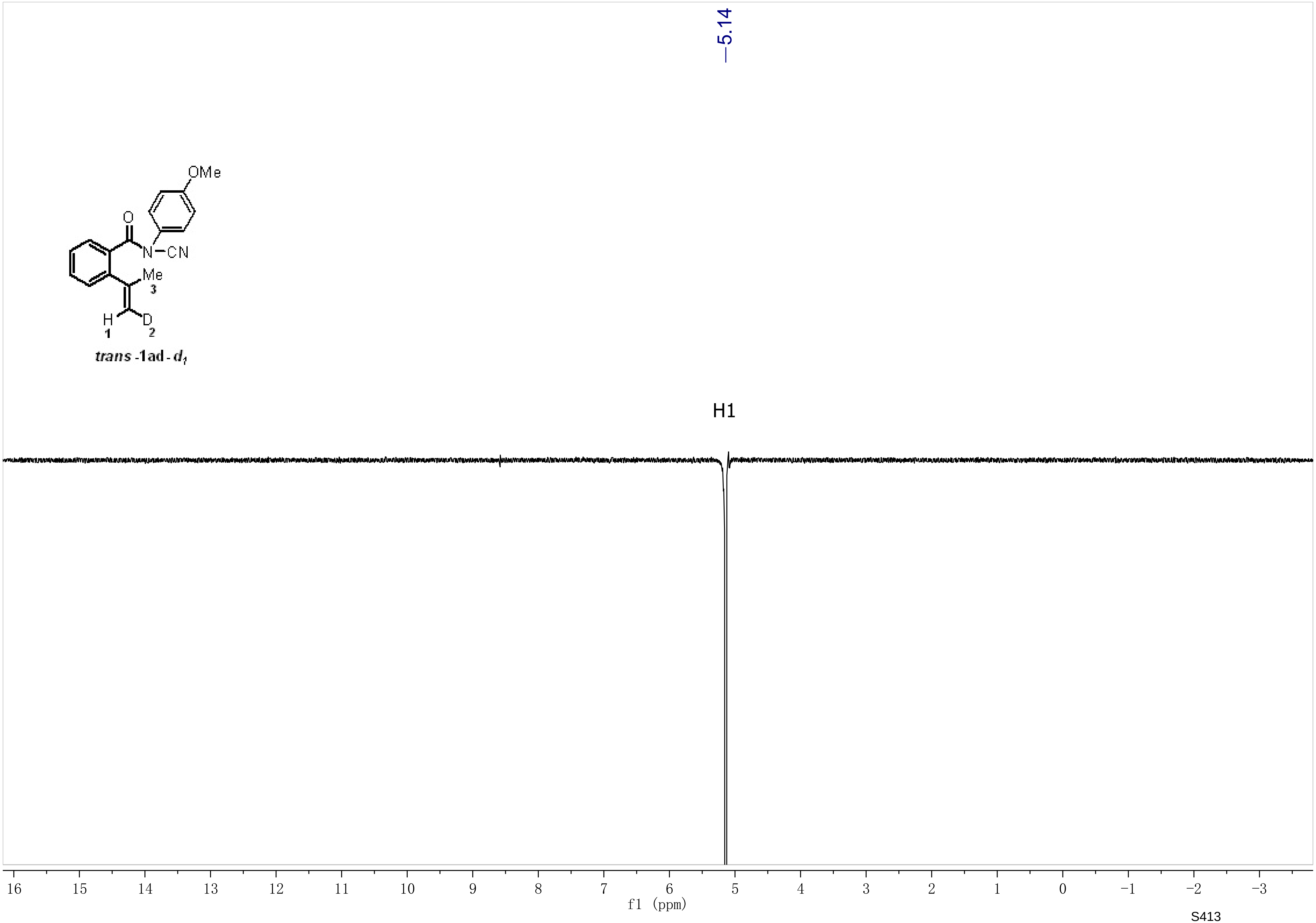

7.97 7.95 7.69 7.68 7.66 7.65 7.63 7.59 7.57 7.56 7.23 7.23 7.21 7.21 7.04 7.03 7.02
3.86
2.88
1.68
O
N
OMe
Me
NC
D
2ad-d_1
1.00 1.08 1.09 1.06 2.13 2.19
3.31
1.00
3.46
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

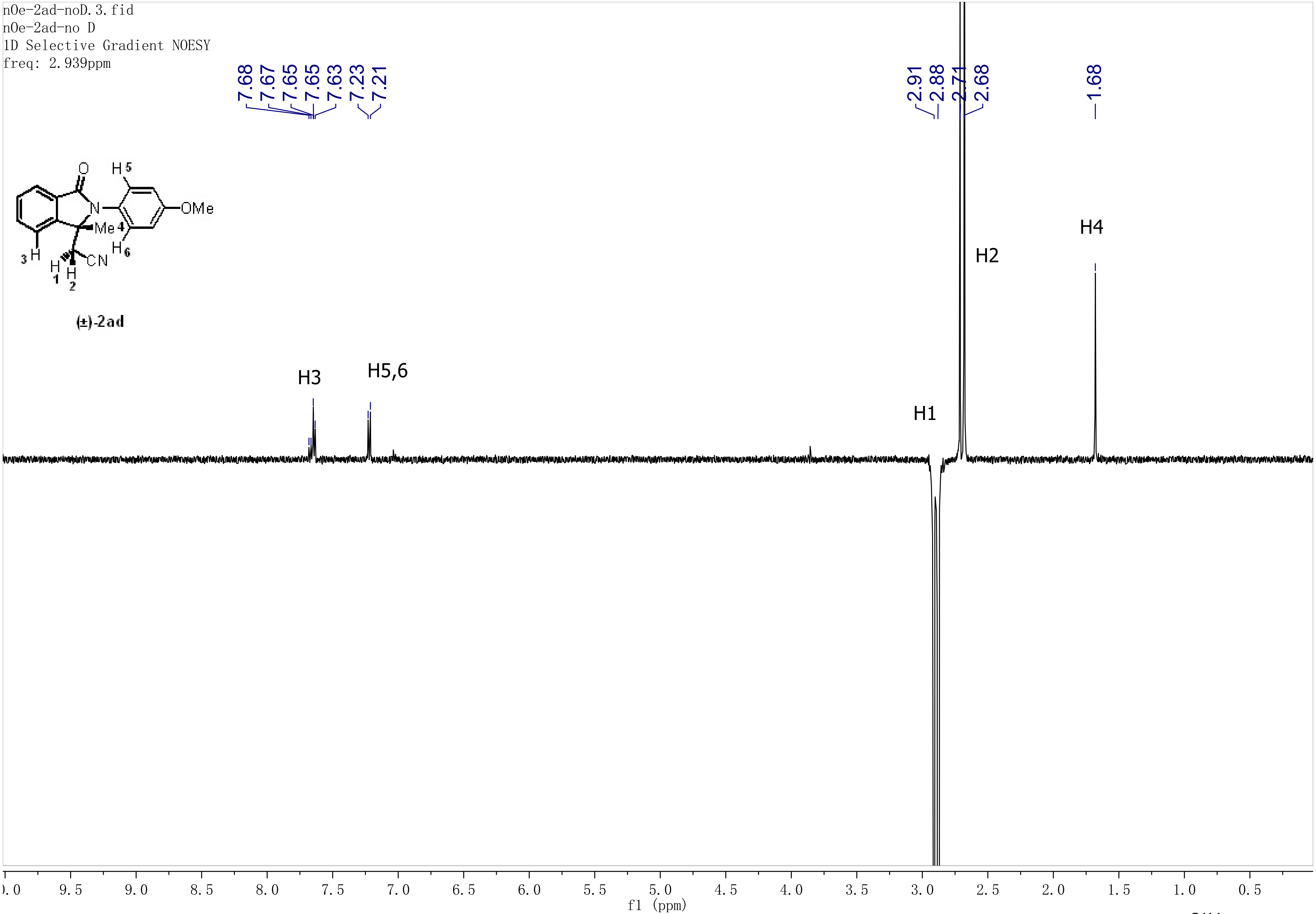

167.72
159.98
147.12
132.75
130.99
130.87
129.50
126.68
124.70
121.30
115.97
115.26
77.31
77.06
76.80
63.68
55.56
28.54
28.38
28.21
24.86
-0.01
O
N
OMe
Me
NC
D
2ad-d_1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

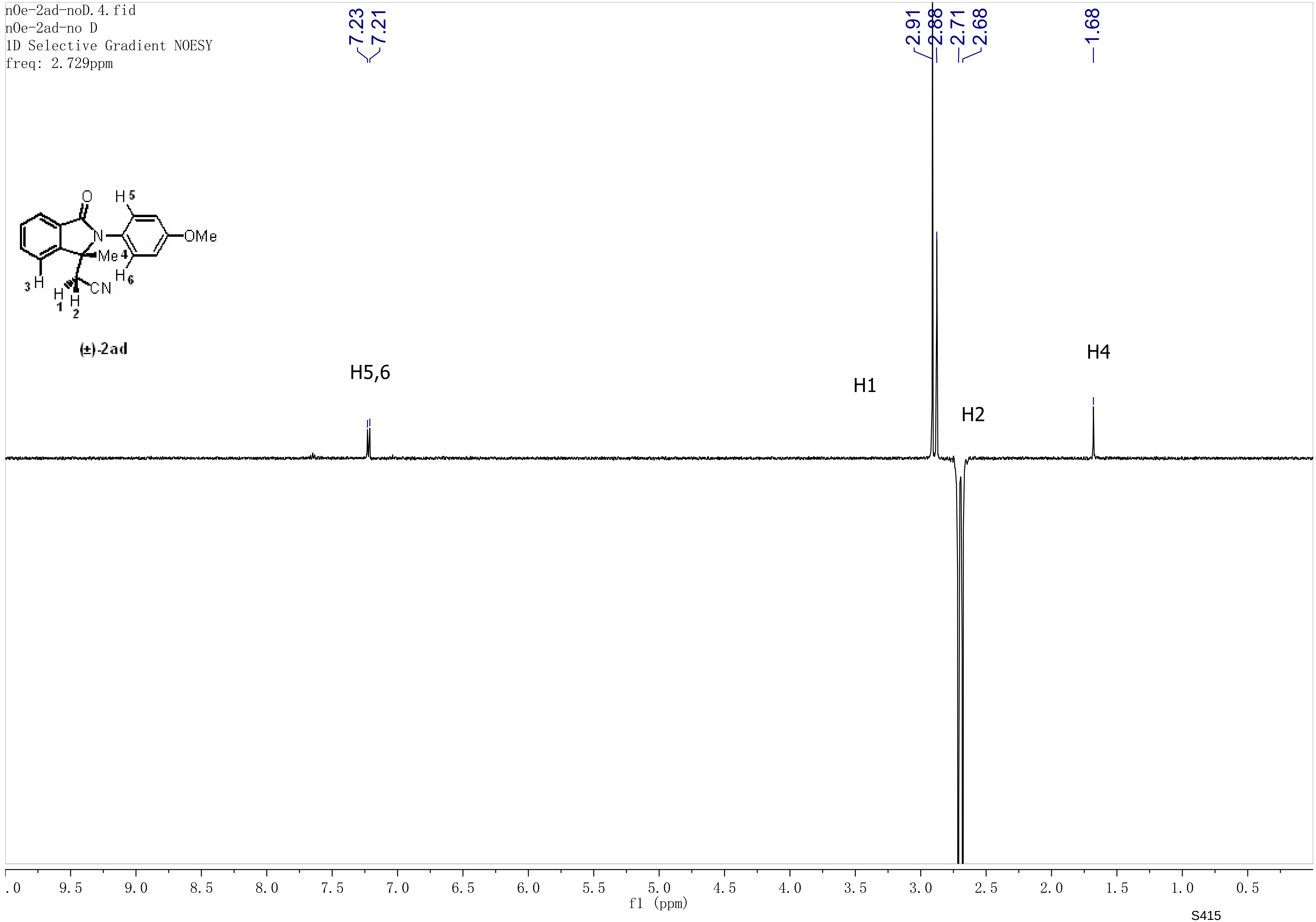

cdoshw-180130-av500.3.fid
nOe-Me
1D Selective Gradient NOESY
freq: 5.149ppm
5.35
5.16
5.15
OMe
O
N
CN
Me
3
H
1
H
2
1ad
H2
H1
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

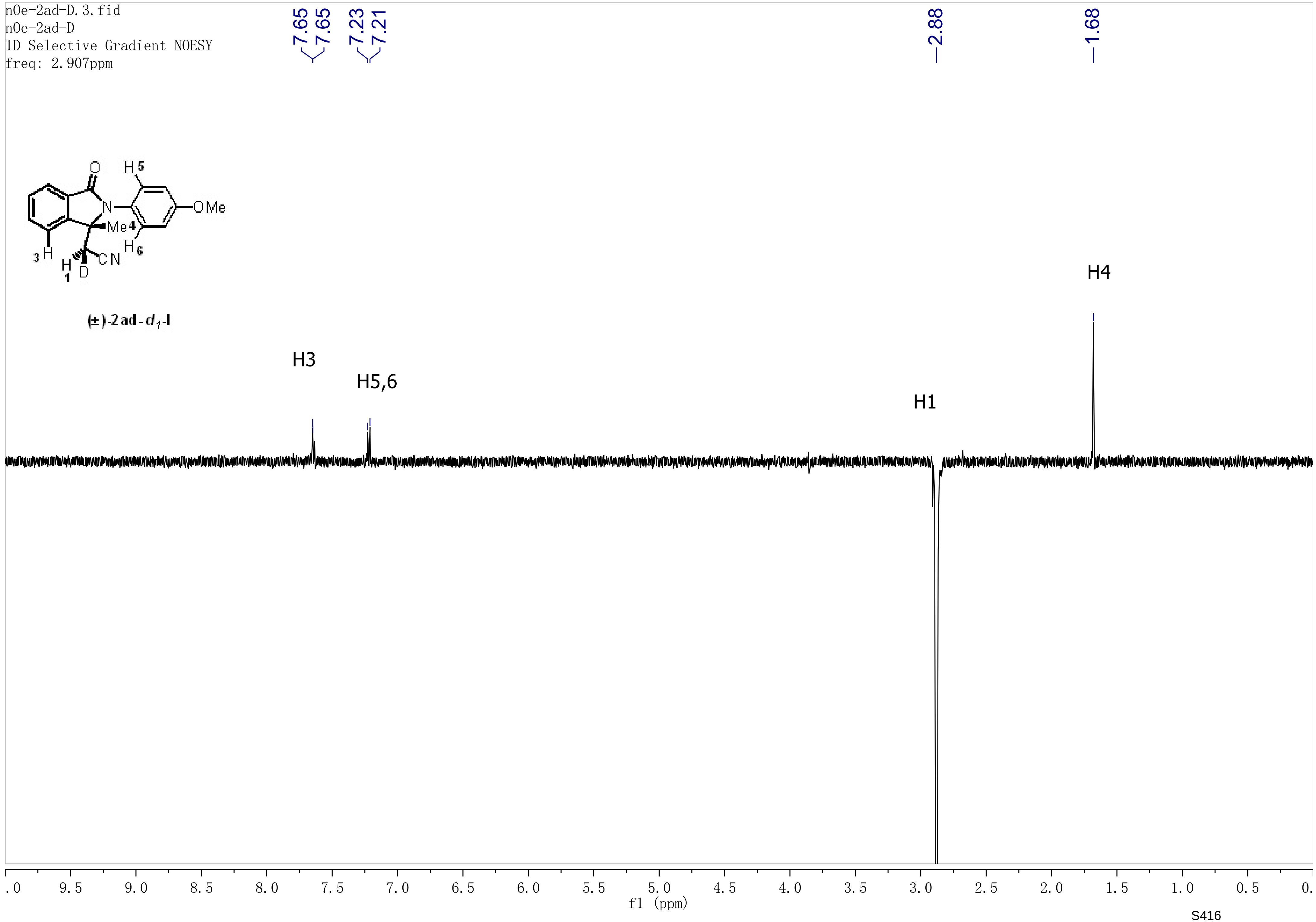
cdoshw-180130-av500.2.fid
nOe-Me
1D Selective Gradient NOESY
freq: 2.258ppm




5.14
OMe
O
N
CN
Me
3
H
1
D
2
trans-1ad-d1
H1
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)


nOe-2ad-noD.3.fid
nOe-2ad-no D
1D Selective Gradient NOESY
freq: 2.939ppm
7.68
7.67
7.65
7.65
7.63
7.23
7.21
2.91
2.88
2.71
2.68
1.68
H3
H5,6
H1
H2
H4
O
H5
N
OMe
Me 4
H6
3 H
H 1
H 2
CN
(±)-2ad
f1 (ppm)


nOe-2ad-noD.4.fid
nOe-2ad-no D
1D Selective Gradient NOESY
freq: 2.729ppm
7.23
7.21
2.91
2.88
2.71
2.68
1.68
(±)-2ad
H5,6
H1
H2
H4
f1 (ppm)


nOe-2ad-D.3.fid
nOe-2ad-D
1D Selective Gradient NOESY
freq: 2.907ppm
7.65
7.65
7.23
7.21
2.88
1.68
O
H5
N
OMe
Me4
H6
3H
H1
D
CN
(±)-2ad-d_1-I
H4
H3
H5,6
H1
f1 (ppm)