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Repurposing a Supramolecular Iridium Catalyst via Secondary Zn···O=C Weak Interactions between Ligand and Substrate Leads to *ortho*-selective C(sp^2)-H Borylation of Benzamides with Unusual Kinetics

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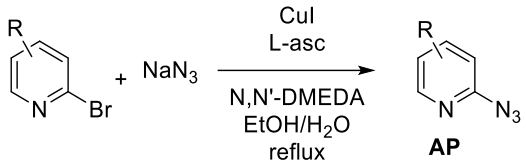
1. General methods.

Solvents were purified with an MB SPS-800 purification system. Pyrrole was dried with CaH_2 and distilled prior to use. $CDCl_3$ was filtered through alumina and stored under argon over molecular sieves. All the other employed chemicals were purchased from commercial sources and used as received. Unless otherwise specified, reactions were carried out under argon atmosphere by employing standard Schlenk and vacuum-line techniques. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker GPX (400 MHz) spectrometer. ^{1}H NMR spectra were referenced to residual protiated solvent (δ = 7.26 ppm for $CDCl_3$). ^{13}C NMR spectra were referenced to $CDCl_3$ (δ = 77.0 ppm).[1] ^{19}F NMR spectra were referenced to external $CFCl_3$ (δ = 0 ppm).[2] Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; tdd, doublet of doublet of triplets. Coupling constants, *J*, were reported in hertz unit (Hz). The reactions were monitored by using a Shimadzu 2014 gas chromatograph equipped with an EquityTM-1 Fused Silica capillary column (30 m x 0.25 mm x 0.25 μm) and an FID detector; conversion and selectivity were determined by using dodecane as internal standard. UV/Vis absorption spectra were recorded with a Specord 205 UV/Vis/NIR spectrophotometer and quartz cuvettes of 1 cm path length. Mass spectroscopy and microanalysis were performed in the laboratories of the Centre Regional de Mesures Physiques de l'Ouest (CRMPO, Université de Rennes 1, Rennes, France). PM3-semiempirical molecular modeling calculations were performed with the Spartan molecular modeling program. The ligands **L1**-**L6**, and **L1***-**2*** were prepared as described in the literature.[3]

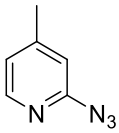
2. Synthesis and characterization of the chemicals prepared in this study.

Synthesis and characterization of azidopyridines AP:

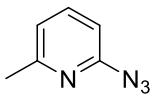


General procedure for the synthesis of 2-azidopyridine AP: In a two-necked dried round bottom flask, 2-bromopyridine derivative (1 equiv.), sodium azide (2 equiv.), CuI (0.1 equiv.), sodium ascorbate (0.05 equiv) and *N*,*N*'-dimethylethylenediamine (0.15 equiv.) were dissolved in a mixture of EtOH:H_2O (v/v 7:3). The reaction mixture was stirred for 2 hours at reflux under air atmosphere. Then, the mixture was evaporated to dryness. A mixture of EtOAc and H_2O were added and the aqueous layer was extracted with EtOAc three times. Then the combined organic layers were washed with water two times and once with brine solution. After drying over $MgSO_4$ and filtration, the solvents were evaporated under reduced pressure. If needed, the product was further purified by column chromatography (SiO_2, *n*-heptane:EtOAc).

Important Note: Azide are sensitive compound that are prone to explosion or decomposition under harsh conditions (high temperature, low pressure…). Careful attention should be taken to prevent any unwanted reactivity as well as safety incident. In the same regard, quenching the remaining aqueous sodium azide at the end of reaction should be carried out for safety and toxicity reason.

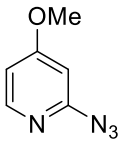


Synthesis and characterization of 2-azido-4-methylpyridine (AP3): According to the general procedure, 2-bromo-4-methylpyridine (0.314 mL, 0.485 g, 2.66 mmol, 1equiv.), sodium azide (0.345 g, 5.32 mmol, 2 equiv.), CuI (0.050 g, 0.27 mmol, 0.1 equiv.), sodium ascorbate (0.026 g, 0.13 mmol, 0.05 equiv.) and *N*,*N*'-dimethylethylenediamine (0.04 mL, 0.033 g, 0.40 mmol, 0.15 equiv.) were dissolved in a mixture of EtOH:H_2O (12 mL, v/v 7:3). The final product was isolated as an analytically pure white powder (0.362 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (d, *J* = 7.0 Hz, 1H), 7.77 (dd, *J* = 1.4, 1.1 Hz 1H), 7.03 (dd, *J* = 7.1, 1.4 Hz, 1H), 2.56 (d, *J* = 1.1 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 143.7, 135.5, 124.3, 119.2, 114.0, 21.7 ppm. HRMS (ESI, MeOH/DCM : 95/5): *m/z* calcd for $C_6H_6N_4$: 157.04847 $[M+Na]^+$; found: 157.0486 (1 ppm).

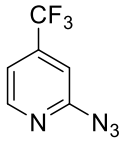


Synthesis and characterization of 2-azido-6-methylpyridine (AP4): According to the general procedure, 2-bromo-6-methylpyridine (0.321 mL, 0.485 g, 2.66 mmol, 1 equiv.), sodium azide (0.345 g, 5.32 mmol, 2 equiv.), CuI (0.050 g, 0.27 mmol, 0.1 equiv.), sodium ascorbate (0.026 g, 0.13 mmol, 0.05 equiv.) and *N*,*N*'-dimethylethylenediamine (0.04 mL, 0.033 g, 0.40 mmol, 0.15 equiv.) were dissolved in a mixture of EtOH:H_2O (12 mL, v/v 7:3). The final product was isolated as an analytically pure white powder (370 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (dt, *J* = 9.1, 1.0 Hz, 1H), 7.60 (dd, *J* = 9.0, 6.8 Hz, 1H), 7.00 (dt, *J* = 6.8, 1.0 Hz, 1H), 2.95 (t, *J* = 1.0 Hz, 3H) ppm. $^{13}C\{^1H\}$

NMR (101 MHz, $CDCl_3$): δ = 152.7, 136.8, 131.7, 115.2, 113.1, 17.4 ppm. HRMS (ESI, DCM): *m/z* calcd for $C_6H_7N_4$: 135.06652 $[M+H]^+$; found: 135.0664 (1 ppm). The spectral data match those found in literature.[4]

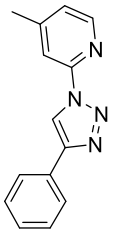


Synthesis and characterization of 2-azido-4-methoxylpyridine (AP5): According to the general procedure, 2-bromo-4-methoxypyridine (0.324 mL, 0.500 g, 2.66 mmol, 1 equiv.), sodium azide (0.345 g, 5.32 mmol, 2 equiv.), CuI (0.050 g, 0.27 mmol, 0.1 equiv.), sodium ascorbate (0.026 g, 0.13 mmol, 0.05 equiv.) and *N*,*N*'-dimethylethylenediamine (0.04 mL, 0.033 g, 0.40 mmol, 0.15 equiv.) were dissolved in a mixture of EtOH:H_2O (12 mL, v/v 7:3). The final product was isolated as an analytically pure white powder (0.390 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (dd, *J* = 7.5, 0.6 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 7.5, 2.4 Hz, 1H), 3.97 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 162.3, 150.4, 125.4, 112.0, 91.8, 56.4 ppm. HRMS (ESI, MeOH/DCM : 90/10): *m/z* calcd for $C_6H_6N_4O$: 173.04338 $[M+Na]^+$; found: 173.0435 (1 ppm).The spectral data match those found in literature.[5]

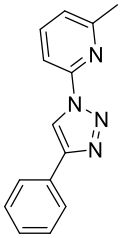


Synthesis and characterization of 2-azido-4-trifluoromethylpyridine (AP6): According to the general procedure, 2-bromo-4-trifluoromethylpyridine (0.255 mL, 0.465 g, 2.66 mmol, 1 equiv.), sodium azide (0.345 g, 5.32 mmol, 2 equiv.), CuI (0.050 g, 0.27 mmol, 0.1 equiv.), sodium ascorbate (0.026 g, 0.13 mmol, 0.05 equiv.) and *N*,*N*'-dimethylethylenediamine (0.04 mL, 0.033 g, 0.40 mmol, 0.15 equiv.) were dissolved in a mixture of EtOH:H_2O (12 mL, v/v 7:3). The reaction mixture was stirred at reflux for 45 minutes. It is important to note that longer reaction time induce partial to full decomposition of the expected product. The final product was isolated as an analytically pure white powder (0.320 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.00 (d, *J* = 7.2 Hz, 1H), 8.37 (d, *J* = 1.7 Hz, 1H), 7.43 (dd, *J* = 7.2, 1.7 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 147.8, 134.3 (q, *J* = 35.2 Hz), 126.9, 121.99 (d, *J* = 273.5 Hz), 114.4 (q, *J* = 4.8 Hz), 112.8 (q, *J* = 2.8 Hz) ppm. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ = -64.3 (s) ppm. HRMS (ESI, DCM): *m/z* calcd for $C_6H_3N_4F_3$: 211.02020 $[M+Na]^+$; found: 211.0203 (0 ppm). The spectral data match those found in literature.[6]

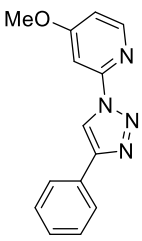
General procedure for L3*-L6* synthesis: Into a dried Schlenk tube charged with a stirring bar, azidopyridine AP (1 equiv.), $Cu(PPh_3)_3Br$ (0.1 equiv.) and dry toluene were added followed by phenylacetylene (1.2 equiv.) addition. The reaction mixture was stirred for 24 hours at 120°C. Back at room temperature, the solvents were evaporated and the crude mixture was purified by column chromatography (SiO_2, *n*-heptane:EtOAc).



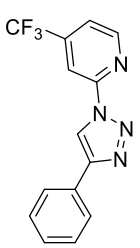
Synthesis and characterization of ligand L3*: According to the general procedure, 2-azido-4-methylpyridine **AP3** (0.228 g, 1.7 mmol, 1 equiv.) and $Cu(PPh_3)_3Br$ (0.158 g, 0.17 mmol, 0.1 equiv.) were suspended in dry toluene (12 mL) in a dry Schlenk tube. Then, phenylacetylene (0.208 mg, 0.224 mL, 2 mmol, 1.2 equiv.) was introduced and the reaction mixture was stirred at 120°C immediately for 24 hours. Back at room temperature, the solvent was evaporated under reduced pressure and the crude mixture was purified by column chromatography (SiO_2, n-heptane:EtOAc, 1:0 to 7:3) to afford **L3*** (0.145 g, 36% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (s, 1H), 8.37 (dd, *J* = 5.1, 0.8 Hz, 1H), 8.08 (dt, *J* = 1.6, 0.8 Hz, 1H), 7.97–7.92 (m, 2H), 7.50–7.44 (m, 2H), 7.40–7.33 (m, 1H), 7.17 (ddd, *J* = 5.1, 1.6, 0.8 Hz, 1H), 2.50 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 150.9, 149.3, 148.2, 148.0, 130.3, 128.9, 128.4, 125.9, 124.6, 116.9, 114.4, 21.3 ppm. HRMS (ESI, MeOH/DCM, 95/5): *m/z* calcd for $C_{14}H_{12}N_4$: 259.09542 $[M+Na]^+$; found: 259.0955 (0 ppm).



Synthesis and characterization of Ligand L4*: According to the general procedure, 2-azido-6-methylpyridine **AP4** (0.228 g, 1.7 mmol, 1 equiv.) and $Cu(PPh_3)_3Br$ (0.158 g, 0.17 mmol, 0.1 equiv.) were suspended in dry toluene (12 mL) in a dry Schlenk tube. Then, phenylacetylene (0.208 mg, 0.224 mL, 2 mmol, 1.2 equiv.) was introduced and the reaction mixture was stirred at 120°C immediately for 24 hours. Back at room temperature, the solvent was evaporated under reduced pressure and the crude mixture was purified by column chromatography (SiO_2, n-heptane:EtOAc, 1:0 to 7:3) to afford **L4*** (0.164 g, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.99–7.93 (m, 2H), 7.80 (t, *J* = 7.9 Hz, 1H), 7.50–7.43 (m, 2H), 7.40–7.33 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 2.62 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 158.2, 148.6, 147.8, 139.2, 130.4, 128.9, 128.3, 125.9, 123.0, 116.8, 110.7, 24.2 ppm. HRMS (ESI, MeOH/DCM, 95/5): *m/z* calcd for $C_{14}H_{12}N_4$: 259.09542 $[M+Na]^+$; found: 259.0954 (0 ppm).



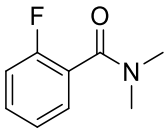
Synthesis and characterization of ligand L5*: According to the general procedure, 2-azido-4-tertbutylpyridine **AP5** (0.255 g, 1.7 mmol, 1 equiv.) and $Cu(PPh_3)_3Br$ (0.158 g, 0.17 mmol, 0.1 equiv.) were suspended in dry toluene (12 mL) in a dry Schlenk tube. Then, phenylacetylene (0.208 mg, 0.224 mL, 2 mmol, 1.2 equiv.) was introduced and the reaction mixture was stirred at 120°C immediately for 24 hours. Back at room temperature, the solvent was evaporated under reduced pressure and the crude mixture was purified by column chromatography (SiO_2, n-heptane:EtOAc, 1:0 to 7:3) to afford **L5*** (0.192 g, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (s, 1H), 8.31 (d, *J* = 5.7 Hz, 1H), 8.03–7.87 (m, 2H), 7.78 (d, *J* = 2.4 Hz, 1H), 7.47 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.43–7.34 (m, 1H), 6.88 (dd, *J* = 5.8, 2.4 Hz, 1H), 3.99 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 168.1, 151.0, 149.5, 148.2, 130.4, 129.1, 128.6, 126.0, 117.2, 111.4, 98.9, 56.0 ppm. HRMS (ESI, MeOH/DCM, 95/5): *m/z* calcd for $C_{14}H_{12}N_4O$: 252.10111 $[M+Na]^+$; found: 252.1011 (0 ppm).



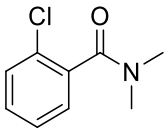
Synthesis and characterization of Ligand L6*: According to the general procedure, 2-azido-4-tertbutylpyridine **AP6** (0.320 g, 1.7 mmol, 1 equiv.) and $Cu(PPh_3)_3Br$ (0.158 g, 0.17 mmol, 0.1 equiv.) were suspended in dry toluene (12 mL) in a dry Schlenk tube. Then, phenylacetylene (0.208 mg, 0.224 mL, 2 mmol, 1.2 equiv.) was introduced and the reaction mixture was stirred at 120°C immediately for 24 hours. Back at room temperature, the solvent was evaporated under reduced pressure and the crude mixture was purified by column chromatography (SiO_2, n-heptane:EtOAc, 1:0 to 7:3) to afford **L6*** (0.262 g, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (s, 1H), 8.72 (d, *J* = 5.2 Hz, 1H), 8.52 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.99–7.93 (m, 2H), 7.58 (d, *J* = 5.2 Hz, 0H), 7.48 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.42–7.37 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.9, 148.5, 141.5, 129.8, 129.0, 128.7, 126.0, 122.2 (d, *J* = 273.5 Hz), 119.1 (d, *J* = 4.1 Hz), 116.8, 110.2 (d, *J* = 4.0 Hz) ppm. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ = -64.9 (s) ppm. HRMS (ESI, MeOH/DCM, 95/5): *m/z* calcd for $C_{14}H_9N_4F_3$: 313.06715 $[M+Na]^+$; found: 313.0673 (0 ppm).

Synthesis of non-commercial starting materials 1:

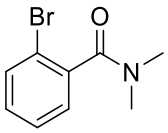
General method: To an oven dried round bottom flask was added carboxylic acid (10 mmol, 1 equiv.), DMF (10 mL). Then freshly distillated $POCl_3$ (1.53 g, 0.930 mL, 10 mmol, 1 equiv.) was slowly added and the reaction mixture was heated to 120°C for 16h. Then the reaction mixture was quench by addition of a saturated solution of $NaHCO_3$ until no bubbling was noticed. EtOAc was added, and the aqueous layer was extracted 3 times with EtOAc. The combined organic layer was washed with a saturated solution of K_2CO_3 and then brine solution. After drying over $MgSO_4$ and filtration, the solvents were evaporated under reduced pressure. The crude mixture was further purified by column chromatography (SiO_2, n-heptane:EtOAc (1:0 to 2:8).



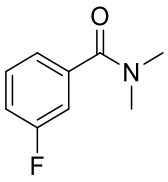
Synthesis and characterization of 2-fluoro-*N*,*N*'-dimethylbenzamide (1f): According to the general method, 2-fluoro-*N*,*N*'-dimethylbenzamide was isolated as a yellow oil (1.57 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.32 (m, 2H), 7.21–7.13 (m, 1H), 7.10–7.03 (m, 1H), 3.11 (q, *J* = 1.3 Hz, 3H), 2.91 (q, *J* = 1.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 166.7, 158.2 (d, *J* = 247.5 Hz), 131.1 (d, *J* = 8.0 Hz), 129.0 (d, *J* = 3.9 Hz), 124.7, 124.5 (d, *J* = 3.4 Hz), 115.6 (d, *J* = 21.6 Hz), 38.2 (d, *J* = 2.8 Hz), 34.9 ppm. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ = -115.3 (s) ppm. The spectral data match those found in literature.[7]



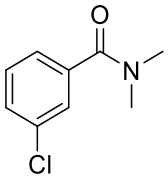
Synthesis and characterization of 2-chloro-*N*,*N*'-dimethylbenzamide (1g): According to the general method, 2-chloro-*N*,*N*'-dimethylbenzamide was isolated as a yellow oil (1.67 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.31 (m, 1H), 7.31–7.22 (m, 3H), 3.09 (d, *J* = 0.9 Hz, 3H), 2.81 (d, *J* = 0.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 168.2, 136.2, 130.0, 129.9, 129.3, 127.5, 127.0, 37.8, 34.4 ppm. The spectral data match those found in literature.[8]



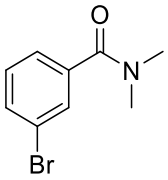
Synthesis and characterization of 2-bromo-*N*,*N*'-dimethylbenzamide (1h): According to the general method, 2-bromo-*N*,*N*'-dimethylbenzamide was isolated as a yellow oil (1.98 g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.35 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.29–7.20 (m, 2H), 3.13 (s, 3H), 2.85 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 169.2, 138.6, 132.7, 130.1, 127.7, 127.7, 119.1, 38.2, 34.6 ppm. The spectral data match those found in literature.[9]



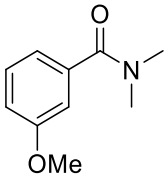
Synthesis and characterization of 3-fluoro-*N*,*N*'-dimethylbenzamide (1i): According to the general method, 3-methoxy-*N*,*N*'-dimethylbenzamide was isolated as a yellow oil (1.49 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (td, *J* = 7.7, 5.6 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.10 (ddt, *J* = 10.9, 8.4, 4.0 Hz, 2H), 3.09 (s, 3H), 2.96 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 170.1 (d, *J* = 2.4 Hz), 163.7, 161.2, 138.4 (d, *J* = 6.9 Hz), 130.1 (d, *J* = 8.1 Hz), 122.7 (d, *J* = 3.2 Hz), 116.5 (d, *J* = 21.1 Hz), 114.3 (d, *J* = 22.8 Hz), 39.4, 35.3 ppm. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ = -112.1 (s) ppm. The spectral data match those found in literature.[10]



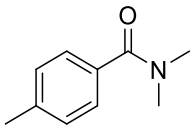
Synthesis and characterization of 3-chloro-*N*,*N*'-dimethylbenzamide (1j): According to the general method, 3-chloro-*N*,*N*'-dimethylbenzamide was isolated as a yellow oil (1.76 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.22 (m, 4H), 3.09 (s, 3H), 2.96 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 170.0, 138.1, 134.4, 129.8, 129.6, 127.3, 125.1, 39.5, 35.4 ppm. The spectral data match those found in literature.[10]



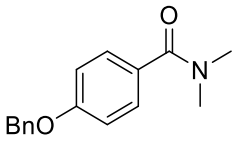
Synthesis and characterization of 3-bromo-*N*,*N*'-dimethylbenzamide (1k): According to the general method, 3-bromo-*N*,*N*'-dimethylbenzamide was isolated as a yellow oil (1.84 g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.48 (m, 2H), 7.36–7.23 (m, 2H), 3.09 (s, 3H), 2.96 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 169.9, 138.3, 132.6, 130.1, 130.0, 125.6, 122.5, 39.5, 35.4 ppm. The spectral data match those found in literature.[11]



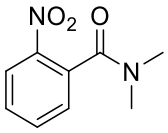
Synthesis and characterization of 3-methoxy-*N*,*N*'-dimethylbenzamide (1l): According to the general method, 3-methoxy-*N*,*N*'-dimethylbenzamide was isolated as a yellow oil (1.49 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (t, *J* = 7.7 Hz, 1H), 6.99–6.90 (m, 3H), 3.82 (s, 3H), 3.10 (s, 3H), 2.97 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 171.4, 159.6, 137.7, 129.43, 119.2, 115.4, 112.4, 55.3, 39.5, 35.3 ppm. The spectral data match those found in literature.[12]



Synthesis and characterization of 4-methyl-*N*,*N*'-dimethylbenzamide (1n): According to the general method, 4-methyl-*N*,*N*'-dimethylbenzamide was isolated as a white solid (1.50 g, 92% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.15 (d, J = 5.2 Hz, 4H), 3.08 (s, 3H), 2.98 (s, 3H), 2.36 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 171.8, 139.6, 133.4, 128.9, 127.2, 39.6, 35.4, 21.4 ppm. The spectral data match those found in literature.[8]

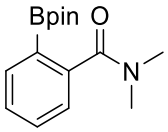


Synthesis and characterization of 4-(phenylmethoxy)-*N*,*N*'-dimethylbenzamide (1o): According to the general method, 4-(phenylmethoxy)-*N*,*N*'-dimethylbenzamide was isolated as a white solid (1.58 g, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.29 (m, 7H), 7.00–6.94 (m, 2H), 5.09 (s, 2H), 3.05 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 171.4, 159.7, 136.6, 129.1, 128.7, 128.6, 128.0, 127.4, 114.5, 70.0 ppm. The spectral data match those found in literature.[13]



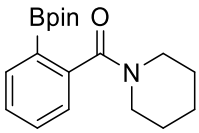
Synthesis and characterization of 2-nitro-*N*,*N*'-dimethylbenzamide (1p): According to the general method, 2-nitro-*N*,*N*'-dimethylbenzamide was isolated as a yellow solid (0.99 g, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (dd, J = 8.3, 1.2 Hz, 1H), 7.70 (td, J = 7.5, 1.2 Hz, 1H), 7.55 (td, J = 8.3, 7.5, 1.5 Hz, 1H), 7.39 (dd, J = 7.5, 1.5 Hz, 1H), 3.16 (s, 3H), 2.83 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 167.9, 145.1, 134.5, 133.3, 129.6, 128.1, 124.7, 38.2, 34.9 ppm. The spectral data match those found in literature.[14]

General method for the borylation catalysis experiment: To an oven dried round bottom flask was added $[Ir(COD)(Cl)]_2$ (1.7 mg, 2.43x10^{-3} mmol, 0.015 equiv.), ligand **L** (4.86x10^{-3} mmol, 0.03 equiv.), B_2pin_2 (61.7 mg, 0.243 mmol, 1.5 equiv.). Then *p*-xylene (1 mL) and the corresponding benzamide **1** (0.162 mmol, 1 equiv.) and cyclohexene (13 mg, 16 µL, 0.162 mmol, 1 equiv.) were introduced and the reaction mixture was heated at 100 °C during 30 hours. Back at room temperature, the crude mixture was analyzed by GC-MS and evaporated under vacuum until full evaporation of *p*-xylene. Heptane (1 mL) was added and the mixture was filtrated on celite. The solid was washed with heptane and the filtrate was further purified by column chromatography (SiO_2, n-heptane:EtOAc, v/v 1:0 to 1:1) to afford the pure borylated products **2**.

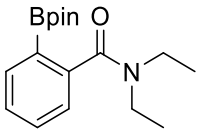


Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*,*N*'-dimethylbenzamide (2a): Following the general procedure, *N*,*N*'-dimethylbenzamide **1a** (24 mg, 0.162 mmol, 1 equiv.) was borylated at 100 °C during 30 hours using cyclohexene (13 mg, 16 µL, 0.162 mmol, 1 equiv.) as a pinacolborane scavenger. A conversion of 99% and a selectivity of 97% toward the *ortho* derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **2a** was

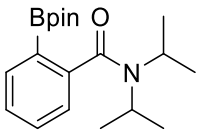
isolated as a solid (39 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.46 (td, *J* = 7.5, 1.2 Hz, 1H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.30 (dd, *J* = 7.5, 1.2 Hz, 1H), 2.98 (s, 6H), 1.33 (s, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz, CDCl3): δ = 172.5, 142.7, 135.0, 130.9, 128.1, 125.5, 83.6, 24.9 ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 29.6 (s) ppm. The spectral data match those found in literature.[15]



Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoylpiperidine (2b): Following the general procedure **A**, benzoylpiperidine **1b** (31 mg, 0.162 mmol, 1 equiv.) was borylated at 100 °C during 30 hours using cyclohexene (13 mg, 16 µL, 0.162 mmol, 1 equiv.) as a pinacolborane scavenger. A conversion of 99% and a selectivity of 98% toward the *ortho* derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **2b** was isolated as a solid (46 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.45 (td, *J* = 7.5, 1.3 Hz, 1H), 7.35 (td, *J* = 7.5, 1.3 Hz, 1H), 7.25 (dt, *J* = 7.5, 1.3 Hz, 1H), 3.73 (t, *J* = 5.4 Hz, 2H), 3.17 (t, *J* = 5.4 Hz, 2H), 1.74–1.62 (m, 4H), 1.53–1.46 (m, 2H), 1.34 (s, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 170.84, 143.28, 135.41, 130.91, 127.76, 125.42, 83.81, 48.31, 42.61, 25.76, 25.15, 24.94, 24.68 ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 30.32 (s) ppm. The data match those found in the literature.[16]

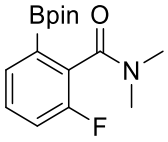


Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)- *N*,N'-diethylbenzamide (2c): Following the general procedure, *N*,*N*'-diethylbenzamide **1c** (29 mg, 0.162 mmol, 1 equiv.) was borylated at 100 °C during 40 hours using cyclohexene (13 mg, 16 µL, 0.162 mmol, 1 equiv.) as a pinacolborane scavenger. A conversion of 92% and a selectivity of 86% toward the *ortho* derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **2c** was isolated as a solid (40 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1H), 7.35 (td, *J* = 7.5, 1.3 Hz, 1H), 7.26 (dd, *J* = 7.5, 1.3 Hz, 1H), 3.57 (q, *J* = 7.1 Hz, 2H), 3.21 (q, *J* = 7.1 Hz, 2H), 1.31 (m, 3 H), 1.30 (s, 12H), 1.06 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 171.7, 142.4, 135.1, 130.5, 128.2, 125.4, 83.4, 43.0, 39.8, 24.9, 13.7, 12.5 ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 28.35 (s) ppm. The data match those found in the literature.[16]

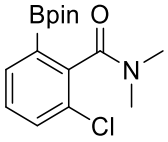


Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)- *N*,*N*'-diisopropylbenzamide (2d): Following the general procedure, *N*,*N*'-diisopropylbenzamide **1d** (33 mg, 0.162 mmol, 1 equiv.) was borylated at 100 °C during 48 hours using cyclohexene (13 mg, 16 µL, 0.162 mmol, 1 equiv.) as a pinacolborane scavenger. A conversion of 99% and a selectivity of 77% toward the *ortho* derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **2d** was isolated as a solid (46 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.42 (td, *J* = 7.5, 1.3 Hz, 1H), 7.34 (td, *J* = 7.5, 1.3 Hz, 1H), 7.18 (dt, *J* = 7.5, 0.8 Hz, 1H), 3.75 (dt, *J* = 13.0, 5.9 Hz, 1H), 3.53 (q, *J* = 13.0, 5.9 Hz, 1H), 1.60 (d, *J* = 6.8 Hz, 6H),

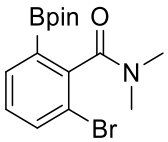
1.33 (s, 12H), 1.14 (d, *J* = 6.8 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 171.3, 145.0, 135.5, 130.5, 127.3, 124.6, 83.8, 50.9, 45.7, 24.9, 20.4, 20.2 ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 30.0 (s) ppm. The data match those found in the literature.[16]



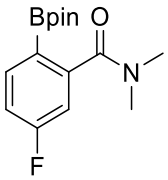
Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-fluoro-*N*,*N*'-dimethylbenzamide (2f): Following the general procedure without cyclohexene, 2-fluoro-*N*,*N*'-dimethylbenzamide **1f** (27 mg, 0.162 mmol, 1 equiv.) was borylated at 100 °C during 30 hours. A conversion of 99% and a selectivity of 94% toward the *ortho* derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **2e** was isolated as a solid (46 mg, 91% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.39–7.32 (m, 1H), 7.18 (td, *J* = 8.2, 7.4, 1.1 Hz, 1H), 3.13 (s, 3H), 2.85 (s, 3H), 1.33 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 167.2, 157.8 (d, *J* = 246.7 Hz), 131.0 (d, *J* = 3.2 Hz), 130.3 (d, *J* = 17.9 Hz), 129.6 (d, *J* = 7.3 Hz), 118.2 (d, *J* = 21.6 Hz), 84.0, 38.3, 34.5, 24.8 ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 30.3 (s) ppm. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ = -117.5 (s) ppm. The data match those found in the literature.[17]



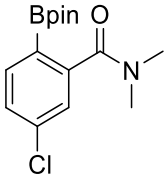
Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-chloro-*N*,*N*'-dimethylbenzamide (2g): Following the general procedure without cyclohexene, 2-chloro-*N*,*N*'-dimethylbenzamide **1g** (30 mg, 0.162 mmol, 1 equiv.) was borylated at 100 °C during 72 hours. A conversion of 85% and a selectivity of 77% toward the *ortho* derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **2g** was isolated as a solid (35 mg,70% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.47 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.30 (t, *J* = 8.1, 7.4 Hz, 1H), 3.12 (s, 3H), 2.80 (s, 3H), 1.33 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 168.8, 142.0, 133.8, 132.0, 130.2, 128.9, 84.1, 38.1, 34.4, 24.9 ppm.$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 30.5 (s) ppm. HRMS (ESI, MeOH/DCM, 95/5): *m/z* calcd for $C_{15}H_{21}NO_3{}^{35}Cl^{11}B$: 332.11952 $[M+Na]^+$; found: 332.1198 (1 ppm).



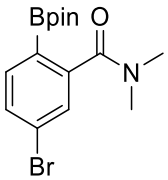
Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-bromo-*N*,*N*'-dimethylbenzamide (2h): Following the general procedure without cyclohexene, 2-bromo-*N*,*N*'-dimethylbenzamide **1h** (37 mg, 0.162 mmol, 1 equiv.) was borylated at 100 °C during 72 hours. A conversion of 30% was determined by GC-MS and GC-FID. The *ortho*-C-H borylated product **2h** was isolated as a solid (16 mg, 28% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.35 (td, *J* = 7.5, 1.2 Hz, 1H), 7.25–7.19 (m, 1H), 3.13 (s, 3H), 2.85 (s, 3H), 1.25 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 169.2, 138.6, 132.7, 130.2, 127.7, 127.7, 119.1, 83.5, 38.2, 34.7, 25.0 ppm.$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 30.5 (s) ppm. The data match those found in the literature.[18]



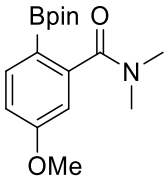
Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-fluoro-*N*,*N*'-dimethylbenzamide (2i): Following the general procedure, 3-fluoro-*N*,*N*'-dimethylbenzamide **1i** (27 mg, 0.162 mmol, 1 equiv.) was borylated at 100 °C during 30 hours using cyclohexene (13 mg, 16 µL, 0.162 mmol, 1 equiv.) as a pinacolborane scavenger. A conversion of 99% and a selectivity of 98% toward the *ortho* derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **2i** was isolated as a solid (48 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.35–7.27 (m, 1H), 7.14 (td, *J* = 8.3, 7.3, 1.1 Hz, 1H), 3.08 (s, 3H), 2.80 (s, 3H), 1.29 (s, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 171.2, 165.9 (d, *J* = 248.3 Hz), 142.0, 131.6 (d, *J* = 8.4 Hz), 121.7 (d, *J* = 3.1 Hz), 117.0 (d, *J* = 24.7 Hz), 83.2, 25.0 ppm.^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 30.3 (s) ppm. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ = -102.9 (s) ppm. HRMS (ESI, MeOH/DCM, 95/5): *m/z* calcd for $C_{15}H_{21}NO_3{}^{19}F^{11}B$: 293.15985 $[M+Na]^+$; found: 293.1599 (0 ppm).



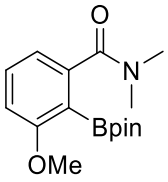
Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-chloro-*N*,*N*'-dimethylbenzamide (2j): Following the general procedure , 3-chloro-*N*,*N*'-dimethylbenzamide **1j** (30 mg, 0.162 mmol, 1 equiv.) was borylated at 100 °C for 48 hours using cyclohexene (13 mg, 16 µL, 0.162 mmol, 1 equiv.) as a pinacolborane scavenger. A conversion of 99% and a selectivity of 90% toward the *ortho* derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **2j** was isolated as a solid (36 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.0 Hz, 1H), 7.36 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.30–7.27 (m, 1H), 3.08 (s, 3H), 2.85 (s, 3H), 1.33 (s, 12H) ppm.^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 170.9, 144.7, 137.4, 136.7, 128.2, 125.9, 83.9, 24.9 ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 30.1 (s) ppm. HRMS (ESI, MeOH/DCM, 95/5): *m/z* calcd for $C_{15}H_{21}NO_3{}^{35}Cl^{11}B$: 332.11952 $[M+Na]^+$; found: 332.1198 (1 ppm).



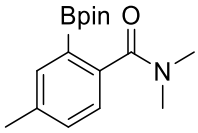
Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-bromo-*N*,*N*'-dimethylbenzamide (2k): Following the general procedure, 3-bromo-*N*,*N*'-dimethylbenzamide **1k** (37 mg, 0.162 mmol, 1 equiv.) was borylated at 100 °C for 40 hours using cyclohexene (13 mg, 16 µL, 0.162 mmol, 1 equiv.) as a pinacolborane scavenger. A conversion of 95% and a selectivity of 87% toward the ortho derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **2k** was isolated as a solid (48 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.42 (d, *J* = 1.8 Hz, 1H), 2.97 (s, 6H), 1.29 (s, 12H) ppm.^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 170.7, 144.8, 136.8, 131.1, 128.7, 125.9, 84.0, 24.9 ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 30.4 (s) ppm. The data match those found in the literature.[16]



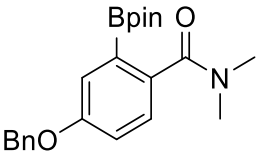
Synthesis and characterization of (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methoxy-*N*,*N*'-dimethylbenzamide (2l): Following the general procedure, 3-methoxy-*N*,*N*'-dimethylbenzamide **1l** (29 mg, 0.162 mmol, 1 equiv.) was borylated at 100 °C during 40 hours using cyclohexene (13 mg, 16 µL, 0.162 mmol, 1 equiv.) as a pinacolborane scavenger. A conversion of 99% and a selectivity of 76% toward the *ortho* derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **2l** was isolated as a solid (33 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.3 Hz, 1H), 6.86 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.79 (d, *J* = 2.5 Hz, 1H), 3.81 (s, 3H), 3.06 (s, 3H), 2.78 (s, 3H), 1.29 (s, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 172.2, 162.1, 145.3, 137.4, 113.7, 111.1, 83.5, 55.3, 24.9 ppm. ^{11}B{^{1}H} NMR (128 MHz, CDCl3): δ = 30.72 (s) ppm. The data match those found in the literature.[17]



2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-methoxy-N,N'-dimethylbenzamide (2m): This *ortho*-C-H borylated isomer product was isolated as a solid (7 mg, 13% yield) during the synthesis of **2l**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (t, *J* = 8.1 Hz, 1H), 6.99 (dd, *J* = 8.1, 0.8 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 3.83 (s, 3H), 3.10 (s, 6H), 1.37 (s, 12H) ppm. . ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 172.0, 163.0, 141.0, 130.5, 118.2, 111.5, 83.1, 55.7, 25.0 ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 27.69 (s) ppm. HRMS (ESI, MeOH/DCM, 95/5): *m/z* calcd for $C_{16}H_{24}NO_4{}^{11}B$: 305.17984 $[M+Na]^+$; found: 305.1798 (0 ppm).

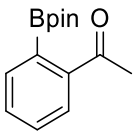


Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-methyl-*N*,*N*'-dimethylbenzamide (2n): Following the general procedure, 4-methyl-*N*,*N*'-dimethylbenzamide **1n** (26 mg, 0.162 mmol, 1 equiv.) was borylated at 100 °C during 24 hours using cyclohexene (13 mg, 16 µL, 0.162 mmol, 1 equiv.) as a pinacolborane scavenger. A conversion of 99% and a selectivity of 97% toward the *ortho* derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **2n** was isolated as a solid (44 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (s, 1H), 7.32–7.12 (m, 2H), 2.99 (s, 6H), 2.35 (s, 3H), 1.31 (s, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 172.68, 139.13, 138.29, 135.25, 131.31, 125.59, 83.26, 24.98, 21.18. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 28.5 (s) ppm. The data match those found in the literature.[17]

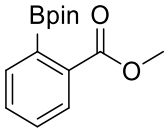


Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(phenylmethoxy)-*N*,*N*'-dimethylbenzamide (2o): Following the general procedure, 4-(phenylmethoxy)-*N*,*N*'-dimethylbenzamide **1o** (41 mg, 0.162 mmol, 1 equiv.) was borylated at 100 °C during 48 hours using cyclohexene (13 mg, 16 µL, 0.162 mmol, 1 equiv.) as a pinacolborane scavenger. A conversion of 82% and a selectivity of 97% toward the *ortho* derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **2o** was isolated as a solid (39 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.32 (m, 7H), 6.97 (dd, *J* = 8.6, 2.6 Hz, 1H), 5.14 (s, 2H), 3.19 (s, 6H), 1.35 (s, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz,

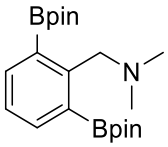
$CDCl_3$): δ = 172.4, 160.4, 136.7, 130.8, 128.6, 128.0, 127.6, 127.4, 118.3, 116.5, 82.1, 70.0, 38.6, 25.1 ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 22.5 (s) ppm. HRMS (ESI, MeOH/DCM, 95/5): *m/z* calcd for $C_{22}H_{28}NO_4{}^{11}B$: 381.21114 $[M+Na]^+$; found: 381.2112 (1 ppm).



Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-acetophenone (2p): Following the general procedure, acetophenone (19 mg, 0.162 mmol, 1 equiv.) was borylated at 80 °C during 24 hours without cyclohexene. A conversion of 55% and a selectivity of 93% toward the ortho derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **7a** was isolated as a solid (20 mg, 49% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.7 Hz, 1H), 7.55–7.48 (m, 2H), 7.45–7.42 (m, 1H), 2.62 (s, 3H), 1.40 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 199.9, 140.7, 137.5, 132.6, 132.4, 129.0, 128.5, 83.8, 25.6, 25.0 ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 31.6 (s) ppm. The data match those found in the literature.[16]



Synthesis and characterization of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-methylbenzoate (2q): Following the general procedure, methylbenzoate (22 mg, 0.162 mmol, 1 equiv.) was borylated at 80 °C during 24 hours without cyclohexene. A conversion of 55% and a selectivity of 93% toward the *ortho* derivative were detected by GC-MS and GC-FID. The *ortho*-C-H borylated product **7b** was isolated in as a solid (19 mg, 49% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.93 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.53–7.48 (m, 2H), 7.45–7.38 (m, 1H), 3.91 (s, 3H), 1.42 (s, 12H) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 30.7 (s) ppm. The data match those found in the literature.[15]



Synthesis and characterization of 1-(2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-N,N-dimethylmethanamine (5): This compound was obtained during the purification of **2a** (*vide supra*). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.3 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 4.14 (s, 2H), 2.60 (s, 6H), 1.29 (s, 24H) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = 22.7 (s) ppm. The data match those found in the literature.[18]

3. Catalytic studies.

Optimization of ligand and kinetic enhancement effect evidence:

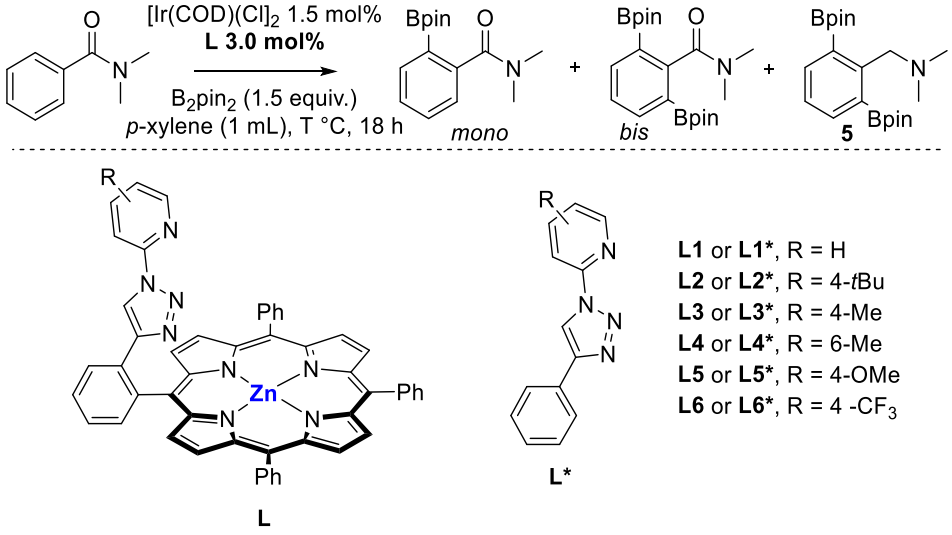


Table S1. Optimization of ligand choice and kinetic enhancement evidence.

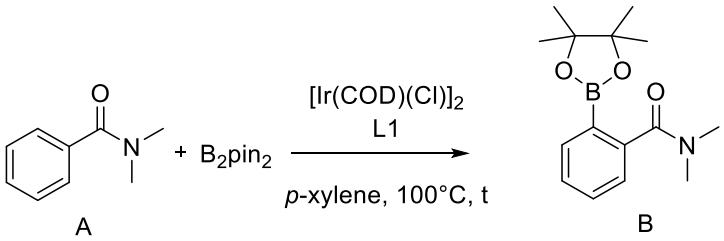
Entry	L	T(°C)	Conversion (%)	Mono (%)	Bis (%)	5 (%)	Ortho selectivity (%)
1	**L1**	**80**	**83**	**64**	**15**	**<5**	**96**
2	L2	80	26	22	2	-	90
3	L3	80	50	37	13	Traces	90
4	**L4**	**80**	**83**	**73**	**8**	**<5**	**97**
5	L5	80	50	38	12	Traces	92
6	L6	80	41	30	11	Traces	91
7	L1*	80	39	33	6	Traces	95
8	L2*	80	7	6.7	0.3	-	96
9	L3*	80	7.4	5	2.4	-	90
10	L4*	80	52	46	6	<5	95
11	L5*	80	25	22	3	traces	93
12	L6*	80	15	12	3	-	89
13	**L1**	**100**	**89**	**60**	**10**	**19**	**97**
14	L1*	100	73	56	4	13	94
15	L1	120	85[a]	53	8	24	95
16	L1*	120	73	47	6	20	94

[a]Full conversion of B_2pin_2, >30% estimated yield of mixture of borylated *p*-xylene.

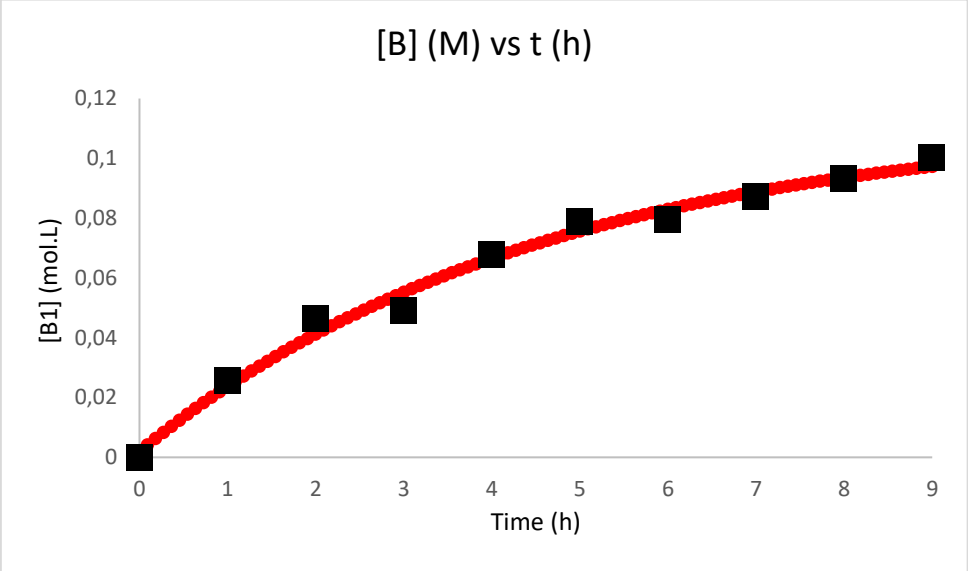
Kinetic isotope effect study.

Reactions in parallel:

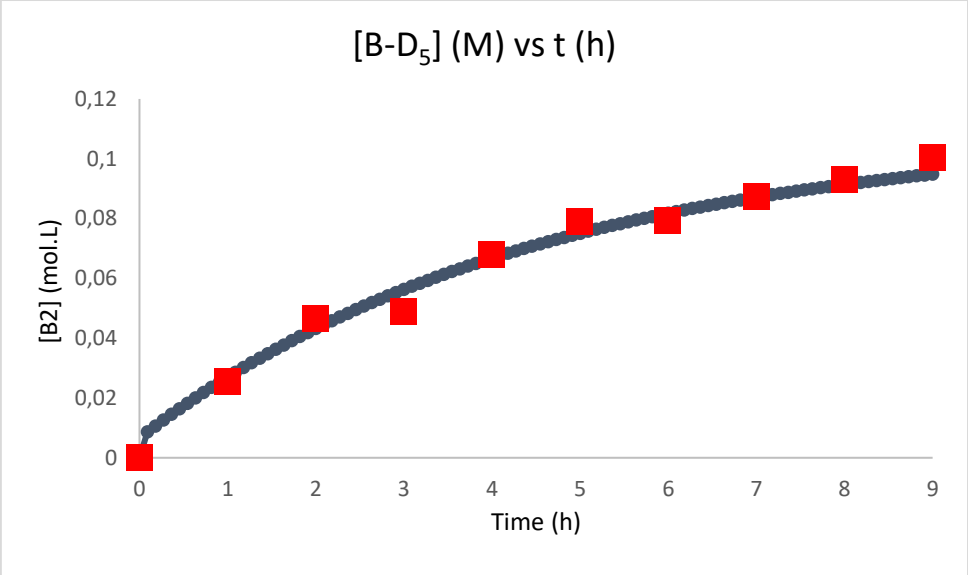
General procedure: $[Ir(COD)(Cl)]_2$, ligand **L1**, B_2pin_2, and dodecane (0.25 eq.) and N,N'-dimethylbenzamide derivative were introduced in an oven dried Schlenk flask. *p*-xylene was added and the reaction mixture was stirred at 100 °C. Small aliquots were taken from the flask under argon flow every 1 hour using a dry pipette. Conversion and yield were estimated by GC-MS/GC-FID using dodecane as the internal standard. Fitting of the experimental data was done using sigmoidal Boltzmann function.



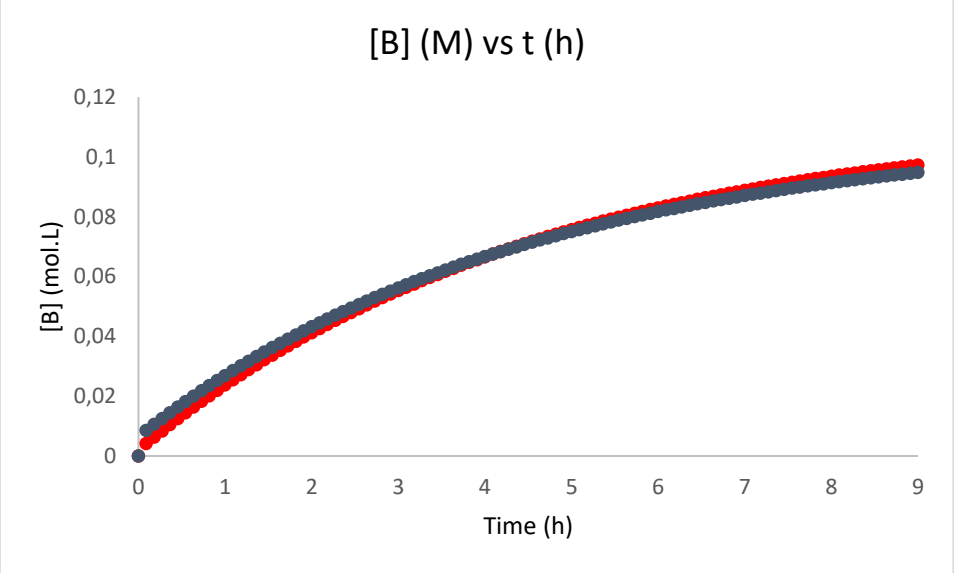
Reaction at standard conditions with ligand L1. Following the general procedure, $[Ir(COD)(Cl)]_2$ (16.5 mg, 2.43 x 10^{-5} mol, 0.015 eq.), ligand **L1** (41 mg, 4.86 x 10^{-5} mol, 0.03 eq.), B_2pin_2 (617 mg, 2.43 x 10^{-3} mol, 1.5 eq.) and N,N'-dimethylbenzamide (242 mg, 1.62 x 10^{-3} mol, 1 eq.) were dissolved in *p*-xylene (10 mL). The reaction mixture was stirred at 100 °C for 10 hours. Formation of *ortho*-borylated product [B1] versus time (h) is plotted below (fitted values are shown in red, and experimental values are shown in black squares highlighting the error of the measurement):



Reaction at standard conditions with ligand L1. Following the general procedure, $[Ir(COD)(Cl)]_2$ (16.5 mg, 2.43 x 10^{-5} mol, 0.015 eq.), ligand L1 (41 mg, 4.86 x 10^{-5} mol, 0.03 eq.), B_2pin_2 (617 mg, 2.43 x 10^{-3} mol, 1.5 eq.) and 2,3,4,5,6-D_5-N,N'-dimethylbenzamide (250 mg, 1.62 x 10^{-3} mol, 1 eq.) were dissolved in *p*-xylene (10 mL). The reaction mixture was stirred at 100°C for 10 hours. Formation of ortho-borylated product [B-d_5] versus time (h) is plotted below (fitted values are shown in blue, and experimental values are shown in red squares highlighting the error of the measurement):

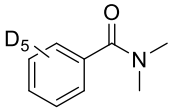


Summary of kinetic profil



Summary of kinetic profile: The kinetic profiles are plotted as follow: N,N'-dimethylbenzamide kinetic profile in red and 2,3,4,5,6-d_5-N,N'-dimethylbenzamide kinetic profile in blue.

Intermolecular competition:



Synthesis and characterization of 2,3,4,5,6-d$_5$-*N*,*N*'-dimethylbenzamide (1a-*d*$_5$): According to the general method, 2,3,4,5,6-d$_5$-*N*,*N*'-dimethylbenzamide was synthesized starting from 2,3,4,5,6-d$_5$-benzoic acid and isolated as a white solid upon cooling (1.51 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.10 (s, 3H), 2.97 (s, 3H) ppm.

KIE evaluation by substrate competition: $[Ir(COD)(Cl)]_2$ (1.65 mg, 2.43 x 10^{-6} mol, 0.015 eq.), ligand **L1** (4.1 mg, 4.86 x 10^{-6} mol, 0.03 eq.), B_2pin_2 (41.1 mg, 1.62 x 10^{-4} mol, 1 eq.), *N*,*N*'-dimethylbenzamide **1a** (48.4 mg, 1.62 x 10^{-4} mol, 1 eq), 2,3,4,5,6-D$_5$-*N*,*N*'-dimethylbenzamide **1a**-*d*$_5$ (49.8 mg, 1.62 x 10^{-4} mol, 1 eq.) and dodecane (0.25 eq.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at 80 °C for 16 hours before full conversion of both benzamide starting materials. The reaction mixture was then cooled at room temperature, evaporated and the mixture of borylated product was purified by column chromatography (SiO_2, n-heptane:EtOAc, v/v 1:0 to 1:1) affording the mixture as a colorless oil.

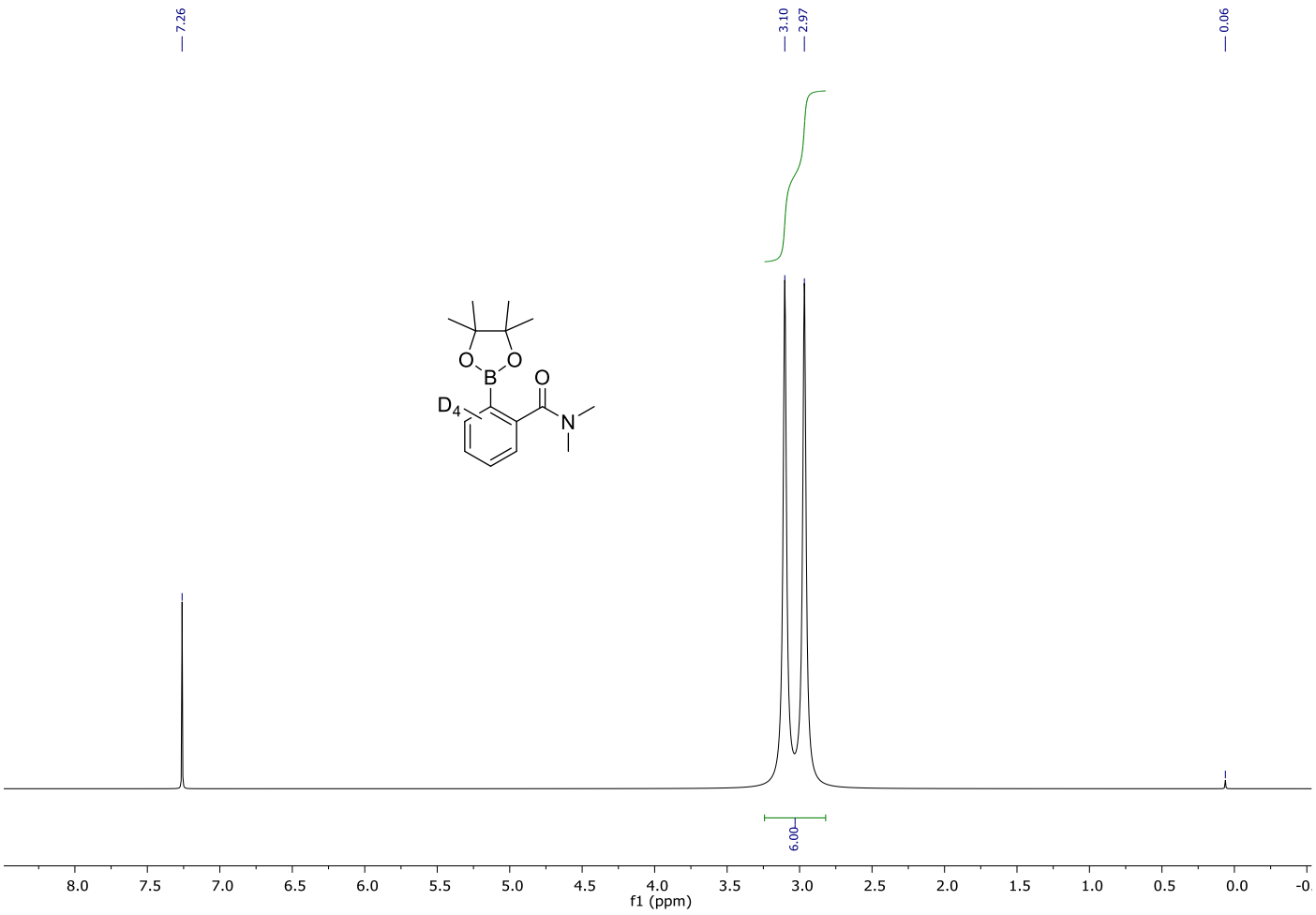
The KIE was calculated as it follows:

Relative number of non deuterated mono-borylated product (based on aromatic hydrogen): N = 1.19 + 1.25 + 1.29 + 1.21 = 4.94.

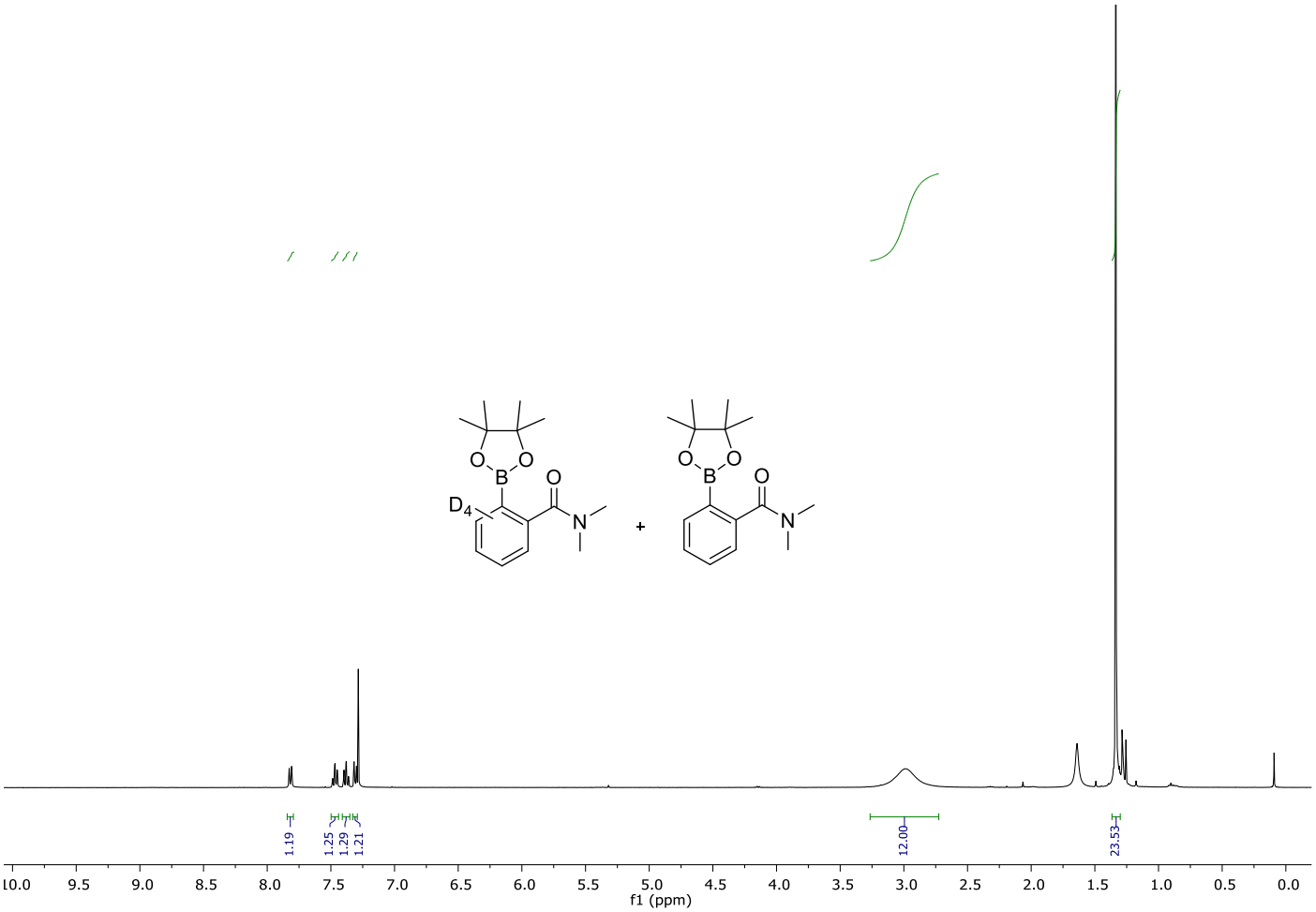
Relative number of deuterated mono-borylated product: N_d = (8 - 4.94) = 3.06.

KIE = N/N_d = (4.94/3.06) = 1.61

See details in the NMR spectra below.

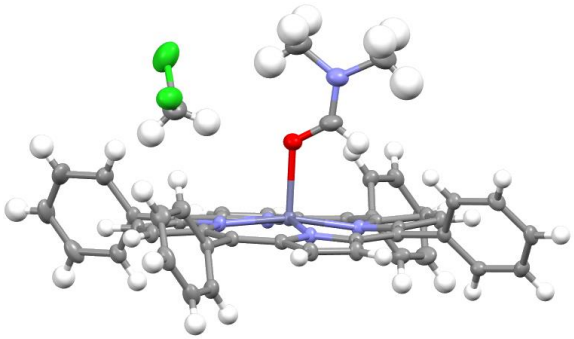


^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4,5,6-D_5-*N*,*N*'-dimethylbenzamide **1a**-d_5.



^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of the mixture of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4,5,6-D_4-*N*,*N*'-dimethylbenzamide **2a**-d_4 and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*,*N*'-dimethylbenzamide **2a**

4. X-ray crystallographic data for ZnTPP⊂DMF.



(C_{47} H_{35} N_5 O Zn, C H_2 Cl_2); M = 836.09. APEXII, Bruker-AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), T = 150(2) K; Triclinic P -1 (I.T.#2), a = 11.1934(5), b = 12.5189(6), c = 14.5833(6) Å, α = 98.996(2), β = 94.719(2), γ = 103.136(2) °, V = 1950.79(15) $Å^3$.Z = 2, d = 1.423 $g.cm^{-3}$, μ = 0.812 mm^{-1}. The structure was solved by direct methods using the *SIR97* program,[19] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-97*).[20] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 8916 unique intensities and 516 parameters converged at $\omega R(F^2)$ = 0.0917 ($R(F)$ = 0.0370) for 7536 observed reflections with $I > 2\sigma(I)$.

Structural data

Empirical formula	C_{48} H_{37} Cl_2 N_5 O Zn
Extended formula	C_{47} H_{35} N_5 O Zn, C H_2 Cl_2
Formula weight	836.09
Temperature	150(2) *K*
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, *P* -1
Unit cell dimensions	a = 11.1934(5) Å, α = 98.996(2) ° b = 12.5189(6) Å, β = 94.719(2) ° c = 14.5833(6) Å, γ = 103.136(2) °
Volume	1950.79(15) $Å^3$
Z, Calculated density	2, 1.423 ($g.cm^{-3}$)
Absorption coefficient	0.812 mm^{-1}
F(000)	864
Crystal size	0.370 x 0.250 x 0.210 mm
Crystal color	red
Theta range for data collection	2.914 to 27.543 °
h_min, h_max	-12, 14
k_min, k_max	-16, 16
l_min, l_max	-18, 16
Reflections collected / unique	21741 / 8916 [R(int)[a] = 0.0294]
Reflections [I>2σ]	7536
Completeness to theta_max	0.992
Absorption correction type	multi-scan
Max. and min. transmission	0.843 , 0.795
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8916 / 0 / 516
[b]Goodness-of-fit	1.051
Final *R* indices [I>2σ]	$R1^c$ = 0.0370, $wR2^d$ = 0.0917
R indices (all data)	$R1^c$ = 0.0461, $wR2^d$ = 0.0962
Largest diff. peak and hole	0.544 and -0.552 $e^-.Å^{-3}$

[a] $R_{int} = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum [F_o^2]$

[b] $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$

[c] $R1 = \sum | |F_o| - |F_c| | / \sum |F_o|$

[d] $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

$w = 1 / [\sigma(F_o^2) + aP^2 + bP]$ where $P = [2F_c^2 + MAX(F_o^2, 0)] / 3$

Atomic coordinates, site occupancy (%) and equivalent isotropic displacement parameters (Å^2). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	occ.	U(eq)
Zn1	0.57107(2)	0.43779(2)	0.77875(2)	1	0.01677(7)
C1	0.69589(17)	0.25101(15)	0.70736(12)	1	0.0191(4)
C2	0.79886(17)	0.32578(16)	0.68562(13)	1	0.0195(4)
C3	0.82101(17)	0.44260(15)	0.70462(13)	1	0.0197(4)
C4	0.92887(17)	0.51834(16)	0.68374(14)	1	0.0239(4)
H4	0.9956	0.4984	0.6547	1	0.029
C5	0.91732(17)	0.62310(16)	0.71324(14)	1	0.0230(4)
H5	0.9749	0.6905	0.7097	1	0.028
C6	0.80126(16)	0.61303(15)	0.75110(12)	1	0.0188(4)
C7	0.75307(16)	0.70346(15)	0.78647(12)	1	0.0184(4)
C8	0.63990(16)	0.69423(15)	0.82283(12)	1	0.0184(4)
C9	0.58498(17)	0.78645(16)	0.84928(13)	1	0.0222(4)
H9	0.6186	0.8622	0.8454	1	0.027
C10	0.47679(18)	0.74499(15)	0.88067(14)	1	0.0228(4)
H10	0.4198	0.7860	0.9026	1	0.027
C11	0.46411(16)	0.62670(15)	0.87454(12)	1	0.0180(4)
C12	0.36460(16)	0.55245(15)	0.90142(12)	1	0.0185(4)
C13	0.35002(16)	0.43656(15)	0.89176(13)	1	0.0184(4)
C14	0.25376(17)	0.36266(16)	0.92725(14)	1	0.0230(4)
H14	0.1925	0.3836	0.9626	1	0.028
C15	0.26691(17)	0.25798(16)	0.90092(14)	1	0.0228(4)
H15	0.2161	0.1914	0.9136	1	0.027
C16	0.37295(16)	0.26650(15)	0.84985(13)	1	0.0189(4)
C17	0.41701(16)	0.17555(15)	0.80954(13)	1	0.0189(4)
C18	0.52281(17)	0.18307(15)	0.76331(13)	1	0.0191(4)
C19	0.57507(18)	0.09015(16)	0.73178(14)	1	0.0233(4)
H19	0.5413	0.0141	0.7347	1	0.028
C20	0.68112(17)	0.13201(16)	0.69735(14)	1	0.0226(4)
H20	0.7357	0.0908	0.6714	1	0.027
C21	0.89460(17)	0.27648(16)	0.64016(14)	1	0.0225(4)
C22	0.8692(2)	0.21693(19)	0.54948(15)	1	0.0314(5)
H22	0.7902	0.2073	0.5155	1	0.038
C23	0.9578(2)	0.1711(2)	0.50759(17)	1	0.0412(6)
H23	0.9391	0.1301	0.4455	1	0.049
C24	1.0725(2)	0.1855(2)	0.55642(17)	1	0.0404(6)
H24	1.1334	0.1549	0.5277	1	0.048
C25	1.0996(2)	0.24400(19)	0.64663(18)	1	0.0363(5)
H25	1.1788	0.2534	0.6801	1	0.044
C26	1.01046(18)	0.28953(17)	0.68897(15)	1	0.0263(4)
H26	1.0291	0.3296	0.7514	1	0.032
C31	0.26488(16)	0.59928(15)	0.94258(13)	1	0.0188(4)
C32	0.29163(17)	0.67791(16)	1.02479(13)	1	0.0214(4)
H32	0.3739	0.7021	1.0554	1	0.026
C33	0.19941(18)	0.72123(17)	1.06247(14)	1	0.0247(4)
H33	0.2191	0.7756	1.1183	1	0.030
C34	0.07848(18)	0.68588(16)	1.01931(14)	1	0.0249(4)
H34	0.0154	0.7160	1.0452	1	0.030
C35	0.05040(17)	0.60627(16)	0.93818(14)	1	0.0245(4)
H35	-0.0324	0.5804	0.9088	1	0.029

C36	0.14358(17)	0.56427(15)	0.89980(13)	1	0.0212(4)
H36	0.1240	0.5108	0.8435	1	0.025
C41	0.82842(16)	0.81921(15)	0.78766(13)	1	0.0195(4)
C42	0.85198(18)	0.85971(16)	0.70577(14)	1	0.0238(4)
H42	0.8212	0.8125	0.6470	1	0.029
C43	0.91949(18)	0.96755(17)	0.70858(15)	1	0.0268(4)
H43	0.9350	0.9937	0.6519	1	0.032
C44	0.96444(19)	1.03739(17)	0.79327(15)	1	0.0296(5)
H44	1.0118	1.1112	0.7951	1	0.035
C45	0.9402(2)	0.99934(18)	0.87558(16)	1	0.0343(5)
H45	0.9692	1.0475	0.9341	1	0.041
C46	0.8732(2)	0.89050(17)	0.87227(14)	1	0.0289(4)
H46	0.8579	0.8645	0.9290	1	0.035
C51	0.34681(17)	0.06216(15)	0.82041(14)	1	0.0211(4)
C52	0.3371(2)	0.03452(17)	0.90879(15)	1	0.0279(4)
H52	0.3800	0.0865	0.9624	1	0.034
C53	0.2661(2)	-0.06719(18)	0.91968(16)	1	0.0329(5)
H53	0.2592	-0.0840	0.9806	1	0.040
C54	0.2052(2)	-0.14458(17)	0.84258(17)	1	0.0338(5)
H54	0.1556	-0.2143	0.8501	1	0.041
C55	0.2170(2)	-0.11985(18)	0.75425(17)	1	0.0343(5)
H55	0.1775	-0.1738	0.7008	1	0.041
C56	0.28630(19)	-0.01672(16)	0.74292(15)	1	0.0277(4)
H56	0.2924	0.0000	0.6819	1	0.033
O61	0.46635(13)	0.43070(12)	0.64573(10)	1	0.0304(3)
C62	0.3857(2)	0.4841(2)	0.64143(16)	1	0.0368(5)
H62	0.3740	0.5277	0.6979	1	0.044
N63	0.31549(18)	0.48496(17)	0.56533(13)	1	0.0379(4)
C64	0.3254(3)	0.4194(3)	0.47825(18)	1	0.0575(8)
H64A	0.3924	0.3819	0.4865	1	0.086
H64B	0.3431	0.4678	0.4318	1	0.086
H64C	0.2474	0.3634	0.4566	1	0.086
C65	0.2213(3)	0.5476(3)	0.5657(2)	1	0.0641(9)
H65A	0.2223	0.5878	0.6292	1	0.096
H65B	0.1401	0.4963	0.5450	1	0.096
H65C	0.2381	0.6011	0.5232	1	0.096
C101	0.4900(3)	0.1792(2)	0.51183(19)	1	0.0530(7)
H10A	0.5595	0.1503	0.5358	1	0.064
H10B	0.4886	0.2477	0.5556	1	0.064
N1	0.59774(14)	0.27980(12)	0.74697(10)	1	0.0178(3)
N2	0.74467(13)	0.50255(13)	0.74574(11)	1	0.0185(3)
N3	0.56354(14)	0.59760(12)	0.83740(11)	1	0.0184(3)
N4	0.42261(14)	0.37619(12)	0.84619(11)	1	0.0183(3)
Cl1	0.35036(6)	0.07889(7)	0.50755(5)	1	0.05400(18)
Cl2	0.51350(9)	0.21186(6)	0.40039(6)	1	0.0677(2)

Anisotropic displacement parameters ($Å^2$)

The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 a^{*2} U_{11} + ... + 2 h k a* b* U_{12}].

Atom	U11	U22	U33	U23	U13	U12
Zn1	0.01554(11)	0.01495(11)	0.01942(12)	0.00280(8)	0.00501(8)	0.00211(8)
C1	0.0191(9)	0.0197(9)	0.0183(9)	0.0021(7)	0.0030(7)	0.0047(7)
C2	0.0178(9)	0.0233(10)	0.0188(9)	0.0033(7)	0.0053(7)	0.0069(7)
C3	0.0188(9)	0.0216(9)	0.0193(9)	0.0048(7)	0.0046(7)	0.0045(7)
C4	0.0184(9)	0.0266(10)	0.0277(10)	0.0072(8)	0.0079(8)	0.0045(8)
C5	0.0178(9)	0.0220(10)	0.0285(10)	0.0069(8)	0.0055(8)	0.0013(7)
C6	0.0171(9)	0.0197(9)	0.0177(9)	0.0028(7)	0.0022(7)	0.0013(7)
C7	0.0193(9)	0.0169(9)	0.0171(9)	0.0040(7)	0.0023(7)	0.0001(7)
C8	0.0191(9)	0.0162(9)	0.0177(9)	0.0016(7)	0.0024(7)	0.0005(7)
C9	0.0234(10)	0.0166(9)	0.0256(10)	0.0029(7)	0.0063(8)	0.0025(7)
C10	0.0240(10)	0.0174(9)	0.0271(10)	0.0024(8)	0.0070(8)	0.0051(8)
C11	0.0171(9)	0.0180(9)	0.0177(9)	0.0011(7)	0.0029(7)	0.0029(7)
C12	0.0161(8)	0.0190(9)	0.0196(9)	0.0021(7)	0.0036(7)	0.0032(7)
C13	0.0143(8)	0.0201(9)	0.0206(9)	0.0043(7)	0.0036(7)	0.0030(7)
C14	0.0187(9)	0.0212(10)	0.0307(10)	0.0069(8)	0.0106(8)	0.0043(7)
C15	0.0189(9)	0.0207(10)	0.0304(10)	0.0086(8)	0.0096(8)	0.0028(7)
C16	0.0158(9)	0.0186(9)	0.0216(9)	0.0041(7)	0.0025(7)	0.0024(7)
C17	0.0181(9)	0.0151(9)	0.0223(9)	0.0038(7)	0.0025(7)	0.0015(7)
C18	0.0194(9)	0.0159(9)	0.0203(9)	0.0014(7)	0.0021(7)	0.0021(7)
C19	0.0237(10)	0.0164(9)	0.0287(10)	0.0015(8)	0.0051(8)	0.0041(7)
C20	0.0216(9)	0.0192(9)	0.0269(10)	0.0006(8)	0.0060(8)	0.0059(7)
C21	0.0221(9)	0.0210(10)	0.0276(10)	0.0083(8)	0.0110(8)	0.0067(8)
C22	0.0322(11)	0.0401(13)	0.0260(11)	0.0054(9)	0.0081(9)	0.0160(10)
C23	0.0503(15)	0.0526(16)	0.0297(12)	0.0065(11)	0.0183(11)	0.0270(12)
C24	0.0408(13)	0.0504(15)	0.0460(14)	0.0199(12)	0.0273(11)	0.0286(12)
C25	0.0222(11)	0.0397(13)	0.0557(15)	0.0228(11)	0.0127(10)	0.0129(9)
C26	0.0225(10)	0.0243(10)	0.0337(11)	0.0087(9)	0.0056(8)	0.0058(8)
C31	0.0184(9)	0.0175(9)	0.0218(9)	0.0058(7)	0.0060(7)	0.0046(7)
C32	0.0199(9)	0.0231(10)	0.0205(9)	0.0045(8)	0.0015(7)	0.0039(7)
C33	0.0291(10)	0.0246(10)	0.0216(10)	0.0037(8)	0.0084(8)	0.0074(8)
C34	0.0229(10)	0.0259(10)	0.0319(11)	0.0107(8)	0.0141(8)	0.0109(8)
C35	0.0149(9)	0.0264(10)	0.0330(11)	0.0103(8)	0.0042(8)	0.0031(8)
C36	0.0202(9)	0.0186(9)	0.0240(10)	0.0035(7)	0.0038(7)	0.0032(7)
C41	0.0150(8)	0.0173(9)	0.0259(10)	0.0043(7)	0.0045(7)	0.0024(7)
C42	0.0257(10)	0.0226(10)	0.0235(10)	0.0043(8)	0.0068(8)	0.0050(8)
C43	0.0277(10)	0.0247(10)	0.0324(11)	0.0127(9)	0.0101(9)	0.0076(8)
C44	0.0271(11)	0.0182(10)	0.0417(13)	0.0096(9)	0.0025(9)	-0.0004(8)
C45	0.0393(12)	0.0232(11)	0.0322(12)	0.0029(9)	-0.0040(9)	-0.0049(9)
C46	0.0362(12)	0.0224(10)	0.0237(10)	0.0064(8)	0.0010(8)	-0.0022(9)
C51	0.0179(9)	0.0164(9)	0.0301(10)	0.0055(8)	0.0074(7)	0.0043(7)
C52	0.0357(11)	0.0213(10)	0.0287(11)	0.0050(8)	0.0087(9)	0.0089(9)
C53	0.0398(12)	0.0287(11)	0.0392(12)	0.0177(10)	0.0179(10)	0.0140(10)
C54	0.0268(11)	0.0201(10)	0.0568(15)	0.0152(10)	0.0109(10)	0.0027(8)
C55	0.0287(11)	0.0231(11)	0.0453(13)	0.0042(10)	0.0003(10)	-0.0028(9)
C56	0.0272(10)	0.0220(10)	0.0315(11)	0.0058(8)	0.0027(8)	0.0009(8)
O61	0.0319(8)	0.0315(8)	0.0274(8)	0.0047(6)	-0.0006(6)	0.0086(7)
C62	0.0337(12)	0.0473(14)	0.0266(11)	0.0068(10)	-0.0017(9)	0.0059(11)
N63	0.0334(10)	0.0471(12)	0.0334(10)	0.0094(9)	0.0007(8)	0.0099(9)
C64	0.0594(18)	0.079(2)	0.0339(14)	0.0030(14)	-0.0035(12)	0.0233(16)
C65	0.0458(16)	0.100(3)	0.0560(18)	0.0127(17)	-0.0001(14)	0.0395(17)

C101	0.0528(17)	0.0557(18)	0.0461(16)	-0.0003(13)	-0.0100(13)	0.0163(14)
N1	0.0165(7)	0.0163(8)	0.0200(8)	0.0025(6)	0.0052(6)	0.0026(6)
N2	0.0169(7)	0.0178(8)	0.0208(8)	0.0028(6)	0.0056(6)	0.0036(6)
N3	0.0172(7)	0.0166(8)	0.0205(8)	0.0033(6)	0.0049(6)	0.0016(6)
N4	0.0171(7)	0.0161(8)	0.0220(8)	0.0032(6)	0.0052(6)	0.0037(6)
Cl1	0.0432(4)	0.0780(5)	0.0434(4)	0.0092(3)	0.0078(3)	0.0203(3)
Cl2	0.0896(6)	0.0502(4)	0.0589(5)	0.0017(3)	0.0246(4)	0.0082(4)

Bond lengths [Å]

Zn1 - N1 = 2.0543(15)
Zn1 - N2 = 2.0554(15)
Zn1 - N4 = 2.0608(15)
Zn1 - N3 = 2.0723(15)
Zn1 - O61 = 2.1609(14)
C1 - N1 = 1.375(2)
C1 - C2 = 1.403(3)
C1 - C20 = 1.444(3)
C2 - C3 = 1.405(3)
C2 - C21 = 1.503(2)
C3 - N2 = 1.374(2)
C3 - C4 = 1.442(2)
C4 - C5 = 1.353(3)
C4 - H4 = 0.9500
C5 - C6 = 1.440(2)
C5 - H5 = 0.9500
C6 - N2 = 1.371(2)
C6 - C7 = 1.407(3)
C7 - C8 = 1.401(2)
C7 - C41 = 1.499(2)
C8 - N3 = 1.371(2)
C8 - C9 = 1.443(3)
C9 - C10 = 1.351(3)
C9 - H9 = 0.9500
C10 - C11 = 1.443(3)
C10 - H10 = 0.9500
C11 - N3 = 1.373(2)
C11 - C12 = 1.405(2)
C12 - C13 = 1.406(3)
C12 - C31 = 1.499(2)
C13 - N4 = 1.373(2)
C13 - C14 = 1.440(2)
C14 - C15 = 1.351(3)
C14 - H14 = 0.9500
C15 - C16 = 1.445(2)
C15 - H15 = 0.9500
C16 - N4 = 1.371(2)
C16 - C17 = 1.407(3)
C17 - C18 = 1.402(2)
C17 - C51 = 1.497(2)
C18 - N1 = 1.374(2)
C18 - C19 = 1.447(3)
C19 - C20 = 1.354(3)
C19 - H19 = 0.9500

C20 - H20 = 0.9500
C21 - C22 = 1.385(3)
C21 - C26 = 1.389(3)
C22 - C23 = 1.391(3)
C22 - H22 = 0.9500
C23 - C24 = 1.376(4)
C23 - H23 = 0.9500
C24 - C25 = 1.375(4)
C24 - H24 = 0.9500
C25 - C26 = 1.397(3)
C25 - H25 = 0.9500
C26 - H26 = 0.9500
C31 - C36 = 1.389(3)
C31 - C32 = 1.391(3)
C32 - C33 = 1.384(3)
C32 - H32 = 0.9500
C33 - C34 = 1.387(3)
C33 - H33 = 0.9500
C34 - C35 = 1.385(3)
C34 - H34 = 0.9500
C35 - C36 = 1.390(3)
C35 - H35 = 0.9500
C36 - H36 = 0.9500
C41 - C46 = 1.386(3)
C41 - C42 = 1.390(3)
C42 - C43 = 1.382(3)
C42 - H42 = 0.9500
C43 - C44 = 1.380(3)
C43 - H43 = 0.9500
C44 - C45 = 1.384(3)
C44 - H44 = 0.9500
C45 - C46 = 1.389(3)
C45 - H45 = 0.9500
C46 - H46 = 0.9500
C51 - C56 = 1.390(3)
C51 - C52 = 1.392(3)
C52 - C53 = 1.379(3)
C52 - H52 = 0.9500
C53 - C54 = 1.379(3)
C53 - H53 = 0.9500
C54 - C55 = 1.381(3)
C54 - H54 = 0.9500
C55 - C56 = 1.389(3)
C55 - H55 = 0.9500
C56 - H56 = 0.9500
O61 - C62 = 1.243(3)
C62 - N63 = 1.309(3)
C62 - H62 = 0.9500
N63 - C64 = 1.427(3)
N63 - C65 = 1.450(3)
C64 - H64A = 0.9800
C64 - H64B = 0.9800
C64 - H64C = 0.9800
C65 - H65A = 0.9800

C65 - H65B = 0.9800
C65 - H65C = 0.9800
C101 - Cl1 = 1.757(3)
C101 - Cl2 = 1.763(3)
C101 - H10A = 0.9900
C101 - H10B = 0.9900

Angles [°]

N1 - Zn1 - N2 = 89.81(6)
N1 - Zn1 - N4 = 89.47(6)
N2 - Zn1 - N4 = 164.75(6)
N1 - Zn1 - N3 = 168.17(6)
N2 - Zn1 - N3 = 88.92(6)
N4 - Zn1 - N3 = 88.67(6)
N1 - Zn1 - O61 = 95.17(6)
N2 - Zn1 - O61 = 98.52(6)
N4 - Zn1 - O61 = 96.72(6)
N3 - Zn1 - O61 = 96.66(6)
N1 - C1 - C2 = 125.61(16)
N1 - C1 - C20 = 109.44(15)
C2 - C1 - C20 = 124.82(17)
C1 - C2 - C3 = 125.45(17)
C1 - C2 - C21 = 117.05(16)
C3 - C2 - C21 = 117.49(16)
N2 - C3 - C2 = 125.87(16)
N2 - C3 - C4 = 109.41(16)
C2 - C3 - C4 = 124.72(17)
C5 - C4 - C3 = 107.20(17)
C5 - C4 - H4 = 126.4
C3 - C4 - H4 = 126.4
C4 - C5 - C6 = 107.03(17)
C4 - C5 - H5 = 126.5
C6 - C5 - H5 = 126.5
N2 - C6 - C7 = 125.57(16)
N2 - C6 - C5 = 109.71(15)
C7 - C6 - C5 = 124.71(17)
C8 - C7 - C6 = 125.00(17)
C8 - C7 - C41 = 116.67(16)
C6 - C7 - C41 = 118.32(15)
N3 - C8 - C7 = 125.98(16)
N3 - C8 - C9 = 109.54(15)
C7 - C8 - C9 = 124.48(16)
C10 - C9 - C8 = 107.23(16)
C10 - C9 - H9 = 126.4
C8 - C9 - H9 = 126.4
C9 - C10 - C11 = 107.01(16)
C9 - C10 - H10 = 126.5
C11 - C10 - H10 = 126.5
N3 - C11 - C12 = 125.20(16)
N3 - C11 - C10 = 109.58(15)
C12 - C11 - C10 = 125.21(16)
C11 - C12 - C13 = 125.05(16)
C11 - C12 - C31 = 117.99(16)
C13 - C12 - C31 = 116.95(15)

N4 - C13 - C12 = 125.86(16)
N4 - C13 - C14 = 109.60(16)
C12 - C13 - C14 = 124.53(16)
C15 - C14 - C13 = 107.20(16)
C15 - C14 - H14 = 126.4
C13 - C14 - H14 = 126.4
C14 - C15 - C16 = 107.00(16)
C14 - C15 - H15 = 126.5
C16 - C15 - H15 = 126.5
N4 - C16 - C17 = 125.60(16)
N4 - C16 - C15 = 109.54(15)
C17 - C16 - C15 = 124.86(17)
C18 - C17 - C16 = 125.39(17)
C18 - C17 - C51 = 117.93(16)
C16 - C17 - C51 = 116.65(15)
N1 - C18 - C17 = 125.72(16)
N1 - C18 - C19 = 109.42(15)
C17 - C18 - C19 = 124.71(17)
C20 - C19 - C18 = 107.07(17)
C20 - C19 - H19 = 126.5
C18 - C19 - H19 = 126.5
C19 - C20 - C1 = 107.25(16)
C19 - C20 - H20 = 126.4
C1 - C20 - H20 = 126.4
C22 - C21 - C26 = 118.80(18)
C22 - C21 - C2 = 120.92(18)
C26 - C21 - C2 = 120.28(18)
C21 - C22 - C23 = 120.9(2)
C21 - C22 - H22 = 119.6
C23 - C22 - H22 = 119.6
C24 - C23 - C22 = 119.8(2)
C24 - C23 - H23 = 120.1
C22 - C23 - H23 = 120.1
C25 - C24 - C23 = 120.4(2)
C25 - C24 - H24 = 119.8
C23 - C24 - H24 = 119.8
C24 - C25 - C26 = 120.0(2)
C24 - C25 - H25 = 120.0
C26 - C25 - H25 = 120.0
C21 - C26 - C25 = 120.3(2)
C21 - C26 - H26 = 119.9
C25 - C26 - H26 = 119.9
C36 - C31 - C32 = 118.61(17)
C36 - C31 - C12 = 120.66(17)
C32 - C31 - C12 = 120.73(17)
C33 - C32 - C31 = 120.58(18)
C33 - C32 - H32 = 119.7
C31 - C32 - H32 = 119.7
C32 - C33 - C34 = 120.46(19)
C32 - C33 - H33 = 119.8
C34 - C33 - H33 = 119.8
C35 - C34 - C33 = 119.45(17)
C35 - C34 - H34 = 120.3
C33 - C34 - H34 = 120.3

C34 - C35 - C36 = 119.90(18)
C34 - C35 - H35 = 120.1
C36 - C35 - H35 = 120.1
C35 - C36 - C31 = 120.98(18)
C35 - C36 - H36 = 119.5
C31 - C36 - H36 = 119.5
C46 - C41 - C42 = 118.14(18)
C46 - C41 - C7 = 119.83(17)
C42 - C41 - C7 = 122.00(17)
C43 - C42 - C41 = 120.99(19)
C43 - C42 - H42 = 119.5
C41 - C42 - H42 = 119.5
C44 - C43 - C42 = 120.31(18)
C44 - C43 - H43 = 119.8
C42 - C43 - H43 = 119.8
C43 - C44 - C45 = 119.62(19)
C43 - C44 - H44 = 120.2
C45 - C44 - H44 = 120.2
C44 - C45 - C46 = 119.8(2)
C44 - C45 - H45 = 120.1
C46 - C45 - H45 = 120.1
C41 - C46 - C45 = 121.16(19)
C41 - C46 - H46 = 119.4
C45 - C46 - H46 = 119.4
C56 - C51 - C52 = 118.36(18)
C56 - C51 - C17 = 120.92(17)
C52 - C51 - C17 = 120.68(18)
C53 - C52 - C51 = 121.0(2)
C53 - C52 - H52 = 119.5
C51 - C52 - H52 = 119.5
C54 - C53 - C52 = 120.3(2)
C54 - C53 - H53 = 119.8
C52 - C53 - H53 = 119.8
C53 - C54 - C55 = 119.41(19)
C53 - C54 - H54 = 120.3
C55 - C54 - H54 = 120.3
C54 - C55 - C56 = 120.5(2)
C54 - C55 - H55 = 119.7
C56 - C55 - H55 = 119.7
C55 - C56 - C51 = 120.3(2)
C55 - C56 - H56 = 119.8
C51 - C56 - H56 = 119.8
C62 - O61 - Zn1 = 119.75(14)
O61 - C62 - N63 = 125.2(2)
O61 - C62 - H62 = 117.4
N63 - C62 - H62 = 117.4
C62 - N63 - C64 = 120.7(2)
C62 - N63 - C65 = 122.3(2)
C64 - N63 - C65 = 116.9(2)
N63 - C64 - H64A = 109.5
N63 - C64 - H64B = 109.5
H64A - C64 - H64B = 109.5
N63 - C64 - H64C = 109.5
H64A - C64 - H64C = 109.5

H64B - C64 - H64C = 109.5
N63 - C65 - H65A = 109.5
N63 - C65 - H65B = 109.5
H65A - C65 - H65B = 109.5
N63 - C65 - H65C = 109.5
H65A - C65 - H65C = 109.5
H65B - C65 - H65C = 109.5
Cl1 - C101 - Cl2 = 111.32(15)
Cl1 - C101 - H10A = 109.4
Cl2 - C101 - H10A = 109.4
Cl1 - C101 - H10B = 109.4
Cl2 - C101 - H10B = 109.4
H10A - C101 - H10B = 108.0
C18 - N1 - C1 = 106.81(14)
C18 - N1 - Zn1 = 126.72(12)
C1 - N1 - Zn1 = 126.45(12)
C6 - N2 - C3 = 106.64(14)
C6 - N2 - Zn1 = 126.94(12)
C3 - N2 - Zn1 = 126.10(12)
C8 - N3 - C11 = 106.61(14)
C8 - N3 - Zn1 = 125.35(12)
C11 - N3 - Zn1 = 125.75(12)
C16 - N4 - C13 = 106.63(14)
C16 - N4 - Zn1 = 126.73(12)
C13 - N4 - Zn1 = 126.56(12)

Torsion angles [°]

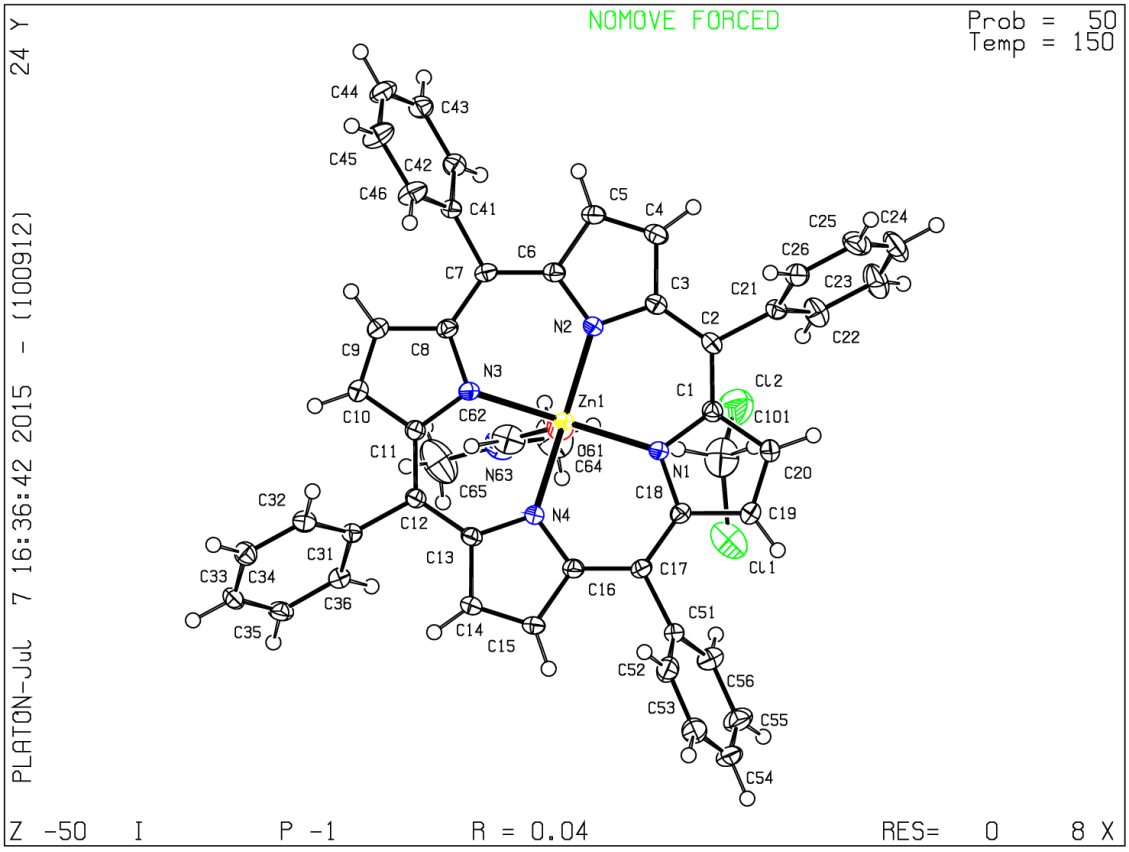
N1 - C1 - C2 - C3 = 3.0(3)
C20 - C1 - C2 - C3 = -172.46(18)
N1 - C1 - C2 - C21 = -178.46(17)
C20 - C1 - C2 - C21 = 6.1(3)
C1 - C2 - C3 - N2 = -1.4(3)
C21 - C2 - C3 - N2 = -179.91(17)
C1 - C2 - C3 - C4 = 178.47(18)
C21 - C2 - C3 - C4 = -0.1(3)
N2 - C3 - C4 - C5 = 0.6(2)
C2 - C3 - C4 - C5 = -179.26(18)
C3 - C4 - C5 - C6 = -1.0(2)
C4 - C5 - C6 - N2 = 1.1(2)
C4 - C5 - C6 - C7 = -177.85(18)
N2 - C6 - C7 - C8 = 0.8(3)
C5 - C6 - C7 - C8 = 179.57(18)
N2 - C6 - C7 - C41 = 179.53(17)
C5 - C6 - C7 - C41 = -1.7(3)
C6 - C7 - C8 - N3 = 6.1(3)
C41 - C7 - C8 - N3 = -172.66(17)
C6 - C7 - C8 - C9 = -172.79(18)
C41 - C7 - C8 - C9 = 8.5(3)
N3 - C8 - C9 - C10 = 0.8(2)
C7 - C8 - C9 - C10 = 179.77(18)
C8 - C9 - C10 - C11 = 0.4(2)
C9 - C10 - C11 - N3 = -1.4(2)
C9 - C10 - C11 - C12 = 179.28(18)

N3 - C11 - C12 - C13 = -2.0(3)
C10 - C11 - C12 - C13 = 177.22(18)
N3 - C11 - C12 - C31 = 178.82(16)
C10 - C11 - C12 - C31 = -2.0(3)
C11 - C12 - C13 - N4 = -7.3(3)
C31 - C12 - C13 - N4 = 171.95(17)
C11 - C12 - C13 - C14 = 174.05(18)
C31 - C12 - C13 - C14 = -6.8(3)
N4 - C13 - C14 - C15 = -1.5(2)
C12 - C13 - C14 - C15 = 177.38(18)
C13 - C14 - C15 - C16 = 0.8(2)
C14 - C15 - C16 - N4 = 0.1(2)
C14 - C15 - C16 - C17 = -179.30(18)
N4 - C16 - C17 - C18 = 3.5(3)
C15 - C16 - C17 - C18 = -177.10(18)
N4 - C16 - C17 - C51 = -178.76(17)
C15 - C16 - C17 - C51 = 0.6(3)
C16 - C17 - C18 - N1 = -2.5(3)
C51 - C17 - C18 - N1 = 179.81(17)
C16 - C17 - C18 - C19 = 172.46(18)
C51 - C17 - C18 - C19 = -5.2(3)
N1 - C18 - C19 - C20 = 0.3(2)
C17 - C18 - C19 - C20 = -175.33(18)
C18 - C19 - C20 - C1 = 0.1(2)
N1 - C1 - C20 - C19 = -0.6(2)
C2 - C1 - C20 - C19 = 175.49(18)
C1 - C2 - C21 - C22 = 69.1(2)
C3 - C2 - C21 - C22 = -112.3(2)
C1 - C2 - C21 - C26 = -110.6(2)
C3 - C2 - C21 - C26 = 68.1(2)
C26 - C21 - C22 - C23 = -0.2(3)
C2 - C21 - C22 - C23 = -179.8(2)
C21 - C22 - C23 - C24 = -0.4(4)
C22 - C23 - C24 - C25 = 0.6(4)
C23 - C24 - C25 - C26 = -0.2(3)
C22 - C21 - C26 - C25 = 0.5(3)
C2 - C21 - C26 - C25 = -179.81(18)
C24 - C25 - C26 - C21 = -0.3(3)
C11 - C12 - C31 - C36 = 119.7(2)
C13 - C12 - C31 - C36 = -59.6(2)
C11 - C12 - C31 - C32 = -60.9(2)
C13 - C12 - C31 - C32 = 119.81(19)
C36 - C31 - C32 - C33 = -0.8(3)
C12 - C31 - C32 - C33 = 179.81(17)
C31 - C32 - C33 - C34 = 0.8(3)
C32 - C33 - C34 - C35 = 0.3(3)
C33 - C34 - C35 - C36 = -1.3(3)
C34 - C35 - C36 - C31 = 1.3(3)
C32 - C31 - C36 - C35 = -0.2(3)
C12 - C31 - C36 - C35 = 179.19(17)
C8 - C7 - C41 - C46 = 63.4(2)
C6 - C7 - C41 - C46 = -115.4(2)
C8 - C7 - C41 - C42 = -114.4(2)
C6 - C7 - C41 - C42 = 66.8(2)

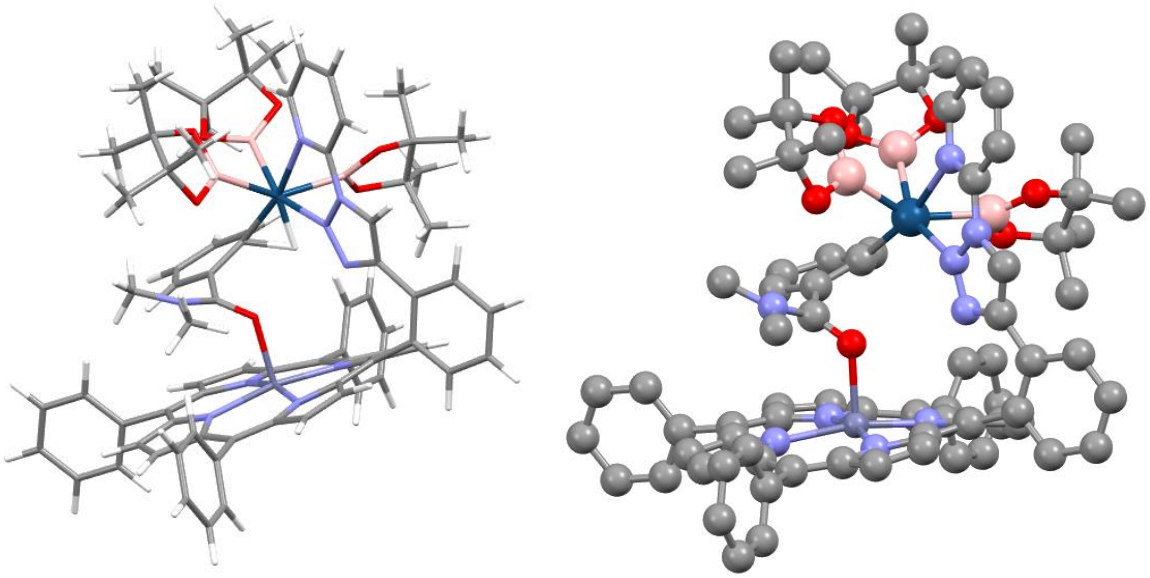
C46 - C41 - C42 - C43 = 0.8(3)
C7 - C41 - C42 - C43 = 178.60(17)
C41 - C42 - C43 - C44 = -0.3(3)
C42 - C43 - C44 - C45 = -0.9(3)
C43 - C44 - C45 - C46 = 1.5(3)
C42 - C41 - C46 - C45 = -0.2(3)
C7 - C41 - C46 - C45 = -178.03(19)
C44 - C45 - C46 - C41 = -0.9(3)
C18 - C17 - C51 - C56 = -66.0(2)
C16 - C17 - C51 - C56 = 116.1(2)
C18 - C17 - C51 - C52 = 116.2(2)
C16 - C17 - C51 - C52 = -61.7(2)
C56 - C51 - C52 - C53 = -2.0(3)
C17 - C51 - C52 - C53 = 175.85(18)
C51 - C52 - C53 - C54 = 1.3(3)
C52 - C53 - C54 - C55 = 0.7(3)
C53 - C54 - C55 - C56 = -2.1(3)
C54 - C55 - C56 - C51 = 1.3(3)
C52 - C51 - C56 - C55 = 0.7(3)
C17 - C51 - C56 - C55 = -177.17(18)
Zn1 - O61 - C62 - N63 = -178.99(18)
O61 - C62 - N63 - C64 = 1.6(4)
O61 - C62 - N63 - C65 = 178.8(2)
C17 - C18 - N1 - C1 = 174.91(17)
C19 - C18 - N1 - C1 = -0.7(2)
C17 - C18 - N1 - Zn1 = -3.6(3)
C19 - C18 - N1 - Zn1 = -179.21(12)
C2 - C1 - N1 - C18 = -175.24(18)
C20 - C1 - N1 - C18 = 0.8(2)
C2 - C1 - N1 - Zn1 = 3.3(3)
C20 - C1 - N1 - Zn1 = 179.31(12)
C7 - C6 - N2 - C3 = 178.23(17)
C5 - C6 - N2 - C3 = -0.7(2)
C7 - C6 - N2 - Zn1 = 4.5(3)
C5 - C6 - N2 - Zn1 = -174.43(12)
C2 - C3 - N2 - C6 = 179.93(17)
C4 - C3 - N2 - C6 = 0.1(2)
C2 - C3 - N2 - Zn1 = -6.3(3)
C4 - C3 - N2 - Zn1 = 173.88(12)
C7 - C8 - N3 - C11 = 179.39(17)
C9 - C8 - N3 - C11 = -1.6(2)
C7 - C8 - N3 - Zn1 = -17.0(3)
C9 - C8 - N3 - Zn1 = 161.96(12)
C12 - C11 - N3 - C8 = -178.83(18)
C10 - C11 - N3 - C8 = 1.9(2)
C12 - C11 - N3 - Zn1 = 17.7(3)
C10 - C11 - N3 - Zn1 = -161.63(12)
C17 - C16 - N4 - C13 = 178.37(18)
C15 - C16 - N4 - C13 = -1.1(2)
C17 - C16 - N4 - Zn1 = 1.7(3)
C15 - C16 - N4 - Zn1 = -177.78(12)
C12 - C13 - N4 - C16 = -177.30(18)
C14 - C13 - N4 - C16 = 1.6(2)
C12 - C13 - N4 - Zn1 = -0.6(3)

C14 - C13 - N4 - Zn1 = 178.29(12)

Structure visualisation



5. PM3-minimized molecular modelling.



HETATM 1 N UNK 0001 1.155 -2.560 -1.984

HETATM 2 C UNK 0001 1.375 -2.303 -3.325

HETATM 3 C UNK 0001 2.347 -2.447 -1.294

HETATM 4 C UNK 0001 2.711 -1.942 -3.451

HETATM 5 C UNK 0001 3.309 -2.024 -2.196

HETATM 6 C UNK 0001 2.555 -2.753 0.073

HETATM 7 C UNK 0001 1.571 -3.118 0.904

HETATM 8 N UNK 0001 0.265 -3.228 0.631

HETATM 9 C UNK 0001 -0.363 -3.478 1.774

HETATM 10 C UNK 0001 0.573 -3.613 2.896

HETATM 11 C UNK 0001 1.751 -3.408 2.314

HETATM 12 C UNK 0001 -1.786 -3.640 1.981

HETATM 13 C UNK 0001 -2.510 -3.888 0.886

HETATM 14 N UNK 0001 -2.167 -3.902 -0.474

HETATM 15 C UNK 0001 -3.315 -4.217 -1.211

HETATM 16 C UNK 0001 -3.904 -4.293 0.985

HETATM 17 C UNK 0001 -4.360 -4.540 -0.240

HETATM 18 C UNK 0001 -3.613 -4.221 -2.512

HETATM 19 C UNK 0001 -2.603 -3.705 -3.401

HETATM 20 N UNK 0001 -1.418 -3.188 -3.104

HETATM 21 C UNK 0001 -0.795 -2.860 -4.238

HETATM 22 C UNK 0001 -2.839 -3.673 -4.853

HETATM 23 C UNK 0001 -1.718 -3.133 -5.324

HETATM 24 C UNK 0001 0.459 -2.432 -4.396

HETATM 25 C UNK 0001 2.054 -3.069 -7.781

HETATM 26 C UNK 0001 0.698 -1.007 -6.474

HETATM 27 C UNK 0001 1.609 -3.248 -6.471

HETATM 28 C UNK 0001 1.822 -1.862 -8.436

HETATM 29 C UNK 0001 1.145 -0.831 -7.785

HETATM 30 C UNK 0001 0.926 -2.218 -5.805

HETATM 31 C UNK 0001 -7.198 -4.171 -3.726

HETATM 32 C UNK 0001 -5.131 -6.010 -3.351

HETATM 33 C UNK 0001 -7.395 -5.517 -4.034

HETATM 34 C UNK 0001 -5.967 -3.741 -3.229

HETATM 35 C UNK 0001 -4.924 -4.659 -3.039

HETATM 36 C UNK 0001 -6.364 -6.435 -3.848

HETATM 37 C UNK 0001 -2.358 -3.627 3.339

HETATM 38 C UNK 0001 -3.443 -3.795 5.916

HETATM 39 C UNK 0001 -2.469 -4.868 4.002

HETATM 40 C UNK 0001 -2.799 -2.444 3.970

HETATM 41 C UNK 0001 -3.336 -2.559 5.270

HETATM 42 C UNK 0001 -3.010 -4.950 5.281

HETATM 43 C UNK 0001 4.357 -1.458 1.256

HETATM 44 C UNK 0001 6.096 -3.638 1.111

HETATM 45 C UNK 0001 3.930 -2.650 0.651

HETATM 46 C UNK 0001 5.644 -1.360 1.785

HETATM 47 C UNK 0001 6.511 -2.450 1.713

HETATM 48 C UNK 0001 4.810 -3.740 0.579

HETATM 49 C UNK 0001 -2.686 -1.115 3.356

HETATM 50 C UNK 0001 -3.449 -0.000 3.751

HETATM 51 H UNK 0001 -4.246 0.122 4.470

HETATM 52 N UNK 0001 -1.740 -0.756 2.363

HETATM 53 N UNK 0001 -1.872 0.543 2.292

HETATM 54 N UNK 0001 -2.832 1.035 3.105

HETATM 55 C UNK 0001 -2.911 2.407 3.291

HETATM 56 C UNK 0001 -2.736 5.117 3.657

HETATM 57 C UNK 0001 -3.804 3.019 4.164

HETATM 58 C UNK 0001 -1.871 4.444 2.800

HETATM 59 C UNK 0001 -3.714 4.397 4.340

HETATM 60 N UNK 0001 -1.987 3.121 2.629

HETATM 61 Ir UNK 0001 -0.564 1.970 1.181

HETATM 62 Zn UNK 0001 -0.605 -3.032 -1.091

HETATM 63 H UNK 0001 0.070 0.448 0.971

HETATM 64 B UNK 0001 0.629 1.816 3.075

HETATM 65 B UNK 0001 0.698 3.870 0.963

HETATM 66 O UNK 0001 1.343 4.536 2.053

HETATM 67 O UNK 0001 0.963 4.514 -0.313

HETATM 68 C UNK 0001 2.005 5.485 -0.030

HETATM 69 C UNK 0001 3.345 4.836 -0.391

HETATM 70 C UNK 0001 1.784 6.692 -0.942

HETATM 71 C UNK 0001 1.850 5.778 1.498

HETATM 72 C UNK 0001 3.149 6.121 2.227

HETATM 73 C UNK 0001 0.810 6.864 1.810

HETATM 74 O UNK 0001 1.997 1.388 3.108

HETATM 75 O UNK 0001 0.094 2.068 4.386

HETATM 76 C UNK 0001 2.232 1.054 4.496

HETATM 77 C UNK 0001 1.243 1.985 5.266

HETATM 78 C UNK 0001 0.776 1.445 6.616

HETATM 79 C UNK 0001 1.751 3.422 5.441

HETATM 80 C UNK 0001 3.707 1.286 4.813

HETATM 81 C UNK 0001 1.908 -0.440 4.634

HETATM 82 H UNK 0001 -5.830 -2.691 -2.992

HETATM 83 H UNK 0001 -8.008 -3.461 -3.874

HETATM 84 H UNK 0001 -8.355 -5.852 -4.422

HETATM 85 H UNK 0001 -6.520 -7.484 -4.090

HETATM 86 H UNK 0001 -4.334 -6.739 -3.212

HETATM 87 H UNK 0001 -4.552 2.457 4.716

HETATM 88 H UNK 0001 -4.396 4.910 5.020

HETATM 89 H UNK 0001 -2.649 6.193 3.793

HETATM 90 H UNK 0001 -1.107 4.942 2.235

HETATM 91 H UNK 0001 2.100 3.840 4.492

HETATM 92 H UNK 0001 2.570 3.478 6.165

HETATM 93 H UNK 0001 0.944 4.079 5.785

HETATM 94 H UNK 0001 0.084 2.148 7.095

HETATM 95 H UNK 0001 1.617 1.276 7.294

HETATM 96 H UNK 0001 0.213 0.512 6.505

HETATM 97 H UNK 0001 2.095 -0.807 5.648

HETATM 98 H UNK 0001 2.524 -1.027 3.944

HETATM 99 H UNK 0001 0.866 -0.650 4.369

HETATM 100 H UNK 0001 4.340 0.604 4.234

HETATM 101 H UNK 0001 4.027 2.294 4.528

HETATM 102 H UNK 0001 3.918 1.132 5.875

HETATM 103 H UNK 0001 3.548 3.963 0.237

HETATM 104 H UNK 0001 4.178 5.538 -0.281

HETATM 105 H UNK 0001 3.338 4.486 -1.429

HETATM 106 H UNK 0001 2.483 7.502 -0.712

HETATM 107 H UNK 0001 1.916 6.412 -1.994

HETATM 108 H UNK 0001 0.760 7.073 -0.870

HETATM 109 H UNK 0001 3.632 7.003 1.796

HETATM 110 H UNK 0001 3.855 5.284 2.213

HETATM 111 H UNK 0001 2.956 6.320 3.288

HETATM 112 H UNK 0001 1.173 7.861 1.537

HETATM 113 H UNK 0001 -0.129 6.686 1.277

HETATM 114 H UNK 0001 0.564 6.871 2.878

HETATM 115 H UNK 0001 -3.696 -4.021 -5.403

HETATM 116 H UNK 0001 -1.524 -2.984 -6.376

HETATM 117 H UNK 0001 0.167 -0.194 -5.992

HETATM 118 H UNK 0001 0.966 0.106 -8.306

HETATM 119 H UNK 0001 2.170 -1.725 -9.458

HETATM 120 H UNK 0001 2.583 -3.872 -8.290

HETATM 121 H UNK 0001 1.798 -4.197 -5.971

HETATM 122 H UNK 0001 3.219 -1.683 -4.373

HETATM 123 H UNK 0001 4.354 -1.839 -1.975

HETATM 124 H UNK 0001 4.498 -4.669 0.107

HETATM 125 H UNK 0001 6.776 -4.484 1.053

HETATM 126 H UNK 0001 7.516 -2.375 2.123

HETATM 127 H UNK 0001 5.976 -0.437 2.253

HETATM 128 H UNK 0001 3.685 -0.607 1.318

HETATM 129 H UNK 0001 2.695 -3.447 2.834

HETATM 130 H UNK 0001 0.366 -3.847 3.924

HETATM 131 H UNK 0001 -3.668 -1.684 5.824

HETATM 132 H UNK 0001 -3.860 -3.853 6.919

HETATM 133 H UNK 0001 -3.089 -5.913 5.781

HETATM 134 H UNK 0001 -2.129 -5.783 3.516

HETATM 135 H UNK 0001 -4.476 -4.432 1.890

HETATM 136 H UNK 0001 -5.360 -4.885 -0.459

HETATM 137 C UNK 0001 0.656 1.254 -0.432

HETATM 138 C UNK 0001 2.188 1.374 -2.721

HETATM 139 C UNK 0001 2.018 1.512 -0.327

HETATM 140 C UNK 0001 0.115 0.737 -1.615

HETATM 141 C UNK 0001 0.882 0.894 -2.781

HETATM 142 C UNK 0001 2.773 1.614 -1.489

HETATM 143 C UNK 0001 -1.092 -0.132 -1.639

HETATM 144 O UNK 0001 -1.313 -1.043 -0.758

HETATM 145 H UNK 0001 0.528 0.543 -3.744

HETATM 146 H UNK 0001 2.787 1.449 -3.627

HETATM 147 H UNK 0001 3.828 1.871 -1.427

HETATM 148 H UNK 0001 2.486 1.681 0.638

HETATM 149 B UNK 0001 -2.009 3.143 -0.085

HETATM 150 O UNK 0001 -1.958 4.603 -0.208

HETATM 151 O UNK 0001 -3.116 2.580 -0.804

HETATM 152 C UNK 0001 -3.949 3.729 -1.126

HETATM 153 C UNK 0001 -2.936 4.914 -1.226

HETATM 154 C UNK 0001 -4.943 3.859 0.039

HETATM 155 C UNK 0001 -4.731 3.456 -2.408

HETATM 156 C UNK 0001 -2.158 4.977 -2.546

HETATM 157 C UNK 0001 -3.530 6.287 -0.922

HETATM 158 N UNK 0001 -2.171 0.161 -2.494

HETATM 159 C UNK 0001 -2.099 1.024 -3.661

HETATM 160 C UNK 0001 -3.426 -0.555 -2.332

HETATM 161 H UNK 0001 -1.461 1.888 -3.478

HETATM 162 H UNK 0001 -3.098 1.377 -3.926

HETATM 163 H UNK 0001 -1.705 0.440 -4.497

HETATM 164 H UNK 0001 -4.227 0.178 -2.195

HETATM 165 H UNK 0001 -3.629 -1.129 -3.238

HETATM 166 H UNK 0001 -3.420 -1.213 -1.462

HETATM 167 H UNK 0001 -1.350 5.715 -2.482

HETATM 168 H UNK 0001 -1.671 4.022 -2.766

HETATM 169 H UNK 0001 -2.801 5.250 -3.388

HETATM 170 H UNK 0001 -5.372 4.303 -2.673

HETATM 171 H UNK 0001 -5.674 4.655 -0.136

HETATM 172 H UNK 0001 -4.429 4.063 0.983

HETATM 173 H UNK 0001 -4.340 6.537 -1.615

HETATM 174 H UNK 0001 -2.762 7.067 -0.995

HETATM 175 H UNK 0001 -3.908 6.346 0.104

HETATM 176 H UNK 0001 -5.360 2.566 -2.298

HETATM 177 H UNK 0001 -5.489 2.920 0.187

HETATM 178 H UNK 0001 -4.068 3.252 -3.252

CONECT 1 2 3 62

CONECT 2 1 4 24

CONECT 3 1 5 6

CONECT 4 2 5 122

CONECT 5 3 4 123

CONECT 6 3 7 45

CONECT 7 6 8 11

CONECT 8 7 9 62

CONECT 9 8 10 12

CONECT 10 9 11 130

CONECT 11 7 10 129

CONECT 12 9 13 37

CONECT 13 12 14 16

CONECT 14 13 15 62

CONECT 15 14 17 18

CONECT 16 13 17 135

CONECT 17 16 15 136

CONECT 18 15 19 35

CONECT 19 18 20 22

CONECT 20 19 21 62

CONECT 21 20 23 24

CONECT 22 19 23 115

CONECT 23 22 21 116

CONECT 24 21 2 30

CONECT 25 28 27 120

CONECT 26 29 30 117

CONECT 27 30 25 121

CONECT 28 25 29 119

CONECT 29 28 26 118

CONECT 30 26 27 24

CONECT 31 34 33 83

CONECT 32 35 36 86

CONECT 33 36 31 84

CONECT 34 31 35 82

CONECT 35 34 32 18

CONECT 36 32 33 85

CONECT 37 40 39 12

CONECT 38 41 42 132

CONECT 39 42 37 134

CONECT 40 37 41 49

CONECT 41 40 38 131

CONECT 42 38 39 133

CONECT 43 46 45 128

CONECT 44 47 48 125

CONECT 45 48 43 6

CONECT 46 43 47 127

CONECT 47 46 44 126

CONECT 48 44 45 124

CONECT 49 40 50 52

CONECT 50 49 51 54

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CONECT 57 59 55 87

CONECT 58 56 60 90

CONECT 59 56 57 88

CONECT 60 58 55 61

CONECT 61 53 60 63 64

CONECT 61 65 137 149

CONECT 62 8 14 20 1

CONECT 62 144

CONECT 63 61 137

CONECT 64 61 74 75

CONECT 65 61 66 67

CONECT 66 65 71

CONECT 67 65 68

CONECT 68 67 69 70 71

CONECT 69 68 103 104 105

CONECT 70 68 106 107 108

CONECT 71 68 72 73 66

CONECT 72 71 109 110 111

CONECT 73 71 112 113 114

CONECT 74 64 76

CONECT 75 64 77

CONECT 76 77 80 81 74

CONECT 77 76 78 79 75

CONECT 78 77 94 95 96

CONECT 79 77 91 92 93

CONECT 80 76 100 101 102

CONECT 81 76 97 98 99

CONECT 82 34

CONECT 83 31

CONECT 84 33

CONECT 85 36

CONECT 86 32

CONECT 87 57

CONECT 88 59

CONECT 89 56

CONECT 90 58

CONECT 91 79

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CONECT 109 72

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CONECT 115 22

CONECT 116 23

CONECT 117 26

CONECT 118 29

CONECT 119 28

CONECT 120 25

CONECT 121 27

CONECT 122 4

CONECT 123 5

CONECT 124 48

CONECT 125 44

CONECT 126 47

CONECT 127 46

CONECT 128 43

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CONECT 130 10

CONECT 131 41

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CONECT 137 140 139 61 63

CONECT 138 141 142 146

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CONECT 142 138 139 147

CONECT 143 140 144 158

CONECT 144 143 62

CONECT 145 141

CONECT 146 138

CONECT 147 142

CONECT 148 139

CONECT 149 61 151 150

CONECT 150 153 149

CONECT 151 149 152

CONECT 152 151 153 154 155

CONECT 153 152 150 156 157

CONECT 154 152 171 172 177

CONECT 155 152 170 176 178

CONECT 156 153 167 168 169

CONECT 157 153 173 174 175

CONECT 158 143 159 160

CONECT 159 158 161 162 163

CONECT 160 158 164 165 166

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CONECT 175 157

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CONECT 177 154

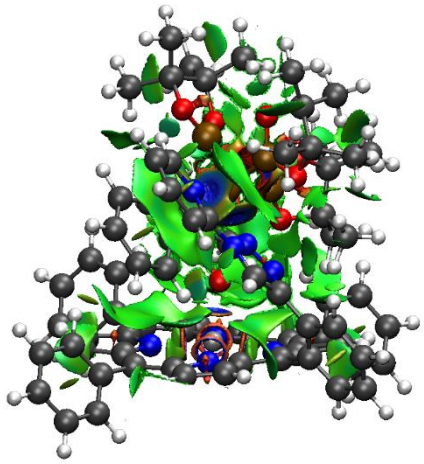
CONECT 178 155

6. Computational details.

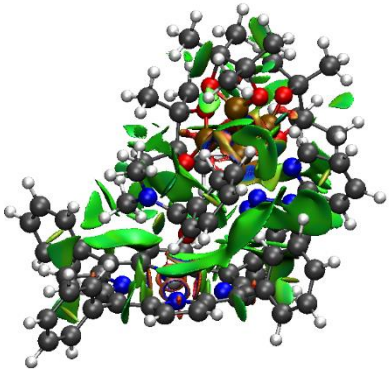
All the DFT calculations were performed with the Gaussian 16 set of programs.[21] Geometry optimizations were performed without symmetry constraints. Analytical frequency calculations were then carried out for the characterization of the located stationary points. These frequencies were used to calculate unscaled zero-point energies (ZPEs) as well as thermal corrections and entropy effects at 353.15 K. For this calculations, we used the BP86 functional of Becke and Perdew,[22-24] together with the Grimme D3 correction term to the electronic energy.[25] The electronic configuration of the molecular systems was described with the double-ζ basis set with polarization of Ahlrichs for main-group atoms (Def2SVP keyword in Gaussian),[26] whereas for iridium the small-core quasi-relativistic Stuttgart/Dresden effective core potential, with an associated valence basis set (standard SDD keywords in Gaussian16) were employed.[27-29] Energies were obtained by single-point calculations on the optimized geometries with the M06L functional,[30] coupled with the Def2TZVP basis set.[31] Solvent corrections were considered using the polarization continuum solvation model (PCM),[32,33] using p-xylene as the solvent. The reported free energies in this work include energies obtained at the M06L/Def2TZVP~sdd level of theory (with solvent corrections included) corrected with zero-point energies, thermal corrections and entropy effects evaluated at 353.15 K, achieved at the BP86-D3/Def2SVP~sdd level. Other four functionals (B3LYP-D3//SMD, B3LYP-D3//PCM, PBEPBE-D3BJ//SMD and M06L//SMD) led to less accurate data.

Table S2. NCI plots for a selected list of intermediates and transitions states. The isosurface represents a value of 0.5 with a color scale for the reduced density gradient from -0.05 to 0.05.

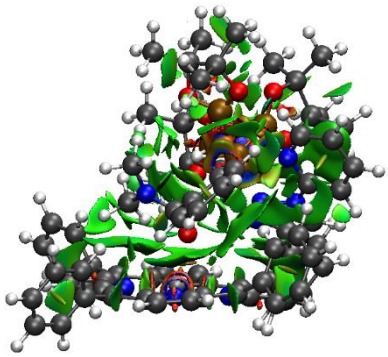
A



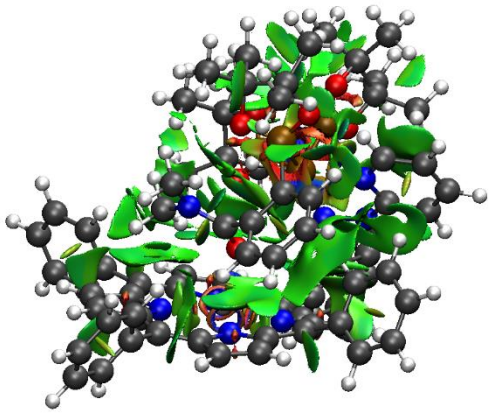
TS_{AB}



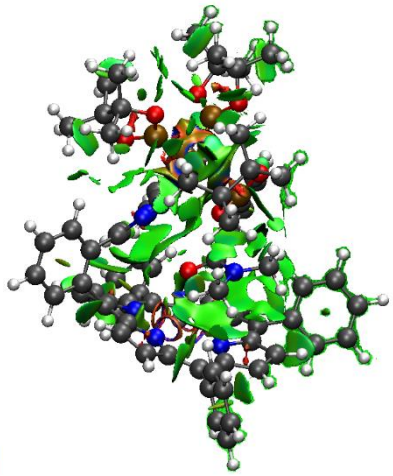
B



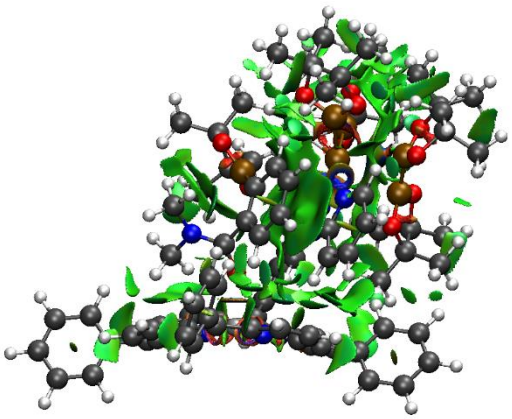
TS_{BC}



C

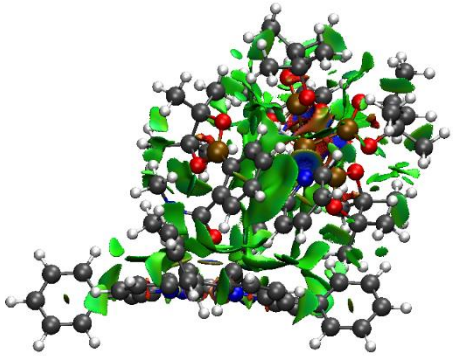


TS_{CD}



D

D'



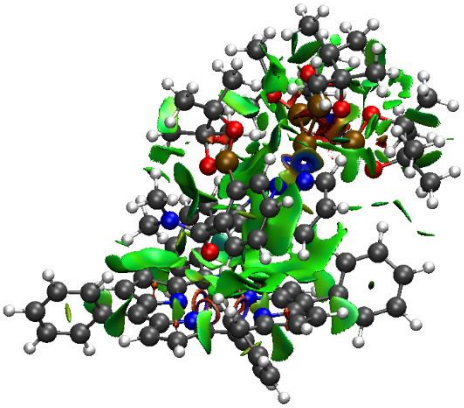


Table S3. xyz coordinates and absolute energies (in a.u.) of all optimized geometries.

Ir-1

Thermal correction to Gibbs Free Energy= 1.224983
SCF Done: -5831.35899691 A.U.

N	2.720589	-0.716300	-0.480008
C	3.150229	-0.453300	-1.767668
C	3.796415	-1.261770	0.197367
C	4.542362	-0.845728	-1.909289
C	3.790329	-1.719867	1.539867
C	2.661582	-1.705119	2.398277
N	1.399118	-1.252804	2.064137
C	0.628923	-1.334099	3.207579
C	1.425677	-1.866112	4.299187
C	2.682192	-2.105178	3.796632
C	-0.725052	-0.941606	3.321001
C	-1.532585	-0.466269	2.260140
N	-1.117019	-0.257117	0.960528
C	-2.223829	0.168113	0.248959
C	-2.951419	-0.172604	2.374415
C	-3.381245	0.215858	1.126883
C	-2.238028	0.533303	-1.118708
C	-1.115677	0.499148	-1.983098
N	0.156858	0.073057	-1.644757
C	0.960514	0.309966	-2.744959
C	-1.117587	1.011762	-3.341997
C	0.168975	0.898701	-3.813207
C	2.353833	0.058737	-2.823563
C	3.351471	-0.097706	-6.510825
C	4.038178	1.345050	-4.201365
C	2.705189	-0.370717	-5.293913
C	4.342553	0.898027	-6.577256
C	4.683974	1.618249	-5.418455
C	3.038879	0.347557	-4.122442
C	-5.176203	2.875350	-1.771627
C	-4.268493	0.357360	-2.624488
C	-5.920941	2.145869	-2.716217
C	-3.981948	2.348638	-1.252092
C	-3.517376	1.080861	-1.672050
C	-5.463304	0.886028	-3.142226
C	-1.371941	-1.059900	4.665373
C	-2.689736	-1.341869	7.160039
C	-1.652265	-2.335657	5.200719
C	-1.754733	0.094539	5.403558
C	-2.412219	-0.067089	6.645895
C	-2.303728	-2.483004	6.435413
C	6.197684	-1.392997	2.237146
C	6.396315	-4.071821	3.054249
C	5.075817	-2.242843	2.099429
C	7.400018	-1.874262	2.779820
C	7.503224	-3.215070	3.191588
C	5.193095	-3.589954	2.512619
C	-1.491819	1.461981	4.917097

C	-2.336755	2.563322	5.006270
H	-3.360596	2.664009	5.372629
N	-0.297426	1.867367	4.363231
N	-0.357988	3.149868	4.134751
N	-1.609498	3.610356	4.502347
C	-1.879080	4.985941	4.470824
C	-2.201548	7.708323	4.575607
C	-3.129143	5.497222	4.869699
C	-0.999340	7.120257	4.179619
C	-3.296030	6.884184	4.912178
N	-0.830332	5.770875	4.102372
Ir	1.127719	4.727354	3.928433
Zn	0.804422	-0.491538	0.245280
B	2.716956	3.639342	4.662231
B	0.978896	4.870376	6.009633
B	2.390958	6.330865	4.066155
O	1.953440	7.668613	4.160179
O	3.792188	6.301262	4.014705
C	4.277089	7.584429	4.482708
C	4.406590	7.473907	6.012201
C	5.630841	7.875219	3.836999
C	3.105385	8.546339	4.047777
C	2.893674	9.756688	4.957628
C	3.204696	8.981407	2.576690
O	1.144614	6.017832	6.781880
O	0.484470	3.813511	6.786509
C	0.996311	5.652591	8.184313
C	0.132094	4.328643	8.094757
C	0.465060	3.264189	9.140593
C	-1.381752	4.600183	8.061644
C	0.320546	6.810447	8.919953
C	2.409057	5.407969	8.732492
H	-3.384605	2.921173	-0.523584
H	-5.523515	3.867362	-1.440853
H	-6.857182	2.560341	-3.122970
H	-6.042040	0.308693	-3.880930
H	-3.906212	-0.629378	-2.953682
H	-3.947572	4.819013	5.146353
H	-4.260720	7.316614	5.217634
H	-2.278604	8.804689	4.614270
H	-0.098135	7.706415	3.937701
H	-1.623541	5.379392	7.310843
H	-1.775469	4.921286	9.047319
H	-1.899053	3.666111	7.759573
H	-0.177798	2.373948	8.984154
H	0.291293	3.644919	10.168560
H	1.518404	2.937431	9.053414
H	2.397754	5.132088	9.806386
H	3.005200	6.334844	8.616546
H	2.910215	4.617396	8.143602
H	0.994891	7.690512	8.928523
H	-0.621652	7.113208	8.424888
H	0.100836	6.533968	9.972298
H	3.414516	7.271583	6.463713
H	4.845583	8.387196	6.463612

H	5.055420	6.607823	6.248322
H	5.981832	8.895868	4.096567
H	6.381955	7.147237	4.205267
H	5.583696	7.782939	2.735067
H	3.807199	10.386210	4.995843
H	2.632888	9.440626	5.985009
H	2.062210	10.381669	4.571338
H	4.017751	9.717958	2.413482
H	3.382497	8.105059	1.921155
H	2.244756	9.446465	2.273342
H	-1.989714	1.430042	-3.856967
H	0.555691	1.210061	-4.789910
H	4.299579	1.910831	-3.293307
H	5.455958	2.403006	-5.462885
H	4.849190	1.112136	-7.531703
H	3.083060	-0.671141	-7.412469
H	1.934239	-1.155166	-5.237126
H	5.128824	-0.774633	-2.832077
H	4.326622	-4.260225	2.399202
H	6.471189	-5.125708	3.366574
H	8.446032	-3.592533	3.618344
H	8.259936	-1.194292	2.888302
H	6.110305	-0.341350	1.925037
H	3.557056	-2.482306	4.336983
H	1.075420	-2.015496	5.326199
H	-2.676582	0.831059	7.226591
H	-3.195413	-1.444156	8.133024
H	-2.513574	-3.489930	6.829258
H	-1.359737	-3.222878	4.617773
H	-3.545043	-0.273294	3.290141
H	-4.393690	0.500135	0.819085
O	3.468380	3.946200	5.813657
O	3.096318	2.385186	4.167770
C	4.506632	2.941989	5.955277
C	3.858024	1.718532	5.210389
C	5.756827	3.486145	5.244710
C	4.790882	2.706607	7.438691
C	4.843488	0.754467	4.557616
C	2.834288	0.972544	6.083163
H	3.866274	2.459203	7.993625
H	5.230243	3.618445	7.891877
H	5.512800	1.873536	7.569193
H	6.014542	4.471654	5.681217
H	5.553277	3.644088	4.167180
H	6.627541	2.808266	5.358791
H	5.480516	1.271322	3.815132
H	4.286467	-0.041233	4.027646
H	5.497596	0.272640	5.313598
H	3.321815	0.341357	6.854607
H	2.143889	1.692160	6.569734
H	2.225503	0.326258	5.423213
C	4.940507	-1.351612	-0.694798
H	5.916613	-1.774112	-0.432121
C	-1.601382	4.674517	1.317823
C	-1.244581	3.385989	1.138379

C	-0.010902	2.890278	0.436209
C	1.201860	2.622100	1.346739
C	1.914930	3.840234	1.906272
C	1.665899	5.210745	1.665813
C	0.682238	5.891369	0.705740
C	-0.846403	5.925419	0.944001
H	-2.563065	4.866273	1.829154
H	-1.903521	2.603427	1.558074
H	2.956126	3.606714	2.175203
H	2.577264	5.824685	1.773686
H	-0.266307	1.941626	-0.064325
H	0.282349	3.575530	-0.382086
H	0.932982	1.920662	2.168386
H	1.962668	2.068312	0.744164
H	0.995509	6.955792	0.652081
H	0.887411	5.487337	-0.310806
H	-1.049732	6.672719	1.737760
H	-1.312788	6.366809	0.030495

COD

Thermal correction to Gibbs Free Energy= 0.135201
SCF Done: -312.06501155 A.U.

C	-1.487188	4.692933	1.375935
C	-1.202741	3.401471	1.095592
C	-0.013038	2.827985	0.351294
C	1.252009	2.669547	1.228127
C	1.864115	3.914273	1.826332
C	1.658700	5.219629	1.541374
C	0.715353	5.835596	0.527087
C	-0.742586	5.960915	1.029935
H	-2.417022	4.872504	1.948296
H	-1.911875	2.650499	1.490726
H	2.601823	3.700891	2.623002
H	2.226552	5.946060	2.151931
H	-0.286076	1.821101	-0.030106
H	0.227261	3.426951	-0.548978
H	1.017332	1.973791	2.066881
H	2.037217	2.138567	0.637322
H	1.076103	6.857484	0.283269
H	0.734947	5.281364	-0.431747
H	-0.751425	6.613514	1.933643
H	-1.338904	6.525464	0.272845

B_2pin_2

Thermal correction to Gibbs Free Energy= 0.290388
SCF Done: -822.729730458 A.U.

B	-3.746289	6.412156	5.448946
C	-3.752023	5.228665	7.415478

C	-5.147912	5.081289	6.686784
B	-3.186671	7.411992	4.175063
C	-2.407699	8.034555	2.107825
C	-2.558333	9.304329	3.038370
C	-1.341281	10.229029	3.068592
H	-1.127588	10.626680	2.054846
H	-1.538573	11.087331	3.741942
H	-0.441587	9.705833	3.442948
C	-3.837694	10.108692	2.758485
H	-3.991605	10.833549	3.582560
H	-3.770860	10.669339	1.804326
H	-4.723899	9.443961	2.719970
C	-0.958724	7.533192	2.001257
H	-0.961736	6.528450	1.533612
H	-0.334263	8.208000	1.381666
H	-0.495876	7.440199	3.004182
C	-3.027481	8.177135	0.717538
H	-2.551768	9.011312	0.161370
H	-2.872097	7.243766	0.139885
H	-4.116508	8.361979	0.774079
C	-3.129347	3.914346	7.886647
H	-2.158982	4.115601	8.383536
H	-3.793290	3.407102	8.616967
H	-2.939982	3.227258	7.040841
C	-3.774117	6.253525	8.560593
H	-4.327727	5.873214	9.442734
H	-2.731161	6.470721	8.865831
H	-4.237040	7.205677	8.232348
C	-6.367491	5.329304	7.574638
H	-7.295503	5.203219	6.981428
H	-6.392975	4.604851	8.414873
H	-6.367833	6.354854	7.988915
C	-5.296248	3.752139	5.929446
H	-5.433610	2.897051	6.621714
H	-6.182574	3.815275	5.267213
H	-4.410140	3.556841	5.292811
O	-2.724303	8.701375	4.360696
O	-3.149054	7.016029	2.851227
O	-2.910897	5.798054	6.362791
O	-5.081350	6.133493	5.672712

$NMe_2C(=O)Ph$

Thermal correction to Gibbs Free Energy= 0.132249
SCF Done: -479.6711441 A.U.

C	0.359305	0.495023	-0.010858
C	1.682538	0.616485	0.467070
C	2.294197	1.878784	0.552342
C	1.593452	3.029845	0.150991
C	0.269730	2.916784	-0.314332
C	-0.348884	1.659113	-0.378807
H	2.229448	-0.282031	0.794194
H	3.322236	1.964414	0.939112
H	2.075767	4.018490	0.210861

H	-0.286543	3.817717	-0.618503
H	-1.395466	1.558171	-0.705140
C	-0.390774	-0.818237	-0.004028
O	-1.527596	-0.870619	0.475272
N	0.254460	-1.937551	-0.510229
C	1.418936	-1.912545	-1.383550
H	1.699384	-0.875303	-1.640436
H	2.298447	-2.411625	-0.915930
H	1.192081	-2.450160	-2.332248
C	-0.389991	-3.235199	-0.359678
H	0.337695	-3.983369	0.024466
H	-1.233817	-3.132310	0.346900
H	-0.786088	-3.605881	-1.333062

A

Thermal correction to Gibbs Free Energy= 1.224793
SCF Done: -5995.53986227 A.U.

N	2.664463	-0.673619	-0.226126
C	3.157213	-0.108302	-1.380162
C	3.681337	-1.422917	0.323917
C	4.525263	-0.555223	-1.602394
C	3.640289	-2.072260	1.587486
C	2.520695	-2.085254	2.463201
N	1.275109	-1.570613	2.183793
C	0.519360	-1.697791	3.326035
C	1.313836	-2.321638	4.376502
C	2.552473	-2.574559	3.837422
C	-0.825847	-1.275803	3.471438
C	-1.620227	-0.672577	2.460518
N	-1.184975	-0.291458	1.210144
C	-2.262866	0.270779	0.556348
C	-3.034205	-0.362104	2.601258
C	-3.434296	0.222922	1.421319
C	-2.219605	0.914956	-0.710722
C	-1.040131	1.119454	-1.477217
N	0.223106	0.679831	-1.140792
C	1.073629	1.089276	-2.146383
C	-0.986902	1.832069	-2.747367
C	0.329182	1.844298	-3.143891
C	2.451778	0.767904	-2.245015
C	3.796272	1.608172	-5.732098
C	4.218294	2.363228	-3.062362
C	3.039331	1.016036	-4.706699
C	4.766061	2.579645	-5.425550
C	4.976023	2.955026	-4.086378
C	3.238516	1.388049	-3.358416

C	-4.903383	3.326744	-1.992916
C	-4.589687	0.579186	-1.518064
C	-5.971525	2.448665	-2.249770
C	-3.684497	2.834148	-1.498062
C	-3.508068	1.451602	-1.249740
C	-5.808936	1.072092	-2.011272
C	-1.469469	-1.463970	4.808635
C	-2.793170	-1.845319	7.290807
C	-1.749971	-2.759782	5.293528
C	-1.850853	-0.342516	5.599584
C	-2.515278	-0.549807	6.829589
C	-2.402652	-2.955100	6.521221
C	6.067679	-1.960763	2.289251
C	6.103721	-4.712449	2.841996
C	4.894961	-2.723058	2.075735
C	7.239724	-2.564021	2.772946
C	7.262039	-3.942555	3.051478
C	4.931068	-4.108151	2.359334
C	-1.585550	1.038952	5.151684
C	-2.467675	2.115038	5.141308
H	-3.524894	2.184324	5.407231
N	-0.366718	1.470719	4.673806
N	-0.453277	2.733047	4.384403
N	-1.740931	3.164781	4.647070
C	-2.069653	4.527587	4.498085
C	-2.518755	7.228293	4.302737
C	-3.348901	5.014979	4.821015
C	-1.284179	6.652790	3.980008
C	-3.573055	6.393511	4.716584
N	-1.061197	5.319018	4.066539
Ir	0.969442	4.370026	3.984472
Zn	0.828282	-0.229790	0.650733
B	2.655469	3.353068	4.540713
B	1.028986	4.802438	5.958126
B	2.181571	5.987015	3.760519
O	1.721010	7.322436	3.766303
O	3.567814	5.981632	3.505082
C	4.073280	7.317484	3.759919
C	4.444506	7.366733	5.252447
C	5.300042	7.563452	2.882380
C	2.815704	8.207690	3.416978
C	2.694848	9.490370	4.240793
C	2.692038	8.515278	1.915352
O	1.429678	5.997948	6.552822
O	0.403677	3.959529	6.890753
C	1.280451	5.854813	7.991894
C	0.164537	4.738984	8.091666
C	0.277373	3.821618	9.308303
C	-1.260284	5.307872	7.964481
C	0.887257	7.210565	8.578965
C	2.637399	5.391916	8.539927
H	-2.851378	3.522959	-1.291553
H	-5.020278	4.407154	-2.175812
H	-6.927160	2.835433	-2.638171
H	-6.635866	0.373994	-2.218461

H	-4.458417	-0.499630	-1.339763
H	-4.145096	4.336024	5.154443
H	-4.560131	6.810434	4.968136
H	-2.647622	8.317744	4.226418
H	-0.407441	7.244531	3.670060
H	-1.334912	5.985476	7.089035
H	-1.577112	5.861176	8.871835
H	-1.963804	4.465944	7.801884
H	-0.543664	3.076057	9.296122
H	0.205126	4.402976	10.251061
H	1.235695	3.269036	9.301346
H	2.632082	5.299015	9.644887
H	3.409672	6.132497	8.251038
H	2.922200	4.426996	8.081245
H	1.727157	7.925178	8.462535
H	0.007217	7.637691	8.061608
H	0.659372	7.120039	9.661537
H	3.546939	7.178263	5.875718
H	4.905655	8.334497	5.537550
H	5.165599	6.551512	5.459892
H	5.654154	8.610702	2.981821
H	6.123232	6.889969	3.196017
H	5.086040	7.362084	1.814940
H	3.582407	10.140744	4.094211
H	2.592361	9.259490	5.317538
H	1.795836	10.059926	3.926995
H	3.446053	9.253742	1.574768
H	2.808491	7.591469	1.313045
H	1.683088	8.929944	1.715003
H	-1.844734	2.261181	-3.276334
H	0.752561	2.299727	-4.046138
H	4.374255	2.653358	-2.011456
H	5.733317	3.715818	-3.837770
H	5.359810	3.042229	-6.229961
H	3.631985	1.303321	-6.778071
H	2.286176	0.247752	-4.941952
H	5.147710	-0.287923	-2.464088
H	4.023527	-4.709055	2.191724
H	6.114148	-5.794039	3.051888
H	8.180997	-4.416327	3.431860
H	8.139721	-1.951105	2.940998
H	6.043021	-0.880081	2.082920
H	3.422340	-3.015454	4.336836
H	0.977208	-2.519285	5.400312
H	-2.787331	0.325430	7.441137
H	-3.304014	-1.988241	8.255948
H	-2.613841	-3.977101	6.873667
H	-1.459586	-3.622858	4.674581
H	-3.646589	-0.576640	3.485025
H	-4.431027	0.599120	1.164675
O	3.445904	3.695225	5.662865
O	3.046835	2.099141	4.059870
C	4.465297	2.675097	5.829035
C	3.794378	1.442487	5.118450
C	5.722812	3.176932	5.100442

C	4.749422	2.473740	7.317471
C	4.759017	0.426446	4.512257
C	2.757551	0.733238	6.007422
H	3.820281	2.260644	7.879051
H	5.208934	3.387406	7.746384
H	5.453372	1.628810	7.468793
H	5.999914	4.168974	5.510246
H	5.515204	3.308553	4.019563
H	6.583334	2.488398	5.227386
H	5.457579	0.892433	3.792899
H	4.185166	-0.354738	3.976033
H	5.355676	-0.071418	5.304354
H	3.236676	0.117034	6.795913
H	2.077196	1.472408	6.477675
H	2.138825	0.078485	5.363950
C	4.845070	-1.384555	-0.552195
H	5.780784	-1.931769	-0.391896
O	1.447867	1.420531	1.729518
C	1.808278	2.582040	1.419048
C	0.730062	3.643360	1.377660
N	3.108991	2.830436	1.092633
C	0.886279	5.058609	1.283640
C	-0.601081	3.130900	1.353693
C	3.660077	4.104015	0.637676
C	4.098617	1.776397	1.307928
C	-0.233282	5.891864	1.051168
H	1.875717	5.520838	1.286994
C	-1.704734	3.964337	1.174423
H	-0.727951	2.048484	1.476885
H	3.023278	4.559676	-0.144851
H	3.804007	4.813684	1.483468
H	4.648312	3.903705	0.180178
H	4.896757	2.163118	1.973805
H	3.612094	0.917978	1.795329
H	4.542907	1.455177	0.341430
C	-1.521661	5.352830	0.989000
H	-0.070101	6.975382	0.951816
H	-2.712035	3.520890	1.159003
H	-2.390011	6.009344	0.820362

TS_{AB}

Thermal correction to Gibbs Free Energy= 1.221979
SCF Done: 5998.91460995 A.U.

N	2.605312	-1.186793	-0.375600
C	2.973715	-0.859470	-1.666081
C	3.679777	-1.834638	0.198616
C	4.329598	-1.326841	-1.919402
C	3.754935	-2.296180	1.539161
C	2.700646	-2.241106	2.486289
N	1.433651	-1.753305	2.246169
C	0.736495	-1.839231	3.430806
C	1.598414	-2.392273	4.467879
C	2.814786	-2.648432	3.880084

C	-0.606953	-1.426506	3.628439
C	-1.431406	-0.808826	2.651194
N	-1.007938	-0.383901	1.415473
C	-1.970103	0.470145	0.934153
C	-2.786593	-0.326511	2.895955
C	-3.102895	0.507555	1.849627
C	-1.887596	1.232620	-0.255640
C	-0.922104	1.052793	-1.277537
N	0.204257	0.271144	-1.171443
C	0.898287	0.400830	-2.352935
C	-0.970454	1.677405	-2.591184
C	0.142270	1.242059	-3.275603
C	2.191826	-0.128732	-2.601450
C	3.632654	-0.580471	-6.115467
C	3.175020	1.490108	-4.275865
C	3.047657	-0.863783	-4.869717
C	3.989191	0.739268	-6.445948
C	3.758067	1.774252	-5.521942
C	2.810442	0.167574	-3.932879
C	-3.153276	4.742272	0.394011
C	-3.923934	2.520135	-1.151570
C	-4.301102	4.816358	-0.416482
C	-2.400281	3.559329	0.439574
C	-2.775253	2.436991	-0.338007
C	-4.685192	3.703347	-1.186622
C	-1.129483	-1.464223	5.028957
C	-2.111074	-1.515787	7.693273
C	-1.338474	-2.685534	5.705173
C	-1.419171	-0.247199	5.713875
C	-1.911278	-0.291264	7.037239
C	-1.822540	-2.717416	7.023154
C	6.176803	-1.952753	2.156597
C	6.469391	-4.660292	2.836883
C	5.071694	-2.823940	2.017367
C	7.411056	-2.427794	2.629743
C	7.561167	-3.783882	2.971710
C	5.234776	-4.184012	2.364118
C	-1.277854	1.065232	5.049968
C	-2.243284	2.060447	4.969659
H	-3.267024	2.113765	5.346774
N	-0.157660	1.490920	4.371128
N	-0.366353	2.685591	3.909634
N	-1.659046	3.057454	4.240402
C	-2.121148	4.350202	3.951144
C	-2.878930	6.952143	3.538190
C	-3.494603	4.647863	3.928388
C	-1.534024	6.560418	3.542952
C	-3.876700	5.978190	3.719328
N	-1.155520	5.273659	3.733821
Ir	0.972895	4.539715	3.742631
Zn	0.908962	-0.525818	0.640432
B	2.571594	3.495765	4.557229
B	0.704424	4.642118	5.838027
B	1.934201	6.312859	3.997254
O	1.263851	7.551896	3.935266

O	3.305093	6.515499	4.150256
C	3.512162	7.901092	4.532436
C	3.479214	7.946185	6.069485
C	4.866878	8.367371	4.000507
C	2.262428	8.609722	3.877813
C	1.737985	9.824930	4.642172
C	2.474133	8.947519	2.393478
O	0.765953	5.801002	6.610982
O	0.237390	3.565867	6.602373
C	0.591627	5.433166	8.009621
C	-0.196954	4.065904	7.893257
C	0.148344	3.024173	8.957177
C	-1.720200	4.256323	7.795052
C	-0.166790	6.555532	8.718595
C	1.997595	5.266051	8.601980
H	-1.489292	3.502031	1.057526
H	-2.826795	5.611486	0.985839
H	-4.893776	5.744610	-0.454818
H	-5.583513	3.756329	-1.822679
H	-4.218694	1.647427	-1.755589
H	-4.237164	3.847151	4.044987
H	-4.943416	6.246929	3.689842
H	-3.132703	8.011732	3.389986
H	-0.700700	7.275964	3.448443
H	-1.971448	4.992184	7.003562
H	-2.166697	4.592987	8.752392
H	-2.177740	3.286199	7.514148
H	-0.426200	2.094197	8.770063
H	-0.101304	3.392674	9.973777
H	1.222634	2.762804	8.925715
H	1.968308	4.997309	9.677306
H	2.548266	6.221281	8.493411
H	2.557239	4.498609	8.036026
H	0.459924	7.469906	8.743310
H	-1.108931	6.806878	8.195472
H	-0.402470	6.271517	9.765408
H	2.491535	7.605625	6.439788
H	3.699993	8.959758	6.462296
H	4.239885	7.239473	6.456776
H	5.009921	9.452696	4.184236
H	5.679606	7.819867	4.519145
H	4.966344	8.173071	2.915602
H	2.521387	10.607141	4.721381
H	1.408195	9.545196	5.660196
H	0.869328	10.263212	4.108920
H	3.180451	9.791144	2.255849
H	2.854620	8.064852	1.841205
H	1.500448	9.233321	1.945894
H	-1.761128	2.349937	-2.943568
H	0.434973	1.481430	-4.304278
H	2.998187	2.296454	-3.546237
H	4.038937	2.810259	-5.770726
H	4.447084	0.961118	-7.423067
H	3.806341	-1.396176	-6.835517
H	2.762409	-1.895232	-4.609480

H	4.878330	-1.202864	-2.859929
H	4.377569	-4.866989	2.256183
H	6.580672	-5.724872	3.098280
H	8.528639	-4.157602	3.343157
H	8.259449	-1.733101	2.737329
H	6.052053	-0.890654	1.895673
H	3.715850	-3.054808	4.352946
H	1.320051	-2.548349	5.515832
H	-2.115458	0.657788	7.558591
H	-2.486195	-1.531030	8.728607
H	-1.980056	-3.684643	7.526155
H	-1.123503	-3.623080	5.169328
H	-3.398906	-0.576398	3.770584
H	-4.026532	1.075432	1.683893
O	3.294516	3.839147	5.708812
O	2.945265	2.225264	4.108227
C	4.273988	2.790486	5.953455
C	3.614922	1.561448	5.225478
C	5.585880	3.247288	5.295220
C	4.461007	2.610075	7.458964
C	4.600600	0.512678	4.713651
C	2.518757	0.881067	6.063340
H	3.495738	2.419508	7.964270
H	4.909297	3.522541	7.901652
H	5.138604	1.755650	7.665243
H	5.846223	4.253305	5.680010
H	5.460041	3.328212	4.196436
H	6.424302	2.554095	5.511518
H	5.372686	0.941645	4.048660
H	4.059373	-0.276187	4.154846
H	5.115882	0.028218	5.568634
H	2.949398	0.290862	6.897976
H	1.805380	1.629135	6.464163
H	1.947451	0.201786	5.402012
C	4.764186	-1.937324	-0.765132
H	5.731353	-2.419404	-0.581960
O	1.283794	1.401285	1.355924
C	1.968810	2.398606	1.047885
C	1.287670	3.660961	0.601097
N	3.326809	2.394324	1.037032
C	1.022703	4.710033	1.512759
C	0.947162	3.764094	-0.762786
C	4.142672	3.574658	0.781243
C	4.055352	1.192836	1.413804
C	0.510645	5.916141	0.973582
H	2.138578	4.526966	2.600780
C	0.353430	4.935661	-1.253243
H	1.159080	2.922048	-1.437837
H	3.537308	4.382537	0.333882
H	4.585175	3.948534	1.731949
H	4.966250	3.316810	0.082222
H	4.841498	1.459327	2.145111
H	3.362748	0.476142	1.885636
H	4.521403	0.723206	0.520815
C	0.154663	6.021697	-0.382072

H	0.383128	6.789096	1.631468
H	0.064547	5.001403	-2.313618
H	-0.280136	6.961618	-0.759841

B

Thermal correction to Gibbs Free Energy= 1.221559
SCF Done: -5998.94100183 A.U.

N	2.712106	-0.923336	-0.297909
C	3.122109	-0.499986	-1.546483
C	3.791661	-1.546867	0.292136
C	4.515732	-0.868430	-1.753142
C	3.816632	-2.115410	1.593078
C	2.709443	-2.194083	2.476506
N	1.441815	-1.717948	2.217680
C	0.691210	-1.929720	3.352573
C	1.513277	-2.564856	4.373955
C	2.763141	-2.738480	3.826930
C	-0.665805	-1.552967	3.525873
C	-1.461589	-0.874697	2.566582
N	-1.005787	-0.367341	1.374106
C	-1.981147	0.473266	0.896032
C	-2.835162	-0.439313	2.791633
C	-3.144403	0.431333	1.773646
C	-1.900483	1.273589	-0.270228
C	-0.893853	1.170254	-1.264124
N	0.266619	0.443525	-1.135701
C	0.998689	0.648475	-2.283457
C	-0.925110	1.829127	-2.561924
C	0.232776	1.471775	-3.213790
C	2.335489	0.217912	-2.487888
C	3.965766	0.011519	-5.941813
C	3.285744	1.967555	-4.046497
C	3.343357	-0.361912	-4.738665
C	4.248808	1.364456	-6.201684
C	3.906518	2.341804	-5.249843
C	2.994073	0.610842	-3.774625
C	-3.532436	4.587048	0.565385
C	-3.927869	2.493433	-1.273435
C	-4.591768	4.656484	-0.357959
C	-2.679575	3.473288	0.572719
C	-2.866701	2.413821	-0.347197
C	-4.786039	3.608232	-1.276467
C	-1.243298	-1.700824	4.897769
C	-2.329731	-1.959940	7.509049
C	-1.479414	-2.970820	5.466100
C	-1.561619	-0.540484	5.665375
C	-2.104118	-0.687759	6.961253
C	-2.015803	-3.105547	6.757159
C	6.188348	-1.723513	2.359367
C	6.571497	-4.461941	2.839420
C	5.130730	-2.625157	2.097536
C	7.419483	-2.183199	2.855216
C	7.614747	-3.554804	3.098144

C	5.340376	-4.000965	2.342939
C	-1.392345	0.815972	5.105668
C	-2.322693	1.847905	5.108029
H	-3.335394	1.916481	5.511901
N	-0.268434	1.243118	4.429623
N	-0.448446	2.464399	4.035489
N	-1.717031	2.864933	4.419309
C	-2.114537	4.191087	4.229092
C	-2.730525	6.860987	4.083421
C	-3.465650	4.570033	4.297315
C	-1.413874	6.400021	3.976648
C	-3.777227	5.931876	4.222726
N	-1.104567	5.077756	4.024015
Ir	0.889101	4.293489	3.730024
Zn	0.943338	-0.397905	0.672643
B	2.394038	3.267347	4.796280
B	0.805836	4.529599	5.848118
B	1.970282	6.008004	3.644857
O	1.426512	7.300010	3.684033
O	3.360148	6.064664	3.508903
C	3.768471	7.427117	3.806596
C	4.023485	7.487368	5.322694
C	5.037231	7.748834	3.019115
C	2.491300	8.244568	3.371139
C	2.254121	9.533229	4.156394
C	2.429685	8.498182	1.857032
O	1.001654	5.756950	6.468990
O	0.167096	3.624906	6.702307
C	0.702606	5.605810	7.886407
C	-0.261920	4.350118	7.889289
C	-0.122024	3.426787	9.098648
C	-1.735130	4.725841	7.658945
C	0.067311	6.902407	8.389419
C	2.037516	5.342075	8.594429
H	-1.826883	3.427522	1.269185
H	-3.349917	5.409857	1.275318
H	-5.263287	5.530177	-0.368626
H	-5.615135	3.656906	-2.000739
H	-4.082799	1.668039	-1.986205
H	-4.246574	3.803947	4.392390
H	-4.825980	6.261512	4.271285
H	-2.924486	7.942428	4.045082
H	-0.547142	7.074190	3.870305
H	-1.838160	5.408645	6.791634
H	-2.187135	5.212572	8.546498
H	-2.305613	3.801589	7.435109
H	-0.821435	2.571826	8.999149
H	-0.359807	3.964901	10.039549
H	0.902304	3.015583	9.172138
H	1.917129	5.249787	9.692687
H	2.725734	6.184485	8.382811
H	2.508721	4.427062	8.191199
H	0.812400	7.722295	8.348359
H	-0.796595	7.201176	7.765881
H	-0.269248	6.794420	9.441454

H	3.093777	7.250441	5.879317
H	4.410243	8.476759	5.641867
H	4.769540	6.710618	5.583428
H	5.314632	8.816959	3.137428
H	5.877896	7.131109	3.395118
H	4.910253	7.531029	1.941536
H	3.110493	10.228830	4.035839
H	2.111807	9.325171	5.233568
H	1.343225	10.043680	3.781709
H	3.170145	9.256835	1.531765
H	2.599298	7.556969	1.296524
H	1.415787	8.861695	1.594813
H	-1.730895	2.476462	-2.925811
H	0.553313	1.760281	-4.221302
H	3.022478	2.729478	-3.295571
H	4.129054	3.403544	-5.442862
H	4.736073	1.657046	-7.145435
H	4.226905	-0.759745	-6.684122
H	3.116062	-1.419863	-4.533554
H	5.101618	-0.656117	-2.654675
H	4.522281	-4.708654	2.136100
H	6.718801	-5.538733	3.020840
H	8.579675	-3.916691	3.487522
H	8.229875	-1.464736	3.057988
H	6.029370	-0.650269	2.172691
H	3.648468	-3.174027	4.303546
H	1.186879	-2.830807	5.385477
H	-2.324858	0.216733	7.550755
H	-2.744418	-2.056540	8.524741
H	-2.193399	-4.109094	7.175177
H	-1.242917	-3.863393	4.866342
H	-3.469203	-0.750113	3.630559
H	-4.082354	0.972899	1.602129
O	3.268545	3.741023	5.784230
O	2.618846	1.919494	4.533458
C	4.215118	2.670090	6.083163
C	3.421293	1.385717	5.617907
C	5.463410	2.955256	5.234888
C	4.558689	2.696475	7.570854
C	4.291046	0.248083	5.087786
C	2.428280	0.857257	6.668136
H	3.653586	2.602751	8.199534
H	5.061736	3.649828	7.830183
H	5.244165	1.860616	7.821242
H	5.834637	3.971503	5.474922
H	5.209284	2.939407	4.156166
H	6.274642	2.224113	5.425516
H	4.942356	0.569224	4.255489
H	3.643038	-0.565891	4.709411
H	4.931831	-0.162814	5.895101
H	2.941815	0.362319	7.517399
H	1.783192	1.676604	7.046310
H	1.766562	0.121412	6.168520
C	4.928404	-1.524072	-0.615464
H	5.912167	-1.962239	-0.411688

O	1.311725	1.480255	1.476831
C	1.918829	2.521115	1.142837
C	1.142533	3.718635	0.671261
N	3.275905	2.615971	1.186617
C	0.600619	4.629873	1.615898
C	0.938070	3.860322	-0.715728
C	4.004244	3.855061	0.933352
C	4.068165	1.476354	1.629880
C	-0.101547	5.731545	1.071974
H	2.321159	3.759949	3.239011
C	0.188197	4.936796	-1.212764
H	1.361979	3.113577	-1.404466
H	3.327746	4.611127	0.498120
H	4.405512	4.271874	1.883404
H	4.842007	3.663953	0.229591
H	4.790033	1.808878	2.402993
H	3.399249	0.716073	2.069493
H	4.625666	1.030921	0.777530
C	-0.320658	5.883942	-0.309456
H	-0.499732	6.510601	1.741296
H	0.006860	5.028669	-2.294933
H	-0.899887	6.746055	-0.679178

TS_{BC}

Thermal correction to Gibbs Free Energy= 1.227072
SCF Done: -5998.91225946 A.U.

N	2.709514	-0.899764	-0.269008
C	3.070959	-0.525391	-1.548194
C	3.822132	-1.467315	0.315267
C	4.472499	-0.849125	-1.773569
C	3.886852	-2.015438	1.623534
C	2.790802	-2.133668	2.516351
N	1.514020	-1.668040	2.283229
C	0.769191	-1.952388	3.407691
C	1.607545	-2.614315	4.397381
C	2.859846	-2.734600	3.841965
C	-0.599249	-1.628597	3.595614
C	-1.412723	-0.953100	2.650026
N	-0.969017	-0.405072	1.470029
C	-1.980646	0.390256	0.990901
C	-2.799334	-0.567395	2.878794
C	-3.136830	0.308538	1.874035
C	-1.966575	1.130177	-0.217159
C	-1.010521	0.966315	-1.253783
N	0.189099	0.311054	-1.108173
C	0.865479	0.439914	-2.300942
C	-1.132729	1.481276	-2.609570
C	0.017735	1.120161	-3.274129
C	2.222126	0.081399	-2.512902
C	3.783775	-0.254678	-5.988988
C	3.009713	1.776927	-4.213268
C	3.217449	-0.585707	-4.746381
C	3.964346	1.093215	-6.347787

C	3.575154	2.108630	-5.455701
C	2.822338	0.425375	-3.841235
C	-3.653516	4.419929	0.582007
C	-4.026182	2.295352	-1.224998
C	-4.718925	4.459631	-0.335626
C	-2.779914	3.322482	0.597318
C	-2.955070	2.246789	-0.307179
C	-4.901932	3.395708	-1.238317
C	-1.176293	-1.843142	4.961694
C	-2.260707	-2.245052	7.556675
C	-1.366711	-3.141942	5.479633
C	-1.544140	-0.724888	5.773770
C	-2.083818	-0.944631	7.059836
C	-1.901167	-3.347675	6.762256
C	6.262114	-1.550704	2.328966
C	6.738676	-4.271884	2.820699
C	5.224269	-2.484809	2.104393
C	7.519007	-1.969285	2.795488
C	7.760827	-3.332173	3.045165
C	5.481919	-3.851979	2.352991
C	-1.433799	0.646492	5.241318
C	-2.375688	1.669791	5.283038
H	-3.345731	1.751459	5.779017
N	-0.381157	1.052944	4.449245
N	-0.619873	2.241442	3.992101
N	-1.853681	2.654970	4.481922
C	-2.299582	3.938708	4.180586
C	-2.976108	6.571078	3.759799
C	-3.639329	4.326260	4.362412
C	-1.674621	6.106582	3.559085
C	-3.983077	5.663582	4.147222
N	-1.336491	4.796937	3.732295
Ir	0.656812	4.081197	3.436460
Zn	0.966458	-0.354216	0.740249
B	2.238196	3.107387	4.432416
B	0.701795	4.809491	5.352958
B	1.547022	5.709118	2.457392
O	1.086480	7.038070	2.726995
O	2.948373	5.766678	2.157893
C	3.443603	7.028713	2.644892
C	3.871284	6.829315	4.110224
C	4.641372	7.448125	1.788869
C	2.171084	7.962414	2.500322
C	2.083368	9.074228	3.547647
C	2.008660	8.524089	1.077606
O	0.952611	6.126305	5.714845
O	0.152076	4.084672	6.418925
C	0.808298	6.237460	7.159079
C	-0.145322	5.016866	7.493898
C	0.136403	4.328394	8.829138
C	-1.637107	5.367340	7.367526
C	0.224855	7.613610	7.480557
C	2.213724	6.087126	7.757521
H	-1.920684	3.300792	1.287781
H	-3.485127	5.253891	1.281124

H	-5.406093	5.320868	-0.351243
H	-5.738609	3.418689	-1.955046
H	-4.179786	1.453421	-1.918301
H	-4.388437	3.580408	4.660571
H	-5.023293	5.995375	4.283357
H	-3.191419	7.639045	3.613128
H	-0.832701	6.769869	3.293566
H	-1.842128	5.882888	6.407839
H	-1.988853	6.013307	8.197179
H	-2.224454	4.426827	7.379975
H	-0.571702	3.487487	8.974905
H	0.014915	5.036243	9.675174
H	1.162358	3.915184	8.854984
H	2.211124	6.192605	8.861149
H	2.868343	6.872664	7.329846
H	2.643159	5.108275	7.474881
H	0.956053	8.400895	7.206976
H	-0.703758	7.804337	6.909895
H	0.006280	7.706401	8.564680
H	3.004993	6.540233	4.735002
H	4.346155	7.739232	4.532161
H	4.601797	5.997135	4.151357
H	4.978993	8.471916	2.053182
H	5.488482	6.753739	1.966003
H	4.399035	7.420370	0.709225
H	2.976460	9.732178	3.508202
H	1.991969	8.639255	4.560859
H	1.186260	9.700315	3.361035
H	2.765466	9.300047	0.841237
H	2.079344	7.709372	0.328919
H	1.001839	8.980324	0.986117
H	-1.988364	2.040440	-3.003983
H	0.280604	1.317025	-4.319794
H	2.709000	2.569808	-3.509909
H	3.717027	3.167159	-5.726630
H	4.407959	1.352269	-7.322329
H	4.081407	-1.055770	-6.684452
H	3.069916	-1.639946	-4.464006
H	5.027178	-0.660632	-2.699785
H	4.681836	-4.586150	2.169456
H	6.923023	-5.342405	3.005219
H	8.745896	-3.662075	3.411759
H	8.313181	-1.225637	2.969408
H	6.067426	-0.484628	2.134650
H	3.753500	-3.176205	4.296807
H	1.287823	-2.937462	5.394194
H	-2.345204	-0.074098	7.682795
H	-2.674832	-2.397225	8.565791
H	-2.041569	-4.372895	7.139781
H	-1.095706	-4.001382	4.846909
H	-3.424400	-0.913823	3.710232
H	-4.094965	0.814511	1.705546
O	3.036244	3.689911	5.426463
O	2.549993	1.767525	4.250084
C	4.004292	2.691904	5.865165

C	3.325046	1.339288	5.403869
C	5.310228	3.002921	5.119267
C	4.204352	2.811549	7.375438
C	4.306777	0.257403	4.963776
C	2.314476	0.783268	6.420484
H	3.237958	2.767550	7.911903
H	4.694913	3.774434	7.623035
H	4.851306	1.989617	7.745866
H	5.612386	4.044920	5.345696
H	5.157720	2.925795	4.024104
H	6.133227	2.322568	5.416908
H	4.934545	0.590535	4.117304
H	3.747448	-0.637194	4.632518
H	4.970985	-0.037287	5.802288
H	2.815171	0.359596	7.314629
H	1.601972	1.573729	6.735305
H	1.729051	-0.014451	5.921522
C	4.935743	-1.441881	-0.620532
H	5.937845	-1.840825	-0.426083
O	1.332258	1.668889	1.287465
C	1.951880	2.663010	0.840527
C	1.130507	3.814869	0.302256
N	3.304634	2.729832	0.793995
C	0.661141	4.889513	1.114840
C	0.710283	3.679363	-1.035476
C	4.035493	3.822836	0.165445
C	4.106785	1.640962	1.339831
C	-0.298921	5.751991	0.528002
H	2.200915	3.707904	3.073741
C	-0.211717	4.576265	-1.592387
H	1.098771	2.845245	-1.637034
H	4.747206	4.266156	0.890591
H	4.591523	3.444055	-0.720653
H	3.338353	4.622701	-0.136993
H	4.866216	2.061562	2.032021
H	3.453525	0.950007	1.901123
H	4.625646	1.090216	0.526571
C	-0.733351	5.609681	-0.797698
H	-0.676750	6.597542	1.121425
H	-0.535701	4.444320	-2.635982
H	-1.480857	6.305873	-1.209852

C

Thermal correction to Gibbs Free Energy= 1.224849
SCF Done: -5998.94999858 A.U.

N	2.582592	-0.449538	-1.408239
C	2.711194	0.599309	-2.295507
C	3.758968	-1.164938	-1.447351
C	4.035346	0.565124	-2.901705
C	4.135121	-2.207306	-0.554568
C	3.406019	-2.570133	0.608059
N	2.157224	-2.091527	0.933858
C	1.887177	-2.492310	2.222389

C	3.013342	-3.256461	2.743198
C	3.926071	-3.360736	1.718016
C	0.660156	-2.263518	2.897172
C	-0.533600	-1.820143	2.264864
N	-0.593305	-1.168976	1.058010
C	-1.903533	-0.809626	0.841364
C	-1.868953	-1.938827	2.824382
C	-2.726894	-1.324875	1.932506
C	-2.351096	0.059812	-0.198808
C	-1.493796	0.728613	-1.120281
N	-0.123015	0.586564	-1.179871
C	0.340085	1.434317	-2.158383
C	-1.917847	1.686689	-2.136320
C	-0.777454	2.150823	-2.752929
C	1.687460	1.532505	-2.606123
C	2.709821	3.633882	-5.642835
C	1.930741	4.002785	-2.969622
C	2.403789	2.520843	-4.841563
C	2.632098	4.933247	-5.109590
C	2.239267	5.114059	-3.771108
C	2.016678	2.690373	-3.492691
C	-5.705205	1.902743	-0.237037
C	-4.742677	-0.727070	-0.432590
C	-6.612184	0.837724	-0.382400
C	-4.324535	1.652012	-0.184758
C	-3.817657	0.333486	-0.275989
C	-6.123819	-0.477516	-0.483100
C	0.696266	-2.347340	4.392873
C	1.178937	-2.421187	7.183532
C	0.767005	-3.575054	5.082822
C	0.823366	-1.129077	5.131238
C	1.087218	-1.188947	6.517382
C	0.996644	-3.617488	6.468567
C	6.555907	-2.554006	0.111238
C	6.990270	-4.200479	-2.121289
C	5.483189	-2.820759	-0.770922
C	7.826752	-3.107738	-0.116581
C	8.047586	-3.934186	-1.232986
C	5.719125	-3.647102	-1.893015
C	0.639507	0.204619	4.504311
C	-0.510617	0.680664	3.885730
H	-1.473167	0.209048	3.678790
N	1.548969	1.239952	4.580021
N	1.018895	2.302536	4.036398
N	-0.252418	1.987069	3.609585
C	-1.142558	2.995581	3.199587
C	-2.892578	5.051137	2.727161
C	-2.379683	2.687297	2.606802
C	-1.617315	5.269659	3.256295
C	-3.276229	3.740266	2.387397
N	-0.747544	4.257961	3.497020
Ir	1.275921	4.490827	4.205605
Zn	1.105217	-0.534551	0.057845
B	0.933305	4.198459	6.177290
B	1.180750	6.422604	4.848681

O	2.213585	7.368372	4.830940
O	0.029179	6.979834	5.450180
C	1.851011	8.447288	5.731383
C	0.273687	8.391765	5.689608
C	-0.419307	8.800188	6.989652
C	-0.319656	9.157192	4.494817
C	2.463835	9.751693	5.221757
C	2.422561	8.079160	7.112154
H	-3.614407	2.483677	-0.066534
H	-6.075786	2.938099	-0.162078
H	-7.695553	1.032260	-0.422614
H	-6.824767	-1.317849	-0.610552
H	-4.361982	-1.756241	-0.524334
H	-2.623712	1.653191	2.321465
H	-4.265568	3.532272	1.954101
H	-3.571681	5.903173	2.578542
H	-1.255088	6.266571	3.545013
H	0.188914	8.862014	3.554167
H	-0.234751	10.256329	4.615143
H	-1.394794	8.900300	4.402245
H	-1.519427	8.719339	6.874284
H	-0.174184	9.849608	7.255641
H	-0.117807	8.142973	7.827033
H	2.242941	8.873367	7.865428
H	3.516216	7.930928	7.010478
H	1.994039	7.120401	7.468604
H	3.569034	9.696732	5.290750
H	2.202181	9.937845	4.162706
H	2.121733	10.613665	5.831963
H	-2.953080	1.955215	-2.373290
H	-0.701682	2.873322	-3.573807
H	1.621743	4.140870	-1.921144
H	2.174122	6.127585	-3.344151
H	2.873385	5.804652	-5.738896
H	3.003795	3.485433	-6.694264
H	2.448355	1.503763	-5.261550
H	4.427990	1.293212	-3.620435
H	4.889017	-3.852175	-2.587209
H	7.155321	-4.846541	-2.998344
H	9.044211	-4.367820	-1.412353
H	8.652085	-2.885635	0.578683
H	6.384161	-1.894858	0.976782
H	4.877139	-3.905151	1.723868
H	3.081050	-3.693118	3.746011
H	1.208240	-0.244354	7.070158
H	1.379818	-2.445402	8.266135
H	1.046040	-4.587903	6.987469
H	0.660209	-4.507844	4.507242
H	-2.113948	-2.428534	3.775411
H	-3.813572	-1.213406	2.022857
O	1.751255	4.585004	7.243920
O	-0.175450	3.473005	6.624852
C	1.298495	3.858802	8.420901
C	-0.218785	3.592854	8.075188
C	2.128574	2.565454	8.484432

C	1.536599	4.724067	9.657336
C	-0.796114	2.304130	8.659011
C	-1.118542	4.798173	8.392480
H	1.084643	5.727217	9.539831
H	2.625334	4.859433	9.817621
H	1.109795	4.243986	10.562457
H	3.204060	2.831261	8.510915
H	1.961192	1.952962	7.574567
H	1.891934	1.960548	9.383259
H	-0.267080	1.413621	8.269224
H	-1.865034	2.209566	8.379677
H	-0.727352	2.306459	9.766821
H	-1.256509	4.940672	9.483620
H	-0.695287	5.722024	7.948454
H	-2.112224	4.631595	7.930520
C	4.669660	-0.552050	-2.406482
H	5.679469	-0.909021	-2.639457
O	1.545304	1.057851	1.389072
C	2.304718	2.027077	1.111816
C	1.763942	3.423445	1.180305
N	3.606007	1.856708	0.767254
C	2.421395	4.436395	1.964269
C	0.569292	3.692518	0.495769
C	4.419031	2.874178	0.114499
C	4.319333	0.655439	1.176922
C	1.852441	5.751788	1.929046
H	2.741723	4.620408	4.781067
C	0.044077	5.003397	0.465785
H	0.070162	2.872073	-0.039141
H	3.791175	3.712195	-0.236144
H	5.198444	3.266181	0.803265
H	4.909509	2.415426	-0.770893
H	4.995538	0.925180	2.014463
H	3.597843	-0.103424	1.520812
H	4.908255	0.247681	0.334088
C	0.699856	6.031042	1.151705
H	2.396394	6.570620	2.423229
H	-0.873853	5.206810	-0.107203
H	0.308674	7.060319	1.119002
B	3.689138	4.234920	2.887579
O	4.206785	3.013701	3.289728
O	4.516009	5.303003	3.187378
C	5.249416	3.267888	4.270646
C	5.510036	4.859524	4.147212
C	6.459414	2.404194	3.892929
C	4.708302	2.816402	5.637001
C	6.879259	5.228197	3.560596
C	5.270070	5.632525	5.452725
H	7.310916	2.583941	4.579621
H	6.796492	2.598059	2.856396
H	6.181786	1.333308	3.969604
H	5.469261	2.941350	6.433774
H	3.796125	3.372857	5.917741
H	4.425893	1.747382	5.570092
H	7.039816	4.748412	2.575451

H	7.708056	4.938182	4.237355
H	6.920690	6.325742	3.410671
H	5.986555	5.321917	6.240021
H	5.402826	6.715599	5.259528
H	4.237154	5.491528	5.822700

TS_{CD}

Thermal correction to Gibbs Free Energy= 1.548879
SCF Done: -6821.68980487 A.U.

N	2.170509	-0.870233	-2.023751
C	1.841646	-0.080493	-3.106697
C	3.356082	-1.506266	-2.322495
C	2.867075	-0.214154	-4.132973
C	4.136969	-2.288184	-1.424898
C	3.875971	-2.427510	-0.034531
N	2.737504	-1.989091	0.600046
C	2.948627	-2.103742	1.957182
C	4.288365	-2.625724	2.196725
C	4.837045	-2.888941	0.960772
C	1.963616	-1.850478	2.948880
C	0.585618	-1.646431	2.665189
N	0.088239	-1.185488	1.468161
C	-1.265070	-0.972764	1.643871
C	-0.492473	-1.795569	3.621879
C	-1.650767	-1.420804	2.973888
C	-2.101211	-0.280230	0.726424
C	-1.663326	0.250922	-0.521766
N	-0.415855	0.065602	-1.076962
C	-0.387304	0.756052	-2.268797
C	-2.452203	1.119656	-1.386527
C	-1.657891	1.439064	-2.466192
C	0.678014	0.728671	-3.211979
C	0.168069	1.823178	-6.841914
C	0.571329	2.994867	-4.321783
C	0.320532	1.010900	-5.705725
C	0.216343	3.223661	-6.721827
C	0.418164	3.806702	-5.458095
C	0.525925	1.585683	-4.430743
C	-5.120372	1.062035	2.654257
C	-4.595612	-0.494969	0.376552
C	-6.188771	0.560380	1.889905
C	-3.794975	0.785178	2.282359
C	-3.511546	0.001901	1.137748
C	-5.921452	-0.219159	0.749856
C	2.390312	-1.776487	4.380945
C	3.354758	-1.703578	7.044448
C	2.835452	-2.947859	5.033586
C	2.399628	-0.532764	5.096078
C	2.901721	-0.532349	6.424964
C	3.312036	-2.925858	6.352717
C	6.668544	-2.360140	-1.603362
C	6.527804	-4.476653	-3.441987
C	5.403175	-2.872348	-1.971703

C	7.847495	-2.902330	-2.141726
C	7.780852	-3.963620	-3.061998
C	5.349184	-3.934872	-2.902327
C	1.878091	0.759099	4.590252
C	1.167707	1.128240	3.446051
H	0.923521	0.619738	2.513256
N	1.933065	1.871178	5.418705
N	1.295546	2.857275	4.873838
N	0.799930	2.427343	3.656344
C	-0.127066	3.239657	2.977903
C	-2.082193	4.859197	1.940190
C	-0.905913	2.742162	1.925084
C	-1.210791	5.302970	2.941963
C	-1.909189	3.569876	1.408077
N	-0.242435	4.507022	3.451051
Ir	1.181086	5.031553	5.006626
Zn	1.267432	-0.747639	-0.173786
B	2.063961	5.386646	6.829239
B	1.514013	6.972321	4.480898
O	2.823441	7.399414	4.164856
O	0.622886	8.040849	4.237457
C	2.848912	8.839859	4.069154
C	1.351211	9.176558	3.685286
C	0.823110	10.477334	4.297489
C	1.096608	9.188628	2.170386
C	3.883814	9.248201	3.018093
C	3.256599	9.366234	5.456977
H	-2.963562	1.199121	2.872448
H	-5.316461	1.680588	3.544454
H	-7.228627	0.777026	2.181658
H	-6.752406	-0.621142	0.148452
H	-4.384732	-1.109955	-0.512402
H	-0.727565	1.738424	1.519936
H	-2.540168	3.193802	0.588850
H	-2.862683	5.534928	1.562449
H	-1.255074	6.310262	3.380303
H	1.534765	8.298424	1.684362
H	1.521798	10.091391	1.686870
H	0.002106	9.176246	1.993092
H	-0.221588	10.658498	3.972520
H	1.438416	11.336621	3.958191
H	0.837178	10.450565	5.401463
H	3.343727	10.471628	5.480662
H	4.241314	8.928507	5.717211
H	2.541971	9.027829	6.232130
H	4.898896	8.974916	3.370563
H	3.714569	8.728887	2.055759
H	3.862840	10.344152	2.843479
H	-3.485347	1.434971	-1.199037
H	-1.918062	2.056924	-3.333404
H	0.739125	3.452347	-3.334374
H	0.462235	4.902746	-5.355228
H	0.095841	3.860248	-7.612711
H	0.003566	1.358624	-7.827290
H	0.272082	-0.085783	-5.794626

H	2.879879	0.315816	-5.092211
H	4.366253	-4.334176	-3.197925
H	6.466775	-5.307777	-4.162582
H	8.704909	-4.388543	-3.484979
H	8.824531	-2.488024	-1.845743
H	6.719435	-1.520203	-0.893171
H	5.815900	-3.332876	0.747108
H	4.737507	-2.808427	3.179379
H	2.915102	0.421704	6.971566
H	3.732086	-1.660463	8.078327
H	3.646546	-3.857634	6.835299
H	2.795967	-3.896161	4.475227
H	-0.377069	-2.159705	4.649437
H	-2.672726	-1.432572	3.368655
O	2.436885	6.607378	7.391215
O	2.367560	4.322420	7.681439
C	3.172438	6.337480	8.614101
C	2.698763	4.870401	8.986400
C	4.664363	6.411253	8.250856
C	2.818570	7.403566	9.650785
C	3.780130	3.988250	9.614292
C	1.419485	4.845598	9.834955
H	1.726668	7.447543	9.820236
H	3.153155	8.399101	9.294024
H	3.319834	7.194173	10.618553
H	4.868851	7.393103	7.778739
H	4.922184	5.624149	7.515351
H	5.318546	6.299064	9.139257
H	4.637937	3.844323	8.929890
H	3.355393	2.989039	9.839701
H	4.148319	4.429473	10.563913
H	1.614699	5.175180	10.876370
H	0.632083	5.475499	9.377820
H	1.026737	3.810555	9.853155
C	3.791011	-1.116947	-3.658571
H	4.703838	-1.466700	-4.154486
O	2.124096	1.029022	0.603696
C	2.825006	2.046656	0.379713
C	2.184266	3.395803	0.419170
N	4.154201	1.964624	0.105321
C	2.612561	4.396300	1.328879
C	1.096063	3.610537	-0.451108
C	4.947933	3.058247	-0.454057
C	4.809256	0.663246	0.159700
C	1.942319	5.638665	1.297473
H	2.728560	5.143500	5.307915
C	0.456462	4.856808	-0.470263
H	0.751880	2.784660	-1.092925
H	4.307715	3.927472	-0.683260
H	5.730774	3.388828	0.260656
H	5.431883	2.712911	-1.392639
H	5.865550	0.796114	0.465287
H	4.292971	0.020352	0.892707
H	4.780511	0.164084	-0.831062
C	0.883950	5.872769	0.403922

H	2.248515	6.412104	2.018246
H	-0.395440	5.023970	-1.148084
H	0.368412	6.845474	0.410912
B	3.764706	4.156145	2.376130
O	3.747730	3.152733	3.314050
O	4.917777	4.905035	2.375386
C	5.059985	3.117154	3.963684
C	5.701445	4.518655	3.549512
C	5.781420	1.903459	3.362036
C	4.889701	2.931224	5.471198
C	7.172371	4.436380	3.134020
C	5.511686	5.623419	4.594720
H	6.759016	1.720245	3.850808
H	5.948781	2.038489	2.277098
H	5.142283	1.007945	3.498469
H	5.869848	3.048374	5.977960
H	4.167527	3.643964	5.908164
H	4.505609	1.916849	5.688213
H	7.323740	3.759414	2.271708
H	7.794964	4.075216	3.977939
H	7.533915	5.443355	2.844644
H	6.116241	5.430091	5.502235
H	5.832803	6.589160	4.157109
H	4.449201	5.749490	4.875099
B	-0.996757	3.938136	6.663225
O	-0.953320	3.430175	7.948774
O	-1.457165	3.001013	5.744524
C	-1.955163	1.850086	6.488485
C	-3.484501	2.004621	6.526065
C	-1.572658	0.583066	5.733447
C	-1.262900	2.009930	7.910162
C	-2.175841	1.687552	9.096902
C	0.066862	1.256600	8.045887
H	-3.775335	2.941198	7.042299
H	-3.978866	1.148558	7.027507
H	-3.857390	2.064057	5.483567
H	-1.945295	-0.321748	6.256053
H	-2.021831	0.600974	4.722696
H	-0.480970	0.486259	5.603738
H	-2.502610	0.627485	9.064860
H	-3.071050	2.337245	9.116185
H	-1.621391	1.849427	10.043038
H	-0.074646	0.156921	8.031235
H	0.770664	1.547137	7.243196
H	0.537443	1.535233	9.010047
B	-0.899948	5.652133	6.517790
O	-0.668538	6.337735	7.713018
O	-1.737433	6.391414	5.669999
C	-2.289254	7.500979	6.432728
C	-2.384746	8.722566	5.519584
C	-3.688161	7.046024	6.884167
C	-1.266654	7.655593	7.640704
C	-0.146670	8.665369	7.372558
C	-1.921395	7.947607	8.995481
H	-1.412565	8.900255	5.027960

H	-2.687152	9.623445	6.092271
H	-3.145580	8.544524	4.731655
H	-4.229753	7.846805	7.427452
H	-4.278461	6.767628	5.988053
H	-3.620693	6.152754	7.537502
H	-0.528891	9.706619	7.378535
H	0.327611	8.452375	6.400593
H	0.627762	8.560869	8.154788
H	-2.483159	8.904192	8.964712
H	-2.607677	7.136804	9.304042
H	-1.133859	8.036482	9.771225

D’

Thermal correction to Gibbs Free Energy= 1.548962
SCF Done: -6821.73749292 A.U.

N	2.422381	-0.940682	-1.931409
C	2.093782	-0.211660	-3.053203
C	3.623174	-1.567869	-2.186156
C	3.123723	-0.387709	-4.067571
C	4.403682	-2.285794	-1.238274
C	4.093691	-2.399010	0.142455
N	2.925715	-1.959343	0.728966
C	3.062514	-2.130341	2.088693
C	4.381781	-2.669741	2.385269
C	4.998105	-2.891080	1.174091
C	2.026852	-1.926993	3.036169
C	0.664421	-1.709965	2.705117
N	0.209178	-1.244548	1.488410
C	-1.136539	-0.966448	1.642377
C	-0.433928	-1.788576	3.646861
C	-1.559711	-1.360017	2.977977
C	-1.945949	-0.282678	0.696490
C	-1.502567	0.151057	-0.585926
N	-0.264462	-0.104940	-1.135712
C	-0.201758	0.564752	-2.339096
C	-2.257003	1.022640	-1.477566
C	-1.444096	1.293735	-2.555291
C	0.907625	0.551309	-3.229915
C	-0.166564	2.052413	-6.585713
C	1.753838	2.492095	-4.586408
C	-0.118583	1.210261	-5.462219
C	0.742230	3.118803	-6.711166
C	1.704308	3.335227	-5.708363
C	0.839772	1.420966	-4.444704
C	-4.796607	1.358186	2.639810

C	-4.460672	-0.314932	0.409640
C	-5.921853	0.921371	1.917978
C	-3.507539	0.960664	2.250325
C	-3.320699	0.118450	1.126167
C	-5.749624	0.082161	0.802428
C	2.394328	-1.859213	4.485160
C	3.209363	-1.745068	7.192743
C	2.741073	-3.030772	5.191292
C	2.438412	-0.596926	5.158613
C	2.861017	-0.571146	6.512598
C	3.142460	-2.985838	6.535475
C	6.937381	-2.285993	-1.286905
C	6.957844	-4.420614	-3.110118
C	5.709180	-2.839320	-1.717447
C	8.158927	-2.795589	-1.757913
C	8.173000	-3.865290	-2.670744
C	5.736444	-3.911635	-2.638119
C	2.036990	0.696006	4.556161
C	1.356558	1.031844	3.381184
H	1.018762	0.468132	2.513214
N	2.220586	1.862432	5.273878
N	1.683758	2.851223	4.626489
N	1.124534	2.372942	3.467307
C	0.164714	3.152756	2.770562
C	-1.847329	4.654136	1.684878
C	-0.465815	2.666023	1.616579
C	-1.118857	5.084148	2.799112
C	-1.502500	3.435421	1.077129
N	-0.134093	4.337560	3.341864
Ir	1.042853	4.829310	5.191757
Zn	1.428935	-0.792244	-0.127368
B	2.235247	4.954344	6.839568
B	1.754343	6.806414	4.722079
O	2.803130	7.473896	5.369484
O	1.051121	7.692327	3.876233
C	2.675771	8.897109	5.129540
C	1.798873	8.937956	3.806142
C	0.810004	10.102210	3.738390
C	2.648885	8.878917	2.525480
C	4.079023	9.490948	4.979530
C	1.972403	9.507728	6.349508
H	-2.628757	1.319848	2.808256
H	-4.919725	2.020356	3.511296
H	-6.932439	1.234079	2.225163
H	-6.626154	-0.271902	0.236616
H	-4.324064	-0.978090	-0.459031
H	-0.130543	1.737895	1.137848
H	-2.018716	3.075388	0.175720
H	-2.655536	5.283325	1.285289
H	-1.313084	6.037419	3.307975
H	3.335124	8.008125	2.550574
H	3.237375	9.806509	2.373527
H	1.975789	8.756481	1.652659
H	0.212256	10.034256	2.806671
H	1.346002	11.073965	3.736914

H	0.110079	10.088281	4.594603
H	1.856742	10.606822	6.257269
H	2.577929	9.292162	7.251768
H	0.989030	9.027690	6.501435
H	4.632568	9.371381	5.932750
H	4.658686	8.985440	4.184510
H	4.024662	10.574258	4.744322
H	-3.272895	1.392694	-1.297040
H	-1.668567	1.933446	-3.416142
H	2.502243	2.659195	-3.795587
H	2.418737	4.169053	-5.797775
H	0.702506	3.778964	-7.592051
H	-0.915384	1.870219	-7.373010
H	-0.821545	0.367909	-5.367329
H	3.114038	0.063898	-5.066288
H	4.783154	-4.345184	-2.979045
H	6.960343	-5.260164	-3.823484
H	9.130477	-4.265031	-3.040598
H	9.106024	-2.349978	-1.413981
H	6.924574	-1.442315	-0.578980
H	5.982526	-3.339144	0.997867
H	4.766725	-2.896067	3.386127
H	2.907351	0.401619	7.023495
H	3.528322	-1.688707	8.245407
H	3.401718	-3.915832	7.065547
H	2.687273	-3.993138	4.658577
H	-0.353062	-2.141330	4.681636
H	-2.587081	-1.315755	3.355737
O	3.574719	4.526340	6.728018
O	1.964220	5.347577	8.147197
C	4.115431	4.393443	8.063354
C	3.220703	5.417362	8.865432
C	3.890351	2.932073	8.490360
C	5.608146	4.723399	8.029079
C	2.976475	5.046835	10.328272
C	3.726901	6.864639	8.738220
H	5.790773	5.707037	7.556985
H	6.148016	3.956656	7.435932
H	6.036333	4.731930	9.053228
H	4.355193	2.270395	7.732133
H	2.806311	2.701475	8.515824
H	4.334486	2.710451	9.482464
H	2.446427	4.079067	10.413283
H	2.345324	5.820516	10.810692
H	3.934561	4.983023	10.885879
H	4.660680	7.035584	9.312587
H	3.889035	7.117097	7.670617
H	2.942049	7.544454	9.126220
C	4.063861	-1.241227	-3.536040
H	4.982233	-1.607036	-4.009298
O	2.088515	1.199635	0.398810
C	2.717627	2.154816	-0.126252
C	2.053913	3.504699	-0.185597
N	3.973742	2.036970	-0.616617
C	2.363119	4.501158	0.783112

C	1.044518	3.712553	-1.143991
C	4.681321	3.135984	-1.258803
C	4.786733	0.876486	-0.286093
C	1.578723	5.679898	0.782809
H	2.223040	5.601064	4.147453
C	0.330442	4.920499	-1.162298
H	0.808952	2.917587	-1.865423
H	3.974395	3.926423	-1.567680
H	5.425771	3.576787	-0.559977
H	5.211144	2.754555	-2.156519
H	5.616641	1.195454	0.380351
H	4.164070	0.134327	0.238699
H	5.200857	0.416838	-1.205588
C	0.581787	5.895431	-0.181431
H	1.754200	6.430826	1.567604
H	-0.448866	5.079655	-1.924190
H	-0.010167	6.823794	-0.156160
B	3.583109	4.424392	1.768619
O	4.392206	3.322073	1.928483
O	4.021001	5.534270	2.455248
C	5.428175	3.660348	2.914996
C	5.367334	5.249392	2.956696
C	6.754743	3.085139	2.415117
C	5.030272	3.008270	4.238936
C	6.327389	5.924506	1.964685
C	5.520864	5.846609	4.353045
H	7.587945	3.405332	3.073241
H	6.984252	3.400394	1.378983
H	6.710394	1.977275	2.438463
H	5.842971	3.099317	4.986656
H	4.132406	3.470886	4.682727
H	4.828237	1.932218	4.067619
H	6.210727	5.509363	0.942405
H	7.385139	5.812107	2.275610
H	6.089700	7.006064	1.919461
H	6.511591	5.576113	4.773534
H	5.455483	6.949844	4.298290
H	4.732866	5.503433	5.048286
B	-0.281034	3.649160	6.328739
O	-0.601501	3.622761	7.681051
O	-0.900311	2.582601	5.653511
C	-1.832650	1.945052	6.564787
C	-3.204822	2.585146	6.304389
C	-1.855363	0.447237	6.263316
C	-1.224818	2.339150	7.966038
C	-2.247267	2.525398	9.085728
C	-0.091282	1.395594	8.403360
H	-3.162469	3.675683	6.496623
H	-4.007564	2.127866	6.917696
H	-3.456106	2.447694	5.233592
H	-2.465331	-0.102007	7.010492
H	-2.295466	0.275777	5.260684
H	-0.831880	0.025776	6.250147
H	-2.805509	1.583894	9.270003
H	-2.970878	3.326315	8.841540

H	-1.728950	2.812222	10.022820
H	-0.468747	0.398769	8.708974
H	0.642996	1.266244	7.582037
H	0.438945	1.853732	9.262073
B	-0.341790	6.122992	6.004827
O	-0.192155	7.152067	6.934300
O	-1.705737	5.998014	5.647852
C	-2.430911	7.121703	6.210067
C	-2.493531	8.196077	5.111594
C	-3.834190	6.660604	6.602716
C	-1.505643	7.529789	7.421458
C	-1.511726	9.022747	7.753458
C	-1.762593	6.693972	8.686127
H	-1.468934	8.486753	4.803762
H	-3.053213	9.098223	5.431980
H	-3.005590	7.770672	4.224093
H	-4.392251	7.479252	7.103166
H	-4.399210	6.357557	5.697694
H	-3.794803	5.791774	7.286370
H	-2.525513	9.347265	8.068247
H	-1.196917	9.640423	6.891178
H	-0.809277	9.222880	8.587288
H	-2.725811	6.956070	9.170315
H	-1.739039	5.612051	8.448544
H	-0.938886	6.883696	9.402277

D

Thermal correction to Gibbs Free Energy= 1.379928
SCF Done: -6409.75561175 A.U.

N	2.386888	-0.816727	-2.318013
C	1.662463	-0.325235	-3.385824
C	3.654580	-1.100321	-2.784571
C	2.491902	-0.328582	-4.581134
C	4.736127	-1.607616	-2.015376
C	4.664569	-1.998874	-0.651852
N	3.525275	-2.009490	0.120905
C	3.919484	-2.267559	1.418017
C	5.366034	-2.439888	1.466478
C	5.824446	-2.303684	0.177503
C	3.049563	-2.338601	2.536455
C	1.636024	-2.215324	2.475827
N	0.922821	-1.675712	1.426003
C	-0.376446	-1.517092	1.870662
C	0.749413	-2.480467	3.594426
C	-0.501690	-2.053130	3.217889
C	-1.419942	-0.860520	1.168278
C	-1.328013	-0.413946	-0.178803
N	-0.213499	-0.530109	-0.989893
C	-0.536364	0.045391	-2.203866
C	-2.378643	0.293303	-0.893208
C	-1.889441	0.576957	-2.148156
C	0.317251	0.128543	-3.337375
C	-1.856827	0.859446	-6.398585

C	0.350239	1.970268	-5.067138
C	-1.339254	0.232043	-5.253310
C	-1.275605	2.046412	-6.879931
C	-0.168716	2.599059	-6.211061
C	-0.230419	0.780121	-4.567637
C	-3.575469	0.775142	3.847116
C	-3.936855	-0.902670	1.612918
C	-4.869113	0.360769	3.482864
C	-2.472666	0.347050	3.095511
C	-2.631479	-0.486174	1.961196
C	-5.044959	-0.483417	2.370067
C	3.655044	-2.389871	3.904470
C	4.847387	-2.484959	6.475915
C	4.407931	-3.510156	4.319300
C	3.488785	-1.294972	4.813368
C	4.094143	-1.367504	6.091124
C	5.002559	-3.565136	5.589399
C	6.691772	-0.458547	-3.120519
C	8.053774	-2.894091	-3.419188
C	6.080242	-1.652297	-2.668487
C	7.965701	-0.481495	-3.711528
C	8.651461	-1.700259	-3.862199
C	6.780064	-2.870610	-2.827171
C	2.649979	-0.113002	4.516411
C	2.237749	0.462707	3.305511
H	2.496549	0.290391	2.256597
N	2.051714	0.582826	5.543698
N	1.283083	1.512253	5.044673
N	1.366952	1.445182	3.661389
C	0.503658	2.267559	2.890567
C	-1.385461	3.818939	1.663001
C	0.129432	1.934593	1.583351
C	-0.927705	4.099236	2.954994
C	-0.845754	2.725806	0.965643
N	0.003930	3.328847	3.566570
Ir	0.661010	3.515871	5.676137
Zn	1.732123	-1.032207	-0.371873
B	1.431460	3.446951	7.557052
H	-1.466281	0.674111	3.390283
H	-3.395105	1.442580	4.703311
H	-5.741783	0.690379	4.069742
H	-6.054629	-0.825088	2.090612
H	-4.075752	-1.570645	0.748148
H	0.578863	1.078029	1.073403
H	-1.173019	2.476630	-0.052572
H	-2.152681	4.461261	1.207090
H	-1.276519	4.957558	3.549796
H	-3.357681	0.560182	-0.480984
H	-2.398190	1.111488	-2.958016
H	1.217830	2.401691	-4.543619
H	0.293391	3.528470	-6.580474
H	-1.682795	2.538314	-7.777451
H	-2.717450	0.414229	-6.922826
H	-1.788586	-0.701134	-4.879282
H	2.162717	-0.028814	-5.582383

H	6.308059	-3.804450	-2.483797
H	8.581682	-3.853398	-3.540685
H	9.650296	-1.720012	-4.326133
H	8.427825	0.458387	-4.053638
H	6.149841	0.493176	-2.999426
H	6.861685	-2.356604	-0.171856
H	5.956156	-2.635201	2.368572
H	3.955644	-0.523502	6.783665
H	5.309080	-2.514492	7.475376
H	5.579677	-4.454380	5.888361
H	4.507793	-4.357598	3.623310
H	1.051573	-2.934669	4.545200
H	-1.431165	-2.100243	3.795901
O	2.767845	3.819077	7.820712
O	0.838273	2.932809	8.717873
C	3.117836	3.312472	9.133651
C	1.706910	3.244018	9.834345
C	3.745576	1.921371	8.926529
C	4.116847	4.267292	9.787636
C	1.565615	2.155738	10.898472
C	1.252327	4.608887	10.382364
H	3.742292	5.308202	9.774714
H	5.078652	4.245739	9.234847
H	4.317195	3.970730	10.838739
H	4.605980	2.020429	8.233403
H	3.011380	1.234090	8.458776
H	4.109222	1.478306	9.876497
H	1.715550	1.148250	10.466026
H	0.546277	2.187833	11.334396
H	2.297836	2.307390	11.719277
H	1.808571	4.902985	11.296238
H	1.375089	5.392972	9.608116
H	0.172740	4.548130	10.625150
C	3.726145	-0.807383	-4.208498
H	4.600440	-0.976792	-4.847180
O	2.729813	0.799042	0.337315
C	3.243050	1.890731	-0.017780
C	2.341836	3.043314	-0.364716
N	4.585633	2.052988	-0.088223
C	2.241451	4.200137	0.461530
C	1.509784	2.878897	-1.487845
C	5.231508	3.265292	-0.568492
C	5.471951	1.043768	0.477568
C	1.305047	5.191135	0.082741
C	0.592952	3.881565	-1.841431
H	1.576510	1.949794	-2.072401
H	4.512809	3.903391	-1.112545
H	5.651891	3.844612	0.282128
H	6.060128	2.991799	-1.255029
H	6.124229	1.519403	1.240241
H	4.869157	0.252798	0.953241
H	6.101732	0.580865	-0.310674
C	0.495671	5.044207	-1.056422
H	1.209072	6.088780	0.714036
H	-0.052633	3.738760	-2.722665

H	-0.227258	5.831491	-1.322632
B	3.092741	4.433620	1.760229
O	3.886137	3.471791	2.347581
O	3.164302	5.662585	2.380029
C	4.485319	4.068753	3.552216
C	4.322935	5.620277	3.280820
C	5.928554	3.575044	3.651385
C	3.682789	3.590395	4.759228
C	5.494641	6.224616	2.490807
C	4.035594	6.451400	4.527203
H	6.447397	4.063045	4.501191
H	6.500074	3.775782	2.724652
H	5.932838	2.480779	3.829036
H	4.068133	3.964588	5.725104
H	2.624982	3.955946	4.684120
H	3.686827	2.486182	4.793740
H	5.722845	5.626961	1.584708
H	6.411567	6.293650	3.109136
H	5.215324	7.244735	2.160663
H	4.868421	6.352311	5.252746
H	3.953272	7.521327	4.248721
H	3.101664	6.155411	5.039919
B	-1.139848	3.762739	6.516428
O	-1.461397	4.554434	7.628090
O	-2.306054	3.177433	5.979121
C	-3.447237	3.843514	6.596522
C	-3.810281	5.024124	5.680297
C	-4.618916	2.868283	6.716706
C	-2.841762	4.303717	7.978413
C	-3.449930	5.586685	8.546070
C	-2.841577	3.186063	9.034700
H	-2.959539	5.731625	5.611213
H	-4.715663	5.562000	6.028994
H	-4.007368	4.628713	4.662877
H	-5.423272	3.307747	7.342927
H	-5.050194	2.655463	5.717452
H	-4.302601	1.908989	7.168296
H	-4.535197	5.458096	8.740499
H	-3.312424	6.438940	7.853751
H	-2.954388	5.843976	9.503992
H	-3.857999	2.982007	9.429272
H	-2.417343	2.252910	8.614176
H	-2.186622	3.495477	9.873028
B	0.446747	5.529981	5.852406
O	1.288827	6.424779	6.527906
O	-0.570661	6.255414	5.182137
C	-0.273715	7.671065	5.270683
C	0.459022	8.054258	3.973032
C	-1.587794	8.444095	5.394301
C	0.649303	7.728678	6.551216
C	1.722945	8.816153	6.516742
C	-0.152031	7.794183	7.862338
H	1.401418	7.481907	3.864773
H	0.684909	9.139046	3.923458
H	-0.188200	7.793639	3.110652

H	-1.397388	9.525421	5.557092
H	-2.180032	8.334092	4.462878
H	-2.200599	8.062330	6.232472
H	1.259346	9.823097	6.458210
H	2.404236	8.689113	5.655032
H	2.332456	8.769039	7.441667
H	-0.656103	8.772697	7.999344
H	-0.898423	6.975896	7.894948
H	0.545916	7.638511	8.709318

$NMe_2C(=O)PhBpin$

Thermal correction to Gibbs Free Energy= 0.281395
SCF Done: -890.456832316 A.U.

O	10.887937	4.959065	-9.872013
C	11.321168	5.411162	-10.936940
C	10.881429	6.789481	-11.395240
N	12.190473	4.722665	-11.755448
C	11.506792	7.935534	-10.833509
C	9.776072	6.929845	-12.256345
C	12.917757	5.356216	-12.844107
C	12.746184	3.472125	-11.264152
C	10.984068	9.210123	-11.147792
C	9.284122	8.209183	-12.569167
H	9.295641	6.031633	-12.676526
H	12.383977	6.260432	-13.189178
H	13.935644	5.662289	-12.510300
H	13.014494	4.655053	-13.700821
H	13.770113	3.633313	-10.851640
H	12.096246	3.089331	-10.455769
H	12.810867	2.725989	-12.084429
C	9.886372	9.352455	-12.013024
H	11.453014	10.103397	-10.703784
H	8.419876	8.313222	-13.244955
H	9.495349	10.354271	-12.252139
B	12.728464	7.757871	-9.877524
O	13.632870	6.719837	-10.017132
O	13.002313	8.580766	-8.807931
C	14.377278	6.646453	-8.762302
C	14.276337	8.138685	-8.238980
C	15.795419	6.162218	-9.057687
C	13.631005	5.639310	-7.874624
C	15.362752	9.054974	-8.821199
C	14.206526	8.277642	-6.719195
H	16.416998	6.192496	-8.139249
H	16.283526	6.775360	-9.838527
H	15.764596	5.113494	-9.416655
H	14.158334	5.467670	-6.914833
H	12.595387	5.975858	-7.670419
H	13.550188	4.676764	-8.416555
H	15.429621	8.941449	-9.922007
H	16.357802	8.843166	-8.380778
H	15.098862	10.108609	-8.601012
H	15.115776	7.851448	-6.247205

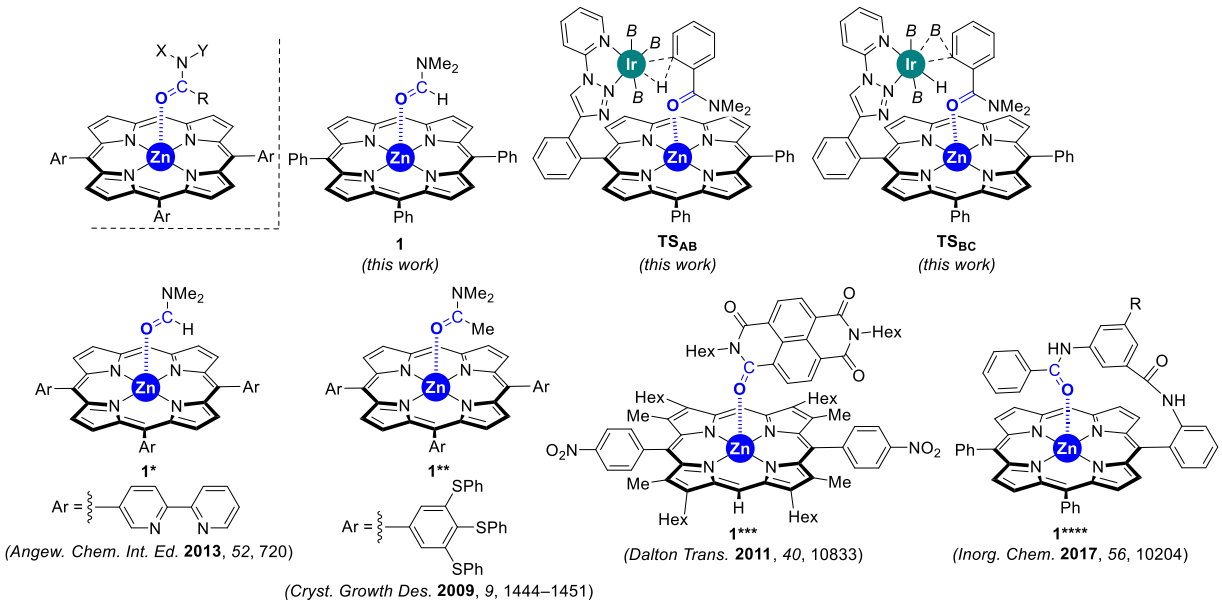
H	14.141469	9.348714	-6.440816
H	13.317186	7.764558	-6.308143

HBpin

Thermal correction to Gibbs Free Energy= 0.142987
SCF Done: -411.962551424 A.U.

B	1.714190	0.128961	15.052543
O	2.563091	1.118399	15.486168
O	1.203985	-0.653712	16.059863
C	2.476026	1.148654	16.947354
C	1.923473	-0.299394	17.284750
C	3.035857	-1.345486	17.456831
C	0.950062	-0.357322	18.461960
C	1.488291	2.270610	17.303656
C	3.860838	1.456060	17.516897
H	0.048713	0.256131	18.276478
H	1.440205	-0.000021	19.390993
H	0.620539	-1.403037	18.625213
H	2.579282	-2.355195	17.463419
H	3.589679	-1.203248	18.406456
H	3.756667	-1.303483	16.615799
H	3.850002	1.390973	18.624451
H	4.163218	2.484337	17.234095
H	4.626091	0.759281	17.126877
H	1.837701	3.214950	16.840885
H	0.476298	2.051812	16.907836
H	1.416016	2.421151	18.399490
H	1.439676	-0.038220	13.886189

Table S4. Key parameters involved in the coordination of carbonyl groups from amides to tetra-aryl-zinc-porphyrin derivatives: current work versus precedents from the literature.



Entry	$d_{Zn...N}$ (Å)	$d_{Zn...O}$ (Å)	$d_{Zn...C}$ (Å)	$d_{O...C}$ (Å)	$d_{C...R}$ (Å)	$d_{C...N}$ (Å)	angle (°) N-Zn-O	angle (°) Zn-O-C	angle (°) O-C-R	angle (°) O-C-N
1 (X-ray)	2.054 2.055 2.061 2.072	2.161	2.980	1.243	0.950 (R = H)	1.309	95.16 98.52 96.65 96.72	119.74	117.39 (R = H)	125.20
TS_{AB}	2.085 2.100 2.073 2.088	2.090	3.138	1.249	1.502 (R = Ph)	1.358	90.33 108.26 103.49 88.55	138.66	119.74 (R = Ph)	123.19
TS_{BC}	2.088 2.112 2.069 2.099	2.127	3.176	1.254	1.514 (R = Ph)	1.355	89.36 95.37 111.18 103.25	138.39	117.51 (R = Ph)	123.04
1* (X-ray)	2.077 2.067 2.065 2.071	2.107	2.968	1.241	0.950 (R = H)	1.320	98.37 101.29 100.49 97.25	122.76	117.84 (R = H)	124.14
1** (X-ray)	2.060 2.060 2.077 2.093	2.102	3.090	1.247	1.483 (R = Me)	1.365	92.65 95.90 108.17 102.88	133.02	120.70 (R = Me)	119.48
1*** (synch roton X-ray)	2.216 2.073 1.991 2.172	2.325	2.857	1.306	1.375 (R = Ph)	1.463	96.19 100.83 107.54 100.90	99.98	124.11 (R = Ph)	113.17
1**** (X-ray)	2.055 2.054 2.054 2.047	2.246	3.149	1.232	1.495 (R = Ph)	1.353	98.30 87.77 97.63 105.50	127.32	121.53 (R = Ph)	123.59

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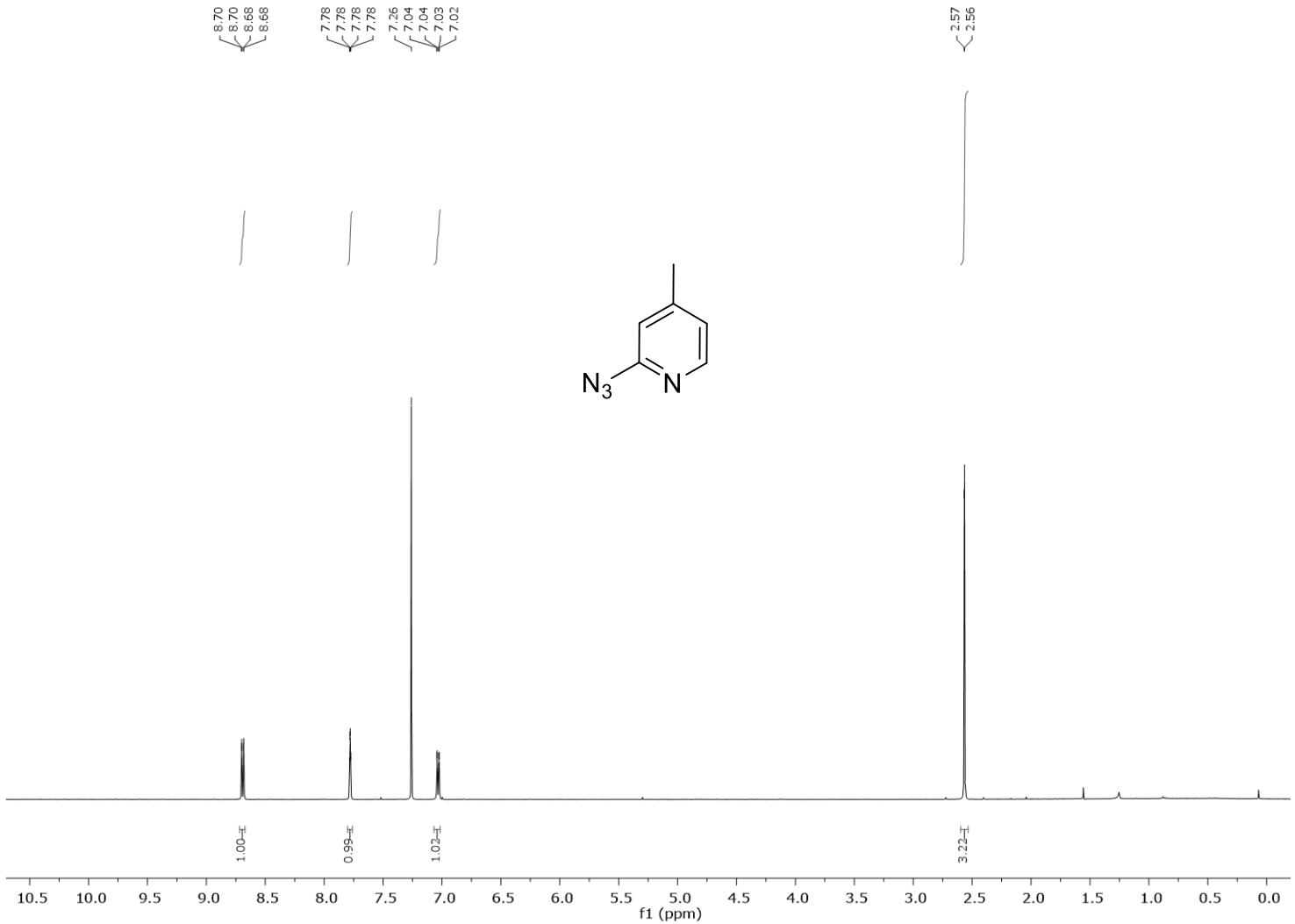
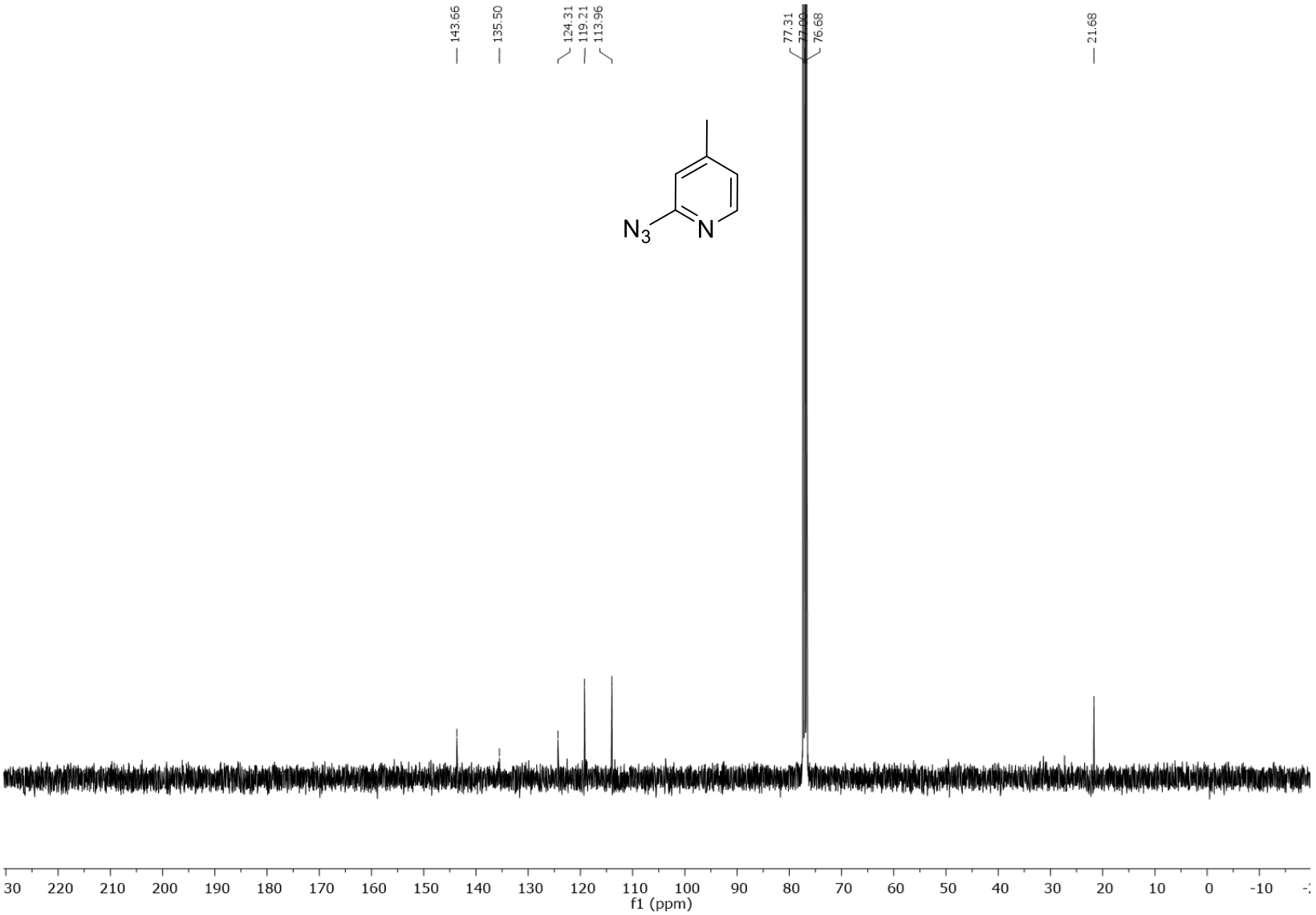
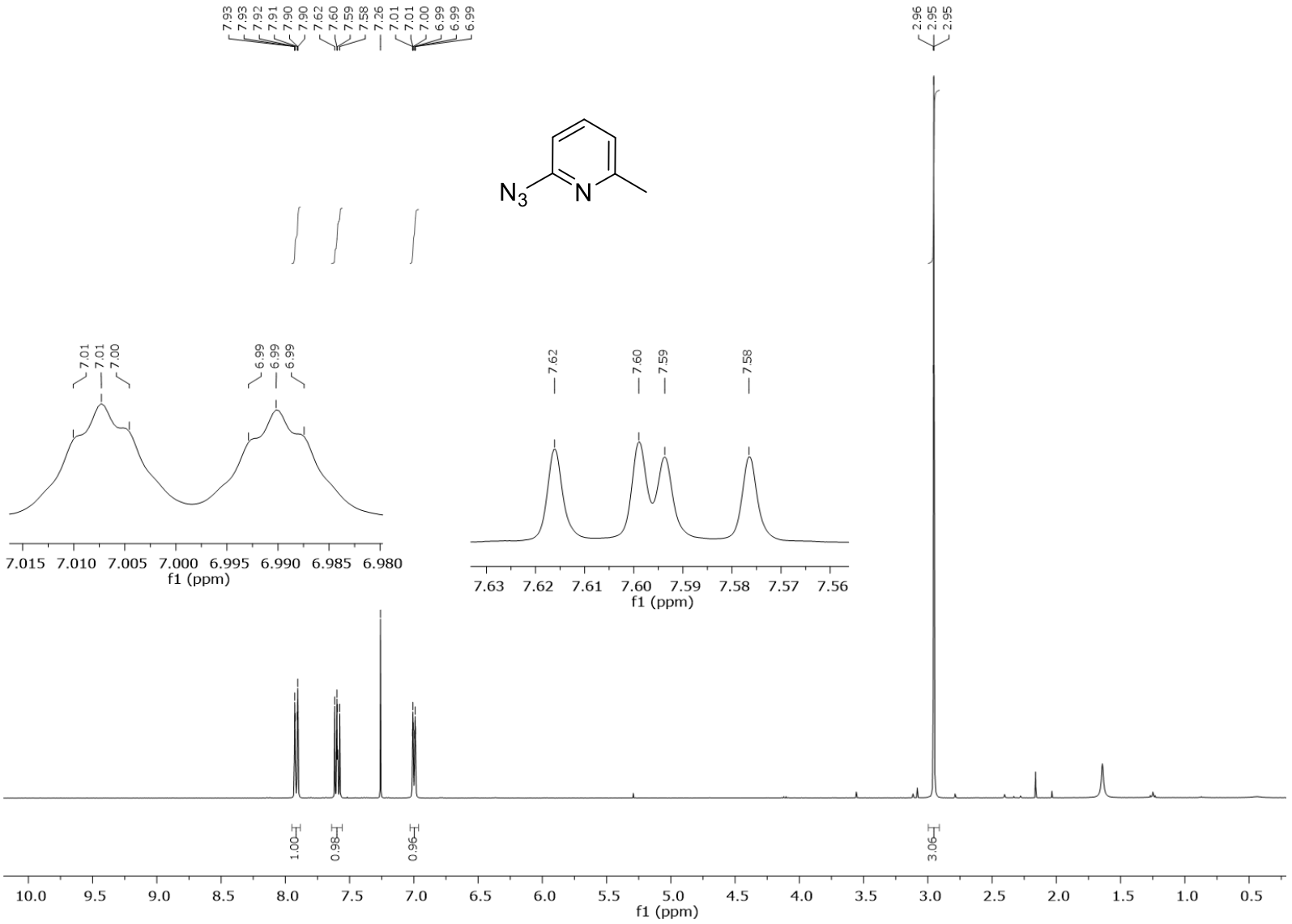
8. NMR data.



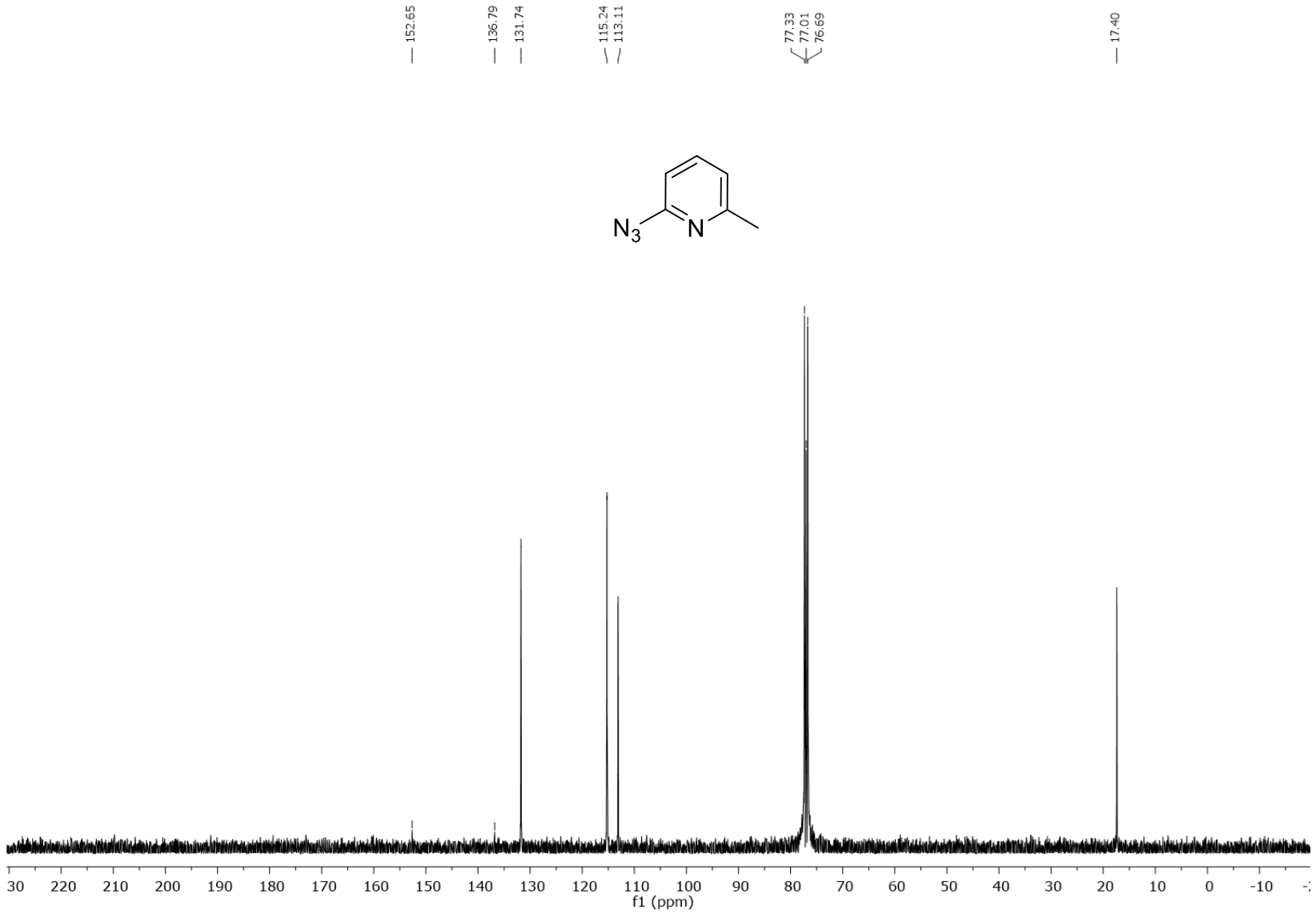
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of of 2-azido-4-methylpyridine (**AP3**).



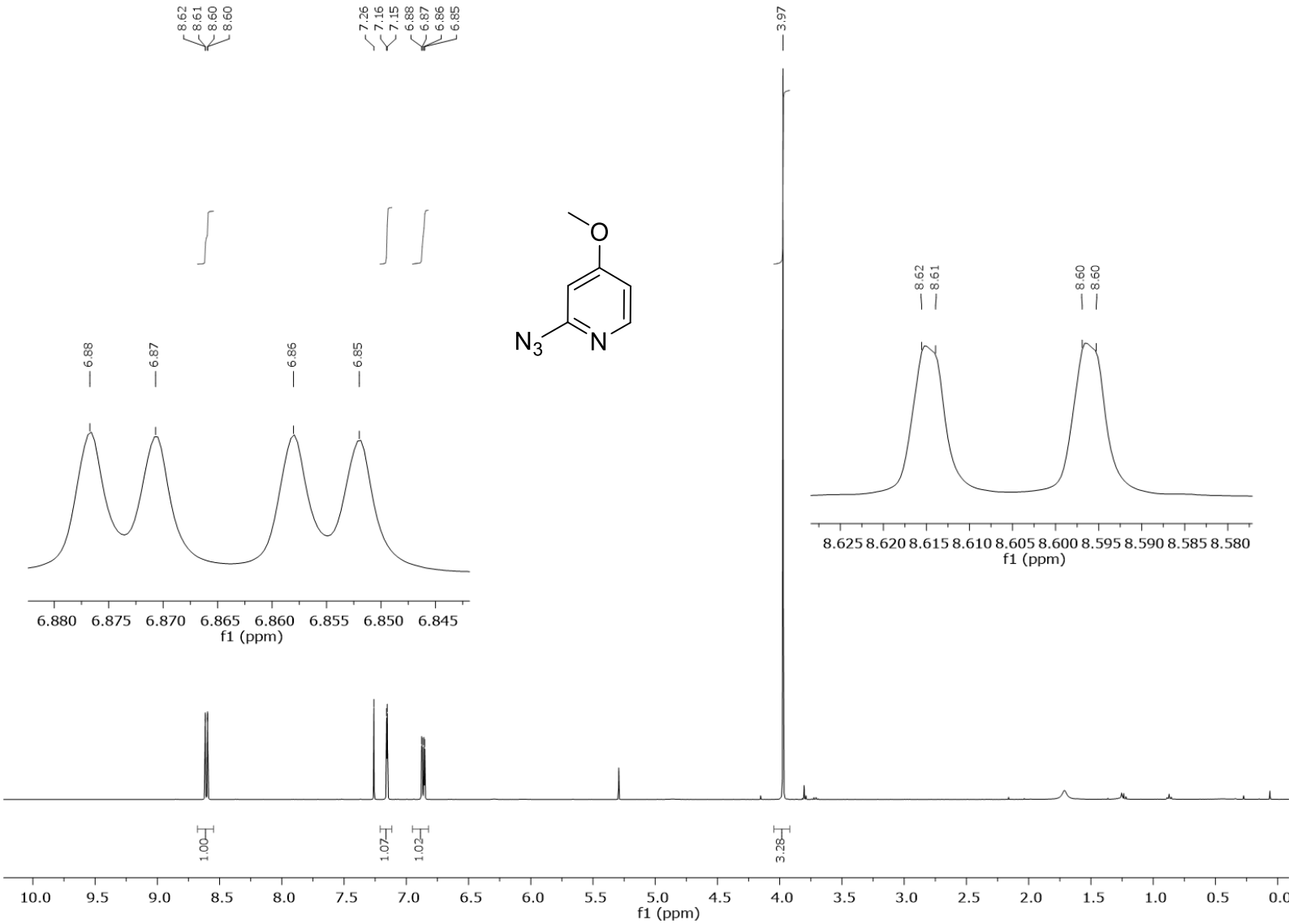
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of 2-azido-4-methylpyridine (**AP3**).



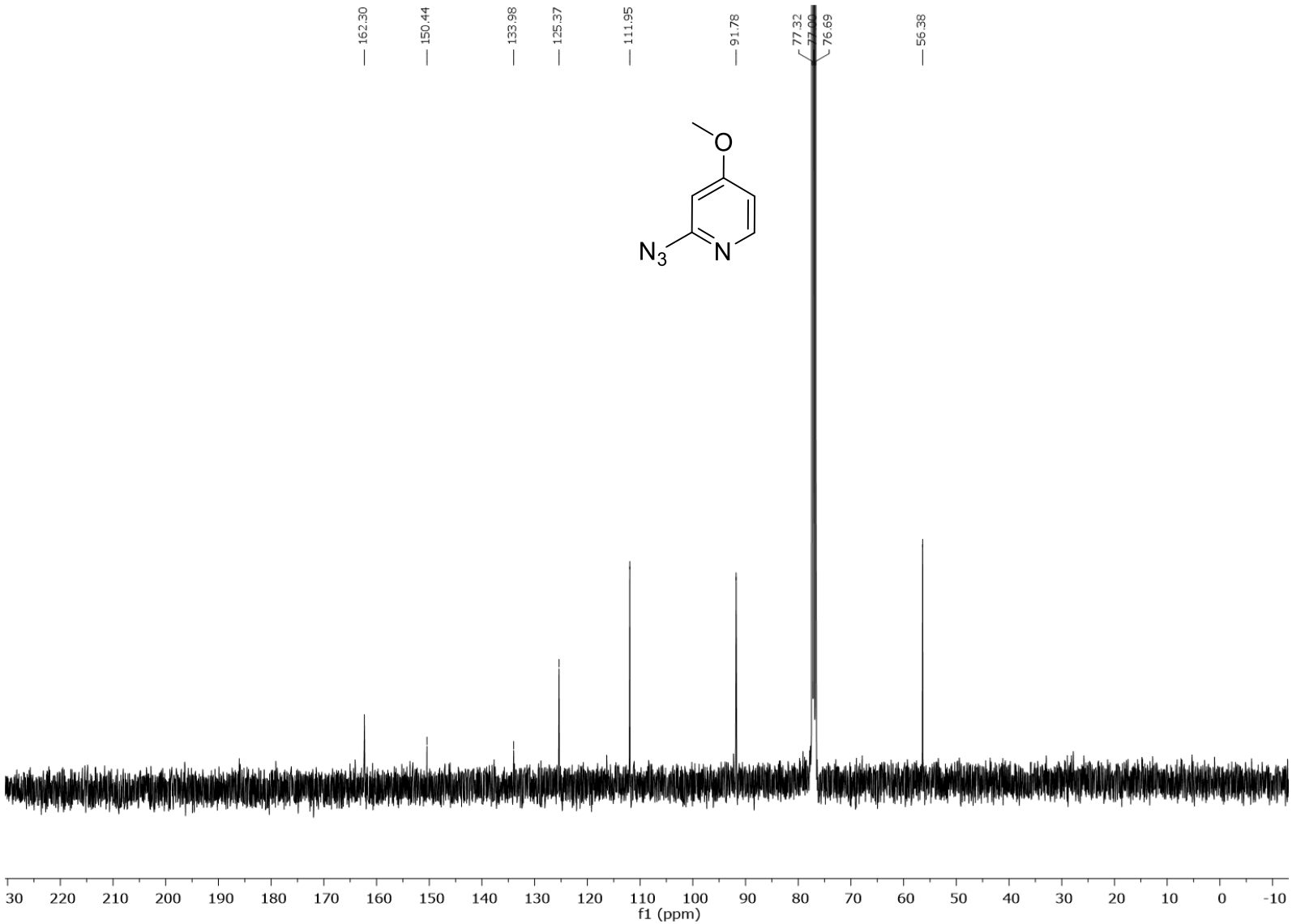
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of 2-azido-6-methylpyridine (**AP4**).



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of 2-azido-6-methylpyridine (**AP4**).



^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of 2-azido-4-methoxypyridine (**AP5**).



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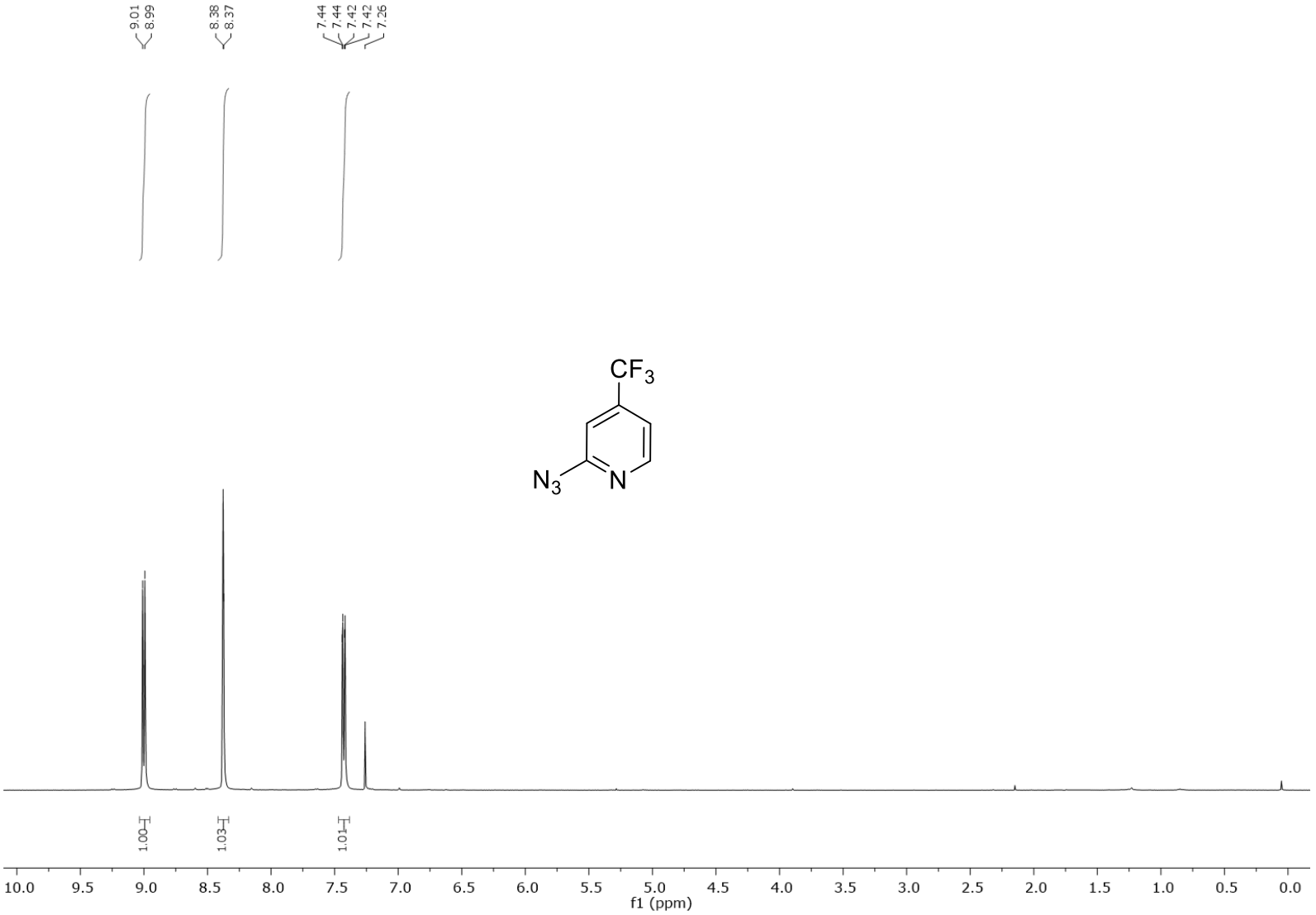

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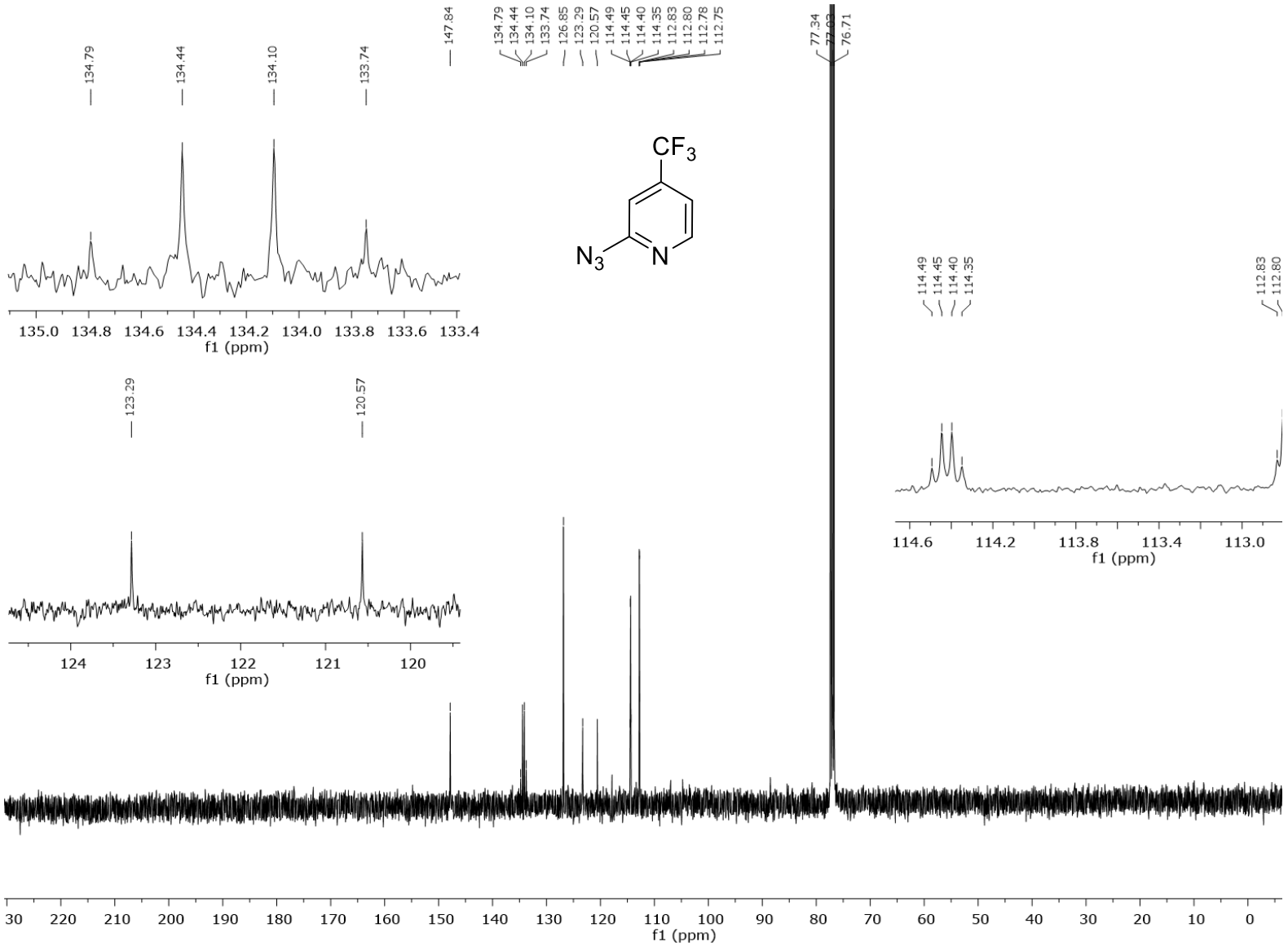

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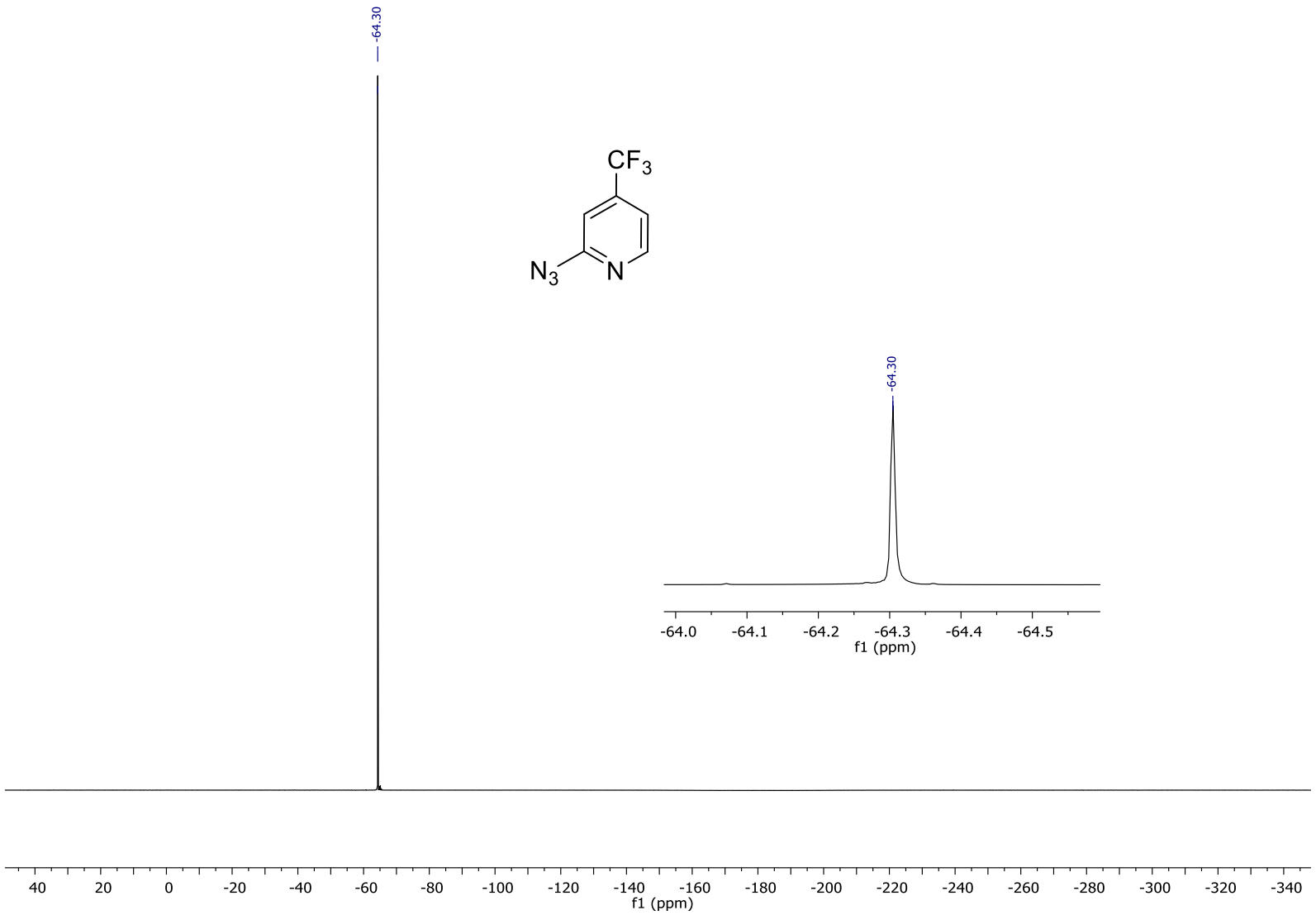

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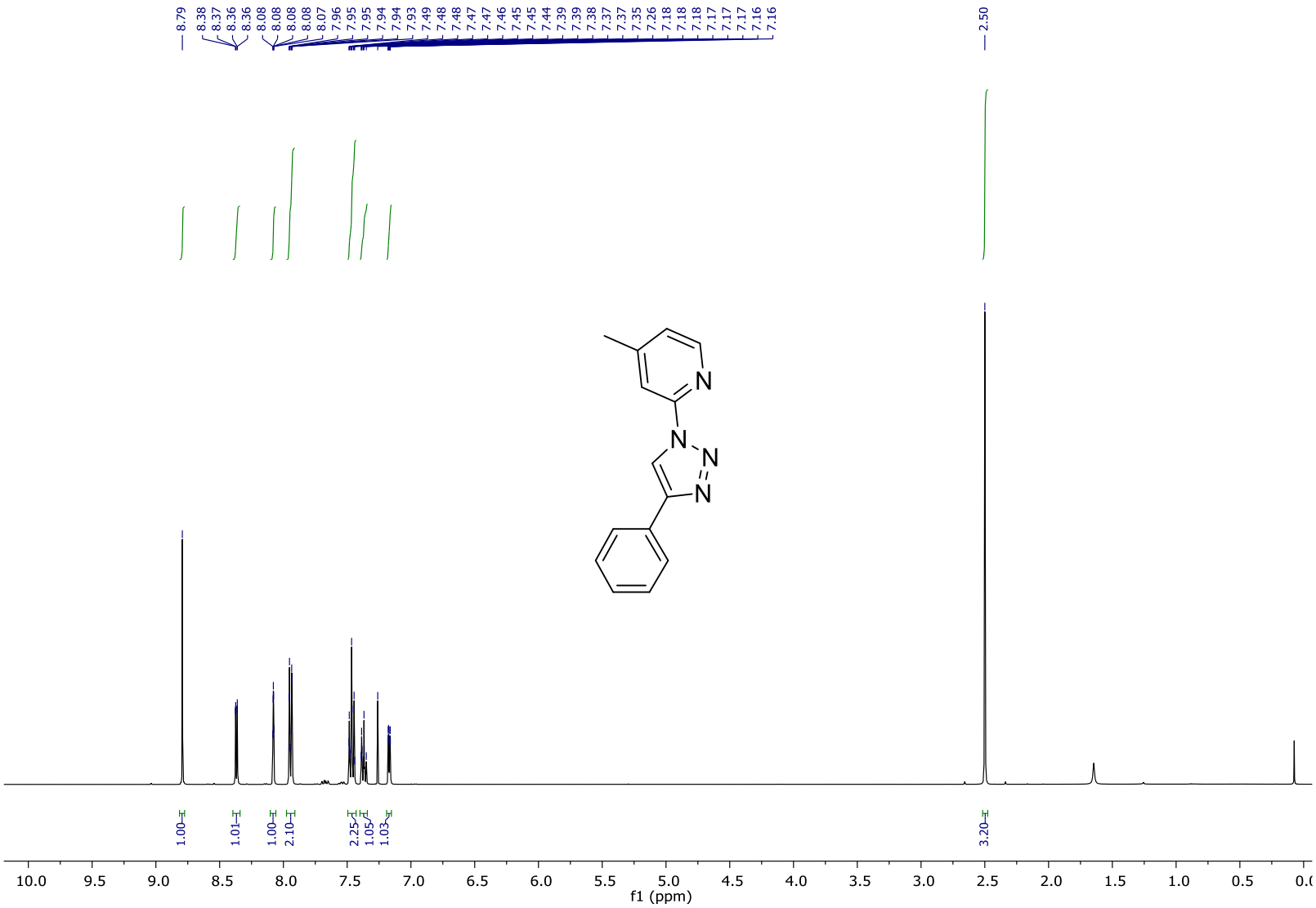

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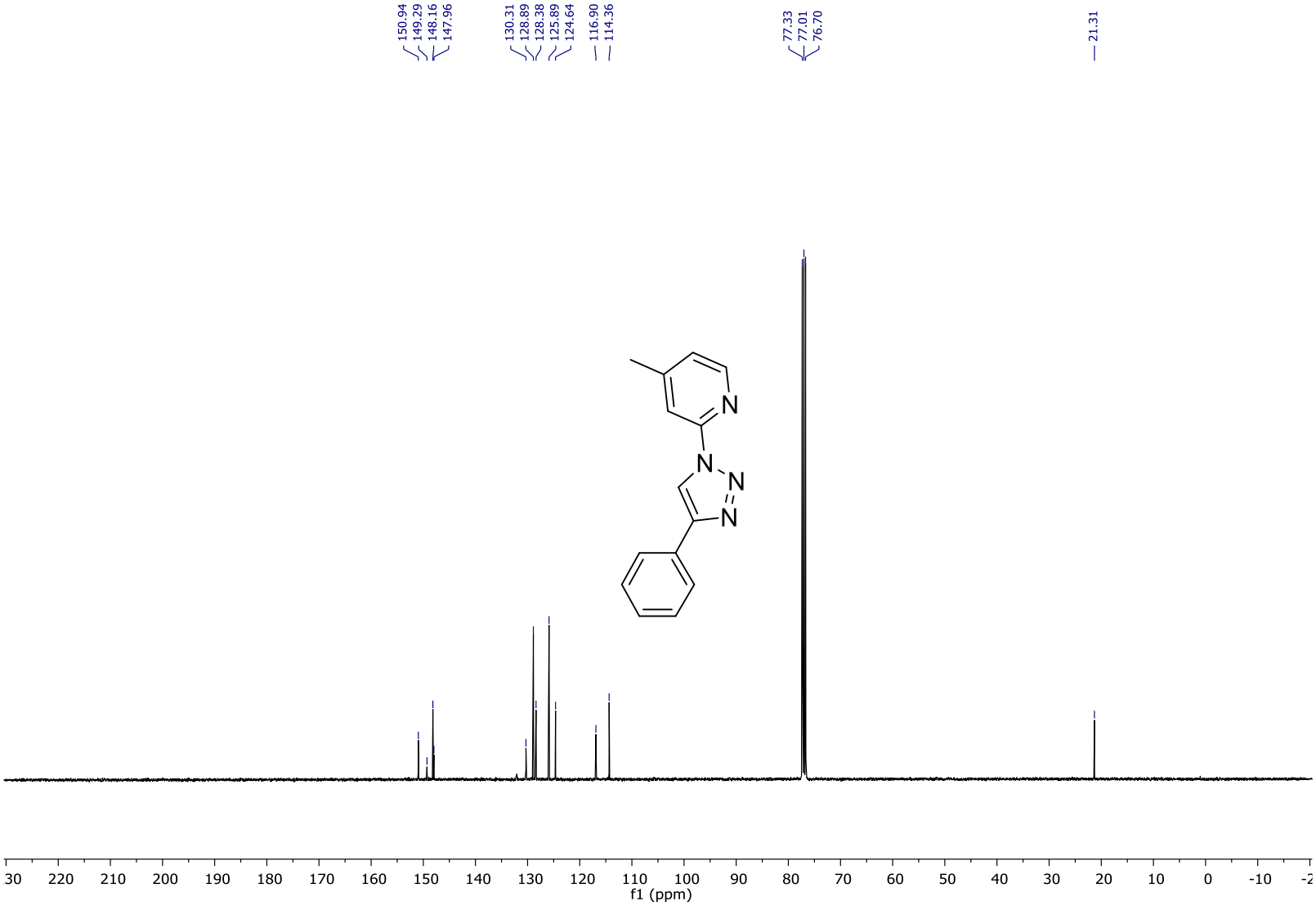

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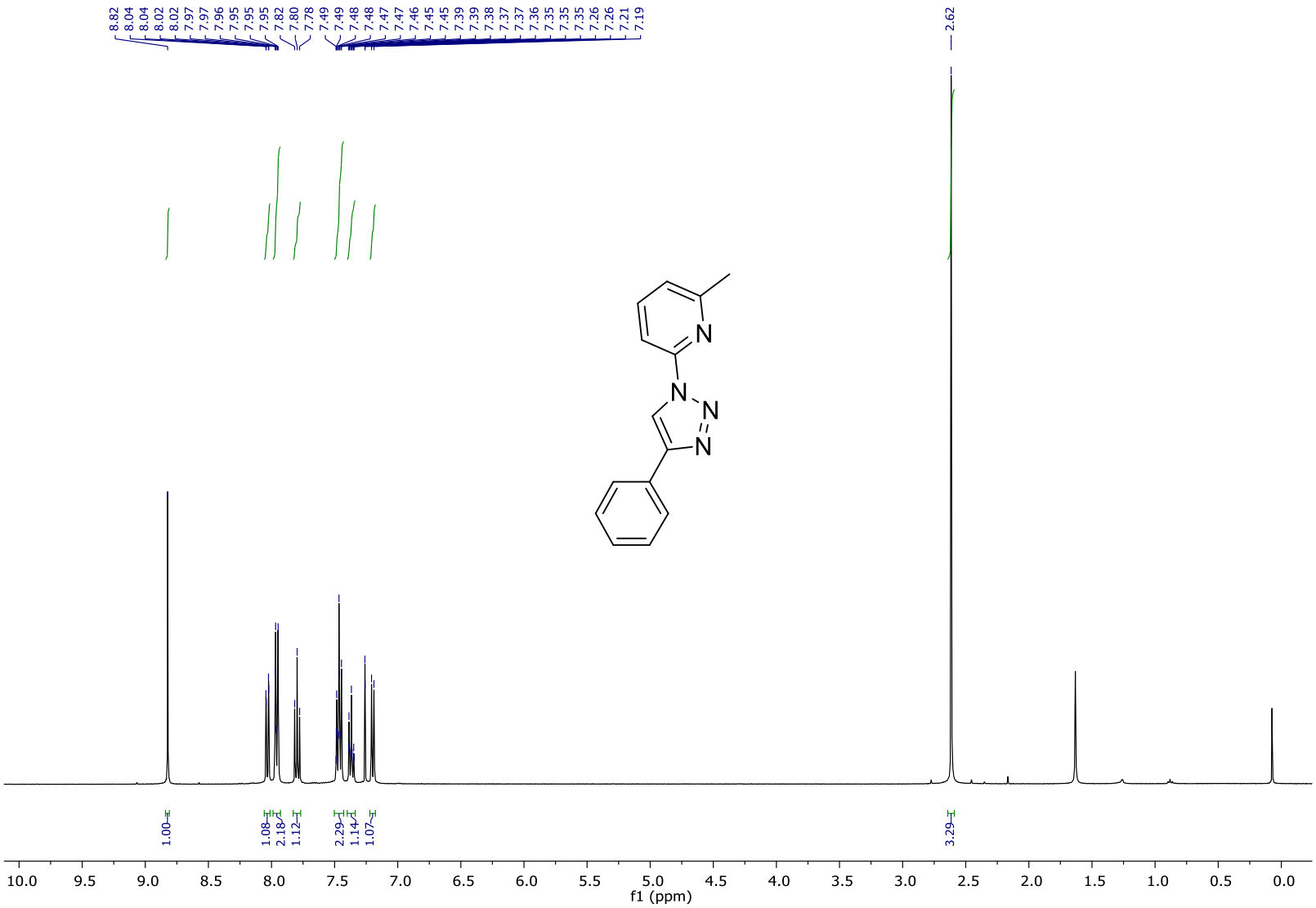

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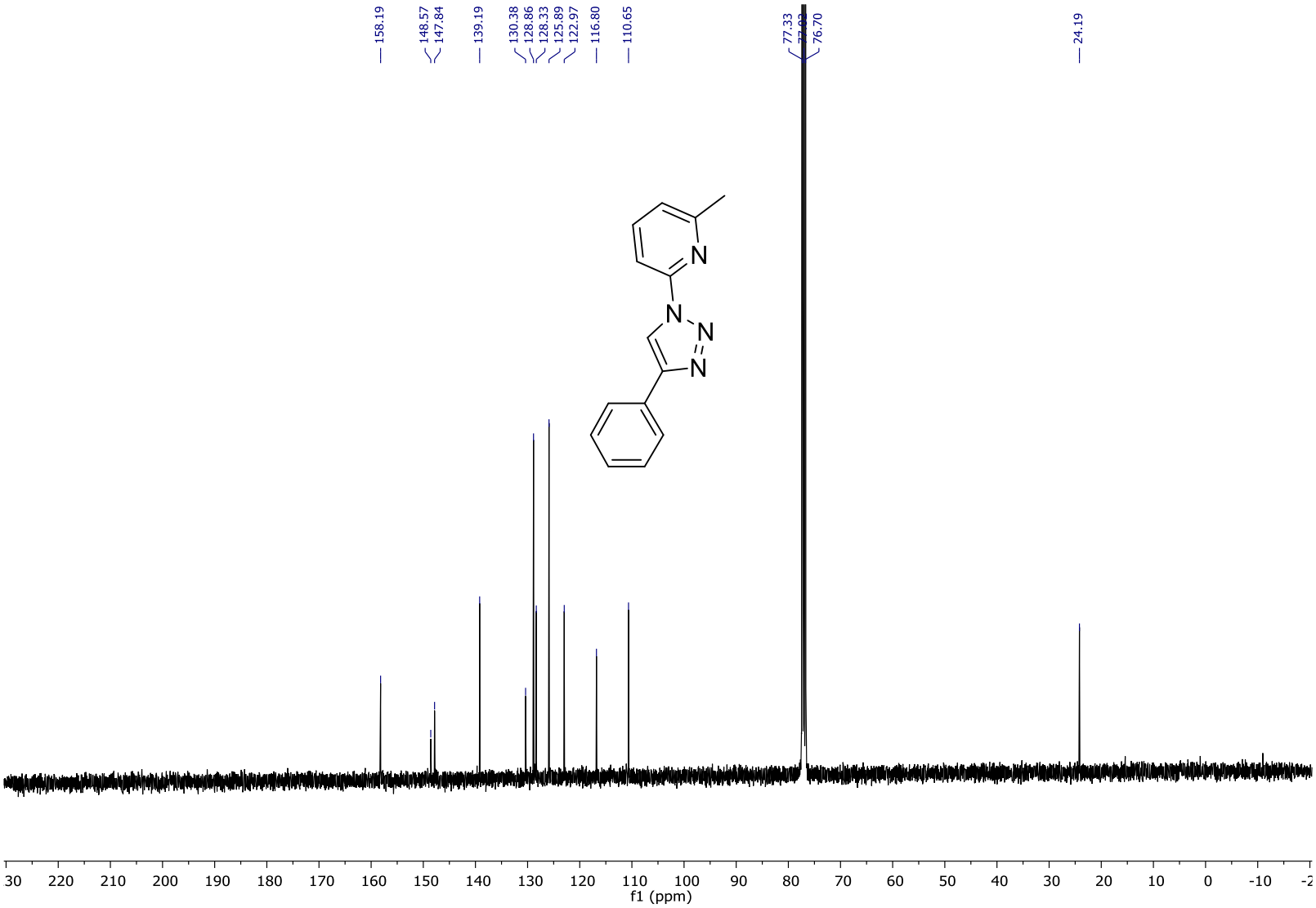

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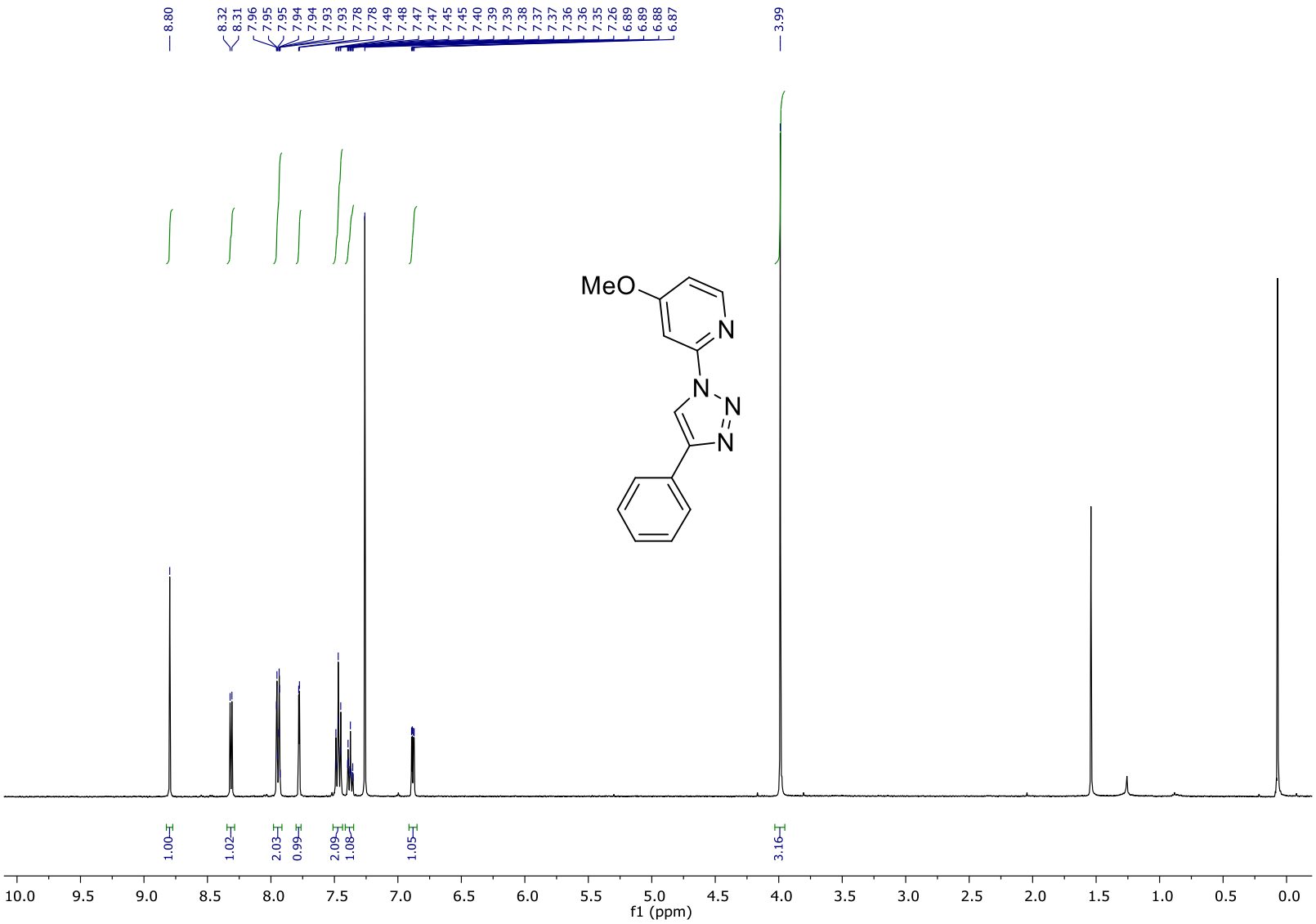

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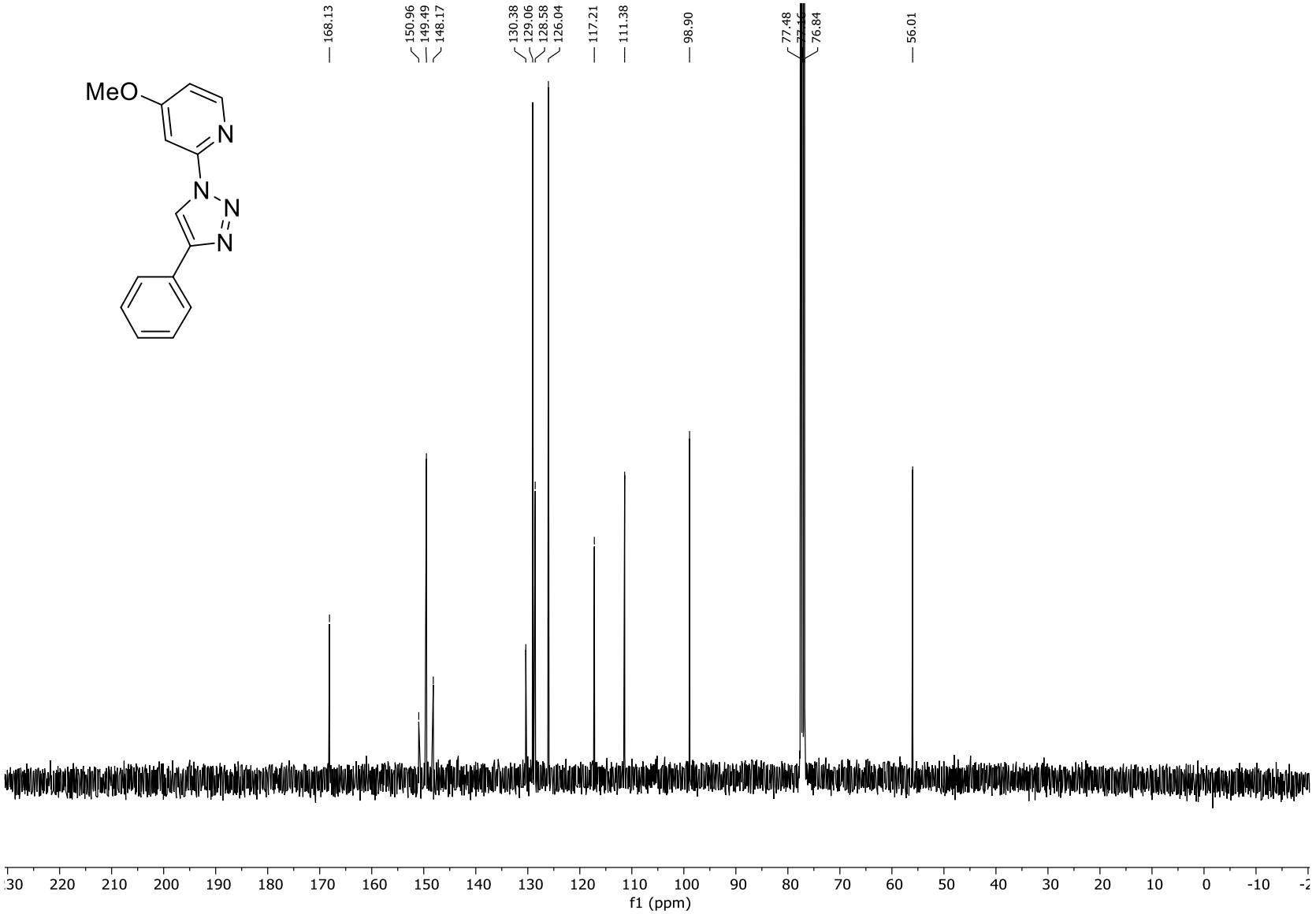

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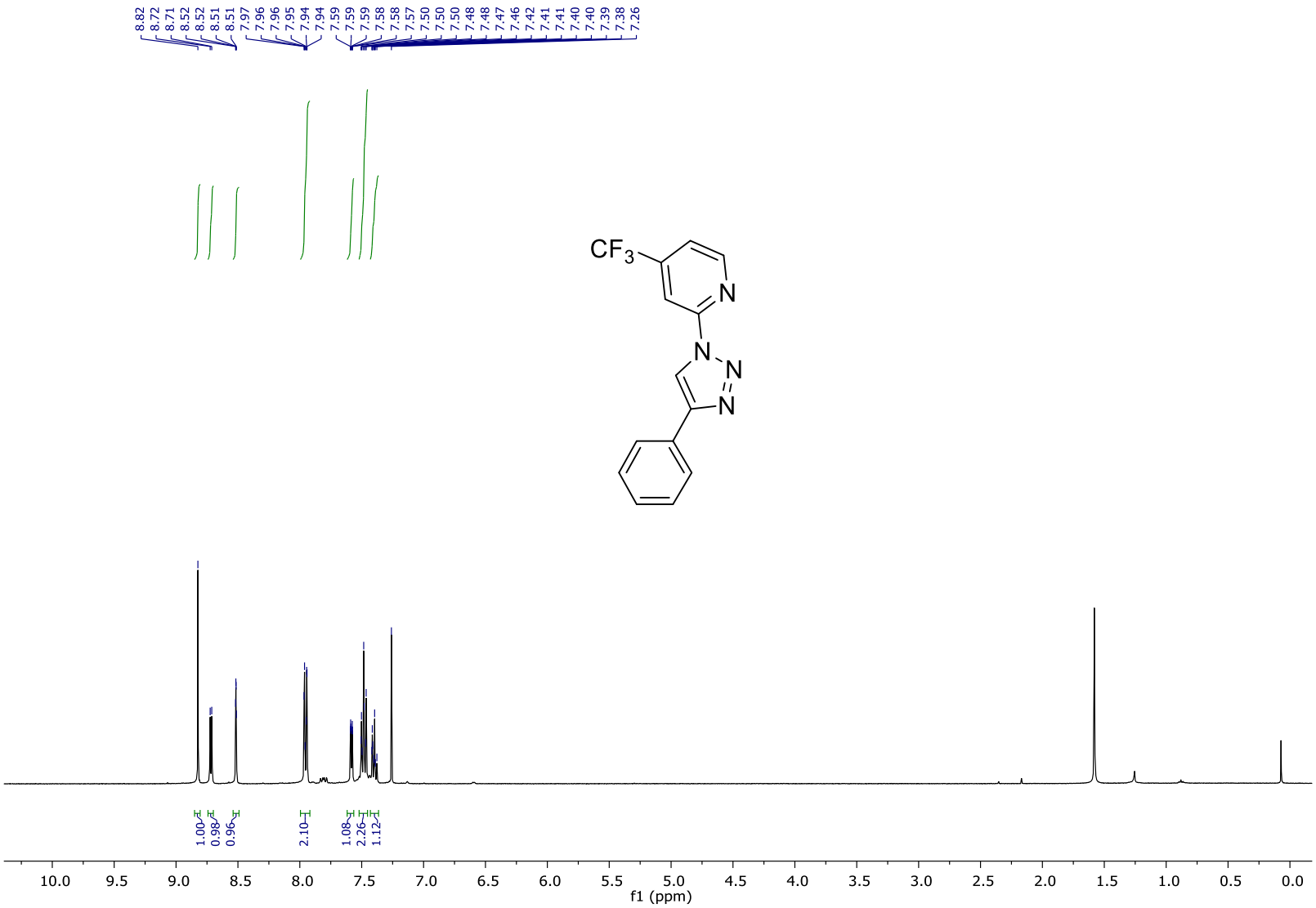
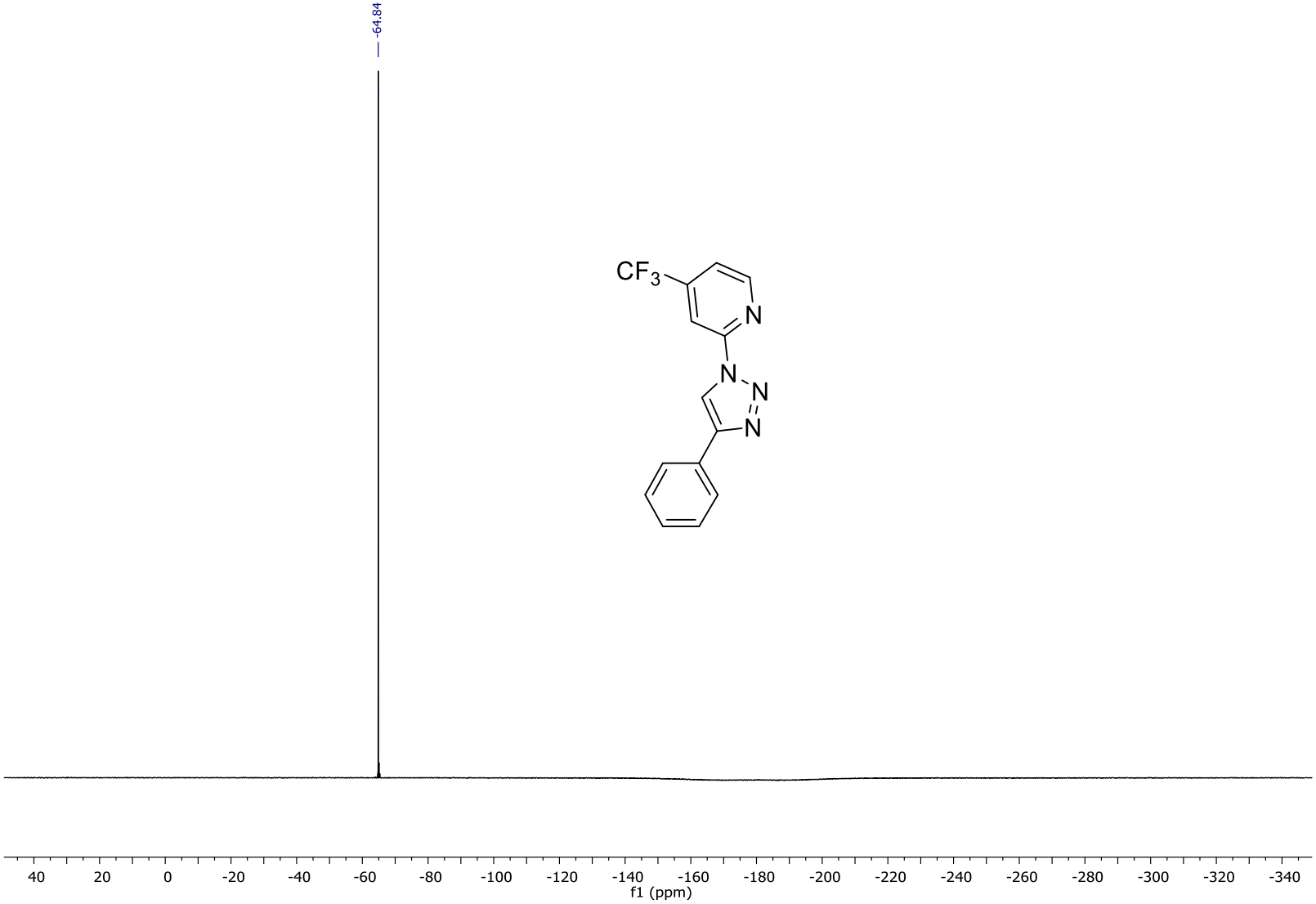
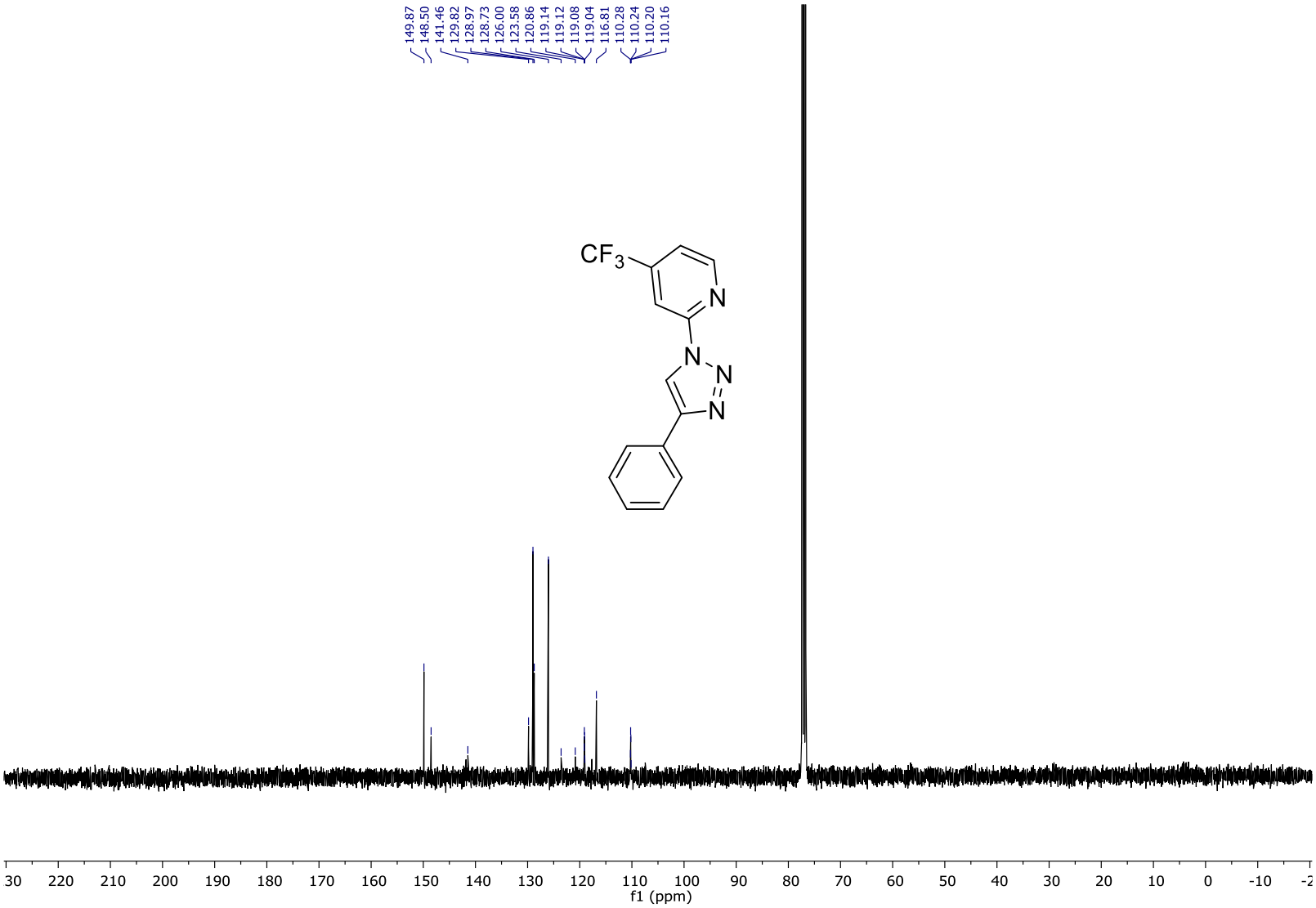


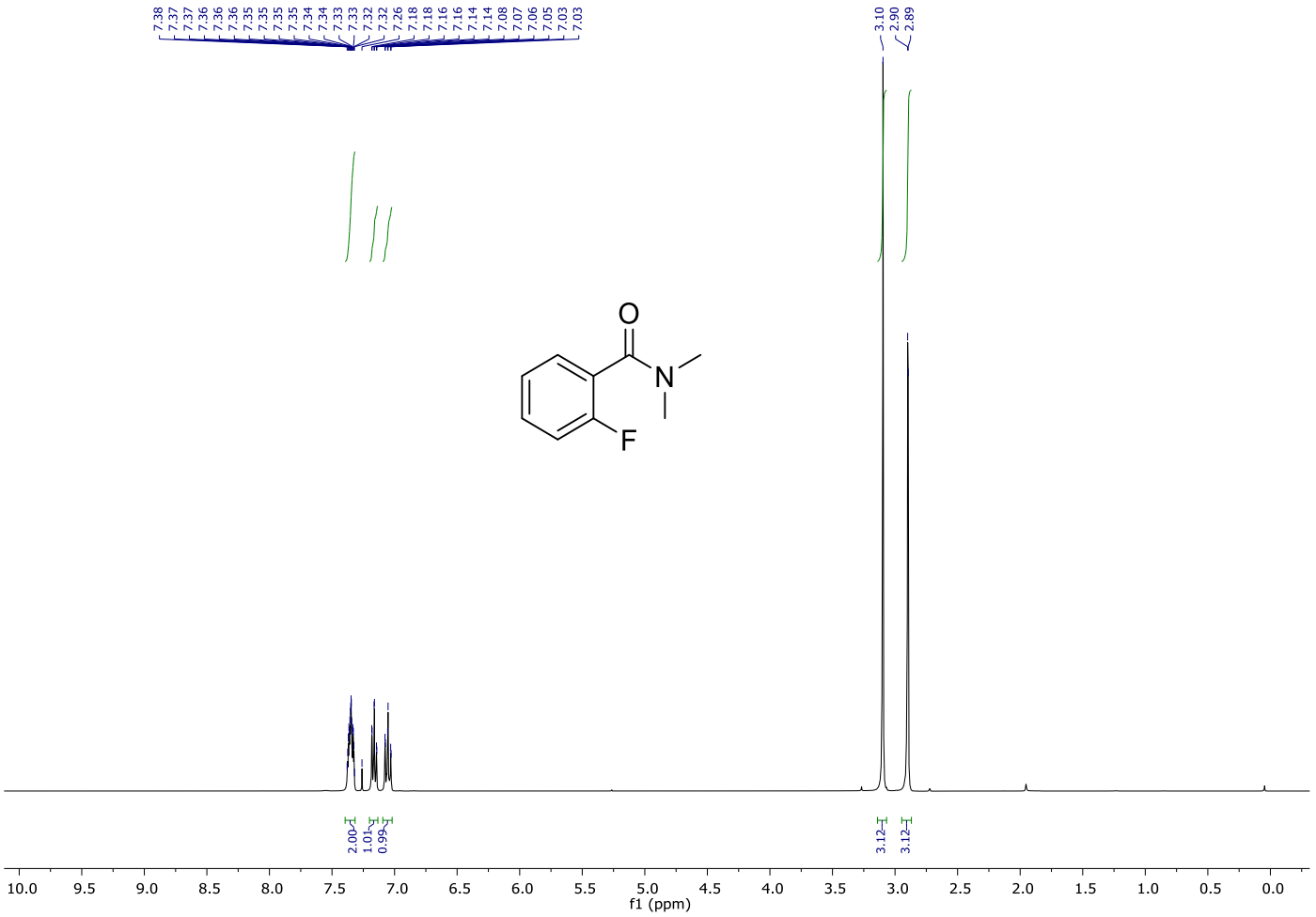
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **L6***.



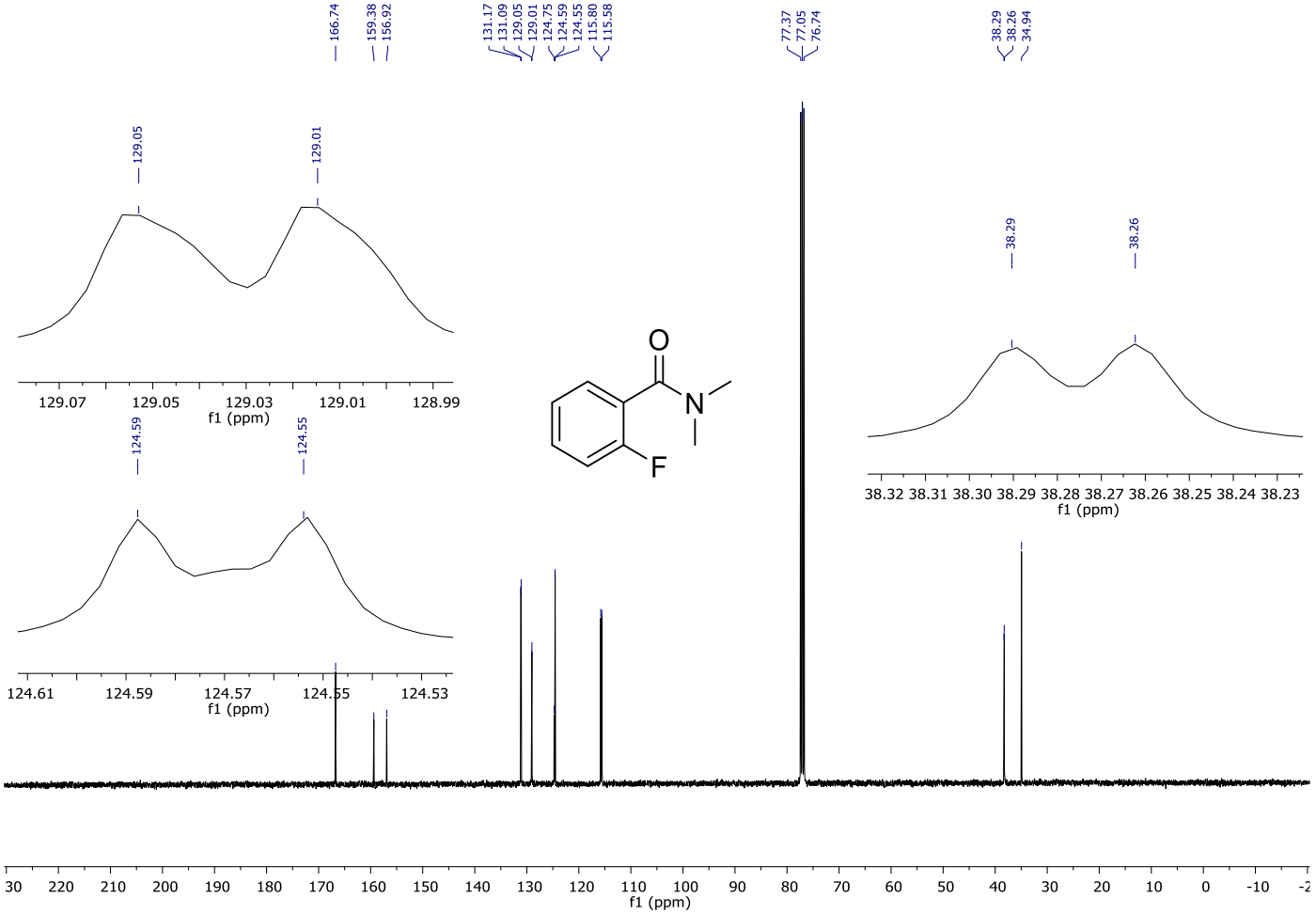
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376 MHz) spectrum of **L6***.



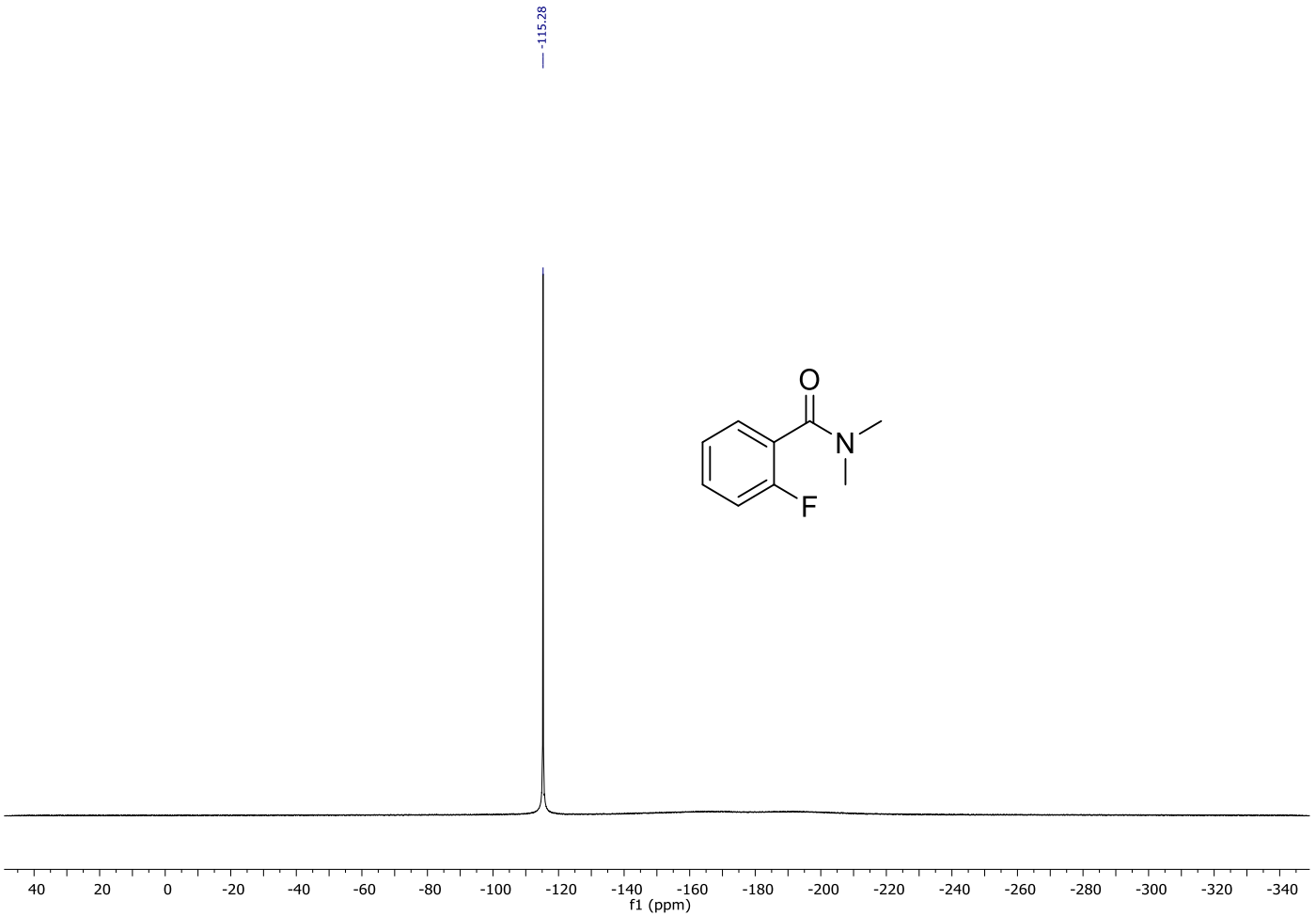
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **L6***.



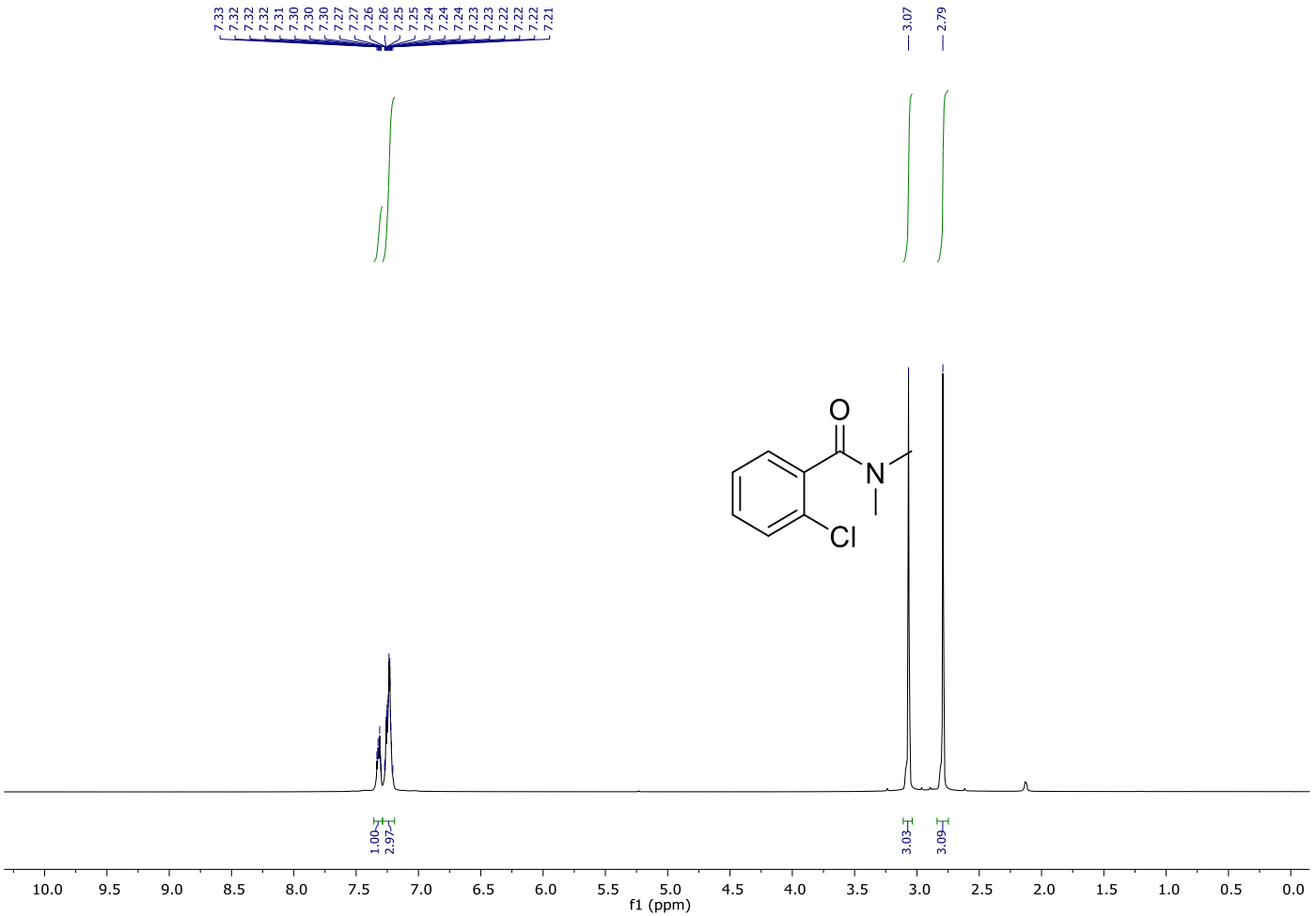
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **1f**.



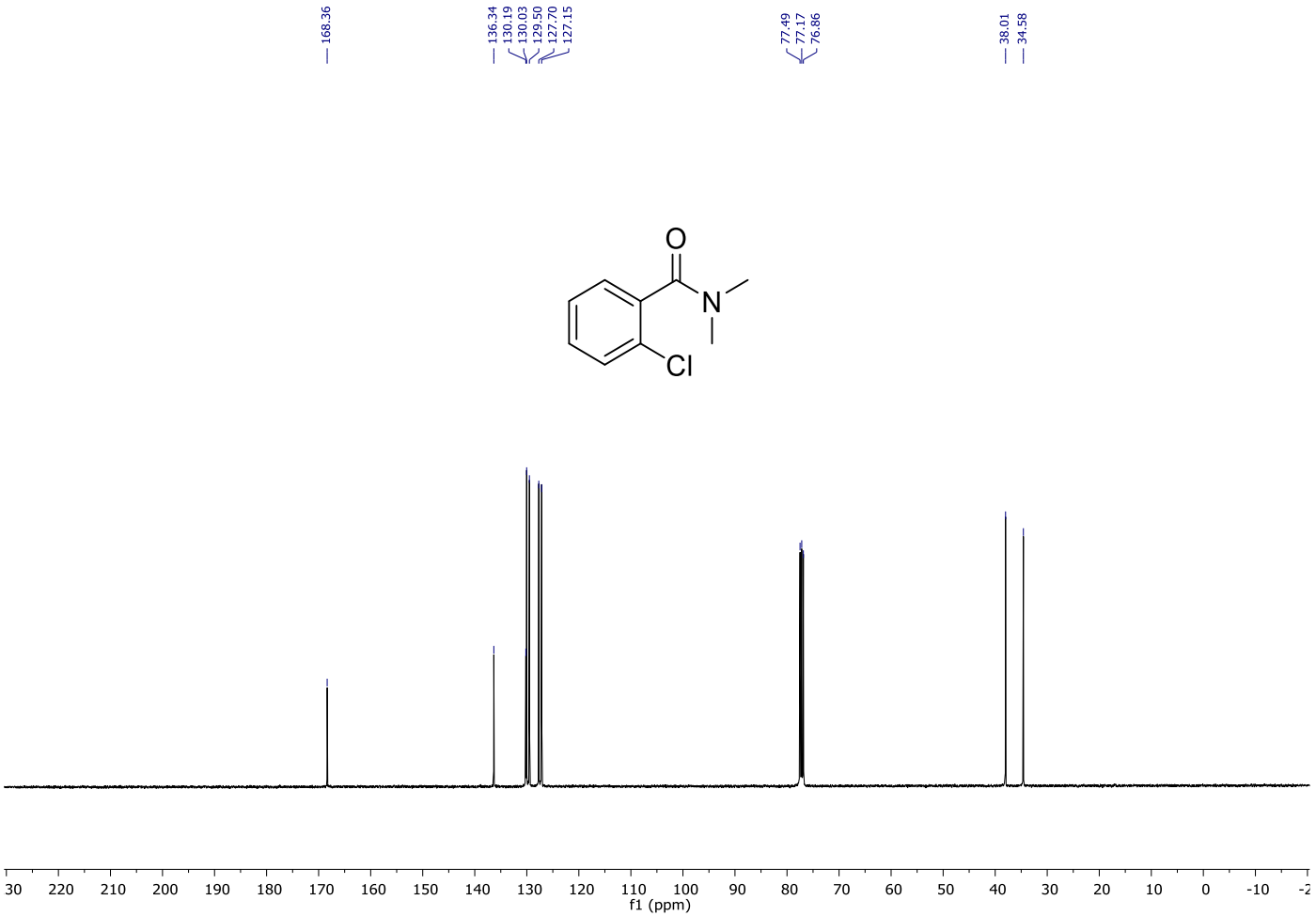
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **1f**.



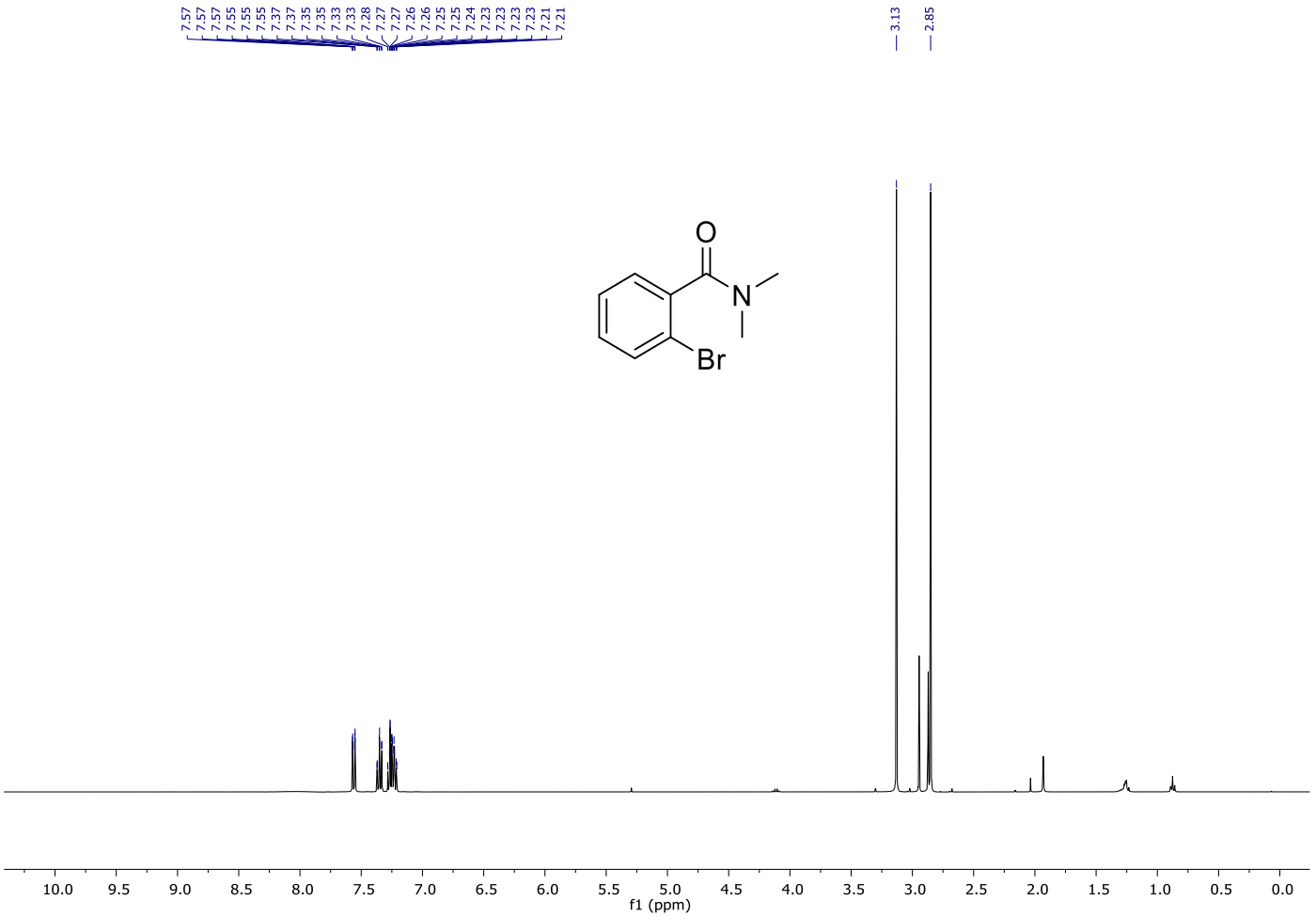
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376 MHz) spectrum of **1f**.



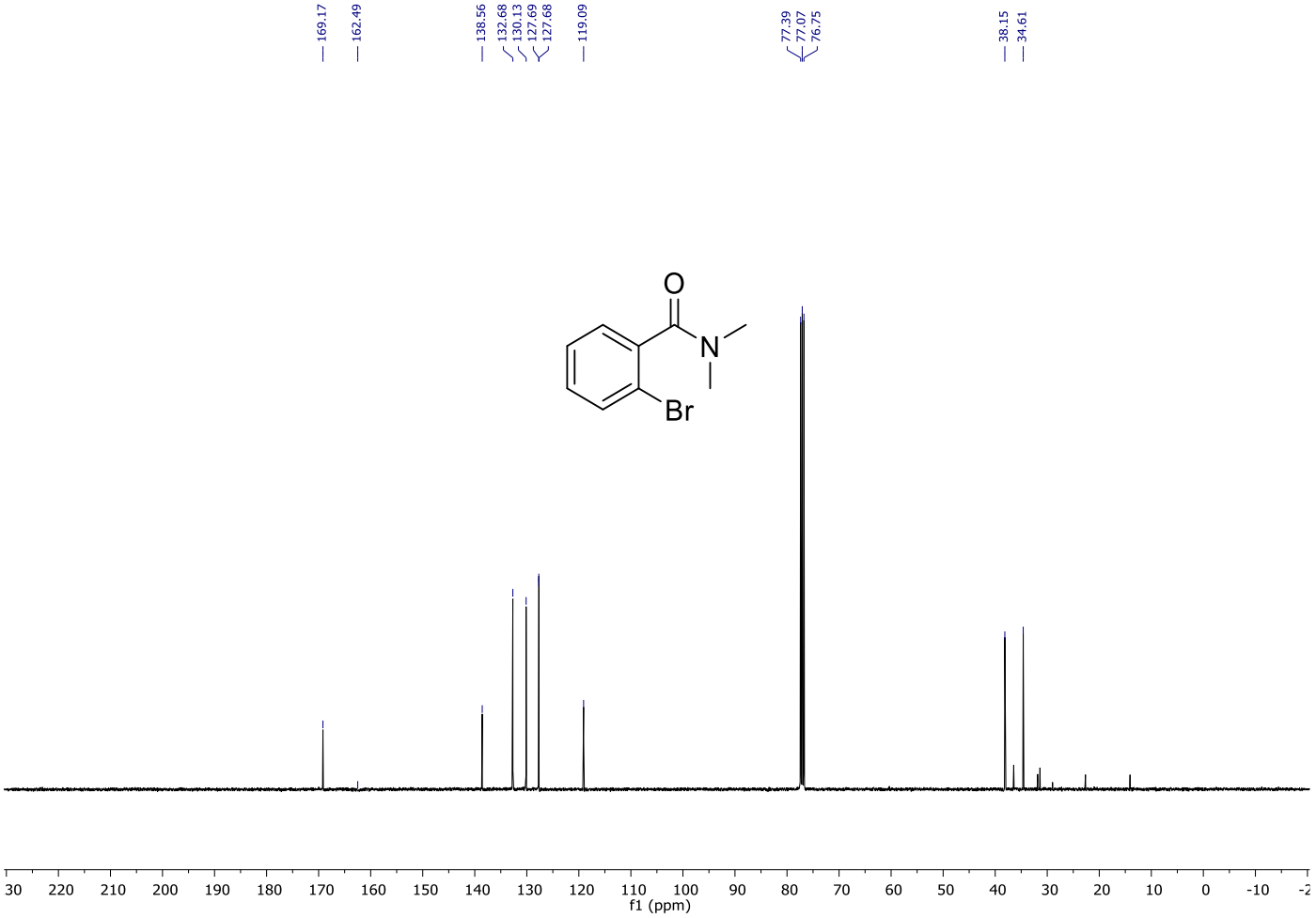
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **1g**.



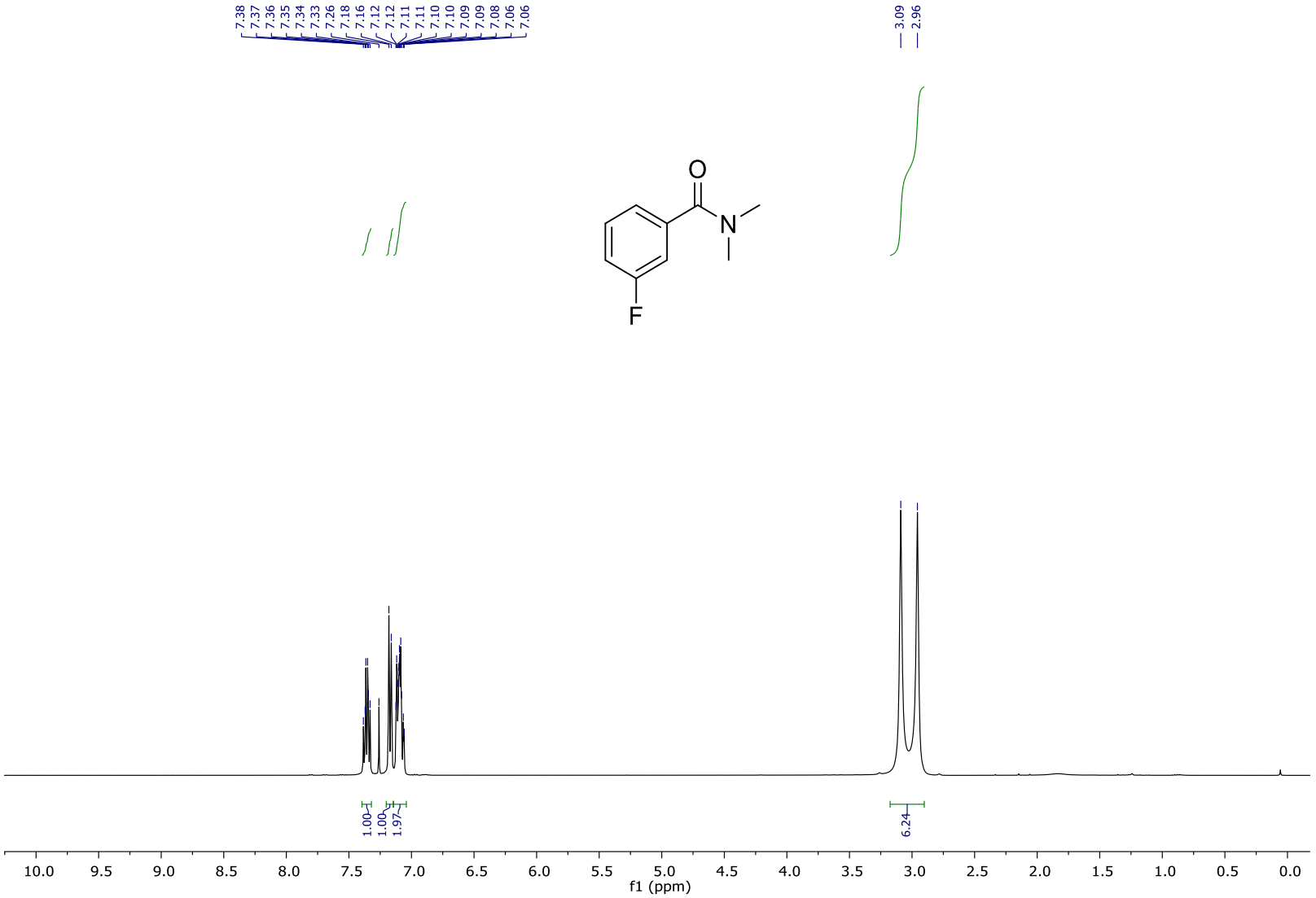
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **1g**.



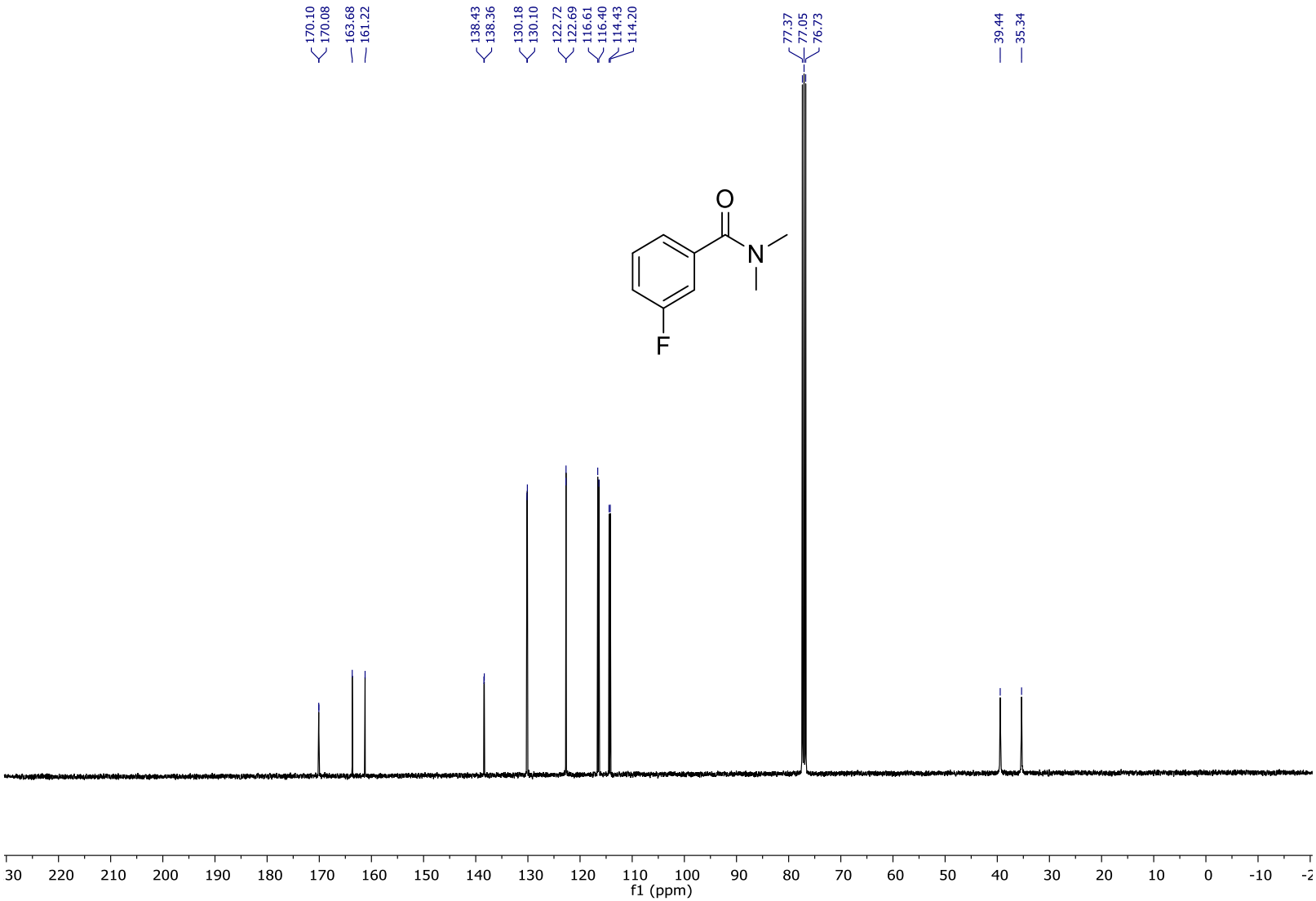
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **1h**.



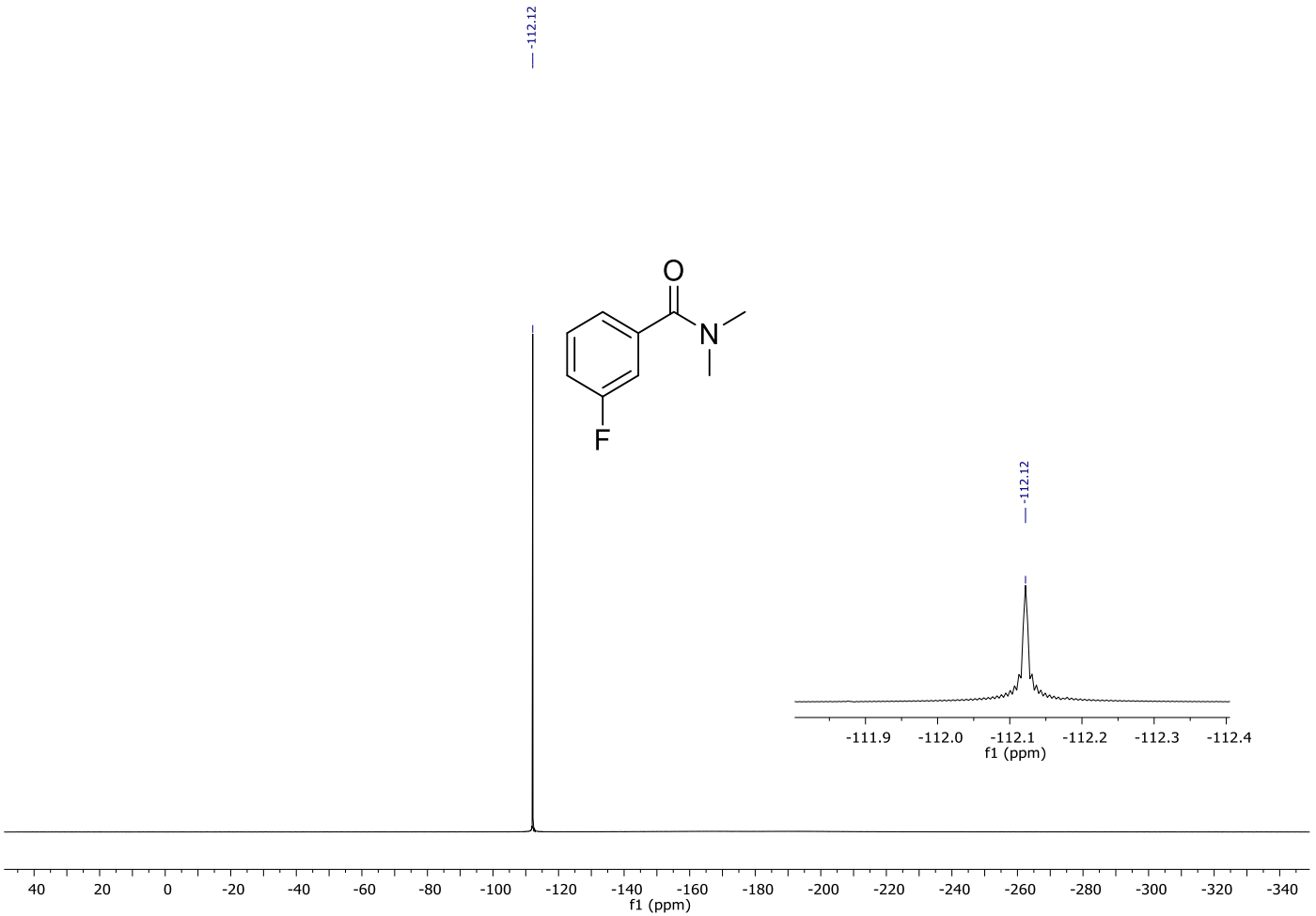
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **1h**.



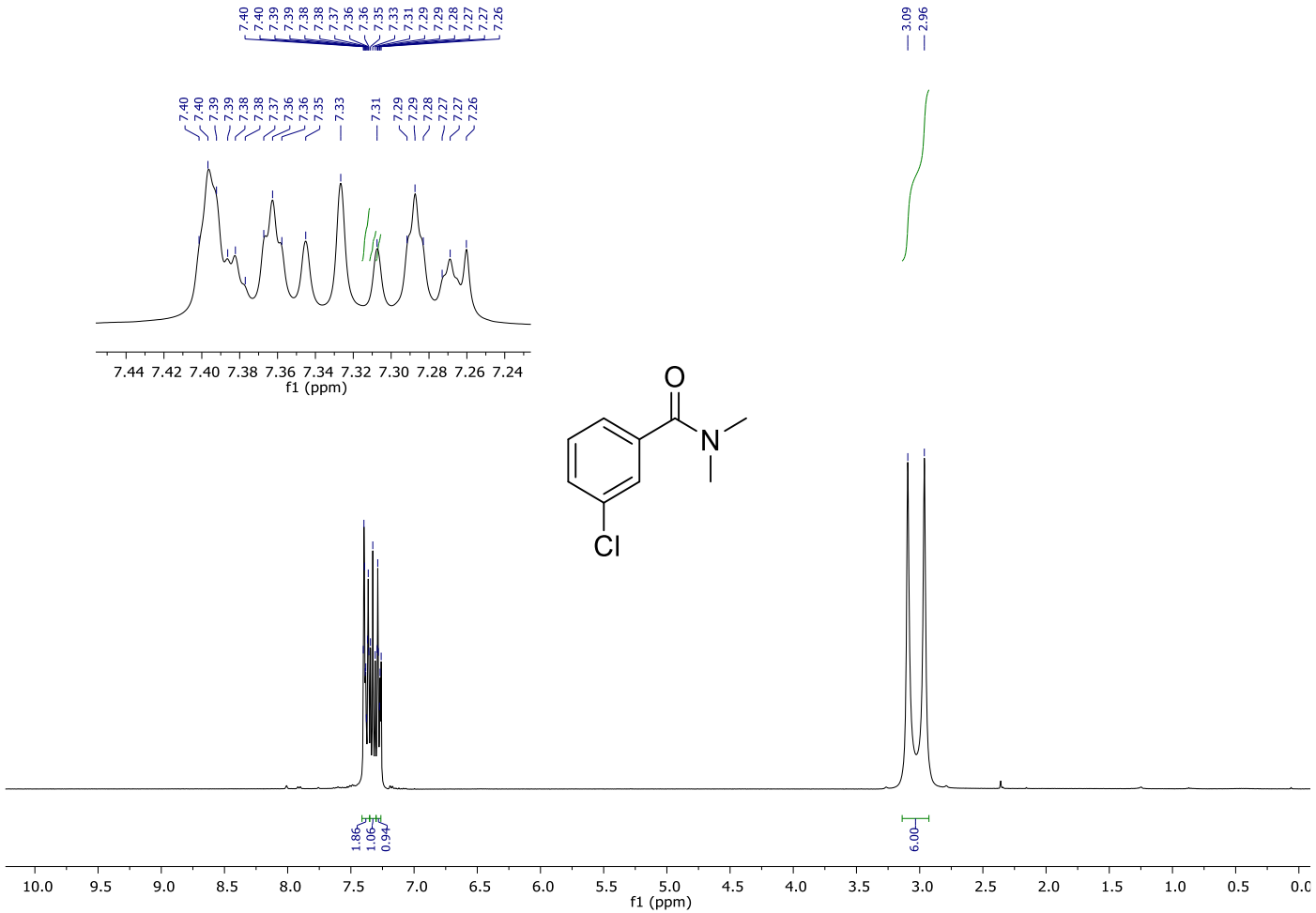
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **1i**.



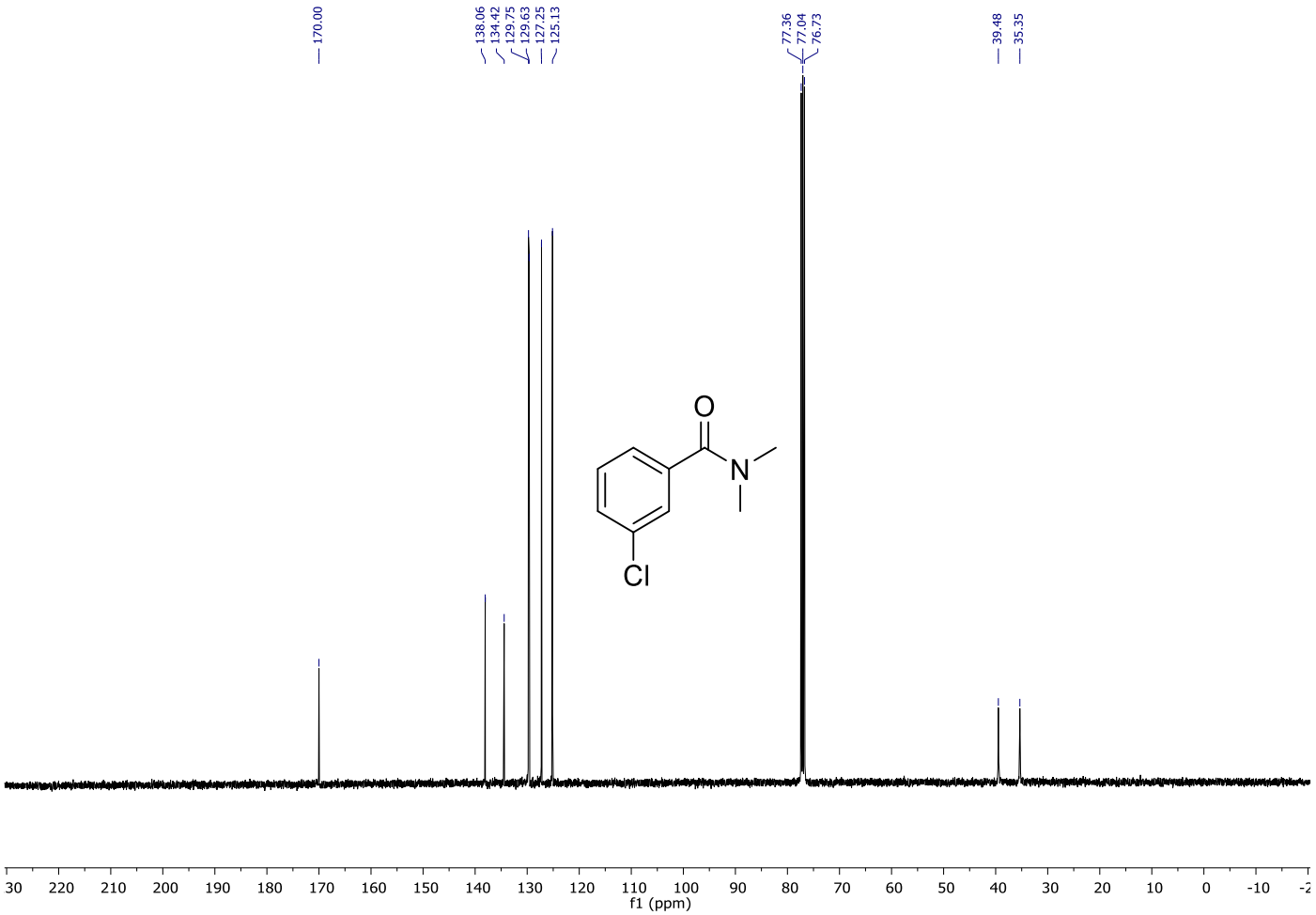
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **1i**..



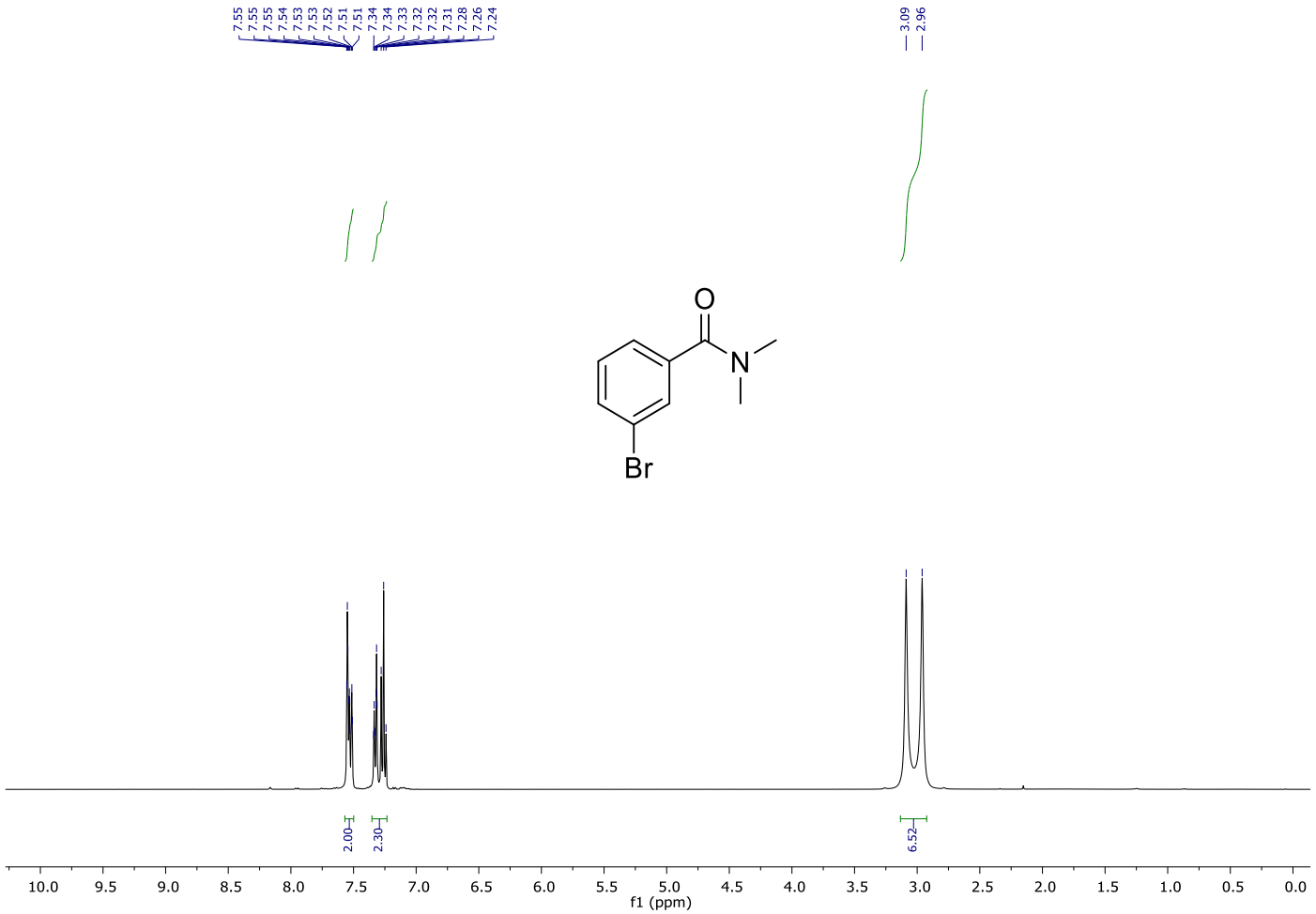
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376 MHz) spectrum of **1i**.



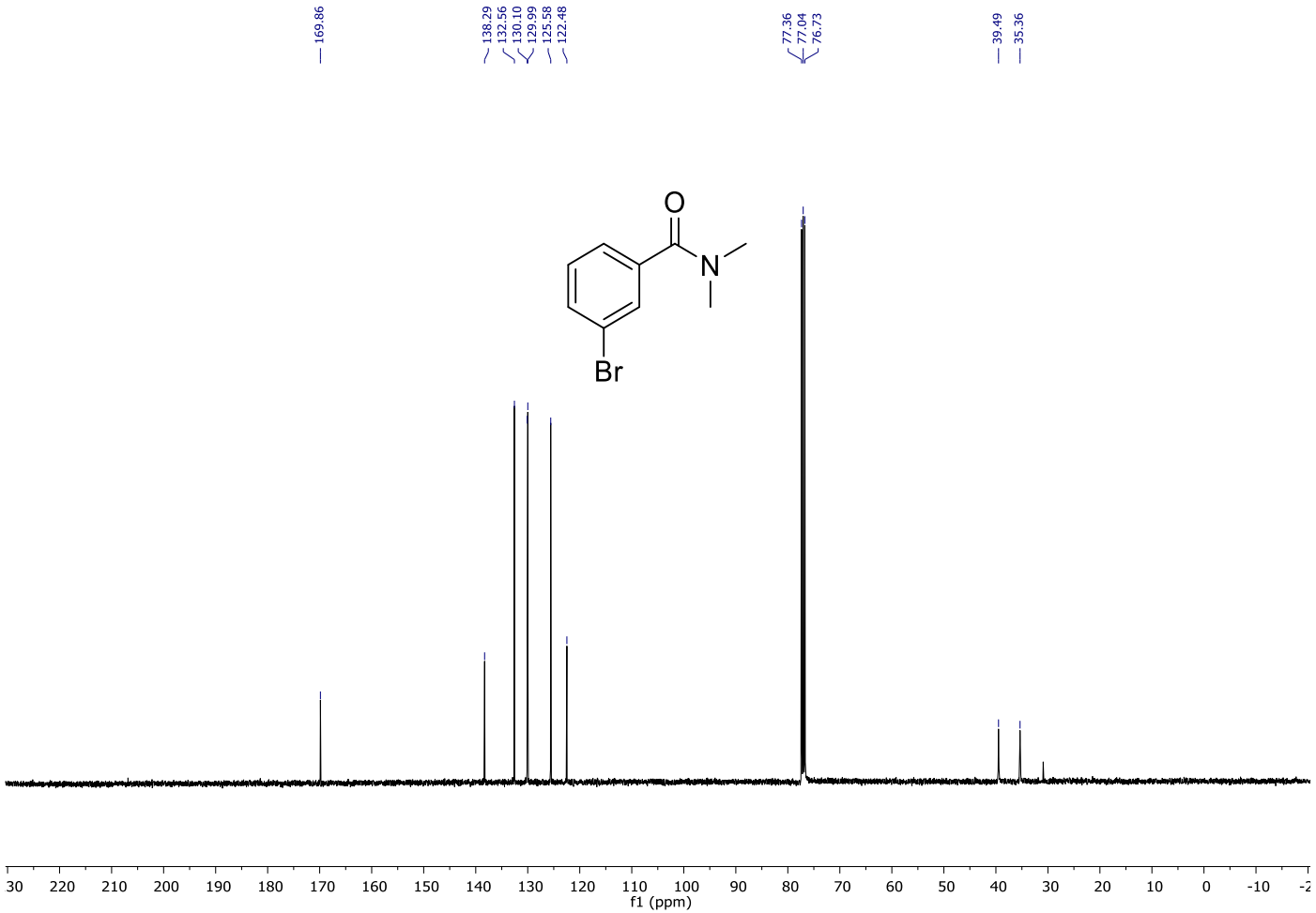
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **1j**.



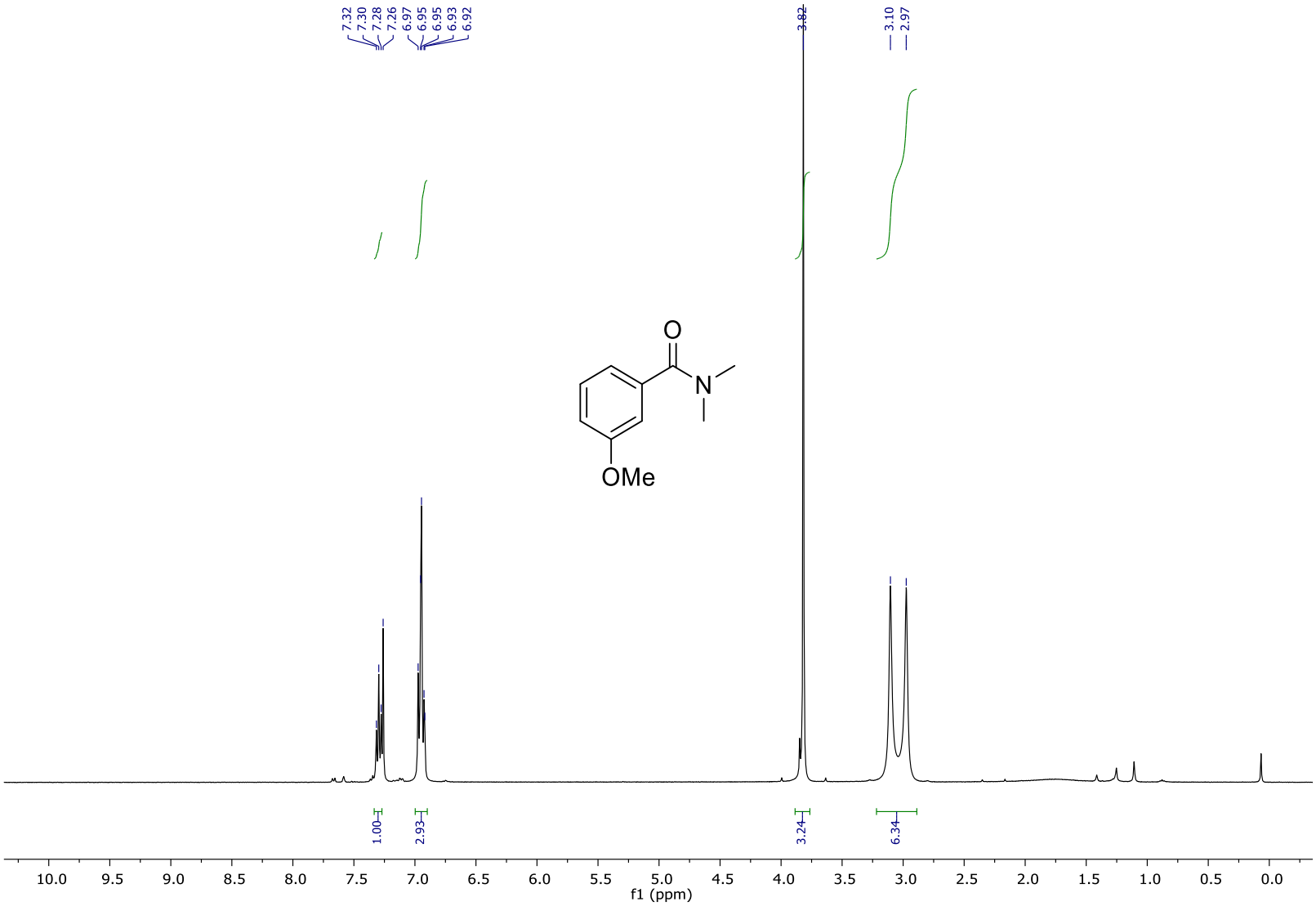
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **1j**.



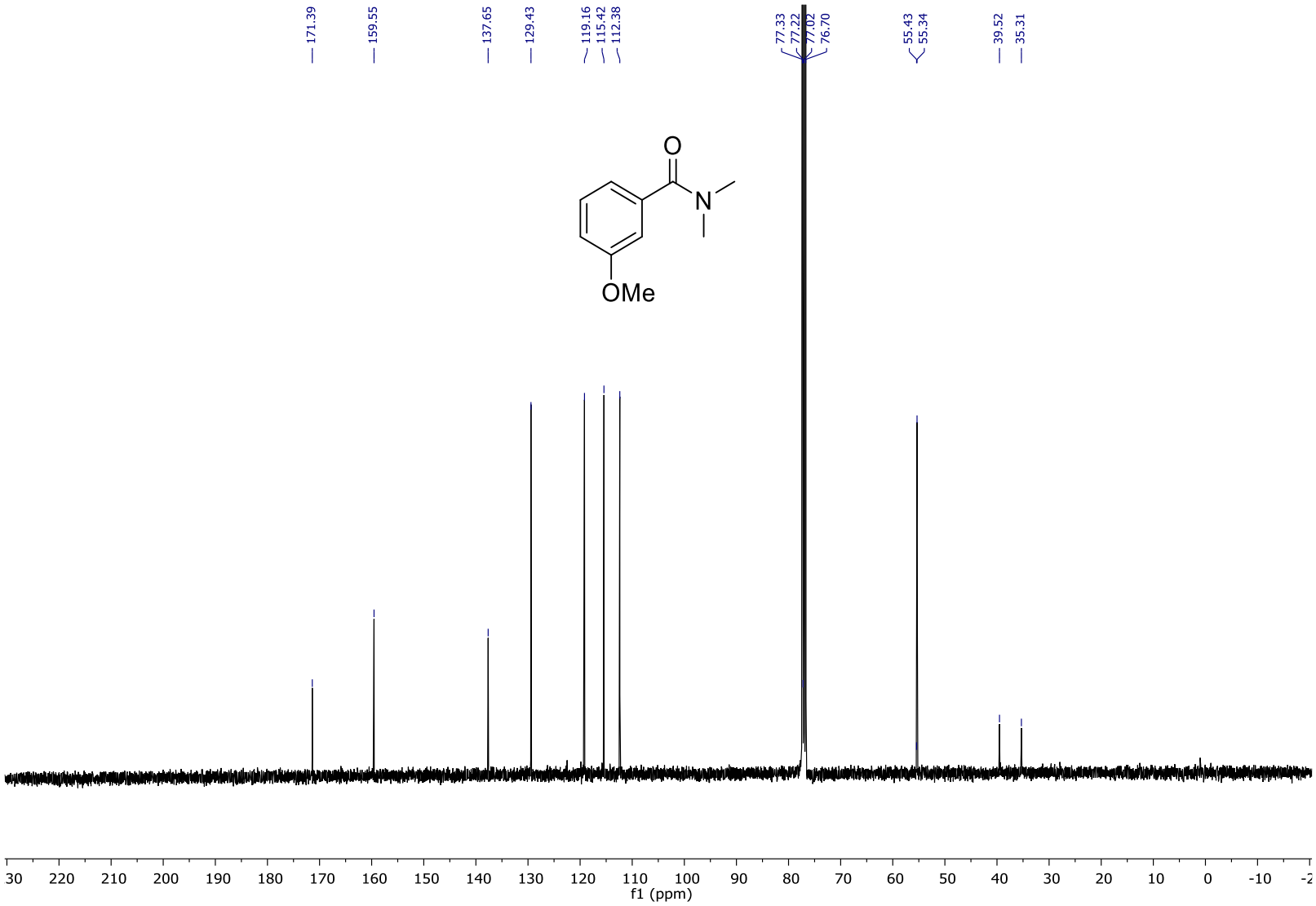
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **1k**.



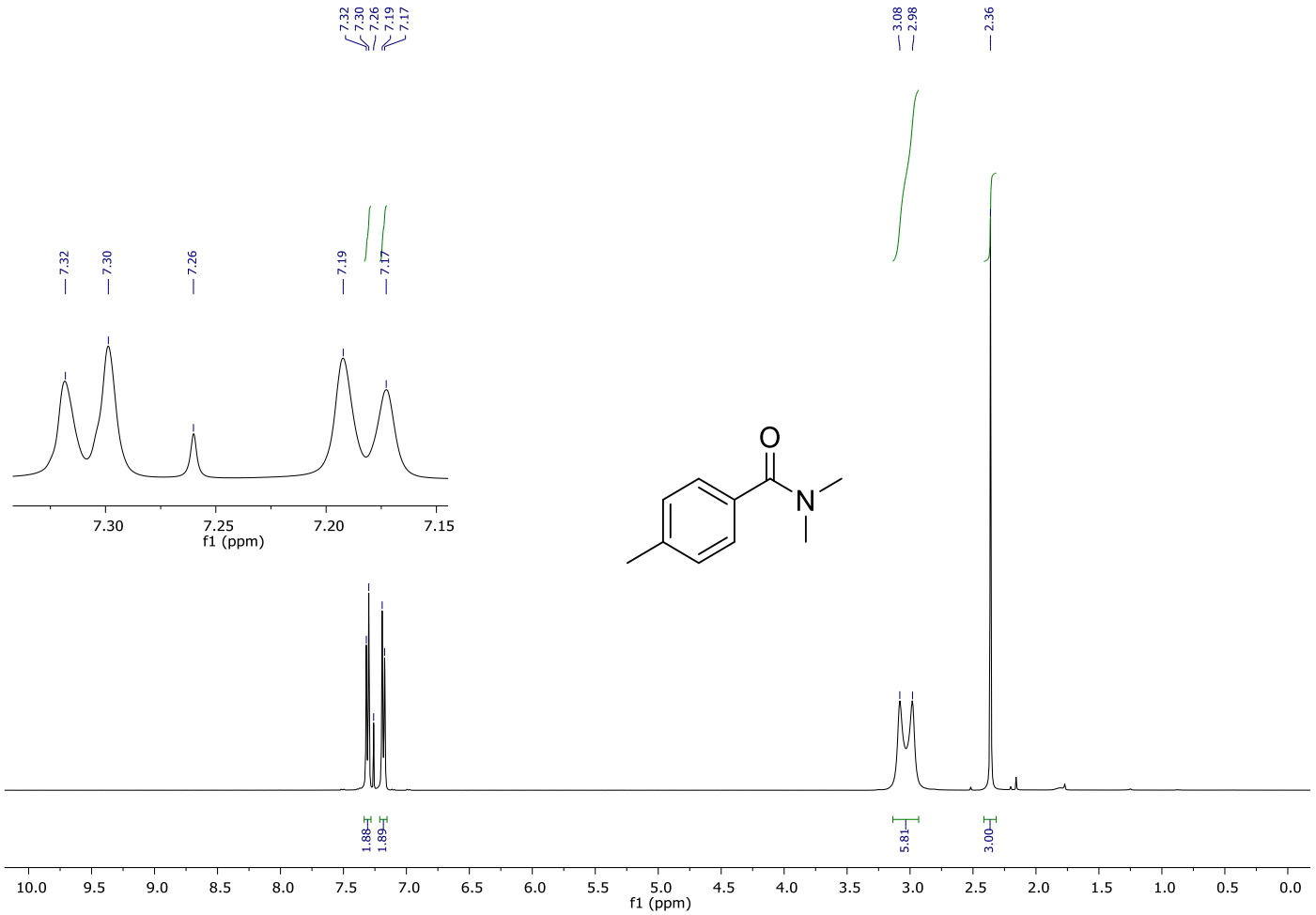
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **1k**



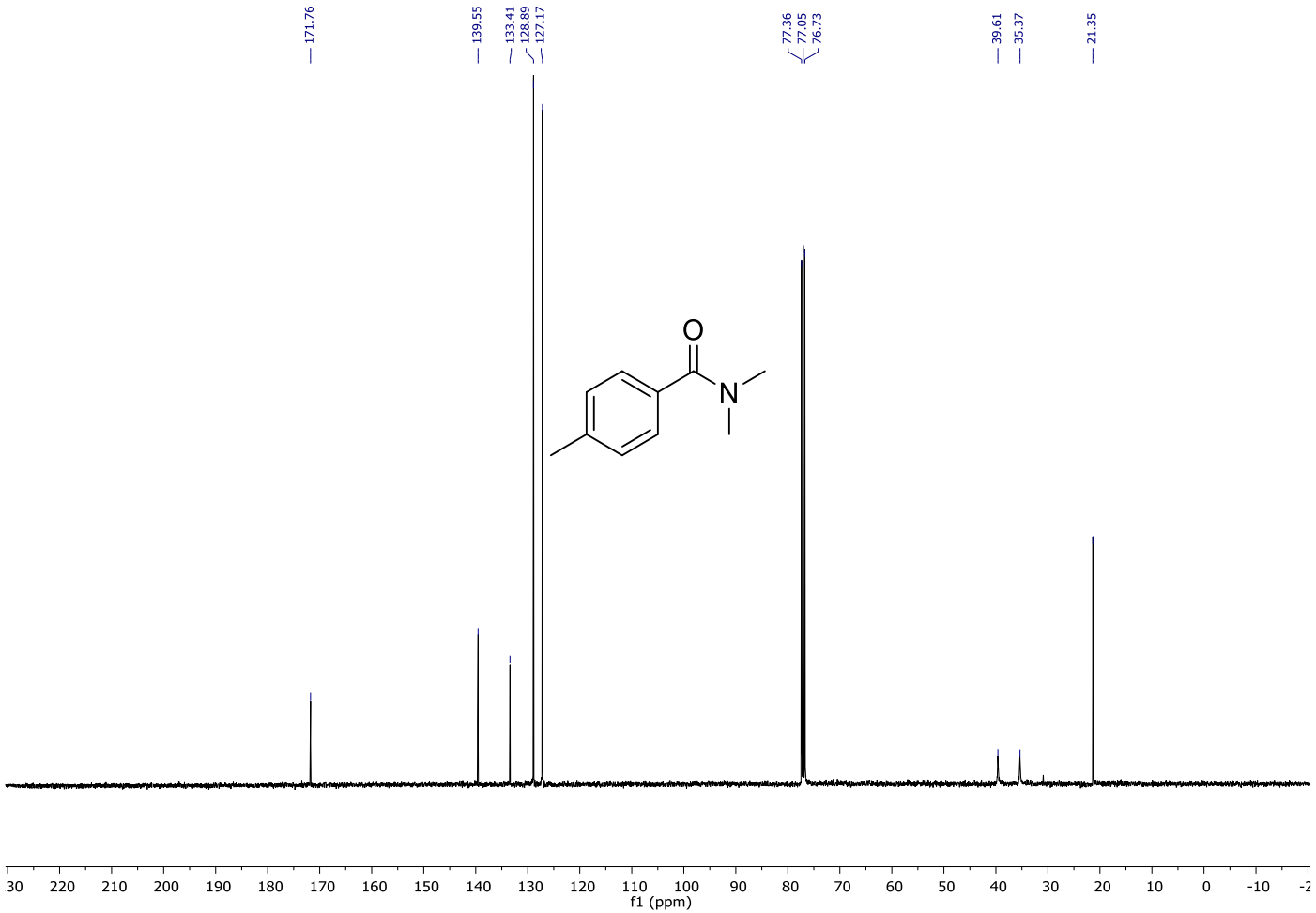
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **1l**.



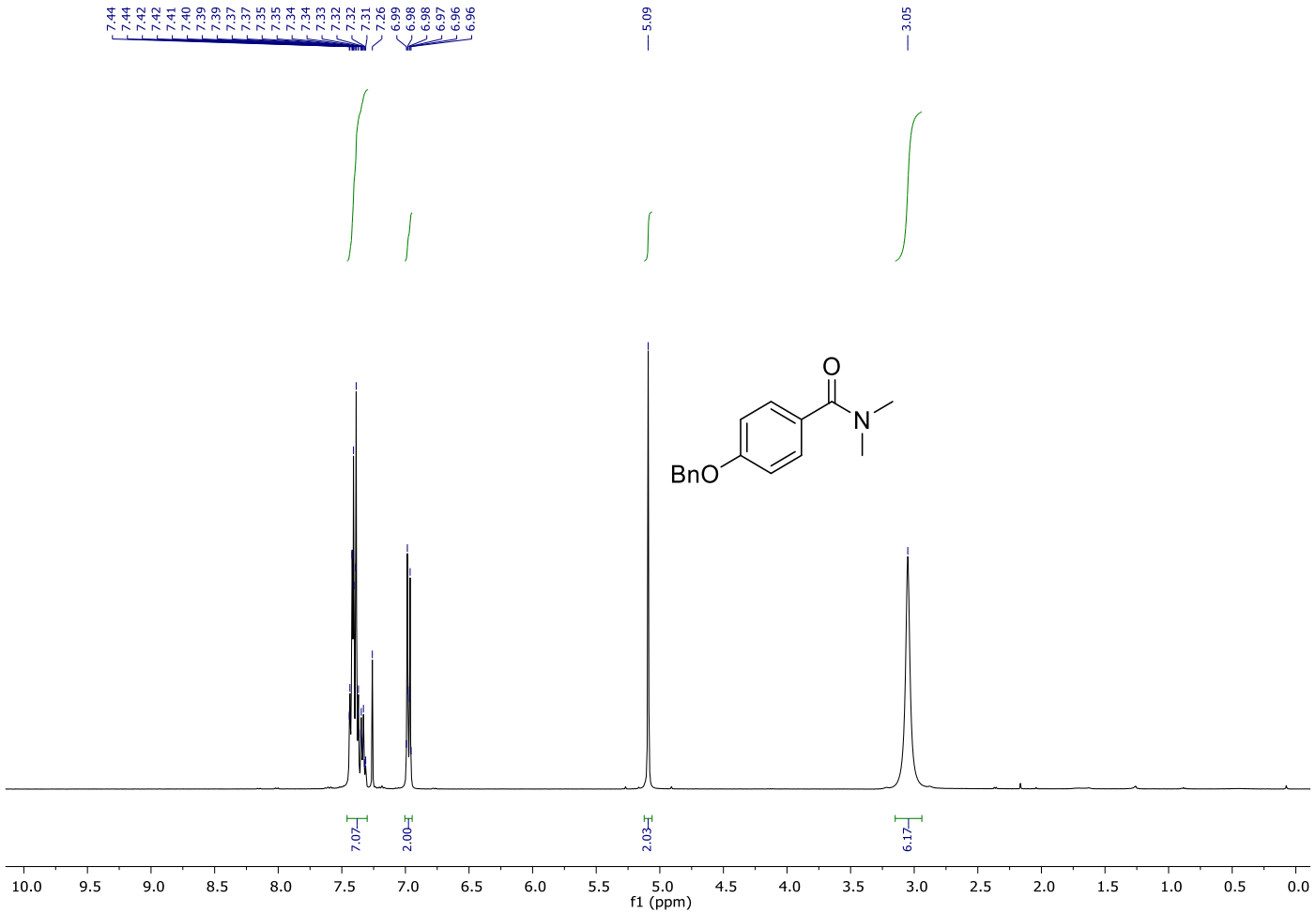
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **1l**.



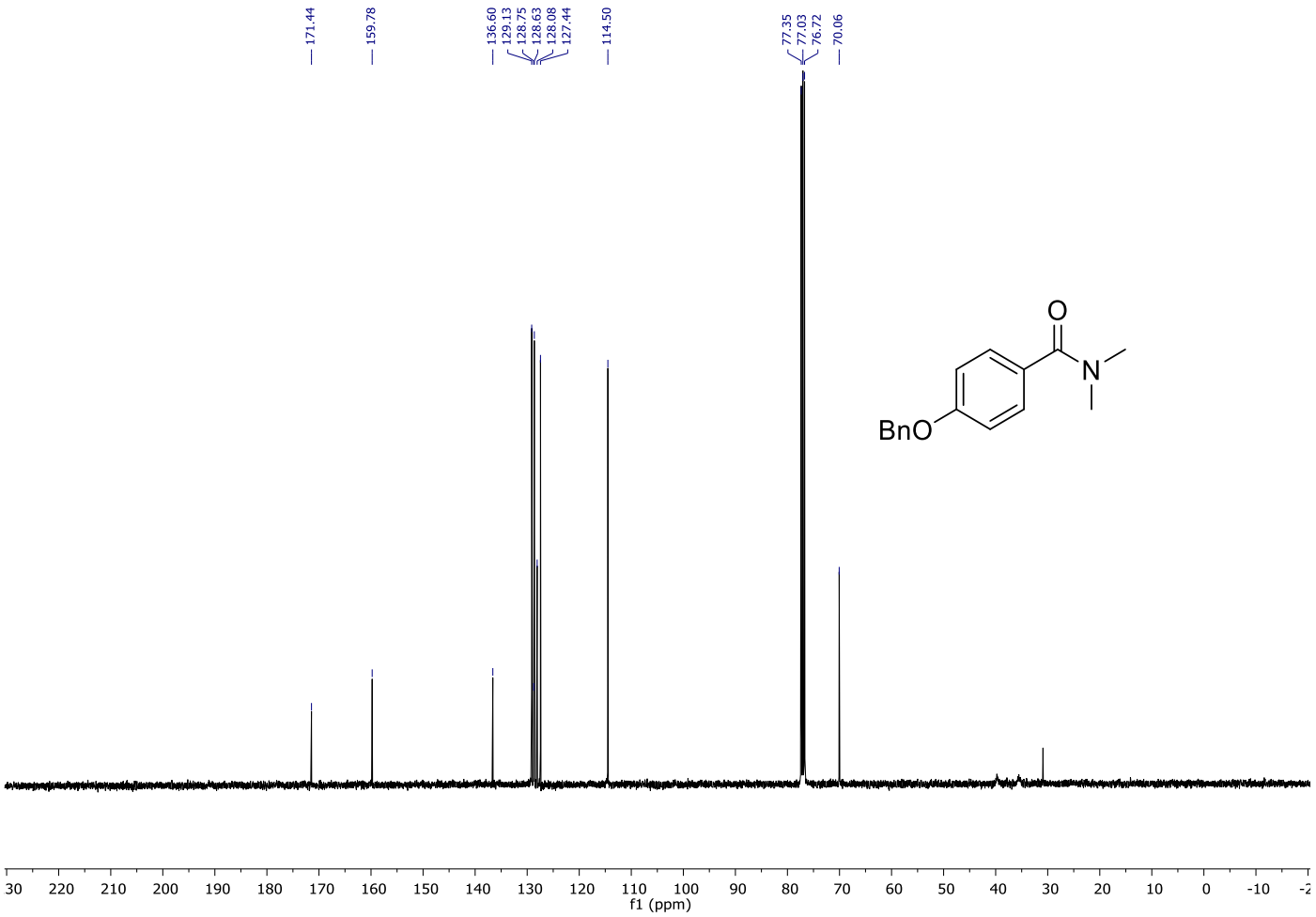
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **1n**.



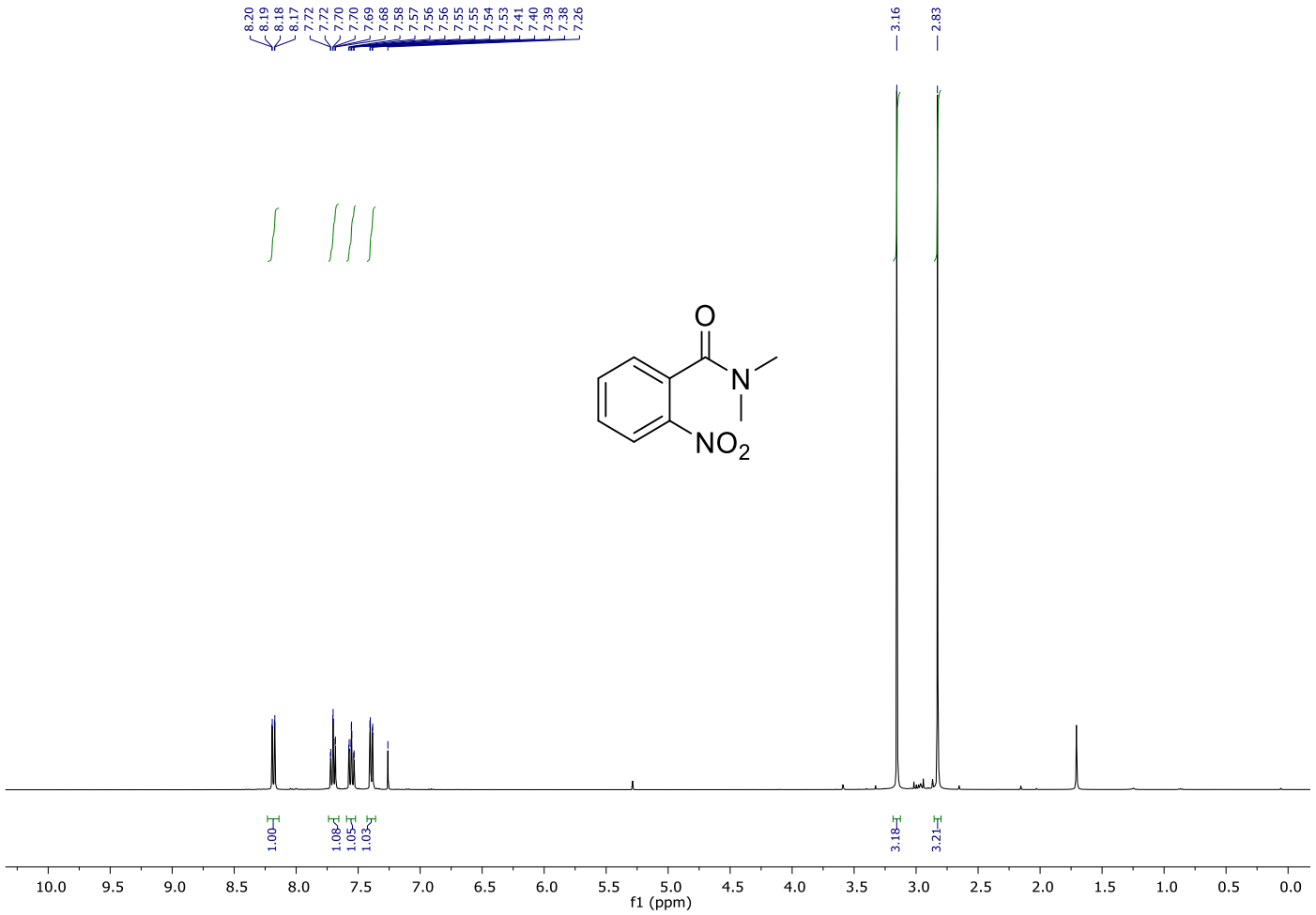
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **1n**.



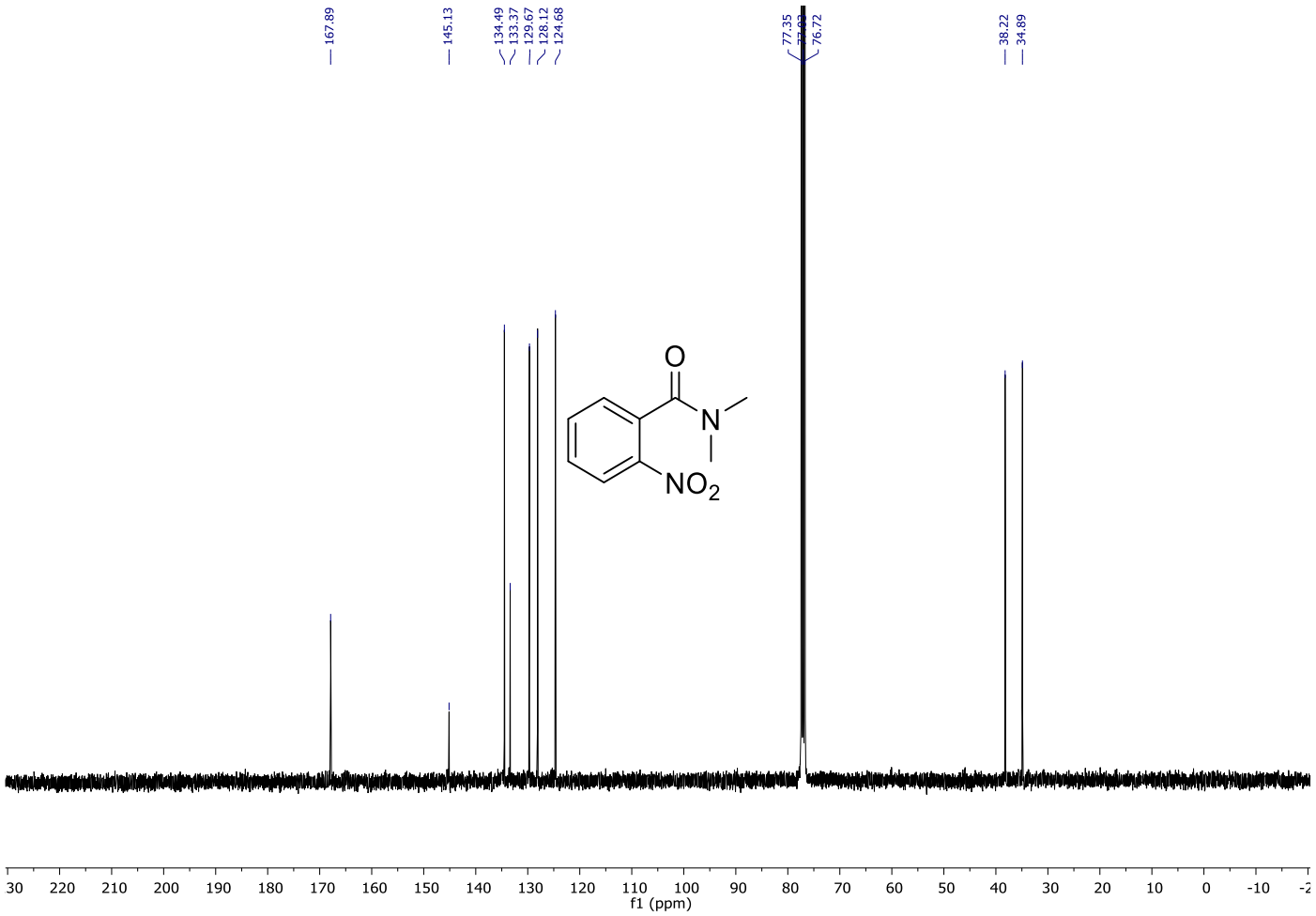
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **1o**.



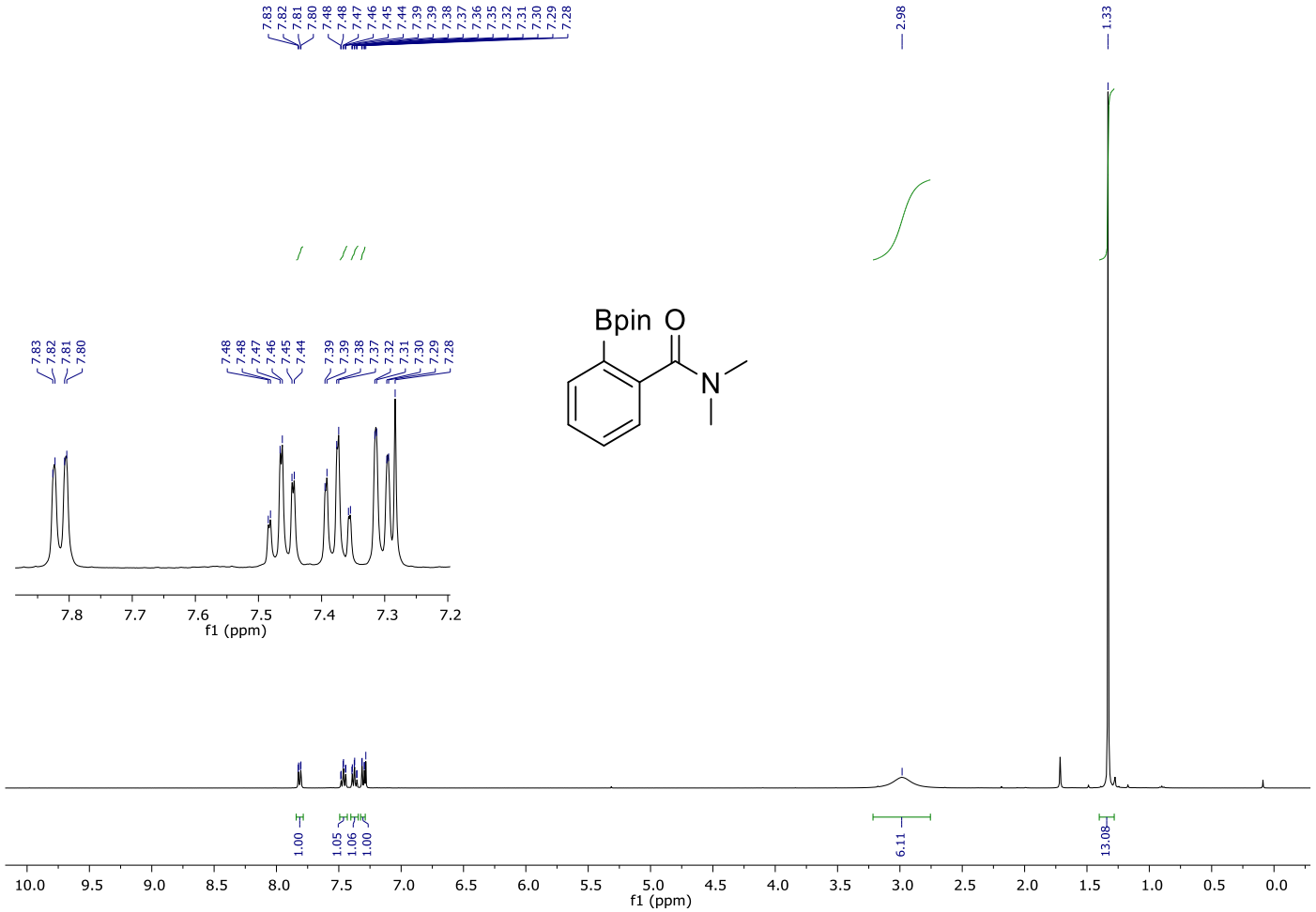
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **1o**.



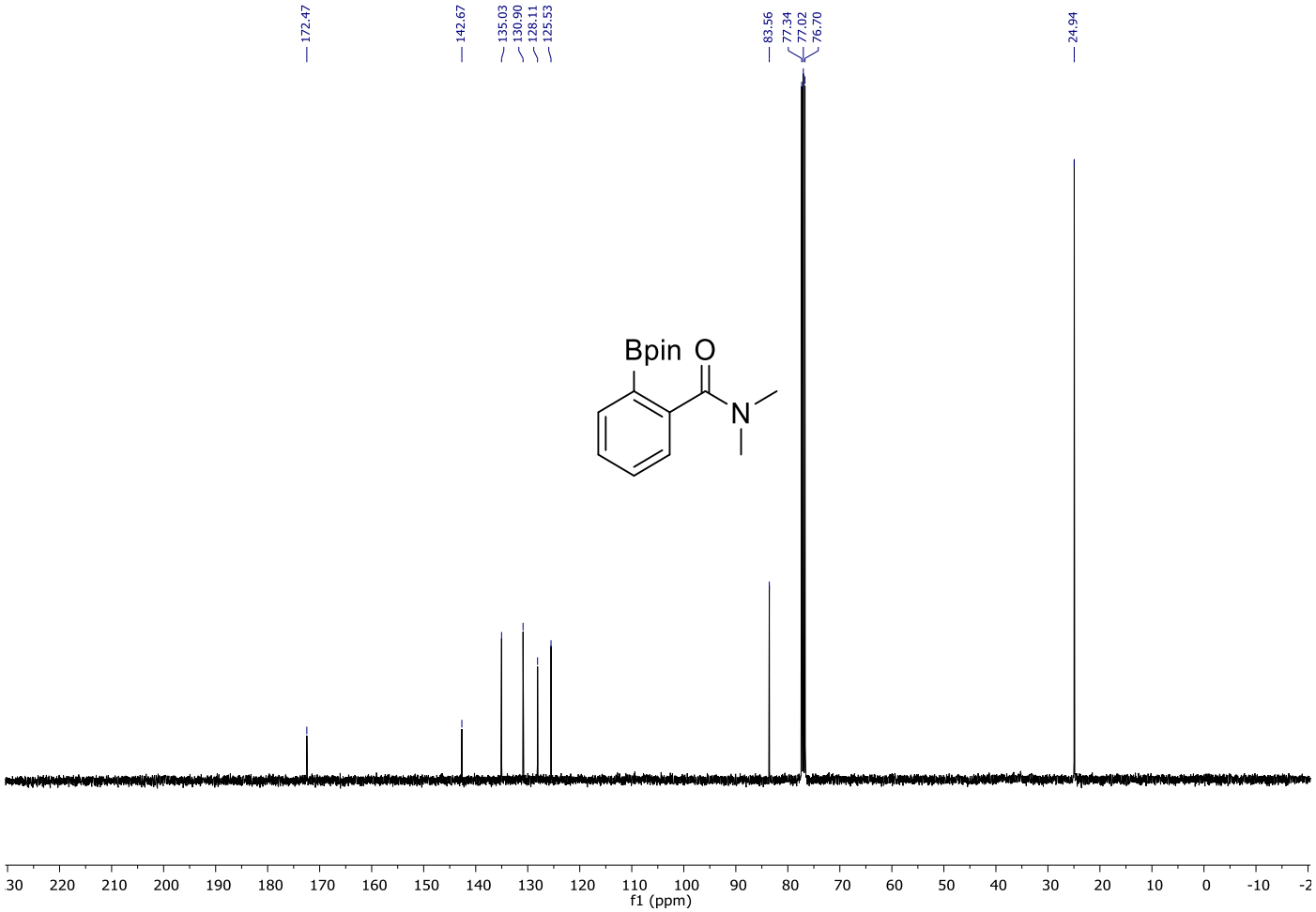
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **1p**.



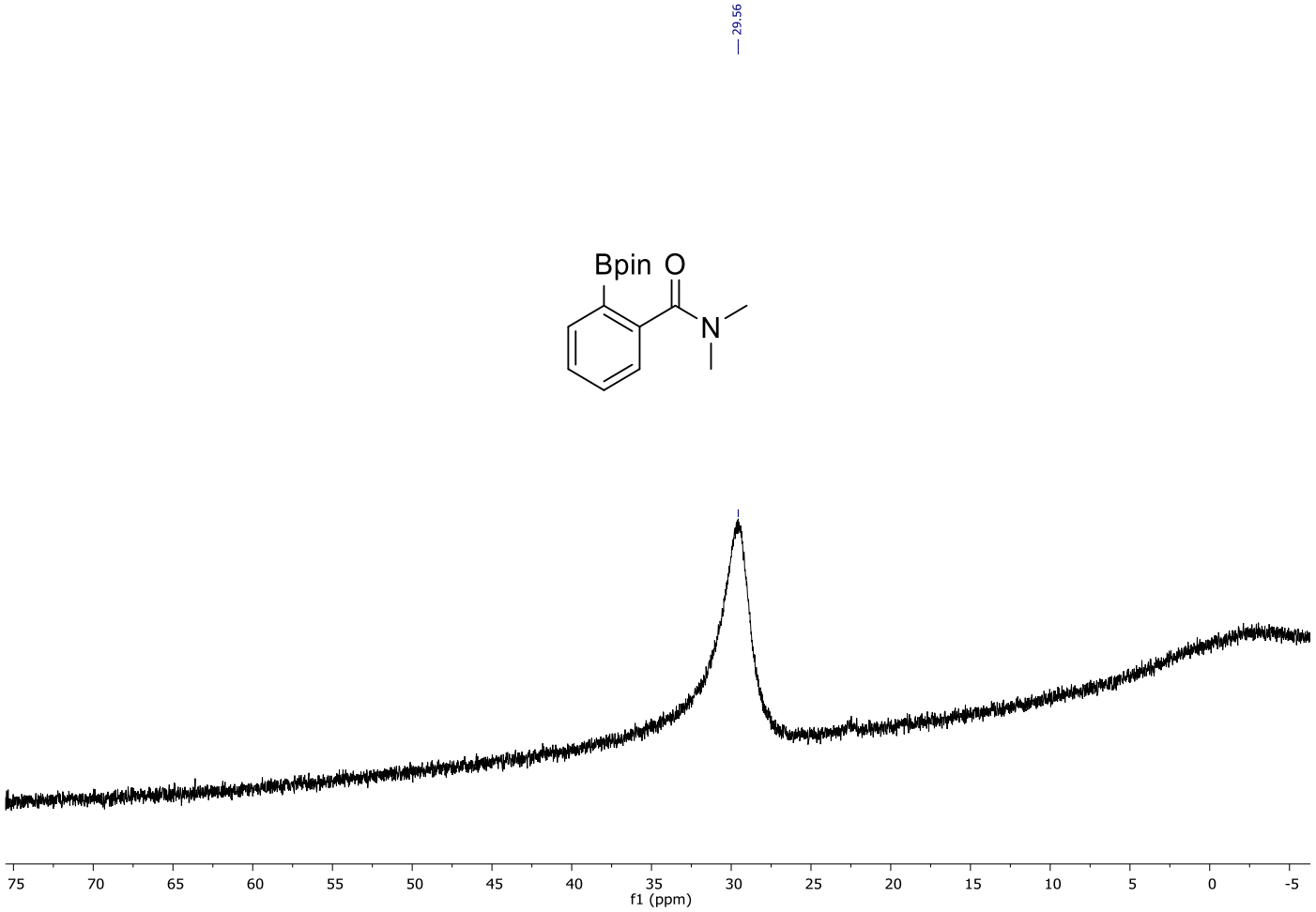
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **1p**.



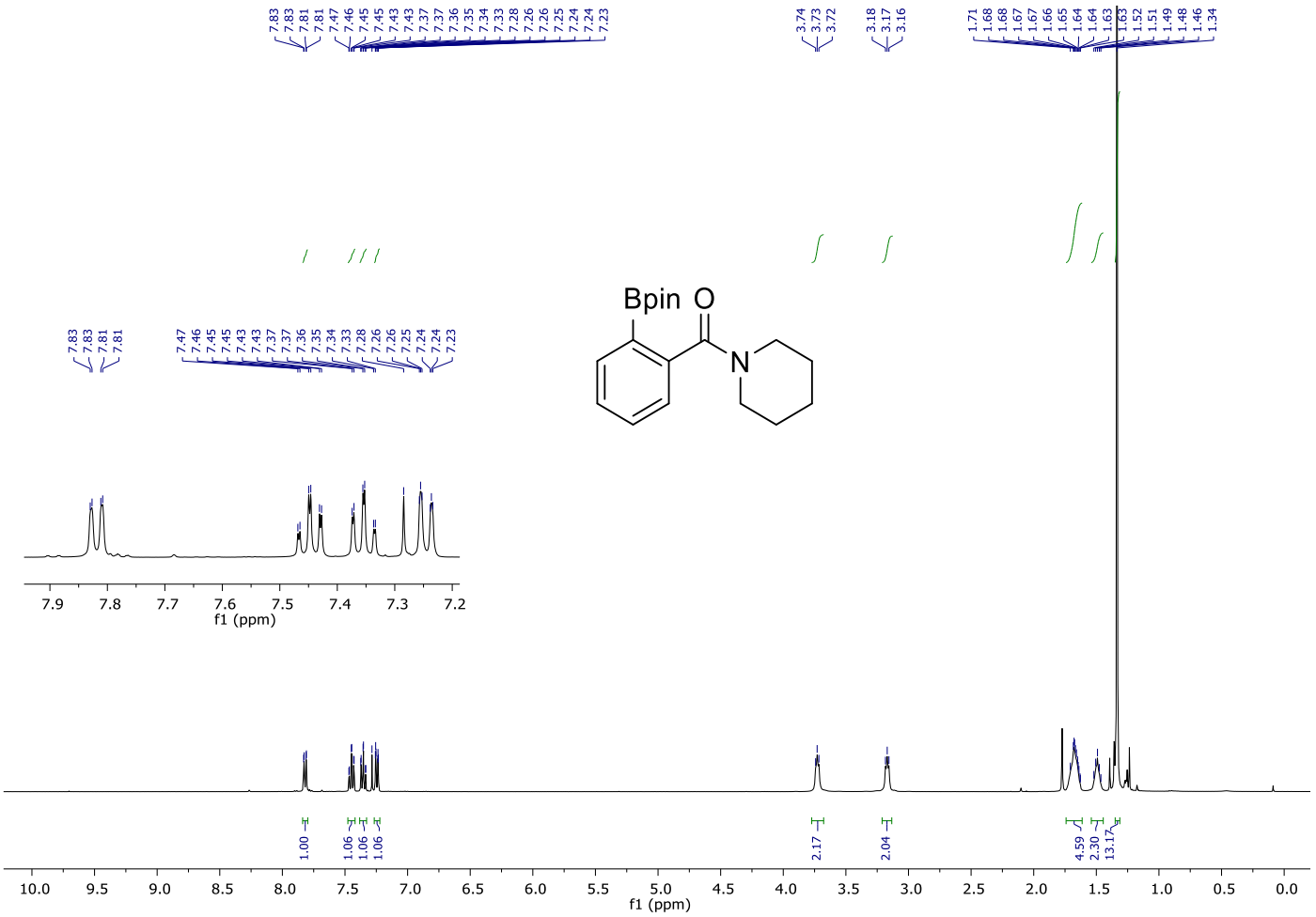
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2a**.



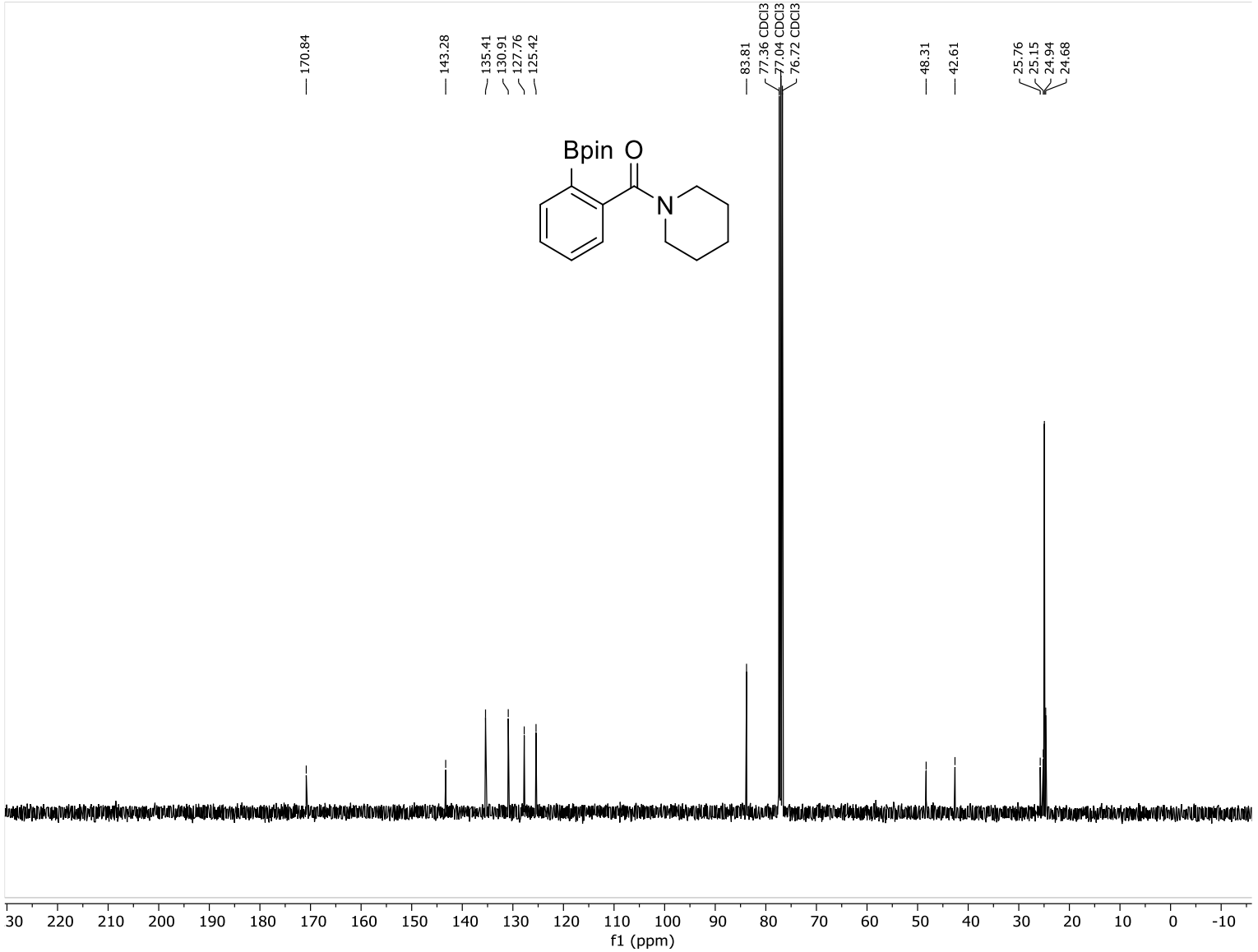
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2a**.



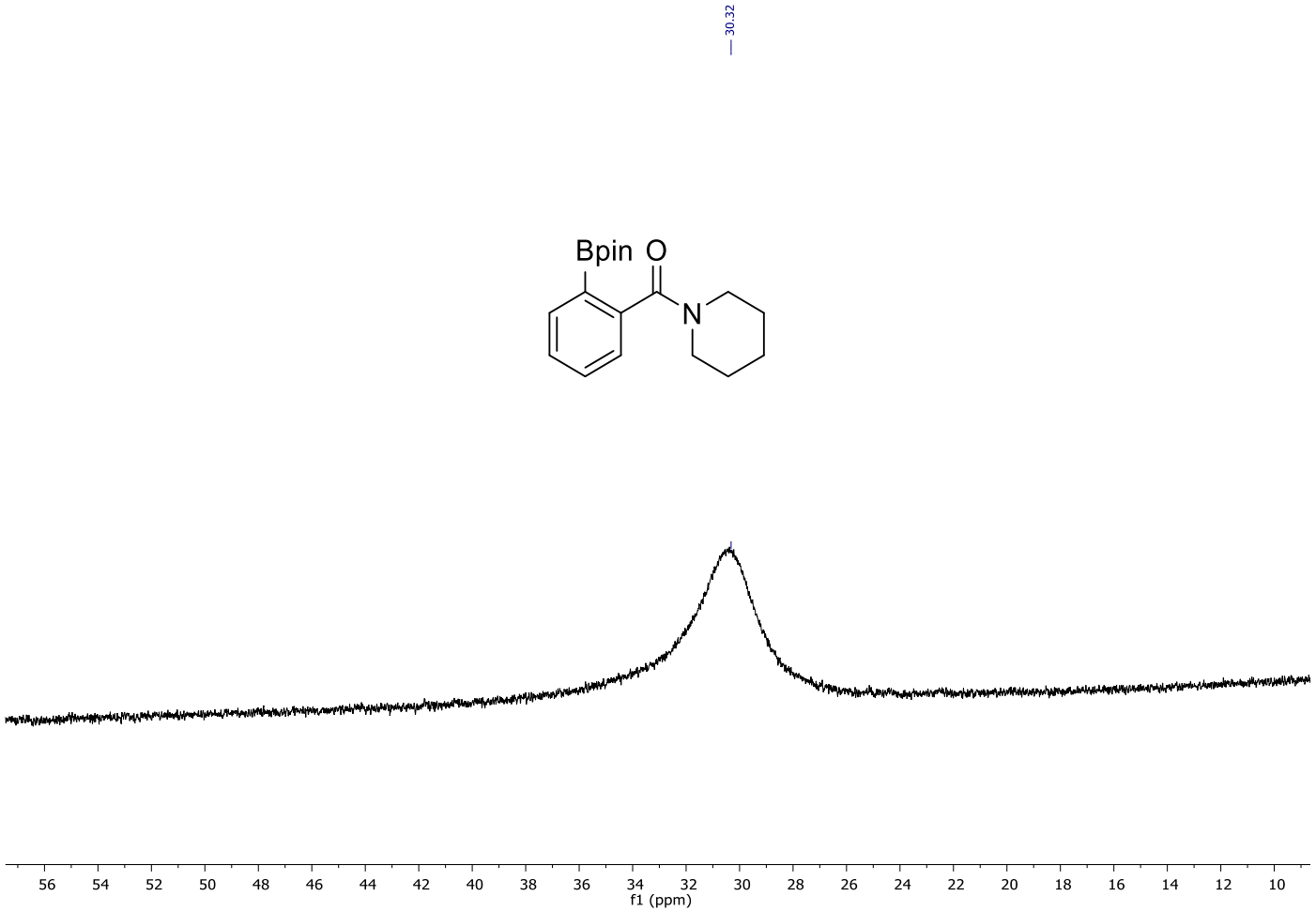
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2a**.



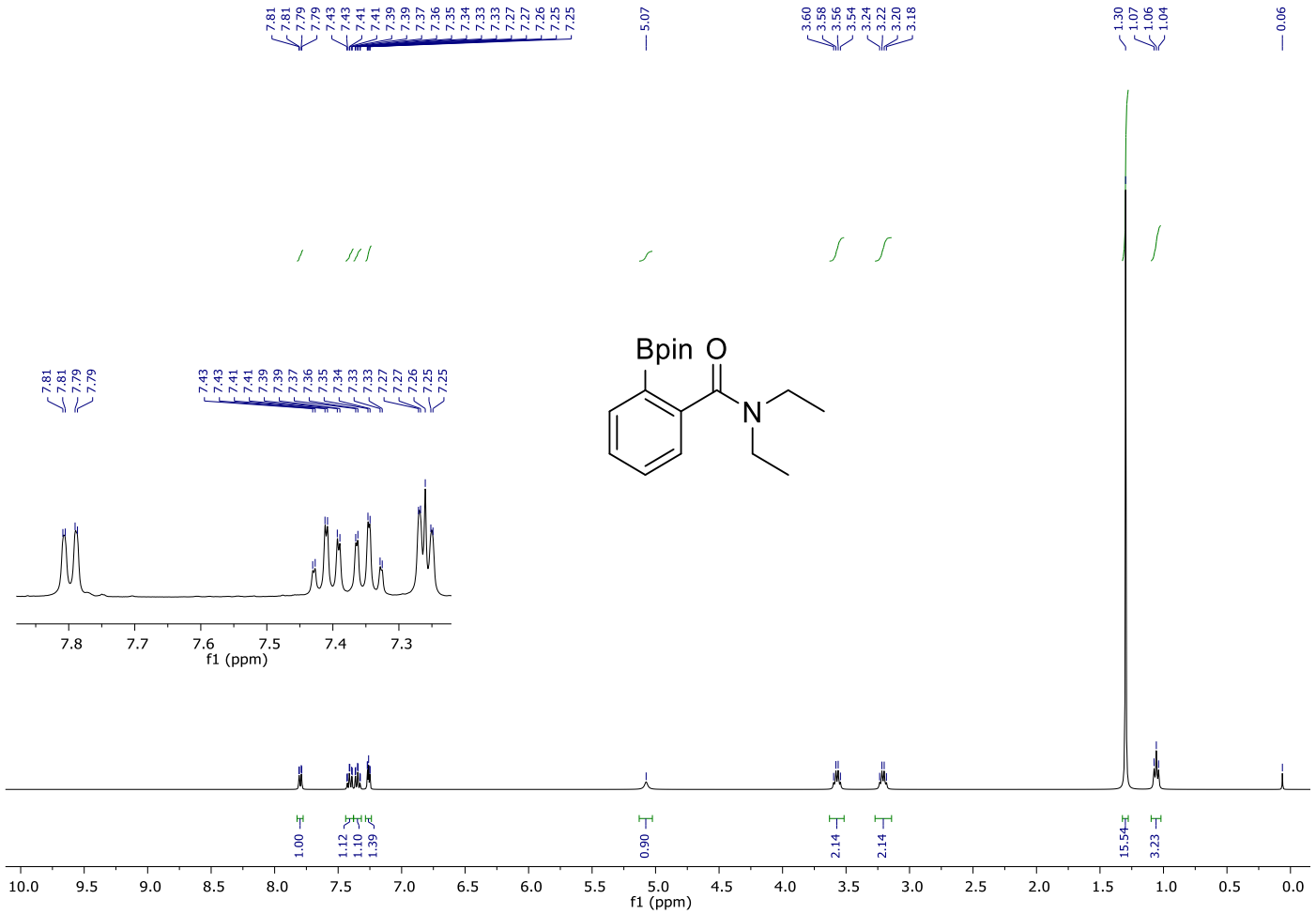
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2b**.



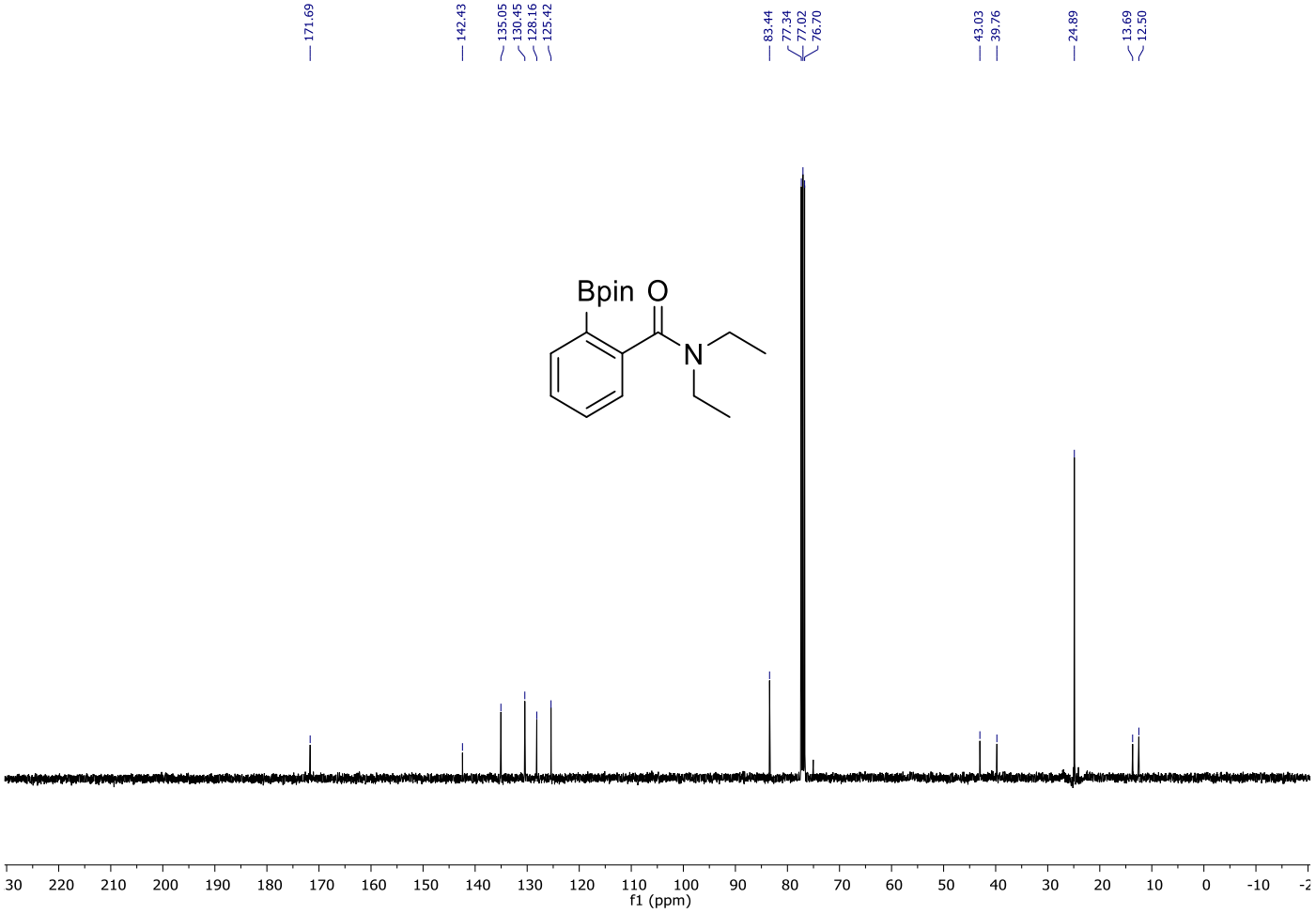
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2b**.



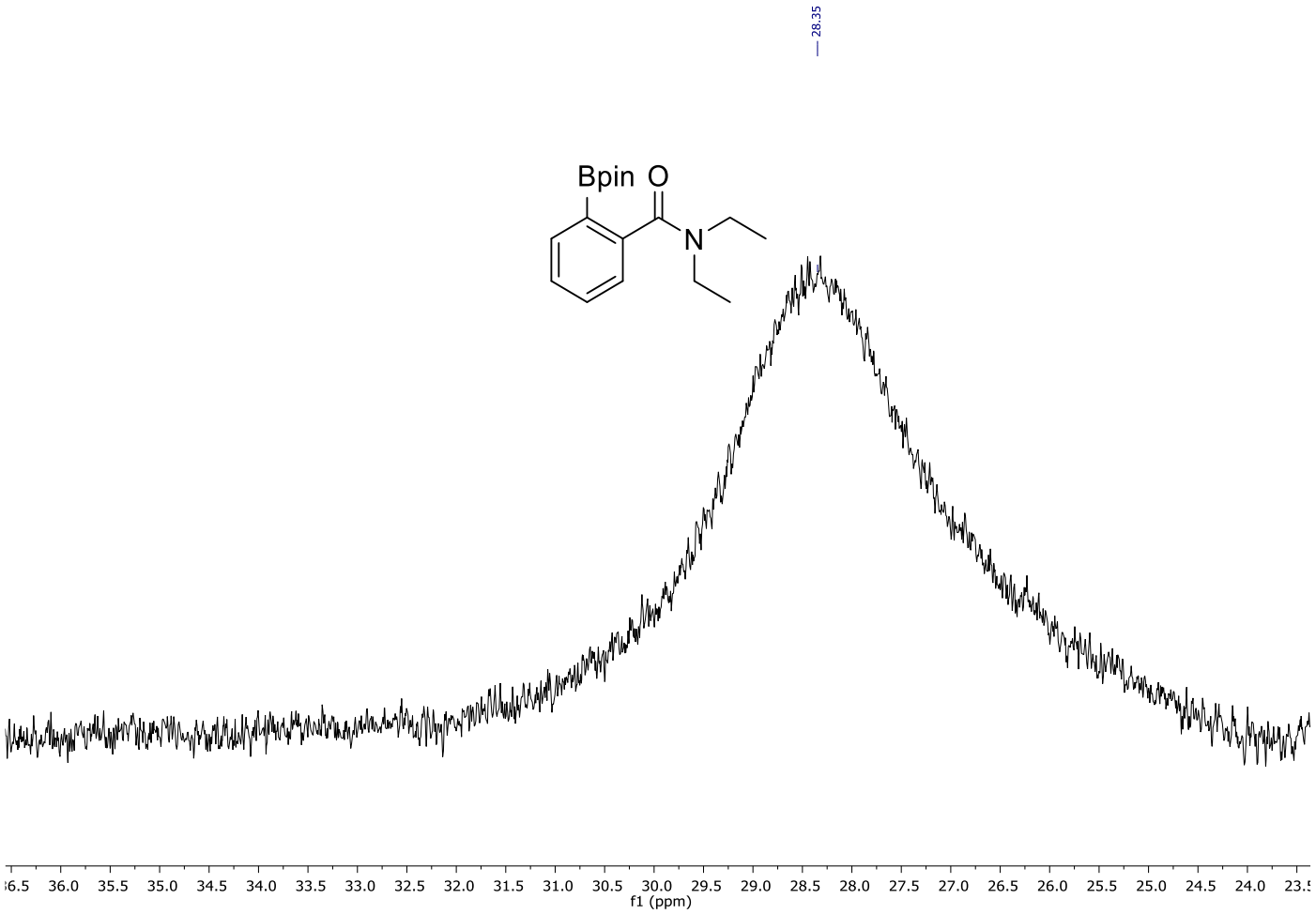
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2b**.



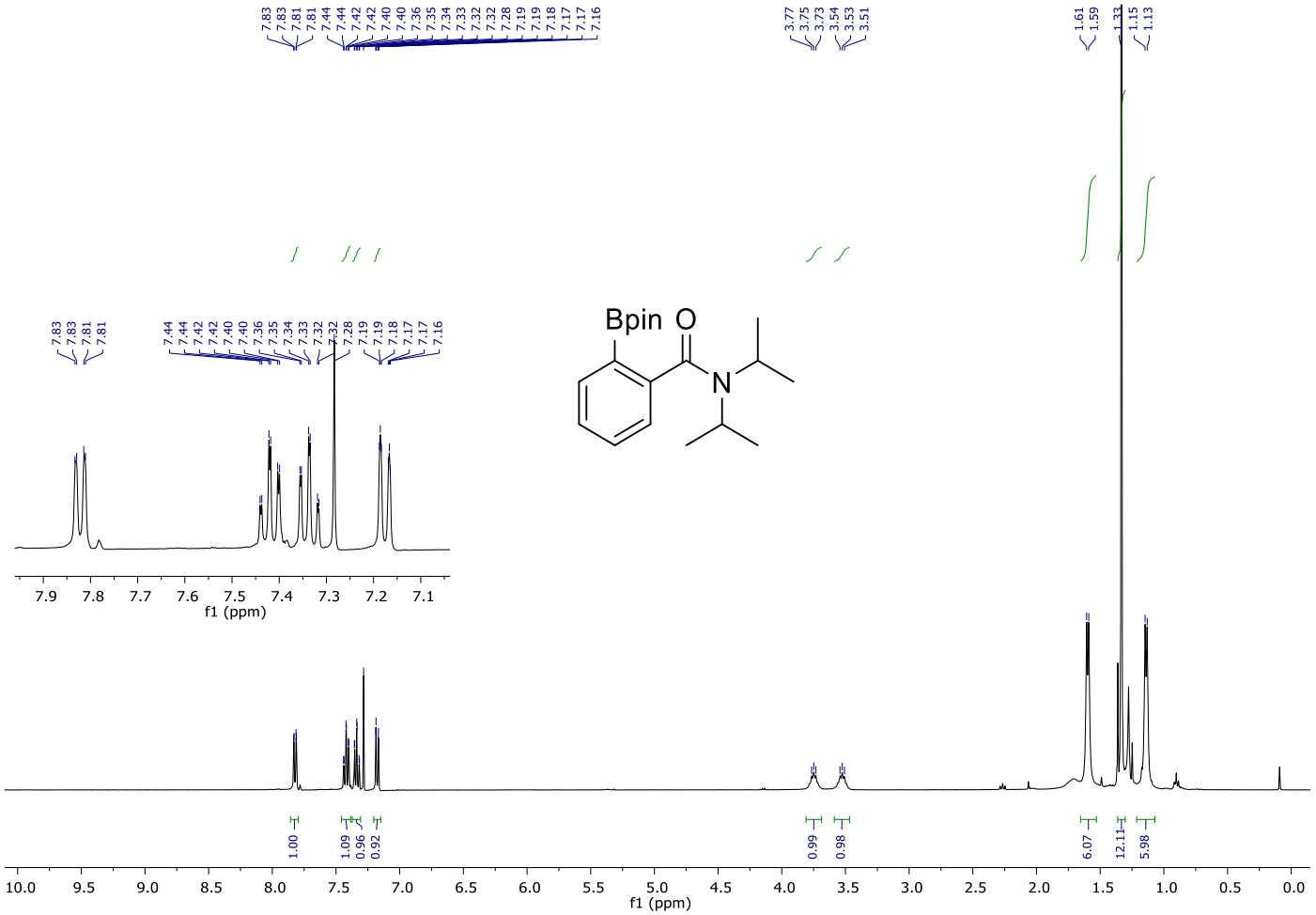
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2c**.



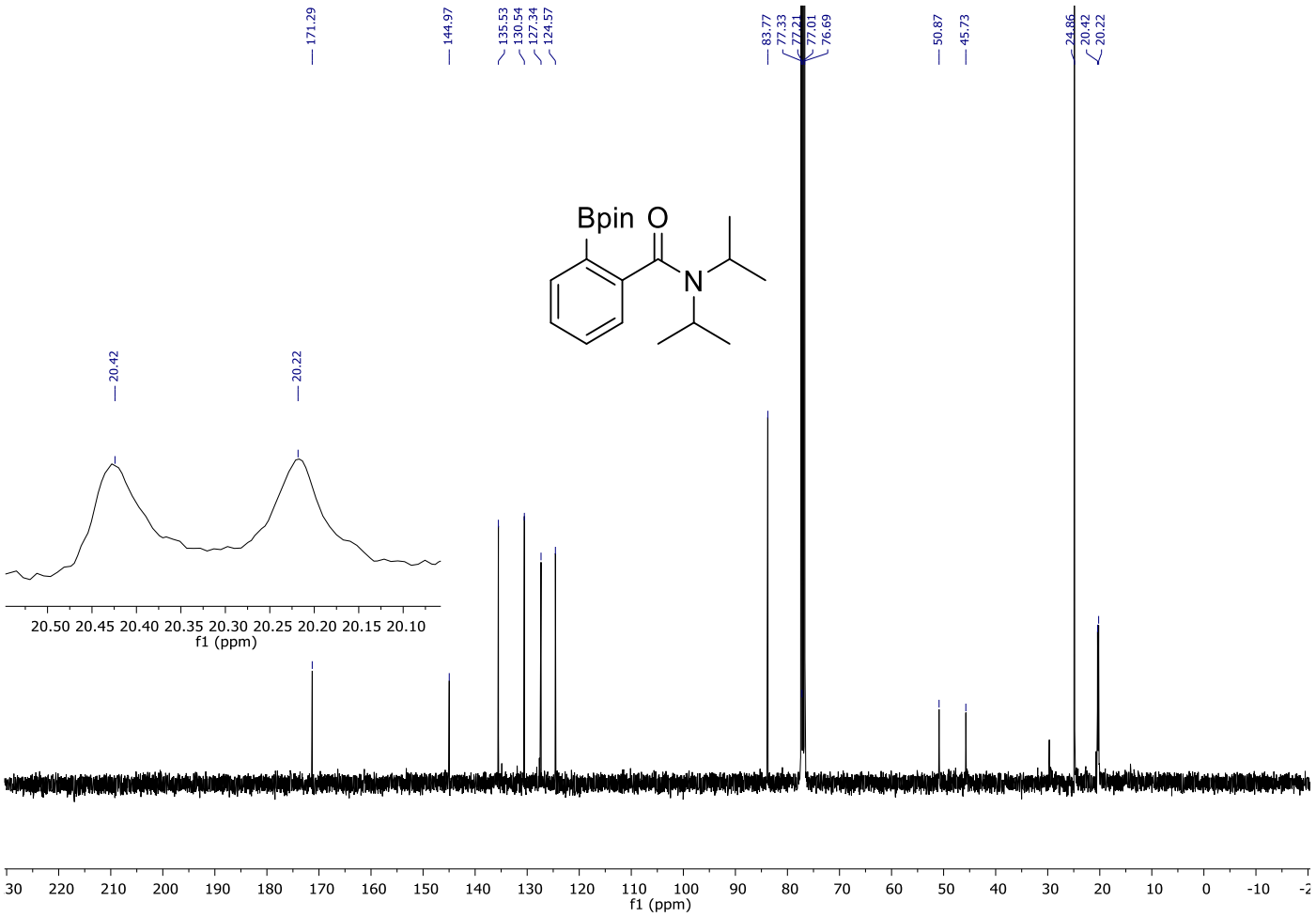
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2c**.



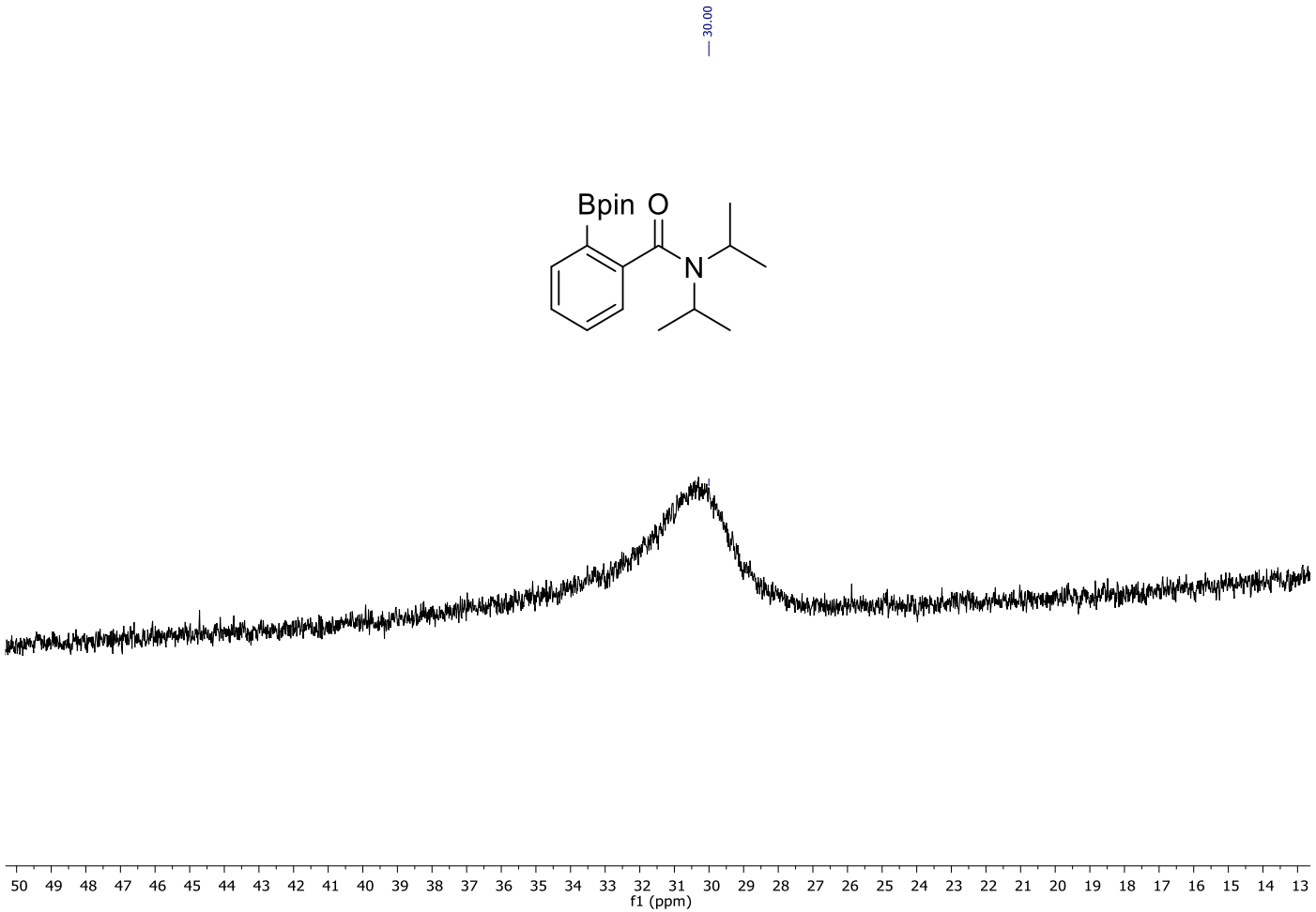
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2c**.



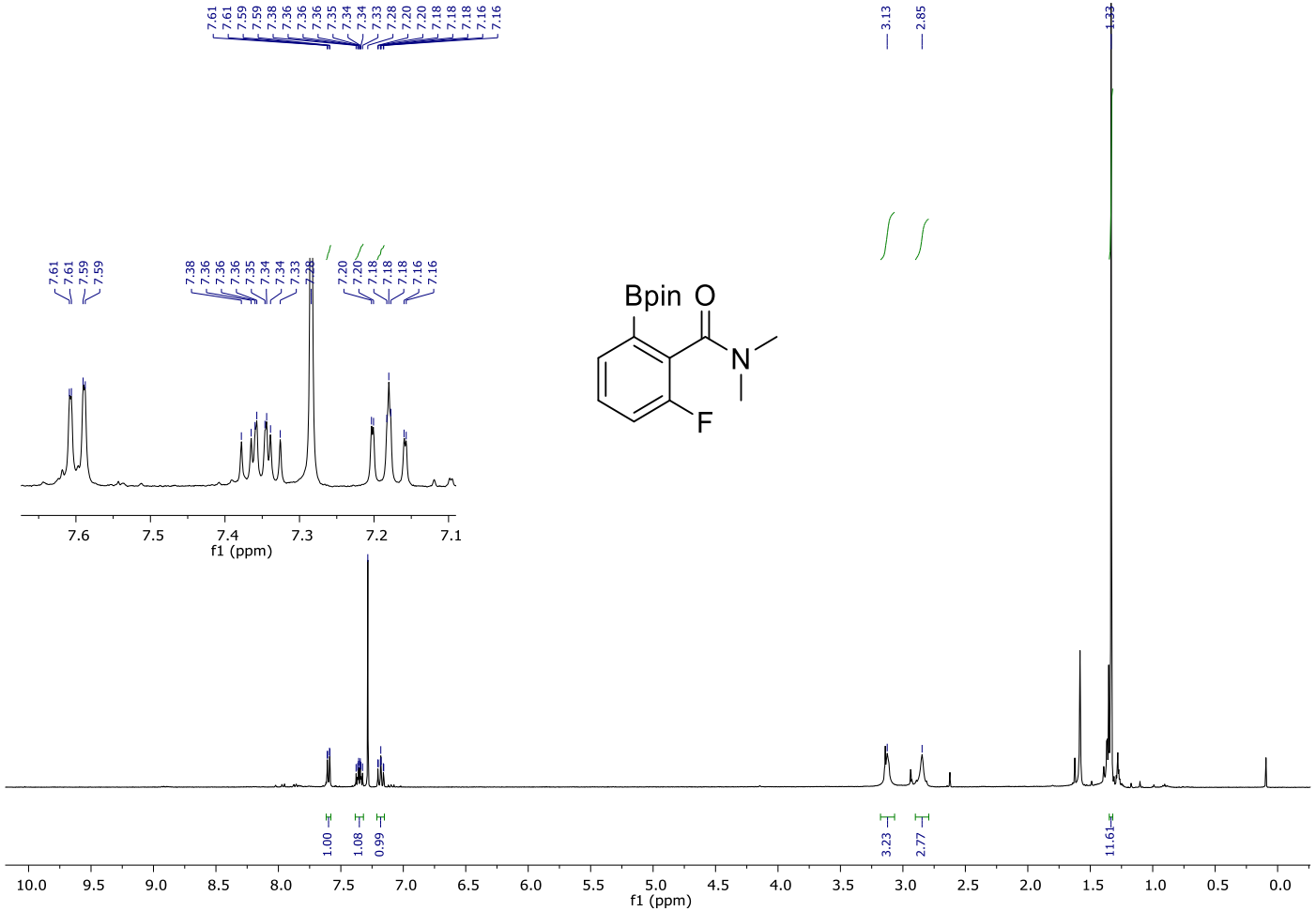
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2d**.



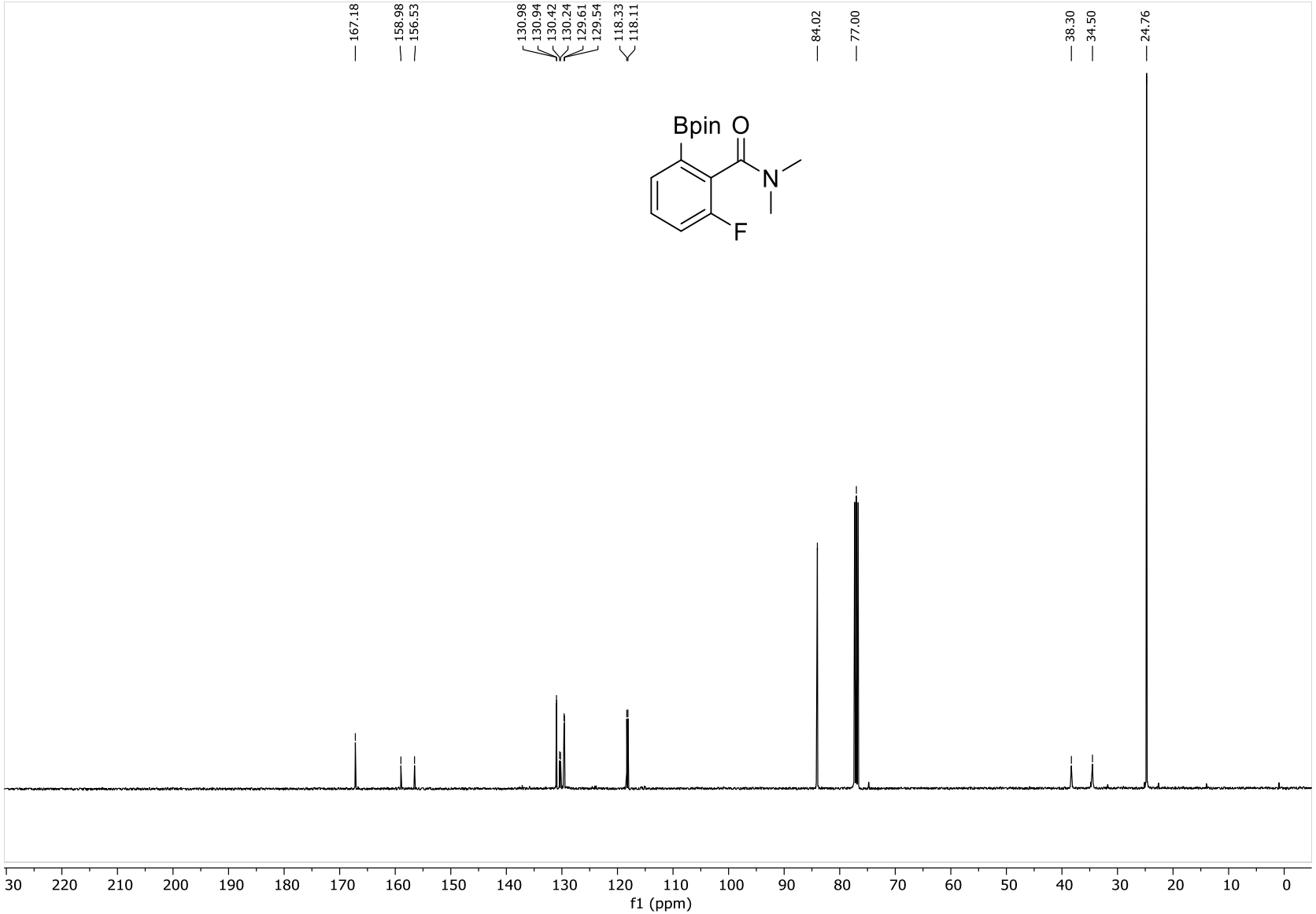
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2d**.



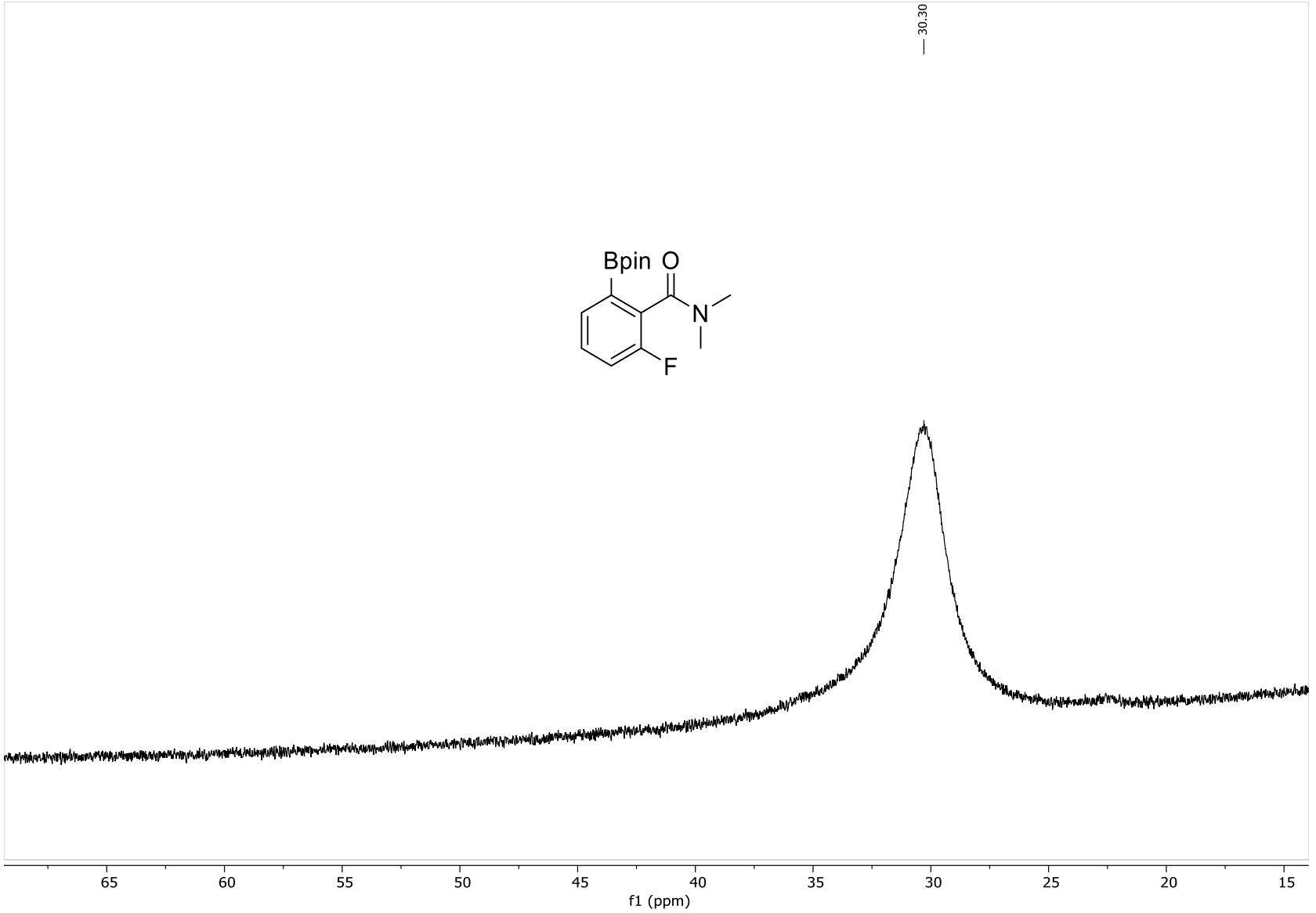
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2d**.



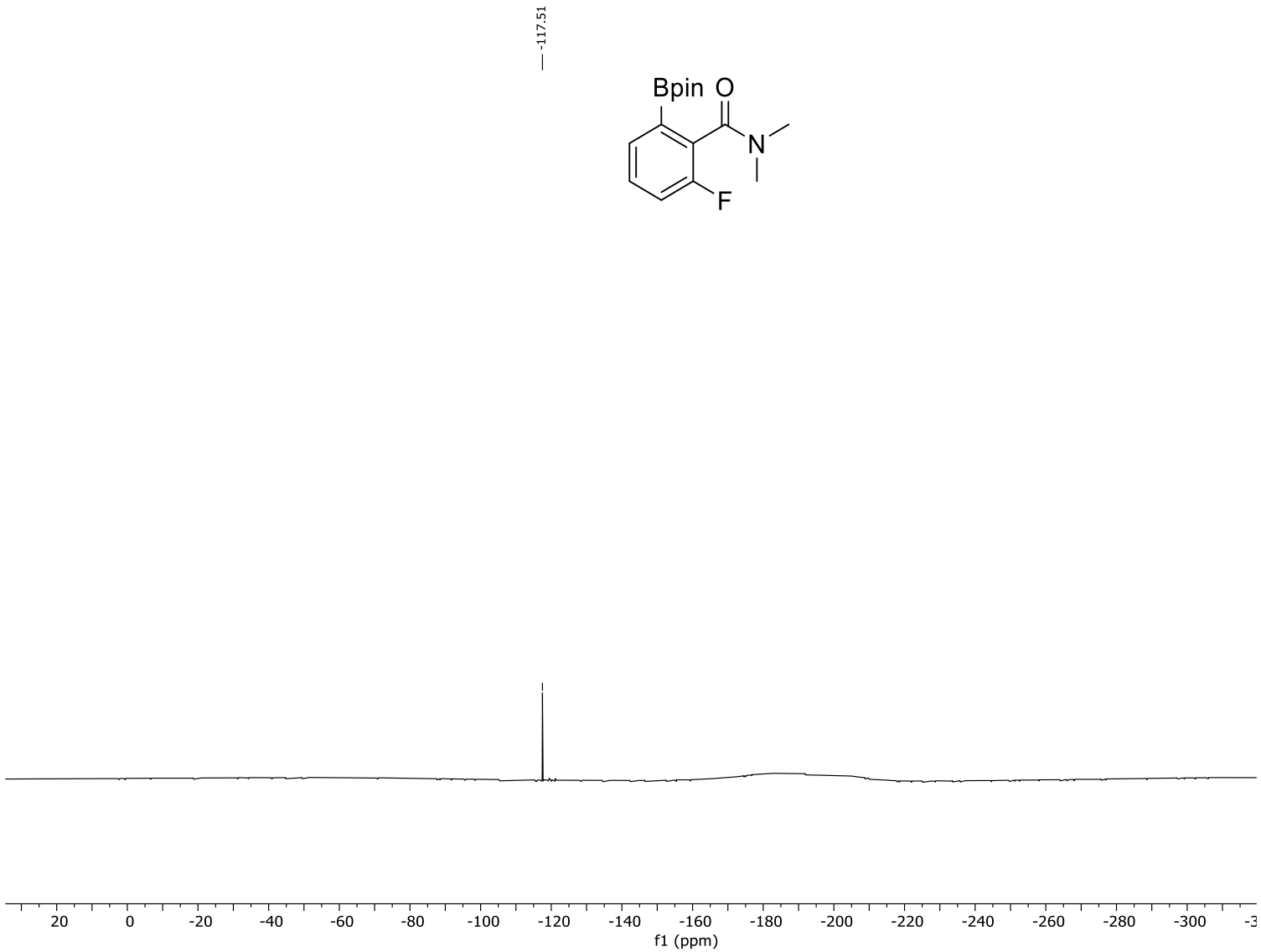
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2f**.



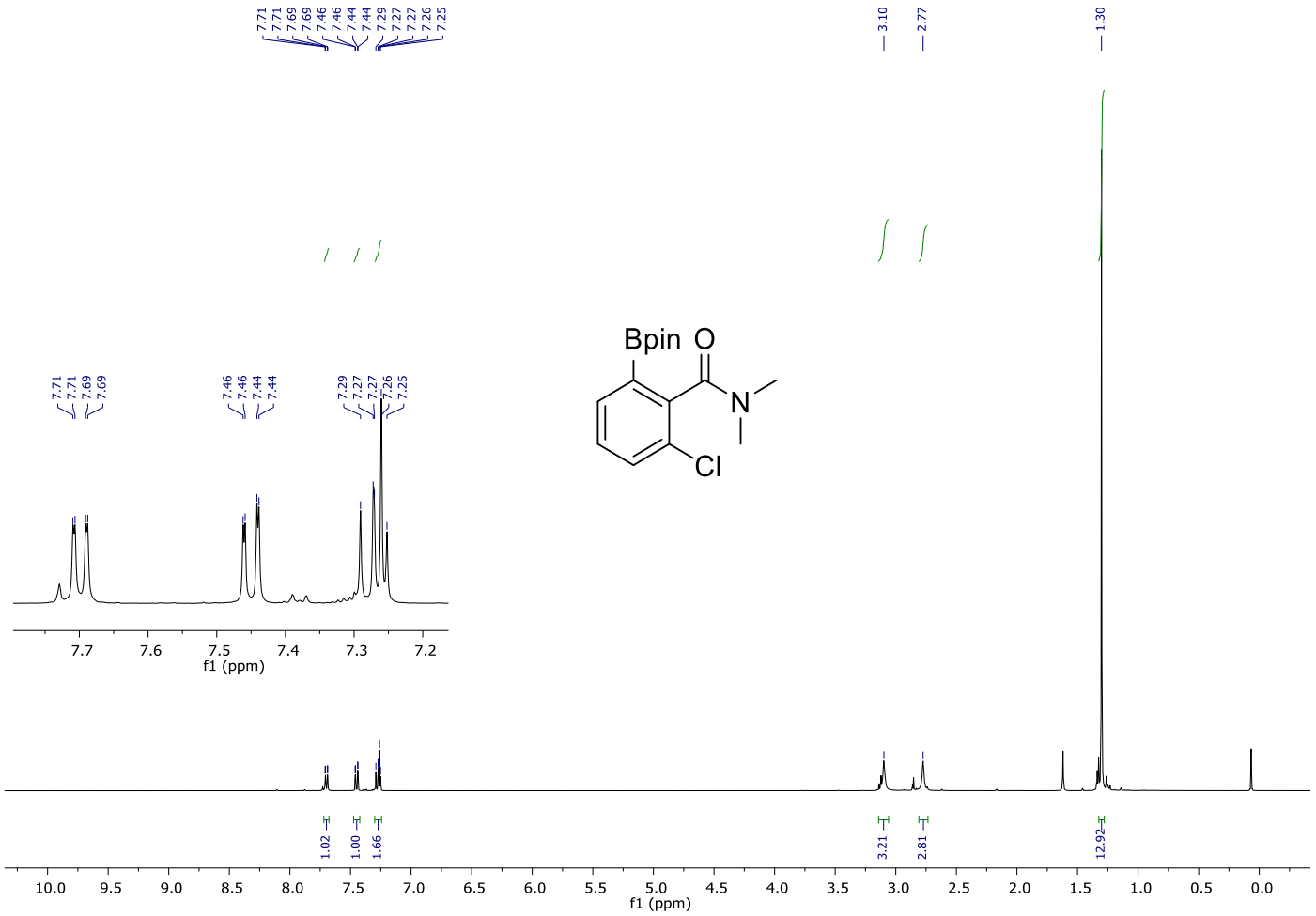
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2f**.



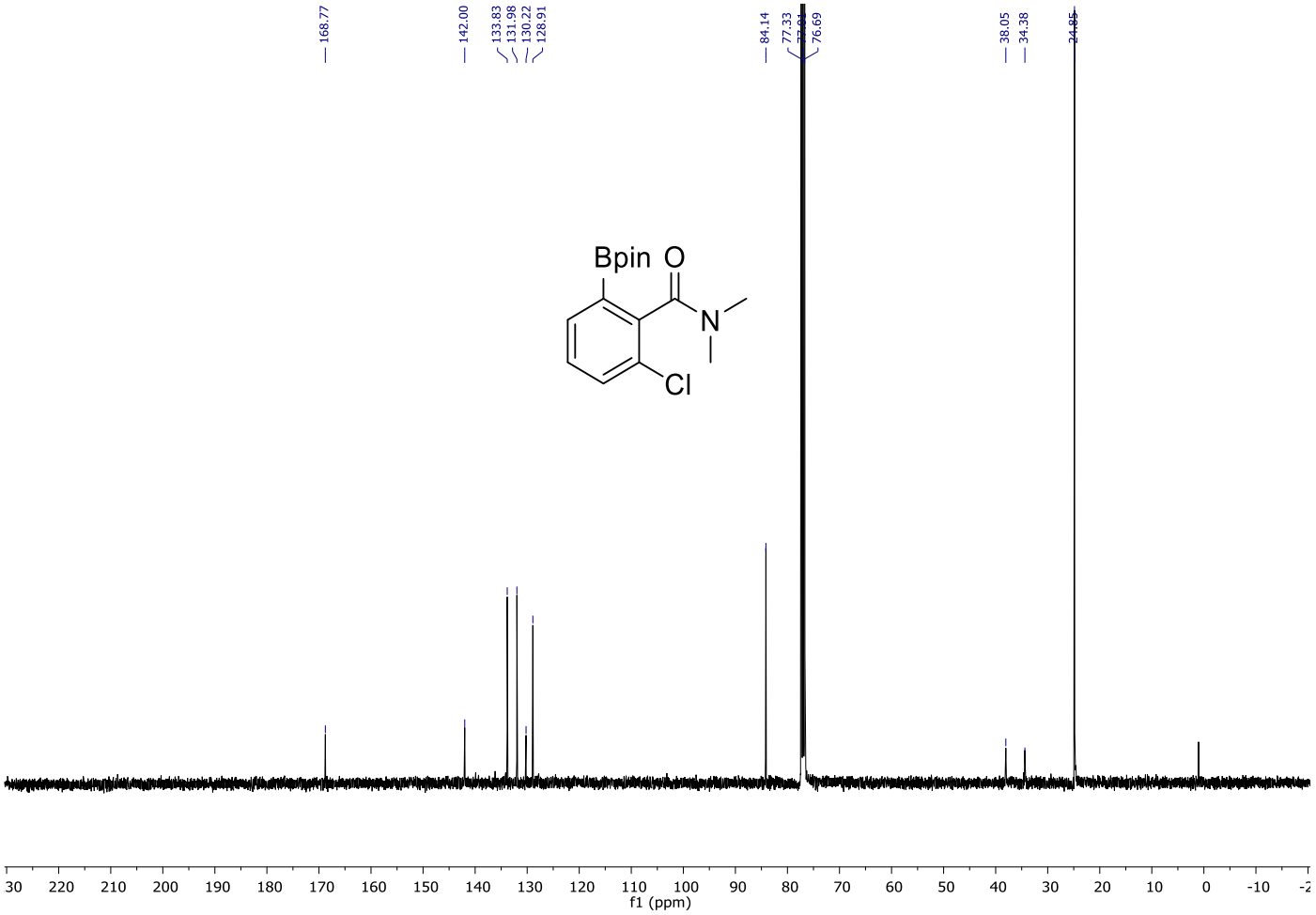
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2f**.



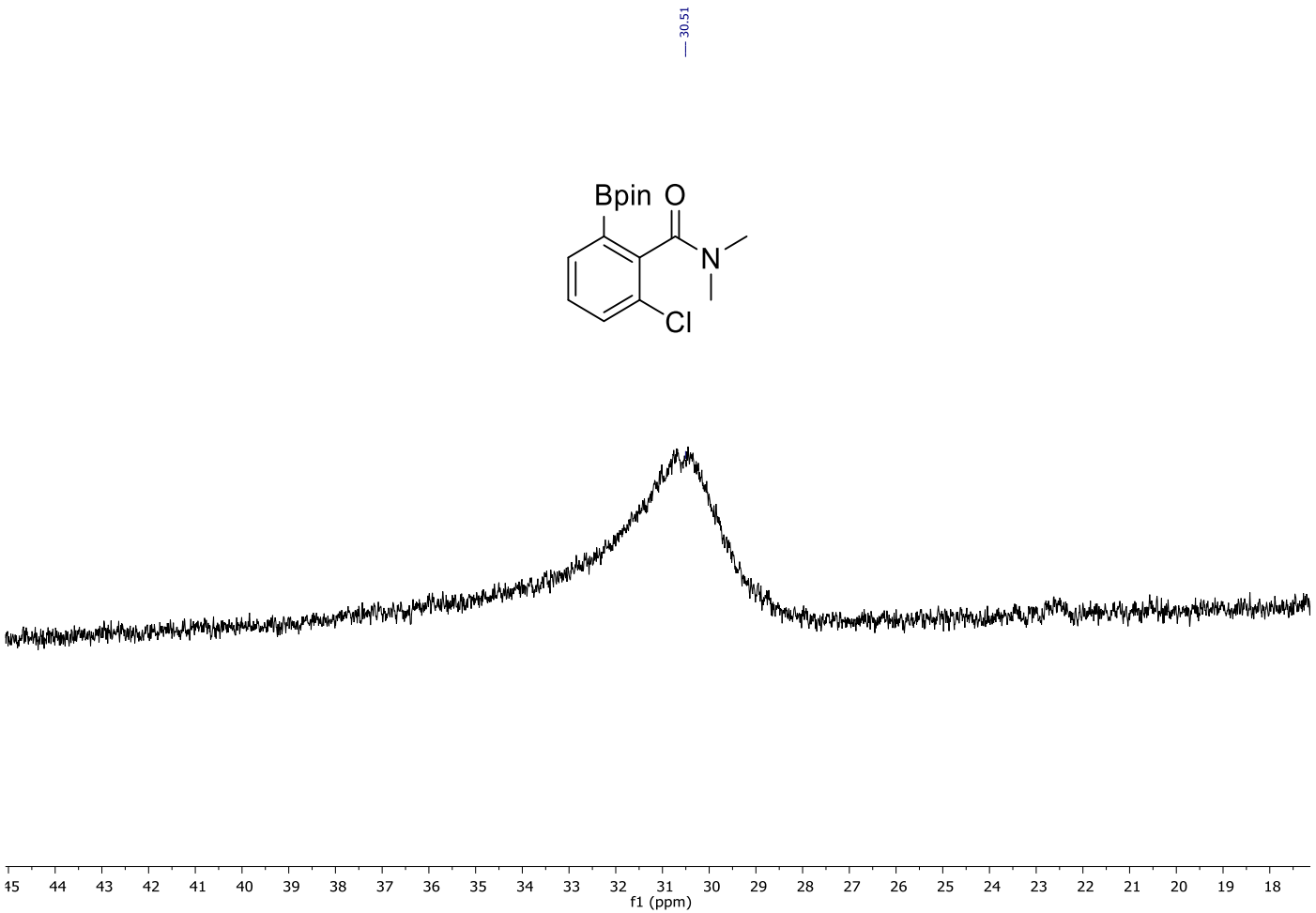
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376 MHz) spectrum spectrum of **2f**.



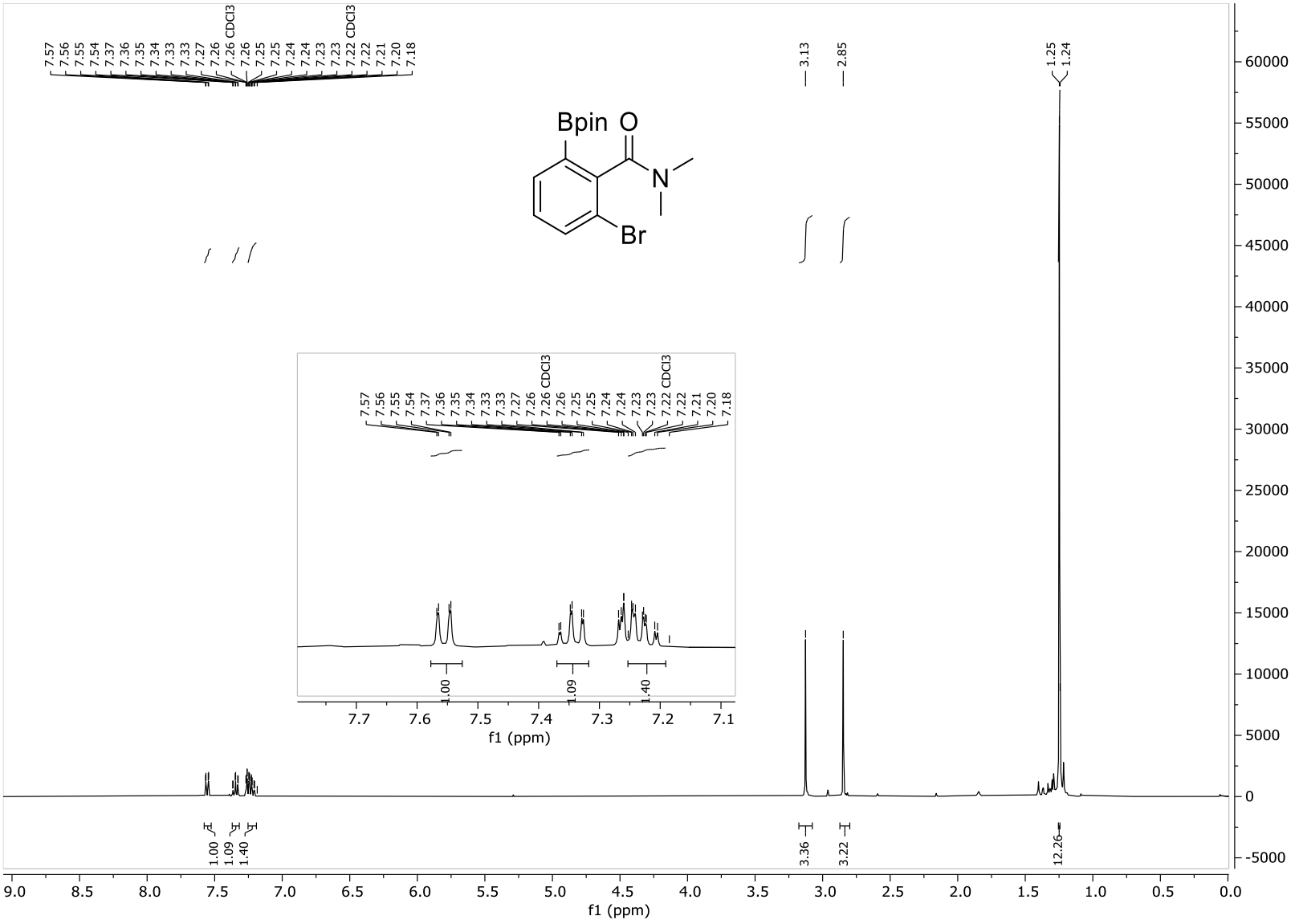
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2g**.



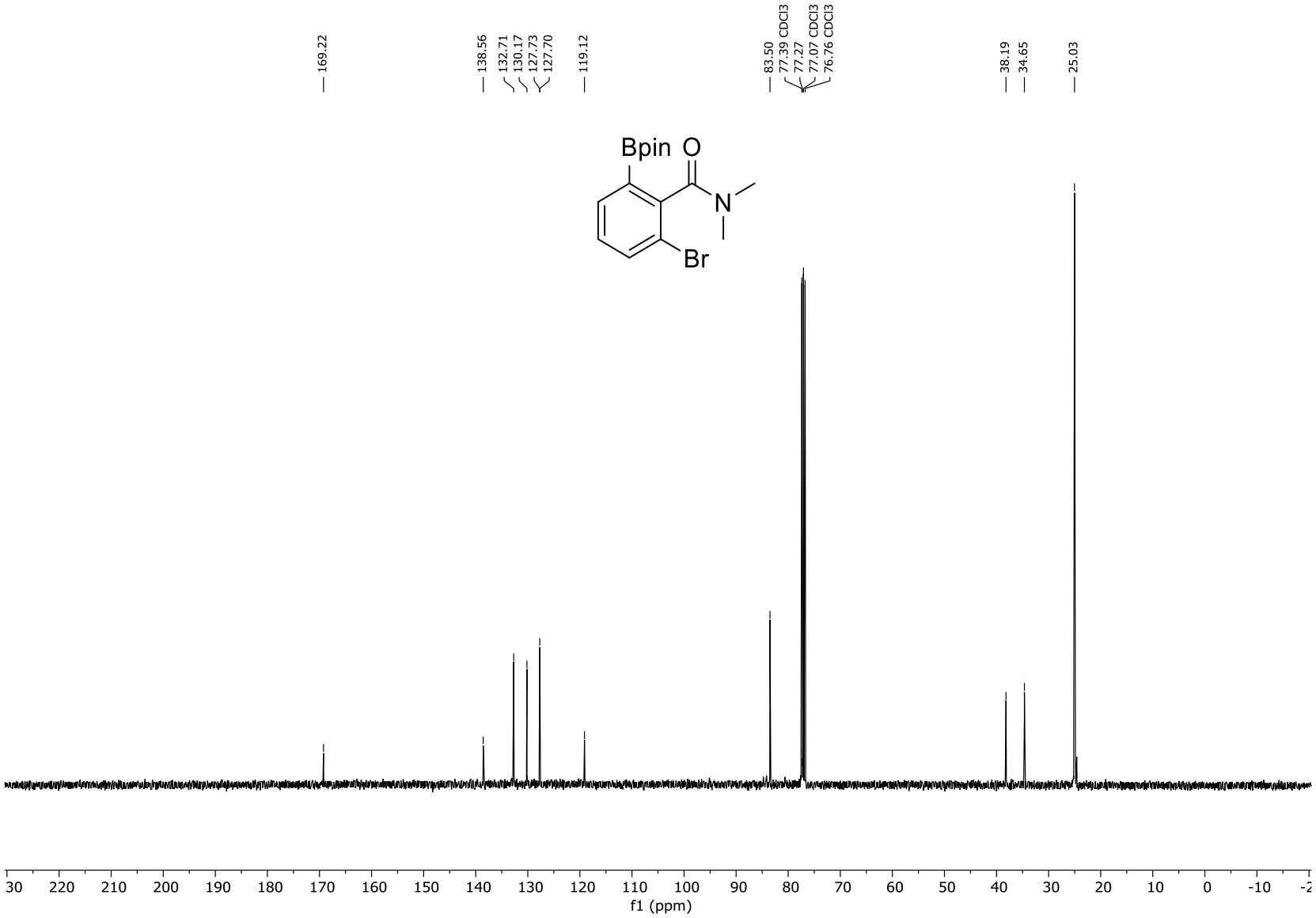
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2g**.



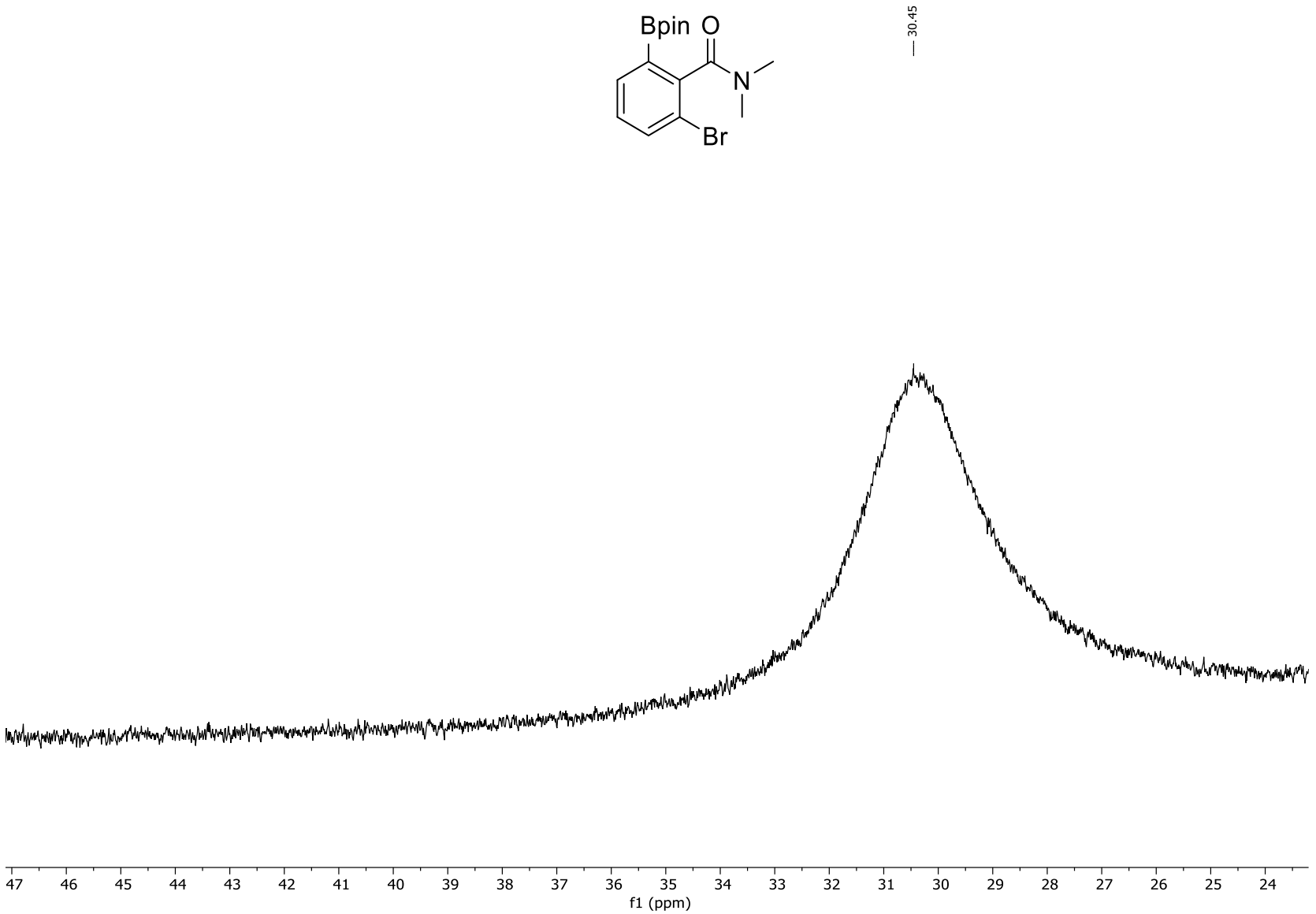
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2g**.



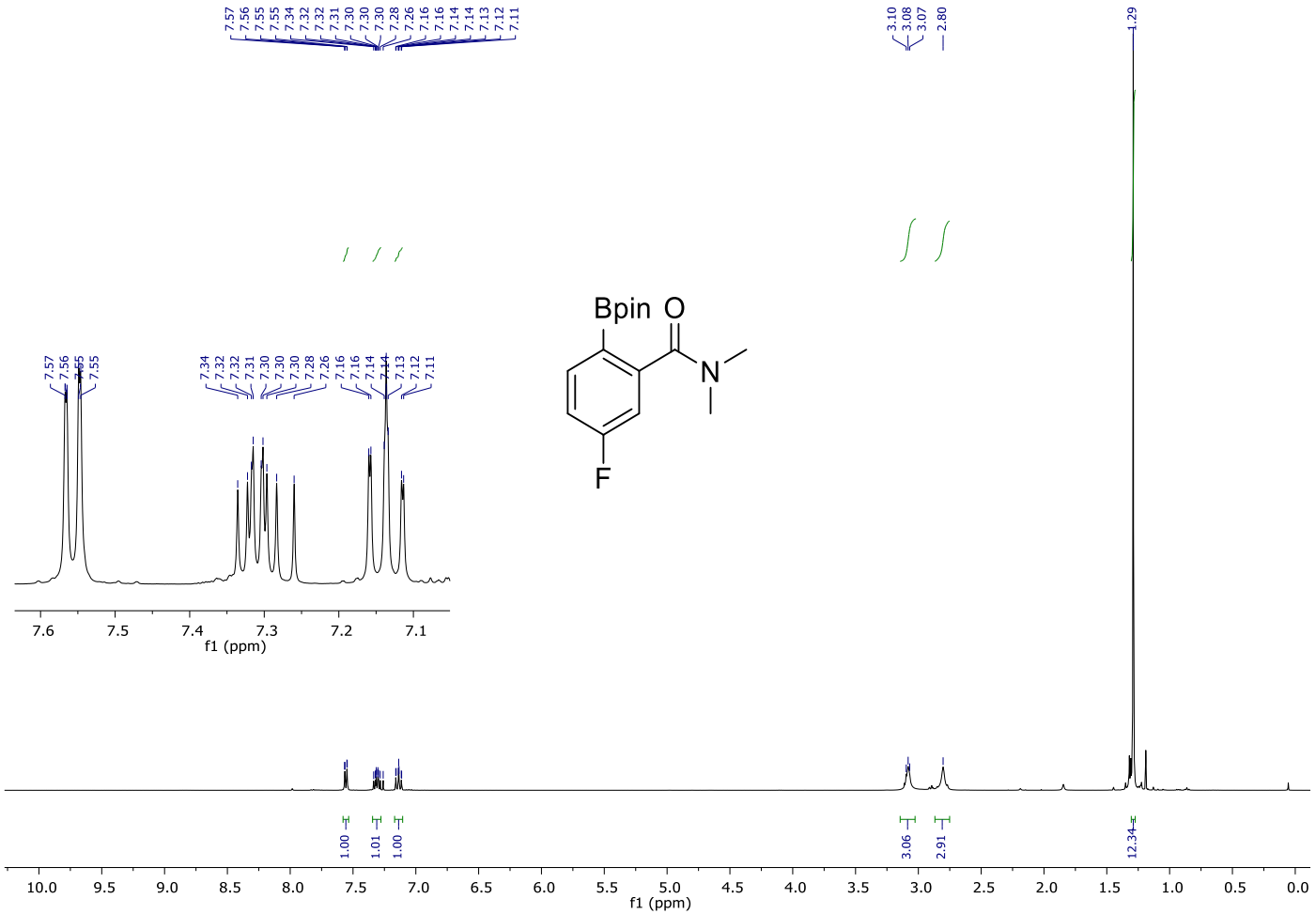
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2h**.



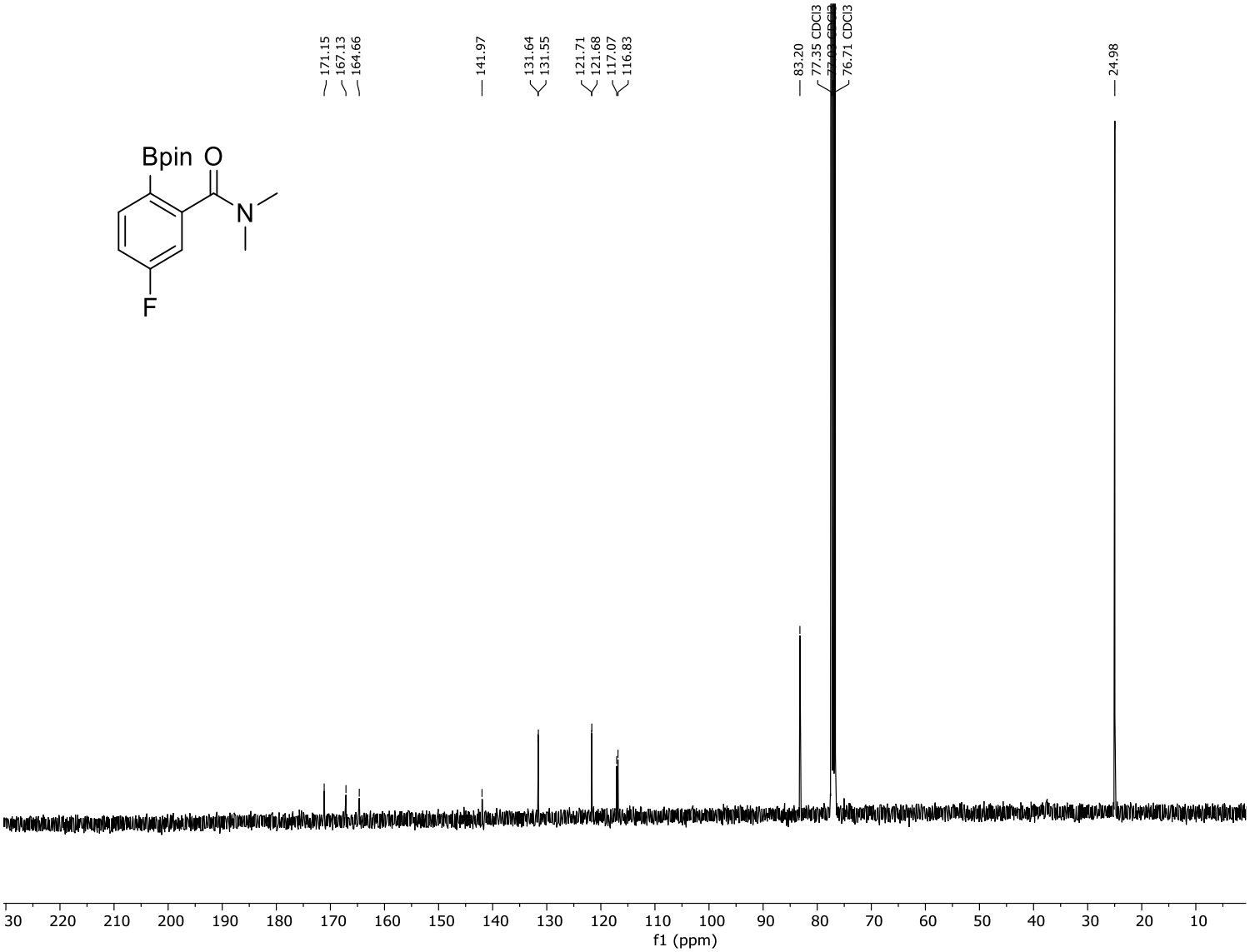
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2h**.



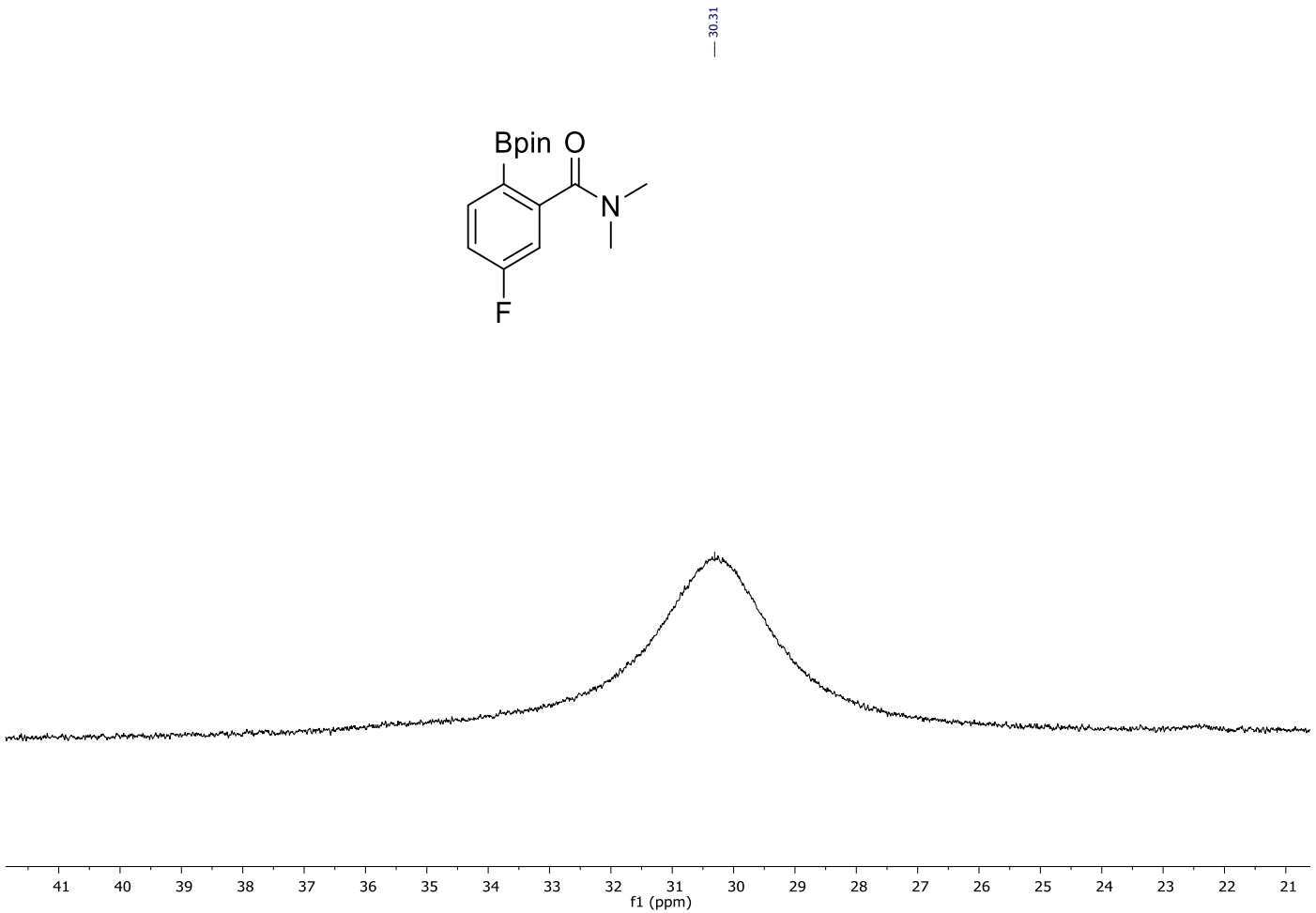
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2h**.



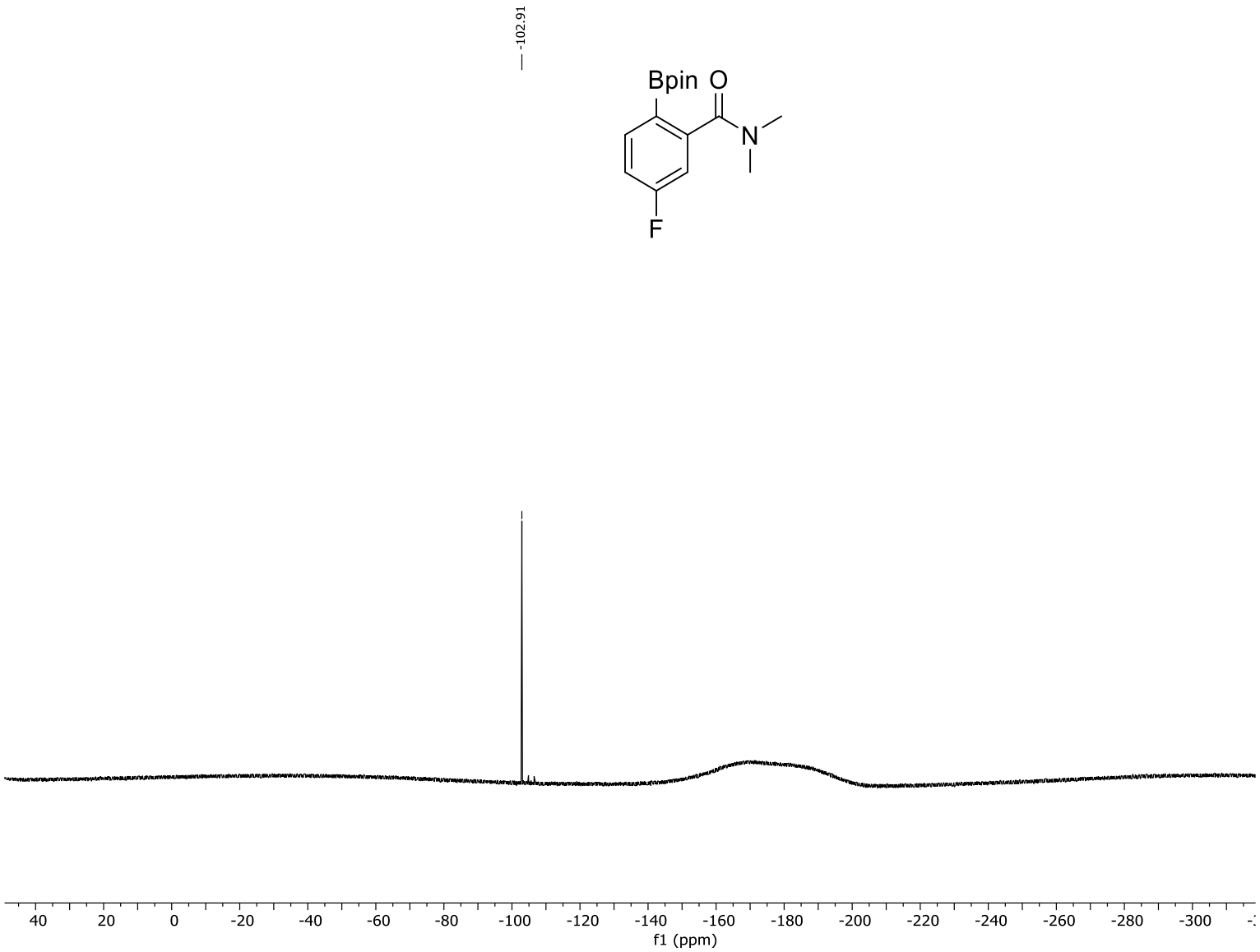
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2i**.



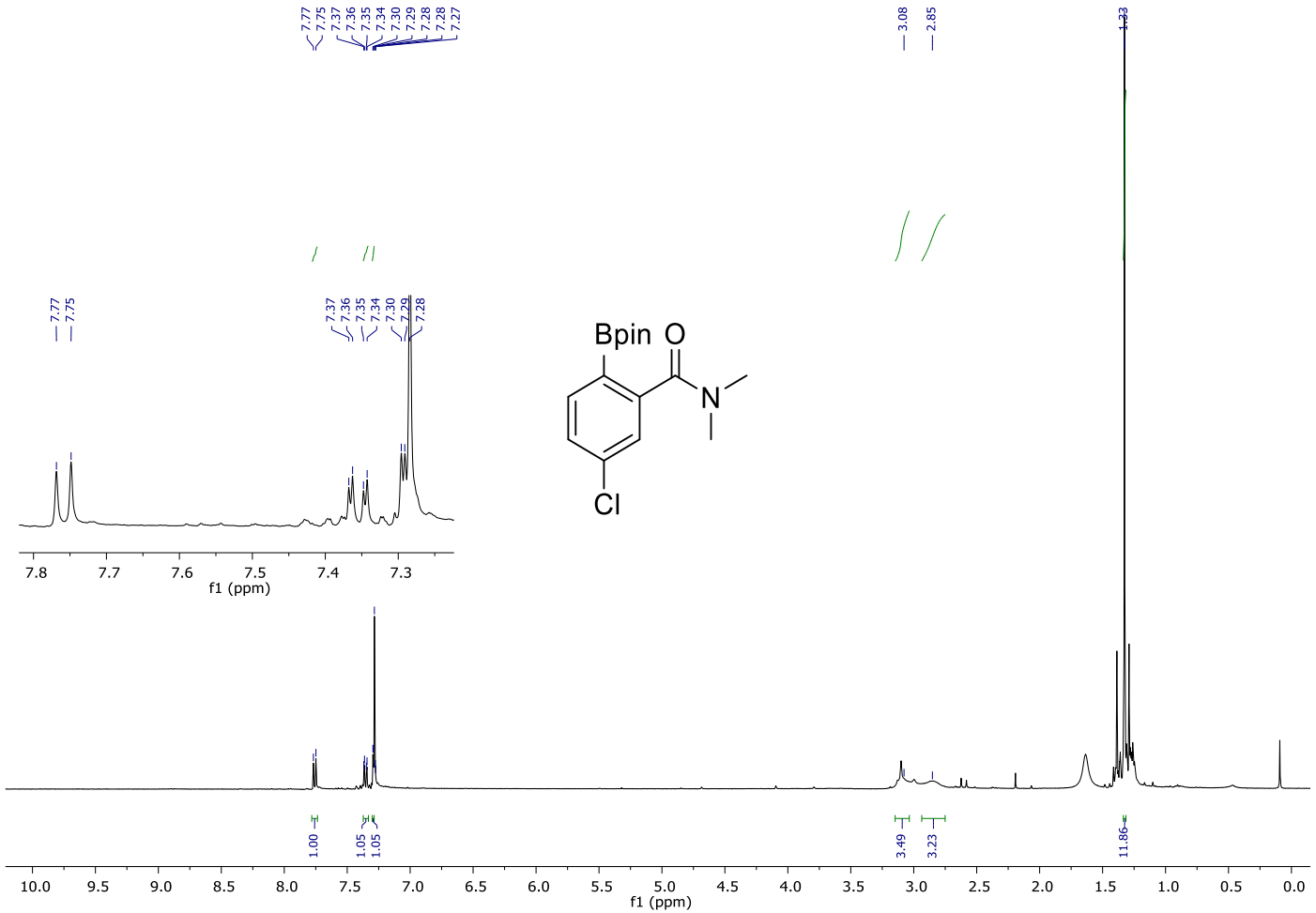
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2i**.



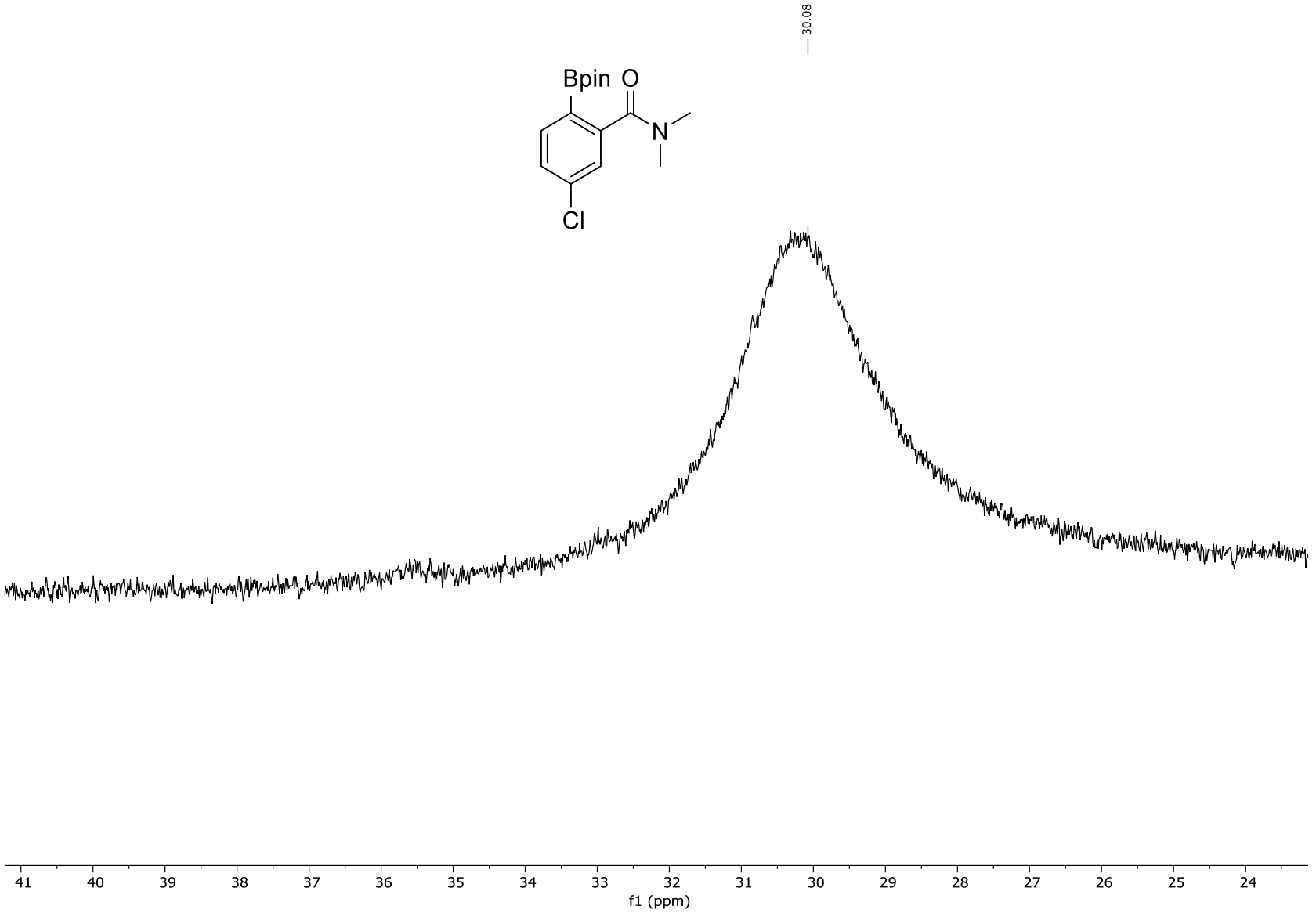
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2i**.



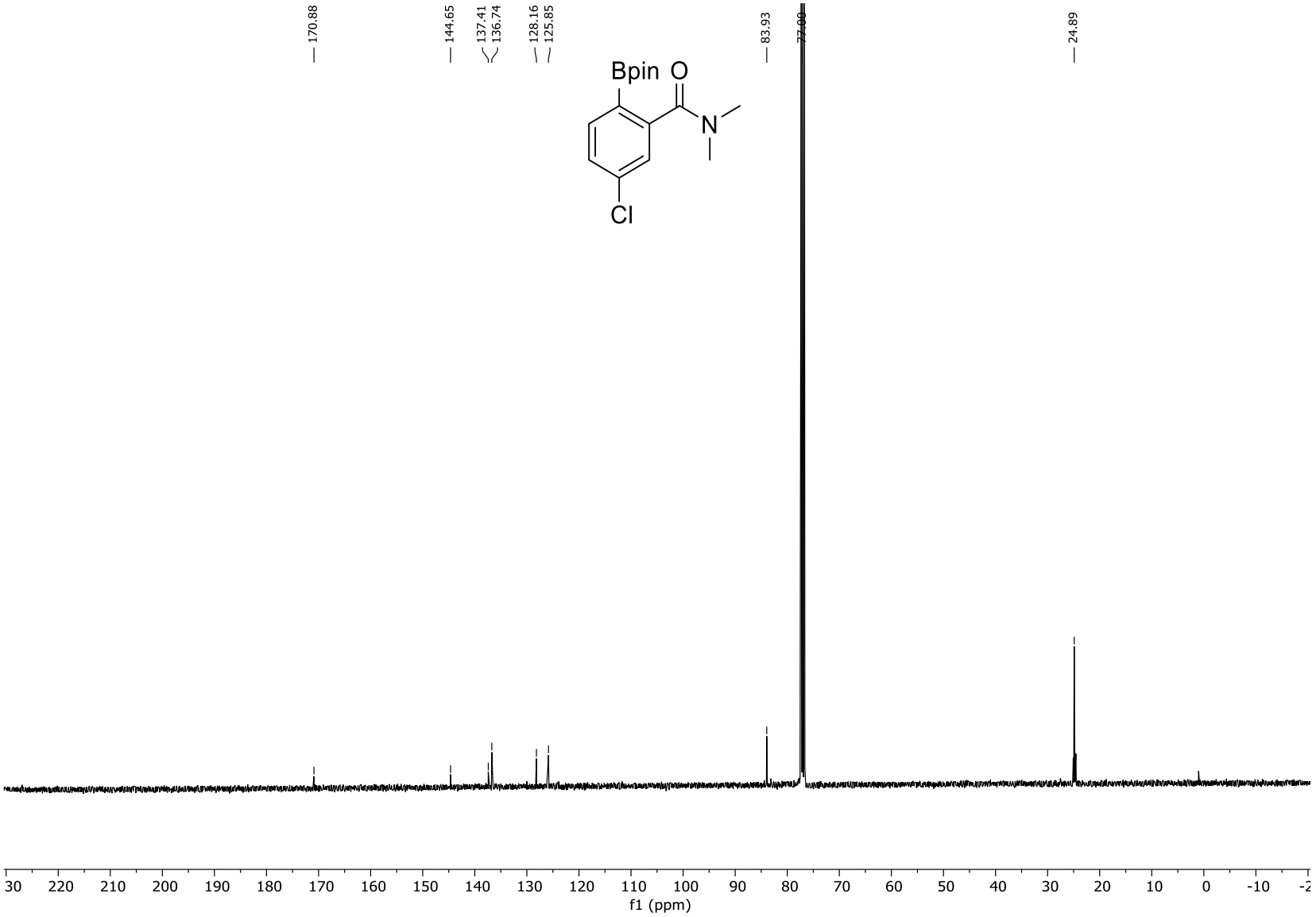
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376 MHz) spectrum of **2i**.



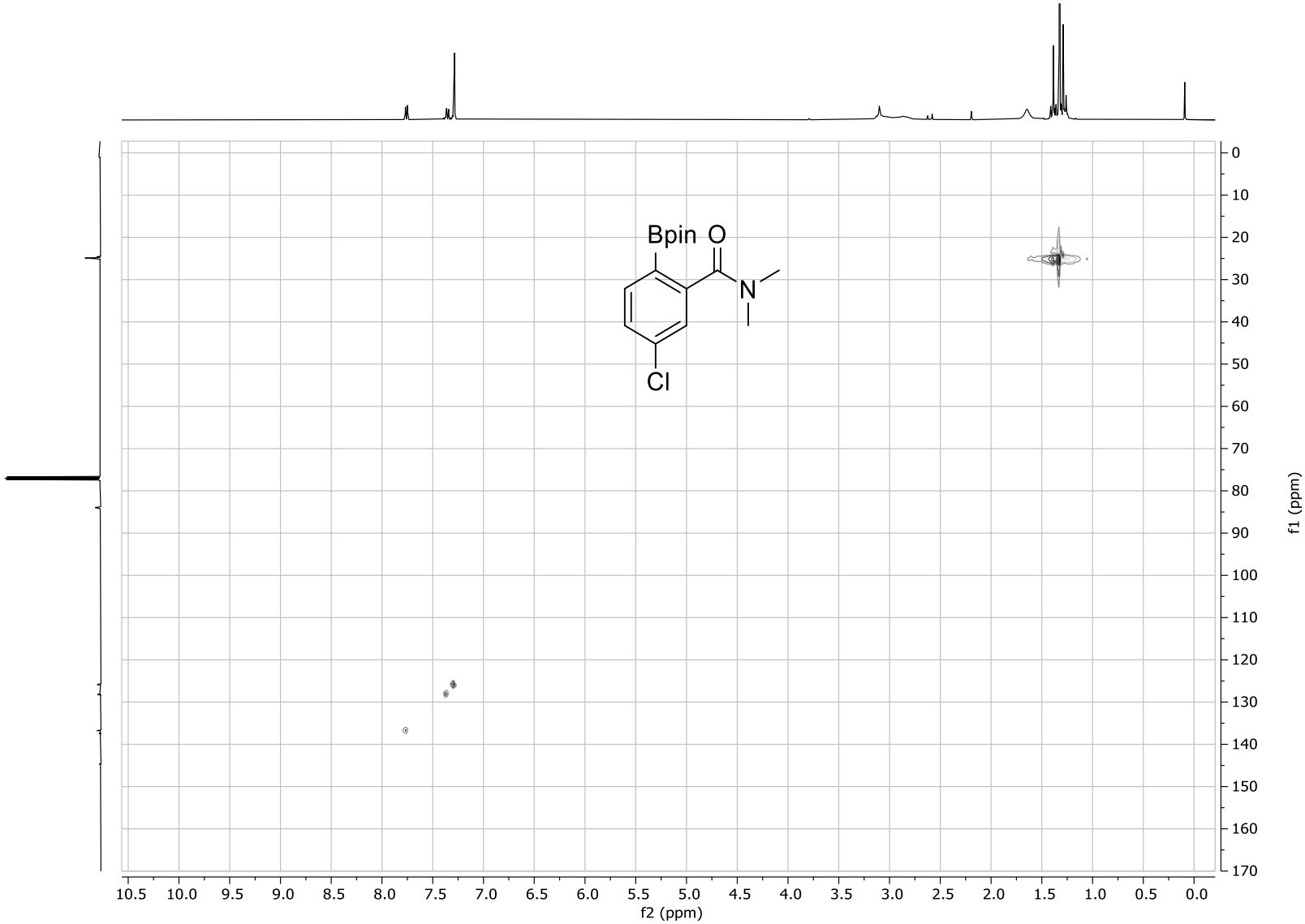
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2j**.



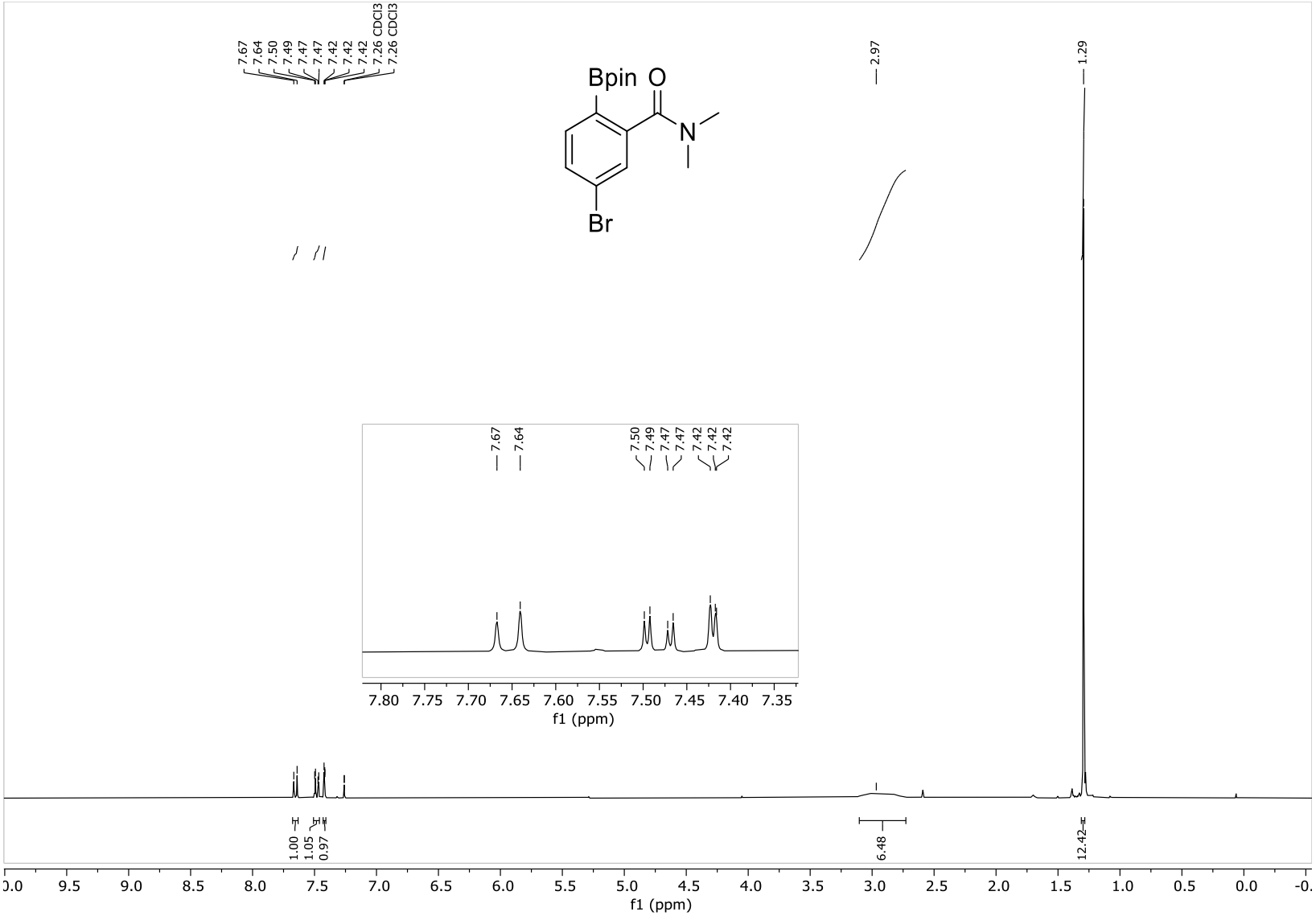
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2j**.



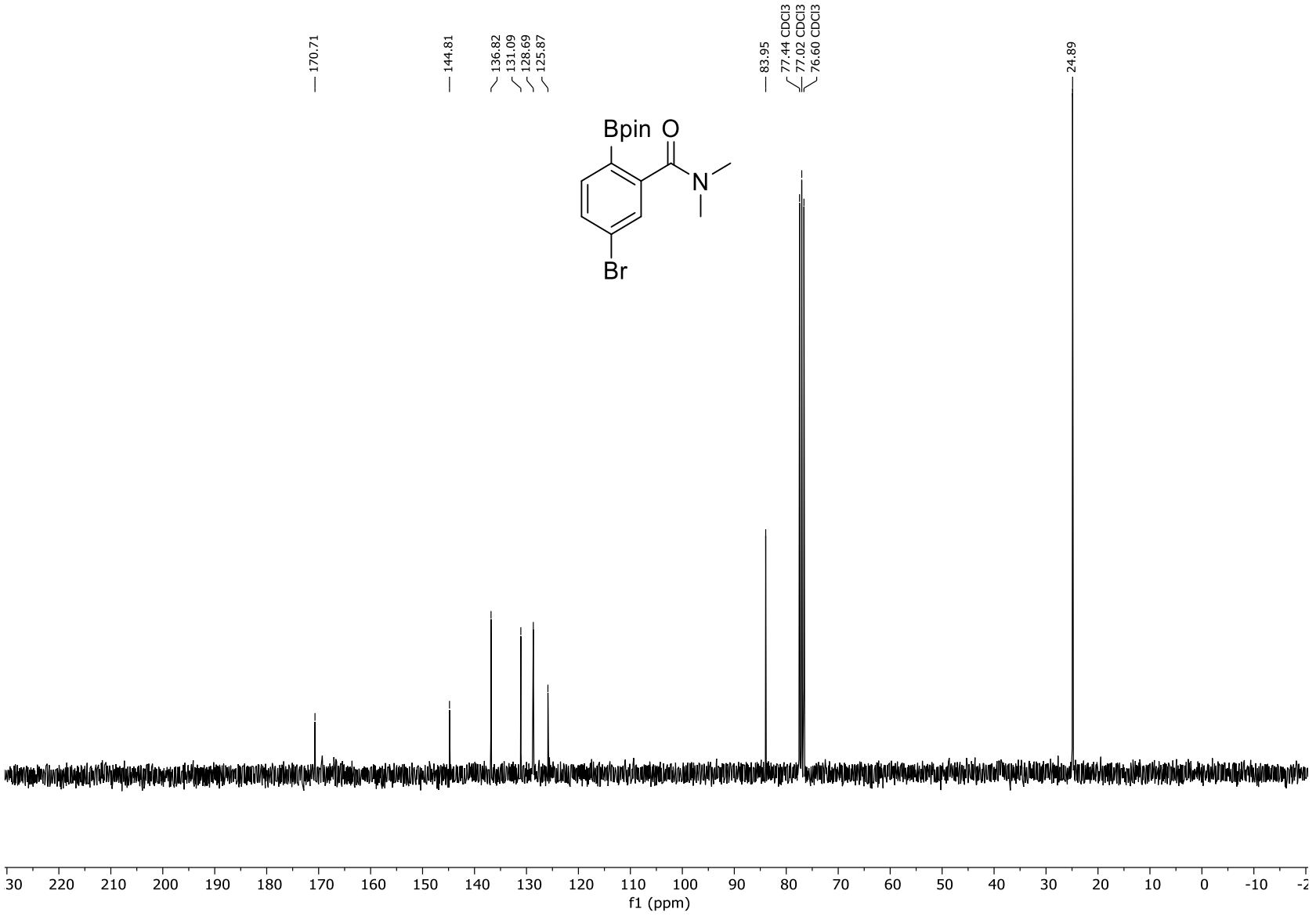
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2j**.



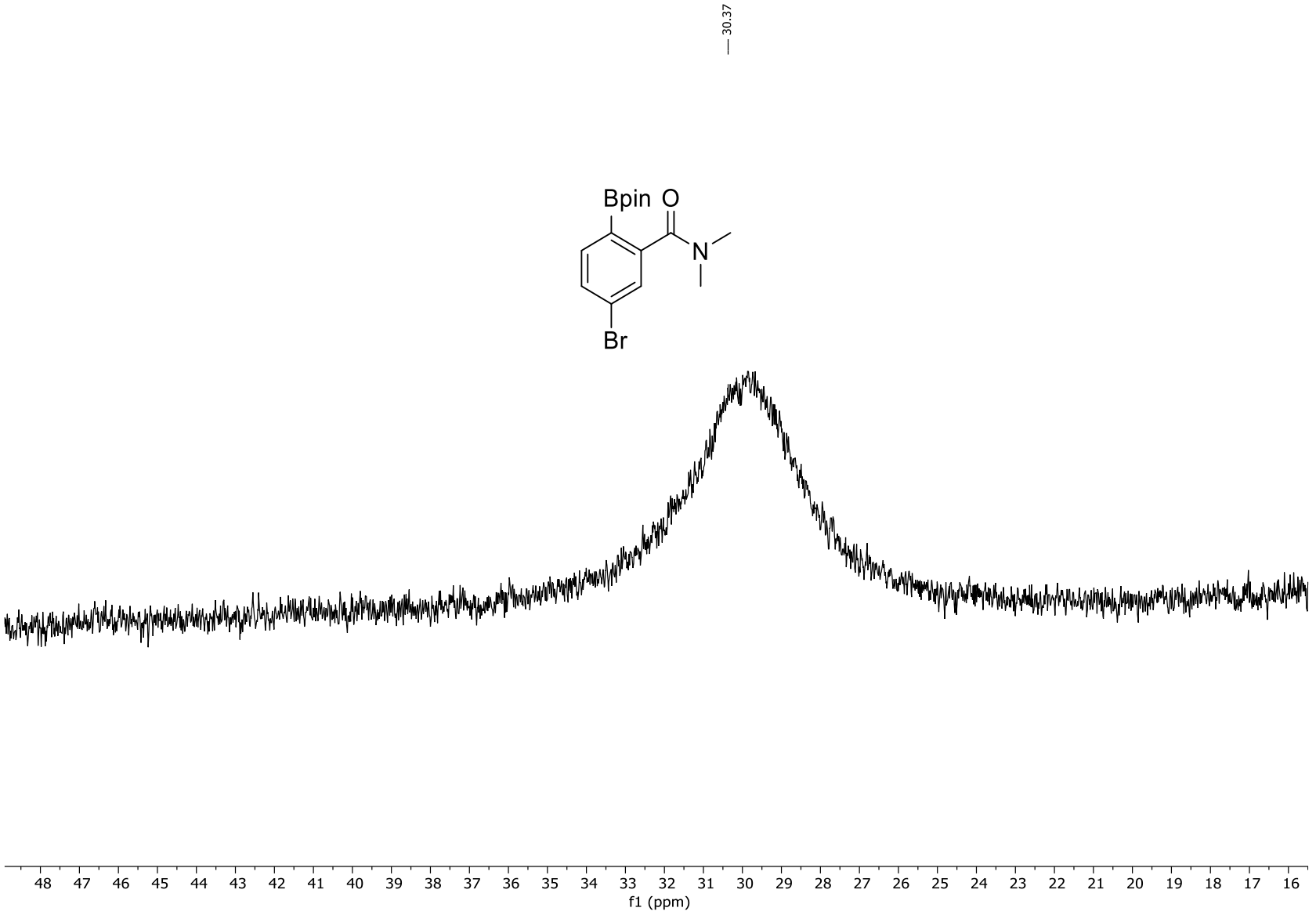
^{1}H-^{13}C HSQC NMR ($CDCl_3$) spectrum of **2j**.



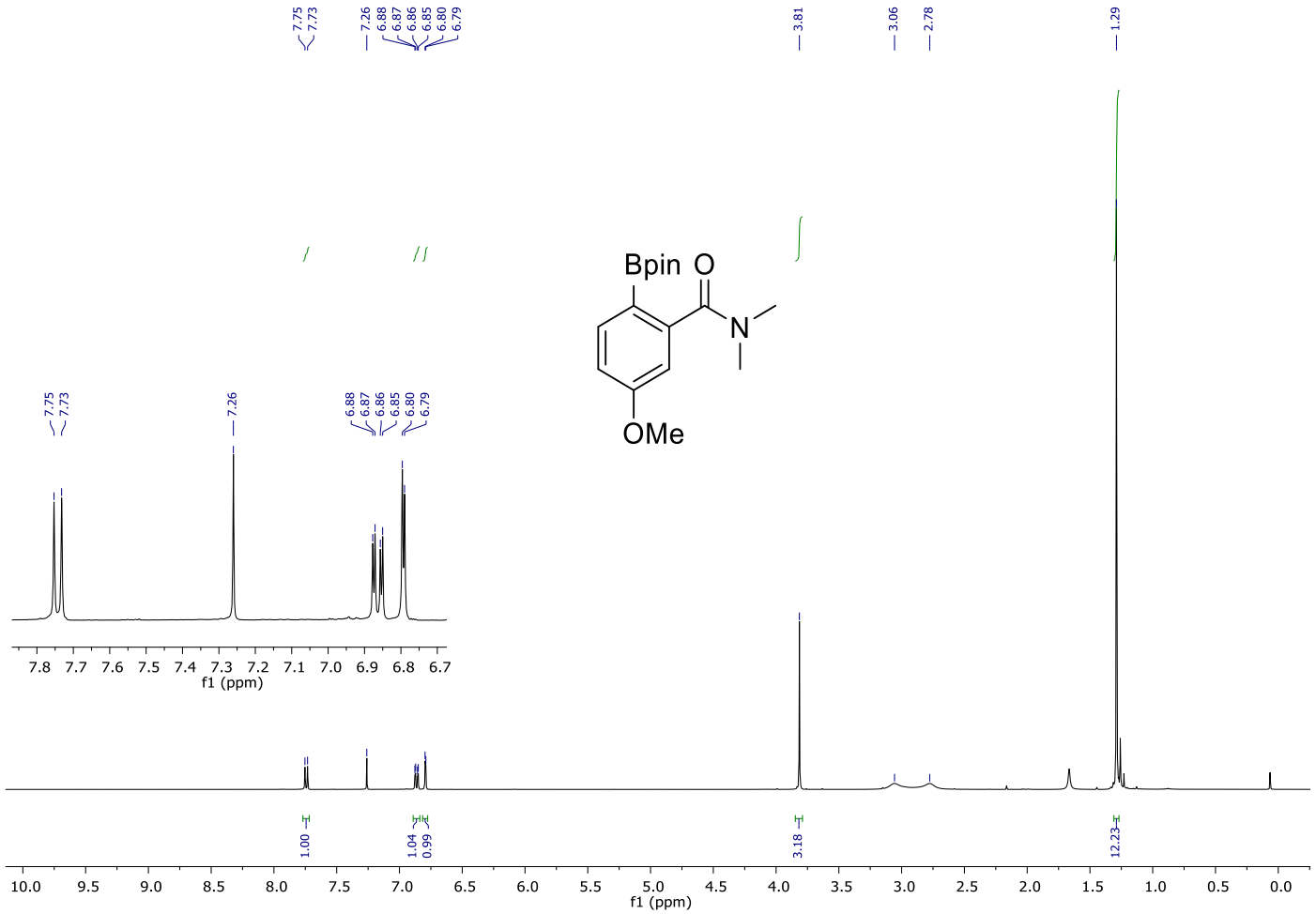
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2k**.



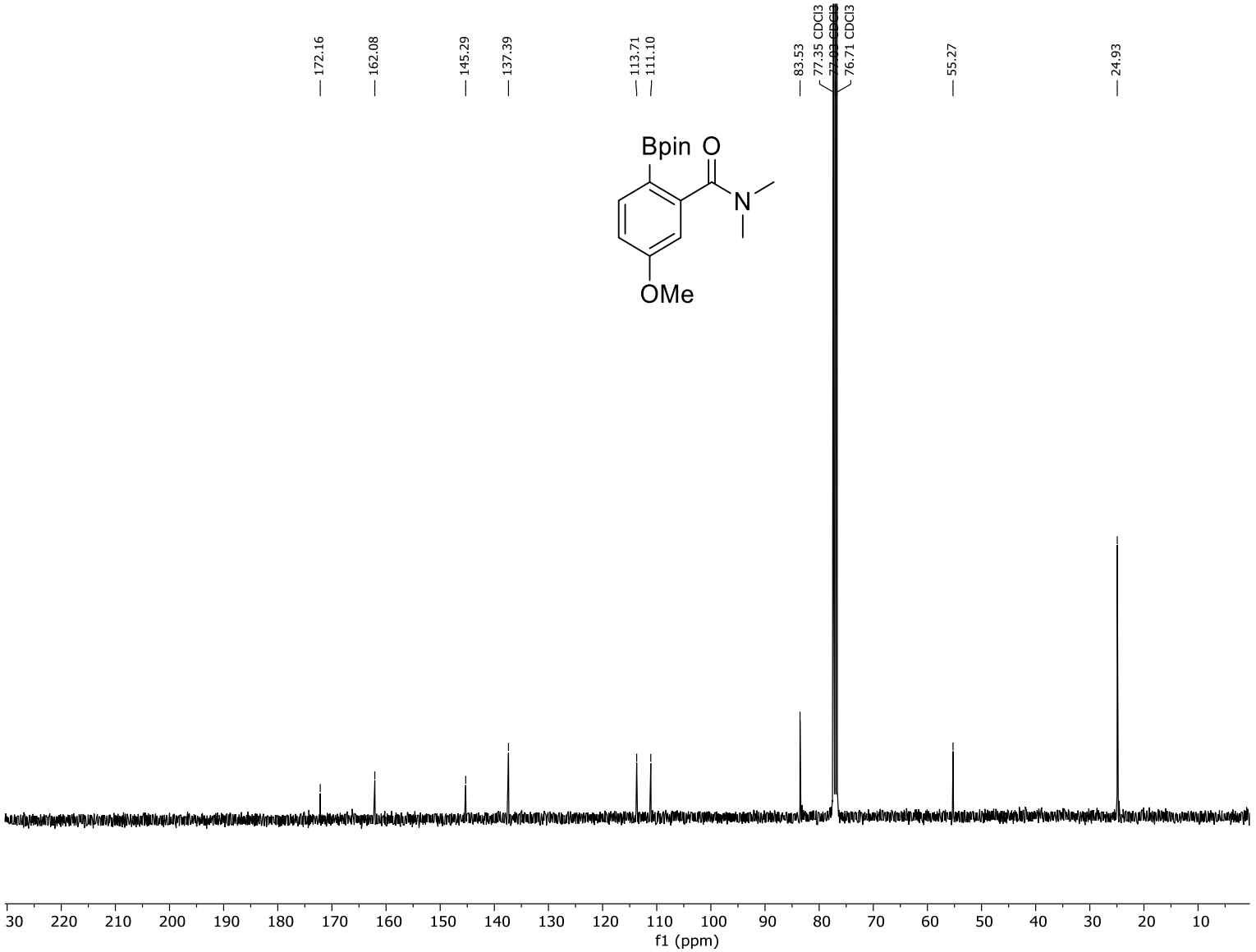
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2k**.



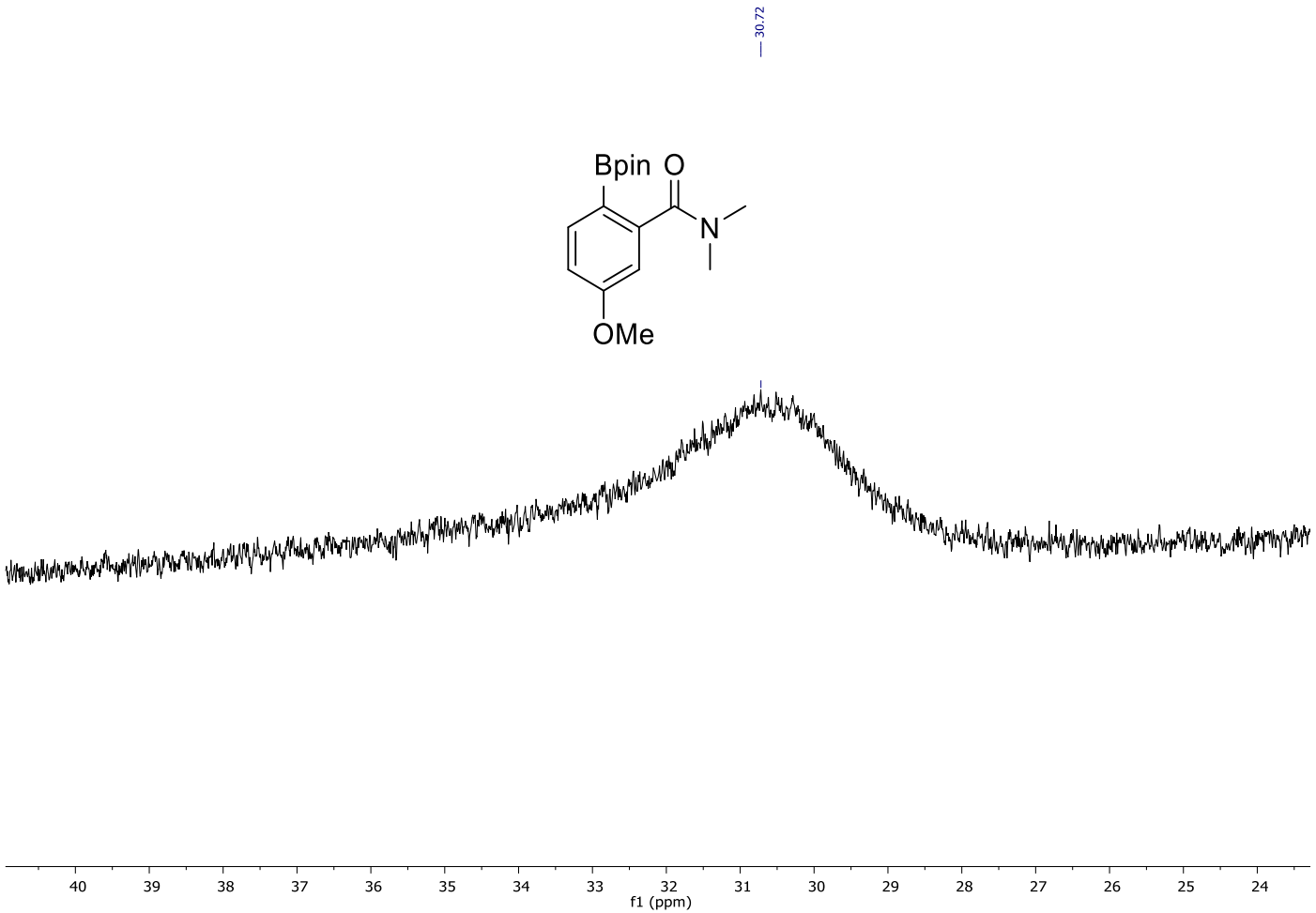
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2k**.



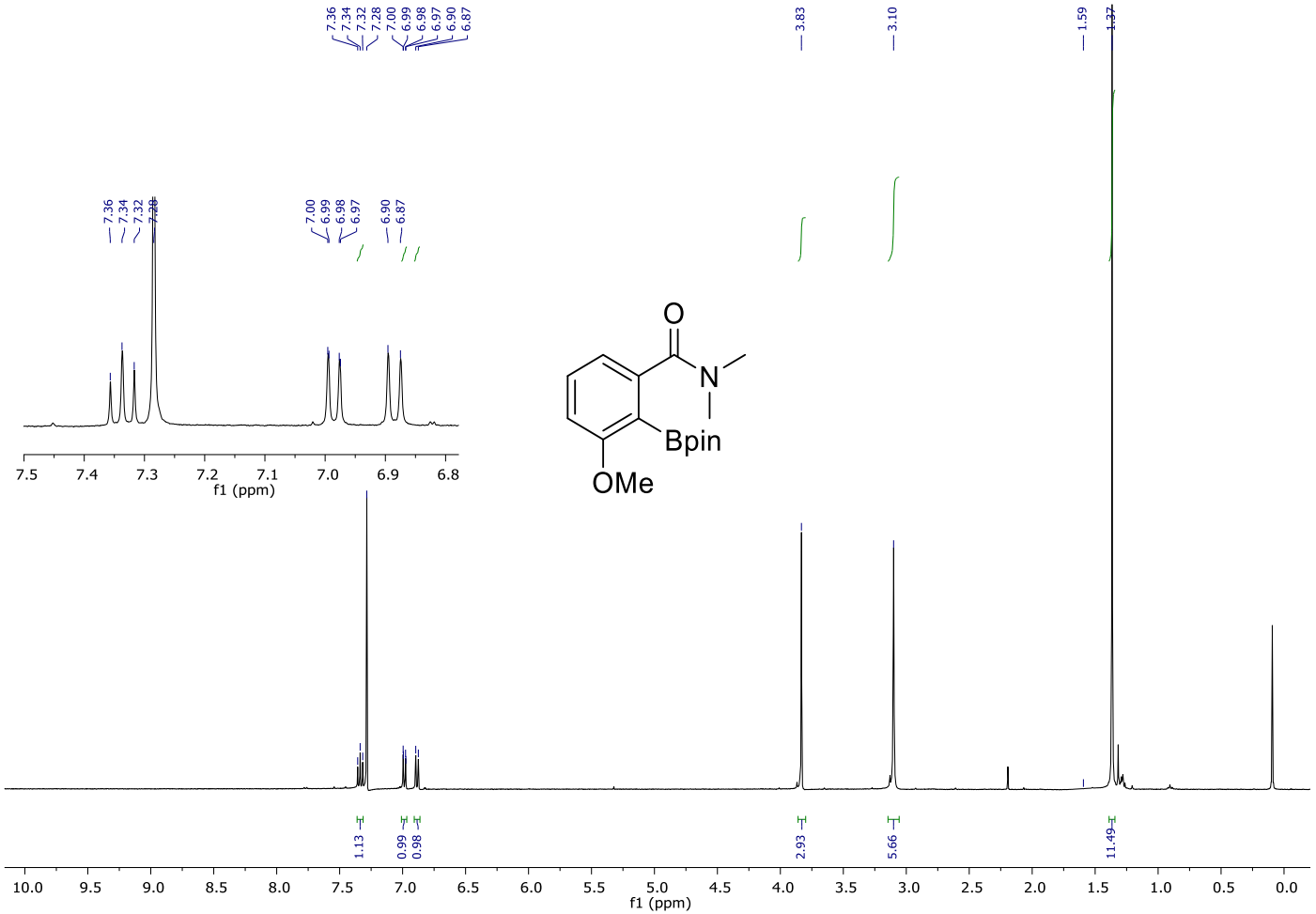
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2l**.



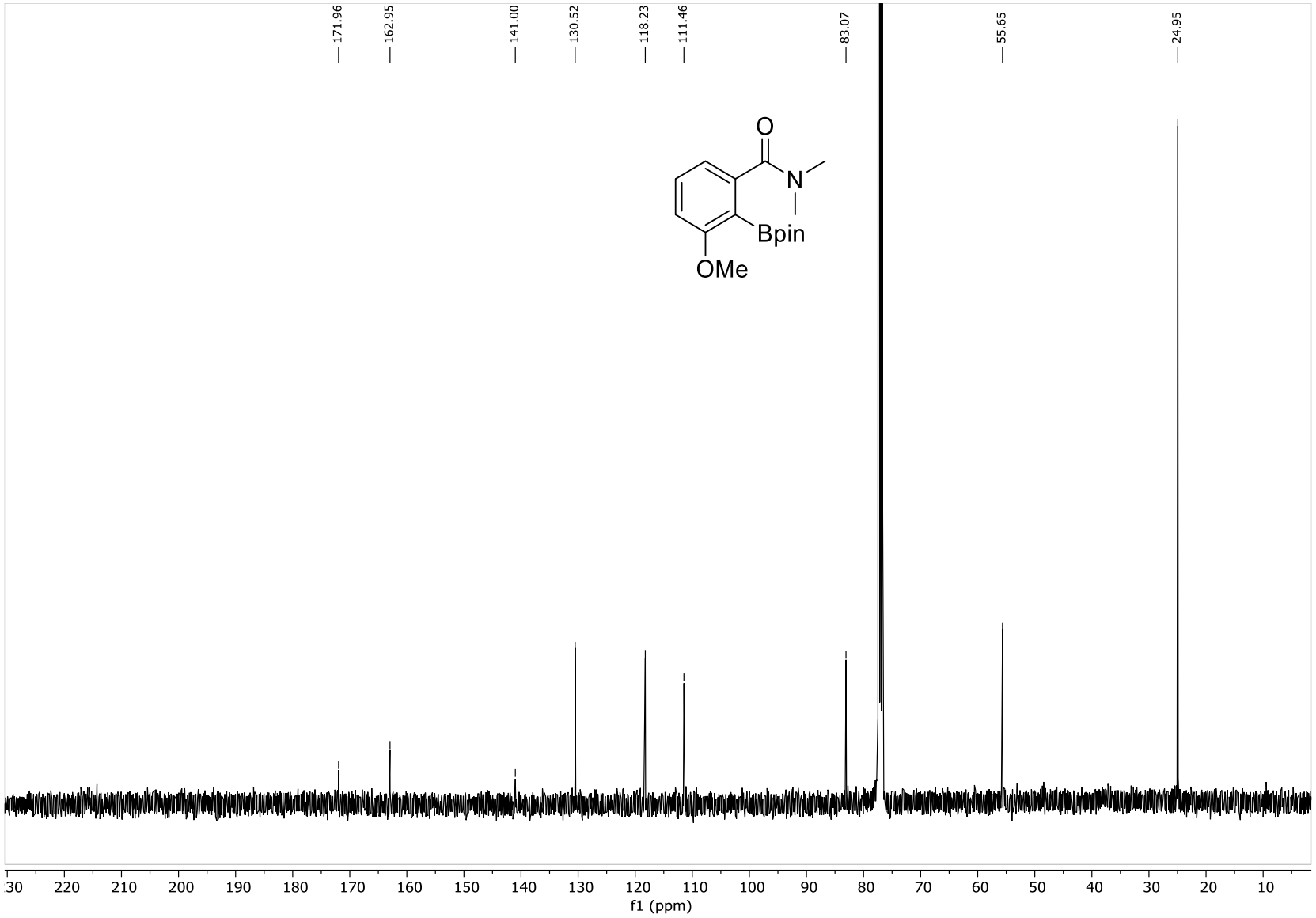
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2l**.



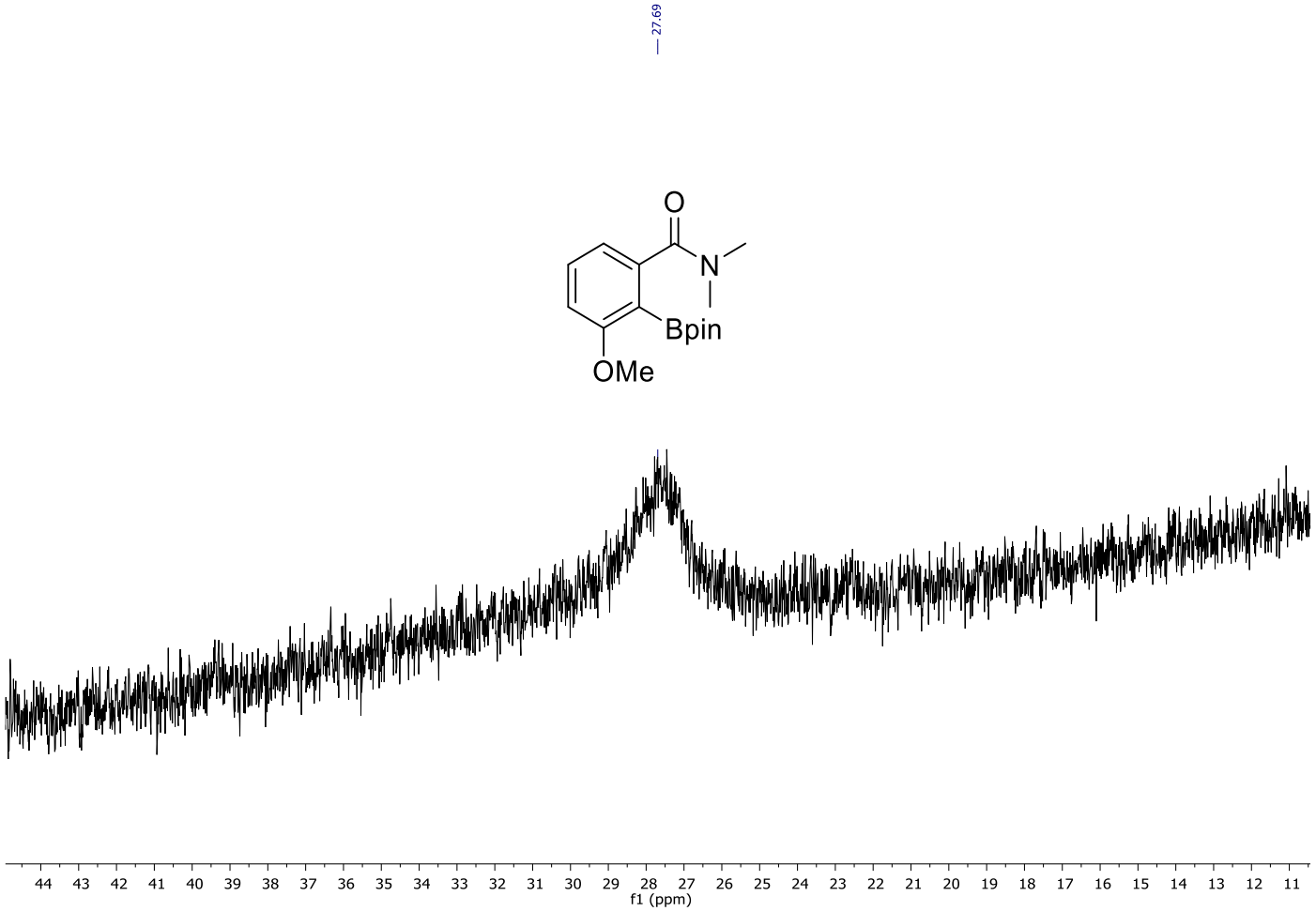
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2l**.



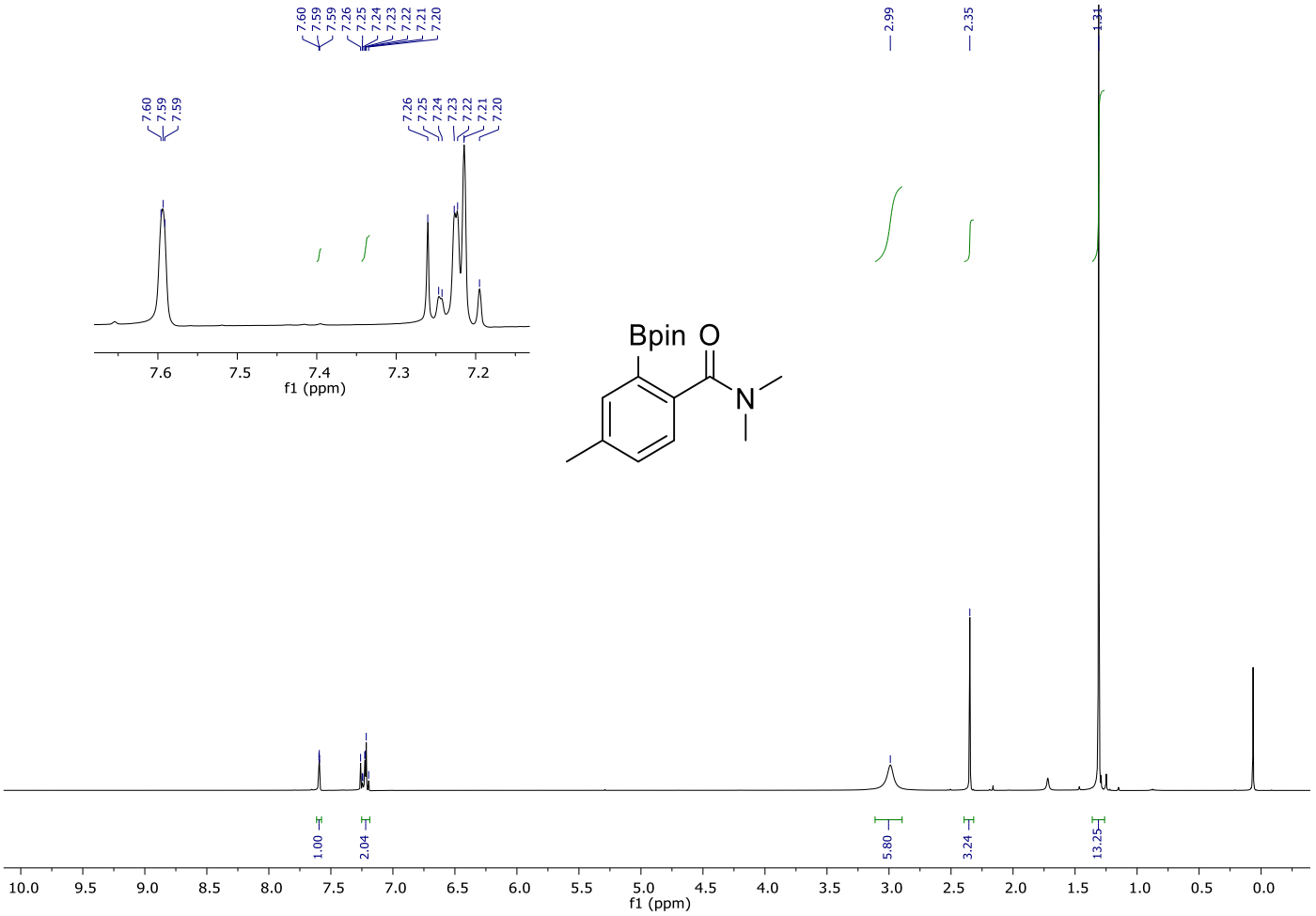
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2m**.



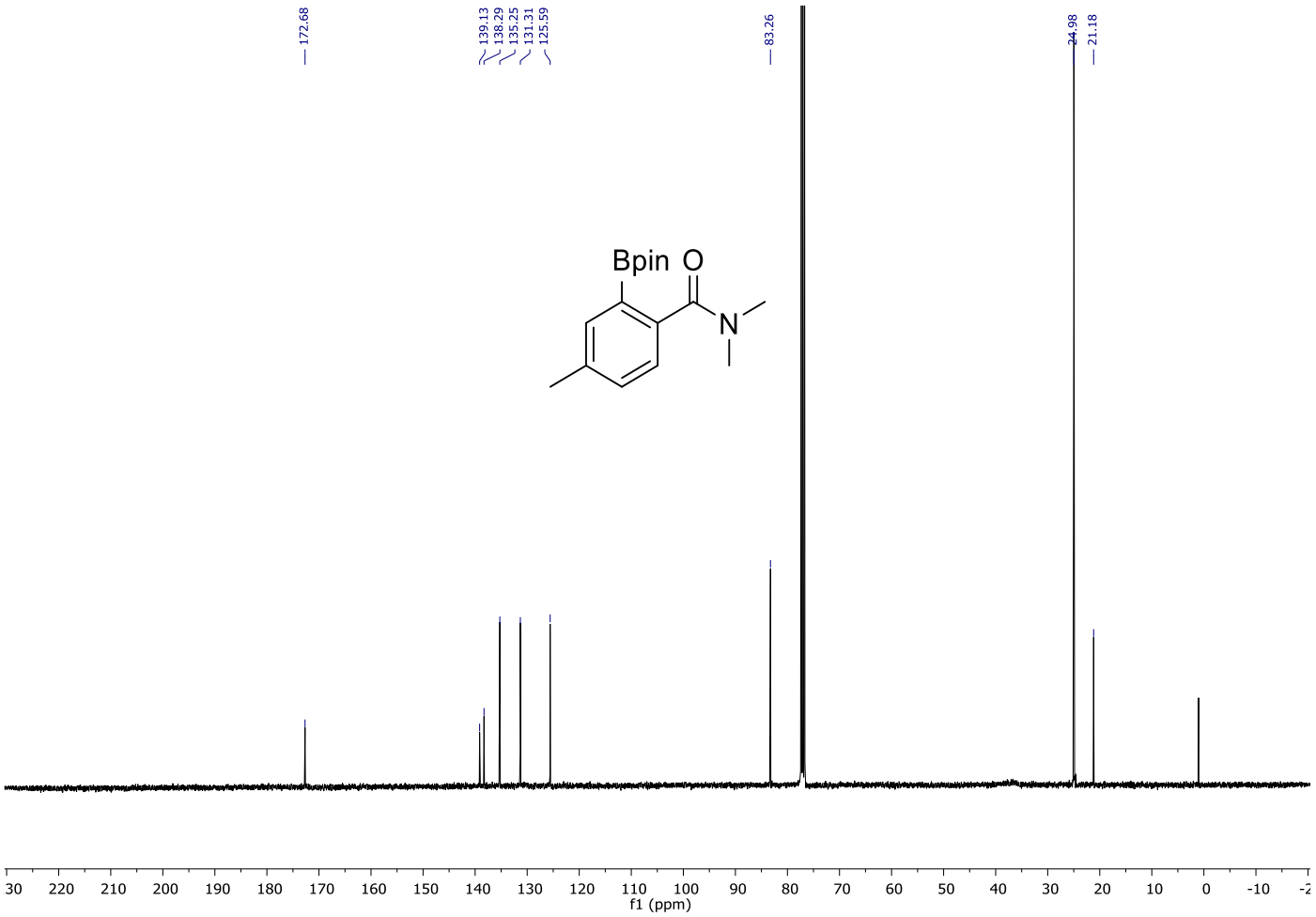
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2m**.



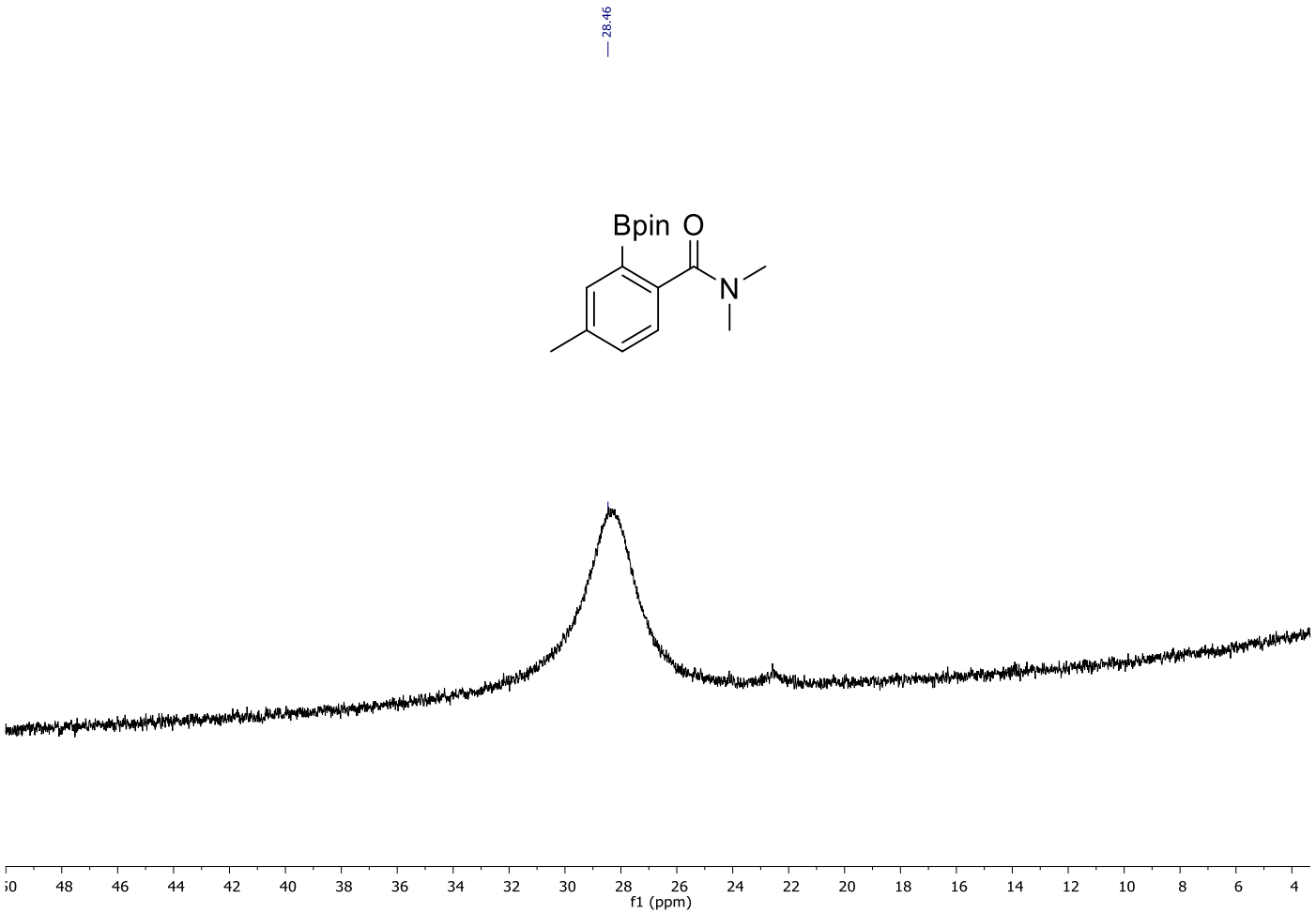
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2m**.



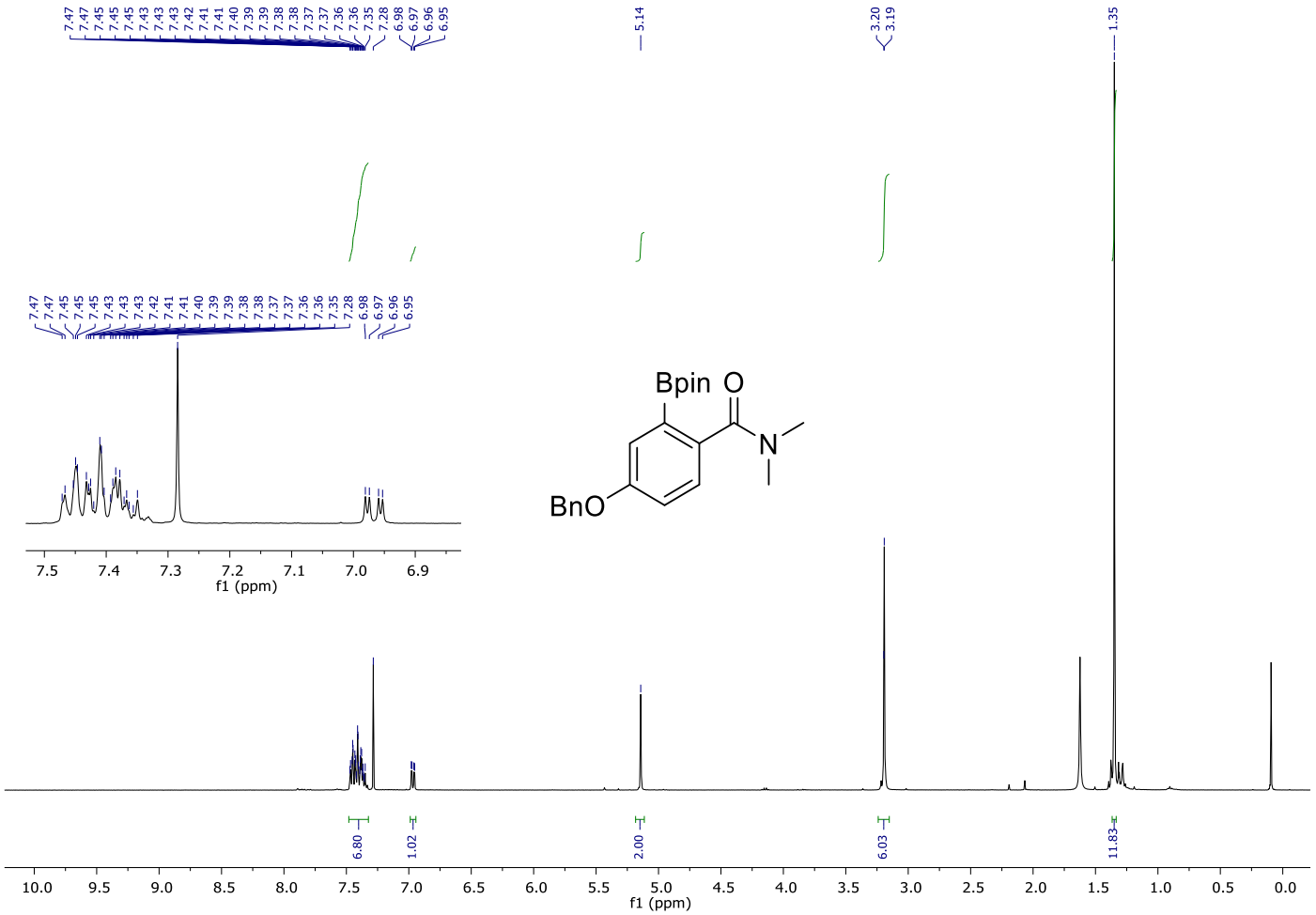
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2n**.



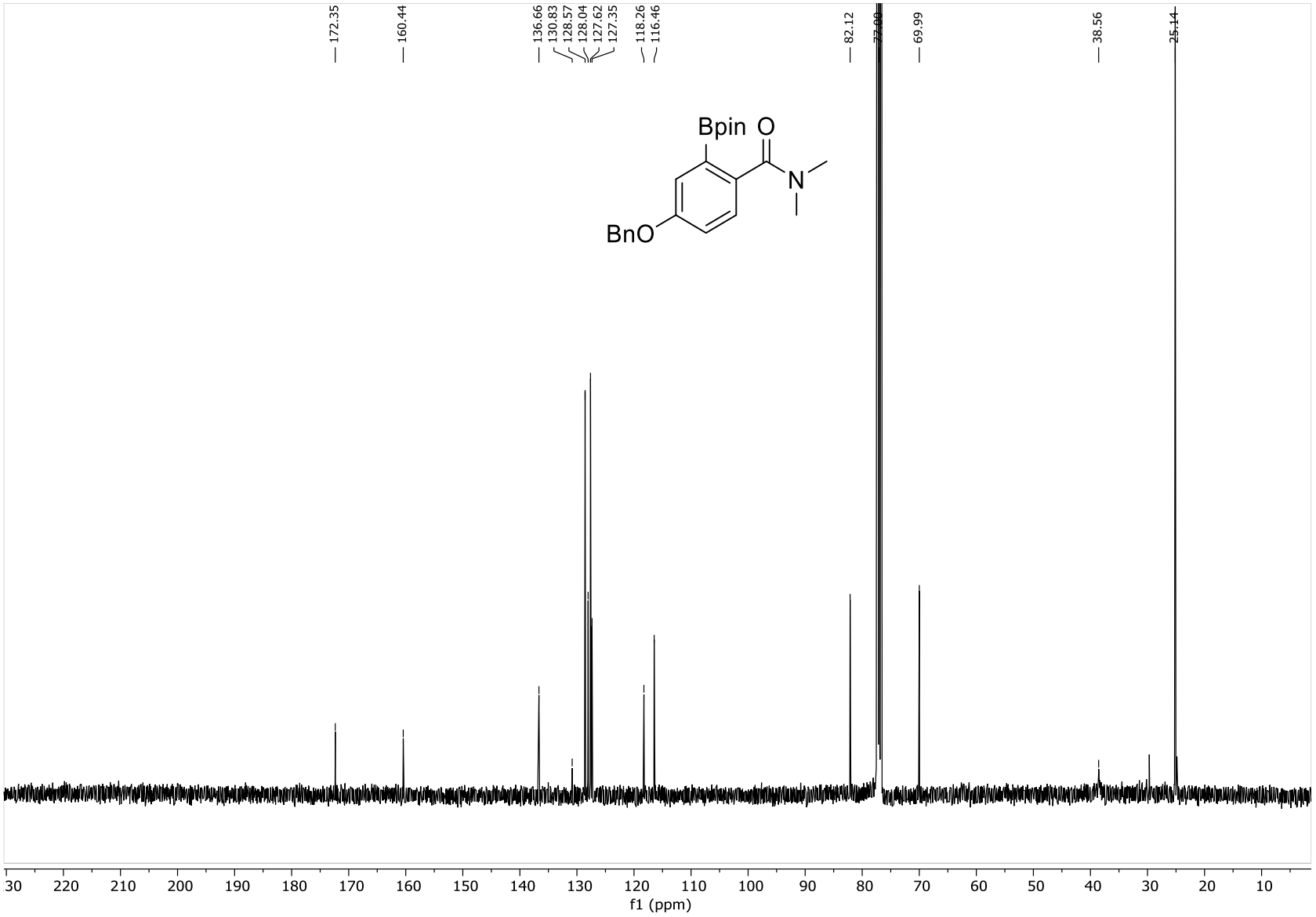
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2n**.



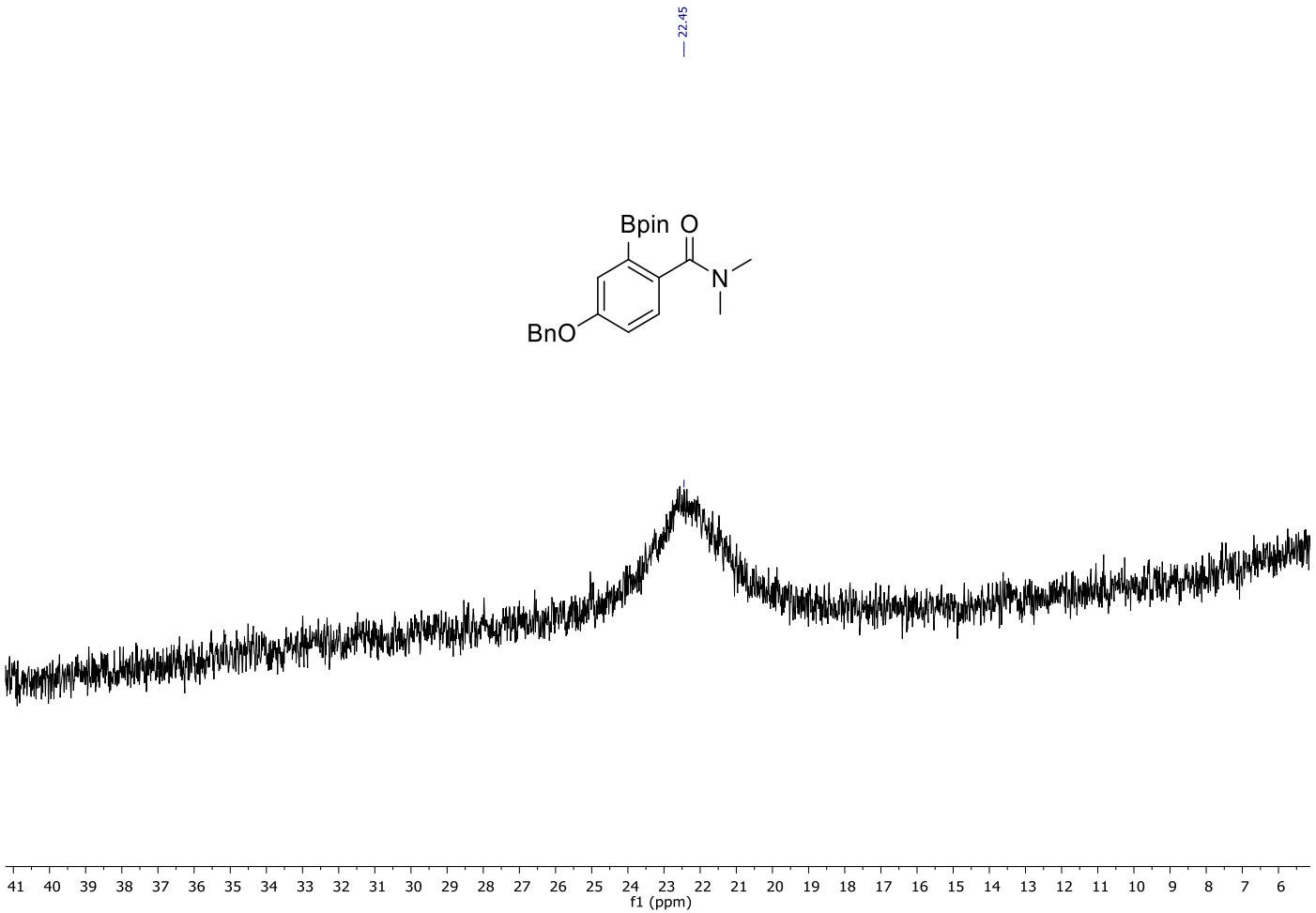
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2n**.



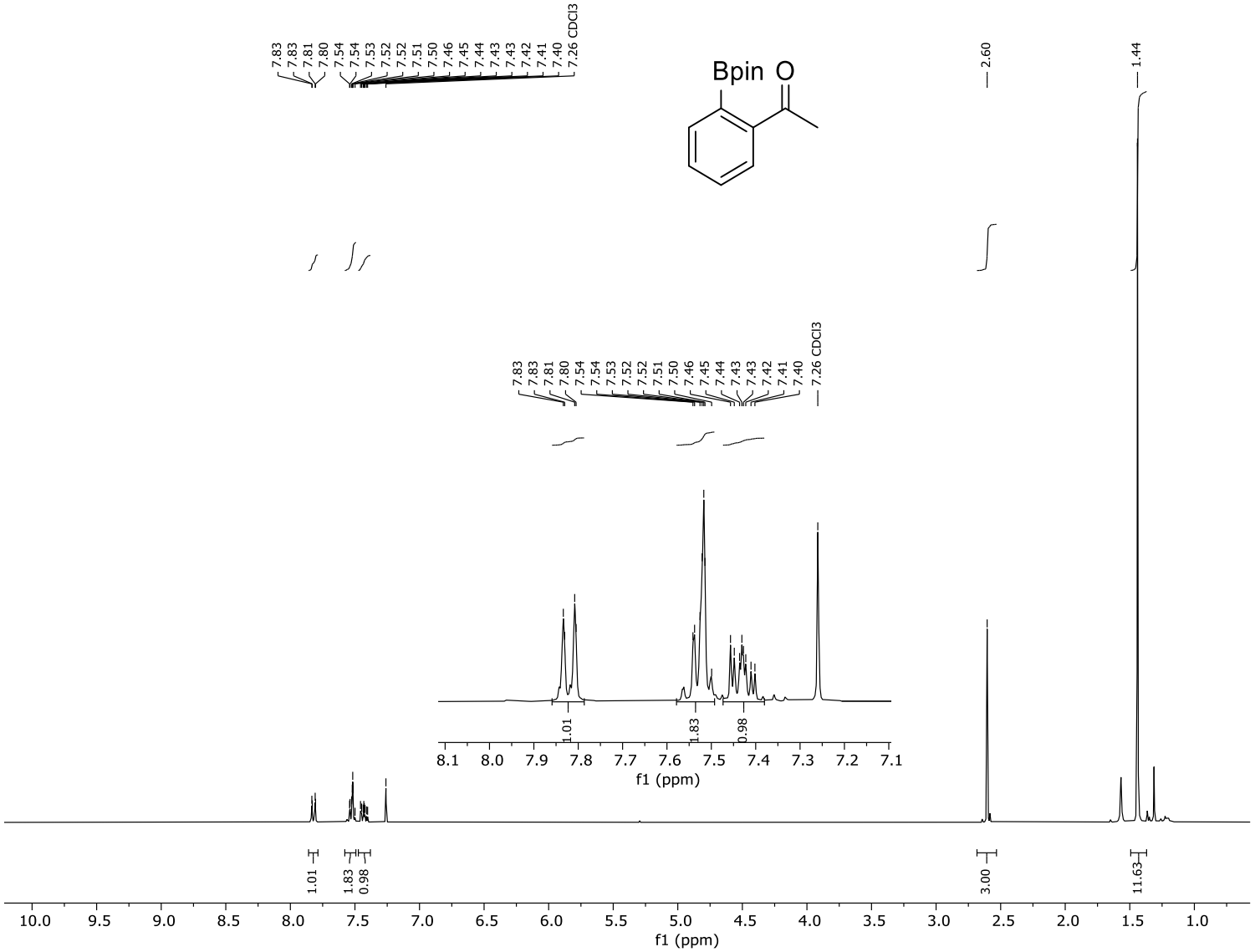
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2o**.



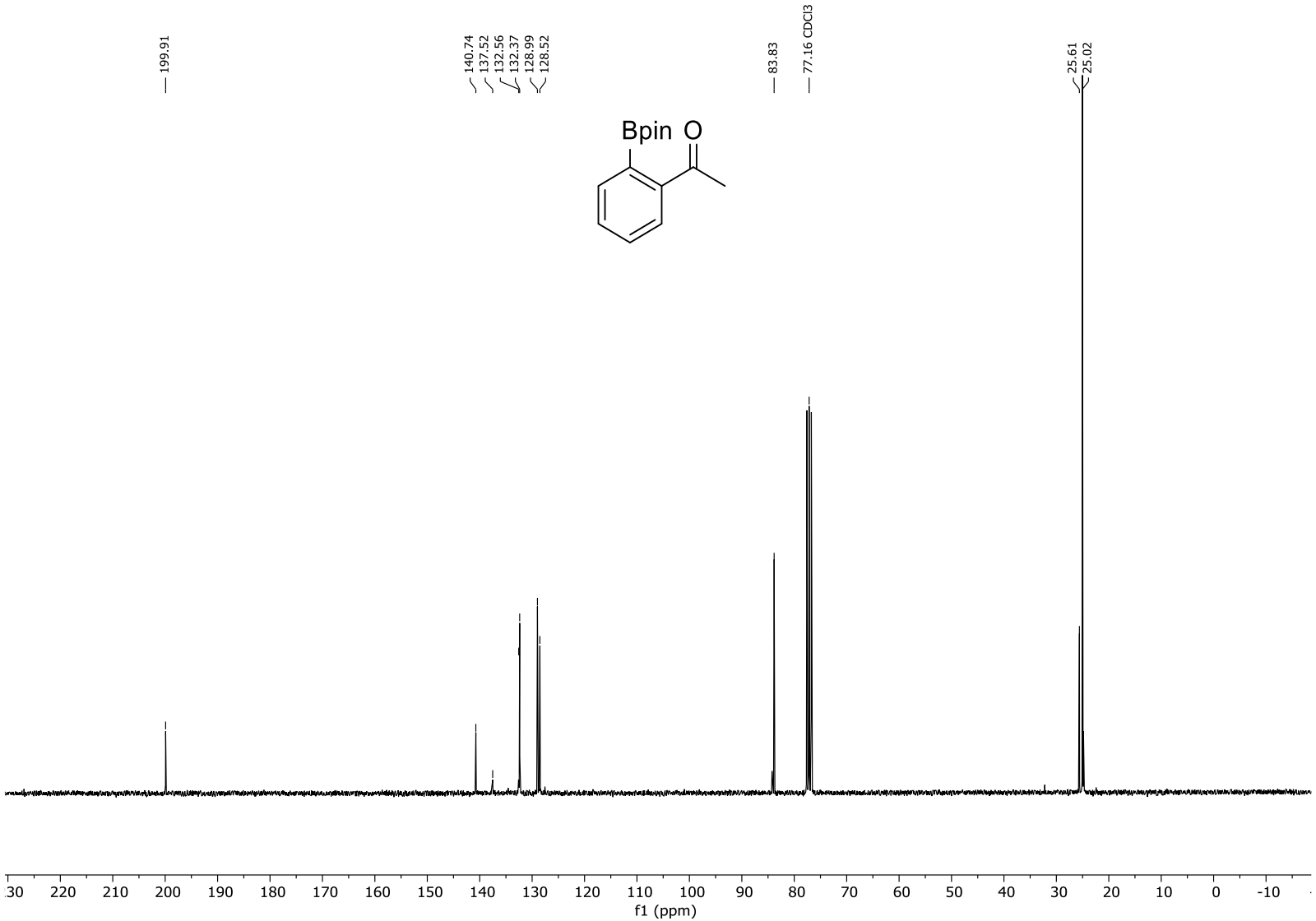
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2o**.



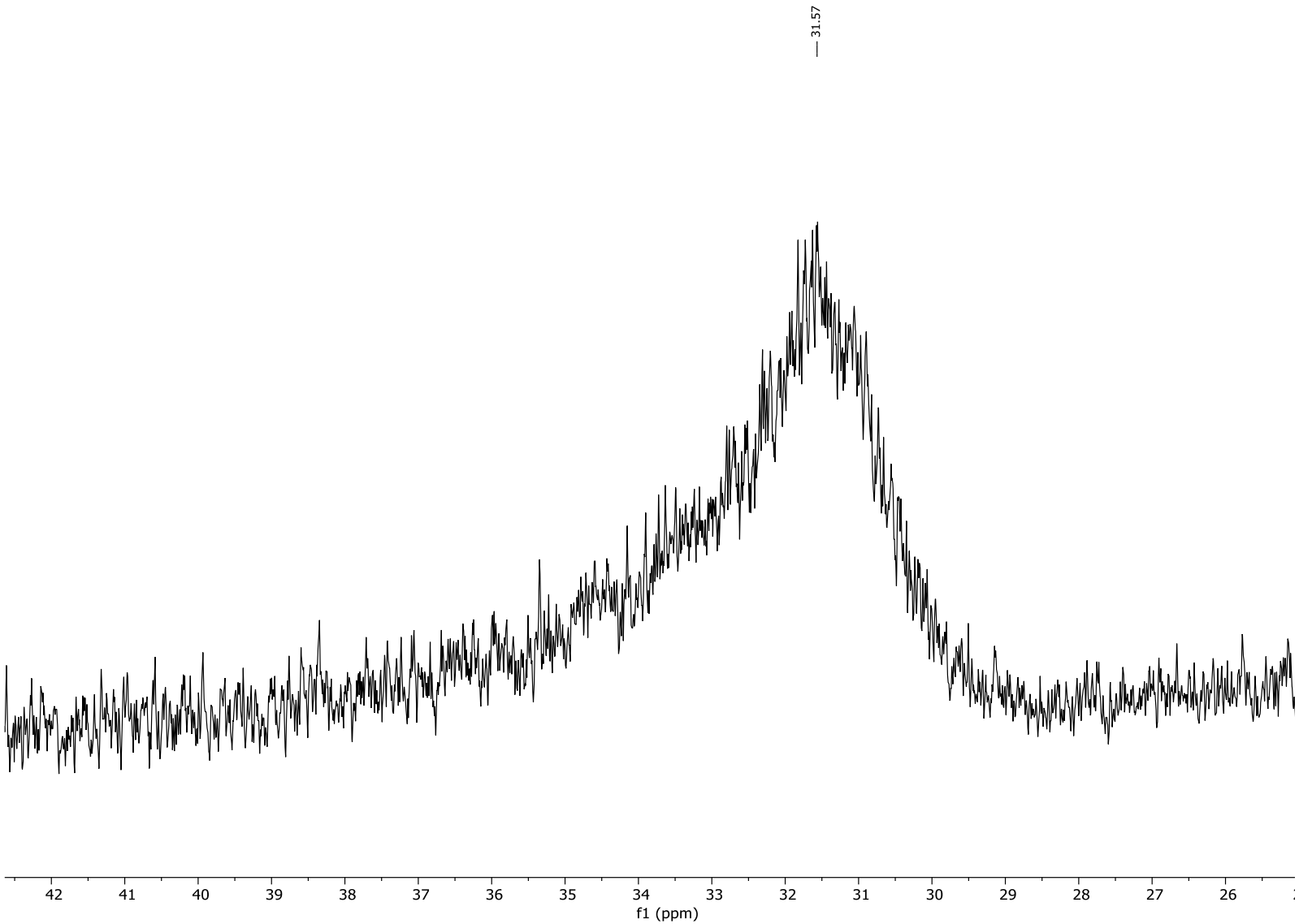
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2o**.



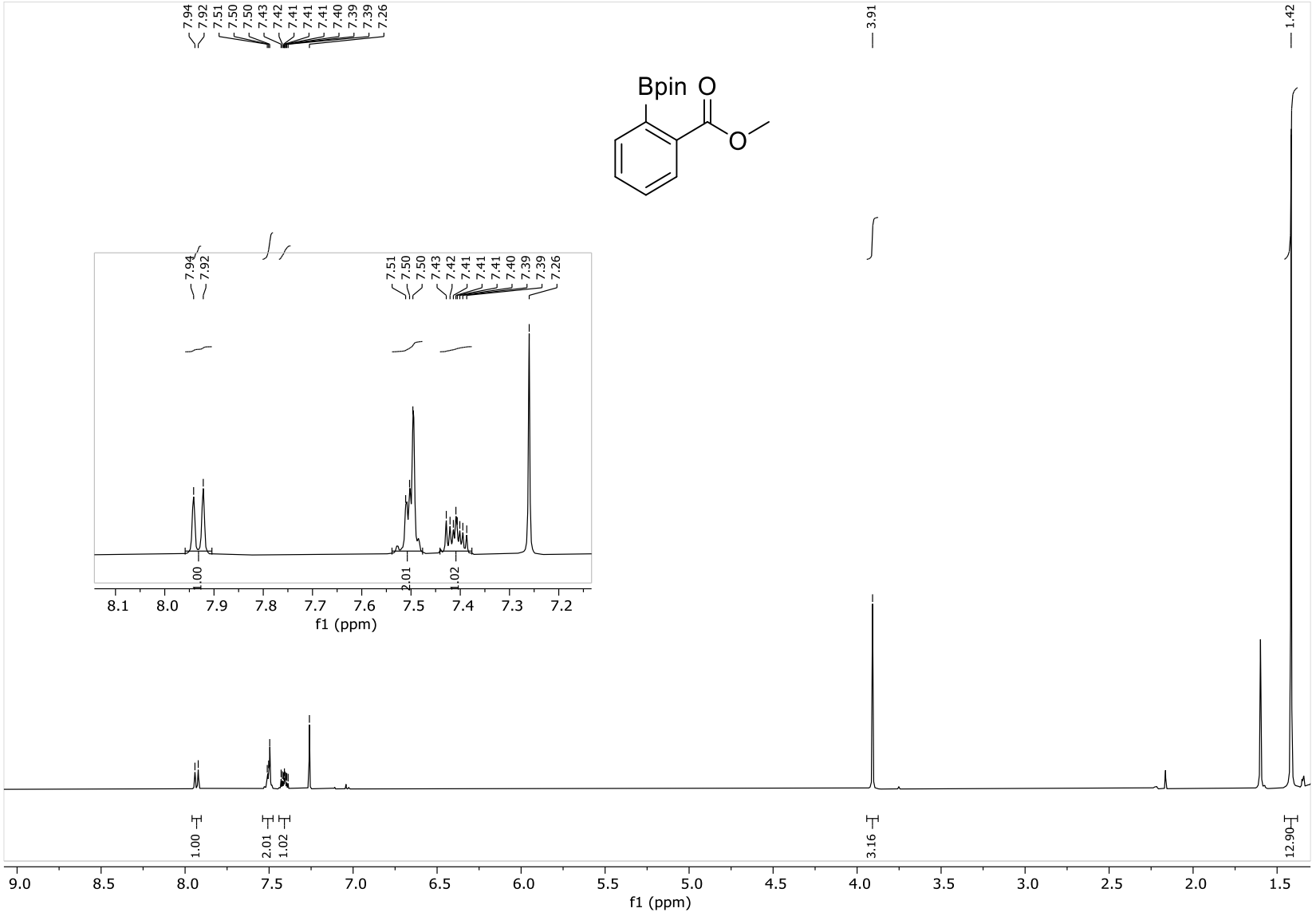
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2p**.



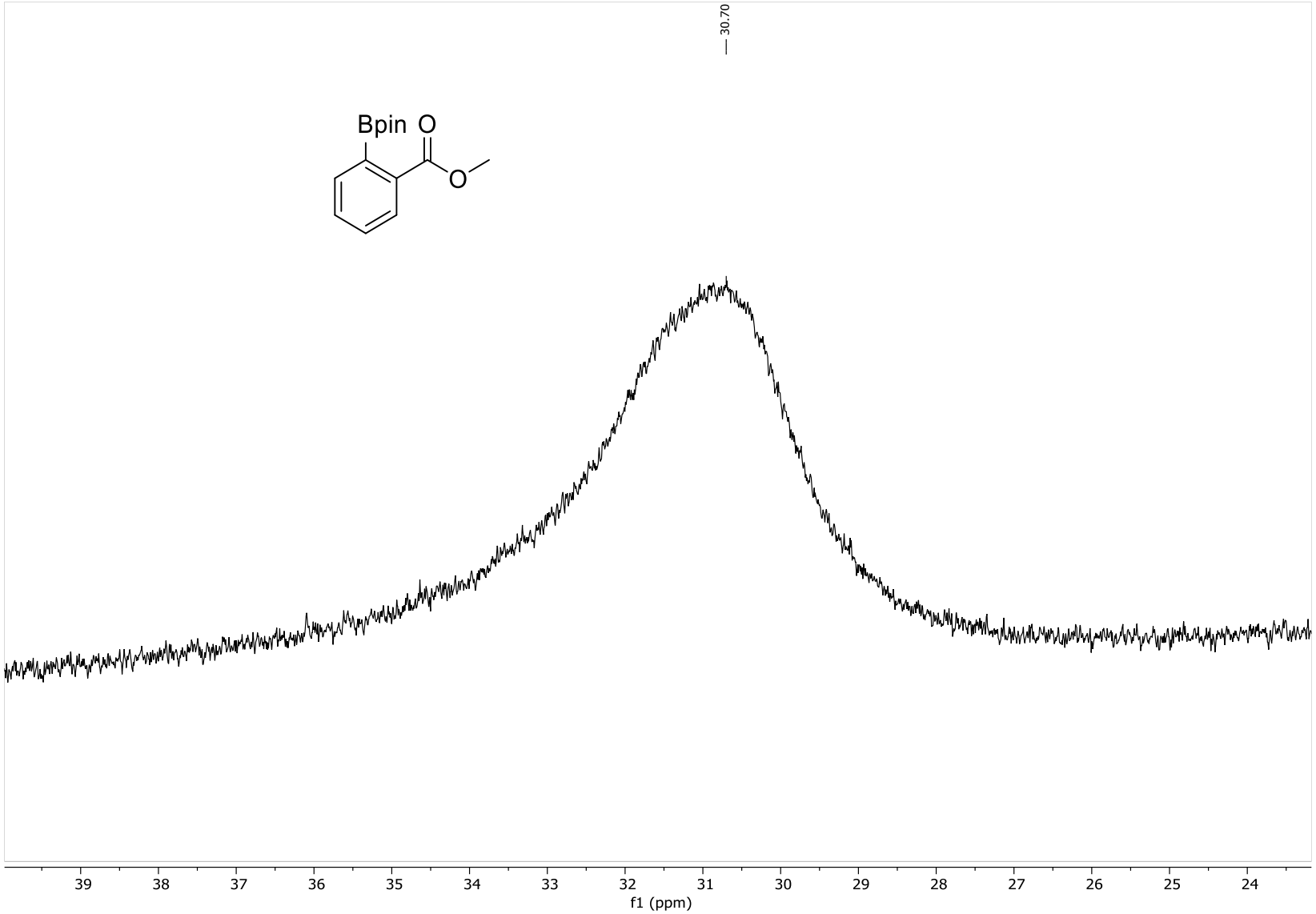
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of **2p**.



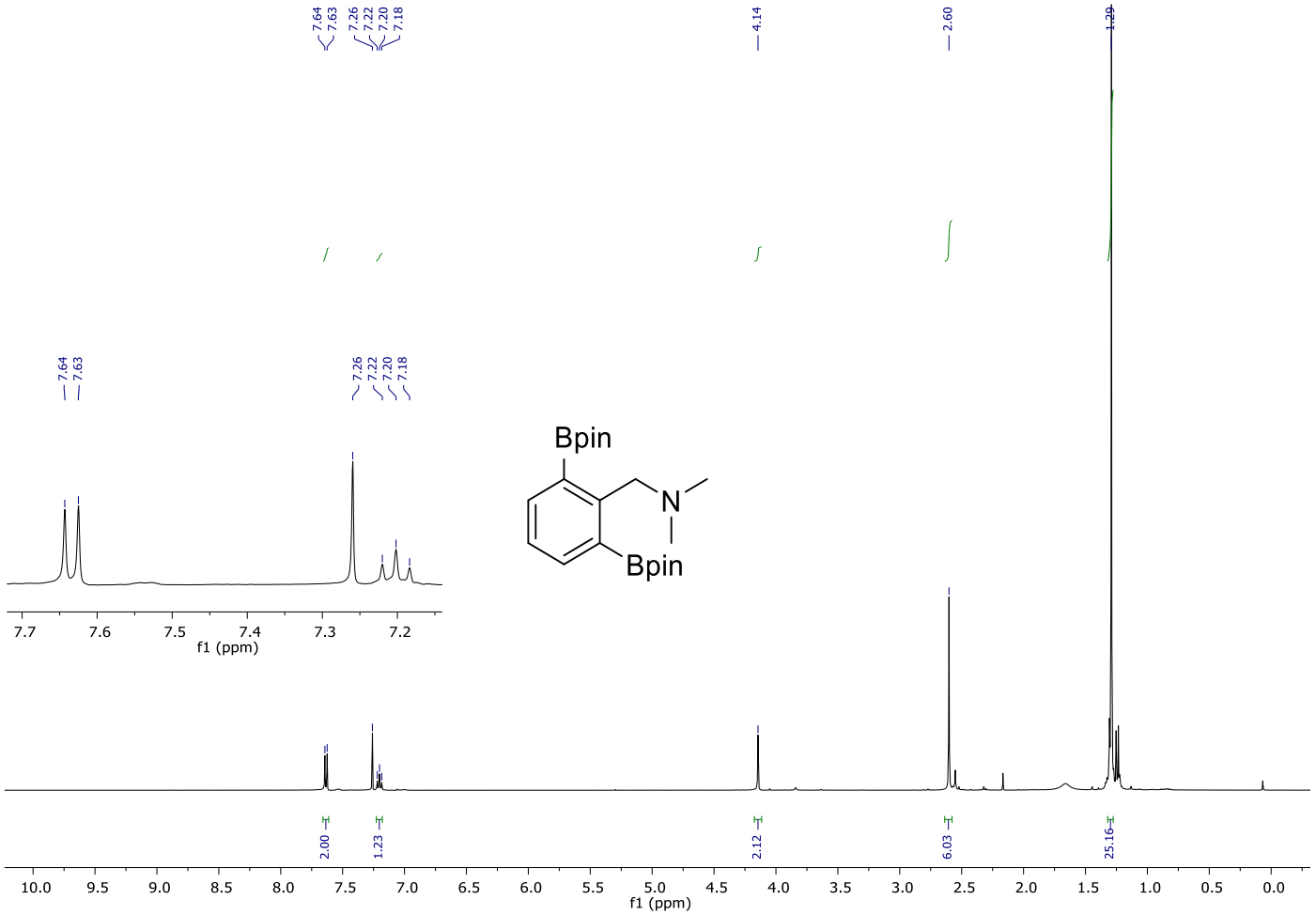
$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2p**.



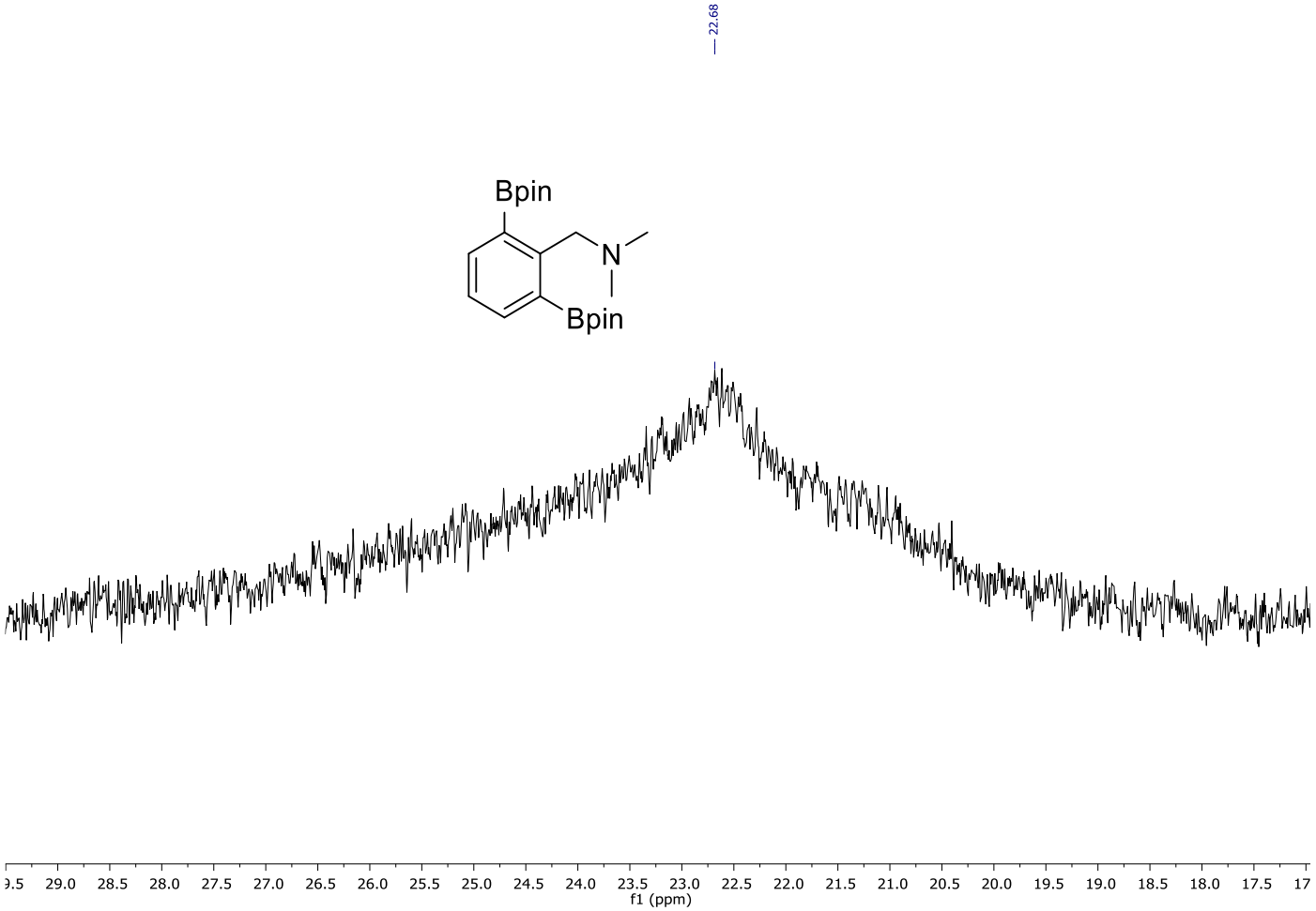
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **2q**.



$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **2q**.



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



$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz) spectrum spectrum of **5**.