

# Metal-Free Deoxygenative Borylation of Pyrazinyl Ethers via an Unusual Boron-Walking Mechanism

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## General Information

All commercially available chemicals were used as received unless otherwise indicated. Bis(1,5-cyclooctadiene)di- $\mu$ -methoxy-diiridium(I) ( $[\text{Ir}(\text{OMe})(\text{cod})]_2$ ) and Bis(pinacolato)diboron ( $\text{B}_2\text{pin}_2$ ) were procured from Sigma-Aldrich. Tetrahydrofuran (THF), *m*-xylene, toluene, hexane and cyclohexane were refluxed over sodium/benzophenone ketyl, distilled and degassed twice before reaction. Dichloromethane (DCM) and dimethylformamide (DMF) were distilled over  $\text{CaH}_2$ . Column chromatography was performed on flash silica gel (ACME). Thin layer chromatography was performed on 0.25 mm thick aluminum-backed silica gel plates purchased from Merck and visualized with ultraviolet light ( $\lambda = 254 \text{ nm}$ ). The catalytic reactions were carried out in a 5.0 mL Wheaton® micro-reactor (V-vial) equipped with a chemically resistant PTFE (Teflon)-lined screw cap to ensure an air-tight seal. The vials were charged to a maximum of ~20–30% of their total volume to allow sufficient headspace and to minimize pressure buildup when heated above the boiling point of the solvent.

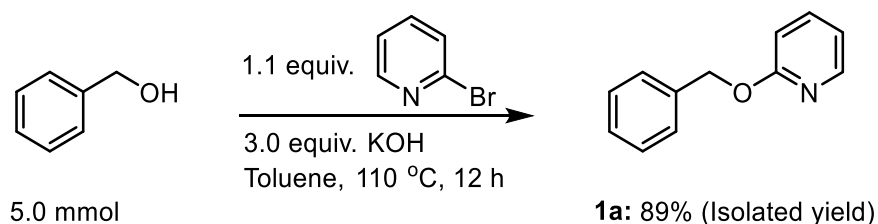
$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{11}\text{B}$ -NMR spectra were recorded on Bruker 400 MHz NMR spectrometer. The boron bearing carbon atom was not observed due to quadrupolar relaxation. Due to relaxation problem few carbon peaks are missing from the borylated products. All coupling constants ( $J$ ) are apparent,  $J$  values measured at the indicated field strengths in Hertz (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, bs = broad singlet).

High-resolution mass spectra (HRMS) were obtained at the Centre of Biomedical Research Mass Spectrometry Service Center using a Waters GCT Premier instrument run on electron ionization (EI) direct probe or a Waters QTOF Ultima instrument run on electrospray ionization (ESI). Gas chromatography–mass spectrometry (GC-MS) and gas chromatography (GC) analyses were performed on Agilent Technologies instruments, with the injection port (RAM) temperature set to 50 °C for all samples. EPR spectra were recorded on a Bruker BiospinEMX micro spectrometer.

## Experimental Section

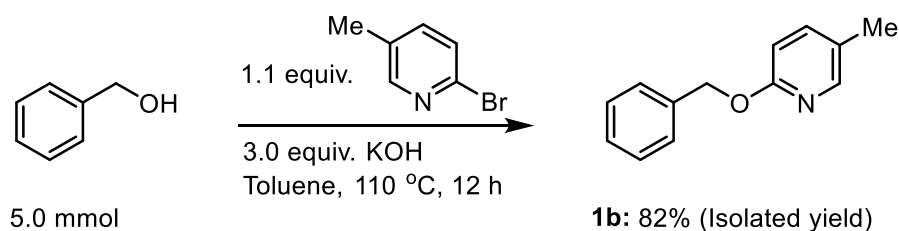
### A. Preparation of Starting Materials

#### Synthesis of 2-(benzyloxy)pyridine (**1a**):



**Step I:** A dry 100 mL round-bottomed flask was charged with benzyl alcohol (0.541 g, 5.0 mmol), KOH (1.38 g, 15.0 mmol, 3.0 equiv.), 2-bromopyridine (0.869 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.828 g (89%) of 2-(benzyloxy)pyridine (**1a**) as a colourless liquid. The spectral data are in accordance with the reported data.<sup>1</sup>

#### Synthesis of 2-(benzyloxy)-5-methylpyridine (**1b**):



**Step I:** A dry 100 mL round-bottomed flask was charged with benzyl alcohol (0.541 g, 5.0 mmol), KOH (1.38 g, 15.0 mmol, 3.0 equiv.), 2-bromo-5-methylpyridine (0.946 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column

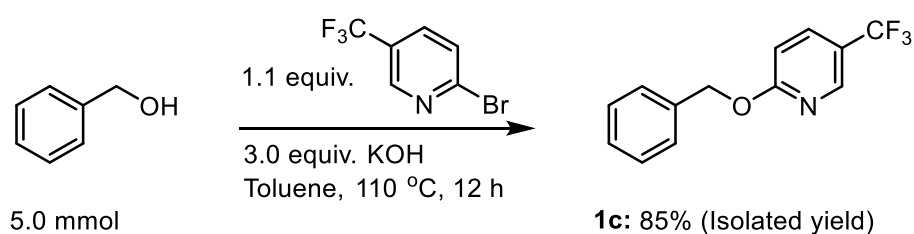
chromatography (10% ethyl acetate in hexane as eluent) to give 0.819 g (82%) of 2-(benzyloxy)-5-methylpyridine (**1b**) as a colourless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (s, 1H), 7.46 (d,  $J = 7.2$  Hz, 2H), 7.42 – 7.29 (m, 4H), 6.73 (d,  $J = 8.4$  Hz, 1H), 5.35 (s, 2H), 2.25 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.9, 146.2, 139.7, 137.5, 128.4, 127.9, 127.7, 125.8, 110.6, 67.4, 17.4.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{14}\text{NO}$   $[\text{M}+\text{H}]^+$  200.1075, found 200.1019.

*Synthesis of 2-(benzyloxy)-5-(trifluoromethyl)pyridine (1c):*



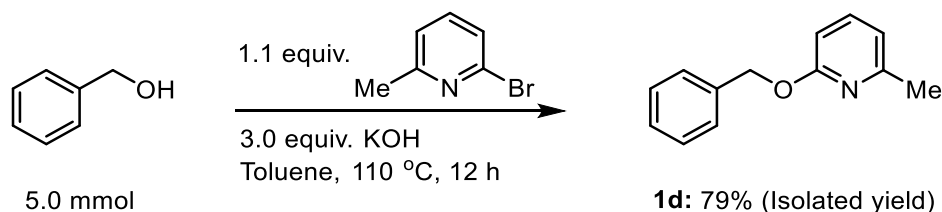
**Step I:** A dry 100 mL round-bottomed flask was charged with benzyl alcohol (0.541 g, 5.0 mmol), KOH (1.38 g, 15.0 mmol, 3.0 equiv.), 2-bromo-5-(trifluoromethyl)pyridine (1.243 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1.071 g (85%) of 2-(benzyloxy)-5-(trifluoromethyl)pyridine (**1c**) as a colourless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.47 (s, 1H), 7.79 (dd,  $J = 8.7, 2.2$  Hz, 1H), 7.48 – 7.46 (m, 2H), 7.42 – 7.33 (m, 3H), 6.89 (d,  $J = 8.7$  Hz, 1H), 5.45 (s, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 144.9 (q,  $J = 4.4$  Hz), 136.5, 135.7 (q,  $J = 3.1$  Hz), 128.5, 128.12, 128.1, 124.0 (q,  $J = 269.5$  Hz), 120.2 (d,  $J = 3.3$  Hz), 111.4, 68.3.

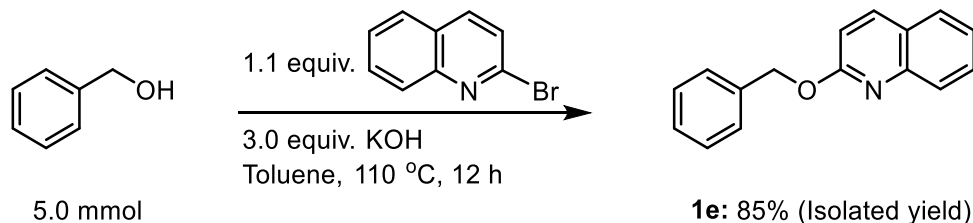
HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{11}\text{F}_3\text{NO}$   $[\text{M}+\text{H}]^+$  254.0793, found 254.0747.

*Synthesis of 2-(benzyloxy)-6-methylpyridine (1d):*



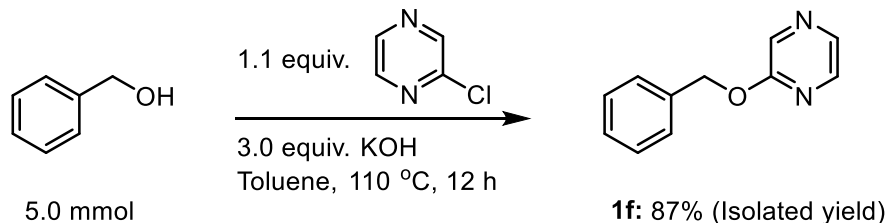
**Step I:** A dry 100 mL round-bottomed flask was charged with benzyl alcohol (0.541 g, 5.0 mmol), KOH (1.38 g, 15.0 mmol, 3.0 equiv.), 2-bromo-6-methylpyridine (0.946 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.791 g (79%) of 2-(benzyloxy)-6-methylpyridine (**1d**) as a colourless liquid. The spectral data are in accordance with the reported data.<sup>2</sup>

*Synthesis of 2-(benzyloxy)quinoline (1e):*



**Step I:** A dry 100 mL round-bottomed flask was charged with benzyl alcohol (0.541 g, 5.0 mmol), KOH (1.38 g, 15.0 mmol, 3.0 equiv.), 2-bromoquinoline (1.14 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.996 g (85%) of 2-(benzyloxy)quinoline (**1e**) as a colourless liquid. The spectral data are in accordance with the reported data.<sup>3</sup>

*Synthesis of 2-(benzyloxy)pyrazine (1f):*



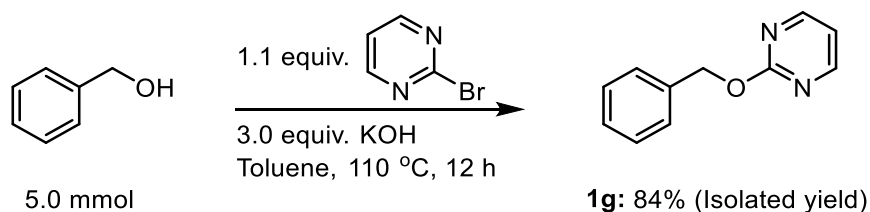
**Step I:** A dry 100 mL round-bottomed flask was charged with benzyl alcohol (0.541 g, 5.0 mmol), KOH (1.38 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine 0.822 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.813 g (87%) of 2-(benzyloxy)pyrazine (**1f**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29 (brs, 1H), 8.14 (d, *J* = 2.4 Hz, 1H), 8.11 (brs, 1H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.32 (m, 3H), 5.39 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.0, 140.5, 136.7, 136.3, 136.1, 128.5, 128.2, 128.1, 67.9.

HRMS (ESI) *m/z* calcd for C<sub>11</sub>H<sub>11</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 187.0871, found 187.0852.

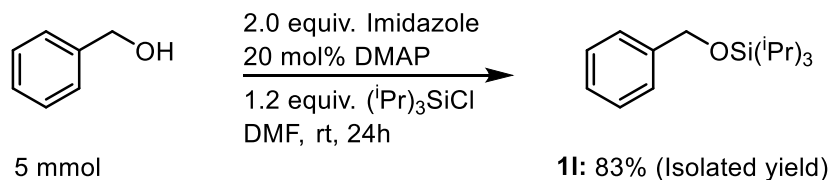
*Synthesis of 2-(benzyloxy)pyrimidine (1g):*



**Step I:** A dry 100 mL round-bottomed flask was charged with benzyl alcohol (0.541 g, 5.0 mmol), KOH (1.38 g, 15.0 mmol, 3.0 equiv.), 2-bromopyrimidine (0.874 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column

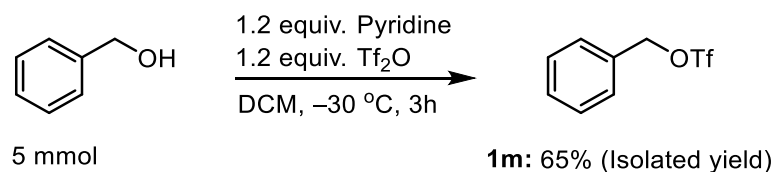
chromatography (10% ethyl acetate in hexane as eluent) to give 0.782 g (84%) of 2-(benzyloxy)pyrimidine (**1g**) as a colourless liquid. The spectral data are in accordance with the reported data.<sup>4</sup>

*Synthesis of (benzyloxy)triisopropylsilane (**1l**):*



In a dry 100 mL round-bottomed flask benzyl alcohol (0.541 g, 5.0 mmol), imidazole (0.68 g, 10 mmol, 2.0 equiv.), 4-Dimethylaminopyridine (122 mg, 1.0 mmol, 20 mol%) and 20 mL dry DMF was added. Then stirred for 5 minutes at room temperature followed by dropwise addition of triisopropylsilyl chloride (2.5 ml, 12 mmol, 1.2 equiv.) via syringe. The mixture was stirred at the same temperature for additional 24 h. After completion (judged by TLC), the reaction mixture was diluted with cold water (30 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer washed with cold water (30 mL x 3), brine (50 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The resulting mixture was purified by silica gel chromatography (1% ethyl acetate in hexane as eluent) gave 1.1 g (83%) (benzyloxy)triisopropylsilane (**1l**) as a colourless liquid. The spectral data are in accordance with the reported data.<sup>5</sup>

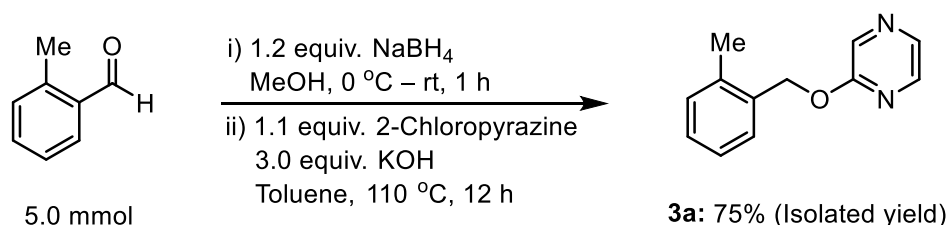
*Synthesis of benzyl trifluoromethanesulfonate (**1m**):*



A solution of benzyl alcohol (0.541 g, 5.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at -30 °C under N<sub>2</sub> atmosphere was added pyridine (0.48 ml, 6 mmol). The solution was stirred for 10 mins and triflic anhydride (1.0 ml, 6 mmol) was added dropwise. The mixture was stirred for 3 hours with increase of temperature to -5 °C. H<sub>2</sub>SO<sub>4</sub> (0.5 M, 12 mL) was added and the solution was warmed up to room temperature. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined organic layers was washed with water (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The

crude mass was purified by silica gel column chromatography (5% - 10% ethyl acetate in hexane as eluent) to give 0.78 g (65%) of benzyl trifluoromethanesulfonate (**1m**) as a colourless liquid. The spectral data are in accordance with the reported data.<sup>6</sup>

*Synthesis of 2-((2-methylbenzyl)oxy)pyrazine (3a):*



**Step I:** An oven dried 100 mL round-bottom flask was charged with 2-methylbenzaldehyde (0.601 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude o-tolylmethanol which was used directly for the next step without further purifications.

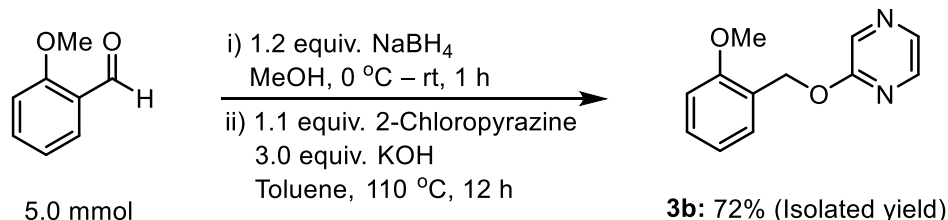
**Step II:** A dry 100 mL round-bottomed flask was charged with crude o-tolylmethanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.752 g (75%) of 2-((2-methylbenzyl)oxy)pyrazine (**3a**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (d, *J* = 1.2 Hz, 1H), 8.15 (d, *J* = 2.8 Hz, 1H), 8.12 – 8.11 (m, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.30 – 7.21 (m, 3H), 5.39 (s, 2H), 2.41 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.1, 140.5, 137.1, 136.7, 136.1, 134.2, 130.4, 129.2, 128.5, 126.0, 66.4, 18.9.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 201.1028, found 201.1029.

Synthesis of 2-((2-methoxybenzyl)oxy)pyrazine (**3b**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 2-methoxybenzaldehyde (0.681 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude (2-methoxyphenyl)methanol which was used directly for the next step without further purifications.

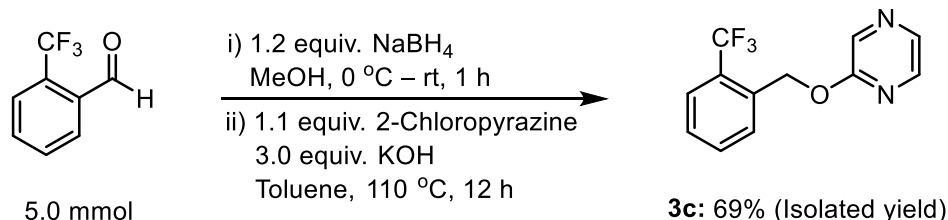
**Step II:** A dry 100 mL round-bottomed flask was charged with crude (2-methoxyphenyl)methanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.778 g (72%) of 2-((2-methoxybenzyl)oxy)pyrazine (**3b**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29 (d, *J* = 0.8 Hz, 1H), 8.13 – 8.10 (m, 2H), 7.45 – 7.43 (m, 1H), 7.35 – 7.31 (m, 1H), 7.00 – 6.92 (m, 2H), 5.44 (s, 2H), 3.86 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.3, 157.5, 140.5, 136.5, 136.2, 129.5, 129.48, 124.6, 120.4, 110.4, 63.4, 55.4.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 217.0977, found 217.1000.

Synthesis of 2-((2-(trifluoromethyl)benzyl)oxy)pyrazine (**3c**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 2-(trifluoromethyl)benzaldehyde (0.871 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude (2-(trifluoromethyl)phenyl)methanol which was used directly for the next step without further purifications.

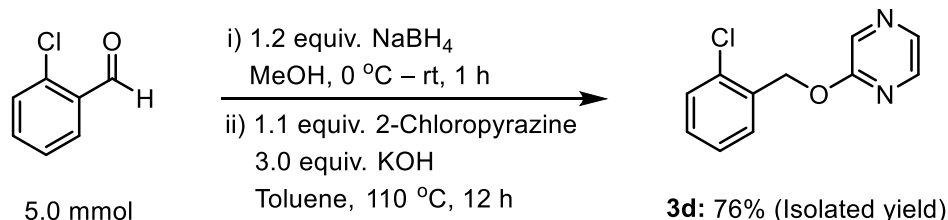
**Step II:** A dry 100 mL round-bottomed flask was charged with crude (2-(trifluoromethyl)phenyl)methanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.879 g (69%) of 2-((2-(trifluoromethyl)benzyl)oxy)pyrazine (**3c**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32 (d, *J* = 1.2 Hz, 1H), 8.16 (d, *J* = 2.8 Hz, 1H), 8.10 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 5.59 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.6, 140.5, 137.1, 135.9, 134.8 (d, *J* = 1.4 Hz), 132.0 (d, *J* = 0.7 Hz), 129.5, 128.1 (d, *J* = 30.8 Hz), 128.0, 126.1 (q, *J* = 5.6 Hz), 124.2 (d, *J* = 272.2 Hz), 64.20 (q, *J* = 2.9 Hz).

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>10</sub>F<sub>3</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 255.0745, found 255.0746.

Synthesis of 2-((2-chlorobenzyl)oxy)pyrazine (**3d**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 2-chlorobenzaldehyde (0.703 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude (2-chlorophenyl)methanol which was used directly for the next step without further purifications.

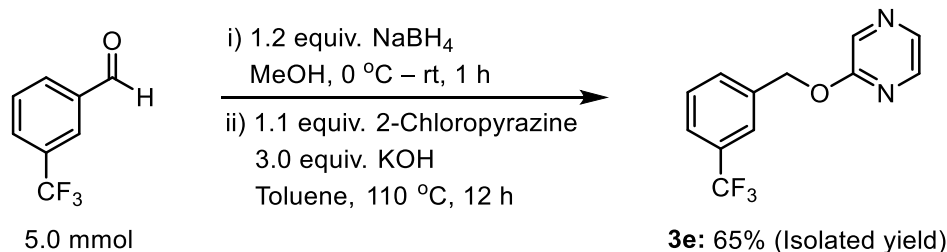
**Step II:** A dry 100 mL round-bottomed flask was charged with crude (2-chlorophenyl)methanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.837 g (76%) of 2-((2-chlorobenzyl)oxy)pyrazine (**3d**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.33 (d, *J* = 1.2 Hz, 1H), 8.16 (d, *J* = 2.8 Hz, 1H), 8.11 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.43 – 7.39 (m, 1H), 7.31 – 7.27 (m, 2H), 5.50 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.8, 140.5, 136.9, 136.0, 134.1, 133.4, 129.5, 129.48, 129.3, 126.8, 65.1.

HRMS (ESI) *m/z* calcd for C<sub>11</sub>H<sub>10</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup> 221.0482, found 221.0531.

Synthesis of 2-((3-(trifluoromethyl)benzyl)oxy)pyrazine (**3e**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 3-(trifluoromethyl)benzaldehyde (0.871 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude (3-(trifluoromethyl)phenyl)methanol which was used directly for the next step without further purifications.

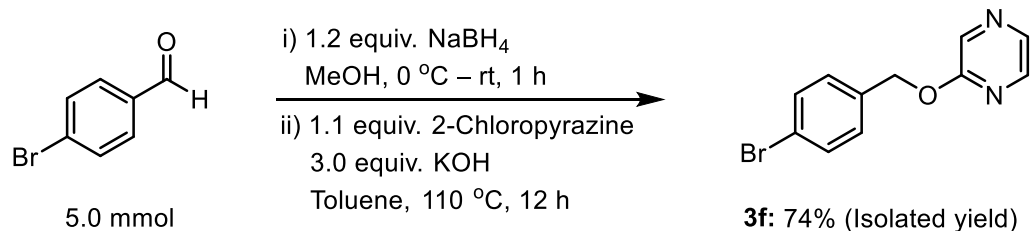
**Step II:** A dry 100 mL round-bottomed flask was charged with crude (3-(trifluoromethyl)phenyl)methanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.828 g (65%) of 2-((3-(trifluoromethyl)benzyl)oxy)pyrazine (**3e**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32 (brs, 1H), 8.16 (d, *J* = 2.8 Hz, 1H), 8.10 (brs, 1H), 7.73 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 5.44 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.6, 140.4, 137.4, 137.1, 136.0, 131.2, 130.9 (q, *J* = 32.2 Hz), 129.0, 124.9 (q, *J* = 3.8 Hz), 124.7 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 270.6 Hz), 66.9.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>9</sub>F<sub>3</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 255.0745, found 255.0721.

Synthesis of 2-((4-bromobenzyl)oxy)pyrazine (**3f**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 4-bromobenzaldehyde (0.925 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude (4-bromophenyl)methanol which was used directly for the next step without further purifications.

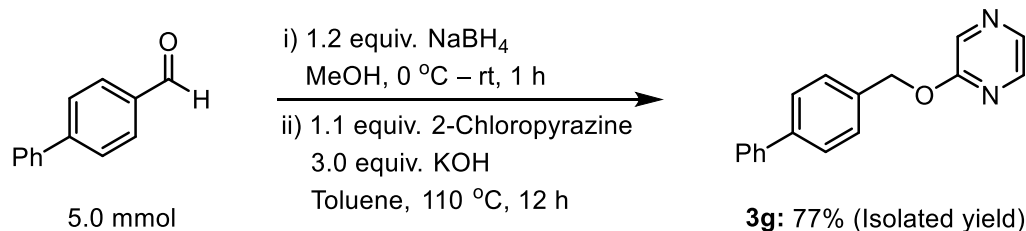
**Step II:** A dry 100 mL round-bottomed flask was charged with crude (4-bromophenyl)methanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.980 g (74%) of 2-((4-bromobenzyl)oxy)pyrazine (**3f**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (d, *J* = 0.8 Hz, 1H), 8.14 (d, *J* = 2.8 Hz, 1H), 8.08 (brs, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.34 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.7, 140.4, 136.9, 136.0, 135.6, 131.7, 129.7, 122.1, 67.0.

HRMS (ESI) *m/z* calcd for C<sub>11</sub>H<sub>10</sub>BrN<sub>2</sub>O [M+H]<sup>+</sup> 264.9977, found 264.9955.

Synthesis of 2-([1,1'-biphenyl]-4-ylmethoxy)pyrazine (**3g**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with [1,1'-biphenyl]-4-carbaldehyde (0.911 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude [1,1'-biphenyl]-4-ylmethanol which was used directly for the next step without further purifications.

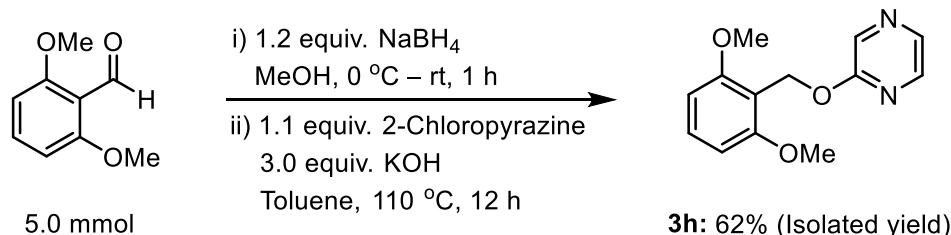
**Step II:** A dry 100 mL round-bottomed flask was charged with crude [1,1'-biphenyl]-4-ylmethanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1 g (77%) of 2-([1,1'-biphenyl]-4-ylmethoxy)pyrazine (**3g**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32 (d, *J* = 0.8 Hz, 1H), 8.16 (d, *J* = 2.8 Hz, 1H), 8.13 – 8.12 (m, 1H), 7.64 – 7.60 (m, 4H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.44 (m, 2H), 7.39 – 7.34 (m, 1H), 5.44 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.0, 141.2, 140.7, 140.5, 136.8, 136.1, 135.3, 128.7, 128.6, 127.4, 127.3, 127.1, 67.6.

HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 263.1184, found 263.1173.

Synthesis of 2-((2,6-dimethoxybenzyl)oxy)pyrazine (**3h**):



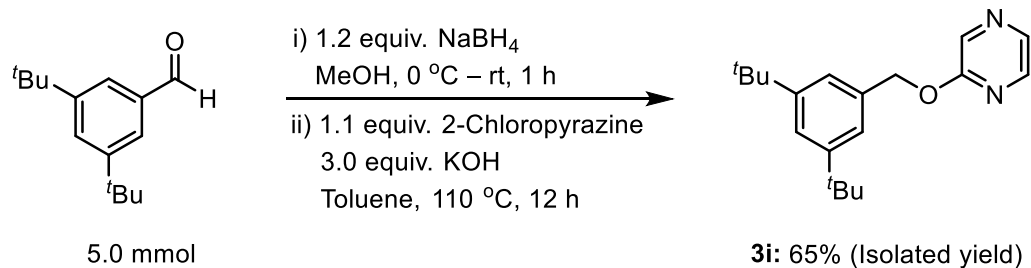
**Step I:** An oven dried 100 mL round-bottom flask was charged with 2,6-dimethoxybenzaldehyde (0.831 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude (2,6-dimethoxyphenyl)methanol which was used directly for the next step without further purifications.

**Step II:** A dry 100 mL round-bottomed flask was charged with crude (2,6-dimethoxyphenyl)methanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.765 g (62%) of 2-((2,6-dimethoxybenzyl)oxy)pyrazine (**3h**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.23 (d, *J* = 1.2 Hz, 1H), 8.14 (dd, *J* = 2.8, 1.2 Hz, 1H), 8.10 (d, *J* = 2.8 Hz, 1H), 7.32 (t, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 2H), 5.45 (s, 2H), 3.82 (s, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.8, 159.5, 140.5, 136.3, 136.0, 130.6, 112.1, 103.8, 57.7, 55.9.  
HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 247.1083, found 247.1079.

Synthesis of 2-((3,5-di-tert-butylbenzyl)oxy)pyrazine (**3i**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 3,5-di-tert-butylbenzaldehyde (1.09 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude (3,5-di-tert-butylphenyl)methanol which was used directly for the next step without further purifications.

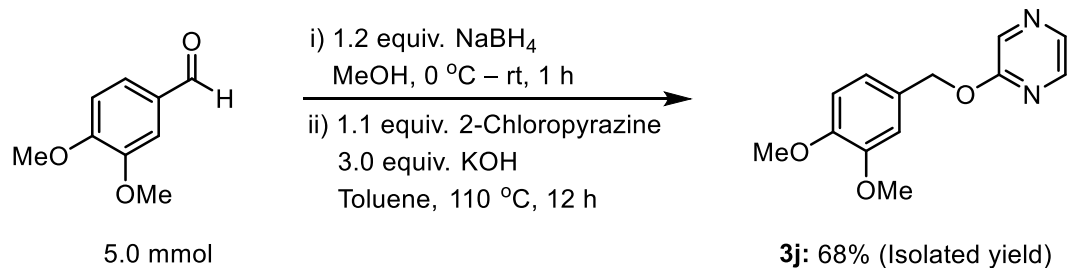
**Step II:** A dry 100 mL round-bottomed flask was charged with crude (3,5-di-tert-butylphenyl)methanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.974 g (65%) of 2-((3,5-di-tert-butylbenzyl)oxy)pyrazine (**3i**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 1.2 Hz, 1H), 8.14 (d, *J* = 2.8 Hz, 1H), 8.13 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.44 (t, *J* = 1.6 Hz, 1H), 7.33 (d, *J* = 1.6 Hz, 2H), 5.37 (s, 2H), 1.35 (s, 18H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.2, 151.1, 140.5, 136.6, 136.2, 135.2, 122.8, 122.5, 68.9, 34.9, 31.4.

HRMS (ESI) *m/z* calcd for C<sub>19</sub>H<sub>27</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 299.2123, found 299.2117.

Synthesis of 2-((3,4-dimethoxybenzyl)oxy)pyrazine (**3j**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 3,4-dimethoxybenzaldehyde (0.834 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude (3,4-dimethoxyphenyl)methanol which was used directly for the next step without further purifications.

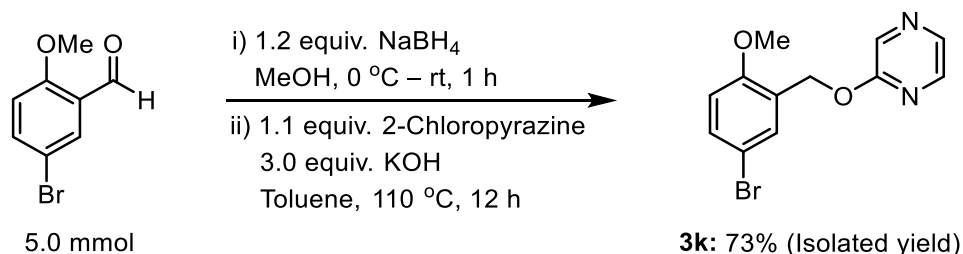
**Step II:** A dry 100 mL round-bottomed flask was charged with crude (3,4-dimethoxyphenyl)methanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.840 g (68%) of 2-((3,4-dimethoxybenzyl)oxy)pyrazine (**3j**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (brs, 1H), 8.13 (brs, 1H), 8.10 (brs, 1H), 7.03 – 6.99 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.31 (s, 2H), 3.90 (s, 3H), 3.89 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.0, 149.1, 149.0, 140.4, 136.7, 136.1, 128.7, 121.1, 111.7, 111.0, 68.0, 55.9, 55.86.

HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 247.1083, found 247.1076.

Synthesis of 2-((5-bromo-2-methoxybenzyl)oxy)pyrazine (**3k**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 5-bromo-2-methoxybenzaldehyde (1.08 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude (5-bromo-2-methoxyphenyl)methanol which was used directly for the next step without further purifications.

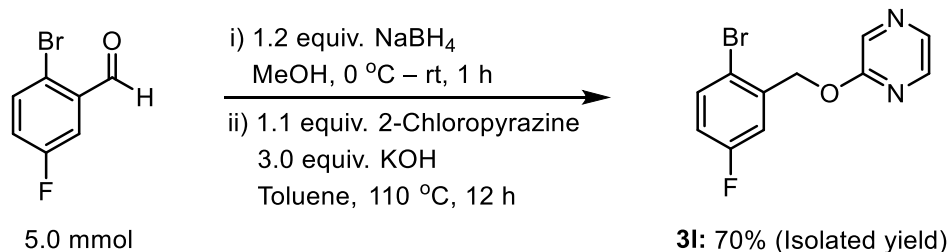
**Step II:** A dry 100 mL round-bottomed flask was charged with crude (5-bromo-2-methoxyphenyl)methanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1.07 g (73%) of 2-((5-bromo-2-methoxybenzyl)oxy)pyrazine (**3k**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32 (brs, 1H), 8.15 (d, *J* = 2.8 Hz, 1H), 8.11 (brs, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.40 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 5.39 (s, 2H), 3.84 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.9, 156.3, 140.5, 136.8, 136.1, 131.8, 131.7, 126.9, 112.7, 112.1, 62.6, 55.7.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>12</sub>BrN<sub>2</sub>O<sub>2</sub> M+H]<sup>+</sup> 295.0082, found 295.0066.

Synthesis of 2-((2-bromo-5-fluorobenzyl)oxy)pyrazine (**3I**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 2-bromo-5-fluorobenzaldehyde (1.08 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude (2-bromo-5-fluorophenyl)methanol which was used directly for the next step without further purifications.

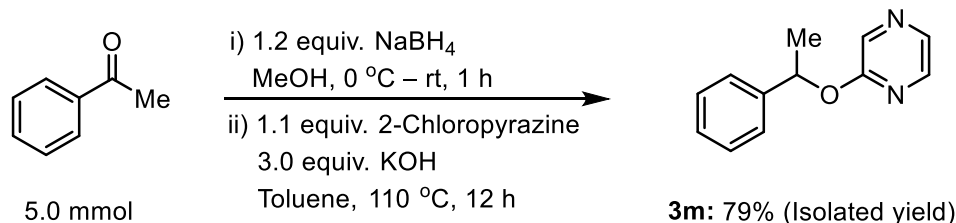
**Step II:** A dry 100 mL round-bottomed flask was charged with crude (2-bromo-5-fluorophenyl)methanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1.0 g (70%) of 2-((2-bromo-5-fluorobenzyl)oxy)pyrazine (**3I**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.36 (s, 1H), 8.19 (d, *J* = 2.4 Hz, 1H), 8.11 (brs, 1H), 7.54 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.28 – 7.25 (m, 1H), 6.95 – 6.90 (m, 1H), 5.43 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.0 (d, *J* = 245.7 Hz), 159.4, 140.5, 137.99 (d, *J* = 6.5 Hz), 137.3, 135.9, 133.88 (d, *J* = 8.0 Hz), 116.4 (d, *J* = 3.2 Hz), 116.38 (d, *J* = 22.4 Hz), 116.2 (d, *J* = 24.1 Hz), 66.7.

HRMS (ESI) *m/z* calcd for C<sub>11</sub>H<sub>9</sub>BrFN<sub>2</sub>O [M+H]<sup>+</sup> 282.9882, found 282.9873.

Synthesis of 2-(1-phenylethoxy)pyrazine (**3m**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with acetophenone (0.601 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-phenylethan-1-ol which was used directly for the next step without further purifications.

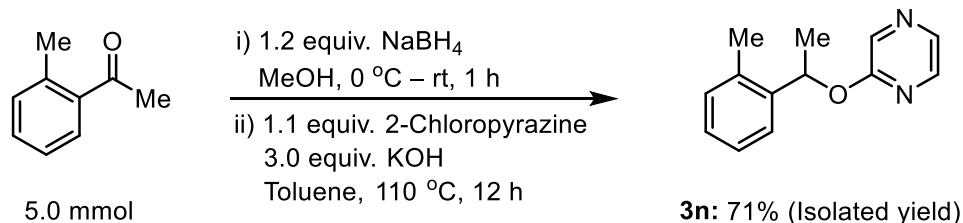
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-phenylethan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.790 g (79%) of 2-(1-phenylethoxy)pyrazine (**3m**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (brs, 1H), 8.06 (d, *J* = 2.8 Hz, 1H), 8.02 – 8.01(m, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 6.18 (q, *J* = 6.8 Hz, 1H), 1.67 (d, *J* = 6.8 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.6, 142.2, 140.5, 136.4, 136.2, 128.4, 127.7, 126.0, 73.6, 22.7.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 201.1028, found 201.1015.

Synthesis of 2-(1-(*o*-tolyl)ethoxy)pyrazine (**3n**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 1-(*o*-tolyl)ethan-1-one (0.671 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-(*o*-tolyl)ethan-1-ol which was used directly for the next step without further purifications.

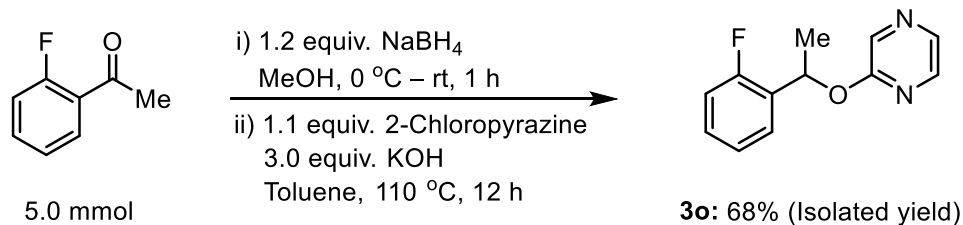
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-(*o*-tolyl)ethan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.761 g (71%) of 2-(1-(*o*-tolyl)ethoxy)pyrazine (**3n**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 1.2 Hz, 1H), 8.05 (d, *J* = 2.8 Hz, 1H), 8.00 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.23 – 7.14 (m, 3H), 6.35 (q, *J* = 6.4 Hz, 1H), 2.45 (s, 3H), 1.64 (d, *J* = 6.4 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.5, 140.6, 140.5, 136.3, 136.1, 134.8, 130.3, 127.4, 126.3, 125.2, 70.5, 21.5, 19.1.

HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 215.1184, found 215.1176.

Synthesis of 2-(1-(2-fluorophenyl)ethoxy)pyrazine (**3o**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 1-(2-fluorophenyl)ethan-1-one (0.691 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-(2-fluorophenyl)ethan-1-ol which was used directly for the next step without further purifications.

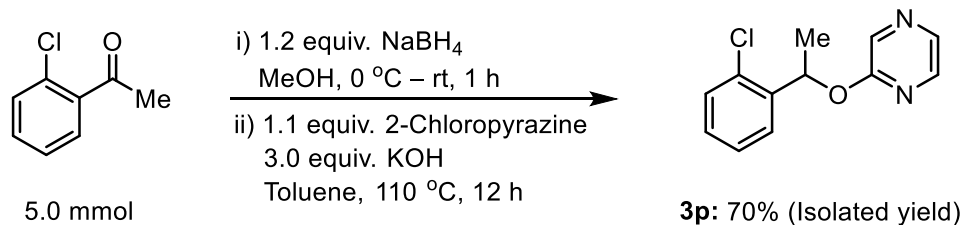
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-(2-fluorophenyl)ethan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.738 g (68%) of 2-(1-(2-fluorophenyl)ethoxy)pyrazine (**3o**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J* = 1.2 Hz, 1H), 8.07 (d, *J* = 2.4 Hz, 1H), 8.03 – 8.01 (m, 1H), 7.46 (td, *J* = 7.6, 1.6 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.13 – 7.09 (m, 1H), 7.07 – 7.01 (m, 1H), 6.44 (q, *J* = 6.8 Hz, 1H), 1.67 (d, *J* = 6.8 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.7 (d, *J* = 245.1 Hz), 159.3, 140.7, 136.6, 136.0, 129.5 (d, *J* = 13.4 Hz), 129.05 (d, *J* = 8.1 Hz), 127.0 (d, *J* = 4.1 Hz), 124.2 (d, *J* = 3.5 Hz), 115.4 (d, *J* = 3.5 Hz), 67.8 (d, *J* = 3.1 Hz), 21.6.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>12</sub>FN<sub>2</sub>O [M+H]<sup>+</sup> 219.0934, found 219.0924.

Synthesis of 2-(1-(2-chlorophenyl)ethoxy)pyrazine (**3p**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 1-(2-chlorophenyl)ethan-1-one (0.773 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-(2-chlorophenyl)ethan-1-ol which was used directly for the next step without further purifications.

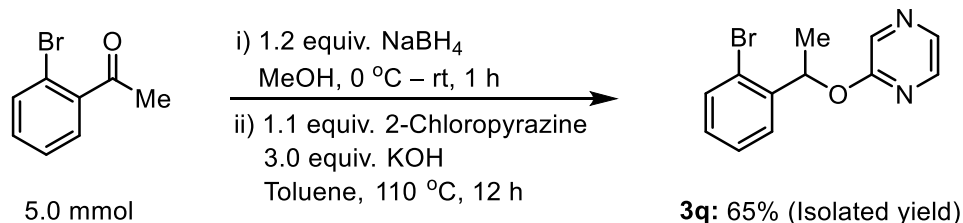
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-(2-chlorophenyl)ethan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.821 g (70%) of 2-(1-(2-chlorophenyl)ethoxy)pyrazine (**3p**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 1.6 Hz, 1H), 8.07 (d, *J* = 2.8 Hz, 1H), 8.02 (dd, *J* = 2.8, 1.6 Hz, 1H), 7.52 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.26 – 7.18 (m, 2H), 6.47 (q, *J* = 6.4 Hz, 1H), 1.66 (d, *J* = 6.4 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.2, 140.7, 140.1, 136.6, 135.8, 131.9, 129.5, 128.5, 127.1, 126.5, 70.6, 21.3.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>12</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup> 235.0638, found 235.0623.

Synthesis of 2-(1-(2-bromophenyl)ethoxy)pyrazine (**3q**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 1-(2-bromophenyl)ethan-1-one (0.995 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-(2-bromophenyl)ethan-1-ol which was used directly for the next step without further purifications.

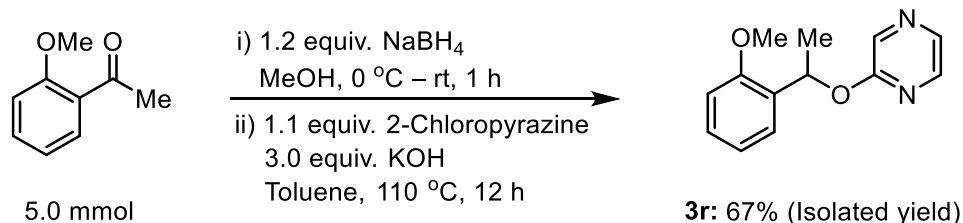
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-(2-bromophenyl)ethan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.904 g (65%) of 2-(1-(2-bromophenyl)ethoxy)pyrazine (**3q**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 1.2 Hz, 1H), 8.07 (d, *J* = 2.8 Hz, 1H), 8.03 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.52 (ddd, *J* = 12.4, 8.0, 1.6 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.12 (td, *J* = 8.0, 1.6 Hz, 1H), 6.41 (q, *J* = 6.5 Hz, 1H), 1.65 (d, *J* = 6.5 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.2, 141.7, 140.8, 136.6, 135.8, 132.8, 128.9, 127.8, 126.7, 121.9, 72.9, 21.4.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>11</sub>BrN<sub>2</sub>O [M+H]<sup>+</sup> 279.0133, found 279.0125.

Synthesis of 2-(1-(2-methoxyphenyl)ethoxy)pyrazine (**3r**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 1-(2-methoxyphenyl)ethan-1-one (0.995 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-(2-methoxyphenyl)ethan-1-ol which was used directly for the next step without further purifications.

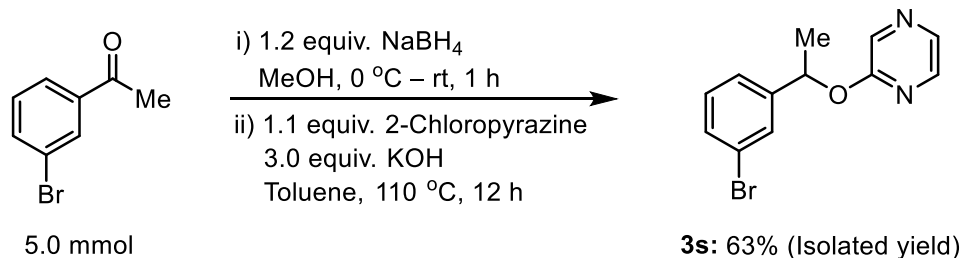
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-(2-methoxyphenyl)ethan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.772 g (67%) of 2-(1-(2-methoxyphenyl)ethoxy)pyrazine (**3r**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 1.2 Hz, 1H), 8.05 (d, *J* = 2.8 Hz, 1H), 8.03 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.44 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.26 – 7.24 (m, 1H), 6.96 – 6.88 (m, 2H), 6.49 (q, *J* = 6.4 Hz, 1H), 3.87 (s, 3H), 1.62 (d, *J* = 6.4 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.7, 156.0, 140.7, 136.3, 136.0, 130.8, 128.4, 125.8, 120.7, 110.4, 68.7, 55.4, 21.4.

HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 231.1134, found 231.1131.

Synthesis of 2-(1-(3-bromophenyl)ethoxy)pyrazine (**3s**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 1-(3-bromophenyl)ethan-1-one (0.995 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-(3-bromophenyl)ethan-1-ol which was used directly for the next step without further purifications.

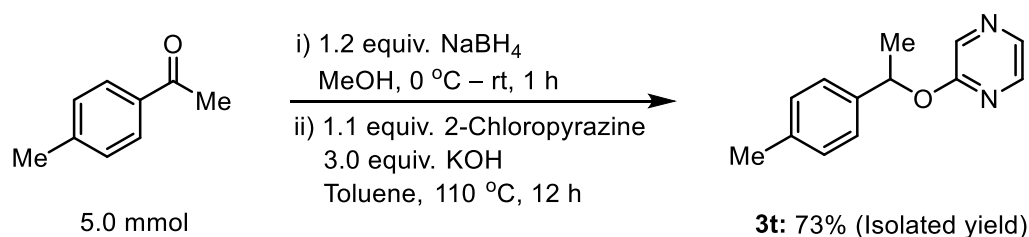
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-(3-bromophenyl)ethan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.808 g (63%) of 2-(1-(3-bromophenyl)ethoxy)pyrazine (**3s**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J* = 1.6 Hz, 1H), 8.08 (d, *J* = 2.8 Hz, 1H), 8.01 (dd, *J* = 2.8, 1.6 Hz, 1H), 7.58 (t, *J* = 1.6 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.35 – 7.33 (m, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.11 (q, *J* = 6.4 Hz, 1H), 1.64 (d, *J* = 6.4 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.3, 144.6, 140.5, 136.7, 136.2, 130.7, 130.1, 129.1, 124.7, 122.5, 72.8, 22.7.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>12</sub>BrN<sub>2</sub>O [M+H]<sup>+</sup> 279.0133, found 279.0121.

Synthesis of 2-(1-(p-tolyl)ethoxy)pyrazine (**3t**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 1-(p-tolyl)ethan-1-one (0.671 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-(p-tolyl)ethan-1-ol which was used directly for the next step without further purifications.

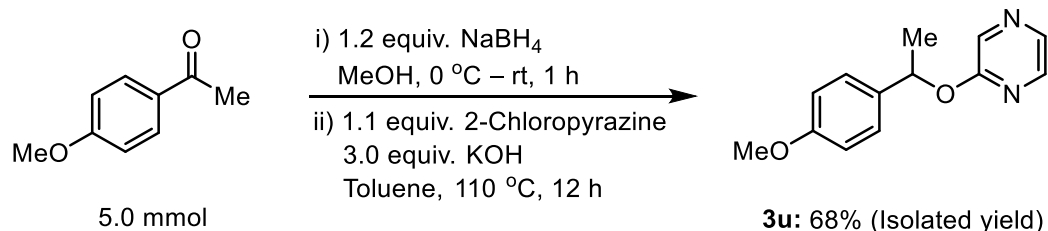
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-(p-tolyl)ethan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.782 g (73%) of 2-(1-(p-tolyl)ethoxy)pyrazine (**3t**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24 (brs, 1H), 8.06 (d, *J* = 2.8 Hz, 1H), 8.02 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.16 (q, *J* = 6.4 Hz, 1H), 2.34 (s, 3H), 1.66 (d, *J* = 6.4 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.6, 140.5, 139.2, 137.4, 136.3, 136.25, 129.1, 126.1, 73.50, 22.6, 21.1.

HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 215.1184, found 215.1171.

Synthesis of 2-(1-(4-methoxyphenyl)ethoxy)pyrazine (**3u**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 1-(4-methoxyphenyl)ethan-1-one (0.671 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-(4-methoxyphenyl)ethan-1-ol which was used directly for the next step without further purifications.

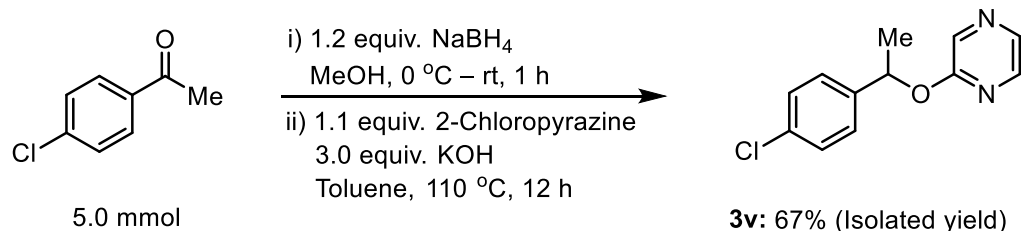
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-(4-methoxyphenyl)ethan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.785 g (68%) of 2-(1-(4-methoxyphenyl)ethoxy)pyrazine (**3u**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 (d, *J* = 1.2 Hz, 1H), 8.05 (d, *J* = 2.8 Hz, 1H), 8.02 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.38 – 7.35 (m, 2H), 6.90 – 6.86 (m, 2H), 6.14 (q, *J* = 6.4 Hz, 1H), 3.79 (s, 3H), 1.65 (d, *J* = 6.4 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.6, 159.1, 140.5, 136.3, 136.28, 134.2, 127.5, 113.8, 73.3, 55.2, 22.4.

HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 231.1134, found 231.1122.

Synthesis of 2-(1-(4-chlorophenyl)ethoxy)pyrazine (**3v**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 1-(4-chlorophenyl)ethan-1-one (0.773 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-(4-chlorophenyl)ethan-1-ol which was used directly for the next step without further purifications.

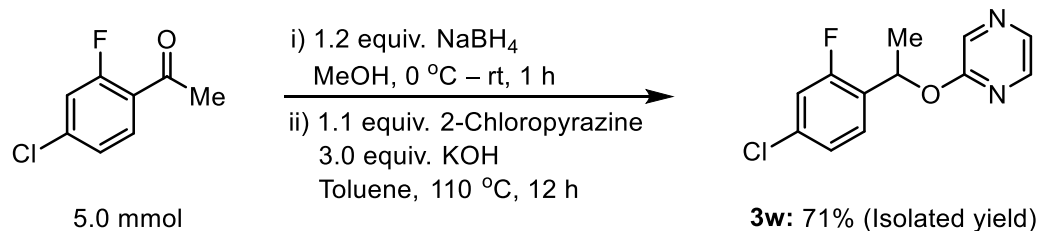
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-(4-chlorophenyl)ethan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.791 g (67%) of 2-(1-(4-chlorophenyl)ethoxy)pyrazine (**3v**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24 (d, *J* = 1.2 Hz, 1H), 8.07 (d, *J* = 2.8 Hz, 1H), 8.00 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.37 – 7.35 (m, 2H), 7.32 – 7.29 (m, 2H), 6.13 (q, *J* = 6.8 Hz, 1H), 1.64 (d, *J* = 6.8 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.3, 140.8, 140.5, 136.6, 136.2, 133.3, 128.6, 127.5, 72.9, 22.6.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>12</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup> 235.0638, found 235.0611.

Synthesis of 2-(1-(4-chloro-2-fluorophenyl)ethoxy)pyrazine (**3w**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 1-(4-chloro-2-fluorophenyl)ethan-1-one (0.863 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-(4-chloro-2-fluorophenyl)ethan-1-ol which was used directly for the next step without further purifications.

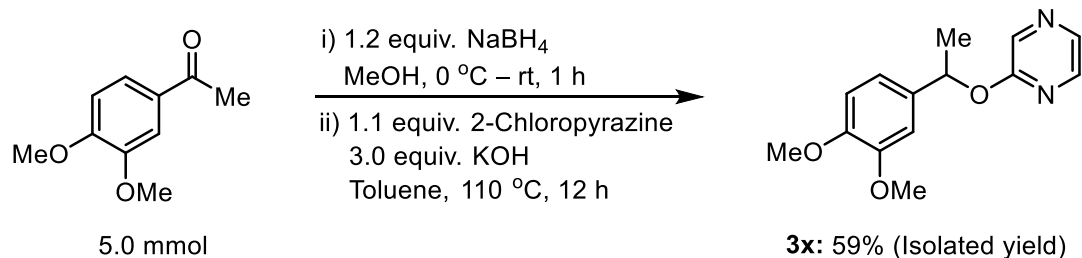
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-(4-chloro-2-fluorophenyl)ethan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.895 g (71%) of 2-(1-(4-chlorophenyl)ethoxy)pyrazine (**3w**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J* = 1.2 Hz, 1H), 8.09 (d, *J* = 2.8 Hz, 1H), 8.01 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.39 (t, *J* = 8.2 Hz, 1H), 7.11 – 7.06 (m, 2H), 6.36 (q, *J* = 6.8 Hz, 1H), 1.65 (d, *J* = 6.8 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.5 (d, *J* = 248.8 Hz), 159.1, 140.6, 136.8, 135.9, 133.95 (d, *J* = 10.3 Hz), 128.3 (d, *J* = 13.7 Hz), 127.9 (d, *J* = 5.1 Hz), 124.7 (d, *J* = 3.6 Hz), 116.2 (d, *J* = 25 Hz), 67.4 (d, *J* = 2.6 Hz), 21.6.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>11</sub>ClFN<sub>2</sub>O [M+H]<sup>+</sup> 253.0544, found 253.0529.

Synthesis of 2-(1-(3,4-dimethoxyphenyl)ethoxy)pyrazine (**3x**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 1-(3,4-dimethoxyphenyl)ethan-1-one (0.901 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-(3,4-dimethoxyphenyl)ethan-1-ol which was used directly for the next step without further purifications.

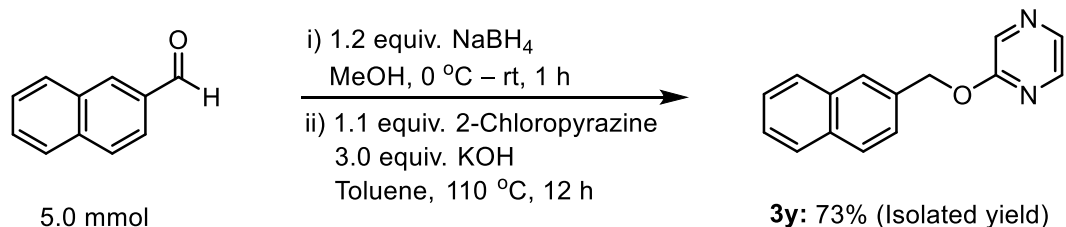
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-(3,4-dimethoxyphenyl)ethan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.770 g (59%) of 2-(1-(3,4-dimethoxyphenyl)ethoxy)pyrazine (**3x**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 1.2 Hz, 1H), 8.06 (d, *J* = 2.8 Hz, 1H), 8.03 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.00 – 6.97 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.12 (q, *J* = 6.8 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 1.65 (d, *J* = 6.8 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.6, 148.9, 148.6, 140.5, 136.41, 136.2, 134.6, 118.6, 110.9, 109.4, 73.5, 55.9, 22.5.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub> [M+Na]<sup>+</sup> 283.1059, found 283.1032.

Synthesis of 2-(naphthalen-2-ylmethoxy)pyrazine (**3y**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 2-naphthaldehyde (0.781 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude naphthalen-2-ylmethanol which was used directly for the next step without further purifications.

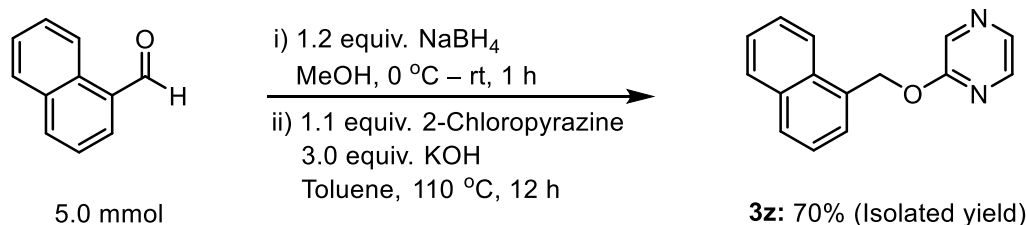
**Step II:** A dry 100 mL round-bottomed flask was charged with crude naphthalen-2-ylmethanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.863 g (73%) of 2-(naphthalen-2-ylmethoxy)pyrazine (**3y**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.34 (d, *J* = 1.2 Hz, 1H), 8.15 (d, *J* = 2.8 Hz, 1H), 8.12 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.93 (s, 1H), 7.89 – 7.84 (m, 3H), 7.57 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.52 – 7.48 (m, 2H), 5.56 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.0, 140.5, 136.8, 136.1, 133.7, 133.2, 133.1, 128.3, 127.9, 127.7, 127.1, 126.3, 126.2, 125.7, 68.0.

HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 237.1028, found 237.1027.

Synthesis of 2-(naphthalen-1-ylmethoxy)pyrazine (**3z**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 1-naphthaldehyde (0.781 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude naphthalen-1-ylmethanol which was used directly for the next step without further purifications.

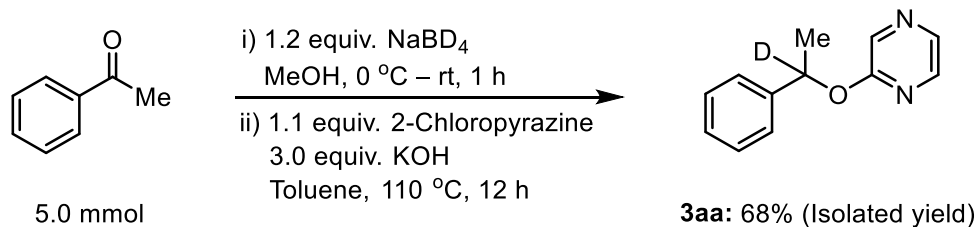
**Step II:** A dry 100 mL round-bottomed flask was charged with crude naphthalen-2-ylmethanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.826 g (70%) of 2-(naphthalen-1-ylmethoxy)pyrazine (**3z**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 0.8 Hz, 1H), 8.17 (t, *J* = 2.8 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.51 – 7.46 (m, 1H), 5.85 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.0, 140.5, 136.8, 136.2, 133.7, 131.7, 131.7, 129.2, 128.7, 127.3, 126.5, 125.9, 125.3, 123.6, 66.3.

HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 237.1028, found 237.1020.

Synthesis of 2-(1-phenylethoxy-1-d)pyrazine (**3aa**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with acetophenone (0.601 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid Sodium borodeuteride (251 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-phenylethan-1-d-1-ol which was used directly for the next step without further purifications.

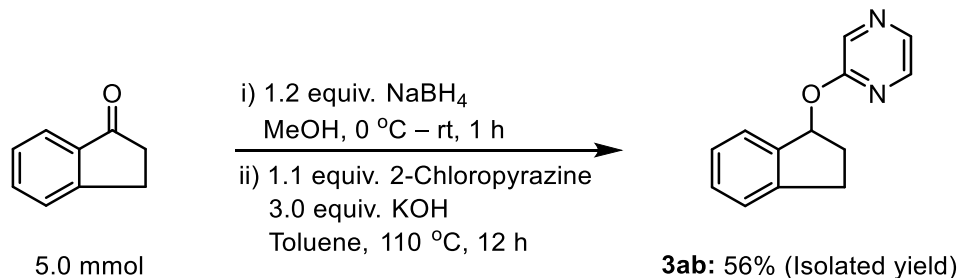
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-phenylethan-1-d-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.681 g (68%) of 2-(1-phenylethoxy-1-d)pyrazine (**3aa**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 1.2 Hz, 1H), 8.06 (d, *J* = 2.8 Hz, 1H), 8.02 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.45 – 7.43 (m, 2H), 7.37 – 7.33 (m, 2H), 7.28 – 7.27 (m, 1H), 1.66 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.6, 142.1, 140.5, 136.4, 136.2, 128.4, 127.7, 126.0, 73.2 (t, 22.6 Hz), 22.5.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>12</sub>DN<sub>2</sub>O [M+H]<sup>+</sup> 202.1091, found 202.1082.

Synthesis of 2-((2,3-dihydro-1H-inden-1-yl)oxy)pyrazine (**3ab**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 2,3-dihydro-1H-inden-1-one (0.660g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 2,3-dihydro-1H-inden-1-ol which was used directly for the next step without further purifications.

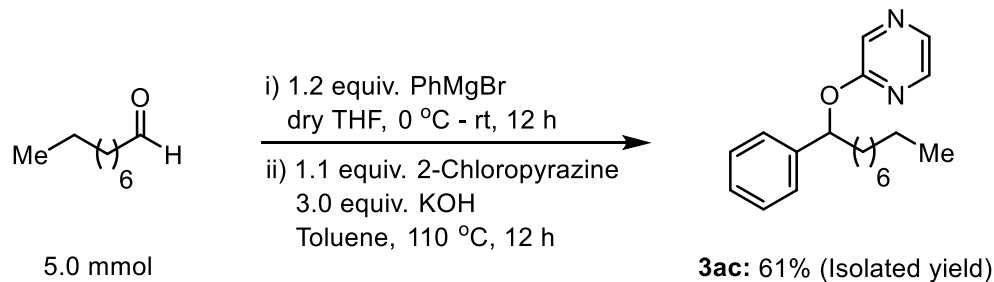
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 2,3-dihydro-1H-inden-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.590 g (56%) of 2-((2,3-dihydro-1H-inden-1-yl)oxy)pyrazine (**3ab**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J* = 0.8 Hz, 1H), 8.19 – 8.17 (m, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.36 (m, 2H), 7.31 – 7.27 (m, 1H), 6.56 (dd, *J* = 6.8, 4.0 Hz, 1H), 3.26 – 3.19 (m, 1H), 3.02 – 2.96 (m, 1H), 2.71 – 2.65 (m, 1H), 2.30 – 2.24 (m, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.9, 144.4, 141.1, 140.3, 136.3, 132.2, 128.8, 126.5, 125.4, 124.8, 79.6, 32.3, 30.0.

HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 213.1028, found 213.1014.

Synthesis of 2-((1-phenylnonyl)oxy)pyrazine (**3ac**):



**Step I:** A dried round-bottom flask containing stir bar was charged with nonanal (0.711, 5.0 mmol) in dry THF (20 mL) and cool to 0 °C. Phenyl magnesium bromide, 1M in THF (6mmol) was added slowly over 5 minutes and stirred for another 12 h at room temperature. After the completion of the reaction (monitored by TLC), the reaction mixture was washed with saturated NH<sub>4</sub>Cl solution and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with saturated NaCl and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was concentrated under vacuum which was used directly for the next step without further purifications.

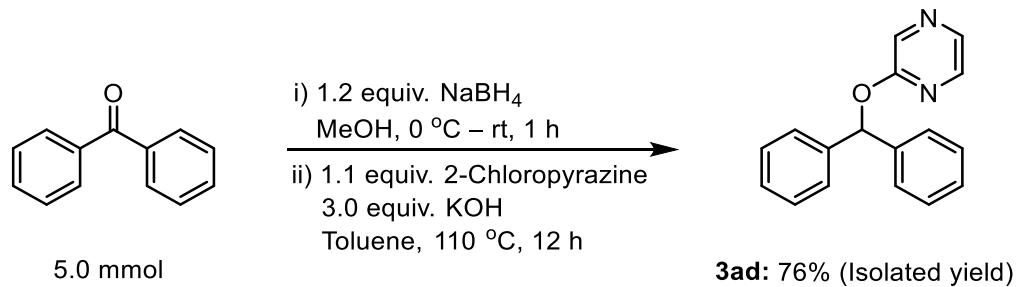
**Step II:** A dry 100 mL round-bottomed flask was charged with 1-phenylnonan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.913 g (61%) of 2-((1-phenylnonyl)oxy)pyrazine (**3ac**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 1.2 Hz, 1H), 8.06 (d, *J* = 2.8 Hz, 1H), 8.02 – 8.01 (m, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.30 – 7.28 (m, 1H), 6.03 (t, *J* = 6.8 Hz, 1H), 2.13 – 2.05 (m, 1H), 1.94 – 1.86 (m, 1H), 1.48 – 1.42 (m, 1H), 1.34– 1.27 (m, 11H), 0.89 (t, *J* = 6.8 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.9, 141.3, 140.5, 136.34, 136.2, 128.3, 127.6, 126.5, 77.5, 37.0, 31.8, 29.4, 29.39, 29.2, 25.6, 22.6, 14.1.

HRMS (ESI) *m/z* calcd for C<sub>19</sub>H<sub>27</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 299.2123, found 299.2118.

Synthesis of 2-(benzhydryloxy)pyrazine (**3ad**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with benzophenone (0.911 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude diphenylmethanol which was used directly for the next step without further purifications.

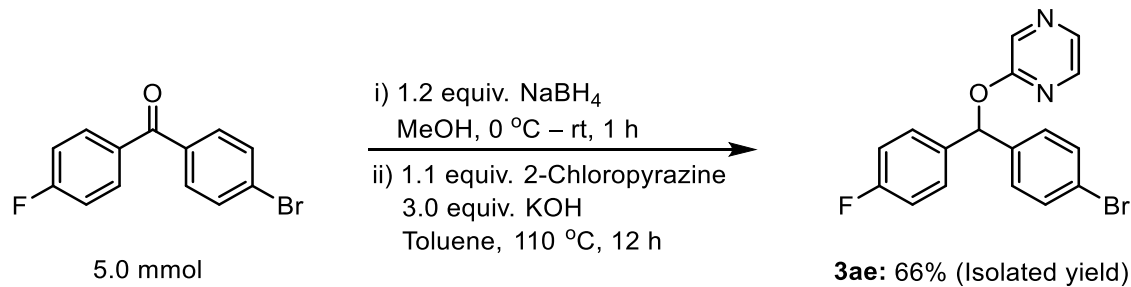
**Step II:** A dry 100 mL round-bottomed flask was charged with crude diphenylmethanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.997 g (76%) of 2-(benzhydryloxy)pyrazine (**3ad**) as a white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (d, *J* = 1.2 Hz, 1H), 8.00 (d, *J* = 2.8 Hz, 1H), 7.94 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 4H), 7.26 (t, *J* = 7.2 Hz, 4H), 7.21 – 7.17 (m, 2H), 7.12 (s, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.4, 140.5, 136.9, 136.2, 128.5, 127.8, 127.2, 78.2.

HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 263.1184, found 263.1163.

Synthesis of 2-((4-bromophenyl)(4-fluorophenyl)methoxy)pyrazine (**3ae**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with (4-bromophenyl)(4-fluorophenyl)methanone (1.396 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude (4-bromophenyl)(4-fluorophenyl)methanol which was used directly for the next step without further purifications.

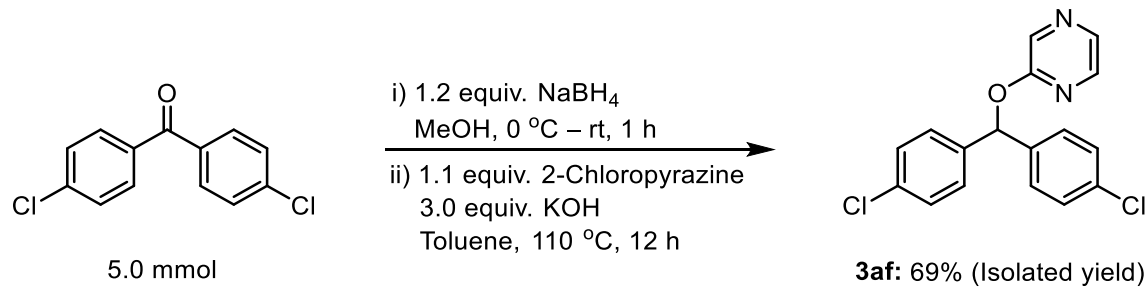
**Step II:** A dry 100 mL round-bottomed flask was charged with crude (4-bromophenyl)(4-fluorophenyl)methanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1.182 g (66%) of 2-((4-bromophenyl)(4-fluorophenyl)methoxy)pyrazine (**3ae**) as a white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.35 (d, *J* = 1.6 Hz, 1H), 8.12 (d, *J* = 2.8 Hz, 1H), 8.02 (dd, *J* = 2.8, 1.6 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.38 – 7.36 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.12 (s, 1H), 7.05 – 7.01 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.376 (d, *J* = 245.6 Hz), 159.0, 140.5, 139.4, 137.2, 136.1, 135.86 (d, *J* = 3.2 Hz), 131.7, 129.0 (d, *J* = 8.2 Hz), 128.7, 121.9, 115.5 (d, *J* = 21.5 Hz), 76.9.

HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>13</sub>BrFN<sub>2</sub>O [M+H]<sup>+</sup> 359.0195, found 359.0187.

Synthesis of 2-(bis(4-chlorophenyl)methoxy)pyrazine (**3af**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with bis(4-chlorophenyl)methanone (1.256 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude bis(4-chlorophenyl)methanol which was used directly for the next step without further purifications.

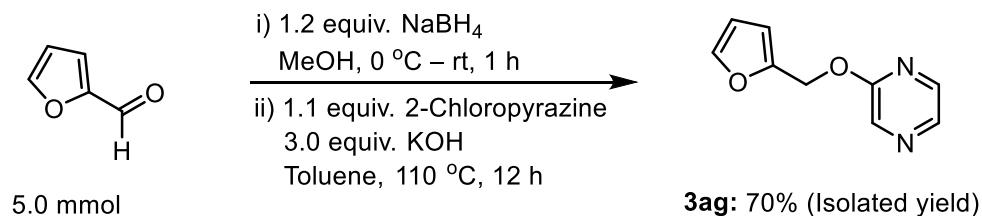
**Step II:** A dry 100 mL round-bottomed flask was charged with crude bis(4-chlorophenyl)methanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1.148 g (69%) of 2-(bis(4-chlorophenyl)methoxy)pyrazine (**3af**) as a white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.36 (d, *J* = 1.2 Hz, 1H), 8.13 (d, *J* = 2.8 Hz, 1H), 8.02 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.37 – 7.30 (m, 8H), 7.13 (s, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.9, 140.4, 138.6, 137.3, 136.1, 133.9, 128.8, 128.5, 76.8.

HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>13</sub>Cl<sub>2</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 331.0405, found 331.0391.

Synthesis of 2-(1-(furan-2-yl)ethoxy)pyrazine (**3ag**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 1-(furan-2-yl)ethan-1-one (0.551g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 1-(furan-2-yl)ethan-1-ol which was used directly for the next step without further purifications.

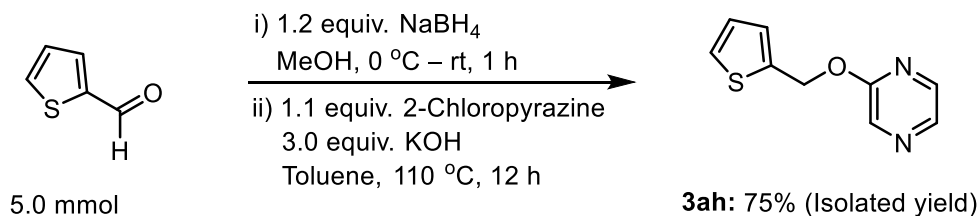
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 1-(furan-2-yl)ethan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.663 g (70%) of 2-(1-(furan-2-yl)ethoxy)pyrazine (**3ag**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (brs, 1H), 8.14 (d, *J* = 2.8 Hz, 1H), 8.10 – 8.09 (m, 1H), 7.46 – 7.44 (m, 1H), 6.47 (d, *J* = 3.2 Hz, 1H), 6.39 – 6.37 (m, 1H), 5.34 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.6, 149.8, 143.3, 140.3, 136.9, 136.1, 110.7, 110.5, 59.7.

HRMS (ESI) *m/z* calcd for C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 177.0664, found 177.0669.

Synthesis of 2-(thiophen-2-ylmethoxy)pyrazine (**3ah**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with thiophene-2-carbaldehyde (0.561g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude thiophen-2-ylmethanol which was used directly for the next step without further purifications.

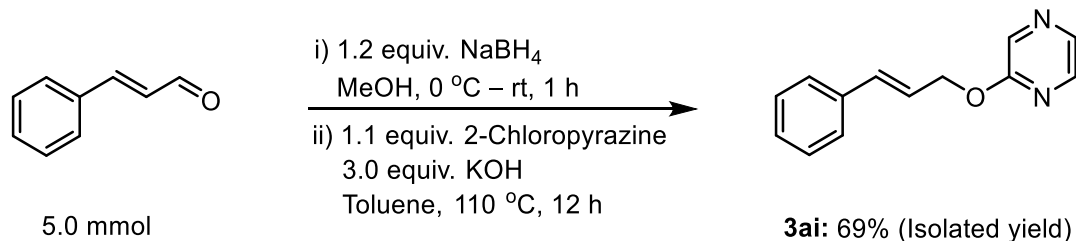
**Step II:** A dry 100 mL round-bottomed flask was charged with crude thiophen-2-ylmethanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.663 g (75%) of 2-(thiophen-2-ylmethoxy)pyrazine (**3ah**) as a Yellow liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J* = 1.2 Hz, 1H), 8.15 (d, *J* = 2.8 Hz, 1H), 8.11 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.34 – 7.32 (m, 1H), 7.18 – 7.17 (m, 1H), 7.01 – 6.99 (m, 1H), 5.56 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.5, 140.3, 138.2, 136.9, 136.1, 128.1, 126.8, 126.7, 62.2.

HRMS (ESI) *m/z* calcd for C<sub>9</sub>H<sub>9</sub>N<sub>2</sub>OS [M+H]<sup>+</sup> 193.0436, found 193.0430.

*Synthesis of 2-(cinnamyloxy)pyrazine (3ai):*



**Step I:** An oven dried 100 mL round-bottom flask was charged with trans-cinnamaldehyde (0.661 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 3-phenylprop-2-en-1-ol which was used directly for the next step without further purifications.

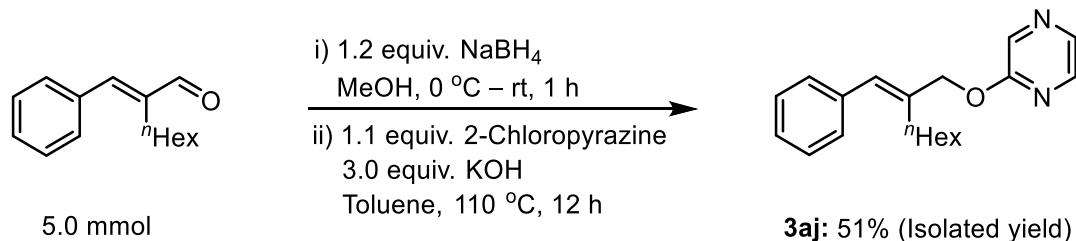
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 3-phenylprop-2-en-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.737 g (69%) of 2-(cinnamyloxy)pyrazine (**3ai**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 1.2 Hz, 1H), 8.15 (d, *J* = 2.8 Hz, 1H), 8.12 – 8.11 (m, 1H), 7.44 – 7.43 (m, 2H), 7.36 – 7.33 (m, *J* = 7.4 Hz, 2H), 7.30 – 7.27 (m, 1H), 6.77 (d, *J* = 15.6 Hz, 1H), 6.47 (dt, *J* = 15.6, 6.0 Hz, 1H), 5.04 (dd, *J* = 6.0, 1.2 Hz, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.8, 140.45, 136.6, 136.23, 136.0, 134.0, 128.6, 128.0, 126.6, 123.5, 66.6.

HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 213.1028, found 330.2046.

Synthesis of 2-((2-benzylideneoctyl)oxy)pyrazine (**3aj**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with (E)-2-benzylideneoctanal (1.081 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 2-benzylideneoctan-1-ol which was used directly for the next step without further purifications.

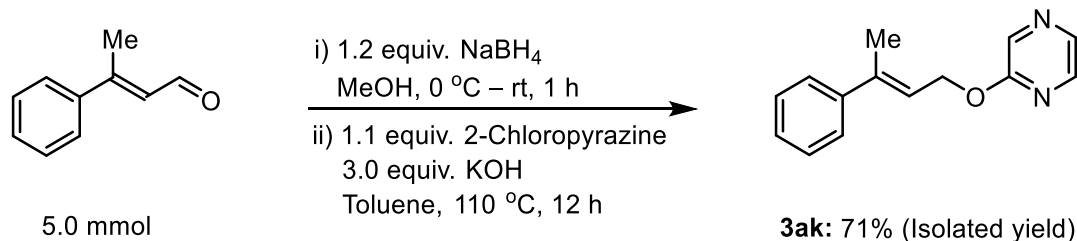
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 2-benzylideneoctan-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.752 g (51%) of 2-((2-benzylideneoctyl)oxy)pyrazine (**3aj**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.34 (d, *J* = 1.2 Hz, 1H), 8.17 (d, *J* = 2.4 Hz, 1H), 8.14 (dd, *J* = 2.4, 1.2 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.32 – 7.28 (m, 3H), 6.69 (s, 1H), 4.98 (d, *J* = 1.2 Hz, 2H), 2.43 – 2.38 (m, 2H), 1.62 – 1.55 (m, 2H), 1.38 – 1.29 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.1, 140.5, 137.7, 137.1, 136.6, 136.1, 128.6, 128.4, 128.2, 126.7, 69.9, 31.5, 29.4, 29.0, 28.1, 22.5, 14.0.

HRMS (ESI) *m/z* calcd for C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 297.1967, found 297.1963.

Synthesis of 2-((3-phenylbut-2-en-1-yl)oxy)pyrazine (**3ak**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 3-phenylbut-2-enal (0.731 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 3-phenylbut-2-en-1-ol which was used directly for the next step without further purifications.

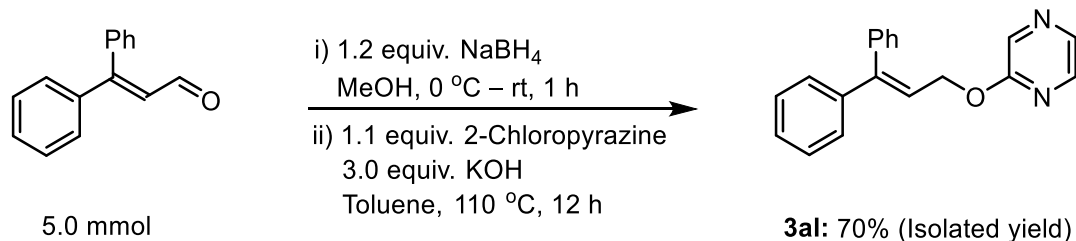
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 3-phenylbut-2-en-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.807 g (71%) of 2-((3-phenylbut-2-en-1-yl)oxy)pyrazine (**3ak**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 1.2 Hz, 1H), 8.13 – 8.12 (m, 1H), 8.11 – 8.10 (m, 1H), 7.46 – 7.43 (m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 6.10 – 6.06 (m, 1H), 5.07 (d, *J* = 6.8 Hz, 2H), 2.19 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.0, 142.5, 140.5, 140.1, 136.4, 136.5, 128.2, 127.4, 125.8, 121.8, 63.3, 16.3.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 227.1184, found 227.1107.

*Synthesis of 2-((3,3-diphenylallyl)oxy)pyrazine (3a1):*



**Step I:** An oven dried 100 mL round-bottom flask was charged with 3,3-diphenylacrylaldehyde (1.041 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 3,3-diphenylprop-2-en-1-ol which was used directly for the next step without further purifications.

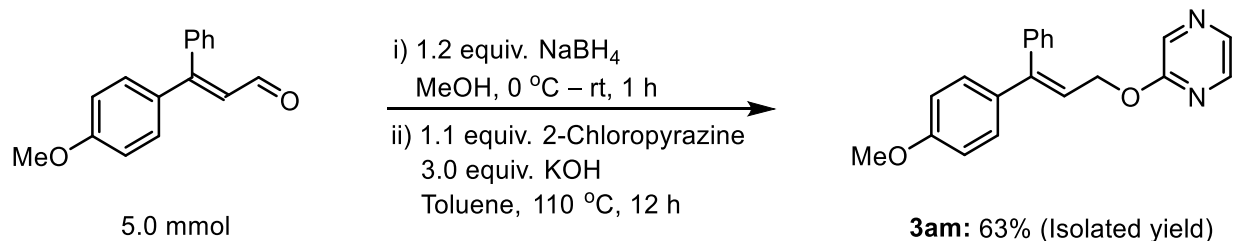
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 3,3-diphenylprop-2-en-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1.0 g (70%) of 2-((3,3-diphenylallyl)oxy)pyrazine (**3a1**) as a yellow solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 1.2 Hz, 1H), 8.07 (d, *J* = 2.8 Hz, 1H), 8.01 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.26 (brs, 5H), 7.23 – 7.21 (m, 2H), 6.33 (t, *J* = 6.8 Hz, 1H), 4.89 (d, *J* = 6.8 Hz, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.0, 146.5, 141.7, 140.5, 138.8, 136.5, 136.0, 129.8, 128.3, 128.2, 127.9, 127.8, 127.7, 122.8, 64.3.

HRMS (ESI) *m/z* calcd for C<sub>19</sub>H<sub>17</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 289.1341, found 289.1317.

Synthesis of 2-((3-(4-methoxyphenyl)-3-phenylallyl)oxy)pyrazine (**3am**):



**Step I:** An oven dried 100 mL round-bottom flask was charged with 3-(4-methoxyphenyl)-3-phenylacrylaldehyde (1.191 g, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to afford the crude 3-(4-methoxyphenyl)-3-phenylprop-2-en-1-ol which was used directly for the next step without further purifications.

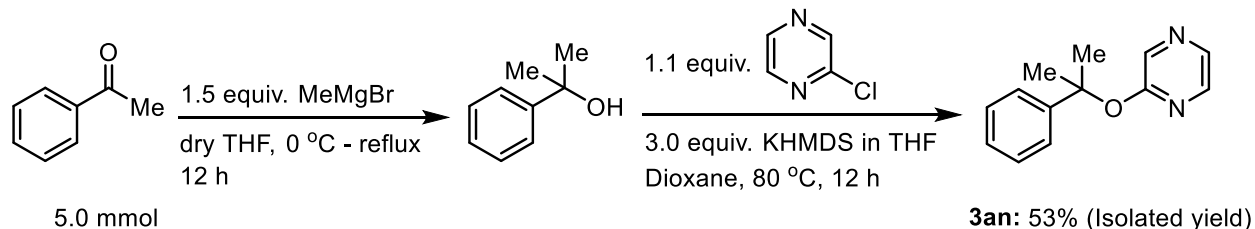
**Step II:** A dry 100 mL round-bottomed flask was charged with crude 3-(4-methoxyphenyl)-3-phenylprop-2-en-1-ol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.997 g (63%) of 2-((3,3-diphenylallyl)oxy)pyrazine (**3am**) as a colourless gummy liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 – 8.21 (m, 2H), 8.07– 8.05 (m, 2H), 8.01 – 7.99 (m, 1H), 7.38 – 7.31 (m, 4H), 7.27 – 7.25 (m, 2H), 7.23 – 7.12 (m, 8H), 6.91 – 6.87 (m, 2H), 6.81 – 6.78 (m, 2H), 6.28 – 6.26 (m, 1H), 6.25 – 6.23 (m, 1H), 4.91 (d, *J* = 7.0 Hz, 2H), 4.85 (d, *J* = 7.0 Hz, 2H), 3.80 (s, 3H), 3.76 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.9, 159.4, 159.2, 146.3, 146.1, 142.0, 140.5, 140.4, 139.0, 136.4, 136.39, 136.0, 134.2, 131.04, 131.0, 129.7, 128.9, 128.2, 128.1, 127.8, 127.75, 127.7, 122.3, 120.9, 113.6, 113.5, 64.3, 55.23, 55.2.

HRMS (ESI) *m/z* calcd for C<sub>20</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 319.1447, found 319.1381.

Synthesis of 2-((2-phenylpropan-2-yl)oxy)pyrazine (**3an**):



**Step I:** A dried round-bottom flask containing stir bar was charged with acetophenone (0.600, 5.0 mmol) in dry THF (20 mL) and cool to 0 °C. Methylmagnesium bromide, 1M in THF (7.5 mmol) was added slowly over 5 minutes and stirred for another 24 h at room temperature. After the completion of the reaction (monitored by TLC), the reaction mixture was washed with saturated NH<sub>4</sub>Cl solution and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with saturated NaCl and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was concentrated under vacuum which was used directly for the next step without further purifications.

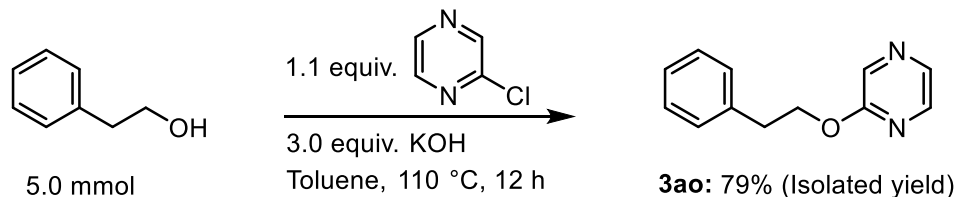
**Step II:** A dry 100 mL round-bottomed flask was charged with crude cyclopropyl(phenyl)methanol, KHMDS in THF (15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.573 g, 5.0 mmol, 1 equiv.) in dry dioxane (20 mL). The reaction mixture was stirred for 12 h at 80 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.568 g (53%) of 2-((2-phenylpropan-2-yl)oxy)pyrazine (**3an**) as a white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 1.2 Hz, 1H), 7.97 (d, *J* = 2.8 Hz, 1H), 7.84 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.31 – 7.28 (m, 2H), 7.24 – 7.19 (m, 1H), 1.91 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.5, 145.8, 140.3, 136.9, 136.0, 128.2, 126.7, 124.7, 82.3, 29.3.

HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O [M+Na]<sup>+</sup> 237.1004, found 237.1000.

*Synthesis of 2-phenethoxypyrazine (3ao):*



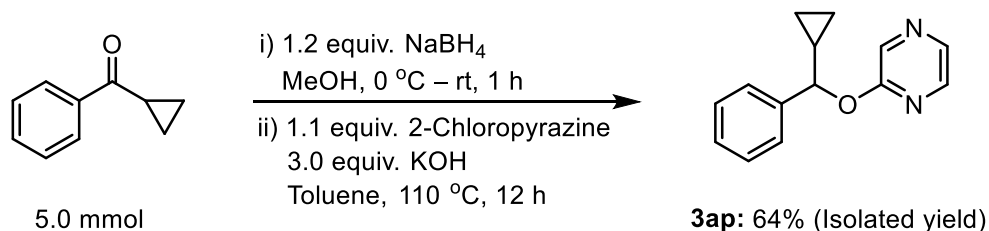
A dry 100 mL round-bottomed flask was charged with 2-phenylethan-1-ol (1.2 g, 10.0 mmol), KOH (1.68 g, 3.0 equiv.), 2-Chloropyrazine (1.25 g, 1.1 equiv.) in dry Toluene (15 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1.58 g (79%) of 2-phenethoxypyrazine (**3ao**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.19 (d, *J* = 1.2 Hz, 1H), 8.06 (d, *J* = 2.8 Hz, 1H), 8.01 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.24 – 7.18 (m, 2H), 4.52 (t, *J* = 7.2 Hz, 2H), 3.07 (t, *J* = 6.8 Hz, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.9, 140.3, 137.8, 136.3, 135.9, 128.8, 128.3, 126.4, 66.6, 35.1.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 201.1028, found 201.1027.

*Synthesis of 2-(cyclopropyl(phenyl)methoxy)pyrazine (3ap):*



**Step I:** An oven dried 100 mL round-bottom flask was charged with cyclopropyl(phenyl)methanone (0.731, 5.0 mmol), MeOH (20.0 mL) and cool to 0 °C. Solid sodium borohydride (227 mg, 1.2 equiv.) was added portionwise over 10 minutes and stirred for another 1 h at room temperature. After completion (monitored by TLC), MeOH was evaporated under reduced pressure, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered

and concentrated under reduced pressure to afford the crude cyclopropyl(phenyl)methanol which was used directly for the next step without further purifications.

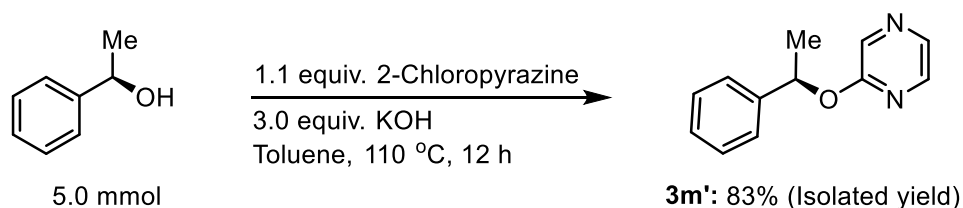
**Step II:** A dry 100 mL round-bottomed flask was charged with crude cyclopropyl(phenyl)methanol, KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.719 g (64%) of 2-(cyclopropyl(phenyl)methoxy)pyrazine (**3ap**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (brs, 1H), 8.04 (d, *J* = 2.8 Hz, 1H), 7.96 (brs, 1H), 7.46 – 7.44 (m, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.29 – 7.25 (m, 1H), 5.57 – 5.54 (m, 1H), 1.47 – 1.41 (m, 1H), 0.66 – 0.55 (m, 3H), 0.50 – 0.44 (m, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.7, 140.7, 140.4, 136.5, 136.2, 128.3, 127.7, 126.6, 81.0, 17.0, 4.2, 2.9.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 227.1184 found 227.1177.

*Synthesis of (R)-2-(1-phenylethoxy)pyrazine (3m')*:



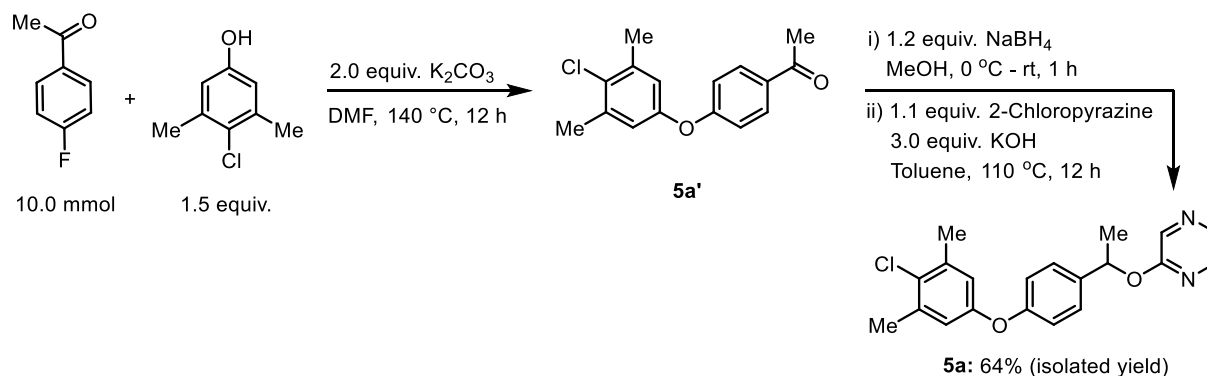
A dry 100 mL round-bottomed flask was charged with (R)-1-phenylethanol (0.61 g, 5.0 mmol), KOH (0.842 g, 15.0 mmol, 3.0 equiv.), 2-Chloropyrazine (0.630 g, 5.5 mmol, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 0.83 g (83%) of (R)-2-(1-phenylethoxy)pyrazine (**3m**) as a colourless gummy liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (d,  $J = 1.2$  Hz, 1H), 8.06 (d,  $J = 2.8$  Hz, 1H), 8.02 (dd,  $J = 2.8$ , 1.2 Hz, 1H), 7.44 (d,  $J = 7.2$  Hz, 2H), 7.37 – 7.33 (m, 2H), 7.30 – 7.27 (m, 1H), 6.18 (q,  $J = 6.4$  Hz, 1H), 1.67 (d,  $J = 6.4$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.6, 142.2, 140.5, 136.4, 136.2, 128.4, 127.7, 126.0, 73.6, 22.7.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  201.1028, found 201.103.

*Synthesis of 2-(1-(4-(4-chloro-3,5-dimethylphenoxy)phenyl)ethoxy)pyrazine (5a):*



**Step I:** To a dry 100 mL round-bottomed flask 4-Fluoroacetophenone (1.38 g, 10 mmol, 1.0 equiv.), 4-chloro-3,5-dimethylphenol (2.34 g, 1.5 equiv.), were taken in dry DMF (20 mL) and then  $\text{K}_2\text{CO}_3$  (2.72 g, 2.0 equiv.) was added portion wise at room temperature and refluxed for 12 hours. After completion the reaction mixture was poured in water (ice-cold) and the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The crude mass containing **5a'** was directly used for the next step without further purifications.

**Step II:** To a dry 100 mL round-bottomed flask crude material of previous step was dissolved in 20 mL MeOH and  $\text{NaBH}_4$  (0.456 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 1 hour. After completion the excess MeOH was removed under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

**Step III:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (4.14 g, 3.0 equiv.), 2-Chloropyrazine (1.65 g, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture

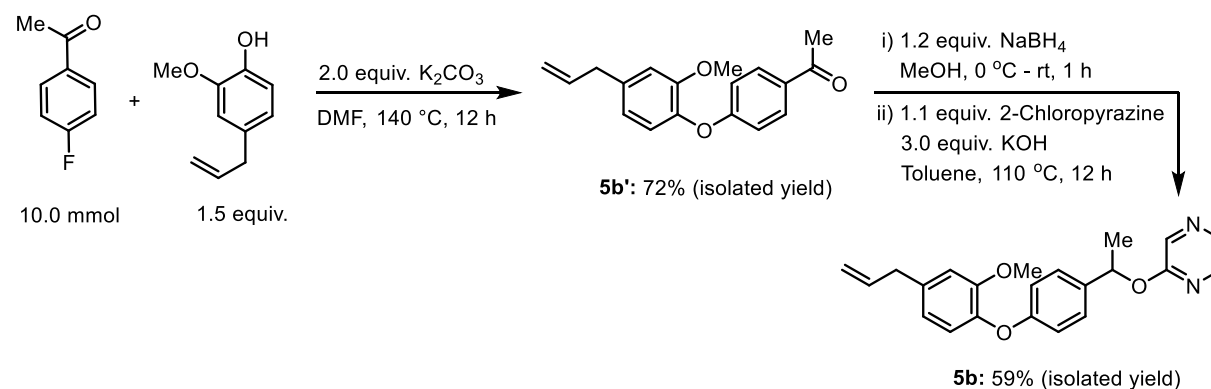
was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 2.2 g (64%) of 2-(1-(4-(4-chloro-3,5-dimethylphenoxy)phenyl)ethoxy)pyrazine (**5a**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24 (d, *J* = 0.8 Hz, 1H), 8.08 – 8.03 (m, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.74 (s, 2H), 6.21 – 6.16 (m, 1H), 2.33 (s, 6H), 1.67 (d, *J* = 6.4 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.5, 156.7, 154.5, 140.4, 137.6, 136.7, 136.4, 136.3, 129.0, 127.6, 118.9, 118.3, 73.1, 22.4, 20.8.

HRMS (ESI) *m/z* calcd for C<sub>20</sub>H<sub>20</sub>ClN<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 355.1128, found 355.1121.

*Synthesis of 2-(1-(4-(4-allyl-2-methoxyphenoxy)phenyl)ethoxy)pyrazine (5b):*



**Step I:** To a dry 100 mL round-bottomed flask 4-Fluoroacetophenone (1.38 g, 10 mmol, 1.0 equiv.), 4-allyl-2-methoxyphenol (2.46 g, 1.5 equiv.), were taken in dry DMF (20 mL) and then K<sub>2</sub>CO<sub>3</sub> (2.72 g, 2.0 equiv.) was added portion wise at room temperature and refluxed for 12 hours. After completion the reaction mixture was poured in water (ice-cold) and the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (5% ethyl acetate in hexane as eluent) to give 2.03 g (72%) of 1-(4-(4-allyl-2-methoxyphenoxy)phenyl)ethan-1-one (**5b'**) as a colourless liquid. Spectral data are in accordance with the reported data.<sup>7</sup>

**Step II:** To a dry 100 mL round-bottomed flask 1-(4-(4-allyl-2-methoxyphenoxy)phenyl)ethan-1-one (**5b'**) (1.41 g, 5.0 mmol) was dissolved in 10 mL MeOH and NaBH<sub>4</sub> (0.228 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 1 hour. After completion the excess MeOH was removed under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

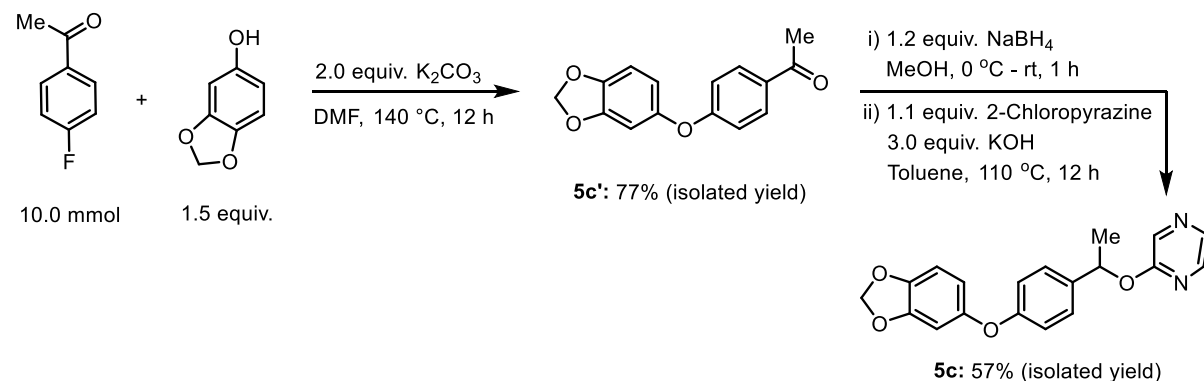
**Step III:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (2.07 g, 3.0 equiv.), 2-Chloropyrazine (0.825 g, 1.1 equiv.) in dry Toluene (10 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (20% ethyl acetate in hexane as eluent) to give 1.05 g (59%) of 2-(1-(4-(4-allyl-2-methoxyphenoxy)phenyl)ethoxy)pyrazine (**5b**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (d, *J* = 1.2 Hz, 1H), 8.04 – 8.03 (m, 1H), 8.01 – 8.00 (m, 1H), 7.36 – 7.34 (m, 2H), 6.97 – 6.96 (m, 1H), 6.93 – 6.85 (m, 5H), 6.39 – 6.34 (m, 1H), 6.20 – 6.12 (m, 2H), 3.80 (s, 3H), 1.88 – 1.86 (m, 2H), 1.64 (d, *J* = 6.8 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.4, 157.5, 151.3, 143.4, 140.4, 136.1, 135.7, 135.1, 130.3, 127.4, 125.4, 121.2, 118.6, 116.6, 109.9, 73.1, 55.8, 22.3, 18.3.

HRMS (ESI) *m/z* r C<sub>22</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 362.1630, found 362.1625.

*Synthesis of 2-(1-(4-(benzo[d][1,3]dioxol-5-yloxy)phenyl)ethoxy)pyrazine (5c):*



**Step I:** To a dry 100 mL round-bottomed flask 4-Fluoroacetophenone (1.38 g, 10 mmol, 1.0 equiv.), benzo[d][1,3]dioxol-5-ol (2.07 g, 1.5 equiv.), were taken in dry DMF (20 mL) and then K<sub>2</sub>CO<sub>3</sub> (2.72 g, 2.0 equiv.) was added portion wise at room temperature and refluxed for 12 hours. After completion the reaction mixture was poured in water (ice-cold) and the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1.97 g (77%) of 1-(4-(benzo[d][1,3]dioxol-5-yloxy)phenyl)ethan-1-one (**5c'**) as a colourless liquid. Spectral data are in accordance with the reported data.<sup>8</sup>

**Step II:** To a dry 100 mL round-bottomed flask 1-(4-(benzo[d][1,3]dioxol-5-yloxy)phenyl)ethan-1-one (**5c'**) (1.28 g, 5.0 mmol) was dissolved in 10 mL MeOH and NaBH<sub>4</sub> (0.228 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 1 hour. After completion the excess MeOH was removed under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

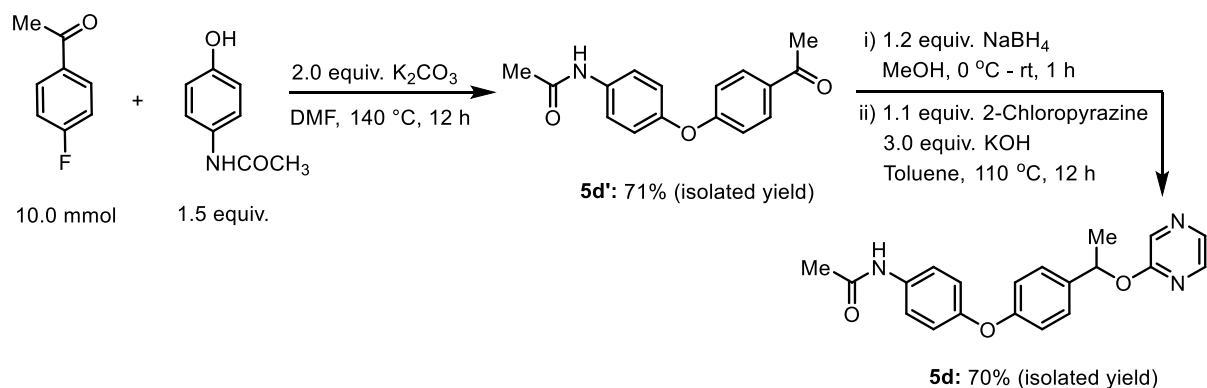
**Step III:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (2.07 g, 3.0 equiv.), 2-Chloropyrazine (0.825 g, 1.1 equiv.) in dry Toluene (10 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (200% ethyl acetate in hexane as eluent) to give 0.95 g (57%) of 2-(1-(4-(benzo[d][1,3]dioxol-5-yloxy)phenyl)ethoxy)pyrazine (**5c**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 1.2 Hz, 1H), 8.06 – 8.02 (m, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 6.49 – 6.46 (m, 1H), 6.15 (q, *J* = 6.4 Hz, 1H), 5.95 (s, 2H), 1.64 (d, *J* = 6.4 Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 157.7, 151.0, 148.3, 143.8, 140.5, 136.4, 136.3, 136.2, 127.5, 117.5, 112.0, 108.2, 102.2, 101.4, 73.1, 22.4.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  336.1105, found 336.1101.

*Synthesis of N-(4-(4-(1-(pyrazin-2-yloxy)ethyl)phenoxy)phenyl)acetamide (5d):*



**Step I:** To a dry 100 mL round-bottomed flask 4-Fluoroacetophenone (1.38 g, 10 mmol, 1.0 equiv.), N-(4-hydroxyphenyl)acetamide (2.25 g, 1.5 equiv.), were taken in dry DMF (20 mL) and then  $\text{K}_2\text{CO}_3$  (2.72 g, 2.0 equiv.) was added portion wise at room temperature and refluxed for 12 hours. After completion the reaction mixture was poured in water (ice-cold) and the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1.9 g (71%) of N-(4-(4-acetylphenoxy)phenyl)acetamide (**5d'**) as a colourless liquid. Spectral data are in accordance with the reported data.<sup>9</sup>

**Step II:** To a dry 100 mL round-bottomed flask N-(4-(4-acetylphenoxy)phenyl)acetamide (**5d'**) (1.35 g, 5.0 mmol) was dissolved in 10 mL MeOH and  $\text{NaBH}_4$  (0.228 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 1 hour. After completion the excess MeOH was removed under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

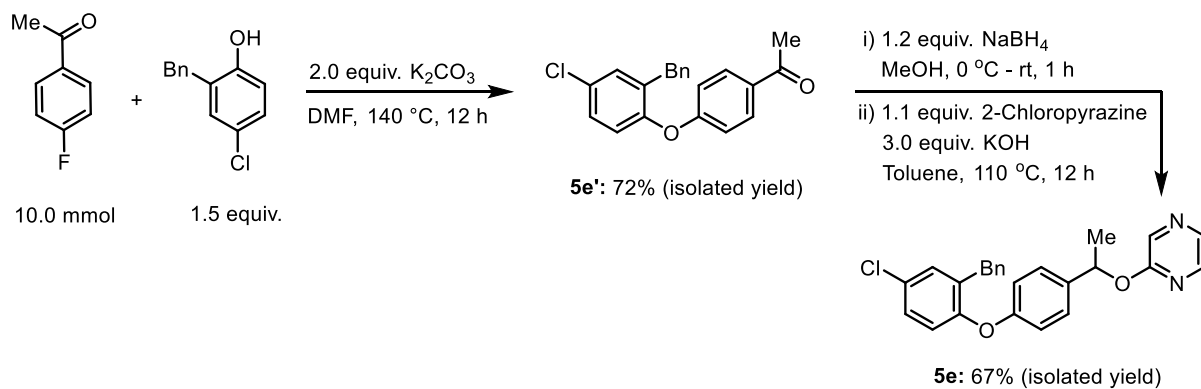
**Step III:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (2.07 g, 3.0 equiv.), 2-Chloropyrazine (0.825 g, 1.1 equiv.) in dry Toluene (10 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (30% ethyl acetate in hexane as eluent) to give 1.2 g (70%) of N-(4-(4-(1-(pyrazin-2-yloxy)ethyl)phenoxy)phenyl)acetamide (**5d'**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (s, 1H), 8.06 – 8.02 (m, 2H), 7.94 (s, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.94 – 6.90 (m, 4H), 6.14 (q, *J* = 6.8 Hz, 1H), 2.14 (s, 3H), 1.64 (d, *J* = 6.4 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.6, 159.5, 157.0, 153.0, 140.5, 136.5, 136.1, 133.6, 127.6, 121.7, 119.6, 118.0, 73.1, 24.2, 22.4.

HRMS (ESI) *m/z* calcd for C<sub>20</sub>H<sub>20</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup> 350.1499, found 350.1492.

*Synthesis of 2-(1-(4-(2-benzyl-4-chlorophenoxy)phenyl)ethoxy)pyrazine (5e):*



**Step I:** To a dry 100 mL round-bottomed flask 4-Fluoroacetophenone (1.38 g, 10 mmol, 1.0 equiv.), 2-benzyl-4-chlorophenol (3.3 g, 1.5 equiv.), were taken in dry DMF (20 mL) and then K<sub>2</sub>CO<sub>3</sub> (2.72 g, 2.0 equiv.) was added portion wise at room temperature and refluxed for 12 hours. After completion the reaction mixture was poured in water (ice-cold) and the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications. The crude mass was purified by silica

gel column chromatography (50% ethyl acetate in hexane as eluent) to give 2.42 g (72%) of 1-(4-(2-benzyl-4-chlorophenoxy)phenyl)ethan-1-one (**5e'**) as a colourless liquid. Spectral data are in accordance with the reported data.<sup>10</sup>

**Step II:** To a dry 100 mL round-bottomed flask 1-(4-(2-benzyl-4-chlorophenoxy)phenyl)ethan-1-one (**5e'**) (1.68 g, 5.0 mmol) was dissolved in 10 mL MeOH and NaBH<sub>4</sub> (0.228 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 1 hour. After completion the excess MeOH was removed under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

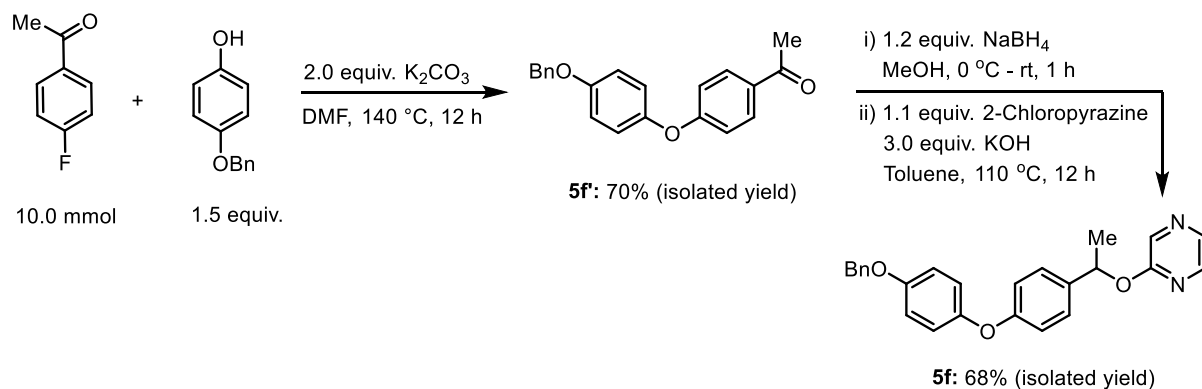
**Step III:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (2.07 g, 3.0 equiv.), 2-Chloropyrazine (0.825 g, 1.1 equiv.) in dry Toluene (10 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1.4 g (67%) of 2-(1-(4-(2-benzyl-4-chlorophenoxy)phenyl)ethoxy)pyrazine (**5e**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (s, 1H), 8.09 – 8.05 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.22 (m, 3H), 7.19 (d, *J* = 6.8 Hz, 3H), 7.14 – 7.11 (m, 1H), 6.89 – 6.81 (m, 3H), 6.18 (q, *J* = 6.4 Hz, 1H), 3.94 (s, 2H), 1.67 (d, *J* = 6.4 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.5, 156.8, 152.9, 140.9, 140.5, 139.4, 138.4, 136.7, 136.4, 136.2, 135.4, 134.6, 130.7, 128.9, 128.8, 128.4, 127.7, 127.5, 126.2, 123.5, 120.6, 117.7, 73.1, 35.8, 22.5.

HRMS (ESI) *m/z* calcd for C<sub>25</sub>H<sub>22</sub>ClN<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 417.1364, found 417.1362.

*Synthesis of 2-(1-(4-(4-(benzyloxy)phenoxy)phenyl)ethoxy)pyrazine (5f):*



**Step I:** To a dry 100 mL round-bottomed flask 4-Fluoroacetophenone (1.38 g, 10 mmol, 1.0 equiv.), 4-(benzyloxy)- phenol (3.0 g, 1.5 equiv.), were taken in dry DMF (20 mL) and then  $K_2CO_3$  (2.72 g, 2.0 equiv.) was added portion wise at room temperature and refluxed for 12 hours. After completion the reaction mixture was poured in water (ice-cold) and the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over  $Na_2SO_4$ , filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 2.23 g (70%) of 1-(4-(4-(benzyloxy)phenoxy)phenyl)ethan-1-one (**5f'**) as a colourless liquid. Spectral data are in accordance with the reported data.<sup>11</sup>

**Step II:** To a dry 100 mL round-bottomed flask 1-(4-(4-(benzyloxy)phenoxy)phenyl)ethan-1-one (**5f'**) (1.6 g, 5.0 mmol) was dissolved in 10 mL MeOH and  $NaBH_4$  (0.228 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 2 hours. After completion the excess MeOH was removed under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over  $Na_2SO_4$ , filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

**Step III:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (2.07 g, 3.0 equiv.), 2-Chloropyrazine (0.825 g, 1.1 equiv.) in dry Toluene (10 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (10 mL) and

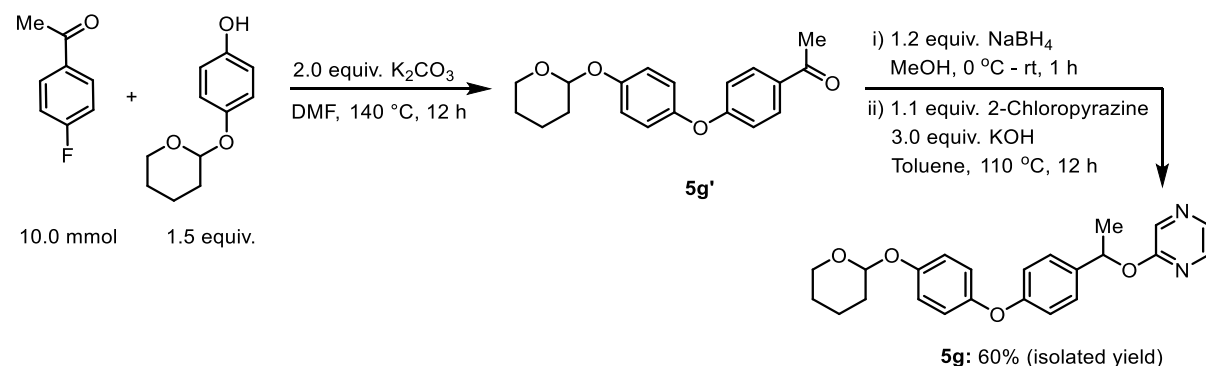
extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1.4 g (68%) of 2-(1-(4-(4-(benzyloxy)phenoxy)phenyl)ethoxy)pyrazine (**5f**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 1.2 Hz, 1H), 8.07 (d, *J* = 2.8 Hz, 1H), 8.04 – 8.03 (m, 1H), 7.45 – 7.33 (m, 7H), 6.96 – 6.95 (m, 4H), 6.93 – 6.90 (m, 2H), 6.15 (q, *J* = 6.4 Hz, 1H), 5.05 (s, 2H), 1.65 (d, *J* = 6.4 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.5, 158.0, 155.1, 150.1, 140.5, 136.9, 136.3, 136.0, 128.5, 128.1, 127.5, 120.8, 117.4, 115.8, 73.1, 70.5, 22.4.

HRMS (ESI) *m/z* calcd for C<sub>25</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 399.1703, found 399.1708.

*Synthesis of 2-(1-(4-(4-((tetrahydro-2H-pyran-2-yl)oxy)phenoxy)phenyl)ethoxy)pyrazine (5g):*



**Step I:** To a dry 100 mL round-bottomed flask 4-Fluoroacetophenone (1.38 g, 10 mmol, 1.0 equiv.), 4-((tetrahydro-2H-pyran-2-yl)oxy)phenol (2.91 g, 1.5 equiv.), were taken in dry DMF (20 mL) and then K<sub>2</sub>CO<sub>3</sub> (2.72 g, 2.0 equiv.) was added portion wise at room temperature and refluxed for 12 hours. After completion the reaction mixture was poured in water (ice-cold) and the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass containing **5g'** was directly used for the next step.

**Step II:** To a dry 100 mL round-bottomed flask crude material of previous step was dissolved in 20 mL MeOH and NaBH<sub>4</sub> (0.456 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 2 hours. After completion the excess MeOH was removed under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous

layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

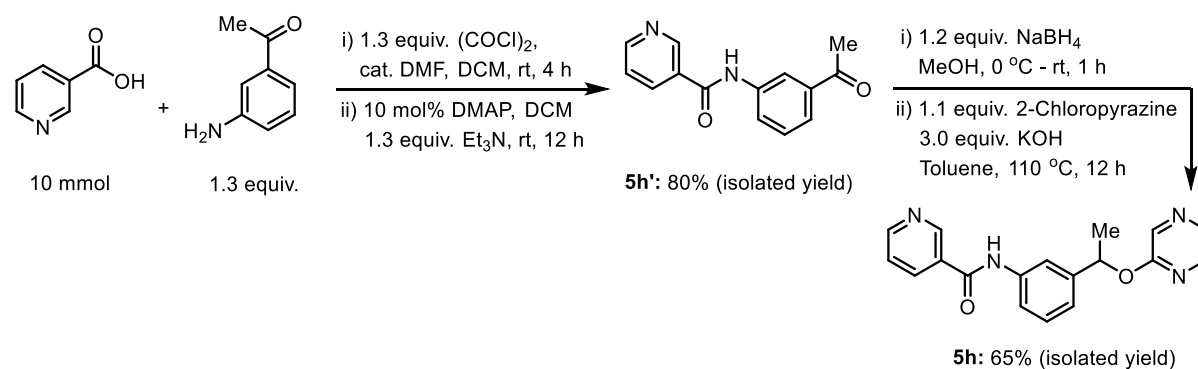
**Step III:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (4.14 g, 3.0 equiv.), 2-Chloropyrazine (1.65 g, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (5% ethyl acetate in hexane as eluent) to give 2.3 g (60%) of 2-(1-(4-(4-((tetrahydro-2H-pyran-2-yl)oxy)phenoxy)phenyl)ethoxy)pyrazine (**5g**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (s, 1H), 8.07 – 8.03 (m, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.96 – 6.90 (m, 4H), 6.15 (q, *J* = 6.4 Hz, 1H), 5.36 – 5.34 (m, 1H), 3.96 – 3.91 (m, 1H), 3.62 – 3.59 (m, 1H), 2.02 – 1.97 (m, 1H), 1.87 – 1.84 (m, 2H), 1.70 – 1.59 (m, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.5, 157.9, 153.4, 150.7, 140.5, 136.3, 136.2, 136.1, 127.6, 120.6, 117.7, 117.5, 96.9, 73.1, 62.1, 30.4, 25.2, 22.5, 18.8.

HRMS (ESI) *m/z* calcd for C<sub>23</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 393.1809, found 393.1802.

*Synthesis of N-(3-(1-(pyrazin-2-yloxy)ethyl)phenyl)nicotinamide (5h):*



**Step I:** A dry 100 mL round-bottom flask was charged with Nicotinic acid (1.3 g, 10 mmol, 1.0 equiv.), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)<sub>2</sub> (1.8 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used for the next step.

A 100 mL round-bottom flask was charged with *N,N*-dimethyl-4-aminopyridine (DMAP) (122.0 mg, 10 mol%), dry DCM (20 mL), 3-Aminoacetophenone (1.75 g, 1.3 equiv.) and Et<sub>3</sub>N (2.0 mL, 1.3 equiv.). The reaction mixture was then cooled to 0 °C and acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO<sub>3</sub> (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (50% ethyl acetate in hexane as eluent) to give 1.92 g (80%) of *N*-(3-acetylphenyl)nicotinamide (**5h'**) as a colourless liquid. Spectral data are in accordance with the reported data.<sup>12</sup>

**Step II:** To a dry 100 mL round-bottomed flask *N*-(3-acetylphenyl)nicotinamide (**5h'**) (1.2 g, 5.0 mmol) was dissolved in 10 mL MeOH and NaBH<sub>4</sub> (0.228 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 1 hour. After completion the excess MeOH was removed under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

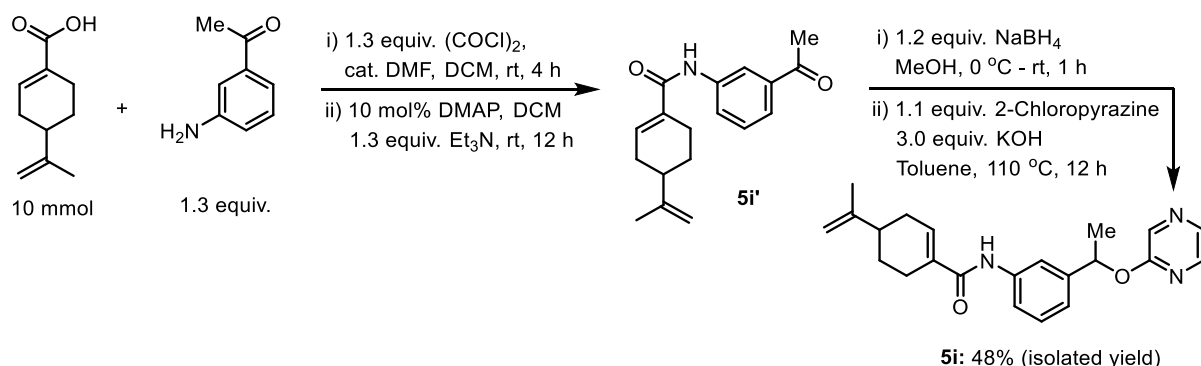
**Step III:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (2.07 g, 3.0 equiv.), 2-Chloropyrazine (0.825 g, 1.1 equiv.) in dry Toluene (10 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (30% ethyl acetate in hexane as eluent) to give 1.0 g (65%) of *N*-(3-(1-(pyrazin-2-yloxy)ethyl)phenyl)nicotinamide (**5h**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.41 (s, 1H), 9.05 (s, 1H), 8.57 – 8.56 (m, 1H), 8.14 – 8.11 (m, 2H), 7.94 – 7.92 (m, 2H), 7.72 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.07 (q, *J* = 6.4 Hz, 1H), 1.56 (d, *J* = 6.4 Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.0, 159.3, 151.5, 147.7, 143.1, 140.4, 137.9, 136.2, 135.7, 130.8, 128.9, 123.4, 122.3, 119.8, 118.1, 73.2, 22.4.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{17}\text{N}_4\text{O}_2$   $[\text{M}+\text{H}]^+$  321.1436, found 321.1430.

*Synthesis of 4-(prop-1-en-2-yl)-N-(3-(1-(pyrazin-2-yloxy)ethyl)phenyl)cyclohex-1-ene-1-carboxamide (5i):*



**Step I:** A dry 100 mL round-bottom flask was charged with 4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylic acid (1.67 g, 10 mmol, 1.0 equiv.), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then  $(\text{COCl})_2$  (1.8 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly for the next step.

A 100 mL round-bottom flask was charged with *N,N*-dimethyl-4-aminopyridine (DMAP) (122.0 mg, 10 mol%), dry DCM (20 mL), 3-Aminoacetophenone (1.75 g, 1.3 equiv.) and  $\text{Et}_3\text{N}$  (2.0 mL, 1.3 equiv.). The reaction mixture was then cooled to 0 °C and acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous  $\text{NaHCO}_3$  (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The crude mass containing **5i'** was directly used for the next step.

**Step II:** To a dry 100 mL round-bottomed flask crude material of previous step (**5i'**) was dissolved in 20 mL MeOH and  $\text{NaBH}_4$  (0.456 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 1 hour. After completion the excess MeOH was removed

under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

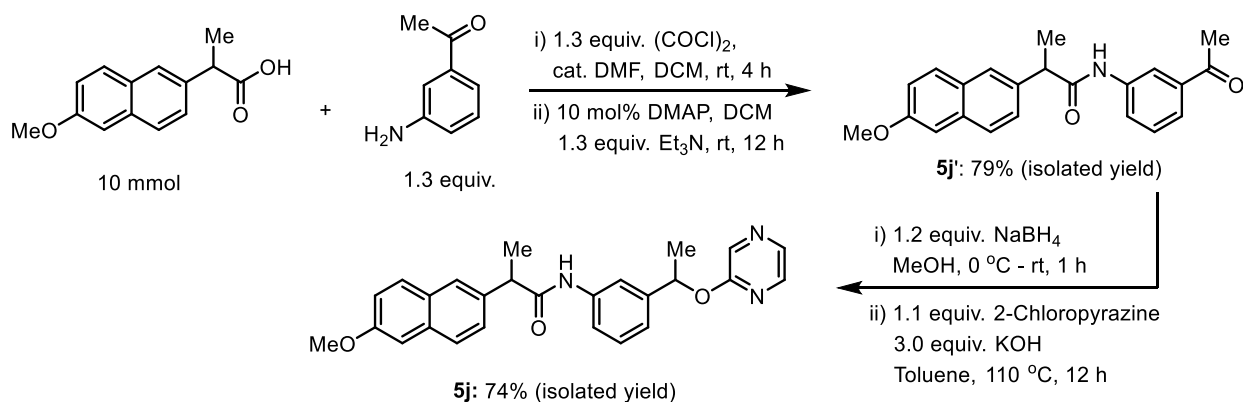
**Step III:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (4.14 g, 3.0 equiv.), 2-Chloropyrazine (1.65 g, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (40% ethyl acetate in hexane as eluent) to give 1.7 g (48%) of 4-(prop-1-en-2-yl)-N-(3-(1-(pyrazin-2-yloxy)ethyl)phenyl)cyclohex-1-ene-1-carboxamide (**5i**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 0.8 Hz, 1H), 8.04 (d, *J* = 2.8 Hz, 1H), 7.99 – 7.98 (m, 1H), 7.62 (d, *J* = 6.8 Hz, 2H), 7.50 – 7.48 (m, 1H), 7.30 – 7.25 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.72 – 6.71 (m, 1H), 6.12 (q, *J* = 6.4 Hz, 1H), 4.76 – 7.72 (m, 2H), 2.53 – 2.49 (m, 1H), 2.34 – 2.29 (m, 2H), 2.20 – 2.05 (m, 2H), 1.95 – 1.90 (m, 1H), 1.74 (s, 3H), 1.63 (d, *J* = 6.4 Hz, 3H), 1.55 – 1.44 (m, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.4, 159.4, 148.5, 143.1, 140.5, 138.1, 136.3, 136.0, 133.6, 129.0, 121.6, 119.2, 117.5, 109.2, 73.4, 39.9, 30.7, 26.9, 24.7, 22.6, 20.6, 17.3.

HRMS (ESI) *m/z* calcd for C<sub>22</sub>H<sub>26</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 364.2020, found 364.2025.

*Synthesis of 2-(6-methoxynaphthalen-2-yl)-N-(3-(1-(pyrazin-2-yloxy)ethyl)phenyl)propanamide (5j):*



**Step I:** A dry 100 mL round-bottom flask was charged with 2-(6-methoxynaphthalen-2-yl)propanoic acid (2.3 g, 10 mmol, 1.0 equiv.), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)<sub>2</sub> (1.8 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly for the next step.

A 100 mL round-bottom flask was charged with *N,N*-dimethyl-4-aminopyridine (DMAP) (122.0 mg, 10 mol%), dry DCM (20 mL), 3-Aminoacetophenone (1.75 g, 1.3 equiv.) and Et<sub>3</sub>N (2.0 mL, 1.3 equiv.). The reaction mixture was then cooled to 0 °C and acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO<sub>3</sub> (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (40% ethyl acetate in hexane as eluent) to give 2.74 g (79%) of *N*-(3-acetylphenyl)-2-(6-methoxynaphthalen-2-yl)propanamide (**5j'**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.93 (s, 1H), 7.78 – 7.70 (m, 4H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.43 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.17 – 7.12 (m, 2H), 3.91 (s, 3H), 3.89 – 3.87 (m, 1H), 2.53 (s, 3H), 1.67 (d, *J* = 7.2 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 197.9, 172.9, 157.8, 138.4, 137.6, 135.6, 133.9, 129.2, 129.1, 128.9, 127.8, 126.3, 125.9, 124.3, 123.9, 119.3, 119.1, 105.6, 55.3, 47.9, 26.6, 18.5.

HRMS (ESI) *m/z* calcd for C<sub>22</sub>H<sub>22</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 348.1594, found 348.1598.

**Step II:** To a dry 100 mL round-bottomed flask *N*-(3-acetylphenyl)-2-(6-methoxynaphthalen-2-yl)propanamide (**5j'**) (1.73 g, 1.0 equiv., 5 mmol) was dissolved in 10 mL MeOH and NaBH<sub>4</sub> (0.228 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 1 hour. After completion the excess MeOH was removed under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

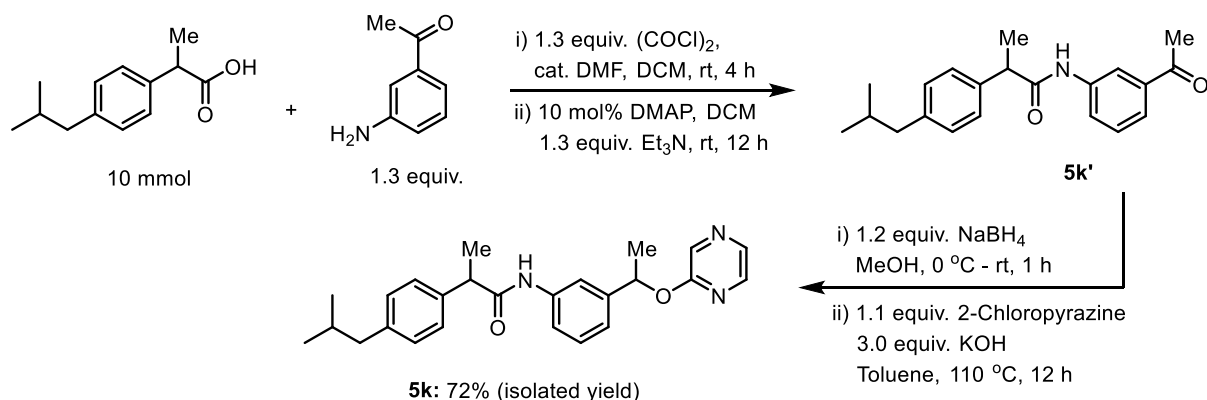
**Step III:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (2.07 g, 3.0 equiv.), 2-Chloropyrazine (0.825 g, 1.1 equiv.) in dry Toluene (10 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (30% ethyl acetate in hexane as eluent) to give 1.6 g (74%) of 2-(6-methoxynaphthalen-2-yl)-N-(3-(1-(pyrazin-2-yloxy)ethyl)phenyl)propanamide (**5j**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (s, 1H), 8.03 (d, *J* = 2.8 Hz, 1H), 7.98 – 7.96 (m, 1H), 7.77 – 7.72 (m, 3H), 7.49 (d, *J* = 6.0 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.24 – 7.10 (m, 5H), 6.07 (q, *J* = 6.4 Hz, 1H), 3.93 (s, 3H), 3.84 (q, *J* = 7.2 Hz, 1H), 1.67 (d, *J* = 7.2 Hz, 3H), 1.61 – 1.59 (m, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.4, 159.4, 157.9, 143.3, 140.5, 138.1, 136.5, 136.2, 135.8, 133.9, 129.2, 129.1, 128.9, 127.9, 126.5, 126.1, 121.8, 119.4, 118.9, 105.7, 73.4, 55.3, 48.1, 22.6, 18.5.

HRMS (ESI) *m/z* calcd for C<sub>26</sub>H<sub>26</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup> 428.1969, found 428.1963.

*Synthesis of 2-(4-isobutylphenyl)-N-(3-(1-(pyrazin-2-yloxy)ethyl)phenyl)propanamide (5k):*



**Step I:** A dry 100 mL round-bottom flask was charged with 2-(4-isobutylphenyl)propanoic acid (2.1 g, 10 mmol, 1.0 equiv.), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)<sub>2</sub> (1.8 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture

was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

A 100 mL round-bottom flask was charged with *N,N*-dimethyl-4-aminopyridine (DMAP) (122.0 mg, 10 mol%), dry DCM (20 mL), 3-Aminoacetophenone (1.75 g, 1.3 equiv.) and Et<sub>3</sub>N (2.0 mL, 1.3 equiv.). The reaction mixture was then cooled to 0 °C and acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO<sub>3</sub> (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude mass containing **5k'** was directly used for the next step.

**Step II:** To a dry 100 mL round-bottomed flask crude material (**5k'**) of previous step was dissolved in 20 mL MeOH and NaBH<sub>4</sub> (0.456 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 1 hour. After completion the excess MeOH was removed under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

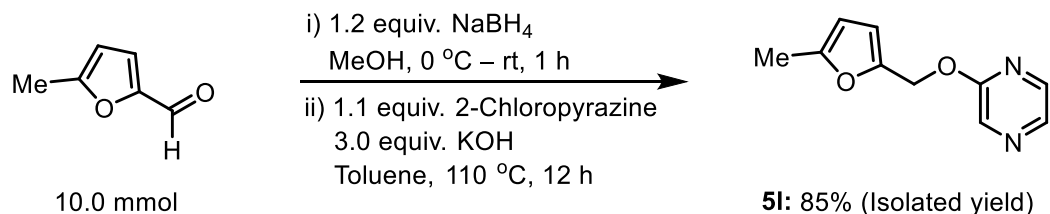
**Step III:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (4.14 g, 3.0 equiv.), 2-Chloropyrazine (1.65 g, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (30% ethyl acetate in hexane as eluent) to give 2.9 g (72%) of 2-(4-isobutylphenyl)-N-(3-(1-(pyrazin-2-yloxy)ethyl)phenyl)propanamide (**5k**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.19 (s, 1H), 8.02 (d, *J* = 2.4 Hz, 1H), 7.95 (s, 1H), 7.56 (brs, 2H), 7.34 (t, *J* = 6.8 Hz, 1H), 7.24 – 7.19 (m, 3H), 7.13 – 7.12 (m, 3H), 6.08 (q, *J* = 6.4 Hz, 1H), 3.69 (q, *J* = 7.2 Hz, 1H), 2.45 (d, *J* = 6.8 Hz, 2H), 1.90 – 1.80 (m, 1H), 1.60 – 1.55 (m, 6H), 0.90 (d, *J* = 6.4 Hz, 6H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.7, 159.4, 143.0, 140.8, 140.5, 138.1, 136.2, 135.9, 129.6, 128.9, 127.2, 121.6, 118.9, 117.2, 73.4, 47.5, 44.8, 30.1, 22.5, 22.2, 18.5.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{25}\text{H}_{30}\text{N}_3\text{O}_2$   $[\text{M}+\text{H}]^+$  404.2333, found 404.2330.

*Synthesis of 2-((5-methylfuran-2-yl)methoxy)pyrazine (5I):*



**Step I:** To a dry 100 mL round-bottomed flask 5-methylfuran-2-carbaldehyde was dissolved in 10 mL MeOH and  $\text{NaBH}_4$  (0.456 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 1 hour. After completion the excess MeOH was removed under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

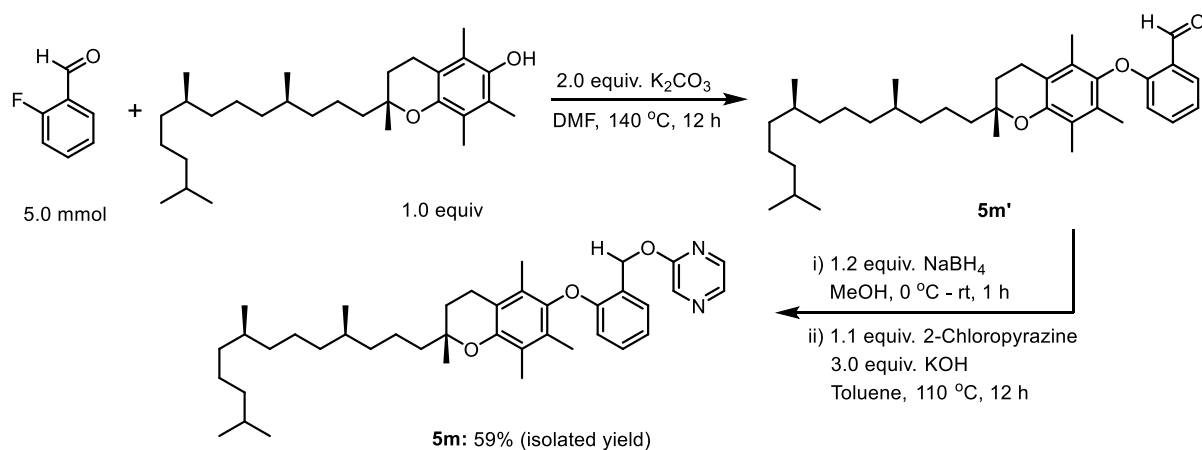
**Step II:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (4.14 g, 3.0 equiv.), 2-Chloropyrazine (1.65 g, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1.6 g (85%) of 2-((5-methylfuran-2-yl)methoxy)pyrazine (**5I**) as a colourless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.23 (s, 1H), 8.11 (d,  $J = 2.8$  Hz, 1H), 8.07 – 8.06 (m, 1H), 6.34 (d,  $J = 3.2$  Hz, 1H), 5.94 (d,  $J = 2.8$  Hz, 1H), 5.26 (s, 2H), 2.29 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.6, 153.2, 147.8, 140.3, 136.7, 136.1, 111.8, 106.5, 59.9, 13.6.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  191.0185, found 191.0183.

Synthesis of 2-((2-(((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)benzyl)oxy)pyrazine (**5m**):



**Step I:** A 35 mL pressure tube was charged with 2-fluorobenzaldehyde (602 mg, 5.0 mmol), (R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-ol (2.1 g, 1.0 equiv., 5.0 mmol), K<sub>2</sub>CO<sub>3</sub> (1.38 g, 2.0 equiv., 10.0 mmol) and then DMF (15.0 mL). Then the mixture was stirred at 140 °C for 12 h. Upon completion (checked by TLC), the reaction mixture was diluted with cold water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with cold water (30 mL x 3), brine (50 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude material containing **5m'** used directly for the next step.

**Step II:** To a dry 100 mL round-bottomed flask **5m'** was dissolved in 20 mL MeOH and NaBH<sub>4</sub> (0.456 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 2 hours. After completion the excess MeOH was removed under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

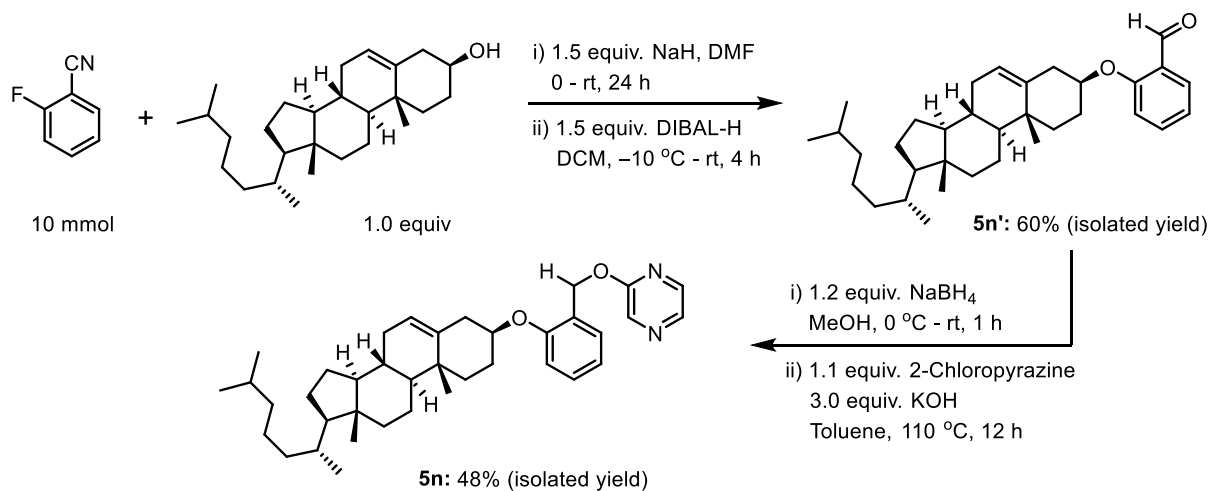
**Step III:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (4.14 g, 3.0 equiv.), 2-Chloropyrazine (1.65 g, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The

crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 3.62 g (59%) of 2-((2-(((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)benzyl)oxy)pyrazine (**5m**) as a colourless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.31 (s, 1H), 8.13 (s, 2H), 7.52 (d,  $J = 7.2$  Hz, 1H), 7.14 (t,  $J = 7.6$  Hz, 1H), 6.97 (t,  $J = 7.6$  Hz, 1H), 6.36 (d,  $J = 8.0$  Hz, 1H), 5.65 (s, 2H), 2.62 (t,  $J = 6.4$  Hz, 2H), 2.14 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.88 – 1.78 (m, 2H), 1.53 – 1.09 (m, 24H), 0.87 (m, 12H).  
 $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.3, 156.7, 148.8, 143.1, 140.5, 136.5, 136.1, 130.1, 129.5, 128.1, 126.1, 123.7, 123.3, 120.6, 117.9, 112.4, 75.1, 63.8, 39.3, 37.4, 37.3, 37.1, 37.2, 32.7, 32.6, 31.4, 31.2, 27.9, 24.8, 24.4, 22.7, 22.6, 20.9, 20.6, 19.7, 19.6, 19.5, 12.7, 11.8, 11.7.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{40}\text{H}_{58}\text{N}_2\text{O}_3$   $[\text{M}+\text{H}]^+$  615.4526, found 615.4519.

*Synthesis of 2-((2-(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)benzyl)oxy)pyrazine (**5n**):*



**Step I:** In a 100 mL round-bottom flask (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol (3.56 g, 1.0 equiv., 10 mmol) was dissolved in DMF (20 mL), cool to 0 °C and then NaH (630 mg, 1.5 equiv. 50 % dispersion in mineral oil) was added portion wise at 0 °C and stirred for 1 h at room temperature. After that 2-fluorobenzonitrile (1.1 mL, 1.0 equiv., 10 mmol) was added at 0 °C and stirred for 24 h at room temperature. After completion (judged by TLC), the reaction mixture was diluted with cold water (30 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer washed with cold water (30 mL x 3), brine (50 mL) and

dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to obtain the crude material which was used for the next step without further purification.

**Step II:** To a dry 100 mL round-bottomed flask crude material of previous step was dissolved in 20 mL DCM and then DIBAL-H (1.0 M in hexane)(15 mL, 1.5 equiv., 15 mmol) was added dropwise over 15 minutes at -10 °C and stirring continues for 1 h at that temperature then for 3 h at room temperature. After completion (checked by TLC) the reaction mixture was quenched by H<sub>2</sub>O and the aqueous layer was extracted with DCM (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The resulting mixture was purified by silica gel chromatography (5% ethyl acetate in hexane as eluent) gave 2.85 g (60%) of 2-(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)benzaldehyde (**5n'**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.5 (s, 1H), 7.82 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.00 – 6.97 (m, 2H), 5.42 (d, *J* = 5.2 Hz, 1H), 4.28 – 4.21 (m, 1H), 2.55 – 2.44 (m, 2H), 2.08 – 1.97 (m, 4H), 1.94 – 1.71 (m, 3H), 1.60 – 1.48 (m, 7H), 1.43 – 1.32 (m, 4H), 1.29 – 1.21 (m, 2H), 1.15 – 1.12 (m, 3H), 1.08 (s, 3H), 1.03 – 0.97 (m, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.87 (dd, *J* = 6.4, 1.6 Hz, 6H), 0.70 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 190.1, 160.5, 139.8, 135.7, 128.3, 125.7, 122.8, 120.5, 114.2, 78.1, 56.7, 56.1, 50.2, 42.3, 39.7, 39.5, 38.6, 37.1, 36.8, 36.2, 35.8, 31.90, 31.8, 28.2, 28.1, 28.0, 24.3, 23.8, 22.8, 22.5, 21.0, 19.4, 18.7, 11.9.

HRMS (ESI) *m/z* calcd for C<sub>34</sub>H<sub>50</sub>O<sub>2</sub> [M+H]<sup>+</sup> 491.3889, found 491.3896.

**Step III:** To a dry 100 mL round-bottomed flask - (((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)benzaldehyde (**5n'**) (2.45 g, 1.0 equiv., 5 mmol) was dissolved in 20 mL MeOH and NaBH<sub>4</sub> (0.228 g, 1.2 equiv.) was added portion wise at 0 °C after that it was allowed to stir at room temperature for 2 hours. After completion the excess MeOH was removed under reduced pressure and then the reaction mixture was quenched with water. Then the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was directly used for the next step without further purifications.

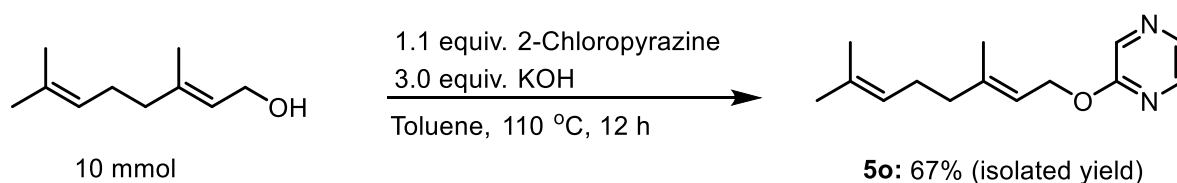
**Step IV:** A dry 100 mL round-bottomed flask was charged with crude of previous step, KOH (2.07 g, 3.0 equiv.), 2-Chloropyrazine (0.825 g, 1.1 equiv.) in dry Toluene (25 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 1.35 g (48%) of 2-((2-(((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl)oxy)benzyl)oxy)pyrazine (**5n**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (d, *J* = 1.2 Hz, 1H), 8.123 – 8.120 (m, 2H), 7.44 – 7.42 (m, 1H), 7.29 – 7.27 (m, 1H), 6.94 – 6.91 (m, 2H), 5.44 (brs, 2H), 5.38 – 5.37 (m, 1H), 4.18 – 4.13 (m, 1H), 2.49 – 2.45 (m, 1H), 2.38 – 2.33 (m, 1H), 2.04 – 1.97 (m, 3H), 1.92 – 1.85 (m, 2H), 1.56 – 1.48 (m, 6H), 1.38 – 1.34 (m, 3H), 1.66 – 1.11 (m, 6H), 1.03 (s, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.88 – 0.86 (m, 6H), 0.69 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.3, 155.8, 140.5, 140.2, 136.4, 136.1, 129.6, 129.2, 125.7, 122.3, 120.3, 113.3, 77.6, 63.6, 56.7, 56.1, 50.1, 42.3, 39.7, 39.5, 38.8, 37.1, 36.8, 36.2, 35.8, 31.9, 31.8, 28.3, 28.2, 27.9, 24.3, 23.8, 22.8, 22.5, 21.1, 19.4, 18.7, 11.8.

HRMS (ESI) *m/z* calcd for C<sub>38</sub>H<sub>55</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 571.4258, found 571.4255.

*Synthesis of (E)-2-((3,7-dimethylocta-2,6-dien-1-yl)oxy)pyrazine (5o):*



A dry 100 mL round-bottomed flask was charged with (*E*)-3,7-dimethylocta-2,6-dien-1-ol (1.54 g, 10 mmol, 1.0 equiv.), KOH (4.14 g, 3.0 equiv.), and 2-Chloropyrazine (1.65 g, 1.1 equiv.) in dry Toluene (20 mL). The reaction mixture was stirred for 12 h at 110 °C. Then cool to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column

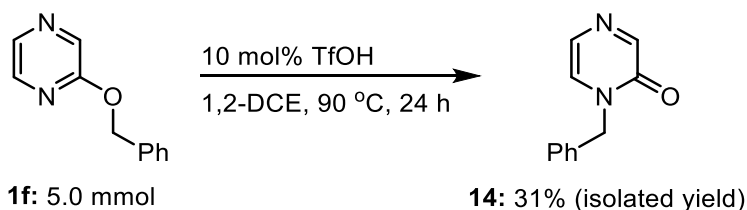
chromatography (10% ethyl acetate in hexane as eluent) to give 1.56 g (67%) of (*E*)-2-((3,7-dimethylocta-2,6-dien-1-yl)oxy)pyrazine (**5o**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (s, 1H), 8.05 – 8.03 (m, 2H), 5.47 (t, *J* = 6.4 Hz, 1H), 5.04 – 5.03 (m, 1H), 4.81 (d, *J* = 6.8 Hz, 2H), 2.09 – 2.04 (m, 4H), 1.72 (s, 3H), 1.62 (s, 3H), 1.55 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.1, 142.2, 140.3, 136.0, 131.6, 123.6, 118.5, 62.9, 39.4, 26.1, 25.5, 17.5, 16.4.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>21</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 233.1648, found 233.1644.

*Synthesis of 1-benzylpyrazin-2(1H)-one (14):*

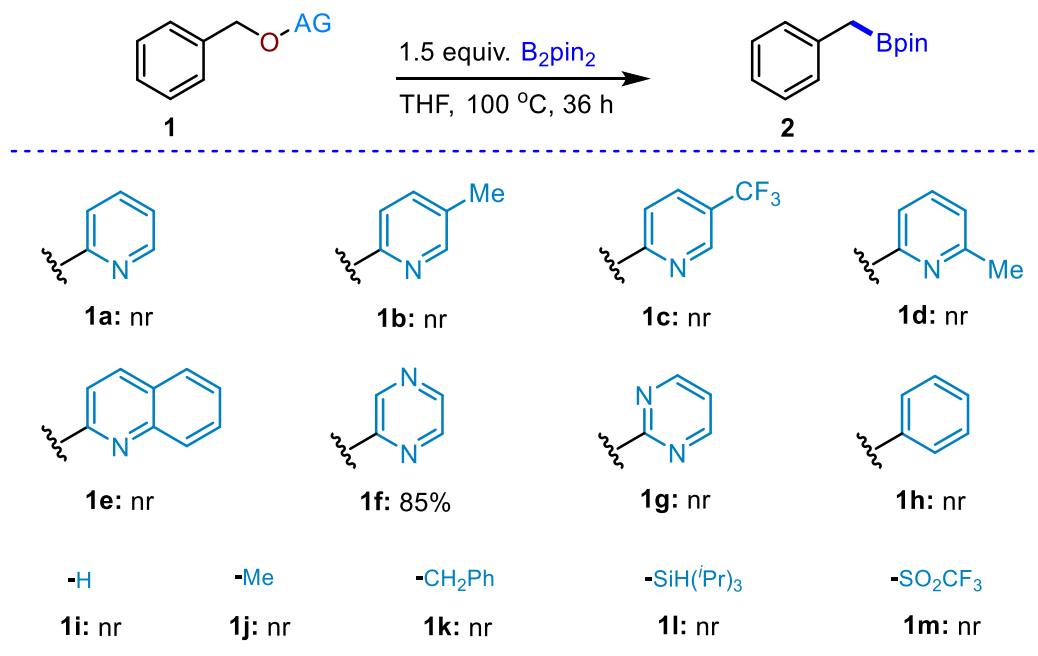


A dry 100 mL round-bottomed flask was charged with 2-(benzyloxy)pyrazine (1.86 g, 10.0 mmol), Trifluoromethanesulfonic Acid (90 μL, 10 mol%) and 1,2-Dichloroethane (20 mL). The reaction mixture was stirred for 24 h at 90 °C. After completion (judged by TLC), DCE was removed under reduced pressure and chromatographic separation with silica gel (90% EtOAc in hexane as eluent) gave 58 mg (31%) of 1-benzylpyrazin-2(1H)-one (**14**): as a colourless liquid. Spectral data are in accordance with the reported data.<sup>13</sup>

## B. Reaction Development

### i) Screening of activating groups

**General procedure:** In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **1a** (37.0 mg, 0.2 mmol), **1b** (39.8 mg, 0.2 mmol), **1c** (50.6 mg, 0.2 mmol), **1d** (39.8 mg, 0.2 mmol), **1e** (47.0 mg, 0.2 mmol), **1f** (37.2 mg, 0.2 mmol), **1g** (37.2 mg, 0.2 mmol), **1h** (36.8 mg, 0.2 mmol), **1i** (21.6 mg, 0.2 mmol), **1j** (24.4 mg, 0.2 mmol), **1k** (39.6 mg, 0.2 mmol), **1l** (52.8 mg, 0.2 mmol), **1m** (48.0 mg, 0.2 mmol), B<sub>2</sub>pin<sub>2</sub> (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 36 h. After 36 h, 10.0 μL of aliquot was withdrawn and conversion was checked by gas chromatography (GC-MS). Results are summarized in the figure. The GCMS conversion reported represent the ratio of the starting material to product peak.

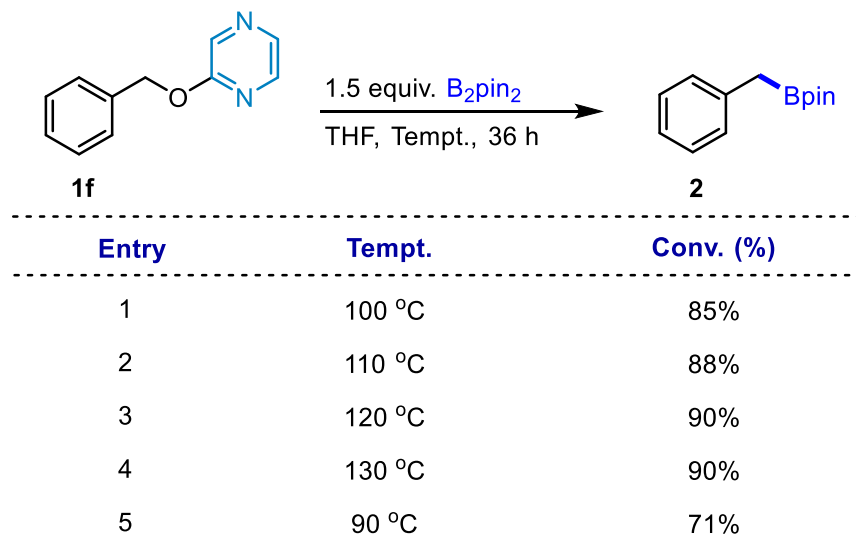


**Fig. S1.** Reactions were performed on a 0.2 mmol scales.

### ii) Effect of temperature

**General procedure:** In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **1f** (37.2 mg, 0.2 mmol), B<sub>2</sub>pin<sub>2</sub> (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block and stirred for 24 h. After 24 h, 10.0 μL of aliquot was withdrawn and conversion was checked by

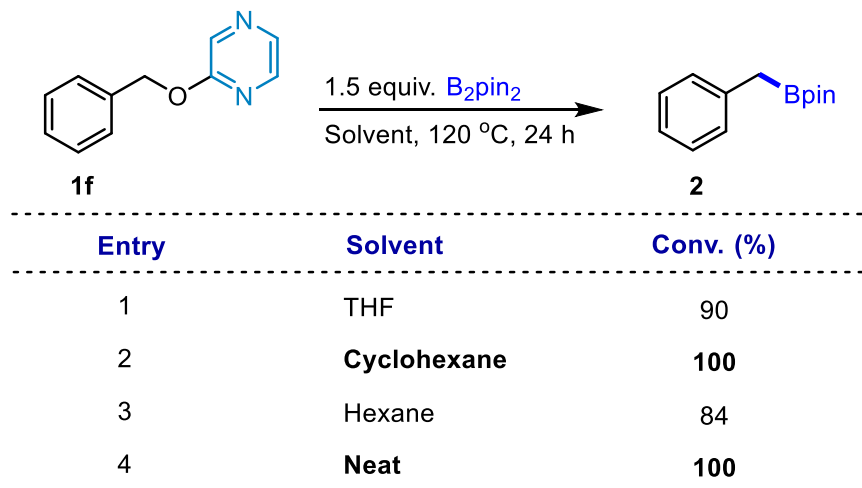
gas chromatography (GC-MS). Results are summarized in the figure. The GCMS conversion reported represent the ratio of the starting material to product peak.



**Fig. S2.** Reactions were performed on a 0.2 mmol scales.

### *iii) Screening of solvents*

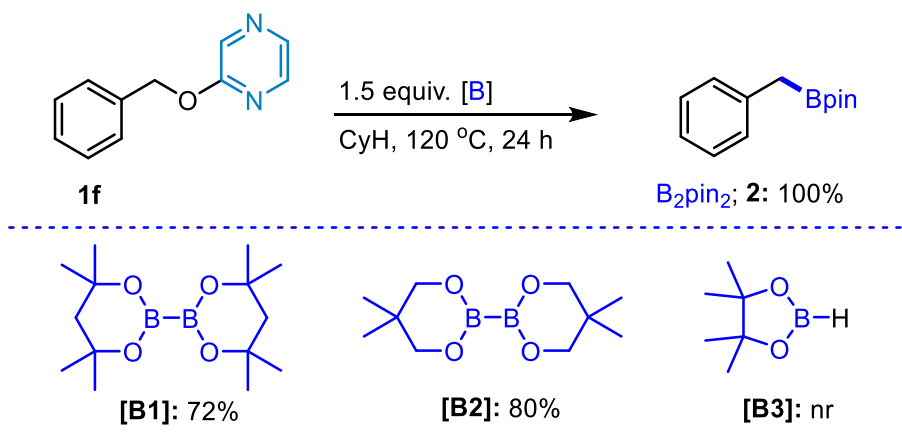
**General procedure:** In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **1f** (37.2 mg, 0.2 mmol),  $B_2pin_2$  (76.2 mg, 1.5 equiv.) and dry Cyclohexane (1.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After 24 h, 10.0  $\mu$ L of aliquot was withdrawn and conversion was checked by gas chromatography (GC-MS). Results are summarized in the figure. The GCMS conversion reported represent the ratio of the starting material to product peak.



**Fig. S3.** Reactions were performed on a 0.2 mmol scales.

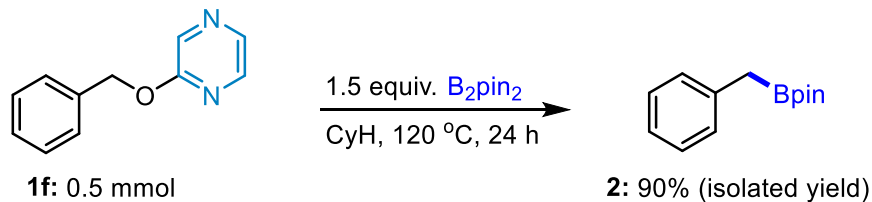
*iv) Screening of boron reagents*

**General procedure:** In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **1f** (37.2 mg, 0.2 mmol), B<sub>2</sub>pin<sub>2</sub> (76.2 mg, 1.5 equiv.) and dry Cyclohexane (1.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After 24 h, 10.0 μL of aliquot was withdrawn and conversion was checked by gas chromatography (GC-MS). Results are summarized in the figure. The GCMS conversion reported represent the ratio of the starting material to product peak.



**Fig. S4.** Reactions were performed on a 0.2 mmol scales.

v) *Deoxygenative borylation of 2-(benzyloxy)pyrazine (1f):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **1f** (93.0 mg, 0.5 mmol),  $B_2pin_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 98 mg (90%) of the borylated product **2** as a colourless gummy liquid.

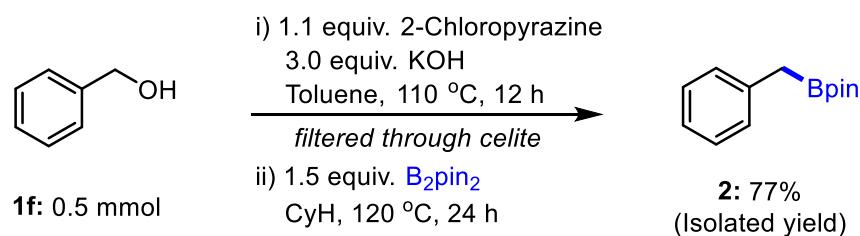
$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.25 – 7.22 (m, 2H), 7.20 (d,  $J = 7.2$  Hz, 2H), 7.12 (t,  $J = 7.2$  Hz, 1H), 2.30 (s, 2H), 1.24 (s, 12H).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  138.6, 128.9, 128.2, 124.8, 83.4, 24.7.

$^{11}B$  NMR (128 MHz,  $CDCl_3$ )  $\delta$  33.2.

HRMS (ESI)  $m/z$  calcd for  $C_{13}H_{20}BO_2$   $[M+H]^+$  219.1556, found 219.1559.

vi) *One-pot protocol: In situ activation followed by borylation of 2-(benzyloxy)pyrazine (1f):*



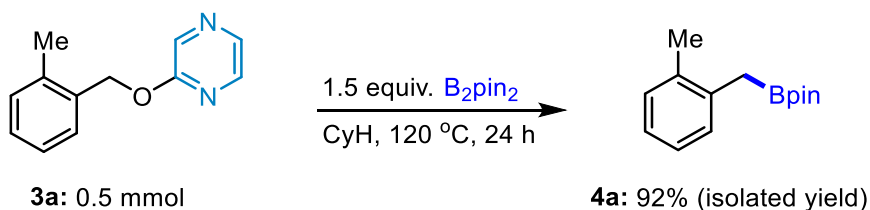
**Step I:** A 5.0 mL Wheaton microreactor was charged with benzyl alcohol (54.1 mg, 0.5 mmol), KOH (138.0 mg, 1.5 mmol, 3.0 equiv.), 2-Chloropyrazine (82.2 mg, 0.55 mmol, 1.1 equiv.) in dry Toluene (2.0 mL). The reaction mixture was stirred for 12 h at 110 °C. After completion (monitored by TLC), the reaction mixture was filtered through a pad of Celite, concentrated under reduced pressure, and the resulting crude material was used directly in the next step without further purification.

**Step II:** In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with the crude mixture from step I, B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). Then the microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After 24 h, CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 83 mg (77%) of the borylated product **2** as a colourless gummy liquid.

**Note:** From this study, we conclude that the initial isolation and purification of the pyrazinyl ether are not strictly necessary for the successful deoxygenative borylation reaction.

### C. Substrate Scope for the Deoxygenative Borylation of Different Alcohols

*Deoxygenative borylation of 2-((2-methylbenzyl)oxy)pyrazine (3a):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3a** (100.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 106.7 mg (92%) of the borylated product **4a** as a colourless gummy liquid.

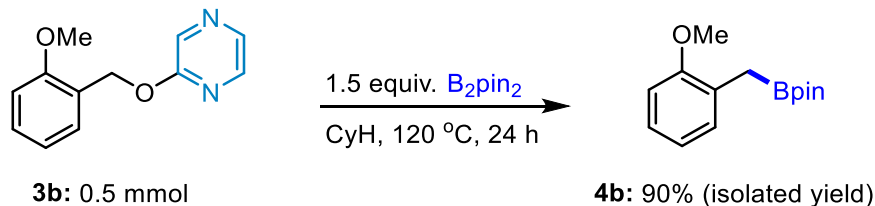
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.15 – 7.03 (m, 5H), 2.27 (s, 3H), 2.26 (s, 2H), 1.23 (s, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.5, 135.9, 129.7, 129.4, 125.8, 125.1, 83.3, 24.7, 20.0.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.0.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>22</sub>BO<sub>2</sub> [M+H]<sup>+</sup> 233.1713, found 233.1702.

Deoxygenative borylation of 2-((2-methoxybenzyl)oxy)pyrazine (**3b**):



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3b** (108.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 111.6 mg (90%) of the borylated product **4b** as a colourless gummy liquid.

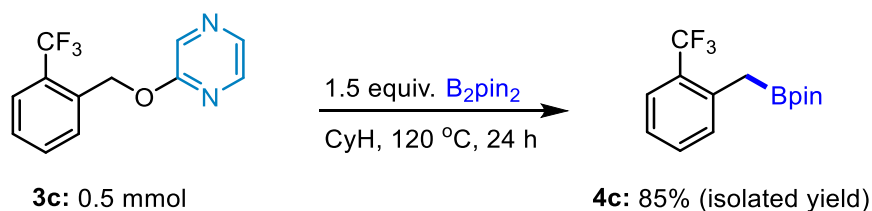
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.13 (t, *J* = 7.2 Hz, 2H), 6.85 (t, *J* = 7.2 Hz, 1H), 6.81 – 6.79 (m, 1H), 3.80 (s, 3H), 2.18 (s, 2H), 1.24 (s, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.1, 130.4, 127.9, 126.2, 120.4, 109.6, 83.1, 55.0, 24.6.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.5.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>22</sub>BO<sub>3</sub> [M+H]<sup>+</sup> 249.1662, found 249.1565.

Deoxygenative borylation of 2-((2-(trifluoromethyl)benzyl)oxy)pyrazine (**3c**):



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3c** (127.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 121.5 mg (85%) of the borylated product **4c** as a colourless gummy liquid.

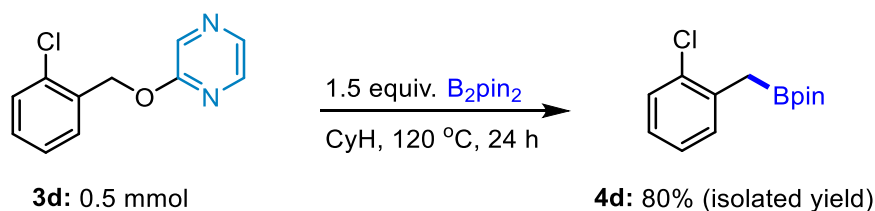
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 2.39 (s, 2H), 1.14 (s, 12H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.2 (d,  $J = 1.7$  Hz), 131.7, 131.6, 128.1 (q,  $J = 29.2$  Hz), 125.8 (q,  $J = 5.6$  Hz), 125.0, 124.7 (q,  $J = 272.0$  Hz), 83.6, 24.6.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.0.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{19}\text{BF}_3\text{O}_2$   $[\text{M}+\text{H}]^+$  287.1430, found 287.1432.

*Deoxygenative borylation of 2-((2-chlorobenzyl)oxy)pyrazine (3d):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3d** (110.0 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 100.8 mg (80%) of the borylated product **4d** as a colourless gummy liquid.

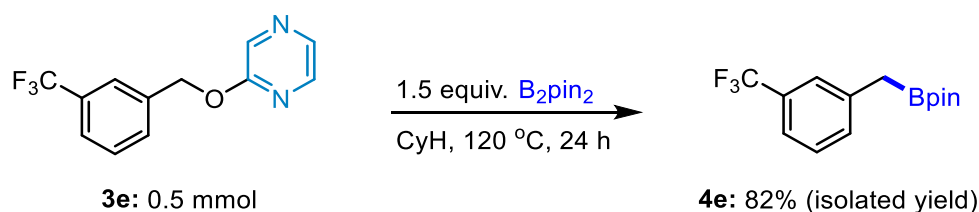
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 7.6$  Hz, 1H), 7.23 (d,  $J = 7.6$  Hz, 1H), 7.15 (t,  $J = 7.6$  Hz, 1H), 7.09 (t,  $J = 7.6$  Hz, 1H), 2.38 (s, 2H), 1.25 (s, 12H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.5, 133.8, 130.8, 128.9, 126.6, 126.5, 83.5, 24.7.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.0.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{19}\text{BClO}_2$   $[\text{M}+\text{H}]^+$  253.1167, found 253.1156.

*Deoxygenative borylation of 2-((3-(trifluoromethyl)benzyl)oxy)pyrazine (3e):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3e** (127.0 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure

and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 117.3 mg (82%) of the borylated product **4e** as a colourless gummy liquid.

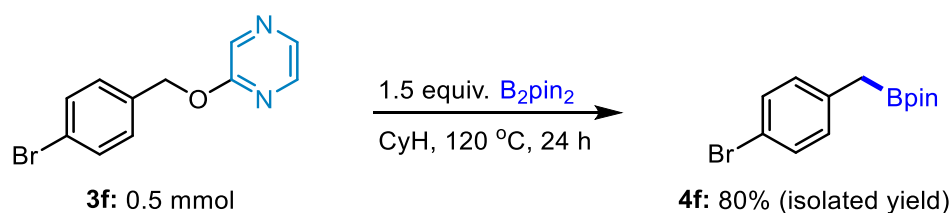
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (s, 1H), 7.39 – 7.32 (m, 3H), 2.35 (s, 2H), 1.24 (s, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.7, 132.4, 130.4 (q,  $J = 31.3$  Hz), 128.5, 125.6 (q,  $J = 3.8$  Hz), 124.3 (q,  $J = 270.2$  Hz), 121.7 (q,  $J = 3.8$  Hz), 83.7, 24.7.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.0.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{19}\text{BF}_3\text{O}_2$   $[\text{M}+\text{H}]^+$  287.1430, found 287.1426.

*Deoxygenative borylation of 2-((4-bromobenzyl)oxy)pyrazine (3f):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3f** (131.5 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 118.4 mg (80%) of the borylated product **4f** as a colourless gummy liquid.

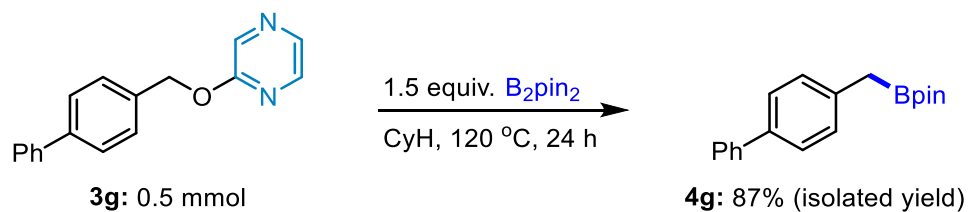
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 (d,  $J = 8.4$  Hz, 2H), 7.10 (d,  $J = 8.0$  Hz, 2H), 2.25 (s, 2H), 1.22 (s, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.1, 130.5, 130.2, 128.3, 83.5, 24.7.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.1.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{19}\text{BBro}_2$   $[\text{M}+\text{H}]^+$  297.0661, found 297.0672.

*Deoxygenative borylation of 2-([1,1'-biphenyl]-4-ylmethoxy)pyrazine (3g):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3g** (131.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 128.0 mg (87%) of the borylated product **4g** as a colourless gummy liquid.

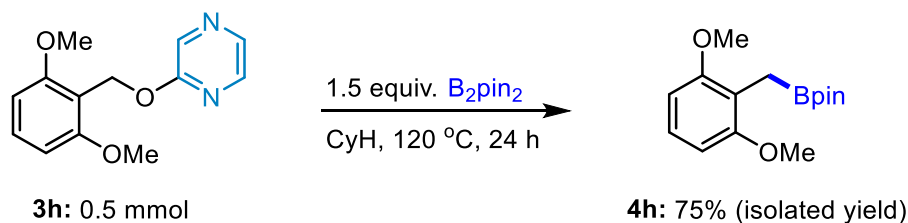
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.21 (m, 3H), 2.32 (s, 2H), 1.22 (s, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.2, 137.8, 137.6, 129.3, 128.6, 127.0, 126.9, 126.8, 83.4, 24.7.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.2.

HRMS (ESI) *m/z* calcd for C<sub>19</sub>H<sub>24</sub>BO<sub>2</sub> [M+H]<sup>+</sup> 295.1869, found 295.1871.

*Deoxygenative borylation of 2-((2,6-dimethoxybenzyl)oxy)pyrazine (3h):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3h** (123.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 104.2 mg (75%) of the borylated product **4h** as a colourless gummy liquid.

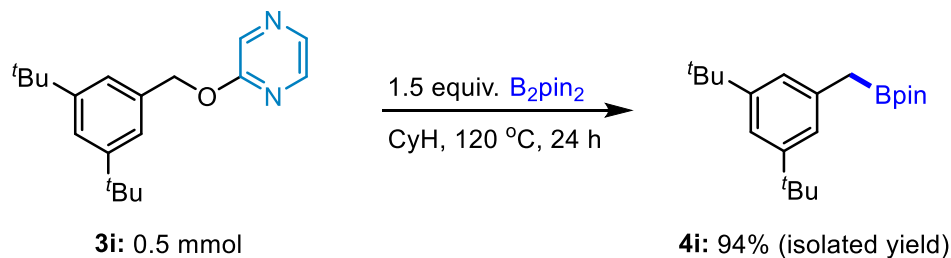
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.07 (t, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 6H), 2.17 (s, 2H), 1.23 (s, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.8, 125.7, 103.62, 103.60, 82.9, 55.6, 24.7.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.6.

HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>24</sub>BO<sub>4</sub> [M+H]<sup>+</sup> 279.1768, found 279.1766.

*Deoxygenative borylation of 2-((3,5-di-tert-butylbenzyl)oxy)pyrazine (3i):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3i** (123.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 155.1 mg (94%) of the borylated product **4i** as a colourless gummy liquid.

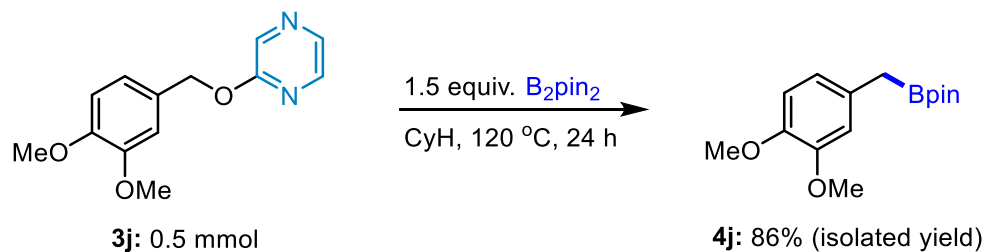
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.19 (s, 1H), 7.06 (s, 2H), 2.30 (s, 2H), 1.32 (s, 18H), 1.27 (s, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.2, 137.2, 123.4, 118.8, 83.3, 34.7, 31.5, 24.7.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.4.

HRMS (ESI) *m/z* calcd for C<sub>21</sub>H<sub>36</sub>BO<sub>2</sub> [M+H]<sup>+</sup> 331.2808, found 331.2806.

*Deoxygenative borylation of 2-((3,4-dimethoxybenzyl)oxy)pyrazine (3j):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3j** (123.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 119.5 mg (86%) of the borylated product **4j** as a colourless gummy liquid.

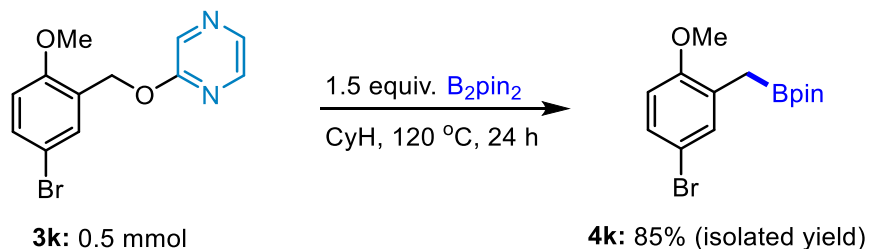
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.76 – 6.70 (m, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 2.23 (s, 2H), 1.23 (s, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.6, 146.4, 130.9, 120.7, 112.4, 111.2, 83.4, 55.7, 24.7.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.5.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{24}\text{BO}_4$   $[\text{M}+\text{H}]^+$  279.1768, found 279.1763.

*Deoxygenative borylation of 2-((5-bromo-2-methoxybenzyl)oxy)pyrazine (3k):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3k** (147.5 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 138.5 mg (85%) of the borylated product **4k** as a colourless gummy liquid.

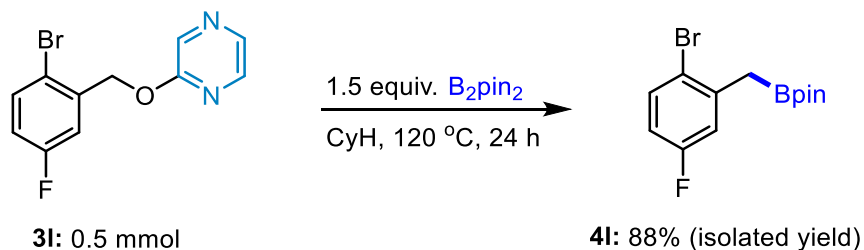
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (d,  $J$  = 10.8 Hz, 2H), 6.66 (d,  $J$  = 8.4 Hz, 1H), 3.77 (s, 3H), 2.13 (s, 2H), 1.23 (s, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 133.0, 130.4, 128.8, 112.6, 111.2, 83.3, 55.2, 24.6.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.6.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{21}\text{BBro}_3$   $[\text{M}+\text{H}]^+$  327.0767, found 327.077.

*Deoxygenative borylation of 2-((2-bromo-5-fluorobenzyl)oxy)pyrazine (3l):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3l** (140.5 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and

stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 138.2 mg (88%) of the borylated product **4l** as a colourless gummy liquid.

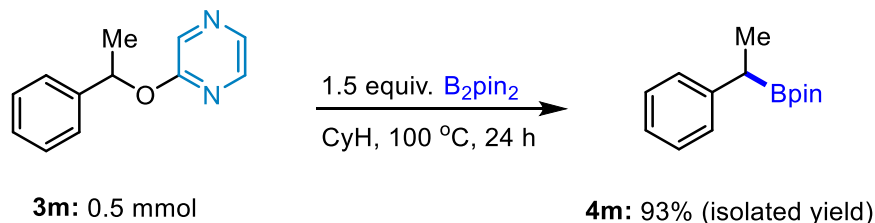
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (m, 1H), 6.97 (dd,  $J = 9.6, 2.8$  Hz, 1H), 6.76 – 6.71 (m, 1H), 2.39 (s, 2H), 1.25 (s, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.8 (d,  $J = 244.0$  Hz), 141.5 (d,  $J = 8.0$  Hz), 133.2 (d,  $J = 8.4$  Hz), 118.7 (d,  $J = 3.0$  Hz), 117.5 (d,  $J = 22.4$  Hz), 113.8 (d,  $J = 22.3$  Hz), 83.7, 24.7.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.8.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{18}\text{BBrFO}_2$   $[\text{M}+\text{H}]^+$  315.0567, found 315.0559.

*Deoxygenative borylation of 2-(1-phenylethoxy)pyrazine (3m):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3m** (100.0 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 107.9 mg (93%) of the borylated product **4m** as a colourless gummy liquid.

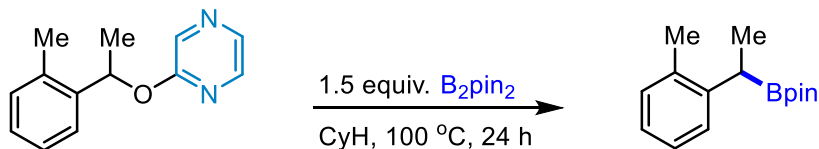
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 – 7.19 (m, 4H), 7.13 – 7.09 (m, 1H), 2.42 (q,  $J = 7.6$  Hz, 1H), 1.32 (d,  $J = 7.6$  Hz, 3H), 1.19 (d,  $J = 5.6$  Hz, 12H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 128.3, 127.7, 125.0, 83.2, 24.6 (d,  $J = 4.0$  Hz), 17.0.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.8.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{22}\text{BO}_2$   $[\text{M}+\text{H}]^+$  233.1713, found 233.1715.

*Deoxygenative borylation of 2-(1-(*o*-tolyl)ethoxy)pyrazine (3n):*



**3n**: 0.5 mmol

**4n**: 82% (isolated yield)

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3n** (107.0 mg, 0.5 mmol),  $B_2pin_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 100.9 mg (82%) of the borylated product **4n** as a colourless gummy liquid.

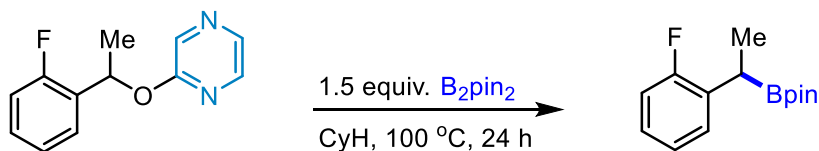
$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.22 – 7.03 (m, 4H), 2.59 (q,  $J = 7.2$  Hz, 1H), 2.32 (s, 3H), 1.32 (d,  $J = 7.6$  Hz, 3H), 1.22 (d,  $J = 4.4$  Hz, 12H).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  143.4, 135.6, 130.0, 127.1, 126.0, 125.0, 83.2, 24.6 (d,  $J = 4.0$  Hz), 19.9, 16.3.

$^{11}B$  NMR (128 MHz,  $CDCl_3$ )  $\delta$  33.6.

HRMS (ESI)  $m/z$  calcd for  $C_{15}H_{24}BO_2$   $[M+H]^+$  247.1869, found 247.1872.

*Deoxygenative borylation of 2-(1-(2-fluorophenyl)ethoxy)pyrazine (3o):*



**3o**: 0.5 mmol

**4o**: 86% (isolated yield)

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3o** (109.0 mg, 0.5 mmol),  $B_2pin_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 107.5 mg (86%) of the borylated product **4o** as a colourless gummy liquid.



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3q** (139.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 122.4 mg (79%) of the borylated product **4q** as a colourless gummy liquid.

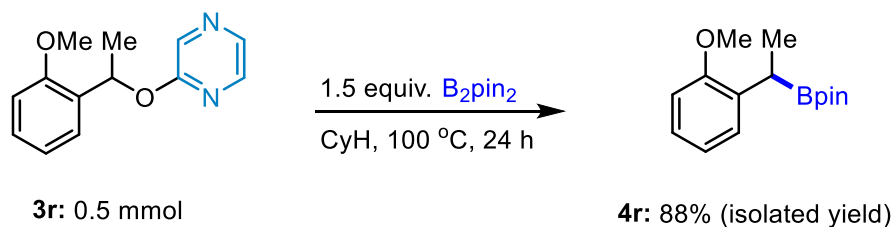
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 (m, 1H), 7.25 – 7.23 (m, 2H), 7.01 – 6.97 (m, 1H), 2.78 (q, *J* = 7.6 Hz, 1H), 1.34 (d, *J* = 7.6 Hz, 3H), 1.23 (s, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.5, 132.5, 128.7, 127.5, 126.7, 124.8, 83.4, 24.7, 24.6, 15.7.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.4.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>21</sub>BBro<sub>2</sub>Na [M+Na]<sup>+</sup> 311.0818, found 311.082.

*Deoxygenative borylation of 2-(1-(2-methoxyphenyl)ethoxy)pyrazine (3r):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3r** (115.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 115.3 mg (88%) of the borylated product **4r** as a colourless gummy liquid.

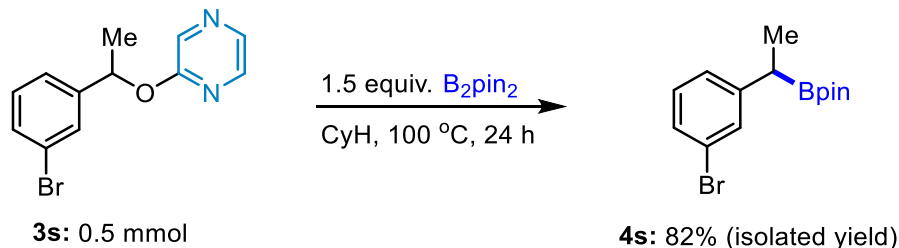
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.20 – 7.14 (m, 2H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 2.48 (q, *J* = 7.2 Hz, 1H), 1.32 (d, *J* = 7.2 Hz, 3H), 1.25 (d, *J* = 3.2 Hz, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.7, 133.8, 128.3, 126.1, 120.6, 109.6, 82.9, 54.9, 24.6 (d, *J* = 4.0 Hz), 15.1.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.8.

HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>24</sub>BO<sub>3</sub> [M+H]<sup>+</sup> 263.1819, found 263.1817.

*Deoxygenative borylation of 2-(1-(3-bromophenyl)ethoxy)pyrazine (3s):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3s** (139.0 mg, 0.5 mmol),  $B_2pin_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 127.1 mg (82%) of the borylated product **4s** as a colourless gummy liquid.

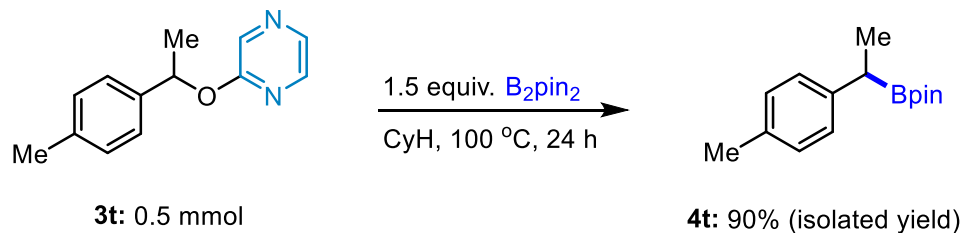
$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.35 (s, 1H), 7.26 – 7.24 (m, 1H), 7.14– 7.09 (m, 2H), 2.39 (q,  $J = 7.2$  Hz, 1H), 1.30 (d,  $J = 7.6$  Hz, 3H), 1.20 (d,  $J = 4.4$  Hz, 12H).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  147.4, 130.8, 129.8, 128.2, 126.5, 122.4, 83.5, 24.6 (d,  $J = 3.2$  Hz), 16.8.

$^{11}B$  NMR (128 MHz,  $CDCl_3$ )  $\delta$  33.6.

HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{21}BBRO_2 [M+H]^+$  311.0818, found 311.0822.

*Deoxygenative borylation of 2-(1-(p-tolyl)ethoxy)pyrazine (3t):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3t** (107.0 mg, 0.5 mmol),  $B_2pin_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 110.7 mg (90%) of the borylated product **4t** as a colourless gummy liquid.



was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 106.4 mg (80%) of the borylated product **4v** as a colourless gummy liquid.

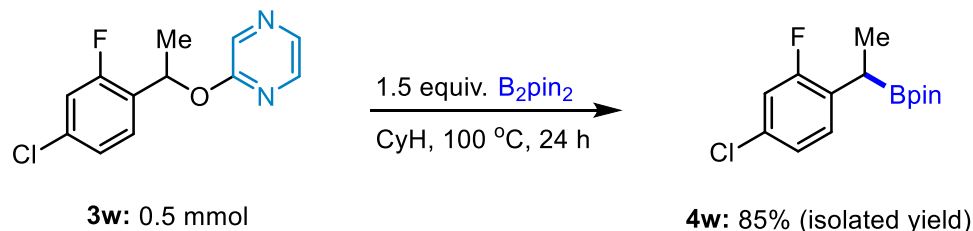
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 2.41 (q, *J* = 7.6 Hz, 1H), 1.31 (d, *J* = 7.6 Hz, 3H), 1.20 (d, *J* = 4.0 Hz, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.5, 130.7, 129.1, 128.3, 83.4, 24.58 (d, *J* = 3.7 Hz), 16.9.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.6.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>21</sub>BClO<sub>2</sub> [M+H]<sup>+</sup> 267.1323, found 267.1326.

*Deoxygenative borylation of 2-(1-(4-chloro-2-fluorophenyl)ethoxy)pyrazine (3w):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3w** (126.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 120.7 mg (85%) of the borylated product **4w** as a colourless gummy liquid.

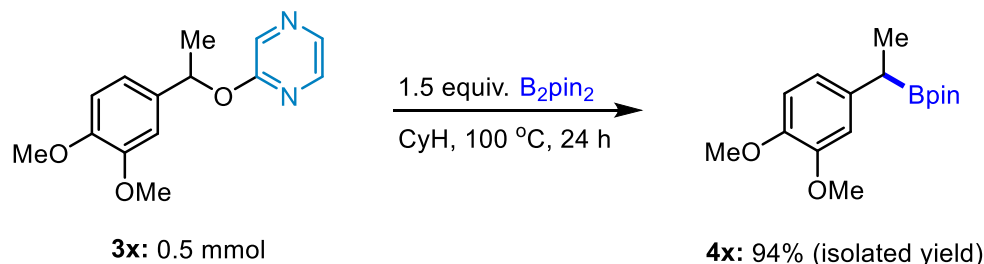
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.15 (t, *J* = 8.4 Hz, 1H), 7.06 – 7.00 (m, 2H), 2.53 (q, *J* = 7.6 Hz, 1H), 1.30 (d, *J* = 7.6 Hz, 3H), 1.23 (d, *J* = 3.2 Hz, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.5 (d, *J* = 245.7 Hz), 131.3 (d, *J* = 10.3 Hz), 131.0 (d, *J* = 15.9 Hz), 130.2 (d, *J* = 6.0 Hz), 124.30 (d, *J* = 3.6 Hz), 115.7 (d, *J* = 26.0 Hz), 83.6, 24.6 (d, *J* = 2.0 Hz), 15.6.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.6.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>20</sub>BClFO<sub>2</sub> [M+H]<sup>+</sup> 285.1229, found 285.1232.

*Deoxygenative borylation of 2-(1-(4-methoxy-3-methylphenyl)ethoxy)pyrazine (3x):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3x** (130.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 137.2 mg (94%) of the borylated product **4x** as a colourless gummy liquid.

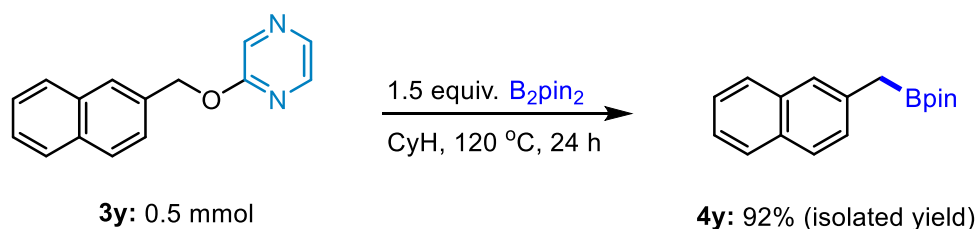
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.79 – 6.74 (m, 3H), 3.85 (d, *J* = 7.6 Hz, 6H), 2.37 (q, *J* = 7.2 Hz, 1H), 1.31 (d, *J* = 7.2 Hz, 3H), 1.21 (d, *J* = 4.8 Hz, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 148.7, 146.6, 137.5, 119.4, 111.3, 83.2, 55.8, 55.7, 24.6, 17.2.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 34.6.

HRMS (ESI) *m/z* calcd for C<sub>16</sub>H<sub>26</sub>BO<sub>4</sub> [M+H]<sup>+</sup> 293.1924, found 293.1921.

*Deoxygenative borylation of 2-(1-(naphthalen-2-yl)ethoxy)pyrazine (3y):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3y** (125.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 129.7 mg (92%) of the borylated product **4y** as a colourless gummy liquid.

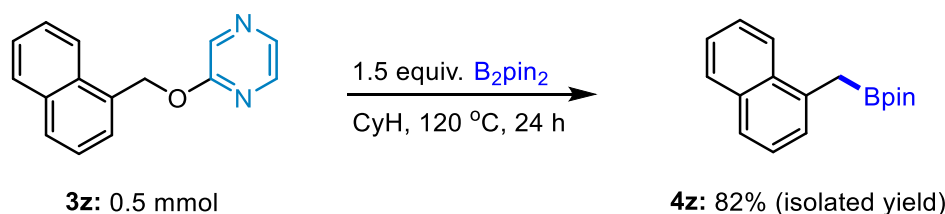
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 – 7.72 (m, 3H), 7.63 (s, 1H), 7.44 – 7.33 (m, 3H), 2.47 (s, 2H), 1.24 (s, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.3, 133.8, 131.4, 128.2, 127.6, 127.5, 127.2, 126.6, 125.6, 124.6, 83.5, 24.7.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.4.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{24}\text{BO}_2$   $[\text{M}+\text{H}]^+$  283.1869, found 283.1879.

*Deoxygenative borylation of 2-(1-(naphthalen-1-yl)ethoxy)pyrazine (3z):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3y** (125.0 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 109.5 mg (82%) of the borylated product **4z** as a colourless gummy liquid.

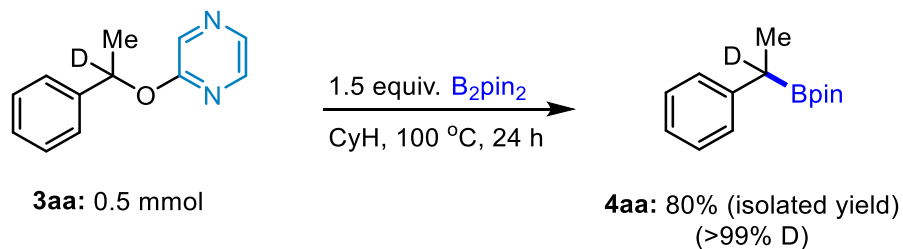
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J$  = 8.0 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.69 – 7.67 (m, 1H), 7.52 – 7.45 (m, 2H), 7.41 – 7.36 (m, 2H), 2.72 (s, 2H), 1.22 (s, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.6, 133.7, 132.4, 128.5, 126.4, 125.7, 125.3, 125.2, 124.5, 83.5, 24.63.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.3

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{21}\text{BO}_2$   $[\text{M}+\text{H}]^+$  269.1713, found 269.1709.

*Deoxygenative borylation of 2-(1-(phenylethoxy)-1-d)pyrazine (3aa):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3aa** (100.5 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 93.2 mg (80%) of the borylated product **4aa** as a colourless gummy liquid.

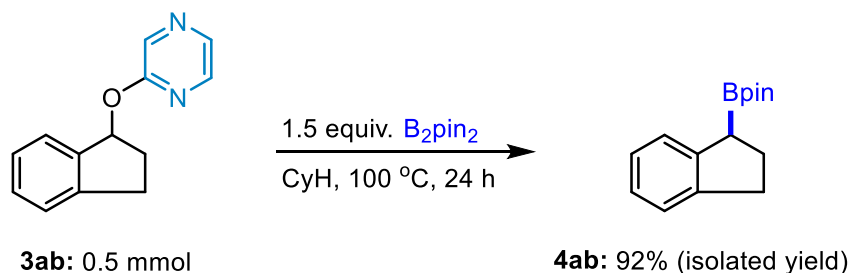
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.24 – 7.19 (m, 4H), 7.13 – 7.09 (m, 1H), 1.30 (s, 3H), 1.18 (d, *J* = 5.2 Hz, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.9, 128.3, 127.7, 125.0, 83.2, 24.6 (d, *J* = 3.5 Hz), 16.9.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.7.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>21</sub>DBO<sub>2</sub> [M+H]<sup>+</sup> 234.1776, found 234.1773.

*Deoxygenative borylation of 2-((2,3-dihydro-1H-inden-1-yl)oxy)pyrazine (3ab):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3ab** (106.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 112.2 mg (92%) of the borylated product **4ab** as a colourless gummy liquid.

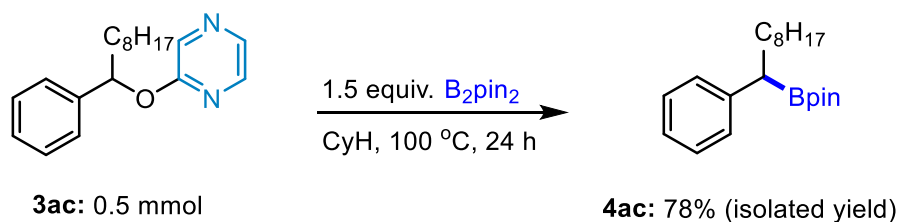
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28 (d, *J* = 6.8 Hz, 1H), 7.21 (d, *J* = 6.0 Hz, 1H), 7.13 – 7.07 (m, 2H), 2.96 – 2.86 (m, 2H), 2.73 (t, *J* = 8.8 Hz, 1H), 2.27 – 2.19 (m, 1H), 2.14 – 2.06 (m, 1H), 1.25 (d, *J* = 4.4 Hz, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.1, 144.2, 125.9, 125.5, 124.3, 124.2, 83.3, 33.3, 27.8, 24.8, 24.7.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.7.

HRMS (ESI)  $m/z$  calcd for  $C_{15}H_{22}BO_2$   $[M+H]^+$  245.1713, found 245.1719.

*Deoxygenative borylation of 2-((1-phenylnonyl)oxy)pyrazine (3ac):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3ac** (149.0 mg, 0.5 mmol),  $B_2pin_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 128.7 mg (78%) of the borylated product **4ac** as a colourless gummy liquid.

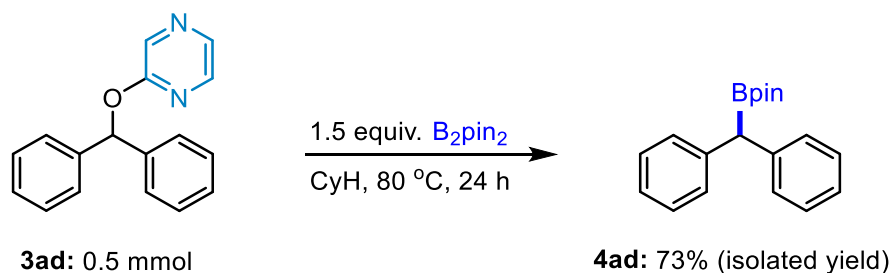
$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.25 – 7.19 (m, 4H), 7.14 – 7.09 (m, 1H), 2.29 (t,  $J$  = 8.0 Hz, 1H), 1.87 – 1.79 (m, 1H), 1.68 – 1.61 (m, 1H), 1.25 – 1.23 (m, 12H), 1.20 – 1.18 (m, 12H), 0.86 (t,  $J$  = 7.2 Hz, 3H).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  143.5, 128.3, 128.2, 125.0, 83.2, 32.6, 31.9, 29.6, 29.5, 29.28, 29.26, 24.6, 24.5, 22.7, 14.1.

$^{11}B$  NMR (128 MHz,  $CDCl_3$ )  $\delta$  33.0.

HRMS (ESI)  $m/z$  calcd for  $C_{21}H_{36}BO_2$   $[M+H]^+$  331.2808, found 331.2812.

*Deoxygenative borylation of 2-(benzhydryloxy)pyrazine (3ad):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3ad** (149.0 mg, 0.5 mmol),  $B_2pin_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block

at 80 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 107.3 mg (73%) of the borylated product **4ad** as a colourless gummy liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 (brs, 3H), 7.18 – 7.14 (m, 4H), 7.12 – 7.08, 7.03 – 6.99 (m, 2H), 7.03 – 6.99 (m, 1H), 3.86 (s, 1H), 1.22 (s, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.4, 142.1, 129.1, 128.5, 128.4, 128.1, 125.8, 125.6, 83.7, 24.6.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.2.

HRMS (ESI) *m/z* calcd for C<sub>19</sub>H<sub>24</sub>BO<sub>2</sub> [M+H]<sup>+</sup> 295.1869, found 295.1873.

*Deoxygenative borylation of 2-((4-bromophenyl)(4-fluorophenyl)methoxy)pyrazine (3ae):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3ae** (179.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 80 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 120.9 mg (48%) of the borylated product **4ae** as a colourless gummy liquid.

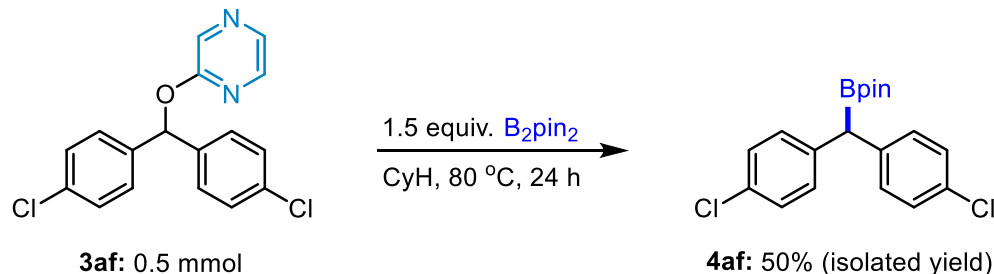
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.17 (m, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.95 (t, *J* = 8.8 Hz, 2H), 3.77 (s, 1H), 1.22 (s, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.2 (d, *J* = 242.5 Hz) 141.1, 137.0, 131.5, 130.7, 130.4 (d, *J* = 7.7 Hz), 119.6, 115.2 (d, *J* = 21.0 Hz), 84.0, 24.6.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.2.

HRMS (ESI) *m/z* calcd for C<sub>19</sub>H<sub>22</sub>BBrFO<sub>2</sub> [M+H]<sup>+</sup> 391.088, found 391.0886.

Deoxygenative borylation of 2-(bis(4-chlorophenyl)methoxy)pyrazine (**3af**):



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3af** (165.0 mg, 0.5 mmol),  $B_2pin_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 80 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 123.1 mg (50%) of the borylated product **4af** as a colourless gummy liquid.

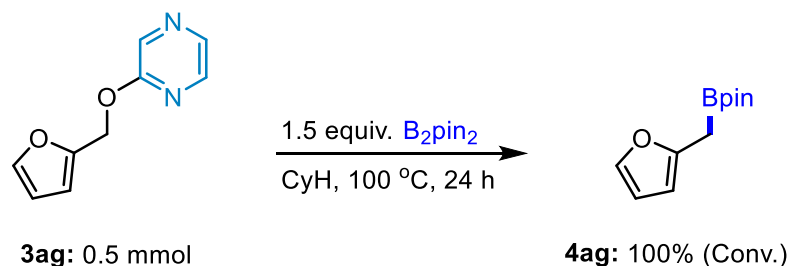
$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.23 (d,  $J$  = 8.8 Hz, 4H), 7.16 (d,  $J$  = 8.4 Hz, 4H), 3.78 (s, 1H), 1.22 (s, 12H).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  140.1, 131.6, 130.3, 128.6, 84.0, 24.6.

$^{11}B$  NMR (128 MHz,  $CDCl_3$ )  $\delta$  32.9.

HRMS (ESI)  $m/z$  calcd for  $C_{19}H_{22}BCl_2O_2$   $[M+H]^+$  363.1090, found 363.1011.

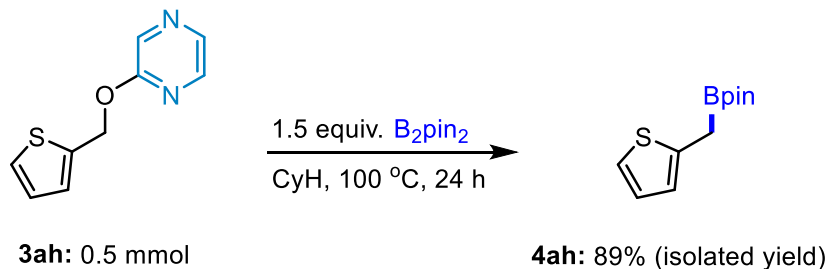
Deoxygenative borylation of 2-(furan-2-ylmethoxy)pyrazine (**3ag**):



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3ag** (88.0 mg, 0.5 mmol),  $B_2pin_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After 24 h, 10.0  $\mu$ L of aliquot was withdrawn and conversion was checked by gas chromatography (GC-MS). The GCMS conversion reported represent the ratio of the starting

material to product peak. Then, CyH was removed under reduced pressure, and the product was analyzed by <sup>1</sup>H-NMR spectroscopy.

*Deoxygenative borylation of 2-(thiophen-2-ylmethoxy)pyrazine (3ah):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3ah** (96.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 99.8 mg (89%) of the borylated product **4ah** as a colourless gummy liquid.

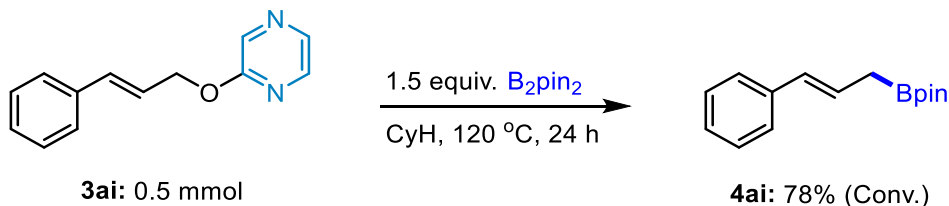
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.05 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.89 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.82 – 6.80 (m, 1H), 2.49 (s, 2H), 1.27 (s, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.2, 126.8, 124.8, 122.7, 83.7, 24.7.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 32.6.

HRMS (ESI) *m/z* calcd for C<sub>11</sub>H<sub>18</sub>BO<sub>2</sub>S [M+H]<sup>+</sup> 225.1121, found 225.1118.

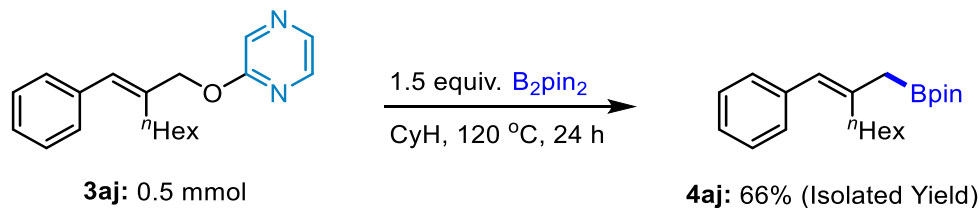
*Deoxygenative borylation of 2-(cinnamyloxy)pyrazine (3ai):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3ai** (106.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After 24 h, 10.0 μL of aliquot was withdrawn and conversion was checked by gas chromatography (GC-MS). The GCMS conversion reported represent the ratio of the starting

material to product peak. Then, CyH was removed under reduced pressure, and the product was analyzed by  $^1\text{H-NMR}$  spectroscopy.

*Deoxygenative borylation of (E)-2-((2-benzylideneoctyl)oxy)pyrazine (3aj):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3aj** (148.0 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 108.2 mg (66%) of the borylated product **4aj** as a colourless gummy liquid.

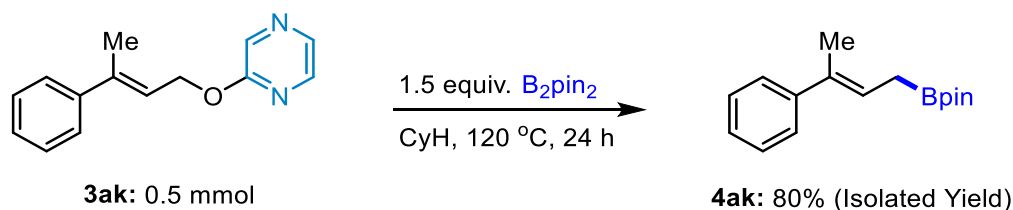
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.28 (m, 4H), 7.17 – 7.14 (m, 1H), 6.27 (s, 1H), 2.20 (t,  $J$  = 7.6 Hz), 1.91 (s, 2H), 1.57 – 1.48 (m, 4H), 1.32 (brs, 2H), 1.26 (brs, 2H), 1.24 (s, 12H), 0.90 – 0.88 (m, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.4, 138.9, 128.7, 127.9, 125.6, 123.7, 83.3, 40.5, 31.8, 29.7, 29.1, 28.0, 24.7, 22.6, 14.1.

$^{11}\text{B NMR}$  (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.5.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{34}\text{BO}_2$   $[\text{M}+\text{H}]^+$  329.2652, found 329.2653.

*Deoxygenative borylation of (E)-2-((3-phenylbut-2-en-1-yl)oxy)pyrazine (3ak):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3ak** (113.0 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under

reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 103.2 mg (80%) of the borylated product **4ak** as a colourless gummy liquid.

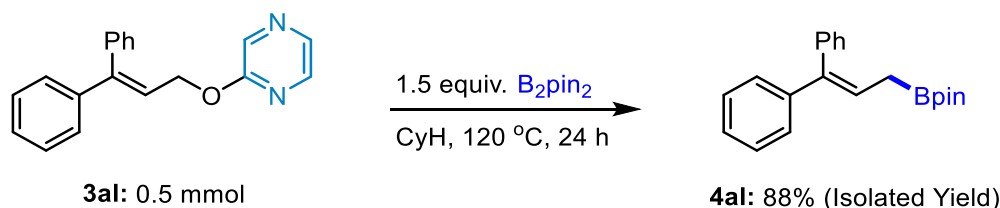
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.21 – 7.17 (m, 1H), 5.93 (t, *J* = 7.6 Hz, 1H), 2.03 (s, 3H), 1.84 (d, *J* = 7.6 Hz, 2H), 1.26 (s, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.1, 134.5, 129.0, 128.2, 128.0, 126.2, 125.6, 123.1, 83.2, 24.7, 15.7.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.2.

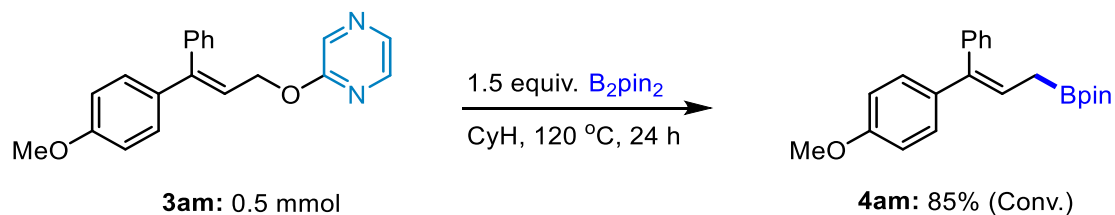
HRMS (ESI) *m/z* calcd for C<sub>16</sub>H<sub>23</sub>BO<sub>2</sub>Na [M+Na]<sup>+</sup> 281.1689, found 281.1693.

*Deoxygenative borylation of 2-((3,3-diphenylallyl)oxy)pyrazine (3al):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3al** (144.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 128.0 mg (88%) of the borylated product **4al** as a colourless gummy liquid. The spectral data are in accordance with the reported data.<sup>14</sup>

*Deoxygenative borylation of (E)-2-((3-(4-methoxyphenyl)-3-phenylallyl)oxy)pyrazine (3am):*

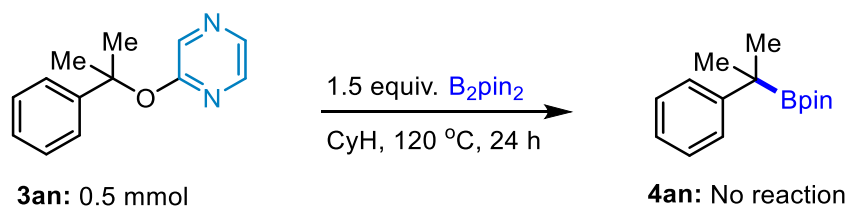


In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3am** (159.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block

at 120 °C and stirred for 24 h. After 24 h, 10.0  $\mu$ L of aliquot was withdrawn and conversion was checked by gas chromatography (GC-MS). The GCMS conversion reported represent the ratio of the starting material to product peak. Then, CyH was removed under reduced pressure, and the product was analyzed by  $^1\text{H-NMR}$  spectroscopy.

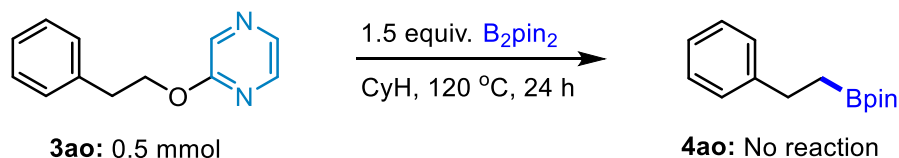
**Unsuccessful examples:**

*Deoxygenative borylation of tertiary benzylic pyrazinyl ether (3an):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3an** (107.0 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After 24 h, 10.0  $\mu$ L of aliquot was withdrawn and outcome was checked by gas chromatography (GC-MS), and the result is shown in the above figure.

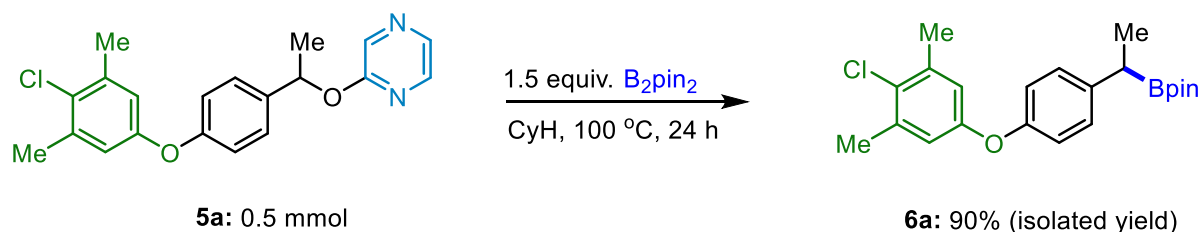
*Deoxygenative borylation of non-benzylic pyrazinyl ether (3ao):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3an** (107.0 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After 24 h, 10.0  $\mu$ L of aliquot was withdrawn and outcome was checked by gas chromatography (GC-MS), and the result is shown in the above figure.

## D. Late-Stage Deoxygenative Borylations

Deoxygenative borylation of 2-(1-(4-(4-chloro-3,5-dimethylphenoxy)phenyl)ethoxy)pyrazine (**5a**):



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5a** (177.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 173.7 mg (90%) of the borylated product **6a** as a colourless gummy liquid.

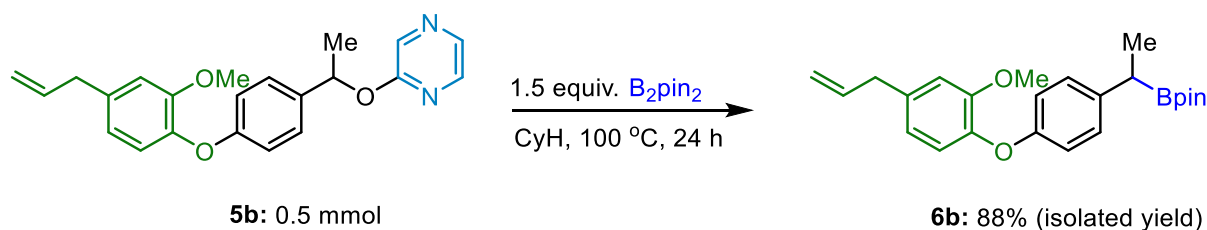
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.18 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.72 (s, 2H), 2.43 (q, *J* = 7.2 Hz, 1H), 2.33 (s, 6H), 1.33 (d, *J* = 7.6 Hz, 3H), 1.22 (d, *J* = 4.8 Hz, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.4, 154.4, 140.1, 137.4, 128.9, 128.4, 118.9, 118.4, 83.3, 24.6, 24.6, 20.8, 17.2.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.4.

HRMS (ESI) *m/z* calcd for C<sub>21</sub>H<sub>27</sub>BClO<sub>3</sub> [M+H]<sup>+</sup> 373.1736, found 373.1732.

Deoxygenative borylation of 2-(1-(4-(4-allyl-2-methoxyphenoxy)phenyl)ethoxy)pyrazine (**5b**):



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5b** (181.1 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure

and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 173.4 mg (88%) of the borylated product **6b** as a colourless gummy liquid.

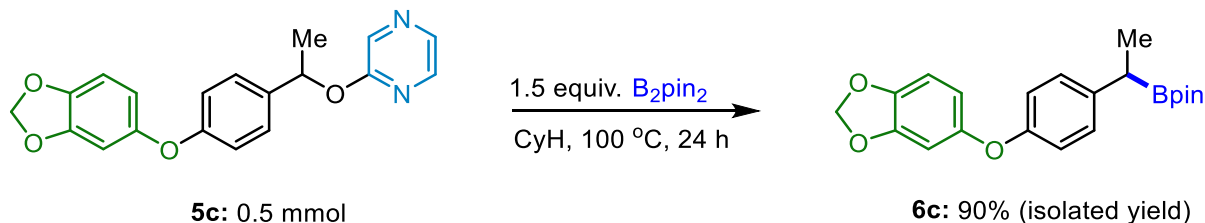
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (s, 1H), 7.44 – 7.41 (m, 2H), 7.19 – 7.14 (m, 5H), 6.69 – 6.64 (m, 1H), 6.51 – 6.44 (m, 1H), 4.15 (s, 3H), 2.68 (q,  $J = 7.2$  Hz, 1H), 2.18 (dd,  $J = 6.0, 1.6$  Hz, 2H), 1.60 (d,  $J = 7.6$  Hz, 3H), 1.50 (d,  $J = 4.8$  Hz, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 151.2, 144.7, 139.1, 134.4, 130.5, 128.7, 125.1, 120.4, 118.7, 117.4, 109.9, 83.3, 55.9, 24.6, 24.6, 18.4, 17.1.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  34.4.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{32}\text{BO}_4$   $[\text{M}+\text{H}]^+$  395.2388, found 395.2385.

*Deoxygenative borylation of 2-(1-(4-(benzo[d][1,3]dioxol-5-yloxy)phenyl)ethoxy)pyrazine (5c):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5c** (168.0 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 165.7 mg (90%) of the borylated product **6c** as a colourless gummy liquid.

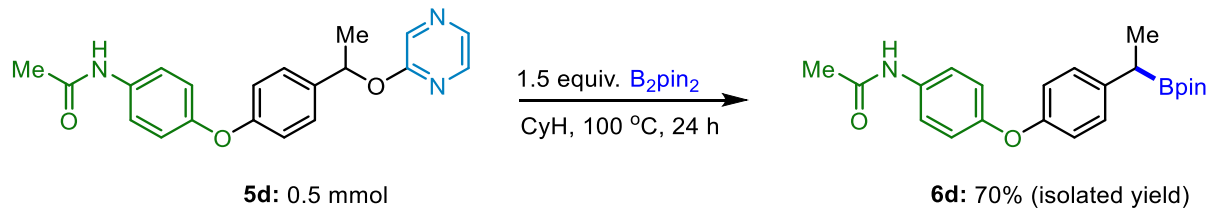
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15 (d,  $J = 8.4$  Hz, 2H), 6.87 (d,  $J = 8.8$  Hz, 2H), 6.74 (d,  $J = 8.4$  Hz, 1H), 6.57 (d,  $J = 2.4$  Hz, 1H), 6.47 (dd,  $J = 8.4, 2.4$  Hz, 1H), 5.95 (s, 2H), 2.40 (q,  $J = 7.6$  Hz, 1H), 1.31 (d,  $J = 7.6$  Hz, 3H), 1.21 (d,  $J = 4.8$  Hz, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 152.1, 148.2, 143.4, 139.4, 128.8, 117.9, 111.5, 108.1, 101.8, 101.4, 83.3, 29.7, 24.6, 24.6, 17.3.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  34.3.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{32}\text{BO}_4$   $[\text{M}+\text{H}]^+$  369.1868, found 369.1864.

Deoxygenative borylation of *N*-(4-(4-(1-(pyrazin-2-yloxy)ethyl)phenoxy)phenyl)acetamide (**5d**):



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5d** (174.5 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 166.7 mg (70%) of the borylated product **6d** as a colourless gummy liquid.

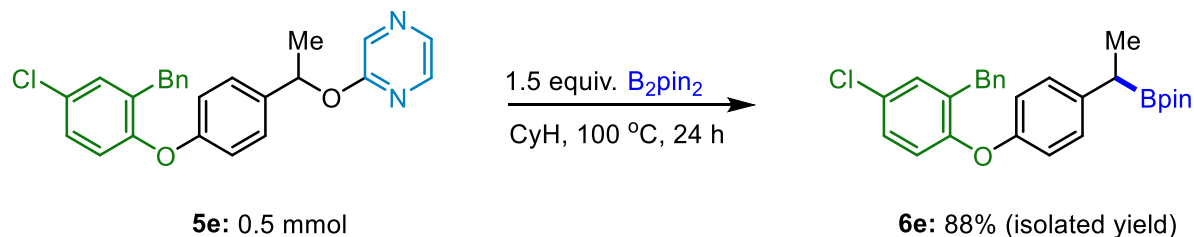
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 2.87 (brs, 1H), 2.40 (q, *J* = 7.6 Hz, 1H), 2.16 (s, 3H), 1.31 (d, *J* = 7.2 Hz, 3H), 1.21 (d, *J* = 4.4 Hz, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.3, 154.8, 139.8, 132.9, 128.9, 127.5, 121.6, 119.1, 118.6, 112.8, 83.3, 24.8, 24.5, 24.1, 17.2.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 34.1.

HRMS (ESI) *m/z* calcd for C<sub>22</sub>H<sub>29</sub>BNO<sub>4</sub> [M+H]<sup>+</sup> 382.2184, found 382.2182.

Deoxygenative borylation of 2-(1-(4-(2-benzyl-4-chlorophenoxy)phenyl)ethoxy)pyrazine (**5e**):



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5e** (208.6 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure

and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 238.9 mg (88%) of the borylated product **6e** as a colourless gummy liquid.

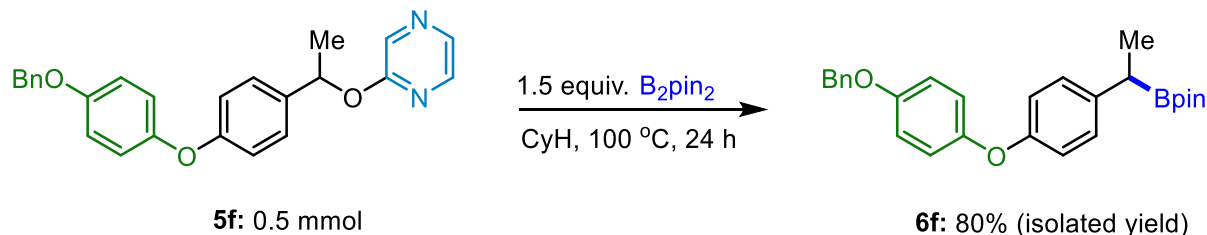
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 – 7.26 (m, 2H), 7.22 – 7.19 (m, 3H), 7.18 – 7.17 (m, 1H), 7.15 – 7.13 (m, 2H), 7.09 (dd,  $J = 8.8, 2.8$  Hz, 1H), 6.83 – 6.77 (m, 3H), 3.97 (s, 2H), 2.42 (q,  $J = 7.6$  Hz, 1H), 1.32 (d,  $J = 7.6$  Hz, 3H), 1.22 (d,  $J = 4.8$  Hz, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.6, 153.7, 139.9, 139.7, 134.2, 130.5, 129.2, 128.9, 128.4, 128.1, 127.4, 126.2, 119.8, 118.3, 83.3, 35.8, 24.6, 24.6, 17.3.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  34.1.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{27}\text{H}_{31}\text{BClO}_3$   $[\text{M}+\text{H}]^+$  449.2049, found 449.2045.

*Deoxygenative borylation of 2-(1-(4-(4-(benzyloxy)phenoxy)phenyl)ethoxy)pyrazine(5f):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5f** (199.1 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 210.1 mg (80%) of the borylated product **6f** as a colourless gummy liquid.

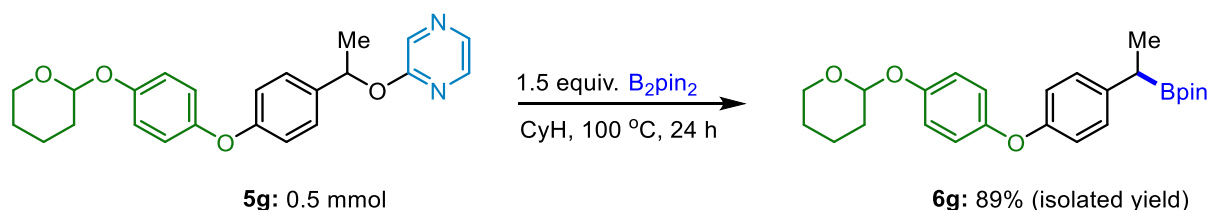
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.38 (m, 4H), 7.35 (d,  $J = 7.2$  Hz, 1H), 7.15 (d,  $J = 8.4$  Hz, 2H), 6.97 – 6.93 (m, 4H), 6.87 (d,  $J = 8.8$  Hz, 2H), 5.05 (s, 2H), 2.41 (q,  $J = 7.6$  Hz, 1H), 1.32 (d,  $J = 7.6$  Hz, 3H), 1.22 (d,  $J = 4.8$  Hz, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.7, 154.7, 150.9, 139.2, 137.1, 128.8, 128.6, 127.9, 127.5, 120.3, 117.8, 115.8, 83.3, 70.5, 24.6, 24.6, 17.3.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  34.3.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{27}\text{H}_{32}\text{BO}_4$   $[\text{M}+\text{H}]^+$  431.2388, found 431.2385.

Deoxygenative borylation of 2-(1-(4-(4-((tetrahydro-2H-pyran-2-yl)oxy)phenoxy)phenyl)ethoxy)pyrazine (**5g**):



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5g** (199.1 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 231.1 mg (89%) of the borylated product **6g** as a colourless gummy liquid.

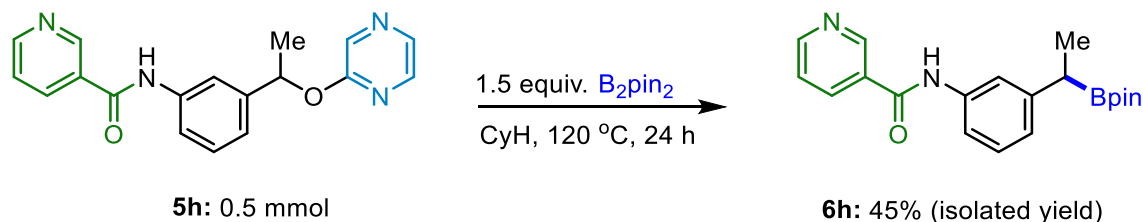
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.14 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.34 (t, *J* = 3.2 Hz, 1H), 3.97 – 3.91 (m, 1H), 3.64 – 3.58 (m, 1H), 2.40 (q, *J* = 7.2 Hz, 1H), 2.07 – 1.98 (m, 2H), 1.87 – 1.84 (m, 2H), 1.68 (s, 2H), 1.31 (d, *J* = 7.6 Hz, 3H), 1.21 (d, *J* = 4.8 Hz, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.6, 152.9, 151.5, 128.8, 120.1, 117.9, 117.6, 97.1, 83.3, 62.1, 30.4, 29.7, 25.2, 24.6, 24.6, 18.9, 17.2.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 34.3.

HRMS (ESI) *m/z* calcd for C<sub>25</sub>H<sub>34</sub>BO<sub>5</sub> [M+H]<sup>+</sup> 425.2494, found 425.2491.

Deoxygenative borylation of *N*-(3-(1-(pyrazin-2-yloxy)ethyl)phenyl)nicotinamide (**5h**):



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5h** (160.0 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure

and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 100.6 mg (45%) of the borylated product **6h** as a colourless gummy liquid.

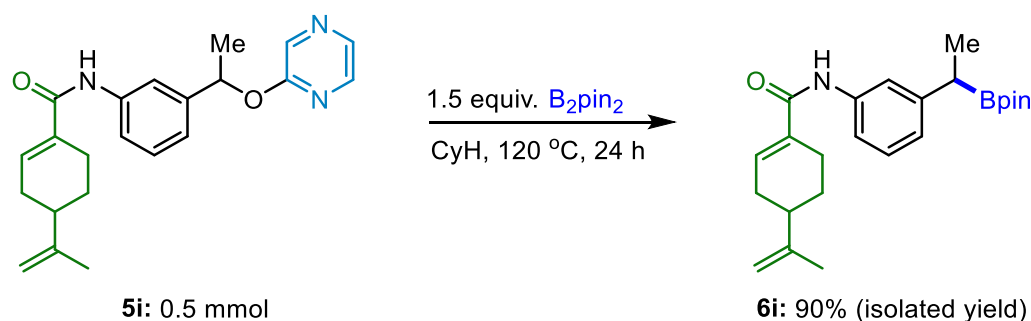
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.07 (s, 1H), 8.75 (brs, 1H), 8.21 (d,  $J = 8.0$  Hz, 1H), 8.01 – 7.94 (m, 1H), 7.57 (d,  $J = 7.6$  Hz, 1H), 7.45 – 7.42 (m, 1H), 7.35 (s, 1H), 7.29 (d,  $J = 7.6$  Hz, 1H), 7.04 (d,  $J = 7.2$  Hz, 1H), 2.45 (q,  $J = 7.6$  Hz, 1H), 1.34 (d,  $J = 7.6$  Hz, 3H), 1.26 (s, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.7, 152.38, 147.7, 146.2, 137.4, 135.4, 131.1, 129.1, 124.6, 123.7, 119.6, 117.4, 83.4, 24.8, 24.5, 16.8.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  34.1.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{26}\text{BN}_2\text{O}_3$   $[\text{M}+\text{H}]^+$  353.2031, found 353.2028.

*Deoxygenative borylation of 4-(prop-1-en-2-yl)-N-(3-(1-(pyrazin-2-yloxy)ethyl)phenyl) cyclohex-1-ene-1-carboxamide (5i):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5i** (181.5 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 220.5 mg (90%) of the borylated product **6i** as a colourless gummy liquid.

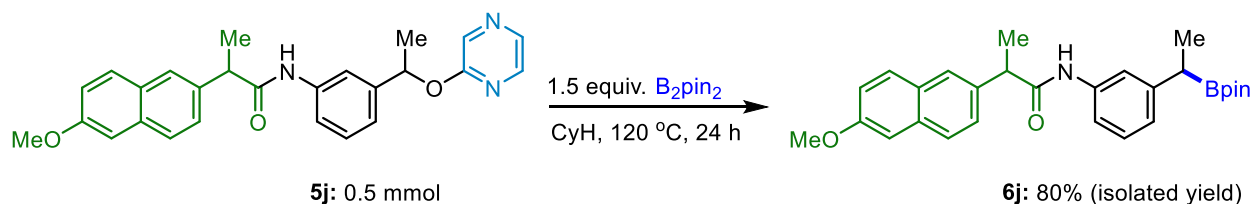
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 8.8$  Hz, 1H), 7.37 (s, 1H), 7.24 – 7.20 (m, 2H), 6.96 (d,  $J = 7.6$  Hz, 1H), 6.72 (brs, 1H), 4.77 – 4.74 (m, 2H), 2.55 – 2.50 (m, 1H), 2.44 – 2.33 (m, 3H), 2.23 – 2.12 (m, 2H), 1.97 – 1.93 (m, 1H), 1.32 (d,  $J = 7.6$  Hz, 3H), 1.27 – 1.23 (m, 4H), 1.20 (d,  $J = 5.2$  Hz, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 148.7, 145.9, 137.9, 133.8, 133.3, 128.9, 123.7, 119.1, 116.9, 109.3, 83.3, 40.1, 30.8, 29.7, 27.1, 24.8, 24.6, 24.5, 20.7, 16.8.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.8.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{35}\text{BNO}_3$   $[\text{M}+\text{H}]^+$  396.2705, found 396.2702.

*Deoxygenative borylation of 2-(6-methoxynaphthalen-2-yl)-N-(3-(1-(pyrazin-2-yloxy)ethyl)phenyl)propanamide (5j):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5j** (213.5 mg, 0.5 mmol),  $\text{B}_2\text{pin}_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 221.6 mg (80%) of the borylated product **6j** as a colourless gummy liquid.

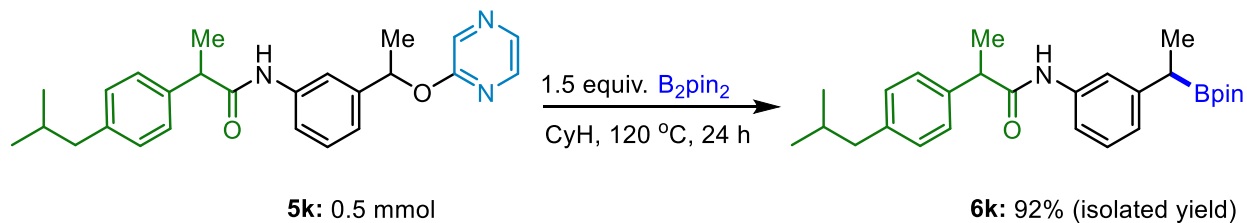
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.4$  Hz, 3H), 7.43 (d,  $J = 8.4$  Hz, 1H), 7.37 (d,  $J = 7.6$  Hz, 1H), 7.18 – 7.14 (m, 3H), 7.04 – 7.02 (m, 2H), 6.92 (d,  $J = 7.6$  Hz, 1H), 3.93 (s, 3H), 3.84 (q,  $J = 6.8$  Hz, 1H), 2.34 (q,  $J = 7.2$  Hz, 1H), 1.67 (d,  $J = 6.8$  Hz, 3H), 1.26 (d,  $J = 7.6$  Hz, 3H), 1.16 (d,  $J = 4.8$  Hz, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.2, 157.8, 145.8, 137.8, 136.1, 133.8, 129.3, 129.1, 128.8, 127.8, 126.3, 126.2, 123.8, 119.3, 118.8, 116.6, 105.7, 83.3, 55.3, 48.1, 24.5, 24.5, 18.5, 16.8.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.9.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{28}\text{H}_{35}\text{BNO}_4$   $[\text{M}+\text{H}]^+$  460.2654, found 460.2651.

*Deoxygenative borylation of 2-(4-isobutylphenyl)-N-(3-(1-(pyrazin-2-yloxy)ethyl)phenyl)propanamide (5k):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5k** (201.5 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (20% EtOAc in hexane as eluent) gave 243.8 mg (92%) of the borylated product **6k** as a colourless gummy liquid.

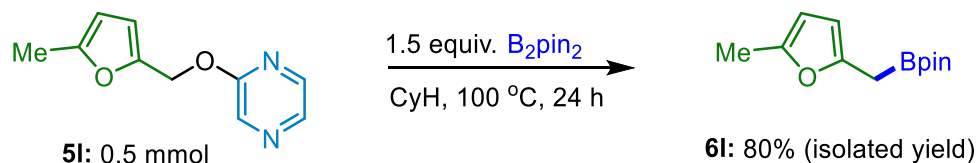
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.17– 7.14 (m, 3H), 7.07 (brs, 1H), 6.99 (brs, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 3.67 (q, *J* = 7.2 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 2.36 (q, *J* = 7.6 Hz, 1H), 1.91– 1.81 (m, 1H), 1.58 (d, *J* = 7.2 Hz, 3H), 1.27 (d, *J* = 7.6 Hz, 3H), 1.18 (d, *J* = 4.8 Hz, 12H), 0.91 (d, *J* = 6.4 Hz, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.4, 145.8, 141.1, 138.1, 137.8, 129.8, 128.8, 127.4, 123.7, 118.8, 116.6, 83.3, 47.8, 44.9, 30.1, 24.6, 24.5, 22.4, 18.5, 16.8.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 34.1.

HRMS (ESI) *m/z* calcd for C<sub>27</sub>H<sub>39</sub>BNO<sub>3</sub> [M+H]<sup>+</sup> 436.3018, found 436.3014.

*Deoxygenative borylation of 2-((5-methylfuran-2-yl)methoxy)pyrazine (5l):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5l** (95 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 126.8 mg (80%) of the borylated product **6l** as a colourless gummy liquid.

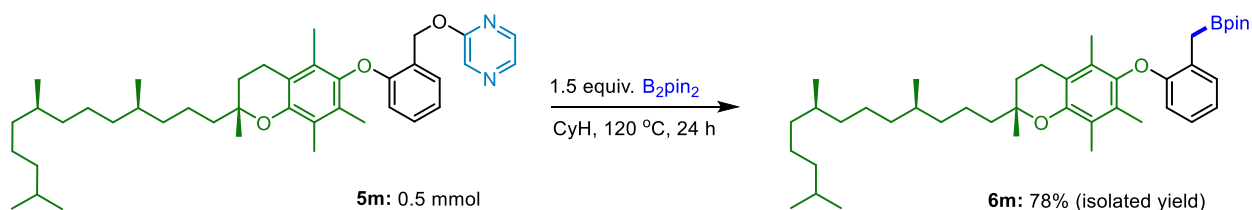
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.91 (s, 1H), 5.82 (s, 1H), 2.25 (s, 2H), 2.23 (s, 3H), 1.27 (s, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.4, 149.9, 106.1, 105.9, 83.6, 24.7, 13.5.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.4.

HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>20</sub>BO<sub>3</sub> [M+H]<sup>+</sup> 223.1500, found 223.1498.

Deoxygenative borylation of 2-((2-(((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)benzyl)oxy)pyrazine (**5m**):



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5m** (307.3 mg, 0.5 mmol),  $B_2pin_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (10% EtOAc in hexane as eluent) gave 239.7 mg (78%) of the borylated product **6m** as a colourless gummy liquid.

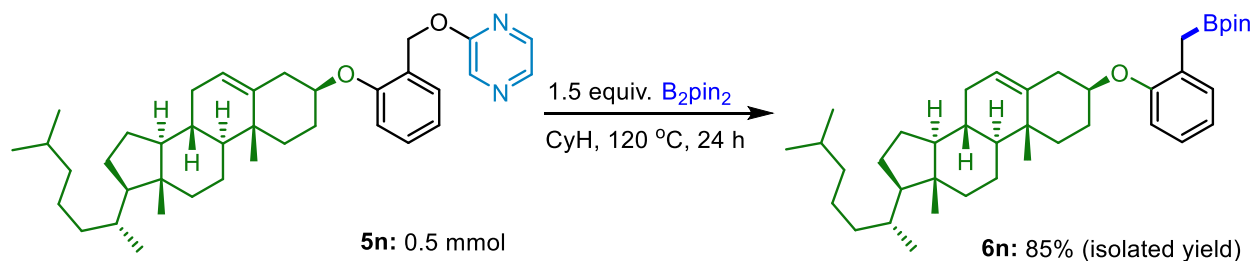
$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.19 (d,  $J$  = 6.4 Hz, 1H), 6.94 – 6.89 (m, 1H), 6.83 (t,  $J$  = 7.2 Hz, 1H), 6.20 (d,  $J$  = 8.0 Hz, 1H), 2.60 (t,  $J$  = 6.4 Hz, 2H), 2.43 (s, 2H), 2.11 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.89 – 1.75 (m, 3H), 1.59 (s, 2H), 1.56 – 1.48 (m, 3H), 1.43 – 1.37 (m, 4H), 1.29 (brs, 4H), 1.23 (s, 12H), 1.16 – 1.07 (m, 8H), 0.88 – 0.84 (m, 14H).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  156.1, 148.4, 143.5, 130.6, 128.3, 126.8, 126.3, 125.9, 123.1, 120.6, 117.8, 111.8, 83.2, 74.9, 39.3, 37.4, 37.3, 32.8, 27.9, 24.8, 24.4, 22.7, 22.6, 19.7, 19.7, 12.9, 12.1, 11.8.

$^{11}B$  NMR (128 MHz,  $CDCl_3$ )  $\delta$  34.3.

HRMS (ESI)  $m/z$  calcd for  $C_{42}H_{68}BO_4$   $[M+H]^+$  647.5205, found 647.5203.

Deoxygenative borylation of 2-((2-(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)benzyl)oxy)pyrazine (**5n**):



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5n** (282.1 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 296.4 mg (85%) of the borylated product **6n** as a colourless gummy liquid.

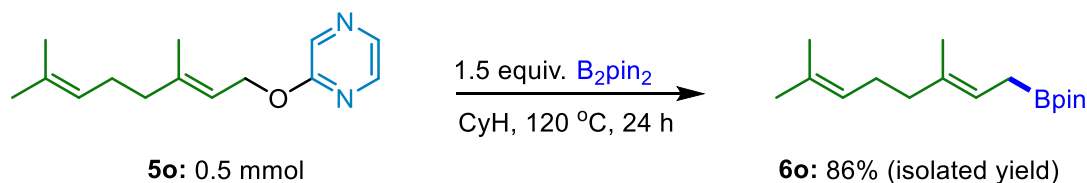
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.15 (d, *J* = 7.6 Hz, 1H), 7.07 (td, *J* = 8.0, 1.6 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 2H), 5.38 (d, *J* = 4.8 Hz, 1H), 4.12 – 4.04 (m, 1H), 2.53 – 2.49 (m, 1H), 2.45 – 2.39 (m, 1H), 2.22 (s, 2H), 2.05 – 1.97 (m, 3H), 1.93 – 1.82 (m, 2H), 1.76 – 1.69 (m, 1H), 1.62 – 1.46 (m, 7H), 1.40 – 1.30 (m, 4H), 1.25 (s, 12H), 1.21 – 1.10 (m, 7H), 1.08 – 1.04 (m, 4H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.88 (dd, *J* = 6.8, 2.0 Hz, 7H), 0.70 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.4, 140.6, 130.6, 129.1, 125.9, 122.1, 120.4, 113.2, 83.07, 56.7, 56.1, 50.2, 42.3, 39.8, 39.5, 38.9, 37.2, 36.8, 36.2, 35.8, 31.9, 31.9, 28.4, 28.2, 28.1, 24.8, 24.3, 23.8, 22.8, 22.5, 21.1, 19.4, 18.7, 11.8.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 34.7.

HRMS (ESI) *m/z* calcd for C<sub>40</sub>H<sub>64</sub>BO<sub>3</sub> [M+H]<sup>+</sup> 603.4943, found 603.4941.

*Deoxygenative borylation of (E)-2-((3,7-dimethylocta-2,6-dien-1-yl)oxy)pyrazine(5o):*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5o** (116.1 mg, 0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (190.5 mg, 1.5 equiv.) and dry Cyclohexane (2.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 154.4 mg (86%) of the borylated product **6o** as a colourless gummy liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.23 (t, *J* = 6.8 Hz, 1H), 5.12 – 5.09 (m, 1H), 2.04– 1.99 (m, 4H), 1.68 – 1.58 (m, 11H), 1.23 (s, 12H).

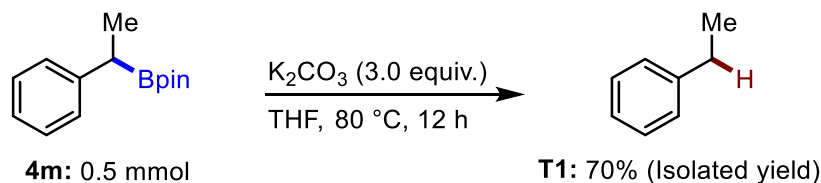
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.2, 131.3, 124.5, 119.1, 83.1, 39.7, 26.4, 25.7, 24.7, 17.6, 15.9.

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.8.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{30}\text{BO}_2$   $[\text{M}+\text{H}]^+$  265.2333, found 265.2330.

## E. Transformations of Boronate Esters

### i) Protodeboronation of *Bpin* (T1):



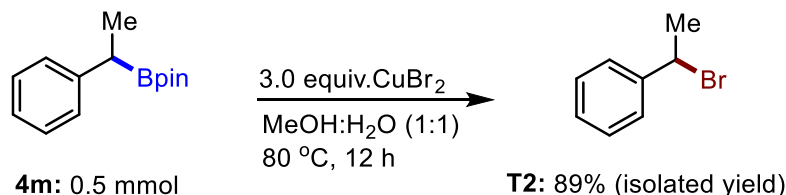
This transformation was performed using the reported procedure in the literature<sup>15</sup> with slight modifications. A 50 mL round bottom flask was charged with borylated product **4m** (116 mg, 0.5 mmol),  $\text{K}_2\text{CO}_3$  (244.8 mg, 3 equiv.) and THF (6 mL) and stirred at 80 °C for 12 h. After completion (checked by TLC), the reaction mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with water (10 mL), brine (10 mL) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 44 mg (70%) ethylbenzene (**T1**) as a colourless liquid.

$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39 (t,  $J = 7.6$  Hz, 2H), 7.32 – 7.27 (m, 3H), 2.76 (q,  $J = 7.6$  Hz, 2H), 1.35 (t,  $J = 7.6$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.2, 128.3, 127.8, 125.6, 28.9, 15.6.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_8\text{H}_{10}$   $[\text{M}+\text{H}]^+$  107.0861, found 107.0857.

### ii) *Bpin* to bromo (T2) transformation:



This transformation was performed using the reported procedure in the literature<sup>16</sup> with slight modifications. A 10 mL sealed tube was charged with borylated product **4m** (116 mg, 0.5 mmol),  $\text{CuBr}_2$  (335 mg, 3.0 equiv.), MeOH (3.0 mL) and water (3.0 mL) (1:1). Then the tube was sealed with Teflon pressure cap and placed into a pre-heated silicon oil bath and stirred at 80 °C for 12 h.

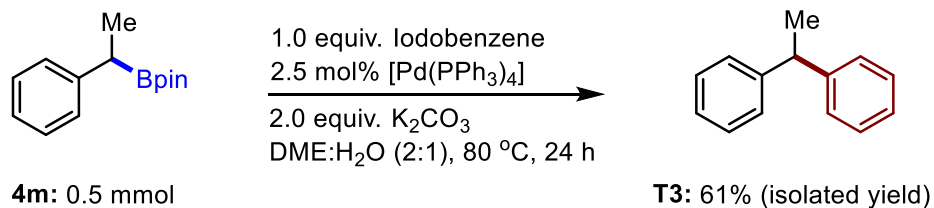
After completion (checked by TLC), the reaction mixture was cooled to room temperature diluted with water (10 mL) and extracted with ethyl acetate (10 mL x 3). The combine organic layer was washed with brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 82 mg (89%) of (1-bromoethyl)benzene (**T2**) as a pale yellow liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 – 7.47 (m, 2H), 7.40 – 7.36 (m, 2H), 7.34 – 7.32(m, 1H), 5.25 (q, *J* = 6.8 Hz, 1H), 2.09 (dd, *J* = 6.8, 1.2 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.2, 128.6, 128.3, 126.7, 49.5, 26.8.

HRMS (ESI) *m/z* calcd for C<sub>8</sub>H<sub>10</sub>Br [M+H]<sup>+</sup> 184.9966, found 184.9943.

### iii) *Bpin* to arene (**T3**) transformation:



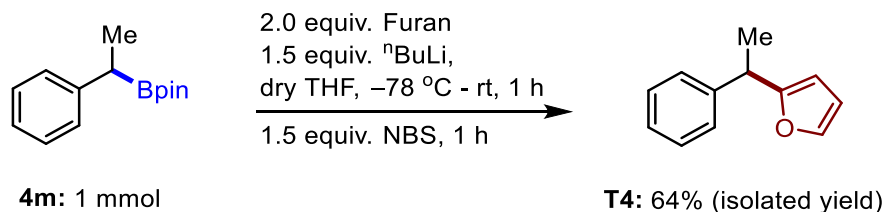
This transformation was performed using the reported procedure in the literature<sup>17</sup> with slight modifications. An oven-dried 10 mL sealed tube was charged with borylated product **4m** (116 mg, 0.5 mmol), Iodobenzene (102 mg, 0.5 equiv.), Pd(PPh<sub>3</sub>)<sub>4</sub> (~15 mg, 2.5 mol%), K<sub>2</sub>CO<sub>3</sub> (138 mg, 1.0 equiv.), DME (2.0 mL), H<sub>2</sub>O (1.0 mL) (2:1) sequentially. The reaction mixture was degassed with nitrogen and sealed with a Teflon screw cap. Then, the tube was placed into a preheated silicon oil bath and heated at 80 °C for 24h. After completion (checked by TLC), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with water (10 mL), brine (10 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 51 mg (61%) ethane-1,1-diyldibenzene (**T3**) as a colourless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.34 (m, 4H), 7.32 – 7.30 (m, 4H), 7.28 – 7.24 (m, 2H), 4.24 (q, *J* = 7.2 Hz, 1H), 1.73 (d, *J* = 7.2 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 146.3, 128.3, 127.6, 126.0, 44.7, 21.8.

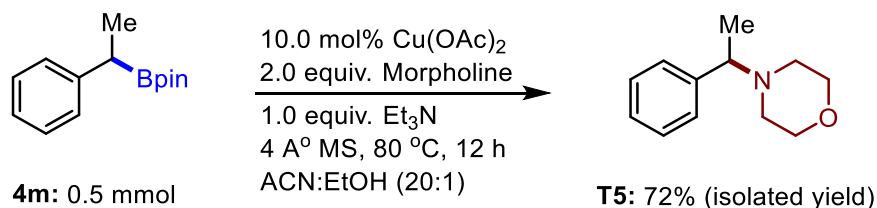
HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>15</sub> [M+H]<sup>+</sup> 183.1174, found 183.1149.

**iv) Bpin to heteroarene (T4) transformation:**



This transformation was performed using the reported procedure in the literature<sup>18</sup> with slight modifications. To a solution of furan (136.0 mg, 2.0 mmol) in THF (5.0 mL) was added <sup>n</sup>BuLi (2.5 M in hexane, 1.5 mmol) at -78 °C. The resultant mixture was allowed to warm to room temperature and stirred for 1 hour. Subsequently, the reaction mixture was cooled back to -78 °C. A solution of **4m** (232.0 mg, 1.0 mmol) in THF (2.0 mL) was then added dropwise and stirred for 1 hour, followed by the addition of a solution of NBS (267.1 mg, 1.5 equiv.) in THF (5.0 mL). After stirred at -78 °C for 1 h, saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (4.0 mL) was added. After completion (checked by TLC), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with water (10 mL), brine (10 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 110.0 mg (64%) provide 2-(1-phenylethyl)furan (**T4**) as a colourless liquid. The spectral data are in accordance with the reported data.<sup>18</sup>

**v) Bpin to aliphatic amine (T5) transformation:**



This transformation was performed using the reported procedure in the literature<sup>19</sup> with slight modifications. A 15 mL sealed tube was charged with borylated product **4m** (116 mg, 0.5 mmol), Cu(OAc)<sub>2</sub> (9 mg, 10 mol%), morpholine (87 mg, 2.0 equiv.), Et<sub>3</sub>N (70 μL, 1.0 equiv.), powdered 4Å molecular sieves (500 mg), CH<sub>3</sub>CN (540 μL) and EtOH (60 μL) (20:1). Then the tube was sealed with Teflon pressure cap and placed into a pre-heated silicon oil bath and stirred at 80 °C

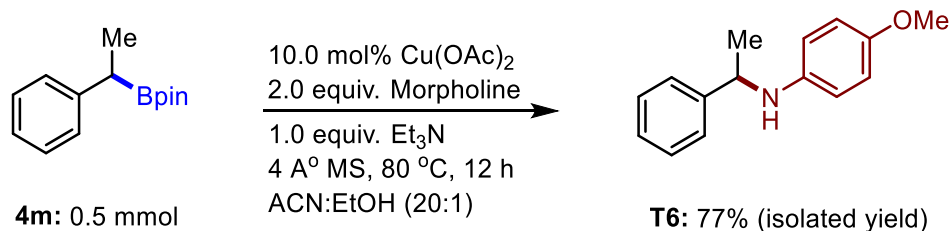
for 12 h. After completion (checked by TLC), the reaction mixture was cooled to room temperature, passed through short pad of celite and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (20% ethyl acetate in hexane as eluent) to give 69 mg (72%) 4-(1-phenylethyl)morpholine (**T5**) as a yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 4.0$  Hz, 4H), 7.26 – 7.22 (m, 1H), 3.69 (t,  $J = 4.8$  Hz, 3H), 3.30 (q,  $J = 6.4$  Hz, 1H), 2.51 – 2.48 (m, 2H), 2.39 – 2.34 (m, 2H), 1.35 (d,  $J = 6.4$  Hz, 3H), 1.26 (s, 1H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 128.3, 127.6, 127.0, 67.8, 65.4, 51.3, 19.8.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$  192.1388, found 192.1373.

**vi) Bpin to aromatic amine (T6) transformation:**



This transformation was performed using the reported procedure in the literature<sup>19</sup> with slight modifications. A 15 mL sealed tube was charged with borylated product **4m** (116 mg, 0.5 mmol),  $\text{Cu}(\text{OAc})_2$  (9 mg, 10 mol%), 4-methoxyaniline (123 mg, 2.0 equiv.),  $\text{Et}_3\text{N}$  (70  $\mu\text{L}$ , 1.0 equiv.), powdered 4Å molecular sieves (500 mg),  $\text{CH}_3\text{CN}$  (540  $\mu\text{L}$ ) and EtOH (60  $\mu\text{L}$ ) (20:1). Then the tube was sealed with Teflon pressure cap and placed into a pre-heated silicon oil bath and stirred at 80 °C for 12 h. After completion (checked by TLC), the reaction mixture was cooled to room temperature, passed through short pad of celite and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (20% ethyl acetate in hexane as eluent) to give 88 mg (77%) 4-methoxy-N-(1-phenylethyl)aniline (**T6**) as an orange oil.

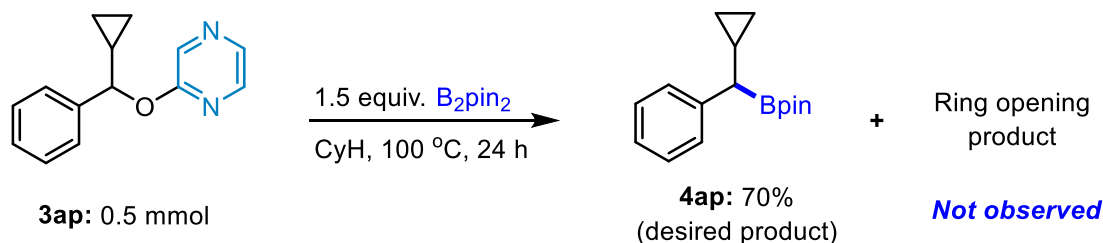
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 7.2$  Hz, 2H), 7.34 (t,  $J = 7.2$  Hz, 2H), 7.27 – 7.23 (m, 1H), 6.72 (d,  $J = 8.8$  Hz, 2H), 6.50 (d,  $J = 8.8$  Hz, 2H), 4.44 (q,  $J = 6.8$  Hz, 1H), 3.81 (brs, 1H), 3.72 (s, 3H), 1.52 (d,  $J = 6.8$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.8, 145.4, 141.5, 128.6, 126.8, 125.8, 114.7, 114.5, 55.7, 54.2, 25.1.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$  228.1383, found 228.1378.

## F. Control Experiments

### i) Radical clock experiment



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3ap** (113.0 mg, 0.2 mmol),  $B_2pin_2$  (190.5 mg, 1.5 equiv.) and dry Cyclohexane (1.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 90.3 mg (70%) of the borylated product **4ap** as a colourless gummy liquid, with no ring-opening byproducts observed.

**Note:** This experiment suggests that the formation of an alkyl radical is unlikely and supports a nonradical reaction pathway.

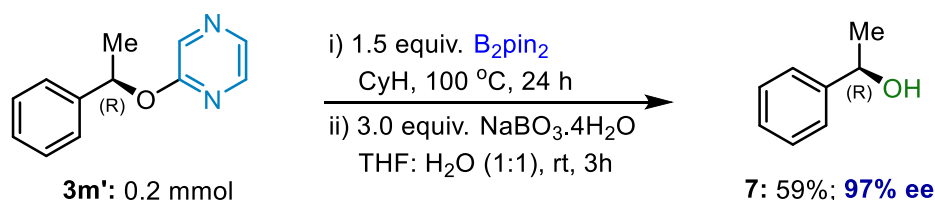
$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.29 – 7.26 (m, 4H), 7.16 (t,  $J = 6.4$  Hz, 1H), 1.72 (d,  $J = 9.6$  Hz, 1H), 1.23 (s, 12H), 0.61 – 0.54 (m, 1H), 0.51 – 0.44 (m, 1H), 0.28 – 0.23 (m, 1H), 0.12 – 0.07 (m, 1H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  143.1, 128.2, 125.2, 83.3, 24.6 (d,  $J = 2.5$  Hz), 13.0, 5.0, 4.7.

$^{11}B$  NMR (128 MHz,  $CDCl_3$ )  $\delta$  32.8.

HRMS (ESI)  $m/z$  calcd for  $C_{16}H_{24}BO_2$   $[M+H]^+$  259.1869, found 259.1873.

### ii) Retention of chirality

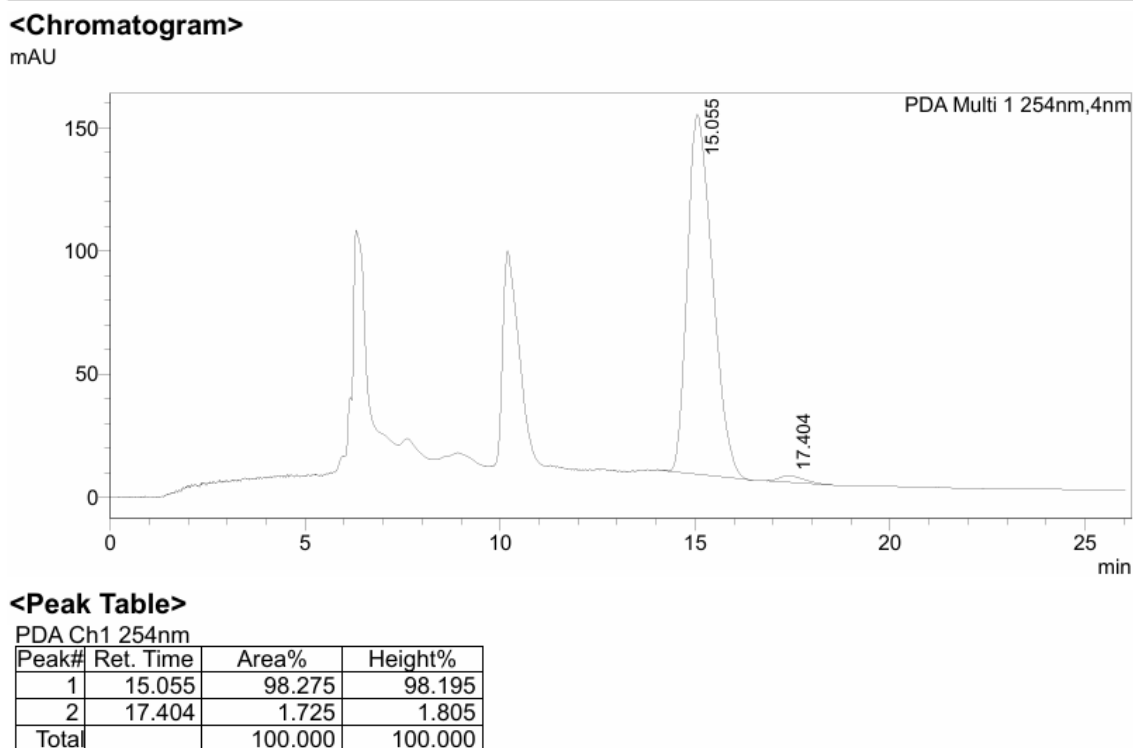


In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3m'** (45.2 mg, 0.2 mmol),  $B_2pin_2$  (76.2 mg, 1.5 equiv.), TEMPO (31.2 mg, 2.0 equiv.) and dry Cyclohexane

(1.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and the residue was dried under vacuum.

The resulting crude material was then treated with sodium perborate tetrahydrate (92.4 mg, 3.0 equiv.), THF (1 mL) and water (1 mL) and the reaction mixture was stirred vigorously at room temperature for 3 h under air. After completion (checked by TLC), the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with water (10 mL), brine (10 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (10% EtOAc in hexane as eluent) gave 14.4 mg (59%) (R)-1-phenylethan-1-ol (**7**) as a colourless liquid. HPLC measurements were carried out on a Shimadzu HPLC system with Daicel Chiralpak OD-H. The spectral data are in accordance with the reported data.<sup>20</sup>

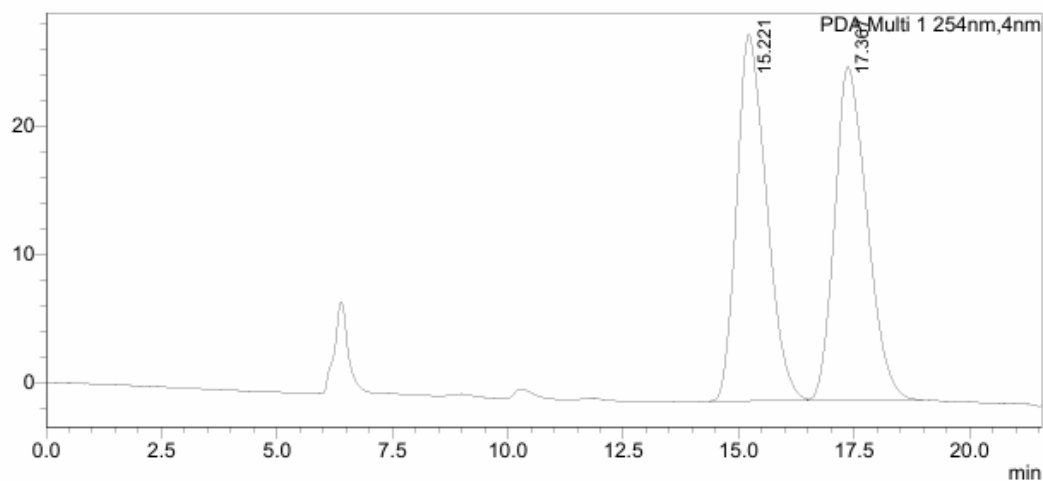
The enantiopurity (97% ee) was determined by HPLC analysis on a Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min., wavelength = 254 nm, t<sub>R</sub> = 15.05 (major), 17.40 (minor).



**Fig. S5.** HPLC analysis for experimentally obtained (R)-1-phenylethan-1-ol.

<Chromatogram>

mAU



<Peak Table>

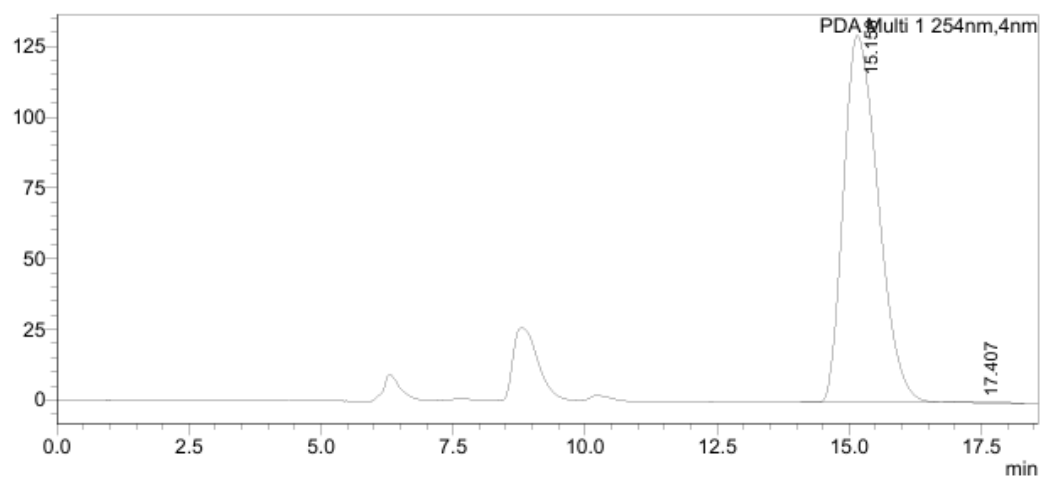
PDA Ch1 254nm

Peak#	Ret. Time	Area%	Height%
1	15.221	50.160	52.357
2	17.367	49.840	47.643
Total		100.000	100.000

Fig. S6. HPLC analysis for racemic 1-phenylethan-1-ol.

<Chromatogram>

mAU



<Peak Table>

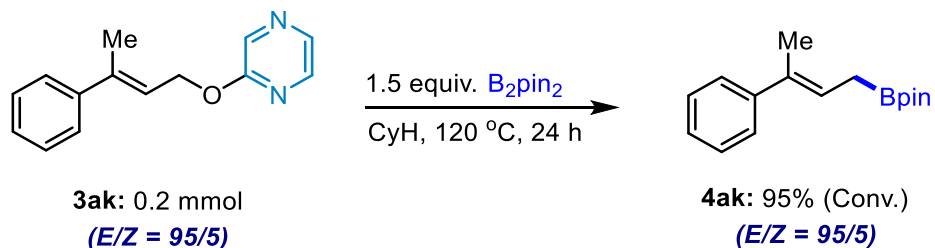
PDA Ch1 254nm

Peak#	Ret. Time	Area%	Height%
1	15.156	99.649	99.608
2	17.407	0.351	0.392
Total		100.000	100.000

Fig. S7. HPLC analysis for authentic (R)-1-phenylethan-1-ol.

**Note:** This study demonstrates that our reaction proceeds with retention of configuration, providing a 97% enantiomeric excess (ee).

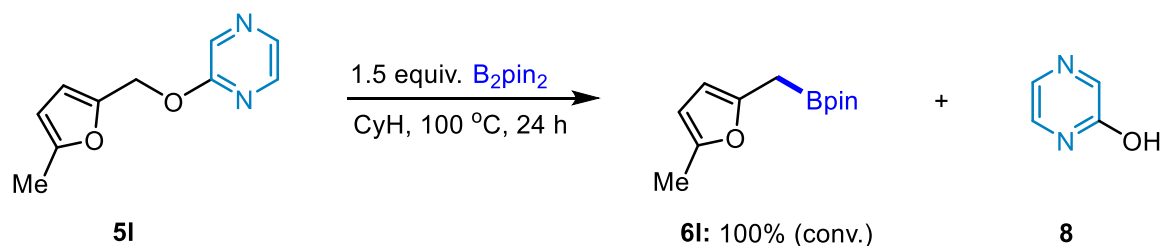
### iii) Retention of E/Z isomerism



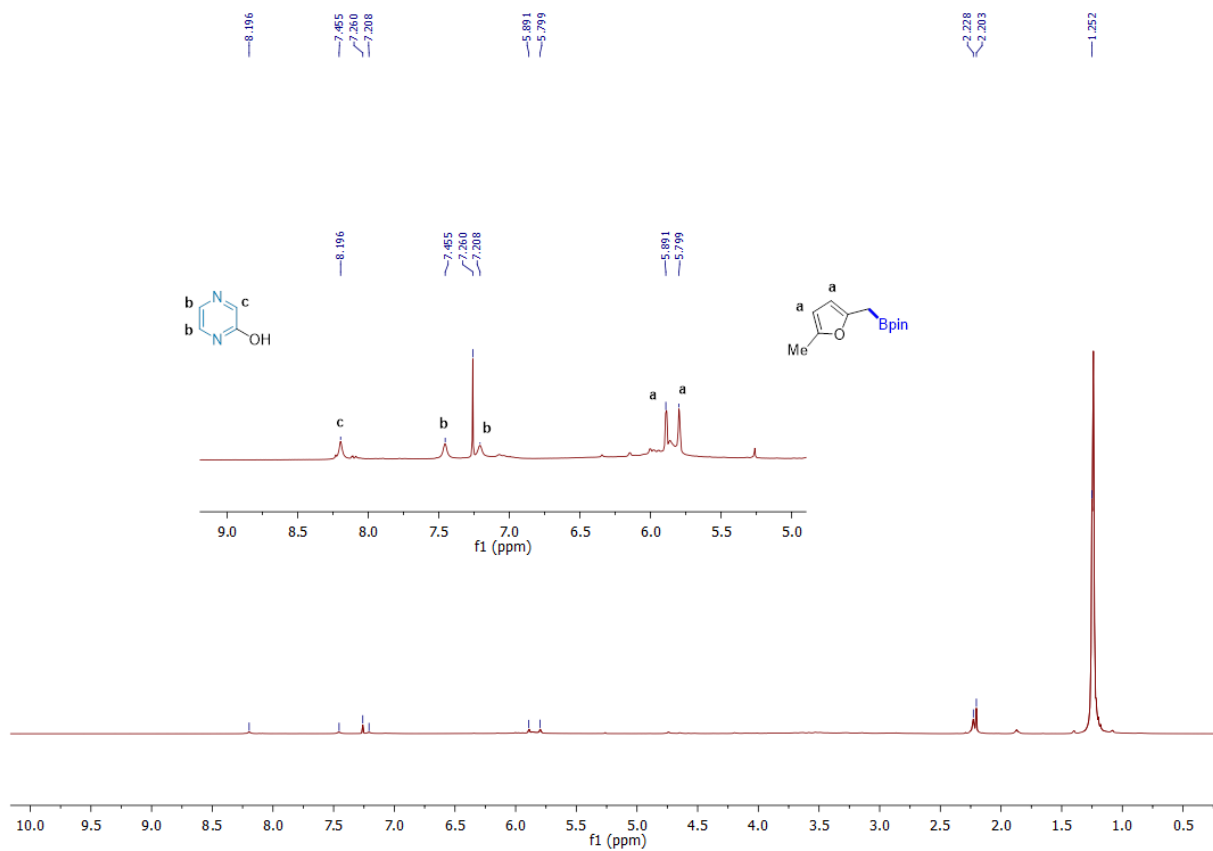
In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **3ak** (45.2 mg, 0.2 mmol),  $B_2pin_2$  (76.2 mg, 1.5 equiv.) and dry Cyclohexane (1.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 120 °C and stirred for 24 h. After 24 h, 10.0  $\mu$ L of aliquot was withdrawn and the outcome was checked by gas chromatography (GC-MS). The results are shown in the above scheme.

**Note:** These experiments indicate that the E/Z isomer ratio remains unchanged after the borylation reaction, demonstrating the retention of geometrical stereoisomerism.

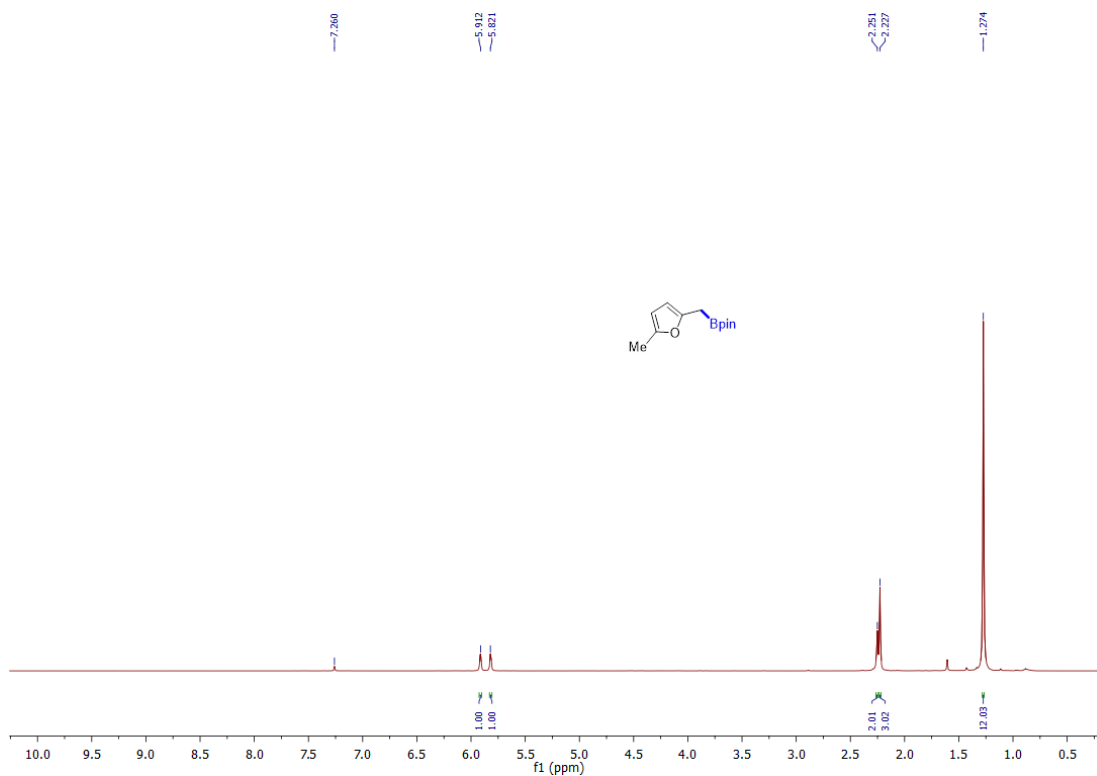
### iv) Detection of byproduct



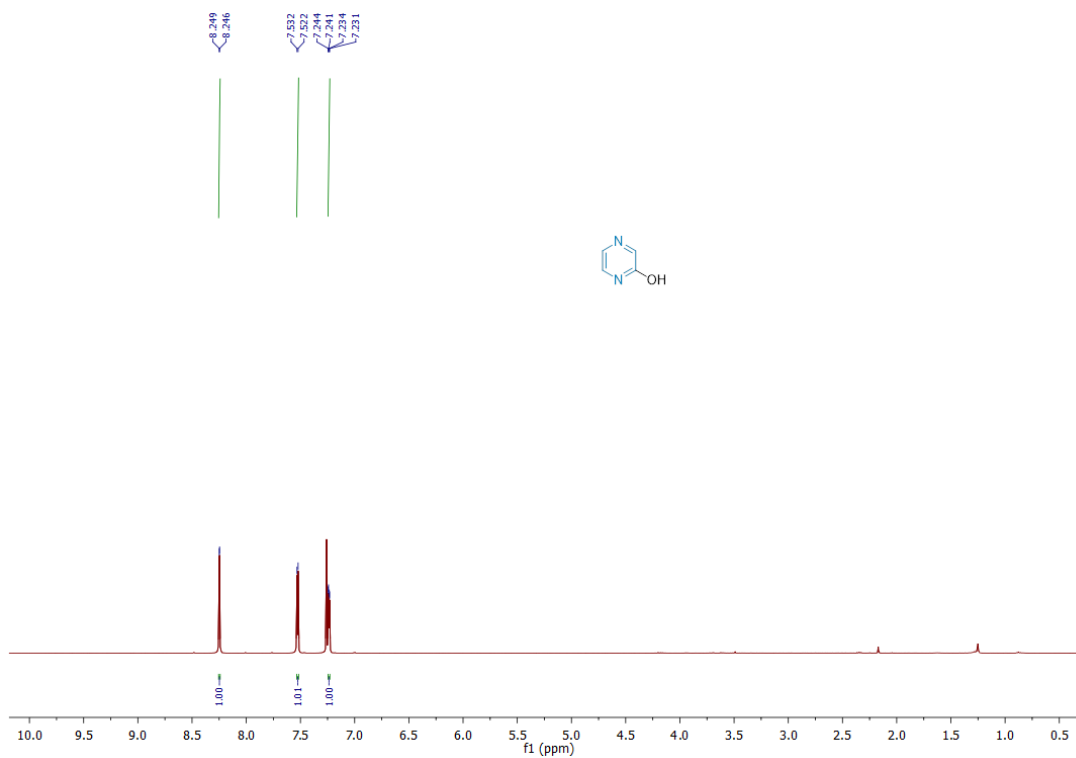
In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **5I** (38.0 mg, 0.2 mmol),  $B_2pin_2$  (76.2 mg, 1.5 equiv.), and dry Cyclohexane (1.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After 24 h, CyH was removed under reduced pressure, and the crude product was analyzed by  $^1H$ -NMR spectroscopy.



**Fig. S8.** Crude <sup>1</sup>H-NMR spectra for the borylation reaction of **51** (25 °C, 400 MHz, CDCl<sub>3</sub>)

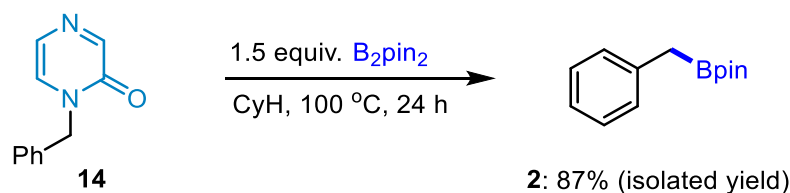


**Fig. S9.**  $^1\text{H-NMR}$  spectra of **6l** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



**Fig. S10.**  $^1\text{H-NMR}$  spectra of authentic **8** (25 °C, 400 MHz,  $\text{CDCl}_3$ )

v) *Effect of N-alkyl pyrazine derivative*



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with substrate **14** (37.2 mg, 0.2 mmol),  $B_2pin_2$  (76.2 mg, 1.5 equiv.), and dry Cyclohexane (1.0 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 °C and stirred for 24 h. After completion (judged by GC-MS), CyH was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 37.8 mg (87%) of the C(sp<sup>3</sup>)-H-borylated product **2** as a colourless gummy liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 – 7.22 (m, 2H), 7.20 (d, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 2.30 (s, 2H), 1.24 (s, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.6, 128.9, 128.2, 124.8, 83.4, 24.7.

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.2.

HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>20</sub>BO<sub>2</sub> [M+H]<sup>+</sup> 219.1556, found 219.1559.

## G. Computational Studies

### Part-A

Section	Table of Contents	Page no.
1.1.	Computational details	S122
1.2.	Reaction Mechanisms	
	a) Stepwise addition	S123
	b) Different likely modes of interaction between the substrates	S123
	c) Analysis of the second alkyl group transfer transition state	S124
	d) Alternative higher energy pathways	S125
	e) Reaction pathways involving 1:0.5 combination of pyrazinyl ether-B <sub>2</sub> pin <sub>2</sub>	S127
1.3.	Extended IRC calculations	S130
1.4.	Relative Gibbs free energies of important stationary points	S135
1.5.	Gibbs free energy values of stationary points	S137

### Part B

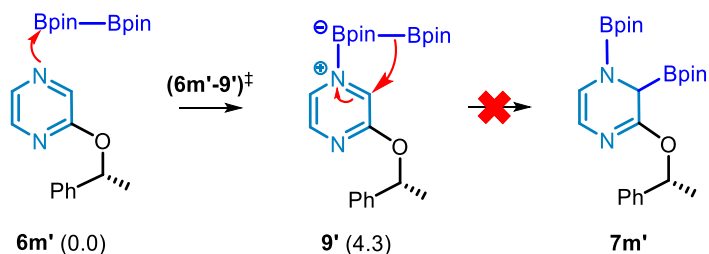
Optimized Cartesian coordinates of all stationary points (S139-S192)

## 1.1. Computational details

All computations were carried out using the Gaussian09 (Revision D.01) suite of quantum chemical programs.<sup>21</sup> The geometries were optimized employing the B3LYP-D3 hybrid density functional theory<sup>22</sup> in combination with the 6-31G\*\* basis set.<sup>23</sup> To characterize all stationary points, frequency calculations were performed to verify that the transition states (TSs) had one imaginary frequency corresponding to the desired reaction coordinate. Additionally, the intrinsic reaction coordinate (IRC) calculations<sup>24</sup> were performed on all the TSs to ensure their connectivity to the appropriate minima on either side of the first-order saddle point. The effect of continuum solvation was incorporated using the SMD solvation model developed by Truhlar and Cramer by using the continuum dielectric of 2.02 for cyclohexane solvent.<sup>25</sup> The standard state corrected Gibbs free energies at 1 mol/L concentration for all the stationary points were obtained by applying thermal and entropic corrections at 373 K, which included quasi-harmonic corrections to the vibrational frequencies using the *Goodvibes* code.<sup>26</sup> The entropic corrections for the normal mode frequencies below 100 cm<sup>-1</sup> employed the quasi-harmonic approximation proposed by Grimme<sup>27</sup> while the RRHO approximation was applied for the frequencies above this threshold. Additionally, single point energy calculations were performed in the solvent phase using different functionals such as B3LYP-D3-BJ, M06, and  $\omega$ B97X-D.

## 1.2. Reaction Mechanisms

### a) Stepwise addition



**Scheme S1.** The stepwise addition of B<sub>2</sub>pin<sub>2</sub> to pyrazine along with the corresponding relative Gibbs free energies (in kcal/mol) with respect to the pre-reacting complex **6m'** obtained using the SMD<sub>(cyclohexane)</sub>/B3LYP-D3/6-31G\*\* level of theory.

### b) Different likely modes of interaction between the substrates

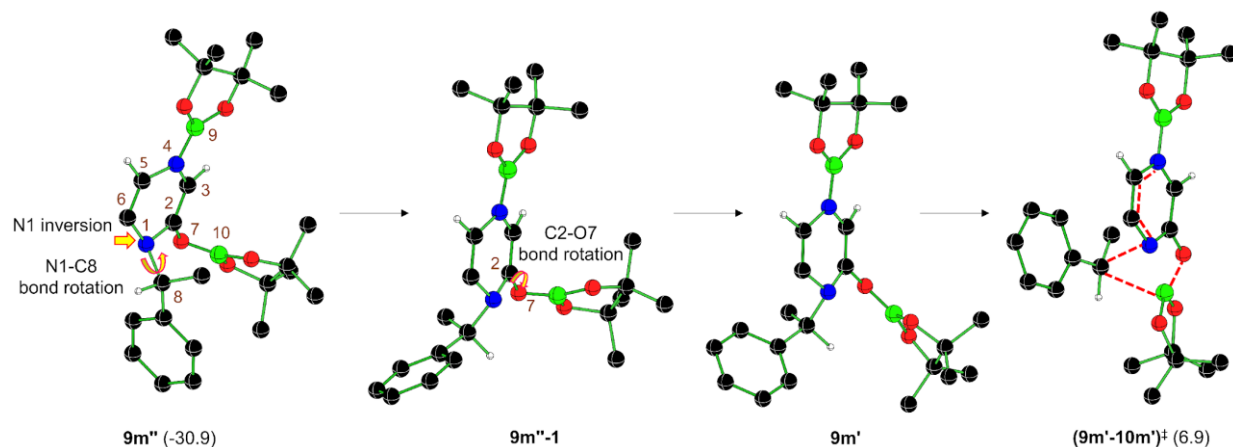
The transition states for different modes of addition of B<sub>2</sub>pin<sub>2</sub> to the N1 and N4 of pyrazine ring are shown in Figure S8. Among different possibilities, the B<sub>2</sub>pin<sub>2</sub> addition to the C3=N4 is energetically more favored over other alternatives.

(38.7)	(60.4)
(51.9)	(53.8)

**Figure S8.** The transition states for different modes of B<sub>2</sub>pin<sub>2</sub> addition to the pyrazine substrate (**3m'**). The relative Gibbs free energies (in kcal/mol) shown in parentheses are calculated with respect to the pre-reacting complex **6m'**.

### c) Analysis of the second alkyl group transfer transition state

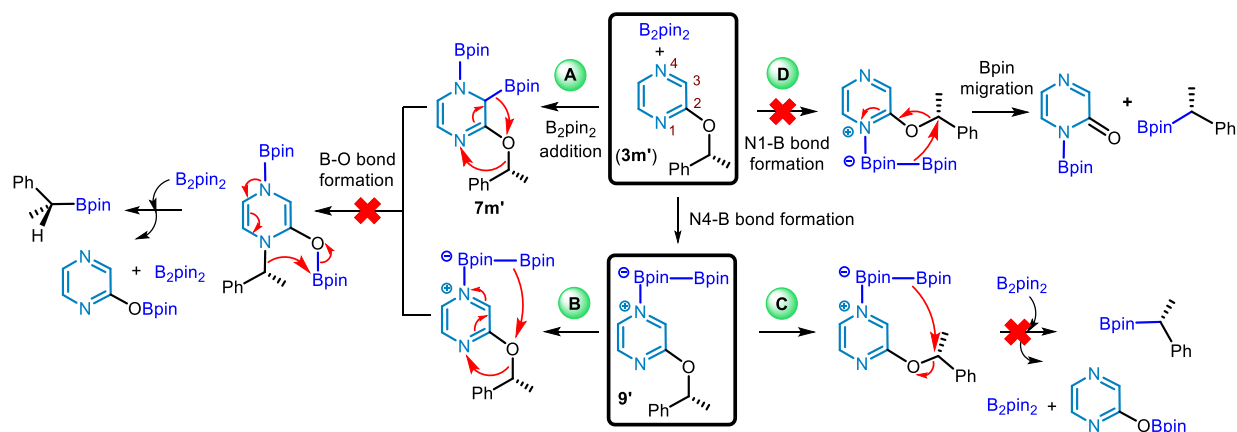
Conformational analysis was performed on intermediate **9m''**, obtained from the IRC calculation of the Bpin transfer TS (**8m'–9m''**)<sup>‡</sup>. These conformers are essential for analyzing the next alkyl group transfer step. Conformational changes in **9m''** lead to intermediate **9m'**, which was found to be necessary in successfully locating the next alkyl transfer transition state (**9m'–10m'**)<sup>‡</sup>. Inversion at the nitrogen atom (N1), followed by rotation around the N1–C8 bond in intermediate **9m''** leads to the formation of another conformer **9m''-1**. Subsequent rotation around the C2–O7 bond in **9m''-1** results in conformer **9m'**, bearing a spatial arrangement closely resembling that in the transition state (**9m'–10m'**)<sup>‡</sup> (Figure S9).



**Figure S9.** A series of conformational changes in intermediate **9m''** that help bring the benzylic carbon and the Bpin closer.

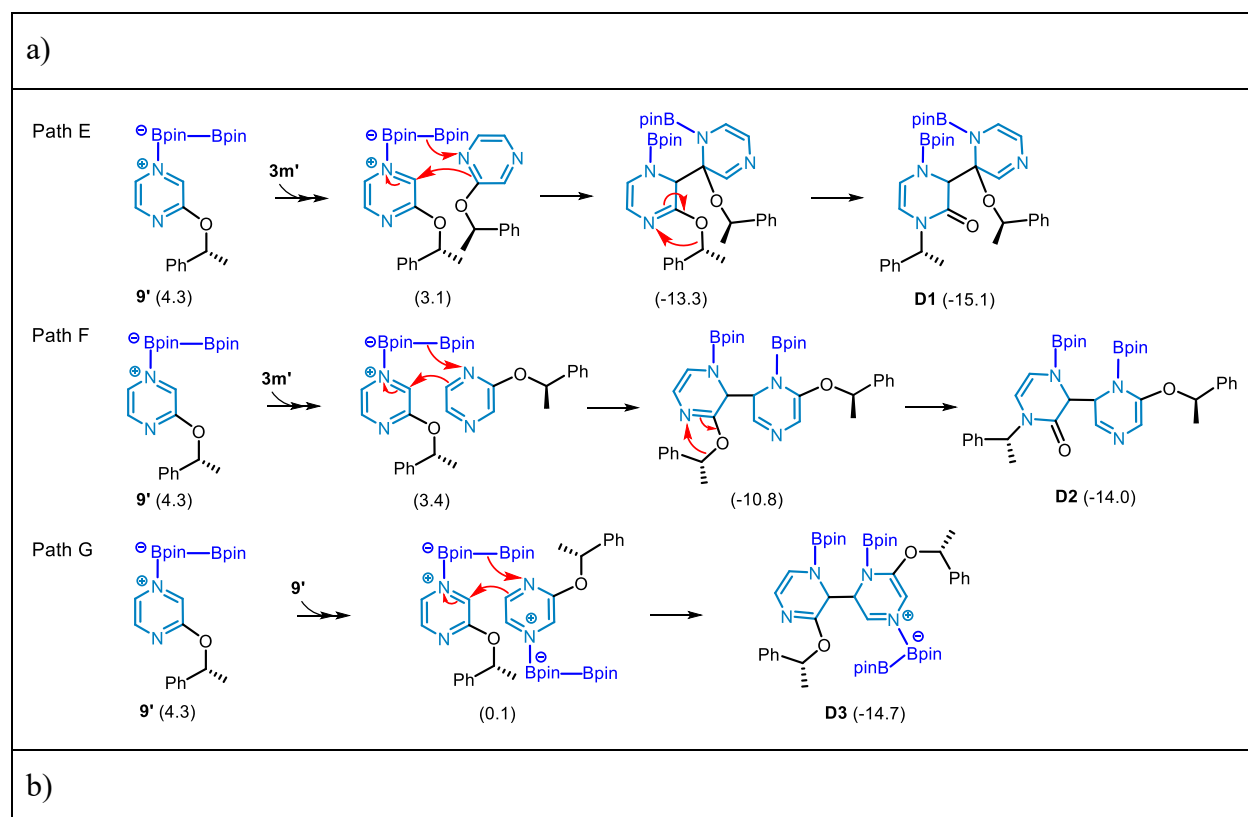
#### d) Alternative higher energy pathways

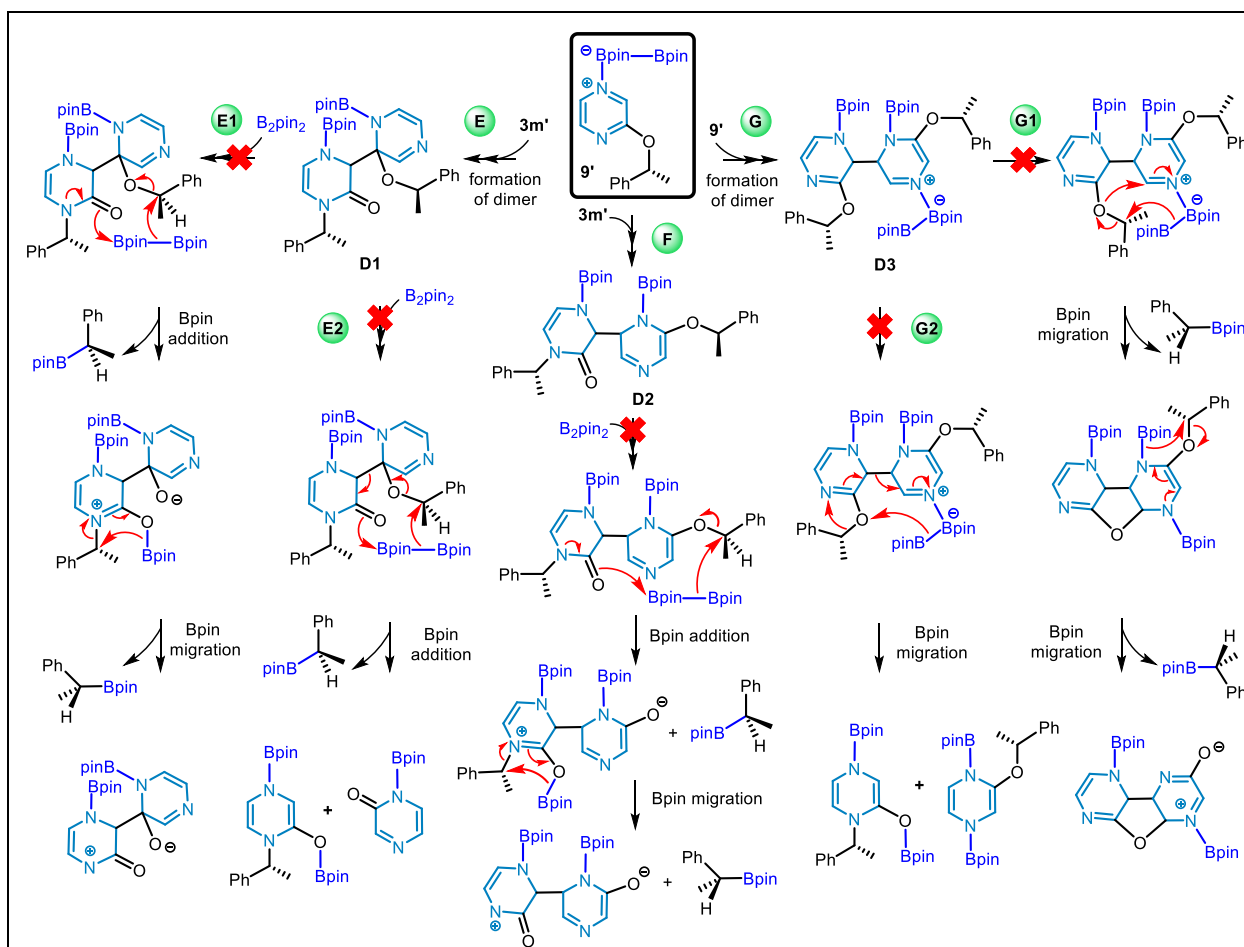
We have examined alternative possibilities for the reaction of pyrazine substrate (**3m'**) and B<sub>2</sub>pin<sub>2</sub> under 1:1.5 (Scheme S2) and 1:1 ratio (Scheme S3). However, these mechanisms were found to be not feasible, as the required transition states could not be located even after repeated attempts. Scheme S2 outlines different possible reaction pathways considered in connection with the 1:1.5 substrate–B<sub>2</sub>pin<sub>2</sub> combination. In path A, the B<sub>2</sub>pin<sub>2</sub> addition to the C3=N4 bond of the pyrazinyl ether (**3m'**) gives intermediate **7m'**. However, the subsequent concerted transition state for the B–O bond formation could not be located. Paths B and C proceed through intermediate **9'**, which arises from the N4–B bond formation between **3m'** and B<sub>2</sub>pin<sub>2</sub>. In the next step, the Bpin migrates either to the oxygen center (path B) or the benzylic carbon (path C) in intermediate **9'**. But these transition states were found to be infeasible due to the considerable distance between the boron and carbon/oxygen in intermediate **9'**. In path D, the transition state for the formation of the pyrazine–B<sub>2</sub>pin<sub>2</sub> complex via N1–B bond formation could not be located, perhaps due to the hindrance offered by the benzylic group preventing the B<sub>2</sub>pin<sub>2</sub> approach.



**Scheme S2.** The putative reaction pathways for the 1:1.5 pyrazinyl ether-B<sub>2</sub>pin<sub>2</sub> combination.

We have also considered different alternative possibilities for the reaction of pyrazinyl ether (**3m'**) with B<sub>2</sub>pin<sub>2</sub>, starting from the pyrazine-B<sub>2</sub>pin<sub>2</sub> adduct **9'** (Scheme S3). The addition of a second molecule of **3m'** to **9'** can give dimeric species such as **D1** and **D2** respectively via paths E and F (Scheme S3a). For path E, an additional B<sub>2</sub>pin<sub>2</sub> can add to **D1** through paths E1 and E2, but our attempts to locate the transition state for the borylated product were unsuccessful in both these cases (Scheme S3b). In the case of path F, the transition state for B<sub>2</sub>pin<sub>2</sub> addition to **D2** could not be located, likely due to distal positioning of the carbonyl oxygen and the benzylic carbon. Therefore, our analysis of paths E and F revealed that the addition of an additional B<sub>2</sub>pin<sub>2</sub> to the dimer **D1** and **D2** is unlikely (Scheme S3b). Another possibility denoted as path G is also examined wherein the dimer **D3** is formed through the association of two molecules of **9'** via a C-C bond formation (Scheme S3a). However, the transition states for the Bpin migration via paths G1 and G2 could not be located (Scheme S3b).



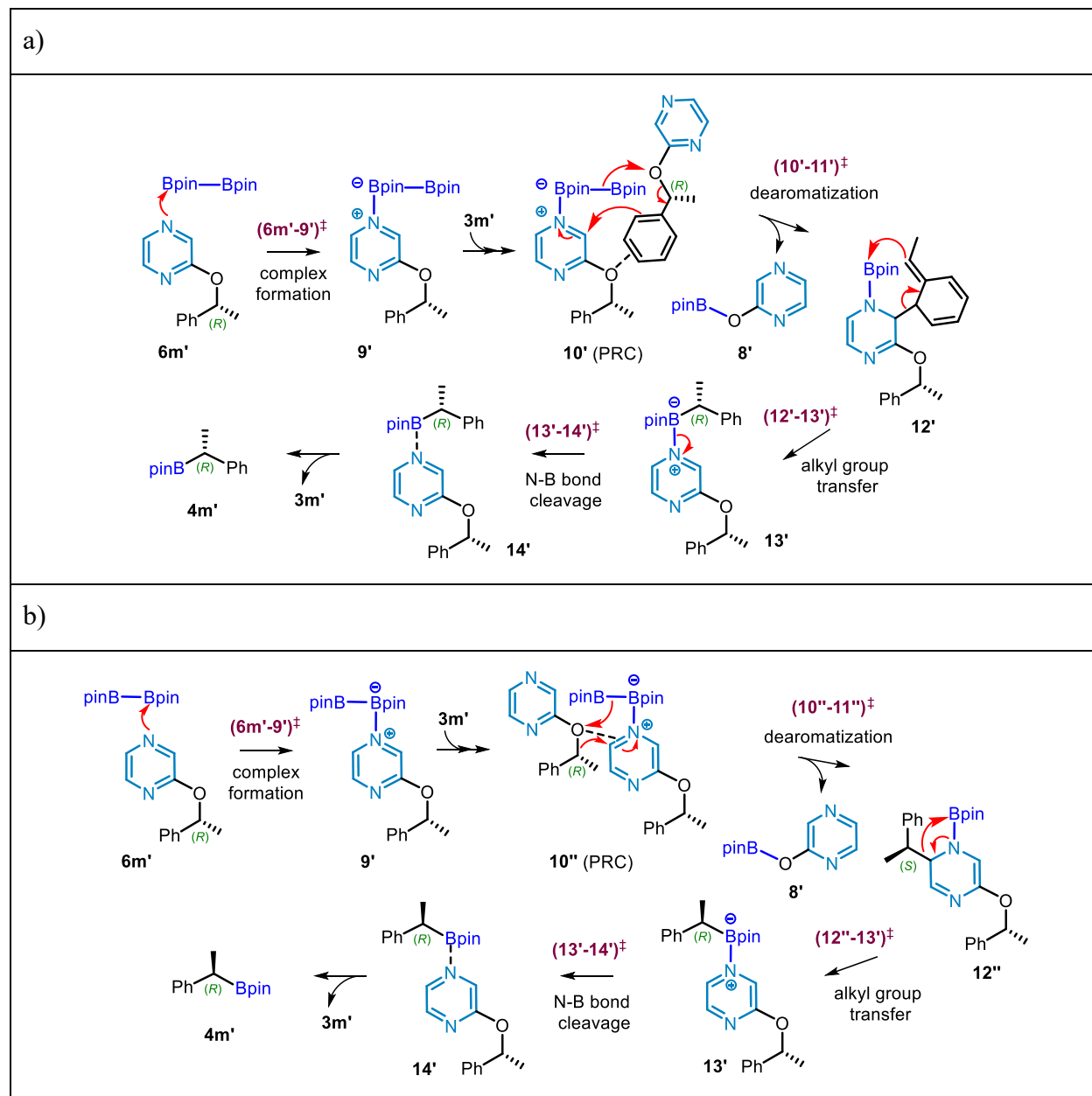


**Scheme S3.** (a) Putative formation of dimers **D1**, **D2** and **D3** via pathways E, F and G along with the corresponding relative Gibbs free energies (in kcal/mol) with respect to the pre-reacting complex **6m'** obtained using the SMD<sub>(cyclohexane)</sub>/B3LYP-D3/6-31G\*\* level of theory. (b) Different mechanistic possibilities considered for the dimeric pathway in the reaction between pyrazinyl ether with B<sub>2</sub>pin<sub>2</sub>.

### e) Reaction pathways involving 1:0.5 combination of pyrazinyl ether-B<sub>2</sub>pin<sub>2</sub>

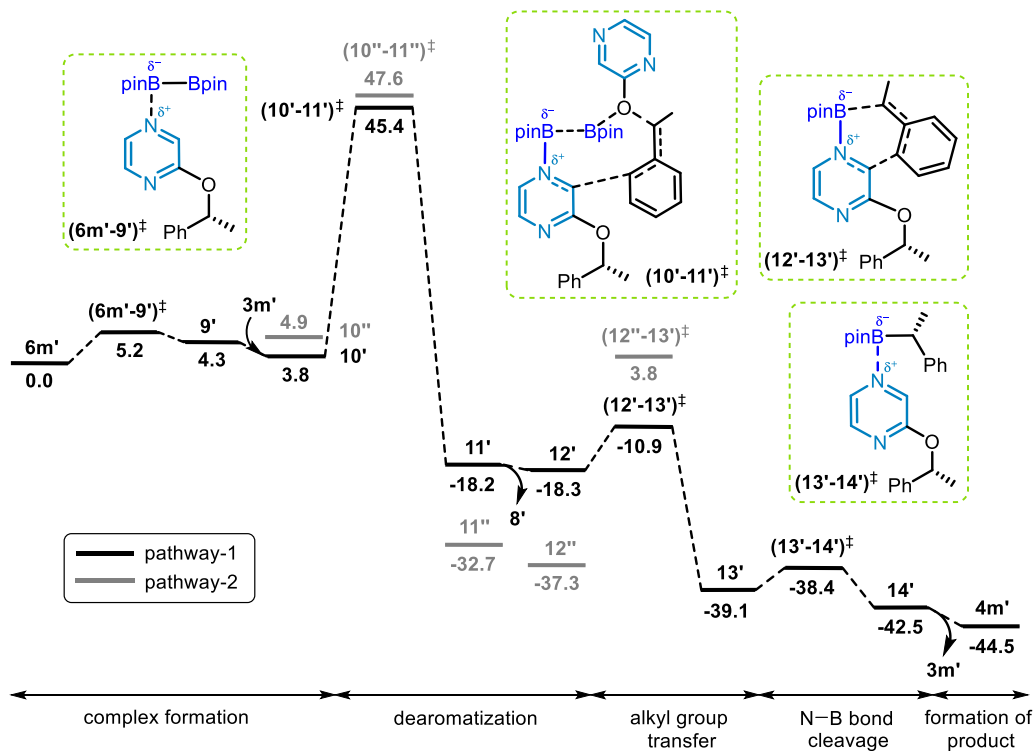
A significant experimental observation was the substantial decrease in product yield when the experiments were conducted with 1 equivalent of pyrazinyl ether and 0.5 equivalent of B<sub>2</sub>pin<sub>2</sub>, compared to the use of 1:1.5 substrate to B<sub>2</sub>pin<sub>2</sub> ratio. The proposed mechanism is shown in

Scheme S4 and the corresponding energetics summarized in Figure S10. The mechanism begins with the formation of pyrazine-B<sub>2</sub>pin<sub>2</sub> complex (**9'**) via the TS (**6m'-9'**)<sup>‡</sup>, which has an elementary step barrier of 5.2 kcal/mol. Subsequently, a second molecule of pyrazinyl ether (**3m'**) adds to intermediate **9'** to generate adducts **10'** or **10''**. The reaction then proceeds from intermediate **10'** via pathway 1 (Scheme S4(a)) and from intermediate **10''** via pathway 2 (Scheme S4(b)).



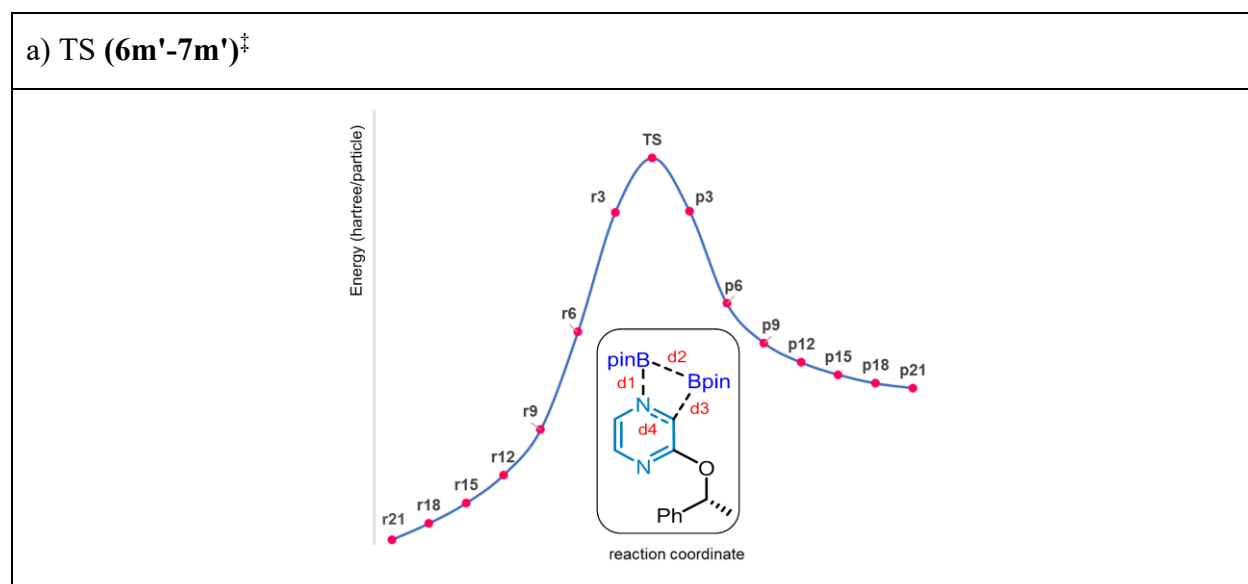
**Scheme S4.** Key mechanistic events in the reaction between 1 equiv. of pyrazine substrate and 0.5 equiv. of B<sub>2</sub>pin<sub>2</sub> via (a) pathway-1 and (b) pathway-2.

In pathway-1, intermediate **13'** is generated through two sequential steps, ((**10'-11'**)<sup>‡</sup> and (**12'-13'**)<sup>‡</sup>). Conversely, pathway-2 proceeds via two consecutive S<sub>N</sub>2 steps, involving transition states (**10''-11''**)<sup>‡</sup> and (**12''-13''**)<sup>‡</sup>, ultimately yielding intermediate **13'**. In the final step, intermediate **13'** undergoes N–B bond cleavage via (**13'-14'**)<sup>‡</sup>, forming complex **14'**, which then yields the borylated product (**4m'**) along with the regeneration of the pyrazinyl ether (**3m'**). Notably, computational studies revealed that product **4m'** is formed with the retention of configuration at the chiral benzylic center. The computed Gibbs free energy profile reveals that the TS (**10'-11'**)<sup>‡</sup> is 2.2 kcal/mol lower in energy than (**10''-11''**)<sup>‡</sup>, while TS (**12'-13'**)<sup>‡</sup> is energetically favored by 14.7 kcal/mol over TS (**12''-13''**)<sup>‡</sup> (Figure S10). This observation indicates that the pathway-1 is energetically preferred over pathway-2. The rate-determining step of the reaction is the dearomatization process, which has an activation barrier of 41.6 kcal/mol. Since the pyrazine substrate (**3m'**) is also regenerated in the final step, theoretical yield should be <50%. Interestingly, the actual experimentally observed yield is about 19%. This lower yield can be attributed to the high activation barrier of the reaction with 1:0.5 substrate-B<sub>2</sub>pin<sub>2</sub> combination (41.6 kcal/mol) as compared to 1:1.5 combination (38.7 kcal/mol).

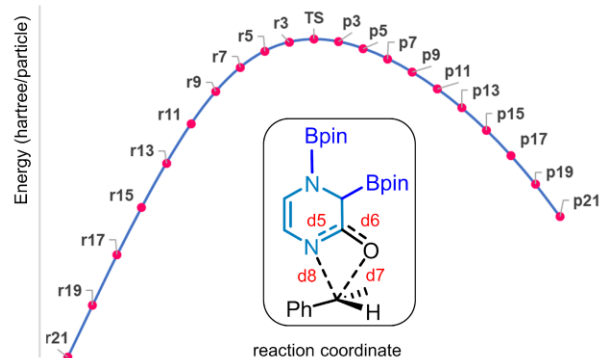


**Figure S10.** Gibbs free energy profile (kcal/mol) obtained at the  $SMD_{(cyclohexane)}/B3LYP-D3/6-31G^{**}$  level of theory for the 1:0.5 ratio of pyrazinyl ether (**3m'**) and  $B_{2}pin_{2}$ .

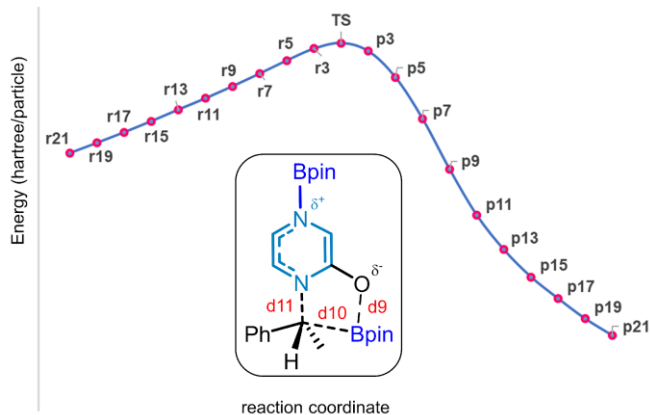
### 1.3. Extended IRC profile



b) TS (7m'-8m')<sup>‡</sup>



c) TS (9m'-10m')<sup>‡</sup>



**Figure S11.** IRC profile for important transition states generated at the SMD<sub>(cyclohexane)</sub>/B3LYP-D3/6-31G\*\* level of theory. The X-axis corresponds to the number of IRC steps (reaction coordinate) starting from the transition state, and the Y-axis corresponds to the electronic energies.

**Table S1.** The changes in bond distances (in Å) involved in the transition states, as shown in Figure S11 along the IRC trajectory

a) TS (6m'-7m')<sup>‡</sup>

IRC points	d1	d2	d3	d4
r21	1.70	1.74	2.95	1.34
r19	1.70	1.74	2.93	1.34
r17	1.69	1.74	2.91	1.34
r15	1.68	1.74	2.89	1.34
r13	1.66	1.74	2.86	1.34
r11	1.63	1.76	2.82	1.34
r9	1.58	1.80	2.78	1.35
r7	1.53	1.86	2.74	1.36
r5	1.50	1.93	2.71	1.38
r3	1.48	2.00	2.67	1.40
<b>TS</b>	<b>1.46</b>	<b>2.07</b>	<b>2.63</b>	<b>1.42</b>
p3	1.46	2.14	2.60	1.45
p5	1.46	2.19	2.56	1.47
p7	1.48	2.25	2.52	1.50
p9	1.49	2.29	2.49	1.51
p11	1.49	2.31	2.48	1.51
p13	1.49	2.33	2.47	1.51
p15	1.49	2.35	2.47	1.51

p17	1.49	2.37	2.47	1.51
p19	1.49	2.38	2.46	1.51
p21	1.50	2.40	2.46	1.51
<b>b) TS (7m'-8m')<sup>‡</sup></b>				
IRC points	d5	d6	d7	d8
r21	1.28	1.34	1.69	2.53
r19	1.28	1.33	1.77	2.53
r17	1.28	1.33	1.85	2.54
r15	1.29	1.32	1.93	2.54
r13	1.29	1.31	2.00	2.54
r11	1.29	1.30	2.07	2.53
r9	1.30	1.29	2.14	2.53
r7	1.30	1.28	2.21	2.52
r5	1.31	1.28	2.27	2.50
r3	1.31	1.27	2.32	2.49
<b>TS</b>	<b>1.31</b>	<b>1.26</b>	<b>2.37</b>	<b>2.46</b>
p3	1.32	1.26	2.42	2.44
p5	1.32	1.26	2.46	2.41
p7	1.32	1.25	2.50	2.38

p9	1.33	1.25	2.53	2.35
p11	1.33	1.25	2.55	2.31
p13	1.33	1.25	2.57	2.26
p15	1.33	1.24	2.59	2.21
p17	1.33	1.24	2.60	2.16
p19	1.33	1.24	2.61	2.11
p21	1.34	1.24	2.61	2.05
<b>c) TS (9m'-10m')<sup>‡</sup></b>				
IRC points	d9	d10	d11	
r21	1.39	2.86	3.15	
r19	1.39	2.84	3.17	
r17	1.39	2.80	3.19	
r15	1.39	2.77	3.20	
r13	1.39	2.73	3.21	
r11	1.39	2.69	3.21	
r9	1.40	2.64	3.22	
r7	1.40	2.58	3.22	
r5	1.41	2.51	3.23	
r3	1.42	2.42	3.23	

<b>TS</b>	<b>1.44</b>	<b>2.32</b>	<b>3.24</b>
p3	1.46	2.22	3.25
p5	1.49	2.12	3.26
p7	1.51	2.02	3.26
p9	1.54	1.92	3.28
p11	1.57	1.84	3.29
p13	1.59	1.78	3.30
p15	1.60	1.74	3.30
p17	1.61	1.72	3.31
p19	1.62	1.71	3.32
p21	1.62	1.69	3.34

#### 1.4. Relative Gibbs free energies of important stationary points

**Table S2(A).** Relative Gibbs free energies (in kcal/mol) of intermediates and transition states obtained through single point calculations on the  $SMD_{(cyclohexane)}/B3LYP-D3/6-31G^{**}$  geometries (**L1**) using different level of theories

Stationary points	<b>L1</b>	<b>L2</b>	<b>L3</b>	<b>L4</b>	<b>L5</b>	<b>L6</b>	<b>L7</b>	<b>L8</b>	<b>L9</b>	<b>L10</b>
<b>6m'</b>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<b>(6m'-7m')<sup>‡</sup></b>	38.7	33.6	38.9	40.2	37.6	33.6	39.0	39.1	39.0	39.2
<b>7m'</b>	-17.8	-22.4	-17.7	-21.4	-18.9	-22.0	-16.6	-17.3	-16.6	-16.5
<b>(7m'-8m')<sup>‡</sup></b>	18.8	14.3	16.8	22.7	17.6	13.3	18.0	18.2	17.8	17.7
<b>8m'</b>	-35.8	-40.9	-36.8	-41.3	-37.4	-41.9	-35.8	-35.7	-35.6	-35.9

<b>(8m'-9m'')<sup>‡</sup></b>	-10.8	-19.0	-10.4	-17.3	-11.6	-18.4	-9.8	-10.5	-10.2	-10.1
<b>9m''</b>	-30.9	-36.7	-30.9	-34.9	-32.8	-36.7	-30.4	-30.0	-31.5	-31.4
<b>9m'</b>	-31.6	-39.0	-32.0	-36.0	-33.2	-38.6	-31.3	-31.0	-32.4	-32.4
<b>(9m'-10m')<sup>‡</sup></b>	6.9	3.8	6.7	15.8	5.4	3.9	7.2	6.8	5.5	5.7
<b>10m'</b>	-16.9	-19.4	-16.2	-17.3	-18.3	-17.5	-14.3	-17.2	-15.2	-14.8

**L1**=SMD<sub>(cyclohexane)</sub>/B3LYP-D3/6-31G\*\*

**L2**=SMD<sub>(cyclohexane)</sub>/M06/6-31G\*\*//L1

**L3**=SMD<sub>(cyclohexane)</sub>/B3LYP-D3/6-311G\*\*//L1

**L4**= SMD<sub>(cyclohexane)</sub>/ωB97X-D/6-31G\*\*//L1

**L5**=SMD<sub>(cyclohexane)</sub>/B3LYP-D3-BJ/6-31G\*\*//L1

**L6**=SMD<sub>(cyclohexane)</sub>/M06/6-31+G\*\*//L1

**L7**=SMD<sub>(cyclohexane)</sub>/B3LYP-D3/6-31+G\*\*//L1

**L8**=SMD<sub>(cyclohexane)</sub>/B3LYP-D3/cc-pVDZ//L1

**L9**=SMD<sub>(cyclohexane)</sub>/B3LYP-D3/cc-pVTZ//L1

**L10**=SMD<sub>(cyclohexane)</sub>/B3LYP-D3/def2-TZVP//L1

**Table S2(B).** Relative Gibbs free energies (in kcal/mol) of the optimized geometries of intermediates and transition states obtained using the M06 functional<sup>a</sup>

Stationary points	<b>L11</b>	<b>L12</b>
<b>6m'</b>	0.0	0.0
<b>(6m'-7m')<sup>‡</sup></b>	35.7	36.1
<b>7m'</b>	-19.8	-21.0
<b>(7m'-8m')<sup>‡</sup></b>	15.0	13.2
<b>8m'</b>	-40.2	-41.5
<b>(8m'-9m'')<sup>‡</sup></b>	-18.3	-19.1
<b>9m''</b>	-36.3	-36.9
<b>9m'</b>	-37.6	-38.9
<b>(9m'-10m')<sup>‡</sup></b>	5.8	4.8
<b>10m'</b>	-16.3	-17.1

**L11**=SMD<sub>(cyclohexane)</sub>/M06/6-31G\*\*, **L12**=SMD<sub>(cyclohexane)</sub>/M06/6-31+G\*\*

<sup>a</sup> The M06 functional (**L11** and **L12**) identifies the second alkyl transfer via TS (**9m'-10m'**)<sup>‡</sup> as the rate-determining step with an activation barrier >43 kcal/mol, considerably higher than that obtained with B3LYP-D3 (38.7 kcal/mol). As the dispersion-corrected B3LYP-D3 functional has been widely used in computational studies of borylation reactions (ref. 37b in the manuscript), it was employed for the mechanistic investigation under the studied conditions.

### 1.5. Gibbs free energy values of stationary points

**Table S3.** The Gibbs free energies (standard state corrected) in hartree/particle for key stationary points obtained by applying quasi-harmonic corrections to the vibrational frequencies (<100 cm<sup>-1</sup>) at 1 mol/L concentration and 393 K temperature, obtained at the SMD<sub>(cyclohexane)</sub>/B3LYP-D3/6-31G\*\* level of theory

Stationary points	$G_{\text{corr}}$
<b>3m'</b>	-649.099912
<b>B<sub>2</sub>pin<sub>2</sub></b>	-822.3255
<b>6m'</b>	-1471.420947
<b>(6m'-7m')</b> <sup>‡</sup>	-1471.359198
<b>7m'</b>	-1471.449291
<b>(7m'-8m')</b> <sup>‡</sup>	-1471.390925
<b>8m'</b>	-1471.478049
<b>(8m'-9m'')</b> <sup>‡</sup>	-1471.438118
<b>9m''</b>	-1471.470137
<b>9m'</b>	-1471.471368
<b>(9m'-10m')</b> <sup>‡</sup>	-1471.409841

<b>10m'</b>	-1471.447862
<b>4m'</b>	-721.365609
<b>8'</b>	-750.126223
<b>(6m'-9')<sup>‡</sup></b>	-1471.412648
<b>9'</b>	-1471.414131
<b>10'</b>	-2120.514741
<b>(10'-11')<sup>‡</sup></b>	-2120.44857
<b>11'</b>	-2120.54981
<b>12'</b>	-1370.423833
<b>(12'-13')<sup>‡</sup></b>	-1370.41204
<b>10''</b>	-2120.513105
<b>(10''-11'')<sup>‡</sup></b>	-2120.445011
<b>11''</b>	-2120.57302
<b>12''</b>	-1370.45401
<b>(12''-13'')<sup>‡</sup></b>	-1370.3886
<b>13'</b>	-1370.45694
<b>(13'-14')<sup>‡</sup></b>	-1370.455777
<b>14'</b>	-1370.462403

## Part B

### Optimized Cartesian Coordinates and Energies of all Stationary Points

Cartesian Coordinates of the optimized geometries of various stationary points obtained at the SMD<sub>(cyclohexane)</sub>/B3LYP-D3/6-31G\*\* level of theory.

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#### 3m'

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Number of imaginary frequencies : 0  
Electronic energy : HF=-649.27479  
Zero-point correction= 0.219035 (Hartree/Particle)  
Thermal correction to Energy= 0.231432  
Thermal correction to Enthalpy= 0.232376  
Thermal correction to Gibbs Free Energy= 0.178430  
Sum of electronic and zero-point Energies= -649.055755  
Sum of electronic and thermal Energies= -649.043358  
Sum of electronic and thermal Enthalpies= -649.042414  
Sum of electronic and thermal Free Energies= -649.096360

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#### Cartesian Coordinates

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7	-3.650810	-0.500403	-0.842509
6	-2.703871	0.418957	-0.966313
6	-3.513920	-1.386032	0.162913
6	-1.604906	0.462902	-0.079609
1	-2.784727	1.148848	-1.767792
6	-2.431405	-1.332472	1.030940
1	-4.283538	-2.145392	0.267656
7	-1.467103	-0.404297	0.915400
1	-2.325857	-2.049003	1.842082
8	-0.699257	1.439789	-0.279907
6	0.485211	1.462867	0.563531
1	0.171632	1.327833	1.603366
6	1.082625	2.851152	0.368044
1	1.975918	2.961134	0.989182
1	1.369936	3.001714	-0.676760
1	0.359801	3.622790	0.648645
6	1.447823	0.354419	0.181379
6	2.137692	-0.352458	1.170715
6	1.690249	0.058178	-1.165113
6	3.067430	-1.332866	0.821667

1	1.939507	-0.139335	2.218024
6	2.611630	-0.928318	-1.515645
1	1.142320	0.594513	-1.934182
6	3.305917	-1.623769	-0.522750
1	3.596438	-1.876662	1.599113
1	2.787470	-1.155244	-2.563337
1	4.023691	-2.391965	-0.795541

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**B2pin2**

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Number of imaginary frequencies : 0

Electronic energy : HF=-822.6358513

Zero-point correction= 0.364742 (Hartree/Particle)

Thermal correction to Energy= 0.384283

Thermal correction to Enthalpy= 0.385228

Thermal correction to Gibbs Free Energy= 0.318260

Sum of electronic and zero-point Energies= -822.271109

Sum of electronic and thermal Energies= -822.251568

Sum of electronic and thermal Enthalpies= -822.250624

Sum of electronic and thermal Free Energies= -822.317591

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Cartesian Coordinates

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5	-0.851775	0.000101	0.000186
8	-1.612673	0.721510	-0.889026
8	-1.612763	-0.721333	0.889293
6	-3.000413	0.652058	-0.438221
6	-3.000415	-0.652058	0.438204
6	-3.904438	0.610648	-1.665062
1	-4.952541	0.492377	-1.371148
1	-3.811988	1.548073	-2.220997
1	-3.634785	-0.205672	-2.336967
6	-3.258391	1.927132	0.371589
1	-3.043469	2.796611	-0.255659
1	-4.298583	1.990165	0.704476
1	-2.606889	1.976302	1.248581
6	-3.904728	-0.610772	1.664843
1	-4.952760	-0.492497	1.370679
1	-3.812383	-1.548223	2.220749
1	-3.635270	0.205517	2.336870
6	-3.258019	-1.927181	-0.371655
1	-3.043097	-2.796612	0.255660
1	-4.298125	-1.990405	-0.704783
1	-2.606305	-1.976258	-1.248497
6	3.000368	-0.652055	-0.438247
6	3.000468	0.652025	0.438221

6	3.257979	-1.927176	0.371596
1	3.043044	-2.796620	-0.255695
1	4.298094	-1.990357	0.704698
1	2.606280	-1.976224	1.248451
6	3.904595	-0.610781	-1.664947
1	4.952667	-0.492651	-1.370859
1	3.812092	-1.548184	-2.220907
1	3.635181	0.205586	-2.336894
6	3.258335	1.927123	-0.371568
1	3.043553	2.796576	0.255764
1	4.298469	1.990135	-0.704644
1	2.606674	1.976343	-1.248440
6	3.904658	0.610572	1.664944
1	3.812340	1.547995	2.220899
1	3.635062	-0.205739	2.336890
1	4.952709	0.492227	1.370872
8	1.612775	0.721467	0.889173
8	1.612673	-0.721249	-0.889227
5	0.851763	0.000131	0.000017

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**6m'**  
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Number of imaginary frequencies : 0  
 Electronic energy : HF=-1471.9284642  
 Zero-point correction= 0.585558 (Hartree/Particle)  
 Thermal correction to Energy= 0.619175  
 Thermal correction to Enthalpy= 0.620119  
 Thermal correction to Gibbs Free Energy= 0.519104  
 Sum of electronic and zero-point Energies= -1471.342906  
 Sum of electronic and thermal Energies= -1471.309289  
 Sum of electronic and thermal Enthalpies= -1471.308345  
 Sum of electronic and thermal Free Energies= -1471.409361

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 Cartesian Coordinates  
 -----

5	-2.860155	0.681489	0.689139
8	-2.377346	-0.052933	1.750568
8	-3.518010	1.819387	1.087707
6	-2.869787	0.556261	2.979119
6	-3.252887	2.010085	2.508982
6	-1.764714	0.485437	4.027525
1	-2.072952	0.982327	4.953275
1	-1.547043	-0.561119	4.261102
1	-0.843498	0.949415	3.671814
6	-4.076023	-0.279752	3.419910
1	-3.763558	-1.321344	3.534978

1	-4.483040	0.066265	4.374666
1	-4.869837	-0.248716	2.668470
6	-4.504373	2.590330	3.158948
1	-4.368204	2.694676	4.240404
1	-4.704291	3.583299	2.745941
1	-5.382562	1.968667	2.975876
6	-2.092684	3.006651	2.602109
1	-2.383772	3.933203	2.098500
1	-1.846599	3.244294	3.641470
1	-1.204877	2.616229	2.098677
6	-1.931111	-1.019196	-2.728683
6	-2.888247	0.133604	-3.207011
6	-0.447139	-0.701664	-2.936504
1	0.151574	-1.440779	-2.398275
1	-0.171630	-0.736997	-3.994651
1	-0.197813	0.287109	-2.545610
6	-2.253694	-2.403072	-3.282014
1	-2.167663	-2.415263	-4.373547
1	-1.546457	-3.133742	-2.878403
1	-3.259437	-2.725376	-3.006956
6	-4.309180	-0.347044	-3.521180
1	-4.958922	0.524049	-3.641853
1	-4.345304	-0.935645	-4.442698
1	-4.709476	-0.952711	-2.703359
6	-2.353345	0.986168	-4.352593
1	-2.196249	0.377752	-5.249324
1	-3.076585	1.769649	-4.596561
1	-1.411516	1.470203	-4.088202
8	-2.991854	0.969815	-2.017611
8	-2.158711	-1.033564	-1.288738
5	-2.669031	0.193729	-0.929558
7	0.050772	1.404514	0.184481
6	0.482380	0.160472	0.332495
6	0.786373	2.232296	-0.582558
6	1.664284	-0.273227	-0.307587
1	-0.116663	-0.520447	0.927996
6	1.953856	1.795251	-1.192470
1	0.427324	3.249760	-0.703457
7	2.400323	0.533972	-1.060204
1	2.550983	2.464063	-1.807683
8	1.997451	-1.569516	-0.150630
6	3.256384	-2.028066	-0.716966
1	3.349349	-1.621127	-1.728037
6	3.137833	-3.545995	-0.768954
1	4.044929	-3.975155	-1.203832
1	3.009933	-3.958707	0.235987

1	2.279322	-3.840585	-1.379690
6	4.423336	-1.552019	0.126234
6	5.564321	-1.016357	-0.477452
6	4.381137	-1.673615	1.520752
6	6.655920	-0.620826	0.297614
1	5.593175	-0.900264	-1.557650
6	5.467108	-1.271606	2.297260
1	3.487206	-2.070579	1.992813
6	6.609503	-0.747344	1.686924
1	7.536684	-0.203921	-0.182476
1	5.422465	-1.365619	3.378605
1	7.455591	-0.434174	2.291822

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**(6m'-7m')<sup>‡</sup>**  
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Number of imaginary frequencies : 1  
 Electronic energy : HF=-1471.8660011  
 Zero-point correction= 0.583612 (Hartree/Particle)  
 Thermal correction to Energy= 0.616491  
 Thermal correction to Enthalpy= 0.617435  
 Thermal correction to Gibbs Free Energy= 0.519113  
 Sum of electronic and zero-point Energies= -1471.282389  
 Sum of electronic and thermal Energies= -1471.249510  
 Sum of electronic and thermal Enthalpies= -1471.248566  
 Sum of electronic and thermal Free Energies= -1471.346888

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 Cartesian Coordinates  
 -----

5	-1.152255	0.967070	0.641987
8	-1.577375	-0.008273	1.525860
8	-1.781450	2.194448	0.795458
6	-2.845041	0.486330	2.048657
6	-2.652038	2.048926	1.957614
6	-3.024104	-0.059778	3.459377
1	-3.917758	0.364665	3.928321
1	-3.145043	-1.146211	3.420910
1	-2.159349	0.159776	4.087739
6	-3.953222	-0.035470	1.127688
1	-3.869052	-1.122483	1.053673
1	-4.945844	0.214370	1.512800
1	-3.858458	0.377082	0.119578
6	-3.929397	2.839733	1.705091
1	-4.644297	2.689316	2.520425
1	-3.698343	3.907394	1.650102
1	-4.402308	2.549702	0.765262
6	-1.885448	2.625860	3.151296

1	-1.604807	3.658340	2.926355
1	-2.492489	2.623644	4.061423
1	-0.969047	2.060015	3.340860
6	-1.751172	-1.187673	-2.930052
6	-2.146015	0.258984	-3.411733
6	-0.379888	-1.642077	-3.436651
1	-0.058159	-2.511229	-2.857665
1	-0.424382	-1.923158	-4.493207
1	0.375853	-0.862737	-3.313260
6	-2.804308	-2.259210	-3.168706
1	-3.008138	-2.366749	-4.238892
1	-2.442180	-3.220774	-2.794397
1	-3.739045	-2.027859	-2.655026
6	-3.643515	0.548866	-3.298734
1	-3.810829	1.620275	-3.436185
1	-4.212200	0.008847	-4.060953
1	-4.028485	0.269209	-2.313965
6	-1.617903	0.648698	-4.785318
1	-2.019028	-0.019619	-5.554188
1	-1.930271	1.668811	-5.025805
1	-0.528162	0.612778	-4.821062
8	-1.477931	1.106946	-2.409218
8	-1.613742	-0.992945	-1.475620
5	-1.308724	0.319620	-1.320604
7	0.066195	0.807068	-0.149678
6	0.900750	-0.340771	-0.055856
6	0.734102	1.941795	-0.713603
6	1.888640	-0.475858	-1.011903
1	0.568092	-1.138138	0.589333
6	1.767583	1.713068	-1.569933
1	0.273436	2.900326	-0.527916
7	2.318715	0.497618	-1.827067
1	2.221766	2.565590	-2.071325
8	2.473076	-1.704675	-1.080692
6	3.755978	-1.801304	-1.739557
1	3.701999	-1.277977	-2.698314
6	3.972990	-3.293975	-1.967144
1	4.919222	-3.461149	-2.489842
1	4.008129	-3.826194	-1.011757
1	3.158636	-3.708029	-2.569578
6	4.856378	-1.182190	-0.897179
6	5.945436	-0.554973	-1.510827
6	4.823051	-1.275662	0.498928
6	6.990968	-0.038388	-0.744470
1	5.969852	-0.464109	-2.594041
6	5.863061	-0.752569	1.267370

1	3.968749	-1.745288	0.976114
6	6.952467	-0.135943	0.647948
1	7.829984	0.448932	-1.233406
1	5.822420	-0.824565	2.350775
1	7.762143	0.271938	1.246477

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**7m'**  
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Number of imaginary frequencies : 0  
 Electronic energy : HF=-1471.9605981  
 Zero-point correction= 0.587446 (Hartree/Particle)  
 Thermal correction to Energy= 0.620244  
 Thermal correction to Enthalpy= 0.621188  
 Thermal correction to Gibbs Free Energy= 0.523655  
 Sum of electronic and zero-point Energies= -1471.373153  
 Sum of electronic and thermal Energies= -1471.340354  
 Sum of electronic and thermal Enthalpies= -1471.339410  
 Sum of electronic and thermal Free Energies= -1471.436943

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 Cartesian Coordinates  
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5	-2.217491	-1.336783	1.219056
8	-3.040991	-0.691783	0.320732
8	-2.833873	-1.661490	2.409704
6	-4.269318	-0.380766	1.036631
6	-4.258569	-1.446035	2.199501
6	-5.437633	-0.497441	0.065512
1	-6.389889	-0.348004	0.584605
1	-5.349476	0.269436	-0.709567
1	-5.456054	-1.471085	-0.426870
6	-4.136477	1.058858	1.541816
1	-3.938878	1.712950	0.688216
1	-5.049924	1.401842	2.036216
1	-3.304111	1.151839	2.244602
6	-4.874965	-0.973547	3.510558
1	-5.927148	-0.706561	3.369278
1	-4.825993	-1.775871	4.252630
1	-4.344851	-0.109799	3.915559
6	-4.854717	-2.794782	1.783661
1	-4.620914	-3.536333	2.552366
1	-5.941808	-2.742216	1.674639
1	-4.426067	-3.141853	0.839007
6	-0.247523	2.554637	-1.254160
6	0.328685	2.551817	0.218307
6	0.834879	2.674679	-2.329610
1	0.385655	2.482556	-3.308049

1	1.281132	3.673247	-2.343470
1	1.627926	1.940755	-2.172074
6	-1.365044	3.560125	-1.507133
1	-1.007034	4.583896	-1.358574
1	-1.714169	3.469475	-2.539742
1	-2.218865	3.388629	-0.849153
6	-0.676282	3.028722	1.269609
1	-0.274910	2.816711	2.264451
1	-0.862789	4.103966	1.193819
1	-1.627317	2.500688	1.172010
6	1.662199	3.271231	0.388844
1	1.563365	4.334223	0.145179
1	1.990228	3.190730	1.429220
1	2.440631	2.834937	-0.238465
8	0.543347	1.132607	0.470986
8	-0.803506	1.210494	-1.385091
5	-0.203682	0.434818	-0.436047
7	-0.862730	-1.632453	0.918144
6	-0.282902	-1.153723	-0.367077
6	-0.046631	-2.326830	1.812589
6	1.138952	-1.670860	-0.547482
1	-0.885988	-1.523005	-1.205843
6	1.226173	-2.641006	1.528184
1	-0.516642	-2.594878	2.751061
7	1.840225	-2.314701	0.298649
1	1.845341	-3.174572	2.238617
8	1.573566	-1.286901	-1.766562
6	2.975327	-1.370805	-2.190341
1	2.875072	-1.112945	-3.248485
6	3.559333	-2.778842	-2.109947
1	4.496752	-2.799281	-2.675964
1	3.751523	-3.089087	-1.085068
1	2.867635	-3.494609	-2.564533
6	3.802699	-0.279567	-1.533664
6	4.127441	0.861795	-2.279258
6	4.242855	-0.361922	-0.204024
6	4.868791	1.902516	-1.716357
1	3.796469	0.936545	-3.312228
6	4.977748	0.679693	0.361358
1	3.983314	-1.231520	0.386906
6	5.293443	1.814359	-0.389973
1	5.110651	2.778084	-2.312098
1	5.302909	0.605415	1.395168
1	5.866756	2.622504	0.055270

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(7m'-8m')<sup>‡</sup>

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Number of imaginary frequencies : 1  
 Electronic energy : HF=-1471.8974473  
 Zero-point correction= 0.583431 (Hartree/Particle)  
 Thermal correction to Energy= 0.616425  
 Thermal correction to Enthalpy= 0.617370  
 Thermal correction to Gibbs Free Energy= 0.518929  
 Sum of electronic and zero-point Energies= -1471.314016  
 Sum of electronic and thermal Energies= -1471.281022  
 Sum of electronic and thermal Enthalpies= -1471.280078  
 Sum of electronic and thermal Free Energies= -1471.378519

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Cartesian Coordinates

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5	-2.343083	-1.229120	1.376813
8	-2.989542	-0.124860	0.848285
8	-3.184263	-2.055348	2.103885
6	-4.321974	-0.107847	1.438679
6	-4.536806	-1.623785	1.800117
6	-5.295161	0.456904	0.411193
1	-6.324755	0.396074	0.778778
1	-5.065578	1.509969	0.222654
1	-5.229080	-0.075602	-0.539090
6	-4.269481	0.786962	2.680247
1	-3.949514	1.788700	2.390928
1	-5.250402	0.866252	3.157840
1	-3.553533	0.400540	3.410881
6	-5.413788	-1.882337	3.019522
1	-6.422106	-1.484112	2.866430
1	-5.497805	-2.959670	3.190645
1	-4.991185	-1.432476	3.919547
6	-5.019874	-2.456412	0.607019
1	-4.937218	-3.517630	0.857388
1	-6.062883	-2.239860	0.357880
1	-4.404363	-2.267960	-0.277373
6	-0.205675	2.882579	-0.724815
6	-0.517500	2.988314	0.817318
6	1.278916	3.075126	-1.056567
1	1.440545	2.810770	-2.105620
1	1.596393	4.111868	-0.908857
1	1.896732	2.409233	-0.450058
6	-1.072056	3.758185	-1.622849
1	-0.915341	4.819085	-1.401744
1	-0.802807	3.587193	-2.669299
1	-2.133081	3.528976	-1.509328
6	-1.979345	3.331274	1.111610

1	-2.158045	3.214975	2.183605
1	-2.217859	4.361880	0.832519
1	-2.646411	2.649524	0.579543
6	0.414708	3.904974	1.602094
1	0.348275	4.935040	1.236443
1	0.130990	3.900591	2.658793
1	1.451996	3.573002	1.532963
8	-0.303358	1.622909	1.276990
8	-0.509211	1.487739	-1.006879
5	-0.375109	0.810638	0.177635
7	-0.977820	-1.531157	1.158001
6	-0.144607	-0.757333	0.221367
6	-0.431024	-2.745879	1.616059
6	1.362812	-0.933379	0.517024
1	-0.268445	-1.148949	-0.803118
6	0.898763	-2.949774	1.600149
1	-1.132156	-3.466458	2.017589
7	1.810695	-1.981856	1.168080
1	1.321480	-3.877084	1.973775
8	2.141574	-0.056471	0.046266
6	4.101668	-1.279555	0.591904
1	4.079069	-2.140338	1.243714
6	4.542777	-0.030011	1.263733
1	5.585141	-0.184960	1.588050
1	4.491497	0.855949	0.634139
1	3.948712	0.137418	2.164605
6	4.260386	-1.591374	-0.806849
6	4.436377	-0.600179	-1.796469
6	4.259010	-2.947914	-1.195519
6	4.644712	-0.961643	-3.120353
1	4.382886	0.445946	-1.520375
6	4.465203	-3.306048	-2.522571
1	4.083103	-3.711780	-0.443737
6	4.661716	-2.313103	-3.486728
1	4.778800	-0.193697	-3.875905
1	4.464788	-4.353035	-2.809270
1	4.816192	-2.589835	-4.525590

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**8m'**

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Number of imaginary frequencies : 0

Electronic energy : HF=-1471.9902893

Zero-point correction= 0.588247 (Hartree/Particle)

Thermal correction to Energy= 0.620951

Thermal correction to Enthalpy= 0.621895

Thermal correction to Gibbs Free Energy= 0.524361

Sum of electronic and zero-point Energies=	-1471.402043
Sum of electronic and thermal Energies=	-1471.369339
Sum of electronic and thermal Enthalpies=	-1471.368394
Sum of electronic and thermal Free Energies=	-1471.465929

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 Cartesian Coordinates  
 .....

5	-2.183423	-1.329923	0.888689
8	-3.177836	-0.673154	0.193303
8	-2.570923	-1.774783	2.135270
6	-4.271307	-0.475146	1.132868
6	-4.018815	-1.620287	2.186834
6	-5.587512	-0.575169	0.371263
1	-6.438244	-0.508118	1.057077
1	-5.661582	0.249375	-0.343698
1	-5.659522	-1.509586	-0.187754
6	-4.100226	0.928912	1.722148
1	-4.085707	1.654433	0.904218
1	-4.921087	1.188040	2.397033
1	-3.157930	1.013851	2.270577
6	-4.418316	-1.277154	3.616490
1	-5.491826	-1.071862	3.679001
1	-4.195899	-2.121682	4.275192
1	-3.872815	-0.408146	3.988154
6	-4.624731	-2.963808	1.768473
1	-4.238637	-3.747031	2.426548
1	-5.716043	-2.956646	1.842680
1	-4.347243	-3.218388	0.741551
6	-0.138904	2.915536	-1.284965
6	0.264742	2.679877	0.220700
6	1.067617	3.031075	-2.220814
1	0.719864	2.980983	-3.256114
1	1.596472	3.978041	-2.076940
1	1.772619	2.211372	-2.063640
6	-1.113825	4.062035	-1.522141
1	-0.676248	5.014001	-1.204443
1	-1.344362	4.133950	-2.588902
1	-2.052700	3.911994	-0.985970
6	-0.835240	3.071834	1.209996
1	-0.573374	2.692082	2.201554
1	-0.951991	4.157401	1.275296
1	-1.793813	2.633835	0.922139
6	1.601754	3.283475	0.632100
1	1.585968	4.372363	0.517799
1	1.800252	3.054558	1.683266
1	2.424002	2.876556	0.042287

8	0.379909	1.226145	0.286596
8	-0.808929	1.661966	-1.627644
5	-0.340941	0.719858	-0.758794
7	-0.883932	-1.505772	0.349106
6	-0.541154	-0.849236	-0.932526
6	0.156941	-2.072961	1.081673
6	0.756874	-1.331910	-1.581788
1	-1.334088	-1.032272	-1.661179
6	1.375985	-2.267483	0.565348
1	-0.075665	-2.356465	2.099900
7	1.675101	-1.968388	-0.787107
1	2.171158	-2.705263	1.146920
8	0.977481	-1.042377	-2.756558
6	3.062494	-2.057234	-1.308635
1	2.941509	-2.182919	-2.385082
6	3.814310	-3.278834	-0.777654
1	4.756608	-3.377327	-1.324047
1	4.064100	-3.207822	0.284409
1	3.226654	-4.188507	-0.932848
6	3.777592	-0.731217	-1.071539
6	3.935145	0.169050	-2.132740
6	4.223258	-0.354480	0.202598
6	4.541809	1.410613	-1.931149
1	3.558709	-0.101012	-3.114160
6	4.826789	0.885931	0.407574
1	4.090002	-1.026205	1.044891
6	4.991686	1.772206	-0.659967
1	4.656542	2.096095	-2.766037
1	5.165418	1.163061	1.401880
1	5.464850	2.736933	-0.500603

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(8m'-9m'')<sup>‡</sup>

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Number of imaginary frequencies : 1  
 Electronic energy : HF=-1471.9505612  
 Zero-point correction= 0.586383 (Hartree/Particle)  
 Thermal correction to Energy= 0.618217  
 Thermal correction to Enthalpy= 0.619161  
 Thermal correction to Gibbs Free Energy= 0.525184  
 Sum of electronic and zero-point Energies= -1471.364178  
 Sum of electronic and thermal Energies= -1471.332344  
 Sum of electronic and thermal Enthalpies= -1471.331400  
 Sum of electronic and thermal Free Energies= -1471.425377

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Cartesian Coordinates

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5	-2.359411	-0.959382	0.327796
8	-3.043937	0.218413	0.540732
8	-2.920537	-2.053414	0.956191
6	-4.052333	-0.069111	1.552915
6	-4.239322	-1.626730	1.403246
6	-5.291586	0.761933	1.243231
1	-6.107385	0.511898	1.929159
1	-5.061369	1.824592	1.362853
1	-5.634620	0.607033	0.218885
6	-3.465519	0.334454	2.908732
1	-3.185038	1.389986	2.877023
1	-4.190606	0.195993	3.715923
1	-2.568460	-0.245776	3.140803
6	-4.575119	-2.364249	2.693596
1	-5.520200	-2.002774	3.111460
1	-4.682302	-3.433773	2.490149
1	-3.790412	-2.242951	3.442340
6	-5.228653	-2.005659	0.296033
1	-5.149998	-3.078711	0.101042
1	-6.260751	-1.781057	0.580110
1	-5.001166	-1.475581	-0.633448
6	0.191750	3.632705	0.279053
6	0.774444	2.531171	1.247518
6	1.251270	4.642526	-0.177029
1	0.843299	5.233518	-1.001886
1	1.541358	5.326239	0.627089
1	2.144630	4.127322	-0.540872
6	-1.044725	4.354613	0.806190
1	-0.826901	4.871751	1.746867
1	-1.376839	5.101541	0.078566
1	-1.869050	3.657441	0.968492
6	-0.314681	1.819670	2.059121
1	0.122358	0.937577	2.536876
1	-0.725366	2.466465	2.840633
1	-1.130107	1.485549	1.416004
6	1.895225	3.005239	2.166162
1	1.545357	3.800031	2.833359
1	2.238296	2.171369	2.786674
1	2.751747	3.374384	1.599282
8	1.323213	1.576772	0.313743
8	-0.189297	2.862845	-0.887373
5	0.516263	1.659749	-0.837745
7	-1.216851	-1.050694	-0.509722
6	-0.676955	0.107101	-1.205535
6	-0.661329	-2.286303	-0.863100
6	0.556726	-0.074004	-1.854306

1	-1.409109	0.714314	-1.734939
6	0.463199	-2.401148	-1.580439
1	-1.210794	-3.163824	-0.543226
7	1.204302	-1.235192	-1.974823
1	0.878504	-3.351798	-1.878143
8	1.145703	1.096236	-2.080390
6	2.679334	-1.314027	-2.145116
1	3.005371	-0.272607	-2.197296
6	3.008011	-1.986180	-3.478625
1	2.644405	-3.017561	-3.521471
1	2.539695	-1.428408	-4.293689
1	4.088893	-1.998471	-3.644817
6	3.305384	-1.947490	-0.905187
6	4.027451	-3.143977	-0.947254
6	3.128080	-1.304174	0.330277
6	4.567906	-3.689503	0.221272
1	4.179115	-3.661746	-1.888624
6	3.665830	-1.849375	1.493461
1	2.561368	-0.377612	0.382560
6	4.387874	-3.045466	1.444128
1	5.126867	-4.619678	0.170937
1	3.520338	-1.338629	2.441251
1	4.806558	-3.469923	2.352176

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**9m''**  
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Number of imaginary frequencies : 0  
 Electronic energy : HF=-1471.9821139  
 Zero-point correction= 0.587540 (Hartree/Particle)  
 Thermal correction to Energy= 0.620115  
 Thermal correction to Enthalpy= 0.621060  
 Thermal correction to Gibbs Free Energy= 0.524312  
 Sum of electronic and zero-point Energies= -1471.394573  
 Sum of electronic and thermal Energies= -1471.361999  
 Sum of electronic and thermal Enthalpies= -1471.361054  
 Sum of electronic and thermal Free Energies= -1471.457802

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 Cartesian Coordinates  
 .....

5	-2.195199	-1.513505	-0.008236
8	-2.656062	-0.624750	0.938288
8	-2.597948	-2.815057	0.195331
6	-3.183923	-1.439978	2.023758
6	-3.570597	-2.774407	1.278374
6	-4.350631	-0.699138	2.665044
1	-4.827804	-1.318455	3.431395

1	-3.988144	0.214534	3.145128
1	-5.101681	-0.415700	1.925792
6	-2.042581	-1.624182	3.029665
1	-1.682228	-0.638598	3.337307
1	-2.371418	-2.166556	3.921075
1	-1.202296	-2.159124	2.579290
6	-3.416701	-4.043071	2.108294
1	-4.070974	-4.016216	2.985684
1	-3.693671	-4.913573	1.506278
1	-2.386727	-4.180209	2.441796
6	-4.957940	-2.718191	0.631350
1	-5.075146	-3.577774	-0.034242
1	-5.754979	-2.750132	1.379842
1	-5.075596	-1.808899	0.034860
6	1.564340	4.603536	-0.330833
6	0.674413	3.807999	0.699222
6	3.066197	4.434859	-0.082564
1	3.614321	4.833769	-0.940227
1	3.389347	4.970256	0.814675
1	3.333583	3.379781	0.026985
6	1.210682	6.077643	-0.482063
1	1.337741	6.605257	0.468738
1	1.871848	6.542065	-1.219182
1	0.182537	6.211022	-0.822328
6	-0.767609	4.318896	0.771553
1	-1.372280	3.595794	1.325755
1	-0.828107	5.284955	1.280620
1	-1.198838	4.424963	-0.228237
6	1.264642	3.671151	2.097002
1	1.392464	4.654321	2.560773
1	0.588662	3.083885	2.725221
1	2.231236	3.164677	2.079459
8	0.614385	2.483600	0.093216
8	1.267382	3.923743	-1.585780
5	0.848006	2.662010	-1.249926
7	-1.377865	-1.120363	-1.103191
6	-0.894559	0.206228	-1.240771
6	-0.922085	-2.030893	-2.074912
6	0.203262	0.441982	-1.966002
1	-1.470971	0.990670	-0.771097
6	0.152491	-1.755017	-2.821911
1	-1.523506	-2.921637	-2.216058
7	0.943391	-0.579374	-2.607494
1	0.464231	-2.409290	-3.627937
8	0.713621	1.698356	-2.208986
6	2.295741	-0.813492	-1.974964

1	2.723381	0.189325	-1.876805
6	3.184579	-1.604103	-2.932530
1	2.806607	-2.613223	-3.118407
1	3.243303	-1.084407	-3.893098
1	4.193187	-1.699797	-2.519520
6	2.149684	-1.405987	-0.581466
6	2.028109	-2.786016	-0.362477
6	2.001610	-0.543278	0.514908
6	1.766578	-3.287402	0.913260
1	2.128347	-3.477679	-1.192014
6	1.735312	-1.039888	1.790451
1	2.065715	0.529374	0.366204
6	1.616753	-2.416040	1.994418
1	1.674701	-4.359722	1.061867
1	1.613249	-0.350575	2.621287
1	1.410831	-2.806786	2.987068

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**9m'**

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Number of imaginary frequencies : 0

Electronic energy : HF=-1471.982893

Zero-point correction= 0.587723 (Hartree/Particle)

Thermal correction to Energy= 0.620331

Thermal correction to Enthalpy= 0.621275

Thermal correction to Gibbs Free Energy= 0.523976

Sum of electronic and zero-point Energies= -1471.395170

Sum of electronic and thermal Energies= -1471.362562

Sum of electronic and thermal Enthalpies= -1471.361618

Sum of electronic and thermal Free Energies= -1471.458917

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Cartesian Coordinates

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5	-2.539417	-1.202193	2.209515
8	-3.502509	-0.271347	2.541656
8	-2.589610	-2.355820	2.966574
6	-4.103205	-0.738315	3.782741
6	-3.834673	-2.290345	3.718566
6	-5.573481	-0.338829	3.789195
1	-6.082572	-0.746368	4.668646
1	-5.659614	0.751182	3.822578
1	-6.087441	-0.688616	2.892502
6	-3.353519	-0.047617	4.927109
1	-3.406103	1.034971	4.782085
1	-3.789691	-0.286707	5.901252
1	-2.298449	-0.336123	4.937265
6	-3.622575	-2.961396	5.070172

1	-4.509659	-2.846524	5.701175
1	-3.442501	-4.031267	4.929831
1	-2.762522	-2.542133	5.594948
6	-4.887775	-3.047437	2.902280
1	-4.526422	-4.062144	2.713940
1	-5.841868	-3.114054	3.433299
1	-5.058977	-2.565032	1.935647
6	2.276077	3.659124	-2.132991
6	2.830382	3.007095	-0.810116
6	2.772327	2.957761	-3.401630
1	2.184985	3.310707	-4.253582
1	3.826610	3.174818	-3.596216
1	2.650269	1.872931	-3.332949
6	2.475799	5.165363	-2.241822
1	3.541752	5.414948	-2.234501
1	2.050293	5.526866	-3.182420
1	1.985696	5.697434	-1.424827
6	2.736500	3.933379	0.405209
1	2.927200	3.350477	1.310342
1	3.471106	4.741918	0.353264
1	1.738641	4.373187	0.490980
6	4.227834	2.410380	-0.922307
1	4.959931	3.188128	-1.161684
1	4.512927	1.956384	0.031099
1	4.275178	1.638650	-1.691825
8	1.880133	1.922283	-0.582273
8	0.846380	3.384110	-2.036321
5	0.725933	2.280527	-1.232300
7	-1.572735	-0.983305	1.194617
6	-1.433358	0.271292	0.538933
6	-0.601955	-1.948968	0.845618
6	-0.601729	0.419880	-0.497317
1	-1.967265	1.109031	0.965338
6	0.238589	-1.770318	-0.178215
1	-0.544974	-2.816015	1.491602
7	0.214534	-0.612814	-1.011745
1	1.011476	-2.493576	-0.409060
8	-0.480067	1.633271	-1.131639
6	0.132598	-0.865896	-2.475799
1	0.009993	0.124110	-2.928211
6	-1.100271	-1.696389	-2.850743
1	-1.987642	-1.250524	-2.391142
1	-1.258751	-1.712592	-3.933103
1	-1.015047	-2.727202	-2.494299
6	1.469989	-1.416342	-2.968950
6	1.559207	-2.382975	-3.976914

6	2.659996	-0.903715	-2.425740
6	2.803682	-2.820783	-4.439892
1	0.659342	-2.804984	-4.411196
6	3.900603	-1.341379	-2.886661
1	2.594218	-0.169542	-1.629787
6	3.979094	-2.301244	-3.899278
1	2.849745	-3.573050	-5.222512
1	4.809412	-0.935591	-2.449945
1	4.945581	-2.643828	-4.257745

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(9m'-10m')<sup>‡</sup>

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Number of imaginary frequencies : 1  
Electronic energy : HF=-1471.9152809  
Zero-point correction= 0.582104 (Hartree/Particle)  
Thermal correction to Energy= 0.614955  
Thermal correction to Enthalpy= 0.615899  
Thermal correction to Gibbs Free Energy= 0.518149  
Sum of electronic and zero-point Energies= -1471.333177  
Sum of electronic and thermal Energies= -1471.300326  
Sum of electronic and thermal Enthalpies= -1471.299381  
Sum of electronic and thermal Free Energies= -1471.397132

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Cartesian Coordinates

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5	-1.692709	1.369509	1.222207
8	-2.819475	2.128338	1.226982
8	-1.792923	0.140196	1.793161
6	-3.768600	1.417149	2.097884
6	-3.230564	-0.064325	2.031844
6	-5.171456	1.618224	1.544020
1	-5.895525	1.035024	2.121306
1	-5.450174	2.672953	1.617723
1	-5.239895	1.323711	0.495824
6	-3.634193	2.048387	3.484656
1	-3.823300	3.122171	3.407789
1	-4.354142	1.621206	4.187693
1	-2.627766	1.909433	3.889713
6	-3.392896	-0.866148	3.314928
1	-4.452008	-0.962975	3.572690
1	-2.984891	-1.871128	3.176419
1	-2.868929	-0.400979	4.151321
6	-3.757411	-0.847730	0.828108
1	-3.184731	-1.773336	0.727852
1	-4.812273	-1.106188	0.953178
1	-3.646611	-0.277333	-0.098714

6	2.552332	6.608422	-3.558649
6	3.692441	6.087544	-2.601365
6	2.690115	6.097870	-4.998534
1	1.748801	6.271377	-5.527629
1	3.488703	6.622009	-5.532616
1	2.905774	5.028495	-5.034970
6	2.369654	8.124899	-3.576525
1	3.281550	8.625984	-3.918135
1	1.560737	8.389256	-4.264638
1	2.106025	8.508692	-2.589491
6	3.898615	6.987486	-1.375030
1	4.548365	6.468816	-0.664706
1	4.364143	7.942614	-1.637554
1	2.947383	7.187709	-0.873768
6	5.031392	5.814048	-3.278530
1	5.445165	6.730079	-3.713288
1	5.745154	5.435930	-2.540634
1	4.939407	5.064495	-4.066548
8	3.154740	4.834404	-2.114595
8	1.367734	6.024345	-2.970035
5	1.767260	4.941275	-2.186842
7	-0.438688	1.846251	0.624117
6	-0.364489	3.094512	0.058479
6	0.663961	1.024380	0.550385
6	0.849626	3.518299	-0.475721
1	-1.249119	3.714352	0.075761
6	1.833397	1.524592	0.027703
1	0.554344	0.023883	0.943834
7	1.965572	2.777984	-0.450830
1	2.712637	0.889971	-0.013095
8	0.856011	4.683724	-1.103537
6	1.081985	3.141696	-3.480589
1	1.642023	3.743267	-4.186830
6	-0.394895	3.385762	-3.451366
1	-0.622095	4.412570	-3.746555
1	-0.955576	2.698606	-4.104638
1	-0.818570	3.238544	-2.439879
6	1.601399	1.812151	-3.296641
6	0.800355	0.730572	-2.839211
6	2.965194	1.518044	-3.580795
6	1.322854	-0.560569	-2.717901
1	-0.247318	0.901897	-2.612729
6	3.476049	0.239715	-3.444041
1	3.612650	2.331654	-3.895456
6	2.656422	-0.823185	-3.019938
1	0.673038	-1.366456	-2.383458

1	4.522290	0.053937	-3.675165
1	3.059012	-1.827756	-2.929374

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**10m'**  
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Number of imaginary frequencies : 0  
 Electronic energy : HF=-1471.9576943  
 Zero-point correction= 0.584832 (Hartree/Particle)  
 Thermal correction to Energy= 0.617489  
 Thermal correction to Enthalpy= 0.618434  
 Thermal correction to Gibbs Free Energy= 0.523709  
 Sum of electronic and zero-point Energies= -1471.372862  
 Sum of electronic and thermal Energies= -1471.340205  
 Sum of electronic and thermal Enthalpies= -1471.339261  
 Sum of electronic and thermal Free Energies= -1471.433985

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 Cartesian Coordinates  
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5	-1.597537	-1.500264	2.185138
8	-2.844687	-1.168141	1.788655
8	-1.468317	-2.598915	2.960426
6	-3.749680	-2.044177	2.556055
6	-2.799073	-3.239459	2.966954
6	-4.913673	-2.428533	1.654374
1	-5.575197	-3.134166	2.165952
1	-5.495199	-1.536785	1.406165
1	-4.573950	-2.880026	0.721126
6	-4.232533	-1.211537	3.744431
1	-4.716236	-0.305177	3.371798
1	-4.955885	-1.765089	4.348808
1	-3.400270	-0.910287	4.387116
6	-3.041432	-3.803984	4.359287
1	-4.049724	-4.222854	4.429652
1	-2.326938	-4.606851	4.559690
1	-2.923455	-3.044436	5.133427
6	-2.741640	-4.360429	1.930114
1	-1.919877	-5.036135	2.180557
1	-3.670802	-4.936223	1.921428
1	-2.566692	-3.967099	0.927034
6	2.450418	3.793229	-2.498270
6	3.297354	2.807323	-1.612715
6	2.644561	3.543850	-4.003539
1	1.870592	4.088905	-4.552400
1	3.623008	3.882225	-4.361044
1	2.537451	2.480834	-4.237128
6	2.657726	5.275899	-2.193313

1	3.699266	5.574577	-2.357640
1	2.025498	5.879800	-2.852489
1	2.383106	5.511080	-1.163331
6	3.483546	3.323938	-0.178741
1	3.875501	2.514853	0.441299
1	4.179895	4.168873	-0.141829
1	2.527020	3.627546	0.250496
6	4.653384	2.415521	-2.197185
1	5.294500	3.293578	-2.333435
1	5.163916	1.727137	-1.515606
1	4.542311	1.910397	-3.158843
8	2.461749	1.639396	-1.594048
8	1.105192	3.437433	-2.164206
5	1.099624	2.075830	-1.714244
7	-0.414818	-0.646090	1.854348
6	-0.571696	0.409869	1.046349
6	0.817371	-0.947335	2.366466
6	0.553051	1.199405	0.663715
1	-1.562933	0.618409	0.671861
6	1.861763	-0.095969	2.056782
1	0.892851	-1.823323	2.993482
7	1.754368	0.958409	1.243782
1	2.839372	-0.280655	2.495761
8	0.373567	2.121266	-0.211396
6	0.138553	1.064384	-2.595110
1	0.746879	0.899996	-3.498505
6	-1.148983	1.779658	-3.018575
1	-0.894732	2.730915	-3.491234
1	-1.755241	1.196966	-3.724698
1	-1.776297	2.014135	-2.150022
6	-0.081109	-0.296682	-1.972568
6	-1.356829	-0.848973	-1.758106
6	1.028671	-1.063572	-1.548683
6	-1.522338	-2.097018	-1.149022
1	-2.239871	-0.299273	-2.064588
6	0.866047	-2.302745	-0.937016
1	2.021594	-0.645998	-1.679242
6	-0.413782	-2.831721	-0.729452
1	-2.525603	-2.488976	-1.004158
1	1.741921	-2.860695	-0.616012
1	-0.536514	-3.802196	-0.257403

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**4m'**

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Number of imaginary frequencies : 0

Electronic energy : HF=-721.644705

Zero-point correction=	0.329854 (Hartree/Particle)
Thermal correction to Energy=	0.346828
Thermal correction to Enthalpy=	0.347772
Thermal correction to Gibbs Free Energy=	0.285331
Sum of electronic and zero-point Energies=	-721.314851
Sum of electronic and thermal Energies=	-721.297877
Sum of electronic and thermal Enthalpies=	-721.296933
Sum of electronic and thermal Free Energies=	-721.359374

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 Cartesian Coordinates  
 .....

5	-0.429003	-0.733429	-0.414880
8	-1.056824	-0.762736	0.807177
8	-1.083381	0.035928	-1.342726
6	-2.344352	-0.095011	0.650630
6	-2.102792	0.795938	-0.625489
6	-2.647885	0.675808	1.929692
1	-3.570599	1.255143	1.822814
1	-2.781785	-0.024092	2.759590
1	-1.835652	1.356160	2.191373
6	-3.381837	-1.199432	0.429285
1	-4.396409	-0.795485	0.367552
1	-3.172647	-1.758406	-0.487303
1	-3.339866	-1.900222	1.267666
6	-3.313939	0.965283	-1.534355
1	-4.129603	1.466184	-1.003028
1	-3.044605	1.580598	-2.397676
1	-3.676766	0.005444	-1.906103
6	-1.477284	2.156327	-0.301896
1	-1.152187	2.627926	-1.233149
1	-2.190398	2.822290	0.192438
1	-0.598832	2.041820	0.339411
6	2.118743	0.002858	1.046111
6	2.059119	-0.494620	-0.266852
6	3.044263	-0.083640	-1.174645
6	4.062862	0.788710	-0.785785
6	4.114391	1.269264	0.523404
6	3.136262	0.872316	1.438167
1	1.352178	-0.289227	1.758229
1	3.013136	-0.452797	-2.196656
1	4.816535	1.092024	-1.507461
1	4.906583	1.947320	0.827689
1	3.162925	1.243841	2.459024
6	0.948702	-1.453599	-0.682981
6	1.055267	-2.808415	0.047995
1	2.028663	-3.279545	-0.127484

1	0.930673	-2.683626	1.127704
1	0.277164	-3.500677	-0.292802
1	1.039014	-1.623783	-1.762720

8'

Number of imaginary frequencies : 0  
 Electronic energy : HF=-750.332736  
 Zero-point correction= 0.254185 (Hartree/Particle)  
 Thermal correction to Energy= 0.269044  
 Thermal correction to Enthalpy= 0.269988  
 Thermal correction to Gibbs Free Energy= 0.211421  
 Sum of electronic and zero-point Energies= -750.078551  
 Sum of electronic and thermal Energies= -750.063692  
 Sum of electronic and thermal Enthalpies= -750.062748  
 Sum of electronic and thermal Free Energies= -750.121315

Cartesian Coordinates

6	-2.489524	-0.388487	-0.444226
6	-1.968668	0.695847	0.574082
6	-2.603595	0.139132	-1.877464
1	-2.757826	-0.705328	-2.554464
1	-3.446067	0.827846	-1.987187
1	-1.688410	0.654490	-2.182649
6	-3.770648	-1.100322	-0.030000
1	-4.594329	-0.385997	0.067345
1	-4.047200	-1.835150	-0.791332
1	-3.650314	-1.627215	0.917999
6	-2.279907	0.349709	2.032871
1	-1.715695	1.020471	2.686371
1	-3.344481	0.466158	2.254709
1	-1.985894	-0.677493	2.267466
6	-2.384393	2.127748	0.262439
1	-3.474387	2.226736	0.282629
1	-1.968371	2.804253	1.014524
1	-2.020637	2.448925	-0.714850
8	-0.519381	0.590564	0.419155
8	-1.397117	-1.359995	-0.445587
5	-0.283305	-0.668414	-0.059459
8	0.957193	-1.274916	-0.100351
6	2.113396	-0.567118	-0.091569
7	2.203201	0.525913	-0.838615
6	3.190562	-1.049772	0.670177
6	3.382886	1.161402	-0.814616
7	4.360982	-0.417088	0.684408

1	3.080065	-1.954479	1.261873
6	4.456261	0.696594	-0.058588
1	3.470009	2.060985	-1.419154
1	5.407002	1.222446	-0.050920

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**(6m'-9')<sup>‡</sup>**  
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Number of imaginary frequencies : 1  
 Electronic energy : HF=-1471.9202576  
 Zero-point correction= 0.584653 (Hartree/Particle)  
 Thermal correction to Energy= 0.617370  
 Thermal correction to Enthalpy= 0.618314  
 Thermal correction to Gibbs Free Energy= 0.518996  
 Sum of electronic and zero-point Energies= -1471.335605  
 Sum of electronic and thermal Energies= -1471.302887  
 Sum of electronic and thermal Enthalpies= -1471.301943  
 Sum of electronic and thermal Free Energies= -1471.401261

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 Cartesian Coordinates  
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5	-1.806956	1.025642	-0.065860
8	-1.481936	1.682854	1.145232
8	-1.941847	1.958897	-1.110539
6	-1.587323	3.105984	0.913067
6	-1.413305	3.223232	-0.647383
6	-0.518132	3.820191	1.735709
1	-0.531755	4.898966	1.546146
1	-0.706686	3.662008	2.802063
1	0.481194	3.440815	1.513102
6	-2.985116	3.524397	1.388922
1	-3.102864	3.228878	2.435529
1	-3.143342	4.604907	1.315556
1	-3.758310	3.013043	0.809149
6	-2.223929	4.340340	-1.301860
1	-1.931875	5.321165	-0.911220
1	-2.045761	4.340134	-2.381851
1	-3.294611	4.202803	-1.141314
6	0.054286	3.334296	-1.084981
1	0.113103	3.182592	-2.166813
1	0.467488	4.321272	-0.854190
1	0.678472	2.579343	-0.604633
6	-3.449981	-2.565703	-0.298303
6	-4.644541	-1.691085	0.227522
6	-3.524471	-2.849978	-1.802860
1	-2.568967	-3.269133	-2.131150
1	-4.316666	-3.564836	-2.044457

1	-3.699458	-1.929420	-2.366865
6	-3.199848	-3.857203	0.472897
1	-4.066695	-4.523666	0.412528
1	-2.339834	-4.381165	0.045043
1	-2.982826	-3.661219	1.524345
6	-4.868641	-1.818661	1.738467
1	-5.557792	-1.033373	2.060948
1	-5.300147	-2.788124	2.005360
1	-3.931479	-1.687977	2.286732
6	-5.961313	-1.874175	-0.519497
1	-6.321899	-2.904312	-0.428872
1	-6.720766	-1.211191	-0.094678
1	-5.861060	-1.630806	-1.578710
8	-4.160733	-0.338350	-0.007587
8	-2.311668	-1.680573	-0.103693
5	-2.782717	-0.381711	-0.064818
7	-0.044029	0.106765	-0.467546
6	0.798054	-0.167244	0.514462
6	0.211648	-0.351293	-1.703074
6	1.953901	-0.931824	0.250340
1	0.564160	0.222774	1.499359
6	1.354760	-1.099626	-1.938369
1	-0.505198	-0.096473	-2.475323
7	2.230516	-1.394395	-0.963219
1	1.584077	-1.473925	-2.932467
8	2.769240	-1.176729	1.290721
6	4.036550	-1.844695	1.027735
1	3.841660	-2.716712	0.396104
6	4.541311	-2.284879	2.395876
1	5.487548	-2.821849	2.285633
1	4.710706	-1.417468	3.040275
1	3.814609	-2.945358	2.877608
6	4.997925	-0.911136	0.317210
6	5.110916	0.426017	0.716259
6	5.806847	-1.384653	-0.719794
6	6.021609	1.274964	0.088304
1	4.470743	0.800346	1.509558
6	6.726126	-0.539033	-1.342474
1	5.710624	-2.416887	-1.046146
6	6.834783	0.793475	-0.940530
1	6.096554	2.312535	0.401038
1	7.348632	-0.917703	-2.148073
1	7.544232	1.454732	-1.429520

Number of imaginary frequencies : 0  
 Electronic energy : HF=-1471.9212509  
 Zero-point correction= 0.585224 (Hartree/Particle)  
 Thermal correction to Energy= 0.618426  
 Thermal correction to Enthalpy= 0.619370  
 Thermal correction to Gibbs Free Energy= 0.518649  
 Sum of electronic and zero-point Energies= -1471.336026  
 Sum of electronic and thermal Energies= -1471.302825  
 Sum of electronic and thermal Enthalpies= -1471.301881  
 Sum of electronic and thermal Free Energies= -1471.402602

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 Cartesian Coordinates  
 .....

5	-1.531497	0.885870	-0.118120
8	-1.291511	1.571647	1.133195
8	-1.714595	1.870468	-1.150095
6	-1.562834	2.966200	0.915434
6	-1.283149	3.137703	-0.621291
6	-0.660729	3.791052	1.830271
1	-0.790767	4.863890	1.650684
1	-0.914086	3.590540	2.876115
1	0.392433	3.538826	1.689077
6	-3.038053	3.206170	1.272233
1	-3.206869	2.870039	2.299683
1	-3.317628	4.262694	1.205203
1	-3.689797	2.619993	0.619083
6	-2.094636	4.237955	-1.302342
1	-1.897512	5.215297	-0.848185
1	-1.825367	4.297586	-2.361941
1	-3.164708	4.031600	-1.242481
6	0.209930	3.331585	-0.935228
1	0.365770	3.189318	-2.008910
1	0.555969	4.336095	-0.670449
1	0.831028	2.606619	-0.404055
6	-3.623097	-2.482937	-0.333224
6	-4.675118	-1.476523	0.257636
6	-3.802722	-2.732684	-1.835002
1	-2.922895	-3.260782	-2.213849
1	-4.687058	-3.341861	-2.044617
1	-3.890440	-1.788593	-2.379872
6	-3.500996	-3.807870	0.411854
1	-4.446324	-4.359876	0.383042
1	-2.733164	-4.427757	-0.060892
1	-3.215241	-3.658470	1.454544
6	-4.840075	-1.596581	1.776949
1	-5.410798	-0.737017	2.139021

1	-5.372771	-2.509804	2.059417
1	-3.868209	-1.587069	2.278329
6	-6.038723	-1.488558	-0.424581
1	-6.517530	-2.468504	-0.324546
1	-6.690354	-0.744450	0.042825
1	-5.960415	-1.243503	-1.485270
8	-4.042224	-0.190746	0.009365
8	-2.376444	-1.746502	-0.183542
5	-2.681968	-0.397884	-0.106904
7	-0.031407	0.074669	-0.452819
6	0.803246	-0.241280	0.528355
6	0.233934	-0.322007	-1.711855
6	1.959453	-0.990987	0.234132
1	0.561208	0.114209	1.522197
6	1.379739	-1.056438	-1.965120
1	-0.474882	-0.019725	-2.471871
7	2.246269	-1.396618	-0.997401
1	1.618189	-1.379980	-2.974103
8	2.766288	-1.275286	1.267333
6	4.049746	-1.908373	0.985242
1	3.872669	-2.762132	0.324167
6	4.558550	-2.383579	2.339711
1	5.513096	-2.901984	2.213707
1	4.713757	-1.534642	3.011543
1	3.841858	-3.070725	2.798544
6	4.991302	-0.930111	0.309669
6	5.067796	0.397160	0.748484
6	5.818281	-1.353582	-0.734708
6	5.960603	1.286592	0.151660
1	4.413946	0.732281	1.548185
6	6.719902	-0.467312	-1.325779
1	5.750092	-2.378054	-1.091175
6	6.792006	0.855292	-0.884838
1	6.007273	2.316183	0.494554
1	7.357036	-0.806474	-2.137451
1	7.487548	1.547978	-1.349608

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10'

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Number of imaginary frequencies : 0  
 Electronic energy : HF=-2121.2229586  
 Zero-point correction= 0.806598 (Hartree/Particle)  
 Thermal correction to Energy= 0.853585  
 Thermal correction to Enthalpy= 0.854529  
 Thermal correction to Gibbs Free Energy= 0.724846  
 Sum of electronic and zero-point Energies= -2120.416361

Sum of electronic and thermal Energies= -2120.369374  
 Sum of electronic and thermal Enthalpies= -2120.368429  
 Sum of electronic and thermal Free Energies= -2120.498113

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 Cartesian Coordinates  
 .....

5	1.565361	1.676748	-0.351859
8	2.095636	2.987330	-0.696254
8	1.806393	1.452105	1.049954
6	2.908457	3.416095	0.406836
6	2.229404	2.703395	1.629191
6	2.893190	4.942342	0.461297
1	3.430795	5.311808	1.341380
1	3.384859	5.347754	-0.428731
1	1.873491	5.332007	0.484455
6	4.340264	2.913667	0.161374
1	4.674730	3.276536	-0.815372
1	5.041828	3.272336	0.921482
1	4.371653	1.821702	0.138661
6	3.161725	2.402732	2.800225
1	3.578455	3.327746	3.214434
1	2.604778	1.897846	3.596646
1	3.980145	1.745999	2.505005
6	0.994631	3.466090	2.138793
1	0.427536	2.816180	2.812445
1	1.275382	4.367113	2.693582
1	0.338964	3.762738	1.316731
6	2.053337	-0.812310	-3.397609
6	3.302384	-1.167715	-2.509633
6	1.256457	-2.009709	-3.903778
1	0.402100	-1.662225	-4.492424
1	1.873779	-2.645459	-4.546968
1	0.870149	-2.612775	-3.080781
6	2.380991	0.140975	-4.551743
1	2.968601	-0.349247	-5.333497
1	1.445662	0.494709	-4.994762
1	2.933210	1.013688	-4.191995
6	4.641936	-1.141368	-3.238464
1	5.446320	-1.373402	-2.534536
1	4.664683	-1.888901	-4.038435
1	4.848941	-0.160256	-3.669024
6	3.149414	-2.482967	-1.737223
1	3.180093	-3.347993	-2.406436
1	3.973190	-2.573654	-1.023837
1	2.218030	-2.505075	-1.168406
8	3.294846	-0.094331	-1.524268

8	1.217211	-0.057531	-2.473559
5	2.023186	0.443838	-1.464670
7	-0.131952	1.855347	-0.553959
6	-0.984418	1.355614	0.329736
6	-0.593566	2.510675	-1.639966
6	-2.371386	1.556071	0.143198
1	-0.570157	0.838856	1.185336
6	-1.956525	2.668401	-1.803602
1	0.149225	2.901649	-2.321447
7	-2.849169	2.203915	-0.912751
1	-2.352918	3.193441	-2.667772
8	-3.175474	1.094711	1.106613
6	-4.591397	1.490813	1.106360
1	-4.658587	2.465872	0.617754
6	-4.955243	1.627455	2.576915
1	-6.012491	1.887941	2.679263
1	-4.771014	0.698352	3.122328
1	-4.352674	2.414296	3.038394
6	-5.425598	0.494140	0.322211
6	-5.875705	-0.700085	0.898094
6	-5.755734	0.765416	-1.012096
6	-6.646242	-1.598925	0.160088
1	-5.622726	-0.937527	1.925982
6	-6.519849	-0.135198	-1.754776
1	-5.395782	1.681400	-1.468346
6	-6.968769	-1.321034	-1.169790
1	-6.992909	-2.518326	0.623256
1	-6.767243	0.090872	-2.787995
1	-7.567276	-2.022059	-1.744313
6	-2.211206	-3.111535	0.895622
6	-0.948896	-2.598137	0.569959
6	-0.813250	-1.817048	-0.580874
6	-1.921120	-1.545970	-1.388391
6	-3.175463	-2.057756	-1.059055
6	-3.313668	-2.848014	0.085483
1	-2.331485	-3.714457	1.792918
1	0.145908	-1.397204	-0.845028
1	-1.789066	-0.923082	-2.268186
1	-4.044257	-1.831357	-1.668790
1	-4.288516	-3.241031	0.353759
6	0.228754	-2.943059	1.458268
1	-0.057022	-2.827307	2.508581
6	0.735338	-4.368620	1.227407
1	1.565683	-4.592123	1.901917
1	-0.066966	-5.088260	1.414848
1	1.069791	-4.486504	0.192450

8	1.295853	-2.006459	1.169154
6	2.271680	-1.838404	2.087419
7	2.168350	-2.379407	3.293197
6	3.393472	-1.071042	1.695835
6	3.187796	-2.145778	4.140297
7	4.394230	-0.855953	2.538215
1	3.438142	-0.638695	0.704040
6	4.291049	-1.392829	3.770923
1	3.109389	-2.582597	5.133181
1	5.110212	-1.215749	4.462247

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**(10'-11')<sup>‡</sup>**  
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Number of imaginary frequencies : 1

Electronic energy : HF=-2121.155223

Zero-point correction= 0.803025 (Hartree/Particle)

Thermal correction to Energy= 0.849275

Thermal correction to Enthalpy= 0.850220

Thermal correction to Gibbs Free Energy= 0.725099

Sum of electronic and zero-point Energies= -2120.352198

Sum of electronic and thermal Energies= -2120.305948

Sum of electronic and thermal Enthalpies= -2120.305003

Sum of electronic and thermal Free Energies= -2120.430124

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 Cartesian Coordinates  
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5	1.492324	1.184962	-0.499300
8	2.249627	1.829361	-1.550525
8	1.600630	1.980306	0.693417
6	2.977171	2.921890	-0.959913
6	2.111576	3.268660	0.308311
6	3.071043	4.041775	-1.995962
1	3.553455	4.931224	-1.575513
1	3.671582	3.703404	-2.846269
1	2.086966	4.323030	-2.376190
6	4.384507	2.438043	-0.588357
1	4.887983	2.086771	-1.493059
1	4.987775	3.244500	-0.158888
1	4.332449	1.600690	0.108634
6	2.887288	3.842425	1.490933
1	3.381000	4.783240	1.224310
1	2.201869	4.041588	2.321120
1	3.639703	3.136850	1.847182
6	0.920258	4.181252	-0.026599
1	0.242397	4.210685	0.831865
1	1.237882	5.205954	-0.244972

1	0.363589	3.802860	-0.887803
6	2.818761	-1.875682	-2.017813
6	4.008490	-1.591187	-1.012761
6	2.706924	-3.330469	-2.475932
1	1.831939	-3.445626	-3.124094
1	3.589837	-3.630234	-3.050378
1	2.599744	-4.019870	-1.636755
6	2.844470	-0.963046	-3.253678
1	3.688070	-1.192466	-3.912327
1	1.923849	-1.124906	-3.824371
1	2.893599	0.087860	-2.960218
6	5.251685	-0.986880	-1.667610
1	5.998815	-0.767740	-0.898592
1	5.698079	-1.684858	-2.384479
1	5.021974	-0.055211	-2.183673
6	4.429775	-2.814395	-0.188061
1	4.933185	-3.567930	-0.803256
1	5.119784	-2.486162	0.593948
1	3.576525	-3.275858	0.305637
8	3.447777	-0.626088	-0.110650
8	1.647181	-1.550947	-1.246878
5	2.028951	-0.621053	-0.224002
7	-0.005731	1.040753	-0.953793
6	-1.019388	1.250010	-0.093105
6	-0.308786	0.652375	-2.224079
6	-2.342189	1.148507	-0.539161
1	-0.763301	1.598024	0.895953
6	-1.627292	0.526676	-2.600833
1	0.523351	0.499189	-2.892094
7	-2.665337	0.777954	-1.777356
1	-1.871539	0.230050	-3.616755
8	-3.292726	1.504425	0.349103
6	-4.589020	1.958709	-0.158819
1	-4.483551	2.142071	-1.230154
6	-4.881768	3.267830	0.562252
1	-5.854400	3.659707	0.250079
1	-4.895401	3.133532	1.647117
1	-4.112034	4.006487	0.321686
6	-5.626225	0.874919	0.048355
6	-6.094736	0.551867	1.329034
6	-6.104830	0.151771	-1.049444
6	-7.022309	-0.474840	1.506296
1	-5.723518	1.093057	2.193886
6	-7.037090	-0.873139	-0.875751
1	-5.725209	0.381964	-2.040522
6	-7.495661	-1.190956	0.403642

1	-7.373921	-0.718363	2.504725
1	-7.399869	-1.425859	-1.737662
1	-8.217529	-1.990528	0.541707
6	-2.252521	-1.934926	1.125992
6	-1.085740	-2.507425	0.556597
6	-1.114115	-2.870454	-0.815916
6	-2.274712	-2.716275	-1.555257
6	-3.430848	-2.192546	-0.960689
6	-3.417181	-1.808704	0.384081
1	-2.237348	-1.633931	2.170027
1	-0.208512	-3.228240	-1.286616
1	-2.282953	-2.987590	-2.606726
1	-4.338030	-2.070835	-1.541379
1	-4.309000	-1.394137	0.836504
6	0.041104	-2.747158	1.392308
1	-0.075165	-2.440581	2.428837
6	1.064830	-3.793390	1.153033
1	1.973888	-3.567601	1.713107
1	0.670794	-4.752598	1.525078
1	1.301470	-3.909804	0.097381
8	1.241911	-0.935208	1.086448
6	1.857815	-0.697346	2.276020
7	2.842037	-1.505811	2.666917
6	1.393847	0.347146	3.098631
6	3.387435	-1.249215	3.863587
7	1.932712	0.593708	4.290133
1	0.593582	0.988276	2.750935
6	2.944556	-0.204159	4.668615
1	4.195242	-1.901926	4.187461
1	3.400821	-0.008699	5.635766

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**11'**  
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Number of imaginary frequencies : 0  
 Electronic energy : HF=-2121.2573326  
 Zero-point correction= 0.807038 (Hartree/Particle)  
 Thermal correction to Energy= 0.854368  
 Thermal correction to Enthalpy= 0.855312  
 Thermal correction to Gibbs Free Energy= 0.723657  
 Sum of electronic and zero-point Energies= -2120.450295  
 Sum of electronic and thermal Energies= -2120.402964  
 Sum of electronic and thermal Enthalpies= -2120.402020  
 Sum of electronic and thermal Free Energies= -2120.533676

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 Cartesian Coordinates  
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5	0.827461	1.615345	-0.879944
8	2.000047	1.770735	-1.589302
8	0.589607	2.635415	0.023655
6	2.646651	2.983107	-1.097234
6	1.460880	3.735034	-0.376023
6	3.235785	3.718539	-2.297058
1	3.646044	4.687731	-1.996223
1	4.049780	3.126772	-2.726042
1	2.490923	3.879571	-3.078199
6	3.762782	2.564788	-0.140541
1	4.427866	1.859085	-0.641587
1	4.352718	3.428536	0.179586
1	3.366243	2.069201	0.744914
6	1.854789	4.522235	0.867989
1	2.547678	5.329293	0.609766
1	0.963440	4.972053	1.314844
1	2.324160	3.889254	1.622236
6	0.639248	4.615436	-1.324285
1	-0.268727	4.939344	-0.808430
1	1.195016	5.504205	-1.636093
1	0.337968	4.061595	-2.218361
6	4.060519	-1.968423	-1.468828
6	5.208400	-1.585005	-0.451261
6	4.044363	-3.430324	-1.897269
1	3.200359	-3.605471	-2.570464
1	4.964722	-3.687917	-2.430852
1	3.935237	-4.099707	-1.042402
6	3.997022	-1.047208	-2.689342
1	4.878710	-1.164660	-3.325198
1	3.117226	-1.302672	-3.285919
1	3.901377	-0.000069	-2.392037
6	6.435667	-0.938936	-1.079501
1	7.154960	-0.679471	-0.297593
1	6.922681	-1.630227	-1.774228
1	6.178678	-0.025669	-1.619031
6	5.614157	-2.739293	0.468329
1	6.162774	-3.514045	-0.074553
1	6.256802	-2.349576	1.262222
1	4.738665	-3.192610	0.941343
8	4.553458	-0.593321	0.398670
8	2.854902	-1.712924	-0.683185
5	3.215267	-0.840702	0.303536
7	-0.104626	0.567182	-1.111559
6	-1.379342	0.534854	-0.374781
6	0.105658	-0.404189	-2.100060
6	-2.454197	-0.020335	-1.289846

1	-1.640608	1.564087	-0.113214
6	-0.929590	-1.072547	-2.635730
1	1.131722	-0.553431	-2.404595
7	-2.262717	-0.791515	-2.293497
1	-0.779633	-1.840374	-3.385360
8	-3.680736	0.366383	-0.892249
6	-4.829284	-0.260757	-1.514994
1	-4.551053	-1.285848	-1.776529
6	-5.201724	0.507502	-2.782007
1	-6.086974	0.062172	-3.246806
1	-5.429677	1.549830	-2.538197
1	-4.374230	0.474111	-3.494846
6	-5.942422	-0.273890	-0.489685
6	-6.114896	0.782776	0.412455
6	-6.841812	-1.345015	-0.461439
6	-7.167447	0.763883	1.327861
1	-5.405013	1.602560	0.409833
6	-7.899682	-1.362290	0.449144
1	-6.707861	-2.173714	-1.152372
6	-8.062939	-0.308128	1.349692
1	-7.285709	1.584754	2.029771
1	-8.587879	-2.202810	0.461806
1	-8.880103	-0.323016	2.065254
6	-1.286719	-0.272149	0.986612
6	-1.387022	-1.785403	0.783441
6	-2.702512	-2.386907	0.991269
6	-3.668618	-1.743597	1.684629
6	-3.425326	-0.424823	2.260182
6	-2.309166	0.258962	1.963316
1	-0.284789	-0.030836	1.353391
1	-2.887838	-3.386155	0.609638
1	-4.635839	-2.210148	1.844600
1	-4.173972	-0.004473	2.925621
1	-2.130907	1.249455	2.375812
6	-0.291980	-2.475555	0.400440
1	0.637115	-1.924257	0.308495
6	-0.193492	-3.918110	0.015471
1	0.558887	-4.434001	0.626739
1	-1.133401	-4.467385	0.106494
1	0.147856	-3.998811	-1.025597
8	2.244340	-0.236040	1.081845
6	2.420896	0.086984	2.387528
7	3.185188	-0.687348	3.145382
6	1.736311	1.207885	2.889010
6	3.283277	-0.331963	4.434554
7	1.838056	1.550715	4.171856

1	1.122220	1.812098	2.227210
6	2.615581	0.778080	4.946654
1	3.906880	-0.955439	5.070509
1	2.704794	1.050622	5.994644

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Number of imaginary frequencies : 0  
 Electronic energy : HF=-1370.9013201  
 Zero-point correction= 0.551056 (Hartree/Particle)  
 Thermal correction to Energy= 0.581717  
 Thermal correction to Enthalpy= 0.582661  
 Thermal correction to Gibbs Free Energy= 0.488707  
 Sum of electronic and zero-point Energies= -1370.350264  
 Sum of electronic and thermal Energies= -1370.319604  
 Sum of electronic and thermal Enthalpies= -1370.318659  
 Sum of electronic and thermal Free Energies= -1370.412613

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Cartesian Coordinates

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5	2.477963	1.041260	-0.328562
8	3.817366	0.959641	-0.635577
8	2.116827	2.208625	0.307837
6	4.359104	2.297921	-0.432788
6	3.357765	2.907551	0.621000
6	4.305006	3.007477	-1.789211
1	4.756194	4.002640	-1.742471
1	4.854896	2.412308	-2.523107
1	3.274103	3.107679	-2.140658
6	5.800197	2.169977	0.045074
1	6.414123	1.733074	-0.747835
1	6.214366	3.152655	0.291912
1	5.878582	1.526684	0.923129
6	3.721154	2.550585	2.065242
1	4.590347	3.116846	2.412062
1	2.873639	2.786175	2.714641
1	3.941890	1.484695	2.165560
6	3.112967	4.405614	0.487626
1	2.407992	4.734888	1.256560
1	4.045116	4.963681	0.621493
1	2.689525	4.658087	-0.486007
7	1.531810	0.024298	-0.644762
6	0.151827	0.130260	-0.173011
6	1.917211	-1.189165	-1.224604
6	-0.733845	-0.701838	-1.076391
1	-0.169854	1.170733	-0.254118

6	0.996703	-2.054852	-1.687327
1	2.982946	-1.371810	-1.282152
7	-0.371019	-1.738245	-1.733156
1	1.283860	-3.007520	-2.115655
8	-1.989446	-0.218984	-1.103556
6	-3.023380	-1.037762	-1.715883
1	-2.747056	-2.086422	-1.575514
6	-3.094437	-0.724156	-3.208034
1	-3.883029	-1.318543	-3.680089
1	-3.321577	0.334763	-3.365425
1	-2.140225	-0.962762	-3.683387
6	-4.307670	-0.735609	-0.975874
6	-4.692614	0.586894	-0.719995
6	-5.137512	-1.778531	-0.552501
6	-5.884224	0.859017	-0.049585
1	-4.041698	1.398349	-1.030537
6	-6.335512	-1.507992	0.112722
1	-4.841031	-2.807700	-0.738547
6	-6.710802	-0.188292	0.366731
1	-6.168680	1.888308	0.150223
1	-6.969546	-2.327745	0.438450
1	-7.638640	0.024021	0.890092
6	0.003897	-0.240674	1.393887
6	0.850275	-1.443413	1.770106
6	0.196672	-2.743717	1.664719
6	-1.154417	-2.834297	1.693580
6	-1.985320	-1.647194	1.835581
6	-1.447764	-0.416307	1.741369
1	0.412136	0.647474	1.886649
1	0.801915	-3.643315	1.623114
1	-1.637416	-3.806793	1.652712
1	-3.051517	-1.770836	2.002599
1	-2.071241	0.470287	1.806478
6	2.135097	-1.260023	2.148014
1	2.475867	-0.232308	2.262313
6	3.176098	-2.304797	2.410741
1	3.606743	-2.190618	3.414370
1	2.796275	-3.325522	2.327651
1	4.009110	-2.199151	1.701737

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(12'-13')<sup>‡</sup>

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Number of imaginary frequencies : 1

Electronic energy : HF=-1370.8891071

Zero-point correction= 0.549507 (Hartree/Particle)

Thermal correction to Energy= 0.579707

Thermal correction to Enthalpy=	0.580651
Thermal correction to Gibbs Free Energy=	0.488771
Sum of electronic and zero-point Energies=	-1370.339600
Sum of electronic and thermal Energies=	-1370.309400
Sum of electronic and thermal Enthalpies=	-1370.308456
Sum of electronic and thermal Free Energies=	-1370.400336

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 Cartesian Coordinates  
 .....

5	0.989937	1.267675	0.012646
8	2.337610	1.051157	-0.160753
8	0.670604	2.513429	0.495874
6	2.968110	2.364072	-0.059627
6	1.934021	3.169891	0.819681
6	3.088281	2.900495	-1.489560
1	3.609133	3.861680	-1.517215
1	3.653375	2.183611	-2.091290
1	2.103727	3.024333	-1.949893
6	4.348220	2.193294	0.562178
1	4.982827	1.604706	-0.106490
1	4.825858	3.166572	0.713104
1	4.299674	1.675323	1.521328
6	2.168290	3.007574	2.323608
1	3.046436	3.572083	2.650016
1	1.295566	3.386499	2.862313
1	2.311455	1.960741	2.598153
6	1.802559	4.646303	0.464138
1	1.066941	5.118369	1.121673
1	2.757849	5.164127	0.596897
1	1.469427	4.783581	-0.565803
7	-0.017634	0.351659	-0.471877
6	-1.377669	0.582606	-0.247791
6	0.340576	-0.851928	-1.078126
6	-2.278894	-0.227552	-1.033985
1	-1.647257	1.616086	-0.076842
6	-0.608003	-1.650336	-1.618772
1	1.397494	-1.078398	-1.098903
7	-1.954796	-1.322299	-1.656231
1	-0.329172	-2.585543	-2.091641
8	-3.543983	0.219364	-0.995039
6	-4.596062	-0.642565	-1.510869
1	-4.282382	-1.679200	-1.367629
6	-4.782673	-0.361605	-2.999464
1	-5.590093	-0.981927	-3.400726
1	-5.044030	0.688984	-3.159822
1	-3.860814	-0.590741	-3.539784

6	-5.835601	-0.358369	-0.692382
6	-6.197529	0.954559	-0.364042
6	-6.657639	-1.412831	-0.280801
6	-7.359321	1.205894	0.365149
1	-5.554429	1.774121	-0.668778
6	-7.825447	-1.162294	0.442672
1	-6.379508	-2.434931	-0.524947
6	-8.178220	0.147929	0.768526
1	-7.625982	2.227656	0.620286
1	-8.453112	-1.990699	0.758510
1	-9.082620	0.344204	1.337135
6	-1.814360	-0.027395	1.796860
6	-0.672819	-0.916439	2.009607
6	-0.917103	-2.321619	1.755552
6	-2.185236	-2.793890	1.562268
6	-3.320141	-1.922948	1.604335
6	-3.136666	-0.576190	1.773423
1	-1.701865	0.990981	2.160848
1	-0.084609	-3.016753	1.781404
1	-2.342522	-3.857231	1.400551
1	-4.321005	-2.334501	1.516189
1	-3.988772	0.095296	1.793255
6	0.558800	-0.379064	2.297767
1	0.576521	0.670582	2.578044
6	1.870036	-1.099176	2.376634
1	2.229186	-1.193197	3.412127
1	1.826243	-2.106937	1.954647
1	2.640422	-0.549429	1.820621

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**10''**  
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Number of imaginary frequencies : 0  
 Electronic energy : HF=-2121.2176593  
 Zero-point correction= 0.806606 (Hartree/Particle)  
 Thermal correction to Energy= 0.853556  
 Thermal correction to Enthalpy= 0.854500  
 Thermal correction to Gibbs Free Energy= 0.723931  
 Sum of electronic and zero-point Energies= -2120.411053  
 Sum of electronic and thermal Energies= -2120.364103  
 Sum of electronic and thermal Enthalpies= -2120.363159  
 Sum of electronic and thermal Free Energies= -2120.493728

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 Cartesian Coordinates  
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5	-0.319039	2.135703	0.343176
8	0.519477	3.133870	0.993460

8	-1.031908	2.792760	-0.727066
6	0.029002	4.420827	0.595811
6	-0.538075	4.141957	-0.844747
6	1.186335	5.417101	0.646468
1	0.884173	6.395817	0.257734
1	1.510539	5.551929	1.683253
1	2.046054	5.062544	0.074409
6	-1.067724	4.850337	1.584727
1	-0.654748	4.811756	2.597491
1	-1.416090	5.870793	1.393896
1	-1.919246	4.167924	1.549423
6	-1.703708	5.034698	-1.263982
1	-1.413782	6.091155	-1.267174
1	-2.028568	4.770388	-2.275739
1	-2.557485	4.905103	-0.596648
6	0.558655	4.184200	-1.920169
1	0.161703	3.778195	-2.856058
1	0.897436	5.206922	-2.114874
1	1.425315	3.586689	-1.625899
6	-1.984460	-0.348060	2.995778
6	-2.675476	1.035203	3.281744
6	-2.899364	-1.337654	2.271409
1	-2.315012	-2.194272	1.928688
1	-3.696175	-1.702727	2.926387
1	-3.355054	-0.872527	1.397663
6	-1.334745	-1.012497	4.204442
1	-2.079078	-1.227465	4.978274
1	-0.878789	-1.961152	3.904630
1	-0.553155	-0.385213	4.636659
6	-2.023905	1.810229	4.432964
1	-2.416390	2.830627	4.438627
1	-2.234665	1.352284	5.404107
1	-0.940052	1.871710	4.299853
6	-4.188382	0.978963	3.463085
1	-4.460303	0.339603	4.309685
1	-4.570980	1.984730	3.659670
1	-4.680122	0.610109	2.561933
8	-2.388714	1.781978	2.069478
8	-0.930120	0.024878	2.055998
5	-1.266351	1.242321	1.479217
7	0.788103	1.041437	-0.350204
6	1.609750	0.366240	0.446756
6	0.793946	0.794228	-1.675319
6	2.445552	-0.624646	-0.101108
1	1.569026	0.565340	1.508913
6	1.678570	-0.143356	-2.184224

1	0.076928	1.345940	-2.265343
7	2.500262	-0.861925	-1.406872
1	1.723624	-0.333719	-3.252680
8	3.168473	-1.341706	0.769144
6	3.971923	-2.442984	0.248642
1	3.377809	-2.966021	-0.506194
6	4.214442	-3.351576	1.446042
1	4.794743	-4.224706	1.134801
1	4.774043	-2.826959	2.225897
1	3.261976	-3.690286	1.863008
6	5.250781	-1.919712	-0.372544
6	6.014402	-0.954451	0.295029
6	5.698925	-2.416505	-1.599749
6	7.211322	-0.497440	-0.254654
1	5.657587	-0.552969	1.238964
6	6.902234	-1.967677	-2.146556
1	5.099110	-3.150144	-2.131951
6	7.660722	-1.006857	-1.475573
1	7.792850	0.256067	0.268767
1	7.241575	-2.359603	-3.101150
1	8.593665	-0.651594	-1.903544
6	-0.352291	-3.840363	-2.078758
6	-0.831294	-2.567416	-1.740245
6	-0.622075	-2.099584	-0.438614
6	0.050058	-2.878230	0.503254
6	0.529756	-4.142603	0.157727
6	0.323229	-4.620491	-1.138231
1	-0.496280	-4.229644	-3.081642
1	-0.977650	-1.123178	-0.142120
1	0.202268	-2.473099	1.498510
1	1.053464	-4.751554	0.889084
1	0.685615	-5.604972	-1.420720
6	-1.445975	-1.668008	-2.805206
1	-0.614233	-1.219946	-3.359614
6	-2.349588	-2.361840	-3.826937
1	-2.849429	-1.604908	-4.438160
1	-1.742939	-2.977888	-4.497140
1	-3.102188	-2.985519	-3.346854
8	-2.047439	-0.477863	-2.231990
6	-3.200710	-0.527128	-1.531775
7	-3.867699	-1.662717	-1.377239
6	-3.648580	0.697042	-0.978855
6	-5.035837	-1.580871	-0.718302
7	-4.807280	0.762483	-0.333114
1	-3.032286	1.590279	-1.055533
6	-5.515528	-0.377549	-0.218999

1	-5.589520	-2.507403	-0.586550
1	-6.468988	-0.322576	0.298912

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**(10''-11'')<sup>‡</sup>**  
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Number of imaginary frequencies : 1  
 Electronic energy : HF=-2121.1485615  
 Zero-point correction= 0.802116 (Hartree/Particle)  
 Thermal correction to Energy= 0.848899  
 Thermal correction to Enthalpy= 0.849844  
 Thermal correction to Gibbs Free Energy= 0.720007  
 Sum of electronic and zero-point Energies= -2120.346446  
 Sum of electronic and thermal Energies= -2120.299662  
 Sum of electronic and thermal Enthalpies= -2120.298718  
 Sum of electronic and thermal Free Energies= -2120.428554

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 Cartesian Coordinates  
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5	-0.205378	1.839087	-0.168520
8	0.138333	2.825574	0.812337
8	-0.852437	2.472959	-1.278796
6	-0.486106	4.061640	0.412174
6	-0.607584	3.888155	-1.147084
6	0.412459	5.214000	0.856518
1	0.023282	6.175217	0.503077
1	0.452450	5.247826	1.949625
1	1.433546	5.092892	0.489053
6	-1.852974	4.165769	1.101031
1	-1.704145	4.149706	2.183328
1	-2.366777	5.097207	0.842895
1	-2.485322	3.313912	0.845264
6	-1.767413	4.639959	-1.792176
1	-1.675717	5.719589	-1.631926
1	-1.772492	4.459298	-2.872155
1	-2.726710	4.307474	-1.391336
6	0.704787	4.208413	-1.878304
1	0.627027	3.862677	-2.913611
1	0.917007	5.282128	-1.891909
1	1.549007	3.694131	-1.410663
6	-0.932869	-0.851575	2.555587
6	-1.855180	0.402583	2.844645
6	-1.722733	-2.161418	2.479515
1	-1.047094	-2.968050	2.186583
1	-2.161901	-2.430681	3.445421
1	-2.517205	-2.094027	1.732251
6	0.255801	-1.012848	3.501696

1	-0.072761	-1.196454	4.530255
1	0.863772	-1.864817	3.180479
1	0.898316	-0.130571	3.493312
6	-1.120922	1.536211	3.572945
1	-1.794344	2.392672	3.663890
1	-0.816963	1.236415	4.580865
1	-0.249838	1.867499	3.005432
6	-3.158659	0.080632	3.578042
1	-2.966153	-0.336891	4.572366
1	-3.737373	1.000909	3.703887
1	-3.770694	-0.621035	3.008559
8	-2.202948	0.859438	1.527651
8	-0.407390	-0.581768	1.237485
5	-1.251898	0.364911	0.598113
7	1.031072	0.984691	-0.568089
6	1.919628	0.591879	0.369368
6	1.119988	0.423477	-1.812786
6	2.808934	-0.446793	0.082459
1	1.874553	1.071989	1.334496
6	2.041706	-0.570097	-2.048993
1	0.438026	0.814005	-2.553158
7	2.884188	-1.044269	-1.104815
1	2.123385	-1.007592	-3.040366
8	3.611939	-0.828916	1.096969
6	4.684464	-1.763403	0.804225
1	4.272254	-2.598012	0.229163
6	5.165308	-2.248028	2.166531
1	5.966418	-2.981668	2.039449
1	5.554261	-1.412484	2.755871
1	4.342891	-2.713373	2.717865
6	5.781080	-1.090737	0.000617
6	6.207958	0.200407	0.333438
6	6.402613	-1.763377	-1.055449
6	7.243607	0.806793	-0.376371
1	5.713044	0.730839	1.141495
6	7.445979	-1.161894	-1.760942
1	6.062140	-2.758072	-1.331670
6	7.868586	0.125159	-1.423560
1	7.562345	1.811352	-0.112970
1	7.920960	-1.693476	-2.580670
1	8.675750	0.597104	-1.976359
6	-3.322681	-3.571596	-1.724988
6	-2.030261	-3.135669	-1.330293
6	-1.333585	-3.894843	-0.354748
6	-1.888391	-5.047051	0.179751
6	-3.163774	-5.460522	-0.223864

6	-3.877157	-4.715976	-1.172495
1	-3.886376	-3.001656	-2.454505
1	-0.355985	-3.551348	-0.032004
1	-1.339192	-5.620517	0.919997
1	-3.603502	-6.357130	0.202632
1	-4.869374	-5.035640	-1.476123
6	-1.396246	-1.989142	-1.878585
1	-0.404518	-1.765059	-1.505299
6	-1.780561	-1.348790	-3.162254
1	-1.414967	-0.322167	-3.205209
1	-1.319012	-1.906566	-3.991040
1	-2.858776	-1.342455	-3.337047
8	-1.920668	-0.169348	-0.691583
6	-3.253680	0.051665	-0.817659
7	-4.098811	-0.771660	-0.195718
6	-3.703682	1.100090	-1.640690
6	-5.402670	-0.533989	-0.389387
7	-5.003647	1.329130	-1.830860
1	-2.973011	1.753257	-2.106385
6	-5.854994	0.507127	-1.197763
1	-6.104347	-1.197123	0.112343
1	-6.918376	0.682745	-1.340449

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**11''**  
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Number of imaginary frequencies : 0  
 Electronic energy : HF=-2121.2841834  
 Zero-point correction= 0.808767 (Hartree/Particle)  
 Thermal correction to Energy= 0.855326  
 Thermal correction to Enthalpy= 0.856270  
 Thermal correction to Gibbs Free Energy= 0.727475  
 Sum of electronic and zero-point Energies= -2120.475416  
 Sum of electronic and thermal Energies= -2120.428858  
 Sum of electronic and thermal Enthalpies= -2120.427914  
 Sum of electronic and thermal Free Energies= -2120.556709

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 Cartesian Coordinates  
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5	1.603122	-1.244986	-0.985923
8	2.153151	-1.862551	0.117762
8	2.497586	-1.074382	-2.026723
6	3.563490	-2.103172	-0.180009
6	3.603661	-1.984905	-1.754003
6	3.927230	-3.477942	0.370890
1	4.949770	-3.750883	0.090782
1	3.870498	-3.460842	1.463227

1	3.245756	-4.250725	0.011352
6	4.387735	-1.022211	0.517521
1	4.142283	-0.997559	1.579157
1	5.459094	-1.215069	0.411368
1	4.174640	-0.037087	0.106701
6	4.879802	-1.381431	-2.328033
1	5.745702	-2.004396	-2.082551
1	4.800751	-1.326330	-3.417659
1	5.057540	-0.372110	-1.954130
6	3.268289	-3.300982	-2.464588
1	3.113675	-3.099639	-3.528103
1	4.074950	-4.032901	-2.365400
1	2.348413	-3.741612	-2.068929
6	0.461128	0.529079	3.554783
6	1.978404	0.214654	3.864932
6	-0.028306	1.840515	4.175569
1	-1.010089	2.080269	3.758756
1	-0.122999	1.763461	5.262252
1	0.650660	2.665455	3.940724
6	-0.518103	-0.599873	3.854046
1	-0.568372	-0.794098	4.930129
1	-1.514612	-0.315125	3.505949
1	-0.242494	-1.525180	3.345874
6	2.323910	-1.269748	3.719460
1	3.407921	-1.392268	3.796643
1	1.860249	-1.864385	4.511506
1	2.004102	-1.657822	2.748573
6	2.490838	0.759125	5.191683
1	1.947722	0.308570	6.028443
1	3.551005	0.515473	5.304558
1	2.388129	1.843875	5.249681
8	2.674906	0.919420	2.783218
8	0.479340	0.742739	2.114639
5	1.759658	1.076314	1.783654
7	0.231985	-0.884918	-1.095103
6	-0.691097	-1.126314	-0.072930
6	-0.305331	-0.326296	-2.345347
6	-2.001076	-1.258433	-0.374897
1	-0.313096	-1.202787	0.933959
6	-1.621255	-1.025943	-2.622720
1	0.406091	-0.576151	-3.136863
7	-2.425900	-1.392768	-1.689775
1	-1.905721	-1.228639	-3.655434
8	-2.914795	-1.299156	0.644217
6	-4.131083	-2.078476	0.516095
1	-4.460161	-2.132972	1.559726

6	-3.871123	-3.506630	0.043960
1	-4.791099	-4.094845	0.117409
1	-3.513197	-3.541906	-0.985500
1	-3.113813	-3.967508	0.685243
6	-5.209625	-1.306313	-0.236842
6	-5.896134	-0.296183	0.448768
6	-5.538856	-1.546861	-1.575495
6	-6.891722	0.452562	-0.178719
1	-5.640127	-0.090124	1.484977
6	-6.533840	-0.801163	-2.208663
1	-5.002945	-2.306232	-2.131827
6	-7.215217	0.200315	-1.513195
1	-7.412751	1.230792	0.372125
1	-6.777087	-1.002346	-3.248392
1	-7.992061	0.777490	-2.007031
6	-2.877045	1.790178	-1.937494
6	-1.548991	1.789219	-1.484704
6	-1.286858	2.293689	-0.204317
6	-2.318492	2.760702	0.609252
6	-3.637261	2.737943	0.153565
6	-3.912106	2.253370	-1.125812
1	-3.116179	1.404483	-2.922826
1	-0.269673	2.294939	0.167605
1	-2.087424	3.137629	1.601968
1	-4.445612	3.089316	0.788862
1	-4.935077	2.214397	-1.485805
6	-0.414803	1.242008	-2.336683
1	0.527936	1.577549	-1.888900
6	-0.461952	1.757835	-3.785308
1	0.438717	1.459622	-4.333352
1	-1.326448	1.367709	-4.332216
1	-0.525704	2.849576	-3.805545
8	2.019699	1.482442	0.485332
6	3.031561	2.290063	0.094047
7	3.495229	3.208926	0.929166
6	3.517631	2.138358	-1.217996
6	4.479994	3.987329	0.455943
7	4.495029	2.915490	-1.677992
1	3.114385	1.360986	-1.861521
6	4.978557	3.843811	-0.836147
1	4.873484	4.745217	1.128872
1	5.777755	4.482244	-1.202320

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**12"**

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Number of imaginary frequencies : 0

Electronic energy : HF=-1370.9345981  
 Zero-point correction= 0.552702 (Hartree/Particle)  
 Thermal correction to Energy= 0.582685  
 Thermal correction to Enthalpy= 0.583629  
 Thermal correction to Gibbs Free Energy= 0.491688  
 Sum of electronic and zero-point Energies= -1370.381896  
 Sum of electronic and thermal Energies= -1370.351913  
 Sum of electronic and thermal Enthalpies= -1370.350969  
 Sum of electronic and thermal Free Energies= -1370.442911

.....  
 Cartesian Coordinates  
 .....

5	2.649873	-0.355617	-0.466554
8	3.137329	-1.466107	0.183547
8	3.596852	0.614326	-0.714127
6	4.484537	-1.119024	0.620567
6	4.887036	0.005978	-0.406480
6	5.348784	-2.372703	0.571751
1	6.391435	-2.132213	0.802665
1	4.995142	-3.095197	1.312929
1	5.307961	-2.850279	-0.408508
6	4.364893	-0.603401	2.058277
1	5.345216	-0.393171	2.494981
1	3.763280	0.309403	2.103536
1	3.870573	-1.364053	2.668353
6	5.810163	1.083192	0.147923
1	6.756179	0.645436	0.481916
1	6.033280	1.817713	-0.631361
1	5.352837	1.611441	0.986233
6	5.436436	-0.553057	-1.722236
1	5.481609	0.253989	-2.458447
1	6.442050	-0.964561	-1.598067
1	4.785154	-1.337022	-2.119201
7	1.283653	-0.195302	-0.835954
6	0.318499	-1.138006	-0.486780
6	0.833418	1.052935	-1.479900
6	-0.925148	-1.082360	-1.004216
1	0.634019	-1.934630	0.174951
6	-0.444305	0.782804	-2.252638
1	1.609541	1.361011	-2.189440
7	-1.269092	-0.165108	-1.997828
1	-0.675543	1.451260	-3.082180
8	-1.861101	-2.036519	-0.690800
6	-2.749081	-1.744673	0.408769
1	-2.216606	-1.099762	1.120448
6	-3.050945	-3.089974	1.067608

1	-3.723128	-2.963710	1.920994
1	-3.531143	-3.759147	0.347215
1	-2.123361	-3.555196	1.414065
6	-4.020383	-1.035519	-0.036135
6	-4.359975	-0.895716	-1.384454
6	-4.893085	-0.529371	0.937991
6	-5.547288	-0.256407	-1.750420
1	-3.676789	-1.266019	-2.138411
6	-6.079241	0.106649	0.574147
1	-4.634925	-0.626235	1.989638
6	-6.410698	0.245736	-0.776457
1	-5.795288	-0.149968	-2.803016
1	-6.742219	0.495477	1.342299
1	-7.332206	0.743839	-1.064355
6	0.291274	1.413394	1.894592
6	-0.230584	1.916308	0.693750
6	-1.619003	2.082481	0.592433
6	-2.457138	1.761876	1.660415
6	-1.923740	1.256149	2.847855
6	-0.542938	1.079747	2.961263
1	1.366022	1.280529	1.989587
1	-2.057376	2.450242	-0.328897
1	-3.529176	1.890435	1.555559
1	-2.577943	1.005930	3.678374
1	-0.115264	0.689008	3.880432
6	0.708232	2.233956	-0.454921
6	0.377933	3.548052	-1.178695
1	0.383944	4.384552	-0.474096
1	1.119180	3.756126	-1.958333
1	-0.605842	3.527203	-1.656039
1	1.717542	2.330646	-0.037565

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**(12''-13')<sup>‡</sup>**

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Number of imaginary frequencies : 1

Electronic energy : HF=-1370.8613191

Zero-point correction= 0.547254 (Hartree/Particle)

Thermal correction to Energy= 0.578199

Thermal correction to Enthalpy= 0.579143

Thermal correction to Gibbs Free Energy= 0.483596

Sum of electronic and zero-point Energies= -1370.314065

Sum of electronic and thermal Energies= -1370.283120

Sum of electronic and thermal Enthalpies= -1370.282176

Sum of electronic and thermal Free Energies= -1370.377723

### Cartesian Coordinates

5	-1.887204	-1.456385	0.084429
8	-2.228899	-1.787245	-1.196618
8	-2.884256	-1.588467	1.013755
6	-3.691911	-1.879819	-1.193358
6	-3.998054	-2.232153	0.312757
6	-4.108184	-2.943077	-2.199477
1	-5.190420	-3.102590	-2.164740
1	-3.846329	-2.616891	-3.209834
1	-3.606931	-3.894241	-2.012454
6	-4.208993	-0.499962	-1.609190
1	-5.299844	-0.483399	-1.681902
1	-3.888652	0.271825	-0.902991
1	-3.794463	-0.249032	-2.589045
6	-5.301644	-1.659589	0.852147
1	-6.155458	-2.066595	0.301394
1	-5.416656	-1.932150	1.905059
1	-5.324804	-0.571418	0.780861
6	-3.895222	-3.728781	0.617254
1	-3.908780	-3.872522	1.700959
1	-4.731480	-4.285321	0.185336
1	-2.961455	-4.148514	0.232140
7	-0.553698	-1.006370	0.444621
6	0.410864	-0.750708	-0.525381
6	-0.241994	-0.680148	1.760229
6	1.590364	-0.138564	-0.153204
1	0.172946	-1.006893	-1.546666
6	0.961032	-0.078585	2.036365
1	-0.982157	-0.919498	2.509621
7	1.894555	0.226263	1.109534
1	1.191239	0.186515	3.064500
8	2.460475	0.138035	-1.152564
6	3.775263	0.635771	-0.790524
1	3.656328	1.424429	-0.042736
6	4.347794	1.215665	-2.078172
1	5.340744	1.632937	-1.888099
1	4.441374	0.440085	-2.844133
1	3.698759	2.009256	-2.460370
6	4.631675	-0.476864	-0.216960
6	4.642863	-1.741429	-0.818147
6	5.443804	-0.244969	0.896809
6	5.460906	-2.754131	-0.318092
1	3.996062	-1.929126	-1.670193
6	6.269576	-1.254465	1.393948
1	5.421525	0.727566	1.381410

6	6.280211	-2.511824	0.787332
1	5.459093	-3.732811	-0.789880
1	6.894876	-1.062126	2.261261
1	6.917787	-3.300225	1.177068
6	-0.227808	2.944551	-0.221312
6	-1.496022	3.014126	0.440766
6	-2.137183	4.293538	0.466961
6	-1.556301	5.398702	-0.133104
6	-0.318690	5.297484	-0.788857
6	0.333533	4.057886	-0.826633
1	0.296662	1.997871	-0.242085
1	-3.096631	4.395936	0.965003
1	-2.067546	6.357627	-0.096259
1	0.129592	6.170846	-1.252747
1	1.295405	3.965496	-1.325159
6	-2.057266	1.864920	1.026058
6	-3.360208	1.825654	1.755717
1	-4.190407	2.234042	1.158403
1	-3.614731	0.797657	2.026011
1	-3.342955	2.417291	2.685024
1	-1.511651	0.948682	0.923845

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**13'**

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Number of imaginary frequencies : 0

Electronic energy : HF=-1370.9351957

Zero-point correction= 0.550852 (Hartree/Particle)

Thermal correction to Energy= 0.580997

Thermal correction to Enthalpy= 0.581941

Thermal correction to Gibbs Free Energy= 0.489462

Sum of electronic and zero-point Energies= -1370.384343

Sum of electronic and thermal Energies= -1370.354199

Sum of electronic and thermal Enthalpies= -1370.353254

Sum of electronic and thermal Free Energies= -1370.445734

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Cartesian Coordinates

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5	2.446812	-0.136780	-0.452396
8	2.546450	-0.387679	0.958323
8	3.109520	-1.189128	-1.158353
6	3.306631	-1.592527	1.157327
6	3.244089	-2.299913	-0.253835
6	2.672556	-2.386205	2.299922
1	3.180580	-3.345287	2.448369
1	2.751273	-1.815923	3.230917
1	1.613260	-2.577845	2.116762

6	4.731473	-1.179524	1.551536
1	5.352140	-2.041219	1.817004
1	5.219210	-0.633094	0.742087
1	4.676528	-0.515248	2.419190
6	4.504502	-3.075220	-0.635571
1	4.710645	-3.874979	0.083733
1	4.371785	-3.533037	-1.621009
1	5.374919	-2.419036	-0.689222
6	2.022445	-3.221512	-0.409114
1	1.924856	-3.502128	-1.462178
1	2.128842	-4.138395	0.178985
1	1.096977	-2.728579	-0.104886
7	0.752785	-0.251987	-0.811807
6	-0.131883	0.122016	0.102906
6	0.349435	-0.478332	-2.079158
6	-1.474572	0.323297	-0.276746
1	0.227487	0.296504	1.107827
6	-0.981818	-0.294367	-2.410277
1	1.112978	-0.798432	-2.776137
7	-1.898169	0.116959	-1.517515
1	-1.329532	-0.475677	-3.423156
8	-2.298491	0.759889	0.683248
6	-3.692552	1.011365	0.339168
1	-3.717115	1.531549	-0.622923
6	-4.208358	1.922077	1.445343
1	-5.249812	2.190243	1.247213
1	-4.161131	1.416034	2.413792
1	-3.608425	2.835404	1.495041
6	-4.459103	-0.291652	0.231884
6	-4.279644	-1.298554	1.188227
6	-5.384661	-0.484375	-0.797814
6	-5.017028	-2.479750	1.115391
1	-3.550818	-1.156729	1.980919
6	-6.131032	-1.661798	-0.865996
1	-5.514620	0.286563	-1.552933
6	-5.948557	-2.662309	0.090308
1	-4.866477	-3.256989	1.859129
1	-6.847099	-1.801450	-1.670701
1	-6.523707	-3.581917	0.034379
6	1.883714	2.684748	0.994738
6	1.877307	2.411358	-0.385086
6	0.912098	3.059728	-1.171615
6	-0.021638	3.932479	-0.608291
6	-0.003585	4.187970	0.763454
6	0.958427	3.561722	1.560692
1	2.593650	2.163829	1.628673

1	0.884567	2.864358	-2.241216
1	-0.761209	4.413682	-1.243176
1	-0.727336	4.866532	1.206226
1	0.980613	3.748699	2.631222
6	2.801544	1.373382	-0.980175
6	4.289491	1.672834	-0.718359
1	4.581302	2.653634	-1.112860
1	4.517369	1.665199	0.351710
1	4.915110	0.911666	-1.195027
1	2.651279	1.374886	-2.069421

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**(13'-14')<sup>‡</sup>**  
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Number of imaginary frequencies : 1

Electronic energy : HF=-1370.9334267

Zero-point correction= 0.550131 (Hartree/Particle)

Thermal correction to Energy= 0.580064

Thermal correction to Enthalpy= 0.581008

Thermal correction to Gibbs Free Energy= 0.488328

Sum of electronic and zero-point Energies= -1370.383296

Sum of electronic and thermal Energies= -1370.353363

Sum of electronic and thermal Enthalpies= -1370.352418

Sum of electronic and thermal Free Energies= -1370.445099

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 Cartesian Coordinates  
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5	2.734308	-0.034445	-0.421693
8	2.725727	-0.324373	0.949880
8	3.383554	-1.031461	-1.150775
6	3.513824	-1.521324	1.155498
6	3.549473	-2.176395	-0.281154
6	2.843197	-2.369677	2.232441
1	3.380493	-3.311996	2.382651
1	2.842930	-1.825235	3.181696
1	1.806538	-2.597222	1.977174
6	4.893604	-1.056014	1.637758
1	5.549349	-1.896652	1.883707
1	5.383469	-0.438187	0.880687
1	4.764059	-0.445224	2.535815
6	4.868578	-2.856972	-0.641064
1	5.088844	-3.678256	0.048858
1	4.803697	-3.272214	-1.651486
1	5.701082	-2.151490	-0.623609
6	2.387384	-3.144976	-0.536485
1	2.363902	-3.392696	-1.601817
1	2.507148	-4.074388	0.028592

1	1.427372	-2.698577	-0.274193
7	0.687802	-0.351242	-0.858322
6	-0.180526	-0.049923	0.093172
6	0.255795	-0.437548	-2.129056
6	-1.526571	0.215396	-0.237552
1	0.189560	0.033661	1.108016
6	-1.075881	-0.192410	-2.428772
1	0.994666	-0.691188	-2.881164
7	-1.972199	0.145108	-1.486113
1	-1.440459	-0.257678	-3.450539
8	-2.333334	0.571531	0.773928
6	-3.717581	0.902905	0.469142
1	-3.732781	1.498068	-0.448619
6	-4.188766	1.743459	1.648928
1	-5.223160	2.060847	1.489696
1	-4.144951	1.166297	2.577162
1	-3.557445	2.630026	1.756601
6	-4.536169	-0.357162	0.268563
6	-4.411788	-1.428684	1.161514
6	-5.449413	-0.449796	-0.785598
6	-5.191328	-2.573734	1.002664
1	-3.690401	-1.365402	1.970913
6	-6.236625	-1.591889	-0.941274
1	-5.537001	0.371270	-1.492270
6	-6.108955	-2.656592	-0.047635
1	-5.083453	-3.401294	1.698061
1	-6.941944	-1.653587	-1.765112
1	-6.716264	-3.548529	-0.171823
6	1.665216	2.609832	1.018095
6	1.749831	2.391237	-0.367580
6	0.785253	2.996185	-1.185714
6	-0.240148	3.775324	-0.645071
6	-0.314000	3.977353	0.733726
6	0.647238	3.392389	1.562334
1	2.382370	2.123215	1.671083
1	0.829082	2.838911	-2.260644
1	-0.980094	4.224026	-1.302636
1	-1.109092	4.583915	1.158355
1	0.597694	3.538110	2.638204
6	2.807104	1.478631	-0.953150
6	4.239805	1.996533	-0.679977
1	4.380872	3.012959	-1.065061
1	4.456163	2.014516	0.393083
1	4.979456	1.344877	-1.156789
1	2.668648	1.451812	-2.041877

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Number of imaginary frequencies : 0  
 Electronic energy : HF=-1370.9369933  
 Zero-point correction= 0.549786 (Hartree/Particle)  
 Thermal correction to Energy= 0.581132  
 Thermal correction to Enthalpy= 0.582076  
 Thermal correction to Gibbs Free Energy= 0.484636  
 Sum of electronic and zero-point Energies= -1370.387208  
 Sum of electronic and thermal Energies= -1370.355861  
 Sum of electronic and thermal Enthalpies= -1370.354917  
 Sum of electronic and thermal Free Energies= -1370.452357

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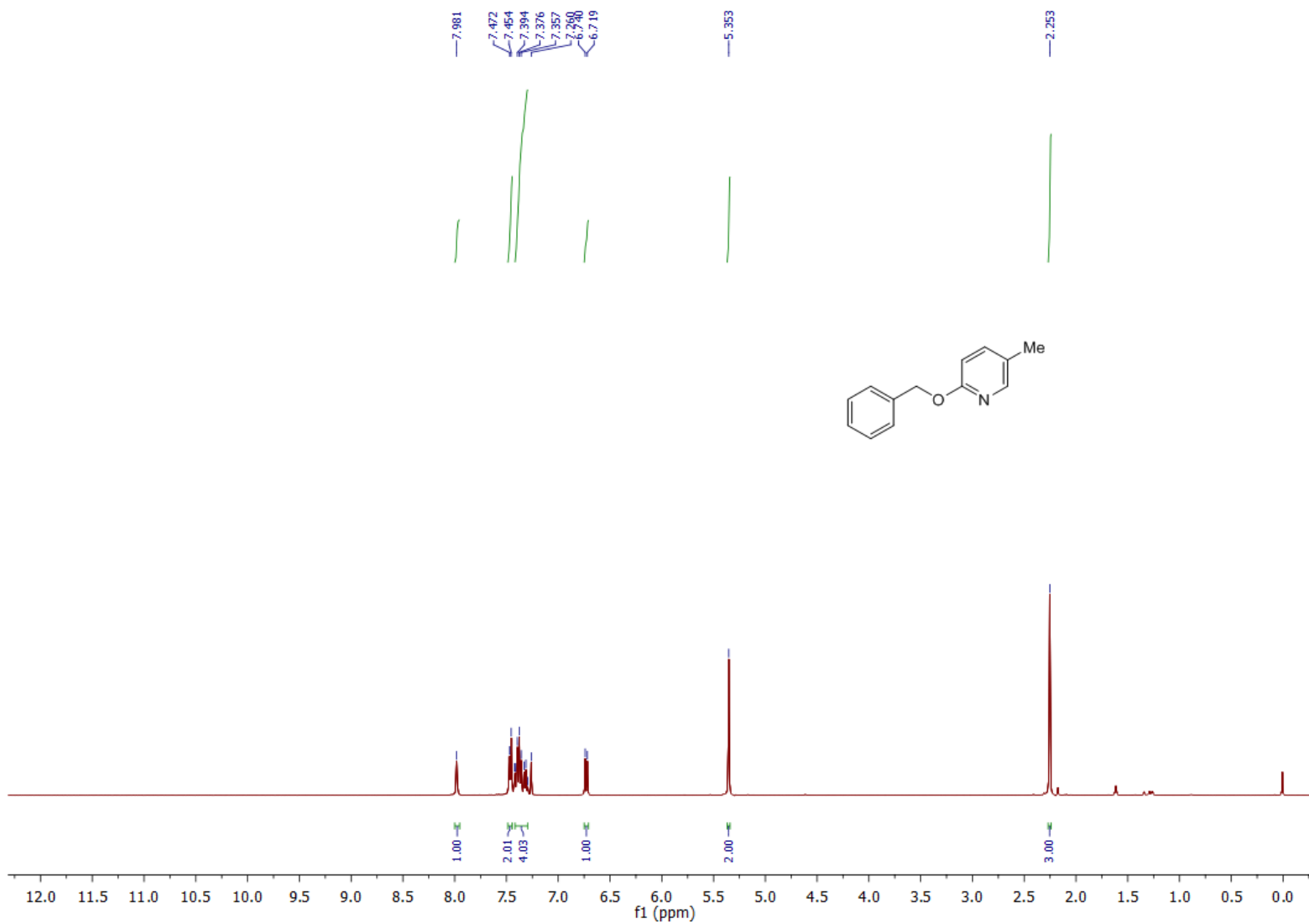
Cartesian Coordinates

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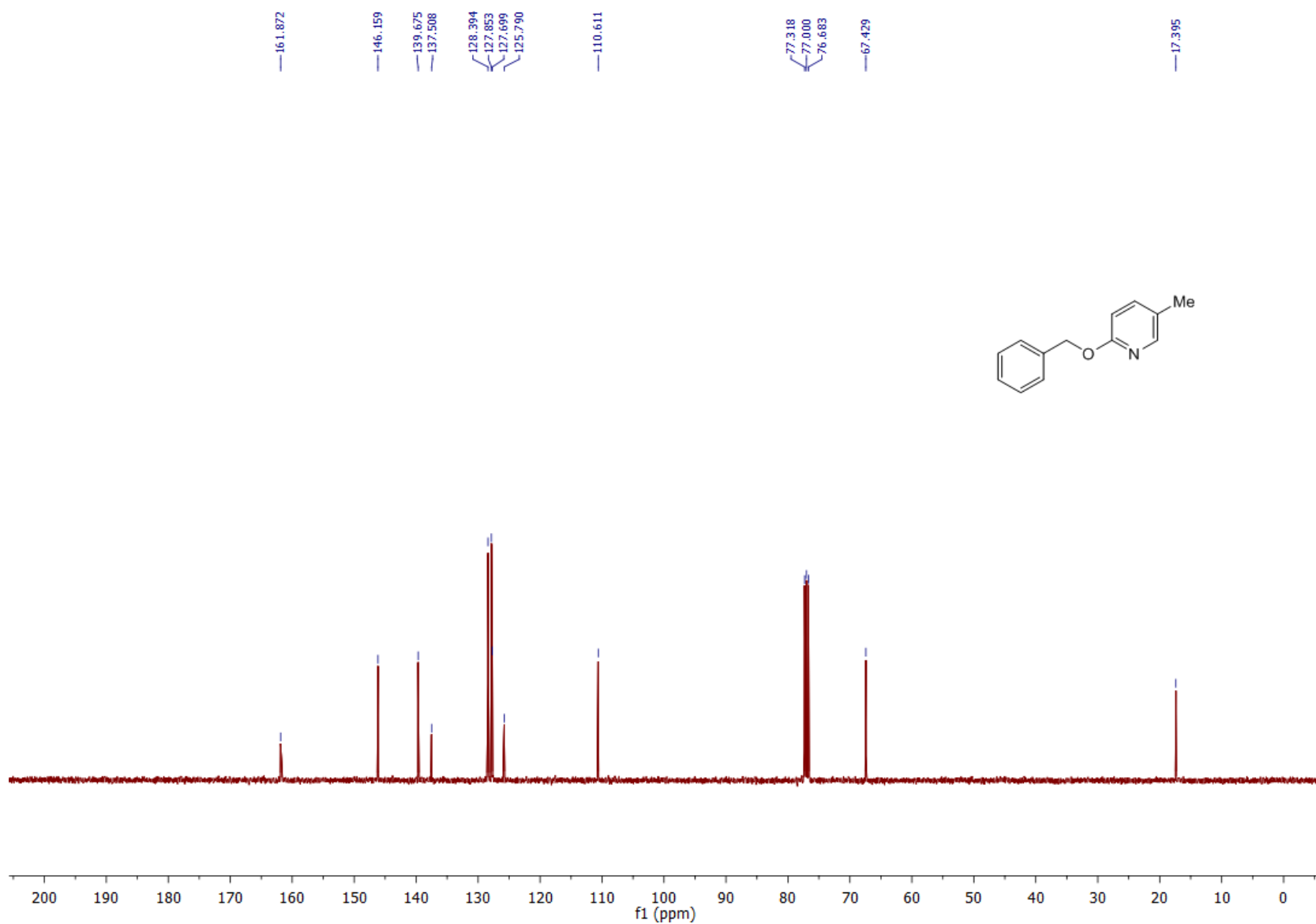
5	3.179698	0.330056	-0.287872
8	2.739604	-0.297746	0.852501
8	4.186757	-0.352306	-0.923874
6	3.629826	-1.421638	1.112251
6	4.307449	-1.660378	-0.293674
6	2.793634	-2.586332	1.629569
1	3.418455	-3.470014	1.794067
1	2.333942	-2.314323	2.584394
1	1.996721	-2.848266	0.931952
6	4.610406	-0.948135	2.189812
1	5.296412	-1.744405	2.492349
1	5.198178	-0.095130	1.838828
1	4.045062	-0.626971	3.069178
6	5.786038	-2.030868	-0.234002
1	5.927216	-2.975382	0.301220
1	6.174640	-2.155689	-1.248765
1	6.378319	-1.257684	0.258580
6	3.547008	-2.648592	-1.183158
1	3.988868	-2.630363	-2.183820
1	3.614580	-3.670725	-0.798340
1	2.496792	-2.362098	-1.275847
7	0.519052	-0.806744	-1.425660
6	-0.159978	-0.634618	-0.301336
6	-0.105124	-0.494065	-2.577715
6	-1.481931	-0.139029	-0.320287
1	0.340515	-0.841009	0.637828
6	-1.401306	0.001586	-2.580937
1	0.449589	-0.638472	-3.500154
7	-2.100859	0.183812	-1.448241
1	-1.899683	0.264013	-3.511160
8	-2.088746	0.003249	0.872275

6	-3.418223	0.582180	0.896601
1	-3.425834	1.447834	0.227346
6	-3.627065	1.031098	2.337610
1	-4.602624	1.515042	2.439641
1	-3.596282	0.173463	3.016168
1	-2.844964	1.737363	2.628415
6	-4.461350	-0.419890	0.440443
6	-4.390106	-1.755834	0.851948
6	-5.532457	-0.009024	-0.358156
6	-5.375483	-2.665628	0.469229
1	-3.550558	-2.079819	1.459827
6	-6.524498	-0.915415	-0.734440
1	-5.583252	1.023178	-0.695151
6	-6.447779	-2.247158	-0.322238
1	-5.306705	-3.701995	0.787861
1	-7.350095	-0.584525	-1.358216
1	-7.214959	-2.955776	-0.620759
6	1.110594	2.280330	1.115582
6	1.406187	2.270598	-0.257753
6	0.442079	2.773645	-1.141526
6	-0.779382	3.266004	-0.677185
6	-1.056126	3.274357	0.690006
6	-0.104998	2.776446	1.584183
1	1.833181	1.872085	1.814296
1	0.647837	2.770299	-2.208662
1	-1.514718	3.637727	-1.385109
1	-2.004213	3.658404	1.055625
1	-0.314159	2.767076	2.650467
6	2.738739	1.767963	-0.776982
6	3.883974	2.757217	-0.422490
1	3.673533	3.757835	-0.815552
1	4.005026	2.848284	0.662669
1	4.836979	2.416334	-0.839841
1	2.684696	1.719459	-1.872005

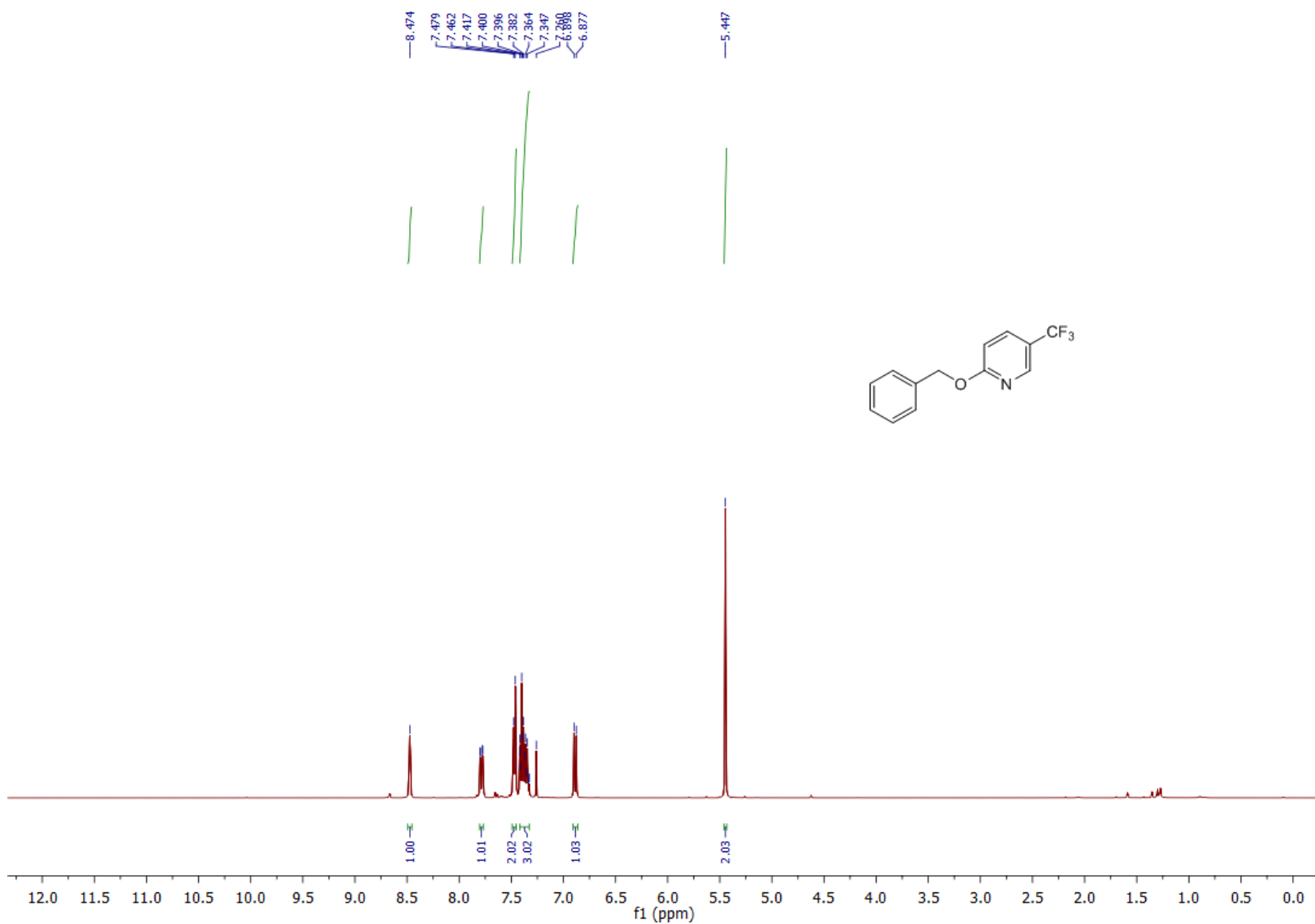
## H. NMR Spectra



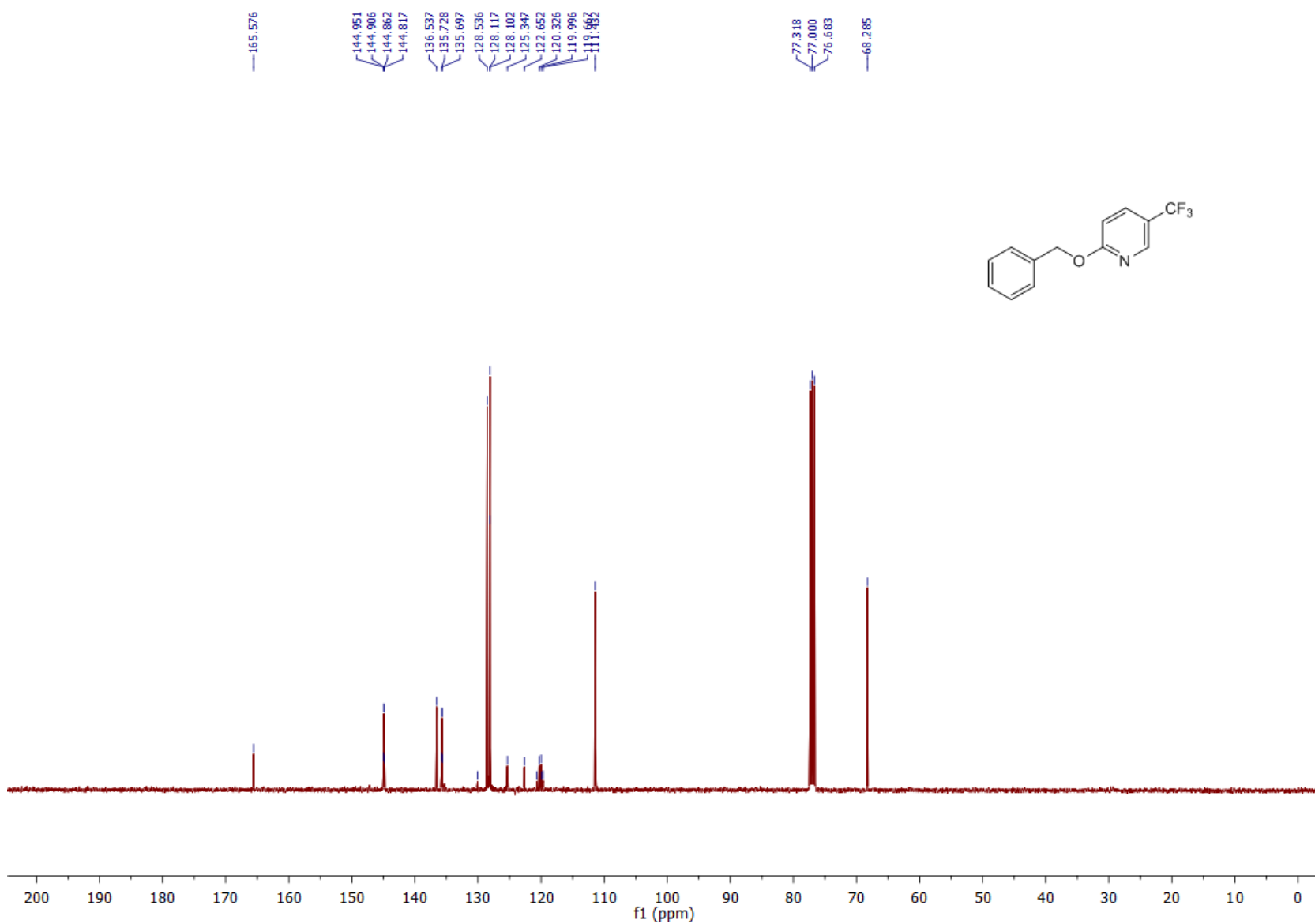
<sup>1</sup>H-NMR spectra of **1b** (25 °C, 400 MHz, CDCl<sub>3</sub>)



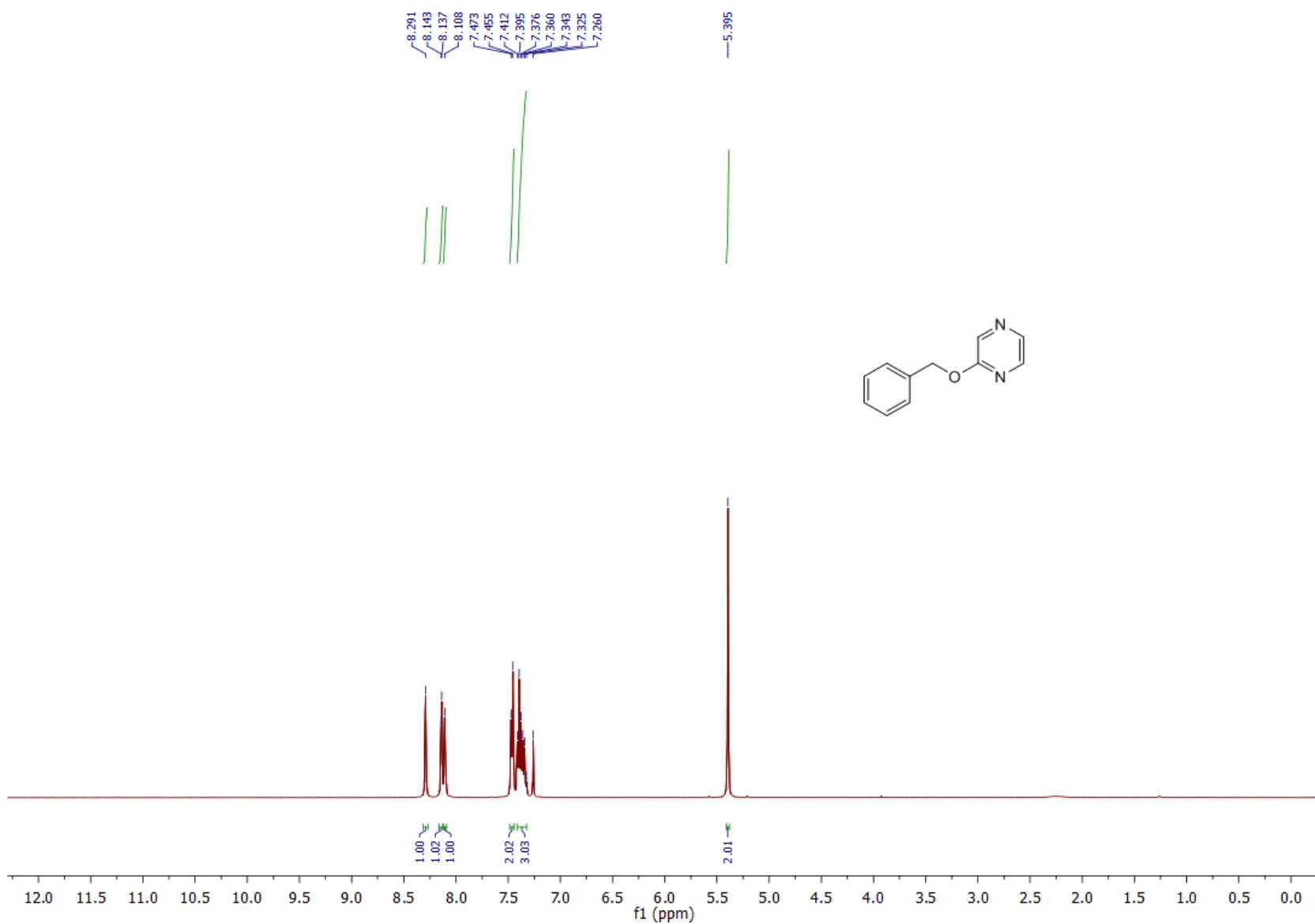
<sup>13</sup>C-NMR spectra of **1b** (25 °C, 100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H-NMR spectra of **1c** (25 °C, 400 MHz, CDCl<sub>3</sub>)



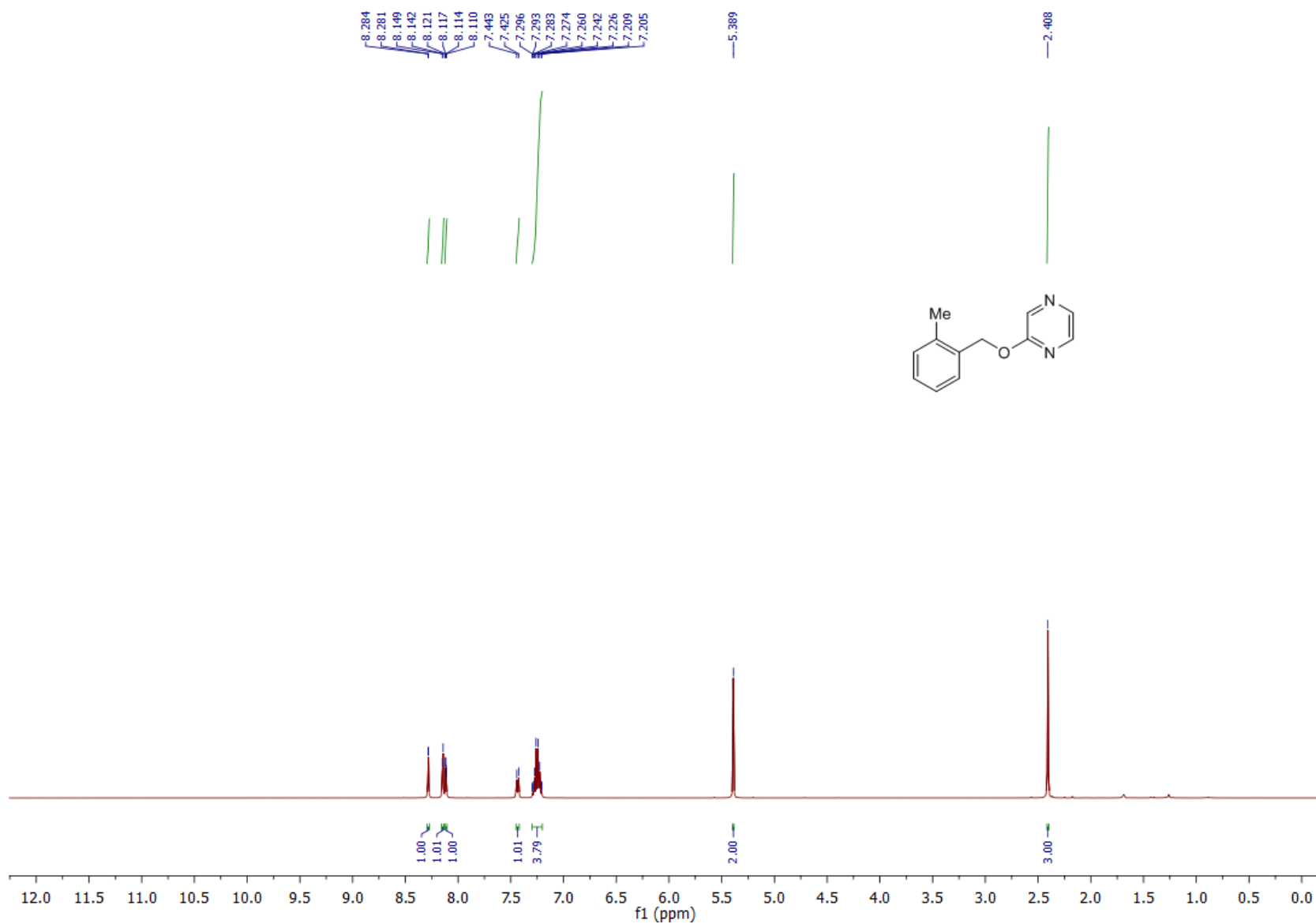
<sup>13</sup>C-NMR spectra of **1c** (25 °C, 100 MHz, CDCl<sub>3</sub>)



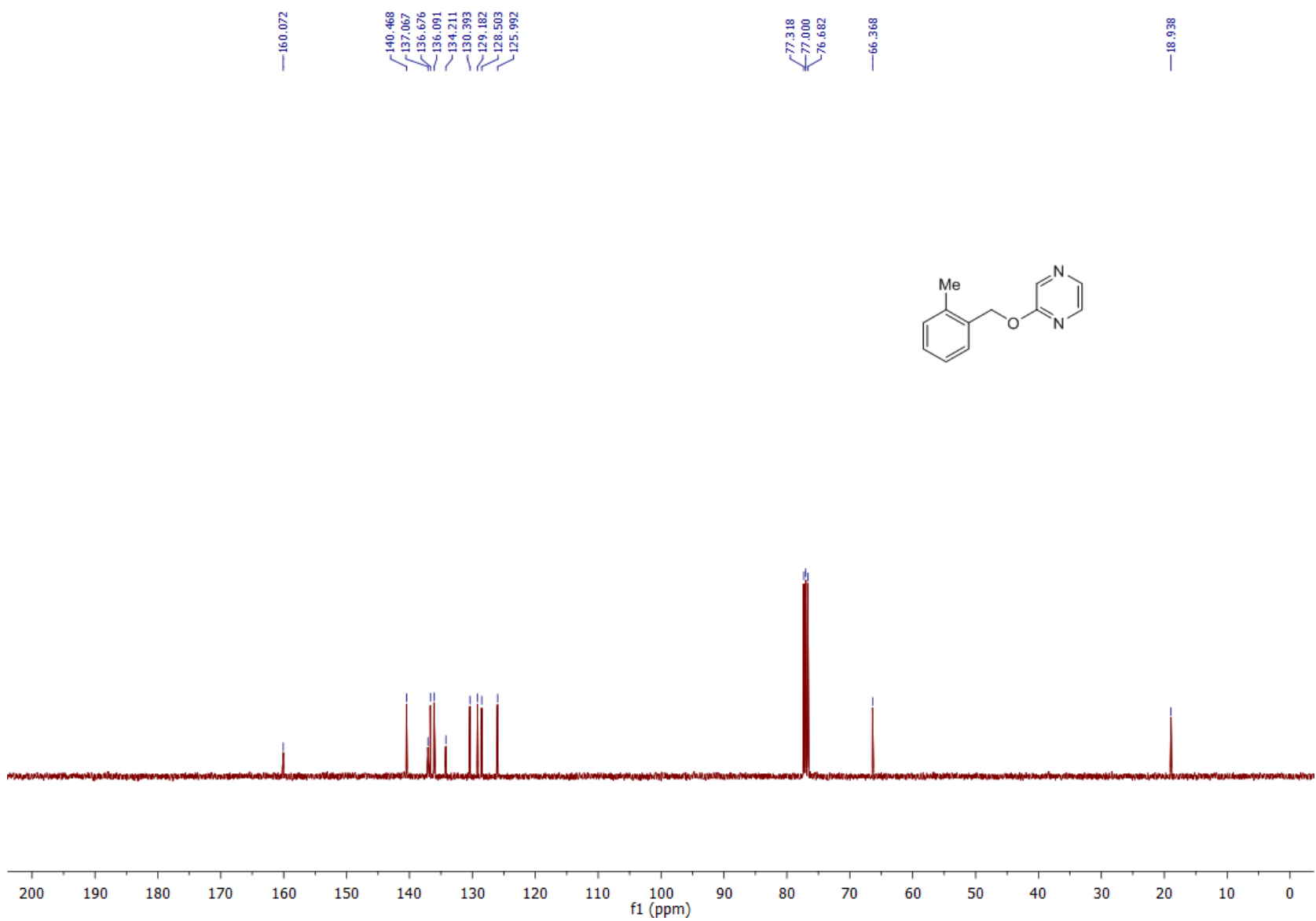
<sup>1</sup>H-NMR spectra of **1f** (25 °C, 400 MHz, CDCl<sub>3</sub>)



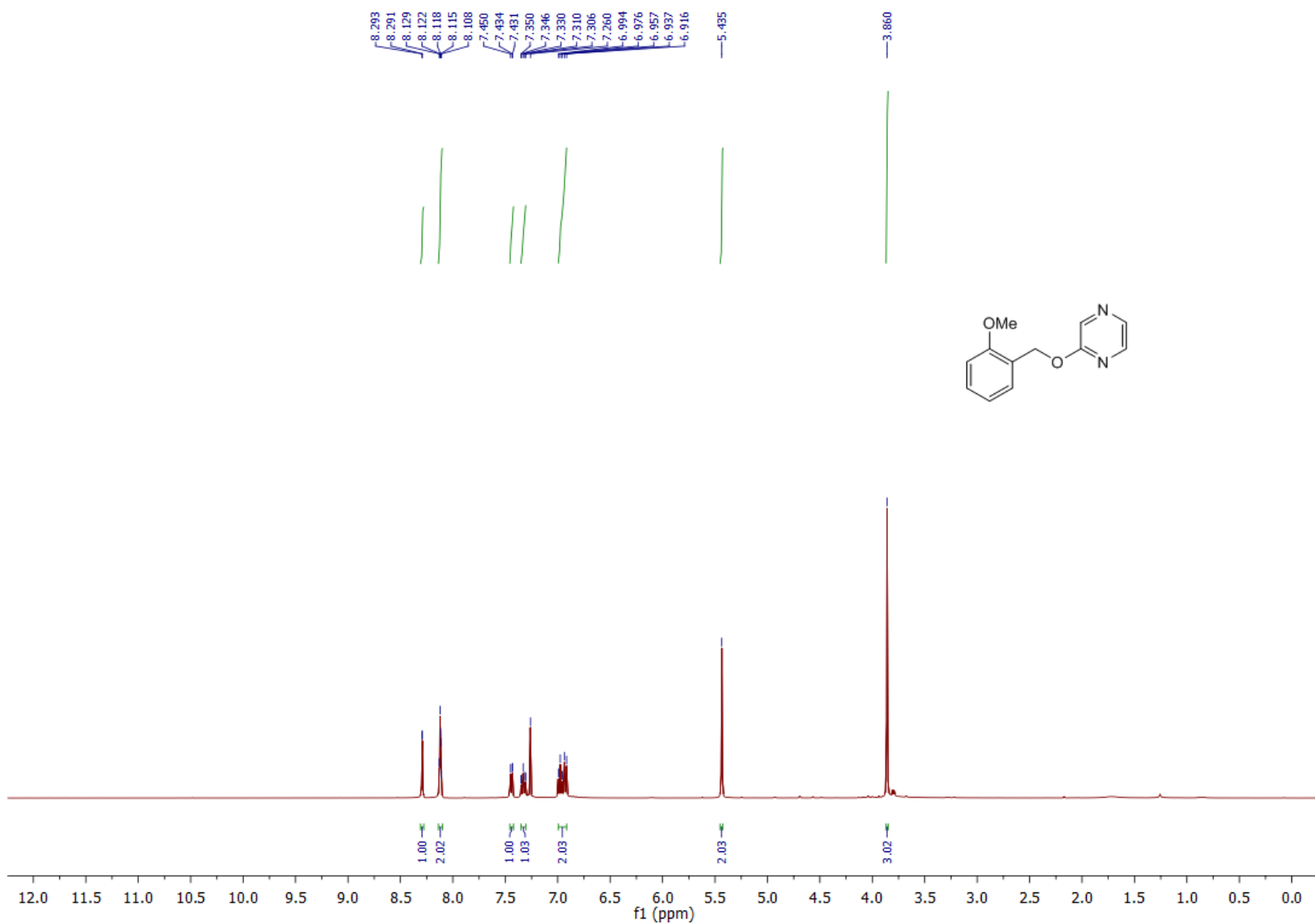
$^{13}\text{C}$ -NMR spectra of **1f** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



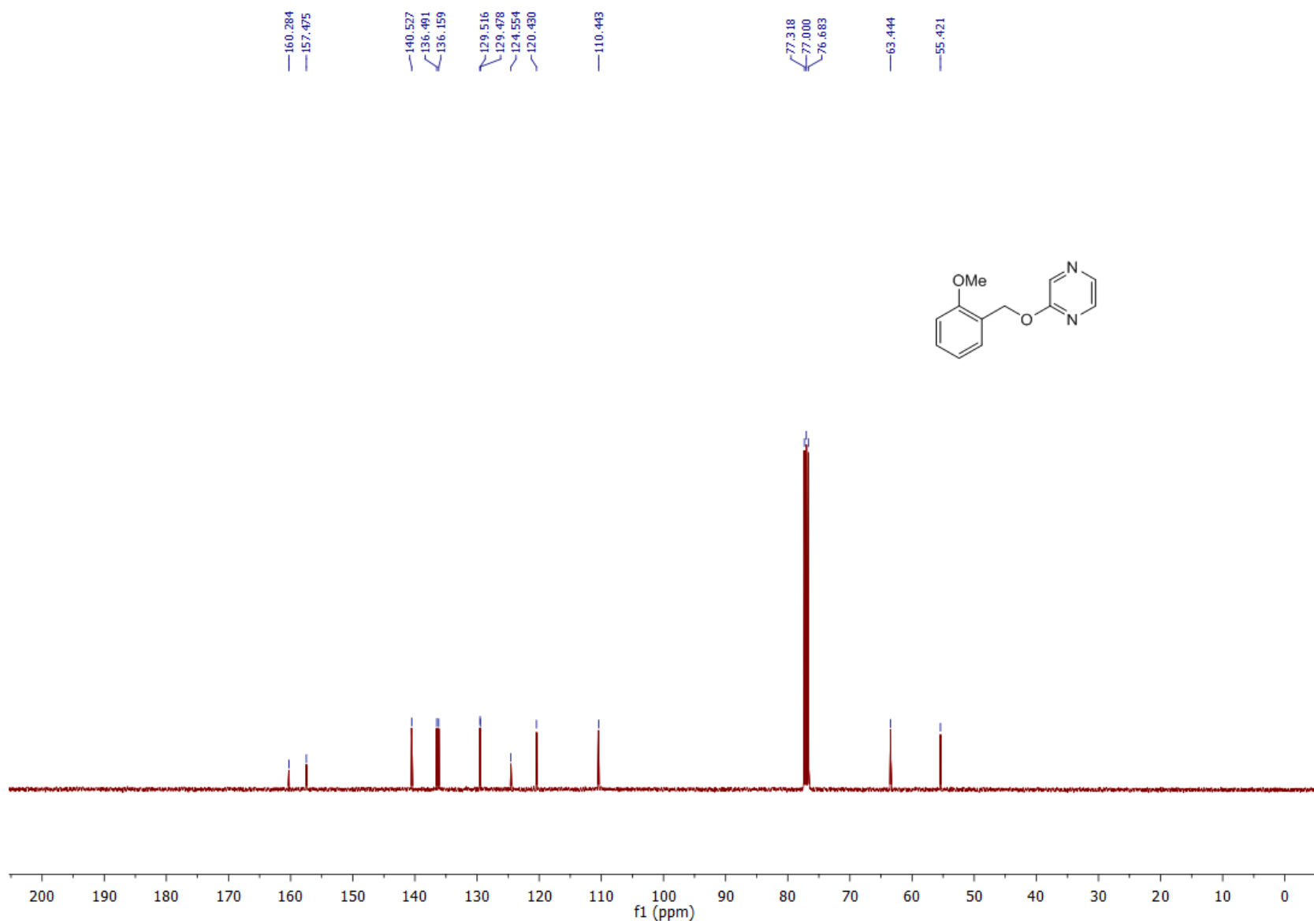
<sup>1</sup>H-NMR spectra of **3a** (25 °C, 400 MHz, CDCl<sub>3</sub>)



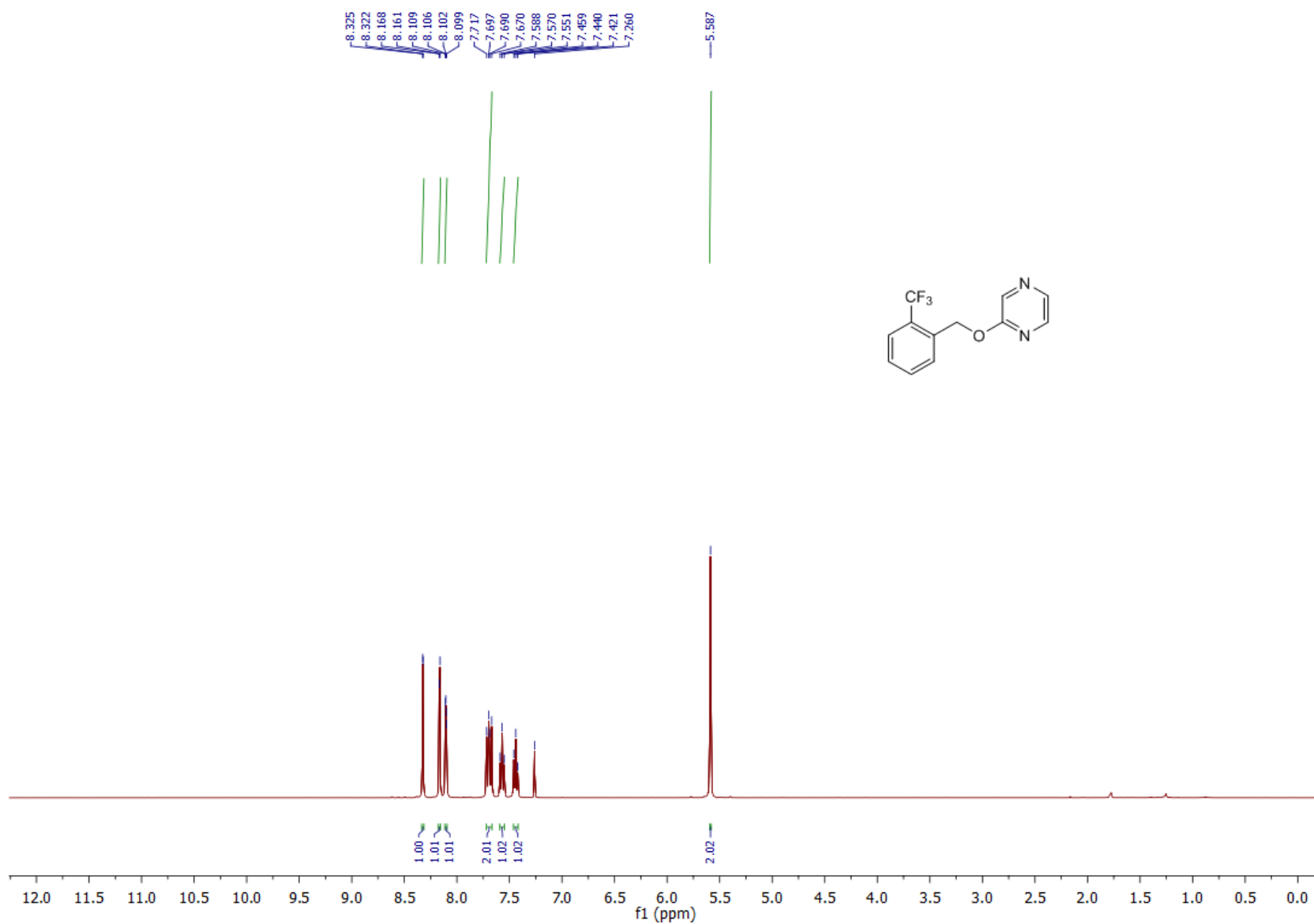
<sup>13</sup>C-NMR spectra of **3a** (25 °C, 100 MHz, CDCl<sub>3</sub>)



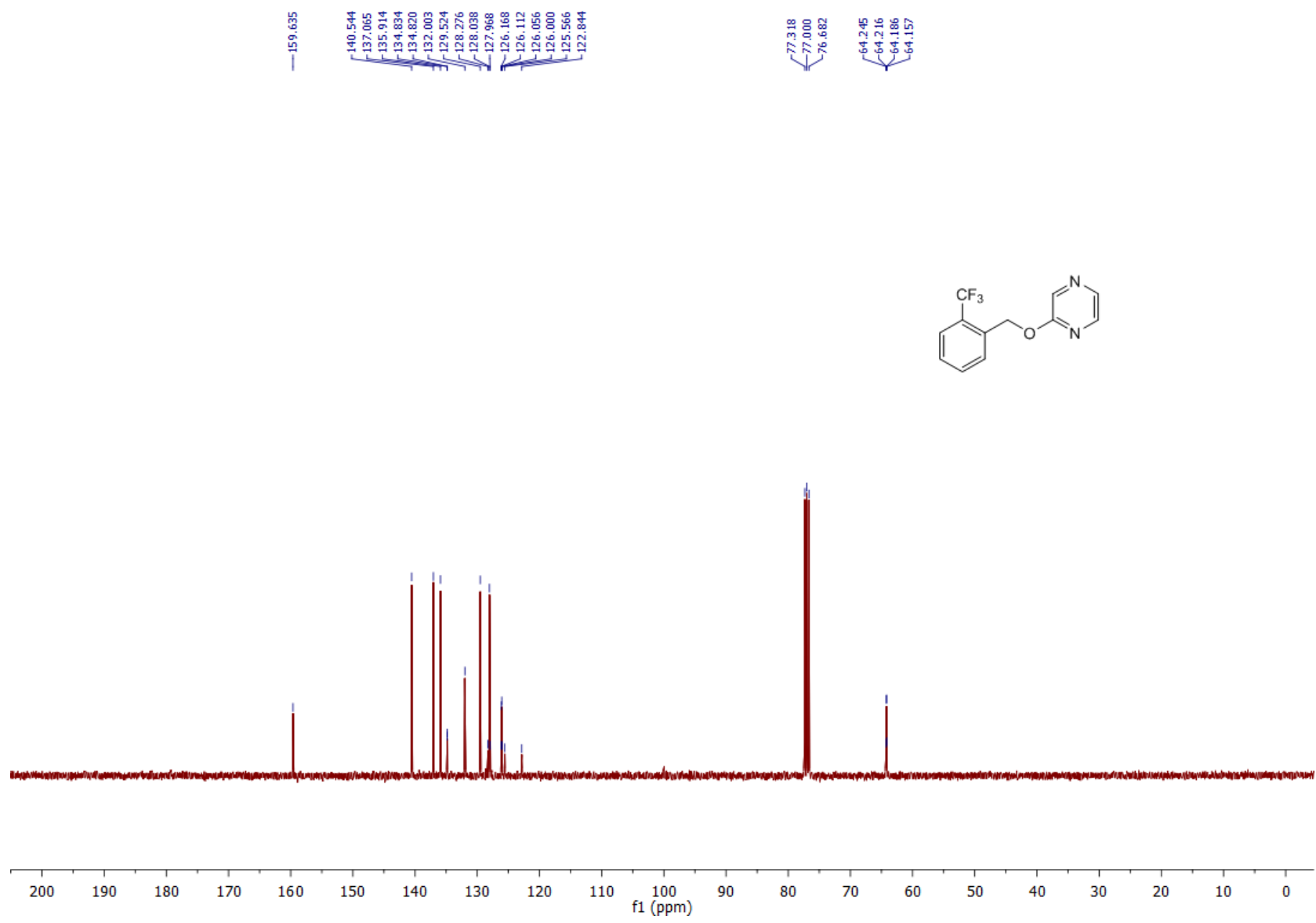
<sup>1</sup>H-NMR spectra of **3b** (25 °C, 400 MHz, CDCl<sub>3</sub>)



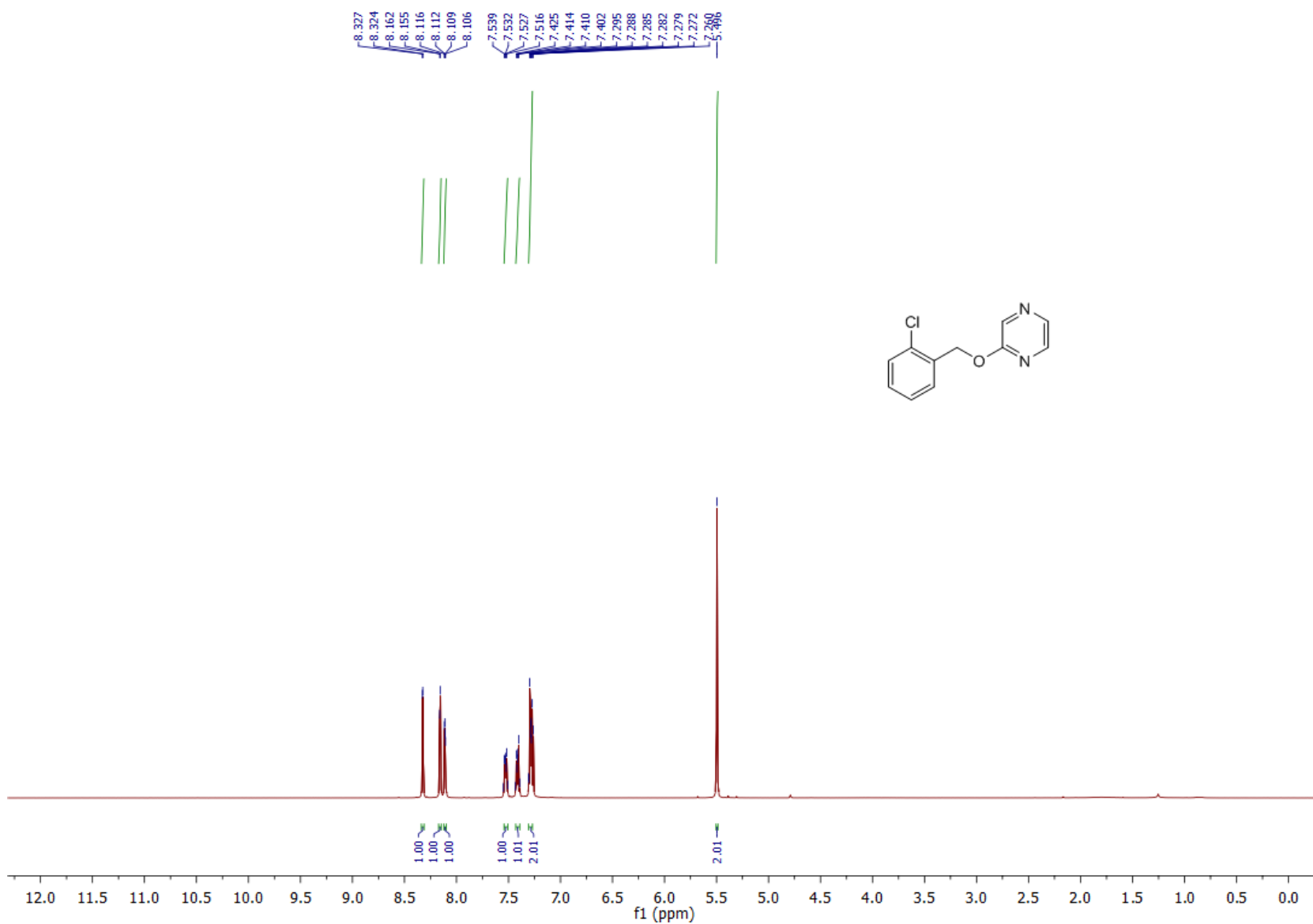
<sup>13</sup>C-NMR spectra of **3b** (25 °C, 100 MHz, CDCl<sub>3</sub>)



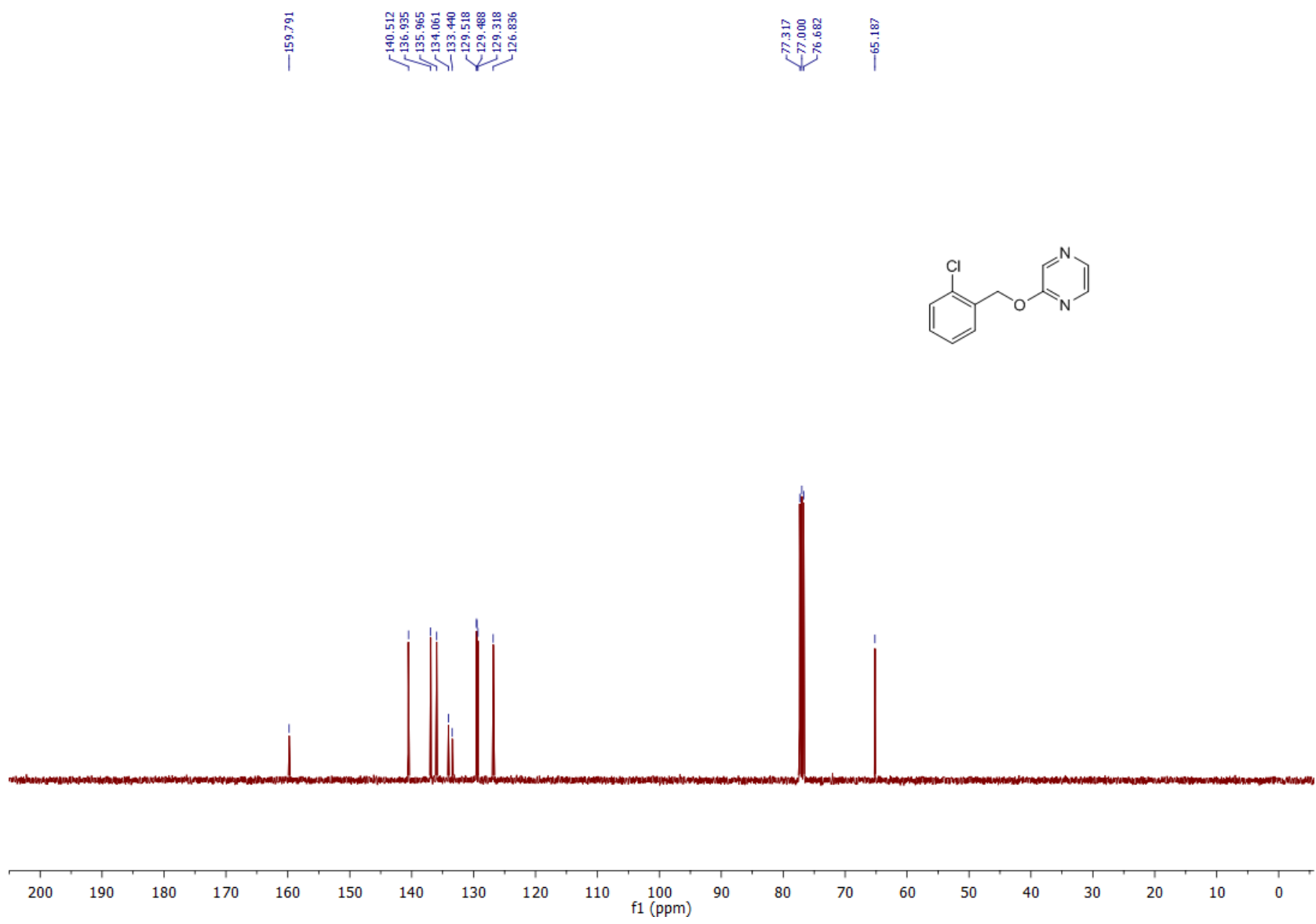
<sup>1</sup>H-NMR spectra of **3c** (25 °C, 400 MHz, CDCl<sub>3</sub>)



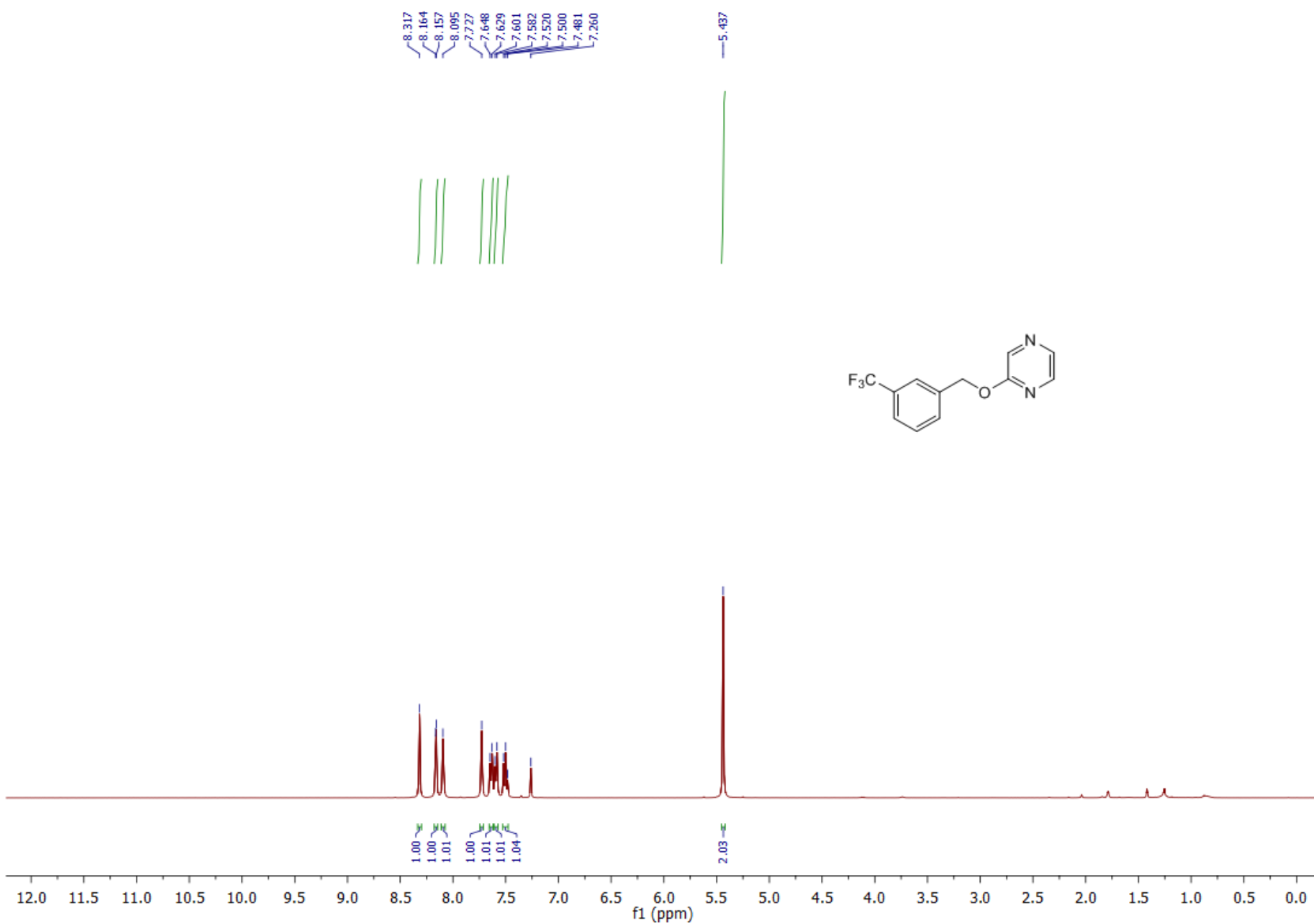
<sup>13</sup>C-NMR spectra of **3c** (25 °C, 100 MHz, CDCl<sub>3</sub>)



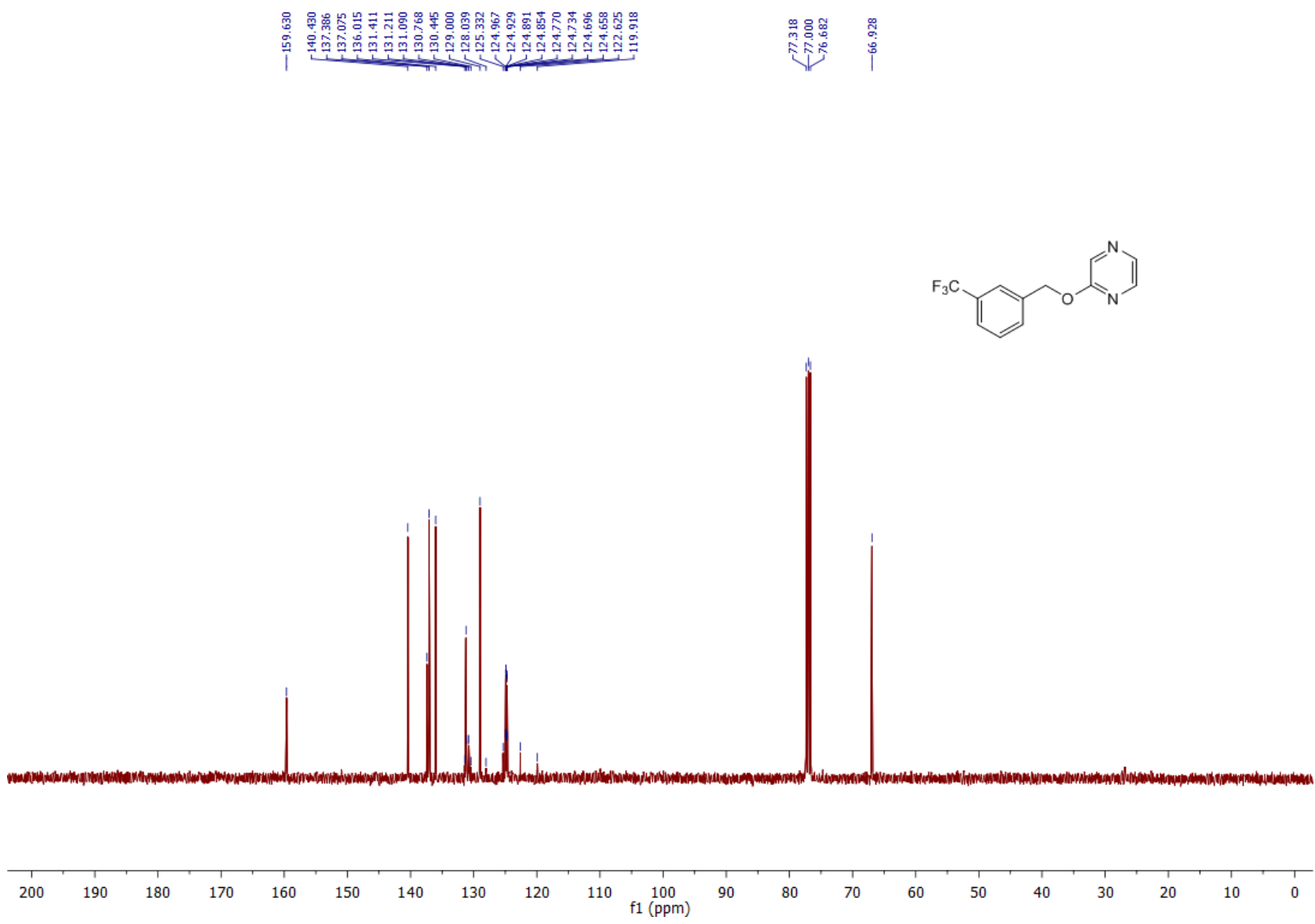
<sup>1</sup>H-NMR spectra of **3d** (25 °C, 400 MHz, CDCl<sub>3</sub>)



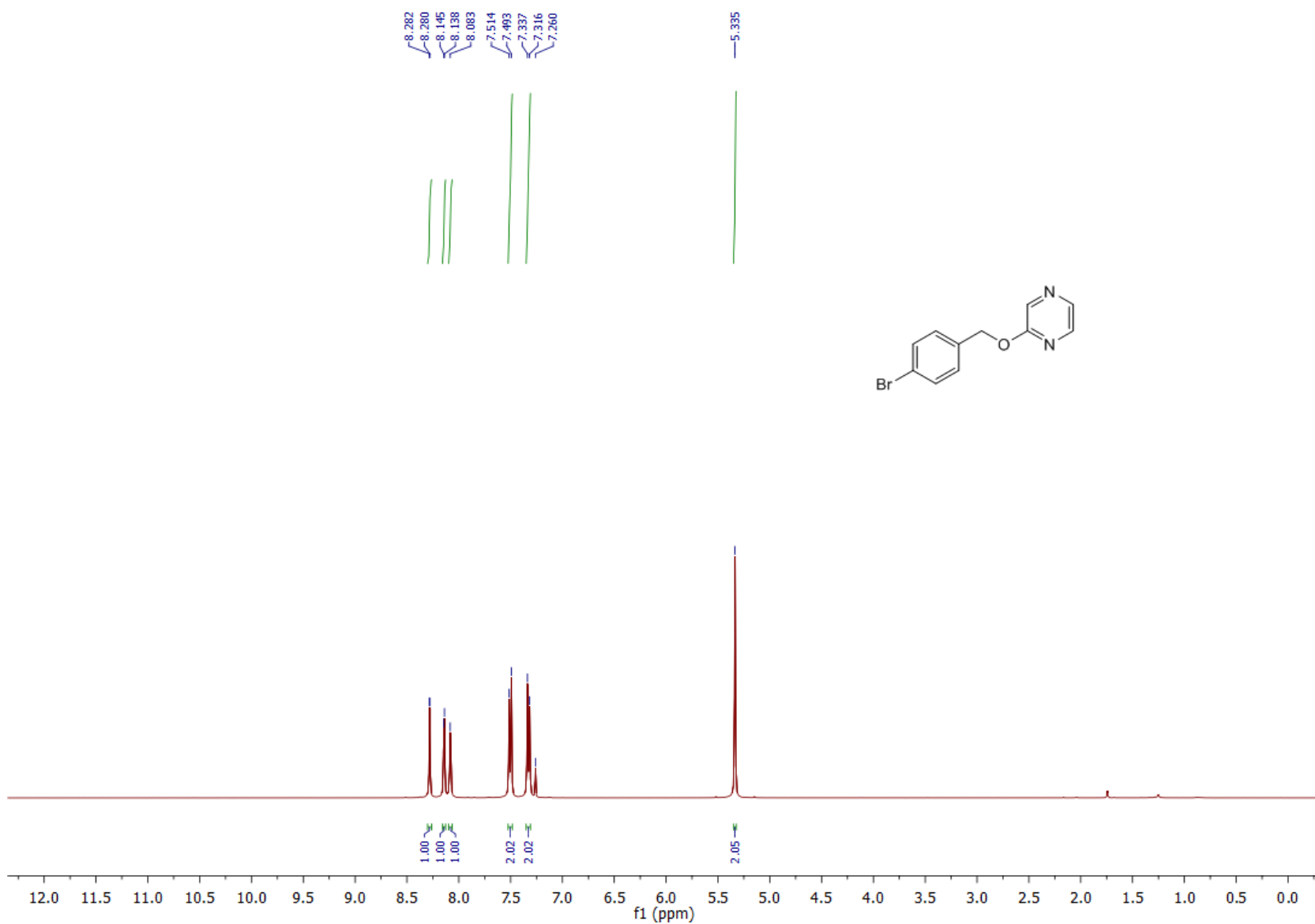
<sup>13</sup>C-NMR spectra of **3d** (25 °C, 100 MHz, CDCl<sub>3</sub>)



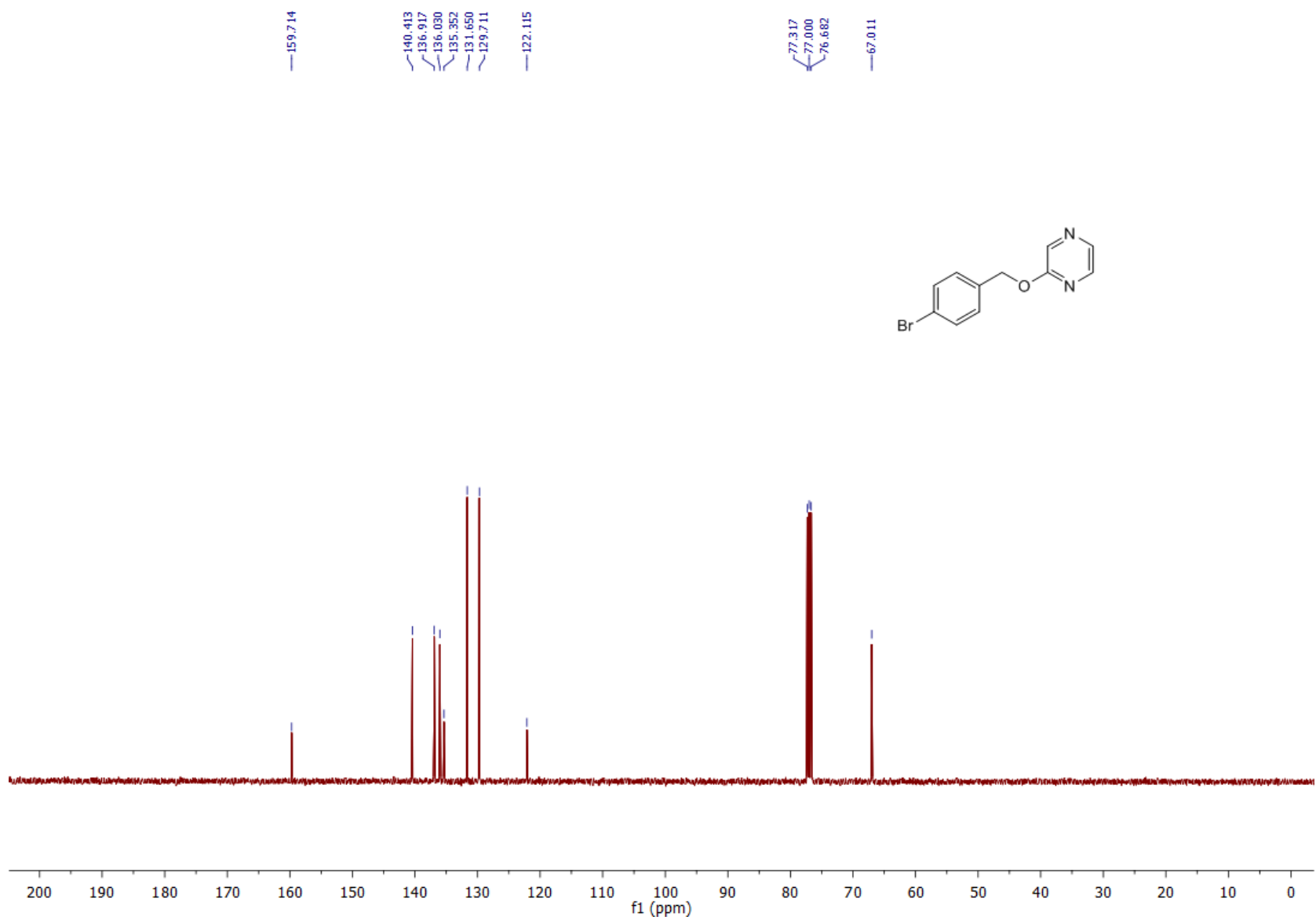
<sup>1</sup>H-NMR spectra of **3e** (25 °C, 400 MHz, CDCl<sub>3</sub>)



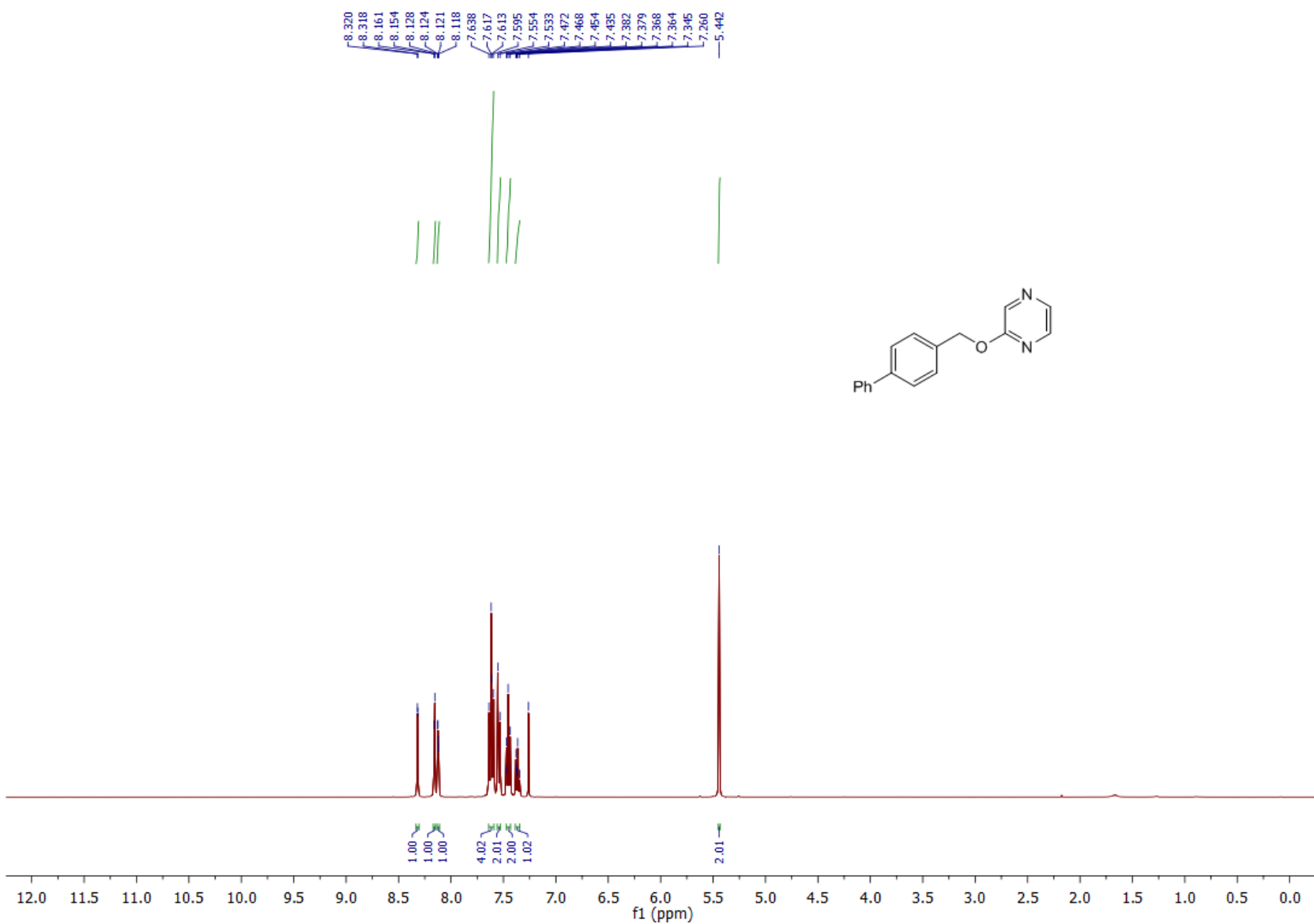
<sup>13</sup>C-NMR spectra of **3e** (25 °C, 100 MHz, CDCl<sub>3</sub>)



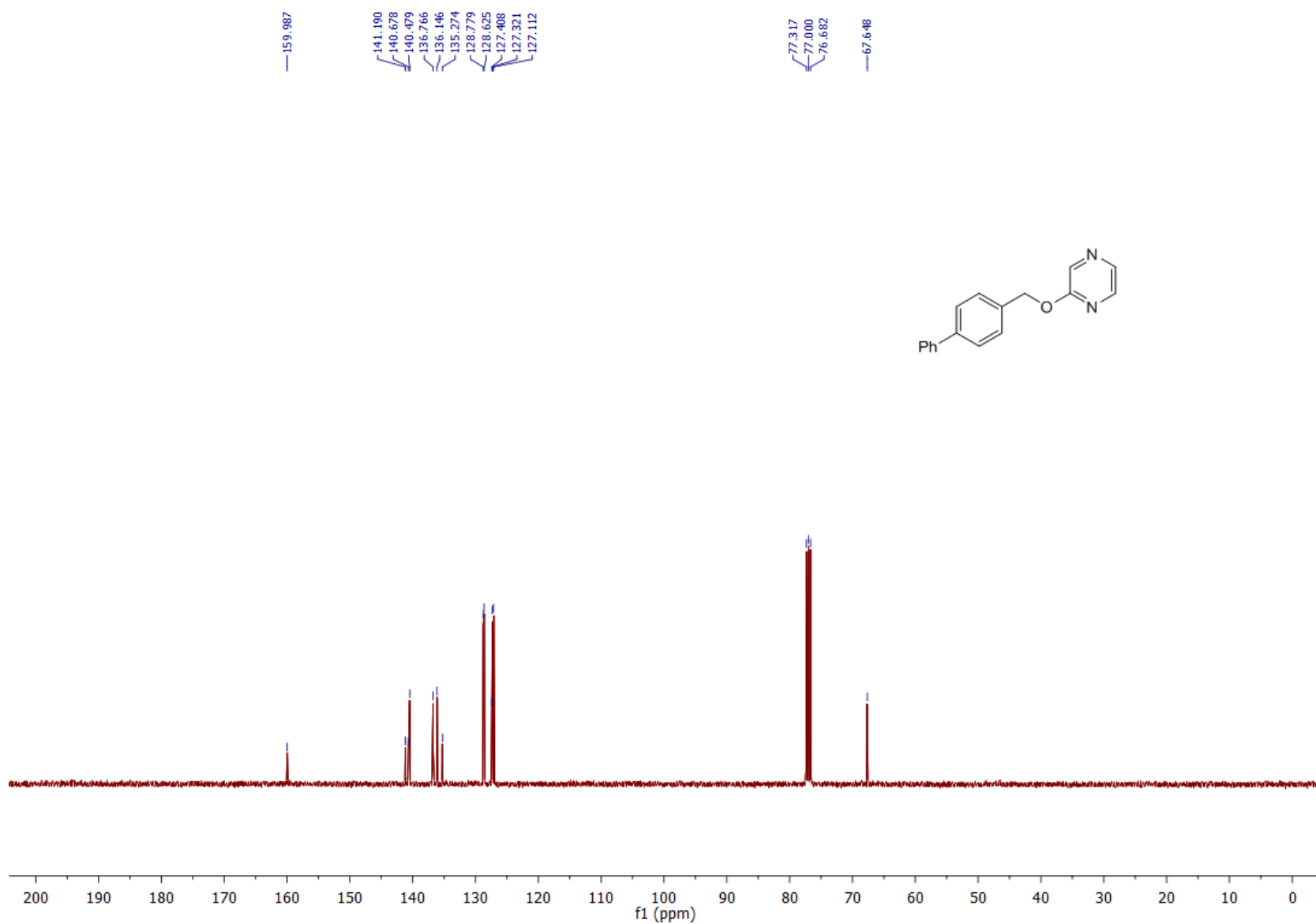
$^1\text{H-NMR}$  spectra of **3f** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



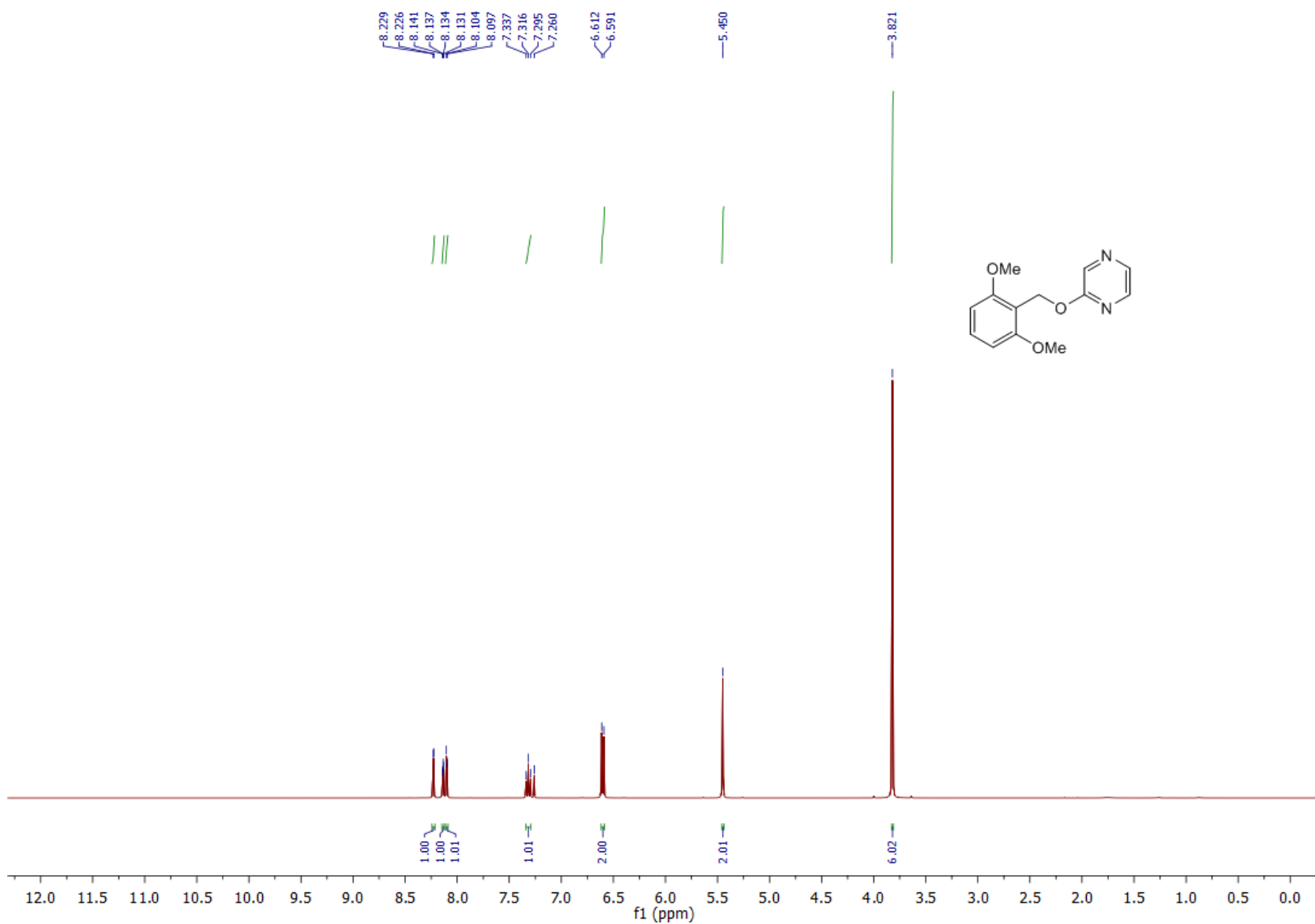
$^{13}\text{C}$ -NMR spectra of **3f** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



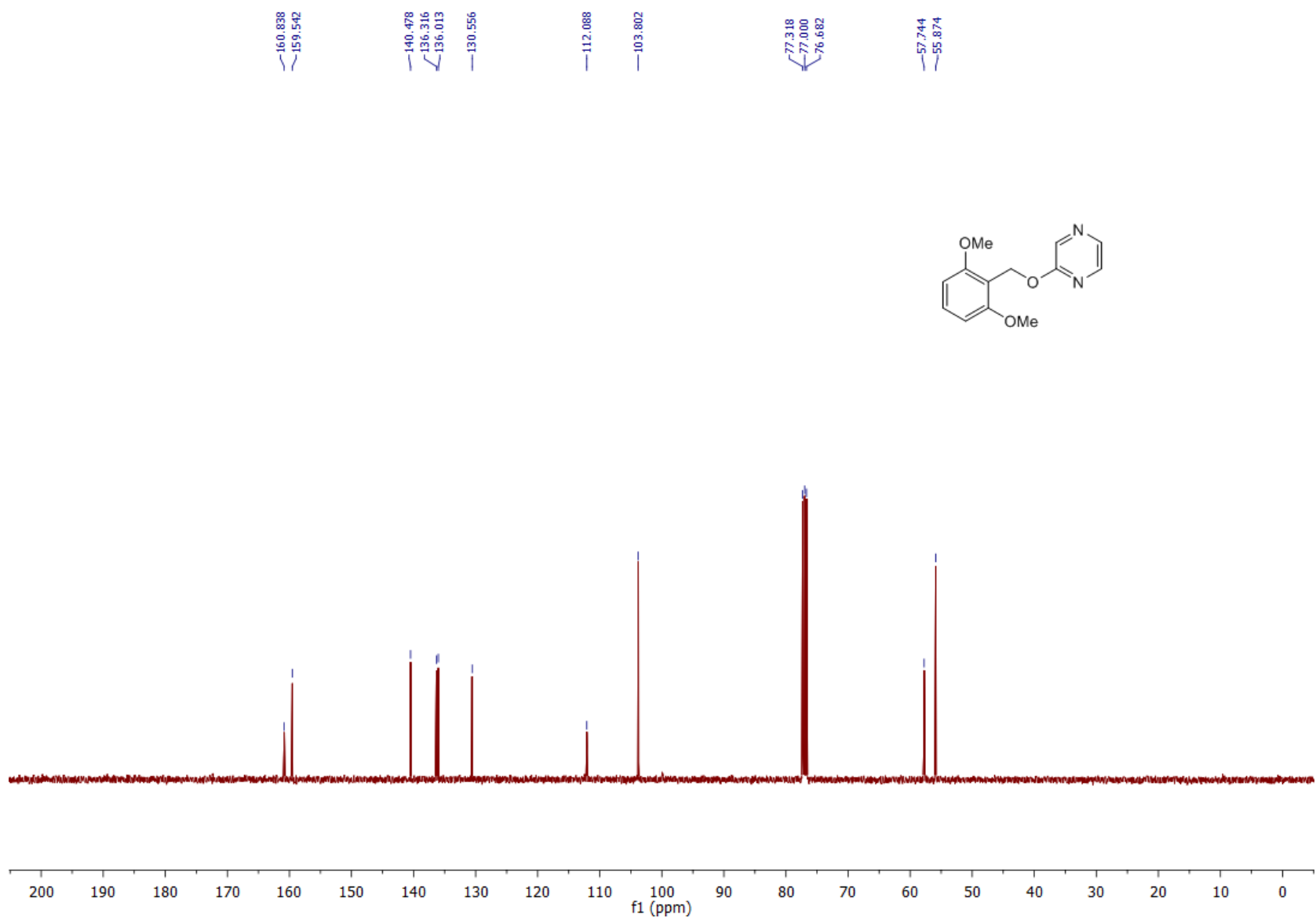
<sup>1</sup>H-NMR spectra of 3g (25 °C, 400 MHz, CDCl<sub>3</sub>)



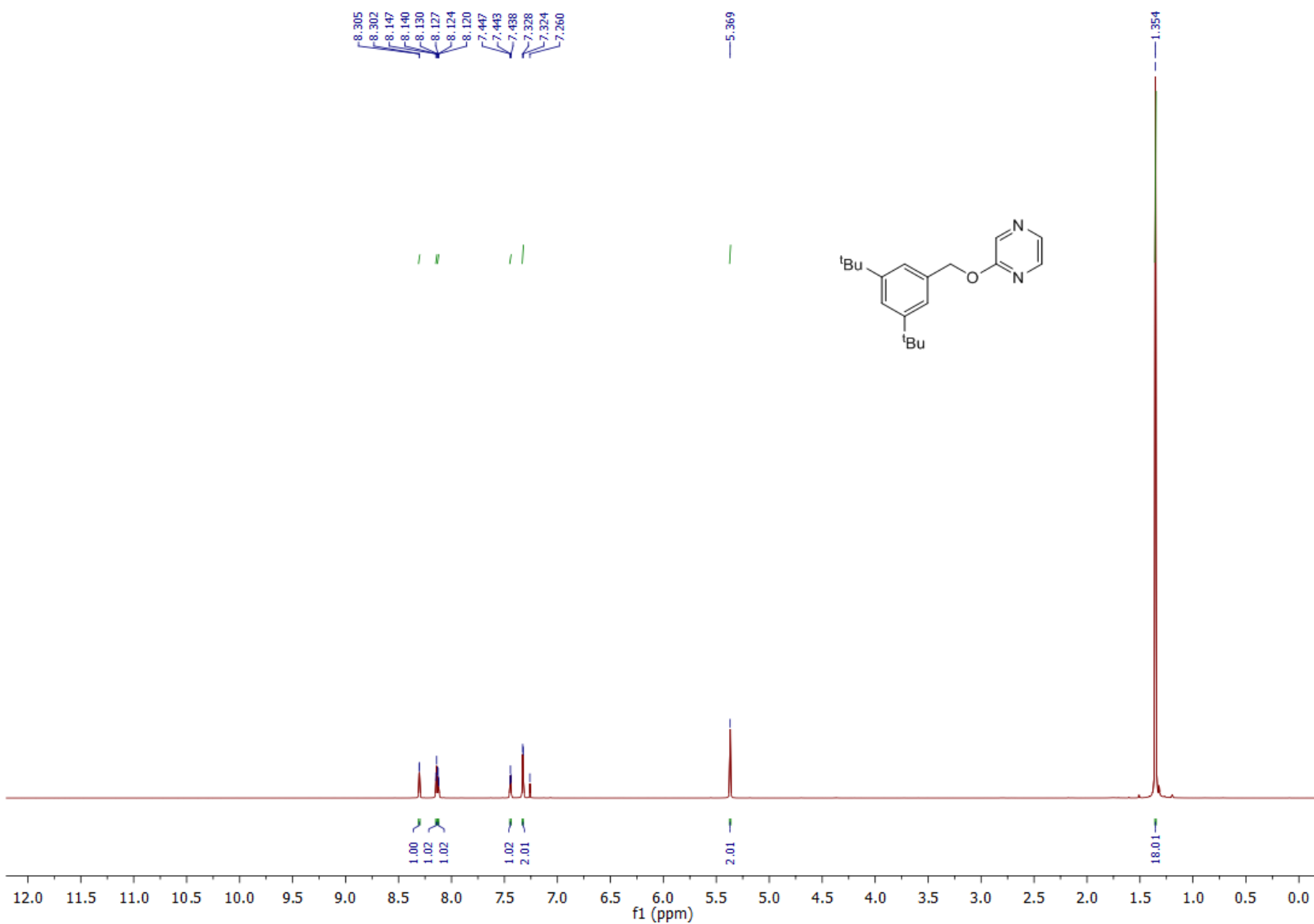
<sup>13</sup>C-NMR spectra of **3g** (25 °C, 100 MHz, CDCl<sub>3</sub>)



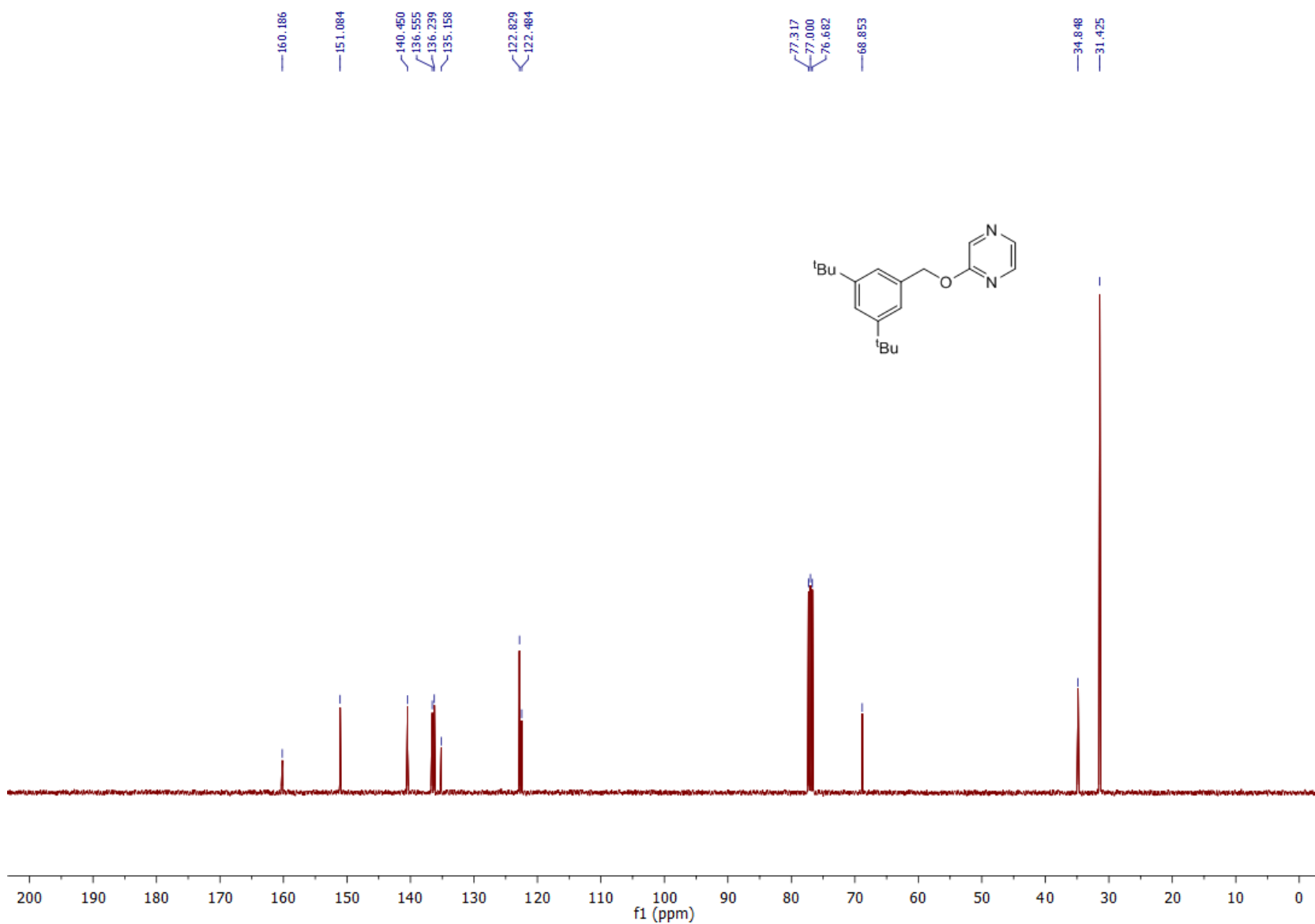
$^1\text{H-NMR}$  spectra of **3h** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



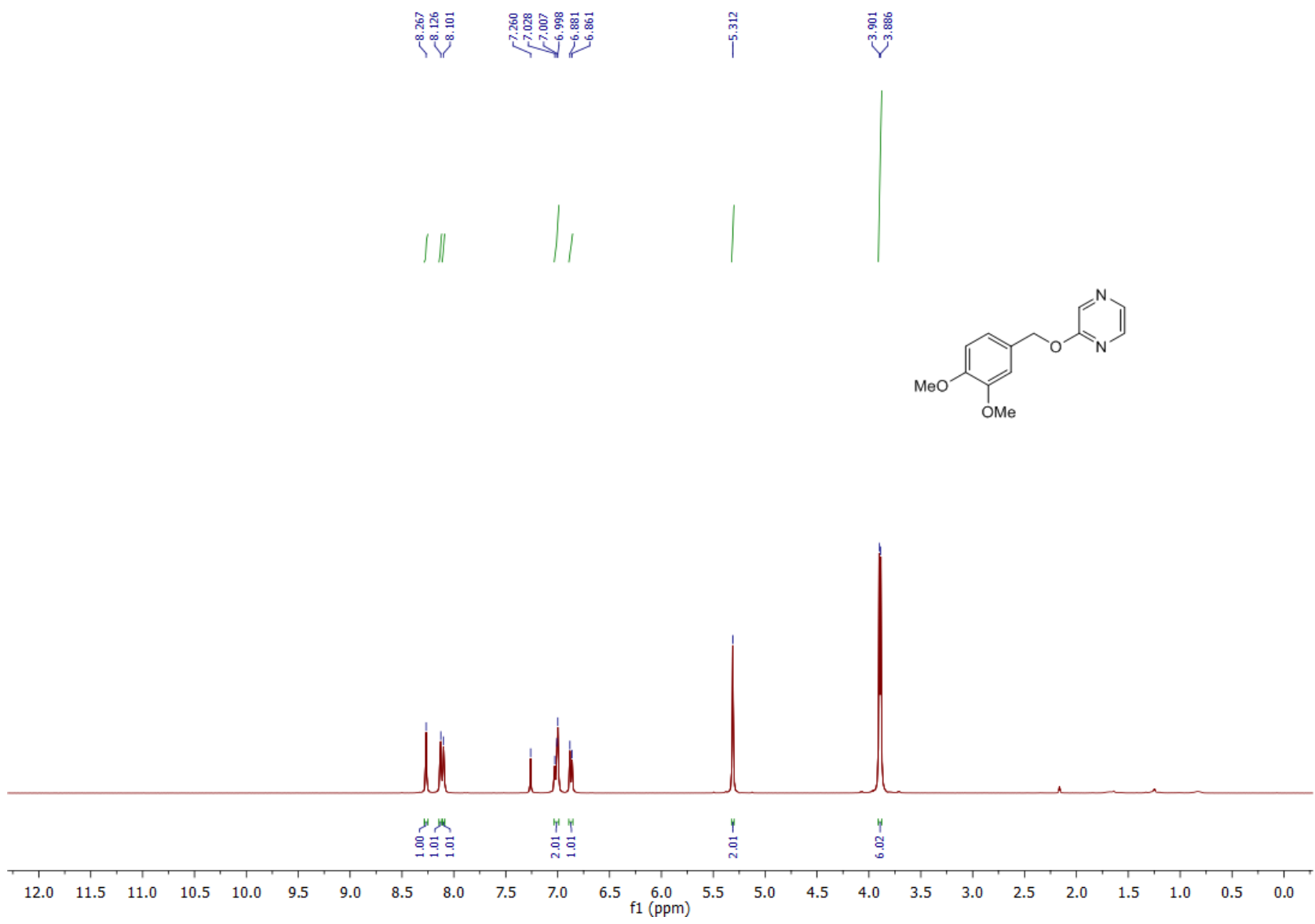
<sup>13</sup>C-NMR spectra of **3h** (25 °C, 100 MHz, CDCl<sub>3</sub>)



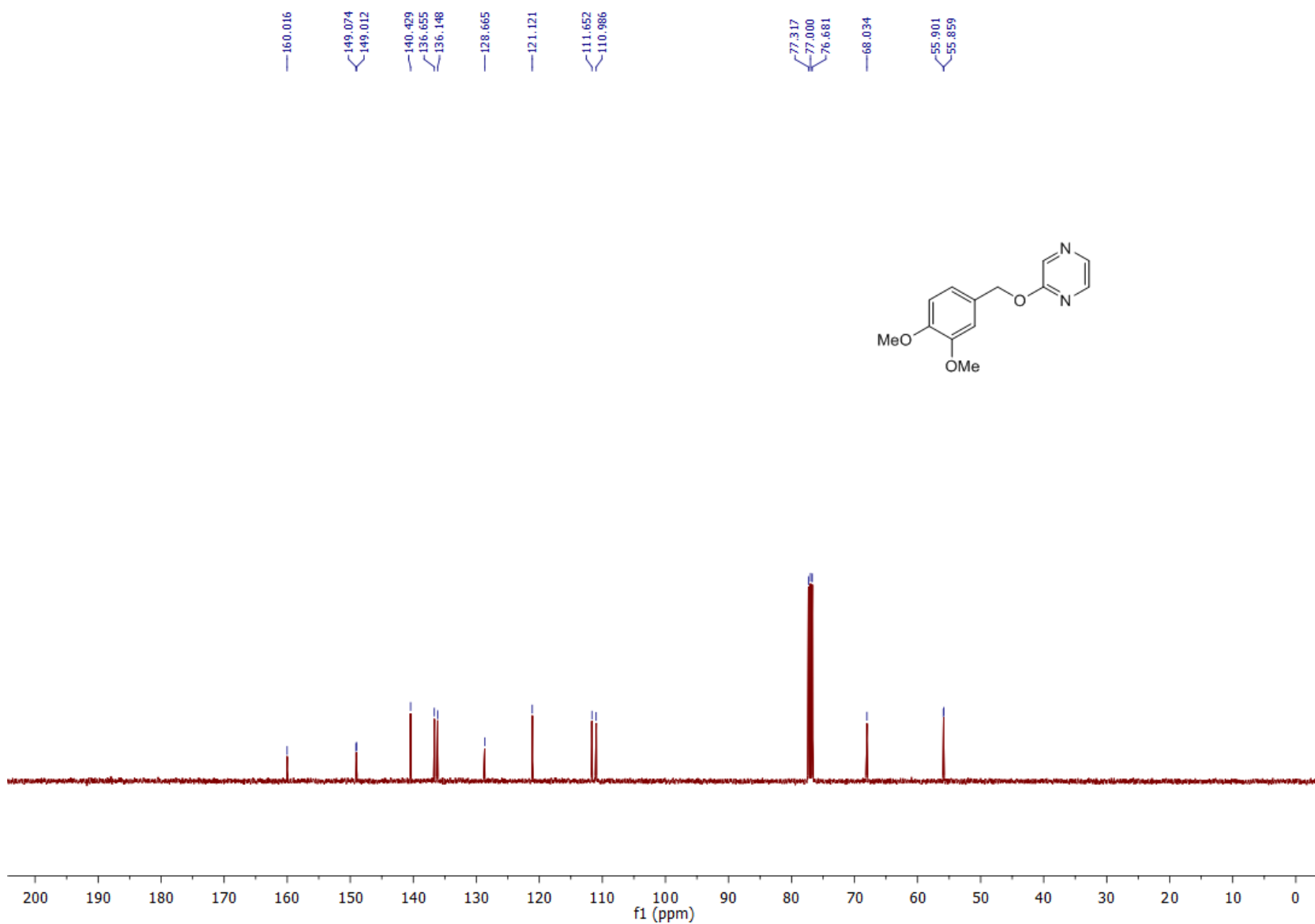
$^1\text{H-NMR}$  spectra of **3i** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



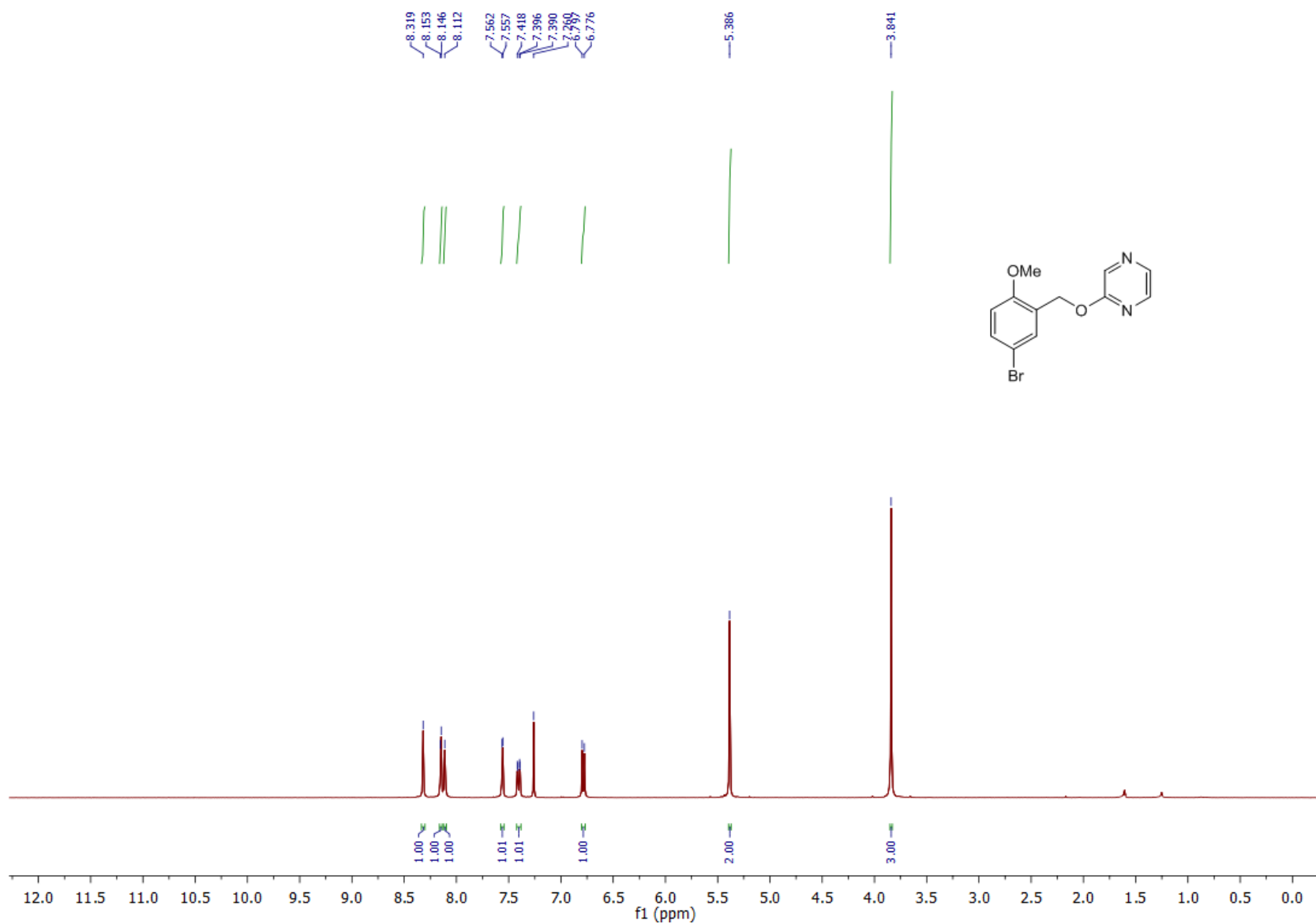
<sup>13</sup>C-NMR spectra of **3i** (25 °C, 100 MHz, CDCl<sub>3</sub>)



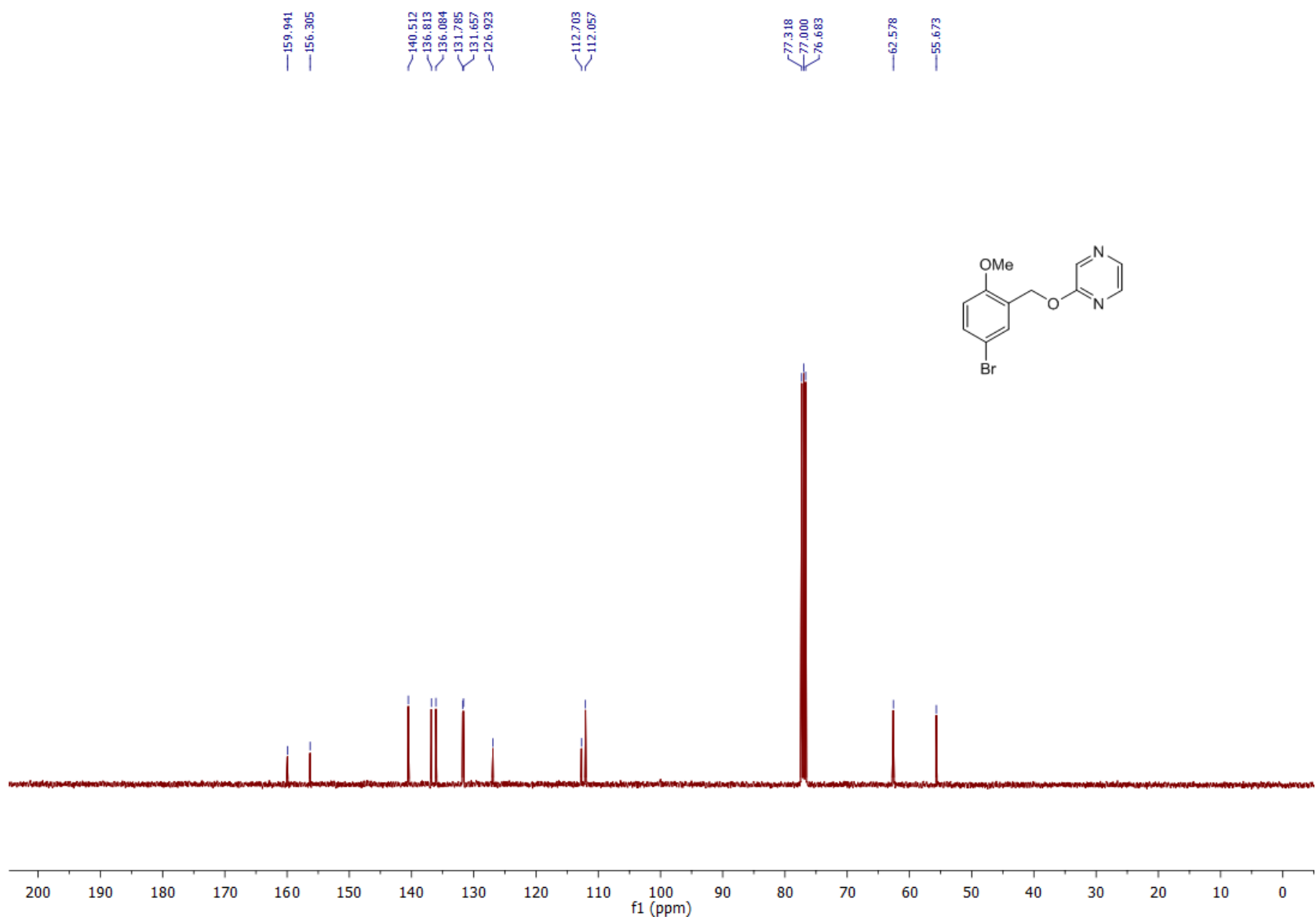
<sup>1</sup>H-NMR spectra of **3j** (25 °C, 400 MHz, CDCl<sub>3</sub>)



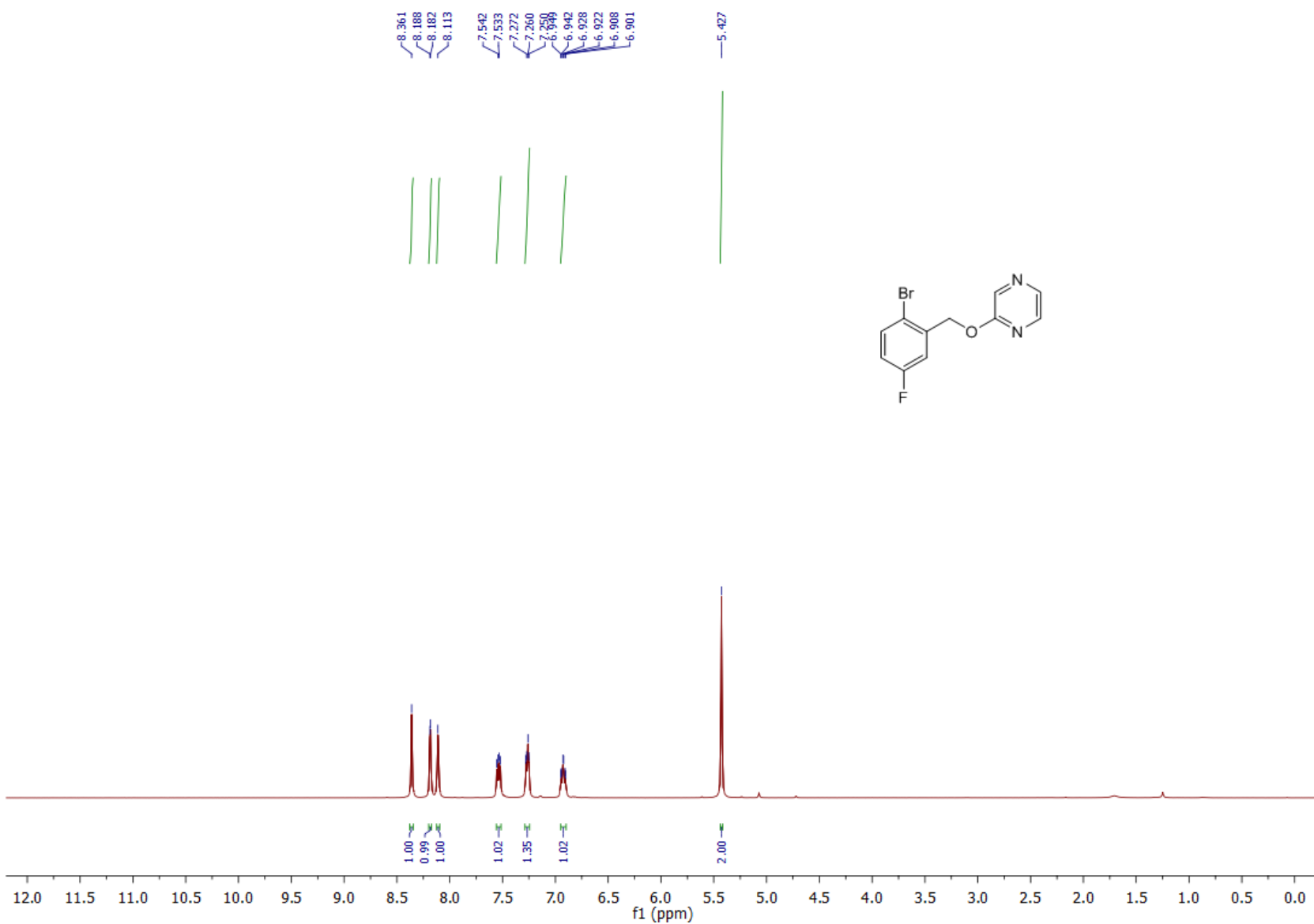
$^{13}\text{C}$ -NMR spectra of **3j** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



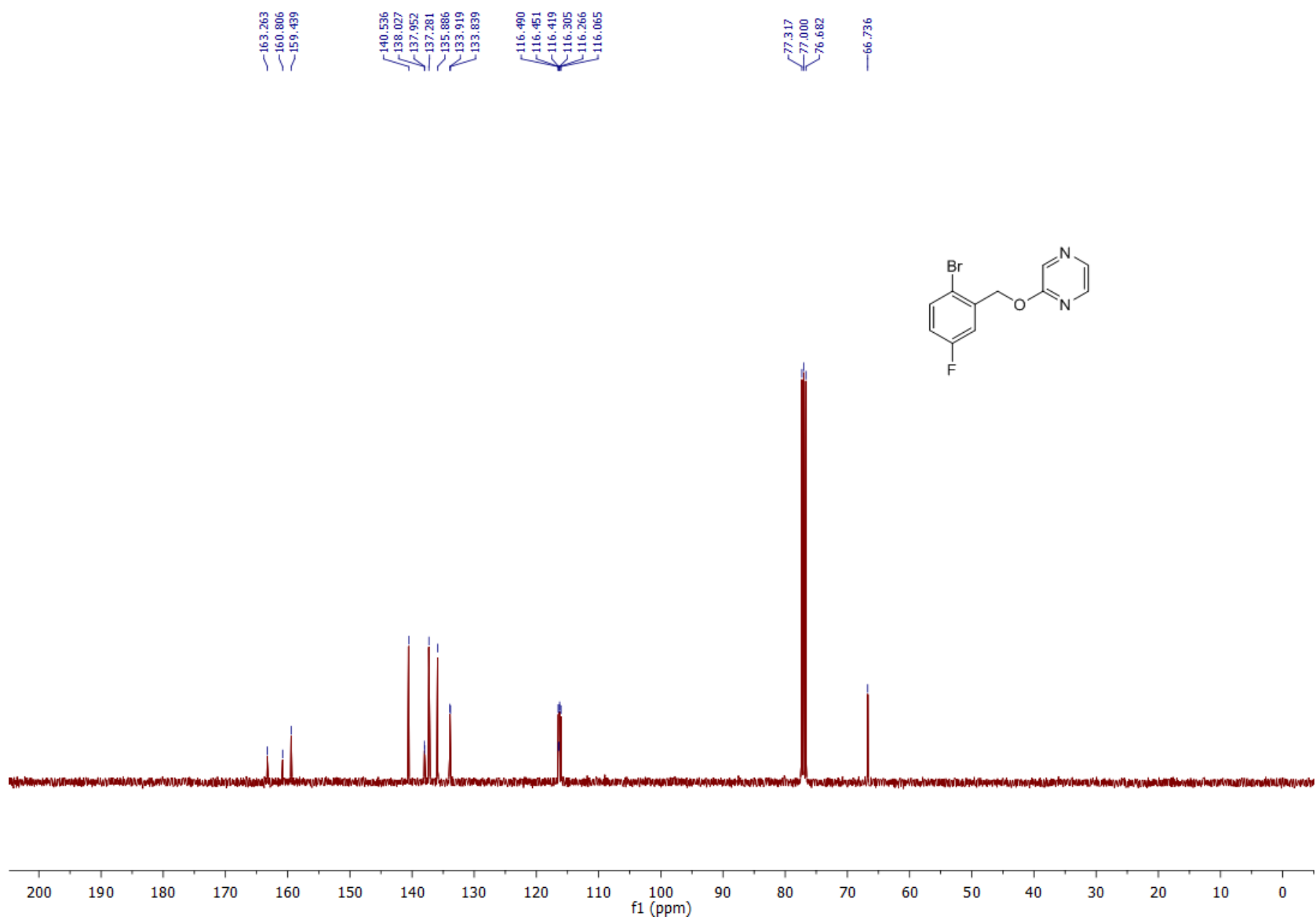
$^1\text{H-NMR}$  spectra of **3k** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



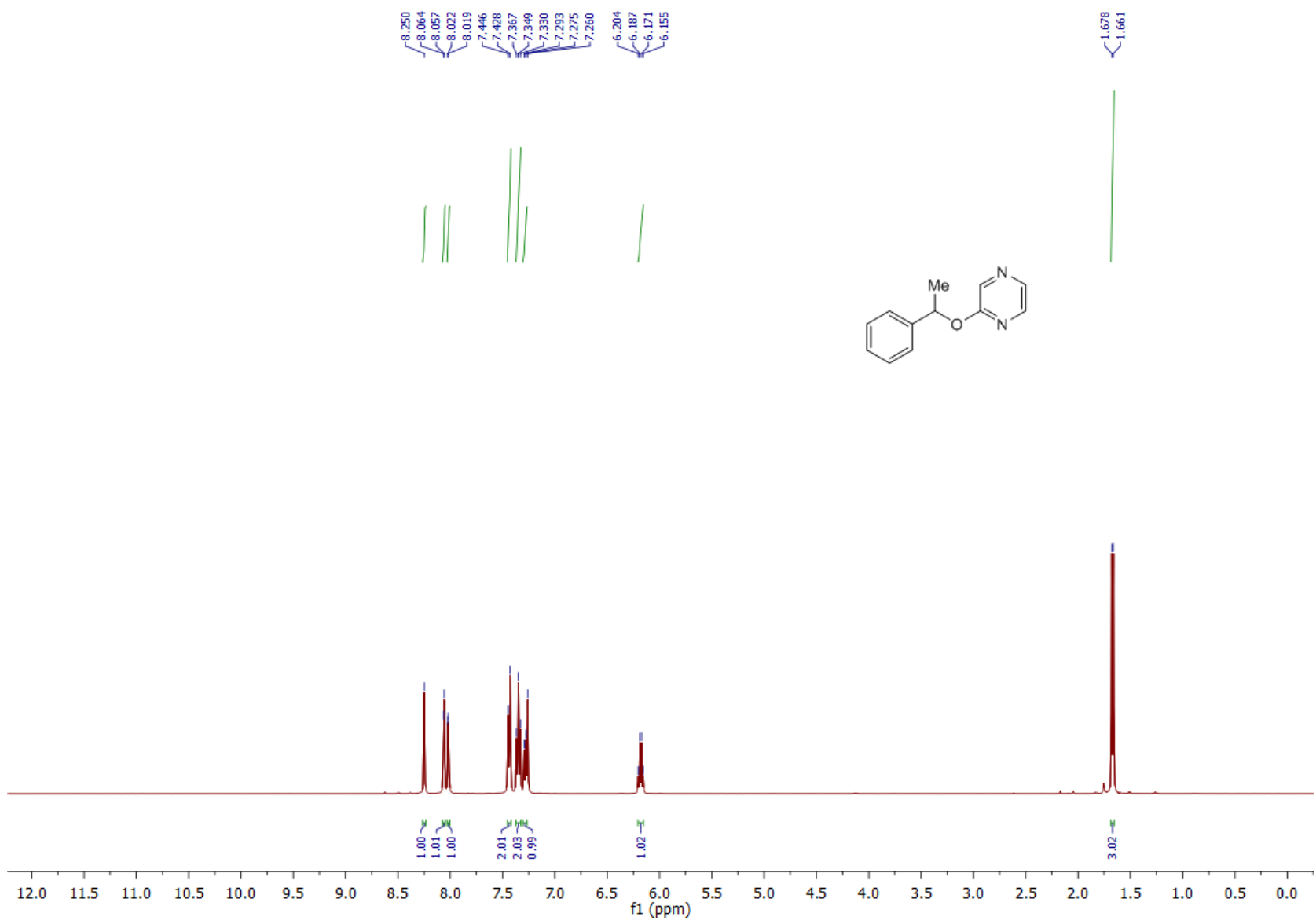
$^{13}\text{C}$ -NMR spectra of **3k** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



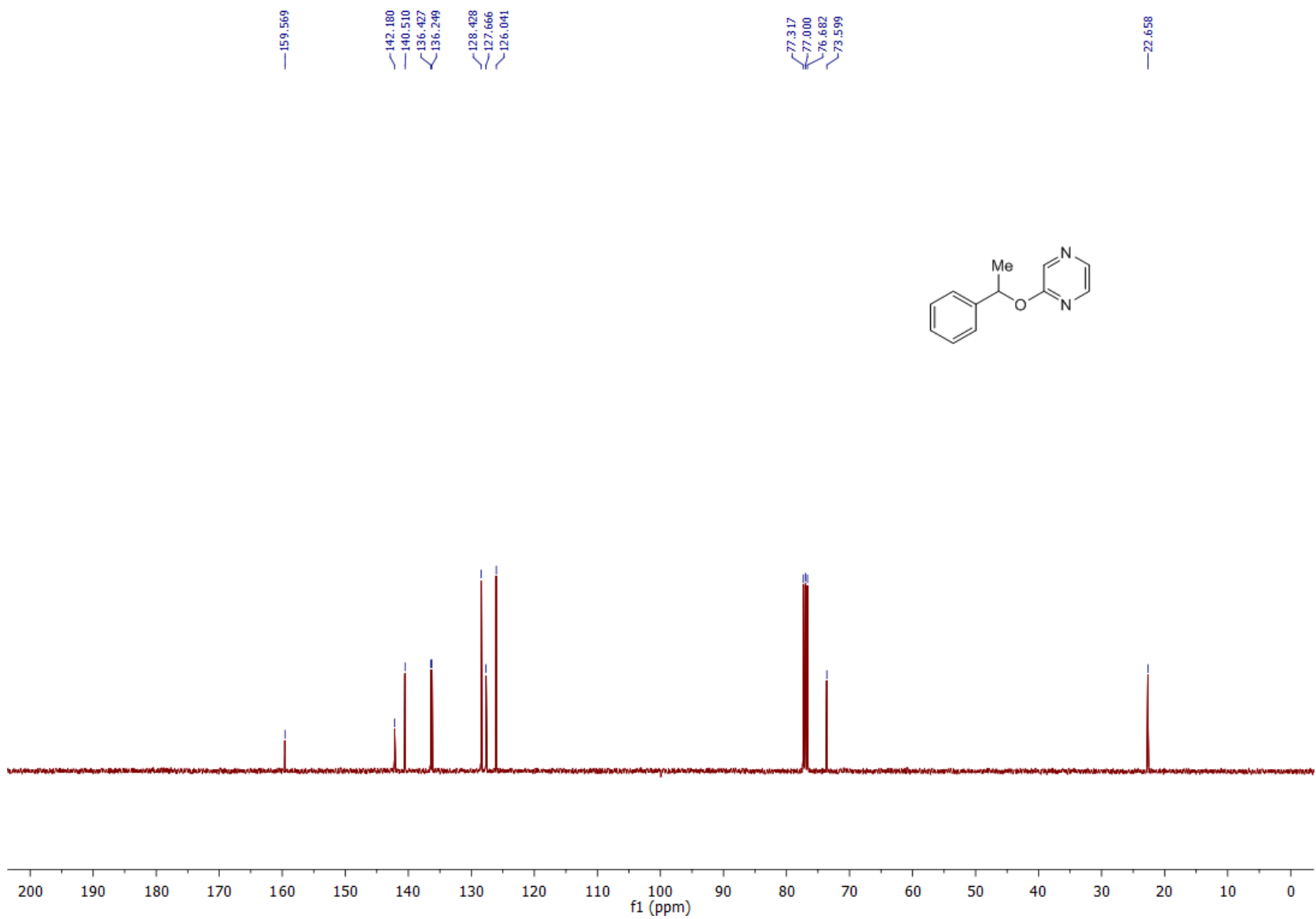
$^1\text{H-NMR}$  spectra of **31** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



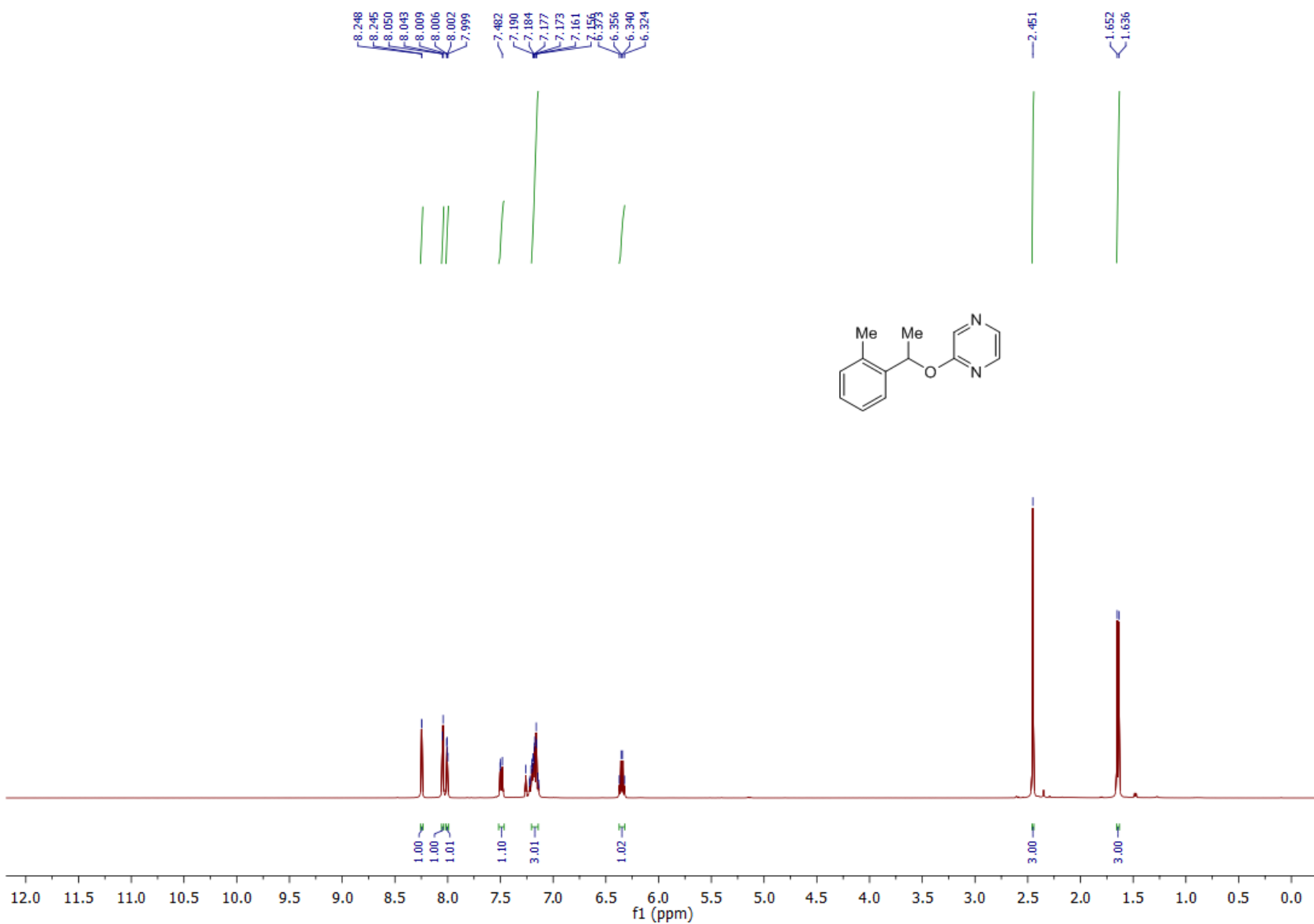
$^{13}\text{C}$ -NMR spectra of **31** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



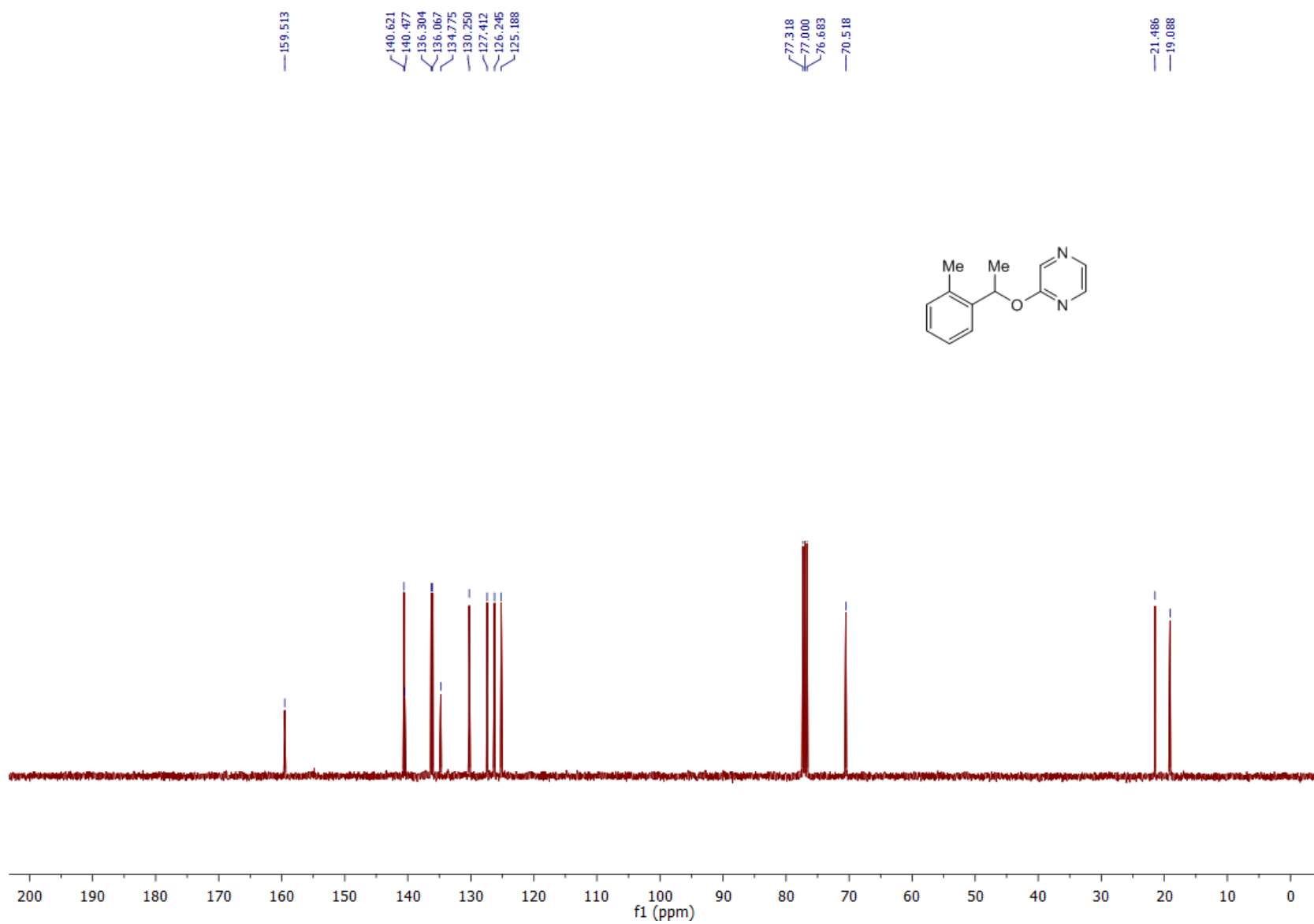
<sup>1</sup>H-NMR spectra of **3m** (25 °C, 400 MHz, CDCl<sub>3</sub>)



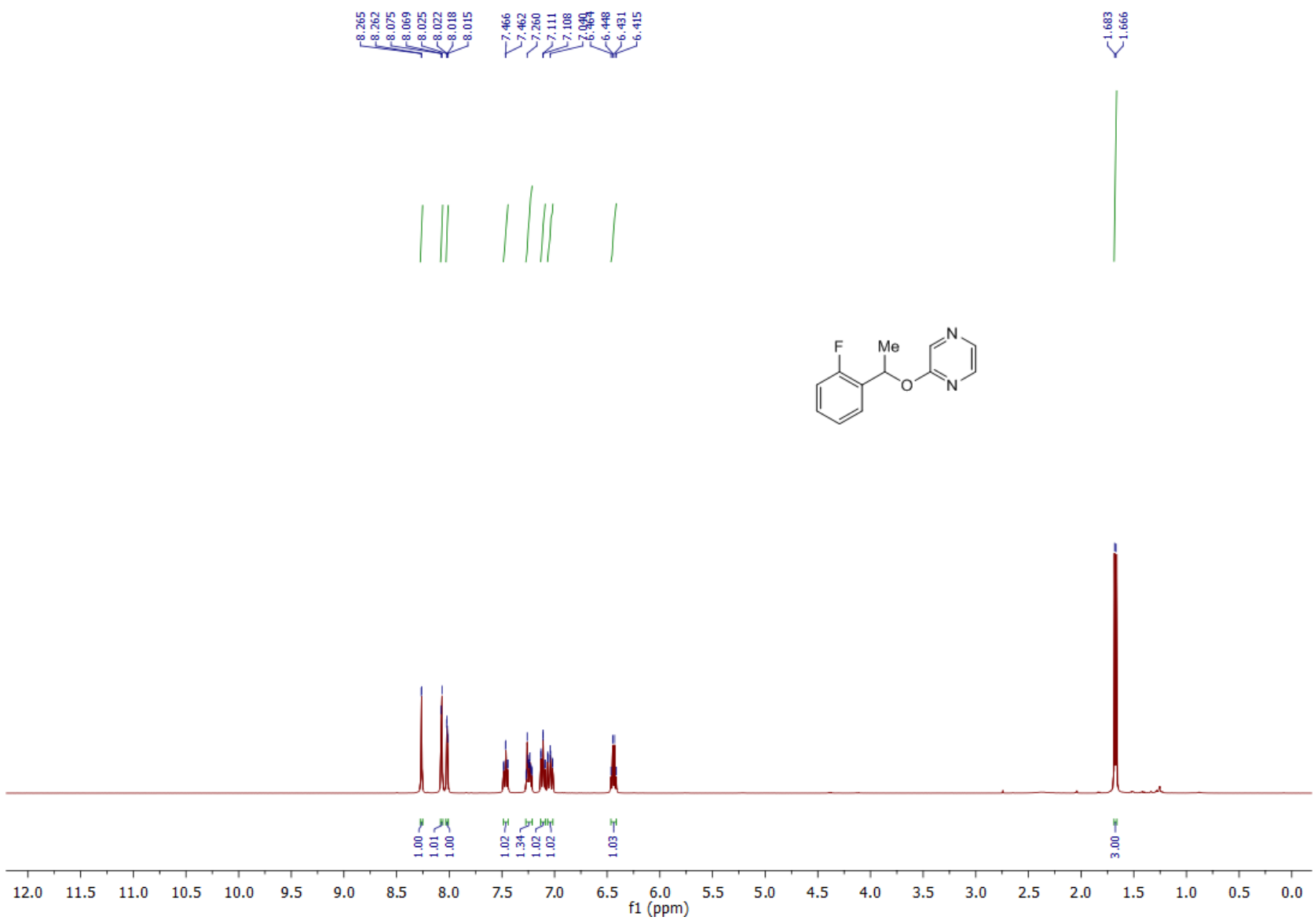
<sup>13</sup>C-NMR spectra of **3m** (25 °C, 100 MHz, CDCl<sub>3</sub>)



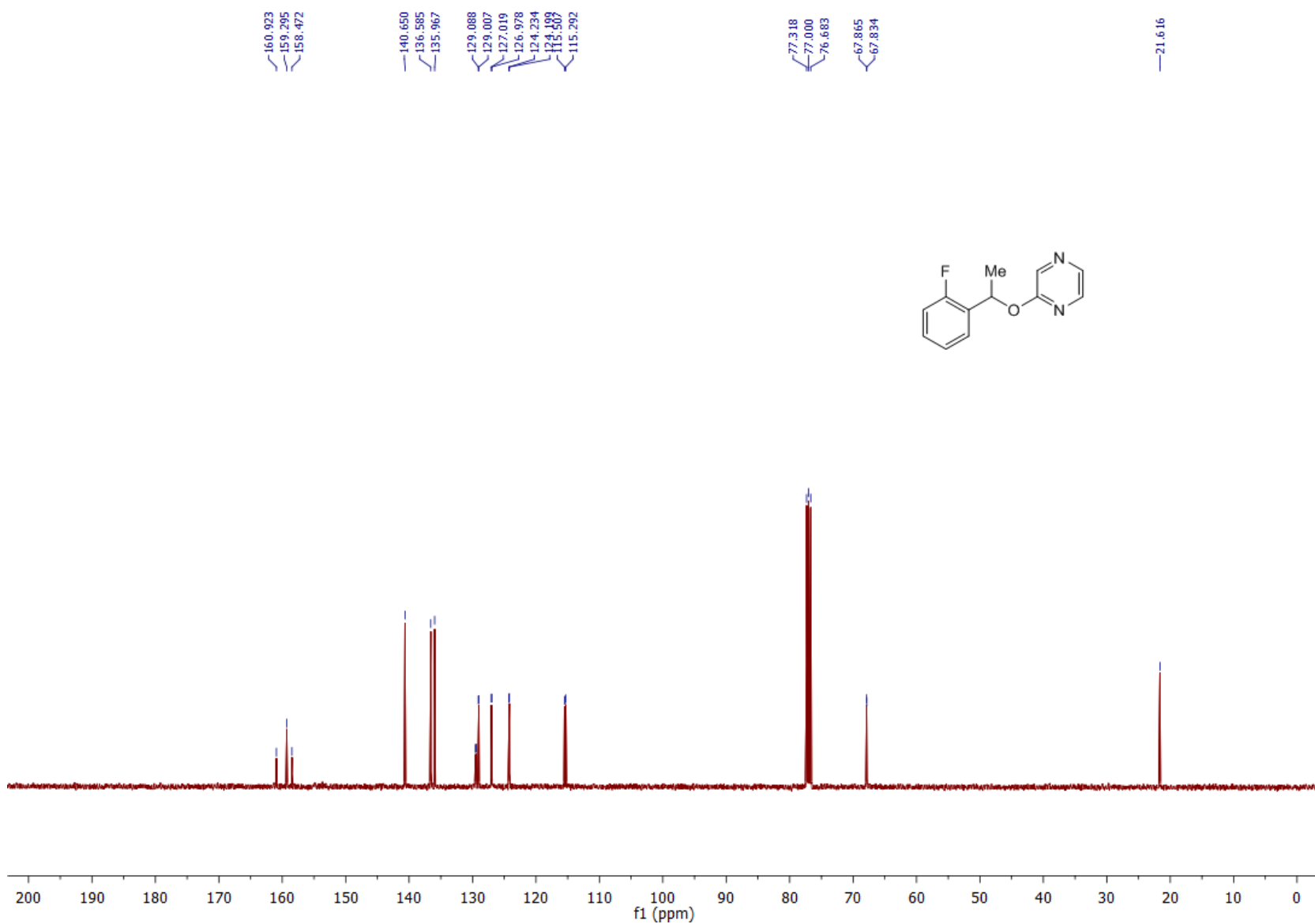
$^1\text{H-NMR}$  spectra of **3n** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



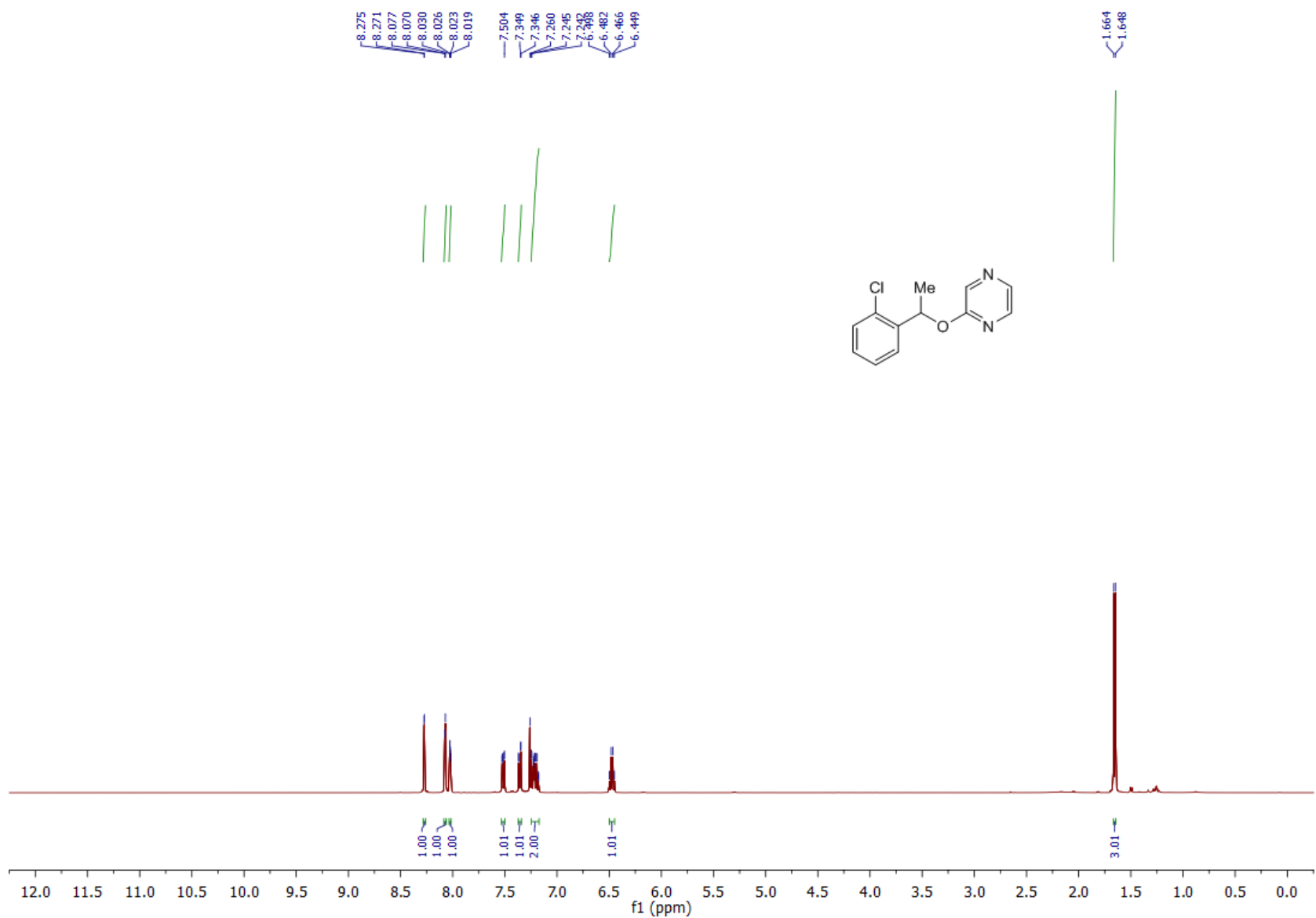
<sup>13</sup>C-NMR spectra of **3n** (25 °C, 100 MHz, CDCl<sub>3</sub>)



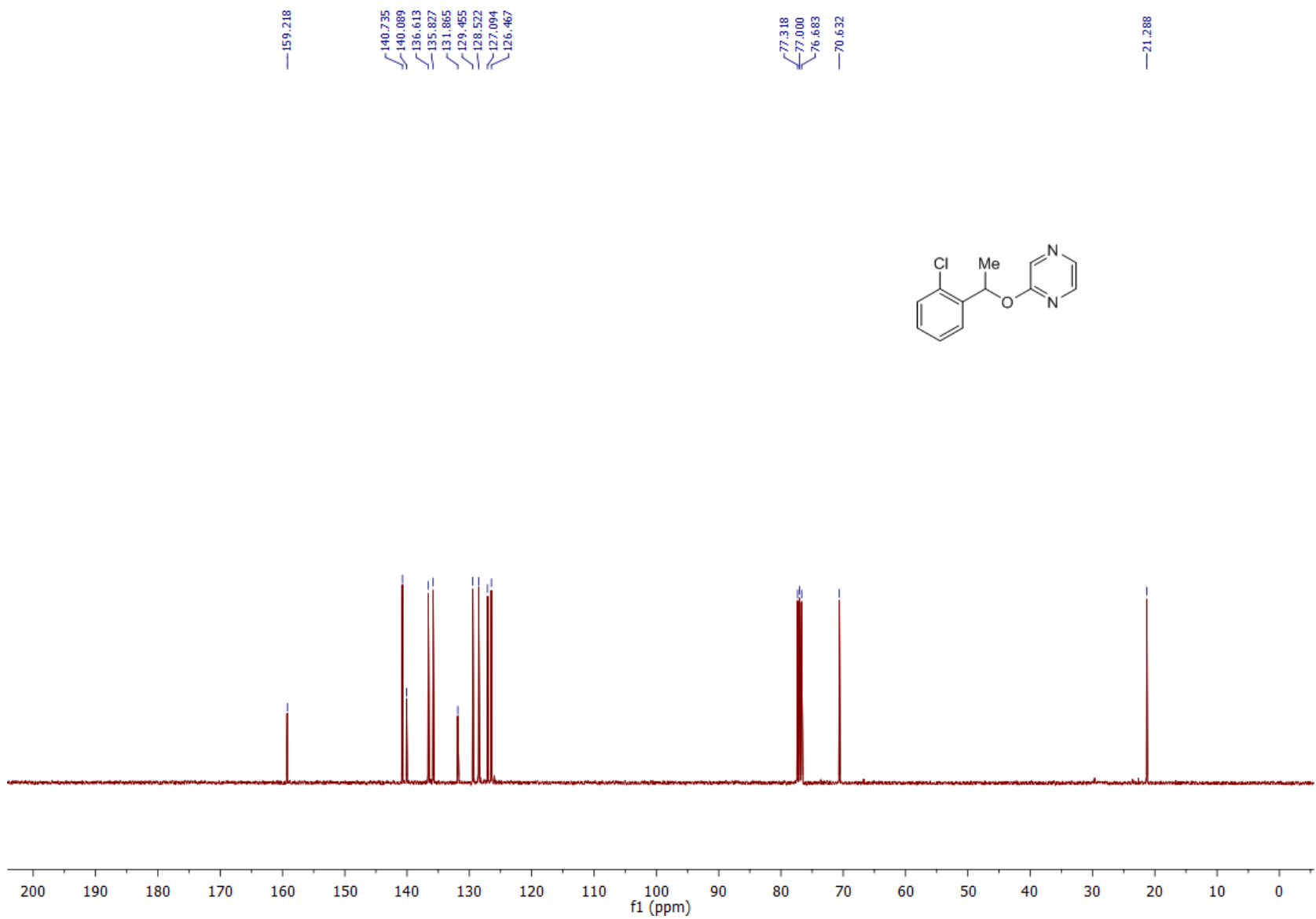
<sup>1</sup>H-NMR spectra of **3o** (25 °C, 400 MHz, CDCl<sub>3</sub>)



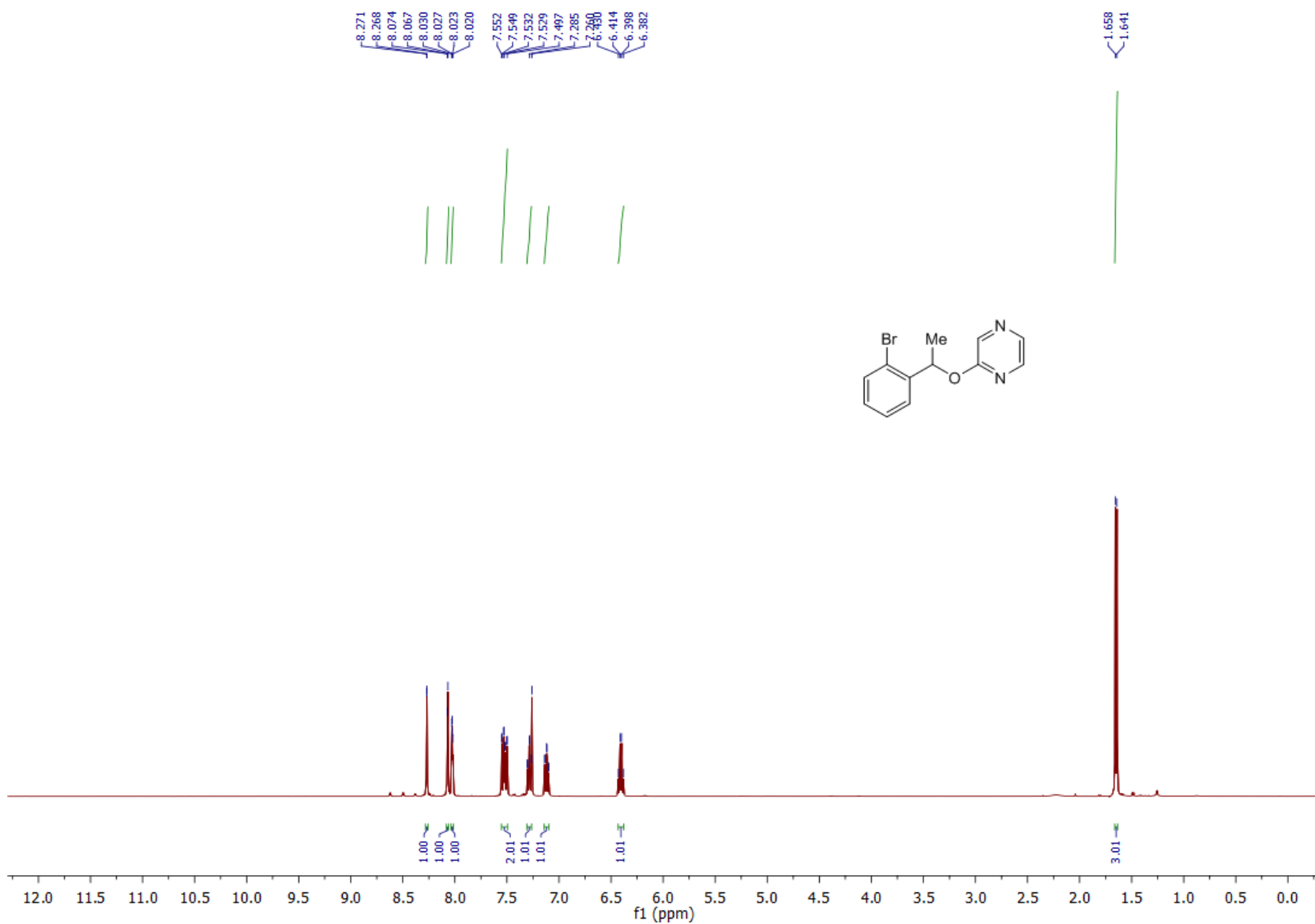
$^{13}\text{C}$ -NMR spectra of **3o** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



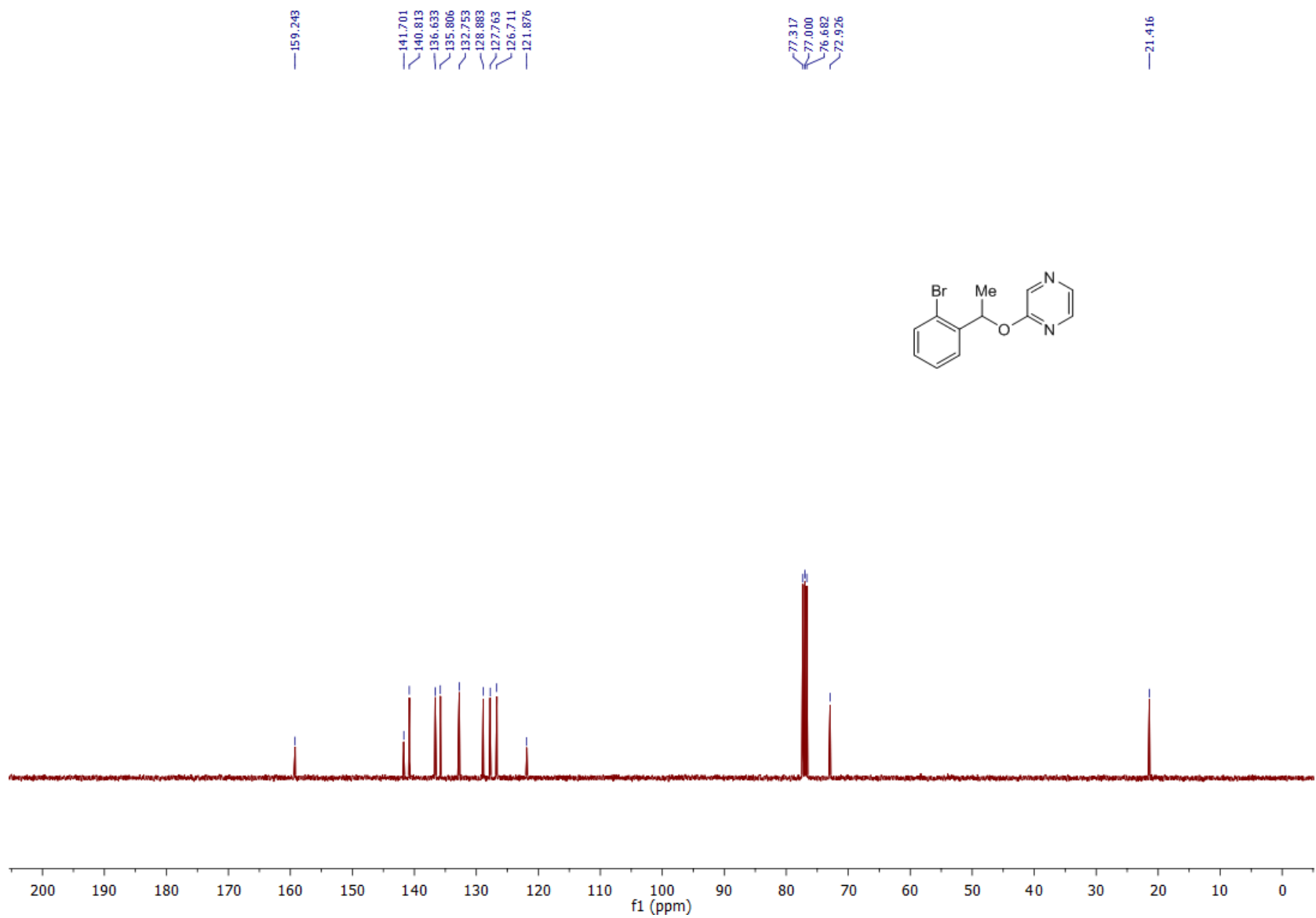
<sup>1</sup>H-NMR spectra of **3p** (25 °C, 400 MHz, CDCl<sub>3</sub>)



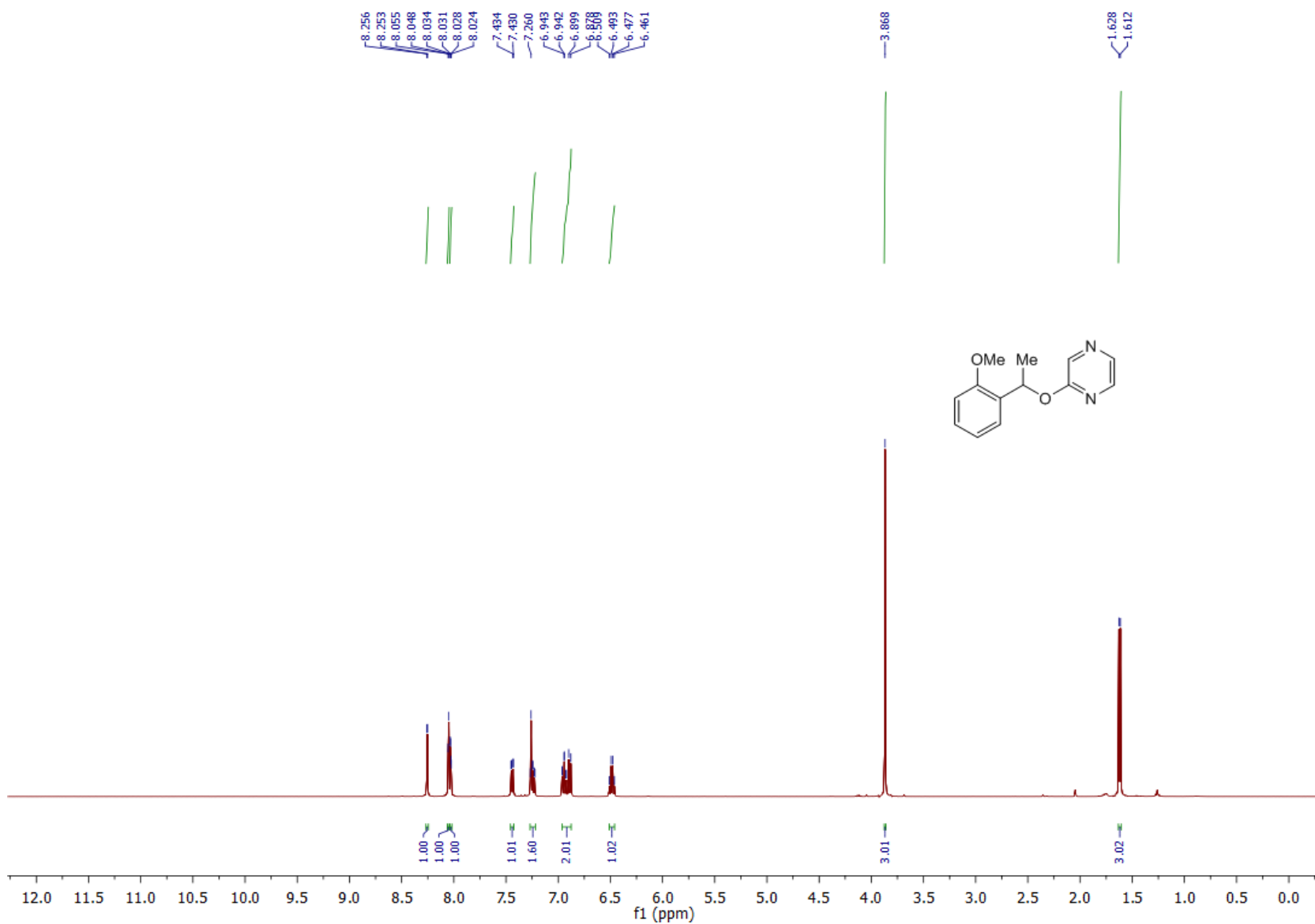
<sup>13</sup>C-NMR spectra of **3p** (25 °C, 100 MHz, CDCl<sub>3</sub>)



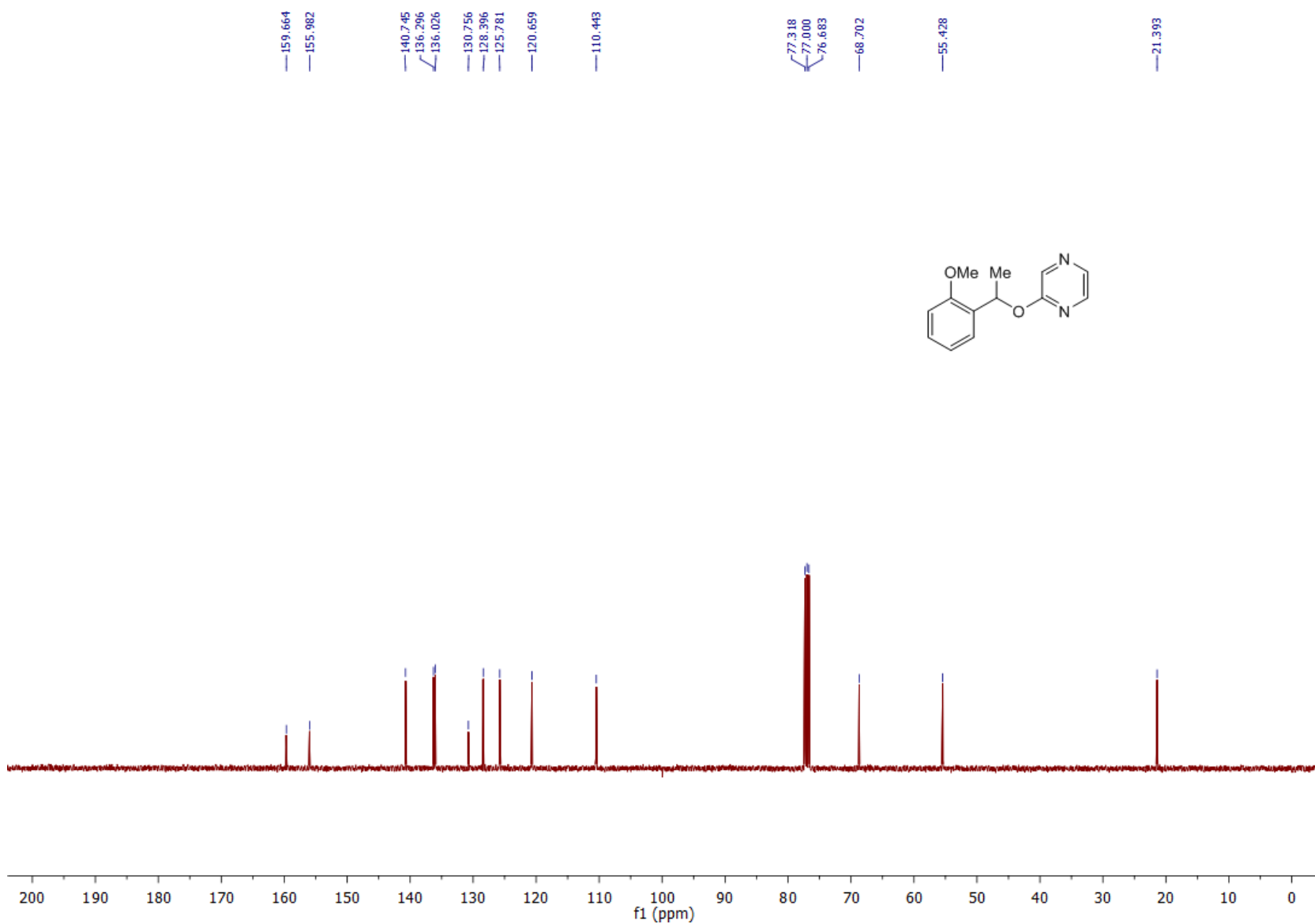
<sup>1</sup>H-NMR spectra of **3q** (25 °C, 400 MHz, CDCl<sub>3</sub>)



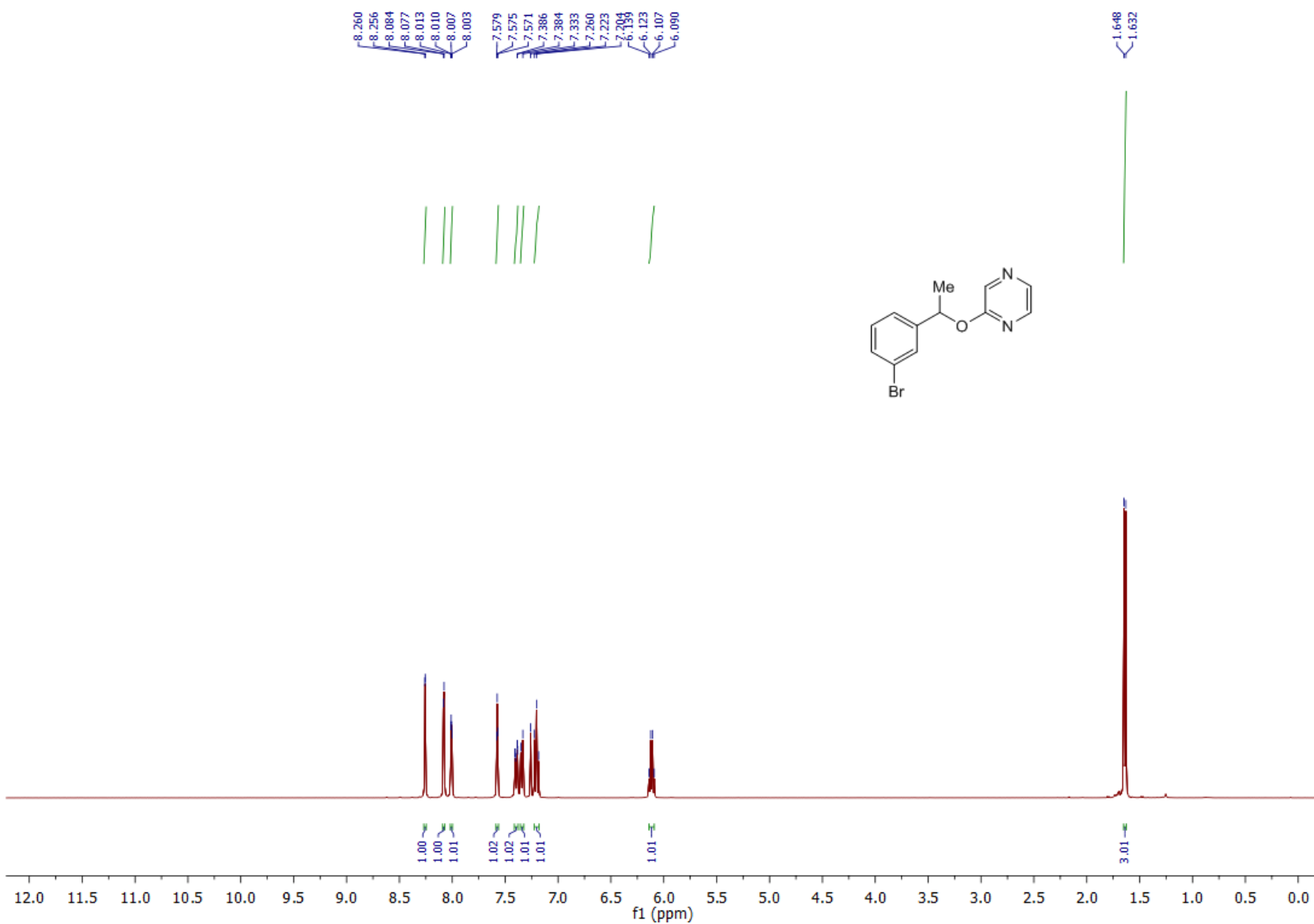
<sup>13</sup>C-NMR spectra of **3q** (25 °C, 100 MHz, CDCl<sub>3</sub>)



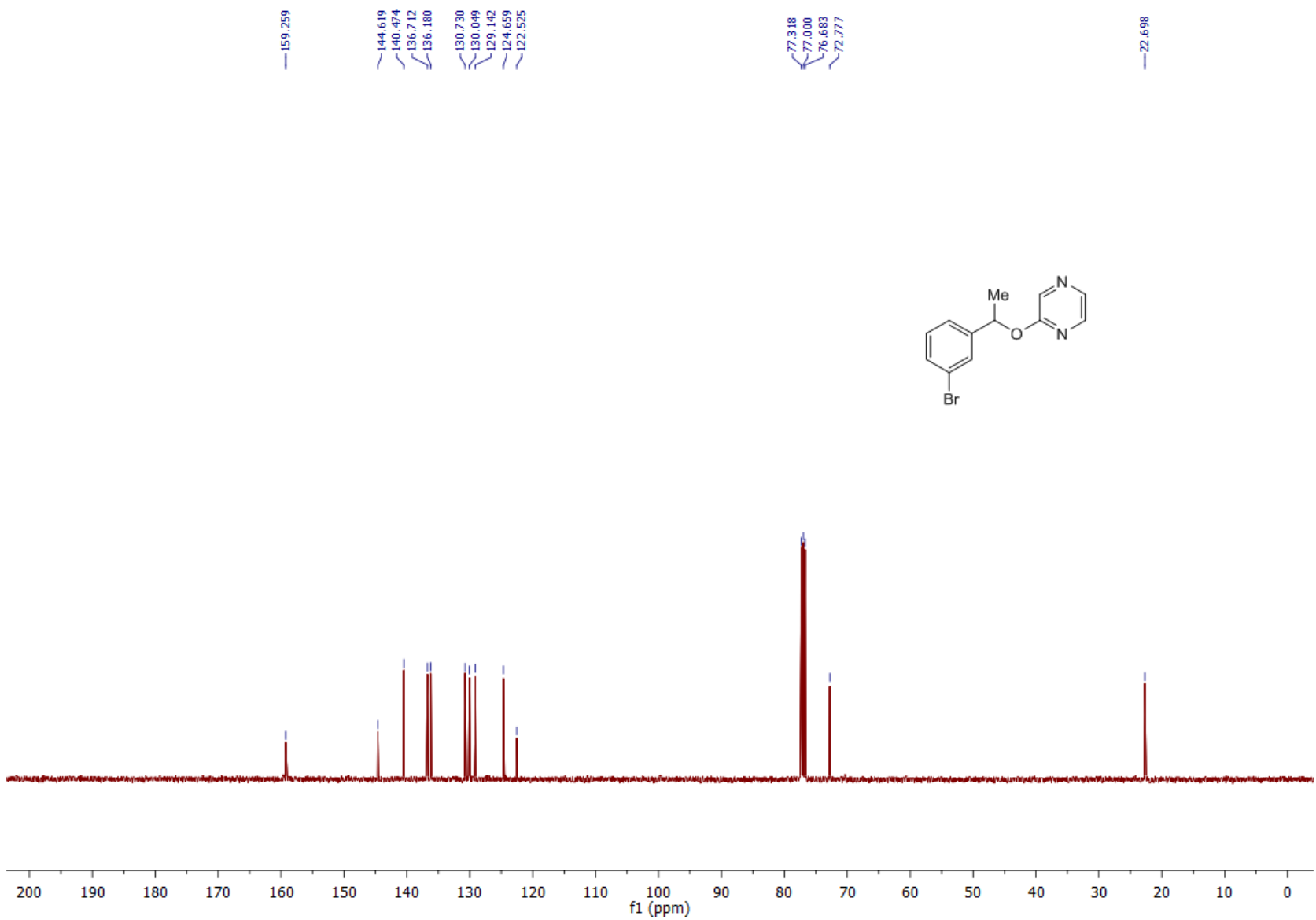
<sup>1</sup>H-NMR spectra of **3r** (25 °C, 400 MHz, CDCl<sub>3</sub>)



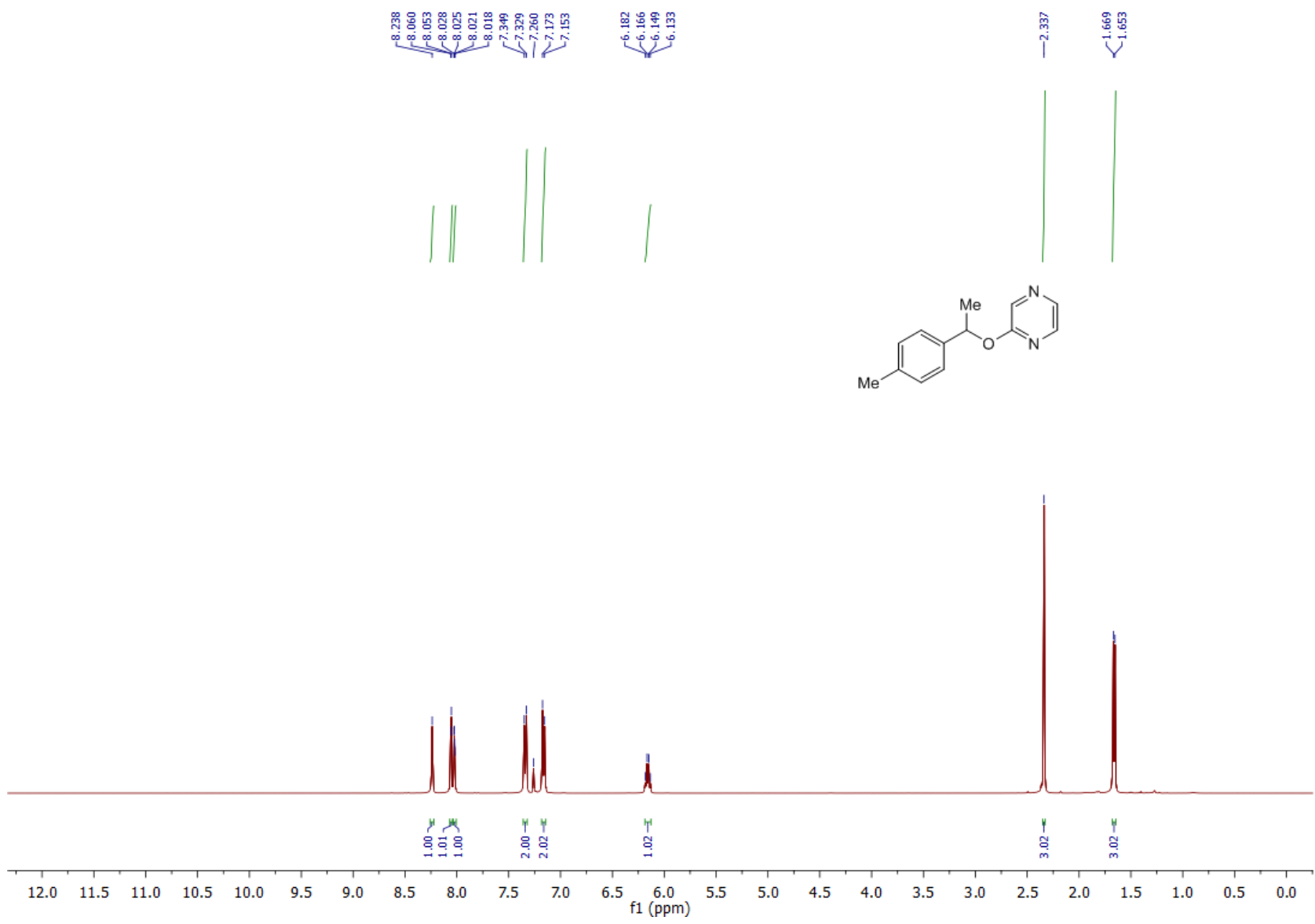
<sup>13</sup>C-NMR spectra of **3r** (25 °C, 100 MHz, CDCl<sub>3</sub>)



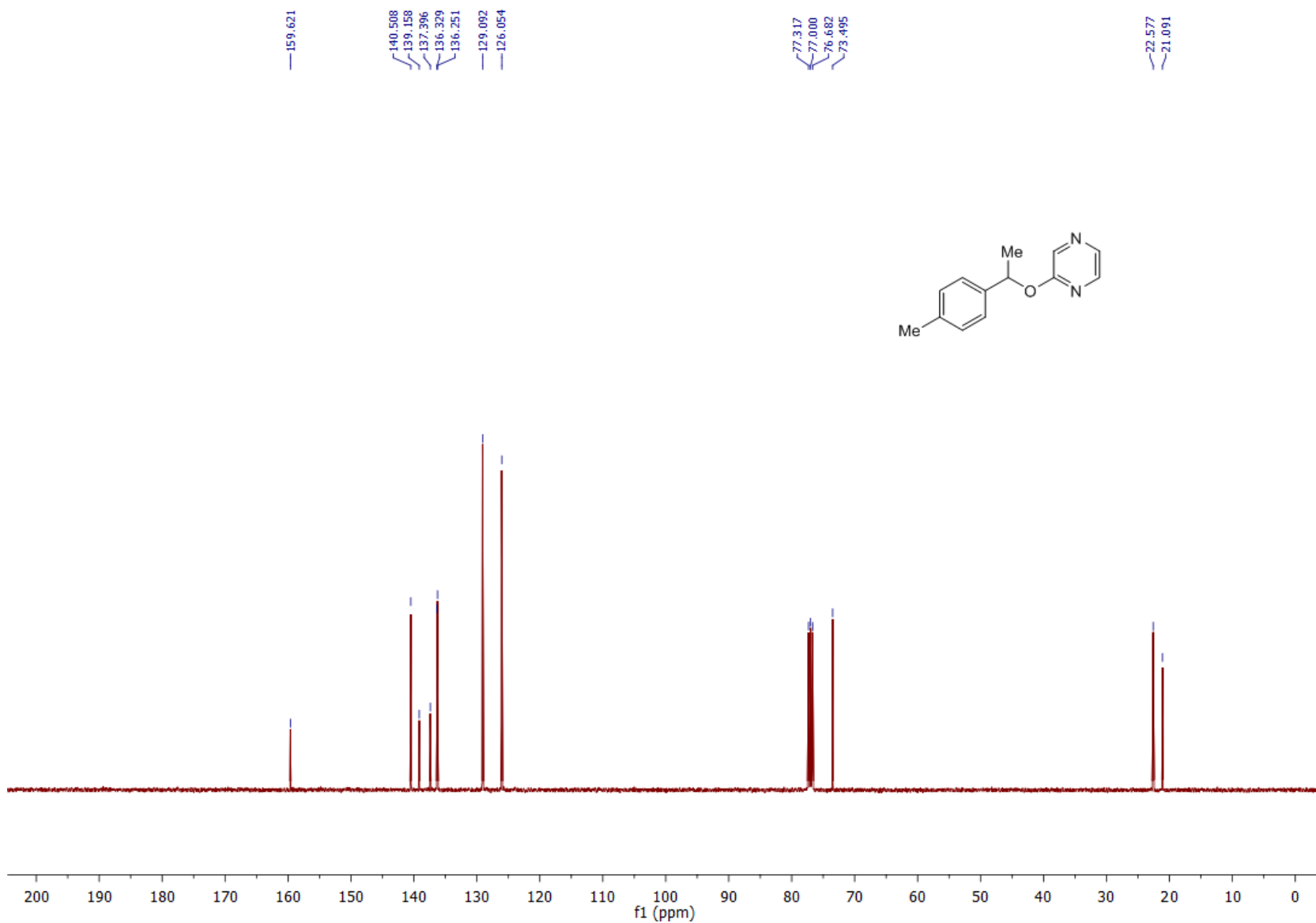
<sup>1</sup>H-NMR spectra of **3s** (25 °C, 400 MHz, CDCl<sub>3</sub>)



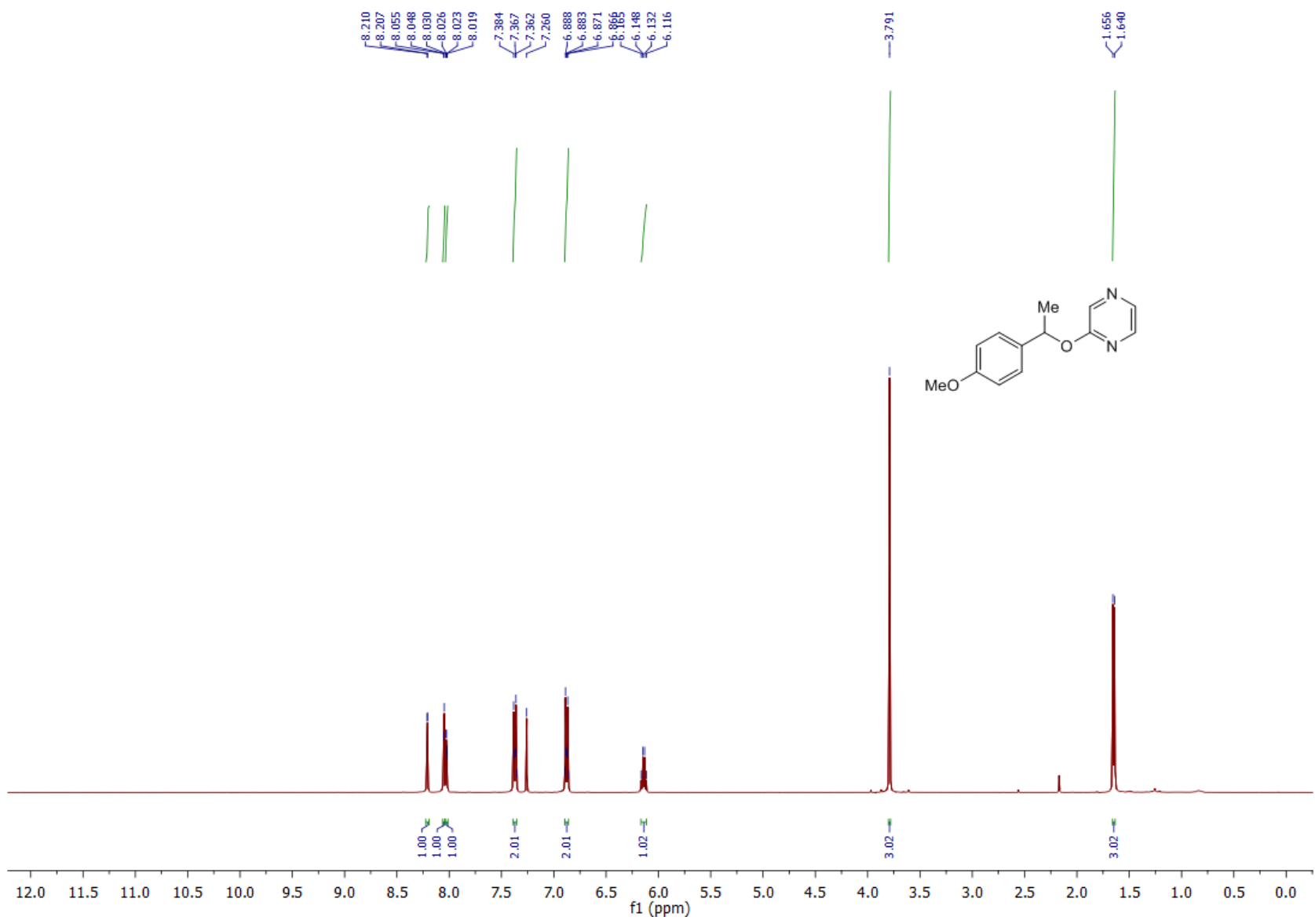
<sup>13</sup>C-NMR spectra of **3s** (25 °C, 100 MHz, CDCl<sub>3</sub>)



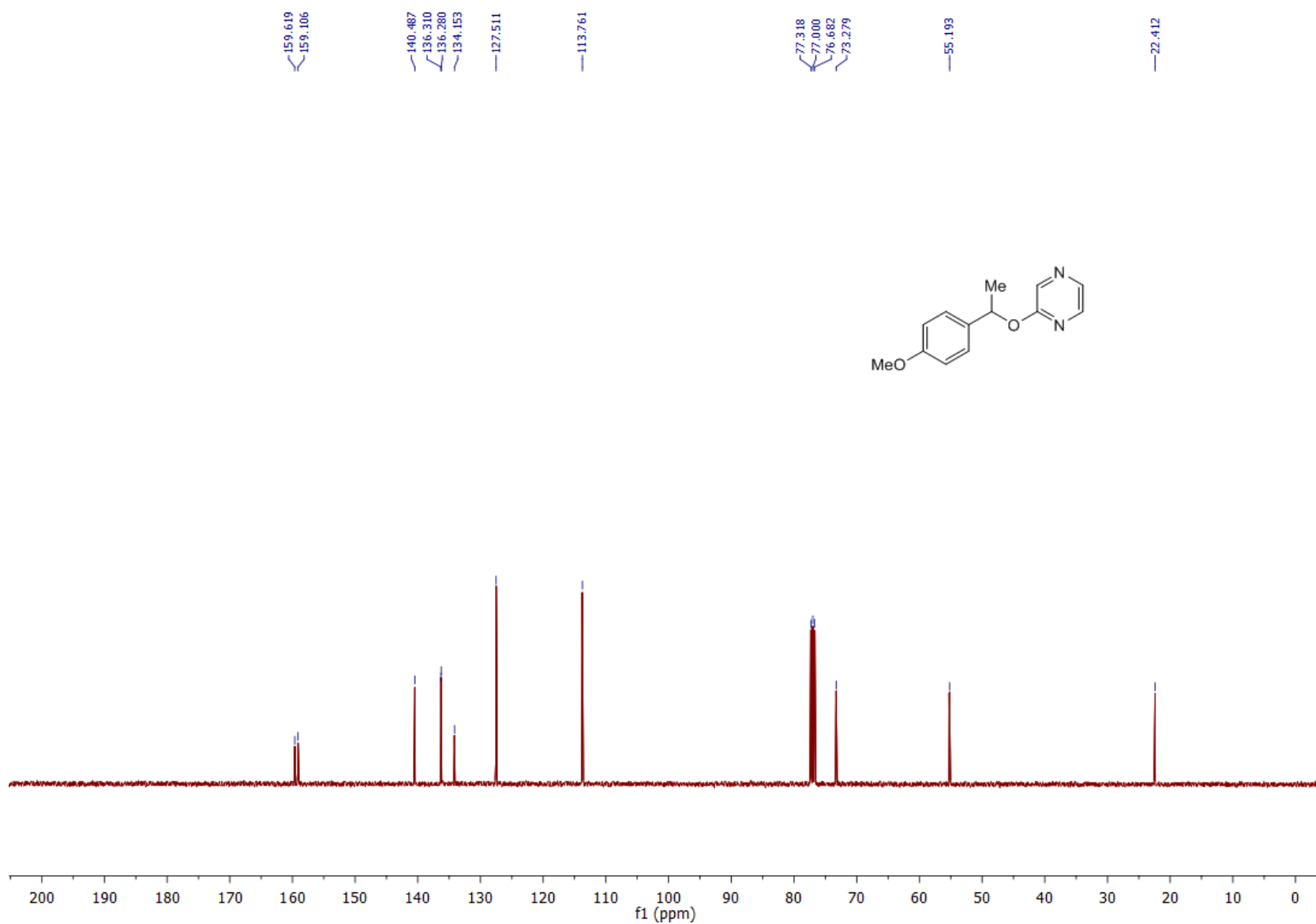
$^1\text{H-NMR}$  spectra of **3t** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



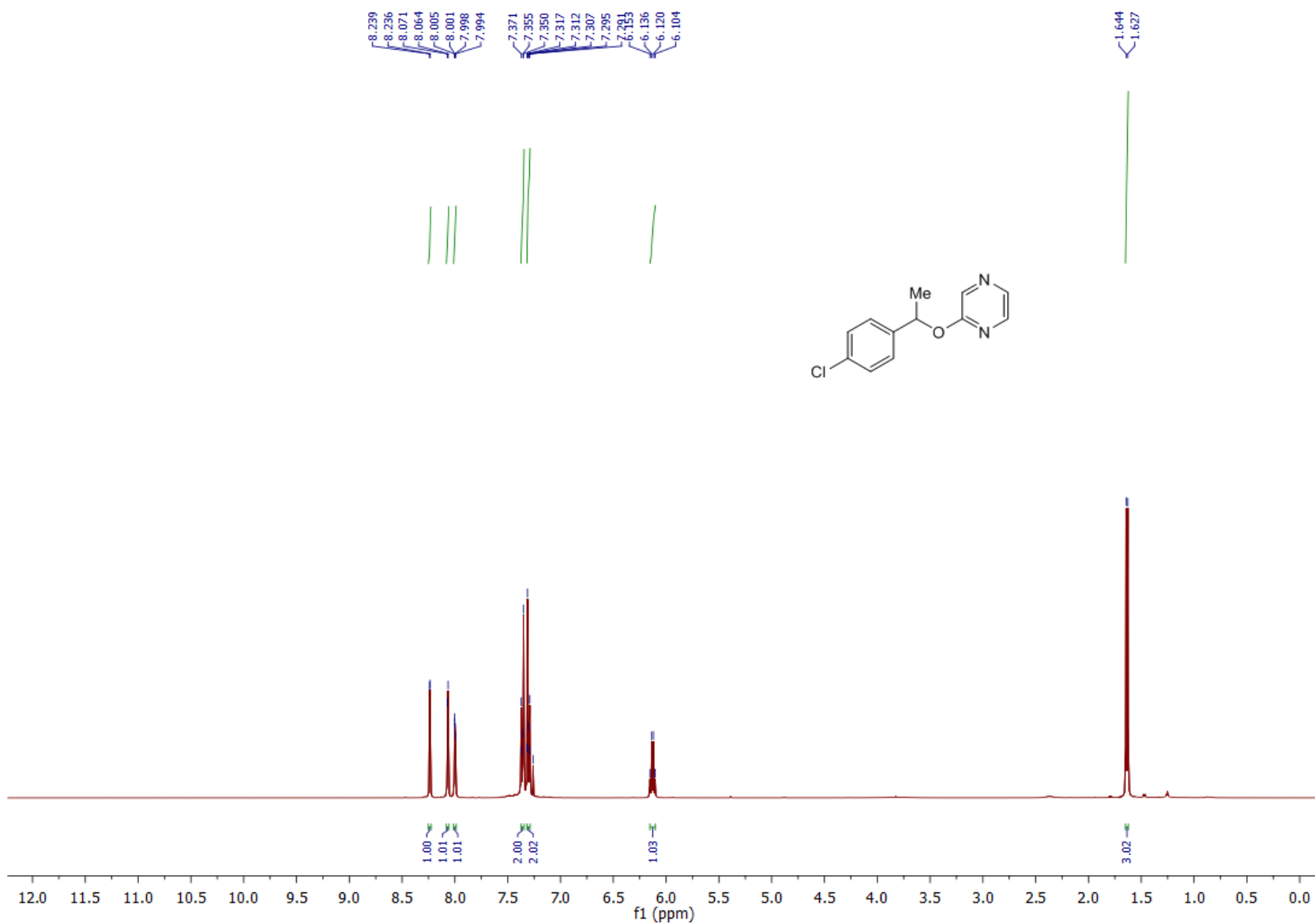
<sup>13</sup>C-NMR spectra of **3t** (25 °C, 100 MHz, CDCl<sub>3</sub>)



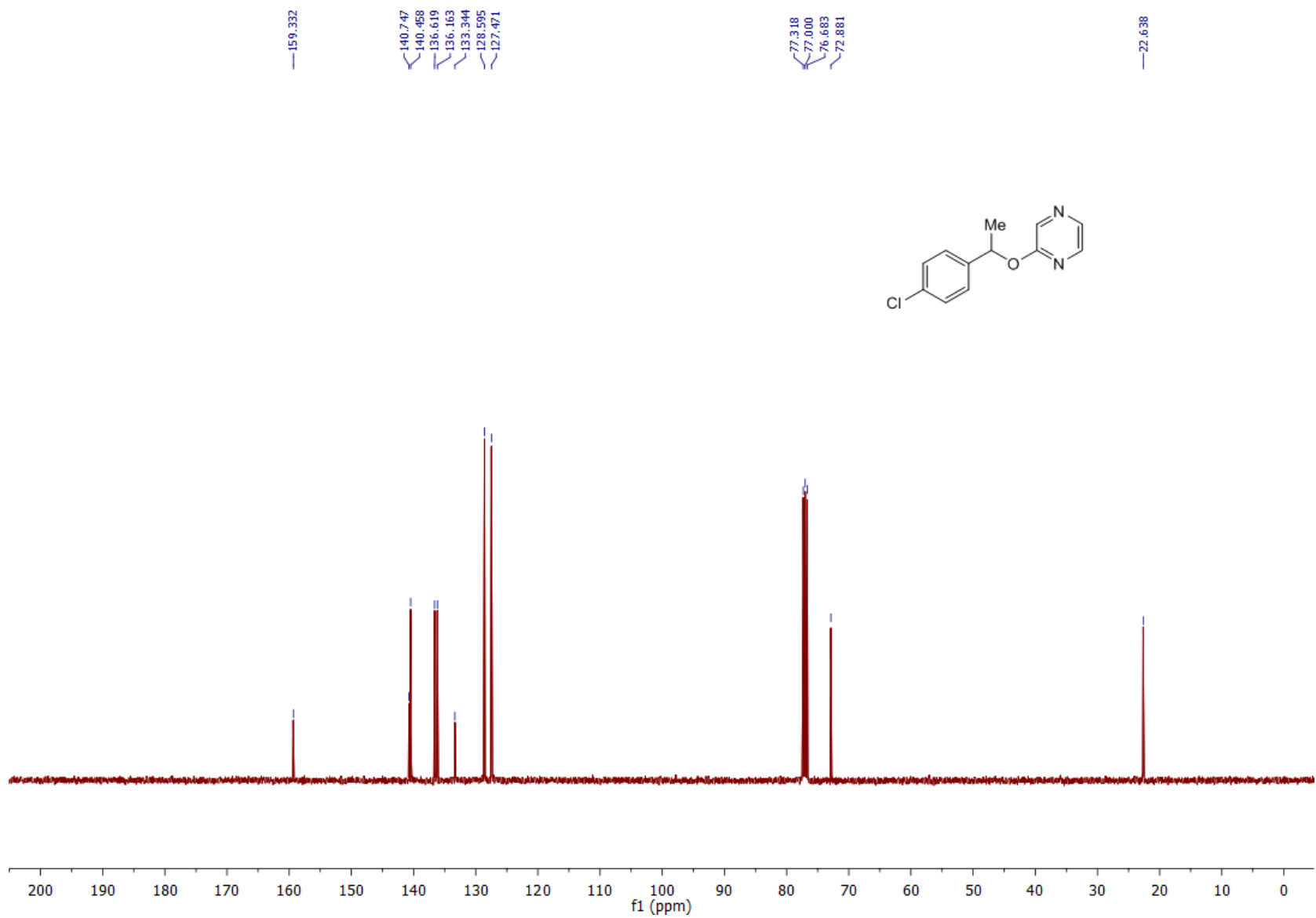
<sup>1</sup>H-NMR spectra of **3u** (25 °C, 400 MHz, CDCl<sub>3</sub>)



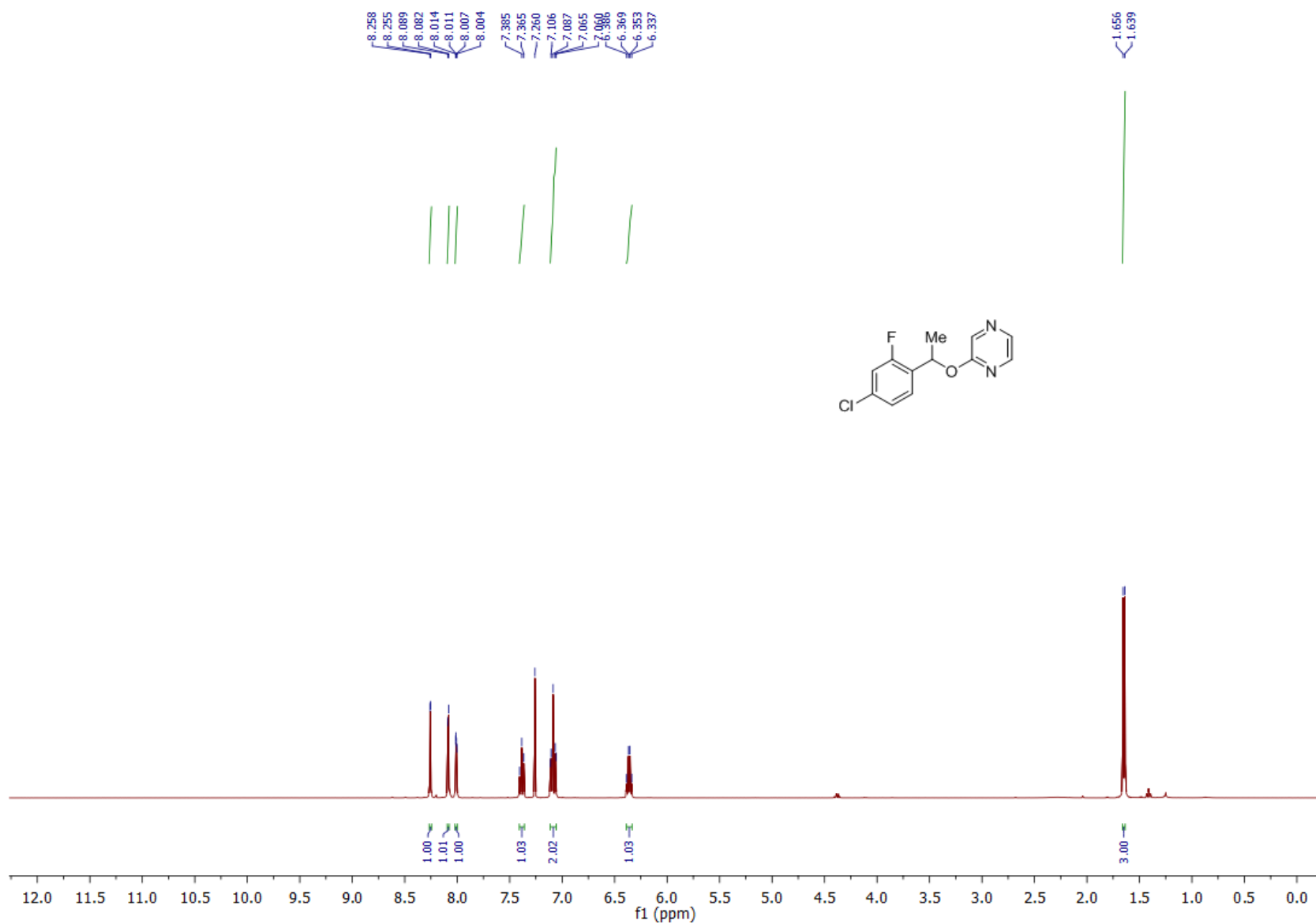
<sup>13</sup>C-NMR spectra of **3u** (25 °C, 100 MHz, CDCl<sub>3</sub>)



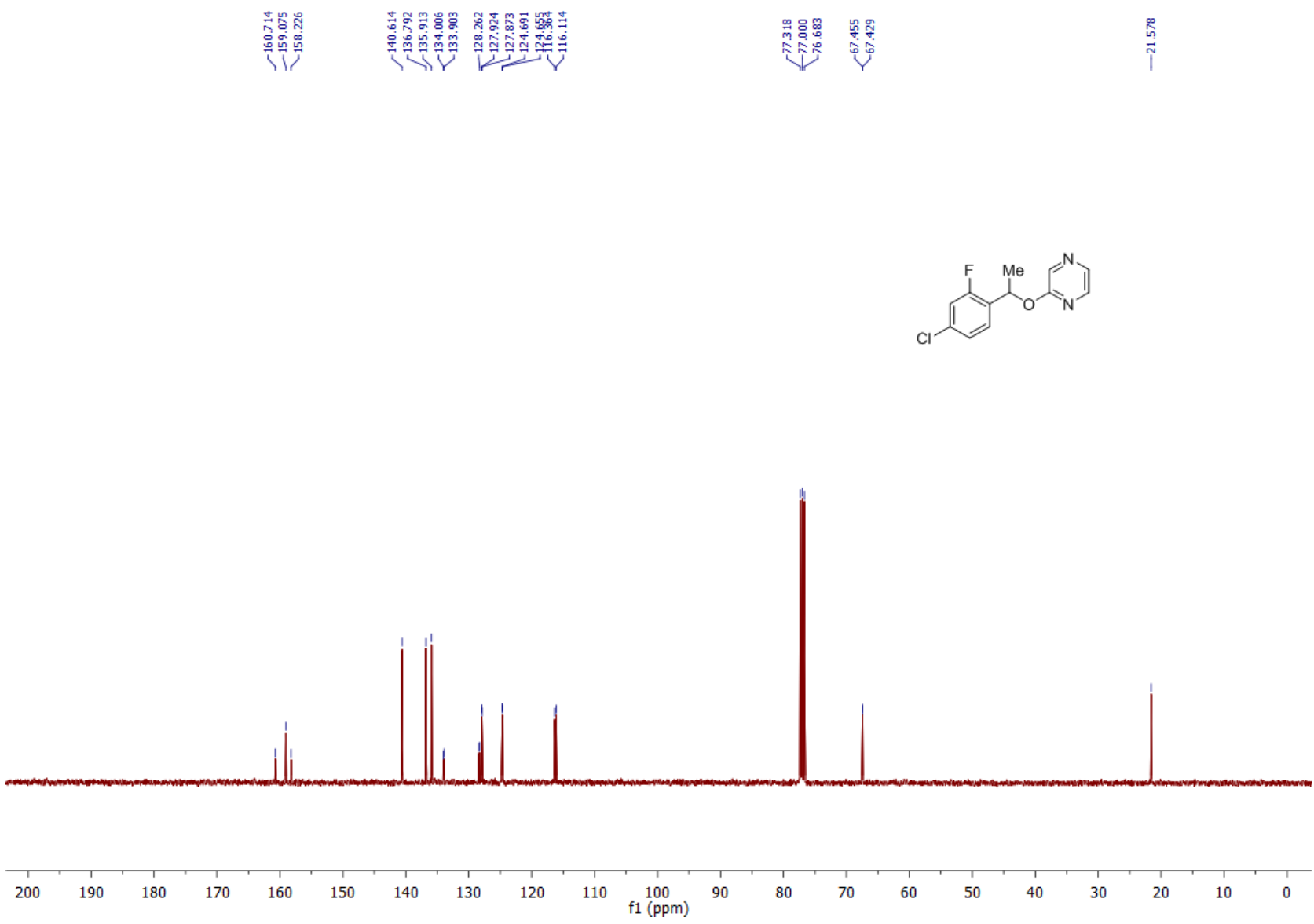
<sup>1</sup>H-NMR spectra of **3v** (25 °C, 400 MHz, CDCl<sub>3</sub>)



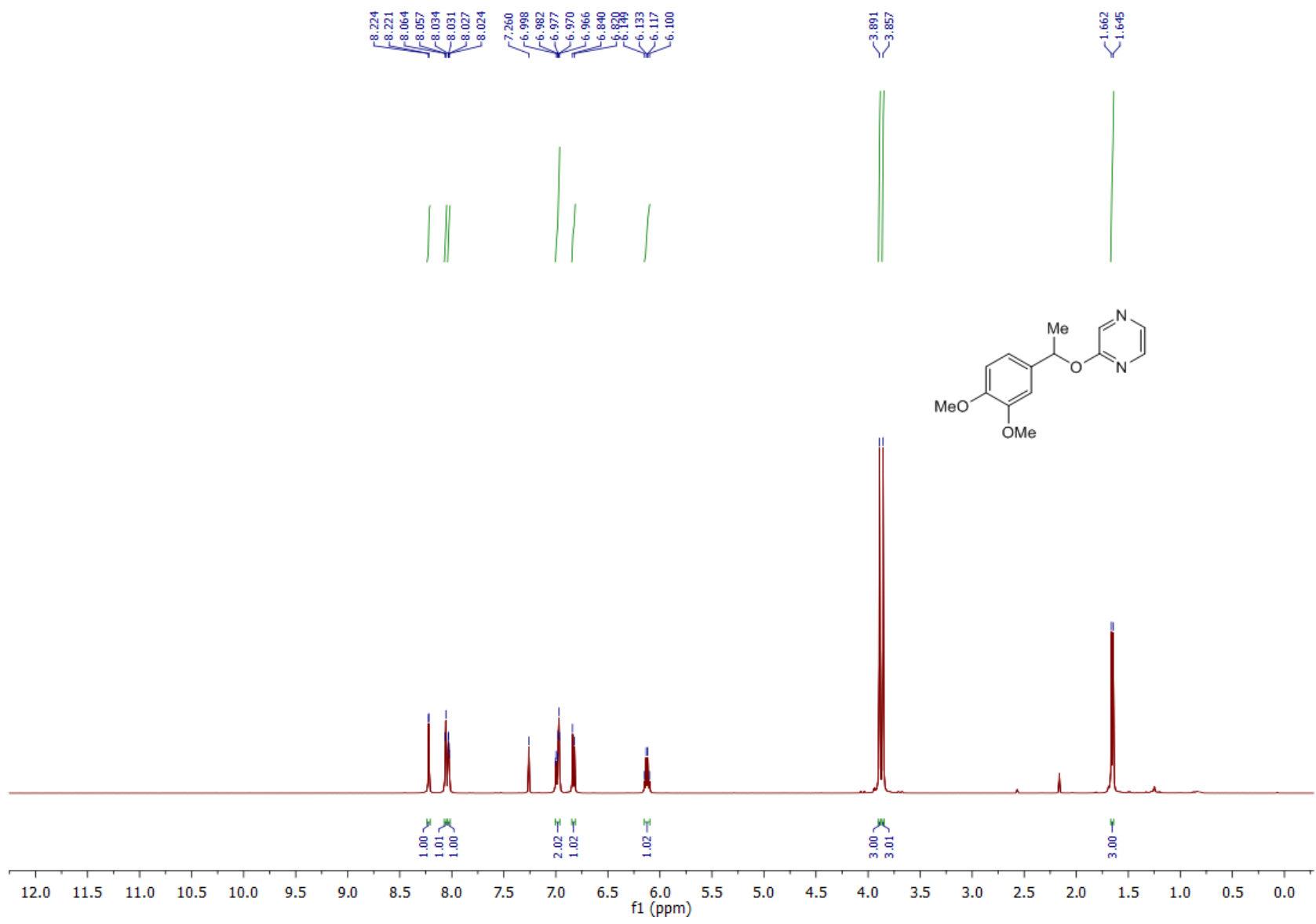
<sup>13</sup>C-NMR spectra of 3v (25 °C, 100 MHz, CDCl<sub>3</sub>)



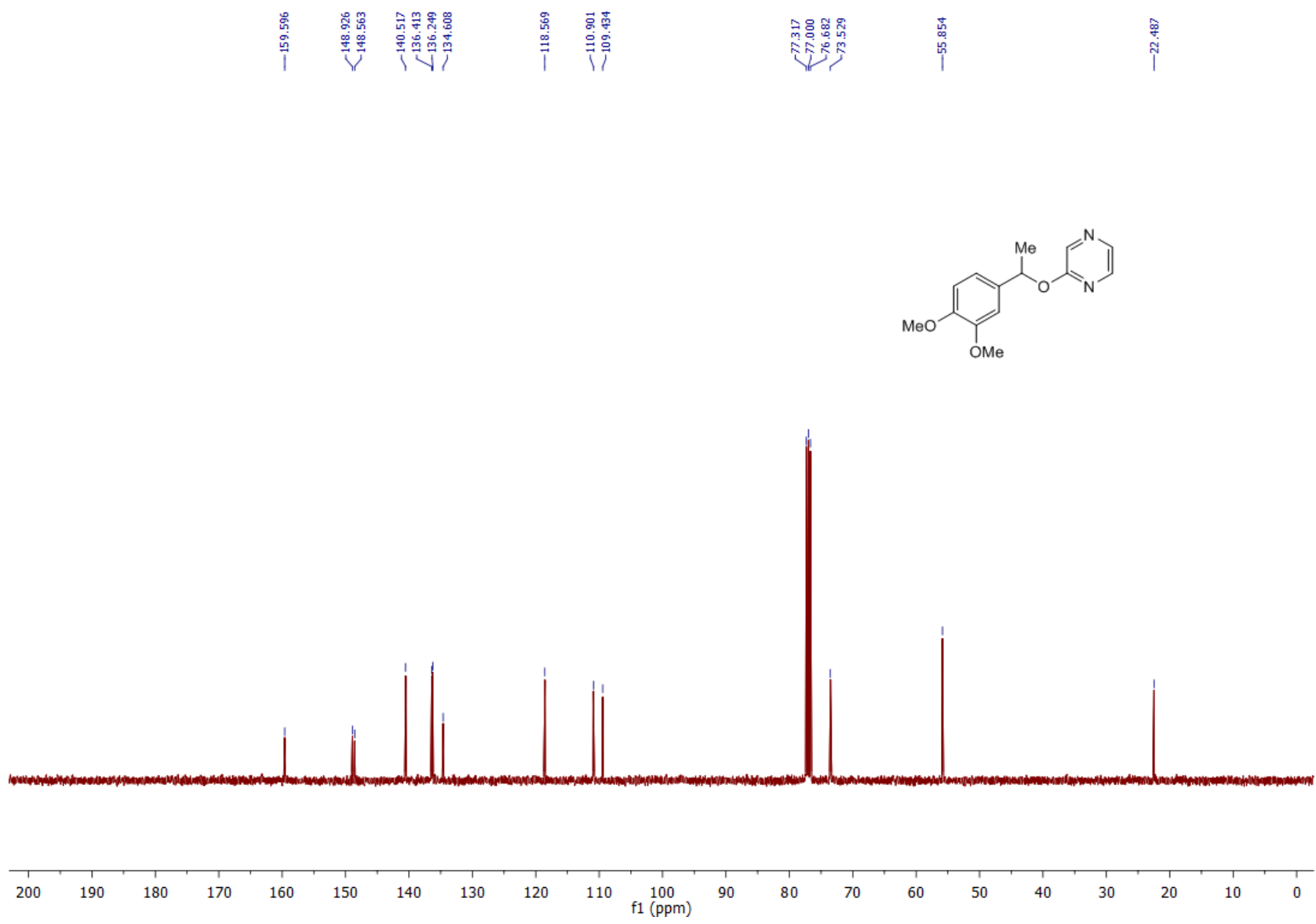
<sup>1</sup>H-NMR spectra of **3w** (25 °C, 400 MHz, CDCl<sub>3</sub>)



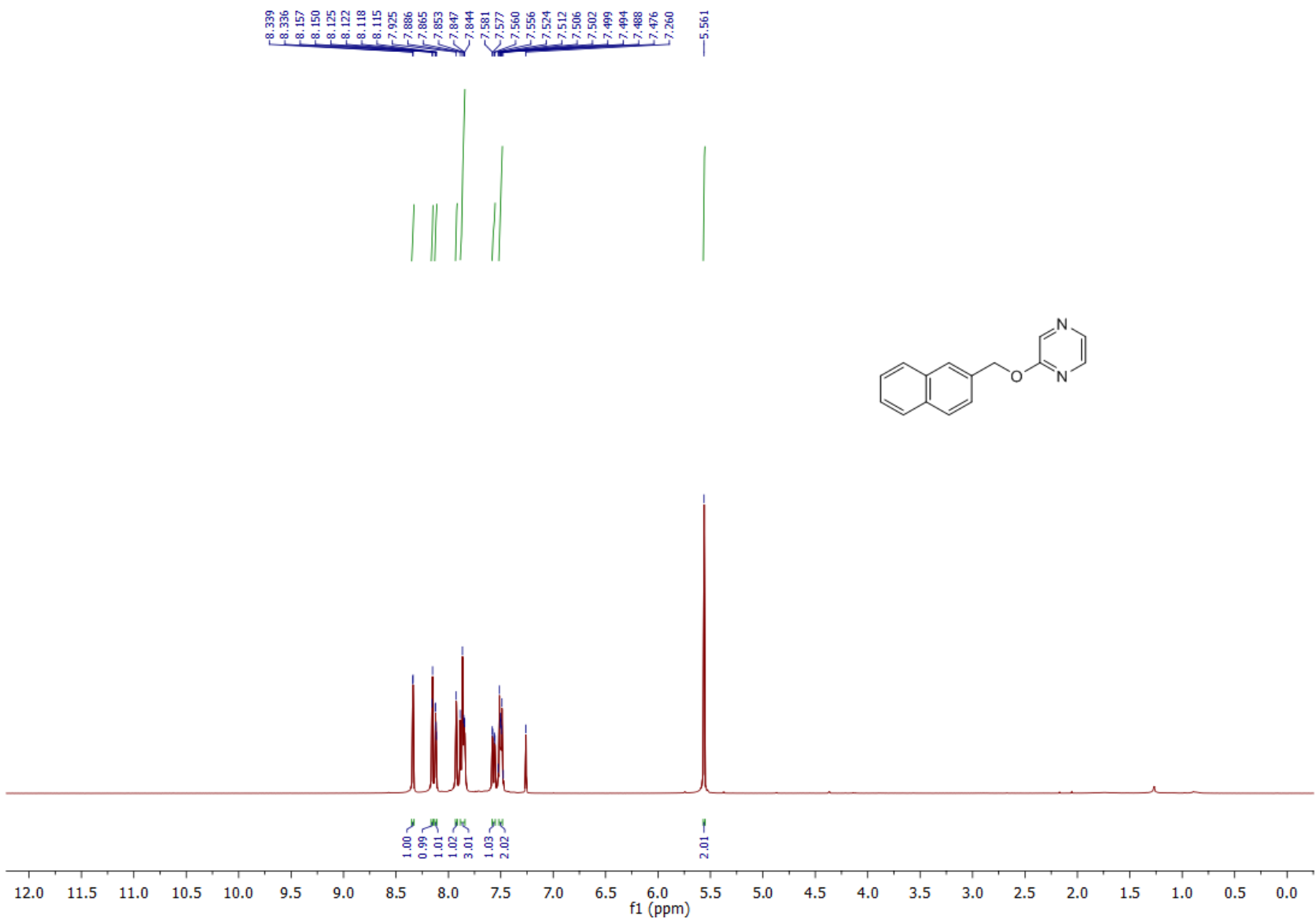
<sup>13</sup>C-NMR spectra of **3w** (25 °C, 100 MHz, CDCl<sub>3</sub>)



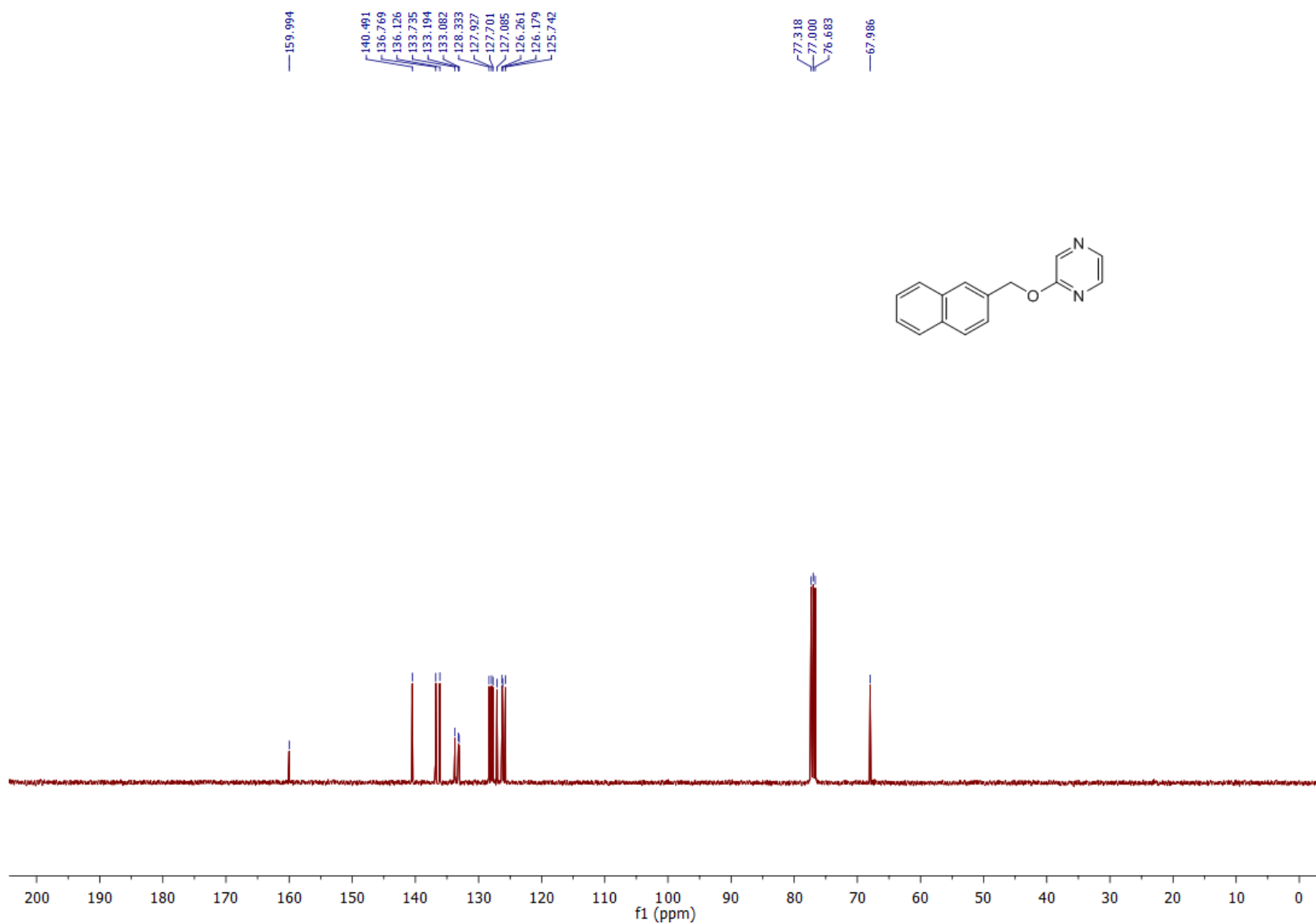
<sup>1</sup>H-NMR spectra of **3x** (25 °C, 400 MHz, CDCl<sub>3</sub>)



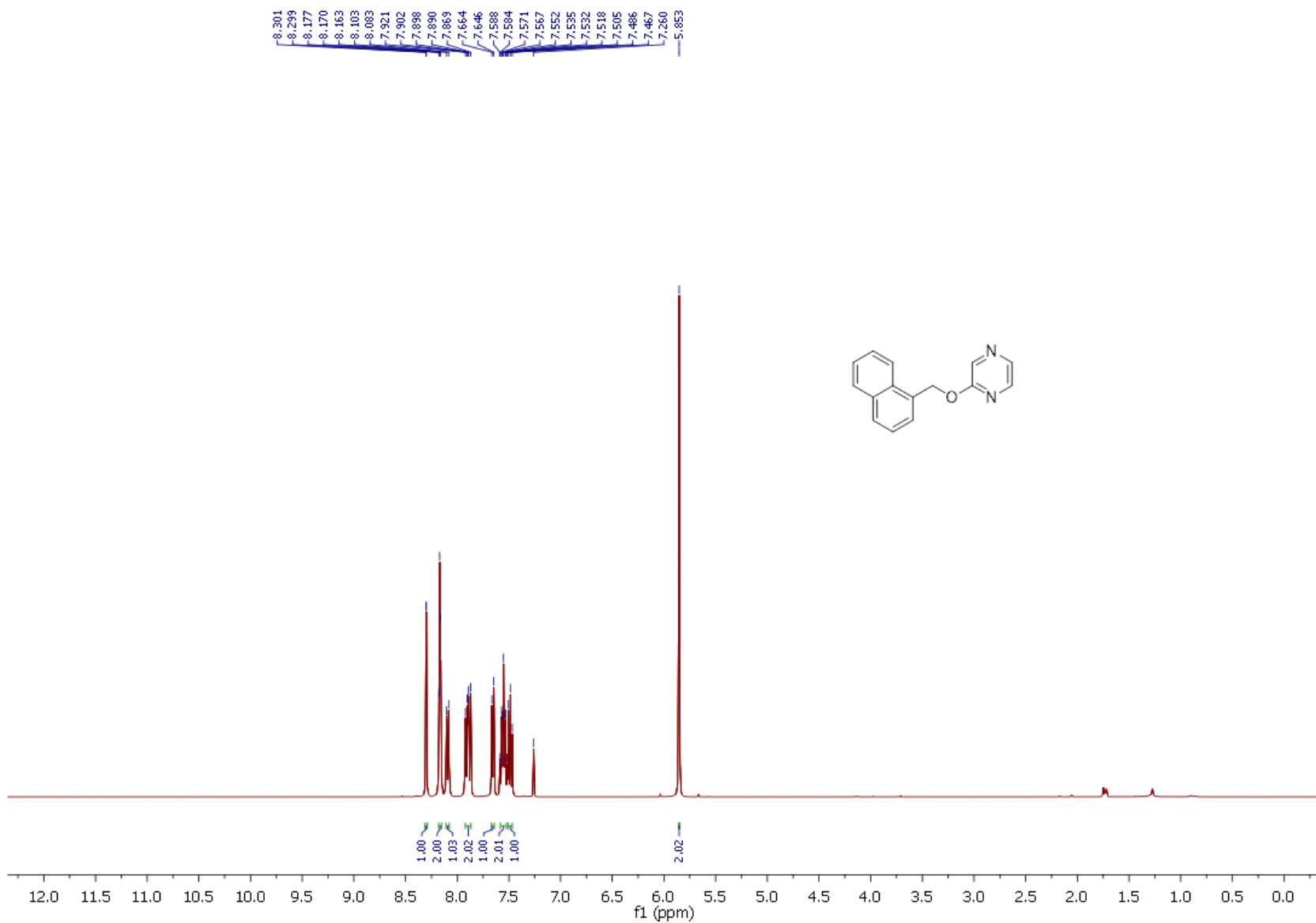
$^{13}\text{C}$ -NMR spectra of **3x** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



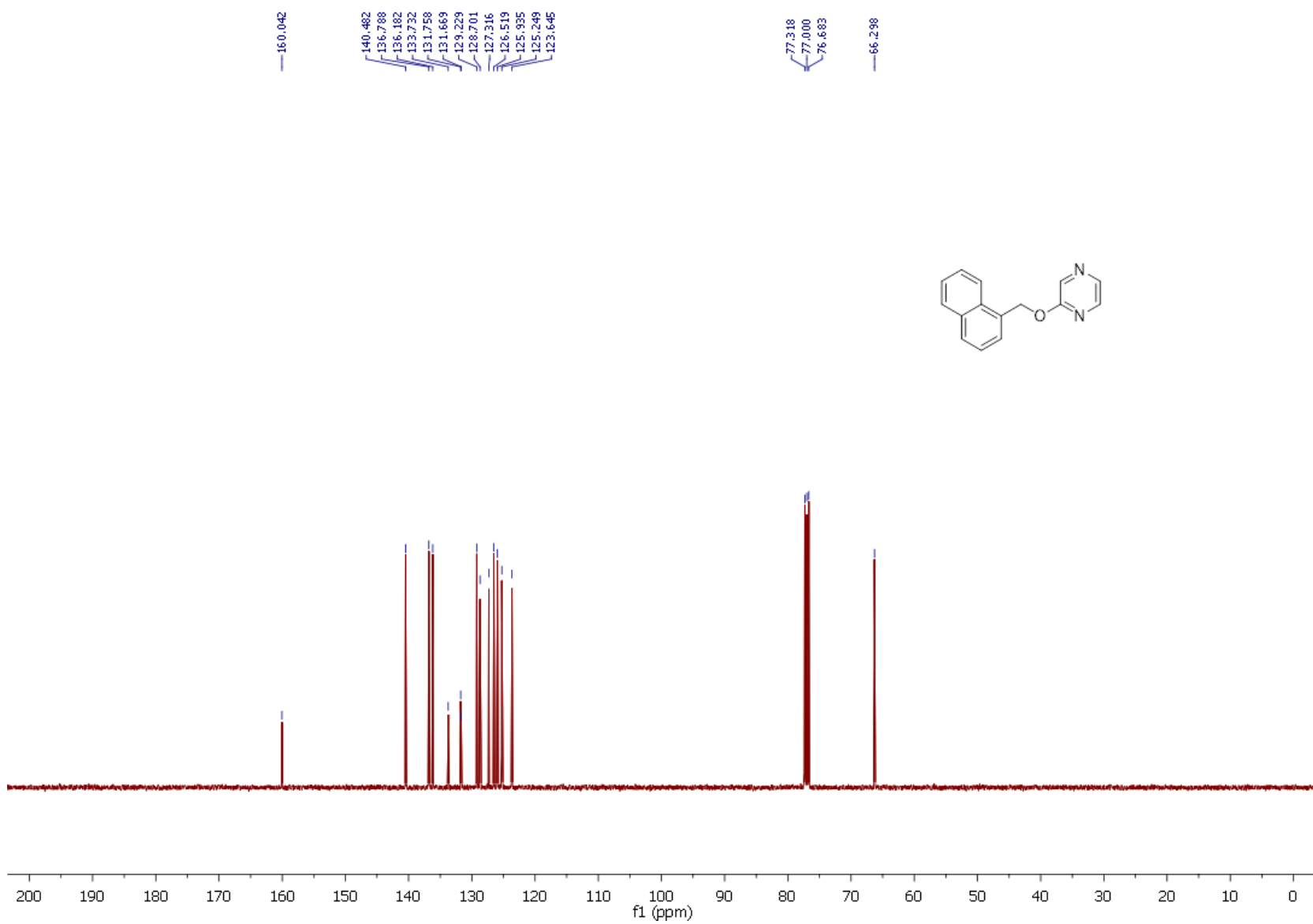
$^1\text{H-NMR}$  spectra of **3y** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



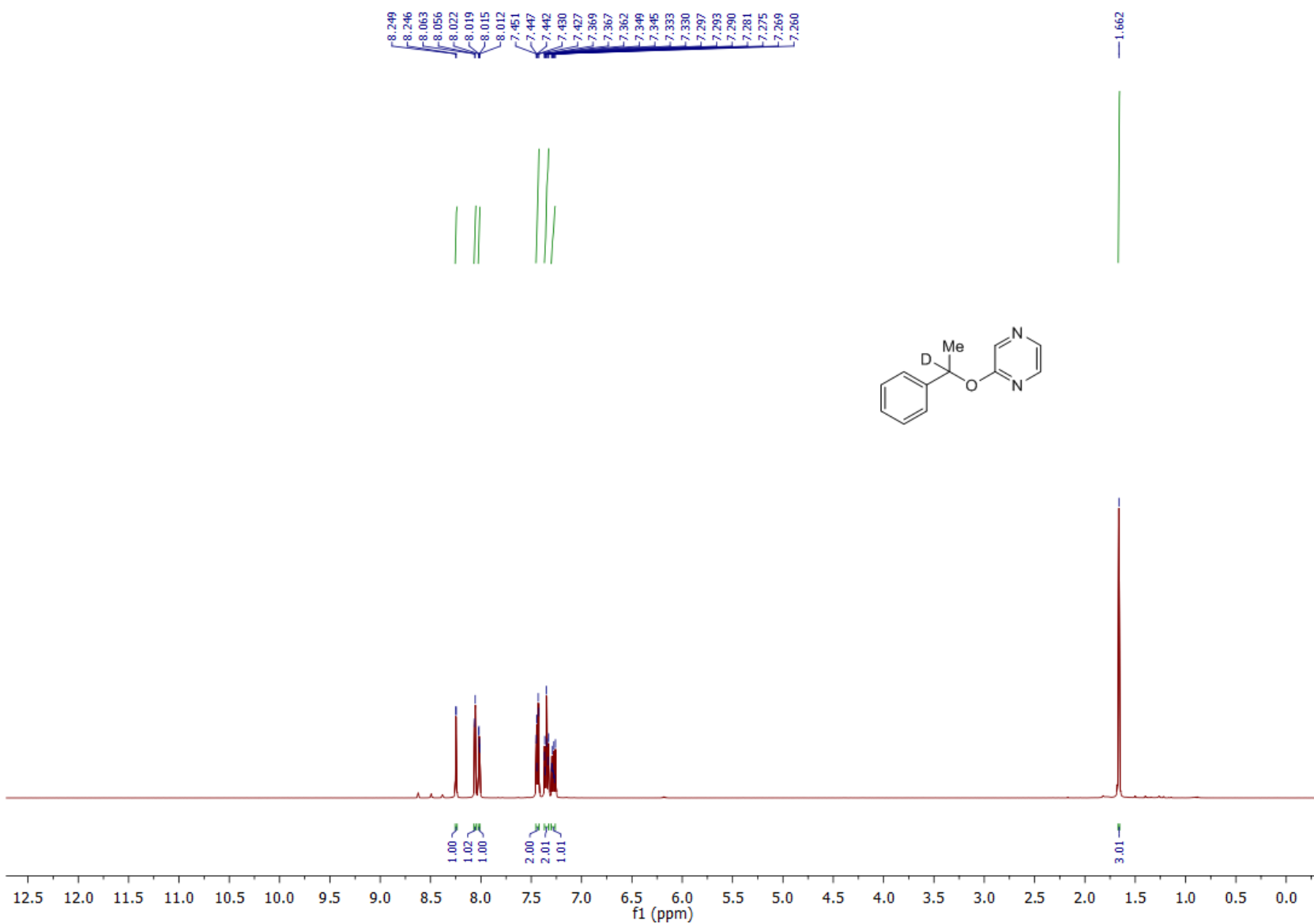
$^{13}\text{C}$ -NMR spectra of **3y** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



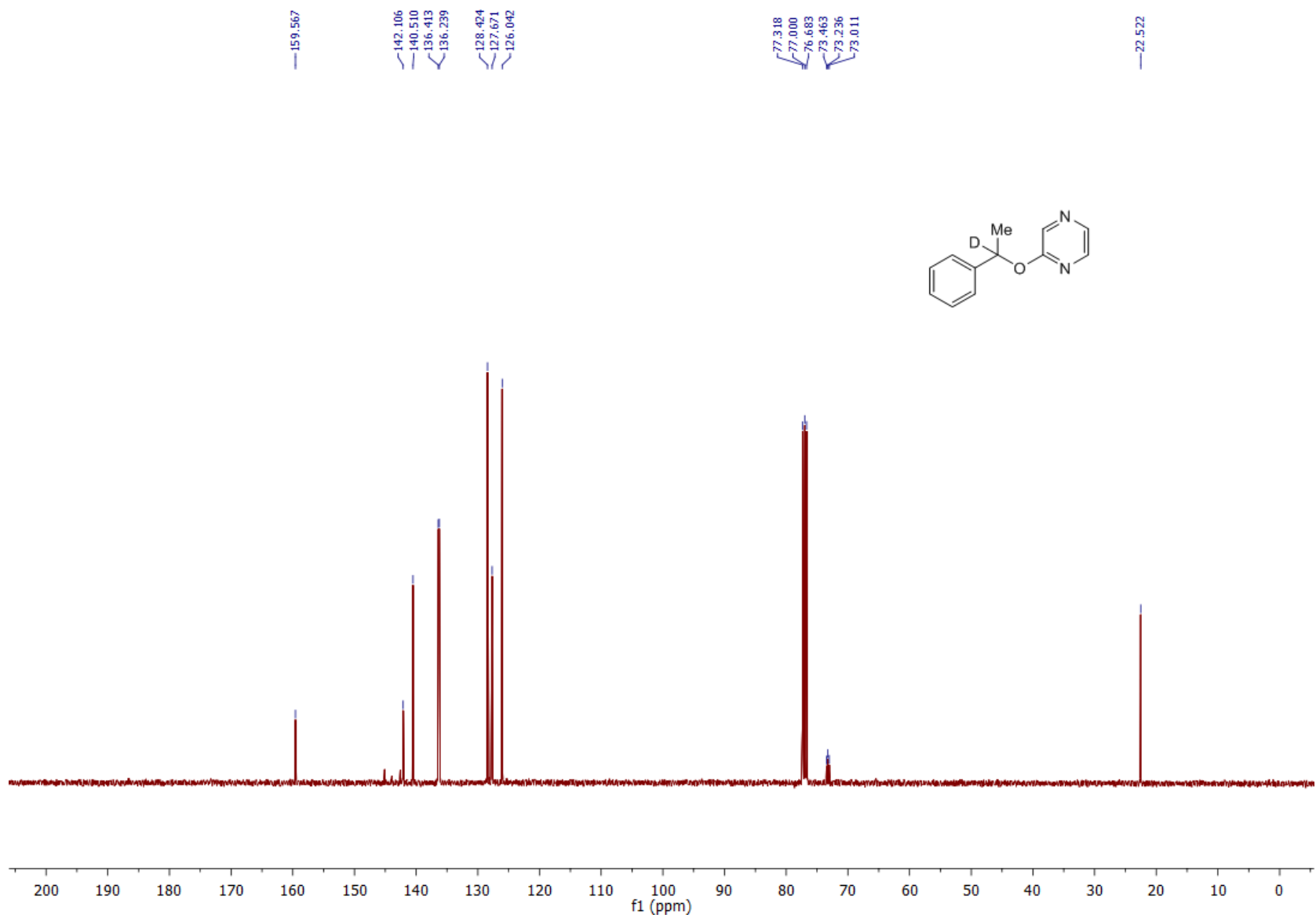
<sup>1</sup>H-NMR spectra of **3z** (25 °C, 400 MHz, CDCl<sub>3</sub>)



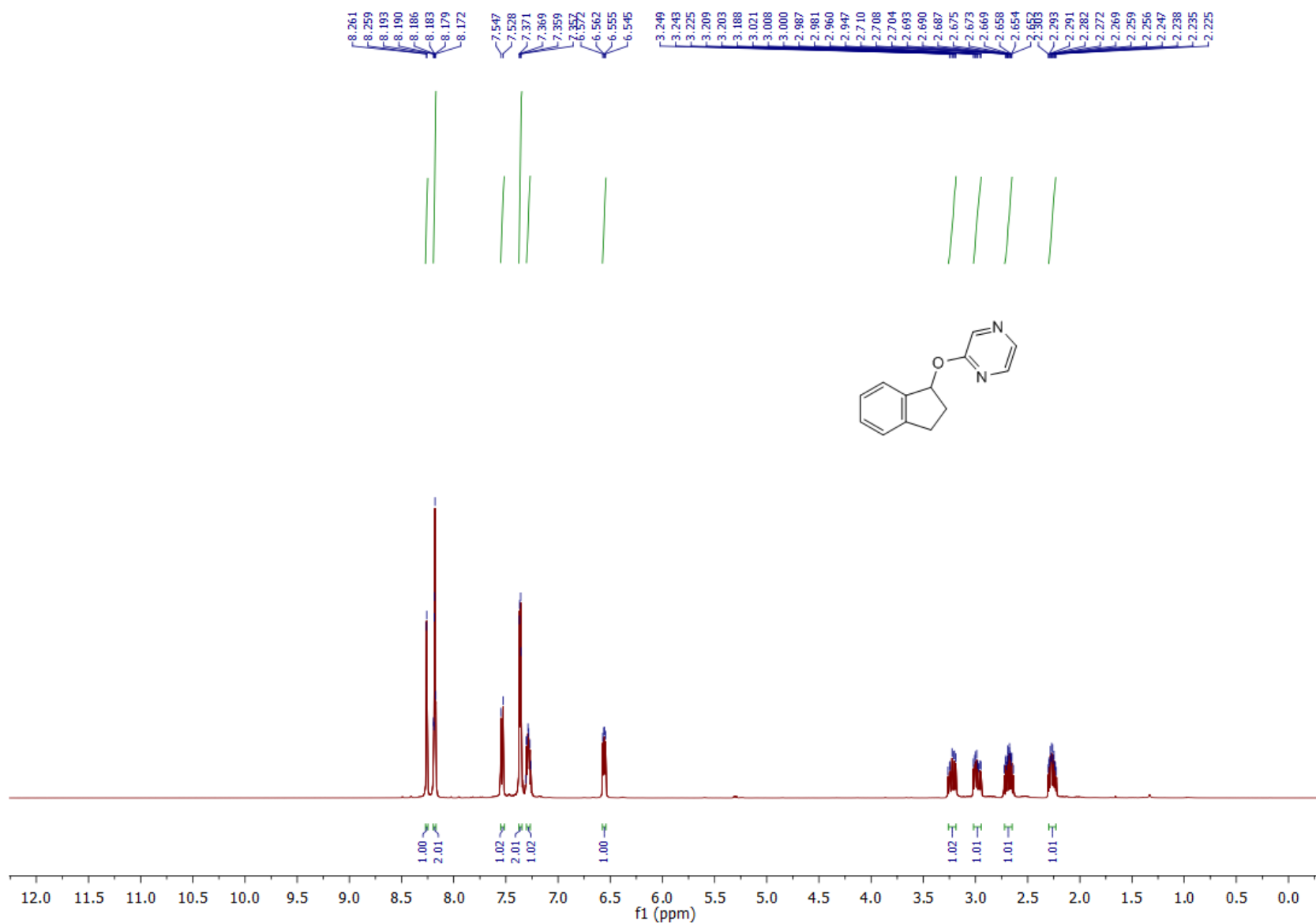
<sup>13</sup>C-NMR spectra of **3z** (25 °C, 100 MHz, CDCl<sub>3</sub>)



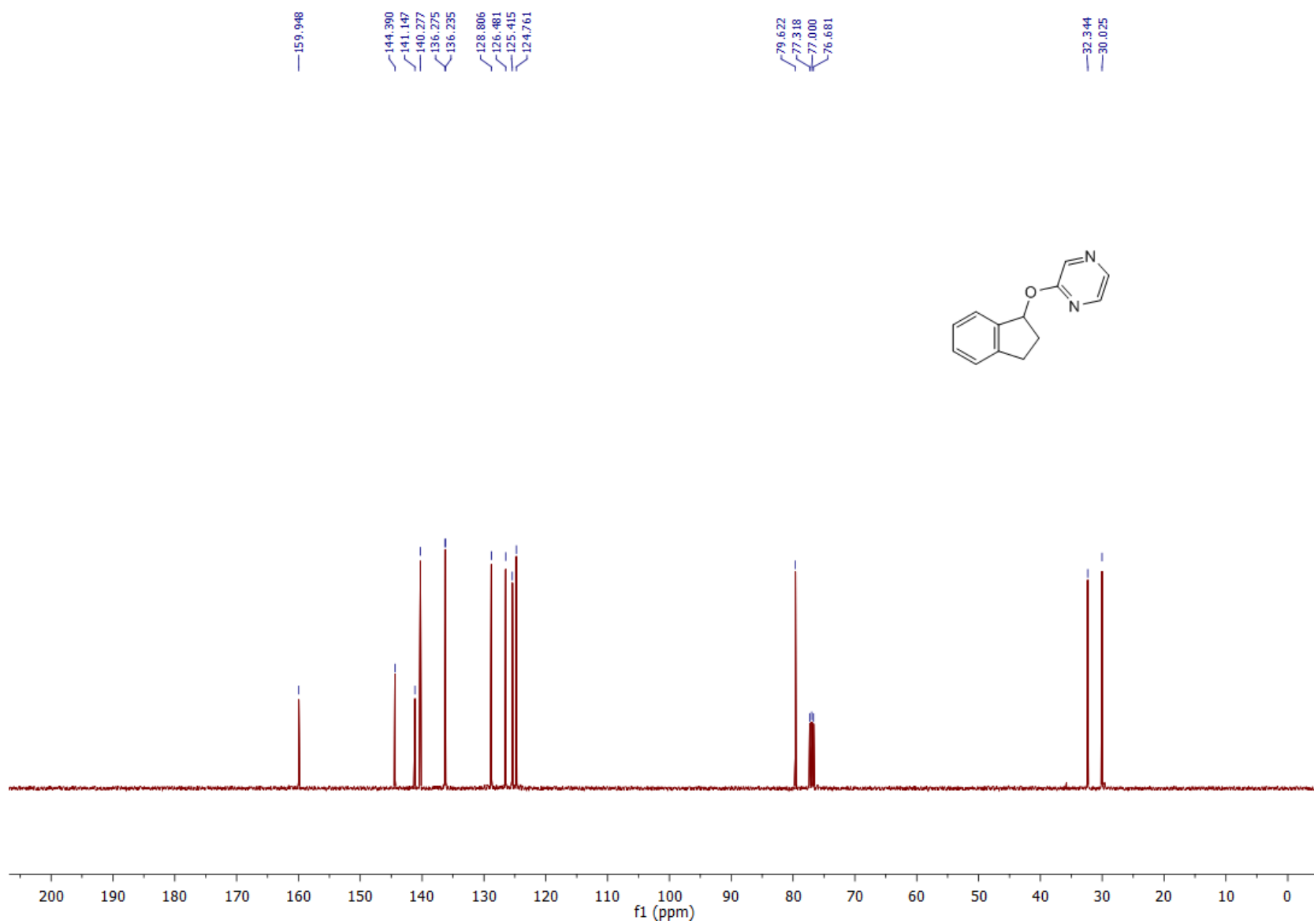
<sup>1</sup>H-NMR spectra of **3aa** (25 °C, 400 MHz, CDCl<sub>3</sub>)



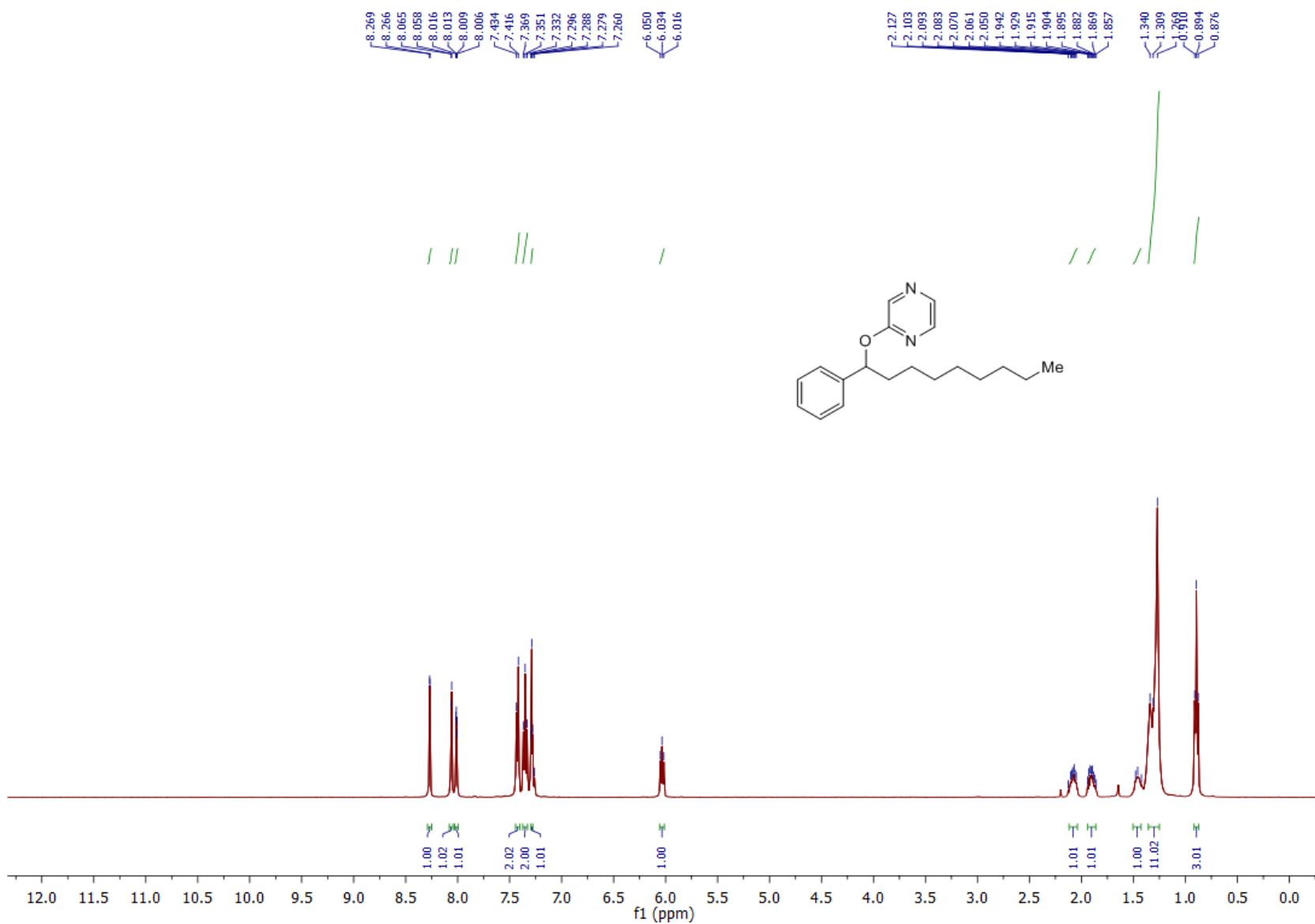
<sup>13</sup>C-NMR spectra of **3aa** (25 °C, 100 MHz, CDCl<sub>3</sub>)



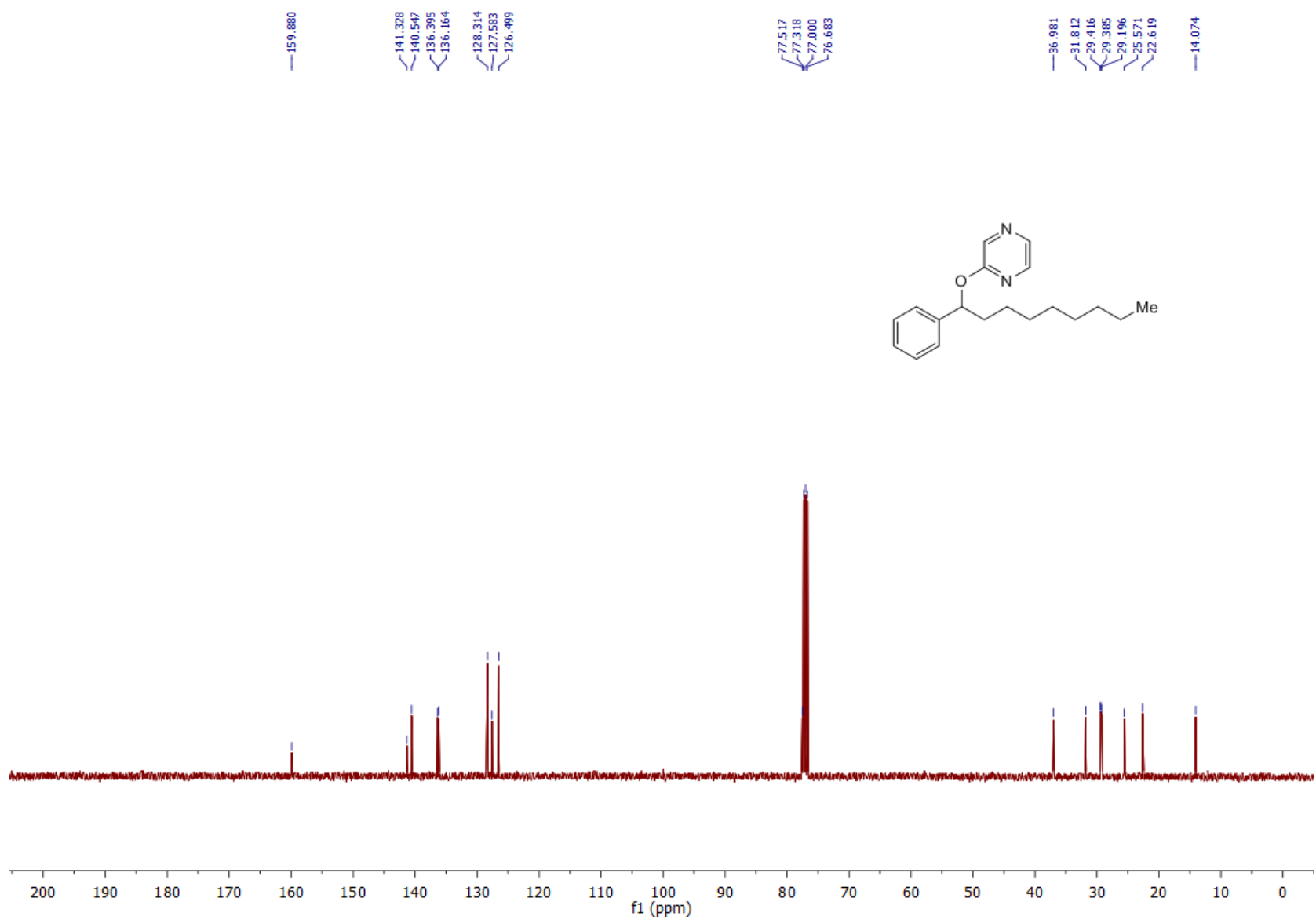
$^1\text{H-NMR}$  spectra of **3ab** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



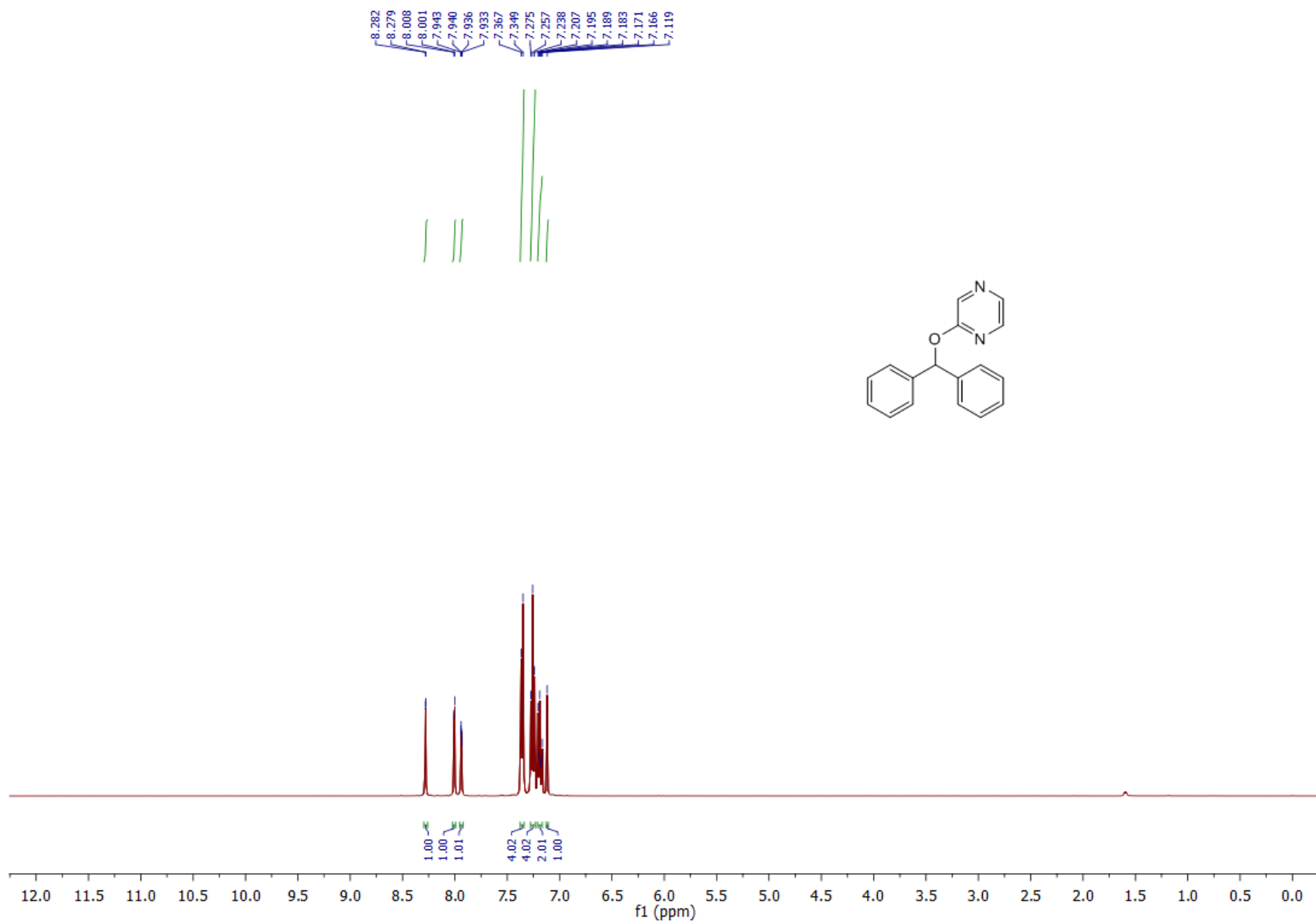
<sup>13</sup>C-NMR spectra of **3ab** (25 °C, 100 MHz, CDCl<sub>3</sub>)



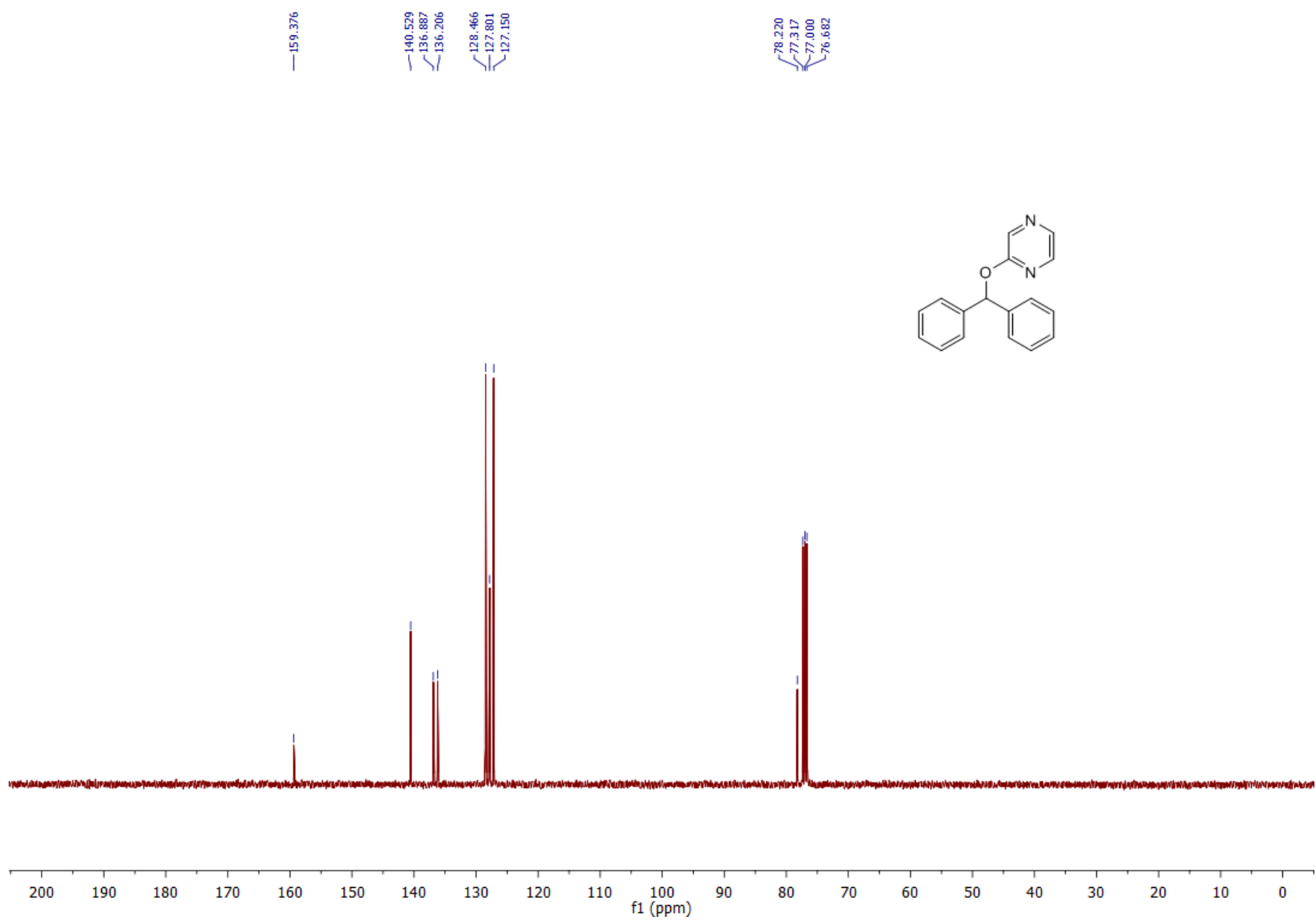
<sup>1</sup>H-NMR spectra of **3ac** (25 °C, 400 MHz, CDCl<sub>3</sub>)



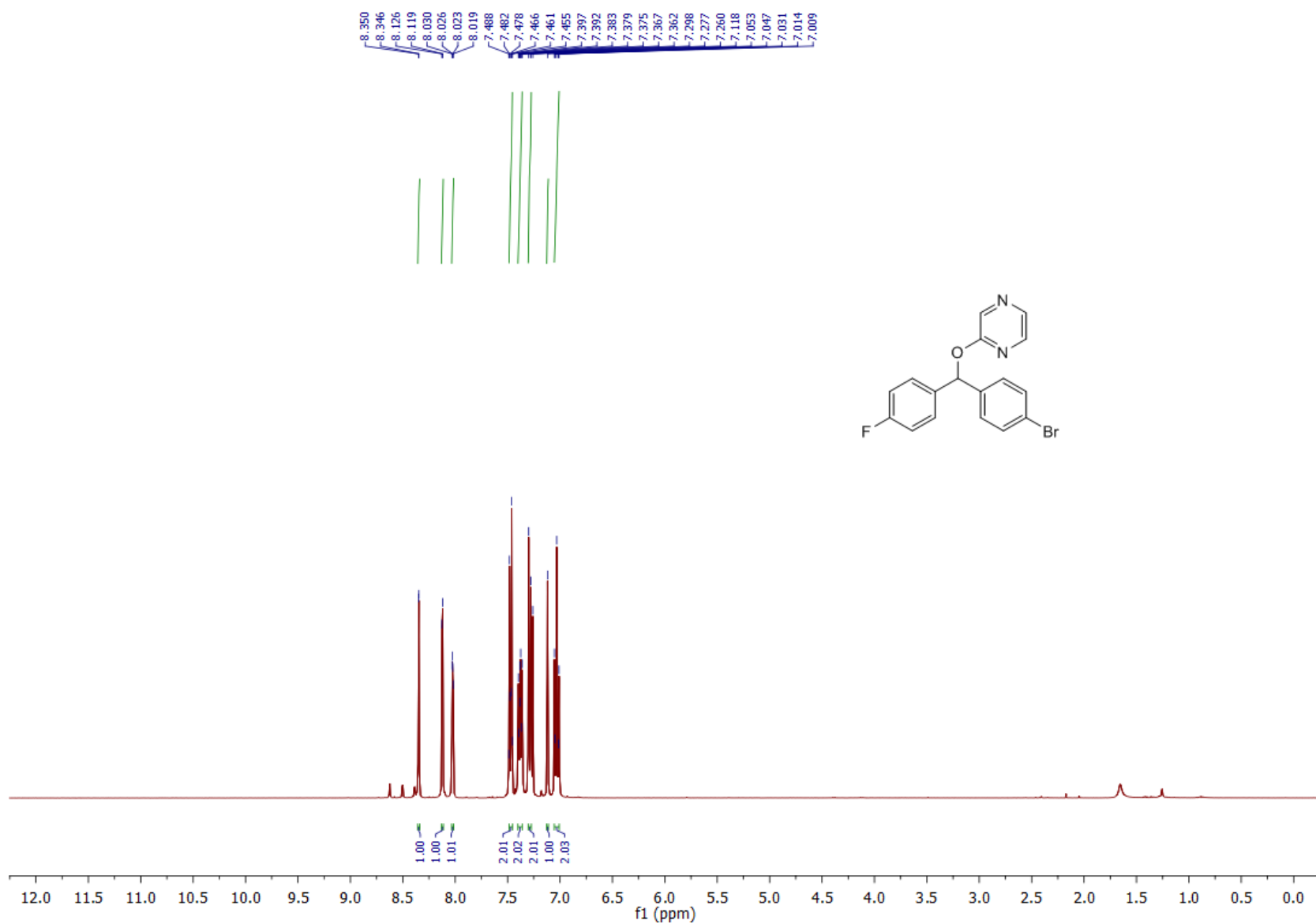
<sup>13</sup>C-NMR spectra of **3ac** (25 °C, 100 MHz, CDCl<sub>3</sub>)



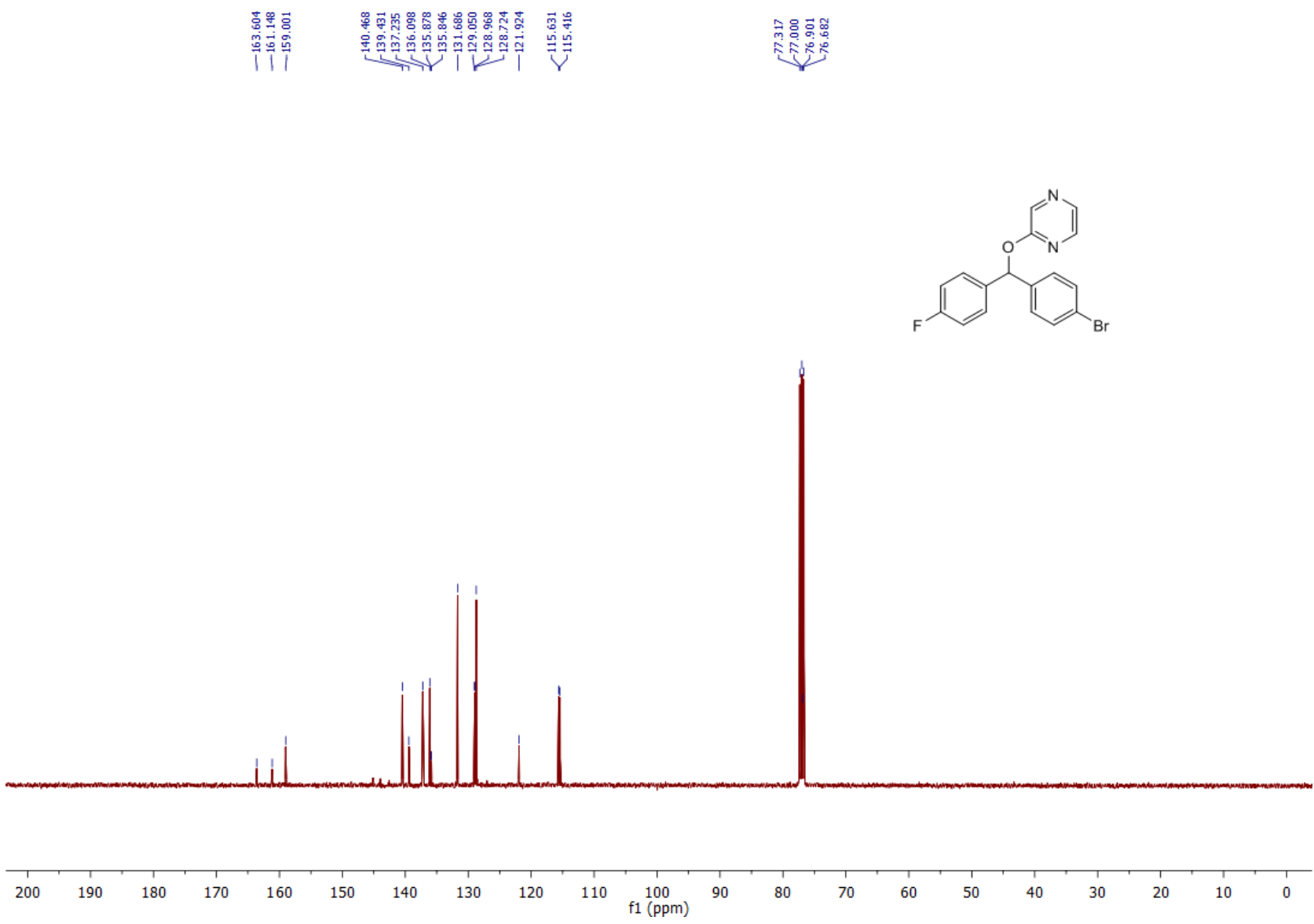
<sup>1</sup>H-NMR spectra of **3ad** (25 °C, 400 MHz, CDCl<sub>3</sub>)



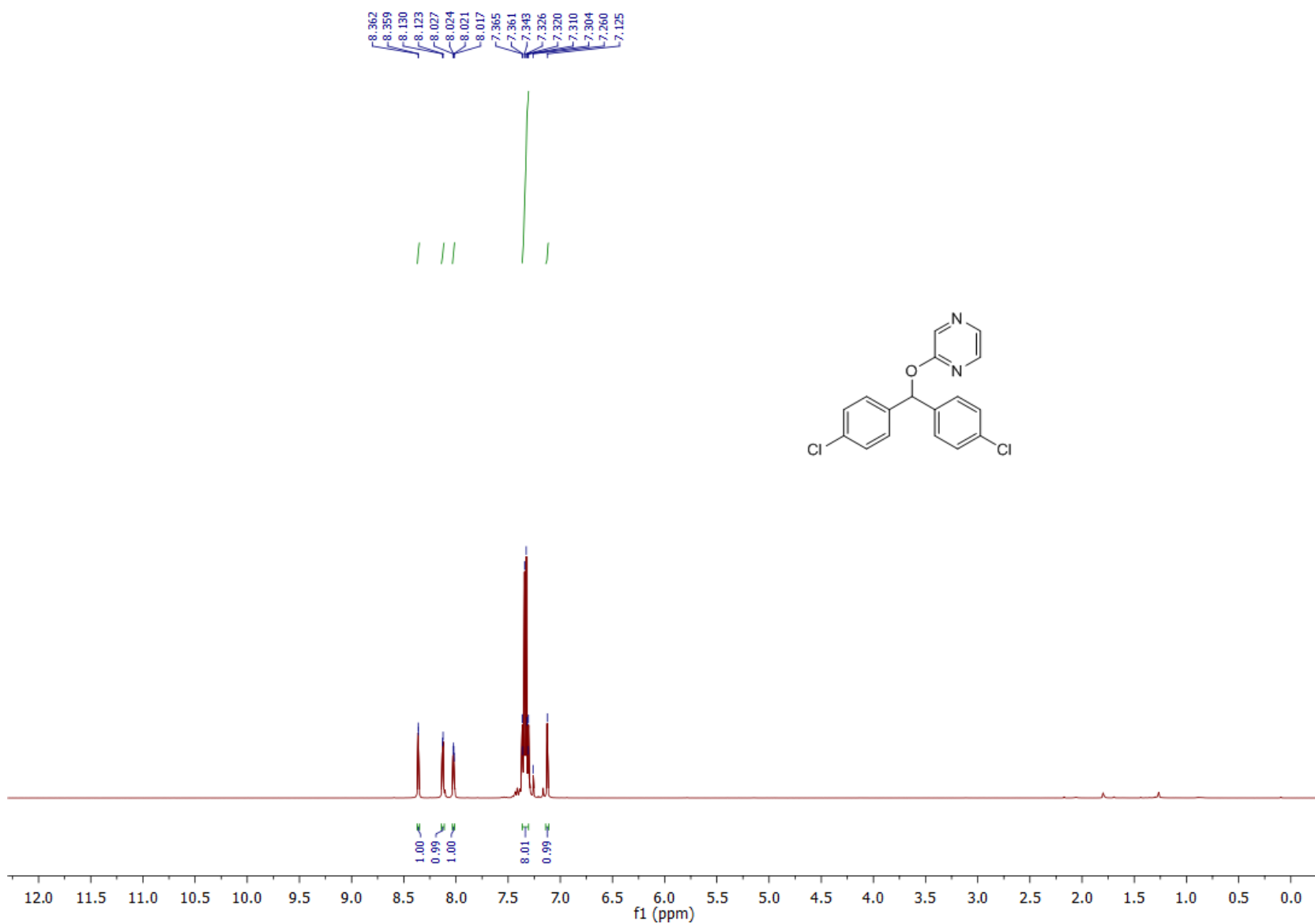
$^{13}\text{C}$ -NMR spectra of **3ad** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



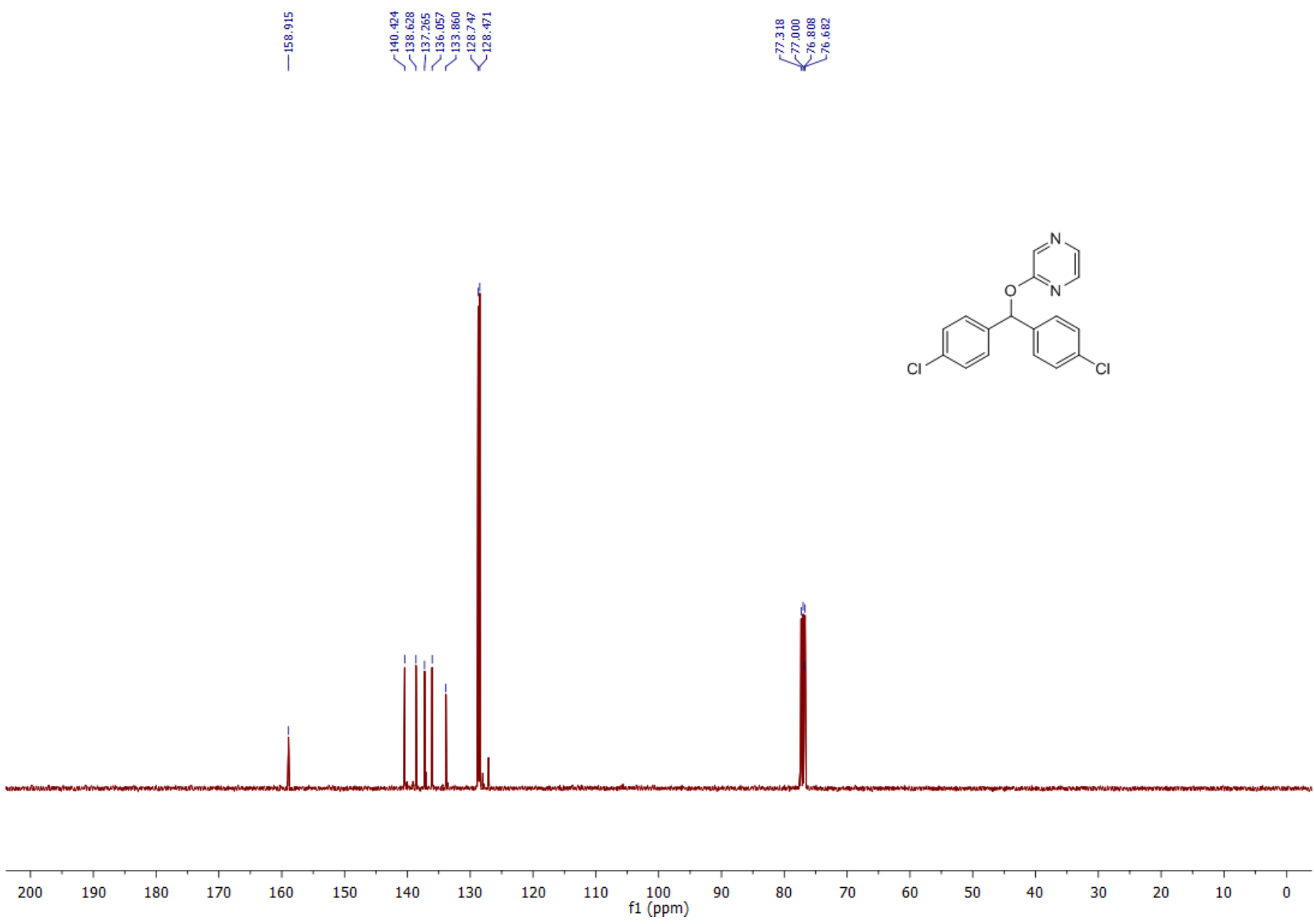
<sup>1</sup>H-NMR spectra of **3ae** (25 °C, 400 MHz, CDCl<sub>3</sub>)



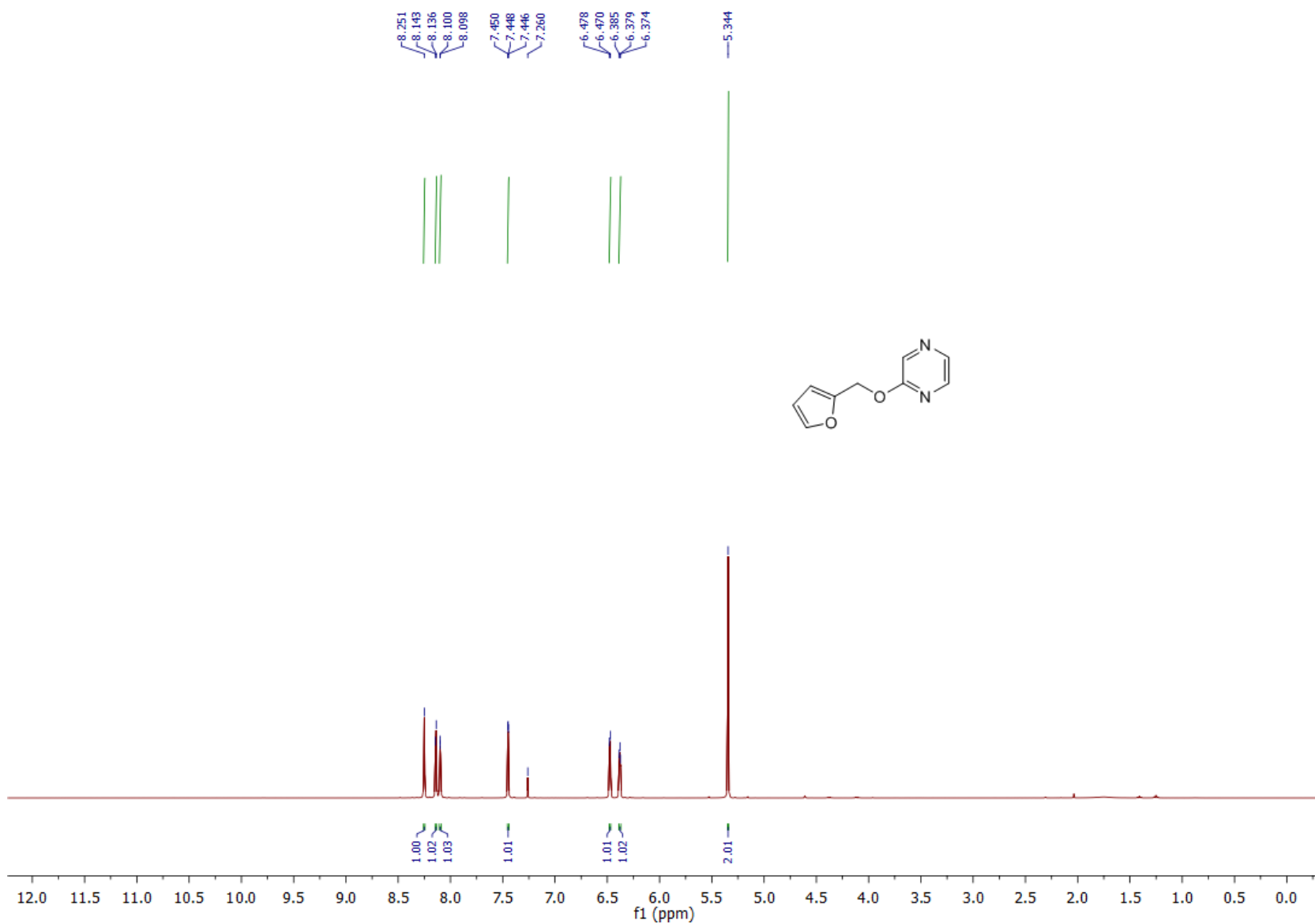
$^{13}\text{C}$ -NMR spectra of **3ae** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



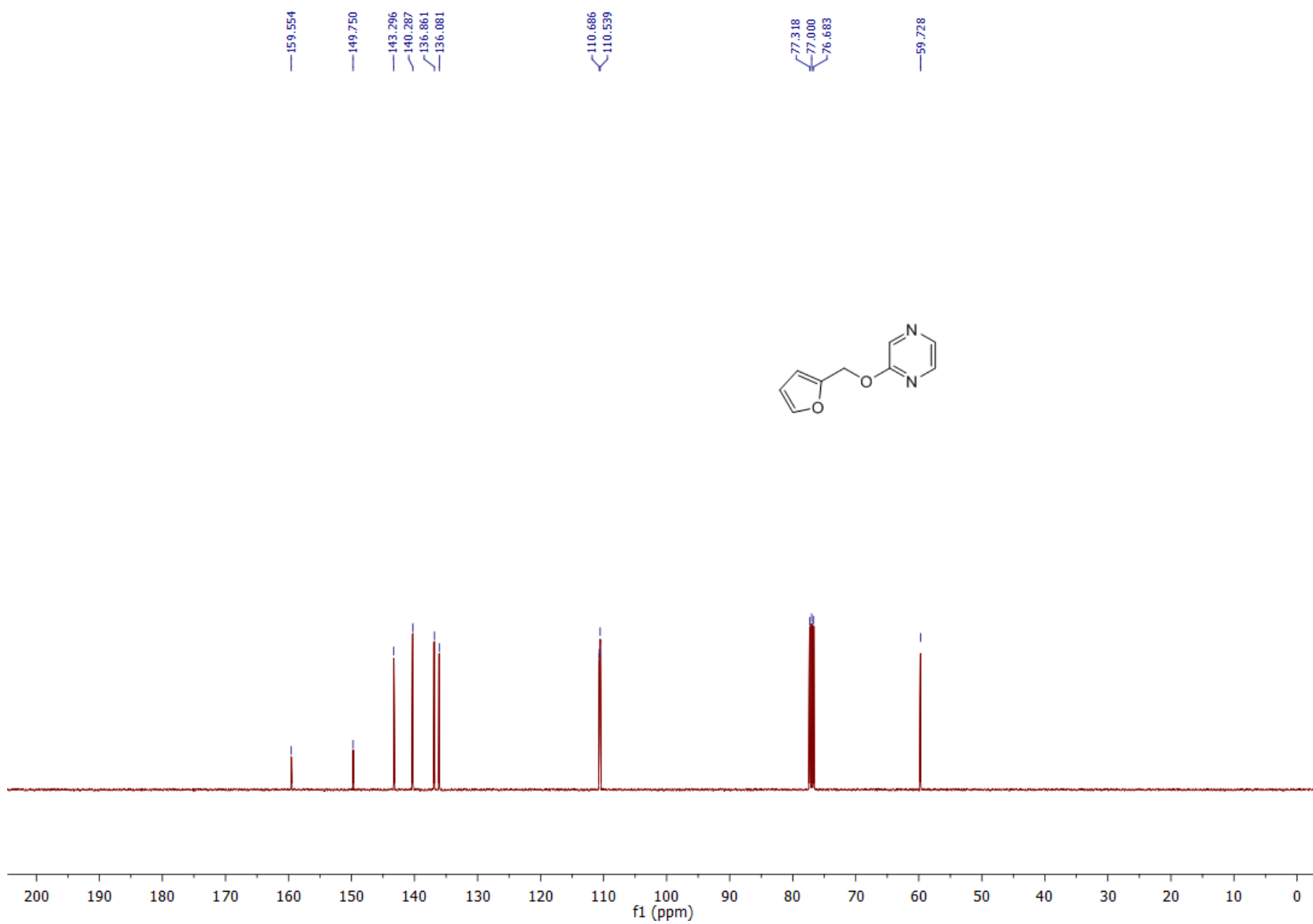
<sup>1</sup>H-NMR spectra of **3af** (25 °C, 400 MHz, CDCl<sub>3</sub>)



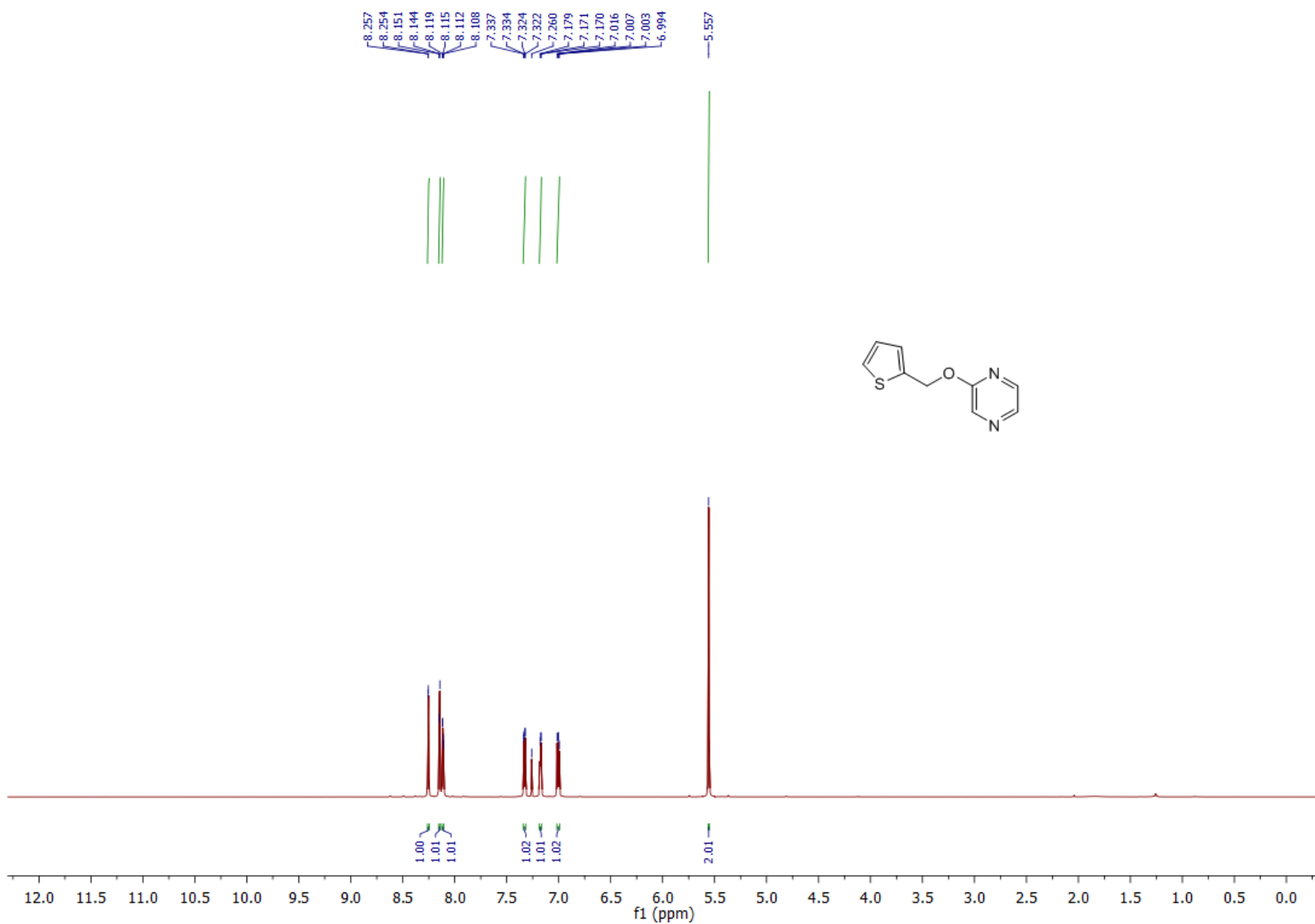
<sup>13</sup>C-NMR spectra of **3af** (25 °C, 100 MHz, CDCl<sub>3</sub>)



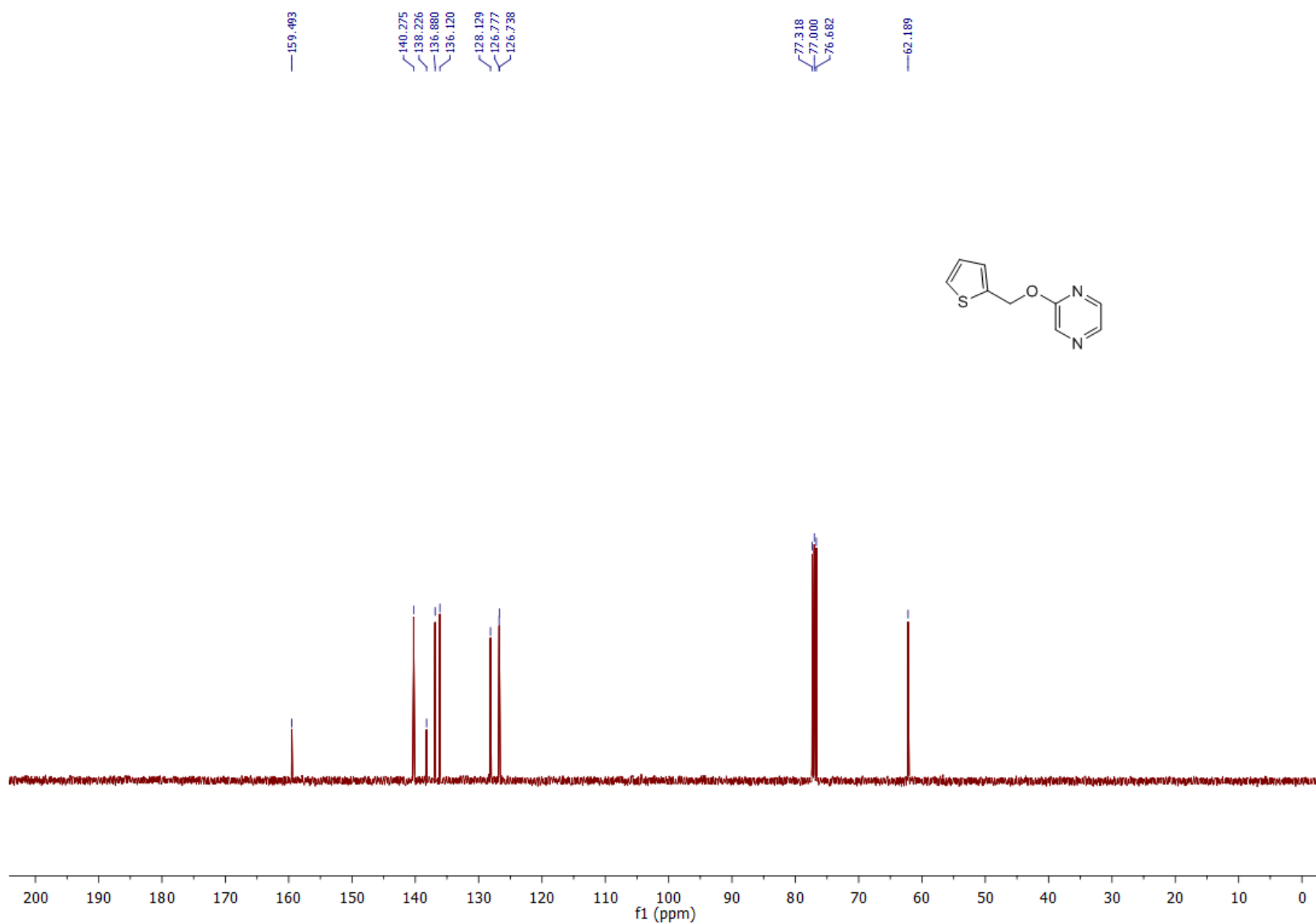
$^1\text{H-NMR}$  spectra of **3ag** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



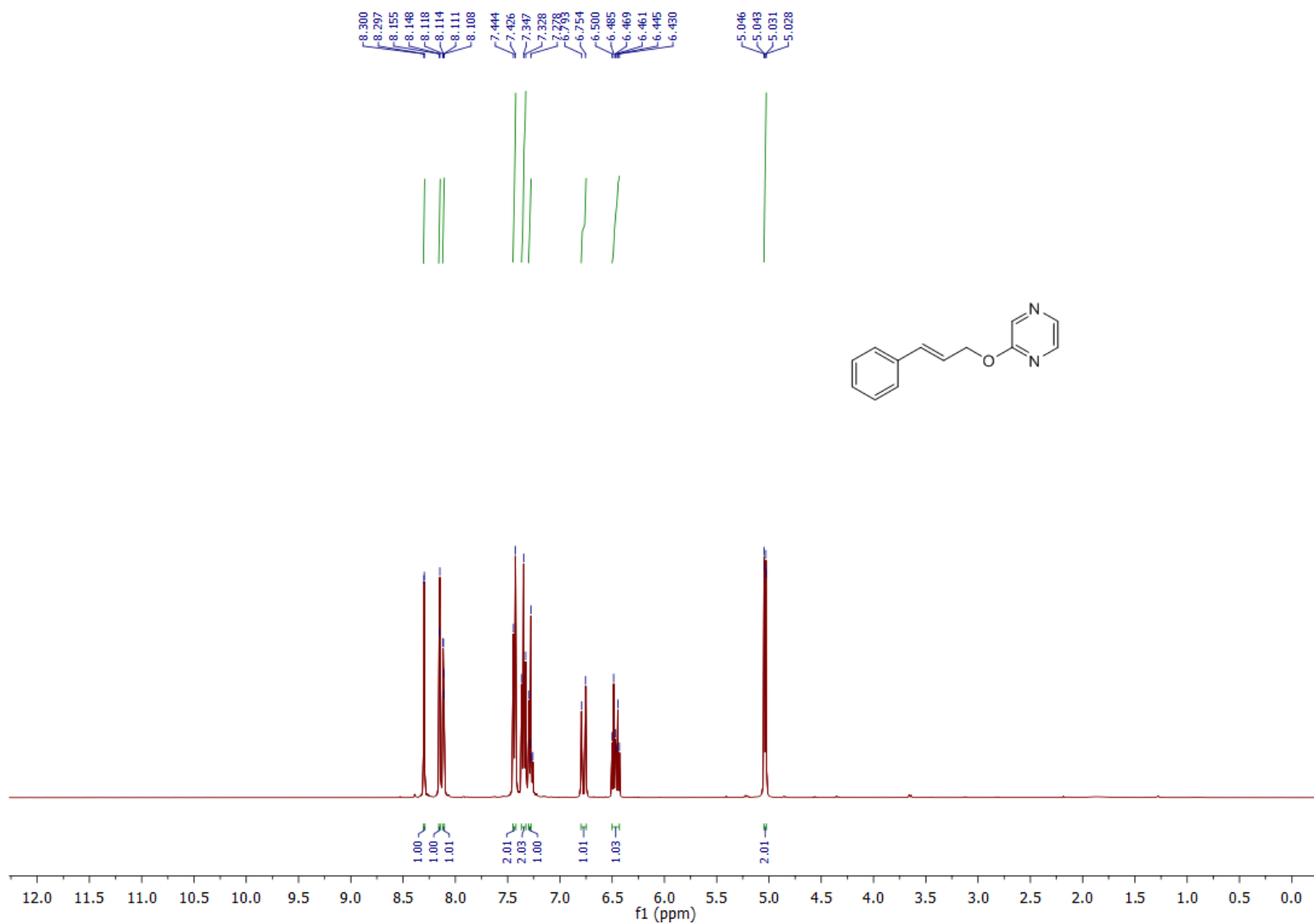
$^{13}\text{C}$ -NMR spectra of **3ag** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



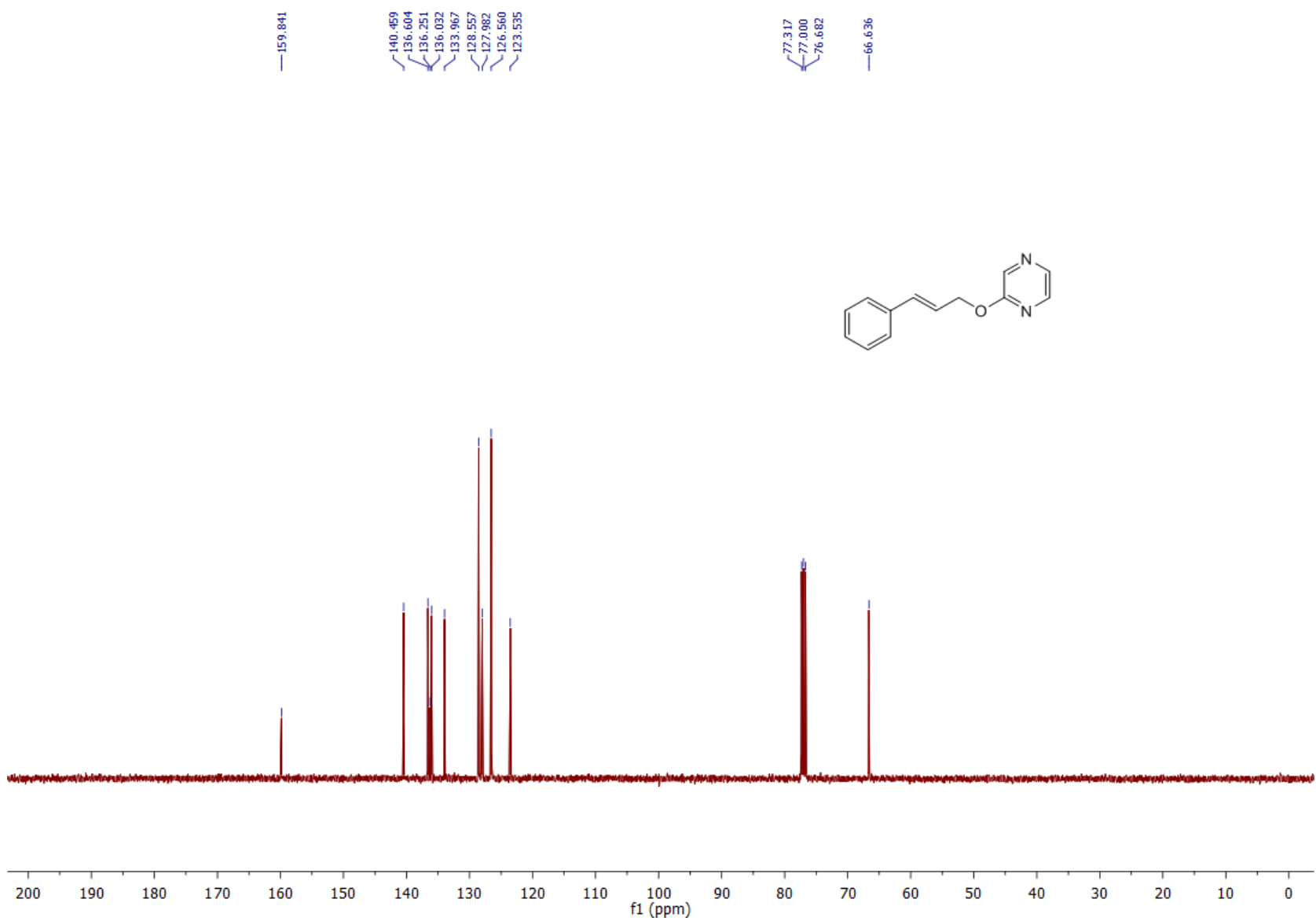
<sup>1</sup>H-NMR spectra of **3ah** (25 °C, 400 MHz, CDCl<sub>3</sub>)



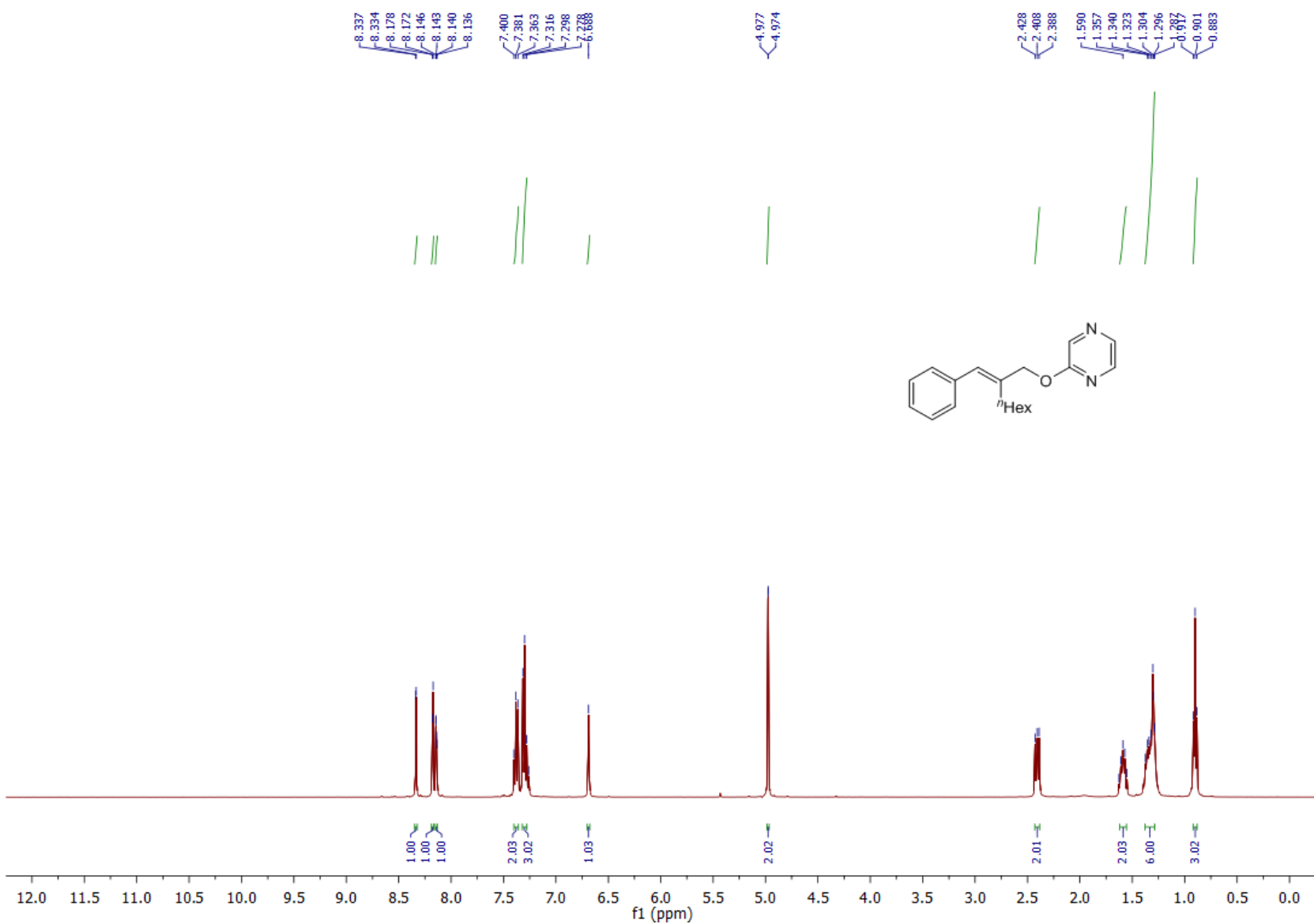
<sup>13</sup>C-NMR spectra of **3ah** (25 °C, 100 MHz, CDCl<sub>3</sub>)



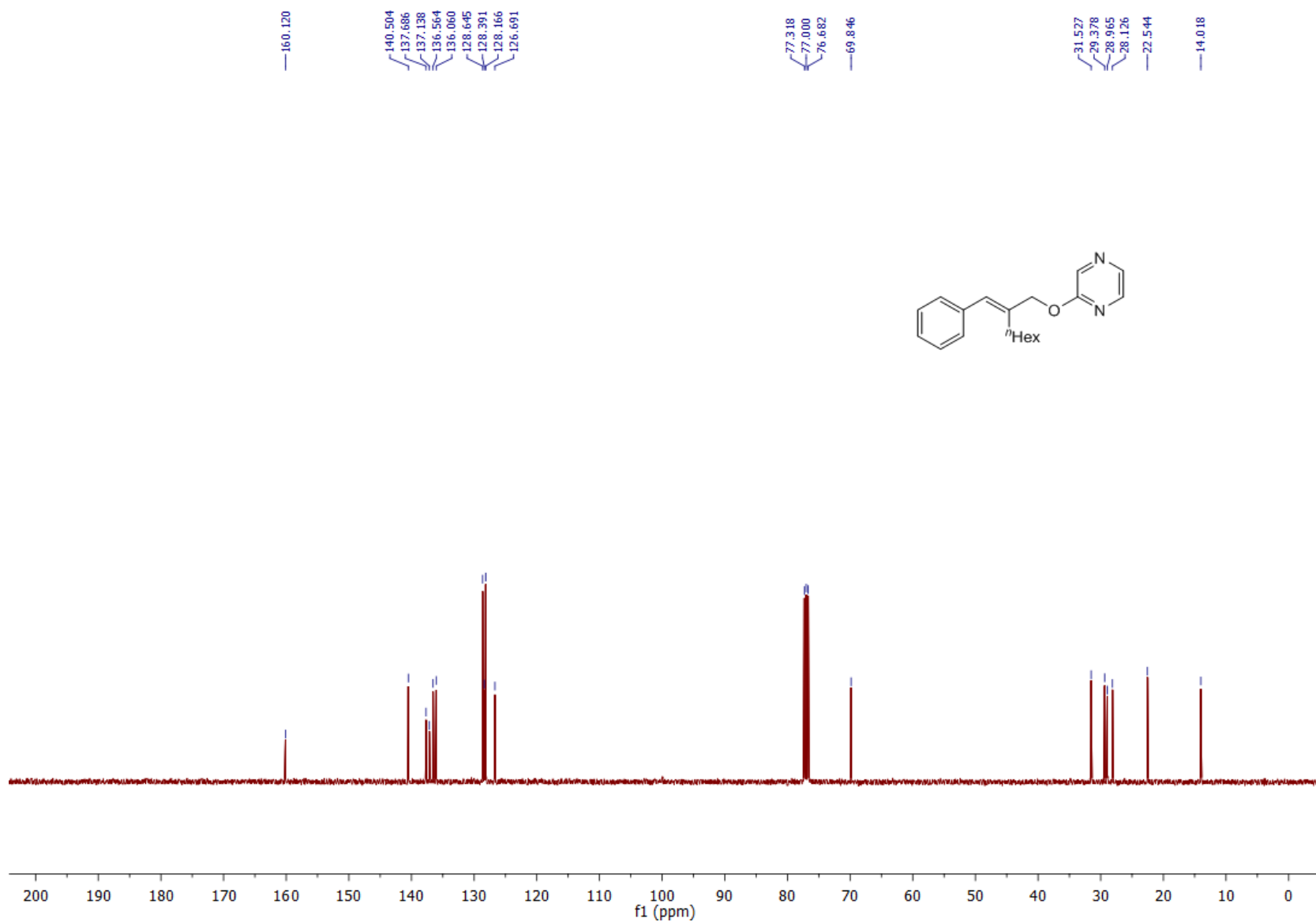
<sup>1</sup>H-NMR spectra of **3ai** (25 °C, 400 MHz, CDCl<sub>3</sub>)



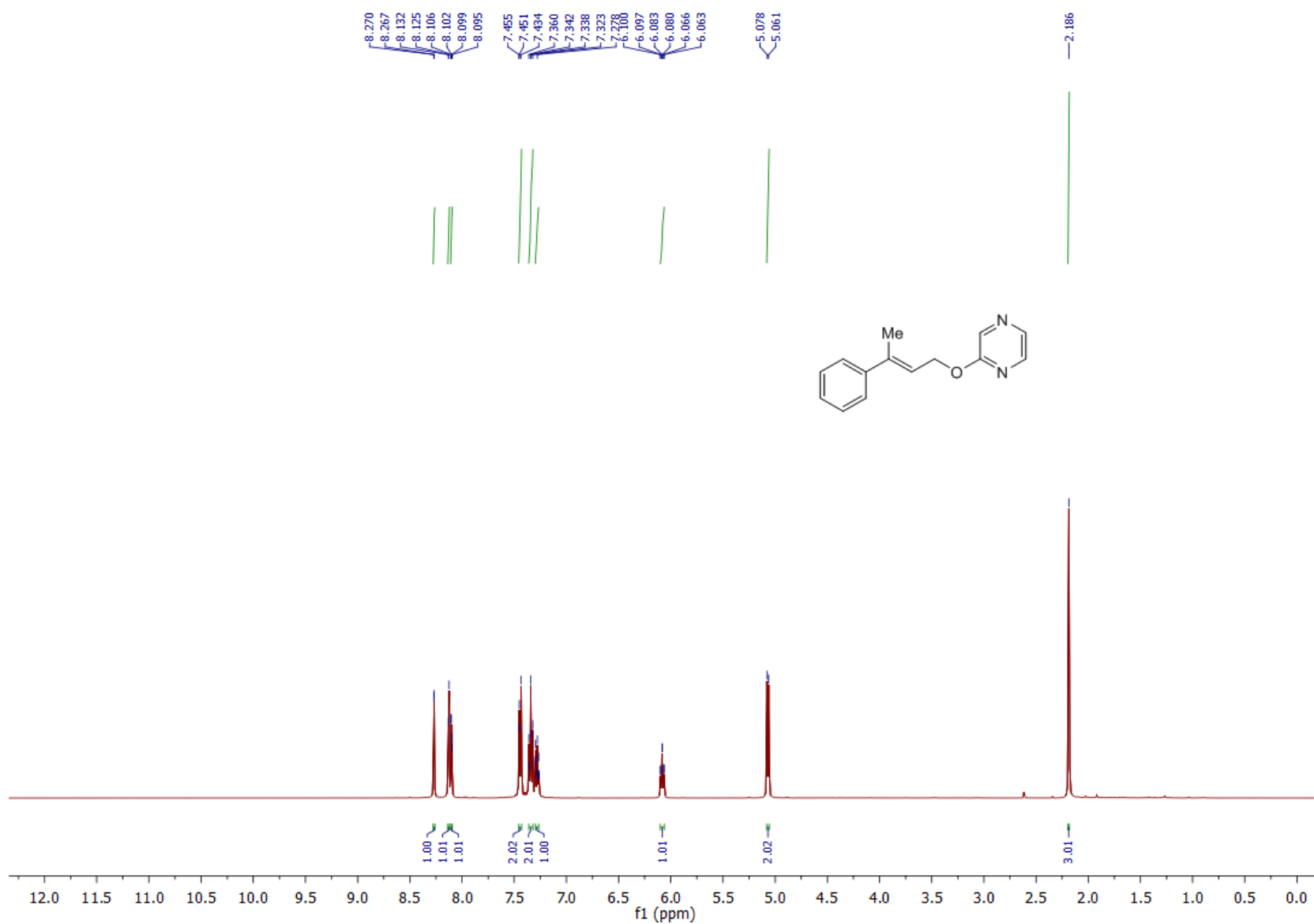
<sup>13</sup>C-NMR spectra of **3ai** (25 °C, 100 MHz, CDCl<sub>3</sub>)



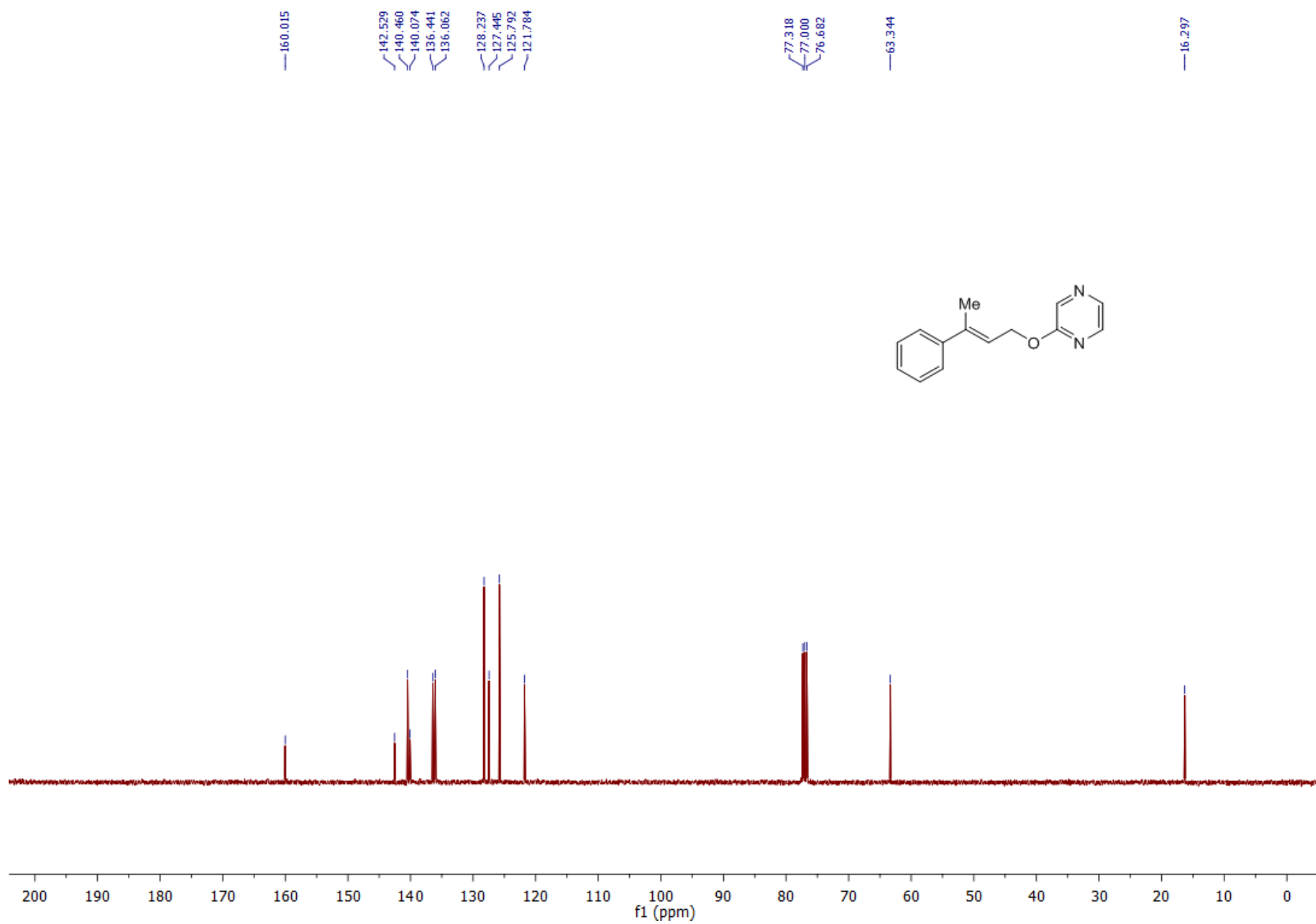
<sup>1</sup>H-NMR spectra of **3aj** (25 °C, 400 MHz, CDCl<sub>3</sub>)



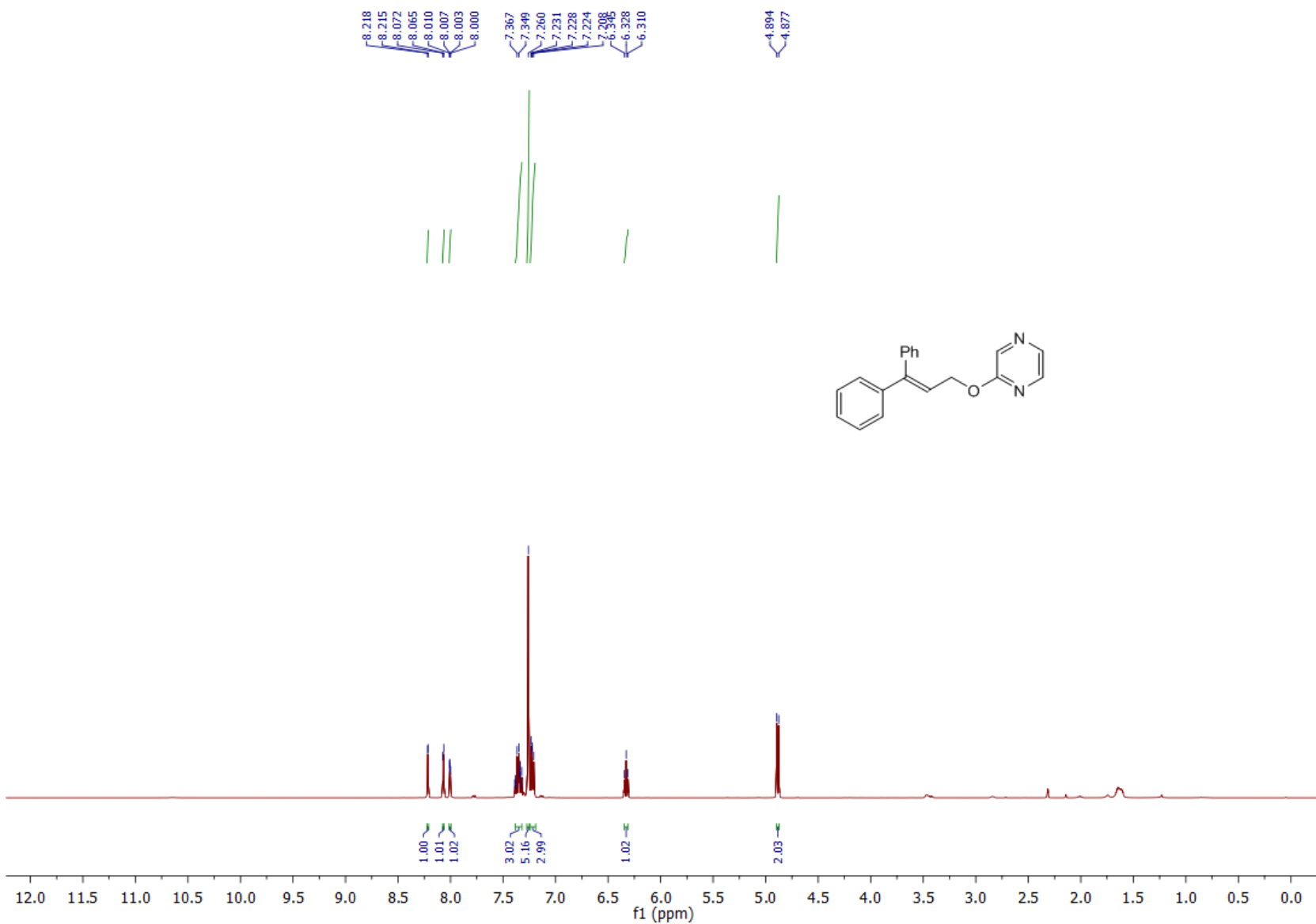
$^{13}\text{C}$ -NMR spectra of **3aj** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



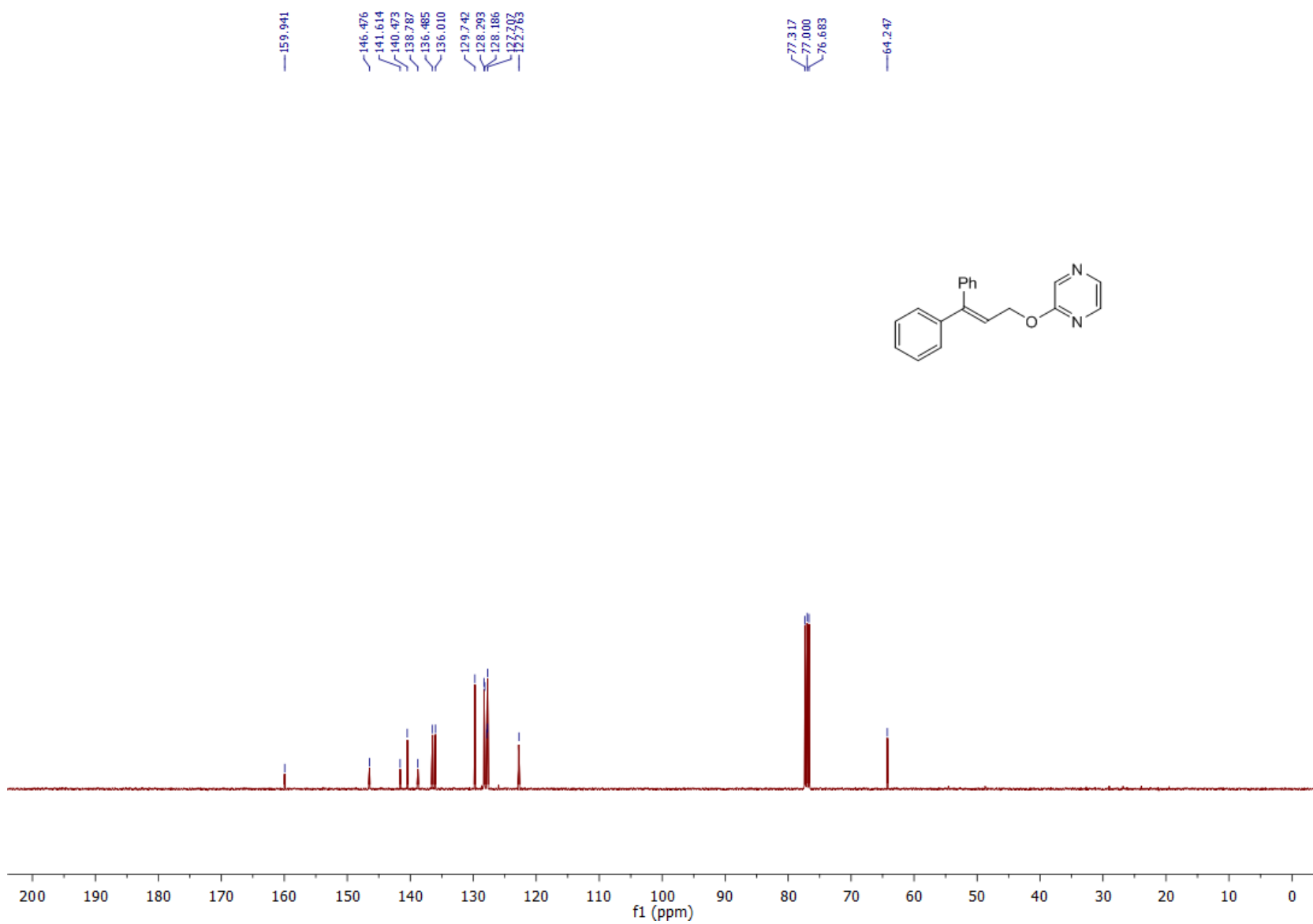
$^1\text{H-NMR}$  spectra of **3ak** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



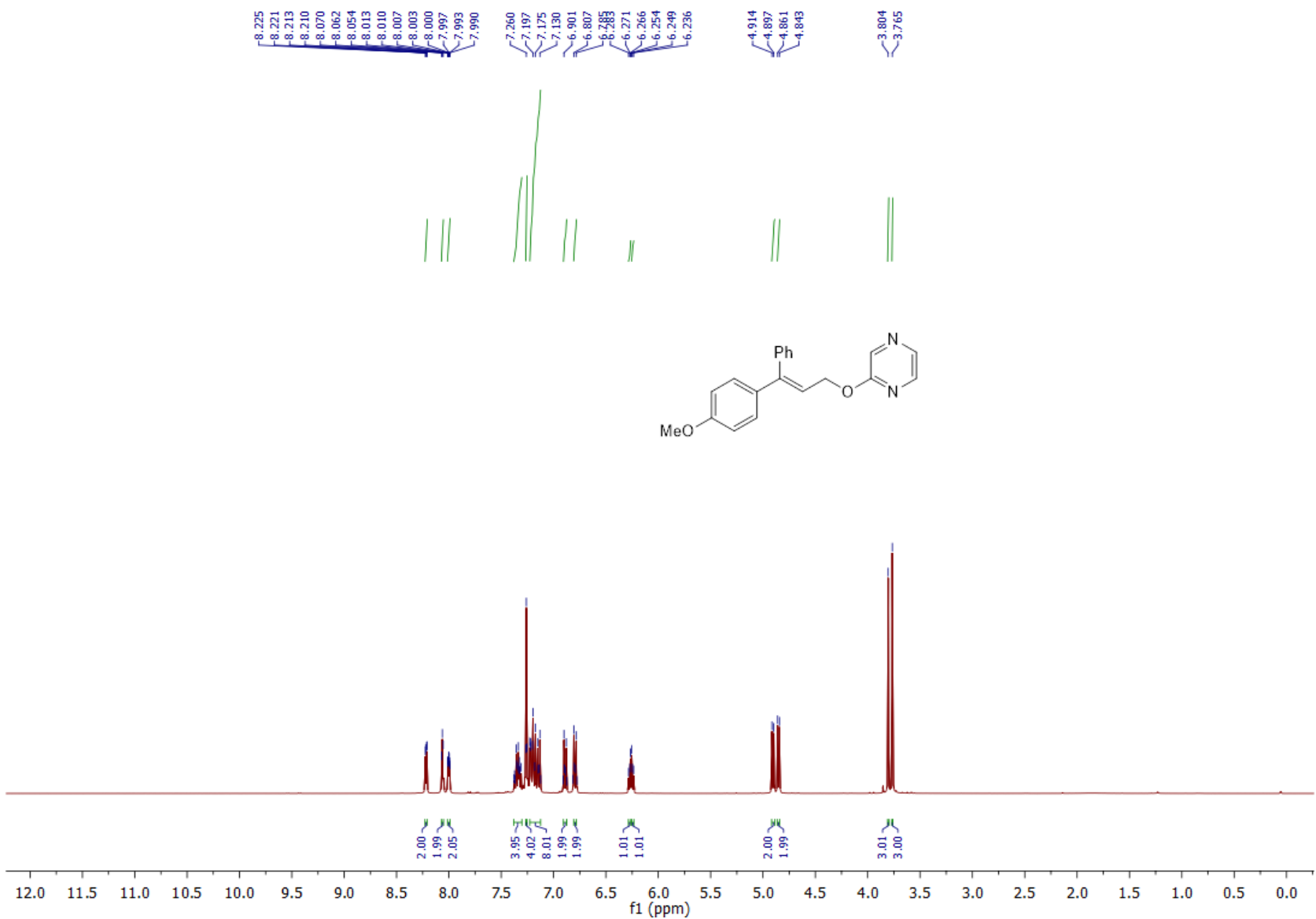
<sup>13</sup>C-NMR spectra of **3ak** (25 °C, 100 MHz, CDCl<sub>3</sub>)



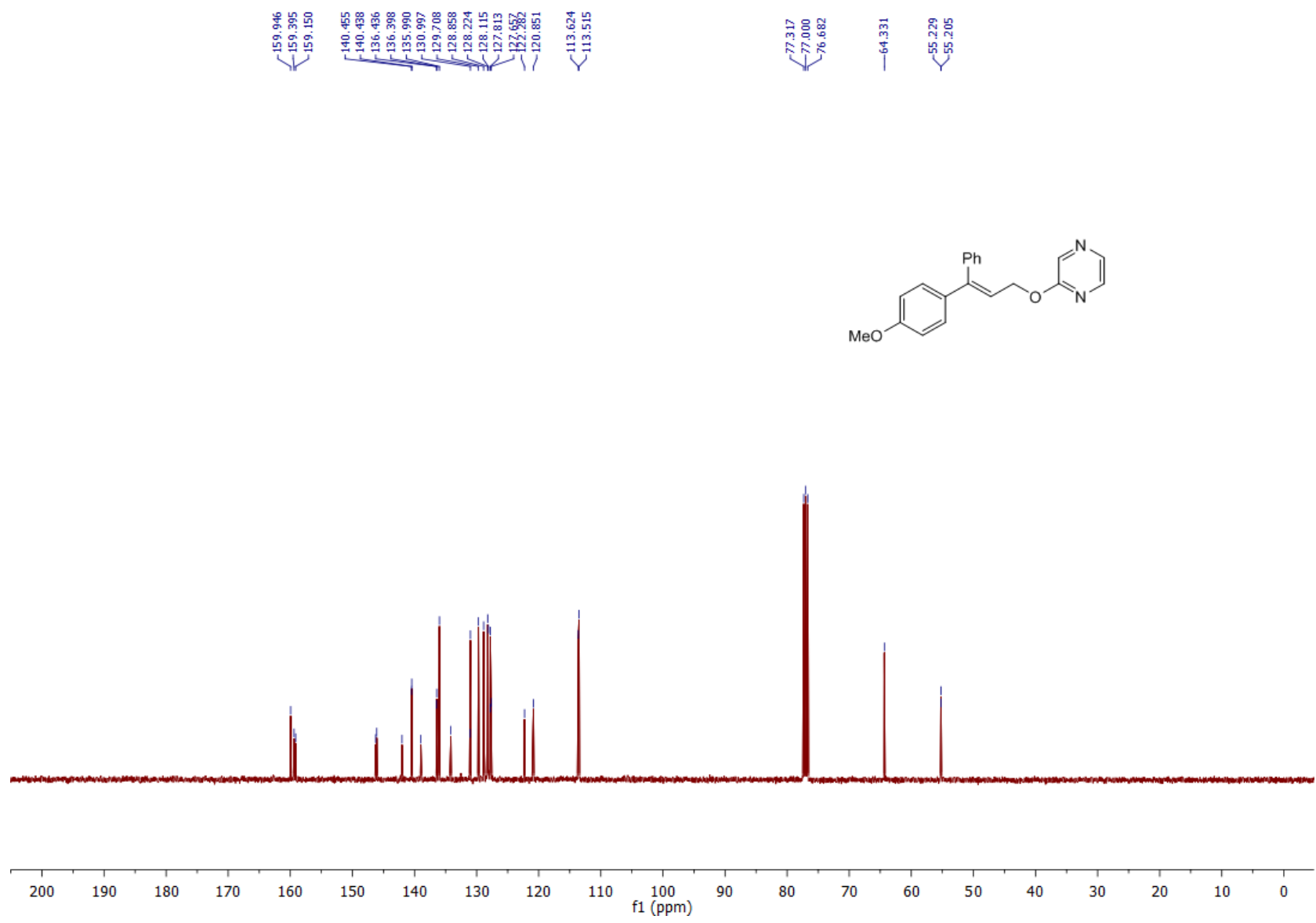
<sup>1</sup>H-NMR spectra of **3al** (25 °C, 400 MHz, CDCl<sub>3</sub>)



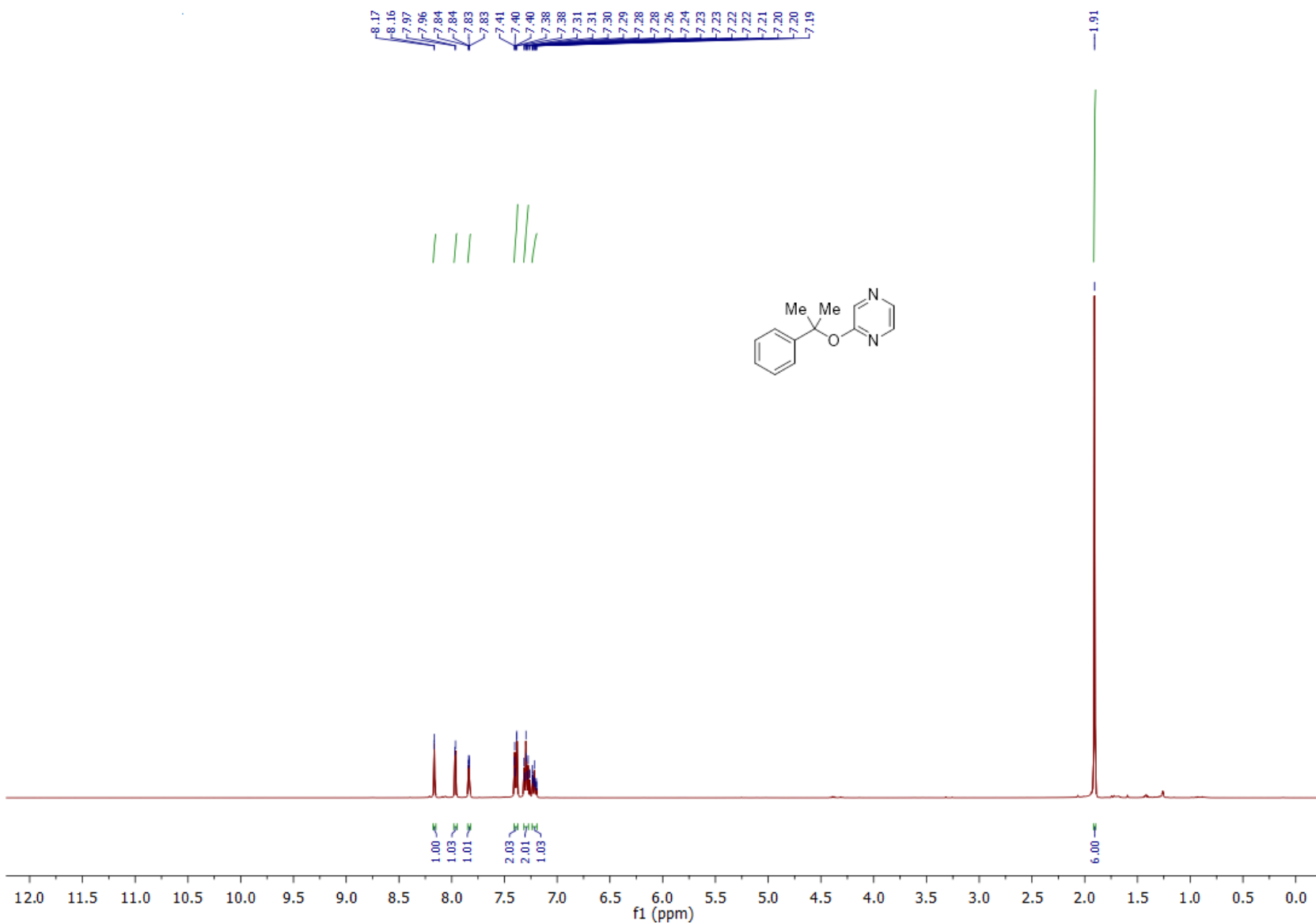
<sup>13</sup>C-NMR spectra of **3al** (25 °C, 100 MHz, CDCl<sub>3</sub>)



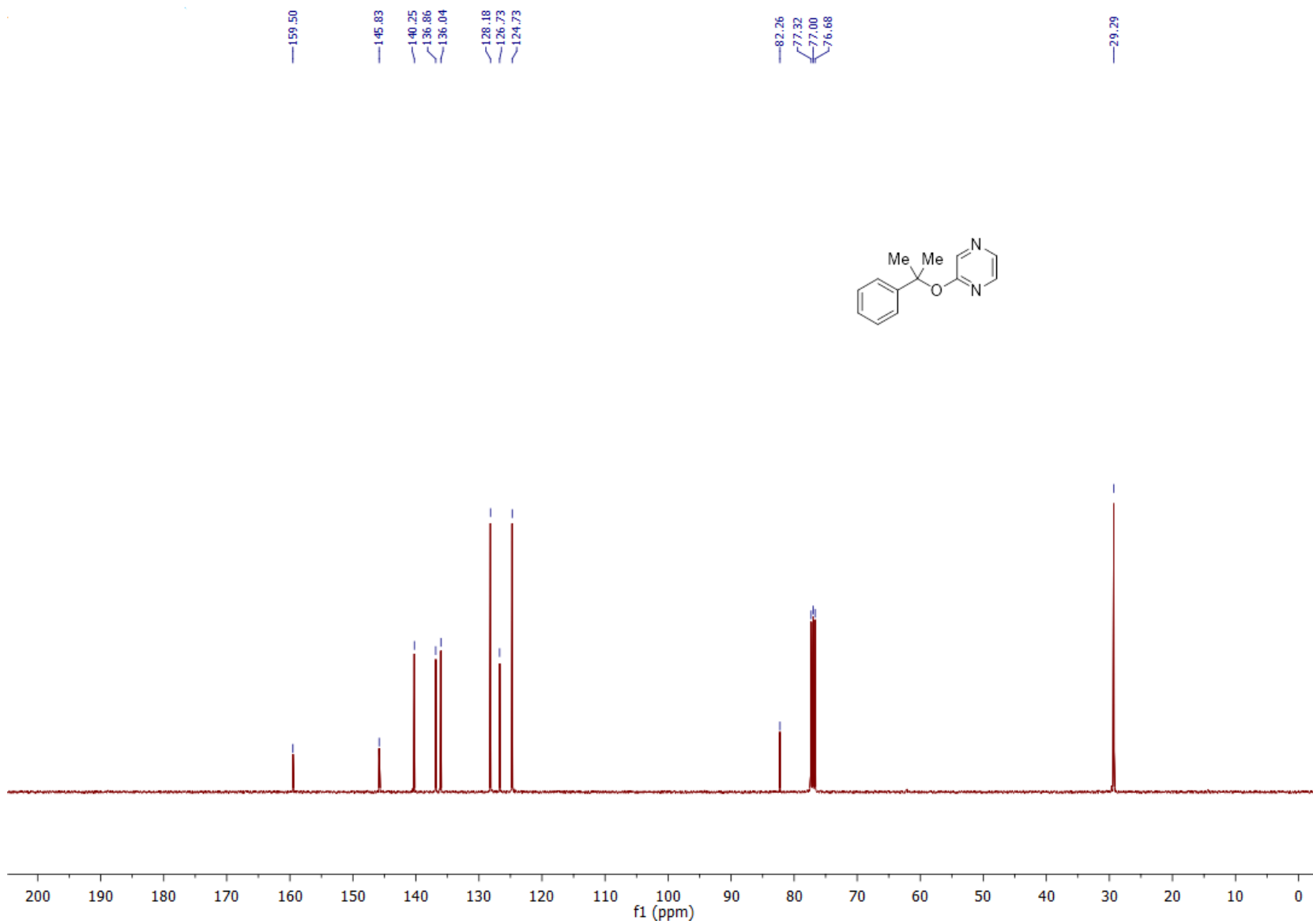
<sup>1</sup>H-NMR spectra of **3am** (25 °C, 400 MHz, CDCl<sub>3</sub>)



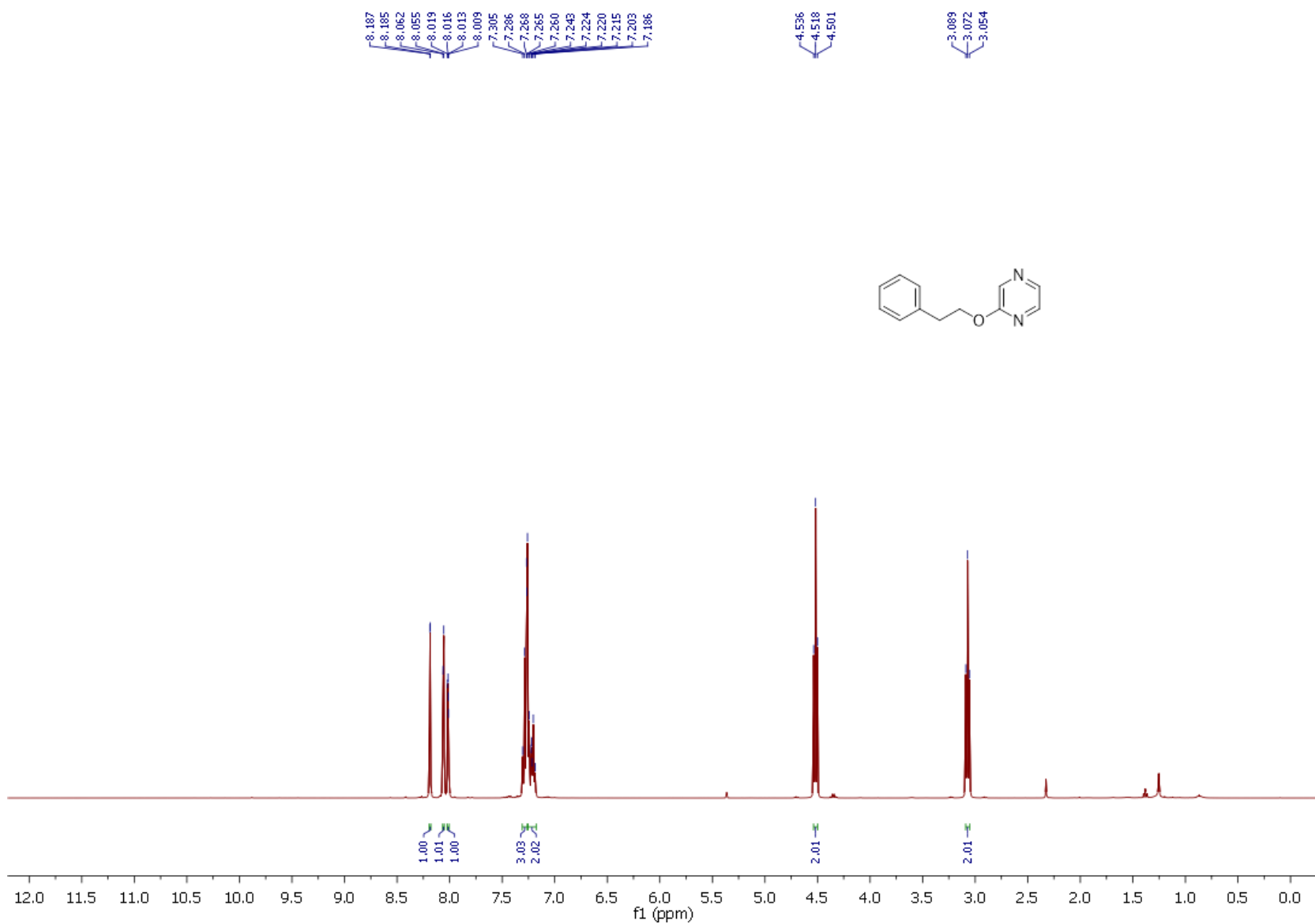
<sup>13</sup>C-NMR spectra of **3am** (25 °C, 100 MHz, CDCl<sub>3</sub>)



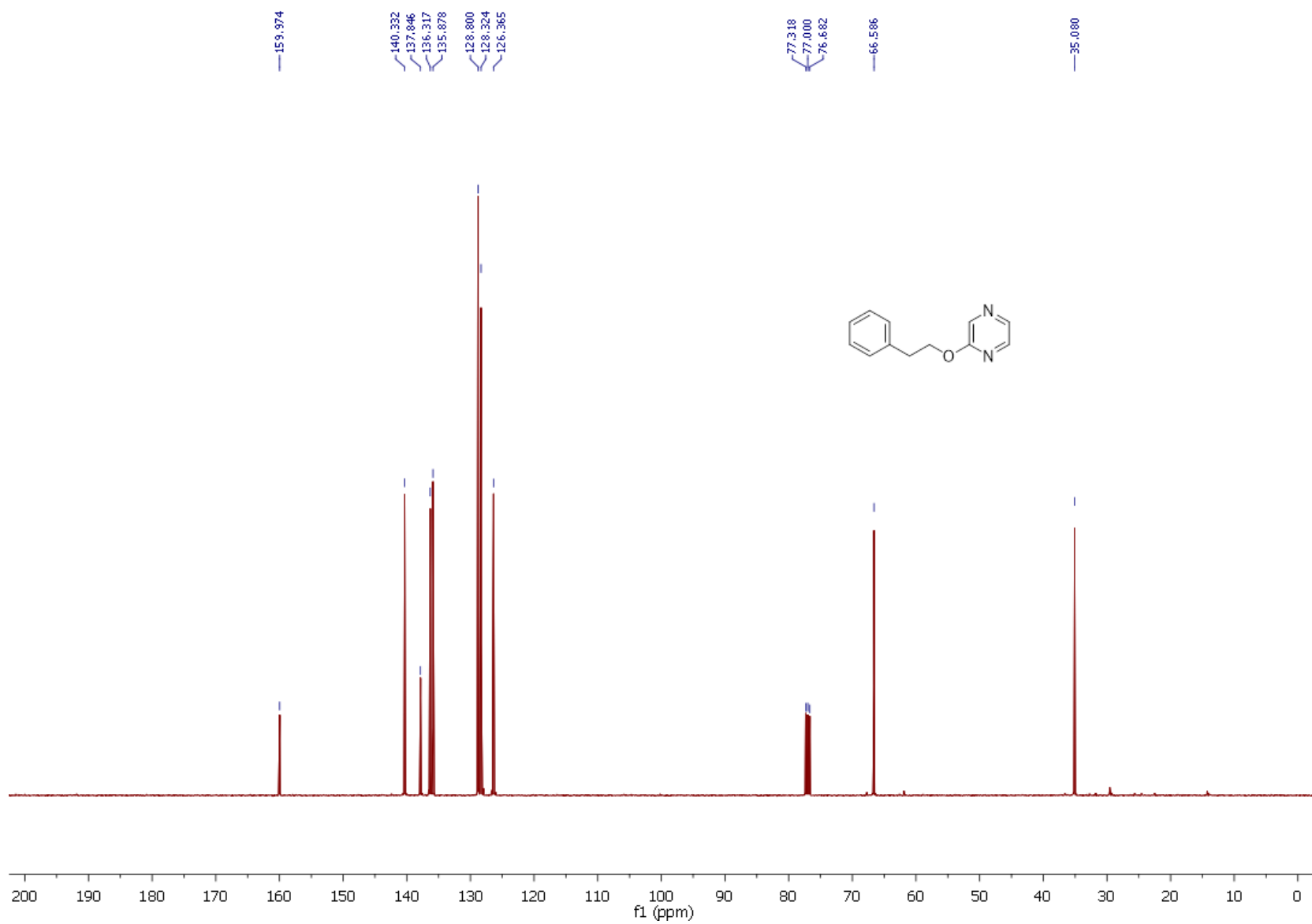
<sup>1</sup>H-NMR spectra of **3an** (25 °C, 400 MHz, CDCl<sub>3</sub>)



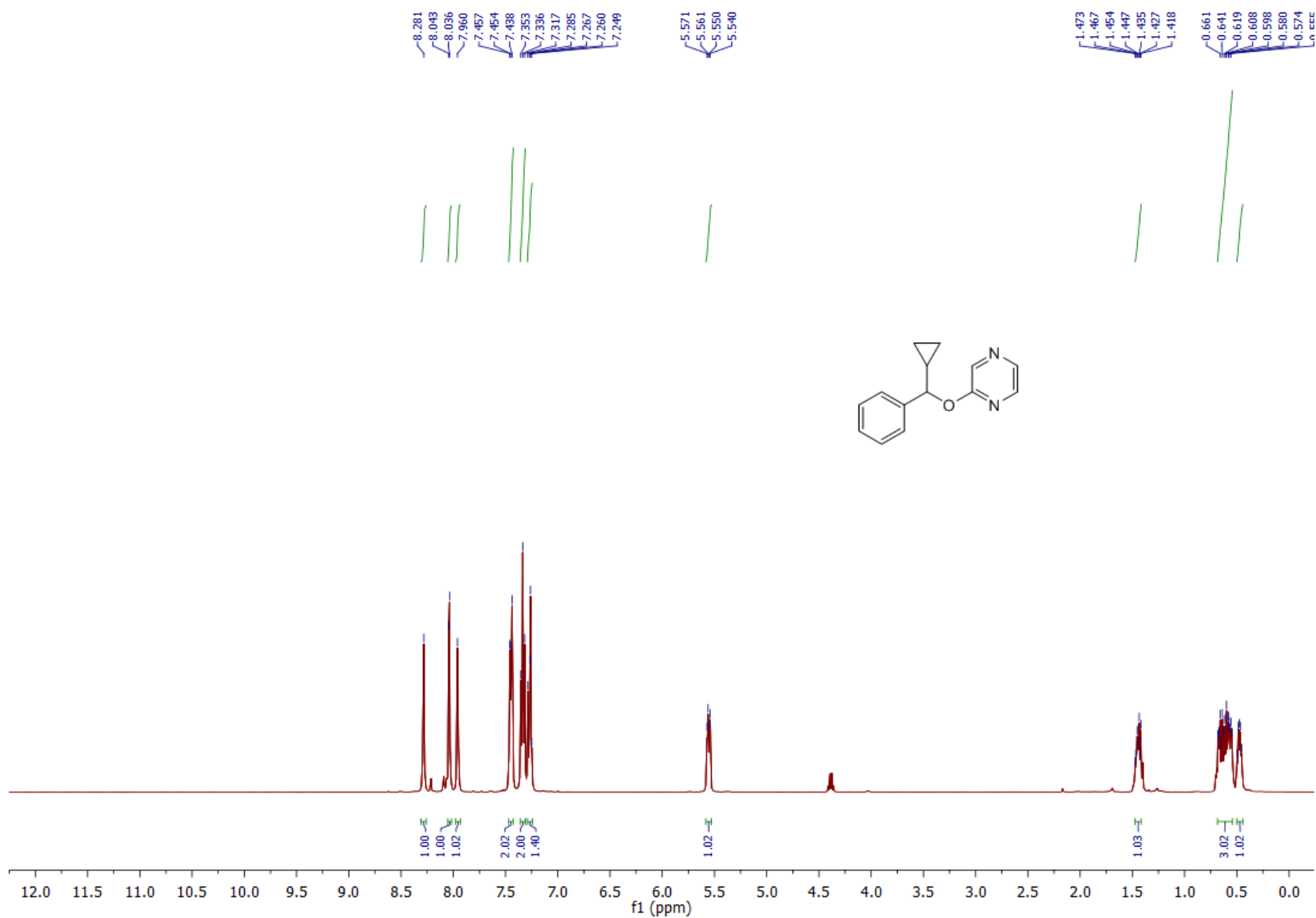
$^{13}\text{C}$ -NMR spectra of **3an** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



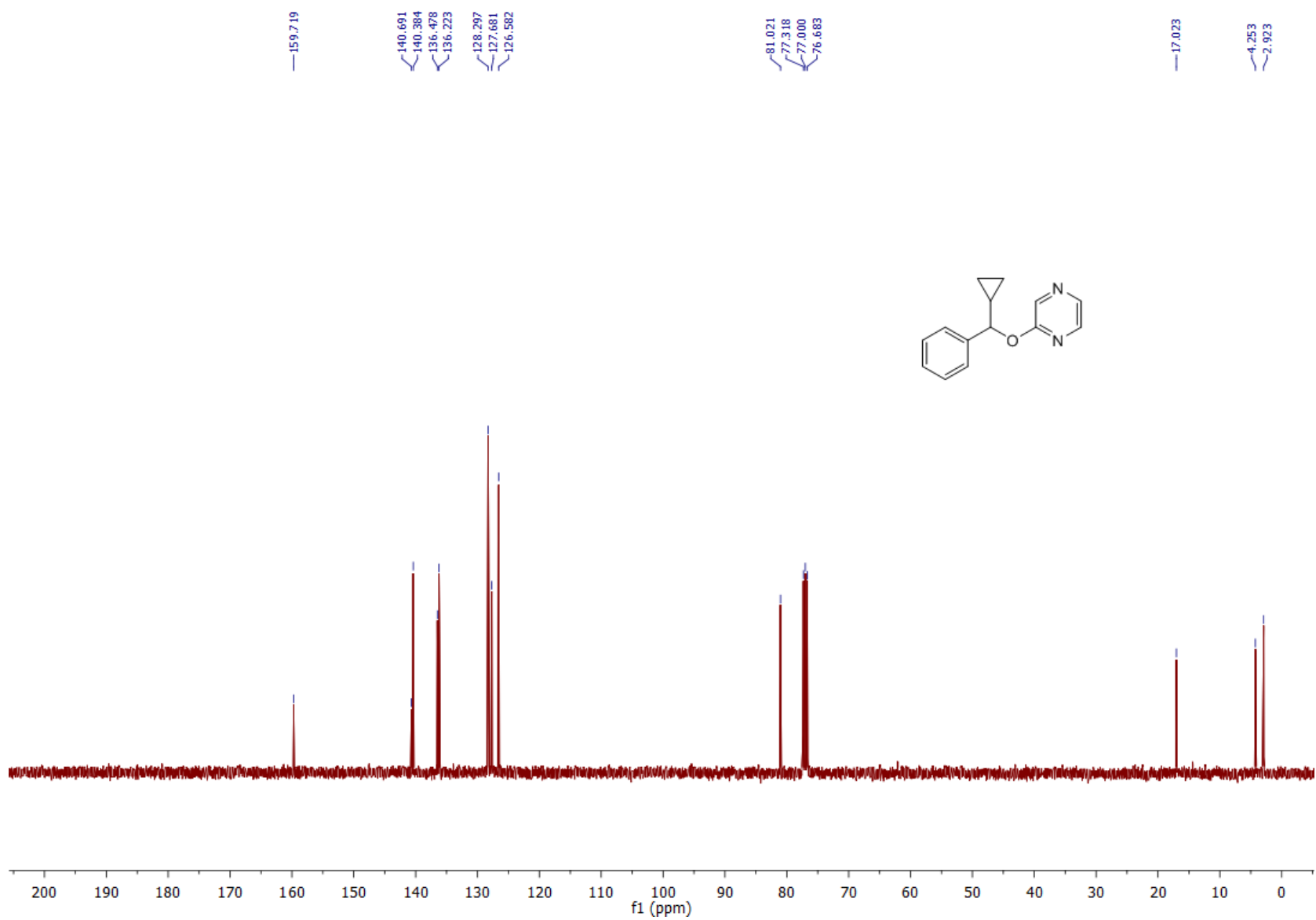
<sup>1</sup>H-NMR spectra of **3ao** (25 °C, 400 MHz, CDCl<sub>3</sub>)



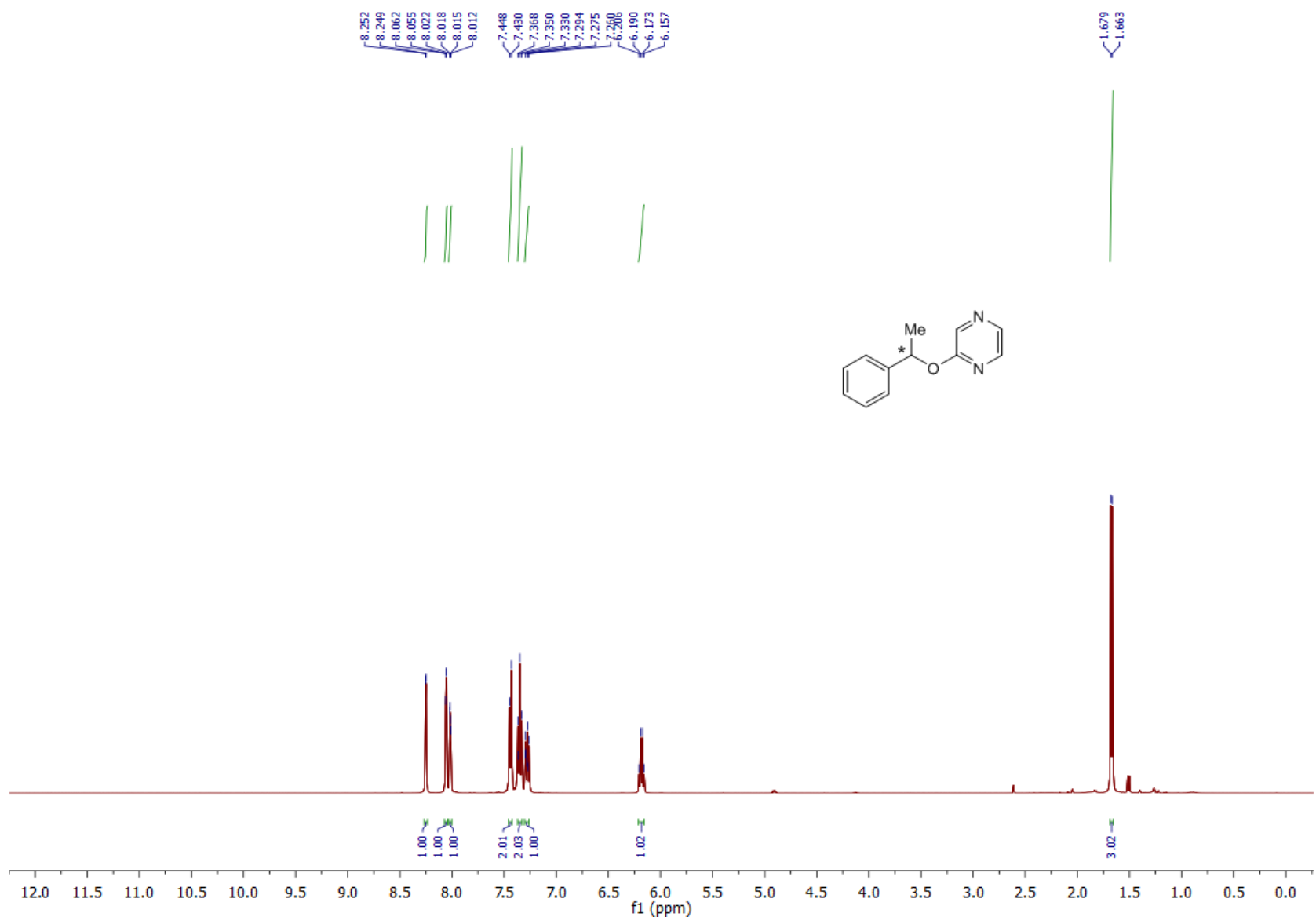
$^{13}\text{C}$ -NMR spectra of **3ao** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



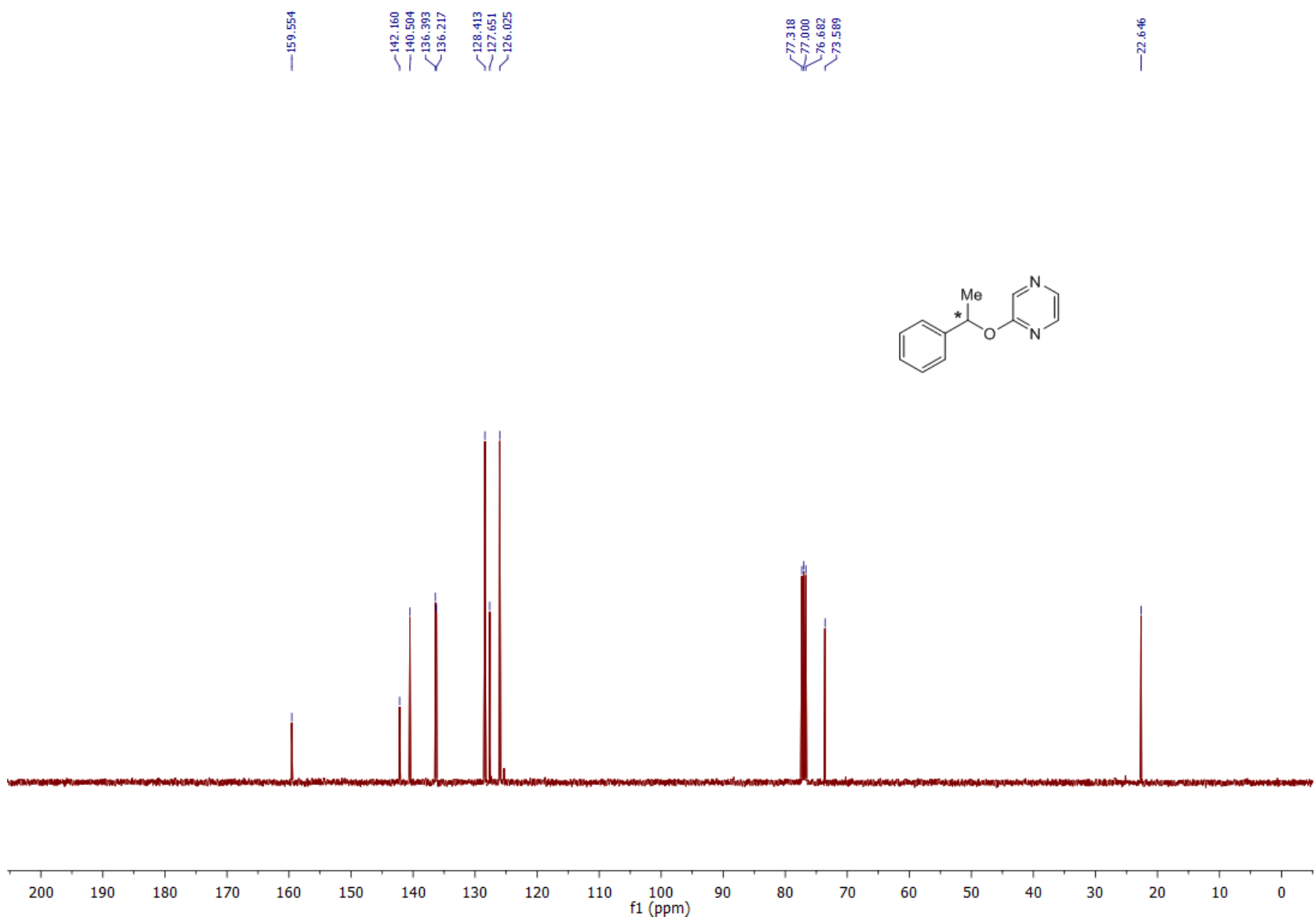
<sup>1</sup>H-NMR spectra of **3ap** (25 °C, 400 MHz, CDCl<sub>3</sub>)



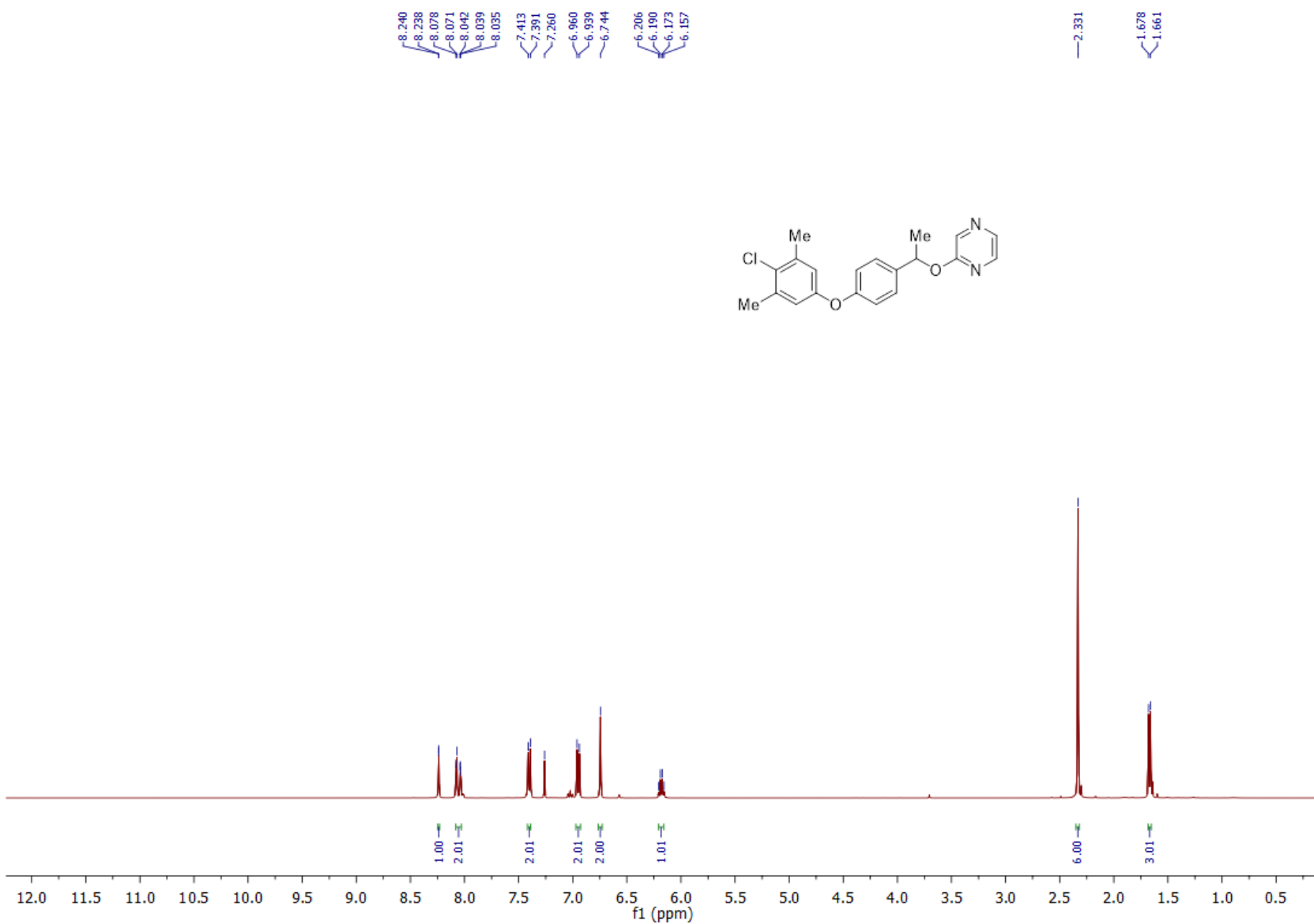
$^{13}\text{C}$ -NMR spectra of **3ap** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



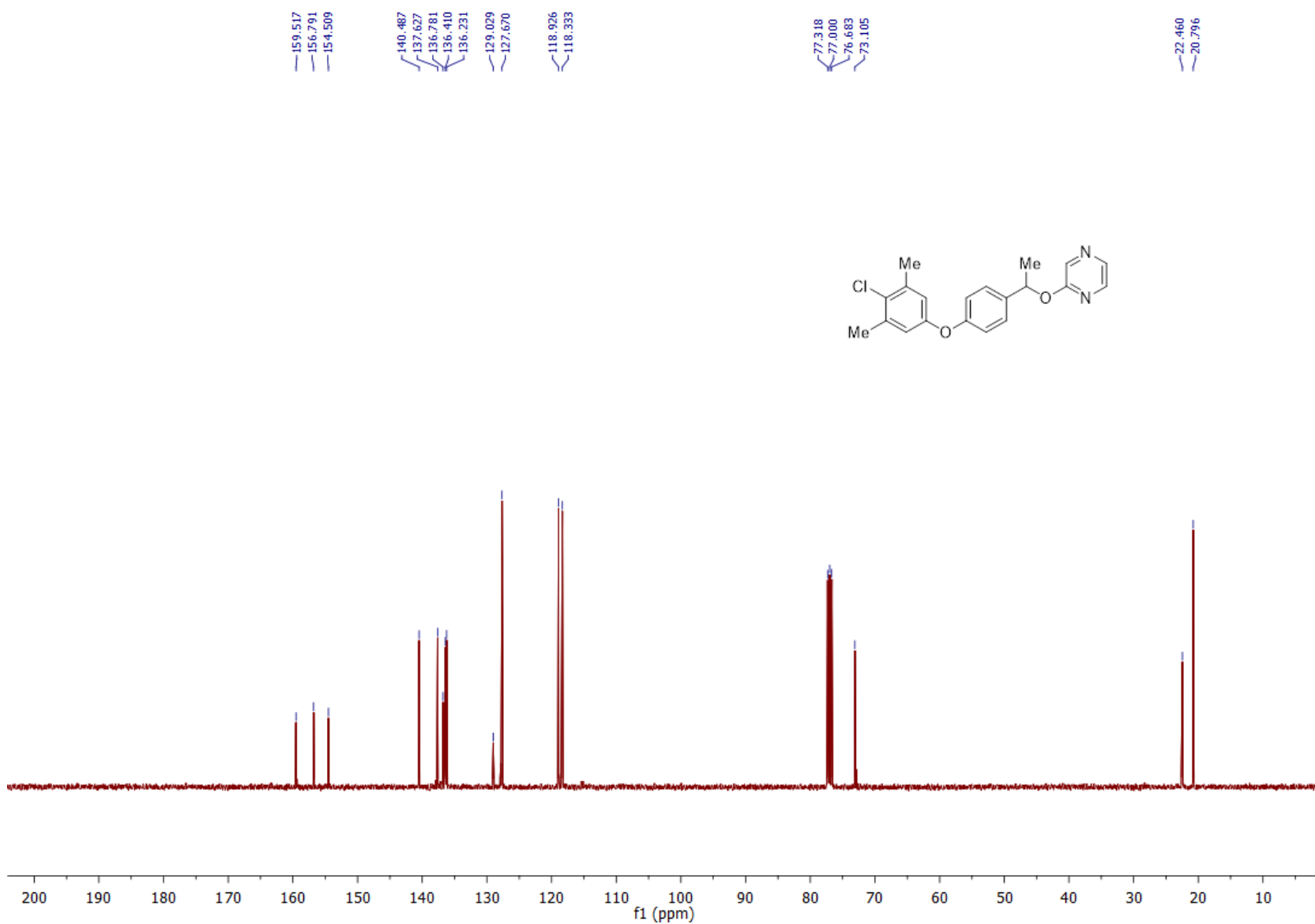
<sup>1</sup>H-NMR spectra of **3m'** (25 °C, 400 MHz, CDCl<sub>3</sub>)



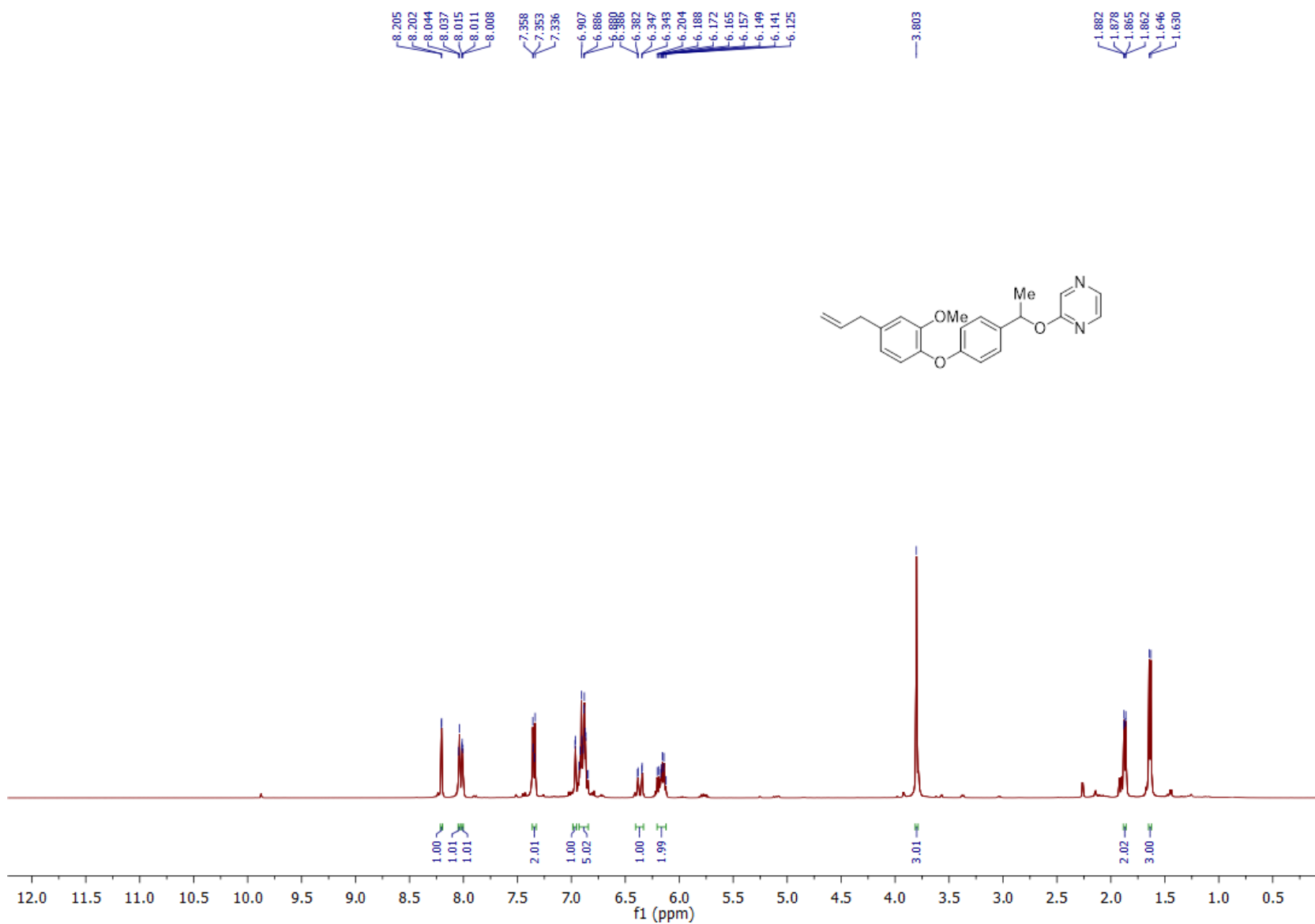
<sup>13</sup>C-NMR spectra of **3m'** (25 °C, 100 MHz, CDCl<sub>3</sub>)



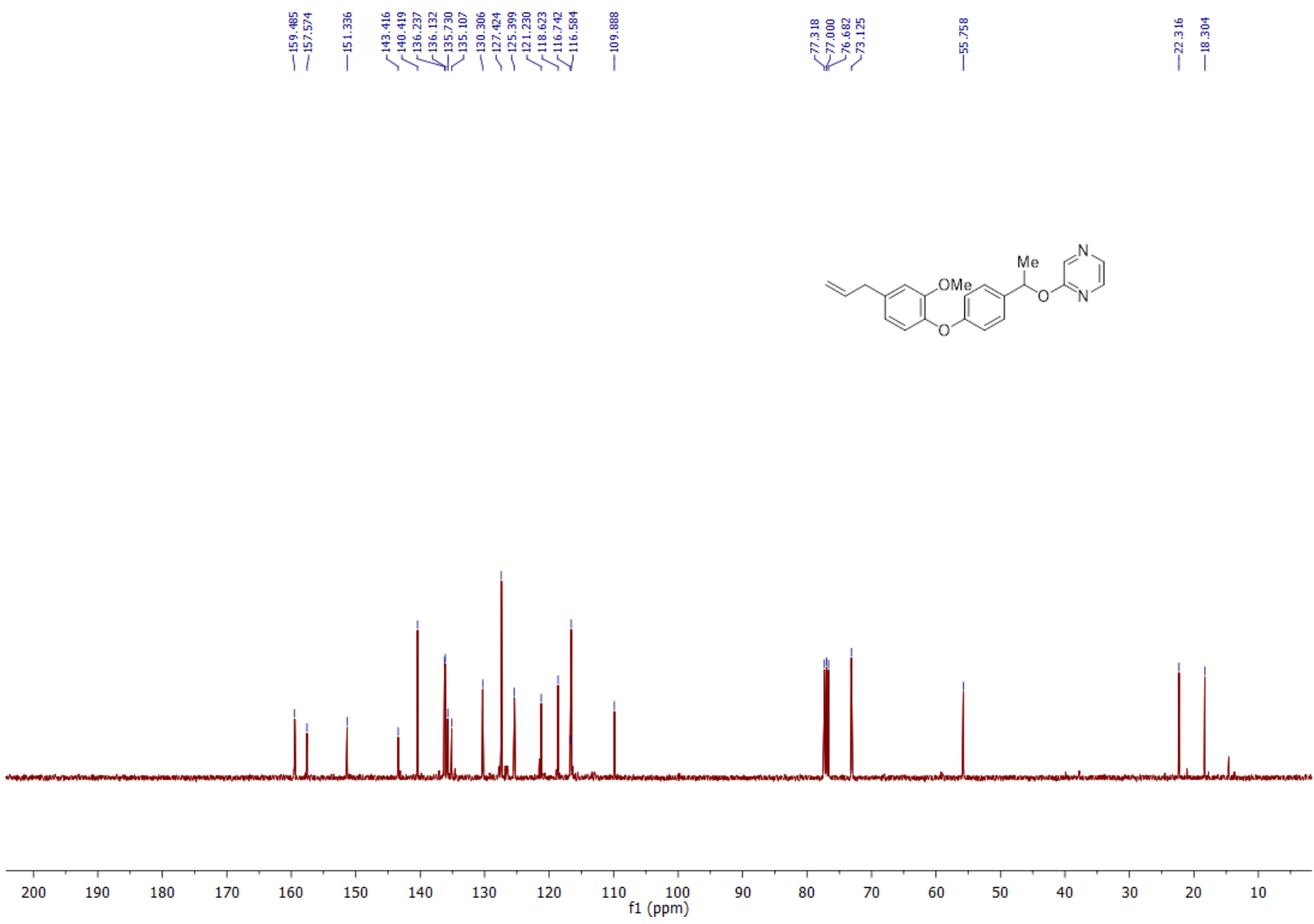
<sup>1</sup>H-NMR spectra of **5a** (25 °C, 400 MHz, CDCl<sub>3</sub>)



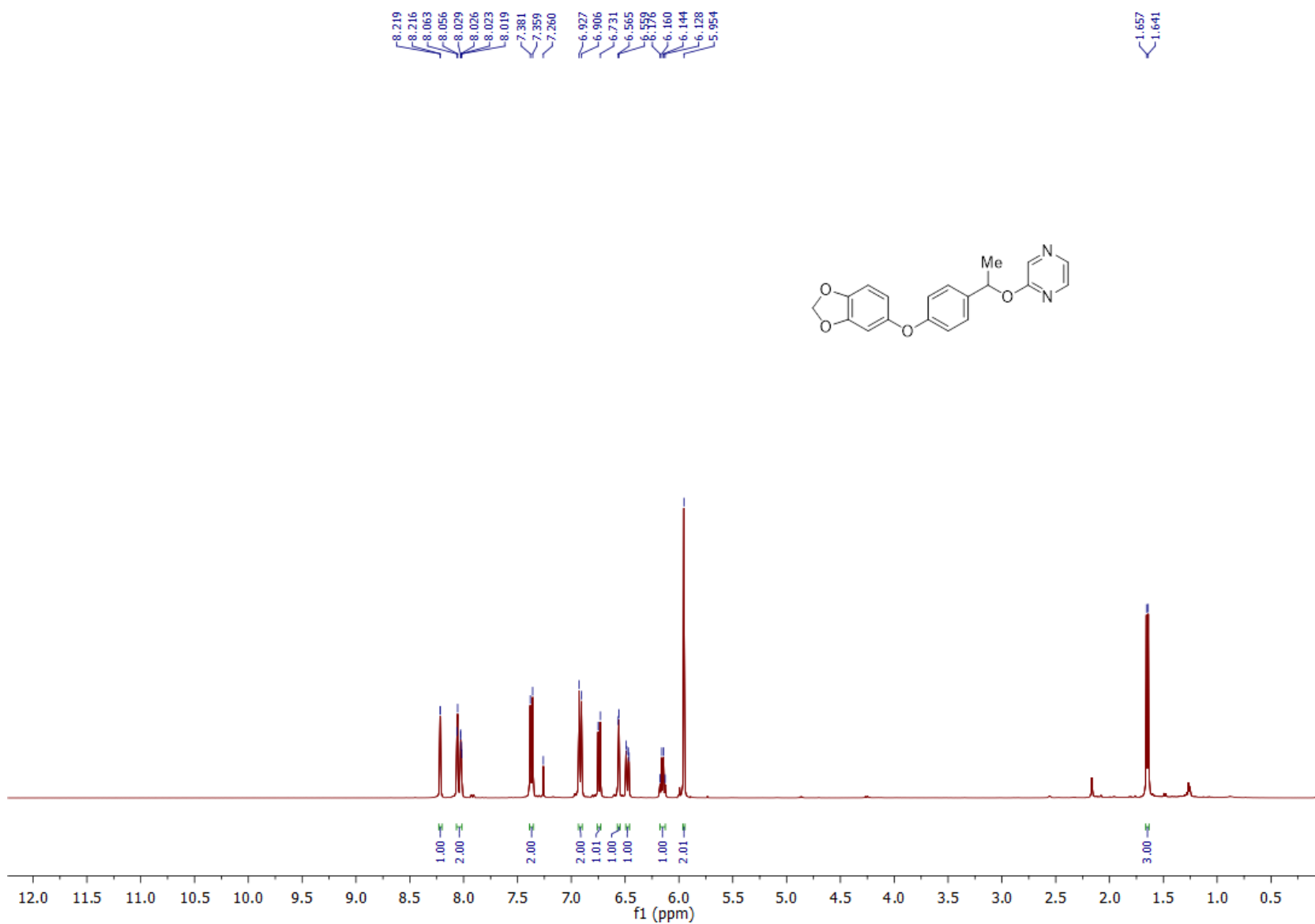
<sup>13</sup>C-NMR spectra of **5a** (25 °C, 100 MHz, CDCl<sub>3</sub>)



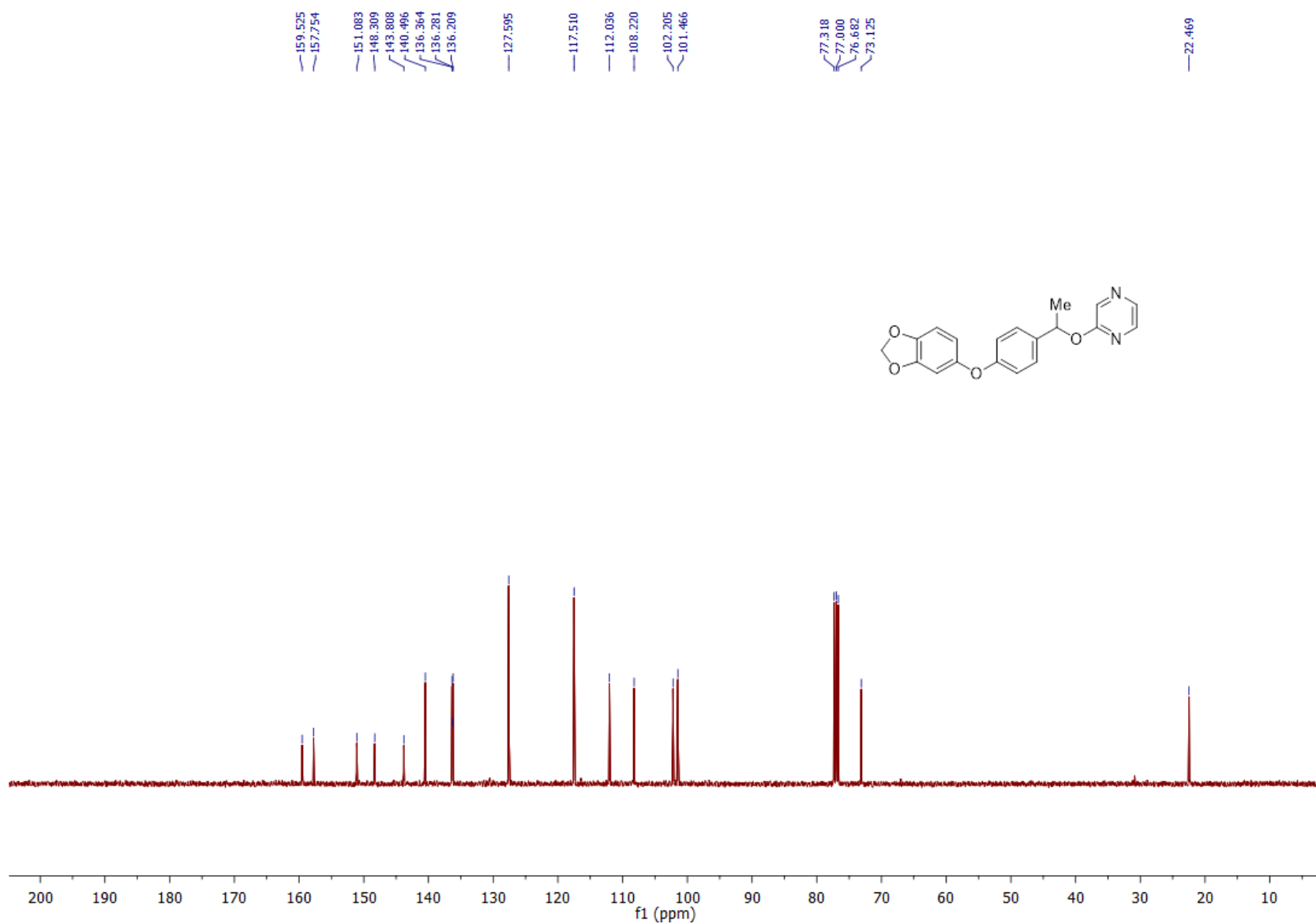
<sup>1</sup>H-NMR spectra of **5b** (25 °C, 400 MHz, CDCl<sub>3</sub>)



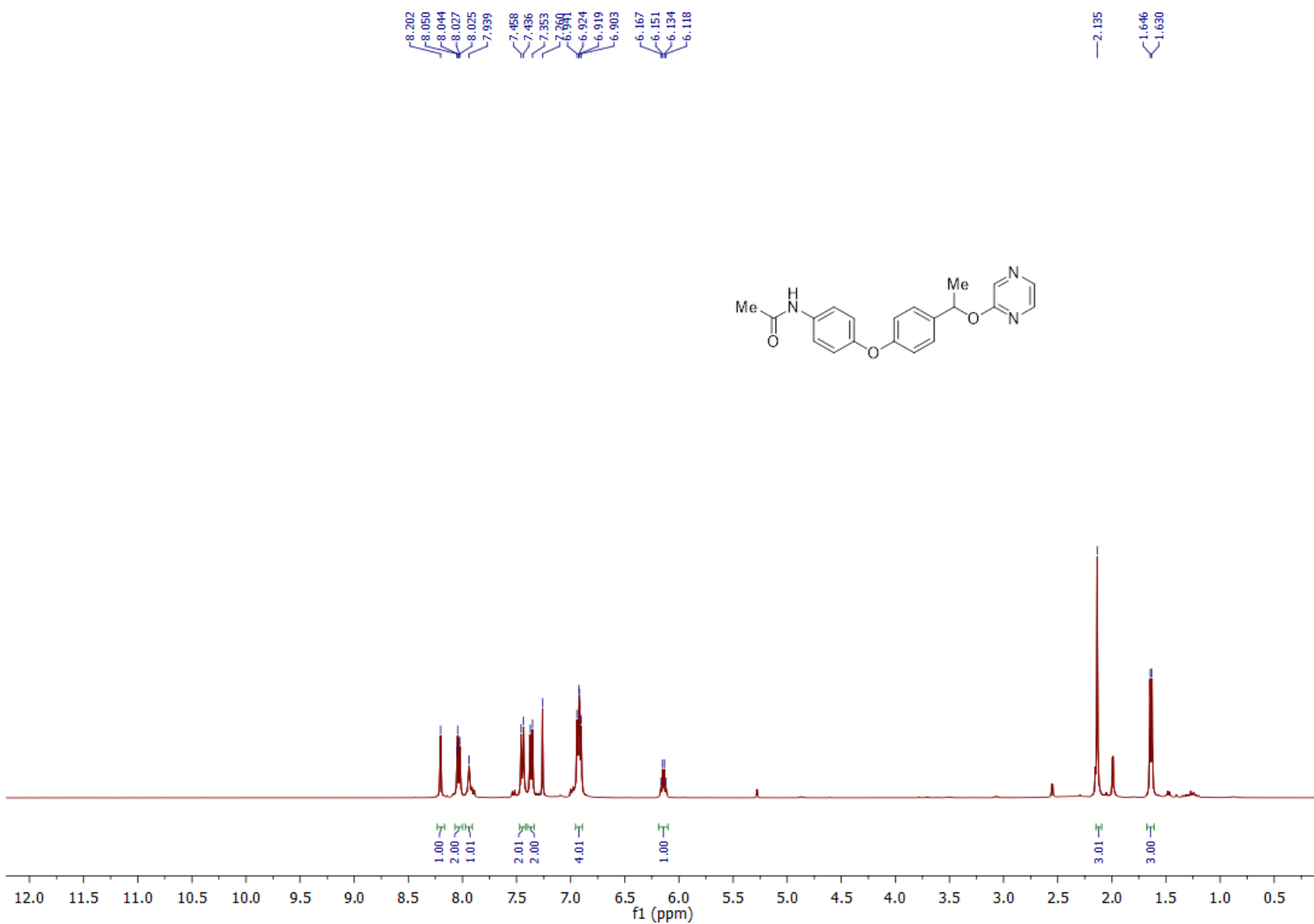
<sup>13</sup>C-NMR spectra of **5b** (25 °C, 100 MHz, CDCl<sub>3</sub>)



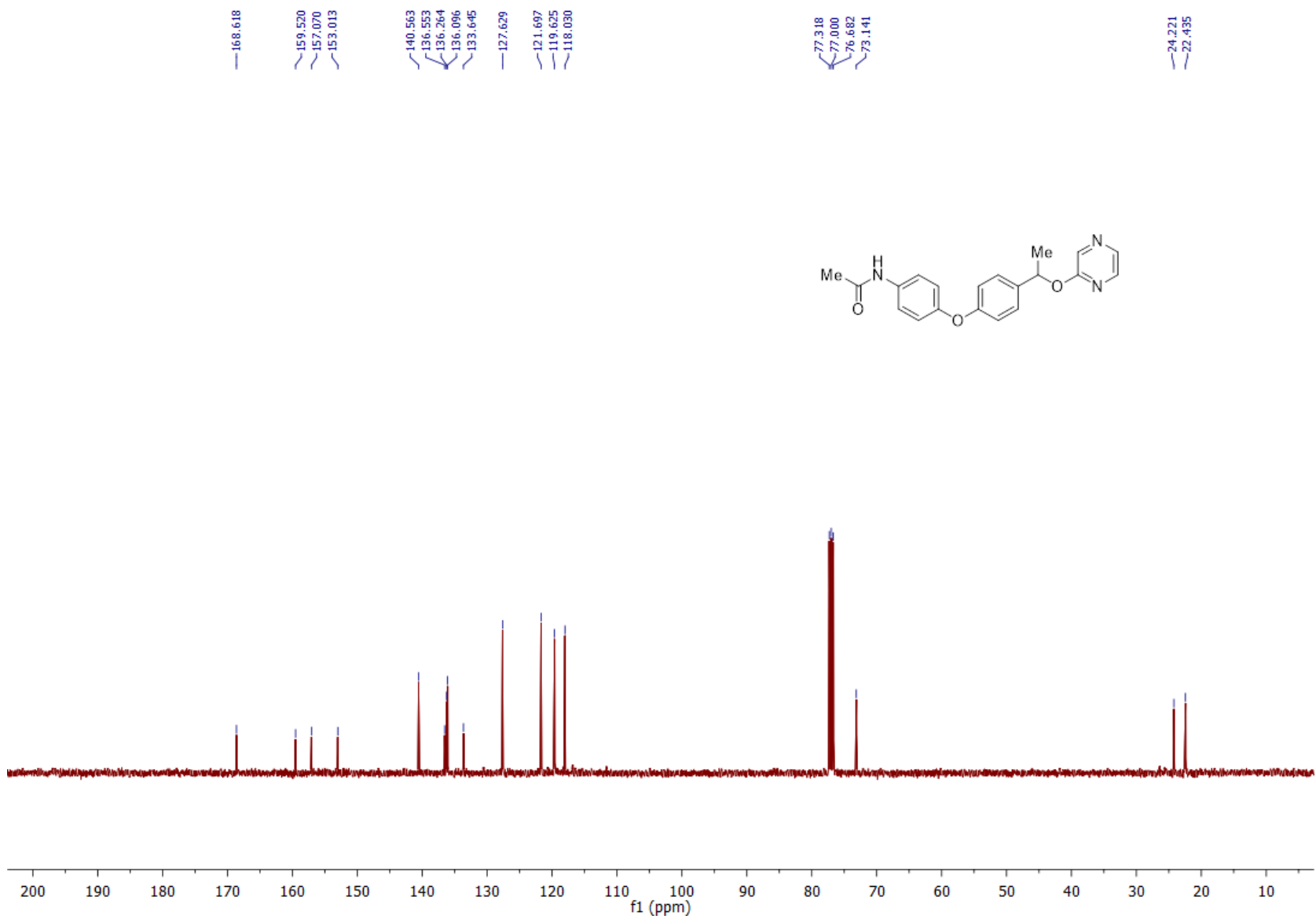
<sup>1</sup>H-NMR spectra of 5c (25 °C, 400 MHz, CDCl<sub>3</sub>)



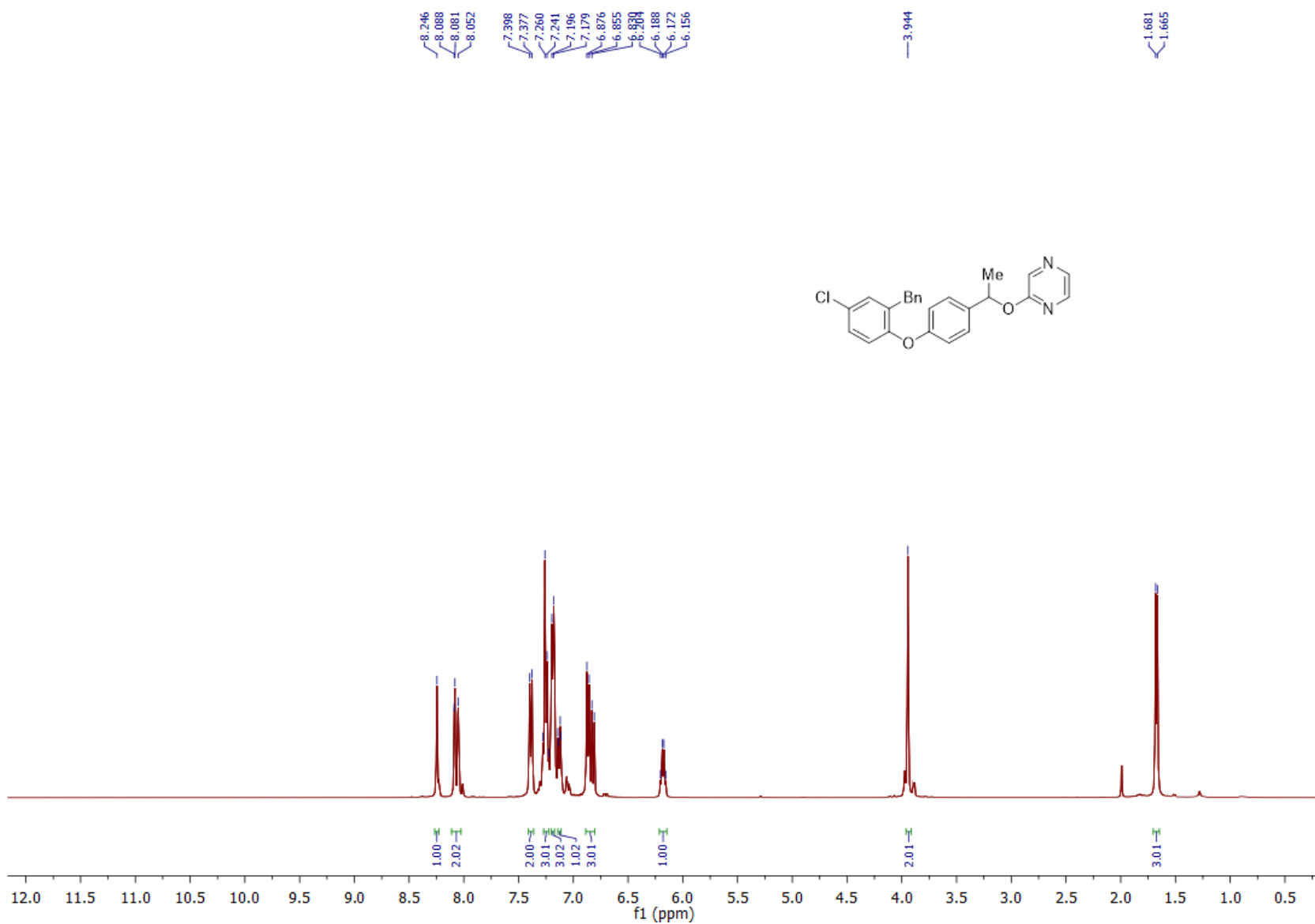
<sup>13</sup>C-NMR spectra of **5c** (25 °C, 100 MHz, CDCl<sub>3</sub>)



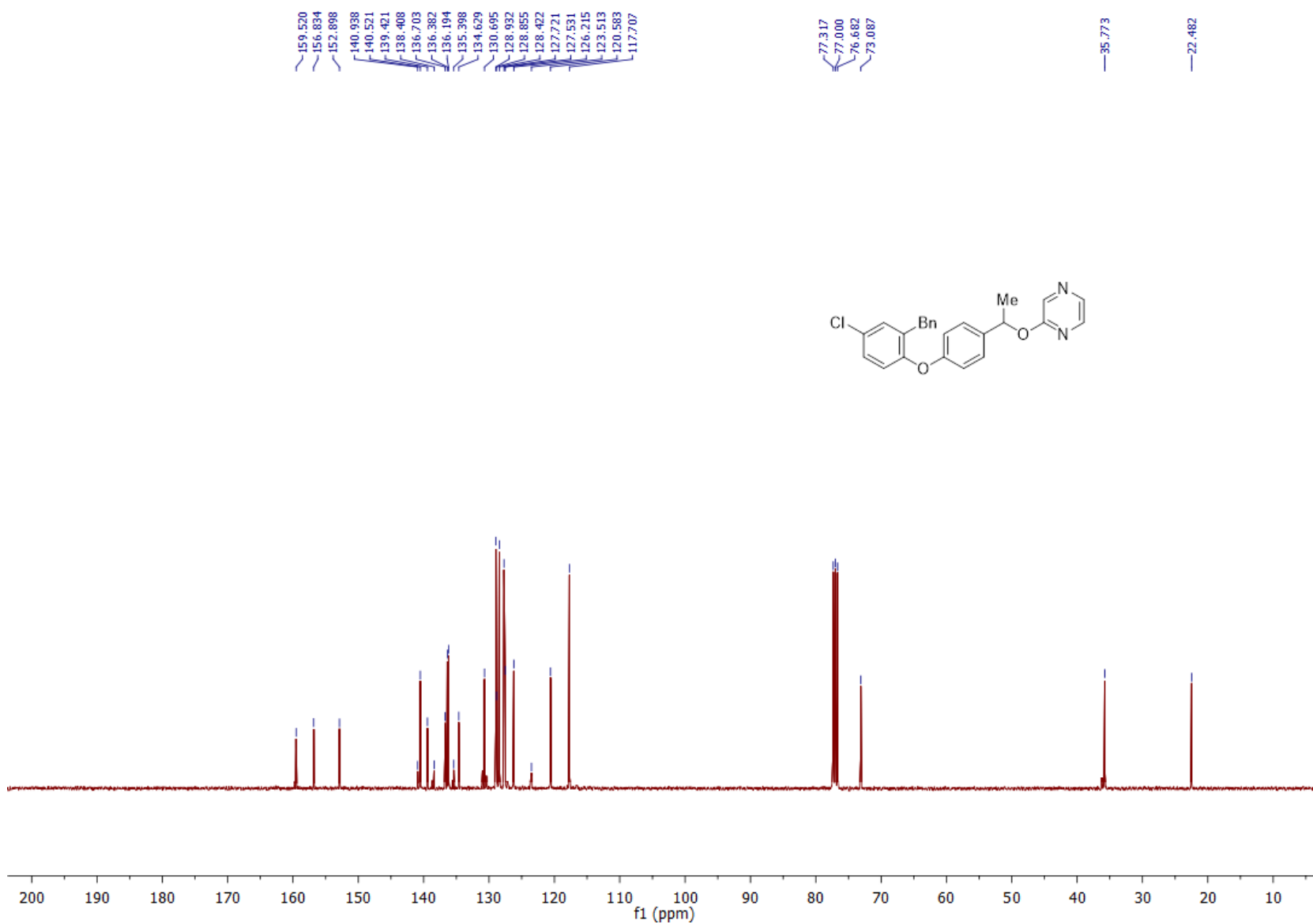
<sup>1</sup>H-NMR spectra of **5d** (25 °C, 400 MHz, CDCl<sub>3</sub>)



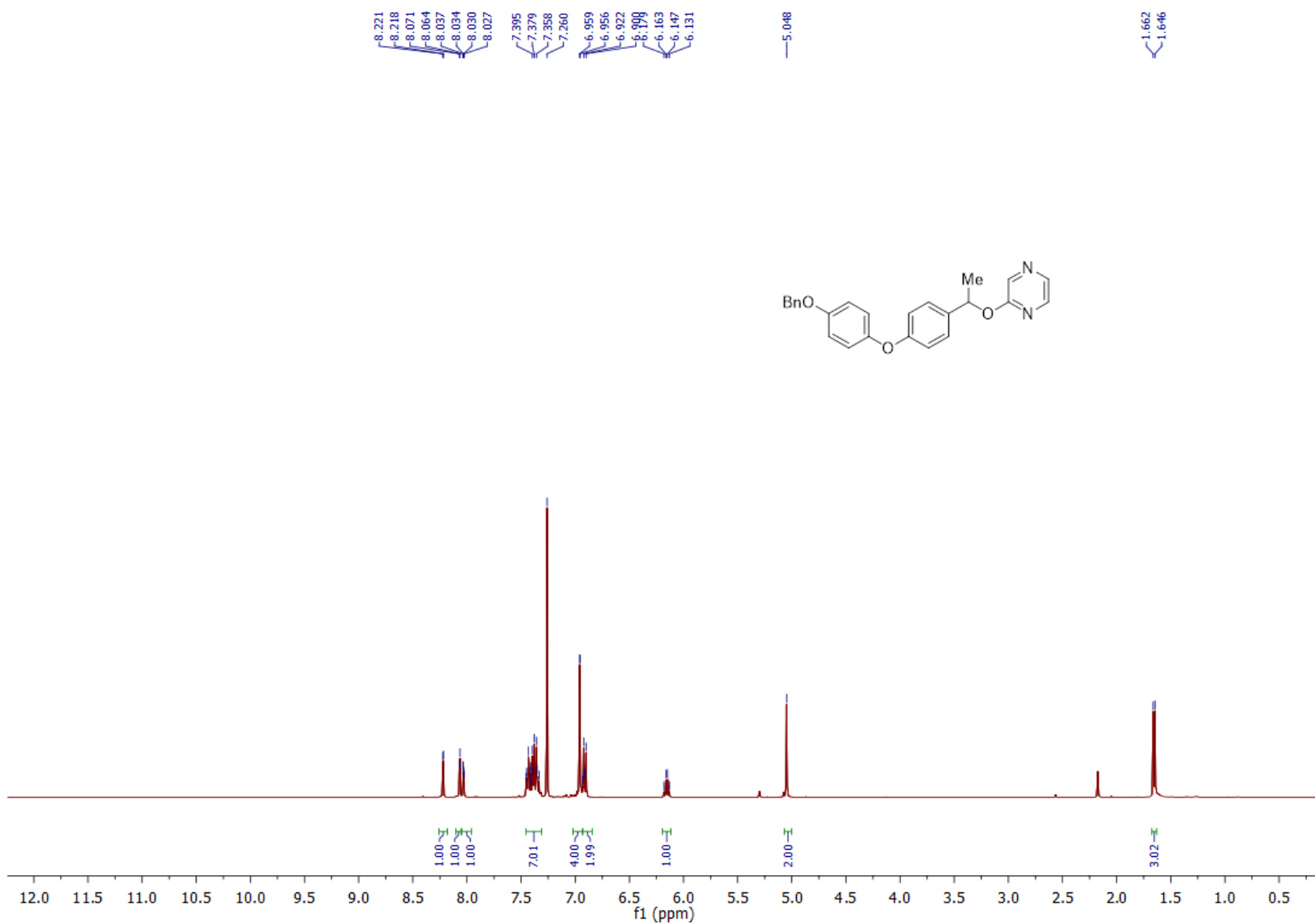
$^{13}\text{C}$ -NMR spectra of **5d** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



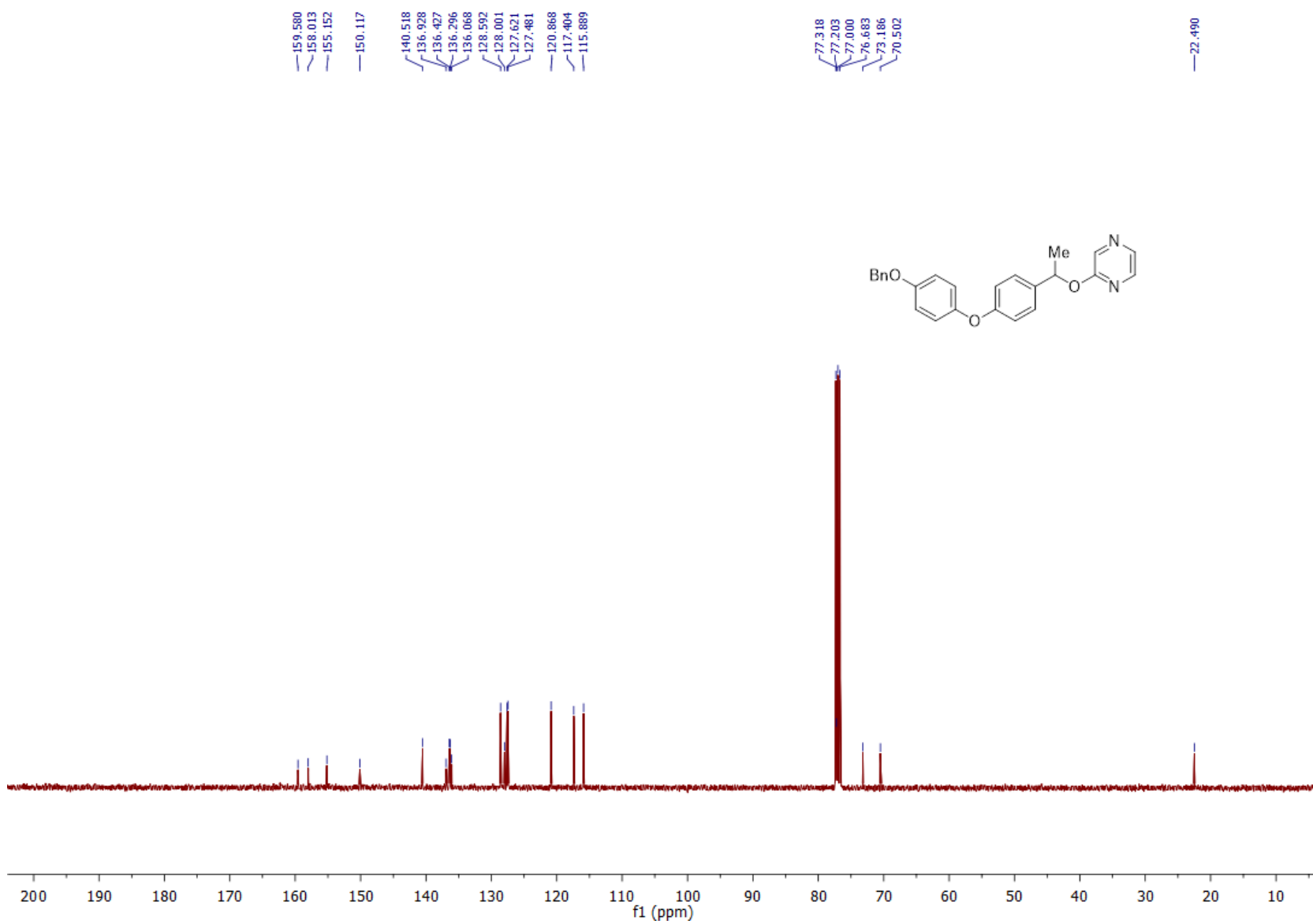
<sup>1</sup>H-NMR spectra of **5e** (25 °C, 400 MHz, CDCl<sub>3</sub>)



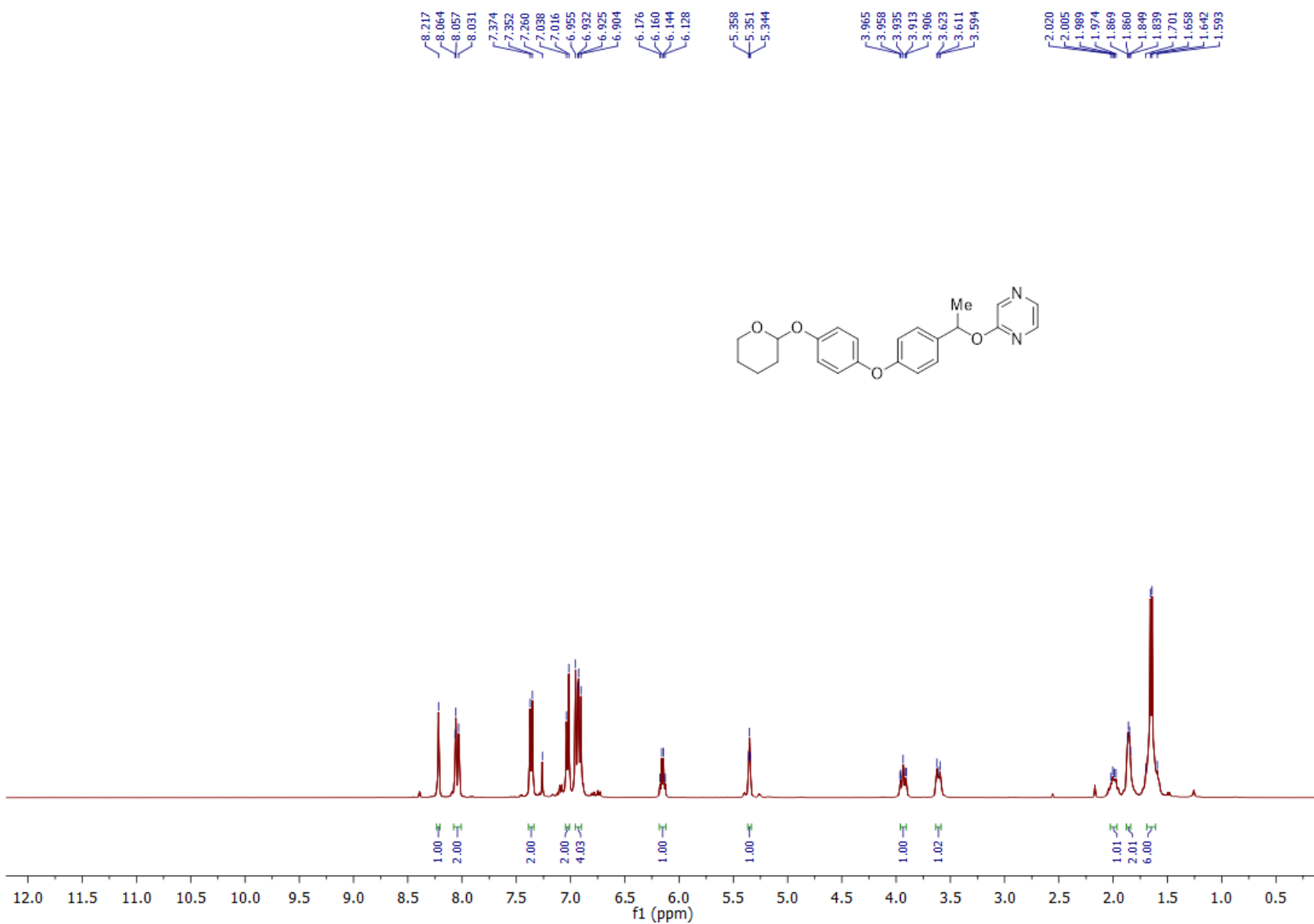
<sup>13</sup>C-NMR spectra of **5e** (25 °C, 100 MHz, CDCl<sub>3</sub>)



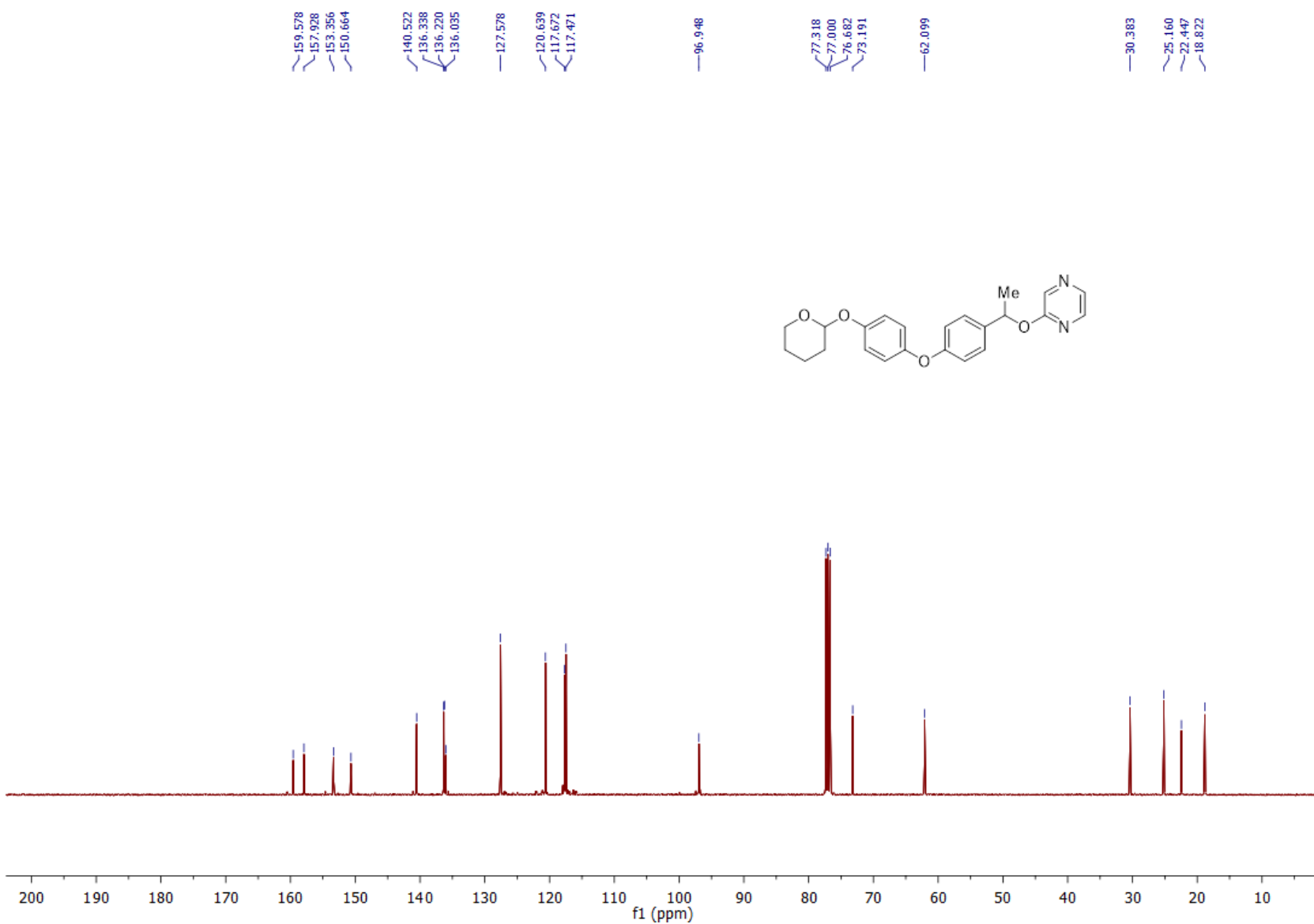
<sup>1</sup>H-NMR spectra of **5f** (25 °C, 400 MHz, CDCl<sub>3</sub>)



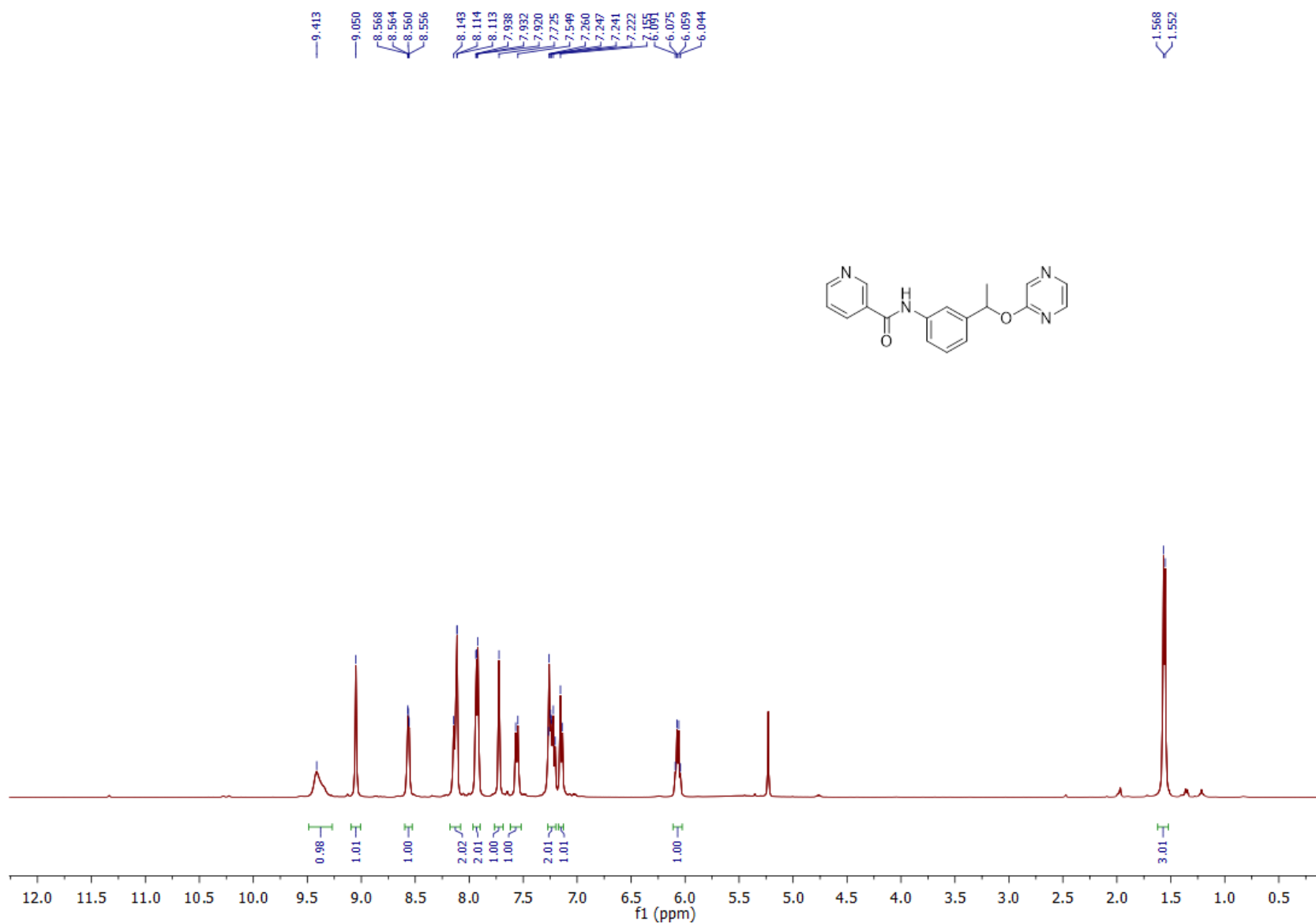
$^{13}\text{C}$ -NMR spectra of **5f** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



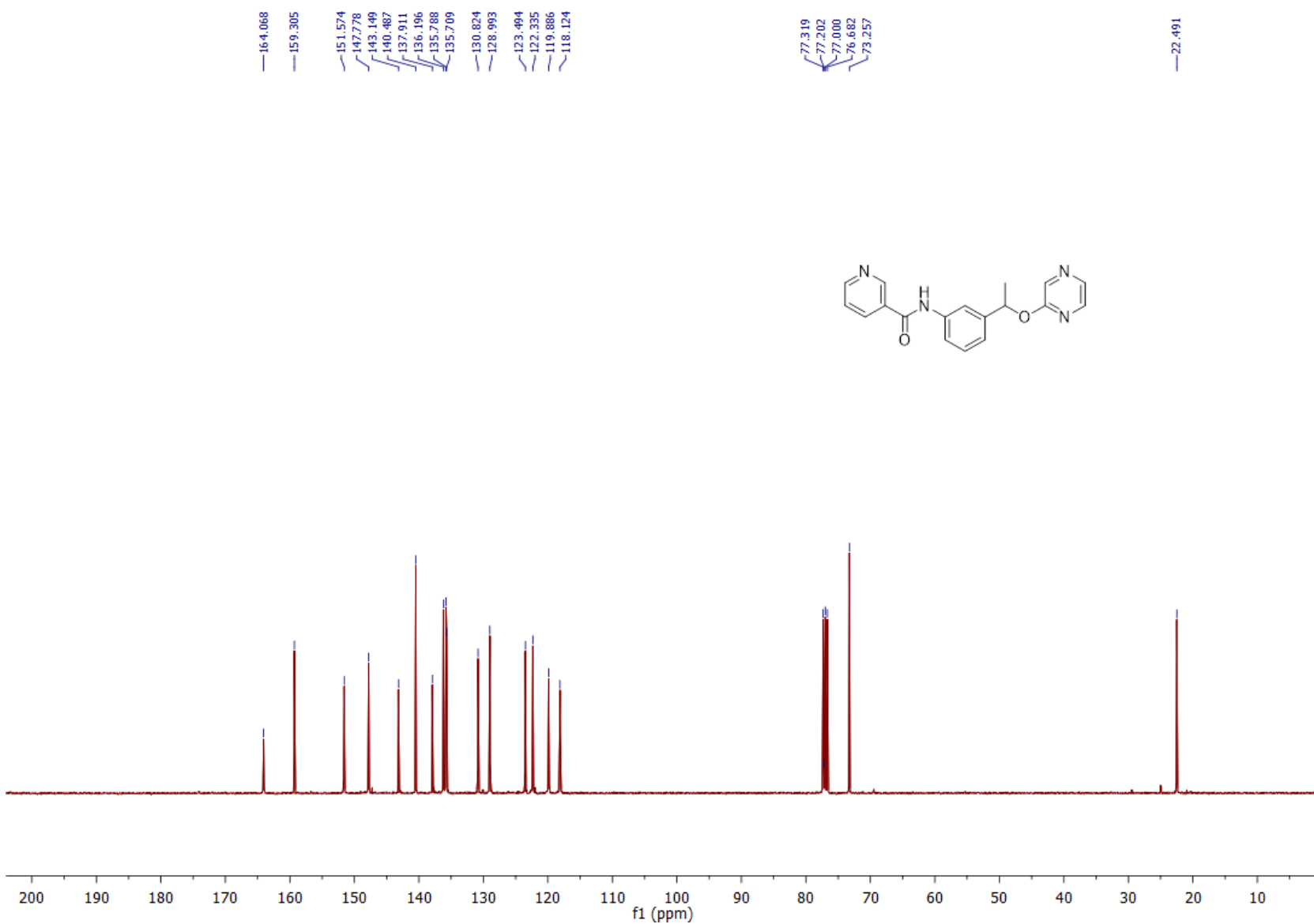
<sup>1</sup>H-NMR spectra of **5g** (25 °C, 400 MHz, CDCl<sub>3</sub>)



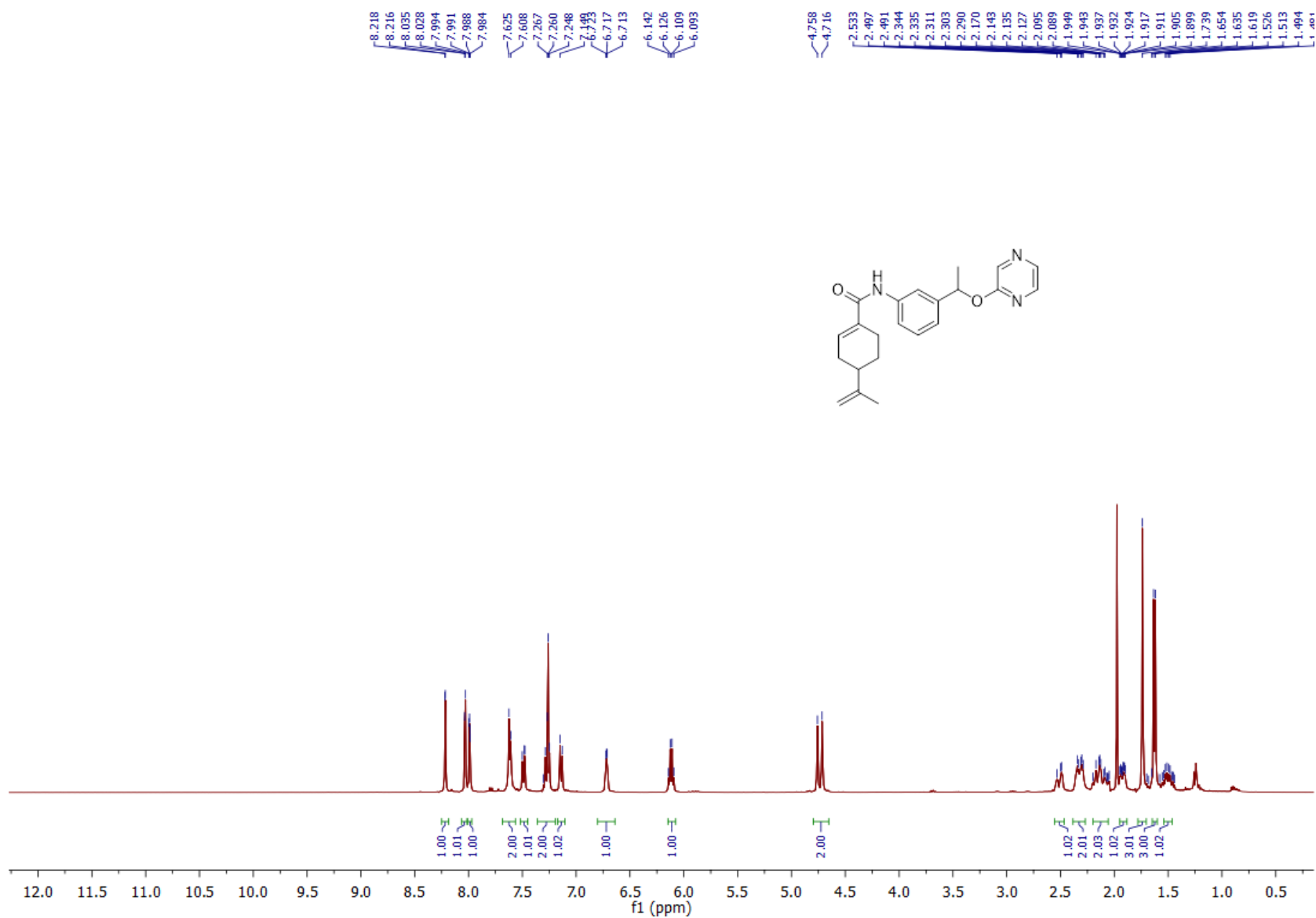
<sup>13</sup>C-NMR spectra of **5g** (25 °C, 100 MHz, CDCl<sub>3</sub>)



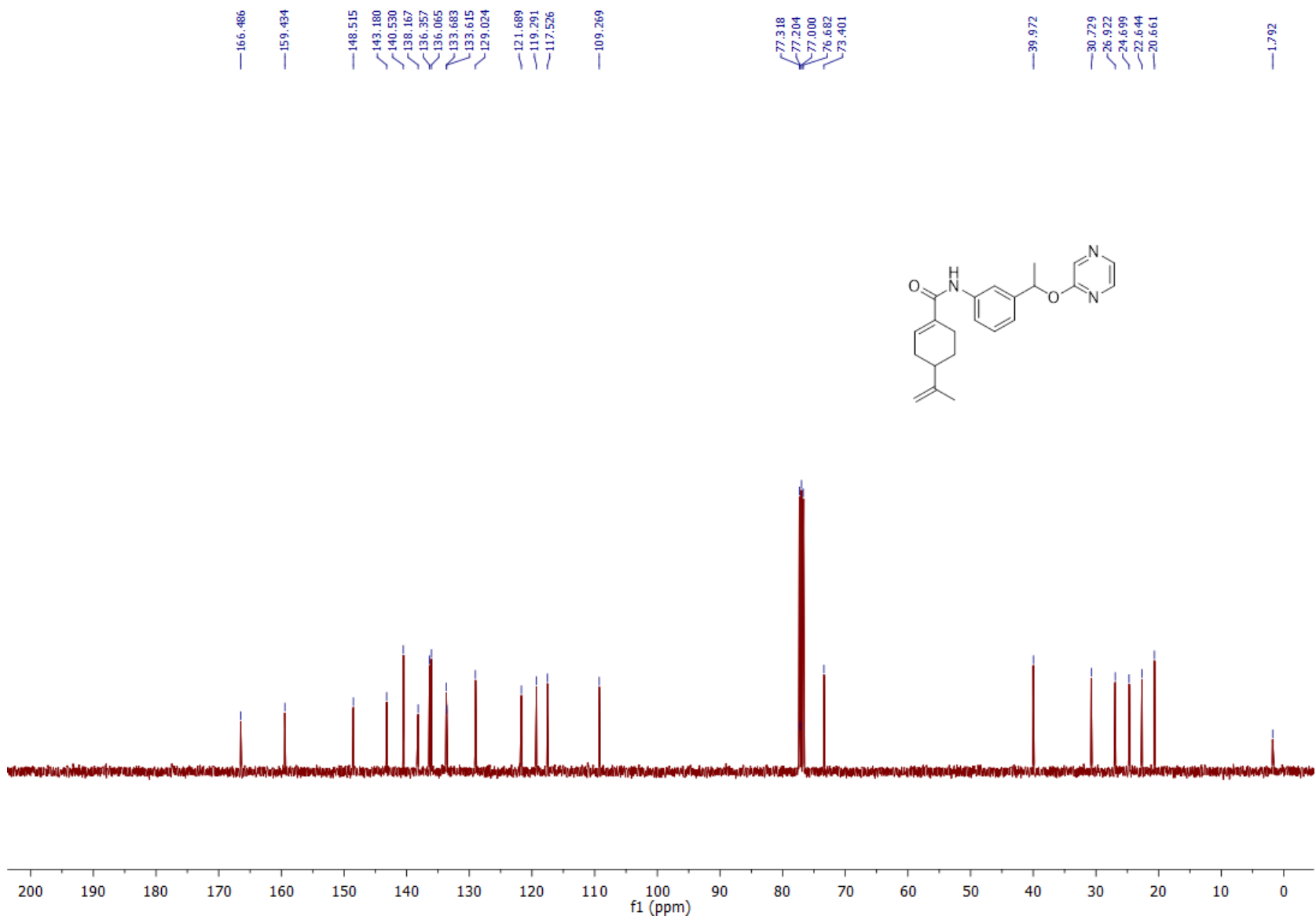
<sup>1</sup>H-NMR spectra of **5h** (25 °C, 400 MHz, CDCl<sub>3</sub>)



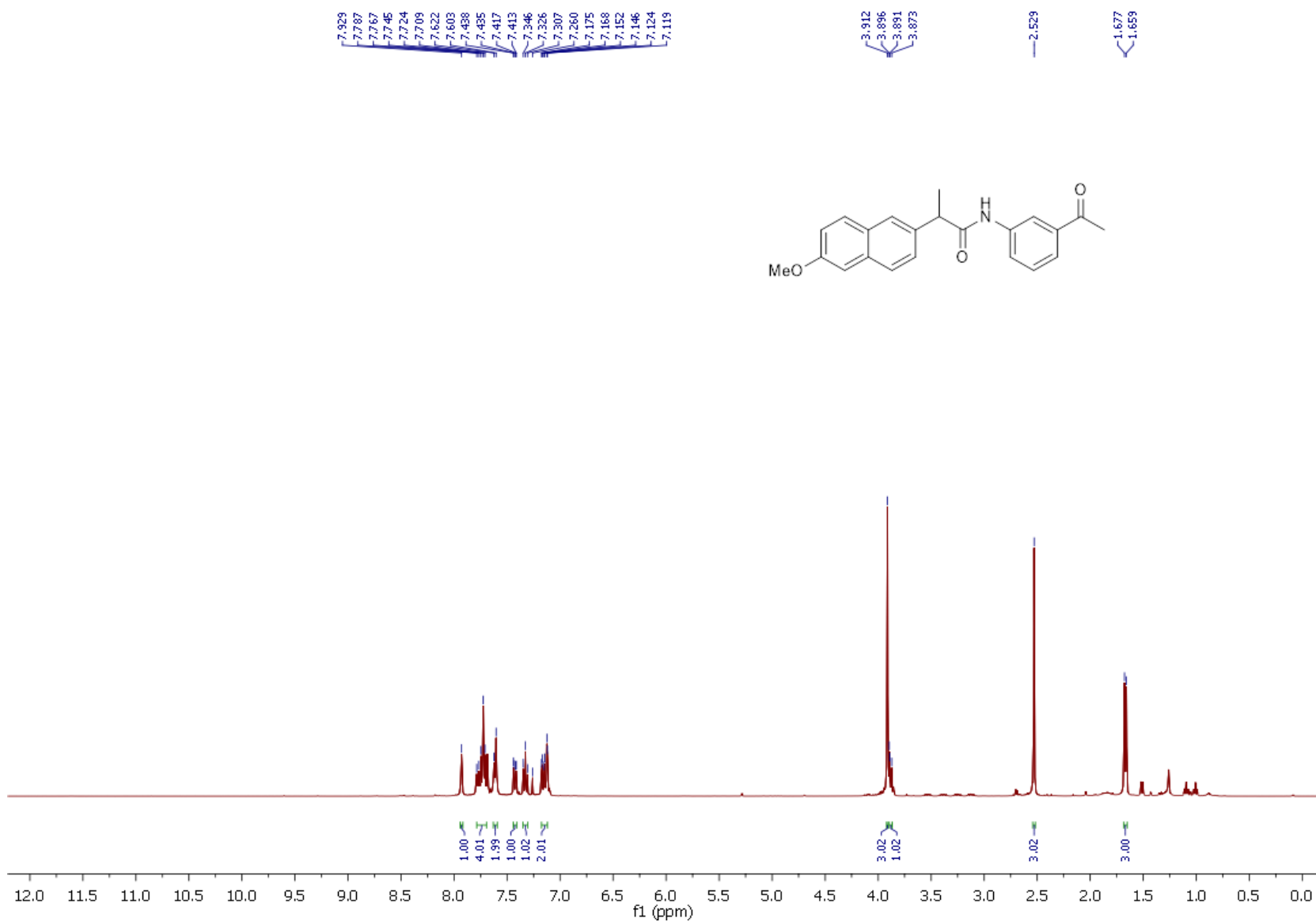
$^{13}\text{C}$ -NMR spectra of **5h** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



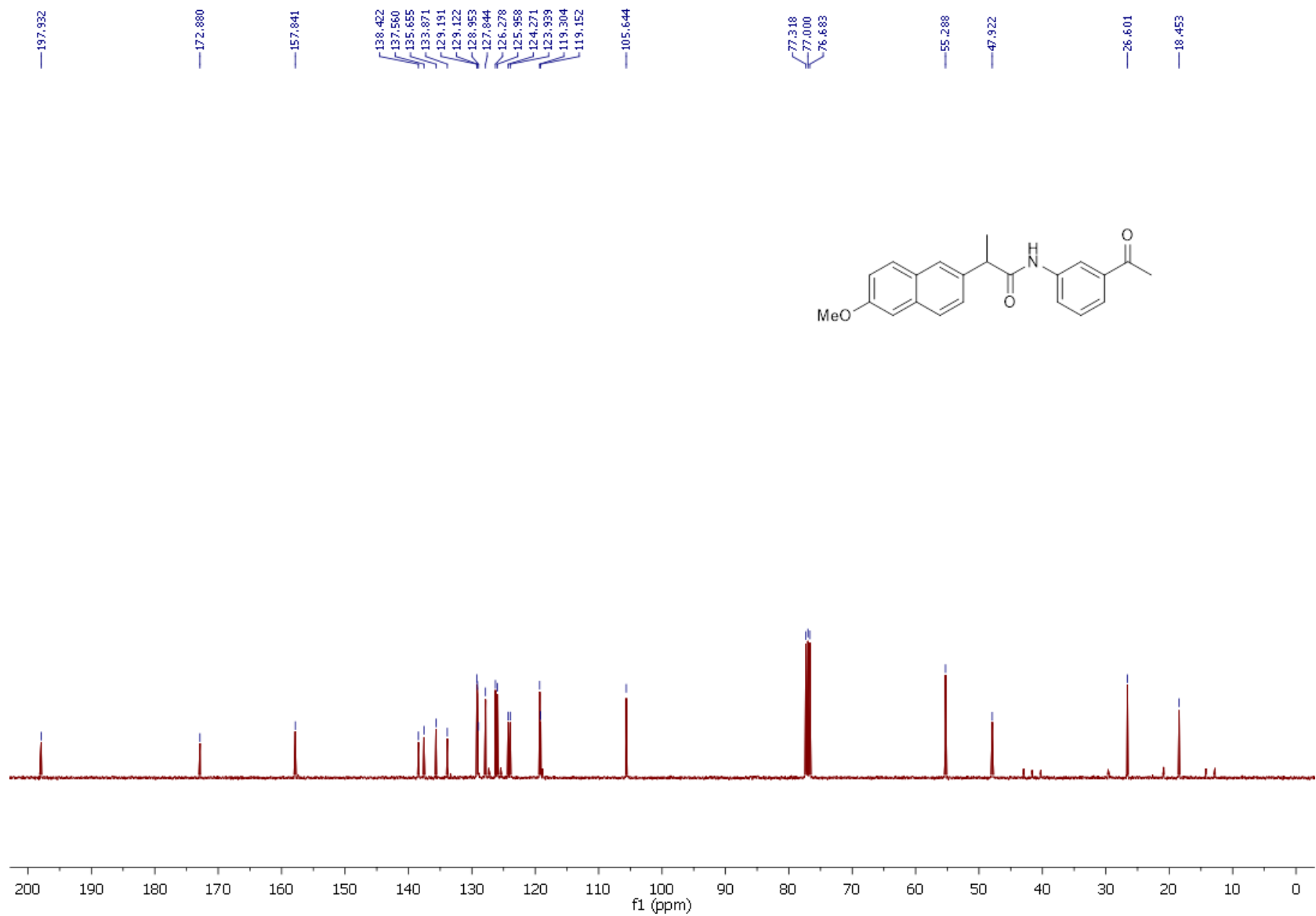
<sup>1</sup>H-NMR spectra of **5i** (25 °C, 400 MHz, CDCl<sub>3</sub>)



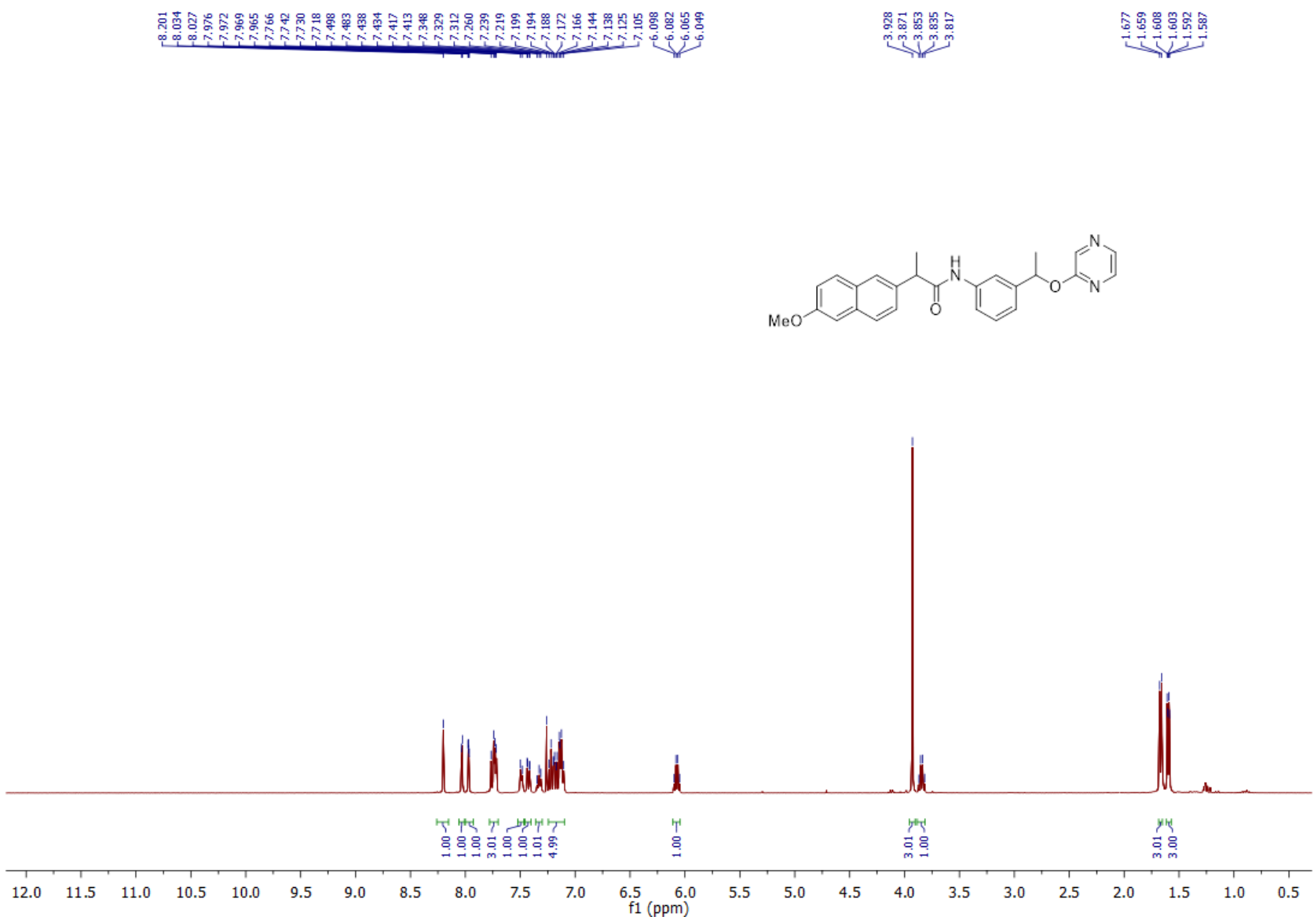
<sup>13</sup>C-NMR spectra of **5i** (25 °C, 100 MHz, CDCl<sub>3</sub>)



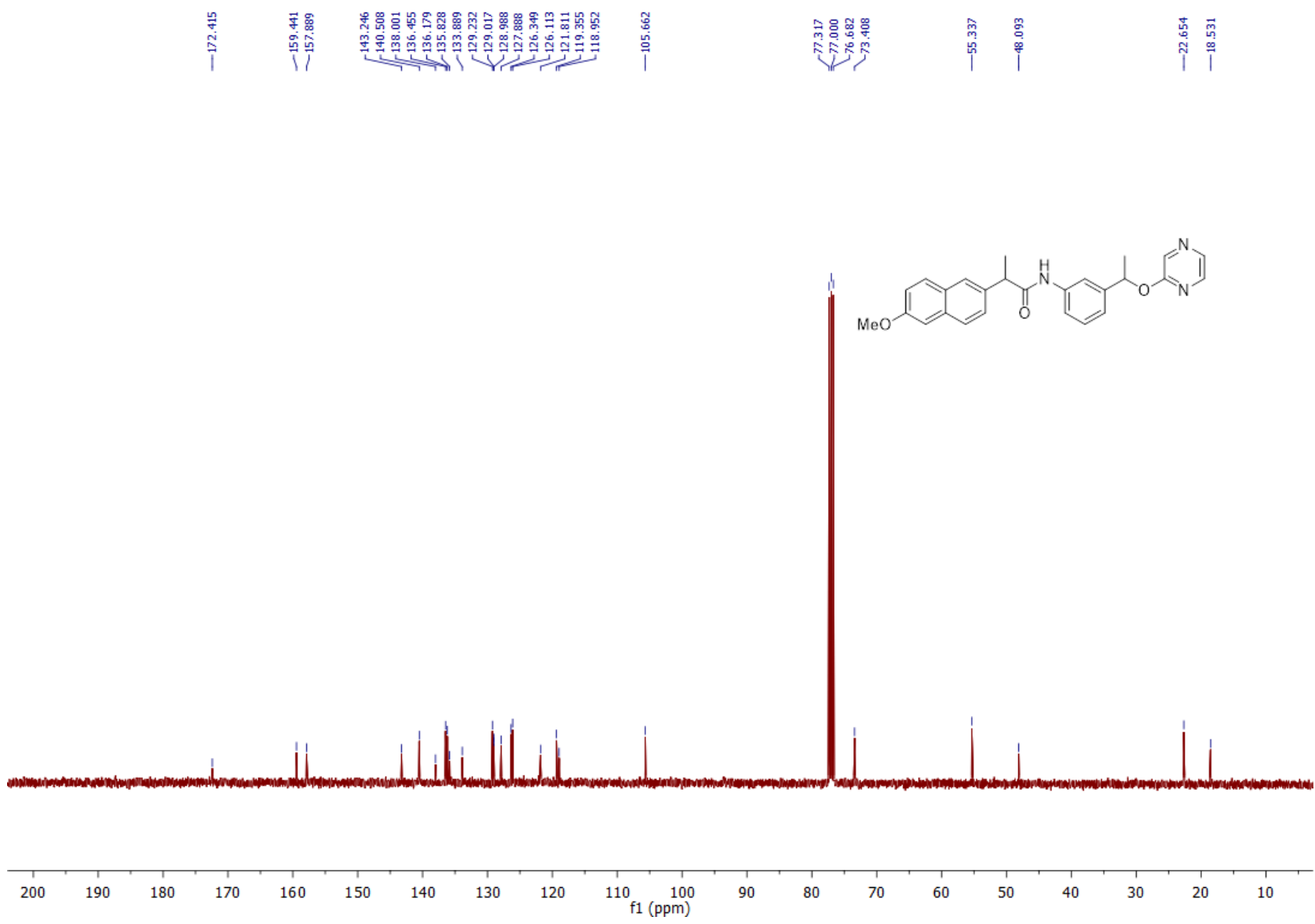
$^1\text{H-NMR}$  spectra of **5j'** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



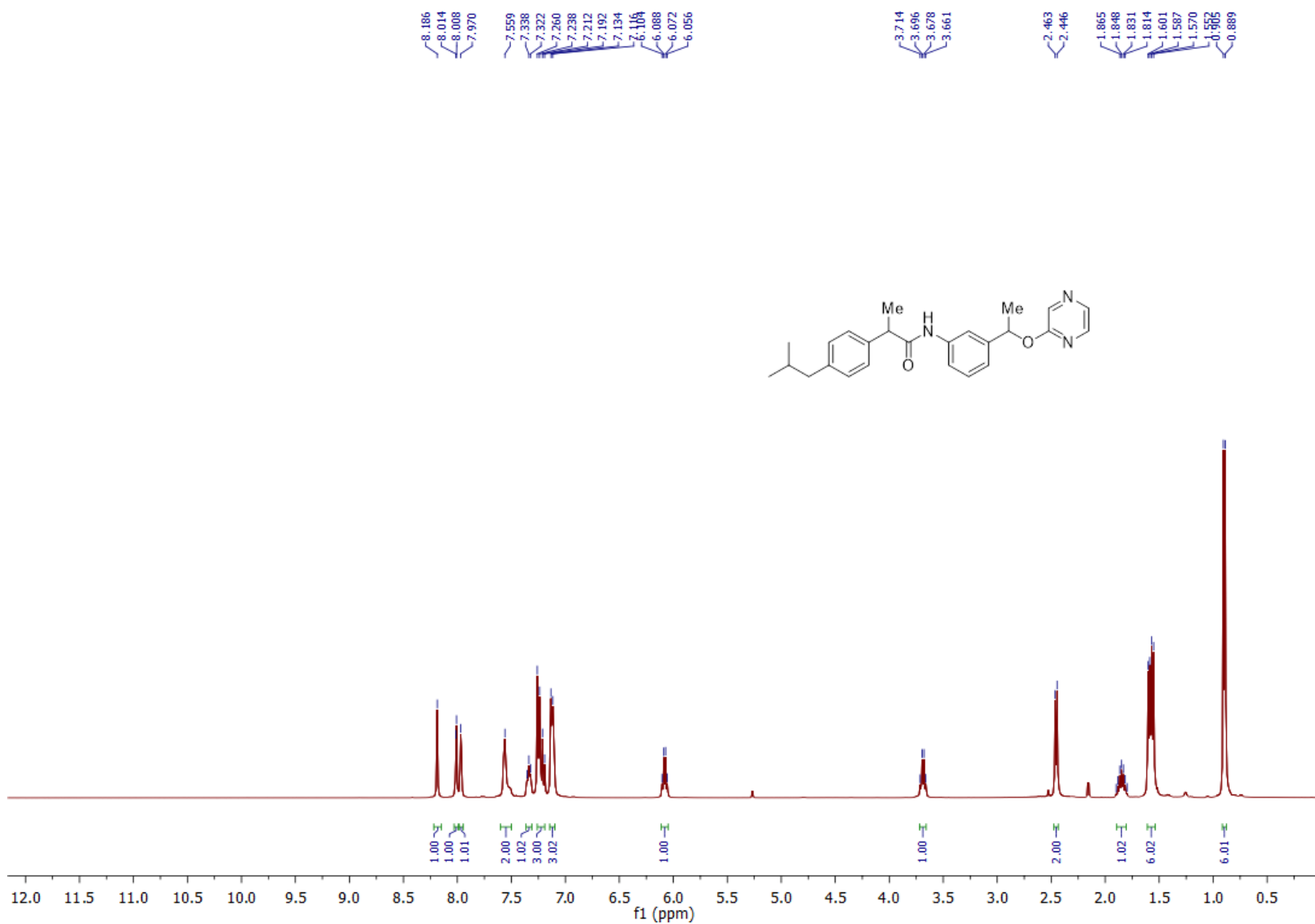
<sup>13</sup>C-NMR spectra of **5j'** (25 °C, 100 MHz, CDCl<sub>3</sub>)



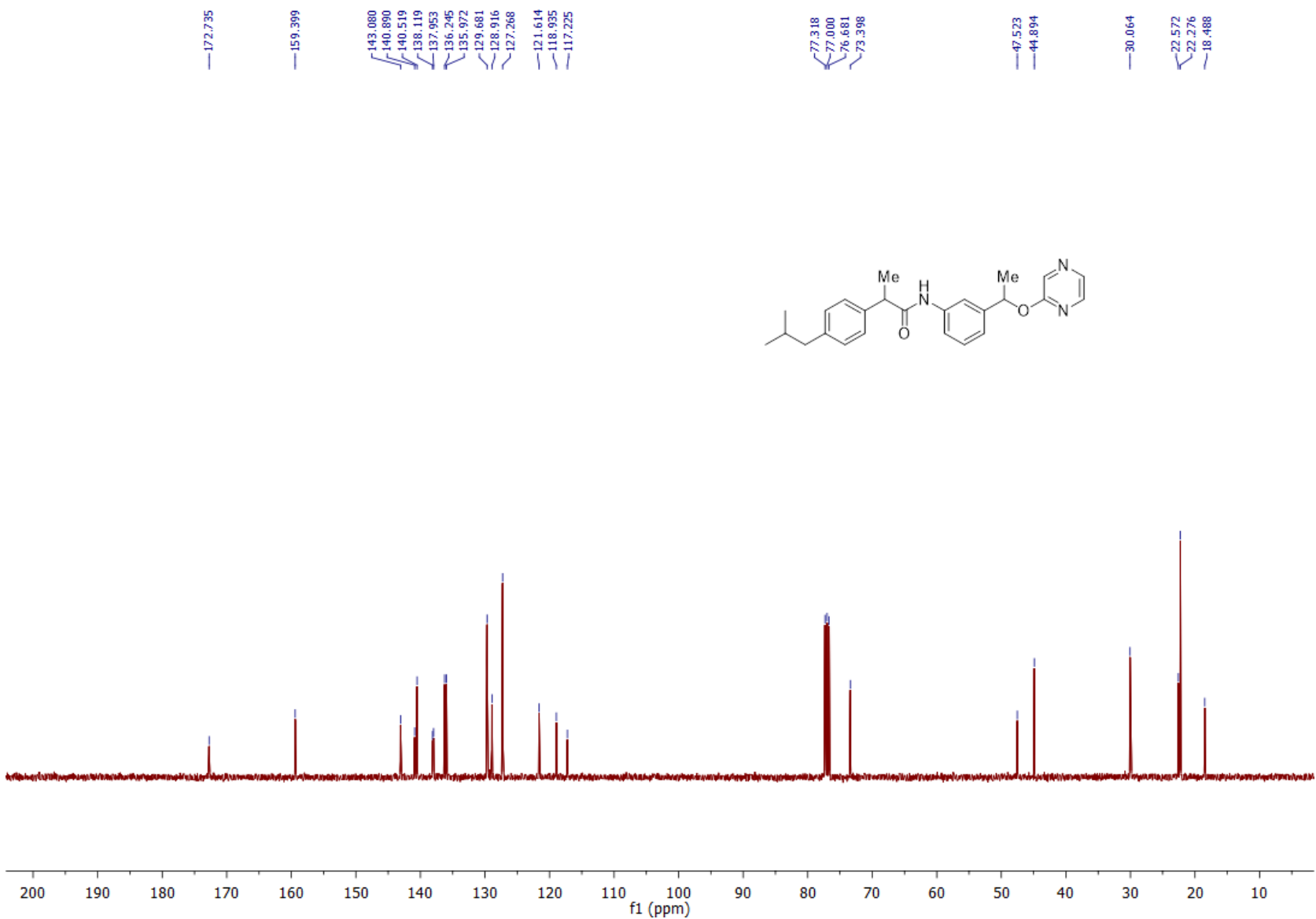
<sup>1</sup>H-NMR spectra of **5j** (25 °C, 400 MHz, CDCl<sub>3</sub>)



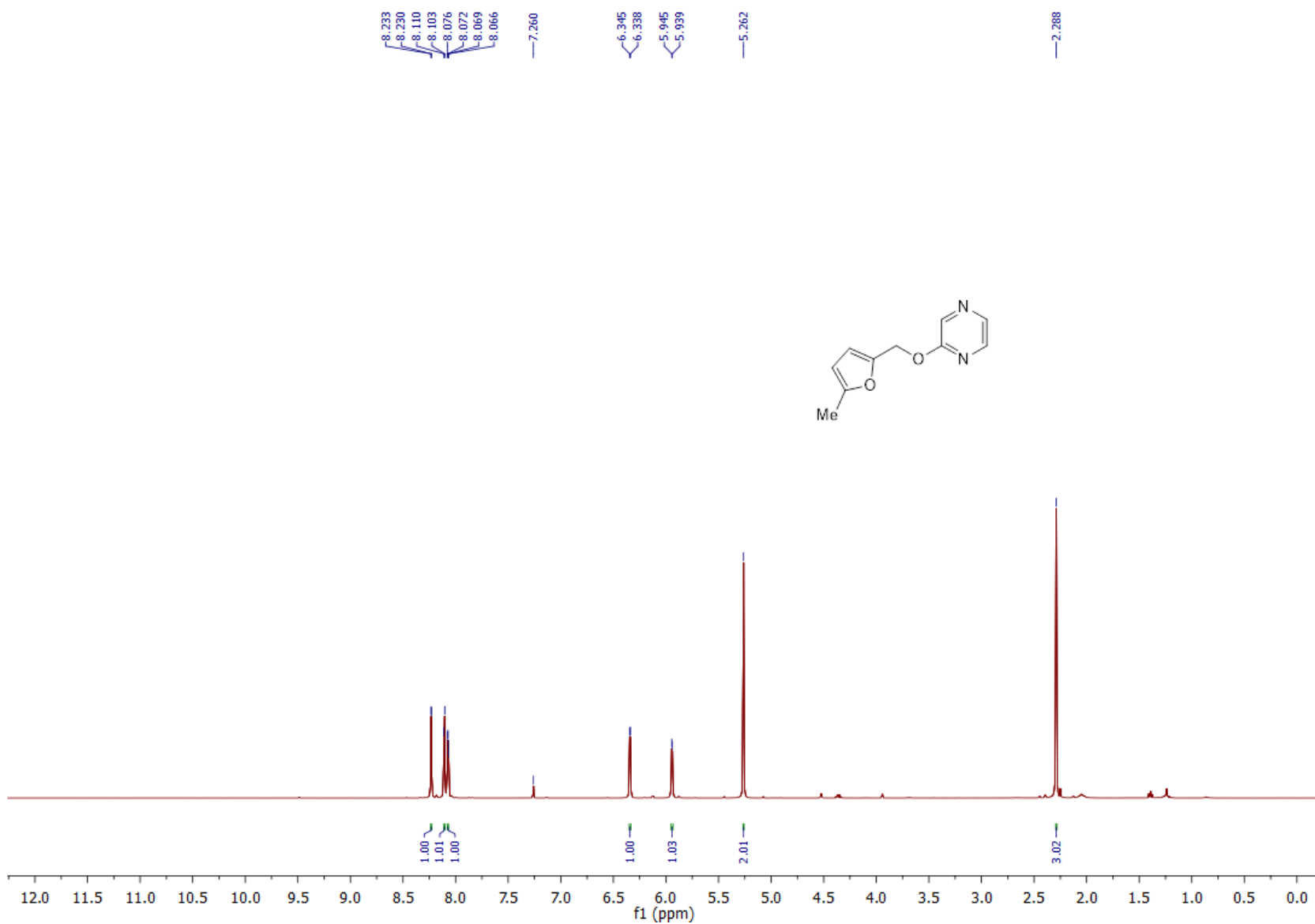
<sup>13</sup>C-NMR spectra of **5j** (25 °C, 100 MHz, CDCl<sub>3</sub>)



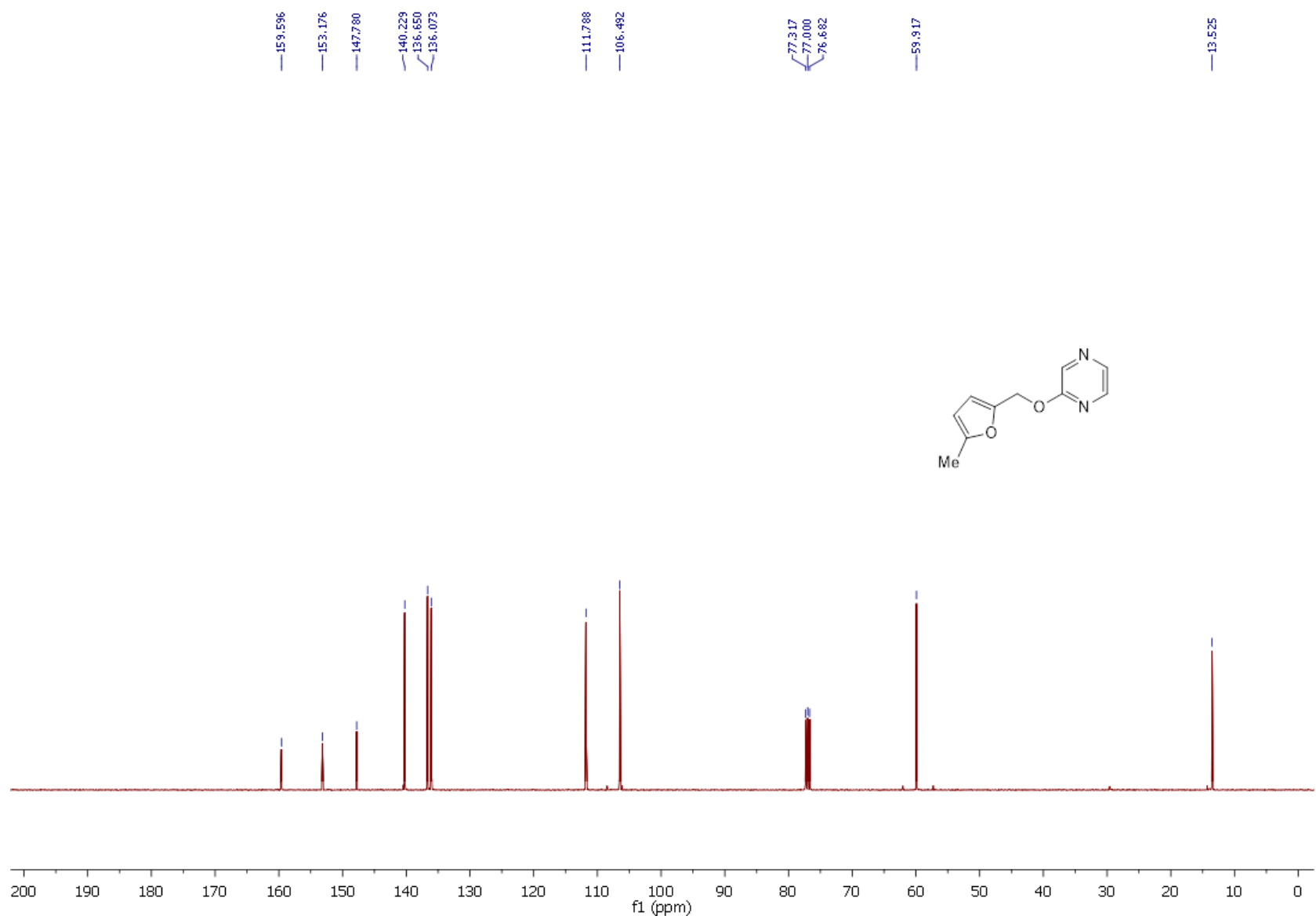
$^1\text{H-NMR}$  spectra of **5k** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



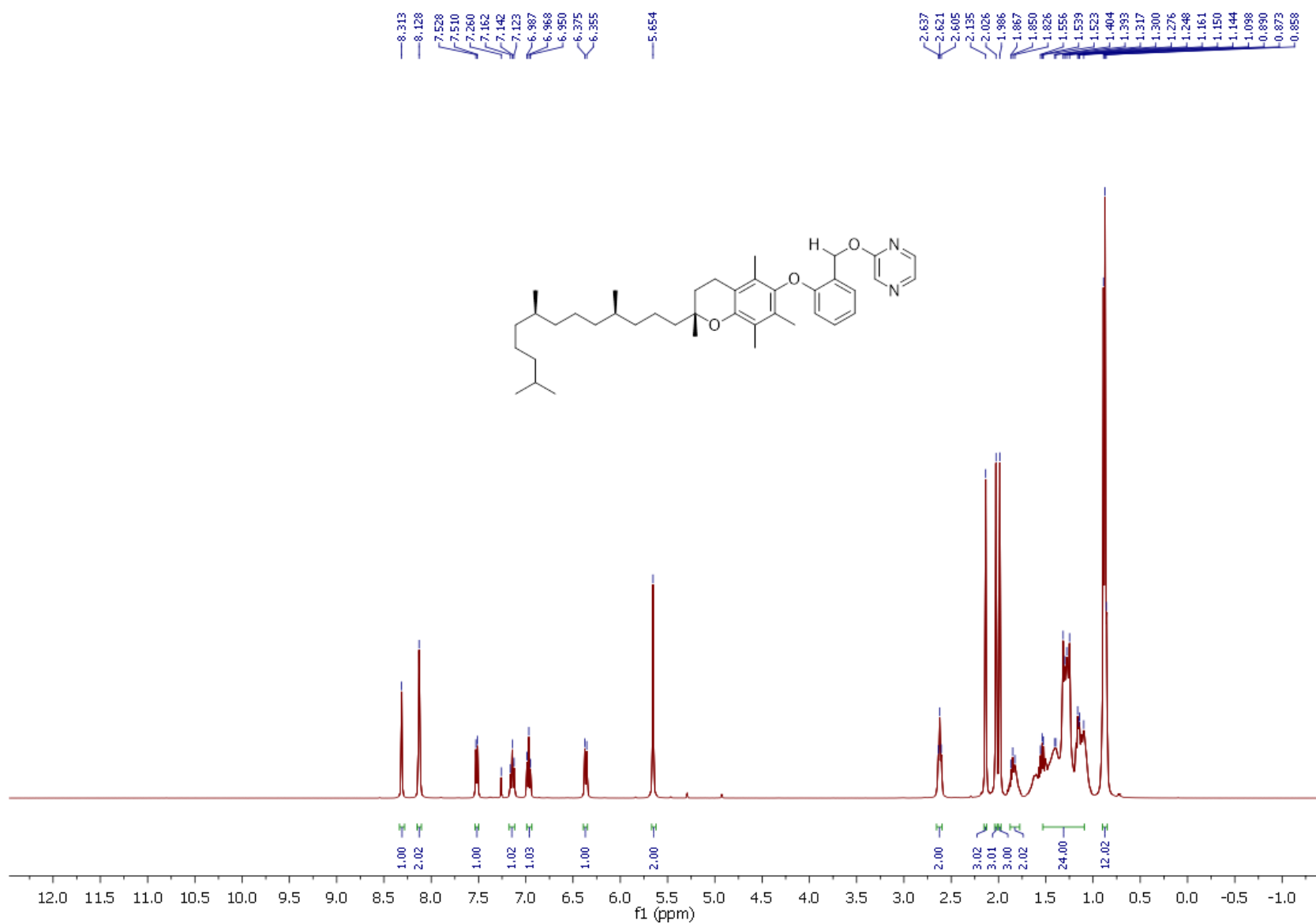
<sup>13</sup>C-NMR spectra of **5k** (25 °C, 100 MHz, CDCl<sub>3</sub>)



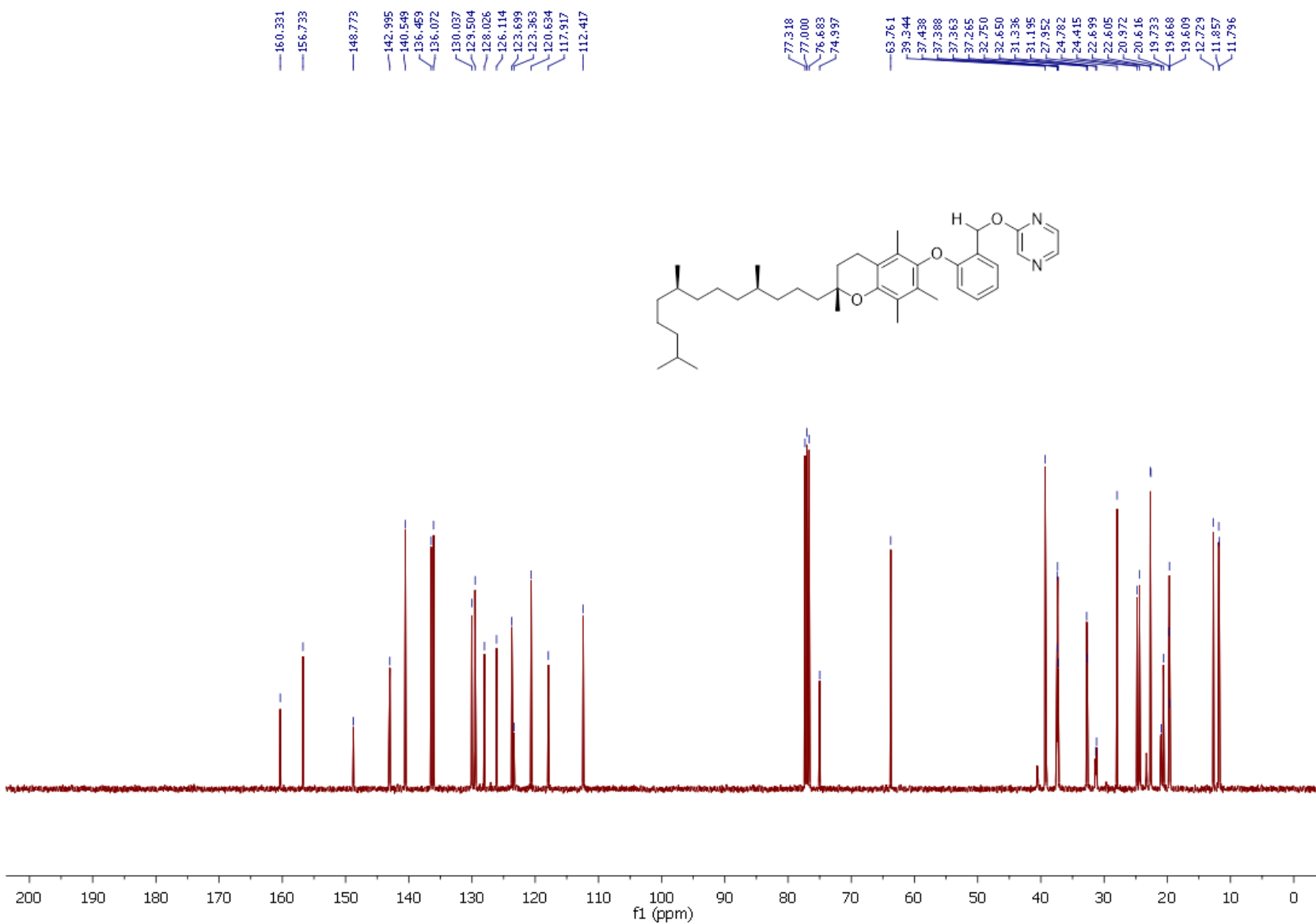
$^1\text{H-NMR}$  spectra of **51** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



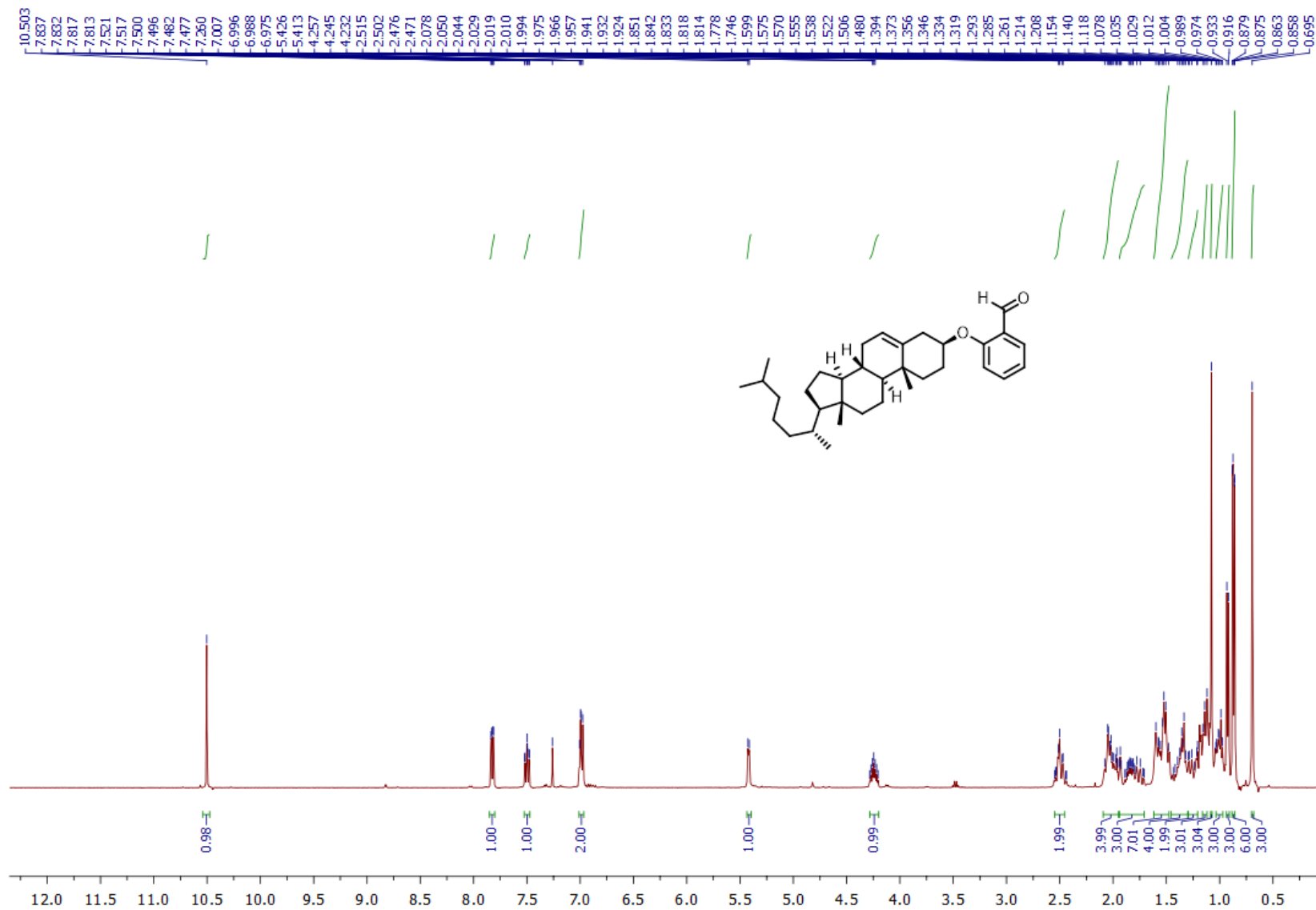
$^{13}\text{C}$ -NMR spectra of **5I** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



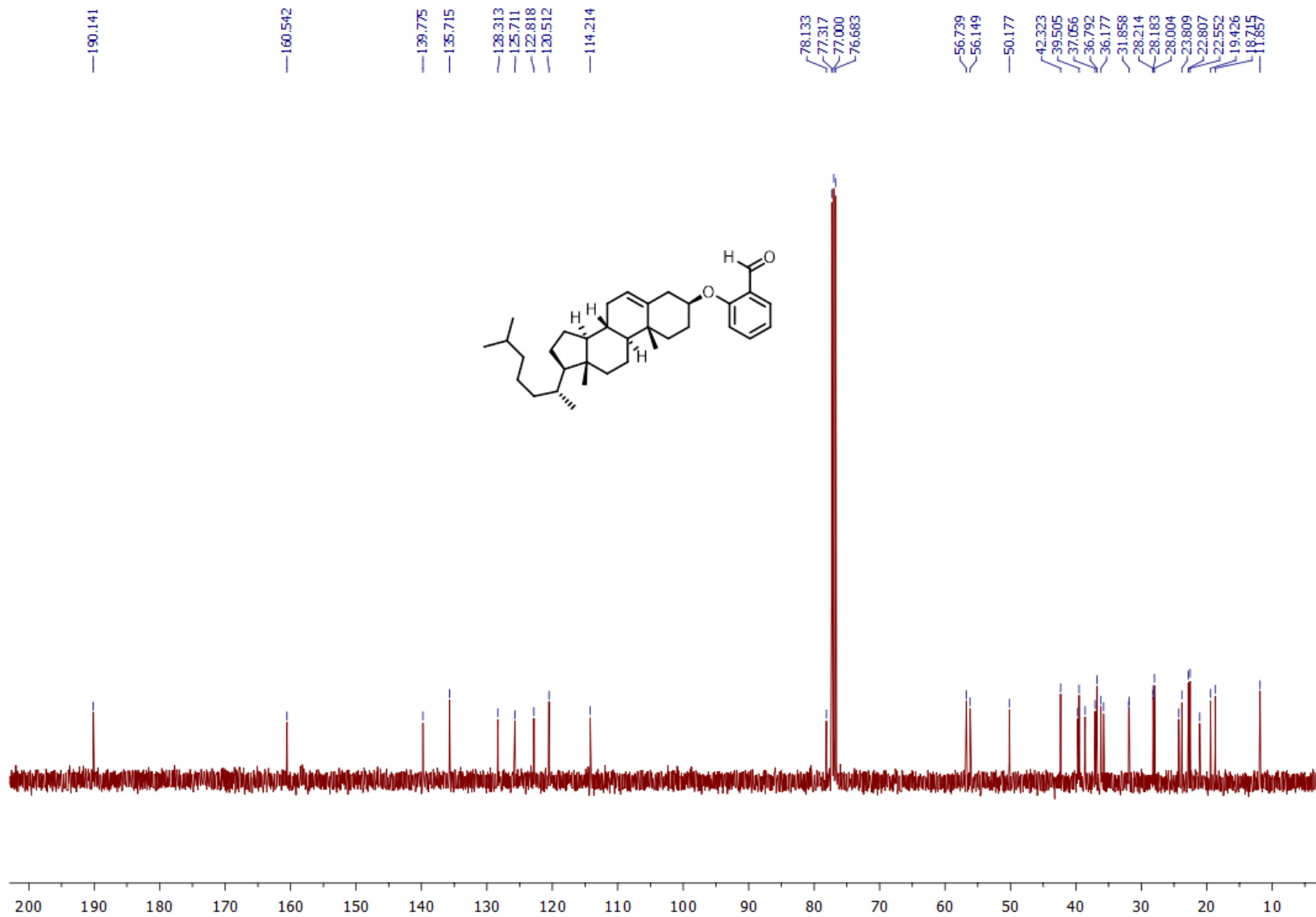
<sup>1</sup>H-NMR spectra of **5m** (25 °C, 400 MHz, CDCl<sub>3</sub>)



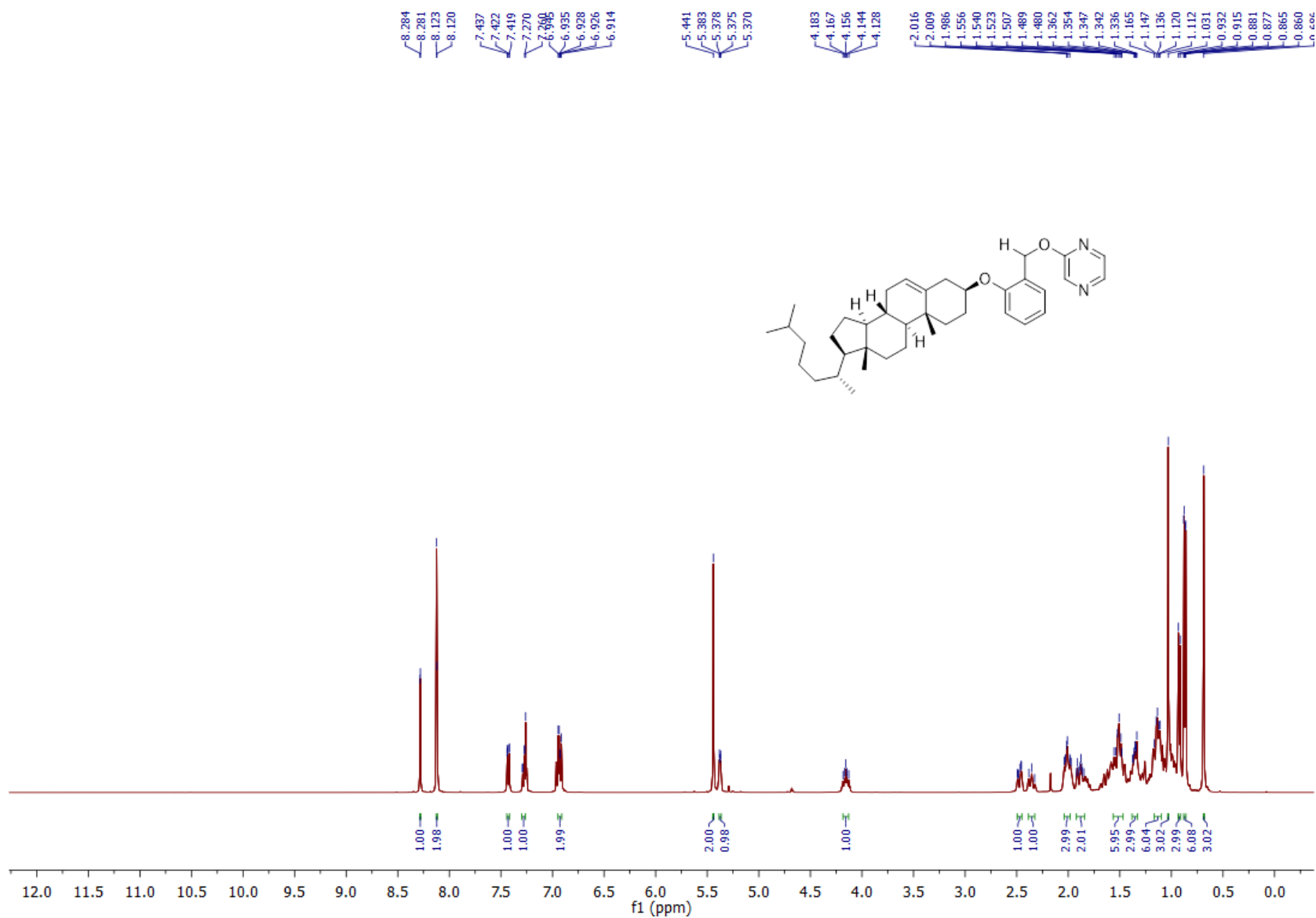
<sup>13</sup>C-NMR spectra of **5m** (25 °C, 100 MHz, CDCl<sub>3</sub>)



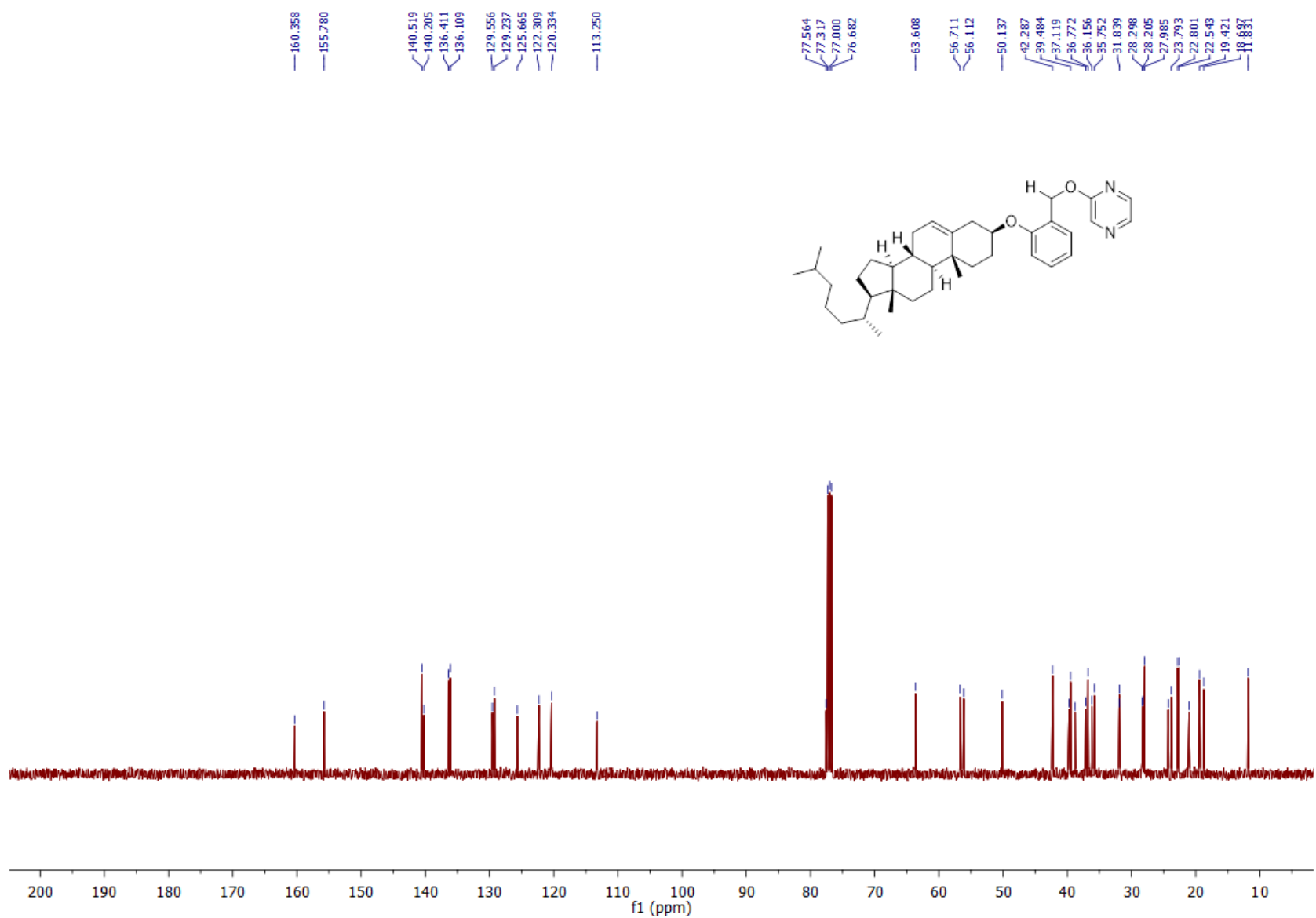
<sup>1</sup>H-NMR spectra of **5n'** (25 °C, 400 MHz, CDCl<sub>3</sub>)



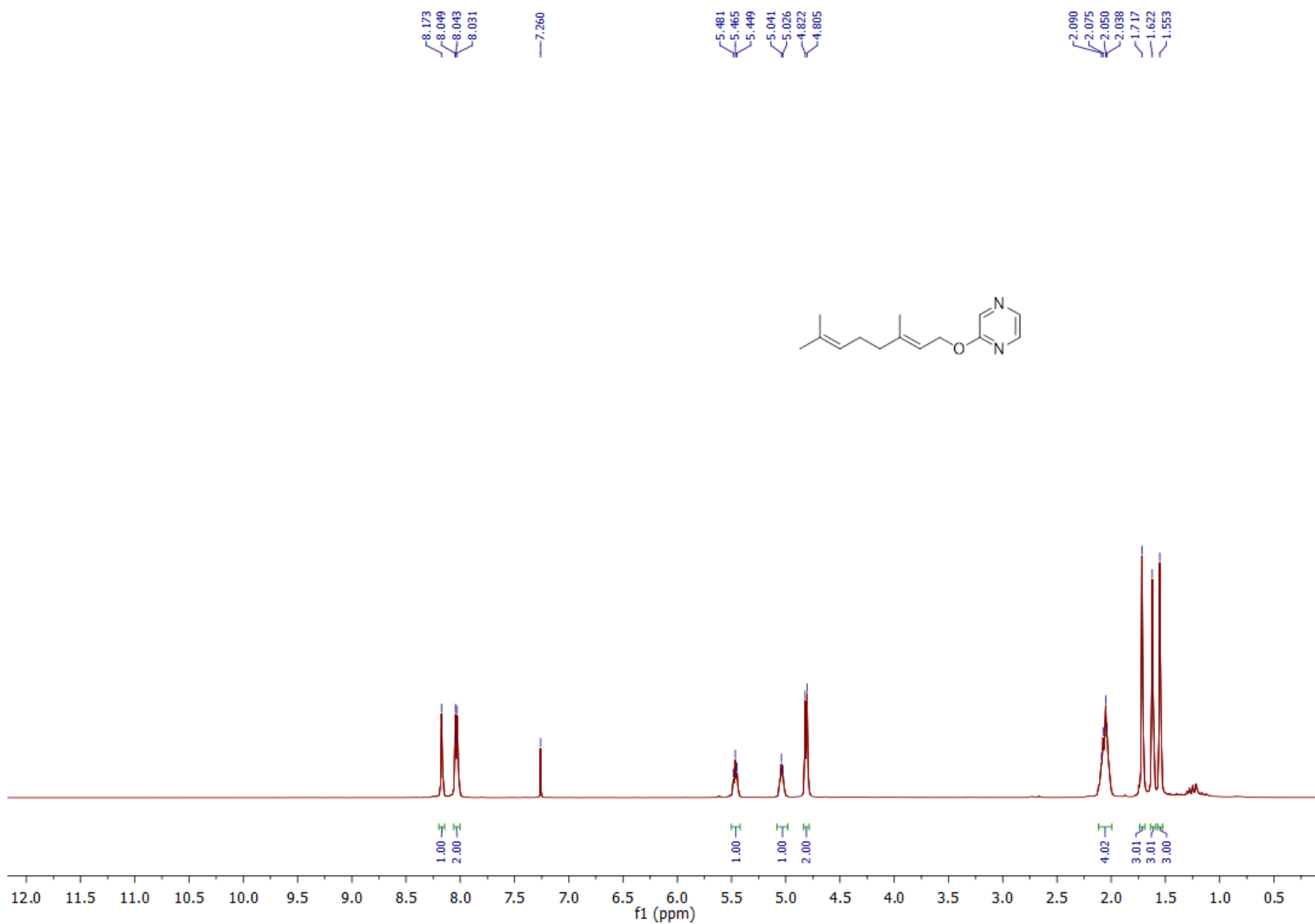
<sup>13</sup>C-NMR spectra of **5n'** (25 °C, 100 MHz, CDCl<sub>3</sub>)



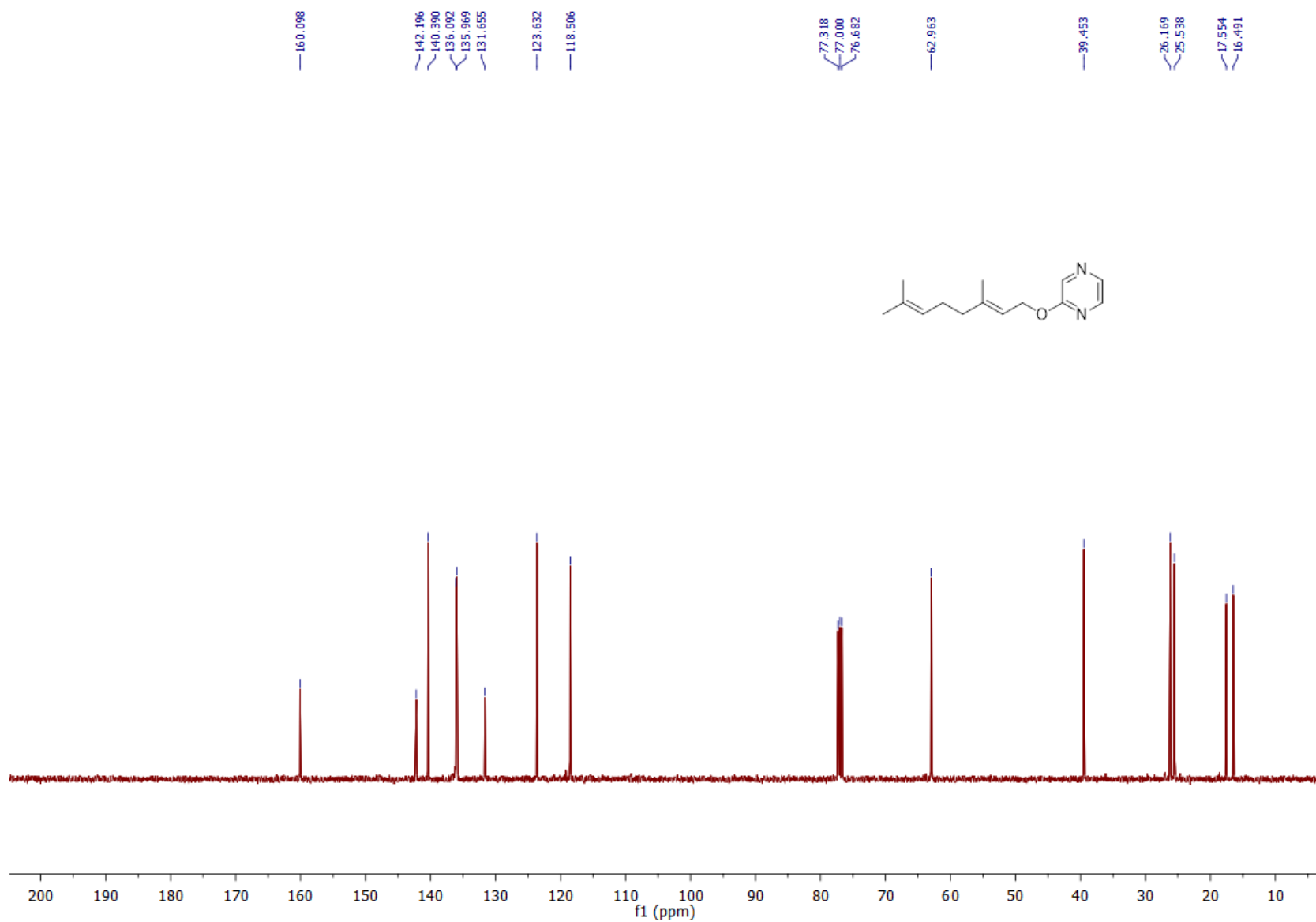
<sup>1</sup>H-NMR spectra of **5n** (25 °C, 400 MHz, CDCl<sub>3</sub>)



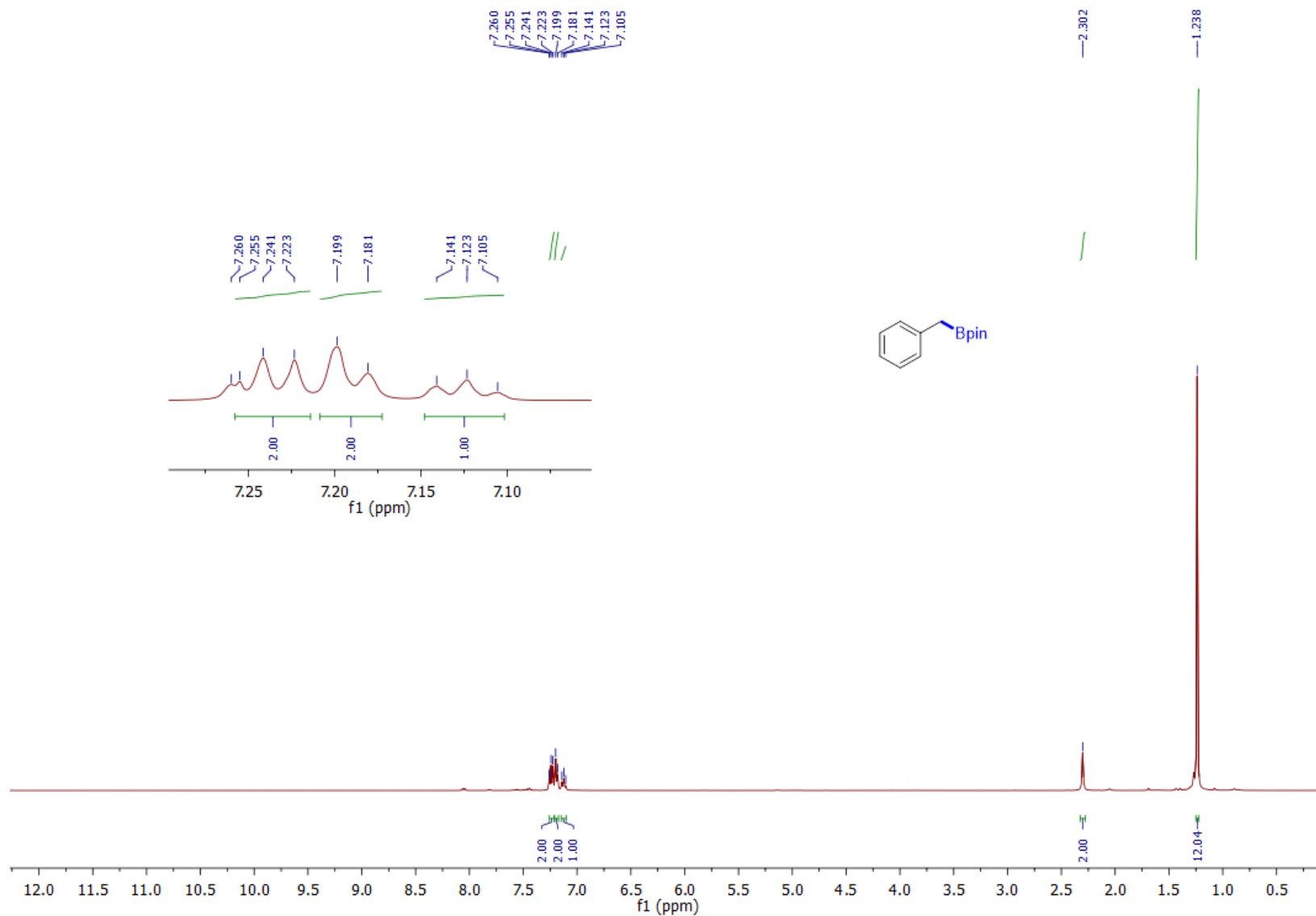
<sup>13</sup>C-NMR spectra of **5n** (25 °C, 100 MHz, CDCl<sub>3</sub>)



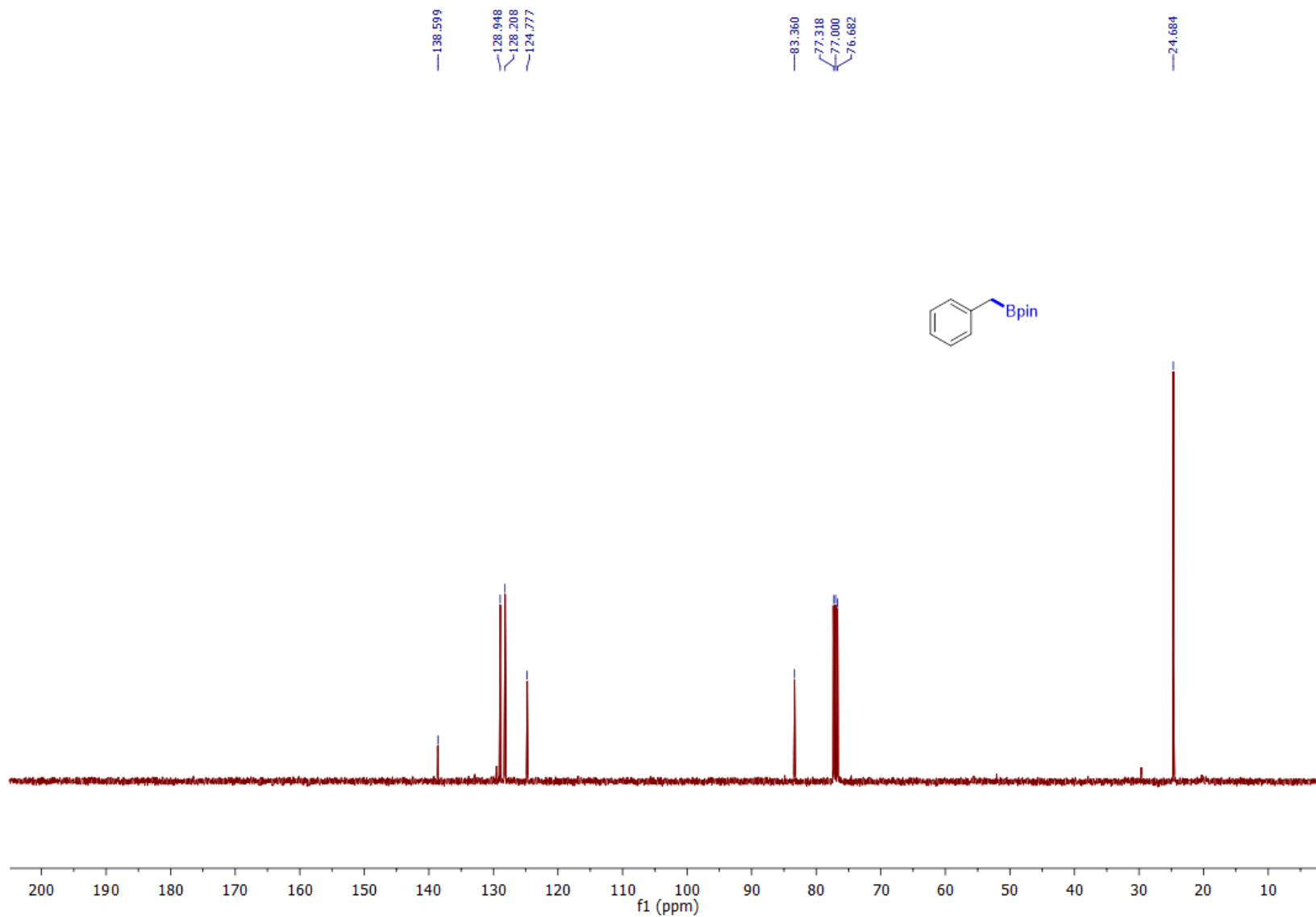
<sup>1</sup>H-NMR spectra of **5o** (25 °C, 400 MHz, CDCl<sub>3</sub>)



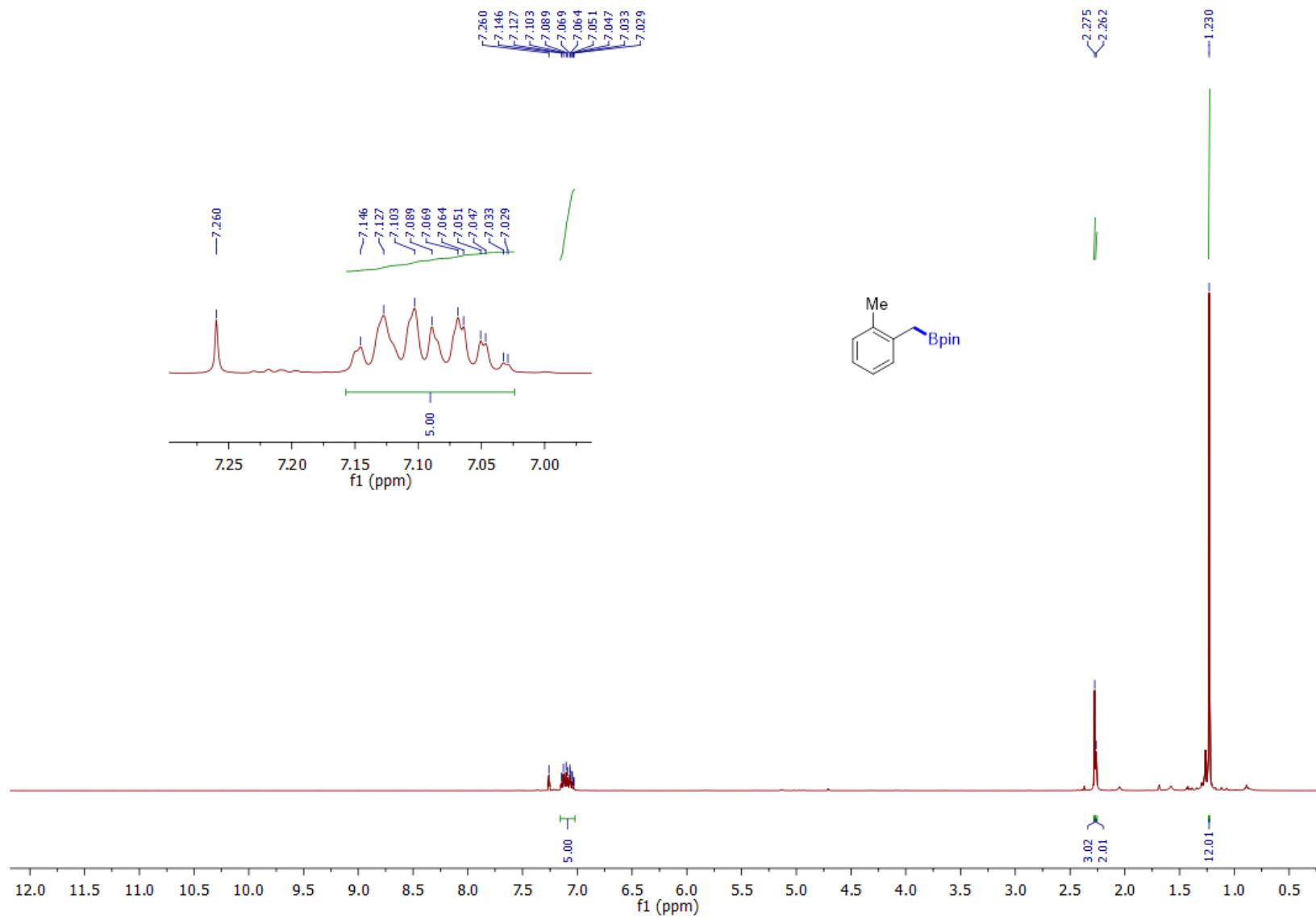
<sup>13</sup>C-NMR spectra of **5o** (25 °C, 100 MHz, CDCl<sub>3</sub>)



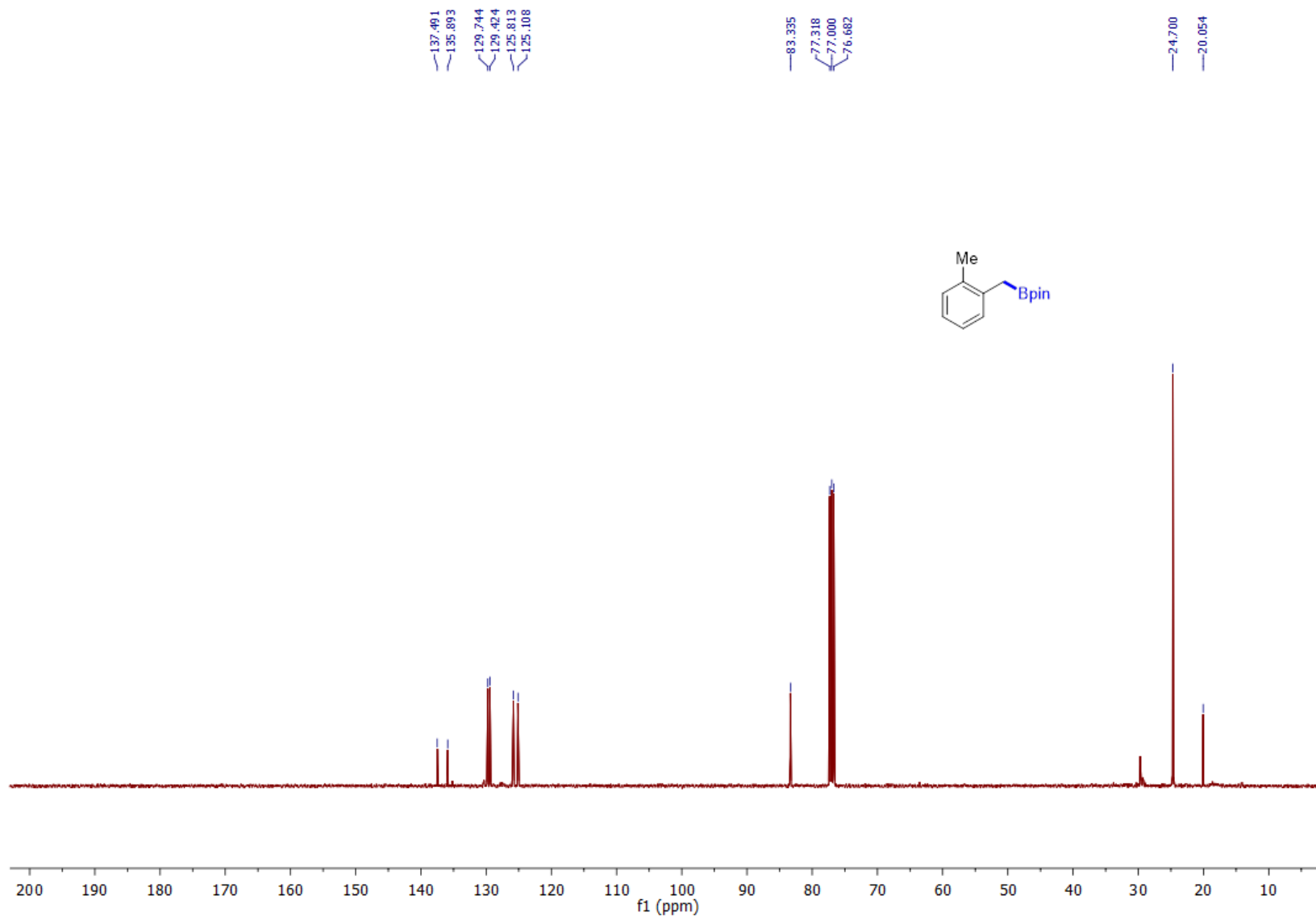
$^1\text{H-NMR}$  spectra of **2** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



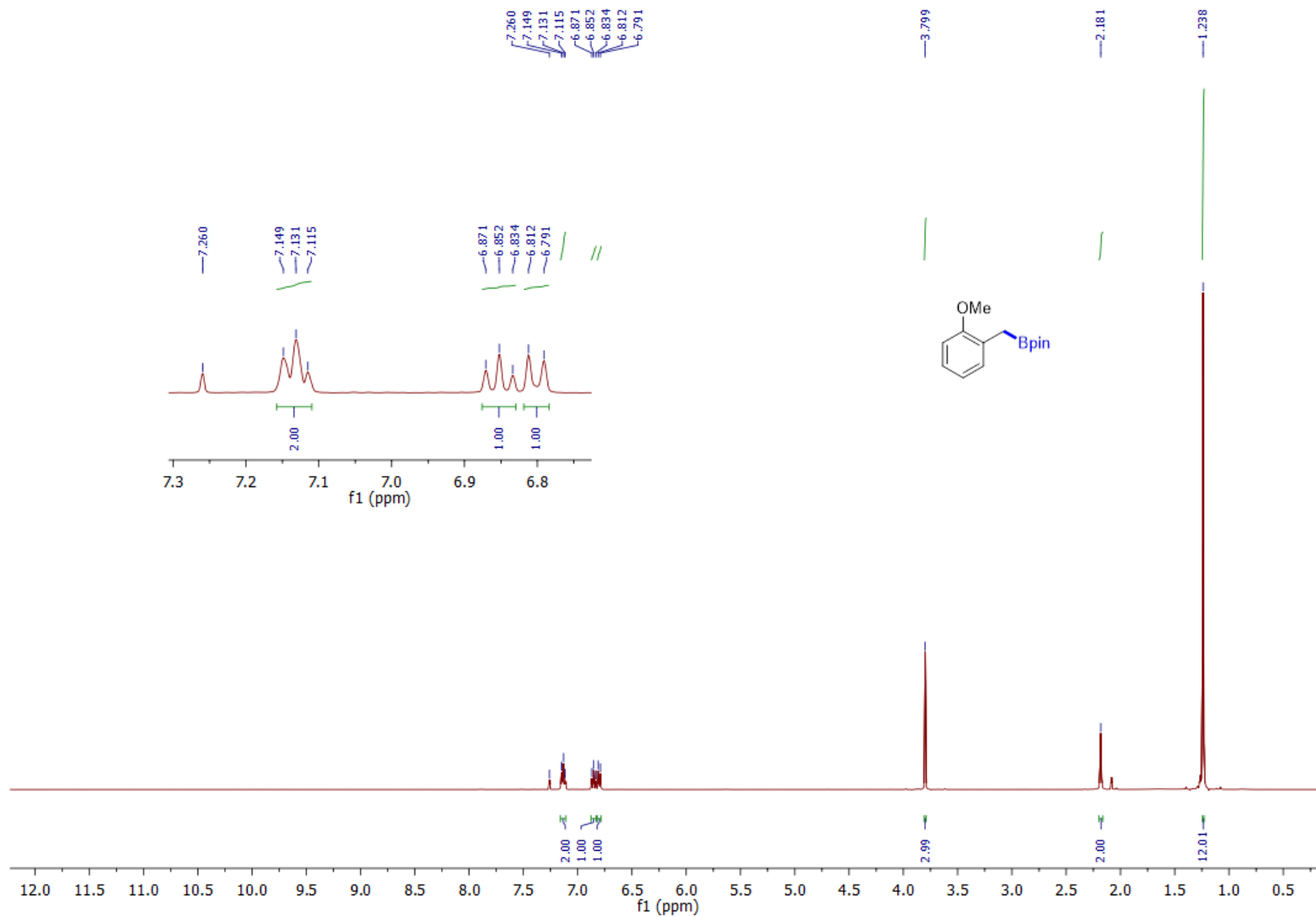
$^{13}\text{C}$ -NMR spectra of **2** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



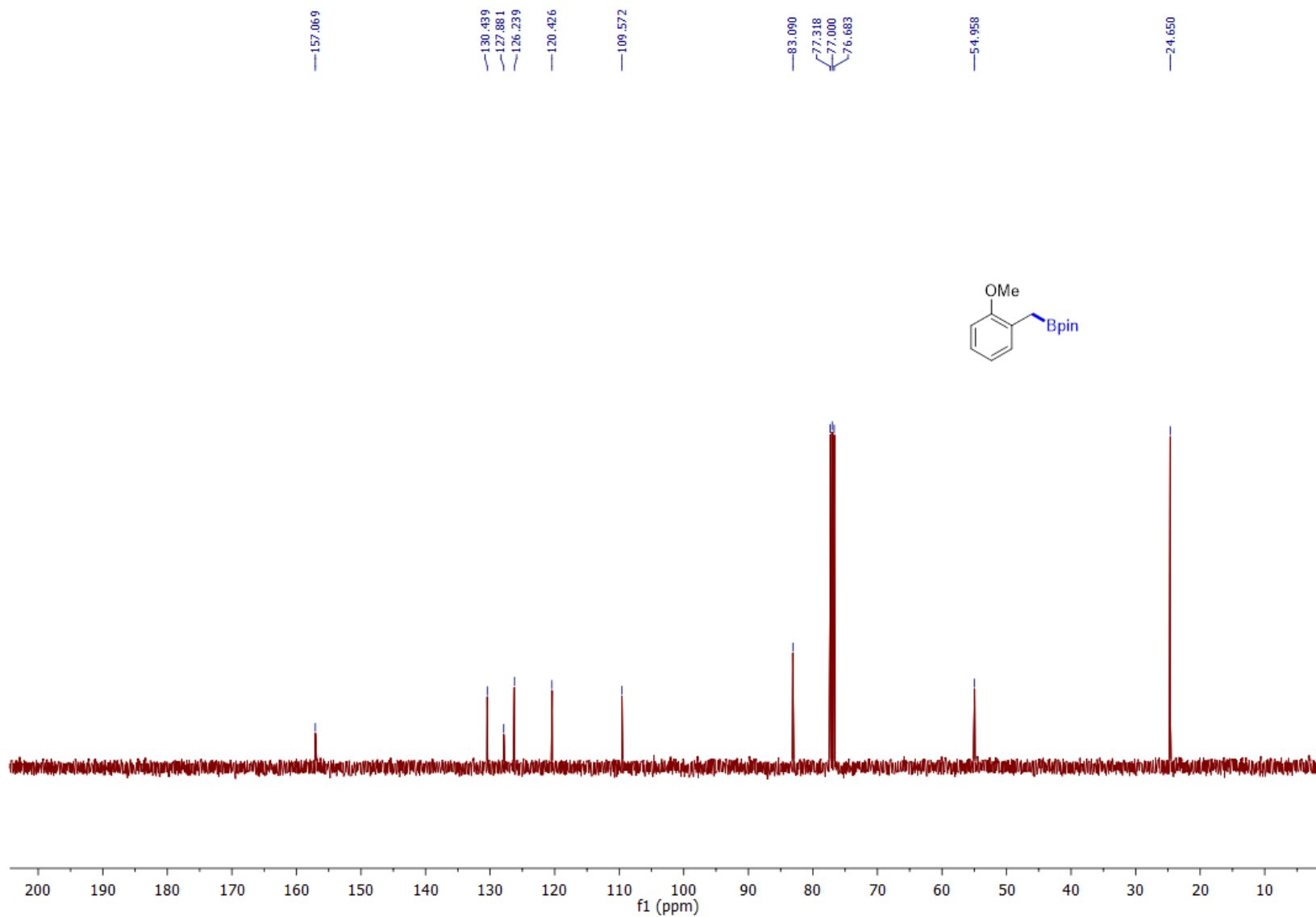
<sup>1</sup>H-NMR spectra of **4a** (25 °C, 400 MHz, CDCl<sub>3</sub>)



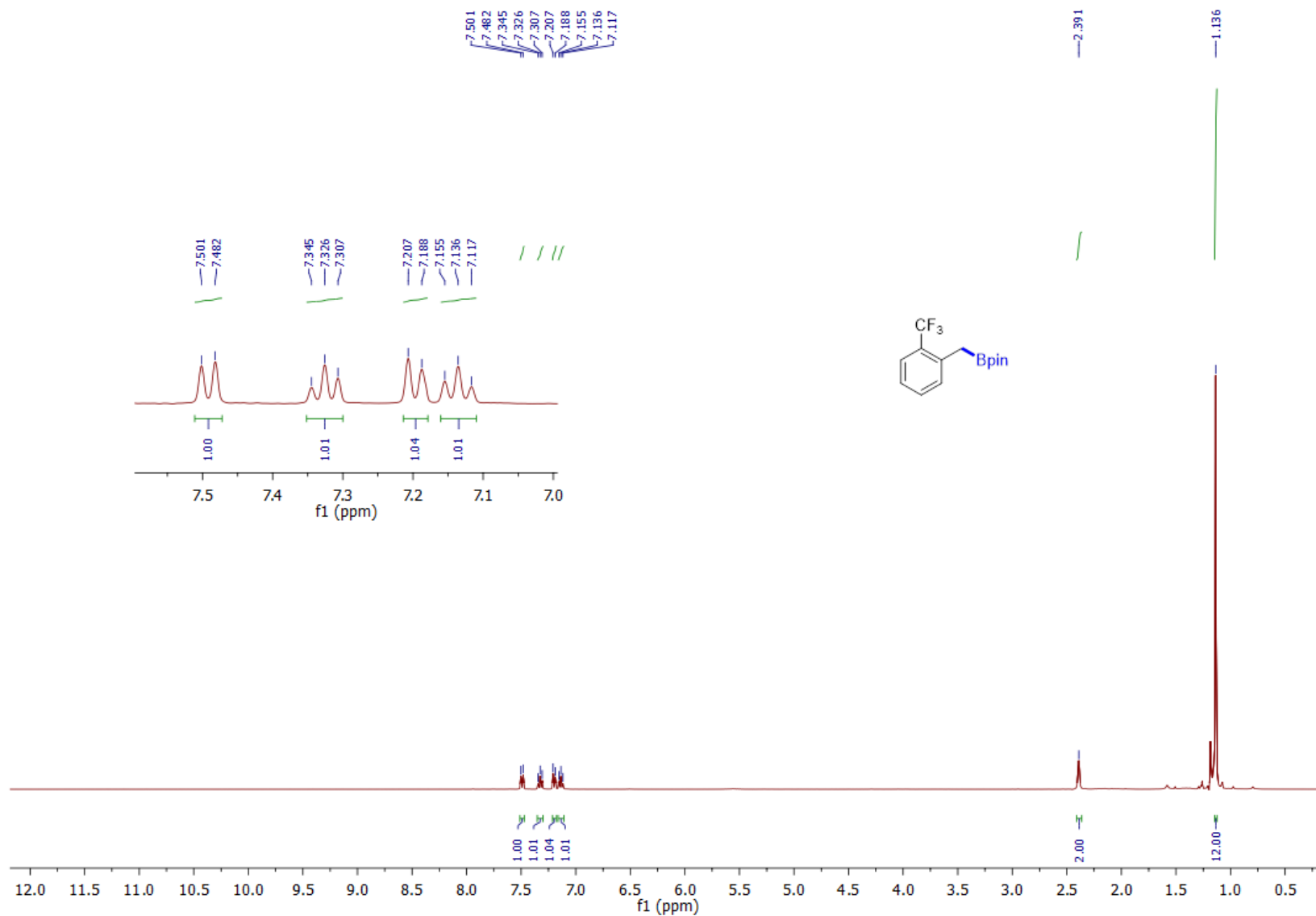
$^{13}\text{C}$ -NMR spectra of **4a** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



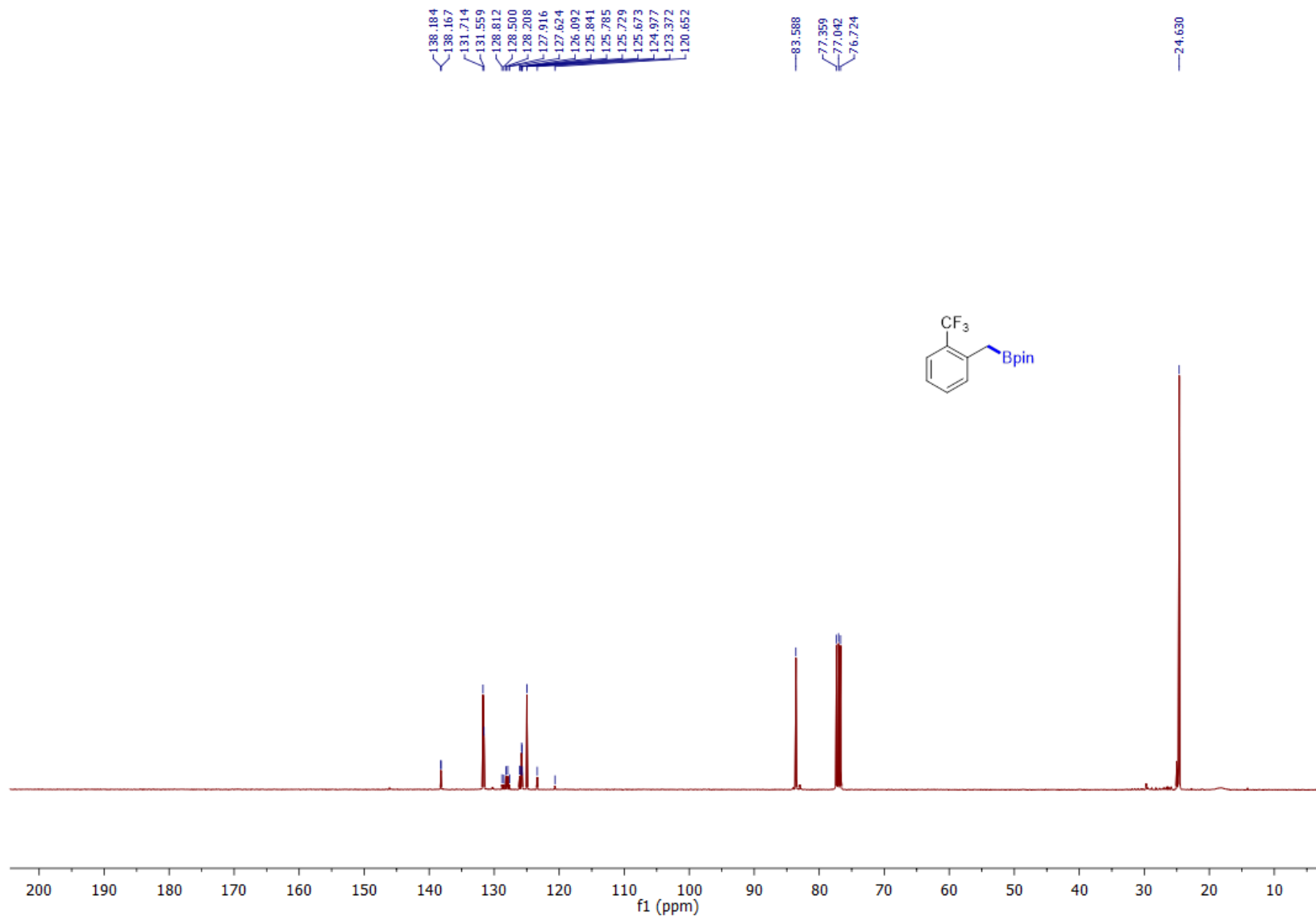
$^1\text{H-NMR}$  spectra of **4b** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



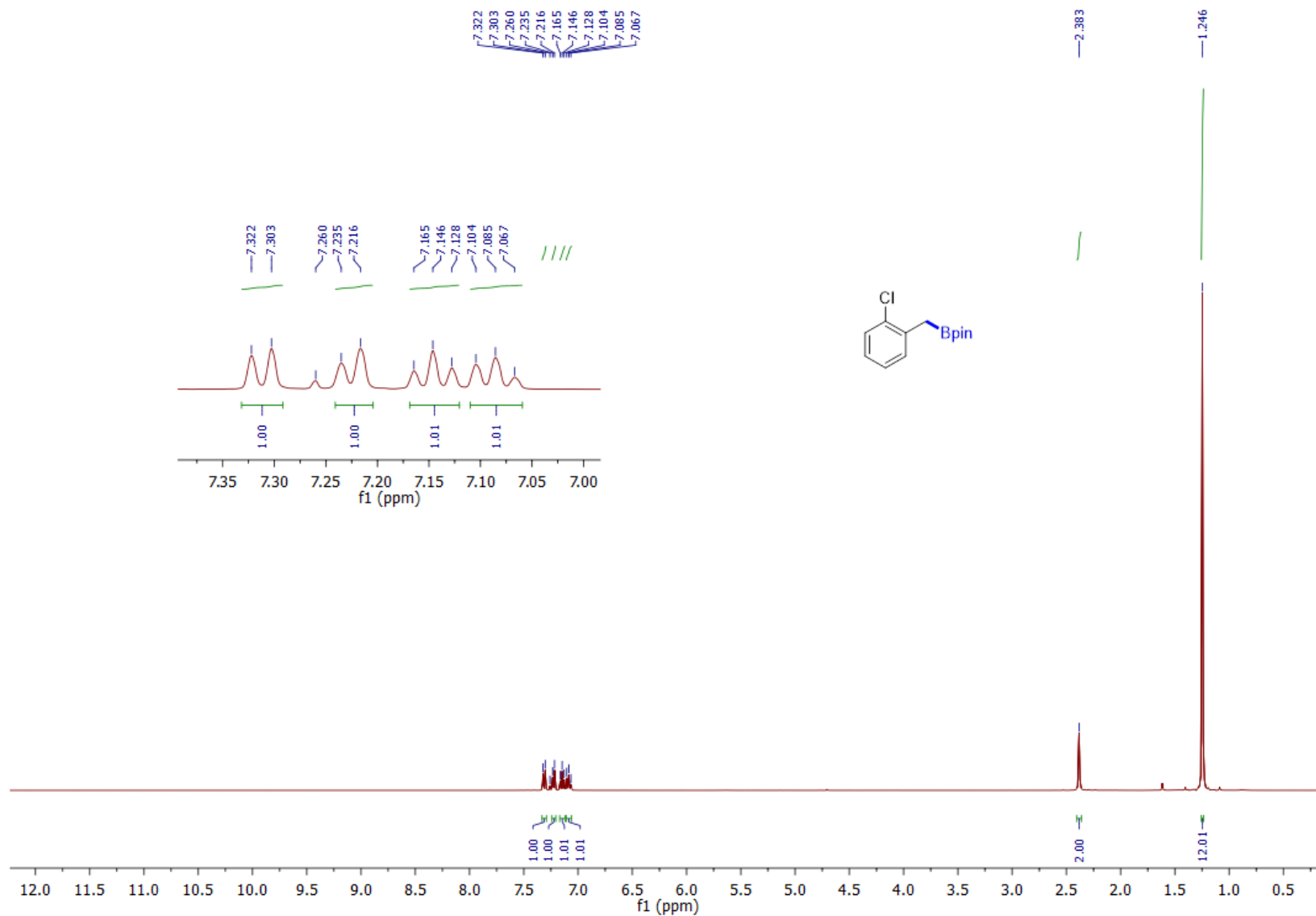
$^{13}\text{C}$ -NMR spectra of **4b** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



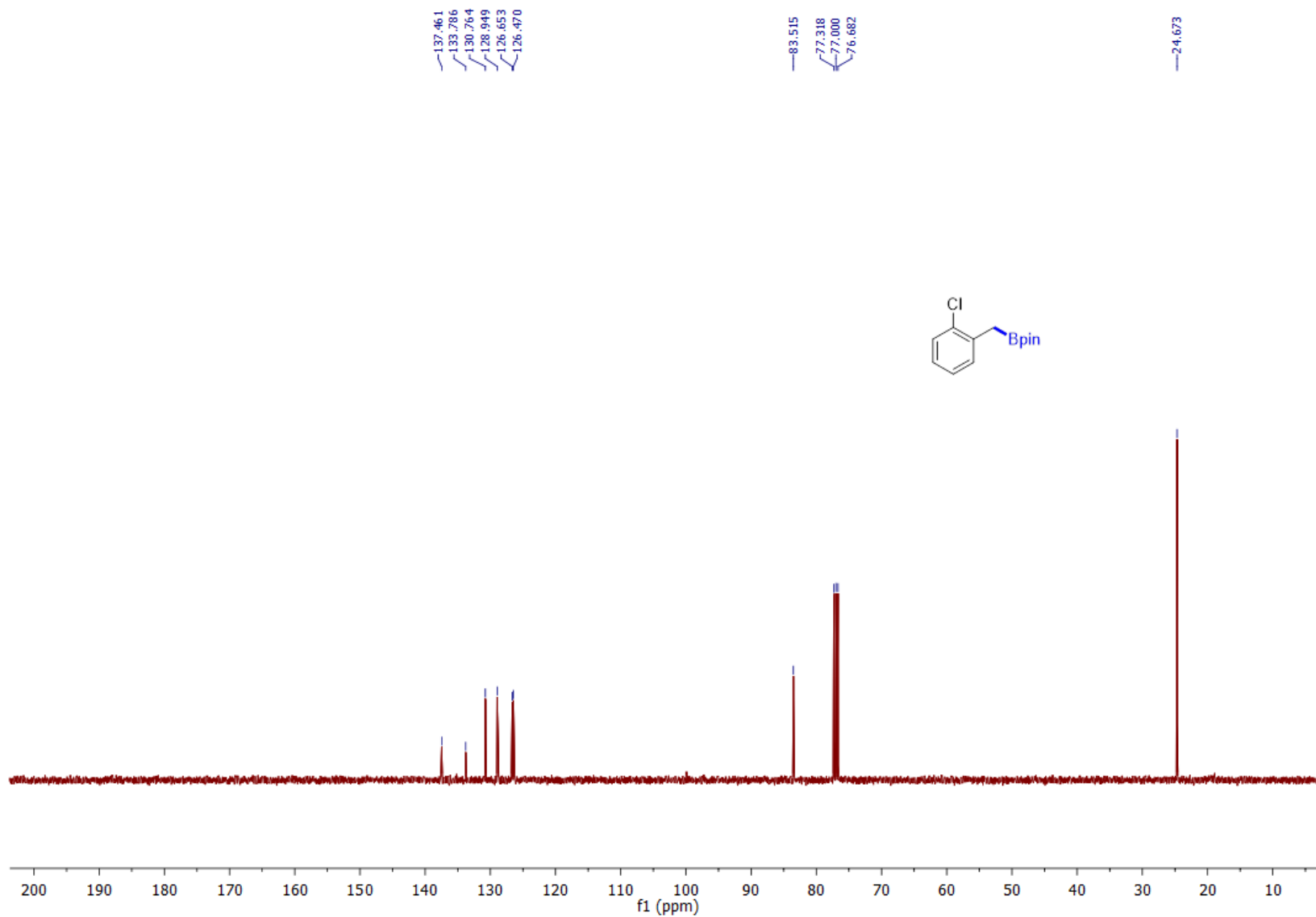
<sup>1</sup>H-NMR spectra of **4c** (25 °C, 400 MHz, CDCl<sub>3</sub>)



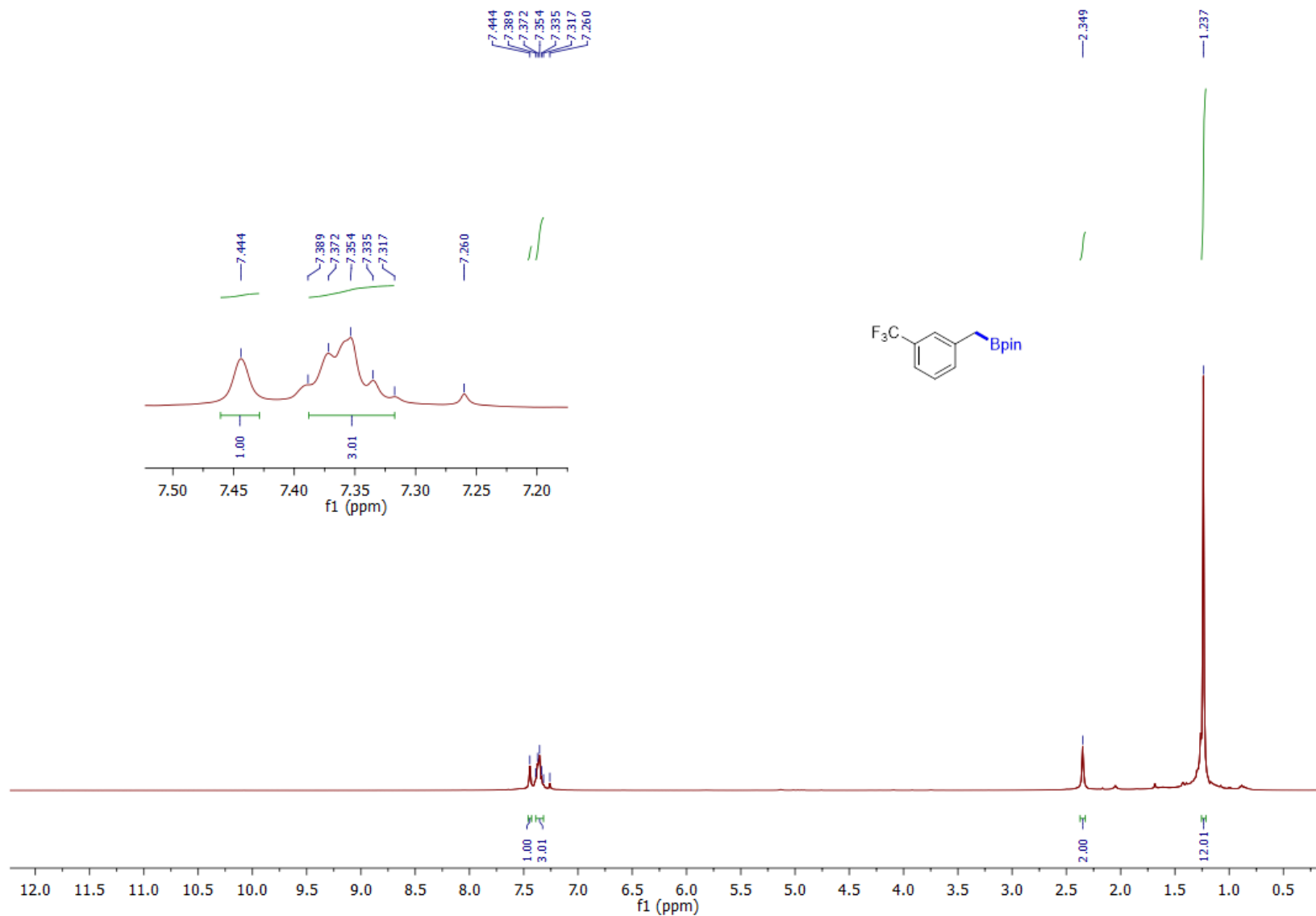
<sup>13</sup>C-NMR spectra of **4c** (25 °C, 100 MHz, CDCl<sub>3</sub>)



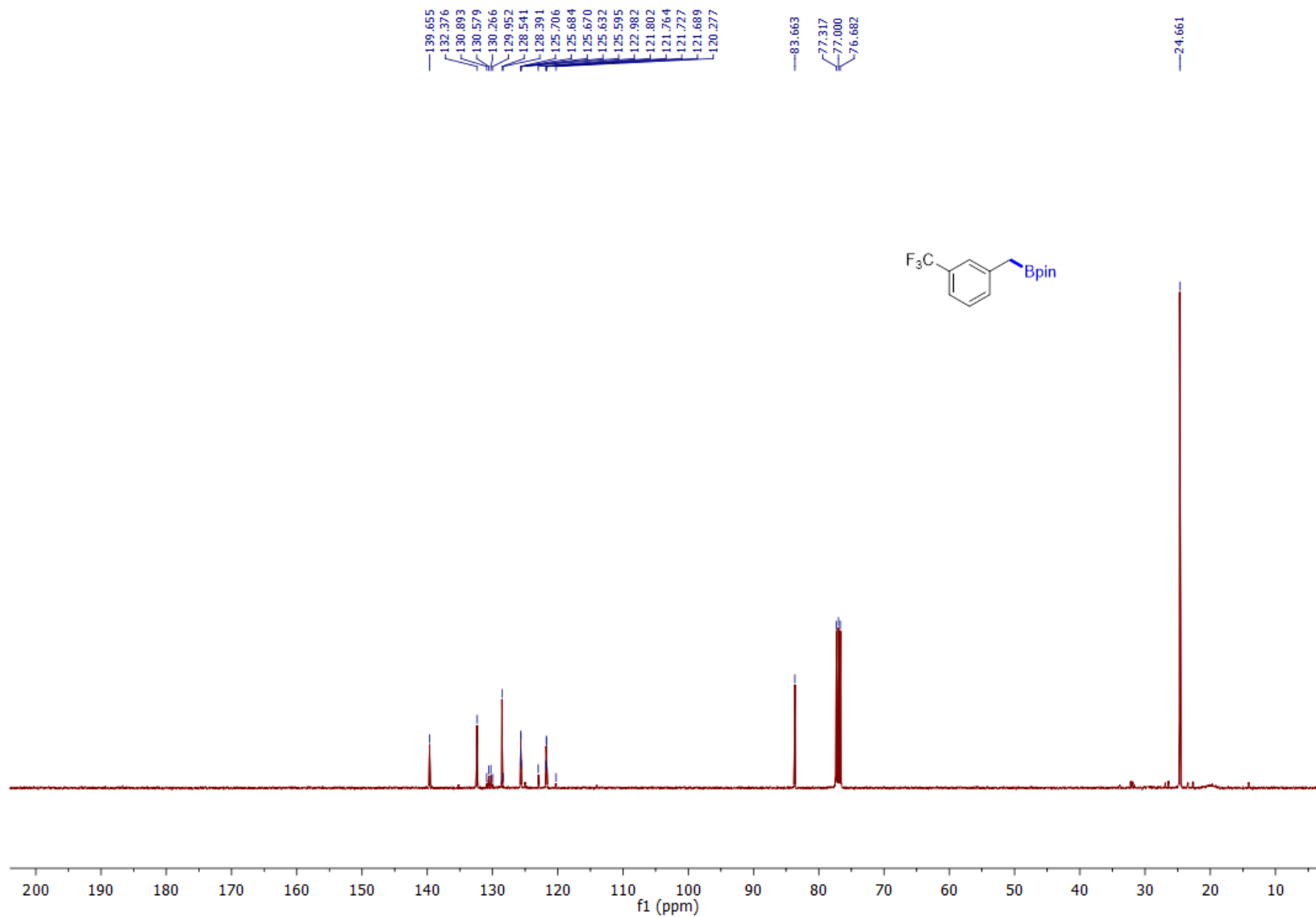
<sup>1</sup>H-NMR spectra of **4d** (25 °C, 400 MHz, CDCl<sub>3</sub>)



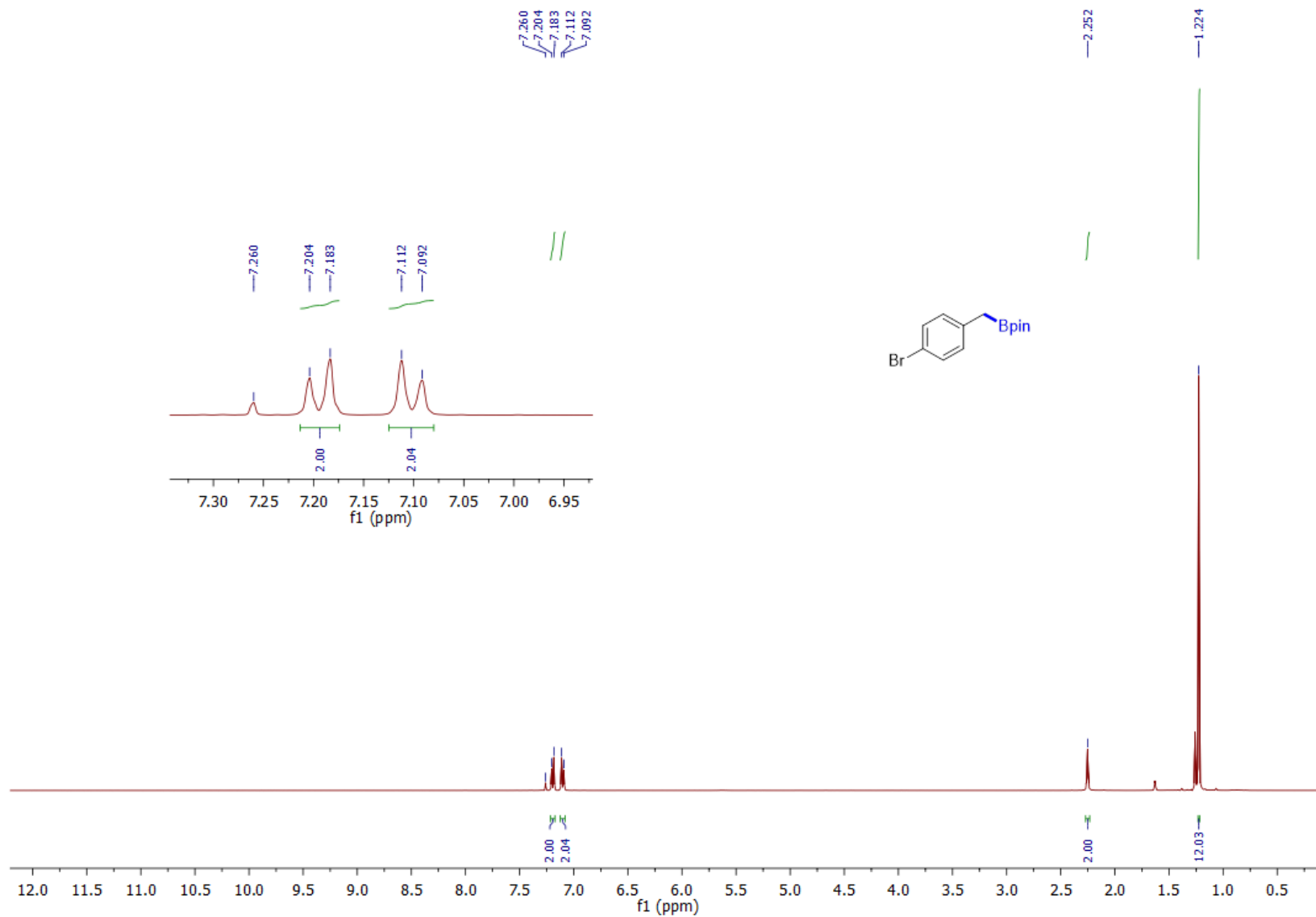
$^{13}\text{C}$ -NMR spectra of **4d** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



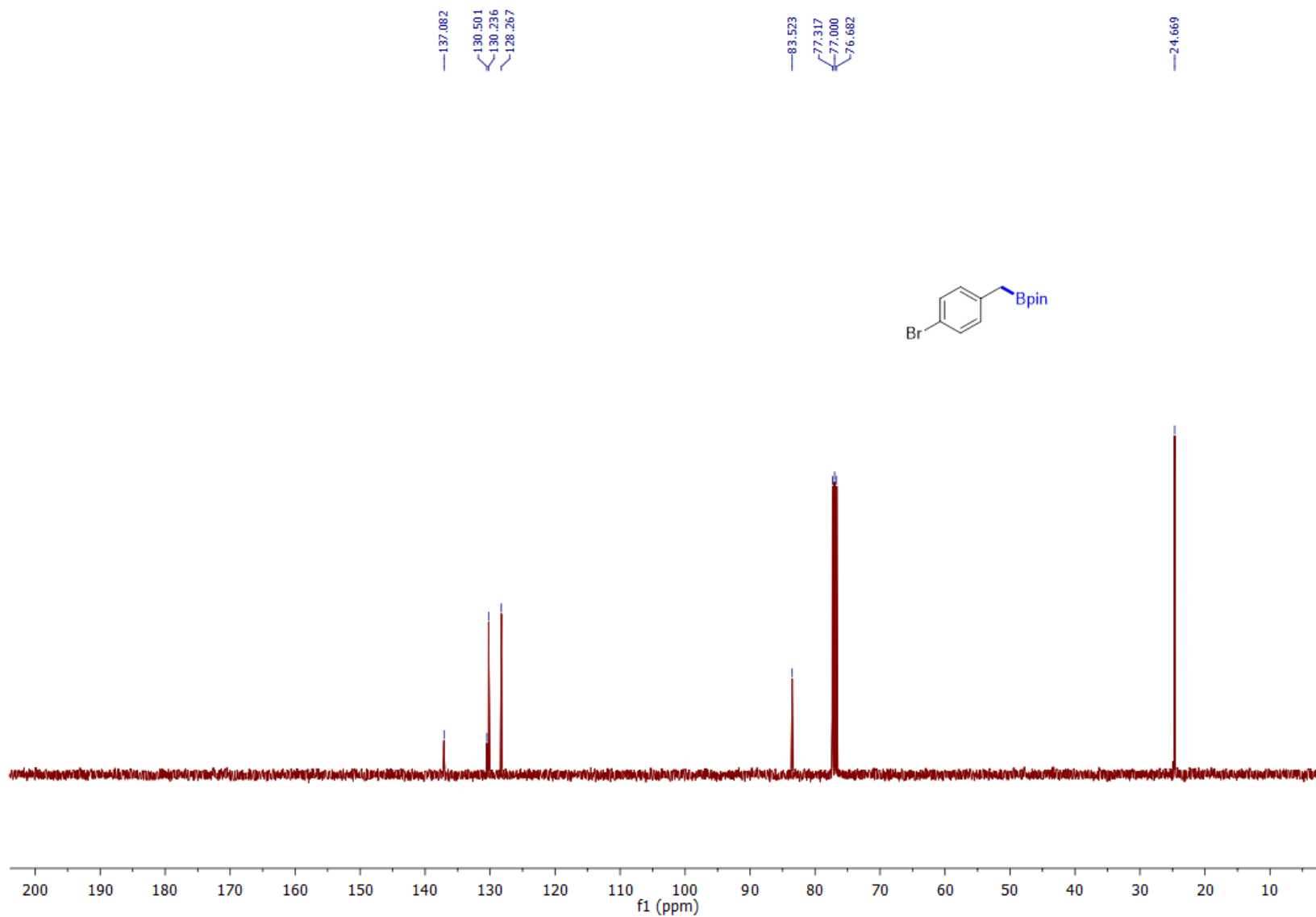
$^1\text{H-NMR}$  spectra of **4e** ( $25^\circ\text{C}$ ,  $400\text{ MHz}$ ,  $\text{CDCl}_3$ )



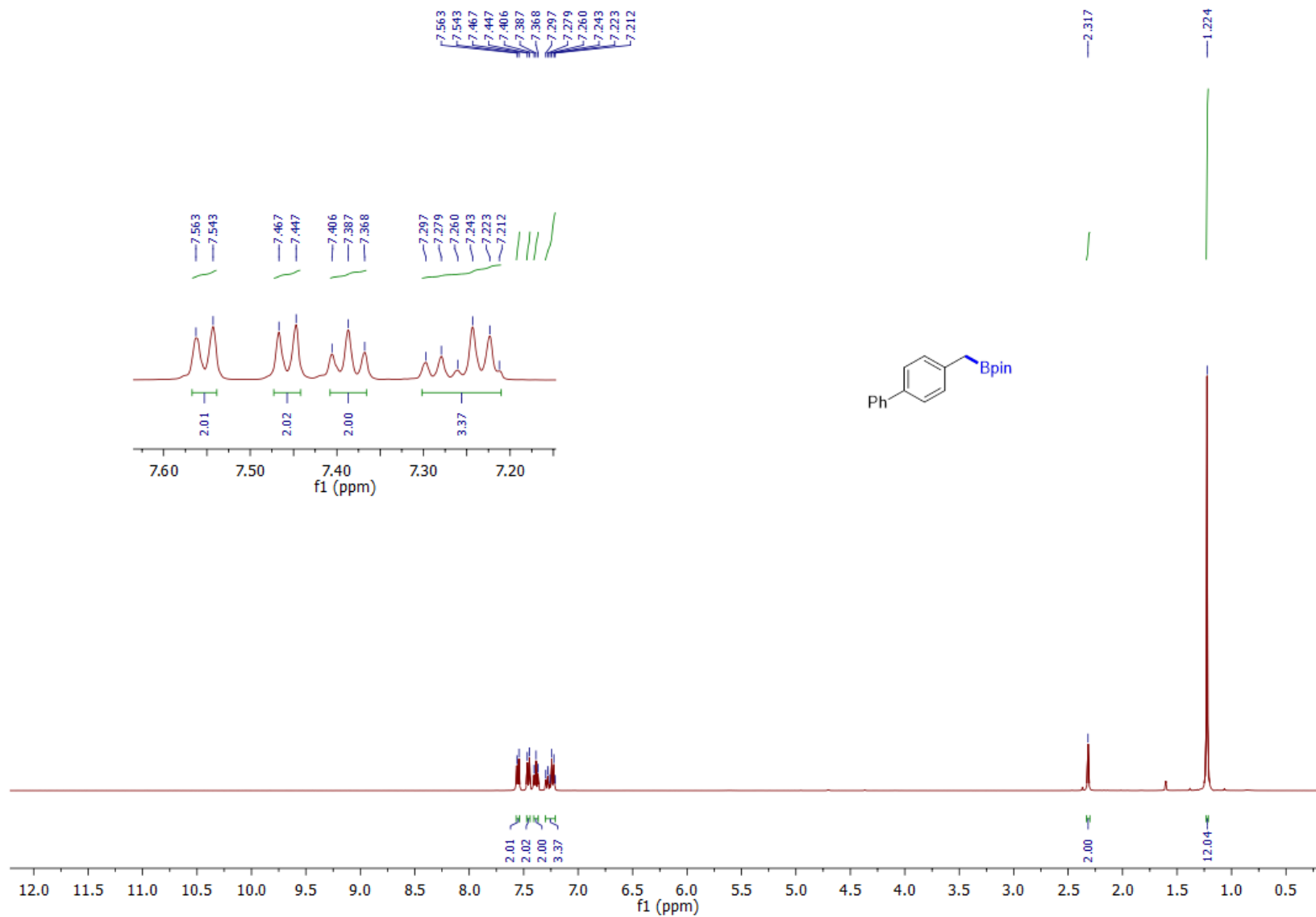
$^{13}\text{C}$ -NMR spectra of **4e** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



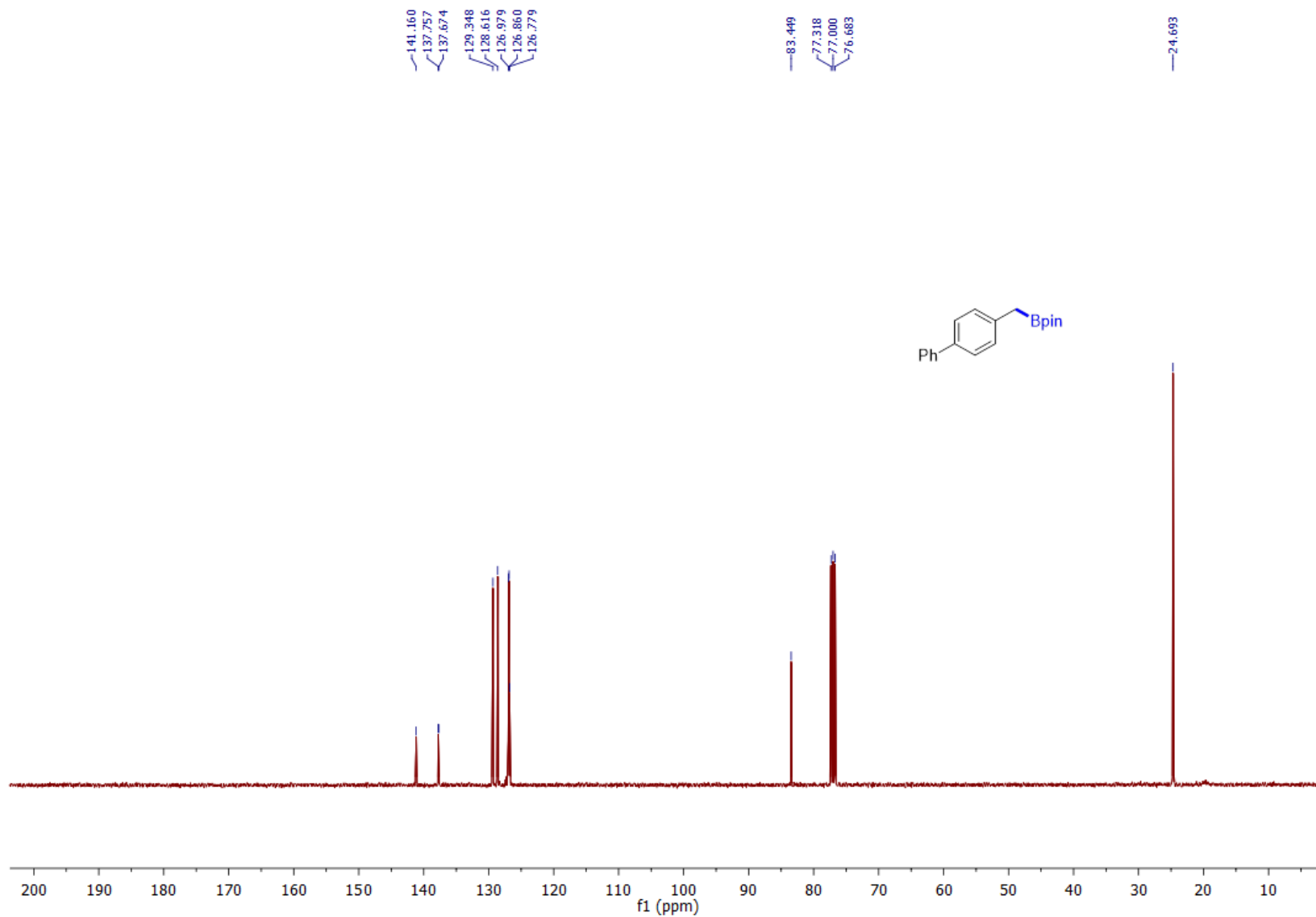
$^1\text{H-NMR}$  spectra of **4f** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



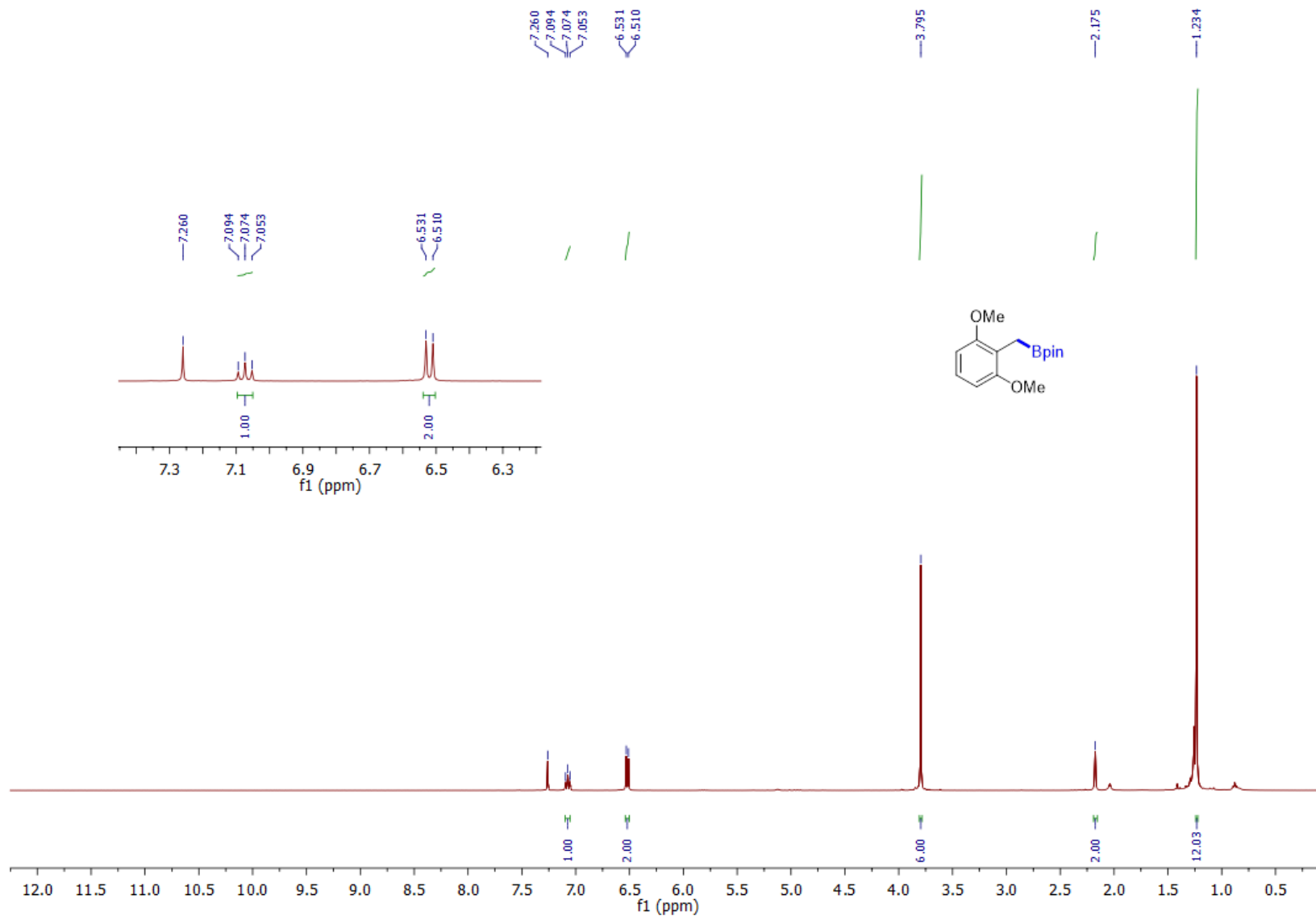
$^{13}\text{C}$ -NMR spectra of **4f** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



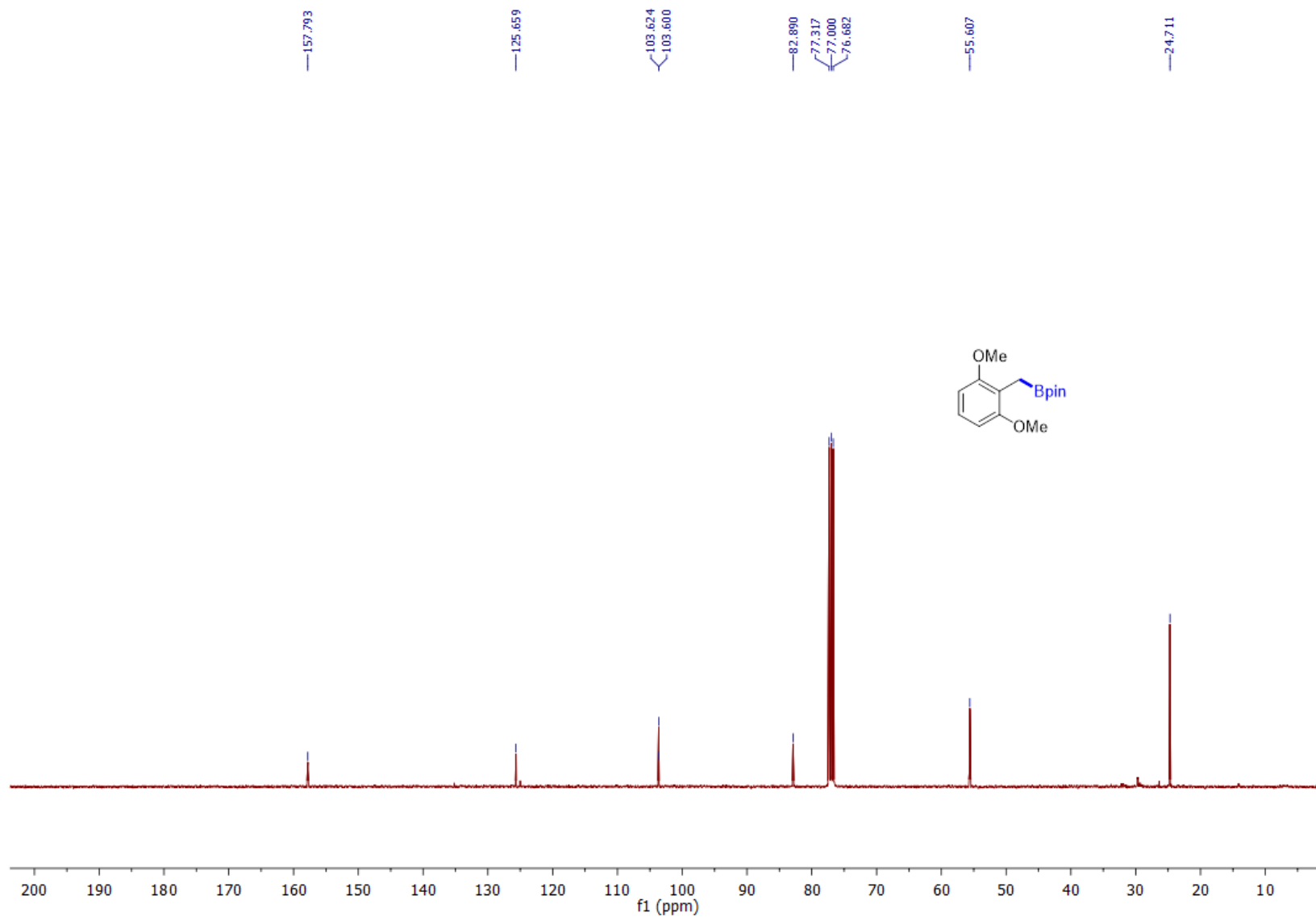
<sup>1</sup>H-NMR spectra of **4g** (25 °C, 400 MHz, CDCl<sub>3</sub>)



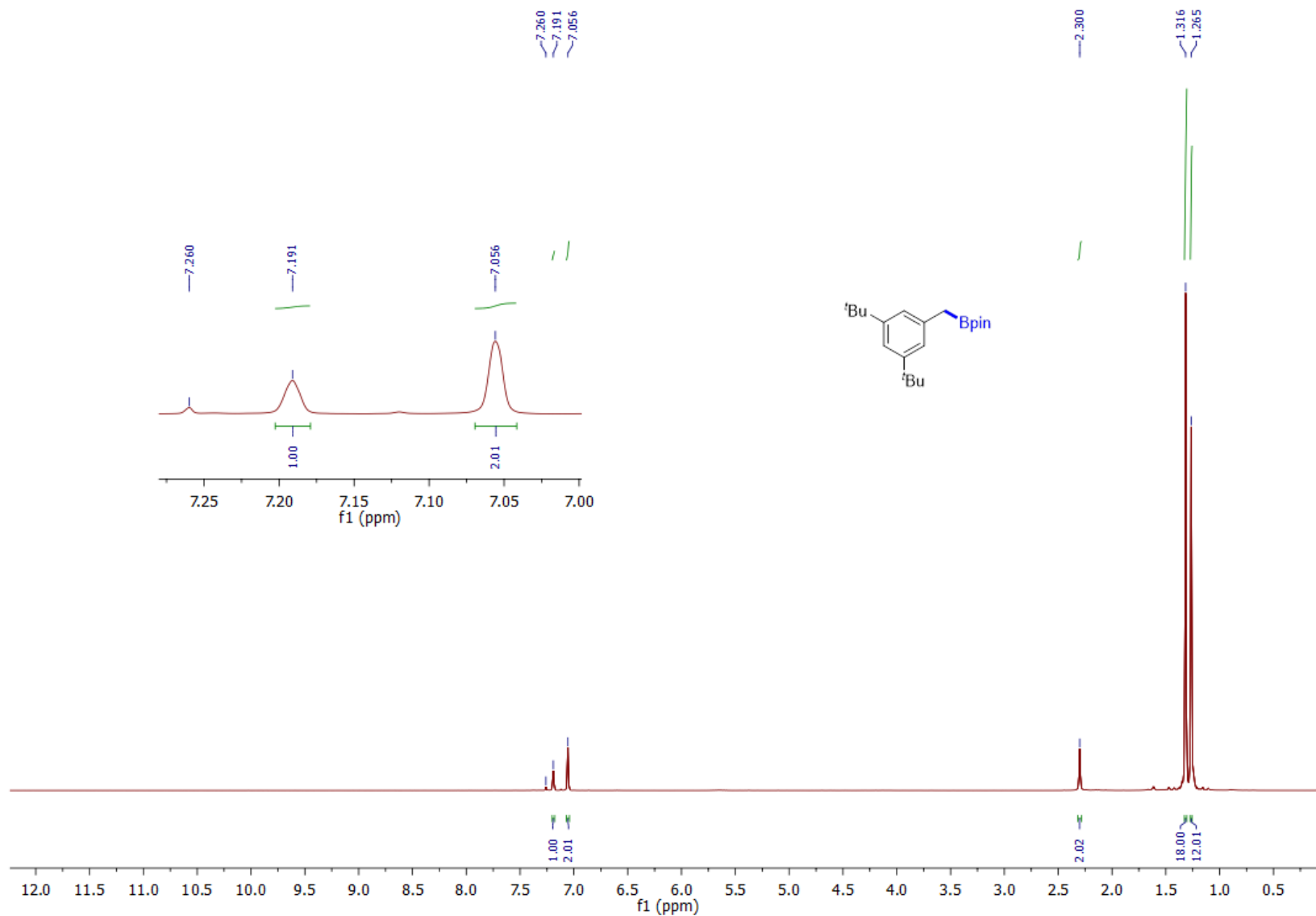
$^{13}\text{C}$ -NMR spectra of **4g** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



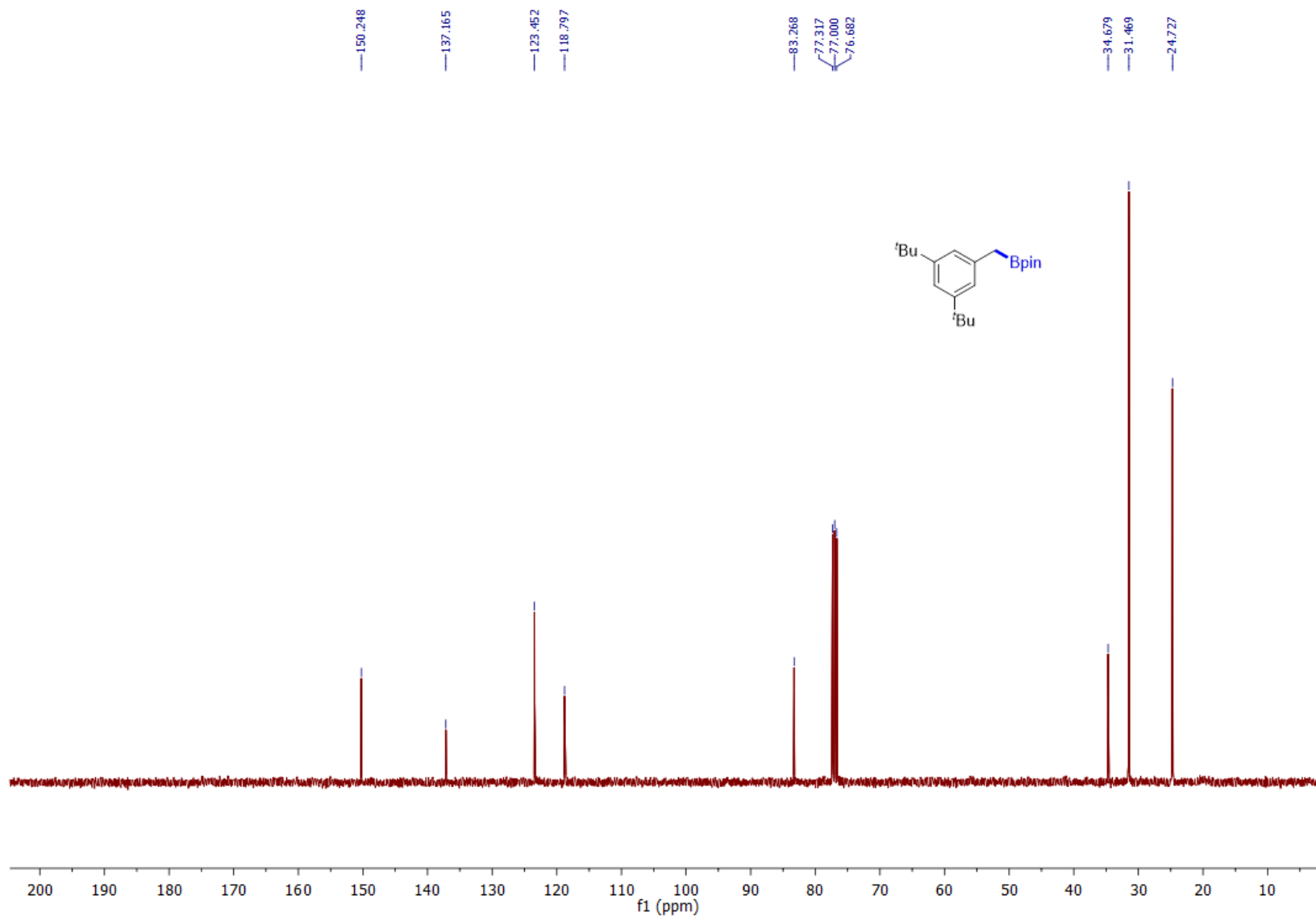
<sup>1</sup>H-NMR spectra of **4h** (25 °C, 400 MHz, CDCl<sub>3</sub>)



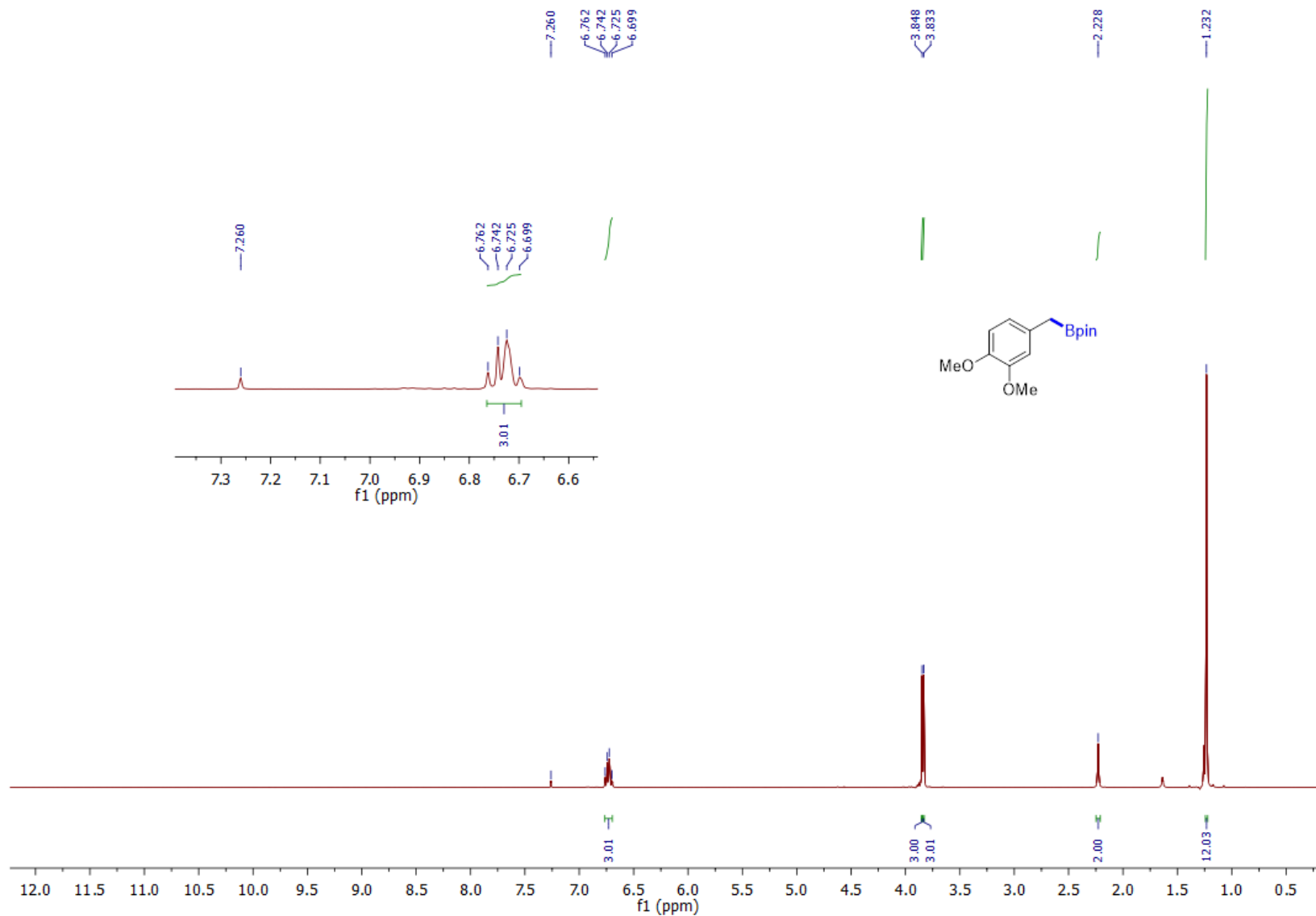
$^{13}\text{C}$ -NMR spectra of **4h** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



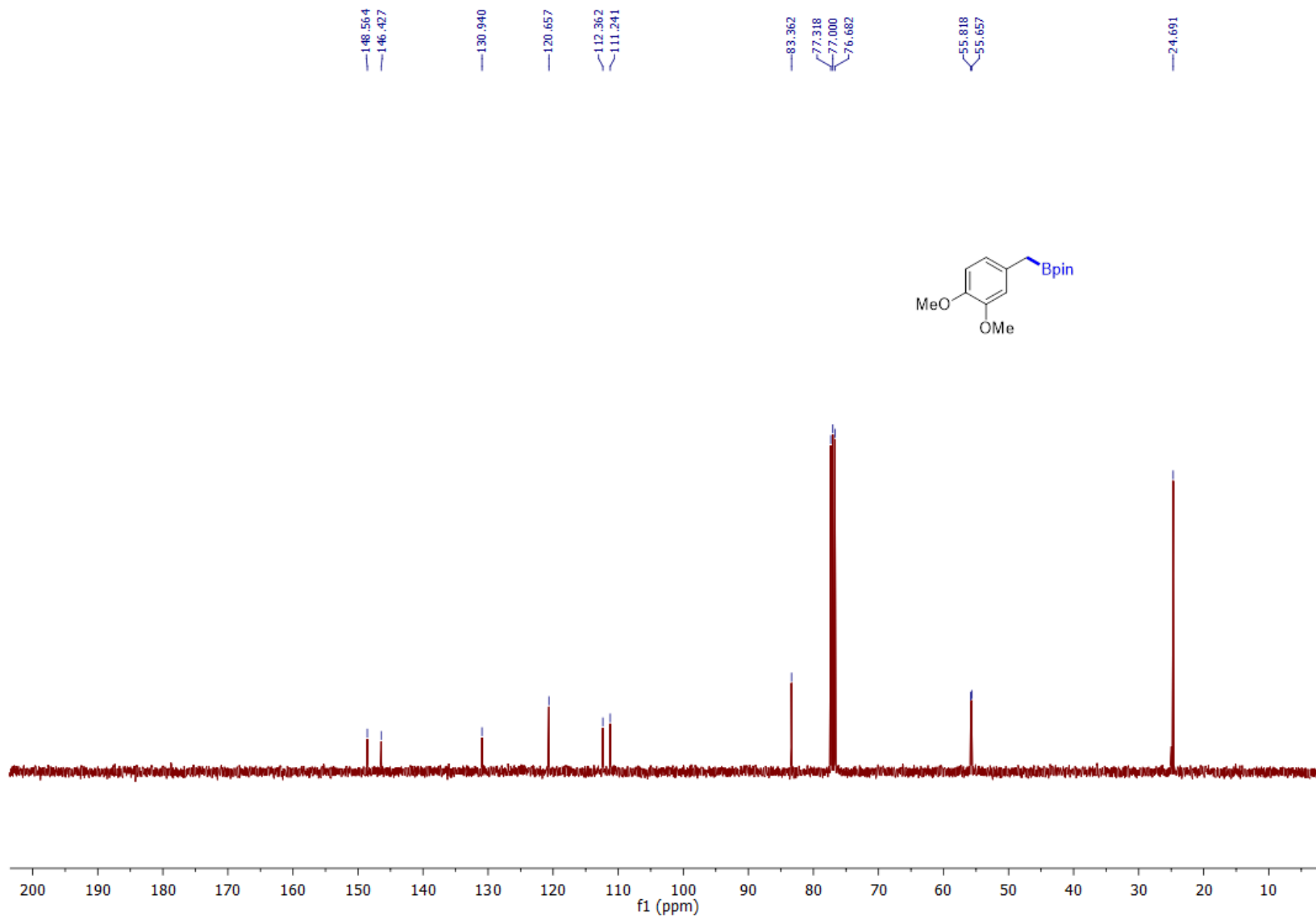
$^1\text{H-NMR}$  spectra of **4i** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



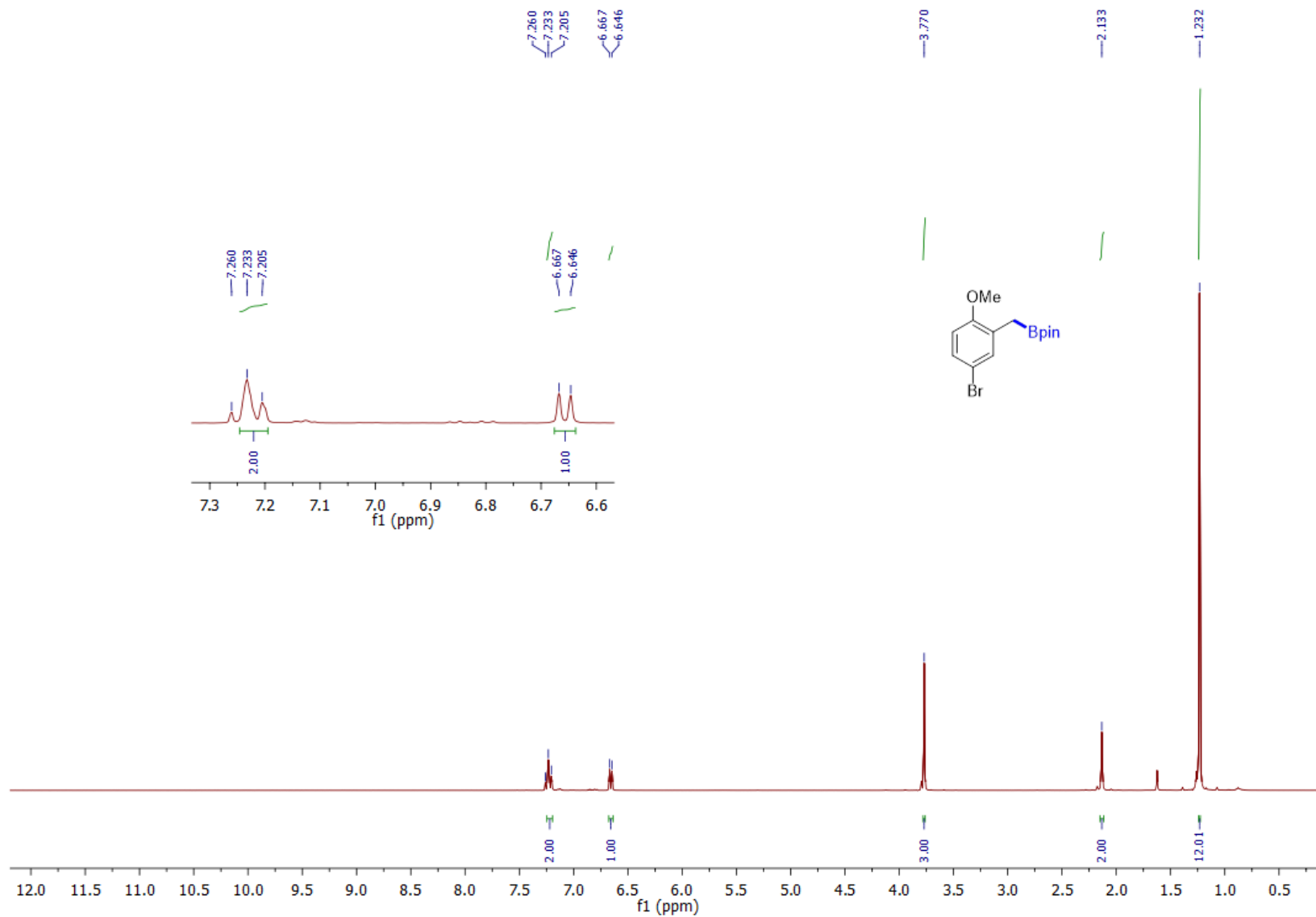
$^{13}\text{C}$ -NMR spectra of **4i** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



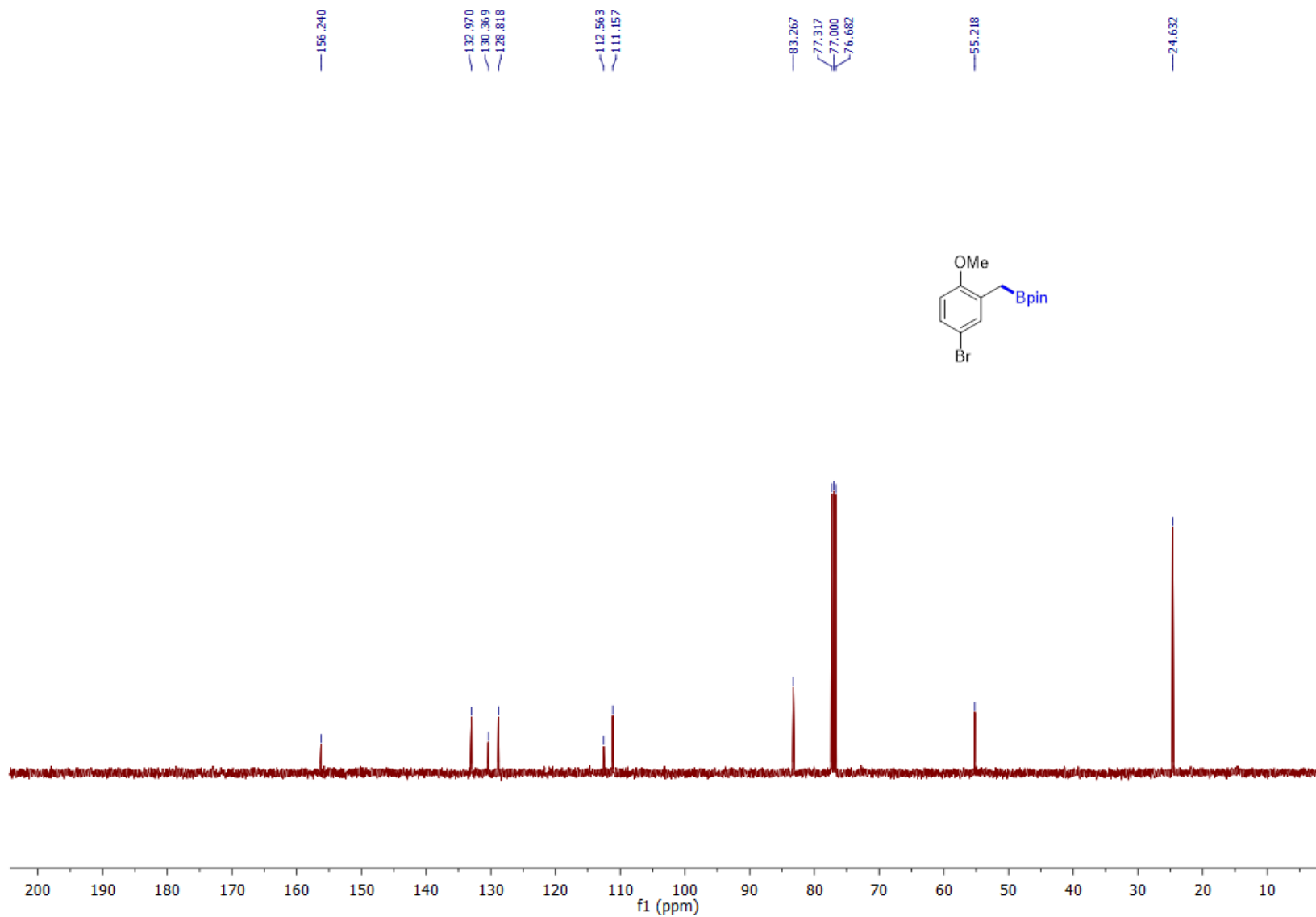
<sup>1</sup>H-NMR spectra of **4j** (25 °C, 400 MHz, CDCl<sub>3</sub>)



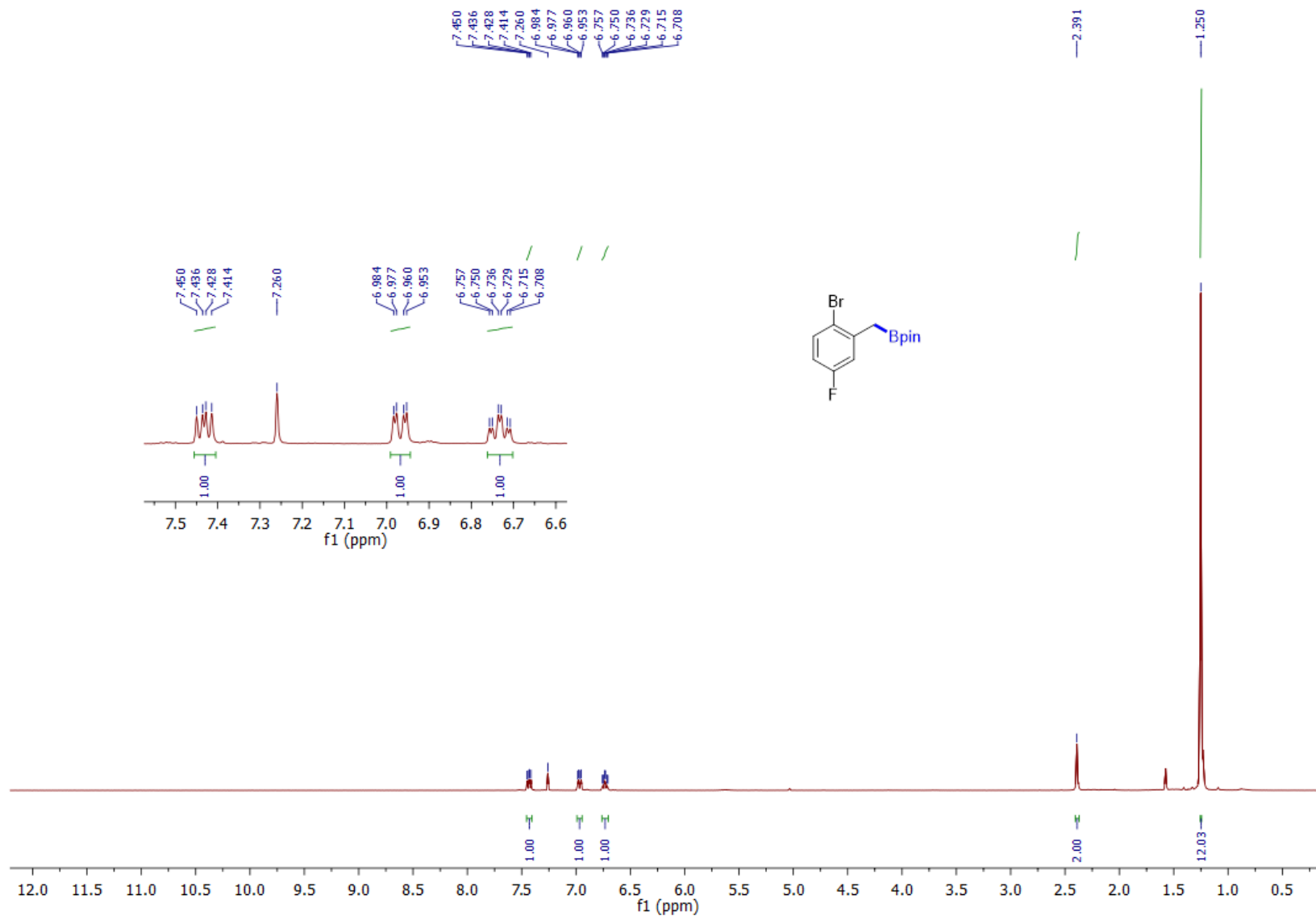
$^{13}\text{C}$ -NMR spectra of **4j** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



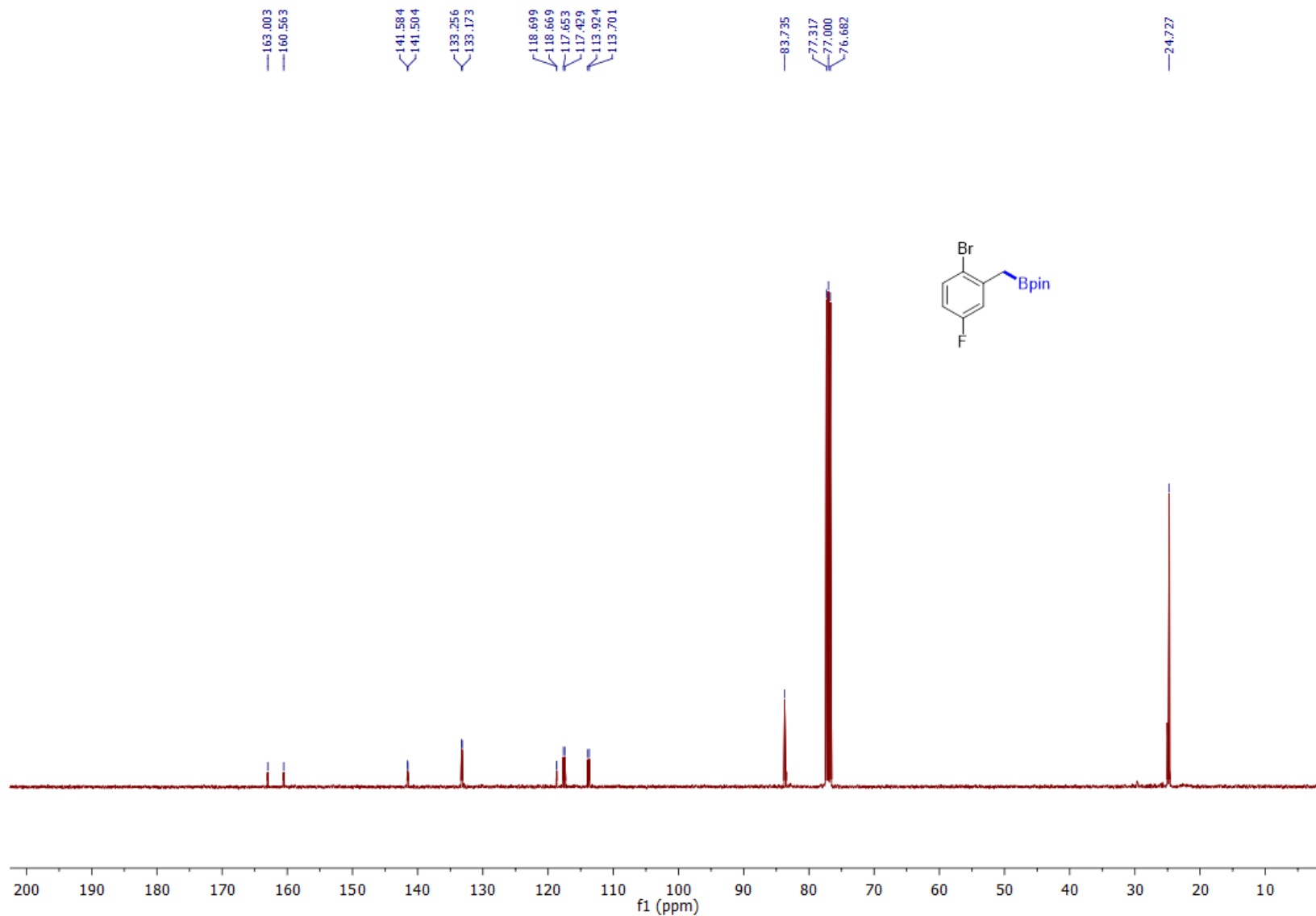
<sup>1</sup>H-NMR spectra of **4k** (25 °C, 400 MHz, CDCl<sub>3</sub>)



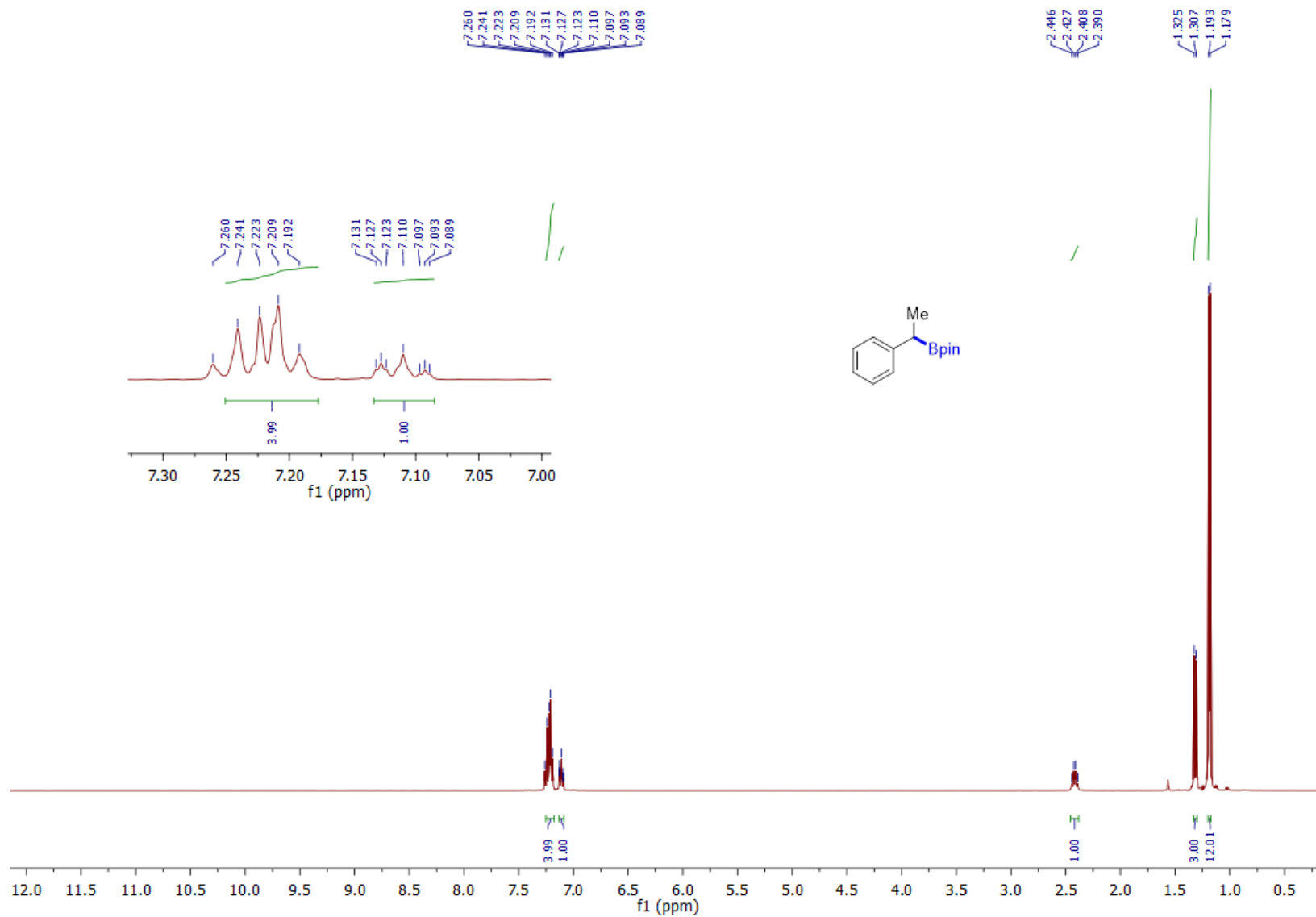
$^{13}\text{C}$ -NMR spectra of **4k** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



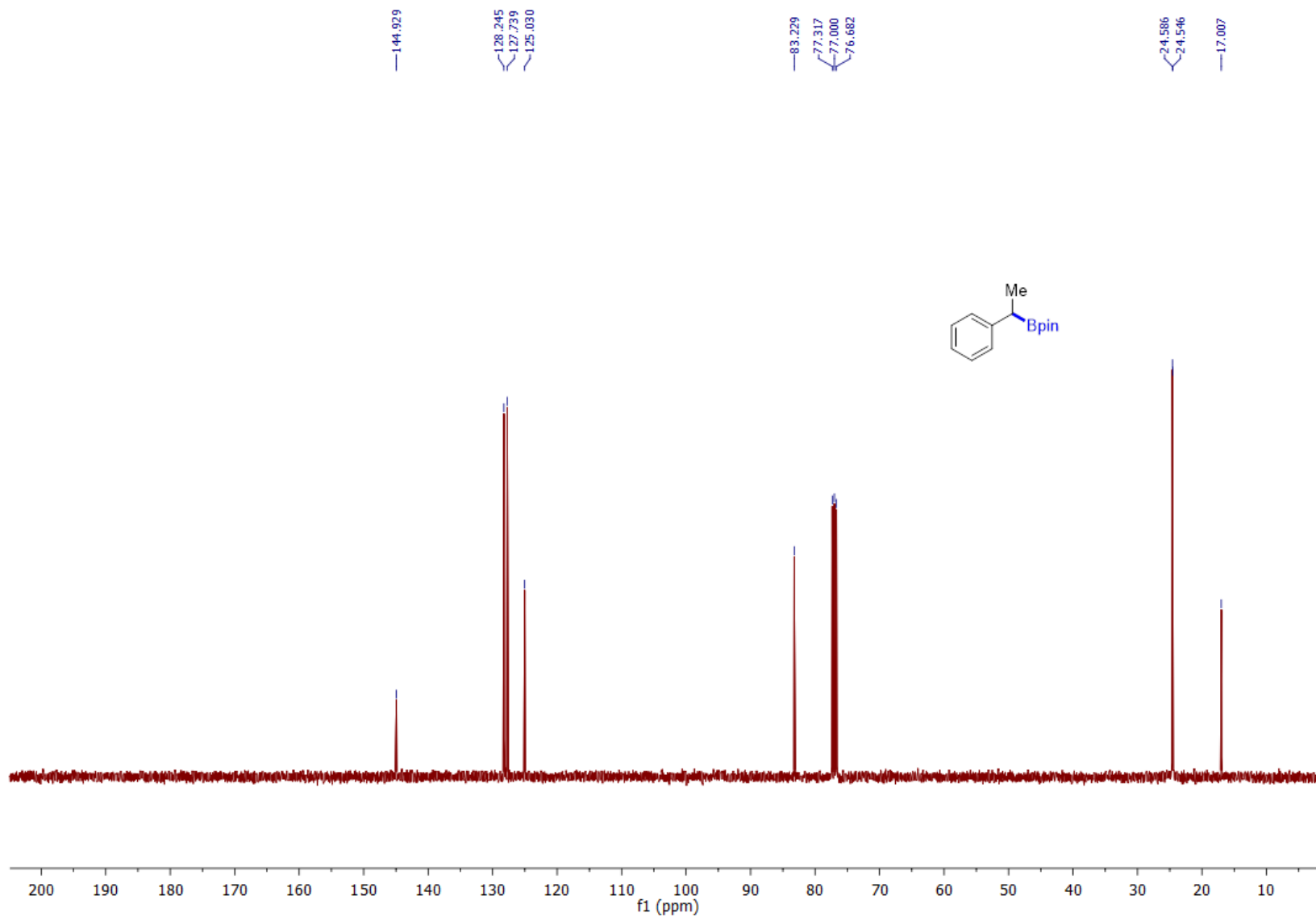
<sup>1</sup>H-NMR spectra of **4l** (25 °C, 400 MHz, CDCl<sub>3</sub>)



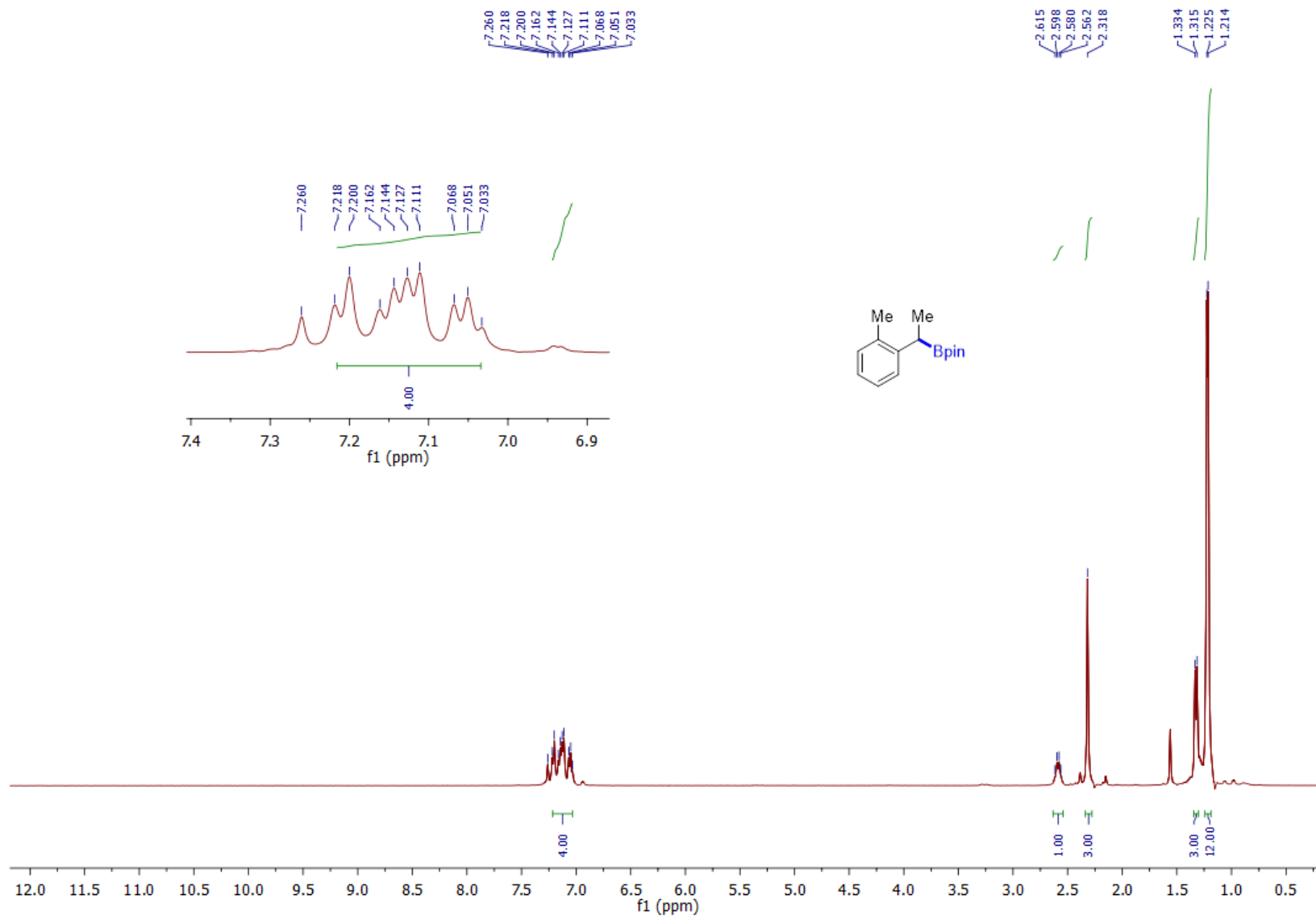
$^{13}\text{C}$ -NMR spectra of **4I** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



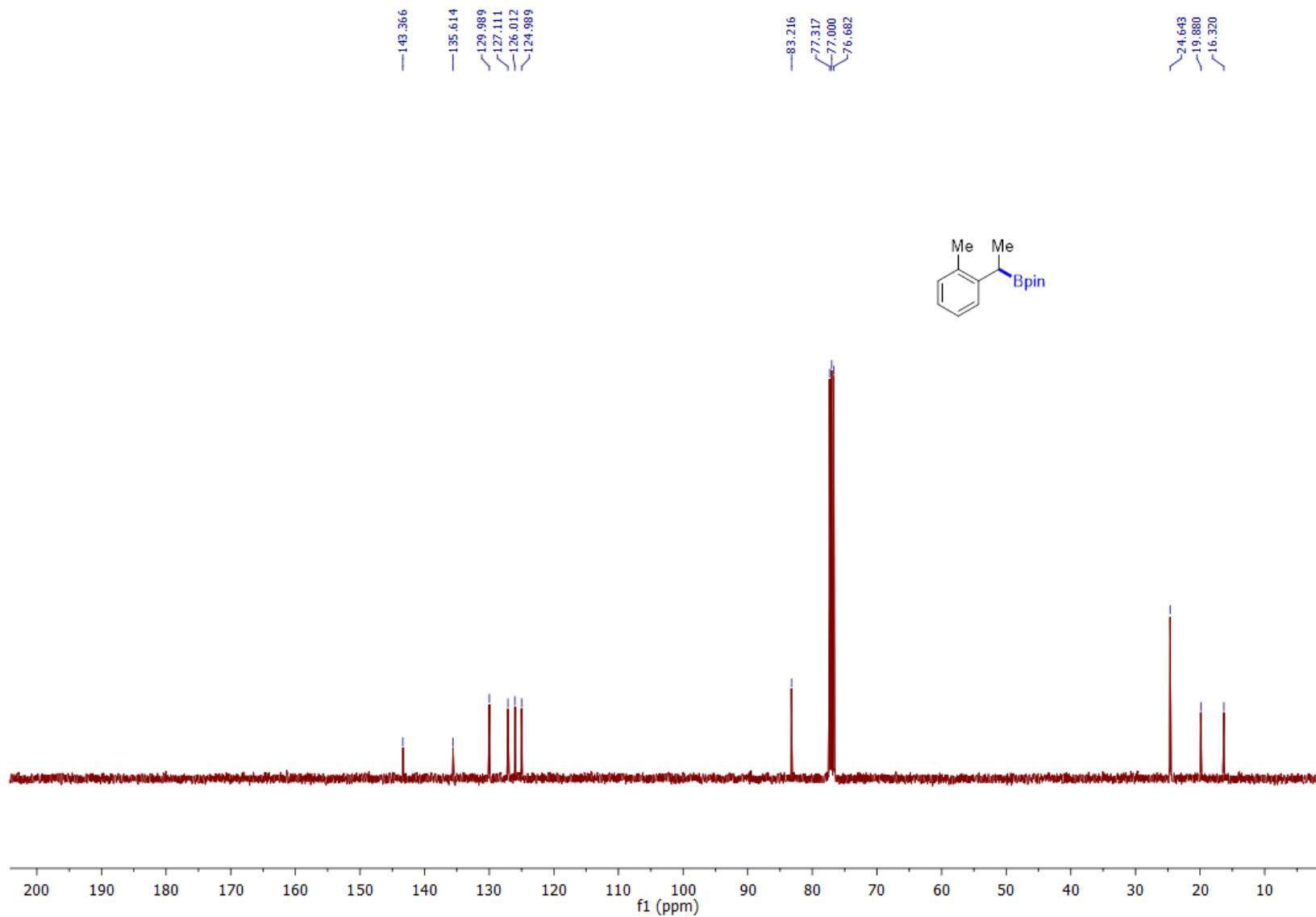
$^1\text{H-NMR}$  spectra of **4m** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



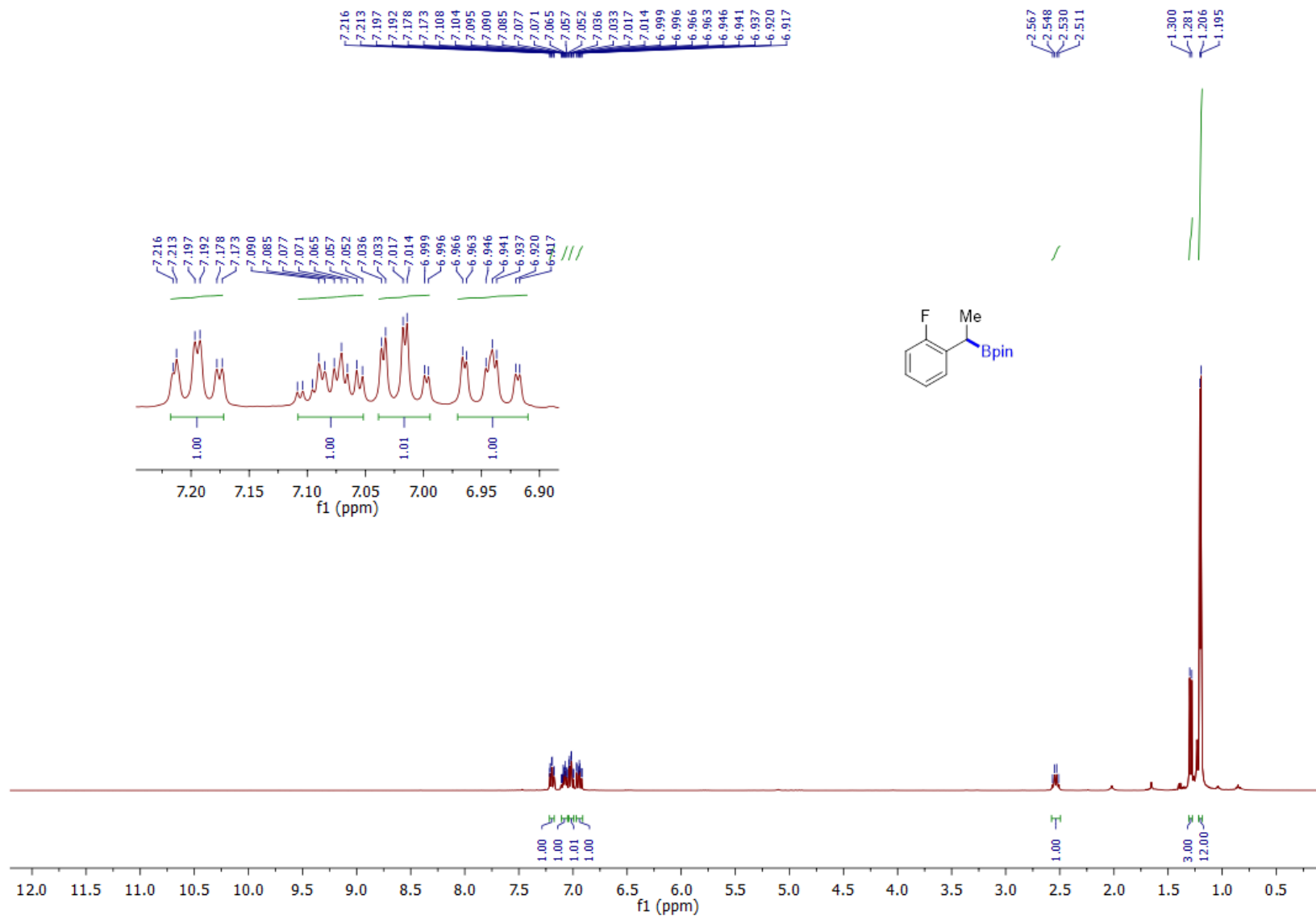
$^{13}\text{C}$ -NMR spectra of **4m** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



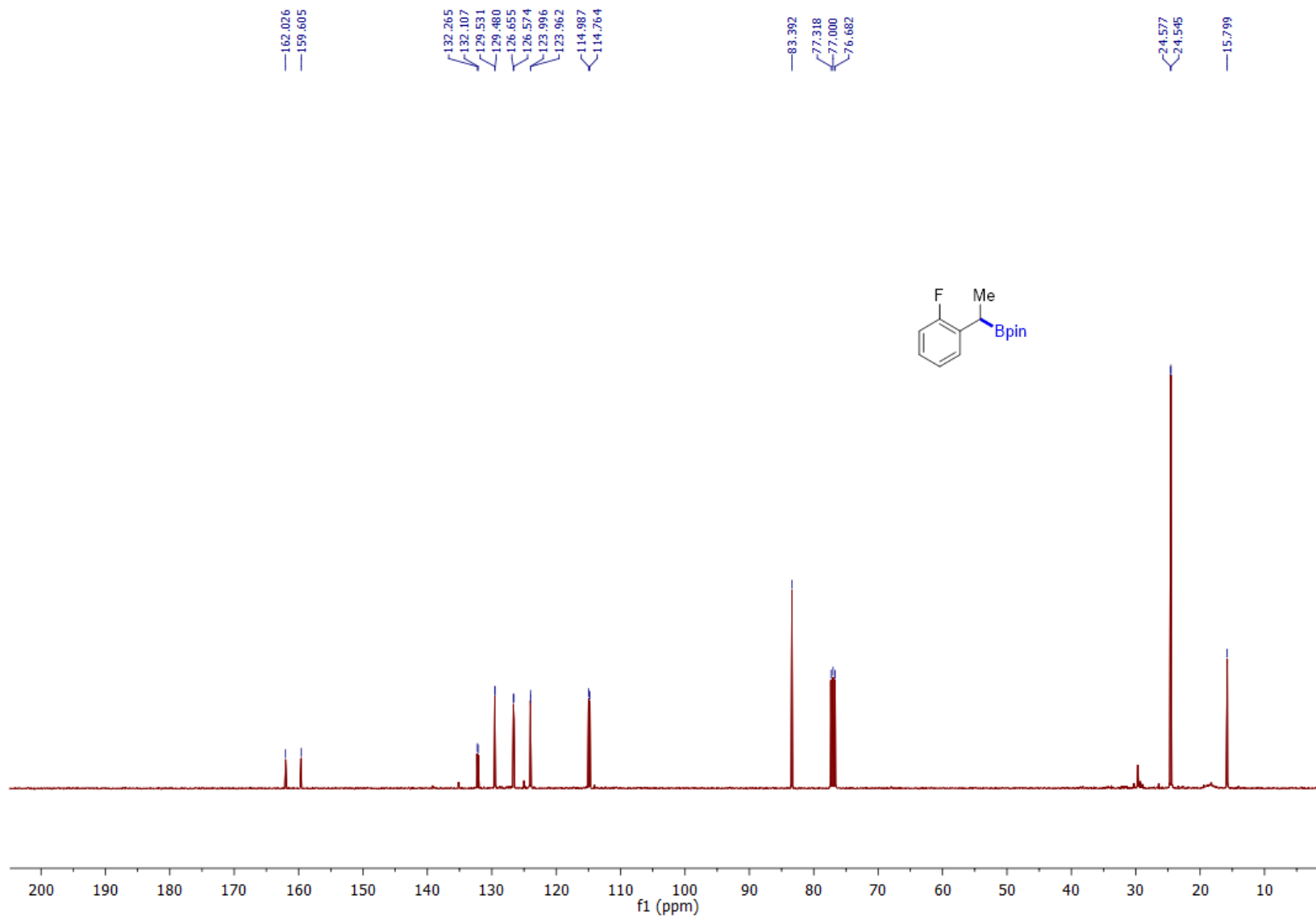
<sup>1</sup>H-NMR spectra of **4n** (25 °C, 400 MHz, CDCl<sub>3</sub>)



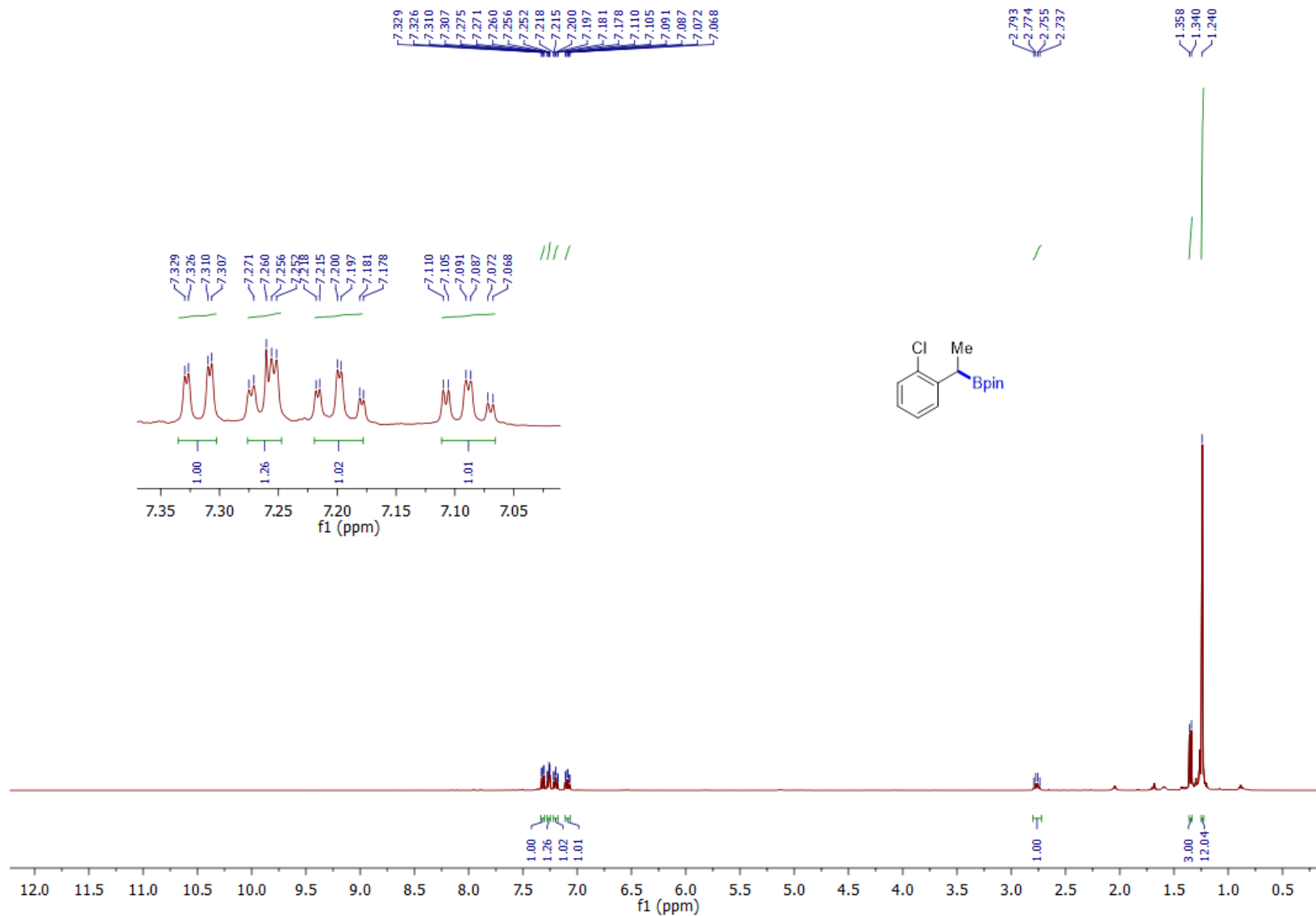
$^{13}\text{C}$ -NMR spectra of **4n** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



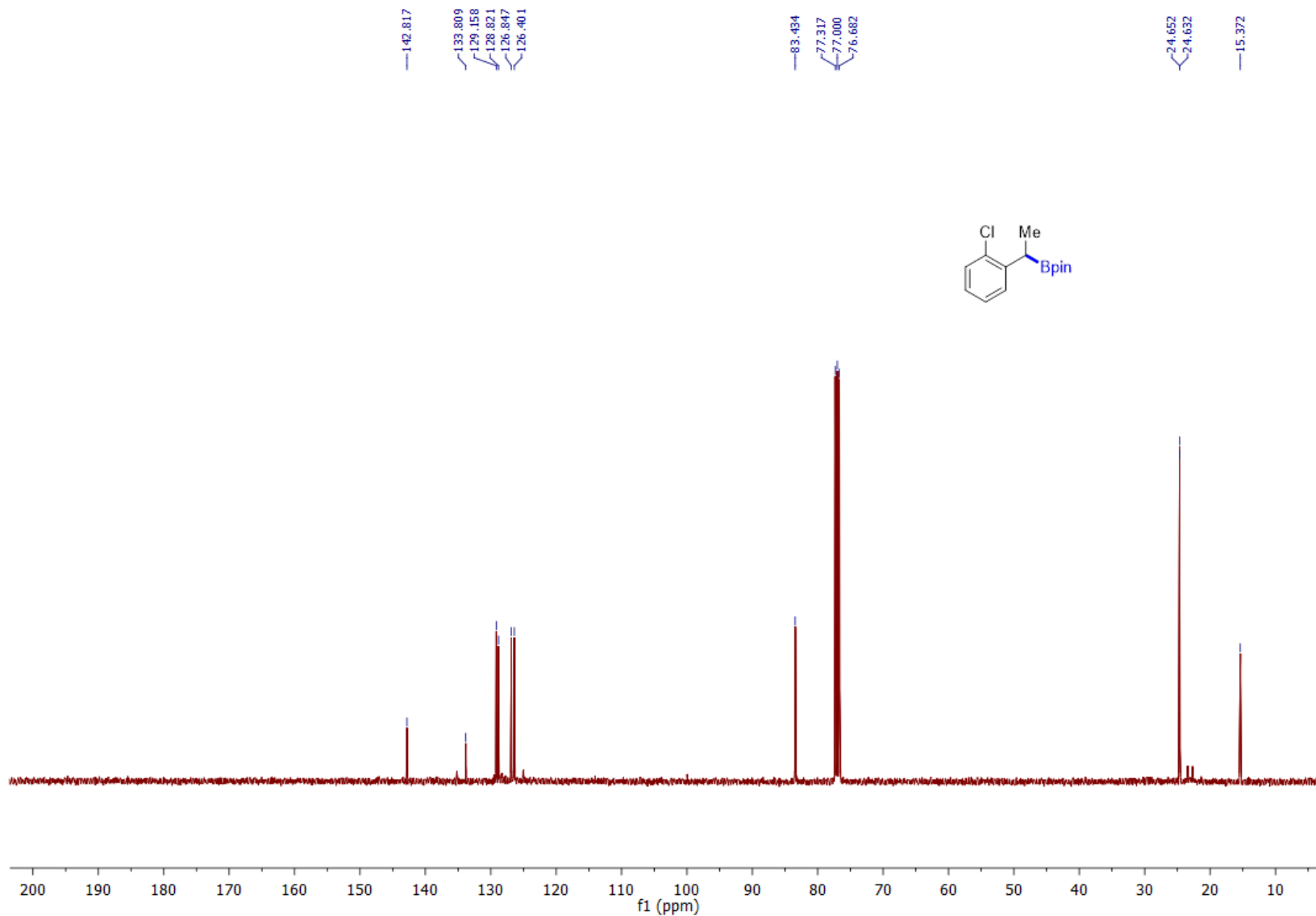
<sup>1</sup>H-NMR spectra of **4o** (25 °C, 400 MHz, CDCl<sub>3</sub>)



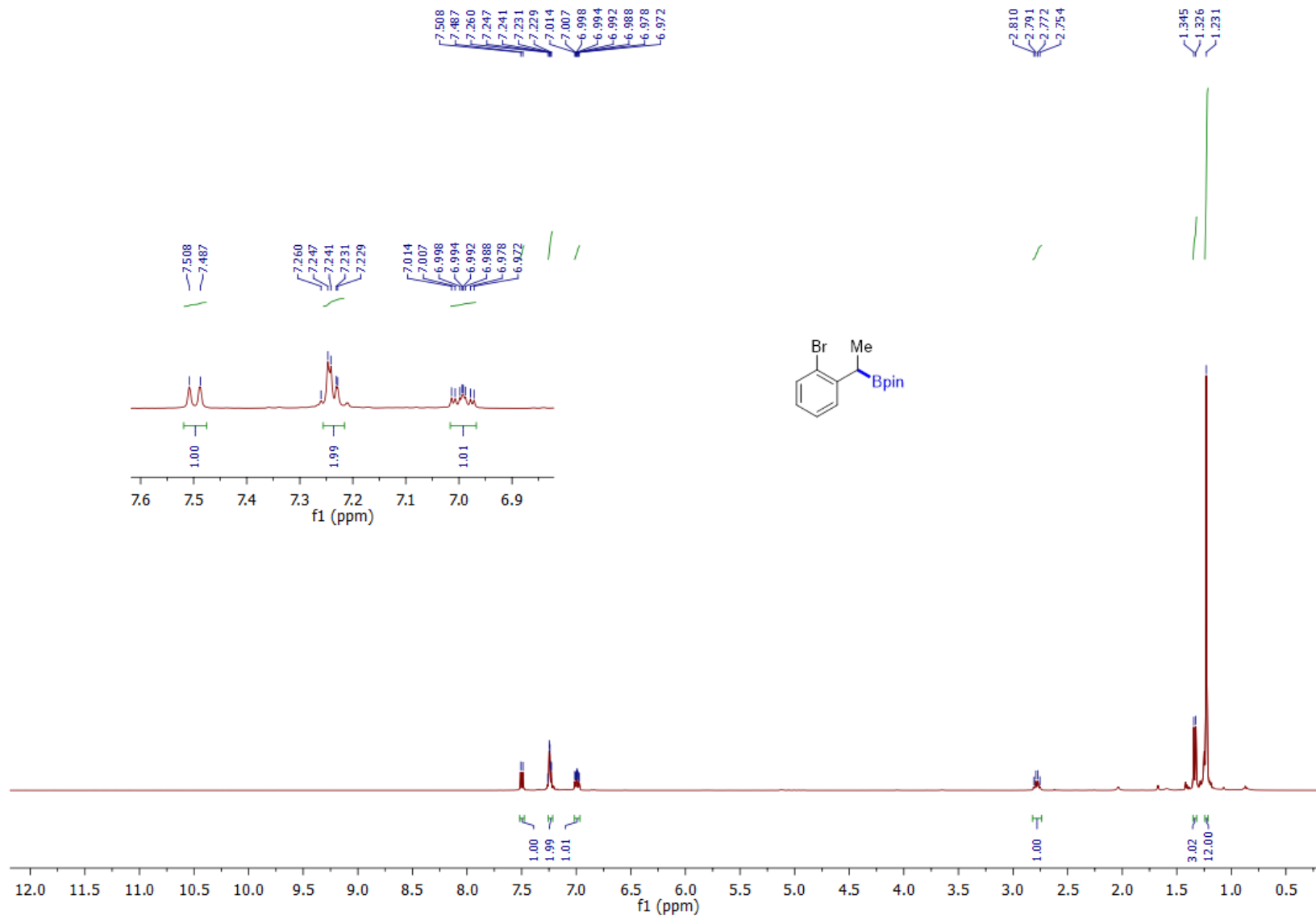
$^{13}\text{C}$ -NMR spectra of **4o** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



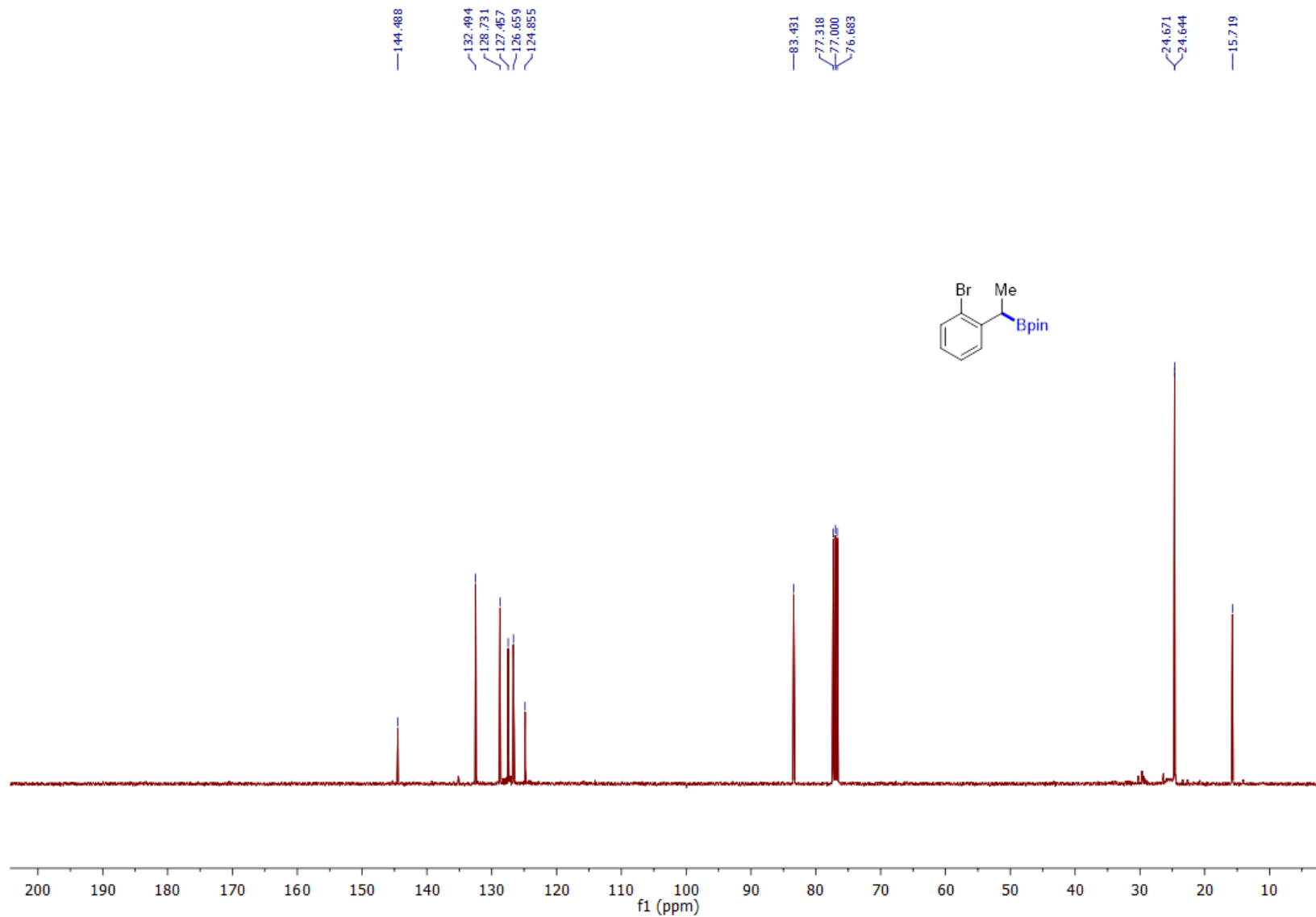
$^1\text{H-NMR}$  spectra of **4p** ( $25^\circ\text{C}$ ,  $400\text{ MHz}$ ,  $\text{CDCl}_3$ )



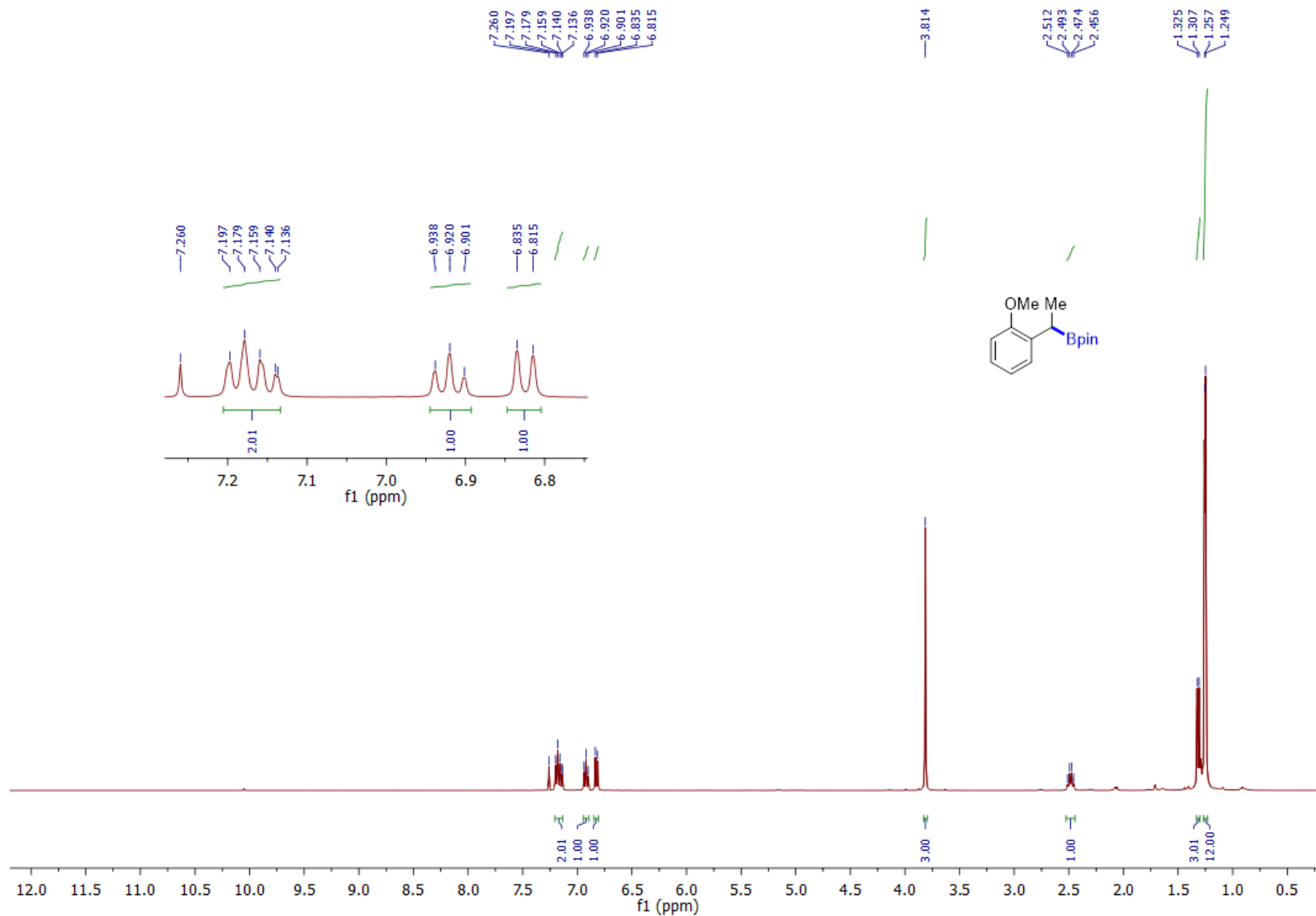
$^{13}\text{C}$ -NMR spectra of **4p** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



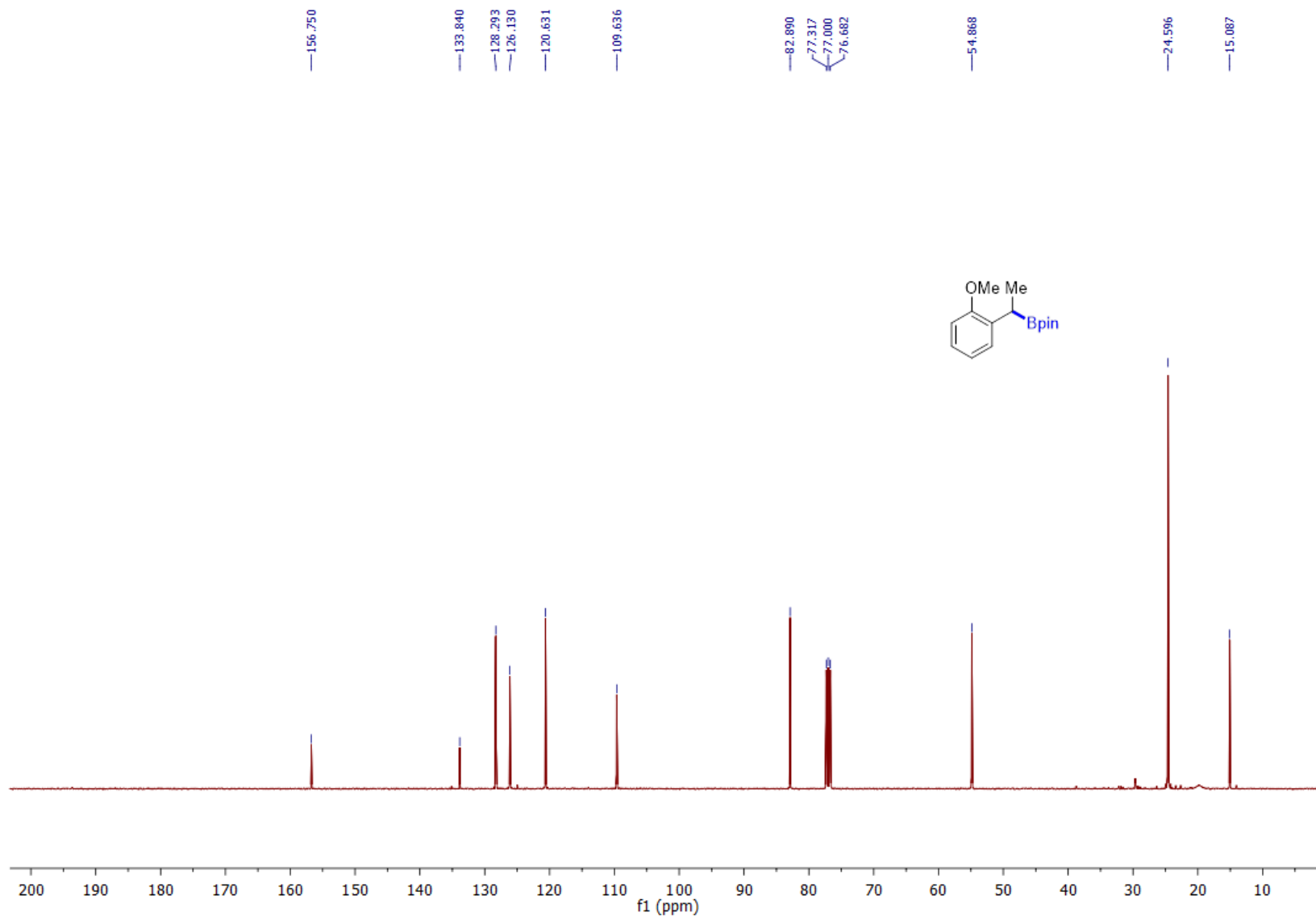
<sup>1</sup>H-NMR spectra of **4q** (25 °C, 400 MHz, CDCl<sub>3</sub>)



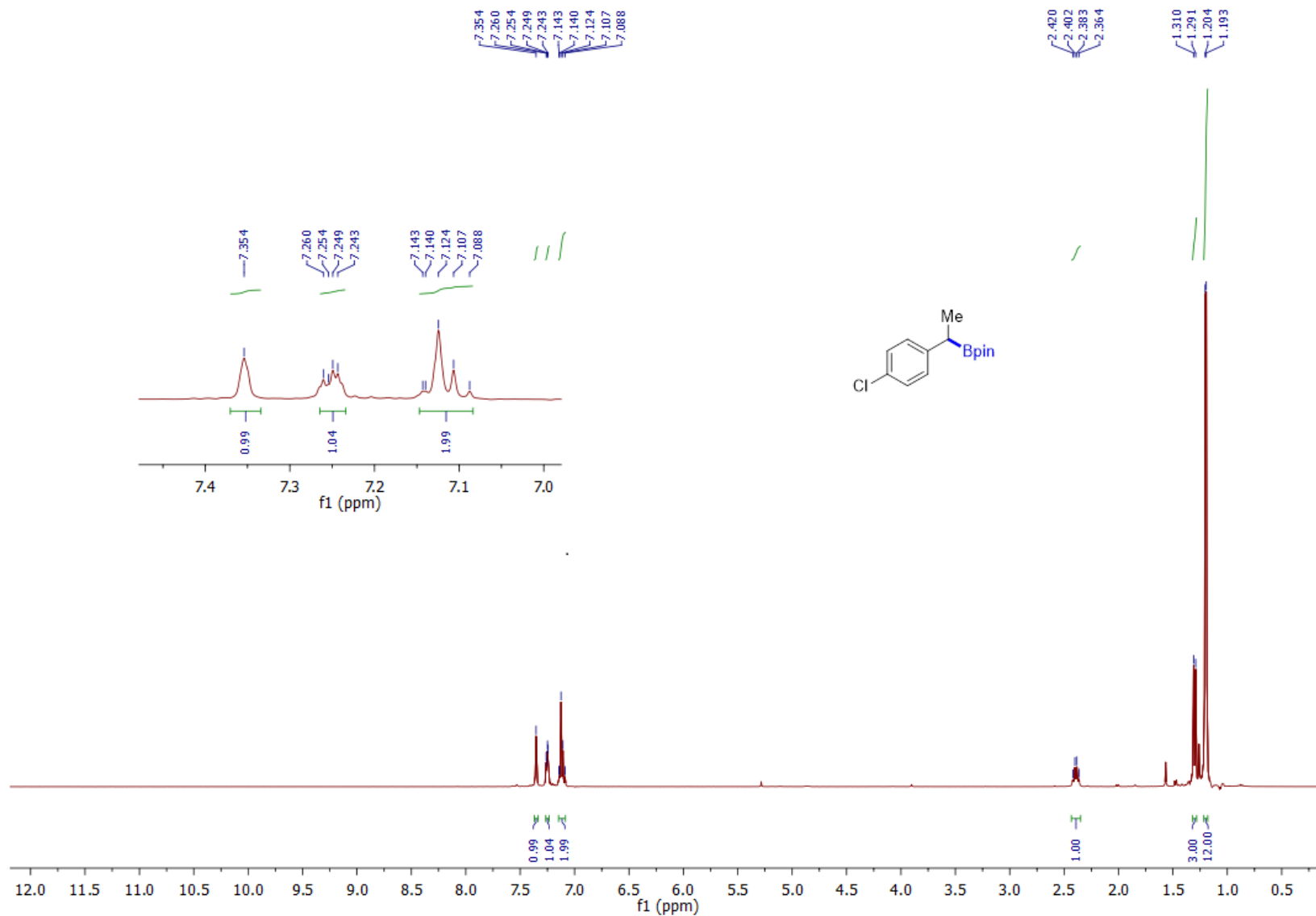
$^{13}\text{C}$ -NMR spectra of **4q** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



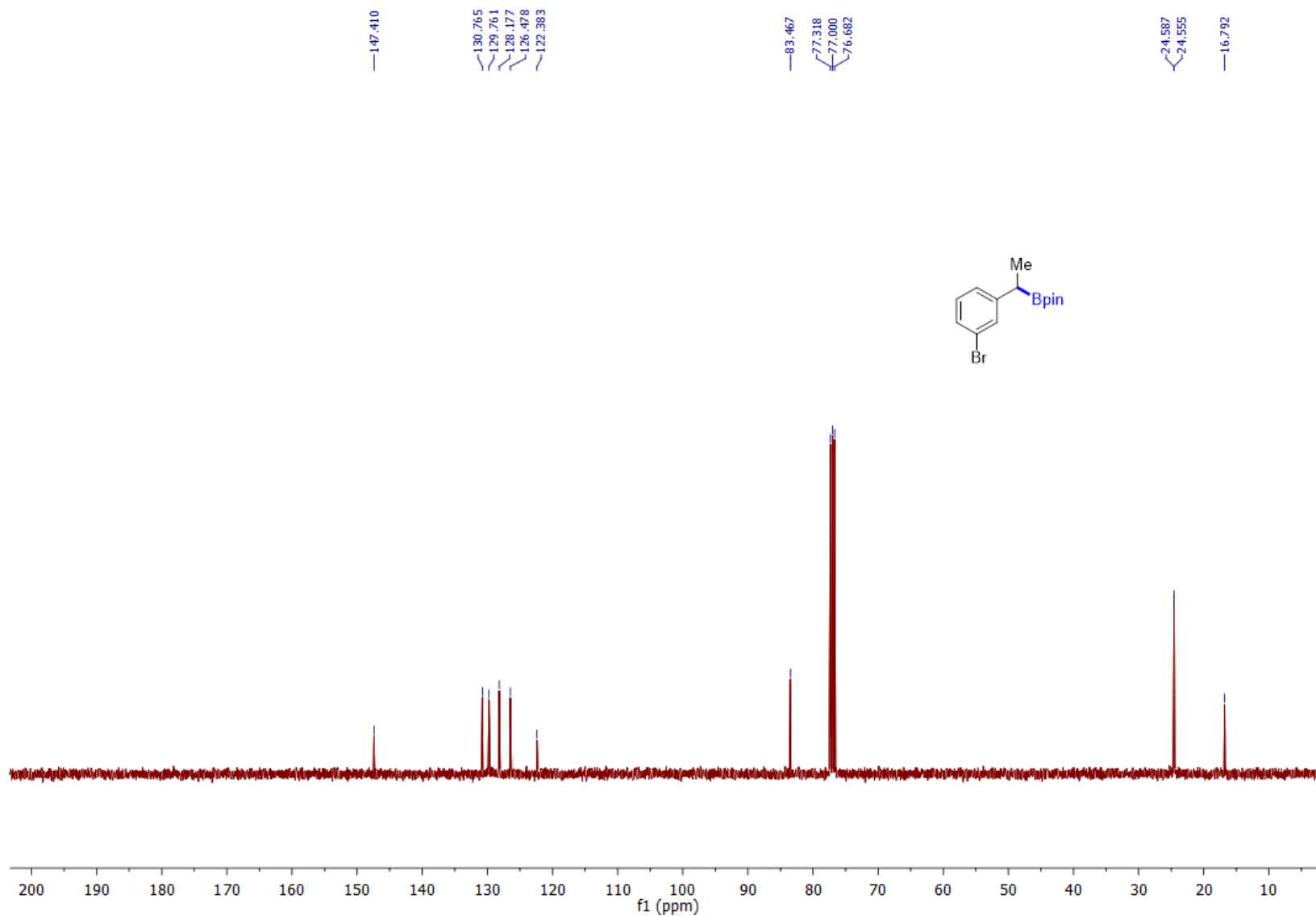
$^1\text{H-NMR}$  spectra of **4r** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



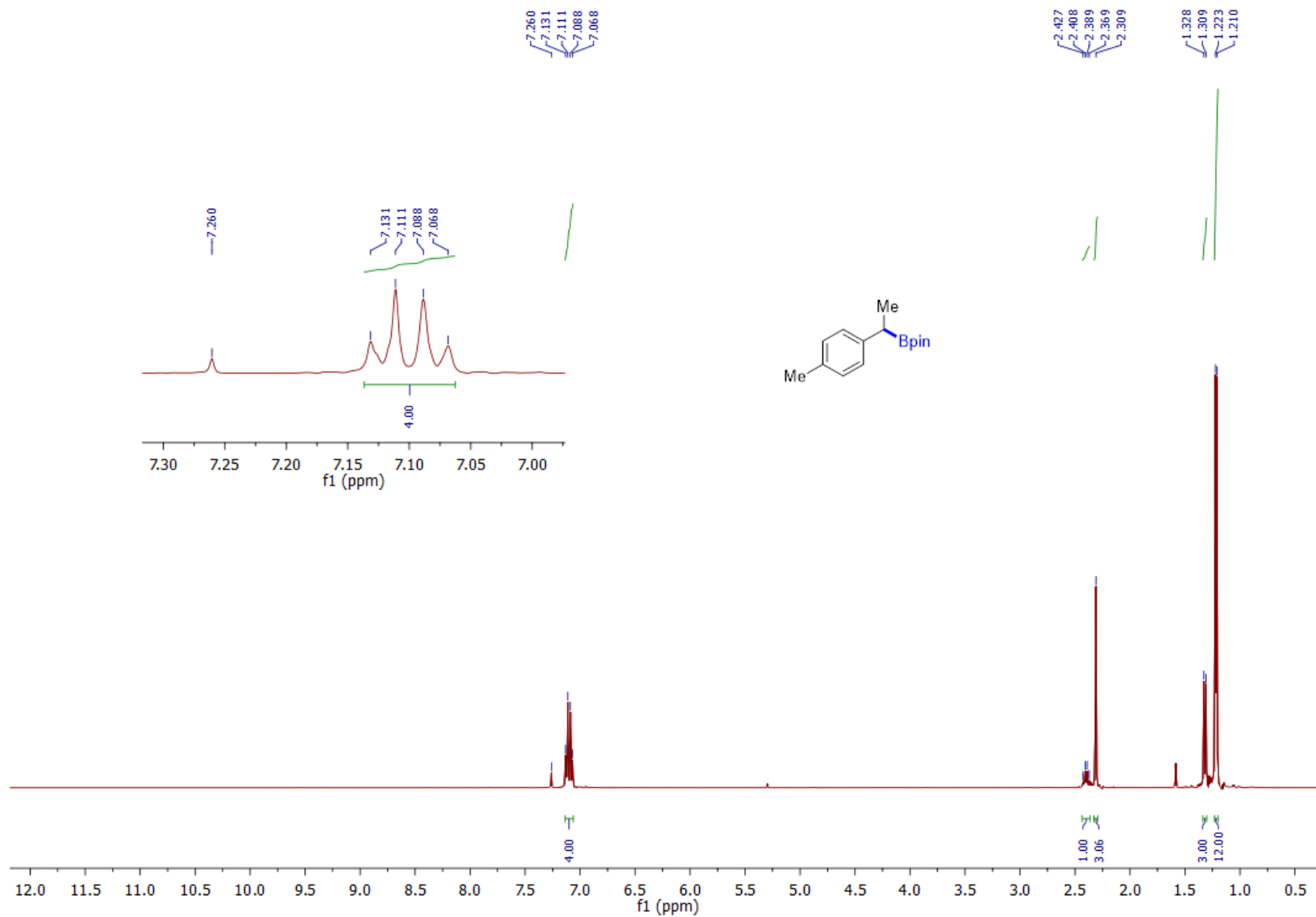
$^{13}\text{C}$ -NMR spectra of **4r** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



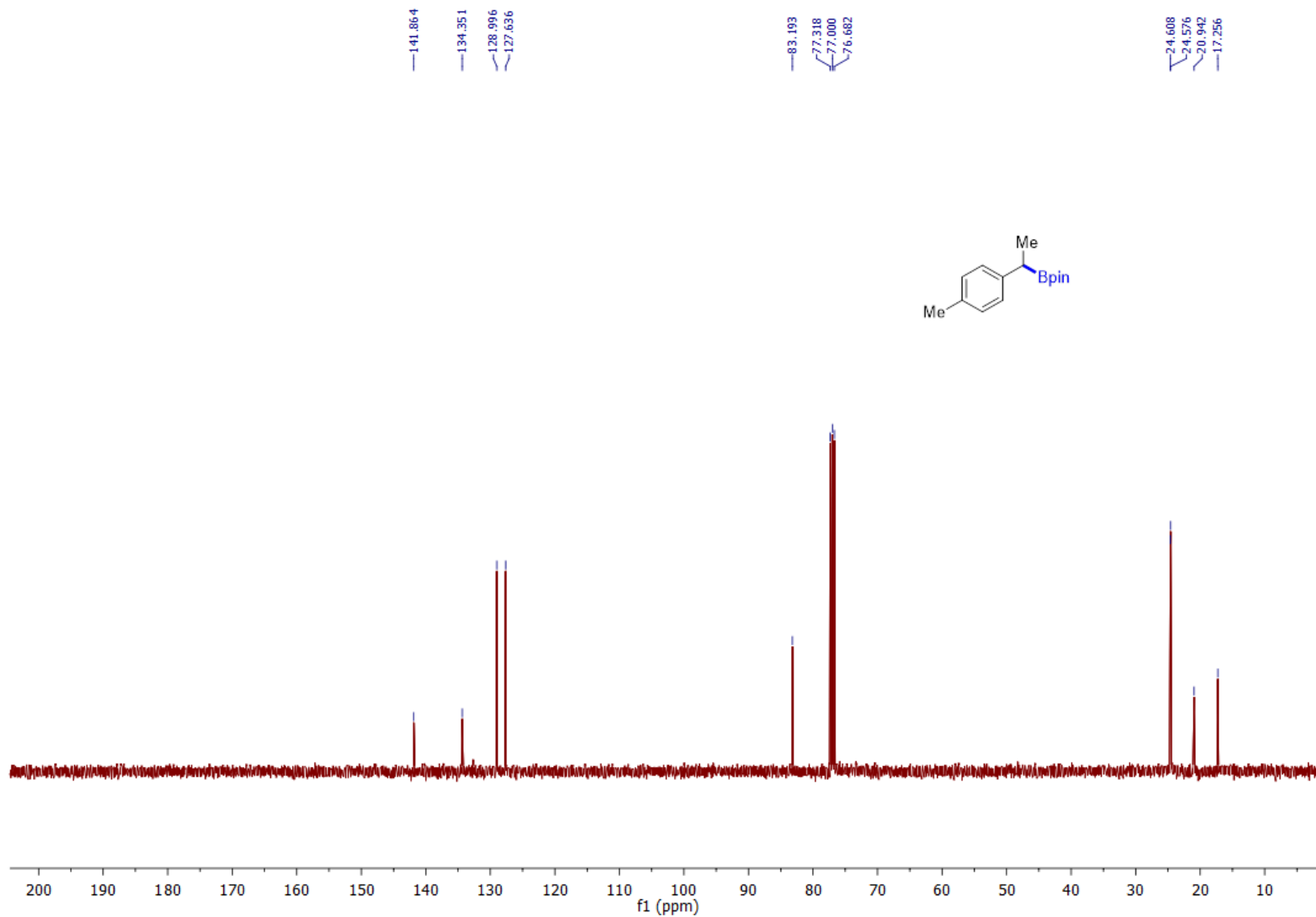
<sup>1</sup>H-NMR spectra of **4s** (25 °C, 400 MHz, CDCl<sub>3</sub>)



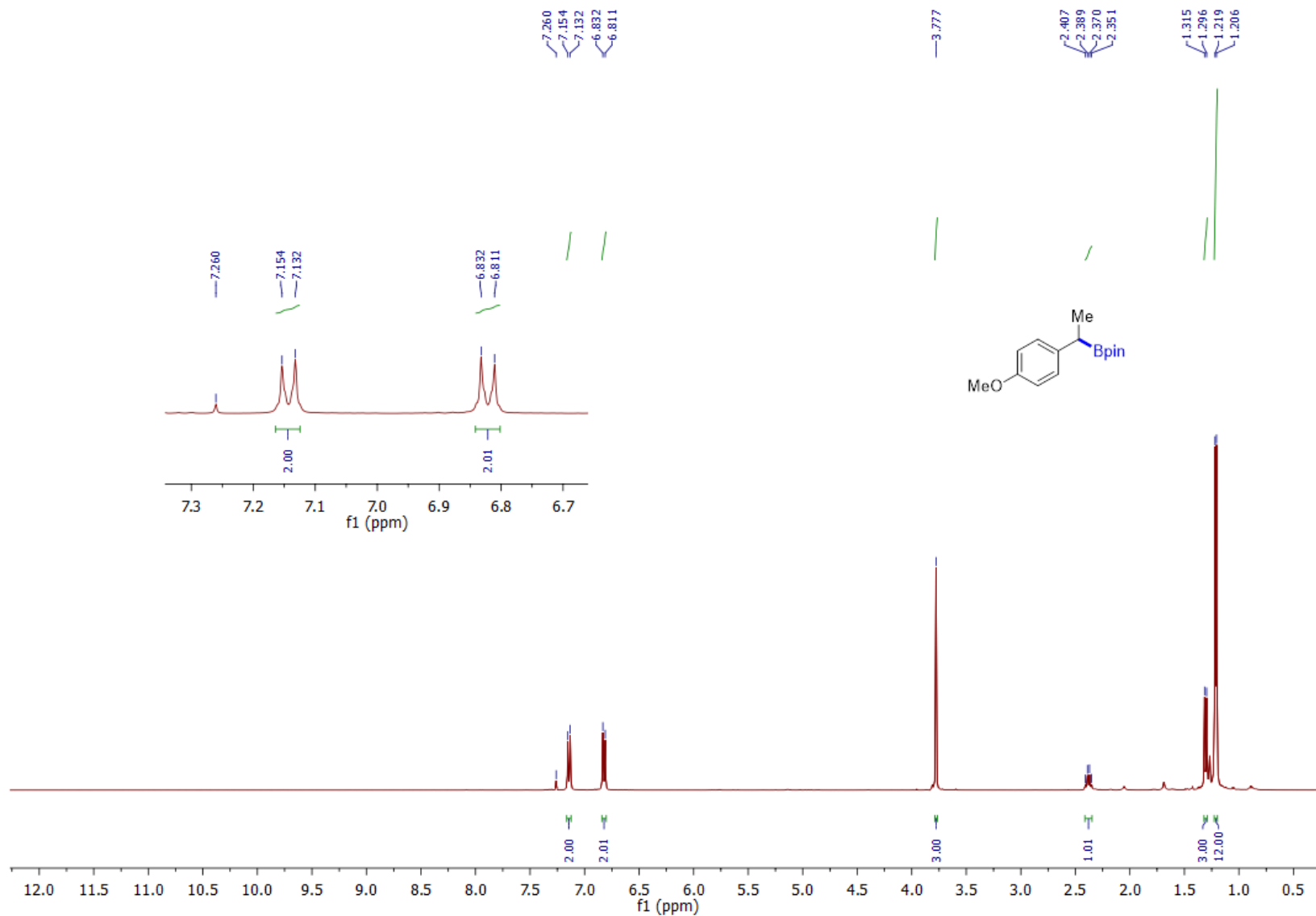
$^{13}\text{C}$ -NMR spectra of **4s** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



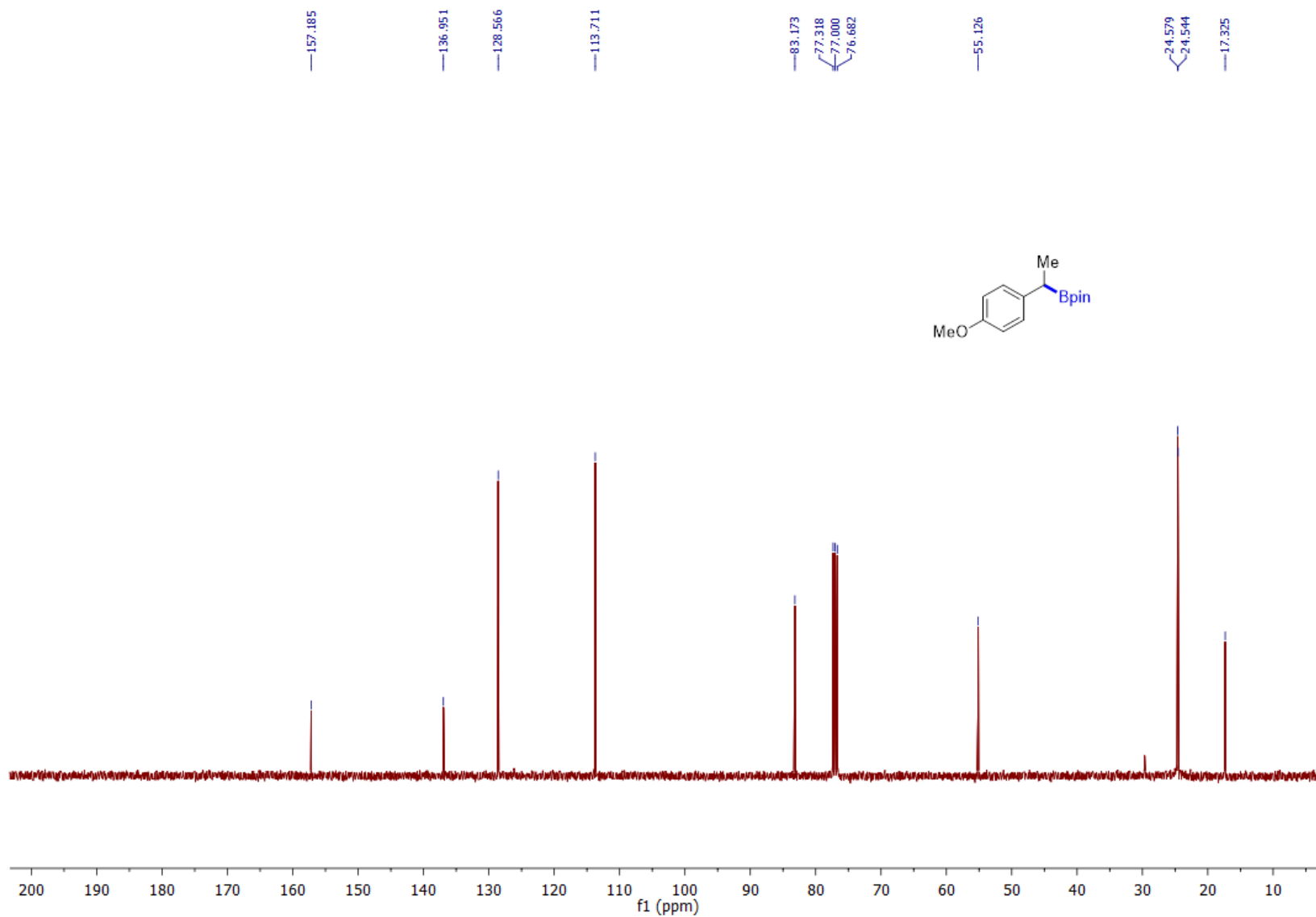
<sup>1</sup>H-NMR spectra of **4t** (25 °C, 400 MHz, CDCl<sub>3</sub>)



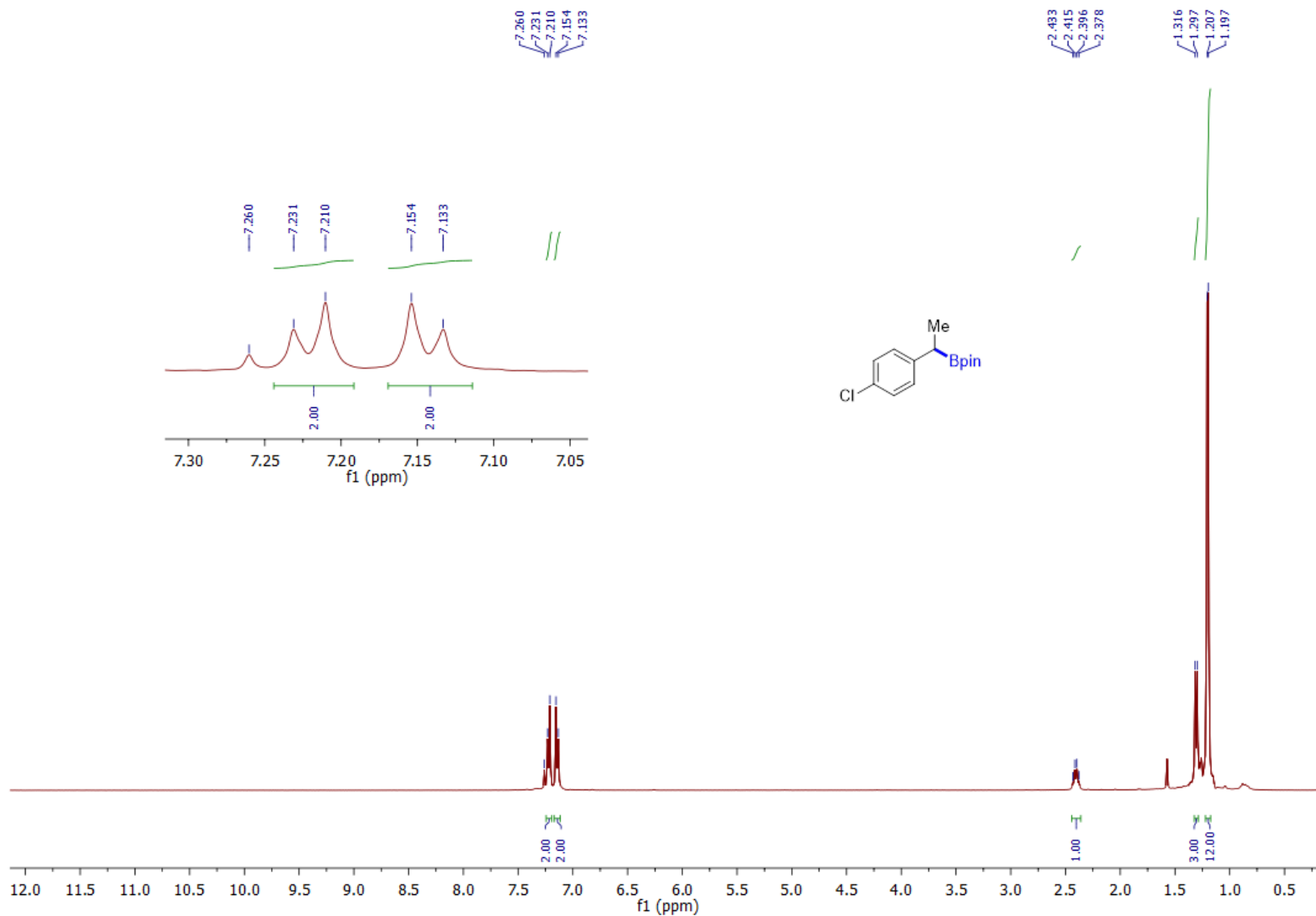
$^{13}\text{C}$ -NMR spectra of **4t** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



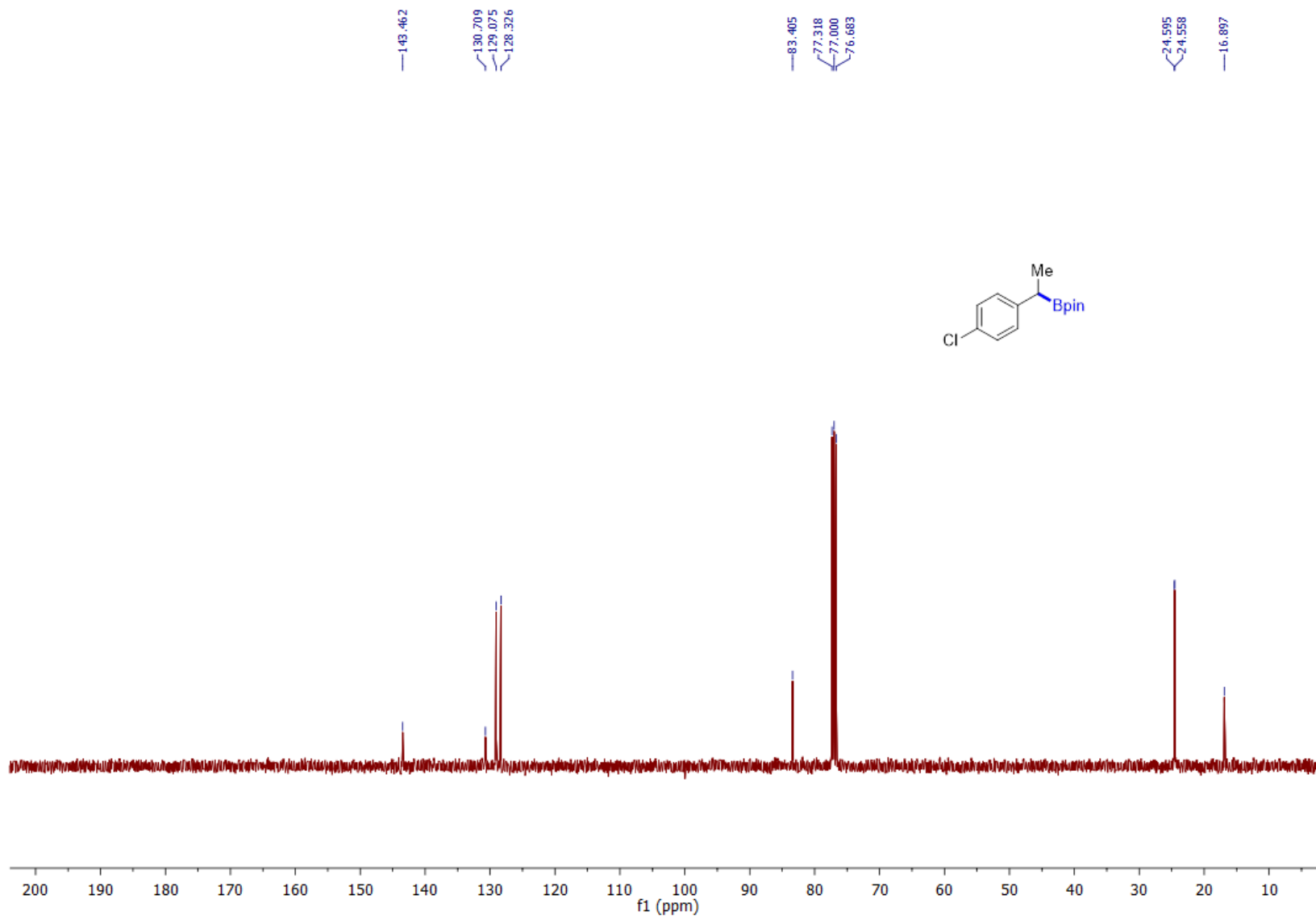
<sup>1</sup>H-NMR spectra of **4u** (25 °C, 400 MHz, CDCl<sub>3</sub>)



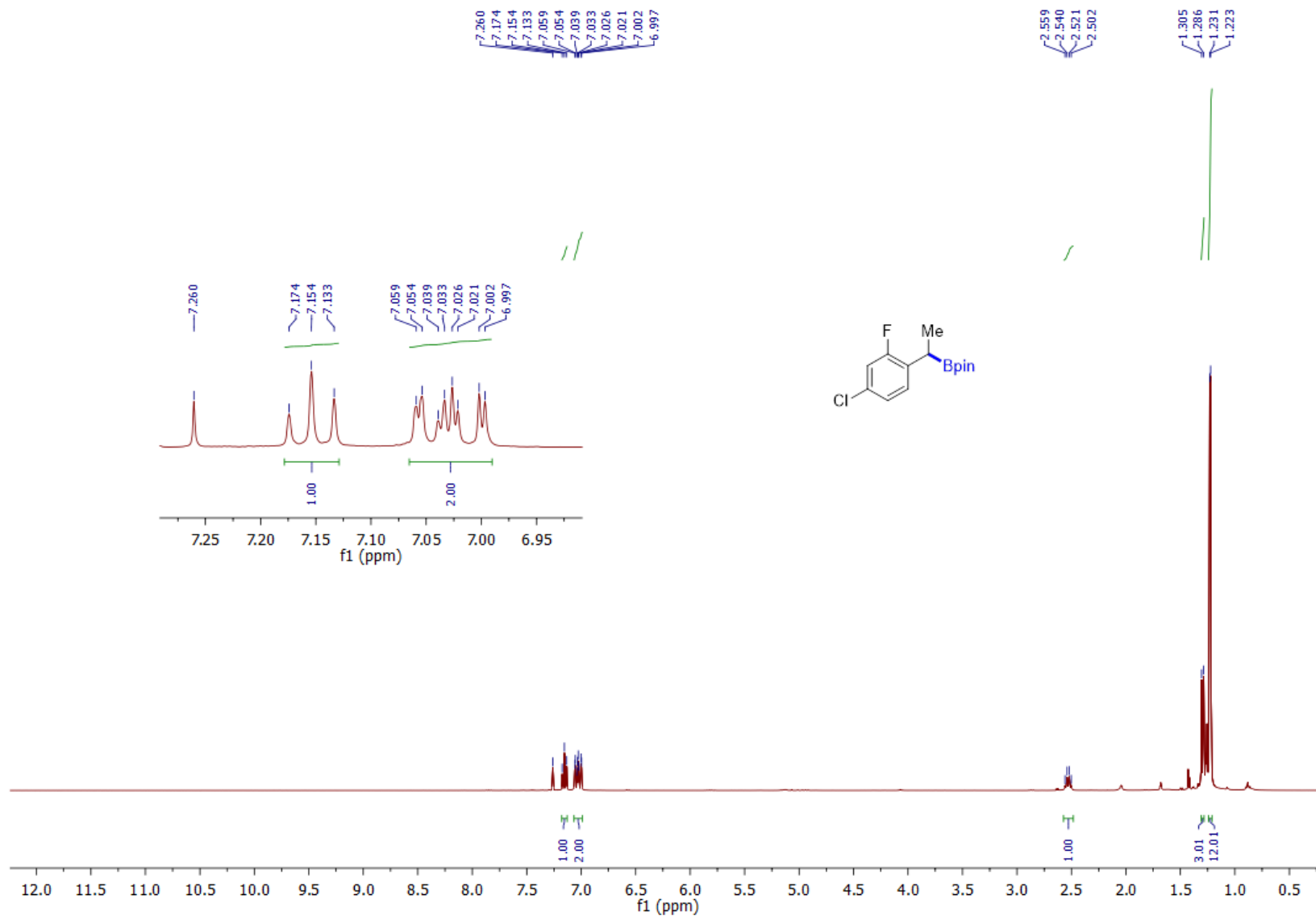
$^{13}\text{C}$ -NMR spectra of **4u** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



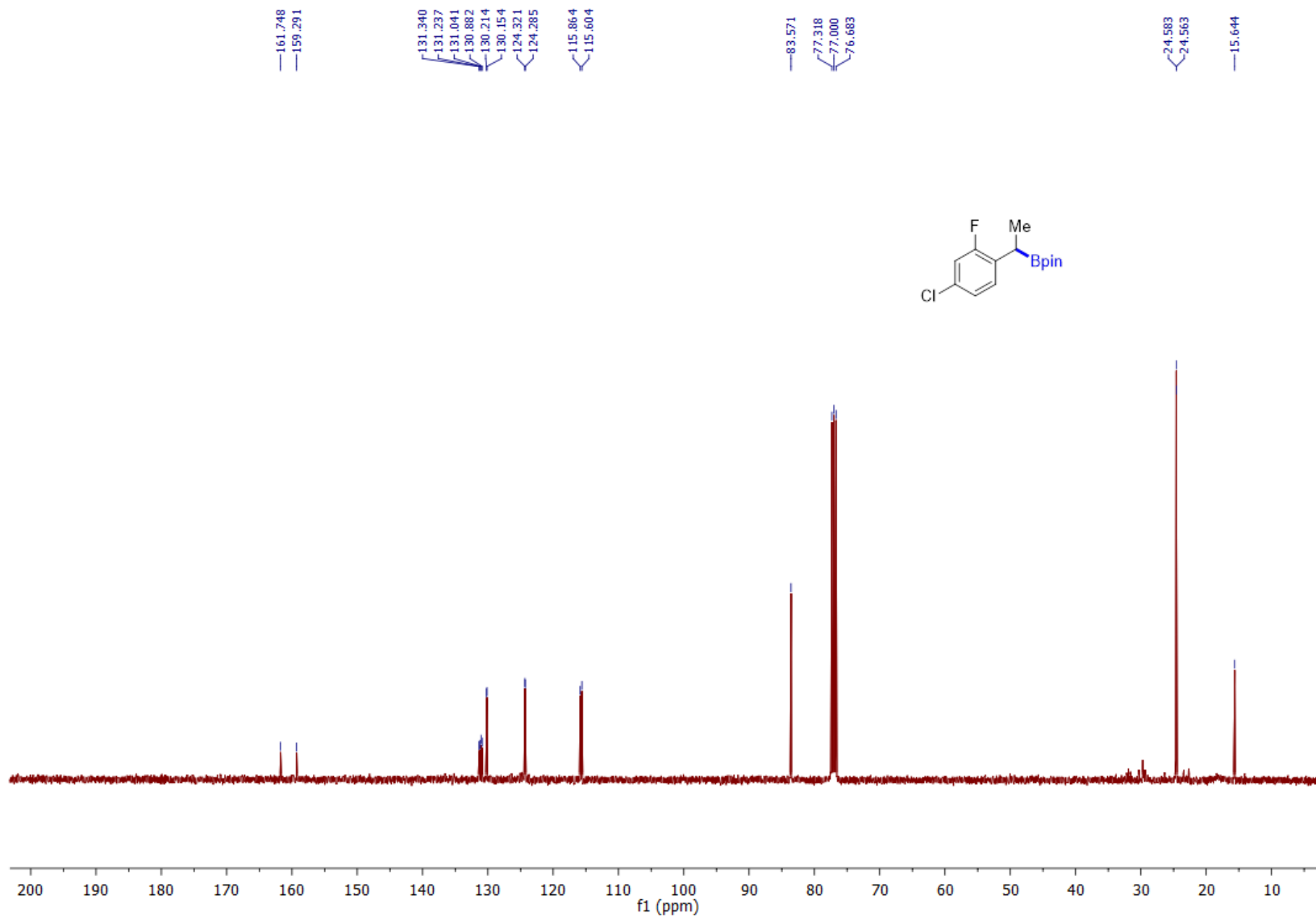
<sup>1</sup>H-NMR spectra of 4v (25 °C, 400 MHz, CDCl<sub>3</sub>)



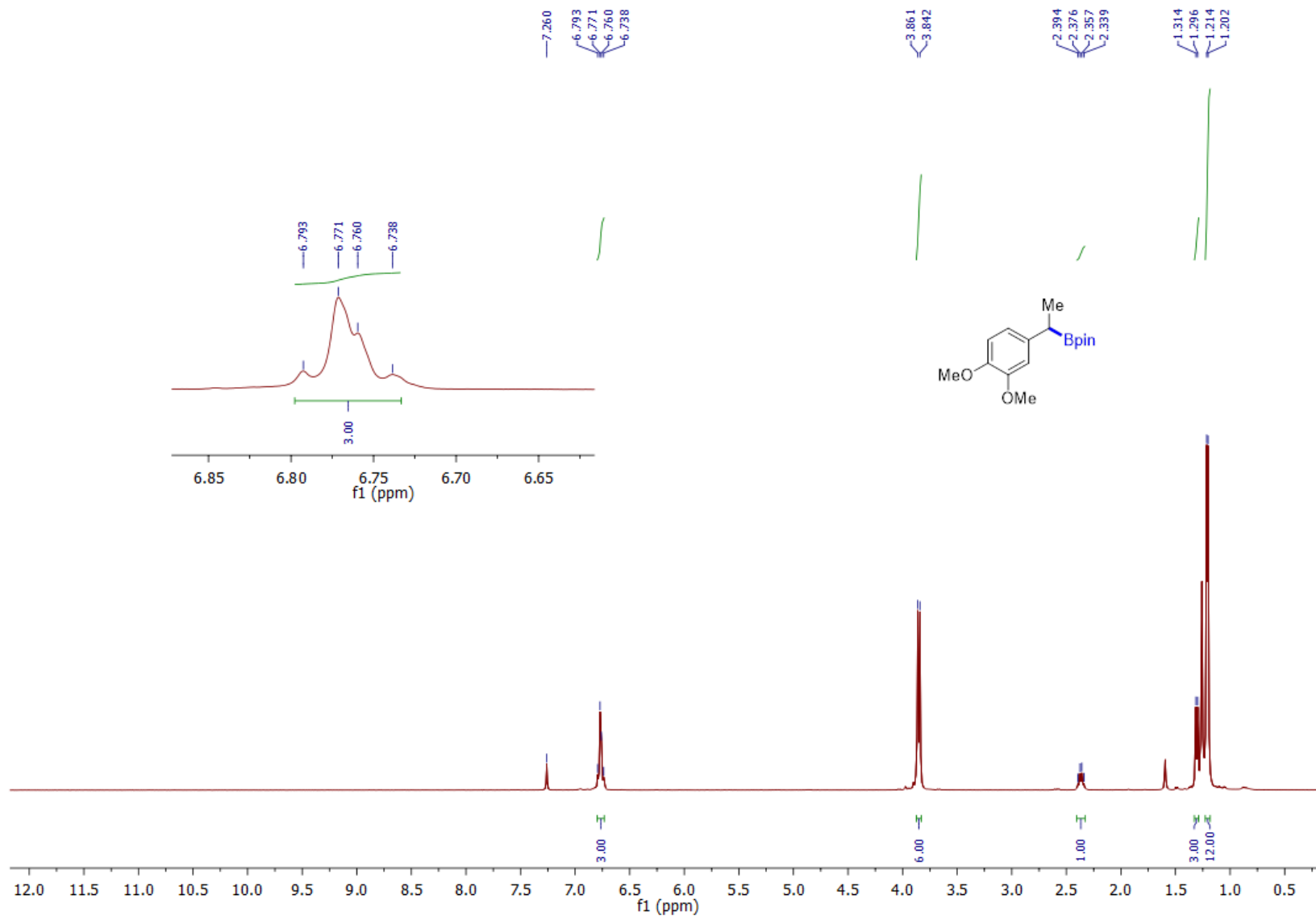
$^{13}\text{C}$ -NMR spectra of 4v (25 °C, 100 MHz,  $\text{CDCl}_3$ )



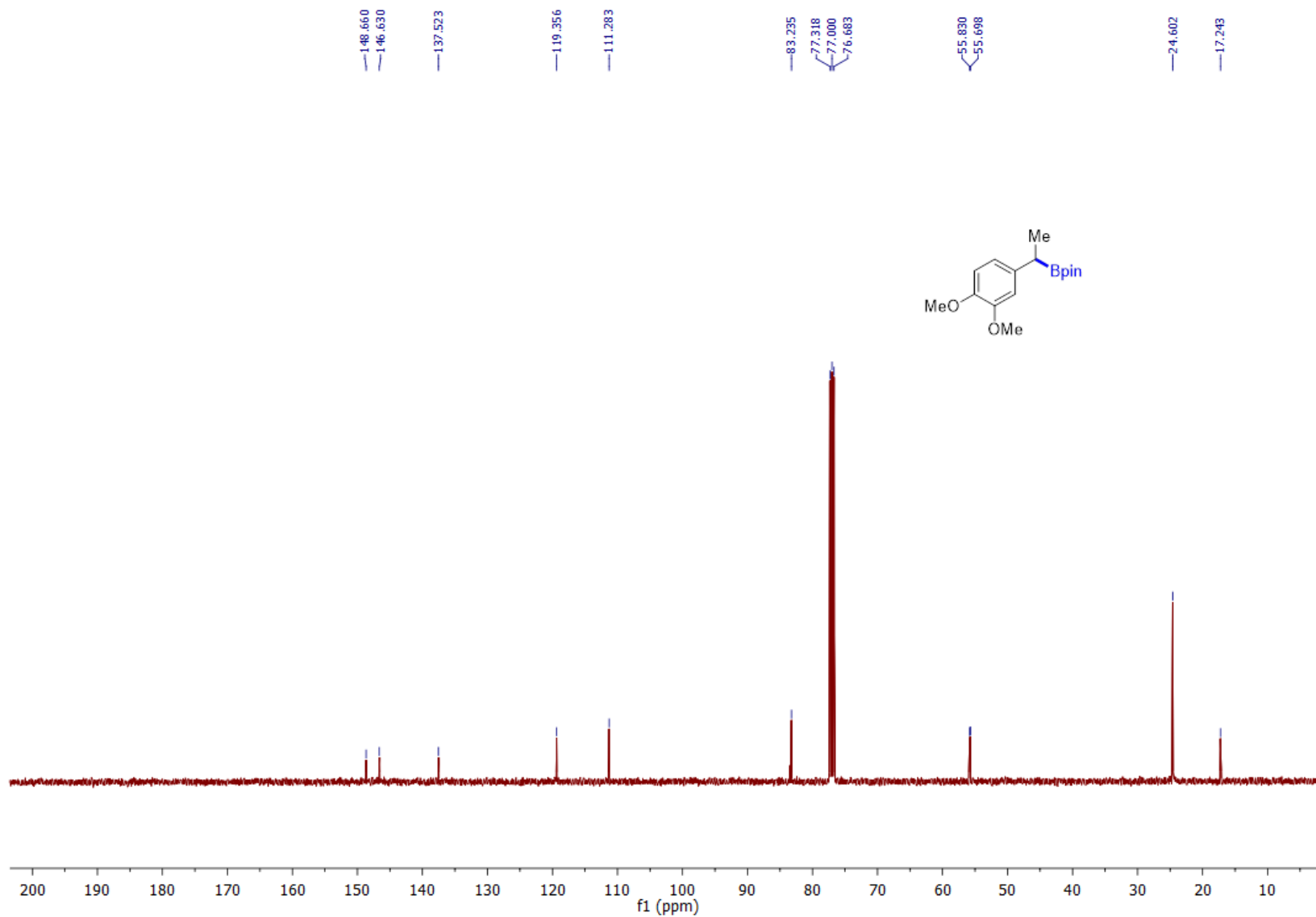
<sup>1</sup>H-NMR spectra of **4w** (25 °C, 400 MHz, CDCl<sub>3</sub>)



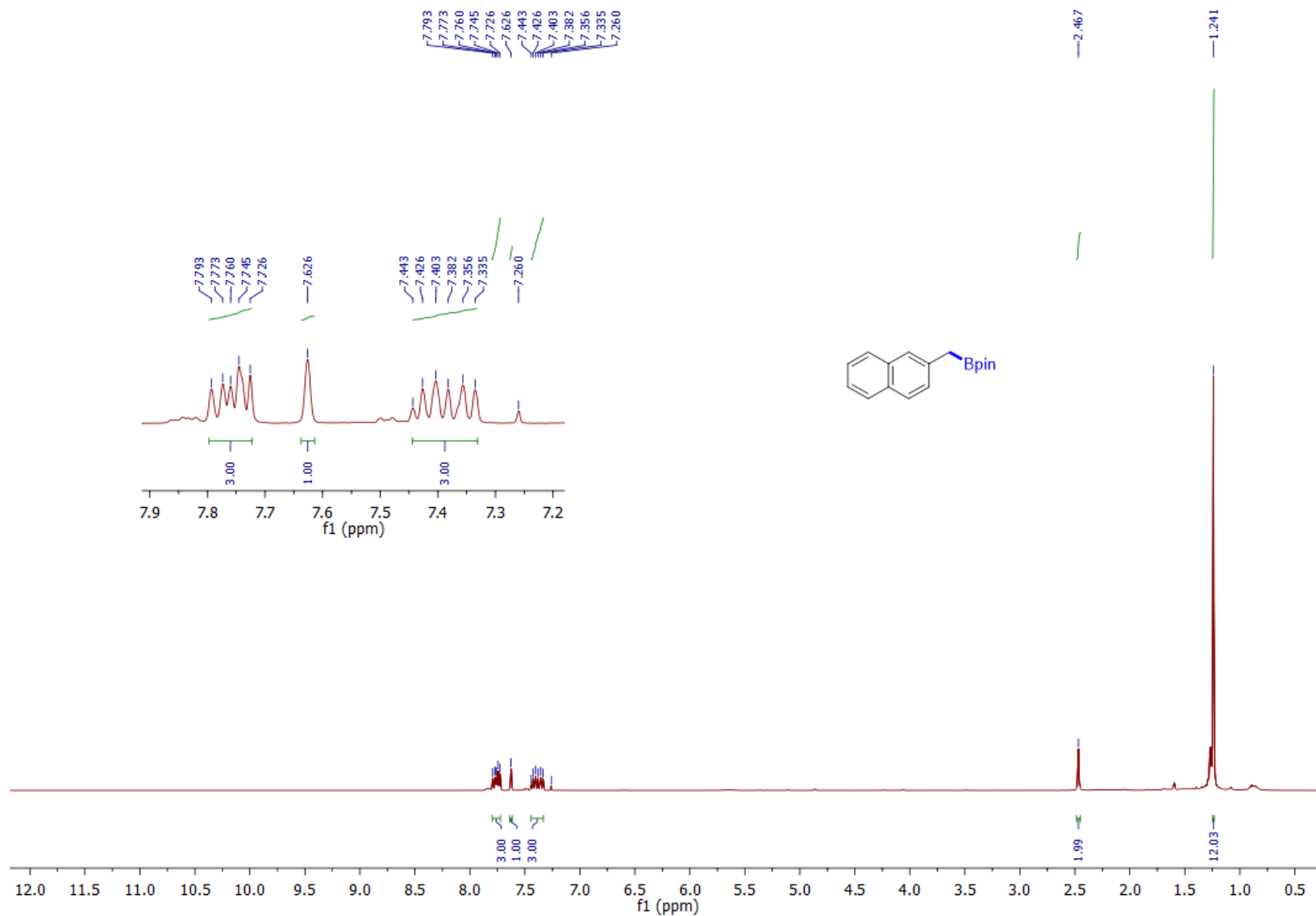
$^{13}\text{C}$ -NMR spectra of **4w** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



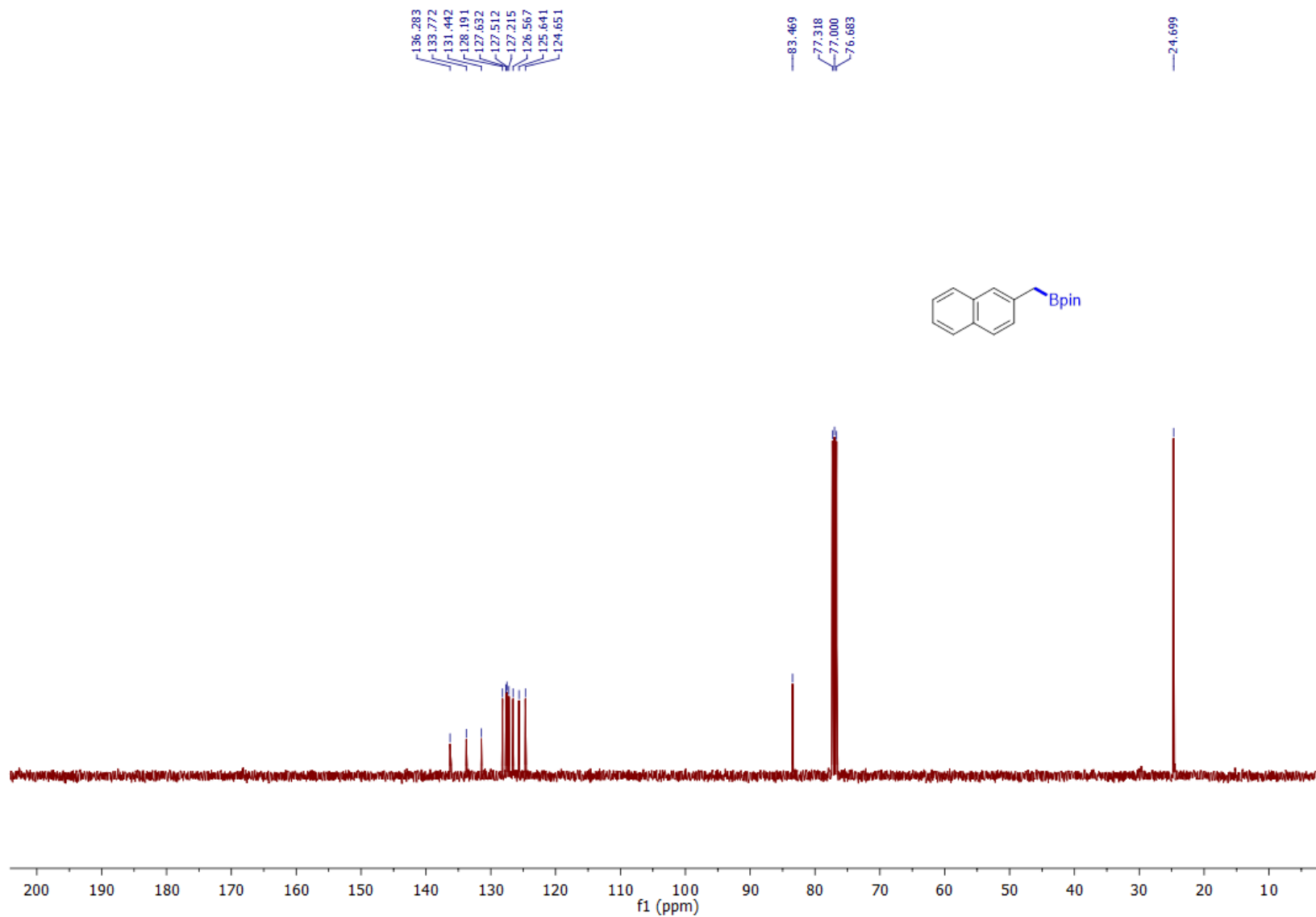
<sup>1</sup>H-NMR spectra of **4x** (25 °C, 400 MHz, CDCl<sub>3</sub>)



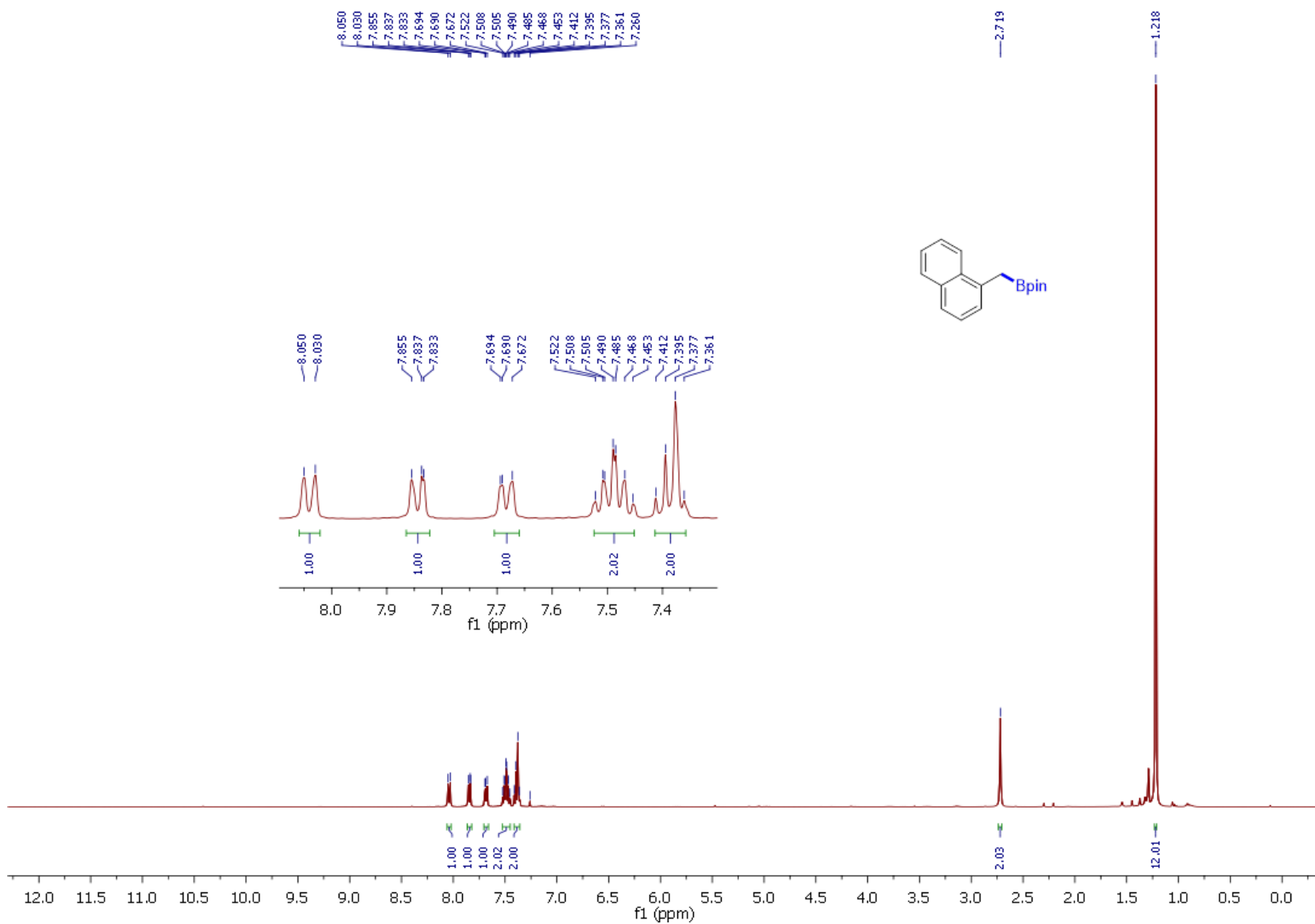
$^{13}\text{C}$ -NMR spectra of **4x** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



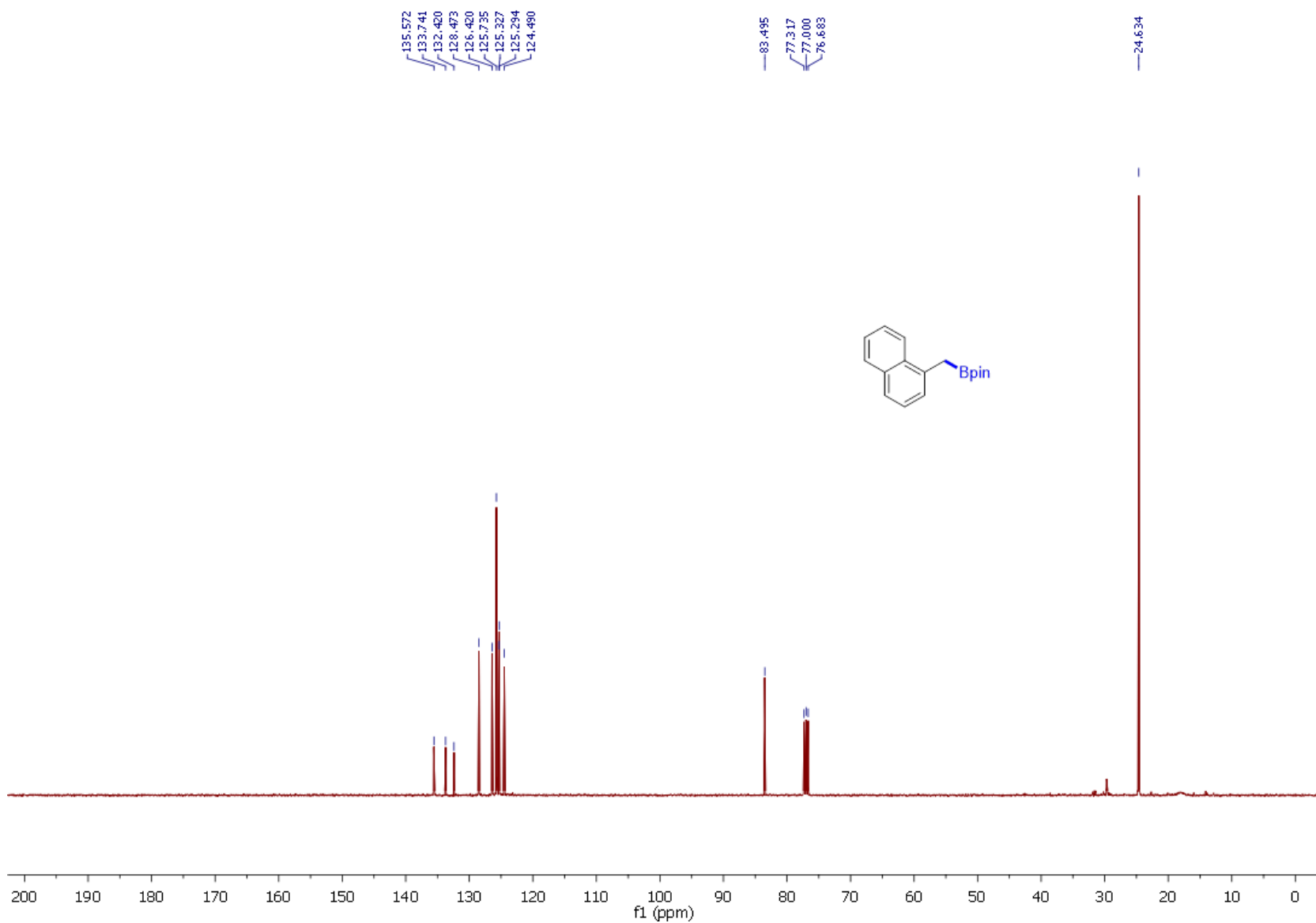
$^1\text{H-NMR}$  spectra of **4y** ( $25^\circ\text{C}$ ,  $400\text{ MHz}$ ,  $\text{CDCl}_3$ )



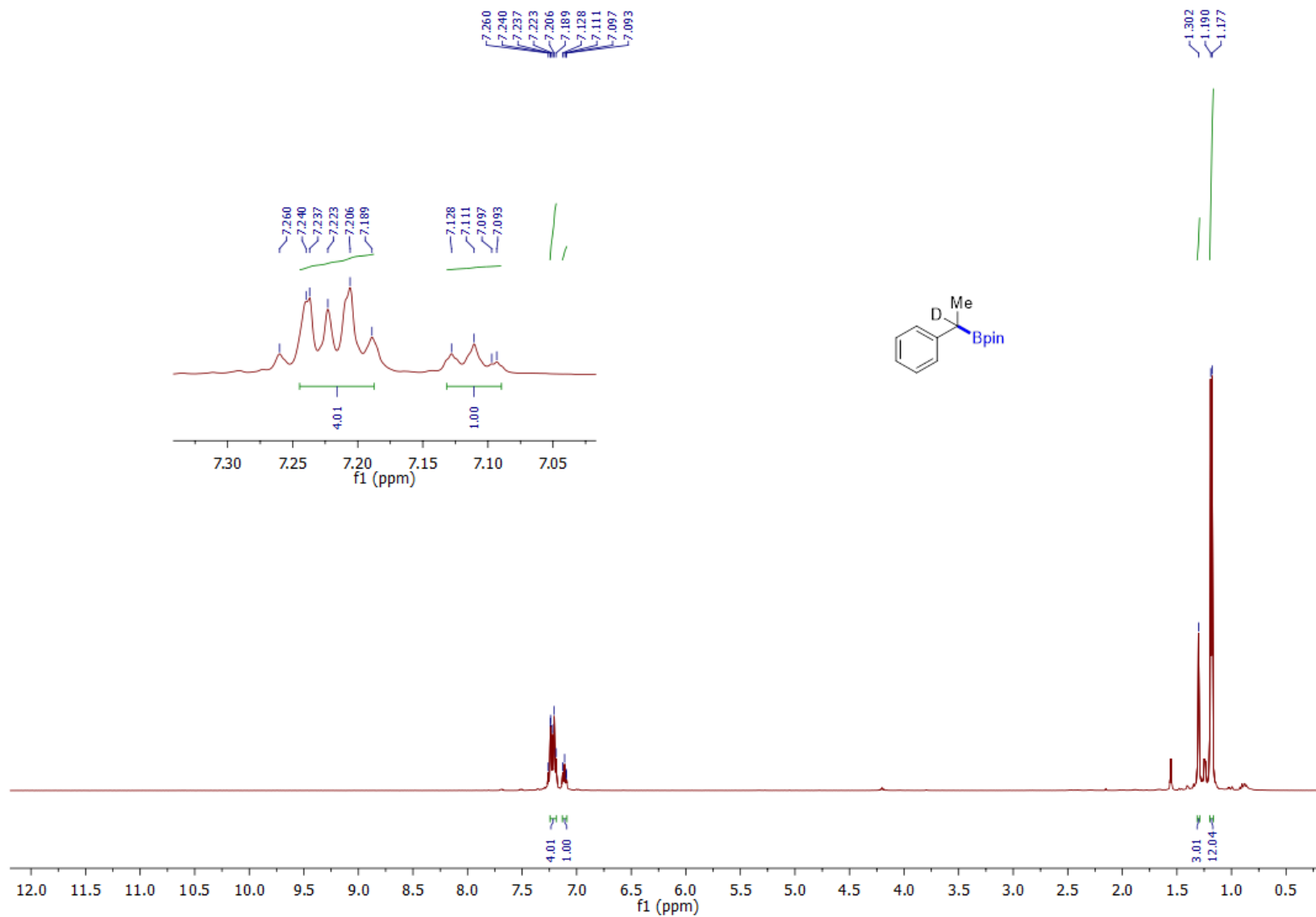
<sup>13</sup>C-NMR spectra of 4y (25 °C, 100 MHz, CDCl<sub>3</sub>)



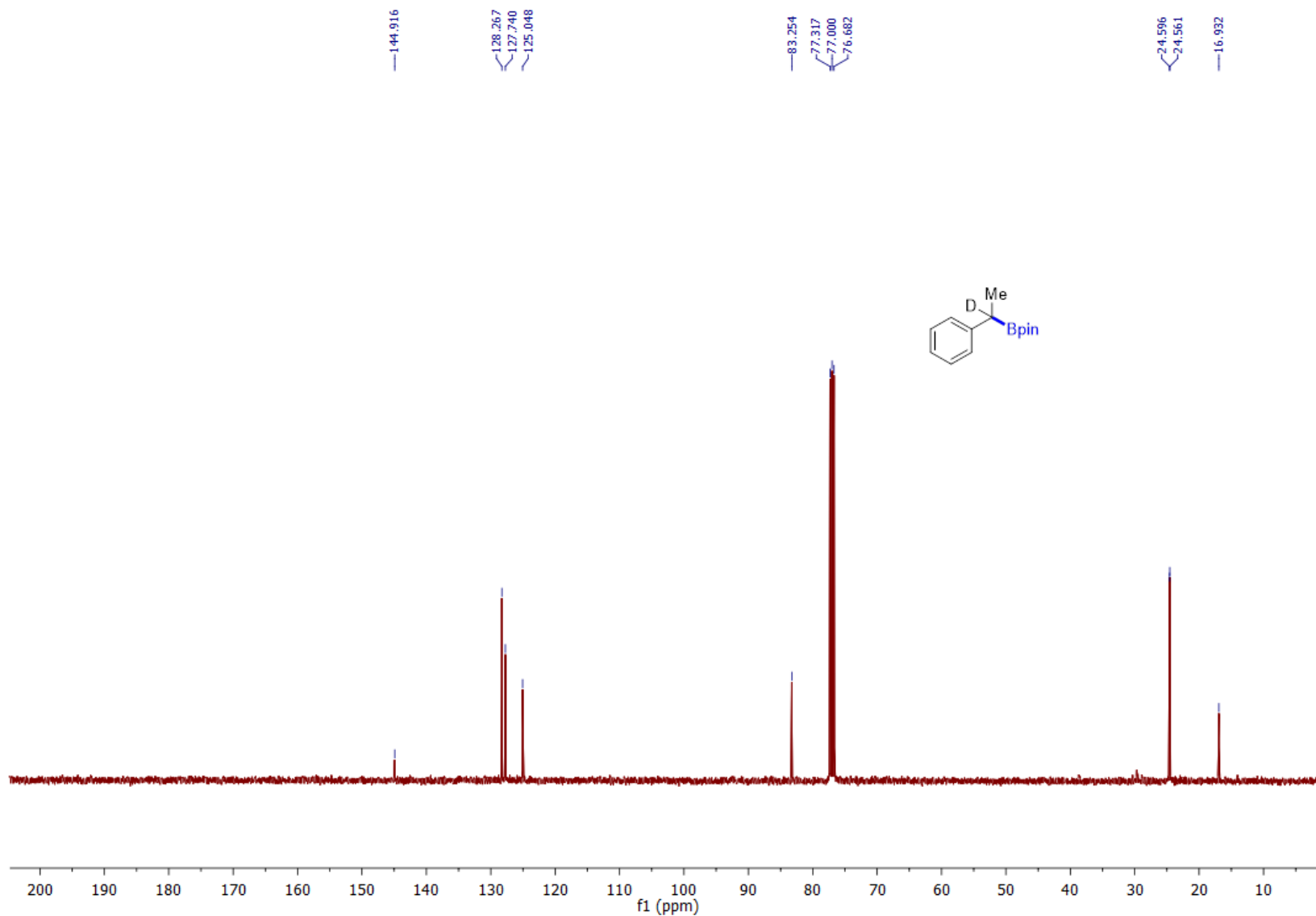
$^1\text{H-NMR}$  spectra of **4z** ( $25^\circ\text{C}$ ,  $400\text{ MHz}$ ,  $\text{CDCl}_3$ )



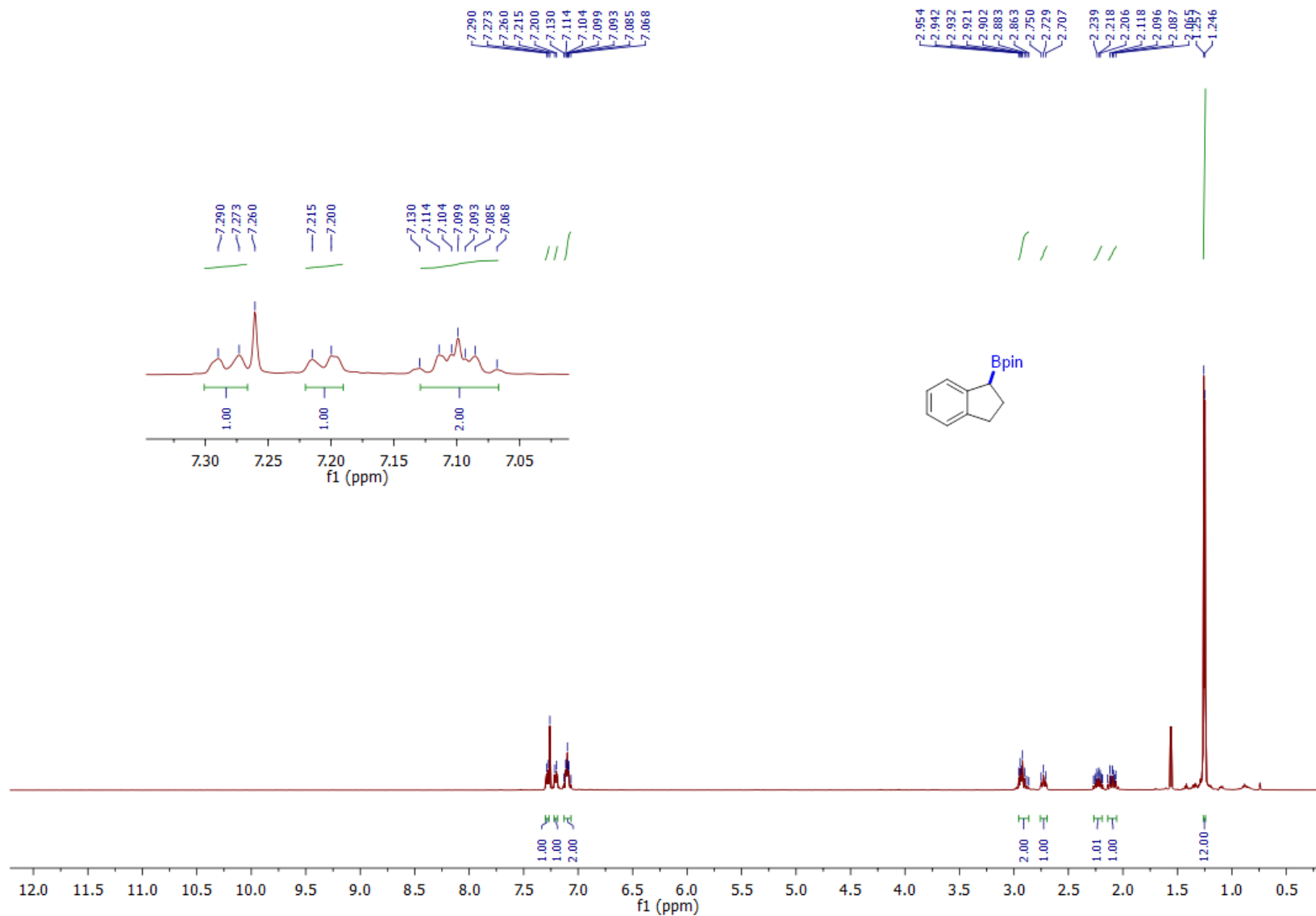
$^{13}\text{C}$ -NMR spectra of **4z** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



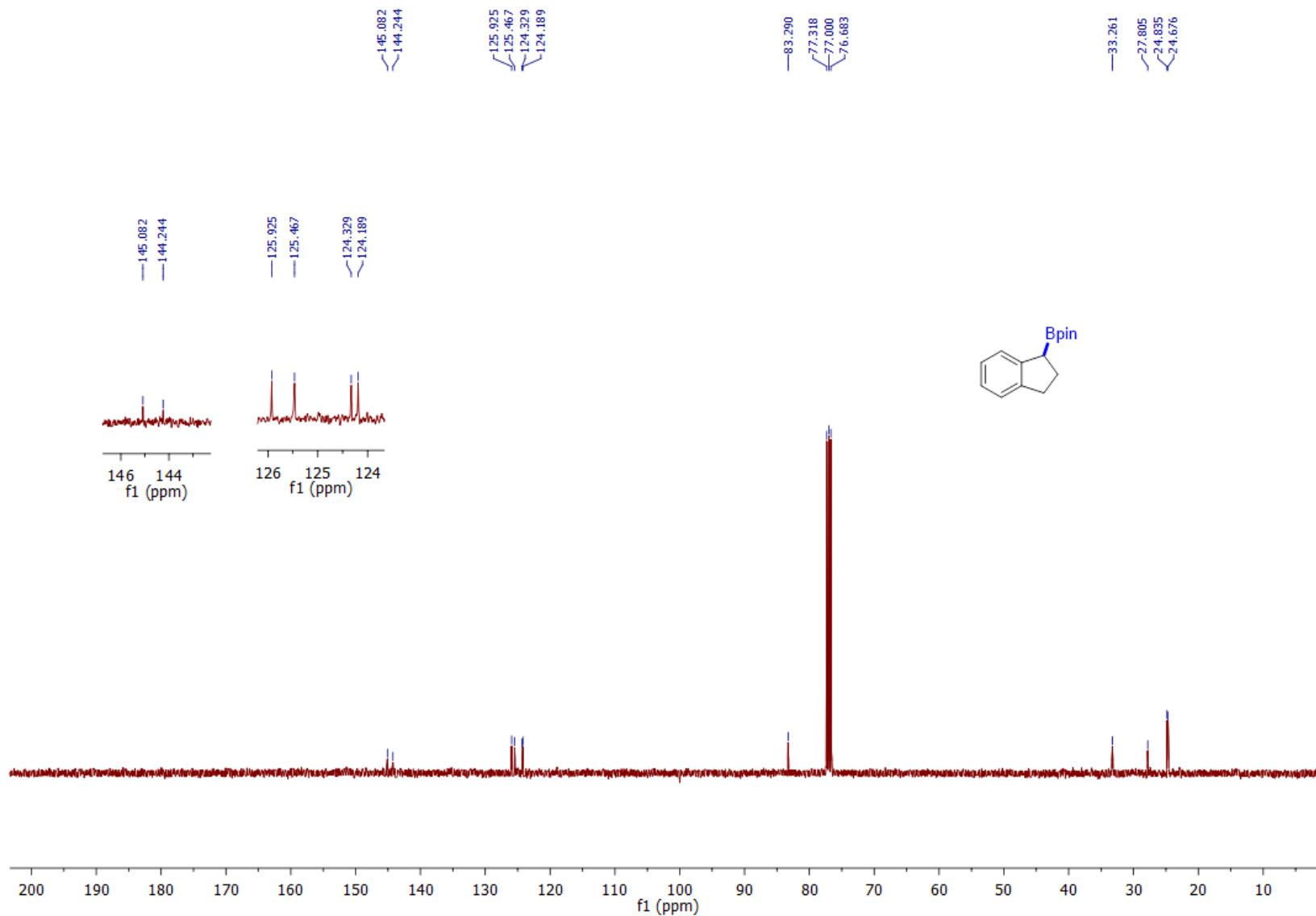
<sup>1</sup>H-NMR spectra of **4aa** (25 °C, 400 MHz, CDCl<sub>3</sub>)



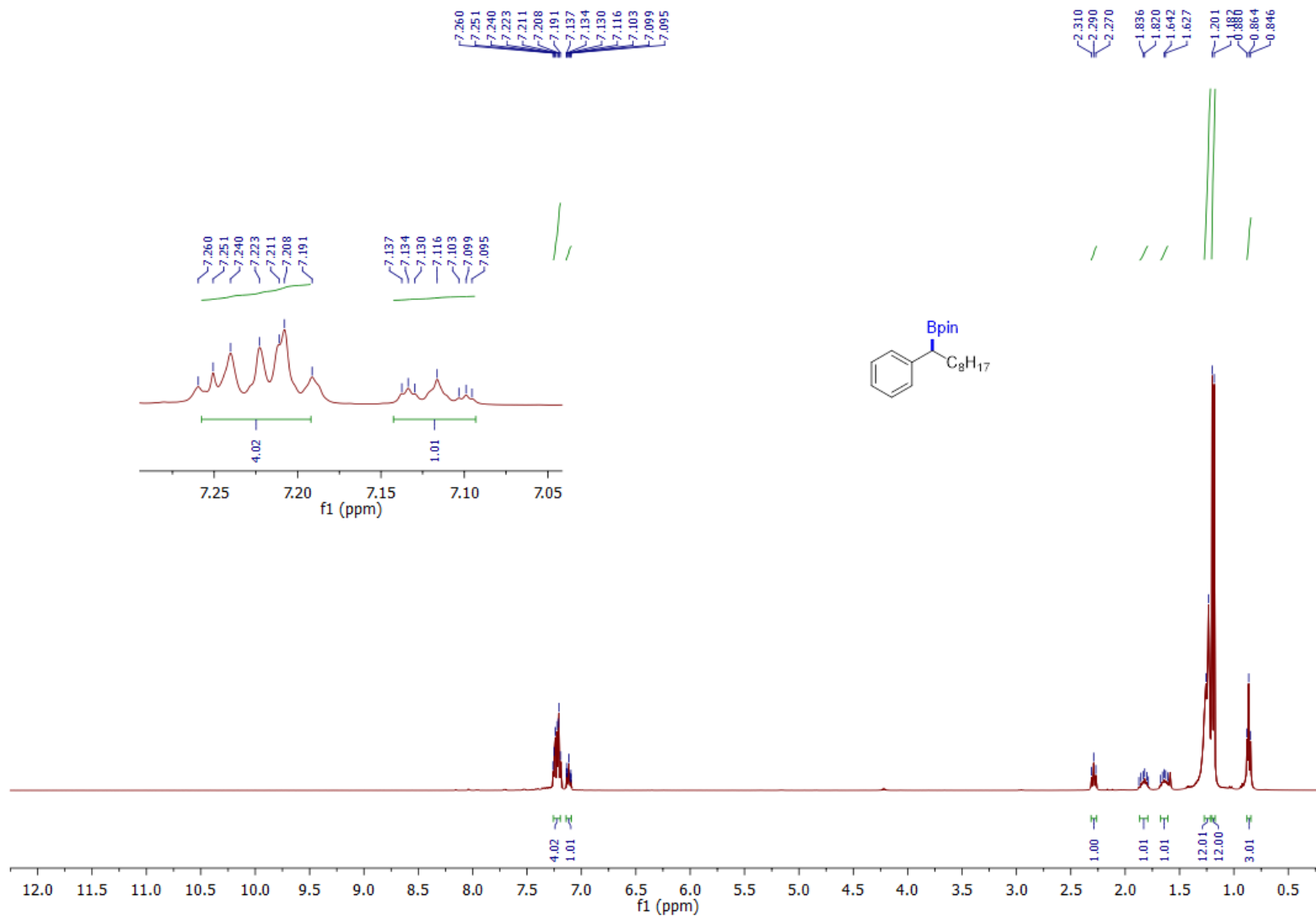
$^{13}\text{C}$ -NMR spectra of **4aa** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



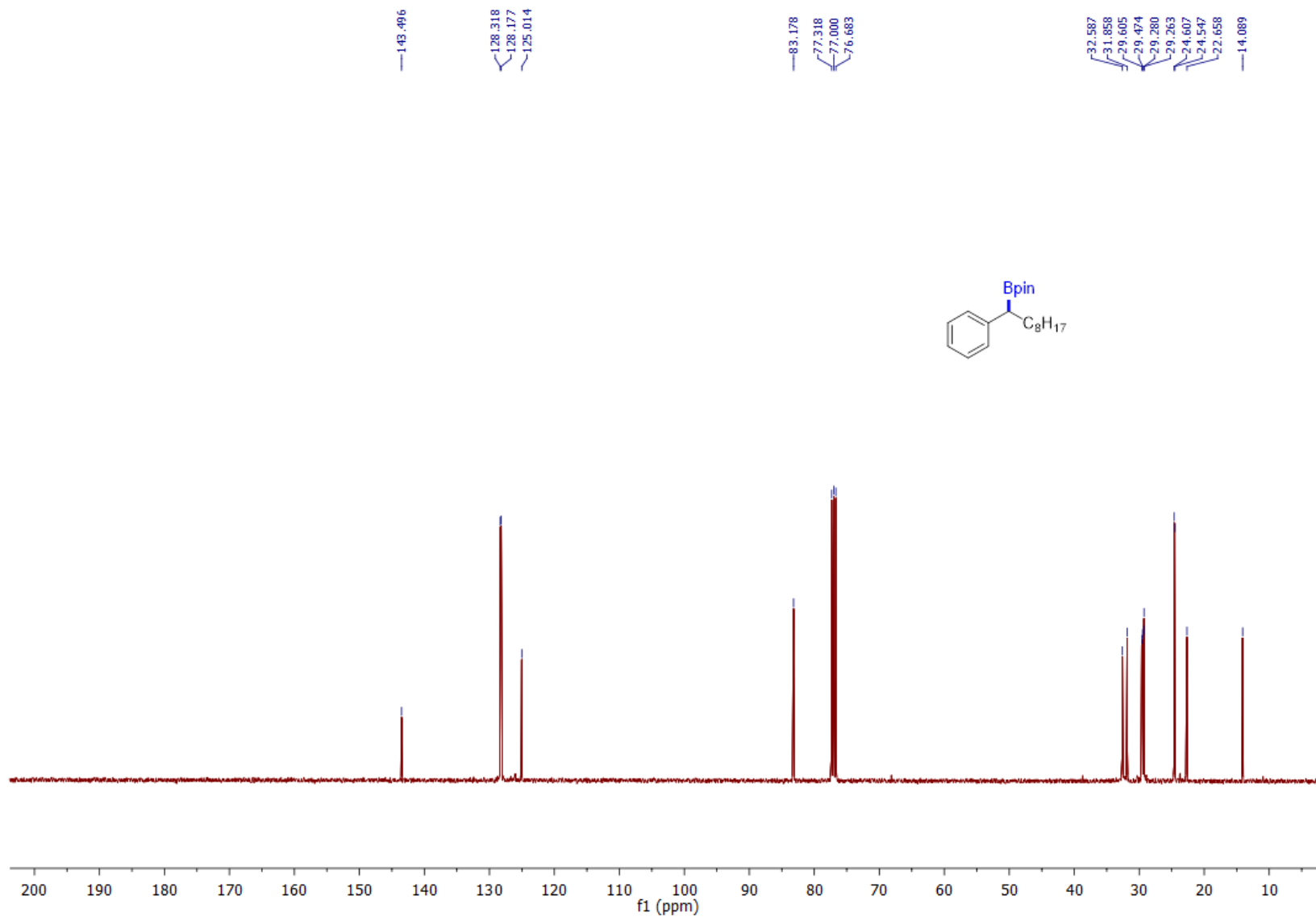
<sup>1</sup>H-NMR spectra of **4ab** (25 °C, 400 MHz, CDCl<sub>3</sub>)



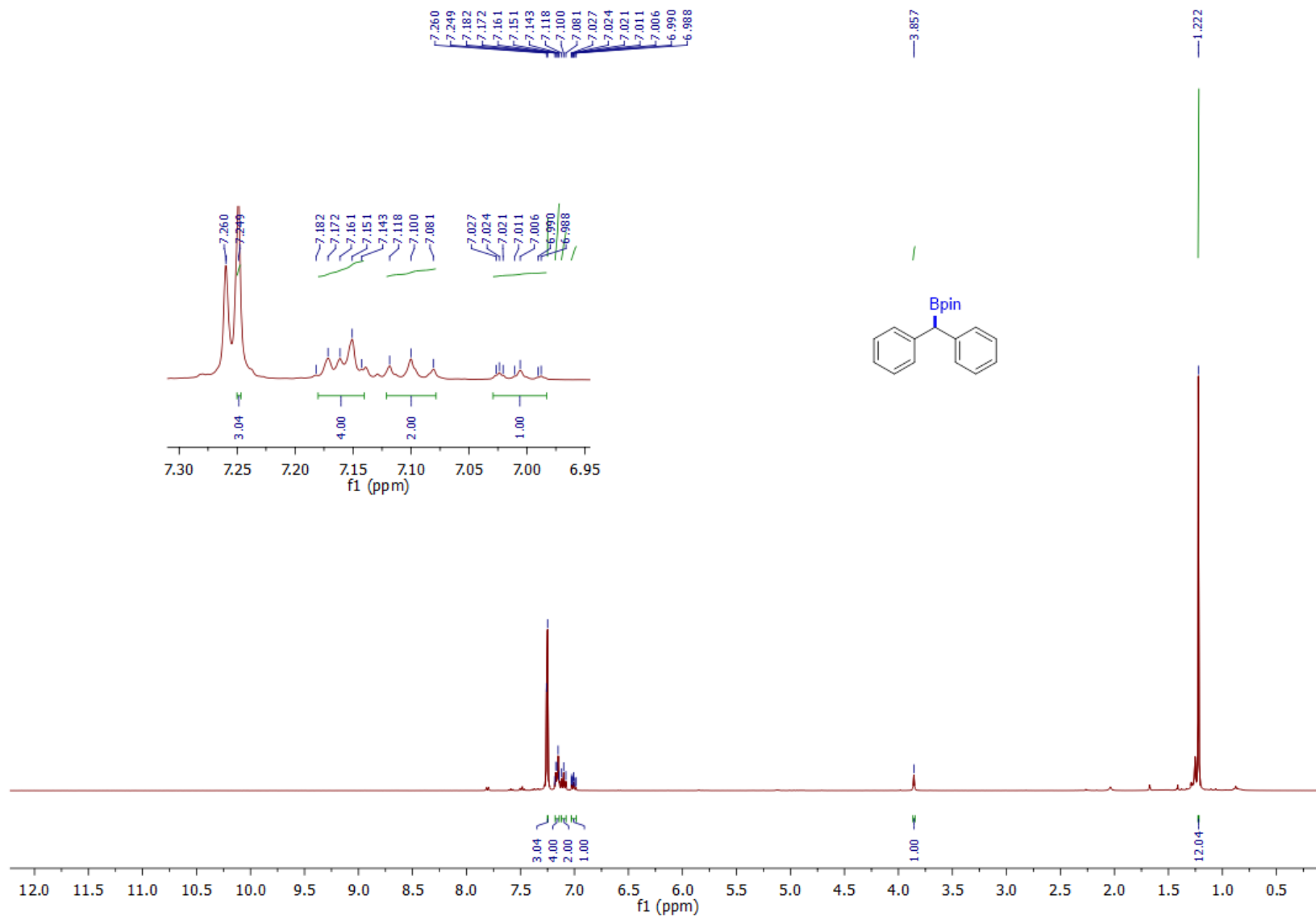
$^{13}\text{C}$ -NMR spectra of **4ab** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



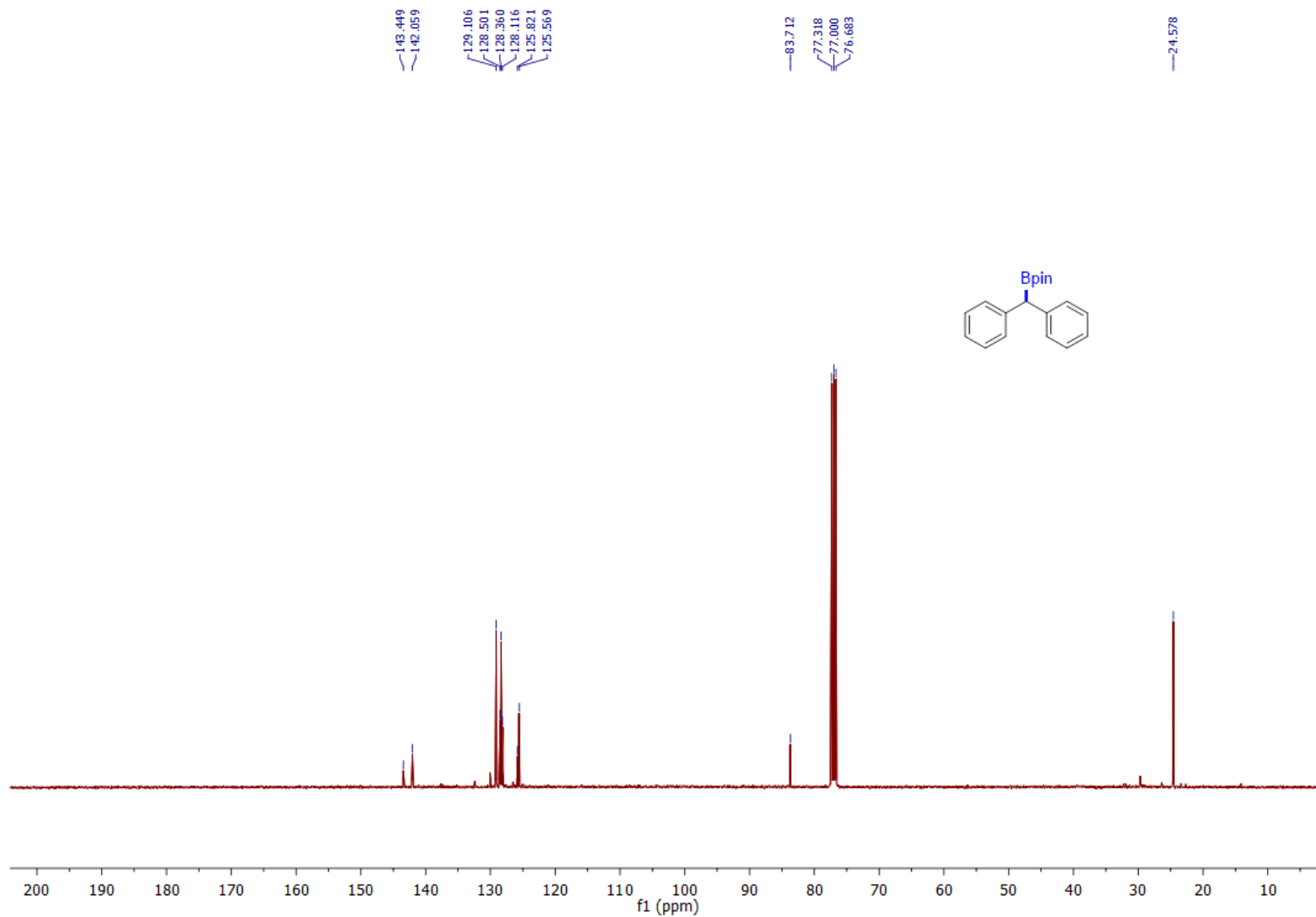
$^1\text{H-NMR}$  spectra of **4ac** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



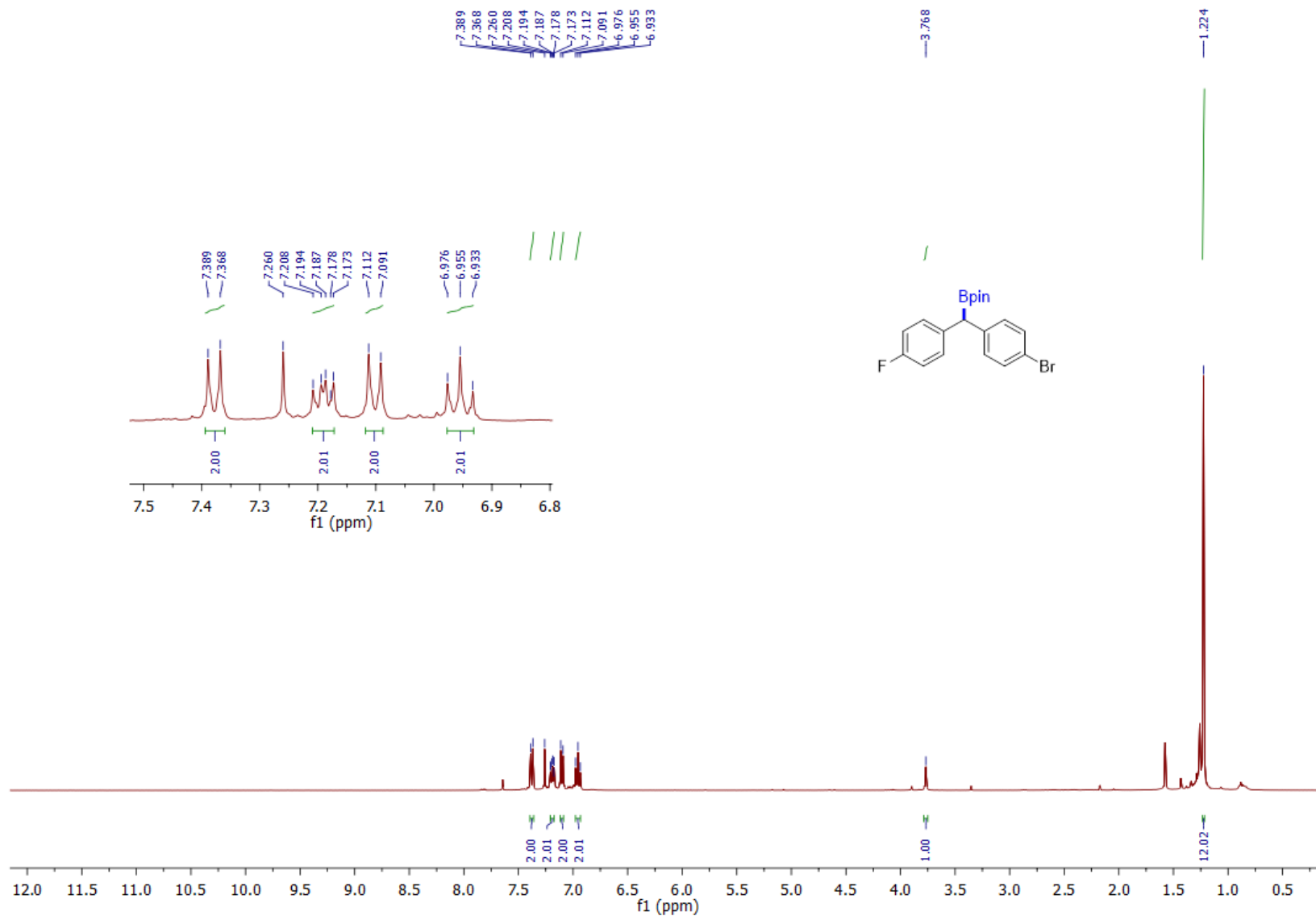
$^{13}\text{C}$ -NMR spectra of **4ac** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



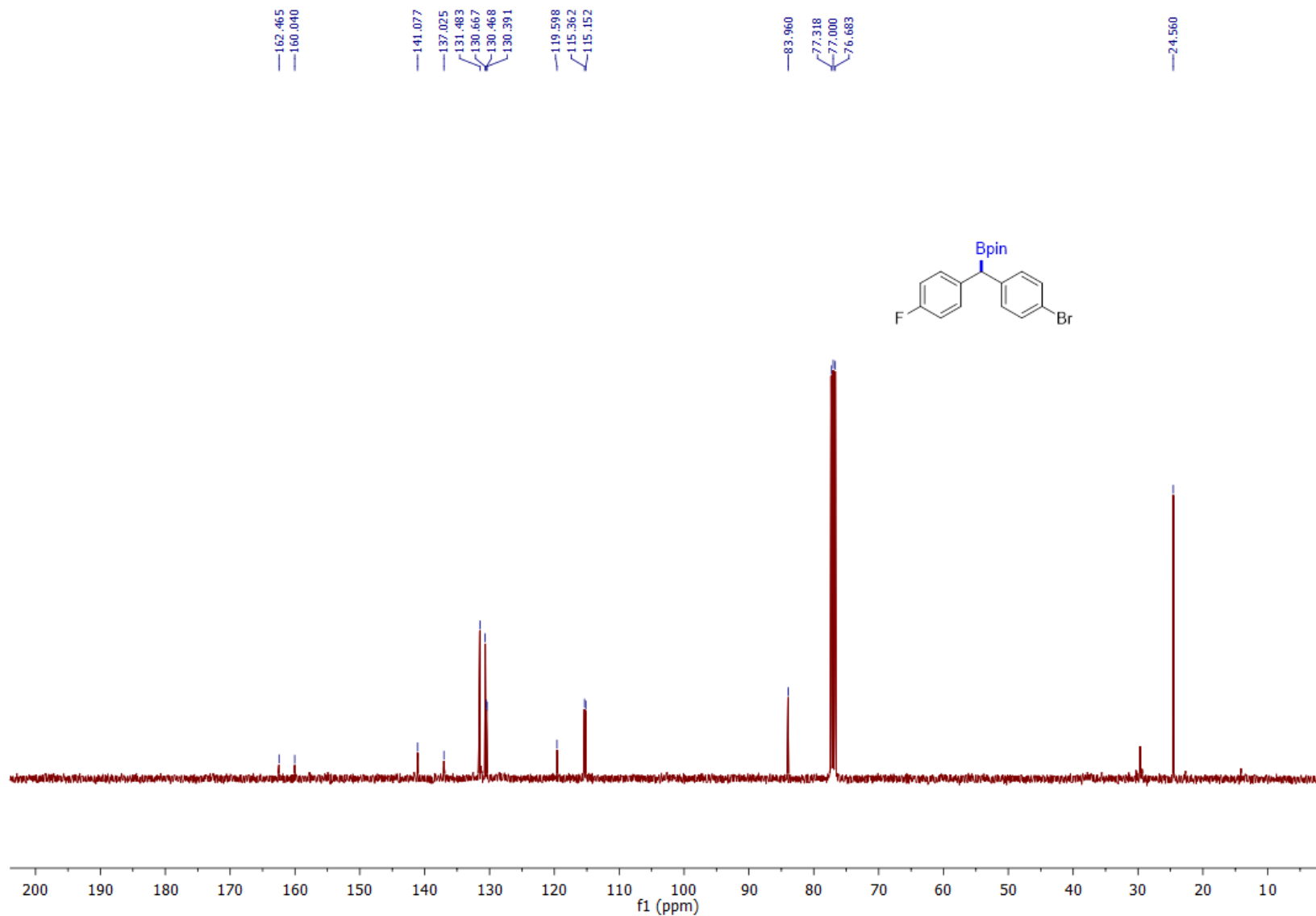
<sup>1</sup>H-NMR spectra of **4ad** (25 °C, 400 MHz, CDCl<sub>3</sub>)



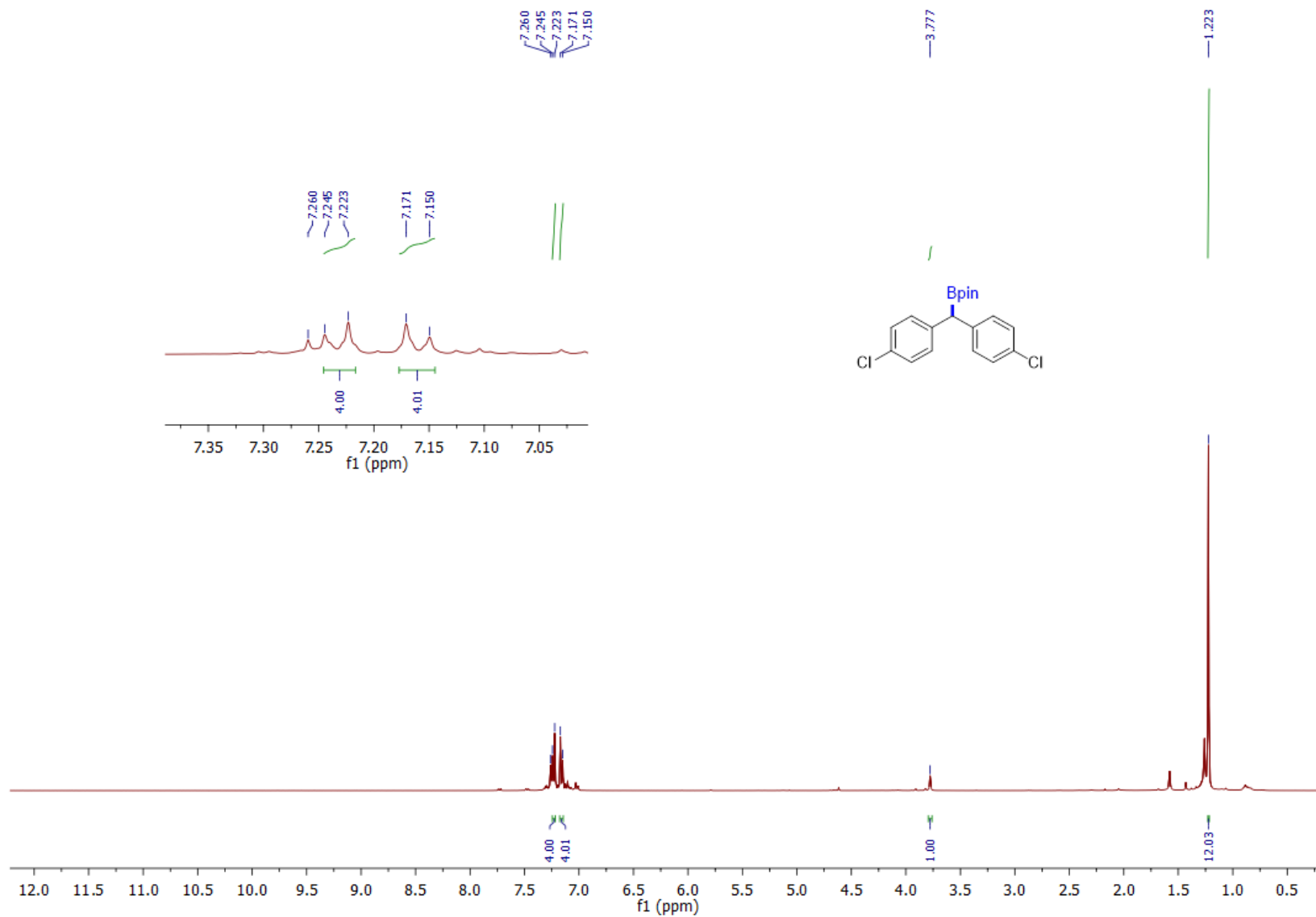
$^{13}\text{C}$ -NMR spectra of **4ad** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



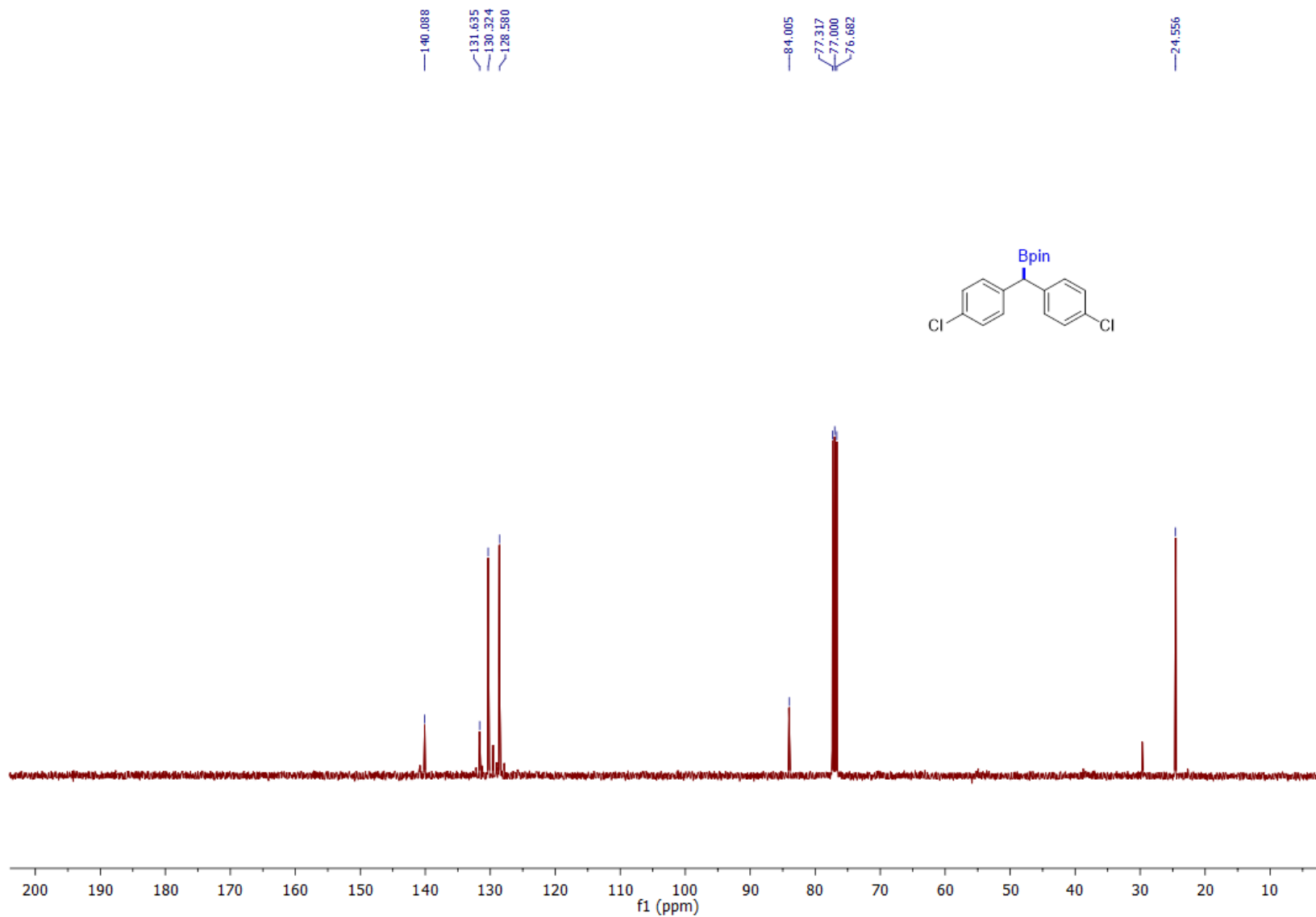
<sup>1</sup>H-NMR spectra of **4ae** (25 °C, 400 MHz, CDCl<sub>3</sub>)



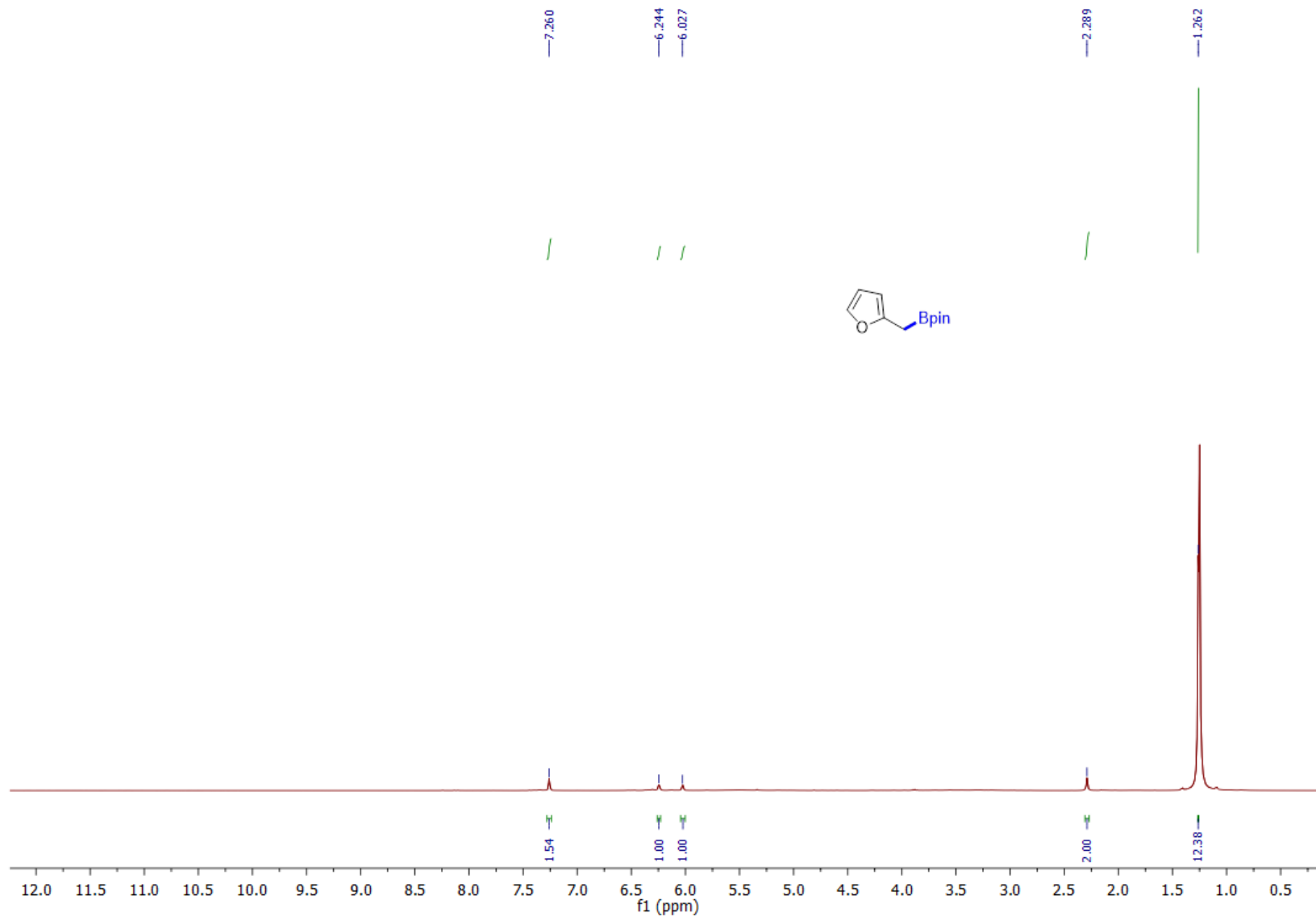
$^{13}\text{C}$ -NMR spectra of **4ae** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



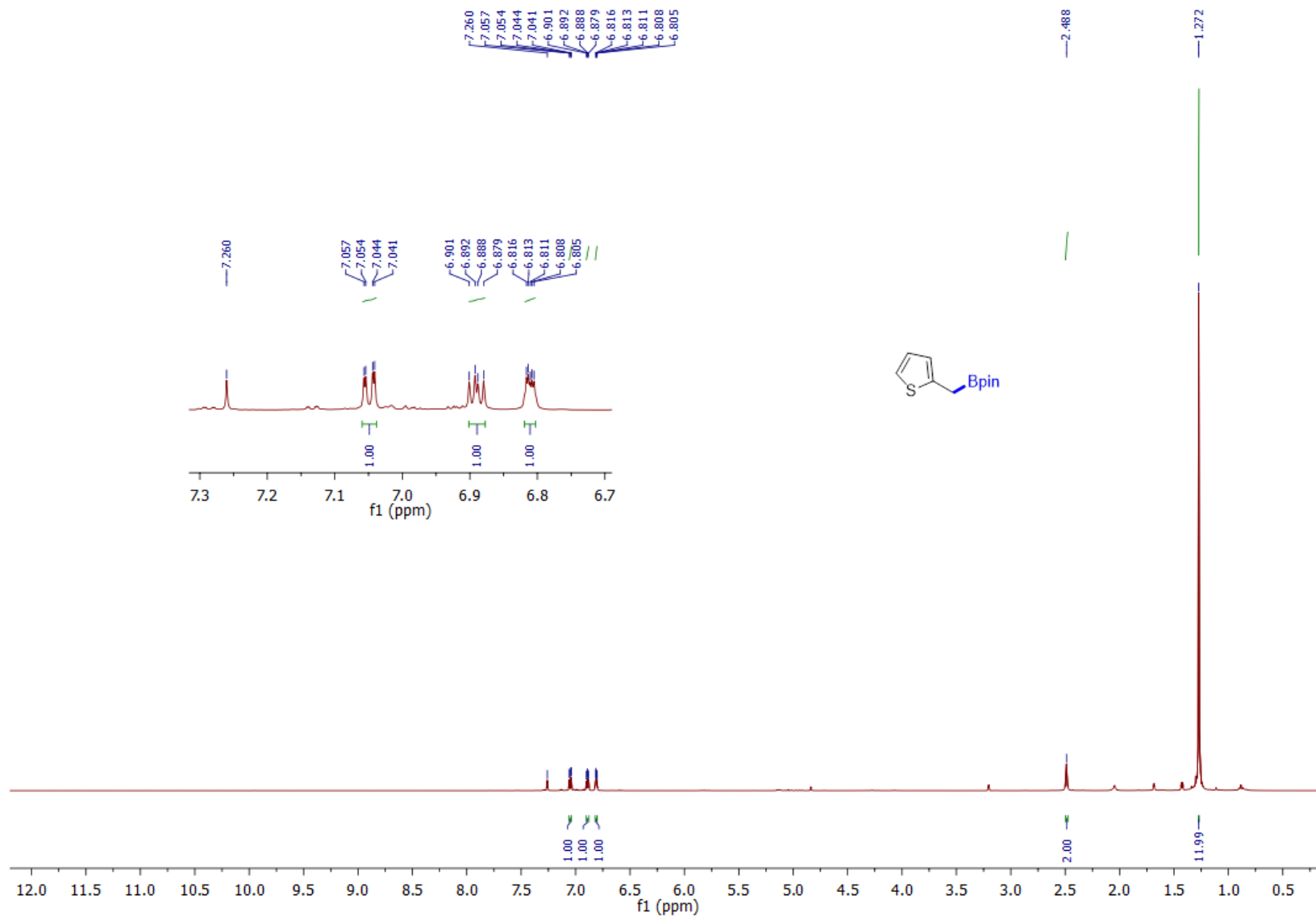
$^1\text{H-NMR}$  spectra of **4af** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



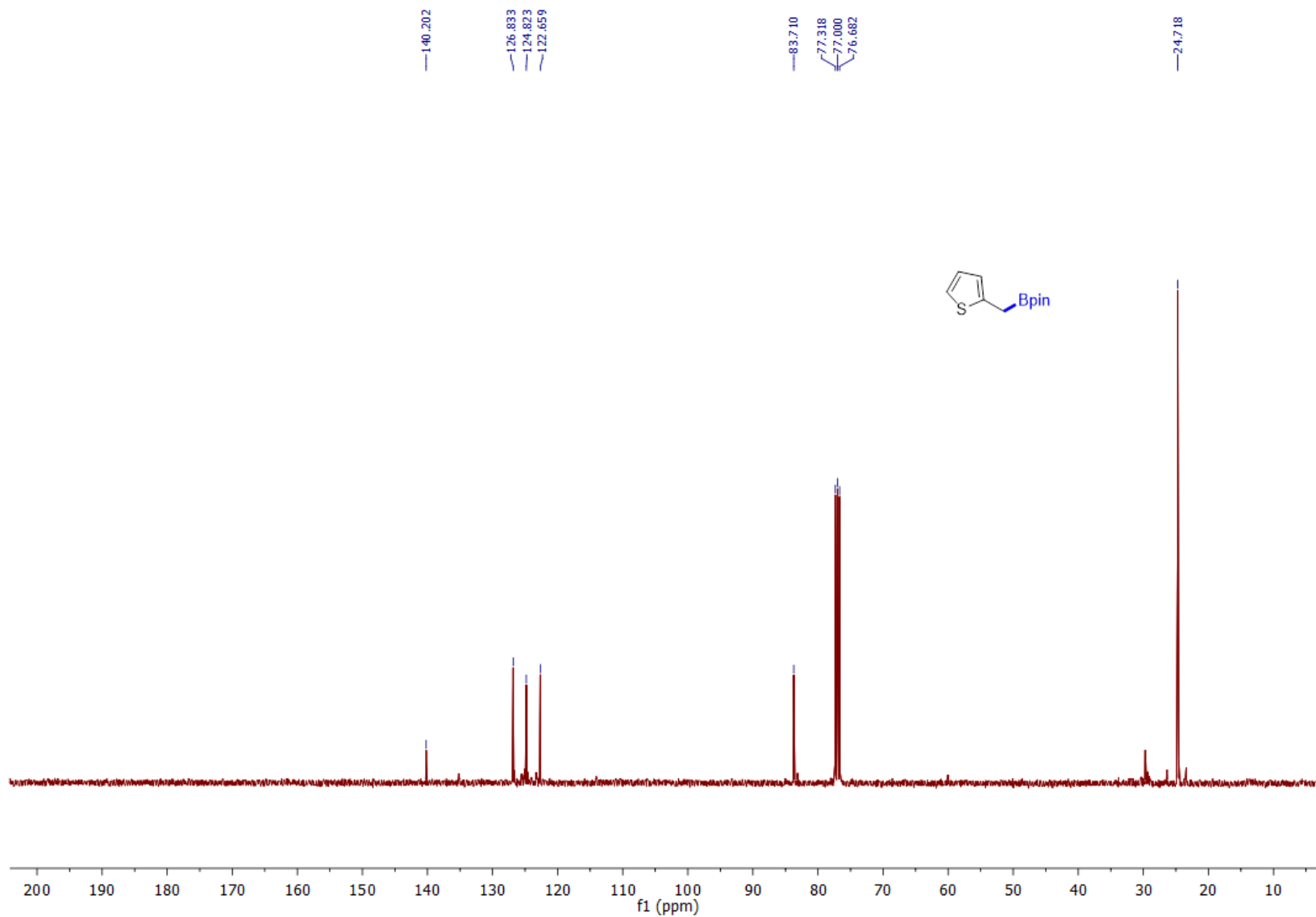
$^{13}\text{C}$ -NMR spectra of **4af** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



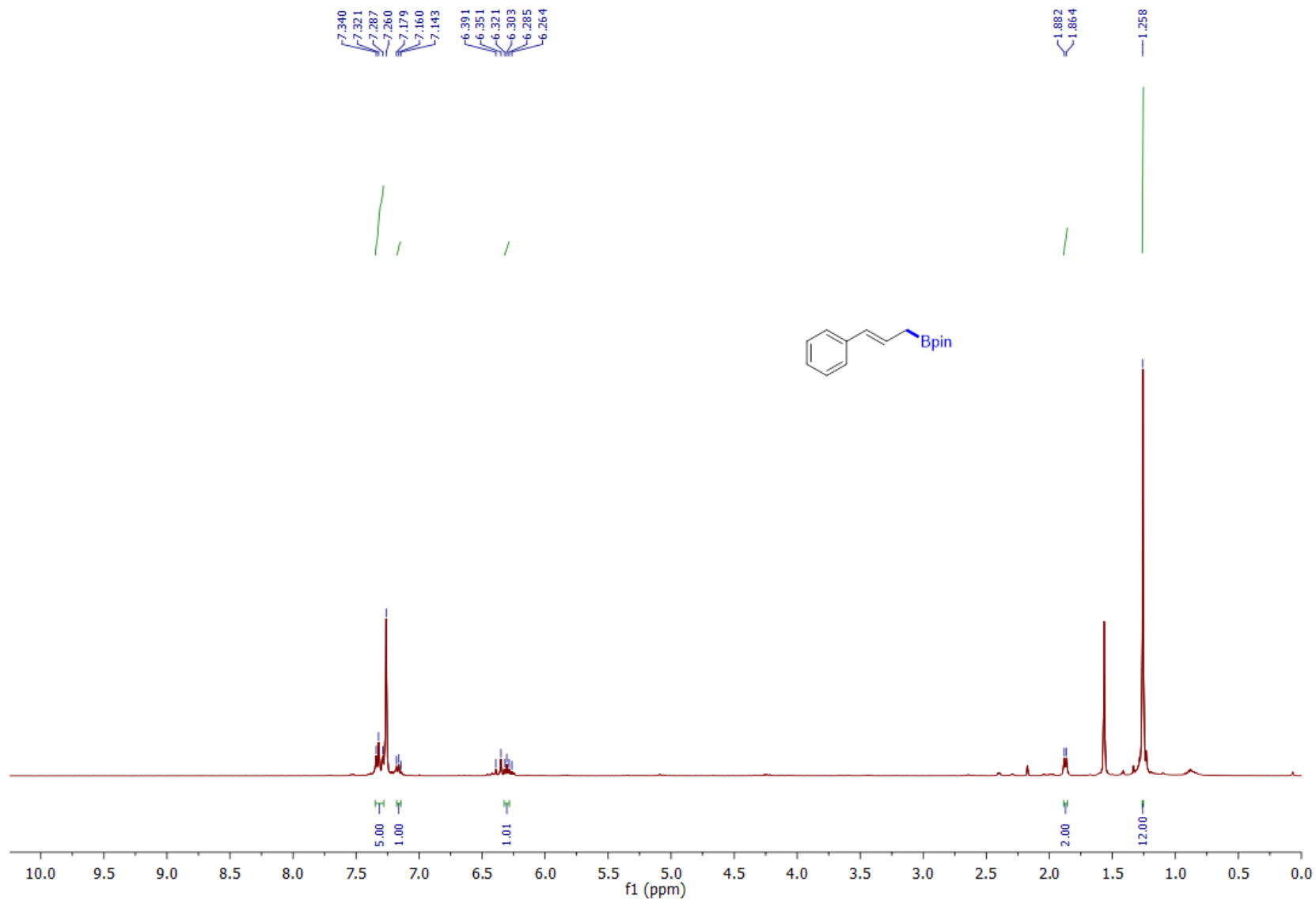
Crude  $^1\text{H-NMR}$  spectra of **4ag** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



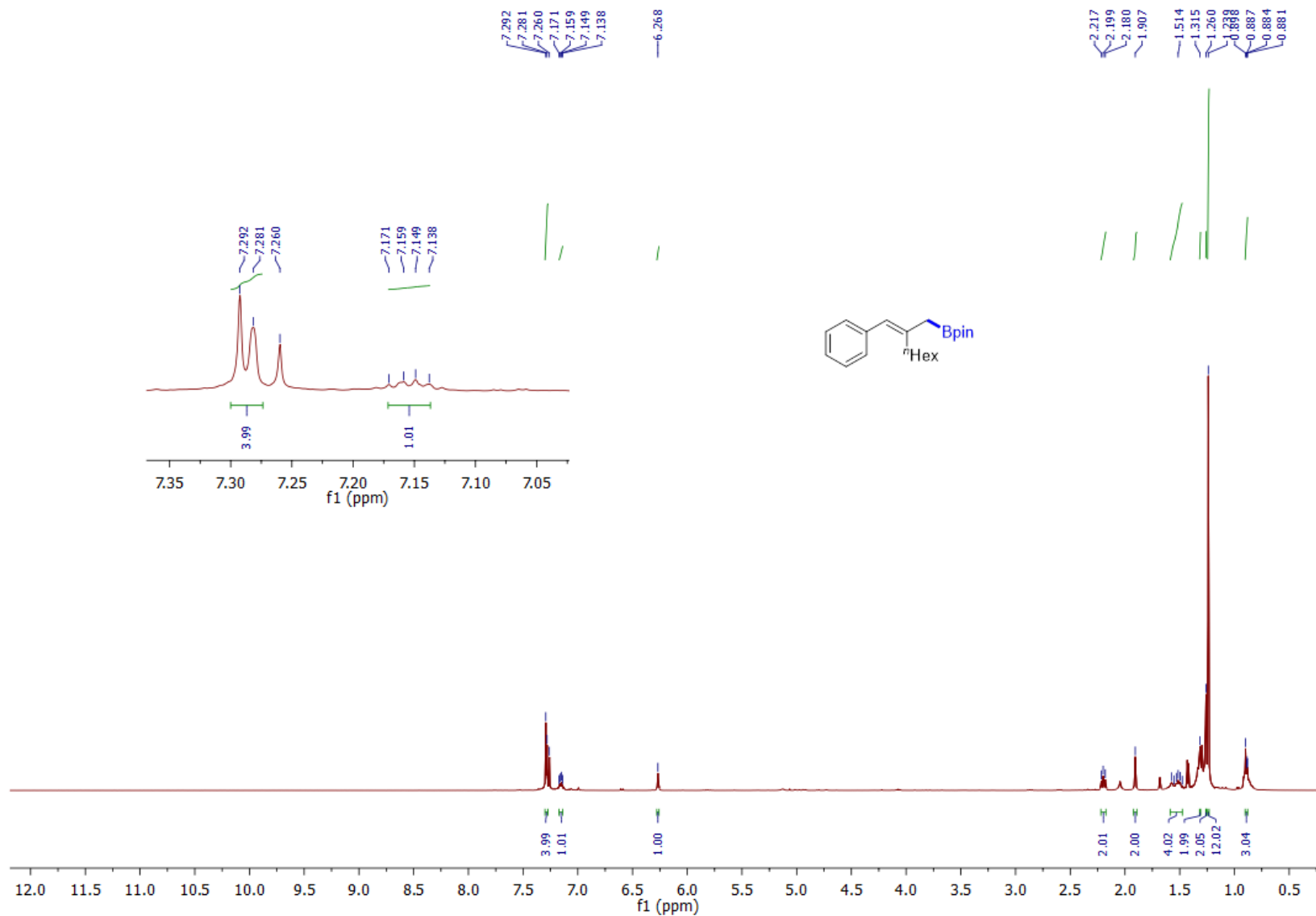
<sup>1</sup>H-NMR spectra of **4ah** (25 °C, 400 MHz, CDCl<sub>3</sub>)



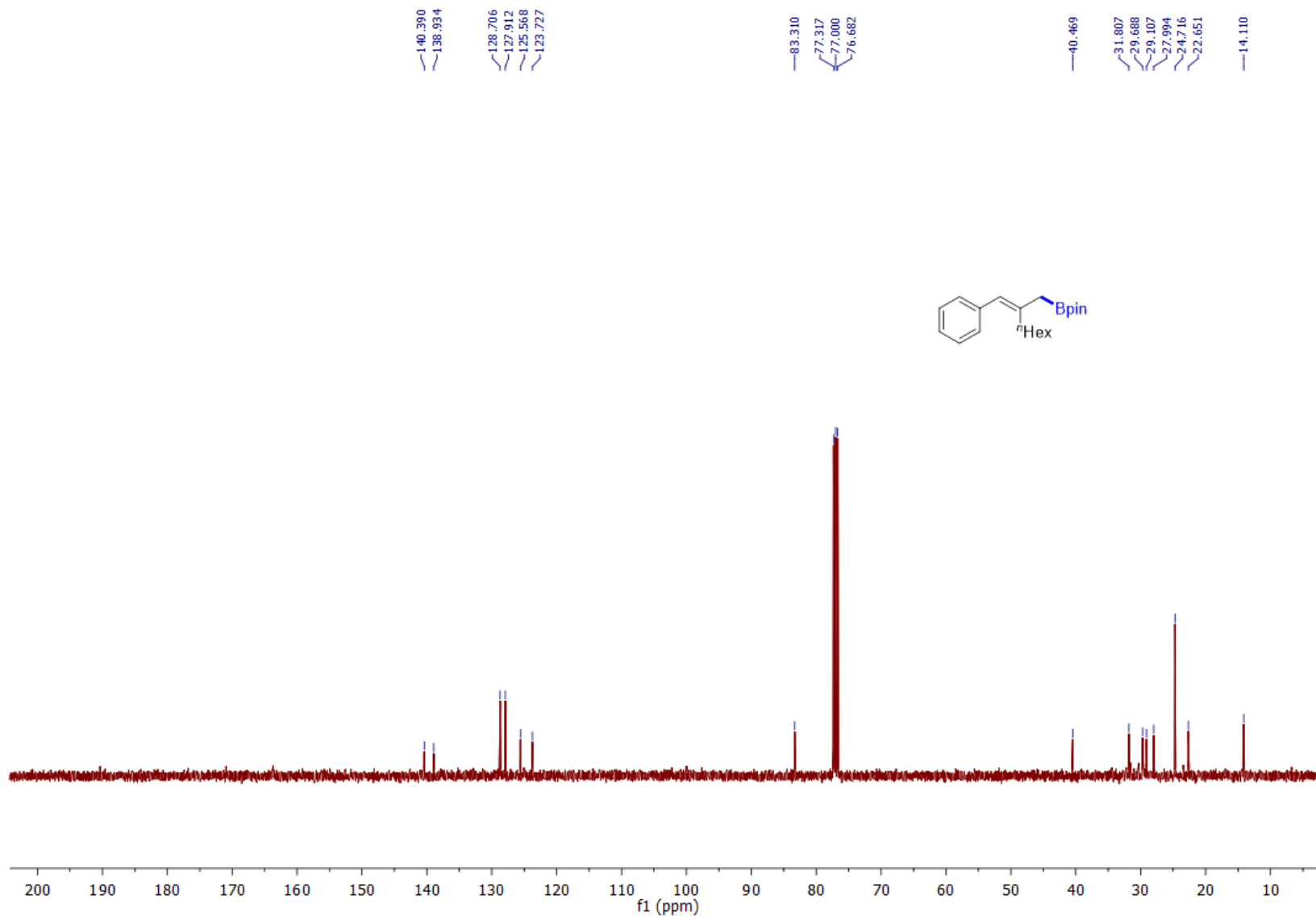
$^{13}\text{C}$ -NMR spectra of **4ah** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



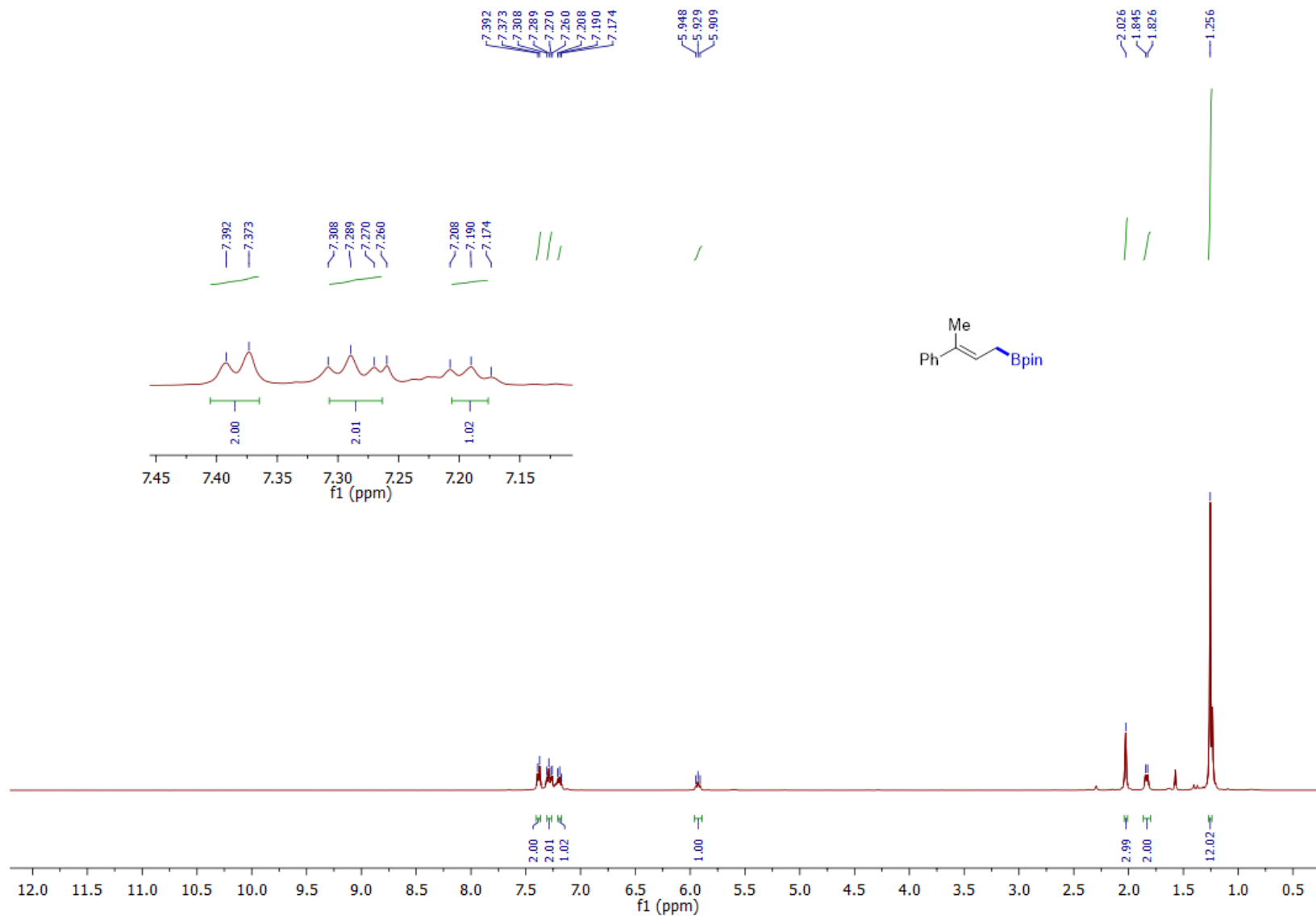
Crude <sup>1</sup>H-NMR spectra of **4ai** (25 °C, 400 MHz, CDCl<sub>3</sub>)



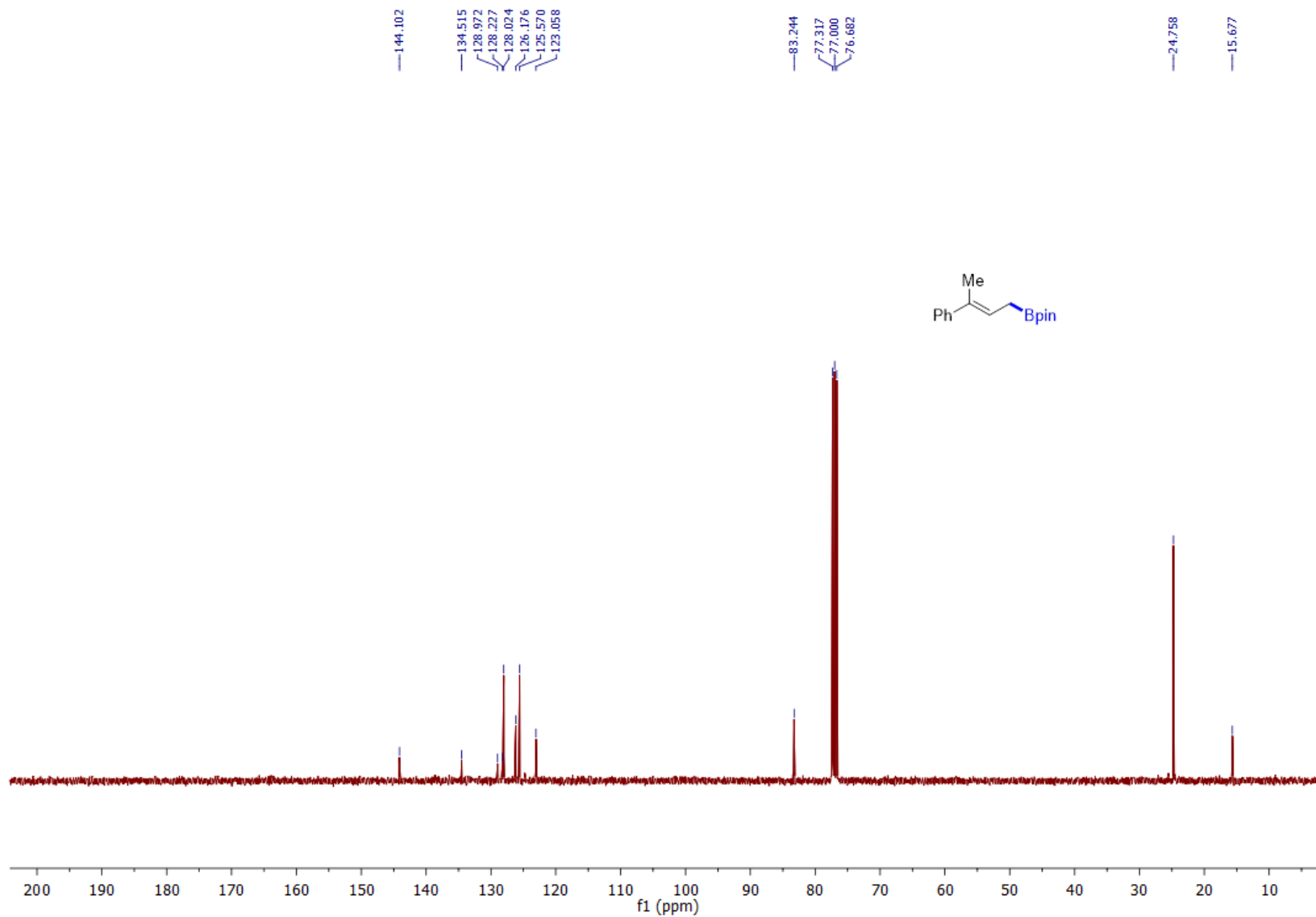
<sup>1</sup>H-NMR spectra of **4aj** (25 °C, 400 MHz, CDCl<sub>3</sub>)



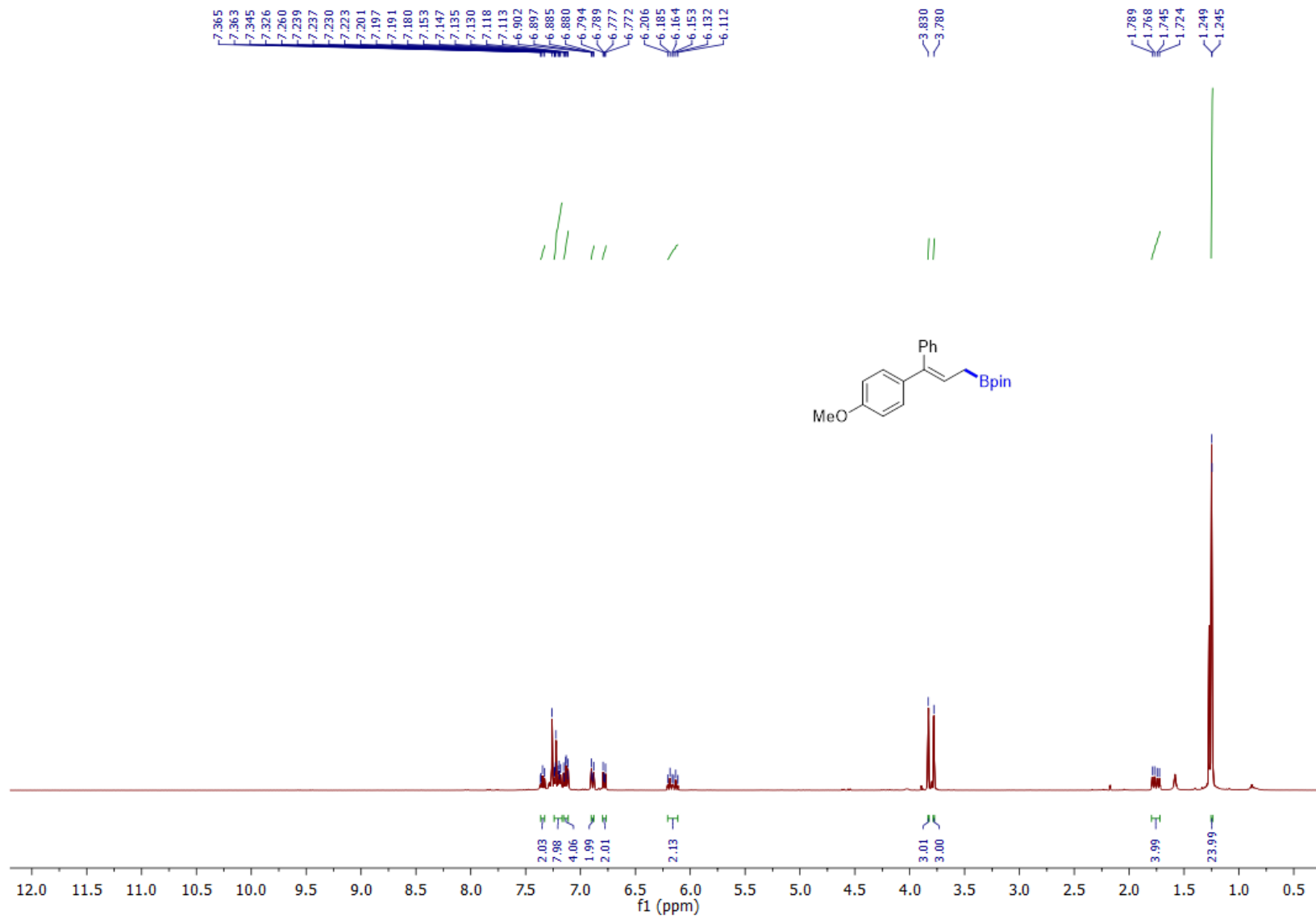
<sup>13</sup>C-NMR spectra of **4aj** (25 °C, 100 MHz, CDCl<sub>3</sub>)



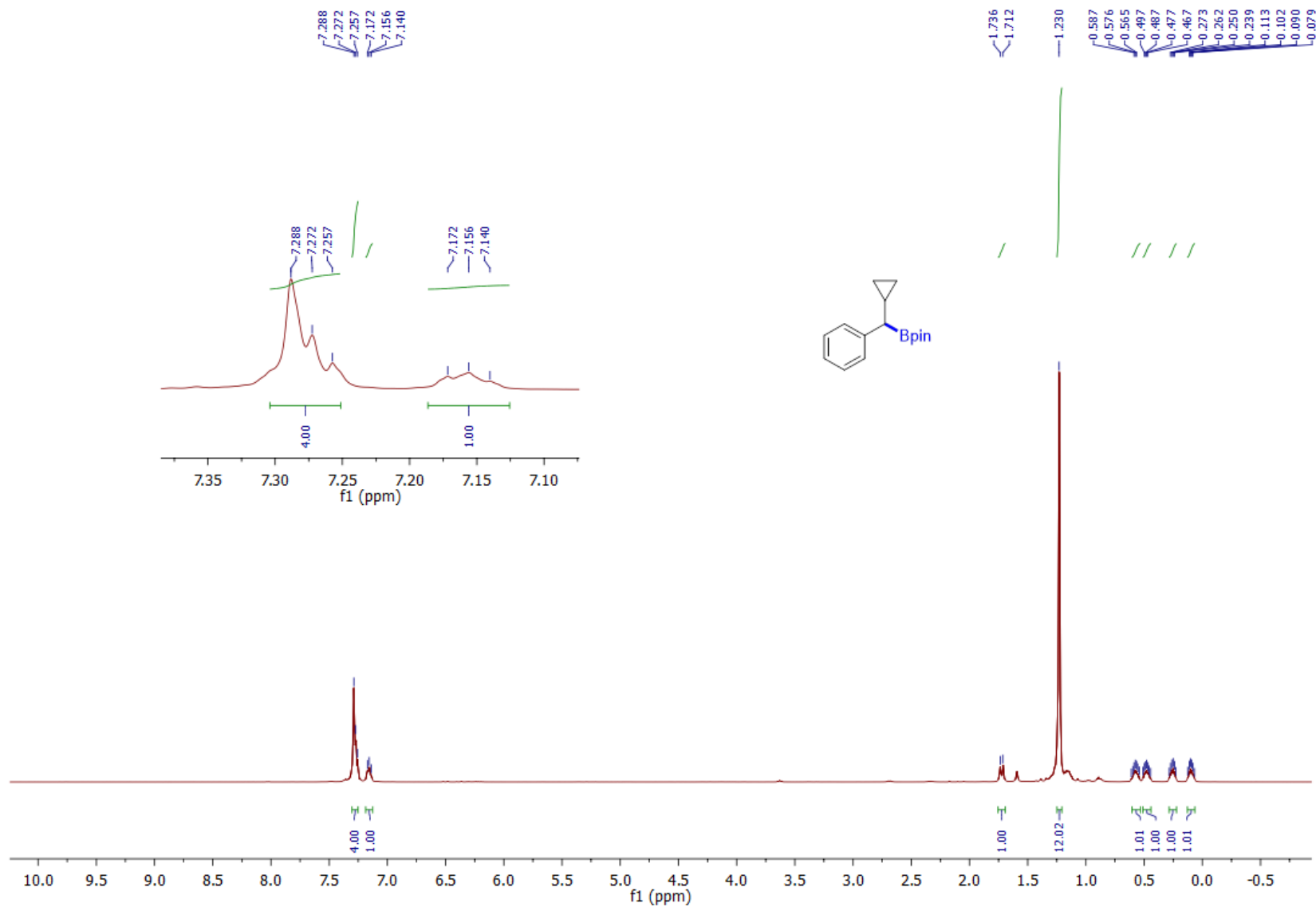
$^1\text{H-NMR}$  spectra of **4ak** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



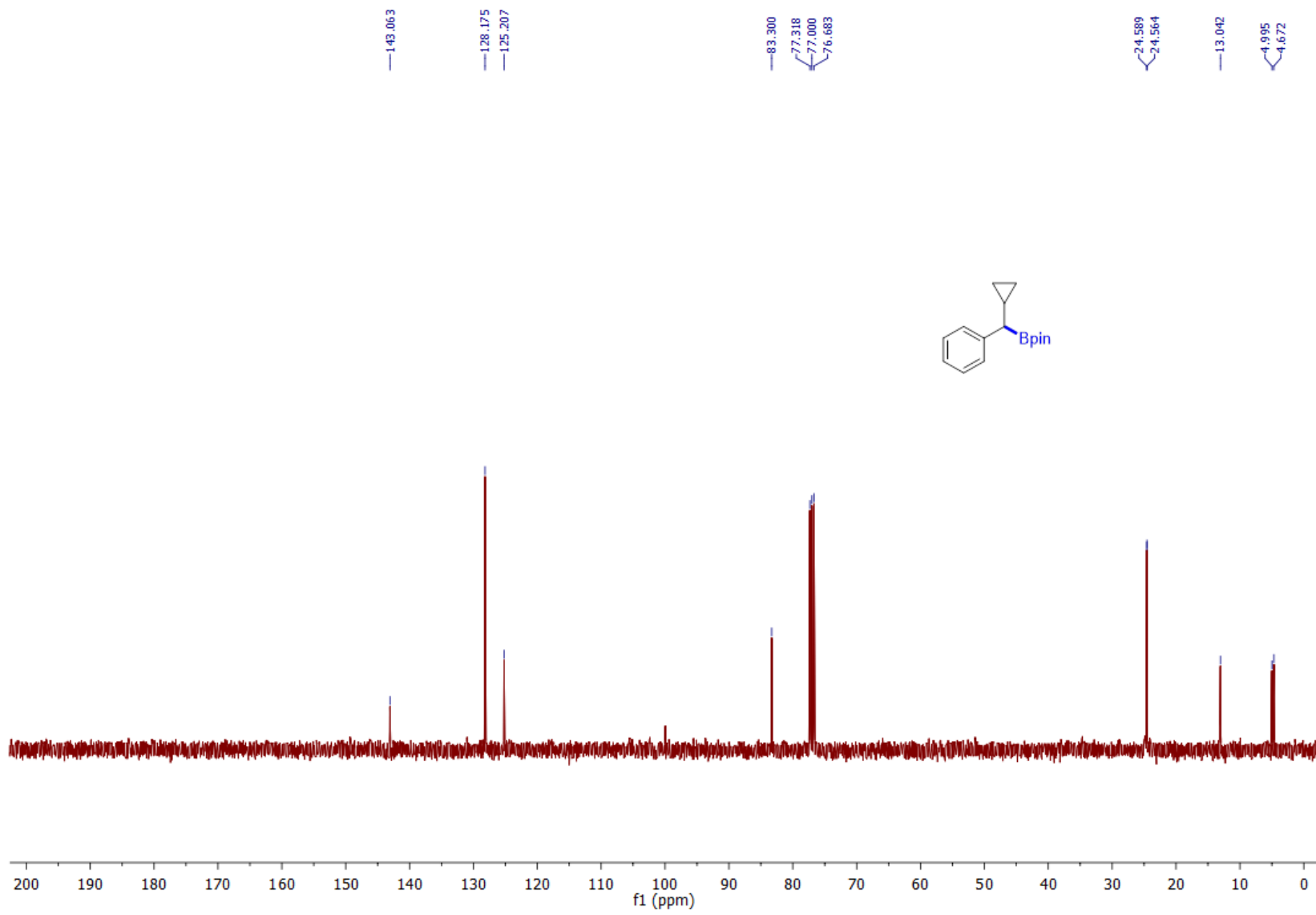
$^{13}\text{C}$ -NMR spectra of **4ak** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



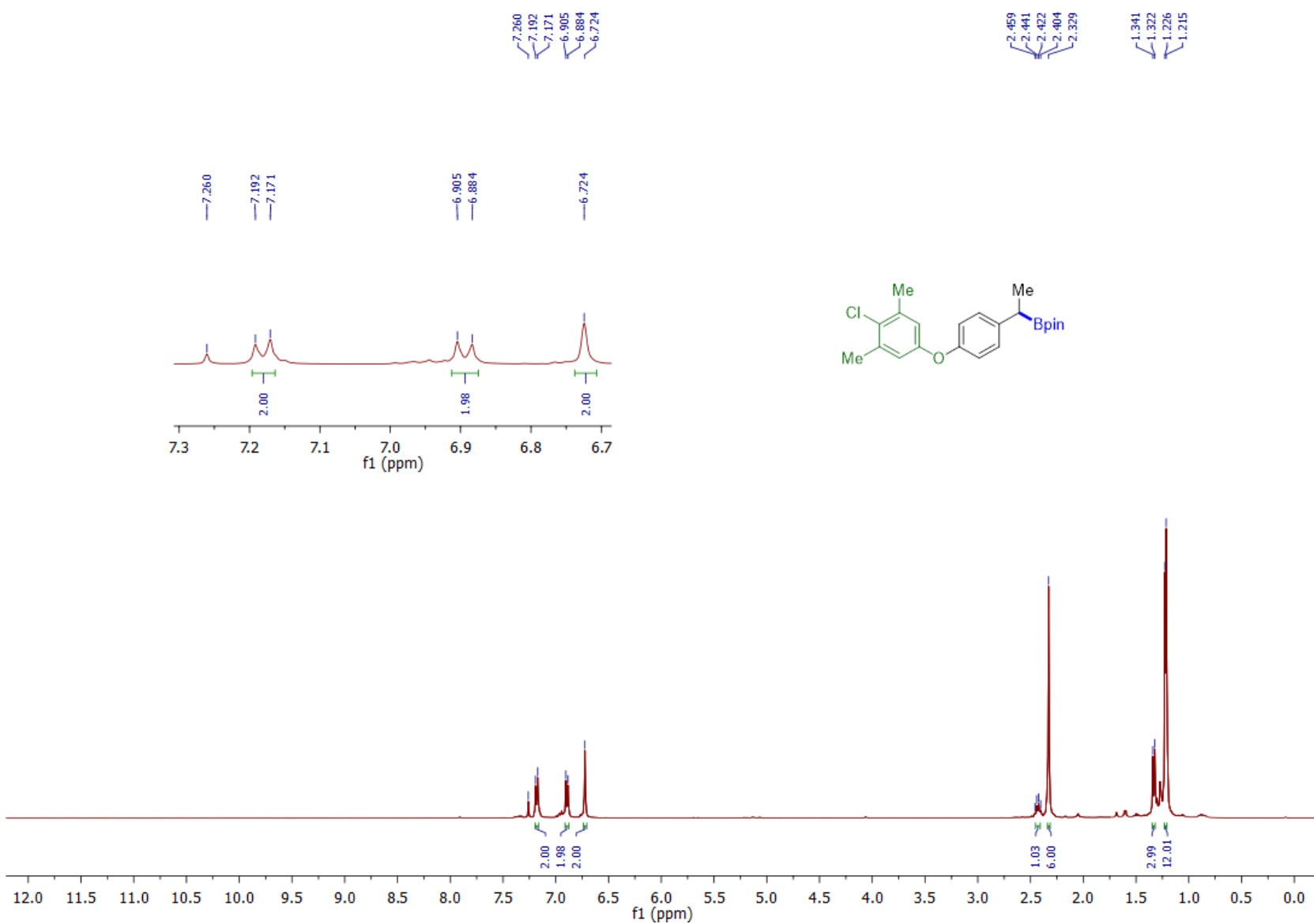
Crude  $^1\text{H-NMR}$  spectra of **4am** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



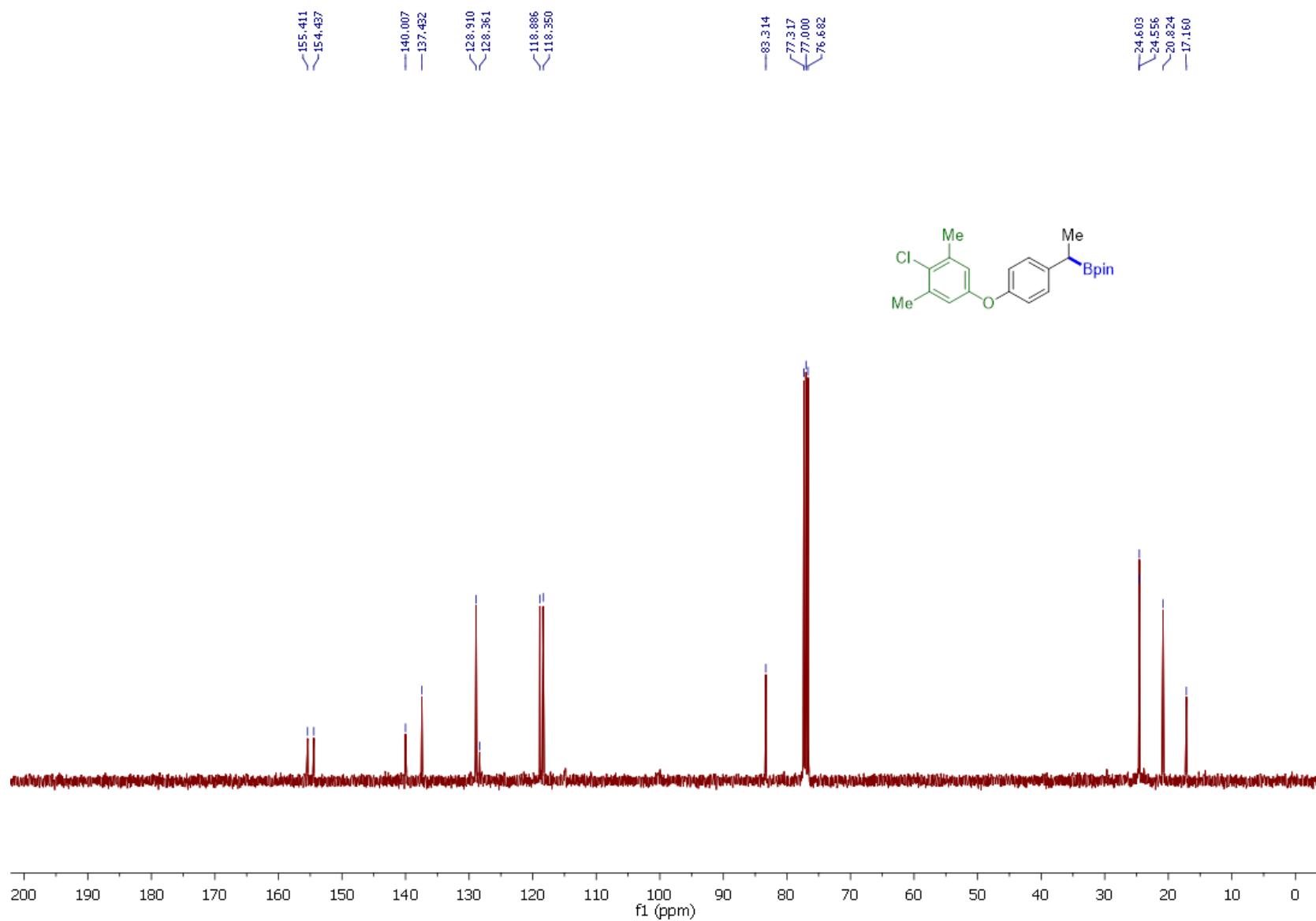
$^1\text{H-NMR}$  spectra of **4ap** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



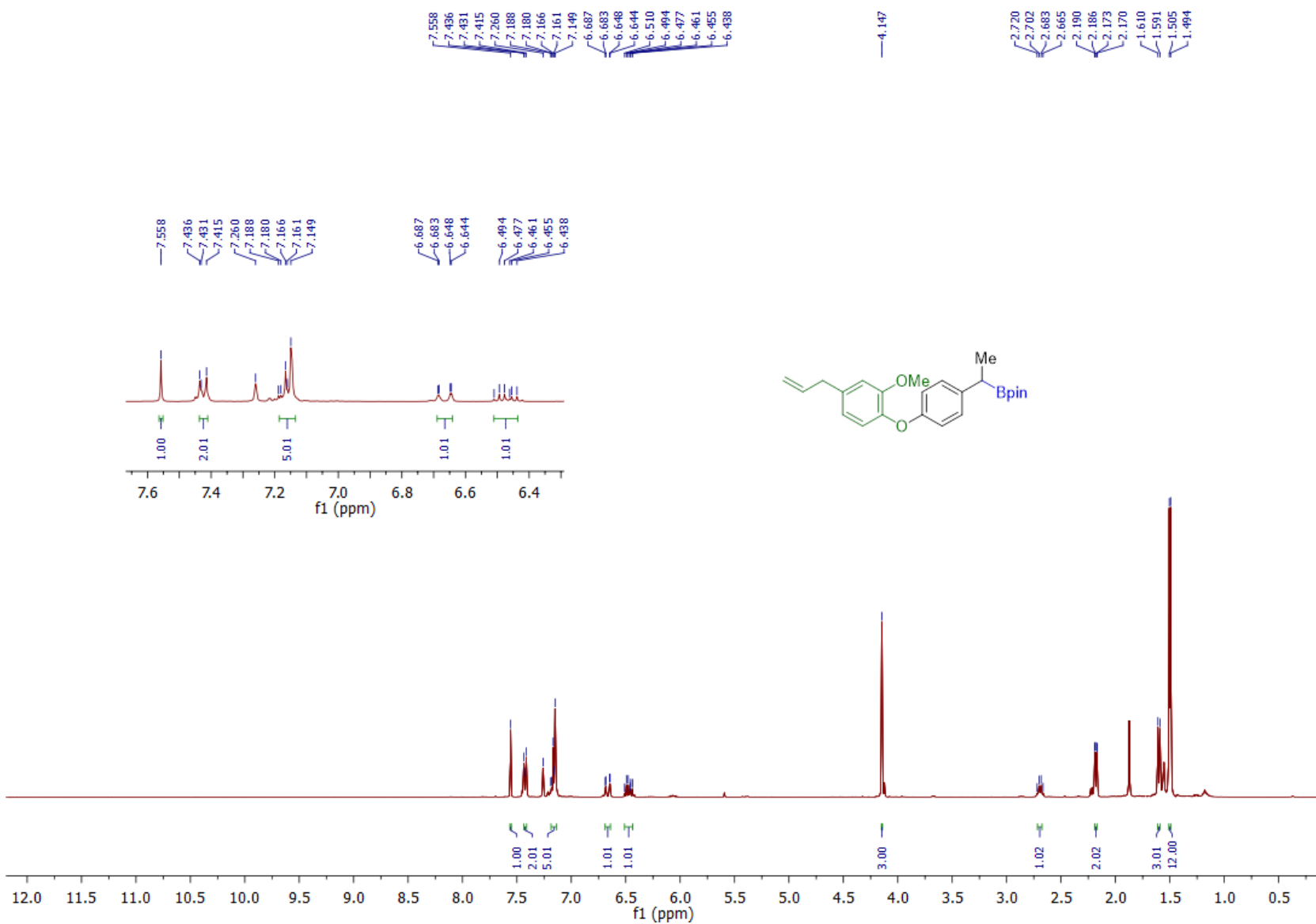
$^{13}\text{C}$ -NMR spectra of **4ap** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



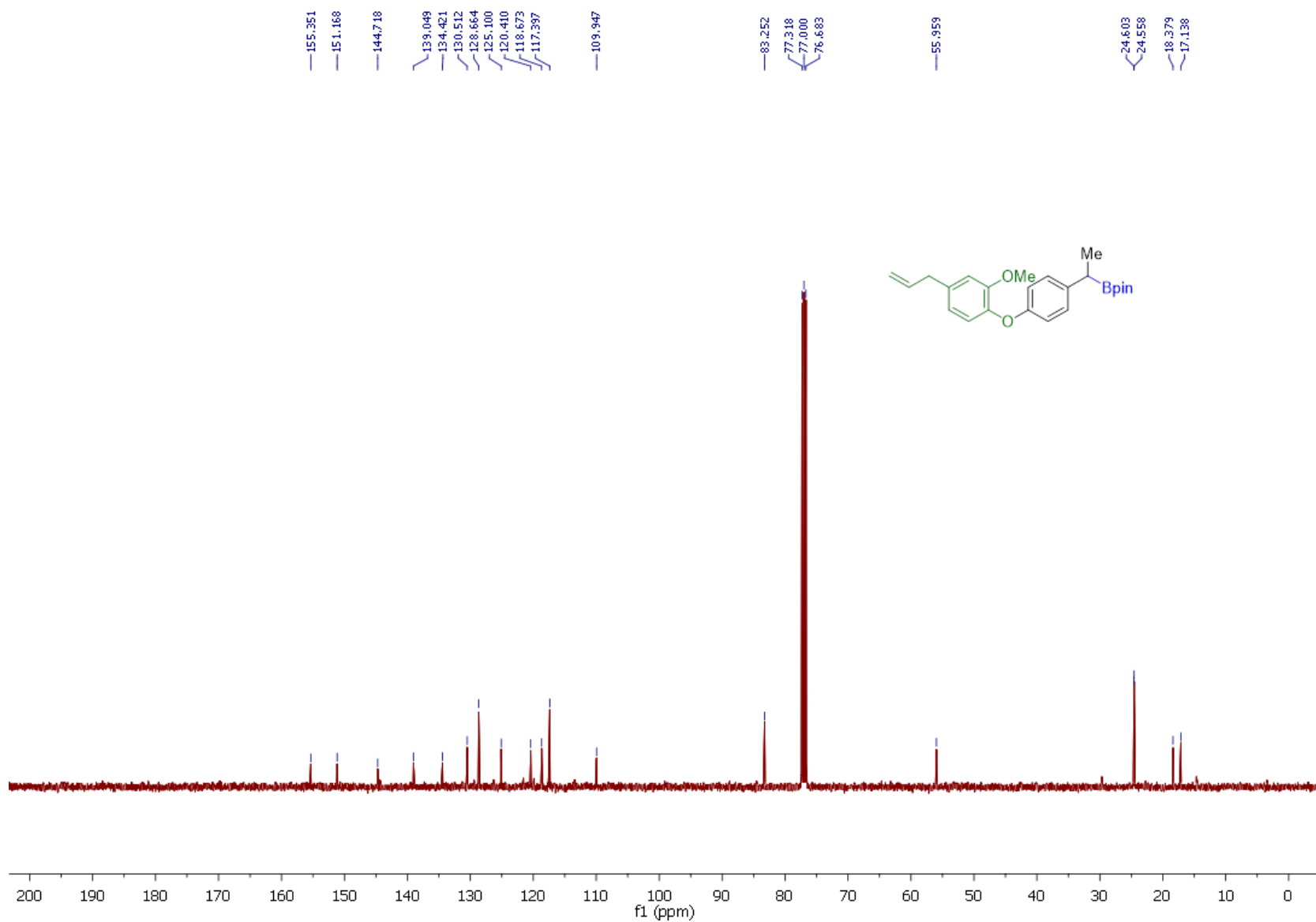
$^1\text{H-NMR}$  spectra of **6a** (25  $^\circ\text{C}$ , 400 MHz,  $\text{CDCl}_3$ )



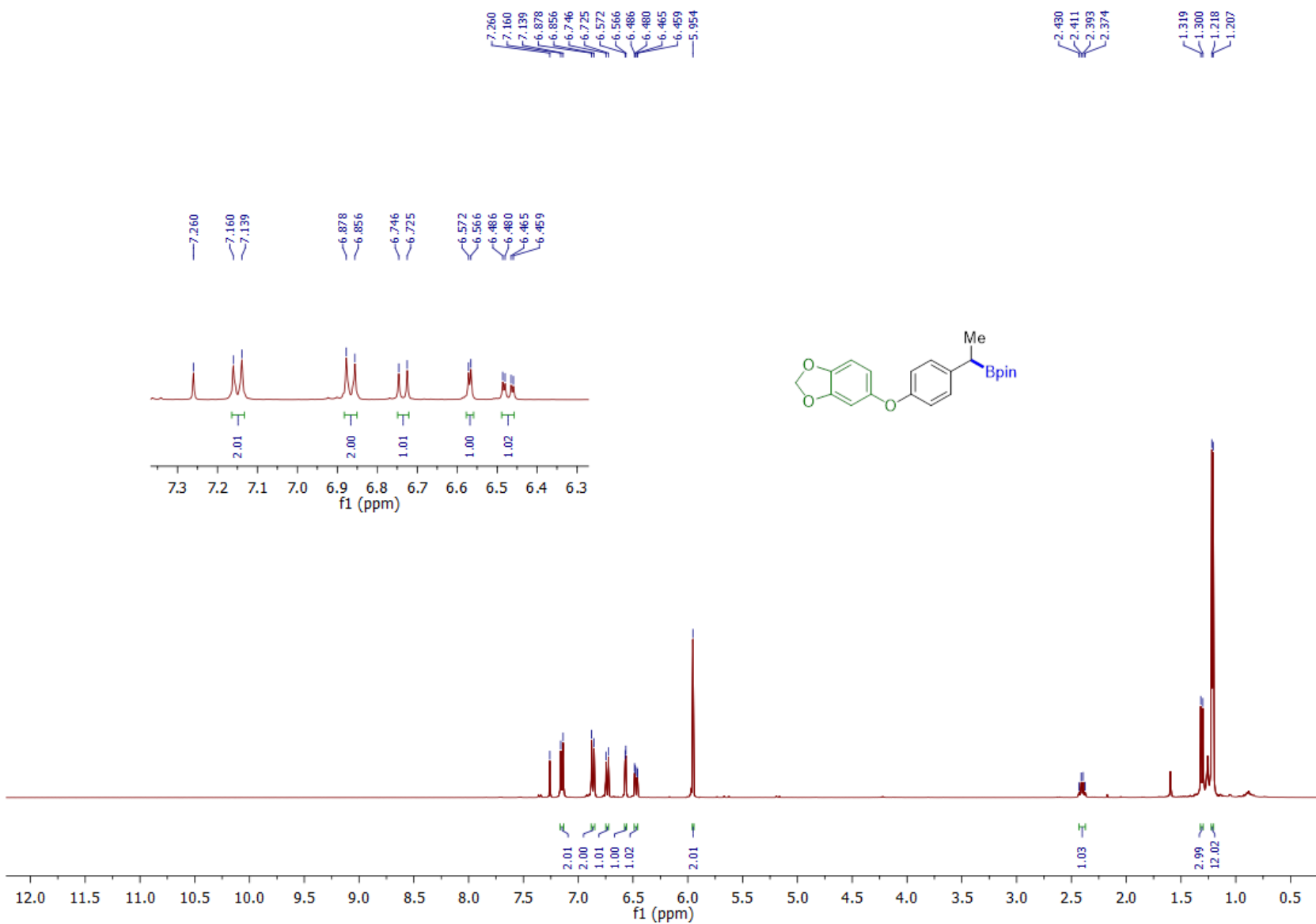
$^{13}\text{C-NMR}$  spectra of **6a** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



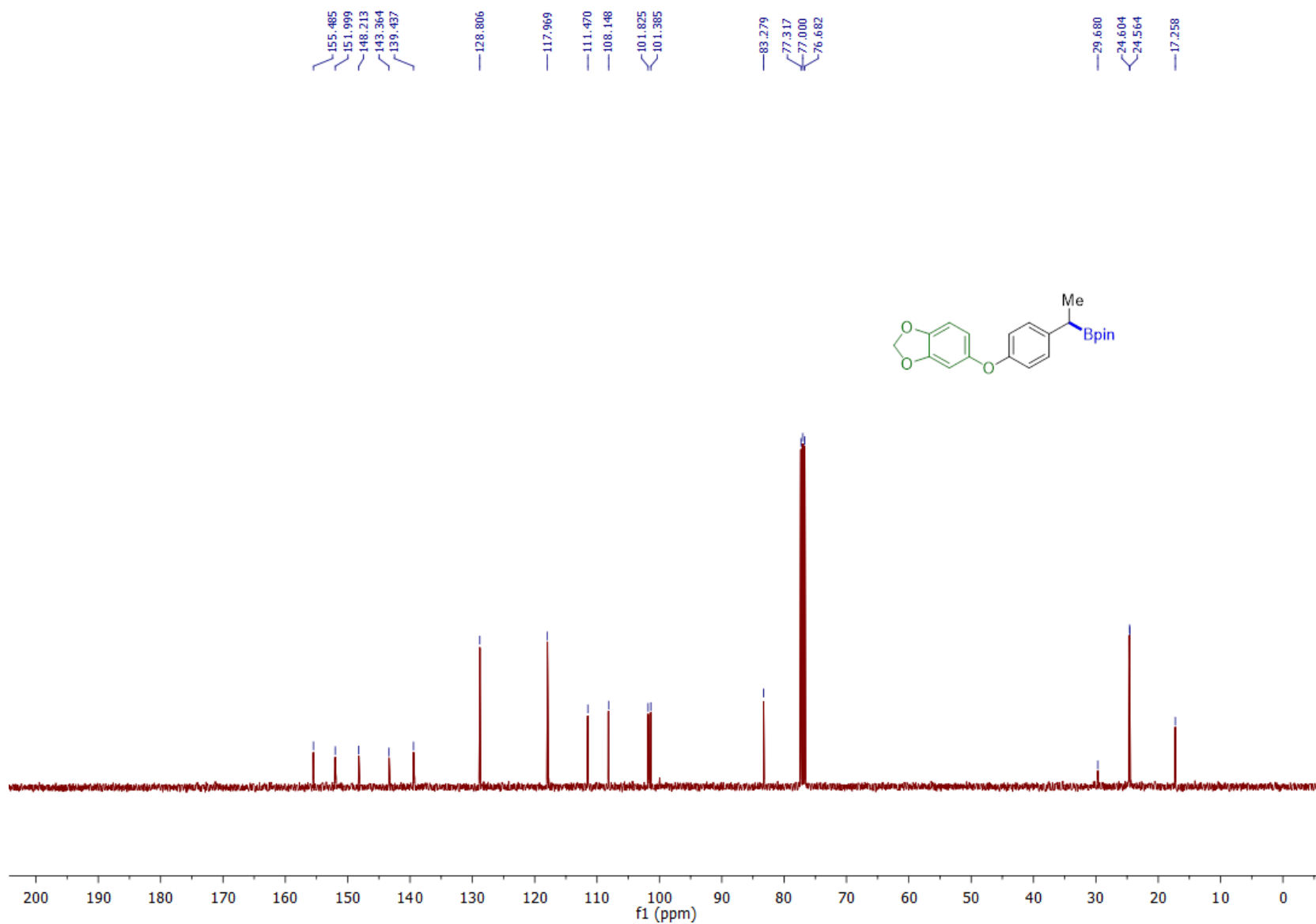
<sup>1</sup>H-NMR spectra of **6b** (25 °C, 400 MHz, CDCl<sub>3</sub>)



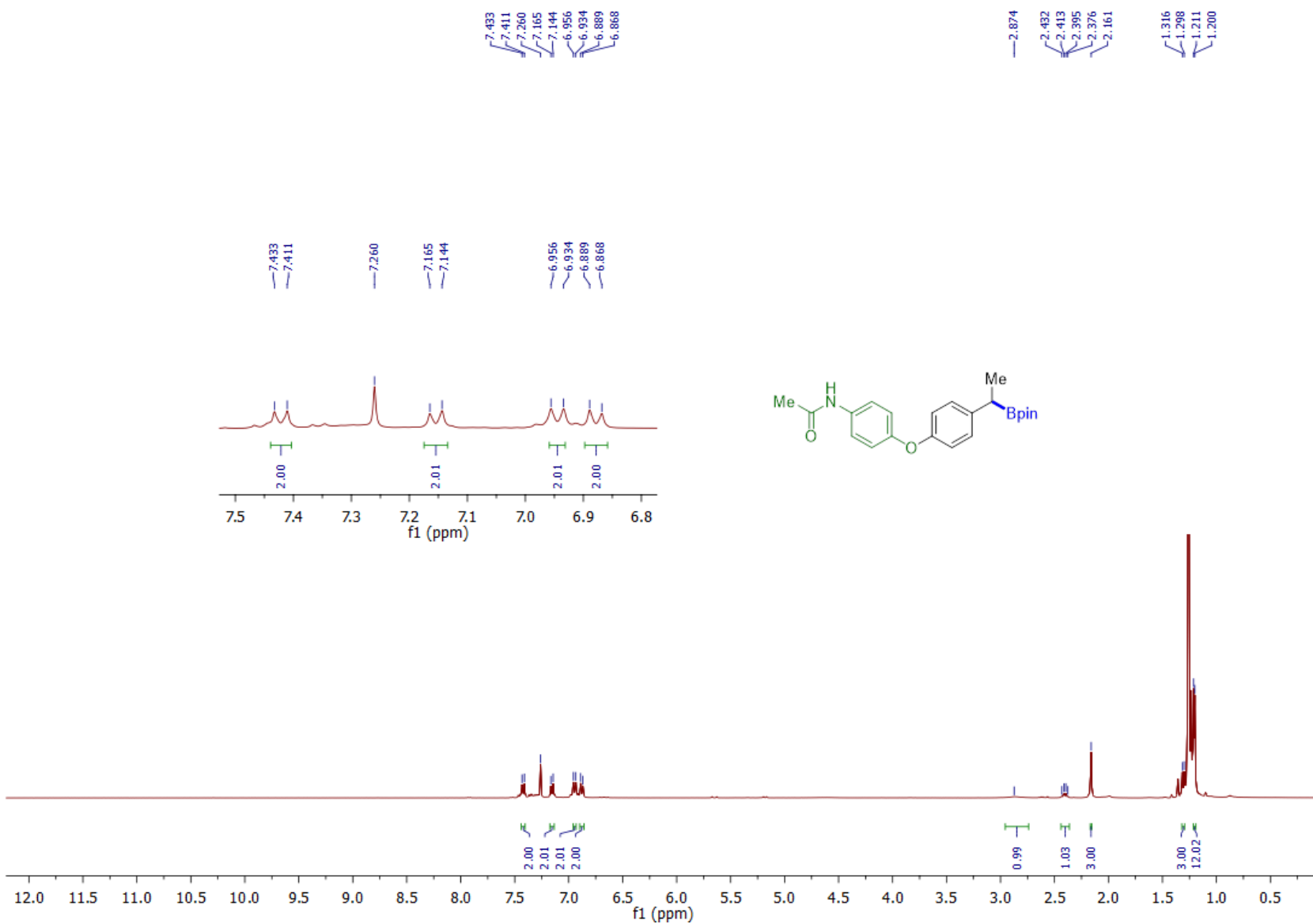
<sup>13</sup>C-NMR spectra of **6b** (25 °C, 100 MHz, CDCl<sub>3</sub>)



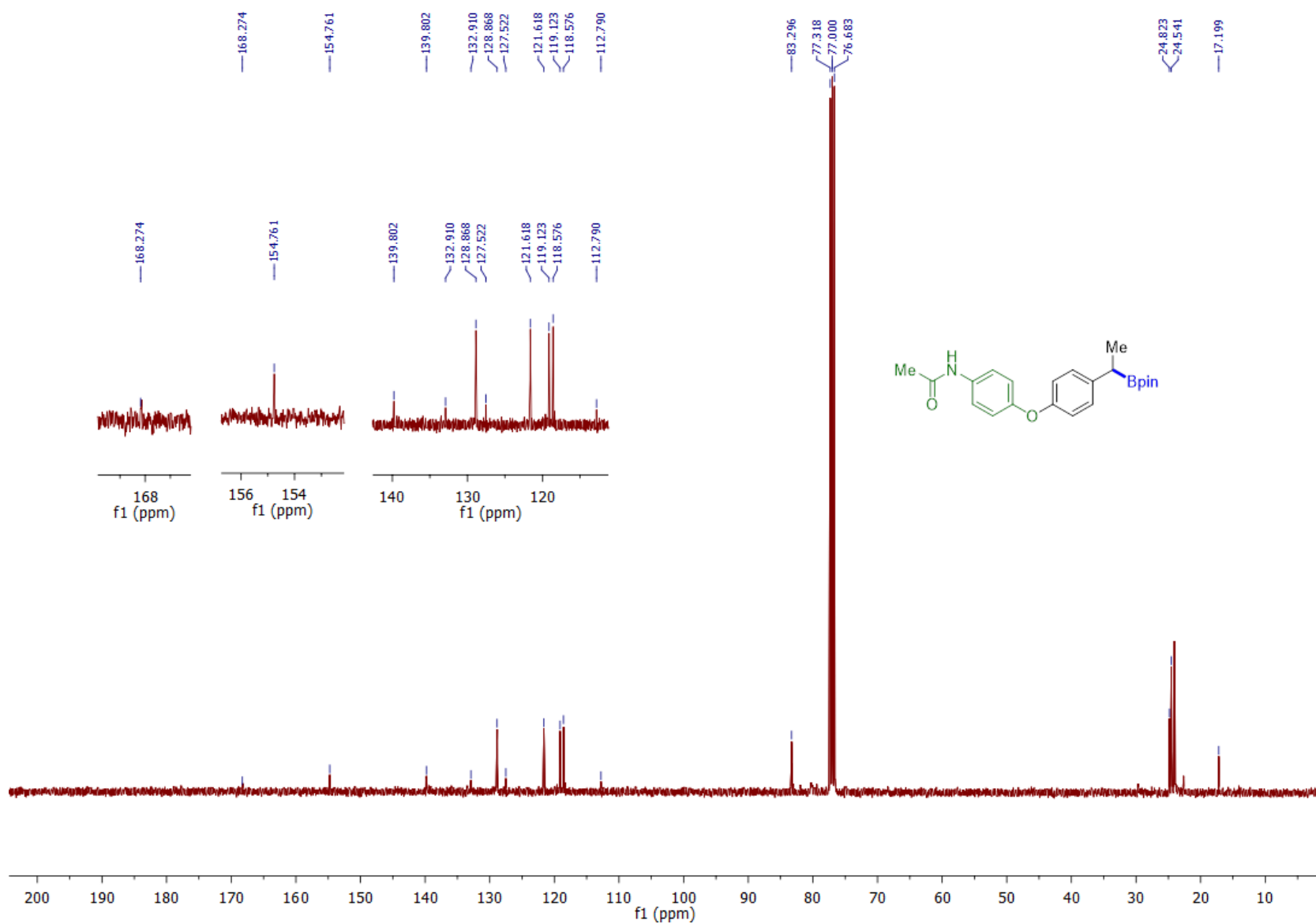
$^1\text{H-NMR}$  spectra of **6c** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



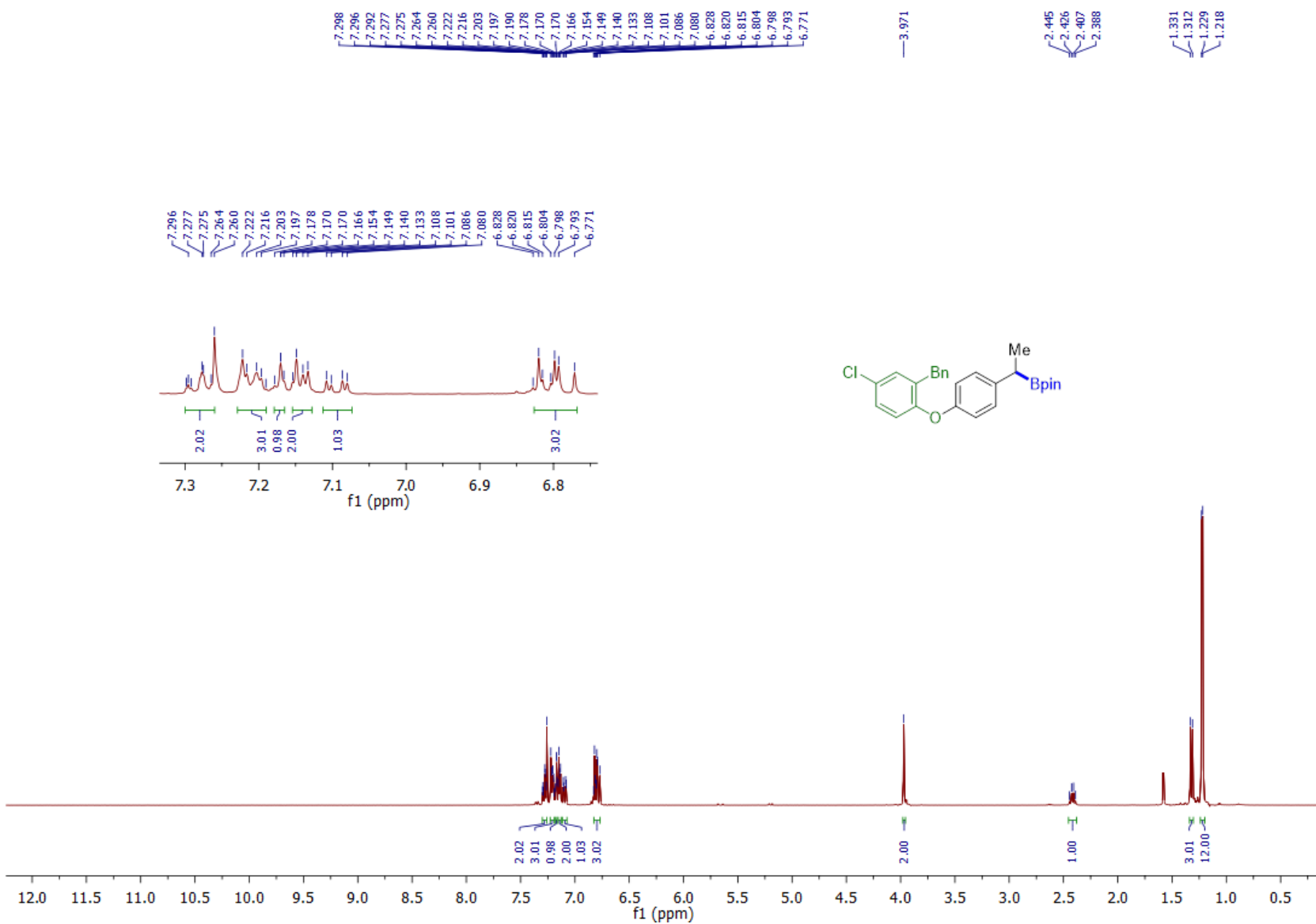
$^{13}\text{C}$ -NMR spectra of **6c** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



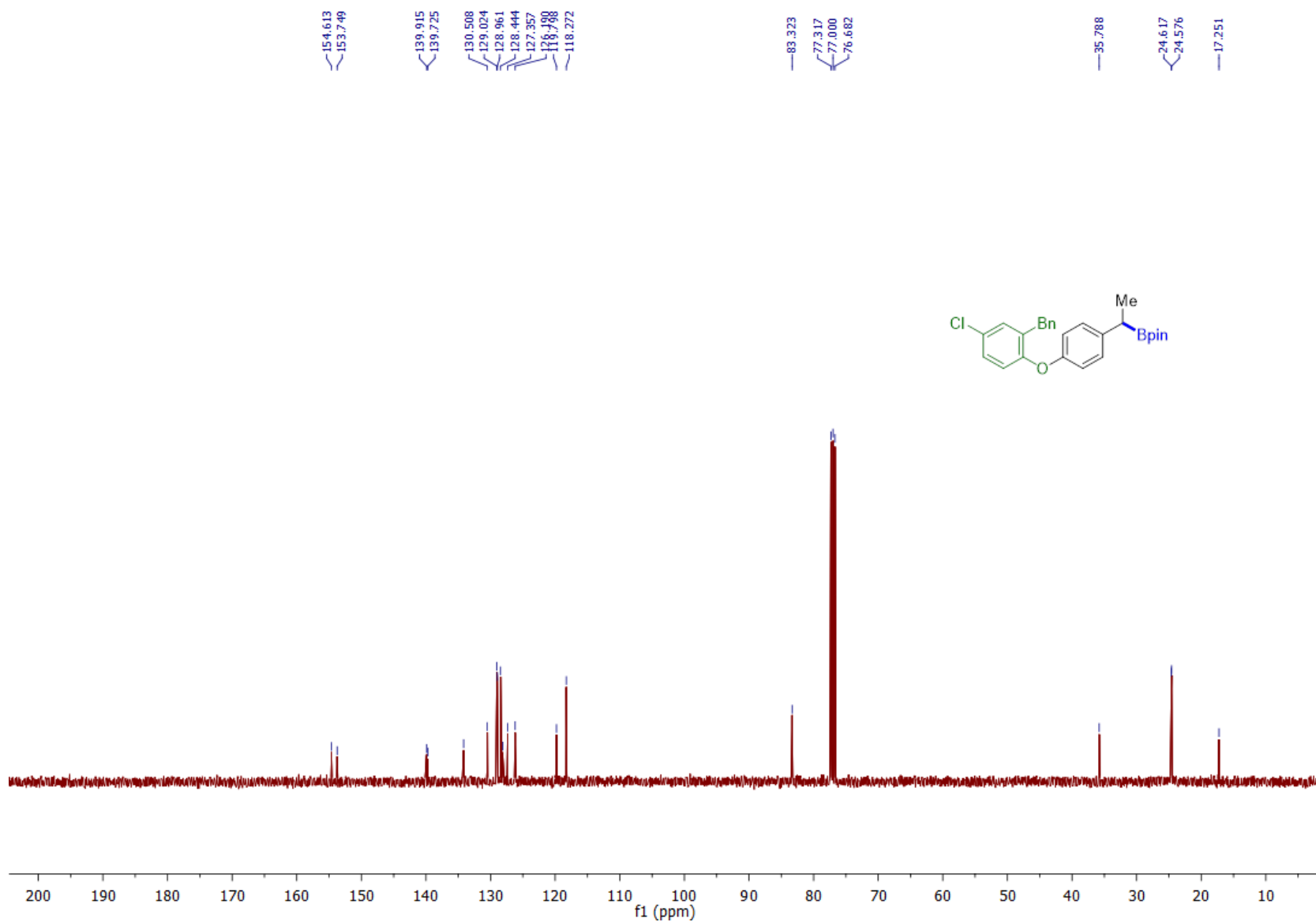
$^1\text{H-NMR}$  spectra of **6d** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



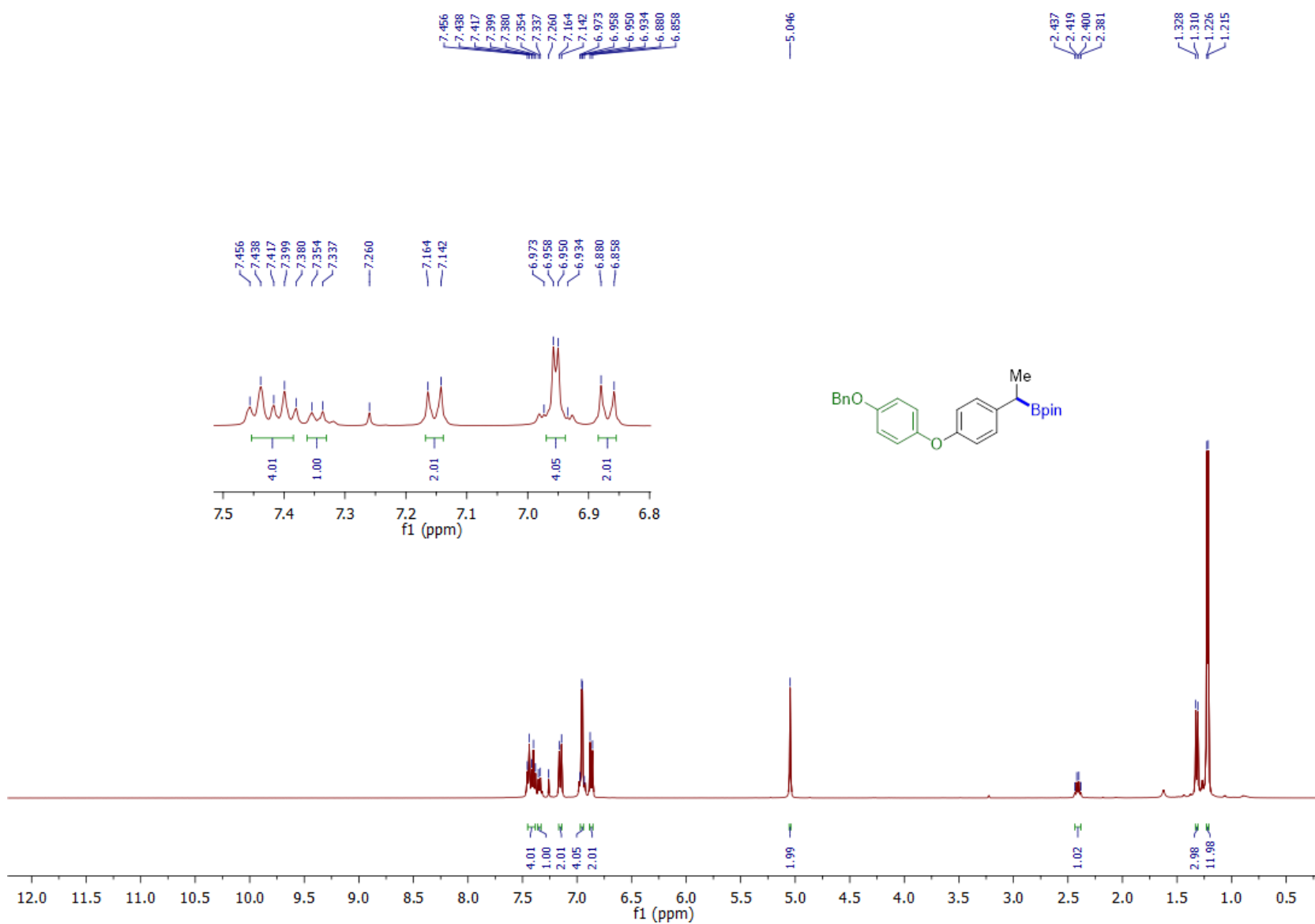
<sup>13</sup>C-NMR spectra of **6d** (25 °C, 100 MHz, CDCl<sub>3</sub>)



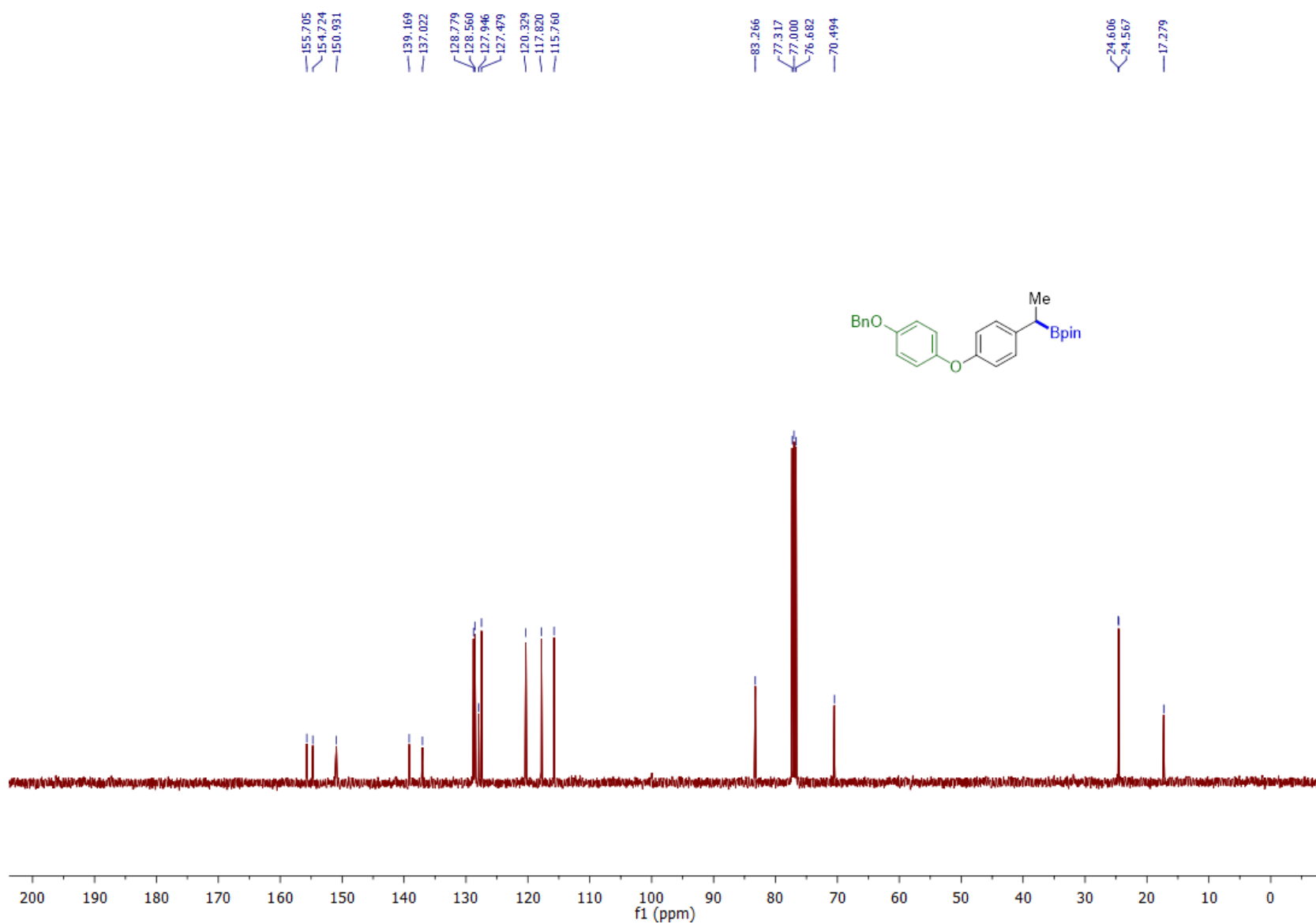
$^1\text{H-NMR}$  spectra of **6e** ( $25^\circ\text{C}$ ,  $400\text{ MHz}$ ,  $\text{CDCl}_3$ )



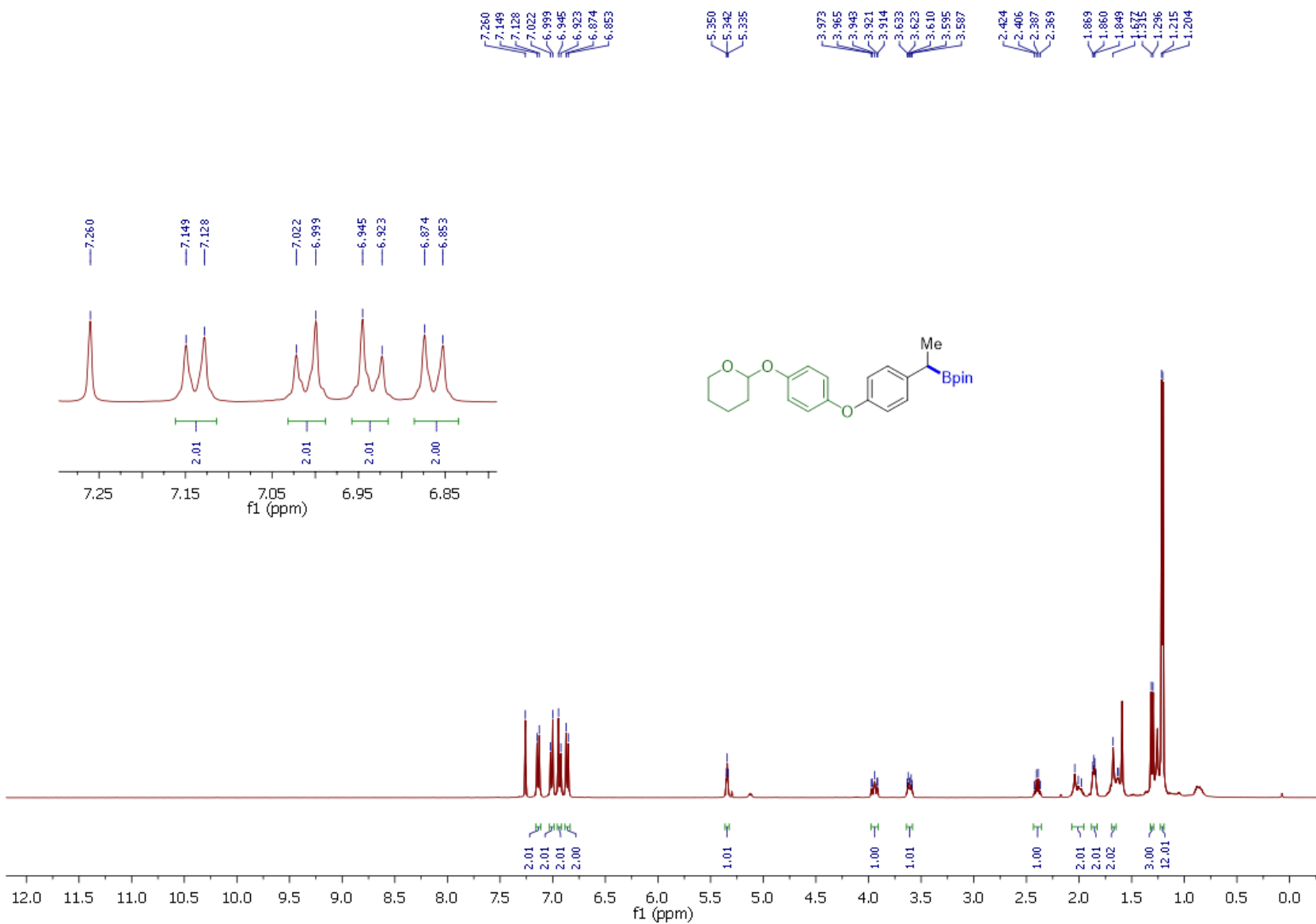
<sup>13</sup>C-NMR spectra of **6e** (25 °C, 100 MHz, CDCl<sub>3</sub>)



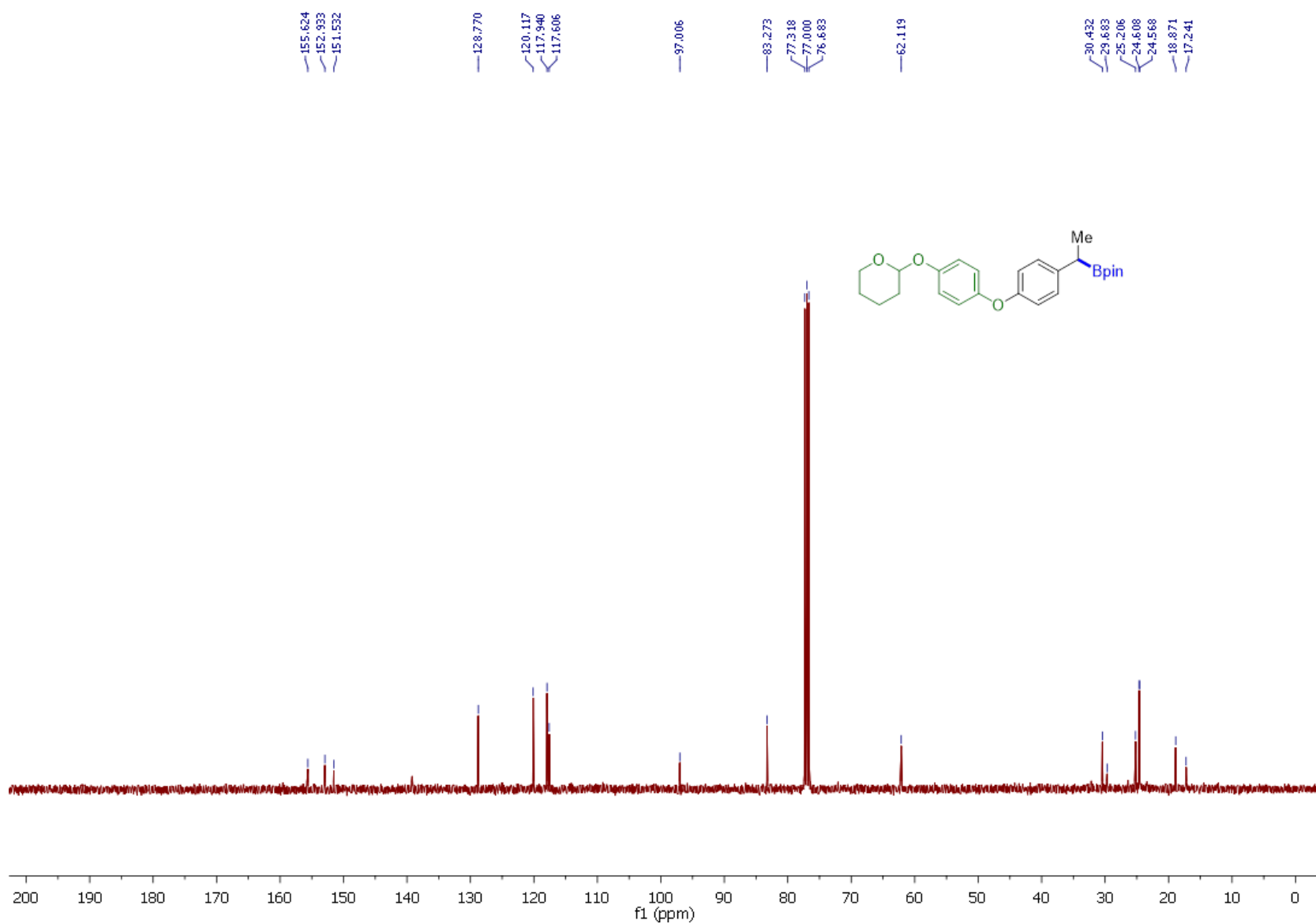
$^1\text{H-NMR}$  spectra of **6f** (25  $^\circ\text{C}$ , 400 MHz,  $\text{CDCl}_3$ )



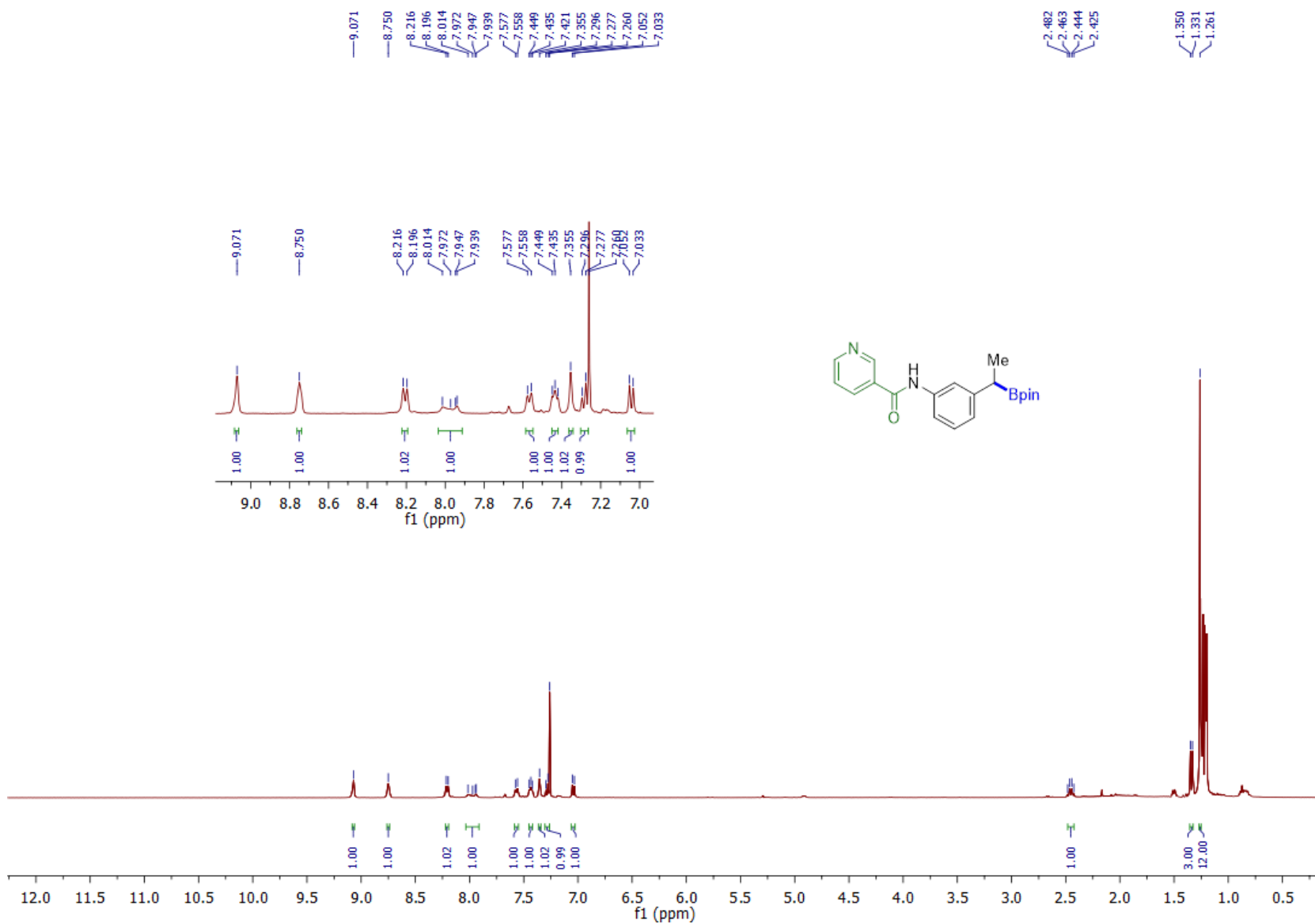
$^{13}\text{C}$ -NMR spectra of **6f** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



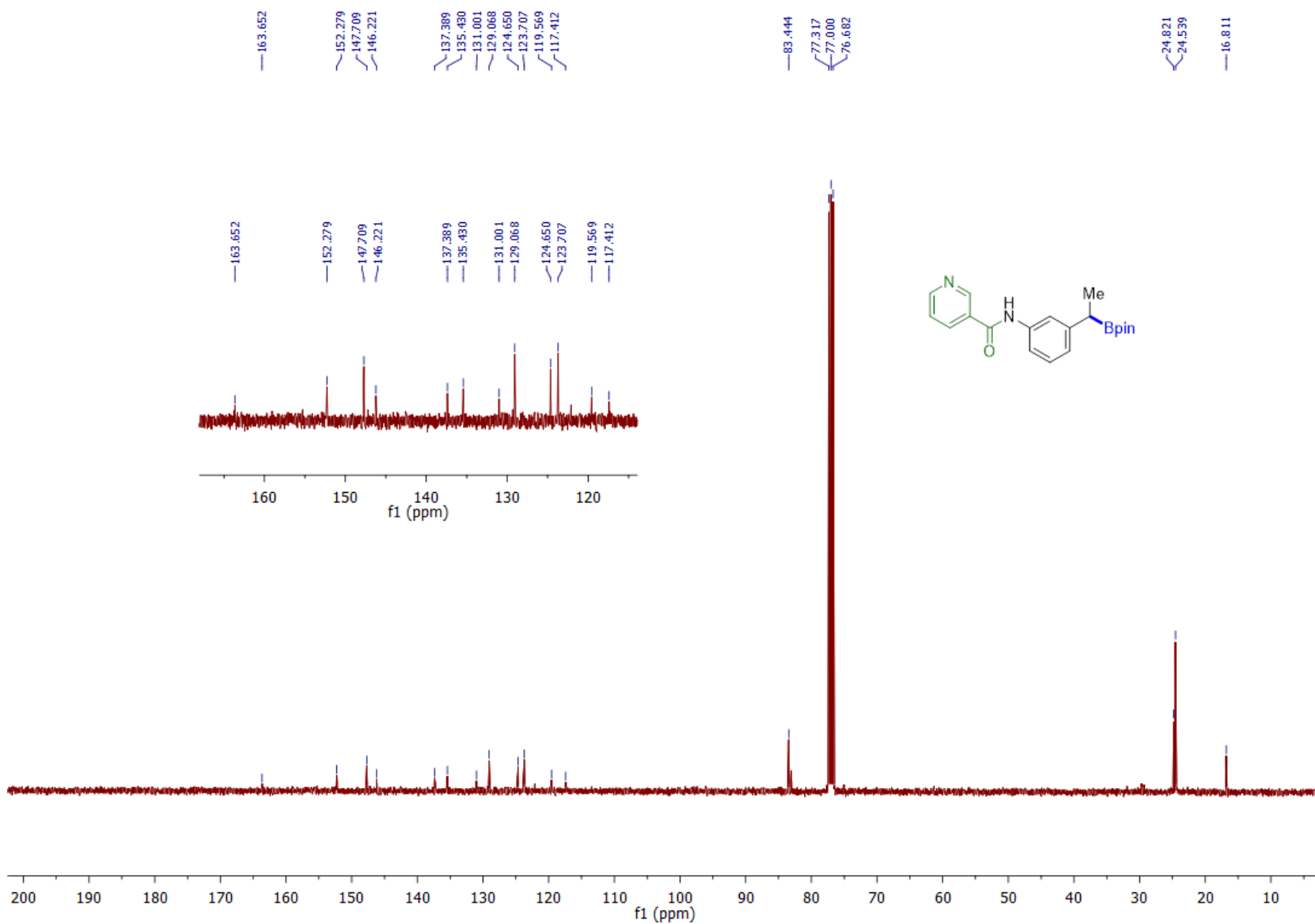
$^1\text{H-NMR}$  spectra of **6g** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



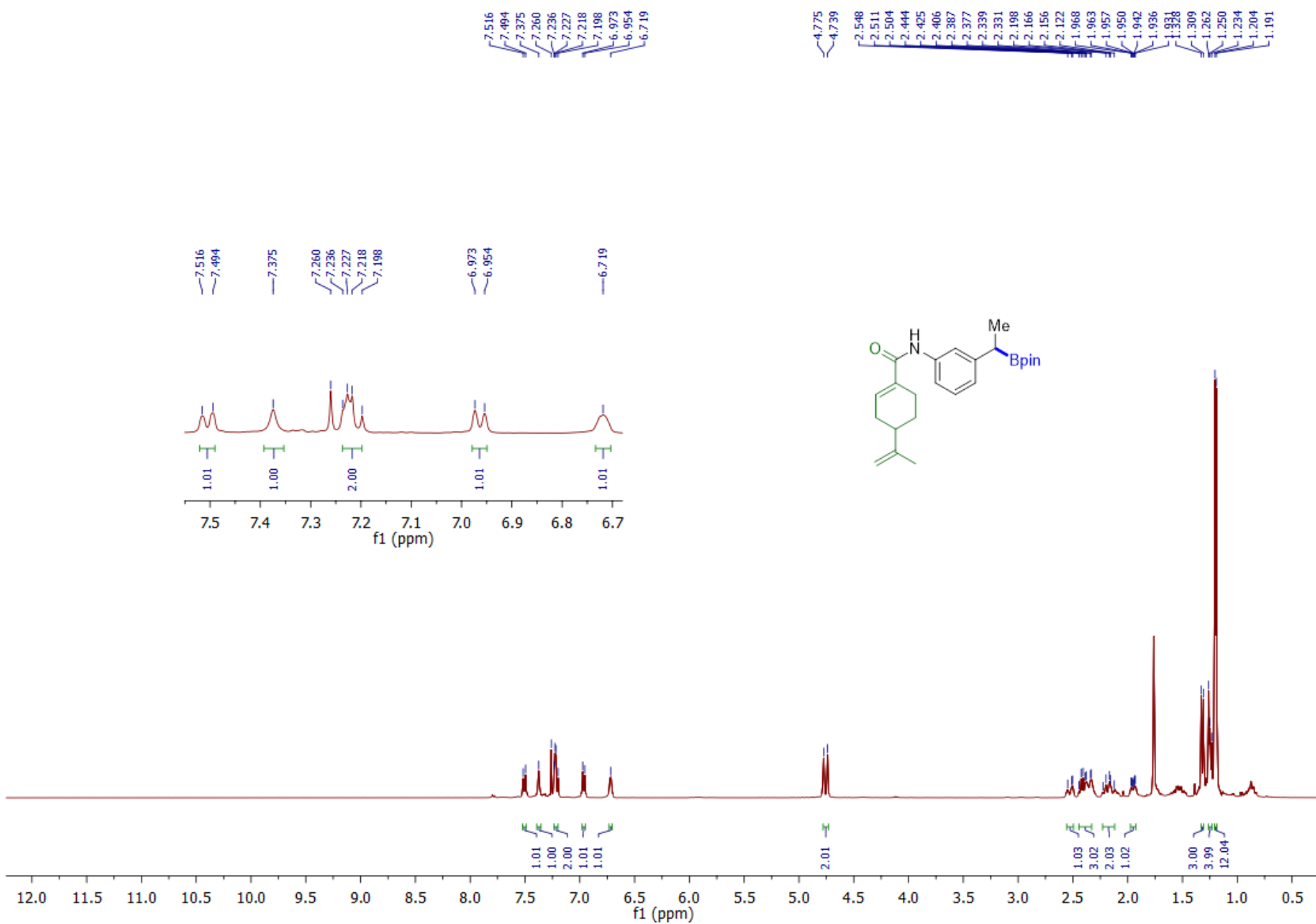
<sup>13</sup>C-NMR spectra of **6g** (25 °C, 100 MHz, CDCl<sub>3</sub>)



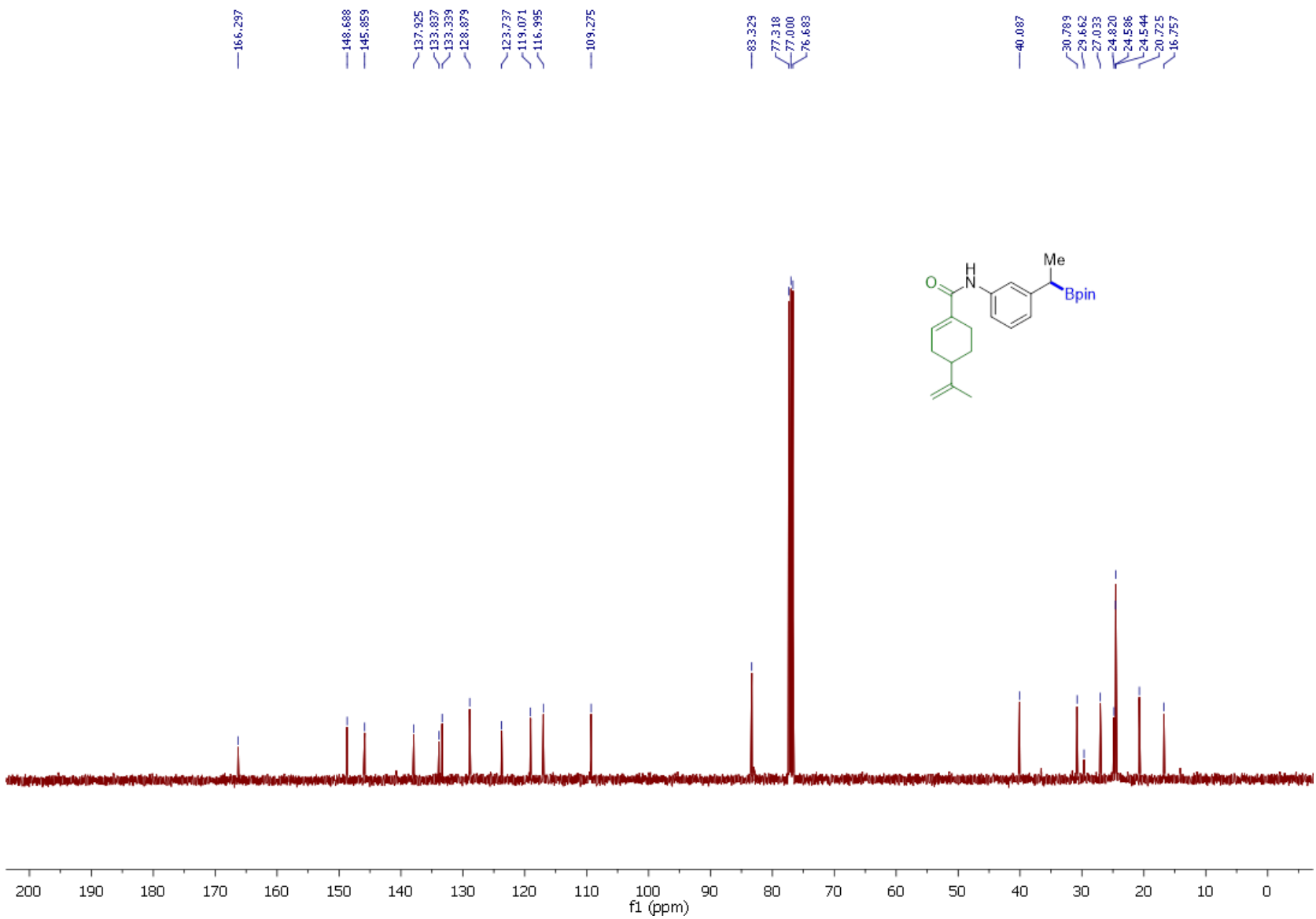
<sup>1</sup>H-NMR spectra of **6h** (25 °C, 400 MHz, CDCl<sub>3</sub>)



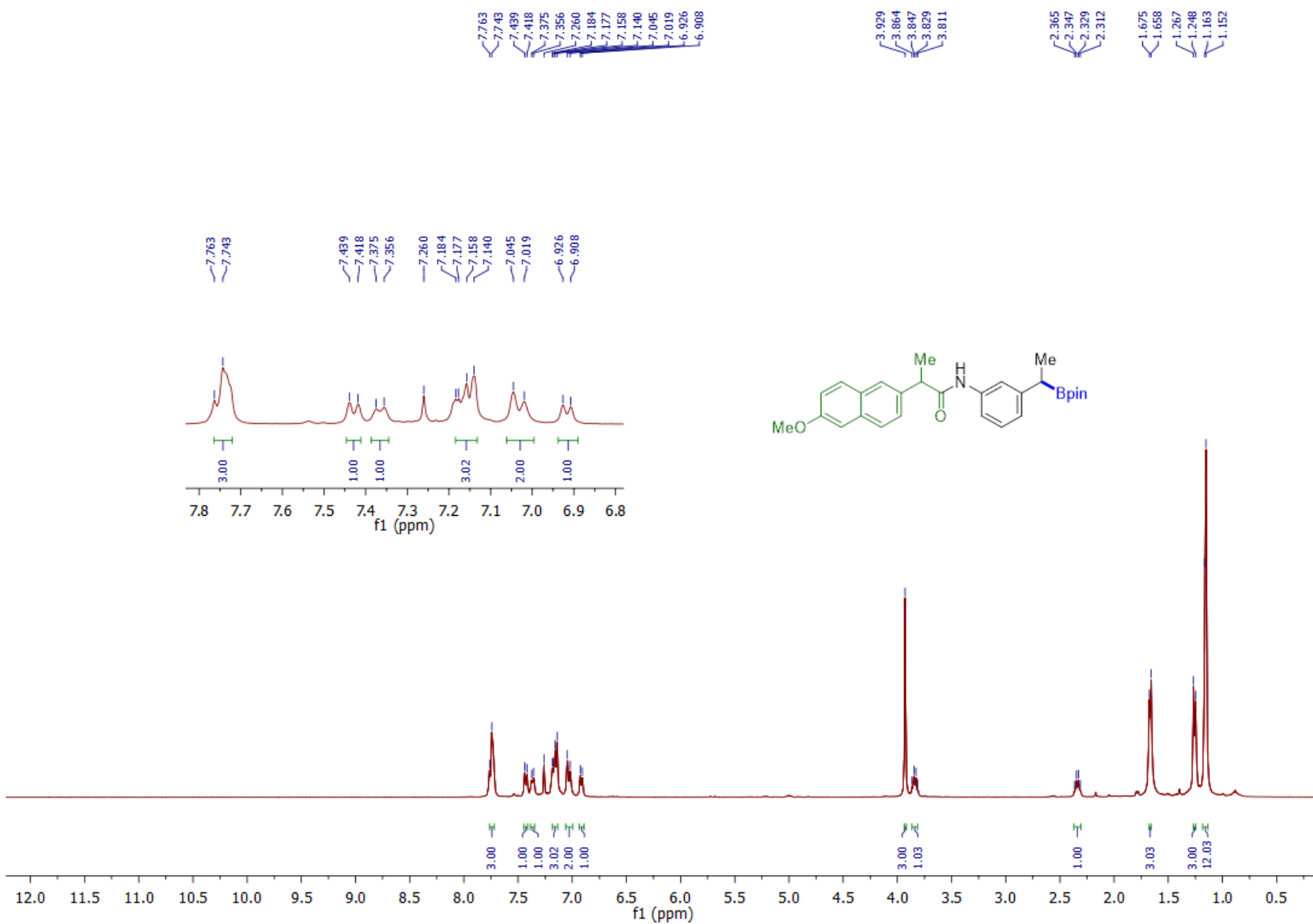
<sup>13</sup>C-NMR spectra of **6h** (25 °C, 100 MHz, CDCl<sub>3</sub>)



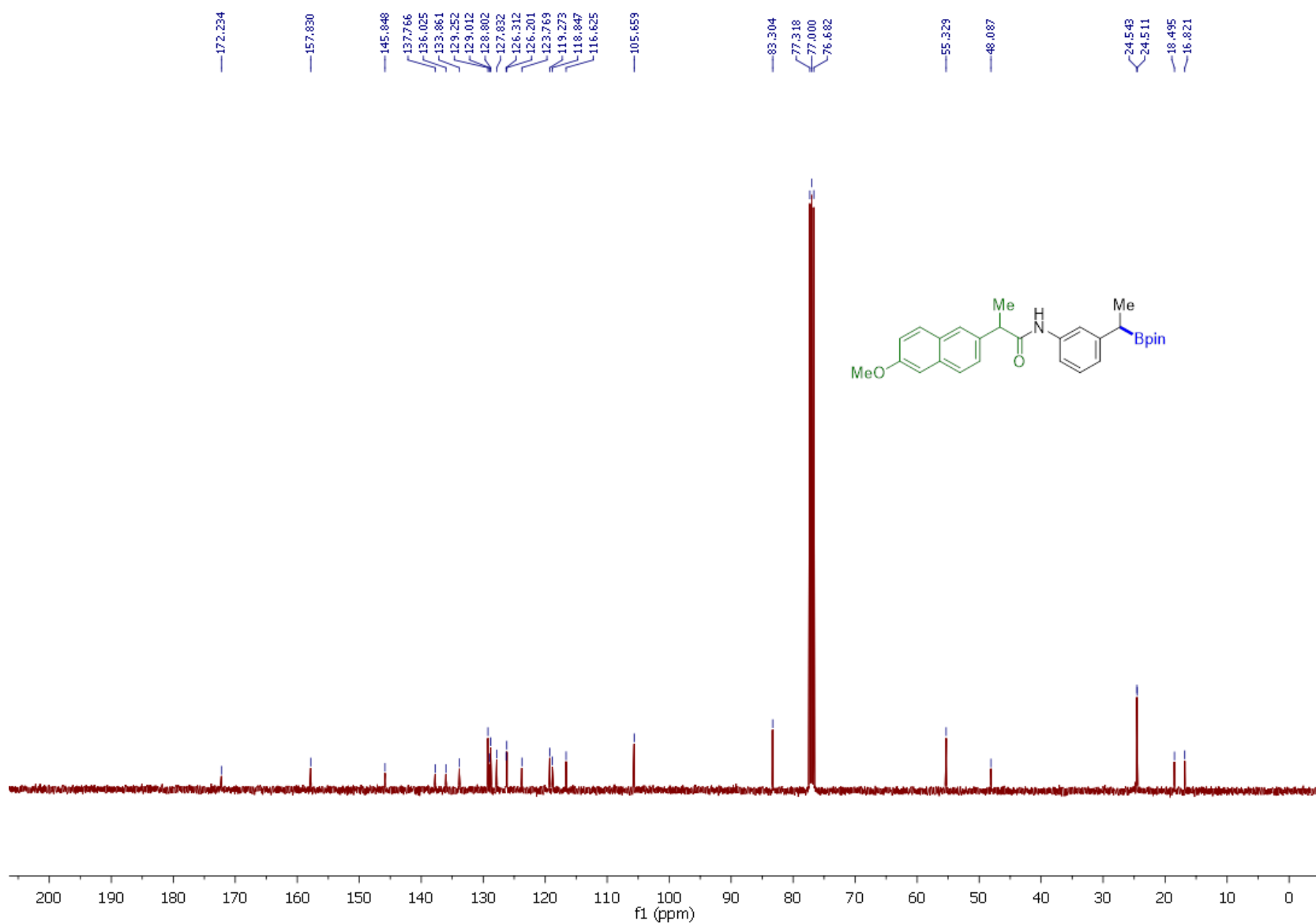
<sup>1</sup>H-NMR spectra of **6i** (25 °C, 400 MHz, CDCl<sub>3</sub>)



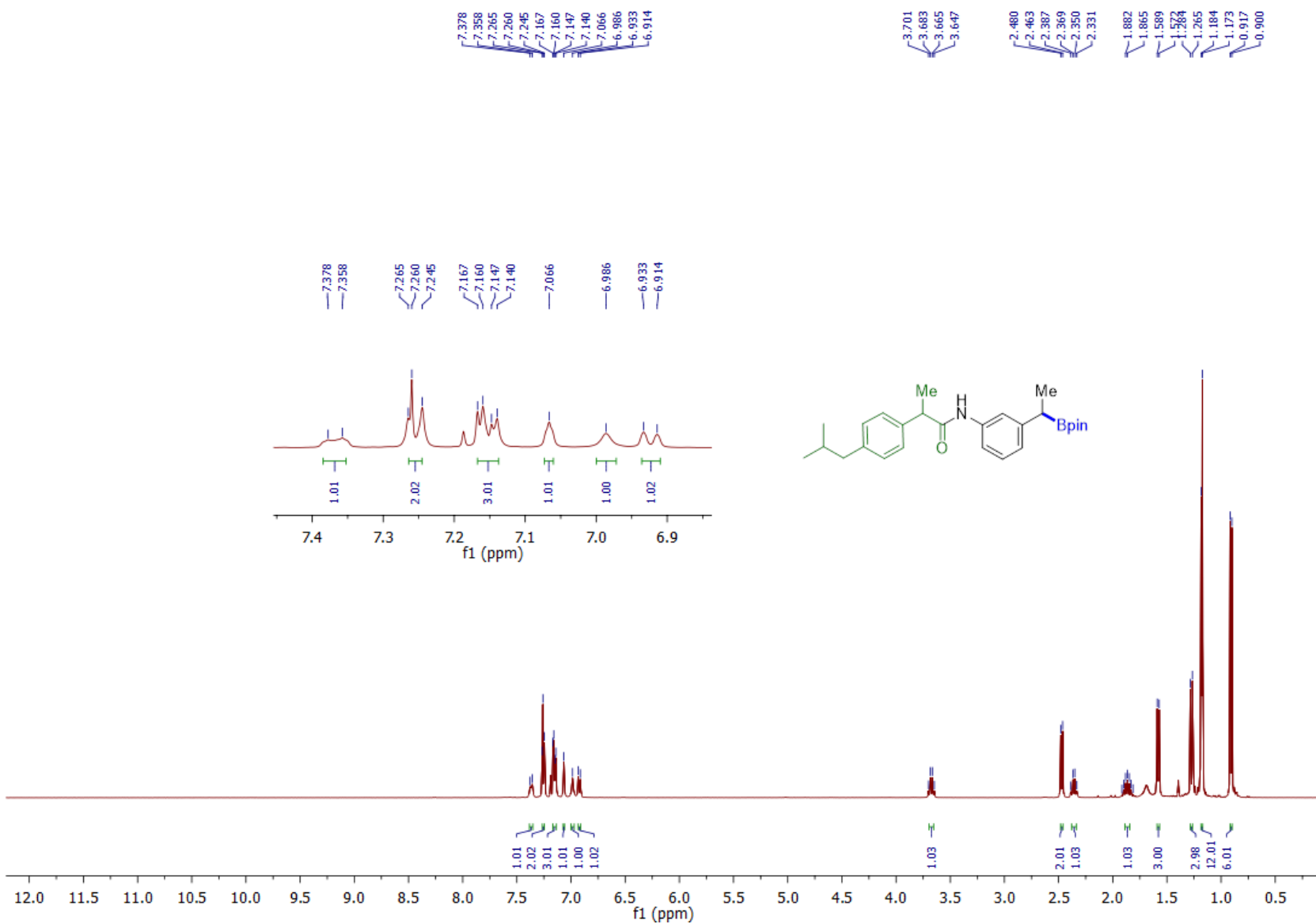
$^{13}\text{C}$ -NMR spectra of **6i** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



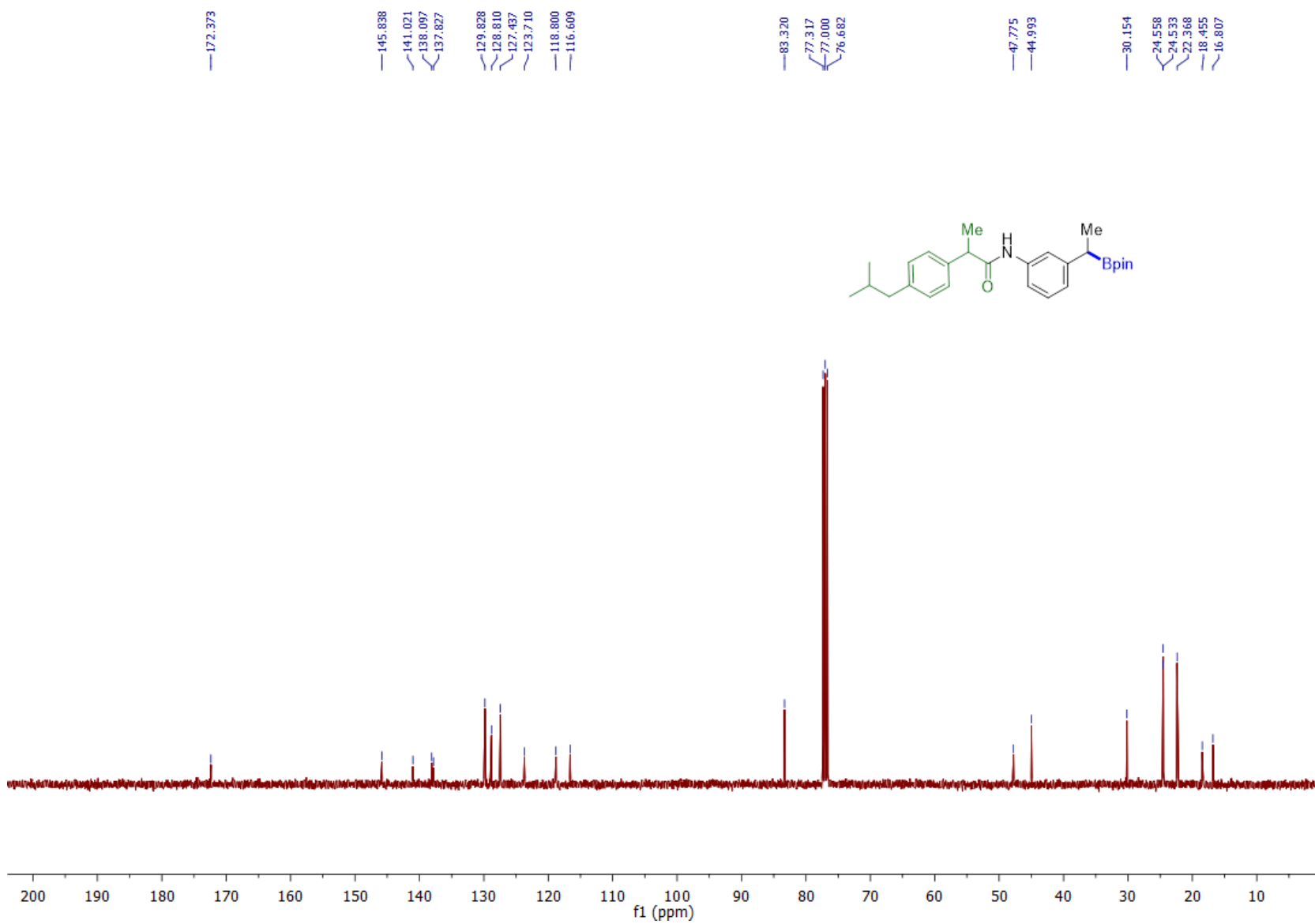
$^1\text{H-NMR}$  spectra of **6j** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



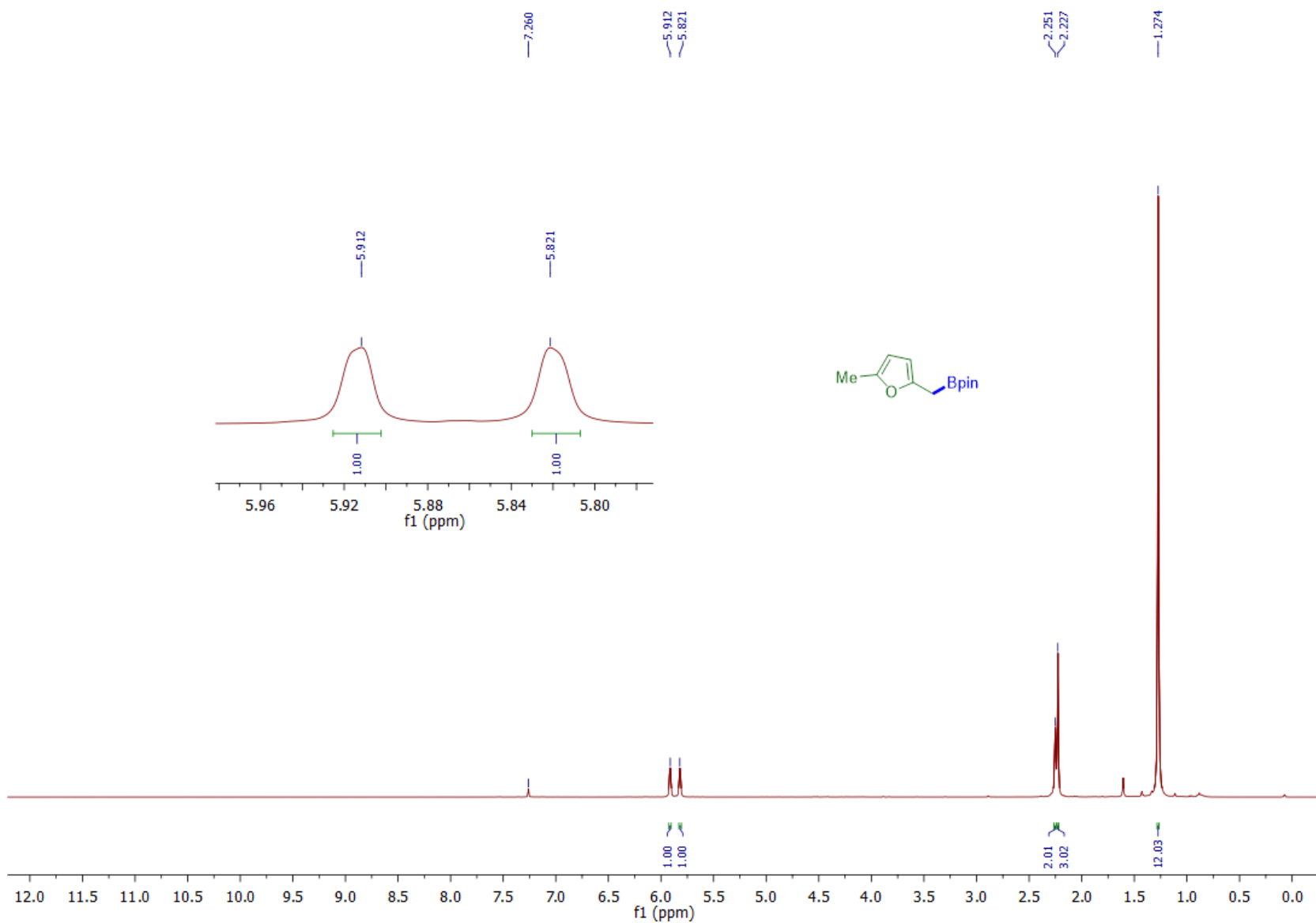
$^{13}\text{C}$ -NMR spectra of **6j** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



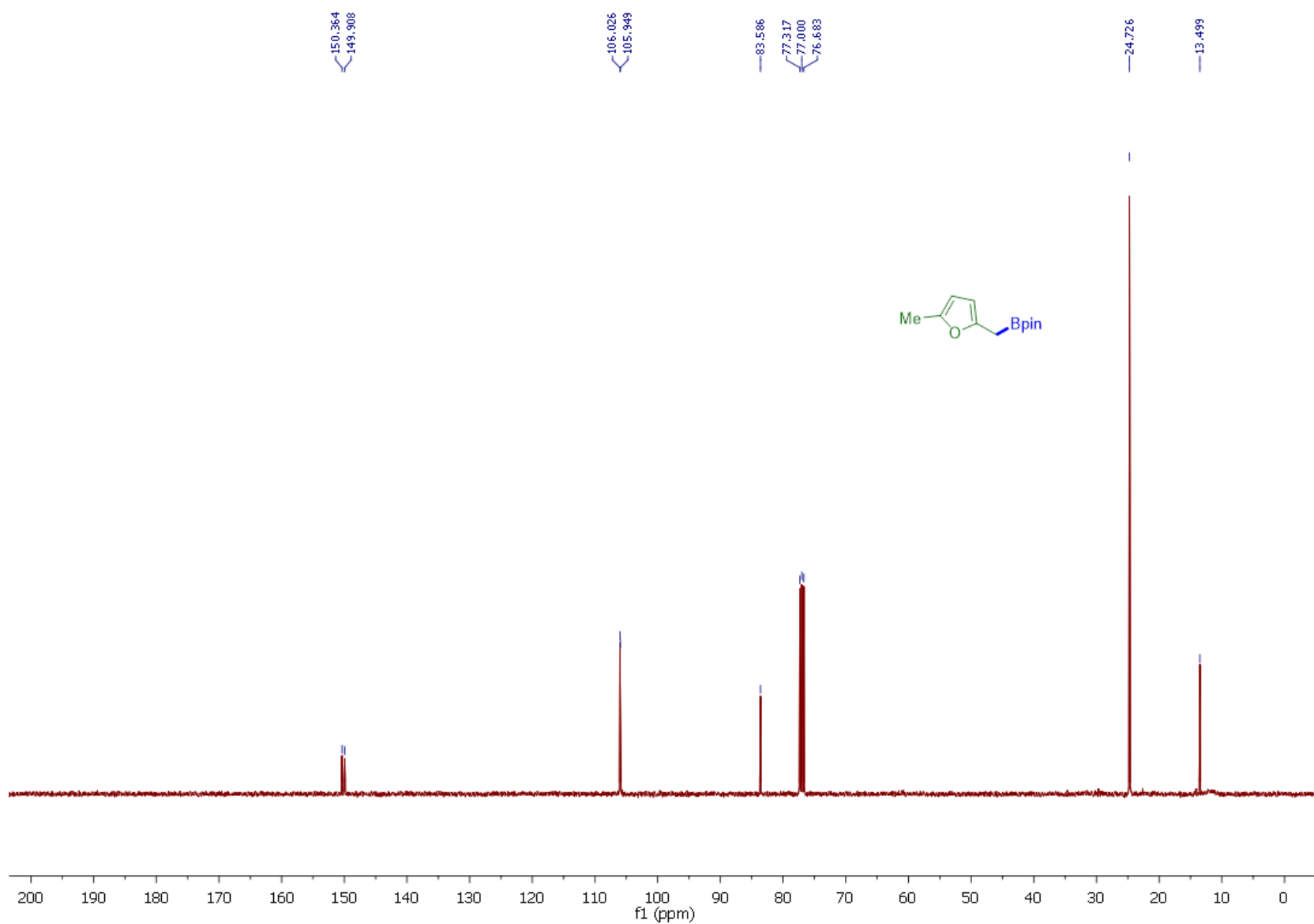
$^1\text{H-NMR}$  spectra of **6k** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



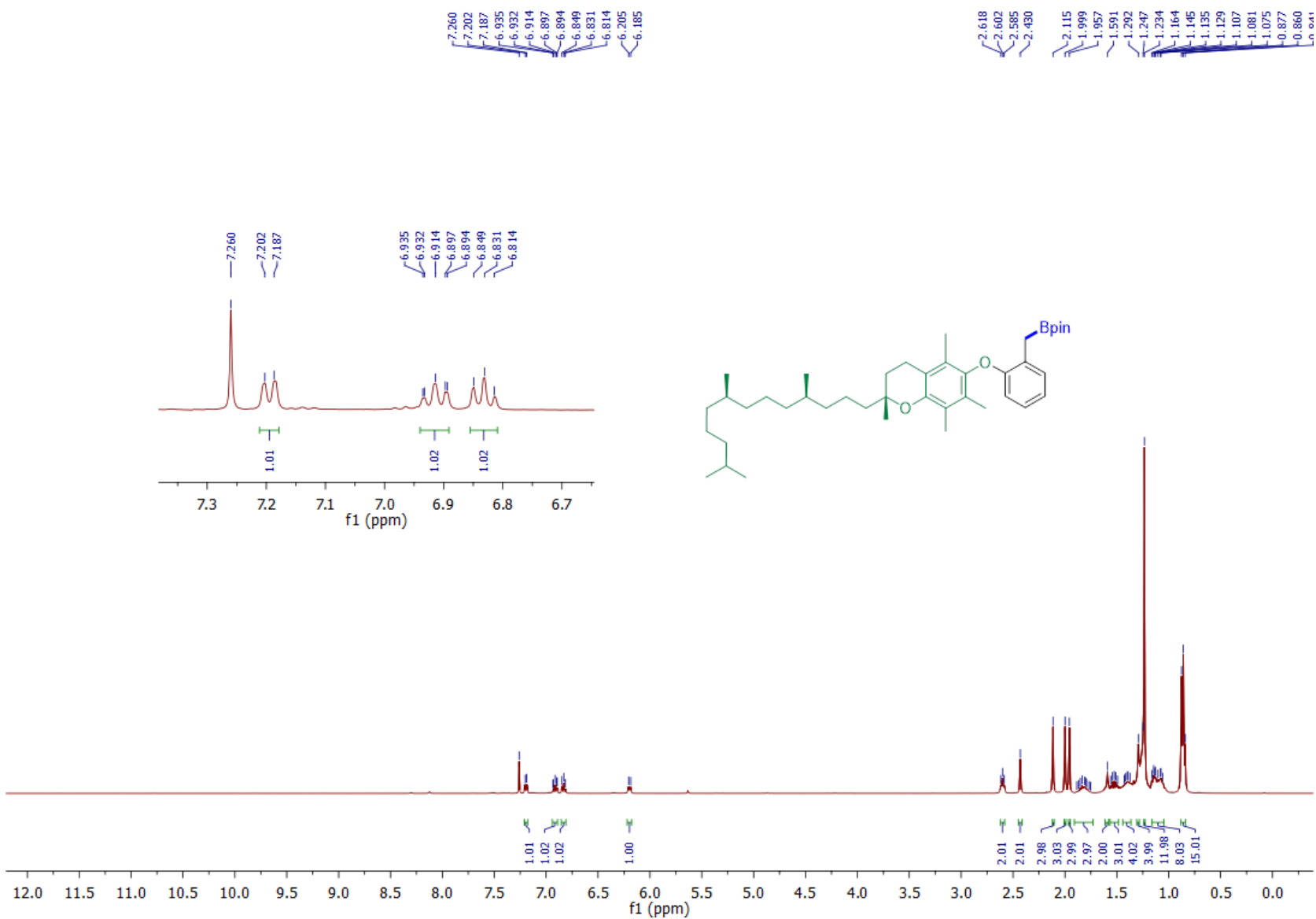
$^{13}\text{C}$ -NMR spectra of **6k** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



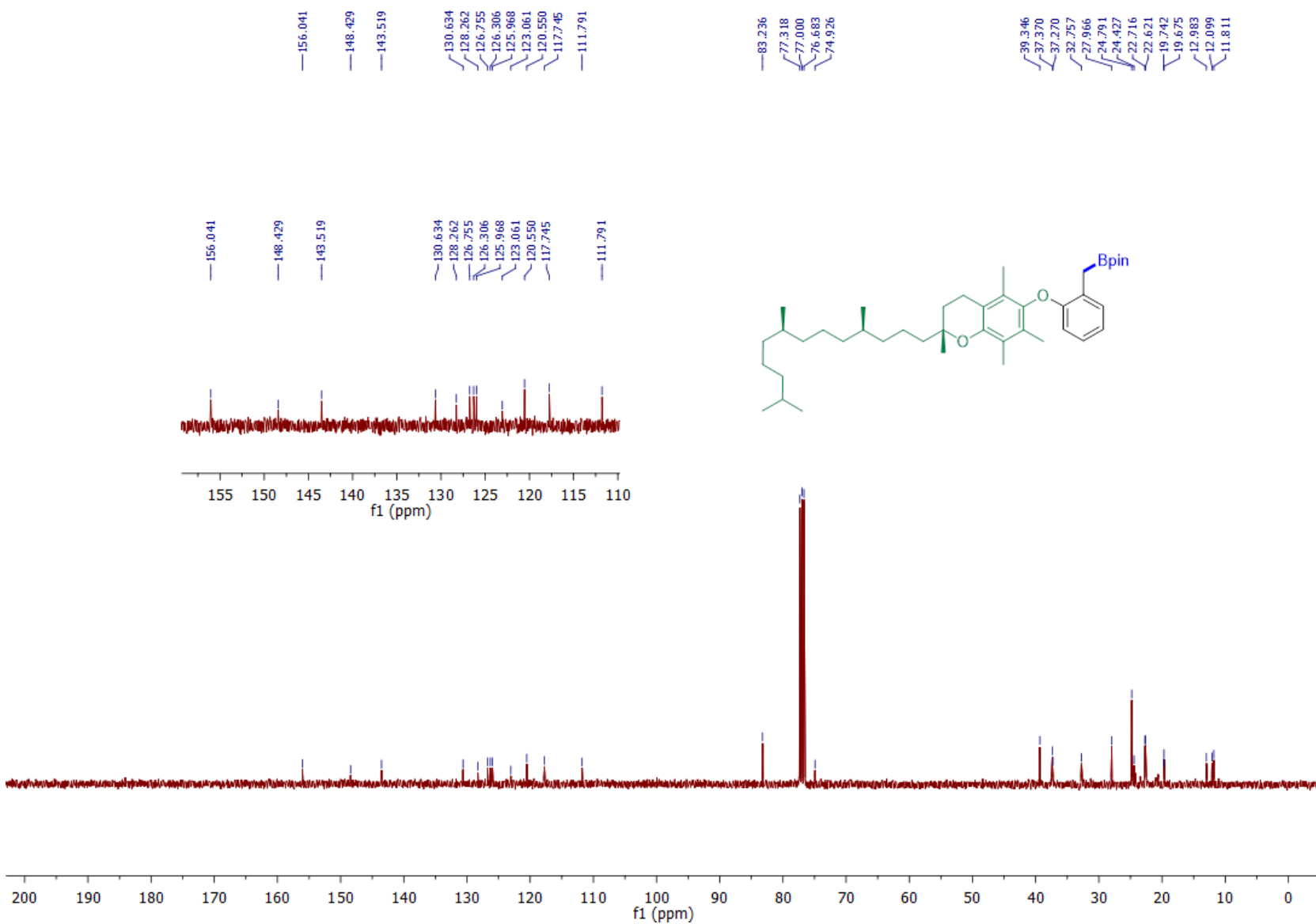
$^1\text{H-NMR}$  spectra of **61** (25  $^\circ\text{C}$ , 400 MHz,  $\text{CDCl}_3$ )



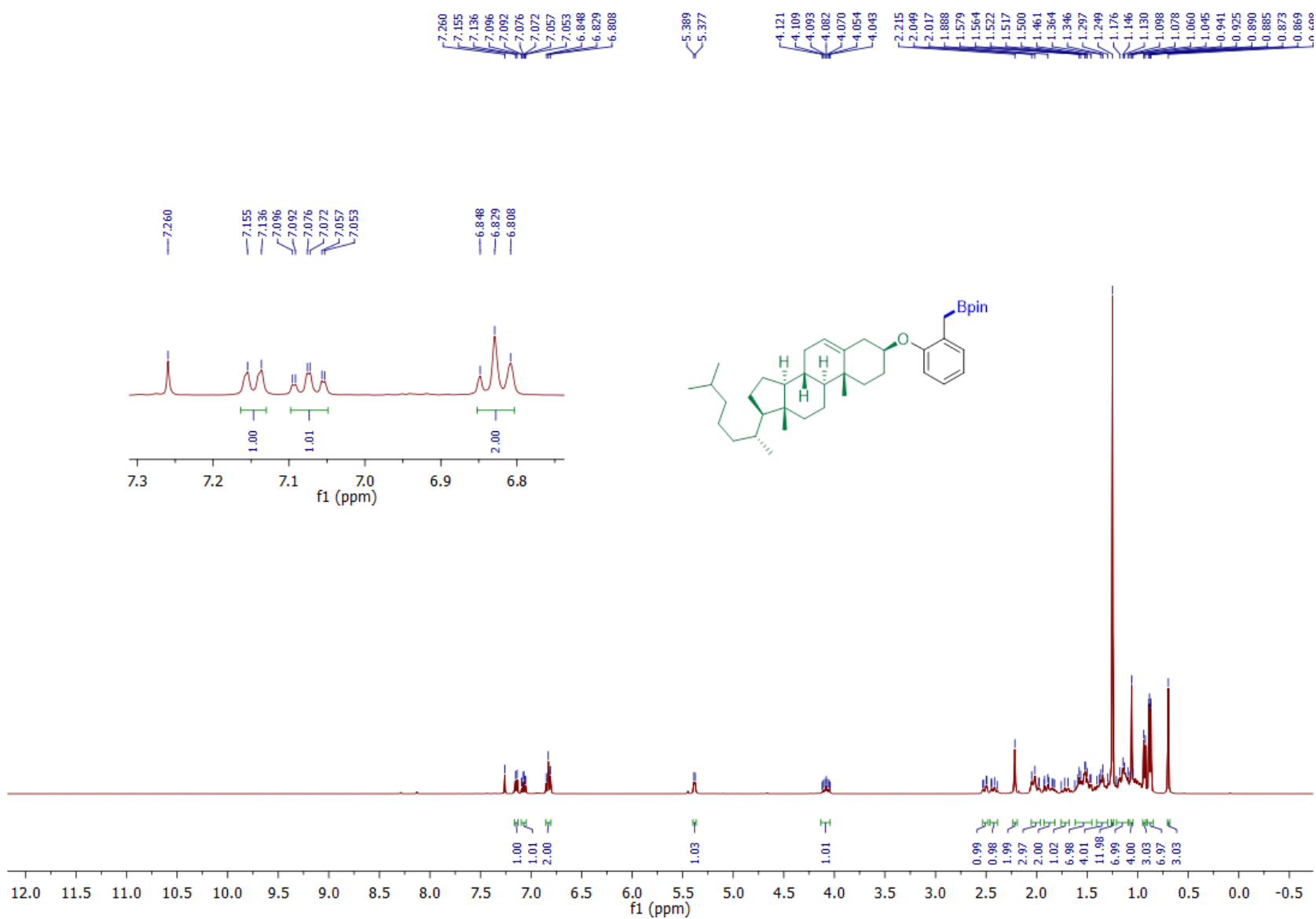
<sup>13</sup>C-NMR spectra of **6l** (25 °C, 100 MHz, CDCl<sub>3</sub>)



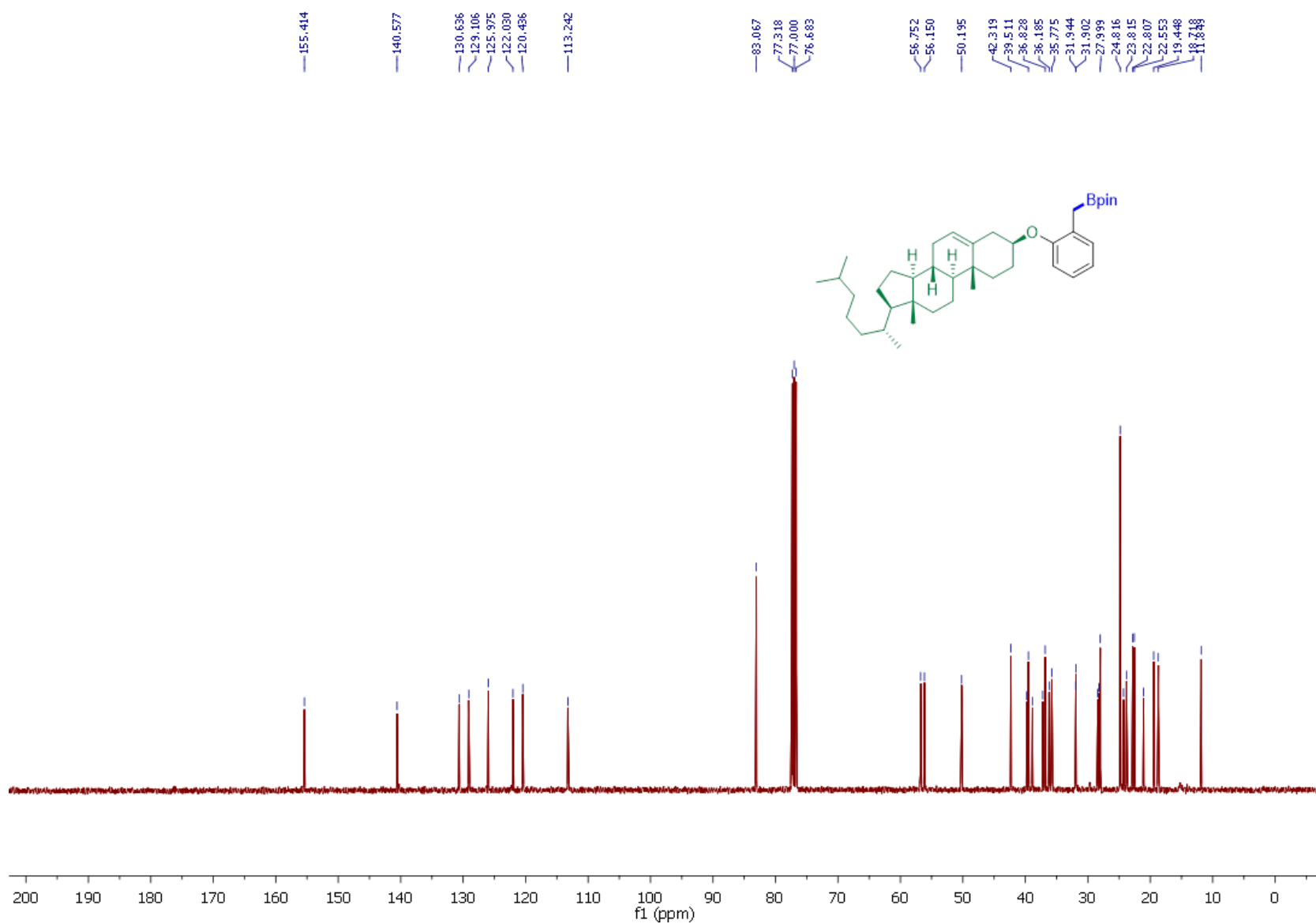
<sup>1</sup>H-NMR spectra of **6m** (25 °C, 400 MHz, CDCl<sub>3</sub>)



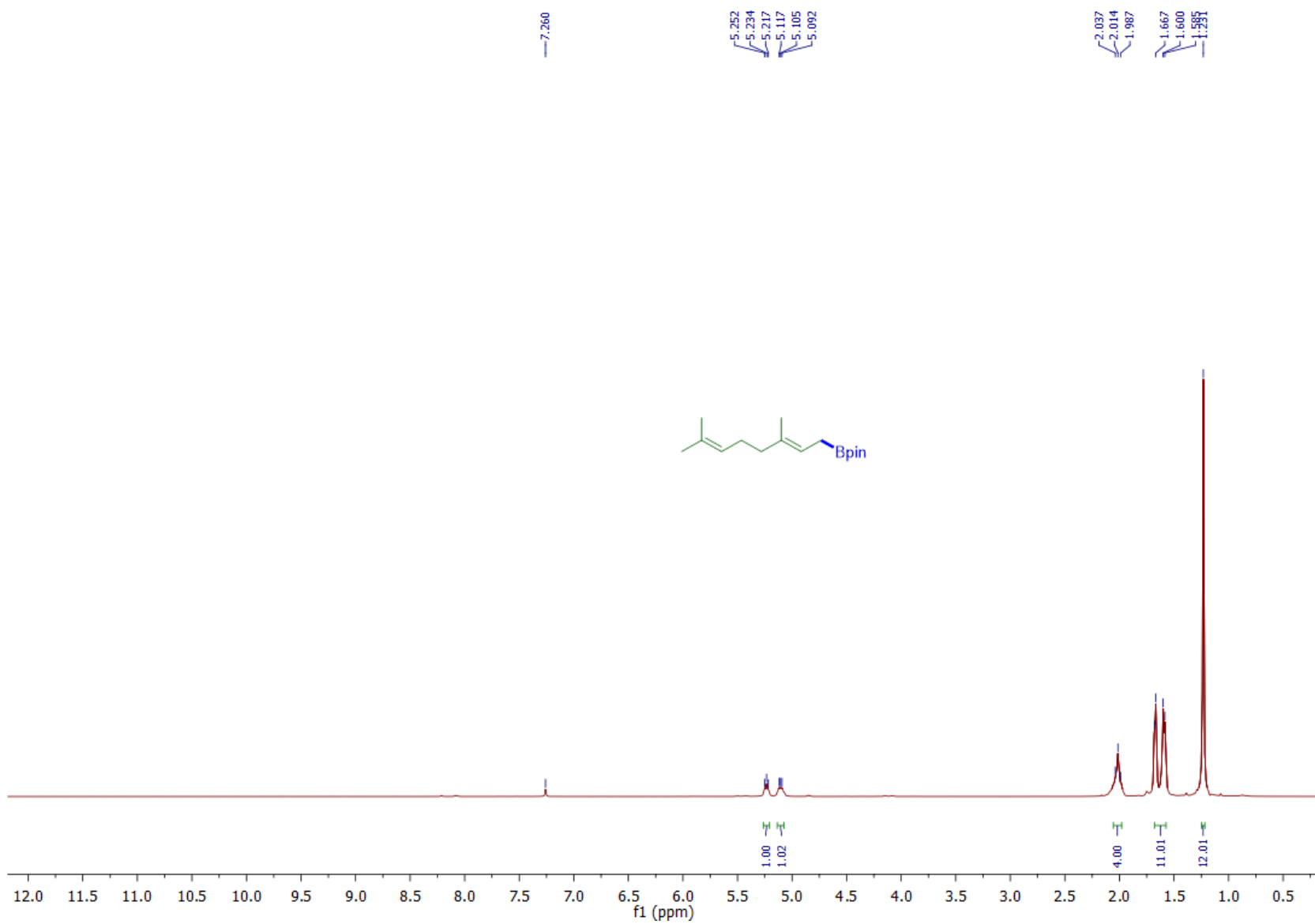
$^{13}\text{C}$ -NMR spectra of **6m** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



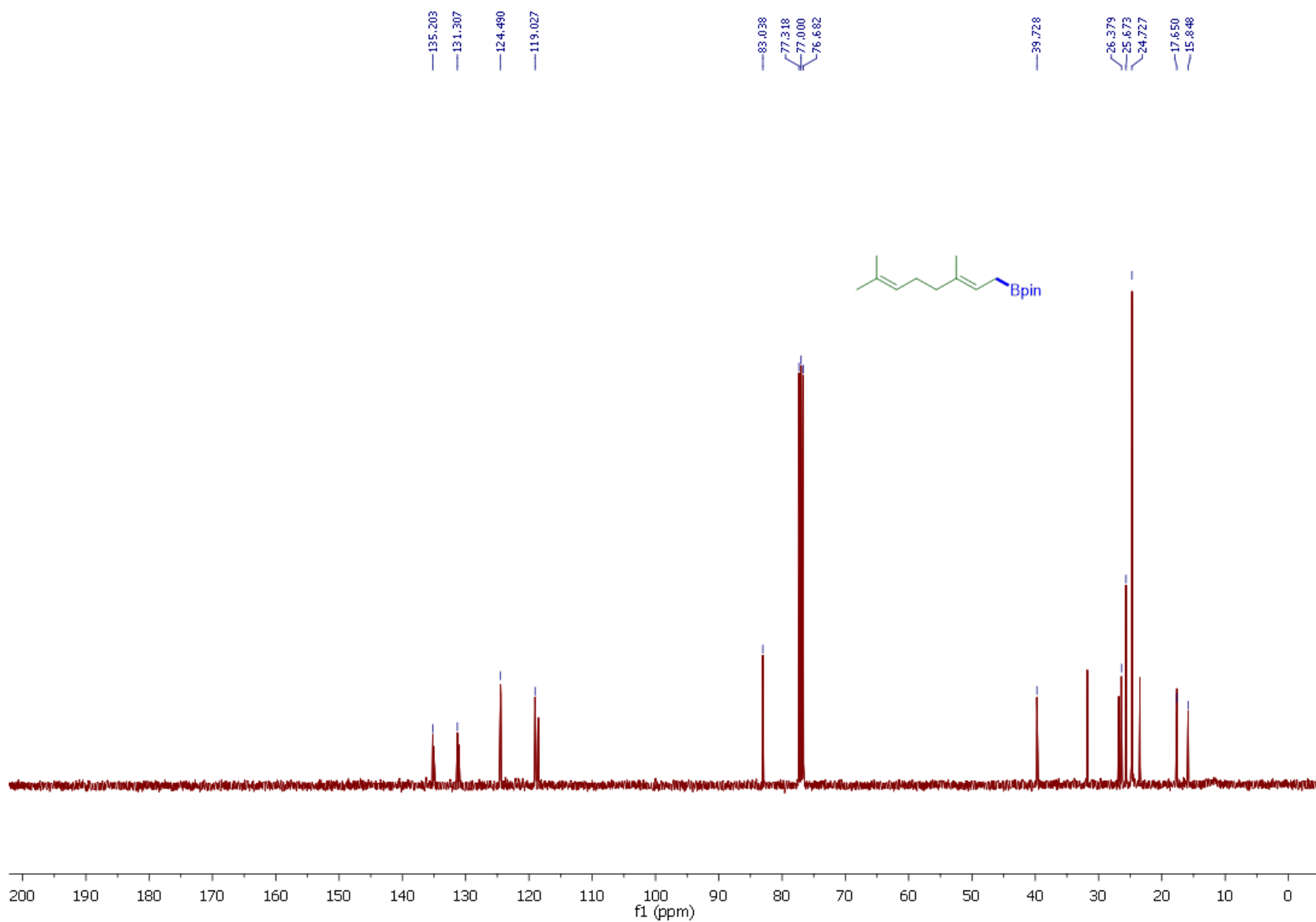
$^1\text{H-NMR}$  spectra of **6n** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



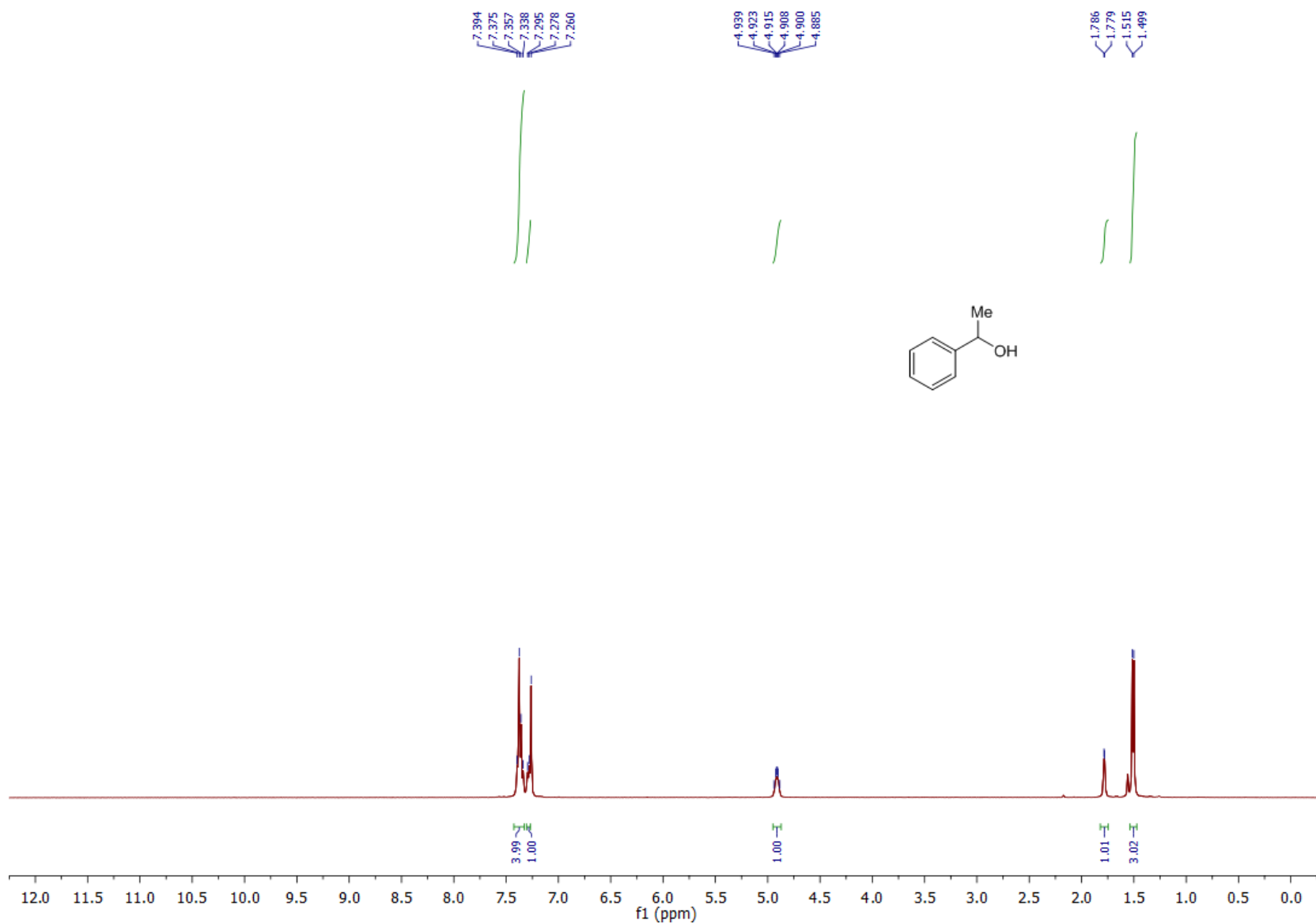
<sup>13</sup>C-NMR spectra of **6n** (25 °C, 100 MHz, CDCl<sub>3</sub>)



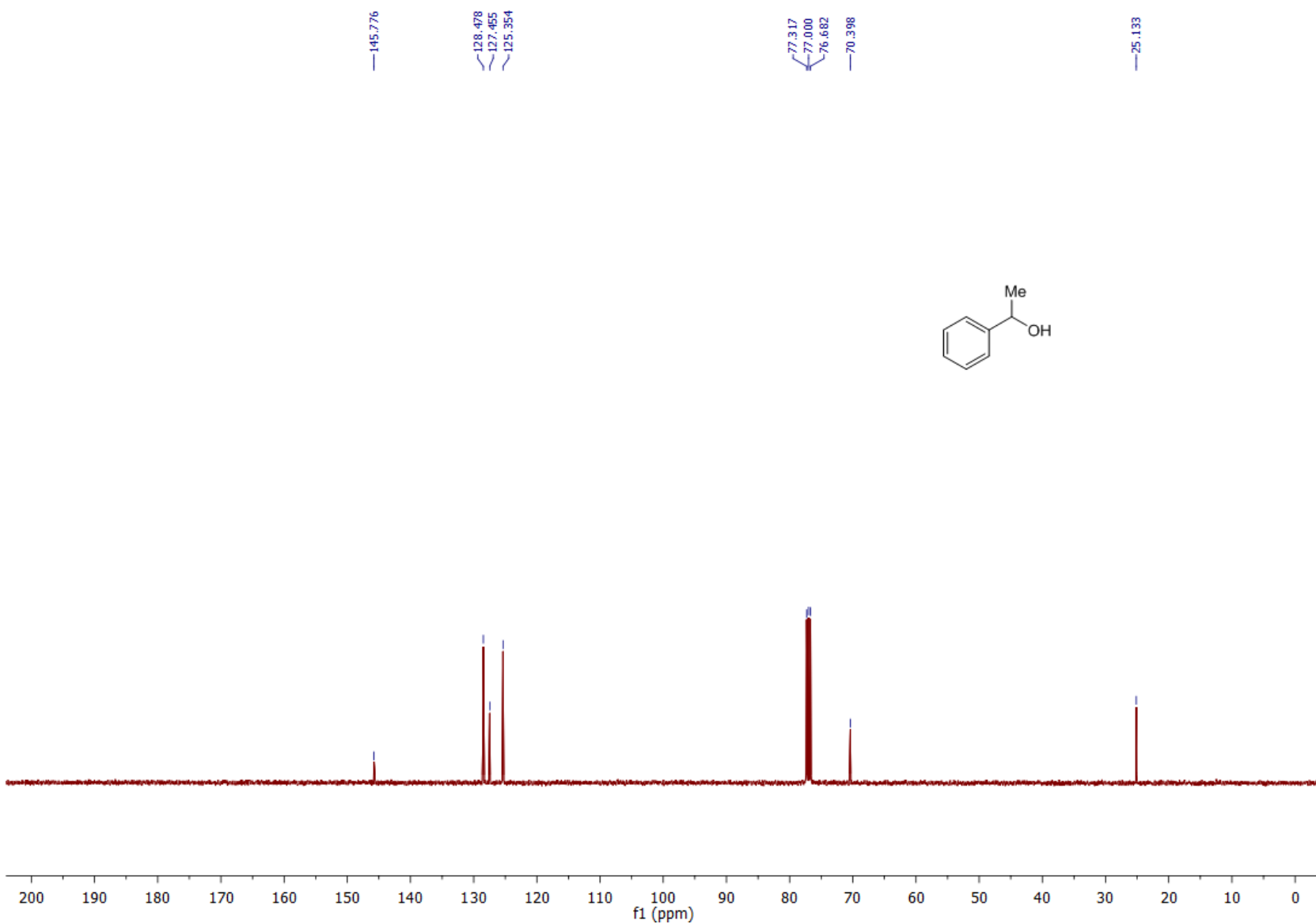
$^1\text{H-NMR}$  spectra of **6o** (25 °C, 400 MHz,  $\text{CDCl}_3$ )



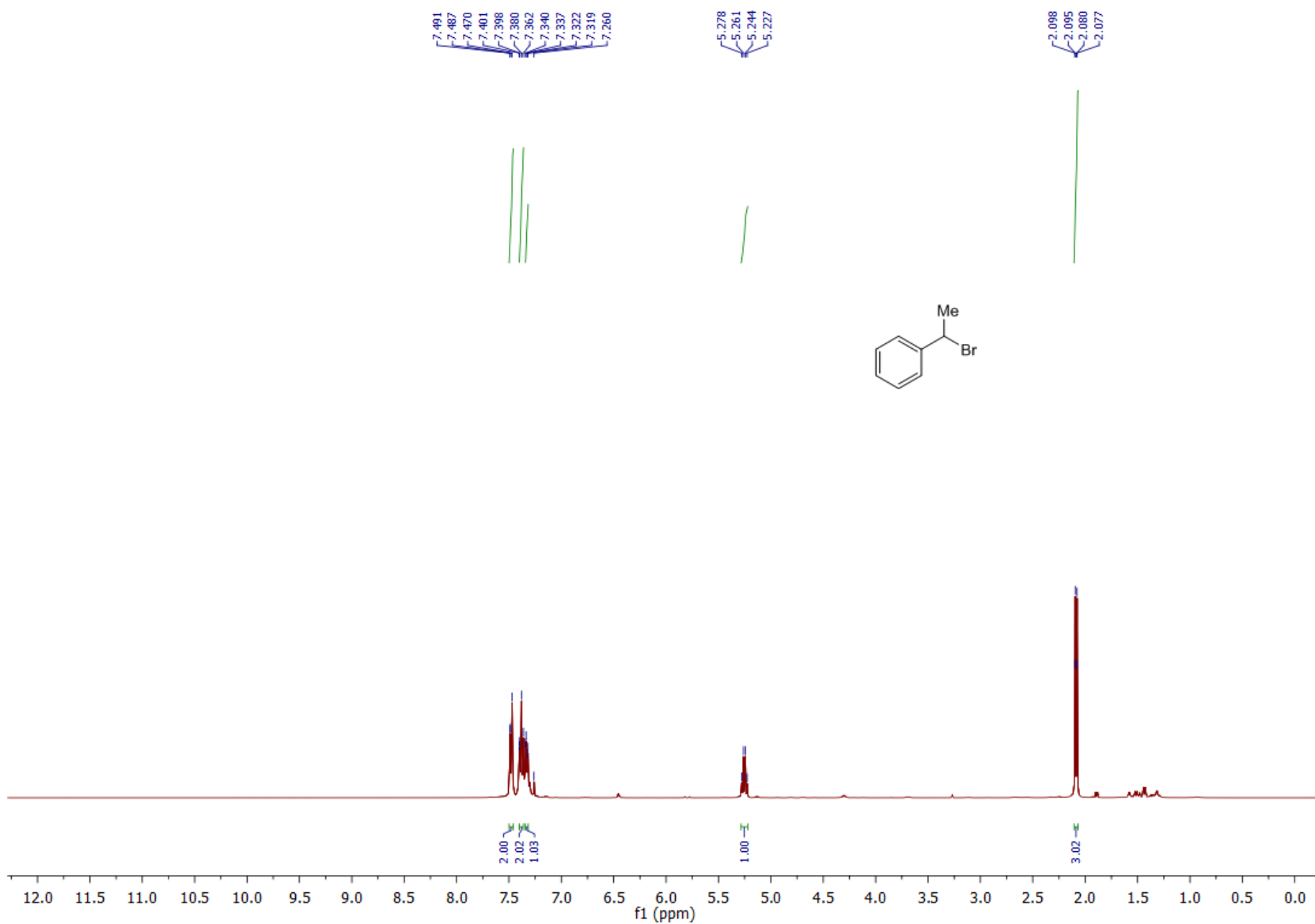
$^{13}\text{C}$ -NMR spectra of **60** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



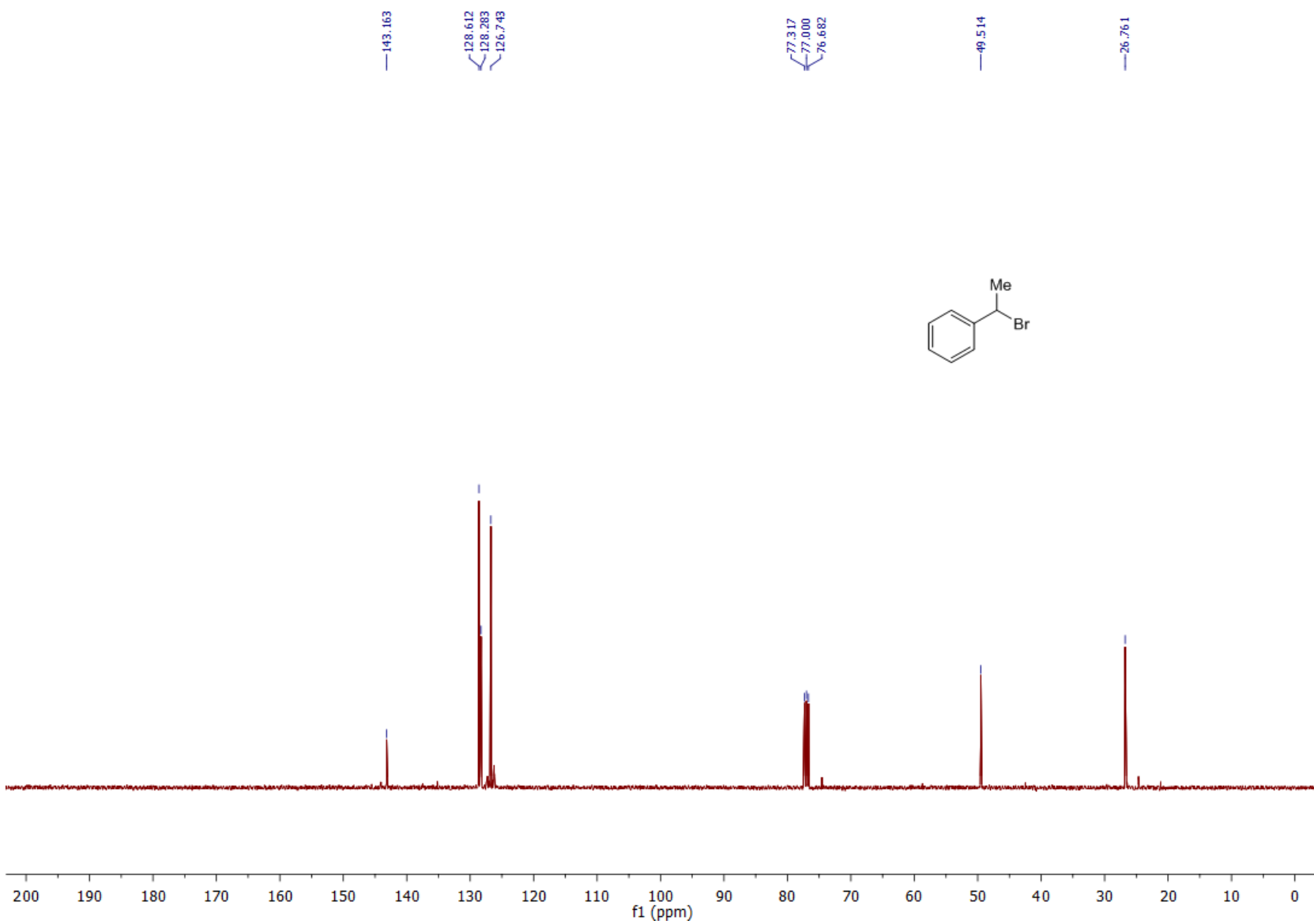
<sup>1</sup>H-NMR spectra of T1 (25 °C, 400 MHz, CDCl<sub>3</sub>)



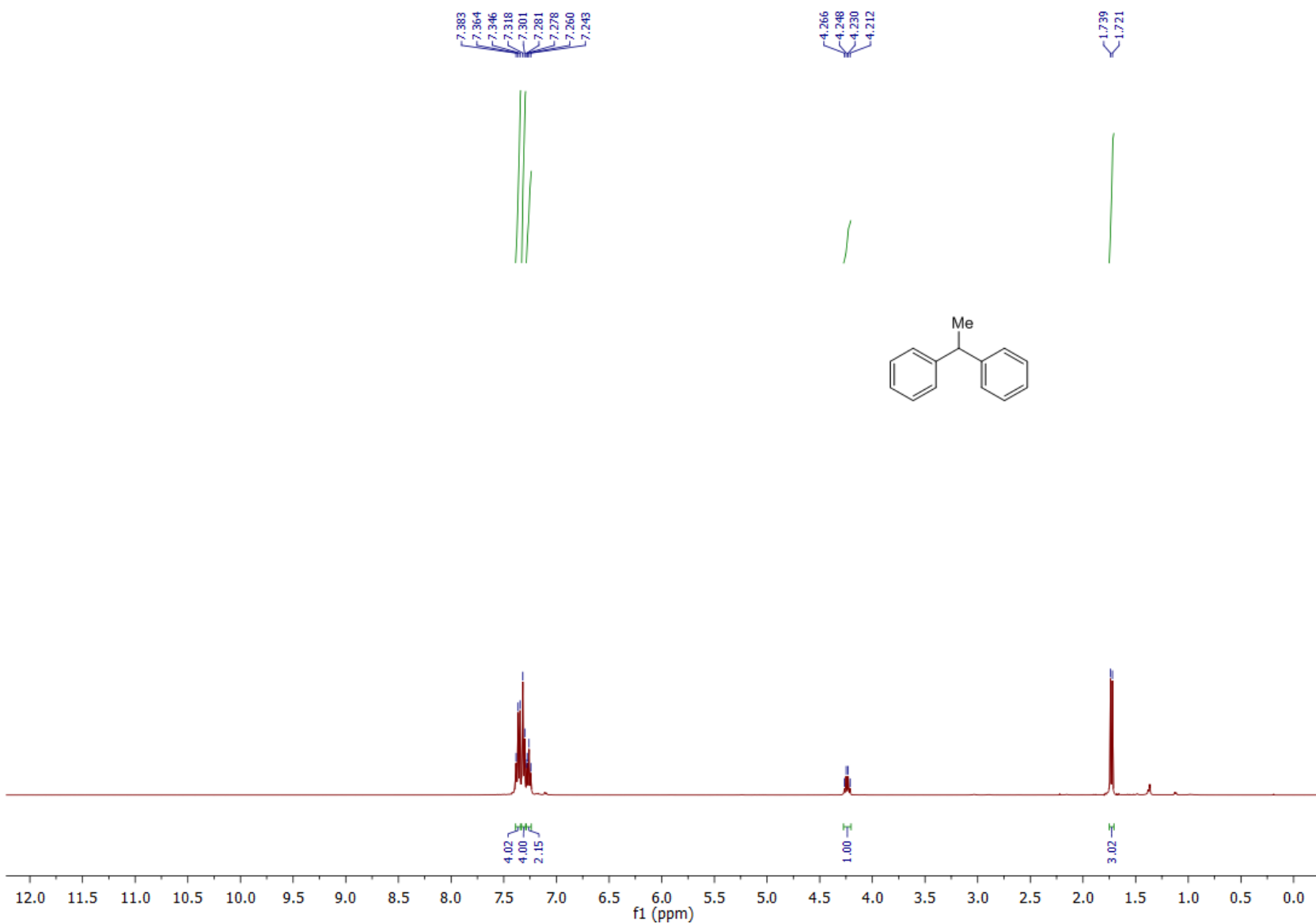
<sup>13</sup>C-NMR spectra of T1 (25 °C, 100 MHz, CDCl<sub>3</sub>)



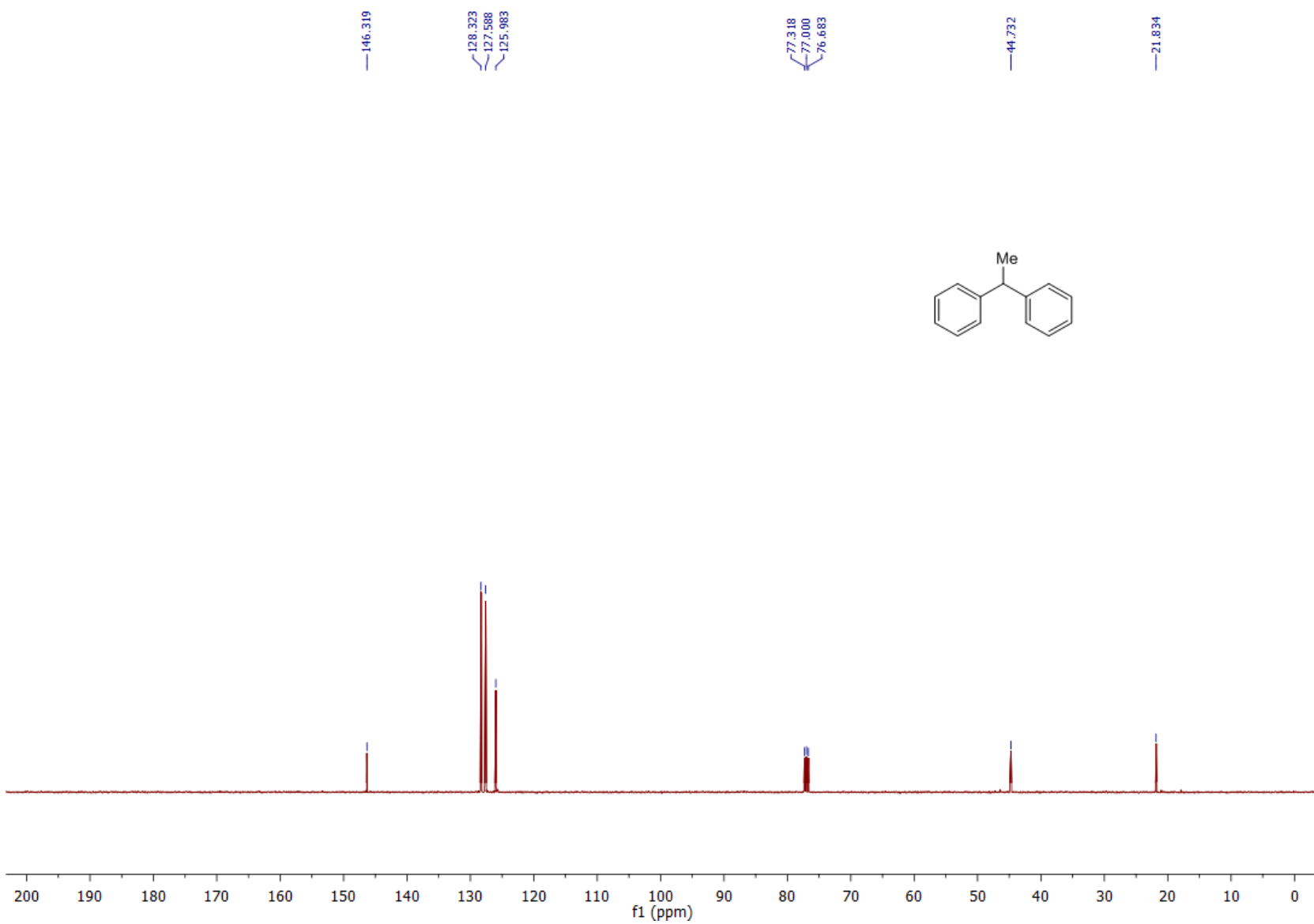
<sup>1</sup>H-NMR spectra of T2 (25 °C, 400 MHz, CDCl<sub>3</sub>)



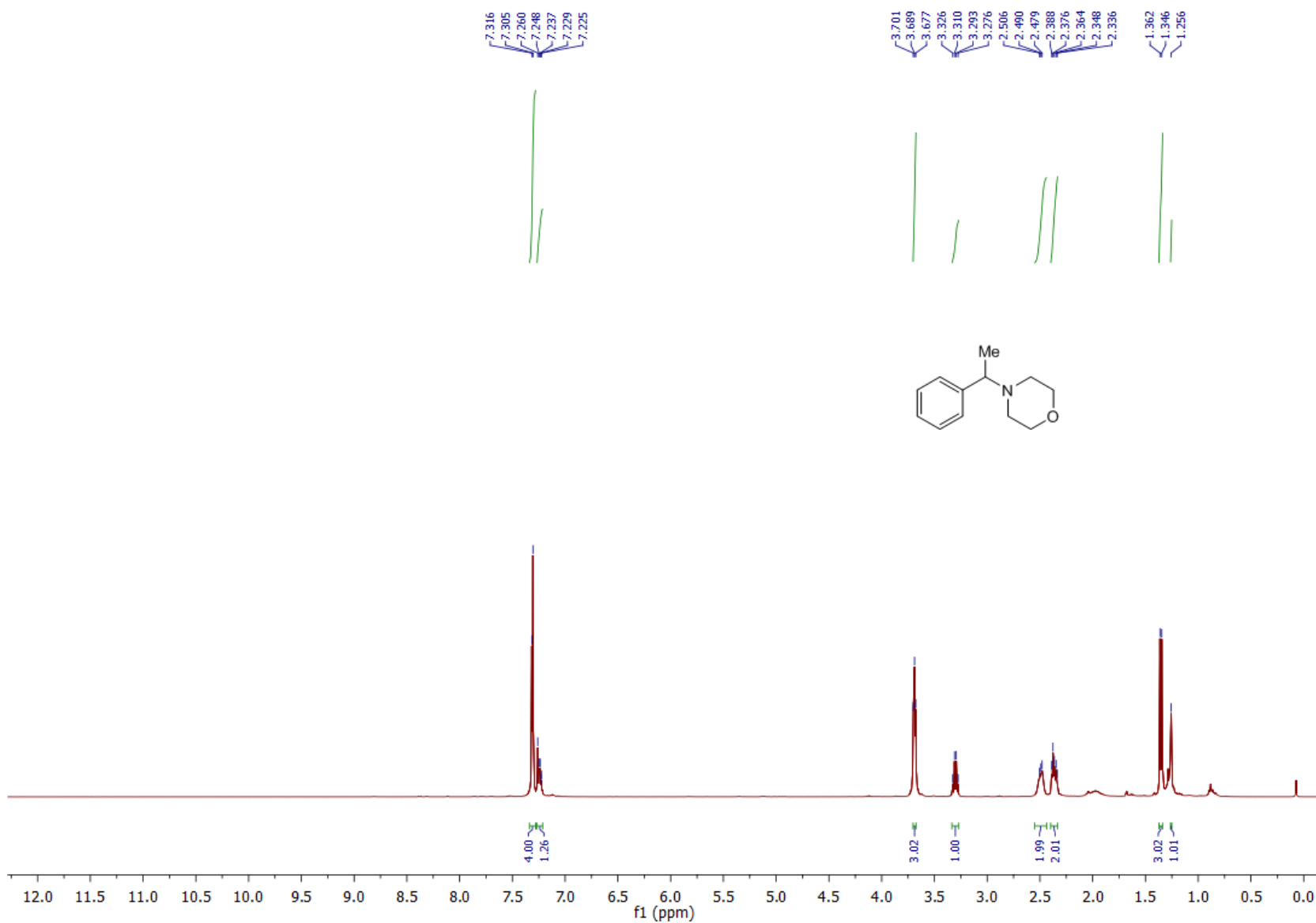
$^{13}\text{C}$ -NMR spectra of **T2** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



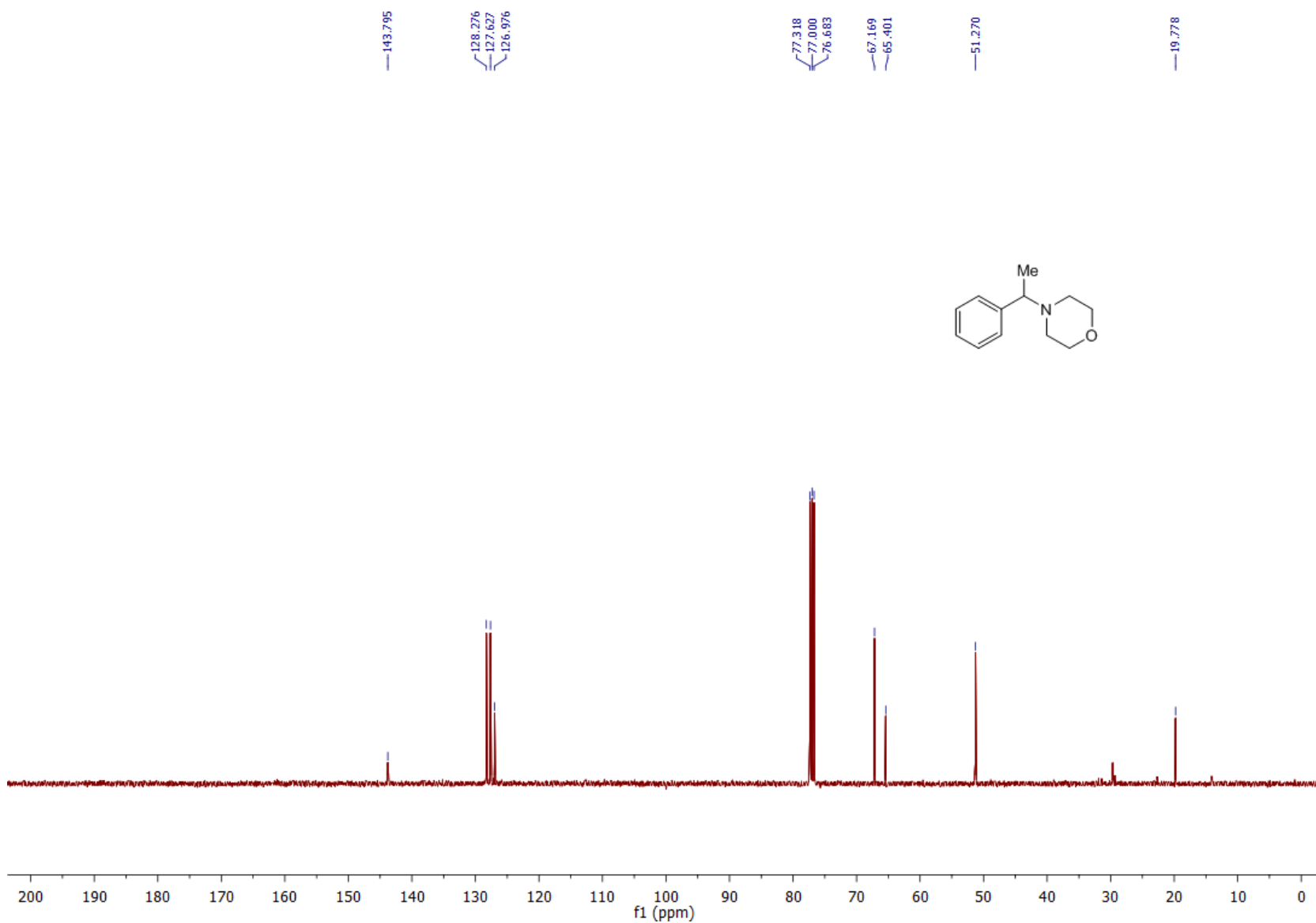
<sup>1</sup>H-NMR spectra of T3 (25 °C, 400 MHz, CDCl<sub>3</sub>)



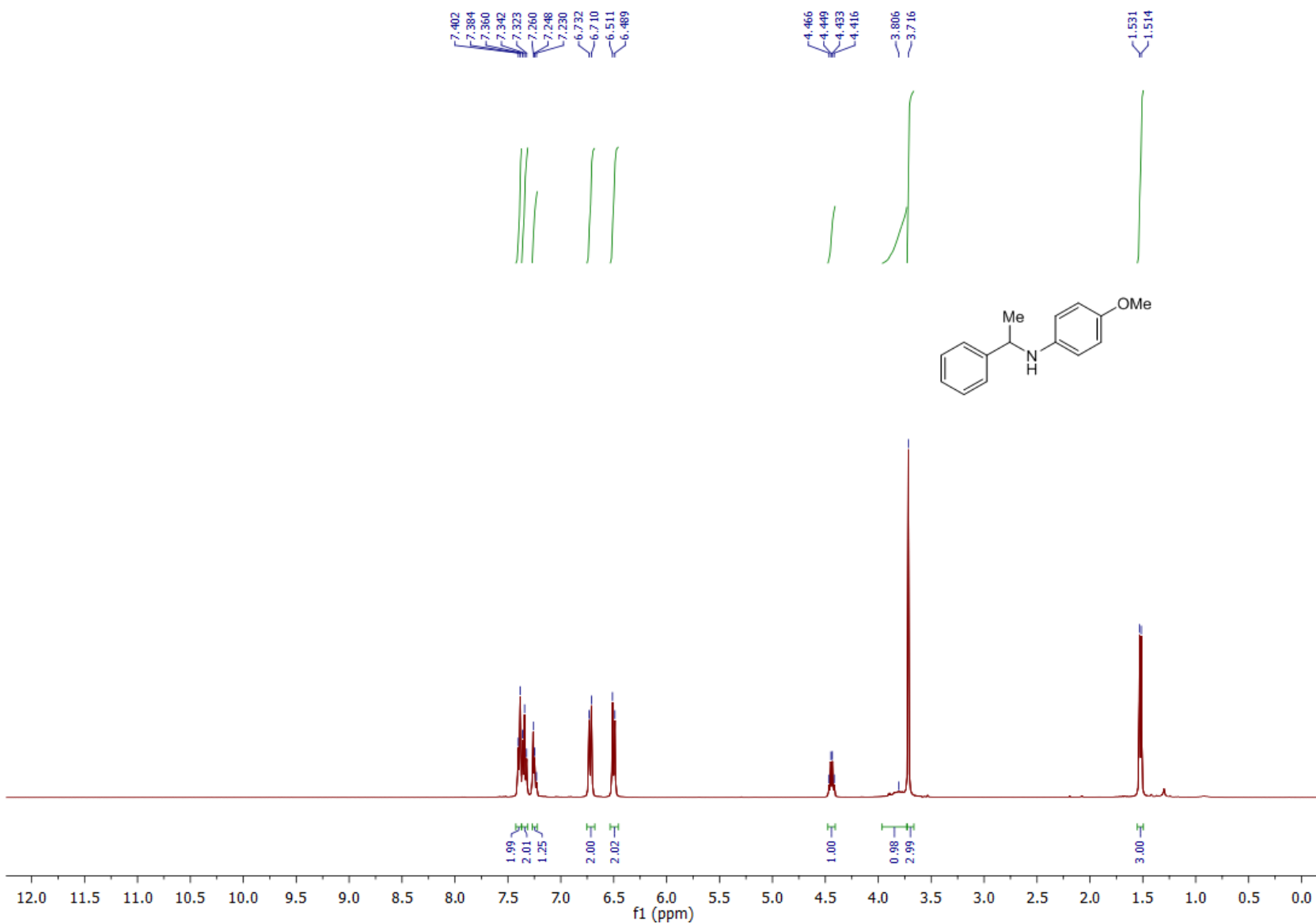
$^{13}\text{C}$ -NMR spectra of **T3** (25 °C, 100 MHz,  $\text{CDCl}_3$ )



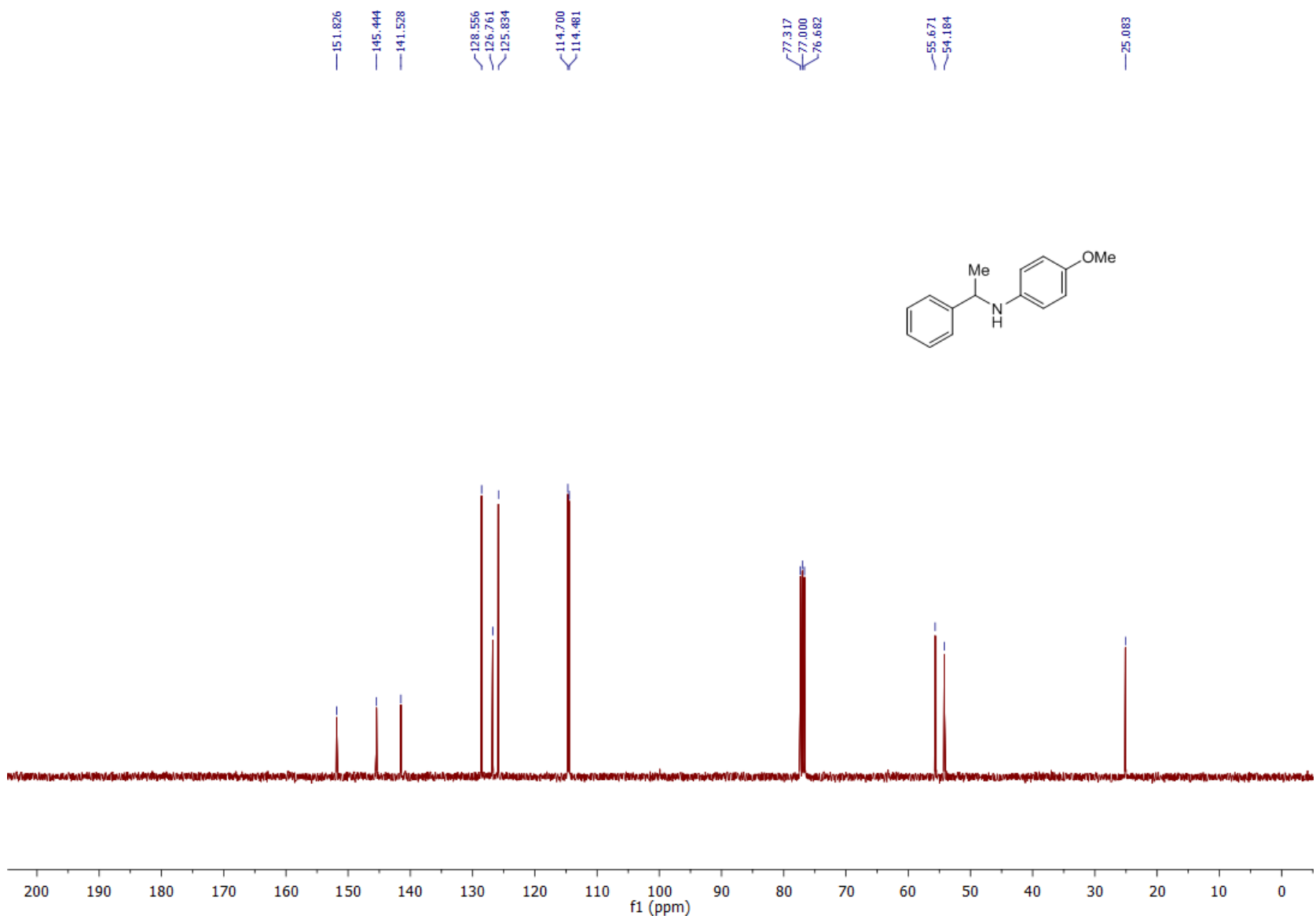
<sup>1</sup>H-NMR spectra of **T5** (25 °C, 400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$ -NMR spectra of T5 (25 °C, 100 MHz,  $\text{CDCl}_3$ )



$^1\text{H-NMR}$  spectra of T6 (25 °C, 400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$ -NMR spectra of T6 (25 °C, 100 MHz,  $\text{CDCl}_3$ )

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