Achieving High Ortho Selectivity in Aniline C–H Borylations by Modifying Boron Substituents

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Supporting Information

Experimental section

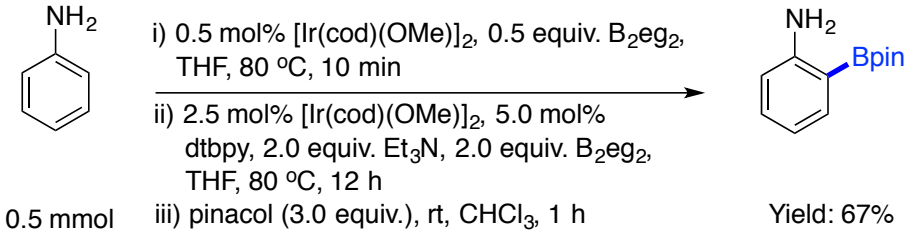
General information

All commercially available chemicals were used as received unless otherwise indicated. Pinacolborane (HBPin) and bis(pinacolato)diboron (B_2Pin_2) were procured from Sigma-Aldrich and A. K. Scientific respectively and used directly. B_2eg_2 was produced as previously reported from $B_2(OH)_4$ and ethylene glycol.[1] Bis(η^4-1,5-cyclooctadiene)-di-μ-methoxy-diiridium(I) $[Ir(OMe)COD]_2$ was procured from Sigma-Aldrich. Tetrahydrofuran (THF) were refluxed over sodium/benzophenone ketyl, distilled and degassed twice before borylation. Column chromatography was performed on flash silica gel (ACME, India). Thin layer chromatography was performed on 0.25 mm thick aluminum-backed silica gel plates purchased from Merck and visualized with ultraviolet light (λ = 254 nm). All borylations were conducted in an argon-filled glovebox, unless otherwise stated.

^1H, ^{13}C, and ^{11}B NMR spectra collected at the Centre of Biomedical Research (CBMR, Lucknow) were recorded on Bruker 400 MHz, 600 MHz and 800 MHz NMR spectrometers. ^1H, ^{13}C, and ^{11}B NMR spectra collected at Michigan State University were recorded on Varian 500 MHz NMR spectrometers. The boron bearing carbon atom was not observed due to quadrupolar relaxation. All coupling constants 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, dt = doublet of triplet, td = triplet of doublet, ttt = triplet of triplet of triplet). 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+). GC-MS (Agilent Technology) was obtained from Centre of Biomedical Research.

Ortho-borylation of aniline derivatives

Ortho-borylation of aniline (2a)

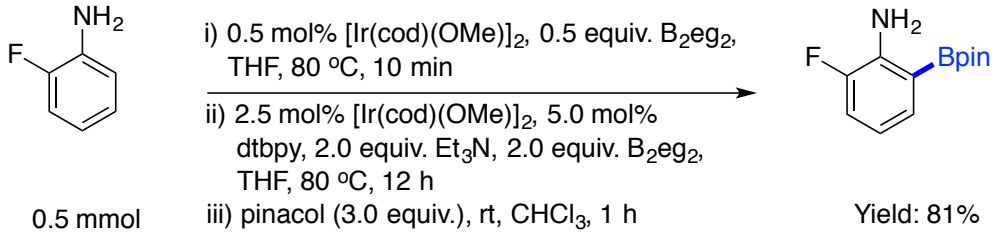


0.5 mmol

Yield: 67%

In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), aniline (46.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 µL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 73.4 mg of ortho-borylated aniline (67%) as a liquid. Spectral data are in accordance with the reported data.[2]

Ortho-borylation of 2-fluoroaniline (2b)



0.5 mmol

Yield: 81%

In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 2-fluoroaniline (55.6 mg, 0.5 mmol) dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 96.0 mg of ortho-borylated 2-fluoroaniline (81%) as a solid (mp = 50-51 °C).

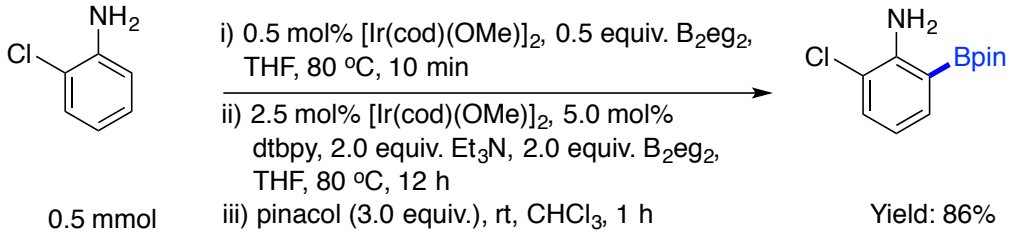
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.2 Hz, 1H), 7.03 (ddd, J = 11.6, J = 8.0, J = 1.2 Hz, 1H), 6.59 (dt, J = 7.6, J = 4.0 Hz, 1H), 4.82 (br, 2H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2 (d, J = 237.7 Hz), 141.7 (d, J = 11.1 Hz), 131.6 (d, J = 3.6 Hz), 117.7 (d, J = 18.1 Hz), 116.4 (d, J = 6.2 Hz), 83.7, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calcd for $C_{12}H_{18}BFNO_2$ $[M+H]^+$ 238.1415, found: 238.1404.

Ortho-borylation of 2-chloroaniline (2c)



0.5 mmol

Yield: 86%

In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 2-chloroaniline (63.8 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C and stirred. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 109.0 mg of ortho-borylated 2-chloroaniline (86%) as a white solid (mp = 84-85 °C).

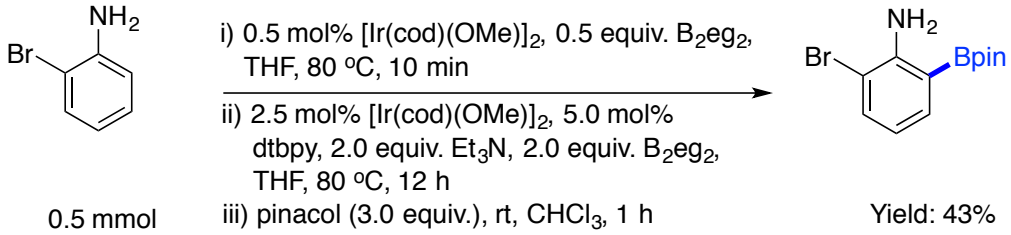
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.31 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 6.60 (t, J = 7.6 Hz, 1H), 5.22 (bs, 2H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 135.3, 132.5, 118.9, 117.1, 83.9, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.2.

HRMS (ESI) *m/z* calcd for $C_{12}H_{18}BClNO_2$ $[M+H]^+$ 254.1119, found: 254.1109.

Ortho-borylation of 2-bromoaniline (2d)



0.5 mmol

Yield: 43%

In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 2-bromoaniline (86.0 mg, 0.5 mmol), dry THF (0.5 ml) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 64.0 mg of ortho-borylated 2-bromoaniline (43%) as a light yellow solid (mp = 82-83 °C).

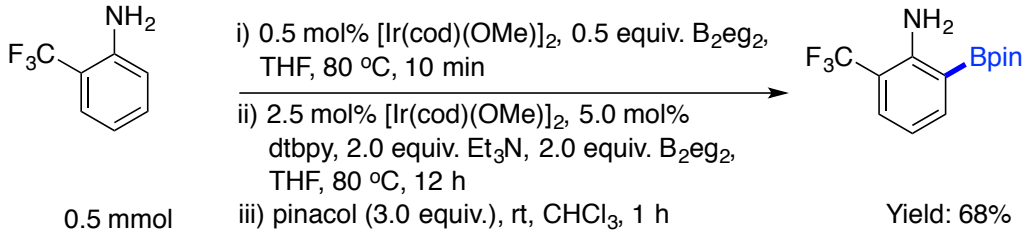
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 7.2 Hz, 1H), 7.48 (dd, J = 7.6 Hz, J = 0.8 Hz, 1H), 6.54 (t, J = 7.6 Hz, 1H), 5.28 (bs, 2H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 136.0, 135.9, 117.6, 109.5, 83.9, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.5.

HRMS (ESI) *m/z* calcd for $C_{12}H_{18}BBrNO_2$ $[M+H]^+$ 298.0614, found: 298.0607.

Ortho-borylation of 2-trifluoromethylaniline (2e)



0.5 mmol

Yield: 68%

In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 2-trifluoromethylaniline (80.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 97.6 mg of ortho-borylated 2-trifluoromethylaniline (68%) as a white solid (mp = 89-90 °C).

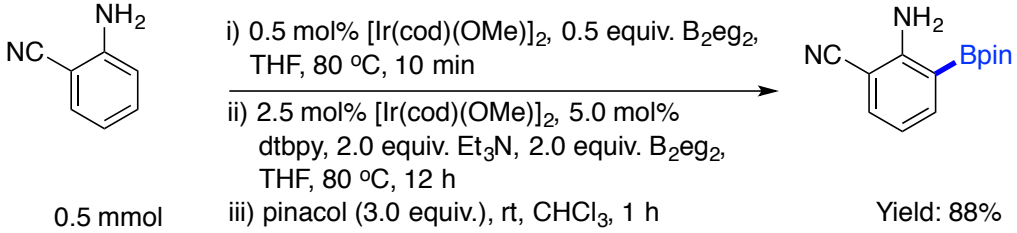
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 7.2 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 6.69 (t, J = 7.6 Hz, 1H), 5.38 (bs, 2H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1 (d, J =1.5 Hz), 140.9, 130.1 (q, J = 5.3 Hz), 125.2 (d, J = 270.7 Hz), 115.7, 112.9 (q, J = 29.1 Hz), 84.0, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$):δ 30.6

HRMS (ESI) *m/z* calcd for $C_{13}H_{18}BF_3NO_2$ $[M+H]^+$ 288.1383, found: 288.1376.

Ortho-borylation of 2-aminobenzonitrile (2f)



0.5 mmol

Yield: 88%

In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 2-aminobenzonitrile (59.1 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a Teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 107.4 mg of ortho-borylated 2-aminobenzonitrile (88%) as a light yellow solid (mp = 95-96 °C).

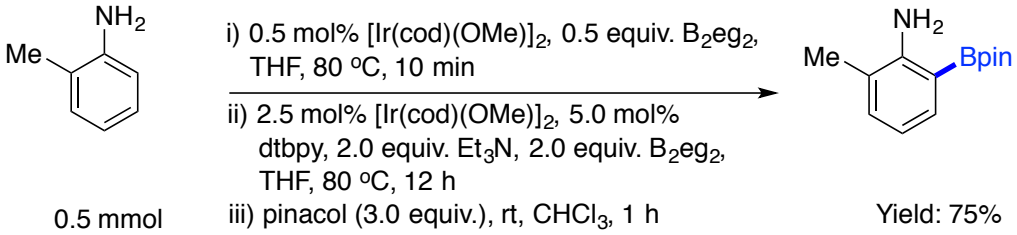
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 7.2 Hz, J = 1.6 Hz, 1H), 7.45 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 6.65 (t, J = 7.6 Hz, 1H), 5.55 (bs, 2H), 1.35 (s, 12H).

^{13}C NMR (200 MHz, $CDCl_3$): δ 155.5, 141.9, 135.9, 117.9, 116.3, 95.4, 84.2, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calcd for $NaC_{13}H_{17}BN_2O_2$ $[M+Na]^+$ 267.1281, found: 267.1275.

Ortho-borylation of 2-methylaniline (2g)



0.5 mmol

Yield: 75%

In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 2-methylaniline (53.6 mg, 0.5 mmol), dry THF (0.5 ml) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 87.4 mg of ortho-borylated 2-methylaniline (75%) as a white solid (mp = 44-45 °C).

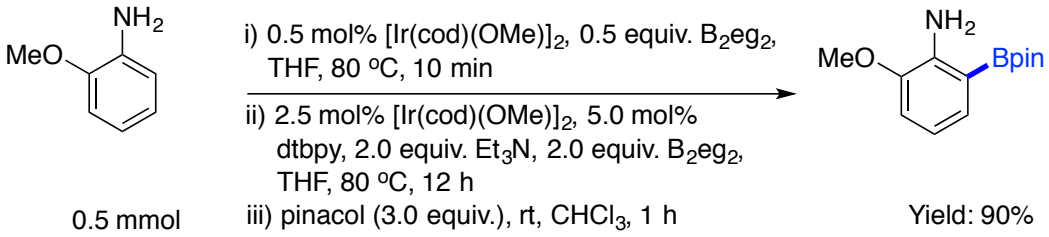
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.2 Hz, 1H), 7.13 (d, J = 6.8 Hz, 1H), 6.65 (t, J = 7.2 Hz, 1H), 4.77 (bs, 2H), 2.14 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 134.7, 133.7, 121.4, 116.8, 83.5, 24.9, 17.5.

^{11}B NMR (128 MHz, $CDCl_3$):δ 31.2.

HRMS (ESI) *m/z* calcd for $C_{13}H_{21}BNO_2$ $[M+H]^+$ 234.1665, found: 234.1662.

Ortho-borylation of 2-methoxyaniline (2h)



0.5 mmol

Yield: 90%

In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 2-methoxyaniline (61.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 µL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 112.0 mg of ortho-borylated 2-methoxyaniline (90%) as a white solid (mp = 102-103 °C).

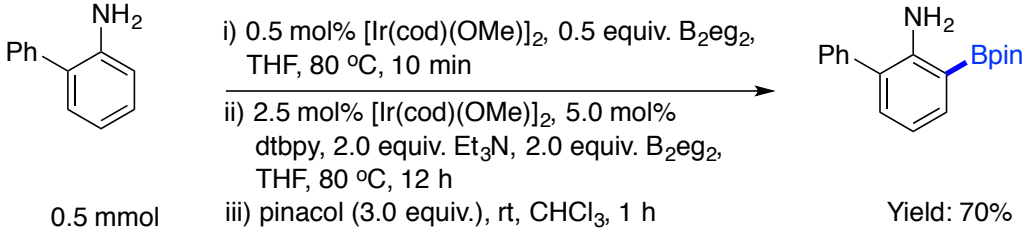
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, J = 7.6 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.64 (t, J = 7.6 Hz, 1H), 4.97 (bs, 2H), 3.84 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 143.9, 128.0, 116.2, 112.8, 83.5, 55.5, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.0.

HRMS (ESI) *m/z* calcd for $C_{13}H_{21}BNO_3$ $[M+H]^+$ 250.1614, found: 250.1612.

Ortho-borylation of 2-phenylaniline (2i)



0.5 mmol

Yield: 70%

In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 2-phenylaniline (84.6 mg, 0.5 mmol) and dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 103.0 mg of ortho-borylated 2-phenylaniline (70%) as a white solid (mp = 39-40 °C).

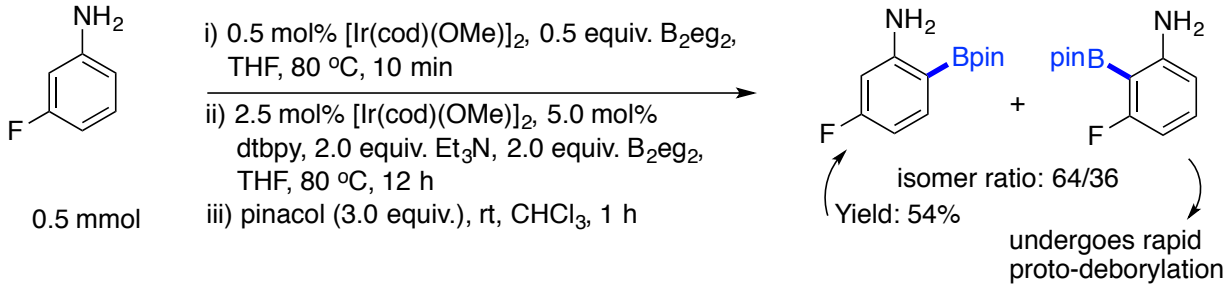
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.44 (s, 2H), 7.43 (d, J = 1.2, 2H), 7.34-7.36 (m, 1H), 7.17 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 6.75 (t, J = 7.6 Hz, 1H), 4.92 (bs, 2H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 139.8, 136.4, 133.8, 129.3, 128.8, 127.1, 127.0, 116.8, 83.6, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.7.

HRMS (ESI) *m/z* calcd for $C_{18}H_{23}BNO_2$ $[M+H]^+$ 296.1822, found: 296.1816.

Ortho-borylation of 3-fluroaniline (2j)



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 3- fluoroaniline (55.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Analyzing the crude reaction mixture it was observed that two ortho isomers were formed and the ratio is shown in the above scheme. Moreover, 4% diborylation was observed, but due to less amount of the product, it was not characterized. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 64.0 mg of ortho-borylated 3-fluoroaniline (major isomer 54%) as a brown solid (mp = 44-46 °C). Minor (mp = 82-84 °C).

Data of Major Isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (t, J = 7.6 Hz, 1H), 6.36 (td, J = 8.4, J = 2.0 Hz, 1H), 6.26 (dd, J = 11.6, J = 2.4 Hz, 1H), 4.87 (br, 2H), 1.33 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4 (d, J = 246.5 Hz), 155.7 (d, J = 11.4 Hz), 138.9 (d, J = 10.5 Hz), 104.2 (d, J = 20.7 Hz), 100.9 (d, J = 23.3 Hz), 83.6, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.2.

HRMS (ESI) *m/z* calcd for $C_{12}H_{18}BFNO_2$ $[M+H]^+$ 238.1415, found: 238.1406.

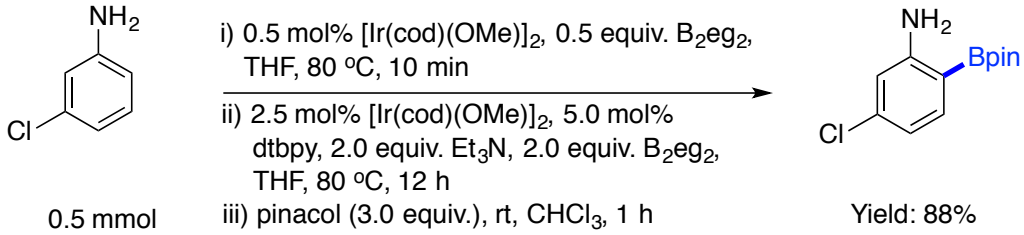
Data of Minor Isomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.09-7.13 (m, 1H), 6.35 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 6.31 (ddd, J = 9.6 Hz, J = 7.8 Hz, J = 0.6 Hz, 1H), 4.95 (bs, 2H), 1.36 (s, 12H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.1 (d, J = 247.2 Hz), 155.4 (d, J = 10.9 Hz), 133.5 (d, J = 11.7 Hz), 110.5 (d, J = 2.4 Hz), 103.5 (d, J = 25.1 Hz), 83.4, 24.8.

^{11}B NMR (192 MHz, $CDCl_3$): δ 30.4.

HRMS (ESI) *m/z* calcd for $C_{12}H_{18}BFNO_2$ $[M+H]^+$ 238.1415, found: 238.1408.

Ortho-borylation of 3-chloroaniline (2k)



0.5 mmol

Yield: 88%

In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 3-chloroaniline (63.8 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 111.3 mg of ortho-borylated 3-chloroaniline (88%) as a white solid (mp = 64-65 °C).

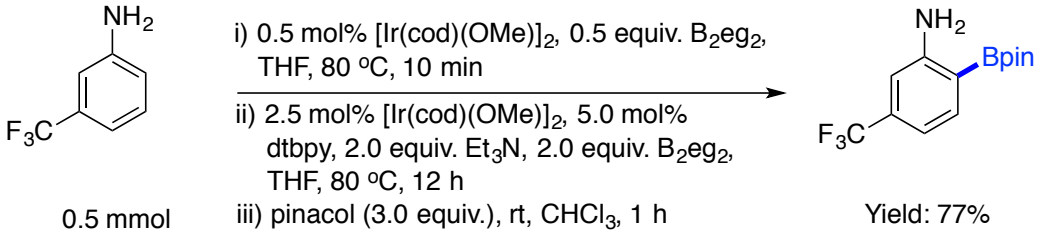
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.0 Hz, 1H), 6.63 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 6.58 (d, J = 1.6 Hz, 1H), 4.81 (bs, 2H), 1.33 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 138.6, 138.0, 117.1, 114.2, 83.7, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.6.

HRMS (ESI) *m/z* calcd for $C_{12}H_{18}BClNO_2$ $[M+H]^+$ 254.1119, found: 254.1114.

Ortho-borylation of 3-trifluoromethylaniline (2l)

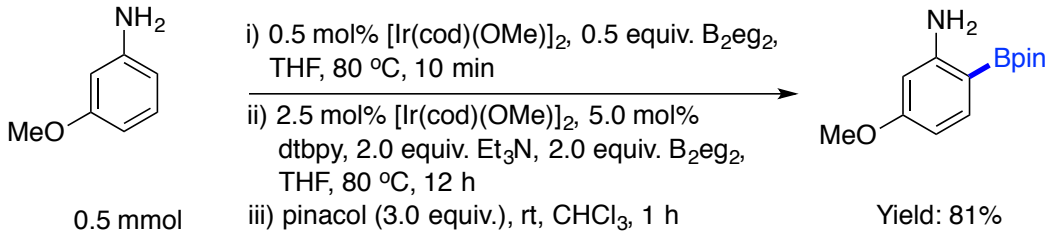


0.5 mmol

Yield: 77%

In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 3-trifluoromethylaniline (80.6 mg, 0.5 mmol), dry THF (0.5 mL), and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 110.5 mg of ortho-borylated 3-trifluoromethylaniline (77%) as a solid (mp = 64-65 °C). Spectral data are in accordance with the reported data.[3]

Ortho-borylation of 3-methoxyaniline (2m)

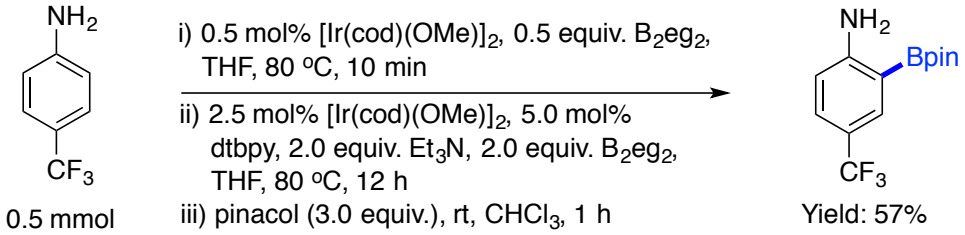


0.5 mmol

Yield: 81%

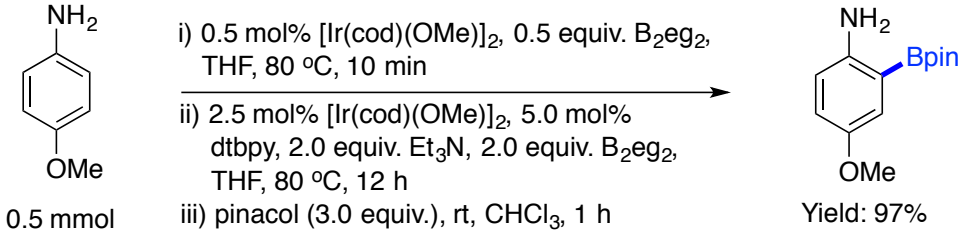
In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 3-methoxyaniline (61.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 101.0 mg of ortho-borylated 3-methoxyaniline (81%) as a white solid (mp = 32-33 °C). Spectral data are in accordance with the reported data.[3]

Ortho-borylation of 4-trifluoromethylaniline (2n)



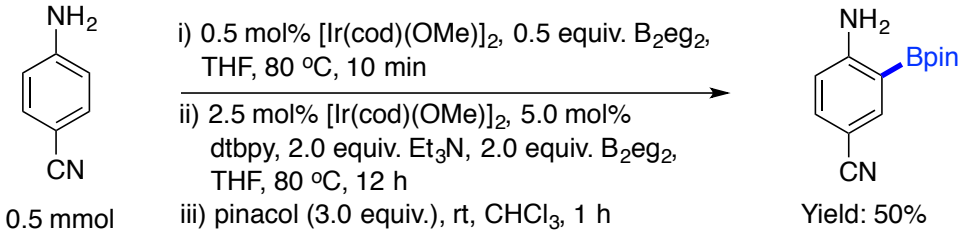
In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 4-trifluoromethylaniline (80.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 82.0 mg of ortho-borylated 4-trifluoromethylaniline (57%) as a solid (mp = 110-113 °C). Spectral data are in accordance with the reported data.[3]

Ortho-borylation of 4-methoxyaniline (2o)



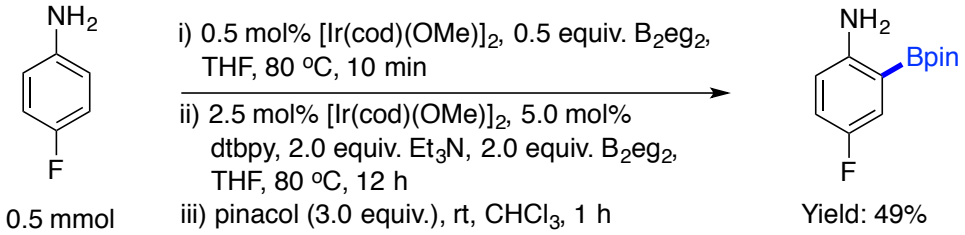
In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 4-methoxyaniline (61.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 120.0 mg of ortho-borylated 4-methoxyaniline (97%) as a white solid (mp = 73-74 °C). Spectral data are in accordance with the reported data.[3]

Ortho-borylation of 4-aminobenzonitrile (2p)



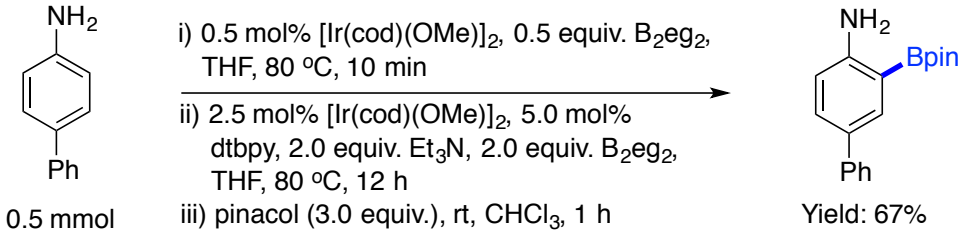
In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 4-aminobenzonitrile (59.1 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 61.0 mg of ortho-borylated 4-aminobenzonitrile (50%) as a white solid (mp = 96-97 °C). Spectral data are in accordance with the reported data.[3]

Ortho-borylation of 4-fluoroaniline (2q)



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 4-fluoroaniline (61.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Analyzing the crude reaction mixture, it was observed that 20% *o,o*-di-borylation, however, due to minor amount, it was not isolated. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 58.0 mg of ortho-borylated 4-fluoroaniline (49%) as a white solid (mp = 29-30 °C). Spectral data are in accordance with the reported data.[3]

Ortho-borylation of 4-phenylaniline (2r)



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 4-phenylaniline (84.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 99.0 mg of ortho-borylated 4-phenylaniline (67%) as a white solid (mp = 146-147 °C).

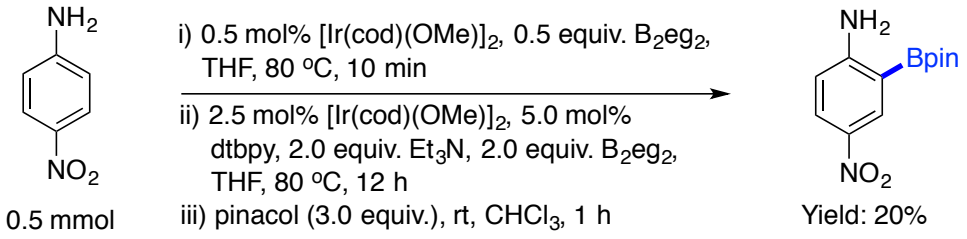
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 2.4 Hz, 1H), 7.57 (d, J = 7.2 Hz, 2H), 7.49 (dd, J = 8.4 Hz, J = 2.4 Hz, 1H), 7.38 (t, J = 7.2 Hz, 2H),7.24 (t, J = 6.8 Hz, 1H),6.68 (d, J = 8.4 Hz, 1H), 4.83 (bs, 2H), 1.36 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 141.2, 135.3, 131.5, 129.8, 128.5, 126.4, 125.9, 115.2, 83.6, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.4.

HRMS (ESI) *m/z* calcd for $C_{18}H_{23}BNO_2$ $[M+H]^+$ 296.1822, found: 296.1818.

Ortho-borylation of 4-nitroaniline (2s)



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 4-nitroaniline (69.1 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 µL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Analyzing the crude mixture, it was found that the GC conversion of the product was 50%, but during isolation via chromatographic separation with silica gel (1% EtOAc in hexane as eluent) 26.4 mg of ortho-borylated 4-nitroaniline (20%) was obtained as a yellow solid (mp = 159-160 °C).

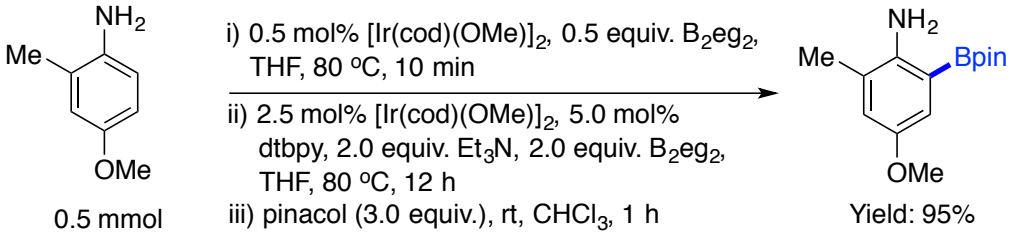
^{1}H NMR (800 MHz, $CDCl_3$): δ 8.54 (d, J = 2.4 Hz, 1H), 8.07 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 6.53 (d, J = 8.8 Hz, 1H), 5.52 (bs, 2H), 1.35 (s, 12H).

^{13}C NMR (200 MHz, $CDCl_3$): δ 158.6, 137.9, 134.2, 128.8, 113.7, 84.4, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 38.3.

HRMS (ESI) *m/z* calcd for $NaC_{12}H_{17}BN_2O_4$ $[M+Na]^+$ 287.1179, found: 287.1170.

Ortho-borylation of 2-methyl-4-methoxyaniline (2t)



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 2-methyl-4-methoxyaniline (68.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 125.0 mg of ortho-borylated 2-methyl-4-methoxyaniline (95%) as a solid (mp = 65-66 °C).

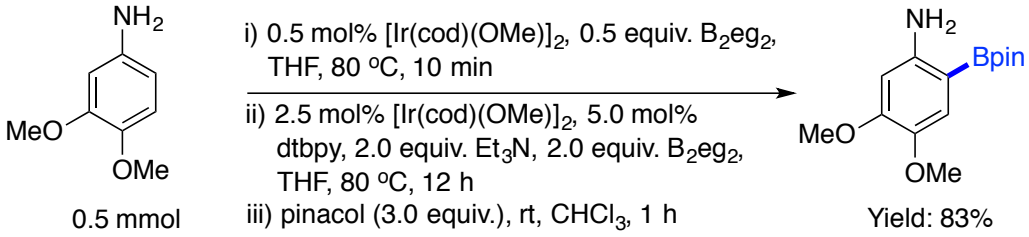
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, J = 3.2 Hz, 1H), 6.79 (d, J = 3.2 Hz 1H), 4.49 (bs, 2H), 3.76 (s, 3H), 2.13 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 146.1, 123.7, 121.8, 117.0, 83.6, 55.8, 24.9, 17.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calcd for $C_{14}H_{23}BNO_3$ $[M+H]^+$ 264.1771, found: 264.1764.

Ortho-borylation of 3,4-dimethoxyaniline (2u)



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 3,4-dimethoxyaniline (76.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 µL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 116.0 mg of ortho-borylated 3,4-dimethoxyaniline (83%) as a solid (mp = 124-125 °C).

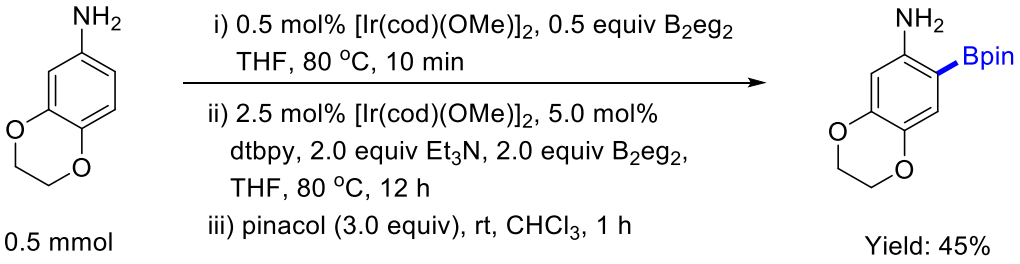
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (s, 1H), 6.18 (s, 1H), 4.56 (bs, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 1.33 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 149.5, 141.1, 118.5, 99.3, 83.3, 56.5, 55.6, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.5.

HRMS (ESI) *m/z* calcd for $C_{14}H_{23}BNO_4$ $[M+H]^+$ 280.1720, found: 280.1714.

Ortho-borylation of 3,4-ethylenedioxy aniline (2v)



0.5 mmol

Yield: 45%

In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2(35.5 mg, 0.5 equiv.), 3,4-ethylenedioxy aniline (75.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (10% EtOAc in hexane as eluent) gave 62.0 mg of ortho-borylated 3,4-ethylenedioxy aniline (45%) as a solid (mp = 49-51 °C).

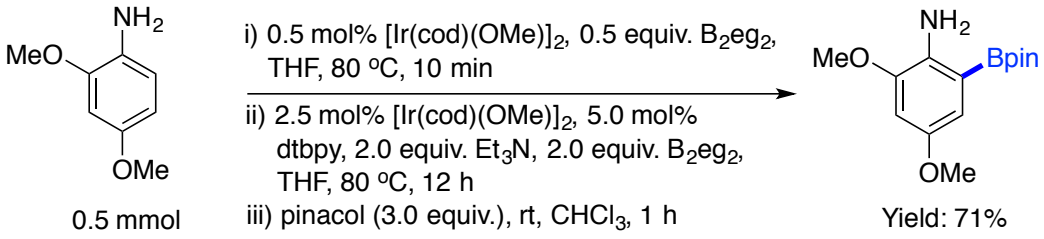
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (s, 1H), 6.13 (s, 1H), 4.44 (bs, 2H), 4.21-4.24 (m, 2H), 4.14-4.17 (m, 2H), 1.31 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 147.5, 135.6, 125.9, 124.3, 102.9, 83.3, 64.9, 63.9, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.7.

HRMS (ESI) *m/z* calcd for $C_{14}H_{21}BNO_4$ $[M+H]^+$ 278.1564, found: 278.1557.

Ortho-borylation of 2,4-dimethoxyaniline (2w)



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 2,4-dimethoxyaniline (76.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 µL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 99.0 mg of ortho-borylated 2,4-dimethoxyaniline (71%) as a solid (mp = 69-71 °C).

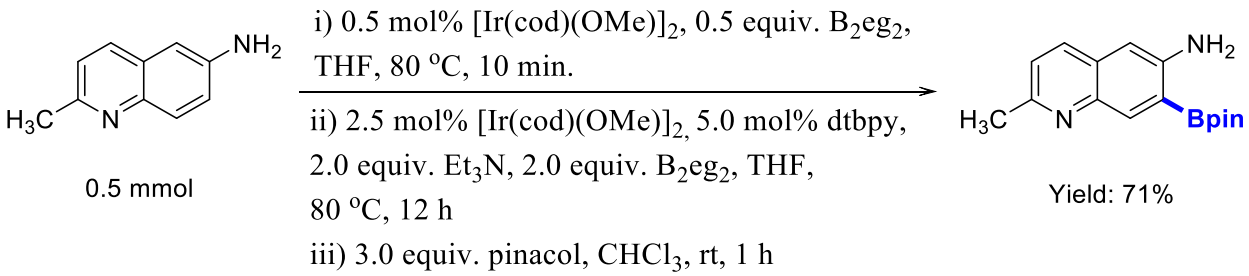
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (d, J = 2.4 Hz, 1H), 6.52 (d, J = 2.8 Hz 1H), 4.68 (bs, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 147.7, 138.4, 108.4, 103.3, 83.5, 55.8, 55.5, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.2.

HRMS (ESI) *m/z* calcd for $C_{14}H_{23}BNO_4$ $[M+H]^+$ 280.1720, found: 280.1712.

Ortho-borylation at 7-position of 2-methylquinolin-6-amine (2x):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 2-methylquinolin-6-amine (31.6 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 µL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (10% EtOAc in hexane as eluent) gave 100.8 mg of 7-borylated 2-methylquinolin-6-amine (71%) as a solid (mp = 62-63 °C).

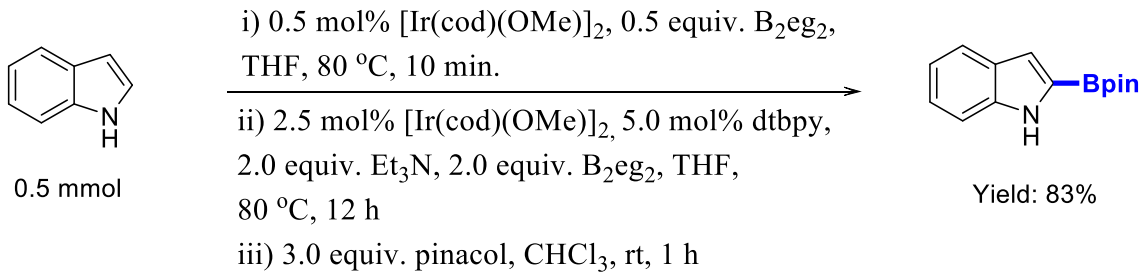
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 6.77 (s, 1H), 4.80 (bs, 2H), 2.63 (s, 3H), 1.36 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 149.2, 141.7, 139.0, 133.6, 130.0, 123.1, 106.9, 83.9, 25.0, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.2.

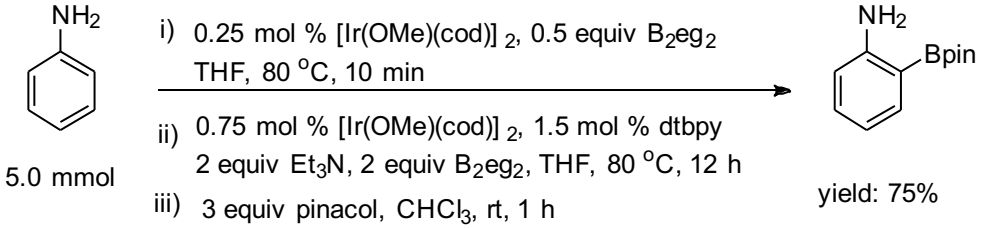
HRMS (ESI) *m/z* calcd for $C_{16}H_{22}BN_2O_2$ $[M+H]^+$ 285.1774, found: 285.1752.

Borylation at 2-position of 1H-indole (2y):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.5 mg, 0.5 equiv.), 1H-indole (58.5 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (142.0 mg, 2.0 equiv.), Et_3N (139.0 μL, 2.0 equiv.) and dry THF (1.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.0 mg, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 100.8 mg of 2-borylated 1H-indole (83%) as a white solid (mp = 85-86 °C). Spectral data are in accordance with the reported data.[4]

Large scale ortho-borylation of aniline:



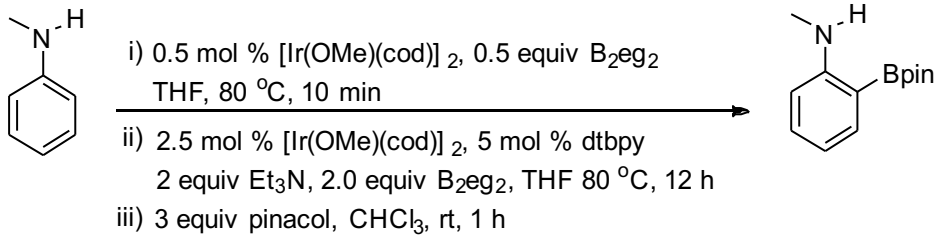
5.0 mmol

yield: 75%

Lower Catalyst loading
Total Ir: 0.5+1.5 = 2.0 mol %

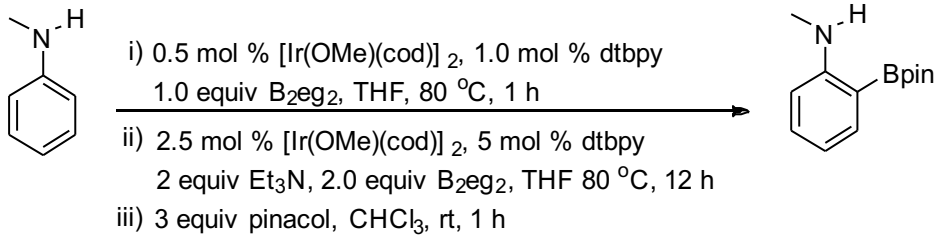
In a glove box, a 15 mL pressure tube was charged with $[Ir(cod)(OMe)]_2$ (8.3 mg, 0.25 mol %), B_2eg_2 (355 mg, 0.5 equiv.), aniline (465.6 mg, 5.0 mmol), dry THF (5.0 mL) and stirred on a preheated oil bath at 80 °C for 10 min. The pressure tube was charged again with $[Ir(cod)(OMe)]_2$ (24.86 mg, 0.75 mol %), dtbpy (20.13 mg, 1.5 mol %), B_2eg_2 (1.42 g, 2.0 equiv.), Et_3N (1.39 mL, 2.0 equiv.) and dry THF (6.0 mL). The Pressure tube was capped with a teflon pressure cap and placed into a preheated oil bath at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (10.0 mL) and pinacol (1.77 g, 3.0 equiv.) at room temperature for 1 h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 821 mg of ortho-borylated aniline (75%) as a solid. Spectral data are in accordance with the reported data.[5]

Ortho-borylation of *N*-methylaniline same conditions as Table 1:



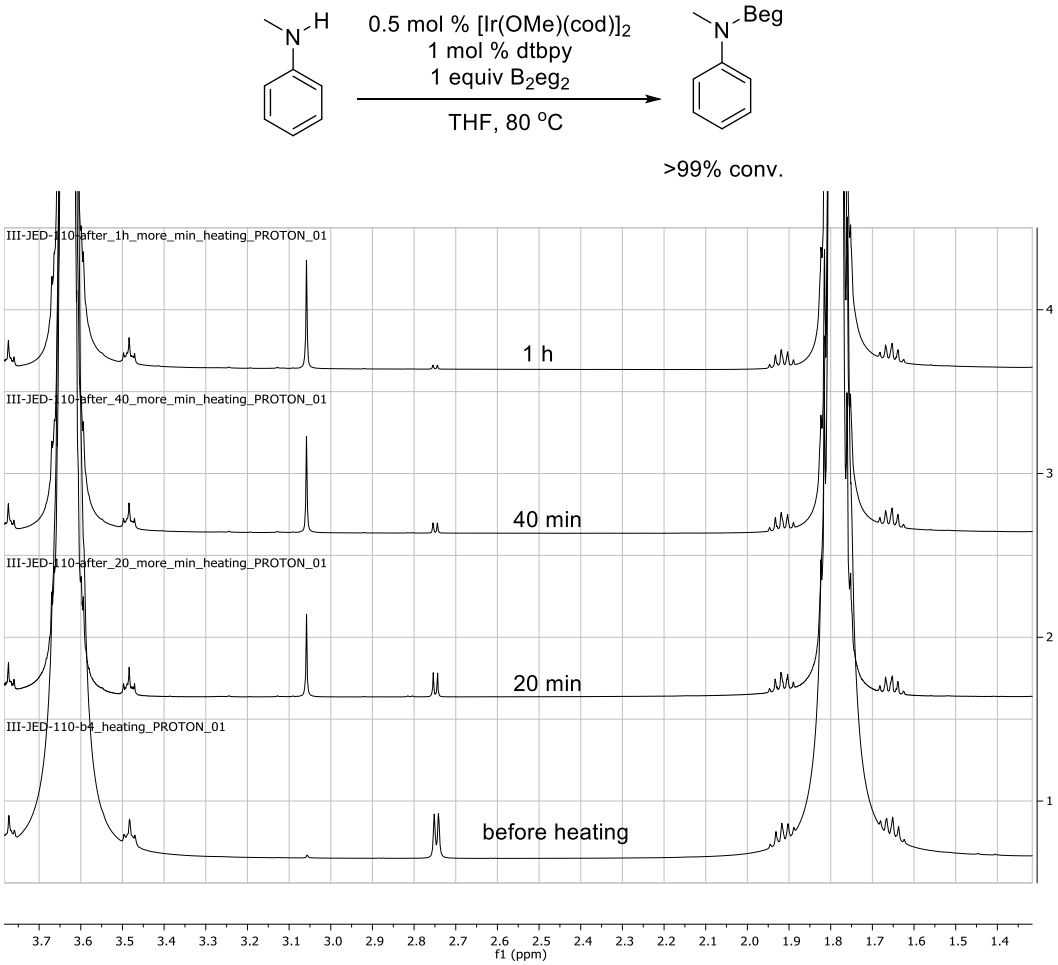
In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (3.3 mg, 0.5 mol %), B_2eg_2 (70.8 mg, 0.5 equiv.), *N*-methylaniline (107.2 mg, 1.0 mmol, 1 equiv), dry THF (1.0 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (16.5 mg, 2.5 mol %), dtbpy (13.4 mg, 5.0 mol %), B_2eg_2 (283.0 mg, 2.0 equiv.), Et_3N (202.3 mg, 2.0 equiv.) and dry THF (4.0 mL). The microreactor was capped with a Teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (355.0 mg, 3.0 equiv.) at room temperature for 1h. Removal of solvent under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane to 5% EtOAc in hexane as eluent) gave 49.3 mg of ortho-borylated *N*-methylaniline (21%) as a solid. Spectra data are in accordance with reported data.[6] It should be noted that by GC ortho-borylation is the only mono-borylated product and conversion was 24%. A trace amount of diborylated material was observed on the GCMS. The remainder of the mass was unreacted starting material.

Ortho-borylation of *N*-methylaniline (eq 1):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.7 mg, 0.5 mol %), B_2eg_2 (70.8 mg, 1.0 equiv.), dtbpy (1.3 mg, 1 mol %) *N*-methylaniline (53.5 mg, 0.5 mmol, 1 equiv), dry THF (1.0 mL) and stirred in a preheated aluminum block at 80 °C for 1 h. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.3 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2eg_2 (141.7 mg, 2.0 equiv.), Et_3N (101.2 mg, 2.0 equiv.) and dry THF (3.0 mL). The microreactor was capped with a Teflon pressure cap and placed into a preheated aluminum block at 80 °C. After 12 h, THF was removed under reduced pressure using dry $CHCl_3$ as transferring solvent and transesterification was performed using dry $CHCl_3$ (4.0 mL) and pinacol (177.2 mg, 3.0 equiv.) at room temperature for 1h. GC showed only the ortho-borylated product in 29% conversion and a trace of diborylation. The remainder of the mass was unreacted starting material.

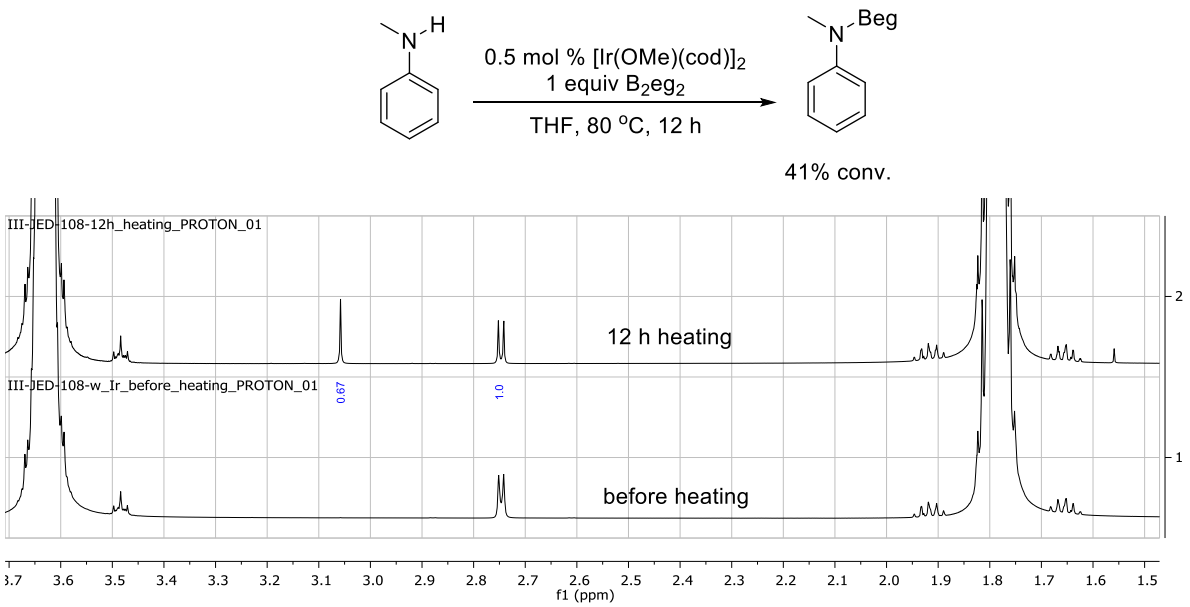
***N*-Borylation of *N*-methylaniline with dtbpy:**



^{1}H NMR (25 °C, 500 MHz, THF)

In a nitrogen filled glove box, a stock solution of $[Ir(OMe)(cod)]_2$ was prepared by dissolving 3.3 mg in 0.5 mL THF and a stock solution of dtbpy was prepared by dissolving 2.7 mg in 0.5 mL THF. *N*-Methylaniline (10.7 mg, 0.1 mmol, 1.0 equiv) and B_2eg_2 (7.1 mg, 0.05 mmol, 0.5 equiv) were dissolved in 0.4 mL deuterated THF respectively. The *N*-methylaniline and B_2eg_2 were transferred to a J-Young tube after which 0.05 mL of the stock $[Ir(OMe)(cod)]_2$ (0.5 mol %) and stock dtbpy (1 mol %) was added. Finally, three drops of THF-d8 was added to enable locking. The J-Young tube sealed and removed from the glove box. ^{1}H NMR was immediately collected. The NMR tube was then heated at 20 min increments after which NMR was collected. The ^{1}H spectra show a new *N*-Methyl peak growing at 3.06 ppm as a singlet and in the ^{11}B NMR *N*–B bond formation via a broad singlet at 25.27 ppm. Over 1 h this conversion was complete.

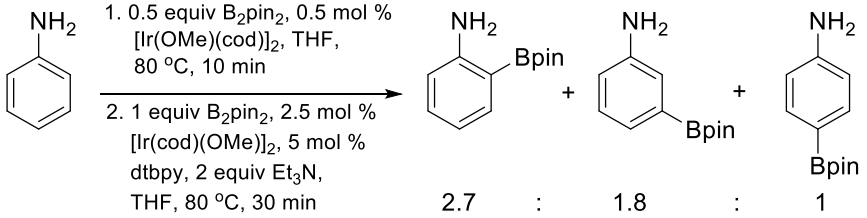
***N*-Borylation of *N*-methylaniline with table 1 conditions:**



^{1}H NMR (25 °C, 500 MHz, THF)

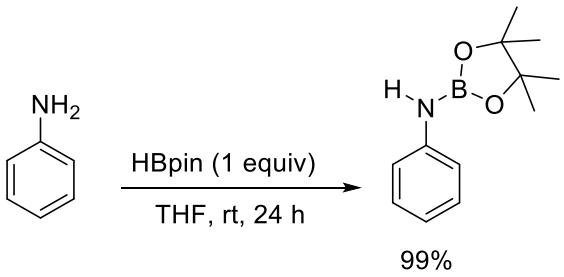
In a nitrogen filled glove box, a stock solution of $[Ir(OMe)(cod)]_2$ was prepared by dissolving 3.3 mg in 0.5 mL THF. *N*-Methylaniline (10.7 mg, 0.1 mmol, 1.0 equiv) and B_2eg_2 (7.1 mg, 0.05 mmol, 0.5 equiv) were dissolved in 0.4 mL deuterated THF respectively. The *N*-methylaniline and B_2eg_2 were transferred to a J-Young tube after which 0.05 mL of the stock $[Ir(OMe)(cod)]_2$ (0.5 mol %). Finally, three drops of THF-d8 was added to enable locking. The J-Young tube sealed and removed from the glove box. ^{1}H and ^{11}B NMR were immediately collected. The NMR tube was then heated at 80 °C for 12 h after which NMR was collected. The ^{1}H spectra show a new *N*-Methyl peak growing at 3.06 ppm as a singlet and in the ^{11}B NMR *N*–B bond formation via a broad singlet at 25.27 ppm; however, even after 12 h of heating the conversion was incomplete at only 41% based on ^{1}H NMR integration.

C–H borylation of aniline with B_2pin_2



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2pin_2 (64.0 mg, 0.5 equiv.), aniline (47 mg, 0.5 mmol), dry THF (0.5 mL) and stirred in a preheated aluminum block at 80 °C for 10 min. The microreactor was charged again with $[Ir(cod)(OMe)]_2$ (8.28 mg, 2.5 mol %), dtbpy (6.7 mg, 5.0 mol %), B_2pin_2 (127.0 mg, 1.0 equiv.), Et_3N (101 mg, 2.0 equiv.) and dry THF (2.0 mL). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminum block at 80 °C and heated for 30 min. The GC (the aliquot taken from reaction mixture was treated with methanol prior to injection in to GC) showed a mixture of monoborylated products (2.7:1.8:1 o:m:p).

Synthesis of 4,4,5,5-tetramethyl-*N*-phenyl-1,3,2-dioxaborolan-2-amine (PhN(H)Bpin)



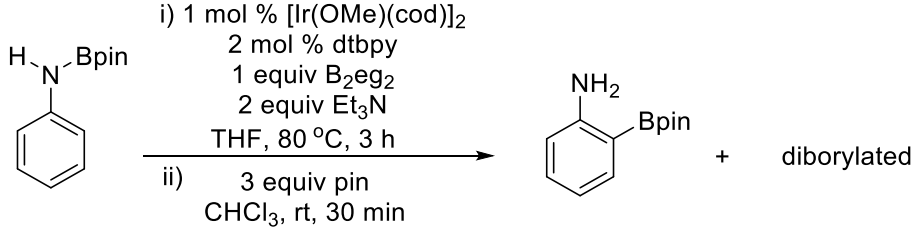
This synthesis was adapted from a previous reported procedure.[7] In a nitrogen filled glove box, a 50 mL Schlenk flask was charged with aniline (1 g, 10.7 mmol, 1 equiv), HBpin (1.374 g, 10.7 mmol, 1 equiv), and dry THF (10 mL). The Schlenk flask was removed from the glove box and allowed to stir under nitrogen for 24 h. After removing the volatiles under reduced pressure, 2.33 g (99%) of a white solid was obtained. It should be noted that this compound is highly hygroscopic and should not be exposed to air.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (dd, J = 8.5, 7.3 Hz, 2H), 7.11 – 7.05 (m, 2H), 6.85 (td, J = 7.3, 1.1 Hz, 1H), 4.62 (bs, 1H), 1.31 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.27, 129.00, 120.07, 117.56, 83.10, 24.64.

^{11}B NMR (160 MHz, $CDCl_3$): δ 23.23 (bs).

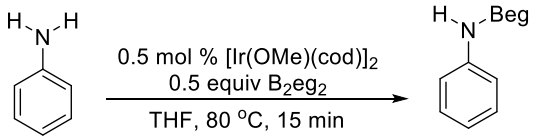
Regioselectivity of C–H borylation of PhN(H)Bpin with B_2eg_2



9.7 1 57%

In a nitrogen filled glove box, a 3.0 mL conical vial was charged with aniline-*N*-Bpin (110 mg, 0.5 mmol, 1.0 equiv), $[Ir(cod)(OMe)]_2$ (3.3 mg, 1 mol %), dtbpy (2.68 mg, 2.0 mol %), B_2eg_2 (70.8 mg, 0.5 mmol, 1.0 equiv), Et_3N (101.1 mg, 1 mmol, 2 equiv) and dry THF (1.5 ml). The vial was capped with a teflon pressure cap and was taken out of the glove box and placed into a preheated aluminum block at 80 °C and heated for 3 h after which the volatiles were removed under reduced pressure. Pinacol (177 mg, 1.5 mmol, 3 equiv) and $CHCl_3$ (5.0 mL) were added to the reaction vial and stirred at room temperature for 30 min. After which ^{1}H NMR showed 57% conversion to the ortho-borylated product with a 9.7:1 ratio of mono:diborylation.

Aniline *N*-Beg formation



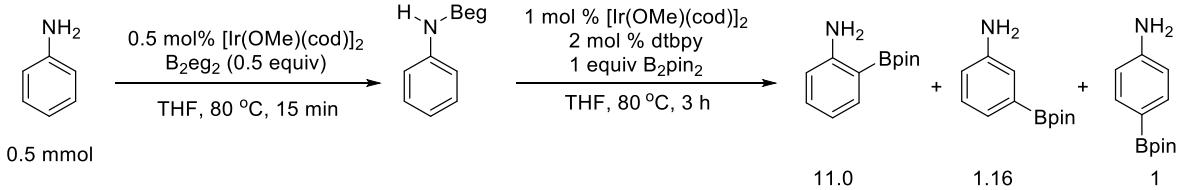
>99%

In a nitrogen filled glove box, a 3.0 mL conical vial was charged with $[Ir(cod)(OMe)]_2$ (3.3 mg, 0.5 mol %), B_2eg_2 (70.9 mg, 0.5 equiv), aniline (93.0 mg, 1.0 mmol, 1.0 equiv), and dry THF (1.0 ml). The vial was capped with a teflon pressure cap, brought out of the glove box and placed into preheated aluminum block at 80 ºC for 15 minutes. After bringing the vial back into the glove box solvent was removed and an aliquot of the black solid was dissolved in C_6D_6.

^{1}H NMR (500 MHz, C_6D_6): δ 7.15 – 7.08 (m, 2H), 7.06 – 7.02 (m, 2H), 6.78 (ddd, J = 8.5, 6.6, 1.2 Hz, 1H), 4.44 (s, 1H), 3.53 (s, 4H).

^{11}B NMR (160 MHz, C_6D_6): δ 24.86 (bs).

Regioselectivity of C–H borylation of PhN(H)Beg with B_2pin_2



Conv:80% (22% diborylated)

In a nitrogen filled glove box, a 3.0 mL conical vial was charged with $[Ir(cod)(OMe)]_2$ (1.65 mg, 0.5 mol %), B_2eg_2 (35.75 mg, 0.5 equiv), aniline (46.5 mg, 0.5 mmol, 1.0 equiv), and dry THF (0.5 ml). The vial was capped with a teflon pressure cap, brought out of the glove box and placed into a preheated aluminum block at 80 °C for 15 minutes then the vial was taken to the glove box and volatiles were removed under reduced pressure and vial was charged with $[Ir(cod)(OMe)]_2$ (3.3 mg, 1.0 mol %), dtbpy (2.68 mg, 2.0 mol %), B_2pin_2 (127.0 mg, 1.0 equiv), and dry THF (1.5 ml). The vial was capped with a teflon pressure cap and was taken out of the glove box and placed into a preheated aluminum block at 80 °C and heated for 3 h. The GC (the aliquot taken from reaction mixture was treated with methanol prior to injection in to GC) showed 80% conversion (58% mono-borylated aniline o**:**m**:**p (11.0**:**1.16**:**1) and 22% of diborylated products).

Computational procedures and results

General

Calculations of structures, energies, and frequencies employed default procedures in Gaussian09[8,9,10] with the following exceptions and all calculations were performed at the Department of Chemistry, Michigan State University. For transition state optimizations, (i) the maximum step size was set to 0.01 Bohr (MaxStep=1), (ii) the 2-electron integral accuracy was set to 10^{-12} (acc2e=12), and (iii) superfine (PhN(H)Beg) or ultrafine (PhN(Me)Beg) grids were used for integration. DFT calculations were performed using the M06 functional with a split 6-31G*/SDD basis set for the light and Ir atoms. An SDD core potential was used for Ir. Complete structures and energetics are provided in sections below. All absolute energies are in Hartrees. All relative energies are presented in kcal/mol. The default self-consistent reaction filed (SCRF) and parameters for THF were used for all calculations.

Guide to structures, structure titles and their organization

The sections below are divided into reactants and transition structures, then divided into specific structures. The first line after the title for a structure is a file name for the original calculation file, so that this file can always be located even if the file title changes.

Calculated Structures, Energies, and Selected NPA Charges

Reactants:

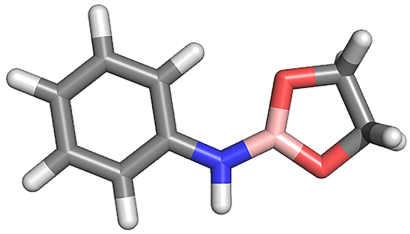
PhN(H)Beg

PhN(H)Beg_superfine_grid
E(RM06) = -579.973272280

Item	Value	Threshold	Converged?
Maximum Force	0.000035	0.000450	YES
RMS Force	0.000010	0.000300	YES
Maximum Displacement	0.000627	0.001800	YES
RMS Displacement	0.000216	0.001200	YES

Zero-point correction = 0.206810 (Hartree/Particle)
Thermal correction to Energy= 0.222466
Thermal correction to Enthalpy= 0.223585
Thermal correction to Gibbs Free Energy= 0.158549
Sum of electronic and zero-point Energies= -579.766462
Sum of electronic and thermal Energies= -579.750806
Sum of electronic and thermal Enthalpies= -579.749688
Sum of electronic and thermal Free Energies= -579.814723

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	139.600	51.547	115.561



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C,-3.696065,0.599968,0.008356
C,-2.593915,1.450565,0.013842
C,-1.298053,0.948532,0.008065
C,-1.08329,-0.435629,-0.003604
C,-2.193232,-1.289649,-0.009255
B,1.480243,-0.377108,-0.00584
O,2.621715,-1.142154,-0.065399
C,3.719889,-0.254488,0.11683
C,3.131497,1.142553,-0.10883
O,1.725131,0.972747,0.057677
H,-4.706597,1.003553,0.013276
H,-0.44578,1.623315,0.012648
H,3.49943,1.883592,0.609132
H,3.326915,1.515251,-1.123599
H,4.516817,-0.500909,-0.593582
H,4.114578,-0.375744,1.135246
N,0.19934,-0.989126,-0.010122
H,-2.740862,2.529879,0.022964
H,-2.035077,-2.368945,-0.018555
H,0.207509,-2.002847,-0.020572
H,-4.329564,-1.460917,-0.007888

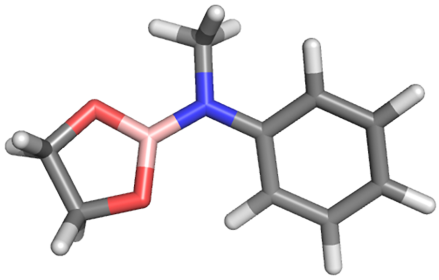
PhN(Me)Beg

MeOPhOBpinprimeM06SB
E(RM06) = -540.7031200

Item	Value	Threshold	Converged?
Maximum Force	0.000047	0.000450	YES
RMS Force	0.000008	0.000300	YES
Maximum Displacement	0.002886	0.001800	NO
RMS Displacement	0.000699	0.001200	YES

Zero-point correction = 0.178465 (Hartree/Particle)
Thermal correction to Energy = 0.192327
Thermal correction to Enthalpy = 0.193445
Thermal correction to Gibbs Free Energy = 0.132344
Sum of electronic and zero-point Energies = -540.524655
Sum of electronic and thermal Energies = -540.510794
Sum of electronic and thermal Enthalpies = -540.509675
Sum of electronic and thermal Free Energies = -540.570776

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	120.687	45.867	108.570



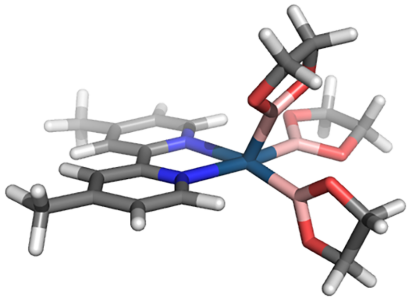
C,-3.46457,-0.67753,0.278879
C,-3.626669,0.676532,0.016203
C,-2.500686,1.434807,-0.29594
C,-1.240002,0.857372,-0.345606
C,-1.066057,-0.508477,-0.070315
C,-2.204525,-1.267112,0.23692
B,1.452855,-0.425579,-0.015991
O,2.651473,-1.096137,-0.125878
C,3.681122,-0.171589,0.204081
C,3.005311,1.200395,0.129559
O,1.611635,0.919601,0.222329
H,-4.613169,1.134739,0.048959
H,-0.377667,1.465489,-0.600664
H,3.30026,1.869238,0.945552
H,3.20439,1.708409,-0.824068
H,4.513235,-0.277377,-0.50085
H,4.052783,-0.394221,1.213973
N,0.206758,-1.110982,-0.128334
H,-2.602686,2.496697,-0.516336
H,-2.11666,-2.328101,0.455686
H,-4.327568,-1.295254,0.523809
C,0.248152,-2.565277,-0.208955
H,-0.055222,-3.040687,0.735103
H,-0.417097,-2.926885,-1.004126
H,1.266754,-2.885282,-0.436185

(4,4′-dimethyl-2,2′-bipyridine)Ir(Beg)$_3$

4,4'-Me2-bipyridine_Ir_(Beg)3_superfine_grid
E(RM06) = -659.807029462

Zero-point correction = 0.426357 (Hartree/Particle)
Thermal correction to Energy = 0.466553
Thermal correction to Enthalpy = 0.467671
Thermal correction to Gibbs Free Energy = 0.343220
Sum of electronic and zero-point Energies = -1439.201607
Sum of electronic and thermal Energies = -1439.161411
Sum of electronic and thermal Enthalpies = -1439.160293
Sum of electronic and thermal Free Energies = -1439.284744

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	292.766	125.248	221.136



C,-3.916953,1.421993,-0.117558
C,-2.711242,0.724928,-0.101524
N,-1.528843,1.374512,-0.07018
C,-1.529066,2.714237,-0.041438
C,-2.693942,3.464353,-0.045913
C,-3.927697,2.814985,-0.093126
C,-2.647857,-0.755708,-0.111396
N,-1.418778,-1.297853,-0.218154
C,-1.3024,-2.631257,-0.214439
C,-2.388861,-3.483085,-0.114942
C,-3.671917,-2.943824,-0.007427
C,-3.783755,-1.555828,-0.001458
Ir,0.376829,0.110811,-0.307007
B,1.841447,1.517676,-0.288722
O,3.182763,1.378074,-0.662476
C,3.894652,2.524468,-0.228329
C,2.815911,3.585306,-0.03976
O,1.625681,2.835,0.152463
B,1.208185,-0.412052,1.410607
O,2.223293,0.248167,2.104654
C,2.387958,-0.387804,3.363128
C,1.699598,-1.738253,3.18998
O,0.772254,-1.524649,2.137131
B,1.877122,-1.061094,-0.962767
O,2.120262,-1.186331,-2.339379
C,3.115088,-2.180235,-2.535874
C,3.759867,-2.33792,-1.162973
O,2.766291,-1.881363,-0.258201
H,-0.285993,-3.015174,-0.283899
H,-4.769809,-1.108202,0.101441
H,-2.237051,-4.560939,-0.116854
C,-4.874452,-3.826335,0.091934
H,-4.864661,0.889691,-0.158802
C,-5.207442,3.586574,-0.131928
H,-2.639501,4.551223,-0.017142
H,-0.543057,3.177634,-0.004941
H,2.640506,-3.114909,-2.875033
H,3.823737,-1.858292,-3.308991
H,4.037141,-3.373492,-0.930202
H,4.658633,-1.7089,-1.062231
H,1.177266,-2.077797,4.092822
H,2.415814,-2.518928,2.888022
H,1.908338,0.220419,4.146027
H,3.454362,-0.476493,3.603857
H,2.707558,4.224023,-0.930777
H,2.996849,4.234797,0.82562
H,4.653305,2.805518,-0.96933
H,4.406796,2.295121,0.719957
H,-6.07549,2.943955,0.051508
H,-5.206061,4.391136,0.613579
H,-5.341862,4.060532,-1.113587
H,-5.779245,-3.255473,0.327507
H,-5.045526,-4.354373,-0.855743
H,-4.737592,-4.593529,0.864191

Transition structures:

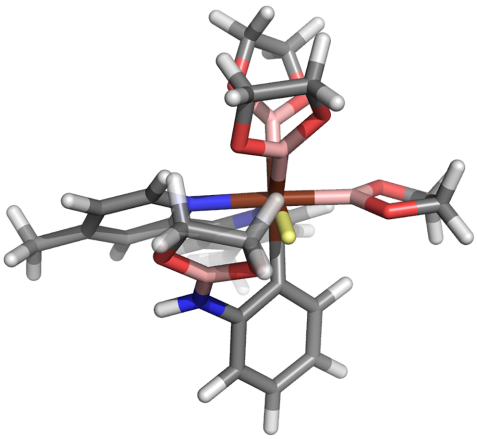
TS1

PhN(H)Beg_left_anti_4,4'-dimethylbipyridine_Ir(Beg)3_superfine_grid
E(RM06) = -1980.29036773

Item	Value	Threshold	Converged?
Maximum Force	0.000010	0.000450	YES
RMS Force	0.000003	0.000300	YES
Maximum Displacement	0.015452	0.001800	NO
RMS Displacement	0.002176	0.001200	NO

Zero-point correction = 0.600770 (Hartree/Particle)
Thermal correction to Energy = 0.656449
Thermal correction to Enthalpy = 0.657567
Thermal correction to Gibbs Free Energy = 0.499537
Sum of electronic and zero-point Energies = -1979.689598
Sum of electronic and thermal Energies = -1979.633919
Sum of electronic and thermal Enthalpies = -1979.632801
Sum of electronic and thermal Free Energies = -1979.790830

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	411.928	176.449	280.802



C,-4.117407,0.388126,-0.733646
C,-2.724633,0.376213,-0.66984
N,-2.05852,-0.726826,-0.27129
C,-2.75437,-1.825669,0.049393
C,-4.137176,-1.873754,0.004914
C,-4.852497,-0.741289,-0.386524
C,-1.900778,1.537215,-1.074707
N,-0.568704,1.349474,-1.065205
C,0.22414,2.332466,-1.50075
C,-0.264694,3.554232,-1.936694
C,-1.639559,3.789568,-1.913364
C,-2.458372,2.75157,-1.474256
Ir,0.167856,-0.559577,0.025916
B,0.578367,-2.298693,0.983977
O,1.582906,-2.476199,1.935326
C,1.562276,-3.824441,2.377133
C,0.181534,-4.327742,1.970488
O,-0.212104,-3.450729,0.923106
C,-0.386794,0.385637,1.972138
C,-1.119969,-0.434334,2.845988
C,-1.896833,0.07705,3.882259
C,-1.935237,1.451552,4.097871
C,-1.158418,2.281711,3.301592
C,-0.371948,1.764053,2.264744
B,1.838667,2.606731,1.382896
O,2.644144,1.690739,2.01736
C,3.97748,1.922624,1.590577
C,3.906884,3.164884,0.679848
O,2.531846,3.511202,0.609539
B,0.413452,-1.509675,-1.855348
O,0.061046,-2.815843,-2.158954
C,0.240764,-3.022576,-3.556438
C,1.132657,-1.866027,-3.989625
O,0.919728,-0.874564,-2.992049
B,2.142954,-0.562997,-0.561238
O,2.817641,0.600735,-0.944415
C,3.990189,0.209756,-1.646336
C,4.253007,-1.208511,-1.157233
O,2.974808,-1.66711,-0.738876
H,1.078667,0.023777,1.258146
H,1.2924,2.122095,-1.470472
H,-3.535267,2.904774,-1.449952
H,0.426365,4.325616,-2.272956
C,-2.214422,5.092711,-2.369881
H,-4.646583,1.279241,-1.063528
C,-6.346919,-0.747727,-0.429657
H,-4.655472,-2.792312,0.274865
H,-2.156176,-2.684862,0.351921
H,3.7882,0.237265,-2.728433
H,4.811761,0.905014,-1.427624
H,4.651365,-1.86862,-1.936924
H,4.945505,-1.228078,-0.301051
H,-1.12483,-1.514887,2.685978
H,-2.540653,1.872785,4.899381
H,-1.129652,3.356392,3.488558
H,0.882161,-1.466607,-4.97922
H,2.197954,-2.148728,-3.987835
H,-0.739546,-2.997365,-4.055668
H,0.691276,-4.006176,-3.732443
H,-0.542117,-4.251013,2.797983
H,0.184211,-5.363924,1.611991
H,1.735721,-3.868983,3.459034
H,2.366371,-4.385301,1.876339
H,4.47528,4.013083,1.08465
H,4.278001,2.956563,-0.332595
H,4.339429,1.036525,1.052609
H,4.615708,2.080564,2.469458
N,0.434235,2.668725,1.531779
H,-0.03317,3.507337,1.207078
H,-2.47379,-0.597888,4.514
H,-6.744739,0.166689,-0.883138
H,-6.720816,-1.60777,-0.999289
H,-6.76257,-0.831103,0.58333
H,-3.214053,5.262342,-1.953841
H,-1.570644,5.933634,-2.085985
H,-2.305043,5.111275,-3.464613

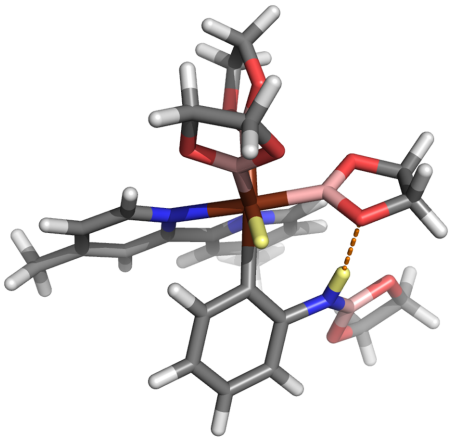
TS2

PhN(H)Beg_H…O–B_TS_front_4,4'-dimethylbipyridine_Ir(Beg)3_superfine_grid
E(RM06) = -1980.29476162

Item	Value	Threshold	Converged?
Maximum Force	0.000004	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.003496	0.001800	NO
RMS Displacement	0.000651	0.001200	YES

Zero-point correction = 0.601453
Thermal correction to Energy = 0.656979
Thermal correction to Enthalpy = .658098
Thermal correction to Gibbs Free Energy = 0.500930
Sum of electronic and zero-point Energies = -1979.693309
Sum of electronic and thermal Energies = -1979.637782
Sum of electronic and thermal Enthalpies = -1979.636664
Sum of electronic and thermal Free Energies = -1979.793832

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	412.261	176.182	279.270



C,2.120282,2.287515,1.81476
C,1.005112,1.758526,1.169163
N,0.843423,0.42474,1.047222
C,1.747738,-0.390761,1.598788
C,2.871951,0.075002,2.261167
C,3.089388,1.448203,2.360342
C,-0.079748,2.608886,0.630271
N,-1.154868,1.964389,0.137644
C,-2.189817,2.683664,-0.30637
C,-2.195181,4.069936,-0.310879
C,-1.079548,4.759997,0.161837
C,-0.014595,4.000649,0.64135
Ir,-0.840499,-0.306323,-0.224634
B,-0.354568,-2.268219,-0.227309
O,-0.008135,-2.990858,0.916852
C,0.678003,-4.172219,0.50958
C,0.250198,-4.362767,-0.938793
O,-0.104666,-3.049134,-1.362618
C,0.381377,0.433265,-1.958022
C,-0.087299,1.526666,-2.697745
C,0.738369,2.28871,-3.521358
C,2.080795,1.943733,-3.641668
C,2.562926,0.824016,-2.975668
C,1.726475,0.056751,-2.155033
B,3.486845,-1.248293,-0.874333
O,4.488886,-0.303558,-0.823623
C,5.481466,-0.798823,0.064353
C,5.146248,-2.285494,0.242281
O,3.793778,-2.403876,-0.179304
B,-1.86416,-0.770847,1.572141
O,-1.551705,-0.125777,2.765068
C,-2.316854,-0.70872,3.815311
C,-3.411794,-1.491913,3.096387
O,-2.912742,-1.66262,1.775399
B,-2.743471,-0.86168,-0.787723
O,-3.813192,0.031383,-0.747207
C,-5.010424,-0.711221,-0.942562
C,-4.543281,-2.022526,-1.572622
O,-3.160888,-2.09788,-1.254008
H,-0.993968,-0.60181,-1.816058
H,-3.035922,2.105207,-0.676786
H,0.868916,4.513027,1.015806
H,-3.061398,4.608666,-0.691079
C,-1.038484,6.254591,0.181101
H,2.243844,3.363841,1.911339
C,4.310458,2.00632,3.017677
H,3.571157,-0.635494,2.700858
H,1.545359,-1.457073,1.506686
H,-5.491077,-0.875317,0.03392
H,-5.702369,-0.146882,-1.578816
H,-5.067433,-2.898159,-1.171304
H,-4.662857,-2.022592,-2.666268
H,-1.139479,1.808235,-2.610227
H,2.748585,2.52558,-4.276034
H,3.601841,0.51767,-3.092918
H,-4.359627,-0.934215,3.053339
H,-3.610342,-2.470466,3.549054
H,-2.709099,0.07813,4.470376
H,-1.666673,-1.362911,4.414406
H,-0.627359,-5.019428,-1.029769
H,1.049024,-4.756134,-1.578275
H,0.404262,-5.00952,1.161167
H,1.763106,-3.996823,0.591202
H,5.779684,-2.928408,-0.385671
H,5.242446,-2.62136,1.2821
H,5.41976,-0.248176,1.016173
H,6.47782,-0.633587,-0.36194
N,2.25375,-1.097324,-1.539797
H,1.577523,-1.852039,-1.45088
H,0.3335,3.141659,-4.065444
H,-0.009204,6.630678,0.190639
H,-1.557644,6.678801,-0.68632
H,-1.539469,6.641447,1.079096
H,4.077426,2.904282,3.602213
H,4.783074,1.27152,3.679463
H,5.052391,2.297702,2.261058

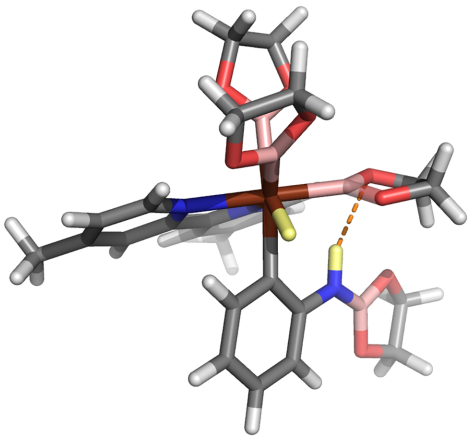
TS3

PhN(H)Beg_H···O–B_TS_rear_4,4'-dimethylbipyridine_Ir(Beg)3_superfine_grid
E(RM06) = -1980.29368534

Item	Value	Threshold	Converged?
Maximum Force	0.000002	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.007538	0.001800	NO
RMS Displacement	0.000925	0.001200	YES

Zero-point correction = 0.601689 (Hartree/Particle)
Thermal correction to Energy = 0.657309
Thermal correction to Enthalpy = 0.658428
Thermal correction to Gibbs Free Energy = 0.498707
Sum of electronic and zero-point Energies = -1979.691997
Sum of electronic and thermal Energies = -1979.636376
Sum of electronic and thermal Enthalpies = -1979.635258
Sum of electronic and thermal Free Energies = -1979.794978

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	412.468	175.978	283.806



C,1.074012,3.008629,2.02546
C,0.290603,2.147028,1.259553
N,0.526668,0.817728,1.248695
C,1.512301,0.331483,2.015692
C,2.325784,1.137916,2.79313
C,2.121578,2.517605,2.799766
C,-0.864955,2.621415,0.467254
N,-1.601948,1.671797,-0.137534
C,-2.695435,2.038674,-0.814024
C,-3.093297,3.359912,-0.939356
C,-2.330134,4.365059,-0.34485
C,-1.202056,3.970999,0.369175
Ir,-0.678227,-0.447734,-0.17803
B,0.265161,-2.243706,-0.048929
O,1.138529,-2.598184,0.984924
C,1.897031,-3.730615,0.567939
C,1.087256,-4.310275,-0.585954
O,0.308476,-3.214531,-1.047273
C,0.54667,0.373273,-1.881109
C,-0.072105,1.156614,-2.863924
C,0.641592,1.882377,-3.81466
C,2.030767,1.816224,-3.80496
C,2.683713,1.035801,-2.859657
C,1.960227,0.310377,-1.90199
B,4.008411,-0.552004,-0.597591
O,5.062448,0.082706,-1.213055
C,6.253383,-0.421321,-0.615435
C,5.781529,-1.092297,0.678031
O,4.396981,-1.339933,0.468487
B,-1.882513,-1.010414,1.474209
O,-1.511311,-1.817681,2.536625
C,-2.577174,-1.840119,3.482154
C,-3.776199,-1.316725,2.701111
O,-3.195604,-0.5652,1.641477
B,-2.333053,-1.508872,-0.802393
O,-3.302941,-0.934685,-1.622814
C,-4.454498,-1.770847,-1.587669
C,-3.914194,-3.121475,-1.132819
O,-2.71012,-2.798929,-0.447215
H,-0.542884,-0.849288,-1.753334
H,-3.253561,1.223411,-1.273878
H,-0.588598,4.73355,0.84373
H,-3.990192,3.605371,-1.505693
C,-2.722574,5.803721,-0.454756
H,0.870943,4.077009,2.033539
C,2.994884,3.43128,3.597883
H,3.115284,0.687386,3.392285
H,1.641242,-0.750076,1.988047
H,-5.175798,-1.356506,-0.866013
H,-4.926475,-1.799479,-2.576316
H,-4.595544,-3.653595,-0.458466
H,-3.681731,-3.781144,-1.981846
H,-1.163956,1.189043,-2.890329
H,2.615953,2.368,-4.540098
H,3.770752,0.983147,-2.851492
H,-4.442423,-0.68086,3.295361
H,-4.37093,-2.137454,2.268246
H,-2.320994,-1.189468,4.331636
H,-2.718016,-2.859533,3.859251
H,0.417813,-5.118488,-0.254564
H,1.71235,-4.693421,-1.40103
H,2.018971,-4.425585,1.406732
H,2.8934,-3.38823,0.248256
H,6.301931,-2.034164,0.885431
H,5.901139,-0.432202,1.549663
H,6.955477,0.401615,-0.440719
H,6.723206,-1.13752,-1.304205
N,2.640998,-0.458164,-0.948718
H,2.010782,-0.924775,-0.303188
H,0.116568,2.47973,-4.559149
H,3.915825,3.660807,3.04459
H,2.49545,4.382221,3.8146
H,3.29438,2.969188,4.545867
H,-3.602157,6.013145,0.16884
H,-1.915895,6.470221,-0.13025
H,-2.992778,6.062126,-1.485938

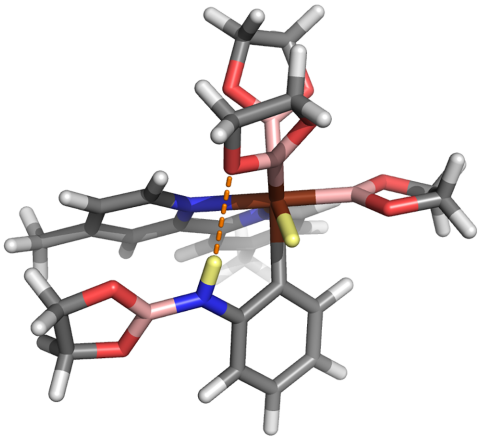
TS4

PhN(H)Beg_H…O–B_TS_left_4,4'-dimethylbipyridine_
Ir(Beg)3_superfine_grid
E(RM06) = -1980.29519479

Item	Value	Threshold	Converged?
Maximum Force	0.000003	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.003225	0.001800	NO
RMS Displacement	0.000385	0.001200	YES

Zero-point correction = 0.601723 (Hartree/Particle)
Thermal correction to Energy = 0.657028
Thermal correction to Enthalpy = 0.658146
Thermal correction to Gibbs Free Energy = 0.501778
Sum of electronic and zero-point Energies = -1979.693472
Sum of electronic and thermal Energies = -1979.638167
Sum of electronic and thermal Enthalpies = -1979.637049
Sum of electronic and thermal Free Energies = -1979.793417

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	412.291	176.033	277.850



C,0.822272,3.506792,-1.614067
C,0.52764,2.194915,-1.250156
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C,-1.606477,2.826492,-0.611223
C,-1.374461,4.145971,-0.963014
C,-0.126937,4.514771,-1.464991
C,1.477463,1.080379,-1.461397
N,1.020555,-0.149545,-1.155809
C,1.772886,-1.207305,-1.462604
C,3.030477,-1.09669,-2.037119
C,3.562587,0.168186,-2.277084
C,2.750252,1.266366,-1.995572
Ir,-0.907087,-0.18232,0.158108
B,-2.647821,0.034211,1.177242
O,-2.986452,-0.643706,2.34746
C,-4.283216,-0.230757,2.754037
C,-4.508284,1.077789,2.004254
O,-3.614705,1.002256,0.900294
C,0.276903,0.673572,1.841672
C,-0.257762,1.793192,2.491014
C,0.507255,2.60873,3.322267
C,1.842881,2.285868,3.543887
C,2.388601,1.148144,2.963845
C,1.615253,0.331121,2.127445
B,3.510866,-1.174153,1.313632
O,4.593221,-0.340243,1.491889
C,5.755061,-1.117543,1.221993
C,5.231317,-2.326457,0.4445
O,3.8567,-2.40658,0.794377
B,-1.989532,-0.820858,-1.553822
O,-3.270063,-0.438249,-1.918725
C,-3.573968,-1.017474,-3.184475
C,-2.52957,-2.114542,-3.350164
O,-1.466329,-1.710605,-2.495488
B,-1.214579,-2.217369,0.211243
O,-0.131524,-3.099207,0.197215
C,-0.635858,-4.398658,-0.095463
C,-2.108554,-4.314051,0.288452
O,-2.408936,-2.924843,0.207972
H,-0.531811,-0.793206,1.623178
H,1.348439,-2.177192,-1.205323
H,3.126225,2.265765,-2.203927
H,3.598095,-1.996167,-2.270859
C,4.951381,0.350148,-2.80087
H,1.79649,3.758481,-2.027106
C,0.180676,5.933844,-1.820549
H,-2.165737,4.883795,-0.842863
H,-2.561652,2.500076,-0.201547
H,-0.50608,-4.596895,-1.170992
H,-0.078294,-5.153337,0.470145
H,-2.763133,-4.876076,-0.387915
H,-2.288264,-4.663808,1.315554
H,-1.305819,2.054599,2.32217
H,2.460366,2.906579,4.192414
H,3.422022,0.871435,3.16429
H,-2.167851,-2.222379,-4.379252
H,-2.906709,-3.092246,-3.008715
H,-3.490876,-0.246402,-3.964873
H,-4.602501,-1.39621,-3.182603
H,-4.247793,1.953015,2.620347
H,-5.536786,1.202625,1.646028
H,-4.315636,-0.114104,3.843718
H,-5.016841,-0.999388,2.467549
H,5.320367,-2.175857,-0.643922
H,5.739535,-3.261644,0.705231
H,6.221228,-1.410763,2.173644
H,6.477173,-0.520251,0.653542
N,2.164148,-0.850685,1.601638
H,1.467904,-1.494966,1.234468
H,0.062166,3.48489,3.792734
H,-0.684509,6.425392,-2.281071
H,0.436015,6.507945,-0.919438
H,1.030229,6.00466,-2.508942
H,5.31921,-0.558758,-3.290855
H,5.008542,1.179982,-3.515464
H,5.640812,0.58581,-1.977812

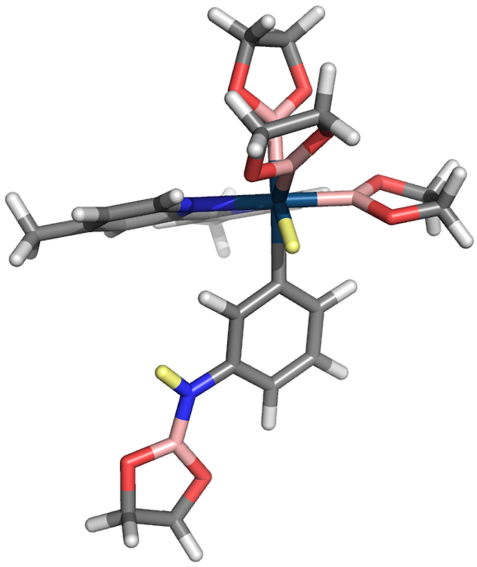
TS_{meta}

PhN(H)Beg_left_meta_4,4´-Me2-bipyridine_Ir_(Beg)3_
superfine_grid
E(RM06) = -1980.29107739

Item	Value	Threshold	Converged?
Maximum Force	0.000010	0.000450	YES
RMS Force	0.000003	0.000300	YES
Maximum Displacement	0.061559	0.001800	NO
RMS Displacement	0.011491	0.001200	NO

Zero-point correction = 0.601119 (Hartree/Particle)
Thermal correction to Energy = 0.657013
Thermal correction to Enthalpy = 0.658131
Thermal correction to Gibbs Free Energy = 0.496329
Sum of electronic and zero-point Energies = -1979.689958
Sum of electronic and thermal Energies = -1979.634065
Sum of electronic and thermal Enthalpies = -1979.632946
Sum of electronic and thermal Free Energies = -1979.794748

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	412.282	176.298	287.505



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N,-0.609373,0.975851,1.630255
C,-0.983675,0.707654,2.888249
C,-0.591641,1.48417,3.965408
C,0.226047,2.594312,3.752548
C,0.529684,2.314423,-0.016553
N,-0.018723,1.494677,-0.93212
C,0.233633,1.709562,-2.227708
C,1.060805,2.729666,-2.670334
C,1.659726,3.579552,-1.739429
C,1.375961,3.35609,-0.394832
Ir,-1.120218,-0.352218,-0.10463
B,-2.057621,-1.889794,0.828633
O,-2.067593,-3.214063,0.389708
C,-2.834511,-3.992099,1.295588
C,-2.912445,-3.132499,2.55347
O,-2.657025,-1.813308,2.089765
C,0.869696,-1.277326,0.250662
C,1.062545,-2.108106,1.365519
C,2.347954,-2.458443,1.771727
C,3.471807,-2.024801,1.077061
C,3.303995,-1.221763,-0.056307
C,2.007012,-0.867564,-0.452498
B,5.783414,-0.975986,-0.671566
O,6.67697,-0.369932,-1.526832
C,7.959436,-0.909754,-1.231147
C,7.791727,-1.581949,0.13606
O,6.386089,-1.769026,0.275767
B,-2.956597,0.699994,-0.280218
O,-4.012358,0.666619,0.616024
C,-4.995179,1.608313,0.196425
C,-4.62544,1.91072,-1.250681
O,-3.246261,1.571595,-1.333089
B,-2.156811,-0.919877,-1.796988
O,-1.655217,-0.683077,-3.077922
C,-2.71869,-0.869074,-4.00449
C,-3.712772,-1.744343,-3.251197
O,-3.420961,-1.496103,-1.88141
H,-0.314504,-1.57667,-0.838242
H,-0.250854,1.017631,-2.917024
H,1.831249,4.002321,0.352437
H,1.243086,2.857854,-3.736028
C,2.550828,4.699882,-2.171696
H,1.222855,3.736468,2.241272
C,0.688205,3.446855,4.890362
H,-0.926437,1.224735,4.968241
H,-1.627342,-0.163551,3.007763
H,-3.150921,0.112134,-4.256379
H,-2.33951,-1.329996,-4.923773
H,-4.758361,-1.490124,-3.462012
H,-3.56653,-2.813629,-3.46511
H,0.206016,-2.474466,1.934332
H,4.470463,-2.31097,1.397533
H,-4.774414,2.960148,-1.530206
H,-5.189186,1.279052,-1.956261
H,-4.935668,2.502971,0.834166
H,-5.995991,1.174642,0.305079
H,-2.14271,-3.413241,3.290021
H,-3.890405,-3.174002,3.047567
H,-2.347844,-4.960211,1.465594
H,-3.829744,-4.179013,0.864059
H,8.300235,-2.550235,0.202618
H,8.150197,-0.944958,0.956759
H,8.706566,-0.107914,-1.223106
H,8.23554,-1.631246,-2.013204
N,4.389311,-0.760532,-0.811536
H,2.481422,-3.089132,2.651363
H,1.095322,4.402617,4.542298
H,-0.130859,3.651341,5.590533
H,1.476202,2.935122,5.459285
H,3.175097,5.062308,-1.347341
H,3.205596,4.39183,-2.995605
H,1.954495,5.548025,-2.534766
H,1.896439,-0.248919,-1.348275
H,4.118707,-0.178757,-1.596751

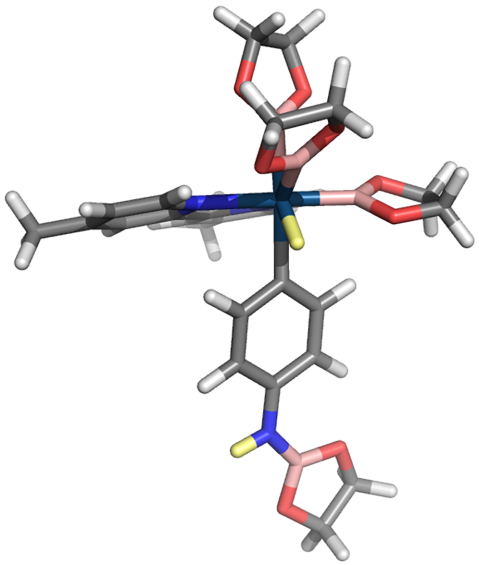
TS5

PhN(H)Beg_para_4,4'-Me2-bipyridine_Ir_(Beg)3_
superfine_grid
E(RM06) = -1980.29037111

Item	Value	Threshold	Converged?
Maximum Force	0.000003	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.010812	0.001800	NO
RMS Displacement	0.001474	0.001200	NO

Zero-point correction = 0.601098 (Hartree/Particle)
Thermal correction to Energy = 0.656941
Thermal correction to Enthalpy = 0.658060
Thermal correction to Gibbs Free Energy = 0.496976
Sum of electronic and zero-point Energies = -1979.689273
Sum of electronic and thermal Energies = -1979.633430
Sum of electronic and thermal Enthalpies = -1979.632311
Sum of electronic and thermal Free Energies = -1979.793395

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	412.237	176.297	286.228



C,0.310189,2.976566,2.35232
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N,-0.331497,0.820732,1.555415
C,0.034715,0.301762,2.734704
C,0.550898,1.074051,3.761369
C,0.702457,2.449182,3.579041
C,-0.647298,2.667252,0.042183
N,-1.195657,1.769732,-0.796538
C,-1.651267,2.185553,-1.983679
C,-1.56203,3.503761,-2.399545
C,-0.977521,4.450811,-1.556456
C,-0.522498,4.009417,-0.317641
Ir,-1.046706,-0.437648,-0.159874
B,-0.816852,-2.311393,0.578156
O,-0.520008,-3.444243,-0.181691
C,-0.45638,-4.5694,0.68057
C,-0.282186,-3.965133,2.070251
O,-0.775033,-2.638449,1.936556
C,1.066418,-0.401184,-0.831356
C,2.03659,-1.136161,-0.132835
C,3.402468,-0.937034,-0.310461
C,3.861567,0.006357,-1.236651
C,2.91261,0.727086,-1.96917
C,1.551416,0.520179,-1.770449
B,6.377424,-0.333797,-0.867578
O,7.637059,0.095405,-1.222753
C,8.562854,-0.775573,-0.584019
C,7.740604,-1.495126,0.490703
O,6.386633,-1.33161,0.077933
B,-2.993614,-0.301362,0.681379
O,-3.392144,-0.827887,1.899941
C,-4.723629,-0.397946,2.167022
C,-5.235197,0.085506,0.815635
O,-4.051562,0.393728,0.089348
B,-2.469722,-1.268346,-1.40081
O,-2.771929,-0.720268,-2.648463
C,-3.992666,-1.298392,-3.093897
C,-4.096032,-2.595474,-2.300733
O,-3.299277,-2.357967,-1.146938
H,-0.294176,-1.096534,-1.456382
H,-2.095809,1.410427,-2.608463
H,-0.062852,4.726326,0.35916
H,-1.941088,3.79188,-3.37872
C,-0.858667,5.882917,-1.970147
H,0.402269,4.047543,2.186599
C,1.271421,3.315168,4.656781
H,0.831265,0.604458,4.702658
H,-0.108583,-0.773944,2.83545
H,-4.821577,-0.612609,-2.858384
H,-3.962553,-1.450927,-4.178929
H,-5.122924,-2.837769,-2.001953
H,-3.685829,-3.4527,-2.855432
H,1.725076,-1.889045,0.595126
H,-5.87966,0.969712,0.882029
H,-5.783904,-0.7063,0.28011
H,-4.700927,0.410373,2.913277
H,-5.307674,-1.229445,2.578126
H,0.776958,-3.929708,2.371674
H,-0.842111,-4.497176,2.848498
H,0.375169,-5.221993,0.387877
H,-1.390647,-5.145732,0.598739
H,7.975743,-2.562578,0.567046
H,7.868632,-1.040047,1.482842
H,9.392837,-0.193648,-0.16731
H,8.970546,-1.475558,-1.327171
N,5.224113,0.240182,-1.459265
H,4.119415,-1.518031,0.265878
H,1.115833,4.379247,4.447605
H,0.821501,3.082539,5.629714
H,2.352382,3.147437,4.755525
H,-0.286501,6.469853,-1.243353
H,-0.367232,5.970083,-2.947412
H,-1.851125,6.341918,-2.070567
H,0.848947,1.100188,-2.373482
H,5.406421,0.941084,-2.168621
H,3.249893,1.455628,-2.709542

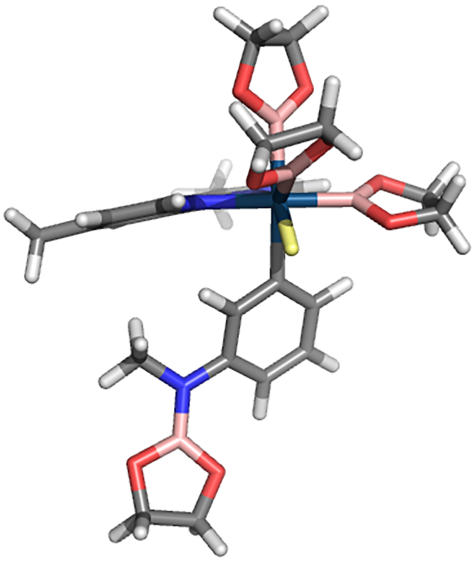
TS6

PhN(Me)Beg_anti_meta_4,4´-Me2-bipyridine_Ir_(Beg)3_ultrafine_grid
E(RM06) = -2019.56206022

Item	Value	Threshold	Converged?
Maximum Force	0.000010	0.000450	YES
RMS Force	0.000004	0.000300	YES
Maximum Displacement	0.007165	0.001800	NO
RMS Displacement	0.001371	0.001200	NO

Zero-point correction = 0.629879 (Hartree/Particle)
Thermal correction to Energy = 0.687155
Thermal correction to Enthalpy = 0.688274
Thermal correction to Gibbs Free Energy = 0.527023
Sum of electronic and zero-point Energies = -2018.932181
Sum of electronic and thermal Energies = -2018.874905
Sum of electronic and thermal Enthalpies = -2018.873787
Sum of electronic and thermal Free Energies = -2019.035037

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	431.196	181.762	286.524



C,0.083109,3.447338,1.843978
C,-0.16724,2.374169,0.989868
N,-0.889004,1.312027,1.403478
C,-1.36416,1.297137,2.656259
C,-1.14282,2.330659,3.550271
C,-0.399937,3.441937,3.148918
C,0.31234,2.346697,-0.409736
N,-0.11651,1.318878,-1.164194
C,0.252202,1.259572,-2.448389
C,1.087098,2.1991,-3.032262
C,1.574554,3.255611,-2.261068
C,1.159735,3.323484,-0.933392
Ir,-1.166829,-0.393751,-0.03171
B,-2.053463,-1.785845,1.147142
O,-1.939091,-3.167215,0.984386
C,-2.710718,-3.811768,1.985953
C,-2.926372,-2.732795,3.042101
O,-2.738206,-1.513543,2.335628
C,0.851035,-1.054823,0.622795
C,1.032318,-1.586725,1.905347
C,2.314264,-1.708171,2.439674
C,3.437019,-1.329041,1.715455
C,3.289737,-0.832829,0.412683
C,1.995169,-0.713849,-0.11055
B,5.727548,-0.947092,-0.200425
O,6.777898,-0.474837,-0.959839
C,7.895343,-1.31302,-0.695249
C,7.518379,-2.064967,0.584662
O,6.102255,-1.948822,0.665867
B,-3.045637,0.459139,-0.537831
O,-4.144703,0.582089,0.296941
C,-5.153254,1.322146,-0.384684
C,-4.724168,1.272471,-1.845653
O,-3.324822,1.024916,-1.784944
B,-2.040084,-1.383583,-1.617283
O,-1.469817,-1.380128,-2.891118
C,-2.450678,-1.844155,-3.810918
C,-3.442636,-2.607828,-2.940431
O,-3.253056,-2.064612,-1.639996
H,-0.23284,-1.674598,-0.443294
H,-0.143551,0.410807,-3.007054
H,1.519591,4.139726,-0.310754
H,1.365291,2.102516,-4.080442
C,2.528822,4.254909,-2.832513
H,0.651581,4.307117,1.496685
C,-0.135364,4.575501,4.087041
H,-1.552531,2.270938,4.557102
H,-1.944117,0.41469,2.925537
H,-2.922263,-0.978187,-4.301074
H,-1.978585,-2.465364,-4.580818
H,-4.484604,-2.469559,-3.253259
H,-3.228457,-3.686687,-2.918045
H,0.171403,-1.887984,2.50557
H,4.427998,-1.422183,2.150441
H,-4.921092,2.202078,-2.392017
H,-5.207871,0.441493,-2.384737
H,-5.174139,2.350895,0.00514
H,-6.133882,0.866322,-0.205897
H,-2.183671,-2.799487,3.853191
H,-3.926739,-2.756808,3.490258
H,-2.173938,-4.688057,2.36917
H,-3.661749,-4.154284,1.549984
H,7.80048,-3.123532,0.559219
H,7.967277,-1.60899,1.478426
H,8.79859,-0.702421,-0.582816
H,8.04274,-1.994436,-1.545161
N,4.409879,-0.42919,-0.349686
H,2.443563,-2.096386,3.450548
H,0.355639,5.414538,3.582134
H,-1.067519,4.940011,4.536674
H,0.511846,4.251633,4.91284
H,2.591579,5.157384,-2.214454
H,3.53842,3.824967,-2.897273
H,2.23897,4.546733,-3.849066
H,1.868543,-0.344239,-1.126991
C,4.170039,0.508089,-1.438603
H,3.672902,0.035645,-2.299342
H,3.533928,1.337963,-1.096685
H,5.124101,0.915614,-1.781992

TS_{para}

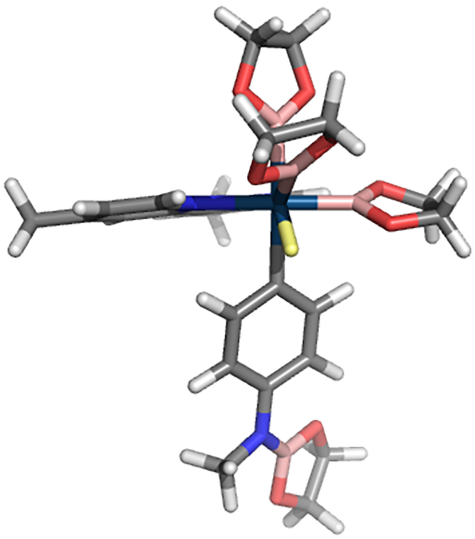
PhN(Me)Beg_para_4,4'-Me2-bipyridine_Ir_(Beg)3_
ultrafine_grid
E(RM06) = -2019.55943016

Item	Value	Threshold	Converged?
Maximum Force	0.000008	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.018462	0.001800	NO
RMS Displacement	0.002295	0.001200	NO

Zero-point correction = 0.629662 (Hartree/Particle)
Thermal correction to Energy = 0.687168
Thermal correction to Enthalpy = 0.688286
Thermal correction to Gibbs Free Energy = 0.524533
Sum of electronic and zero-point Energies = -2018.929768
Sum of electronic and thermal Energies = -2018.872262
Sum of electronic and thermal Enthalpies = -2018.871144
Sum of electronic and thermal Free Energies = -2019.034898

E (Thermal)	CV	S
KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin

Total	431.204	181.874	290.973



C,0.398059,2.794752,2.49018
C,-0.172871,2.041472,1.464882
N,-0.368362,0.714242,1.607
C,-0.011192,0.123033,2.754957
C,0.560511,0.818973,3.806122
C,0.781491,2.191479,3.684001
C,-0.61839,2.644301,0.189003
N,-1.204777,1.811262,-0.689708
C,-1.66167,2.305533,-1.845596
C,-1.537943,3.64177,-2.189473
C,-0.917164,4.523592,-1.30293
C,-0.45922,4.000363,-0.097338
Ir,-1.168272,-0.426827,-0.155646
B,-1.038078,-2.341332,0.499981
O,-0.860717,-3.460369,-0.314867
C,-0.829345,-4.621262,0.500227
C,-0.545795,-4.087289,1.900799
O,-0.949036,-2.725462,1.841853
C,0.934025,-0.485646,-0.858669
C,1.87218,-1.317018,-0.226038
C,3.240198,-1.197491,-0.438847
C,3.749203,-0.233602,-1.321902
C,2.826044,0.579501,-1.990608
C,1.457665,0.445754,-1.762716
B,6.165177,-0.520656,-0.667918
O,7.497403,-0.322784,-0.967222
C,8.254766,-0.968297,0.048289
C,7.253706,-1.203005,1.182195
O,5.977766,-1.123259,0.555877
B,-3.101107,-0.206689,0.697911
O,-3.548238,-0.784787,1.87543
C,-4.846881,-0.27692,2.166409
C,-5.30853,0.33657,0.85014
O,-4.099021,0.604293,0.151141
B,-2.642039,-1.118552,-1.422793
O,-2.904051,-0.507469,-2.650467
C,-4.158991,-0.986959,-3.117049
C,-4.348258,-2.302556,-2.372419
O,-3.544598,-2.157101,-1.207849
H,-0.466822,-1.069091,-1.488508
H,-2.137977,1.580419,-2.505887
H,0.026838,4.665393,0.613093
H,-1.920089,3.994345,-3.146076
C,-0.768177,5.974455,-1.633542
H,0.548245,3.86524,2.370233
C,1.406892,2.974555,4.793492
H,0.83213,0.291801,4.719095
H,-0.206676,-0.947745,2.809008
H,-4.942244,-0.257316,-2.856785
H,-4.136347,-1.100854,-4.206984
H,-5.389789,-2.491068,-2.086281
H,-3.988196,-3.162821,-2.956473
H,1.531595,-2.0909,0.466078
H,-5.885538,1.260037,0.976096
H,-5.910219,-0.372262,0.258323
H,-4.771786,0.473072,2.968063
H,-5.49462,-1.089442,2.515295
H,0.526532,-4.136858,2.148918
H,-1.10371,-4.610632,2.686344
H,-0.058716,-5.313699,0.140028
H,-1.802596,-5.132662,0.445899
H,7.369107,-2.181657,1.661406
H,7.319713,-0.427456,1.95836
H,9.09581,-0.331358,0.344913
H,8.658026,-1.9112,-0.347907
N,5.135617,-0.112679,-1.562964
H,3.924468,-1.864748,0.078421
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H,-0.114775,6.488787,-0.920293
H,-0.355065,6.109126,-2.640939
H,-1.744537,6.477118,-1.618925
H,0.78125,1.098673,-2.319357
H,3.165283,1.331879,-2.699691
C,5.536376,0.581201,-2.77875
H,5.353598,1.664407,-2.718716
H,6.604602,0.428028,-2.947189
H,4.985541,0.1902,-3.644769

TS7

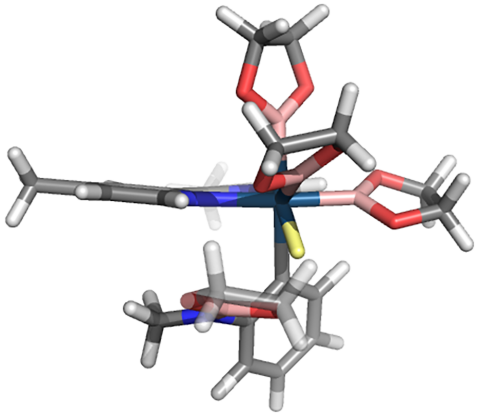
PhN(Me)Beg_left_anti_4,4'-dimethylbipyridine_Ir_(Beg)3_ultrafine_grid
E(RM06) = -2019.56349599

Item	Value	Threshold	Converged?
Maximum Force	0.000006	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.006201	0.001800	NO
RMS Displacement	0.001434	0.001200	NO

Zero-point correction = 0.629878 (Hartree/Particle)
Thermal correction to Energy = 0.686928
Thermal correction to Enthalpy = 0.688046
Thermal correction to Gibbs Free Energy = 0.528049
Sum of electronic and zero-point Energies = -2018.933618
Sum of electronic and thermal Energies = -2018.876568
Sum of electronic and thermal Enthalpies = -2018.875450
Sum of electronic and thermal Free Energies = -2019.035447

	E (Thermal)	CV	S

	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	431.054	181.648	284.297



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N,-2.119479,-0.648631,-0.120977
C,-2.842248,-1.707573,0.26776
C,-4.224398,-1.683324,0.342814
C,-4.91045,-0.513317,0.014957
C,-1.917892,1.590013,-0.981658
N,-0.586652,1.420122,-0.885222
C,0.218317,2.367665,-1.378119
C,-0.258594,3.52071,-1.980065
C,-1.635458,3.723276,-2.085305
C,-2.464907,2.730058,-1.574129
Ir,0.133008,-0.608657,-0.011447
B,0.541852,-2.471387,0.68014
O,1.645146,-2.820317,1.458761
C,1.589553,-4.210365,1.737118
C,0.137819,-4.587428,1.461829
O,-0.327269,-3.563951,0.591471
C,-0.144345,0.097388,2.095667
C,-0.760273,-0.827421,2.957548
C,-1.299643,-0.467831,4.188936
C,-1.200975,0.8504,4.622332
C,-0.544751,1.775262,3.822559
C,-0.007122,1.414108,2.580282
B,2.052723,2.313499,1.524635
O,2.862463,1.284172,1.950534
C,4.170279,1.530151,1.459911
C,4.056939,2.812797,0.614284
O,2.724538,3.268992,0.791354
B,0.138266,-1.328439,-2.006087
O,-0.339381,-2.560856,-2.425019
C,-0.303131,-2.60242,-3.84822
C,0.629446,-1.459047,-4.227951
O,0.582887,-0.588227,-3.104043
B,2.040767,-0.652623,-0.789974
O,2.765318,0.506696,-1.082124
C,3.834984,0.14129,-1.944119
C,4.036313,-1.340852,-1.663672
O,2.764733,-1.772403,-1.198939
H,1.185101,-0.205136,1.181487
H,1.286203,2.178566,-1.277027
H,-3.542731,2.847235,-1.662268
H,0.442315,4.259061,-2.366796
C,-2.190488,4.959246,-2.718559
H,-4.656166,1.498185,-0.674392
C,-6.399688,-0.433833,0.120622
H,-4.764382,-2.573332,0.661388
H,-2.267132,-2.599987,0.513291
H,3.533638,0.32064,-2.988055
H,4.722055,0.75106,-1.726372
H,4.326497,-1.915355,-2.551268
H,4.789274,-1.512089,-0.878282
H,-0.855082,-1.868859,2.643533
H,-1.608334,1.152255,5.586331
H,-0.419069,2.800359,4.172249
H,0.320849,-0.924328,-5.133668
H,1.666015,-1.807316,-4.365503
H,-1.320195,-2.453792,-4.24101
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H,-0.4683,-4.58256,2.382125
H,0.026015,-5.567392,0.983081
H,1.894575,-4.39928,2.773514
H,2.284756,-4.744389,1.071148
H,4.756409,3.594159,0.938736
H,4.227578,2.61687,-0.45284
H,4.501621,0.668696,0.86533
H,4.85613,1.648127,2.309925
N,0.676789,2.418659,1.836778
H,-1.792934,-1.218004,4.806569
H,-6.794813,0.46429,-0.366615
H,-6.87495,-1.312602,-0.332554
H,-6.711075,-0.409311,1.173534
H,-3.273998,4.889228,-2.86516
H,-1.991537,5.839037,-2.091994
H,-1.721314,5.148751,-3.692099
C,-0.056159,3.644512,1.577818
H,-0.212652,4.245782,2.486739
H,0.497889,4.259743,0.861643
H,-1.044579,3.417145,1.150034

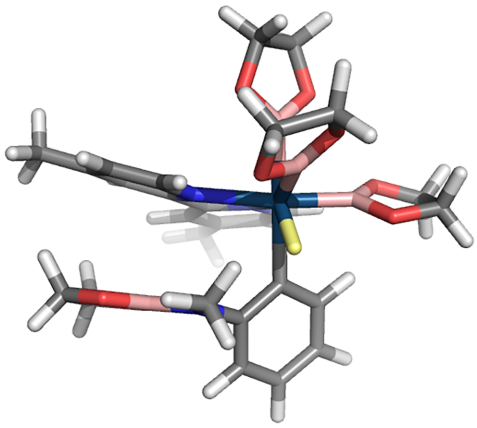
TS8

PhN(Me)Beg_left_syn_4,4'-dimethylbipyridine_Ir_(Beg)3_ultrafine_grid
E(RM06) = -2019.56240728

Item	Value	Threshold	Converged?
Maximum Force	0.000004	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.003059	0.001800	NO
RMS Displacement	0.000449	0.001200	YES

Zero-point correction = 0.629836 (Hartree/Particle)
Thermal correction to Energy = 0.686751
Thermal correction to Enthalpy = 0.687869
Thermal correction to Gibbs Free Energy = 0.531128
Sum of electronic and zero-point Energies = -2018.932572
Sum of electronic and thermal Energies = -2018.875656
Sum of electronic and thermal Enthalpies = -2018.874538
Sum of electronic and thermal Free Energies = -2019.031279

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	430.943	181.769	278.512



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C,0.229663,2.31632,1.984083
C,-0.576445,3.110797,2.780948
C,-1.88542,2.709801,3.055059
C,-1.810669,-0.606348,1.235625
N,-1.039689,-1.105672,0.25173
C,-1.334209,-2.313329,-0.237167
C,-2.399206,-3.074484,0.223408
C,-3.197178,-2.585516,1.256016
C,-2.880805,-1.325867,1.762923
Ir,0.942375,0.054946,-0.147649
B,2.69005,1.080397,-0.18001
O,3.546534,1.203475,-1.273126
C,4.671108,1.980177,-0.889899
C,4.219174,2.691517,0.382552
O,3.137141,1.902123,0.858566
C,0.022471,1.575977,-1.508543
C,0.564861,2.872446,-1.443863
C,-0.075334,3.988596,-1.974459
C,-1.289728,3.837443,-2.634687
C,-1.827068,2.564298,-2.75994
C,-1.190631,1.443114,-2.213425
B,-3.076244,-0.104558,-1.85738
O,-3.687261,0.699168,-0.913605
C,-4.921161,0.098373,-0.562732
C,-4.99169,-1.209185,-1.377357
O,-3.818653,-1.226222,-2.171117
B,1.748585,-1.219011,1.348917
O,2.659471,-0.843951,2.322673
C,2.855405,-1.942289,3.208218
C,2.298825,-3.137656,2.44443
O,1.39374,-2.559843,1.511275
B,2.023328,-1.504181,-0.966658
O,1.430631,-2.469698,-1.780688
C,2.324063,-3.57303,-1.872001
C,3.681388,-2.977595,-1.51719
O,3.361749,-1.821954,-0.752763
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C,-4.339943,-3.372225,1.81672
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H,1.252848,2.596514,1.736927
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H,2.285768,-4.004634,-2.878725
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H,-2.76455,2.410181,-3.295525
H,1.775049,-3.859244,3.081906
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H,2.305782,-1.756542,4.14308
H,3.920215,-2.040655,3.448689
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H,5.003056,2.753892,1.14649
H,4.941957,2.672417,-1.696327
H,5.52811,1.314461,-0.70602
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N,-1.824593,0.183381,-2.432233
H,0.38129,4.973085,-1.874726
H,-3.814145,3.15652,3.909722
H,-2.430285,3.618192,4.920183
H,-2.835781,4.583541,3.501172
H,-5.217968,-2.733775,1.982747
H,-4.629225,-4.192502,1.149661
H,-4.073464,-3.810515,2.787977
C,-1.180577,-0.71155,-3.377342
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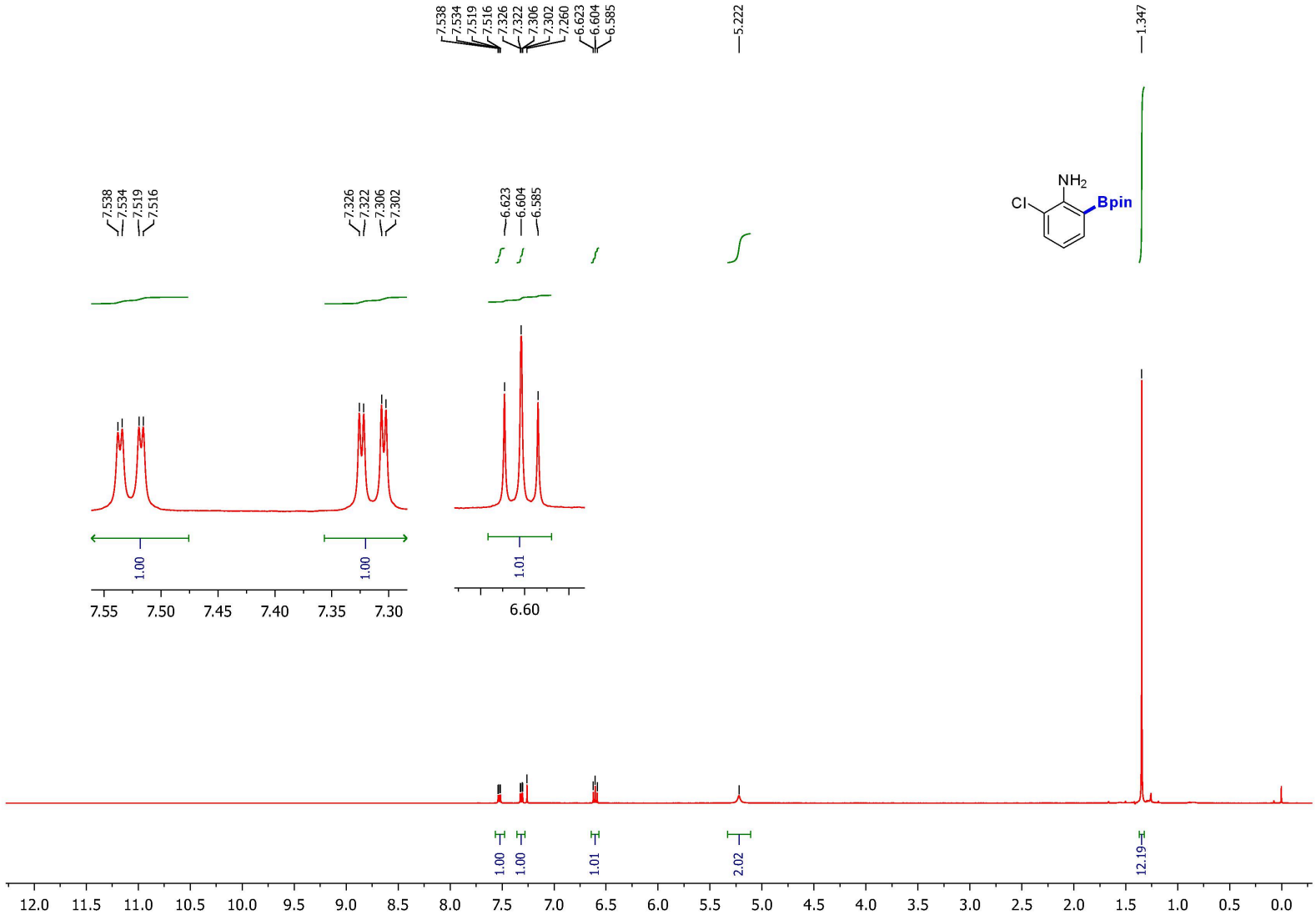
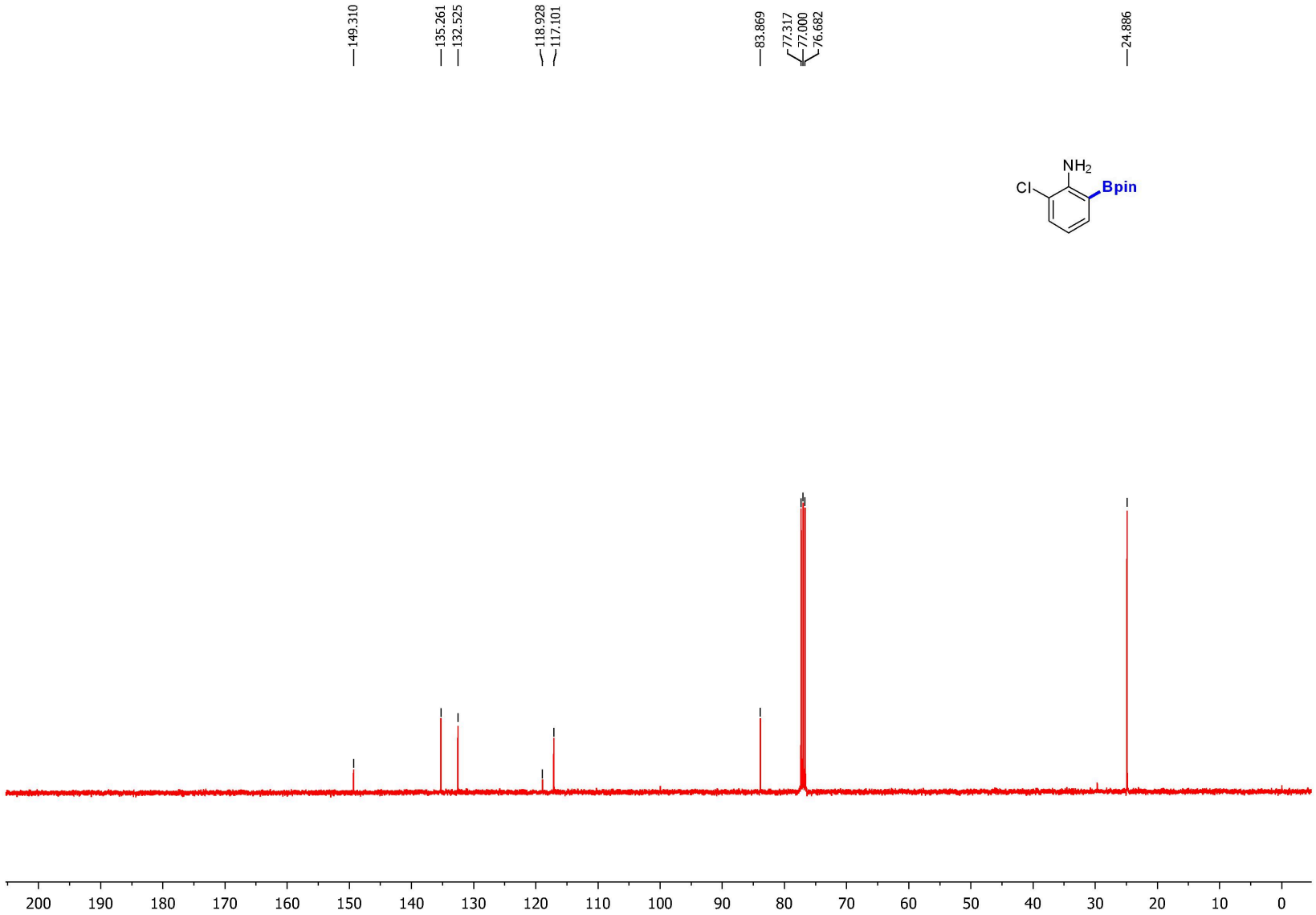
H,-1.002456,-0.200959,-4.336533

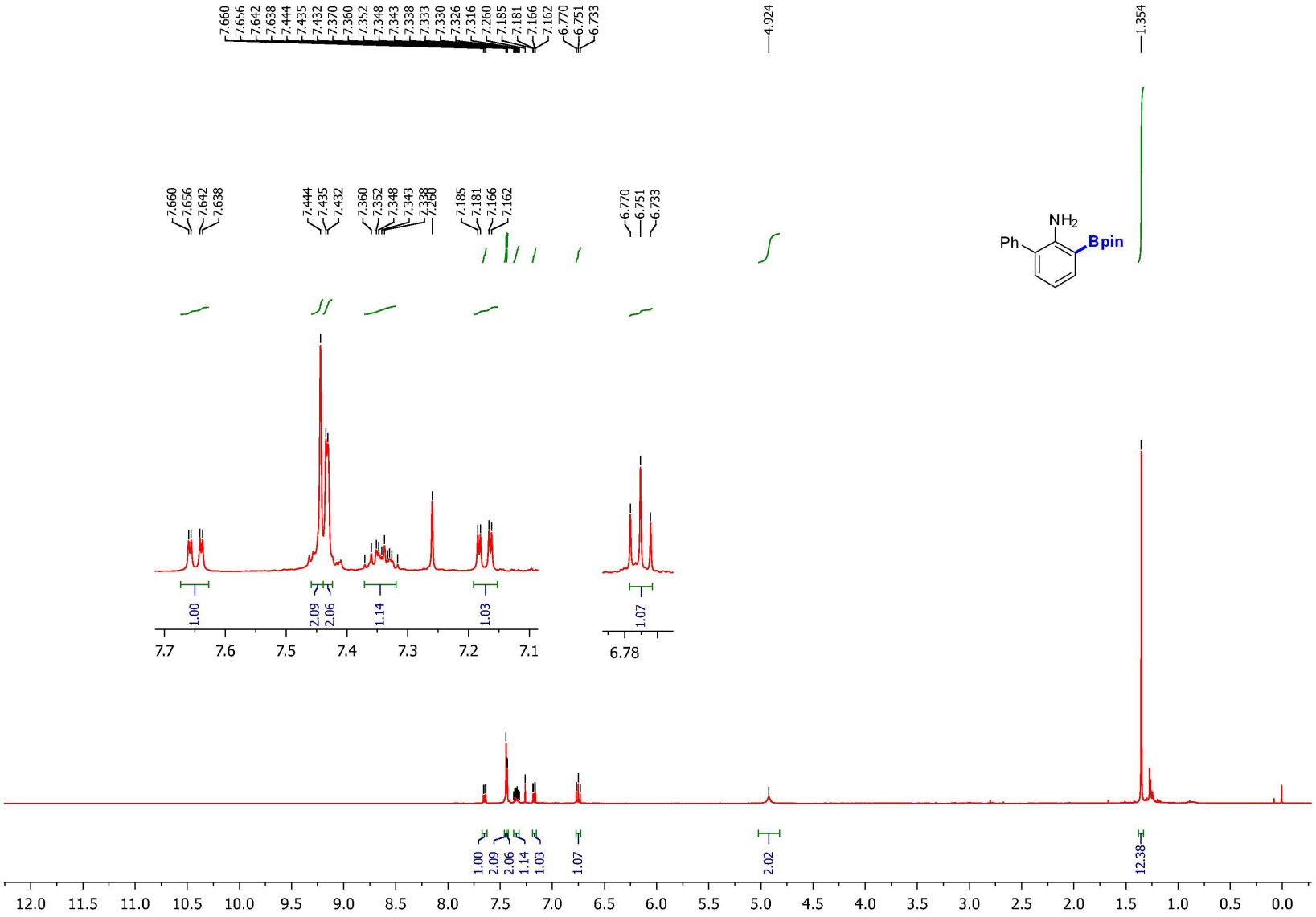
NMR spectra



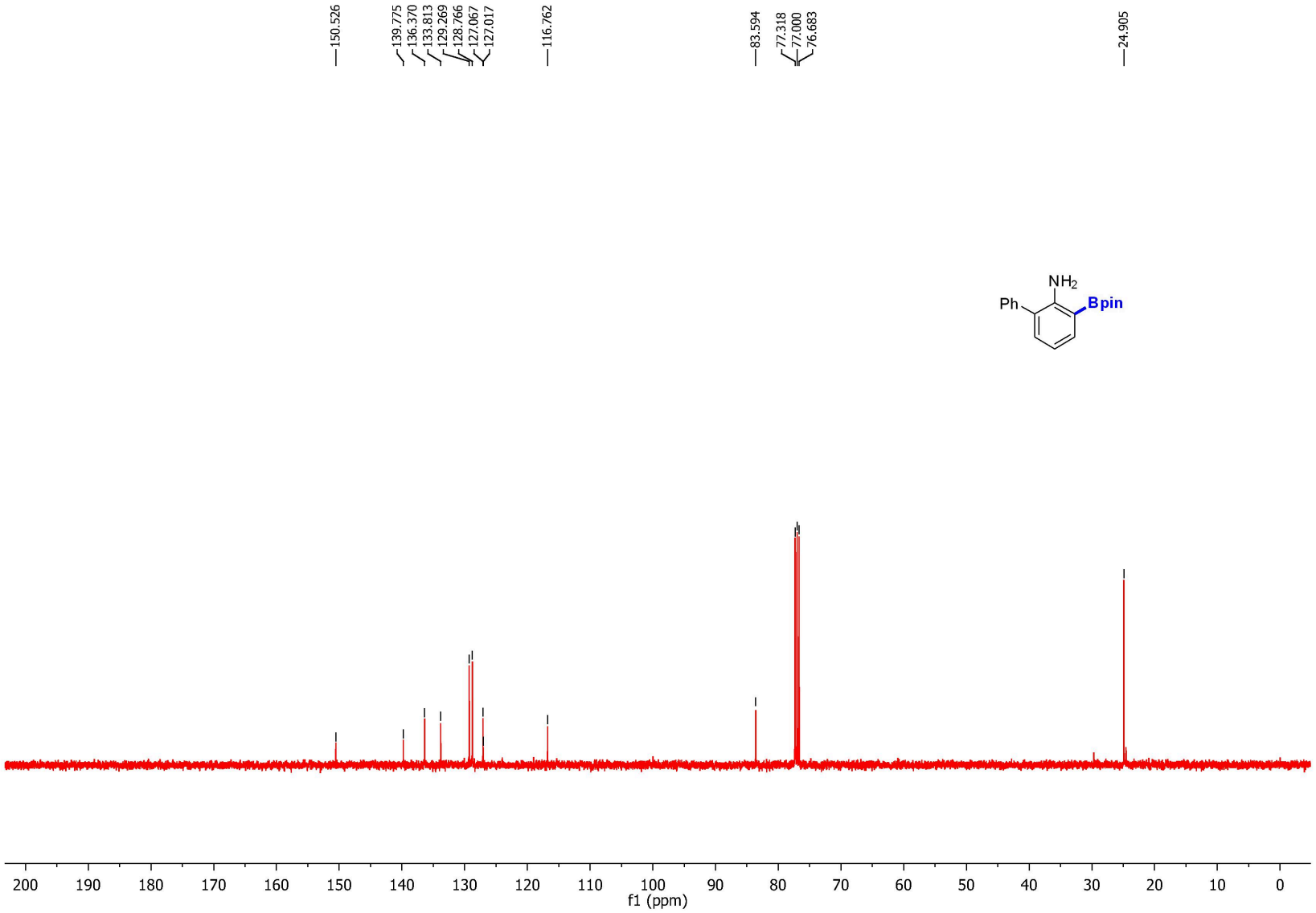
^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



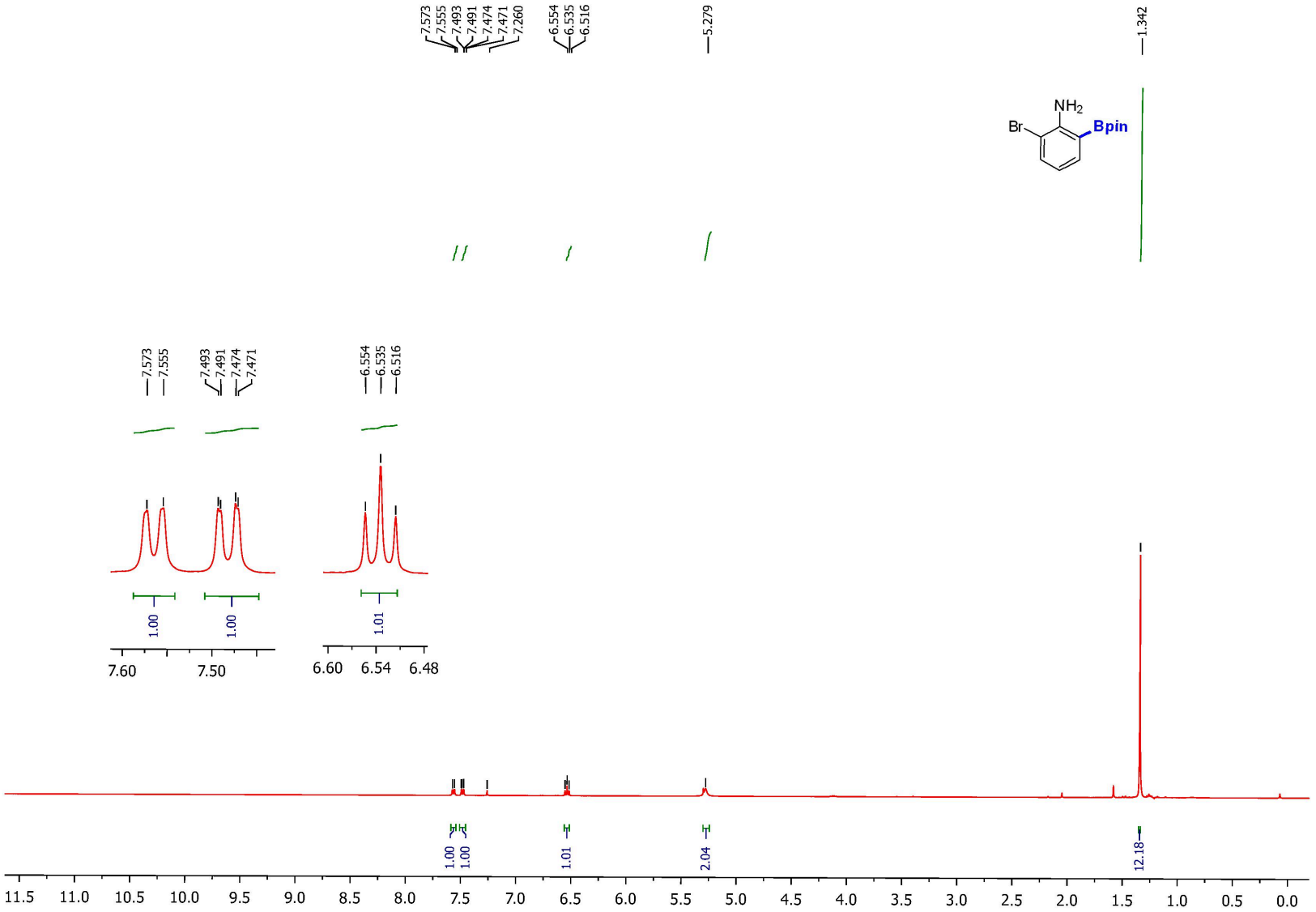
^{13}C-NMR (25 ℃,100 MHz, $CDCl_3$)



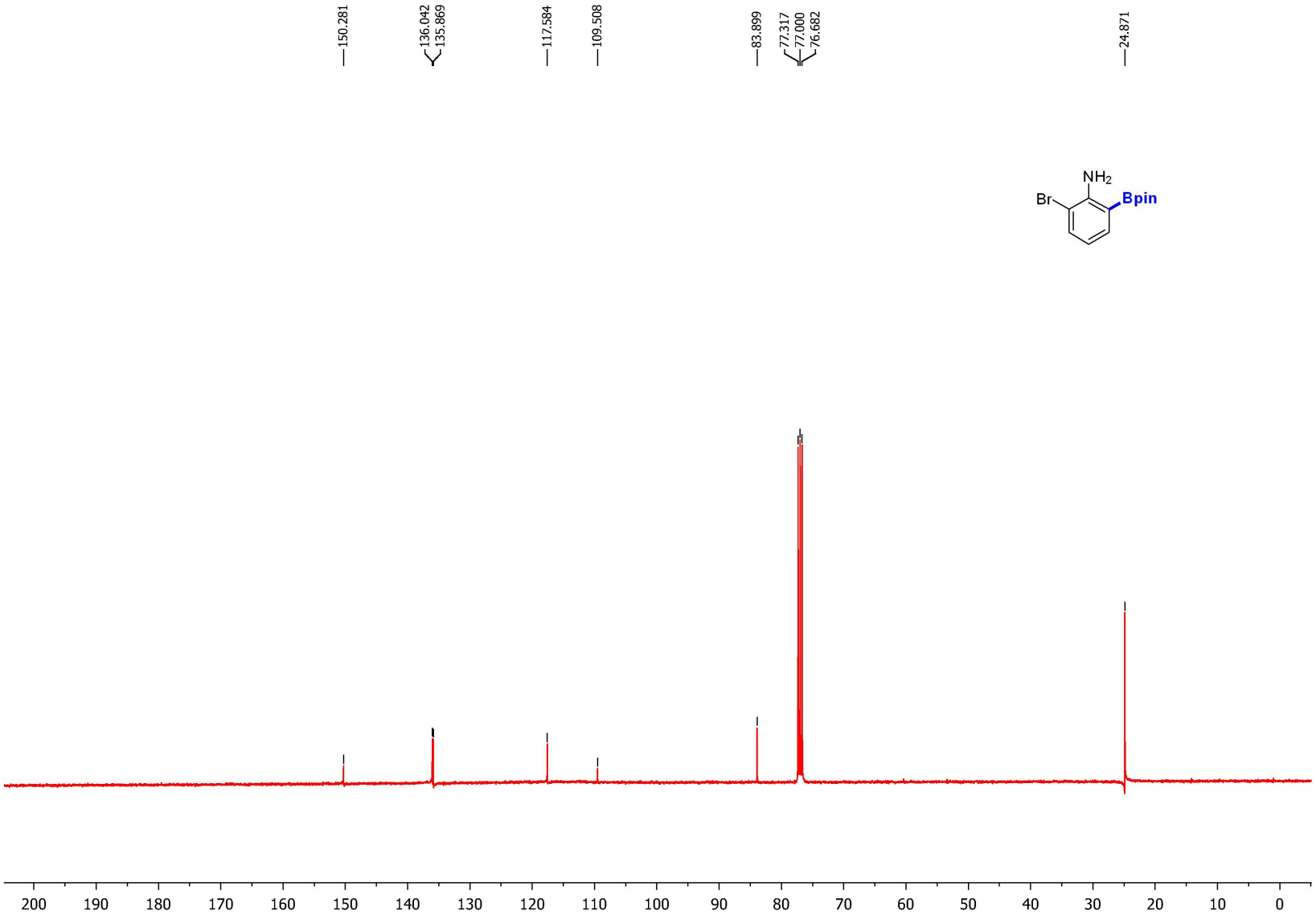
^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



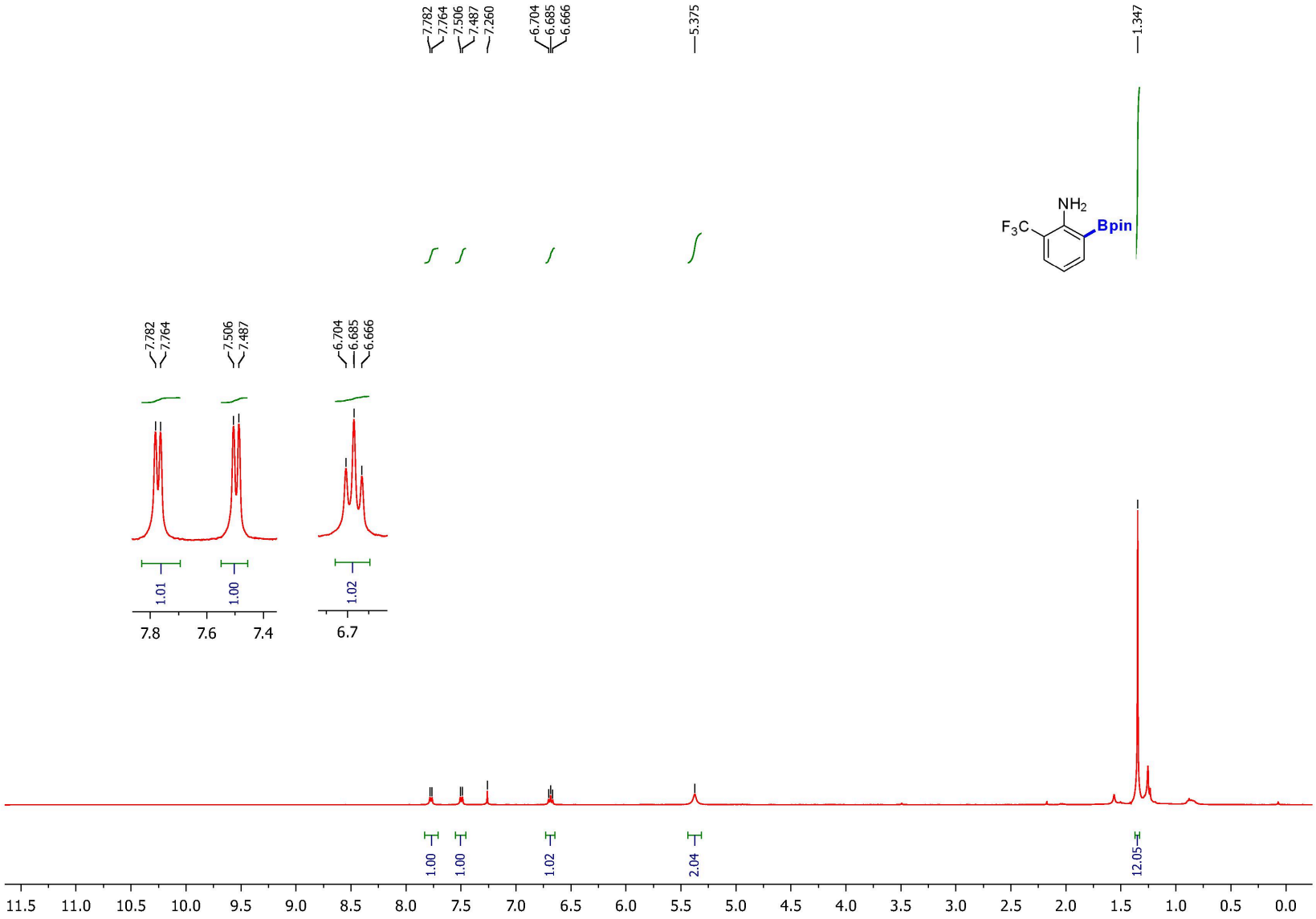
^{13}C-NMR (25 °C,100 MHz, $CDCl_3$)



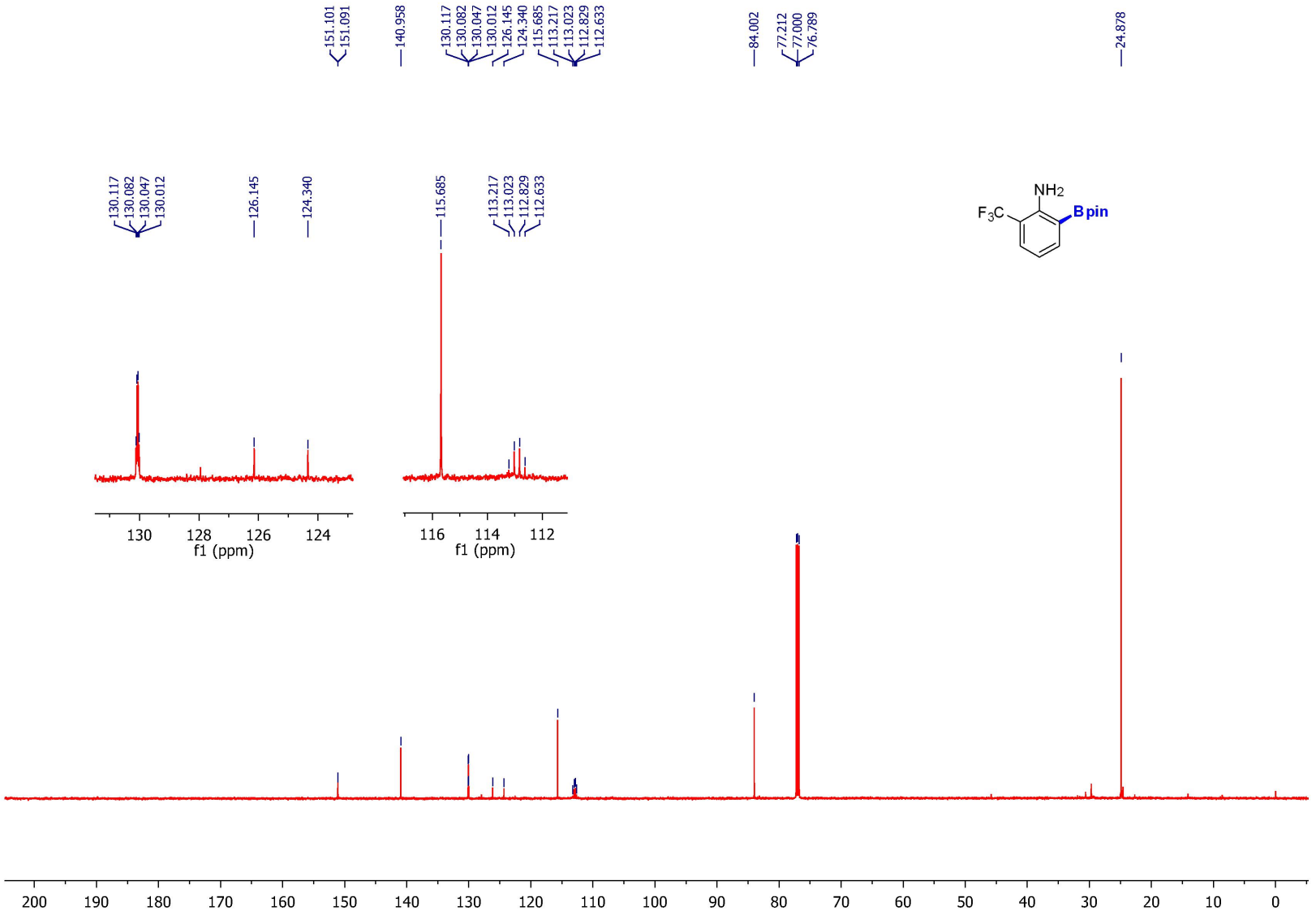
^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



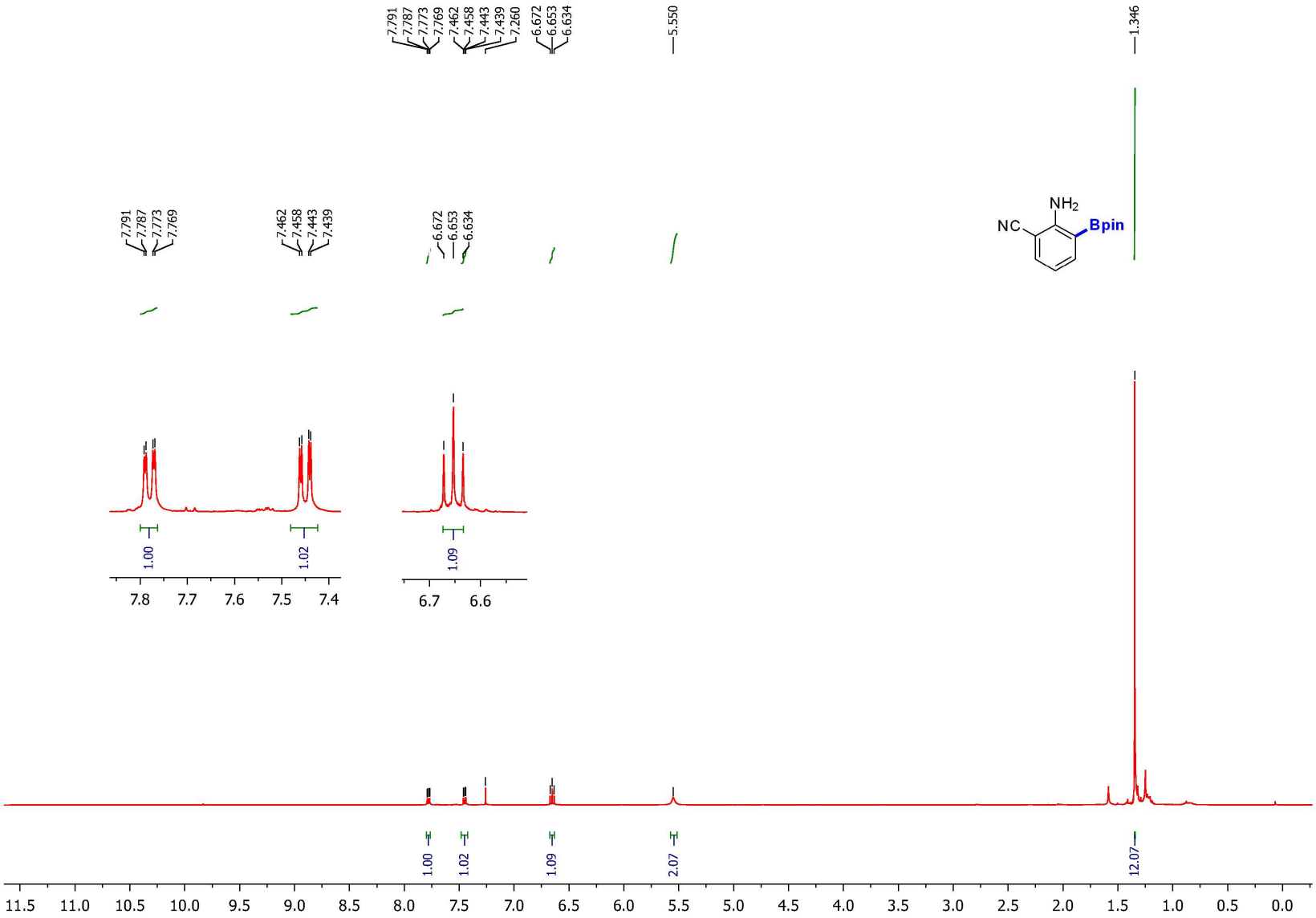
^{13}C-NMR (25 °C,100 MHz, $CDCl_3$)



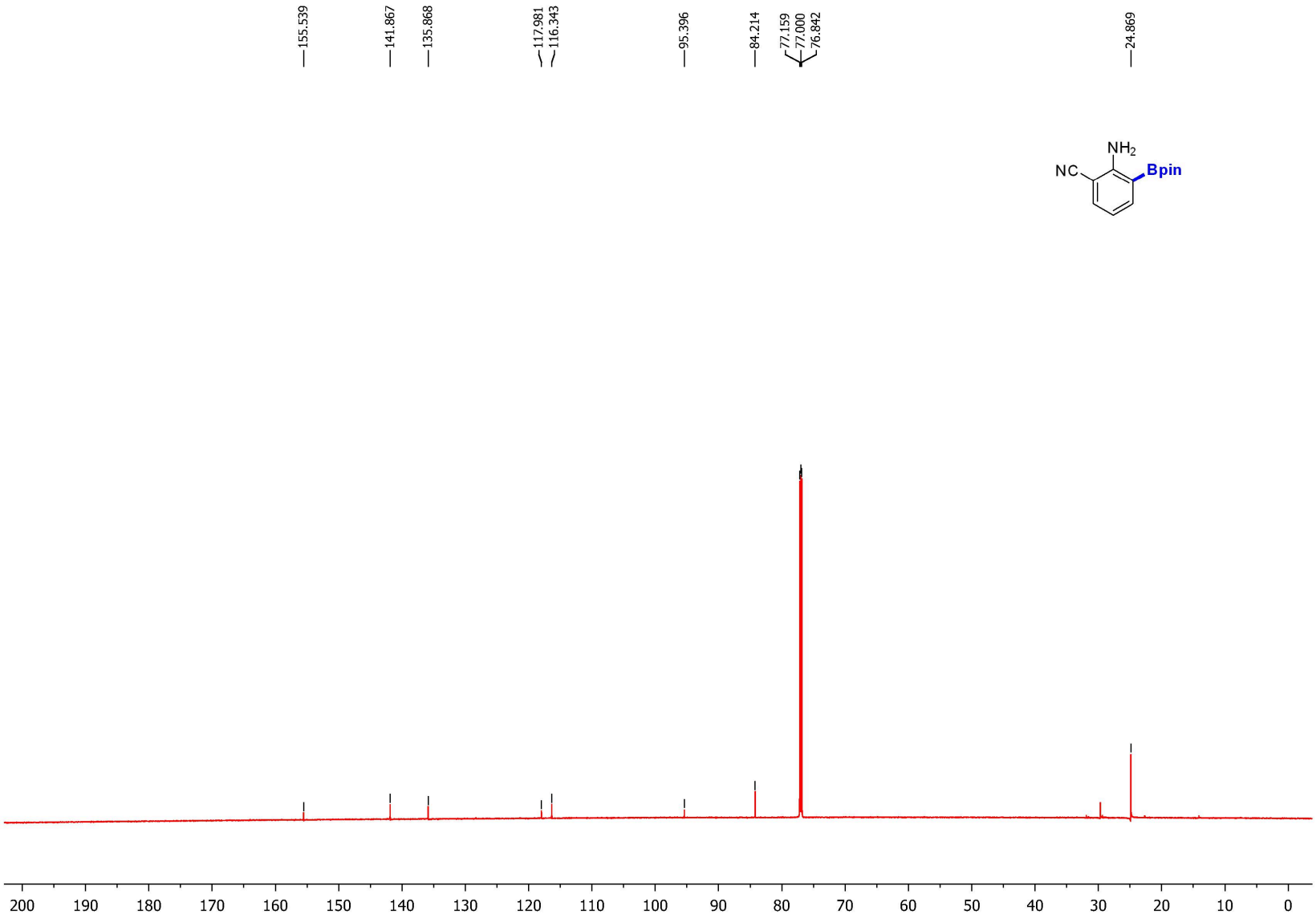
^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



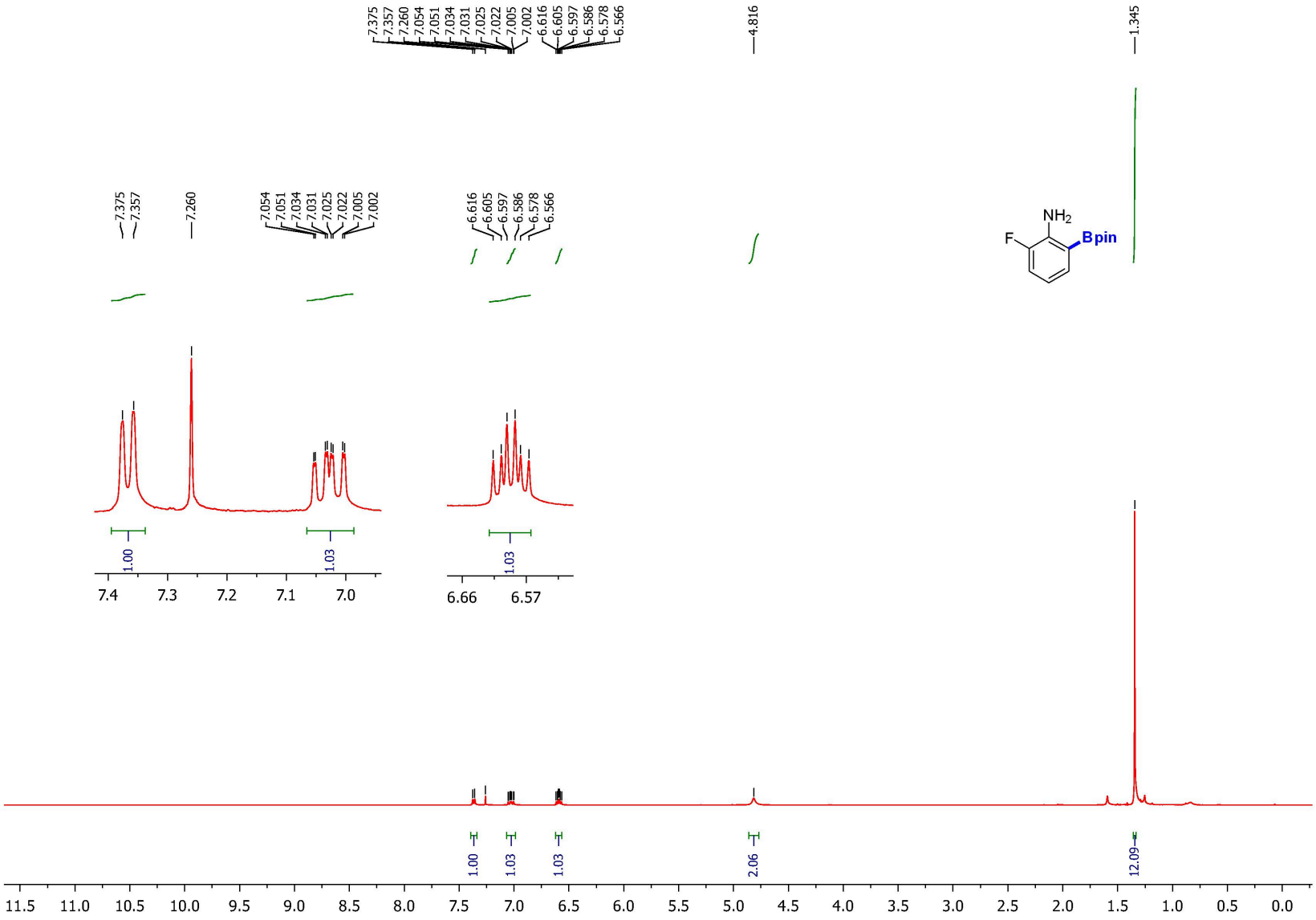
^{13}C-NMR (25 °C, 150 MHz, $CDCl_3$)



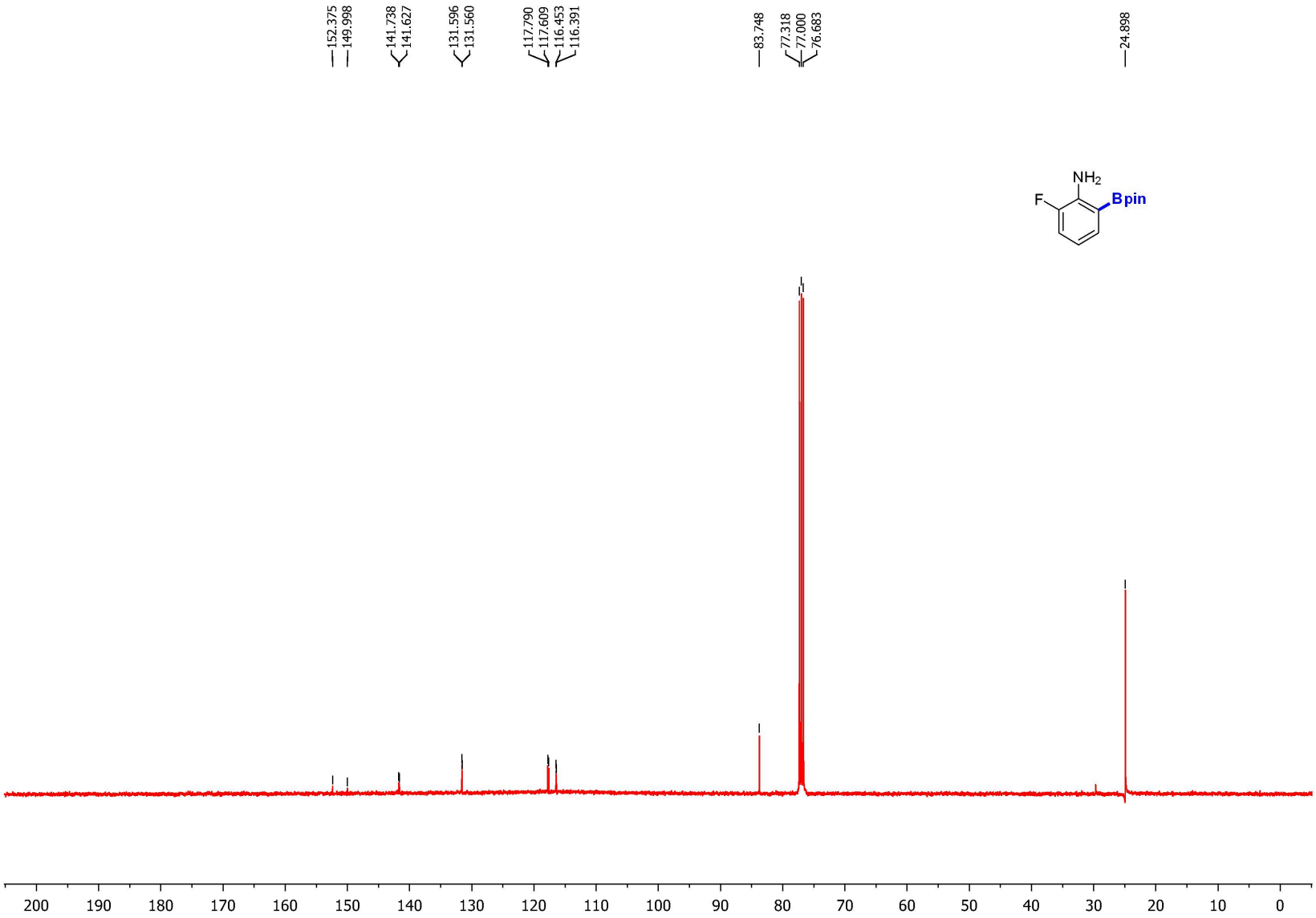
^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



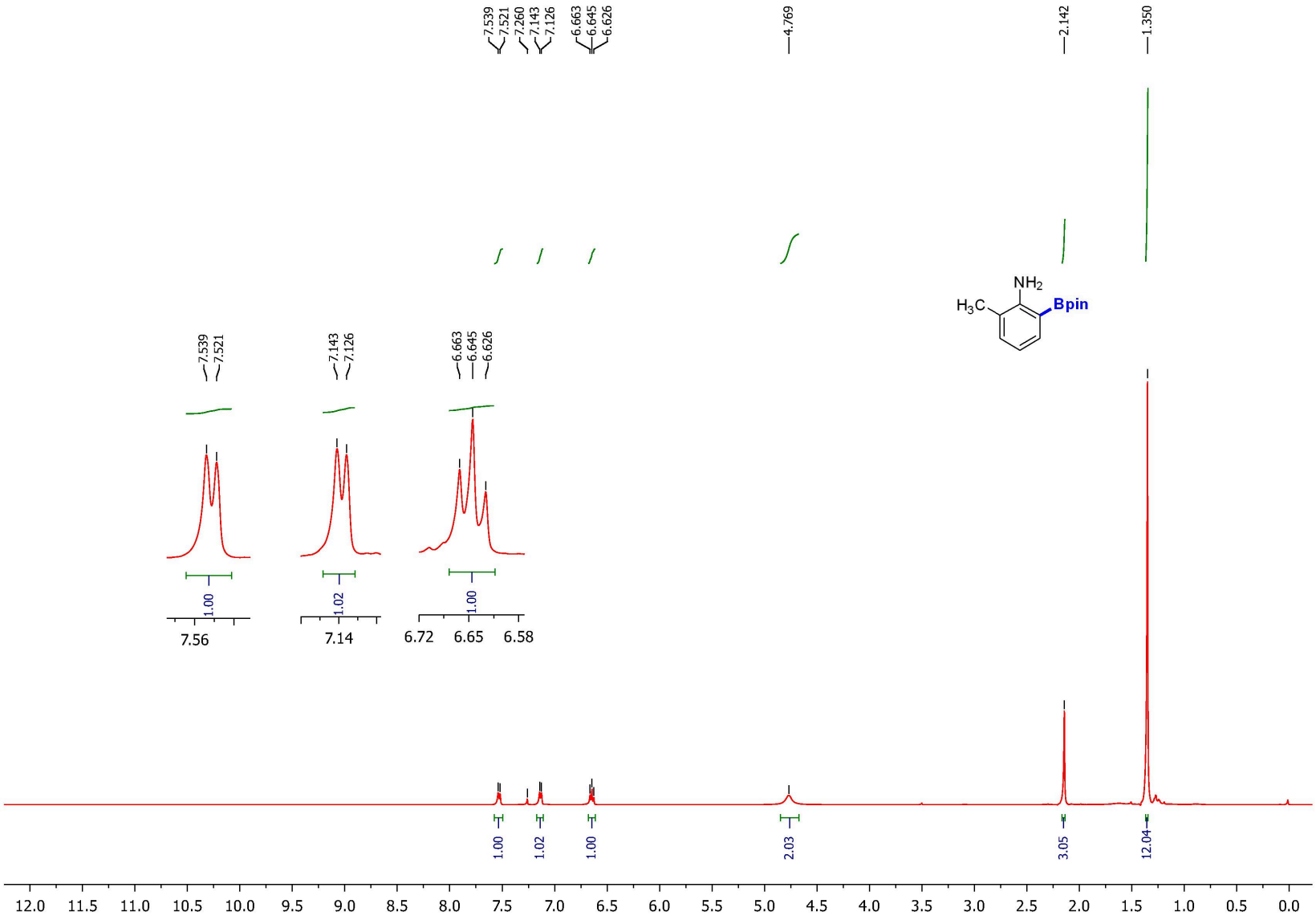
^{13}C-NMR (25 °C, 200 MHz, $CDCl_3$)



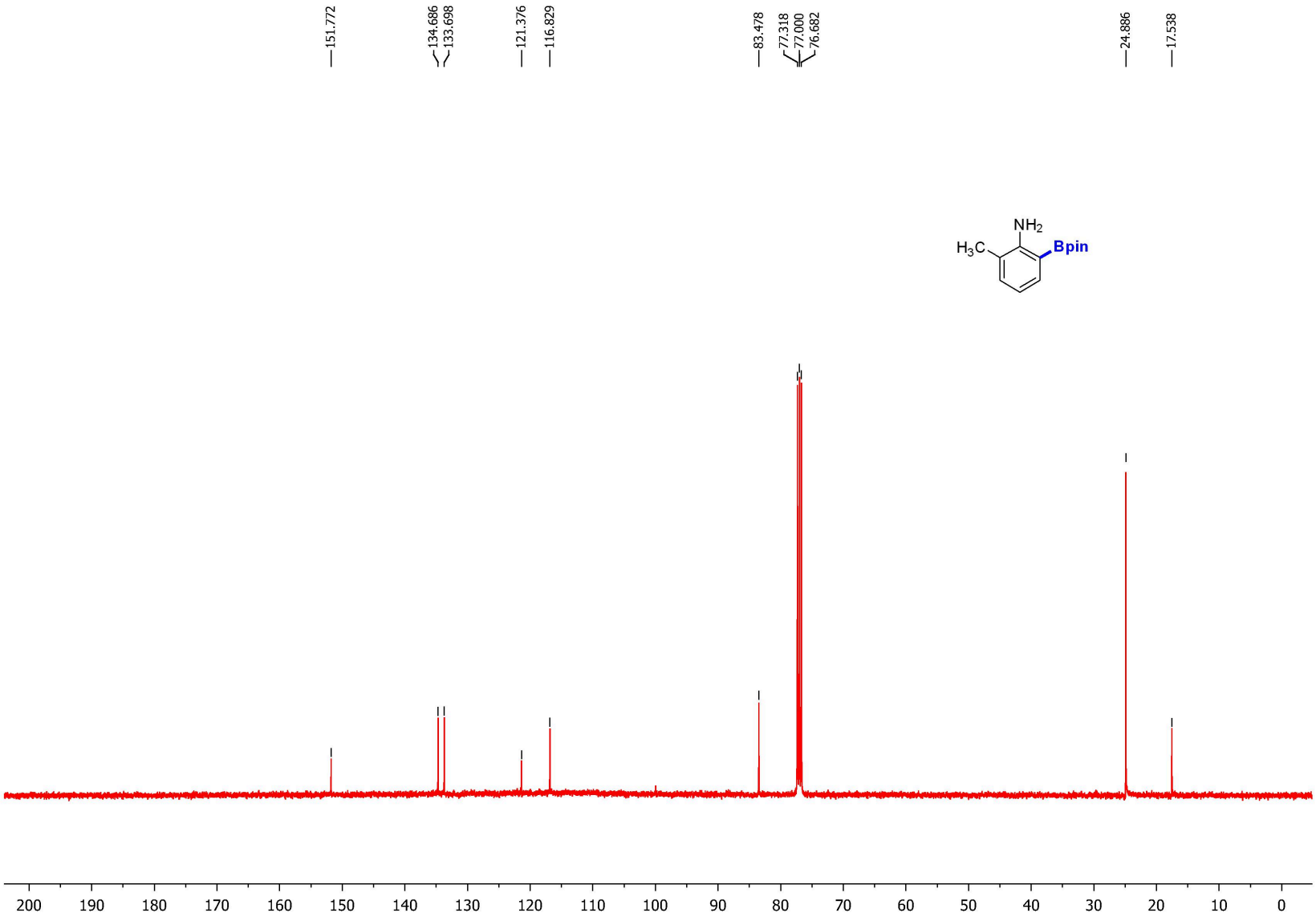
^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



^{13}C-NMR (25 °C, 100 MHz, $CDCl_3$)



^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



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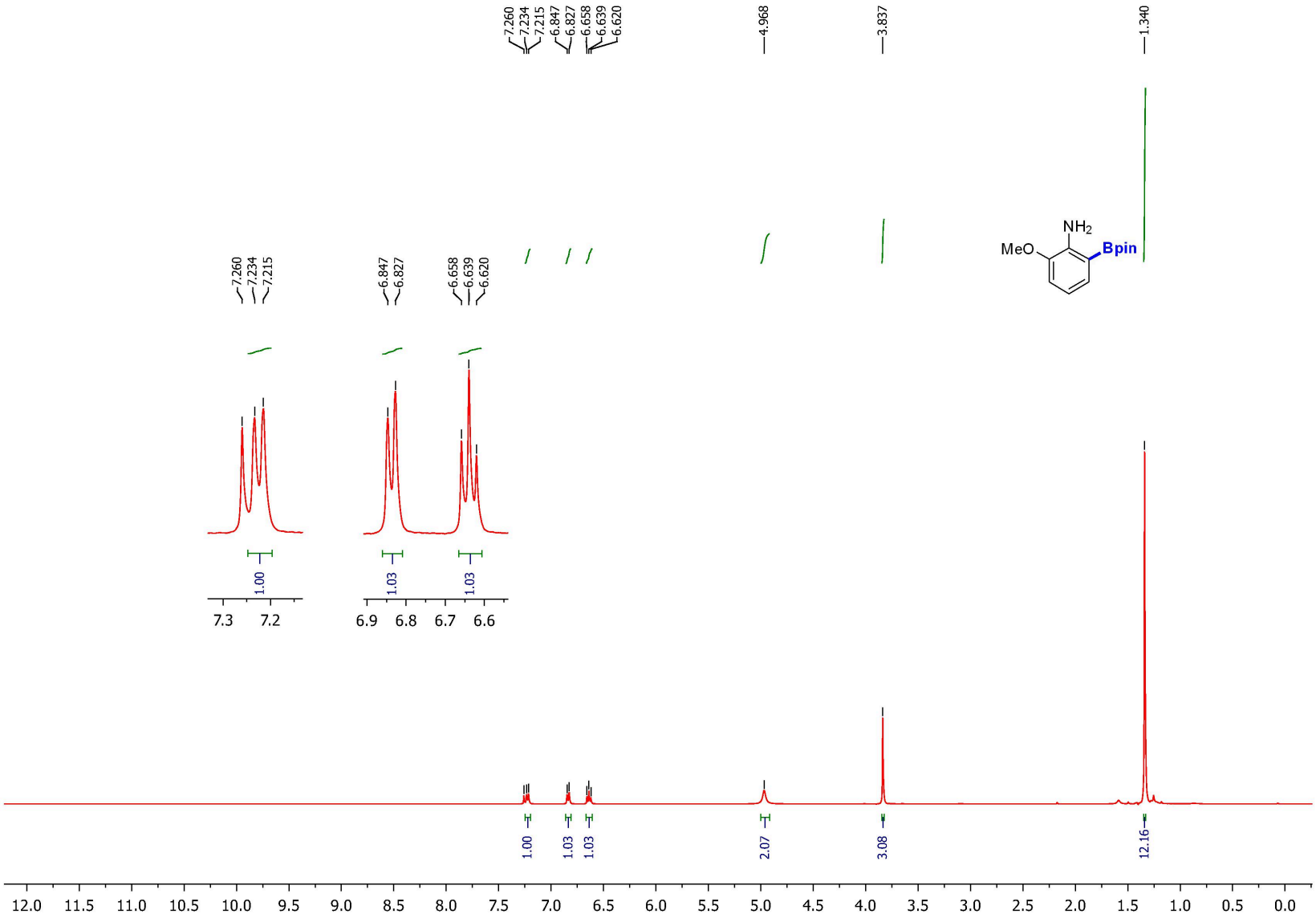
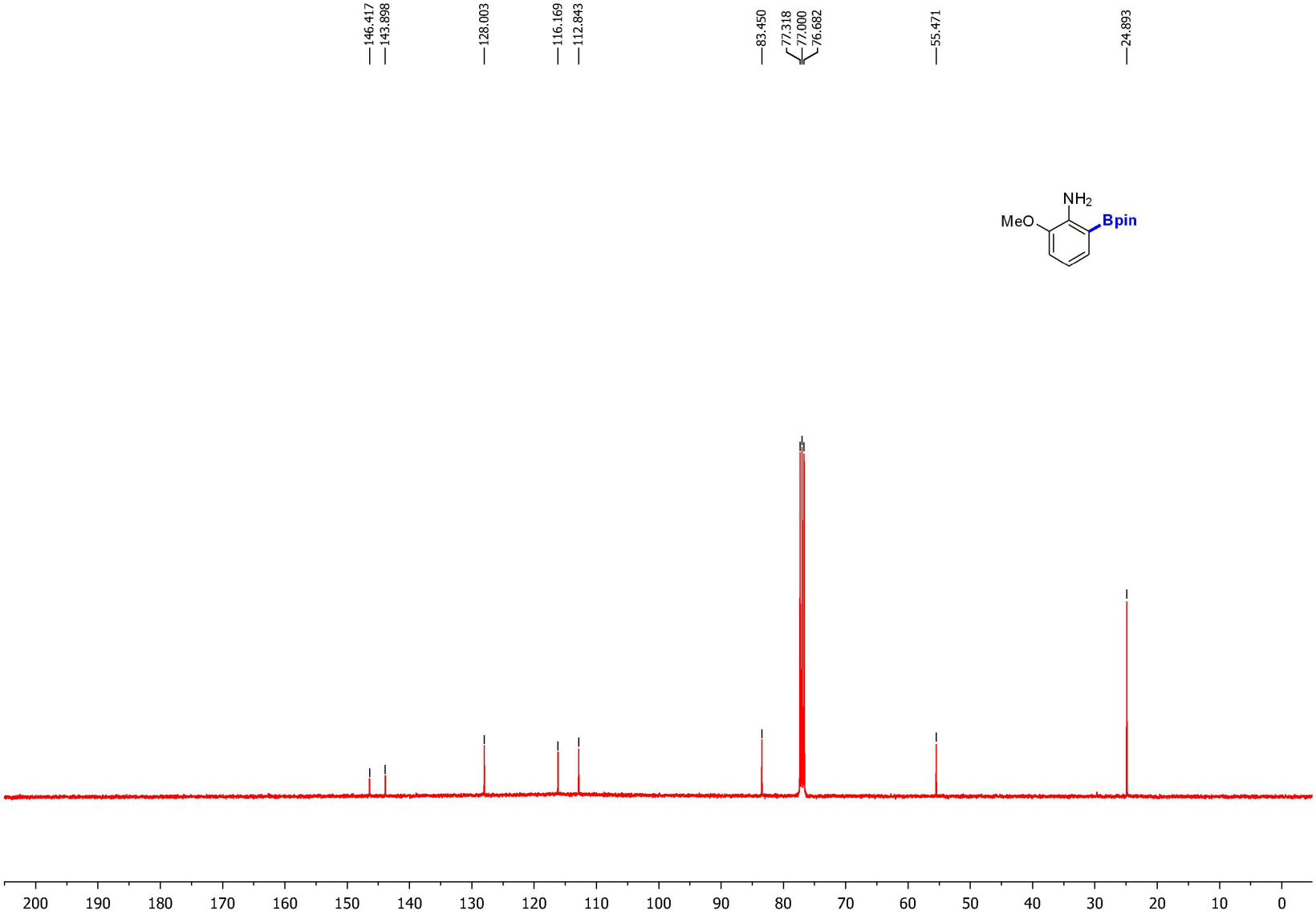
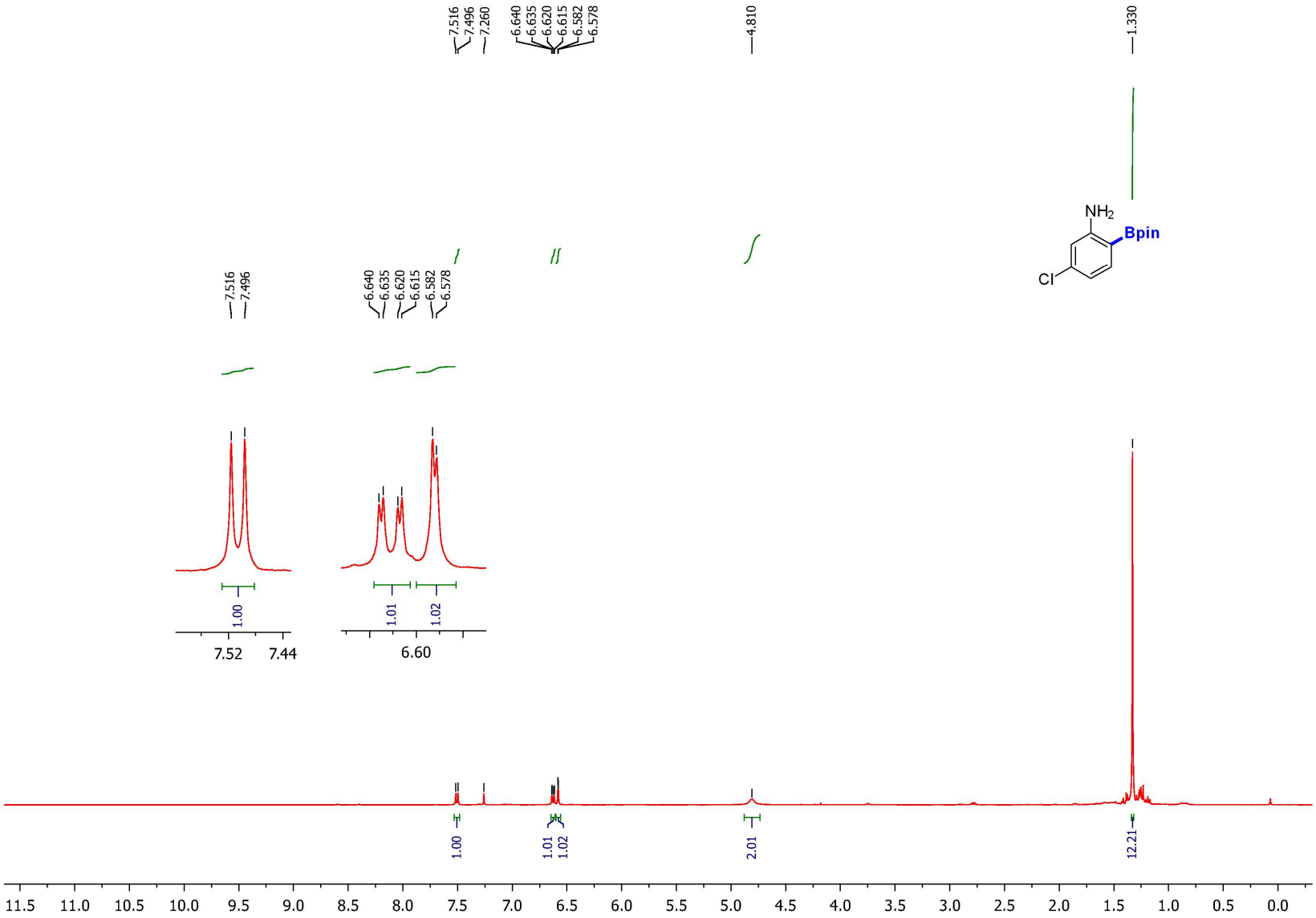


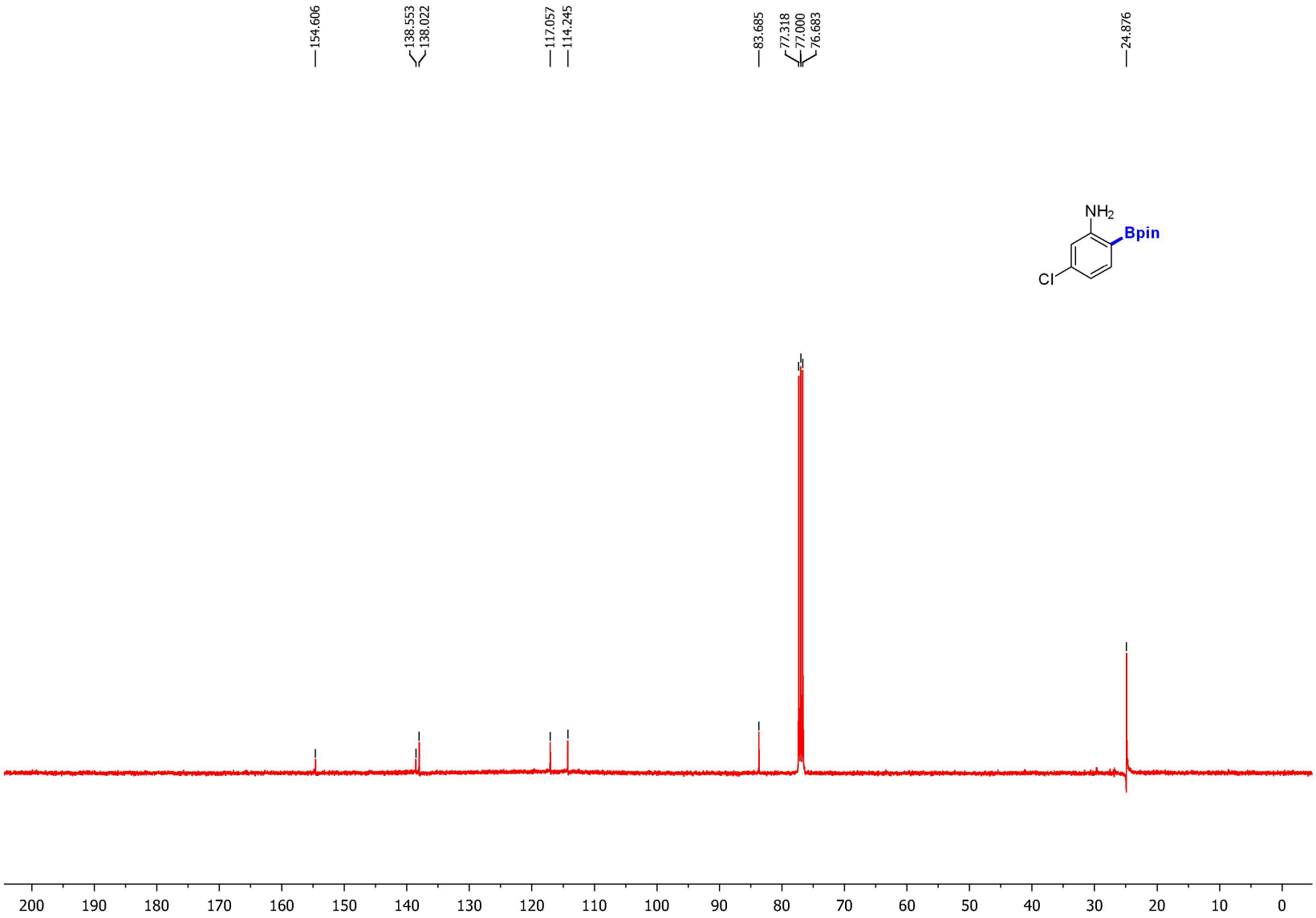
^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



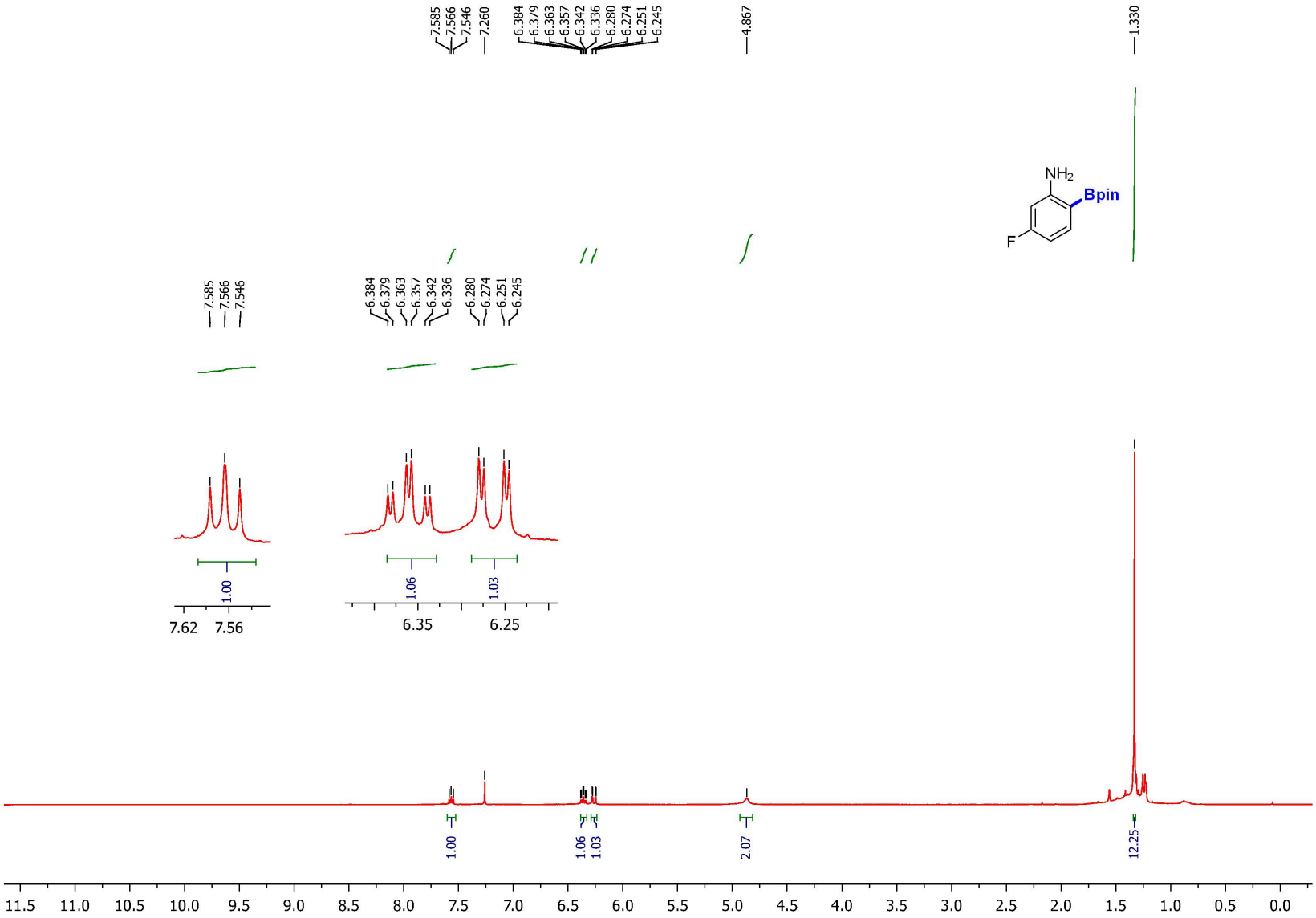
^{13}C-NMR (25 °C, 100 MHz, $CDCl_3$)



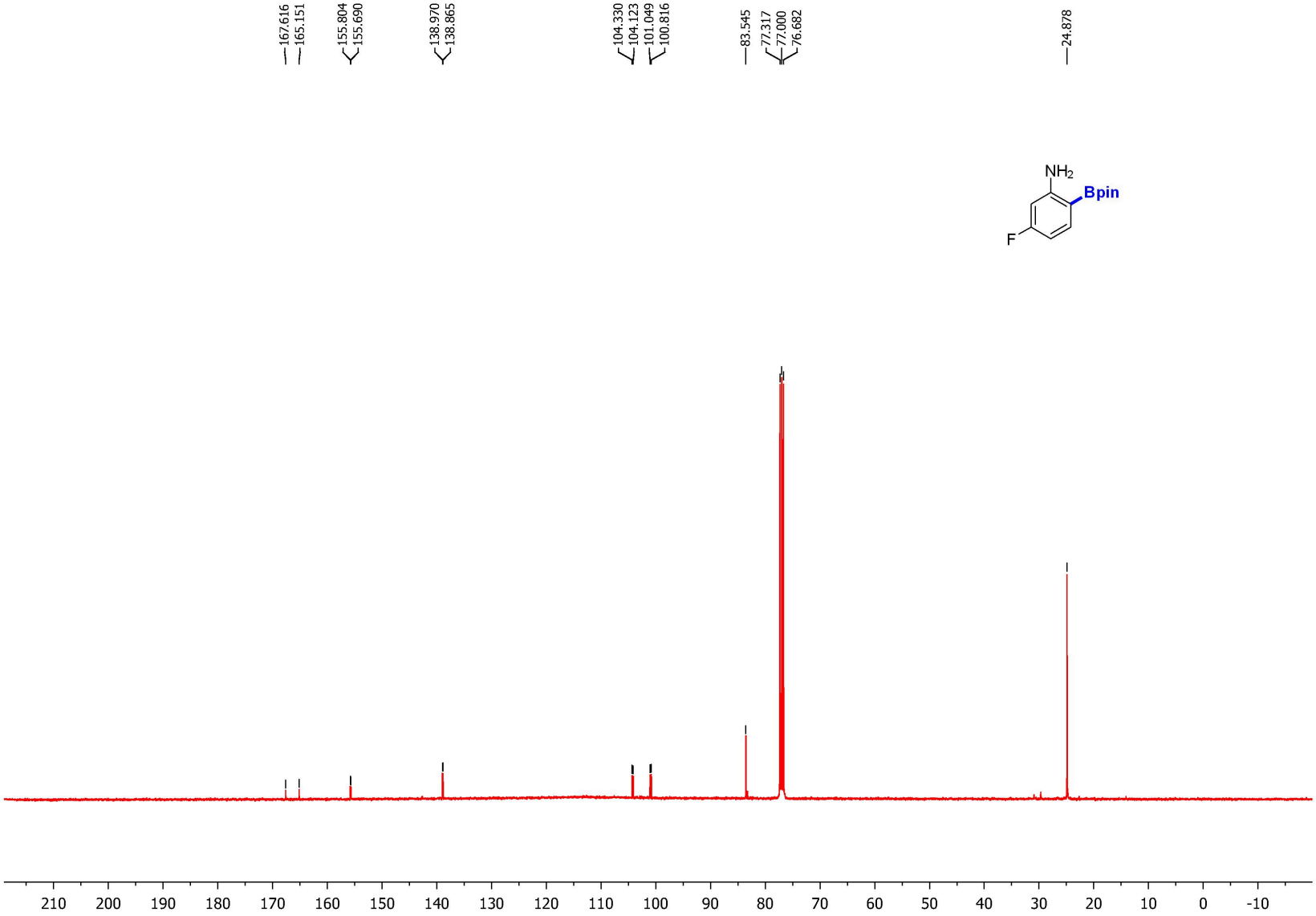
^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



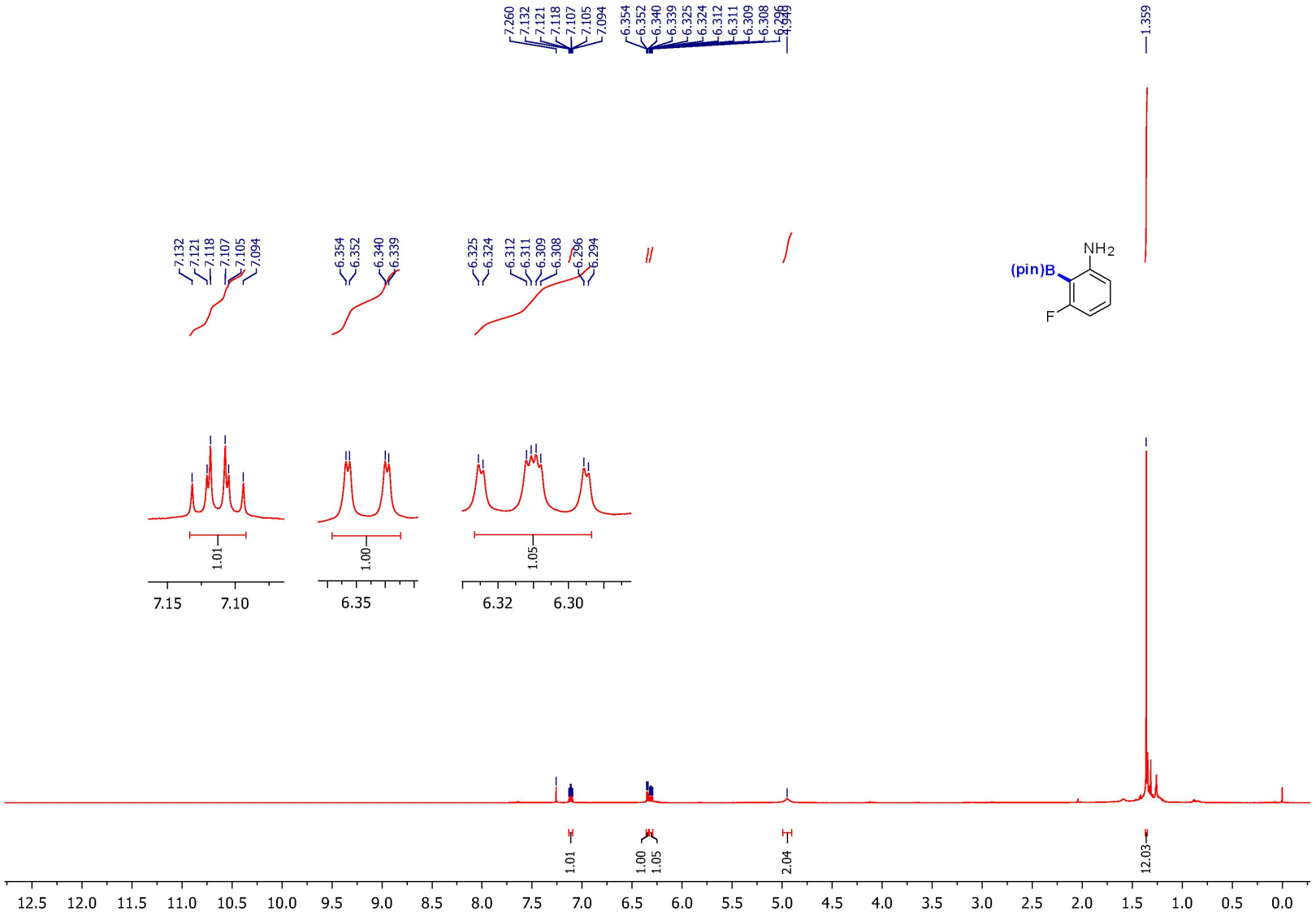
^{13}C-NMR (25 °C, 100 MHz, $CDCl_3$)



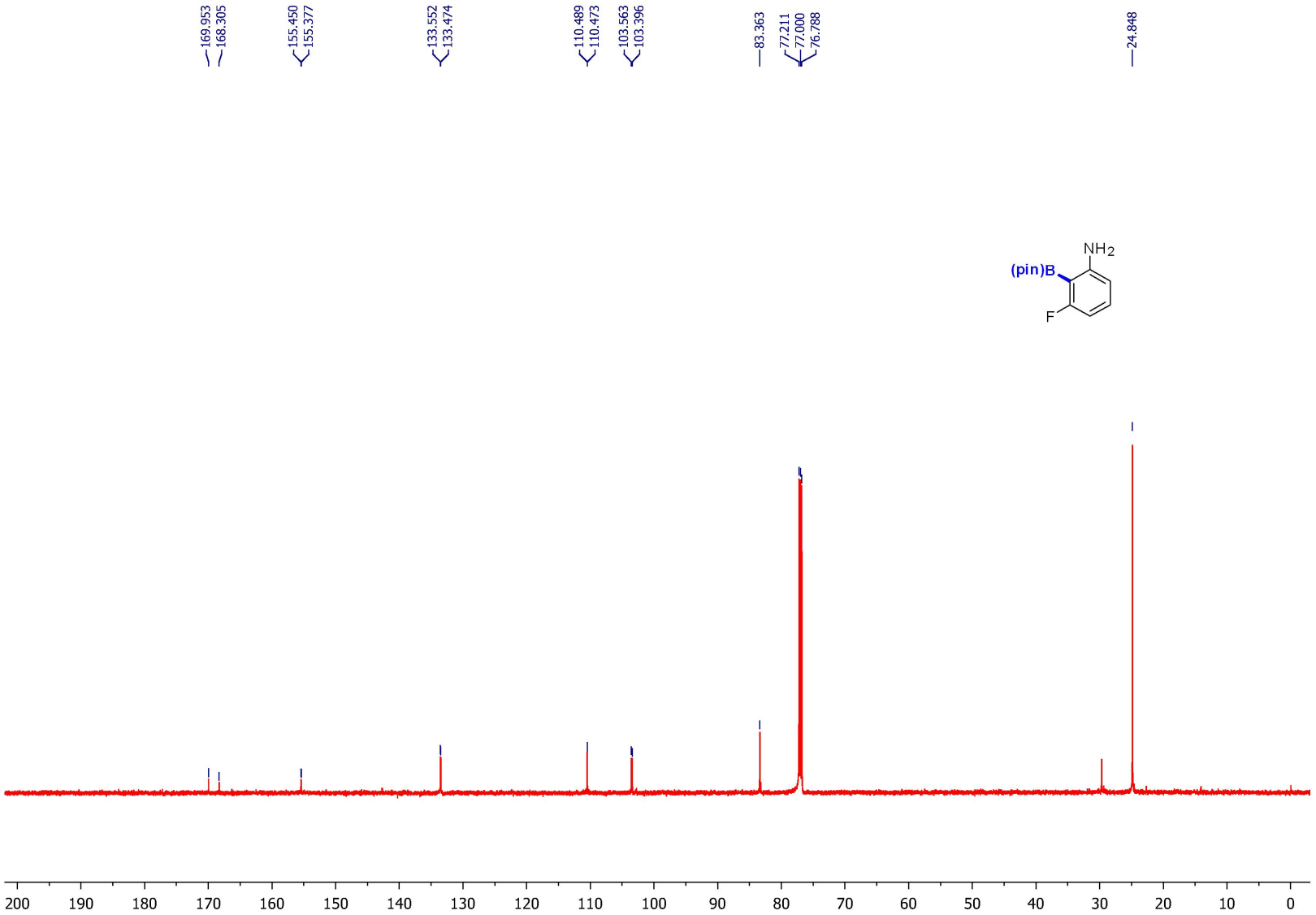
^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



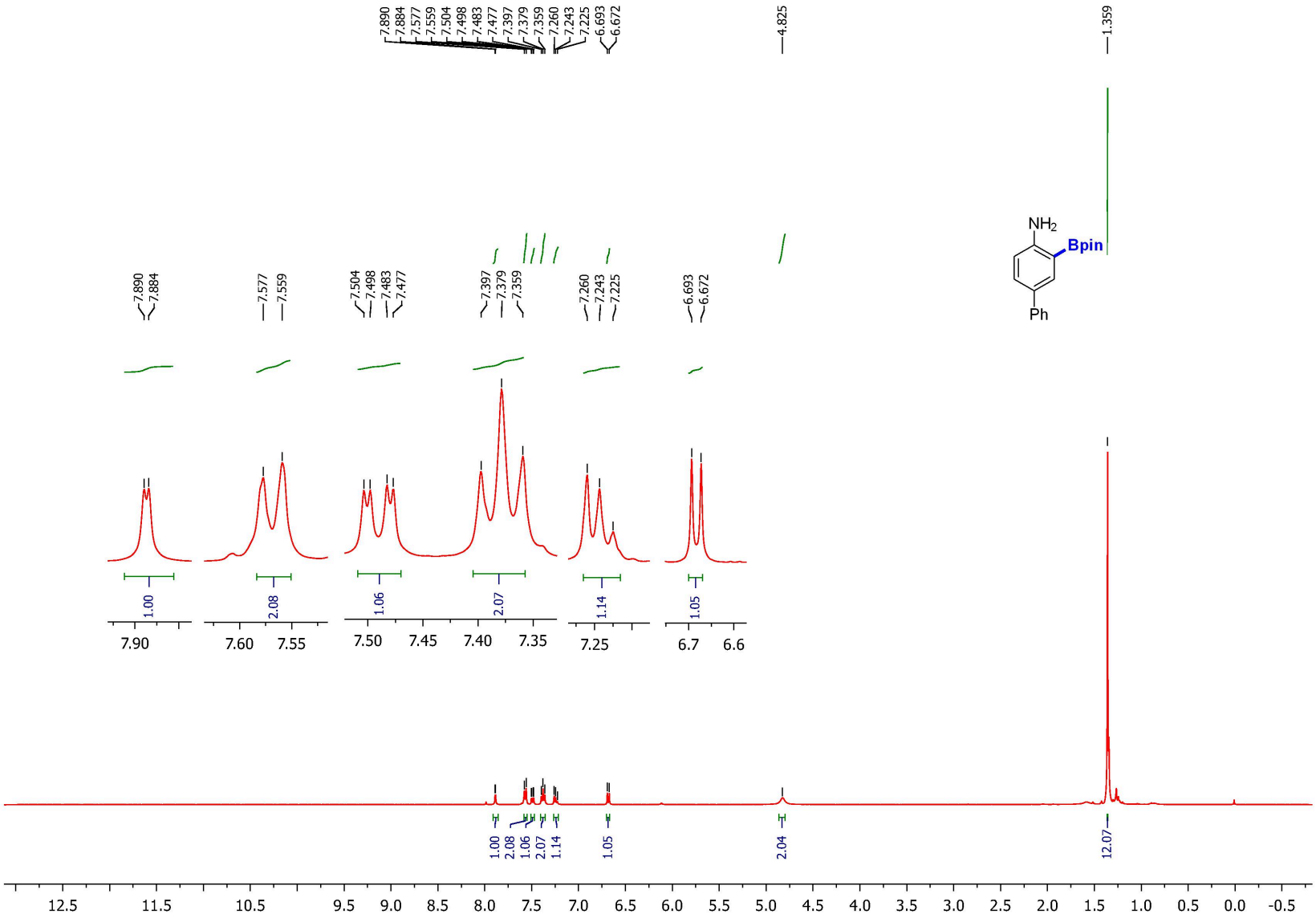
^{13}C-NMR (25 °C, 100 MHz, $CDCl_3$)



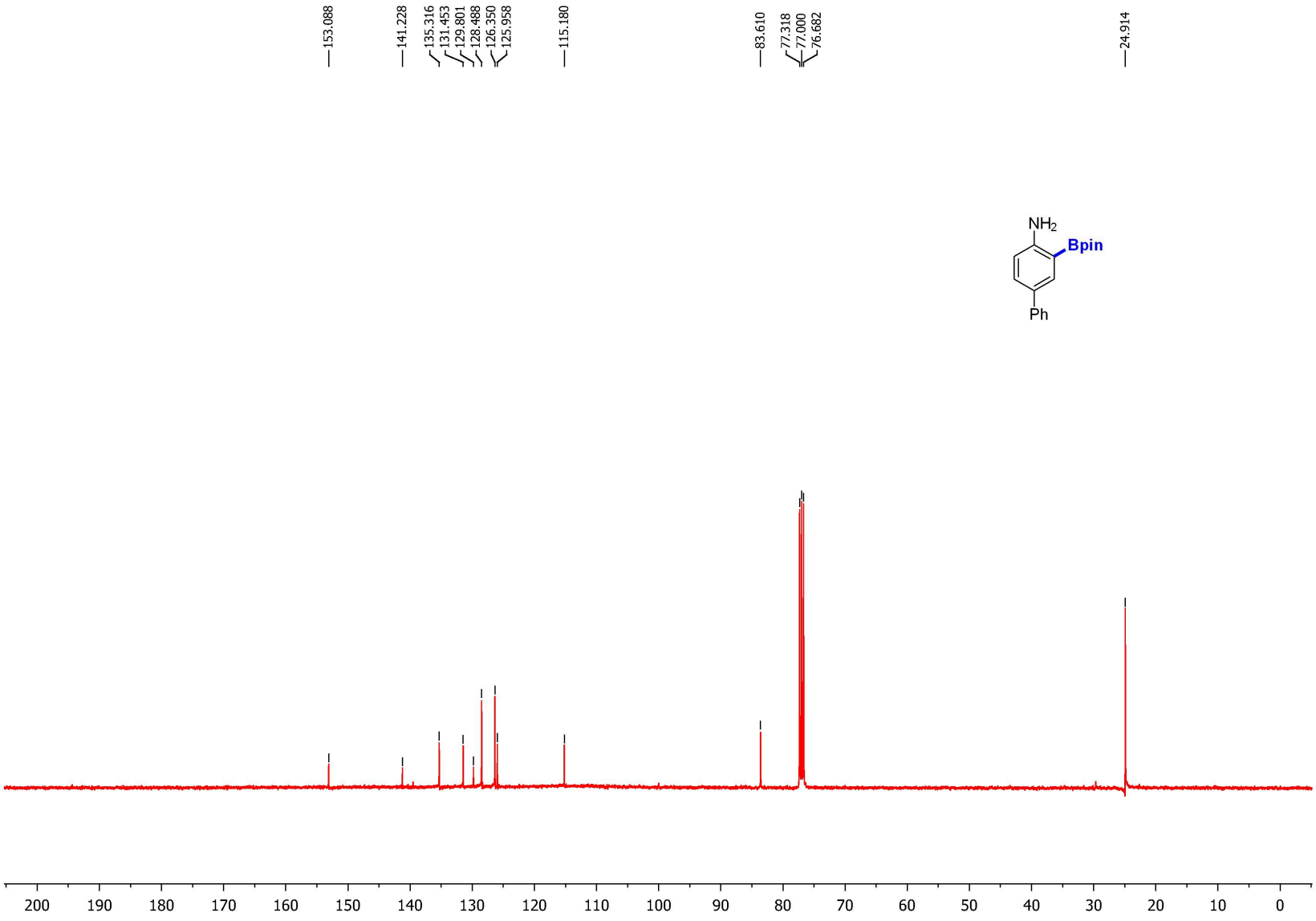
^{1}H-NMR (25 °C, 600 MHz, $CDCl_3$)



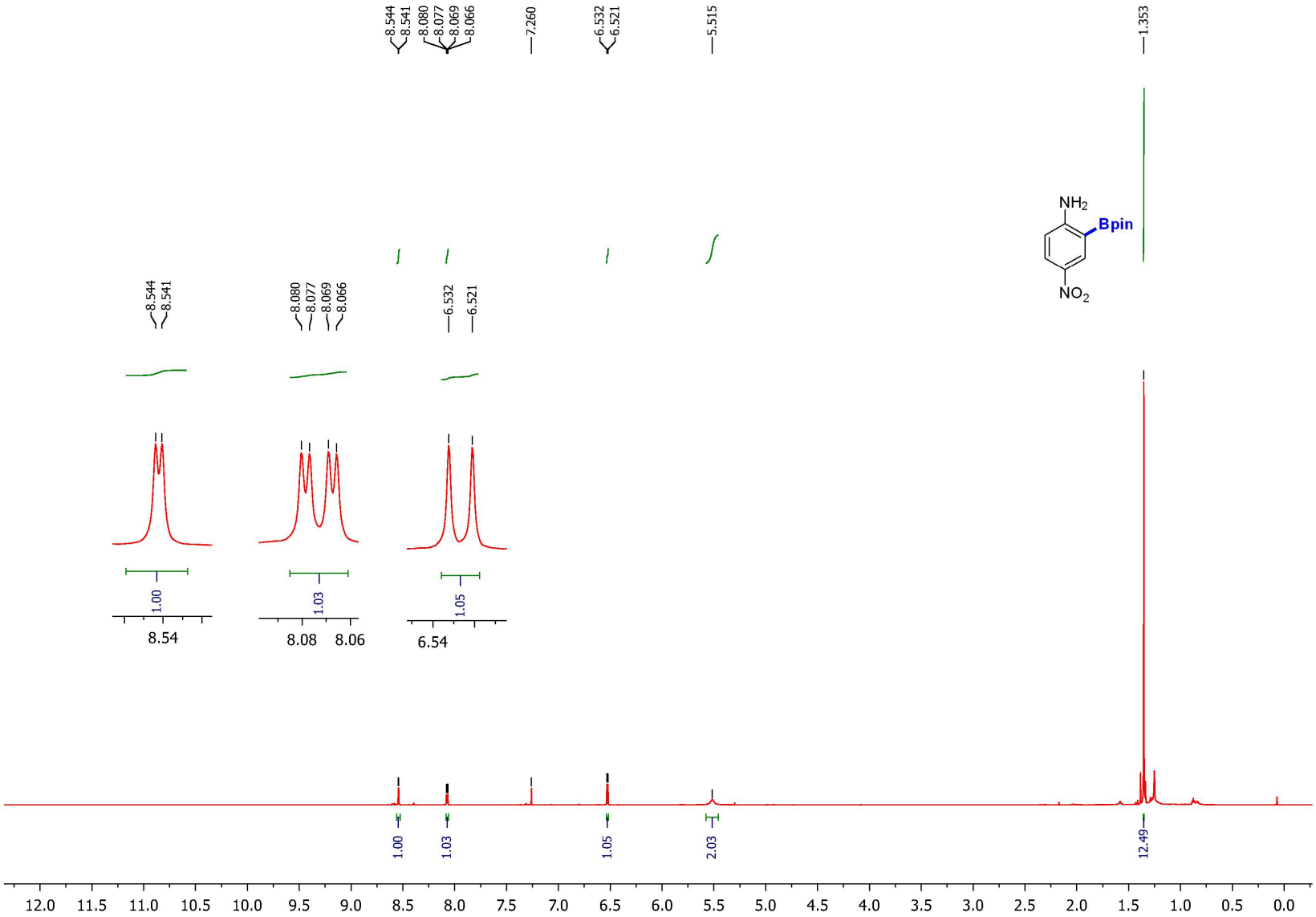
^{13}C-NMR (25 °C, 150 MHz, $CDCl_3$)



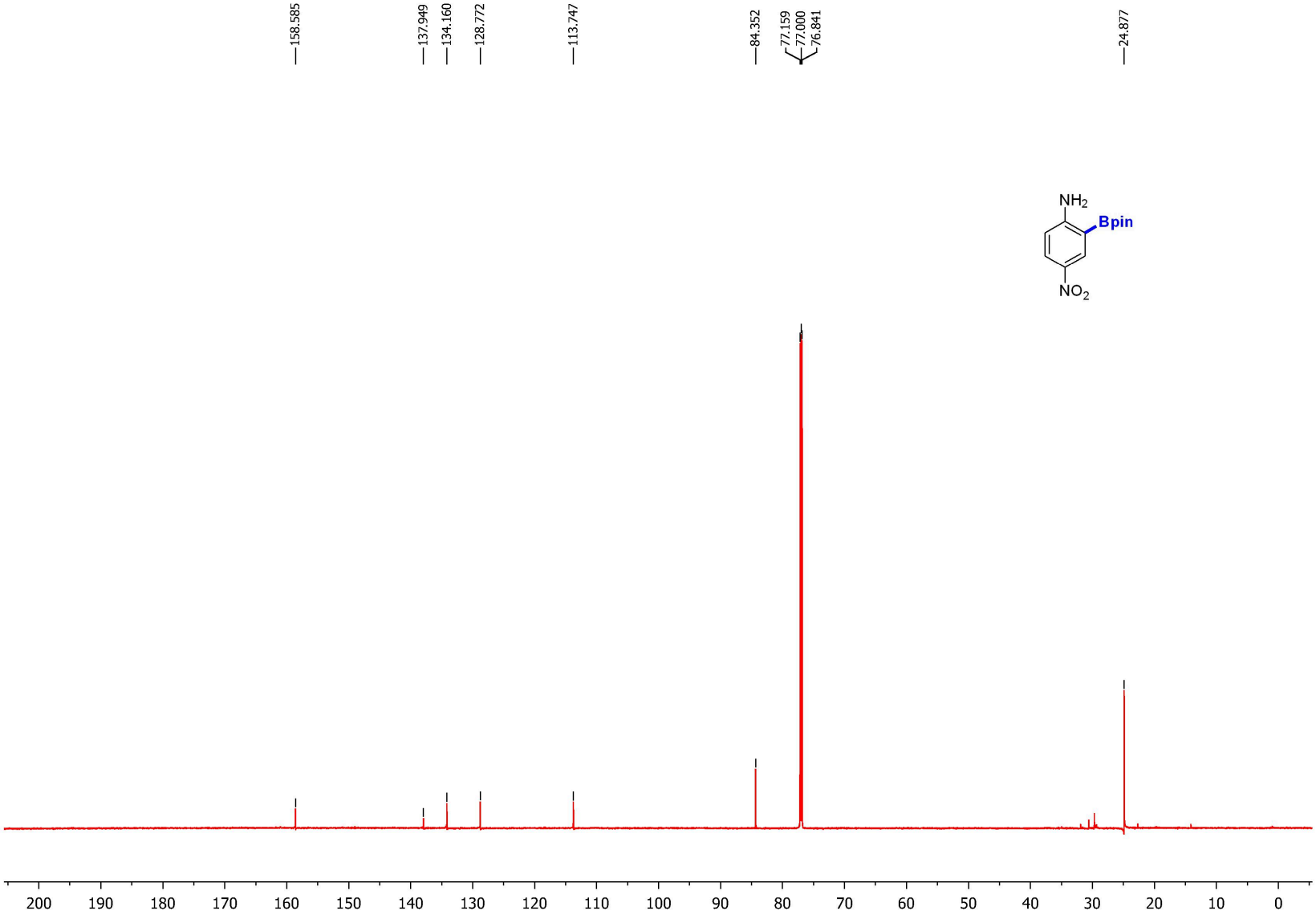
^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



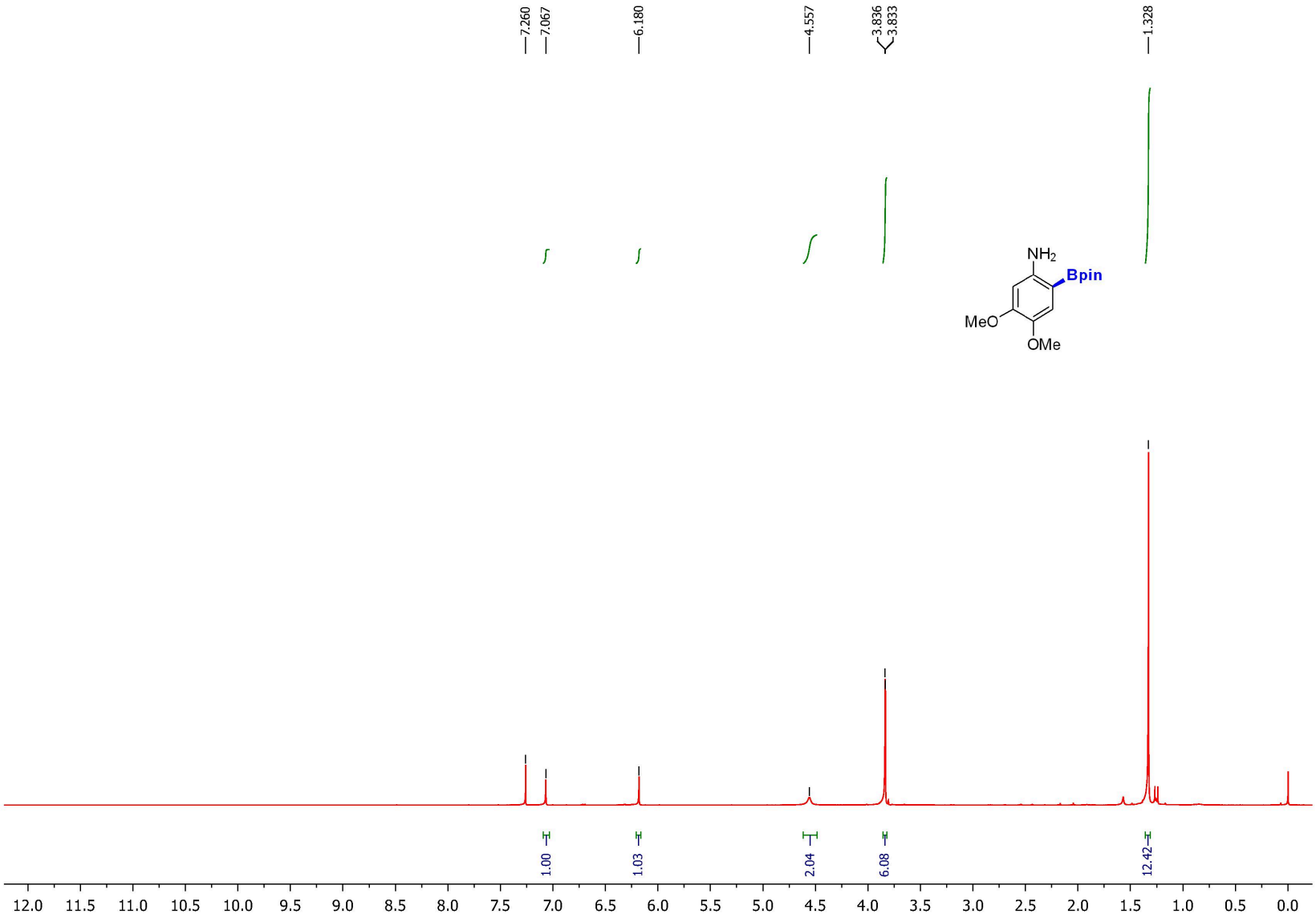
^{13}C-NMR (25 °C, 100 MHz, $CDCl_3$)



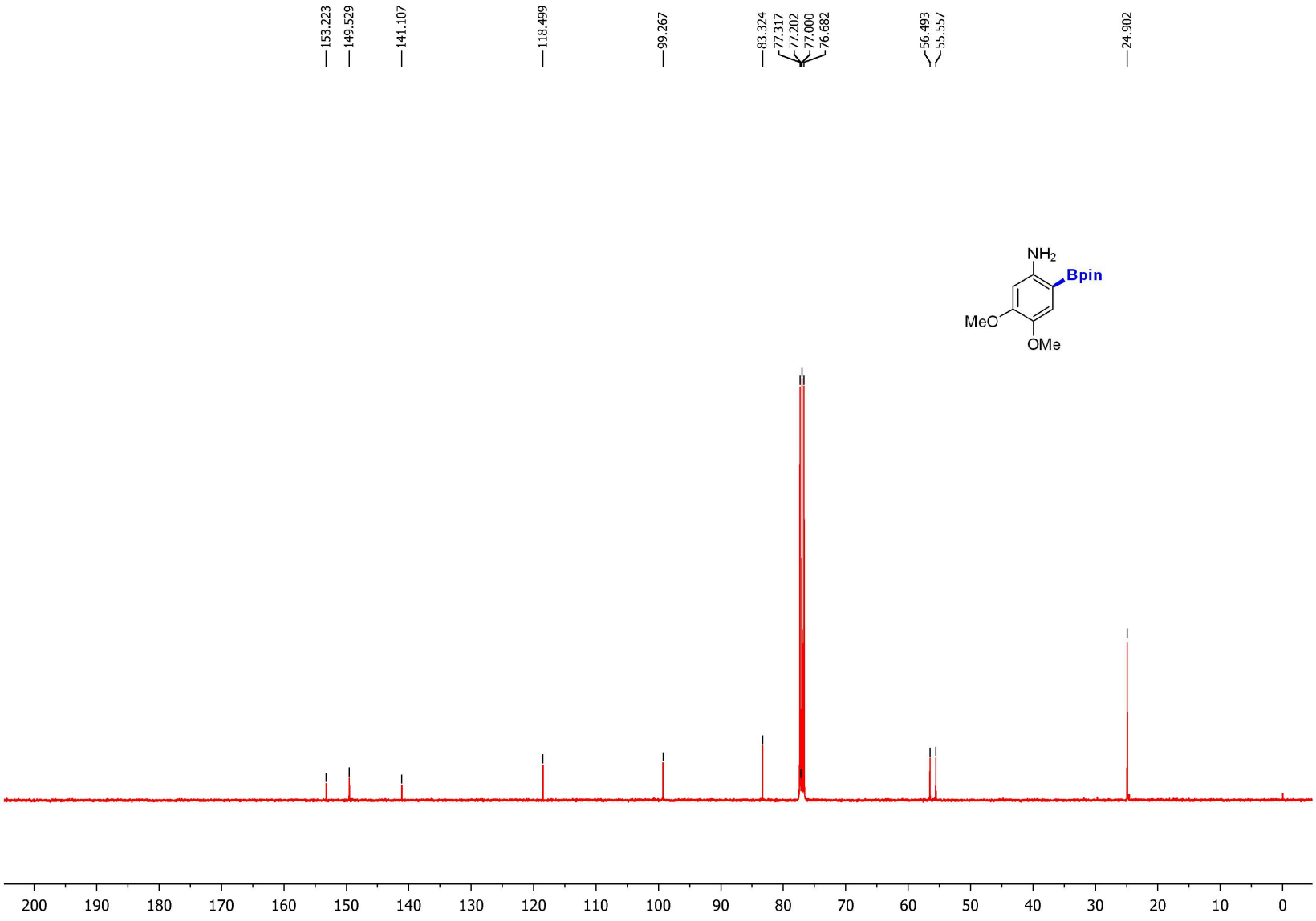
^{1}H-NMR (25 °C, 800 MHz, $CDCl_3$)



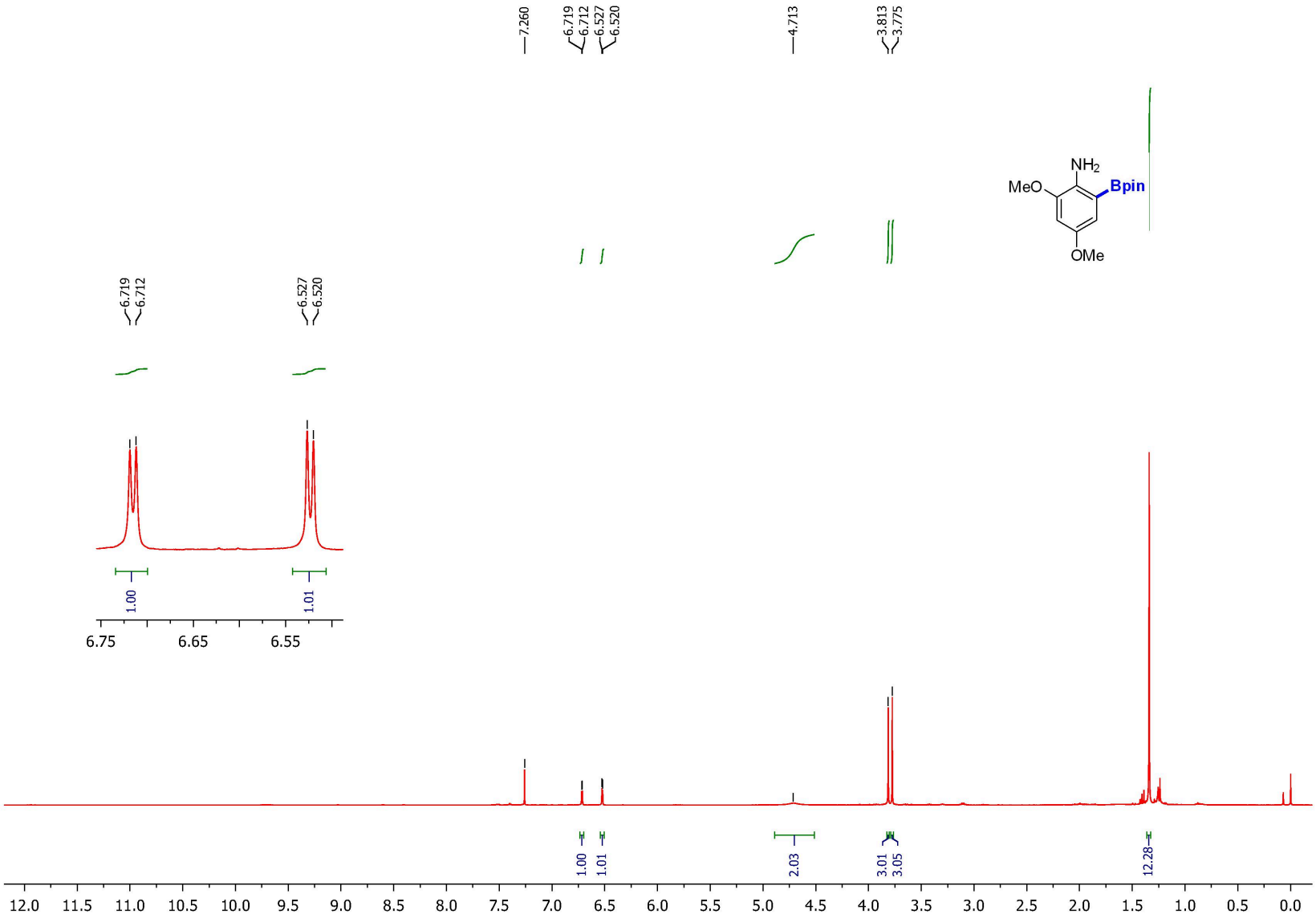
^{13}C-NMR (25 °C, 200 MHz, $CDCl_3$)



^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



^{13}C-NMR (25 °C, 100 MHz, $CDCl_3$)



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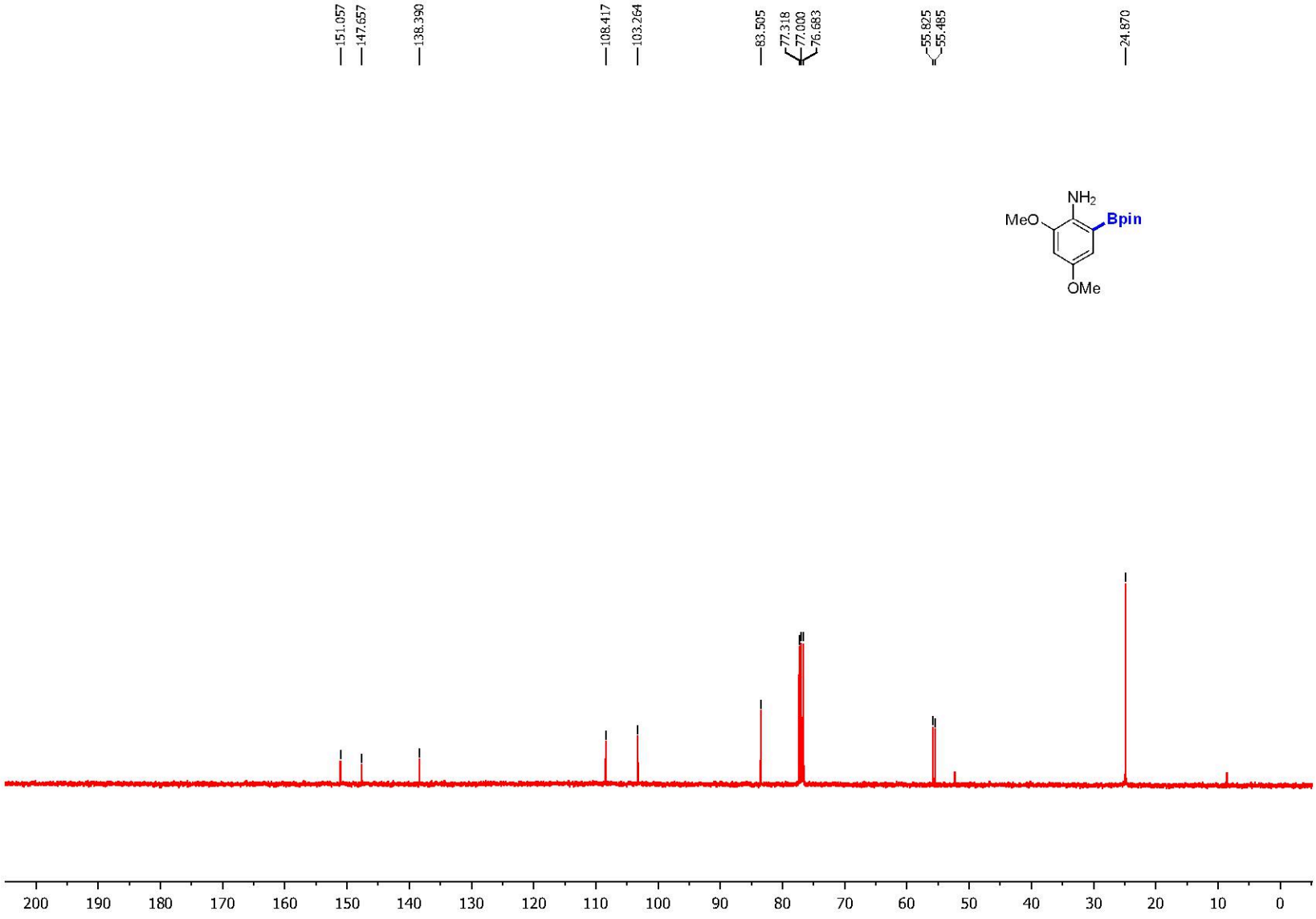
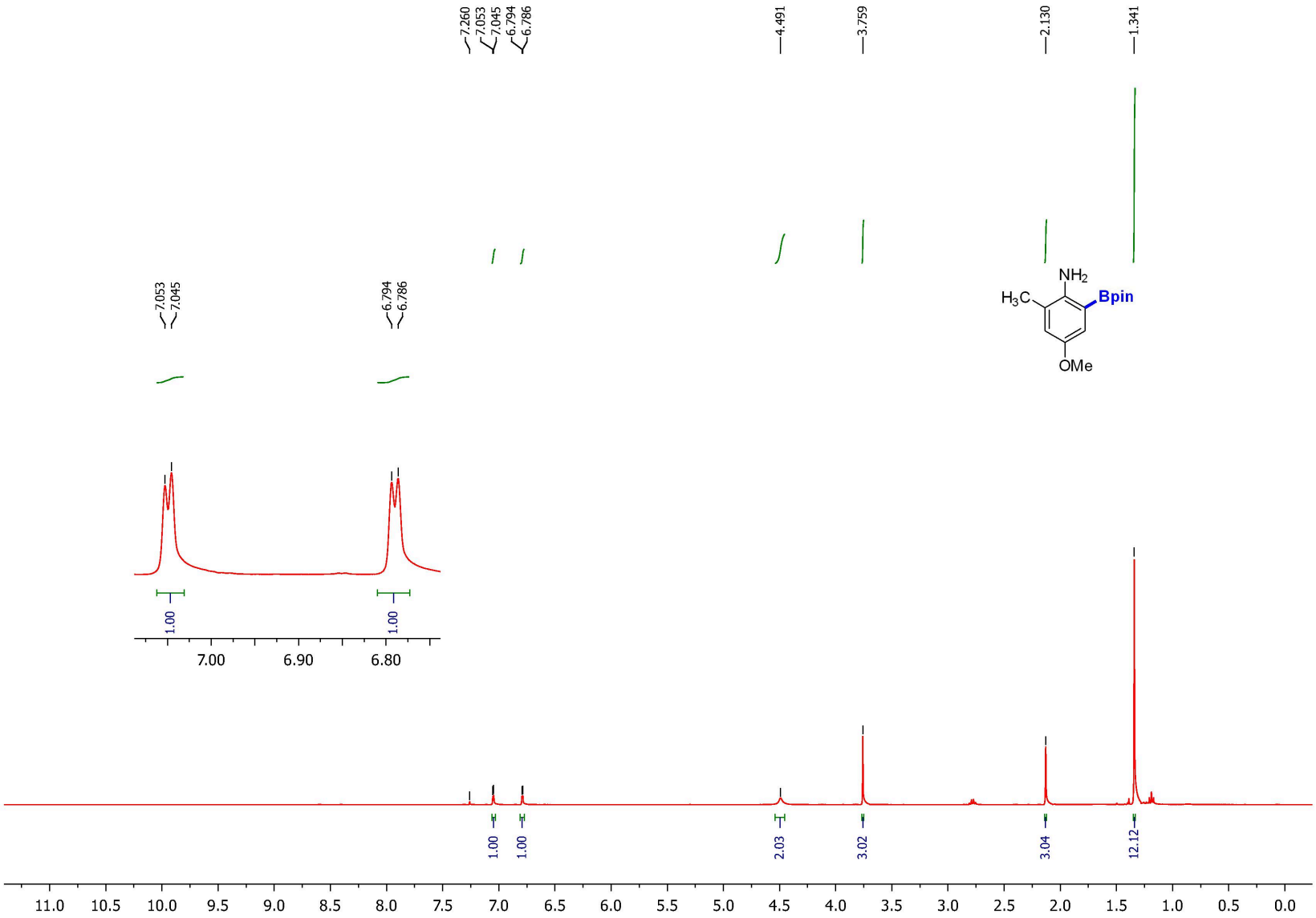
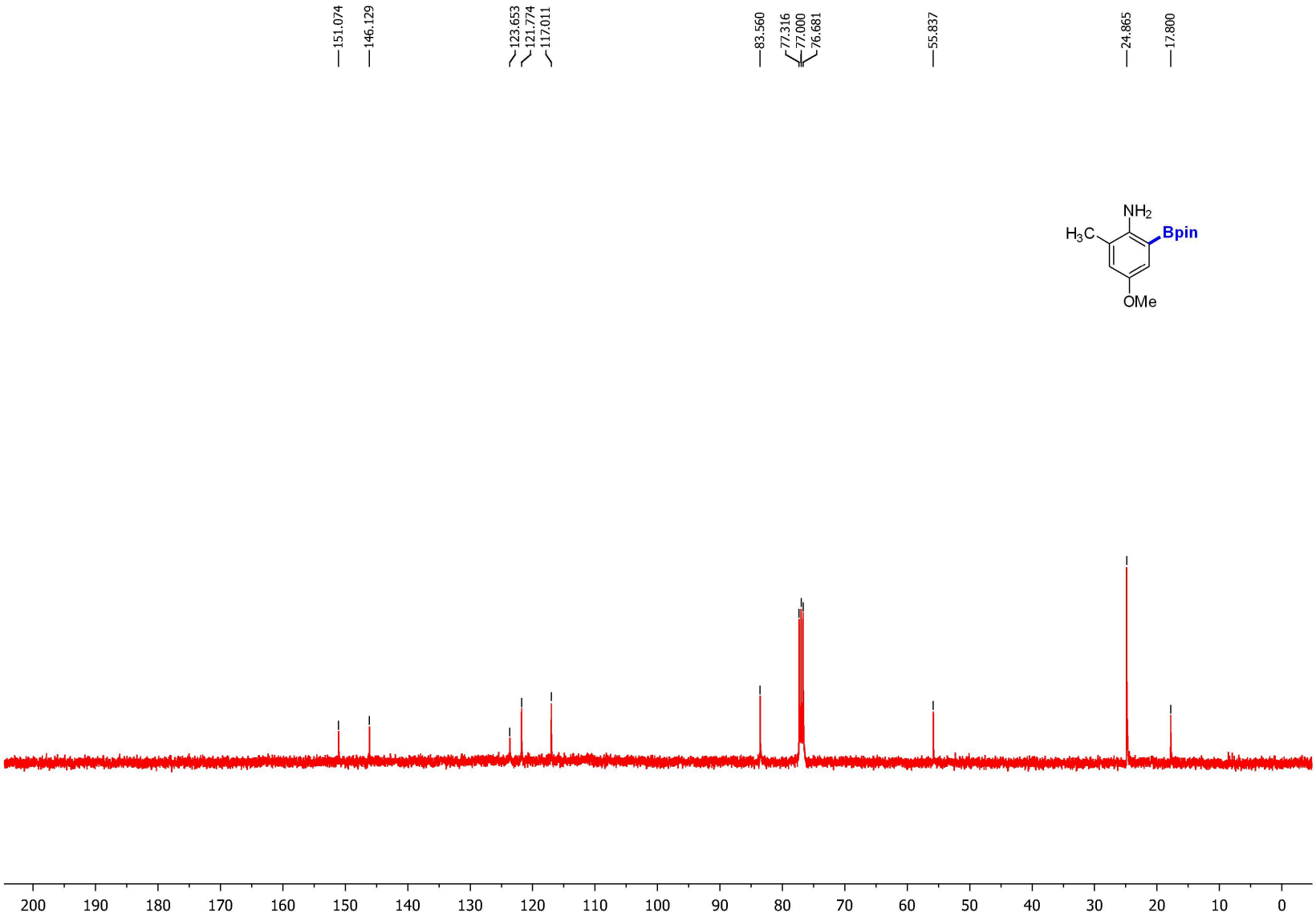


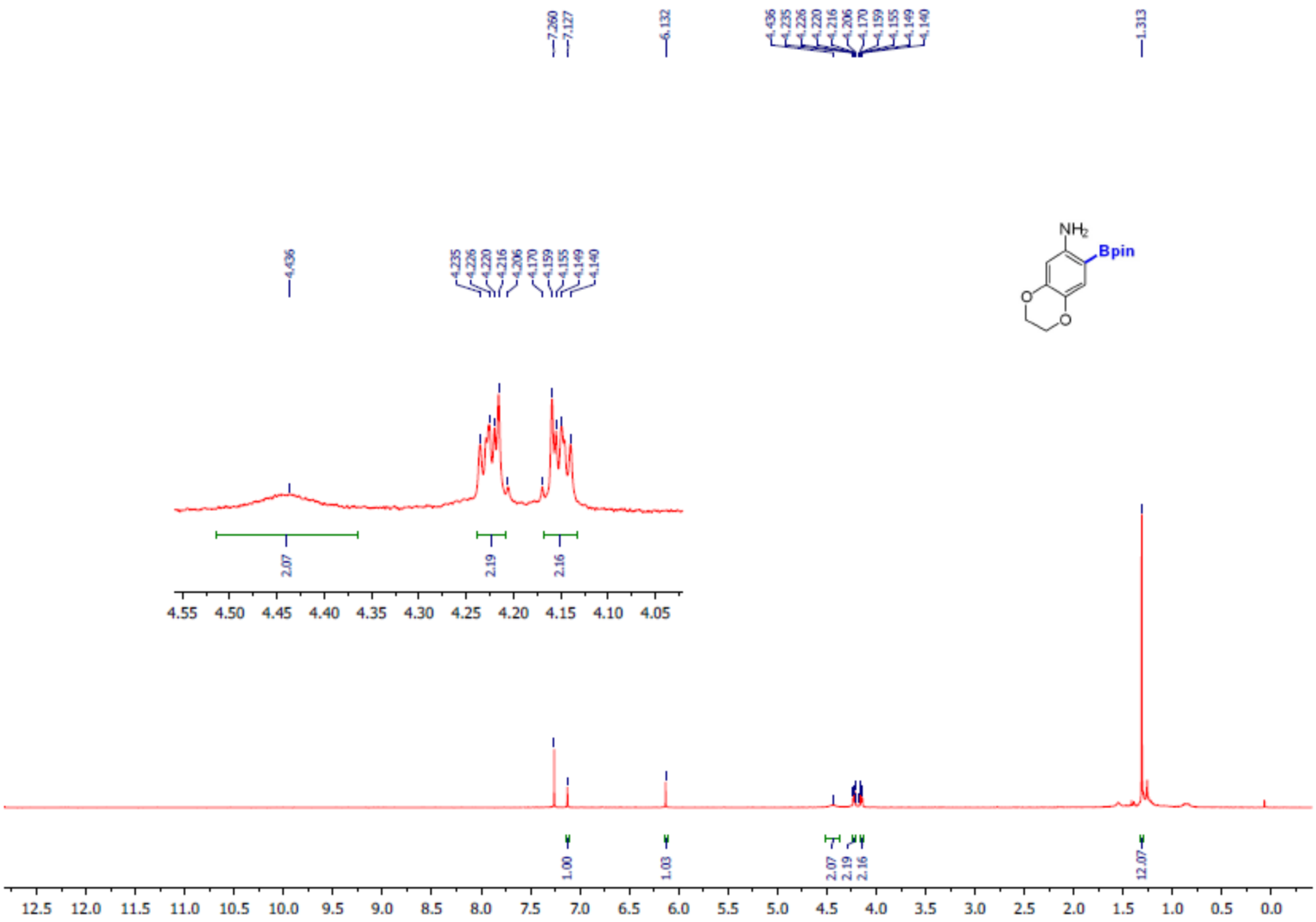
^{13}C-NMR (25 °C, 100 MHz, $CDCl_3$)



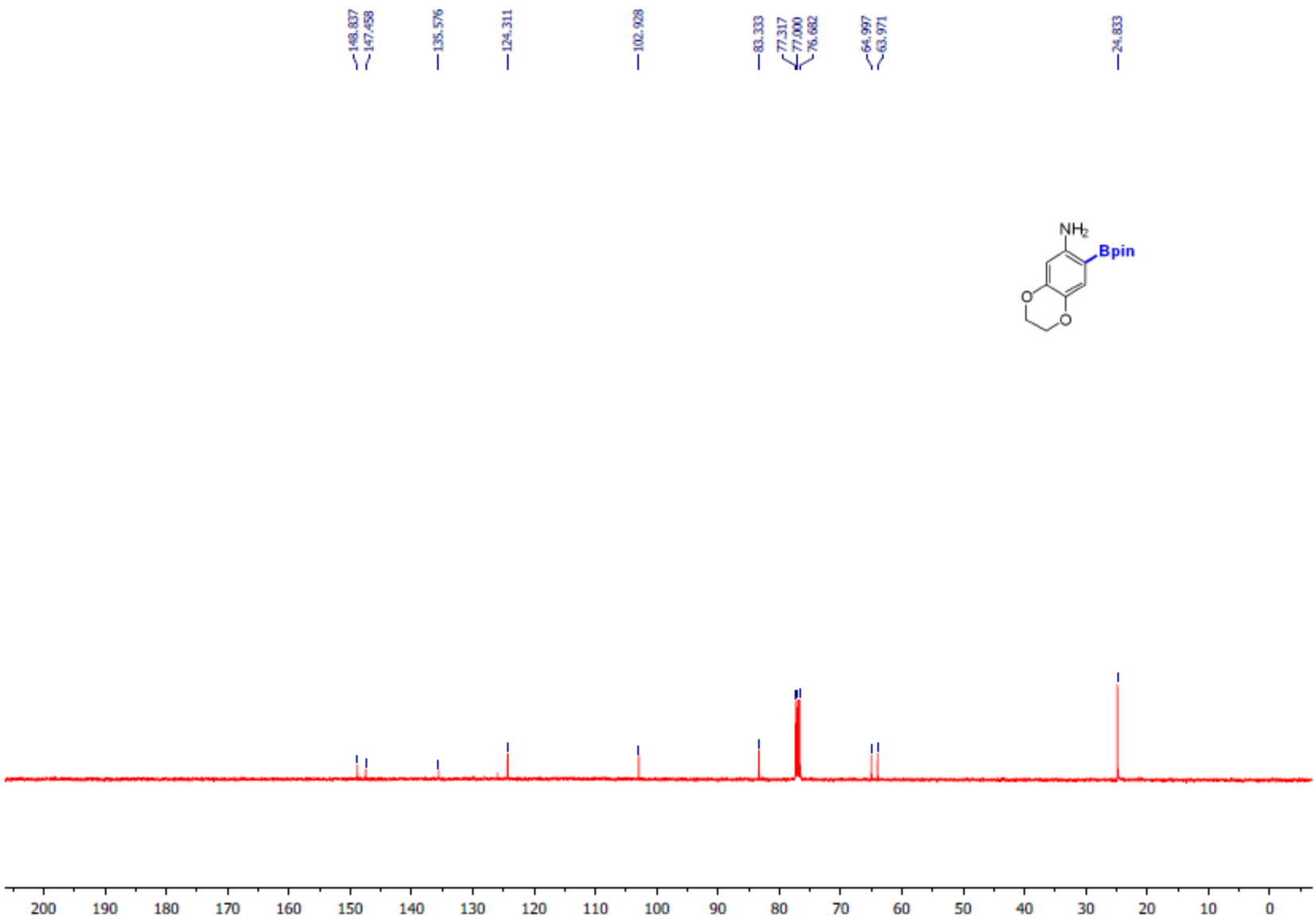
^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



^{13}C-NMR (25 °C, 100 MHz, $CDCl_3$)



^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



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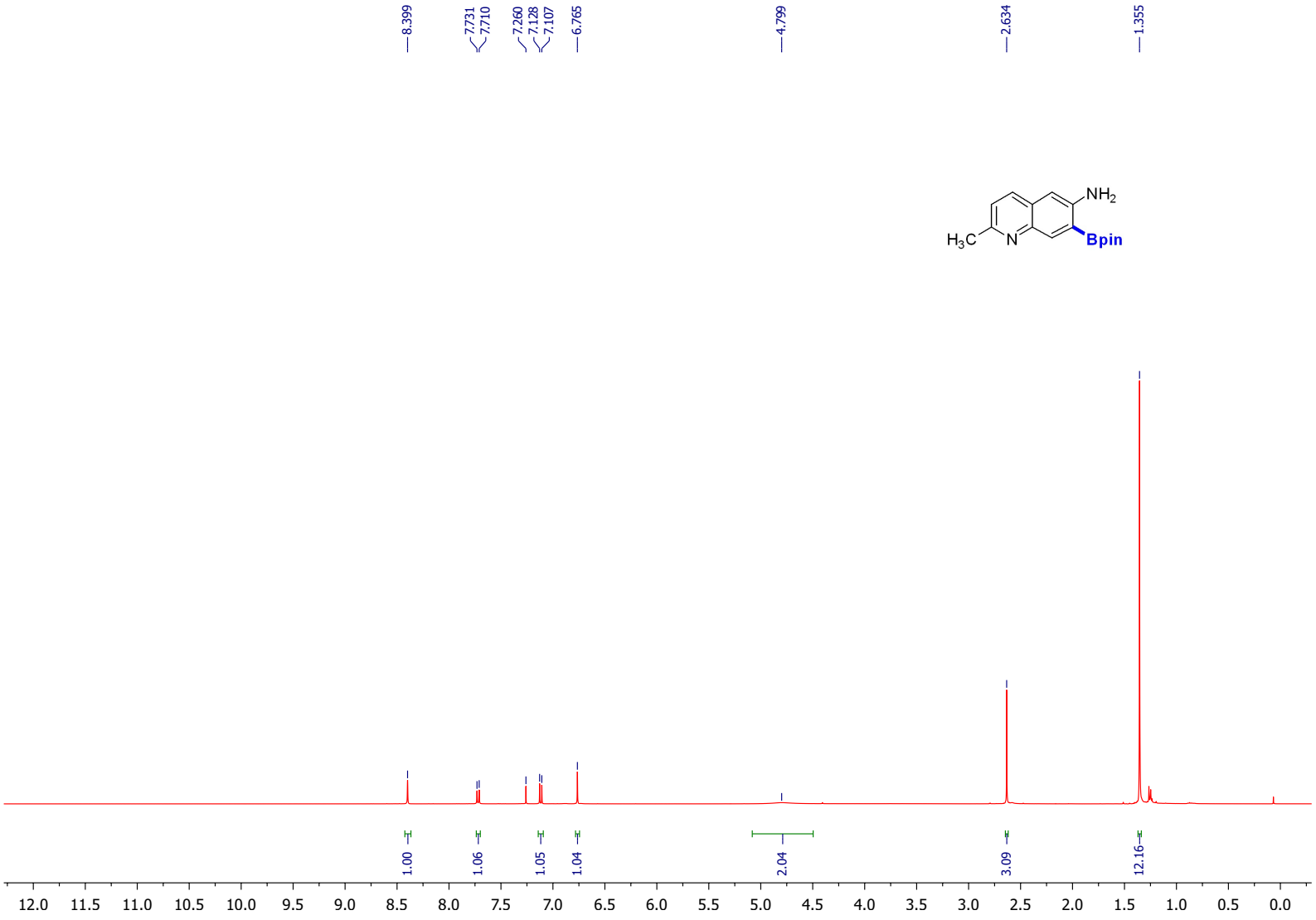
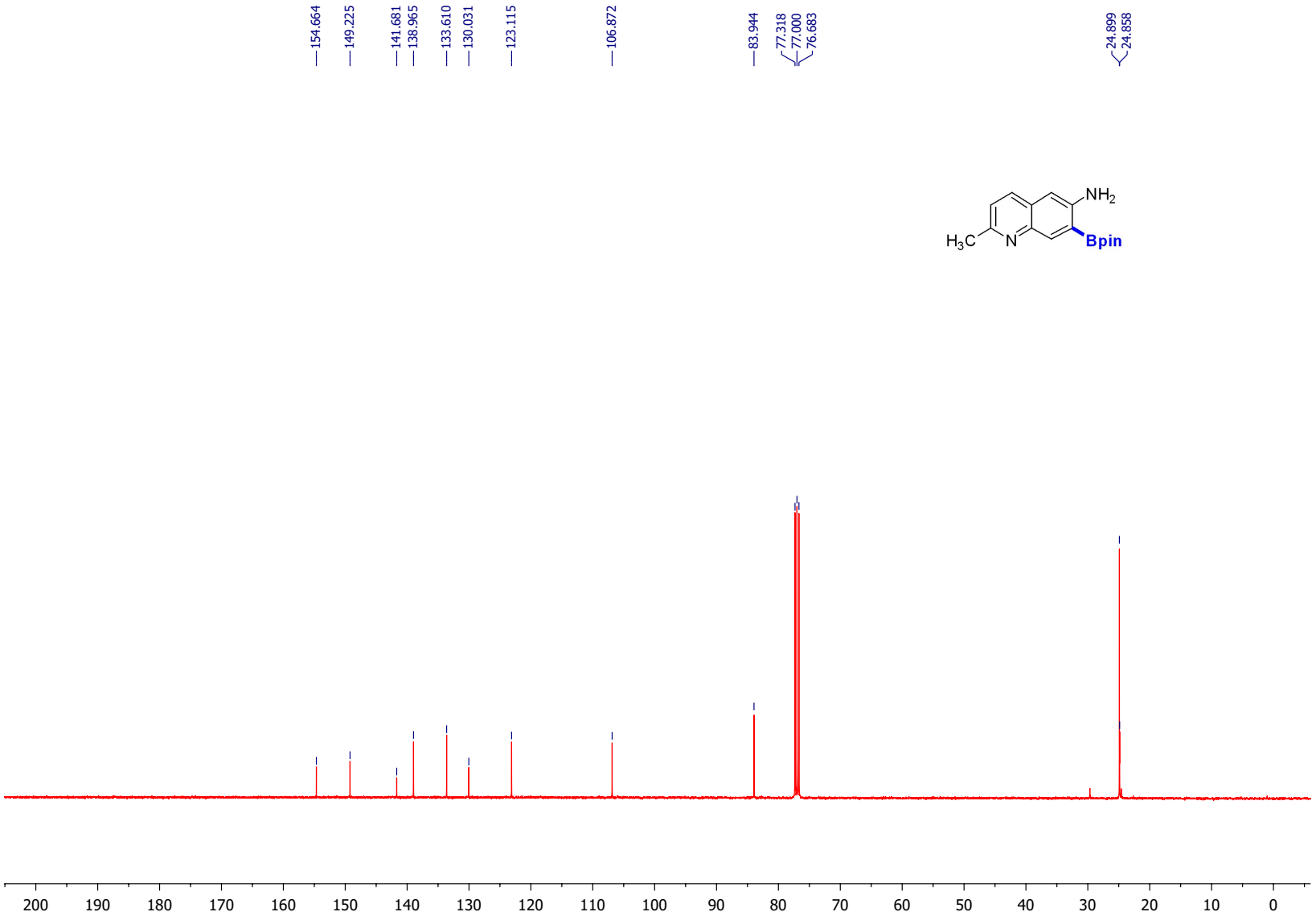
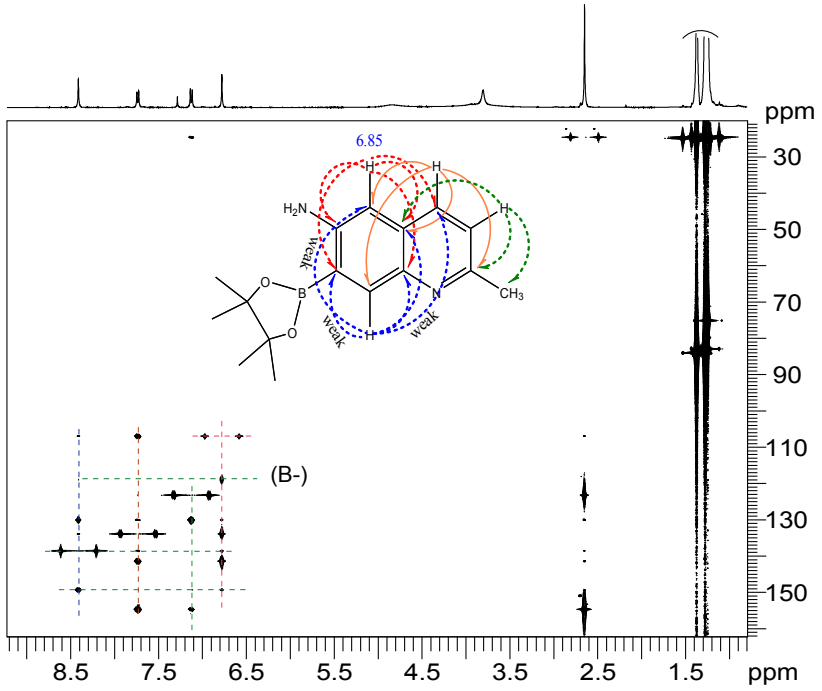


^{1}H-NMR (25 °C, 400 MHz, $CDCl_3$)



^{13}C-NMR (25 °C, 100 MHz, $CDCl_3$)



2-D NMR HMBC (25˚ C, 400 MHz, $CDCl_3$)

References

1) Chattopadhyay, B.; Dannatt, J. E.; Andujar-De Sanctis, I. L.; Gore, K. A.; Maleczka, R. E., Jr.; Singleton, D. A.; Smith, M. R., III *J. Am. Chem. Soc.* **2017**, *139,* 7864.
2) Kong, C.; Jana, N.; Jones, C.; Driver, T. G. *J. Am. Chem. Soc.* **2016**, *138*, 13271.
3) Preshlock, S. M.; Plattner, D. L.; Maligres, P. E.; Krska, S. W.; Maleczka, R. E.; Smith, M. R. *Angew. Chem. Int. Ed.* **2013**, *52*, 12915.
4) Manna, K.; Zhang, T.; Greene, F. X.; Lin, W. *J. Am. Chem. Soc*. **2015**, *137*, 2665.
5) Kong, C.; Jana, N.; Jones, C.; Driver, T. G. *J. Am. Chem. Soc.* **2016**, *138*, 13271.
6) Lam, H.; Tsoung, J.; Lautens, M. *J. Org. Chem.,* **2017**, *82*, 6089.
7) Romero, E. A.; Peltier, J. L.; Jazzar, R.; Bertrand, G. *Chem. Commun.* **2016**, *52*, 10563.
8) Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
9) Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
10) Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.;

Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.