Supporting Information

Aqueous C-H aminomethylation of phenols by iodine catalysis

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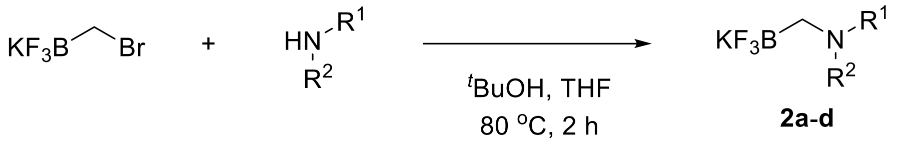
Table of contents

1. General Information

All reactions were carried out in a 10 mL Schlenk tube without exclusion of air. Unless specified, all reagents and solvents were commercially available and were used without further purification. Phenols, iodine and sodium percarbonate ($Na_2CO_3{\cdot}1.5H_2O_2$) were purchased from J&K, TCI and Alfa-Aesar. Potassium trifluoroborates were synthesized according to the reported method given below. Column chromatography was carried out using Merck silica gel 60 with freshly distilled solvents. NMR spectra were recorded on Bruker (500 MHz) or Joel (400 MHz) instruments ($CDCl_3$, DMSO-d_6 or acetone-d_6 as solvents) and chemical shifts (δ) were provided in ppm relative to the deuterated solvent peak or Me_4Si. High-resolution mass spectra (HRMS) were detected by a Waters Q-Tof Permier Spectrometer.

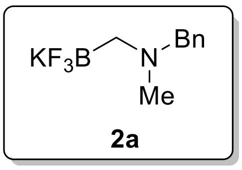
2. Preparation of Starting Materials

2.1 Synthesis of potassium trifluoroborate[1,2]



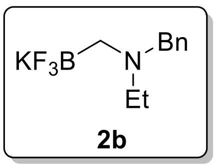
For the synthesis of potassium *N*,*N*-dialkylmethyltrifluoroborate, potassium (bromomethyl)trifluoroborate (10 mmol, 1.56 g) was added to a 25 mL reaction tube. Then, the tube was sealed and degassed with argon. After that, THF (5.5 mL), *tert*-butanol (^{t}BuOH) (2.5 mL) and amine (20 mmol) were sequentially added and the mixture was heated at 80 °C for 2 h. When the reaction finished, the resulting solution was evaporated under reduced pressure and the obtained solids were dissolved in hot acetone, followed by the filtration of insoluble KBr. Then, the filtrate was evaporated using a rotary evaporator, the residue was dissolved with a small amount of hot acetone, and the white solid as the target compound was precipitated after the addition of ether.

Potassium (*N*-benzyl-*N*-methyl)methyltrifluoroborate (2a)[1]



^{1}H NMR (500 MHz, acetone-d_6) δ 7.61 – 7.58 (m, 2H), 7.47 (dd, J = 4.1, 2.4 Hz, 3H), 4.49 (d, J = 13.0 Hz, 1H), 4.33 (d, J = 13.0 Hz, 1H), 2.91 (s, 3H), 2.25 (s, 1H), 2.09 (s, 1H) ppm; ^{13}C NMR (126 MHz, acetone-d_6) δ 131.83, 131.68, 130.22, 129.61, 62.20, 43.16 ppm; ^{19}F NMR (471 MHz, acetone-d_6) δ -141.84 ppm.

Potassium (*N*-benzyl-*N*-ethyl)methyltrifluoroborate (2b)



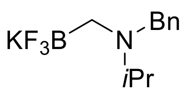
^{1}H NMR (400 MHz, acetone-d_6) δ 7.63-7.59 (m, 2H), 7.49-7.43 (m, 3H), 4.42 (s, 2H), 3.27

(q, *J* = 7.3 Hz, 2H), 2.12 (d, *J* = 3.9 Hz, 2H), 1.37 (t, *J* = 7.3 Hz, 3H) ppm;

^{13}C NMR (100 MHz, acetone-d_6) δ 132.04, 131.90, 130.22, 129.69, 58.85, 58.83, 50.52, 9.28 ppm;

^{19}F NMR (376 MHz, acetone-d_6) δ -141.02 ppm.

Potassium (*N*-benzyl-*N*-isopropyl)methyltrifluoroborate (2c)



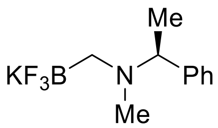
2c

^{1}H NMR (500 MHz, acetone-d_6) δ 7.58 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.48 – 7.43 (m, 3H), 4.54 – 4.45 (m, 1H), 4.31 (dd, *J* = 13.4, 6.7 Hz, 1H), 3.80 – 3.68 (m, 1H), 2.17 (s, 1H), 2.01 (s, 1H), 1.42 (dd, *J* = 6.6, 1.7 Hz, 3H), 1.36 (d, *J* = 6.6 Hz, 3H) ppm;

^{13}C NMR (126 MHz, acetone-d_6) δ 132.12, 131.51, 130.05, 129.63, 56.30, 55.20, 17.33, 15.74 ppm;

^{19}F NMR (471 MHz, acetone-d_6) δ -141.46 ppm.

Potassium ((S)-*N*-methyl-*N*-(1-phenylethyl))methyltrifluoroborate (2d)

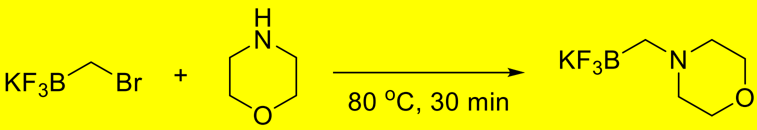


2d

^{1}H NMR (400 MHz, acetone-d_6) δ 7.61 (t, *J* = 2.3 Hz, 1H), 7.49 – 7.43 (m, 3H), 4.64 (t, *J* = 7.0 Hz, 1H), 2.81 (s, 3H), 2.08 (d, *J* = 14.8 Hz, 1H), 1.98 (s, 1H), 1.75 (s, 2H) ppm;

^{13}C NMR (100 MHz, acetone-d_6) δ 136.45, 130.36, 130.18, 129.79, 66.71, 40.57, 16.02 ppm;

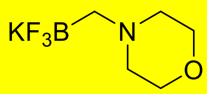
^{19}F NMR (376 MHz, acetone-d_6) δ -142.28 ppm.



2e

For the synthesis of trifluoroborate **2e**, potassium (bromomethyl)trifluoroborate (10 mmol, 2.0 g) was added to morpholine (8 mL) in a 25 mL round-bottom flask. Then, the reaction mixture was heated at 80 °C for 30 min. When finished, the resulting solution was evaporated under reduced pressure and the obtained solids were dissolved in a solution of $KHCO_3$ (10 mmol, 1.4 g) in acetone (100 mL), and stirred at room temperature for 30 min. Then, the insoluble KBr was filtered, and the filtrate was evaporated using a rotary evaporator, the residue was dissolved with a small amount of hot acetone, and the white solid as the target compound was precipitated after the addition of ether.

Potassium 1-morpholinyl-*N*-methyltrifluoroborate (2e)



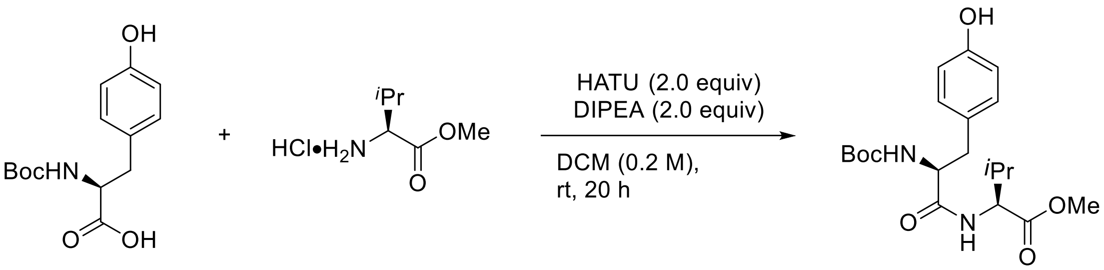
2e

^{1}H NMR (400 MHz, acetone-d_6) δ 3.97 (s, 4H), 3.57 (d, J = 4.9 Hz, 2H), 3.14 (s, 2H), 2.18 (s, 2H) ppm;

^{13}C NMR (100 MHz, acetone-d_6) δ 207.56, 65.72, 56.28 ppm;

^{19}F NMR (376 MHz, acetone-d_6) δ -141.41 ppm.

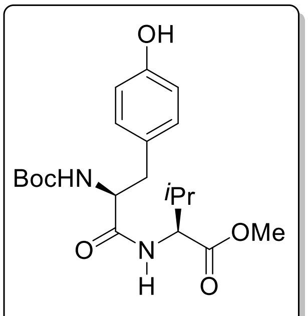
2.2 Synthesis of methyl (*tert*-butoxycarbonyl)-*L*-tyrosyl-*L*-valinate [3]



4j

To a 50 mL reaction bottle, (*tert*-butoxycarbonyl)-*L*-tyrosine (5 mmol, 1.41 g), *L*-valine methyl ester hydrochloride (5 mmol, 0.84 g), HATU (10 mmol, 3.80 g), *N*,*N*-diisopropylethylamine (DIPEA) (10 mmol, 1.29 g) and DCM (10 mL) were sequentially added and the mixture was stirred at room temperature for 20 h. When the reaction finished, the resulting mixture was filtered and the filtrate was concentrated in vacuum. The desired compound was purified by column chromatography.

Methyl (*tert*-butoxycarbonyl)-*L*-tyrosyl-*L*-valinate (4j)



4j

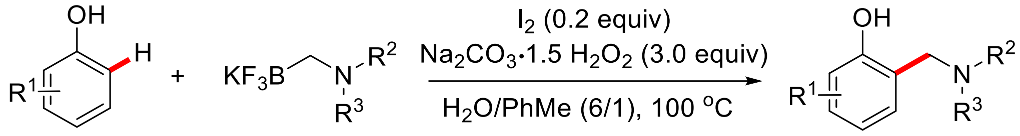
White solid, m.p.: 47-48 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (d, J = 8.1 Hz, 2H), 6.89 (s, 1H), 6.72 (d, J = 8.2 Hz, 2H), 6.50 (d, J = 8.6 Hz, 1H), 5.17 (s, 1H), 4.50 – 4.39 (m, 1H), 4.29 (s, 1H), 3.68 (s, 3H), 2.96 (d, J = 5.6 Hz, 2H), 2.14 – 2.05 (m, 1H), 1.41 (s, 9H), 0.86 (dd, J = 12.9, 6.8 Hz, 6H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.77, 171.63, 155.63, 155.25, 130.32, 127.73, 115.59, 80.42, 57.34, 56.08, 52.14, 37.24, 31.26, 28.21, 18.77, 17.72 ppm.

HRMS (ESI, m/z): calcd for $C_{20}H_{31}N_2O_6^+$ $[M+H]^+$ 395.2182, found: 395.2177.

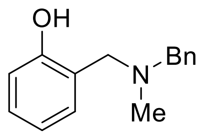
3. General Procedure for the *ortho*-Aminomethylation of Phenols



To a 10 mL Schlenk tube with a stirring bar, $Na_2CO_3 \cdot 1.5H_2O_2$ (0.6 mmol, 94.2 mg), phenols (0.2 mmol), potassium *N*,*N*-dialkylmethyltrifluoroborate (0.3 mmol), H_2O (0.6 mL), toluene (0.1 mL) and I_2 (0.04 mmol, 10.2 mg) were subsequently added. Then, the Schlenk tube was sealed and heated at 100 °C for the desired time. When finished, the resulting mixture was extracted with ethyl acetate. The organic solution was evaporated under reduced pressure after drying over anhydrous Na_2SO_4, and the residue was further purified by flash column chromatography on silica gel to afford the desired product.

4. Characterization Data of Products

2-((Benzyl(methyl)amino)methyl)phenol (3a)[4]



3a

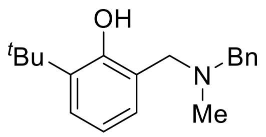
Yellow oil (36.3 mg, 80% yield);

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.46 (dd, *J* = 8.5, 2.2 Hz, 0.08H) (C4), 7.40 – 7.34 (m, 2H), 7.35 – 7.28 (m, 3H), 7.20 (td, *J* = 8.0, 1.6 Hz, 1H), 7.04 – 6.99 (m, 1H), 6.88 (dd, *J* = 8.1, 0.7 Hz, 0.87H) (C2), 6.81 (td, *J* = 7.4, 1.1 Hz, 1H), 6.65 (d, *J* = 8.5 Hz, 0.07H) (C4), 3.77 (s, 1.83H) (C2), 3.70 (s, 0.13H) (C4), 3.62 (s, 1.74H) (C2), 3.60 (s, 0.15H) (C4), 2.26 (s, 2.73H) (C2), 2.25 (s, 0.22H) (C4) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 157.79, 136.80, 129.31, 128.75, 128.55, 128.50, 127.63, 121.83, 119.07, 116.04, 61.38, 60.84, 41.22 ppm;

HRMS (ESI, m/z): calcd for $C_{15}H_{18}NO^+$ $[M+H]^+$ 228.1377, found: 228.1374.

2-((Benzyl(methyl)amino)methyl)-6-(*tert*-butyl)phenol (3b)



3b

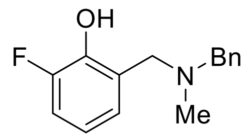
Yellow oil (29.6 mg, 52% yield);

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.36 (s, 1H), 7.48 (d, *J* = 2.2 Hz, 0.11H) (C4), 7.39 – 7.35 (m, 2H), 7.34 – 7.28 (m, 3H), 7.25 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.21 (d, *J* = 2.2 Hz, 0.1H) (C4), 6.93 – 6.90 (m, 1H), 6.77 (t, *J* = 7.6 Hz, 1H), [3.79 (s, 1.80H) (C2), 3.71 (s, 0.23H) (C4)], 3.57 (s, 2H), [2.25 (s, 2.63H) (C2), 2.24 (s, 0.37H) (C4)], [1.49 (s, 8.16H) (C2), 1.44 (s, 0.97H) (C4)] ppm;

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 156.79, 137.03, 136.55, 129.41, 128.45, 127.49, 126.76, 125.96, 122.19, 118.26, 61.57, 60.71, 40.97, 34.66, 29.44 ppm;

HRMS (ESI, m/z): calcd for $C_{19}H_{26}NO^+$ $[M+H]^+$ 284.2003, found: 284.2006.

2-((Benzyl(methyl)amino)methyl)-6-fluorophenol (3c)



3c

Yellow oil (15.4 mg, 31% yield);

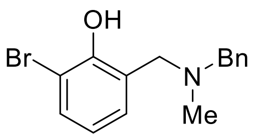
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 5H), 7.28 – 7.24 (m, 1H), 6.94 – 6.90 (m, 1H), 6.76-6.71 (t, J = 7.7 Hz, 1H), 3.78 (s, 2H), 3.66 (s, 2H), 2.25 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.60, 135.97, 129.36, 129.11, 128.66, 127.86, 126.85, 122.86, 120.70, 119.35, 61.50, 60.30, 40.94 ppm;

^{19}F NMR (471 MHz, $CDCl_3$) δ -138.50 ppm;

HRMS (ESI, m/z): calcd for $C_{15}H_{17}FNO^+$ $[M+H]^+$ 246.1283, found: 246.1287.

2-((Benzyl(methyl)amino)methyl)-6-bromophenol (3d)[4]



3d

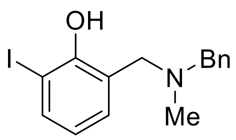
Yellow oil (50.2 mg, 82% yield);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, J = 8.0, 1.4 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.34 – 7.27 (m, 3H), 6.94 (d, J = 7.4 Hz, 1H), 6.67 (t, J = 7.7 Hz, 1H), 3.75 (s, 2H), 3.64 (s, 2H), 2.24 (s, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.66, 136.11, 132.08, 129.37, 128.66, 127.83, 127.50, 122.98, 119.87, 110.10, 77.25, 77.00, 76.75, 61.55, 60.57, 40.98 ppm;

HRMS (ESI, m/z): calcd for $C_{15}H_{17}BrNO^+$ $[M+H]^+$ 306.0483, found: 306.0486.

2-((Benzyl(methyl)amino)methyl)-6-iodophenol (3e)



3e

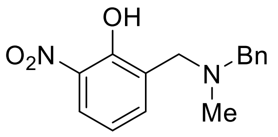
Colorless oil (62.6 mg, 89% yield);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.64 (d, J = 7.9 Hz, 1H), 7.37-7.31 (m, 5H), 7.02-7.00 (d, J = 7.6 Hz, 1H), 6.59-6.55 (t, J = 7.6 Hz, 1H), 3.74 (s, 2H), 3.65 (s, 2H), 2.24 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.92, 138.12, 135.72, 129.55, 128.878, 128.67, 127.92, 121.89, 120.80, 85.97, 61.37, 60.37, 40.85 ppm;

HRMS (ESI, m/z): calcd for $C_{15}H_{17}INO^+$ $[M+H]^+$ 354.0344, found: 354.0344.

2-((Benzyl(methyl)amino)methyl)-6-nitrophenol (3f)



3f

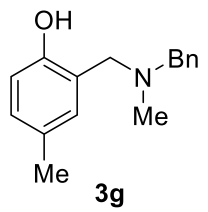
Yellow oil (11.0 mg, 20% yield);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.4, 1.6 Hz, 1H), 7.43 (d, J = 7.3 Hz, 1H), 7.39 – 7.28 (m, 5H), 6.87 (dd, J = 8.3, 7.5 Hz, 1H), 3.83 (s, 2H), 3.69 (s, 2H), 2.29 (s, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.80, 136.34, 136.17, 134.57, 129.29, 128.64, 127.85, 126.12, 124.71, 118.34, 61.54, 58.47, 41.26 ppm;

HRMS (ESI, m/z): calcd for $C_{15}H_{17}N_2O_3^+$ $[M+H]^+$ 273.1228, found: 273.1227.

2-((Benzyl(methyl)amino)methyl)-4-methylphenol (3g)[4]



3g

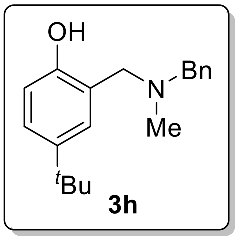
Yellow oil (32.8 mg, 68% yield);

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.86 (s, 1H), 7.38 – 7.28 (m, 5H), 6.98 (d, J = 8.1 Hz, 1H), 6.81 (s, 1H), 6.76 (d, J = 8.2 Hz, 1H), 3.72 (s, 2H), 3.60 (s, 2H), 2.25 (s, 3H), 2.24 (s, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.34, 136.86, 129.27, 129.13, 129.07, 128.50, 128.07, 127.56, 121.48, 115.76, 61.38, 60.88, 41.16, 20.41 ppm;

HRMS (ESI, m/z): calcd for $C_{16}H_{20}NO^+$ $[M+H]^+$ 242.1534, found: 242.1530.

2-((Benzyl(methyl)amino)methyl)-4-(tert-butyl)phenol (3h)[5]



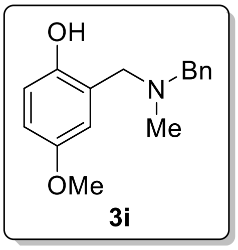
Yellow oil (51.0 mg, 90% yield);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 5H), 7.21 (dd, J = 8.4, 2.4 Hz, 1H), 7.00 (d, J = 2.2 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 3.76 (s, 2H), 3.62 (s, 2H), 2.27 (s, 3H), 1.30 (s, 9H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.25, 141.70, 136.87, 129.30, 128.48, 127.55, 125.42, 125.27, 120.96, 115.38, 61.41, 61.22, 41.29, 33.89, 31.55 ppm;

HRMS (ESI, m/z): calcd for $C_{19}H_{26}NO^+$ $[M+H]^+$ 284.2004, found: 284.2012.

2-((Benzyl(methyl)amino)methyl)-4-methoxyphenol (3i)[4]



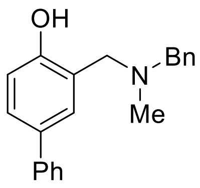
Yellow oil (20.6 mg, 40% yield);

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 7.38 – 7.29 (m, 5H), 6.81 (d, J = 8.7 Hz, 1H), 6.76 (dd, J = 8.8, 2.9 Hz, 1H), 6.61 (d, J = 2.6 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 2H), 3.60 (s, 2H), 2.25 (s, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.48, 151.52, 136.74, 129.30, 128.54, 127.63, 122.48, 116.40, 114.49, 113.54, 61.39, 60.87, 55.71, 41.21 ppm;

HRMS (ESI, m/z): calcd for $C_{16}H_{20}NO_2^+$ $[M+H]^+$ 258.1483, found: 258.1499.

3-((Benzyl(methyl)amino)methyl)-[1,1'-biphenyl]-4-ol (3j)[5]



3j

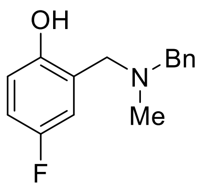
Yellow oil (58.3 mg, 96% yield);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.3 Hz, 2H), 7.41 – 7.26 (m, 9H), 7.24 – 7.22 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 2H), 3.62 (s, 2H), 2.26 (s, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 157.42, 140.89, 136.58, 132.23, 129.32, 128.63, 128.56, 127.68, 127.42, 127.22, 126.50, 126.40, 121.94, 116.44, 61.37, 60.85, 41.19 ppm;

HRMS (ESI, m/z): calcd for $C_{21}H_{22}NO^+$ $[M+H]^+$ 304.1690, found: 304.1690.

2-((Benzyl(methyl)amino)methyl)-4-fluorophenol (3k)[4]



3k

White solid (34.8 mg, 71% yield); m.p.: 30-31 ^{o}C;

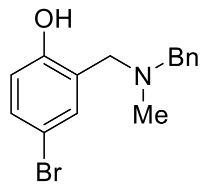
^{1}H NMR (500 MHz, $CDCl_3$) *δ* 10.90 (s, 1H), 7.37 (dd, *J* = 10.1, 4.3 Hz, 2H), 7.34 – 7.28 (m, 3H), 6.88 (td, *J* = 8.6, 3.0 Hz, 1H), 6.79 (dd, *J* = 8.8, 4.8 Hz, 1H), 6.74 (dd, *J* = 8.7, 3.0 Hz, 1H), 3.71 (s, 2H), 3.60 (s, 2H), 2.25 (s, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 157.13, 154.78, 153.68, 136.53, 129.29, 128.59, 127.72, 122.70, 122.64, 116.68, 116.61, 115.01, 114.97, 114.78, 114.75, 61.37, 60.40, 41.21 ppm;

^{19}F NMR (471 MHz, $CDCl_3$) *δ* -125.72 ppm;

HRMS (ESI, m/z): calcd for $C_{15}H_{17}FNO^+$ $[M+H]^+$ 246.1283, found: 246.1281.

2-((Benzyl(methyl)amino)methyl)-4-bromophenol (3l)[4]



3l

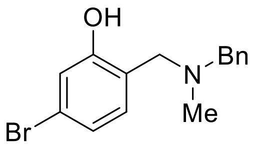
White solid (60.0 mg, 98% yield); m.p.: 69-71 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.22 (s, 1H), 7.38 – 7.32 (m, 2H), 7.28 (ddd, J = 10.6, 7.7, 1.9 Hz, 3H), 7.11 (d, J = 2.4 Hz, 1H), 6.73 (d, J = 8.6 Hz, 1H), 3.70 (s, 2H), 3.59 (s, 2H), 2.23 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.02, 136.40, 131.47, 131.03, 129.30, 128.63, 127.79, 123.82, 117.92, 110.72, 61.40, 60.22, 41.19 ppm;

HRMS (ESI, m/z): calcd for $C_{15}H_{17}BrNO^{+}$ $[M+H]^{+}$ 306.0483, found: 306.0495.

2-((Benzyl(methyl)amino)methyl)-5-bromophenol (3m)



3m

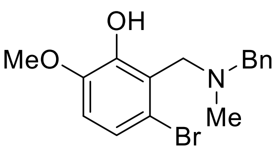
Yellow oil (36.3 mg, 59% yield);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (tdd, J = 7.4, 5.3, 2.2 Hz), 7.05 (d, J = 1.8 Hz), 6.91 (dd, J = 8.0, 1.9 Hz), 6.87 (s), 3.74 (s), 3.64 (s), 2.26 (s) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.69, 135.49, 130.08, 129.51, 128.72, 128.06, 122.36, 122.25, 120.05, 119.58, 61.06, 59.54, 40.85 ppm;

HRMS (ESI, m/z): calcd for $C_{15}H_{17}BrNO^{+}$ $[M+H]^{+}$ 306.0483, found: 306.0481.

2-((Benzyl(methyl)amino)methyl)-3-bromo-6-methoxyphenol (3n)



3n

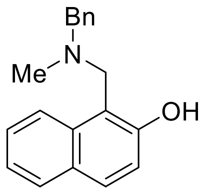
Yellow oil (50.3 mg, 75% yield);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 5H), 6.99-6.97 (d, J = 8.7 Hz, 1H), 6.68-6.66 (d, J = 8.7 Hz, 1H), 4.00 (s, 2H), 3.86 (s, 3H), 3.72 (s, 2H), 2.30 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.51, 147.59, 129.43, 128.71, 127.98, 122.35, 120.05, 113.95, 111.79, 61.51, 59.58, 55.92, 40.99 ppm;

HRMS (ESI, m/z): calcd for $C_{16}H_{19}BrNO_2^+$ $[M+H]^+$ 336.0588, found: 336.0585.

1-((Benzyl(methyl)amino)methyl)naphthalen-2-ol (3o)[6]



3o

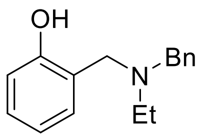
Yellow solid (35.5 mg, 64% yield); m.p.: 116-117 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.6 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.40 – 7.34 (m, 4H), 7.34 – 7.27 (m, 2H), 7.15 (d, J = 8.8 Hz, 1H), 4.22 (s, 2H), 3.71 (s, 2H), 2.35 (s, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.51, 136.57, 132.60, 129.41, 129.24, 128.88, 128.62, 128.50, 127.73, 126.29, 122.40, 120.93, 119.14, 111.41, 61.54, 55.68, 41.44 ppm;

HRMS (ESI, m/z): calcd for $C_{19}H_{20}NO^+$ $[M+H]^+$ 278.1545, found: 278.1549.

2-((Benzyl(ethyl)amino)methyl)phenol (3p)[7]



3p

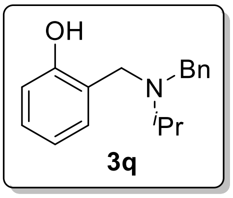
Yellow oil (20.2 mg, 42% yield);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 5H), 7.20-7.16 (m, 1H), 7.02-7.00 (m, 1H), 6.87-6.85 (m, 1H), 6.81-6.77 (m, 1H), 3.80 (s, 1H) , 3.67 (s, 1H) , 2.64-2.59 (m, 2H), 1.18-1.14 (t, J = 7.2 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ157.82, 136.63, 129.49, 128.74, 128.73, 128.57, 127.63, 121.78, 119.11, 116.18, 57.44, 56.66, 46.50, 10.93 ppm;

HRMS (ESI, m/z): calcd for $C_{16}H_{20}NO^+$ $[M+H]^+$ 242.1534, found: 242.1540.

2-((Benzyl(isopropyl)amino)methyl)phenol (3q)



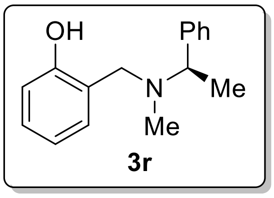
Yellow oil (20.2 mg, 40% yield);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 5H), 7.18-7.14 (m, 1H), 7.02-6.99 (m, 1H), 6.83-6.81 (m, 1H), 6.79-6.75 (m, 1H), 3.80 (s, 2H), 3.61 (s, 2H) , 3.14-3.03 (m, 1H), 1.16 (s, 3H), 1.14 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.92, 137.69, 129.33, 128.74, 128.60, 128.56, 127.48, 121.91, 119.00, 116.04, 53.47, 52.23, 48.24, 16.88 ppm;

HRMS (ESI, m/z): calcd for $C_{17}H_{21}NO^+$ $[M+H]^+$ 256.1690, found: 256.1694.

(*R*)-2-((Methyl(1-phenylethyl)amino)methyl)phenol (3r)



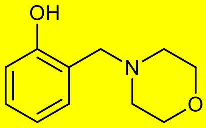
Yellow oil (30.9 mg, 64% yield);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 0.08H) (C4), 7.42 – 7.35 (m, 2H), 7.34 – 7.28 (m, 3H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.3 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 0.81H) (C2), 6.77 (t, *J* = 7.4 Hz, 0.81H) (C2), 6.60 (d, *J* = 8.5 Hz, 0.04H) (C4), 6.53 (t, *J* = 7.6 Hz, 0.06H) (C4), 3.80 (dt, *J* = 13.8, 6.8 Hz, 2H), 3.63 (d, *J* = 13.4 Hz, 1H), [2.24 (d, *J* = 6.9 Hz, 0.15H) (C4), 2.20 (d, *J* = 3.8 Hz, 2.79H) (C2)], [1.51 (d, *J* = 6.9 Hz, 2.71H) (C2), 1.47 (d, *J* = 6.6 Hz, 0.17H) (C4)] ppm;

^{13}C NMR (126 MHz, $CDCl_3$) δ [158.00 (C2), 157.26 (C4)], [140.46 (C2), 137.79 (C4)], 128.56 (C4), 128.52 (C2), 128.45 (C2), 128.40 (C2), 127.99 (C4), 127.96 (C2), 127.88 (C4), 127.77 (C4), 127.59 (C2), 121.90 (C2), 120.57 (C4), 118.98 (C2), 118.40 (C4), 115.93 (C2), [62.93 (C4), 62.47 (C2)], [58.05 (C4), 57.98 (C2)], [37.19 (C4), 37.10 (C2)], [17.80 (C4), 17.17 (C2)] ppm;

HRMS (ESI, m/z): calcd for $C_{16}H_{20}NO^+$ $[M+H]^+$ 242.1545, found: 242.1550.

2-(morpholinomethyl)phenol (3s)[8]



3s

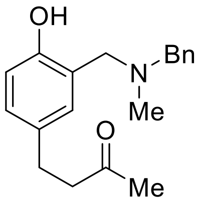
White solid (18.6 mg, 48% yield); m.p.: 84-85 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.17 (dd, J = 11.2, 4.3 Hz, 1H), 6.98 (d, J = 7.3 Hz, 1H), 6.85 – 6.76 (m, 2H), 3.75 (s, 4H), 3.70 (s, 2H), 2.56 (s, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.41, 128.91, 128.73, 120.58, 119.22, 116.01, 66.70, 61.76, 52.81 ppm;

HRMS (ESI, m/z): calcd for $C_{11}H_{16}NO_2^+$ $[M+H]^+$ 194.1170, found: 194.1175.

4-(3-((Benzyl(methyl)amino)methyl)-4-hydroxyphenyl)butan-2-one (5a)



5a

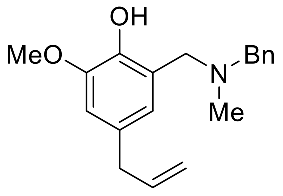
Yellow oil (50.5 mg, 85% yield);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.34 – 7.26 (m, 3H), 7.00 (dd, J = 8.2, 2.1 Hz, 1H), 6.82 (dd, J = 20.5, 5.0 Hz, 2H), 3.74 (s, 2H), 3.61 (s, 2H), 2.85 – 2.79 (m, 2H), 2.77 – 2.70 (m, 2H), 2.25 (d, J = 8.2 Hz, 3H), 2.15 (s, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.25, 155.95, 136.75, 131.35, 129.27, 128.50, 128.40, 128.32, 127.59, 121.69, 115.97, 61.37, 60.79, 45.47, 41.20, 30.05, 28.88 ppm;

HRMS (ESI, m/z): calcd for $C_{19}H_{24}NO_2^+$ $[M+H]^+$ 298.1796, found: 298.1789.

4-Allyl-2-((benzyl(methyl)amino)methyl)-6-methoxyphenol (5b)



5b

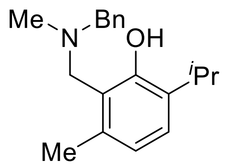
Yellow oil (43.4 mg, 73% yield);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H), 6.64 (d, J = 1.4 Hz, 1H), 6.44 (d, J = 0.5 Hz, 1H), 5.95 (ddt, J = 16.8, 10.0, 6.7 Hz, 1H), 5.11 – 5.02 (m, 2H), 3.87 (s, 3H), 3.73 (s, 2H), 3.62 (s, 2H), 3.29 (d, J = 6.7 Hz, 2H), 2.23 (s, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.72, 145.15, 137.81, 136.79, 130.26, 129.18, 128.50, 127.54, 121.66, 120.24, 115.35, 111.28, 61.63, 60.63, 55.77, 41.09, 39.76 ppm;

HRMS (ESI, m/z): calcd for $C_{19}H_{24}NO_2^+$ $[M+H]^+$ 298.1802, found: 298.1805.

2-((Benzyl(methyl)amino)methyl)-6-isopropyl-3-methylphenol (5c)



5c

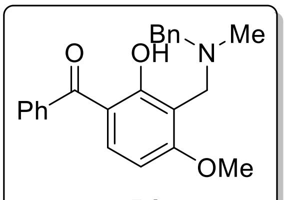
Yellow oil (34.5 mg, 61% yield);

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.85 (s, 1H), 7.39-7.30 (m, 5H), 7.05-7.03 (d, J = 7.8 Hz, 1H), 6.67-6.65 (d, J = 7.8 Hz, 1H), 3.81 (s, 2H), 3.62 (s, 2H), 3.39-3.32 (m, 1H), 2.26 (s, 6H), 1.26 (s, 3H), 1.25 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.36, 133.55, 129.38, 129.00, 128.60, 128.55, 128.41, 127.65, 124.74, 120.84, 119.36, 61.24, 40.98, 26.38, 22.72, 19.67 ppm;

HRMS (ESI, m/z): calcd for $C_{19}H_{26}NO^+$ $[M+H]^+$ 284.2003, found: 284.2007.

(3-((Benzyl(methyl)amino)methyl)-2-hydroxy-4-methoxyphenyl)(phenyl)methanone (5d)



5d

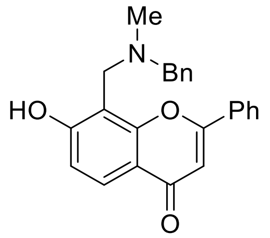
Yellow oil (28.9 mg, 40% yield);

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.70 (s), 7.67 – 7.63 (m), 7.61 – 7.56 (m), 7.52 – 7.46 (m), 7.24 (d, J = 4.7 Hz), 6.50 (s), 3.86 (s), 3.54 (s), 3.47 (s), 2.17 (s) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.05, 165.61, 164.47, 138.31, 135.40, 131.46, 128.93, 128.53, 128.30, 128.16, 127.61, 127.13, 127.01, 112.41, 99.29, 61.57, 55.78, 54.20, 41.94 ppm;

HRMS (ESI, m/z): calcd for $C_{23}H_{24}NO_3^+$ [M+H]$^+$ 362.1756, found: 362.1760.

8-((Benzyl(methyl)amino)methyl)-7-hydroxy-2-phenyl-4*H*-chromen-4-one (5e)



5e

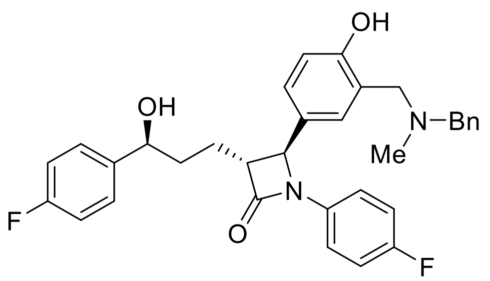
Yellow solid (207.9 mg, 56% yield); m.p.: 159-160 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.8 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.57 – 7.50 (m, 3H), 7.40 – 7.28 (m, 5H), 6.91 (d, J = 8.8 Hz, 1H), 6.74 (s, 1H), 5.29 (s, 1H), 4.19 (s, 2H), 3.75 (s, 2H), 2.38 (s, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.91, 164.03, 162.19, 155.06, 135.72, 132.10, 131.33, 129.43, 129.06, 128.72, 128.01, 126.15, 125.99, 116.56, 115.49, 107.90, 107.31, 61.41, 53.21, 41.51 ppm;

HRMS (ESI, m/z): calcd for $C_{24}H_{22}NO_3^+$ [M+H]$^+$ 372.1589, found: 362.1595.

(3*R*,4*S*)-4-(3-((benzyl(methyl)amino)methyl)-4-hydroxyphenyl)-1-(4-fluorophenyl)-3-((*S*)-3-(4-fluorophenyl)-3-hydroxypropyl)azetidin-2-one (5f)



5f

White solid (47.9 mg, 44% yield); m.p.: 186-187 °C;

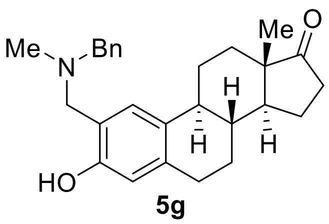
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 – 7.28 (m, 6H), 7.22 (d, J = 7.0 Hz, 2H), 7.09 – 6.99 (m, 4H), 6.95 (s, 1H), 6.87 (d, J = 8.3 Hz, 1H), 6.79 (t, J = 8.6 Hz, 2H), 6.50 (s, 1H), 4.67 – 4.57 (m, 2H), 3.65 (d, J = 14.0 Hz, 1H), 3.54 (d, J = 13.9 Hz, 1H), 3.42 (s, 2H), 2.44 – 2.31 (m, 2H), 2.21 – 2.14 (m, 1H), 2.10 (s, 3H), 2.07 – 2.00 (m, 1H), 1.76 – 1.63 (m, 1H) ppm;

^{13}C NMR (100 MHz, CDCl$_3$) δ 170.82, 163.34, 160.90, 160.49, 158.07, 157.77, 138.29, 138.26, 136.61, 133.08, 131.48, 129.27, 128.59, 127.71, 127.47, 127.39, 126.37, 121.75, 121.67, 116.53, 115.52, 115.30, 115.21, 115.00, 81.89, 79.34, 61.21, 60.51, 53.38, 41.11, 32.67, 27.23 ppm;

^{19}F NMR (CDCl$_3$, 376 MHz) δ -115.17, -117.62 ppm;

HRMS (ESI, m/z): calcd for $C_{33}H_{33}F_2N_2O_3^+$ [M+H]$^+$ 543.2454, found: 543.2462.

(8*R*,9*S*,13*S*,14*S*)-2-((Benzyl(methyl)amino)methyl)-3-hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (5g)



5g

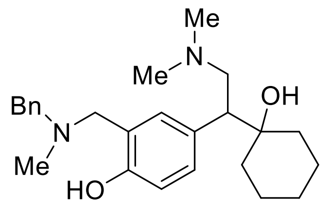
White solid (44.1 mg, 55% yield); m.p.: 179-181 °C;

^{1}H NMR (500 MHz, CDCl$_3$) δ 10.92 (s, 1H), 7.41 – 7.27 (m, 5H), 6.94 (s, 1H), 6.63 (s, 1H), 3.81 – 3.67 (m, 2H), 3.67 – 3.56 (m, 2H), 2.94 – 2.84 (m, 2H), 2.53 (dd, J = 19.0, 8.7 Hz, 1H), 2.41 (dd, J = 10.1, 5.7 Hz, 1H), 2.31 – 2.21 (m, 4H), 2.21 – 2.11 (m, 1H), 2.08 (ddd, J = 11.6, 8.9, 5.6 Hz, 1H), 2.05 – 1.95 (m, 2H), 1.70 – 1.57 (m, 2H), 1.54 (dt, J = 15.5, 9.2 Hz, 3H), 1.46 – 1.38 (m, 1H), 0.93 (d, J = 4.3 Hz, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.51, 136.95, 136.92, 130.28, 129.25, 128.47, 127.52, 125.34, 119.35, 115.87, 61.37, 61.02, 50.36, 47.94, 43.88, 41.19, 38.34, 35.81, 31.54, 29.21, 26.53, 25.97, 21.52, 13.81 ppm;

HRMS (ESI, m/z): calcd for $C_{27}H_{34}NO_2^+$ $[M+H]^+$ 404.2579, found: 404.2576.

2-((Benzyl(methyl)amino)methyl)-4-(2-(dimethylamino)-1-(1-hydroxycyclohexyl)ethyl)phenol (5h)



5h

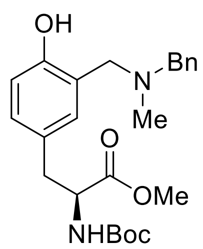
Yellow oil (35.9 mg, 45% yield);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 5H), 6.93-6.90 (m, 1H), 6.76-6.73 (m, 2H), 3.71 (s, 2H), 3.59 (s, 2H), 3.32-3.26 (t, J = 12.5 Hz, 1H), 2.92-2.88 (m, 1H), 2.33 (s, 6H), 2.27 (s, 1H), 2.25 (s, 3H), 1.76-1.59 (m, 3H), 1.56-1.49 (m, 3H), 1.37-1.24 (m, 2H), 1.01-0.81 (m, 2H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.39, 136.66, 131.05, 129.31, 129.21, 128.51, 128.26, 127.62, 121.18, 115.44, 77.32, 77.00, 76.68, 74.17, 61.30, 61.19, 60.75, 51.59, 45.32, 41.33, 37.95, 31.06, 25.92, 21.54, 21.29 ppm;

HRMS (ESI, m/z): calcd for $C_{25}H_{37}N_2O_2^+$ $[M+H]^+$ 397.2844, found: 397.2836.

Methyl (S)-3-(3-((benzyl(methyl)amino)methyl)-4-hydroxyphenyl)-2-((tert-butoxycarbonyl)amino)propanoate (5i)



5i

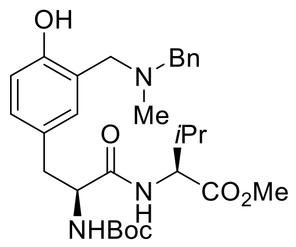
White solid (45.4 mg, 53% yield); m.p.: 39-40 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.41 – 7.25 (m, 5H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.81 – 6.71 (m, 2H), 4.93 (d, *J* = 8.1 Hz, 1H), 4.51 (d, *J* = 7.4 Hz, 1H), 3.73 – 3.66 (m, 5H), 3.58 (s, 2H), 2.97 (qd, *J* = 14.0, 6.1 Hz, 2H), 2.22 (d, *J* = 4.9 Hz, 3H), 1.41 (d, *J* = 6.1 Hz, 9H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 172.39, 156.68, 154.99, 136.59, 129.46, 129.25, 129.20, 128.47, 127.57, 126.27, 121.76, 115.99, 79.66, 61.27, 60.63, 54.51, 51.96, 41.12, 37.40, 28.18 ppm;

HRMS (ESI, m/z): calcd for $C_{24}H_{33}N_2O_5^+$ $[M+H]^+$ 429.2378, found: 429.2384.

Methyl ((*S*)-3-(3-((benzyl(methyl)amino)methyl)-4-hydroxyphenyl)-2-((*tert*-butoxycarbonyl)amino)propanoyl)-*L*-valinate (5j)



5j

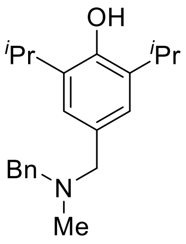
White solid (71.8 mg, 68% yield); m.p.: 51-52 ^{o}C;

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.38 – 7.32 (m, 2H), 7.29 (d, *J* = 7.3 Hz, 3H), 6.99 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.87 (s, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.34 (d, *J* = 6.1 Hz, 1H), 5.04 (s, 1H), 4.42 (dd, *J* = 8.5, 5.1 Hz, 1H), 4.27 (d, *J* = 6.2 Hz, 1H), 3.70 (d, *J* = 8.7 Hz, 2H), 3.65 (s, 3H), 3.59 (d, *J* = 3.4 Hz, 2H), 3.03 – 2.87 (m, 2H), 2.23 (s, 3H), 2.07 (dt, *J* = 9.0, 6.8 Hz, 1H), 1.41 (s, 9H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.81 (d, *J* = 6.9 Hz, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 171.74, 171.30, 156.78, 155.46, 136.72, 129.69, 129.45, 129.37, 128.61, 127.72, 126.98, 122.06, 116.24, 80.17, 61.48, 60.70, 57.23, 52.08, 41.25, 37.27, 31.32, 28.28, 18.83, 17.77 ppm;

HRMS (ESI, m/z): calcd for $C_{29}H_{42}N_3O_6^+$ $[M+H]^+$ 528.3074, found: 528.3082.

4-((Benzyl(methyl)amino)methyl)-2,6-diisopropylphenol (5k)



5k

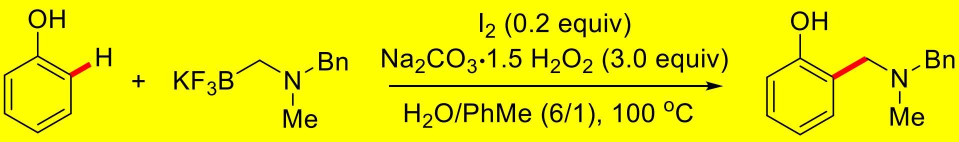
Yellow oil (56.0 mg, 90% yield);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.26 (m), 7.05 (s), 3.55 (d, J = 2.3 Hz), 3.17 (dt, J = 13.7, 6.8 Hz), 2.23 (s), 1.27 (dd, J = 7.9, 5.8 Hz) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.11, 138.24, 133.50, 129.55, 129.23, 128.20, 127.08, 124.43, 61.49, 60.72, 41.66, 27.11, 22.78 ppm;

HRMS (ESI, m/z): calcd for $C_{21}H_{30}NO^+$ $[M+H]^+$ 312.2322, found: 312.2329.

5. Procedure for Gram Scale Experiment



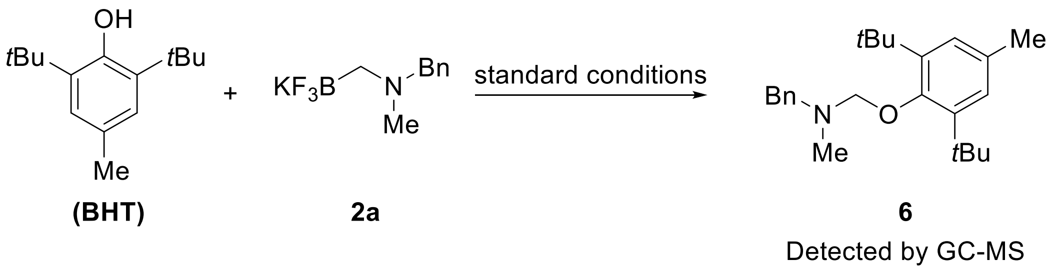
1a **2a** **3a**

To a 100 mL round-bottom flask with a stirring bar, $Na_2CO_3 \cdot 1.5H_2O_2$ (30 mmol, 4.71 g), phenol **1a** (10 mmol, 0.94g), potassium (*N*-benzyl-*N*-methyl)methyltrifluoroborate **2a** (15 mmol, 3.62 g), H_2O (30 mL), toluene (5 mL) and I_2 (2 mmol, 0.51 g) were subsequently added. Then, the flask was heated at 100 °C for 24 h. When finished, the resulting mixture was extracted with ethyl acetate. The organic solution was evaporated under reduced pressure after drying over anhydrous Na_2SO_4, and the residue was further purified by flash column chromatography on silica gel to afford **3a** (1.54 g, 68% yield).

6. Mechanistic Study

6.1 Free radical capture

To a 10 mL Schlenk tube with a stirring bar, $Na_2CO_3 \cdot 1.5H_2O_2$ (0.6 mmol, 94.2 mg), phenol (**1a**) (0.2 mmol, 18.8 mg), potassium (*N*-benzyl-*N*-methyl)methyltrifluoroborate (**2a**) (0.3 mmol, 72.3 mg), 2,2,6,6-tetramethylpiperidinooxy (TEMPO) (0.4 mmol, 62.5 mg) or butylated hydroxytoluene (BHT) (0.4 mmol, 88.1 mg), H_2O (0.6 mL), toluene (0.1 mL) and I_2 (0.04 mmol, 10.2 mg) were subsequently added. Then, the Schlenk tube was sealed and heated at 100 °C for 24 h. The desired product **3a** was isolated in 32% or 18% yield, respectively.



To a 10 mL Schlenk tube with a stirring bar, $Na_2CO_3 \cdot 1.5H_2O_2$ (0.6 mmol, 94.2 mg), butylated hydroxytoluene (BHT) (0.4 mmol, 88.1 mg), potassium (*N*-benzyl-*N*-methyl)methyltrifluoroborate (**2a**) (0.3 mmol, 72.3 mg), H_2O (0.6 mL), toluene (0.1 mL) and I_2 (0.04 mmol, 10.2 mg) were subsequently added. Then, the Schlenk tube was sealed and heated at 100 °C for 24 h. After finished, the resulting mixture was extracted with ethyl acetate and a partion of organic phase was analyzed by GC-MS.

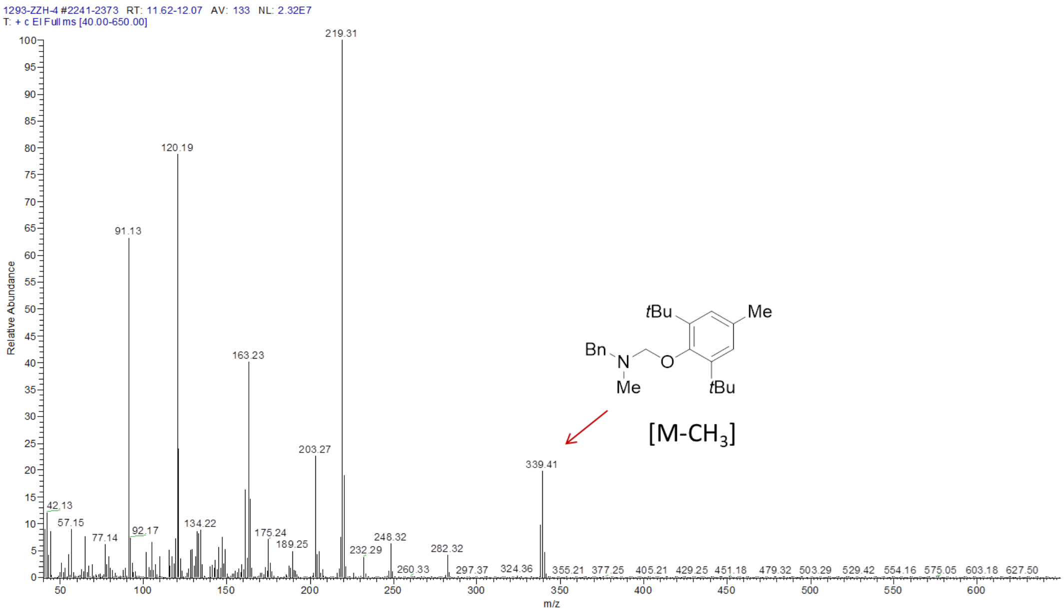
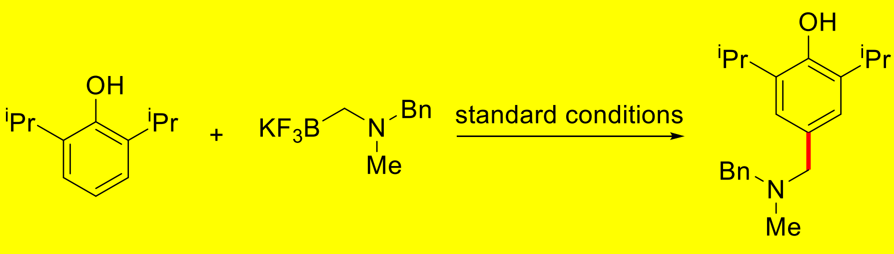
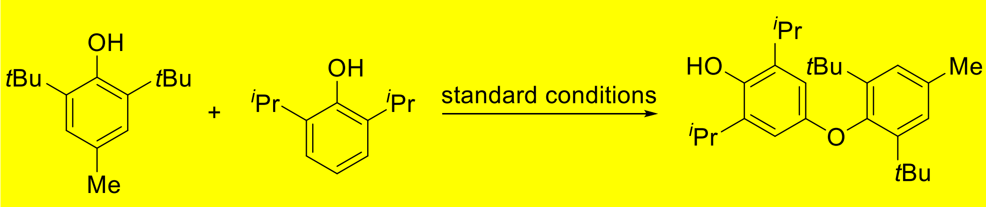


Figure S1. GC-MS spectrum of aminomethyl radical species captured by BHT



To a 10 mL Schlenk tube with a stirring bar, $Na_2CO_3 \cdot 1.5H_2O_2$ (0.6 mmol, 94.2 mg), propofol (**4k**) (0.2 mmol, 35.7 mg), potassium (*N*-benzyl-*N*-methyl)methyltrifluoroborate (**2a**) (0.3 mmol, 72.3 mg), H_2O (0.6 mL), toluene (0.1 mL) and I_2 (0.04 mmol, 10.2 mg) were subsequently added. Then, the Schlenk tube was sealed and heated at 100 °C for 24 h. The *para*-aminomethylated product **5k** was isolated in 90% yield.



To a 10 mL Schlenk tube with a stirring bar, $Na_2CO_3 \cdot 1.5H_2O_2$ (0.6 mmol, 94.2 mg), butylated hydroxytoluene (BHT) (0.4 mmol, 88.1 mg), propofol (**4k**) (0.2 mmol, 35.7 mg) H_2O (0.6 mL), toluene (0.1 mL) and I_2 (0.04 mmol, 10.2 mg) were subsequently added.

Then, the Schlenk tube was sealed and heated at 100 °C for 24 h. After finished, the resulting mixture was extracted with ethyl acetate and a partion of organic phase was analyzed by GC-MS.

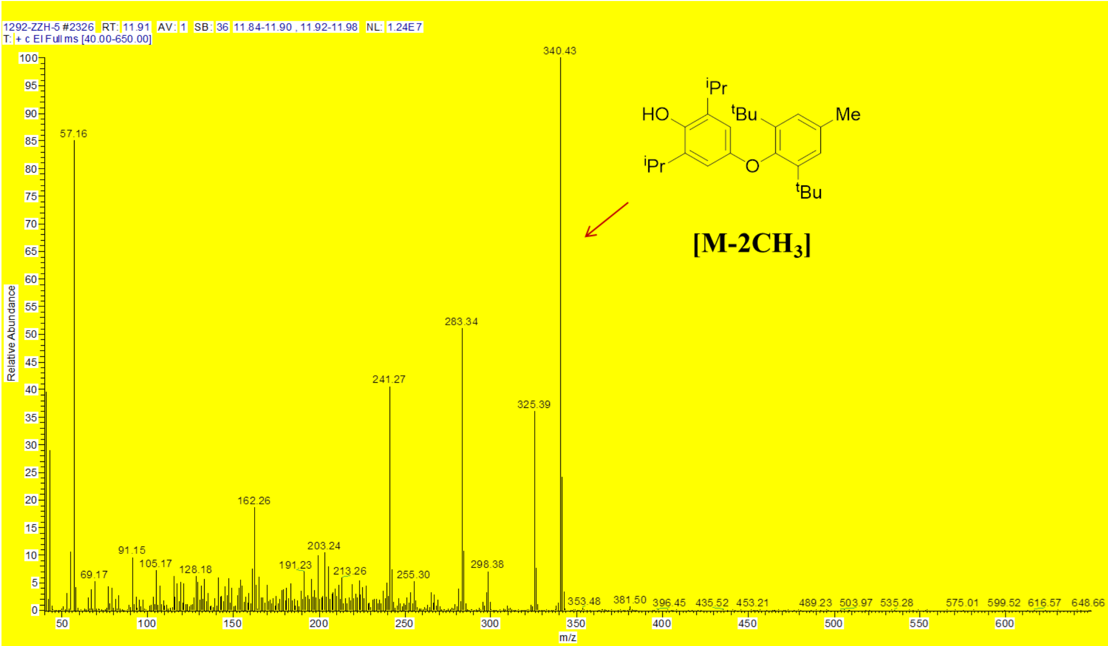
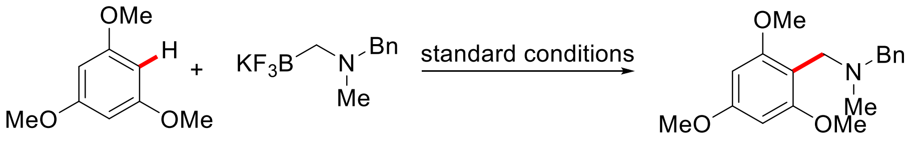
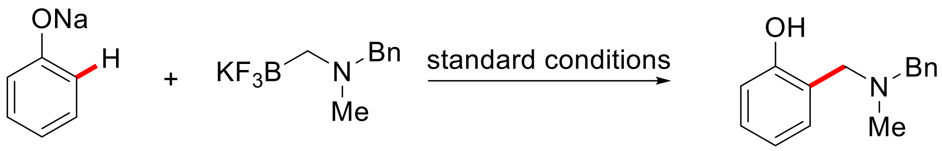


Figure S2. GC-MS spectrum of phenoxy radical species captured by BHT

6.2 Control experiments



To a 10 mL Schlenk tube with a stirring bar, $Na_2CO_3{\cdot}1.5H_2O_2$ (0.6 mmol, 94.2 mg), 1,3,5-trimethoxybenzene (**6**) (0.2 mmol, 33.6 mg), potassium (*N*-benzyl-*N*-methyl)methyltrifluoroborate (**2a**) (0.3 mmol, 72.3 mg), H_2O (0.6 mL), toluene (0.1 mL) and I_2 (0.04 mmol, 10.2 mg) were subsequently added. Then, the Schlenk tube was sealed and heated at 100 °C for 24 h. No desired product but retained starting materials were detected.



7 **2a** No reaction

To a 10 mL Schlenk tube with a stirring bar, $Na_2CO_3{\cdot}1.5H_2O_2$ (0.6 mmol, 94.2 mg), sodium benzenolate (**7**) (0.2 mmol, 23.2 mg), potassium (*N*-benzyl-*N*-methyl)methyltrifluoroborate (**2a**) (0.3 mmol, 72.3 mg), H_2O (0.6 mL), toluene (0.1 mL) and I_2 (0.04 mmol, 10.2 mg) were subsequently added. Then, the Schlenk tube was sealed and heated at 100 °C for 24 h. No desired product was detected.

6.3 Proposed mechanism for *para*-aminomethylation

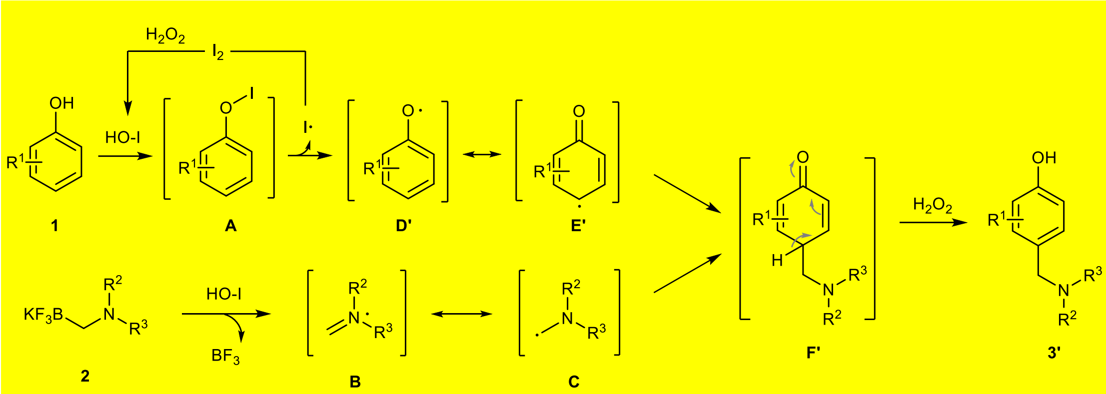


Figure S3. Possible process for the formation of *para*-aminomethylated product

Compared with the process of *ortho*-aminomethylation, homolysis of the O-I bond of **A** may occurr to give the phenoxy radical, and the coupling of *para*-site carbon radical species **E'** with intermediate **C** gives the intermediate **F'**. Finally, the *para*-aminomethylated product **3'** is obtained after an oxidative deprotonation process.

7. References

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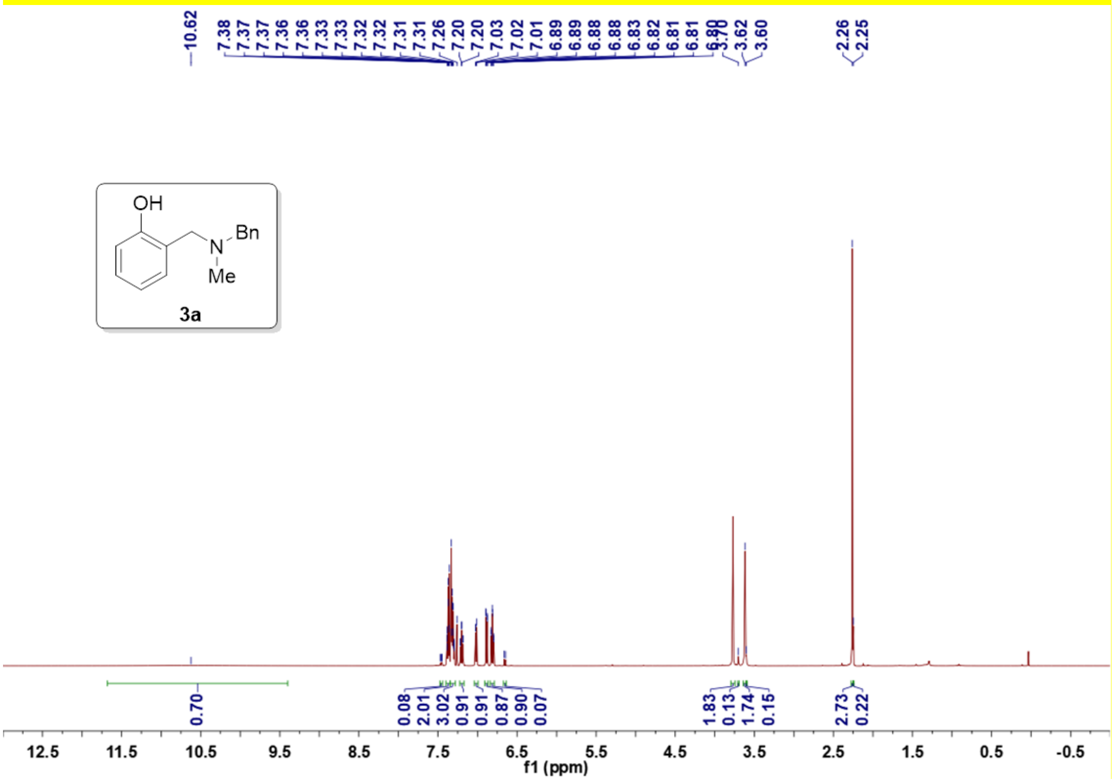
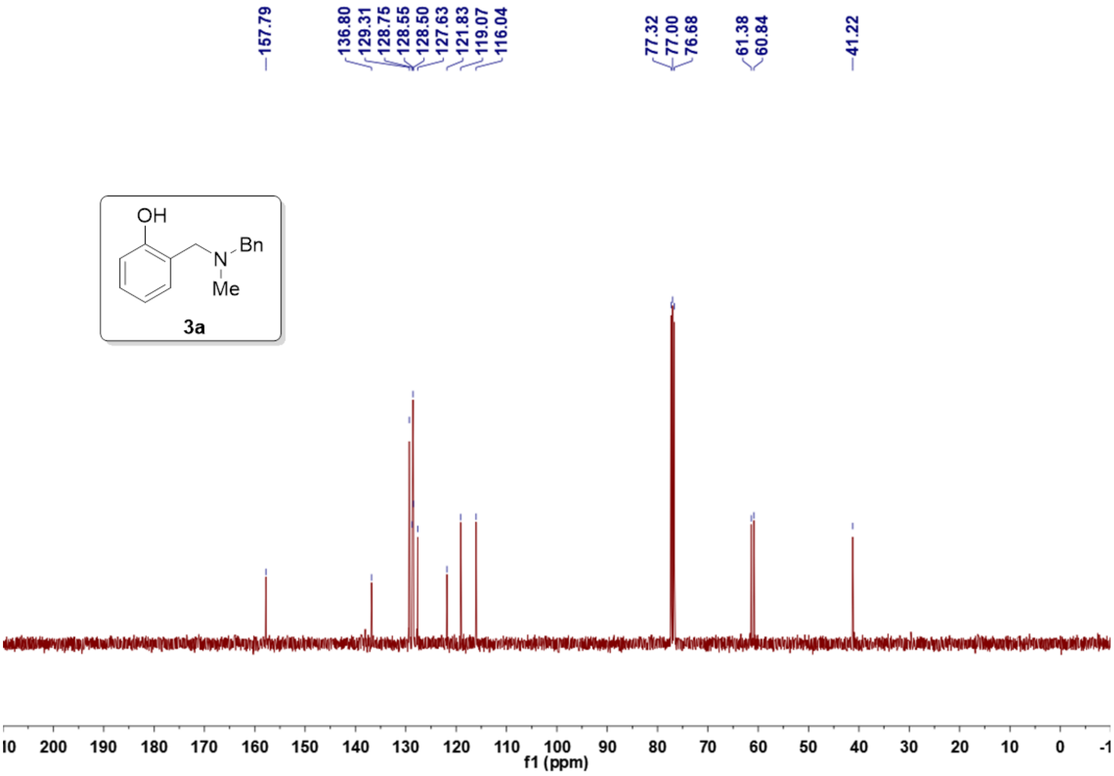
8. NMR Spectra of Products

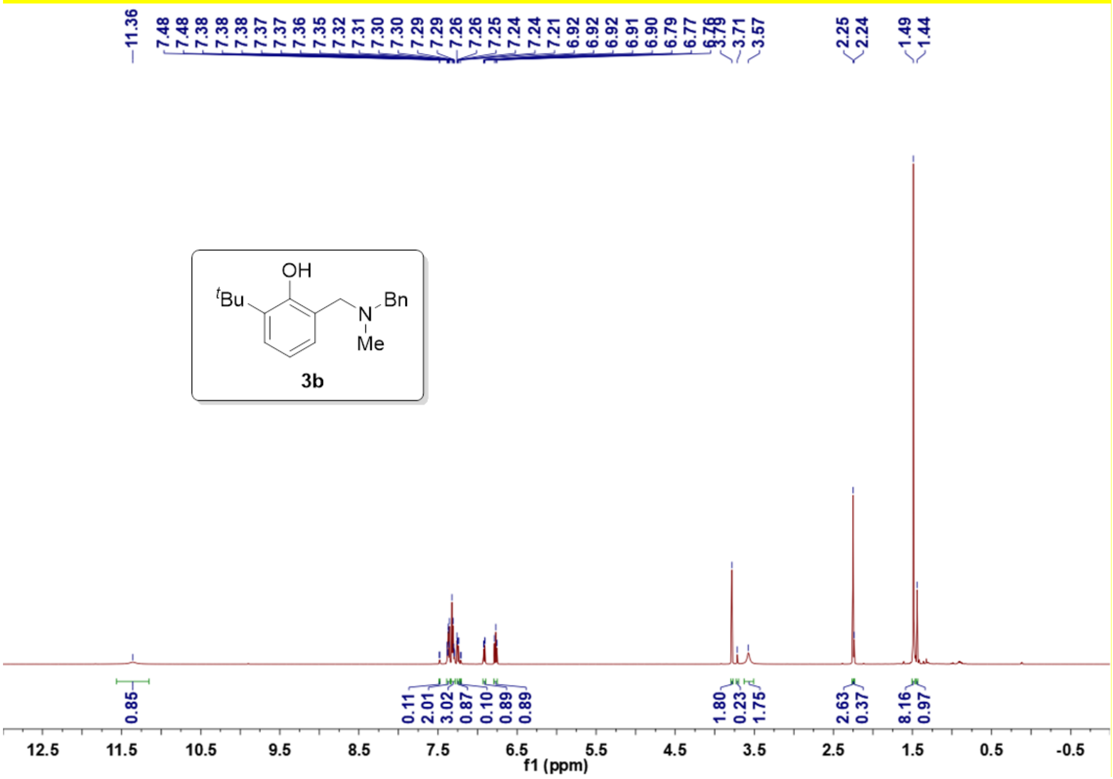
^{1}H NMR (500 MHz, $CDCl_3$) of **3a**



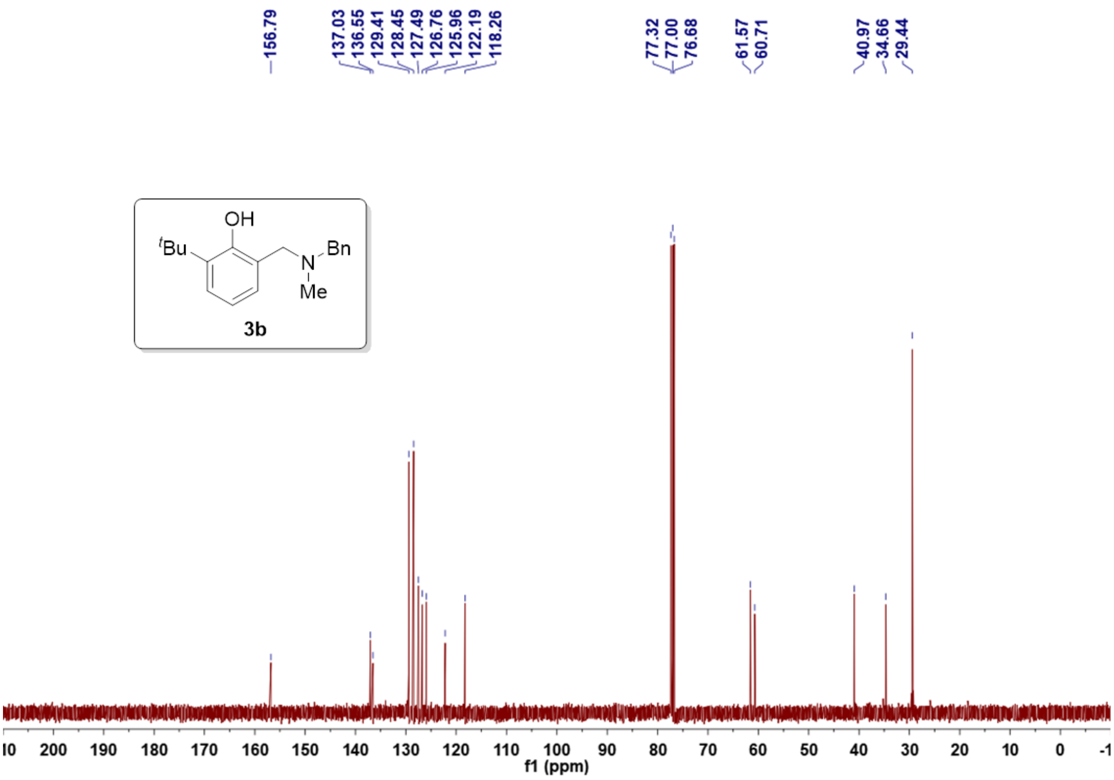
^{13}C NMR (126 MHz, $CDCl_3$) of **3a**



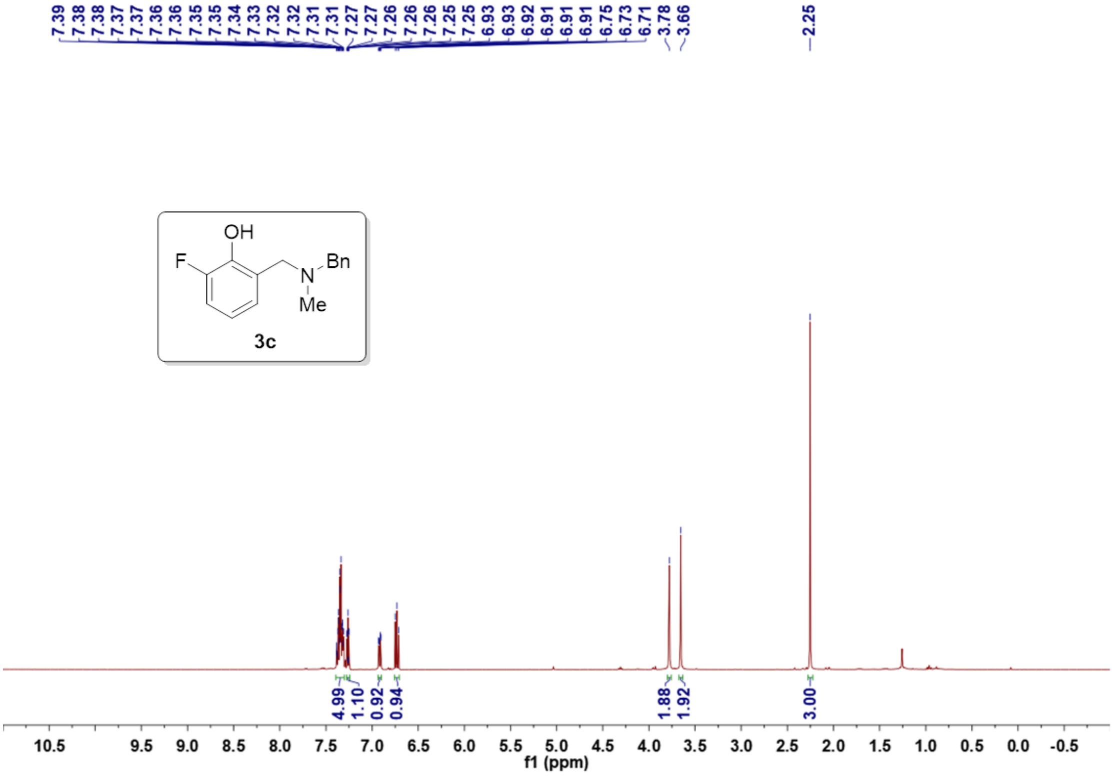
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



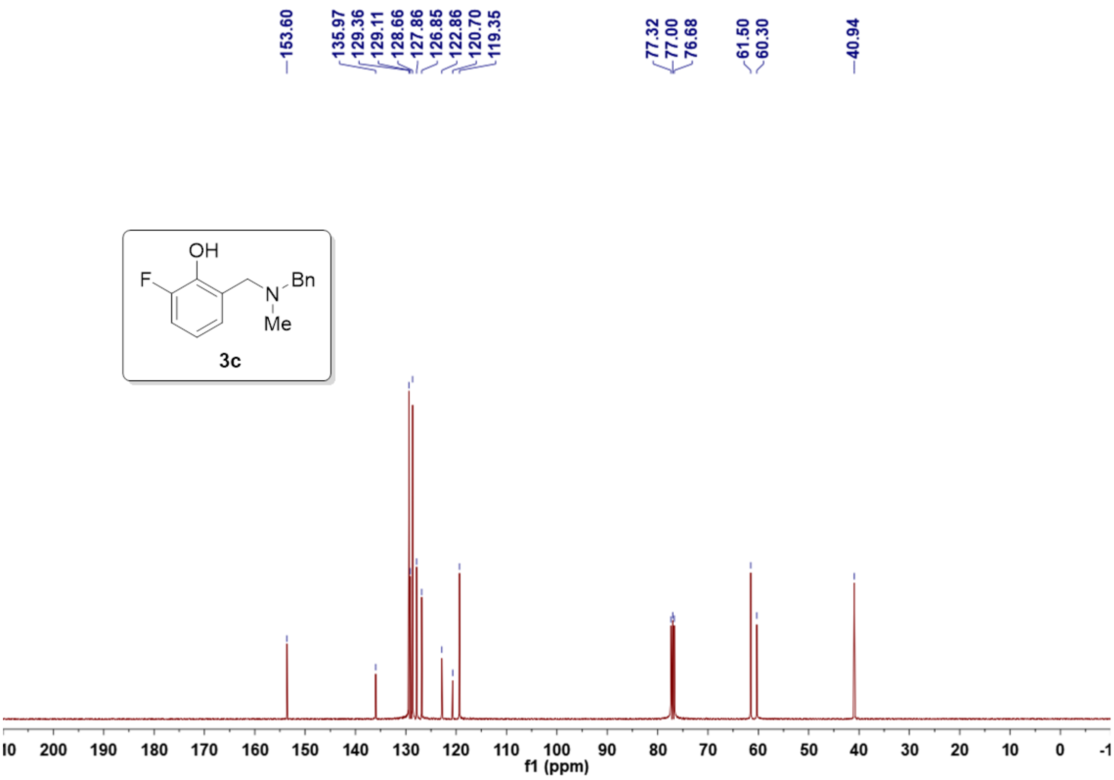
^{13}C NMR (100 MHz, $CDCl_3$) of **3b**



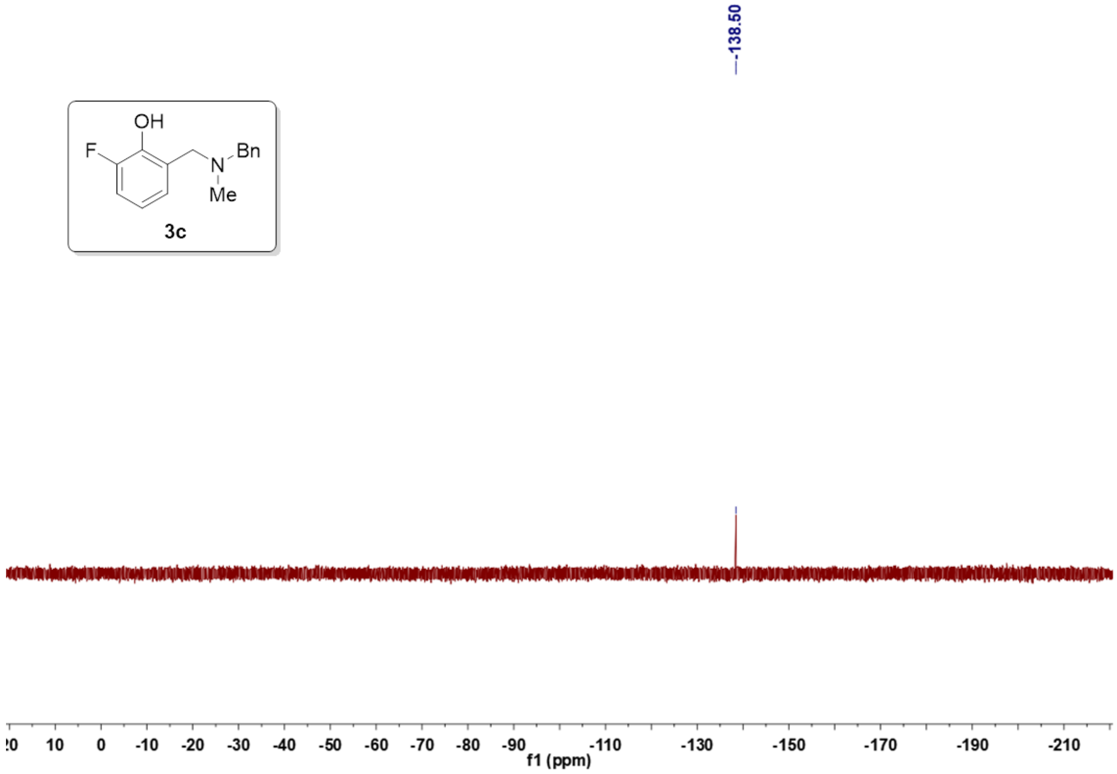
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



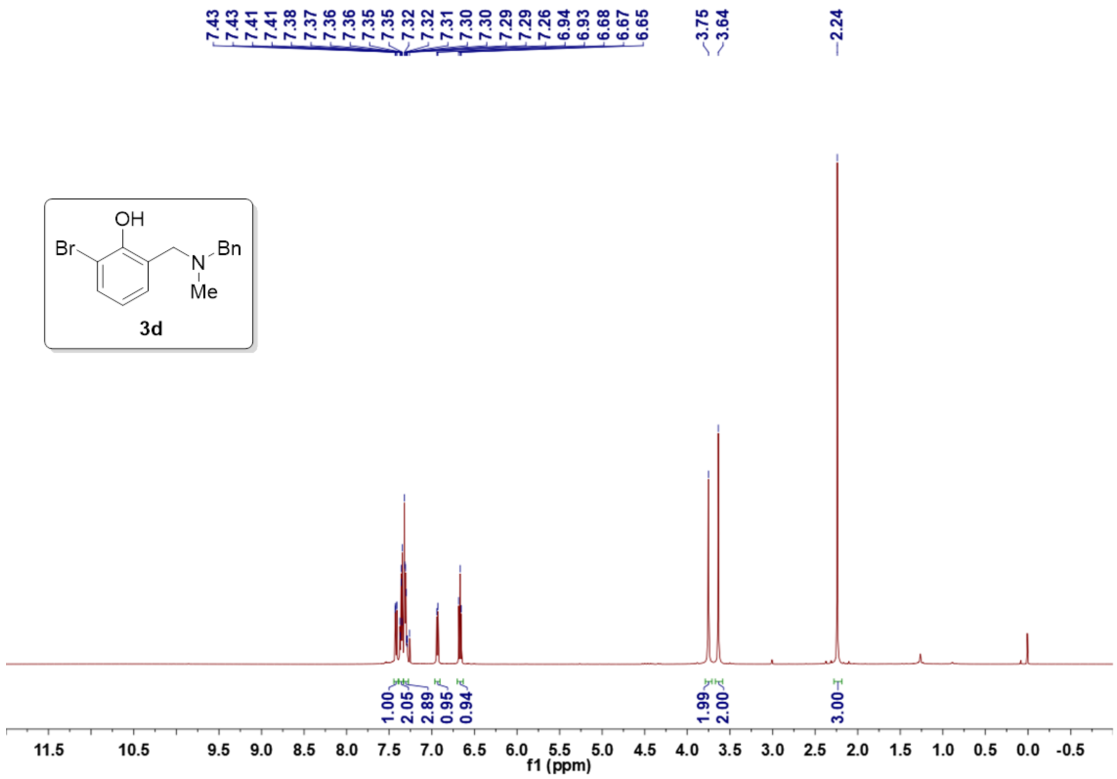
^{13}C NMR (100 MHz, $CDCl_3$) of **3c**



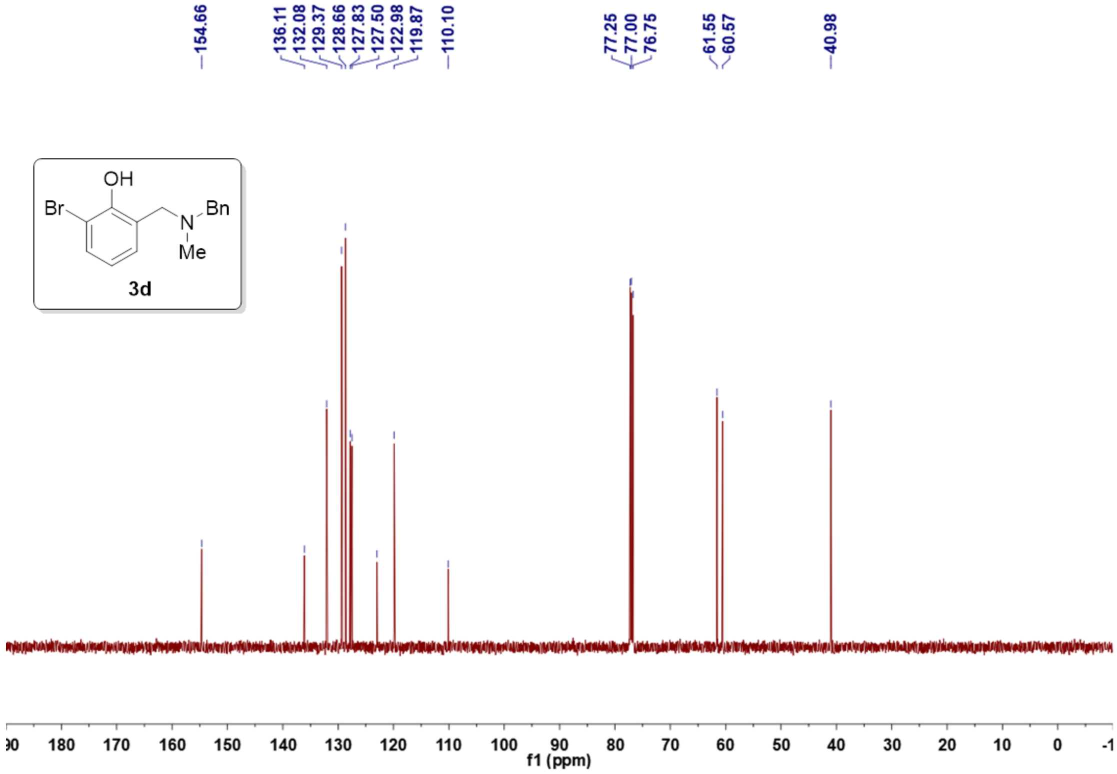
^{19}F NMR (471 MHz, $CDCl_3$) of **3c**



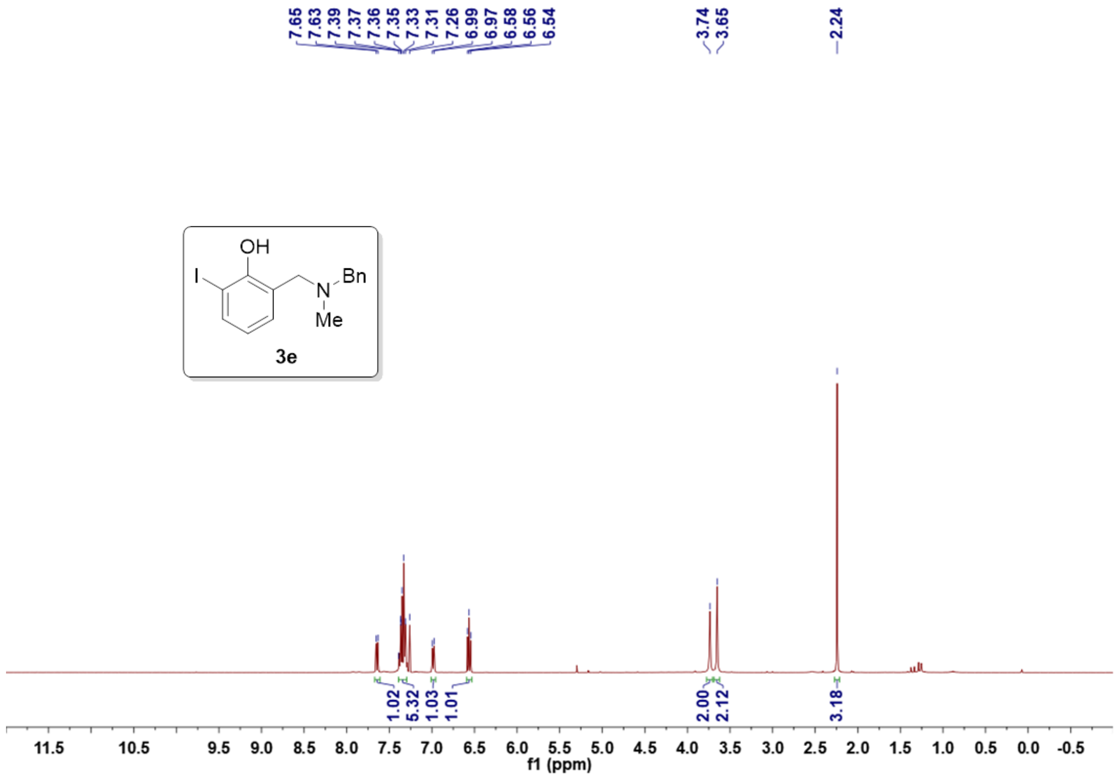
^{1}H NMR (500 MHz, $CDCl_3$) of **3d**



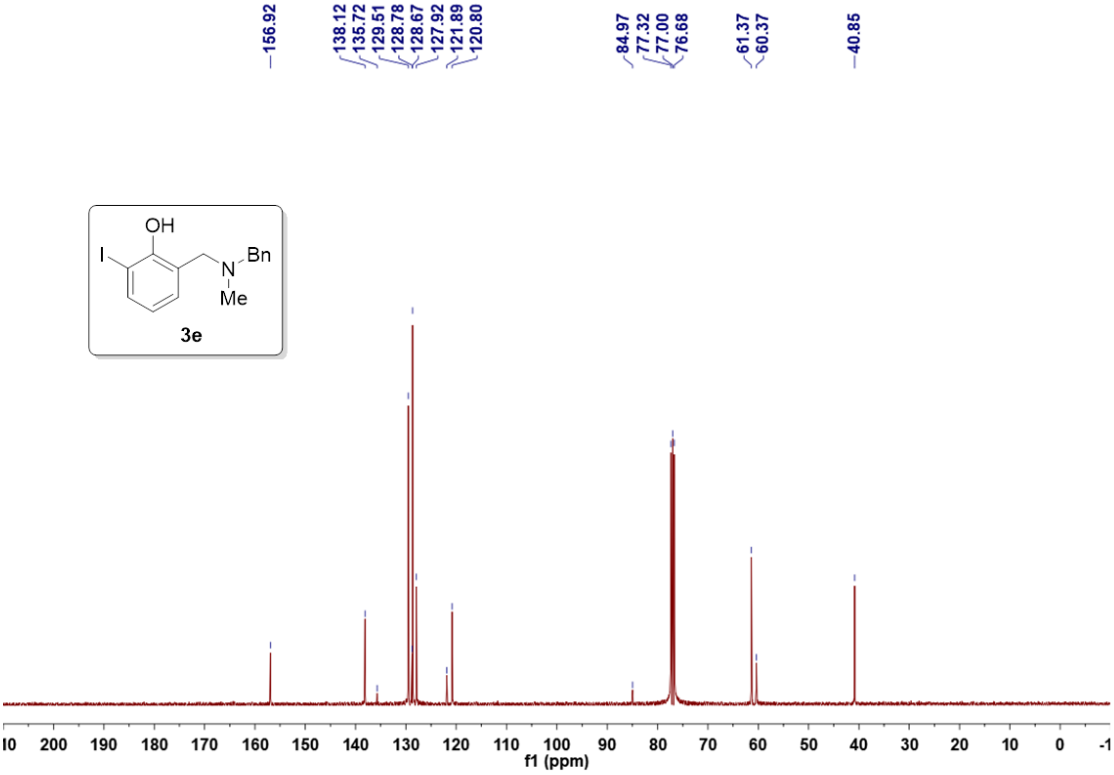
^{13}C NMR (126 MHz, $CDCl_3$) of **3d**



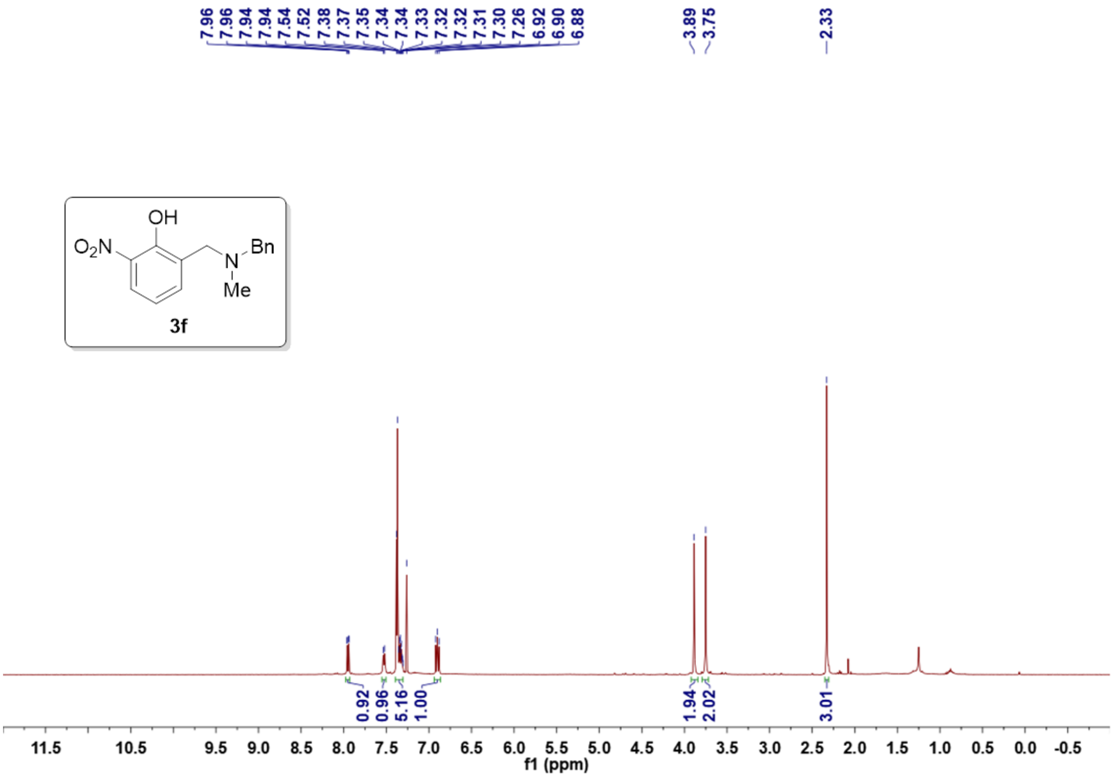
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



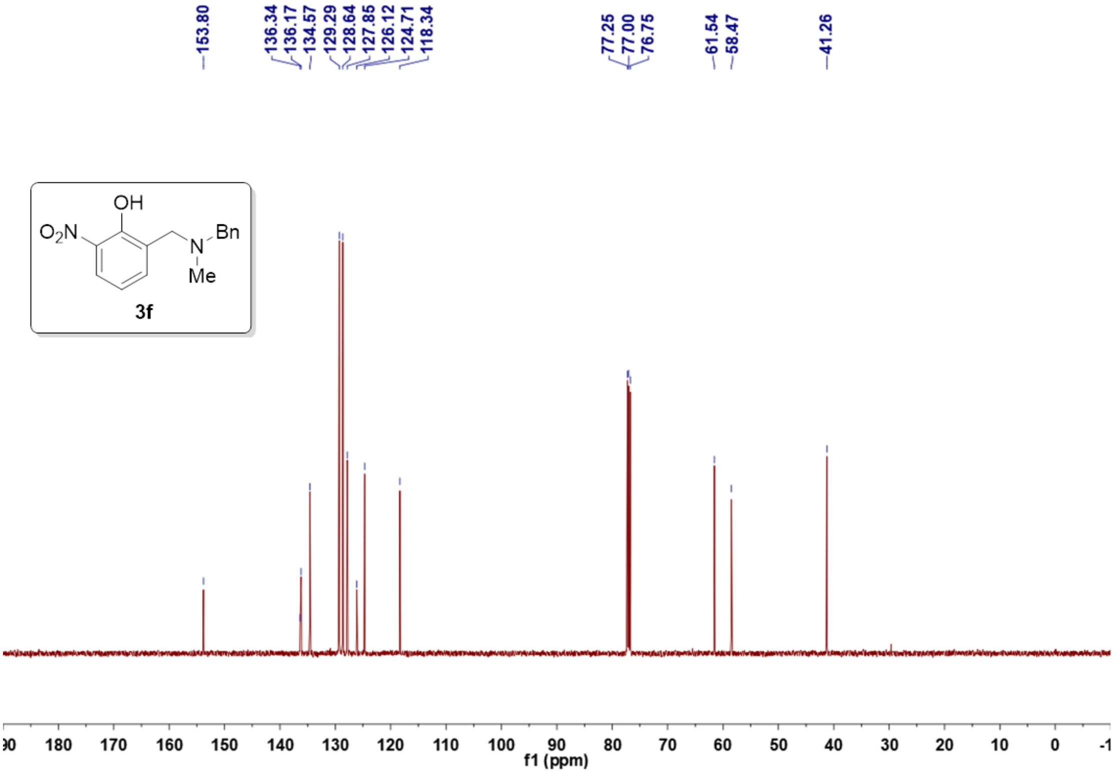
^{13}C NMR (100 MHz, $CDCl_3$) of **3e**



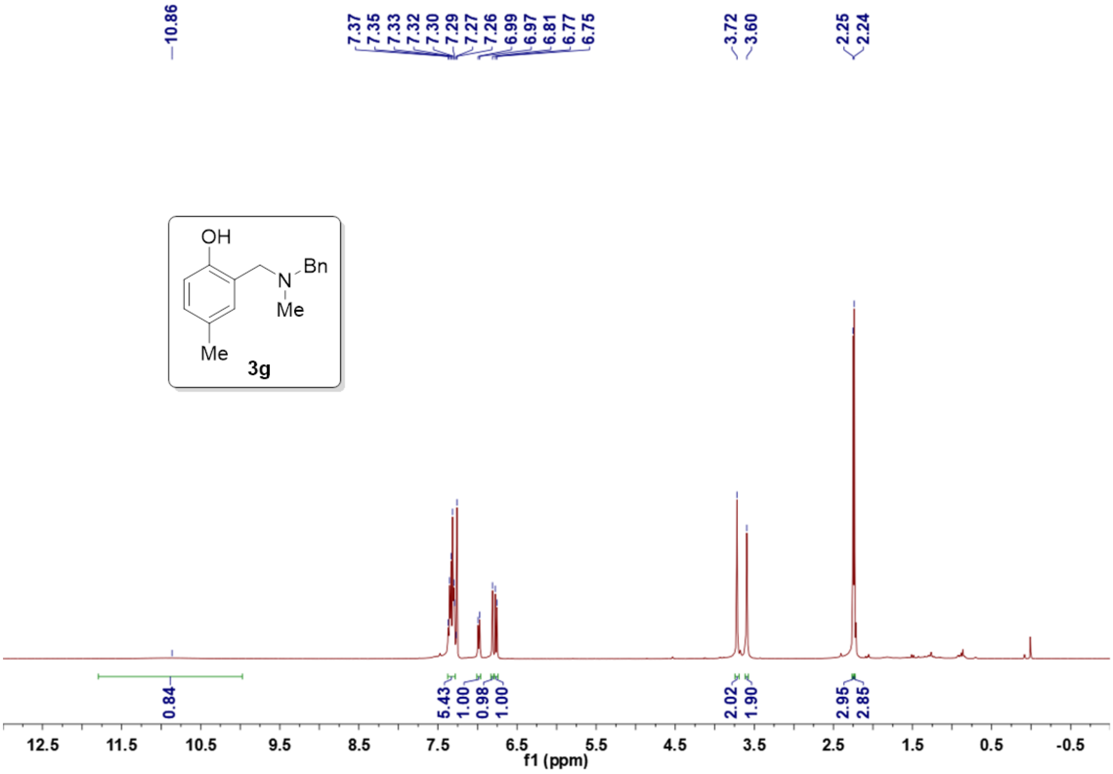
^{1}H NMR (500 MHz, $CDCl_3$) of **3f**



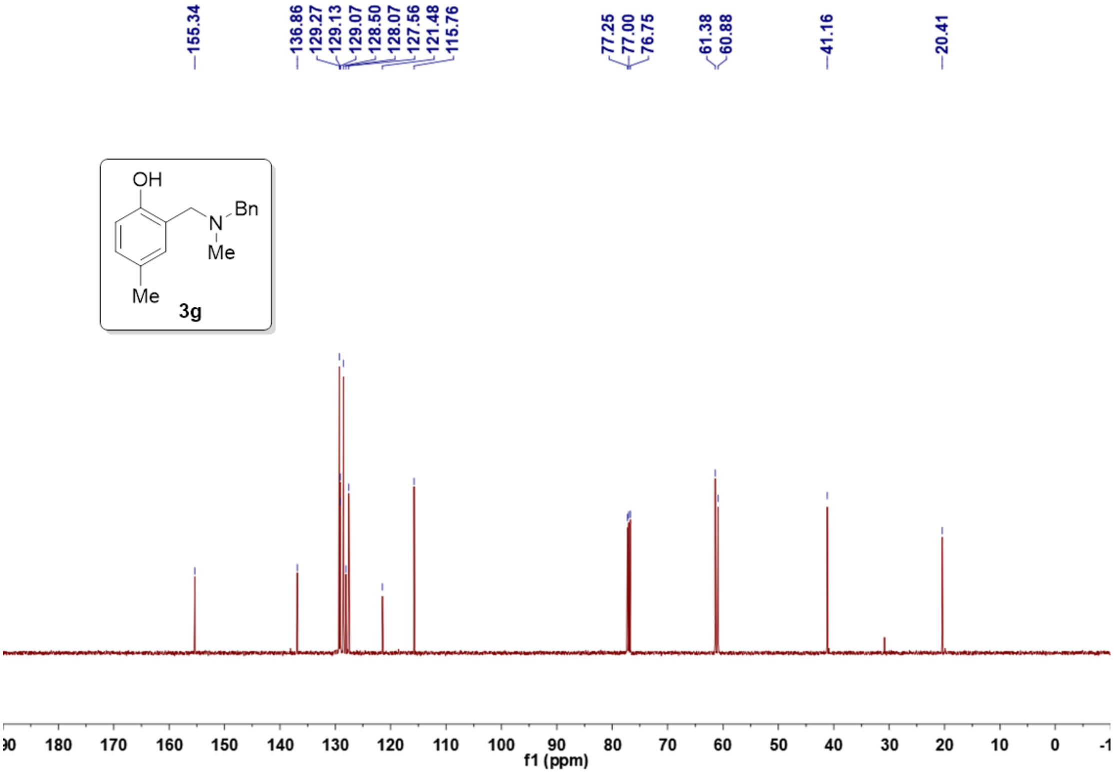
^{13}C NMR (126 MHz, $CDCl_3$) of **3f**



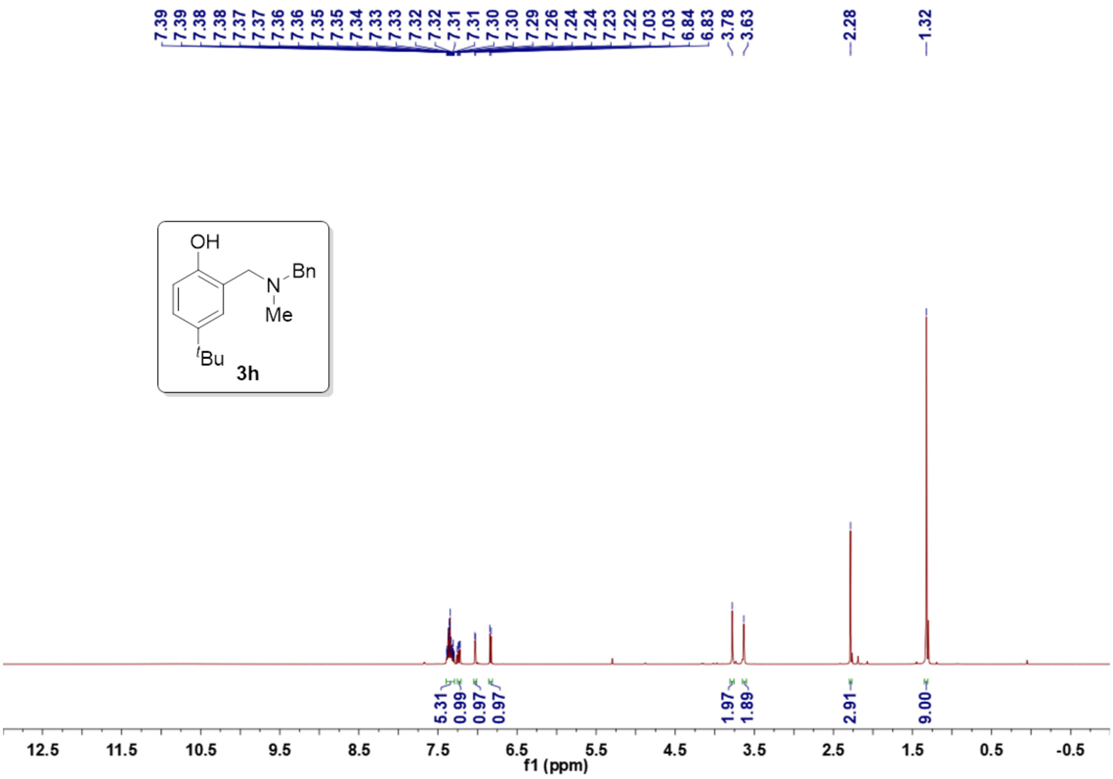
^{1}H NMR (500 MHz, $CDCl_3$) of **3g**



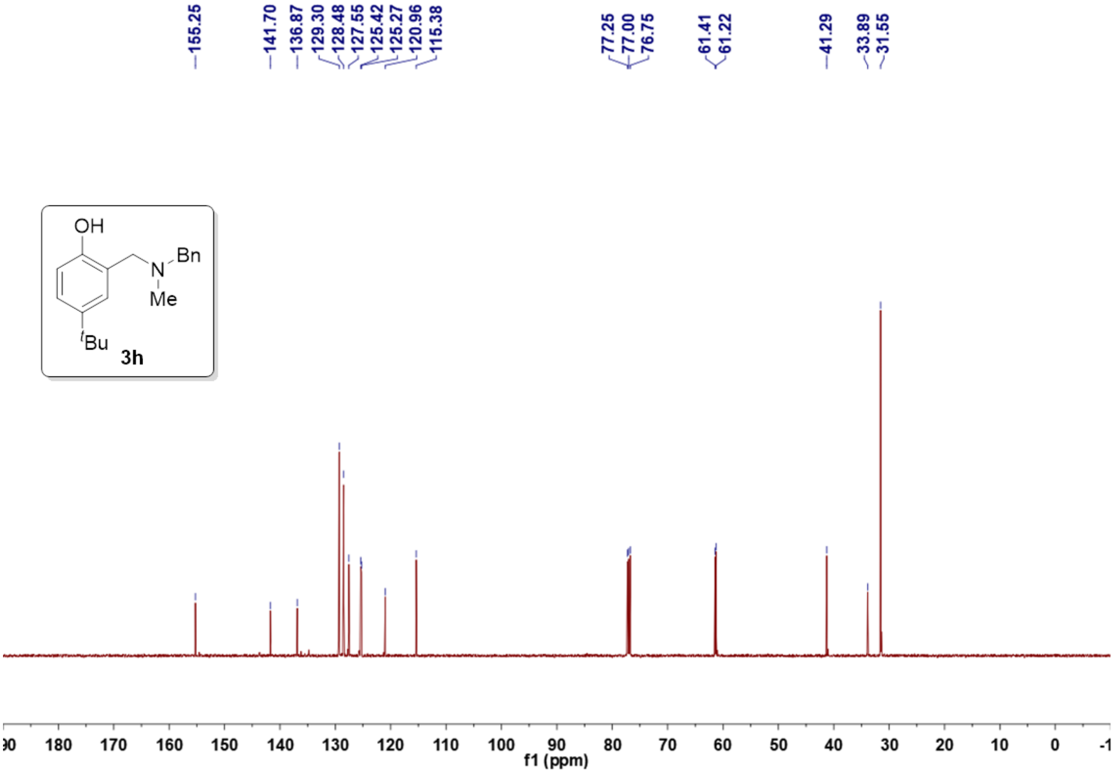
^{13}C NMR (126 MHz, $CDCl_3$) of **3g**



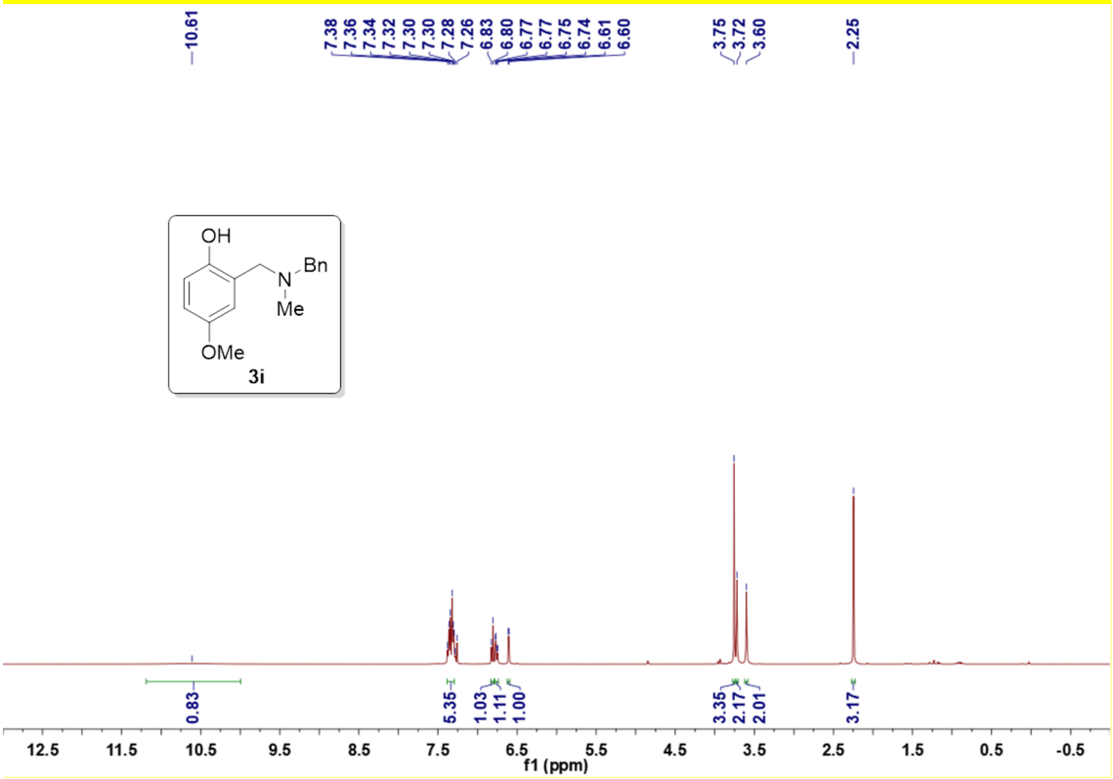
^{1}H NMR (500 MHz, $CDCl_3$) of **3h**



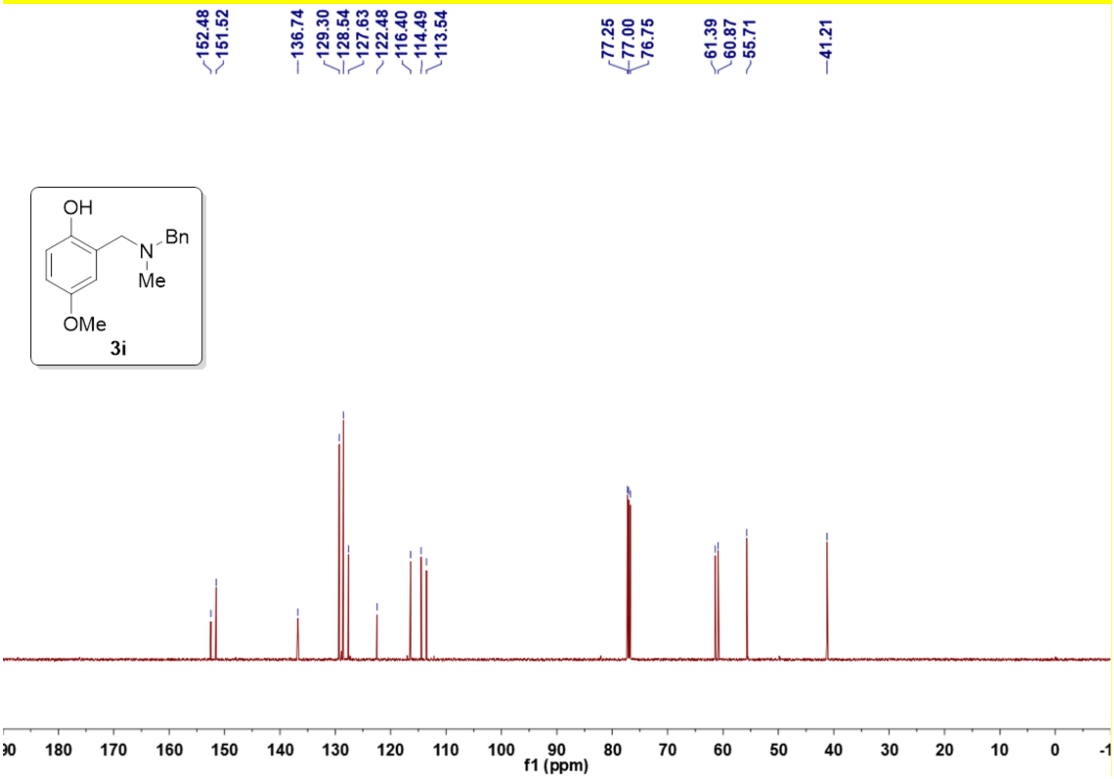
^{13}C NMR (126 MHz, CDCl$_3$) of **3h**



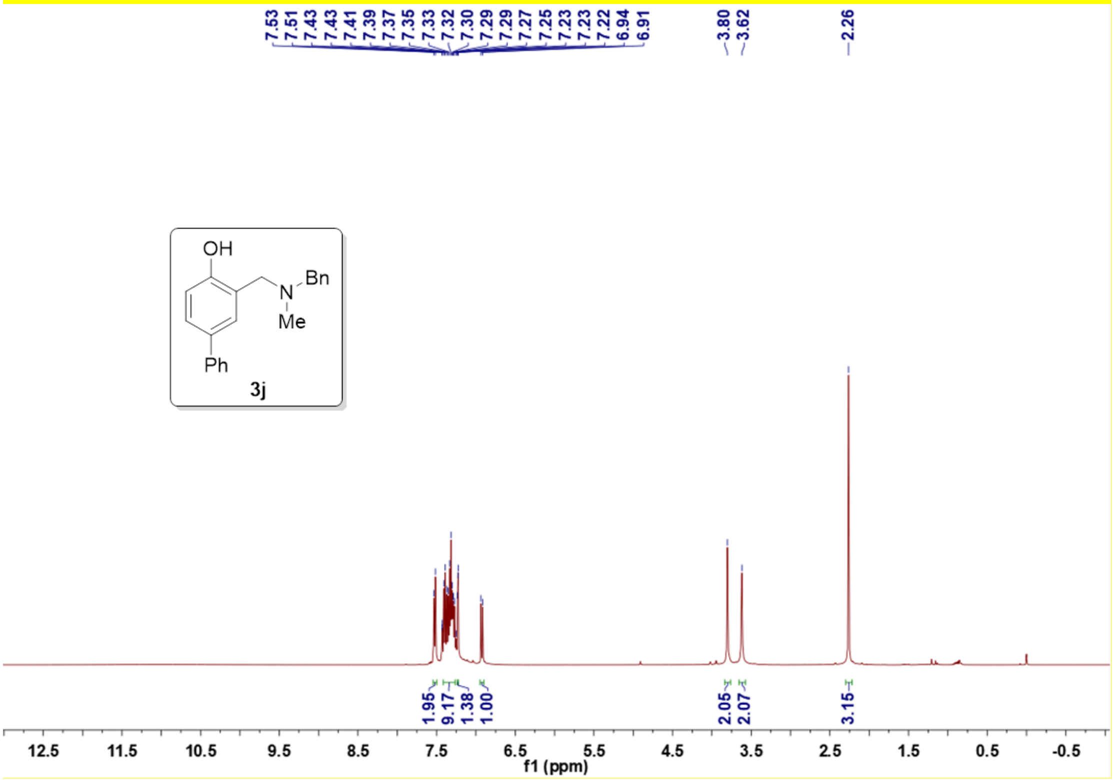
^{1}H NMR (500 MHz, CDCl$_3$) of **3i**



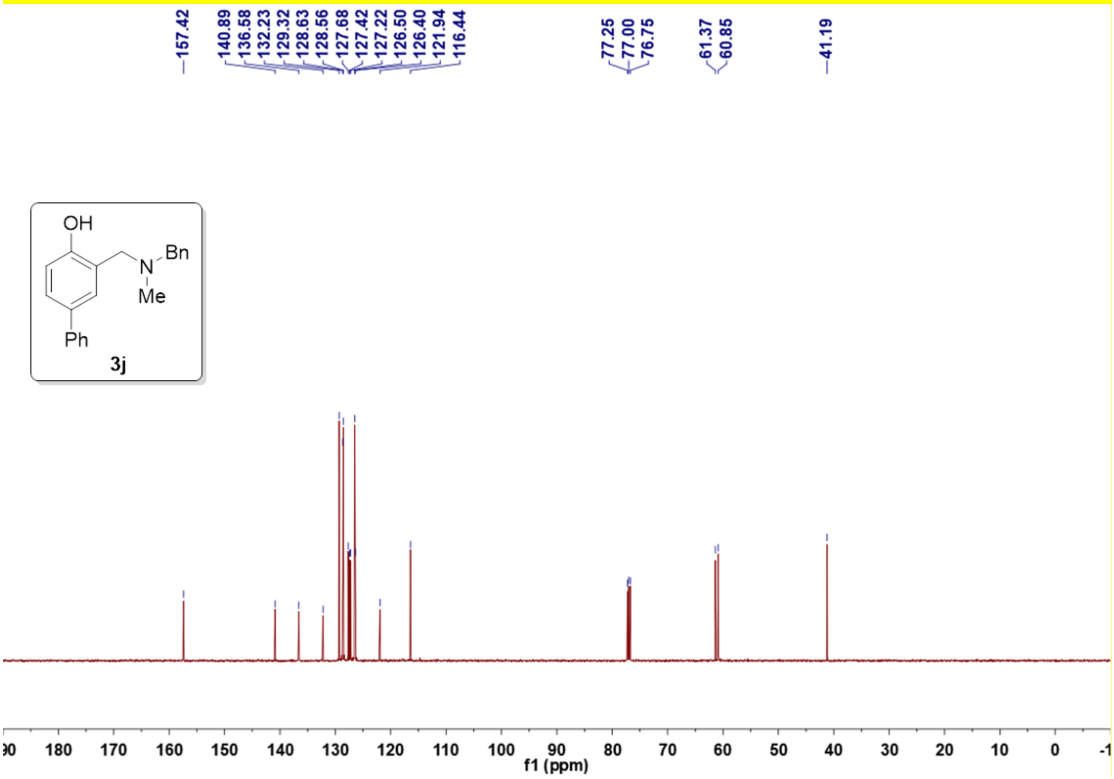
^{13}C NMR (126 MHz, $CDCl_3$) of **3i**



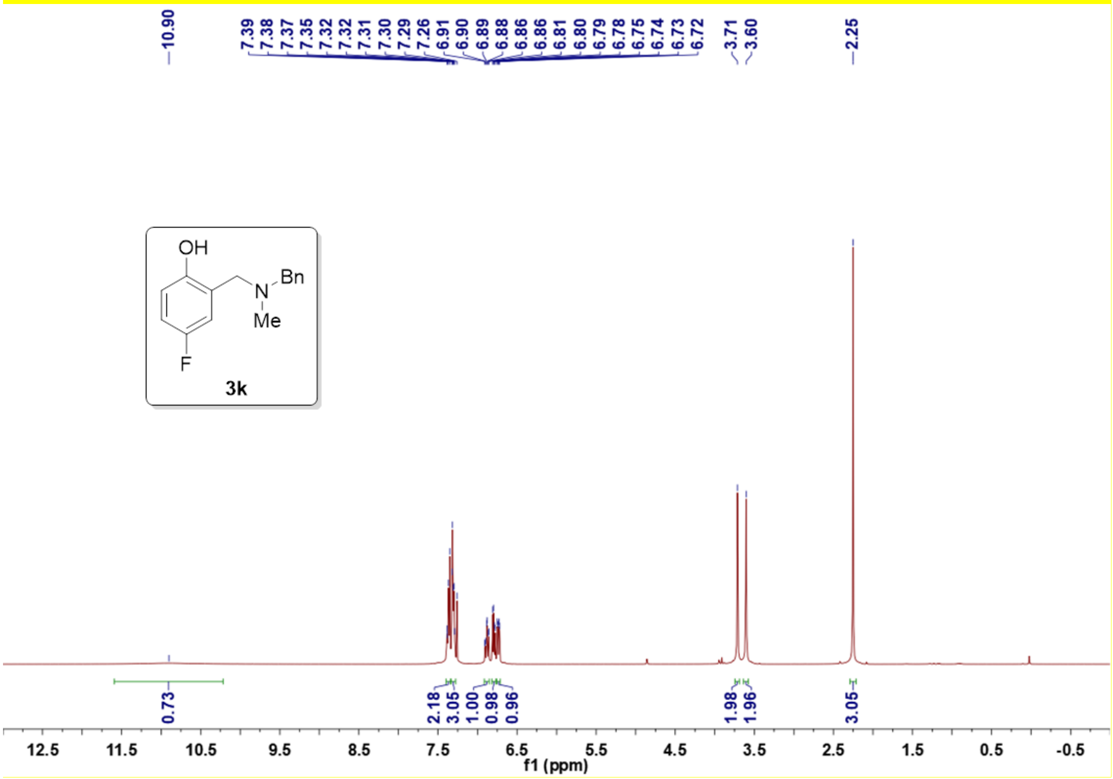
^1H NMR (500 MHz, $CDCl_3$) of **3j**



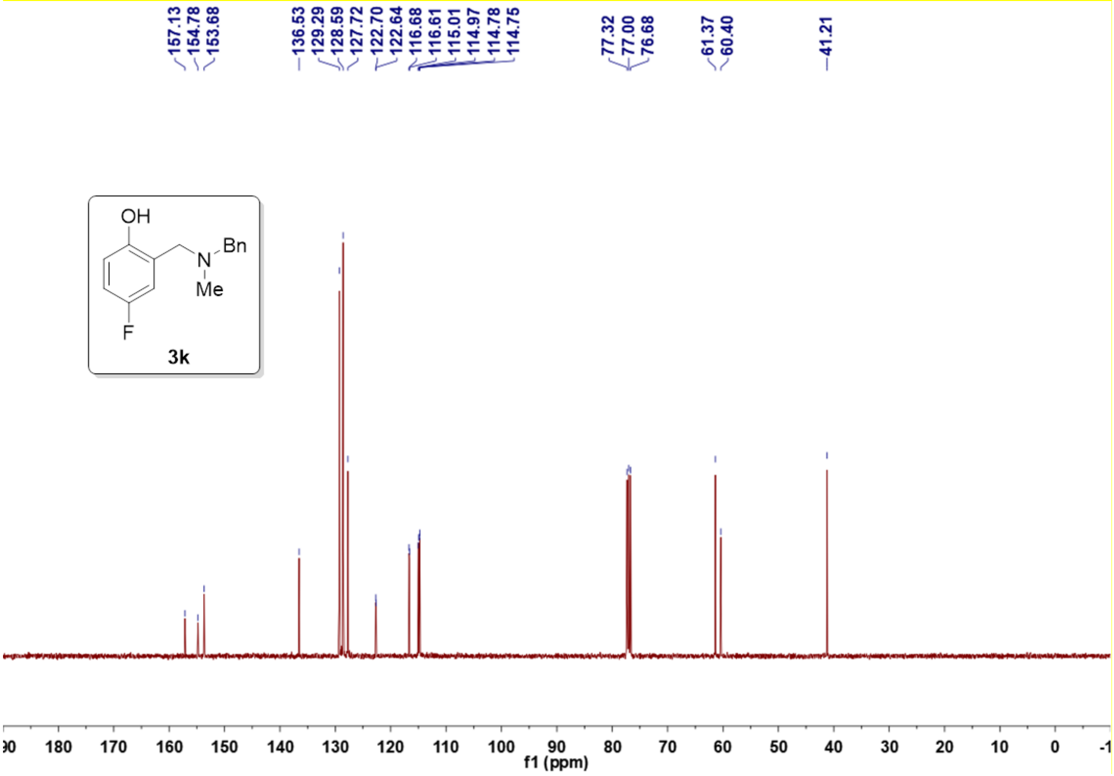
[13]C NMR (126 MHz, $CDCl_3$) of **3j**



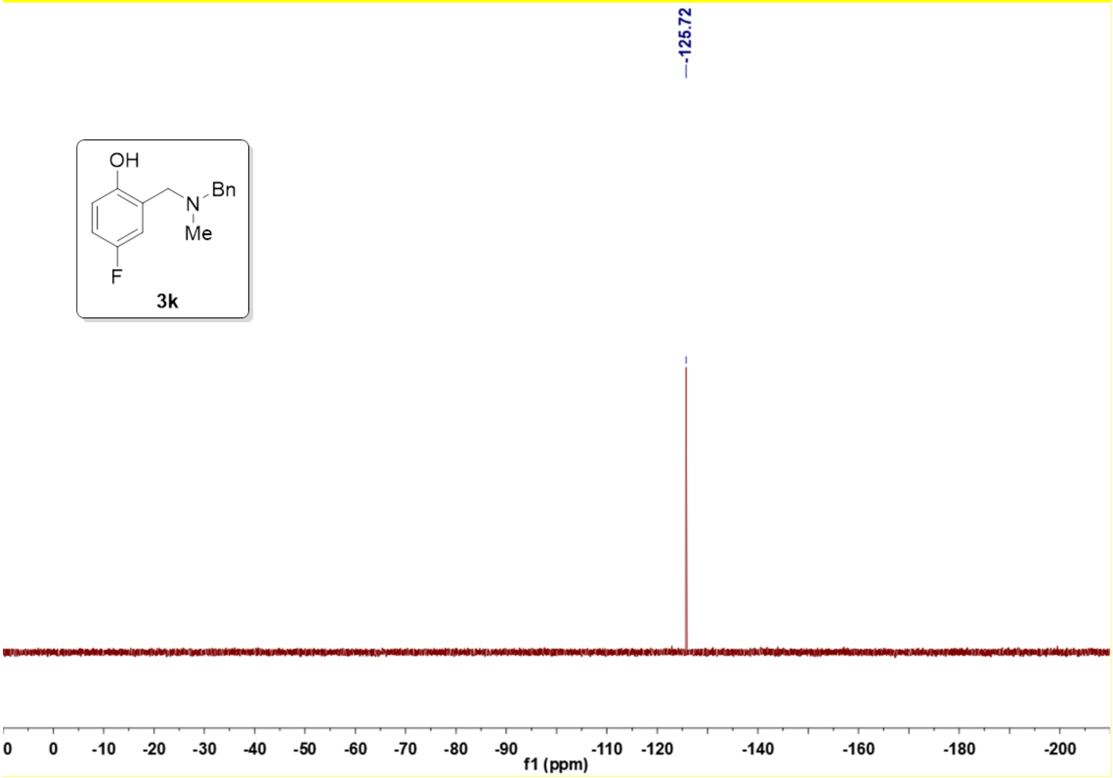
[1]H NMR (500 MHz, $CDCl_3$) of **3k**



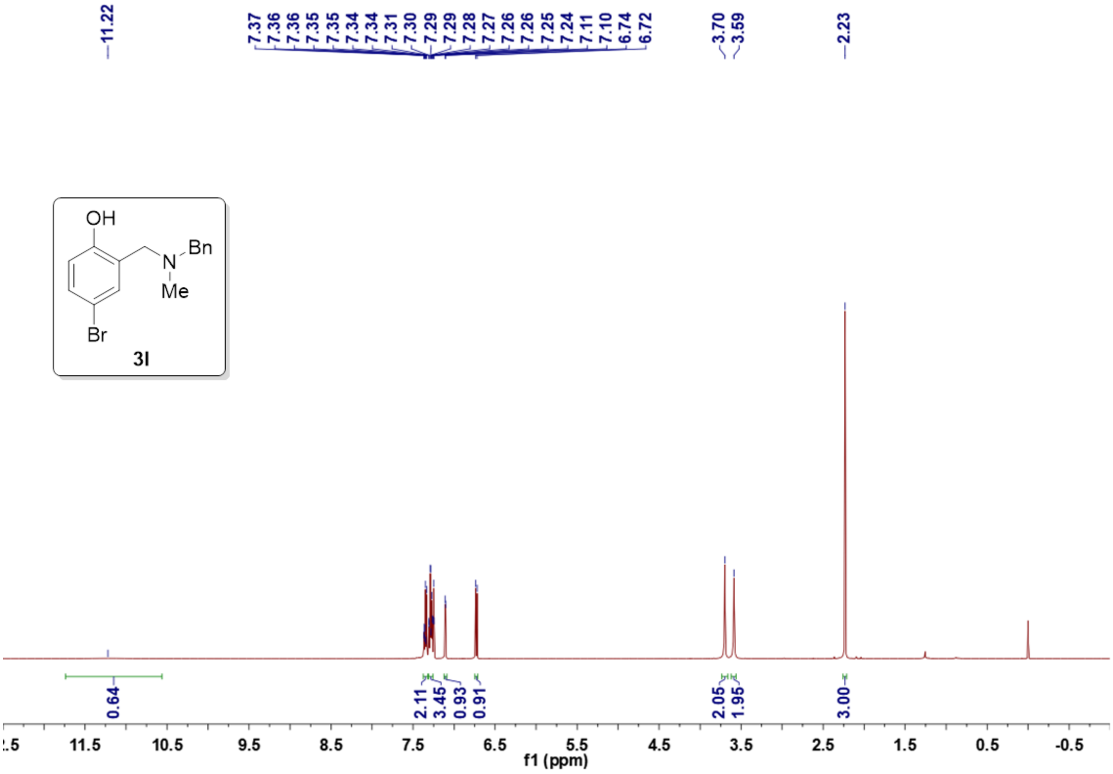
^{13}C NMR (126 MHz, $CDCl_3$) of **3k**



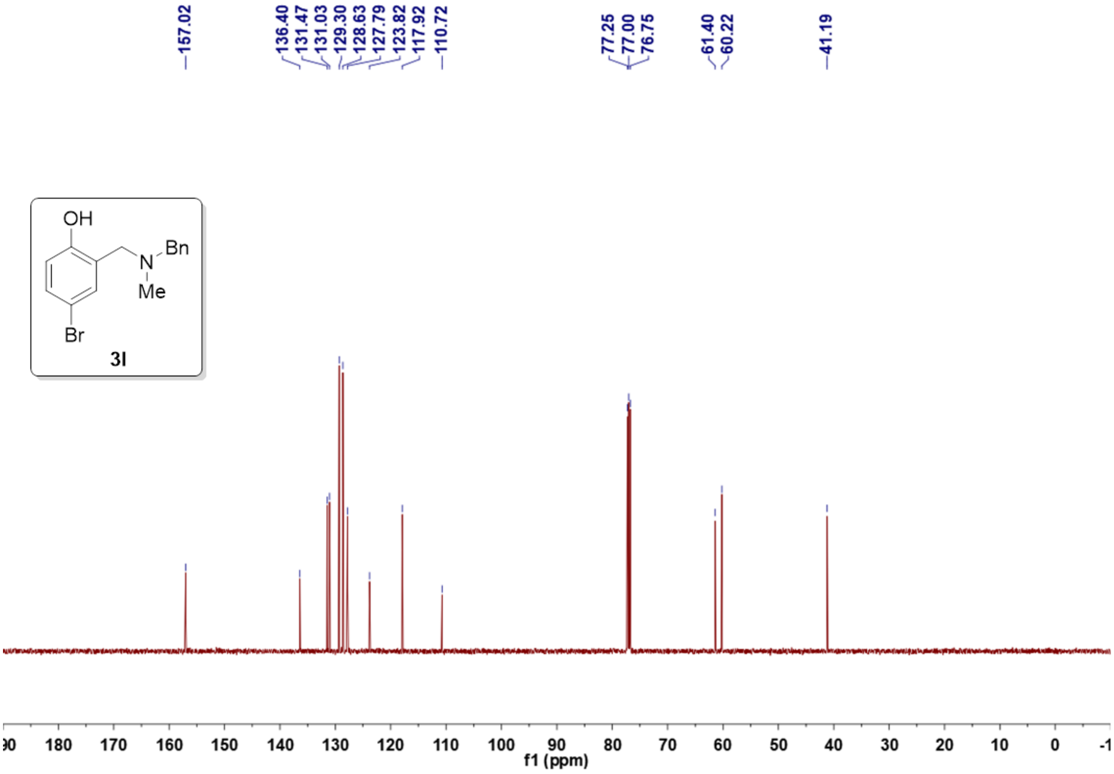
^{19}F NMR (471 MHz, $CDCl_3$) of **3k**



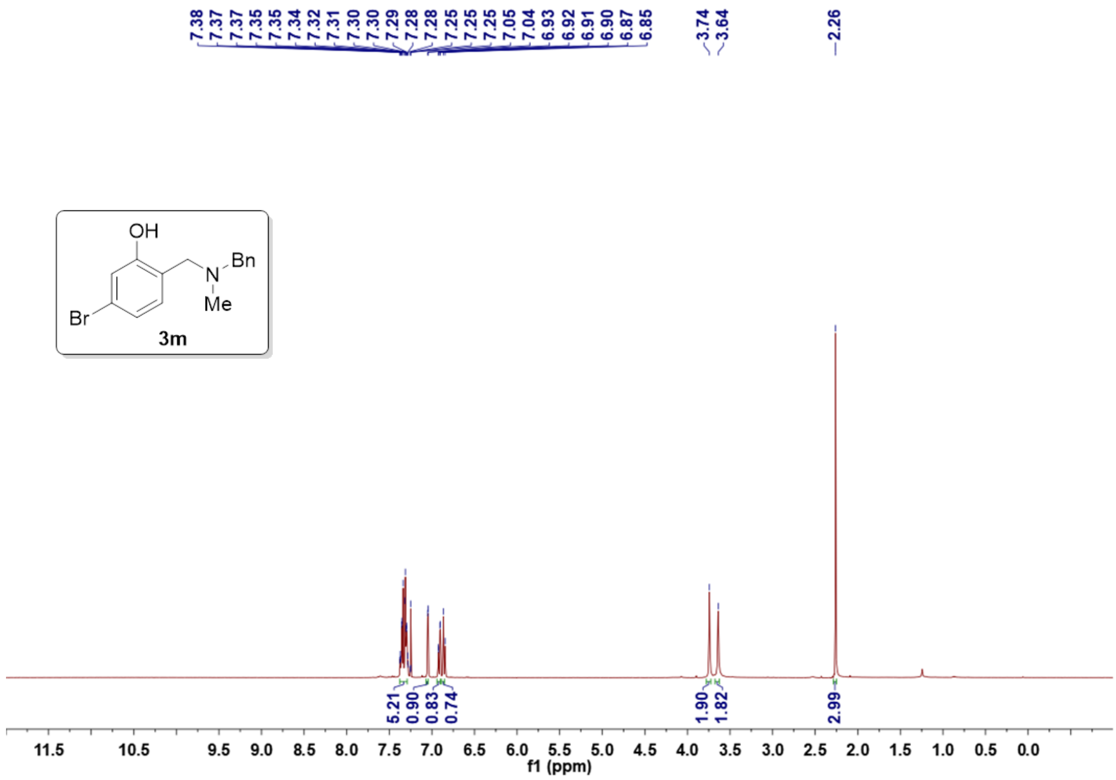
^1H NMR (500 MHz, $CDCl_3$) of **3l**



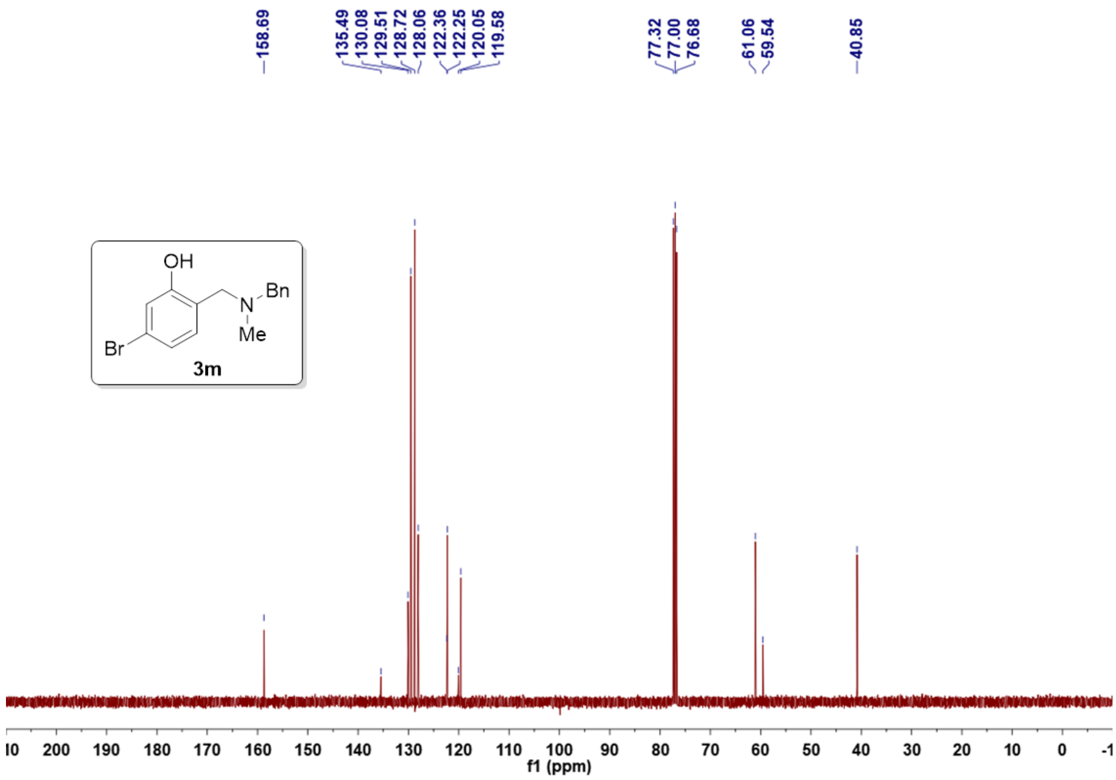
^{13}C NMR (126 MHz, $CDCl_3$) of **3l**



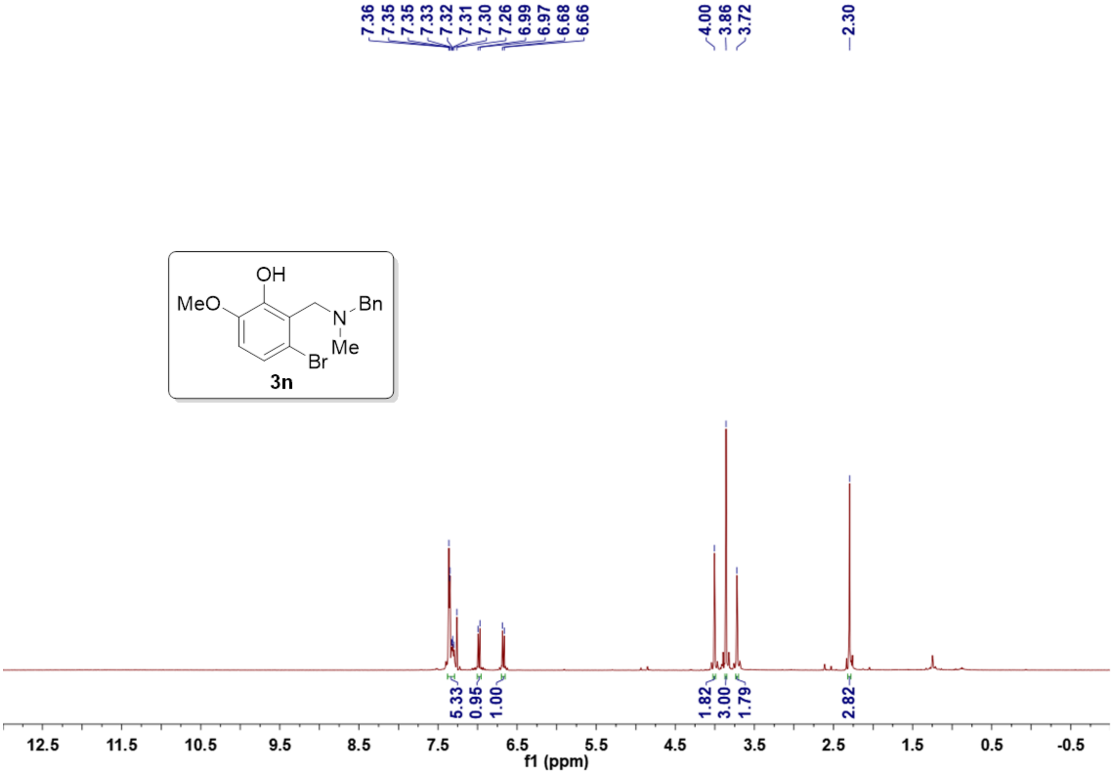
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



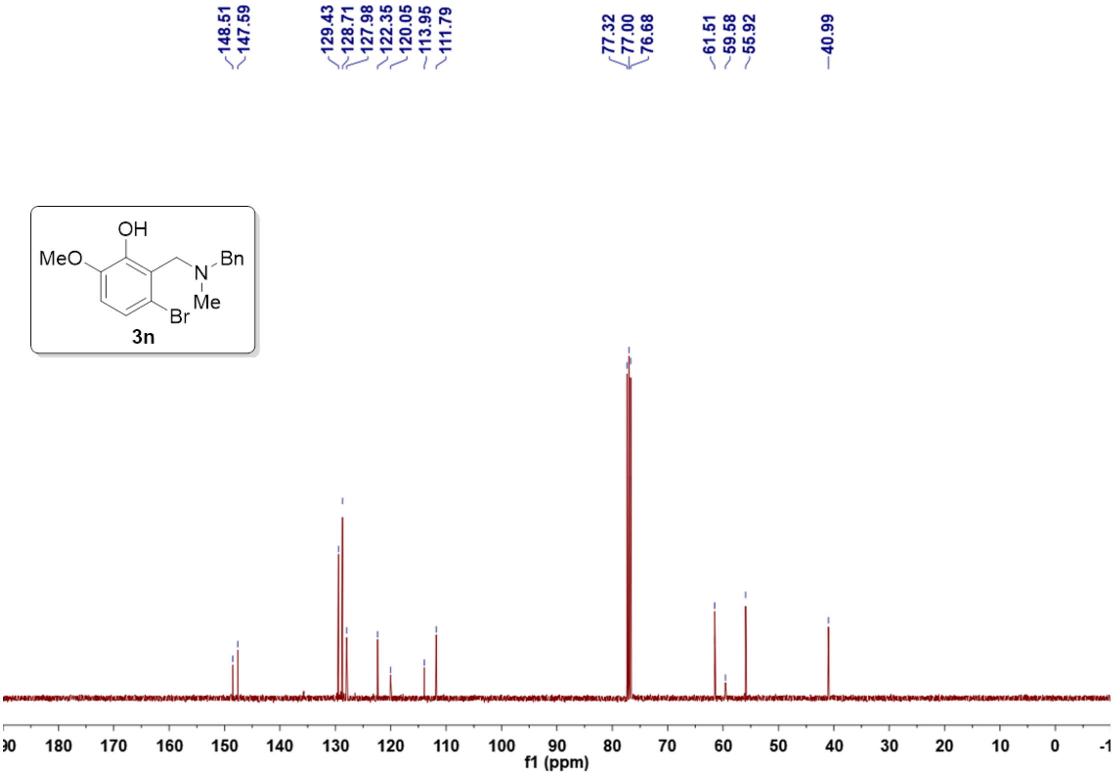
^{13}C NMR (100 MHz, $CDCl_3$) of **3m**



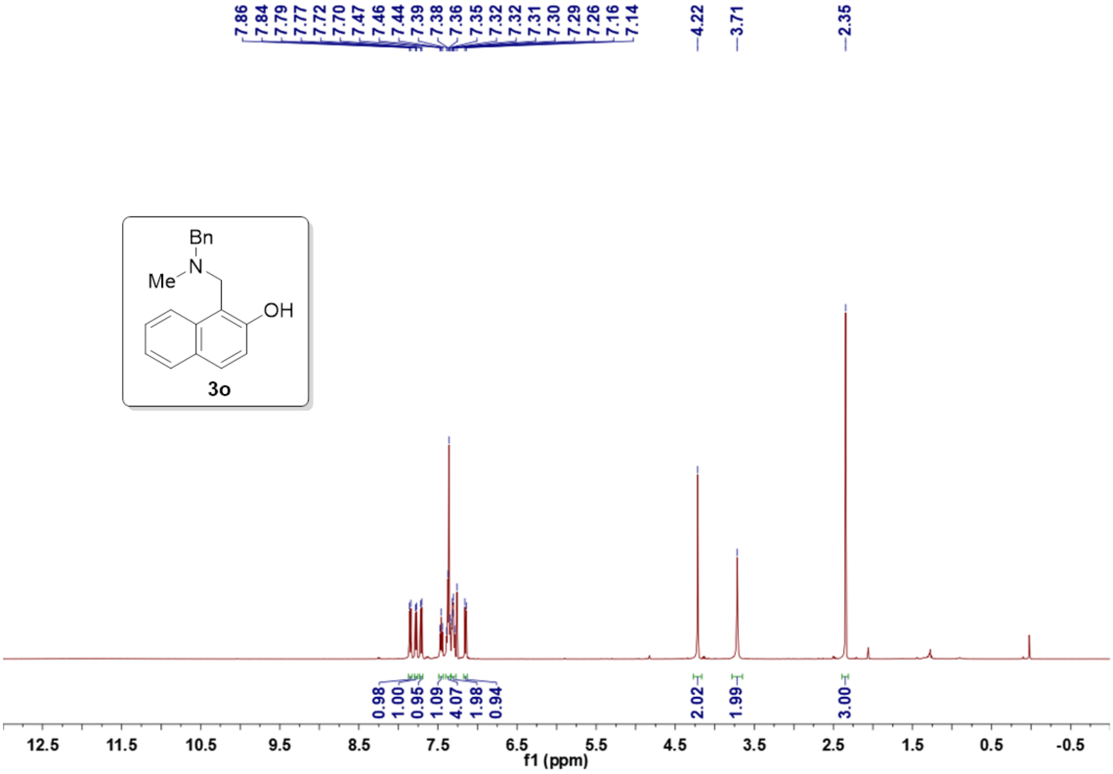
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



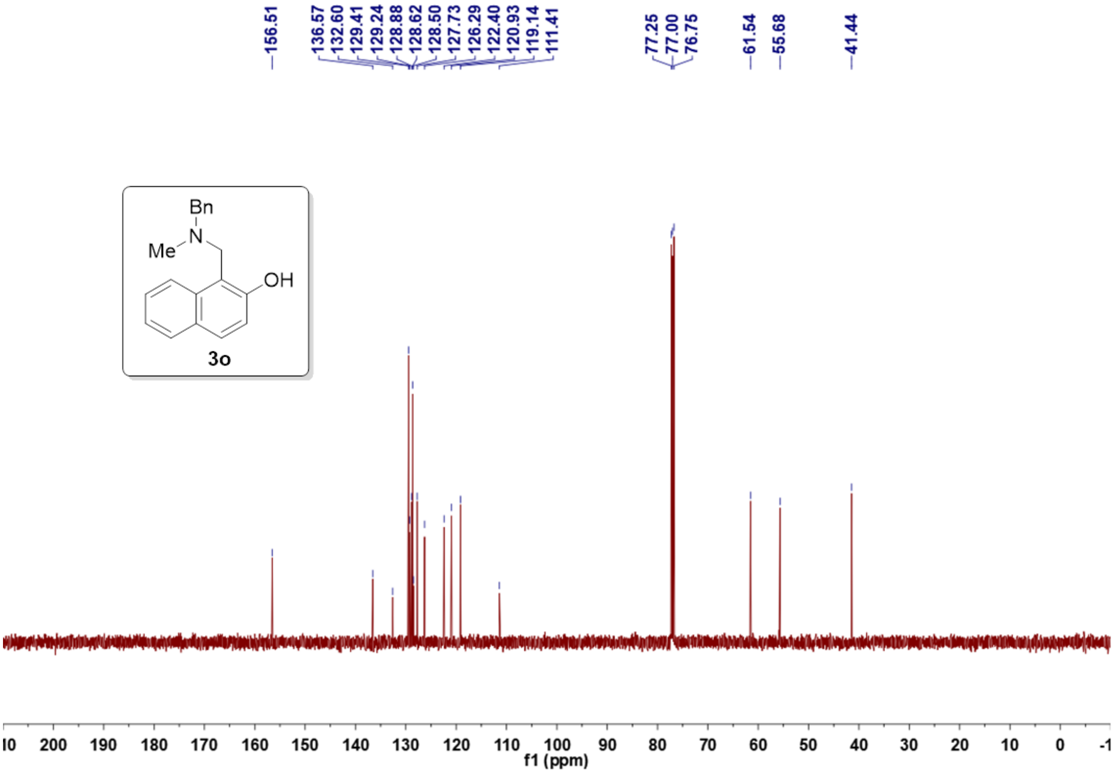
^{13}C NMR (100 MHz, $CDCl_3$) of **3n**



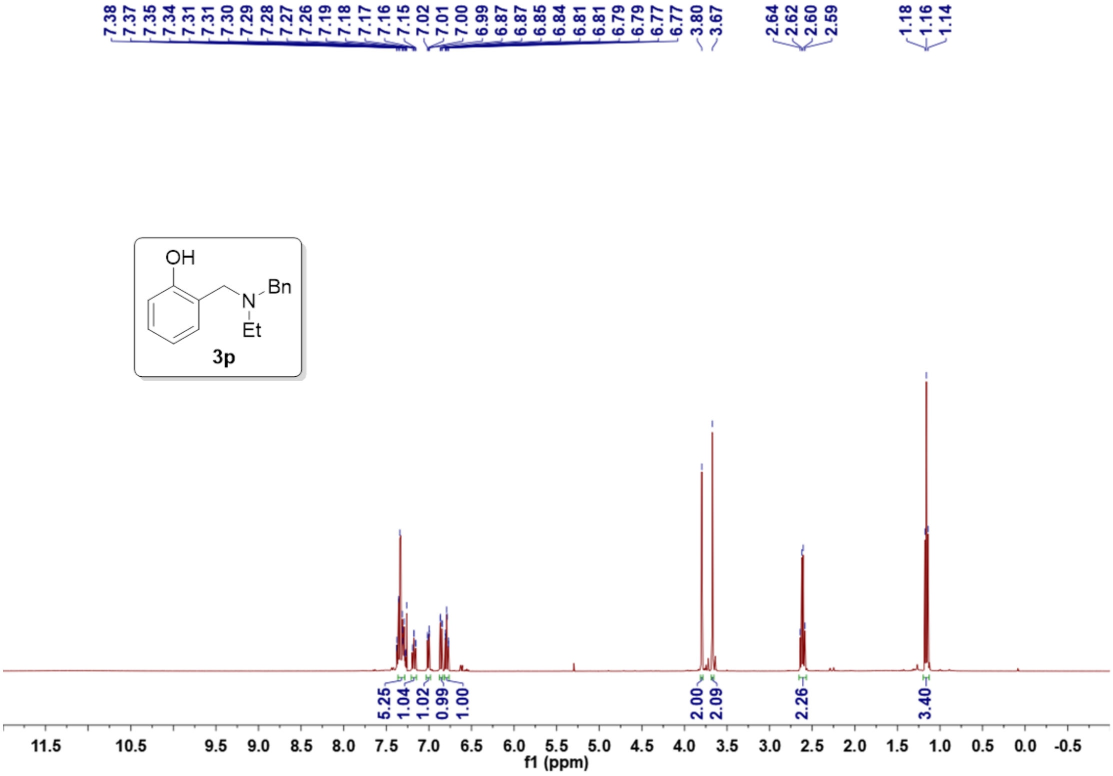
^{1}H NMR (500 MHz, $CDCl_3$) of **3o**



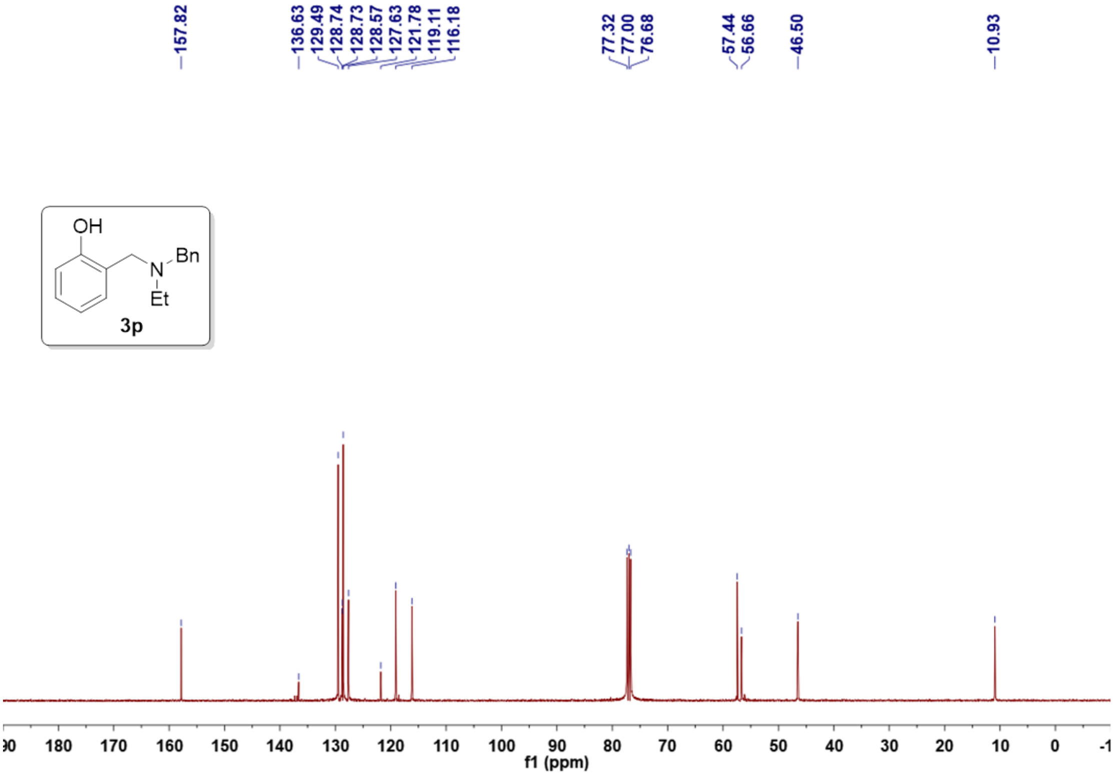
^{13}C NMR (126 MHz, $CDCl_3$) of **3o**



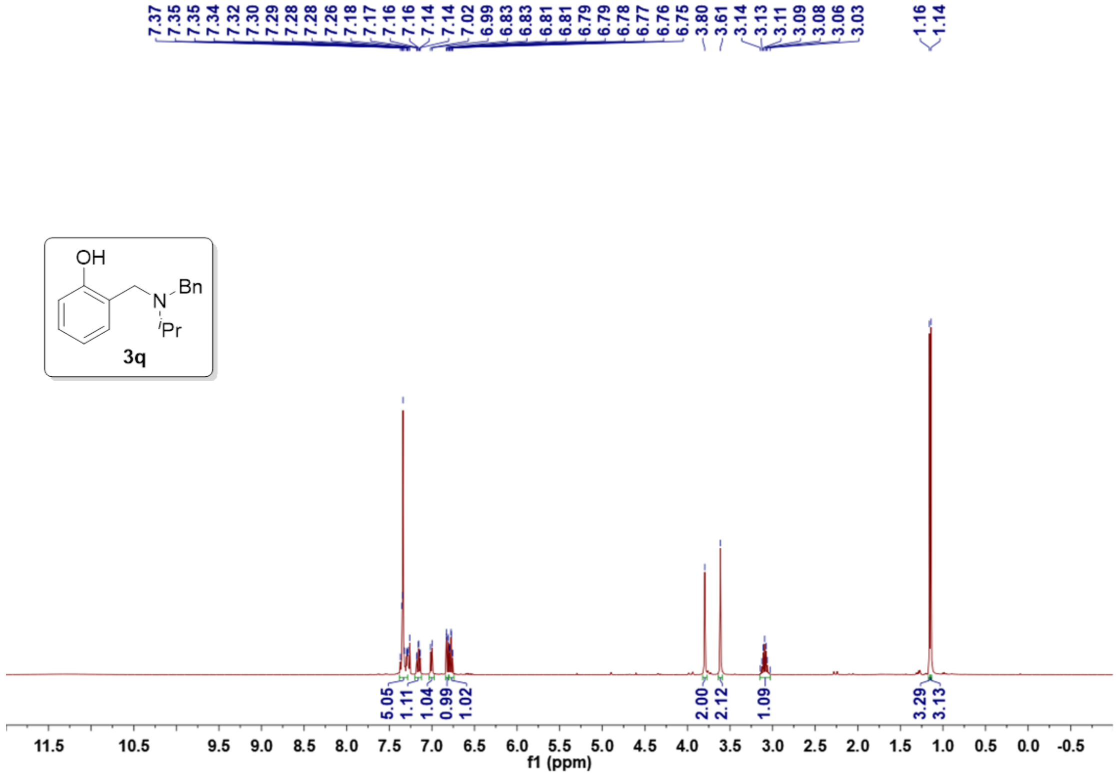
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



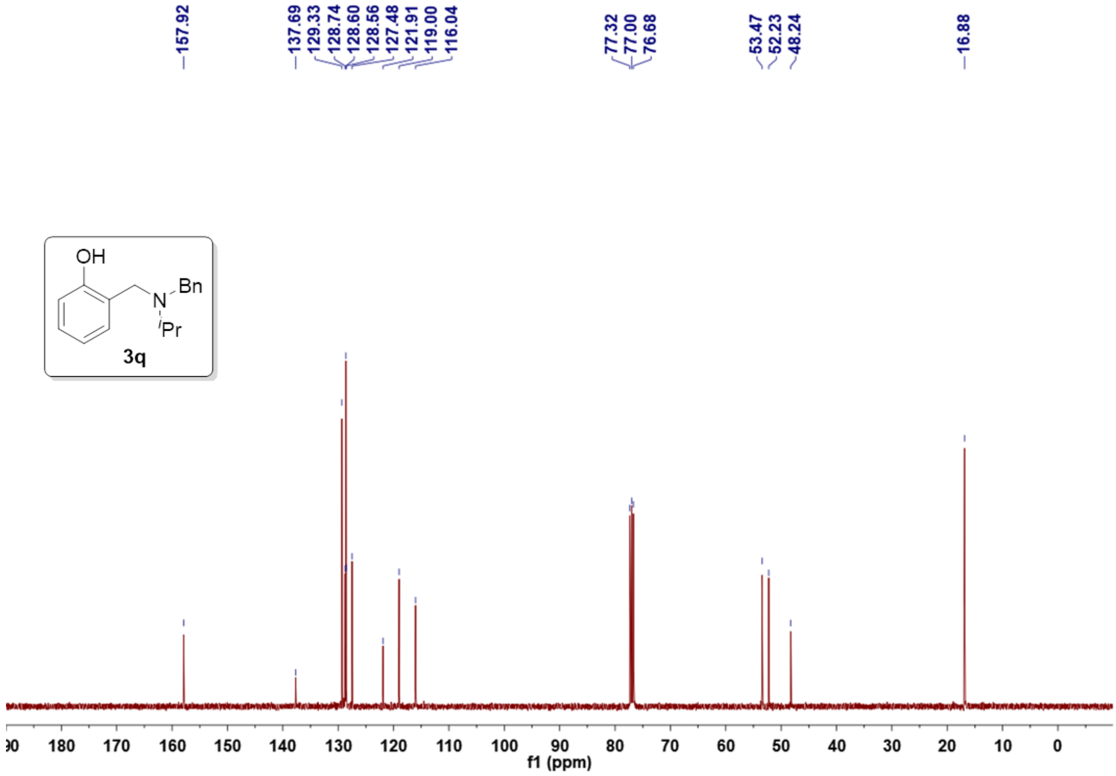
^{13}C NMR (100 MHz, $CDCl_3$) of **3p**



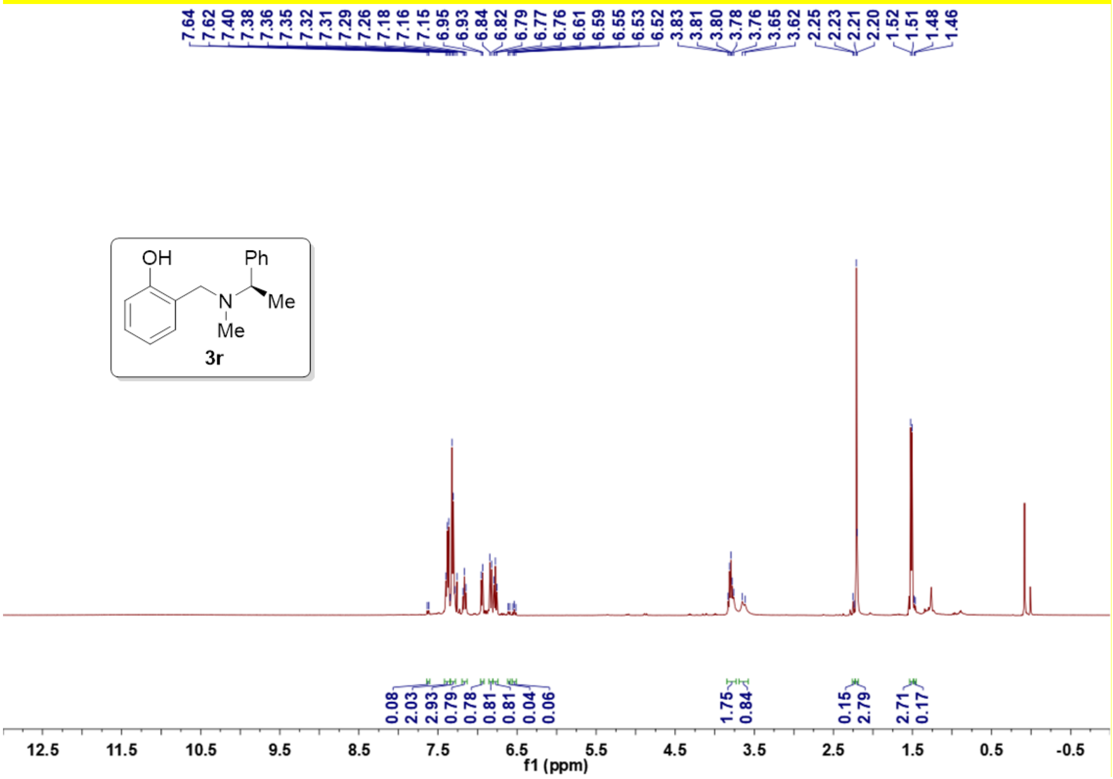
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



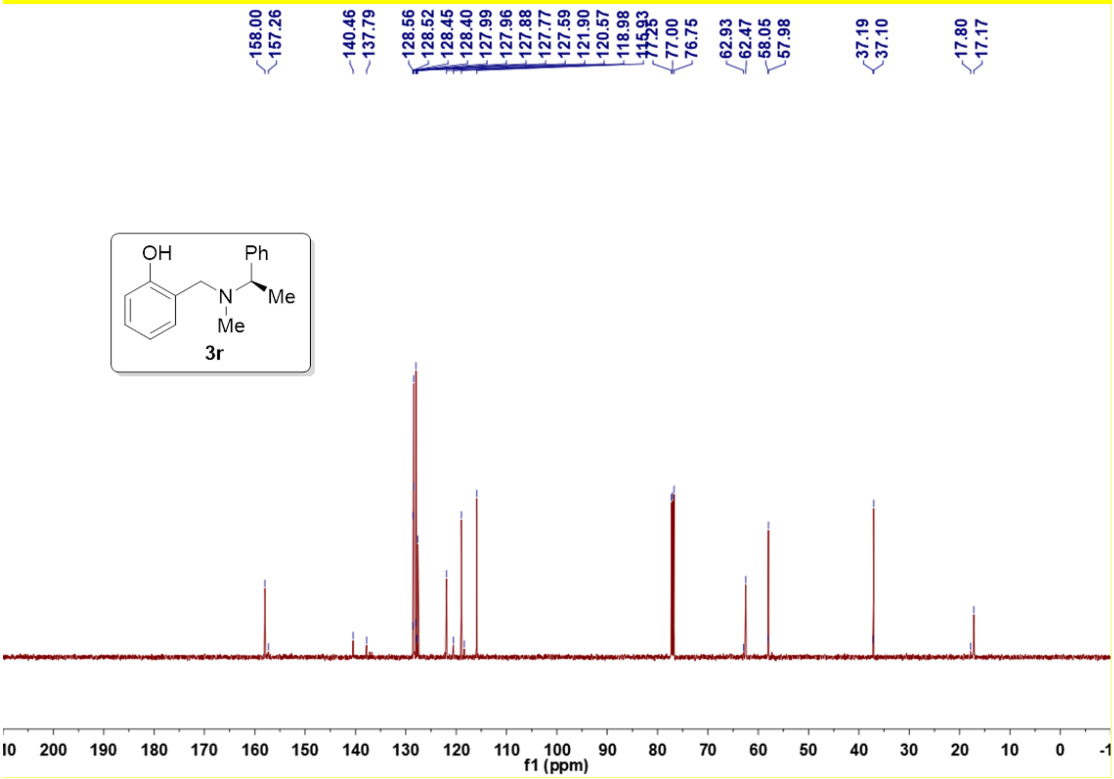
^{13}C NMR (100 MHz, $CDCl_3$) of **3q**



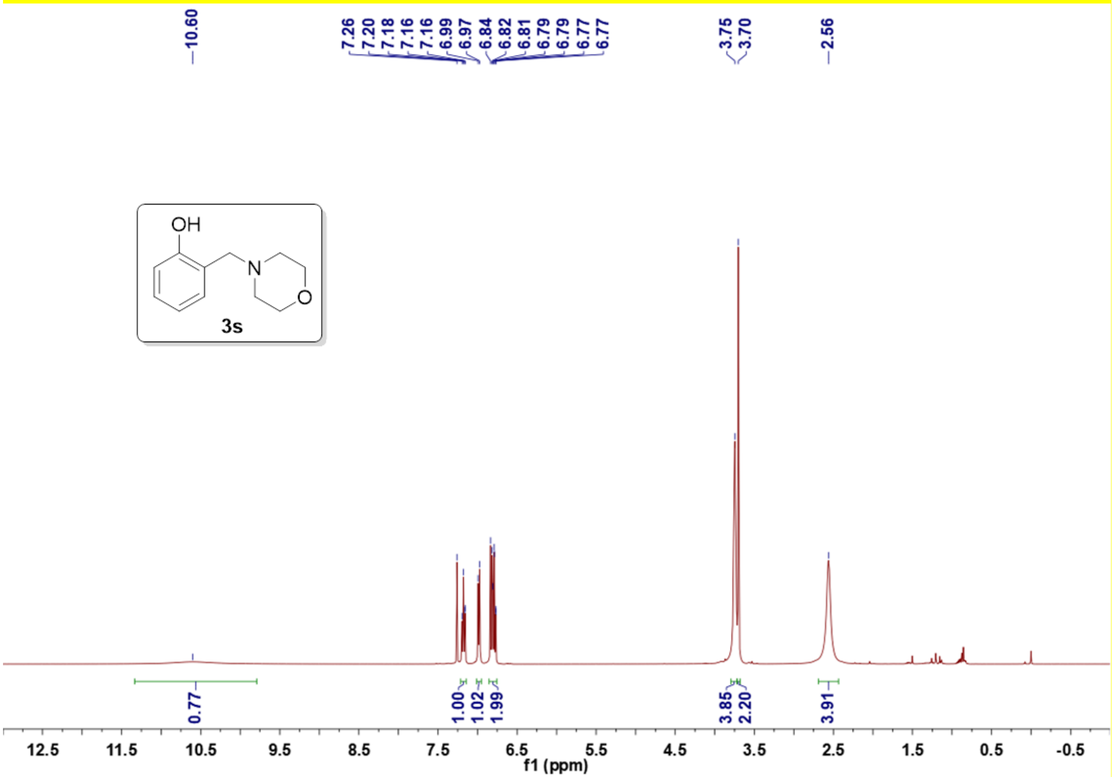
[1]H NMR (500 MHz, $CDCl_3$) of **3r**



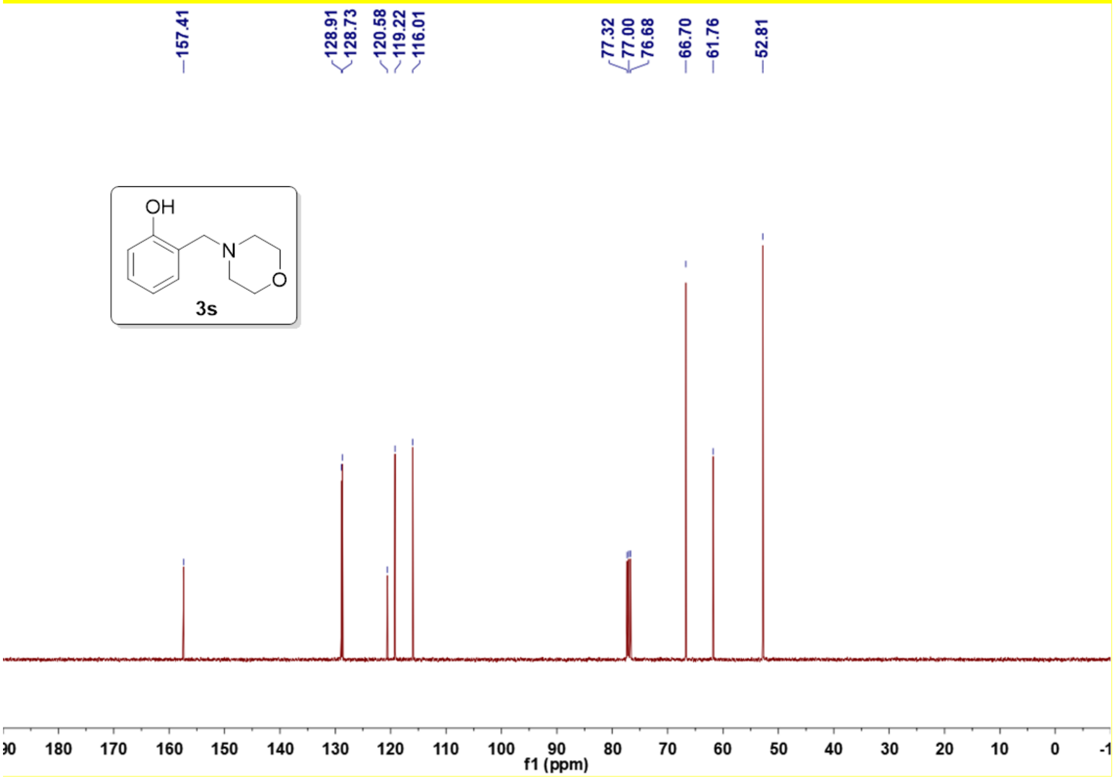
[13]C NMR (126 MHz, $CDCl_3$) of **3r**



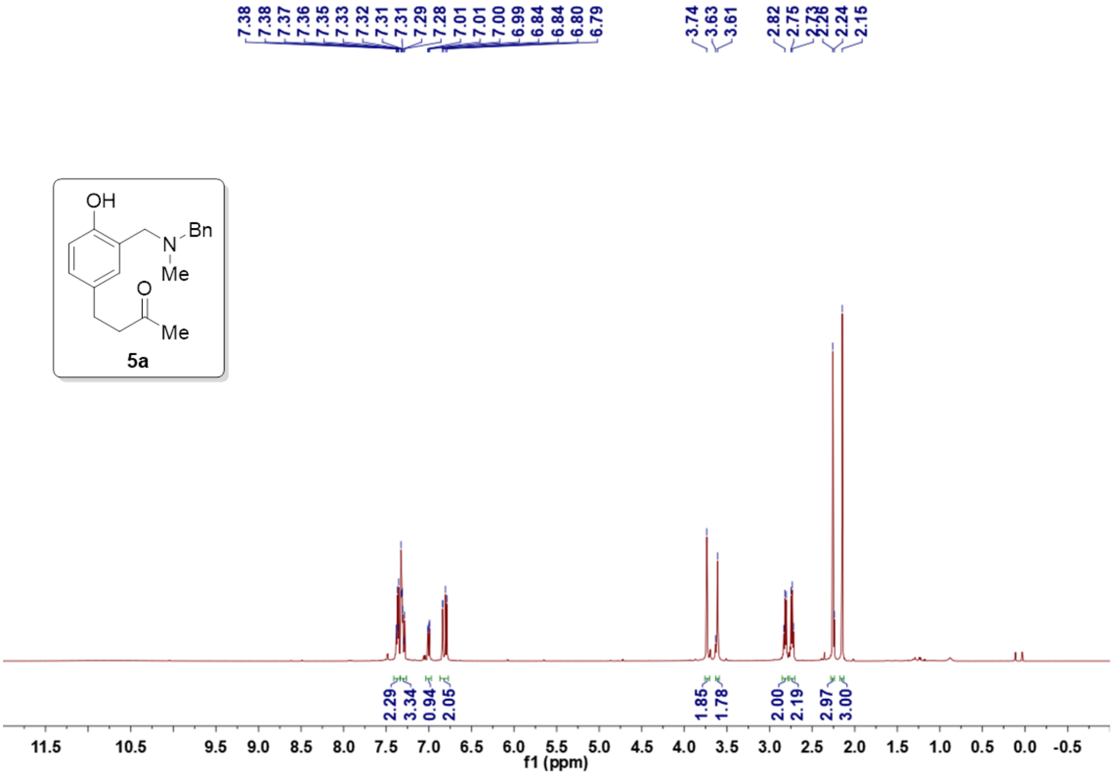
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**



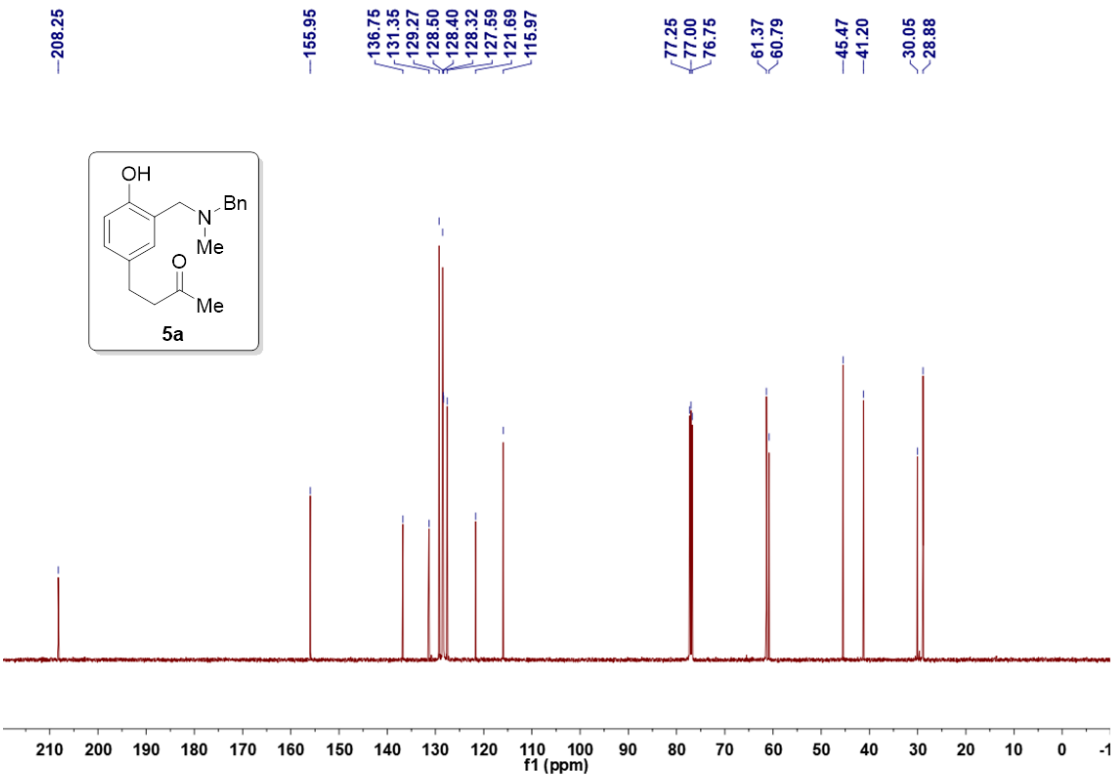
^{13}C NMR (101 MHz, $CDCl_3$) of **3s**



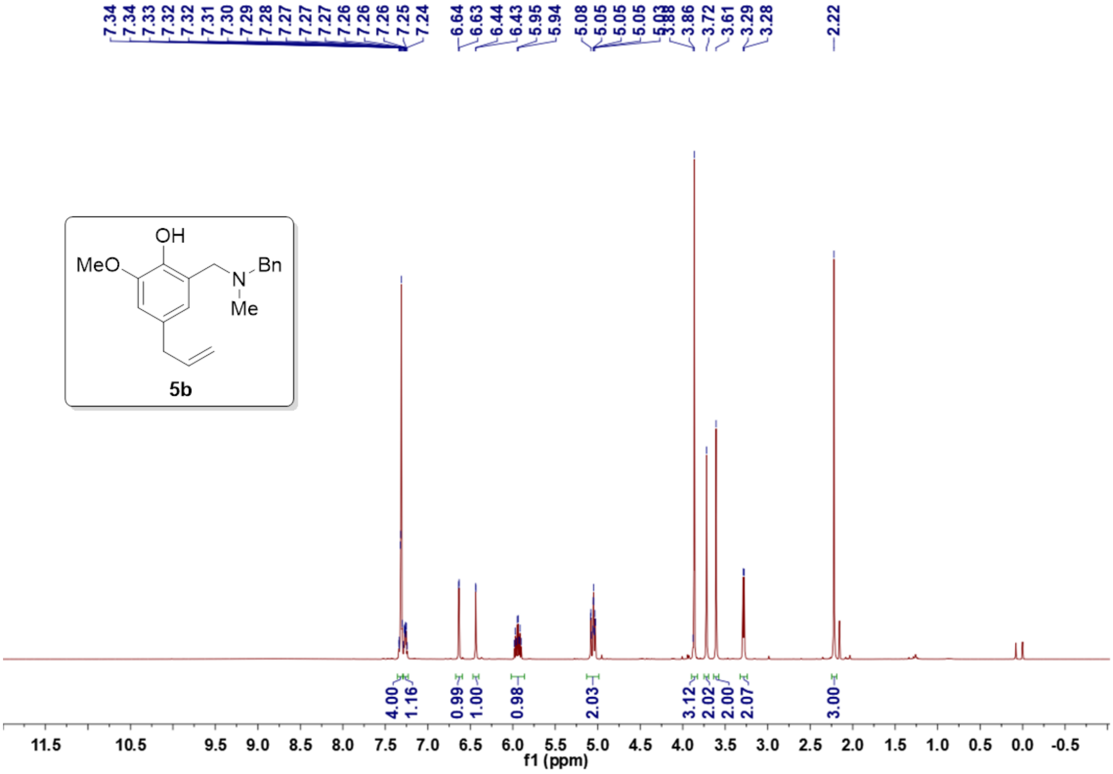
^{1}H NMR (500 MHz, $CDCl_3$) of **5a**



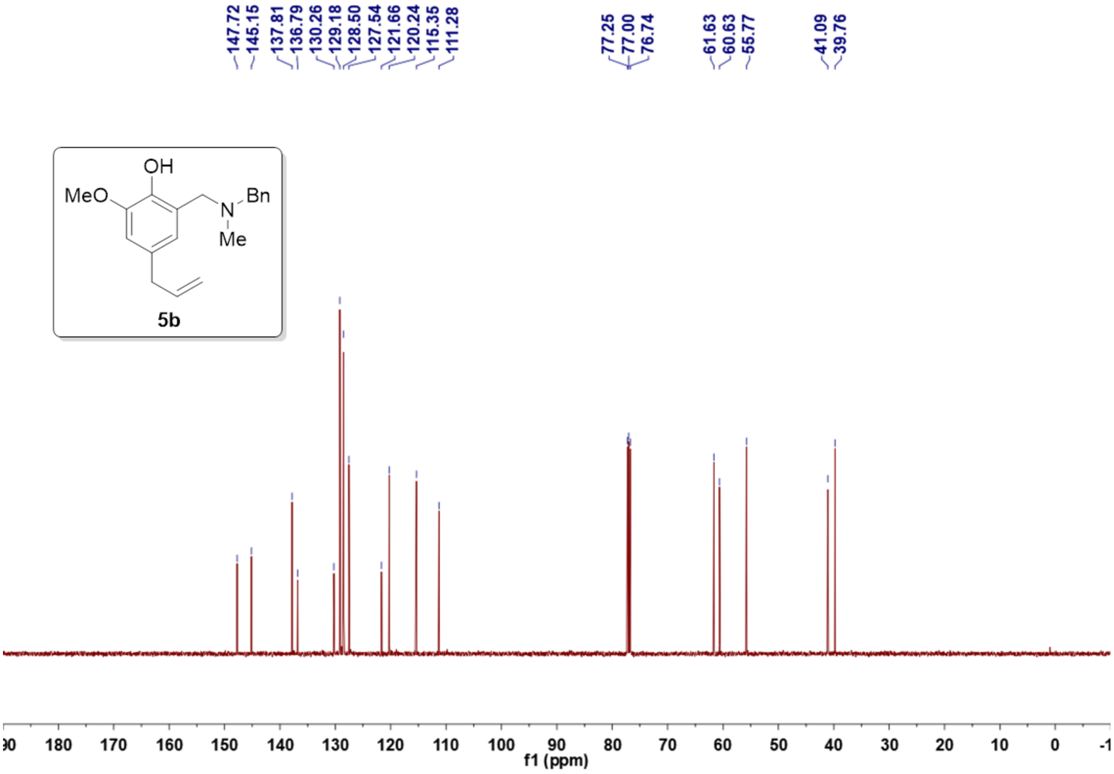
^{13}C NMR (126 MHz, $CDCl_3$) of **5a**



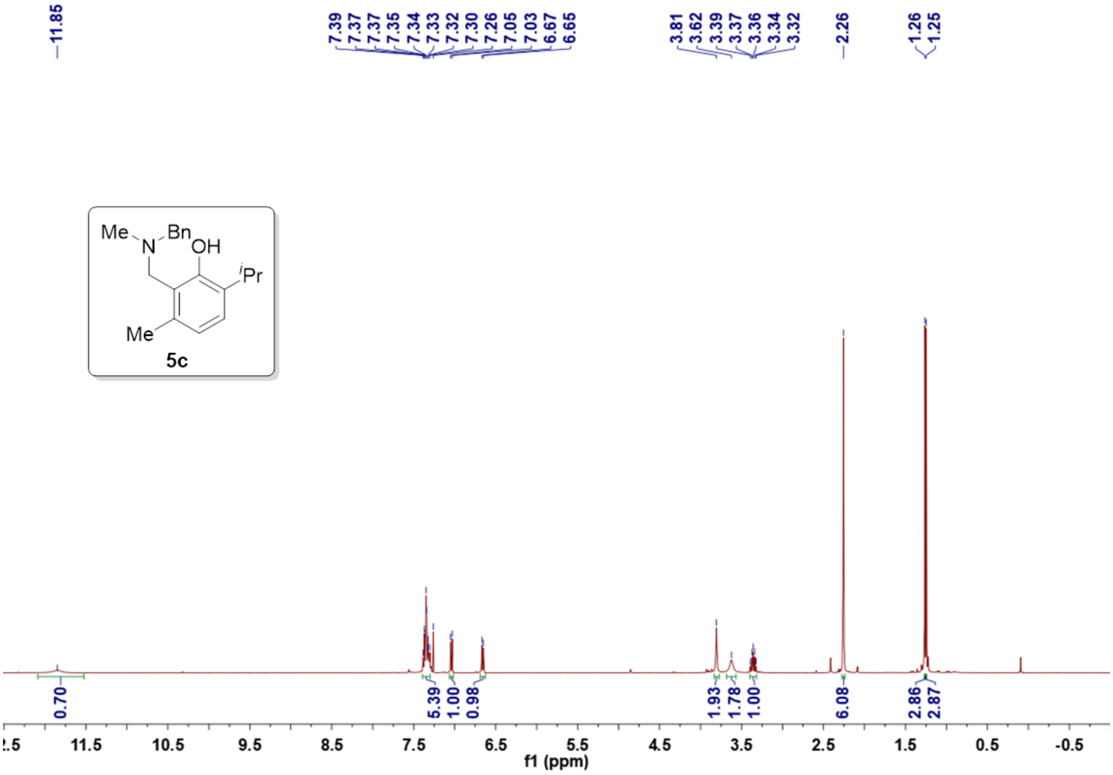
^{1}H NMR (500 MHz, $CDCl_3$) of **5b**



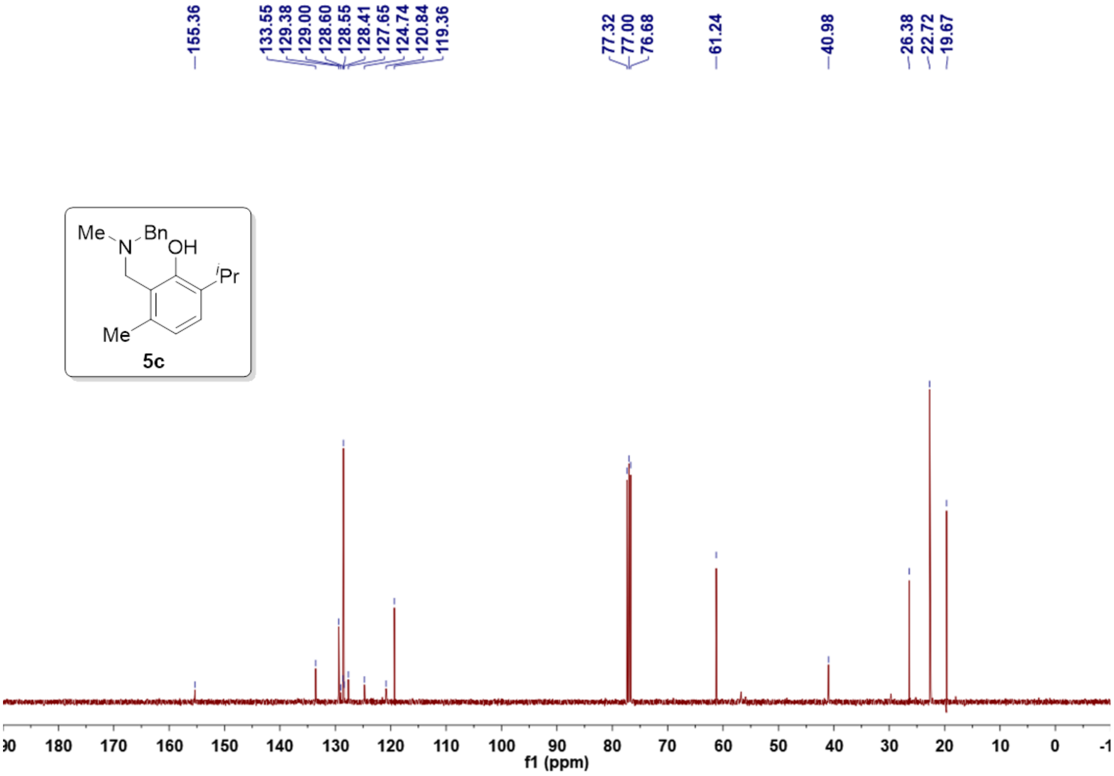
^{13}C NMR (126 MHz, $CDCl_3$) of **5b**



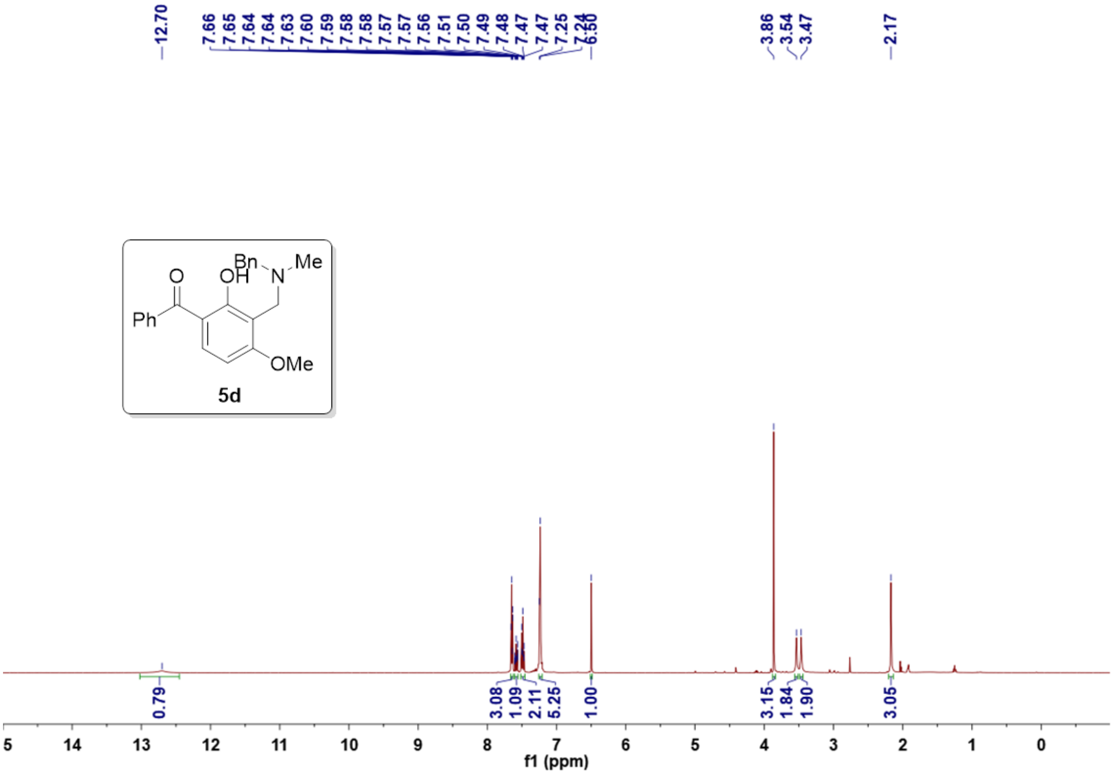
^{1}H NMR (400 MHz, $CDCl_3$) of **5c**



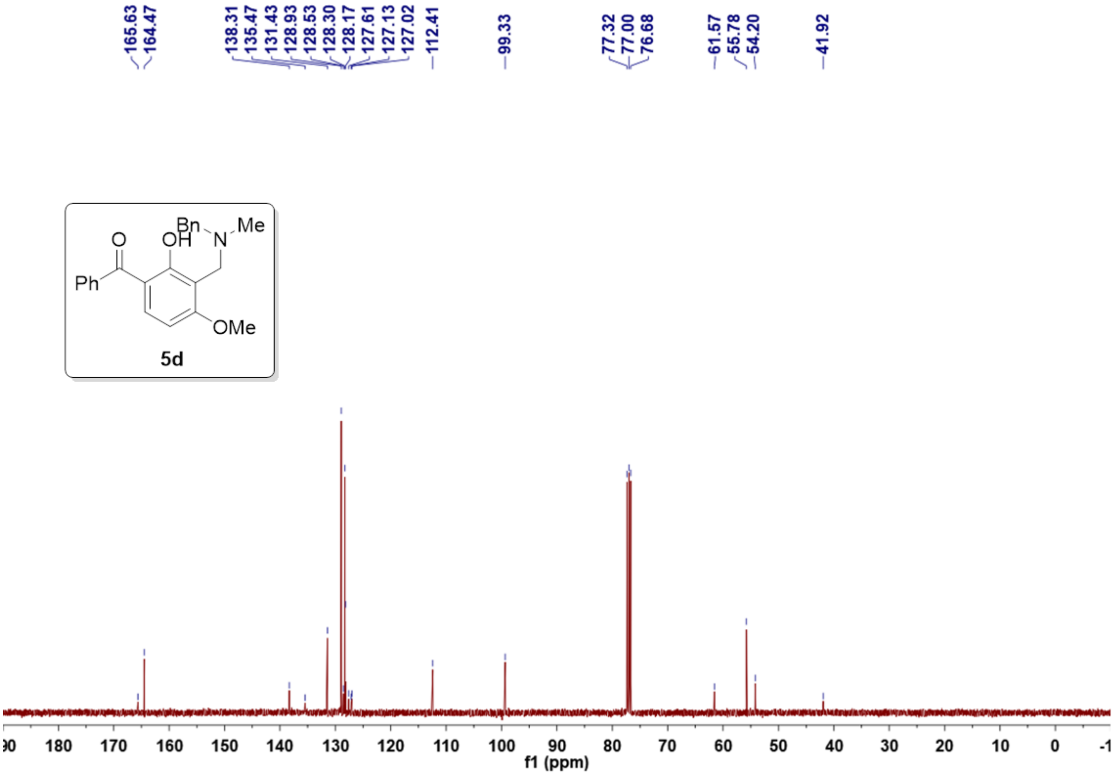
^{13}C NMR (100 MHz, $CDCl_3$) of **5c**



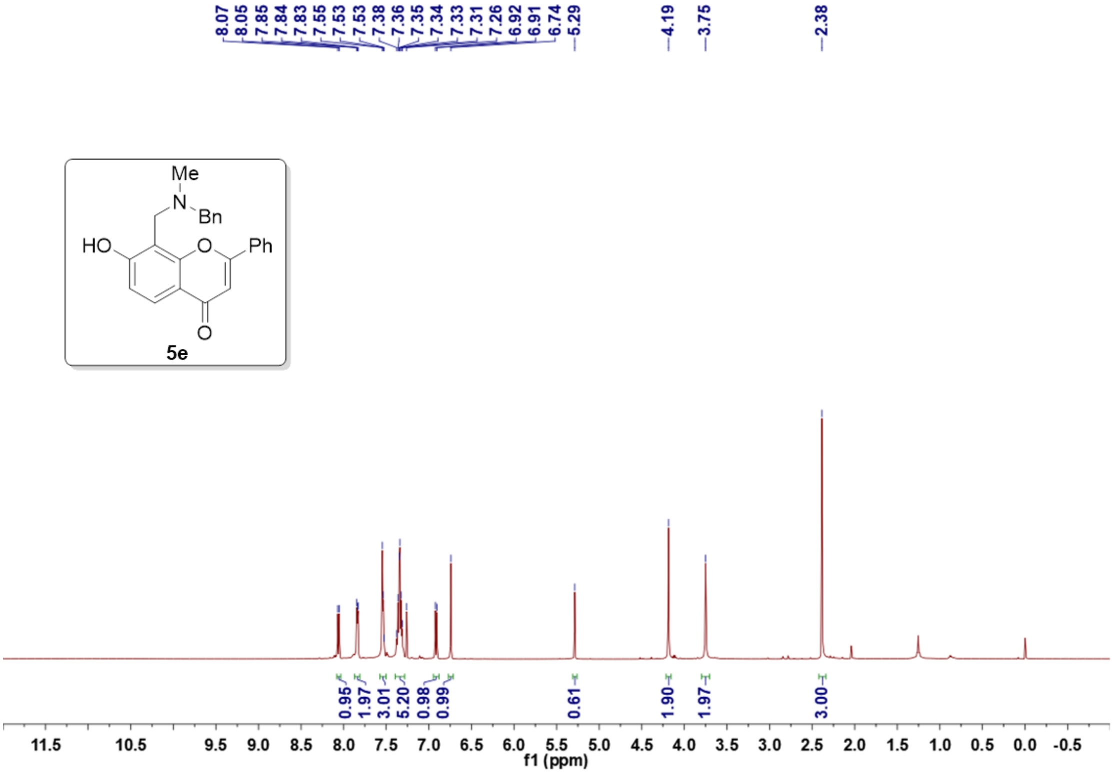
^{1}H NMR (400 MHz, $CDCl_3$) of **5d**



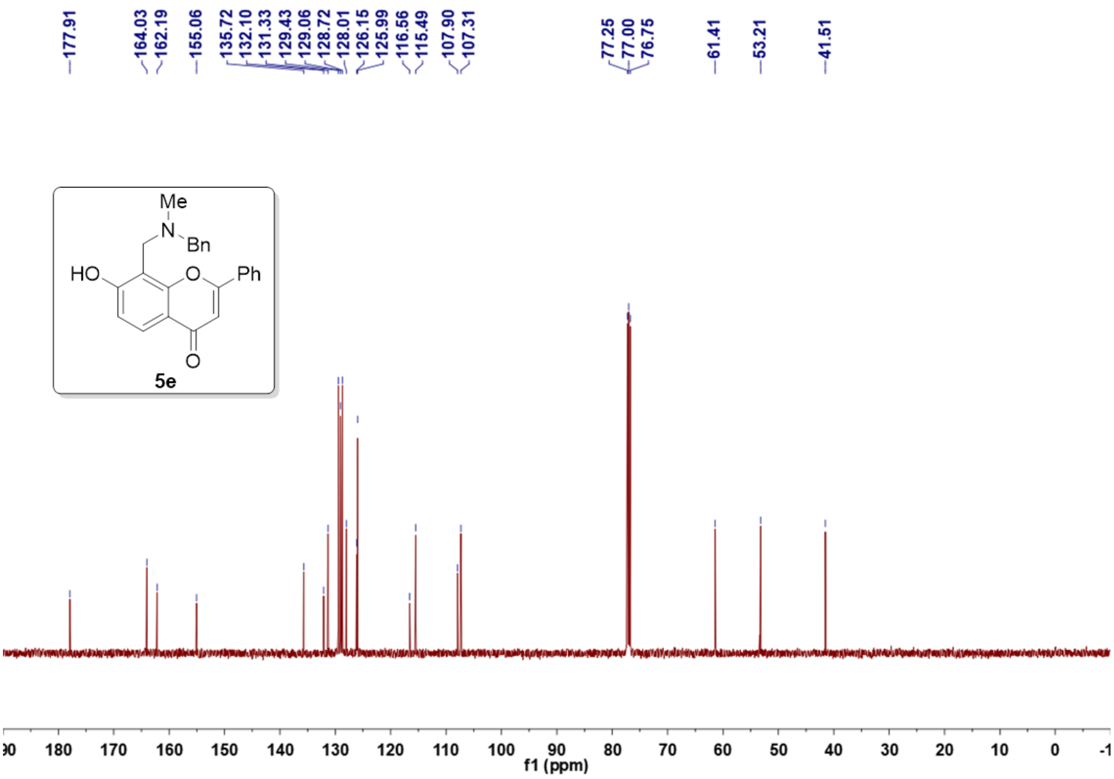
^{13}C NMR (100 MHz, $CDCl_3$) of **5d**



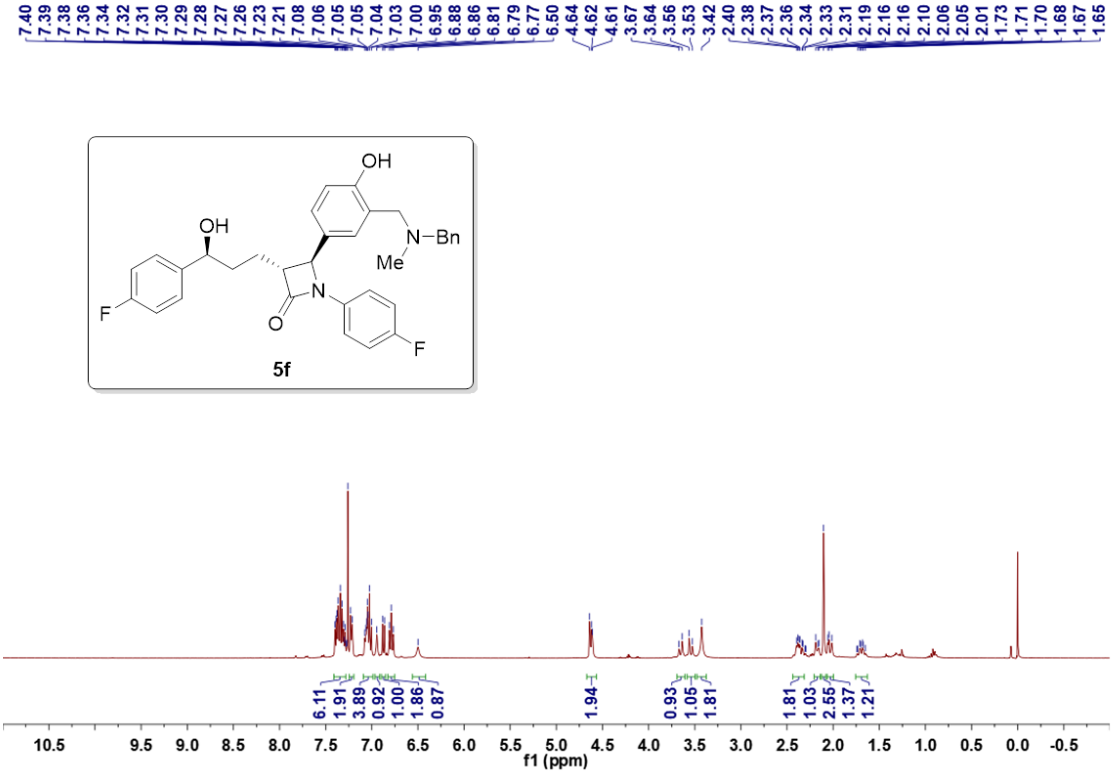
^{1}H NMR (500 MHz, $CDCl_3$) of **5e**



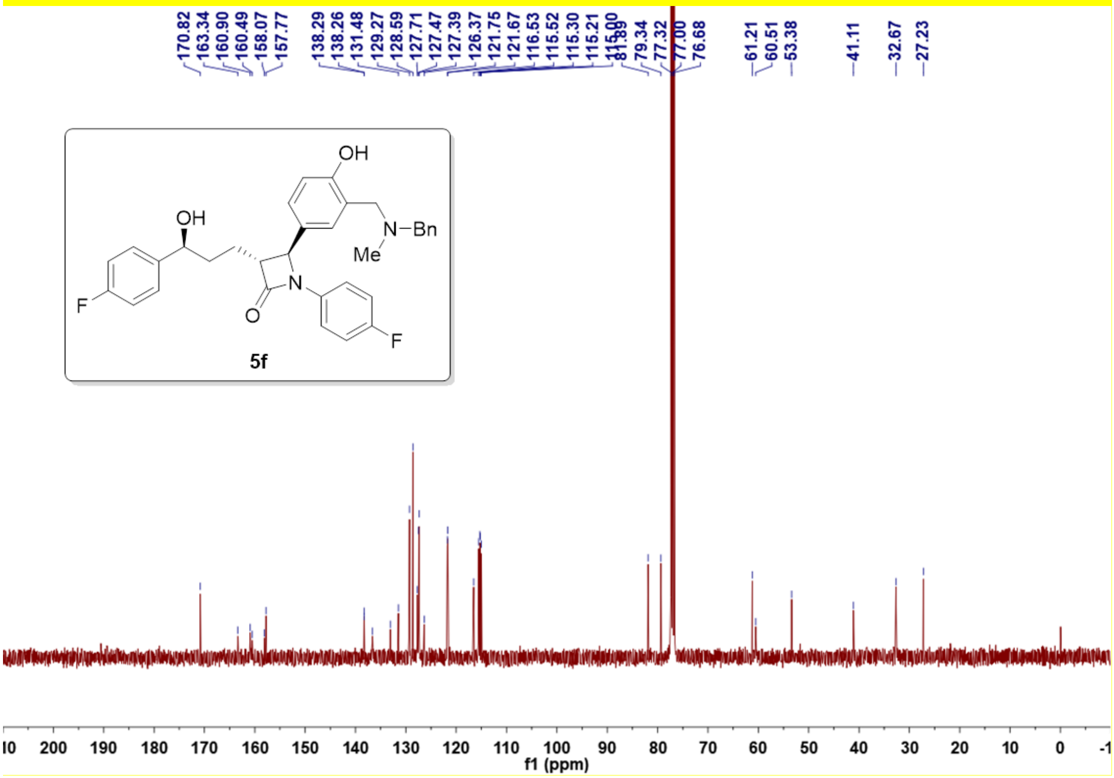
^{13}C NMR (126 MHz, $CDCl_3$) of **5e**



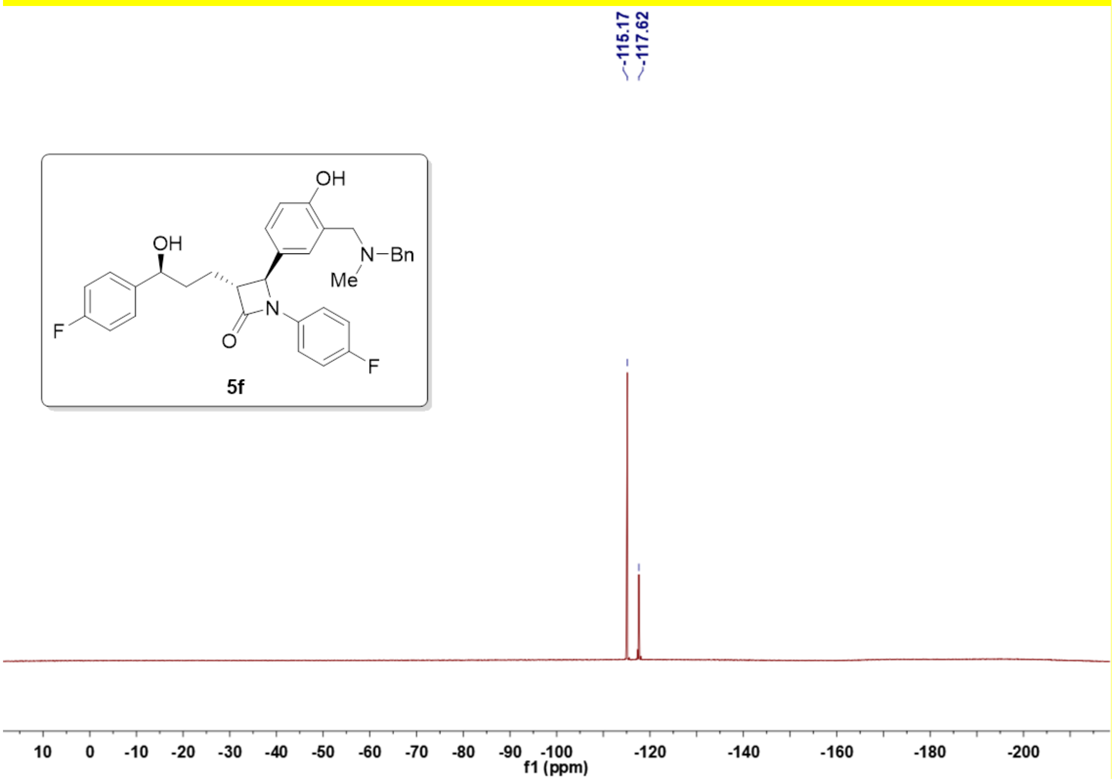
[1]H NMR (400 MHz, $CDCl_3$) of **5f**



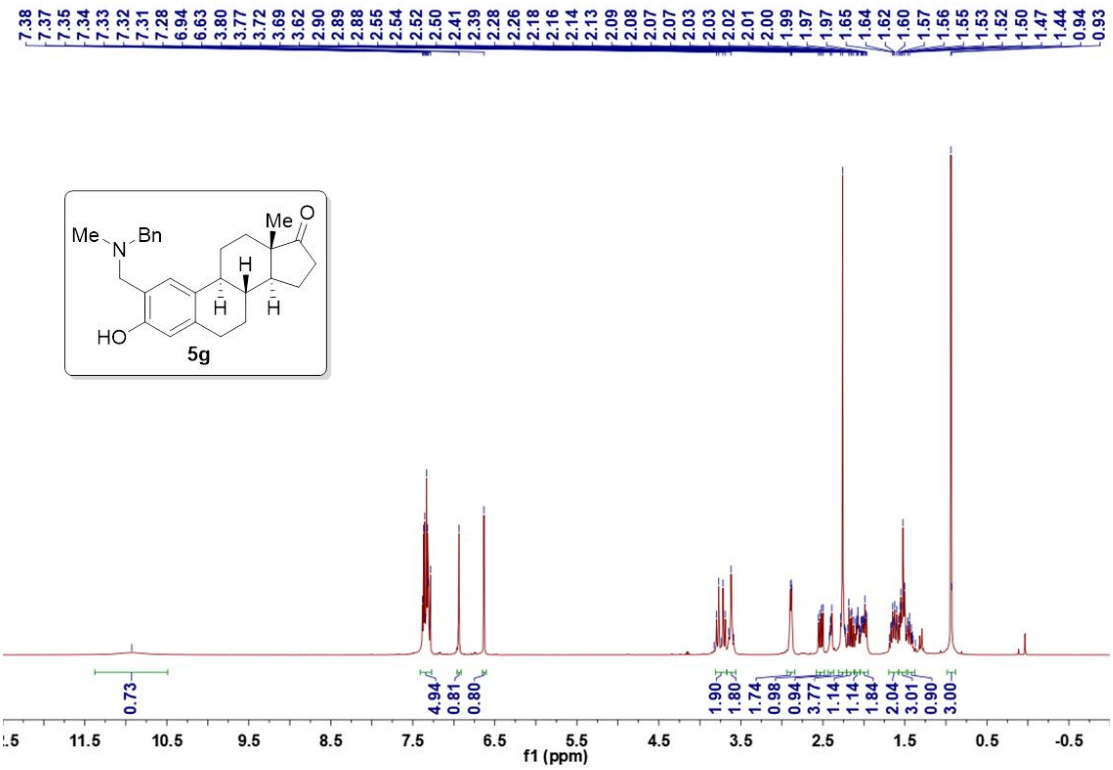
[13]C NMR (100 MHz, $CDCl_3$) of **5f**



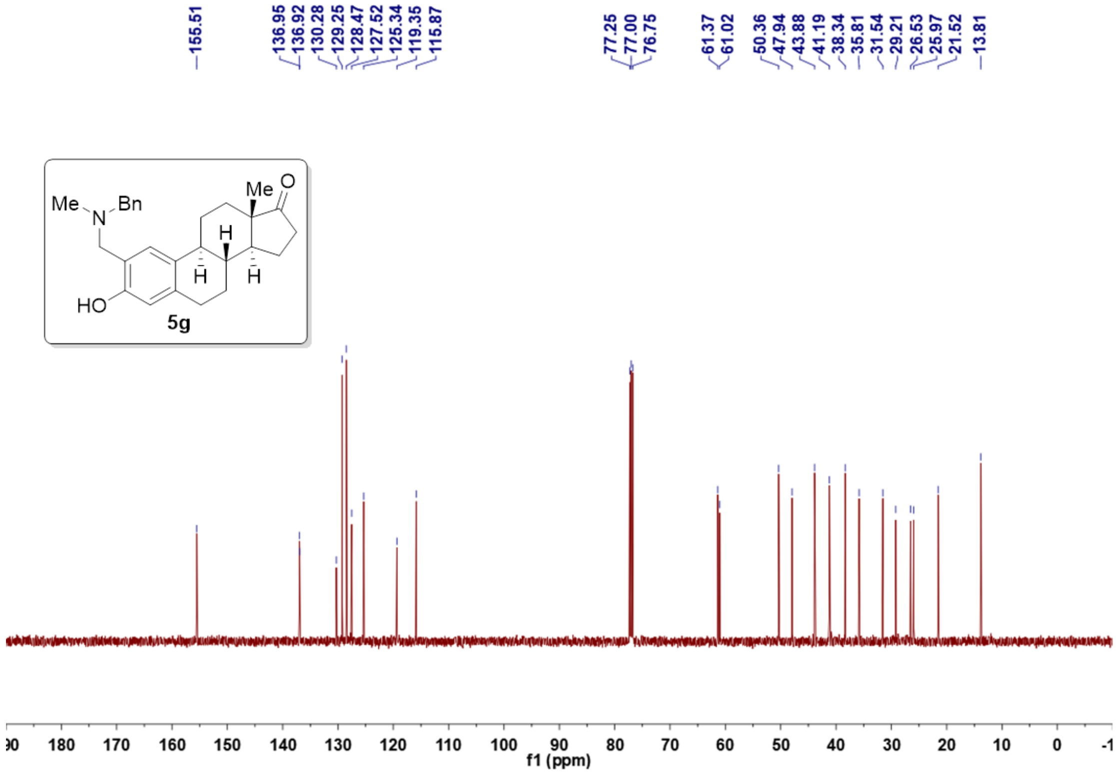
^{19}F NMR (376 MHz, $CDCl_3$) of **5f**



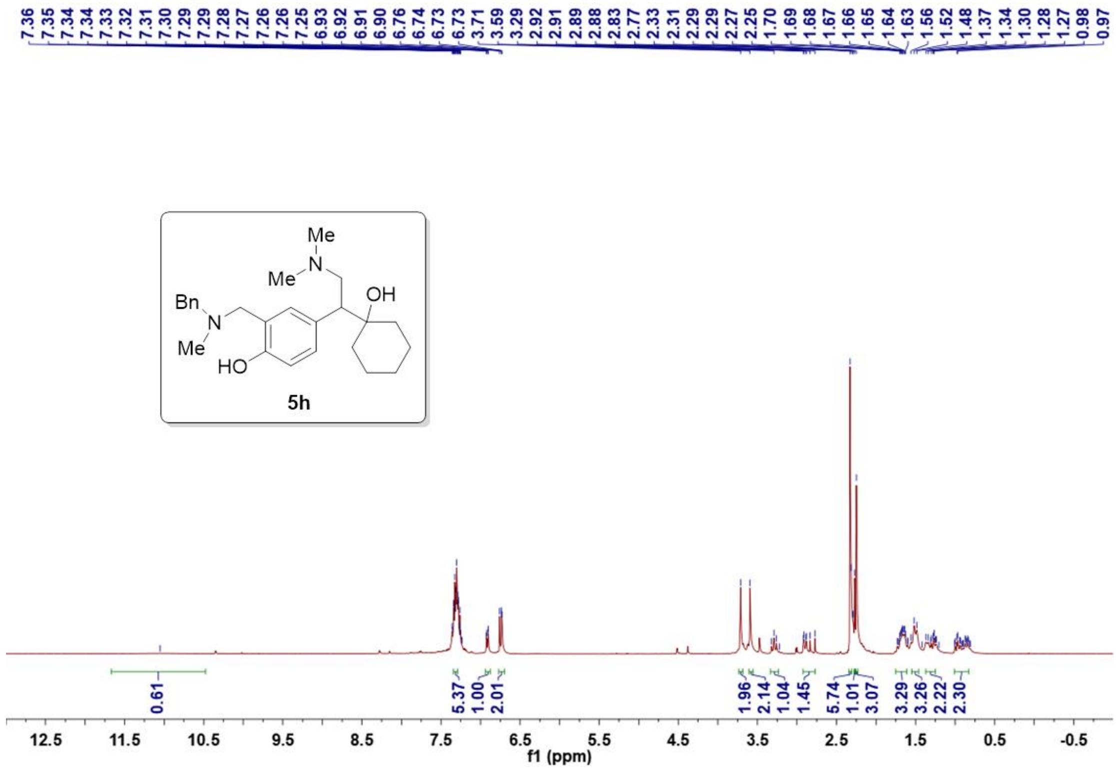
^{1}H NMR (500 MHz, $CDCl_3$) of **5g**



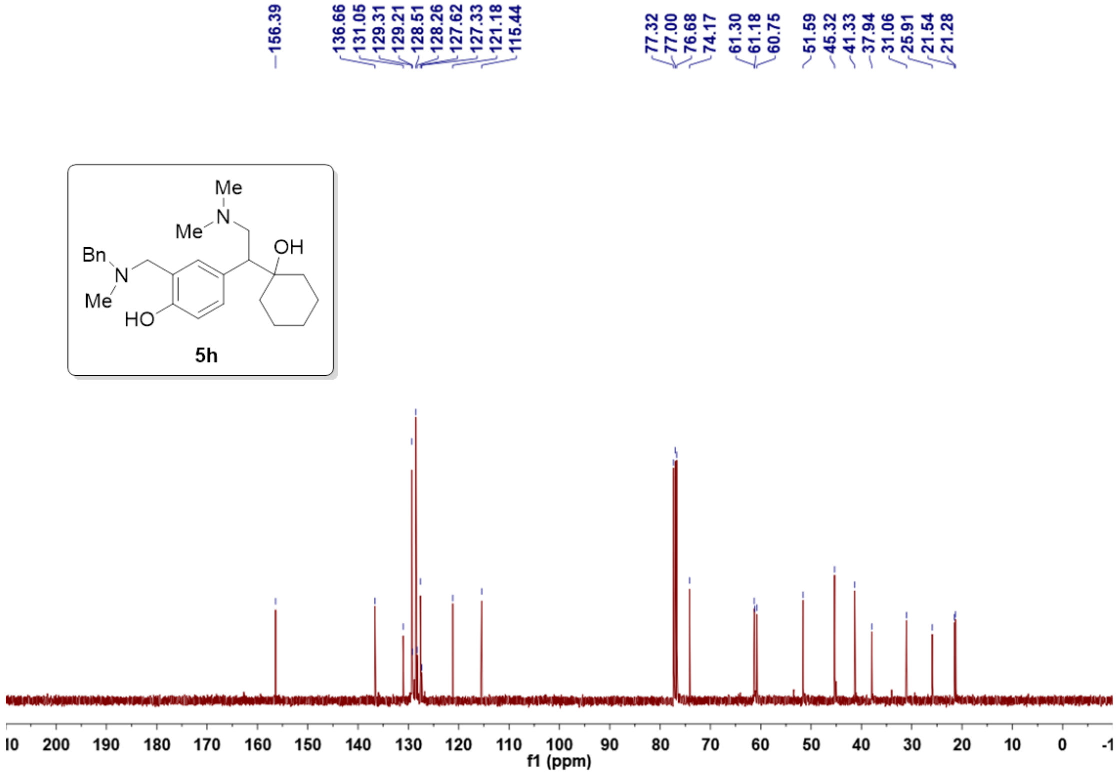
^{13}C NMR (126 MHz, $CDCl_3$) of **5g**



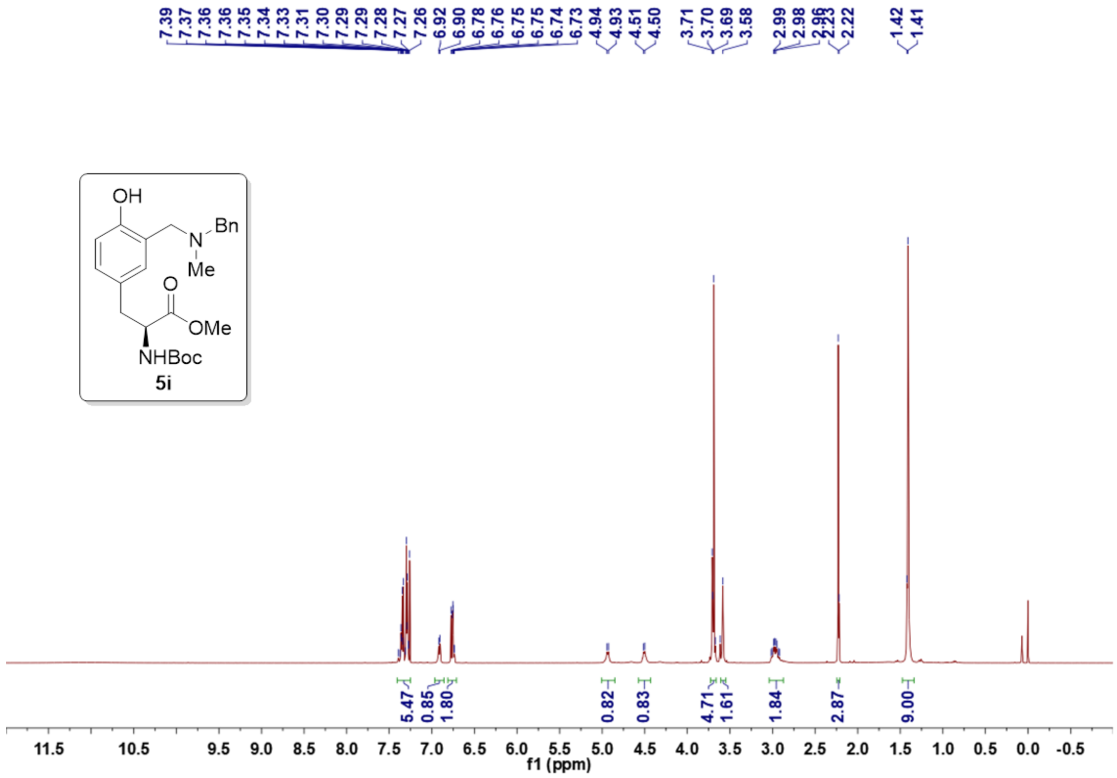
^{1}H NMR (400 MHz, $CDCl_3$) of **5h**



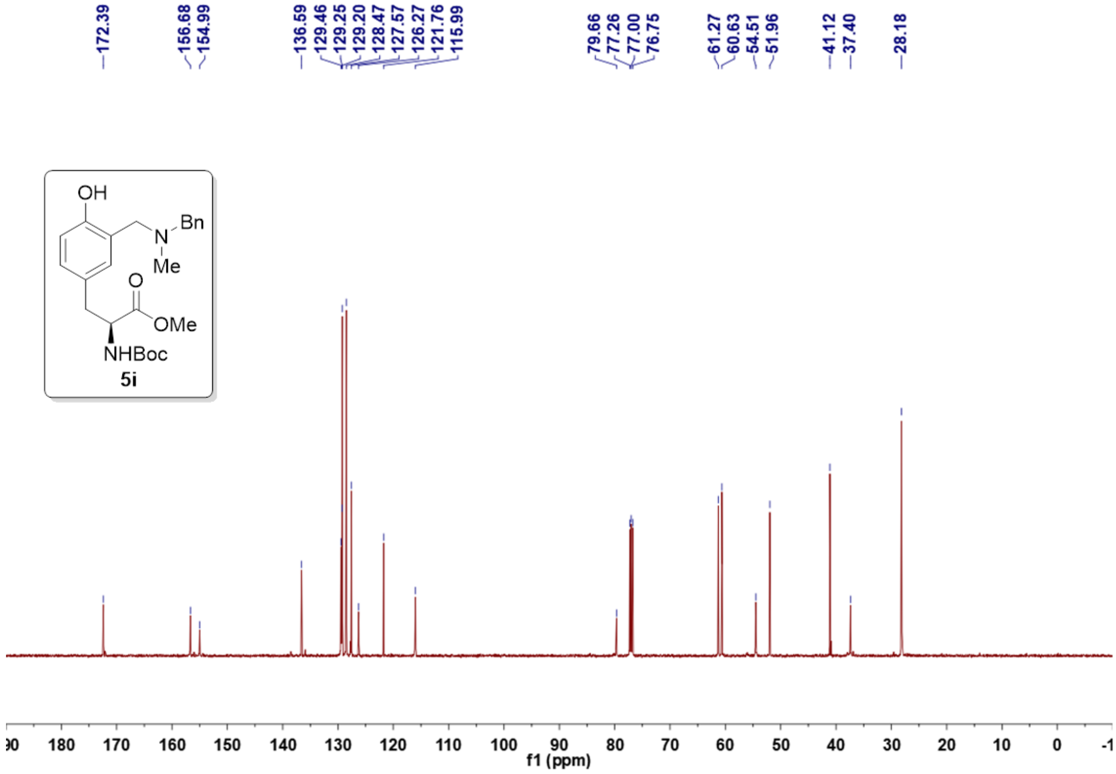
^{13}C NMR (100 MHz, $CDCl_3$) of **5h**



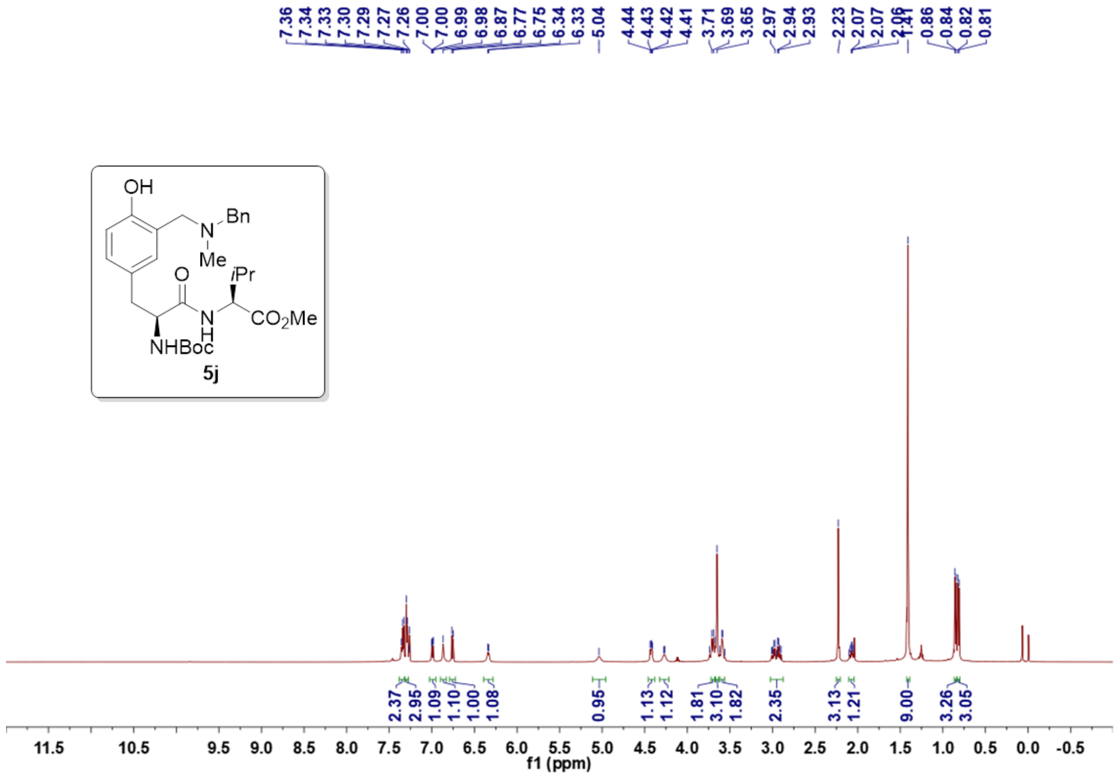
^{1}H NMR (500 MHz, $CDCl_3$) of **5i**



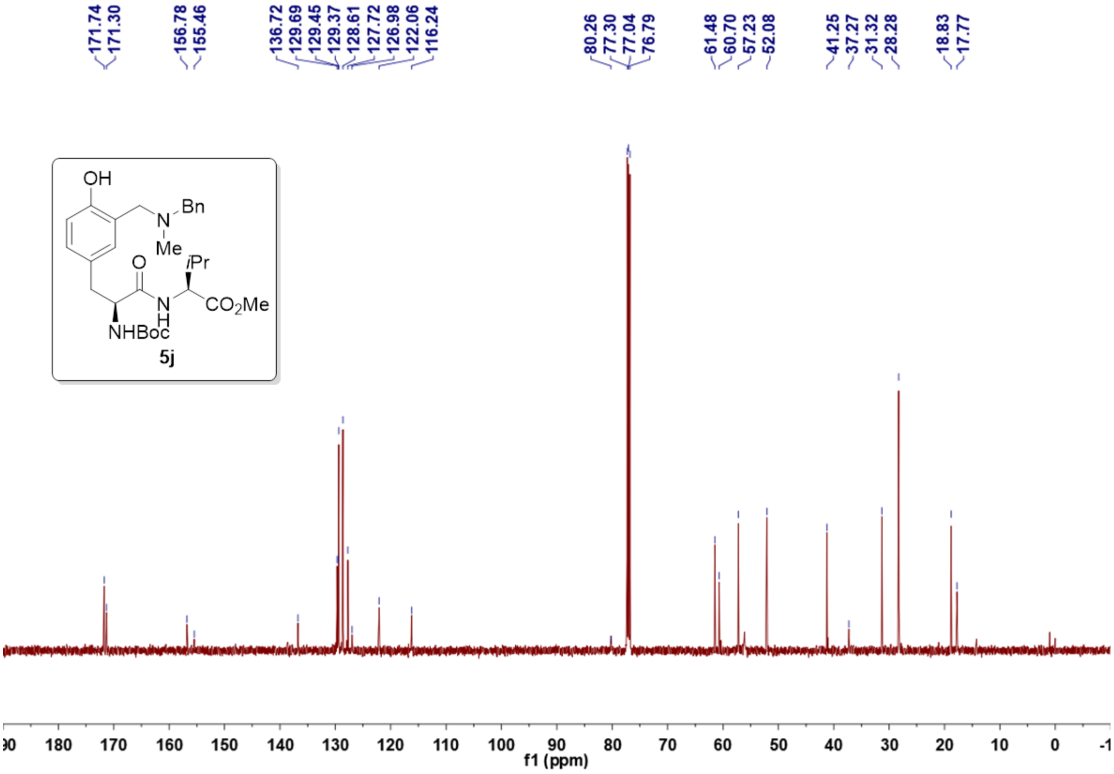
^{13}C NMR (126 MHz, $CDCl_3$) of **5i**



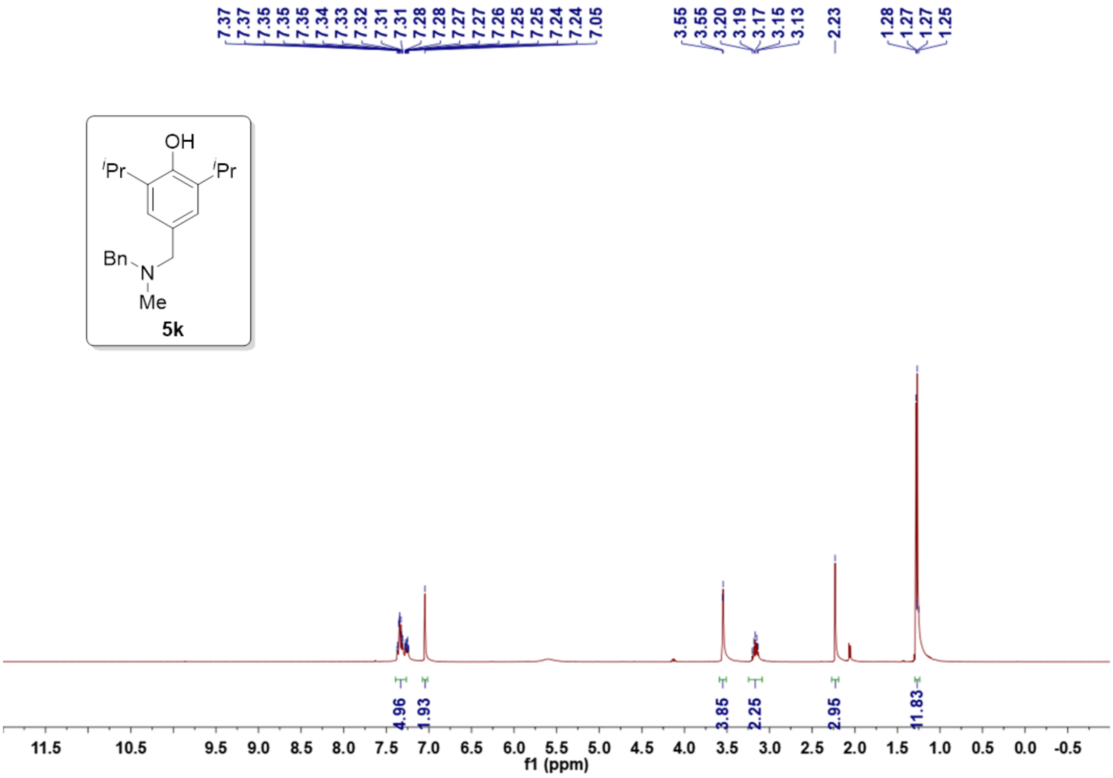
^{1}H NMR (500 MHz, $CDCl_3$) of **5j**



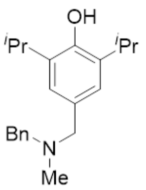
[13]C NMR (126 MHz, $CDCl_3$) of **5j**



[1]H NMR (400 MHz, $CDCl_3$) of **5k**



^{13}C NMR (100 MHz, $CDCl_3$) of **5k**



5k