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Supporting Information: Metal-catalysed Hydroboration of Amide-containing Styrenes

Junning Wang,[a] Benjamin M. Partridge[a,*]

[a] School of Mathematical and Physical Sciences - Chemistry, University of Sheffield, Dainton Building, Sheffield, S3 7HF, United Kingdom

Email: b.m.partridge@sheffield.ac.uk

1. General Information

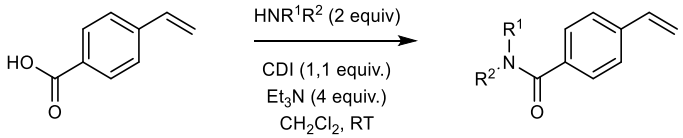
All reagents and solvents used were supplied by commercial sources without further purification. All air-sensitive reactions were carried out under a N_2 atmosphere using oven-dried apparatus. H_2O used for reactions and work-ups was deionised. Anhydrous THF was dried and purified by passage through activated alumina columns using a solvent purification system.

Thin layer chromatography (TLC) was performed on aluminium-backed plates pre-coated with silica. Compounds were visualised by exposure to UV light or by dipping the plates into solutions of vanillin, ninhydrin, phosphomolybdic acid or potassium permanganate followed by heating. All flash chromatography was carried out using silica gel mesh 40-63 unless otherwise stated.

Infra-red spectra were recorded on a Perkin Elmer 100 FT instrument on the neat compound. NMR spectra were recorded on Bruker Advance 400 and 500 instruments at the indicated 101, 128, 126, 377 and 400 MHz as dilute solutions in the indicated deuterated solvent at ambient temperature. All chemical shifts (δ) reported in parts per million (ppm) relative to residual protio solvent (δH: $CHCl_3$ = 7.26 ppm, d_6-DMSO = 2.50 ppm) or the solvent itself (δC: $CDCl_3$ = 77.0 ppm, d_6-DMSO = 39.52 ppm). All multiplets are designated by the following abbreviations: s = singlet, br s = broad singlet, d = doublet, dd = doublet of doublets, dt = doublet triplets, ddd = doublet of doublets of doublets, ddt = doublet of doublets of triplets, dddd = doublet of doublets of doublets of doublets, ddddd = doublet of doublets of doublets of doublets of doublets, t = triplet, tdd = triplet of doublets of doublets, q = quartet, m = multiplet. All coupling constants (*J*) are reported in Hertz (Hz). ^{13}C NMR spectra were acquired as DEPT-Q experiments as standard; regular ^{13}C NMR experiments were acquired when quaternary carbons were hard to distinguish by DEPT-Q. Some quaternary centres were not observed due to quadrupolar relaxation. Compounds which are rotameric and have more signals than expected are labelled “rotamers” after the list of signals. Typically, the signals of carbon atoms attached to boron are not observed due broadening of signals because of quadrupolar relaxation. ^{19}F NMR spectra were acquired as proton decoupled spectra. High-resolution mass spectra were recorded using either electrospray ionization (ESI) or electron ionisation (EI) by the Mass Spectrometry Service at the Department of Chemistry, University of Sheffield. The m/z values of major peaks are reported in Daltons, Da.

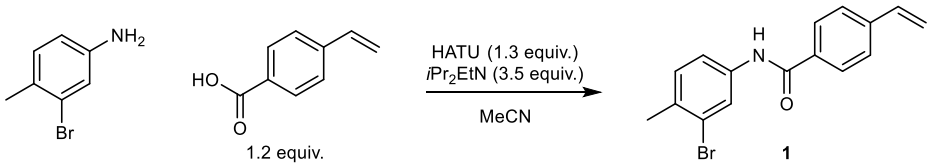
2. Synthesis of Alkenes

General Procedure 1: Amide formation



1,1'-Carbonyldiimidazole (3.61 g, 22.3 mmol, 1.1 equiv.) was added to a mixture of 4-vinylbenzoic acid (3.00 g, 20.3 mmol, 1.0 equiv.) in CH_2Cl_2 (79 mL), and the mixture was stirred for 1 h. Et_3N (11.2 ml, 81.0 mmol, 4.0 equiv.) and the corresponding amine (2.0 equiv.) were added, and the mixture was stirred overnight. The mixture was diluted with water (40 mL) and extracted with CH_2Cl_2 (20 mL). The combined organic phases were washed with brine (3 × 60 mL), dried over $MgSO_4$, filtered, and dried concentrated *in vacuo*.

N-(3-Bromo-4-methyl phenyl)-4-ethenyl benzamide (1)



A solution of 3-bromo-4-methyl aniline (0.83 mL, 6.7 mmol, 1 equiv.) and N,N-diisopropylethylamine (4.08 mL, 23.5 mmol, 3.5 equiv.) in acetonitrile (40 mL) was added to a solution of 4-vinyl benzoic acid (1.19 g, 8 mmol, 1.2 equiv.) and HATU (3.31 g, 8.71 mmol, 1.3 equiv.) in acetonitrile (40 mL). The mixture was stirred at room temperature for 18 h, and the mixture was concentrated *in vacuo*. Ethyl acetate (60 mL) and 5% aqueous sodium bicarbonate (60 mL) were added, and the aqueous phase was extracted with ethyl acetate (20 mL). The combined organic layers were with water (50 mL), saturated aqueous NH_4Cl (50 mL) and water (50 mL), dried over $MgSO_4$, filtered, and dried concentrated *in vacuo*. The crude material was purified by column chromatography (2:3 EtOAc/hexane), and crystallised from EtOAc to give *amide* **1** (1.32 g, 63%) as off-white solid.

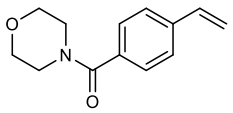
m.p. = 155 – 157 °C.

IR: 3294, 2974, 2918, 1641, 1579, 1519, 1375, 1309, 853 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.3 Hz, 1H, Ar**H**), 7.87 – 7.78 (m, 2H, Ar**H**), 7.74 (s, 1H, N**H**), 7.55 – 7.44 (m, 3H, Ar**H**), 7.23 – 7.17 (m, 1H, Ar**H**), 6.76 (dd, *J* = 17.6, 10.9 Hz, 1H, C**H**=CH_2), 5.87 (dd, *J* = 17.6, 0.7 Hz, 1H, CH=C**H**$_A$H$_B$), 5.39 (dd, *J* = 10.9, 0.7 Hz, 1H, CH=CH$_A$**H**$_B$), 2.38 (s, 3H, C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.1 (C), 141.2 (C), 136.7 (C), 135.8 (CH), 134.0 (C), 133.6 (C), 130.9 (CH), 127.3 (2 × CH), 126.5 (2 × CH), 124.8 (C), 123.9 (CH), 119.1 (CH), 116.4 (CH_2), 22.3 (CH_3).

HRMS (ESI): Exact mass calcd. for $[C_{16}H_{15}{}^{79}BrNO]^+$ $[M+H]^+$: 316.0332, found: 316.0329.



6a

(4-Ethenylphenyl)-4-morpholinylmethanone (6a)

The title compound was prepared according to **General Procedure 1** using morpholine (3.5 ml, 40.5 mmol). The crude material was purified by column chromatography (2:3 EtOAc/hexane) to give *amide* **6a** (0.814 g, 56%) as light-yellow solid.

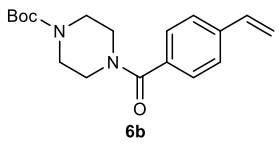
m.p. = 57 – 59 °C.

IR: 2962, 2905, 2856, 1619, 1605, 1429, 1276, 1258, 1110 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.42 (m, 2H, Ar**H**), 7.40 – 7.35 (m, 2H, Ar**H**), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H, C**H**=CH_2), 5.80 (d, *J* = 17.6 Hz, 1H, CHC**H$_A$**H$_B$), 5.33 (d, *J* = 10.9 Hz, 1H, CHCH$_A$**H$_B$**), 3.91 – 3.37 (m, 8H, 4 × C**H**$_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.2 (C), 139.2 (C), 136.0 (CH), 134.4 (C), 127.5 (2 × CH), 126.3 (2 × CH), 115.5 (CH_2), 66.9 (2 × CH_2). Note: NCH_2 signals from the morpholine group were not observed (including ^{13}C NMR and HSQC experiments, different temperatures and relaxation times, or use of d_6-DMSO as solvent instead of $CDCl_3$),

HRMS (ESI): Exact mass calcd. for $[C_{13}H_{16}NO_2]^+$ $[M+H]^+$: 218.1175, found: 218.1181.



6b

tert-Butyl 4-(4-ethenylbenzoyl)piperazine-1-carboxylate (6b)

The title compound was prepared according to **General Procedure 1** using 1-Boc-piperazine (7.54 g, 40.5 mmol). The crude material was purified by column chromatography (2:3 EtOAc/hexane) to give *amide* **6b** (0.2671 g, 13%) as white solid.

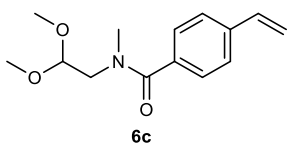
m.p. = 115 – 117 °C.

IR: 3005, 2997, 2927, 1683, 1616, 1428, 1242, 1176, 1008 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.41 (m, 2H, Ar**H**), 7.39 – 7.35 (m, 2H, Ar**H**), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H, C**H**=CH_2), 5.81 (d, *J* = 17.6 Hz, 1H, CHC**H$_A$**H$_B$), 5.33 (d, *J* = 10.9 Hz, 1H, CHCH$_A$**H$_B$**), 3.83 – 3.25 (m, 8H, 4 × C**H**$_2$), 1.47 (s, 9H, 3 × C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4 (C), 154.6 (C), 139.2 (C), 136.0 (CH), 134.6 (C), 127.5 (2 × CH), 126.3 (2 × CH), 115.5 (CH_2), 80.4 (C), 28.4 (3 × CH_3). Note: NCH_2 signals from the piperazine group are not observed (including ^{13}C NMR and HSQC experiments, different temperatures and relaxation times, or use of d_6-DMSO as solvent instead of $CDCl_3$),

HRMS (ESI): Exact mass calcd. for $[C_{18}H_{25}N_2O_3]^+$ $[M+H]^+$: 317.1865, found: 317.1876.



6c

***N*-(2,2-Dimethoxyethyl)-4-ethenyl-*N*-methylbenzamide (6c)**

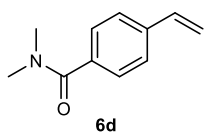
The title compound was prepared according to **General Procedure 1** using 4-vinylbenzoic acid (0.3 g, 2.0 mmol), CH_2Cl_2 (7.89 ml), Et_3N (1.1 ml, 8.1 mmol), CDI (0.36 g, 2.2 mmol), 2,2-dimethoxy-*N*-methylethylamine (0.52 ml, 4.0 mmol) to give *amide* **6c** (0.3626 g, 72%) as colourless oil. No further purification was required.

IR: 2933, 2832, 1626, 1558, 1397, 1125, 1075, 851 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.35 (m, 4H, Ar**H**), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H, C**H**=CH_2), 5.79 (d, *J* = 17.6 Hz, 1H, C**H$_A$**H$_B$), 5.31 (d, *J* = 10.9 Hz, 1H, CH$_A$**H$_B$**), 4.70 (br s, 0.7 H, C**H** rotamer), 4.39 (br s, 0.3 H, C**H** rotamer), 3.70 – 2.93 (m, 11H, 2 × OC**H$_3$** + NC**H$_3$** + C**H$_2$**).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.4 (C), 138.7 (C), 136.1 (CH), 135.5 (C), 127.3 (2 × CH), 126.1 (2 × CH), 115.2 (CH_2), 102.9 (CH), 54.6 (2 × CH_3), 53.0 (CH_2, rotamer) 49.8 (CH_2, rotamer), 39.5 (CH_3, rotamer), 34.3 (CH_3, rotamer).

HRMS (ESI): Exact mass calcd. for $[C_{14}H_{20}NO_3]^+$ $[M+H]^+$: 250.1437, found: 250.1440.



6d

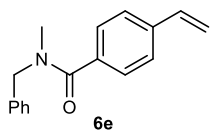
***N*,*N*-Dimethyl-4-vinylbenzamide (6d)**

The title compound was prepared according to **General Procedure 1** using dimethylamine hydrochloride (3.30 g, 40.5 mmol). The crude material was purified by column chromatography (2:3 EtOAc/hexane) to give amide **6d** (0.764 g, 65%) as colourless oil. The data were consistent with the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 4H, Ar**H**), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H, C**H**=CH_2), 5.82 (d, *J* = 17.6 Hz, 1H, C**H$_A$**H$_B$), 5.34 (dd, *J* = 10.9 Hz, 1H, CH$_A$**H$_B$**), 3.13 (s, 3H, C**H$_3$**), 3.02 (s, 3H, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.4 (C), 138.8 (C), 136.1 (C), 135.5 (CH), 127.5 (2 × CH), 126.1 (2 × CH), 115.1 (CH_2), 39.6 (CH_3), 35.4 (CH_3).

HRMS (ESI): Exact mass calcd. for $[C_{11}H_{14}NO]^+$ $[M+H]^+$: 176.1069, found: 176.1074.



6e

***N*-Benzyl-4-ethenyl-*N*-methylbenzamide (6e)**

The title compound was prepared according to **General Procedure 1** using N-benzylmethylamine (4.91 g, 40.5 mmol). The crude material was purified by column chromatography (1:3 EtOAc/hexane) to give amide **6e** (1.07 g, 63%) as white solid. The data were consistent with the literature.[2]

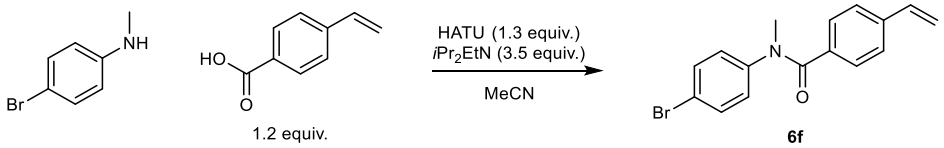
m.p. = 59 – 61 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.31 (m, 8H, Ar**H**), 7.26 – 7.15 (m, 1H, Ar**H**), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H, C**H**=CH_2), 5.81 (d, *J* = 17.6 Hz, 1H, CH=C**H$_A$**H$_B$), 5.33 (d, *J* = 10.9 Hz, 1H, CH=CH$_A$**H$_B$**), 4.78 (s, 1H, NC**H$_A$**H$_B$), 4.56 (s, 1H, NCH$_A$**H$_B$**), 2.98 (m, 3H, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.0 (C), 141.4 (C), 139.0 (C), 136.1 (CH), 131.6 (C), 128.8 (2 × CH), 128.7 (2 × CH), 127.6 (2 × CH), 127.4 (CH), 126.2 (2 × CH), 115.2 (CH_2), 52.8 (CH_2), 31.2 (CH_3).

HRMS (ESI): Exact mass calcd. for $[C_{17}H_{18}NO]^+$ $[M+H]^+$: 252.1382, found: 252.1379.

_N_-(4-Bromophenyl)-4-ethenyl-N-methylbenzamide (6f)



A solution of 4-bromo-*N*-methylaniline (0.85 ml, 6.7 mmol) and *N*,*N*-diisopropylethyl amine (4.1 ml, 24 mmol) in acetonitrile (25 mL) was added to a solution of 4-vinylbenzoic acid (1.20 g, 8 mmol) and HATU (3.35 g, 8.80 mmol) in acetonitrile (25 mL). The mixture was stirred at room temperature for 18 h, and the mixture was concentrated *in vacuo*. Ethyl acetate (20 mL) and 5% aqueous sodium bicarbonate (20 mL) were added, and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were with water (2 × 30 mL) and saturated aqueous NH_4Cl (30 mL), dried over $MgSO_4$, filtered, and dried concentrated *in vacuo*. The crude material was purified by column chromatography (2:3 EtOAc/hexane) to give *amide* **6f** (0.955 g, 45%) as yellow solid.

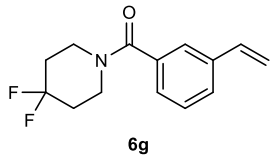
m.p. = 63 – 66 °C.

IR: 2928, 1639, 1608, 1485, 1360, 1010, 847, 571 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.31 (m, 2H, Ar**H**), 7.27 – 7.19 (m, 4H, Ar**H**), 6.94 – 6.88 (m, 2H, Ar**H**), 6.62 (dd, *J* = 17.6, 10.9 Hz, 1H, C**H**=CH_2), 5.73 (dd, *J* = 17.6, 0.8 Hz, 1H, C**H$_A$**H$_B$), 5.27 (dd, *J* = 10.9, 0.8 Hz, 1H, CH$_A$**H$_B$**), 3.46 (s, 3H, C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.2 (C), 144.0 (C), 139.0 (C), 136.0 (CH), 134.6 (C), 132.3 (2 × CH), 129.1 (2 × CH), 128.3 (2 × CH), 125.7 (2 × CH), 119.9 (C), 115.5 (CH_2), 38.4 (CH_3).

HRMS (ESI): Exact mass calcd. for $[C_{16}H_{15}{}^{79}BrNO]^+$ $[M+H]^+$: 316.0332, found: 316.0330.



6g

(4,4-Difluoropiperidin-1-yl)-(3-ethenylphenyl)methanone (6g)

The title compound was prepared according to **General Procedure 1** using 4,4-difluoropiperidine hydrochloride (6.38 g, 40.5 mmol). The crude material was purified by column chromatography (2:3 EtOAc/hexane) to give *amide* **6g** (0.703 g, 82%) as colourless oil which upon standing turns into a white gel.

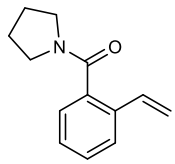
IR: 2922, 1633, 1581, 1422, 1357, 1088, 949 cm^{-1}

^{1}H NMR (400 MHz, DMSO-d6): δ 7.59 – 7.52 (m, 2H, Ar**H**), 7.43 (t, *J* = 7.6 Hz, 1H, Ar**H**), 7.36 – 7.31 (m, 1H, Ar**H**), 6.77 (dd, *J* = 17.7, 10.9 Hz, 1H, C**H**=CH_2), 5.92 (dd, *J* = 17.7, 0.9 Hz, 1H, CH=C**H**$_A$H$_B$), 5.33 (dd, *J* = 10.9, 0.9 Hz, 1H, CH=CH$_A$**H**$_B$), 3.85 – 3.34 (m, 4H, 2 × NC**H**$_2$), 2.04 (br s, 4H, 2 × NCH_2C**H**$_2$).

^{13}C NMR (101 MHz, DMSO-d6): δ 169.0 (C), 137.4 (C), 136.1 (C), 136.0 (CH), 128.8 (CH), 127.2 (CH), 126.1 (CH), 124.4 (CH), 122. 8 (d, *J* = 241.3 Hz, C), 115.4 (CH_2), 43.9 (CH_2), 38.5 (CH_2) 33.2 (2 × CH_2).

^{19}F NMR (376 MHz, $CDCl_3$) δ −95.7

HRMS (ESI): Exact mass calcd. for $[C_{14}H_{16}F_2NO]^+$ $[M+H]^+$: 252.1194, found: 252.1197.



6h

(2-Ethenylphenyl)-pyrrolidin-1-ylmethanone (6h)

The title compound was prepared according to **General Procedure 1** using 2-vinylbenzoic acid (0.20 g, 1.3 mmol), pyrrolidine (0.23 ml, 2.7 mmol), CH_2Cl_2 (5.3 ml), Et_3N (0.75 ml, 5.4 mmol), CDI (0.24 g, 1.5 mmol) to give *amide* **6h** (0.188 g, 69%) as light-yellow oil.

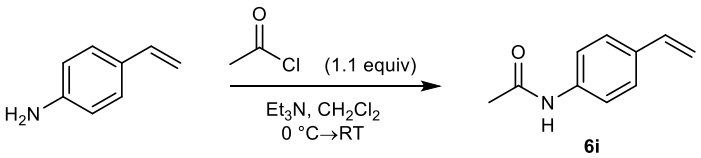
IR: 3238, 2971, 2875, 1621, 1597, 1413, 766 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.54 (m, 1H, Ar**H**), 7.34 (td, *J* = 7.5, 1.9 Hz, 1H, Ar**H**), 7.31 – 7.21 (m, 2H, Ar**H**) 6.76 (dd, *J* = 17.5, 11.0 Hz, 1H, C**H**=CH_2), 5.75 (dd, *J* = 17.5, 1.0 Hz, 1H, CH=C**H**$_A$H$_B$), 5.30 (dd, *J* = 11.0, 1.0 Hz, 1H, CH=CH$_A$**H**$_B$), 3.65 (t, *J* = 7.0 Hz, 2H, NC**H**$_2$), 3.10 (t, *J* = 6.7 Hz, NC**H**$_2$), 1.99 – 1.89 (m, 2H, NCH_2C**H**$_2$), 1.88 – 1.73 (m, 2H, NCH_2C**H**$_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.3 (C), 136.8 (C), 133.8 (C), 133.7 (CH), 128.9 (CH), 127.9 (CH), 126.1 (CH), 125.5 (CH), 116.3 (CH_2), 48.2 (CH_2), 45.5 (CH_2), 25.9 (CH_2), 24.6 (CH_2).

HRMS (ESI): Exact mass calcd. for $[C_{13}H_{16}NO]^+$ $[M+H]^+$: 202.1226, found: 202.1234.

4-Vinylacetanilide (6i)



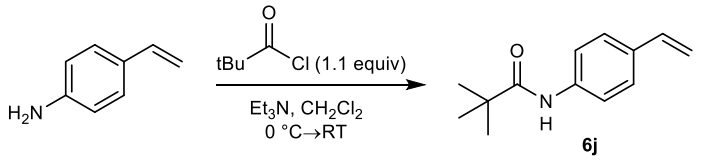
A solution of 4-aminostyrene (2.9 ml, 25 mmol) in CH_2Cl_2 (45 mL) was cooled to 0 °C, and Et_3N (3.8 mL, 28 mmol) was added. Acetyl chloride (2.0 ml, 28 mmol) was added dropwise, and the mixture was stirred at room temperature for 40 hours. Saturated aqueous sodium bicarbonate (40 mL) was added, and the organic phase was washed with aqueous HCl (2M, 2 × 40 mL). The mixture was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give amide **6i** (1.21 g, 30%) as white solid. The data were consistent with the literature.[3]

m.p. = 134 – 136 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.44 (m, 2H, Ar**H**), 7.39 – 7.34 (m, 2H, Ar**H**), 7.14 (br s, 1H, N**H**), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H, C**H**=CH_2), 5.68 (d, *J* = 17.6 Hz, 1H, C$\mathbf{H_A}H_B$), 5.19 (d, *J* = 10.9 Hz, 1H, $CH_A\mathbf{H_B}$), 2.18 (s, 3H, C$\mathbf{H}_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.2 (C), 137.6 (C), 136.1 (CH), 133.7 (C), 126.8 (2 × CH), 119.7 (2 × CH), 113.1 (CH_2), 24.6 (CH_3).

***N*-(4-Ethenylphenyl)-2,2-dimethylpropanamide (6j)**

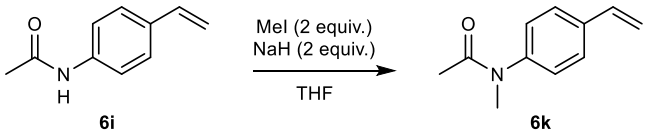


A solution of 4-aminostyrene (1.47 g, 12.6 mmol) in CH_2Cl_2 (22.5 mL) was cooled to 0 °C, and Et_3N (1.9 mL, 14 mmol) was added. Pivaloyl chloride (1.7 ml, 14 mmol) was added dropwise, and the mixture was stirred at room temperature for 40 hours. Saturated aqueous sodium bicarbonate (20 mL). was added, and the organic phase was washed with aqueous HCl (2M, 2 × 20 mL). The mixture was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give amide **6j** (2.49 g, 97%) as colourless oil. The data were consistent with the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.47 (m, 2H, Ar**H**), 7.39 – 7.34 (m, 2H, Ar**H**), 7.31 (br s, 1H, N**H**), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H, C**H**=CH_2), 5.68 (d, *J* = 17.6 Hz, 1H, C$\mathbf{H_A}H_B$), 5.19 (d, *J* = 10.9 Hz, 1H, $CH_A\mathbf{H_B}$), 1.32 (s, 9H, 3 × C$\mathbf{H}_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.5 (**C**), 137.6 (**C**), 136.1 (**C**H), 133.6 (**C**), 126.8 (2 × **C**H), 119.8 (2 × **C**H), 112.9 (**C**H_2), 39.6 (**C**), 27.6 (3 × **C**H_3).

***N*-Methyl-4-vinylacetanilide (6k)**



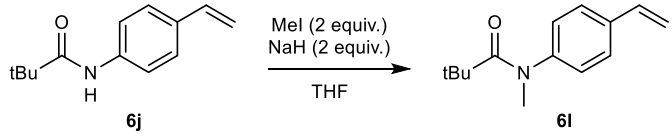
6i **6k**

Sodium hydride (60 wt.% in mineral oil, 0.080 g, 3.3 mmol) was added to a solution amide **6i** (0.27 g, 1.66 mmol) in anhydrous THF (15 mL) under nitrogen, and mixture was stirred at room temperature for 30 minutes. Methyl iodide (0.21 mL, 3.3 mmol) was added dropwise over 10 minutes, and the mixture was stirred for 48 hours. Water (10 mL) was added carefully, followed by of aqueous HCl (1M, 10 mL). The mixture was extracted with ethyl acetate (3 × 10 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (2:3 EtOAc/hexane) to give amide **6k** (0.215 g, 74%) as brown oil. The data were consistent with the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.43 (m, 2H, Ar**H**), 7.21 – 7.14 (m, 2H, Ar**H**), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H, C**H**), 5.80 (d, *J* = 17.6 Hz, 1H, C$\mathbf{H_A}H_B$), 5.34 (d, *J* = 10.9 Hz, 1H, $CH_A\mathbf{H_B}$), 3.28 (s, 3H, NC$\mathbf{H}_3$), 1.91 (s, 3H, CC$\mathbf{H}_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6 (C), 143.9 (C), 137.0 (C), 127.4 (CH), 127.1 (CH), 126.7 (C), 115.0 (CH_2), 37.1 (CH_3), 22.4 (CH_3).

***N*-(4-Ethenylphenyl)-*N*,2,2-trimethylpropanamide (6l)**



6j **6l**

Sodium hydride (60 wt.% in mineral oil, 0.111 g, 4.92 mmol) was added to a solution amide **6j** (0.500 g, 2.46 mmol) in anhydrous THF (28 mL) under nitrogen, and mixture was stirred at room temperature for 30 minutes. Methyl iodide (0.31 mL, 4.9 mmol,) was added dropwise over 10 minutes, and the mixture was stirred for 48 hours. Water (10 mL) was added carefully, followed by of aqueous HCl (1M, 10 mL). The mixture was extracted with ethyl acetate (3 × 10 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (1:4 EtOAc/hexane) to give two fractions containing amide **6j** and amide **6l** respectively. The material containing **6j** was resubjected to the reaction conditions above, and the mixture subjected to purification by column chromatography (1:4 EtOAc/hexane). The two samples of product were combined, giving *amide* **6l** (0.0877 g, 16%) as yellow solid.

m.p. = 55 – 58 °C.

IR: 3060, 2959, 1622, 1596, 1509, 1355, 1119, 901, 562 cm^{-1}

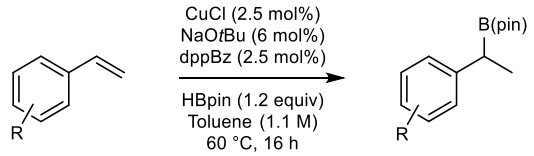
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.40 (m, 2H, Ar**H**), 7.19 – 7.14 (m, 2H, Ar**H**), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H, C**H**), 5.77 (dd, *J* = 17.6, 0.6 Hz, 1H, C$\mathbf{H_A}H_B$), 5.31 (dd, *J* = 10.9, 0.6 Hz, 1H, $CH_A\mathbf{H_B}$), 3.20 (s, 3H, NC$\mathbf{H}_3$), 1.05 (s, 9H, 3 × CC$\mathbf{H}_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 178.1 (C), 144.6 (C), 137.0 (C), 135.7 (CH), 128.8 (2 × CH), 126.9 (2 × CH), 114.9 (CH_2), 41.3 (CH_3), 40.8 (C), 29.5 (3 × CH_3).

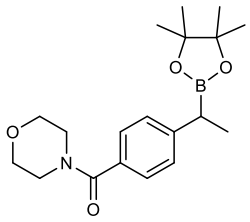
HRMS (ESI): Exact mass calcd. for $[C_{14}H_{20}NO]^+$ $[M+H]^+$: 218.1539, found: 218.1545.

3. Cu-catalysed Hydroboration

General procedure 2: Cu-catalysed Hydroboration of Styrenes



Copper (I) chloride (2.5 mol%), potassium tert-butoxide (6 mol%), 1,2-bis(diphenylphosphino)benzene (2.5 mol%) and the corresponding alkene if a solid (1 equiv.) were added to an oven dried flask and purged with Nitrogen. Anhydrous toluene (1.1M) was added, and the mixture stirred for 10 mins. Pinacolborane (1.2 equiv.) was added and the mixture stirred for 10 mins. If the alkene is an oil, the alkene (1 equiv.) is added at this point. The mixture was heated to 60 °C for 16 hours, cooled to room temperature, filtered through celite eluting with ethyl acetate, and concentrated *in vacuo*. The crude material was purified by column chromatography to give the corresponding boronic ester.



7a

4-{4-[1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzoyl}morpholine amine (7a)

The title compound was prepared according to **General Procedure 2** using copper (I) chloride (0.0046 g, 0.046 mmol), potassium tert-butoxide (0.0139 g, 0.11 mmol), 1,2-bis(diphenylphosphino)benzene (0.0205 g, 0.046 mmol), alkene **6a** (0.400 g, 1.84 mmol), anhydrous toluene (1.67 ml) and pinacolborane (0.32 ml, 2.21 mmol). The crude material was purified by column chromatography (2:1 EtOAc/hexane) to give *boronic ester* **7a** (0.443 g, 70%) as white solid.

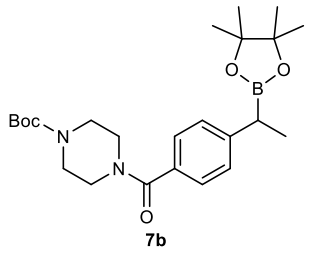
m.p. = 89 – 93 °C.

IR: 2972, 1633, 1315, 1254, 1143, 1115, 1012, 845, 568 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.29 (m, 2H, Ar**H**), 7.26 – 7.22 (m, 2H, Ar**H**), 3.87 – 3.41 (m, 8H, 4 × C**H**$_2$), 2.46 (q, *J* = 7.4 Hz, 1H, C**H**), 1.33 (d, *J* = 7.4 Hz, 3H, CHC**H**$_3$), 1.21 (s, 6H, 2 × CC**H**$_3$), 1.20 (s, 6H, 2 × CC**H**$_3$).**^{13}C NMR** (101 MHz, $CDCl_3$): δ 170.8 (C), 147.4 (C), 131.9 (C), 127.8 (2 × CH), 127.3 (2 × CH_2), 83.4 (2 × C), 66.9 (2 × CH_2), 24.8 (2 × CH_3), 24.6 (2 × CH_3), 16.8 (CH_3). Note: NCH_2 signals from the morpholine group are not observed (including ^{13}C NMR and HSQC experiments, different temperatures and relaxation times, or use of d_6-DMSO as solvent instead of $CDCl_3$),

^{11}B NMR (128.3 MHz, $CDCl_3$): δ 34.2.

HRMS (ESI): Exact mass calcd. for $[C_{19}H_{29}BNO_4]^+$ $[M+H]^+$: 346.2184, found: 346.2197.



***tert*-Butyl 4-[4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzoyl]piperazine-1-carboxylate (7b)**

The title compound was prepared according to **General Procedure 2** using copper (I) chloride (0.0023 g, 0.024 mmol), potassium tert-butoxide (0.0064 g, 0.057 mmol), 1,2-bis(diphenylphosphino)benzene (0.0106 g, 0.024 mmol), alkene **6b** (0.300 g, 0.948 mmol), anhydrous toluene (0.86 ml), and pinacolborane (0.17 ml, 1.14 mmol). The crude material was purified by column chromatography (2:3 EtOAc/hexane) to give *boronic ester* **7b** (0.288 g, 68%) as white solid.

m.p. = 128 – 130 °C.

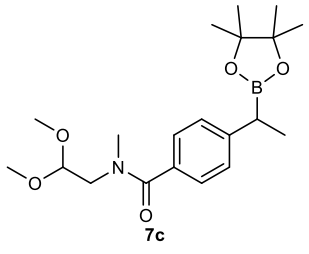
IR: 2975, 2930, 1688, 1618, 1364, 1241, 1145, 998, 850, 537 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.29 (m, 2H, Ar**H**), 7.27 – 7.23 (m, 2H, Ar**H**), 3.79 – 3.33 (m, 8H, 4 × C**H**$_2$), 2.47 (q, *J* = 7.5 Hz, 1H, C**H**), 1.47 (s, 9H, 3 × COCC**H**$_3$), 1.33 (d, *J* = 7.5 Hz, 3H, CHC**H**$_3$), 1.21 (s, 6H, 2 × BOCC**H**$_3$), 1.20 (s, 6H, 2 × BOCC**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.0 (C), 154.6 (C), 147.4 (C), 132.0 (C), 127.9 (2 × CH), 127.3 (2 × CH), 83.4 (C), 80.3 (C), 28.4 (3 × CH_3), 24.6 (2 × CH_3), 24.6 (2 × CH_3), 16.8 (CH_3). Note: NCH_2 signals from the piperazine group are not observed (including ^{13}C NMR and HSQC experiments, different temperatures and relaxation times, or use of d_6-DMSO as solvent instead of $CDCl_3$).

^{11}B NMR (128.3 MHz, $CDCl_3$): δ 34.4.

HRMS (ESI): Exact mass calcd. for $[C_{24}H_{38}BN_2O_5]^+$ $[M+H]^+$: 445.2688, found: 445.2701.



***N*-(2,2-Dimethoxyethyl)-*N*-methyl-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzamide (7c)**

The title compound was prepared according to **General Procedure 2** using copper (I) chloride (0.0015 g, 0.010 mmol), potassium tert-butoxide (0.0027 g, 0.024 mmol), 1,2-bis(diphenylphosphino)benzene (0.0045 g, 0.010 mmol), alkene **6c** (0.075 g, 0.300 mmol), anhydrous toluene (0.36 ml), and pinacolborane (0.07 ml, 0.48 mmol). The crude material was purified by column chromatography (2:3 EtOAc/hexane) to give *boronic ester* **7c** (0.0429 g, 38%) as colourless oil.

IR: 2975, 2932, 1632, 1321, 1141, 1076, 847 cm^{-1}

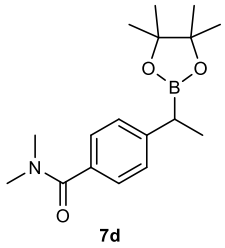
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.9 Hz, 2H, Ar**H**), 7.25 – 7.21 (m, 2H, Ar**H**), 4.69 (s, 0.7 H, C**H** rotamer), 4.35 (s, 0.3 H, C**H** rotamer), 3.70 – 2.98 (m, 11H, 2 × OC**H**$_3$ + C**H**$_2$ + NC**H**$_3$), 2.45

(q, J = 7.5 Hz, 1H, C**H**CH_3), 1.32 (d, J = 7.5 Hz, 3H, CHC**H**$_3$), 1.20 (s, 6H, 2 × C**H**$_3$), 1.19 (s, 6H, 2 × C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9 (C), 146.8 (C , rotamer), 146.6 (C, rotamer), 132.8 (C), 127.5 (2 × CH), 127.1 (2 × CH), 103.5 (CH - rotamer), 102.9 (CH , rotamer), 83.3 (2 × C), 54.7 (2 × CH_3), 52.9 (CH_2 , rotamer), 49.8 (CH_2 , rotamer), 39.5 (CH_3 , rotamer), 34.3 (CH_3, rotamer), 24.5 (2 × CH_3), 24.5 (2 × CH_3), 16.6 (CH_3).

^{11}B NMR (128.3 MHz, CDCl3): δ 33.8.

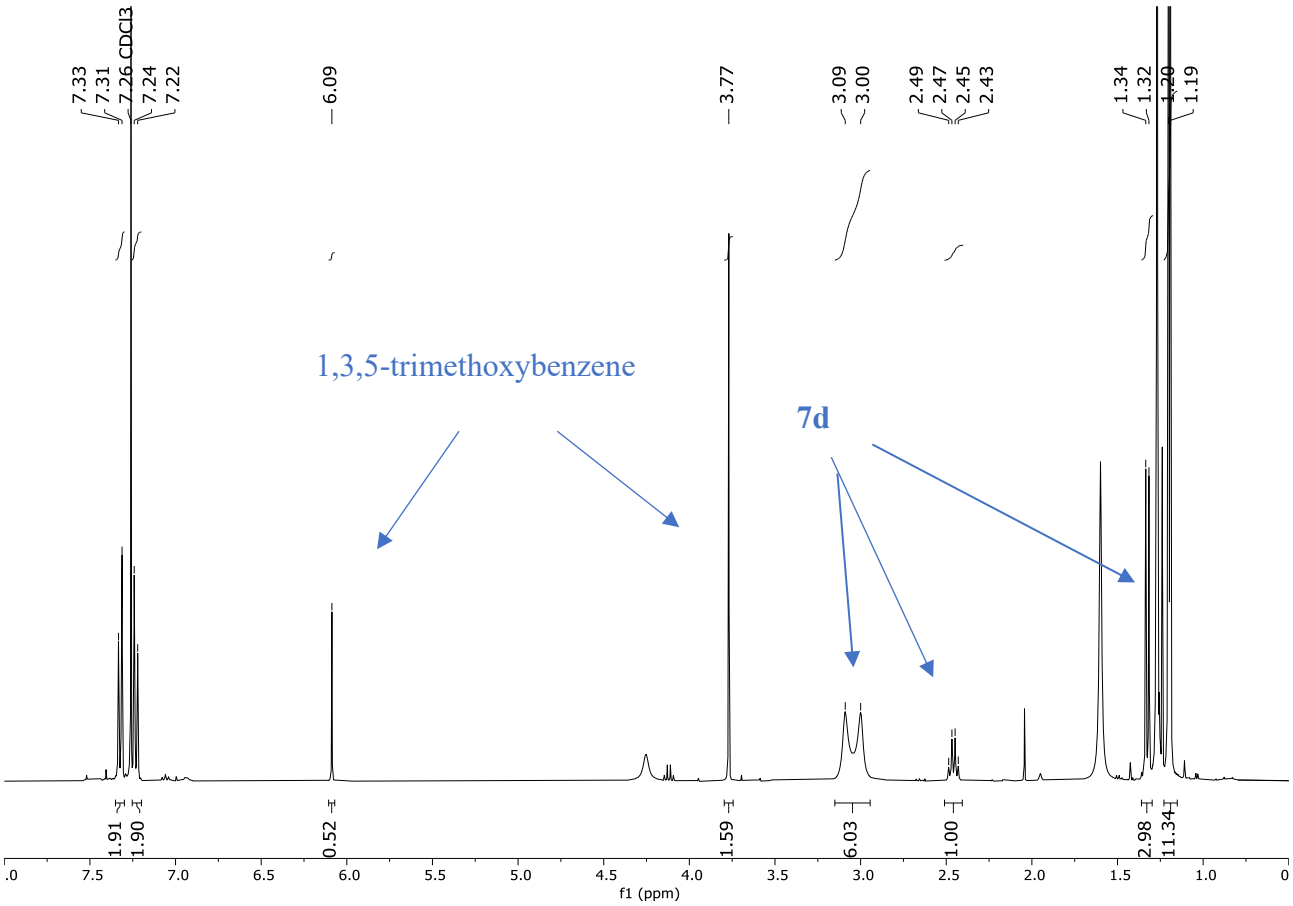
HRMS (ESI): Exact mass calcd. for $[C_{20}H_{32}BNO_5Na]^+$ $[M+Na]^+$: 378.2446, found: 378.2452.



7d

***N,N*-Dimethyl-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzamide (7d)**

The title compound was prepared according to **General Procedure 2** using copper (I) chloride (0.0014 g, 0.014 mmol, potassium tert-butoxide (0.0038g, 0.034 mmol), 1,2-bis(diphenylphosphino)benzene (0.0064 g, 0.014 mmol), alkene **6d** (0.100 g, 0.571 mmol), anhydrous toluene (0.52 ml), and pinacolborane (0.10 ml, 0.68 mmol). 1,3,5-Trimethoxybenzene (10.2 mg, 0.0606 mmol) was added to the crude material, and the mixture was analysed by ^{1}H NMR, which indicated *boronic ester* **7d** was formed in 61% yield.



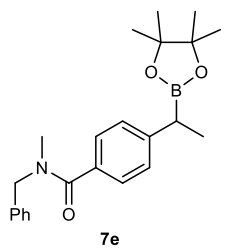
Efficient purification by chromatography was not feasible, due to coelution of the product with (pin)BOB(pin). A sample of **7d** for characterisation was obtained by silica chromatography (2:1 EtOAc/hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.30 (m, 2H, Ar**H**), 7.25 – 7.21 (m, 2H, Ar**H**), 3.04 (br s, 6H, 2 × NC**H**$_3$), 2.45 (q, *J* = 7.5 Hz, 1H, C**H**), 1.32 (d, *J* = 7.5 Hz, 3H, CHC**H**$_3$), 1.20 (s, 6H, 2 × C**H**$_3$), 1.19 (s, 6H, 2 × C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0 (C), 146.8 (C), 132.9 (C), 127.6 (2 × CH), 127.3 (2 × CH), 83.4 (2 × C), 39.1 (CH_3), 36.1 (CH_3), 24.6 (2 × CH_3), 24.6 (2 × CH_3), 16.8 (CH_3).

^{11}B NMR (128.3 MHz, $CDCl_3$): δ 33.7.

HRMS (ESI): Exact mass calcd. for $[C_{17}H_{26}BNNaO_3]^+$ $[M+Na]^+$: 326.1898, found: 326.1914.



7e

_N_-Benzyl-_N_-methyl-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzamide (7e)

The title compound was prepared according to **General Procedure 2** using copper (I) chloride (0.0030 g, 0.030 mmol), potassium tert-butoxide (0.0080 g, 0.072 mmol), 1,2-bis(diphenylphosphino)benzene (0.0133 g, 0.030 mmol), N-

alkene **6e** (0.300 g, 1.19 mmol), anhydrous toluene (1.09 ml), pinacolborane (0.21 ml, 1.43 mmol). The crude material was purified by column chromatography (2:3 EtOAc/hexane) to give *boronic ester* **7e** (0.4145 g, 92%) as colourless oil.

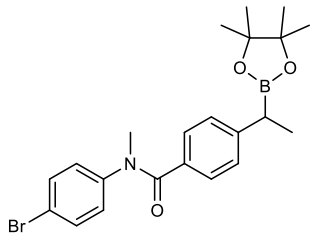
IR: 2975, 2931, 1634, 1622, 1317, 1141, 1068, 849 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.12(m, 9H, Ar**H**), 4.74 (s, 1H, C**H**$_A$H$_B$), 4.54 (s, 1H, CH$_A$**H**$_B$), 3.08 – 2.77 (m, 3H, NC**H**$_3$), 2.45 (q, *J* = 7.5 Hz, 1H, C**H**), 1.31 (d, *J* = 7.5 Hz, 3H, CHC**H**$_3$), 1.19 (s, 6H, 2 × CC**H**$_3$), 1.18 (s, 6H, 2 × C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.6 (C, rotamer), 171.9 (C, rotamer), 146.9 (C), 136.9 (C), 132.7 (C), 128.7 (2 × CH), 128.1 (CH), 127.7 (2 × CH), 127.4 (CH), 127.1 (2 × CH), 126.7 (CH), 83.4 (2 × C), 55.2 (CH_2, rotamer), 50.8 (CH_2, rotamer), 37.1 (CH_3, rotamer), 33.2 (CH_3, rotamer), 25.1 (CH), 24.6 (2 × CH_3), 24.5 (2 × CH_3), 16.7 (CH_3).

^{11}B NMR (128.3 MHz, $CDCl_3$): δ 34.0.

HRMS (ESI): Exact mass calcd. for $[C_{23}H_{31}BNO_3]^+$ $[M+H]^+$: 380.2392, found: 380.2407.



7f

N-(4-Bromophenyl)-N-methyl-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzamide (7f)

The title compound was prepared according to **General Procedure 2** using copper (I) chloride (0.0023 g, 0.024 mmol), potassium tert-butoxide (0.0064 g, 0.057 mmol), 1,2-bis(diphenylphosphino)benzene (0.0106 g, 0.024 mmol), alkene **6f** (0.222 g, 0.701 mmol), anhydrous toluene (0.86 ml), pinacolborane (0.17 ml, 1.14 mmol). The crude material was purified by column chromatography (2:3 EtOAc/hexane) to give *boronic ester* **7f** (0.127 g, 41%) as yellow solid.

m.p. = 103 – 105 °C.

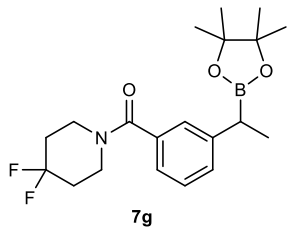
IR: 2975, 2932, 1645, 1334, 1136, 838, 575 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.26 (m, 2H, Ar**H**), 7.20 – 7.11 (m, 2H, Ar**H**), 7.06 – 6.99 (m, 2H, Ar**H**), 6.91 – 6.85 (m, 2H, Ar**H**), 3.43 (s, 3H, NC**H**$_3$), 2.37 (q, *J* = 7.4 Hz, 1H, C**H**), 1.25 (d, *J* = 7.4 Hz, 3H, CHC**H**$_3$), 1.14 (s, 6H, 2 × C**H**$_3$), 1.12 (s, 6H, 2 × C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.8 (C), 147.1 (C), 144.3 (C), 132.1 (2 × CH), 128.7 (2 × CH), 128.3 (2 × CH), 127.1 (2 × CH), 119.5 (C), 83.3 (2 × C), 38.2 (CH_3), 24.5 (2× CH_3), 24.4 (2 × CH_3), 16.0 (CH_3). (One aryl quaternary signal not observed – potentially due to overlap with a CH signal.)

^{11}B NMR (128.3 MHz, CDCl3): δ 33.9.

HRMS (ESI): Exact mass calcd. for $[C_{22}H_{28}B^{79}BrNO_3]^+$ $[M+H]^+$: 444.1340, found: 444.1337.



7g

(4,4-Difluoropiperidin-1-yl)-[3-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]phenyl]methanone (7g)

The title compound was prepared according to **General Procedure 2** using copper (I) chloride (0.0030 g, 0.030 mmol), potassium tert-butoxide (0.0080 g, 0.071 mmol), 1,2-bis(diphenylphosphino)benzene (0.0133 g, 0.030 mmol), alkene **6g** (0.300 g, 1.19 mmol), anhydrous toluene (1.1 ml), pinacolborane (0.20 ml, 1.43 mmol). The crude material was purified by column chromatography (2:3 EtOAc/hexane) to give *boronic ester* **7g** (0.180 g, 40%) as white solid.

m.p. = 97 – 99 °C.

IR: 2978, 2933, 1637, 1359, 1141, 1097, 946, 844 cm^{-1}

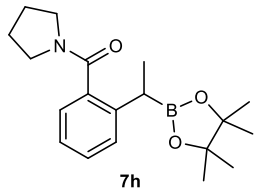
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 2H, Ar**H**), 7.26 – 7.23 (m, 1H, Ar**H**), 7.20 – 7.16 (m, 1H, Ar**H**), 4.00 – 3.36 (m, 4H, 2 × NC**H**$_2$), 2.46 (q, *J* = 7.5 Hz, 1H, C**H**), 2.19 – 1.80 (m, 4H, 2 × CC**H**$_2$), 1.33 (d, *J* = 7.5 Hz, 3H, C**H**$_3$), 1.20 (s, 6H, 2 × C**H**$_3$), 1.19 (s, 6H, 2 × C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.0 (C), 145.5 (C), 135.0 (C), 129.5 (CH), 128.6 (CH), 126.1 (CH), 123.7 (CH), 121.6 (t, *J* = 242.7 Hz, C), 83.4 (2 × C), 34.5 (2 × CH_2), 31.5 (2 × CH_2), 24.6 (2 × CH_3), 24.6 (2 × CH_3), 16.8 (CH_3).

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ −97.7.

HRMS (ESI): Exact mass calcd. for $[C_{20}H_{29}BF_2NO_3]^+$ $[M+H]^+$: 380.2203, found: 380.2203.



7h

Pyrrolidin-1-yl-[2-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]phenyl]methanone (7h)

The title compound was prepared according to **General Procedure 2** using copper (I) chloride (0.0037 g, 0.037 mmol), potassium tert-butoxide (0.010 g, 0.089 mmol), 1,2-bis(diphenylphosphino)benzene (0.0166 g, 0.037 mmol), alkene **6h** (0.300 g, 1.49 mmol), anhydrous toluene (1.36 ml), pinacolborane (0.26 ml, 1.79 mmol). The crude material was

purified by column chromatography (2:1 EtOAc/hexane) to give *boronic ester* **7h** (0.231 g, 47%) as light-yellow solid.

m.p. = 141 – 143 °C.

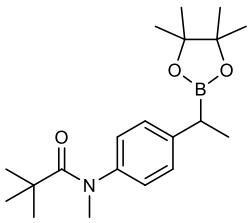
IR: 2973, 2928, 1622, 1429, 1323, 1144, 767 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.27 (m, 2H, Ar**H**), 7.19 – 7.11 (m, 2H, Ar**H**), 3.66 (t, *J* = 7.0 Hz, 2H, NC**H**$_2$), 3.30 (dt, *J* = 10.6, 6.4 Hz, 1H, NC**H**$_A$H$_B$), 3.14 (dt, *J* = 10.7, 7.0 Hz, 1H, NCH$_A$**H$_B$**), 2.48 (q, *J* = 7.4 Hz, 1H, C**H**), 2.01 – 1.88 (m, 2H, NCH$_2$C**H**$_2$), 1.88 – 1.79 (m, 2H, NCH$_2$C**H**$_2$), 1.32 (d, *J* = 7.4 Hz, 3H, CHC**H**$_3$), 1.20 (s, 6H, 2 × C**H**$_3$), 1.19 (s, 6H, 2 × C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.0 (C), 142.0 (C), 136.9 (C), 128.9 (CH), 128.4 (CH), 125.8 (CH), 125.1 (CH), 83.1 (2 × C), 48.6 (CH_2), 45.4 (CH_2), 26.0 (CH_2), 24.7 (2 × CH_3), 24.6 (2 × CH_3), 24.6 (CH_2), 17.5 (CH_3).

^{11}B NMR (128.3 MHz, $CDCl_3$): δ 33.4.

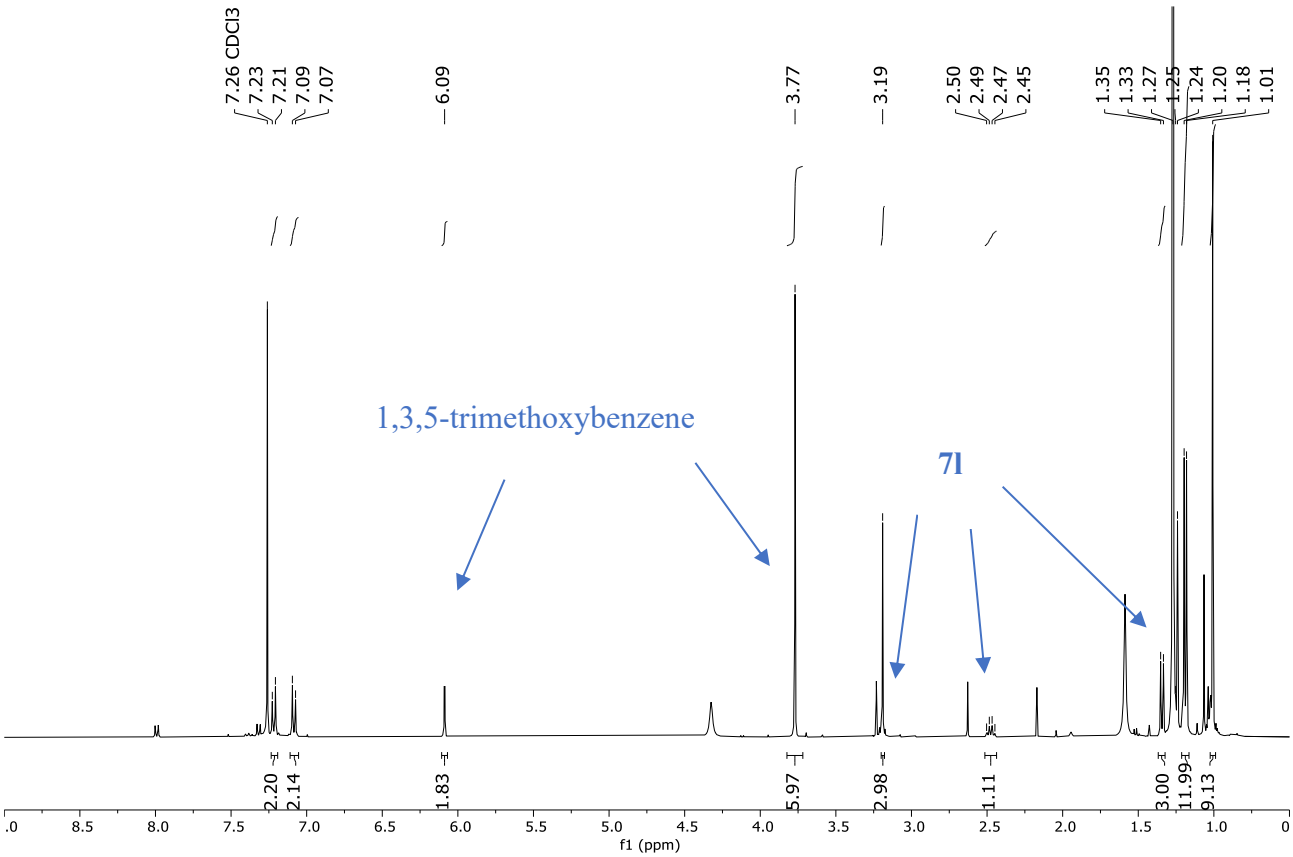
HRMS (ESI): Exact mass calcd. for $[C_{13}H_{16}BNO_2]^+$ [M − pinacol + OH]+: 230.1347, found: 230.1351.



7l

***N*,2,2-Trimethyl-*N*-[4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]phenyl]propanamide (7l)**

The title compound was prepared according to **General Procedure 2** using copper (I) chloride (0.0005 g, 0.0058 mmol), potassium tert-butoxide (0.0015 g, 0.014 mmol), 1,2-bis(diphenylphosphino)benzene (0.0026 g, 0.0058 mmol), alkene **6l** (0.050 g, 0.23 mmol), anhydrous toluene (0.2 ml), and pinacolborane (0.04 ml, 0.28 mmol). 1,3,5-Trimethoxybenzene (11.0 mg, 0.0654 mmol) was added to the crude material, and the mixture was analysed by ^{1}H NMR, which indicated boronic ester **7l** was formed in 47% yield.



Efficient purification by chromatography was not feasible, due to coelution of the product with (pin)BOB(pin). A sample of **7l** for characterisation was obtained by silica chromatography (2:3 EtOAc/hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.19 (m, 2H, Ar**H**), 711 – 7.05 (m, 2H, Ar**H**), 3.19 (s, 3H, NC**H**$_3$), 2.48 (q, *J* = 7.4 Hz, 1H, C**H**), 1.34 (d, *J* = 7.4 Hz, 3H, CHC**H**$_3$), 1.20 (s, 6H, 2 × C**H**$_3$), 1.18 (s, 6H, 2 × OCC**H**$_3$), 1.01 (s, 9H, 3 × C(O)CC**H**$_3$).

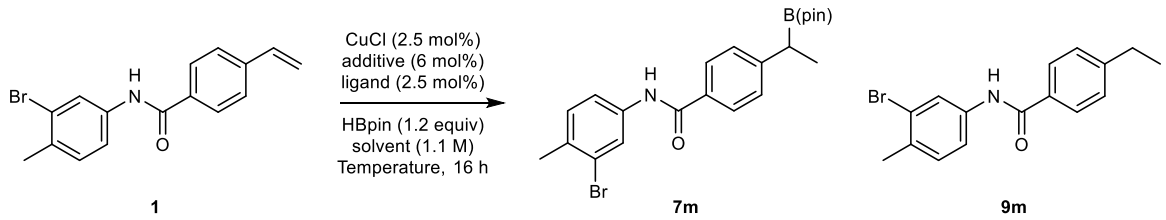
^{13}C NMR (101 MHz, $CDCl_3$): δ 161.5 (C), 149.7 (C), 136.1 (C), 129.5 (2 × CH), 128.8 (2 × CH), 83.1 (2 × C), 41.1 (CH_3), 29.4 (3 × CH_3), 24.5 (4 × CH_3), 16.5 (CH_3).

^{11}B NMR (128 MHz, $CDCl_3$): δ = 33.5.

HRMS (ESI): Exact mass calcd. for $[C_{20}H_{33}BNO_3]^+$ $[M+H]^+$: 346.2548, found: 346.2550.

3.1. Hydroboration of Alkene 1

Table S1: Evaluation of Reaction Conditions

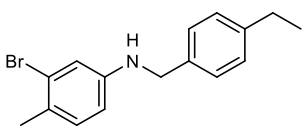


Entry	Ligand	Solvent	Additive	Temperature	Yield[a]		
					1	**7m**	**9m**
1	dppbz	toluene	KOtBu	60 °C	0%	trace	35%
2	dppe	toluene	KOtBu	60 °C	0%	trace	23%
3	dppf	toluene	KOtBu	60 °C	0%	<20%	26%
4	BINAP	toluene	KOtBu	60 °C	0%	0%	26%
5	SImes	toluene	KOtBu	60 °C	0%	0%	15%
6	dppbz	thf	KOtBu	60 °C	0%	0%	34%
7	dppbz	MeCN	KOtBu	60 °C	0%	trace	25%
8	dppbz	iPrOAc	KOtBu	60 °C	0%	trace	24%
9	dppbz	DCE	KOtBu	60 °C	0%	0%	17%
10	dppbz	toluene	NaOtBu	60 °C	0%	0%	21%
11	dppbz	toluene	Na_2CO_3	60 °C	0%	0%	14%
12	dppbz	toluene	NaOMe	60 °C	0%	0%	17%
13	dppbz	toluene	pyridine	60 °C	>95%	0%	0%
14	dppbz	toluene	KOtBu	40 °C	0%	trace	27%
15	dppbz	toluene	KOtBu	80 °C	0%	0%	0%

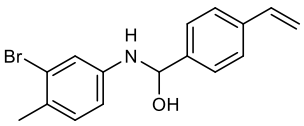
[a] Determined using ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

^{1}H NMR analysis of the crude reaction mixtures indicated that alkene **1** was consumed in each reaction (except entry 14). ^{1}H and ^{11}B NMR analysis indicated that boronic ester **7m** was formed in trace amounts (<10%) at most, and that a major component of the reaction mixture was alkane **9m**. The exception is entry 3, where boronic ester **7m** is observed in approximately 20% yield. However, the error in the quantitative NMR analysis is not sufficient to quote a yield with confidence, and **7m** is a minor component of the reaction mixture.

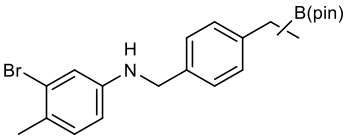
Subsequent LCMS analysis indicated that several of the samples contained signals consistent with possible amide reduction (scheme S1). However, attempts to isolate material were unsuccessful.



m/z observed: 304.0698
predicted m/z for $[M+H]^+$: 304.0695



m/z observed: 318.0489
predicted m/z for $[M+H]^+$: 318.0488

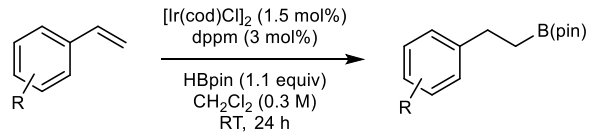


m/z observed: 430.1566
predicted m/z for $[M+H]^+$: 430.1547

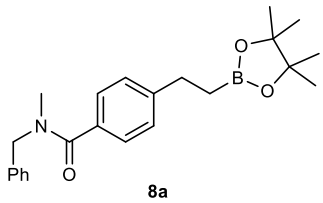
Scheme S1: Structures consistent with LCMS data observed in crude reaction mixture of Table S1 entry 1.

4. Ir-Catalysed Hydroboration

General procedure 3: Ir-catalysed Hydroboration of Styrenes



$[Ir(cod)Cl]_2$ (1.5 mol%) and dppm (3 mol%) were added to an oven dried flask and purged with nitrogen. Anhydrous CH_2Cl_2 (0.3 M solution with respect to the alkene), pinacolborane (1.1 equiv.), and the corresponding alkene (1 equiv.) were added, and the mixture was stirred at room temperature for 24 h. The mixture was concentrated *in vacuo*, dissolved in Et_2O, filtered through a pad of celite, and concentrated *in vacuo*. The crude material was purified by column chromatography to give the corresponding boronic ester.



8a

***N*-Benzyl-*N*-methyl-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzamide (8a)**

The title compound was prepared according to **General Procedure 3** using $[Ir(cod)Cl]_2$ (0.0040 g, 0.0060 mmol), dppm (0.0046 g, 0.012 mmol, 3 mol%), anhydrous CH_2Cl_2 (1.3 ml), pinacolborane (0.06 ml, 0.44 mmol), and alkene **6e** (0.100 g, 0.398 mmol). The crude material was purified by column chromatography (1:1 heptane/EtOAc) to give *boronic ester* **8a** (0.0893 g, 59%) as yellow solid.

m.p. = 71 – 74 °C.

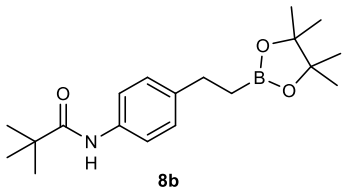
IR: 2978, 2918, 1629, 1370, 1319, 1143, 838, 731 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.09 (m, 9H, Ar**H**), 4.74 (s, 1H, NC$\mathbf{H_A}H_B$), 4.52 (s, 1H, $NCH_A\mathbf{H_B}$), 3.12 – 2.80 (m, 3H,N C$\mathbf{H}_3$), 2.75 (t, J = 8.2 Hz, 2H, ArC$\mathbf{H}_2$), 1.20 (s, 12H, 4 × CC$\mathbf{H}_3$), 1.12 (t, J = 8.2 Hz, 2H, BC$\mathbf{H}_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.6 (C, rotamer), 171.9 (C, rotamer), 146.2 (C), 137.1 (C, rotamer), 136.8 (C, rotamer), 133.4 (C), 128.7 (2 × CH), 128.0 (3 × CH), 127.4 (CH), 126.9 (3 × CH), 83.1 (2 × C), 55.2 (CH_2, rotamer), 50.8 (CH_2, rotamer), 37.0 (CH_3, rotamer), 33.1 (CH_3, rotamer), 29.8 (CH_2), 24.8 (4 × CH_3), 12.6 (CH_2).

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.6.

HRMS (ESI): Exact mass calcd. for $[C_{23}H_{31}BNO_3]^+$ $[M+H]^+$: 380.2428, found: 380.2411.



8b

***N*-2,2-trimethyl-N-[4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]phenyl]propenamide (8b)**

The title compound was prepared according to **General Procedure 3** using $[Ir(cod)Cl]_2$ (0.0050 g, 0.0074 mmol) and dppm (0.0057 g, 0.015 mmol), anhydrous CH_2Cl_2 (1.6 ml), pinacol borane (0.08 ml, 0.54 mmol), and alkene **6j** (0.100 g, 0.492 mmol). The crude material was purified by column chromatography (7:3 heptane/EtOAc) to give *boronic ester* **8b** (0.111 g, 68%) as yellow solid.

m.p. = 128 – 131 °C.

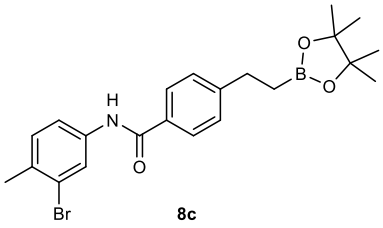
IR: 3347, 2976, 2920, 1653, 1514, 1366, 1316, 1142, 837 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.37 (m, 2H, Ar**H**), 7.25 (br s, 1H, N**H**), 7.18 – 7.13 (m, 2H, Ar**H**), 2.70 (t, *J* = 8.1 Hz, 2H, ArC**H**$_2$), 1.30 (s, 9H, 3 × C**H**$_3$), 1.22 (s, 12H, 4 × C**H**$_3$), 1.10 (t, *J* = 8.1 Hz, 2H, C**H**$_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.4 (C), 140.5 (C), 135.5 (C), 128.4 (2 × CH), 119.9 (2 × CH), 83.1 (2 × C), 39.5 (C), 29.4 (CH_2), 27.6 (3 × CH_3), 24.8 (4 × CH_3).

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.8.

HRMS (ESI): Exact mass calcd. for $[C_{19}H_{31}BNO_3]^+$ $[M+H]^+$: 332.2428, found: 332.2436.



8c

N-(3-bromo-4-methylphenyl)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzamide (8c)

The title compound was prepared according to **General Procedure 3** using $[Ir(cod)Cl]_2$ (0.0032 g, 0.0048 mmol) and dppm (0.0036 g, 0.0096 mmol), anhydrous CH_2Cl_2 (1.1 ml), pinacolborane (0.05 ml, 0.35 mmol), and alkene **1** (0.100 g, 0.316 mmol). The crude material was purified by column chromatography (3:1 heptane/EtOAc) to give *boronic ester* **8c** (0.117 g, 83%) as yellow solid.

m.p. = 166 – 169 °C.

IR: 3308, 2955, 2921, 2852, 1638, 1587, 1502, 1370, 1139, 844, 673 cm^{-1}**.**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 2.2 Hz, 1H Ar**H**), 7.78 – 7.73 (m, 2H, Ar**H**), 7.69 (br s, 1H, N**H**), 7.48 (dd, *J* = 8.3, 2.2 Hz, 1H Ar**H**), 7.37 – 7.30 (m, 2H, Ar**H**), 7.21 (d, *J* = 8.3 Hz, 1H, Ar**H**), 2.82 (t, *J* = 8.1 Hz, 2H, C**H**$_2$), 2.38 (s, 3H, C**H**$_3$), 1.22 (s, 12H, 4 × C**H**$_3$), 1.16 (t, *J* = 8.1 Hz, 2H, C**H**$_2$).

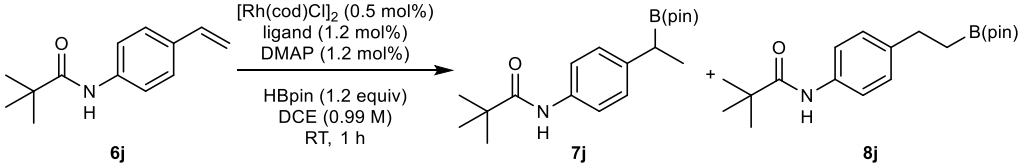
^{13}C NMR (101 MHz, $CDCl_3$): δ 165.5 (C), 149.1 (C), 136.8 (C), 133.8 (C), 131.8 (C), 130.8 (CH), 128.5 (2 × CH), 127.0 (2 × CH), 124.8 (C), 123.8 (CH), 119.03 (CH), 83.3 (2 × C), 29.9 (CH_2), 24.8 (4 × CH_3), 22.3 (CH_3).

^{11}B NMR (128 MHz, $CDCl_3$) δ 35.0.

HRMS (ESI): Exact mass calcd. for $[C_{22}H_{28}B^{79}BrNO_3]^+$ $[M+H]^+$: 444.1376, found: 444.1384.

5. Rh-Catalysed Hydroboration

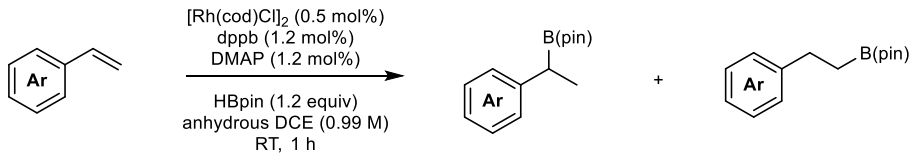
Table S2: Evaluation of Reaction Conditions

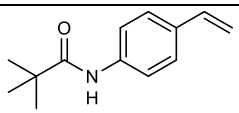
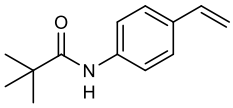
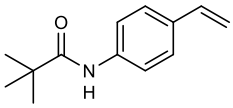
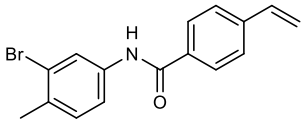
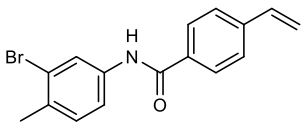
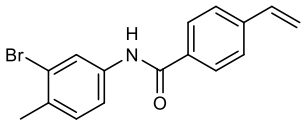


Entry	Ligand	Solvent	Ratio 7j:8j[a]	Yield[a,b]
1	dppb	wet DCE	1.6:1	44%
2	dppm	wet DCE	0.87:1	18%
3	dppf	wet DCE	0.81:1	15%
4	dppe	wet DCE	0.77:1	16%
5	dppbz	wet DCE	0.73:1	15%
6	(±)-Binap	wet DCE	0.95:1	12%
7	dppb	dried DCE[c]	1.7:1	29%
8	(±)-Binap	dried DCE[c]	1.5:1	59%
9	dppb	commercial anhydrous DCE[d]	3.3:1	73%

DCE = dichloroethane. [a] Determined by 1H NMR analysis of the crude material, using 1,3,5-trimethoxybenzene as an internal standard. [b] Yield of **7j** and **8j** combined. [c] DCE dried over activated 4Å molecular sieves for 24 h. [d] Anhydrous DCE purchased from Fisher Scientific (Product code = 10333532).

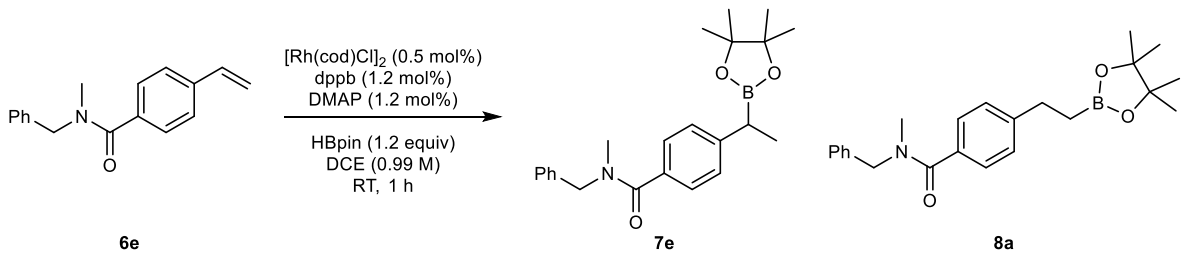
Table S3: Reproducibility of Rh-catalysed Hydroboration.



Entry	Substrate	Branched:linear Ratio[a]	Yield[a,b]
1	 **6j**	4.6:1	87%
2	 **6j**	3.3:1	74%
3	 **6j**	3.3:1	73%
4	 **1**	6.5:1	83%
5	 **1**	2.7:1	75%
6	 **1**	3.3:1	62%

[a] Determined by ^{1}H NMR analysis of the crude material, using 1,3,5-trimethoxybenzene as an internal standard. [b] Yield of branched and linear boronic esters combined.

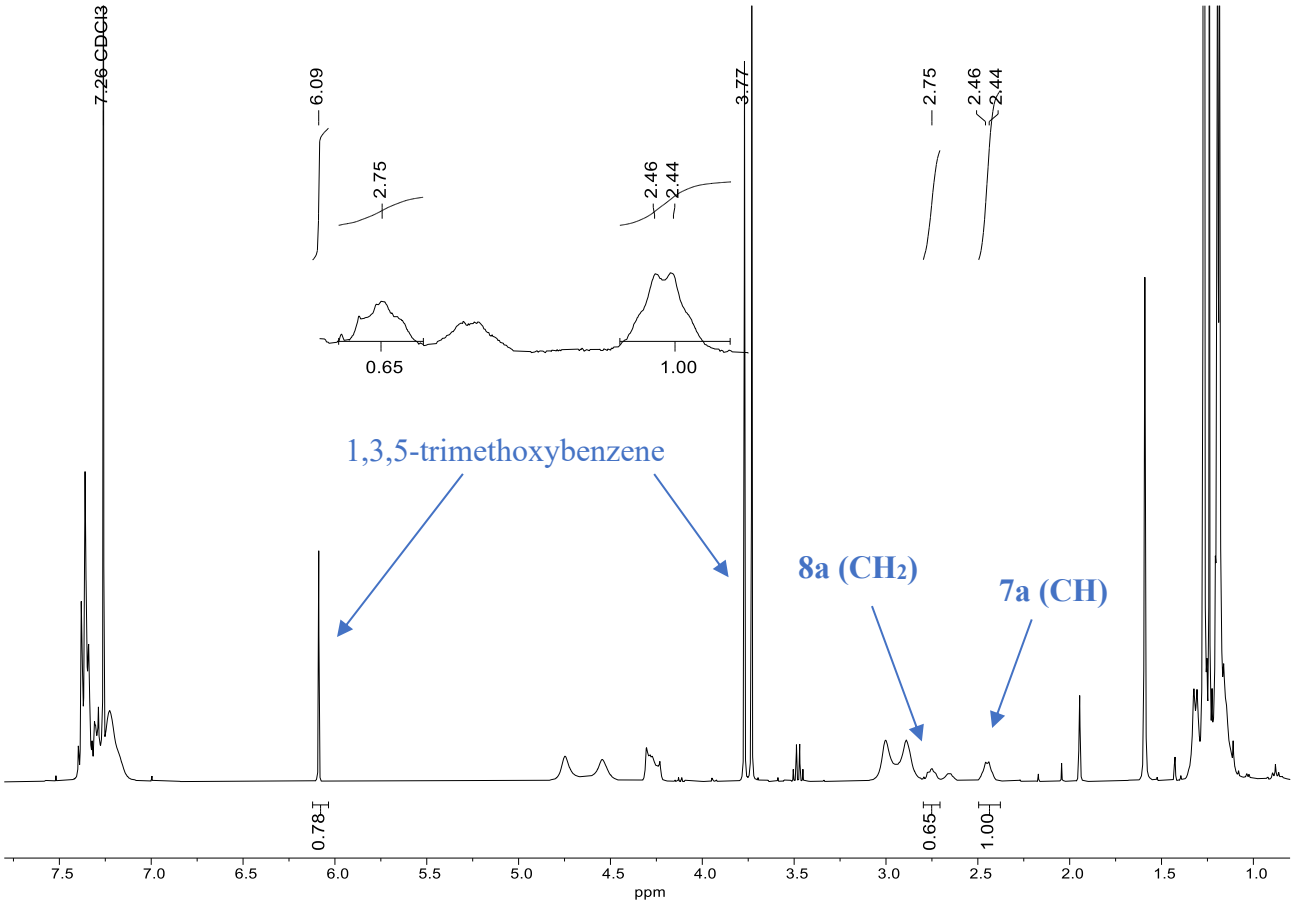
Rh-Catalysed Hydroboration of Alkene 6e



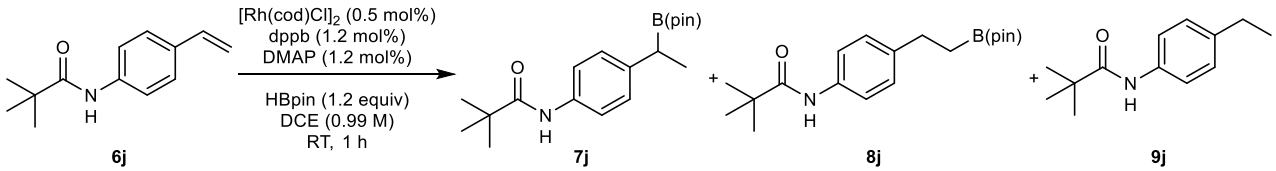
6e **7e** **8a**

Alkene **6e** (0.100 g, 0.398 mmol) and pinacol borane (0.07 ml, 0.48 mmol) were added to a solution of $[RhCl(cod)]_2$ (0.0010 g, 0.0020 mmol), DPPB (0.0020 g, 0.0048 mmol) and DMAP (0.0006 g, 0.0048 mmol) in anhydrous 1,2-dichloroethane (0.4 ml) under nitrogen. The mixture was stirred at

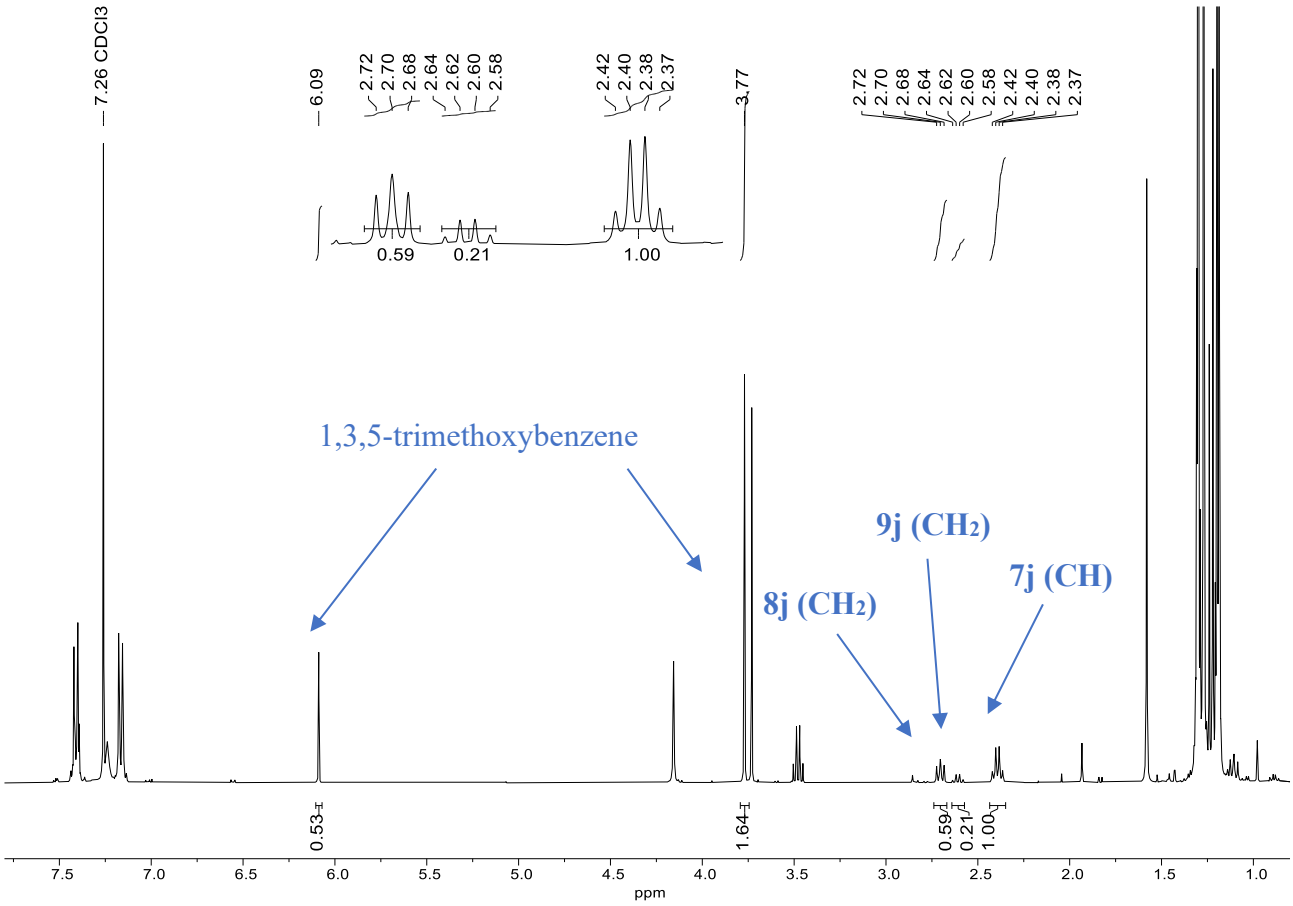
RT for 1 h, filtered through a plug of silica gel eluting with Et_2O (50 mL), and concentrated *in vacuo*. 1,3,5-Trimethoxybenzene (10.0 mg, 0.0596 mmol) was added to the crude material, and the mixture was analysed by ^1H NMR, which indicated *boronic ester* **7e** was formed in 62% yield and boronic ester **8a** was formed in 20% yield. The data of **7e** and **8a** matched that of the values above.



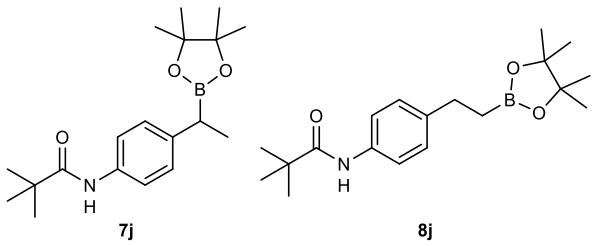
Rh-Catalysed Hydroboration of Alkene 6j.



Alkene **6j** (0.100 g, 0.492 mmol) and pinacol borane (0.09 ml, 0.59 mmol) were added to a solution of $[RhCl(cod)]_2$ (0.0012 g, 0.0025 mmol), DPPB (0.0025 g, 0.0059 mmol) and DMAP (0.0007 g, 0.0059 mmol) in anhydrous 1,2-dichloroethane (0.5 ml) under nitrogen. The mixture was stirred at RT for 1 h, filtered through a plug of silica gel eluting with Et_2O (50 mL), and concentrated *in vacuo*. 1,3,5-Trimethoxybenzene (10.6 mg, 0.0630 mmol) was added to the crude material, and the mixture was analysed by ^1H NMR, which indicated *boronic ester* **7j** was formed in 56% yield, *boronic ester* **8j** was formed in 17% yield and *alkane* **9j** was formed in 15% yield.



Samples for characterisation were obtained through subjecting the crude material to silica chromatography (1:4 EtOAc/heptane).



2,2-Dimethyl-N-[4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]phenyl]propanamide (7j) and 2,2-Dimethyl-N-[4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]phenyl]propanamide (8j).

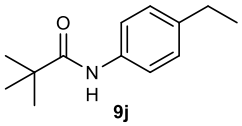
A mixture of **7j** and **8j** was obtained in a 1:0.8 ratio. Characteristic signals are shown below, and the data for **8j** matched that of the values above.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.37 (m, 2H, Ar**H**), 7.24 (s, 1H, N**H**), 7.20 – 7.13 (m, 2H, Ar**H**), 2.73 (t, *J* = 8.1 Hz, 2H, C**H$_2$ - 8j**), 2.39 (q, *J* = 7.5 Hz, 1H, C**H - 7j**), 1.29 (d, *J* = 7.5 Hz, 3H, C**H$_3$ - 1**), 13.0 – 1.29 (m, 12H, CHC**H$_3$ - 7j** and 3 × CCC**H$_3$**), 1.22 (s, 12H, 4 × C**H$_3$ - 8j**), 1.20 (s, 6H, 2 × C**H$_3$ - 7j**), 1.19 (s, 6H, 2 × C**H$_3$ - 7j**), 1.10 (t, J = 8.1 Hz, 2H, C**H$_2$ - 8j**).

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.3 (C), 141.0 (C - **7j**), 140.5 (C - **8j**), 135.6 (C - **8j**), 135.2 (C - **7j**), 128.4 (2 × CH - **8j**), 128.2 (2 × CH - **7j**), 120.1 (2 × CH - **7j**), 119.9 (2 × CH - **8j**), 83.3 (2 × C - **7j**), 83.1 (2 × C - **8j**), 39.5 (C), 29.4 (CH_2 - **8j**), 27.6 (3 × CH_3), 24.8 (4 × CH_3 - **8j**), 24.6 (2 × CH_3 - **7j**), 24.6 (2 × CH_3 - **7j**), 17.1 (CH_3 - **7j**).

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.2

HRMS (ESI): Exact mass calcd. for $[C_{19}H_{31}BNO_3]^+$ $[M+H]^+$: 332.2392, found: 332.2399.



9j

N-(4-Ethylphenyl)-2,2-dimethylpropanamide (9j)

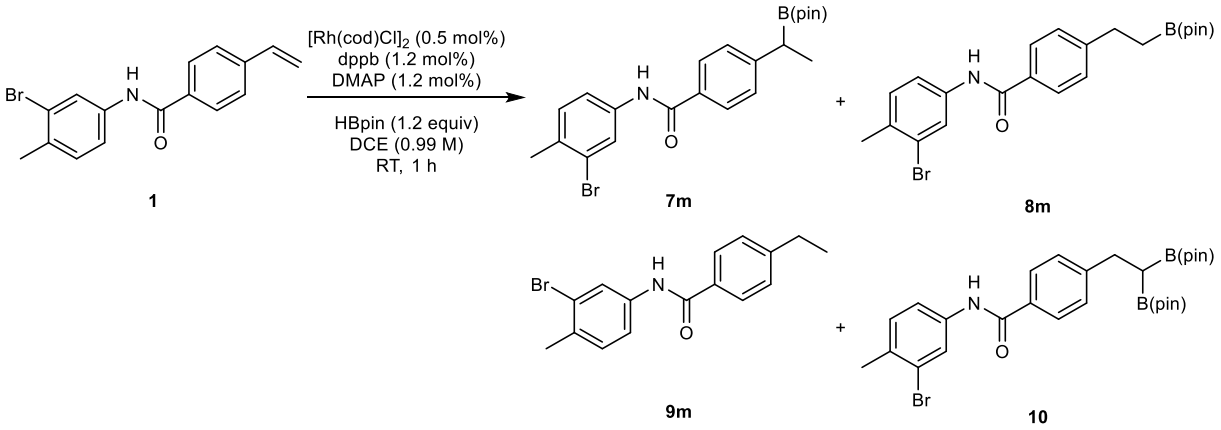
IR: 3323, 2954, 2926, 2867, 1650, 1599, 1524, 1513, 1318, 832, 712 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.39 (m, 2H, Ar**H**), 7.18 – 7.11 (m, 2H, Ar**H**), 2.61 (q, *J* = 7.6 Hz, 2H, C**H**$_2$), 1.31 (s, 9H, 3 × C**H**$_3$), 1.21 (t, J = 7.6 Hz, 3H, C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.4 (C), 140.3 (C), 135.6 (C), 128.3 (2 × CH), 120.1 (2 × CH), 39.5 (C), 28.3 (CH_2), 27.6 (3 × CH_3), 15.7 (CH_3).

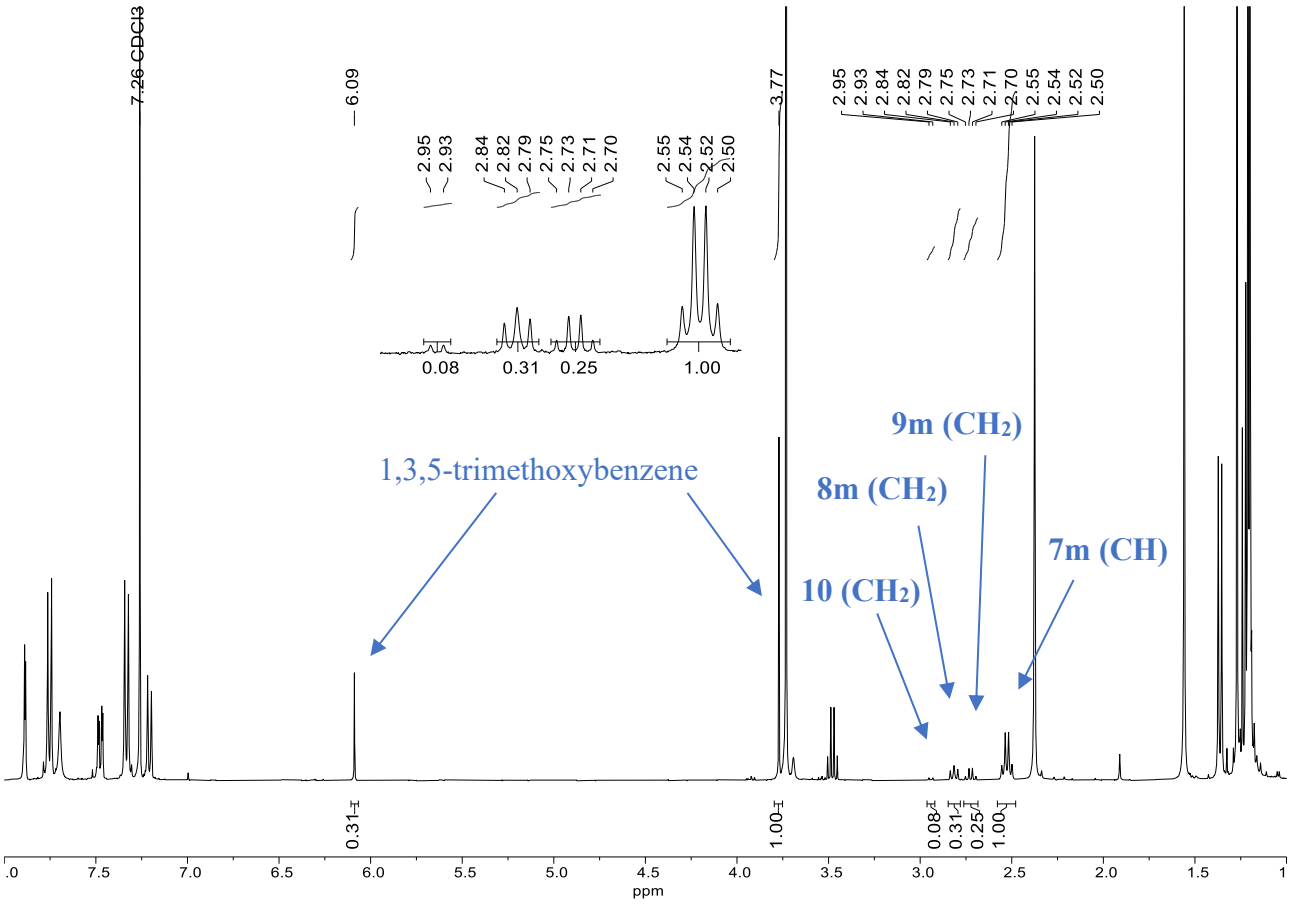
HRMS (ESI): Exact mass calcd. for $[C_{13}H_{20}NO]^+$ $[M+H]^+$: 206.1539, found: 206.1547.

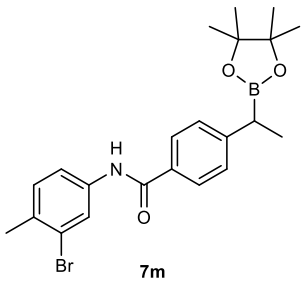
Rh-Catalysed Hydroboration of Alkene 1



1 **7m** **8m** **9m** **10**

Alkene **1** (0.100 g, 0.316 mmol) and pinacol borane (0.06 ml, 0.38 mmol) were added to a solution of $[RhCl(cod)]_2$ (0.0008 g, 0.0016 mmol), DPPB (0.0016 g, 0.0038 mmol) and DMAP (0.0005 g, 0.0038 mmol) in anhydrous 1,2-dichloroethane (0.32 ml) under nitrogen. The mixture was stirred at RT for 1 h, filtered through a plug of silica gel eluting with Et_2O (50 mL), and concentrated *in vacuo*. 1,3,5-Trimethoxybenzene (0.121 g, 0.718 mmol) was added to the crude material, and the mixture was analysed by ^{1}H NMR, which indicated *boronic ester* **7m** was formed in 72% yield, *boronic ester* **8m** was formed in 11% yield, *alkene* **9m** was formed in 9% yield and boronic ester **10** was formed in 3% yield. The data for **8m** match that above.





7m

***N*-Benzyl-*N*-methyl-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzamide (7m)**

The crude material was purified by silica gel chromatography (1:3 EtOAc/heptane) give *boronic ester* **7m** (1.43 g, 34%) as colourless oil.

IR: 2975, 1648, 1587, 1495, 1373, 1304, 1140, 850, 675 cm^{-1}.

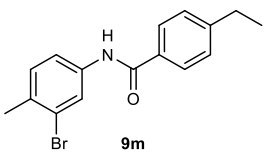
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 2.2 Hz, 1H, Ar**H**), 7.78 – 7.73 (m, 2H, Ar**H**), 7.71 (s, 1H, N**H**), 7.47 (dd, *J* = 8.2, 2.2 Hz, Ar**H**), 7.36 – 7.30 (m, 2H, Ar**H**), 7.20 (d, *J* = 8.2 Hz, 1H, Ar**H**), 2.53 (q, *J* = 7.5 Hz, 1H, C**H**), 2.37 (s, 3H, C**H**$_3$), 1.36 (d, *J* = 7.5 Hz, 3H, C**H**$_3$), 1.21 (s, 6H, 2 × C**H**$_3$), 1.20 (s, 6H, 2 × C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.6 (C), 149.9 (C), 136.9 (C), 133.7 (C), 131.4 (C), 130.8 (CH), 128.1 (2 × CH), 127.0 (2 × CH), 124.8 (C), 123.7 (CH), 119.0 (CH), 83.6 (2 × C), 24.6 (2 × CH_3), 24.6 (2 × CH_3), 22.3 (CH_3), 16.5 (CH_3).

^{11}B NMR (128.3 MHz, $CDCl_3$): δ 33.8.

HRMS (ESI): Exact mass calcd. for $[C_{22}H_{27}B^{79}BrNNaO_3]^+$ $[M+Na]^+$: 466.1160, found: 466.1145.

Samples of **9m** and **10** for characterisation were obtained through subjecting the crude material to silica chromatography (1:1 EtOAc/heptane).



9m

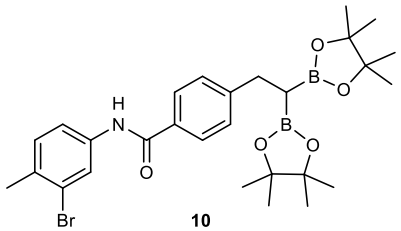
N-(3-bromo-4-methylphenyl)-4-ethylbenzamide (9m)

IR: 3301, 2958, 2920, 2851, 1645, 1580, 1499, 1373, 1298, 814, 673 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 2.2 Hz, 1H, Ar**H**), 7.87 (br s, 1H, N**H**), 7.80 – 7.73 (m, 2H, Ar**H**), 7.47 (dd, *J* = 8.2, 2.2 Hz, 1H, Ar**H**), 7.31 – 7.25 (m, 2H, Ar**H**), 7.18 (d, *J* = 8.2 Hz,1H, Ar**H**), 2.71 (q, *J* = 7.6 Hz, 2H, C**H**$_2$), 2.36 (s, 3H, C**H**$_3$), 1.26 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.6 (C), 148.7 (C), 136.8 (C), 133.7 (C), 131.9 (C), 130.8 (CH), 128.2 (2 × CH), 127.1 (2 × CH), 124.8 (C), 123.9 (CH), 119.2 (CH), 28.8 (CH_2), 22.3 (CH_3), 15.3 (CH_3).

HRMS (ESI): Exact mass calcd. for $[C_{16}H_{17}BrNO]^+$ $[M+H]^+$: 318.0488, found: 318.0502.



10

N-(3-bromo-4-methylphenyl)-4-[2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzamide (10)

IR: 2919, 2850, 1648, 1587, 1499, 1369, 1303, 1135, 840, 675 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 2.3 Hz, 1H, Ar**H**), 7.76 (s, 1H, N**H**), 7.75 – 7.70 (m, 2H, Ar**H**), 7.47 (dd, *J* = 8.3, 2.3 Hz, 1H, Ar**H**), 7.38 – 7.32 (m, 2H, Ar**H**), 7.19 (d, *J* = 8.3 Hz, 1H, Ar**H**), 2.93 (d, *J* = 8.3 Hz, 2H, C**H**$_2$), 2.36z (s, 3H, ArC**H**$_3$), 1.21 – 1.12 (m, 25H, 8 × CC**H**$_3$ and CH).

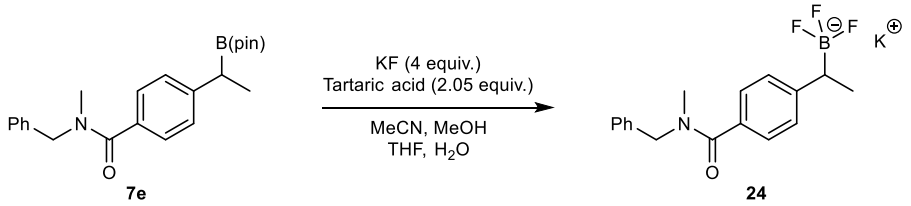
^{13}C NMR (101 MHz, $CDCl_3$): δ 165.6 (C), 149.2 (C), 136.9 (C), 133.7 (C), 131.6 (C), 130.8 (CH), 128.8 (2 × CH), 126.8 (2 × CH), 124.8 (C), 123.8 (CH), 119.0 (CH), 83.3 (2 × C), 31.2 (CH_2), 24.80 (4 × CH_3), 24.5 (4 × CH_3), 22.3 (CH_3).

^{11}B NMR (128MHz, $CDCl_3$): δ 34.3.

HRMS (ESI): Exact mass calcd. for $[C_{28}H_{39}B_2BrNO_5]^+$ $[M+H]^+$: 570.2198, found: 570.2222.

6. Reactions of Boronic Ester 7e

Potassium *N*-benzyl-N-methyl-4-[1-(trifluoro-Λ4- boranyl)ethyl]benzamide (24)



Boronic ester **7e** (0.100 g, 0.26 mmol) was added to a mixture of methanol (2 mL) and acetonitrile (2 mL). Potassium fluoride (0.0613 g, 0.0011 mmol) in H_2O (0.4 mL) was added and the mixture was stirred until the boronic ester completely dissolved. L-(+)-tartaric acid (0.0811 g, 0.0005 mmol) was dissolved in THF (1.5 mL), gentle heat and agitation is required for rapid dissolution) and added drop-wise to the rapidly (≈ 1000 rpm) stirring biphasic mixture over a period of 5 minutes. The mixture was stirred for 2 min, diluted with acetonitrile (3 mL), and stirred for a further 2 min before being diluted again with acetonitrile (1 mL). The mixture was filtered, and the flask and filter cake were rinsed with further portions of acetonitrile (3 × 5 mL). The combined filtrates were concentrated *in vacuo* to give a mixture of the corresponding potassium organotrifluoroborate and pinacol. Pinacol was removed by evaporation at 6 mm Hg with gentle heating using a heat gun, until there were no visible signs of the condensed pinacol around flask. The solid was scrapped off the sides of the flask to give salt **24** (0.0958 g, 100% yield with ~90% purity (estimated by ^{19}F NMR analysis)) as an off-white solid.

m.p. = 228 – 231 °C.

IR: 3315, 2869, 1733, 1700, 1605, 1401, 1303, 1262, 1212, 1066, 904 cm^{-1}

^{1}H NMR (400 MHz, DMSO): δ 7.41 – 7.33 (m, 2H, Ar**H**), 7.33 – 7.13 (m, 5H, Ar**H**), 7.11 – 7.01 (m, 2H, Ar**H**), 4.60 (br s, 2H, C**H**$_2$), 3.42 – 3.22 (m, 3H, C**H**$_3$), 2.86 (s, 3H, NC**H**$_3$), 1.63 (s, 1H, C**H**). 1.04 (d, *J* = 7.2 Hz, 3H, CHC**H**$_3$)

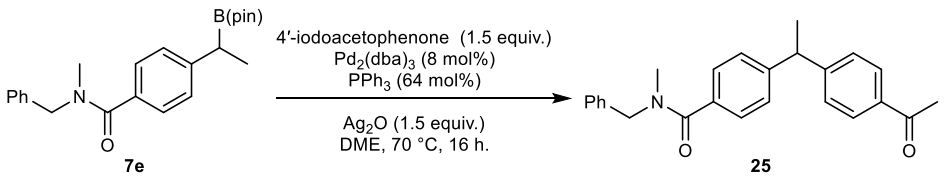
^{13}C NMR (101 MHz, DMSO): δ 154.6 (C), 130.0 (C), 128.6 (CH), 127.1 (CH), 125.8 (CH), 25.3 (CH_3), 16.9 (CH_3). Due to poor solubility of **11** not all carbon environments were observed.

^{11}B NMR (128 MHz, DMSO) δ 3.9.

^{19}F NMR (377 MHz, DMSO) δ −143.1.

HRMS (ESI): Exact mass calcd. for $[C_{17}H_{18}BF_3NO]^-$ $[M]^-$: 320.1434, found: 320.1447.

4-[1-(4-Acetylphenyl)ethyl]-*N*-benzyl-*N*-methylbenzamide (25)



Boronic ester **7e** (0.100 g, 0.260 mmol), tris(dibenzylideneacetone)dipalladium (0.019 g, 0.021 mmol), triphenylphosphine (0.044 g, 0.17 mmol), and silver(I) oxide (0.092 g, 0.40 mmol) were added to a Schlenk tube under nitrogen. Dimethoxyethane (2.6 ml) and 4′-iodoacetophenone (0.097 g, 0.40 mmol) were added, and the mixture was stirred at 70 °C for 16 h. The mixture was cooled to room temperature, filtered through a plug of silica eluting with EtOAc (10 ml), and concentrated *in vacuo*. The crude material was purified by silica gel chromatography (4:3:1 heptane/EtOAc/EtOH) to give *ketone* **25** (0.0656 g, 67%) as yellow oil.

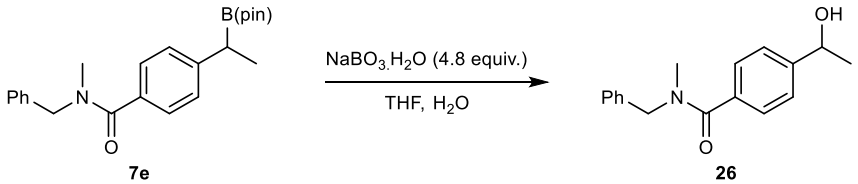
IR: 2967, 2927, 1679, 1627, 1603, 1397, 1266, 1069, 727, 697 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.82 (m, 2H, Ar**H**), 7.44 – 7.37 (m, 2H, Ar**H**), 7.39 – 7.10 (m, 9H, Ar**H**), 4.74 (s, 1H, C**H**$_A$H$_B$), 4.52 (s, 1H, CH$_A$**H**$_B$), 4.21 (br s, 1H, C**H**), 3.09 – 2.78 (m, 3H, C**H**$_3$), 2.56 (s, 3H, CC**H**$_3$), 1.64 (br s, 3H, CHC**H**$_3$).

^{13}C NMR (101 MHz, CDCl3): δ 197.6 (C), 172.1 (C, rotamer), 171.3 (C, rotamer), 151.2 (C), 147.0 (C), 136.9 (C, rotamer), 136.6 (C, rotamer), 135.3 (C), 134.2 (C), 128.7 (CH), 128.7 (CH), 128.5 (2 × CH), 128.1 (CH), 127.8 (2 × CH), 127.6 (2 × CH), 127.5 (CH), 127.4 (CH), 127.1 (CH), 126.6 (CH), 55.1 (CH_2, rotamer), 50.7 (CH_2, rotamer), 44.6 (CH), 37.0 (CH_3, rotamer), 33.1 (CH_3, rotamer), 26.5 (CH_3), 21.3 (CH_3).

HRMS (ESI): Exact mass calcd. for $[C_{25}H_{25}NNaO_2]^+$ $[M+Na]^+$: 394.1778, found: 394.1792.

***N*-Benzyl-4-(1-hydroxyethyl)-*N*-methylbenzamide (26)**



Boronic ester **7e** (0.103 g, 0.272 mmol) was dissolved in THF (1.3 ml) and a solution of $NaBO_3.H_2O$ (0.132 g, 1.32 mmol) in H_2O (1.3 ml) added, and the mixture was stirred at room temperature for 1.5 h. Saturated aqueous NH_4Cl (10 ml) was added, and the mixture was extracted with EtOAc (3 × 10 ml). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by silica gel chromatography (2:1 EtOAc/hexane) to give *alcohol* **26** (0.0706 g, 97%) as colourless oil.

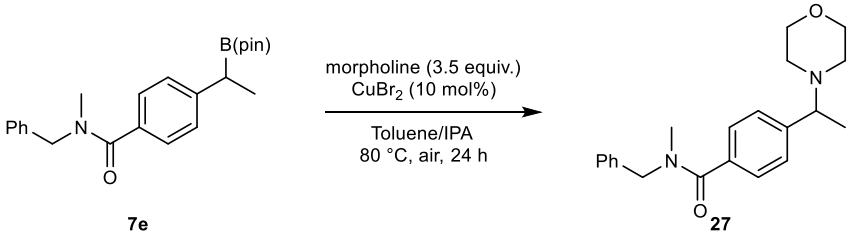
IR: 2971, 2925, 1609, 1399, 1068, 728, 697 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.24 (m, 8H, Ar**H**), 7.19 1 – 7.09 (m, 1H, Ar**H**), 4.83 (s, 1H, C**H**), 4.71 (s, 1H, C**H$_A$**H$_B$), 4.48 (s, 1H, CH$_A$**H$_B$**), 3.10 (s, 1H, O**H**), 3.04 – 2.76 (m, 3H, C**H$_3$**), 1.42 (s, 3H, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.3 (C, rotamer), 171.5 (C, rotamer), 147.8 (C), 136.8 (C, rotamer), 136.4 (C, rotamer), 134.6 (C), 128.7 (CH), 128.6 (CH), 128.0 (CH), 127.5 (CH), 127.0 (CH), 126.8 (CH), 126.6 (CH), 125.3 (CH), 125.2 (CH), 69.5 (CH), 55.1 (CH_2, rotamer), 50.7 (CH_2, rotamer), 36.9 (CH_3, rotamer), 33.1 (CH_3, rotamer), 25.2 (CH_3).

HRMS (ESI): Exact mass calcd. for $[C_{17}H_{20}NO_2]^+$ $[M+H]^+$: 270.1488, found: 270.1493.

N-benzyl-N-methyl-4-(1-morpholine-4-ylethyl)benzamide (27)



7e 27

Isopropyl alcohol (0.38 mL) and toluene (0.38 mL) were added to a flask containing the boronic ester **7e** (0.200 g, 0.530 mmol), morpholine (0.16 ml, 1.85 mmol) and $CuBr_2$ (0.012 g, 0.050 mmol), and the mixture was stirred under air at 80 °C for 24 h. The mixture was cooled to room temperature, passed through a plug of silica eluting with Et_2O, and concentrated *in vacuo*. The crude material was purified by silica gel chromatography (4:3:1 heptane/EtOAc/EtOH) to give *amine* **27** (0.139 g, 78%) as yellow oil.

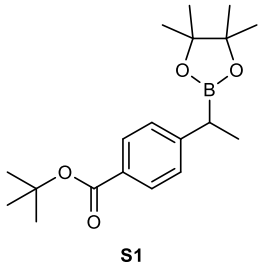
IR: 2957, 2852, 2806, 1628, 1396, 1115, 1067, 946, 727, 697 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H, Ar**H**), 7.37 – 7.22 (m, 6H, Ar**H**), 7.19 – 7.10 (m, 1H, Ar**H**), 4.73 (s, 1H, PhC**H$_A$**H$_B$), 4.52 (s, 1H, PhCH$_A$**H$_B$**), 3.72 – 3.58 (m, 4H, 2 × OC**H$_2$**), 3.29 (s, 1H, C**H**), 3.05 – 2.80 (m, 3H, NC**H$_3$**), 2.50-2.39 (m, 2H, 2 × NC**H$_2$**CH$_2$), 2.37 – 2.27 (m, 2H, 2 × NC**H$_2$**CH$_2$), 1.35 – 1.25 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.1 (C, rotamer), 171.3 (C, rotamer), 145.7 (C), 136.9 (C, rotamer), 136.5 (C, rotamer), 134.7 (C), 128.6 (2 × CH), 127.9 (CH) 127.4 (3 × CH), 127.0 (CH), 126.8 (CH), 126.7 (CH), 66.9 (2 × CH_2), 64.9 (CH), 55.1 (CH_2, rotamer), 51.1 (2 × CH_2), 50.6 (CH_2, rotamer), 36.9 (CH_3, rotamer), 33.0 (CH_3, rotamer), 19.5 (CH_3).

HRMS (ESI): Exact mass calcd. for $[C_{21}H_{27}N_2O_2]^+$ $[M+H]^+$: 339.2067, found: 339.2072.

7. Synthesis of Miscellaneous Materials



Methyl 4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) ethyl] benzoate (S1)

The title compound was prepared according to **General Procedure 2** using copper (I) chloride (0.0033 g, 0.033 mmol), potassium tert-butoxide (0.0089 g, 0.079 mmol), 1,2-bis(diphenylphosphino)benzene (0.015 g, 0.033 mmol), 1,1-dimethylethyl 4-ethenylbenzoate (0.270 g, 1.32 mmol), anhydrous toluene (1.2 ml) and pinacolborane (0.23 ml, 1.6 mmol). The crude material was purified by column chromatography (1:7 EtOAc/hexane) to give *boronic ester* **S1** (0.305 g, 69%) as colourless oil.

IR: 2977, 1705, 1321, 1290, 1140, 1107, 848, 716 cm^{-1}.

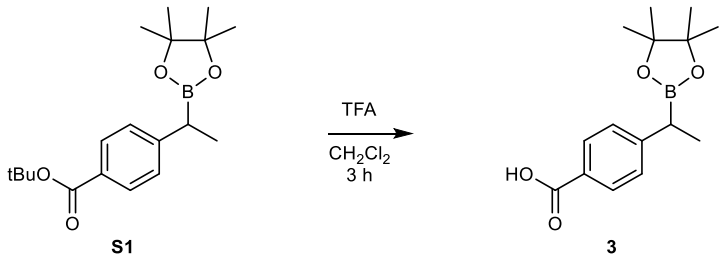
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.84 (m, 2H, Ar**H**), 7.28 – 7.21 (m, 2H, Ar**H**), 2.49 (q, *J* = 7.4 Hz, 1H, C**H**), 1.58 (s, 9H, 3 × COCC**H$_3$**), 1.34 (d, *J* = 7.4 Hz, 3H, CHC**H$_3$**), 1.20 (s, 6H, 2 × BOCC**H$_3$**), 1.18 (s, 6H, 2 × BOCC**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0 (C), 150.2 (C), 129.5 (2 × CH), 128.9 (C), 127.5 (2 × CH_2), 83.4 (2 × C), 80.5 (C), 28.2 (3 × CH_3), 24.6 (2 × CH_3), 24.5 (2 × CH_3), 16.6 (CH_3).

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.5.

HRMS (ESI): Exact mass calcd. for $[C_{19}H_{29}BNaO_4]^+$ $[M+Na]^+$: 355.2057, found: 355.2049. (Base peak: calcd. for $[C_{19}H_{21}BO_4]^+$ $[M - tBu + H_2]^+$: 277.1606, found: 277.1606.)

4-[1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl) ethyl] benzoic acid (3)



Boronic ester **S1** (0.50 g, 1.5 mmol) was dissolved in CH_2Cl_2 (10 ml) and TFA (1 ml, 13.1 mmol) was added. The resulting solution was stirred for 3 h under N_2, after which the mixture was concentrated *in vacuo*. Toluene was added, and the mixture was concentrated *in vacuo* to give boronic ester **3** (0.315 g, 76%) as yellow solid.

m.p. = 116 – 120 °C.

IR: 2977, 1676, 1317, 1281, 1139, 855 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 – 7.97 (m, 2H, Ar**H**), 7.35 – 7.30 (m, 2H, Ar**H**), 2.54 (q, *J* = 7.4 Hz, 1H, C**H**), 1.36 (d, *J* = 7.4 Hz, 3H, CHC**H$_3$**), 1.21 (s, 6H, 2 × CC**H$_3$**), 1.20 (s, 6H, 2 × CC**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.6 (C), 151.8 (C), 130.3 (2 × CH_2), 127.8 (2 × CH_2), 126.1 (C), 83.6 (2 × C), 24.6 (2 × CH_3), 24.5 (2 × CH_3), 16.4 (CH_3).

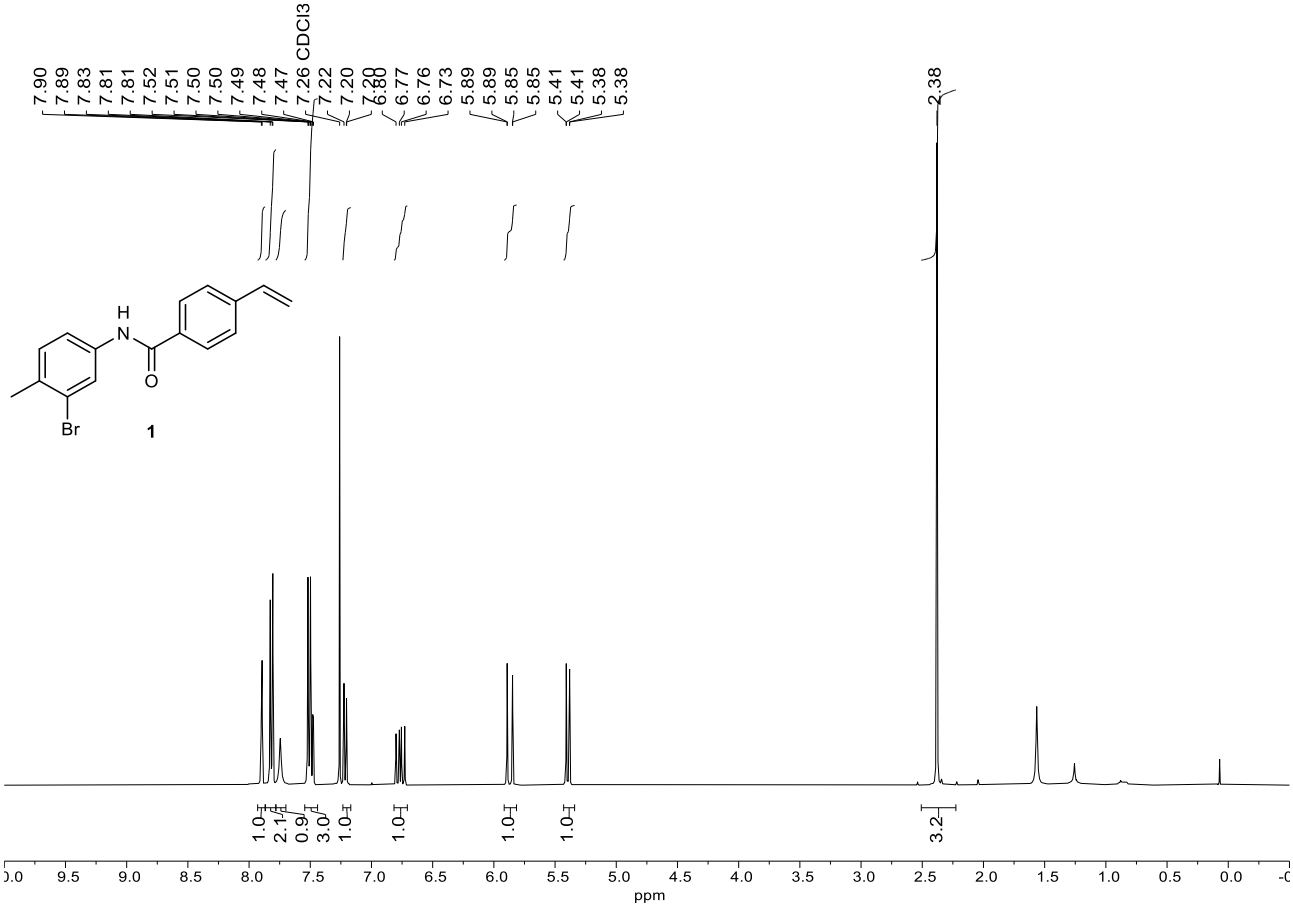
^{11}B NMR (128 MHz, $CDCl_3$): δ 34.1.

HRMS (ESI): Exact mass calcd. for $[C_{15}H_{22}BO_4]^+$ $[M+H]^+$: 277.1606, found: 277.1620.

8. NMR Spectra

8.1. Alkene Substrates

^{1}H NMR:



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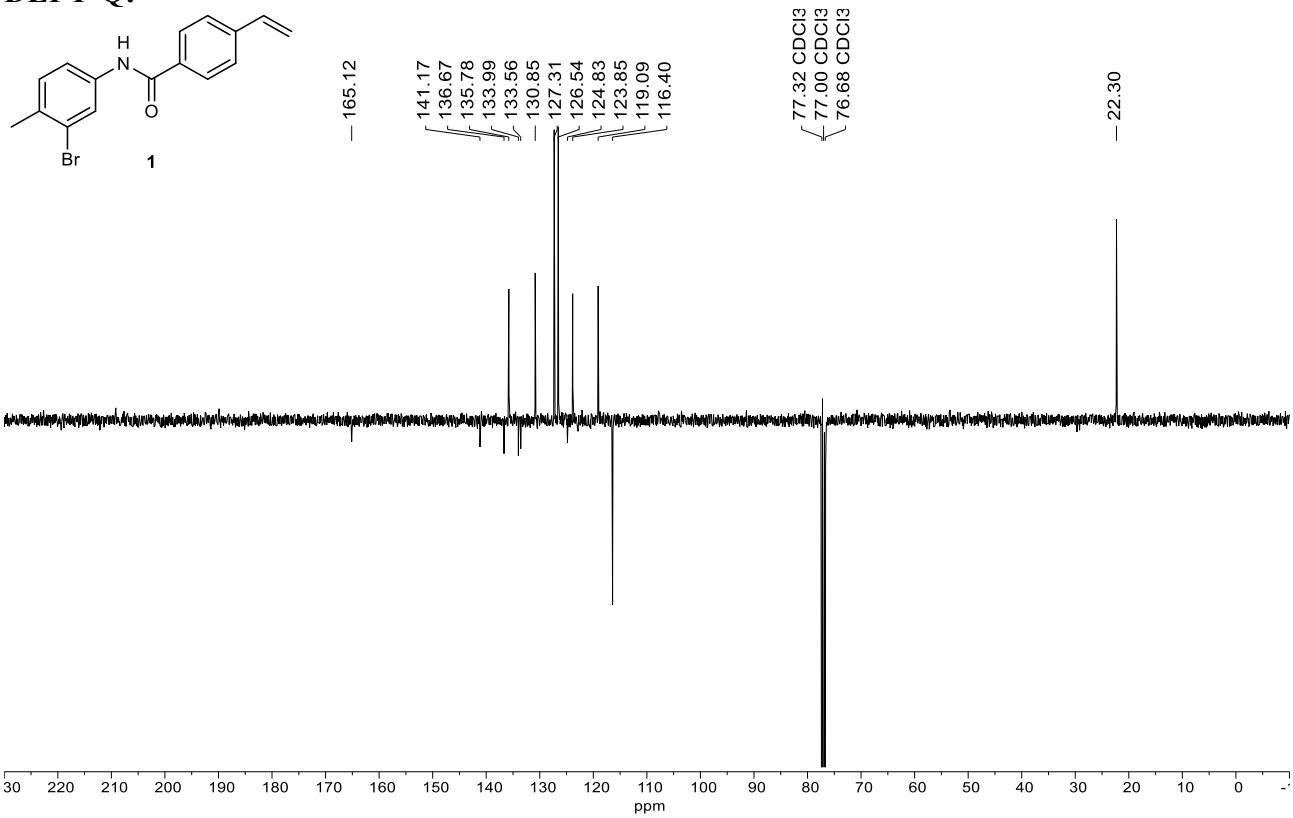

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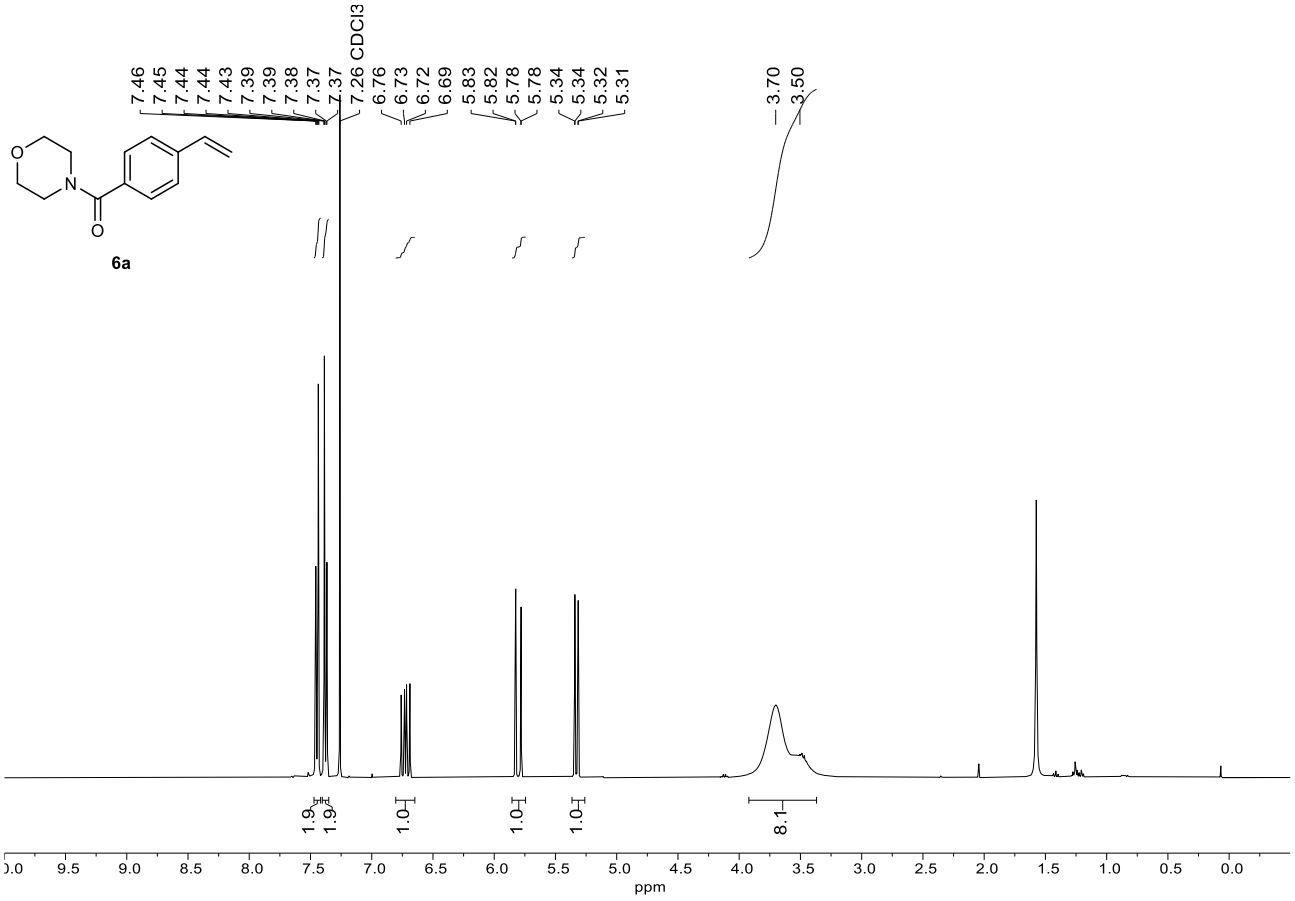
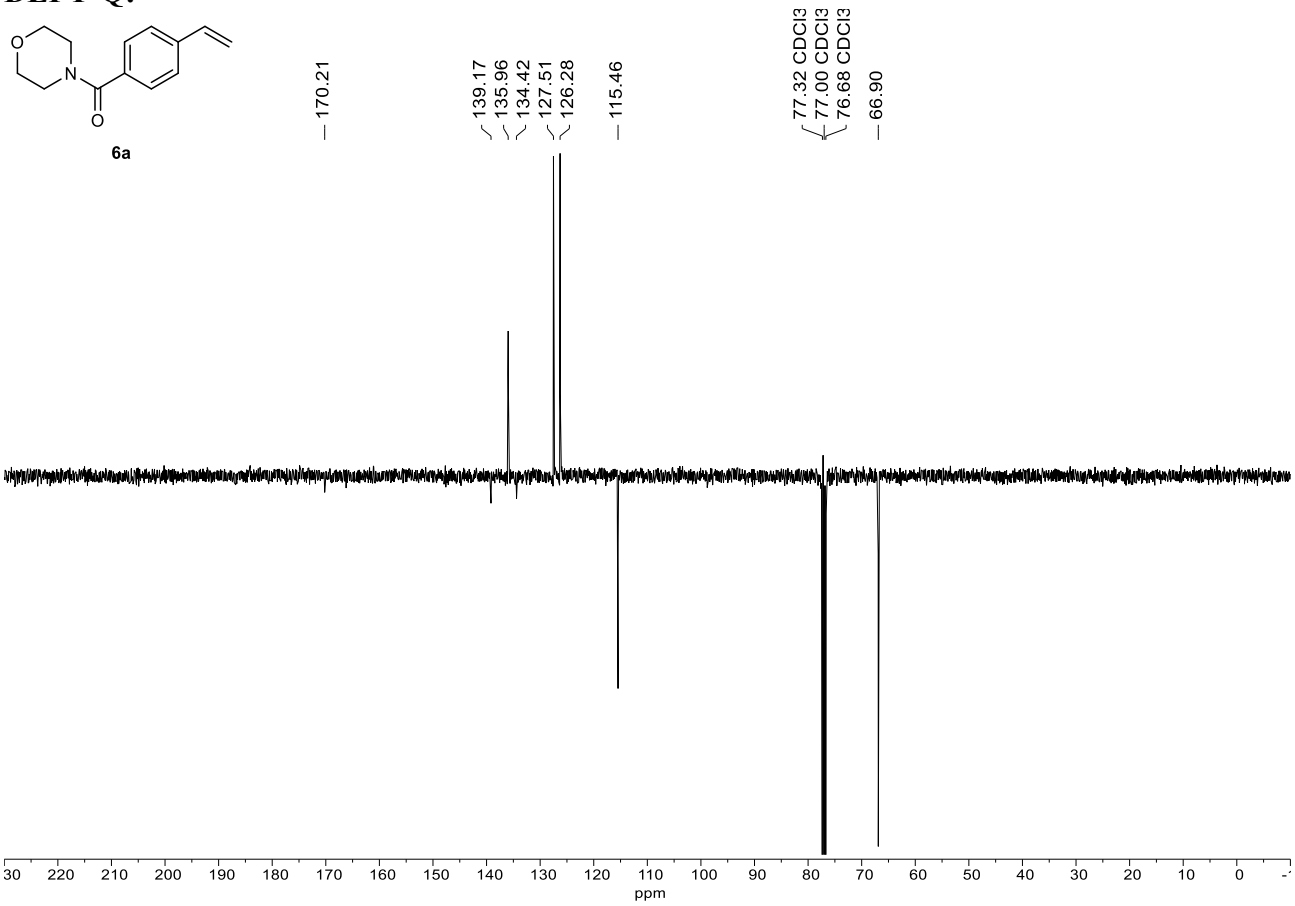
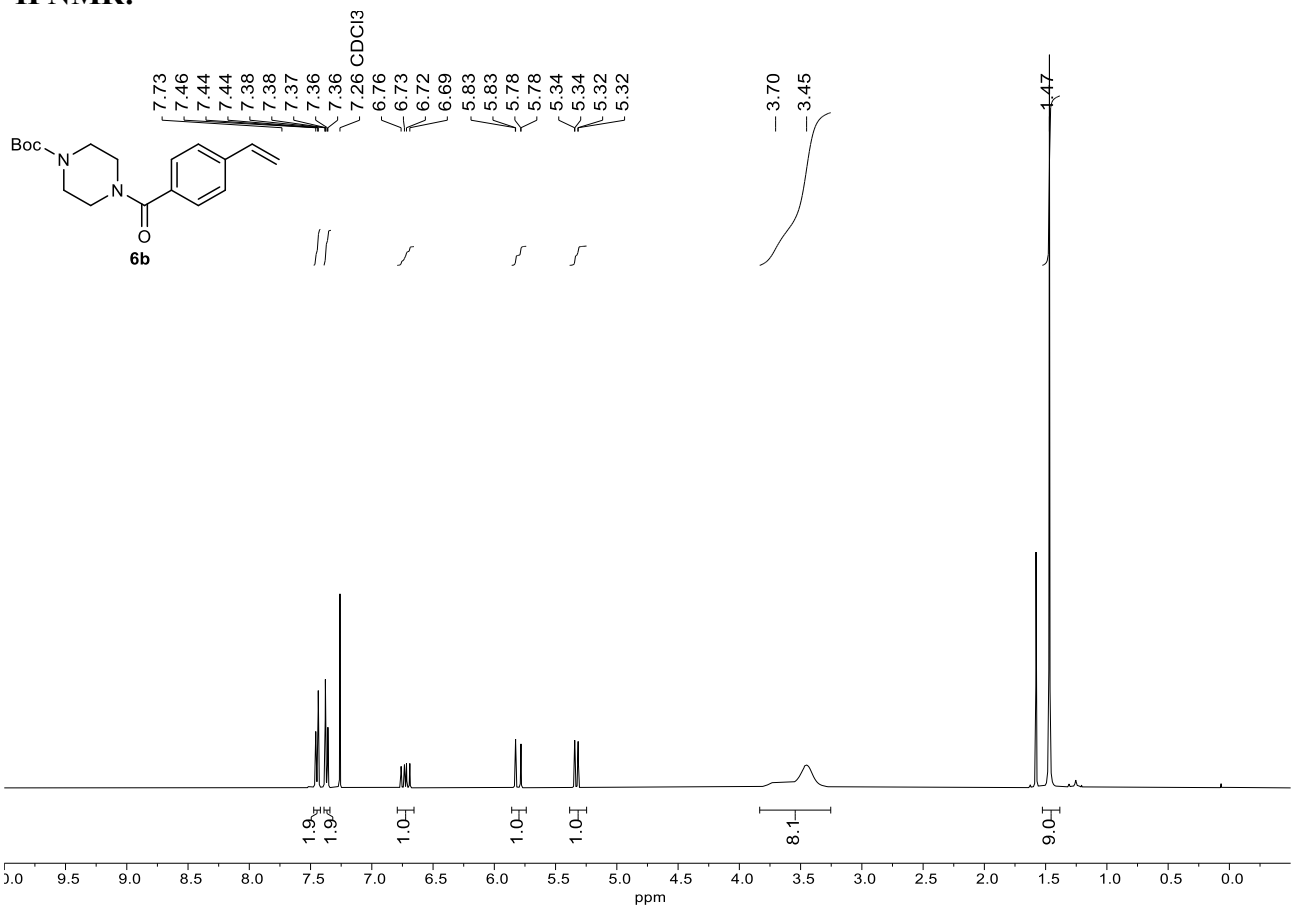

7.46
7.45
7.44
7.44
7.43
7.39
7.39
7.38
7.37
7.37
7.26 CDCl3
6.76
6.73
6.72
6.69
5.83
5.82
5.78
5.78
5.34
5.34
5.32
5.31
3.70
3.50
6a
1.9
1.9
1.0
1.0
1.0
8.1
ppm

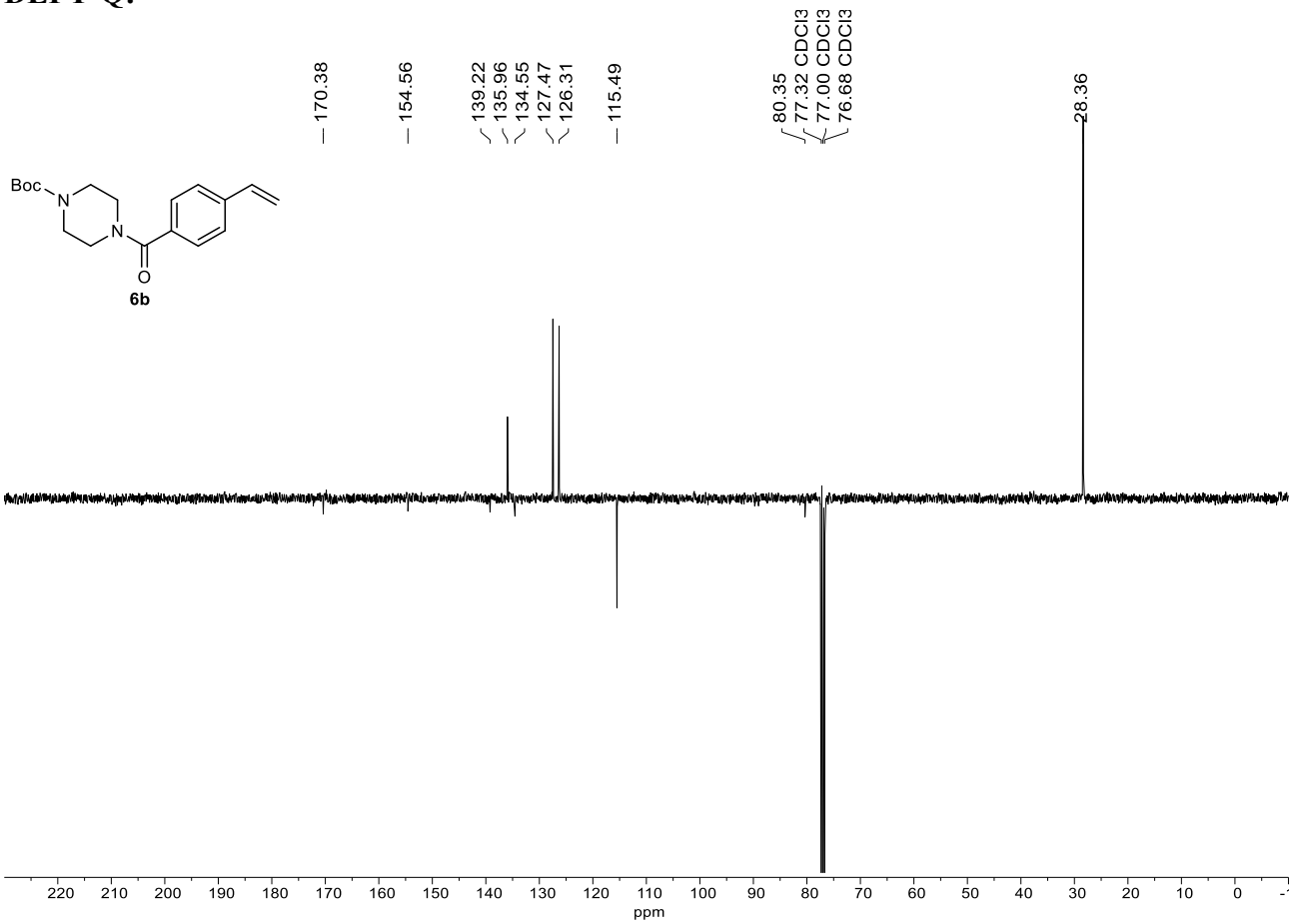
DEPT-Q:


170.21
139.17
135.96
134.42
127.51
126.28
115.46
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
66.90
6a
ppm

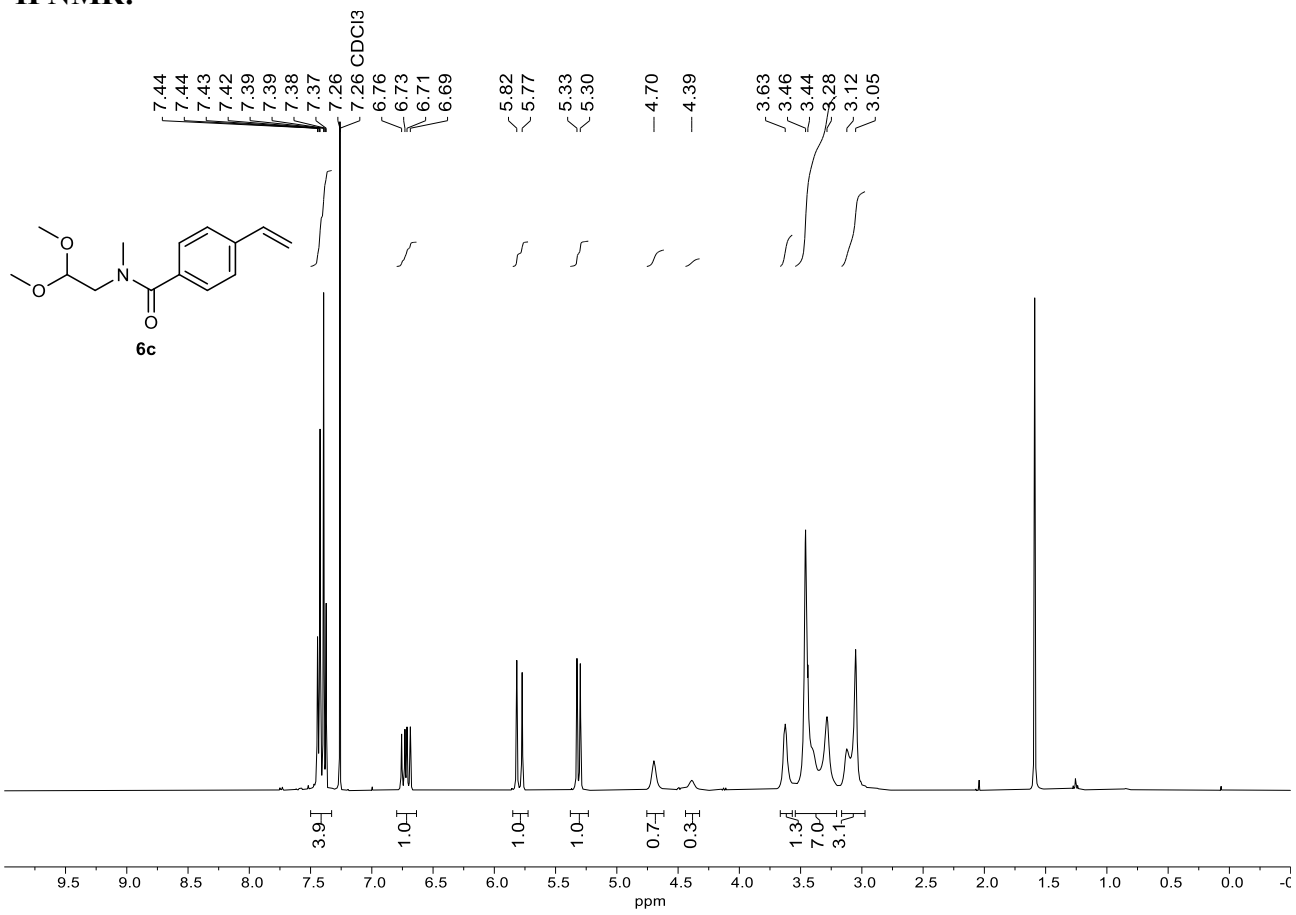
^{1}H NMR:


7.73
7.46
7.44
7.44
7.38
7.38
7.37
7.36
7.36
7.26 CDCl3
6.76
6.73
6.72
6.69
5.83
5.83
5.78
5.78
5.34
5.34
5.32
5.32
3.70
3.45
1.47
Boc
N
N
O
6b
1.9
1.9
1.0
1.0
1.0
8.1
9.0
ppm

DEPT-Q:


170.38
154.56
139.22
135.96
134.55
127.47
126.31
115.49
80.35
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
28.36
Boc
N
N
O
6b
ppm

^{1}H NMR:


7.44
7.44
7.43
7.42
7.39
7.39
7.38
7.37
7.26 CDCl3
6.76
6.73
6.71
6.69
5.82
5.77
5.33
5.30
4.70
4.39
3.63
3.46
3.44
3.28
3.12
3.05
6c
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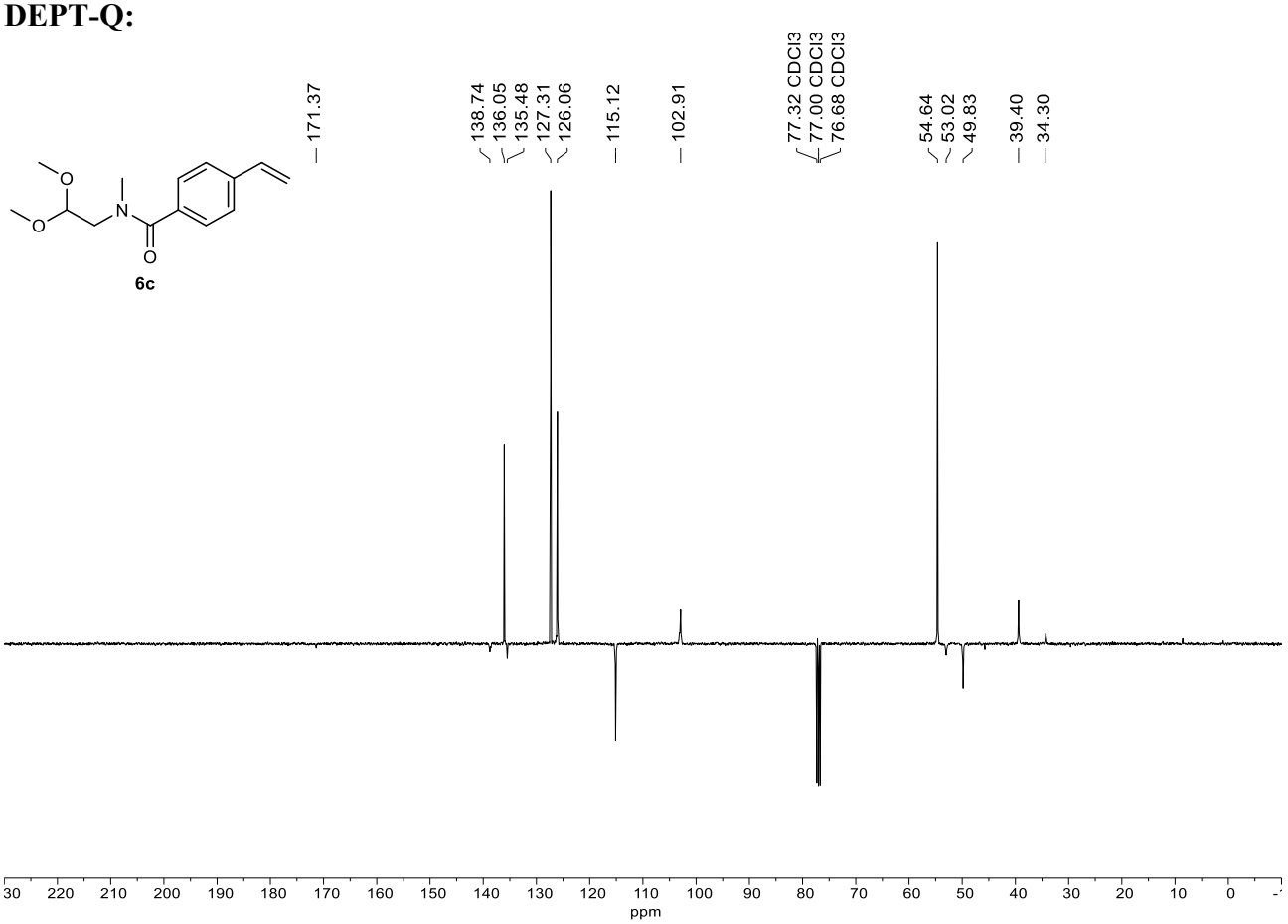
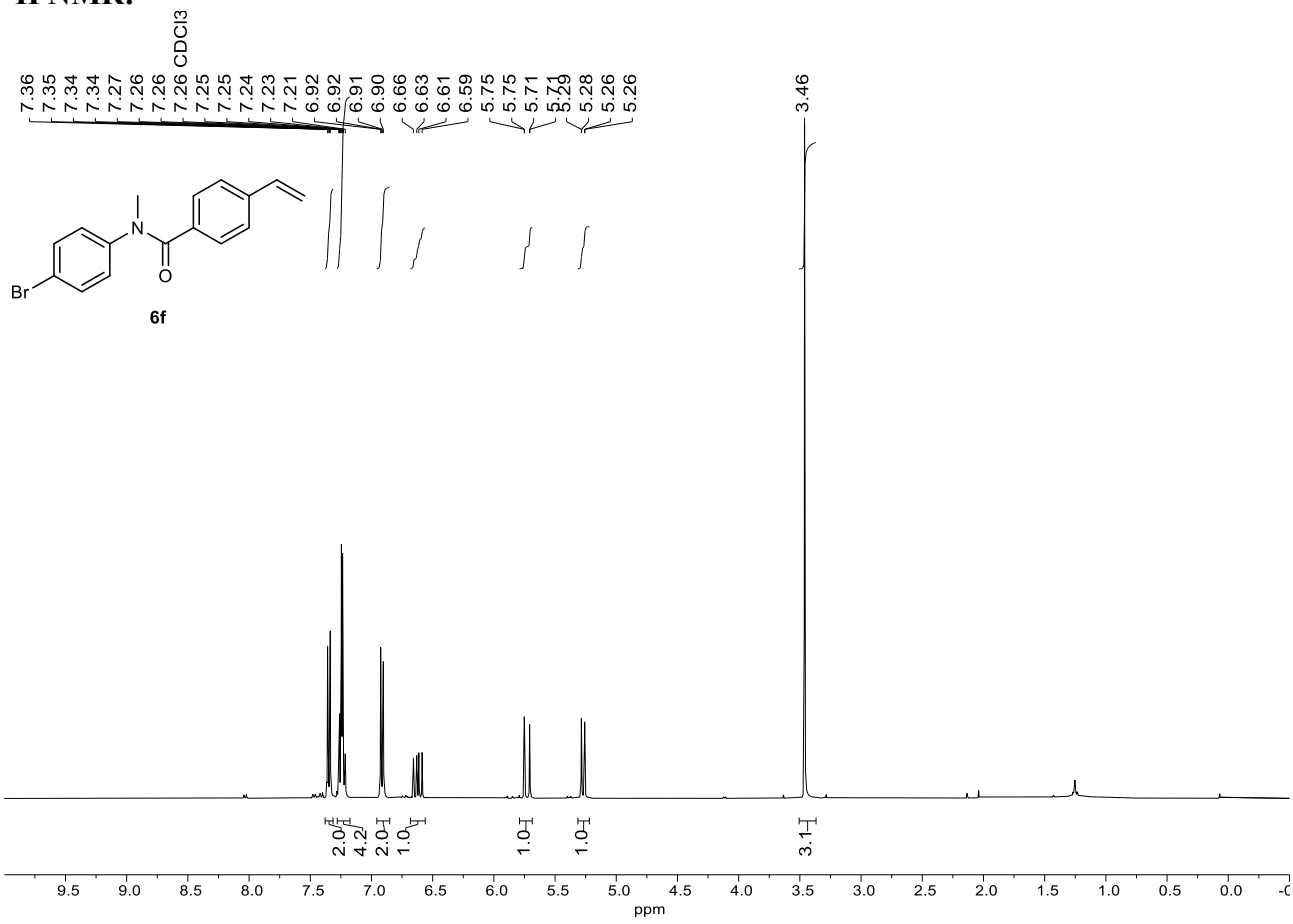
1.0
1.0
0.7
0.3
1.3
7.0
3.1
ppm

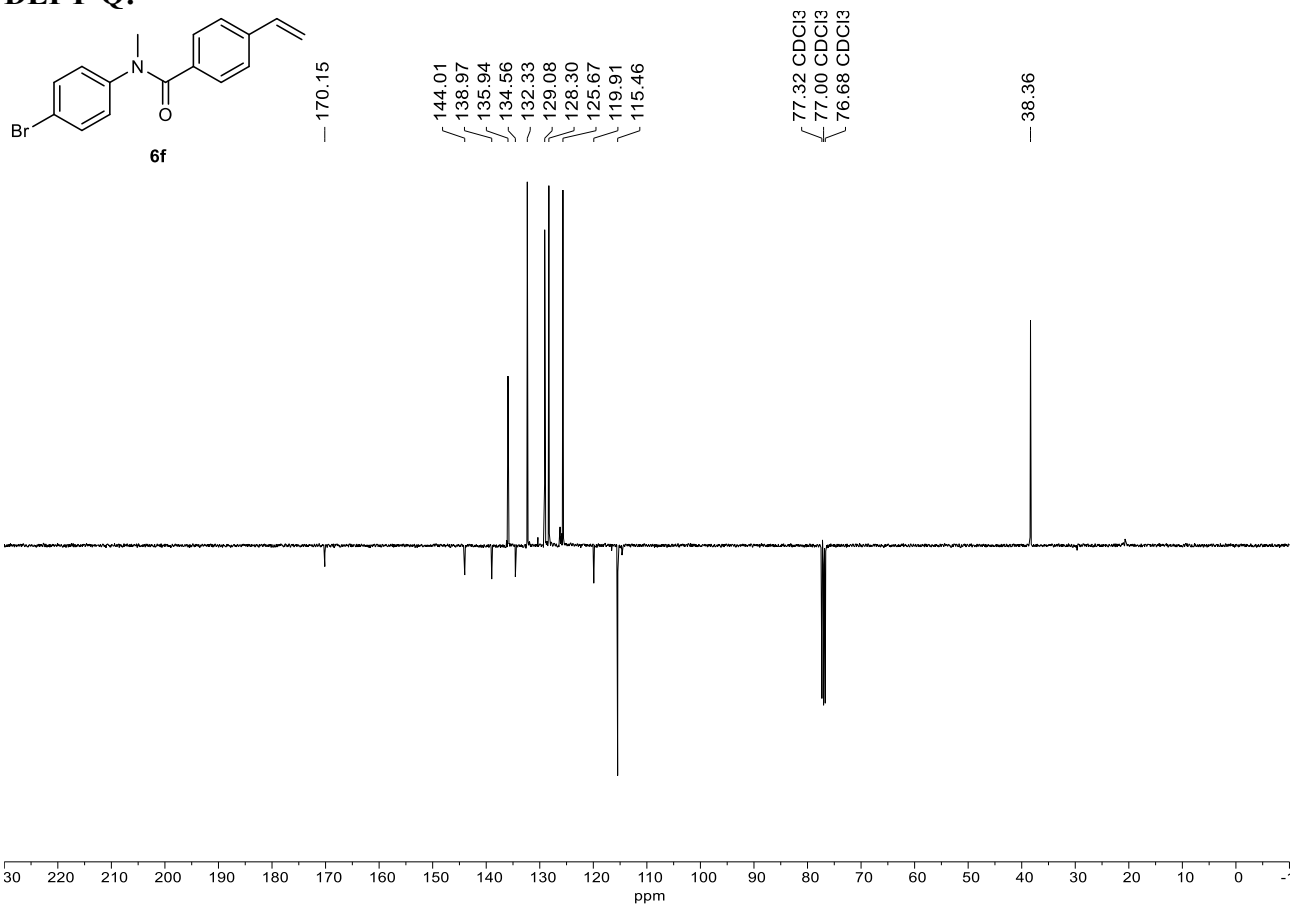
DEPT-Q:


171.37
138.74
136.05
135.48
127.31
126.06
115.12
102.91
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
54.64
53.02
49.83
39.40
34.30
6c
ppm

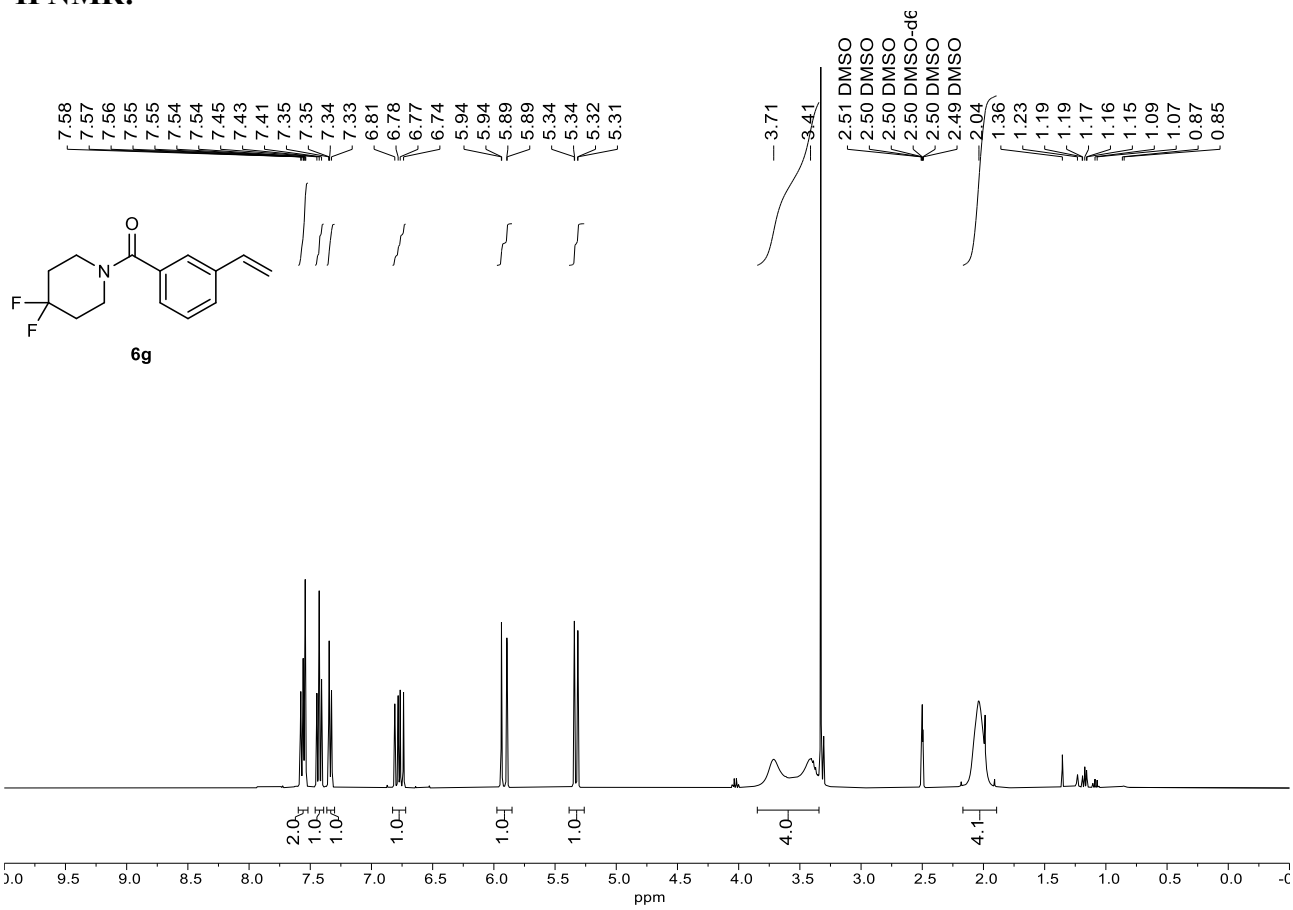
^{1}H NMR:


7.36
7.35
7.34
7.34
7.27
7.26
7.26
7.26 CDCl3
7.25
7.25
7.24
7.23
7.21
6.92
6.92
6.91
6.90
6.66
6.63
6.61
6.59
5.75
5.75
5.71
5.71
5.29
5.28
5.26
5.26
3.46
Br
N
O
6f
2.0
4.2
2.0
1.0
1.0
1.0
3.1
ppm

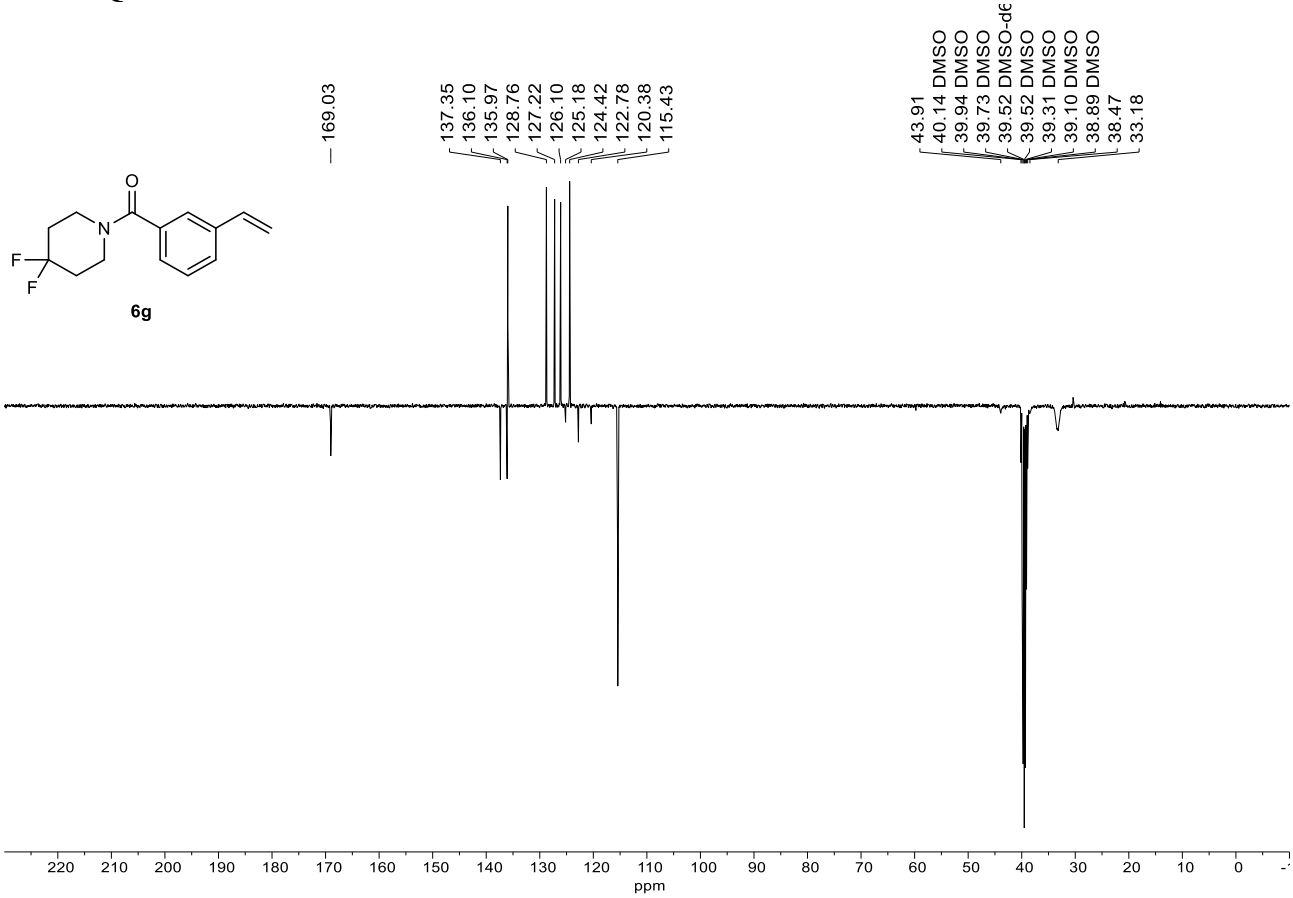
DEPT-Q:


Br
N
O
6f
170.15
144.01
138.97
135.94
134.56
132.33
129.08
128.30
125.67
119.91
115.46
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.36
ppm

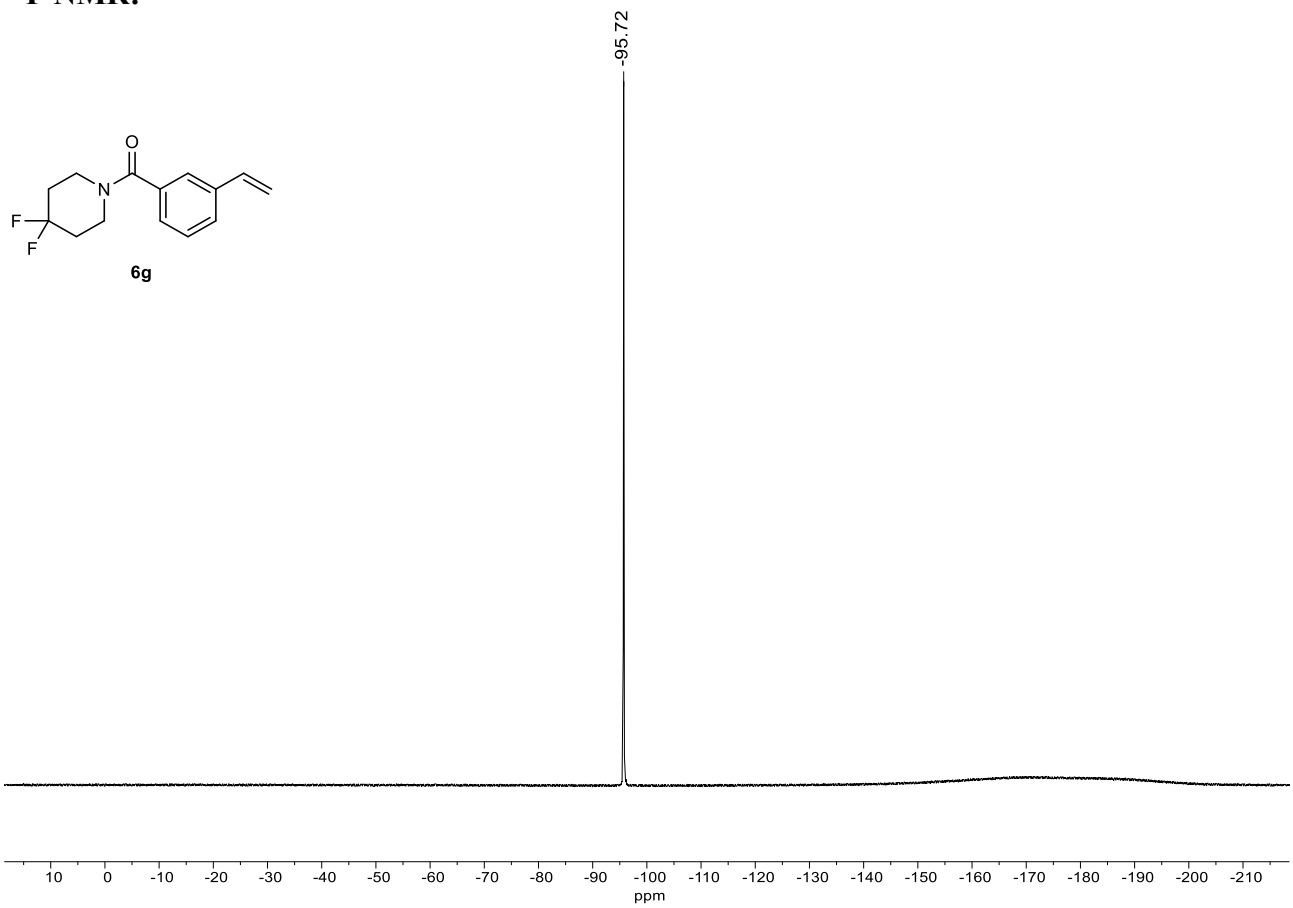
^{1}H NMR:


7.58
7.57
7.56
7.55
7.55
7.54
7.54
7.45
7.43
7.41
7.35
7.35
7.34
7.33
6.81
6.78
6.77
6.74
5.94
5.94
5.89
5.89
5.34
5.34
5.32
5.31
3.71
3.41
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO-d6
2.50 DMSO
2.49 DMSO
2.04
1.36
1.23
1.19
1.19
1.17
1.16
1.15
1.09
1.07
0.87
0.85
O
N
F
F
6g
2.0
1.0
1.0
1.0
1.0
1.0
4.0
4.1
ppm

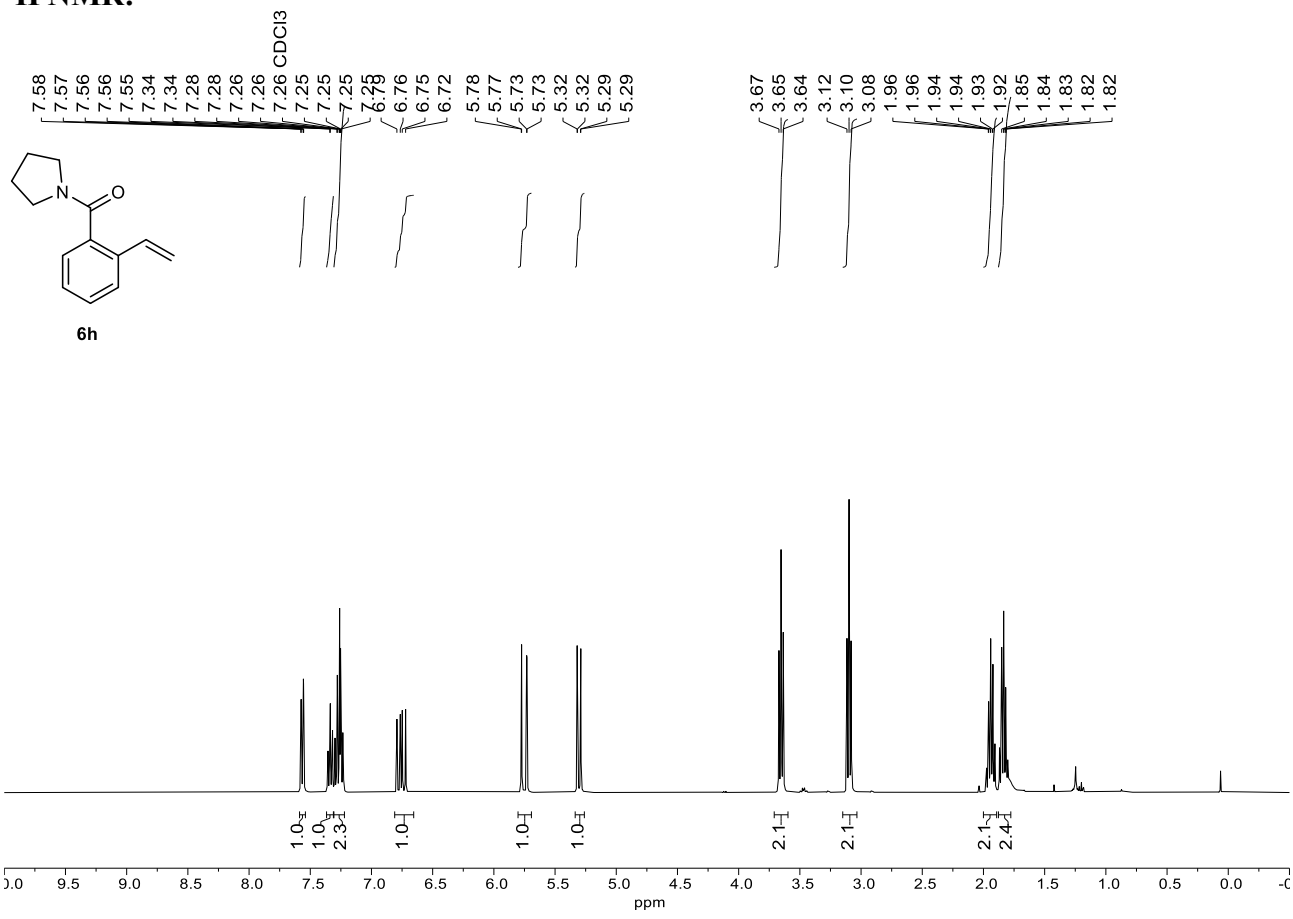
DEPT-Q:


169.03
137.35
136.10
135.97
128.76
127.22
126.10
125.18
124.42
122.78
120.38
115.43
43.91
40.14 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO-d6
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
38.47
33.18
O
N
F
F
6g
ppm

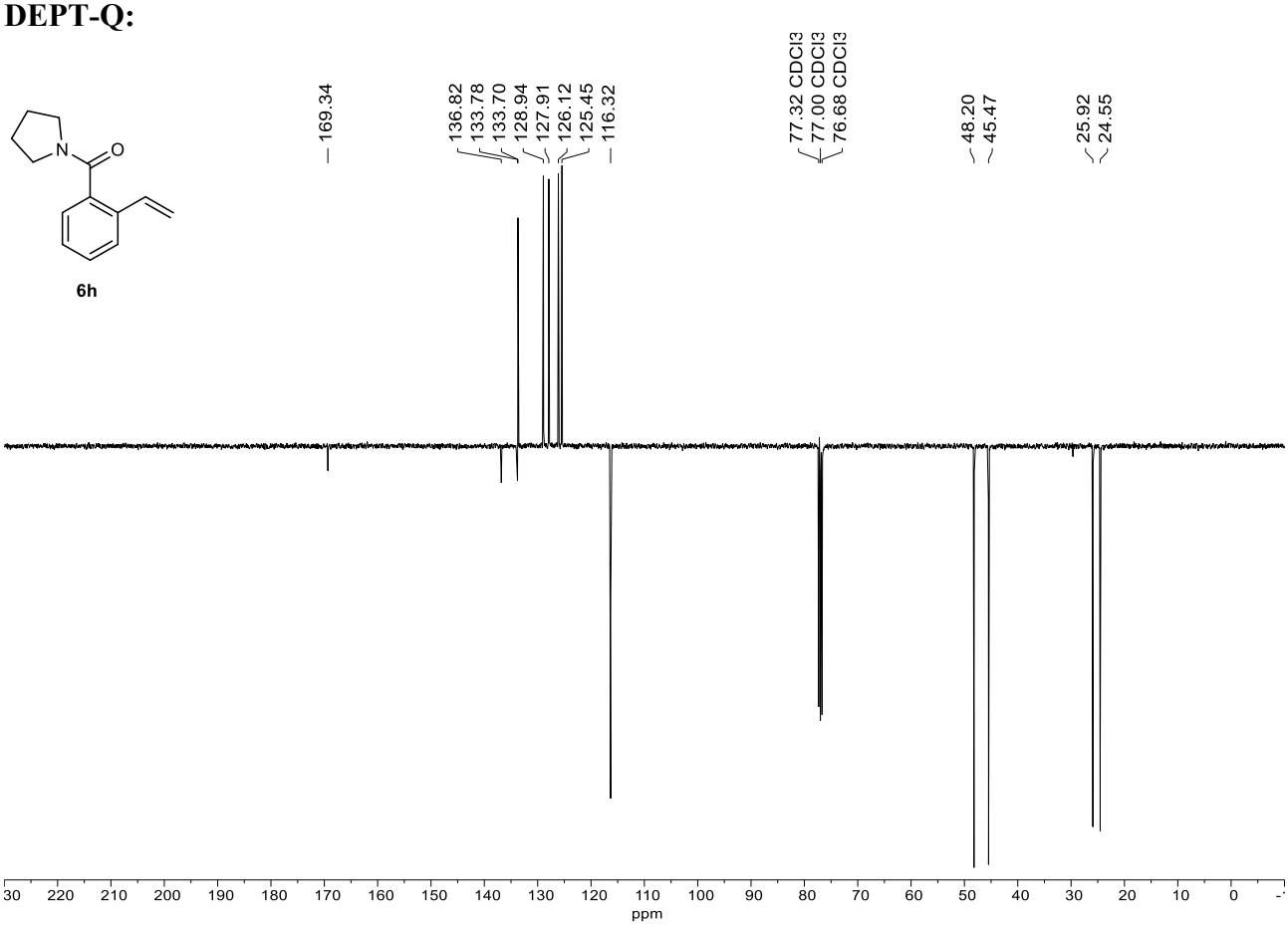
^{19}F NMR:



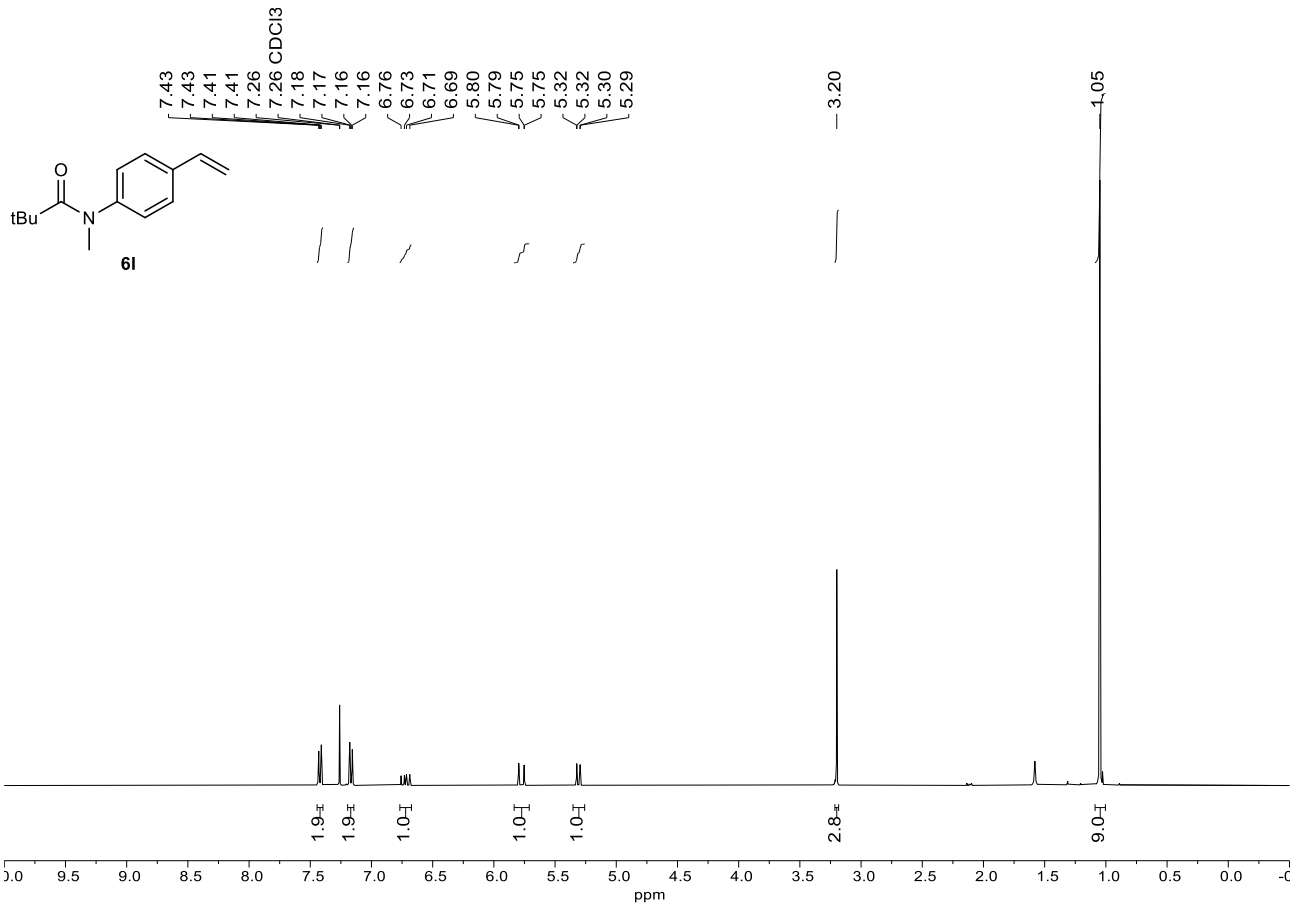
^{1}H NMR:



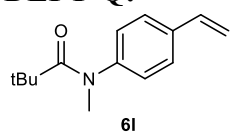
DEPT-Q:


6h
169.34
136.82
133.78
133.70
128.94
127.91
126.12
125.45
116.32
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
48.20
45.47
25.92
24.55
ppm

^{1}H NMR:


6l
7.43
7.43
7.41
7.41
7.26 CDCl3
7.18
7.17
7.16
7.16
6.76
6.73
6.71
6.69
5.80
5.79
5.75
5.75
5.32
5.32
5.30
5.29
3.20
1.05
1.9
1.9
1.0
1.0
1.0
2.8
9.0
ppm

DEPT-Q:

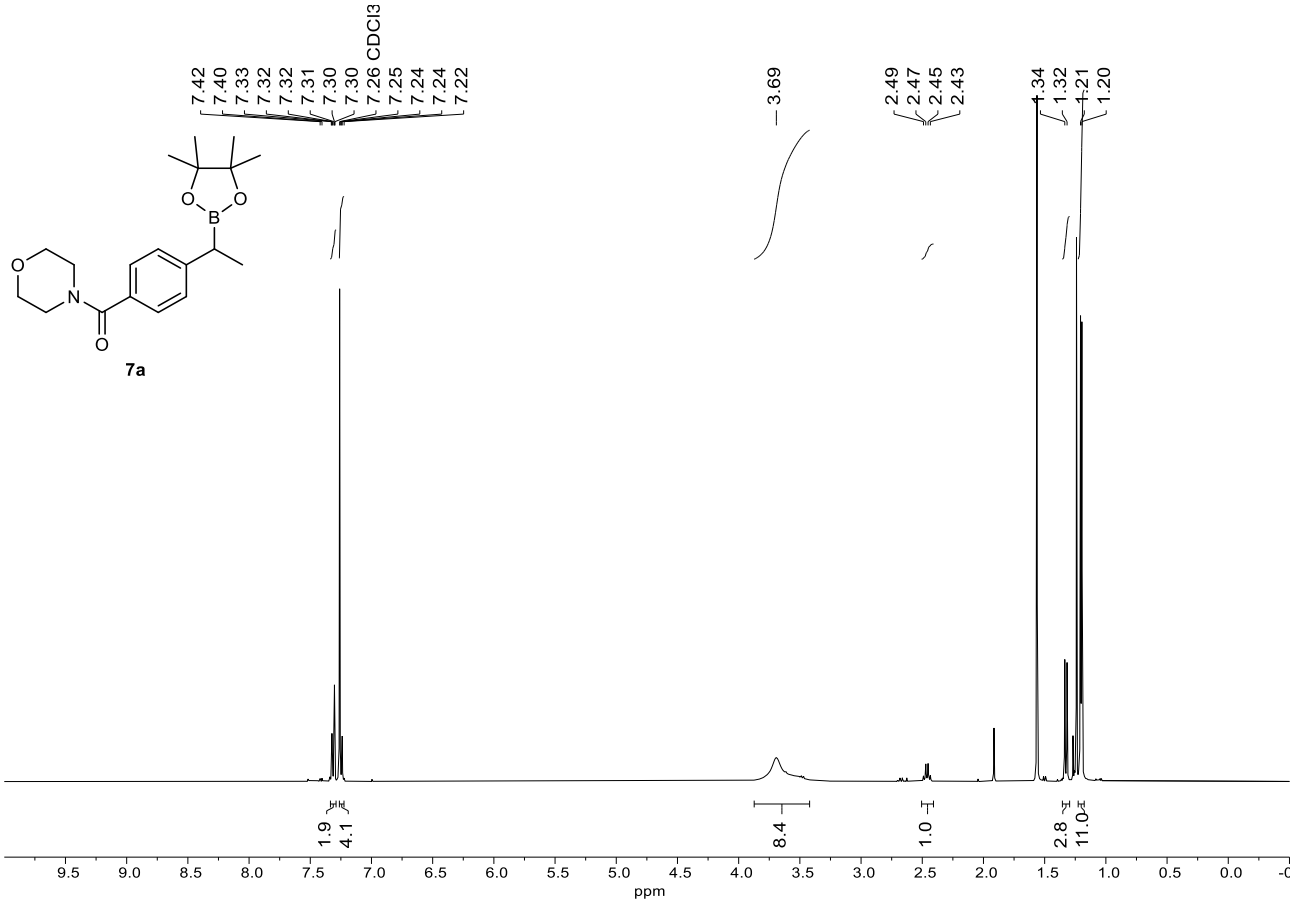

O
tBu
N

6l

178.13
144.62
137.02
135.71
128.83
126.89
114.85
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
41.26
40.79
29.46
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

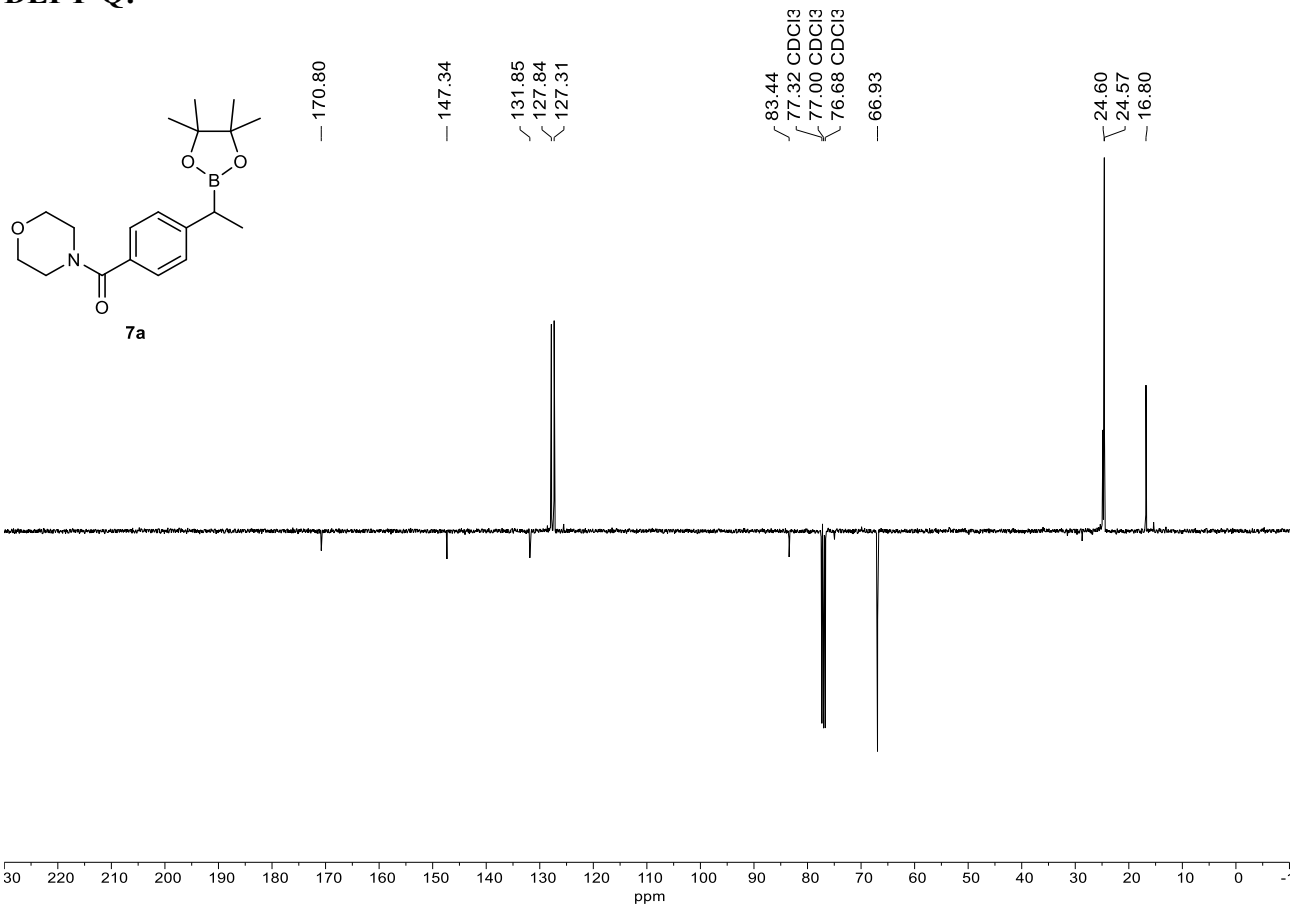
8.2. Cu-Catalysed Hydroboration Products

^{1}H NMR:



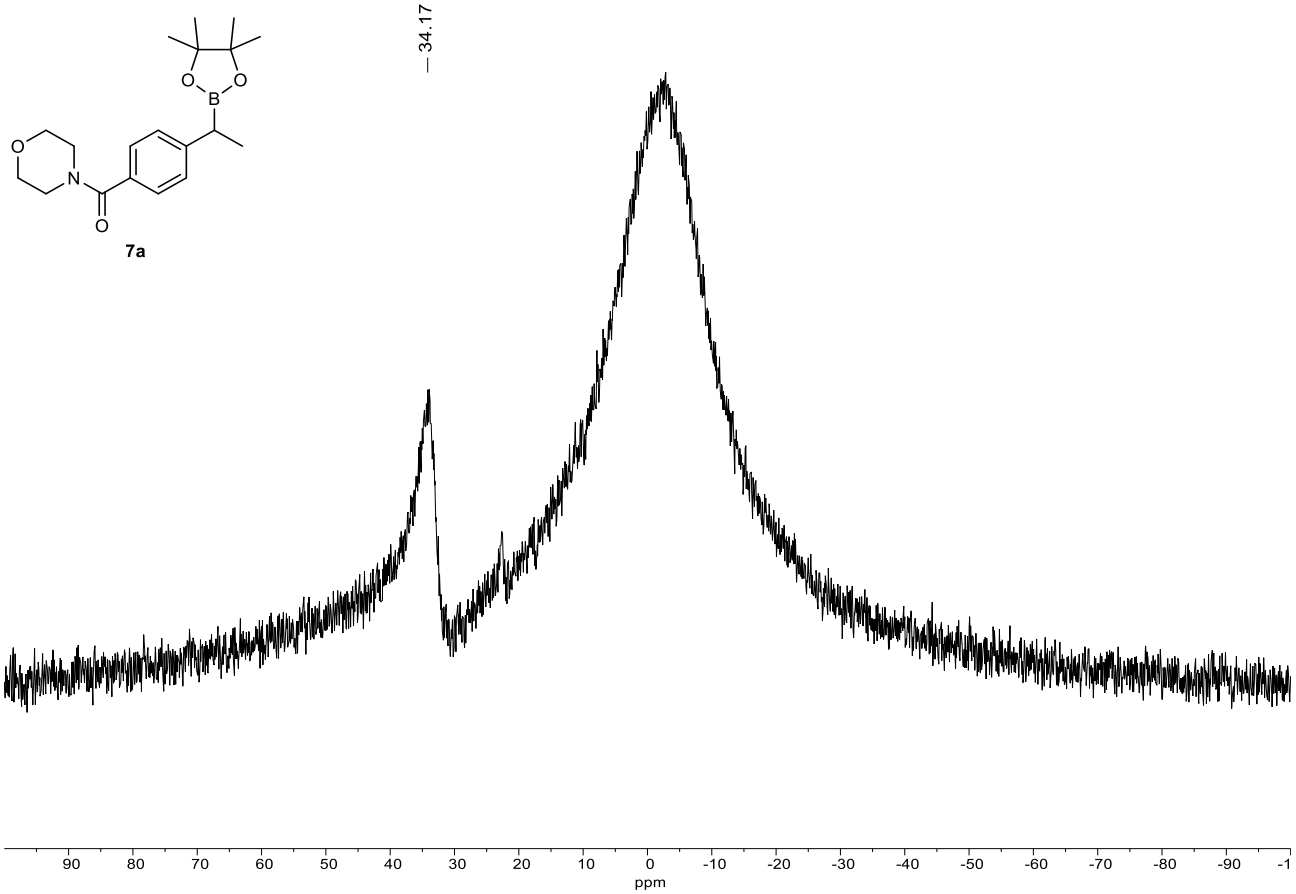
7a

DEPT-Q:

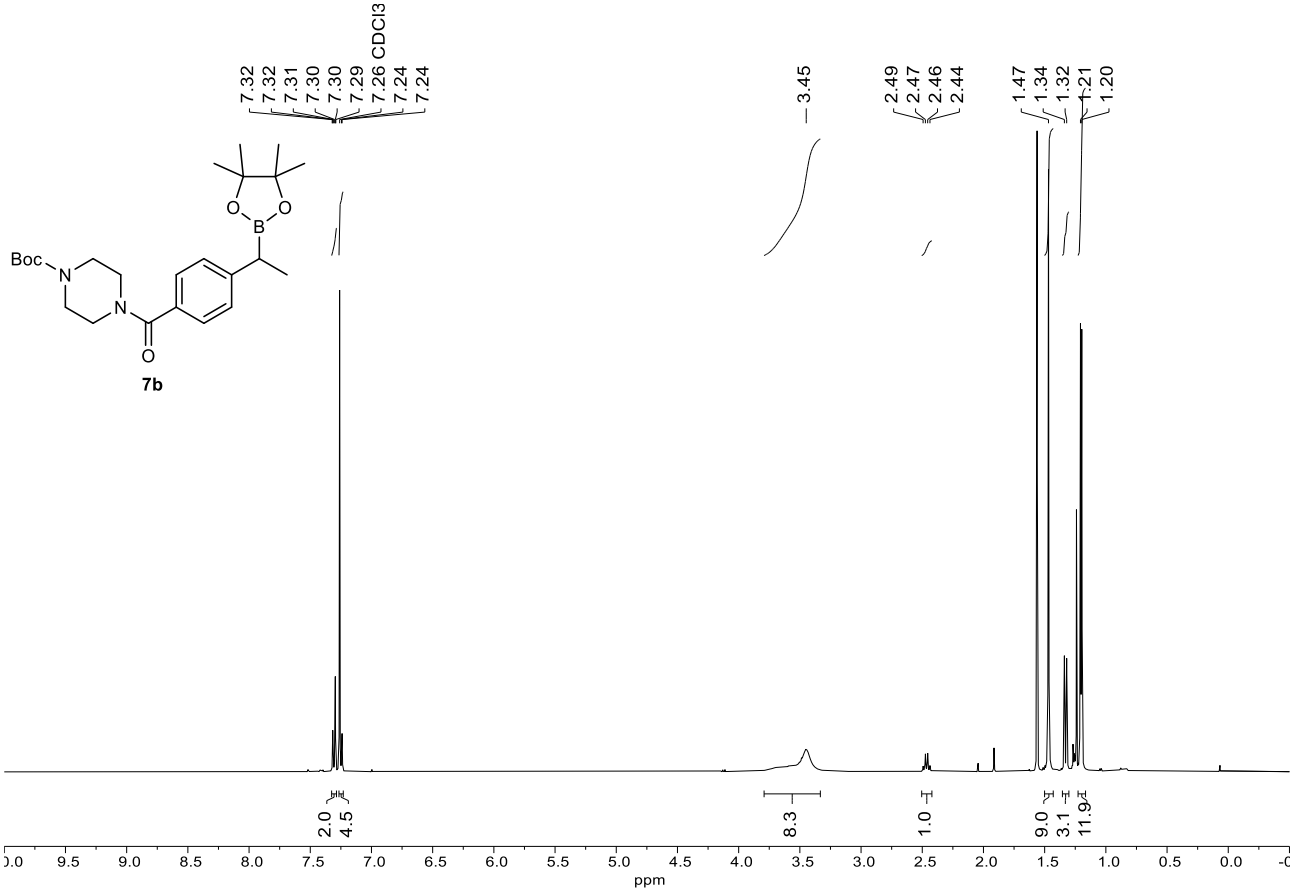


7a

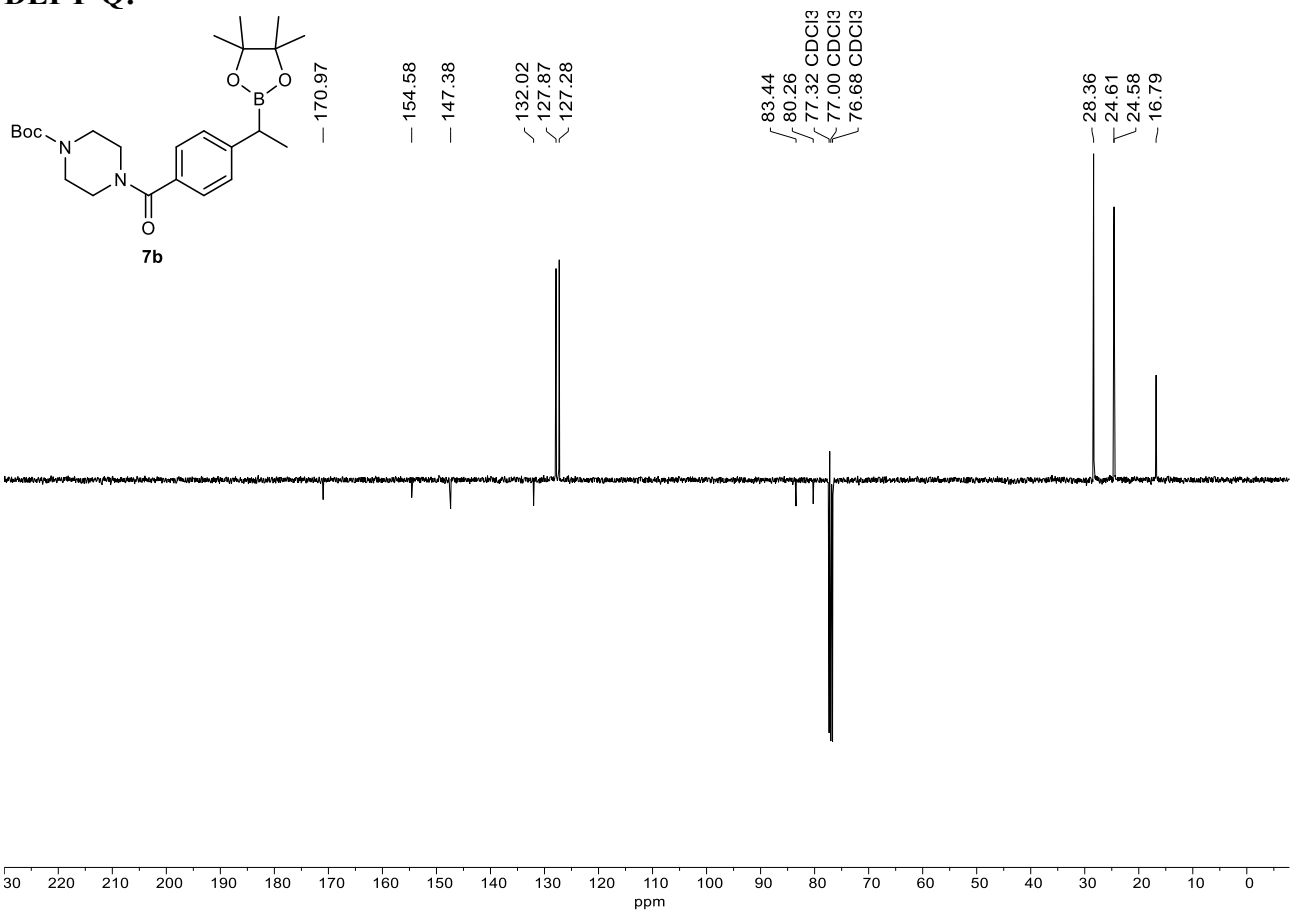
^{11}B NMR:



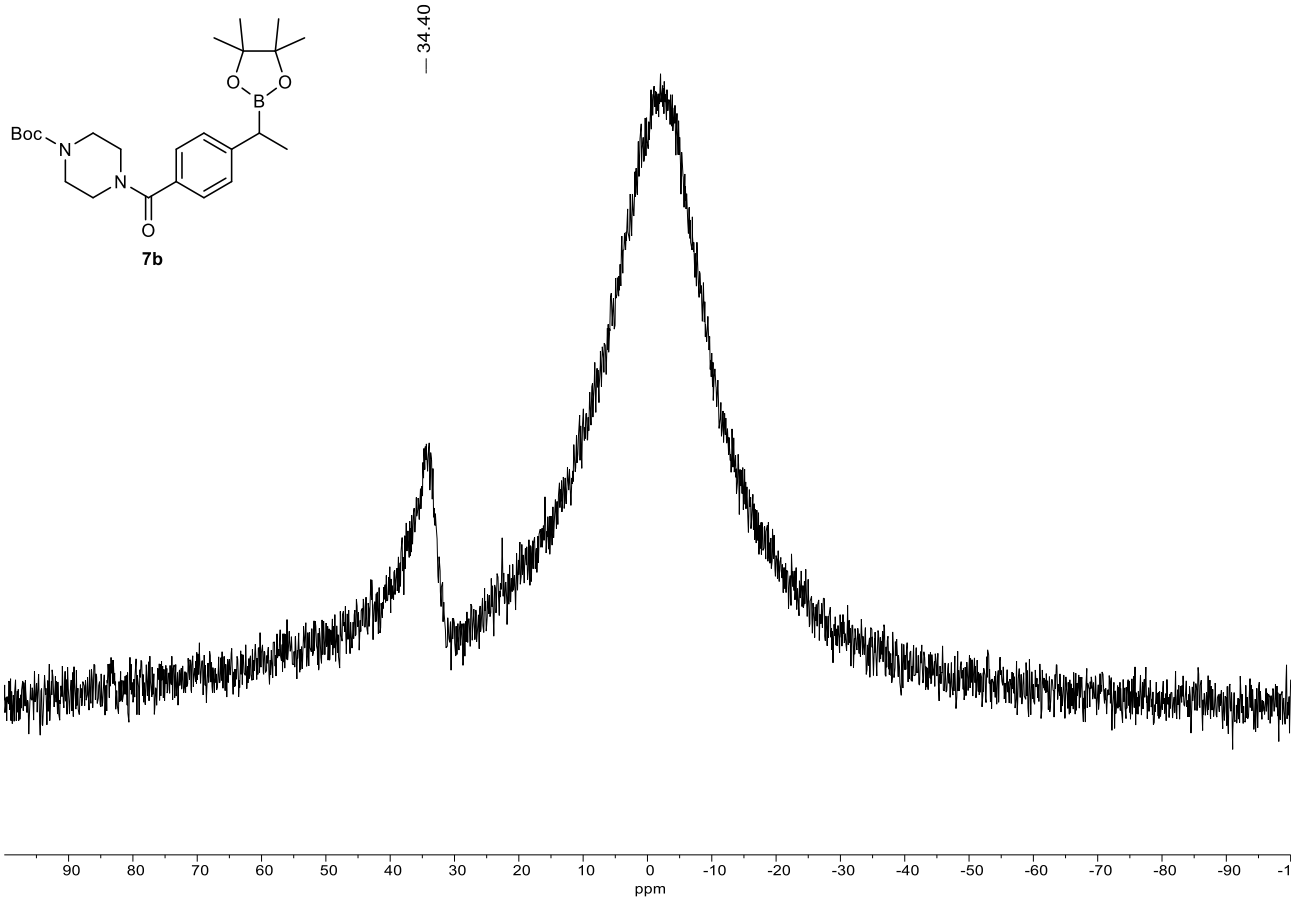
^{1}H NMR:



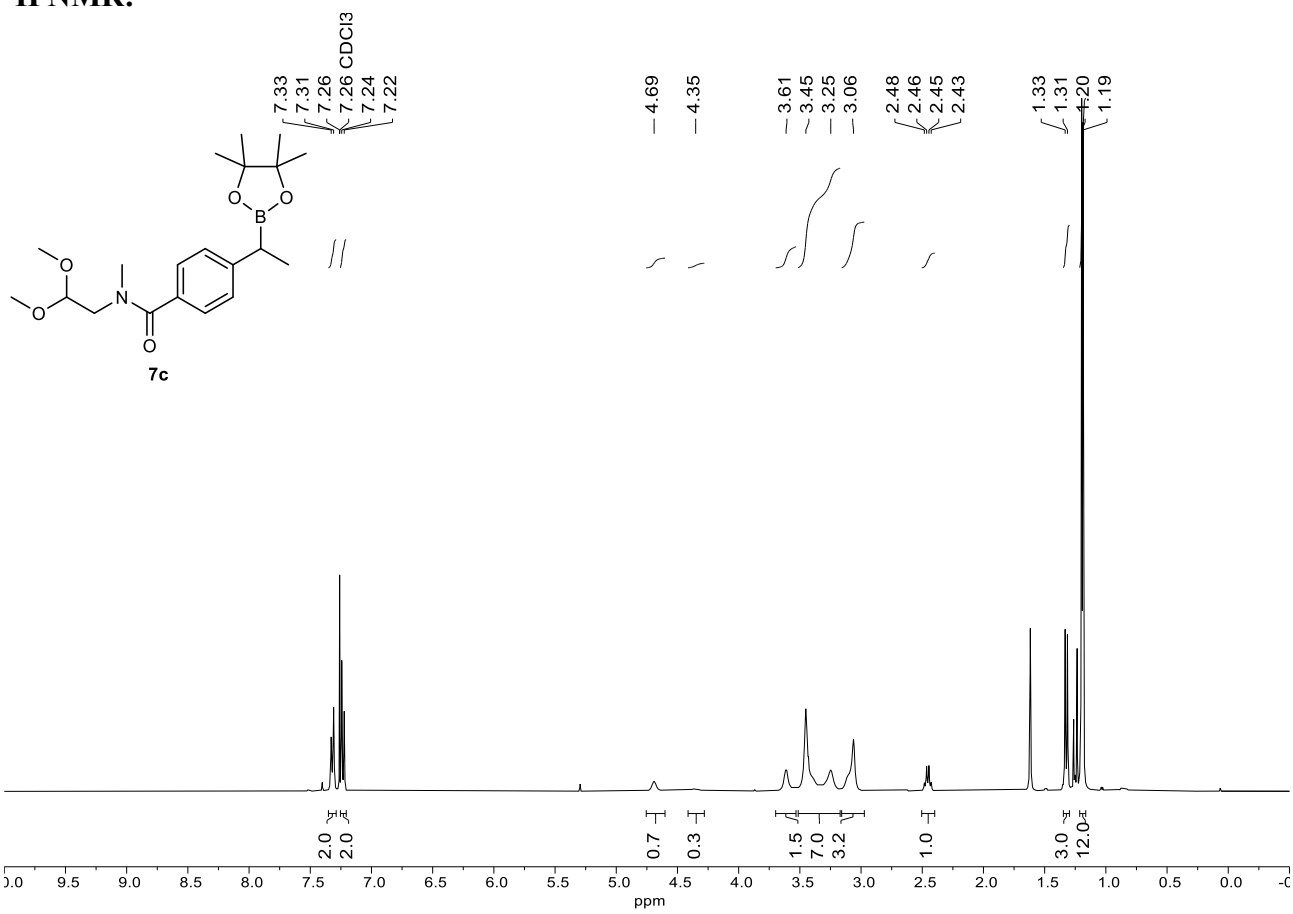
DEPT-Q:



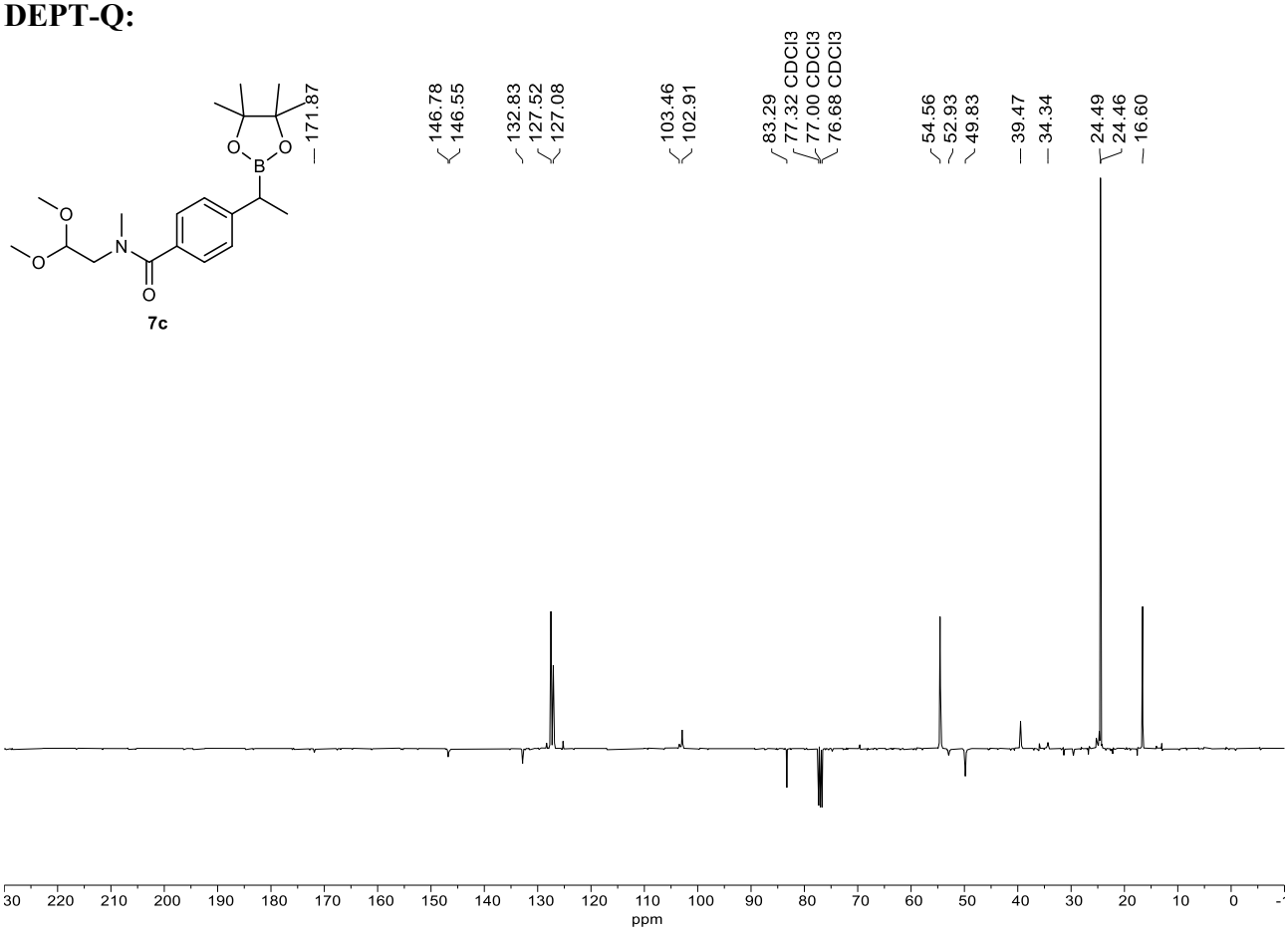
^{11}B NMR:



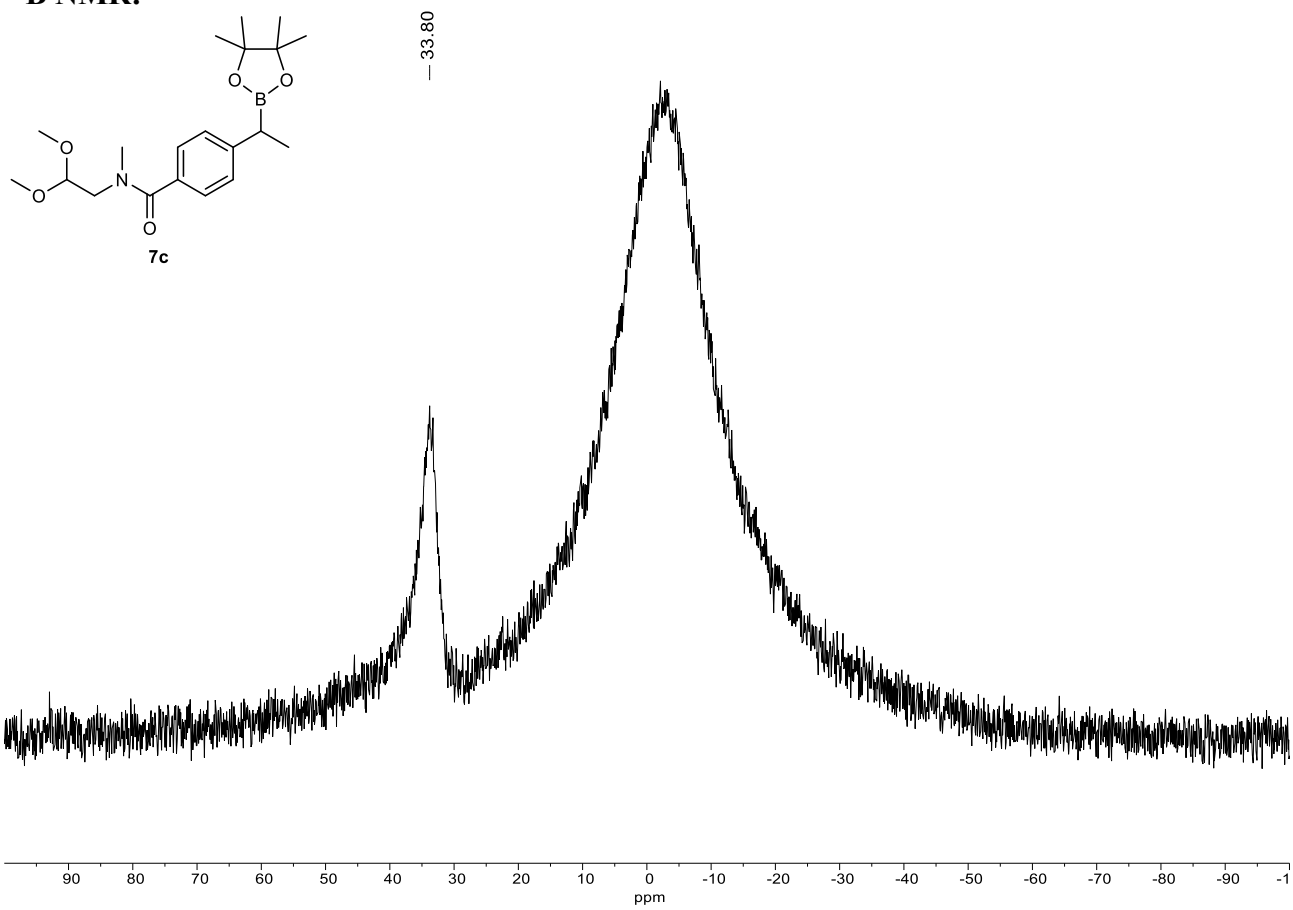
^{1}H NMR:


7.33
7.31
7.26
7.26 CDCl3
7.24
7.22
4.69
4.35
3.61
3.45
3.25
3.06
2.48
2.46
2.45
2.43
1.33
1.31
1.20
1.19
2.0
2.0
0.7
0.3
1.5
7.0
3.2
1.0
3.0
12.0
ppm

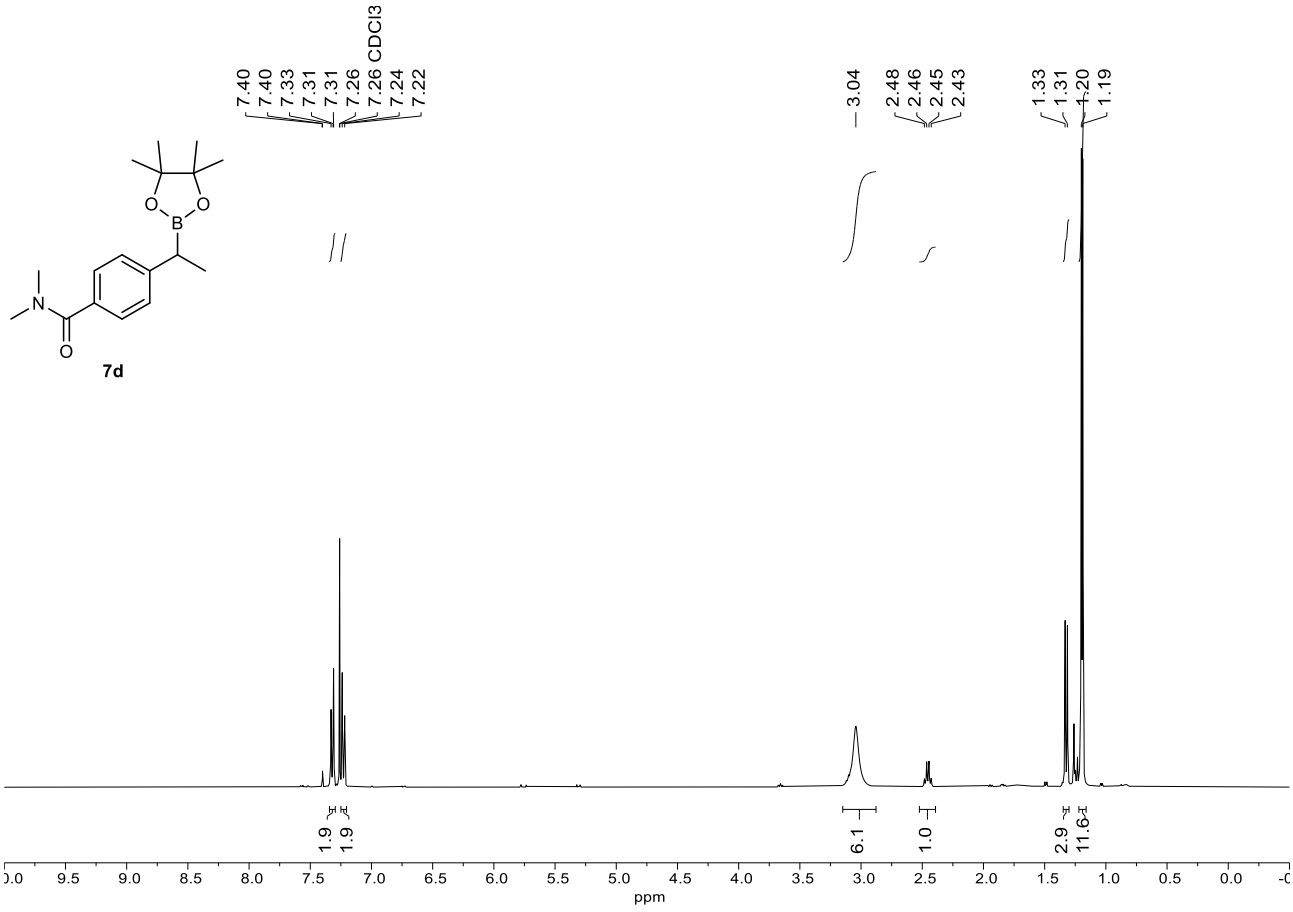
DEPT-Q:


171.87
146.78
146.55
132.83
127.52
127.08
103.46
102.91
83.29
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
54.56
52.93
49.83
39.47
34.34
24.49
24.46
16.60
ppm

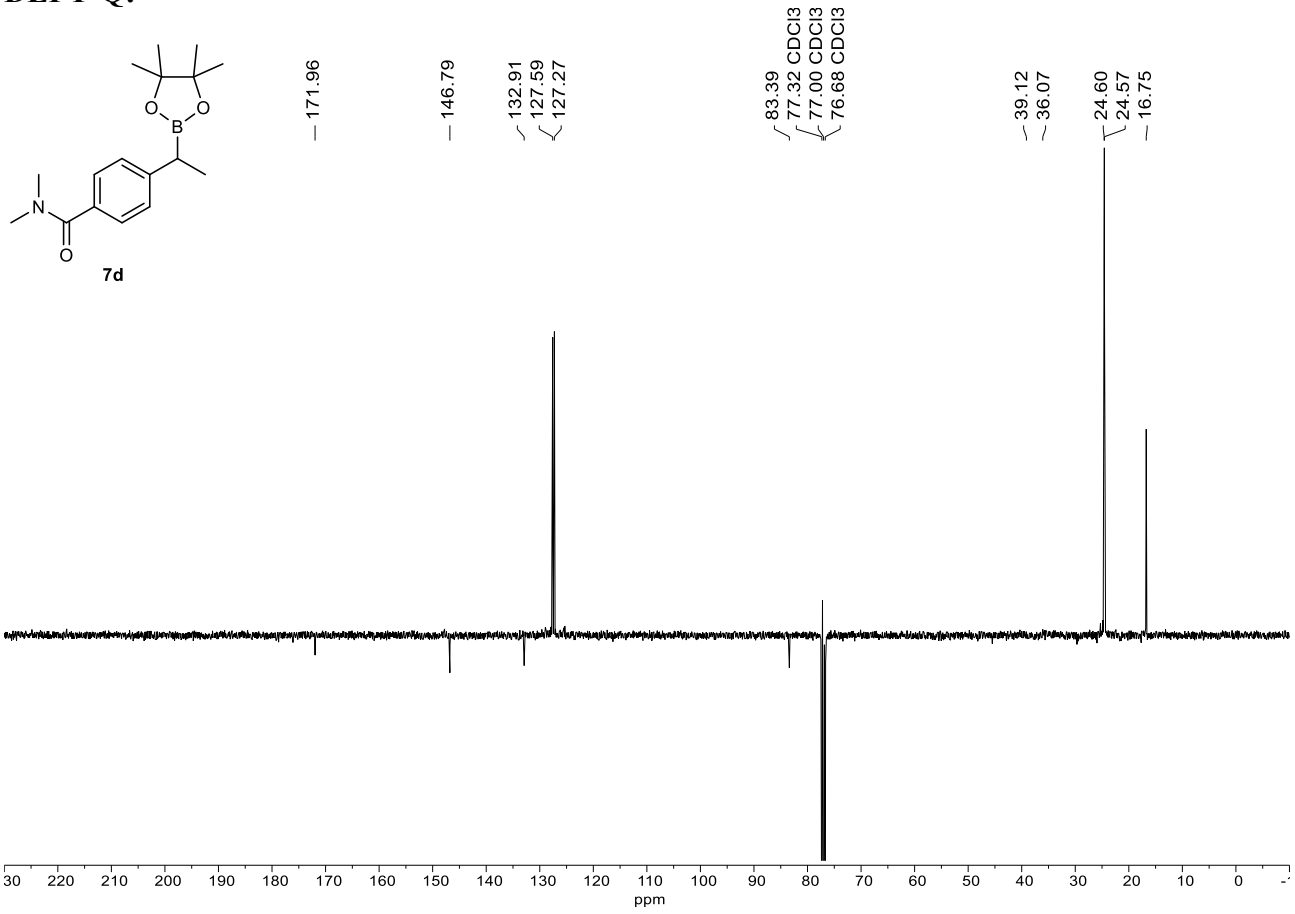
^{11}B NMR:



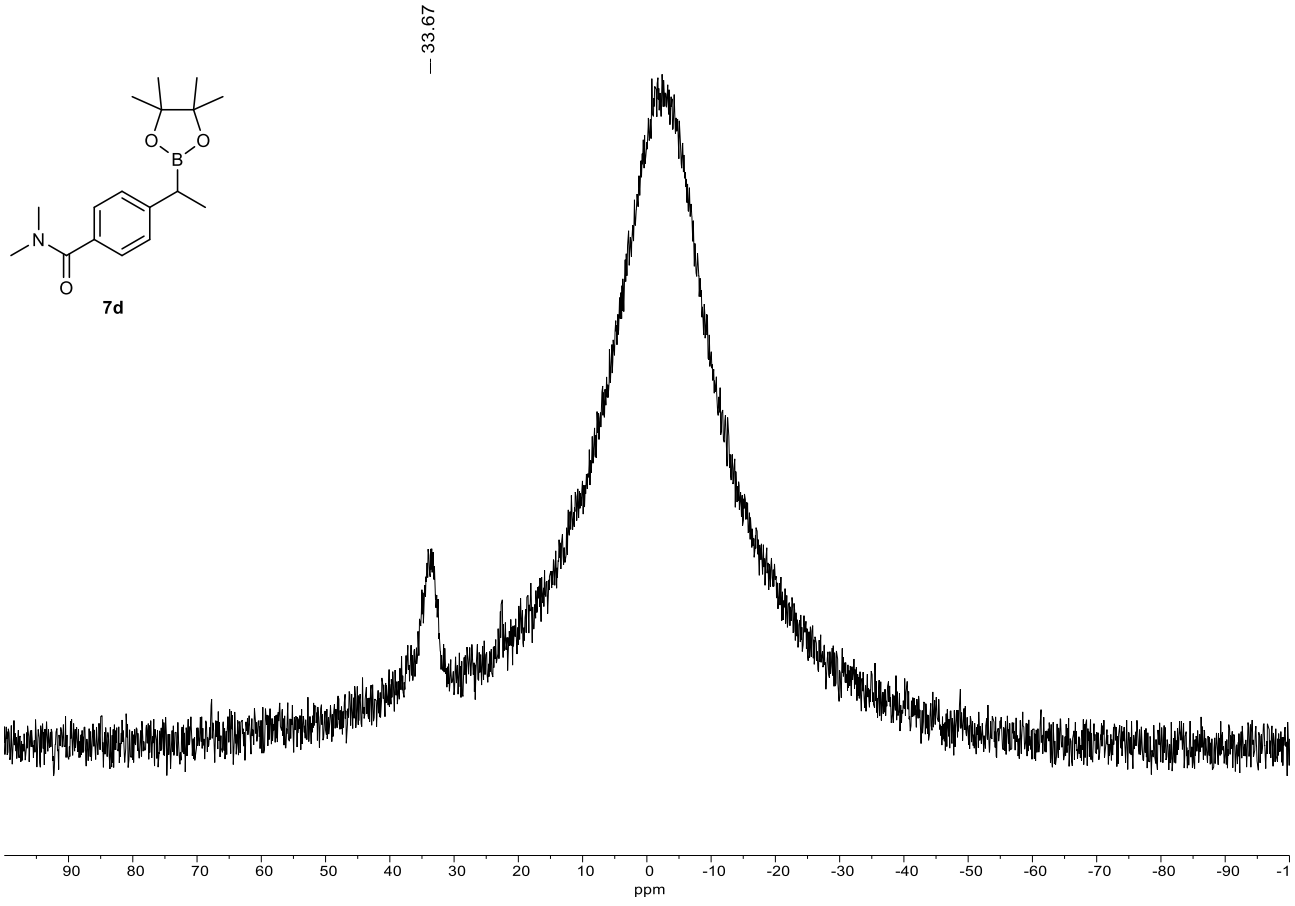
^{1}H NMR:



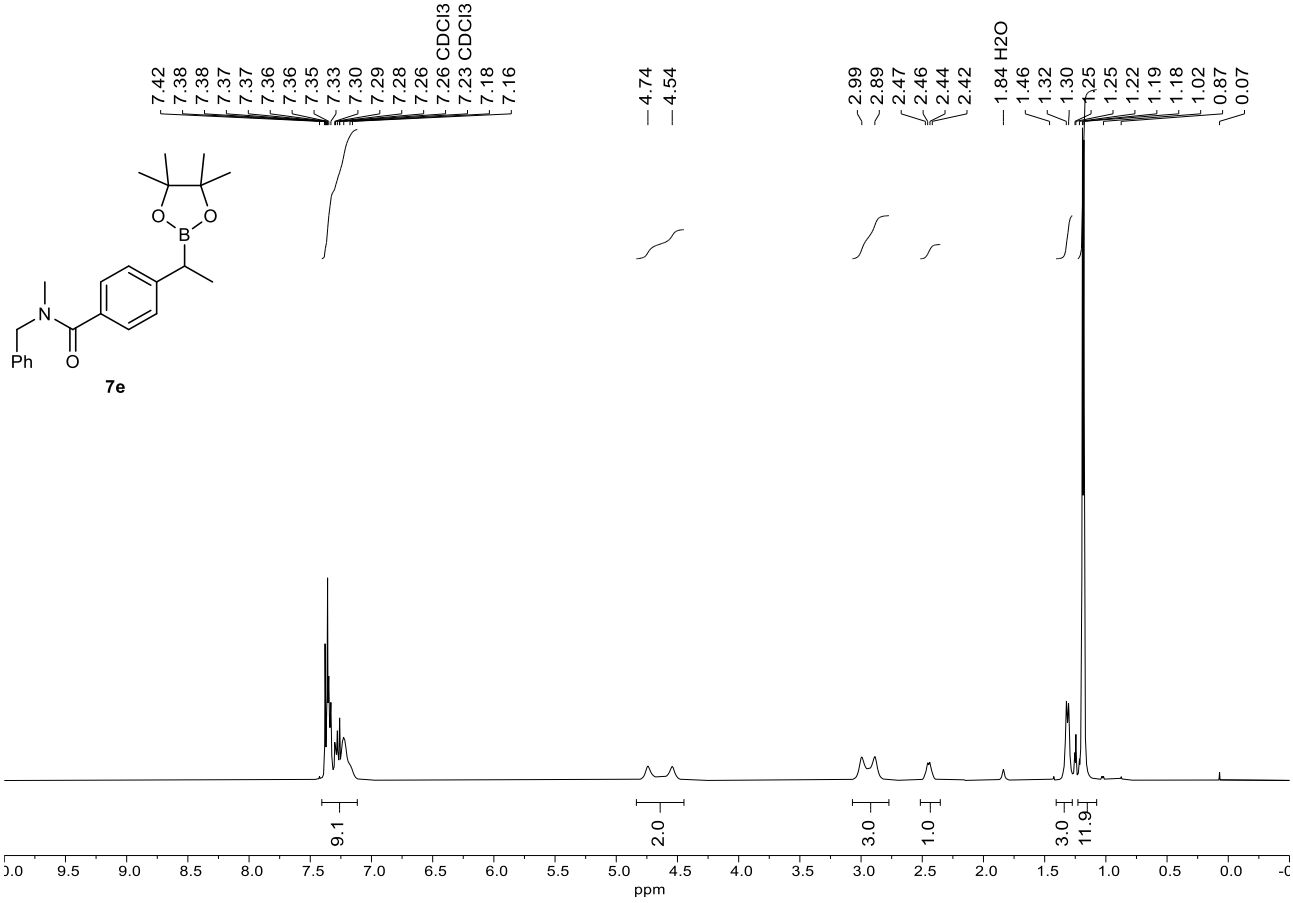
DEPT-Q:



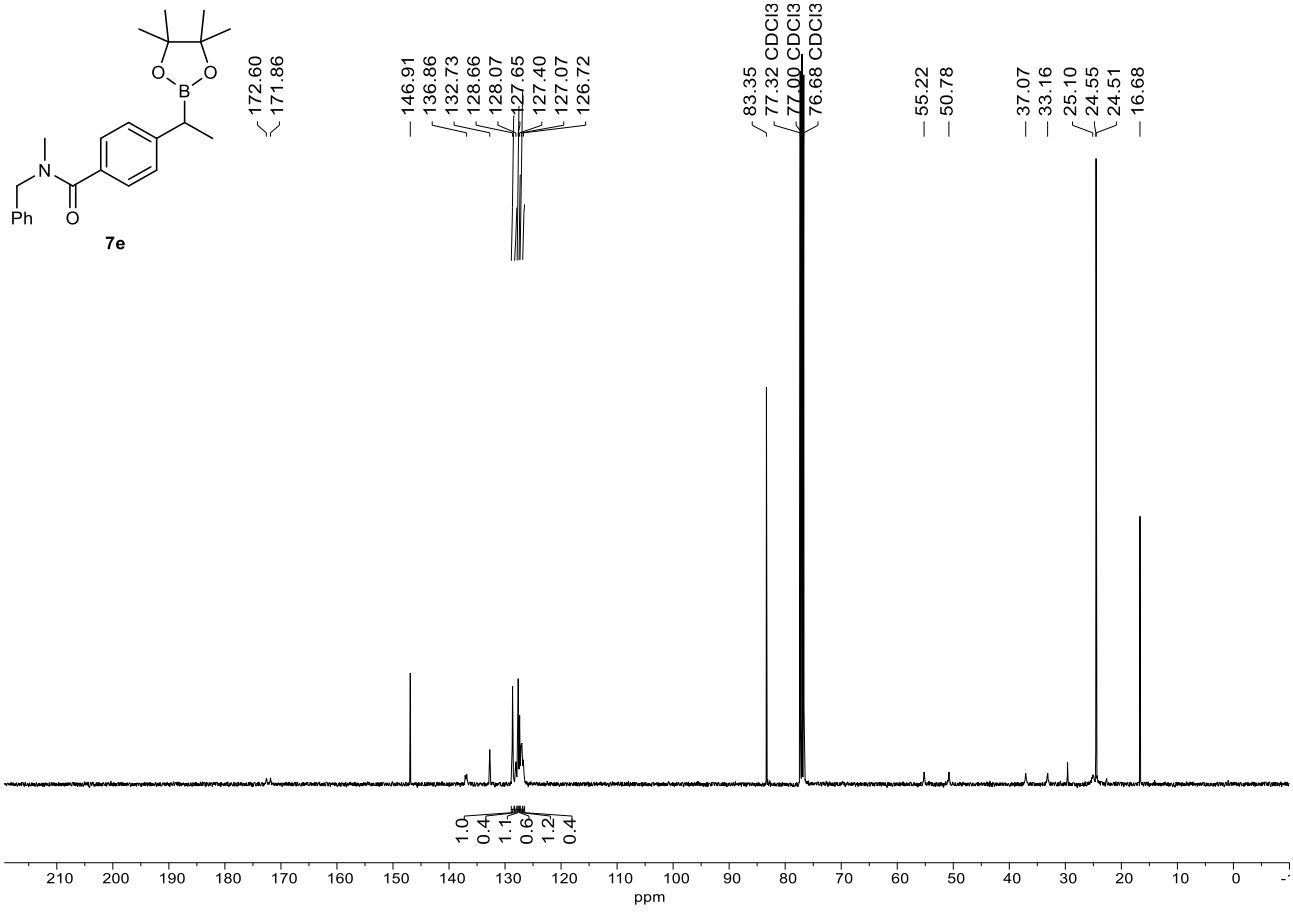
^{11}B NMR



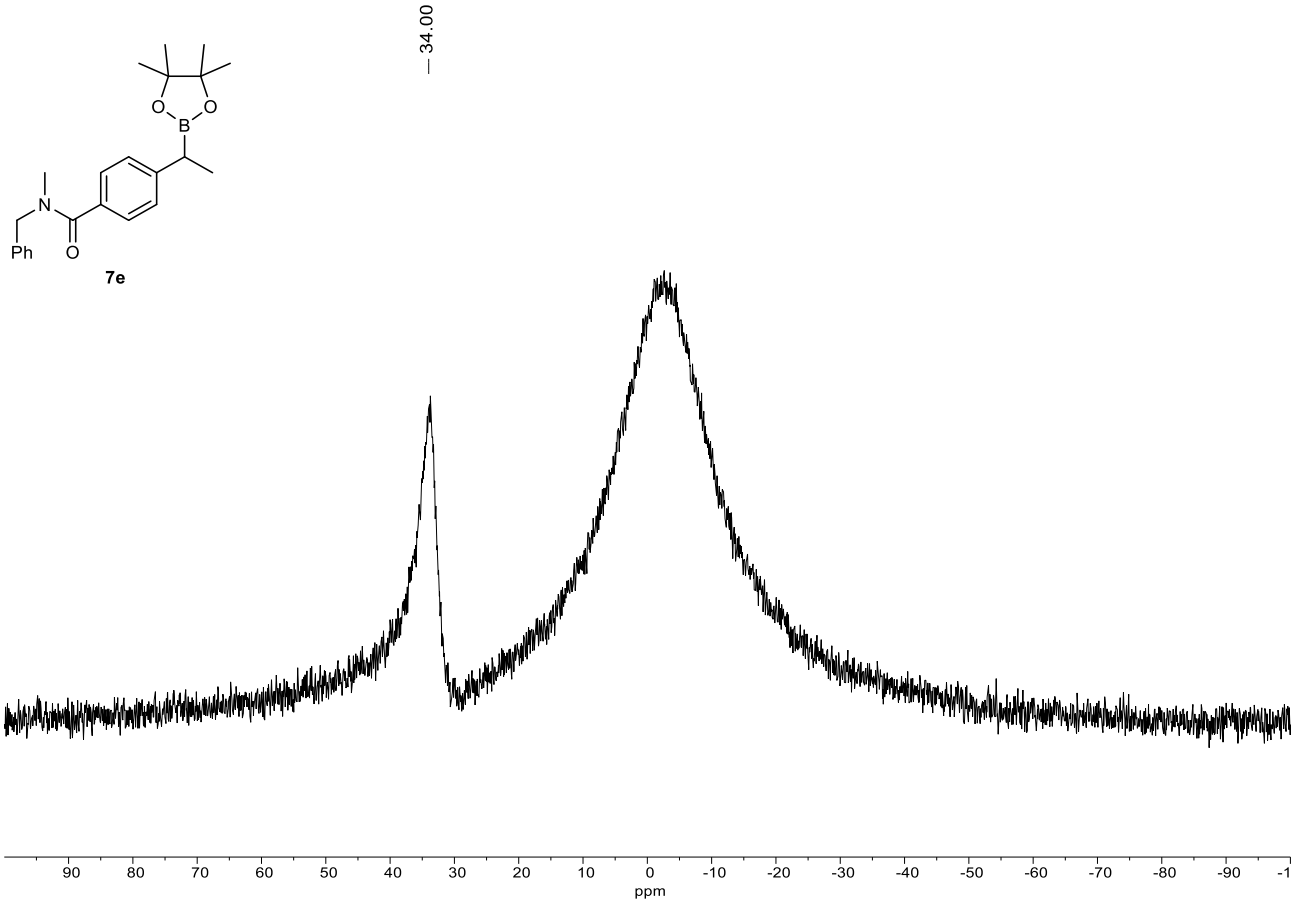
^{1}H NMR:



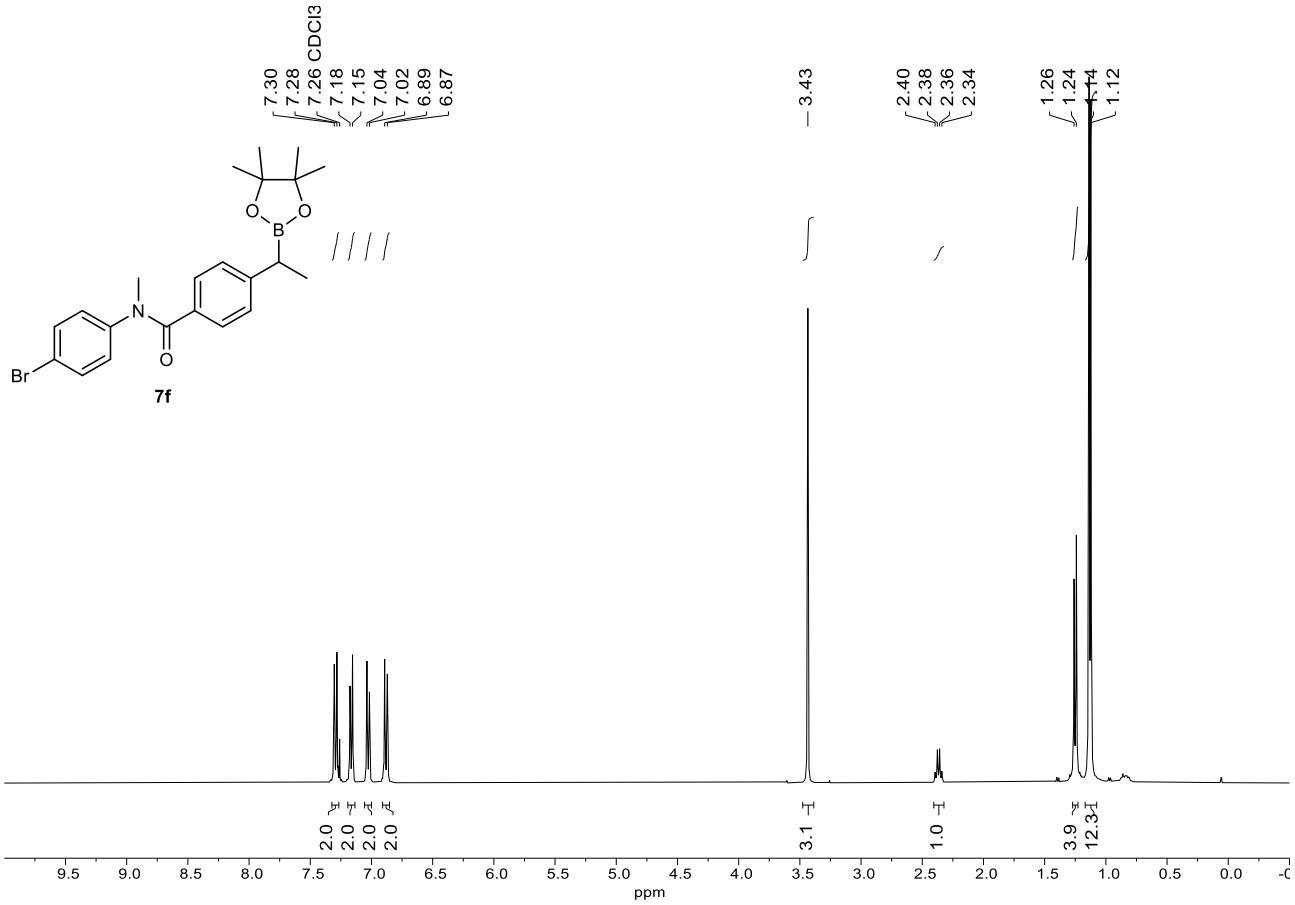
^{13}C NMR:



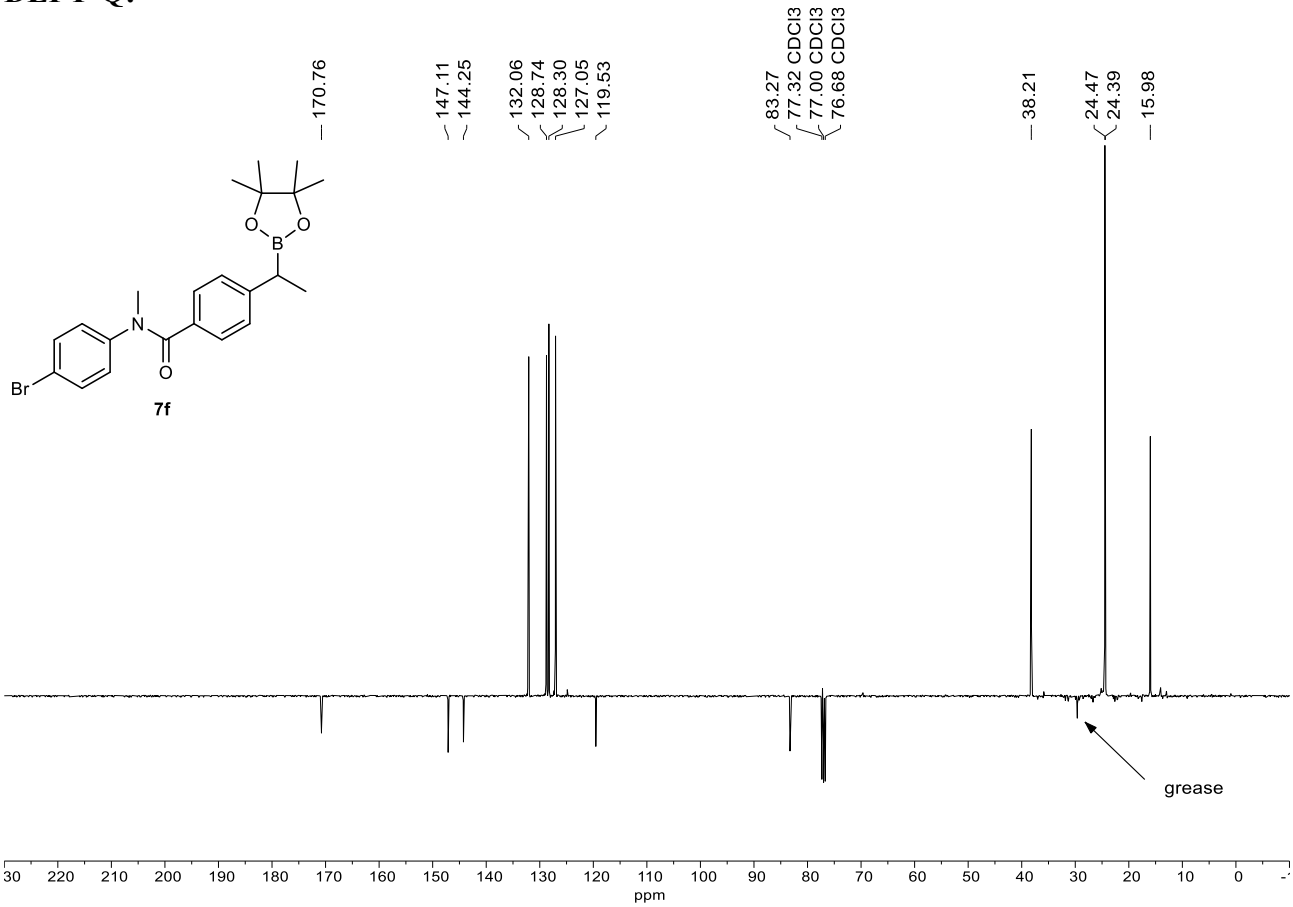
^{11}B NMR:



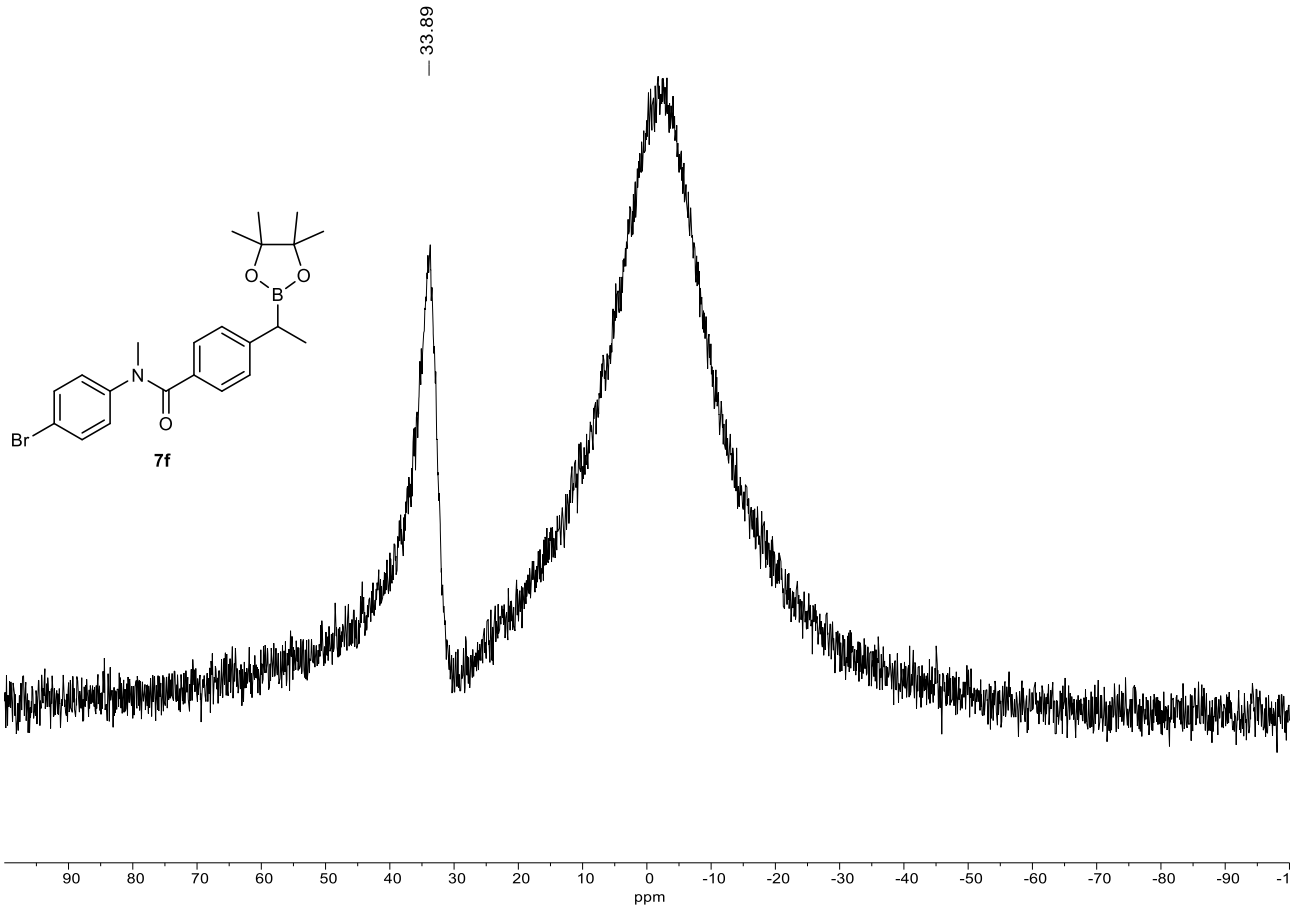
^{1}H NMR:



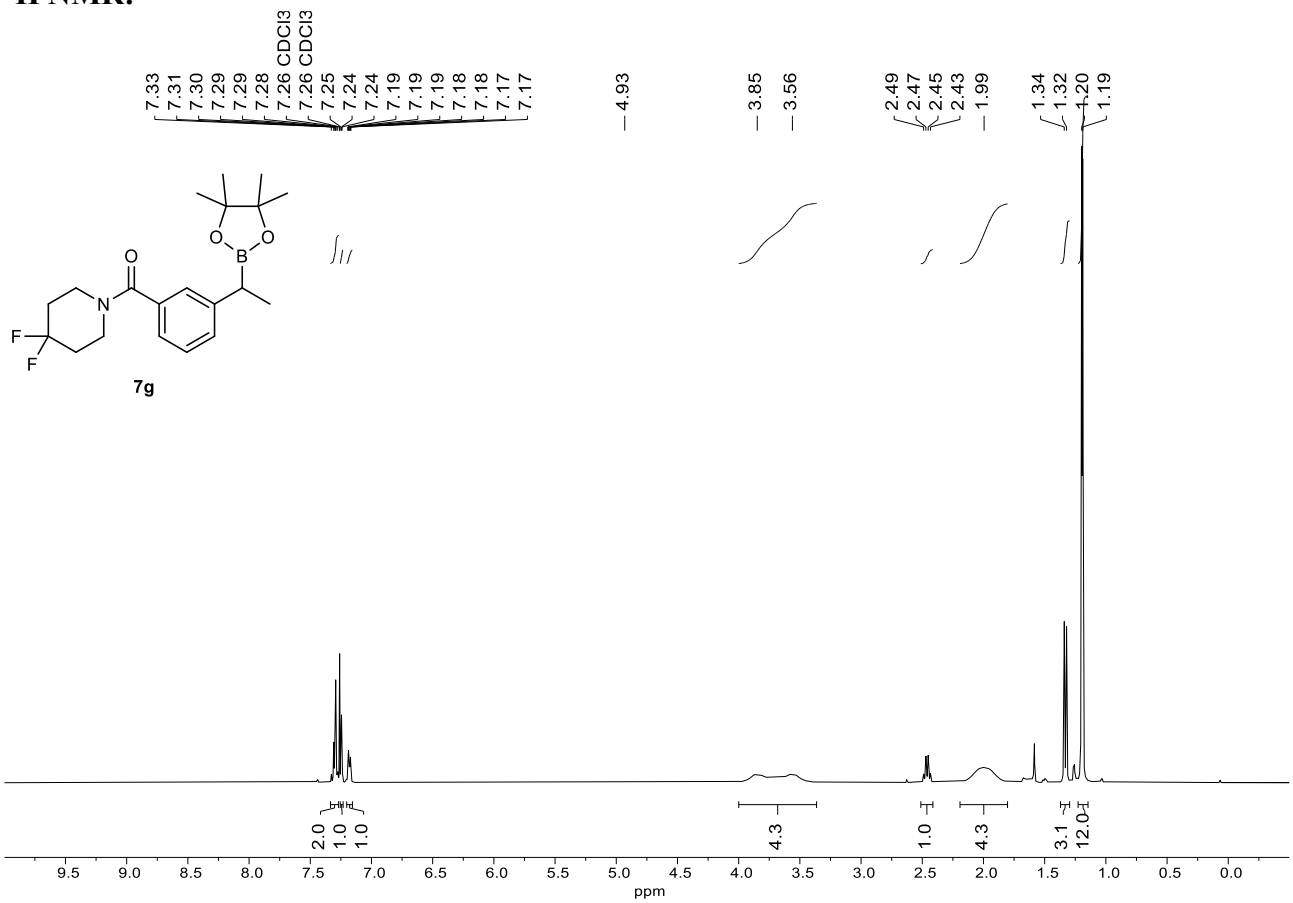
DEPT-Q:



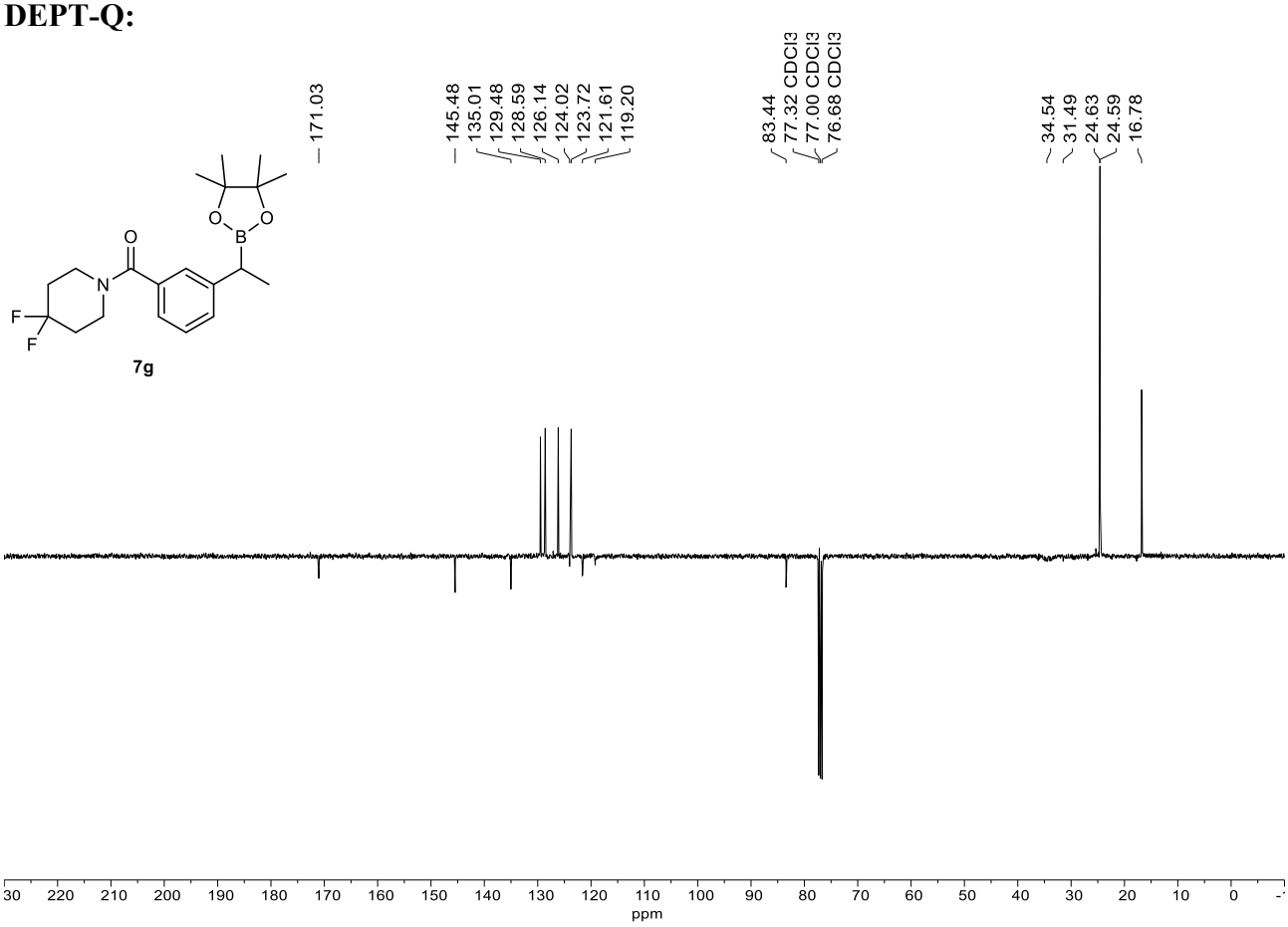
^{11}B NMR:



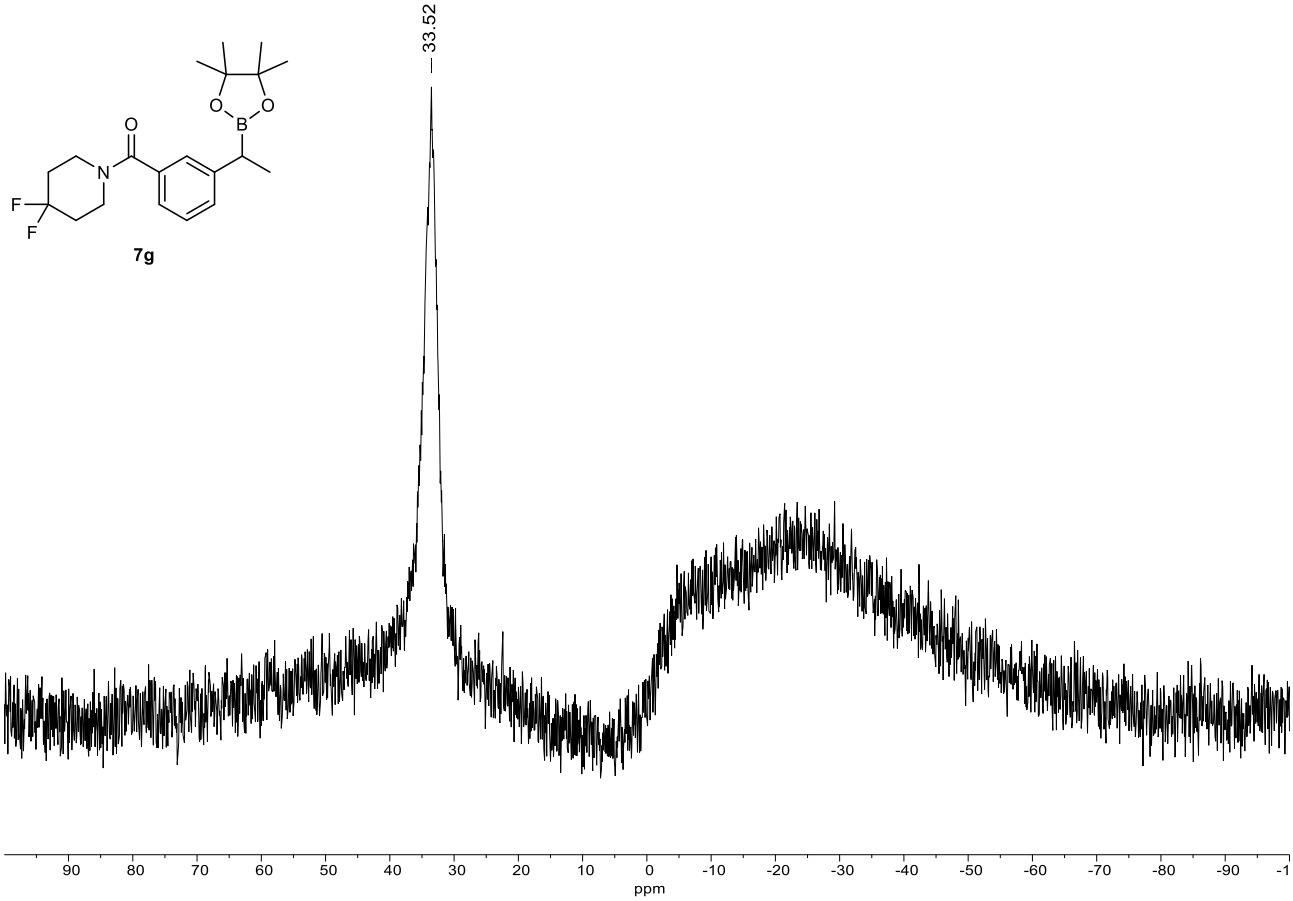
^{1}H NMR:


7.33
7.31
7.30
7.29
7.29
7.28
7.26 CDCl3
7.26 CDCl3
7.25
7.24
7.24
7.19
7.19
7.19
7.18
7.18
7.17
7.17
4.93
3.85
3.56
2.49
2.47
2.45
2.43
1.99
1.34
1.32
1.20
1.19
7g
2.0
1.0
1.0
4.3
1.0
4.3
3.1
12.0
ppm

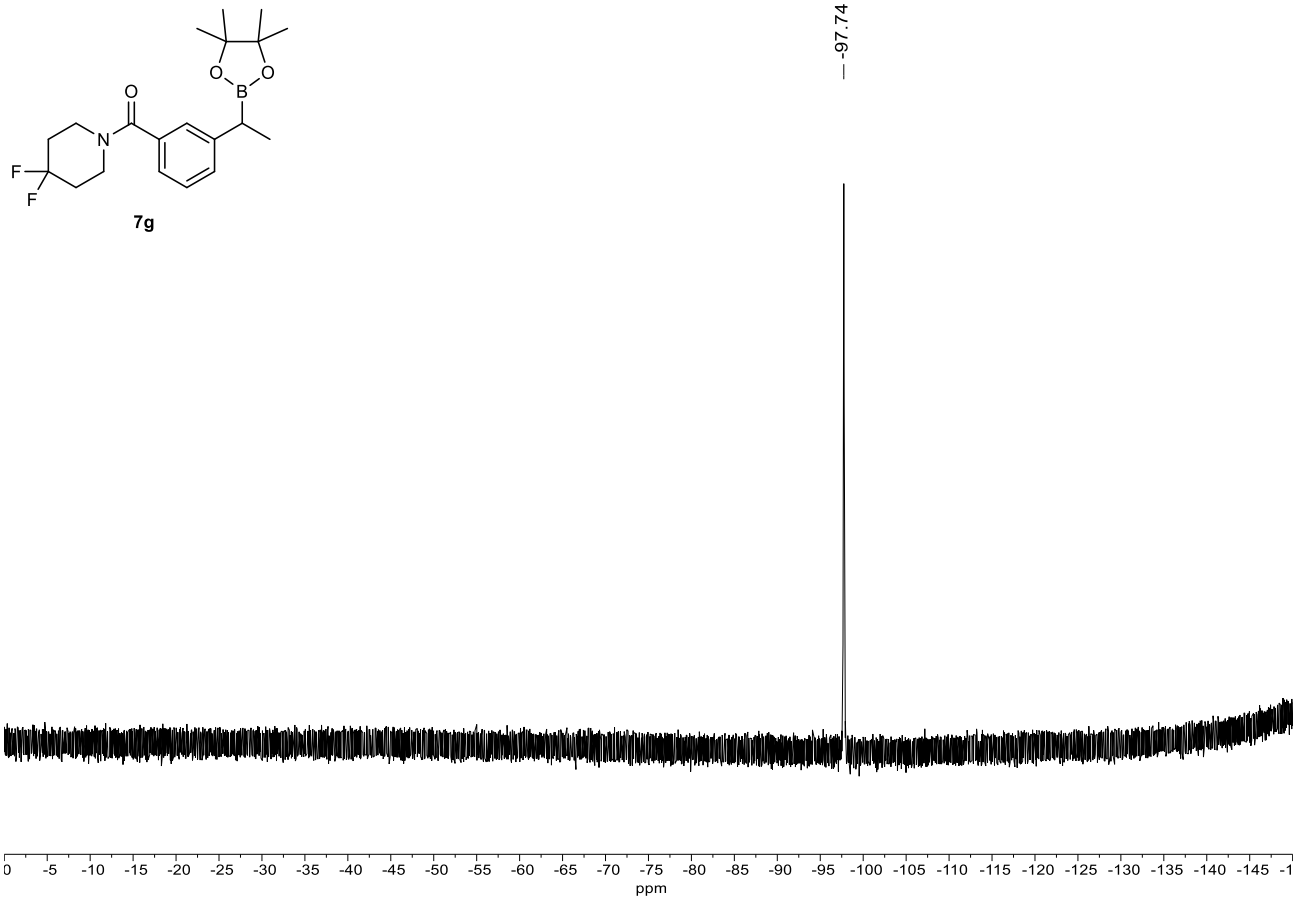
DEPT-Q:


171.03
145.48
135.01
129.48
128.59
126.14
124.02
123.72
121.61
119.20
83.44
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
34.54
31.49
24.63
24.59
16.78
7g
ppm

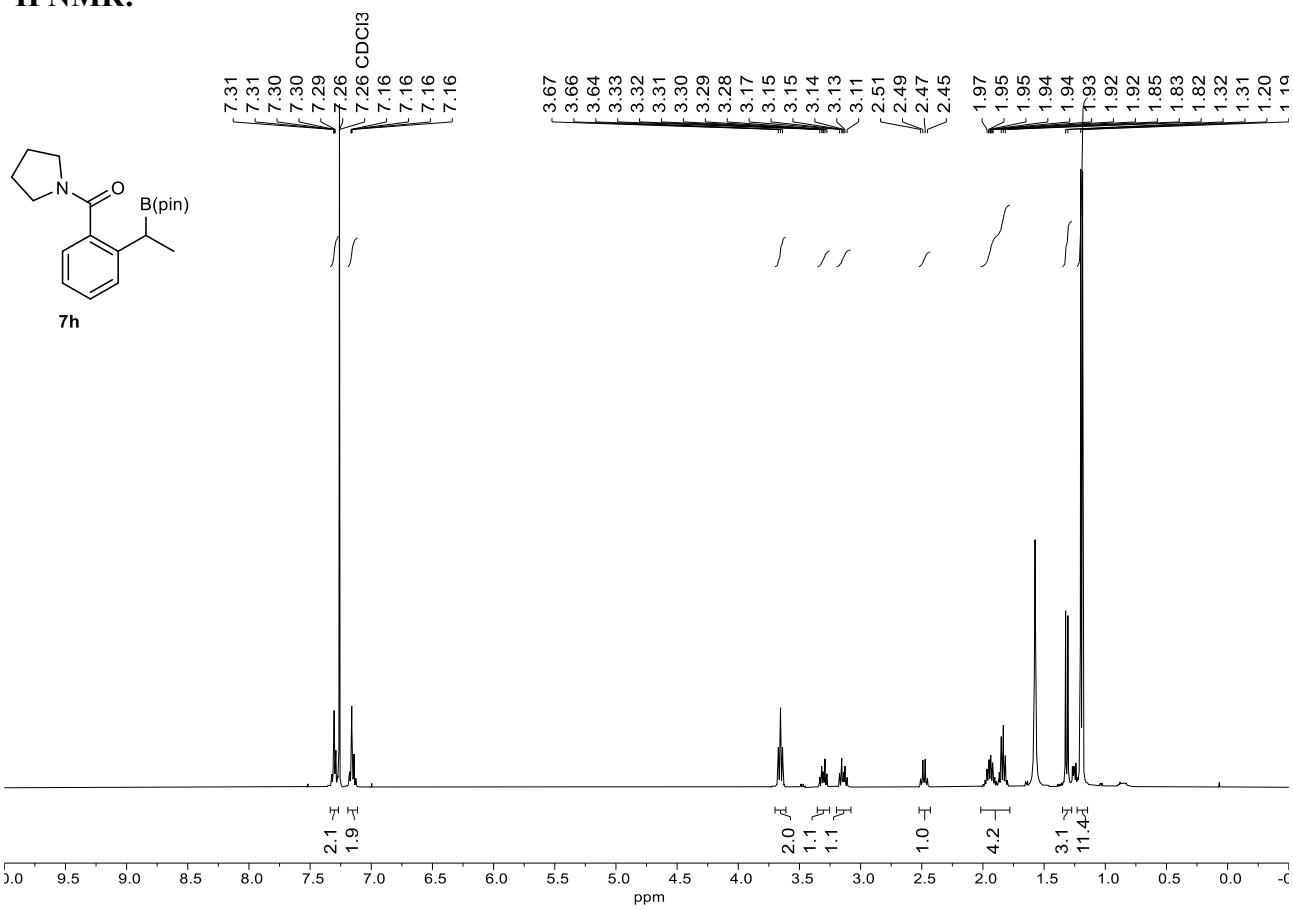
^{11}B NMR:



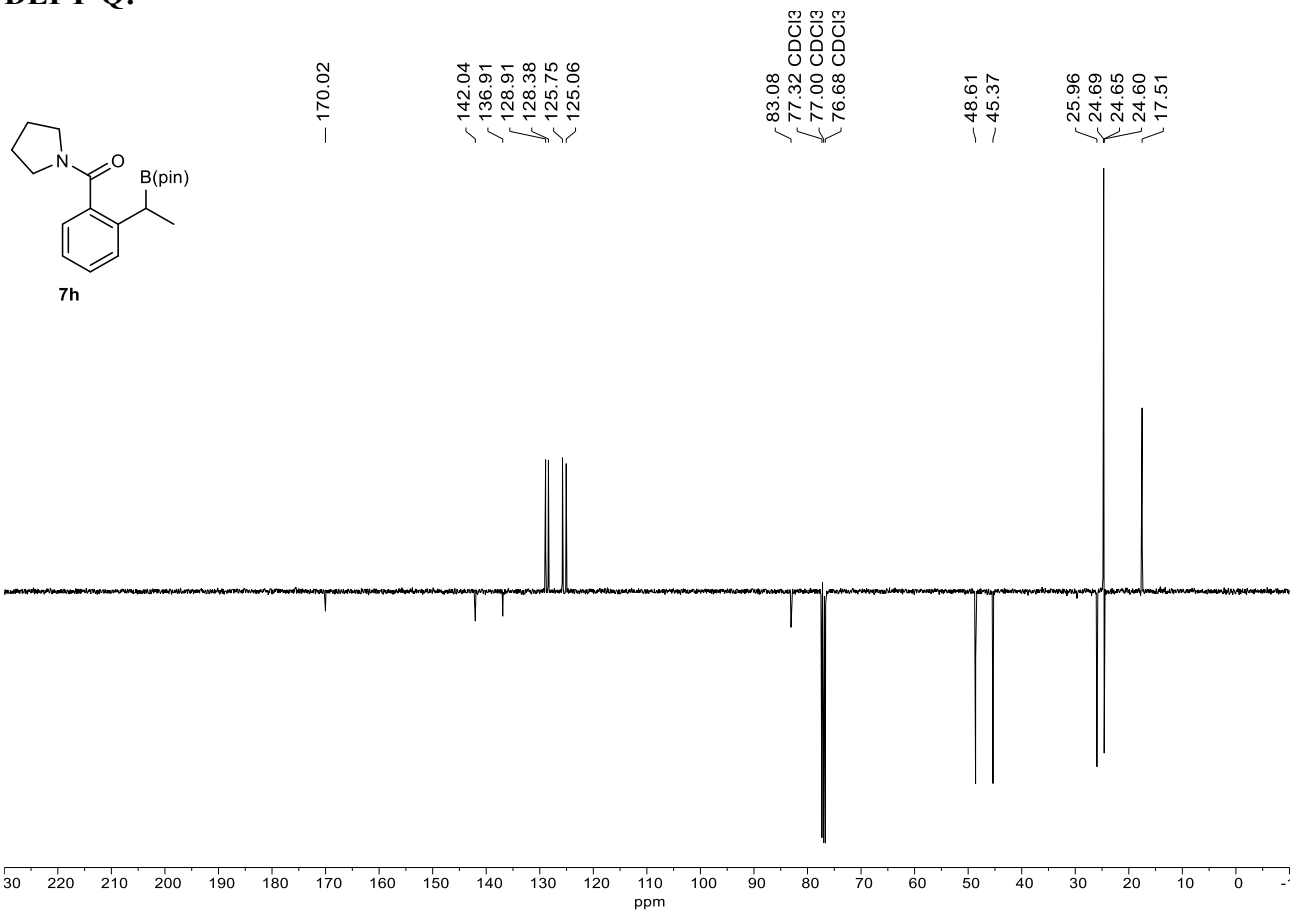
^{19}F NMR:



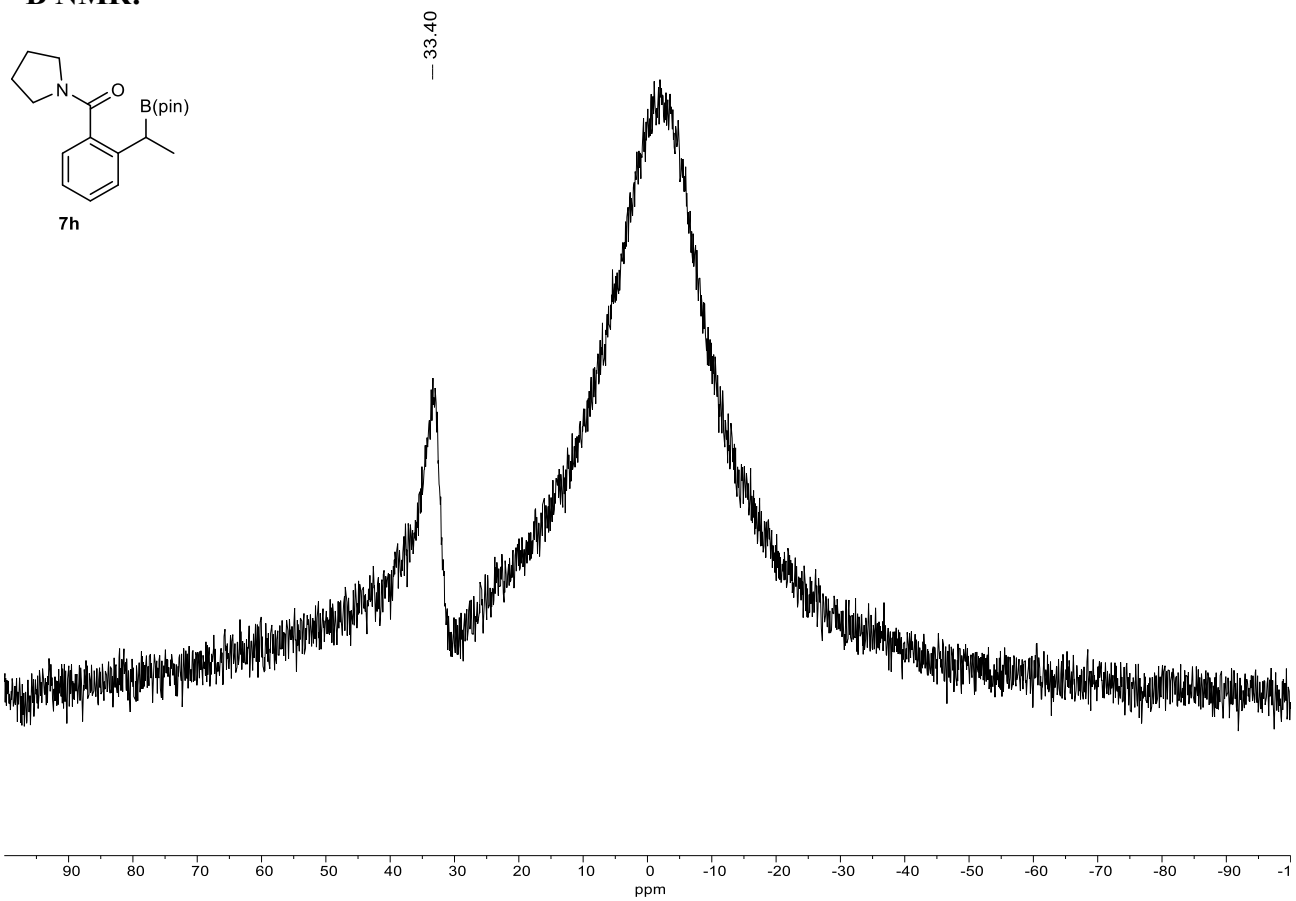
^{1}H NMR:


7.31
7.31
7.30
7.30
7.29
7.26 CDCl3
7.16
7.16
7.16
7.16
3.67
3.66
3.64
3.33
3.32
3.31
3.30
3.29
3.28
3.17
3.15
3.15
3.14
3.13
3.11
2.51
2.49
2.47
2.45
1.97
1.95
1.95
1.94
1.94
1.93
1.92
1.92
1.85
1.83
1.82
1.32
1.31
1.20
N
O
B(pin)
7h
2.1
1.9
2.0
1.1
1.1
1.0
4.2
3.1
11.4
ppm

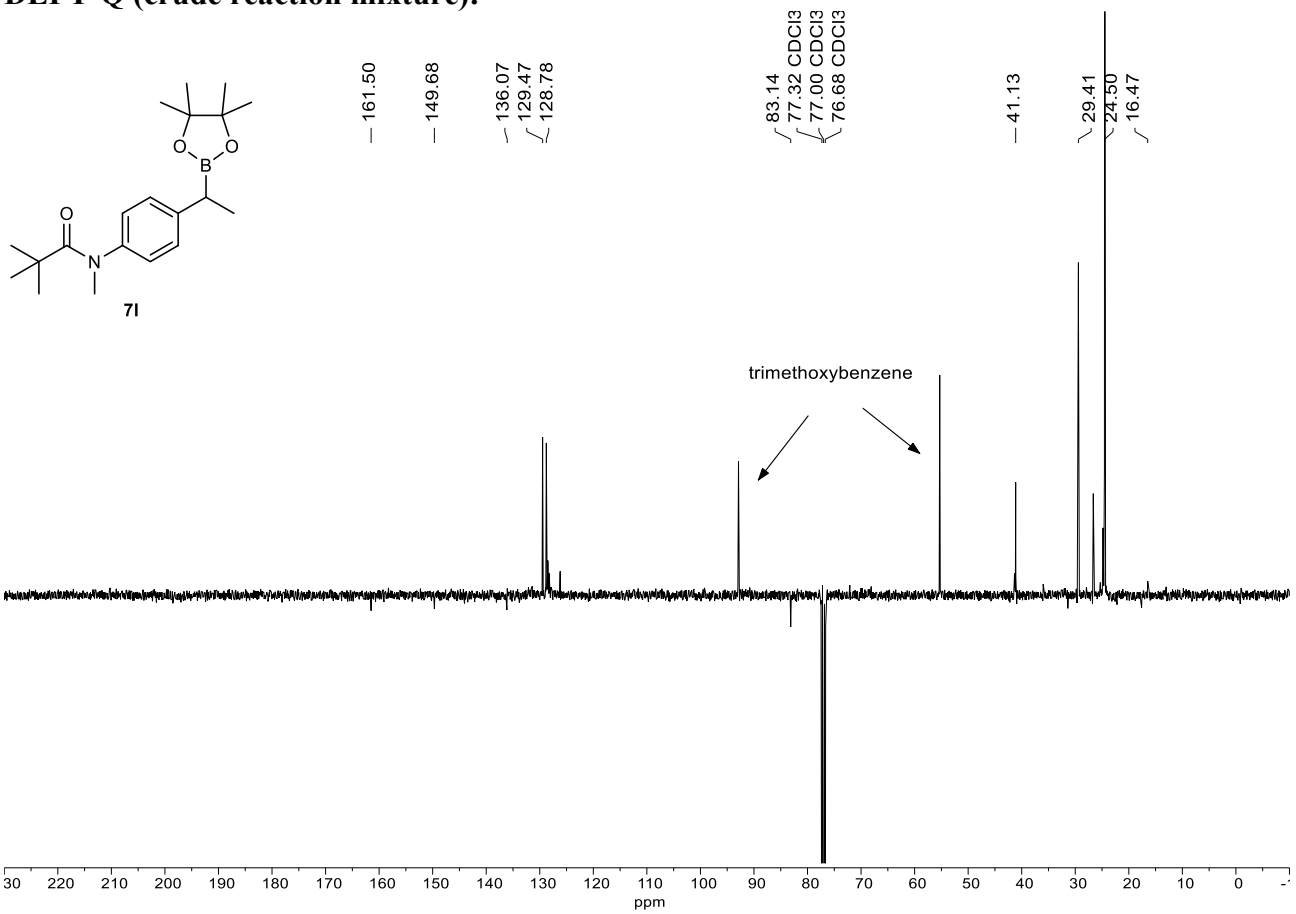
DEPT-Q:


170.02
142.04
136.91
128.91
128.38
125.75
125.06
83.08
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
48.61
45.37
25.96
24.69
24.65
24.60
17.51
N
O
B(pin)
7h
ppm

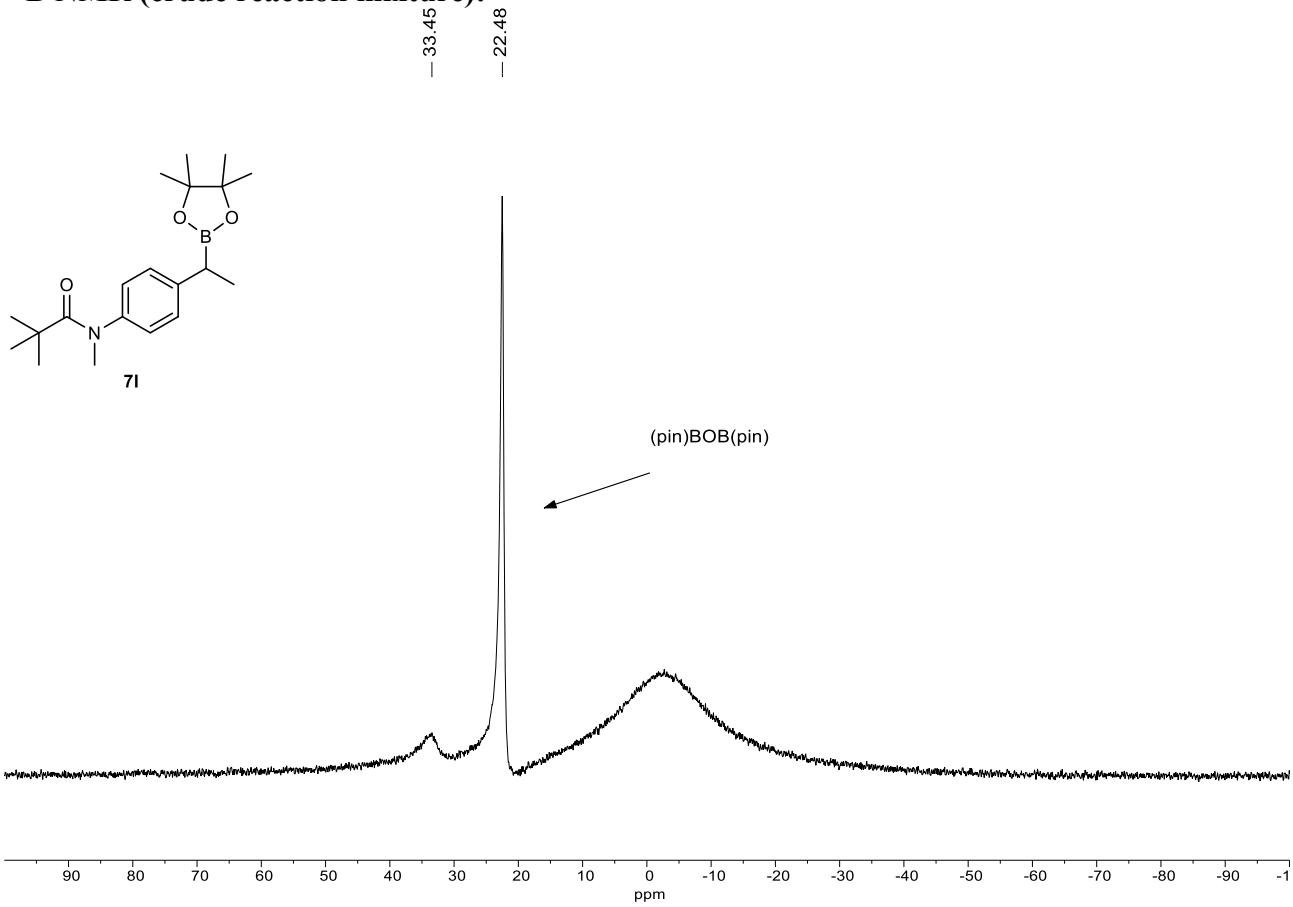
^{11}B NMR:



DEPT-Q (crude reaction mixture):

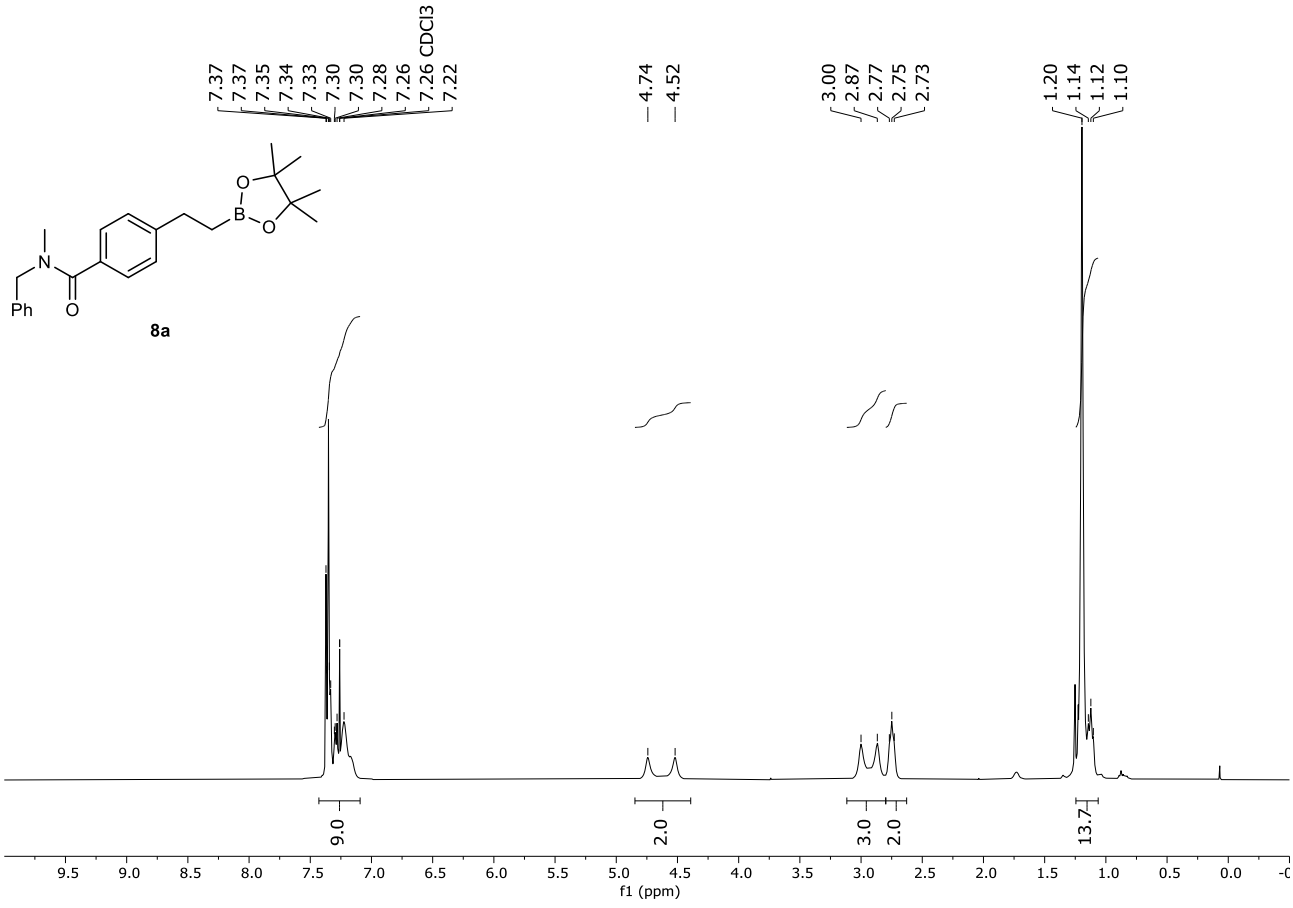


^{11}B NMR (crude reaction mixture):

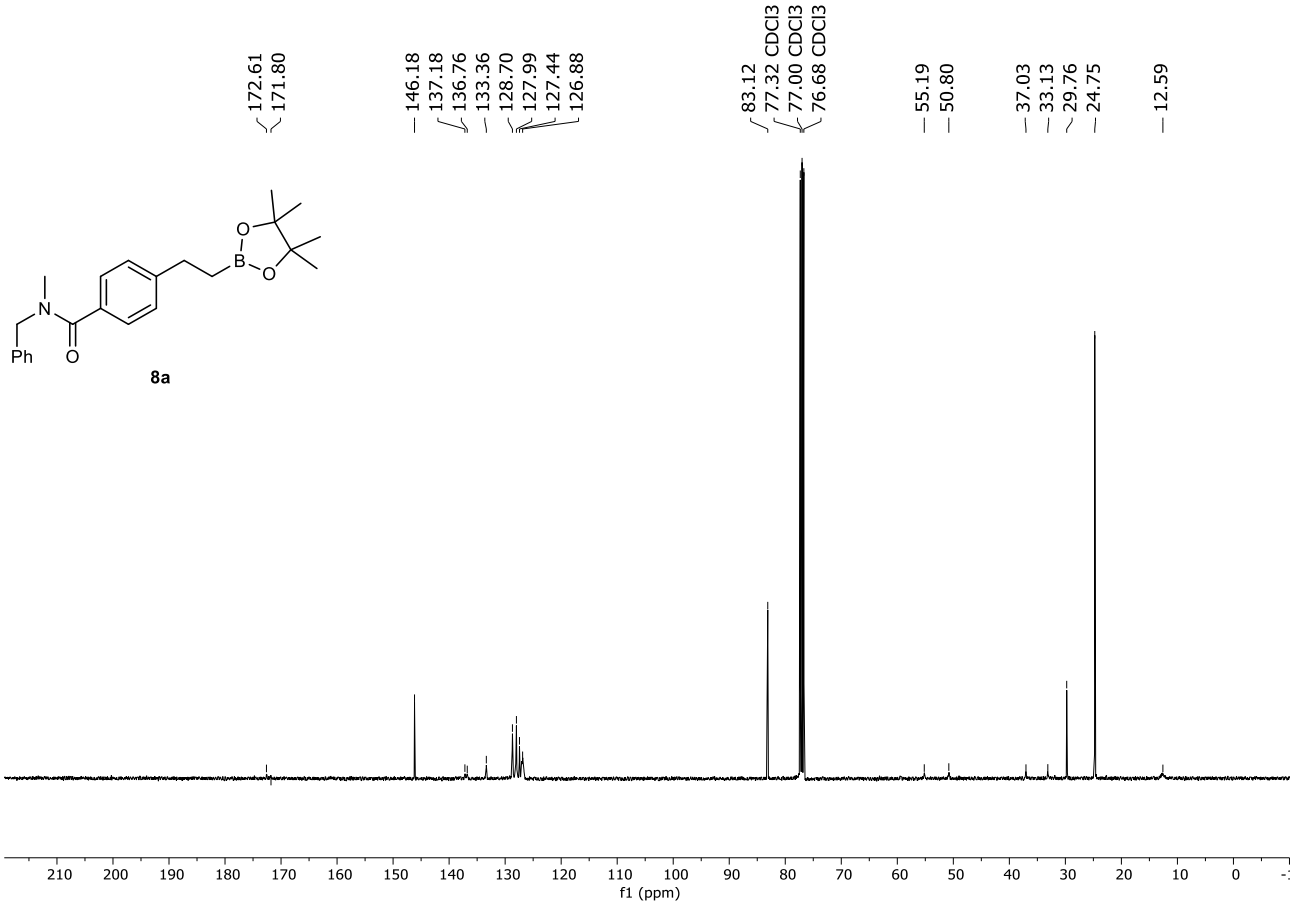


8.3. Ir-catalysed Hydroboration Products

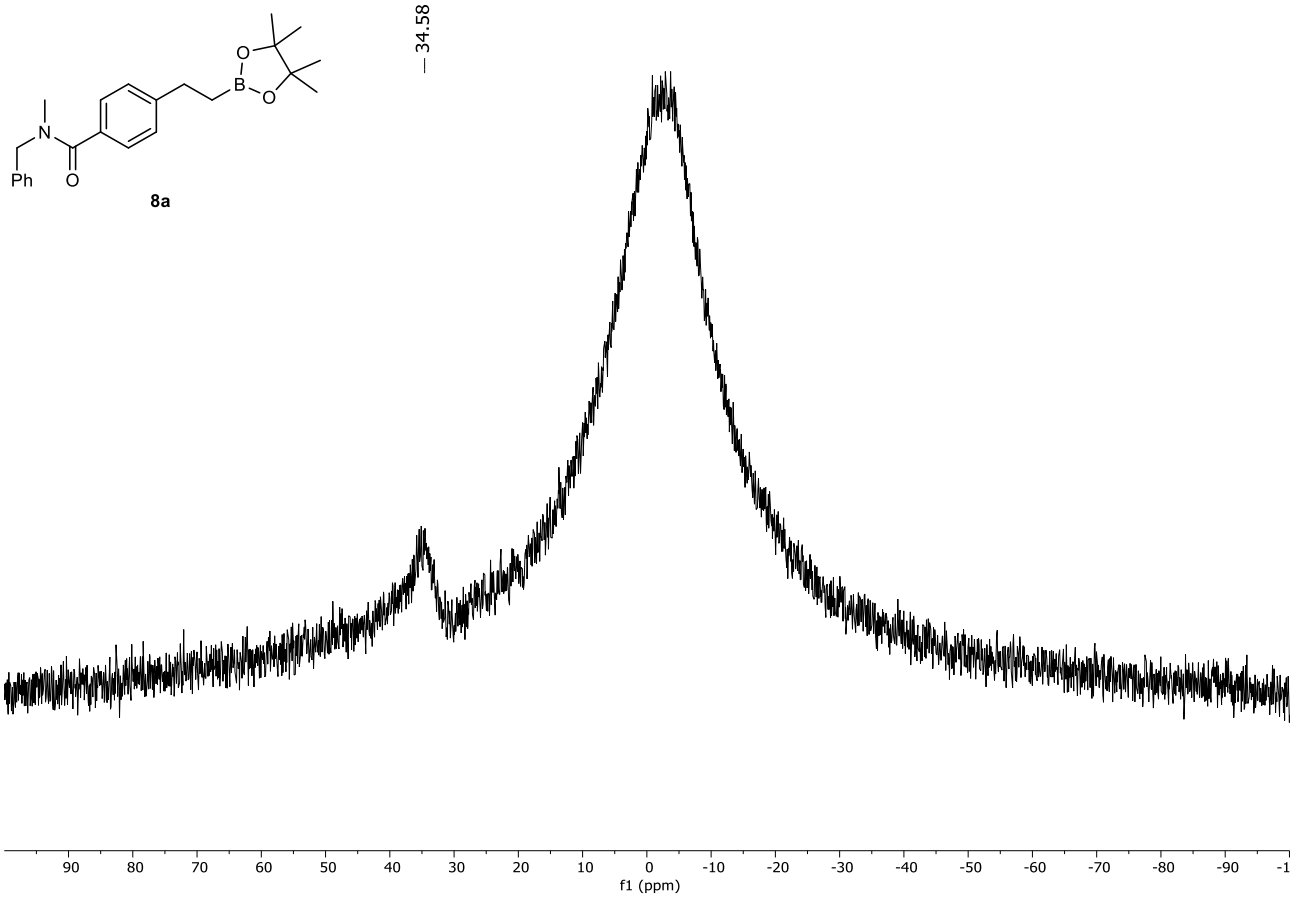
^{1}H NMR:



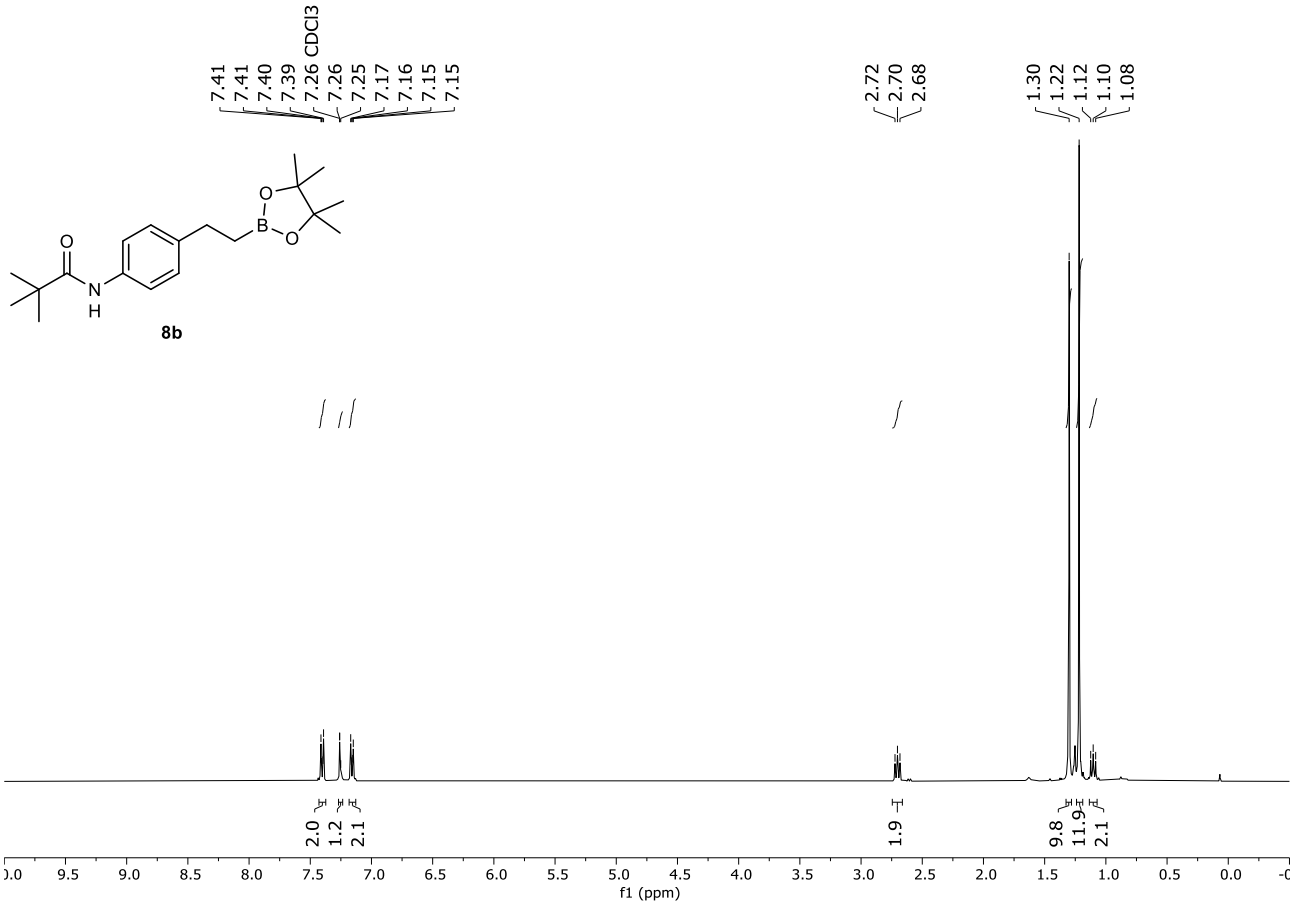
^{13}C NMR:



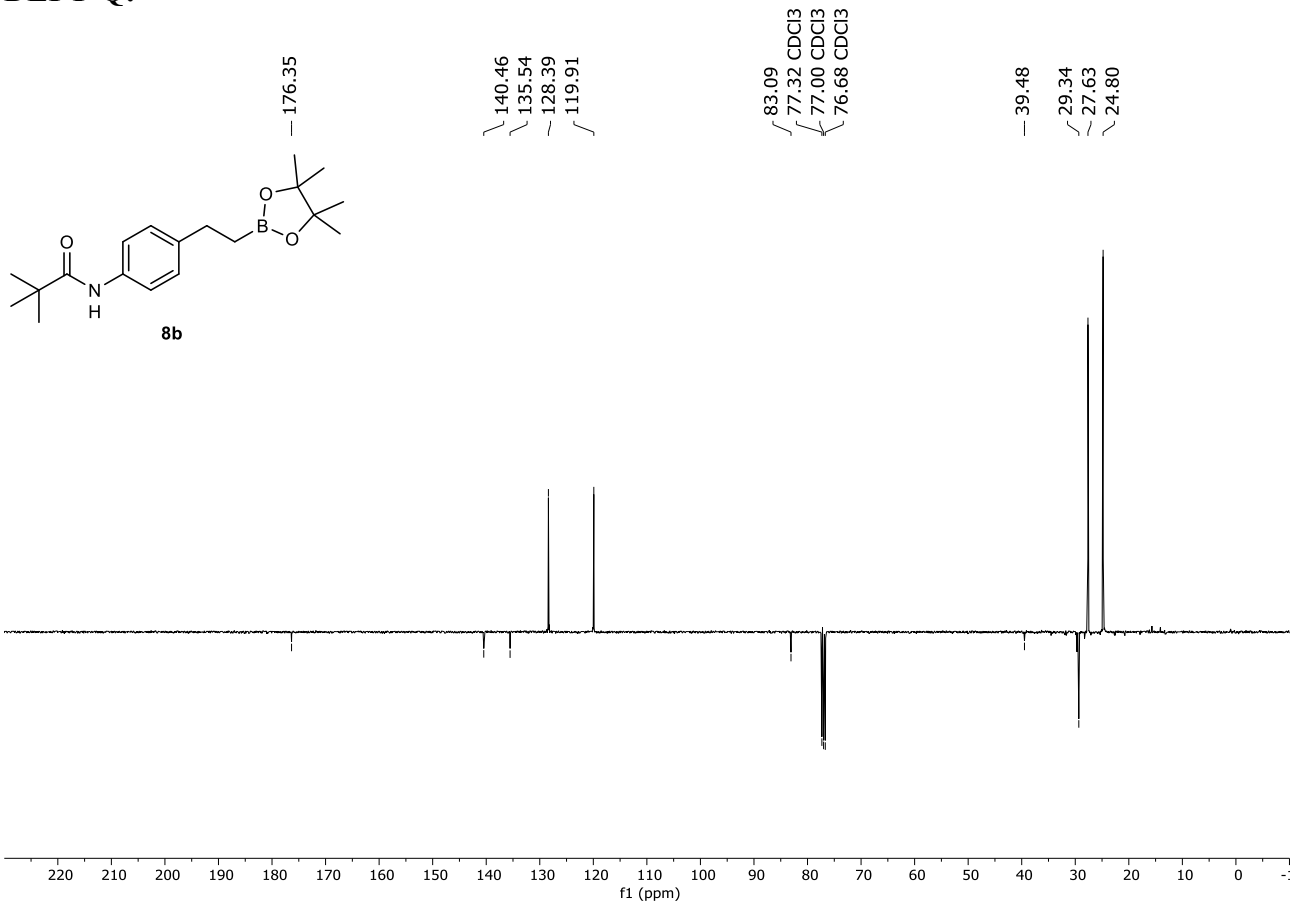
^{11}B NMR:



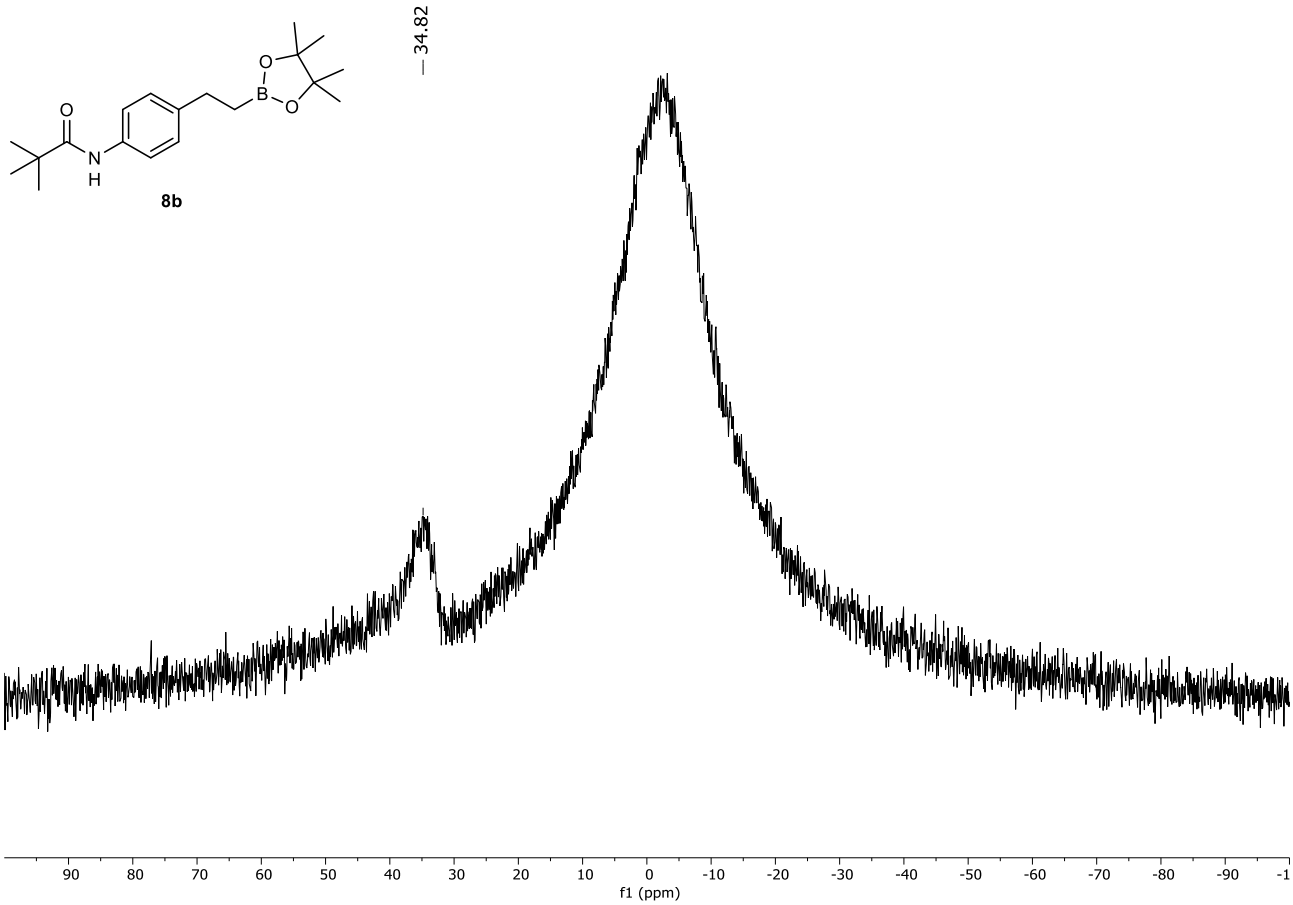
^{1}H NMR:


7.41
7.41
7.40
7.39
7.26 CDCl3
7.26
7.25
7.17
7.16
7.15
7.15
2.72
2.70
2.68
1.30
1.22
1.12
1.10
1.08
8b
2.0
1.2
2.1
1.9
9.8
11.9
2.1
f1 (ppm)

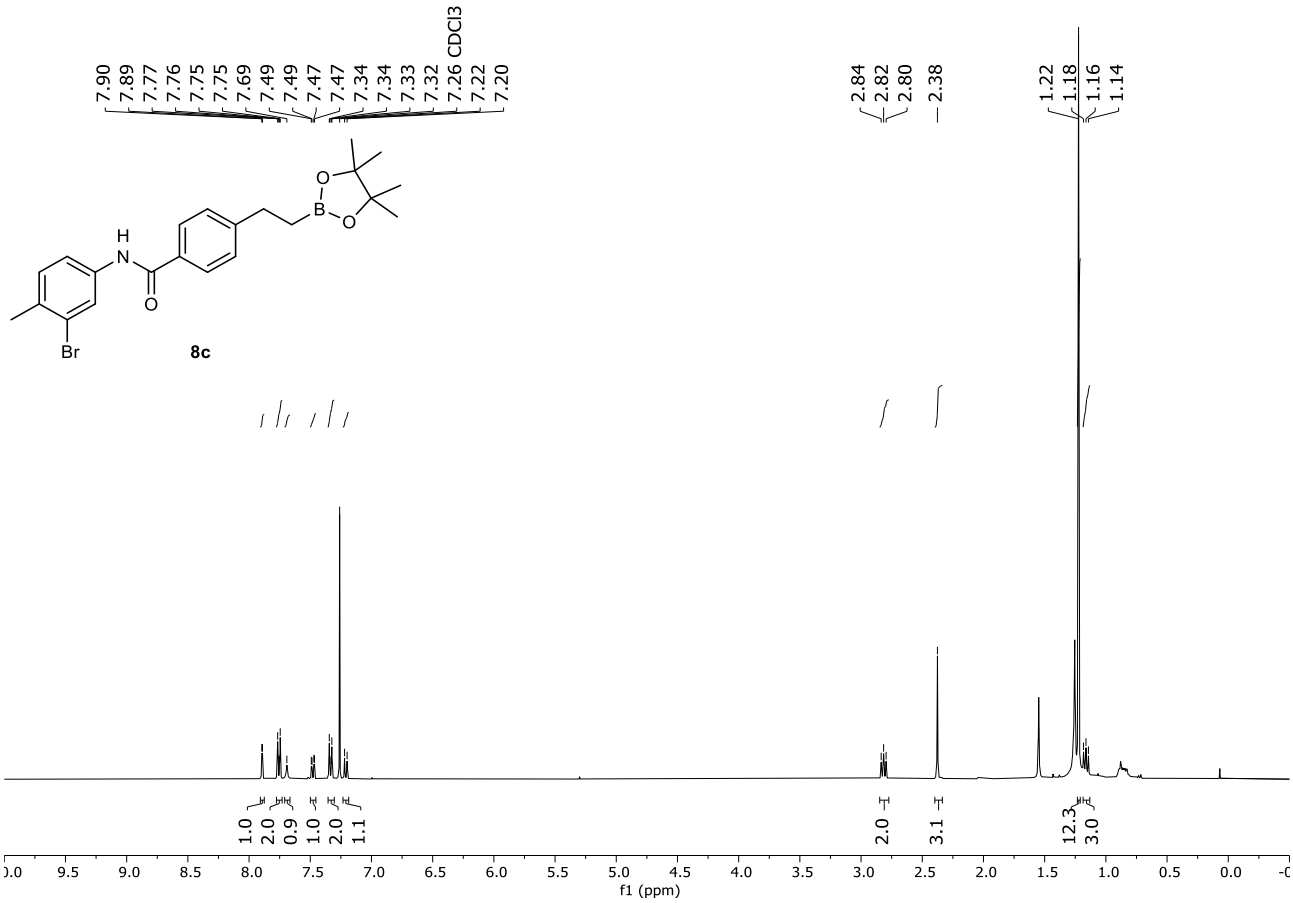
DEPT-Q:


176.35
140.46
135.54
128.39
119.91
83.09
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
39.48
29.34
27.63
24.80
8b
f1 (ppm)

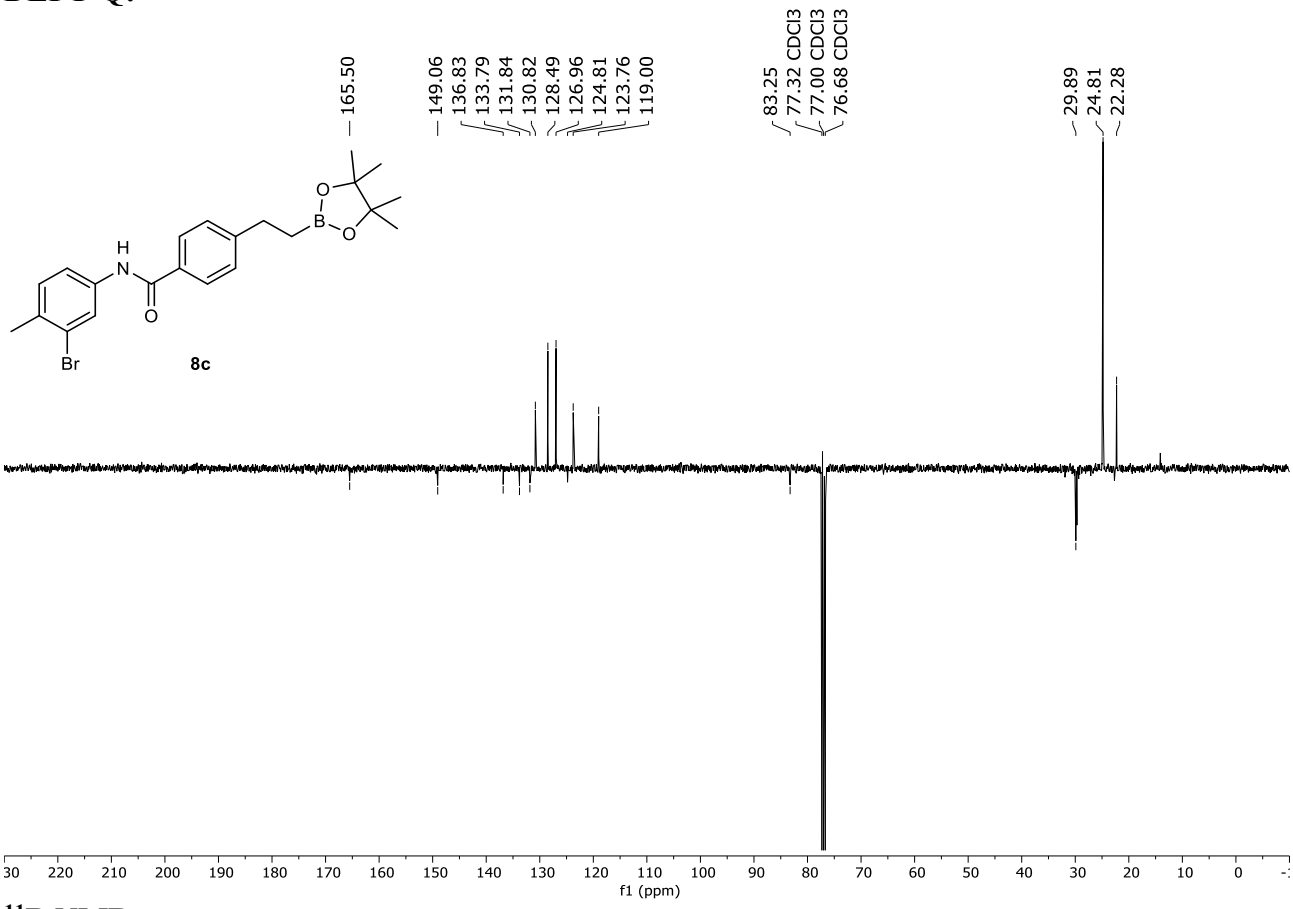
^{11}B NMR:



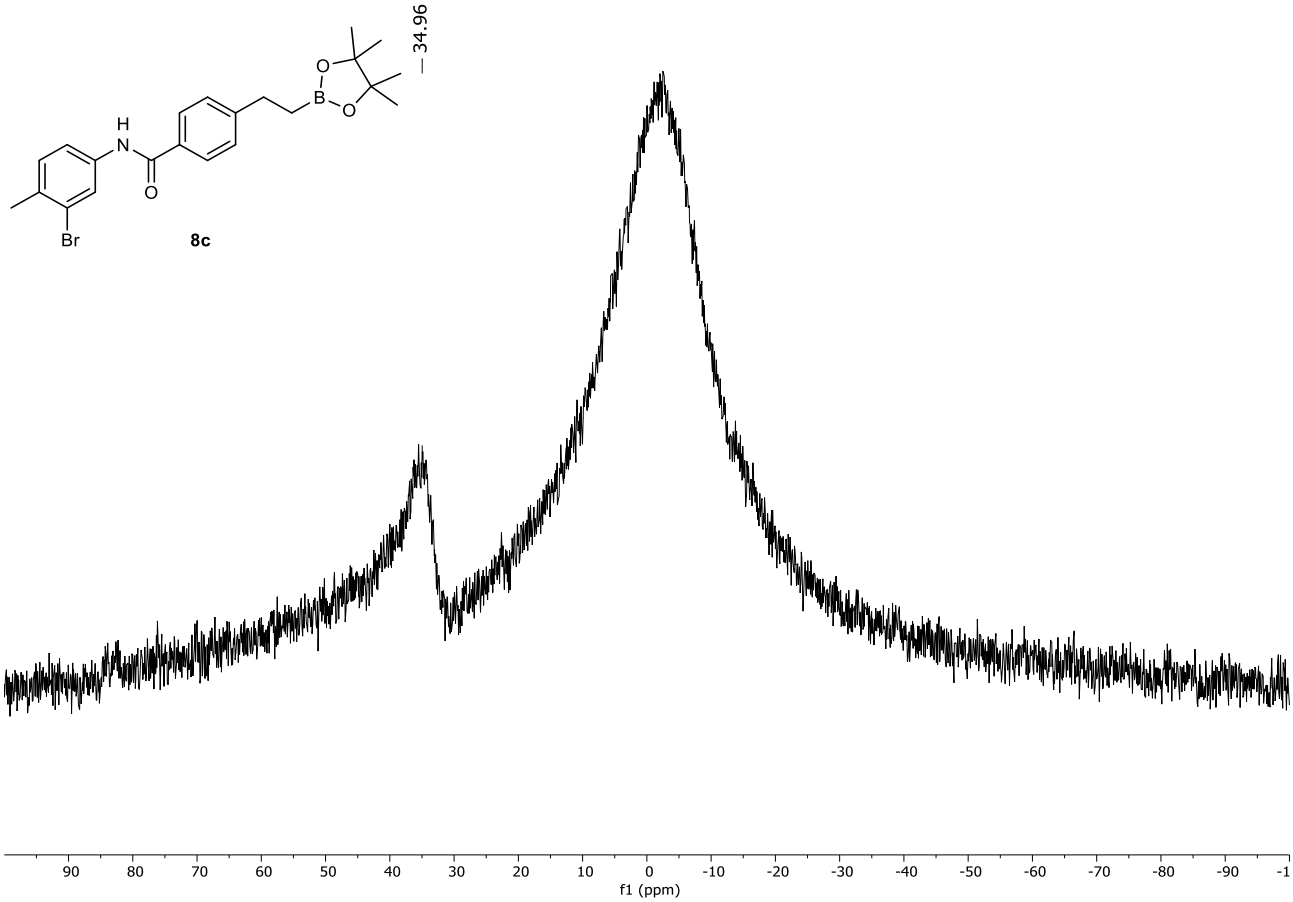
^{1}H NMR:



DEPT-Q:

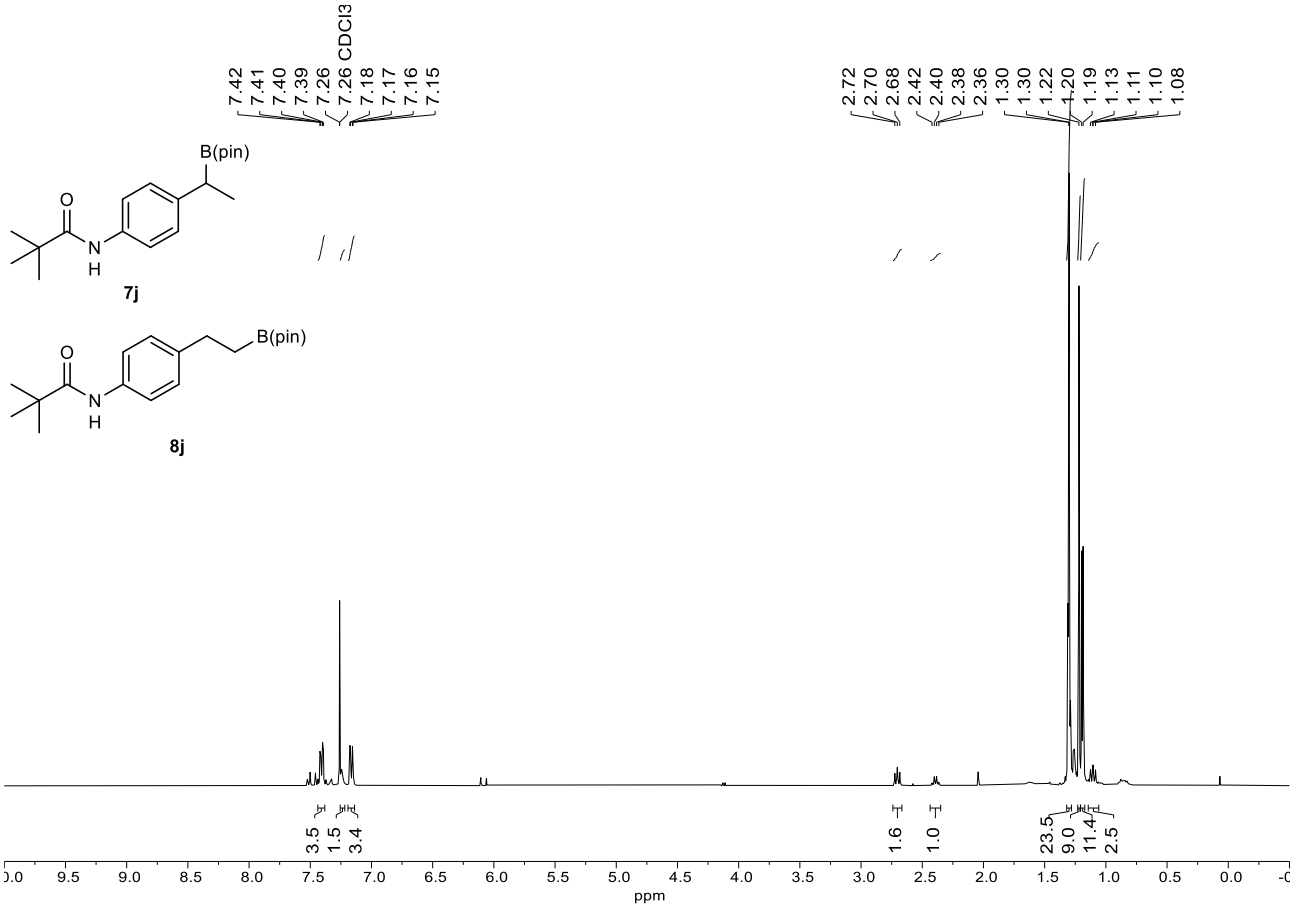


^{11}B NMR:

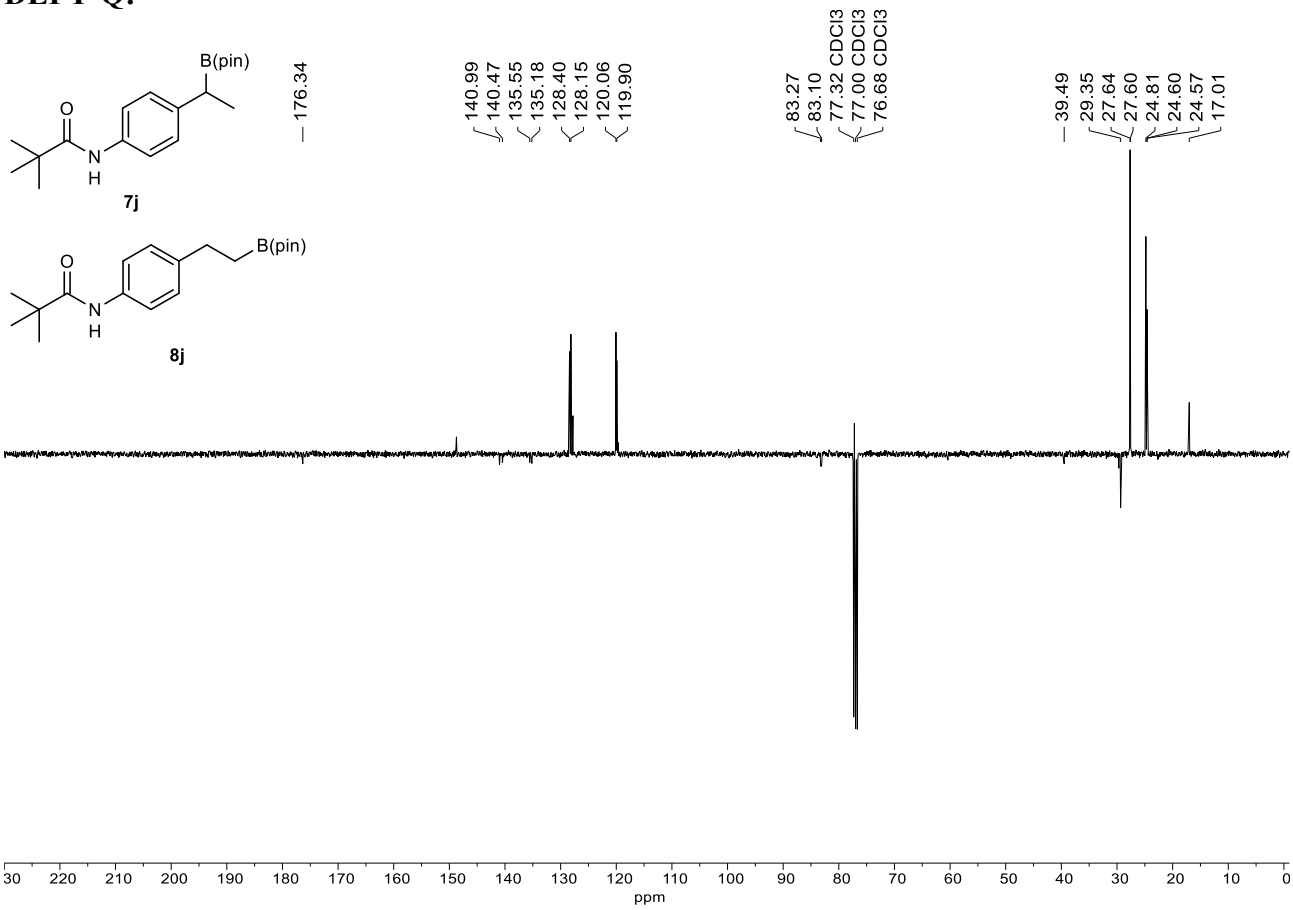


8.4. Rh-catalysed Hydroboration Products

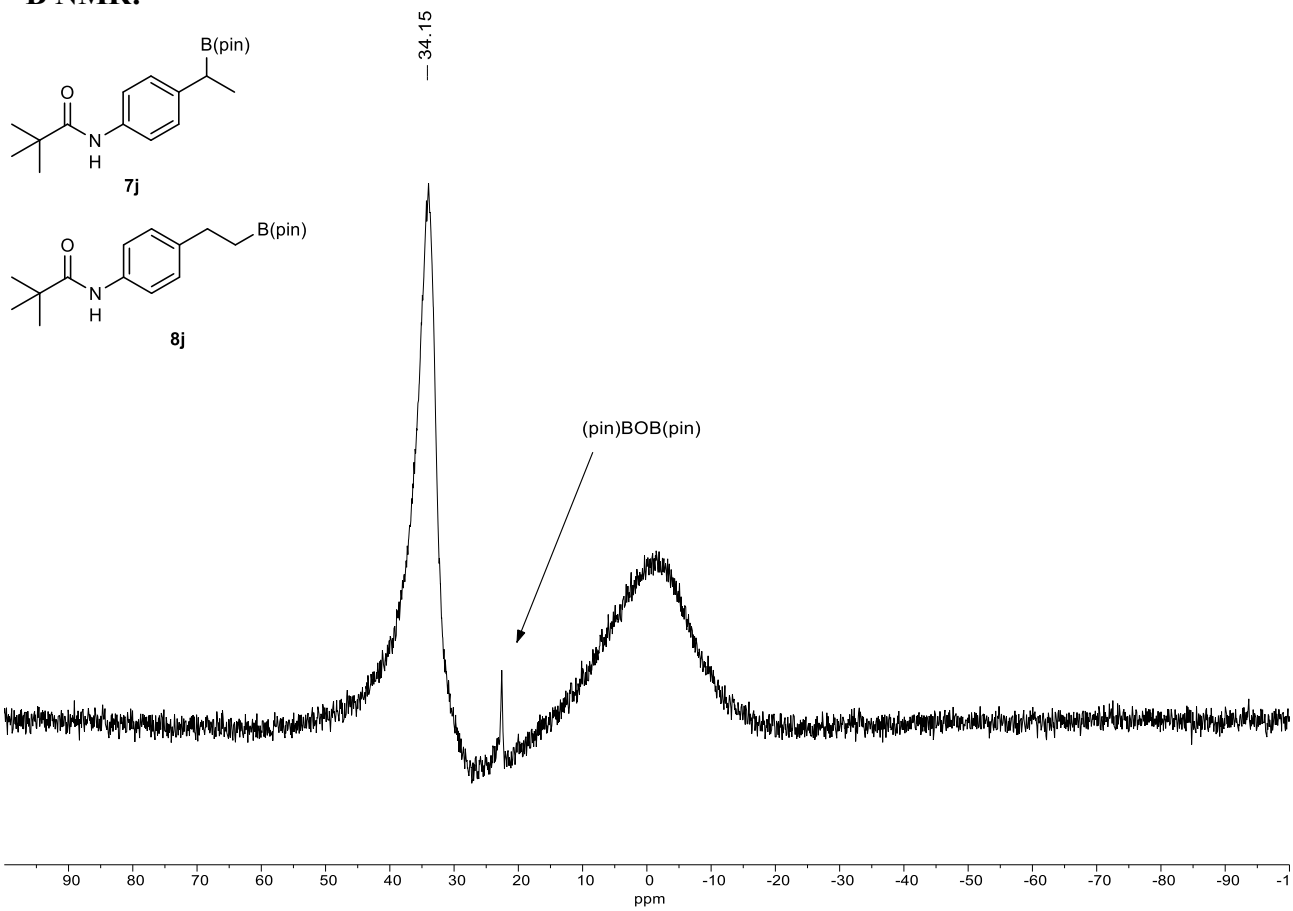
^{1}H NMR:



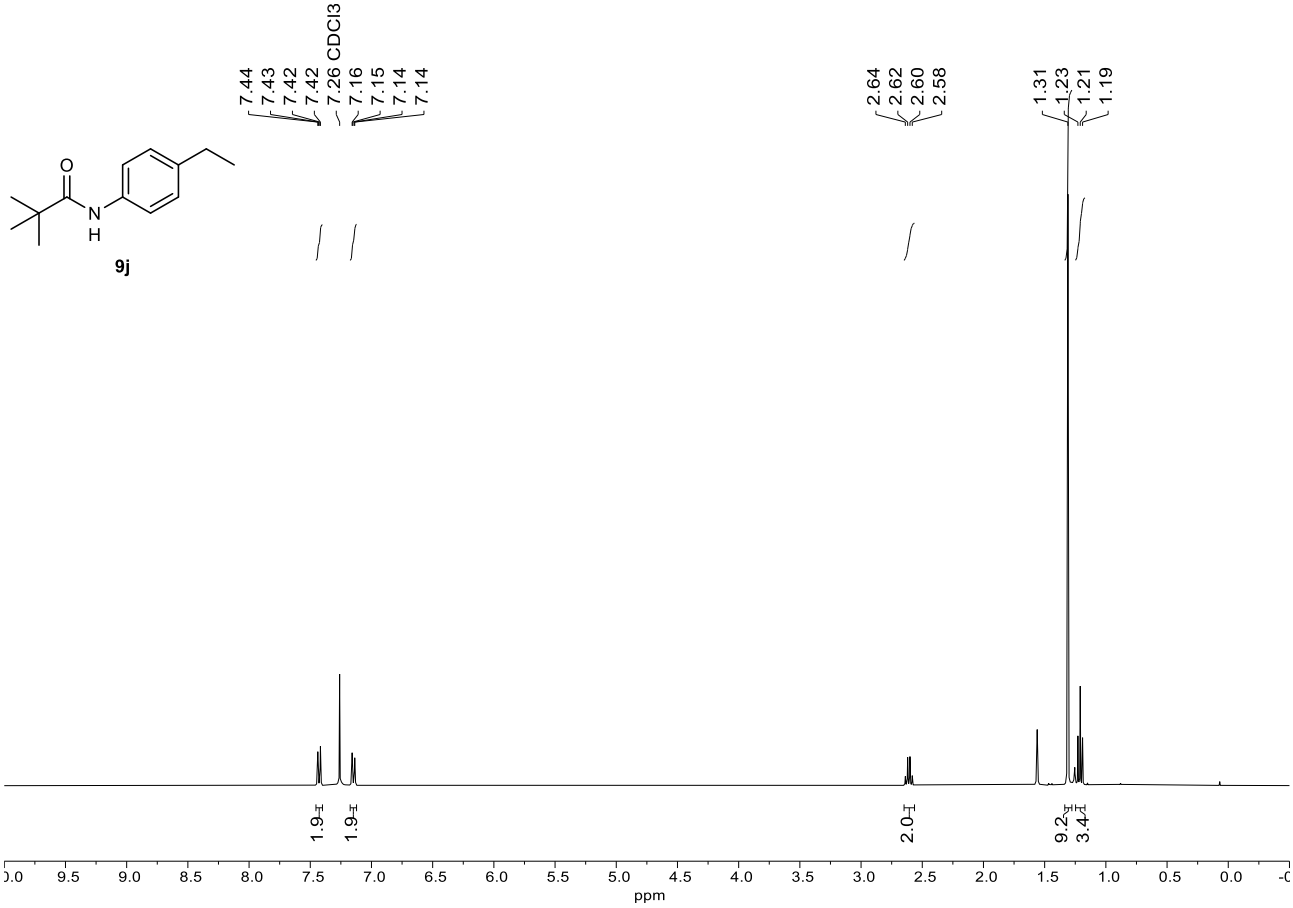
DEPT-Q:



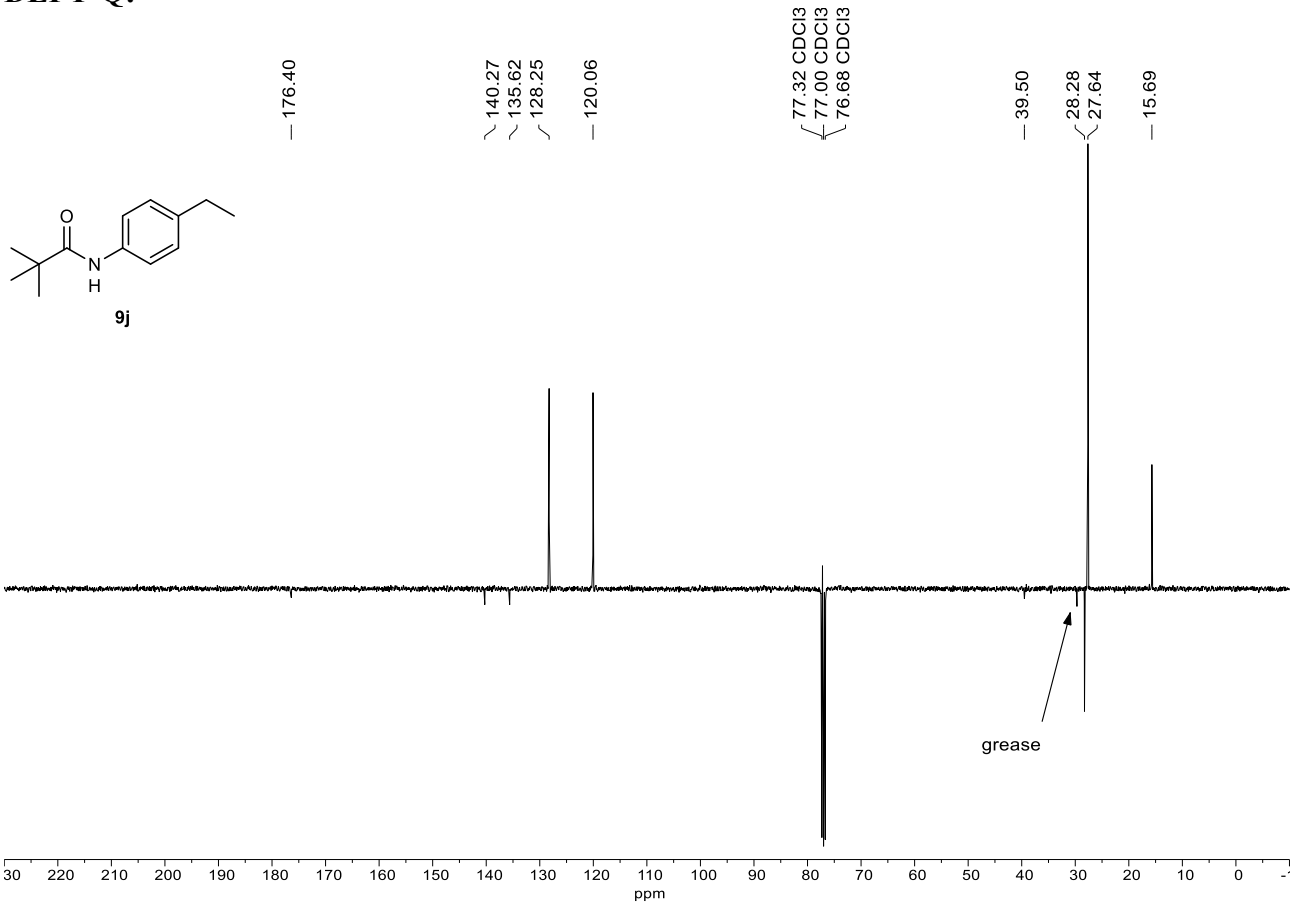
^{11}B NMR:



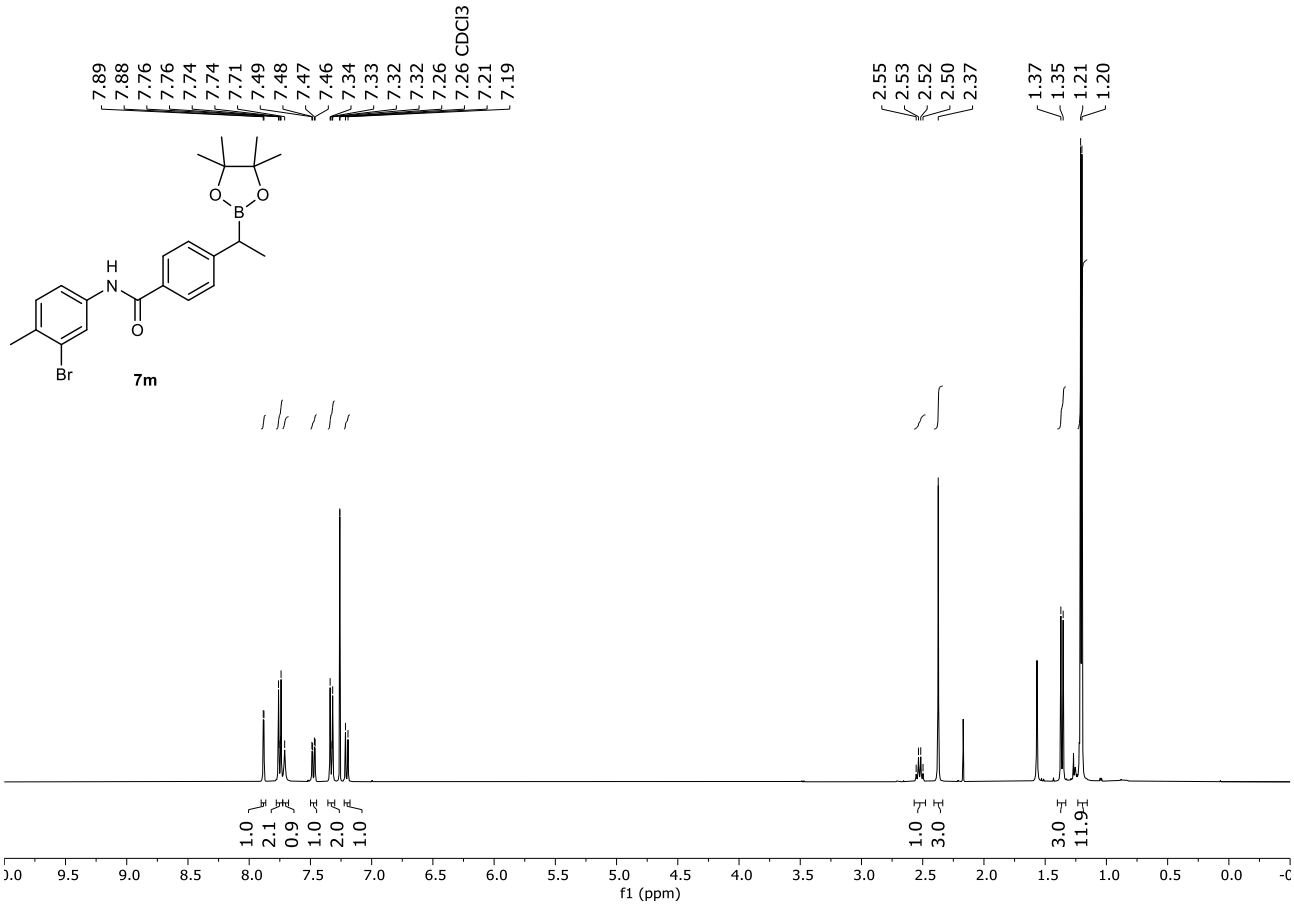
^{1}H NMR:



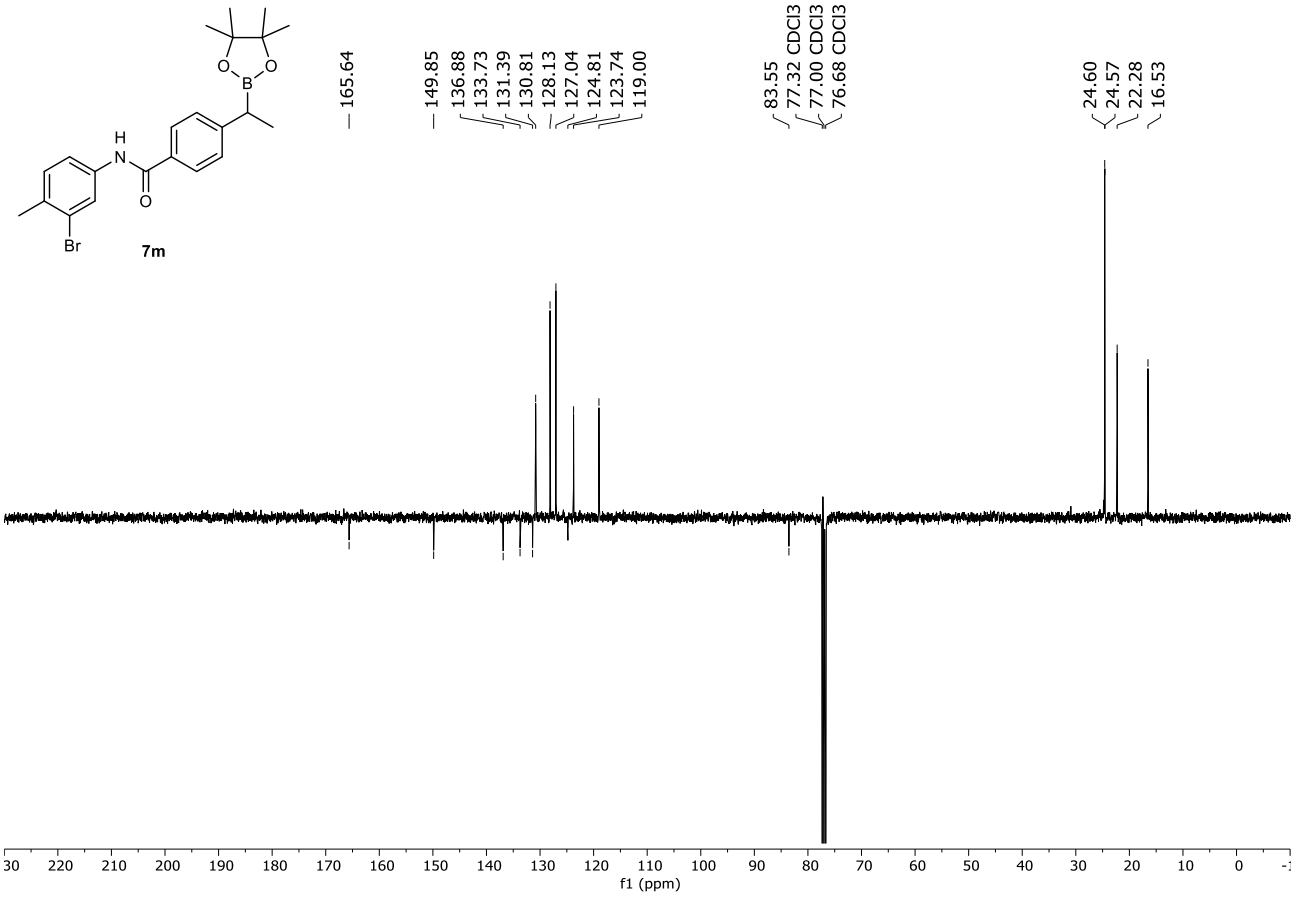
DEPT-Q:


176.40
140.27
135.62
128.25
120.06
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
39.50
28.28
27.64
15.69
9j
grease
ppm

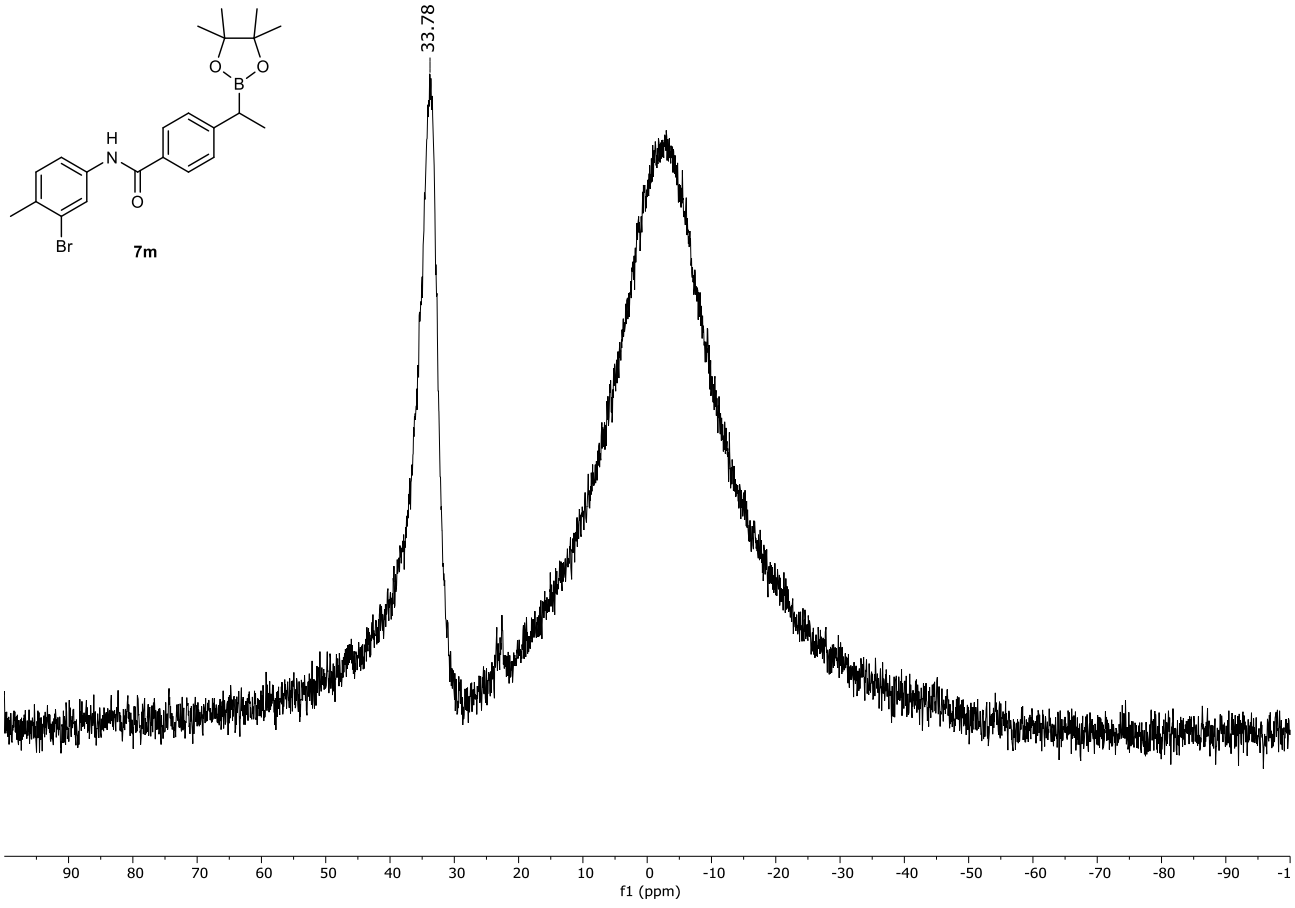
^{1}H NMR:


7.89
7.88
7.76
7.76
7.74
7.74
7.71
7.49
7.48
7.47
7.46
7.34
7.33
7.32
7.26
7.26 CDCl3
7.21
7.19
2.55
2.53
2.52
2.50
2.37
1.37
1.35
1.21
1.20
7m
1.0
2.1
0.9
1.0
2.0
1.0
1.0
3.0
3.0
11.9
f1 (ppm)

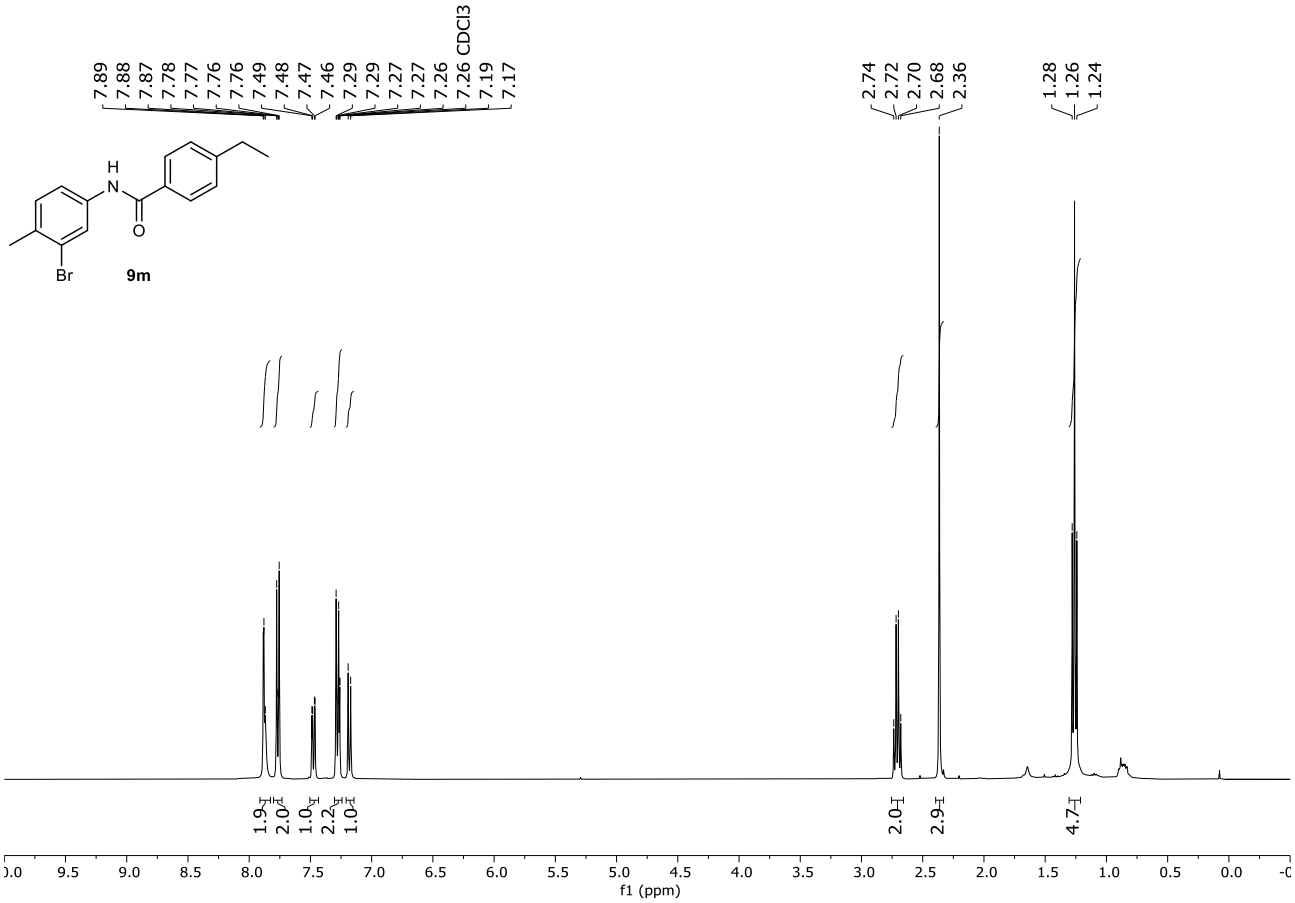
DEPT-Q:



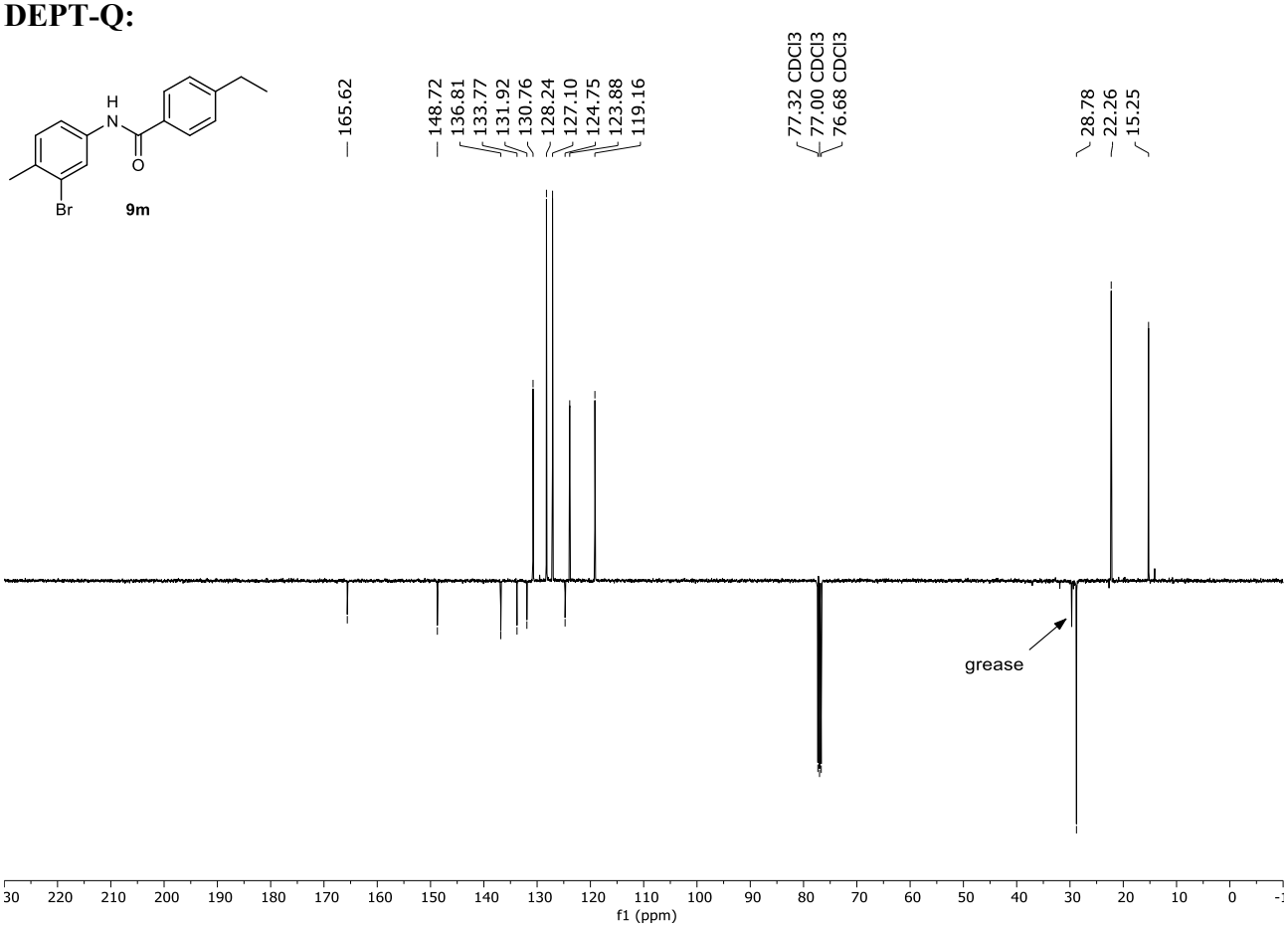
^{11}B NMR:



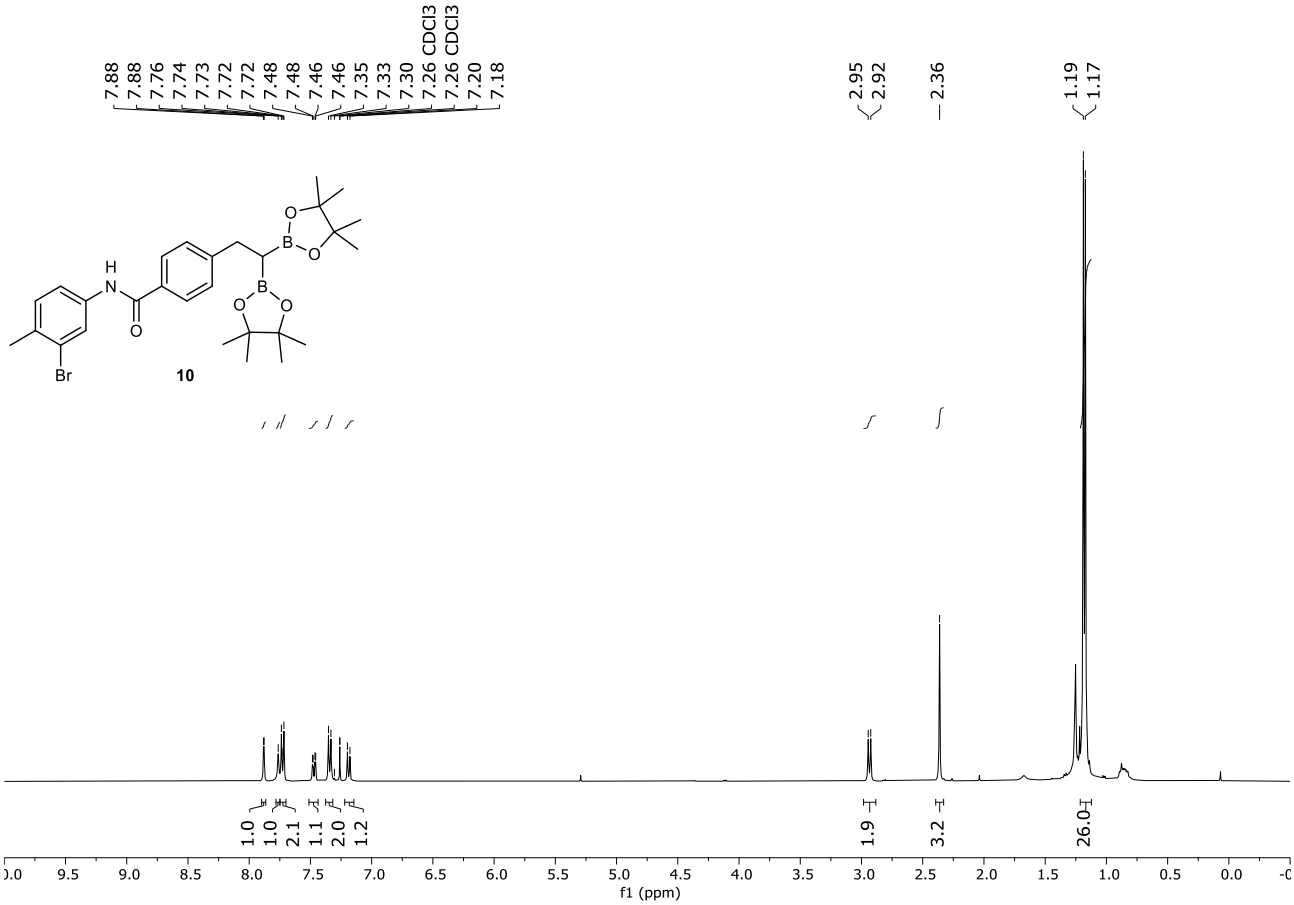
^{1}H NMR:


7.89
7.88
7.87
7.78
7.77
7.76
7.76
7.49
7.48
7.47
7.46
7.29
7.29
7.27
7.27
7.26
7.26 CDCl3
7.19
7.17
2.74
2.72
2.70
2.68
2.36
1.28
1.26
1.24
H
N
O
Br
9m
1.9
2.0
1.0
2.2
1.0
2.0
2.9
4.7
f1 (ppm)

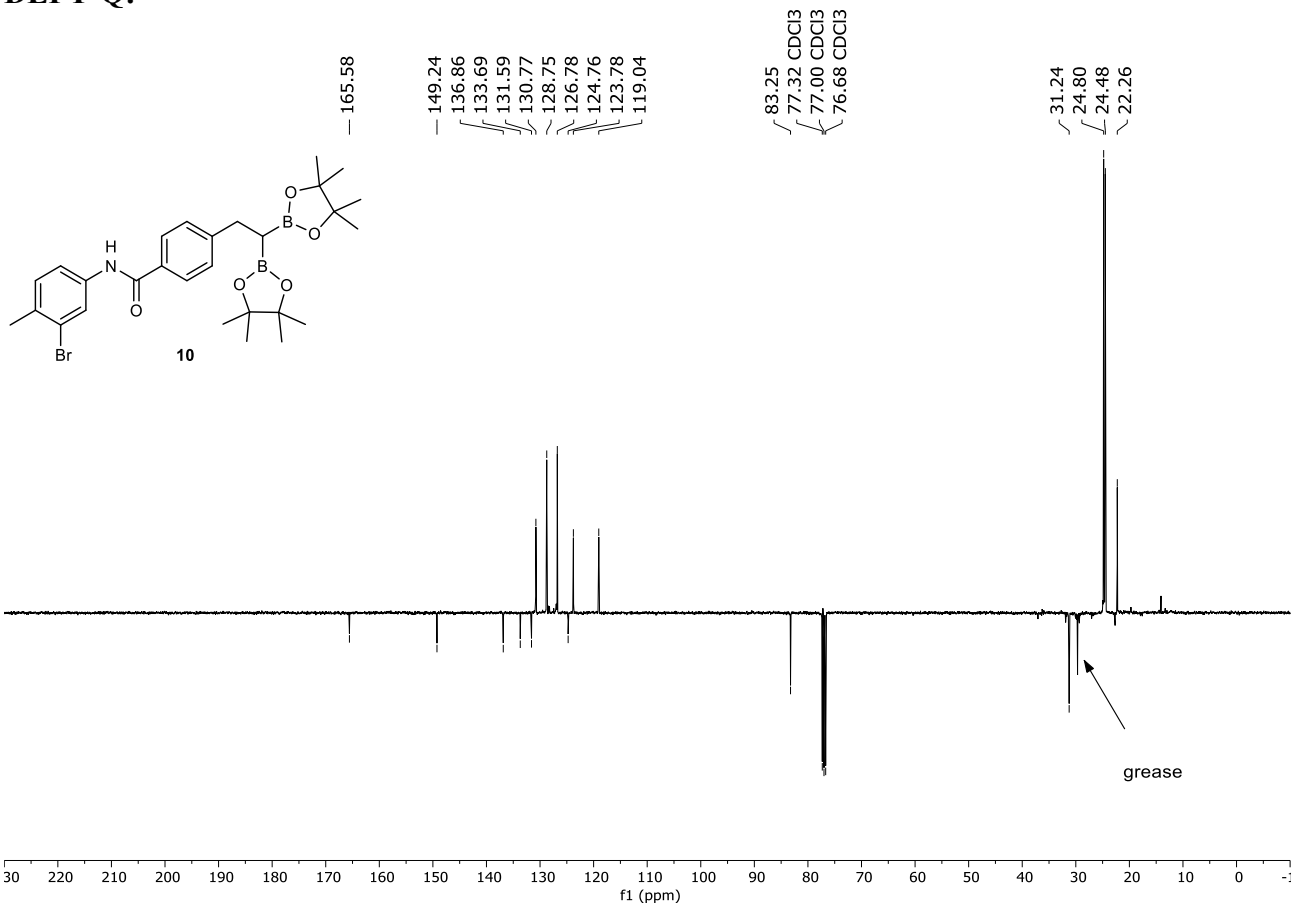
DEPT-Q:


H
N
O
Br
9m
165.62
148.72
136.81
133.77
131.92
130.76
128.24
127.10
124.75
123.88
119.16
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
28.78
22.26
15.25
grease
f1 (ppm)

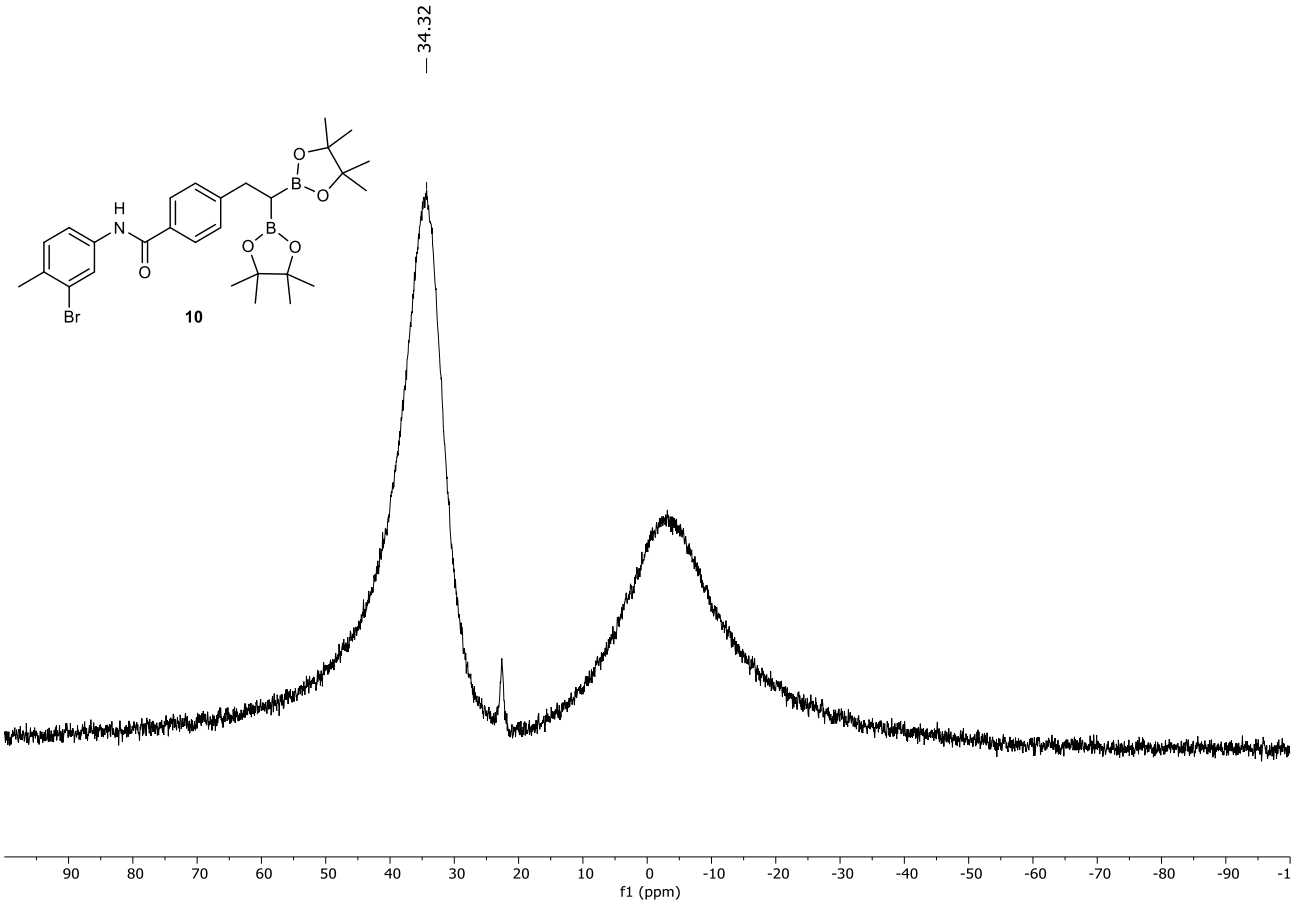
^{1}H NMR:


7.88
7.88
7.76
7.74
7.73
7.72
7.72
7.48
7.48
7.46
7.46
7.35
7.33
7.30
7.26 CDCl3
7.26 CDCl3
7.20
7.18
2.95
2.92
2.36
1.19
1.17
10
1.0
1.0
2.1
1.1
2.0
1.2
1.9
3.2
26.0
f1 (ppm)

DEPT-Q:

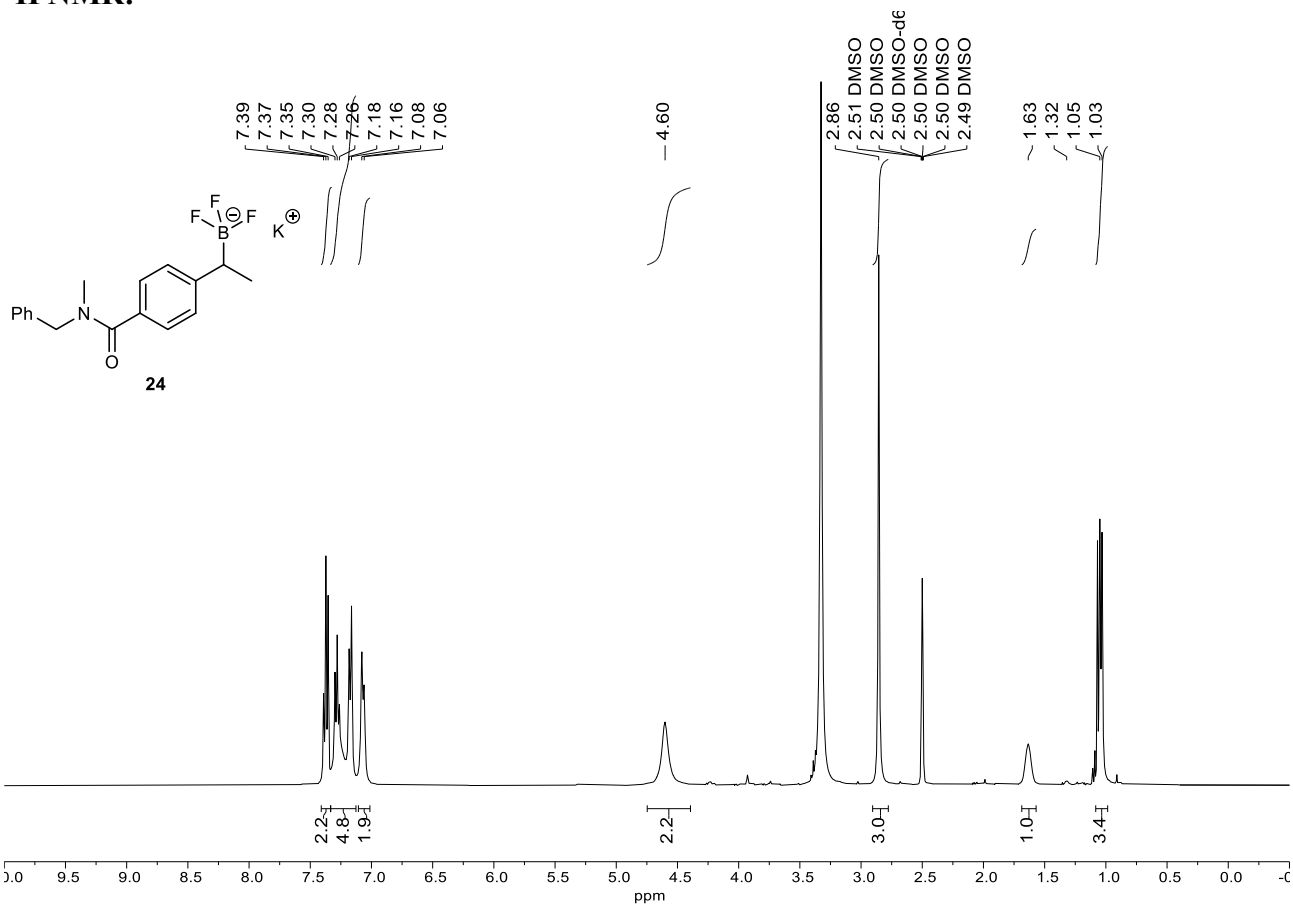

165.58
149.24
136.86
133.69
131.59
130.77
128.75
126.78
124.76
123.78
119.04
83.25
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
31.24
24.80
24.48
22.26
10
grease
f1 (ppm)

^{11}B NMR:

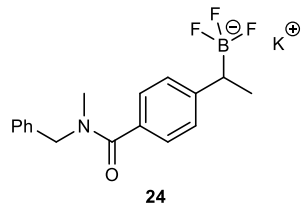


8.5. Reactions of Boronic Ester 7e

^{1}H NMR:

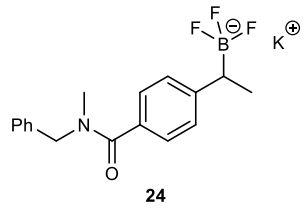


DEPT-Q:



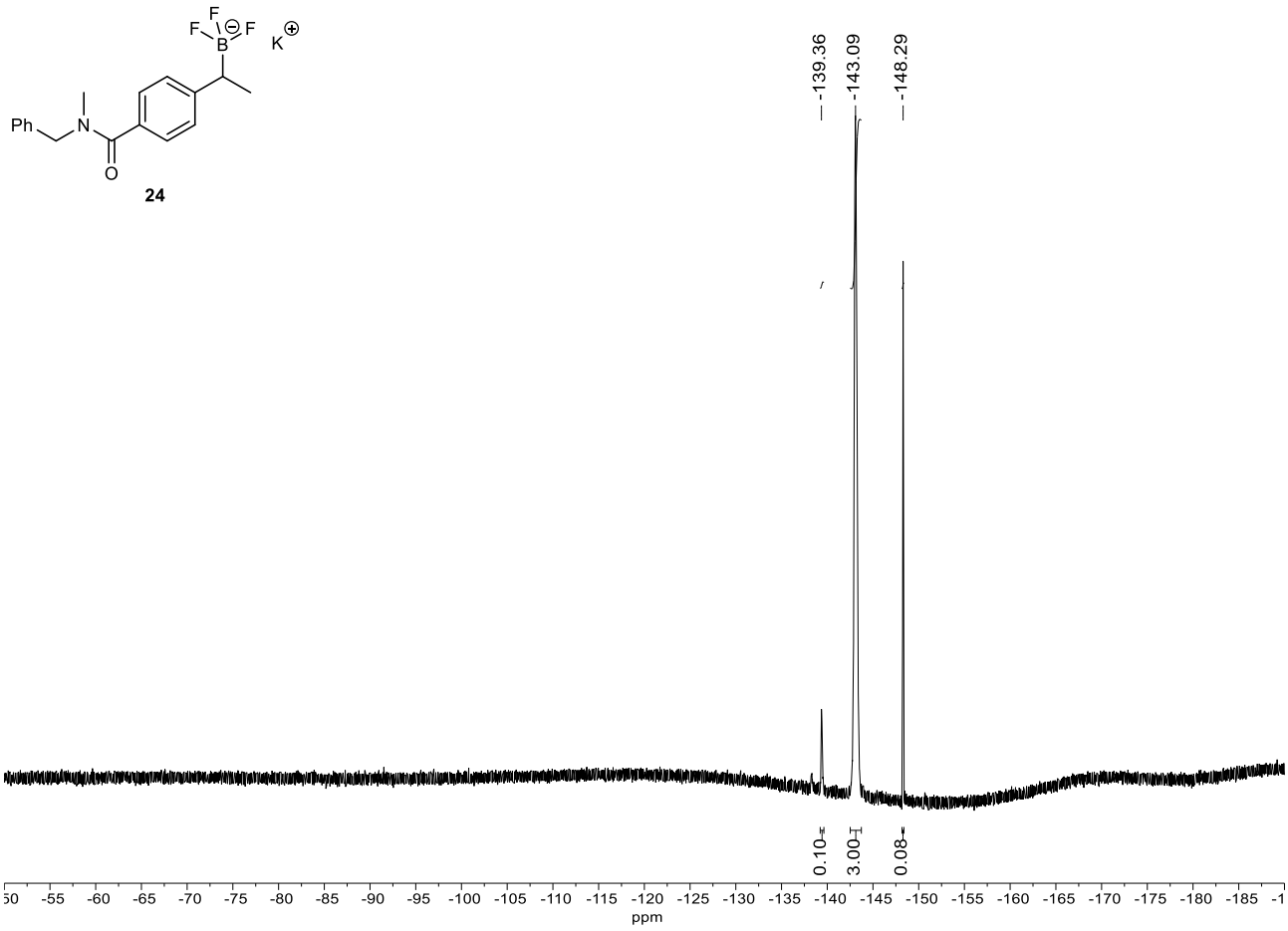
24

^{11}B NMR:

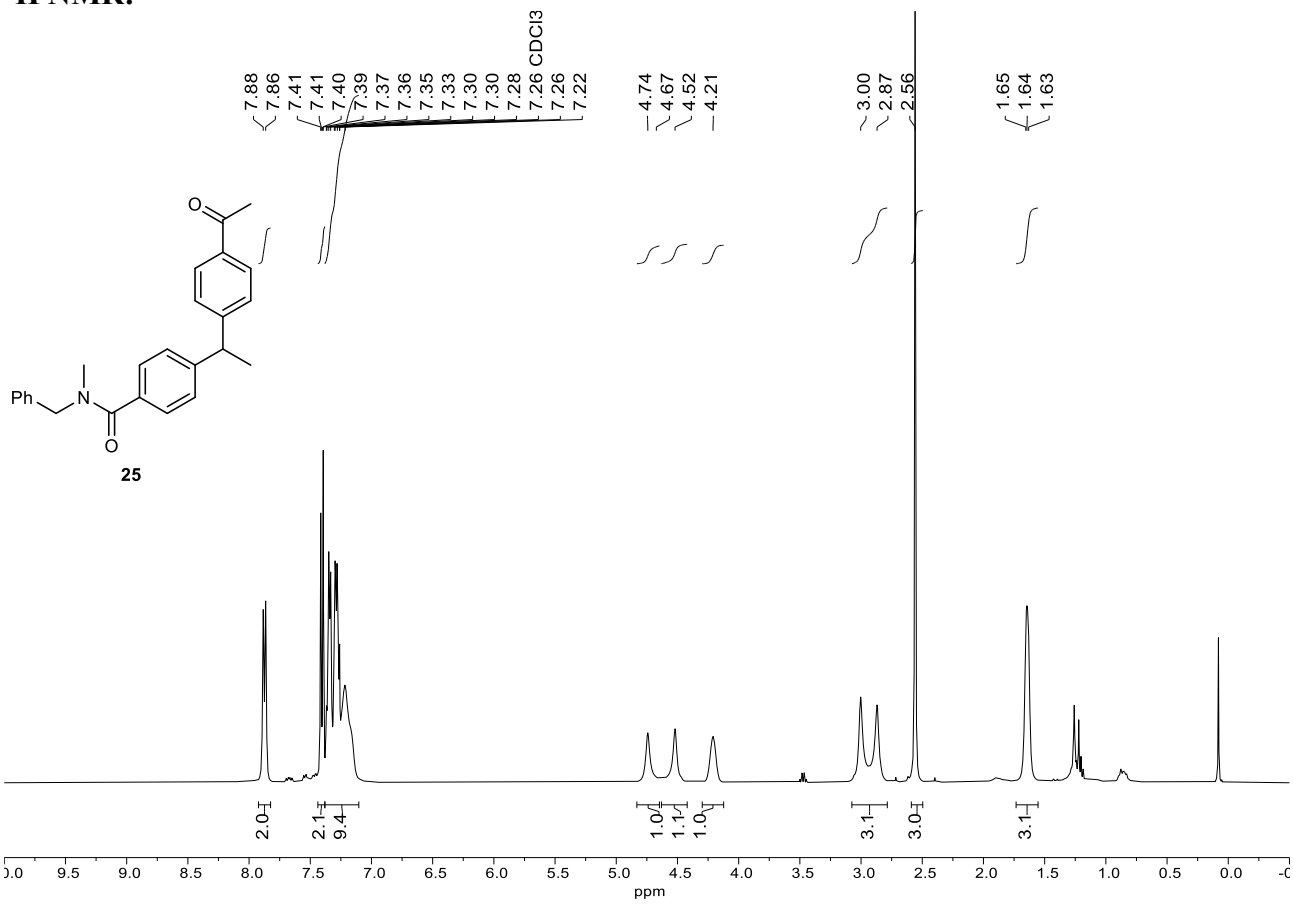


24

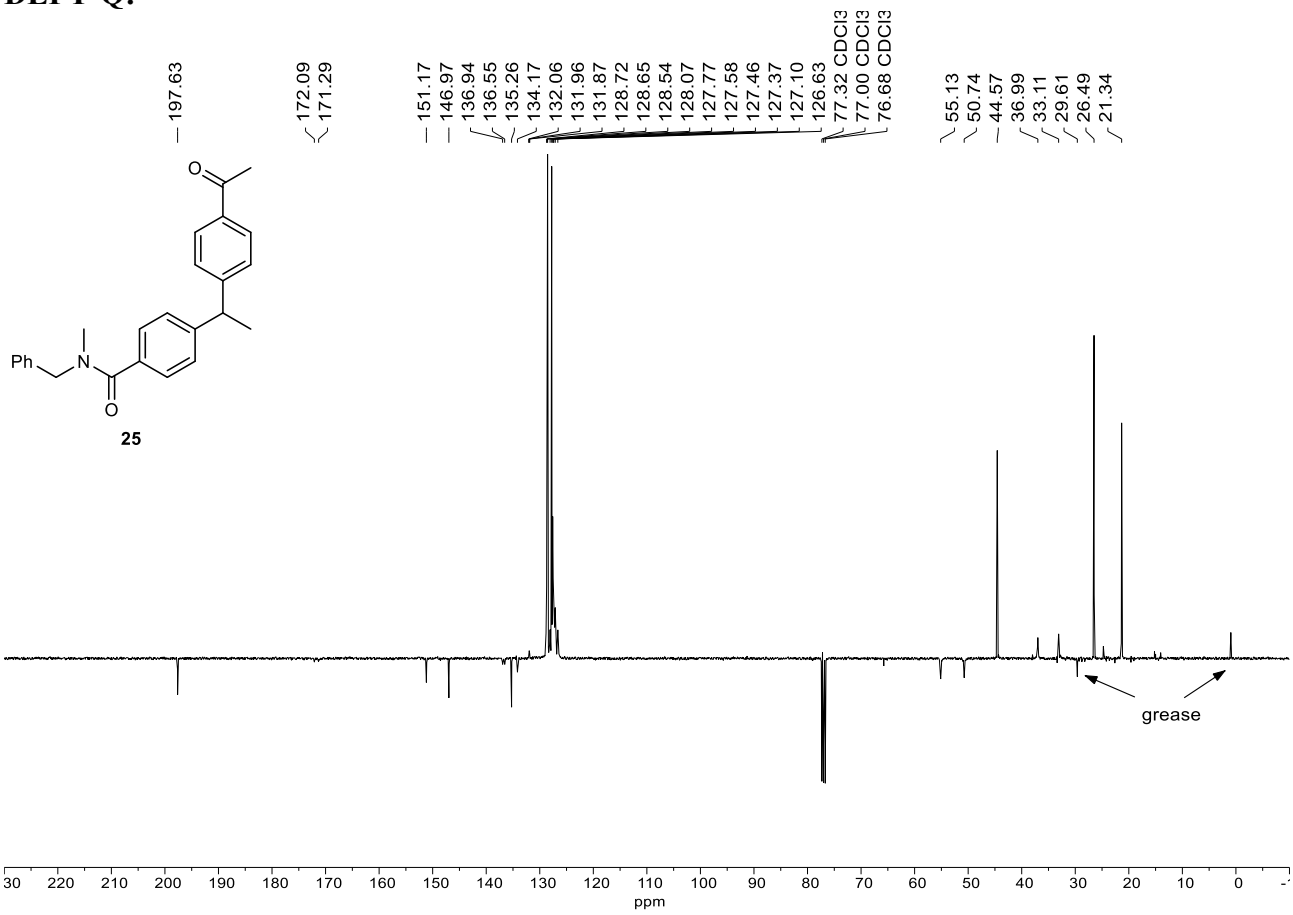
^{19}F NMR:



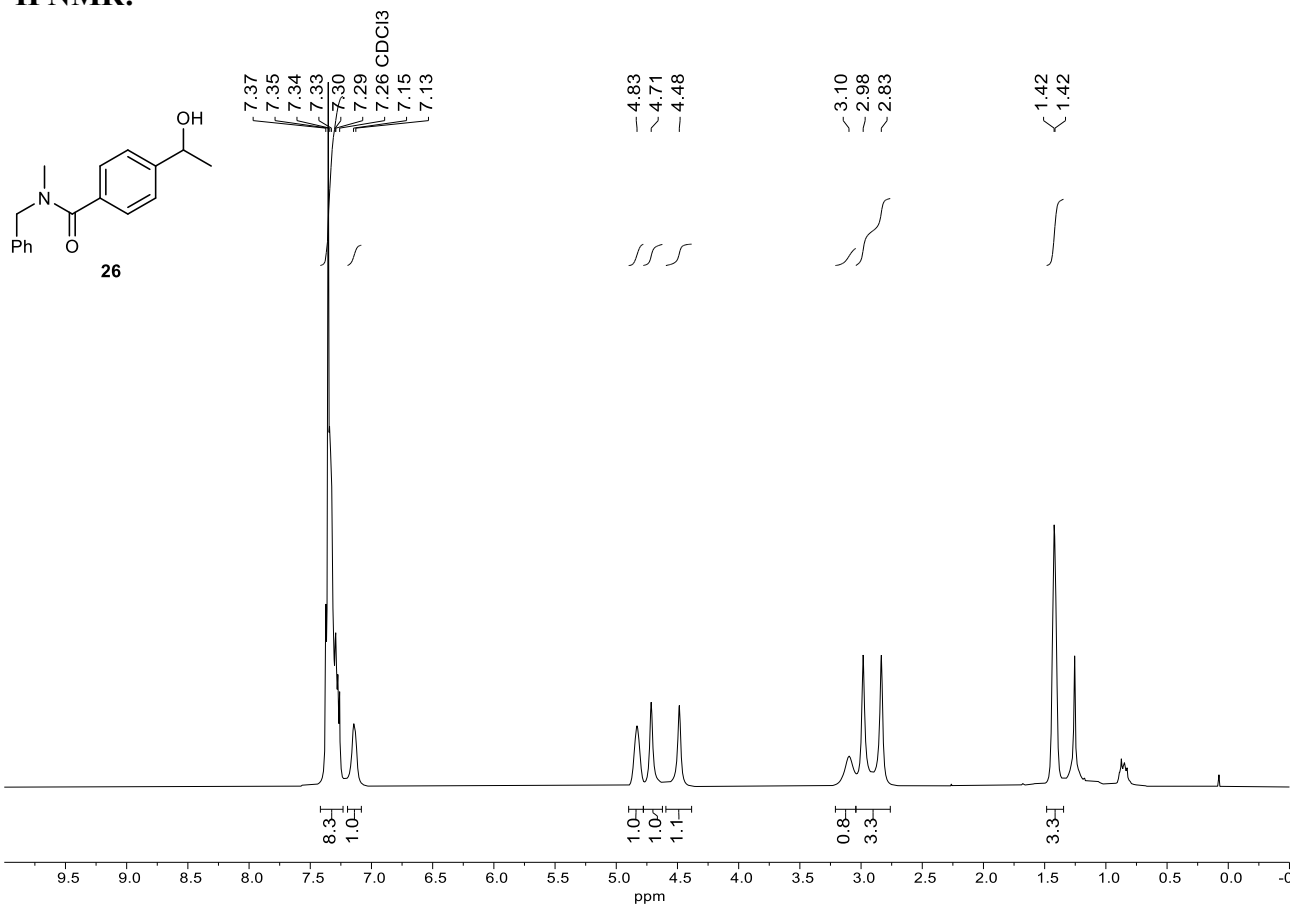
^{1}H NMR:



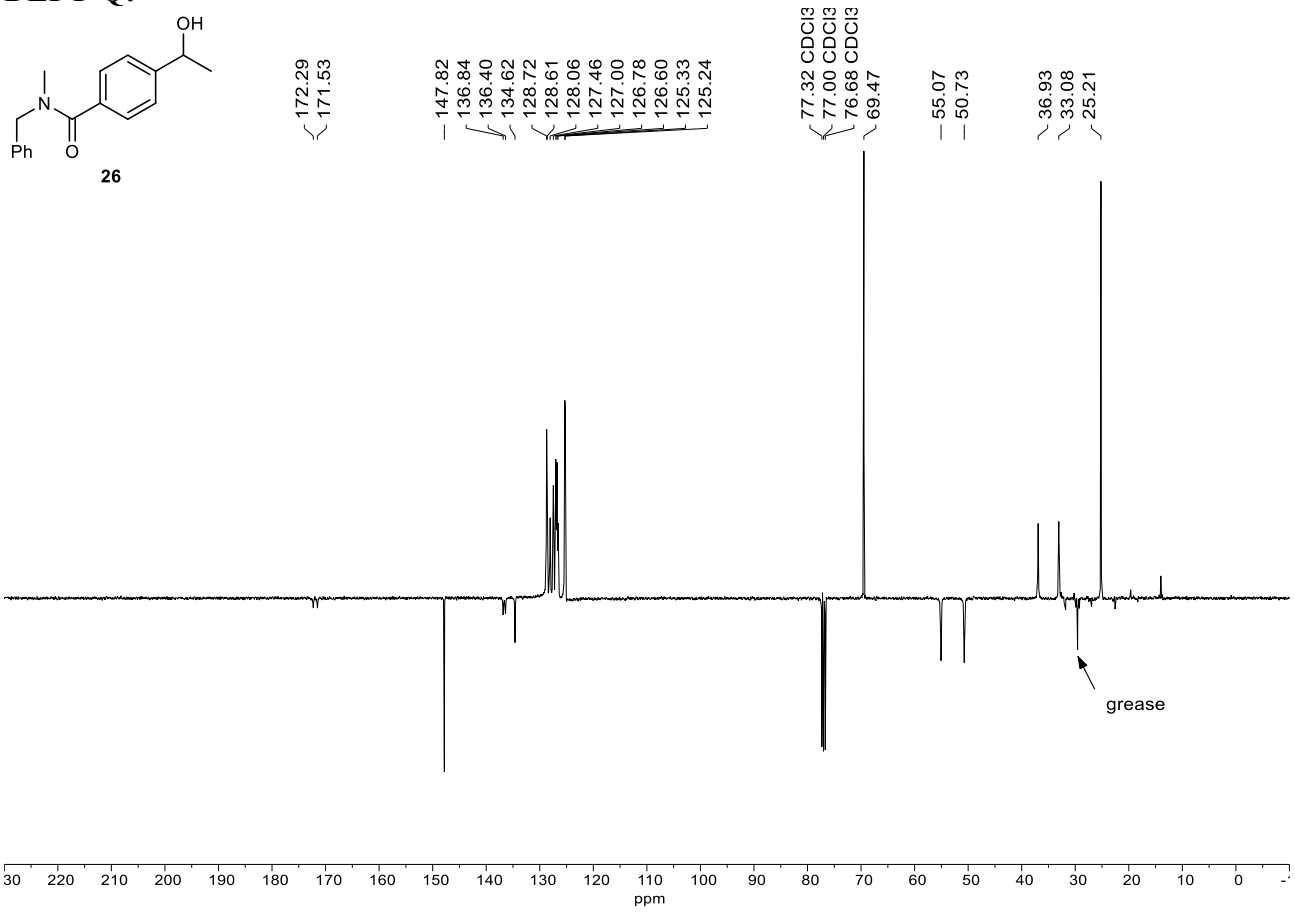
DEPT-Q:


197.63
172.09
171.29
151.17
146.97
136.94
136.55
135.26
134.17
132.06
131.96
131.87
128.72
128.65
128.54
128.07
127.77
127.58
127.46
127.37
127.10
126.63
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.13
50.74
44.57
36.99
33.11
29.61
26.49
21.34
O
Ph
N
O
25
grease
ppm

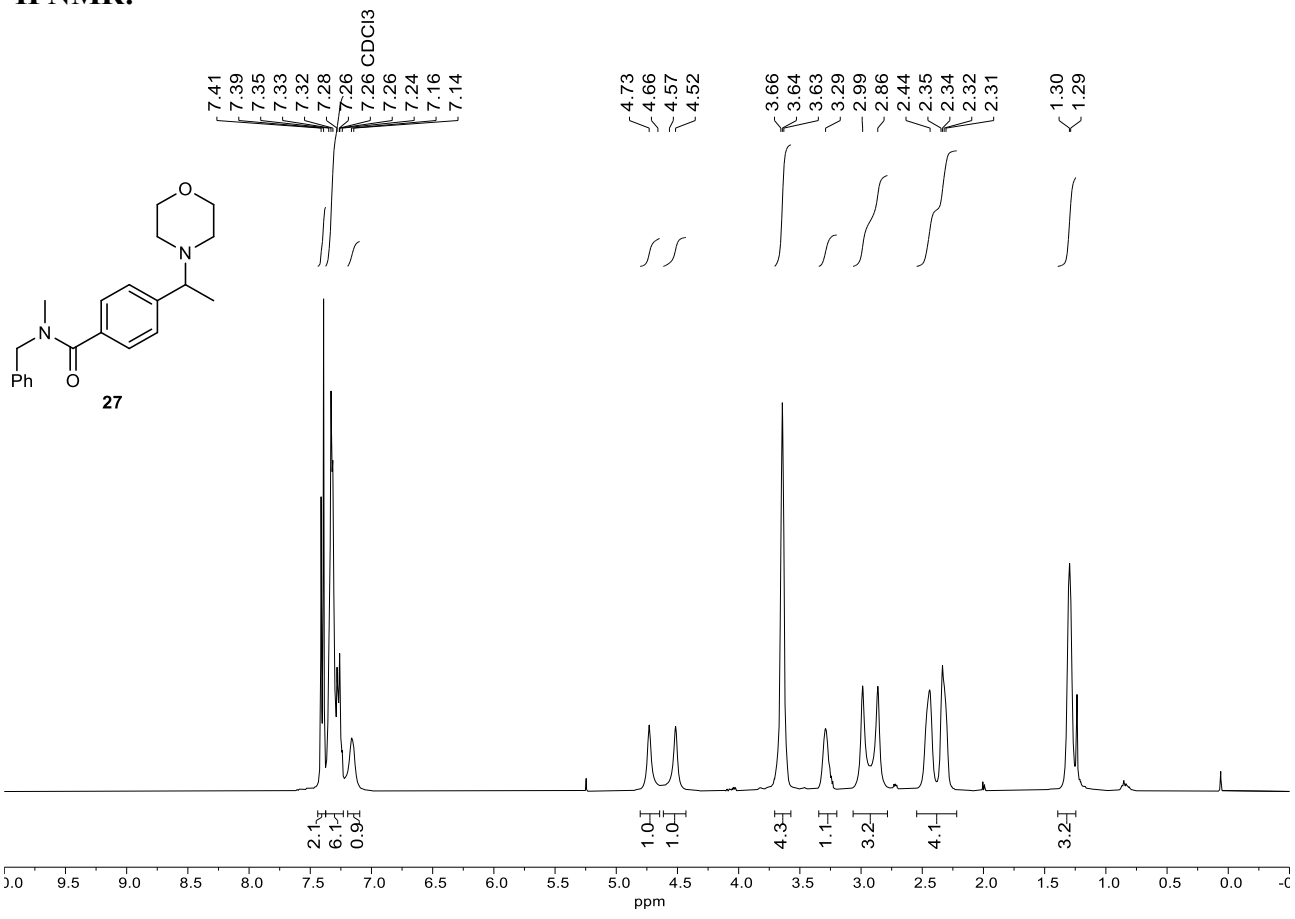
^{1}H NMR:


7.37
7.35
7.34
7.33
7.30
7.29
7.26 CDCl3
7.15
7.13
4.83
4.71
4.48
3.10
2.98
2.83
1.42
1.42
OH
N
Ph
O
26
8.3
1.0
1.0
1.0
1.1
0.8
3.3
3.3
ppm

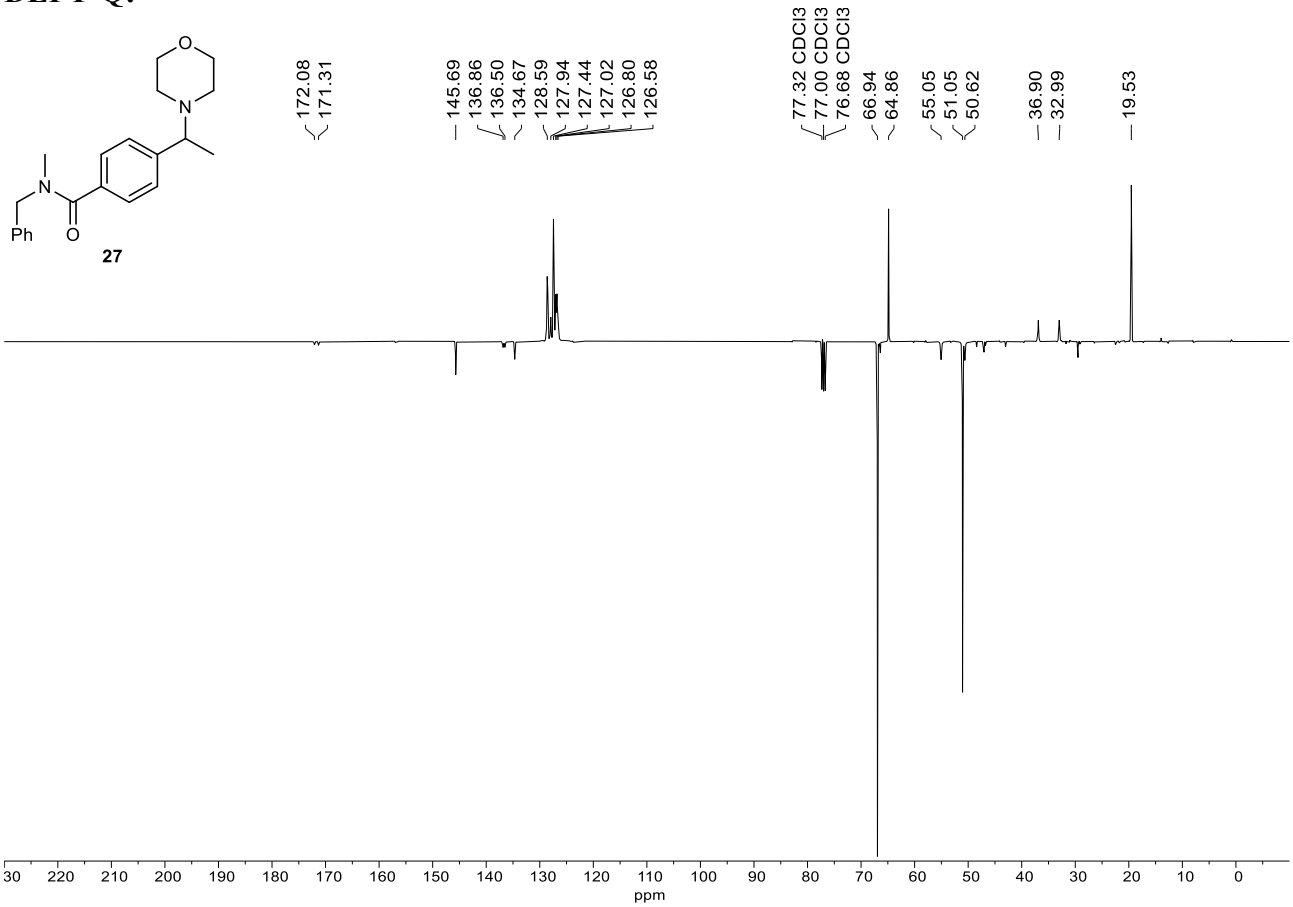
DEPT-Q:


OH
N
Ph
O
26
172.29
171.53
147.82
136.84
136.40
134.62
128.72
128.61
128.06
127.46
127.00
126.78
126.60
125.33
125.24
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.47
55.07
50.73
36.93
33.08
25.21
grease
ppm

^{1}H NMR:

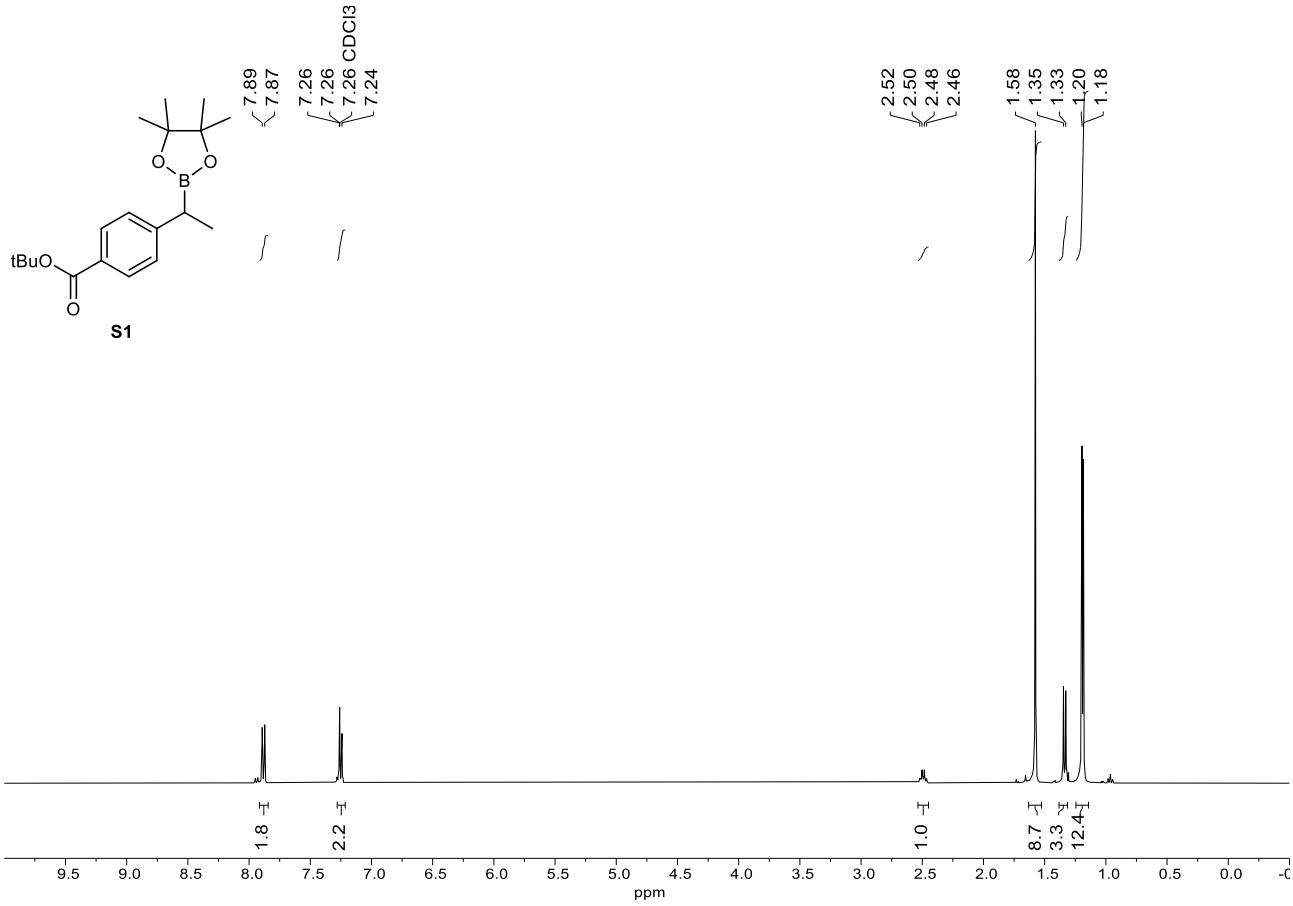

7.41
7.39
7.35
7.33
7.32
7.28
7.26
7.26 CDCl3
7.24
7.16
7.14
4.73
4.66
4.57
4.52
3.66
3.64
3.63
3.29
2.99
2.86
2.44
2.35
2.34
2.32
2.31
1.30
1.29
O
N
N
Ph
O
27
2.1
6.1
0.9
1.0
1.0
4.3
1.1
3.2
4.1
3.2
ppm

DEPT-Q:

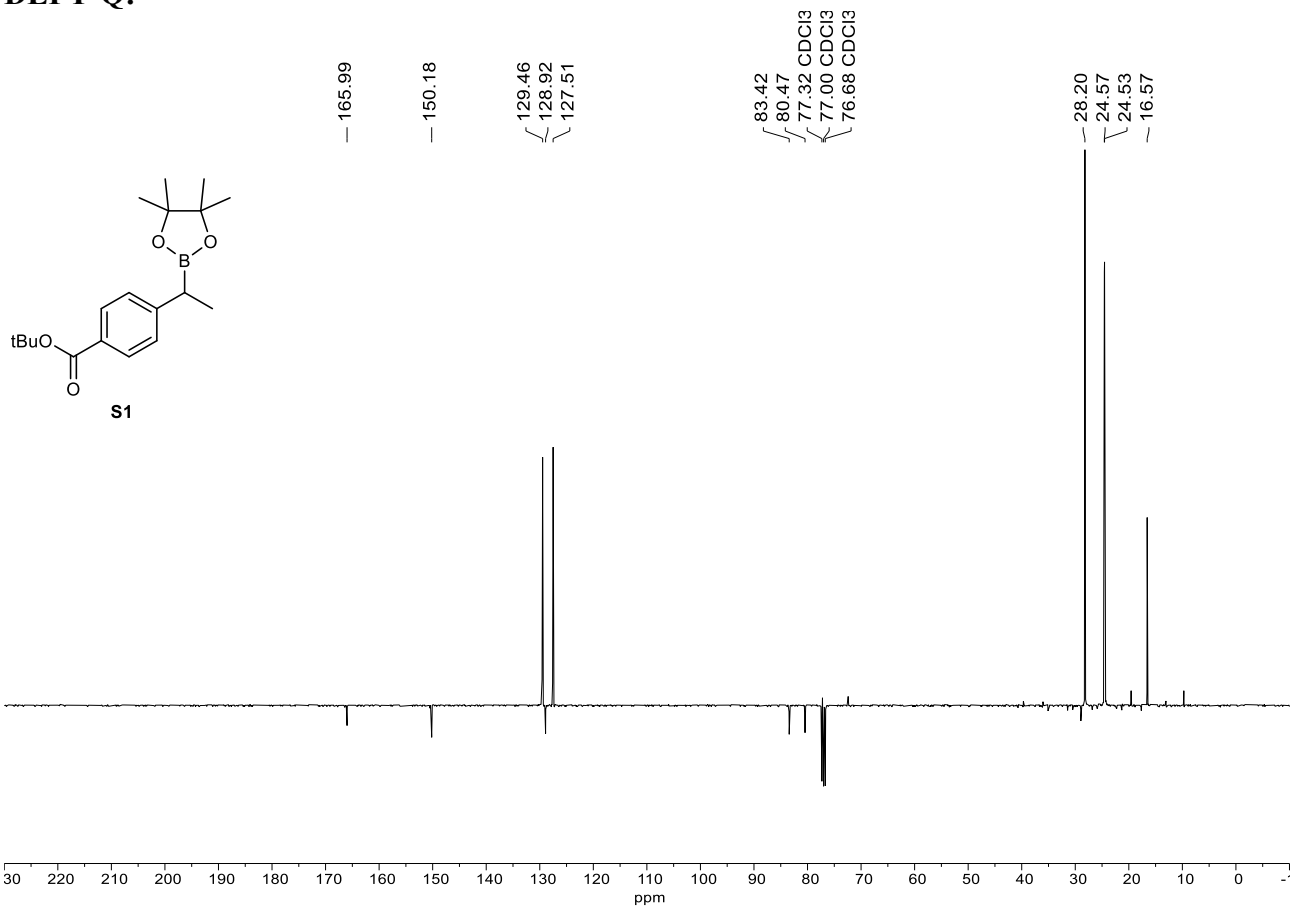

O
N
N
Ph
O
27
172.08
171.31
145.69
136.86
136.50
134.67
128.59
127.94
127.44
127.02
126.80
126.58
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
66.94
64.86
55.05
51.05
50.62
36.90
32.99
19.53
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

8.6. Miscellaneous Compounds

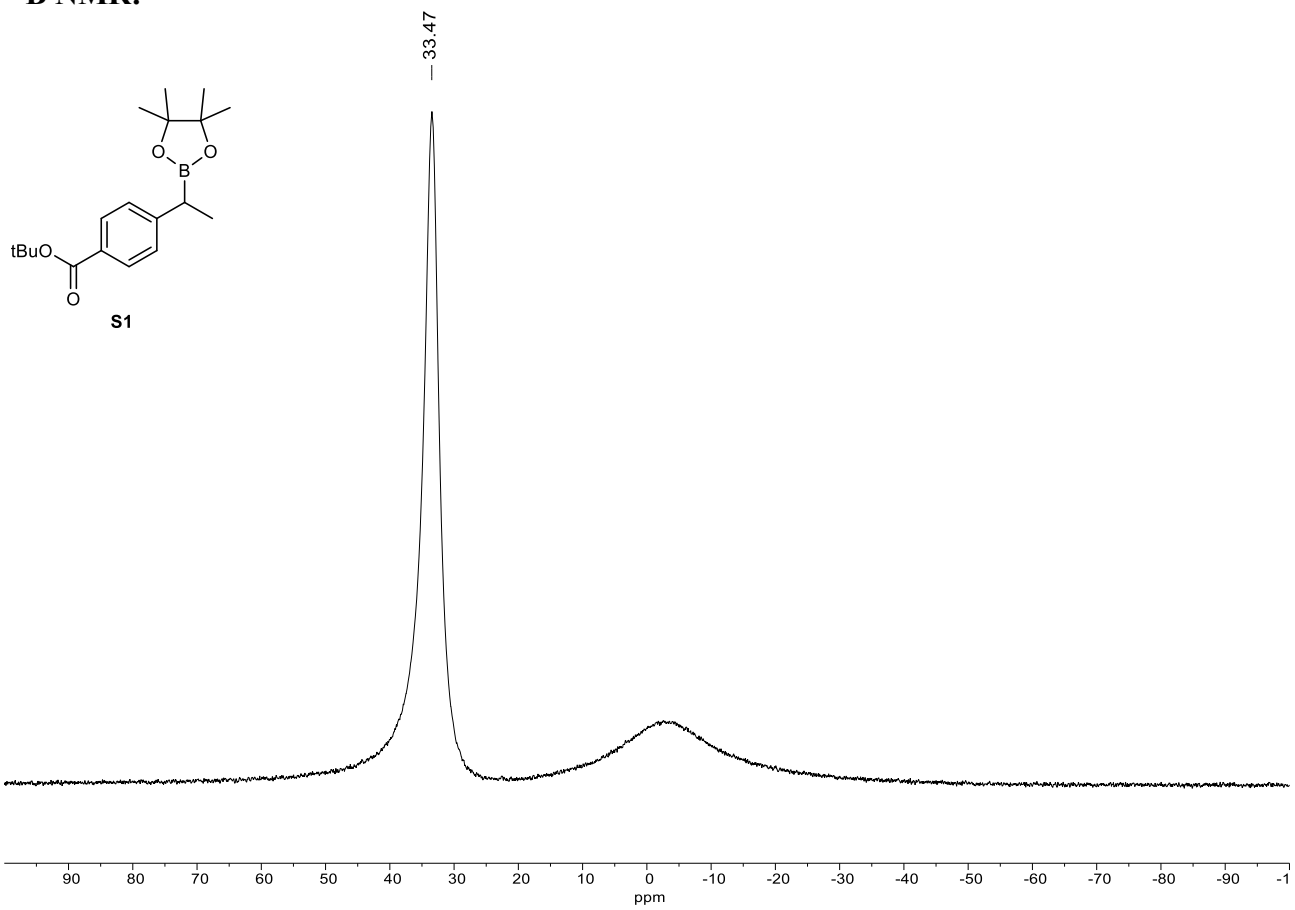
^{1}H NMR:



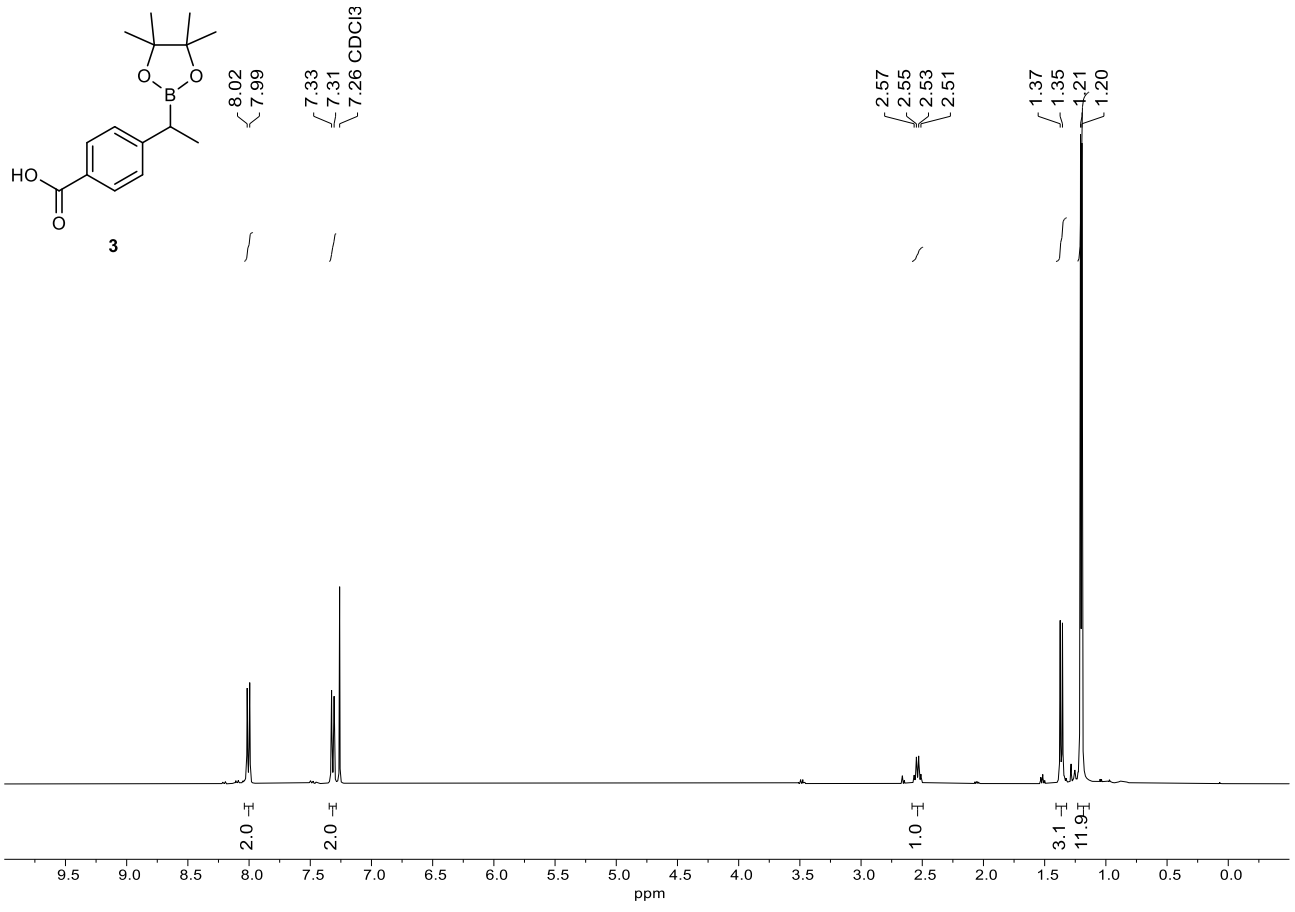
DEPT-Q:



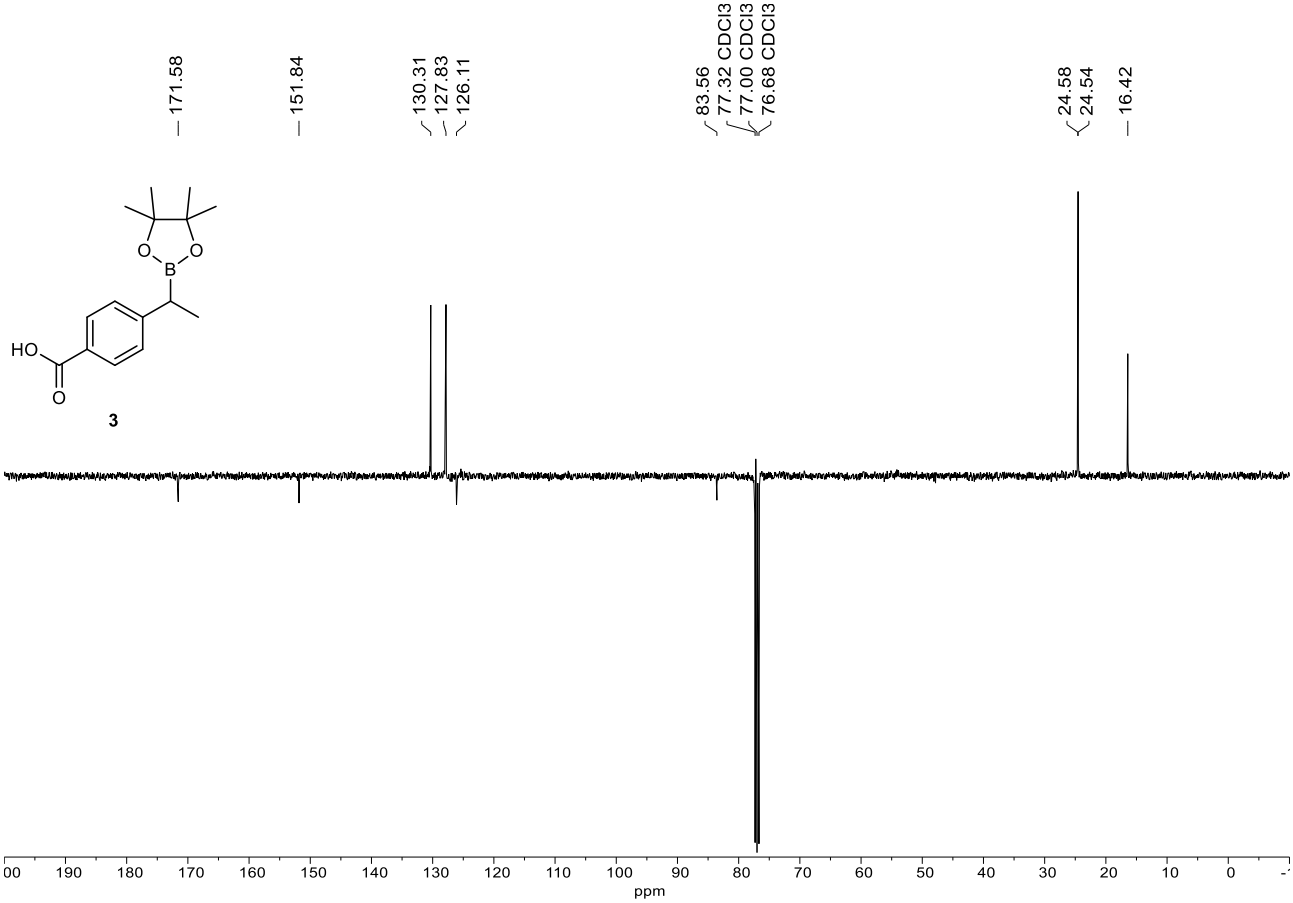
^{11}B NMR:



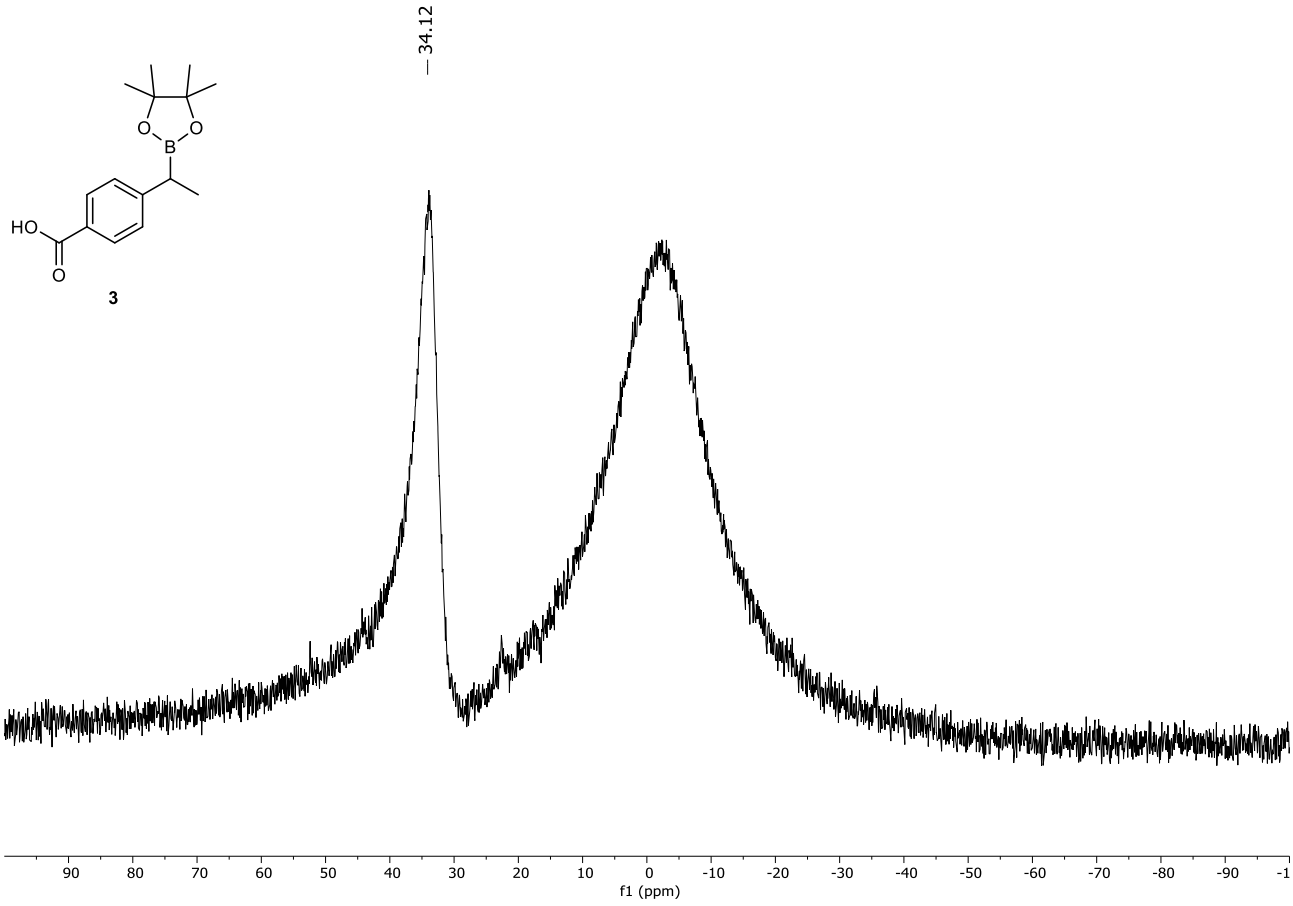
^{1}H NMR:



DEPT-Q:



^{11}B NMR:



9. References

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