Supporting Information: Cu-Catalyzed Coupling of Aliphatic Amines with Alkylboronic Esters

Francesca M. Dennis,[a] Antonio Romero Arenas,[a] George Rodgers,[a] Muralidharan Shanmugam,[b] Jonathan A. Andrews,[a] Samantha L. Peralta-Arriaga,[a] Benjamin M. Partridge[a,*]

[a] Department of Chemistry, University of Sheffield, Dainton Building, Sheffield, S3 7HF, United Kingdom

[b] Department of Chemistry and Photon Science Institute, The University of Manchester, Manchester, M13 9PL, United Kingdom

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

1. General Information

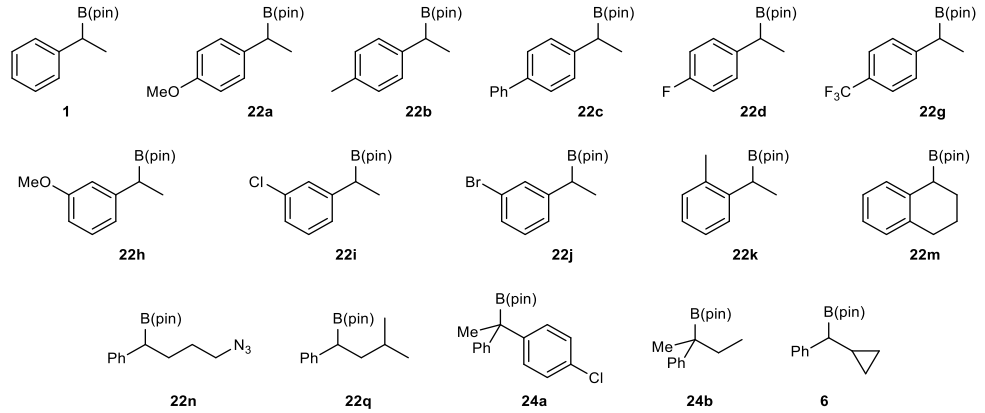
All reagents and solvents used were supplied by commercial sources without further purification unless specified. $CuBr_2$ was typically used as supplied. However, over time the efficiency of the reaction decreases, presumable because $CuBr_2$ is hydroscopic and so water content affects the true loading of the Cu salt. More consistent results can be obtained if the $CuBr_2$ has been dried over P_2O_5.

All air-sensitive reactions were carried out under a nitrogen or argon atmosphere using oven-dried apparatus. Anhydrous Et_2O, THF and toluene were dried and purified by passage through activated alumina columns using a solvent purification system. All petroleum ether used was 40-60 °C petroleum ether. 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 phosphomolybdic acid, ninhydrin, vanillin or $KMnO_4$ followed by heating. All flash chromatography was carried out using silica gel mesh 40-63. It should be noted that the time taken for chromatography of boronic esters should be kept to minimum to avoid extensive decomposition and reduced yields.

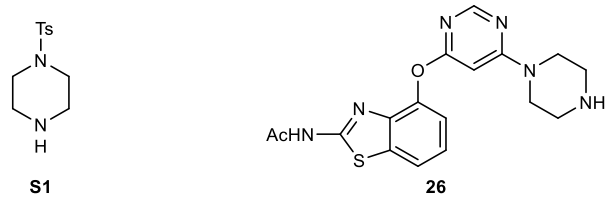
Infra-red spectra were recorded on a Perkin Elmer 100 FT instrument on the neat compound. NMR spectra were recorded on Bruker Advance 400 and 500 instruments at the indicated 101, 128, 126, 377, 400 and 500 MHz as dilute solutions in the indicated deuterated solvent. NMR spectra were recorded at ambient temperature unless otherwise stated. All chemical shifts (δ) reported in parts per million (ppm) relative to residual protio solvent (δH: $CHCl_3$ = 7.27 ppm, DMSO = 2.50 ppm or CH_3CN = 1.94 ppm) or the solvent itself (δC: $CDCl_3$ = 77.0 ppm, DMSO = 39.5 ppm or CH_3CN = 1.32, 118.3 ppm). All multiplets are designated by the following abbreviations: s = singlet, br s = broad singlet, d = doublet, dt = doublet triplet, td = triplet doublet, ddd = doublet of doublets of doublets, q = quartet, br q = broad quartet, m = multiplet. All coupling constants (*J*) are reported in Hertz (Hz). ^{13}C NMR data were acquired as DEPT-Q experiments as standard. For samples where quaternary carbons were not observed by DEPT-Q, ^{13}C NMR spectra were acquired as decoupled spectra. ^{19}F NMR spectra acquired as decoupled spectra. High-resolution mass spectra were recorded using either electrospray ionization (ESI) or electron ionisation (EI) by the Chemistry Mass Spectrometry Facility in the Faculty of Science, University of Sheffield. HPLC analysis was performed using an Agilent 1260 Infinity II LC system. Melting points were measured using Linkam HFs91 heating stage, used in conjunction with a TC92 controller and are uncorrected.

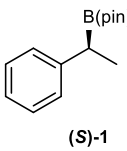
2. Substrate synthesis

Boronic esters (**1**, **6, 22a-d**, **22g-22k**, **22m-q**)[1] and boronic esters (**24a**, **24b**)[2] were prepared by literature methods.



Amines **S1**[3] and amine **26**[4] were prepared were prepared by literature methods.





(*S*)-4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane ((*S*)-1)

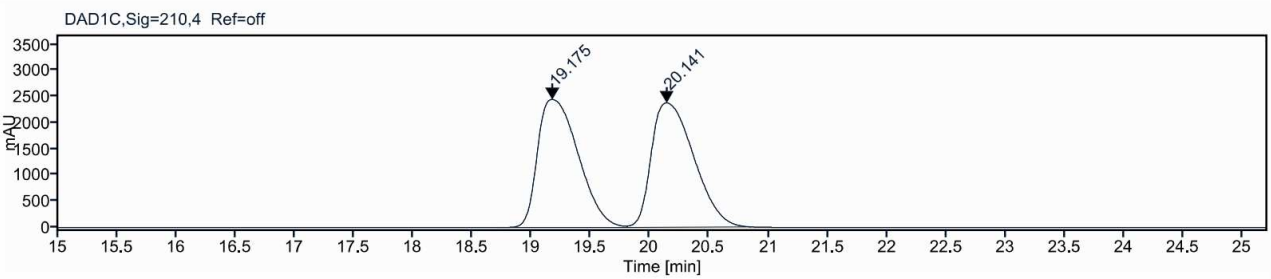
Boronic ester **(*S*)-1** was prepared according to the procedure of Yun and co-workers.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.19 (4H, m, Ar**H**), 7.19-7.08 (1H, m, Ar**H**), 2.45 (1H, q, *J* = 7.5 Hz, C**H**), 1.34 (3H, d, *J* = 7.5 Hz, CHC**H$_3$**), 1.22 (6H, s, 2 × CC**H$_3$**), 1.21 (6H, s, 2 × CC**H$_3$**).

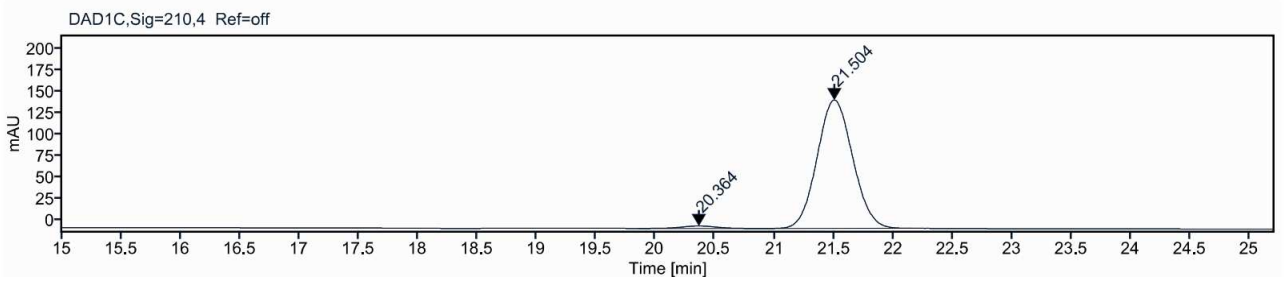
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9 (C), 128.3 (2 × CH), 127.8 (2 × CH), 125.1 (CH), 83.3 (2 × C), 24.6 (2 × CH_3), 24.6 (2 × CH_3), 17.0 (CH_3).

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

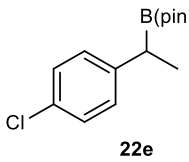
e.r. = 2:98, measured through chiral HPLC analysis of the corresponding alcohol obtained after oxidation. Chiralpak ID column (250 × 4.6 mm), IPA:hexane = 1:99, 0.7 mL/min, column temperature = 22 °C, (*R*)-isomer t_r = 20.4 min and (*S*)-isomer t_r = 21.5 min.



RT [min]	Type	Width [min]	Area	Height	Area%
19.175	MM m	0.3804	58438.0569	2449.1135	49.6661
20.141	MM m	0.3945	59223.8120	2378.5002	50.3339
		Sum	117661.8689		



RT [min]	Type	Width [min]	Area	Height	Area%
20.364	BB	1.0200	57.8583	2.8559	1.8127
21.504	MM m	0.3253	3133.9778	150.2871	98.1873
		Sum	3191.8361		



22e

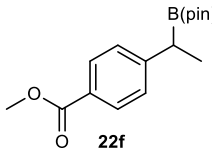
(±)-2-[1-(4-Chlorophenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22e)

Using a modification of the procedure of Yun and co-workers,[6] an oven-dried flask was charged with CuCl (0.045 g, 0.45 mmol), tBuOK (0.121 g, 1.08 mmol) and dppBz (0.200 g, 0.45 mmol) and purged with N_2. Anhydrous toluene (16 mL) was added, and the mixture was stirred at room temperature for 10 min. Pinacolborane (3.13 mL, 21.6 mmol) was added and the mixture was stirred for 10 min. 4-Chlorostyrene (2.16 mL, 18.0 mmol) was added, and the mixture heated to 60 °C for 16 h. The mixture was cooled to room temperature, passed through a plug of Celite eluting with EtOAc (10 mL), and concentrated *in vacuo*. Flash chromatography (2% EtOAc/petroleum ether) of the crude material gave boronic ester **22e** (1.41 g, 81%) as a white solid. The data were consistent with the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) 7.25-7.22 (2H, m, Ar**H**), 7.17-7.14 (2H, m, Ar**H**), 2.41 (1H, q, *J* = 7.5 Hz, C**H**), 1.31 (3H, d, *J* = 7.5 Hz, C**H$_3$**), 1.21 (6H, s, 2 × CC**H$_3$**), 1.20 (6 H, s, 2 × CC**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5 (C), 130.7 (C), 129.1 (2 × CH), 128.3 (2 × CH), 83.4 (2 × C), 24.6 (2 × CH_3), 24.6 (2 × CH_3), 16.9 (CH_3).

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.3.



22f

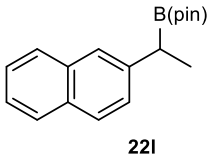
(±)-Methyl 4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzoate (22f)

Using a modification of the procedure of Yun and co-workers,[6] an oven-dried flask was charged with CuCl (0.0147 g, 0.148 mmol), tBuOK (0.0400 g, 0.356 mmol) and dppBz (0.0661 g, 0.148 mmol) and purged with N_2. Anhydrous toluene (3 mL) was added, and the mixture was stirred at room temperature for 10 min. Pinacolborane (1.0 mL, 7.1 mmol) was added and the mixture was stirred for 10 min. A solution of methyl 4-vinylbenzoate (0.963 g, 5.94 mmol) in toluene (4 mL) was added, and the mixture heated to 60 °C for 16 h. The mixture was cooled to room temperature, passed through a plug of Celite eluting with EtOAc (10 mL), and concentrated *in vacuo*. Flash chromatography (100% hexane/0% Et_2O → 90% hexane/10% Et_2O) of the crude material gave boronic ester **22f** (0.756 g, 44%) as a white solid. The data were consistent with the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.91 (m, 2H), 7.30-7.26 (m, 2H), 3.89 (s, 3H), 2.51 (q, *J* = 7.5 Hz, 1H), 1.35 (d, *J* = 7.4 Hz, 4H), 1.20 (s, 7H), 1.19 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3 (C), 150.8 (C), 129.7 (2 × CH), 127.7 (2 × CH), 127.1 (C), 83.5 (C), 51.9 (CH_3), 24.6 (2 × CH_3), 24.5 (2 × CH_3), 16.4 (CH_3).

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



22l

(±)-4,4,5,5-Tetramethyl-2-[1-(2-naphthalen-1-yl)ethyl]-1,3,2-dioxaborolane (22l).

Using a modification of the procedure of Yun and co-workers,[6] an oven-dried flask was charged with CuCl (0.064 g, 0.65 mmol), tBuOK (0.174 g, 1.55 mmol) and dppBz (0.290 g, 0.650 mmol) and purged with N_2. Anhydrous toluene (16 mL) was added, and the mixture was stirred at room temperature for 10 min. Pinacolborane (4.5 mL, 31 mmol) was added and the mixture was stirred for 10 min. 2-Vinylnaphthalene (4.00 g, 26.0 mmol) was added, and the mixture heated to 60 °C for 16 h. The mixture was cooled to room temperature, passed through a plug of Celite eluting with EtOAc (10 mL), and concentrated *in vacuo*. Flash chromatography (4% EtOAc/petroleum ether) of the crude material gave boronic ester **22l** (6.20 g, 84%) as a white solid. The data were consistent with the literature.[8]

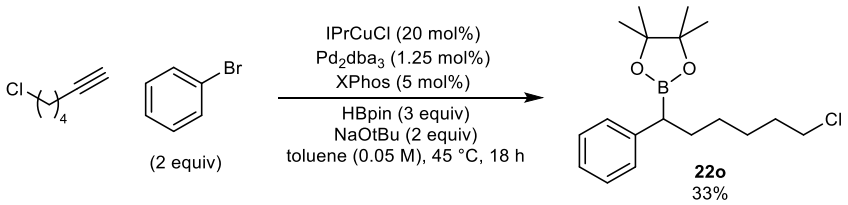
m.p 80-81 °C (EtOAc); literature = 61-63 °C (not specified).[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.74 (3H, m, Ar**H**), 7.65 (1H, s, Ar**H**), 7.45-7.37 (3H, m, Ar**H**), 2.62 (1H, q, *J* = 7.5 Hz, C**H**), 1.43 (3H, d, *J* = 7.5 Hz, CHC**H$_3$**), 1.22 (6H, s, 2 × CC**H$_3$**), 1.21 (6H, s, 2 × CC**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6 (C), 133.8 (C), 131.7 (C), 127.6 (CH), 127.5 (CH), 127.5 (CH), 127.2 (CH), 125.6 (CH), 125.2 (CH), 124.7 (CH), 83.4 (2 × C), 24.6 (2 × CH_3), 24.6 (2 × CH_3), 16.8 (CH_3).

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.0.

2-[6-Chloro-1-(phenyl)hexyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22o)



Using a modification of the procedure by Lalic and Armstrong,[10] a Schlenk flask containing NaO^{t}Bu (0.384 g, 4.00 mmol, 2.0 equiv), IPrCuCl (0.195 g, 0.400 mmol, 0.20 equiv), was backfilled with nitrogen three times. HBpin (0.767 g, 6.00 mmol, 3.0 equiv), anhydrous toluene (40 mL, 0.05 M) and 6-chloro-1-hexyne (0.233 g, 2.00 mmol, 1.0 equiv) were added, and the mixture was stirred at 45 °C until the yellow colour disappeared (~5 mins). Pd_2dba_3 (22.9 mg, 0.025 mmol, 0.0125 equiv), XPhos (47.2 mg, 0.1 mmol, 0.025 equiv) and bromobenzene (0.628 g, 4.00 mmol, 2.0 equiv) were added, and the mixture was vigorously stirred at 45 °C for 18 h. The mixture was cooled to room temperature, diluted with Et_2O (20 mL), and washed with 1 M HCl (20 mL) and brine (20 mL). The organic phase was dried (Na_2SO_4), filtered through a pad a silica gel eluting with Et_2O, and concentrated *in vacuo*. Flash chromatography (100% hexane → 100% CH_2Cl_2) of the crude material gave *boronic ester* **22o** (0.215 g, 33%) as a colourless oil.

IR 2978, 2932, 1371, 1321, 1142 cm^{-1}.

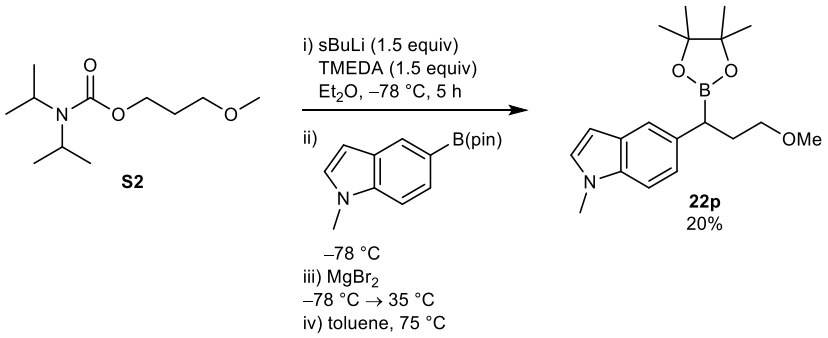
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.17 (4H, m, Ar**H**), 7.15-7.10 (1H, m, Ar**H**), 3.49 (2H, t, *J* = 6.8 Hz, C**H$_2$**Cl), 2.29 (1H, t, *J* = 7.9 Hz, C**H**), 1.90-1.80 (1H, m, C**H$_A$**H$_B$), 1.78-1.69 (2H, m, C**H$_2$**CH$_2$Cl), 1.69-1.60 (1H, m, CH$_A$**H$_B$**), 1.48-1.38 (2H, m, C**H$_2$**), 1.33-1.28 (2H, m, C**H$_2$**), 1.21 (6H, s, 2 × CC**H$_3$**), 1.18 (6H, s, 2 × CC**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2 (C), 128.3 (2 × CH), 128.3 (2 × CH), 125.2 (CH), 83.3 (2 × OC), 45.1 (CH_2), 32.5 (CH_2), 32.3 (CH_2), 28.4 (CH_2), 26.8 (CH_2), 24.6 (2 × CH_3), 24.6 (2 × CH_3).

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.4.

HRMS (QTOF) Exact mass calcd for $[C_{18}H_{28}{}^{11}B^{35}ClO_2]^+$ $[M+H]^+$: 323.1994, found: 323.1959.

(±)-5-[3-Methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl]-1-methylindole (22p)



Using a modification of the procedure by Aggarwal and co-workers,[11] a Schlenck flask containing carbamate **S2**[12] (3.14 g, 14.6 mmol) was backfilled with nitrogen three times. TMEDA (2.18 mL, 14.6 mmol) and anhydrous Et_2O (40 mL) were added, and the mixture was cooled to –78 °C. *s*-BuLi (1.3 M in cyclohexane, 10.4 mL, 14.6 mmol) was added dropwise and the mixture was stirred at –78 °C for 5 h. A solution of 1-methylindole-5-boronic acid pinacol ester (2.49 g, 9.68 mmol) in Et_2O (10 mL) was added dropwise and the mixture was stirred at –78 °C for 1 h. A solution of $MgBr_2$ in Et_2O[1] (2.67 g, 14.6 mmol, 1 M) was added dropwise and the mixture was stirred at 34 °C for 18 h. Toluene (30 mL) was added and mixture heated to 75 °C for 18 h. H_2O (60 mL) was added, and the mixture extracted with Et_2O (3 × 60 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (5% EtOAc/45% hexane/50% CH_2Cl_2) to give *boronic ester* **22p** (0.633 g, 20%) as an off white solid.

m.p. = 91-93 °C (CH_2Cl_2), no literature data available.

IR 2926, 2890, 1668, 1607, 1447, 1336, 1111 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (1H, s, Ar**H**), 7.22 (1H, d, *J* = 8.4 Hz, Ar**H**), 7.12 (1H, d, *J* = 8.4 Hz, Ar**H**), 7.00 (1H, d, *J* = 3.1 Hz, Ar**H**), 6.41 (1H, d, *J* = 3.1 Hz, Ar**H**), 3.76 (3H, s, OC**H$_3$**), 3.40-3.32 (2H, m, OC**H$_2$**), 3.31 (3H, s, NC**H$_3$**), 2.50 (1H, t, *J* = 8.6 Hz, C**H**), 2.23-2.17 (1H, m, CHC**H$_A$**H$_B$), 1.98-1.89 (1H, m, CHCH$_A$**H$_B$**), 1.21 (6H, s, 2 × CC**H$_3$**), 1.19 (6 H, s, 2 × CC**H$_3$**).

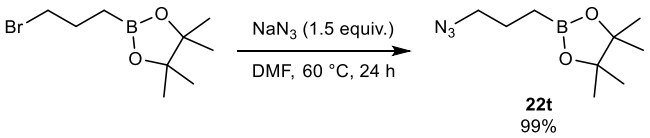
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2 (C), 133.4 (C), 128.7 (C), 128.5 (CH), 122.7 (CH), 120.0 (CH), 108.9 (CH), 100.4 (CH), 83.1 (2 × C), 72.2 (CH_2), 58.4 (CH_3), 33.0 (CH_2), 32.8 (CH_3), 24.6 (2 × CH_3), 24.6 (2 × CH_3).

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.7.

HRMS (QTOF) Exact mass calcd for [$C_{19}H_{28}{}^{11}BNNaO_3$]+ [M+Na]+: 352.2054. Found: 352.2066.

[1] Freshly prepared before use, by the following procedure: A flask was charged with Mg turnings (1.1 equiv.) and purged with N_2. Et_2O (3 mL) followed by 1,2-dibromoethane (1 equiv.) were added, and the mixture was stirred at room temperature for 2 h.

2-(3-Azidopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22t)



22t
99%

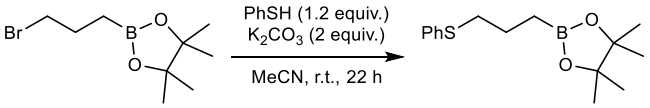
NaN_3 (0.488 g, 7.51 mmol) was added to a solution of 2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.25 g, 5.00 mmol) in DMF (3.30 ml) and the mixture was stirred at 60 °C for 24 h. H_2O (50 mL) was added, and the mixture extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine (100 ml), dried ($MgSO_4$), filtered, and concentrated *in vacuo to* give the azide **22t** as a colourless oil (1.05 g, 99%). The data were consistent with the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.24 (2H, t, *J* = 7.0 Hz, C**H$_2$**N_3), 1.71 (2H, tt, *J* = 7.7, 7.0 Hz, N_3CH_2C**H$_2$**), 1.24 (12H, s, 3 × C**H$_3$**), 0.83 (2H, t, J = 7.7 Hz, C**H$_2$**B).

^{13}C NMR (101 MHz, $CDCl_3$) δ 83.2 (2 × C), 53.4 (CH_2), 24.8 (4 × CH_3), 23.5 (CH_2).

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.8.

4,4,5,5-Tetramethyl-2-[3-(phenylsulfanyl)propyl]-1,3,2-dioxaborolane (22u)



22u
82%

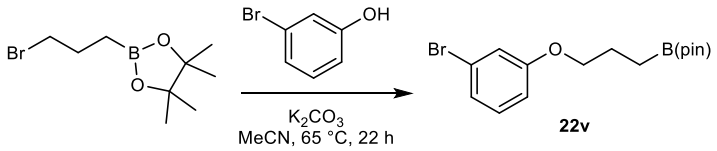
Thiophenol (0.61 ml, 5.98 mmol) was added to a stirring solution of 2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.25 g, 5.01 mmol) and K_2CO_3 (1.38 g, 10.0 mmol) in MeCN (10.0 ml) and stirred at r.t. for 22 h. H_2O (50 mL) was added, and the mixture extracted with Et_2O (3 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Flash column chromatography (99% hexane/1% Et_3N to 89% hexane/10% Et_2O/1% Et_3N) of the crude material gave thioether **22u** (1.21 g, 87%) as a yellow oil. The data were consistent with the literature.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.30 (2H, m, Ar**H**), 7.29-7.22 (2H, m, Ar**H**), 7.18-7.09 (1H, m, Ar**H**), 2.93 (t, *J* = 7.5 Hz, C**H$_2$**S), 1.78 (2H, tt, *J* = 7.7, 7.5 Hz, CC**H$_2$**C), 1.24 (12H, s, 3 × C**H$_3$**), 0.92 (2H, t, *J* = 7.7 Hz, C**H$_2$**B).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1 (C), 128.7 (2 × CH), 128.5 (2 × CH), 125.4 (CH), 83.1 (2 × C), 35.5 (CH_2), 24.8 (4 × CH_3), 23.9 (CH_2).

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.8.

2-[3-(3-Bromophenoxy)propyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22v)



3-Bromophenol (0.981 g, 5.67 mmol) was added to a stirring solution of 2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.90 ml, 4.3 mmol) and K_2CO_3 (1.63 g, 11.8 mmol) in MeCN (10 ml) and stirred at 65 °C for 22 h. The mixture was cooled to room temperature, and saturated aqueous K_2CO_3 (15 mL) and H_2O (10 mL) were added. The mixture was extracted with EtOAc (3 × 50 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Flash column chromatography (100% hexane/0% Et_2O → 100% Et_2O) of the crude material gave *ether* **22v** (0.507 g, 55%) as a colourless oil.

IR 2977, 2933, 1589, 1468, 1371, 1143, 845 cm^{-1}.

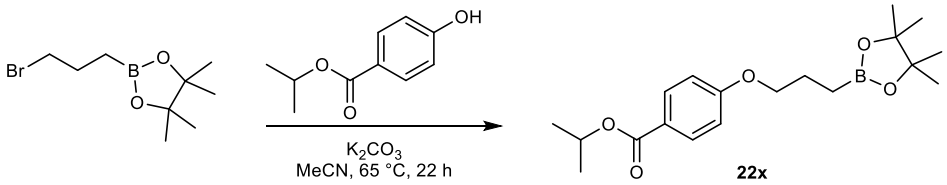
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.07 (1H, m, Ar**H**), 7.08-7.01 (2H, m, Ar**H**), 6.82 (1H, ddd, *J* = 8.2, 2.3, 1.2 Hz, Ar**H**), 3.92 (2H, t, *J* = 6.7 Hz, OC**H$_2$**), 1.88 (2H, tt, *J* = 7.8, 6.7 Hz, OCH_2C**H$_2$**), 1.25 (12H, s, 4 × C**H$_3$**), 0.91 (2H, t, *J* = 7.8 Hz, BC**H$_2$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (C), 130.4 (CH), 123.5 (CH), 122.7 (C), 117.7 (CH), 113.7 (CH), 83.2 (2 × C), 69.8 (CH_2), 24.8 (4 × CH_3), 23.6 (CH_2).

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

HRMS (QTOF) Exact mass calcd for $[C_{15}H_{22}{}^{11}B^{79}BrNaO_3]$+ [M+Na]+: 363.0743 found 363.0738.

Propan-2-yl 4-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy]benzoate (22x)



Isopropyl 4-hydroxybenzoate (1.02 g, 5.67 mmol) was added to a stirring solution of 2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.0 ml, 4.7 mmol) and K_2CO_3 (1.63 g, 11.8 mmol) in MeCN (10 ml) and stirred at 65 °C for 20 h. The mixture was cooled to room temperature, and H_2O (10 mL) was added. The mixture was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Flash column chromatography (100% hexane → 10% EtOAc/90% hexane) of the crude material gave *ether* **22x** (0.510 g, 31%) as a colourless oil.

IR 2978, 2938, 1708, 1606, 1372, 1250, 1099, 771 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.94 (2H, m, Ar**H**), 6.92-6.87 (1H, m, Ar**H**), 5.22 (1H, hept, *J* = 6.2 Hz, C**H**), 3.99 (2H, t, *J* = 6.7 Hz, OC**H$_2$**), 1.95-1.86 (2H, m, OCH_2C**H$_2$**), 1.35 (6H, d, *J* = 6.3 Hz, 2 × CHC**H$_3$**), 1.25 (12H, s, 4 × CC**H$_3$**), 0.92 (2H, t, *J* = 7.8 Hz, BC**H$_2$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 (C), 162.8 (C), 131.4 (2 ×CH), 123.0 (C), 114.0 (2 × CH), 83.2 (2 × C), 69.7 (CH_2), 67.8 (CH), 24.8 (4 × CH_3), 23.6 (CH_2), 22.0 (2 × CH_3).

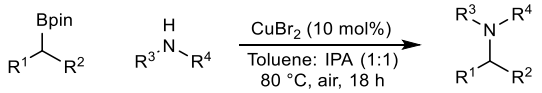
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.4.

HRMS (QTOF) Exact mass calcd for $[C_{19}H_{29}{}^{11}BO_5]$+ [M]+: 348.2217. Found: 348.2228.

3. Cu-catalysed Amination of Alkylboronic Esters

3.1. General Procedures

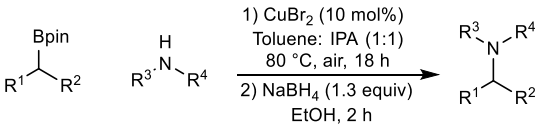
General Procedure 1 (GP1): Preparative scale Cu-catalysed amination of alkylboronic esters



Isopropyl alcohol (0.38 mL) and toluene (0.38 mL) were added to a flask containing the corresponding boronic ester (0.50 mmol, 1 equiv.), amine (1.75 mmol, 3.5 equiv.) and $CuBr_2$ (0.05 mmol, 10 mol%), and the mixture was stirred under air at 80 °C until the reaction was complete (as determined by TLC). 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 column chromatography.

A video guide to help readers see how we set up our reaction, including some tips for problem solving, can be found here: https://digitalmedia.sheffield.ac.uk/id/1_isl6hrng.

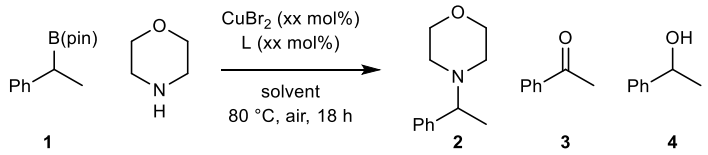
General Procedure 2 (GP2): Preparative scale Cu-catalysed amination of alkylboronic esters with reductive workup.



Isopropyl alcohol (0.38 mL) and toluene (0.38 mL) were added to a flask containing the corresponding boronic ester (0.50 mmol, 1 equiv.), amine (1.75 mmol, 3.5 equiv.) and $CuBr_2$ (0.05 mmol, 10 mol%), and the mixture was stirred under air at 80 °C until the reaction was complete (as determined by TLC). The mixture was cooled to room temperature, passed through a plug of silica eluting with Et_2O, and concentrated *in vacuo*. EtOH (1 mL) and $NaBH_4$ (0.025 g, 0.65 mmol) were added, and the mixture stirred at RT for 2 h. The mixture was diluted with EtOAc (10 mL) and H_2O (10 mL) and 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 column chromatography.

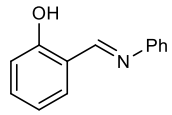
3.2. Optimisation of Reaction Conditions

Reactions conducted as part of the optimisation process were typically conducted on 0.5 mmol scale with respect to boronic ester **1**. It was found that smaller scale reactions (e.g. 0.05 mmol scale) did work but showed lower reproducibility, presumably due to inefficient gas transfer from air to solution limiting catalyst turnover which can be harder to control on smaller scale.

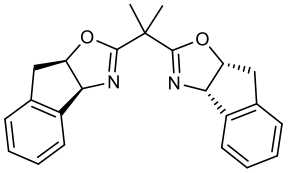


Entry	Cu Source	Cu mol%	L (mol%)	Amine equiv	solvent	T (°C)	Time	Conc.	Yield			
									1	2	3	4
1 [b]	$Cu(OAc)_2$	200	-	4	toluene/pyr	80	16 h	0.1 M	53%	0%	2%	-
2 [b]	$CuBr_2$	200	-	4	toluene/pyr	80	16 h	0.1 M	51%	46%	-	-
3 [b]	CuBr	200	-	4	toluene/pyr	80	16 h	0.1 M	36%	51%	0%	-
4 [b]	CuCl	200	-	4	toluene/pyr	80	16 h	0.1 M	43%	5%	3%	-
5 [b]	CuI	200	-	4	toluene/pyr	80	16 h	0.1 M	84%	0%	0%	-
6 [b]	$CuCl_2$	200	-	4	toluene/pyr	80	16 h	0.1 M	42%	22%	2%	-
7 [b]	$CuBr_2$	200	-	4	toluene/pyr	50	16 h	0.1 M	50%	25%	-	-
8 [b]	$CuBr_2$	200	-	4	toluene/pyr	50	64 h	0.1 M	-	63%	-	-
9 [b,c]	$CuBr_2$	200	-	4	toluene/pyr	80	16 h	0.1 M	51%	26%	0%	-
10 [b,d]	$CuBr_2$	200	-	4	toluene/pyr	80	16 h	0.1 M	32%	30%	0%	-
11 [b,e]	$CuBr_2$	200	-	4	toluene/pyr	80	16 h	0.1 M	0%	35%	0%	-
12 [b]	$CuBr_2$	100	-	4	toluene/pyr	80	16 h	0.16 M	33%	68%	-	-
13 [b]	$CuBr_2$	50	-	4	toluene/pyr	80	16 h	0.16 M	45%	34%	-	-
14 [b]	$CuBr_2$	100	-	40	-	80	16 h	0.025 M	<5%	>95%	<5%	-
15 [b]	$CuBr_2$	50	**L1** (100)	4	toluene/pyr	80	16 h	0.16 M	52%	49%		--
16 [b]	$CuBr_2$	50	**L4** (100)	4	toluene/pyr	80	16 h	0.16 M	63%	22%	-	-
17 [b]	$CuBr_2$	50	**L5** (100)	4	toluene/pyr	80	16 h	0.16 M	65%	32%	-	-
18 [b]	$CuBr_2$	50	**L6** (100)	4	toluene/pyr	80	16 h	0.16 M	67%	23%	-	-
19 [b]	$CuBr_2$	25	**L1** (25)	4	toluene	80	16 h	0.16 M	91%	7%	0%	-
20	$CuBr_2$	25	**L2** (25)	40	-	40	18 h	0.025 M	<5%	95%	-	-
21	$CuBr_2$	25	**L7** (25)	40	-	40	18 h	0.025 M	<5%	84%	-	-
22	$CuBr_2$	25	**L3** (25)	40	-	40	18 h	0.025 M	<5%	67%	-	-
23 [f]	$CuBr_2$	50	**L1** (25)	4	toluene	80	16 h	0.16 M	<5%	30%	34%	-
24 [g]	$CuBr_2$	50	**L1** (25)	4	toluene	80	16 h	0.16 M	<5%	54%	13%	-
25 [h]	$CuBr_2$	50	**L1** (25)	4	toluene	80	16 h	0.16 M	<5%	40%	11%	-
26	$CuBr_2$	50	-	4	toluene	80	16 h	0.16 M	<5%	45%	13%	-
27	$CuBr_2$	25	-	4	toluene	80	16 h	0.16 M	<5%	25%	9%	-
28	$CuBr_2$	25	**L1** (25)	4	toluene	60	18 h	0.3 M	<5%	81%	9%	10%
29	$CuBr_2$	25	**L1** (25)	4	IPA	60	18 h	0.3 M	<5%	95%	<5%	3%
30	$CuBr_2$	25	**L1** (25)	4	dioxane	60	18 h	0.3 M	<5%	88%	10%	2%
31	$CuBr_2$	25	**L1** (25)	4	PrOAc	60	18 h	0.3 M	<5%	91%	6%	3%
32	$CuBr_2$	25	**L1** (25)	4	tol/IPA (1:1)	60	18 h	0.3 M	<5%	95%	<5%	2%
33	$CuBr_2$	25	**L1** (25)	4	tol/IPA (3:1)	60	18 h	0.3 M	<5%	95%	<5%	3%
34	$CuBr_2$	25	**L1** (25)	4	tol/IPA (1:1)	80	18 h	0.3 M	28%	57%	-	-
35	$CuBr_2$	25	**L1** (25)	4	tol/IPA (3:1)	80	18 h	0.6 M	<5%	95%	-	-
36	$CuBr_2$	25	**L1** (25)	4	tol/IPA (3:1)	80	18 h	0.6 M	<5%	95%	-	-
37	$CuBr_2$	15	**L1** (15)	4	tol/IPA (1:1)	80	18 h	0.6 M	<5%	80%	<5%	-

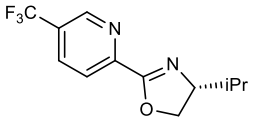
Entry	Cu Source	Cu mol%	L (mol%)	Amine equiv	solvent	T (°C)	Time	Conc.	Yield			
									1	2	3	4
38	$CuBr_2$	15	**L1** (15)	4	tol/IPA (3:1)	80	18 h	0.6 M	<5%	94%	6%	-
39	$CuBr_2$	15	**L1** (15)	3	tol/IPA (1:1)	80	18 h	0.6 M	<5%	84%	9%	-
40	$CuBr_2$	15	**L1** (15)	3.5	tol/IPA (1:1)	80	18 h	0.6 M	<5%	93%	5%	-
41	$CuBr_2$	15	**L1** (15)	2	tol/IPA (1:1)	80	18 h	0.6 M	<5%	77%	7%	-
42	$CuBr_2$	10	**L1** (10)	4	tol/IPA (1:1)	80	18 h	0.6 M	<5%	95%	3%	-
43	$CuBr_2$	10	**L1** (10)	4	tol/IPA (3:1)	80	18 h	0.6 M	<5%	81%	19%	-
44	$CuBr_2$	10	**L1** (10)	3	tol/IPA (1:1)	80	18 h	0.6 M	<5%	79%	6%	-
45	$CuBr_2$	10	-	3.5	tol/IPA (1:1)	80	18 h	0.6 M	<5%	95%	0%	-
46	$CuBr_2$	5	-	3.5	tol/IPA (1:1)	80	18 h	0.6 M	<5%	78%	7%	-
47	$CuBr_2$	10	-	3.5	MeCN	80	18 h	0.6 M	<5%	78%	8%	5%
48	$CuBr_2$	10	-	3.5	MeCN/IPA (1:1)	80	18 h	0.6 M	<5%	77%	7%	6%
49	$CuBr_2$	10	-	3.5	tol/IPA (1:1)	80	4h	0.6 M	44%	55%	-	-
50	$CuBr_2$	10	-	3.5	tol/IPA (1:1)	RT	18 h	0.6 M	51%	13%	6%	30%
51	-	0	-	3.5	tol/IPA (1:1)	80	18 h	0.6 M	<5%	<5%	4%	58%
52 [b]	$CuBr_2$	10	-	3.5	tol/IPA (1:1)	80	18 h	0.6 M	93%	3%	0%	0%
53	**S2**	100	-	4	toluene	80	16 h	0.16 M	n.d.	0%	-	-
54 [i]	$CuBr_2$	10	-	1	tol/IPA (1:1)	80	18 h	0.6 M	20%[j]	46%	35%[j]	12%[j]



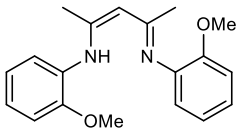
L1



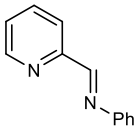
L2



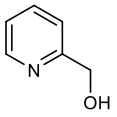
L3



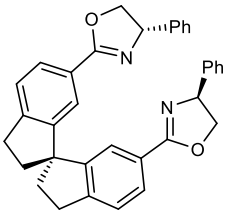
L4



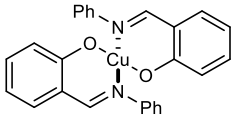
L5



L6



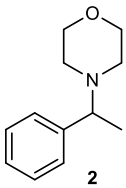
L7



S2

a) Reactions performed using 0.5 mmol of boronic ester **1** unless otherwise stated. Yields determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard; b) reaction carried out under an inert atmosphere (either N_2 or Ar); c) using CsF (2 equiv); d) using Na_2CO_3 (2 equiv); e) using KOtBu (2 equiv); f) using Cs_2CO_3 (0.5 equiv); g) using Na_2CO_3 (0.5 equiv); h) using KOtBu (0.5 equiv); i) reaction using morpholine as the limiting reagent and 3.5 equivalents of boronic ester **1**; j) yield based on boronic ester **1**; pyr = pyridine; tol = toluene; n.d. = not determined

3.3. Scope of Reaction Using Cyclic Amines

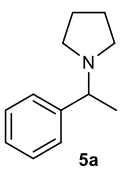

2

(±)-*N*-(1-Phenylethyl)morpholine (2)

Isopropyl alcohol (2.75 mL) and toluene (2.75 mL) were added to a flask containing boronic ester **1** (1.00 g, 4.31 mmol), morpholine (1.31 g, 15.1 mmol) and $CuBr_2$ (96.3 mg, 0.43 mmol), and the mixture was stirred under air at 80 °C for 18 h. The mixture was cooled to room temperature, passed through a plug of silica eluting with Et_2O and EtOAc, and concentrated in vacuo. Flash column chromatography (69% hexane/30% EtOAc/1% Et_3N) of the crude material gave amine **2** (720 mg, 87%) as a colourless oil. The data were consistent with the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (4 H, m, Ar**H**), 7.22-7.16 (1H, m, Ar**H**), 3.68-3.58 (4H, m, 2 × OC**H$_2$**), 3.24 (1H, q, *J* = 6.6 Hz, C**H**), 2.49-2.38 (2H, m, NC**H$_2$**), 2.36-2.27 (2H, m, NC**H$_2$**), 1.30 (3H, d, *J* = 6.6 Hz, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9 (C), 128.3 (2 × CH), 127.6 (2 × CH), 127.0 (CH), 67.2 (2 × CH_2), 65.4 (CH), 51.3 (2 × CH_2), 19.8 (CH_3).


5a

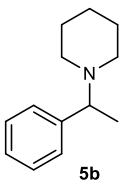
(±)-*N*-(1-Phenylethyl)pyrrolidine (5a)

The title compound was prepared according to **GP1** using boronic ester **1** (0.118 g, 0.508 mmol) and pyrrolidine (124.8 mg, 1.75 mmol), heating for 18 h. Flash column chromatography (99% EtOAc/1% Et_3N) of the crude material gave amine **5a** (60.6 mg, 68%) as a colourless oil. The data were consistent with the literature.[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (4H, m, Ar**H**), 7.25-7.19 (1H, m, Ar**H**) 3.18 (1H, q, *J* = 6.6 Hz, C**H**), 2.61-2.50 (2H, m, NC**H$_2$**), 2.42-2.32 (2H, m, NC**H$_2$**), 1.82-1.70 (4H, m, 2 × C**H$_2$**), 1.41 (3H, d, *J* = 6.6 Hz, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6 (C), 128.2 (2 × CH), 127.2 (2 × CH), 126.8 (CH), 66.0 (CH), 53.0 (2 × CH_2), 23.4 (2 × CH_2), 23.1 (CH_3).

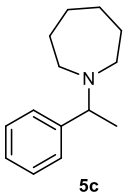
(±)-*N*-(1-Phenylethyl)piperidine (5b)


5b

The title compound was prepared according to **GP1** using boronic ester **1** (0.117 g, 0.504 mmol) and piperidine (0.150 g, 1.76 mmol), heating for 18 h. Flash column chromatography (69% hexane/30% EtOAc/1% Et_3N) of the crude material gave amine **5b** (73.8 mg, 77%) as a colourless oil. The data were consistent with the literature.[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (4H, m, Ar**H**), 7.27-7.18 (1H, m, Ar**H**), 3.38 (1H, q, *J* = 6.7 Hz, C**H**), 2.45-2.37 (4H, m, 2 × NC**H$_2$**), 1.55-1.50 (4H, m, 2 × NCH_2C**H$_2$**), 1.39-1.34 (5H, m, C**H$_3$** and NCH_2CH_2C**H$_2$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7 (C), 128.0 (2 × CH), 127.8 (2 × CH), 126.7 (CH), 65.2 (CH), 51.5 (2 × CH_2), 26.2 (2 × CH_2), 24.5 (CH_2), 19.4 (CH_3).

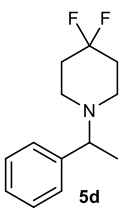


(±)-**1-(1-Phenylethyl)azepane (5c)**

The title compound was prepared according to **GP1** using boronic ester **1** (0.118 g, 0.508 mmol) and 1-acetylpiperazine (0.202 μL, 1.79 mmol), heating for 18 h. The crude was concentrated under vacuo, dissolved in 5 mL EtOAc and extracted with aqueous HCl (1 M, 3 × 3 mL). The aqueous phases were combined and basified to pH > 10 with a solution of sat Na_2CO_3 and extracted with EtOAc (3 × 10 mL). The organic phase was dried over $MgSO_4$ and concentrated under vacuo. Flash column chromatography (100% CH_2Cl_2 to 50% CH_2Cl_2 /50% EtOAc /1% Et_3N) of the crude material gave amine **5c** (62.9 mg, 61%) as a yellow oil. The data were consistent with the literature.[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.36 (2H, m, Ar**H**), 7.35-7.29 (2H, m, Ar**H**), 7.26-7.21 (1H, m, Ar**H**), 3.79 (1H, q, *J* = 6.7 Hz, C**H**), 2.66 (4H, br s, 2 × C**H$_2$**N), 1.60 (8H, br s, 2 × NCH_2C**H_2CH_2**), 1.38 (3H, d, *J* = 6.7 Hz, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8 (C), 127.9 (2 × CH), 127.6 (2 × CH), 126.5 (CH), 63.2 (CH), 52.0 (2 × CH_2), 28.9 (2 × CH_2), 27.0 (2 × CH_2), 18.2 (CH_3).



(±)-**4,4-Difluoro-1-(1-phenylethyl)piperidine (5d)**

The title compound was prepared according to **GP1** using boronic ester **1** (0.116 g, 0.500 mmol) and (0.214 g, 1.77 mmol), heating for 18 h. Flash column chromatography (100% CH_2Cl_2 to 5% Et_2O/95% CH_2Cl_2) of the crude material gave *amine* **5d** (61.5 mg, 55%) as a pale-yellow oil.

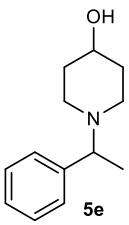
IR 2973, 2813, 1453, 1363, 1098, 927 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.29 (4H, m, Ar**H**), 7.29-7.22 (1H, m, Ar**H**), 3.52 (1H, q, *J* = 6.7 Hz, C**H**), 2.59 (dt, *J* = 11.6, 5.6 Hz, 2H, 2 × NC**H_A**CH_B), 2.51 (dt, *J* = 11.6, 5.6 Hz, 2H, 2 × NCH_AC**H_B**), 2.04-1.88 (4H, m, 2 × C**H$_2$**), 1.38 (3H, d, *J* = 6.7 Hz, CHC**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7 (C), 128.3 (2 × CH), 127.4 (2 × CH), 127.0 (CH), 122.2 (t, $J_{C\text{-}F}$ = 241.6 Hz, CF_2), 63.7 (CH), 47.0 (t, $J_{C\text{-}F}$ = 5.4 Hz, 2 × CH_2), 34.2 (t, $J_{C\text{-}F}$ = 22.7 Hz, 2 × CH_2), 19.3 (CH_3).

^{19}F NMR (377 MHz, $CDCl_3$) δ -97.9.

HRMS (Q-TOF) Exact mass calcd for $[C_{13}H_{18}F_2N]^+$ $[M+H]^+$: 226.1402, found: 226.1413.



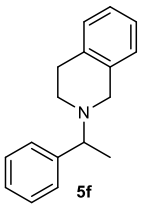
(±)-1-(1-Phenylethyl)piperidin-4-ol (5e)

The title compound was prepared using a modification of **GP1** using boronic ester **1** (0.117 g, 0.504 mmol) and 4-hydroxypiperidine (0.181 g, 1.79 mmol), heating for 18 h. The mixture was cooled to room temperature and concentrated *in vacuo*. The mixture was dissolved in EtOAc (5 mL) and extracted with aqueous HCl (1 M, 3 × 5 mL). The combined aqueous phases were basified using aqueous NaOH (2 M, 3 × 5 mL) and 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 column chromatography (99% EtOAc/ 1% TEA) to give amine **5e** (61.5 mg, 60%) as an off-white solid. The data were consistent with the literature.[19]

m.p. = 100-102 °C (EtOAc), no literature data available.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (4H, m, Ar**H**), 7.26-7.19 (1H, m, Ar**H**), 3.60 (1H, tt, *J* = 8.9, 4.2 Hz, C**H**OH), 3.43 (1H, q, *J* = 6.8 Hz, NC**H**), 2.91-2.80 (1H, m, NC$\mathbf{H_A}H_B$), 2.75-2.66 (1H, m, $NCH_A\mathbf{H_B}$), 2.24 (1H, br s, O**H**), 2.16-2.02 (2H, m, NC$\mathbf{H_2}$), 1.93-1.78 (2H, m, OCHC$\mathbf{H_A}H_B$), 1.64-1.46 (2H, m, $OCHCH_A\mathbf{H_B}$), 1.37 (3H, d, *J* = 6.8 Hz, C$\mathbf{H_3}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6 (C), 128.1 (2 x CH), 127.6 (2 x CH), 126.8 (CH), 68.1 (CH), 64.4 (CH), 48.1 (CH_2), 48.1 (CH_2), 34.7 (CH_2), 34.6 (CH_2), 19.5 (CH_3).

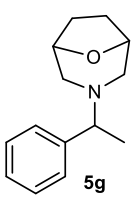


(±)-1,2,3,4-Tetrahydro-2-(1-phenylethyl)isoquinoline (5f)

The title compound was prepared according to **GP2** using boronic ester **1** (0.118 g, 0.506 mmol) and 1,2,3,4-tetrahydroisoquinoline (0.238 g, 1.79 mmol), heating for 18 h. Flash column chromatography (79.5% hexane/20% EtOAc/0.5% Et_3N) of the crude material gave amine **5f** (78.1 mg, 65%) as a yellow oil. The data were consistent with the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (2H, m, Ar**H**), 7.36-7.32 (2H, m, Ar**H**), 7.29-7.25 (1H, m, Ar**H**), 7.14-7.08 (3H, m, Ar**H**), 7.02-6.99 (1H, m, Ar**H**), 3.83 (1H, d, *J* = 14.8 Hz, ArC$\mathbf{H_A}CH_BN$), 3.62-3.54 (2H, m, C**H** and $ArCH_AC\mathbf{H_B}N$), 2.96-2.77 (3H, m, C$\mathbf{H_2}$ **and** $C\mathbf{H_C}CH_D$), 2.67-2.60 (1H, m, $CH_CC\mathbf{H_D}$), 1.49 (3H, d, *J* = 6.7 Hz, C$\mathbf{H_3}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3 (C), 135.2 (C), 134.6 (C), 128.6 (CH), 128.3 (2 × CH), 127.6 (2 × CH), 126.9 (CH), 126.8 (CH), 126.0 (CH), 125.5 (CH), 64.4 (CH), 53.6 (CH_2), 48.0 (CH_2), 29.3 (CH_2), 20.1 (CH_3).



(±)-4-(1-(8-Oxa-3-azabicyclo[3.2.1]oct-3-yl)ethyl)benzene (5g)

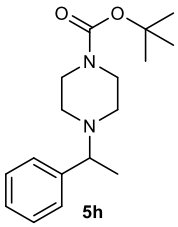
The title compound was prepared according to **GP1** using boronic ester **1** (0.116 g, 0.500 mmol) and 8-oxa-3-azabicyclo[3.2.1]octane (95% w/w, 0.208 mg, 1.75 mmol), heating for 18 h. Flash column chromatography (1: 100% CH_2Cl_2 to 70% hexane/30% EtOAc; 2: 80% hexane/20% Et_2O) of the crude material gave *amine* **5g** (38.3 mg, 35%) as a yellow oil.

IR 2950, 2800, 1451, 1142, 997, 878 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (4H, m, Ar**H**), 7.25-7.17 (1H, m, Ar**H**), 4.35-4.29 (1H, m, OC**H**), 4.20-4.14 (1H, m, OC**H**), 3.29 (1H, q, *J* = 6.7 Hz, C**H**CH_3), 2.75 (1H, dt, *J* = 10.8, 1.8 Hz, NC**H**$_A$H$_B$), 2.40-2.31 (2H, m, NC**H**$_C$H$_D$, NCH$_A$**H**$_B$), 2.19 (dd, *J* = 11.2, 1.5 Hz, 1H, NCH$_C$**H**$_D$), 2.09-1.98 (1H, m, C**H**$_A$H$_B$CH$_2$), 1.94-1.73 (3H, m, CH$_A$**H**$_B$C**H$_2$**), 1.27 (3H, d, *J* = 6.7 Hz, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1 (C), 128.2 (2 × CH), 127.3 (2 × CH), 126.8 (CH), 74.9 (2 × CH), 64.3 (CH), 57.0 (CH_2), 55.2 (CH_2), 28.6 (CH_2), 28.5 (CH_2), 20.0 (CH_3).

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

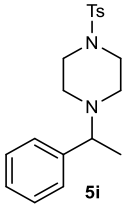


(±)-1-Piperazinecarboxylic acid, 4-(1-phenylethyl)-, 1,1-dimethylethyl ester (5h)

The title compound was prepared according to **GP1** using boronic ester **1** (0.116 g, 0.502 mmol) and *N*-Bocpiperizine (0.326 g, 1.75 mmol), heating for 18 h. Flash column chromatography (69% hexane/30% EtOAc/1% Et_3N) of the crude material gave amine **5h** (0.112 g, 77%) as a colourless oil. The data were consistent with the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.29 (4H, m, Ar**H**), 7.28-7.23 (1H, m, Ar**H**), 3.45-3.35 (5H, m, 2 × C**H$_2$** and C**H**), 2.50-2.40 (2H, m, C**H$_2$**), 2.38-2.30 (2H, m, C**H$_2$**), 1.45 (9H, s, 3 × CC**H$_3$**), 1.38 (3H, d, *J* = 6.7 Hz, CHC**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7 (C), 143.6 (C), 128.2 (2 × CH), 127.6 (2 × CH), 126.9 (CH), 79.4 (C), 64.7 (CH), 50.2 (4 × CH_2), 28.4 (3 × CH_3), 19.6 (CH_3).



(±)-1-[(4-Methylphenyl)sulfonyl]-4-(1-phenylethyl)piperazine (5i)

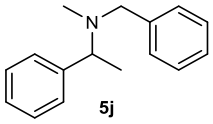
The title compound was prepared according to **GP1** using boronic ester **1** (0.116 g, 0.500 mmol) and *N*-tosylpiperizine (0.420 g, 1.75 mmol), heating for 18 h. Flash column chromatography (99% hexane/1% Et_3N → 99% Et_2O /1% Et_3N) of the crude material gave amine **5i** (84.6 mg, 49%) as a white solid. The data were consistent with the literature.[20]

m.p. 148-149 °C (XX). No literature value available.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.59 (2H, m, Ar**H**), 7.35-7.18 (7H, m, Ar**H**), 3.36 (1H, q, *J* = 6.6 Hz, C**H**), 3.03-2.92 (4H, m, 4 × C**H$_2$**), 2.62-2.52 (2H, m, C**H$_2$**), 2.50-2.40 (5H, m, C**H$_2$** and ArC**H$_3$**), 1.32 (3H, d, *J* = 6.6 Hz, CHC**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6 (C), 143.3 (C), 132.4 (C), 129.6 (2 × CH), 128.3 (2 × CH), 127.9 (2 × CH), 127.5 (2 × CH), 127.1 (CH), 64.4 (CH), 49.5 (2 × CH_2), 46.3 (2 × CH_2), 21.5 (CH_3), 19.5 (CH_3).

3.4. Scope of Reaction Using Acyclic Secondary Amines

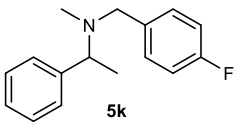


(±)-*N*-α-Dimethyl-*N*-(phenylmethyl)benzenemethanamine (5j)

The title compound was prepared according to **GP1** using boronic ester **1** (0.116 g, 0.503 mmol) and *N*-methylbenzylamine (0.214 g, 1.77 mmol), heating for 18 h. Flash column chromatography (94% hexane/5% EtOAc/1% Et_3N) of the crude material gave amine **5j** (71.2 mg, 63%) as a colourless oil. The data were consistent with the literature.[21]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.41 (2H, m, Ar**H**), 7.37-7.31 (6H, m, Ar**H**), 7.28-7.22 (2H, m, Ar**H**), 3.66 (1H, q, *J* = 6.8 Hz, C**H**), 3.60 (1H, d, *J* = 13.3 Hz, C**H$_A$**H$_B$), 3.32 (1H, d, *J* = 13.3 Hz, CH$_A$**H$_B$**), 2.15 (3H, s, NC**H$_3$**), 1.44 (3H, d, *J* = 6.8 Hz, CHC**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2 (C), 140.1 (C), 128.7 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.7 (2 × CH), 126.8 (CH), 126.7 (CH), 63.2 (CH), 58.9 (CH_2), 38.3 (CH_3), 18.4 (CH_3).



(±)-[(4-Fluorophenyl)methyl](methyl)(1-phenylethyl)amine (5k)

The title compound was prepared according to **GP1** using boronic ester **1** (0.116 g, 0.503 mmol) and *N*-methyl-4-fluorobenzylamine (0.245 g, 1.76 mmol), heating for 18 h. Flash column chromatography (94% hexane/5% EtOAc/1% Et_3N) of the crude material gave *amine* **5k** (64.4 mg, 53%) as a colourless oil.

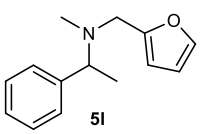
IR 2981, 2790, 1604, 1506, 1453, 1125 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.34 (4H, m, Ar**H**), 7.31-7.24 (3H, m, Ar**H**), 7.04-7.96 (2H, m, Ar**H**), 3.65 (1H, q, *J* = 6.7 Hz, C**H**), 3.55 (1H, d, *J* = 13.3 Hz, C**H$_A$**H$_B$), 3.28 (2H, d, *J* = 13.3 Hz, CH$_A$**H$_B$**), 2.14 (3H, s, NC**H$_3$**), 1.44 (3H, d, *J* = 6.7 Hz, CHC**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (C, d, J_F = 245.5 Hz), 144.1 (C), 135.7 (C), 130.1 (2 × CH, d, J_F = 8.4 Hz), 128.2 (2 × CH), 127.6 (2 × CH), 126.8 (CH), 114.9 (2 × CH, d, J_F = 20.5 Hz), 63.2 (CH), 58.1 (CH_2), 38.2 (CH_3), 18.4 (CH_3).

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.5.

HRMS (Q-TOF) Exact mass calcd for $[C_{16}H_{18}FN]^+$ [M+H]$^+$: 244.1496, found: 244.1508.



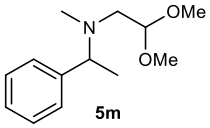
(±)-*N*-Methyl-*N*-(furan-2-ylmethyl)-1-phenylethanamine (5l)

The title compound was prepared according to **GP1** using boronic ester **1** (0.117 g, 0.504 mmol) and *N*-methylfurfurylamine (0.196 g, 1.76 mmol), heating for 18 h. Flash column chromatography (94% hexane/5% EtOAc/1% Et_3N) of the crude material gave amine **5l** (69.6 mg, 64%) as a colourless oil. The data were consistent with the literature.[22]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.32 (5H, m, Ar**H**), 7.29-7.24 (1H, m, Ar**H**), 6.33 (1H, dd, *J* = 3.1, 1.9 Hz, Ar**H**), 6.17 (1H, d, *J* = 3.1 Hz, Ar**H**), 3.67 (d, *J* = 14.4 Hz, C**H$_A$**CH$_B$), 3.58 (1H, q, *J* =

6.7 Hz, C**H**), 3.44 (1H, d, *J* = 14.4 Hz, CH_ACH_B), 2.23 (3H, s, NCH_3), 1.44 (3H, t, *J* = 6.7 Hz, $CHCH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9 (C), 143.8 (C), 141.9 (CH), 128.2 (2 × CH), 127.7 (2 × CH), 126.9 (CH), 109.9 (CH), 108.3 (CH), 62.7 (CH), 51.0 (CH_2), 38.9 (CH_3), 19.6 (CH_3).



(±)-*N*-(2,2-Dimethoxyethyl)-*N*,α-dimethylbenzenemethanamine (5m)

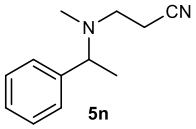
The title compound was prepared according to **GP1** using boronic ester **1** (0.118 g, 0.508 mmol) and 2,2-dimethoxy-*N*-methylethylamine (0.223 g, 1.78 mmol), heating for 18 h. Flash column chromatography (79% hexane / 20% EtOAc /1% Et_3N) of the crude material gave amine **5m** (86.0 mg, 76%) as a green oil.

IR: 2830, 1451, 1124 , 1071 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (4H, m, Ar**H**), 7.26-7.20 (1H, m, Ar**H**), 4.43 (1H, dd, *J* = 5.5, 5.1 Hz, C**H**O), 3.65 (1H, q, *J* = 6.8 Hz, CH_3CH), 3.30 (3H, s, OCH_3), 3.28 (3H, s, OCH_3), 2.60 (1H, dd, *J* = 13.4, 5.3 Hz, CH_ACH_B), 2.42 (1H, dd, *J* = 13.4, 5.3 Hz, CH_ACH_B), 2.28 (3H, s, NCH_3), 1.38 (d, *J* = 6.8 Hz, 1H, $CHCH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1 (C), 128.0 (2 × CH), 127.8 (2 × CH), 126.8 (CH), 103.3 (CH), 63.8 (CH), 55.3 (CH_2), 53.3 (CH_3), 53.0 (CH_3), 39.7 (CH_3), 17.7 (CH_3).

HRMS (QTOF) Exact mass calcd for $[C_{13}H_{22}NO_2]^+$ $[M+H]^+$: 224.1645, found: 224.1654.



(±)-3-(Methyl-(1-phenylethyl)amine)propanenitrile (5n)

The title compound was prepared according to **GP1** using boronic ester **1** (0.116 g, 0.500 mmol) and *N*-(methylamino)propionitrile (0.143 g, 1.70 mmol), heating for 18 h. Flash column chromatography (60% hexane/40% Et_2O) of the crude material gave *amine* **5n** (65.5 mg, 70%) as a colorless oil.

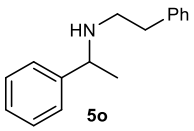
IR 2974, 2799, 2238, 1251, 1371, 1070, 958 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (4H, m, Ar**H**), 7.27-7.24 (1H, m, Ar**H**), 3.62 (1H, q, *J* = 6.7 Hz, NC**H**), 2.77 (1H, dt, *J* = 12.9, 7.2 Hz, NCH_AH_B), 2.62 (1H, dt, *J* = 12.9, 6.8 Hz, NCH_AH_B), 2.42 (2H, dd, *J* = 7.2, 6.8 Hz, CH_2CN), 2.26 (3H, s, NCH_3), 1.37 (3H, d, *J* = 6.7 Hz, $CHCH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3 (C), 128.4 (2 × CH), 127.5 (2 × CH), 127.2 (CH), 118.9 (C), 63.3 (CH), 49.7 (CH_2), 38.4 (CH_3), 18.4 (CH_3), 16.5 (CH_2).

HRMS (Q-TOF) Exact mass calcd for $[C_{12}H_{17}N_2]^+$ $[M+H]^+$: 189.1386, found: 189.1393.

3.5. Scope of Reaction Using Primary amines



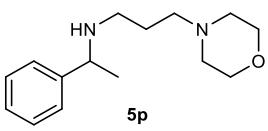
5o

(±)-*N*-Phenethyl-1-phenethanamine (5o)

The title compound was prepared according to **GP1** using boronic ester **1** (0.127 g, 0.547 mmol) and 2-phenylethylamine (240 µL, 1.90 mmol), heating for 18 h. The crude was concentrated under vacuo, dissolved in 5 mL EtOAc and extracted with aqueous HCl (1 M, 3 × 3 mL). The aqueous phases were combined, basified to pH > 10 with a solution of saturated aqueous Na_2CO_3, and extracted with EtOAc (3 × 10 mL). The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. Flash column chromatography (75% hexane/25% EtOAc → 100% EtOAc) of the crude material gave amine **5o** (68.3 mg, 55%) as a yellow oil. The data were consistent with the literature.[23]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.16 (10H, m, Ar**H**), 3.81 (1H, q, *J* = 6.6 Hz, C**H**), 2.87-2.69 (4H, m, 2 × C**H$_2$**), 1.45 (1H, br s, N**H**), 1.37 (d, *J* = 6.6 Hz, 3H, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5 (C), 140.0 (C), 128.6 (2 × CH), 128.3 (4 × CH), 126.8 (CH), 126.5 (2 × CH), 126.0 (CH), 58.1 (CH), 48.9 (CH_2), 36.4 (CH_2), 24.3 (CH_3).



5p

(±)-[3-(Morpholin-4-yl)propyl](1-phenylethyl)amine (5p)

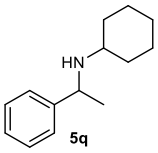
The title compound was prepared according to **GP1** using boronic ester **1** (0.117 g, 0.504 mmol) and 3-morpholinopropylamine (0.253 g, 1.78 mmol), heating for 18 h. Flash column chromatography (97% CH_2Cl_2/2% MeOH/1% Et_3N) of the crude material gave *amine* **5p** (61.7 mg, 49%) as a yellow oil.

IR 2960, 2810, 1675, 1455, 1275, 1118 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (4H, m, Ar**H**), 7.27-7.22 (1H, m, Ar**H**), 3.77 (1H, q, *J* = 6.6 Hz, C**H**), 3.68 (4H, t, *J* = 4.7 Hz, 2 × OC**H$_2$**), 2.65-2.57 (1H, m, CHNC**H$_A$**CH_B), 2.54-2.32 (7H, m, $CHNCH_AC$**H$_B$**, C**H$_2$**N$(CH_2)_2$ and 2 × NC**H$_2$**CH_2O), 1.76-1.63 (2H, m, NCH_2C**H$_2$**CH_2), 1.39 (3H, d, *J* = 6.6 Hz, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1 (C), 128.4 (2 × CH), 127.0 (CH), 126.5 (2 × CH), 66.9 (2 × CH_2), 58.4 (CH), 57.5 (CH_2), 53.7 (2 × CH_2), 46.5 (CH_2), 26.3 (CH_2), 24.0 (CH_3).

HRMS (Q-TOF) Exact mass calcd for $[C_{15}H_{25}N_2O]^+$ $[M+H]^+$: 249.1961, found: 249.1970



5q

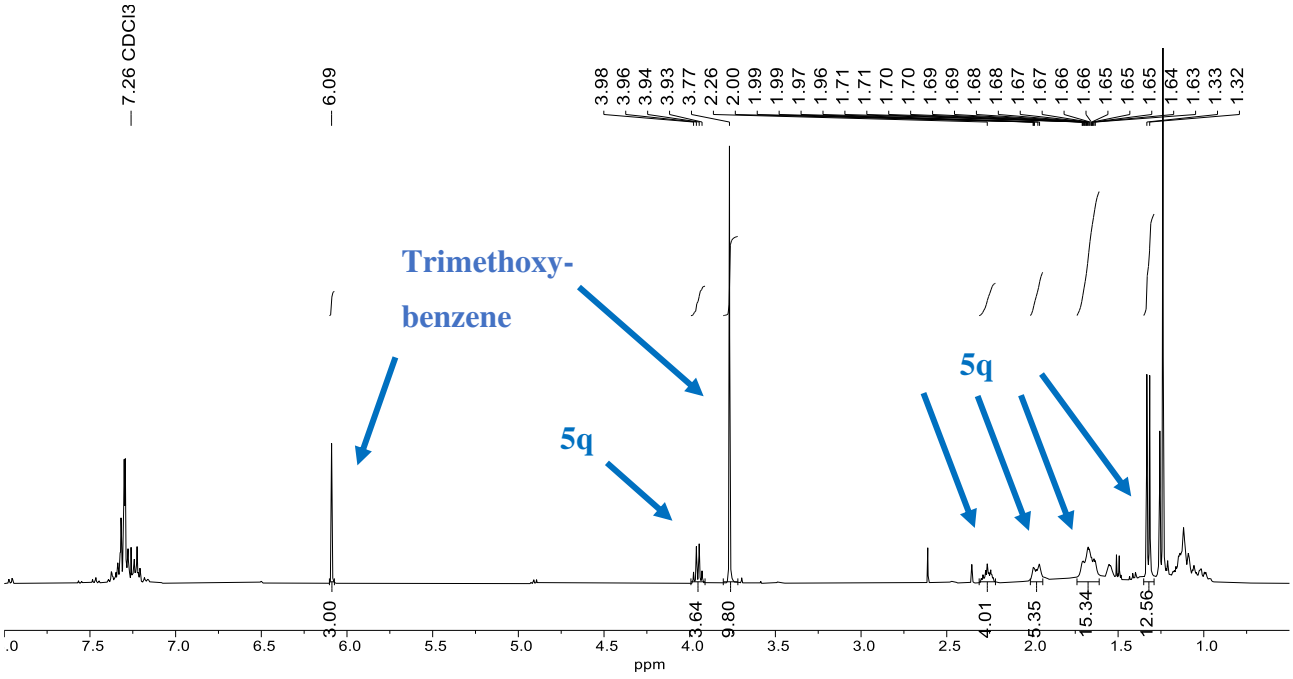
(±)-*N*-(1-phenylethyl)cyclohexanamine (5q)

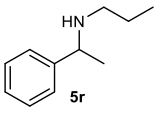
The title compound was prepared using a modification of **GP1** using boronic ester **1** (0.117 g, 0.503 mmol) and cyclohexylamine (0.20 mL, 1.7 mmol), heating for 18 h. The mixture was filtered through a silica plug, eluting with Et_2O (10 mL). 1,3,5-Trimethoxybenzene (16.5 mg, 0.0981 mmol) was added to the filtrate, and the mixture was concentrated *in vacuo*. The

mixture was analysed by ^{1}H NMR, which indicated amine **5q** was formed in 63% yield (average of two reactions). The data matched the literature.[24]

Characteristic peaks for **5q**.

^{1}H NMR (400 MHz, $CDCl_3$): 3.95 (1H, q, *J* = 6.6 Hz, C**H**), 2.31-2.21 (1H, m, CH_2), 2.01-1.94 (1H, m, C**H$_2$**), 1.75-1.61 (3H, m, C**H$_2$**), 1.32 (3H, d, *J* = 6.6 Hz, C**H$_3$**).



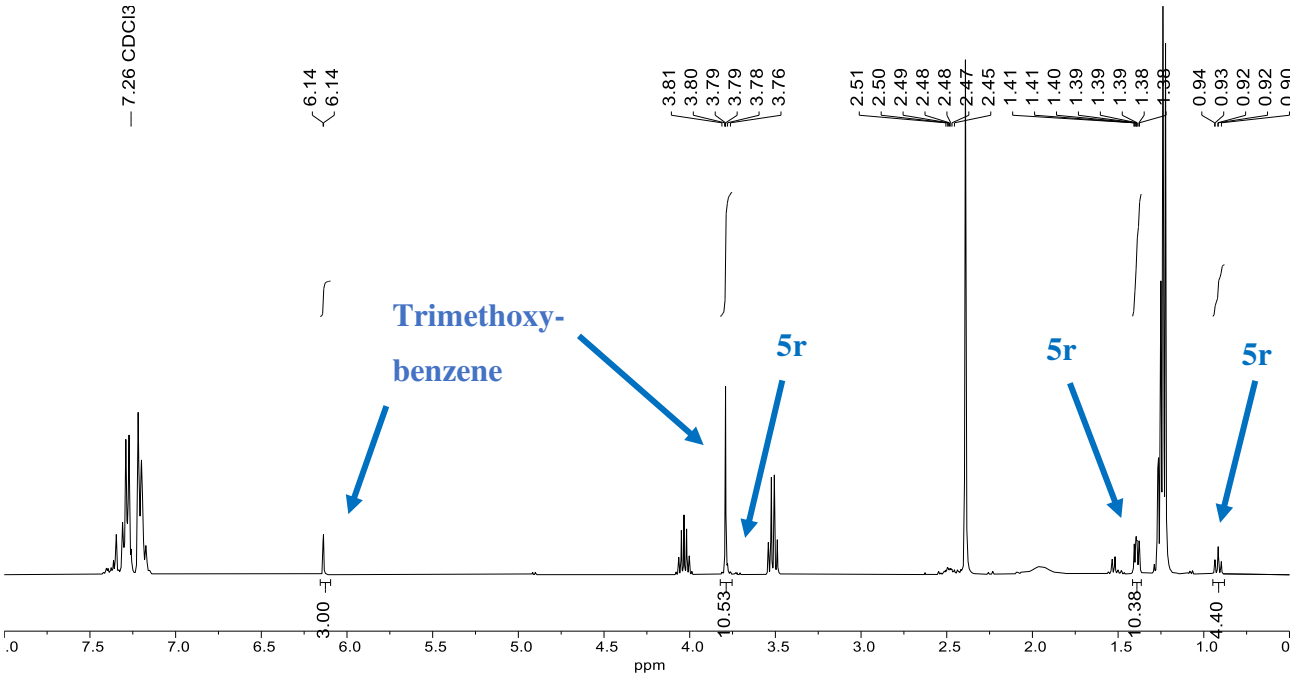


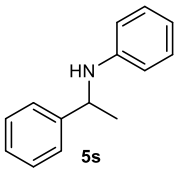
(±)-*N*-(1-phenylethyl)propan-1-amine (5r)

The title compound was prepared using a modification of **GP1** using boronic ester **1** (0.117 g, 0.502 mmol) and propylamine (0.15 mL, 1.8 mmol), heating for 18 h. The mixture was filtered through a silica plug, eluting with Et_2O (10 mL). 1,3,5-Trimethoxybenzene (20.4 mg, 0.121 mmol) was added to the filtrate, and the mixture was concentrated *in vacuo*. The mixture was analysed by ^{1}H NMR, which indicated amine **5r** was formed in 45% yield (average of two reactions). The data matched the literature.[25]

Characteristic peaks for **5r**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (1H, q, *J* = 6.5 Hz, C**H**), 1.41-1.37 (5H, m, C**H$_2$**CH_3 + $CHCH_3$), 0.92 (3H, t, *J* = 7.4 Hz, CH_2C**H$_3$**).



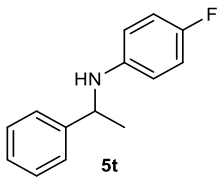


(±)-*N*-(1-Phenylethyl)aniline (5s)

The title compound was prepared according to **GP1** using boronic ester **1** (0.117 g, 0.505 mmol) and aniline (0.163 mg, 1.75 mmol), heating for 18 h. Flash column chromatography (98% hexane/2% EtOAc) of the crude material gave amine **5s** (44.3 mg, 45%) as an orange oil. The data were consistent with the literature.[26]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (2H, m, Ar**H**), 7.37-7.32 (2H, m, Ar**H**), 7.27-7.23 (1H, m, Ar**H**), 7.15-7.09 (2H, m, Ar**H**), 6.70-6.65 (1H, m, Ar**H**), 6.56-6.52 (2H, m, Ar**H**), 4.51 (1H, q, *J* = 6.7 Hz, C**H**), 4.16 (1H, br s, N**H**), 1.55 (3H, d, *J* = 6.7 Hz, C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1 (C), 145.1 (C), 129.1 (2 × CH), 128.6 (2 × CH), 126.9 (CH), 125.8 (2 × CH), 117.3 (CH), 113.4 (2 × CH), 53.5 (CH), 25.0 (CH_3).



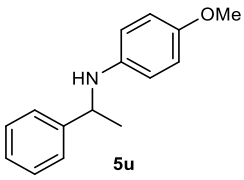
(±)-4-Fluoro-*N*-(1-phenylethyl)aniline (5t)

The title compound was prepared according to **GP1** using boronic ester **1** (0.116 g, 0.500 mmol) and 4-fluoroaniline (0.196 g, 1.76 mmol), heating for 18 h. Flash column chromatography (98% hexane/2% EtOAc) of the crude material gave amine **5t** (53.0 mg, 49%) as an orange oil. The data were consistent with the literature.[26]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (4H, m, Ar**H**), 7.27-7.23 (1H, m, Ar**H**), 6.85-6.78 (2H, m, Ar**H**), 6.48-6.43 (2H, m, Ar**H**), 4.44 (1H, q, *J* = 6.7 Hz, C**H**), 4.04 (1H, br s, N**H**), 1.53 (3H, d, *J* = 6.7 Hz, C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7 (C, d, J_F = 234.6 Hz), 144.9 (C), 143.5 (C), 128.7 (2 × CH), 127.0 (CH), 125.8 (2 × CH), 115.5 (2 × CH, d, J_F = 22.3 Hz), 114.1 (2 × CH, d, J_F = 7.1 Hz), 54.1 (CH), 25.0 (CH_3).

^{19}F NMR (377 MHz, $CDCl_3$) δ -128.2.



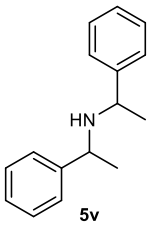
(±)-4-Methoxy-*N*-(1-phenylethyl)aniline (5u)

The title compound was prepared according to **GP1** using boronic ester **1** (0.117 g, 0.505 mmol) and *p*-anisidine (0.217 g, 1.76 mmol), heating for 18 h. Flash column chromatography (96% hexane/4% EtOAc) of the crude material gave amine **5u** (31.6 mg, 28%) as an orange oil. The data were consistent with the literature.[26]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.37 (2H, m, Ar**H**), 7.36-7.32 (2H, m, Ar**H**), 7.31-7.21 (1H, m, Ar**H**), 6.75-6.69 (2H, m, Ar**H**), 6.53-6.47 (2H, m, Ar**H**), 4.44 (1H, q, *J* = 6.7 Hz, C**H**), 3.72 (3H, s, OC**H$_3$**), 1.52 (3H, d, *J* = 6.7 Hz, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9 (C), 145.4 (C), 141.5 (C), 128.6 (2 × CH), 126.8 (CH), 125.9 (2 × CH), 114.7 (2 × CH), 114.6 (2 × CH), 55.7 (CH_3), 54.3 (CH), 25.1 (CH_3).

3.6. Diastereomeric Compounds



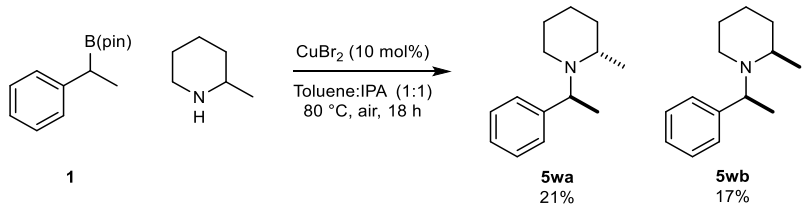
(±)-**Bis(1-phenylethyl)amine (mixture of diastereoisomers) (5v)**

The title compound was prepared according to **GP1** using boronic ester **1** (0.116 g, 0.500 mmol) and (*R*)-methylbenzylamine (212 mg, 1.75 mmol), heating for 18 h. Flash column chromatography (dichloromethane to 69% hexane/ 30% EtOAc/ 1% Et_3N) of the crude material gave amine **5v** (63.6 mg, 56%, *dl/meso* = 1:0.98) as a yellow oil. The data were consistent with the literature.[29]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.22 (20H, m, Ar**H**, *dl* and *meso* isomers), 3.81 (2H, q, *J* = 6.5 Hz, C**H**, *dl* isomer), 3.55 (2H, q, *J* = 6.7 Hz, C**H**, *meso* isomer), 1.66 (2H, br s, N**H**, *dl* and *meso* isomers), 1.40 (6H, d, *J* = 6.6 Hz, C**H$_3$**, *dl* isomer), 1.32 (6H, d, *J* = 6.7 Hz, C**H$_3$**, *meso* isomer).

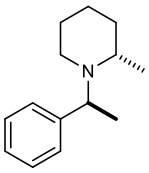
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8 (4 × C, *dl* and *meso* isomers), 128.4 (8 × CH, *dl* and *meso* isomers), 126.8 (4 × CH, *dl* and *meso* isomers), 126.6 (4 × CH, *dl* and *meso* isomers), 126.5 (4 × CH, *dl* and *meso* isomers), 55.1 (2 × CH, *meso*), 54.8 (2 × CH, *dl*), 24.9 (2 × CH_3, *meso*), 23.1 (2 × CH_3, *dl*).

(±)-2-Methyl-1-(1-phenylethyl)piperidine (5w)



1 **5wa** 21% **5wb** 17%

The title compound was prepared according to **GP1** using boronic ester **1** (0.117 g, 0.502 mmol) and 2-methyl piperidine (0.175 g, 1.76 mmol), heating for 18 h. Flash column chromatography (69% hexane/30% EtOAc/1% Et_3N) of the crude material gave amine **5wa** (21.0 mg, 21%) as a yellow oil and amine **5wb** (17.3 mg, 17%) as a yellow oil. The data for **5wa**[27] and **5wb**[28] were consistent with the literature.



5wa

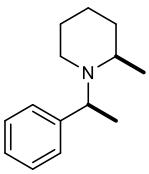
(±)-(*S*,*S*)-2-Methyl-1-(1-phenylethyl)piperidine (5wa)

IR 2930, 2793, 1447, 1373, 1279, 1066 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (2H, m, Ar**H**), 7.35-7.29 (2H, m, Ar**H**), 7.24-7.20 (1H, m, Ar**H**), 4.07 (1H, q, *J* = 6.7 Hz, ArC**H**), 2.87-2.80 (1H, m, NC**H**CH_2), 2.40-2.33 (1H, m, C$\mathbf{H_A}CH_B$), 2.20-2.12 (1H, m, $CH_AC\mathbf{H_B}$),1.75-1.68 (1H, m, C$\mathbf{H_2}$), 1.67-1.59 (1H, m, C$\mathbf{H_2}$), 1.47-1.31 (4H, m, 2 × C$\mathbf{H_2}$), 1.27 (3H, d, *J* = 6.7 Hz, ArCHC$\mathbf{H_3}$), 1.14 (3H, d, *J* = 6.3 Hz, $CH_2CHC\mathbf{H_3}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8 (C), 127.9 (2 × CH), 127.7 (2 × CH), 126.2 (CH), 56.6 (CH), 52.0 (CH), 44.9 (CH_2), 34.7 (CH_2), 26.4 (CH_2), 23.4 (CH_2), 17.0 (CH_3), 12.5 (CH_3).

HRMS (QTOF) Exact mass calcd for $[C_{14}H_{21}N]^+$ $[M+H]^+$: 204.1747, found: 204.1751.



5wb

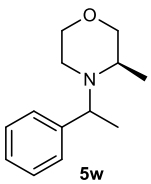
(±)-(*R*,*S*)-2-Methyl-1-(1-phenylethyl)piperidine (5wb)

IR 2940, 2523, 1455, 1205, 1064 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.22 (5H, m, Ar**H**), 4.10 (1H, q, *J* = 6.9 Hz, ArC**H**), 2.89-2.83 (1H. m, NC$\mathbf{H_A}H_B$), 2.39-2.32 (1H, m, NC**H**CH_2), 2.18-2.09 (1H, m, $NCH_A\mathbf{H_B}$), 1.64-1.50 (4H, m, 2 × C$\mathbf{H_2}$), 1.42 (3H, d, *J* = 6.9 Hz, ArCHC$\mathbf{H_3}$), 1.39-1.29 (1H, m, C$\mathbf{H_2}$), 1.25-1.17 (1H, m, C$\mathbf{H_2}$), 1.14 (3H, d, *J* = 6.2 Hz, $CH_2CHC\mathbf{H_3}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8 (C), 128.1 (2 × CH), 127.8 (2 × CH), 126.6 (CH), 57.4 (CH), 52.4 (CH), 44.8 (CH_2), 34.7 (CH_2), 26.5 (CH_2), 22.9 (CH_2), 20.1 (CH_3), 17.3 (CH_3).

HRMS (QTOF) Exact mass calcd for $[C_{14}H_{21}N]^+$ $[M+H]^+$: 204.1747, found: 204.1754.



5w

(±)-3-Methyl-4-(1-phenylethyl)morpholine (5x)

The title compound was prepared according to **GP1** using boronic ester **1** (0.116 g, 0.498 mmol) and (*R*)-3-methylmorpholine (182 mg, 1.80 mmol), heating for 18 h. The mixture was concentrated *in vacuo*, dissolved in 5 mL EtOAc and extracted with aqueous HCl (1

M, 3 × 3 mL). The combined aqueous phases were and basified to pH > 10 using saturated aqueous Na_2CO_3, and extracted with CH_2Cl_2 (3 × 10 mL). Flash column chromatography (75% hexane/25% EtOAc to 50% hexane/50% EtOAc) of the crude material gave two diastereoisomers, *amine* **5xa** (23.5 mg, 23%) as a colourless oil and *amine* **5xb** (23.2 mg, 23%) as a colourless oil.

Mixture of diastereomers:

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

Data for 5xa:

IR 2965, 2848, 1446, 1138, 1125, 1076 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (2H, m, Ar**H**), 7.34-7.28 (2H, m, Ar**H**), 7.25-7.19 (1H, m, Ar**H**), 3.98 (1H, q, *J* = 6.8 Hz, ArC**H**), 3.75 (dd, *J* = 10.9, 3.0 Hz, 1H, CHC**H$_A$**CH$_B$), 3.60 (dt, *J* = 10.8, 4.4 Hz, 1H, $CH_2CH_ACH_B$**H$_B$**), 3.52 (dd, *J* = 10.8, 5.2, 5.0 Hz, 1H, $CH_2CH_ACH_B$**H$_B$**), 3.43 (dd, *J* = 10.9, 6.7 Hz, 1H, CHC**H$_A$**CH$_B$), 2.97 (1H, dqd, *J* = 6.7, 6.5, 3.0 Hz, NC**H**CH$_3$), 2.33-2.25 (2H, m, NC**H$_2$**), 1.29 (3H, d, *J* = 6.8 Hz, ArCHC**H$_3$**), 1.11 (3H, d, *J* = 6.5 Hz, CH_2CHCH_3).

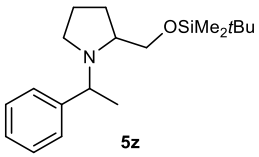
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6 (C), 128.1 (2 x CH), 127.7 (2 x CH), 126.6 (CH), 73.3 (CH_2), 67.8 (CH_2), 56.9 (CH), 51.0 (CH), 44.3 (CH_2), 13.4 (CH_3), 12.0 (CH_3).

Data for 5xb:

IR 2965, 2848, 1452, 1136, 1125, 969 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.20 (5H, m,), 3.97 (1H, q, *J* = 6.9 Hz, ArC**H**), 3.80-3.67 (2H, m, OC**H$_2$**), 3.61 (1H, dd, *J* = 10.9, 3.1 Hz, OCH_A**H$_B$**CH), 3.33 (1H, dd, *J* = 10.9, 6.5 Hz, OCH_A**H$_B$**CH), 2.82-2.72 (1H, m,), 2.50-2.37 (2H, m, NC**H$_2$**), 1.39 (3H, d, *J* = 6.9 Hz, ArCHC**H$_3$**), 1.04 (3H, d, *J* = 6.4 Hz, CH_2CHCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4 (C), 128.1 (2 x CH), 128.0 (2 x CH), 126.9 (CH), 73.2 (CH_2), 67.8 (CH_2), 57.8 (CH), 51.2 (CH), 44.2 (CH_2), 19.9 (CH_3), 12.0 (CH_3).



5z

(±)-2-((*tert*-Butyldimethylsilyloxy)methyl)-1-(1-phenylethyl)pyrrolidine (5y)

The title compound was prepared according to **GP1** using boronic ester **1** (0.116 g, 0.501 mmol) and 2-((*tert*-butyldimethylsilyloxy)methyl)pyrrolidine (378 mg, 1.75 mmol), heating for 18 h. Flash column chromatography (100% CH_2Cl_2 → 69% CH_2Cl_2/30% Et_2O/1% Et_3N) of the crude material gave *amine* **5y** (103 mg, 64%, dr: 1.03:1) as a yellow oil. Upon further purification one of the diastereoisomers (**5ya**) was isolated for further characterisation.

Mixture of diastereoisomers (5ya and 5yb):

IR 2928, 1453, 1252, 1092, 833, 774 cm^{-1}.

^{1}H NMR (400 MHz, CD_3CN) δ 7.39-7.34 (2H, m, Ar**H**, **5yb**), 7.34-7.26 (m, 6H, Ar**H**, **5ya** + **5yb**), 7.25-7.19 (m, 2H, Ar**H**, **5ya** + **5yb**), 3.83-3.70 (m, 2H, ArC**H**, **5ya** + **5yb**), 3.60 (dd, *J* = 10.0, 4.4 Hz,

1H, OC**H**$_A$H$_B$, **5ya**), 3.35 (dd, *J* = 10.0, 8.2 Hz, 1H, OCH$_A$**H$_B$**, **5ya**), 3.15 (1H, dd, J = 9.9, 4.8 Hz, OC**H**$_A$H$_B$, **5yb**) 3.10 (1H, dd, *J* = 9.9, 8.3 Hz, OCH$_A$**H$_B$**, **5yb**), 2.93-2.78 (3H, m, CH$_2$C**H**, **5ya** + **5yb**; NC**H**$_A$H$_B$, **5yb**), 2.77-2.69 (m, 1H, NC**H**$_A$H$_B$, **5ya**), 2.50 (td, *J* = 9.1, 6.8 Hz, 1H, NCH$_A$**H$_B$**, **5yb**), 2.39-2.29 (1H, m, NCH$_A$**H$_B$**, **5ya**), 1.78-1.54 (m, 8H, CHC**H$_2$**C**H$_2$**, **5ya** + **5yb**), 1.36 (3H, d, *J* = 6.7 Hz, CHC**H$_3$**, **5ya**), 1.33 (3H, d, *J* = 6.7 Hz, CHC**H$_3$**, **5yb**), 0.91 (9H, s, 3 × CC**H$_3$**, **5ya**), 0.80 (9H, s, 3 × CC**H$_3$**, **5yb**), 0.07 (3H, s, SiC**H$_3$**, **5ya**), 0.06 (3H, s, SiC**H$_3$**, **5ya**), -0.11 (3H, s, SiC**H$_3$**, **5yb**), -0.13 (3H, s, **5yb**).

^{13}C NMR (101 MHz, CD_3CN) δ 147.1 (C), 145.8 (C), 129.0 (4 × CH), 128.7 (2 × CH), 128.6 (2 × CH), 127.8 (CH), 127.6 (CH), 67.7 (CH_2), 67.0 (CH_2), 63.8 (CH), 63.2 (CH), 63.0 (CH), 62.1 (CH), 52.8 (CH_2), 51.9 (CH_2), 29.0 (CH_2), 28.6 (CH_2), 26.3 (3 × CH_3,), 26.3 (3 × CH_3), 26.1 (CH_3), 24.3 (CH_2), 24.2 (CH_2), 23.2 (CH_3), 19.8 (CH), 18.9 (C), 18.8 (C), -5.0 (CH_3), -5.1 (CH_3), -5.1 (CH_3), -5.2 (CH_3).

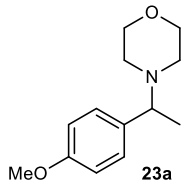
HRMS (QTOF) Exact mass calcd for $[C_{19}H_{34}NOSi]^+$ $[M+H]^+$: 320.2404, found: 320.2414.

Diastereoisomer 5ya:

^{1}H NMR (400 MHz, CD_3CN) δ 7.37-7.26 (4H, m, Ar**H**), 7.25-7.19 (1H, m, Ar**H**), 3.81 (1H q, *J* = 6.7 Hz, ArC**H**), 3.60 (1H, dd, *J* = 10.0, 4.4 Hz, OC**H**$_A$H$_B$), 3.35 (1H, dd, *J* = 10.0, 8.1 Hz, OCH$_A$**H$_B$**), 2.88 (1H, tt, *J* = 8.1, 4.5 Hz, N**H**CH$_2$), 2.77-2.69 (1H, m, NC**H**$_A$H$_B$), 2.39-2.29 (1H, m, NCH$_A$**H$_B$**), 1.77-1.51 (4H, m, CHC**H$_2$**C**H$_2$**), 1.37 (3H, d, *J* = 6.7 Hz, CHC**H$_3$**), 0.90 (9H, s, 3 × CC**H$_3$**), 0.07 (3H, s, SiC**H$_3$**), 0.06 (3H, s, SiC**H$_3$**).

^{13}C NMR (101 MHz, CD_3CN) δ 145.4 (C), 129.1 (2 × CH), 128.7 (2 × CH), 127.7 (CH), 67.6 (CH_2), 63.1 (CH), 62.3 (CH), 52.8 (CH_2), 29.0 (CH_2), 26.3 (3 × CH_3), 24.1 (CH_2), 23.1 (CH_3), 18.9 (C), -5.0 (CH_3), -5.1 (CH_3).

3.7. Scope of Reaction Using Benzylic Boronic Esters



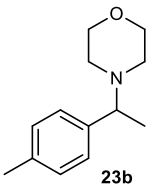
23a

(±)-*N*-[1-(4-Methoxylphenyl)ethyl]morpholine (23a)

The title compound was prepared according to **GP1** using boronic ester **22a** (0.131 g, 0.500 mmol) and morpholine (0.152 g, 1.75 mmol), heating for 18 h. Flash column chromatography (99% hexane/1% Et_3N → 49.5% hexane/49.5% Et_2O/1% Et_3N) of the crude material gave amine **23a** (72.7 mg, 66%) as a colourless oil. The data were consistent with the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (2H, d, *J* = 8.7 Hz, Ar**H**), 6.85 (2H, d, *J* = 8.7 Hz, Ar**H**), 3.80 (3H, s, OC**H₃**), 3.69-3.67 (4H, m, 2 × OC**H₂**), 3.26 (1H, q, *J* = 6.7 Hz, C**H**), 2.49-2.44 (2H, m, NC**H₂**), 2.37-2.32 (2H, m, NC**H₂**), 1.33 (3H, d, *J* = 6.7 Hz, CHC**H₃**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6 (C), 135.8 (C), 128.6 (2 × CH), 113.6 (2 × CH), 67.2 (2 × CH_2), 64.6 (CH), 55.2 (CH_3), 51.2 (2 × CH_2), 19.7 (CH_3).



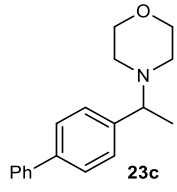
23b

(±)-*N*-[1-(4-Methylphenyl)ethyl]morpholine (23b)

The title compound was prepared according to **GP1** using boronic ester **22b** (0.124 g, 0.504 mmol) and morpholine (0.153 g, 1.76 mmol), heating for 18 h. Flash column chromatography (70% hexane/30% EtOAc) of the crude material gave amine **23b** (75.0 mg, 73%) as a colourless oil. The data were consistent with the literature.[30]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (2H, d, *J* = 7.9 Hz, Ar**H**), 7.13 (2H, d, *J* = 7.9 Hz, Ar**H**), 3.72-3.64 (4H, m, 2 × OC**H₂**), 3.27 (1H, q, *J* = 6.5 Hz, C**H**), 2.47 (2H, br s, NC**H₂**), 2.39-2.34 (2H, m, NC**H₂**), 2.33 (3H, s, ArC**H₃**), 1.35 (3H, d, *J* = 6.5 Hz, CHC**H₃**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7 (C), 136.6 (C), 129.0 (2 × CH), 127.6 (2 × CH), 67.2 (2 × CH_2), 65.1 (CH), 51.3 (2 × CH_2), 21.0 (CH_3), 19.8 (CH_3).



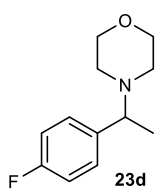
23c

(±)-*N*-[(1-([1,1'-Biphenyl]-4-yl)ethyl)morpholine (23c)

The title compound was prepared according to **GP1** using boronic ester **22c** (0.155 g, 0.503 mmol) and morpholine (0.156 g, 1.79 mmol), heating for 18 h. Flash column chromatography (59% hexane/40% EtOAc/1% Et_3N) of the crude material gave amine **23c** (99.6 mg, 74%) as a colourless oil. The data were consistent with the literature.[30]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.53 (4H, m, Ar**H**), 7.48-7.37 (4H, m, Ar**H**), 7.37-7.29 (1H, m, Ar**H**), 3.76-3.66 (4H, m, 2 × OC**H₂**), 3.37 (1H, q, *J* = 6.6 Hz, C**H**), 2.60-2.49 (2H, m, NC**H₂**), 2.47-2.36 (2H, m, NC**H₂**), 1.40 (3H, d, *J* = 6.6 Hz, C**H₃**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0 (C), 140.9 (C), 139.9 (C), 128.7 (2 × CH), 128.0 (2 × CH), 127.1 (CH), 127.0 (4 × CH), 67.2 (2 × CH), 65.1 (CH), 51.3 (2 × CH), 19.7 (CH_3).



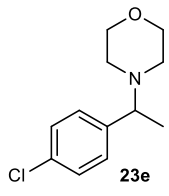
(±)-4-(1-(4-Fluorophenyl)ethyl)morpholine (23d)

The title compound was prepared according to **GP1** using boronic ester **22d** (0.126 g, 0.504 mmol) and morpholine (153 μL, 1.75 mmol), heating for 18 h. Flash column chromatography (79% hexane/20% EtOAc/1% Et_3N to 99% EtOAc/1% Et_3N) of the crude material gave amine **23d** (76.9 mg, 73%) as a colourless oil. The data were consistent with the literature.[31]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.23 (2H, m, Ar**H**), 7.02-6.94 (2H, m, Ar**H**), 3.74-3.60 (4H, m, 2 × OC**H₂**), 3.28 (1H, q, *J* = 6.7 Hz, C**H**), 2.55-2.40 (2H, m, 2 × NC**H**$_A$H$_B$), 2.37-2.27 (2H, m, 2 × NCH$_A$**H$_B$**), 1.31 (3H, d, *J* = 6.7 Hz, C**H₃**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (d, $J_{C\text{-}F}$ = 244.7 Hz, C), 139.7 (d, $J_{C\text{-}F}$ = 3.2 Hz, C), 128.9 (d, $J_{C\text{-}F}$ = 7.8 Hz, 2 × CH), 115.0 (d, $J_{C\text{-}F}$ = 21.0 Hz, 2 × CH), 67.1 (2 × CH_2), 64.5 (CH), 51.1 (2 × CH_2), 19.8 (CH_3).

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.0.



(±)-*N*-[1-(4-Chlorophenyl)ethyl]morpholine (23e)

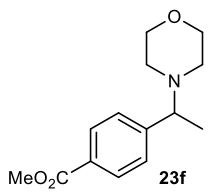
The title compound was prepared according to **GP1** using boronic ester **22e** (0.134 g, 0.504 mmol) and morpholine (0.154 g, 1.77 mmol), heating for 19 h. Flash column chromatography (59% hexane/40% EtOAc/1% Et_3N) of the crude material gave *amine* **23e** (88.0 mg, 78%) as a colourless oil.

IR 2960, 2854, 2907, 1490, 1272, 1116 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.22 (4H, m, Ar**H**), 3.73-3.62 (4H, m, 2 × OC**H₂**), 3.28 (1H, q, *J* = 6.7 Hz, C**H**), 2.52-2.42 (2H, m, NC**H₂**), 2.38-2.29 (2H, m, NC**H₂**), 1.31 (3H, d, *J* = 6.7 Hz, C**H₃**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7 (C), 132.5 (C), 128.9 (2 × CH), 128.5 (2 × CH), 67.2 (2 × CH_2), 64.7 (CH), 51.2 (2 × CH_2), 19.8 (CH_3).

HRMS (Q-TOF) Exact mass calcd for $[C_{12}H_{16}{}^{35}ClNO]^+$ $[M+H]^+$: 226.0993, found: 226.1004.

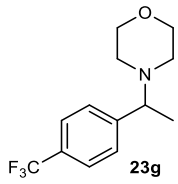


(±)-Methyl 4-(1-morpholin-4-ylethyl)benzoate (23f)

The title compound was prepared according to a modification of **GP1** using boronic ester **22e** (0.146 g, 0.502 mmol) and morpholine (0.154 g, 1.77 mmol) and propyl acetate (0.8 mL), heating for 19 h. Flash column chromatography (20% EtOAc/80% CH_2Cl_2) of the crude material gave amine **23f** (63.0 mg, 50%) as a colourless oil. The data were consistent with the literature.[30]

^{1}H NMR (400 MHz, $CDCl_3$) 8.02-7.91 (2H, m, Ar**H**), 7.44-7.35 (2H, m), 3.90 (3H, s, OC**H₃**), 3.74-3.62 (4H, m, 2 × OC**H₂**), 3.35 (1H, q, *J* = 6.7 Hz, C**H**), 2.54-2.43 (2H, m, NC**H₂**), 2.38-2.28 (2H, m, NC**H₂**), 1.33 (3H, d, *J* = 6.7Hz, CHC**H₃**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0 (CH), 149.6 (CH), 129.7 (2 × CH), 128.9 (C), 127.5 (2 × CH), 67.1 (2 × CH_2), 65.1 (CH_3), 52.0 (CH), 51.3 (2 × CH_2), 19.7 (CH_3).



23g

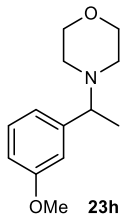
(±)-*N*-[1-[4-(Trifluoromethyl)phenyl]ethyl]morpholine (23g)

The title compound was prepared according to **GP1** using boronic ester **22g** (0.154 g, 0.514 mmol) and morpholine (159 μL, 1.82 mmol), heating for 18 h. Flash column chromatography (89% hexane/10% EtOAc/1% Et_3N → 79% hexane/20% EtOAc/1% Et_3N) of the crude material gave amine **23g** (82.5 mg, 62%) as a colourless oil. The data were consistent with the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.54 (2H, m, Ar**H**), 7.51-7.40 (2H, m, Ar**H**), 3.69 (4H, br s, 2 × O**CH_2**), 3.42-3.29 (1H, m, C**H**), 2.58-2.43 (2H, m, 2 × NC**H_A**H_B), 2.40-2.27 (2H, m, 2 × NCH_A**H_B**), 1.34 (3H, d, J = 4.0 Hz, C**H_3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4 (C), 129.3 (C, q, $J_{C\text{-}F}$ = 31.7 Hz), 127.9 (2 × CH), 125.3 (2 × CH, q, $J_{C\text{-}F}$ = 4.4 Hz), 124.4 (C, q, $J_{C\text{-}F}$ = 271.0 Hz), 67.1 (2 × CH_2), 65.1 (CH), 51.2 (2 × CH_2), 19.7 (CH_3).

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.4.



23h

(±)-*N*-[1-(3-Methoxylphenyl)ethyl]morpholine (23h)

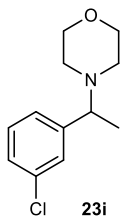
The title compound was prepared according to **GP1** using boronic ester **22h** (0.131 g, 0.500 mmol) and morpholine (0.154 g, 1.77 mmol), heating for 18 h. Flash column chromatography (69% hexane/30% EtOAc/1% Et_3N) of the crude material gave *amine* **23h** (88.0 mg, 80%) as a colourless oil.

IR 2958, 2853, 1585, 1264, 1116 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.20 (1H, m, Ar**H**), 6.93-6.87 (2H, m, Ar**H**), 6.78 (1H, dd, J = 7.8, 2.1 Hz, Ar**H**), 3.81 (3H, s, O**CH_3**), 3.74-3.64 (4H, m, 2 × O**CH_2**), 3.31-3.21 (1H, m, C**H**), 2.56-2.43 (2H, m, NC**H_2**), 2.42-2.32 (2H, m, NC**H_2**), 1.34 (3H, d, J = 6.4 Hz, CHC**H_3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6 (C), 145.8 (C), 129.2 (CH), 120.0 (CH), 113.3 (CH), 112.1 (CH), 67.2 (2 × CH_2) , 65.4 (CH), 55.2 (2 × CH_2), 51.3 (CH_3), 19.9 (CH_3).

HRMS (QTOF) Exact mass calcd for $[C_{13}H_{19}NO_2]^+$ $[M]^+$: 221.1410, found: 221.1417.



23i

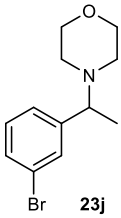
(±)-*N*-[1-(3-Chlorophenyl)ethyl]morpholine (23i)

The title compound was prepared according to **GP1** using boronic ester **22i** (0.135 g, 0.509 mmol) and morpholine (158 μL, 1.81 mmol), heating for 18 h. Flash column

chromatography (59% hexane/40% EtOAc/1% Et_3N) of the crude material gave amine **23i** (79.4 mg, 69%) as a pale-yellow oil. The data were consistent with the literature.[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (1H, t, *J* = 1.8 Hz, Ar**H**), 7.26-7.15 (3H, m, Ar**H**), 3.73-3.62 (4H, m, 2 × OC**H$_2$**), 3.27 (1H, q, *J* = 6.7 Hz, C**H**), 2.53-2.42 (2H, m, 2 × NC**H$_A$**H$_B$), 2.39-2.29 (2H, m, 2 × NCH$_A$**H$_B$**), 1.31 (3H, d, *J* = 6.7 Hz, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3 (C), 134.2 (C), 129.5 (CH), 127.5 (CH), 127.1 (CH), 125.7 (CH), 67.1 (2 × CH_2), 64.9 (CH), 51.1 (2 × CH_2), 19.7 (CH_3).

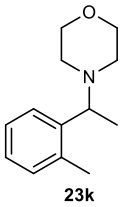


(±)-4-(1-(3-Bromophenyl)ethyl)morpholine (23j)

The title compound was prepared according to **GP1** using boronic ester **22j** (0.156 g, 0.502 mmol) and morpholine (155 μL, 1.77 mmol), heating for 18 h. Flash column chromatography (90% hexane/ 10% EtOAc to 100% EtOAc) of the material gave amine **23j** (88.2 mg, 65%) as a colourless oil. The data were consistent with the literature.[30]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (1H, t, *J* = 1.8 Hz, Ar**H**), 7.39-7.33 (1H, m, Ar**H**), 7.25-7.21 (1H, m, Ar**H**), 7.17 (1H, t, *J* = 7.7 Hz, Ar**H**), 3.74-3.62 (4H, m, 2 × OC**H$_2$**), 3.26 (1H, q, *J* = 6.7 Hz, C**H**), 2.52-2.42 (2H, m, 2 × NC**H$_A$**H$_B$), 2.39-2.30 (2H, m, 2 × NCH$_A$**H$_B$**), 1.31 (3H, d, *J* = 6.7 Hz, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6 (C), 130.4 (CH), 130.0 (CH), 129.9 (CH), 126.2 (CH), 122.5 (C), 67.1 (CH_2), 64.9 (CH), 51.2 (CH_2), 19.7 (CH_3).



(±)-*N*-[1-(2-Methylphenyl)ethyl]morpholine (23k)

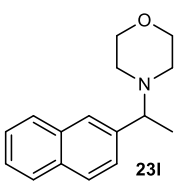
The title compound was prepared according to **GP1** using boronic ester **22k** (0.124 g, 0.505 mmol) and morpholine (0.153 g, 1.76 mmol), heating for 19 h. Flash column chromatography (69% hexane/30% EtOAc/1% Et_3N) of the crude material gave *amine* **23k** (87.7 mg, 85%) as a colourless oil.

IR 2958, 2852, 1454, 1261, 1116 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (1H, d, *J* = 7.5 Hz, Ar**H**), 7.21-7.14 (1H, m, Ar**H**), 7.12 (2H, d, *J* = 3.9 Hz, Ar**H**), 3.74-3.63 (4H, m, 2 × OC**H$_2$**), 3.53 (1H, q, *J* = 6.6 Hz, C**H**), 2.56-2.45 (2H, m, NC**H$_2$**), 2.42-2.36 (2H, m, NC**H$_2$**), 2.36 (3H, s, ArC**H$_3$**), 1.28 (3H, d, *J* = 6.6 Hz, CHC**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6 (C), 135.8 (C), 130.4 (CH), 126.8 (CH), 126.4 (CH), 126.0 (CH), 67.3 (2 × CH_2), 60.8 (CH), 51.3 (2 × CH_2), 19.5 (CH_3), 18.6 (CH_3).

HRMS (Q-TOF) Exact mass calcd for $[C_{13}H_{19}NO]^+$ $[M+H]^+$: 206.1539, found: 206.1549.

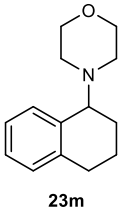


(±)-*N*-[1-(2-Naphthalenyl)ethyl]morpholine (23l)

The title compound was prepared according to **GP1** using boronic ester **22l** (0.142 g, 0.503 mmol) and morpholine (0.155 mg, 1.78 mmol), for 18 h. Flash column chromatography (69% hexane/30% EtOAc/1% Et_3N) of the crude material gave amine **23l** (86.3 mg, 71%) as a colourless oil. The data were consistent with the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.78 (3H, m, Ar**H**), 7.72 (1H, s, Ar**H**), 7.55-7.42 (3H, m, Ar**H**), 3.76-3.65 (4H, m, 2 × OC**H₂**), 3.46 (1H, q, *J* = 6.5 Hz, C**H**), 2.60-2.51 (2H, m, NC**H₂**), 2.45-2.35 (2H, m, NC**H₂**), 1.44 (3H, d, *J* = 6.5 Hz, C**H₃**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7 (C), 133.3 (C), 132.8 (C), 128.1 (CH), 127.7 (CH), 127.6 (CH), 126.2 (CH), 126.0 (CH), 125.8 (CH), 125.6 (CH), 67.2 (2 × CH_2), 65.6 (CH), 51.5 (2 × CH_2), 19.8 (CH_3).

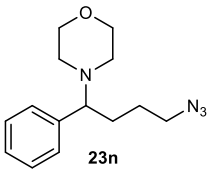


(±)-4-(1,2,3,4-Tetrahydro-1-naphthalenyl)morpholine (23m)

The title compound was prepared according to modification of **GP1** using boronic ester **22m** (0.134 g, 0.519 mmol) and morpholine (158 μL, 1.81 mmol), heating for 18 h. The crude was concentrated under vacuo, dissolved in EtOAc (5 mL) and extracted with aqueous HCl (1 M, 3 × 3 mL). The aqueous phases were combined, basified to pH > 10 with saturated aqueous Na_2CO_3, and extracted with EtOAc (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), and concentrated *in vacuo*. Flash column chromatography (90% hexane/ 10% Et_2O → 100% Et_2O) of the crude material gave amine **23m** (77.5 mg, 69%) as a colourless oil. The data were consistent with the literature.[32]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (1H, dd, J = 7.1, 1.3 Hz, Ar**H**), 7.23-7.11 (2H, m, Ar**H**), 7.11-7.05 (1H, m, Ar**H**), 3.86-3.67 (5H, m, C**H** and 2 × OC**H₂**), 2.89-2.69 (2H, m, ArC**H₂**), 2.69-2.59 (2H, m, 2 × NC**H$_A$**H$_B$), 2.56-2.45 (2H, m, 2 × NCH$_A$**H$_B$**), 2.08-1.91 (2H, m, CHC**H$_A$**H$_B$ and ArCH$_2$C**H$_A$**H$_B$), 1.82-1.63 (2H, m, CHCH$_A$**H$_B$** and ArCH$_2$CH$_A$**H$_B$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3 (C), 137.6 (C), 128.8 (CH), 128.1 (CH), 126.3 (CH), 125.6 (CH), 67.6 (2 × CH_2), 63.0 (CH), 48.9 (2 × CH_2), 29.6 (CH_2), 21.5 (CH_2), 21.5 (CH_2).



(±)-4-(4-Azido-1-phenylbutyl)morpholine (23n)

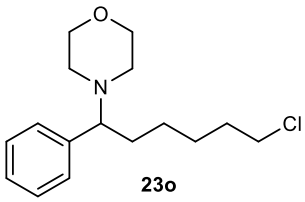
The title compound was prepared according to **GP1** using boronic ester **22n** (154 mg, 0.514 mmol) and morpholine (87.0 mg, 0.99 mmol), for 18 h. Flash column chromatography (69% hexane/30% EtOAc/1% Et_3N) of the crude material gave *amine* **23n** (94.9 mg, 71%) as a colourless oil.

IR 2954, 2853, 2092, 1450, 1731, 1116.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.19 (5H, m, Ar**H**), 3.68 (4H, t, *J* = 4.7 Hz, 2 × OC**H$_2$**), 3.26 (1H, dd, *J* = 8.9, 5.2 Hz, C**H**), 3.21 (2H, t, *J* = 6.8 Hz, C**H$_2$**N_3), 2.52-2.33 (4H, m, 2 × C**H$_2$**CH_2O), 2.06-1.94 (1H, m, CHC**H$_A$**H_b), 1.85-1.70 (1H, m, $CHCH_A$**H$_b$**), 1.55-1.31 (2H, m, C**H$_2$**CH_2N_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6 (C), 128.4 (2 × CH), 128.2 (2 × CH), 127.3 (CH), 69.9 (CH), 67.0 (2 × CH_2), 51.4 (CH_2), 50.9 (2 × CH_2), 29.4 (CH_2), 25.5 (CH_2).

HRMS (Q-TOF) Exact mass calcd for $[C_{14}H_{21}N_4O]^+$ $[M+H]^+$: 261.1715, found: 261.1722.



23o

(±)-*N*-(6-Chloro-1-phenylhexyl)morpholine (23o)

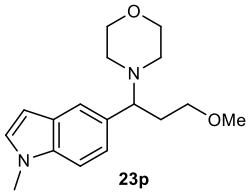
The title compound was prepared according to **GP1** using boronic ester **22o** (89.8 mg, 0.28 mmol) and morpholine (87.0 mg, 0.99 mmol), for 18 h. Flash column chromatography (69% hexane/30% EtOAc/1% Et_3N) of the crude material gave *amine* **23o** (31.5 mg, 40%, ~90% purity) as a colourless oil.

IR 2935, 2856, 1450, 1683, 1273, 1116.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (2H, m, Ar**H**), 7.28-7.21 (3H, m, Ar**H**), 3.72-3.65 (4H, m, 2 × OC**H$_2$**), 3.46 (2H, t, *J* = 6.7 Hz, C**H$_2$**Cl), 3.24-3.20 (1H, m, C**H**), 50-2.32 (4H, m, 2 × NC**H$_2$**), 1.96-1.87 (1H, m, C**H$_A$**CH_B), 1.76-1.64 (3H, m, CH_AC**H$_B$** and C**H$_2$**), 1.44-1.34 (2H, m, C**H$_2$**), 1.20-1.02 (2H, m, C**H$_2$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7 (C), 128.6 (2 × CH), 128.1 (2 × CH), 127.2 (CH), 70.5 (CH), 67.2 (2 × CH_2), 51.1 (2 × CH_2), 45.0 (CH_2), 32.4 (2 × CH_2), 26.9 (CH_2), 25.4 (CH_2).

HRMS (Q-TOF) Exact mass calcd for $[C_{16}H_{24}{}^{35}ClNO]^+$ $[M+H]^+$: 282.1619 found: 282.1631.



23p

(±)-3-[3-Methoxy-1-(moprholinyl)propyl]--1*H*-1-methyl-indole (23p)

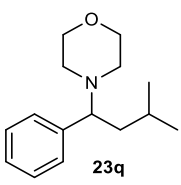
The title compound was prepared according to **GP1** using boronic ester **22p** (0.165 g, 0.501 mmol) and morpholine (155 μL, 1.75 mmol), heating for 18 h. Flash column chromatography (1: 95% CH_2Cl_2/5% MeOH; 2: 50% hexane/50% isopropanol) gave *amine* **23p** (80.1 mg, 55%) as a brown oil.

IR 2924 (CH), 1447, 1115 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (1H, s, Ar**H**), 7.28 (1H, d, *J* = 8.5 Hz, Ar**H**), 7.14 (1H, dd, *J* = 8.5, 1.3 Hz, Ar**H**), 7.05 (1H, d, *J* = 3.1 Hz, Ar**H**), 6.46 (1H, d, *J* = 3.1 Hz, Ar**H**), 3.79 (3H, s, NC**H$_3$**), 3.67 (4H, t, *J* = 4.7 Hz, (C**H$_2$**)$_2$O), 3.45 (1H, dd, *J* = 9.9, 4.9 Hz, NC**H**), 3.27-3.19 (4H, m, OC**H$_3$** and C**H$_a$**$H_B$$OCH_3$), 3.14 (1H, dt, *J* = 9.3, 7.3 Hz, CH_a**H$_B$**OCH_3), 2.57-2.44 (2H, m, 2 × NC**H$_A$**H_B), 2.44-2.36 (2H, m, 2 × NCH_A**H$_B$**), 2.36-2.26 (1H, m, CHC**H$_A$**CH_B), 2.03-1.89 (1H, m, $CHCH_A$**H$_B$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2 (C), 130.8 (C), 129.0 (CH), 128.2 (C), 122.2 (CH), 120.8 (CH), 108.9 (CH), 100.8 (CH), 70.3 (CH_2), 67.8 (CH), 67.3 (2 × CH_2), 58.6 (CH_3), 51.3 (2 × CH_2), 32.9 (CH_2), 32.9 (CH_3).

HRMS (Q-TOF) Exact mass calcd for $[C_{17}H_{25}N_2O_2]^+$ $[MH]^+$ calcd. 289.1922, found 289.1927.



(±)-4-(2-Phenylbutan-2-yl)morpholine (23q)

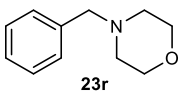
The title compound was prepared according to **GP1** using boronic ester **22q** (0.137 g, 0.501 mmol) and morpholine (153 mg, 1.76 mmol), for 18 h. Flash column chromatography (79% hexane/20% EtOAc/1% Et_3N) of the crude material gave *amine* **23q** (19.8 mg, 17%) as a colourless oil.

IR 2955, 2854, 1451, 1270, 1117 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (2H, m, Ar**H**), 7.27-7.19 (3H, m, Ar**H**), 3.71-3.59 (4H, m, 2 × OC**H₂**), 3.32 (1H, dd, *J* = 9.4, 5.6 Hz, ArC**H**), 2.48-2.39 (2H, m, NC**H₂**), 2.39-2.30 (2H, m, NC**H₂**), 1.77-1.62 (2H, m, CHC**H₂**), 1.32-1.25 (1H, m, C**H**CH_3), 0.86 (3H, d, *J* = 6.6 Hz, C**H₃**), 0.83 (3H, d, *J* = 6.6 Hz, C**H₃**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1 (C), 128.7 (2 × CH), 128.0 (2 × CH), 127.1 (CH), 68.5 (CH), 67.3 (2 × CH_2), 50.9 (2 × CH_2), 41.3 (CH_2), 25.0 (CH_3), 23.7 (CH), 21.9 (CH_3).

HRMS (Q-TOF) Exact mass calcd for $[C_{15}H_{24}NO]^+$ $[M+H]^+$: 234.1852 found: 234.1862.



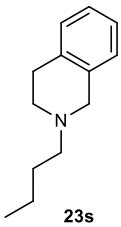
***N*-Benzylmorpholine (23r)**

The title compound was prepared according to **GP1** using boronic ester **22r** (0.109 g, 0.500 mmol) and morpholine (0.152 mg, 1.74 mmol), for 18 h. Flash column chromatography (99% hexane/1% Et_3N to 99% Et_2O/1% Et_3N) of the crude material gave amine **23r** (66.3 mg, 75%) as a colourless oil. The data were consistent with the literature.[23]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (4H, m, Ar**H**), 7.27-7.23 (1H, m, Ar**H**), 3.72-3.70 (4H, m, 2 × OC**H₂**), 3.50 (2H, s, ArC**H₂**), 2.46-2.43 (4H, m, 2 × NC**H₂**CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8 (C), 129.2 (2 × CH), 128.2 (2 × CH), 127.1 (CH), 67.0 (2 × CH_2), 63.5 (CH_2), 53.6 (2 × CH_2).

3.8. Scope of Reaction Using Aliphatic Boronic Esters



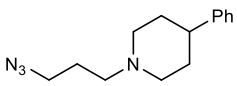
23s

2-Butyl-1,2,3,4-tetrahydroisoquinoline (23s)

The title compound was prepared according to **GP1** using *n*-butyl pinacol boronic ester (0.103 g, 0.560 mmol) and 1,2,3,4-tetrahydroisoquinoline (253 μL, 2.02 mmol), heating for 18 h. Flash column chromatography (70% hexane/ 29% EtOAc/ 1% Et_3N) of the material gave amine **23s** (36.6 mg, 35%) as an orange oil. The data were consistent with the literature.[33]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.06 (3H, m, Ar**H**), 7.05-6.98 (1H, m, Ar**H**), 3.63 (2H, s, NC**H$_2$**Ar), 2.92 (2H, t, *J* = 5.9 Hz, NC**H$_2$**CH_2Ar), 2.74 (2H, t, *J* = 5.9 Hz, ArC**H$_2$**CH_2), 2.55-2.46 (2H, m, NC**H$_2$**CH_2CH_2), 1.65-1.54 (2H, m, **CH$_2$**CH_2CH_3), 1.46-1.32 (2H, m, C**H$_2$**CH_3), 0.96 (3H, t, *J* = 7.3 Hz, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9 (C), 134.3 (C), 128.6 (CH), 126.6 (CH), 126.0 (CH), 125.5 (CH), 58.3 (CH_2), 56.2 (CH_2), 51.0 (CH_2), 29.3 (CH_2), 29.21(CH_2), 20.8 (CH_2), 14.1 (CH_3).



23t

1-(3-Azidopropyl)-4-phenylpiperidine (23t)

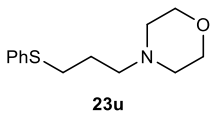
The title compound was prepared according to **GP1** using boronic ester **22t** (0.106 g, 0.502 mmol) and 4-phenylpiperidine (0.282 g, 1.75 mmol), heating for 18 h. Flash column chromatography (59% hexane/40% Et_2O/1% Et_3N) of the material gave *amine* **23t** (74.8 mg, 61%) as a colourless oil.

IR 2932, 2093, 1452, 1253, 1131 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (2H, dd, *J* = 8.0, 7.7 Hz, Ar**H**), 7.23 (2H, d, *J* = 7.7 Hz, Ar**H**), 7.21 (1H, t, *J* = 8.0 Hz, Ar**H**), 3.38 (2H, t, *J* = 6.7 Hz, C**H$_2$**N_3), 3.08 (2H, d, *J* = 11.9 Hz, 2 × NC**H$_A$**$H_B$$CH_2$CH), 2.56-2.48 (3H, m, NC**H$_2$**CH_2CH_2 + C**H**), 2.15-2.09 (2H, m, C**H$_2$**CH_2N_3), 1.89-1.82 (6H, m, NCH_A**H$_B$**CH_2CH + 2 × C**H$_2$**CH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1 (C), 128.4 (2 × CH), 126.8 (2 × CH), 126.2 (CH), 55.7 (CH_2), 54.3 (2 × CH_2), 49.7 (2 × CH_2), 42.6 (CH), 33.3 (CH_2), 26.4 (CH_2).

HRMS (Q-TOF) Exact mass calcd for $C_{14}H_{21}N_4]^+$ $[M+H]^+$: 245.1761 found: 245.1764.



23u

4-[3-(Phenylsulfanyl)propyl]morpholine (23u)

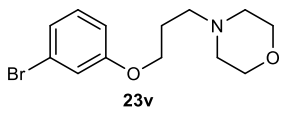
The title compound was prepared according to **GP1** using boronic ester **22u** (0.139 g, 0.500 mmol) and morpholine (0.152 g, 1.74 mmol), heating for 18 h. Flash column chromatography (99% hexane/1% Et_3N → 49.5% hexane/49.5% Et_2O/1% Et_3N) of the material gave *amine* **23u** (72.5 mg, 61%) as a colourless oil.

IR 2853, 1584, 1439, 1259, 1116 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (2H, d, *J* = 8.1 Hz, Ar**H**), 7.27 (1H, dd, *J* = 8.1, 7.2 Hz, Ar**H**), 7.17 (1H, t, *J* = 7.2 Hz, Ar**H**), 3.71 (4H, t, *J* = 4.6 Hz, OC**H**$_2$), 2.97 (2H, t, *J* = 7.2 Hz, SC**H**$_2$), 2.58-2.25 (6H, m, $CH_2CH_2C\mathbf{H}_2N$ + 2 × $OCH_2C\mathbf{H}_2N$), 1.83 (2H, p, *J* = 7.2 Hz, $SCH_2C\mathbf{H}_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5 (C), 129.1 (2 × CH), 128.9 (2 × CH), 125.9 (CH), 66.9 (CH_2), 57.5 (CH_2), 53.6 (2 × CH_2), 31.4 (2 × CH_2), 26.0 (CH_2).

HRMS (Q-TOF) Exact mass calcd for $[C_{13}H_{20}NOS]^+$ $[M+H]^+$: 238.1260 found: 238.1268.



23v

4-[3-(3-Bromophenoxy)propyl]morpholine (23v)

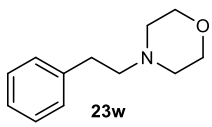
The title compound was prepared according to **GP1** using boronic ester **22v** (0.169 g, 0.496 mmol) and morpholine (0.152 g, 1.74 mmol), heating for 18 h. Flash column chromatography (40% EtOAc/59% hexane/1% Et_3N) of the material gave *amine* **23v** (96.6 mg, 65%) as a pale yellow oil.

IR 2954, 2810, 1588, 1467, 1229, 1116, 860 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.09 (1H, m, Ar**H**), 7.09-7.02 (2H, m, Ar**H**), 6.86-6.78 (1H, m, Ar**H**), 4.00 (2H, t, *J* = 6.3 Hz, ArOC**H**$_2$), 3.72 (4H, t, *J* = 4.6, Hz, OC**H**$_2$$CH_2N$), 2.50 (2H t, *J* = 7.2, Hz, $CH_2CH_2C\mathbf{H}_2N$), 2.48-2.44 (4H, m, $OCH_2C\mathbf{H}_2N$), 1.95 (2H, tt, *J* = 7.2, 6.3 Hz, $ArOCH_2C\mathbf{H}_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (C), 130.5 (CH), 123.7 (CH), 122.8 (C), 117.7 (CH), 113.6 (CH), 67.0 (2 × CH_2), 66.3 (CH_2), 55.4 (CH_2), 53.7 (2 × CH_2), 26.3 (CH_2).

HRMS (Q-TOF) Exact mass calcd for $[C_{13}H_{19}{}^{79}BrNO_2]^+$ $[M+H]^+$: 300.0594 found: 300.0599.



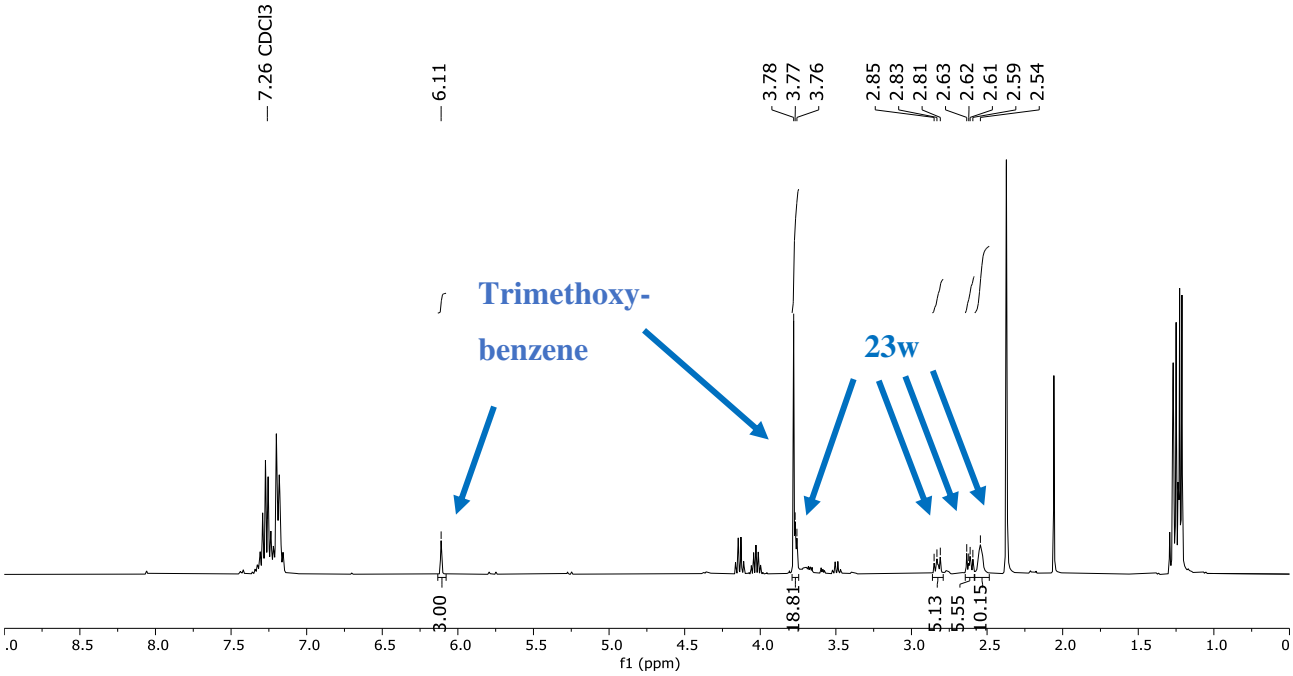
23w

4-(2-Phenylethyl)morpholine (23w)

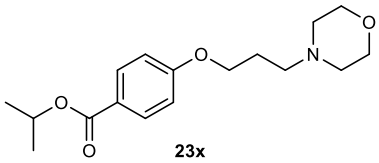
The title compound was prepared using a modification of **GP1** using 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (0.117 g, 0.503 mmol) and morpholine (0.16 mL, 1.8 mmol), heating for 18 h. The mixture was filtered through a silica plug, eluting with EtOAc (10 mL). 1,3,5-Trimethoxybenzene (21.1 mg, 0.125 mmol) was added to the filtrate, and the mixture was concentrated *in vacuo*. The mixture was analysed by ^{1}H NMR, which indicated amine **23w** was formed in 72% yield (average of two reactions). The data matched the literature.[34]

Characteristic peaks for **23w**.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77-3.75 (4H, m, 2 × OC**H**$_2$), 2.86-2.80 (2H, m, NC**H**$_2$), 2.64-2.58 (2H, m, PhC**H**$_2$), 2.54 (4H, s, 2 × NC**H**$_2$).



HRMS (Q-TOF) Exact mass calcd for $[C_{12}H_{18}NO]^+$ $[M+H]^+$: 192.1383 found: 192.1388.



Propan-2-yl 4-(3-morpholin-4-ylpropoxy)benzoate (23x)

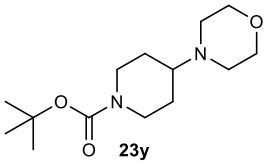
The title compound was prepared according to **GP1** using boronic ester **22x** (0.174 g, 0.500 mmol) and morpholine (0.16 mL, 1.8 mmol), heating for 18 h. Flash column chromatography (1: 100% EtOAc, 2: 2% EtOH/98% CH_2Cl_2) of the material gave *amine* **23x** (86.0 mg, 56%) as a pale yellow oil.

IR 2956, 2854, 1705, 1605, 1251, 1099, 771 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (2H, m, Ar**H**), 6.93 – 6.87 (2H, m, Ar**H**), 5.22 (1H, hept, *J* = 6.3 Hz, C**H**), 4.08 (2H t, *J* = 6.3 Hz, ArOC**H₂**), 3.77 – 3.69 (4H, m, 2 × OC**H₂**CH_2N), 2.58 – 2.41 (6H, m, 3 × NC**H₂**), 1.99 (1H, tt, *J* = 6.4, 6.3 Hz, ArOCH_2C**H₂**), 1.35 (6H, d, *J* = 6.3 Hz, 2 × C**H₃**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C), 162.6 (C), 131.5 (2 × CH), 123.3 (C), 113.9 (2 × CH), 67.9 (CH), 67.0 (2 × CH_2), 66.2 (CH_2), 55.4 (CH_2), 53.7 (2 × CH_2), 26.3 (CH_2), 22.0 (2 × CH_3).

HRMS (Q-TOF) Exact mass calcd for $[C_{17}H_{26}NO_4]^+$ $[M+H]^+$: 308.1866 found: 308.1856.

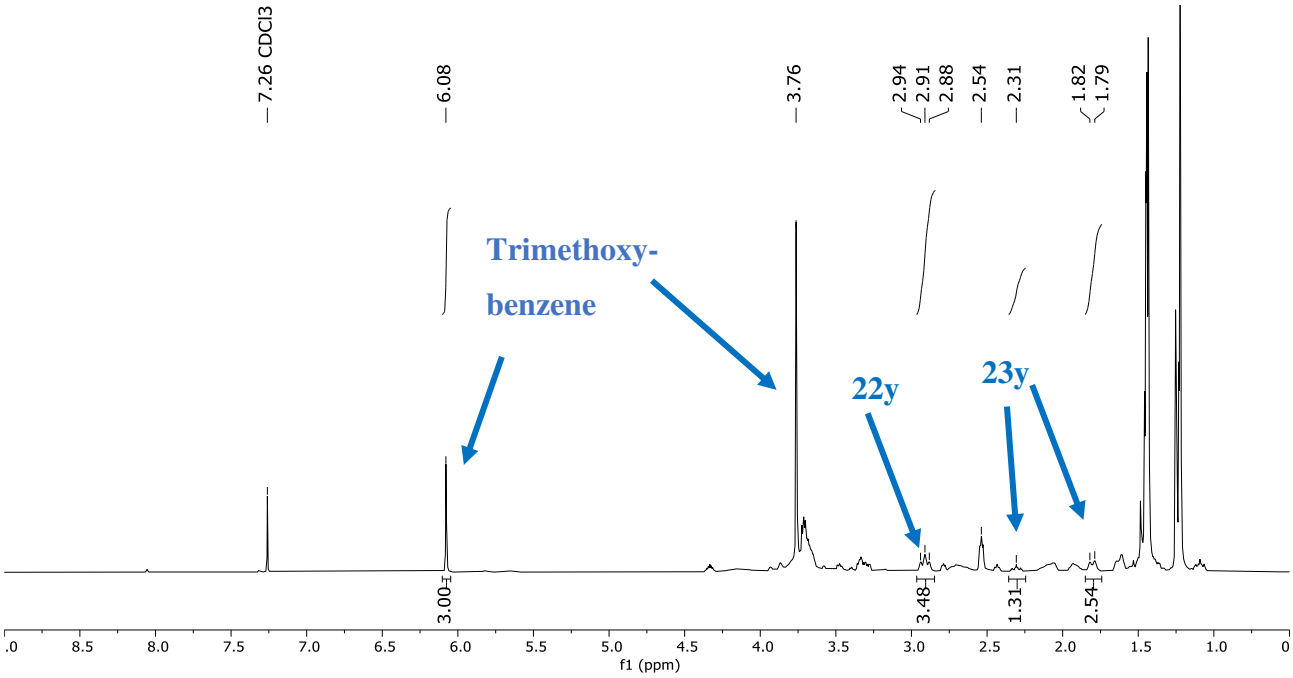


tert-Butyl 4-morpholinopiperidine-1-carboxylate (23y)

The title compound was prepared using a modification of **GP1** using *N*-Boc-piperidine-4-boronic acid pinacol ester **22y** (0.156 g, 0.503 mmol) and morpholine (0.16 mL, 1.8 mmol), heating for 18 h. The mixture was filtered through a silica plug, eluting with EtOAc (10 mL). 1,3,5-Trimethoxybenzene (18.9 mg, 0.112 mmol) was added to the filtrate, and the mixture was concentrated *in vacuo*. The mixture was analysed by ^{1}H NMR, which indicated amine **23y** was formed in 29% yield (average of two reactions). The data matched the literature.[35]

Characteristic peaks for **10y**.

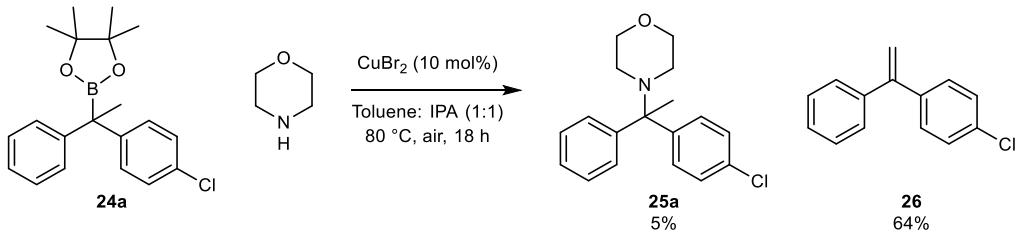
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36-2.25 (1H, m, C**H**), 1.80 (2H, d, *J* = 13.0 Hz, C**H$_2$**).



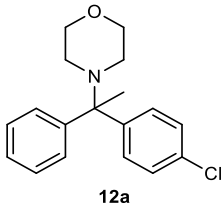
HRMS (Q-TOF) Exact mass calcd for $[C_{14}H_{27}N_2O_3]^+$ $[M+H]^+$: 271.2016 found: 271.2020.

3.9. Coupling of Tertiary Boronic Esters

4-[1-(4-Chlorophenyl)-1-phenylethyl]morpholine (25a)



The title compounds were prepared according to **GP1** using boronic ester **23a** (0.171 g, 0.502 mmol) and morpholine (0.153 g, 1.76 mmol). Flash chromatography (89% hexane/10% EtOAc/1% Et_3N) of the crude material gave and *amine* **25a** (8.0 mg, 5%) as a colourless oil and alkene **26** (68.5 mg, 64%) as a colourless oil.



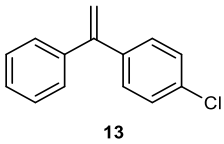
4-[1-(4-Chlorophenyl)-1-phenylethyl]morpholine (25a)

IR 2958, 2851, 1488, 1267, 1114 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.39 (4H, m, Ar**H**), 7.31-7.21 (4H, m, Ar**H**), 7.21-7.14 (1H, m, Ar**H**), 3.81-3.67 (4H, m, 2 × OC**H$_2$**), 2.47-2.32 (4H, m, 2 × NC**H$_2$**), 1.76 (3H, s, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8 (C), 144.2 (C), 132.0 (C), 128.9 (2 × CH), 128.1 (4 × CH), 127.4 (2 × CH), 126.5 (CH), 67.7 (2 × CH_2), 66.4 (C), 47.7 (2 × CH_2), 18.9 (CH_3).

HRMS (Q-TOF) Exact mass calcd for $[C_{18}H_{20}{}^{35}ClNO]^+$ $[M]^+$: 301.1228 found: 301.1220.


13

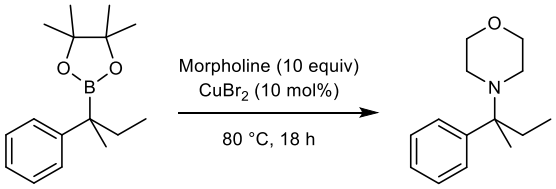
1-(4-Chlorophenyl)-1-phenylethylene (26)

The data were consistent with the literature.[36]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (9H, m, Ar**H**), 5.48-5.44 (2H, m, C**H$_2$**)

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0 (C), 141.0 (C), 139.9 (C), 133.6 (C), 129.5 (2 × CH), 128.3 (2 × CH), 128.3 (2 × CH), 128.2 (2 × CH), 127.9 (CH), 114.7 (CH_2).

(±)-4-(3-Methyl-1-phenylbutyl)morpholine (25b)



24b 25b 11%

Morpholine (0.218 g, 2.5 mmol) was added to a flask containing boronic ester **24b** (0.065 g, 0.25 mmol) and $CuBr_2$ (5.6 mg, 0.025 mmol), and the mixture was stirred under air at 80 °C for 18 h. The mixture was cooled to room temperature, passed through a plug of silica eluting with Et_2O, and concentrated *in vacuo*. Flash chromatography (89% hexane/10% EtOAc/1% Et_3N) of the crude material gave and *amine* **25b** (5.8 mg, 11%) as a colourless oil.

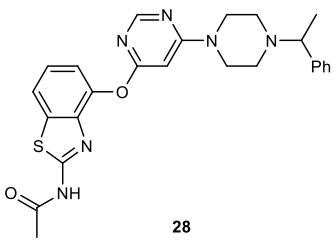
IR 2966, 2851, 1493, 1446, 1273, 1118 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.44 (2H, m, Ar**H**), 7.33-7.27 (2H, m, Ar**H**), 7.22-7.17 (1H, m, Ar**H**), 3.74-3.63 (4H, m, 2 × OC**H$_2$**), 2.59-2.50 (2H, m, 2 × NC**H$_A$**H$_B$), 2.43-2.36 (2H, m, 2 × NCH$_A$**H$_B$**), 1.81-1.71 (1H, m, CC**H$_A$**H$_B$), 1.66-1.56 (1H, m, CCH$_A$**H$_B$**), 1.33 (3H, s, CC**H$_3$**), 0.57 (3H, t, J = 7.4 Hz, CH_2C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8 (C), 127.7 (2 × CH), 127.3 (2 × CH), 126.1 (CH), 67.9 (2 × CH_2), 62.8 (C), 46.8 (2 × CH_2), 33.8 (CH_2), 15.7 (CH_3), 8.7 (CH_3).

HRMS (Q-TOF) Exact mass calcd for $[C_{14}H_{22}NO]^+$ $[M+H]^+$: 220.1696 found: 220.1703.

3.10. Synthesis of a TRVP1 Inhibitor


28

(±)-*N*-[5-[6-[4-(1-Phenylethyl)piperazin-1-yl]pyrimidin-4-yl]oxy-1,3-benzothiazol-2-yl]acetamide (28)

The title compound was prepared using a modification of the **GP1** using boronic ester **1** (0.117 g, 0.504 mmol), $CuBr_2$ (22.6 mg, 0.100 mmol) and amine **27** (0.324 g, 1.75 mmol) in DMSO (0.75 mL) heating for 18 h. The mixture was diluted in CH_2Cl_2, filtered, and the filtrate concentrated *in vacuo*. Flash column

chromatography (100% EtOAc) of the crude material gave amine **28** (88.4 mg, 37%) as an off-white solid. The data were consistent with the literature.[4]

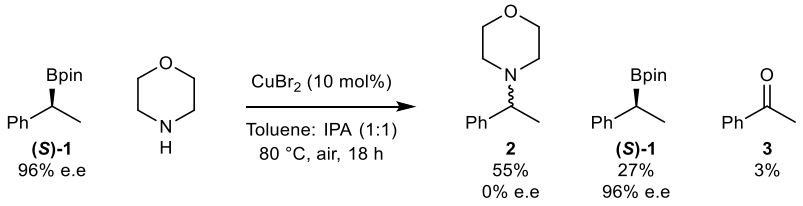
m.p. 175-178 °C (DMSO). Literature 132-135 °C (Not reported).[4]

^{1}H NMR (400 MHz, DMSO-d^6) δ 12.41 (1H, br s, N**H**), 8.05 (1H, s, Ar**H**), 7.84 (1H, dd, *J* = 7.9, 1.1 Hz, Ar**H**), 7.36-7.23 (6H, m, Ar**H**), 7.18 (1H, d, *J* = 7.9, 1.1 Hz, Ar**H**), 6.31 (1H, s, Ar**H**), 3.59-3.56 (4H, m, 2 × ArNC**H$_2$**), 3.45 (1H, q, *J* = 6.7 Hz, C**H**CH$_3$), 2.49-2.43 (2H, m, 2 × CHNC**H$_A$**H$_B$), 2.38-2.32 (2H, m, 2 × CHNCH$_A$**H$_B$**), 2.15 (3H, s, COC**H$_3$**), 1.32 (3H, d, *J* = 6.7 Hz, CHC**H$_3$**).

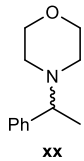
^{13}C NMR (101 MHz, DMSO-d^6) δ 169.9 (C), 169.5 (C), 163.6 (C), 158.0 (C), 157.3 (CH), 144.2 (C), 143.1 (C), 141.8 (C), 133.4 (C), 128.2 (2 × CH), 127.5 (2 × CH), 127.0 (CH), 124.0 (CH), 119.2 (CH), 118.9 (CH), 85.7 (CH), 63.7 (CH), 49.5 (2 × CH$_2$), 43.9 (2 × CH$_2$), 22.6 (CH$_3$), 19.3 (CH$_3$).

3.11. Mechanistic Studies

Reaction With Enantiomerically Enriched Boronic Ester



IPA (0.38 mL) and toluene (0.38 mL) were added to a flask containing boronic ester **(*S*)-1** (0.117 g, 0.503 mmol), morpholine (0.155 µl, 1.75 mmol) and $CuBr_2$ (11.3 mg, 0.05 mmol), and the mixture was stirred under air at 80 °C for 1.5 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 column chromatography (5% EtOAc/95% hexane then 1% Et_3N/30% EtOAc/69% hexane) to give amine **2** (53.2 mg, 55%), boronic ester **1** (31 mg, 27%), and acetophenone (2.0 mg, 3%).

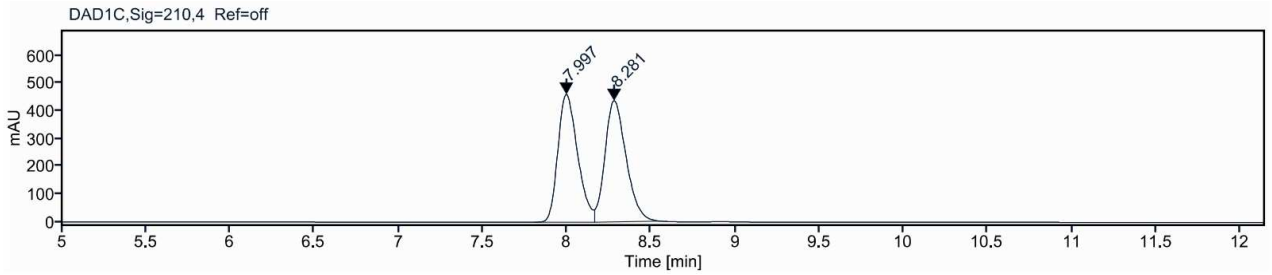


(±)-*N*-(1-Phenylethyl)morpholine (2).

See above for data.

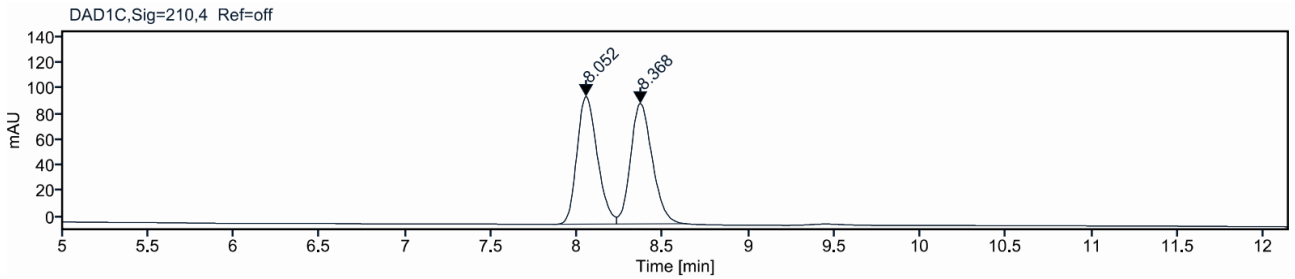
e.r. = 50:50, Chiralpak ID column (250 × 4.6 mm), IPA:hexane = 1:99, 0.7 mL/min, column temperature = 22 °C, t_r = 8.1 min and t_r = 8.4 min.

Racemate

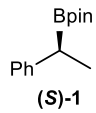


RT [min]	Type	Width [min]	Area	Height	Area%
7.997	BM m	0.1270	3765.7788	462.3245	49.5545
8.281	MM m	0.1339	3833.4956	438.8471	50.4455
	Sum		7599.2744		

Reaction:



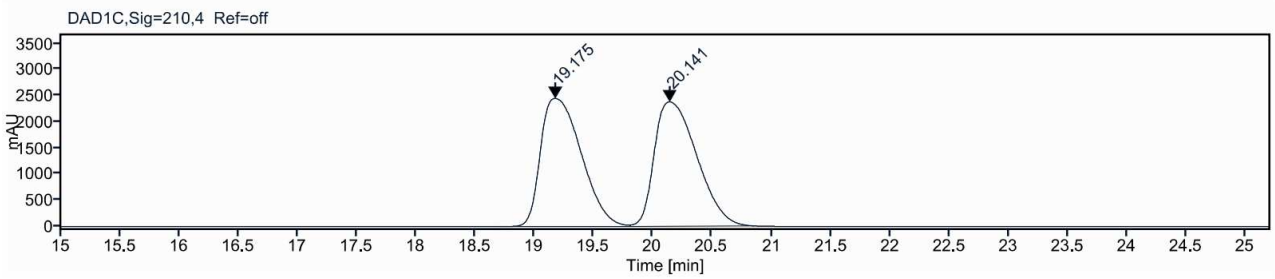
RT [min]	Type	Width [min]	Area	Height	Area%
8.052	MM m	0.1281	822.2641	99.8313	49.7669
8.368	MM m	0.1369	829.9678	94.1140	50.2331
	Sum		1652.2318		



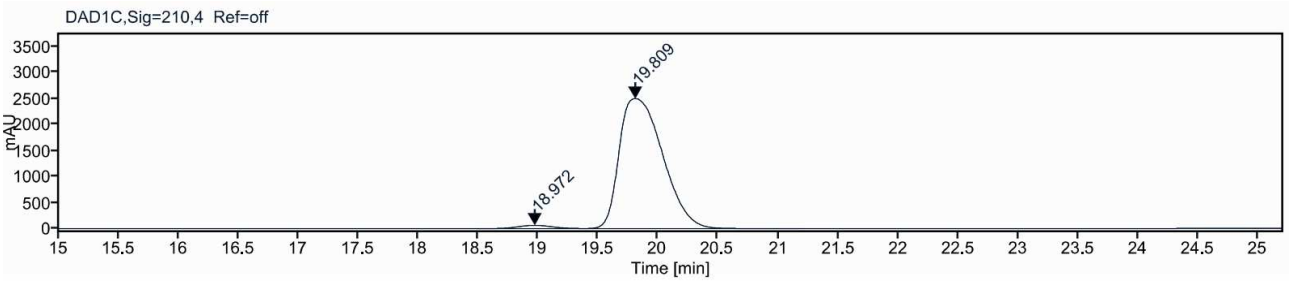
(*S*)-4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane ((*S*)-1)

See above for data.

e.r. = 2:98, measured through chiral HPLC analysis of the corresponding alcohol obtained after oxidation. Chiralpak ID column (250 × 4.6 mm), IPA:hexane = 1:99, 0.7 mL/min, column temperature = 22 °C, (*R*)- isomer t_r = 19.0 min and (*S*)-isomer t_r = 19.8 min.

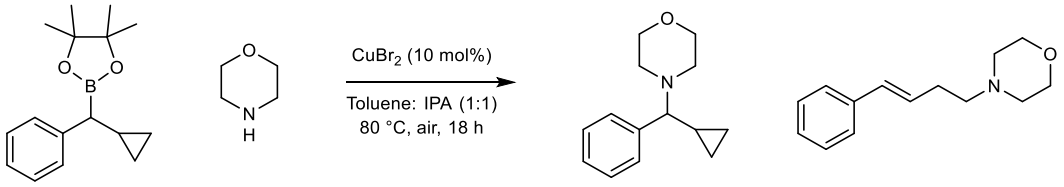


RT [min]	Type	Width [min]	Area	Height	Area%
19.175	MM m	0.3804	58438.0569	2449.1135	49.6661
20.141	MM m	0.3945	59223.8120	2378.5002	50.3339
		Sum	117661.8689		



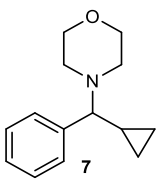
RT [min]	Type	Width [min]	Area	Height	Area%
18.972	MM m	0.3057	1260.7191	64.0195	1.9641
19.809	MB m	0.3995	62926.0405	2501.1997	98.0359
		Sum	64186.7596		

(±)-*N*-[Cyclopropyl(phenyl)methyl]morpholine (6) and (±)-*N*-[(3*E*)-4-Phenylbut-3-en-1-yl]morpholine (8)



6 | **7** 36% | **8** 37%

The title compounds were prepared according to **GP1** using boronic ester **6** (0.129 g, 0.501 mmol) and morpholine (0.154 mg, 1.78 mmol), heating for 18 h. Flash column chromatography (69% hexane/30% EtOAc/1% Et_3N) of the crude material gave *amine* **7** (39.6 mg, 36%, ~94% purity) as a colourless oil and *amine* **8** (40.3 mg, 37%) as a pale yellow oil.



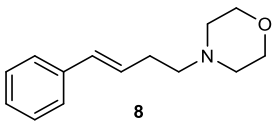
(±)-*N*-[Cyclopropyl(phenyl)methyl]morpholine (7)

IR 2959, 2804, 1451, 1278, 1117 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (4H, m, Ar**H**), 7.27-7.22 (1H, m, Ar**H**), 3.77-3.63 (4H, m, 2 × OC**H$_2$**), 2.81-2.64 (2H, m, NC**H$_2$**), 2.41-2.30 (2H, m, NC**H$_2$**), 2.23 (1H, d, *J* = 9.2 Hz, NC**H**), 1.09-0.94 (1H, m, C**H**CH$_2$), 0.80-0.70 (1H, m, CHC**H$_A$**H$_B$), 0.47-0.39 (1H. m, CHCH$_A$**H$_B$**), 0.39-0.30 (1H, m, CHC**H$_C$**H$_D$), 0.06-−0.03 (1H, m, CHCH$_C$**H$_D$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3 (C), 128.2 (2 × CH), 127.9 (2 × CH), 126.9 (CH), 76.6 (CH), 67.2 (2 × CH_2), 52.4 (2 × CH_2), 15.5 (CH), 8.6 (CH_2), 2.00 (CH_2).

HRMS (Q-TOF) Exact mass calcd for $[C_{14}H_{20}NO]^+$ $[M+H]^+$: 218.1539 found: 218.1549.



***N*-[(3*E*)-4-Phenylbut-3-en-1-yl]morpholine (8)**

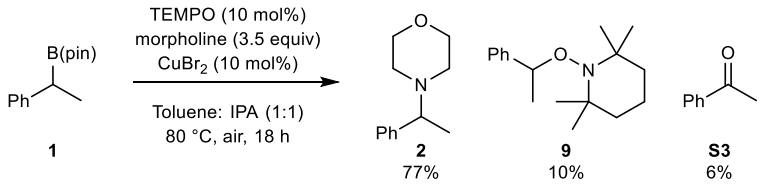
IR 2956, 2854, 2806, 1698, 1447, 1271, 1116 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (4H, m, Ar**H**), 7.24-7.18 (1H, m, Ar**H**), 6.45 (1H, d, *J* = 15.9 Hz, C**H**), 6.22 (1H, dt, *J* = 15.9, 6.1 Hz, C**H**CH$_2$), 3.79-3.71 (4H, m, 2 × OC**H$_2$**), 2.59-2.48 (6H, m, 3 × NC**H$_2$**), 2.47-2.39 (2H, m, C=CC**H$_2$**).

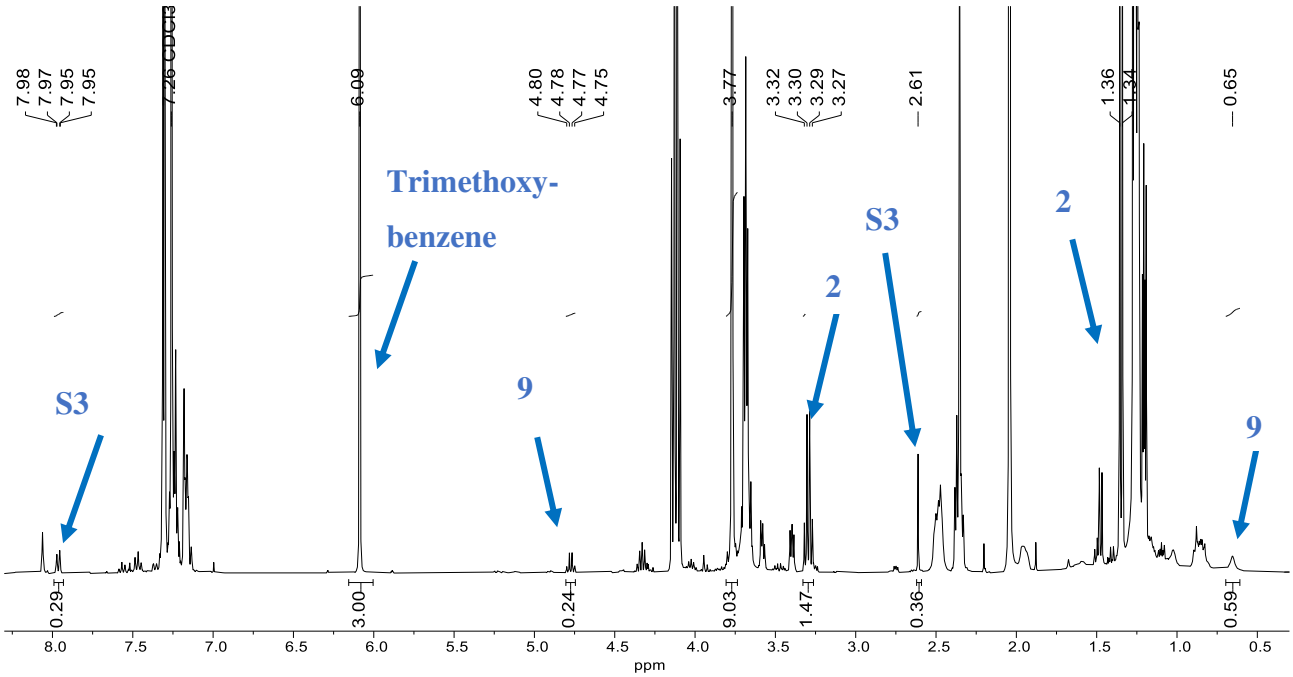
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5 (C), 131.1 (CH), 128.5 (2 × CH), 128.0 (CH), 127.0 (CH), 126.0 (2 × CH), 66.9 (2 × CH_2), 58.6 (CH_2), 53.6 (2 × CH_2), 30.3 (CH_2).

HRMS (Q-TOF) Exact mass calcd for $[C_{14}H_{20}NO]^+$ $[M+H]^+$: 218.1539 found: 218.1541.

Trapping Experiments with TEMPO



Using a modification of **GP1** using boronic ester **1** (0.116 g, 0.500 mmol) and morpholine (0.15 mL) and TEMPO (7.8 mg, 0.050 mmol), the mixture was heated at 80 °C for 18 h, cooled to RT and filtered through Celite eluting with EtOAc. The filtrate was concentrated and analysed by ^{1}H NMR using 1,3,5-trimethoxybenzene (0.0441 g, 0.26 mmol) as an internal standard.



Characteristic peaks for (±)-*N*-(1-Phenylethyl)morpholine (**2**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (q, *J* = 6.7 Hz, 1H), 1.35 (d, *J* = 6.7 Hz, 3H). See earlier for full characterisation data.

Characteristic peaks for 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine (**9**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (q, *J* = 6.7 Hz, 1H), 0.66 (s, 3H).

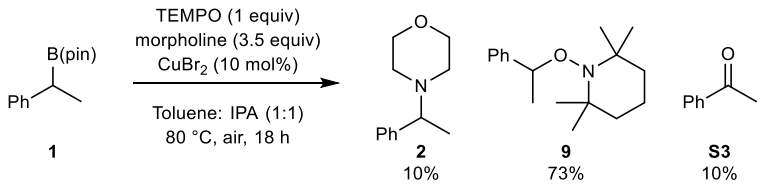
HRMS (Q-TOF) Exact mass calcd for $[C_{17}H_{28}NO]^+$ $[M+H]^+$: 262.2171 found: 262.2167.

The data was consistent with the literature.[37]

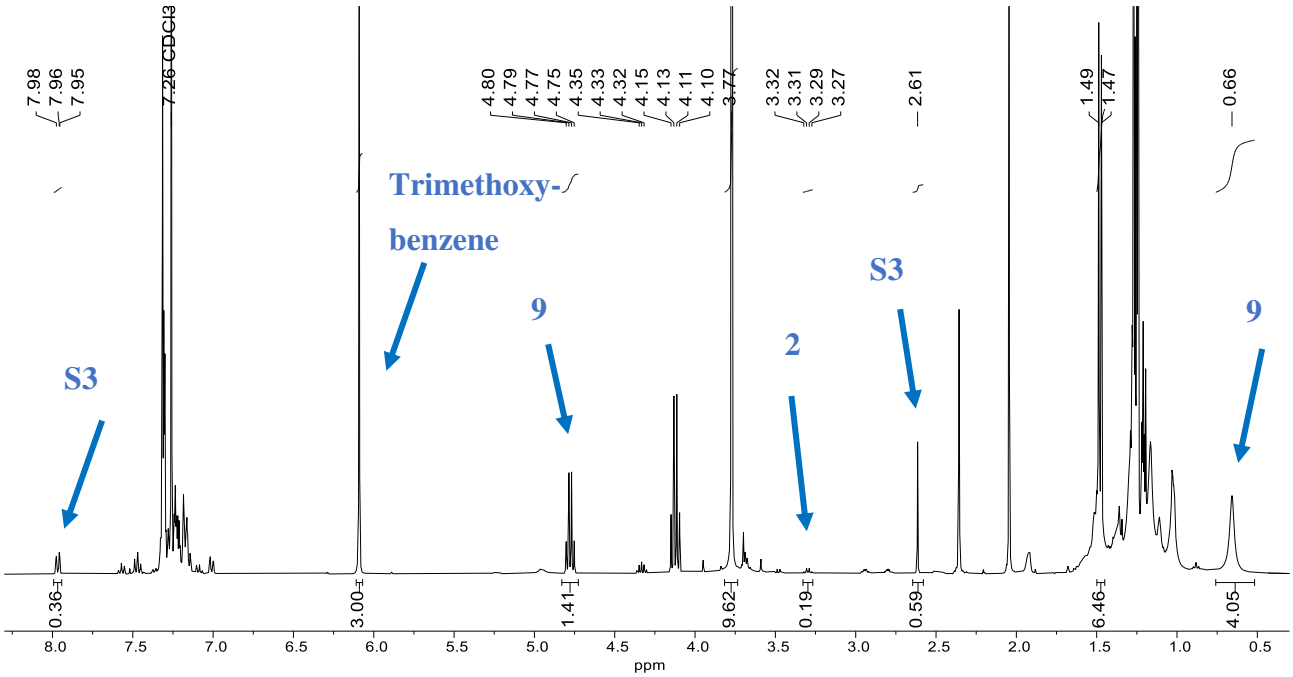
Characteric peaks for acetophenone (**S3**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.94 (m, 2H), 2.61 (s, 3H).

The data was consistent with the literature.[1]



Using a modification of **GP1** using boronic ester **1** (0.116 g, 0.500 mmol) and morpholine (0.15 mL) and TEMPO (7.8 mg, 0.050 mmol), the mixture was heated at 80 °C for 18 h, cooled to RT and filtered through Celite eluting with EtOAc. The filtrate was concentrated and analysed by ^{1}H NMR using 1,3,5-trimethoxybenzene (0.0441 g, 0.26 mmol) as an internal standard.



Characteristic peaks for (±)-*N*-(1-Phenylethyl)morpholine (**2**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.30 (q, *J* = 6.7 Hz, 1H). See earlier for full characterisation data.

Characteristic peaks for 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine (**9**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (q, *J* = 6.7 Hz, 1H), 0.66 (s, 3H).

HRMS (Q-TOF) Exact mass calcd for $[C_{17}H_{28}NO]^+$ $[M+H]^+$: 262.2171 found: 262.2170.

The data was consistent with the literature.[37]

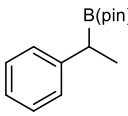
Characteric peaks for acetophenone (**S3**):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.94 (m, 2H), 2.61 (s, 3H).

The data was consistent with the literature.[1]

NMR studies: Boronic ester 1 in the presence of morpholine

An NMR tube was charged with **1** (34.8 g, 0.150 mmol) dissolved in CD_3CN (0.7 mL) and ^{1}H NMR and ^{11}B NMR spectra were recorded. Morpholine (53 µL, 0.60 mmol) was added by microsyringe and ^{1}H NMR and ^{11}B NMR spectra were recorded after homogenization.



1

^{1}H NMR (400 MHz, CD_3CN) δ 7.29-7.10 (5H, m, Ar**H**), 2.38 (1H, q, *J* = 7.6 Hz, C**H**), 1.27 (3H, d, *J* = 7.6 Hz, CHC**H$_3$**), 1.19 (6H, s, 2 × CC**H$_3$**), 1.18 (6H, s, 2 × CC**H$_3$**).

^{11}B NMR (128 MHz, CD_3CN) δ 33.6.

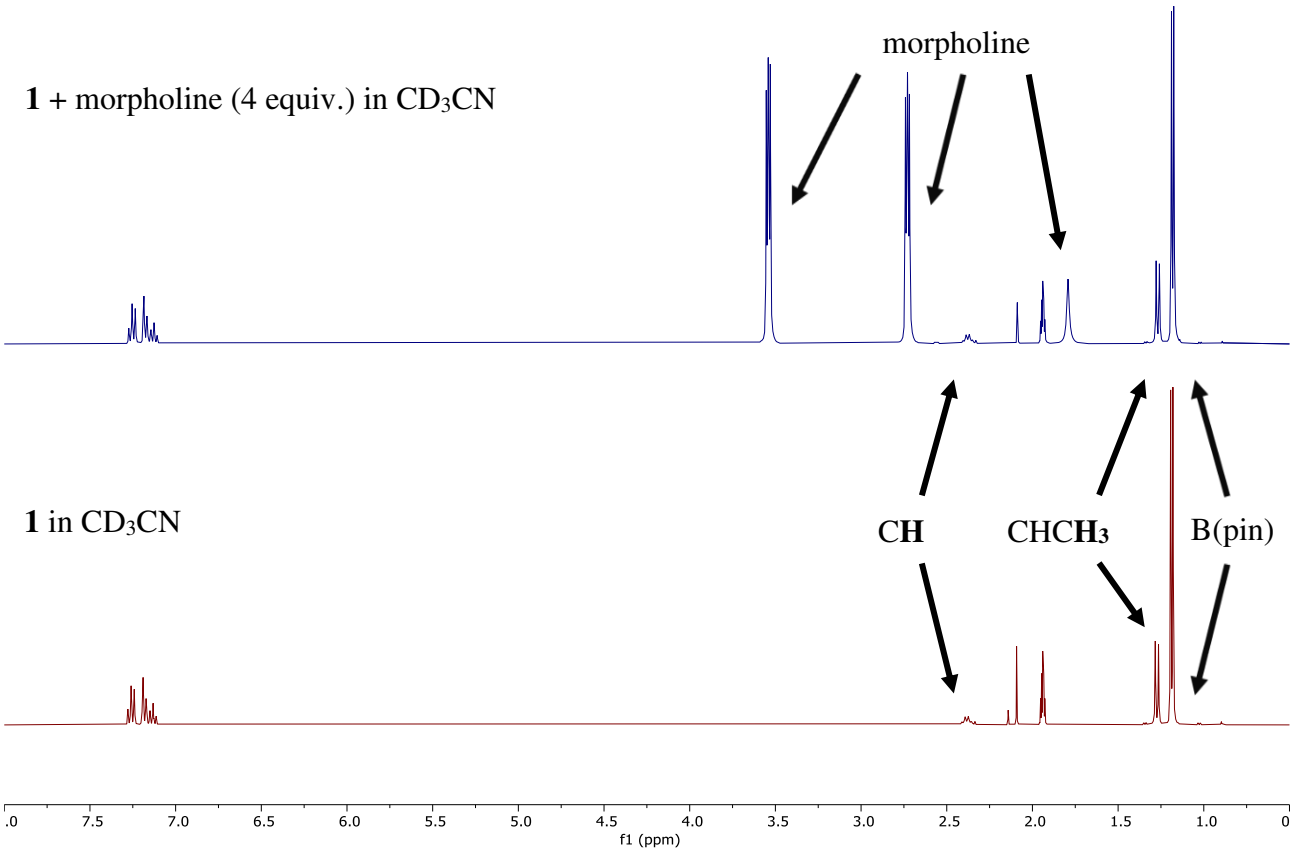


Figure S1: ^{1}H NMR spectra of boronic ester **1** in CD_3CN the absence and presence of morpholine.

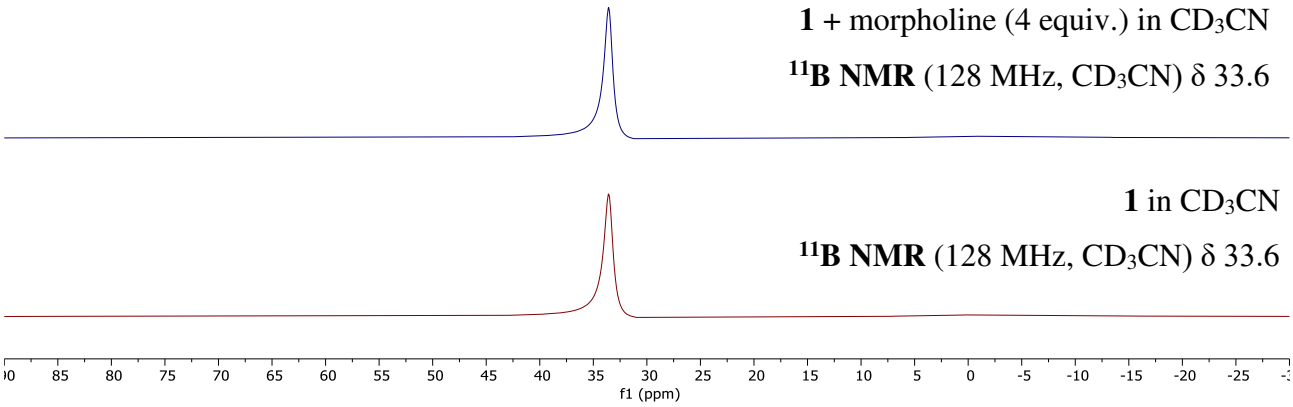


Figure S2: ^{11}B NMR spectra of boronic ester **1** in CD_3CN in the absence and presence of morpholine.

NMR studies: Boronic ester 1 in the presence of IPA and morpholine

An NMR tube was charged with a solution of boronicester **1** (0.023 g, 0.10 mmol) in 0.5 mL CD_3CN and an ^{11}B NMR spectrum was recorded. Isopropanol (0.5 mL) was added, and an ^{11}B NMR spectrum was recorded after homogenization. Morpholine (44 µL, 0.50 mmol,) was added, and an ^{11}B NMR spectrum was recorded after homogenization.

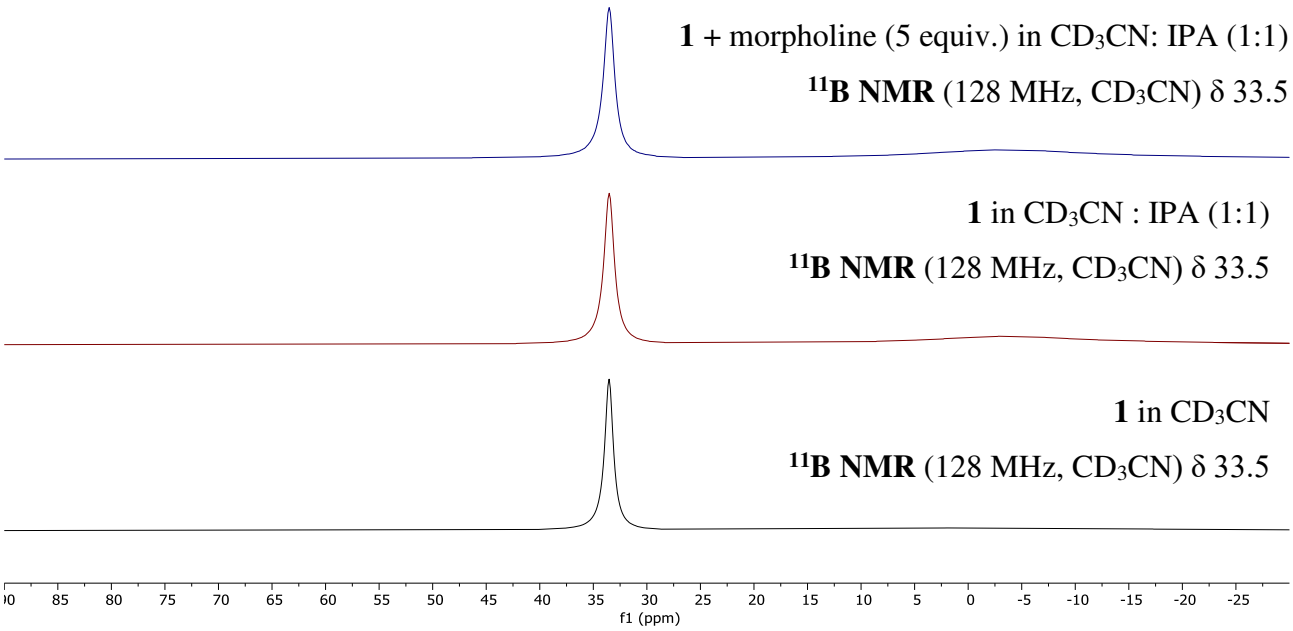


Figure S3: ^{11}B NMR spectra of **1** in in CD_3CN in the absence and presence of IPA, and IPA and morpholine.

Cyclic Voltametry Studies

All cyclic voltammetric measurements were performed at room temperature, using an Autolab® PGSTAT100 potentiostat in a conventional three-electrode cell configuration with a glassy carbon (GC) as working electrode (3 mm diameter), a platinum electrode (2 mm diameter) as counter electrode and Ag/AgCl (KCl 3M) as reference. The cell was purged with N_2 for 10 min before each measurement, and the GC working electrode was polished with alumina before each experiment. Redox potentials were calculated against the Fc^+/Fc^0 couple as an internal reference. (Ferrocene was added in the last experiment of a series, or separately just after an experiment. It was considered that in this period of time, the reference electrode's composition would not change and would be kept constant.) All the experiments were carried out at 100 mV/s.

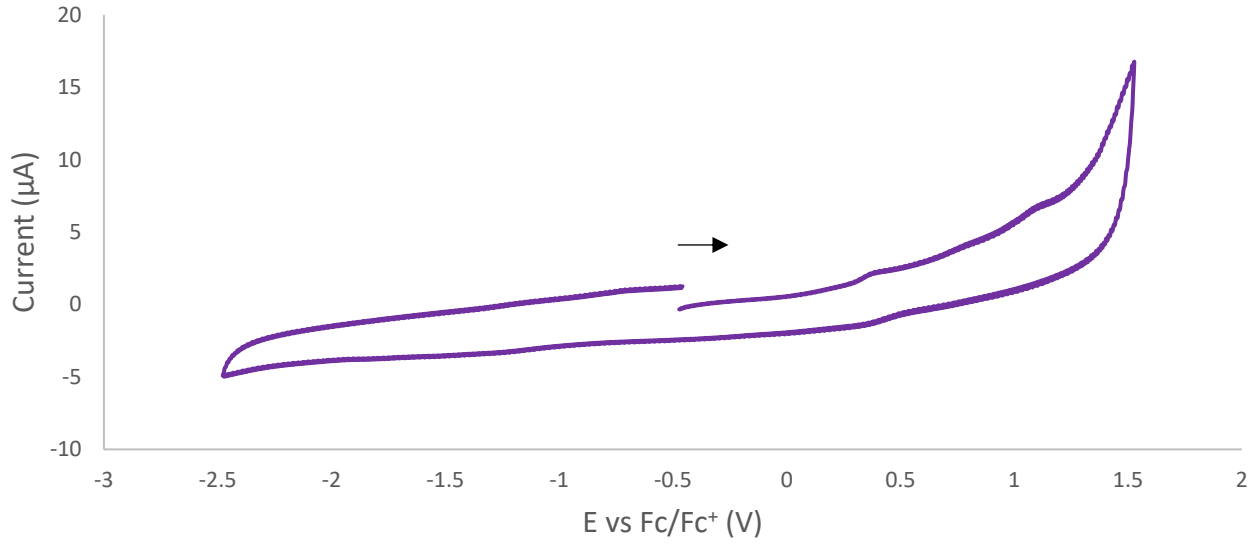


Figure S4. CV trace for MeCN (nBu$_4$NPF$_6$ 0.1 M), 100 mV/s.

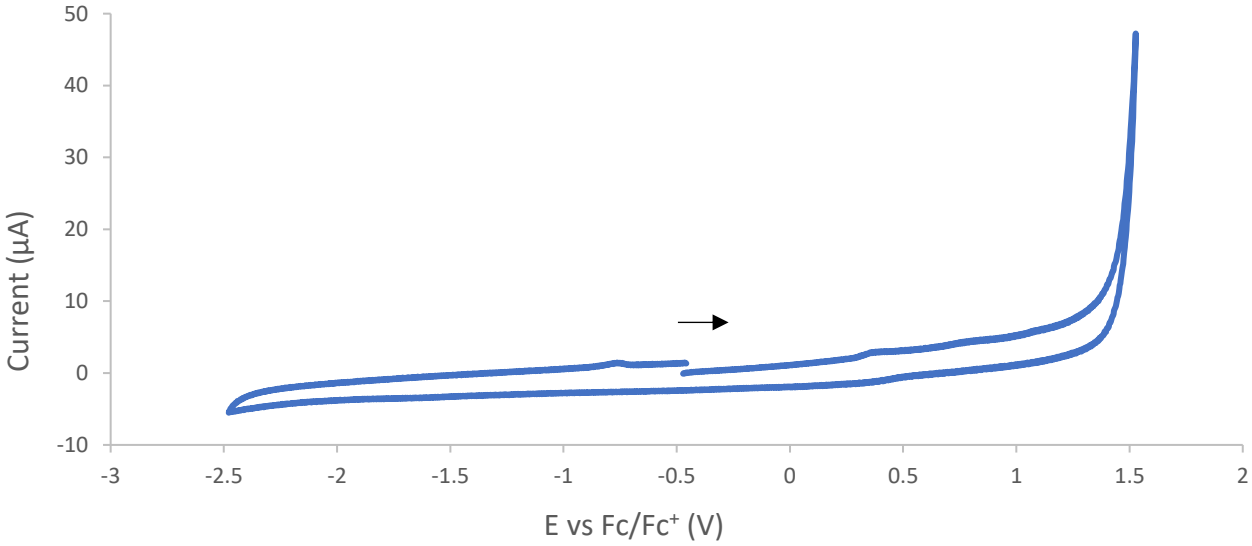


Figure S5. CV trace for boronic ester **1** (3 mM) in MeCN (nBu$_4$NPF$_6$ 0.1 M), 100 mV/s.

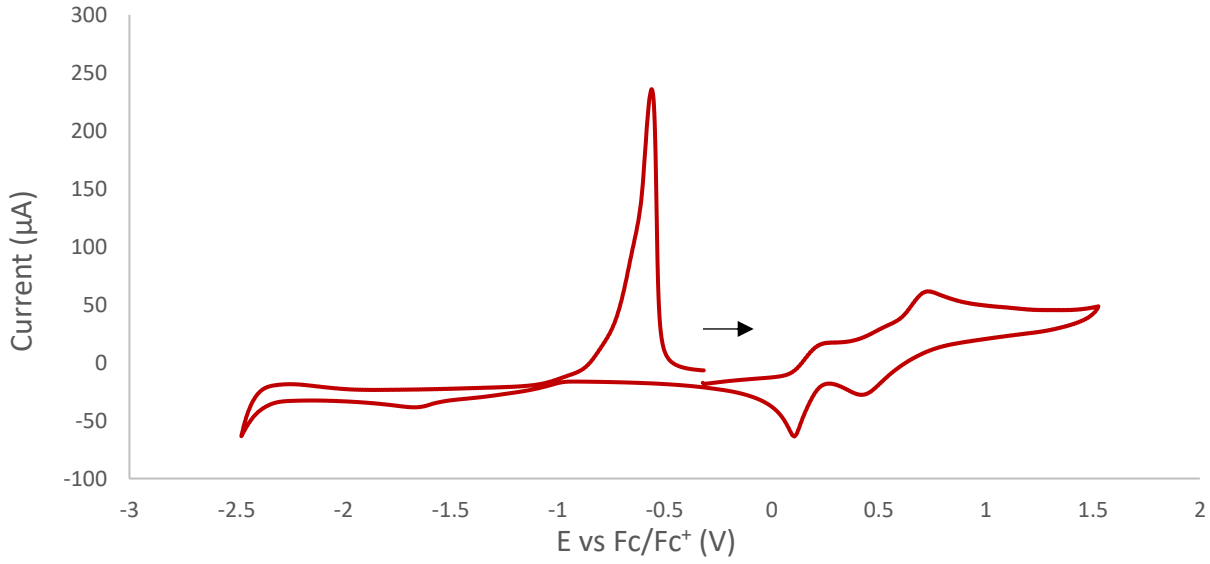


Figure S6. CV trace for $CuBr_2$ (3 mM) in MeCN (nBu$_4$NPF$_6$ 0.1 M), 100 mV/s.

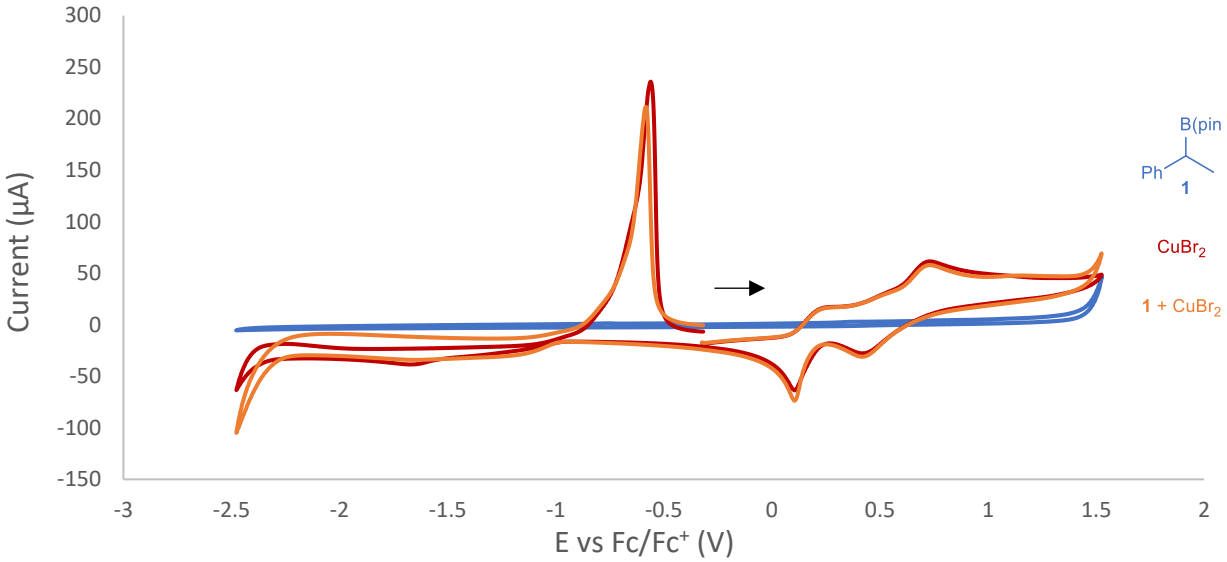


Figure S7. Individual traces of boronic ester **1** (3 mM), $CuBr_2$ (3 mM) and a mixture 1:1 of both (3 mM each) in MeCN (nBu$_4$NPF$_6$ 0.1 M), 100 mV/s.

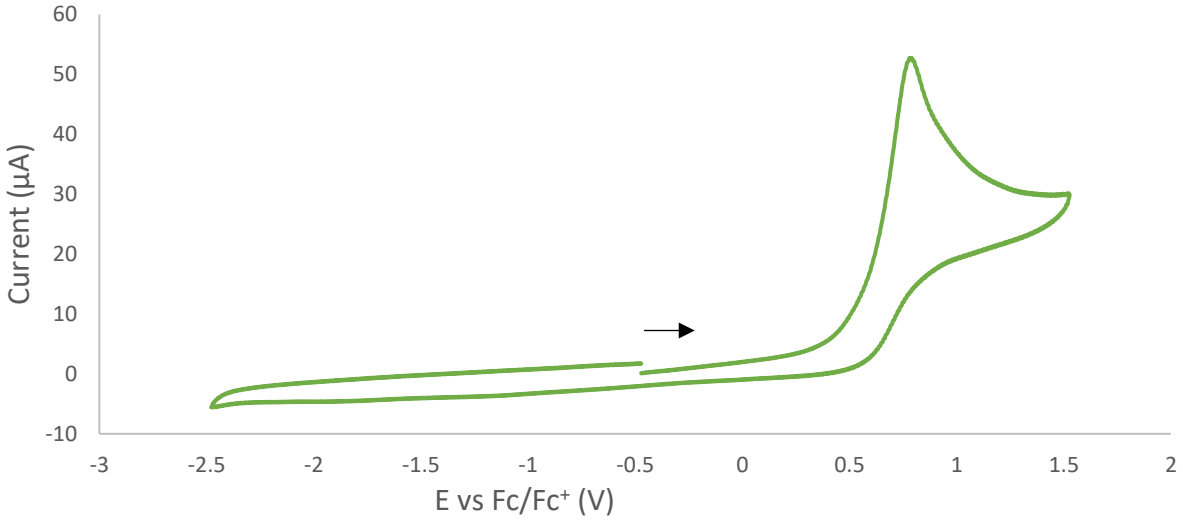


Figure S8. CV trace for morpholine (3 mM) in MeCN (nBu$_4$NPF$_6$ 0.1 M), 100 mV/s.

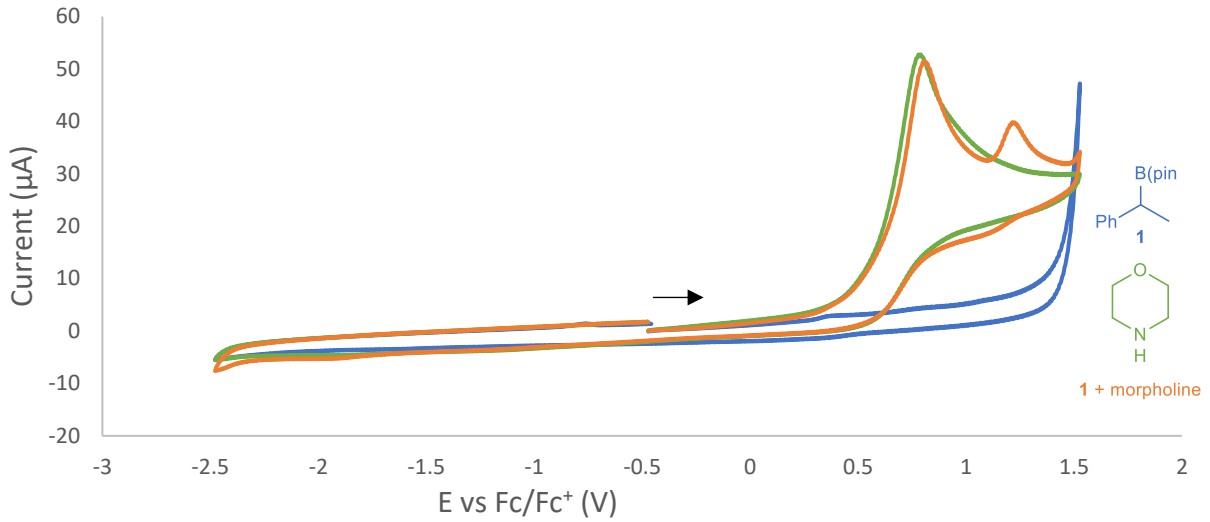


Figure S9. Individual traces of boronic ester **1** (3 mM), morpholine (3 mM) and a mixture 1:1 (3 mM each) in MeCN (nBu$_4$NPF$_6$ 0.1 M), 100 mV/s.

3.12. EPR Experiments

EPR Methods:

All EPR samples were prepared aerobically in 1:1 toluene/isopropyl alcohol solvent mixture. For the spin-trapping EPR experiments, the concentrations of the individual reactants in the reaction mixture were: boronic ester **1** (300 mM), $CuBr_2$ (30 mM), morpholine (1050 mM) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO; 400 mM). Samples were loaded into a 1.3 mm outer diameter/1 mm inner diameter glass capillary EPR tubes (sample ~ 40 mm in height) and inserted into a 4 mm outer diameter/3 mm inner diameter quartz tube (Wilmad LabGlass). The position of the sample inside the active-resonator was optimised by measuring a TEMPO standard. Spectra were measured on a Bruker EMXmicro EPR spectrometer equipped with a Bruker ER 4112SHQ X-band resonator, with a ER4131VT variable temperature unit. The optimum spectrometer conditions were: microwave power 23 dB (1 mW), modulation amplitude 0.5 G, time constant 82 ms, conversion time 1 ms, sweep time 30 s, receiver gain 30 dB. The average microwave frequency was 9.462 GHz. All EPR spectra were measured as a fluid solution at 80 °C. Analysis of the spectra and simulations were performed using the EasySpin toolbox (5.2.35) for the Matlab program package.[38] The extracted spin-Hamiltonian parameters are consistent with previously reported values for DMPO-amine and DMPO-R adducts.[39]

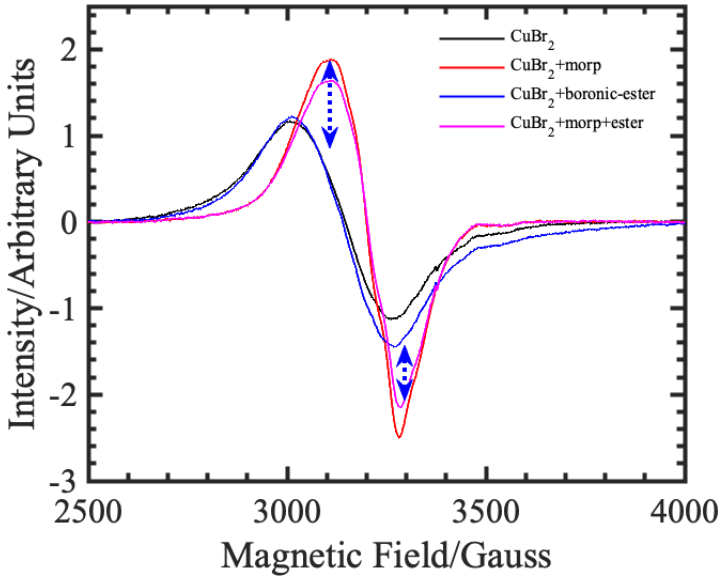


Figure S10: cw-EPR spectra of $CuBr_2$ in the absence (black trace) and presence of boronic ester **1** (blue trace) or morpholine (red trace), or both (magenta trace) measured at 80° C. The shift in the spectra in the presence of morpholine shows that the latter is interacting with the Cu(II). Experimental conditions as described in the EPR methods section.

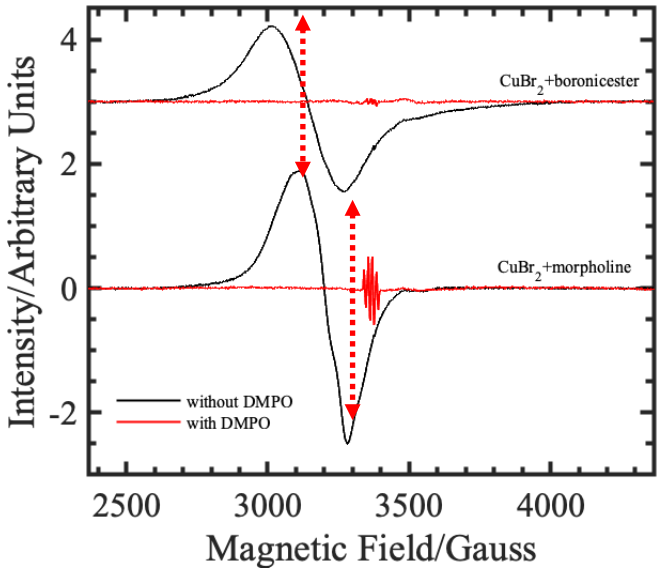


Figure S11: cw-EPR spectra of $CuBr_2$ with morpholine, and of $CuBr_2$ with boronic-ester, in the absence (black traces) and presence (red traces) of DMPO, measured at 80° C. The disappearance of the Cu(II) signals could imply that Cu(II) gets reduced to EPR-silent Cu(I). However, it was noted that Cu(II) signal was regenerated slowly during the catalysis reaction. Experimental conditions as described in the EPR methods section.

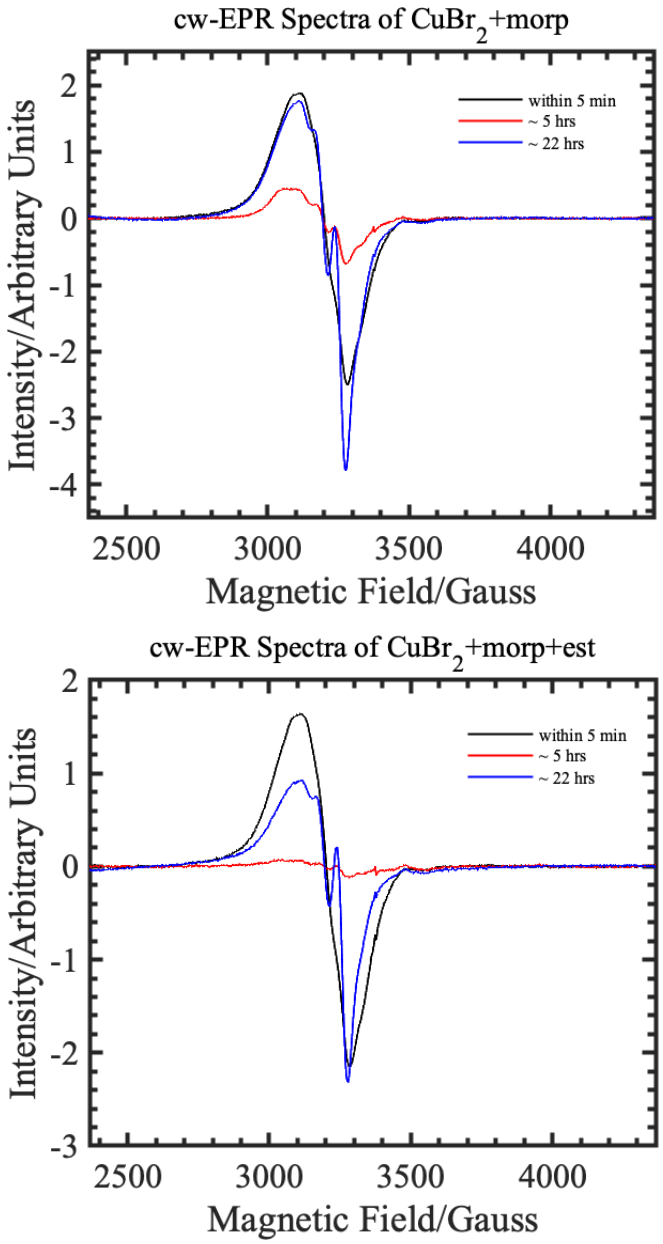


Figure S12: cw-EPR spectra of $CuBr_2$ with morpholine (top panel), and of $CuBr_2$ with morpholine and boronic-ester (bottom panel), in the absence of DMPO, measured at 80° C. The disappearance of the Cu(II) signals could imply that Cu(II) gets reduced to EPR-silent Cu(I) (red traces). However, these signals were regenerated slowly during the catalysis reaction (blue traces). Experimental conditions as described in the EPR methods section.

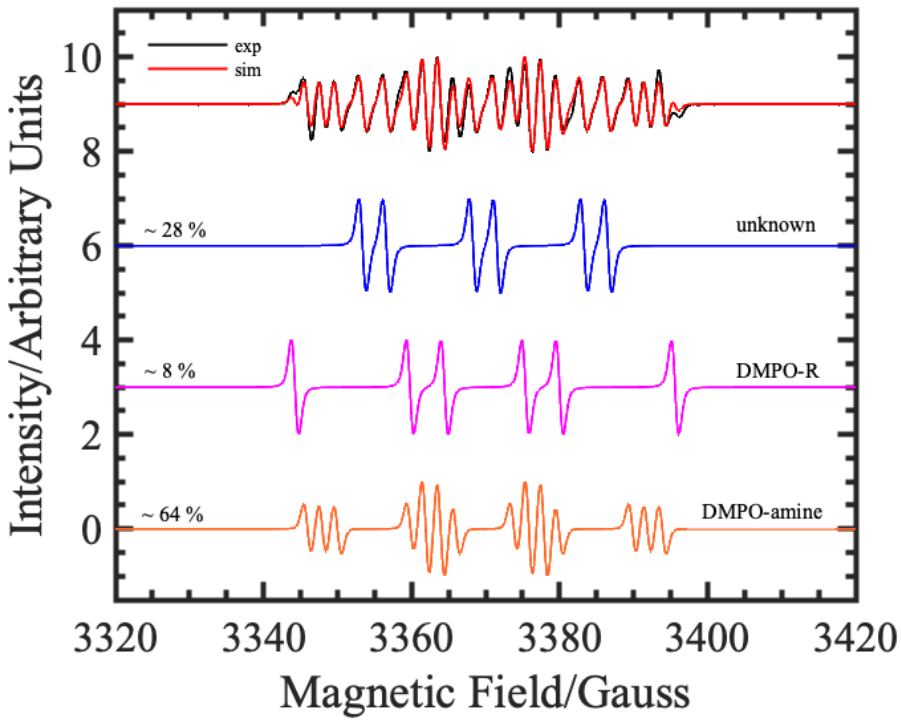
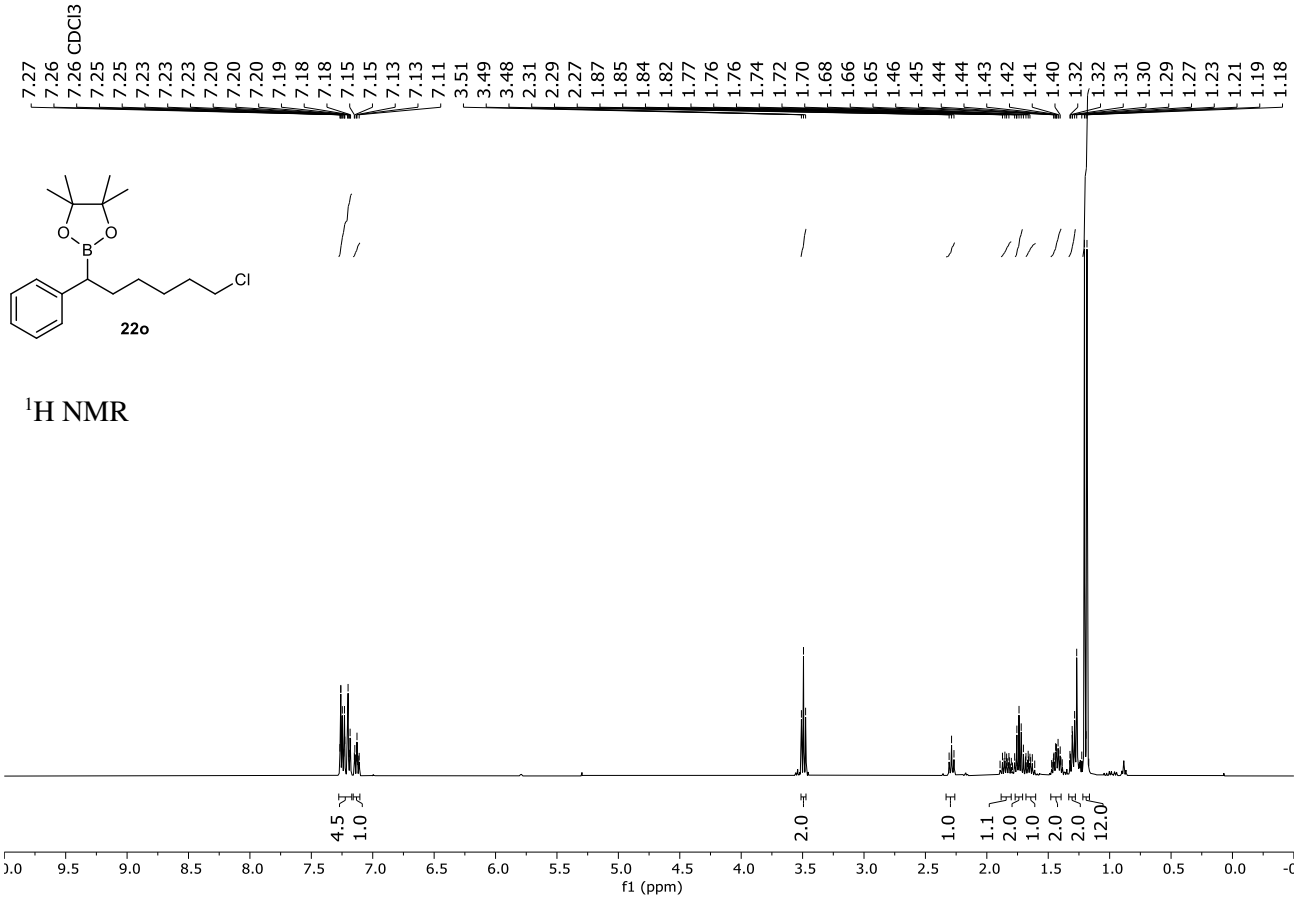


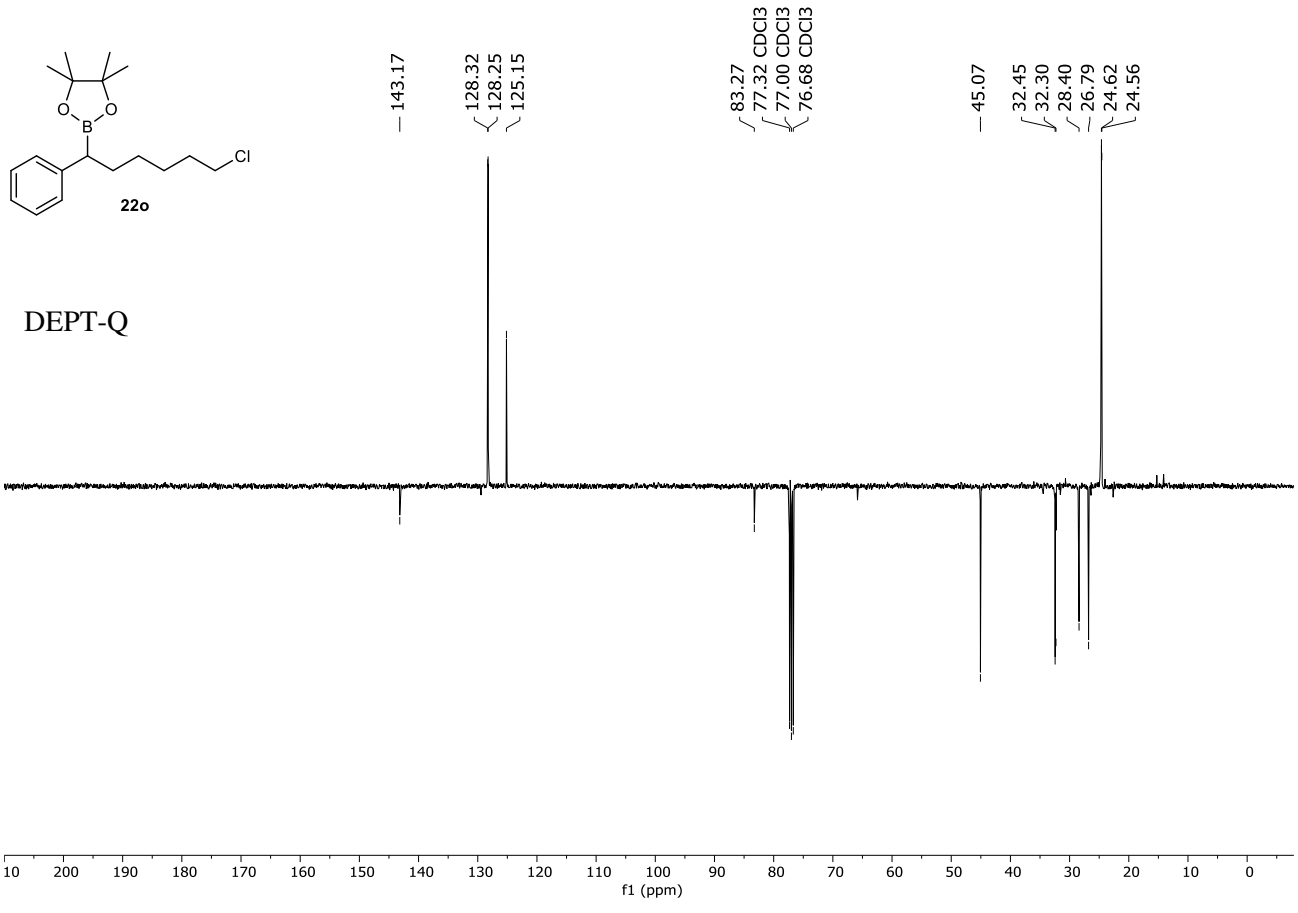
Figure S13: Experimental (black) and simulated (red) cw-EPR spectra of the $CuBr_2$, morpholine and boronic ester mixture with DMPO, measured at 80° C. It was necessary to include three DMPO-adducts to reproduce the experimental spectra (see main text for more details). The spin-Hamiltonian parameters used were (relative weights are given in the figure): *DMPO-amine* - g_{iso} = 2.0059, $a_{iso}(^{14}N)$ = 39.1 MHz, $a_{iso}(^{1}H)$ = 45.0 MHz and $a_{iso}(^{14}N)$ = 5.7 MHz; *DMPO-R* - g_{iso} = 2.0058, $a_{iso}(^{14}N)$ = 43.7 MHz and $a_{iso}(^{1}H)$ = 56.7 MHz; *DMPO-unknown* - g_{iso} = 2.0059, $a_{iso}(^{14}N)$ = 41.8 MHz and $a_{iso}(^{1}H)$ = 9.1 MHz. Experimental conditions as described in the EPR methods section.

4. NMR Spectra

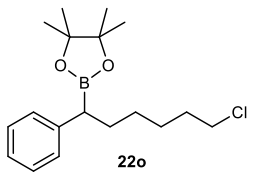
4.1. Boronic Esters



^{1}H NMR

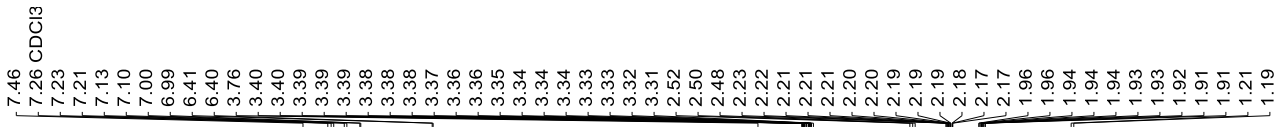


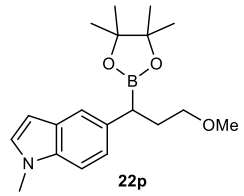
DEPT-Q



22o

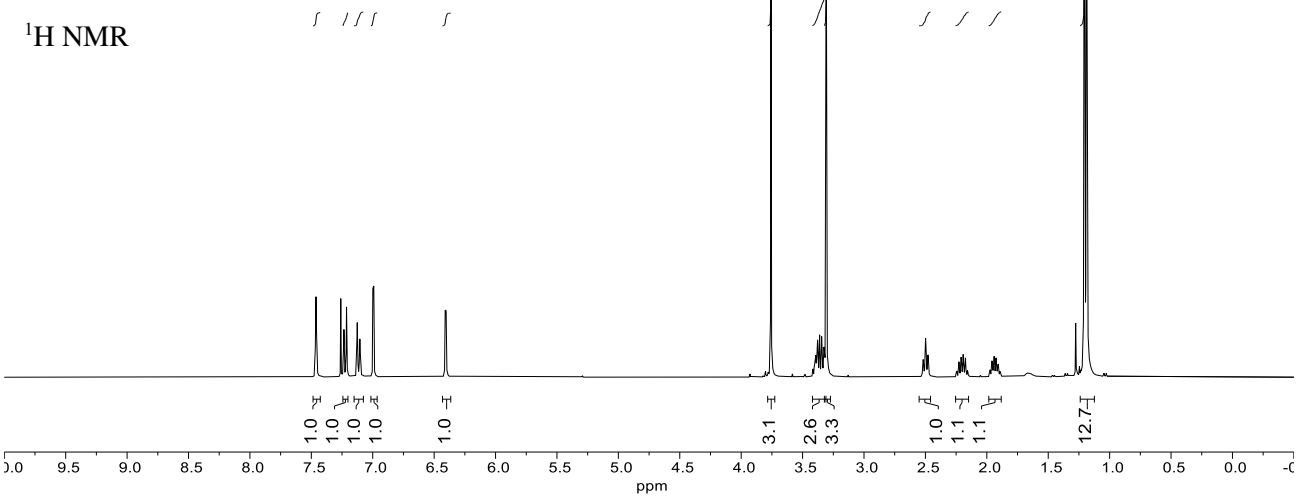
^{11}B NMR

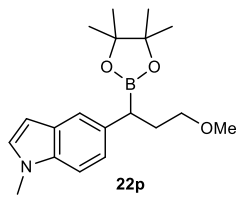




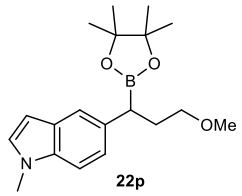
22p

^{1}H NMR

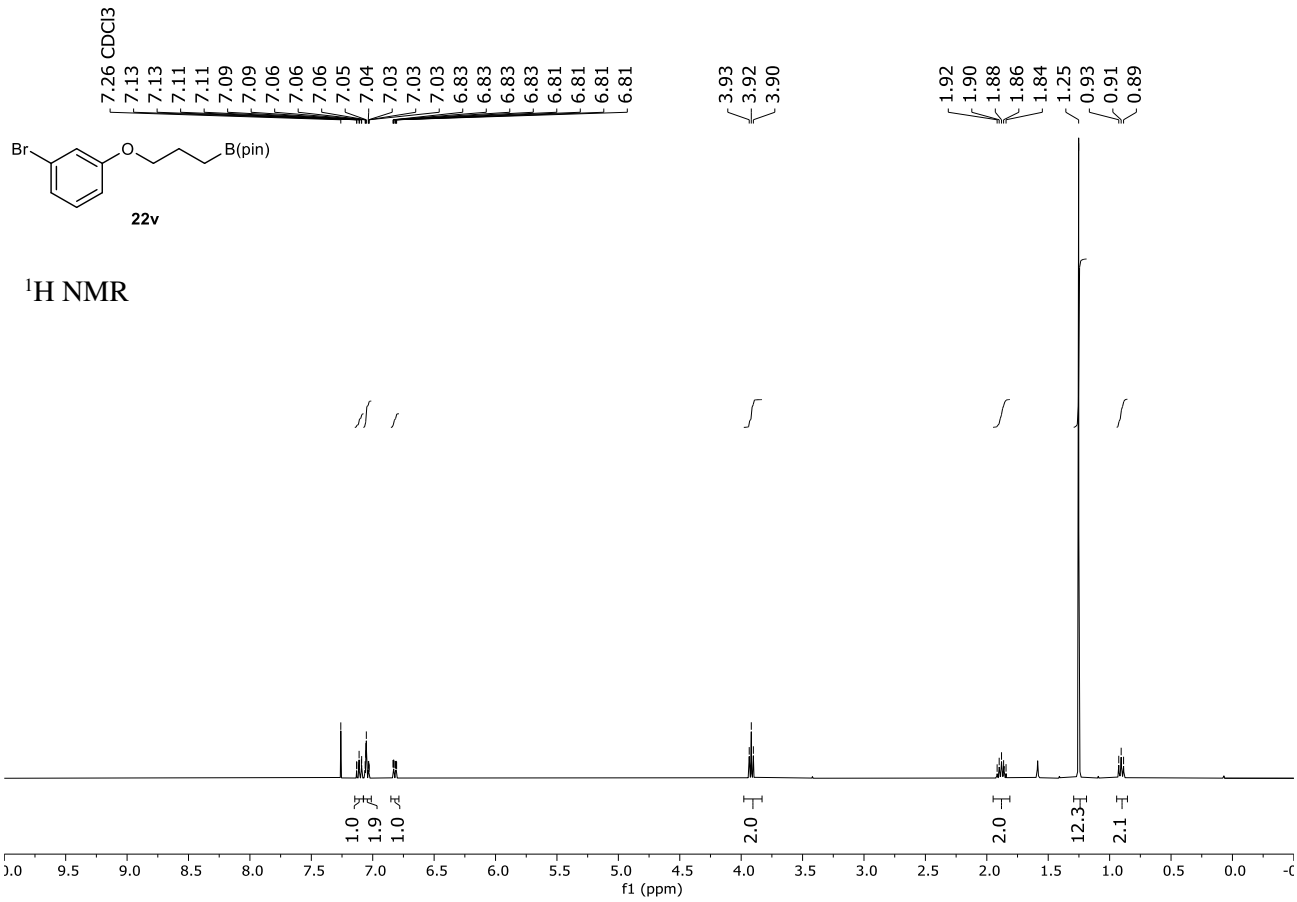



OMe
N
22p

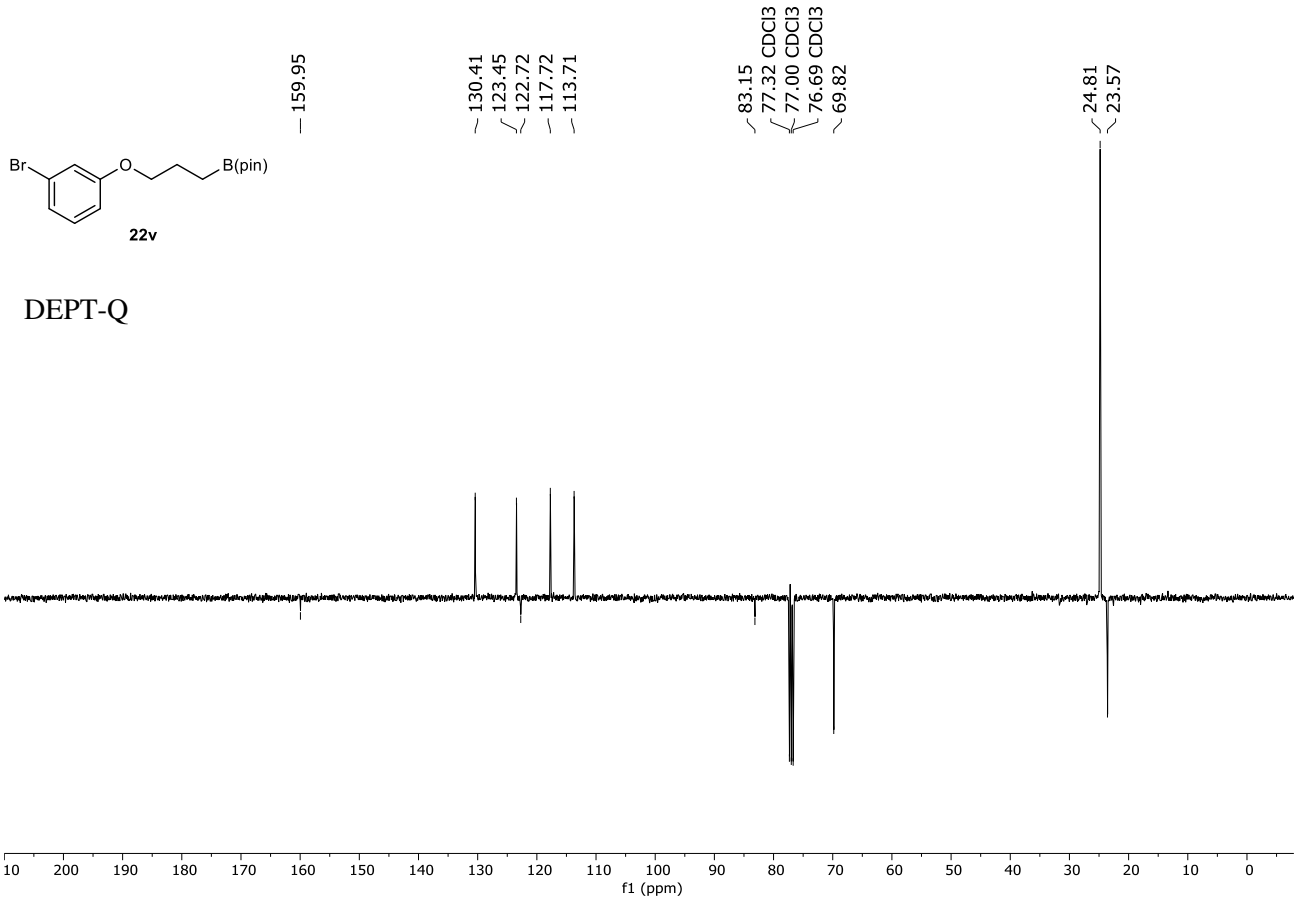
135.16
133.42
128.71
128.53
122.66
120.03
108.92
100.43
83.08
77.32
77.00 CDCl3
76.68
72.17
58.44
33.01
32.77
24.60
24.56
DEPT-Q
ppm


OMe
N
22p

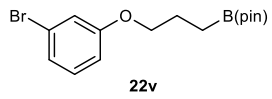
33.65
^{11}B NMR
f1 (ppm)


7.26 CDCl3
7.13
7.13
7.11
7.11
7.09
7.09
7.06
7.06
7.06
7.05
7.04
7.03
7.03
7.03
6.83
6.83
6.83
6.81
6.81
6.81
6.81
3.93
3.92
3.90
1.92
1.90
1.88
1.86
1.84
1.25
0.93
0.91
0.89
Br
O
B(pin)
22v
1.0
1.9
1.0
2.0
2.0
12.3
2.1
f1 (ppm)

^{1}H NMR

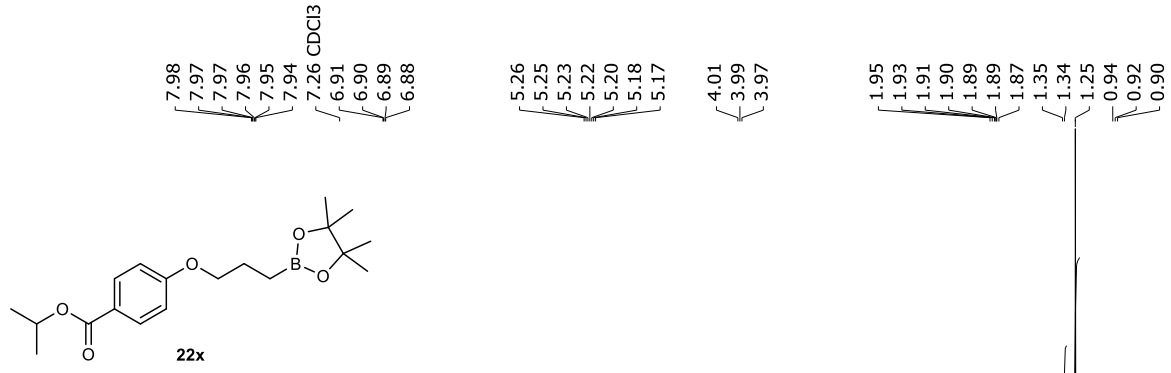

159.95
130.41
123.45
122.72
117.72
113.71
83.15
77.32 CDCl3
77.00 CDCl3
76.69 CDCl3
69.82
24.81
23.57
Br
O
B(pin)
22v
f1 (ppm)

DEPT-Q



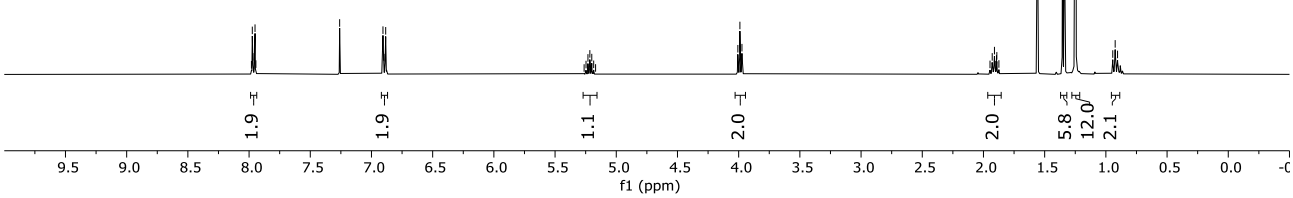
22v

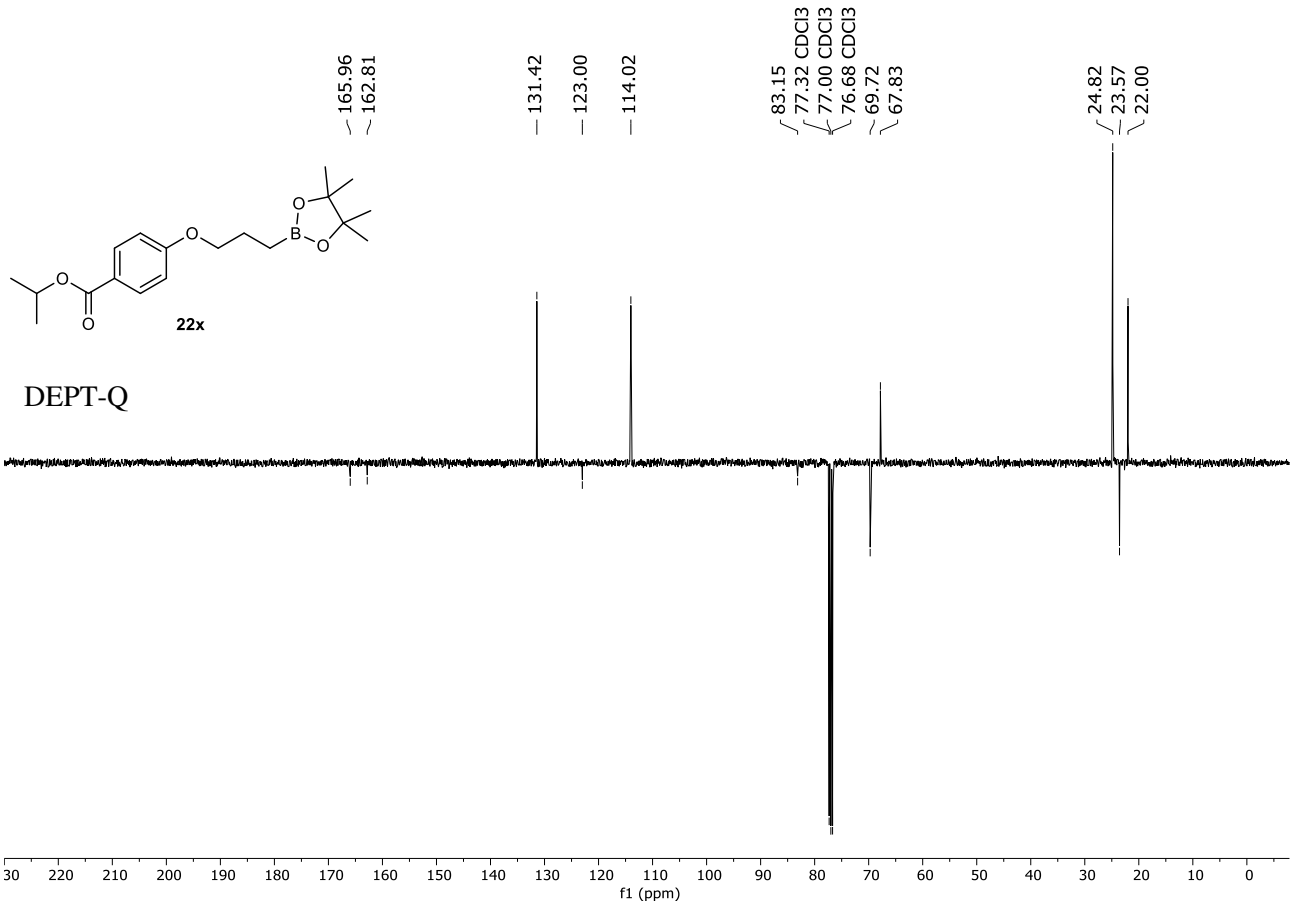
^{11}B NMR

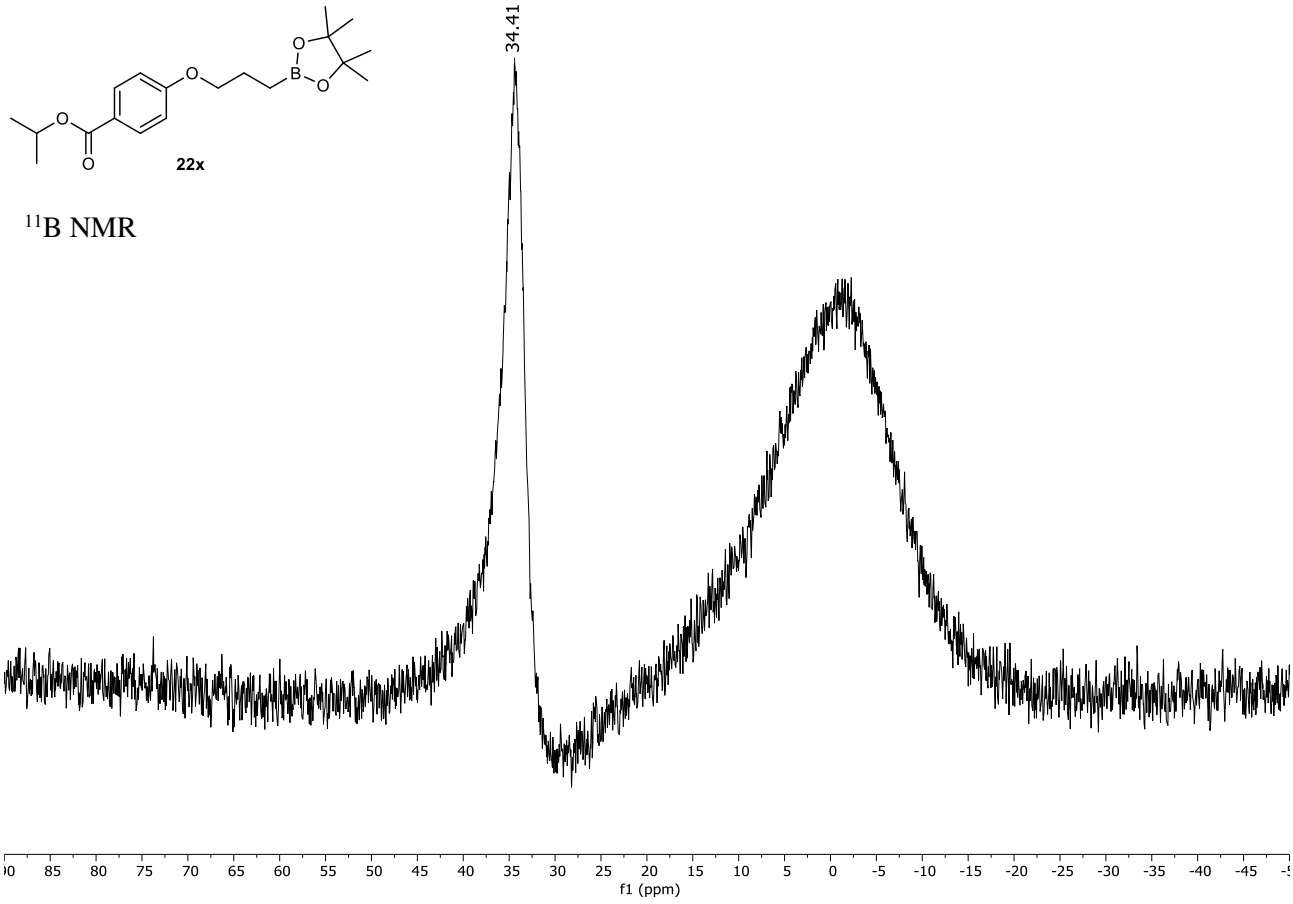


22x

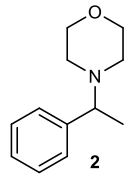
^{1}H NMR



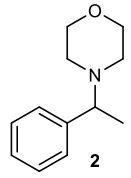

165.96
162.81
131.42
123.00
114.02
83.15
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.72
67.83
24.82
23.57
22.00
22x
DEPT-Q
f1 (ppm)


34.41
22x
11B NMR
f1 (ppm)

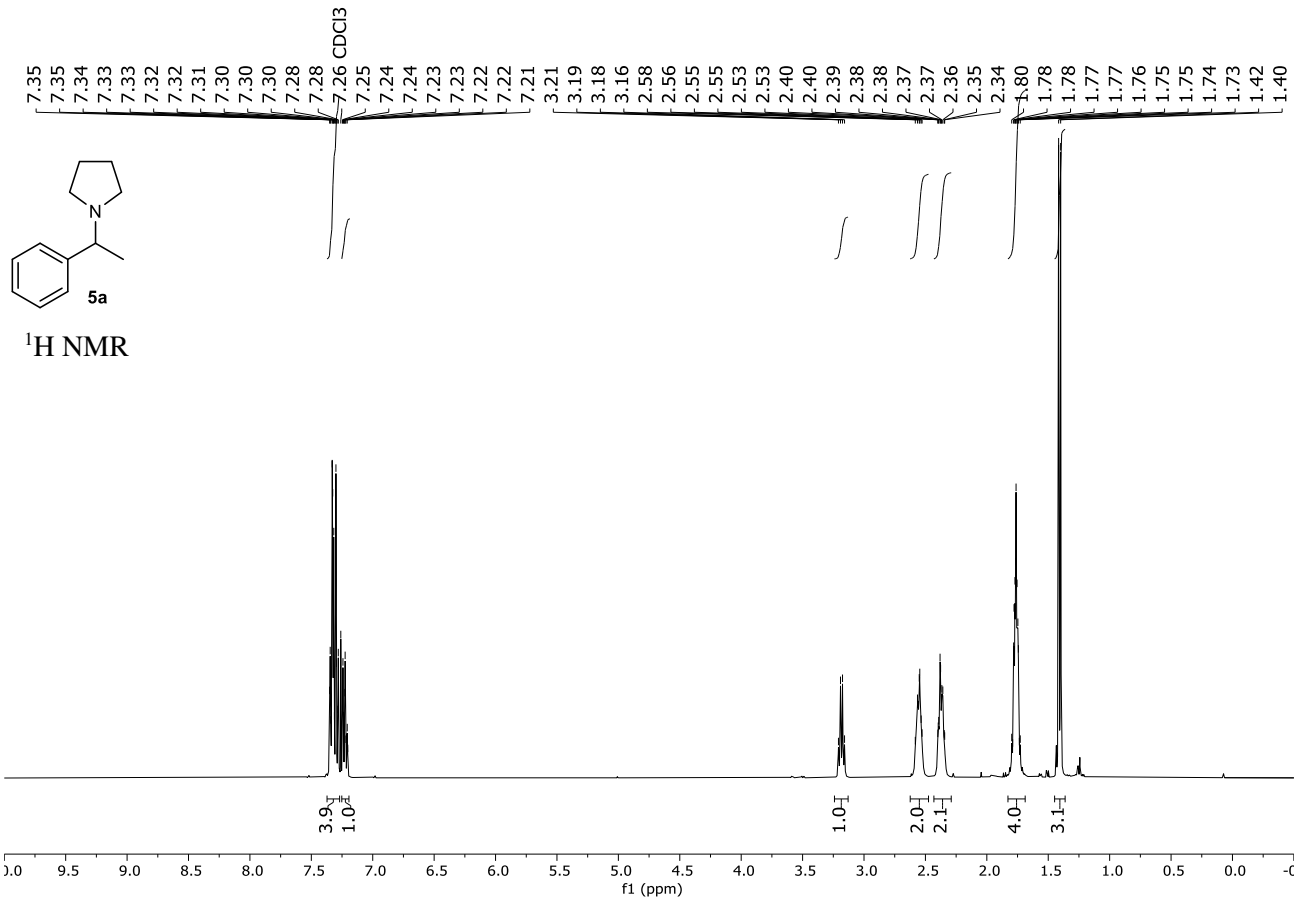
4.2. Coupling of Secondary Amines



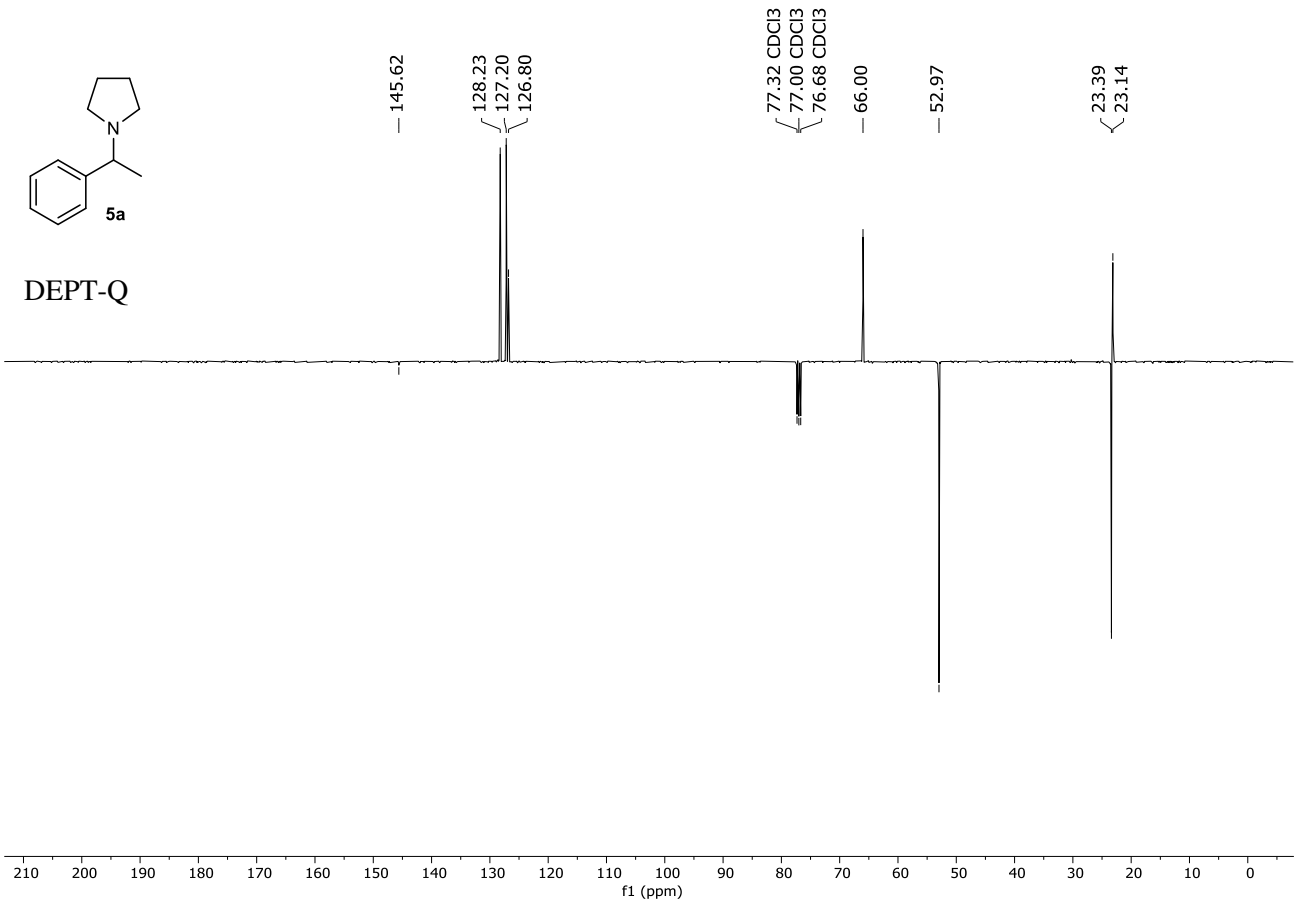
^{1}H NMR



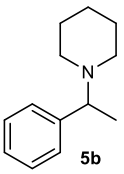
^{13}C NMR


7.35 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.30 7.30 7.28 7.28 7.26 CDCl3 7.25 7.24 7.24 7.23 7.23 7.22 7.22 7.21
3.21 3.19 3.18 3.16 2.58 2.56 2.55 2.55 2.53 2.53 2.40 2.40 2.39 2.38 2.38 2.37 2.37 2.36 2.35 2.34
1.80 1.78 1.78 1.77 1.77 1.76 1.75 1.75 1.74 1.73 1.42 1.40
5a
3.9 1.0 1.0 2.0 2.1 4.0 3.1
f1 (ppm)

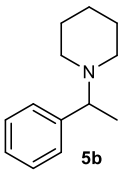
^{1}H NMR


145.62
128.23 127.20 126.80
77.32 CDCl3 77.00 CDCl3 76.68 CDCl3
66.00
52.97
23.39 23.14
5a
f1 (ppm)

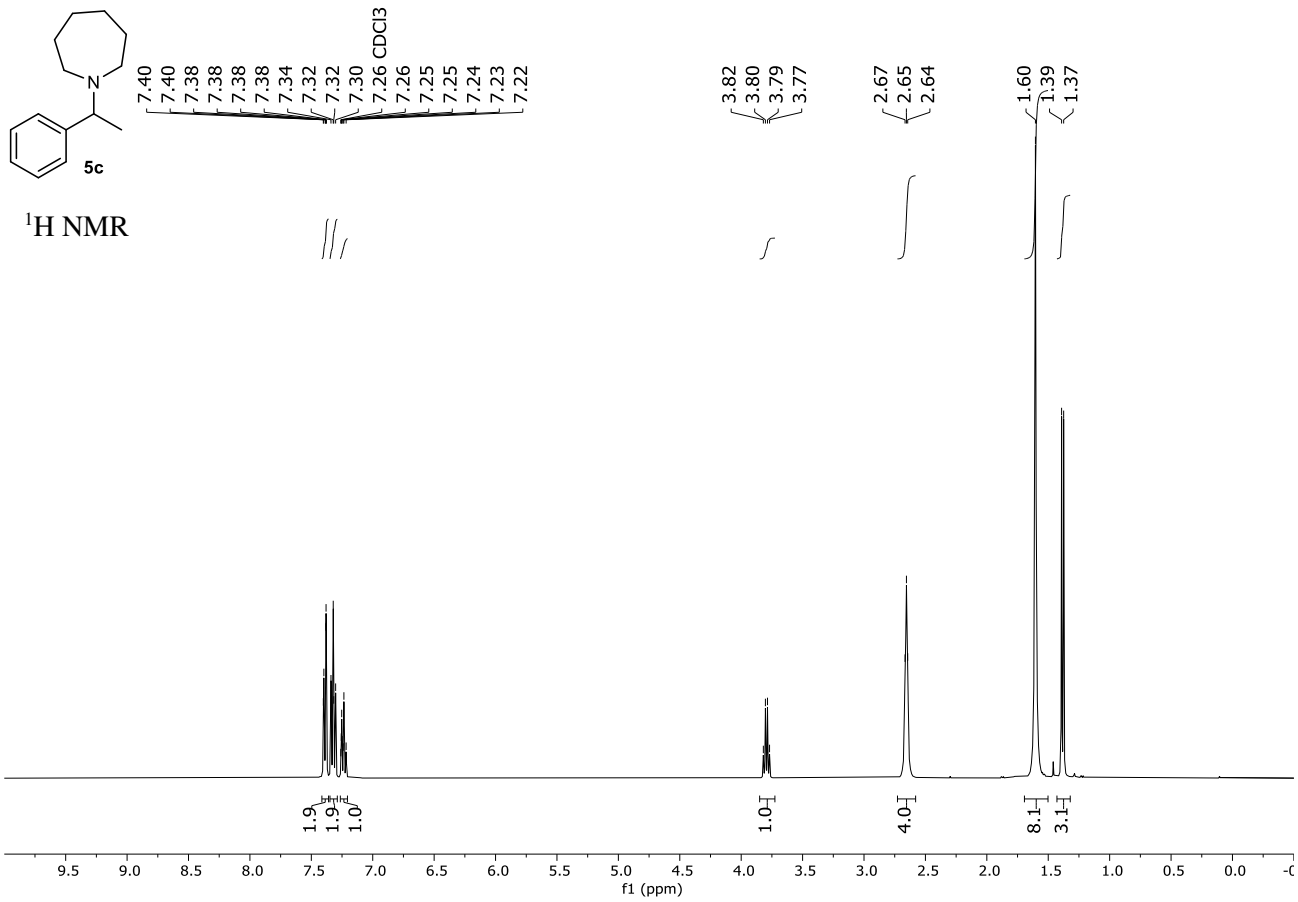
DEPT-Q



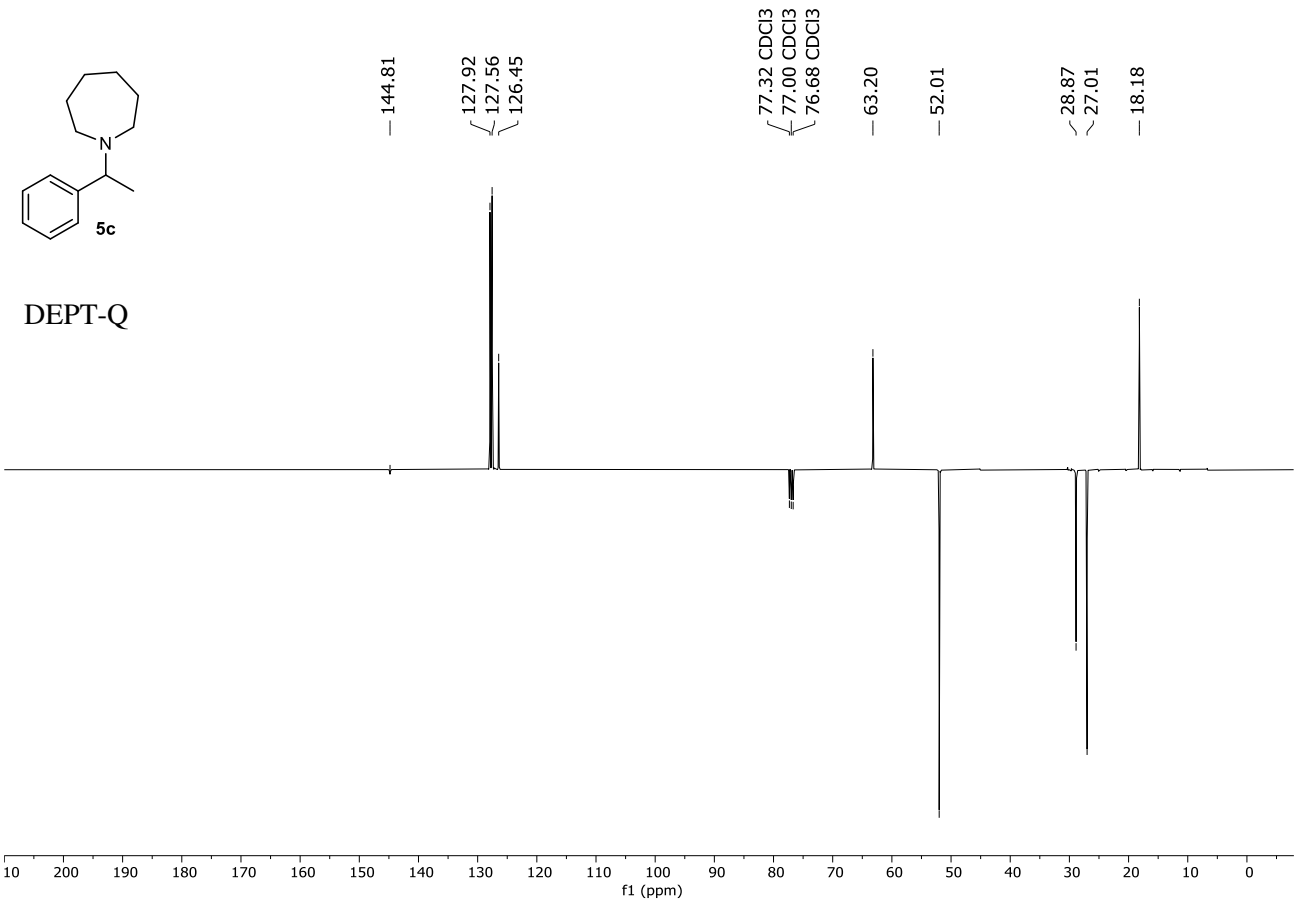
^{1}H NMR



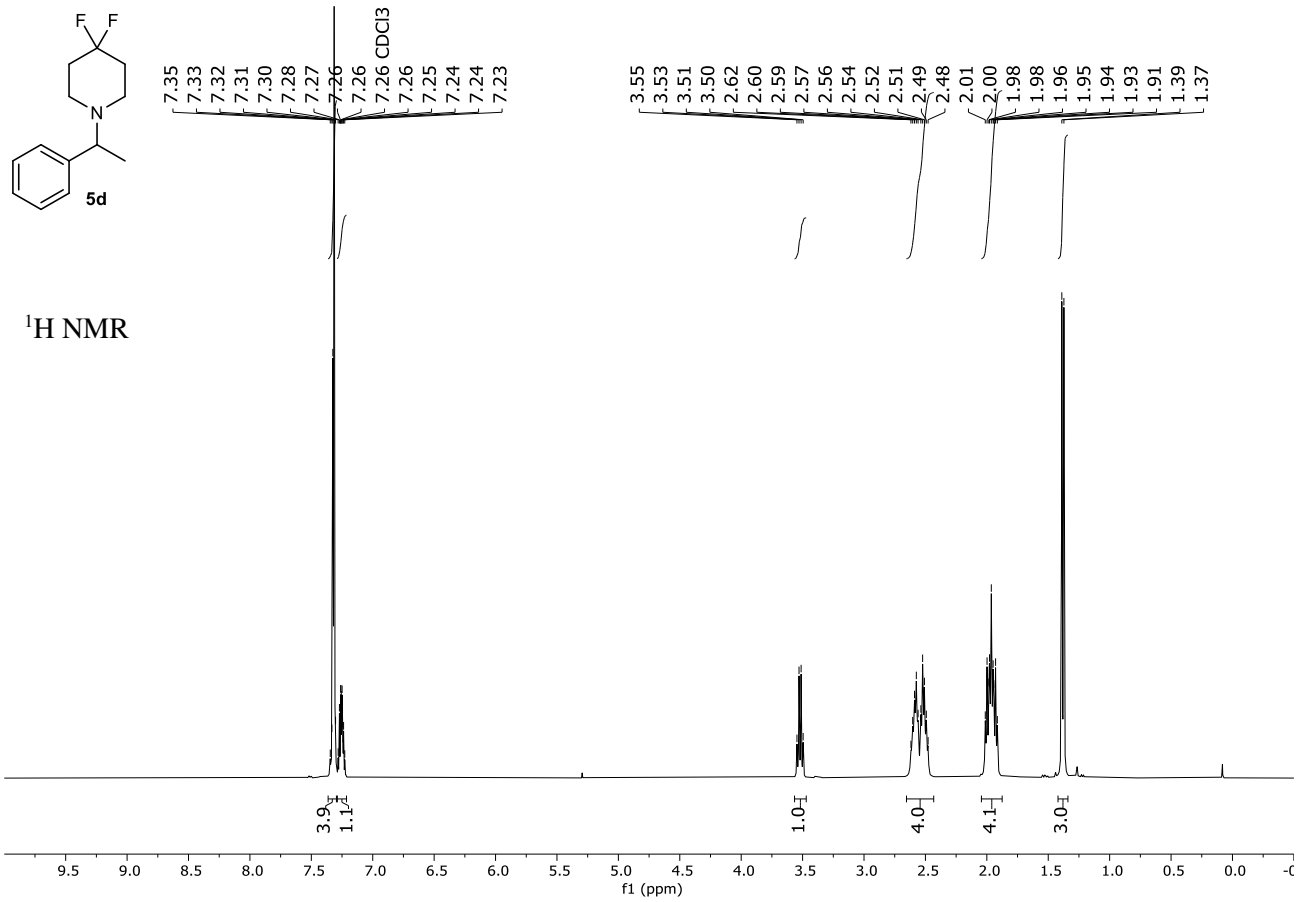
^{13}C NMR


5c
7.40
7.40
7.38
7.38
7.38
7.38
7.34
7.32
7.32
7.30
7.26 CDCl3
7.26
7.25
7.25
7.24
7.23
7.22
3.82
3.80
3.79
3.77
2.67
2.65
2.64
1.60
1.39
1.37
1.9
1.9
1.0
1.0
4.0
8.1
3.1
f1 (ppm)

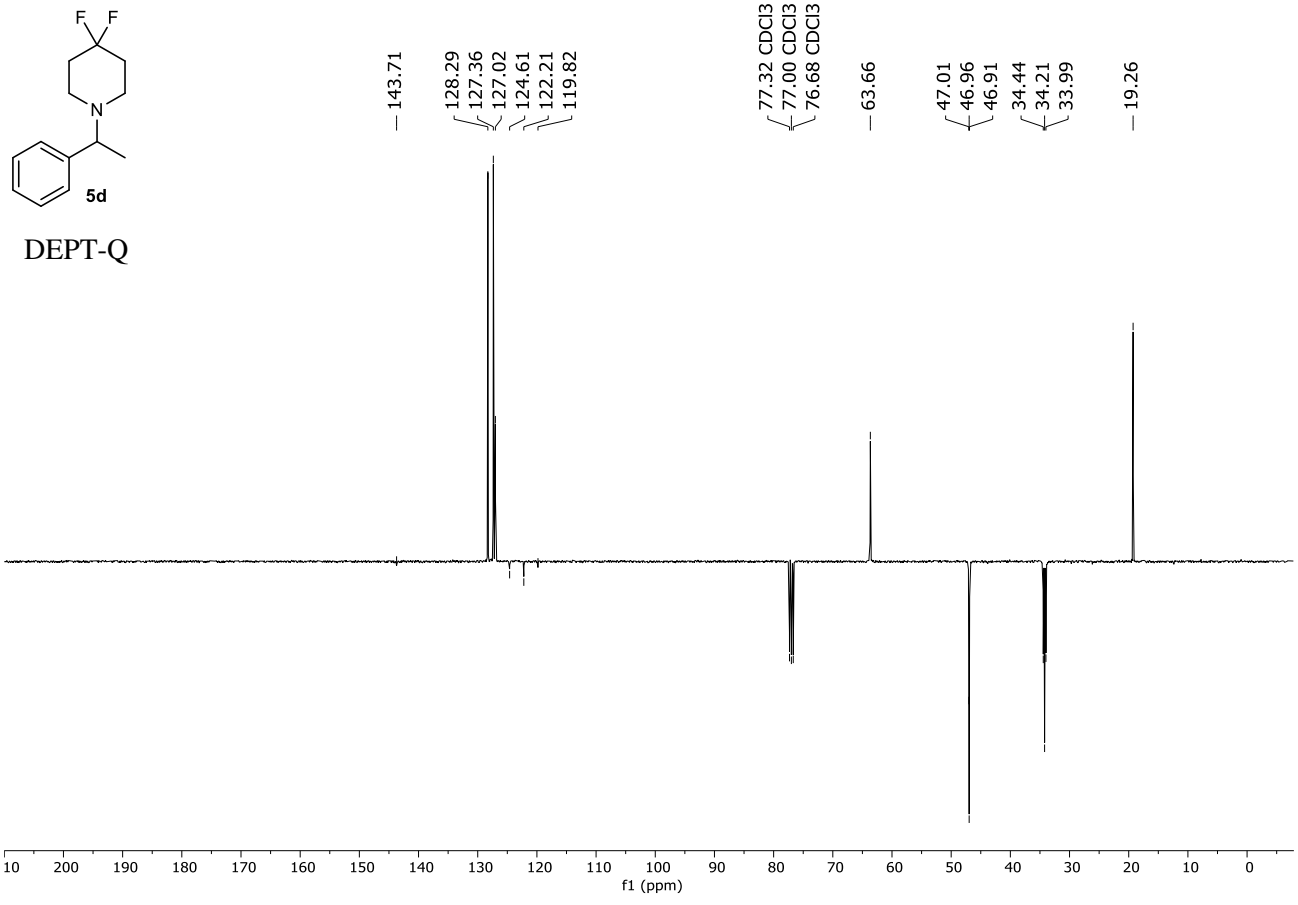
^{1}H NMR


5c
144.81
127.92
127.56
126.45
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
63.20
52.01
28.87
27.01
18.18
f1 (ppm)

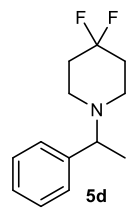
DEPT-Q


F F
N
5d
7.35
7.33
7.32
7.31
7.30
7.28
7.27
7.26
7.26 CDCl3
7.26
7.25
7.24
7.24
7.23
3.55
3.53
3.51
3.50
2.62
2.60
2.59
2.57
2.56
2.54
2.52
2.51
2.49
2.48
2.01
2.00
1.98
1.96
1.95
1.94
1.93
1.91
1.39
1.37
3.9
1.1
1.0
4.0
4.1
3.0
f1 (ppm)

^{1}H NMR

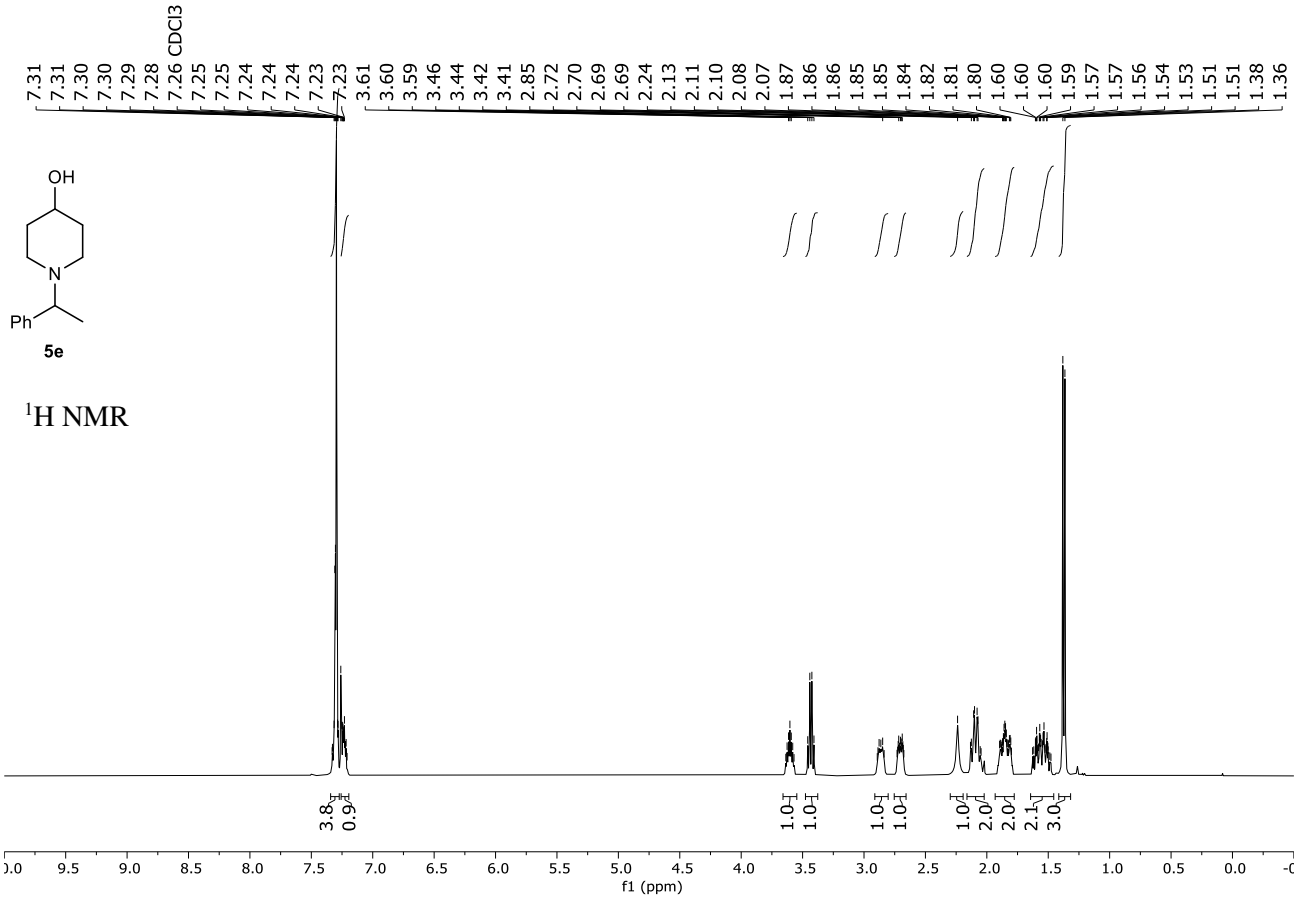

F F
N
5d
143.71
128.29
127.36
127.02
124.61
122.21
119.82
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
63.66
47.01
46.96
46.91
34.44
34.21
33.99
19.26
f1 (ppm)

DEPT-Q



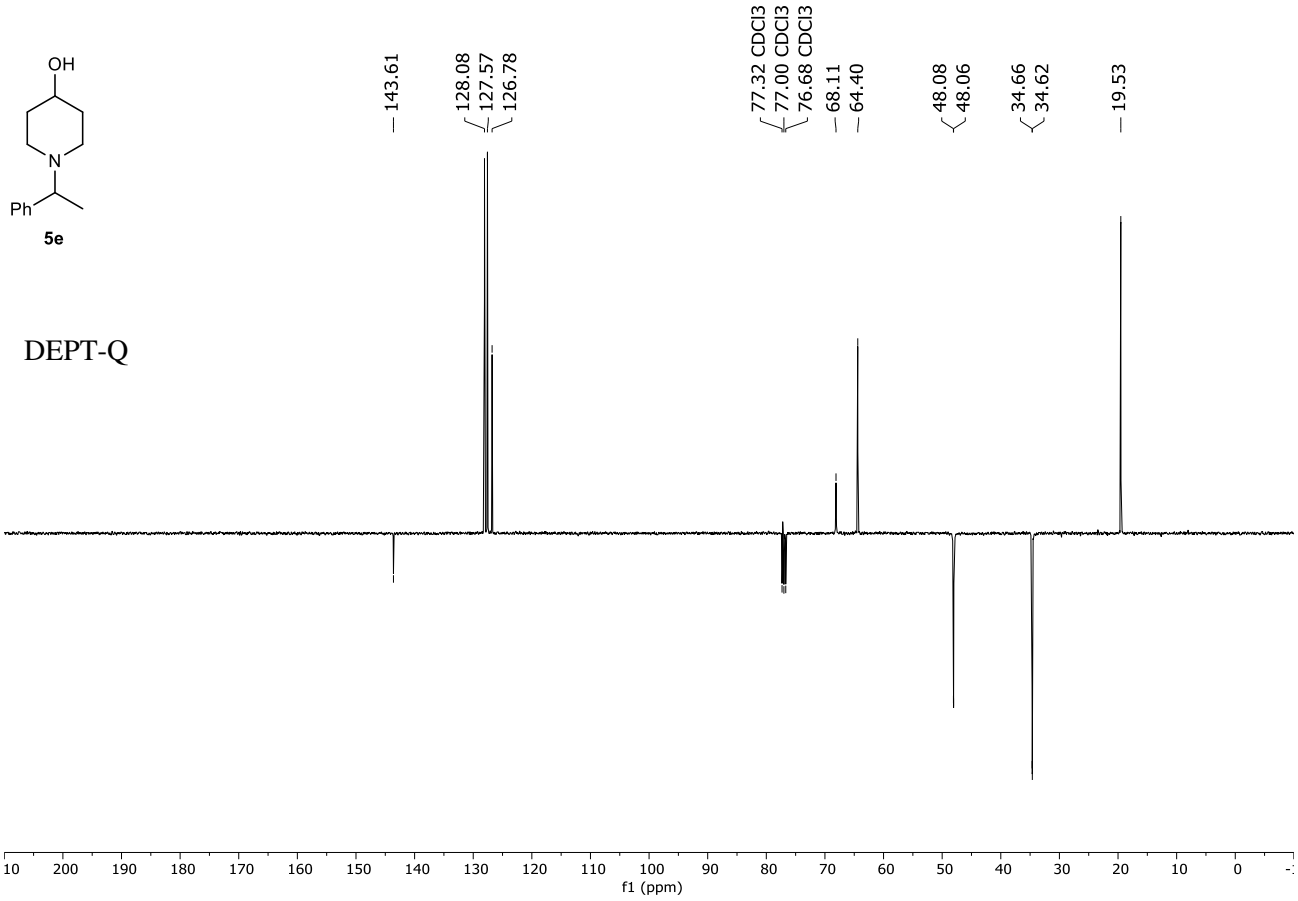
5d

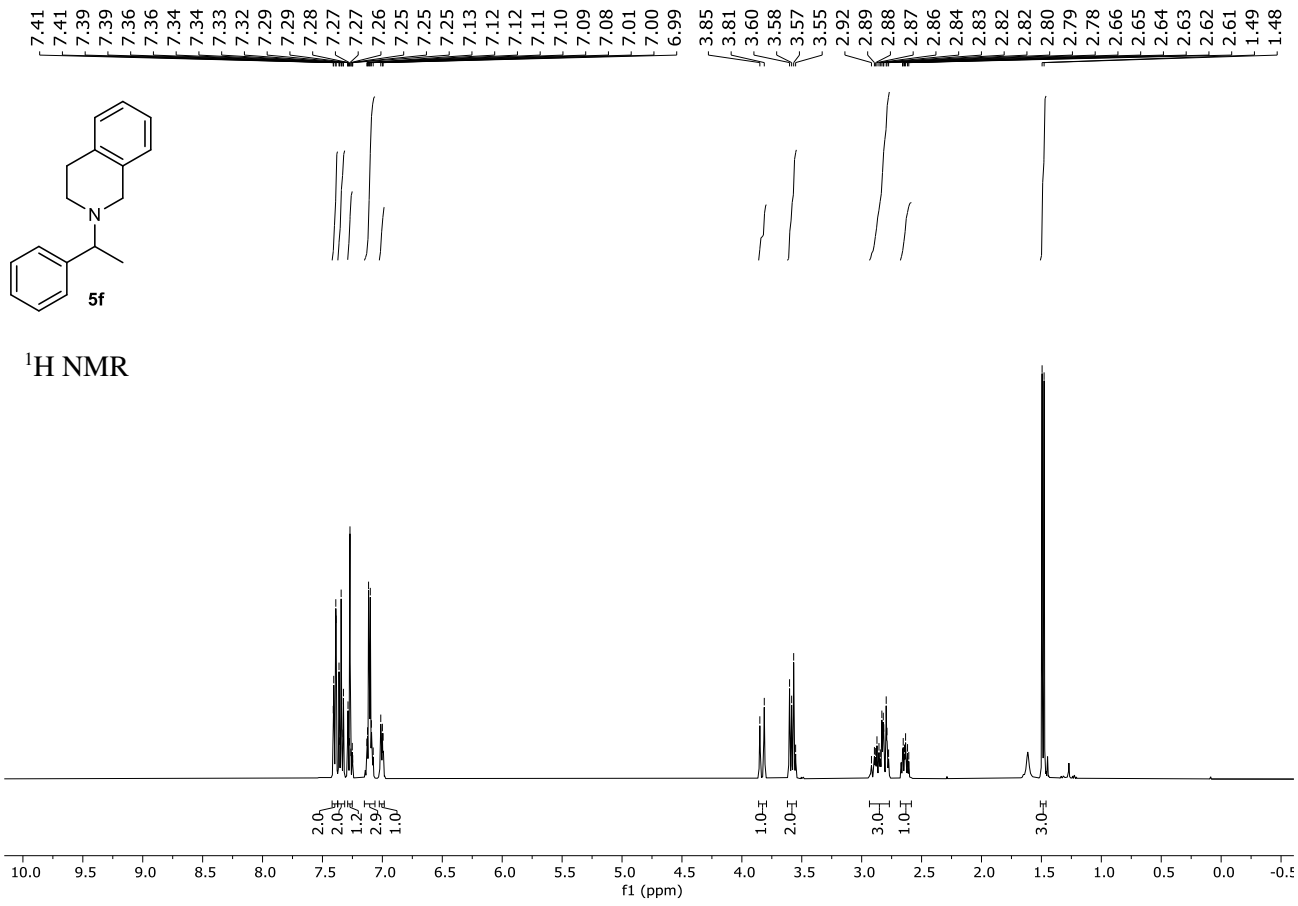
^{19}F NMR

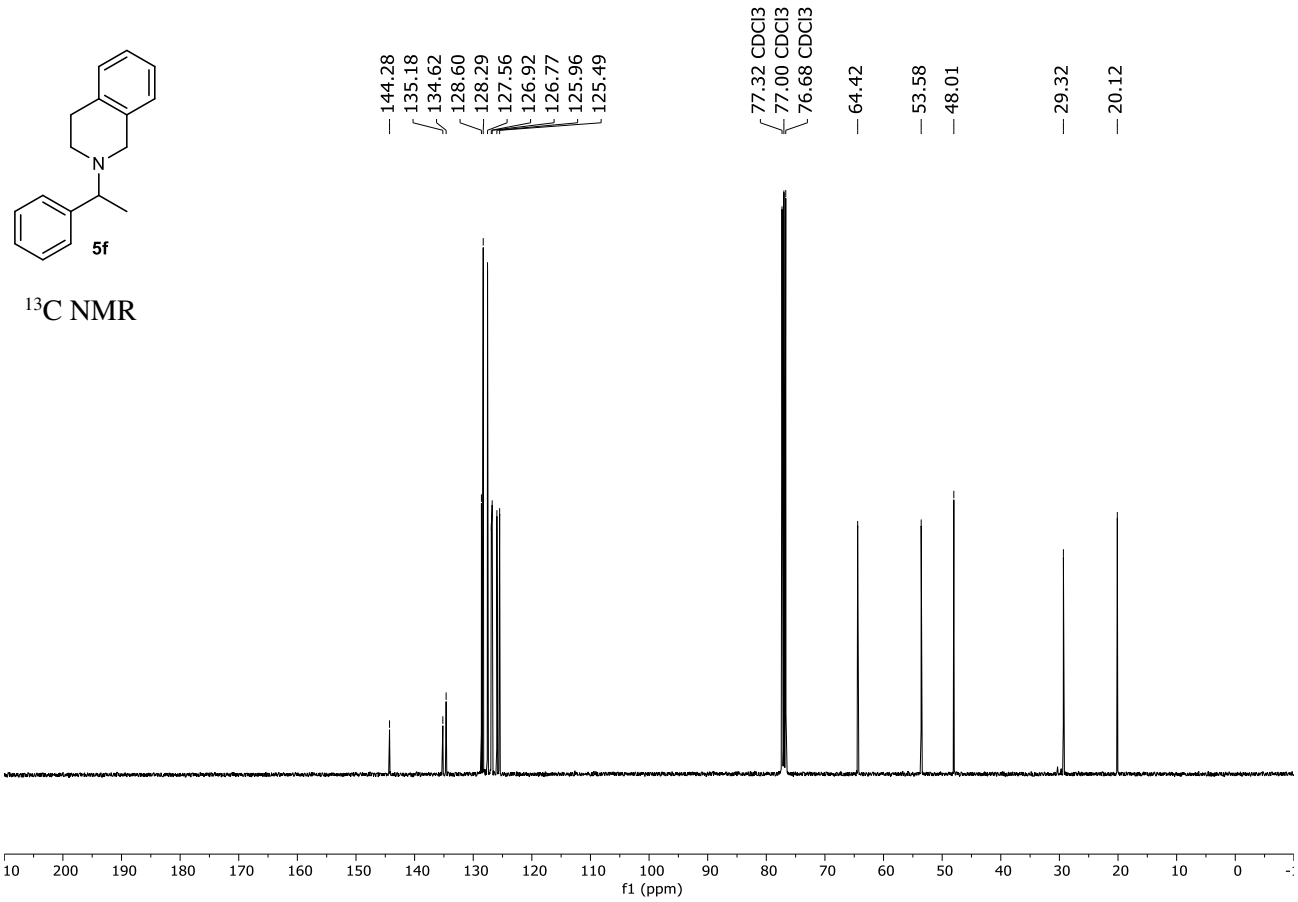


5e

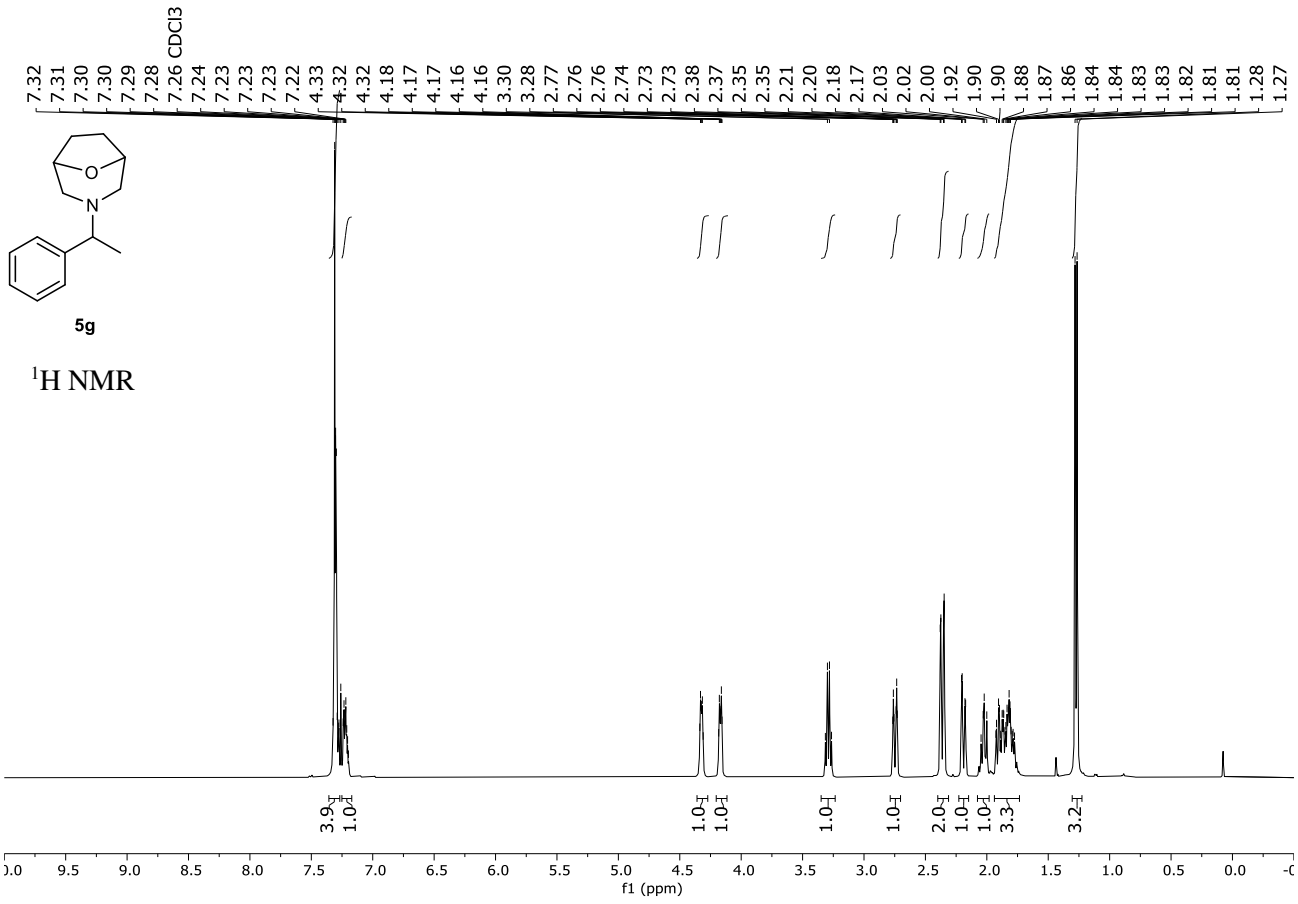
^{1}H NMR


OH
N
Ph
5e
143.61
128.08
127.57
126.78
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
68.11
64.40
48.08
48.06
34.66
34.62
19.53
DEPT-Q
f1 (ppm)

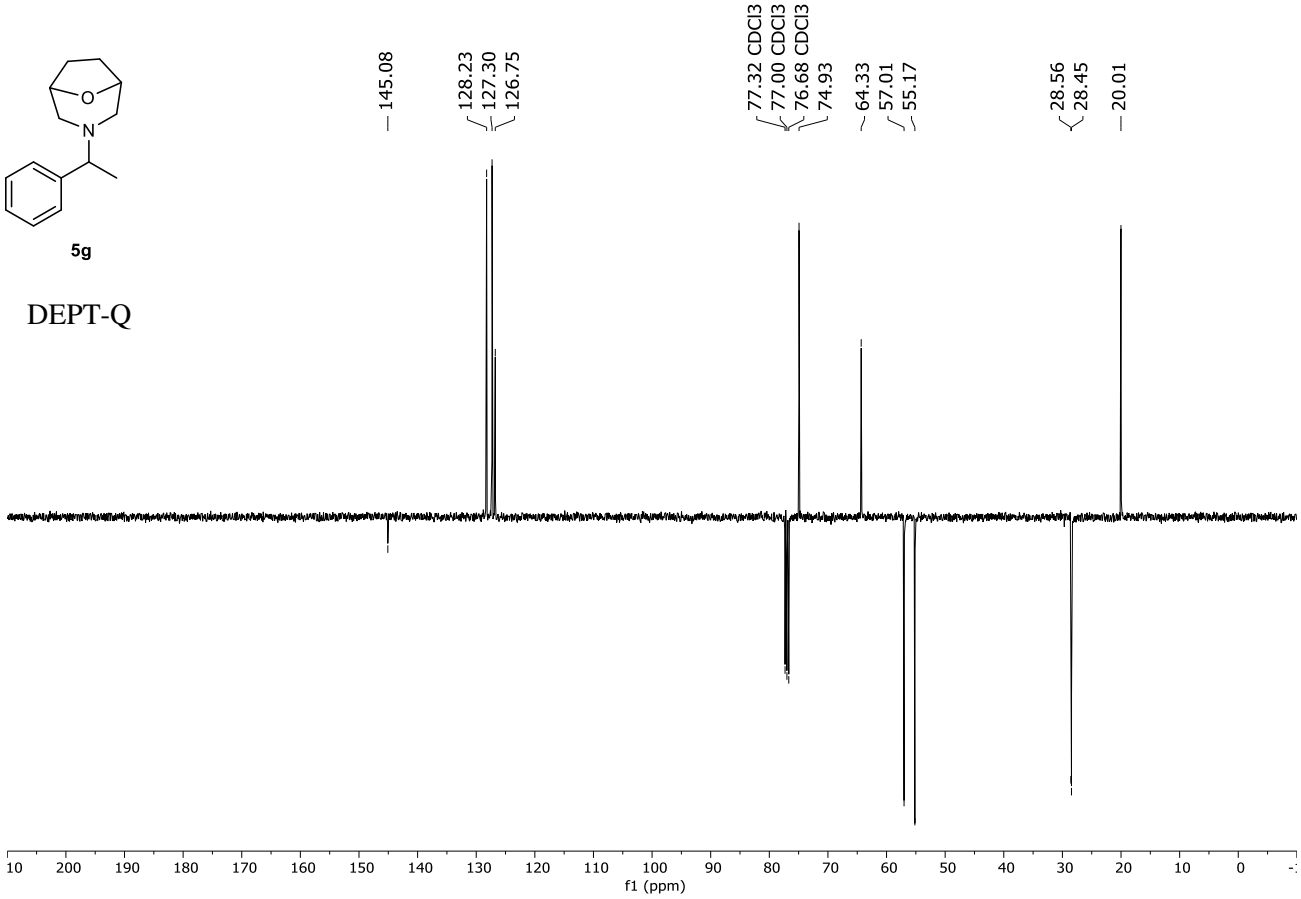

7.41
7.41
7.39
7.39
7.36
7.36
7.34
7.34
7.33
7.32
7.29
7.29
7.28
7.27
7.27
7.26
7.25
7.25
7.25
7.13
7.12
7.12
7.11
7.10
7.09
7.08
7.01
7.00
6.99
3.85
3.81
3.60
3.58
3.57
3.55
2.92
2.89
2.88
2.87
2.86
2.84
2.83
2.82
2.82
2.80
2.79
2.78
2.66
2.65
2.64
2.63
2.62
2.61
1.49
1.48
N
5f
1H NMR
2.0
2.0
1.2
2.9
1.0
1.0
2.0
3.0
1.0
3.0
f1 (ppm)

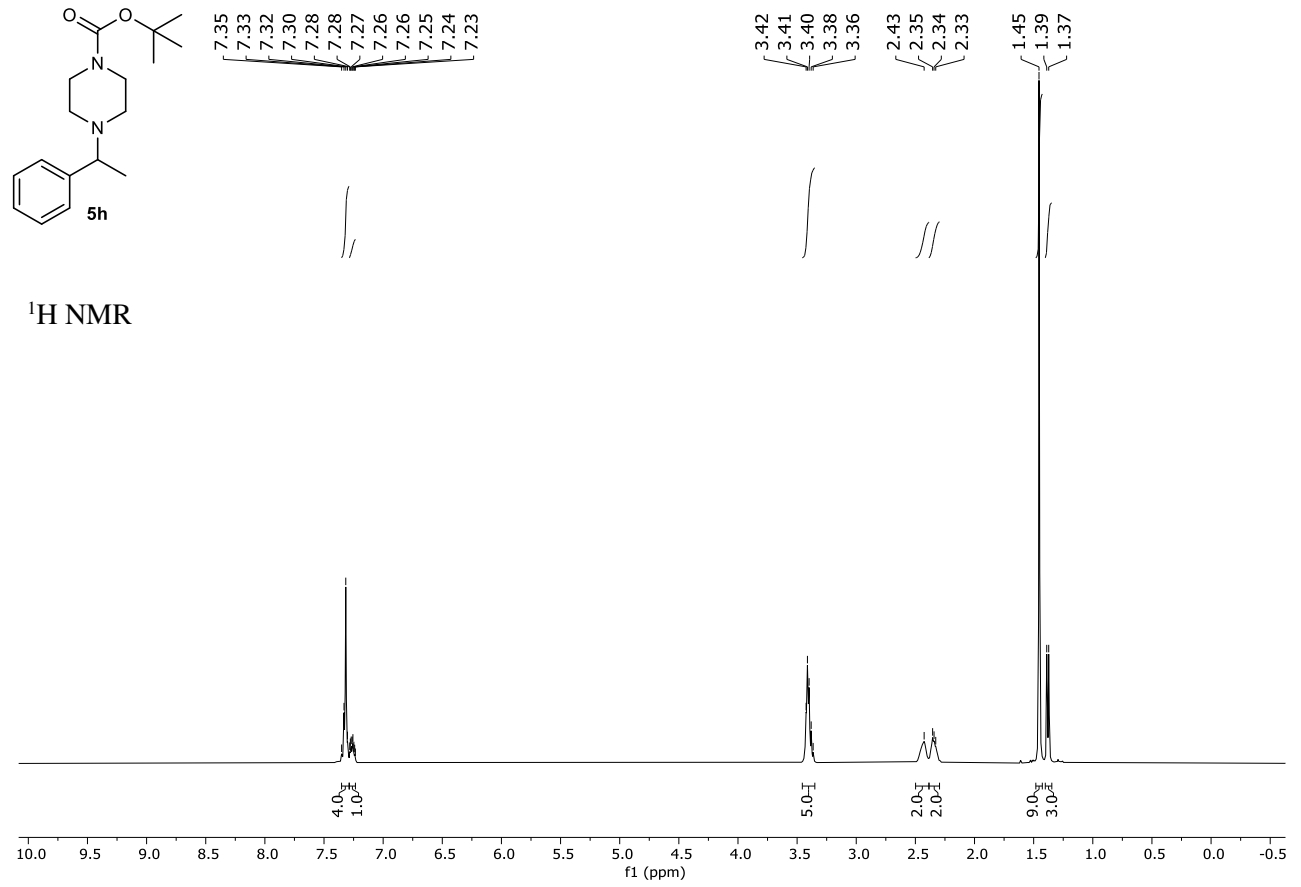


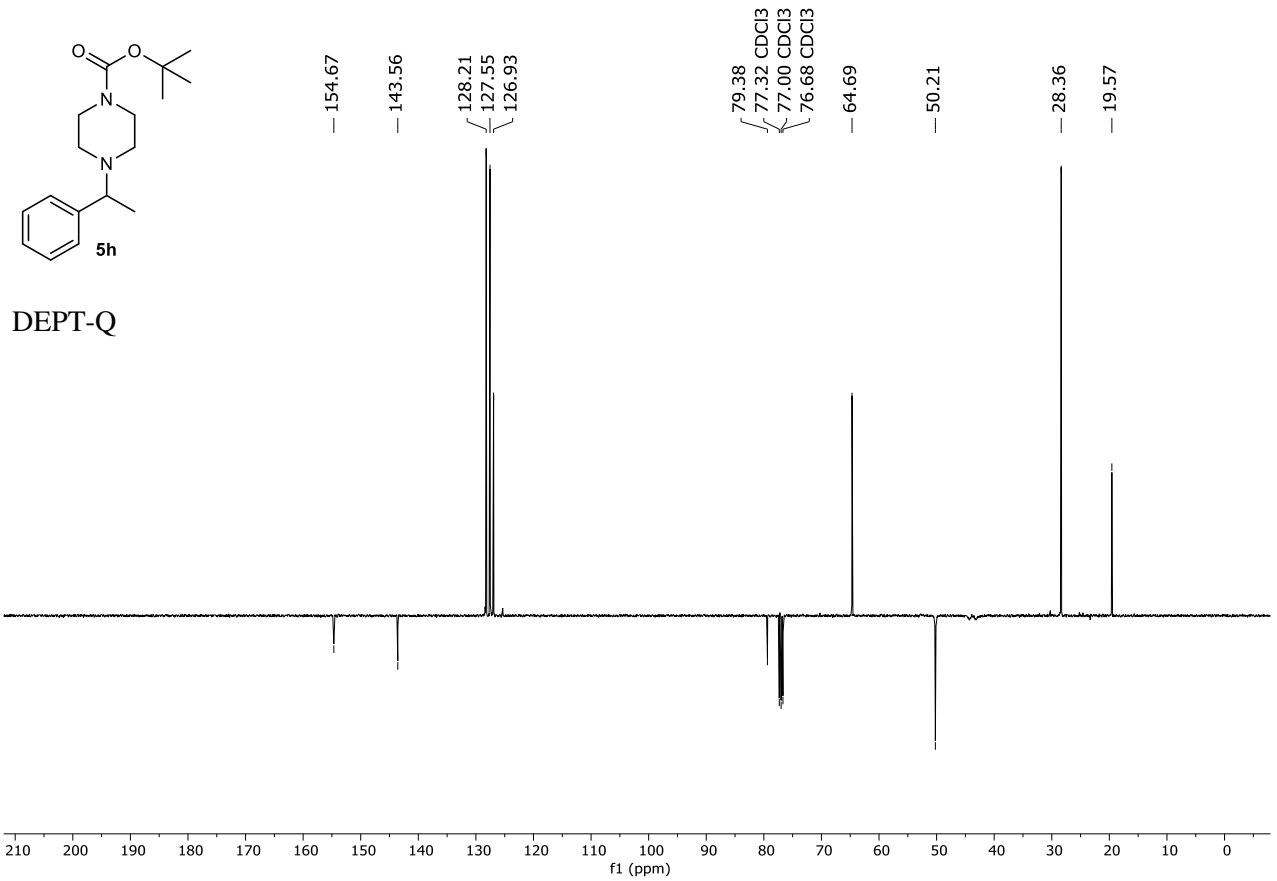
^{13}C NMR



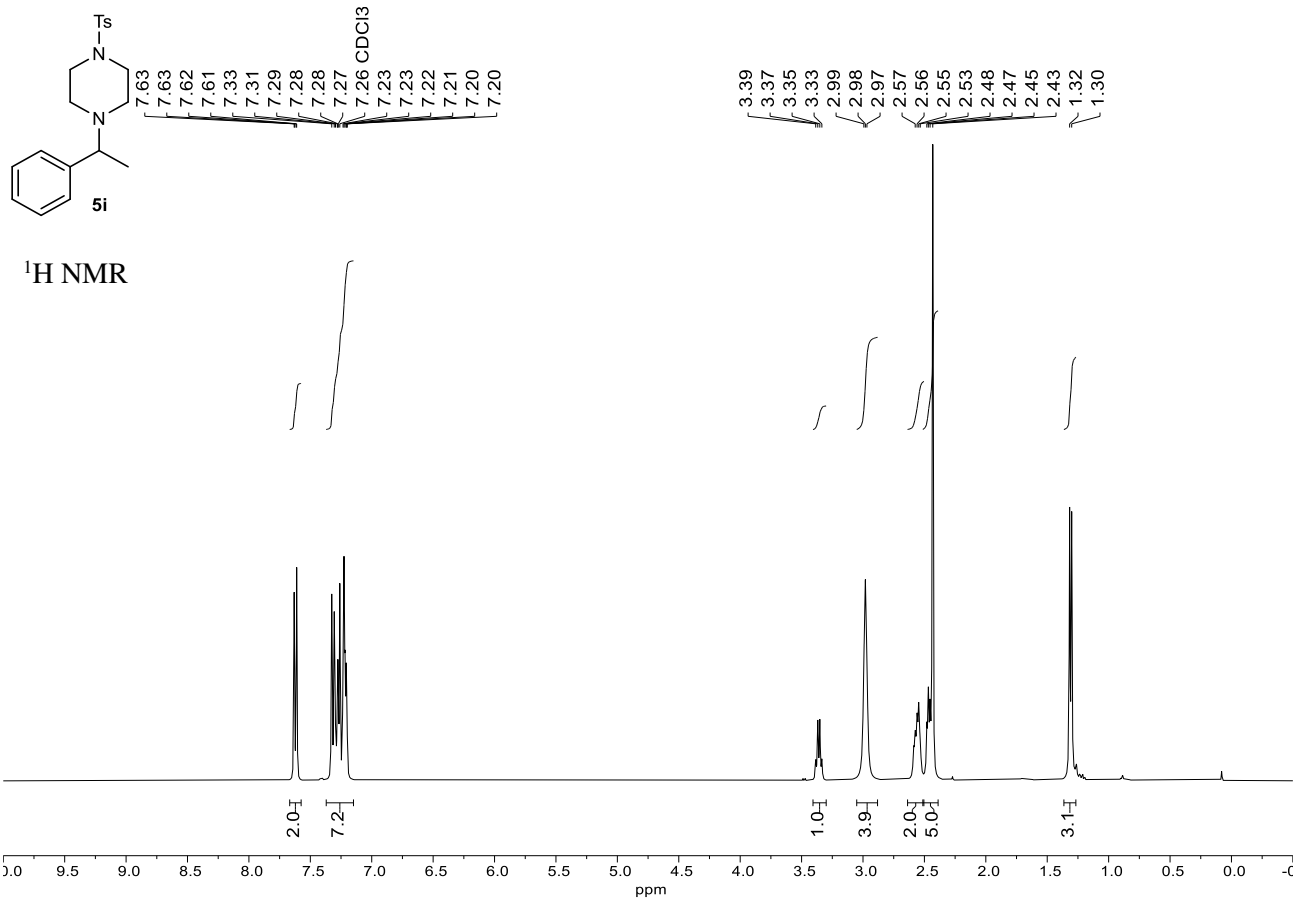
^{1}H NMR


5g
DEPT-Q
145.08
128.23
127.30
126.75
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
74.93
64.33
57.01
55.17
28.56
28.45
20.01
f1 (ppm)

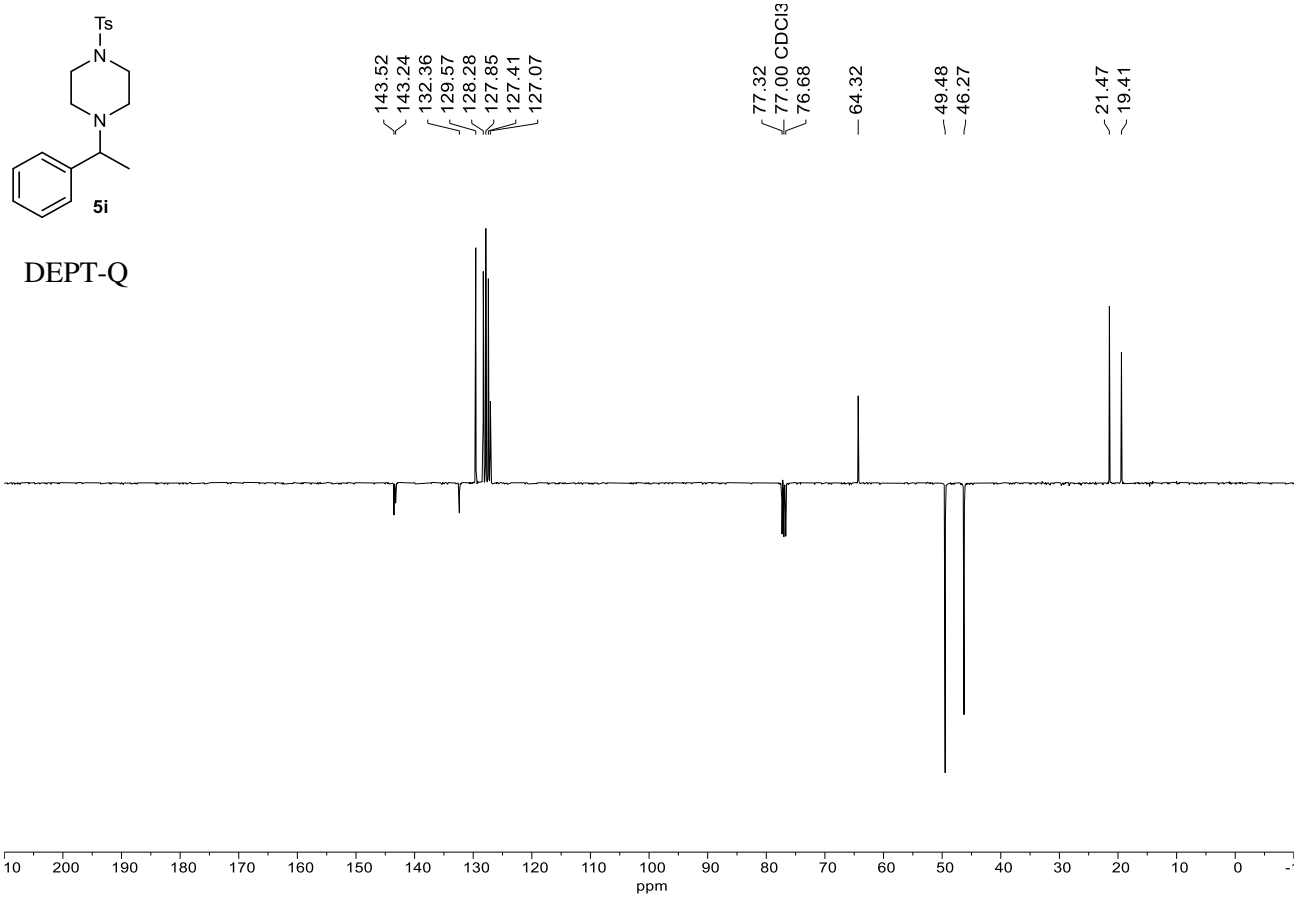

5h
^{1}H NMR
7.35
7.33
7.32
7.30
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.23
3.42
3.41
3.40
3.38
3.36
2.43
2.35
2.34
2.33
1.45
1.39
1.37
4.0
1.0
5.0
2.0
2.0
9.0
3.0
f1 (ppm)

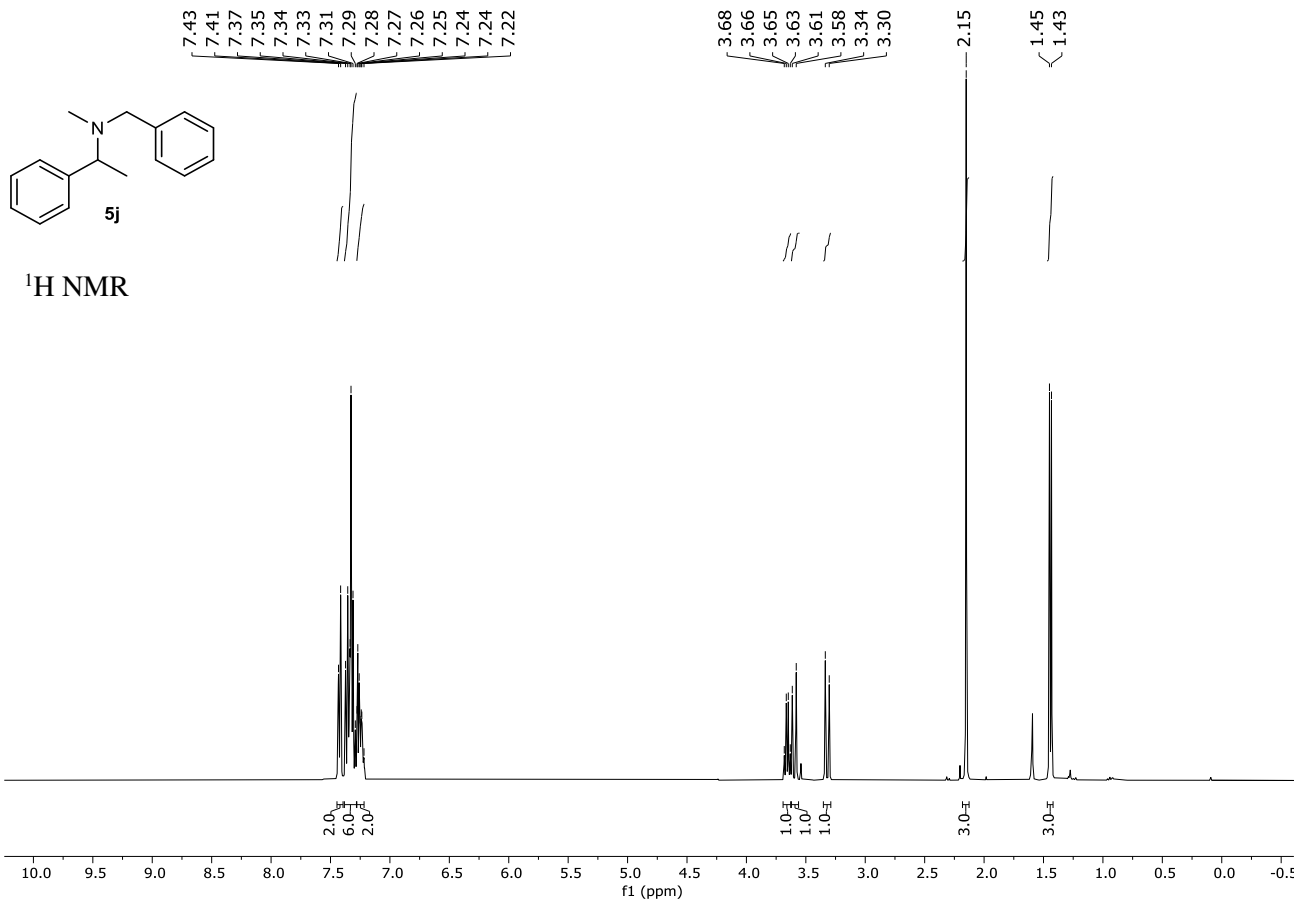

5h
154.67
143.56
128.21
127.55
126.93
79.38
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
64.69
50.21
28.36
19.57
f1 (ppm)

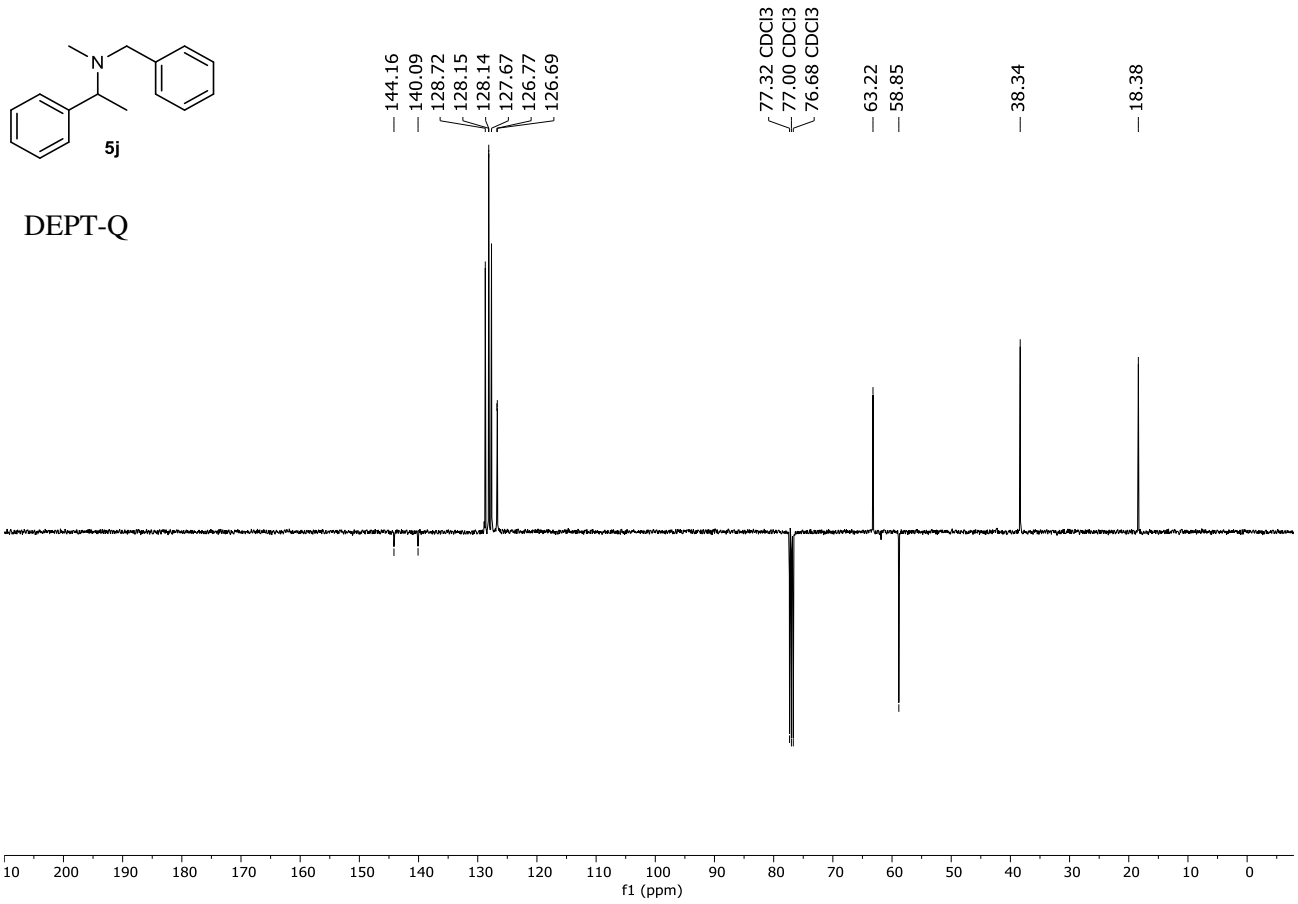
DEPT-Q

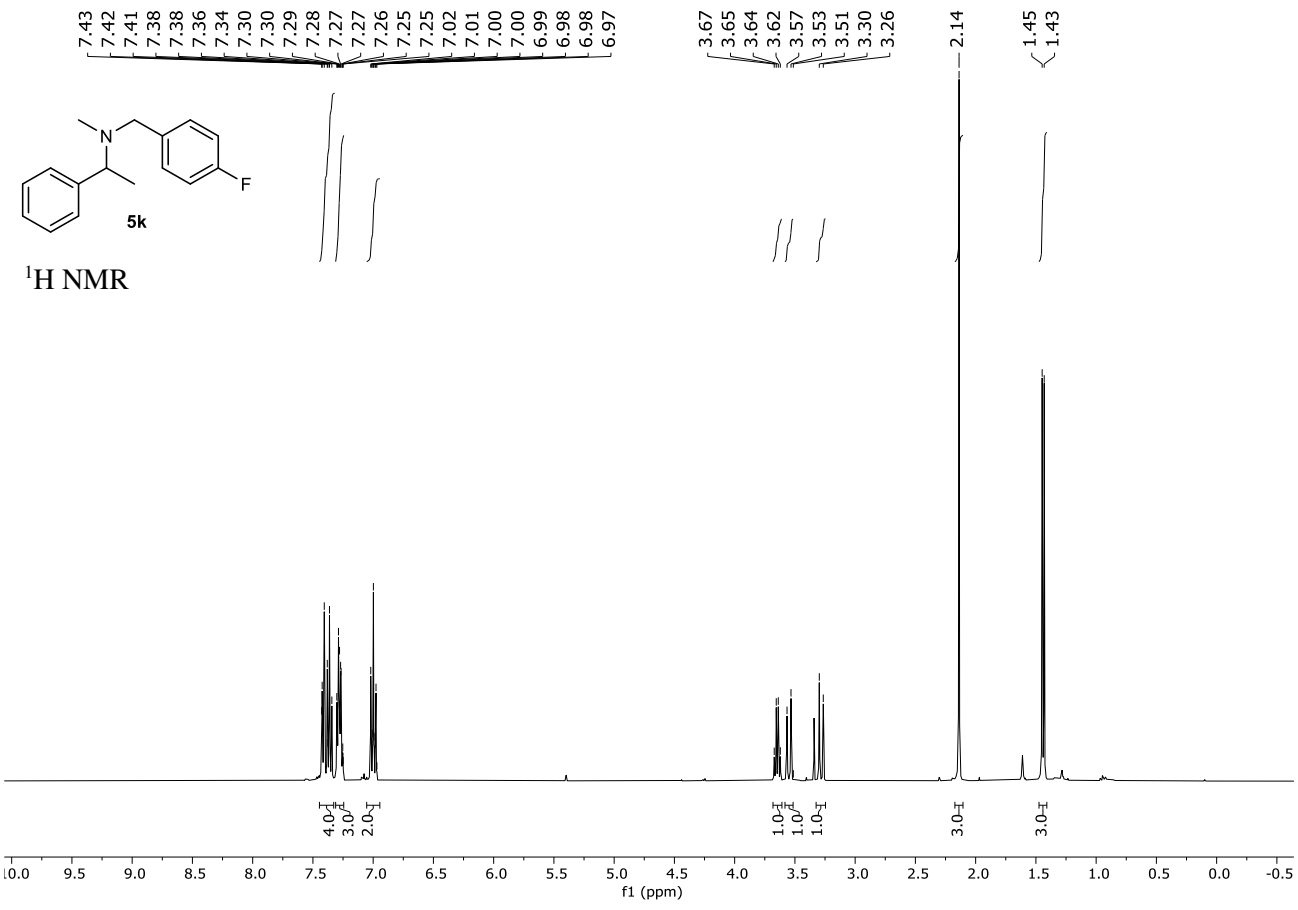

Ts
5i
7.63
7.63
7.62
7.61
7.33
7.31
7.29
7.28
7.28
7.27
7.26 CDCl3
7.23
7.23
7.22
7.21
7.20
7.20
3.39
3.37
3.35
3.33
2.99
2.98
2.97
2.57
2.56
2.55
2.53
2.48
2.47
2.45
2.43
1.32
1.30
2.0
7.2
1.0
3.9
2.0
5.0
3.1
ppm

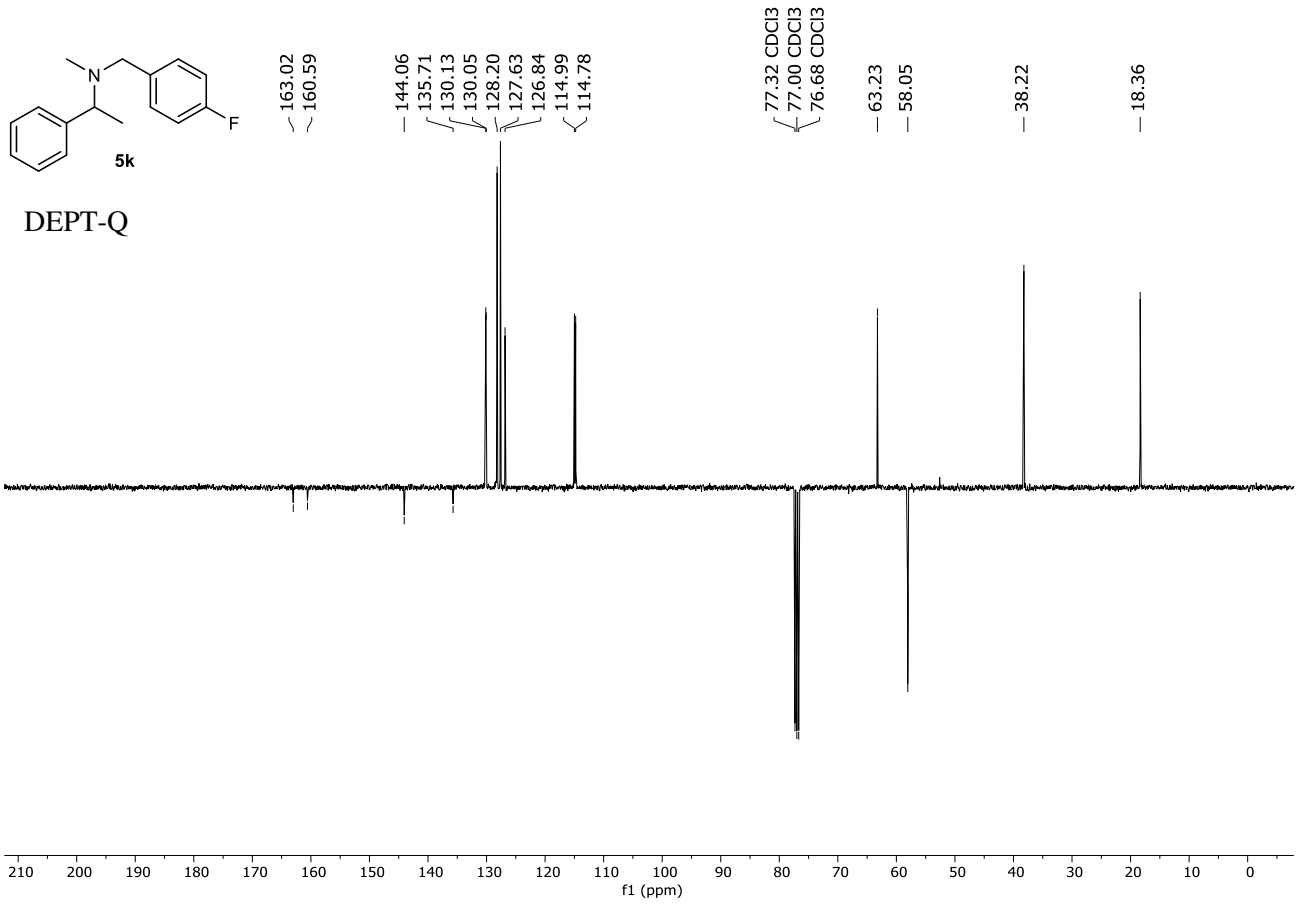
^{1}H NMR


Ts
N
N
5i
143.52
143.24
132.36
129.57
128.28
127.85
127.41
127.07
77.32
77.00 CDCl3
76.68
64.32
49.48
46.27
21.47
19.41
DEPT-Q
ppm

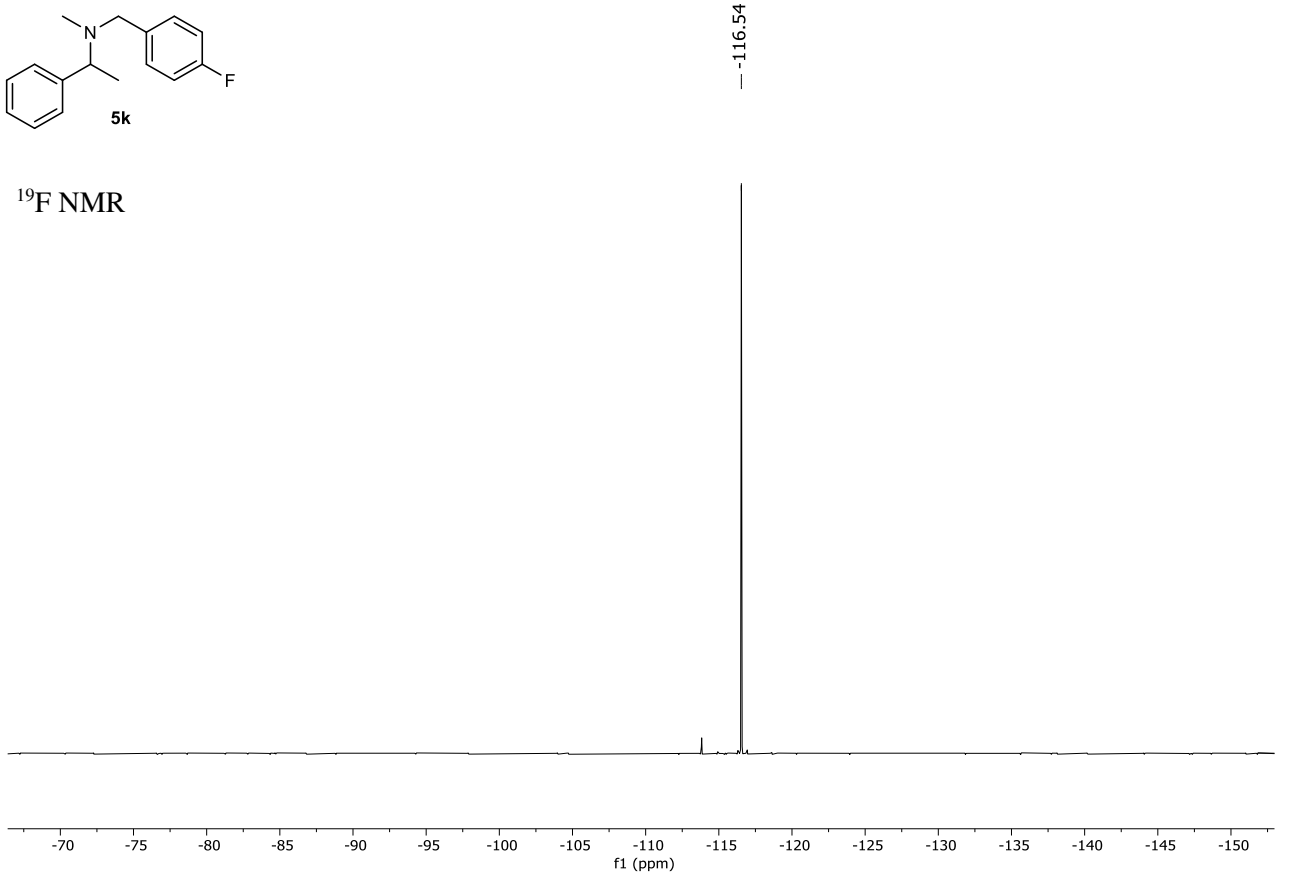

7.43
7.41
7.37
7.35
7.34
7.33
7.31
7.29
7.28
7.27
7.26
7.25
7.24
7.24
7.22
3.68
3.66
3.65
3.63
3.61
3.58
3.34
3.30
2.15
1.45
1.43
N
5j
1H NMR
2.0
6.0
2.0
1.0
1.0
1.0
3.0
3.0
f1 (ppm)


5j
DEPT-Q
144.16
140.09
128.72
128.15
128.14
127.67
126.77
126.69
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
63.22
58.85
38.34
18.38
f1 (ppm)

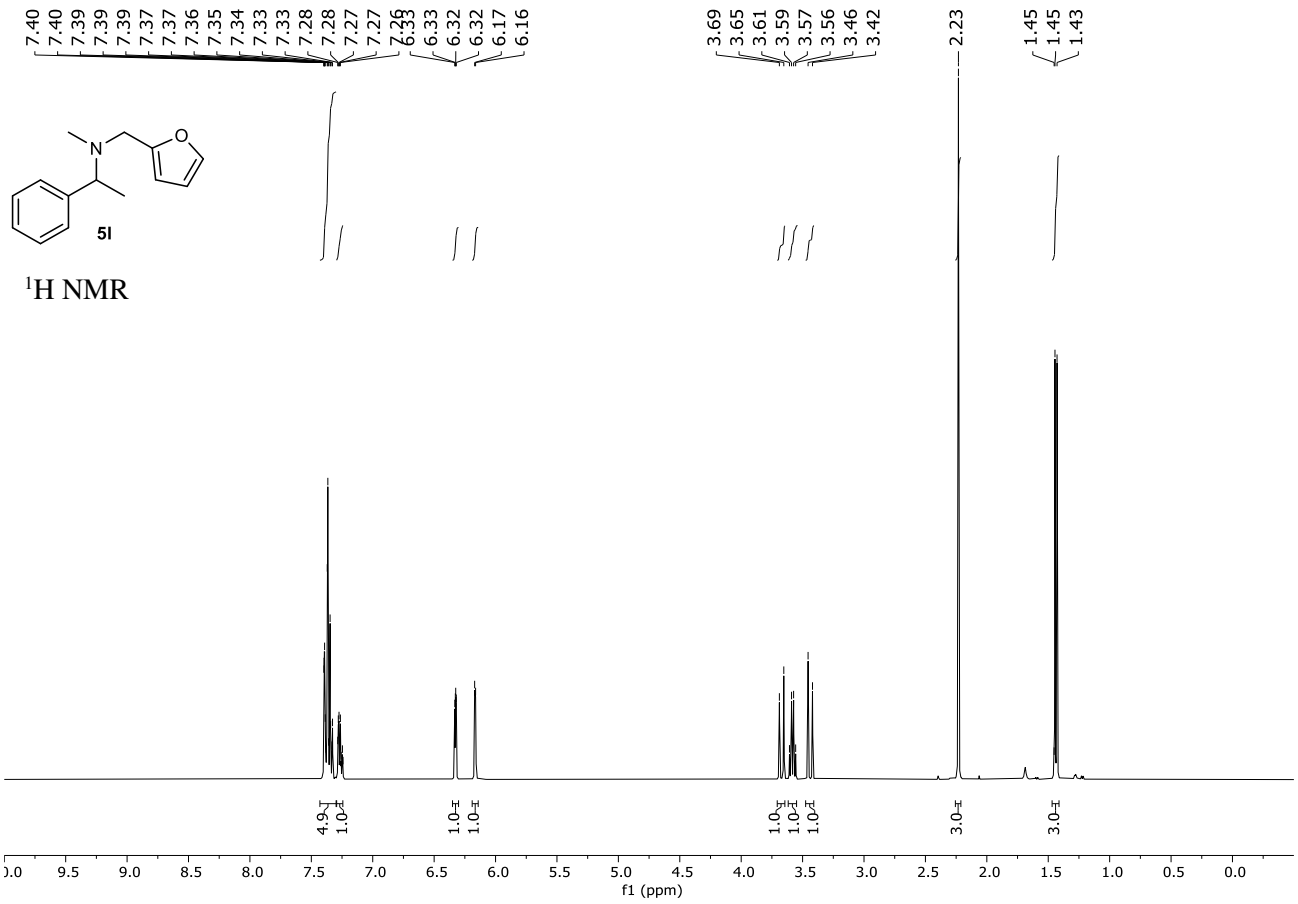

5k
1H NMR
7.43
7.42
7.41
7.38
7.38
7.36
7.34
7.30
7.30
7.29
7.28
7.27
7.27
7.26
7.25
7.25
7.02
7.01
7.00
7.00
6.99
6.98
6.98
6.97
3.67
3.65
3.64
3.62
3.57
3.53
3.51
3.30
3.26
2.14
1.45
1.43
4.0
3.0
2.0
1.0
1.0
1.0
3.0
3.0
f1 (ppm)



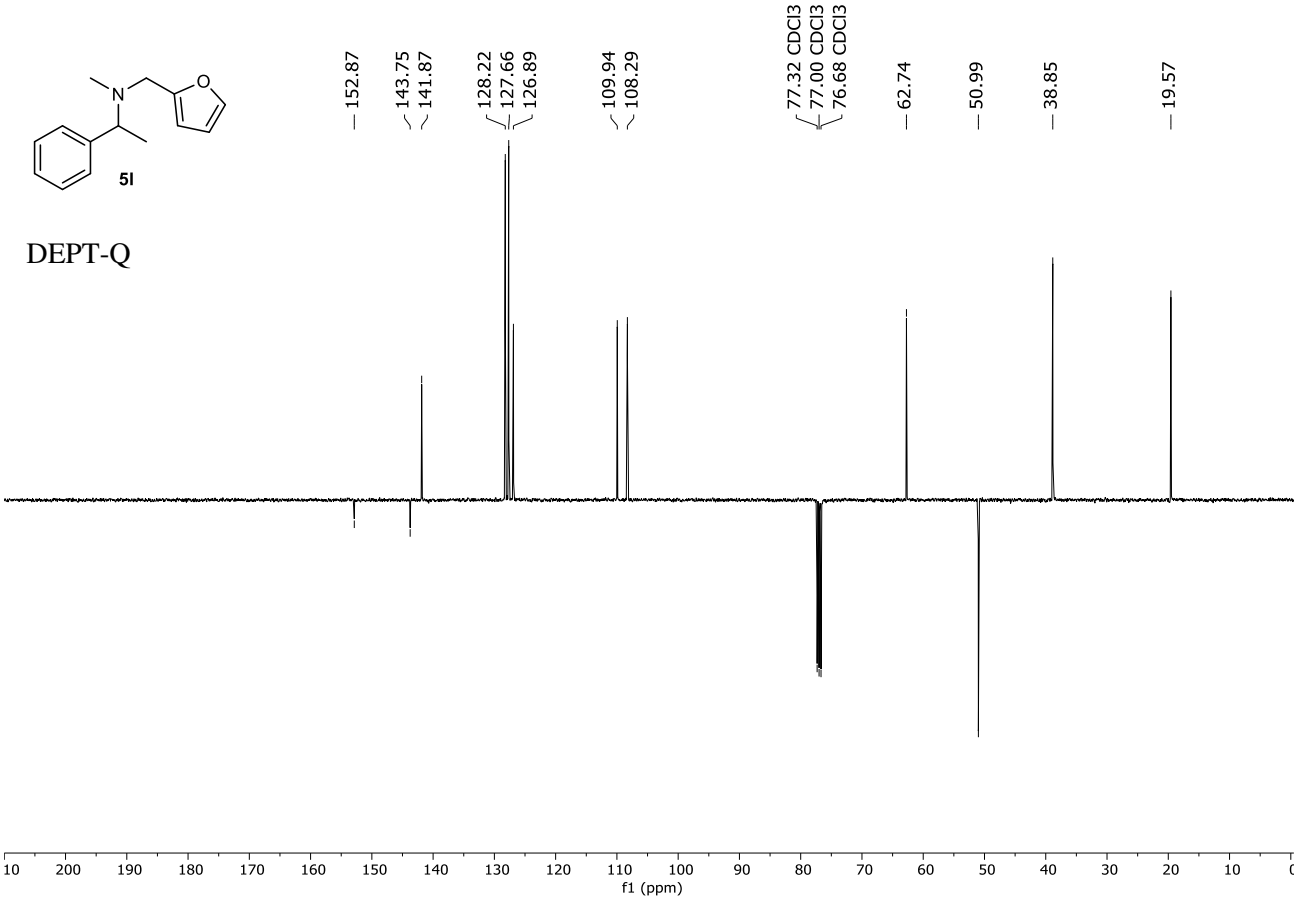
DEPT-Q



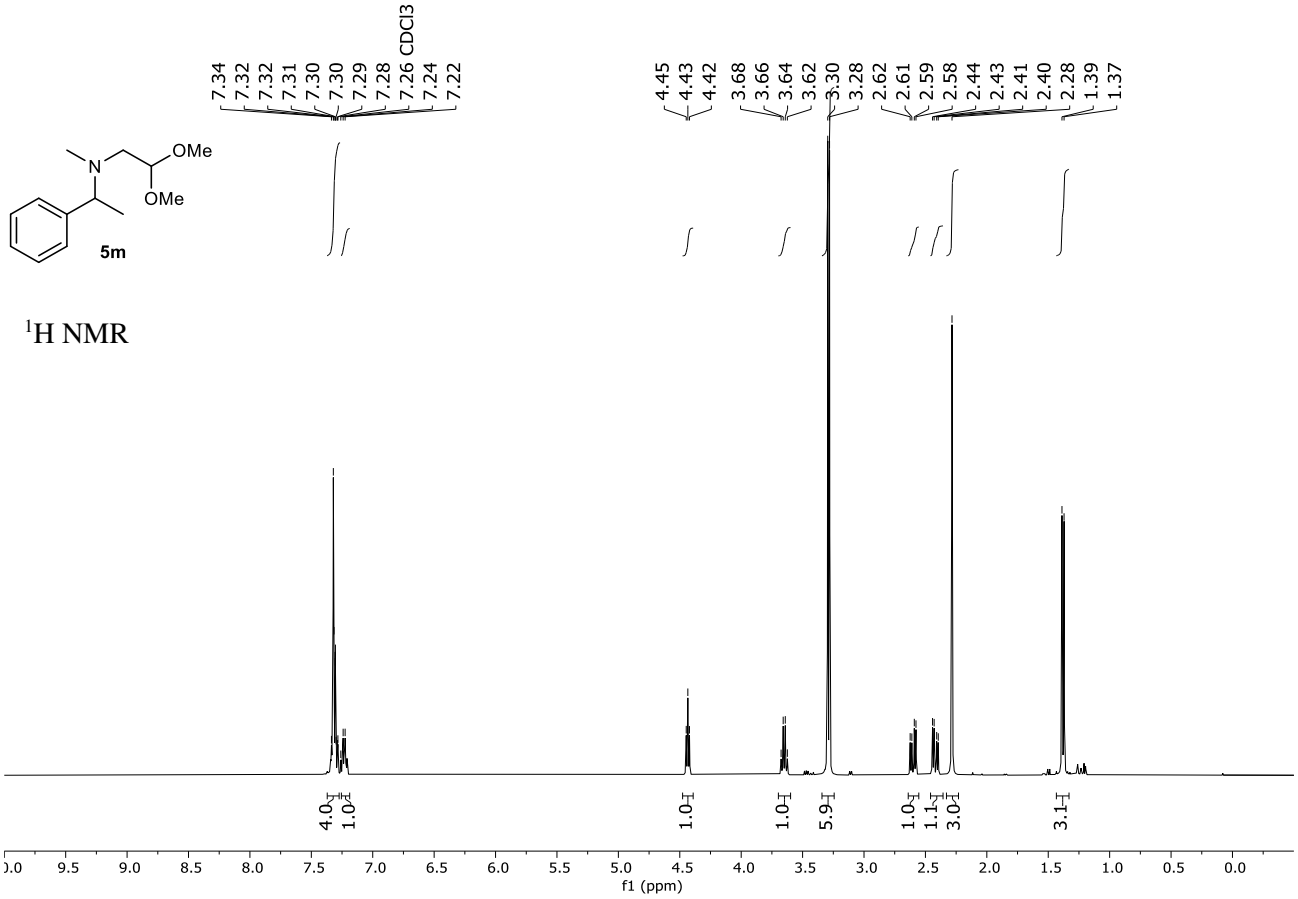
^{19}F NMR


7.40
7.40
7.39
7.39
7.39
7.37
7.37
7.36
7.35
7.34
7.33
7.33
7.28
7.28
7.27
7.27
7.26
6.33
6.33
6.32
6.32
6.17
6.16
3.69
3.65
3.61
3.59
3.57
3.56
3.46
3.42
2.23
1.45
1.45
1.43
N
O
5l
4.9
1.0
1.0
1.0
1.0
1.0
1.0
3.0
3.0
f1 (ppm)

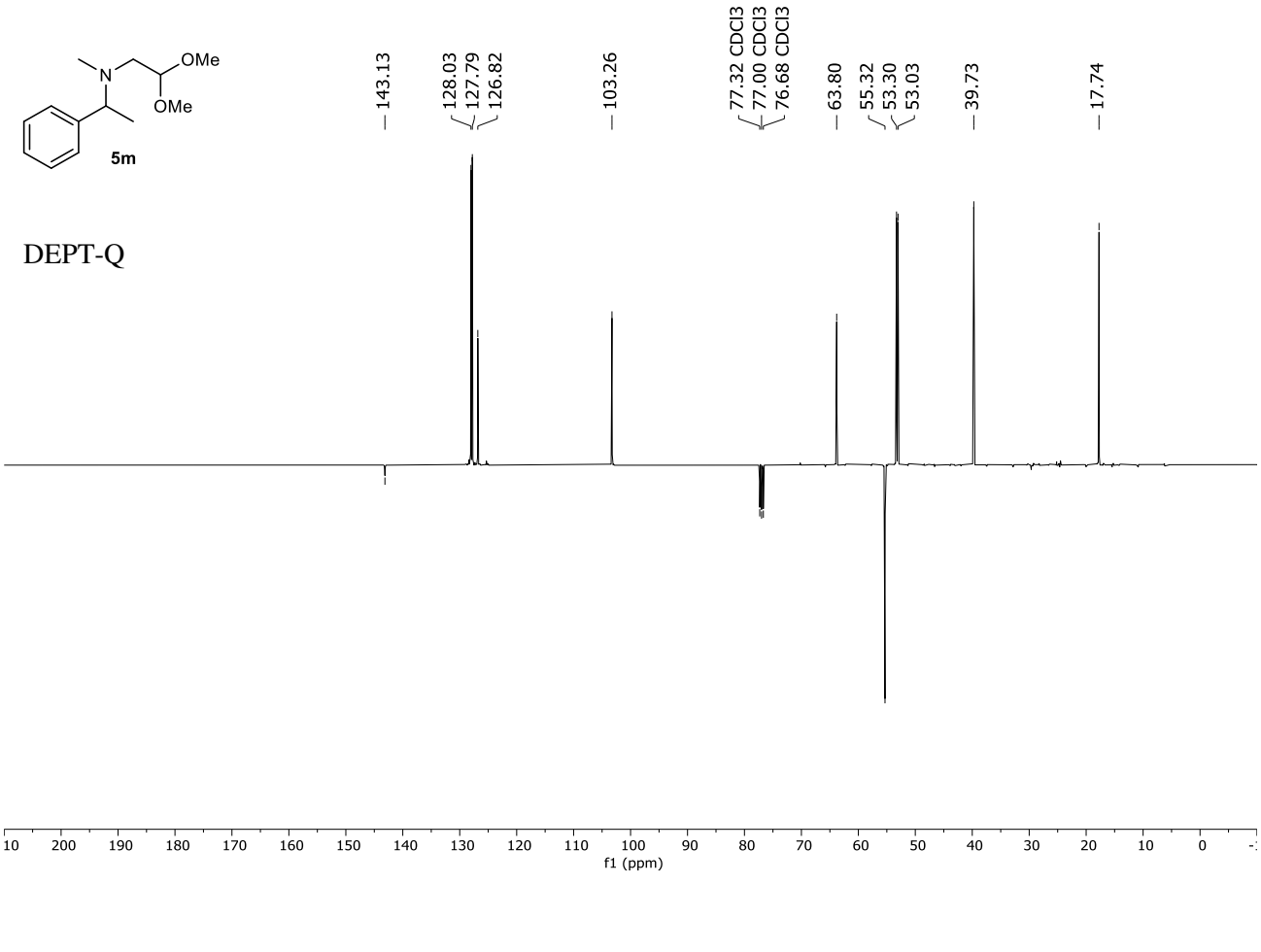
^{1}H NMR


152.87
143.75
141.87
128.22
127.66
126.89
109.94
108.29
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
62.74
50.99
38.85
19.57
N
O
5l
f1 (ppm)

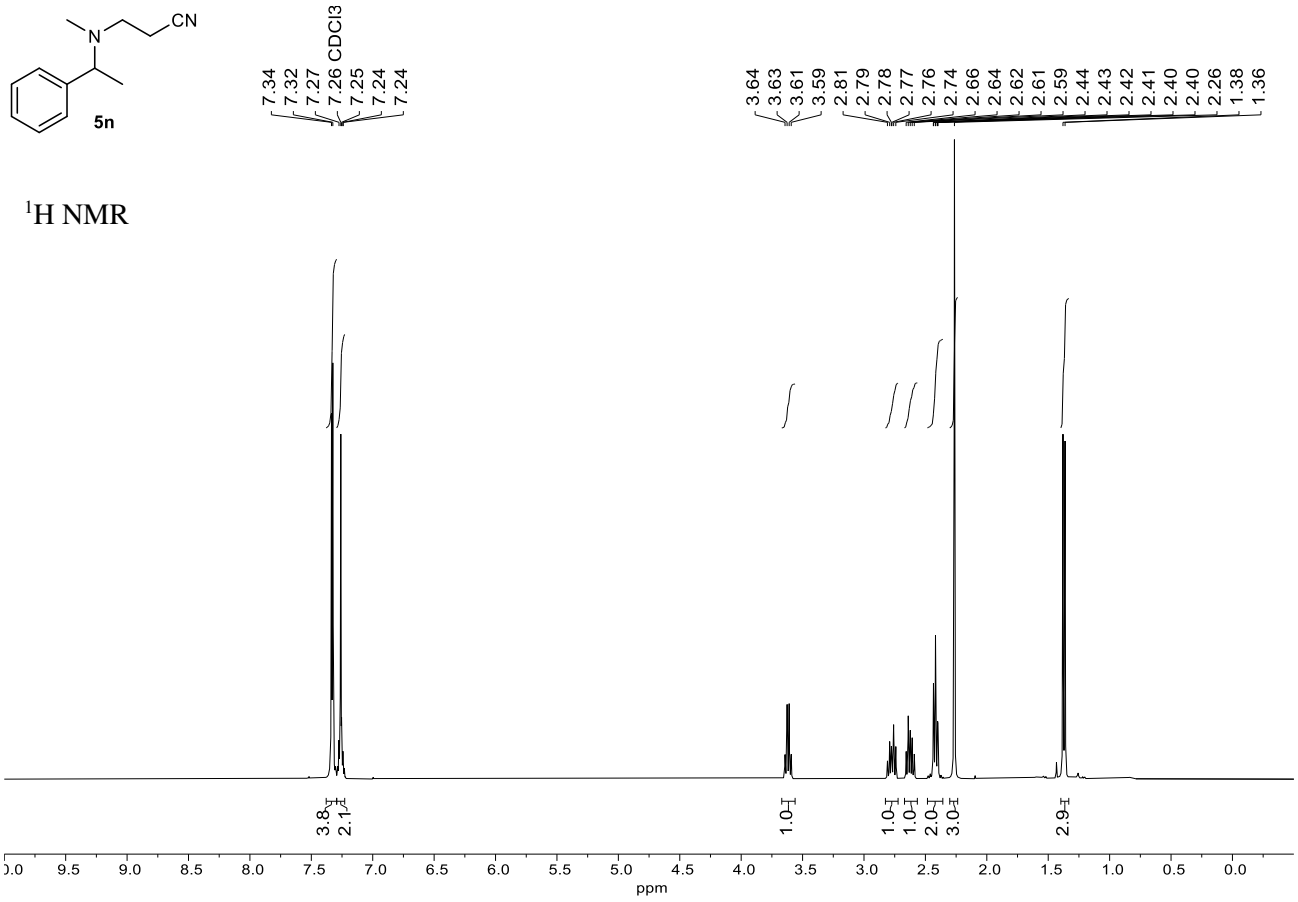
DEPT-Q


7.34
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.26 CDCl3
7.24
7.22
4.45
4.43
4.42
3.68
3.66
3.64
3.62
3.30
3.28
2.62
2.61
2.59
2.58
2.44
2.43
2.41
2.40
2.28
1.39
1.37
N
OMe
OMe
5m
4.0
1.0
1.0
1.0
5.9
1.0
1.1
3.0
3.1
f1 (ppm)

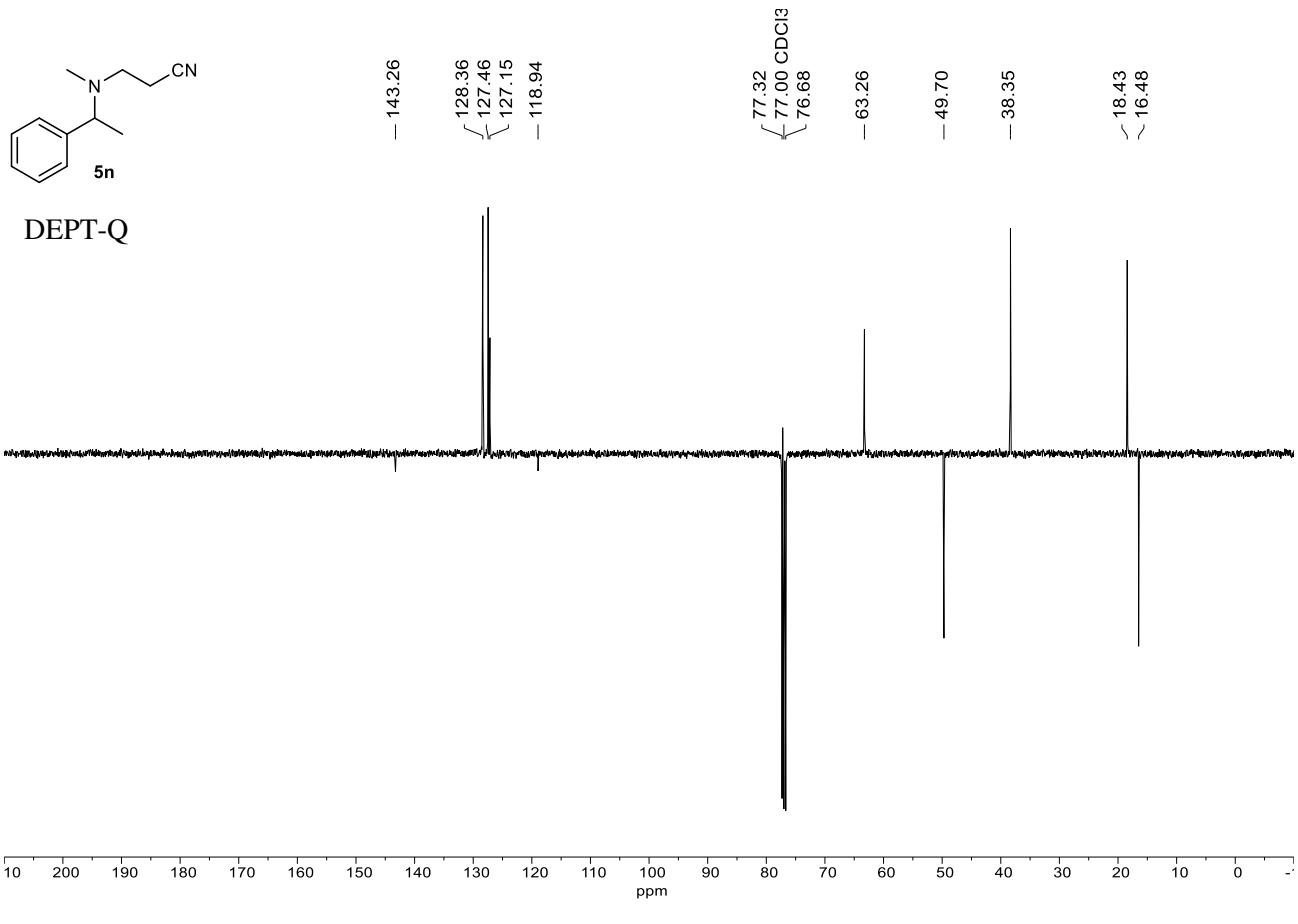
^{1}H NMR


143.13
128.03
127.79
126.82
103.26
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
63.80
55.32
53.30
53.03
39.73
17.74
N
OMe
OMe
5m
f1 (ppm)

DEPT-Q

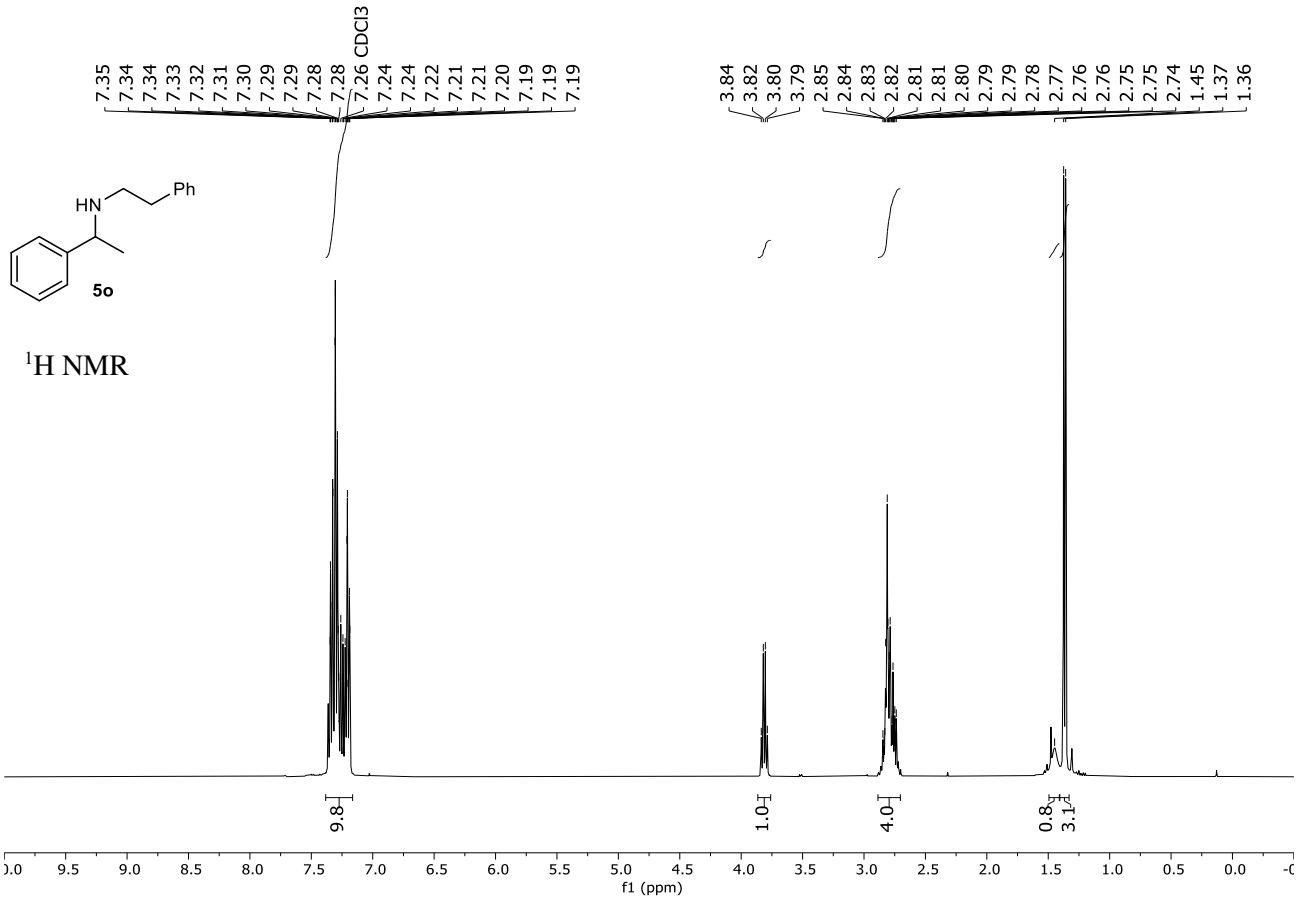

CN
N
5n
7.34
7.32
7.27
7.26 CDCl3
7.25
7.24
7.24
3.64
3.63
3.61
3.59
2.81
2.79
2.78
2.77
2.76
2.74
2.66
2.64
2.62
2.61
2.59
2.44
2.43
2.42
2.41
2.40
2.40
2.26
1.38
1.36
3.8
2.1
1.0
1.0
1.0
2.0
3.0
2.9
ppm

^{1}H NMR

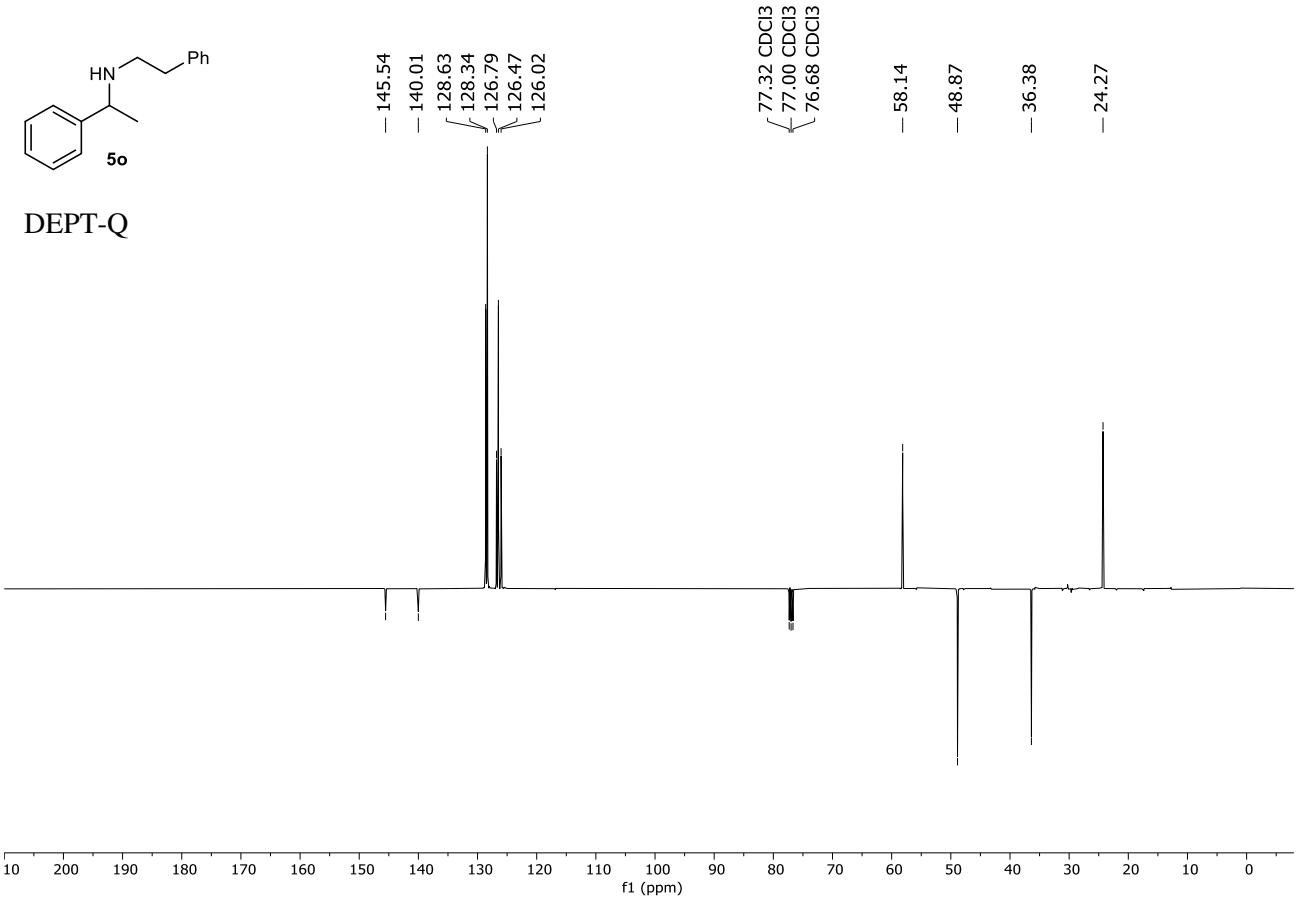

CN
N
5n
143.26
128.36
127.46
127.15
118.94
77.32
77.00 CDCl3
76.68
63.26
49.70
38.35
18.43
16.48
ppm

DEPT-Q

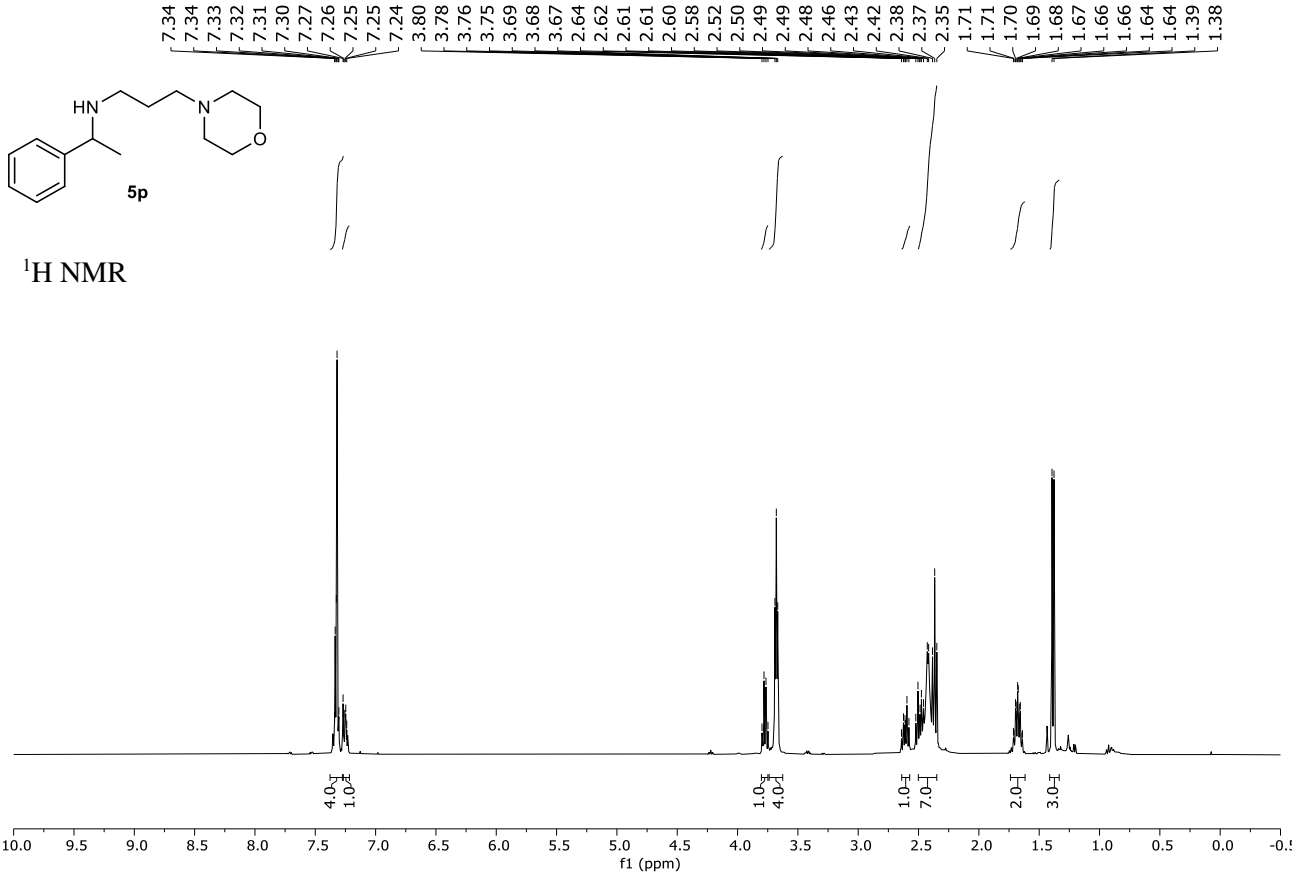
4.3. Coupling of Primary Amines



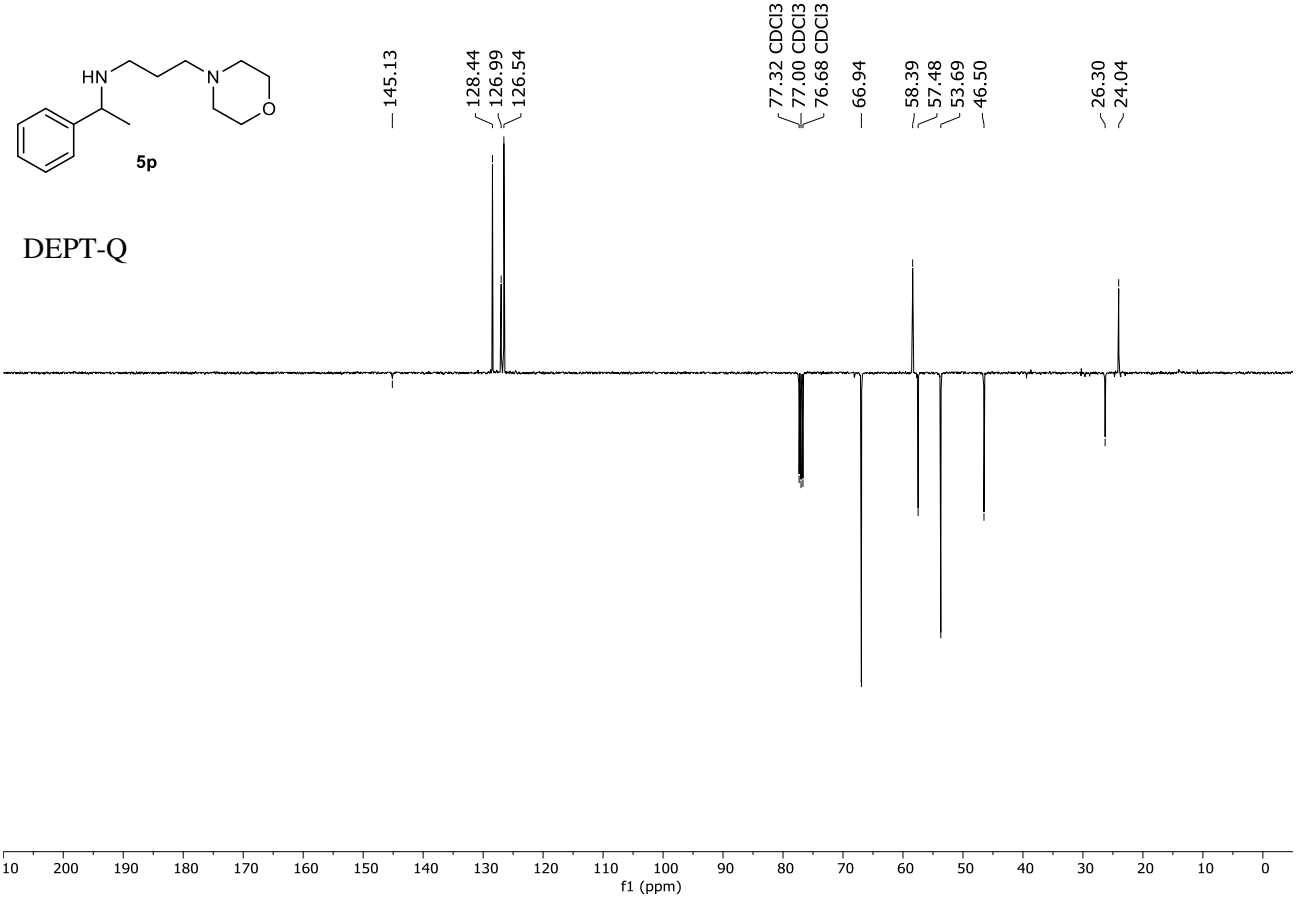
^{1}H NMR



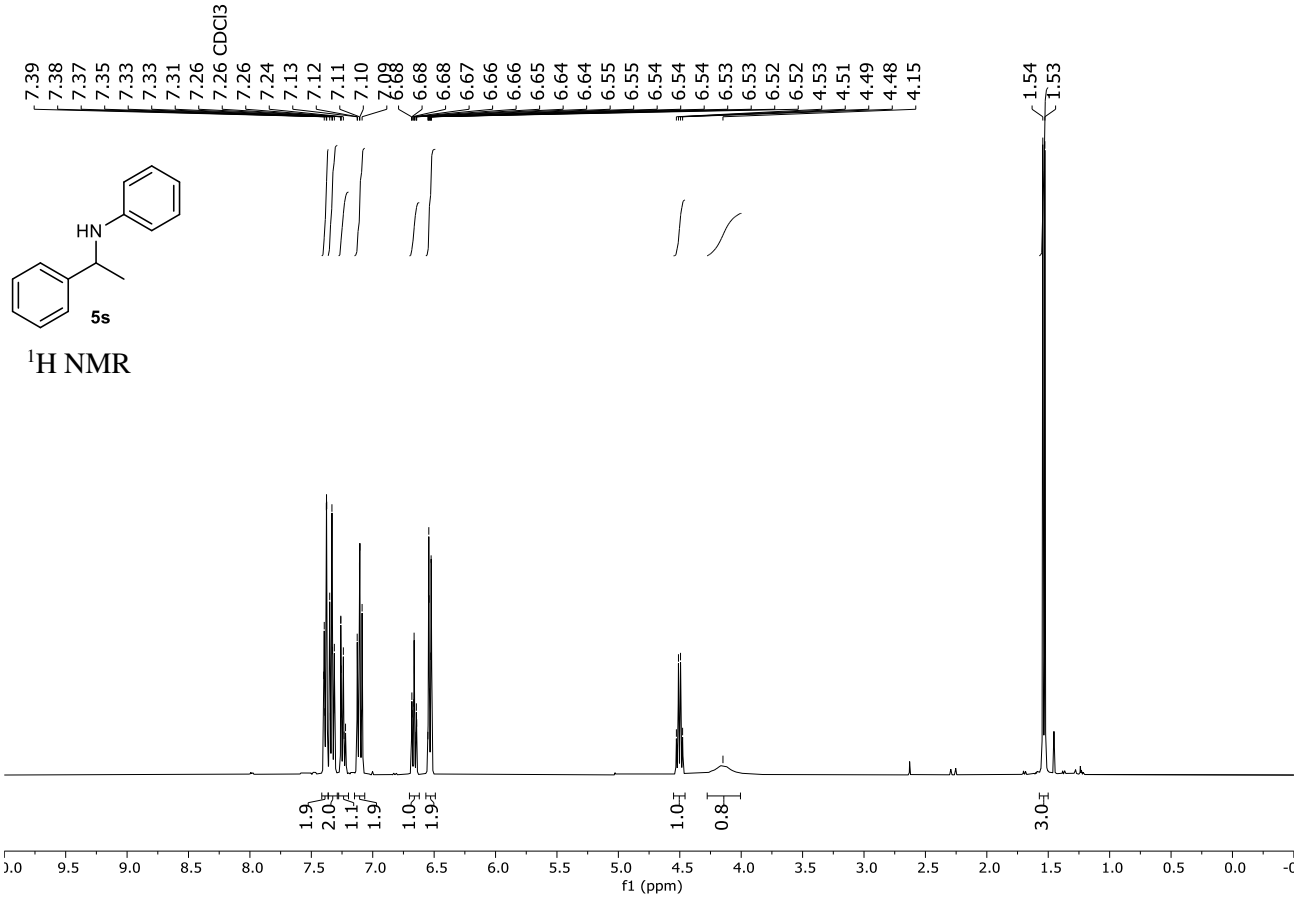
DEPT-Q


7.34
7.34
7.33
7.32
7.31
7.30
7.27
7.26
7.25
7.25
7.24
3.80
3.78
3.76
3.75
3.69
3.68
3.67
2.64
2.62
2.61
2.61
2.60
2.58
2.52
2.50
2.49
2.49
2.48
2.46
2.43
2.42
2.38
2.37
2.35
1.71
1.71
1.70
1.69
1.68
1.67
1.66
1.66
1.64
1.64
1.39
1.38
HN
N
O
5p
4.0
1.0
1.0
4.0
1.0
7.0
2.0
3.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

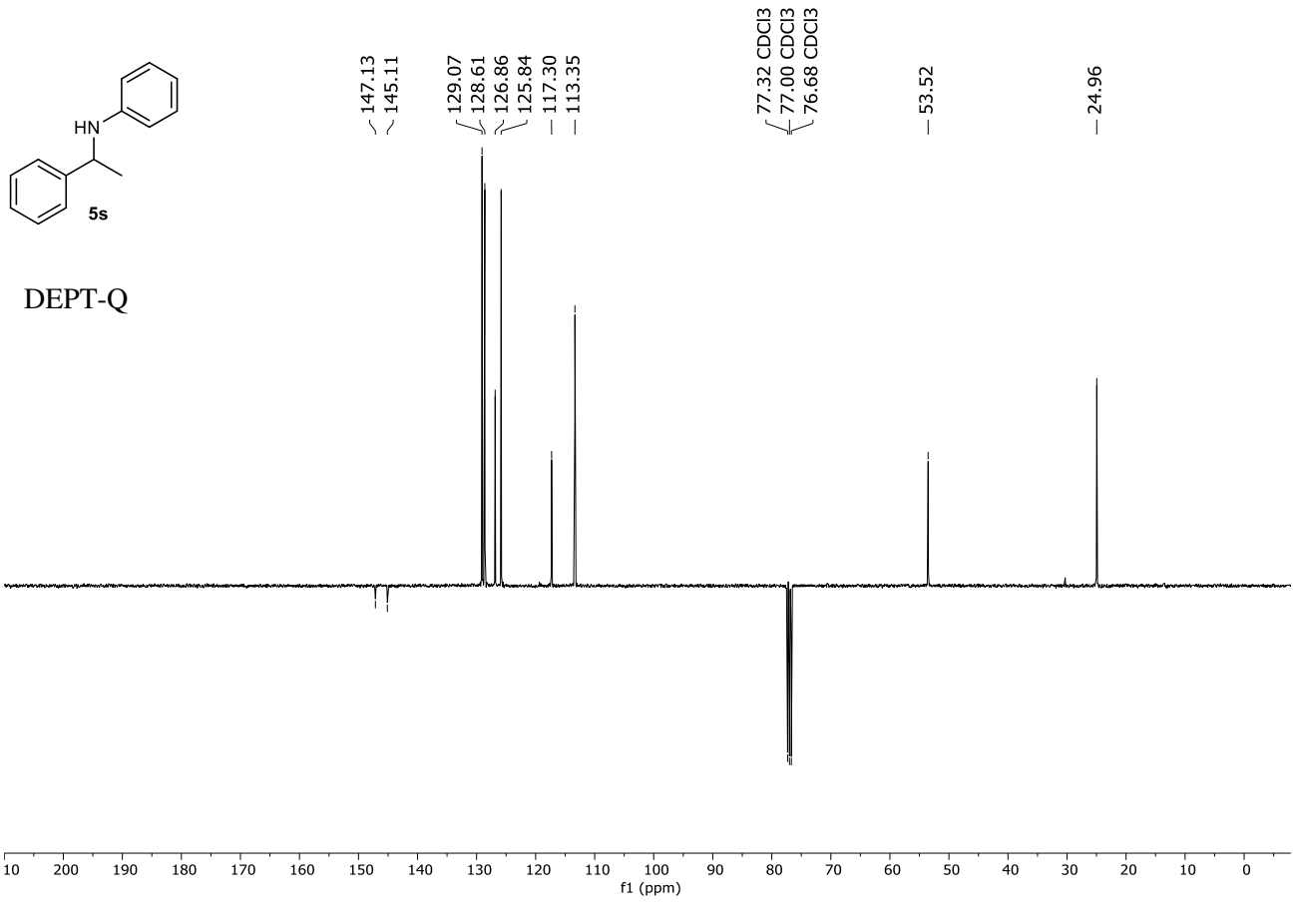
^{1}H NMR


HN
N
O
5p
145.13
128.44
126.99
126.54
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
66.94
58.39
57.48
53.69
46.50
26.30
24.04
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

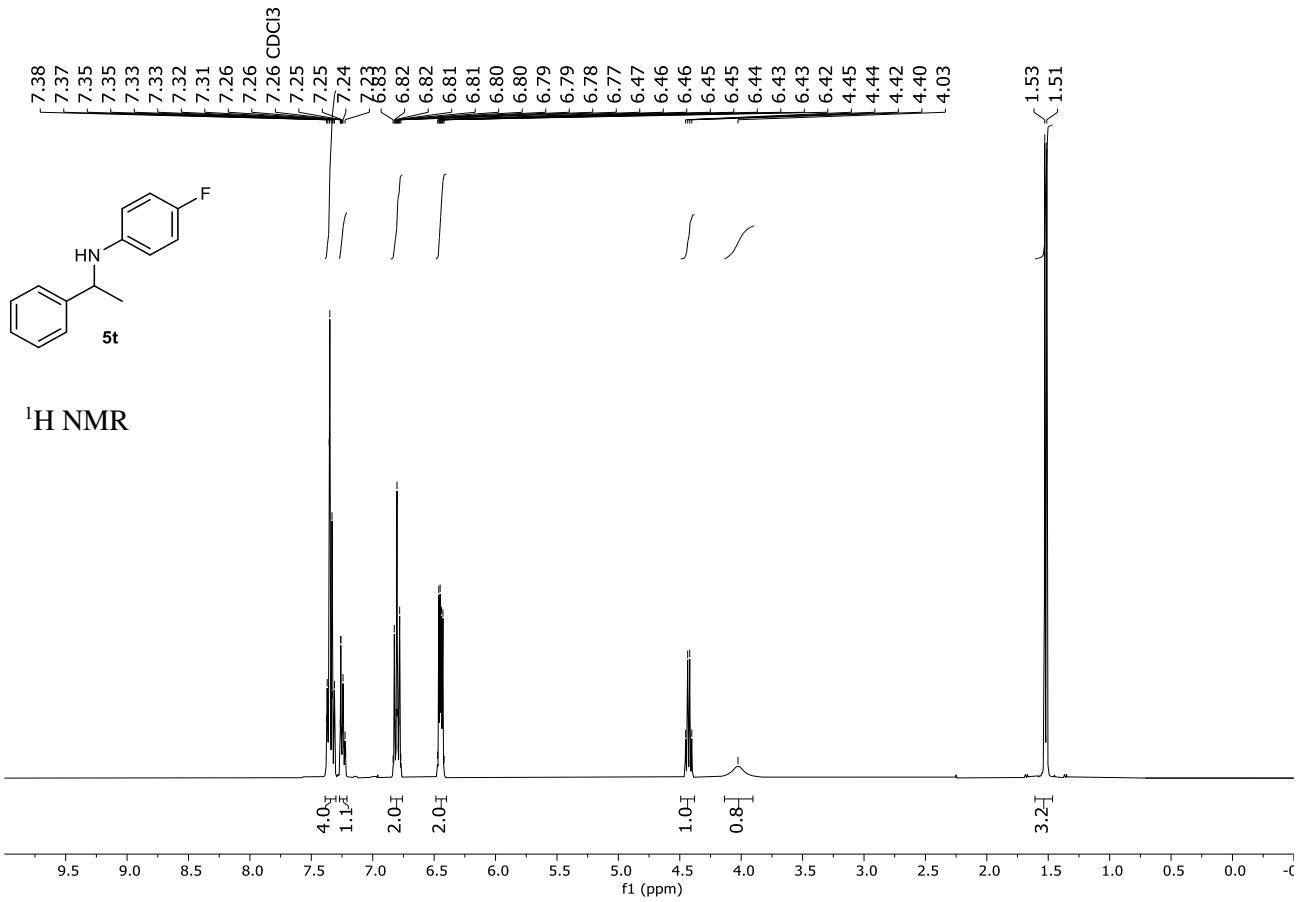
DEPT-Q


7.39
7.38
7.37
7.35
7.33
7.33
7.31
7.26
7.26 CDCl3
7.26
7.24
7.13
7.12
7.11
7.10
7.09
7.08
6.68
6.68
6.67
6.66
6.66
6.65
6.64
6.64
6.55
6.55
6.54
6.54
6.54
6.53
6.53
6.52
6.52
4.53
4.51
4.49
4.48
4.15
1.54
1.53
HN
5s
1.9
2.0
1.1
1.9
1.0
1.9
1.0
0.8
3.0
f1 (ppm)

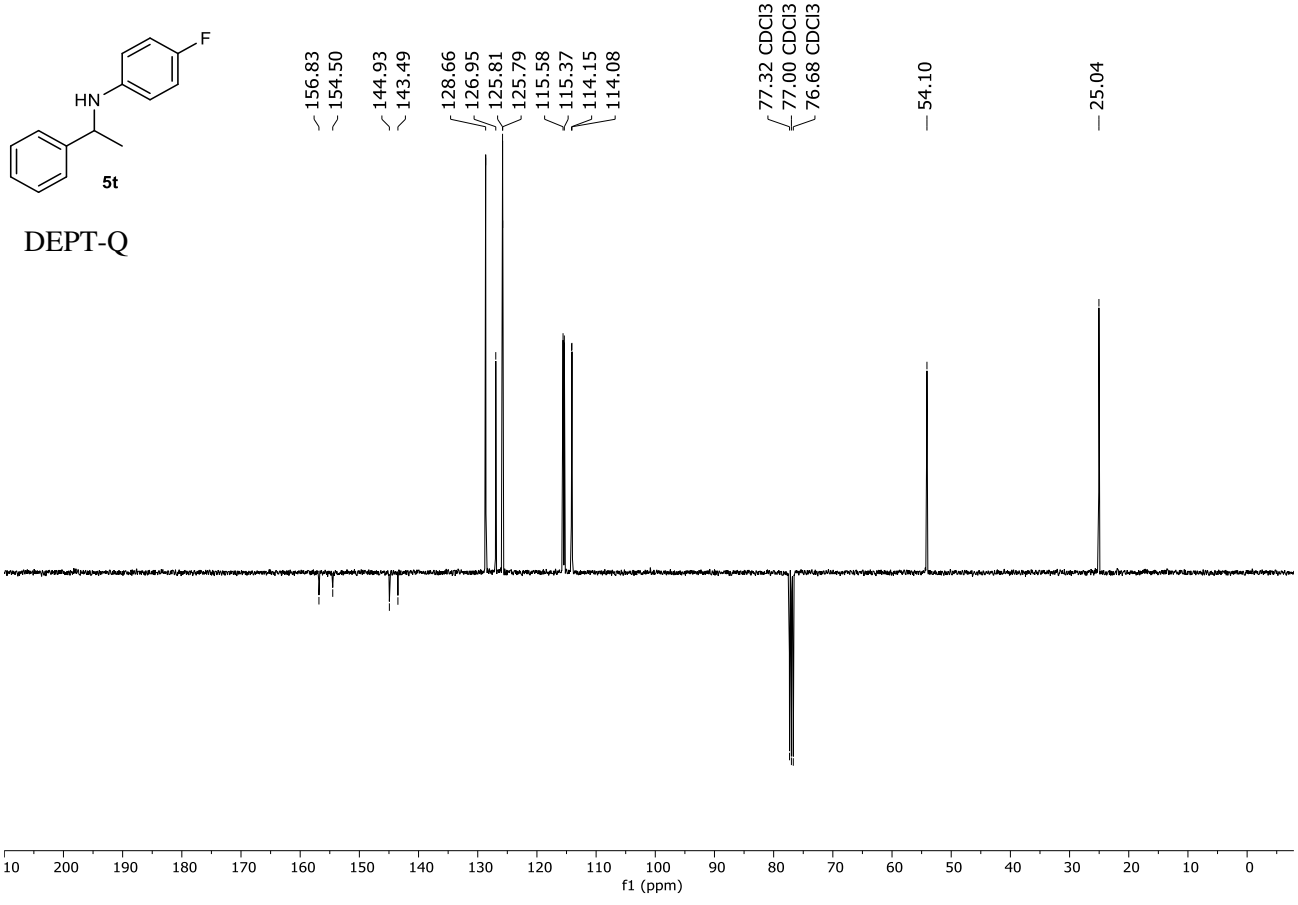
^{1}H NMR


147.13
145.11
129.07
128.61
126.86
125.84
117.30
113.35
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
53.52
24.96
HN
5s
f1 (ppm)

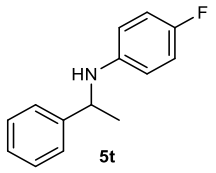
DEPT-Q


7.38
7.37
7.35
7.35
7.33
7.33
7.32
7.31
7.26
7.26 CDCl3
7.25
7.25
7.24
7.23
6.83
6.82
6.82
6.81
6.81
6.80
6.80
6.79
6.79
6.78
6.77
6.47
6.46
6.46
6.45
6.45
6.44
6.43
6.43
6.42
4.45
4.44
4.42
4.40
4.03
1.53
1.51
F
HN
5t
4.0
1.1
2.0
2.0
1.0
0.8
3.2
f1 (ppm)

^{1}H NMR

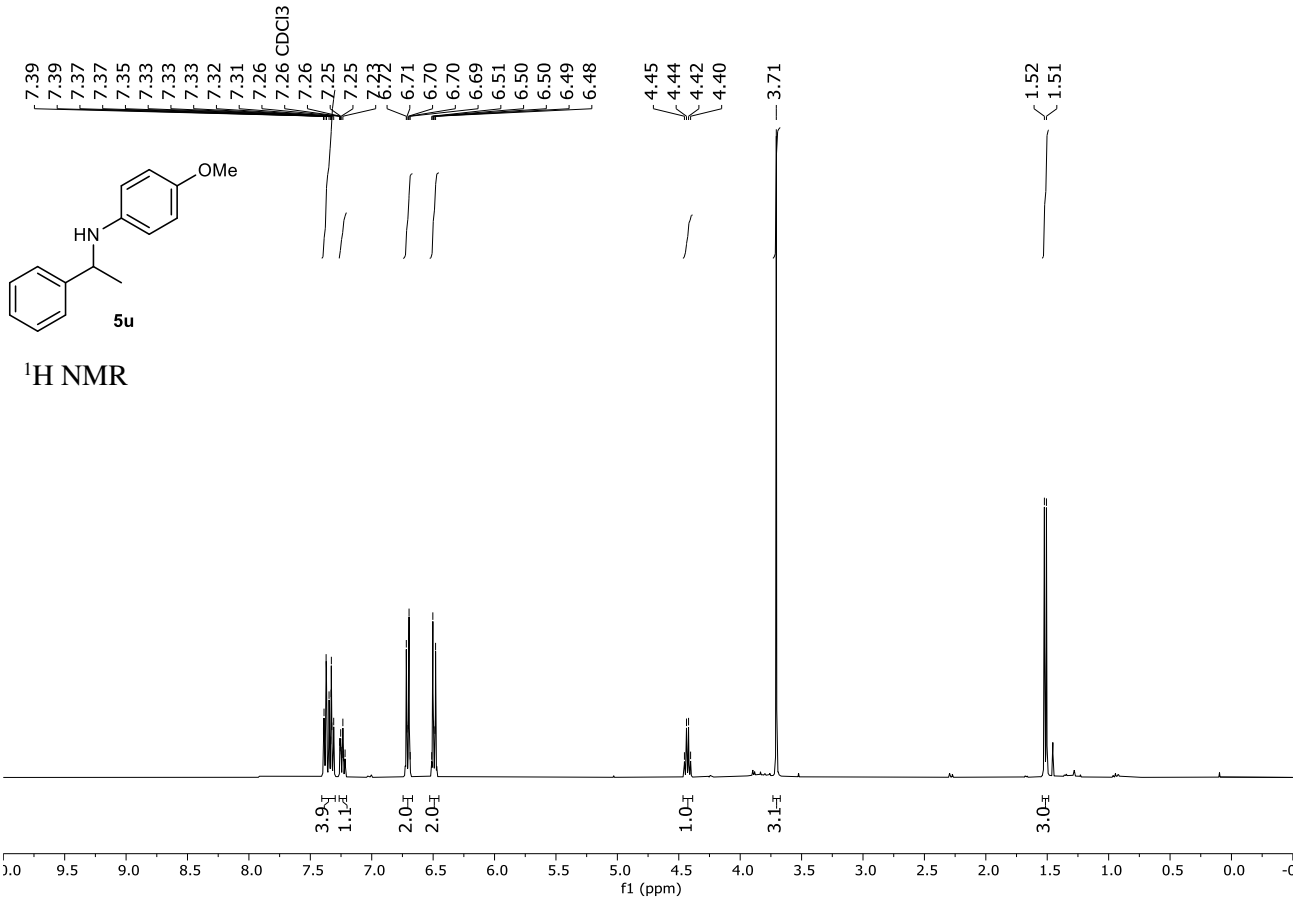

F
HN
5t
156.83
154.50
144.93
143.49
128.66
126.95
125.81
125.79
115.58
115.37
114.15
114.08
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
54.10
25.04
f1 (ppm)

DEPT-Q



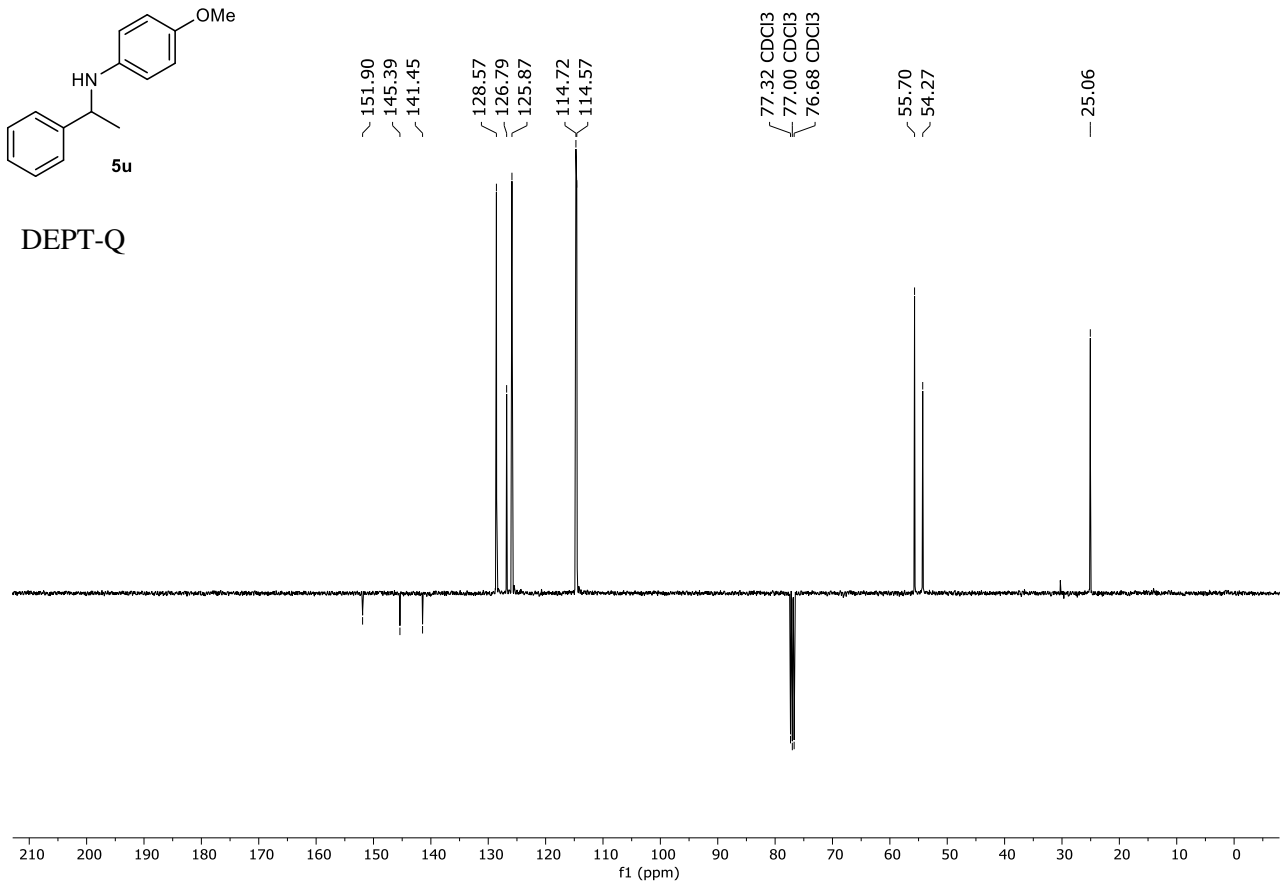
5t

^{19}F NMR

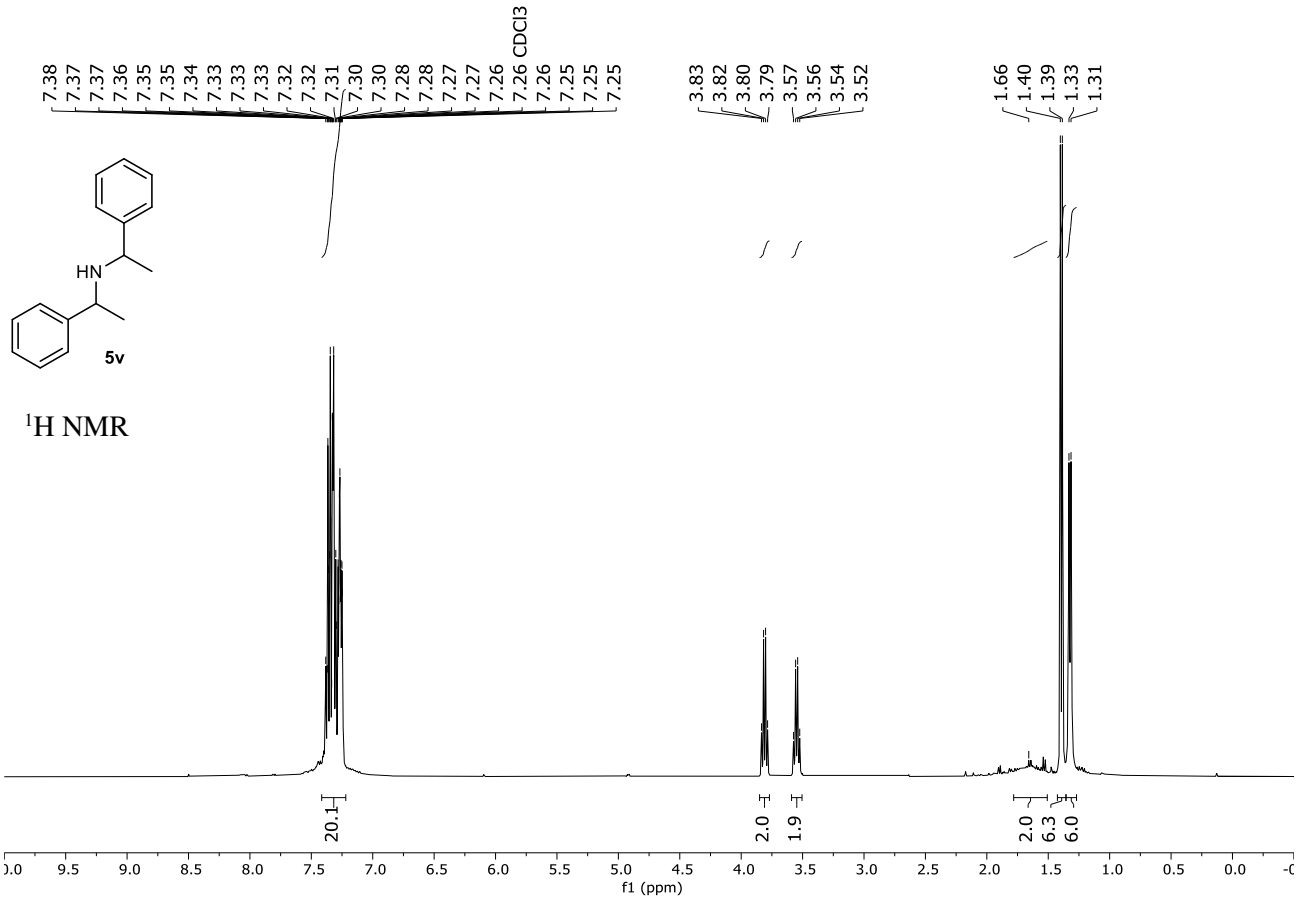


5u

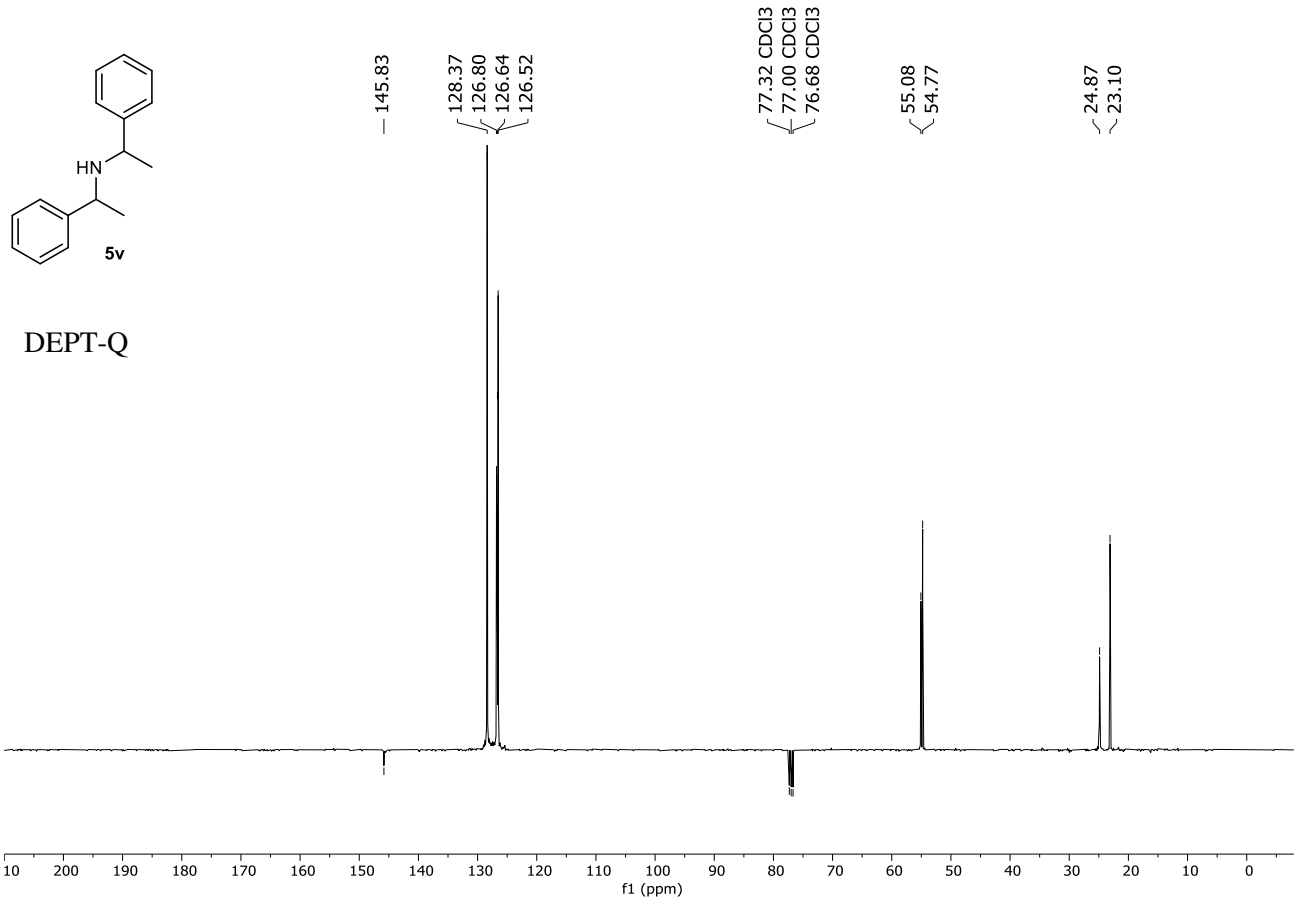
^{1}H NMR


OMe
HN
5u
DEPT-Q
151.90
145.39
141.45
128.57
126.79
125.87
114.72
114.57
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.70
54.27
25.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

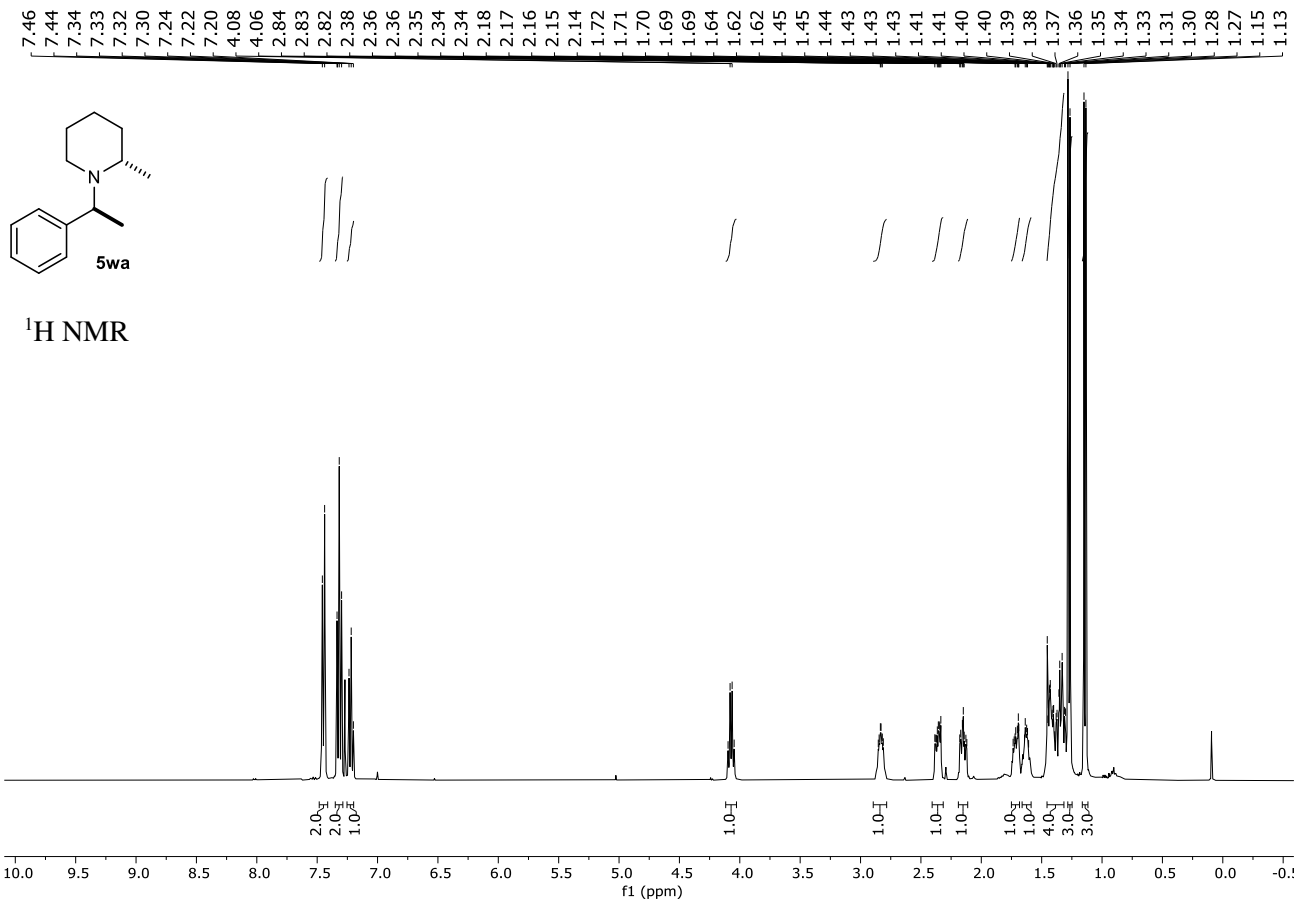
4.4. Diastereomeric Compounds



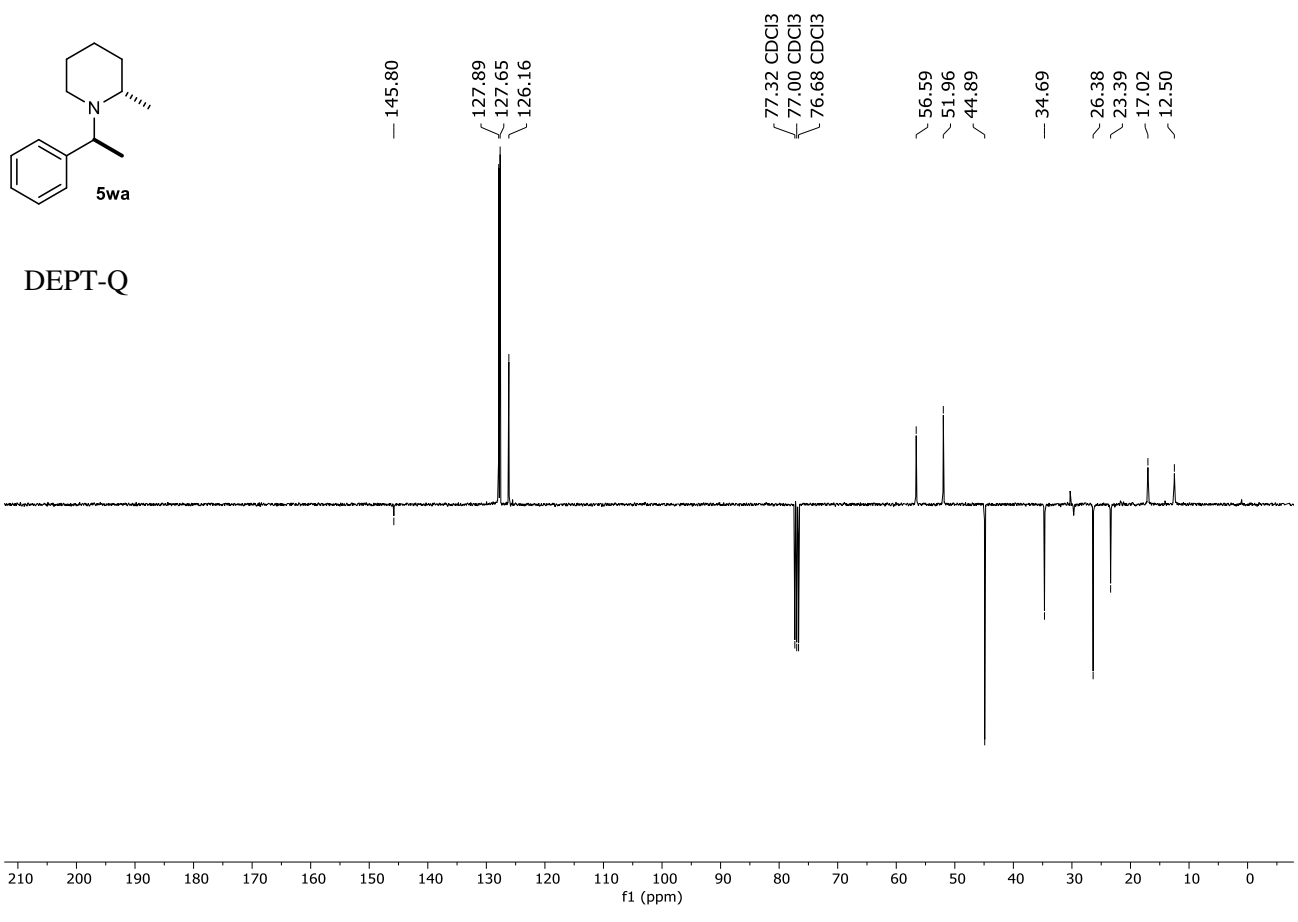
^{1}H NMR



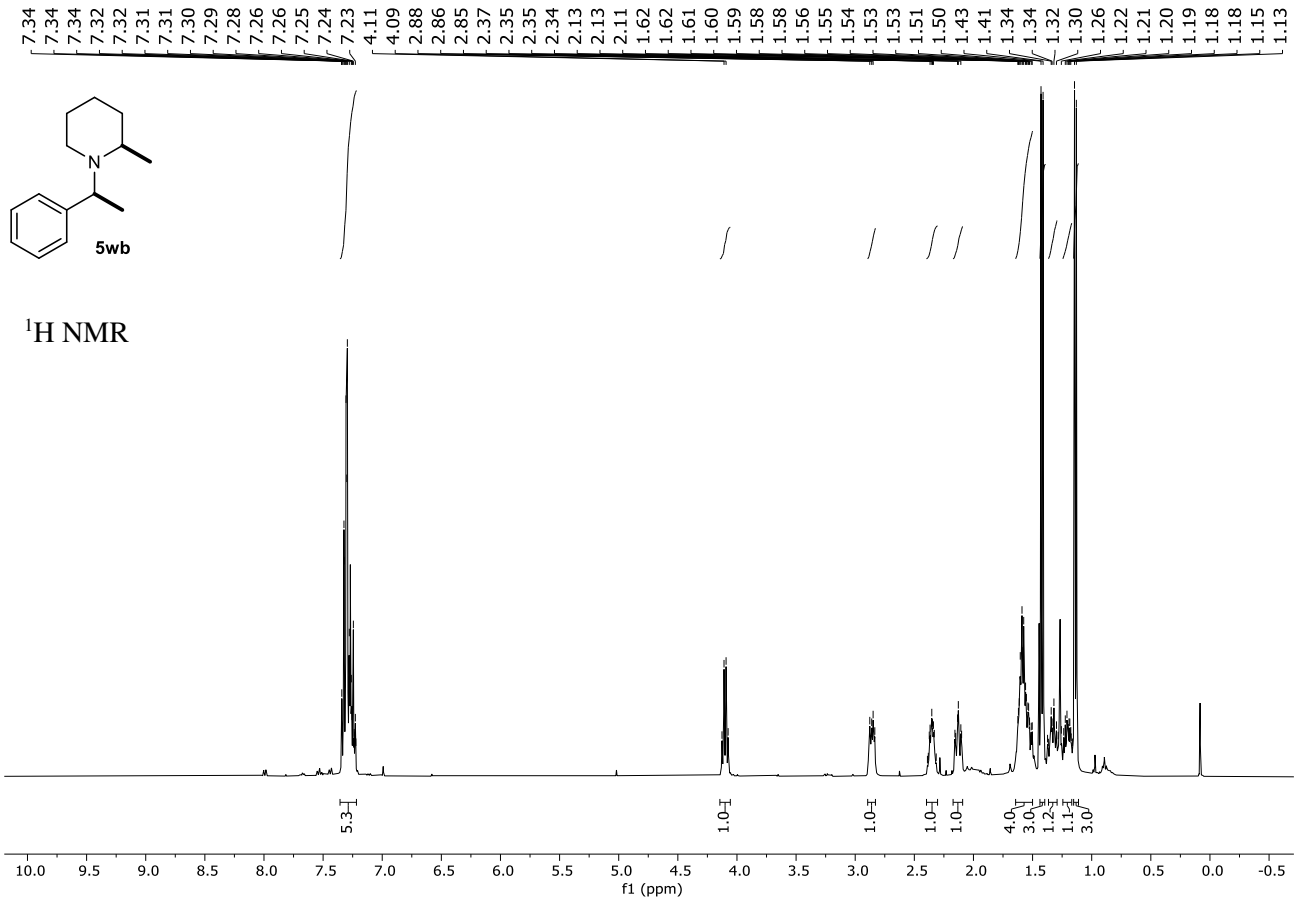
DEPT-Q

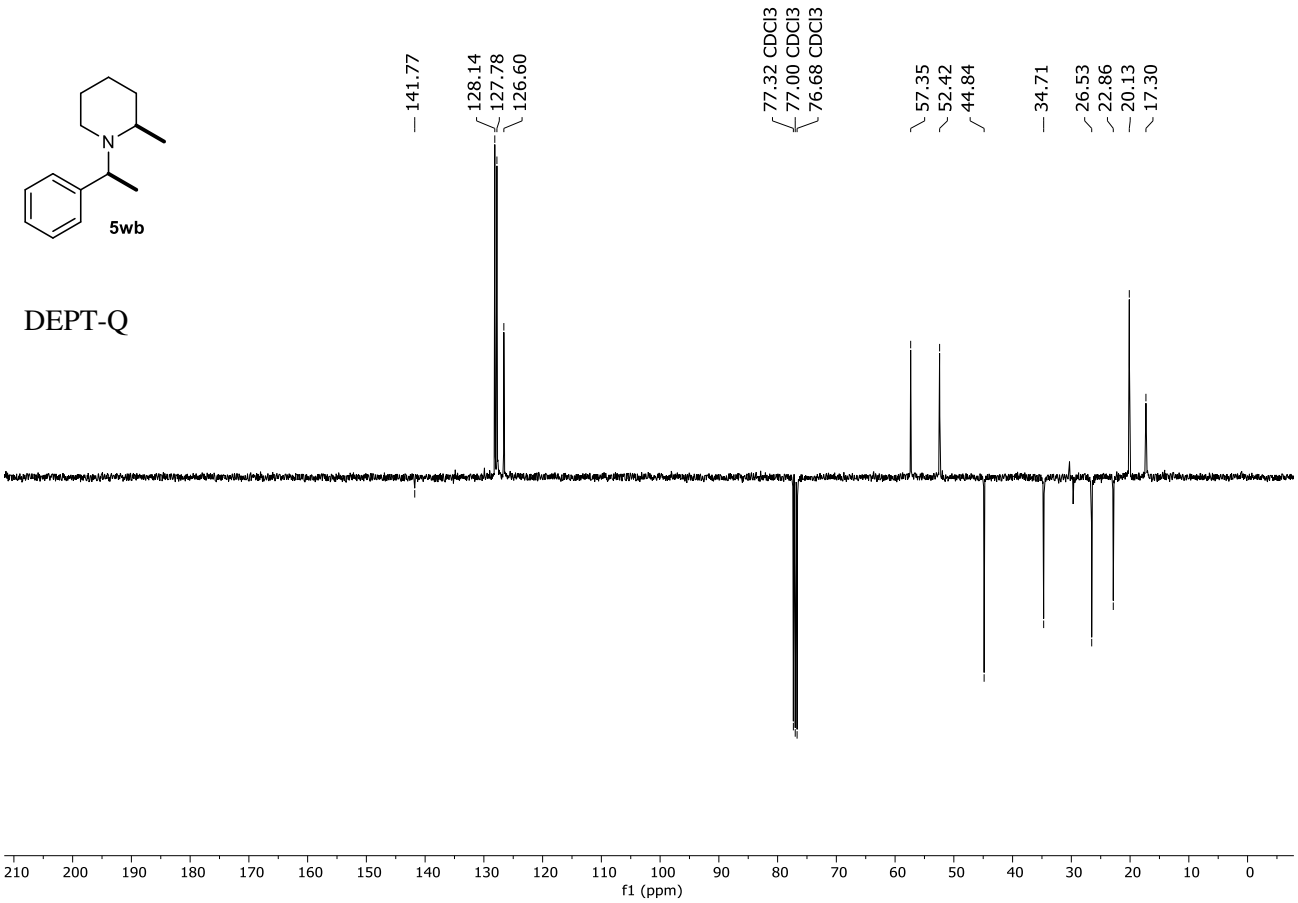

7.46 7.44 7.34 7.33 7.32 7.30 7.24 7.22 7.20 4.08 4.06 2.84 2.83 2.82 2.38 2.36 2.36 2.35 2.34 2.34 2.18 2.17 2.16 2.15 2.14 1.72 1.71 1.70 1.69 1.69 1.64 1.62 1.62 1.45 1.45 1.44 1.43 1.43 1.43 1.41 1.41 1.40 1.40 1.39 1.38 1.37 1.36 1.35 1.34 1.33 1.31 1.30 1.28 1.27 1.15 1.13
5wa
2.0 2.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 4.0 3.0 3.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

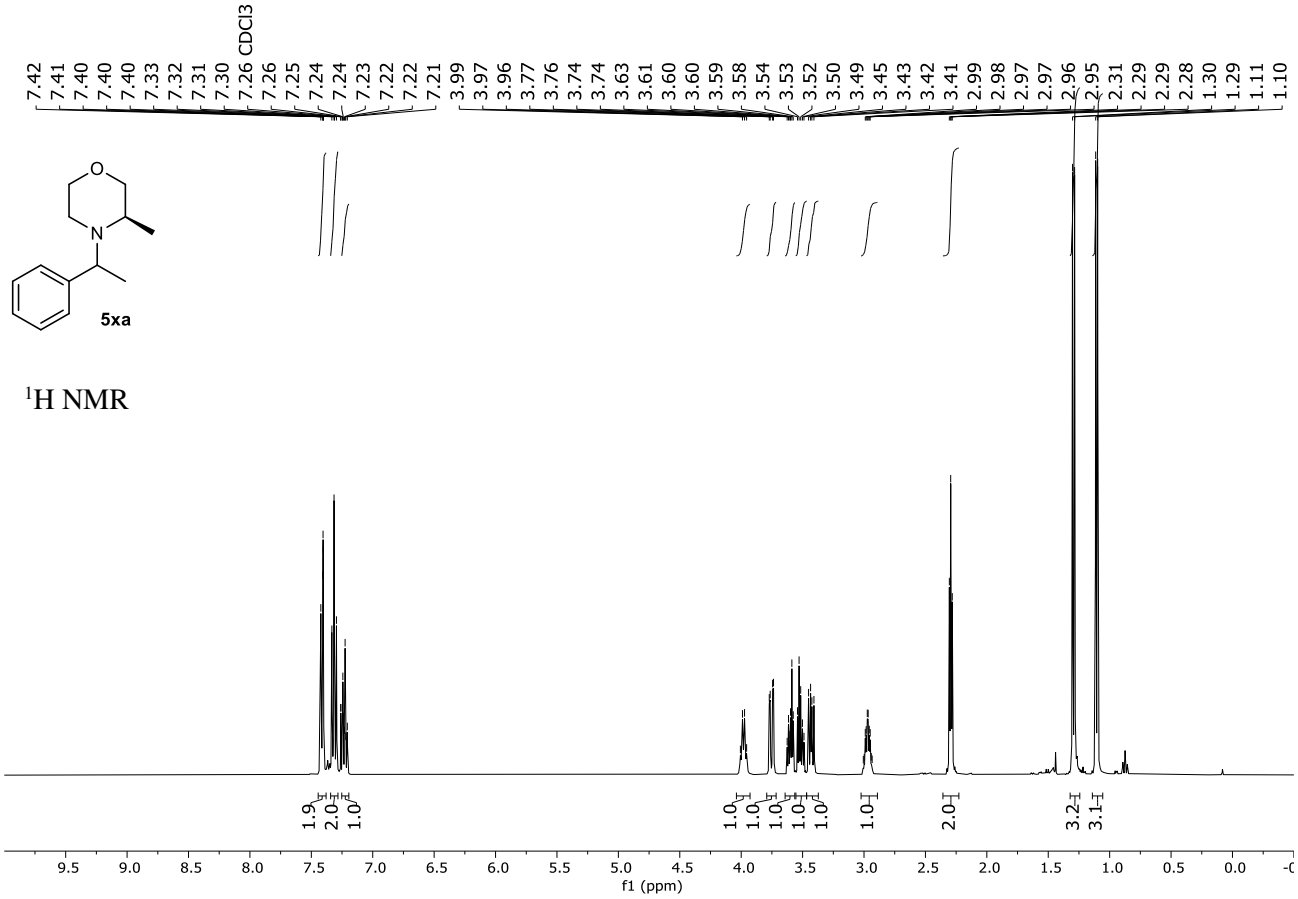
^{1}H NMR


5wa
145.80
127.89 127.65 126.16
77.32 CDCl3 77.00 CDCl3 76.68 CDCl3
56.59 51.96 44.89
34.69
26.38 23.39 17.02 12.50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

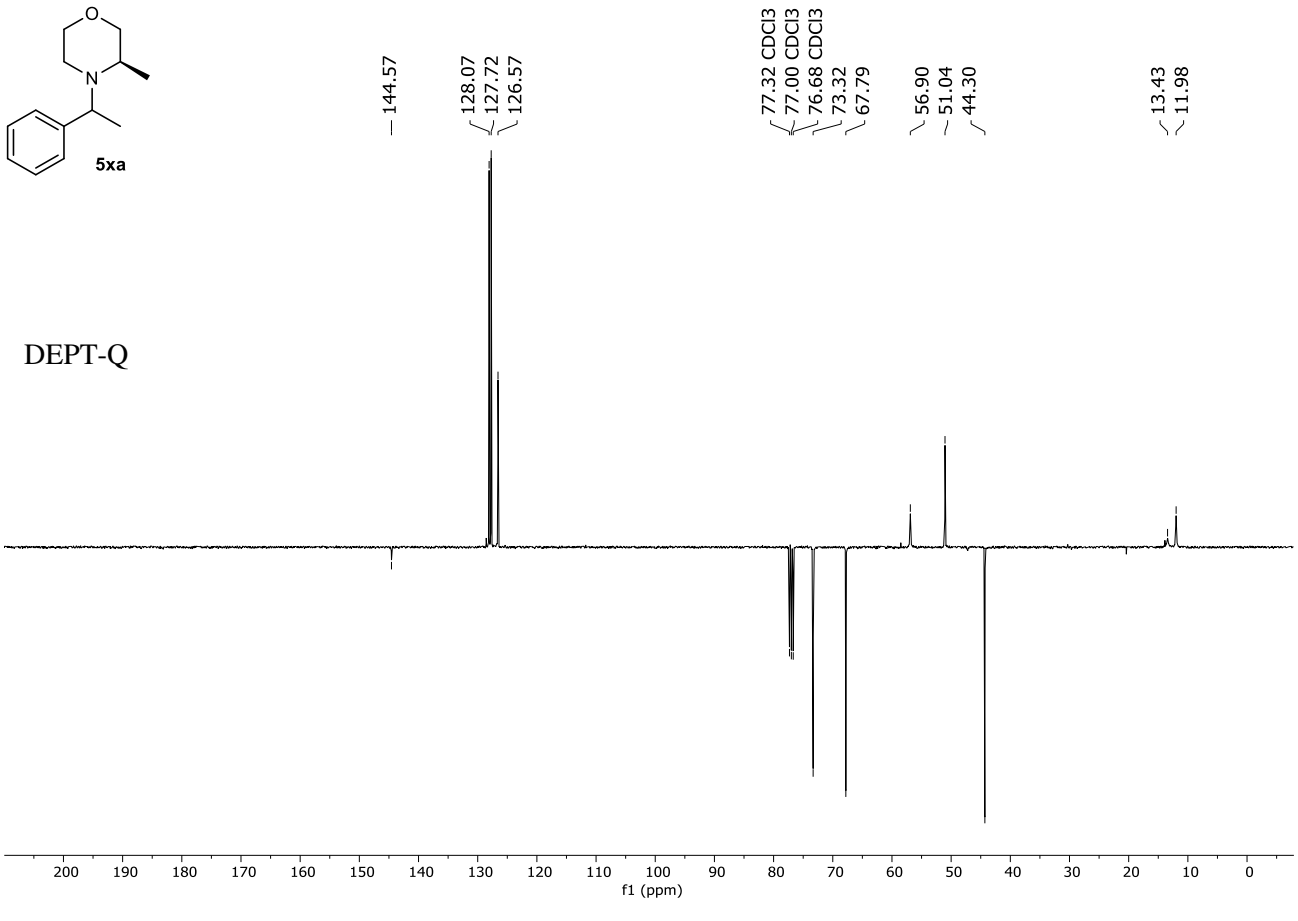
DEPT-Q


7.34 7.34 7.34 7.32 7.32 7.31 7.31 7.30 7.29 7.28 7.26 7.26 7.25 7.24 7.23 4.11 2.88 2.86 2.85 2.37 2.35 2.35 2.34 2.13 2.13 2.11 1.62 1.62 1.61 1.60 1.59 1.58 1.58 1.56 1.55 1.54 1.53 1.53 1.51 1.50 1.43 1.41 1.34 1.32 1.30 1.26 1.22 1.21 1.20 1.19 1.18 1.18 1.15 1.13
5wb
^{1}H NMR
5.3 1.0 1.0 1.0 1.0 4.0 3.0 1.2 1.1 3.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

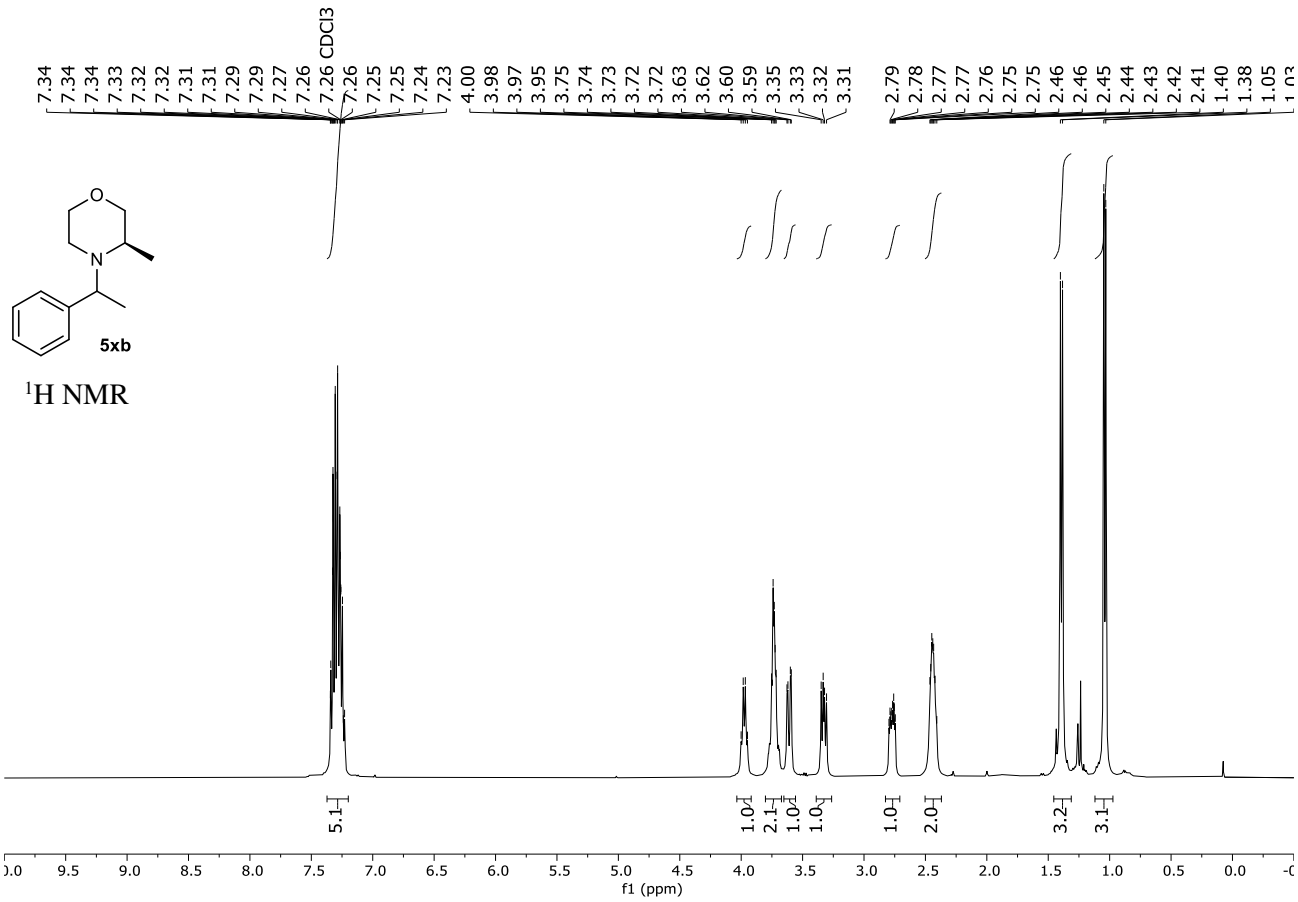

141.77
128.14
127.78
126.60
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
57.35
52.42
44.84
34.71
26.53
22.86
20.13
17.30
5wb
DEPT-Q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.42
7.41
7.40
7.40
7.40
7.33
7.32
7.31
7.30
7.26 CDCl3
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.21
3.99
3.97
3.96
3.77
3.76
3.74
3.74
3.63
3.61
3.60
3.60
3.59
3.58
3.54
3.53
3.52
3.50
3.49
3.45
3.43
3.42
3.41
2.99
2.98
2.97
2.97
2.96
2.95
2.31
2.29
2.29
2.28
1.30
1.29
1.11
1.10
5xa
1.9
2.0
1.0
1.0
1.0
1.0
1.0
1.0
2.0
3.2
3.1
f1 (ppm)

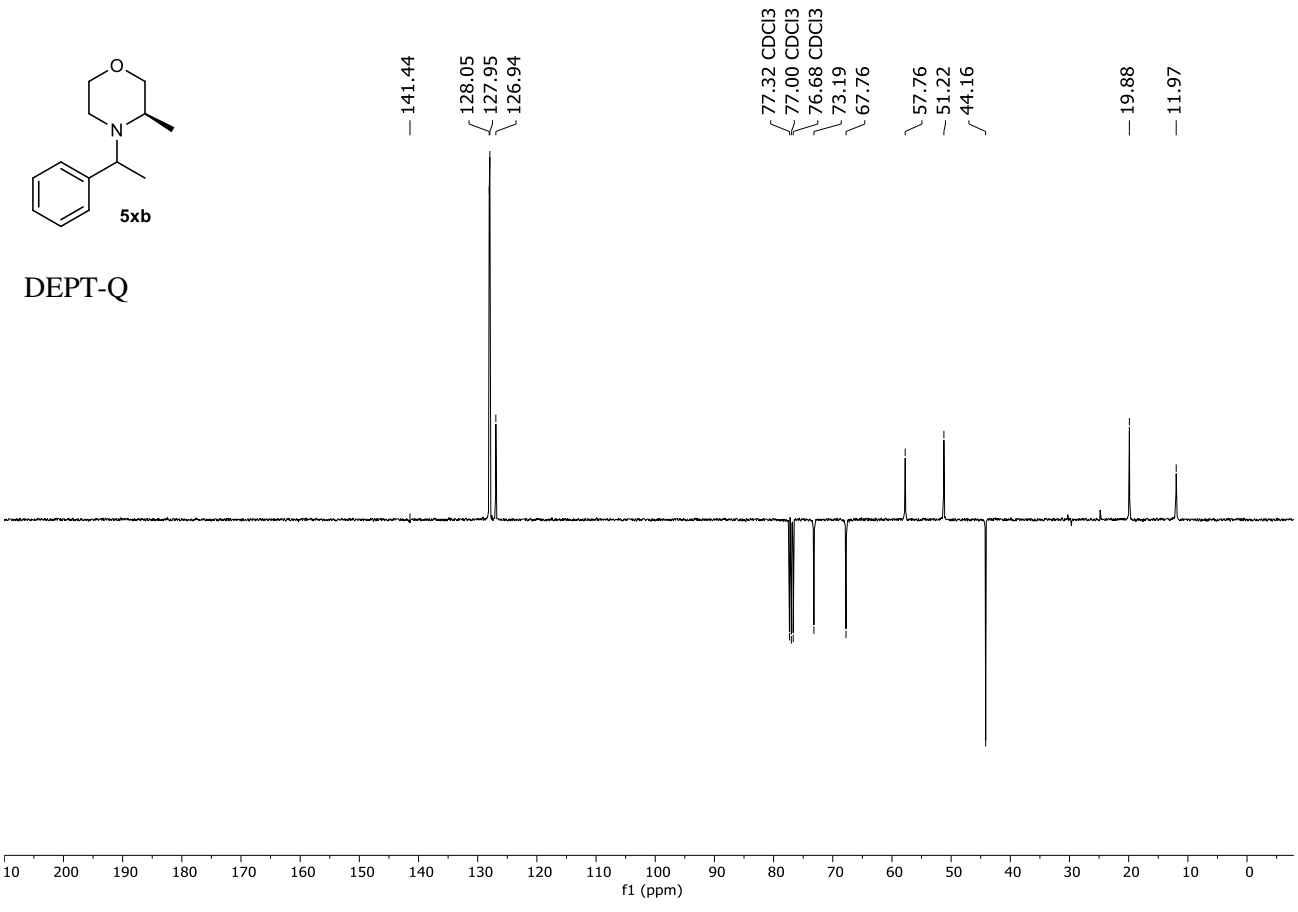
^{1}H NMR


144.57
128.07
127.72
126.57
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
73.32
67.79
56.90
51.04
44.30
13.43
11.98
5xa
f1 (ppm)

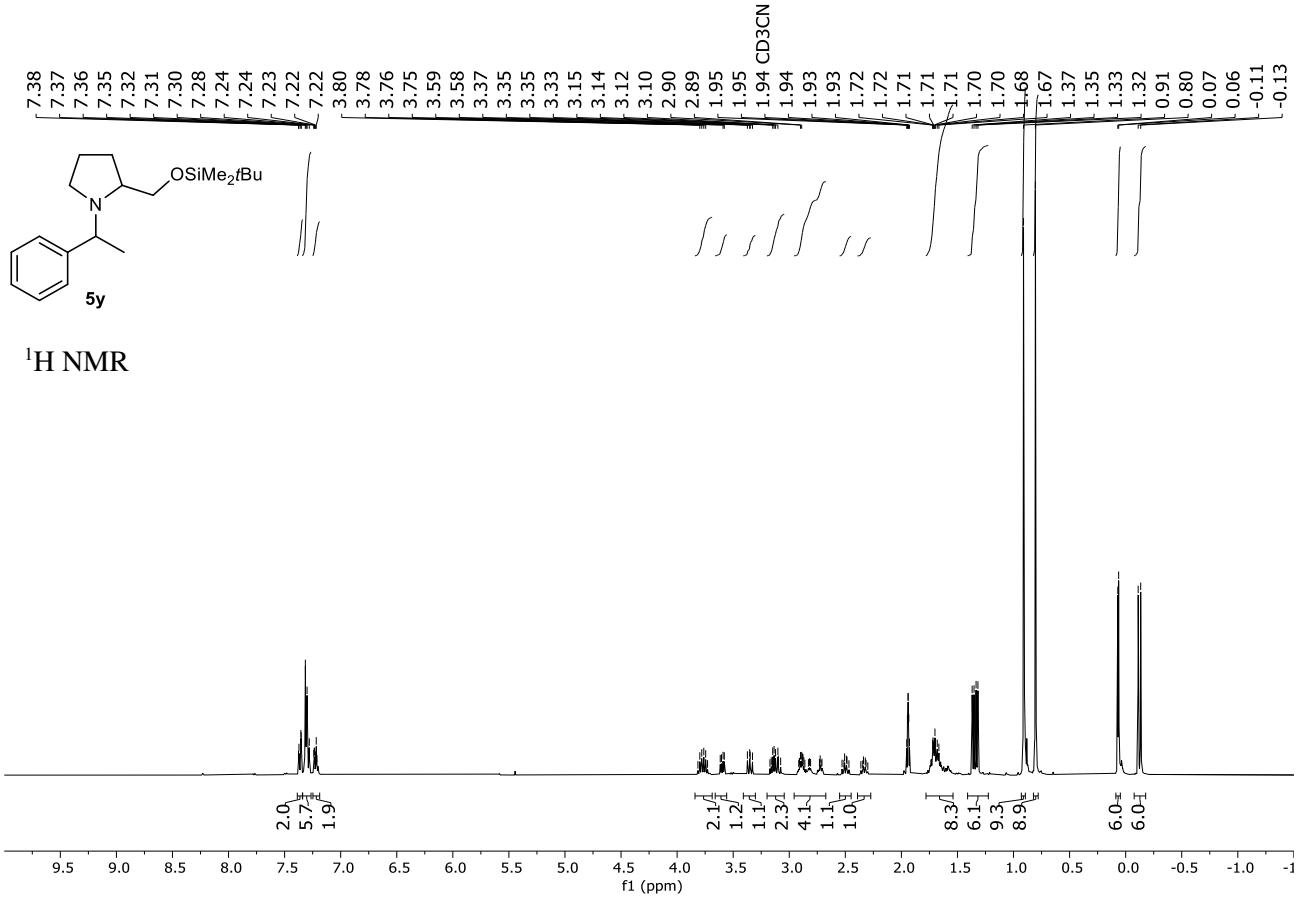
DEPT-Q


7.34
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.29
7.29
7.27
7.26
7.26 CDCl3
7.26
7.25
7.25
7.24
7.23
4.00
3.98
3.97
3.95
3.75
3.74
3.73
3.72
3.72
3.63
3.62
3.60
3.59
3.35
3.33
3.32
3.31
2.79
2.78
2.77
2.77
2.76
2.75
2.75
2.46
2.46
2.45
2.44
2.43
2.42
2.41
1.40
1.38
1.05
5xb
5.1
1.0
2.1
1.0
1.0
1.0
2.0
3.2
3.1
f1 (ppm)

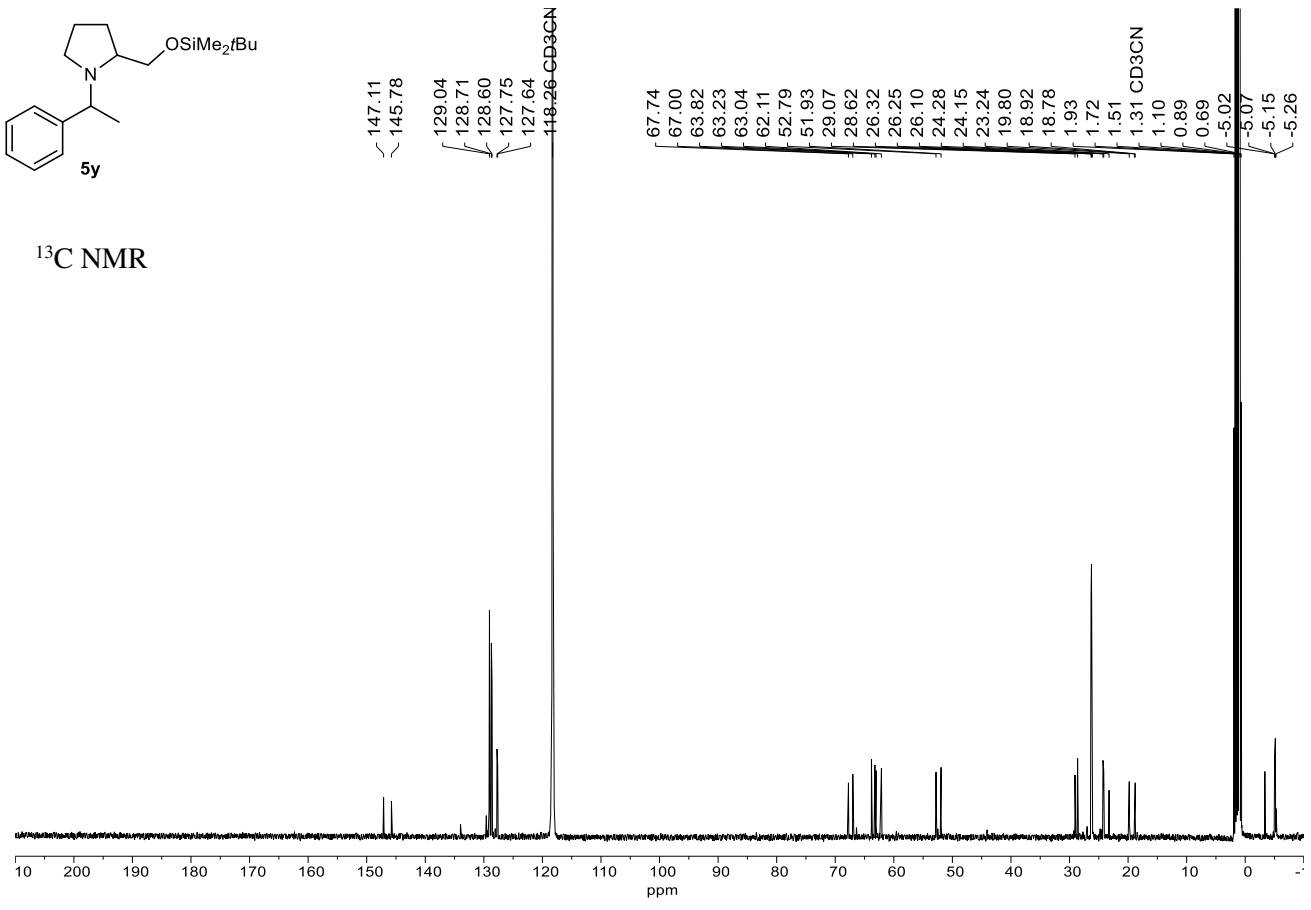
^{1}H NMR


141.44
128.05
127.95
126.94
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
73.19
67.76
57.76
51.22
44.16
19.88
11.97
5xb
f1 (ppm)

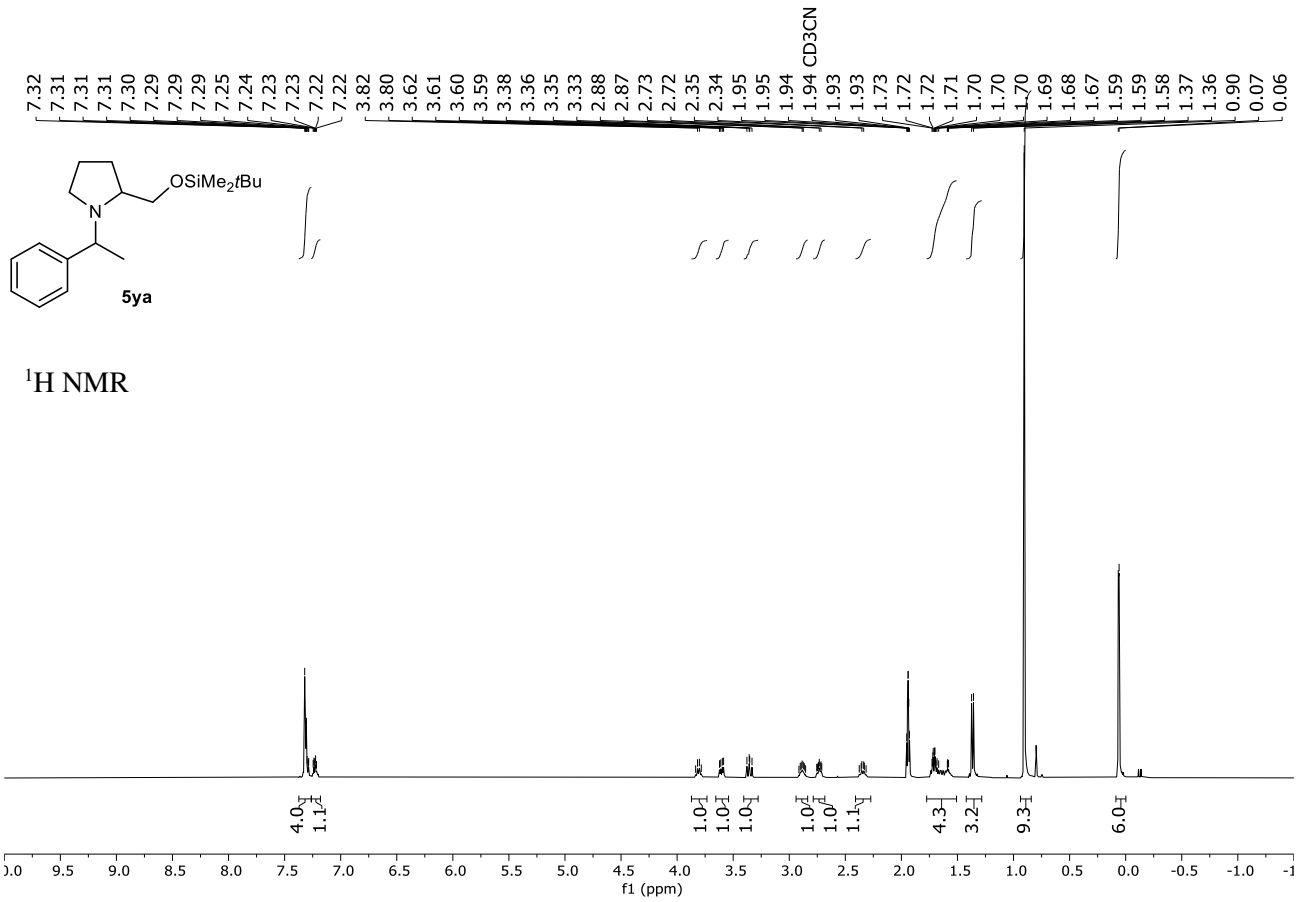
DEPT-Q



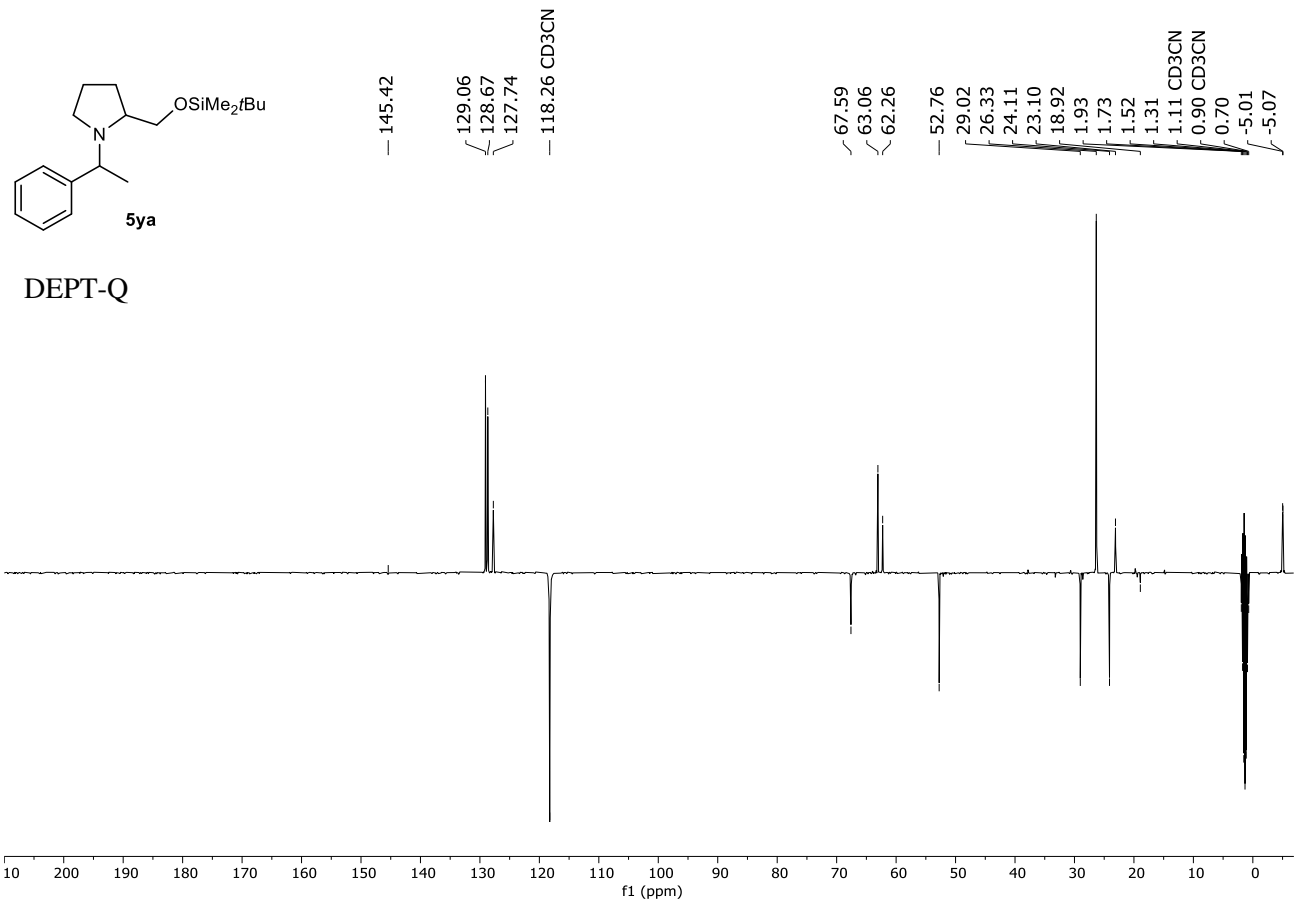
^{1}H NMR



^{13}C NMR

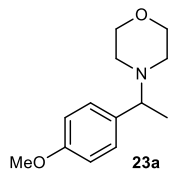

7.32 7.31 7.31 7.31 7.30 7.29 7.29 7.29 7.25 7.24 7.23 7.23 7.22 7.22
3.82 3.80 3.62 3.61 3.60 3.59 3.38 3.36 3.35 3.33 2.88 2.87 2.73 2.72 2.35 2.34 1.95 1.95 1.94 CD3CN 1.93 1.93 1.73 1.72 1.72 1.71 1.70 1.70 1.70 1.69 1.68 1.67 1.59 1.59 1.58 1.37 1.36 0.90 0.07 0.06
OSiMe2tBu
N
5ya
4.0 1.1 1.0 1.0 1.0 1.0 1.0 1.1 4.3 3.2 9.3 6.0
f1 (ppm)

^{1}H NMR

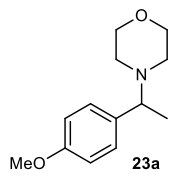

OSiMe2tBu
N
5ya
145.42
129.06 128.67 127.74
118.26 CD3CN
67.59 63.06 62.26
52.76
29.02 26.33 24.11 23.10 18.92 1.93 1.73 1.52 1.31 1.11 CD3CN 0.90 CD3CN 0.70 -5.01 -5.07
f1 (ppm)

DEPT-Q

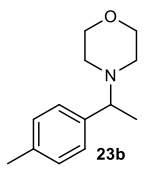
4.5. Coupling of Benzylic Boronic Esters



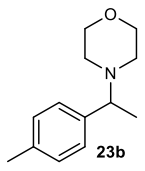
^{1}H NMR



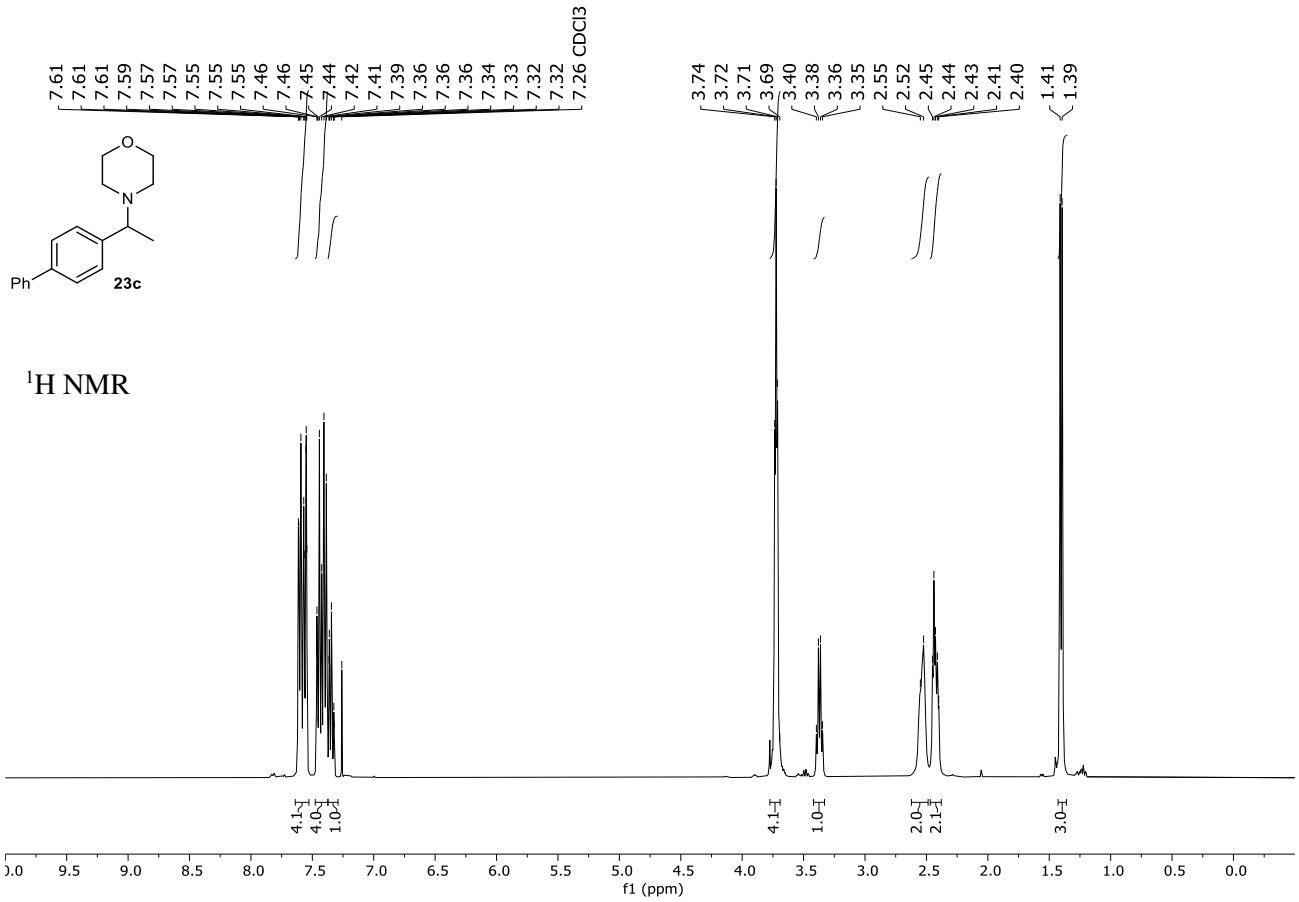
DEPT-Q



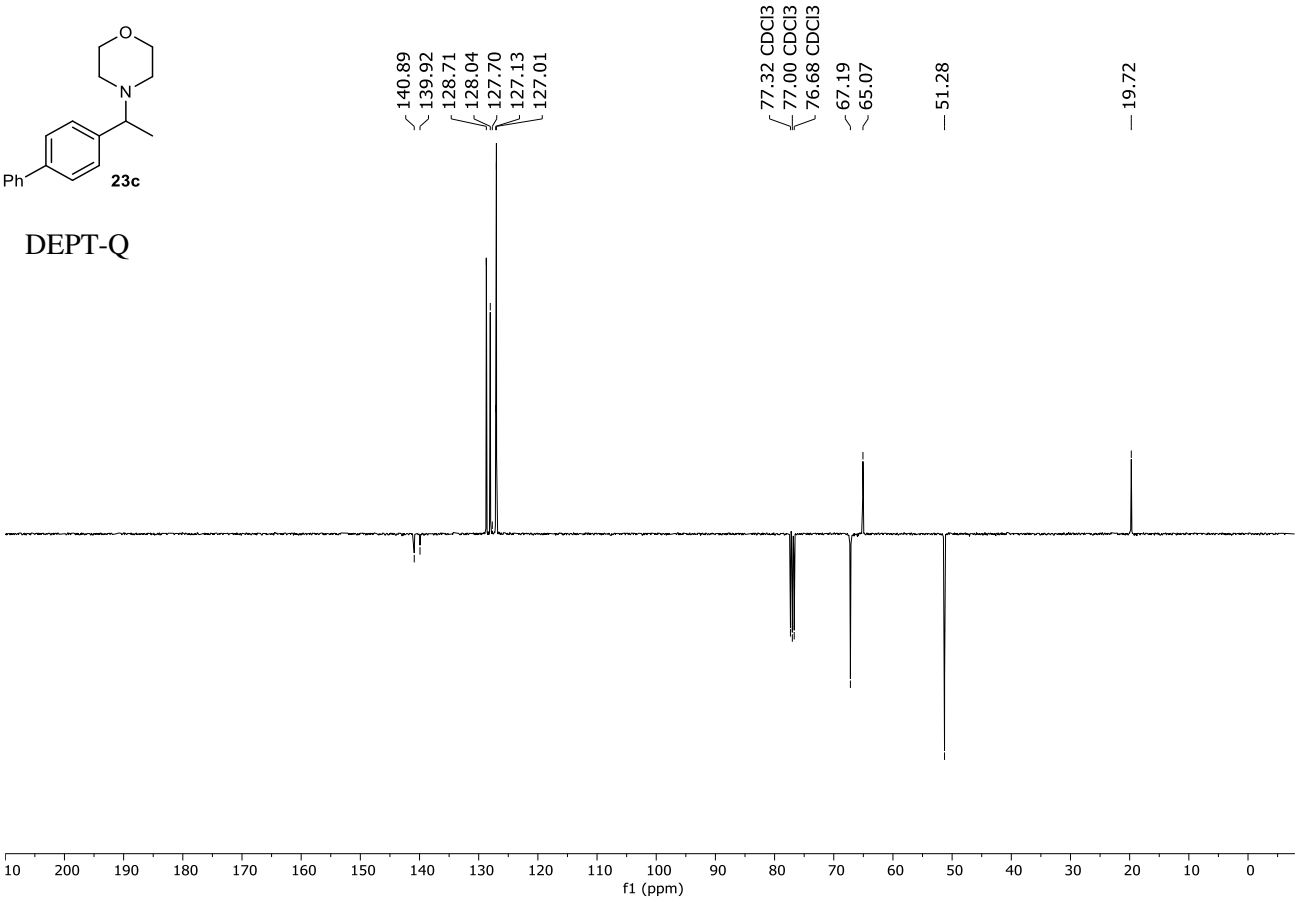
^{1}H NMR



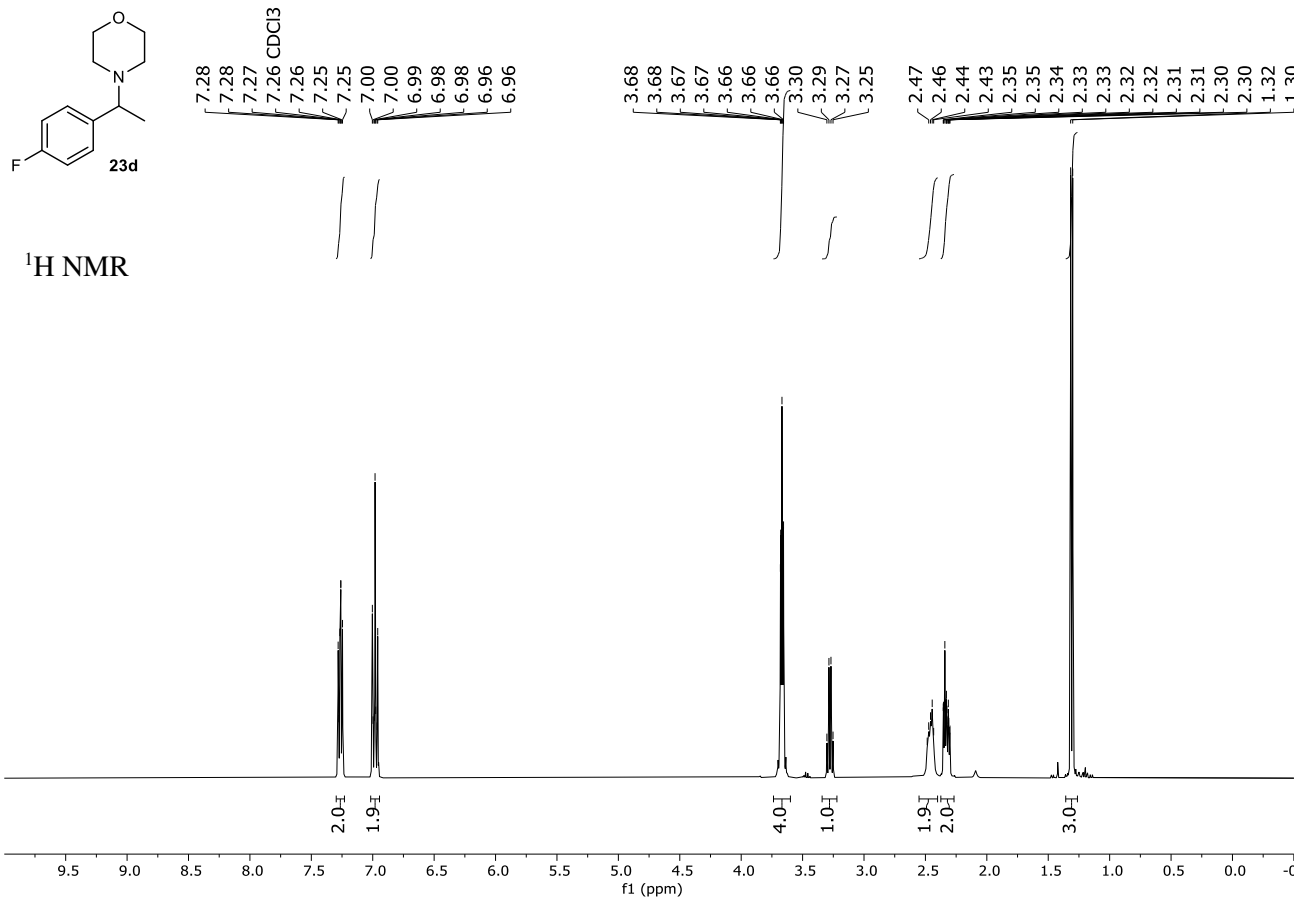
^{13}C NMR


7.61
7.61
7.61
7.59
7.57
7.57
7.55
7.55
7.55
7.46
7.46
7.45
7.44
7.42
7.41
7.39
7.36
7.36
7.34
7.33
7.32
7.26 CDCl3
3.74
3.72
3.71
3.69
3.40
3.38
3.36
3.35
2.55
2.52
2.45
2.44
2.43
2.41
2.40
1.41
1.39
O
N
Ph
23c
4.1
4.0
1.0
4.1
1.0
2.0
2.1
3.0
f1 (ppm)

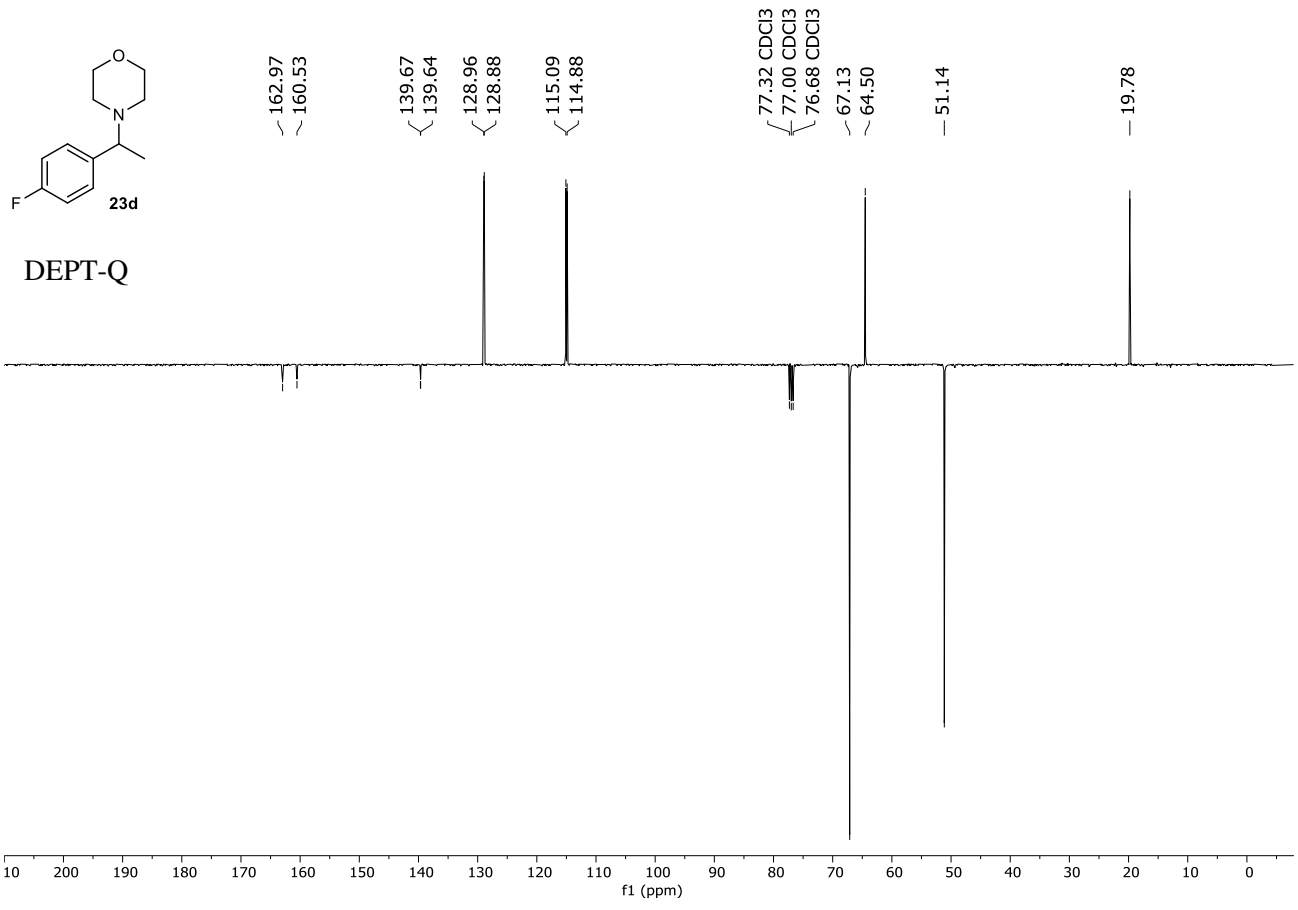
^{1}H NMR


O
N
Ph
23c
140.89
139.92
128.71
128.04
127.70
127.13
127.01
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.19
65.07
51.28
19.72
f1 (ppm)

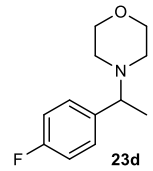
DEPT-Q


23d
7.28
7.28
7.27
7.26 CDCl3
7.26
7.25
7.25
7.00
7.00
6.99
6.98
6.98
6.96
6.96
3.68
3.68
3.67
3.67
3.66
3.66
3.66
3.30
3.29
3.27
3.25
2.47
2.46
2.44
2.43
2.35
2.35
2.34
2.33
2.33
2.32
2.32
2.31
2.31
2.30
2.30
1.32
2.0
1.9
4.0
1.0
1.9
2.0
3.0
f1 (ppm)

^{1}H NMR

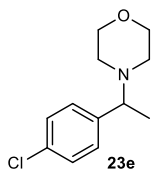

23d
162.97
160.53
139.67
139.64
128.96
128.88
115.09
114.88
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.13
64.50
51.14
19.78
f1 (ppm)

DEPT-Q



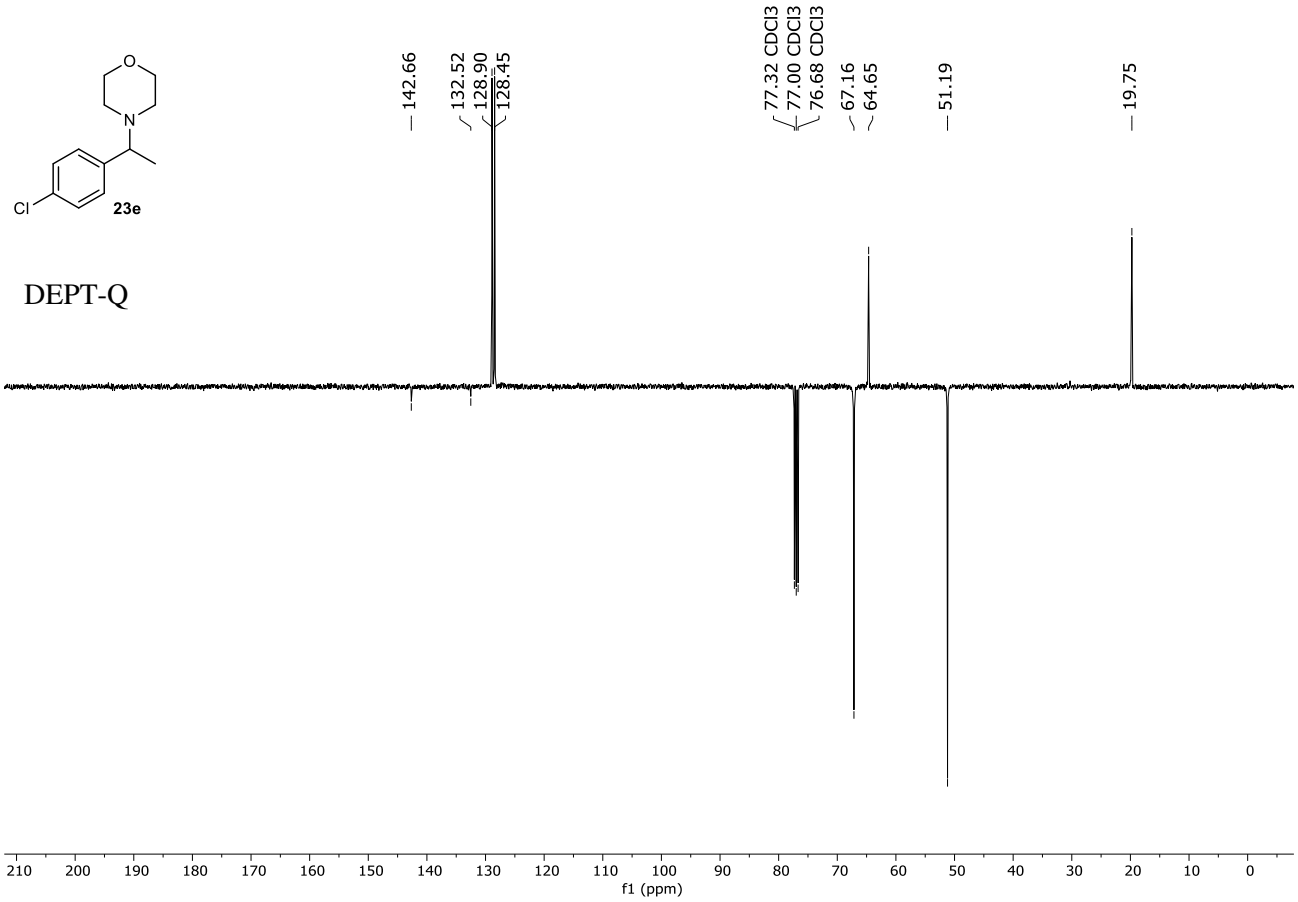
23d

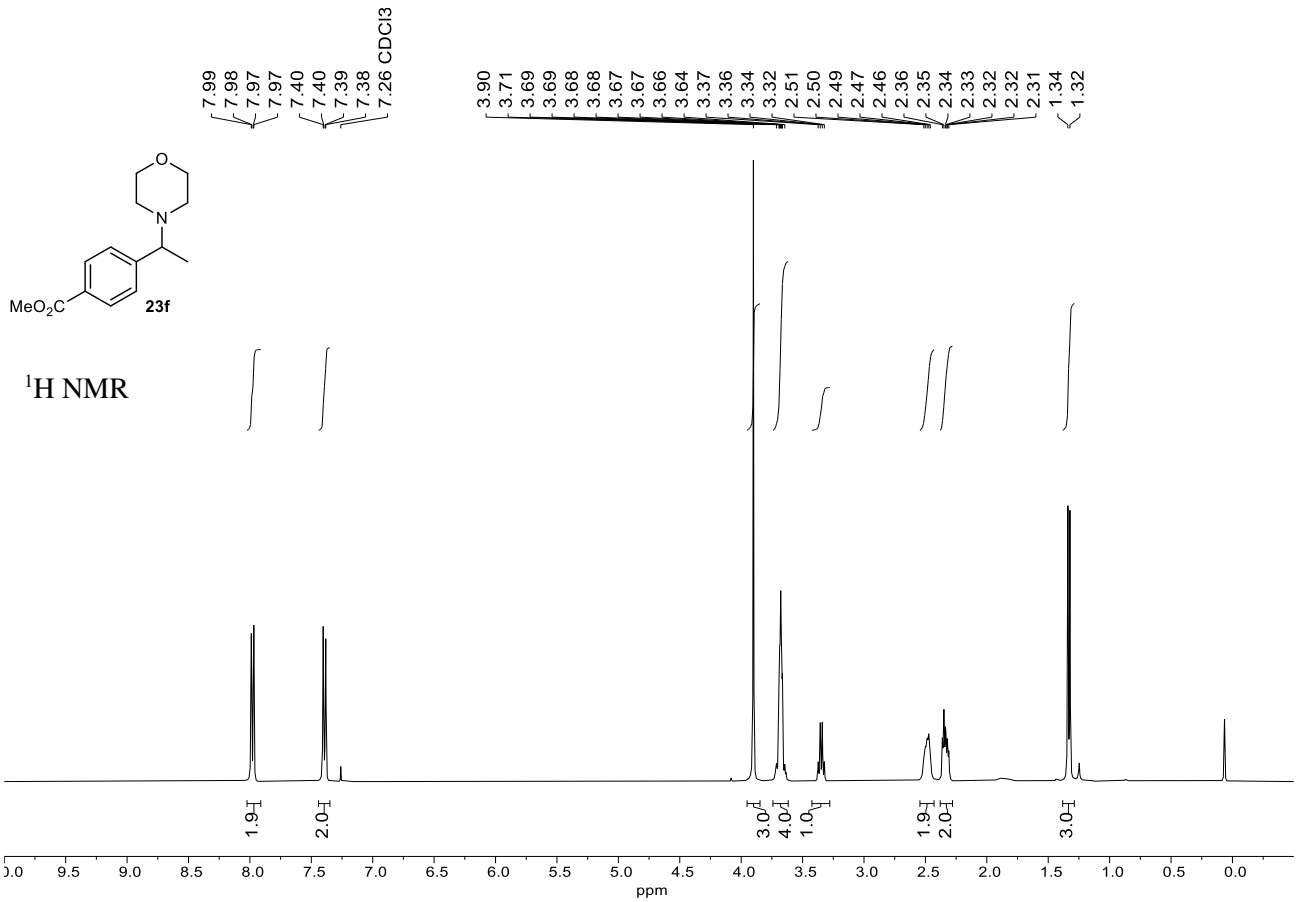
^{19}F NMR

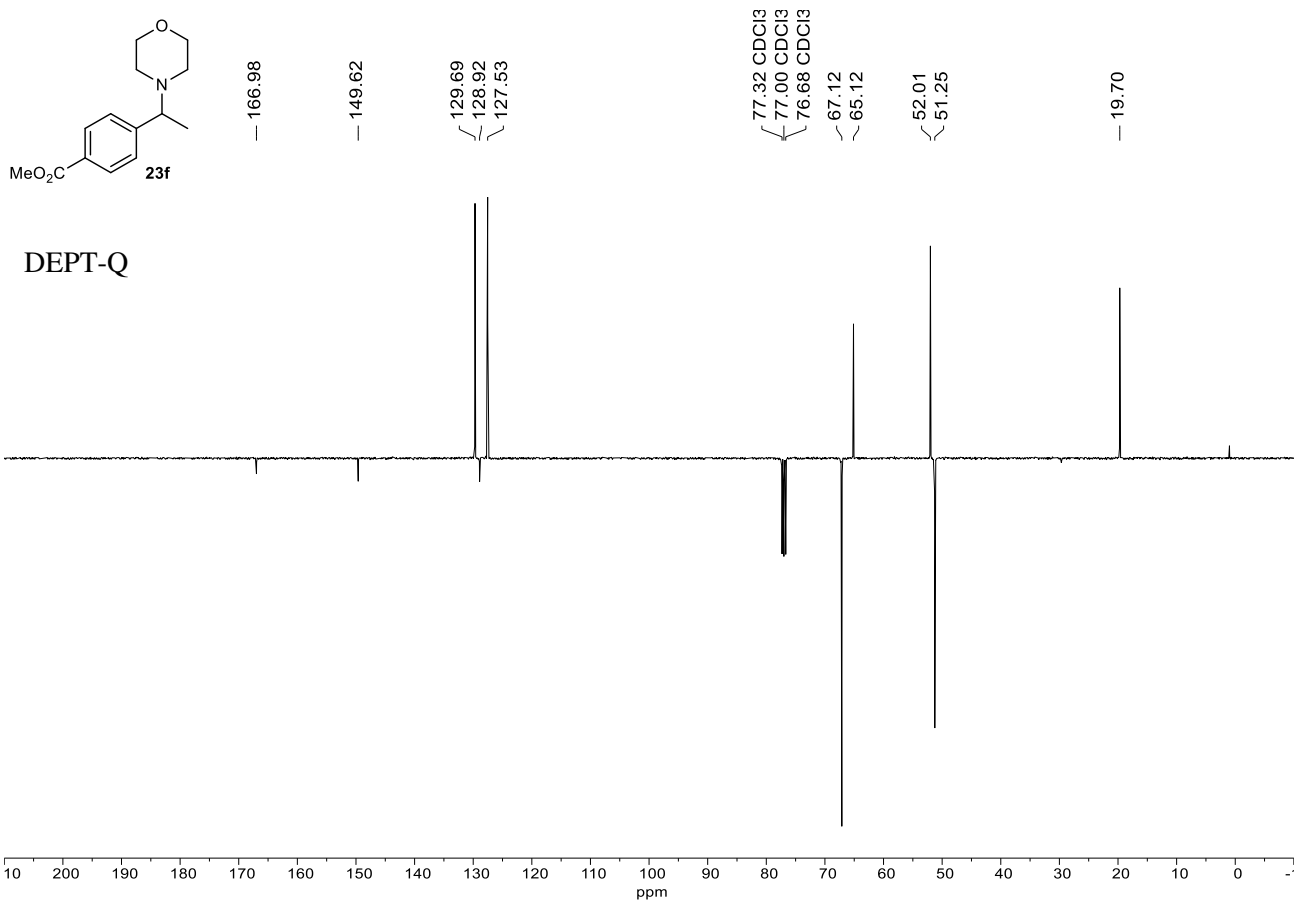


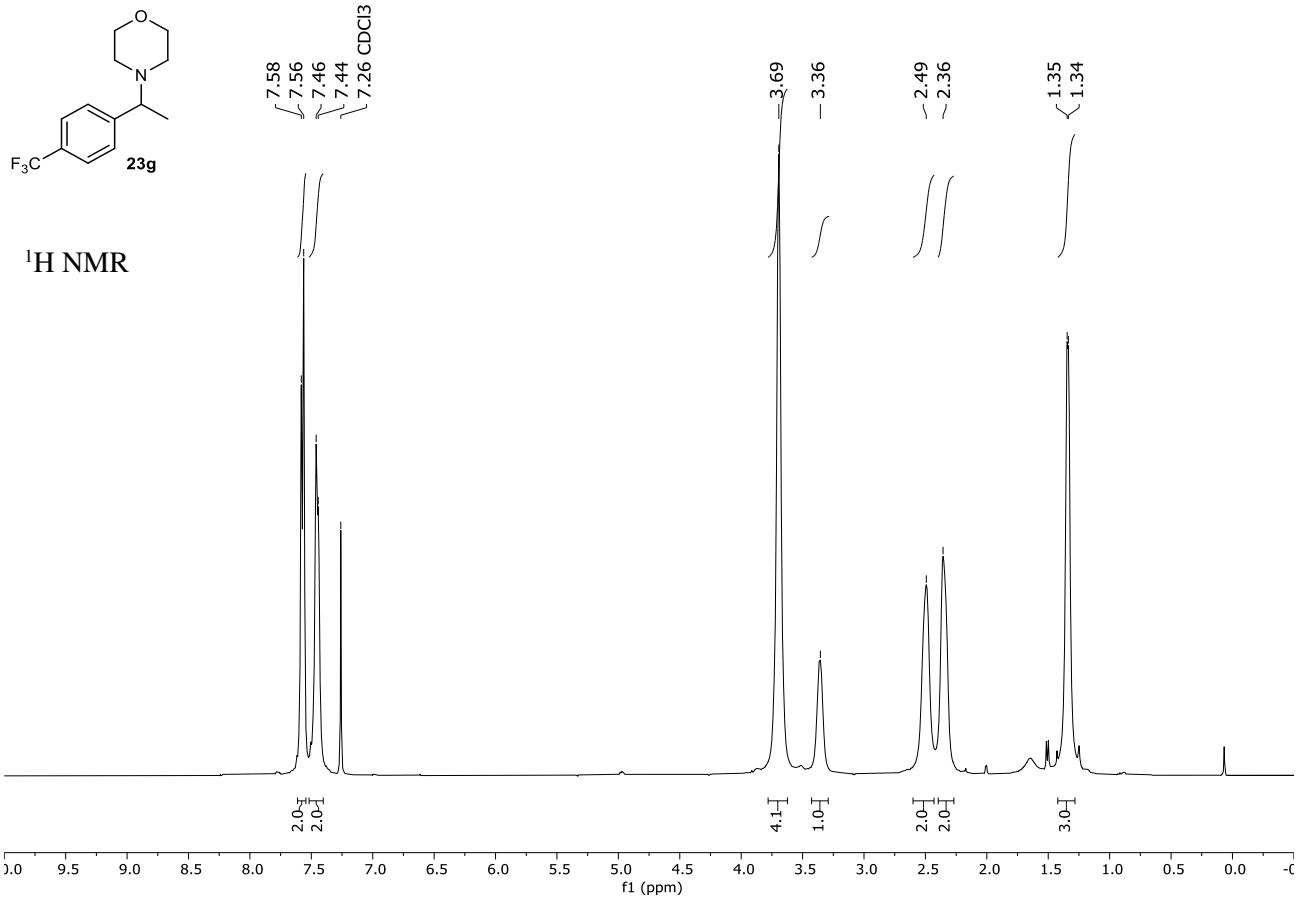
23e

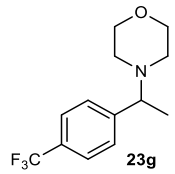
^{1}H NMR


142.66
132.52
128.90
128.45
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.16
64.65
51.19
19.75
Cl
23e
DEPT-Q
f1 (ppm)


7.99
7.98
7.97
7.97
7.40
7.40
7.39
7.38
7.26 CDCl3
3.90
3.71
3.69
3.69
3.68
3.68
3.67
3.67
3.66
3.64
3.37
3.36
3.34
3.32
2.51
2.50
2.49
2.47
2.46
2.36
2.35
2.34
2.33
2.32
2.32
2.31
1.34
1.32
MeO2C
23f
1H NMR
1.9
2.0
3.0
4.0
1.0
1.9
2.0
3.0
ppm

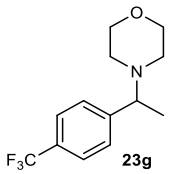

MeO2C
23f
166.98
149.62
129.69
128.92
127.53
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.12
65.12
52.01
51.25
19.70
DEPT-Q
ppm


F3C
23g
7.58
7.56
7.46
7.44
7.26 CDCl3
3.69
3.36
2.49
2.36
1.35
1.34
1H NMR
f1 (ppm)



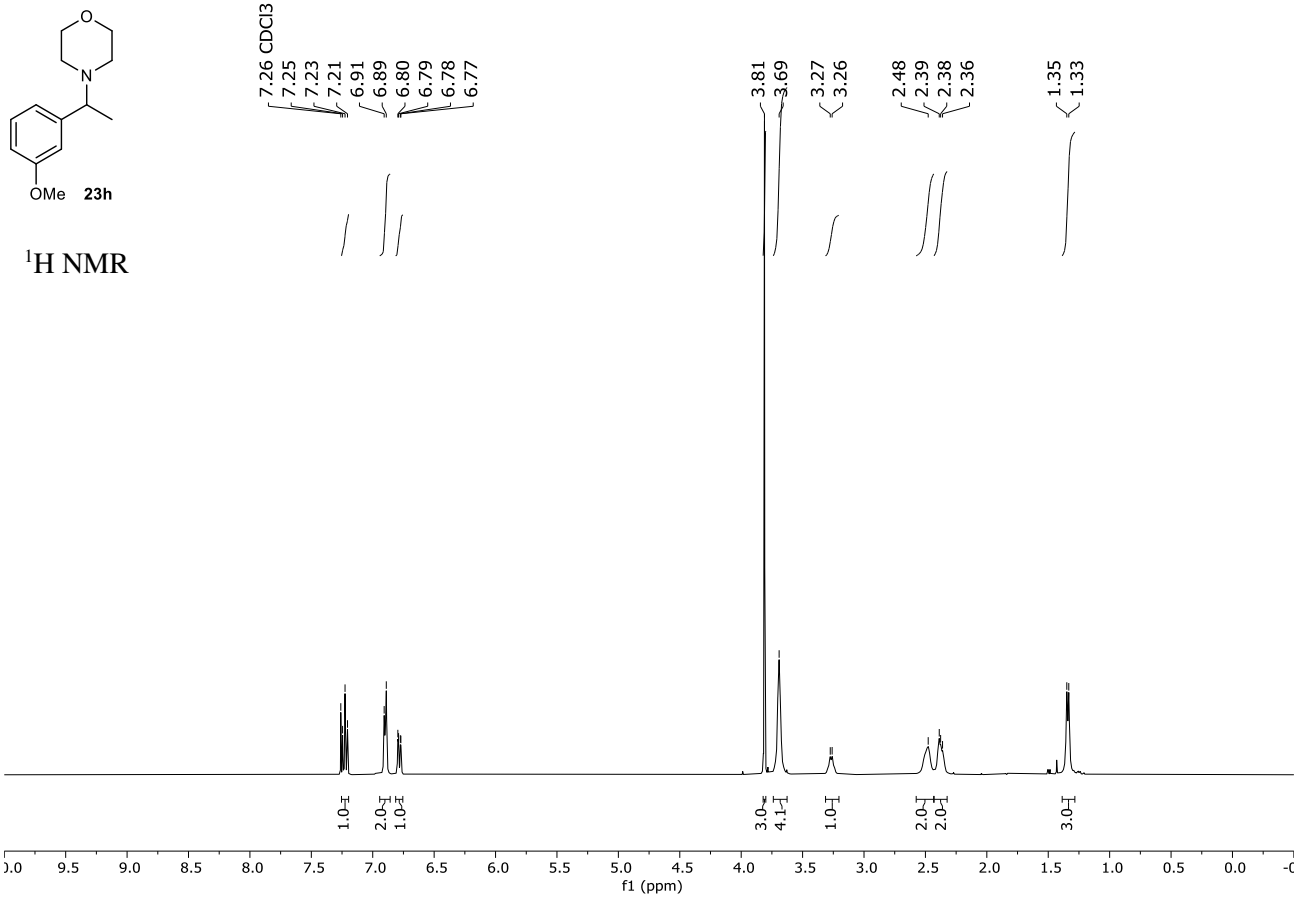
23g

^{13}C NMR

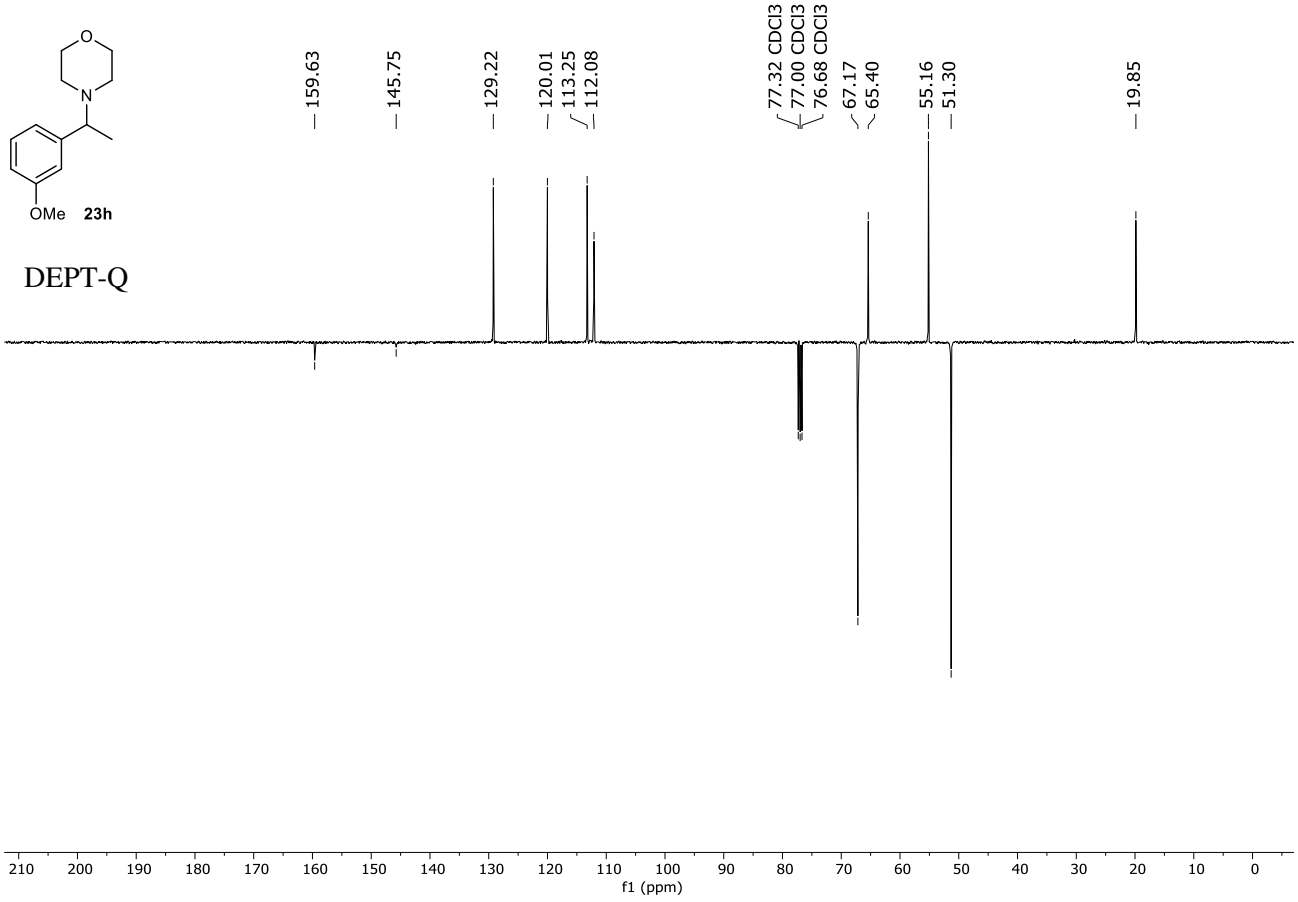


23g

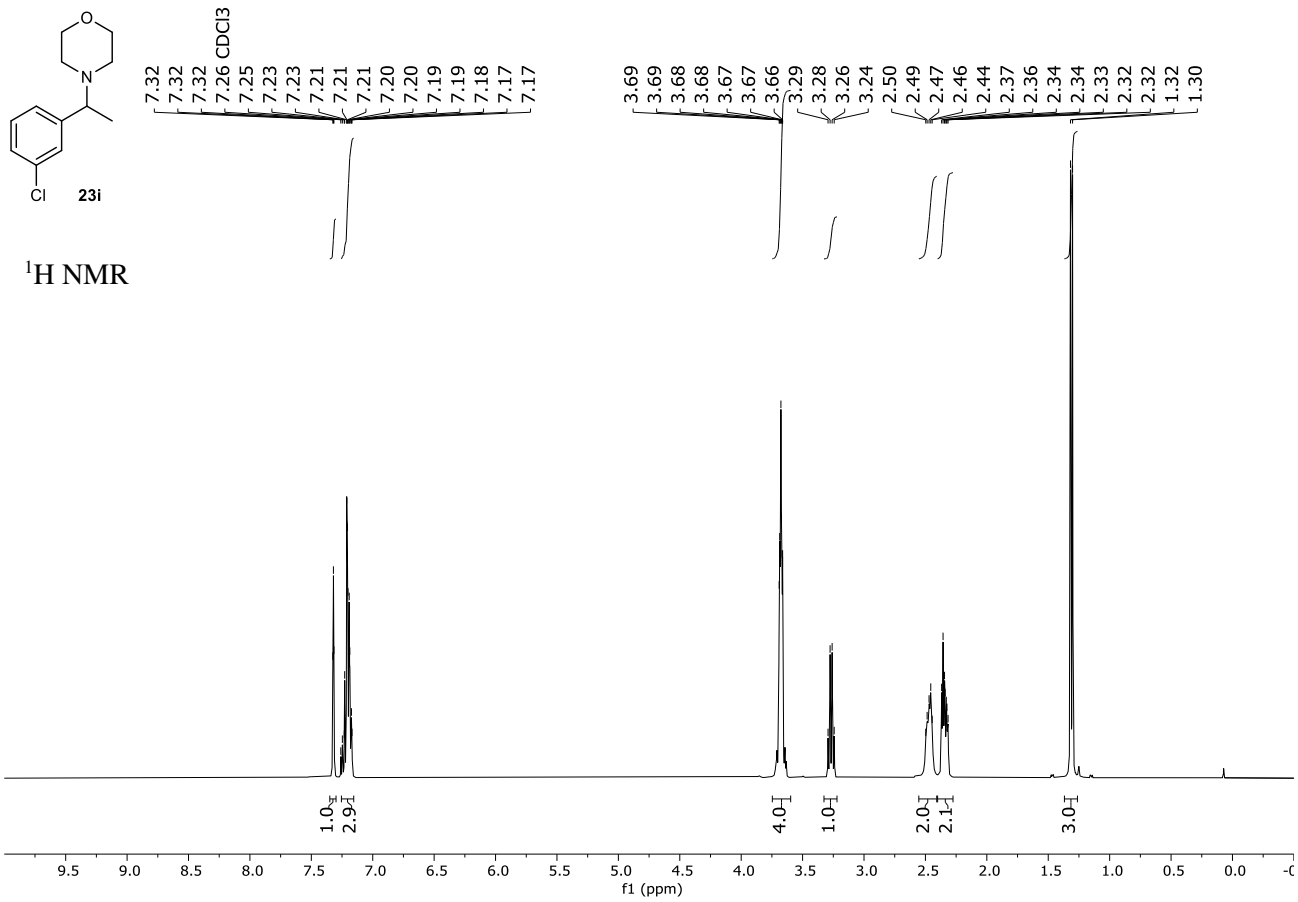
^{19}F NMR


OMe 23h
7.26 CDCl3
7.25
7.23
7.21
6.91
6.89
6.80
6.79
6.78
6.77
3.81
3.69
3.27
3.26
2.48
2.39
2.38
2.36
1.35
1.33
1.0
2.0
1.0
3.0
4.1
1.0
2.0
2.0
3.0
f1 (ppm)

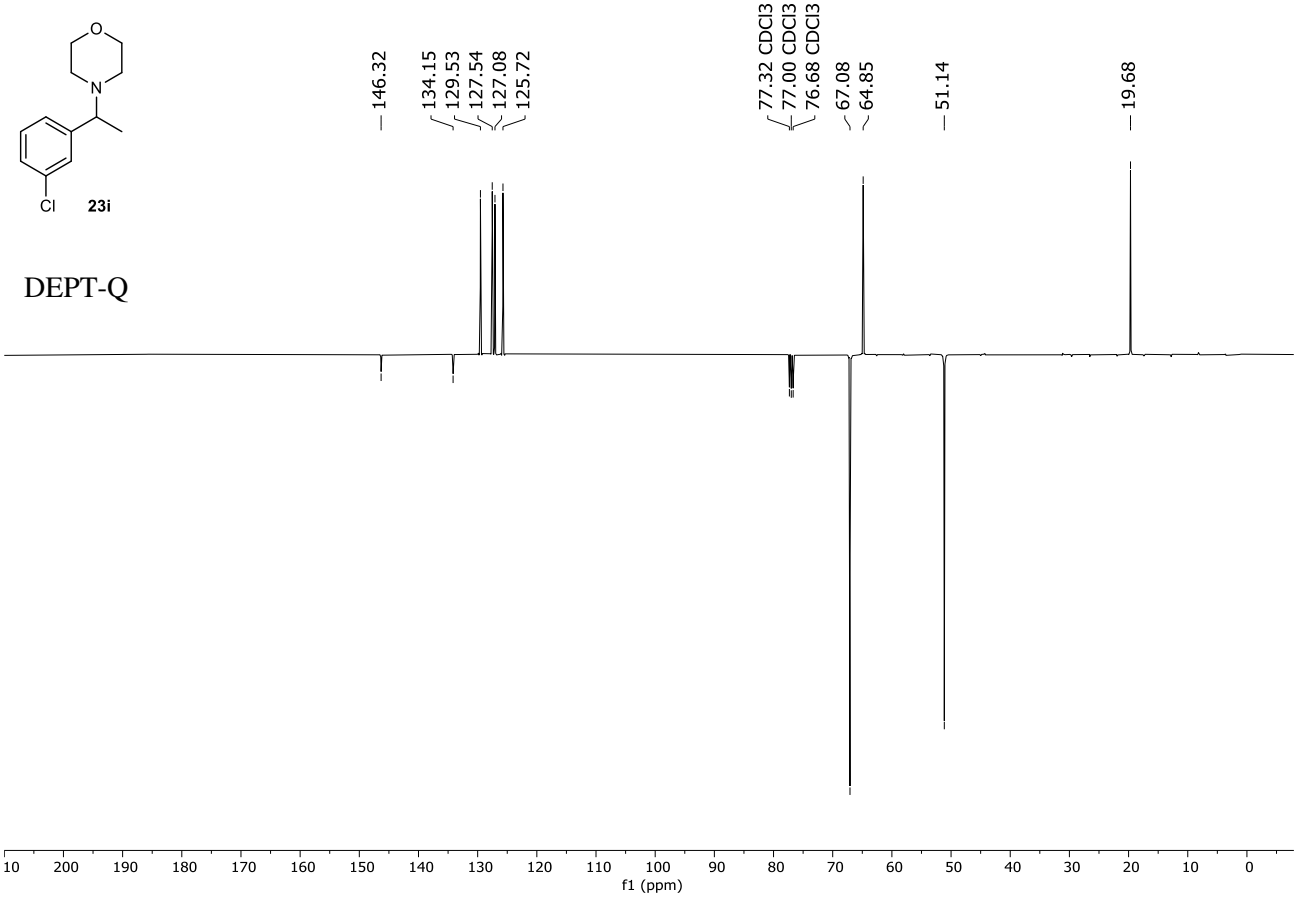
^{1}H NMR


OMe 23h
159.63
145.75
129.22
120.01
113.25
112.08
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.17
65.40
55.16
51.30
19.85
f1 (ppm)

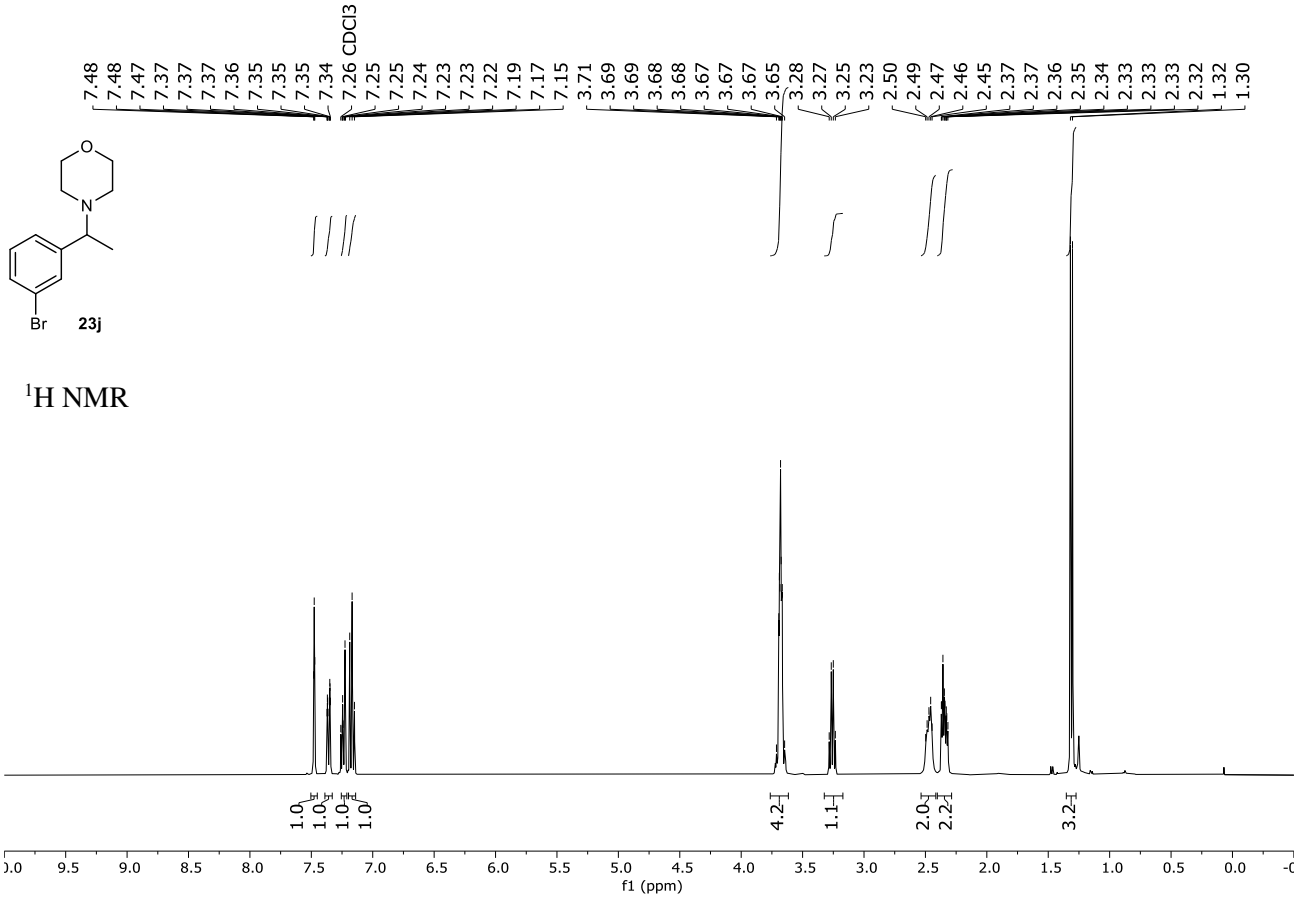
DEPT-Q


23i
7.32
7.32
7.32
7.26 CDCl3
7.25
7.23
7.23
7.21
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.17
3.69
3.69
3.68
3.68
3.67
3.67
3.66
3.29
3.28
3.26
3.24
2.50
2.49
2.47
2.46
2.44
2.37
2.36
2.34
2.34
2.33
2.32
2.32
1.32
1.30
1.0
2.9
4.0
1.0
2.0
2.1
3.0
f1 (ppm)

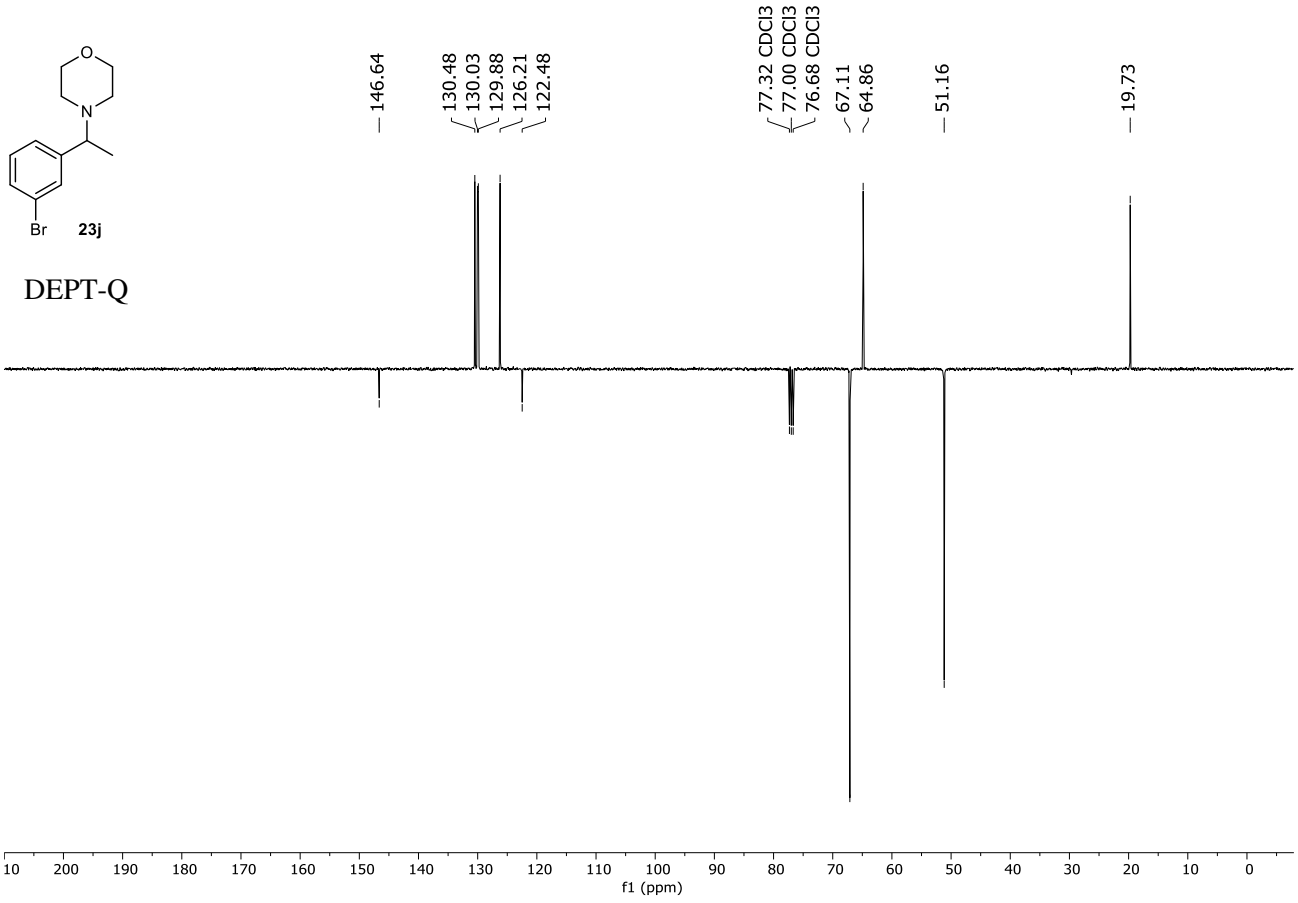
^{1}H NMR


23i
146.32
134.15
129.53
127.54
127.08
125.72
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.08
64.85
51.14
19.68
f1 (ppm)

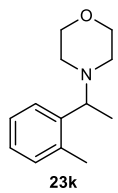
DEPT-Q


7.48 7.48 7.47 7.37 7.37 7.37 7.36 7.35 7.35 7.35 7.34 7.26 CDCl3 7.25 7.25 7.24 7.23 7.23 7.22 7.19 7.17 7.15 3.71 3.69 3.69 3.68 3.68 3.67 3.67 3.67 3.65 3.28 3.27 3.25 3.23 2.50 2.49 2.47 2.46 2.45 2.37 2.37 2.36 2.35 2.34 2.33 2.33 2.32 1.32 1.30
O
N
Br
23j
1.0 1.0 1.0 1.0 4.2 1.1 2.0 2.2 3.2
f1 (ppm)

^{1}H NMR

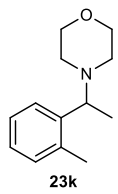

146.64
130.48
130.03
129.88
126.21
122.48
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.11
64.86
51.16
19.73
O
N
Br
23j
f1 (ppm)

DEPT-Q



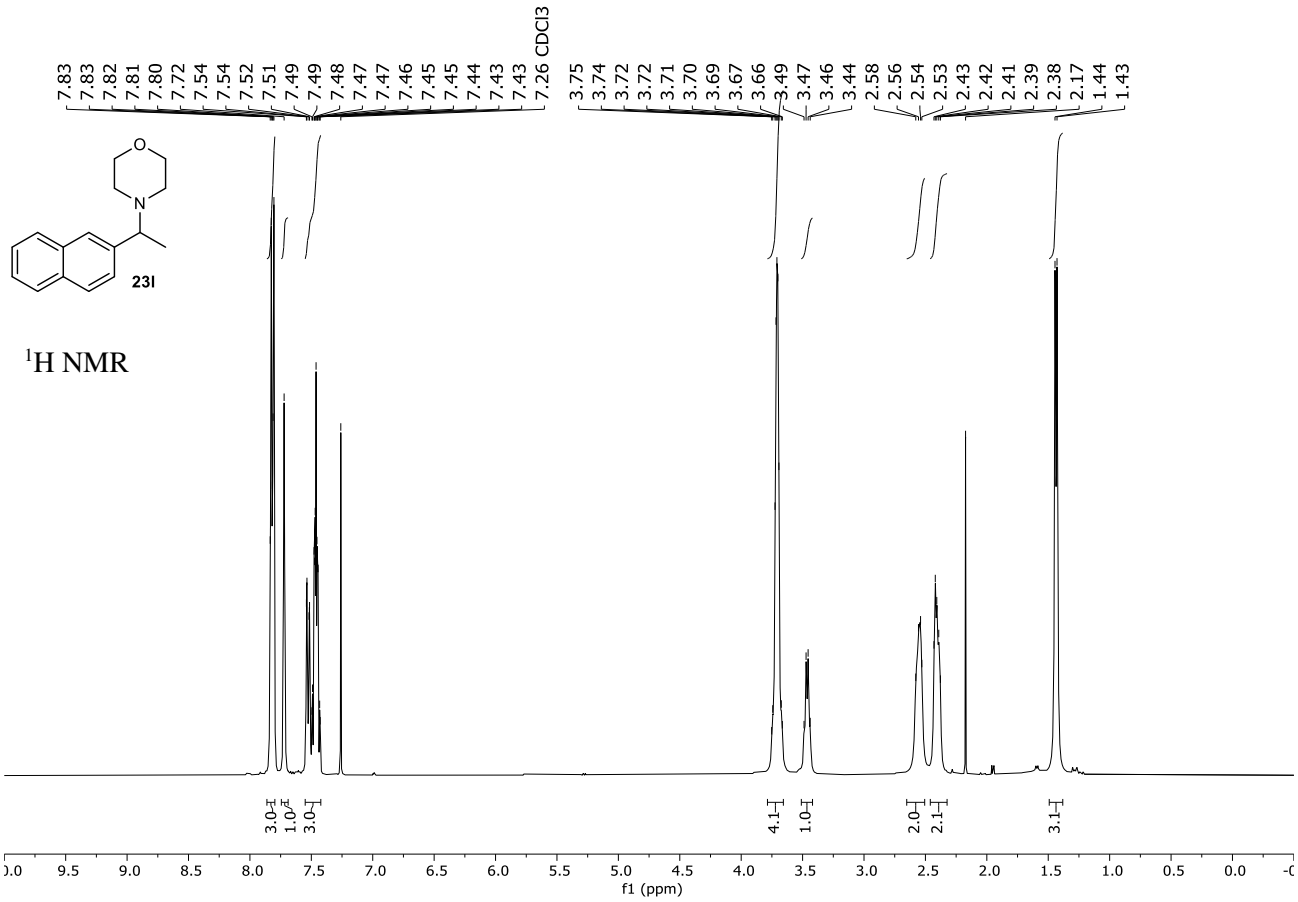
23k

^{1}H NMR

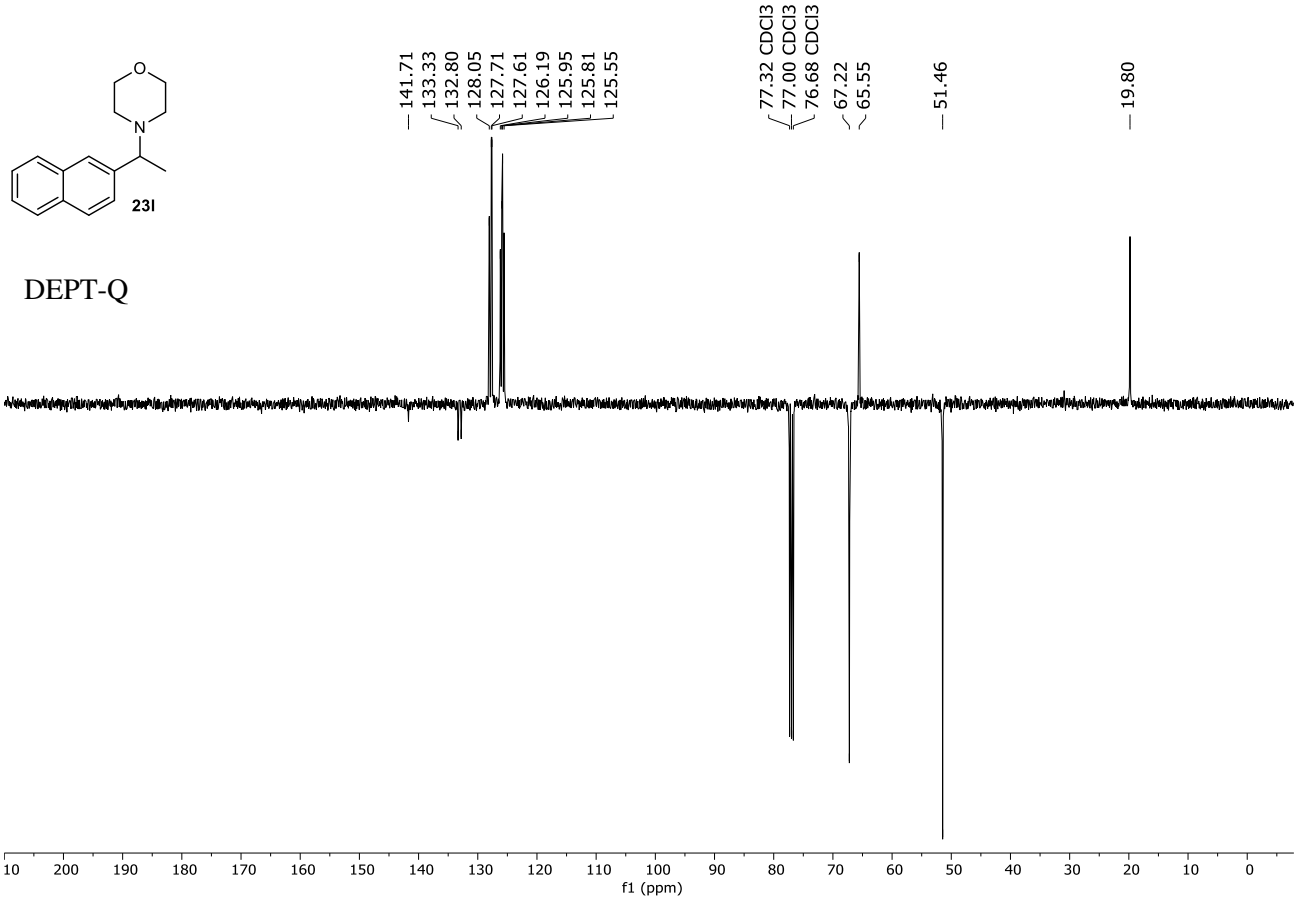


23k

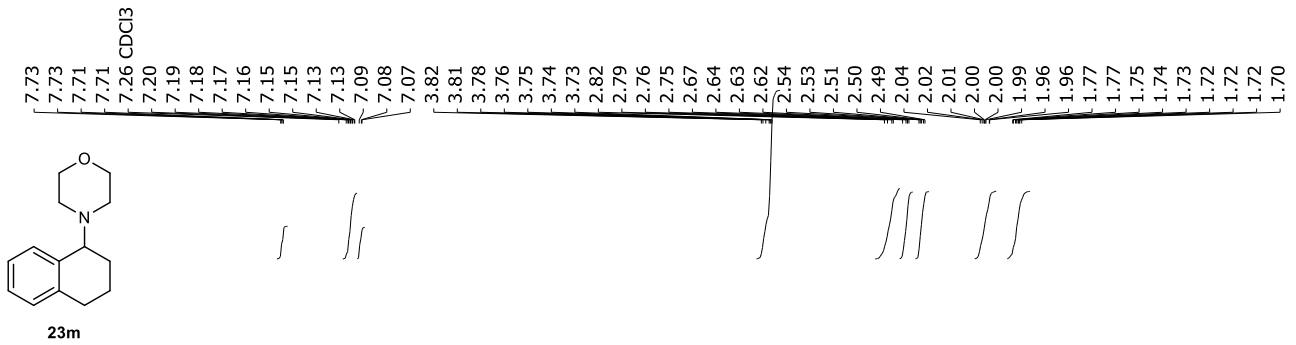
^{13}C NMR


7.83
7.83
7.82
7.81
7.80
7.72
7.54
7.54
7.52
7.51
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.26 CDCl3
3.75
3.74
3.72
3.72
3.71
3.70
3.69
3.67
3.66
3.49
3.47
3.46
3.44
2.58
2.56
2.54
2.53
2.43
2.42
2.41
2.39
2.38
2.17
1.44
1.43
O
N
23l
3.0
1.0
3.0
4.1
1.0
2.0
2.1
3.1
f1 (ppm)

^{1}H NMR

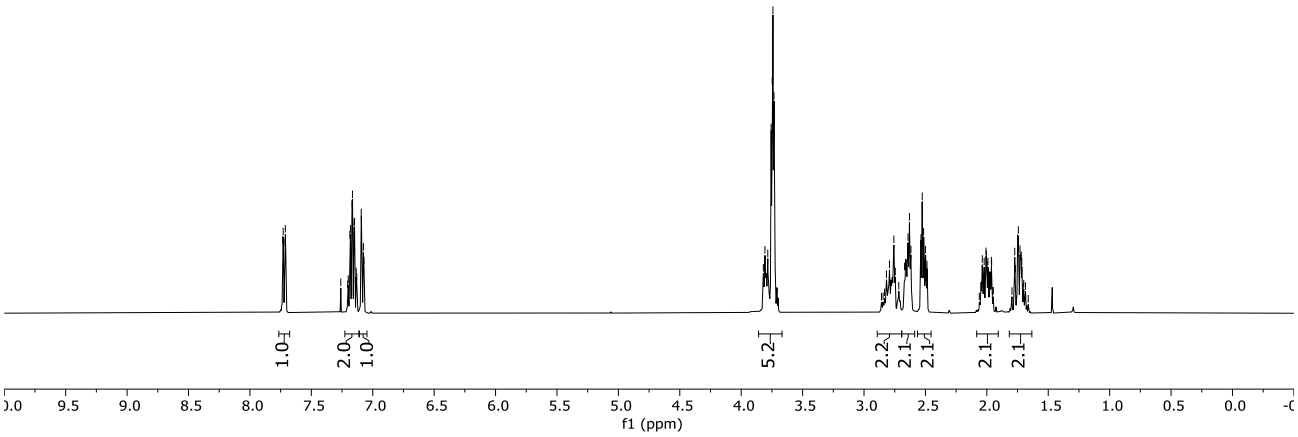

141.71
133.33
132.80
128.05
127.71
127.61
126.19
125.95
125.81
125.55
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.22
65.55
51.46
19.80
O
N
23l
f1 (ppm)

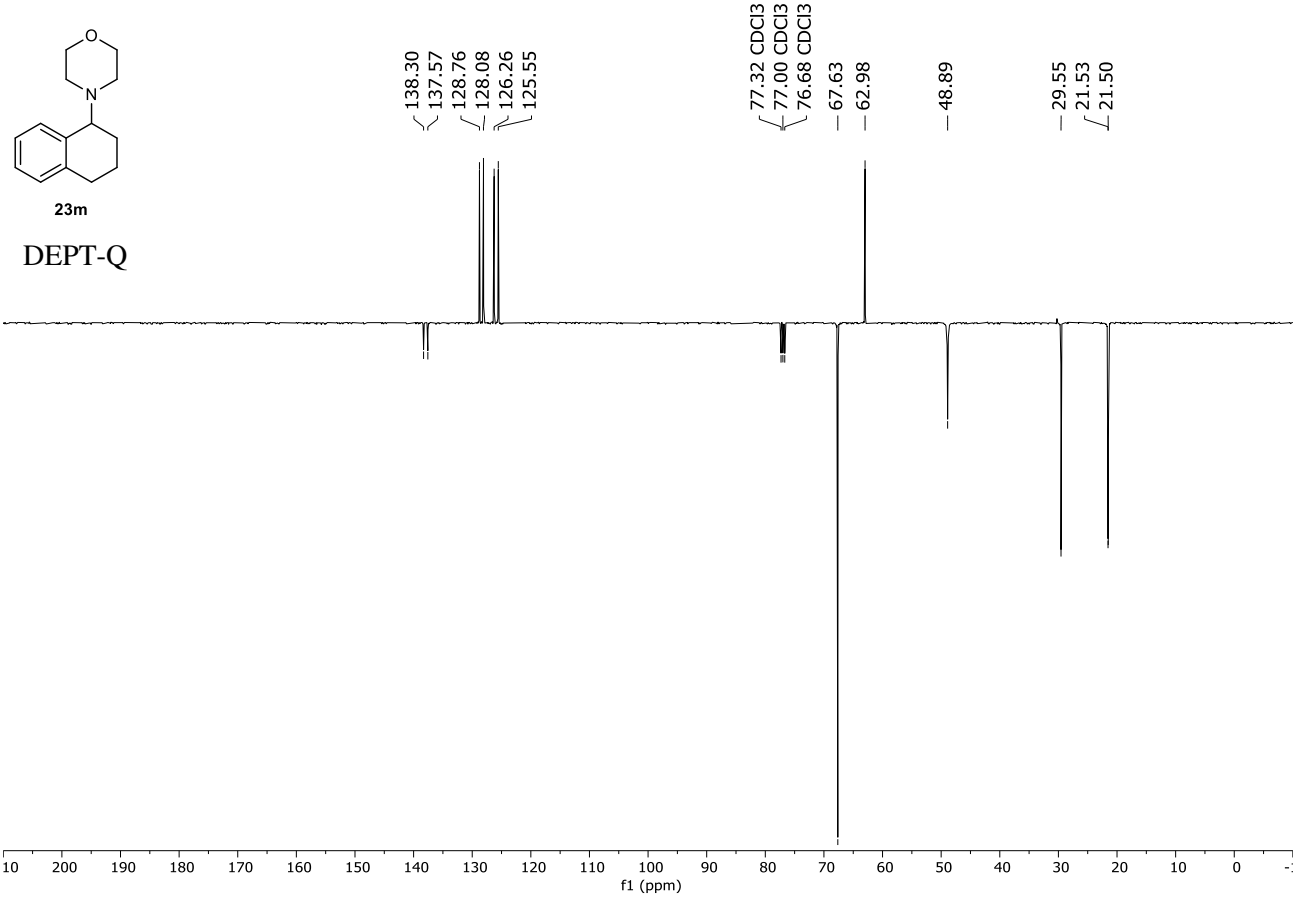
DEPT-Q



23m

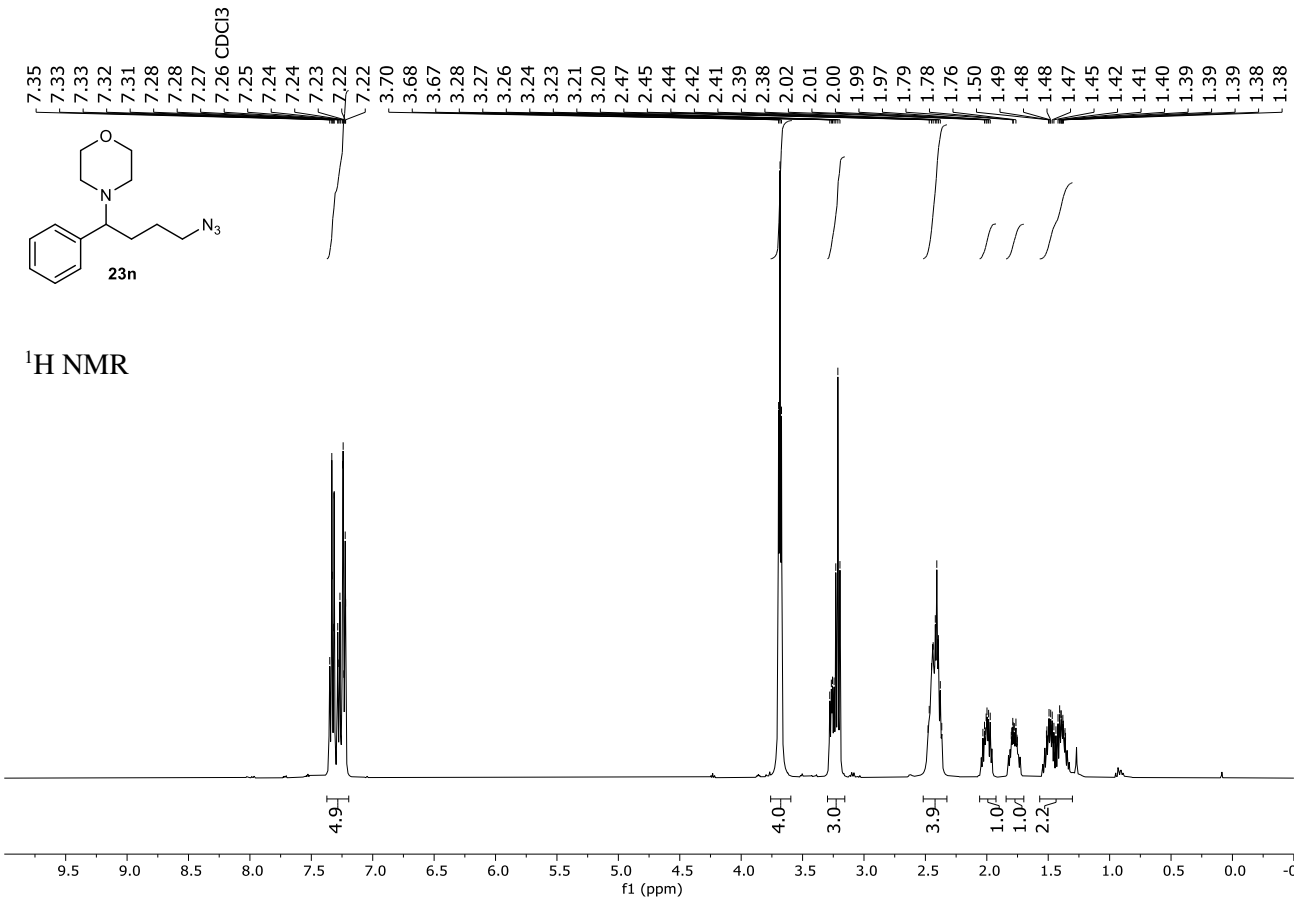
^{1}H NMR

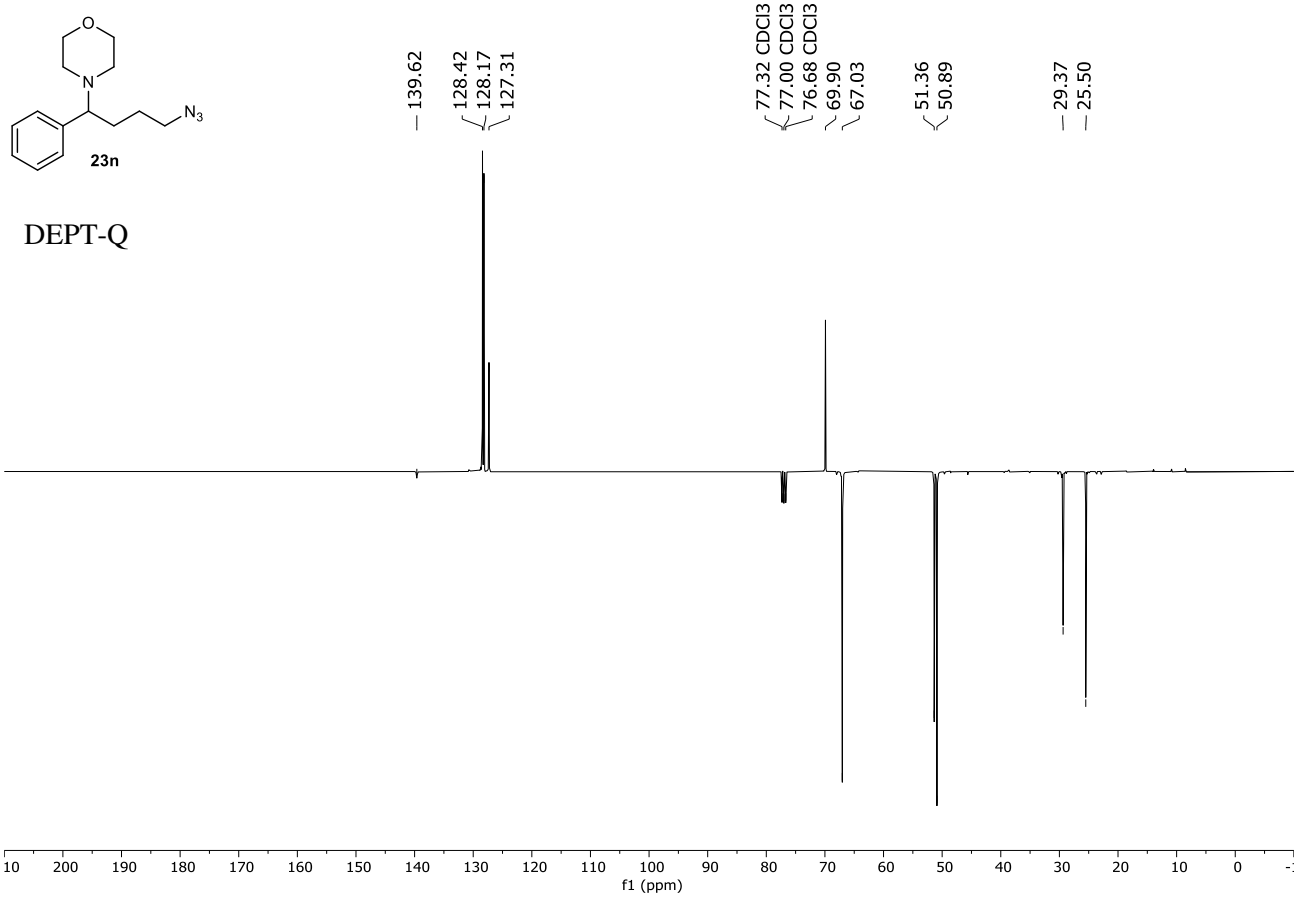


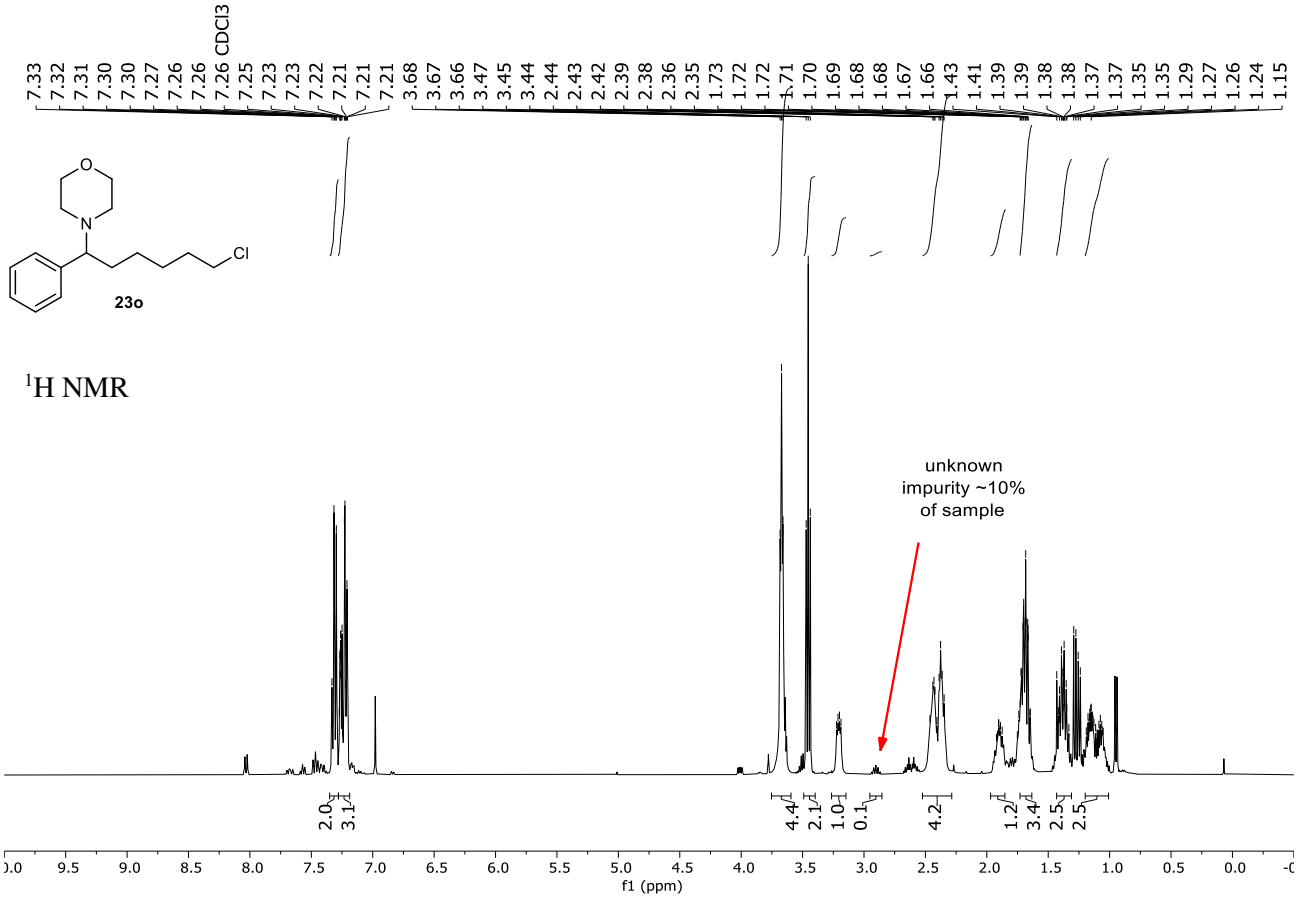


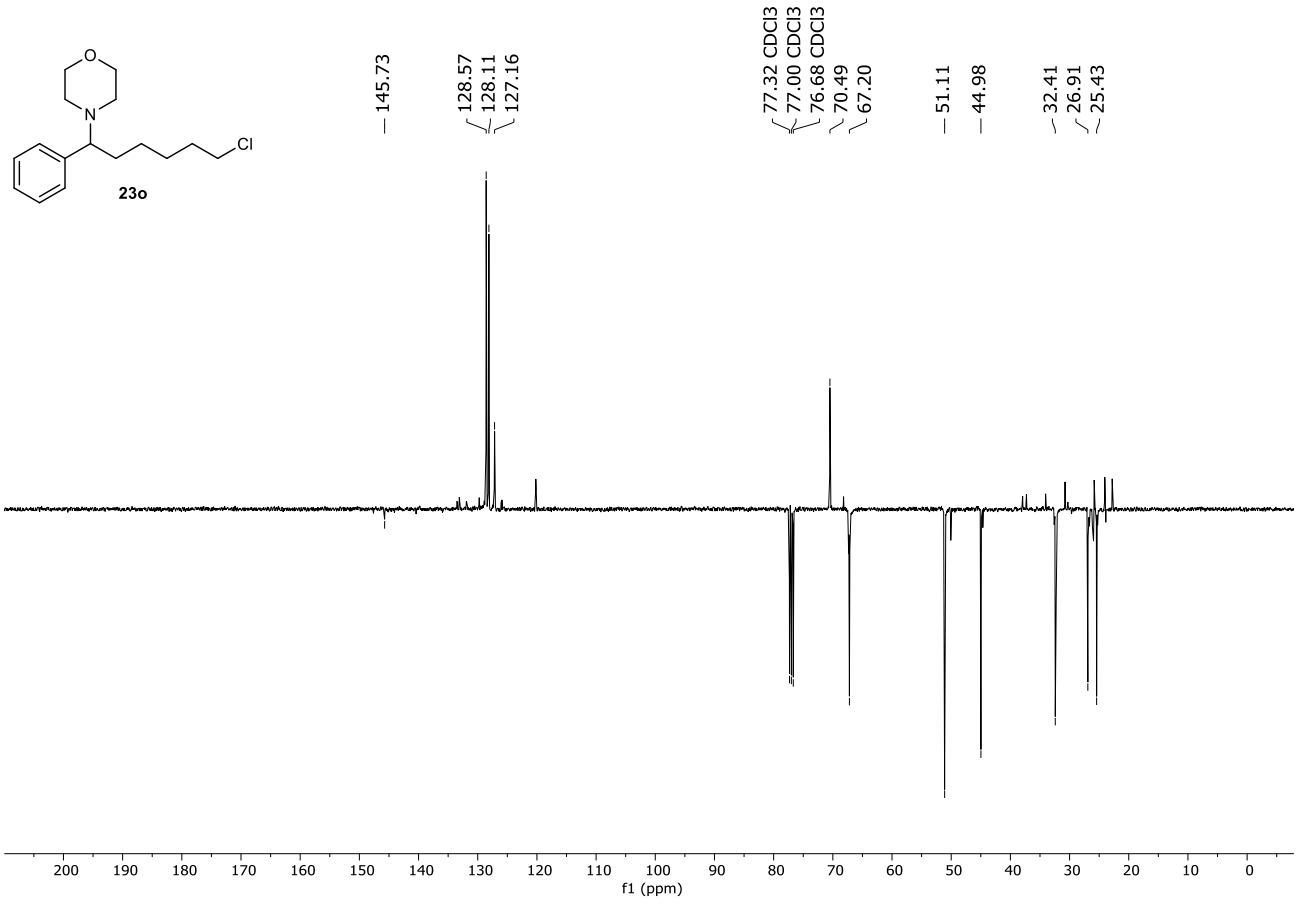
23m

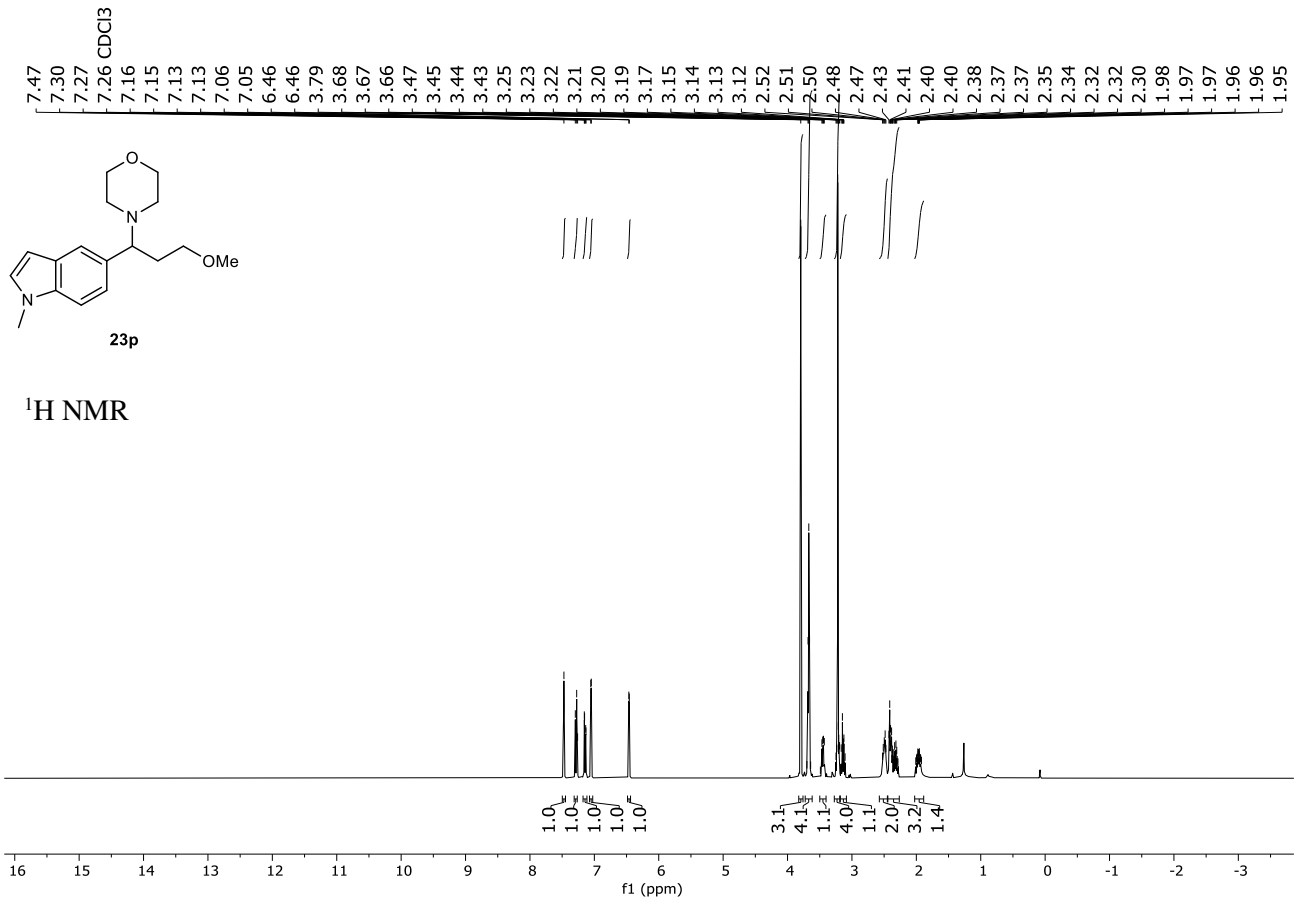
DEPT-Q


7.35 7.33 7.33 7.32 7.31 7.28 7.28 7.27 7.26 CDCl3 7.25 7.24 7.24 7.23 7.22 7.22
3.70 3.68 3.67 3.28 3.27 3.26 3.24 3.23 3.21 3.20 2.47 2.45 2.44 2.42 2.41 2.39 2.38 2.02 2.01 2.00 1.99 1.97 1.79 1.78 1.76 1.50 1.49 1.48 1.48 1.47 1.45 1.42 1.41 1.40 1.39 1.39 1.38 1.38
O
N
N3
23n
1H NMR
4.9
4.0
3.0
3.9
1.0
1.0
2.2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

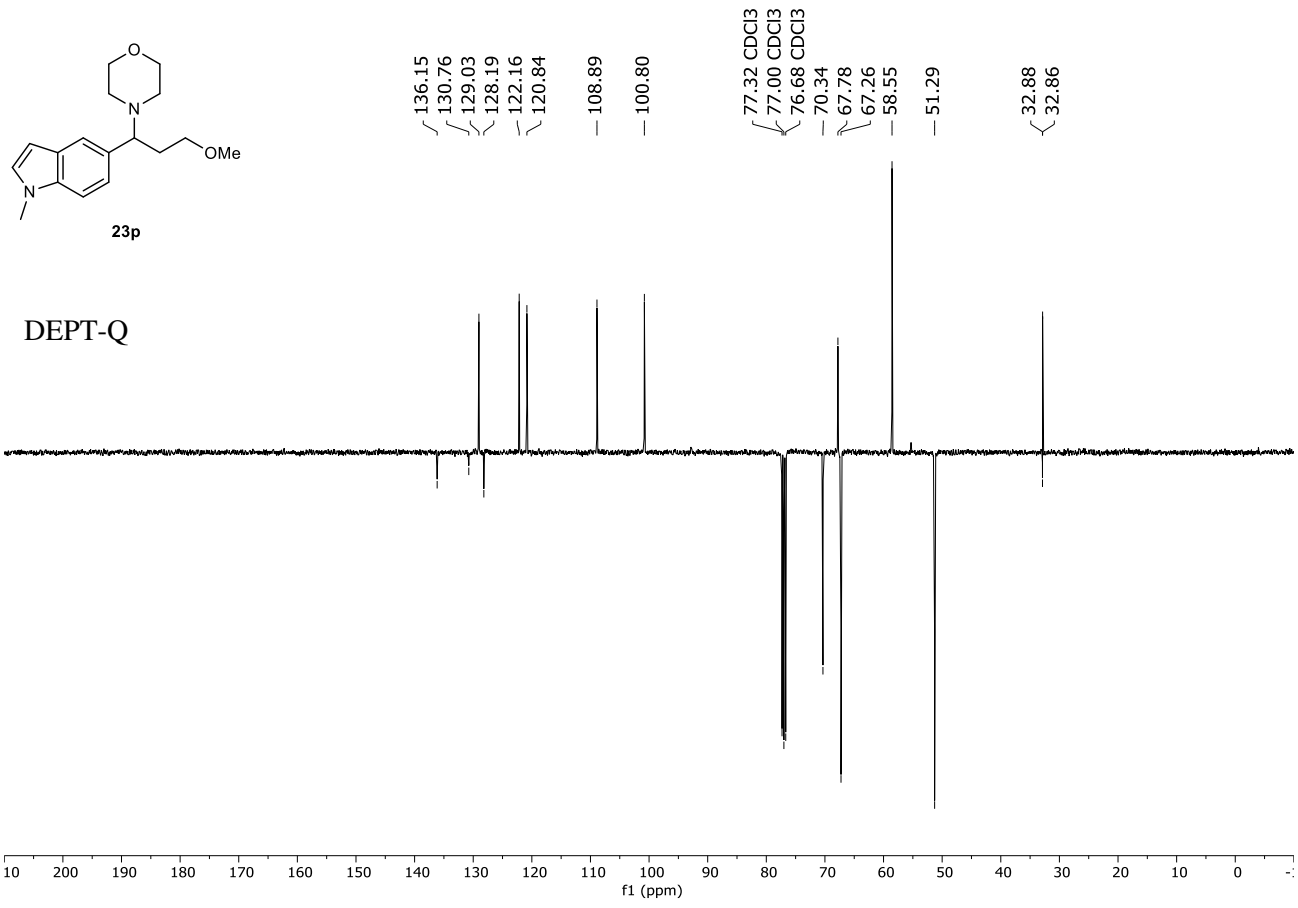

O
N
N3
23n
DEPT-Q
139.62
128.42
128.17
127.31
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.90
67.03
51.36
50.89
29.37
25.50
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.33
7.32
7.31
7.30
7.30
7.27
7.26
7.26
7.26
CDCl3
7.25
7.23
7.23
7.22
7.21
7.21
7.21
3.68
3.67
3.66
3.47
3.45
3.44
2.44
2.43
2.42
2.39
2.38
2.36
2.35
1.73
1.72
1.72
1.71
1.70
1.69
1.68
1.68
1.67
1.66
1.43
1.41
1.39
1.39
1.38
1.38
1.37
1.37
1.35
1.35
1.29
1.27
1.26
1.24
1.15
O
N
Cl
23o
1H NMR
unknown
impurity ~10%
of sample
2.0
3.1
4.4
2.1
1.0
0.1
4.2
1.2
3.4
2.5
2.5
f1 (ppm)

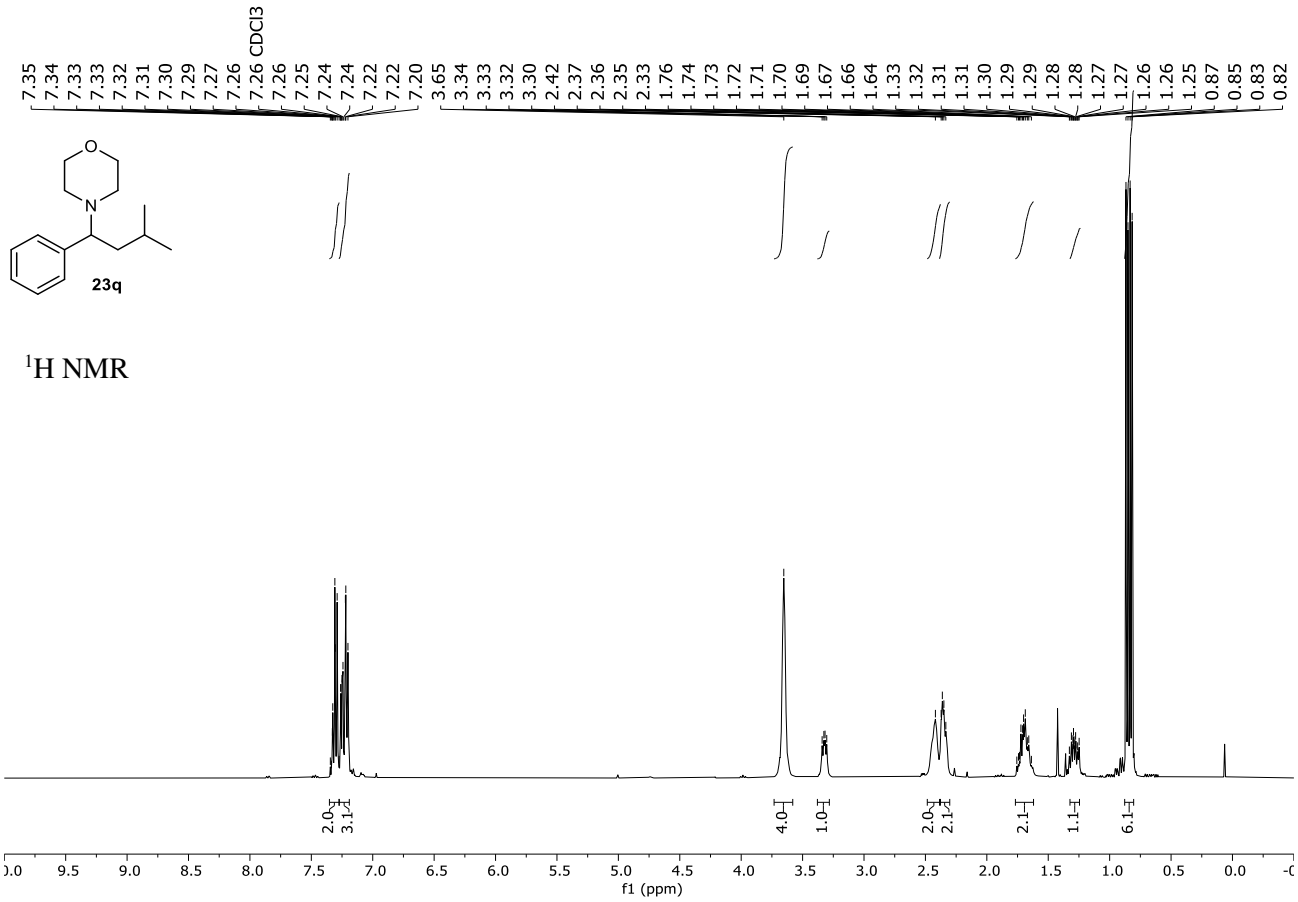

O
N
Cl
23o
145.73
128.57
128.11
127.16
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
70.49
67.20
51.11
44.98
32.41
26.91
25.43
f1 (ppm)


7.47
7.30
7.27
7.26 CDCl3
7.16
7.15
7.13
7.13
7.06
7.05
6.46
6.46
3.79
3.68
3.67
3.66
3.47
3.45
3.44
3.43
3.25
3.23
3.22
3.21
3.20
3.19
3.17
3.15
3.14
3.13
3.12
2.52
2.51
2.50
2.48
2.47
2.43
2.41
2.40
2.40
2.38
2.37
2.37
2.35
2.34
2.32
2.32
2.30
1.98
1.97
1.97
1.96
1.96
1.95
O
N
OMe
N
23p
1.0
1.0
1.0
1.0
1.0
3.1
4.1
1.1
4.0
1.1
2.0
3.2
1.4
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

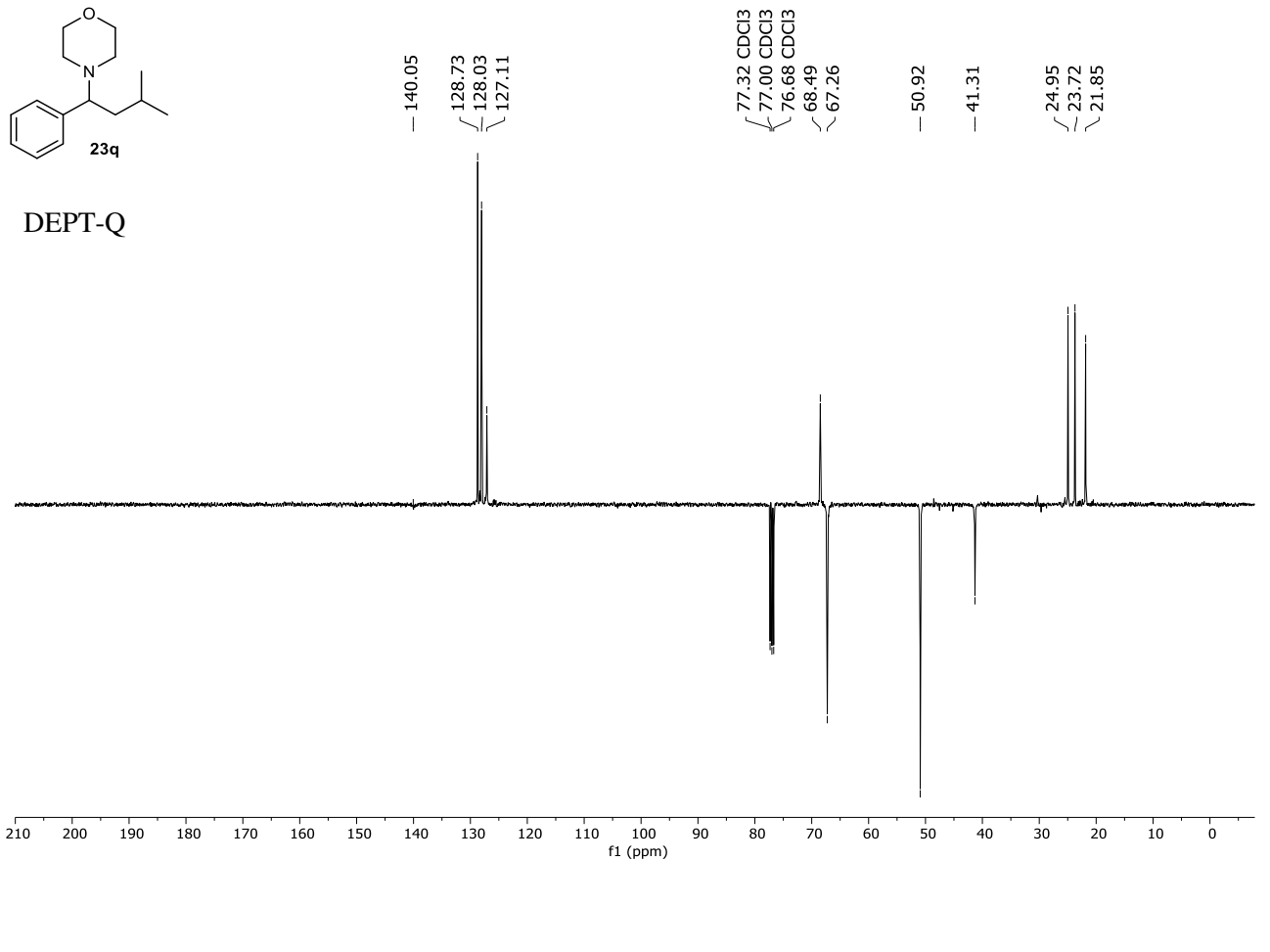
^{1}H NMR


O
N
OMe
N
23p
136.15
130.76
129.03
128.19
122.16
120.84
108.89
100.80
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
70.34
67.78
67.26
58.55
51.29
32.88
32.86
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

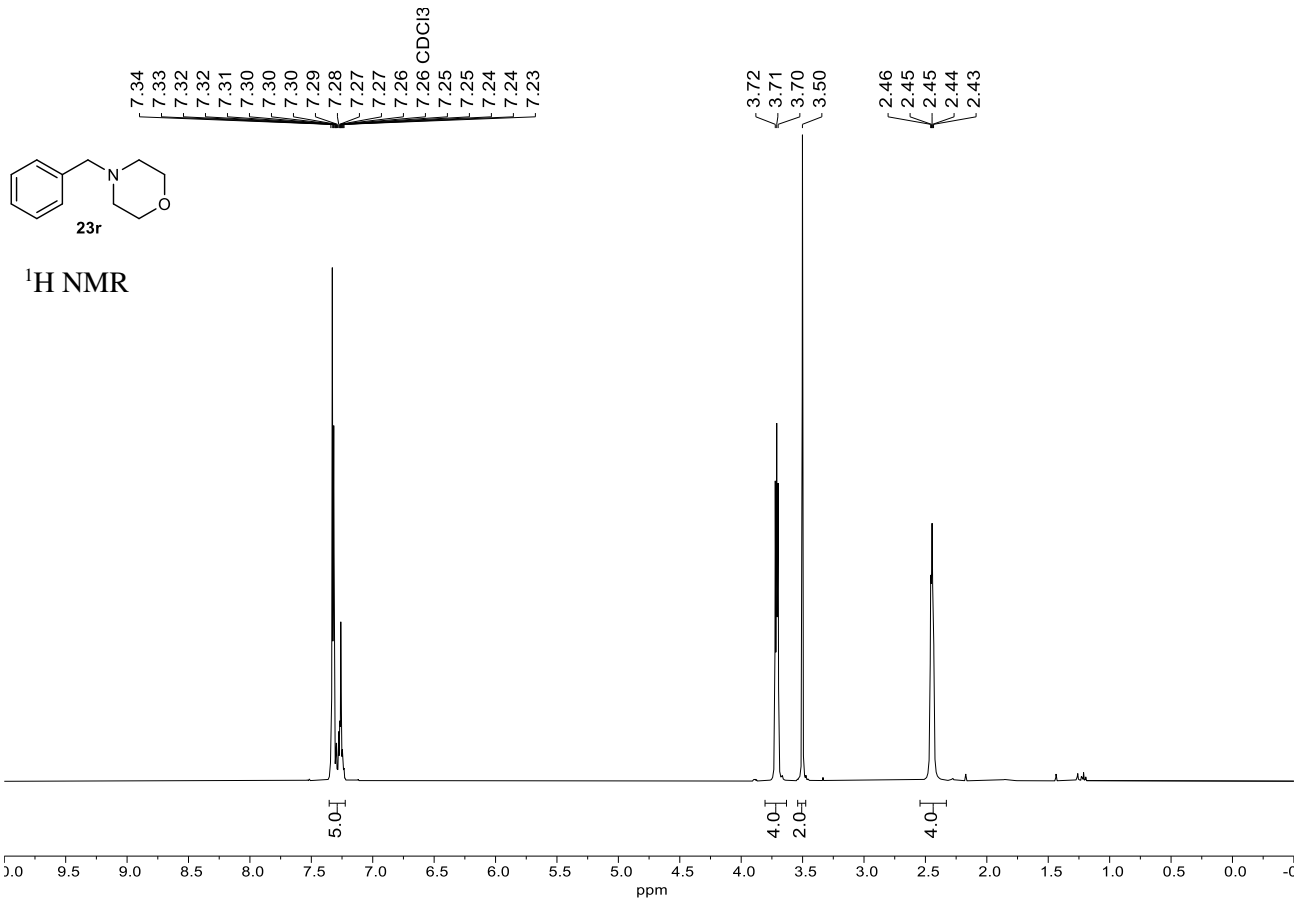
DEPT-Q

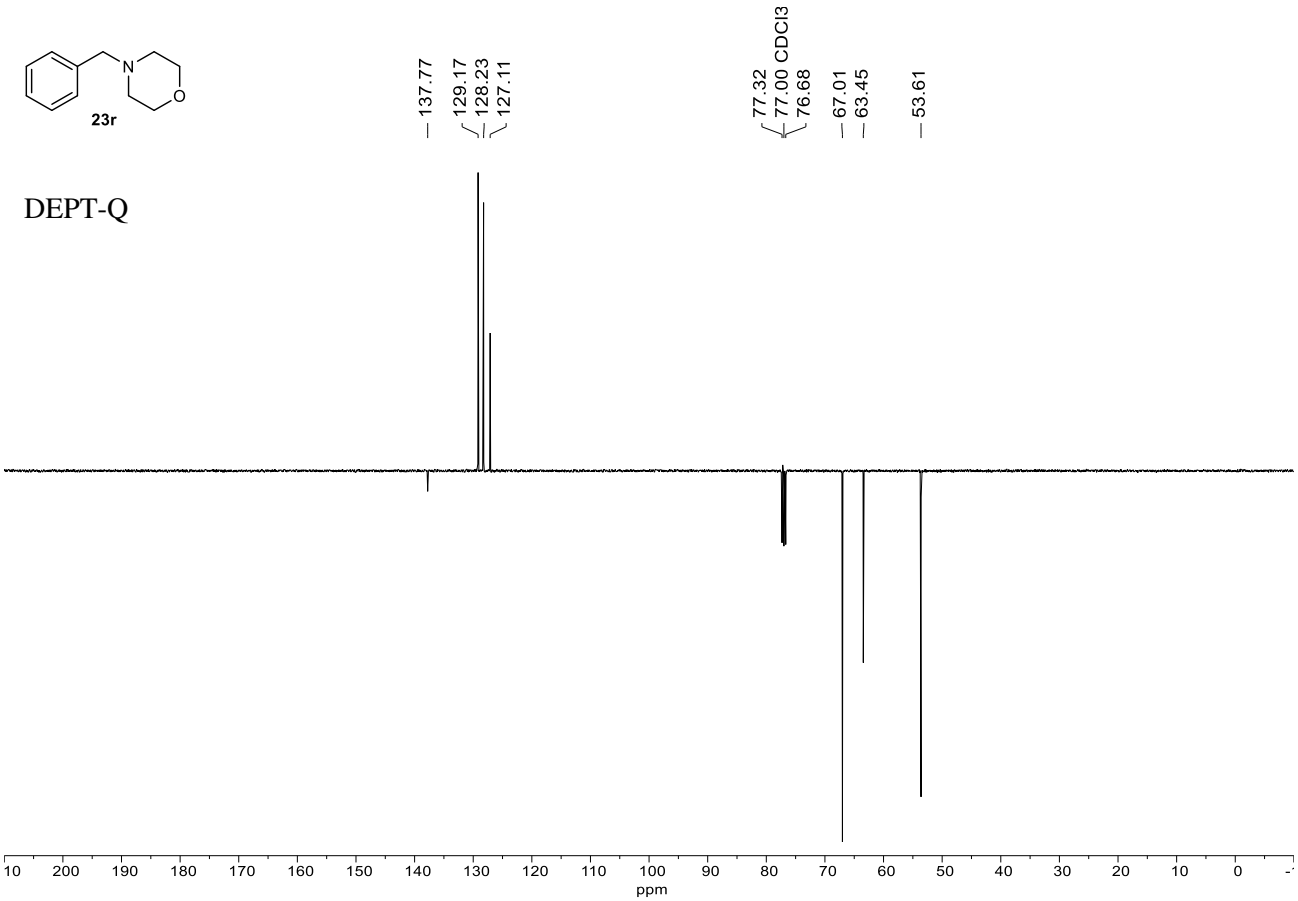

7.35 7.34 7.33 7.33 7.32 7.31 7.30 7.29 7.27 7.26 CDCl3 7.26 7.25 7.24 7.24 7.22 7.20
3.65 3.34 3.33 3.32 3.30 2.42 2.37 2.36 2.35 2.33 1.76 1.74 1.73 1.72 1.71 1.70 1.69 1.67 1.66 1.64 1.33 1.32 1.31 1.31 1.30 1.29 1.29 1.28 1.28 1.27 1.27 1.26 1.26 1.25 0.87 0.85 0.83 0.82
O
N
23q
2.0 3.1 4.0 1.0 2.0 2.1 2.1 1.1 6.1
f1 (ppm)

^{1}H NMR

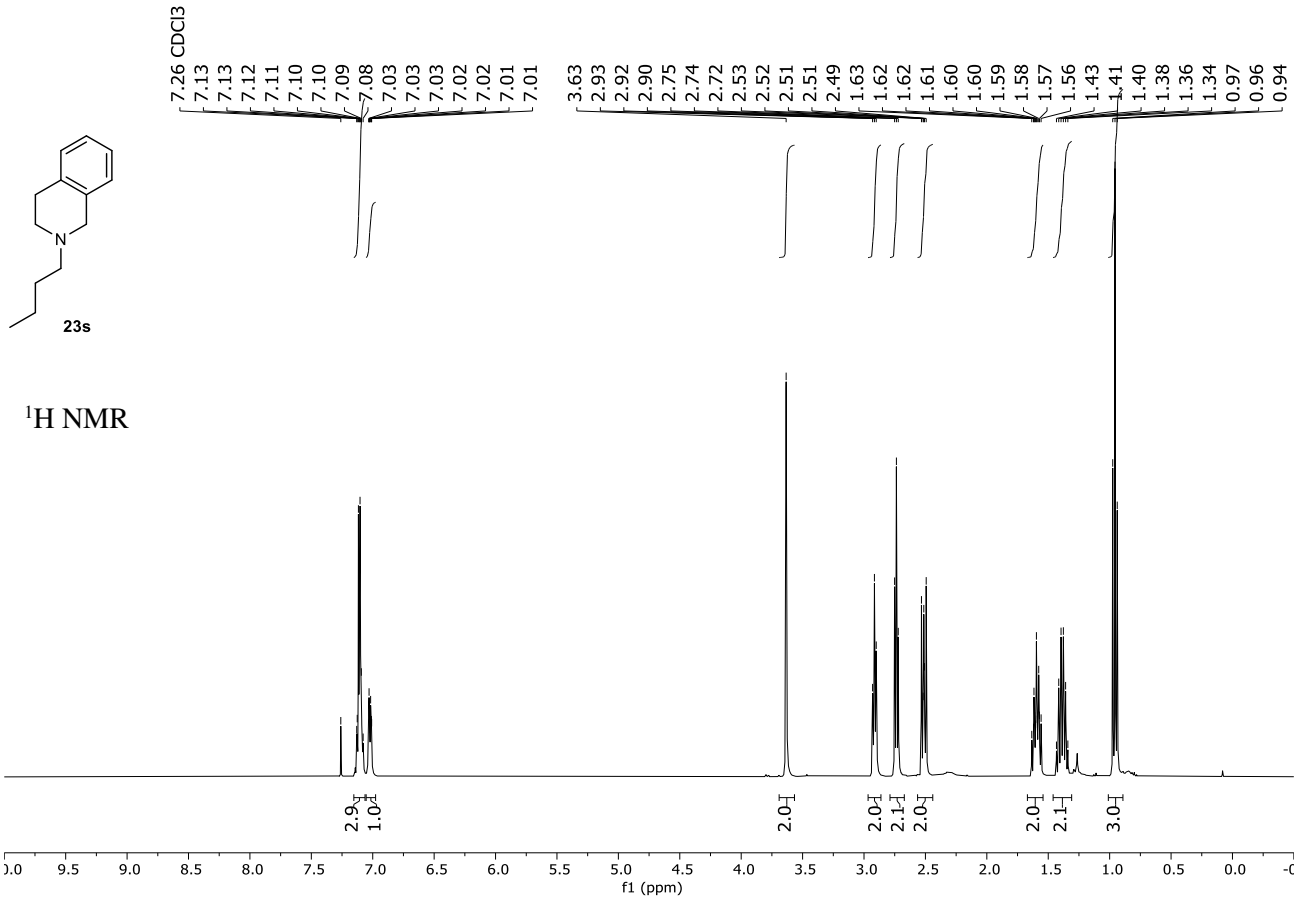

O
N
23q
140.05
128.73
128.03
127.11
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
68.49
67.26
50.92
41.31
24.95
23.72
21.85
f1 (ppm)

DEPT-Q

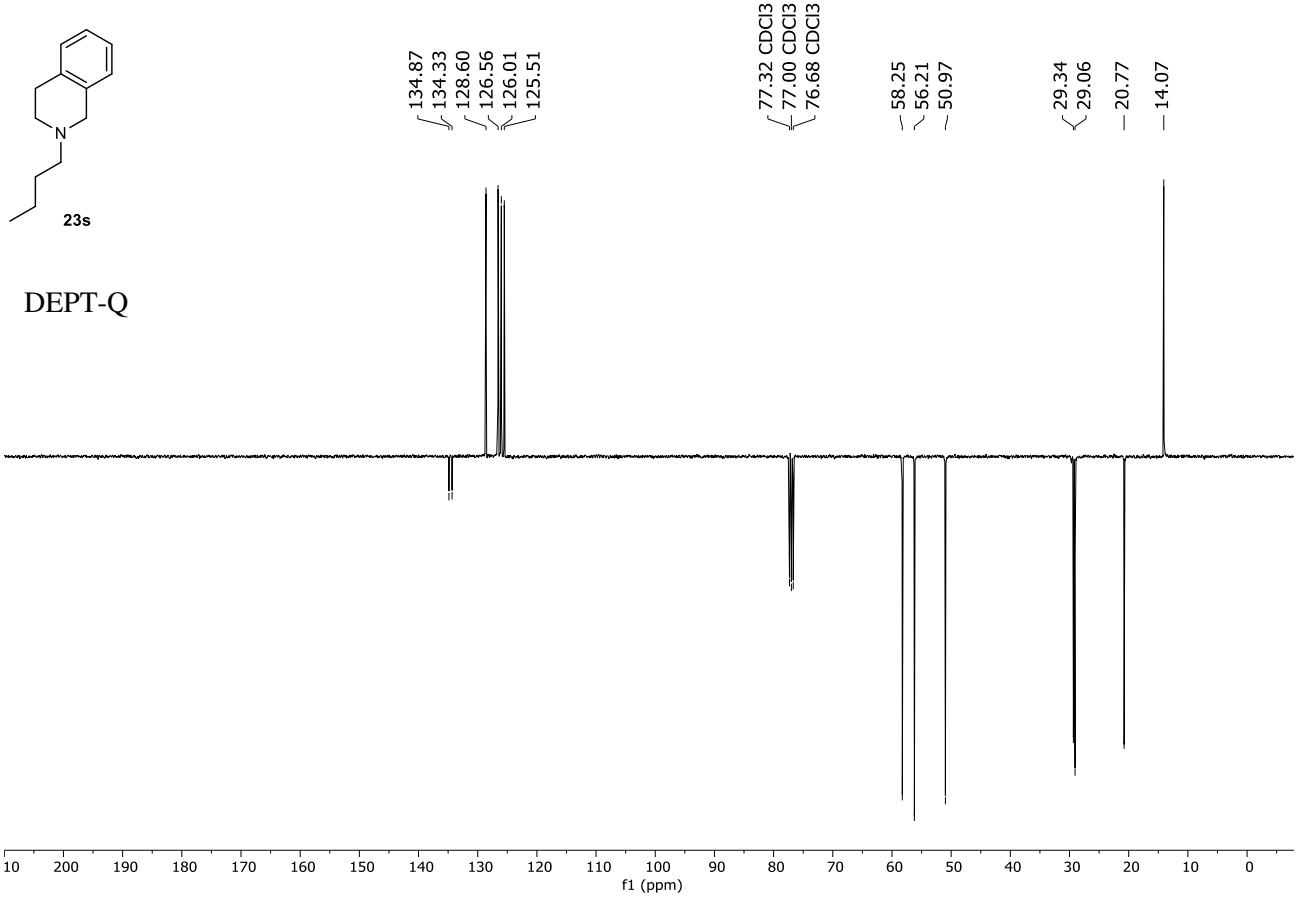

7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.30
7.29
7.28
7.27
7.27
7.26
7.26 CDCl3
7.25
7.25
7.24
7.24
7.23
3.72
3.71
3.70
3.50
2.46
2.45
2.45
2.44
2.43
N
O
23r
1H NMR
5.0
4.0
2.0
4.0
ppm


N
O
23r
DEPT-Q
137.77
129.17
128.23
127.11
77.32
77.00 CDCl3
76.68
67.01
63.45
53.61
ppm

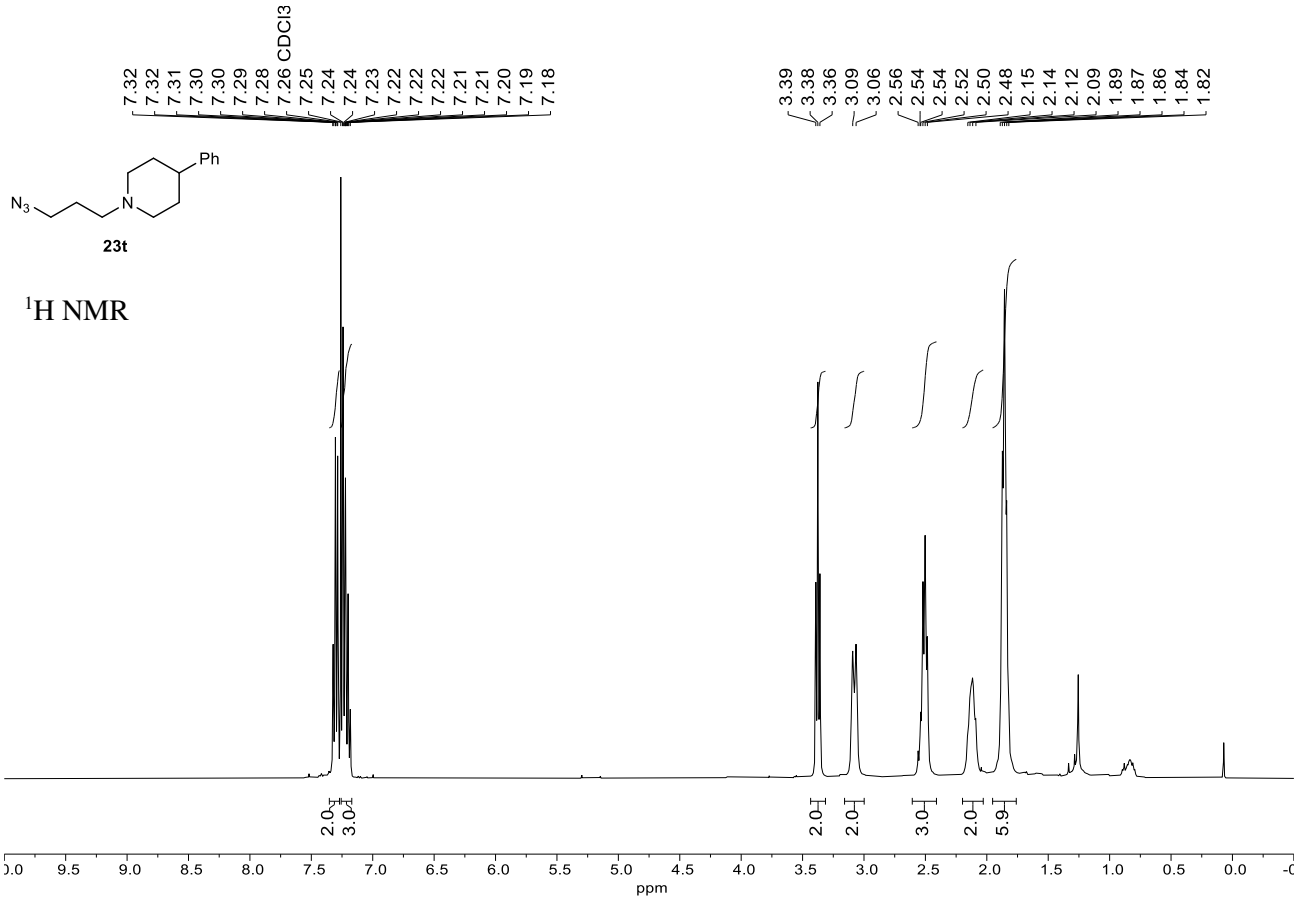
4.6. Coupling of Aliphatic Boronic Esters

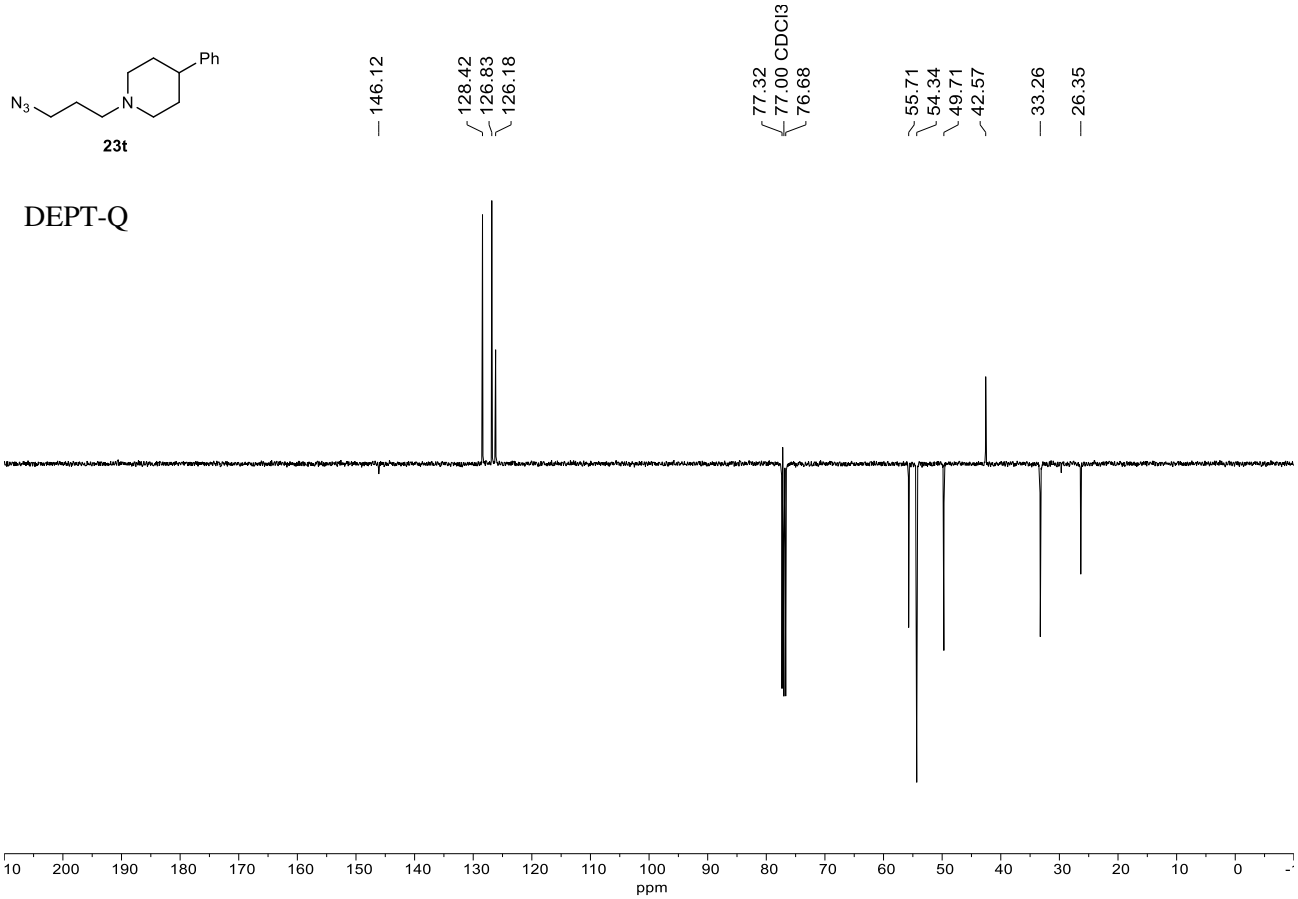


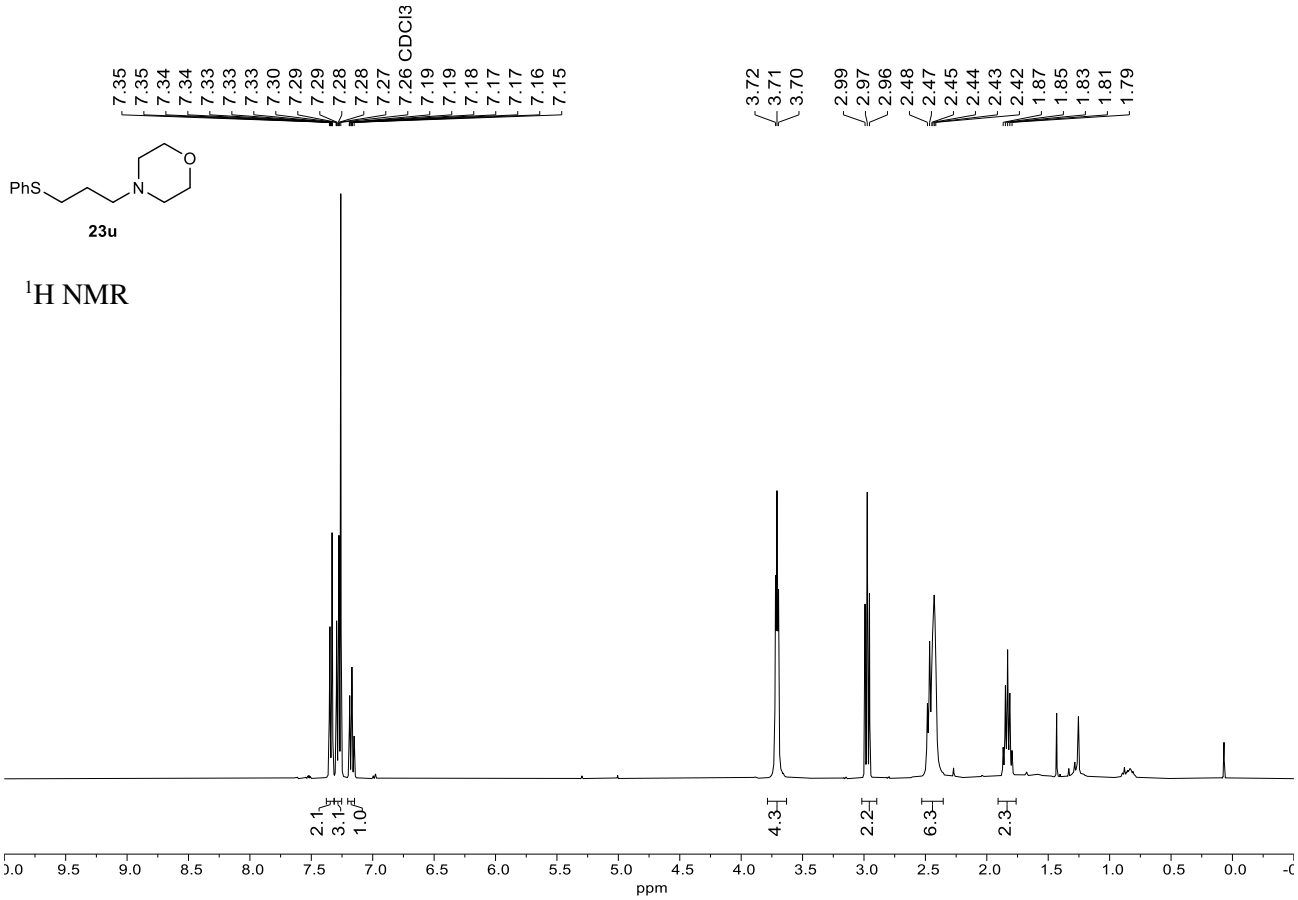
^{1}H NMR



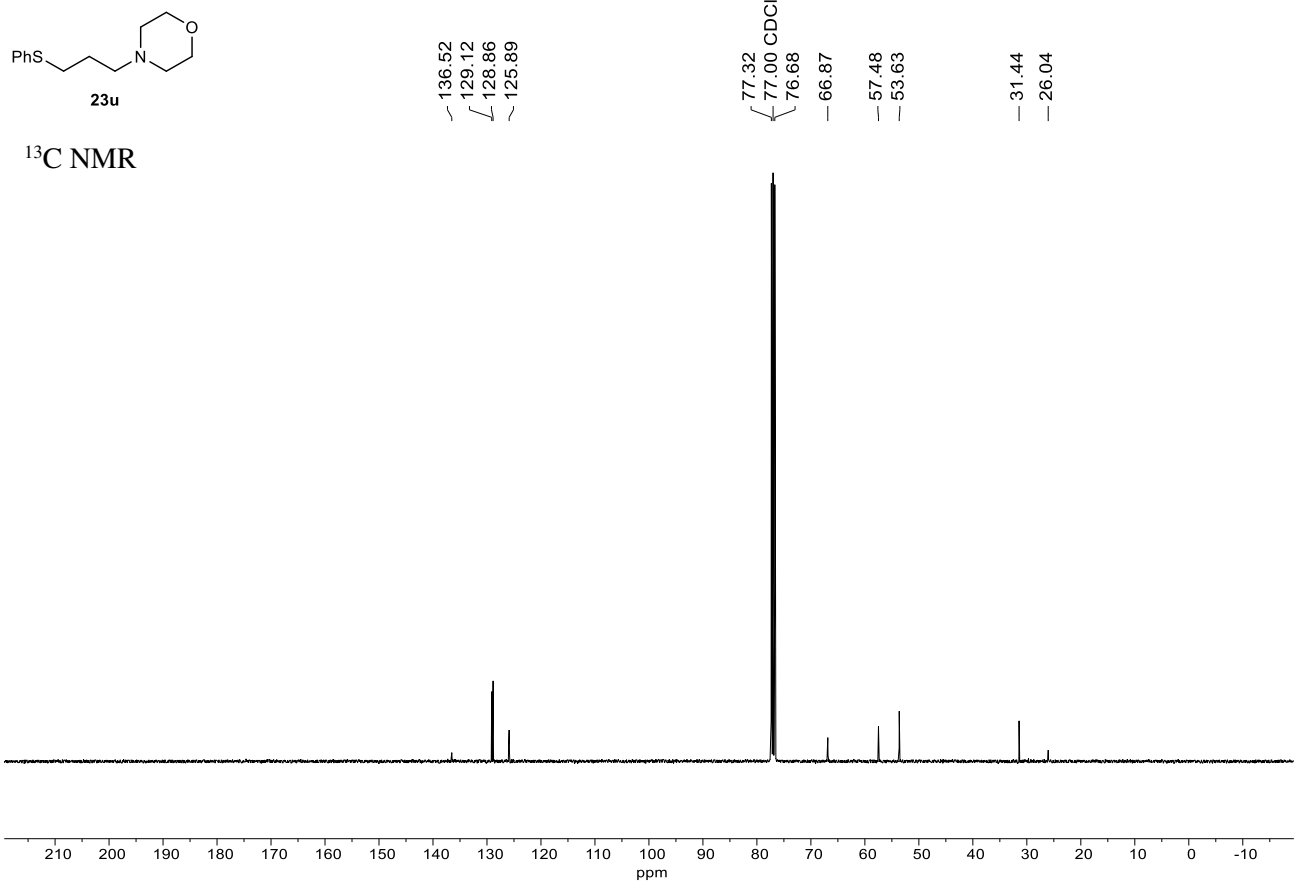
DEPT-Q


7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.26 CDCl3
7.25
7.24
7.24
7.23
7.22
7.22
7.22
7.21
7.21
7.20
7.19
7.18
3.39
3.38
3.36
3.09
3.06
2.56
2.54
2.54
2.52
2.50
2.48
2.15
2.14
2.12
2.09
1.89
1.87
1.86
1.84
1.82
Ph
N3
N
23t
1H NMR
2.0
3.0
2.0
2.0
3.0
2.0
5.9
ppm

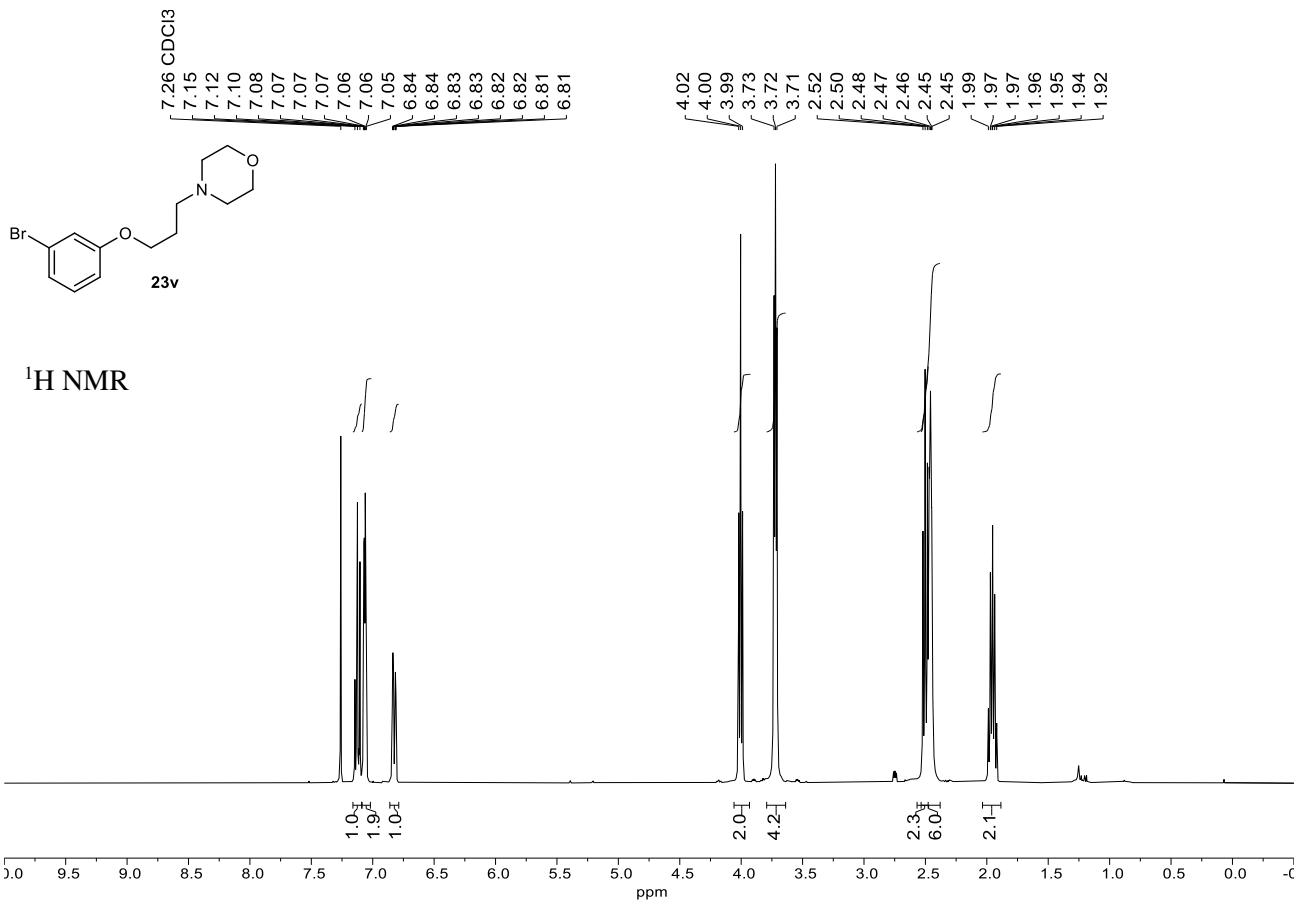

Ph
N3
N
23t
DEPT-Q
146.12
128.42
126.83
126.18
77.32
77.00 CDCl3
76.68
55.71
54.34
49.71
42.57
33.26
26.35
ppm

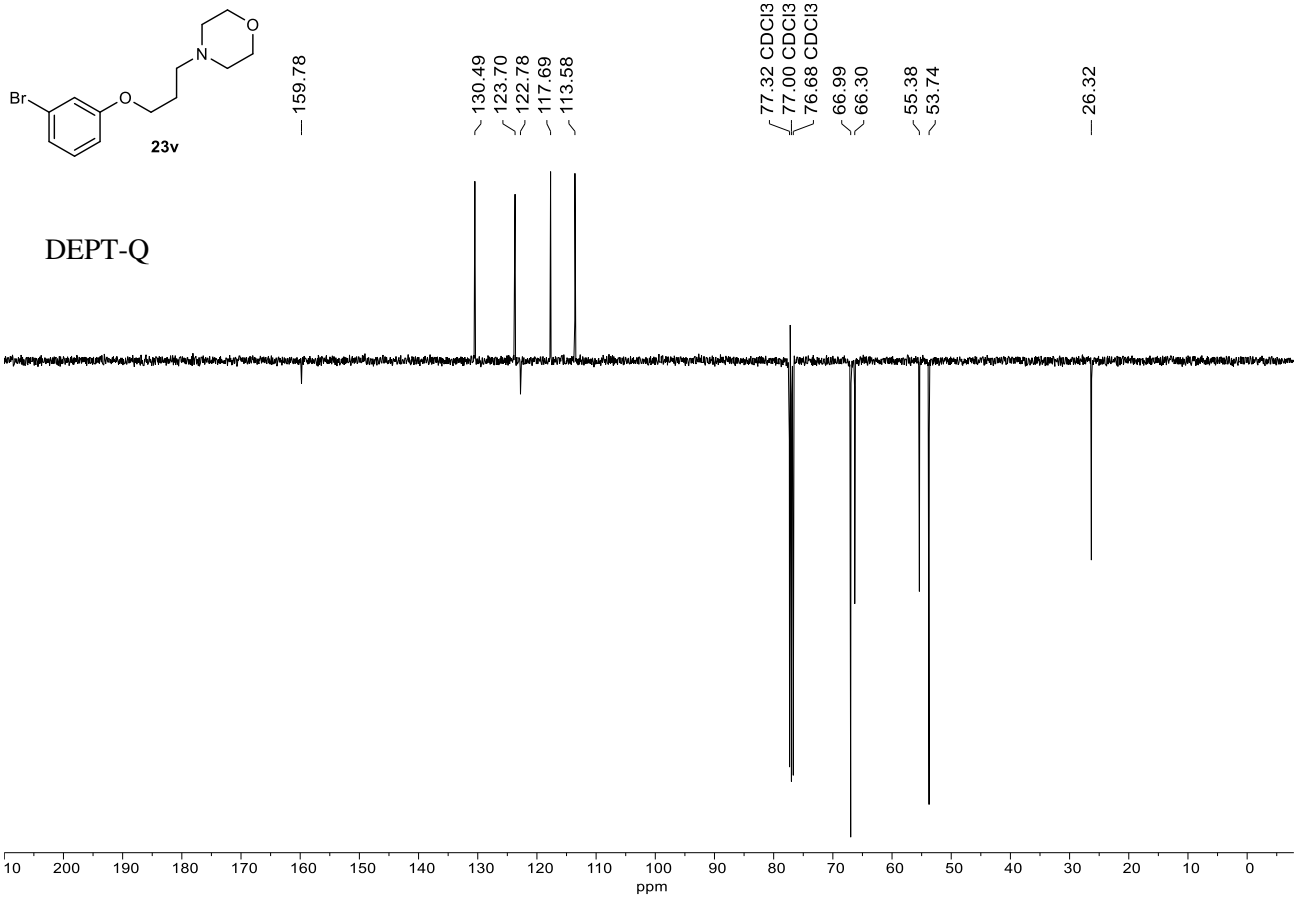


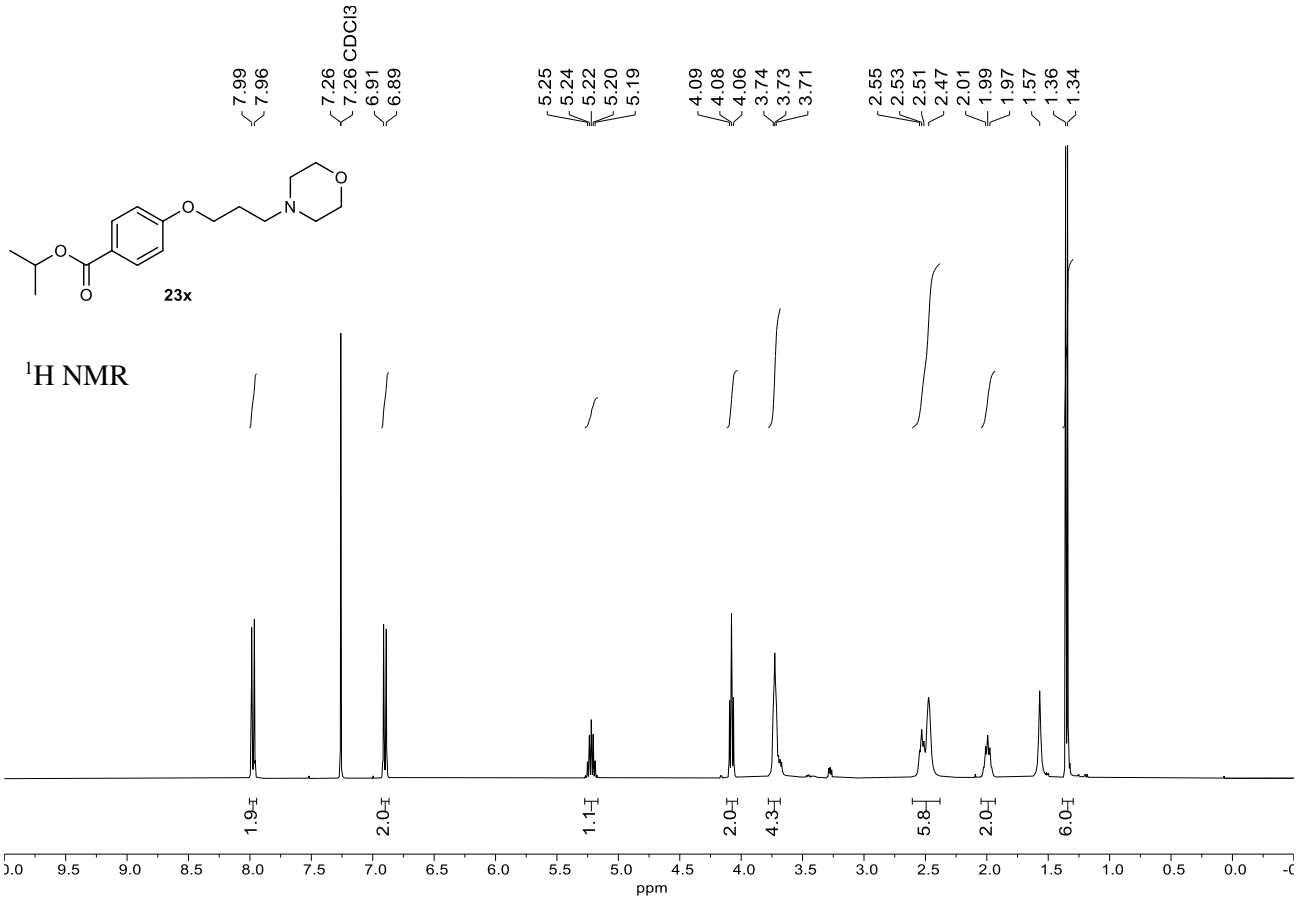
^{1}H NMR

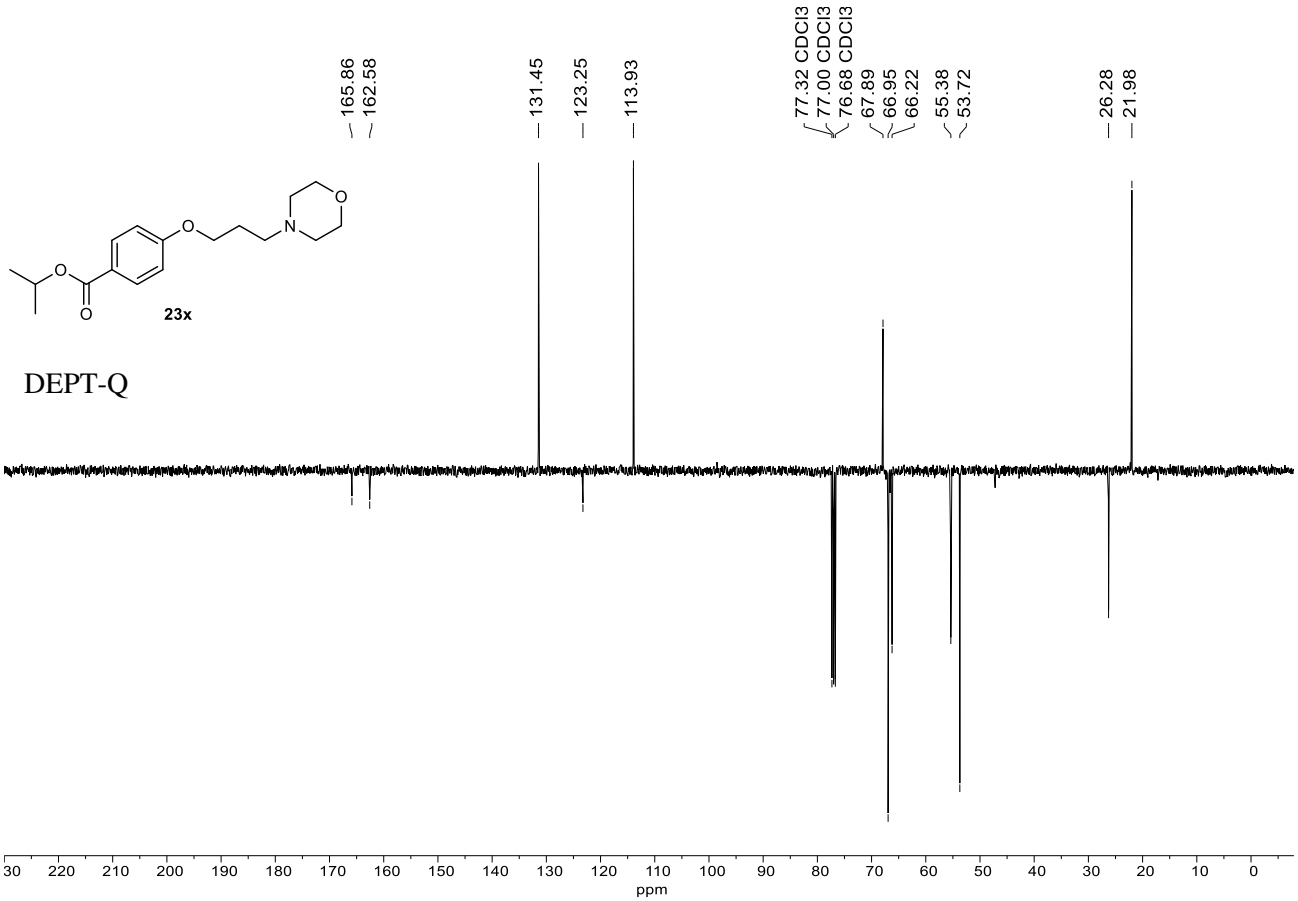


^{13}C NMR

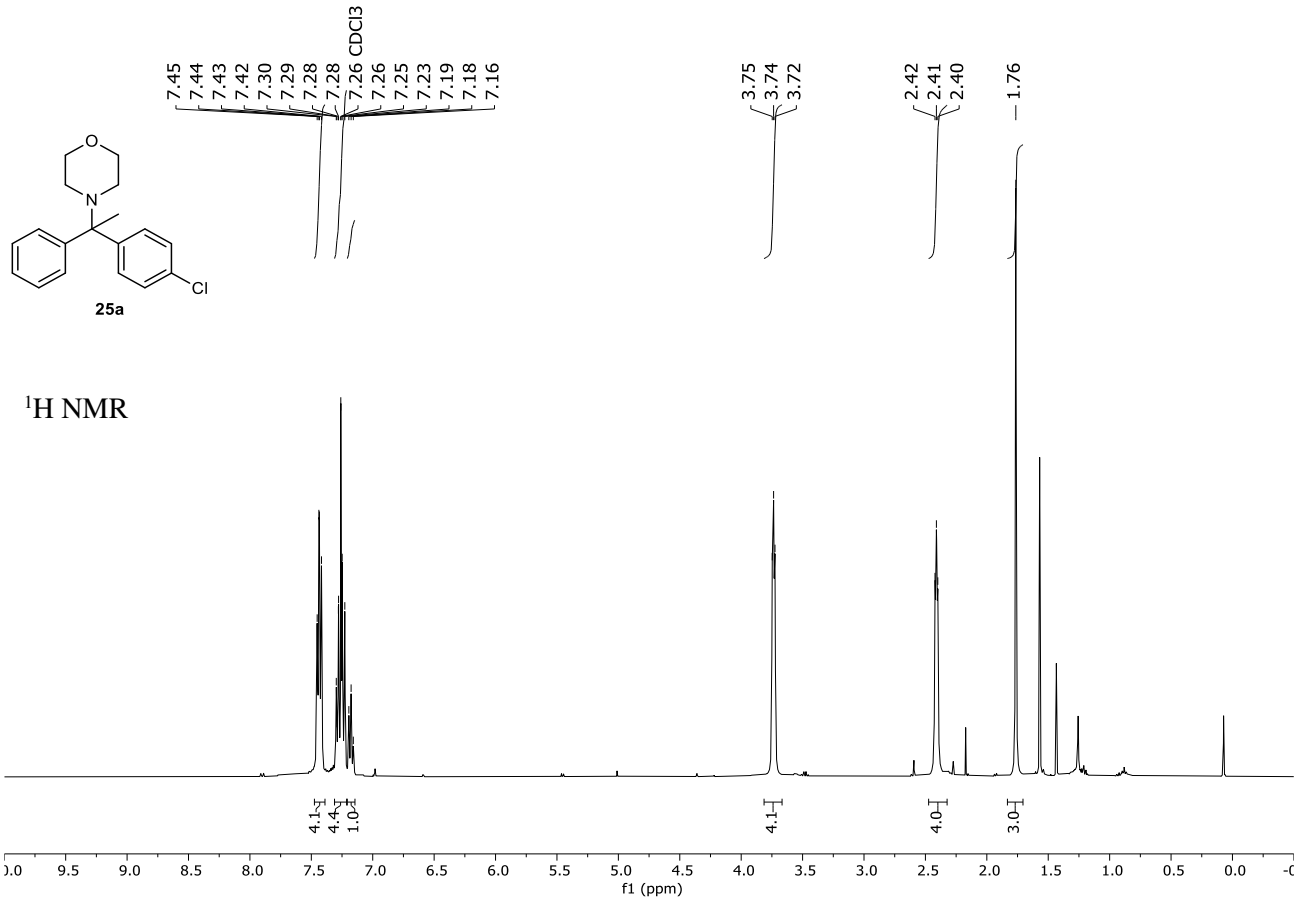

7.26 CDCl3
7.15
7.12
7.10
7.08
7.07
7.07
7.07
7.06
7.06
7.05
6.84
6.84
6.83
6.83
6.82
6.82
6.81
6.81
4.02
4.00
3.99
3.73
3.72
3.71
2.52
2.50
2.48
2.47
2.46
2.45
2.45
1.99
1.97
1.97
1.96
1.95
1.94
1.92
Br
O
N
O
23v
1H NMR
1.0
1.9
1.0
2.0
4.2
2.3
6.0
2.1
ppm


Br
O
N
O
23v
159.78
130.49
123.70
122.78
117.69
113.58
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
66.99
66.30
55.38
53.74
26.32
DEPT-Q
ppm

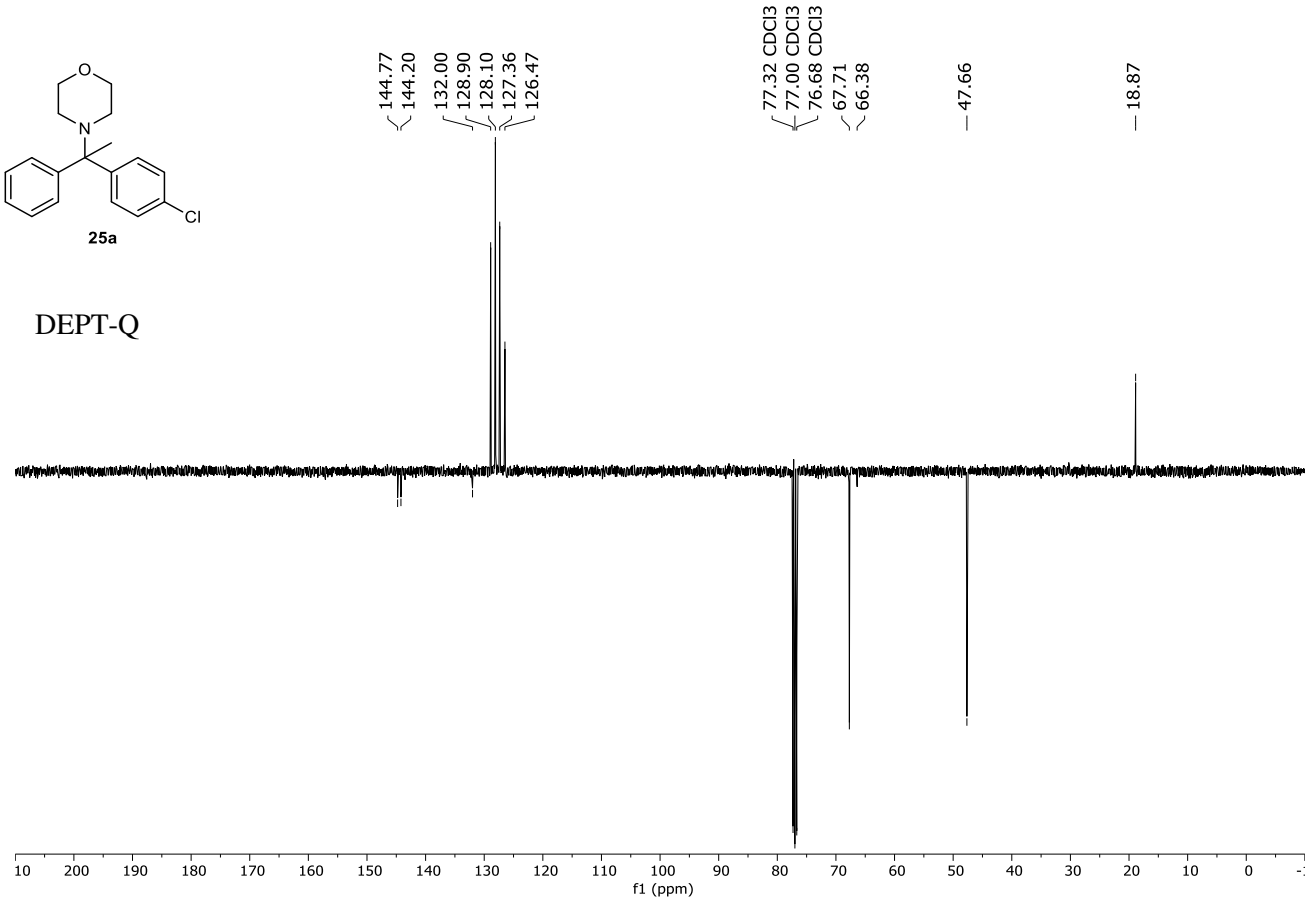

7.99
7.96
7.26
7.26 CDCl3
6.91
6.89
5.25
5.24
5.22
5.20
5.19
4.09
4.08
4.06
3.74
3.73
3.71
2.55
2.53
2.51
2.47
2.01
1.99
1.97
1.57
1.36
1.34
23x
1H NMR
1.9
2.0
1.1
2.0
4.3
5.8
2.0
6.0
ppm


165.86
162.58
131.45
123.25
113.93
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.89
66.95
66.22
55.38
53.72
26.28
21.98
23x
DEPT-Q
ppm

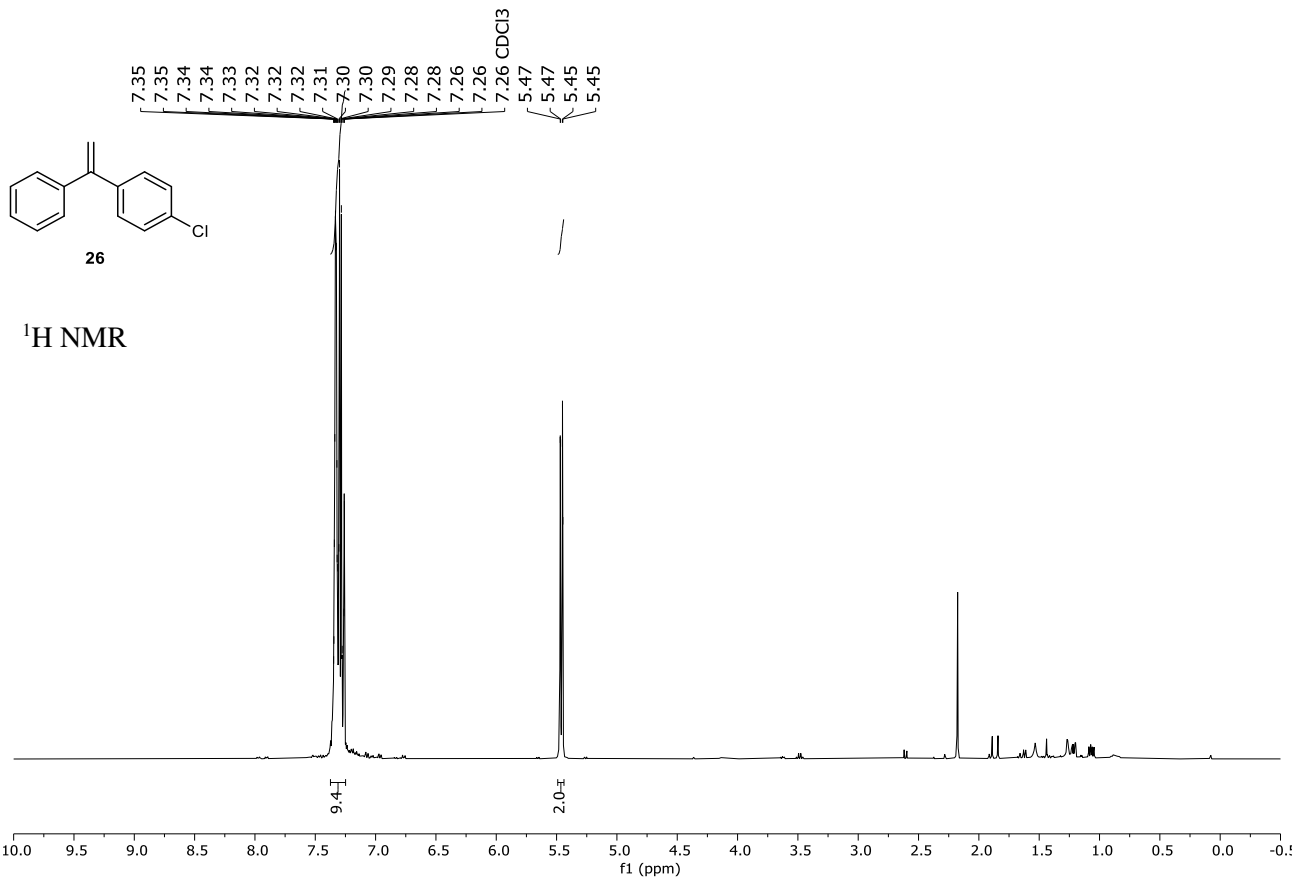
4.7. Coupling of Tertiary Boronic Esters



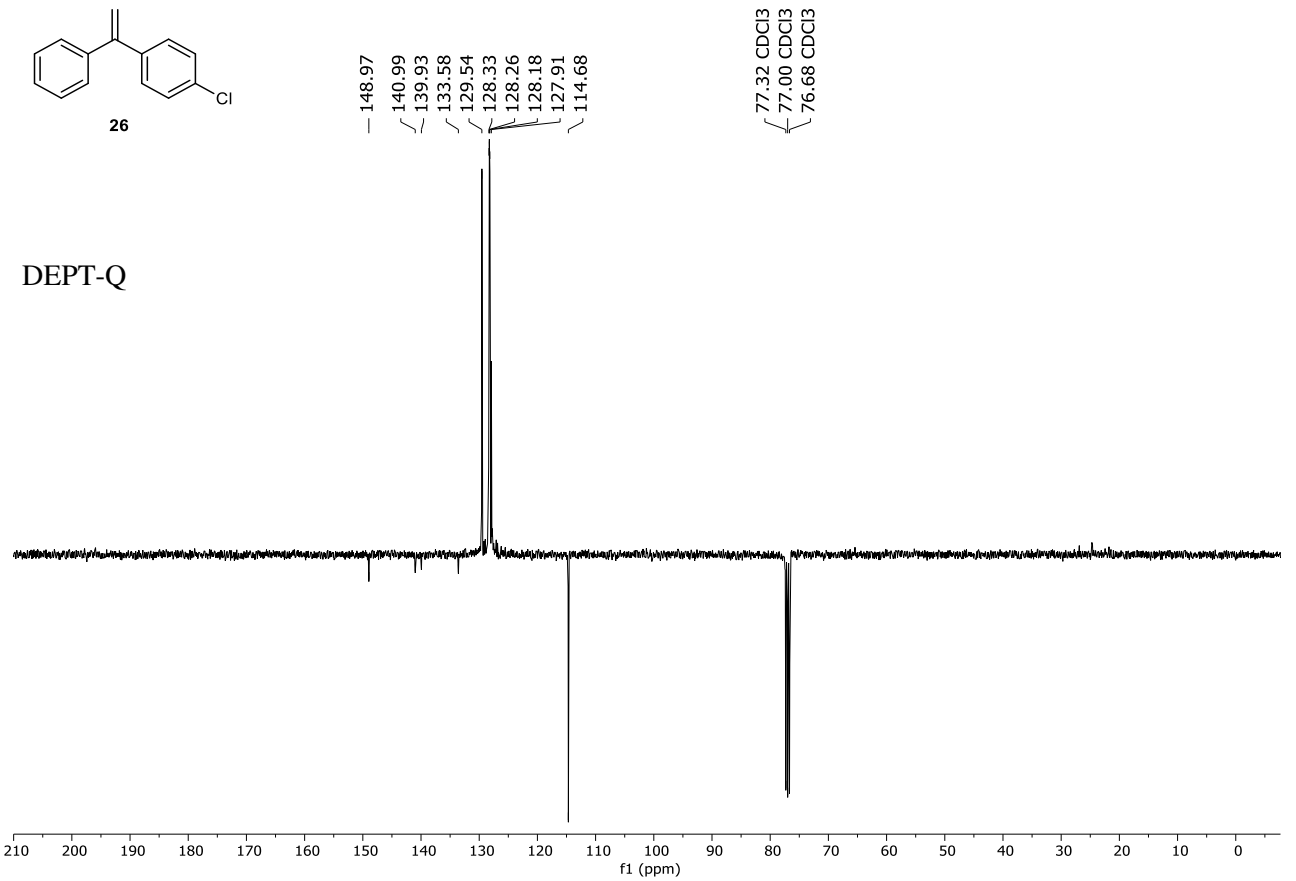
^{1}H NMR



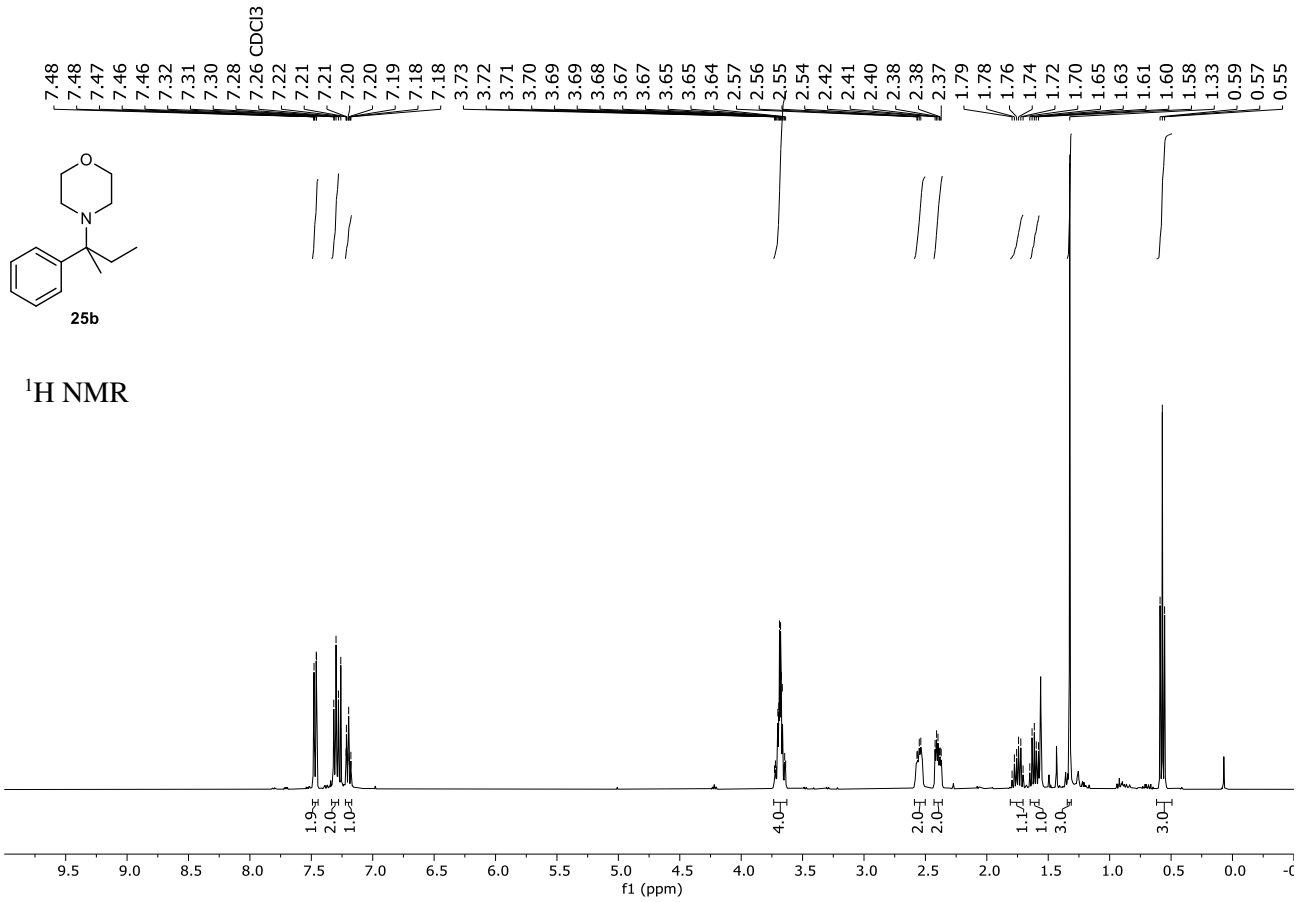
DEPT-Q


7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.26
7.26
7.26 CDCl3
5.47
5.47
5.45
5.45
Cl
26
9.4
2.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

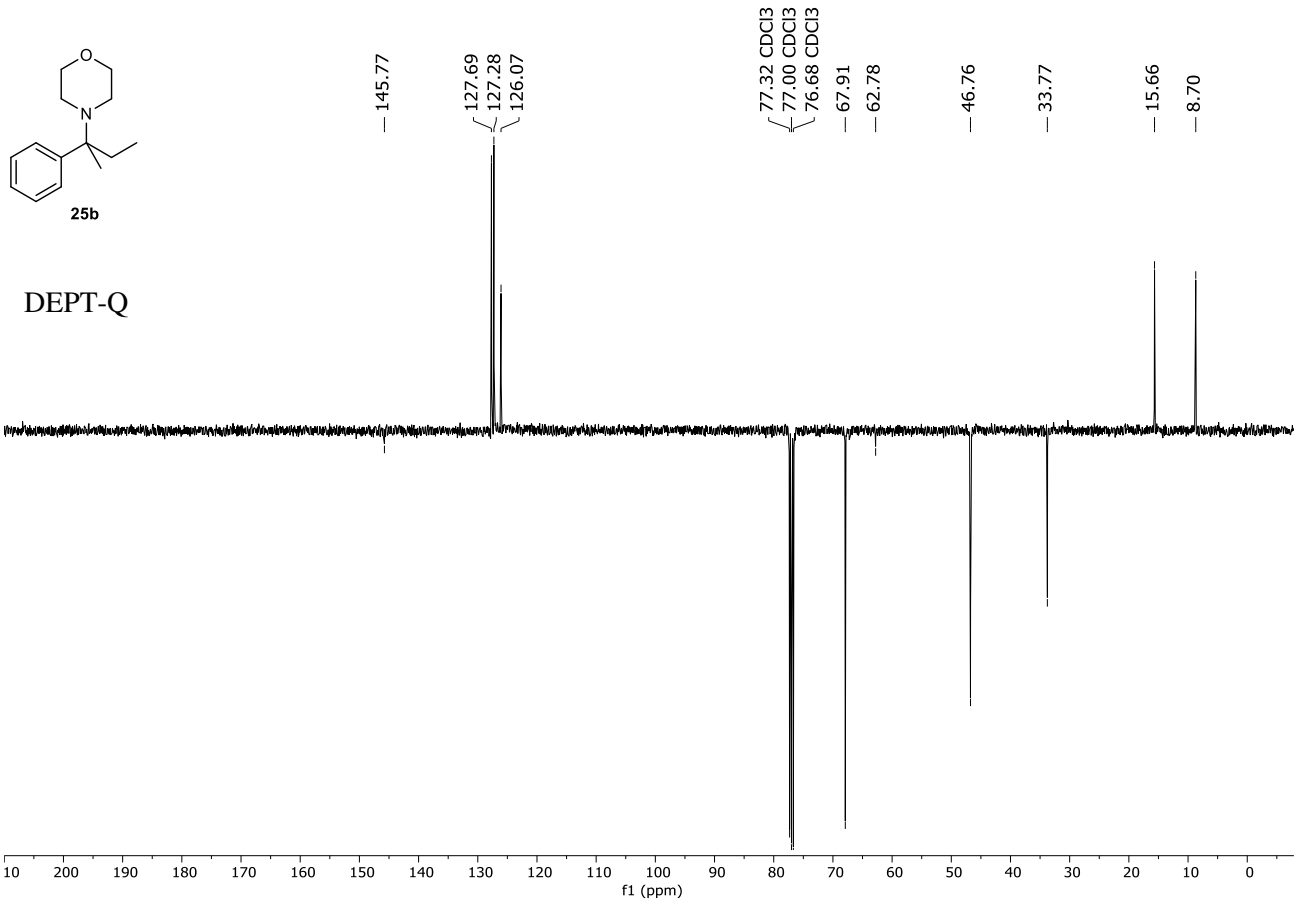
^{1}H NMR


Cl
26
148.97
140.99
139.93
133.58
129.54
128.33
128.26
128.18
127.91
114.68
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

DEPT-Q

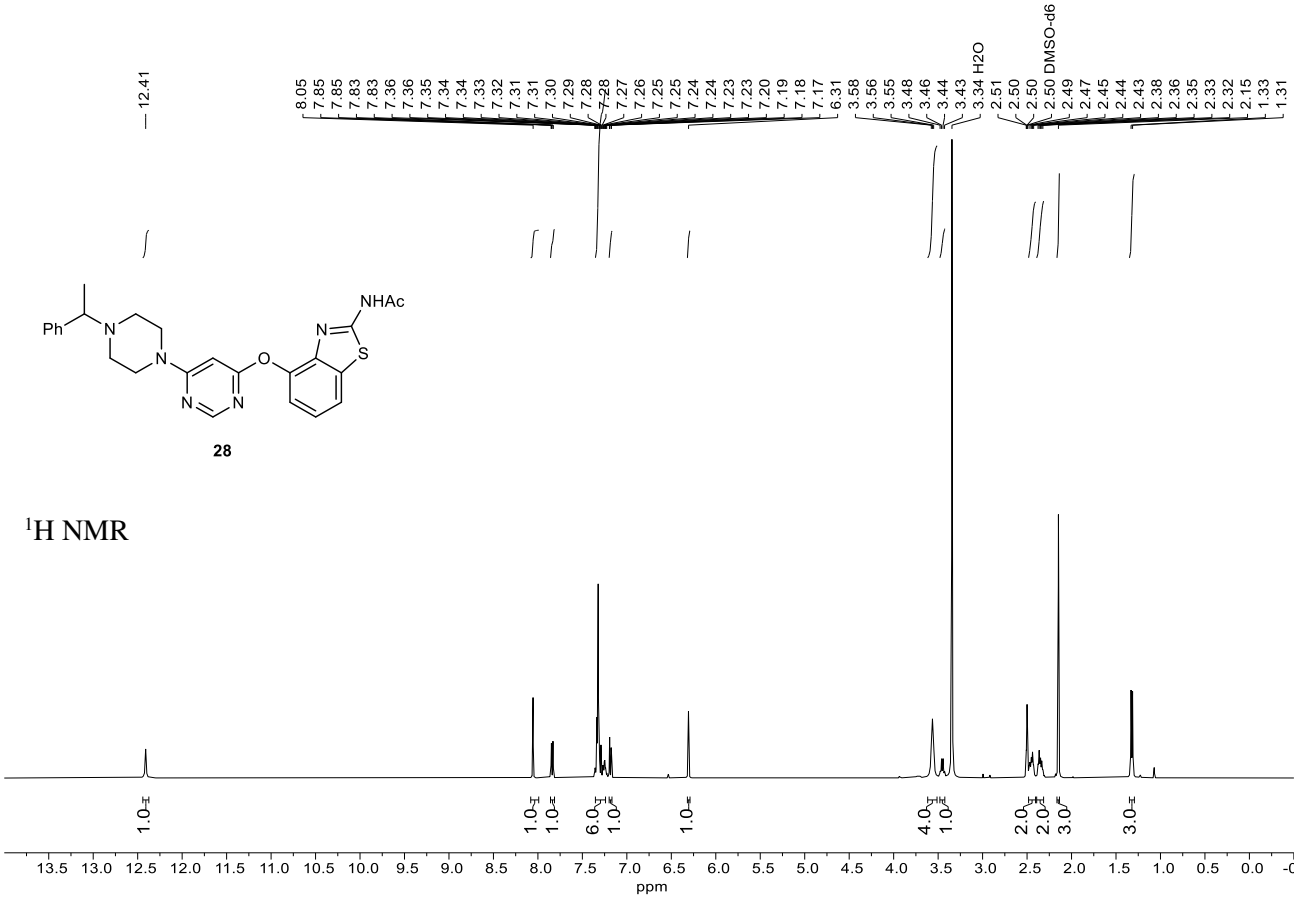

7.48
7.48
7.47
7.46
7.46
7.32
7.31
7.30
7.28
7.26 CDCl3
7.22
7.21
7.21
7.20
7.20
7.19
7.18
7.18
3.73
3.72
3.71
3.70
3.69
3.69
3.68
3.67
3.67
3.65
3.65
3.64
2.57
2.56
2.55
2.54
2.42
2.41
2.40
2.38
2.38
2.37
1.79
1.78
1.76
1.74
1.72
1.70
1.65
1.63
1.61
1.60
1.58
1.33
0.59
0.57
0.55
O
N
25b
1.9
2.0
1.0
4.0
2.0
2.0
1.1
1.0
3.0
3.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

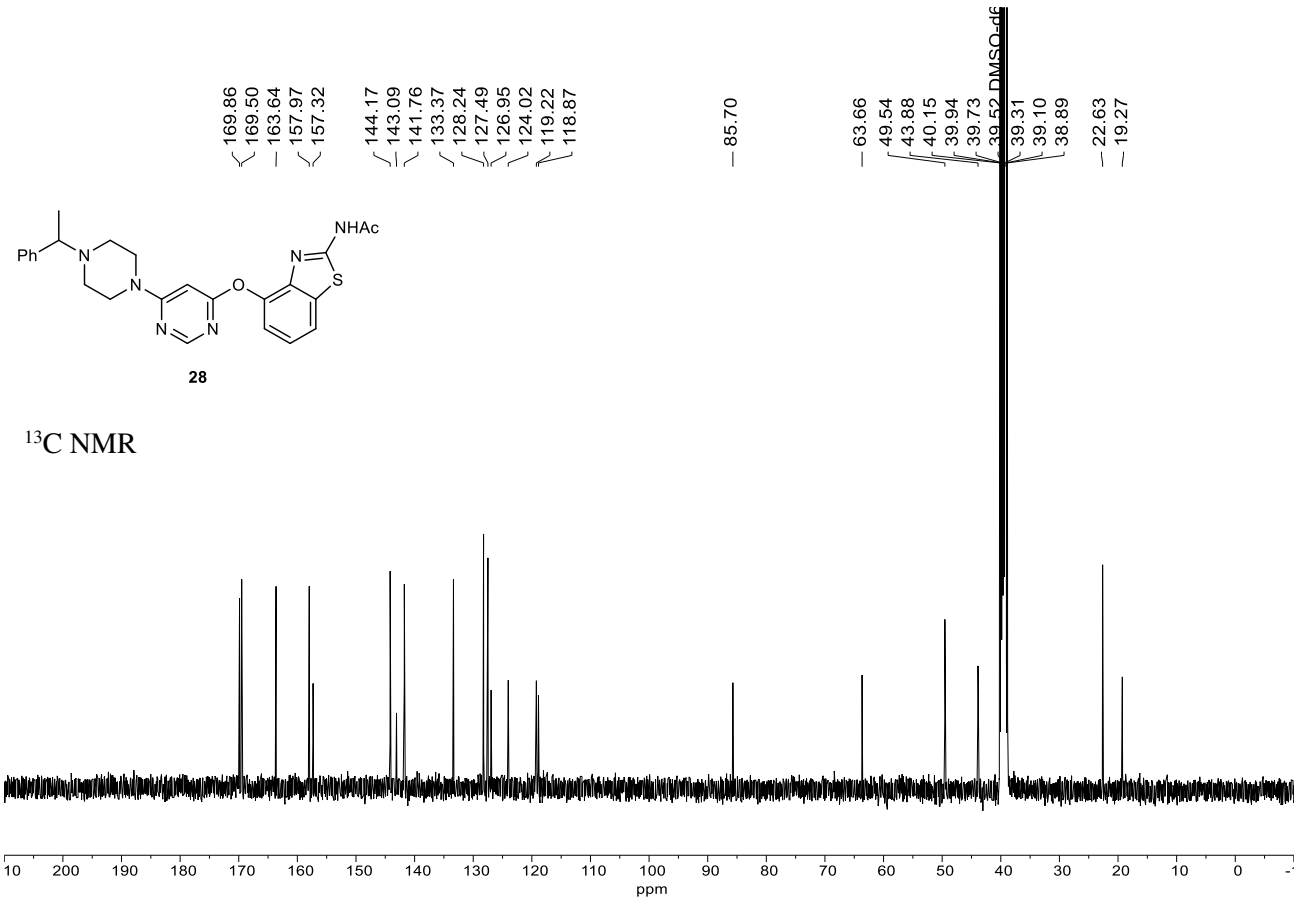
^{1}H NMR


O
N
25b
145.77
127.69
127.28
126.07
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.91
62.78
46.76
33.77
15.66
8.70
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

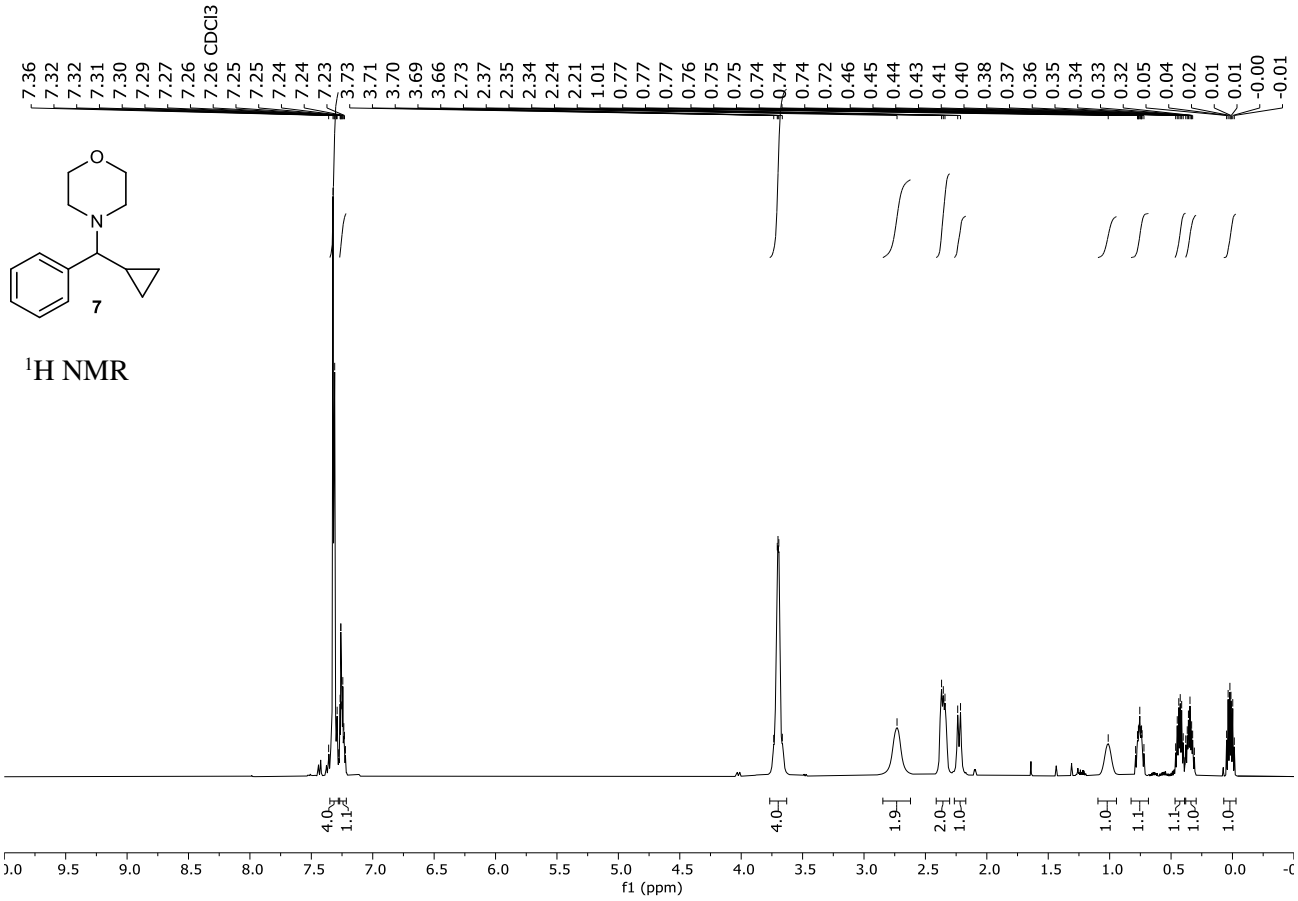
DEPT-Q

4.8. Synthesis of a TRVP 1 Inhibitor

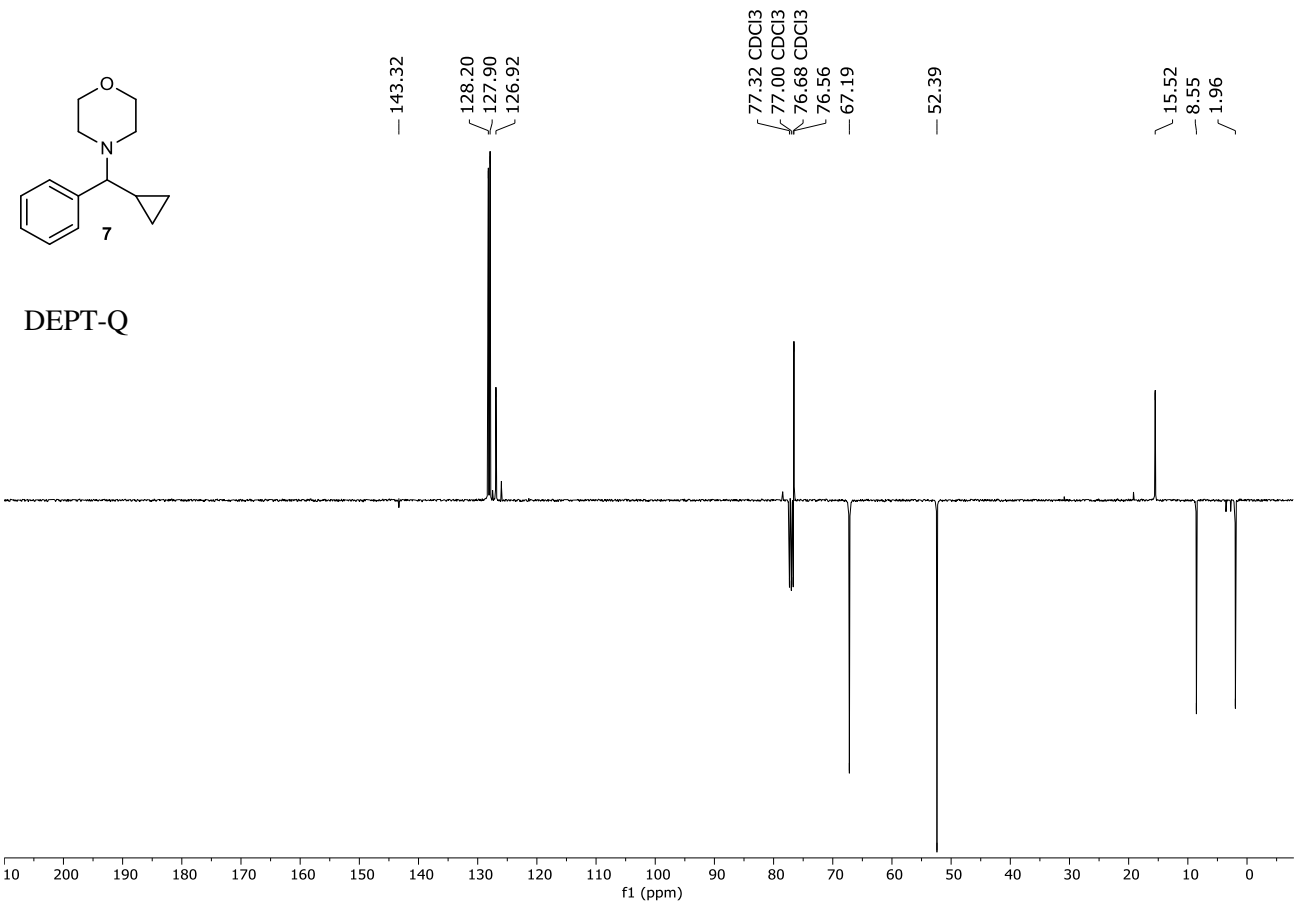




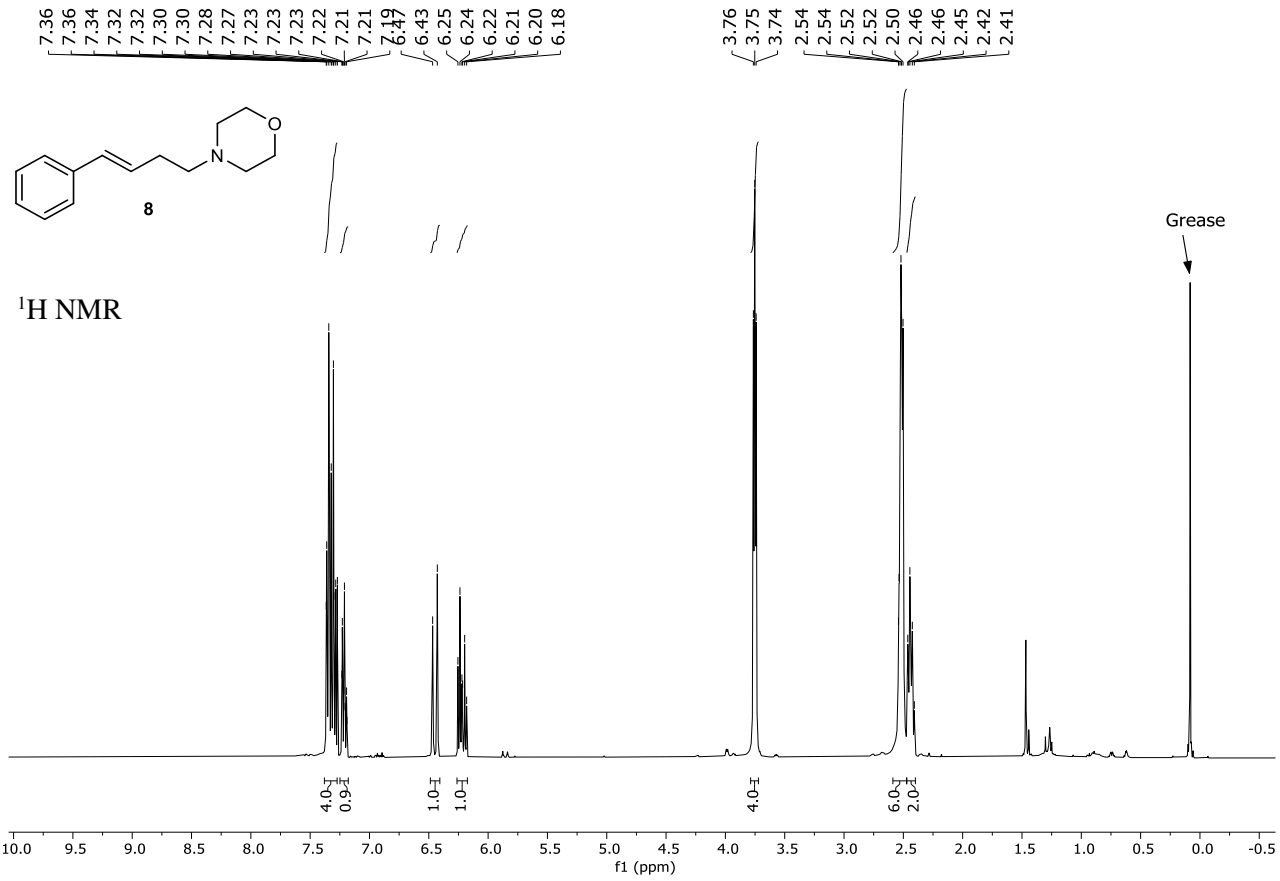
4.9.Mechanistic Studies

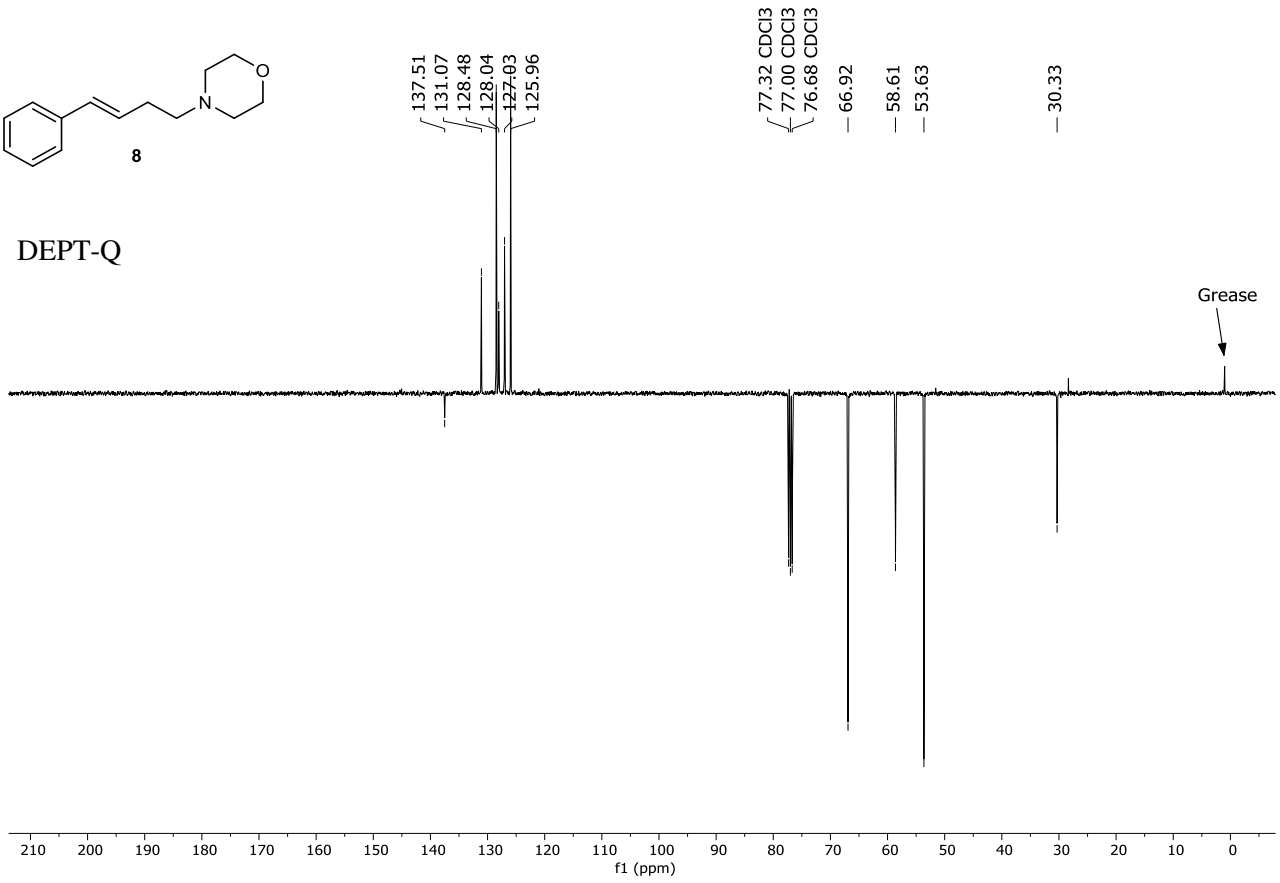


^{1}H NMR



DEPT-Q


7.36
7.36
7.34
7.32
7.32
7.30
7.30
7.28
7.27
7.23
7.23
7.22
7.21
7.21
7.19
6.47
6.43
6.25
6.24
6.22
6.21
6.20
6.18
3.76
3.75
3.74
2.54
2.54
2.52
2.52
2.50
2.46
2.46
2.45
2.42
2.41
O
N
8
Grease
1H NMR
4.0
0.9
1.0
1.0
4.0
6.0
2.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


O
N
8
137.51
131.07
128.48
128.04
127.03
125.96
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
66.92
58.61
53.63
30.33
DEPT-Q
Grease
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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