Electronic Supplementary Material (ESI) for Chemical Science

Supporting Information

Iridium-Catalyzed C-H Borylation of Quinolines and Unsymmetrical 1,2-Disubstituted Benzenes: Insights into Sterics and Electronic Effects on Selectivity

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1.0 General Experimental Considerations

Unless otherwise noted, all manipulations were performed using standard Schlenk techniques or an Innovative Technology Inc. glovebox operating under a nitrogen atmosphere. All borylation reactions were carried out in septum-containing, crimp-capped, sealed Biotage microwave vials. All microwave reactions were heated in an Emrys™ Optimizer (Personal Chemistry) reactor. The wattage was automatically adjusted to maintain the desired temperature for the desired period of time. Room temperature reactions are those run at ambient temperature monitored at 22-25 ˚C.

Anhydrous MTBE (99.8 %) was purchased from Sigma-Aldrich and used as received. All other reaction solvents were dried using an Innovative Technology Solvent Purification System (SPS). Bis(pinacolato)diboron was received as a generous donation of from AllyChem Co. Ltd. (P. R. China) and was used without purification. Unless otherwise stated, all other reagents were purchased from Alfa-Aesar, Acros, Sigma Aldrich or Lancaster, and were used as received.

^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra were recorded in $CDCl_3$ (unless otherwise stated) on Varian Mercury-200 (^{1}H), Varian Mercury-400 (^{1}H, ^{13}C, ^{19}F), Bruker Avance-400 (^{1}H, ^{13}C, ^{11}B) , Varian Inova-500 (^{1}H, ^{13}C) or Varian VNMRS-700 (^{1}H, ^{13}C) spectrometers and reported as follows: chemical shift δ (ppm) (multiplicity, coupling constant *J* (Hz), number of protons, assignment). All ^{13}C NMR spectra were proton decoupled. The chemical shifts are reported using the residual signal of $CHCl_3$ as the internal reference (δH = 7.26 ppm; δC = 77.16 ppm). All chemical shifts are quoted in parts per million relative to tetramethylsilane (δH = 0.00 ppm) and coupling constants are given in Hertz. Assignment of spectra was carried out using COSY, HSQC, and HMBC experiments.

Infrared spectra were measured on a Perkin-Elmer Paragon 1000 FT-IR spectrometer via use of a Diamond ATR (attenuated total reflection) accessory (Golden Gate). GC-MS analyses were performed using an Agilen 6890N gas chromatograph (column: HP-5MS, 10 m, Ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 70 °C (2 min), 70 °C to 250 °C (20 °C min^{-1}), 250 °C (5 min); carrier gas: He (1.6 mL min^{-1})) equipped with an Agilent 5973 inert mass selective detector operating in EI mode and a custom-built Anatune liquid handling system functioning as autosampler/injector. Electrospray mass spectra (ES) were obtained on a Micromass LCT Mass Spectrometer. High-resolution mass spectra were obtained using a Thermo-Finnigan LTQFT mass spectrometer or Xevo QToF mass spectrometer (Waters UK, Ltd) by Durham University Mass Spectrometry service, or performed by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea.

2.0 General Procedures

2.1 General Procedure A: C-H Borylation of Quinolines (Microwave Heating Conditions)

Under N_2, a catalyst stock solution was prepared by weighing $[Ir(OMe)cod]_2$ (104 mg, 0.156 mmol), dtbpy (84 mg, 0.312 mmol) and B_2pin_2 (2644 mg, 10.40 mmol) into a sealable volumetric flask, followed by addition of MTBE to make up a 25 mL solution. The flask was sealed with a crimp top septum cap and shaken to develop a deep red colour. Under N_2, a thick walled microwave synthesis vial (max volume 5 mL) was charged with the corresponding substrate (1.00 mmol) and sealed with a crimp top septum cap. The catalyst stock solution (2.4 mL) (catalyst loading (0.03 mmol Ir), B_2pin_2 (1.00 mmol)) was added and the reaction was heated for the time stated at 100 °C for 1.5 hours in a microwave reactor. Upon completion, the reaction was cooled to room temperature and volatiles were removed under reduced pressure to afford the crude product. This was dry loaded on to silica gel and purified by silica gel flash-column chromatography with gradient elution of solvents, unless otherwise stated.

2.2 General Procedure B: C-H Borylation of Quinolines (Room Temperature Reaction)

Under N_2, a catalyst stock solution was prepared by weighing $[Ir(OMe)cod]_2$ (104 mg, 0.156 mmol), dtbpy (84 mg, 0.312 mmol) and B_2pin_2 (2.644 g, 10.40 mmol) into a sealable volumetric flask, followed by addition of MTBE to make up a 25 mL solution. The flask was sealed with a crimp top septum cap and shaken to develop a deep red colour. Under N_2, a thick walled microwave synthesis vial (max volume 5 mL) was charged with the corresponding substrate (1.00 mmol) and sealed with a crimp top septum cap. The catalyst stock solution (2.4 mL) (catalyst loading (0.03 mmol Ir), B_2pin_2 (1.00 mmol)) was added and the reaction was stirred for the time stated at room temperature on a magnetic stirring block. Upon completion, the volatiles were removed under reduced pressure to afford the crude product. This was dry loaded on to silica gel and purified by silica gel flash-column chromatography with gradient elution of solvents, unless otherwise stated.

2.3 General Procedure C: C-H Borylation of Monosubstituted and Unsymmetrical 1,2-Disubstituted Benzenes with 1,1,2,2-Tetrachloroethane as Internal Standard

Under N_2, a stock solution was prepared by weighing $[Ir(OMe)cod]_2$ (104 mg, 0.156 mmol) and dtbpy (84 mg, 0.312 mmol) into a sealable volumetric flask, followed by addition of MTBE to make up a 25 mL solution. The flask was sealed with a crimp top septum cap and shaken until the solution appears to be completely homogeneous. Under N_2, B_2pin_2 (122 mg, 0.48 mmol) was dissolved in MTBE (2 mL) in a thick walled microwave synthesis vial (max 5 mL) and sealed with a crimp top septum cap. To this was added 1 mL of the stock solution (0.03 mmol Ir) and after 5 min, the arene substrate (0.40 mmol) was added. The reaction was stirred at room temperature on a magnetic stirring block. After the stated time, the mixture was quenched/diluted with DCM and the volatiles removed under reduced pressure to afford the crude mixture. GC-MS analysis of a small sample, was carried out to determine the % conversion. ^{1}H NMR spectroscopy was carried out on the crude sample to determine the product ratios (to some of these crude were added 1,1,2,2-tetrachloroethane as an internal standard). Structures of the products were confirmed by HCOSY, NOESY, HSQC and HMBC spectroscopic experiments.

2.4 General Procedure D: C-H Borylation of Monosubstituted and Unsymmetrical 1,2-Disubstituted Benzenes in an NMR Tube Fitted with a Young's Tap

Under N_2, a catalyst stock solution was prepared by weighing $[Ir(OMe)cod]_2$ (104 mg, 0.156 mmol), dtbpy (84 mg, 0.312 mmol) and B_2pin_2 (3.05 g, 12.0 mmol) into a sealable volumetric flask, followed by addition of MTBE to make up a 25 mL solution. The flask was sealed with a crimp top septum cap and shaken to develop a deep red colour. Under N_2, an NMR tube containing a coaxial tube filled with acetone-d_6 was charged with the corresponding arene (0.20 mmol). The catalyst stock solution (0.5 mL) (catalyst loading (0.006 mmol Ir), B_2pin_2 (0.24 mmol)) was added and the homogeneous solution allowed to stand at room temperature. After the stated time, ^{1}H NMR spectroscopy was carried out on the sample to determine the isomer ratio. GC-MS analysis of a small sample, quenched/diluted with DCM, was carried out to determine the % conversion. Structures of the products were confirmed by HCOSY, NOESY, HSQC and HMBC spectroscopic experiments.

2.5 Catalyst Preparation: $[Ir(Cl)cod]_2$

A 1L 2-necked round bottom flask was charged with $IrCl_3.3H_2O$ (5.29 g, 16.7 mmol), Water (150 mL) and propan-2-ol (250 mL). To the dark purple-black solution, excess 1,5-cyclooctadiene (25 mL) was added. The flask was fitted with a reflux condenser and heated using a heating mantle to reflux for 4 hours. Upon completion, the solution was a bright, clear red-orange colour. The reaction was cooled and fitted with distillation apparatus. The reaction was then heated and solvent removed (200 mL) by distillation. The reaction mixture was left to cool to room temperature for 2 hours allowing a red crystalline solid to form. The solid was filtered and washed with cold methanol (3 × 50 mL) and dried under reduced pressure to afford $(Ir(Cl)cod]_2$ (7.98g, 71%)

2.6 Catalyst Preparation: $[Ir(OMe)COD]_2$

A 500 mL round bottom flask was charged with $[Ir(Cl)cod]_2$ (5.00 g, 7.44 mmol) and KOH (1.00 g, 17.8 mmol). The flask was purged with nitrogen and degassed methanol (150 mL) was added. The reaction was stirred at room temperature for 3 hours under nitrogen, with a continuous flow of nitrogen bubbling through the reaction solvent. Upon completion no orange-red solid remained and a pale yellow precipitate had formed. Degassed water (200 mL) was added to the reaction mixture and the vessel was cooled to 0 °C for 1 hour. The yellow solid was filtered and washed with water (6 × 50 mL) and cold methanol (3 × 25 mL). The solid was transferred to a round bottom flask and placed under reduced pressure. The flask was heated to 40 °C in a water bath for 2 hours, followed by drying under reduced pressure for a further 12 hours affording $[Ir(OMe)cod]_2$ (3.10 g, 63 %) as a fine, free-flowing yellow powder.

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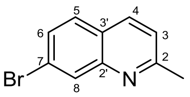
3.0 Experimental Details

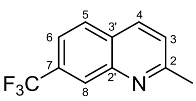
3.1 Quinoline Starting Materials Synthesis (Scheme 1)

7-bromo-2-methylquinoline, 2a[1]



3-bromoaniline (25.0 g, 145 mmol, 15.82 mL) was added to a 250 mL two-necked round bottom flask fitted with a condenser and a septum. Aqueous HCl (5 M, 100 mL) was added and the resultant mixture heated to 110 °C. Crotonaldehyde (12.22 g, 174 mmol, 14.45 mL) was then added as a solution in toluene (10 mL) over a period of 1 hour using a syringe pump. Upon complete addition of the aldehyde the reaction was heated for a further 1 hour and the solution was allowed to cool to 60 °C. To this hot solution, $ZnCl_2$ (19.72 g, 145 mmol) was added slowly as a solution in THF/acetone (50 mL, 1:1), causing a precipitate to form. The reaction vessel was then allowed to cool to room temperature and then cooled in an ice bath for 1 hour. The solid was filtered and washed with cold aq. HCl (5 M, 200 mL), THF (200 mL), isopropyl alcohol (200 mL) and diethyl ether (200 mL).The resultant white solid dissolved in a mixture of hexane (100 mL) and aqueous ammonia (29%, 50 mL) and stirred until complete dissolution had been achieved. The organic layer was separated and the aqueous layer extracted with diethyl ether (3 x 50 mL). The combined organics were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting solid was purified by silica gel flash column chromatography (hexane:ethyl acetate, 8:2) affording 7-bromo-2-methylquinoline as a white solid (10.04 g, 31%); m.p. 77 - 78 °C; Anal. Calcd. For: $C_{10}H_8BrN$ C, 54.1; H, 3.6; N, 6.3%; found: C, 54.1; H, 3.6; N, 6.3%; ν_{max} ($CHCl_3$) 3021, 1525, 1423, 1225, 1016, 928, 669 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.20 (d, *J* = 1.8, 1H, 8-***H***), 7.99 (d, *J* = 8.4, 1H, 4-***H***), 7.62 (d, *J* = 8.6, 1H, 5-***H***), 7.55 (dd, *J* = 1.8, 8.6, 1H, 6-***H***), 7.28 (d, *J* = 8.4, 1H, 3-***H***), 2.73 (s, 3H, 2-***CH₃***); ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.4 (***C***-2), 148.7 (***C***-2′), 136.1 (***C***-4), 131.4 (***C***-8), 129.4 (***C***-6), 128.9 (***C***-5), 125.3 (***C***-3′), 123.6 (***C***-7), 122.5 (***C***-3), 25.6 (2-$\boldsymbol{CH_3}$); GC-MS (EI) *m/z* 223 (98%, M^+(^{81}Br)), 221 (100%, M^+(^{79}Br)), 208 (5%, M^+(^{81}Br) -CH_3), 206 (5%, M^+(^{79}Br) -CH_3), 142 (18%, M^+ -Br), 127 (7%, M^+ -Br,CH_3), 115 (28%); HRMS (ASAP) *m/z* found: 220.9840, $C_{10}H_8{}^{79}BrN$ $(M)^+$ requires: 220.9832.

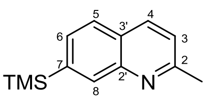
2-methyl-7-(trifluoromethyl)quinoline, 2b[2]



3-(Trifluoromethyl)aniline (6.44 g, 40.0 mmol, 5.0 mL) was added to a 100 mL two-necked round bottom flask fitted with a condenser and a septum. Aqueous HCl (5 M, 20 mL) was added and the mixture heated to

110 °C. Crotonaldehyde (4.21 g, 60.0 mmol, 4.98 mL) was then added as a solution in toluene (5 mL) over a period of 1 hour using a syringe pump. Upon complete addition of the aldehyde, the reaction was heated for a further 1 hour, and the solution was then allowed to cool to room temperature. The aqueous reaction mixture was extracted with diethyl ether (3 x 50 mL) and the combined organic extracts were washed with brine (3 x 25 mL) and dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the resulting oil was purified by silica gel flash-column chromatography eluted with $CHCl_3$ to give 2-methyl-7-(trifluoromethyl)quinoline as a pale yellow crystalline solid (2.16 g, 26%); m.p. 54 - 55 °C; Anal. Calcd. For: $C_{11}H_8F_3N$: C, 62.6; H, 3.8; N, 6.6%; found: C, 62.4; H, 3.9; N, 6.6%; ν_{max} ($CHCl_3$) 3020, 1610, 1518, 1475, 1423, 1375, 1349, 1319, 1281, 1168, 1062, 1016, 905, 792 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, br, 1H, Ar-8-***H***), 8.10 (d, *J* = 8.4, 1H, 4-***H***), 7.89 (d, *J* = 8.4, 1H, 5-***H***), 7.66 (d, *J* = 8.4, 1H, 6-***H***), 7.41 (d, *J* = 8.4, 1H, 3-***H***), 2.78 (s, 3H, 3-***CH₃***); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9 (***C***-2), 147.1 (***C***-2'), 136.2 (***C***-4), 131.4 (q, $^2J_{C\text{-}F}$ = 32.6, ***C***-7), 128.9 (***C***-5), 128.2 (***C***-3'), 126.8 (q, $^3J_{C\text{-}F}$ = 4.4, ***C***-8), 124.3 (q, $^1J_{C\text{-}F}$ = 272.6, 7-$\boldsymbol{CF_3}$), 124.2 (***C***-3), 121.6 (q, $^3J_{C\text{-}F}$ = 3.2, ***C***-6), 25.7 (2-$\boldsymbol{CH_3}$); ^{19}F NMR (188 MHz, $CDCl_3$) δ -62.22; GC-MS (EI) *m/z* 211 (100%, M^+), 196 (10%, M^+-CH_3), 142 (4%, M^+-CF_3); HRMS (ASAP) *m/z* found: 211.0634, $C_{11}H_8F_3N$ $(M)^+$ requires: 211.0609.

2-methyl-7-(trimethylsilyl)quinoline, 2c



To an oven dried flask purged with argon, 7-bromo-2-methylquinoline (1.10 g, 5.00 mmol) was added. To the flask, dry THF (15 mL) and TMEDA (1.0 mL) were added and the resulting solution cooled to -78 °C. *n*-BuLi (1.6M in hexanes) (3.4 mL, 5.5 mmol) was added and stirred for 5 minutes, forming a red-colored solution. TMSCl (1.4 mL, 12 mmol) was then added, and the reaction was allowed to stir at -78 C for 10 minutes and then removed from the cold bath and warmed to room temperature. After 30 minutes, water (2.0 mL) was added to quench the reaction. The reaction mixture was extracted with EtOAc (3 × 20 mL) and washed with brine (3 × 20 mL). The combined organics were dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The resulting oil was purified by silica gel flash column chromatography eluting with 20% EtOAc/hexane affording 2-methyl-7-(trimethylsilyl)quinoline as a colourless oil (692 mg, 64%); ν_{max} ($CHCl_3$) 3019, 2957, 1503, 1475, 1422, 1225, 1084, 927, 840, 665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, br, 1H, 8-***H***), 8.04 (d, *J* = 8.4, 1H, 4-***H***), 7.77 (d, *J* = 8.0, 1H, 5-***H***), 7.62 (dd, *J* = 0.9, 8.0, 1H, 6-***H***), 7.30 (d, *J* = 8.4, 1H, 3-***H***), 2.77 (s, 3H, 2-$\boldsymbol{CH_3}$), 0.37 (s, 9H, 7-Si$\boldsymbol{(CH_3)_3}$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2 (***C***-2), 147.5 (***C***-2'), 142.8 (***C***-3'), 136.3 (***C***-4), 134.6 (***C***-8), 129.9 (***C***-6), 126.83 (***C***-7), 126.75 (***C***-5), 122.5(***C***-3), 25.7 (2-$\boldsymbol{CH_3}$), -1.0 (7-$\boldsymbol{Si(CH_3)_3}$); GC-MS (EI) *m/z* 215 (24%, M^+), 200 (100%, M^+-CH_3), 185 (6%, M^+-2CH_3), 170 (10%, M^+-3CH_3); HRMS (ASAP) *m/z* found: 216.1207; $C_{13}H_{18}NSi$ $(M+H)^+$ requires: 216.1209.

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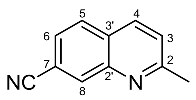
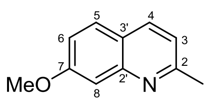
2-methylquinoline-7-carbonitrile, 2d



2-methyl-7-bromoquinoline (2.22 g, 10.0 mmol), $Pd(PPh_3)_4$ (115 mg, 0.1 mmol and $Zn(CN)_2$ (1.23g, 10.5 mmol) were added to a 20 mL microwave vial. The vial was equipped with a magnetic stirrer bar and sealed with a PTFE crimp top. After purging the reaction with argon, dry DMF (15 mL) was added and the reaction heated at 150 °C for 25 minutes in a microwave reactor. The reaction mixture was then cooled to room temperature before being opened and transferred to a separating funnel. Water (100 mL) was added, the layers separated and extracted with EtOAc (4 × 100 mL) and DCM (2 × 100 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure to give a dark brown solid.

The crude product was added to hexane (50 mL) and heated to reflux. The solution was then filtered hot to remove the insoluble impurities. The solute was cooled in a freezer to afford off-white crystals. The resulting crystals were filtered and washed with cold hexane yielding the product as a white crystalline solid (1.40 g, 83%); m.p. 99 - 100 °C; Anal. Calcd. for $C_{11}H_8N_2$ C, 78.6; H, 4.8; N, 16.7%; found: C, 78.2; H, 4.8; N, 16.6%; ν_{max} ($CHCl_3$) 3018, 2231 (C≡N), 1605, 1526, 1475, 1422, 1225, 1016, 928, 846 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.37 (s, br, 1H, 8-***H***), 8.09 (d, *J* = 8.4, 1H, 4-***H***), 7.86 (d, *J* = 8.3, 1H, 5-***H***), 7.64 (dd, *J* = 1.5, 8.3, 1H, 6-***H***), 7.43 (d, *J* = 8.4, 1H, 3-***H***), 2.78 (s, 3H, 2-***CH₃***); ^{13}C NMR (176 MHz, $CDCl_3$) δ 161.6 (***C***-2), 147.0 (***C***-2′), 136.1 (***C***-4), 134.8 (***C***-8), 129.1 (***C***-5), 128.8 (***C***-3′), 126.8 (***C***-6), 124.8 (***C***-3), 118.9 (7-***CN***), 113.0 (***C***-7), 25.7 (2-***CH₃***); GC-MS (EI) *m/z* 168 (100%, M^+), 153 (11%, M^+-CH_3), 142 (11%, M^+-CN); HRMS (ASAP) *m/z* found: 168.0696; $C_{11}H_8N_2$ $(M)^+$ requires: *M* 168.0687.

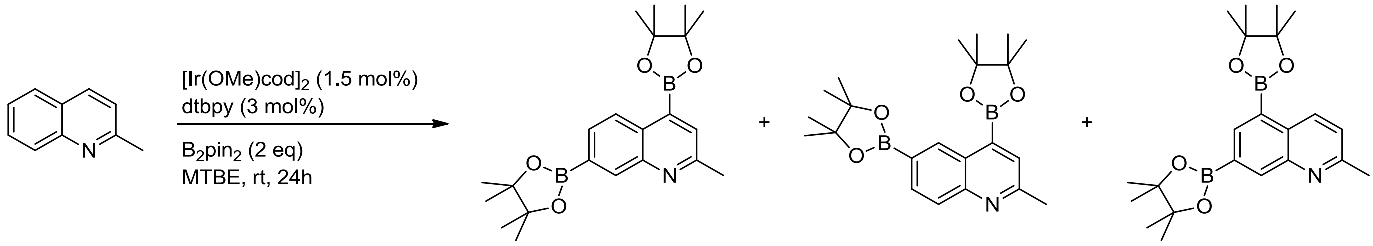
7-methoxy-2-methylquinoline, 2e[3]



In a 50 mL two-necked round bottom flask, equipped with a condenser, sodium (1.00 g, 43.5 mmol) was added to MeOH (5 mL, 123 mmol) to form sodium methoxide *in situ*. Once all of the sodium had reacted the methanol solvent was removed under reduced pressure, 7-bromo-2-methylquinoline (2.22 g, 10.0 mmol) was added along with DMF (5 mL). The reaction vessel was heated to 110 °C. Once at the reaction temperature, CuBr (285 mg, 2.00 mmol) was added as a solution in DMF (1.0 mL). The reaction was heated at 110 °C for a further 45 minutes. The reaction was then transferred to a separating funnel, and water (100 mL) was added. The layers were separated and the aqueous layer was extracted with DCM (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The resulting oil was purified by silica gel flash-column chromatography eluted with 60% EtOAc/hexane, yielding 7-methoxy-2-methylquinoline as a pale yellow oil (1.66 g, 96%); ν_{max} ($CHCl_3$) 3019, 2973, 1621, 1603, 1511, 1459, 1419, 1340, 1211, 1174, 1029, 928, 846, 785, 669 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2, 1H, 4-***H***), 7.62 (d, *J* = 8.9, 1H, 5-***H***), 7.35 (d, *J* = 2.3, 1H, 8-***H***), 7.15 - 7.10 (m, 2H, 3,6-***H***), 3.92 (s, 3H, 7-O***CH₃***), 2.70 (s, 3H, 2-***CH₃***); ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.9 (***C***-2'), 159.4 (***C***-2), 149.8 (***C***-3'), 136.0 (***C***-4), 128.7 (***C***-5), 121.8 (***C***-7), 119.9 (***C***-3), 118.9 (***C***-6), 107.1 (***C***-8), 55.7 (7-O***CH₃***), 25.5 (2-***CH₃***); GC-MS (EI) *m/z* 173 (100%, M^+), 158 (4%, M^+-CH_3), 142 (16%, M^+-OCH_3), 130 (43%), 115 (6%), 103 (11%); HRMS (ASAP) *m/z* found: 173.0852, $C_{11}H_{11}NO$ $(M)^+$ requires: 173.0841.

3.2 Borylation of 2-substituted quinolines (Scheme 2)

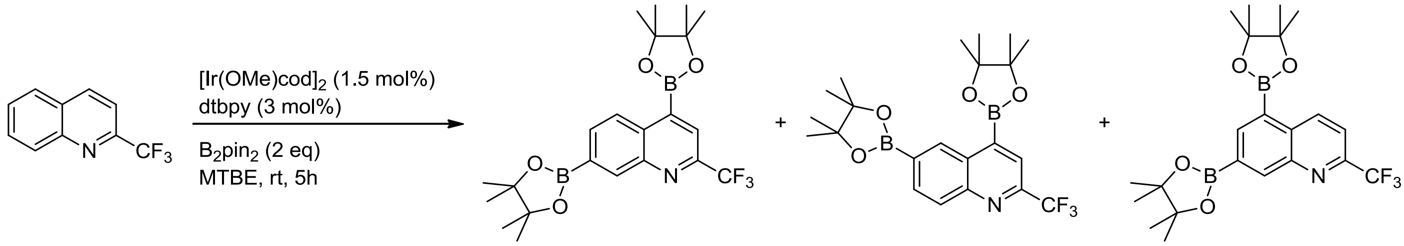
Borylation of 2-methyquinoline, 3a



3a **4a** **5a** **6a**

General procedure C with larger excess of B_2pin_2 (203 mg, 0.80 mmol) was applied to 2-methylquinoline (57 mg, 0.40 mmol). The reaction mixture was stirred for 24 hours giving a conversion of 95% and a mixture of monoborylated products (minor) and bisborylated products (major) (GC-MS). Analysis of ^{1}H NMR spectrum showed **4a** and **5a** in a 68:32 mixture, some unreacted starting material **3a**, and unknown compounds (possibly monoborylated products and/or **6a**).

Borylation of 2-(trifluoromethyl)quinoline, 3b

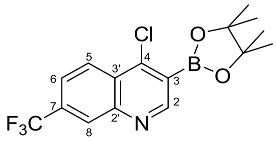


3b **4b** **5b** **6b**

General procedure C with larger excess of B_2pin_2 (203 mg, 0.80 mmol) was applied to 2-(trifluoromethyl)quinoline (79 mg, 0.40 mmol). The reaction mixture was stirred for 5 hours giving a conversion of 90% (GC-MS) and **4b**, **5b** and **6b** in a 51:42:7 mixture (^{1}H NMR spectrum).

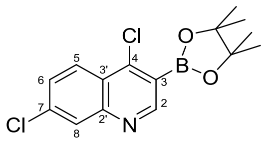
3.3 Borylation of 4,7-Disubstituted Quinolines (Scheme 3)

4-chloro-3-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-7-(trifluoromethyl)quinoline, 9a



General procedure A was applied to 4-chloro-7-(trifluoromethyl)quinoline (231 mg, 1.00 mmol). Purification by recrystallisation from acetonitrile, afforded 4-chloro-3-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-7-(trifluormethyl)quinoline as a white solid (289 mg, 81%); m.p. 93 - 94 °C; Anal. Calcd. for $C_{16}H_{16}BClF_3NO_2$ C, 53.7; H, 4.5; N, 3.9%; found: C, 54.0; H, 4.6; N, 3.7%; ν_{max} ($CHCl_3$) 3019, 1520, 1475, 1422, 1225, 1140, 928, 849, 792 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (s, 1H, 2-***H***), 8.47 (d, *J* = 8.8, 1H, 5-***H***), 8.42 (s, br, 1H, 8-***H***), 7.80 (dd, *J* = 1.6, 8.8, 1H, 6-***H***), 1.43 (s, 12H, pin-***CH₃***); ^{13}C NMR (176 MHz, $CDCl_3$) δ 156.2 (***C***-2), 149.5 (***C***-2′), 149.0 (Ar-***C***), 132.6 (q, $^2J_{C\text{-}F}$ = 32.9, ***C***-7), 127.9 (Ar-***C***), 127.5 (***C***-8), 126.4 (***C***-5), 123.7 (q, $^1J_{C\text{-}F}$ = 272.8, 7-$\boldsymbol{CF_3}$), 123.1 (***C***-6), 84.9 (pin-***C***$(CH_3)_2$), 24.9 (pin-$\boldsymbol{CH_3}$); ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.78; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.88; GC-MS (EI) *m/z* 359 (12%, $M^+(^{37}Cl)$), 357 (38%, $M^+(^{35}Cl)$), 344 (11%, $M^+(^{37}Cl)$ -CH_3), 342 (34%, $M^+(^{35}Cl)$ -CH_3), 322 (100%, M^+-Cl), 301 (15%, $M^+(^{37}Cl)$ -$CO(CH_3)_2$), 299 (48%, $M^+(^{35}Cl)$ -$CO(CH_3)_2$), 280 (62%, M^+ -Cl, $C(CH_3)_2$), 259 (22%, $M^+(^{37}Cl)$ -$CO(CH_3)_2C(CH_3)_2$), 257 (68%, $M^+(^{35}Cl)$ -$CO(CH_3)_2C(CH_3)_2$), 222 (48%, M^+ -Cl, $CO(CH_3)_2C(CH_3)_2$); HRMS (ASAP) *m/z* found: 357.1027, $C_{16}H_{17}{}^{10}B^{35}ClF_3NO_2$ $(M+H)^+$ requires: 357.1029.

4,7-dichloro-3-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)quinoline, 9c

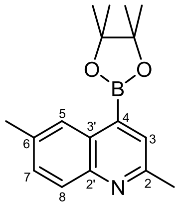


General procedure A was applied to 4,7-dichloroquinoline (196 mg, 1.00 mmol). Purification by recrystallisation from acetonitrile, afforded 4,7-dichloro-3-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)quinoline as a pale yellow crystalline solid (258 mg, 81%); m.p. 127 - 128 °C; ν_{max} ($CHCl_3$) 3020, 1604, 1474, 1422, 1375, 1225, 1016, 928, 849, 793 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s. 1H, 2-***H***), 8.28 (d, *J* = 9.0, 1H, 5-***H***), 8.11 (d, *J* = 2.0, 1H, 8-***H***), 7.58 (dd, *J* = 2.0, 9.0, 1H, 6-***H***), 1.41 (s, 12H, pin-$\boldsymbol{CH_3}$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2 (***C***-2), 150.4 (***C***-2′), 150.0 (Ar-***C***), 149.9 (Ar-***C***), 137.5 (***C***-4), 128.8 (***C***-6), 126.7 (***C***-5), 125.2 (Ar-***C***), 85.0 (pin-***C***$(CH_3)_2$), 25.1 (pin-$\boldsymbol{CH_3}$); ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.32; GC-MS (EI) *m/z* 325 (40%, $M^+(^{37}Cl^{37}Cl)$), 324 (20%, $M^+(^{35}Cl^{37}Cl)$), 323 (62%, $M^+(^{35}Cl^{35}Cl)$), 310 (20%, $M^+(^{37}Cl^{37}Cl)$-CH_3), 309 (10%, $M^+(^{35}Cl^{37}Cl)$-CH_3), 308 (30%, $M^+(^{35}Cl^{35}Cl)$-CH_3), 290 (22%, $M^+(^{37}Cl)$-Cl), 287 (65%, $M^+(^{35}Cl)$-Cl), 267 (26%, $M^+(^{37}Cl^{37}Cl)$-$CO(CH_3)_2$) 266 (11%, $M^+(^{35}Cl^{37}Cl)$-$CO(CH_3)_2$), 265 (40%, $M^+(^{35}Cl^{35}Cl)$-$CO(CH_3)_2$), 245 (15%,

$M^+(^{37}Cl)$-Cl, $3CH_3$), 243 (47%, $M^+(^{35}Cl)$-Cl, $3CH_3$), 225 (64%, $M^+(^{37}Cl^{37}Cl)$-$CO(CH_3)_2C(CH_3)_2$), 224 (25%, $M^+(^{35}Cl^{37}Cl)$-$CO(CH_3)_2C(CH_3)_2$), 223 (100%, $M^+(^{35}Cl^{35}Cl)$-$CO(CH_3)_2C(CH_3)_2$), 190 (15%, $M^+(^{37}Cl)$-Cl, $CO(CH_3)_2C(CH_3)_2$), 188 (46%, $M^+(^{35}Cl)$-Cl, $CO(CH_3)_2C(CH_3)_2$); HRMS (ASAP) *m/z* found: 323.0771, $C_{15}H_{16}{}^{10}B^{35}Cl_2NO_2$ $(M)^+$ requires: 323.0766.

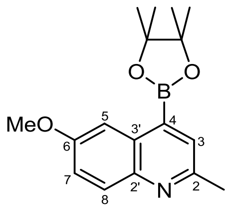
3.4 Borylation of 2,6-Disubstituted Quinolines (Scheme 4)

2,6-dimethyl-4-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)quinoline, 11a



General procedure A was applied to 2,6-dimethylquinoline (157 mg, 1.00 mmol). Purification by flash-column chromatography on neutral alumina with gradient elution of MeOH/DCM from 0.5 - 5% over 25 column volumes, affording 2,6-dimethyl-4-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)quinoline as a white solid (203 mg, 72%); m.p. 96 - 97 °C; ν_{max} ($CHCl_3$) 3021, 1519, 1474, 1423, 1381, 1364, 1331, 1225, 1141, 1016, 928, 849, 793 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, br, 1H, 5-***H***), 7.90 (d, *J* = 8.5, 1H, 8-***H***), 7.70 (s, 1H, 3-***H***), 7.49 (dd, *J* = 1.9, 8.5, 1H, 7-***H***), 2.72 (s, 3H, 2-***CH₃***), 2.54 (s, 3H, 6-***CH₃***), 1.43 (s, 12H, pin-***CH₃***); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2 (***C***-2), 146.4 (***C***-2′), 135.8 (***C***-6), 131.4 (***C***-7), 129.9 (***C***-3), 129.4 (***C***-3′), 128.9 (***C***-8), 127.1 (***C***-5), 84.6 (pin-***C***(CH_3)$_2$, 25.3 (6-***CH₃***), 25.2 (pin-***CH₃***), 22.1 (2-***CH₃***); ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.32; GC-MS (EI) *m/z* 283 (100%, M^+), 268 (15%, M^+-CH_3) , 240 (10%, M^+-$C(CH_3)_2$), 226 (5%, M^+-$CO(CH_3)_2$), 210 (19%), 197 (17%), 183 (78%, M^+-$CO(CH_3)_2C(CH_3)_2$); HRMS (ASAP) *m/z* found: 282.1769, $C_{17}H_{22}{}^{10}BNO_2$ $(M)^+$ requires: 282.1780.

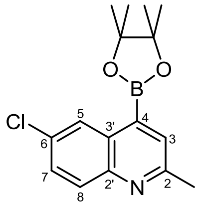
6-methoxy-2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2′-yl)quinoline, 11b



General procedure A was applied to 2-methyl-6-methoxyquinoline (173 mg, 1.00 mmol). Purification by silica gel flash-column chromatography with gradient elution of MeOH/DCM from 0.5 - 12.5% over 25 column volumes, affording 6-methoxy-2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2-dioxaborolan-2-yl)quinoline as an off-white solid (227 mg, 76%); m.p. 121 - 122 °C; ν_{max} ($CHCl_3$) 3020, 1620, 1519, 1475, 1420, 1382, 1364, 1332, 1225, 1142, 963, 928, 849, 718, 666 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.8, 1H, 5-***H***), 7.92 (d, *J* = 9.2, 1H, 8-***H***), 7.70 (s, 1H, 3-***H***), 7.33 (dd, *J* = 2.8, 9.2, 1H, 7-***H***), 3.93 (s, 3H, 6-O***CH₃***), 2.70 (s, 3H, 2-***CH₃***), 1.43 (s, 12H, pin-***CH₃***); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5 (***C***-2), 155.6 (***C***-2′), 143.9 (***C***-6), 130.5 (***C***-3′), 130.4 (***C***-8), 130.1 (***C***-3), 121.3 (***C***-7), 106.7 (***C***-5), 84.6 (pin-***C***(CH_3)$_2$), 55.5 (6-O***CH₃***), 25.2 (pin-***CH₃***), 25.0 (2-***CH₃***); ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.09; GC-MS (EI) *m/z* 299 (100%, M^+), 284 (5%, M^+- CH_3), 226 (21%), 199

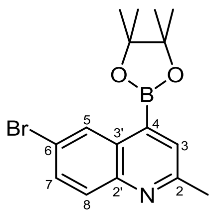
(25%, M^+- $CO(CH_3)_2C(CH_3)_2$), 184 (5%), 156 (11%); HRMS (ASAP) *m/z* found: 299.1805, $C_{17}H_{23}{}^{10}BNO_3$ $(M+H)^+$ requires: 299.1807.

6-chloro-2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline, 11c



General procedure A was applied to 2-methyl-6-chloroquinoline (177 mg, 1.00 mmol). Purification by silica gel flash-column chromatography with gradient elution of MeOH/DCM from 0.5 - 12.5% over 25 column volumes, affording 6-chloro-2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline as a white solid (239 mg, 79%); m.p. 105 - 106 °C; ν_{max} ($CHCl_3$) 3019, 1504, 1473, 1426, 1362, 1225, 1016, 928, 793, 666 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.59 (d, *J* = 2.3, 1H, Ar-5-***H***), 7.94 (d, *J* = 8.9, 1H, Ar-8-***H***), 7.77 (s, 1H, Ar-3-***H***), 7.60 (dd, *J* = 2.3, 8.9, 1H, Ar-7-***H***), 2.73 (s, 3H, Ar-$\boldsymbol{CH_3}$), 1.43 (s, 12H, pin-$\boldsymbol{CH_3}$); ^{13}C NMR (176 MHz, $CDCl_3$) δ 158.3 (Ar-2-***C***), 146.1 (Ar-2'-***C***), 131.6 (Ar-6-***C***), 130.6 (Ar-3-***C***), 130.4 (Ar-8-***C***), 129.81 (Ar-3'-***C***), 129.78 (Ar-7-***C***), 127.0 (Ar-5-***C***), 84.6 (pin-***C***$(CH_3)_2$), 24.9 (Ar-$\boldsymbol{CH_3}$), 24.6 (pin-$\boldsymbol{CH_3}$); ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.60; GC-MS (EI) *m/z* 305 (34%, $M^+(^{37}Cl)$), 303 (100%, $M^+(^{35}Cl)$), 290 (7%, $M^+(^{37}Cl)$ $-CH_3$), 288 (23%, $M^+(^{35}Cl)$ $-CH_3$), 245 (6%, $M^+(^{35}Cl)$ $-CO(CH_3)_2$), 221 (43%, $M^+(^{37}Cl)$ $-C(CH_3)_2C(CH_3)_2$), 219 (15%, $M^+(^{35}Cl)$ $-C(CH_3)_2C(CH_3)_2$), 205 (24%, $M^+(^{37}Cl)$ $-CO(CH_3)_2C(CH_3)_2$), 203 (76%, $M^+(^{35}Cl)$ $-CO(CH_3)_2C(CH_3)_2$), 184 (27%, M^+ $-Cl,C(CH_3)_2C(CH_3)_2$), 141 (9%); HRMS (ASAP) *m/z* found $(M)^+$ 303.1299, $C_{16}H_{19}{}^{10}BNO_2{}^{35}Cl$ requires *M* 303.1312.

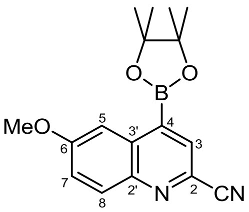
6-bromo-2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline, 11d



General procedure A was applied to 2-methyl-6-bromoquinoline (222 mg, 1.0 mmol). Purification by silica gel flash-column chromatography with gradient elution of MeOH/DCM from 0.5 - 12.5% over 25 column volumes, affording 6-bromo-2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline as a white solid (292 mg, 84%); m.p. 124 - 125 °C; Anal. Calcd. for $C_{16}H_{19}BBrNO_2$: C, 55.2; H, 5.5; N, 4.0%; found: C, 55.0; H, 5.5; N, 4.1%; ν_{max} ($CHCl_3$) 3020, 1601, 1520, 1475, 1423, 1390, 1364, 1332, 1304, 1228, 1141, 1017, 928, 848, 718 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 2.2, 1H, Ar-5-***H***), 7.87 (d, *J* = 8.9, 1H, Ar-8-***H***), 7.76 (s, 1H, Ar-3-***H***), 7.73 (dd, *J* = 2.2, 8.9, 1H, Ar-7-***H***), 2.72 (s, 3H, Ar-$\boldsymbol{CH_3}$), 1.43 (s, 12H, pin-$\boldsymbol{CH_3}$); ^{13}C NMR (126

MHz, CDCl3) δ 158.6 (Ar-2-***C***), 146.4 (Ar-2'-***C***), 132.5 (Ar-***C***), 130.8 (Ar-***C***), 130.7 (Ar-***C***), 130.48 (Ar-***C***), 130.46 (Ar-***C***), 120.1 (Ar-7-***C***), 84.8 (pin-***C***$(CH_3)_2$), 25.3 (Ar-***CH₃***), 25.1 (pin-***CH₃***); ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.19; GC-MS (EI) *m/z* 349 (98%, M^+(^{81}Br)), 347 (100%, M^+(^{79}Br)), 334 (17%, M^+(^{81}Br)-CH_3), 332 (17%, M^+(^{79}Br)-CH_3), 291 (6%, M^+(^{81}Br)-$CO(CH_3)_2$), 289 (6%, M^+(^{79}Br)-$CO(CH_3)_2$), 249 (59%, M^+(^{81}Br)-$CO(CH_3)_2C(CH_3)_2$), 247 (59%, M^+(^{79}Br)-$CO(CH_3)_2C(CH_3)_2$), 226 (18%, M^+-Br, $CO(CH_3)_2C(CH_3)_2$), 211 (29%,-Br, $C(CH_3)_2$,CH_3), 181 (33%, M^+-Br,$CO(CH_3)_2C(CH_3)_2$), 169 (17%), 141 (20%); HRMS (ASAP) *m/z* found: 346.0715, $C_{16}H_{19}{}^{10}B^{79}BrNO_2$ $(M)^+$ requires: 346.0729.

6-methoxy-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline-2-carbonitrile, 11e

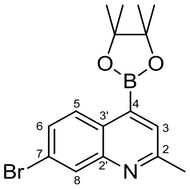


General procedure B was applied to 6-methoxyquinoline-2-carbonitrile (184 mg, 1.00 mmol). The reaction was stirred at room temperature for 48 hours. Upon completion, volatiles were removed under reduced pressure and the remaining residue was purified by silica gel flash-column chromatography with gradient elution of MeOH/DCM from 0.5 - 12.5% over 25 column volumes, affording 6-methoxy-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline-2-carbonitrile as a off-white solid (270 mg, 87%); m.p. 230 - 231 °C; Anal. Calcd. for $C_{17}H_{19}BN_2O_3$: C, 65.8; H, 6.2; N, 9.0; found: C, 65.3; H, 6.1; N, 8.8%; ν_{max} ($CHCl_3$) 3019, 2216, 1619, 1477, 1415, 1372, 1336, 1218, 1140, 1028, 963, 928, 848, 689 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H, Ar-3-***H***), 8.08 (d, *J* = 2.7, 1H, Ar-5-***H***), 8.06 (d, *J* = 9.3, 1H, Ar-8-***H***), 7.48 (dd, *J* = 2.8, 9.3, 1H, Ar-7-***H***), 4.00 (s, 3H, Ar-O***CH₃***), 1.46 (s, 12H, pin-***CH₃***); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4 (Ar-6-***C***), 144.6 (Ar-2'-***C***), 133.8 (Ar-3'-***C***), 131.9 (Ar-8-***C***), 131.4 (Ar-3-***C***), 130.3 (Ar-2-***C***), 124.1 (Ar-7-***C***), 118.2 (Ar-***CN***), 106.2 (Ar-5-***C***) , 85.2 (pin-***C***$(CH_3)_2$), 55.8 (Ar-O***CH₃***), 25.3 (pin-***CH₃***); ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.64; GC-MS (EI) *m/z* 310 (100%, M^+), 295 (19%, M^+-CH_3), 253 (7%, M^+-$CO(CH_3)_2$), 237 (26%), 224 (40%), 210 (64%, M^+-$CO(CH_3)_2C(CH_3)_2$), 180 (11%), 167 (15%); HRMS (ASAP) *m/z* found: 310.1590, $C_{17}H_{19}{}^{10}BN_2O_3$ $(M+H)^+$ requires: 310.1603.

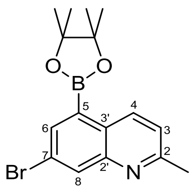
3.5 Borylation of 2,7-Disubstituted Quinolines (Scheme 5, Table 1)

7-bromo-2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline, 13a

7-bromo-2-methyl-5-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)quinoline, 14a



13a



14a

General procedure B was applied to 7-bromo-2-methylquinoline (222 mg, 1.00 mmol). The reaction was stirred at room temperature for 48 hours to afford a mixture of 2 monoborylated isomers in a 80:20 ratio. Purification by silica gel flash-column chromatography with gradient elution of MeOH/DCM from 0.5 - 12.5% over 25 column volumes, afforded the major product, (R_f 0.1) 7-bromo-2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline, as a white solid (225 mg, 65%); m.p. 149 - 150 °C; Anal. Calcd. for $C_{16}H_{19}BBrNO_2$: C, 55.2; H, 5.5; N, 4.0%; found: C, 55.0; H, 5.5; N, 3.8%; ν_{max} ($CHCl_3$) 3018, 1609, 1515, 1475, 1339, 1225, 1011, 935, 838, 709, cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.9, 1H, 5-***H***), 8.20 (d, *J* = 2.0, 1H, 8-***H***), 7.75 (s, 1H, 3-***H***), 7.57 (dd, *J* = 2.0, 8.9, 1H, 6-***H***), 2.72 (s, 3H, 2-$\boldsymbol{CH_3}$), 1.42 (s, 12H, pin-$\boldsymbol{CH_3}$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3 (***C***-2), 148.5 (***C***-2’), 131.4 (***C***-8), 130.3 (***C***-6), 129.8 (***C***-5), 129.5 (***C***-3’), 128.1 (***C***-7), 123.3 (***C***-3), 84.8 (pin-***C***$(CH_3)_2$), 25.3 (2-$\boldsymbol{CH_3}$), 25.2 (pin-$\boldsymbol{CH_3}$); ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.88; GC-MS (EI) *m/z* 349 (98%, $M^+(^{81}Br)$), 347 (100%, $M^+(^{79}Br)$), 334 (24%, $M^+(^{81}Br)-CH_3$), 332 (24%, $M^+(^{79}Br)-CH_3$), 291 (9%, $M^+(^{81}Br)-CO(CH_3)_2$), 289 (9%, $M^+(^{79}Br)-CO(CH_3)_2$), 265 (57%, $M^+(^{81}Br)-C(CH_3)_2C(CH_3)_2$), 263 (58%, $M^+(^{79}Br)-C(CH_3)_2C(CH_3)_2$), 249 (72%, $M^+(^{81}Br)-CO(CH_3)_2C(CH_3)_2$), 247 (73%, $M^+(^{79}Br)-CO(CH_3)_2C(CH_3)_2$), 226 (78%, $M^+-Br,CO(CH_3)_2C(CH_3)_2$), 211 (7%,-Br, $C(CH_3)_2,CH_3$), 181 (9%, $M^+-Br,CO(CH_3)_2C(CH_3)_2$), 168 (14%), 141 (22%); HRMS (ASAP) *m/z* found: 346.0727; $C_{16}H_{19}{}^{10}BNO_2{}^{79}Br$ $(M)^+$ requires: 346.0729.

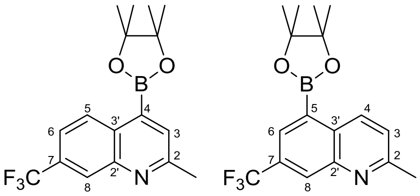
Further elution afforded (R_f 0.05) 7-bromo-2-methyl-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline a white solid (52 mg, 15%); m.p. 151 - 152 °C; ν_{max} ($CHCl_3$) 3020, 1602, 1539, 1520, 1475, 1422, 1225, 1016, 928, 848, 718 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, *J* = 8.7, 1H, 4-***H***), 8.28 (d, *J* = 1.9, 1H, 6-***H***), 8.13 (d, *J* = 1.9, 1H, 8-***H***), 7.32 (d, *J* = 8.7, 1H, 3-***H***), 2.73 (s, 3H, 2-$\boldsymbol{CH_3}$), 1.41 (s, 12H, pin-$\boldsymbol{CH_3}$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8 (***C***-2), 148.7 (***C***-2’), 138.2 (***C***-8), 137.0 (***C***-4), 134.5 (***C***-6), 129.1 (***C***-3’), 123.3 (***C***-7), 122.8 (***C***-3), 84.5 (pin-***C***$(CH_3)_2$), 25.5 (2-$\boldsymbol{CH_3}$), 25.2 (pin-$\boldsymbol{CH_3}$); ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.73; GC-MS (EI) *m/z* 349 (98%, $M^+(^{81}Br)$), 347 (100%, $M^+(^{79}Br)$), 334 (22%, $M^+(^{81}Br)-CH_3$), 332 (22%, $M^+(^{79}Br)-CH_3$), 291 (8%, $M^+(^{81}Br)-CO(CH_3)_2$), 289 (8%, $M^+(^{79}Br)-CO(CH_3)_2$), 265 (50%, $M^+(^{81}Br)-C(CH_3)_2C(CH_3)_2$), 263 (51%, $M^+(^{81}Br)$-

$C(CH_3)_2C(CH_3)_2$), 249 (74%, $M^+(^{81}Br)$-$CO(CH_3)_2C(CH_3)_2$), 247 (75%, $M^+(^{79}Br)$-$CO(CH_3)_2C(CH_3)_2$), 226 (80%, M - Br, $CO(CH_3)_2C(CH_3)_2$), 211 (7%, M^+-Br, $C(CH_3)_2$,CH_3), 181 (9%, M^+-Br,$CO(CH_3)_2C(CH_3)_2$), 168 (11%), 141 (22%); HRMS (ASAP) *m/z* found: 347.0825; $C_{16}H_{20}{}^{10}B^{79}BrNO_2$ $(M+H)^+$ requires: 347.0807.

Application of general procedure A with 7-bromo-2-methylquinoline (221 mg, 1.00 mmol) afforded a mixture of 2 monoborylated products in a 65:35 ratio, as determined by GC-MS.

2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-7-(trifluoromethyl)quinoline, 13b

2-methyl-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-7-(trifluoromethyl)quinoline, 14b

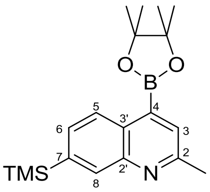


General procedure B was applied to 2-methyl-7-(trifluoromethyl)quinoline (211 mg, 1.00 mmol). The reaction was stirred at room temperature for 20 hours affording 2 monoborylated products in a 70:30 ratio. Volatiles were removed under reduced pressure and the remaining residue was purified by silica gel flash-column chromatography with gradient elution of EtOAc/hexane from 20 - 75% over 15 column volumes, to afford with the major isomer (R_f. 0.15) 2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-7-(trifluoromethyl)quinoline as a white crystalline solid (219 mg, 65%); m.p. 109 - 110 °C; ν_{max} ($CHCl_3$) 3019, 1524, 1476, 1423, 1204, 1016, 928, 849, 786, 662, 626, 492 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.7, 1H, 5-***H***), 8.32 (s, br, 1H, 8-***H***), 7.86 (s, 1H, 3-***H***), 7.68 (dd, *J* = 1.6, 8.7, 1H, 6-***H***), 2.77 (s, 3H, 2-***CH₃***), 1.44 (s, 12H, pin-***CH₃***); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9 (***C***-2), 146.9 (***C***-2'), 131.9 (***C***-3), 130.9 (***C***-3'), 130.86 (q, $^2J_{C\text{-}F}$ = 31.5, ***C***-7), 129.6 (***C***-5), 126.9 (q, $^3J_{C\text{-}F}$ = 4.5, ***C***-8), 124.4 (q, $^1J_{C\text{-}F}$ = 272.4, 7-***CF₃***), 121.7 (q, $^3J_{C\text{-}F}$ = 3.0, ***C***-6), 85.0 (pin-***C***$(CH_3)_2$), 25.4 (2-***CH₃***), 25.2 (pin-***CH₃***); ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.02; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.66; GC-MS (EI) *m/z* 337 (65%, M^+), 322 (41%, M^+-CH_3), 280 (6%, M^+-$CO(CH_3)_2$), 264 (5%), 251 (79%), 237 (100%, M^+-$CO(CH_3)_2C(CH_3)_2$); HRMS (ASAP) *m/z* found: 336.1500; $C_{17}H_{19}{}^{10}BF_3NO_2$ $(M)^+$ requires: 336.1497.

Further elution afforded (R_f. 0.1) 2-methyl-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-7-(trifluoro-methyl)quinoline as an off-white solid (91 mg, 27%); m.p. 99 - 100 °C; Anal. Calcd. for $C_{17}H_{19}BF_3NO_2$: C, 60.6; H, 5.7; N, 4.2%; found: C, 60.2; H, 5.7; N, 4.1%; ν_{max} ($CHCl_3$) 3022, 1520, 1476, 1421, 1195, 1018, 928, 853, 772 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 9.03 (d, *J* = 8.7, 1H, 4-***H***), 8.40 (s, br, 1H, 6-***H***), 8.23 (d, *J* = 1.3, 1H, 8-***H***), 7.41 (d, *J* = 8.7, 1H, 3-***H***), 2.76 (s, 3H, 2-***CH₃***), 1.43 (s, 12H, pin-***CH₃***); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2 (***C***-2), 146.8 (***C***-2'), 136.9 (***C***-4), 132.0 (***C***-3'), 130.5 (q, ${}^{3}J_{C\text{-}F}$ = 3.1, ***C***-6), 130.45 (q, ${}^{2}J_{C\text{-}F}$ = 32.4, ***C***-7), 129.8 (q, ${}^{3}J_{C\text{-}F}$ = 4.3, ***C***-8), 124.14 (***C***-3), 124.14 (q, ${}^{1}J_{C\text{-}F}$ = 273.0, 7-***CF₃***), 84.5 (pin-***C***$(CH_3)_2$), 25.4 (2-***CH₃***), 25.1 (pin-***CH₃***); ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.45; ^{19}F NMR (658 MHz, $CDCl_3$) δ -62.66; GC-MS (EI) *m/z* 337 (65%, M^+), 322 (41%, M^+-CH_3), 280 (6%, M^+-$CO(CH_3)_2$), 264 (5%), 251 (79%), 237 (100%, M^+-$CO(CH_3)_2C(CH_3)_2$); HRMS (ASAP) *m/z* found: 336.1494; $C_{17}H_{19}{}^{10}BF_3NO_2$ $(M)^+$ requires: 336.1497.

Application of general procedure A to 2-methyl-7-(trifluoromethyl)quinoline (211 mg, 1.00 mmol) afforded 2 monoborylated products as a 60:40 ratio.

2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-7-(trimethylsilyl)quinoline, 13c

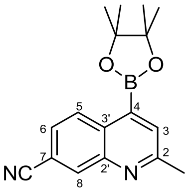


13c

General procedure B was applied to 2-methyl-7-(trimethylsilyl)quinoline (215 mg, 1.00 mmol). The reaction was stirred at room temperature for 72 hours affording a mixture of monoborylated products in an 85:10:5 ratio by GC-MS. Volatiles were removed under reduced pressure and the remaining residue was purified by silica gel flash-column chromatography with gradient elution of MeOH/DCM from 0.5 - 12.5% over 25 column volumes, affording only the major 2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-7-(trimethylsilyl)quinoline product as a white solid (231 mg, 68%); m.p. 110 - 111 °C; ν_{max} ($CHCl_3$) 3016, 1522, 1476, 1423, 1212, 1016, 928, 849, 795 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.2, 1H, 5-***H***), 8.20 (s, br, 1H, 8-***H***), 7.74 (s, 1H, 3-***H***), 7.64 (dd, *J* = 1.1, 8.2, 1H, 6-***H***), 2.74 (s, 3H, Ar-***CH₃***), 1.42 (s, 12H, pin-***CH₃***), 0.34 (s, 9H, Si***(CH₃)₃***; ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2 (***C***-2), 147.1 (***C***-2'), 142.1 (***C***-6), 134.9 (***C***-8), 130.2 (***C***-6), 130.1 (***C***-3), 129.5 (***C***-3'), 127.2 (***C***-5), 84.6 (pin-***C***$(CH_3)_2$), 25.4 (Ar-***CH₃***), 25.2 (pin-***CH₃***), -1.0 (Ar-Si***(CH₃)₃***); ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.82; GC-MS (EI) *m/z* 341 (22%, M^+), 326 (100%, M^+-CH_3), 226 (12%, M^+-CH_3,$CO(CH_3)_2C(CH_3)_2$); HRMS (ASAP) *m/z* found: 341.2096; $C_{19}H_{29}{}^{10}BNO_2Si$ $(M)^+$ requires: 341.2097.

Application of general procedure A with 2-methyl-7-(trimethylsilyl)quinoline (215 mg, 1.00 mmol) afforded a mixture of 3 mono-borylated products in a 70:20:10 ratio, as determined by GC-MS.

2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline-7-carbonitrile, 13d

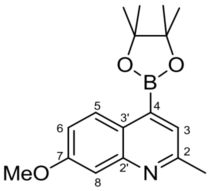


13d

General procedure B was applied to 2-methylquinoline-7-carbonitrile (168 mg, 1.00 mmol). The reaction was stirred at room temperature (25 °C) for 48 hours affording a 95:5 mixture of monoborylated products. Volatiles were removed under reduced pressure and the remaining residue was purified by recrystallisation from acetonitrile, affording only 2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline-7-carbonitrile as a white solid (252 mg, 86%); m.p. 149 - 150 °C; Anal. Calcd. for $C_{17}H_{19}BN_2O_2$ C, 69.4; H, 6.5; N, 9.5%; found: C, 69.1; H, 6.5; N, 9.4%; ν_{max} ($CHCl_3$) 3021, 2230 (C≡N), 1520, 1475, 1423, 1359, 1335, 1225, 1141, 1016, 928, 850 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.6, 1H, 5-***H***), 8.36 (d, *J* = 1.5, 1H, 8-***H***), 7.87 (s, 1H, 3-***H***), 7.64 (dd, *J* = 1.5, 8.6, 1H, 6-***H***), 2.76 (s, 3H, 7-***CH₃***), 1.43 (s, 12H, pin-***CH₃***); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5 (***C***-2), 146.8 (***C***-2'), 135.0 (***C***-8), 132.6 (***C***-3), 131.7 (***C***-3'), 130.0 (***C***-5), 126.9 (***C***-6), 119.2 (7-***CN***), 112.5 (***C***-7), 85.1 (pin-***C***(CH_3)$_2$), 25.5 (pin-***CH₃***), 25.2 (2-***CH₃***); ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.60; *m/z* (GC-MS, EI) 294 (62%, M^+), 279 (36%, M^+-CH_3), 250 (5%), 237 (7%, M^+-CO(CH_3)$_2$), 221 (14%), 208 (100%), 194 (59%, M^+-CO(CH_3)$_2$C(CH_3)$_2$); HRMS (ASAP) *m/z* found: 294.1648; $C_{17}H_{20}{}^{10}BN_2O_2$ $(M+H)^+$ requires: 294.1654.

Application of general procedure A (but with a reaction time of 0.25 hours) with 2-methylquinoline-7-carbonitrile (168 mg, 1.00 mmol) afforded a mixture of 2 monoborylated and 1 bisborylated product in an 82:9:9 ratio, as determined by GC-MS.

7-methoxy-2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline, 13e



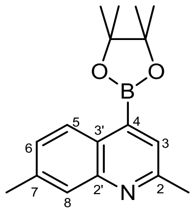
13e

General procedure B was applied to 7-methoxy-2-methylquinoline (173 mg, 1.00 mmol). The reaction was stirred at room temperature for 48 hours affording a 95:5 mixture of 2 monoborylated products as determined by GC-MS. Volatiles were removed under reduced pressure and the remaining residue was purified by silica gel flash-column chromatography with gradient elution of MeOH/DCM from 0.5 - 12.5% over 25 column volumes, affording the major 7-methoxy-2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)quinoline product as a pale yellow solid (218 mg, 73%); m.p. 87 - 88 °C; ν_{max} ($CHCl_3$) 2982, 1604, 1557, 1495, 1331, 1306, 1266, 1204, 1141, 1083, 987, 792 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.47 (d, *J*

= 9.1, 1H, 5-***H***), 7.61 (s, 1H, 3-***H***), 7.36 (d, *J* = 2.6, 1H, 8-***H***), 7.16 (dd, *J* = 2.6, 9.1, 1H, 6-***H***), 3.94 (s, 3H, 7-O***CH₃***), 2.71 (s, 3H, 2-***CH₃***), 1.42 (s, 12H, pin-***CH₃***); ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.2 (***C***-7), 158.2 (***C***-2), 149.4 (***C***-2'), 129.1 (***C***-5), 127.3 (***C***-3), 124.4 (***C***-3'), 118.7 (***C***-6), 107.1 (***C***-8), 84.4 (pin-***C***(CH_3)$_2$), 55.4 (7-O***CH₃***), 25.0 (2-***CH₃***), 24.9 (pin-***CH₃***); ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.95; GC-MS (EI) 299 (100%, M^+), 284 (8%, M^+-CH_3), 242 (6%, M^+-CO(CH_3)$_2$), 226 (28%), 213 (13%), 199 (41%, M^+-CO(CH_3)$_2$C(CH_3)$_2$); HRMS (ASAP) *m/z* found: 298.1749; $C_{17}H_{22}{}^{10}BNO_3$ $(M)^+$ requires: 298.1729.

Application of general procedure A with 7-methoxy-2-methylquinoline (173 mg, 1.00 mmol) afforded a mixture of 2 monoborylated products in a 90:10 ratio, as determined by GC-MS.

2,7-dimethyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline, 13f



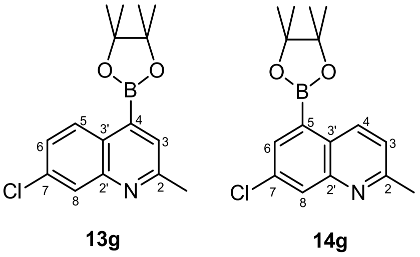
13f

General procedure B was applied to 2,7-dimethylquinoline (157 mg, 1.00 mmol). The reaction was stirred at room temperature (25 °C) for 72 hours. Analysis by GC-MS showed a 95:5 mixture of 2 monoborylated products. Volatiles were removed from the reaction under reduced pressure and the remaining residue was purified by silica gel flash-column chromatography with gradient elution of MeOH/DCM from 0.5 - 12.5% over 25 column volumes, affording the major isomer, 2,7-dimethyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline, as an off-white solid (226 mg, 80%); m.p. 108 - 109 °C (from MeCN); ν_{max} ($CHCl_3$) 3020, 1519, 1475, 1422, 1225, 1016, 928, 849, 718, 666 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.4 Hz, 1H, 5-***H***), 7.79 (s, br, 1H, 8-***H***), 7.67 (s, 1H, 3-***H***), 7.34 (dd, *J* = 8.4, 1.7 Hz, 1H, 6-***H***), 2.72 (s, 3H, 2-***CH₃***), 2.54 (s, 3H, 7-***CH₃***), 1.43 (s, 12H, pin-***CH₃***); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1 (***C***-2), 148.1 (***C***-2'), 139.3 (***C***-7), 129.1 (***C***-3), 128.32 (***C***-6), 128.28 (***C***-8), 127.9 (***C***-5), 127.4 (***C***-3'), 84.6 (pin-***C***(CH_3)$_2$), 25.2 (2-***CH₃***), 25.1 (pin-***CH₃***), 22.0 (7-***CH₃***); ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.34; GC-MS (EI) *m/z* 283 (100%, M^+), 268 (16%, M^+-CH_3), 225 (18%, M^+-CO(CH_3)$_2$), 210 (47%), 197 (30%), 183 (74%, M^+-CO(CH_3)$_2$C(CH_3)$_2$); HRMS (ASAP) *m/z* found: 283.1851; $C_{17}H_{23}{}^{10}BNO_2$ $(M+H)^+$ requires: 283.1858.

Application of general procedure A with 2,7-dimethylquinoline (157 mg, 1.00 mmol) afforded a mixture of 3 monoborylated products in a 82:12:6 ratio, as determined by GC-MS.

7-chloro-2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)quinoline, 13g

7-chloro-2-methyl-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline, 14g



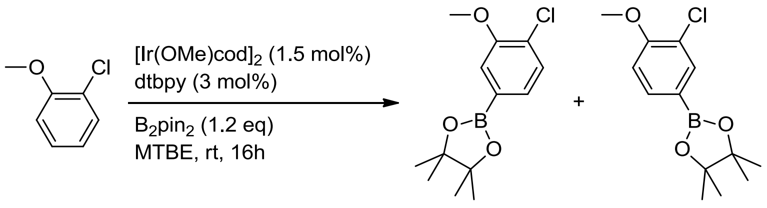
General procedure A was applied to 7-chloro-2-methylquinoline (177 mg. 1.00 mmol). The reaction afforded a 65:35 mixture of 2 monoborylated products at 92% conversion, as determined by GC-MS. Purification by silica gel flash-column chromatography with gradient elution of MeOH/DCM from 0.5 - 12.5% over 25 column volumes, afforded a mixture of 7-chloro-2-methylquinoline and 7-chloro-2-methyl-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline as yellow oil. Recrystallisation from minimum amount of MeCN afforded 7-chloro-2-methyl-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline as a white crystalline solid (33 mg, 11%); m.p. 149 - 150 °C (from MeCN); ν_{max} ($CHCl_3$) 3020, 1475, 1362, 1226, 1016, 928, 793 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.93 (d, *J* = 8.6, 1H, 4-***H***), 8.09 (d, *J* = 2.2, 1H, 6-***H***), 8.00 (d, *J* = 2.2, 1H, 8-***H***), 7.30 (d, *J* = 8.6, 1H, 3-***H***), 2.72 (s, 3H, 2-$\boldsymbol{CH_3}$), 1.41 (s, 12H, pin-$\boldsymbol{CH_3}$); ^{13}C NMR (176 MHz, $CDCl_3$) δ 159.9 (***C***-2), 148.6 (***C***-2'), 136.9 (***C***-4), 135.7 (***C***-8), 134.8 (***C***-7), 131.1 (***C***-6), 128.8 (***C***-3'), 122.6 (***C***-3), 84.5 (pin-***C***$(CH_3)_2$), 25.5 (2-$\boldsymbol{CH_3}$), 25.2 (pin-$\boldsymbol{CH_3}$); ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.64; GC-MS (EI) *m/z* 305 (30%, $M^+(^{37}Cl)$), 303 (91%, $M^+(^{35}Cl)$), 290 (10%, $M^+(^{37}Cl)-CH_3$), 288 (31%, $M^+(^{35}Cl)-CH_3$), 247 (3%, $M^+(^{37}Cl)-CO(CH_3)_2$), 245 (9%, $M^+(^{35}Cl)-CO(CH_3)_2$), 221 (24%, $M^+(^{37}Cl)-C(CH_3)_2C(CH_3)_2$), 219 (78%, $M^+(^{35}Cl)-C(CH_3)_2C(CH_3)_2$), 205 (32%, $M^+(^{37}Cl)-CO(CH_3)_2C(CH_3)_2$), 203 (100%, $M^+(^{35}Cl)-CO(CH_3)_2C(CH_3)_2$), 141 (11%); HRMS (ASAP) *m/z* found: 302.1222; $C_{16}H_{19}{}^{10}BClNO_2$ $(M)^+$ requires: 302.1234.

Further elution afforded 7-chloro-2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline as white crystalline solid (185 mg, 61 %), ν_{max} ($CHCl_3$) 2981, 1589, 1493, 1371, 1329, 1262, 1183, 1138, 964, 933, 928, 843 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.4, 1H, 5-***H***), 8.00 (d, *J* = 2.1, 1H, 8-***H***), 7.74 (s, 1H, 3-***H***), 7.44 (dd, ^2J = 2.1, ^3J = 8.4, 1H, 6-***H***), 2.73 (s, 3H, 2-$\boldsymbol{CH_3}$), 1.42 (s, 12H, pin-$\boldsymbol{CH_3}$); ^{13}C NMR (176 MHz, $CDCl_3$) δ 159.3 (***C***-2), 148.3 (***C***-2'), 134.9 (***C***-7), 130.0 (***C***-3), 129.6 (***C***-5), 128.1 (***C***-8), 127.7 (***C***-3'), 126.9 (***C***-6), 84.8 (pin-***C***$(CH_3)_2$), 25.3 (2-$\boldsymbol{CH_3}$), 25.1 (pin-$\boldsymbol{CH_3}$); ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.90; GC-MS (EI) *m/z* 305 (32%, $M^+(^{37}Cl)$), 303 (100%, $M^+(^{35}Cl)$), 290 (10%, $M^+(^{37}Cl)-CH_3$), 288 (29%, $M^+(^{35}Cl)-CH_3$), 245 (12%, $M^+(^{35}Cl)-CO(CH_3)_2$), 219 (20%, $M^+(^{37}Cl)-C(CH_3)_2C(CH_3)_2$), 217 (56%, $M^+(^{35}Cl)-C(CH_3)_2C(CH_3)_2$), 205 (35%, $M^+(^{37}Cl)-CO(CH_3)_2C(CH_3)_2$), 203 (98%, $M^+(^{35}Cl)-CO(CH_3)_2C(CH_3)_2$), 141 (14%); HRMS (ASAP) *m/z* found: 304.1281; $C_{16}H_{20}{}^{11}B^{35}ClNO_2$ $(M+H)^+$ requires: 304.1276.

Application of general procedure B with 7-chloro-2-methylquinoline (177 mg. 1.00 mmol) for 68 h afforded 73:27 mixture of **13g**:**14g** at 93% conversion, as determined by ^{1}H NMR spectrum analysis of the crude mixture. Purification of the crude mixture, as above, afforded 7-chloro-2-methyl-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline as a white crystalline solid (30 mg, 10%) and 7-chloro-2-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)quinoline as white crystalline solid (200 mg, 66 %).

3.6 Borylation of Unsymmetrical 1,2-Disubstituted Benzenes (Scheme 6, Table 2)

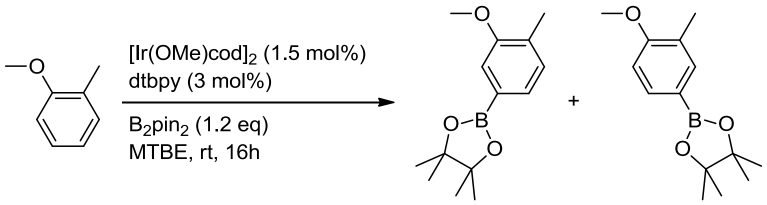
Borylation of 1-chloro-2-methoxybenzene, 15a



15a **16a** **17a**

General procedure C was applied to 1-chloro-2-methoxybenzene **15a** (57 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of 94% (GC-MS) and **16a** and **17a** in a 60:40 mixture which also contained unreacted starting material **15a** (^{1}H NMR spectrum).

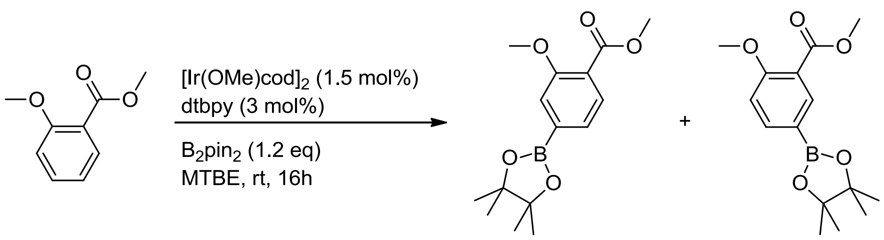
Borylation of 1-methoxy-2-methylbenzene, 15b



15b **16b** **17b**

General procedure C was applied to 1-methoxy-2-methylbenzene **15b** (50 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of 75% (GC-MS) and **16b** and **17b** in a 75:25 mixture which also contained unreacted starting material **15b** (^{1}H NMR spectrum).

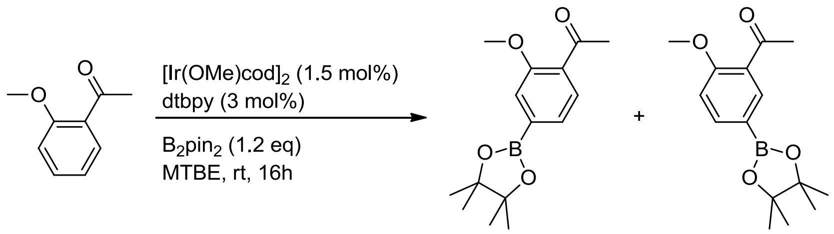
Borylation of methyl 2-methoxybenzoate, 15c



15c **16c** **17c**

General procedure C was applied to methyl 2-methoxybenzoate **15c** (66 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of >99% (GC-MS) and **16c** and **17c** in a 85:15 mixture (^{1}H NMR spectrum).

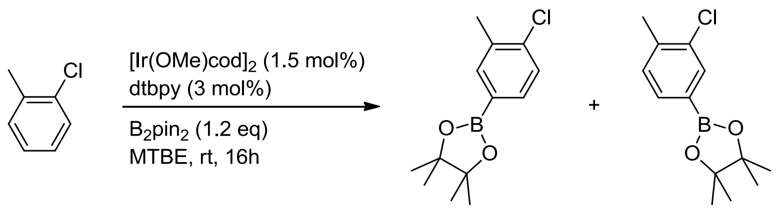
Borylation of 1-(2-methoxyphenyl)ethanone, 15d



15d **16d** **17d**

General procedure C was applied to 1-(2-methoxyphenyl)ethanone **15d** (60 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of >99% (GC-MS) and **16d** and **17d** in a 89:11 mixture (^{1}H NMR spectrum) and some unreacted starting material **15d**.

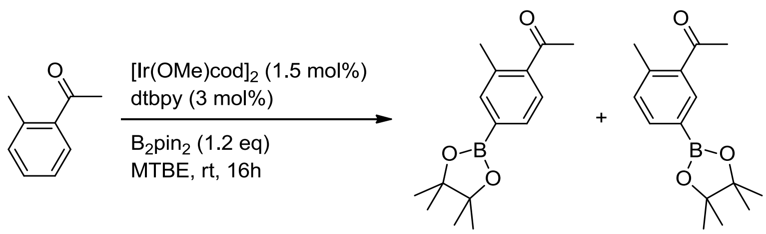
Borylation of 1-chloro-2-methylbenzene, 15e



15e **16e** **17e**

General procedure C was applied to 1-chloro-2-methylbenzene **15e** (51 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 h giving a conversion of >99% (GC-MS) and **16e** and **17e** in a 34:66 mixture (^{1}H NMR spectrum).

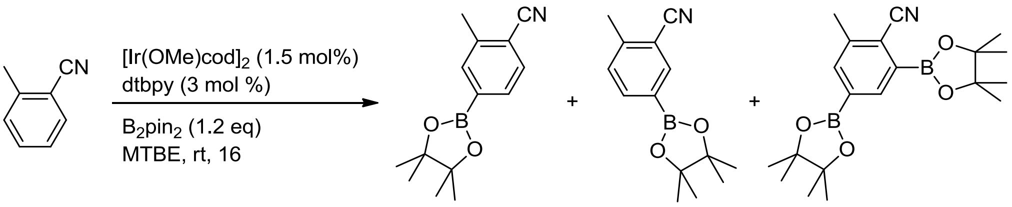
Borylation of 1-(2-methylphenyl)ethanone, 15f



15f **16f** **17f**

General procedure C was applied to 1-(2’-methylphenyl)ethanone **15f** (54 mg, 0.4 mmol). The reaction mixture was was stirred at room temperature for 16 hours giving a conversion of 87% (GC-MS) and **16f** and **17f** in a 56:44 mixture which also contained unreacted starting material **15f** (^{1}H NMR spectrum).

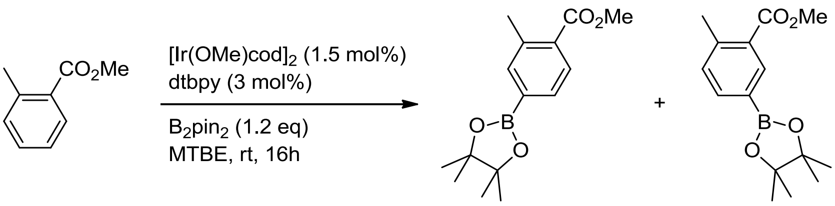
Borylation of 2-methylbenzonitrile, 15g



15g **16g** **17g** **18**

General procedure C was applied to 2-methylbenzonitrile **15g** (47mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of >99% (GCMS) and **16g**, **17g** and **18** in a 52:40:8 mixture (^{1}H NMR spectrum).

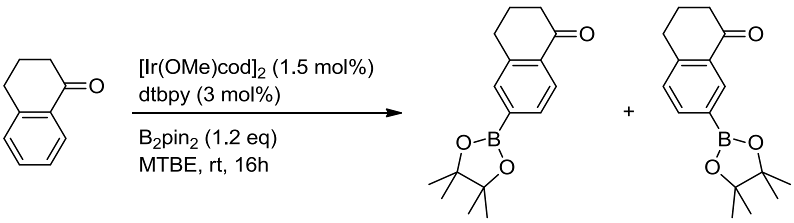
Borylation of methyl 2-methylbenzoate, 15h



15h **16h** **17h**

General procedure D was applied to methyl 2-methylbenzoate **15h** (30 mg, 0.2 mmol). The reaction mixture was allowed to stand for 16 hours giving a conversion of >99% (GC-MS) and **16h** and **17h** in a 73:27 mixture (^{1}H NMR spectrum).

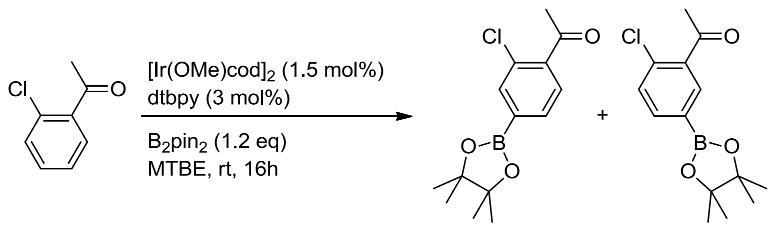
Borylation of 3,4-dihydronaphthalen-1(2*H*)-one, 15i



15i **16i** **17i**

General procedure D was applied to 3,4-dihydronaphthalen-1(2*H*)-one **15i** (29 mg, 0.2 mmol). The reaction mixture was allowed to stand for 16 hours giving a conversion of >99% (GC-MS) and **16i** and **17i** in a 80:20 mixture (^{1}H NMR spectrum).

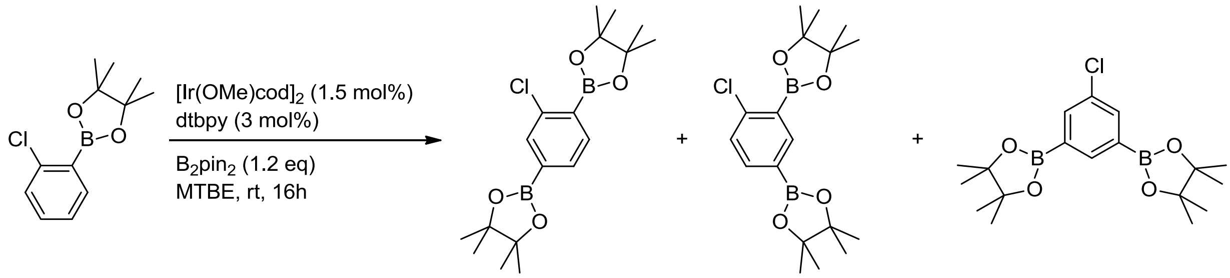
Borylation of 1-(2-chlorophenyl)ethanone, 15j



15j 16j 17j

General procedure C was applied to 1-(2-chlorophenyl)ethanone **15j** (57 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of >99% (GC-MS) and **16j** and **17j** in a 62:38 mixture (^{1}H NMR spectrum).

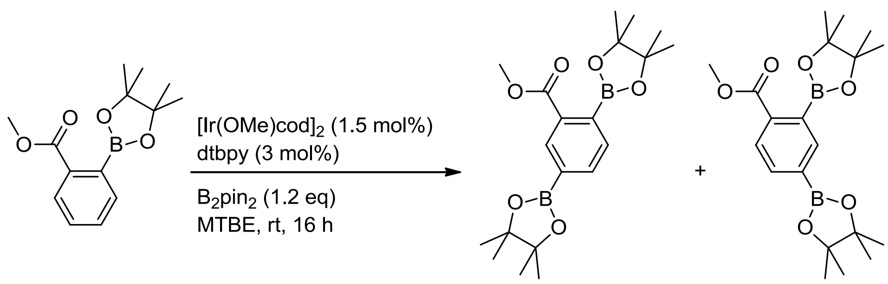
Borylation of 2-(2-chlorophenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane, 15k



15k 16k 17k zz

General procedure C was applied to 2-(2-chlorophenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane **15k** (96 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of >99% (GCMS) and monoborylated products (**16k**+**zz** arising from trace chlorobenzene impurity in the reaction mixture) and **17k** in a 84:16 mixture (^{1}H NMR spectrum).

Borylation of methyl 2-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)benzoate, 15l

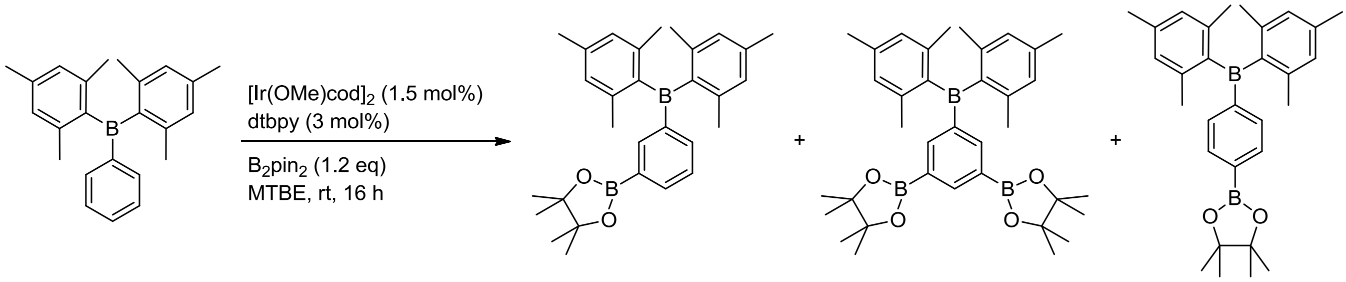


15l 16l 17l

General procedure D was applied to 2-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)benzoate **15l** (52 mg, 0.2 mmol). The reaction mixture was allowed to stand for 16 hours giving a conversion of 35% (GC-MS) and monoborylated products (**16l** and **17l**) in a 53:47 mixture (GC-MS). These peaks were assigned based on the trend of other 1,2-disubstituted benzenes as the structures of both **16l** and **17l** could not be determined unambiguously by NMR spectroscopic techniques.

3.7 Borylation of Monosubstituted Benzenes (Scheme 7, Table 3)

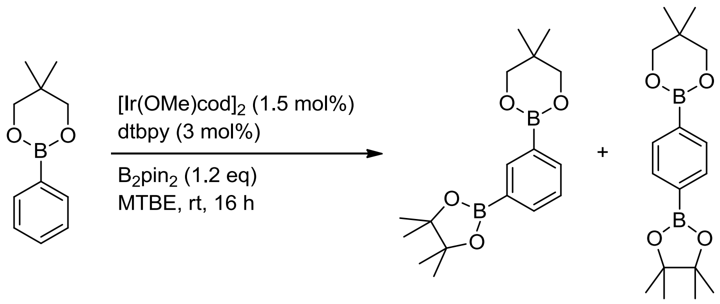
Borylation of (Dimesitylboryl)benzene, 19a



19a **20a** **21a** **22a**

General procedure C was applied to (Dimesitylboryl)benzene **19a** (119 mg, 0.36 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of 69% (^{1}H NMR spectrum) and **20a**, **21a** and **22a** in a 26:6:68 mixture and some unreacted starting material **19a** (^{1}H NMR spectrum).

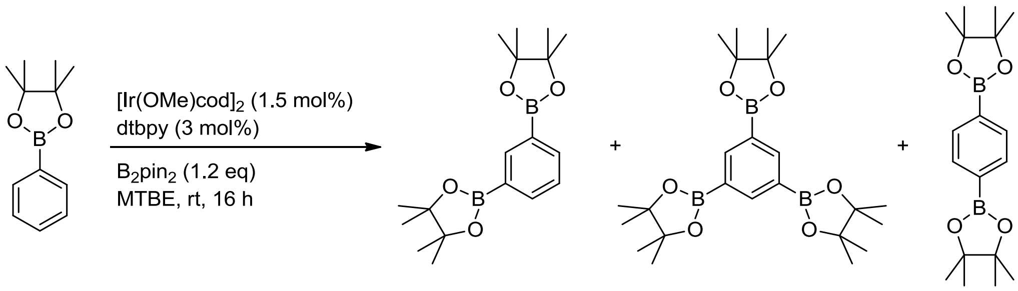
Borylation of 5,5-dimethyl-2-phenyl-[1,3,2]-dioxaborinane, 19b



19b **20b** **22b**

General procedure C was applied to 5,5-dimethyl-2-phenyl-[1,3,2]-dioxaborinane **19b** (76 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of 45% (^{1}H NMR spectrum) and **20b** and **22b** in a 33:67 mixture and some unreacted starting material **19b** (^{1}H NMR spectrum).

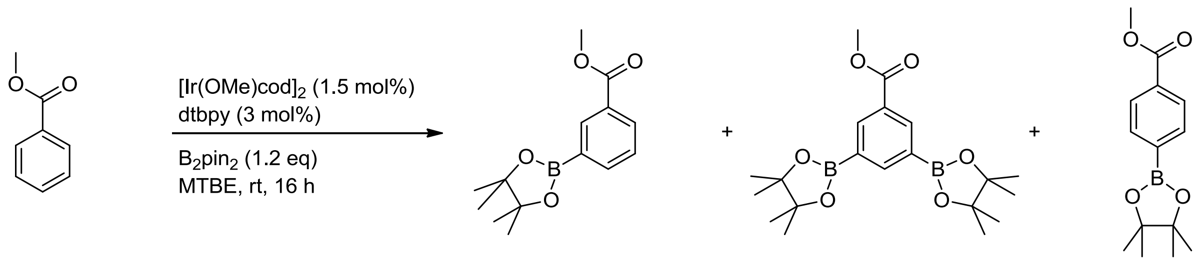
Borylation of 4,4,5,5-tetramethyl-2-phenyl-[1,3,2]-dioxaborolane, 19c



19c **20c** **21c** **22c**

General procedure C was applied to 4,4,5,5-tetramethyl-2-phenyl-[1,3,2]-dioxaborolane **19c** (82 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of 71% (^{1}H NMR spectrum) and **20c, 21c** and **22c** in a 32:4:64 mixture and some unreacted starting material **19c** (^{1}H NMR spectrum).

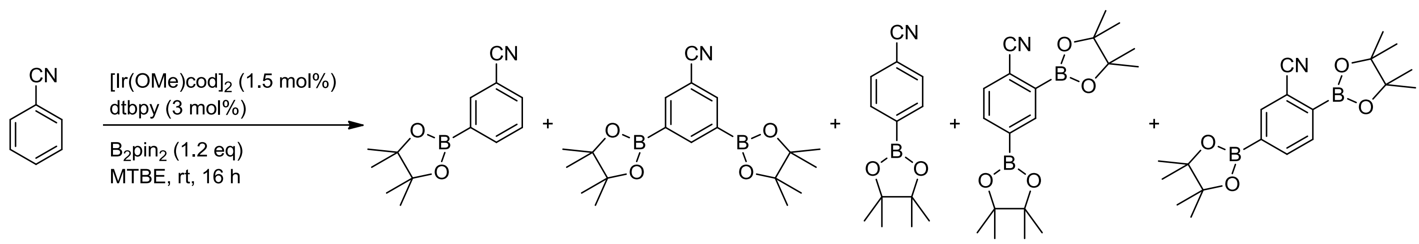
Borylation of methyl benzoate, 19d



19d **20d** **21d** **22d**

General procedure C was applied to methyl benzoate **19f** (54 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of >99% (GC-MS) and **20d**, **21d** and **22d** in a 22:22:56 mixture (^{1}H NMR spectrum).

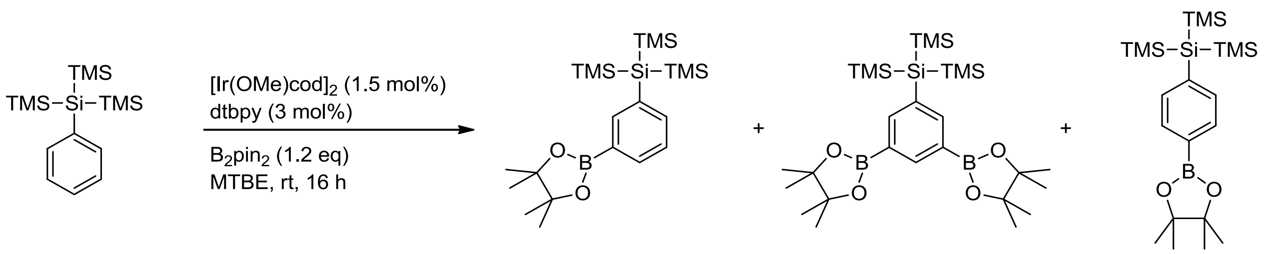
Borylation of benzonitrile, 19e



19e **20e** **21e** **22e** **xx** **yy**

General procedure C was applied to benzonitrile **19e** (41 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of >99% (GC-MS) and **20e**, **21e**, **22e**, **xx** and **yy** in a 30:21:34:7:8 mixture and some unreacted starting material **19e** (^{1}H NMR spectrum).

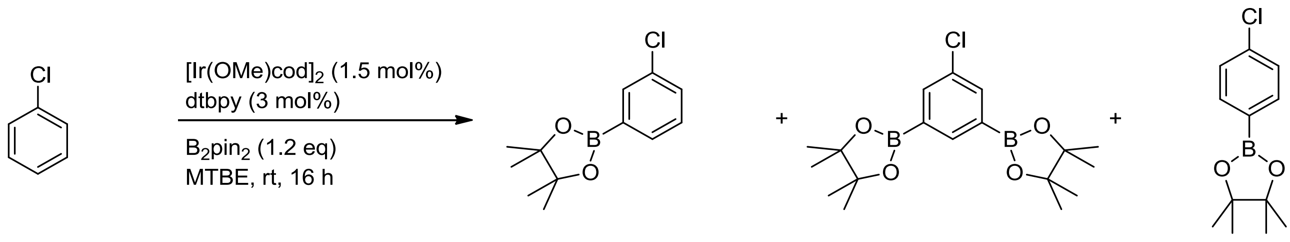
Borylation of 1,1,1,3,3,3-hexamethyl-2-phenyl-2-(trimethylsilyl)trisilane, 19f



19f **20f** **21f** **22f**

General procedure C was applied to 1,1,1,3,3,3-hexamethyl-2-phenyl-2-(trimethylsilyl)trisilane **19f** (130 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of 72% (GC-MS) and **20f**, **21f** and **22f** in a 48:15:37 mixture and some unreacted starting material **19f** (^{1}H NMR spectrum).

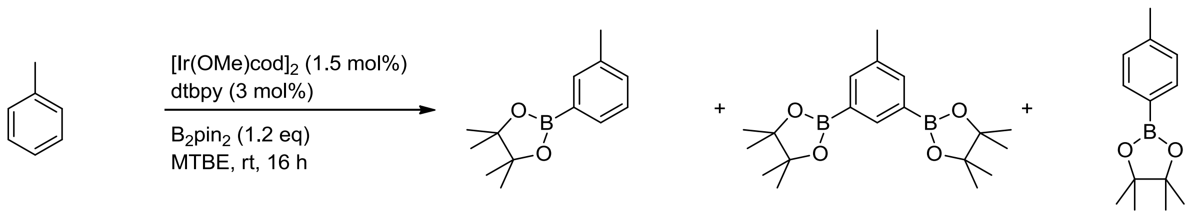
Borylation of chlorobenzene, 19g



19g **20g** **21g** **22g**

General procedure C was applied to chlorobenzene **19g** (45 mg, 0.4 mmol). The reaction mixture was allowed to stand for 16 h giving a conversion of 98% (GCMS) and **20g**, **21g** and **22g** in a 32:33:35 mixture (^{1}H NMR spectrum).

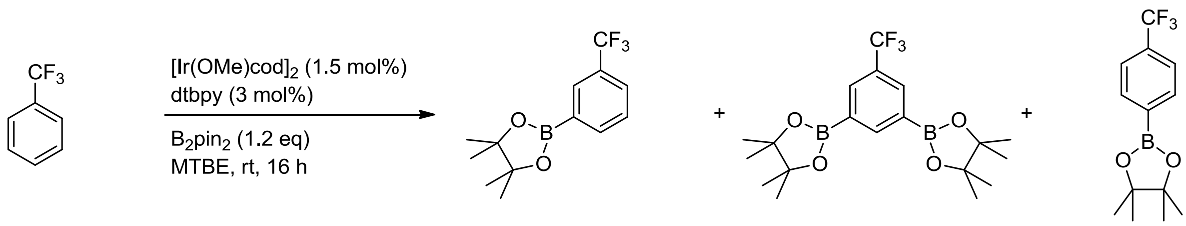
Borylation of toluene, 19h



19h **20h** **21h** **22h**

General procedure D was applied to toluene **19h** (19 mg, 0.2 mmol). The reaction mixture was allowed to stand for 16 hours giving a conversion of 30% (GC-MS) and **20h**, **21h** and **22h** in a 63:6:31 mixture and some unreacted starting material, **19h** (^{1}H NMR spectrum).

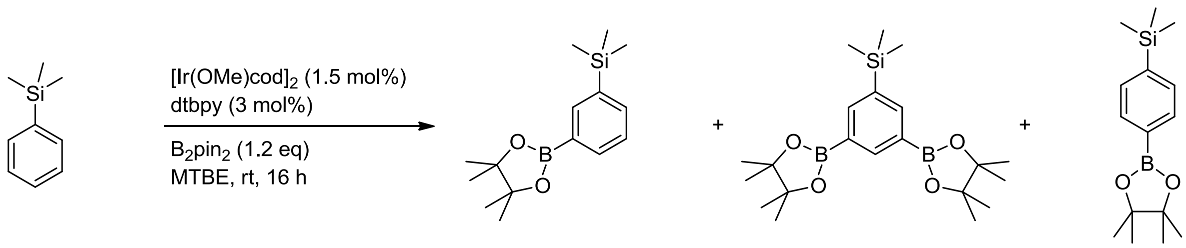
Borylation of (trifluoromethyl)benzene, 19i



19i **20i** **21i** **22i**

General procedure C was applied to (trifluoromethyl)benzene **19i** (58 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of >99% (GC-MS) and **20i**, **21i** and **22i** in a 29:40:31 mixture (^{1}H NMR spectrum).

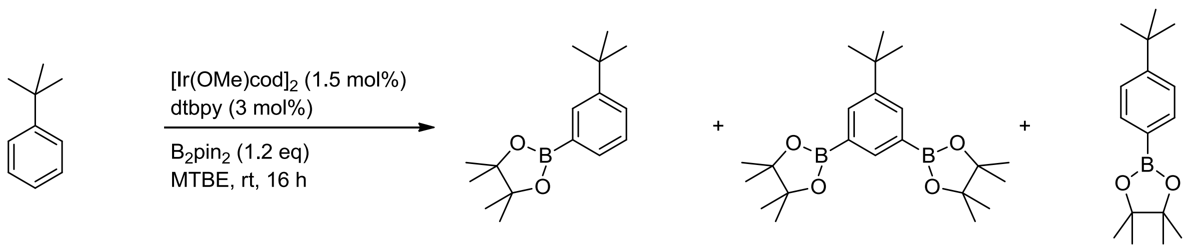
Borylation of trimethyl(phenyl)silane, 19j



19j **20j** **21j** **22j**

General procedure C was applied to trimethyl(phenyl)silane **19j** (60 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of 93% (GC-MS) and **20j**, **21j** and **22j** in a 56:16:28 mixture and some unreacted starting material **19j** (^{1}H NMR spectrum).

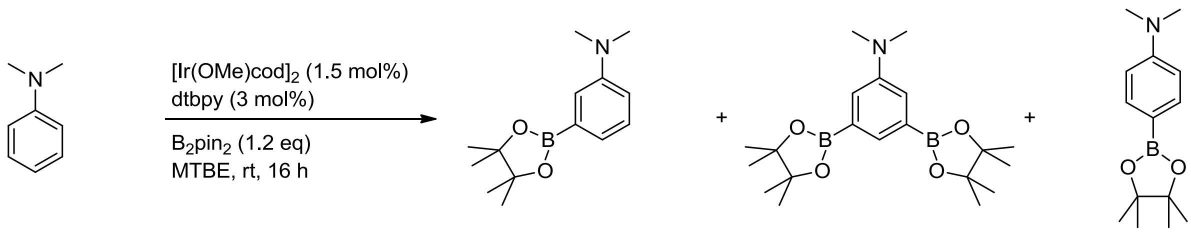
Borylation of *tert*-butylbenzene, 19k



19k **20k** **21k** **22k**

General procedure C was applied to *tert*-butylbenzene **19k** (54 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of 82% (GC-MS) and **20k**, **21k** and **22k** in a 68:8:24 mixture and some unreacted starting material **19k** (^{1}H NMR spectrum).

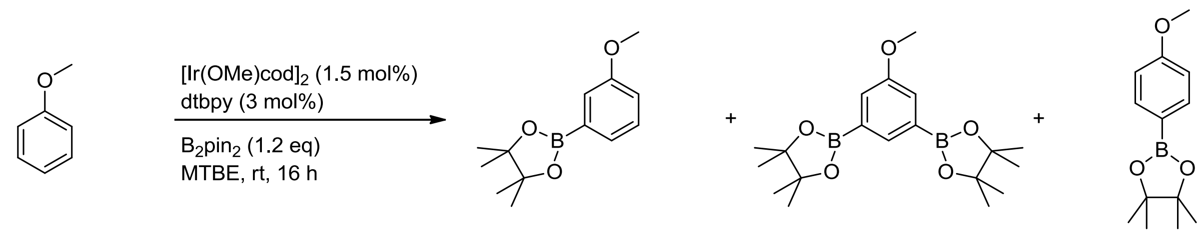
Borylation of *N,N*-dimethylaniline, 19l



19l **20l** **21l** **22l**

General procedure C was applied to N,N-dimethylaniline **19l** (48 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of 69% (GC-MS) and **20l**, **21l** and **22l** in a 75:4:21 mixture and some unreacted starting material **19l** (^{1}H NMR spectrum).

Borylation of anisole, 19m



19m **20m** **21m** **22m**

General procedure C was applied to anisole **19m** (43 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 16 hours giving a conversion of 93% (GCMS) and **20m**, **21m** and **22m** in a 68:16:16 mixture and some unreacted starting material **19m** (^{1}H NMR spectrum).

4.0 Table S1: Literature Reports on the Borylation of Monosubstituted Benzenes

	product ratio ***o*:*m*:*p*** (yield)[a]				
R	method A[4]	method B[5]	method C[6]	method D[6]	method E[7]
Me	**0:69:31** (95 %)	**4:64:32** (35 %)	**4:62:34** (91 %)	**5:63:32** (72 %)	**0:63:37** (39)
OMe	**1:74:25** (95 %)	**5:67:28** (47 %)	**2:79:19** (55 %)	**8:67:25** (65 %)	**0:58:42** (40)
CF_3	**0:70:30** (80%)	**0:69:31** (86 %)	**0:67:33** (99 %)	**0:67:33** (84 %)	**0:60:40** (89)
NMe_2	---	**0:64:35** (< 1 %)	---	**1:63:36** (65 %)	---
Cl	---	**0:76:24** (85 %)	---	---	---
F	---	**17:55:28** (90 %)	---	---	---
iPr	---	---	**1:68:31** (52 %)	**1:66:33** (67 %)	---
CO_2Et	---	---	---	**10:57:33** (---)	---
$CONEt_2$	---	---	---	**58:28:14** (50 %)	---

[a] *reaction conditions:* A:$[IrCl(cod)]_2$ (1.5 mol%), dtbpy (3 mol%), 16 h, 80 ºC, arene (60 equiv.), B_2pin_2 (1 equiv.); B:$[Ir(cod)(NHC)_2][TFA]$ (0.5 mol%), 30 min, 180 ºC microwave, arene (19.2 mmol), HBpin (0.64 mmol)*;* C:$Cp^*Ir(PMe_3)(H)_2$ (20 mol%), 17 – 142 h, 150 ºC, HBpin (1 mmol)*;* D:$Cp^*Rh(\eta^4\text{-}C_6Me_6)$, 0.5 - 3.5 h, 150 ºC, HBpin (1 mmol)*;* E:Nano-Ir(0) (0.006 mmol), tetra-2-pyridinylpyrazine (0.01 mmol) 12 - 20 h, 80 ºC, arene (10 mmol), HBpin (1 mmol), dichloromethane (2 ml), followed by hydrolysis with aqueous HCl

5.0 References

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4. Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F., *J. Am Chem. Soc.* **2002**, 124, 390-391
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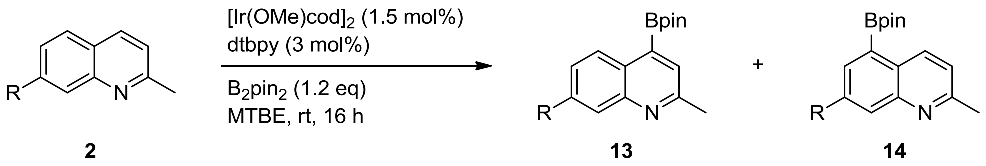
6. Cho, J.-Y.; Iverson, C. N.; Smith, M. R., III, *J. Am. Chem. Soc.* **2000**, 122, 12868-12869
7. Yinghuai, Z.; Chenyan, K.; Peng, A. T.; Emi, A.; Monalisa, W.; Louis, L. K.-J.; Hosmane, N. S.; Maguire, J. A., *Inorg. Chem.* **2008**, 47, 5756-5761.

6.0 Correlation Data

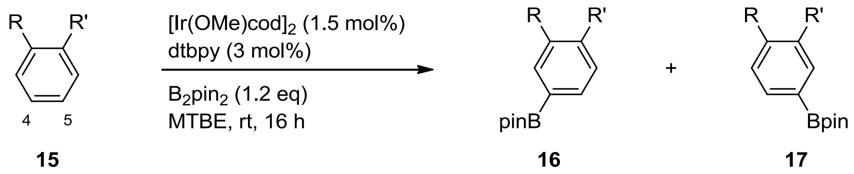
6.1 Table S2 - Correlation of Borylation Regiochemistry with NMR Shifts for 2,7-Disubstituted Quinolines



			^{1}H NMR δ (ppm)[a]		^{13}C NMR δ (ppm)[a]		time	conv.	ratio (%)[c]	yield
entry	**2**	R	4-H	5-H	C-4	C-5	(h)	(%)[b]	**13** : **14** : other	(%)[d]
1	**f**	Me	**7.95**	7.70	**135.7**	127.2	72	93	>95 : <5 : 0	80
2	**e**	OMe	**7.93**	7.62	**136.0**	128.7	48	89	>95 : <5 : 0	73
3	**d**	CN	**8.09**	7.86	**136.1**	129.1	48	92	>95 : <5 : 0	86
4	**c**	$SiMe_3$	**8.04**	7.77	**136.3**	126.8	72	91	85 : 10 : 5	68
5	**a**	Br	**7.99**	7.62	**136.1**	128.9	48	90	80 : 20 : 0	65[e]
6	**g**	Cl	**7.95**	7.64	**135.9**	128.7	68	93	73 : 27 : 0	66[f]
7	**b**	CF_3	**8.10**	7.89	**136.2**	128.9	20	94	70 : 30 : 0	65[g]

[a] Unless otherwise indicated, experimentally determined NMR chemical shifts. Bold values show agreement with experimental results. [b] Conversion determined by GC-MS; [c] Product ratios determined by GC-MS. [d] Isolated yield of major isomer, unless otherwise stated; [e] Minor isomer isolated in 15% yield; [f] Minor isomer isolated in 10% yield; [g] Minor isomer isolated in 27% yield.

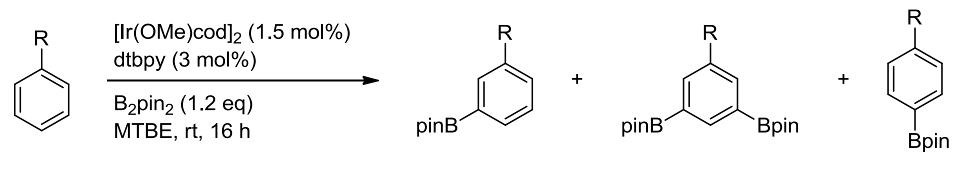
6.2 Table S3 - Correlation of Borylation Regiochemistry with NMR Shifts for Unsymmetrical 1,2-Disubstituted Benzenes



				^{1}H NMR δ (ppm)[a]		^{13}C NMR δ (ppm)[a]		conv	ratio[c]
entry	**15**	R	R'	4-H	5-H	C-4	C-5	(%)[b]	**16 : 17**
1	**a**	OMe	Cl	**7.23**	6.90	**127.9**	121.4	94	60 : 40
2	**b**	OMe	Me	**7.18**	6.88	**126.9**	120.4	75	75 : 25
3	**c**	OMe	CO_2Me	**7.46**	6.97	**133.6**	120.2	>99	85 : 15
4	**d**	OMe	COMe	**7.46**	6.99	**131.8**	120.7	>99	89 : 11
5	**e**	Me	Cl	7.16	7.13	126.7	**127.2**	>99	34 : 66
6	**f**	Me	COMe	**7.37**	7.26	**131.6**	125.8	87	56 : 44
7	**g**	Me	CN	**7.46**	7.26	**132.7**	126.3	>99	60 : 40 [d]
8	**h**	Me	CO_2Me	**7.90**	7.24	**131.9**	125.8	>99	73 : 27
9	**i**	$-CH_2CH_2CH_2CO-$		**7.45**	7.29	**133.5**	126.7	>99	80 : 20
10	**j**	Cl	$COCH_3$	**7.38**	7.31	**132.1**	127.0	>99	62 : 38
11[e]	**k**	Cl	Bpin	7.26	7.26	126.9	127.6	99	84 : 16[f]
12[e]	**l**	CO_2Me	Bpin	7.43	7.50	**127.1**	130.6	35	53 : 47[g]

[a] Unless otherwise indicated, experimentally determined NMR chemical shifts. Bold values show agreement with experimental results. [b] Conversions determined by GC-MS and ^{1}H NMR spectroscopy; [c] Product ratios determined by ^{1}H NMR spectroscopy on the crude reaction mixture; [d] 8% bis borylated product obtained; [e] NMR chemical shifts predicted using NMR Predict from MODGRAPH (http://www.modgraph.co.uk/product_nmr.htm). [f] Product ratio determined by GC-MS: 6% 2,6-bis Bpin-1-chlorobenzene obtained; [g] Product ratio determined by GC-MS.

6.3 Table S4 - Correlation of Borylation Regiochemistry with NMR Shifts for Monosubstituted Benzenes



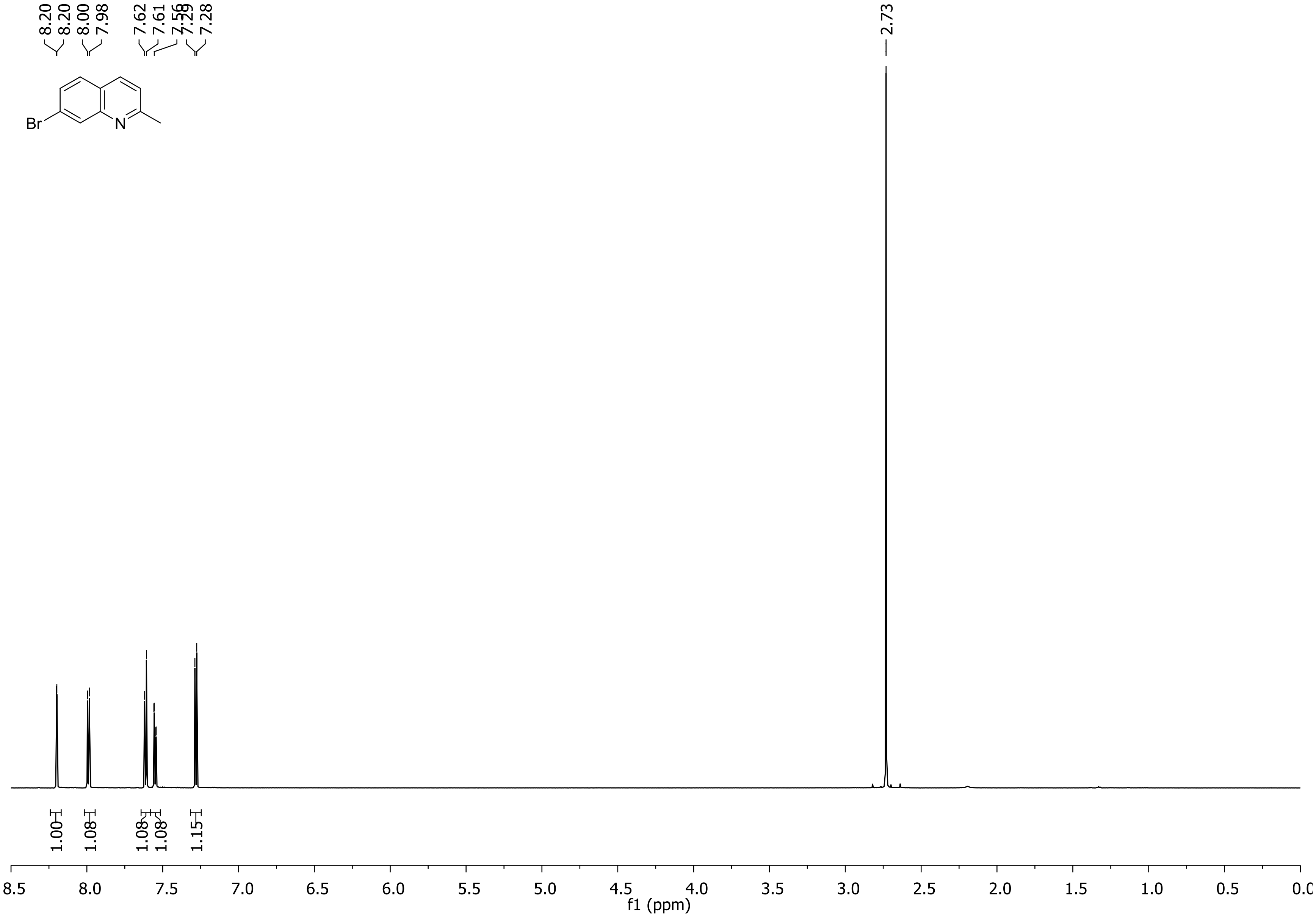
19 20 21 22

			^{1}H NMR δ (ppm)[a]			^{13}C NMR δ (ppm)[a]			conv.	product ratio (%)[c]			m:p ratio	yield
entry	**19**	R	o	m	p	o	m	p	(%)[b]	*meta*	bis	*para*	(**20**+**21**):**22**	(%)[d]
1	**a**	Bmes$_2$[e]	7.51	7.34	**7.47**	134.4	128.5	**130.3**	69[g]	26	6	68	32:68	nd
2	**b**	Bneop[f]	7.81	7.36	**7.44**	134.3	128.0	**130.8**	45[g]	33	0	67	33:67	nd
3	**c**	Bpin	7.82	7.38	**7.48**	133.0	128.2	**130.8**	71[g]	32	4	64	36:64[h]	40
4	**d**	CO_2Me	7.97	7.37	**7.47**	129.6	128.4	**133.1**	>99	22	22	56	44:56	39
5	**e**	CN	7.65	7.46	**7.60**	132.5	129.6	**133.3**	>99	30	36[i]	34	59:41	nd
6	**f**	Si(TMS)$_3$	7.44	7.24	**7.24**	134.3	127.5	**129.2**	72	48	15	37	63:37	nd
7	**g**	Cl	7.29	7.24	7.17	128.6	129.9	126.7	98	32	33	35	65:35	82
8	**h**	CH_3	7.17	**7.25**	7.25	129.1	**128.4**	125.5	30	63	6	31	69:31	nd
9	**i**	CF_3	7.64	7.49	7.56	125.3	129.0	132.0	>99	29	40	31	69:31	nd
10	**j**	TMS	7.68	**7.44**	7.44	133.3	127.7	128.6	93	56	16	28	72:28	52
11	**k**	^{t}Bu	7.28	**7.18**	7.05	125.2	**128.1**	125.3	82	68	8	24	76:24	64
12	**l**	NMe_2	6.60	**7.08**	6.59	113.2	**128.9**	116.9	69	75	4	21	79:21	53
13	**m**	OMe	6.78	**7.17**	6.82	114.6	**129.3**	120.5	93	68	16	16	84:16	76

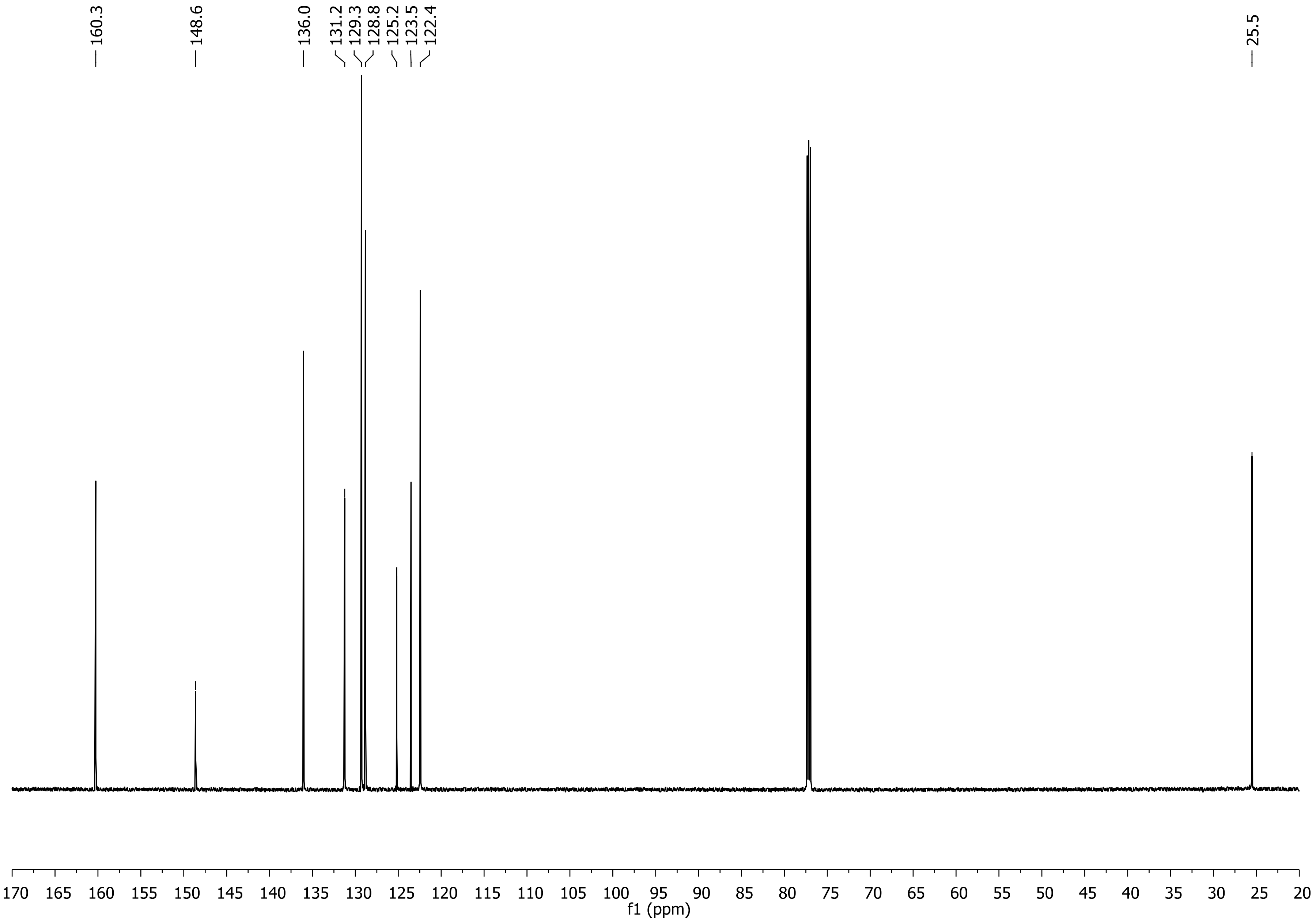
[a] Experimentally determined ^{1}H NMR chemical shifts. ^{13}C NMR chemical shifts predicted using NMR Predict from MODGRAPH (http://www.modgraph.co.uk/product_nmr.htm). Bold values show agreement with experimental results. [b] Unless otherwise indicated, conversions were determined by GCMS analysis of crude reaction mixture using dodecane as an internal standard; [c] Product ratios were determined by ^{1}H NMR spectroscopy and GC-MS analysis; [d] Yield of purified, isolated product mixture (nd = not determined); [e] mes = mesityl = 2,4,6-$Me_3C_6H_2$; [f] neop = neopentaneglycolato = $OCH_2CMe_2CH_2O$; [g] Conversions determined using ^{1}H NMR spectroscopy; [h] The *para*-directing influence of a Bpin substituent has been noted before - see ref 62; [i] a 21 : 7 : 8 mixture of different bisborylated products was isolated reflecting the lower steric demand of the CN group (major bisborylated product = 3,5-bis(Bpin)benzonitrile).

7.0 NMR Spectra

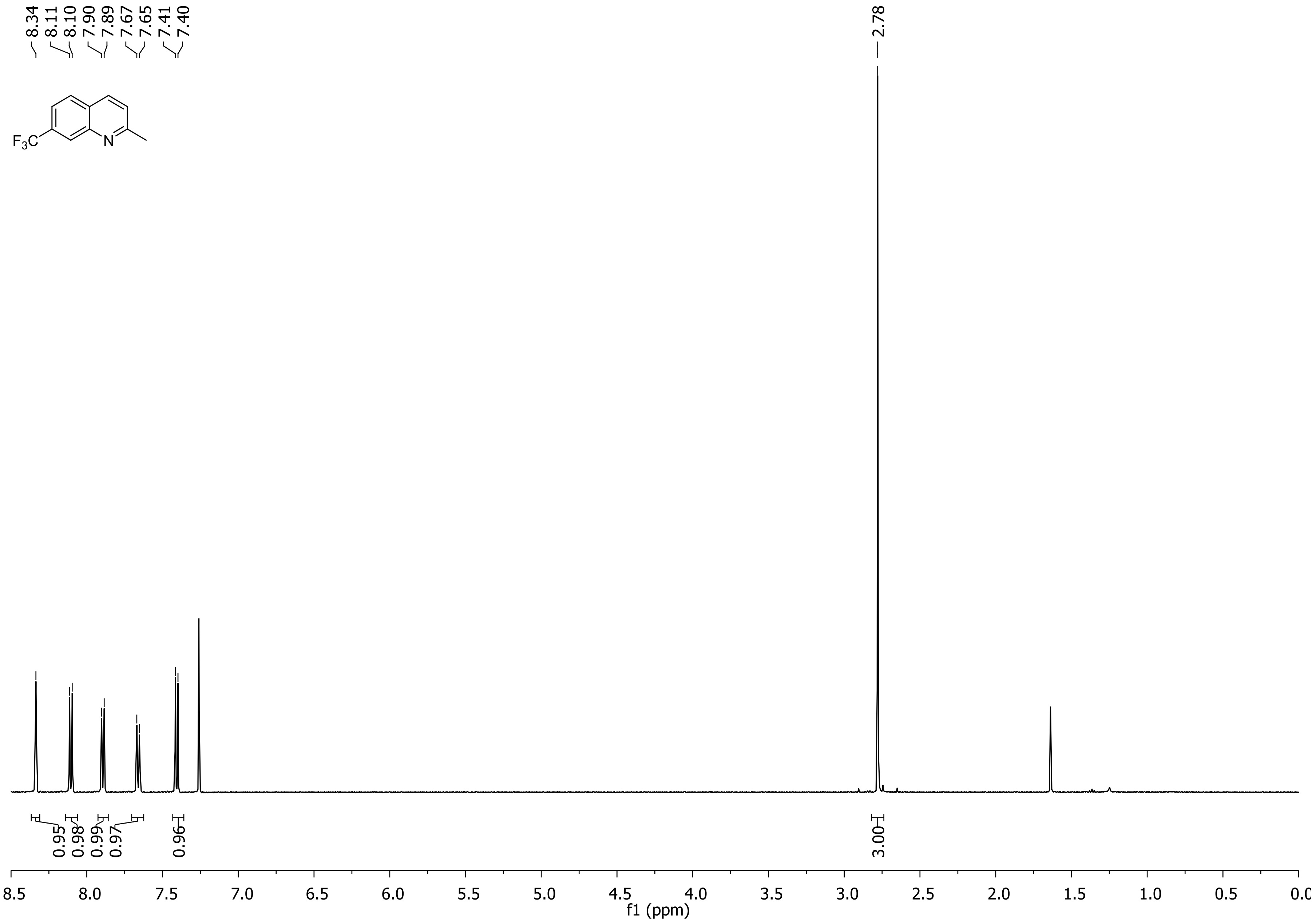
^{1}H NMR (700 MHz, $CDCl_3$), 2a



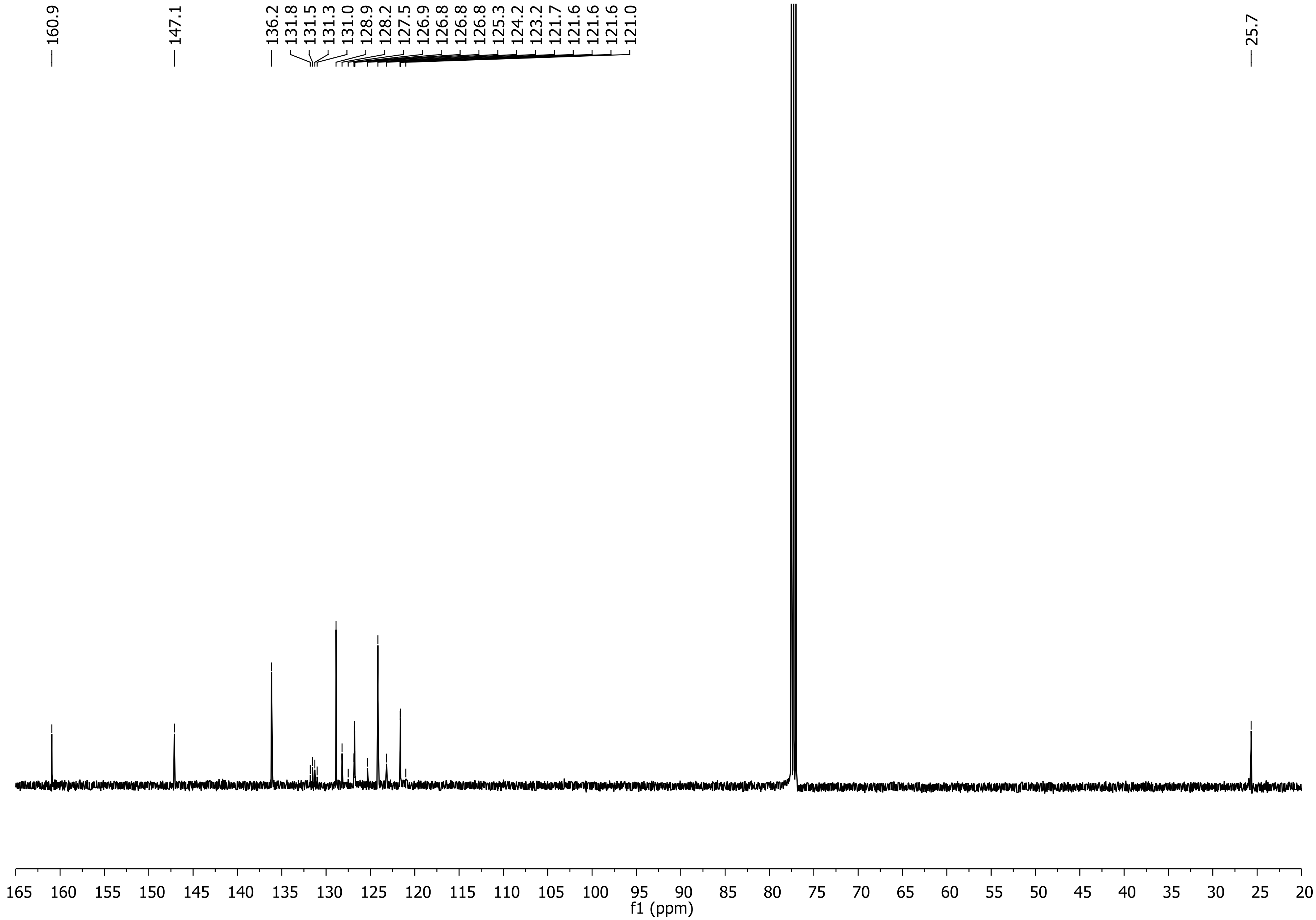
^{13}C NMR (176 MHz, $CDCl_3$), 2a



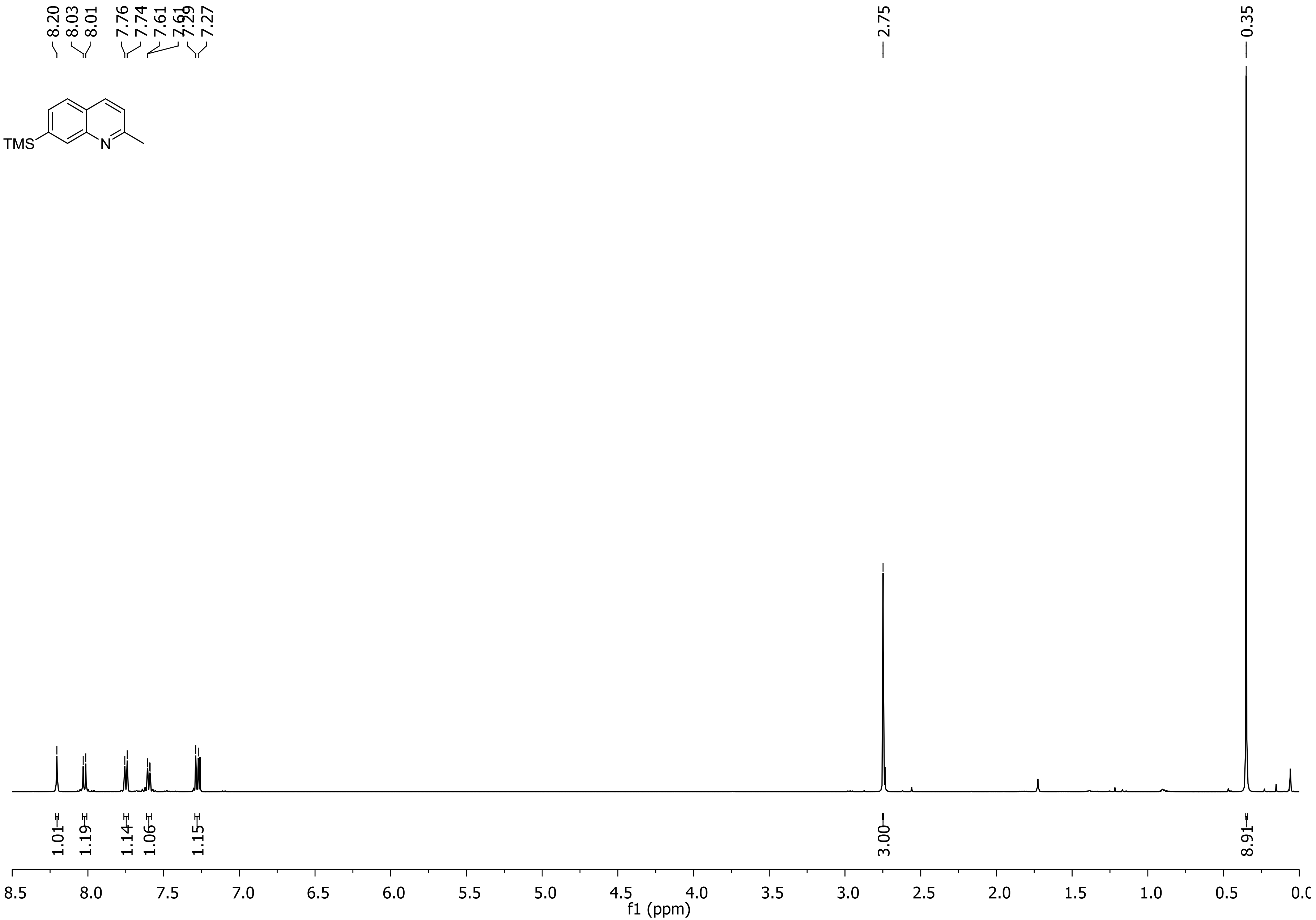
^{1}H NMR (500 MHz, $CDCl_3$), 2b



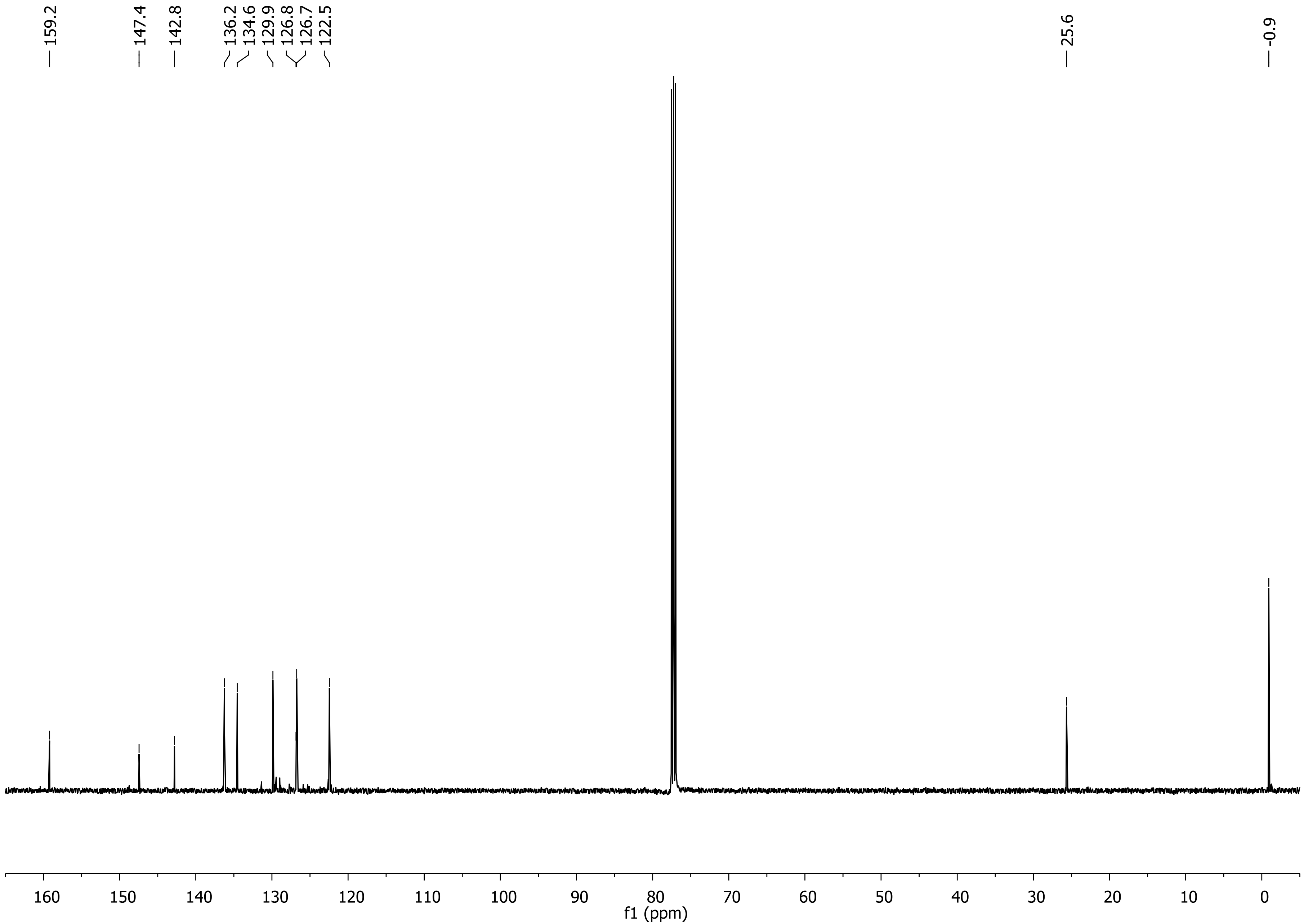
^{13}C NMR (126 MHz, $CDCl_3$), 2b



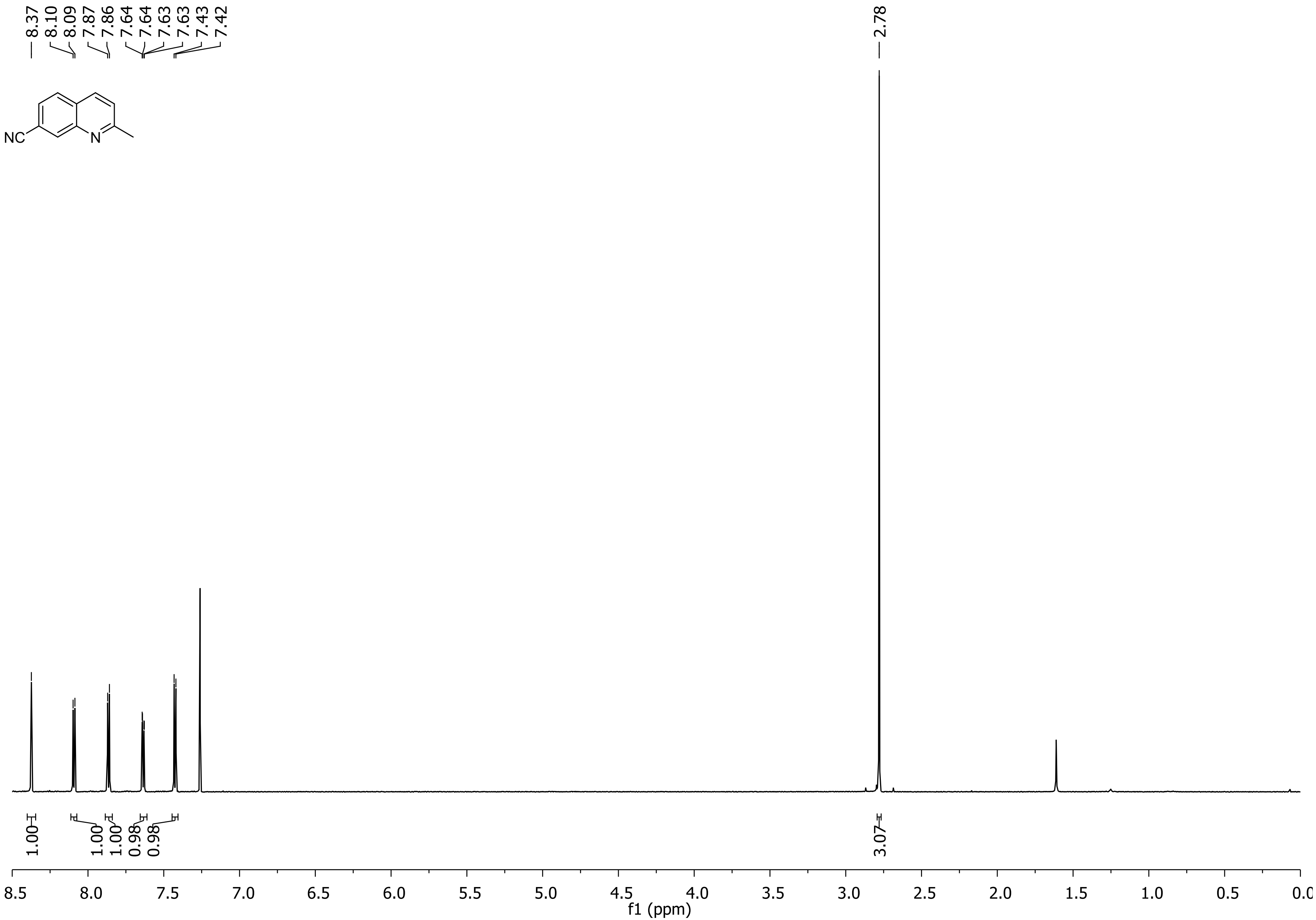
^{1}H NMR (500 MHz, $CDCl_3$), 2c



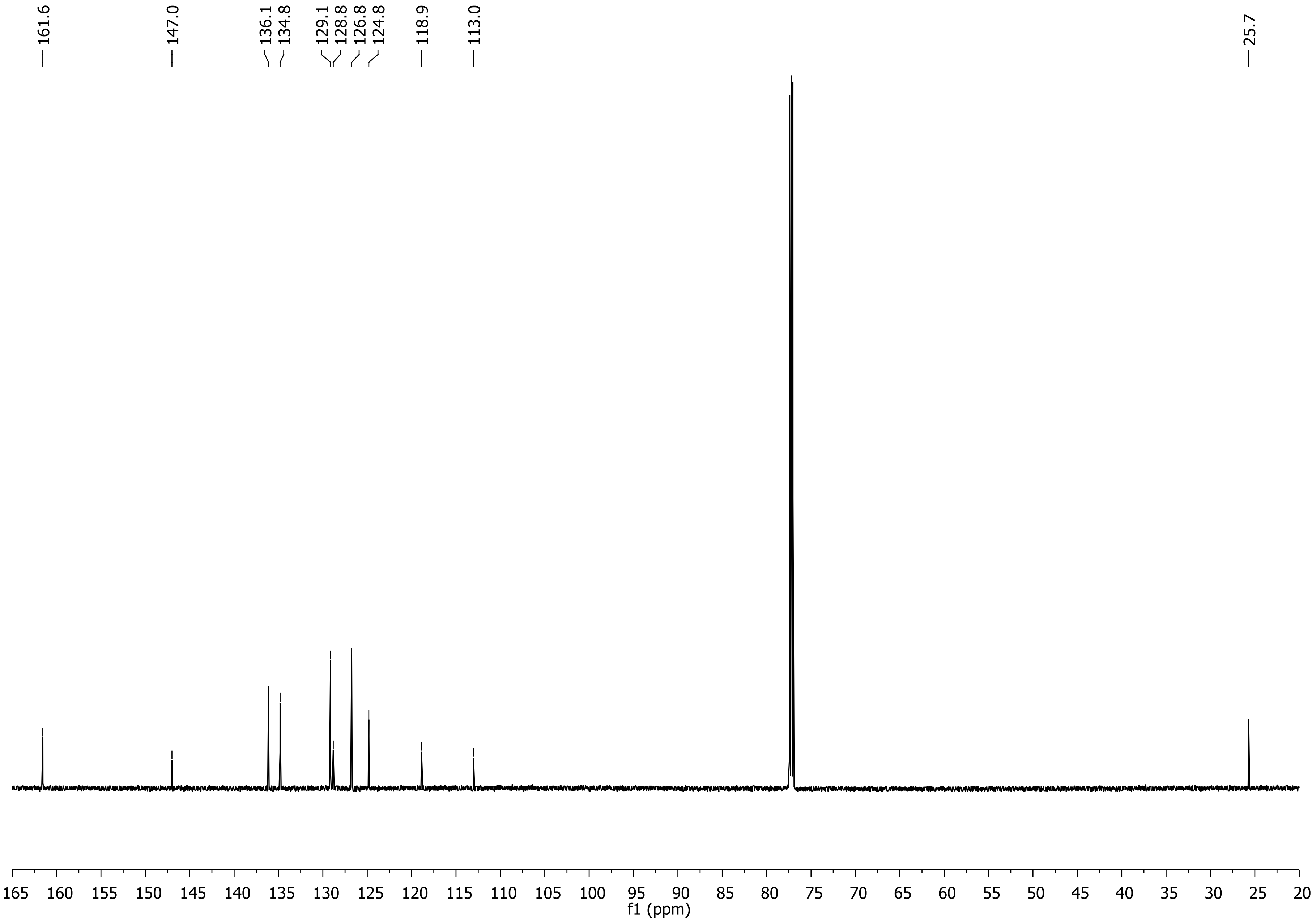
^{13}C NMR (126 MHz, $CDCl_3$), 2c



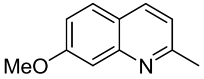
^{1}H NMR (700 MHz, $CDCl_3$), 2d

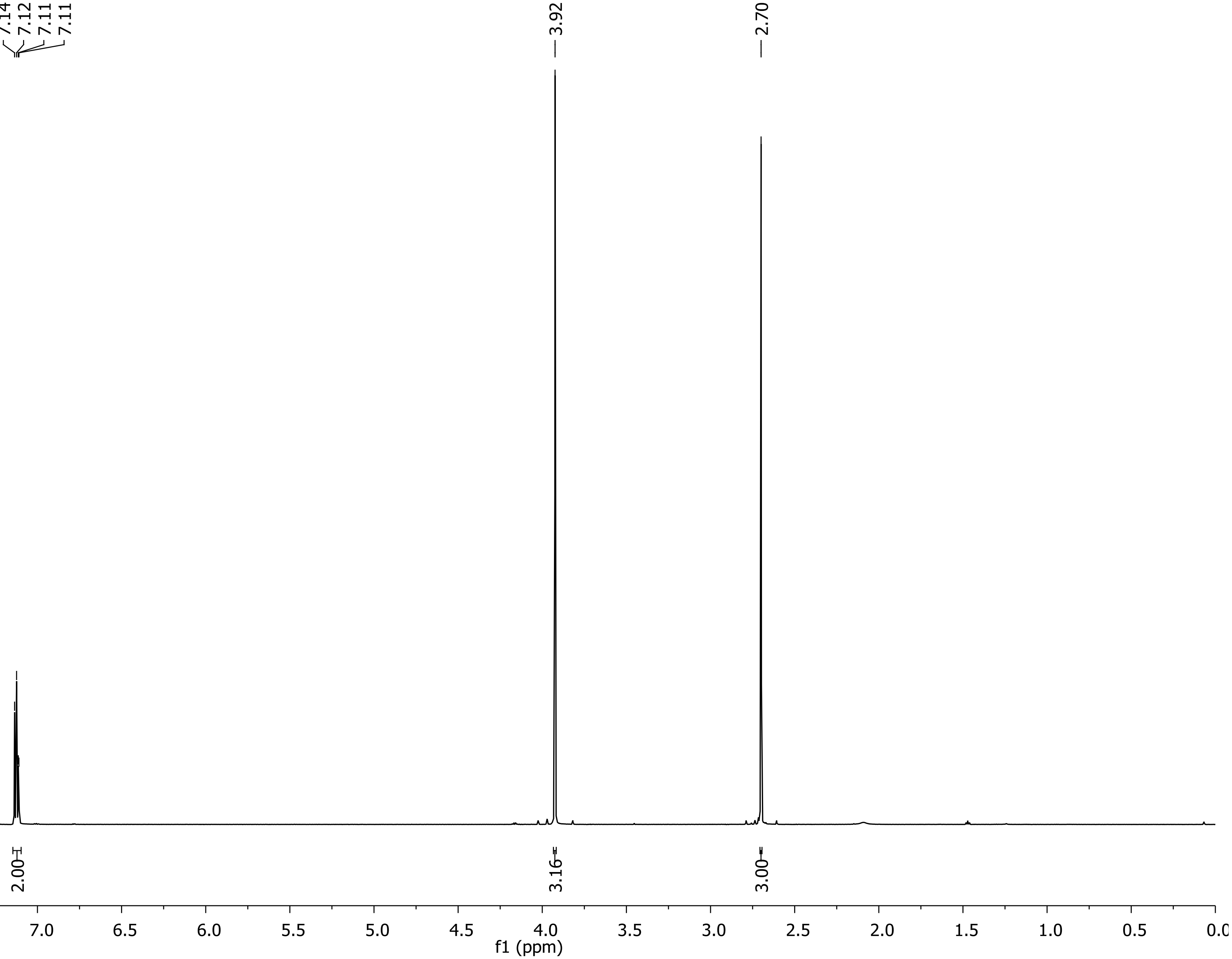


^{13}C NMR (176 MHz, $CDCl_3$), 2d

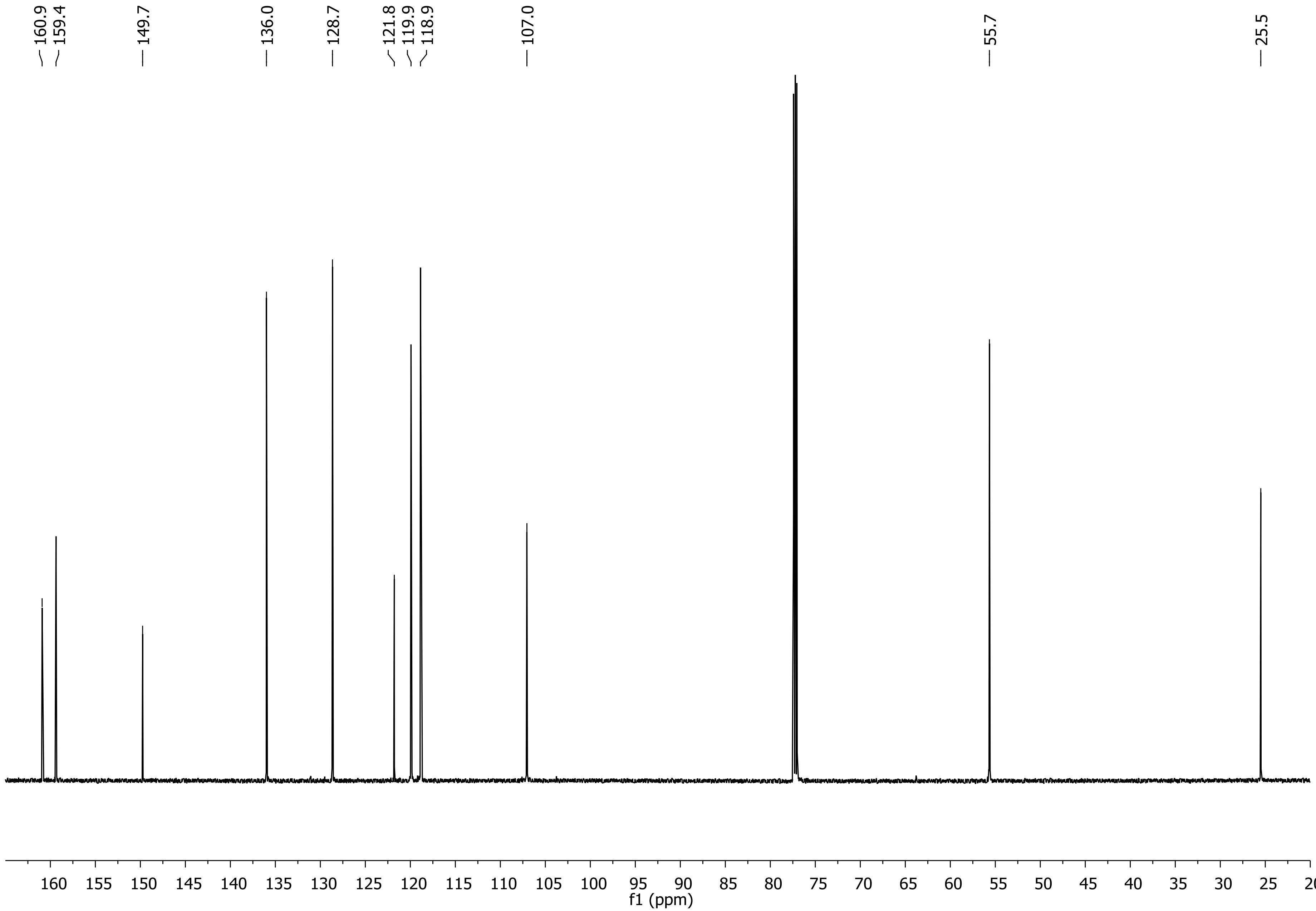


[1]H NMR (700 MHz, $CDCl_3$), 2e

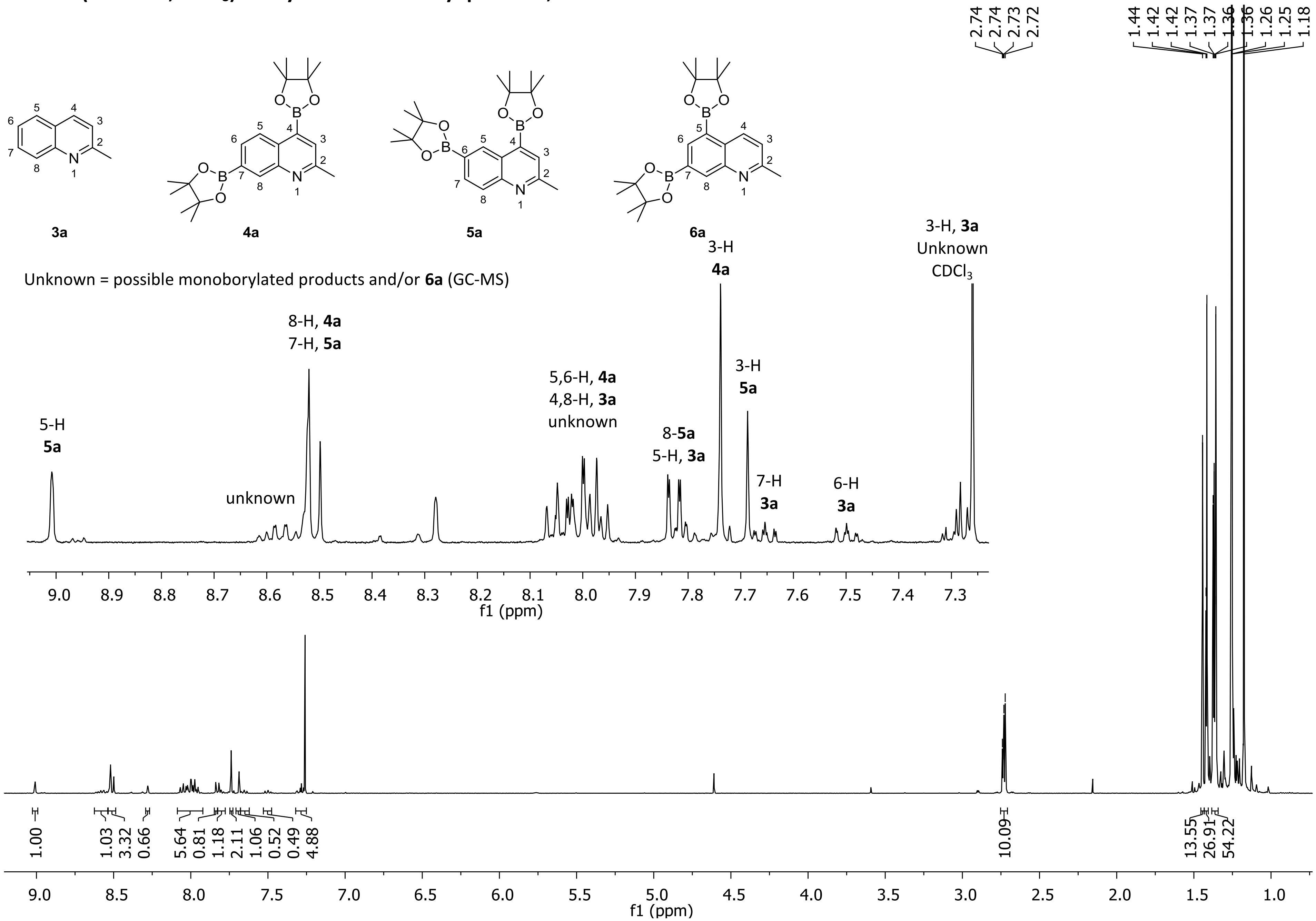




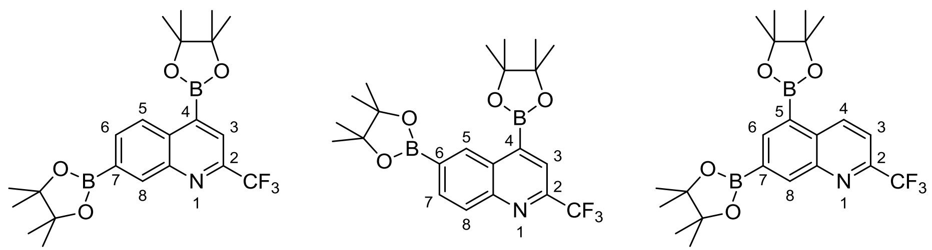
^{13}C NMR (176 MHz, $CDCl_3$), 2e



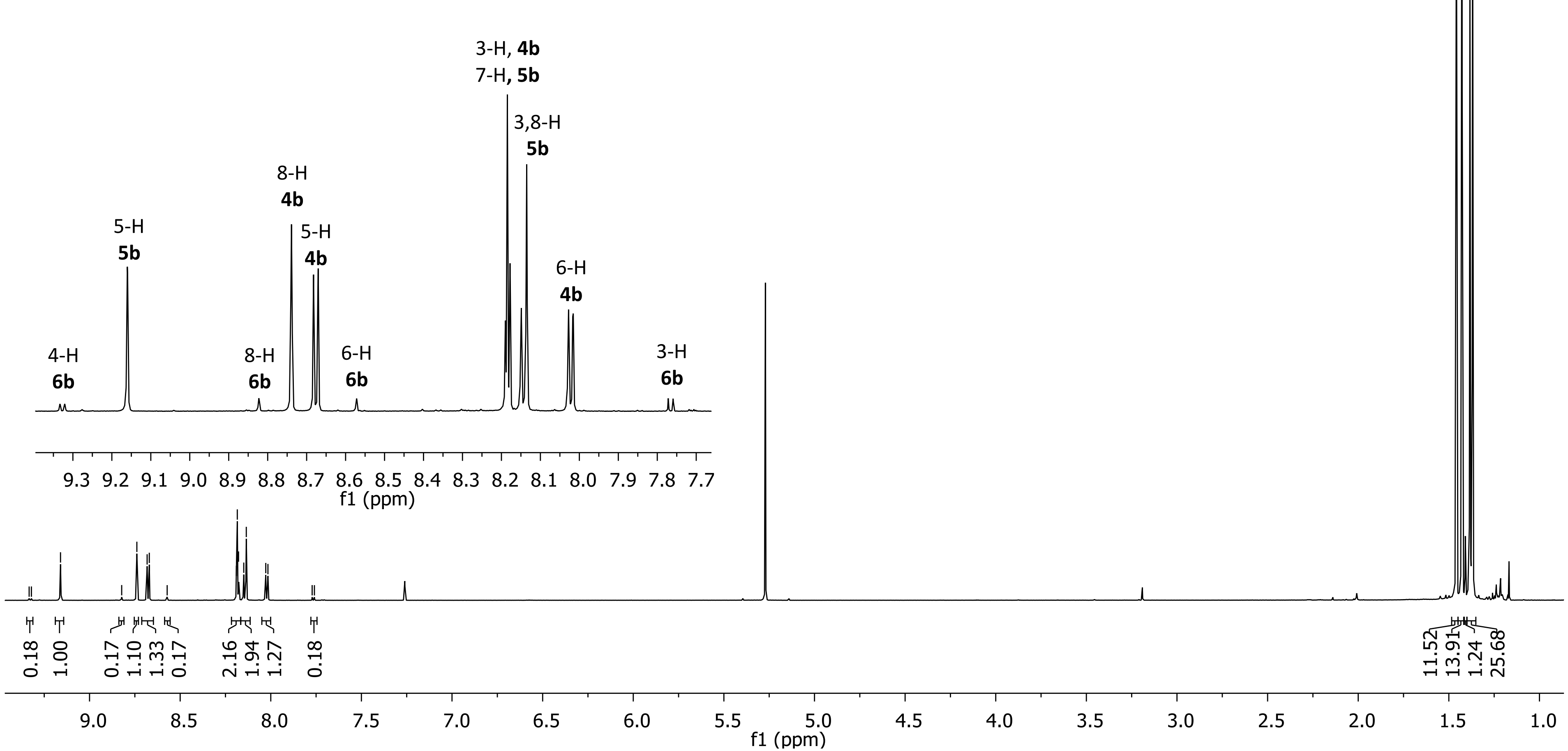
^{1}H NMR (400 MHz, $CDCl_3$) - Borylation of 2-methylquinoline, 3a



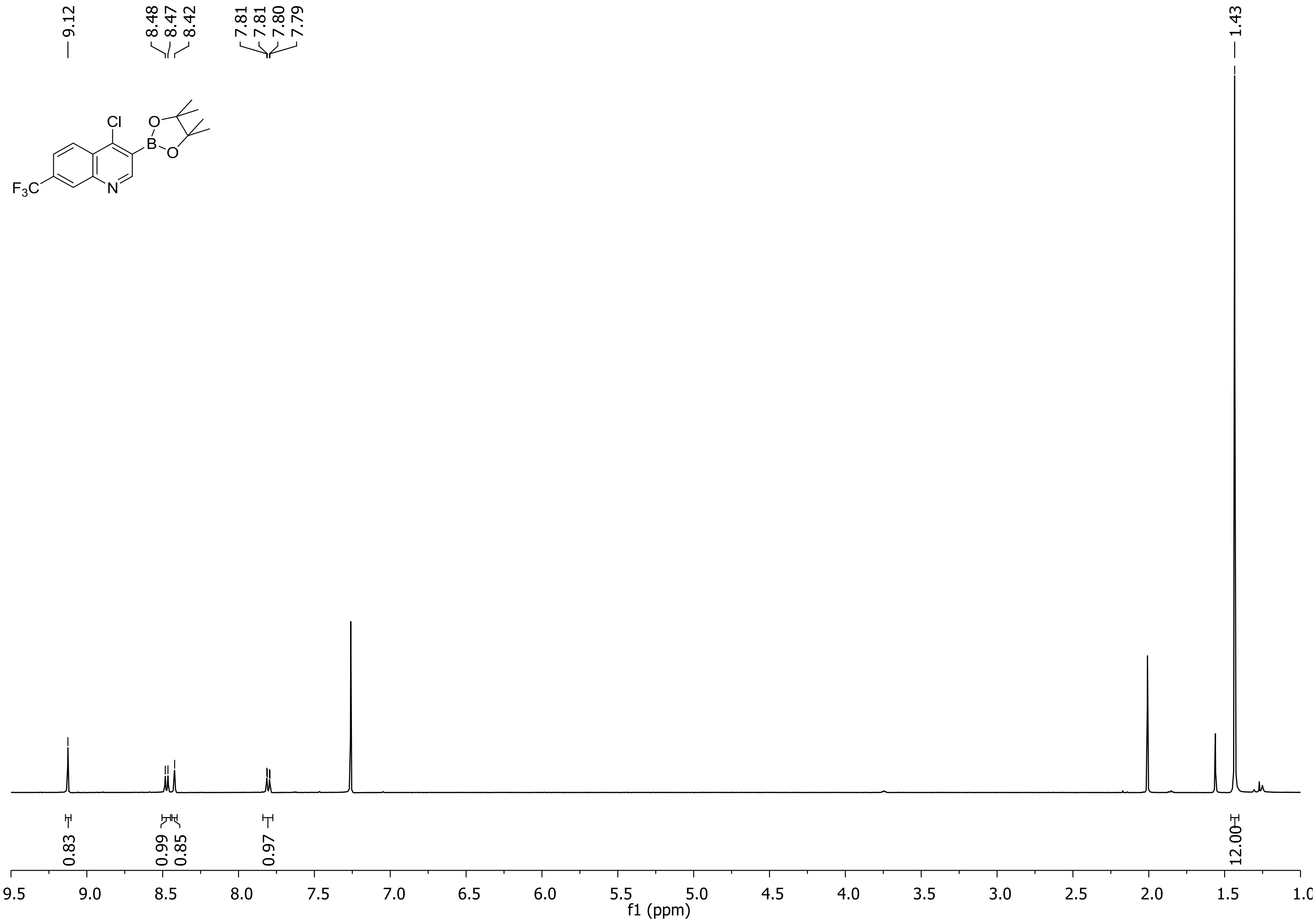
[1]H NMR (600 MHz, $CDCl_3$) - Borylation of 2-(trifluoromethyl)quinoline, 3b



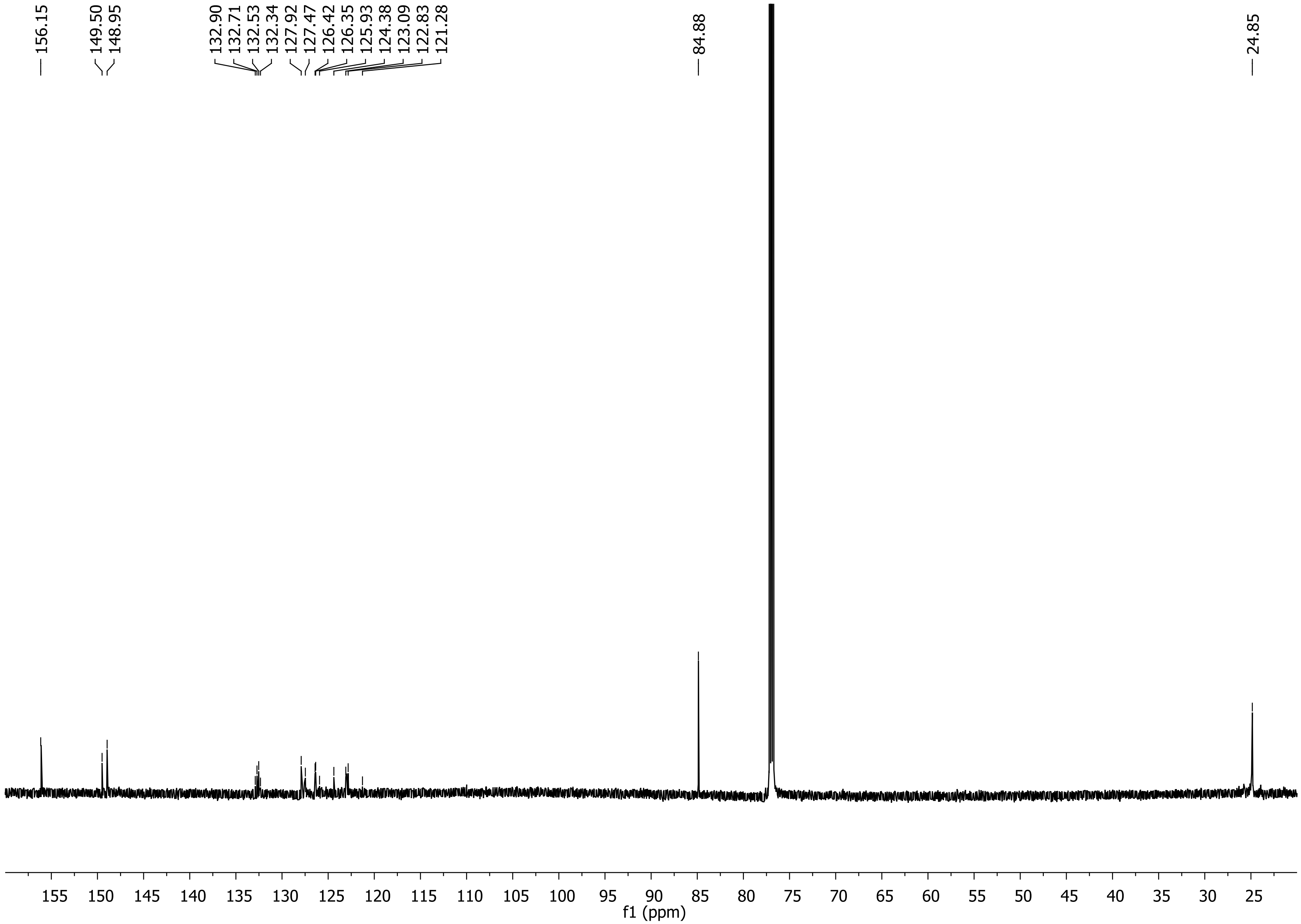
4b 5b 6b



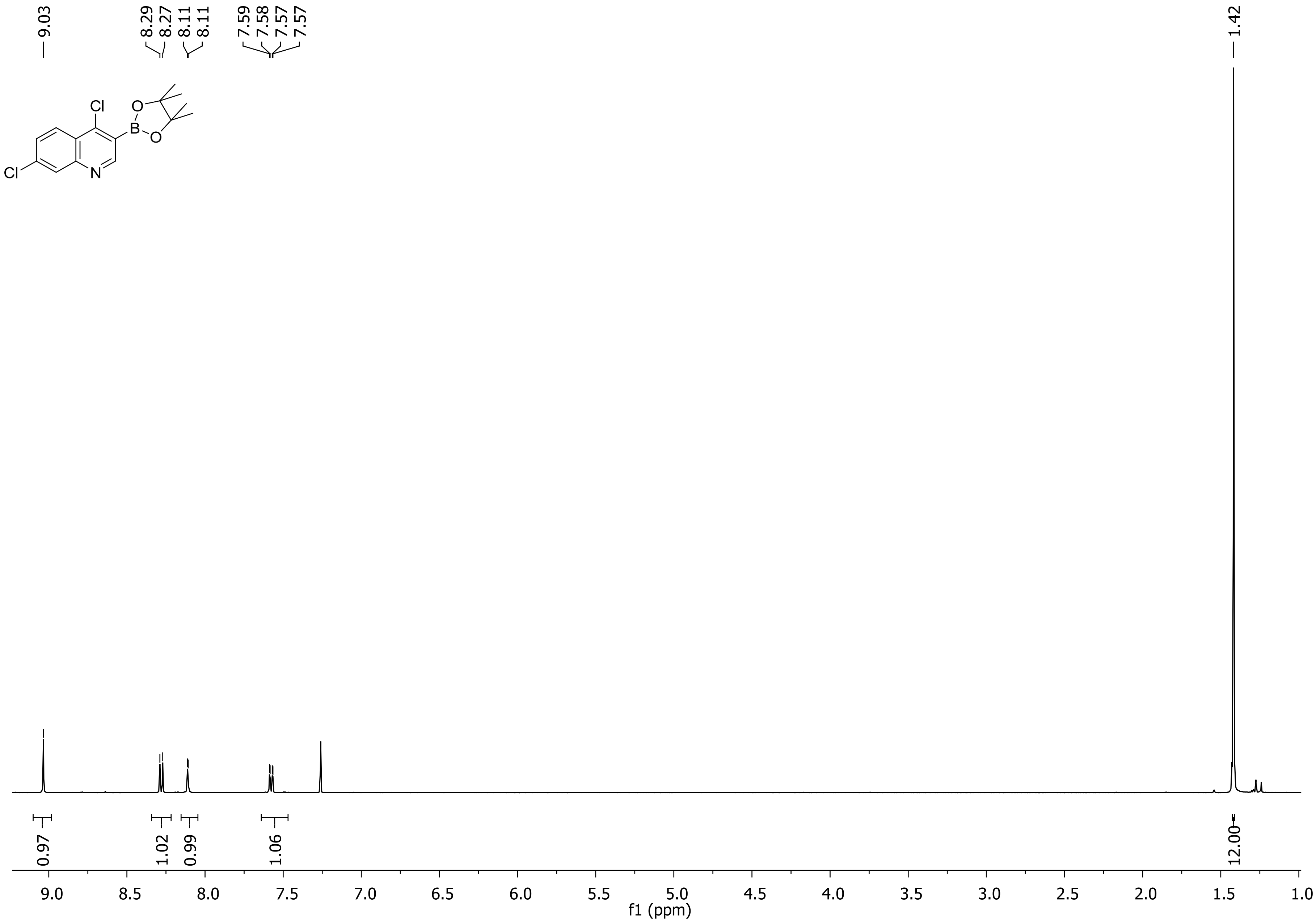
^{1}H NMR (500 MHz, $CDCl_3$), 9a



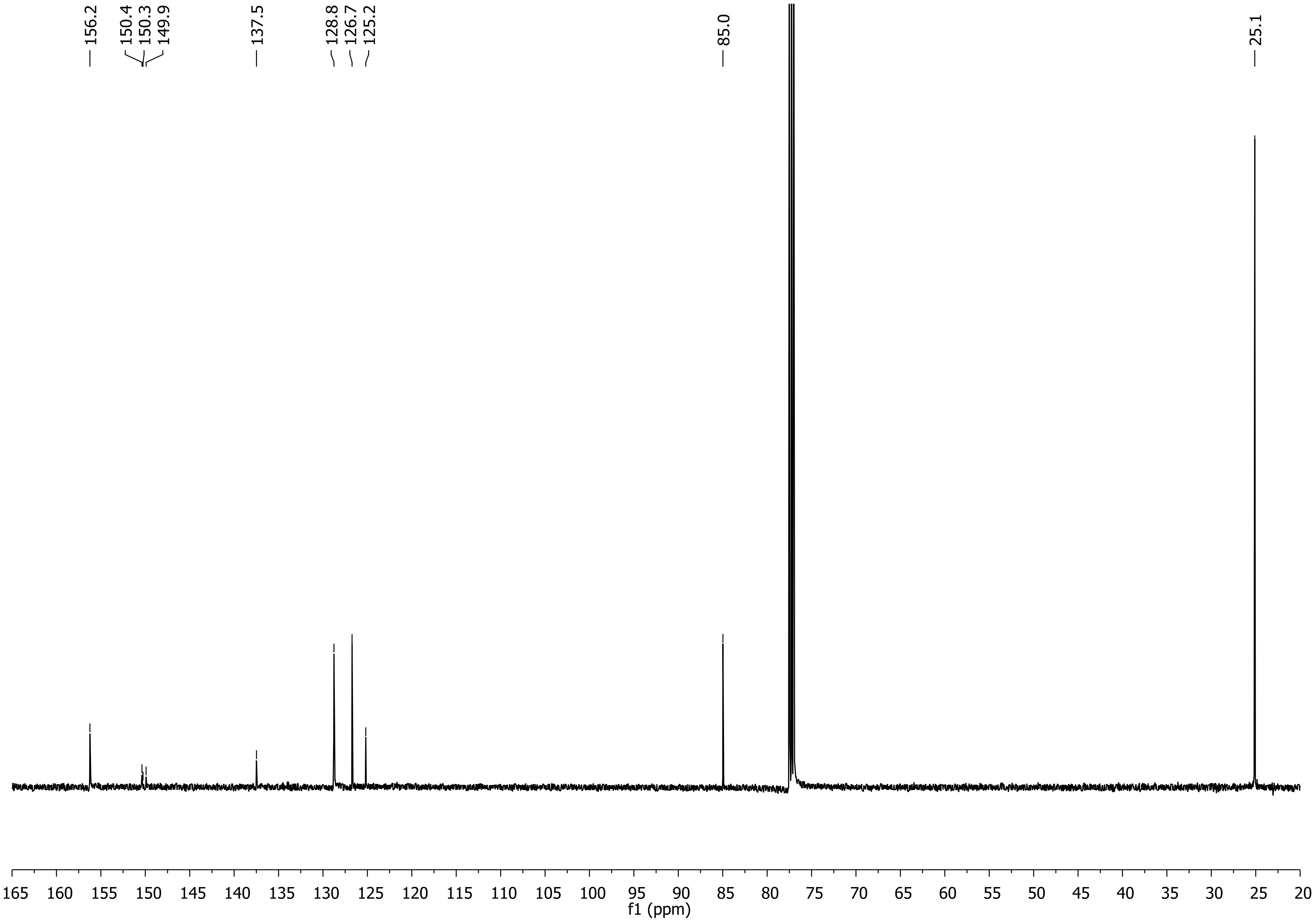
^{13}C NMR (176 MHz, $CDCl_3$), 9a



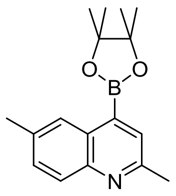
^{1}H NMR (500 MHz, $CDCl_3$), 9c

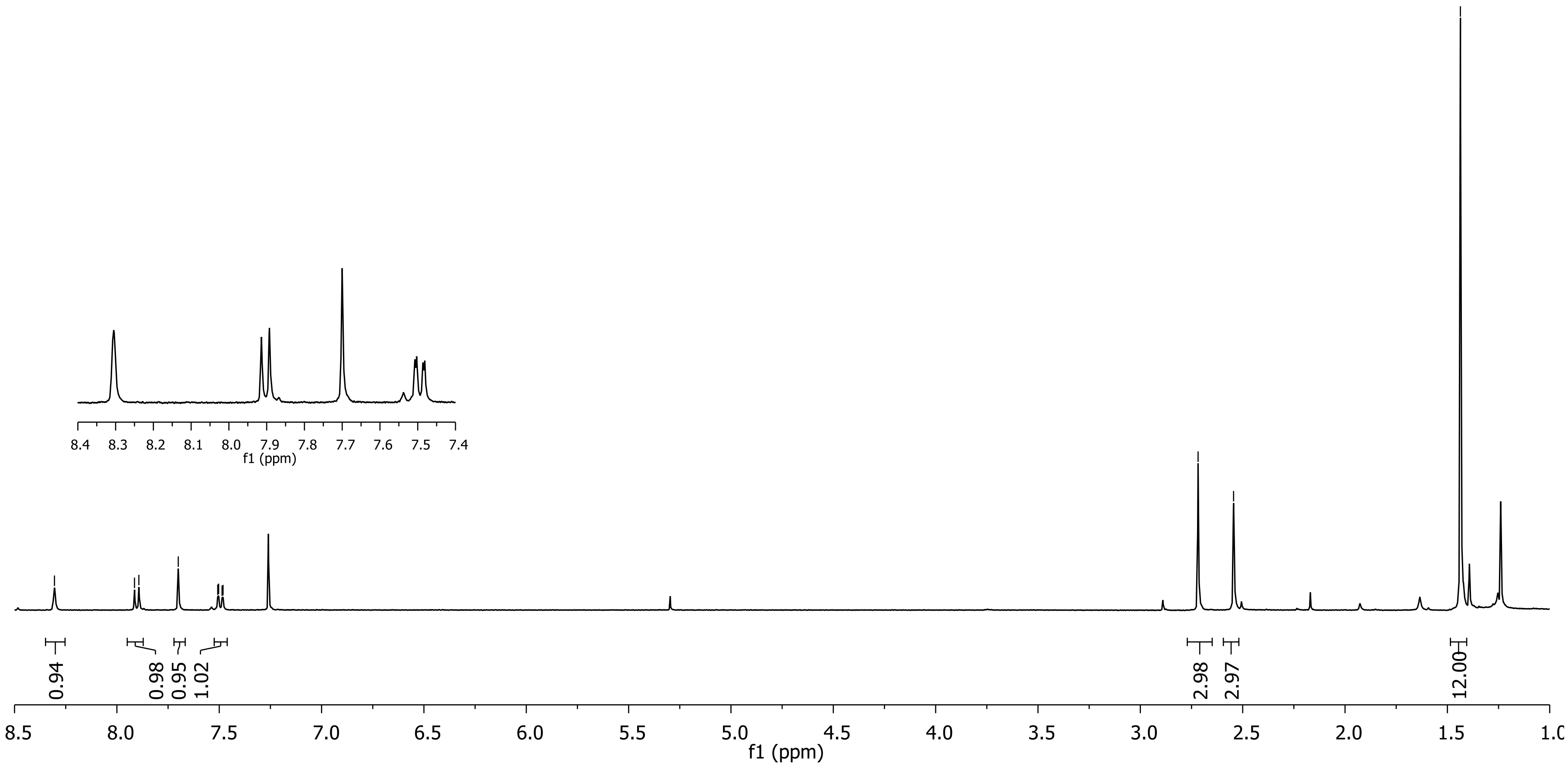


^{13}C NMR (126 MHz, CDCl$_3$), 9c

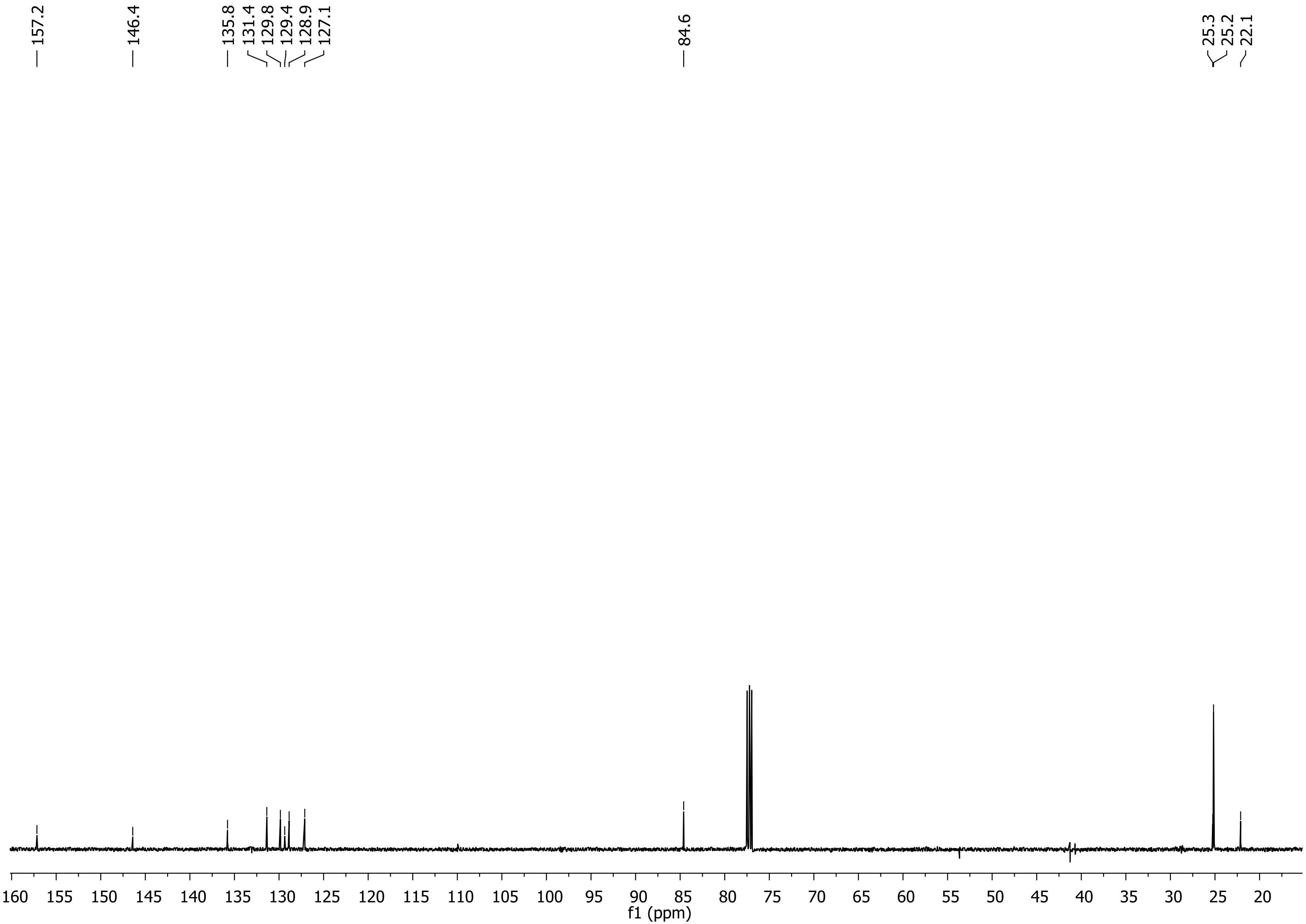


^{1}H NMR (500 MHz, $CDCl_3$), 11a

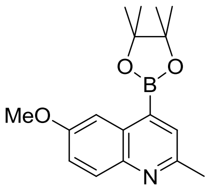


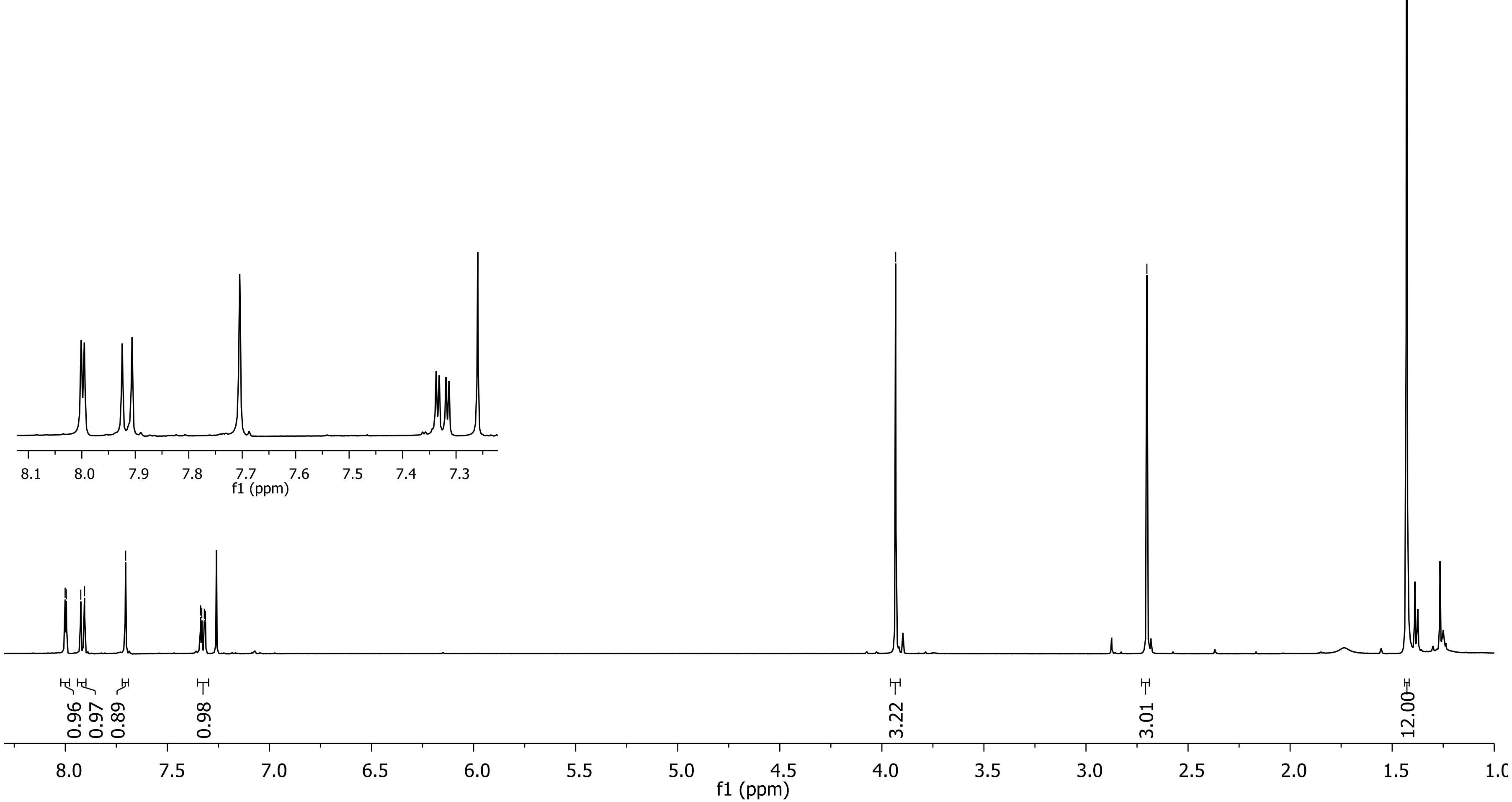


^{13}C NMR (126 MHz, $CDCl_3$), 11a

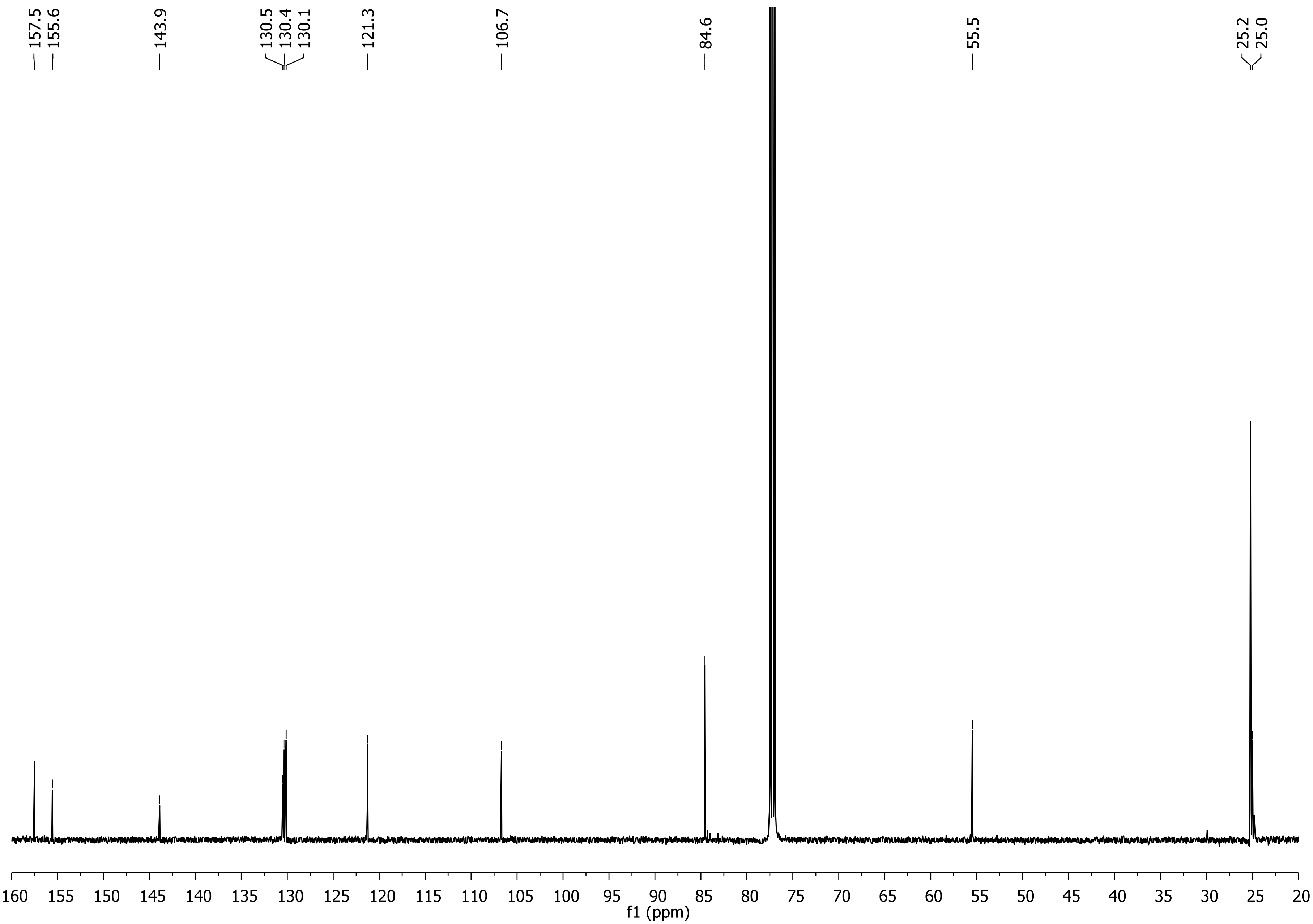


^{1}H NMR (500 MHz, $CDCl_3$), 11b

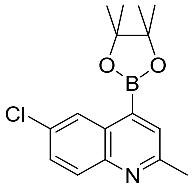


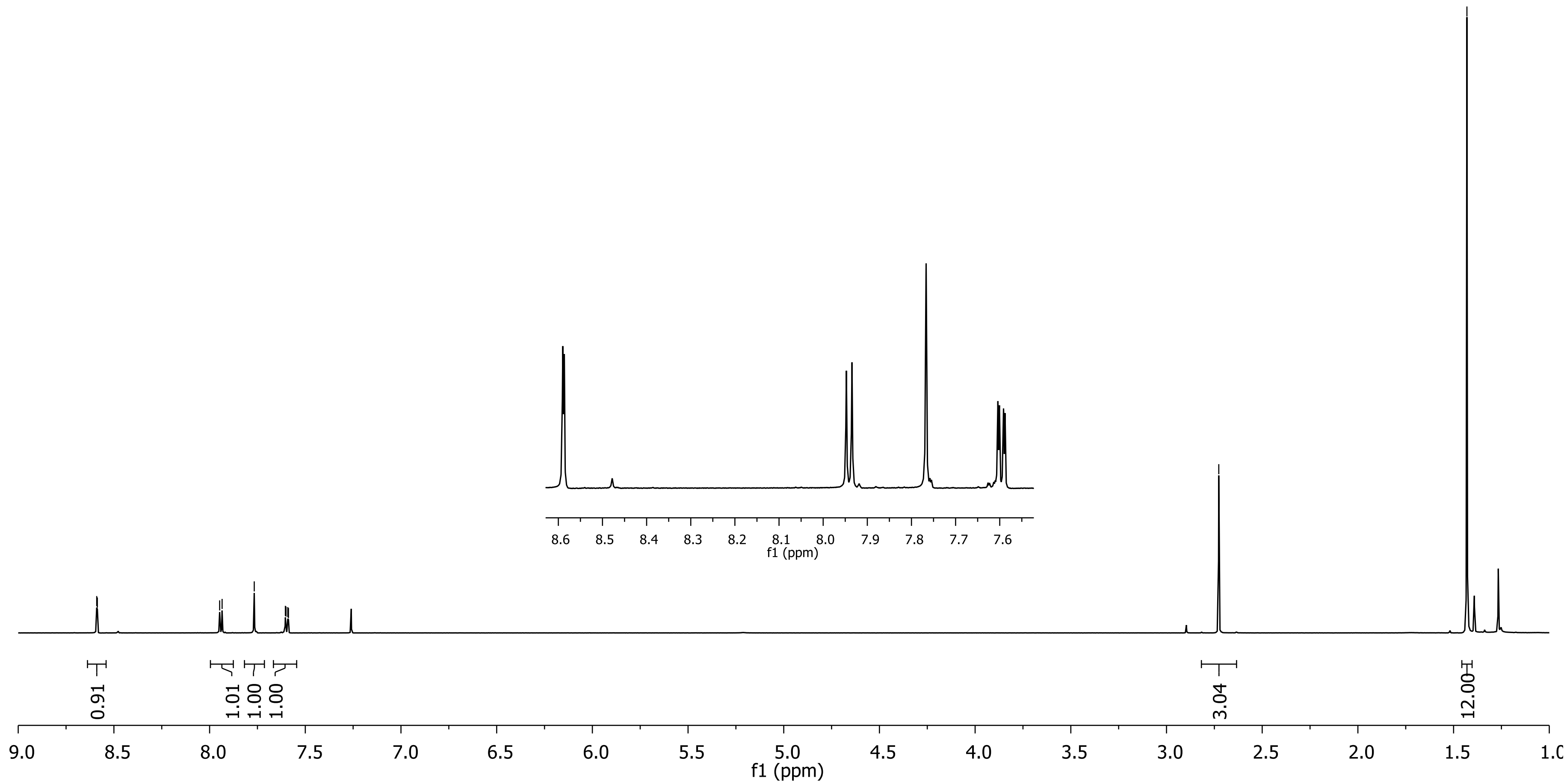


^{13}C NMR (126 MHz, $CDCl_3$), 11b

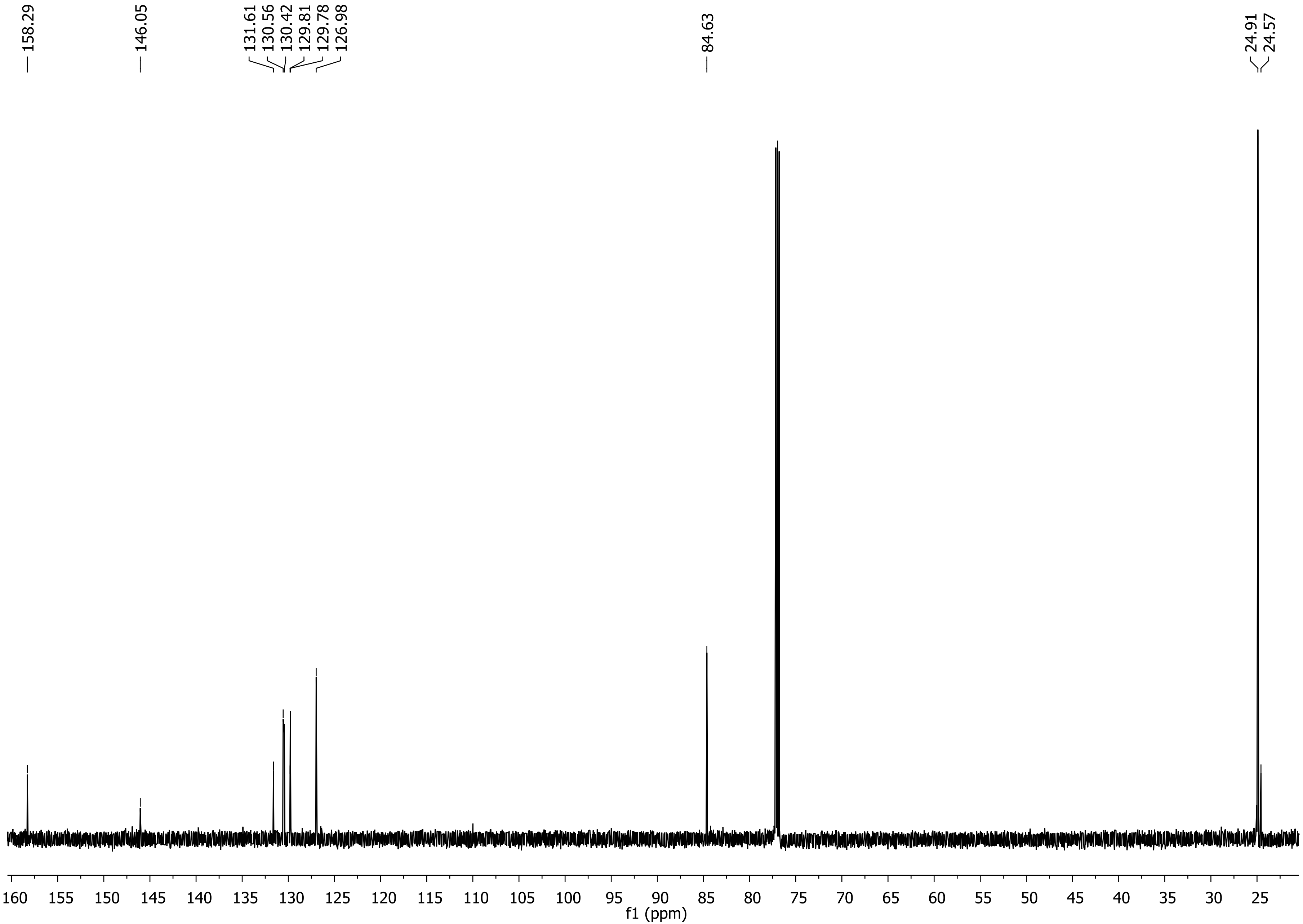


[1]H NMR (700 MHz, $CDCl_3$), 11c



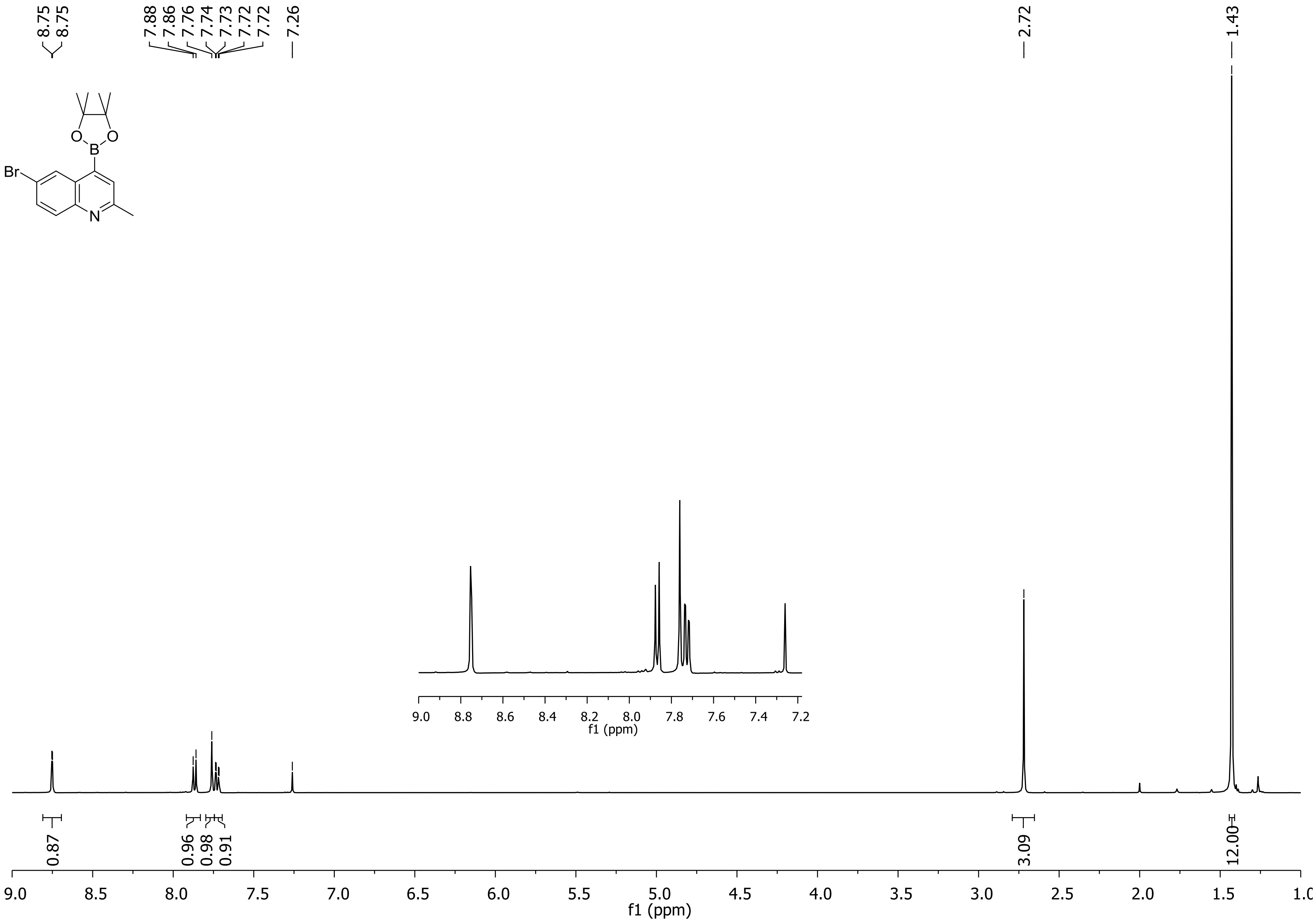


^{13}C NMR (176 MHz, $CDCl_3$), 11c



Electronic Supplementary Material (ESI) for Chemical Science

^{1}H NMR (500 MHz, $CDCl_3$), 11d



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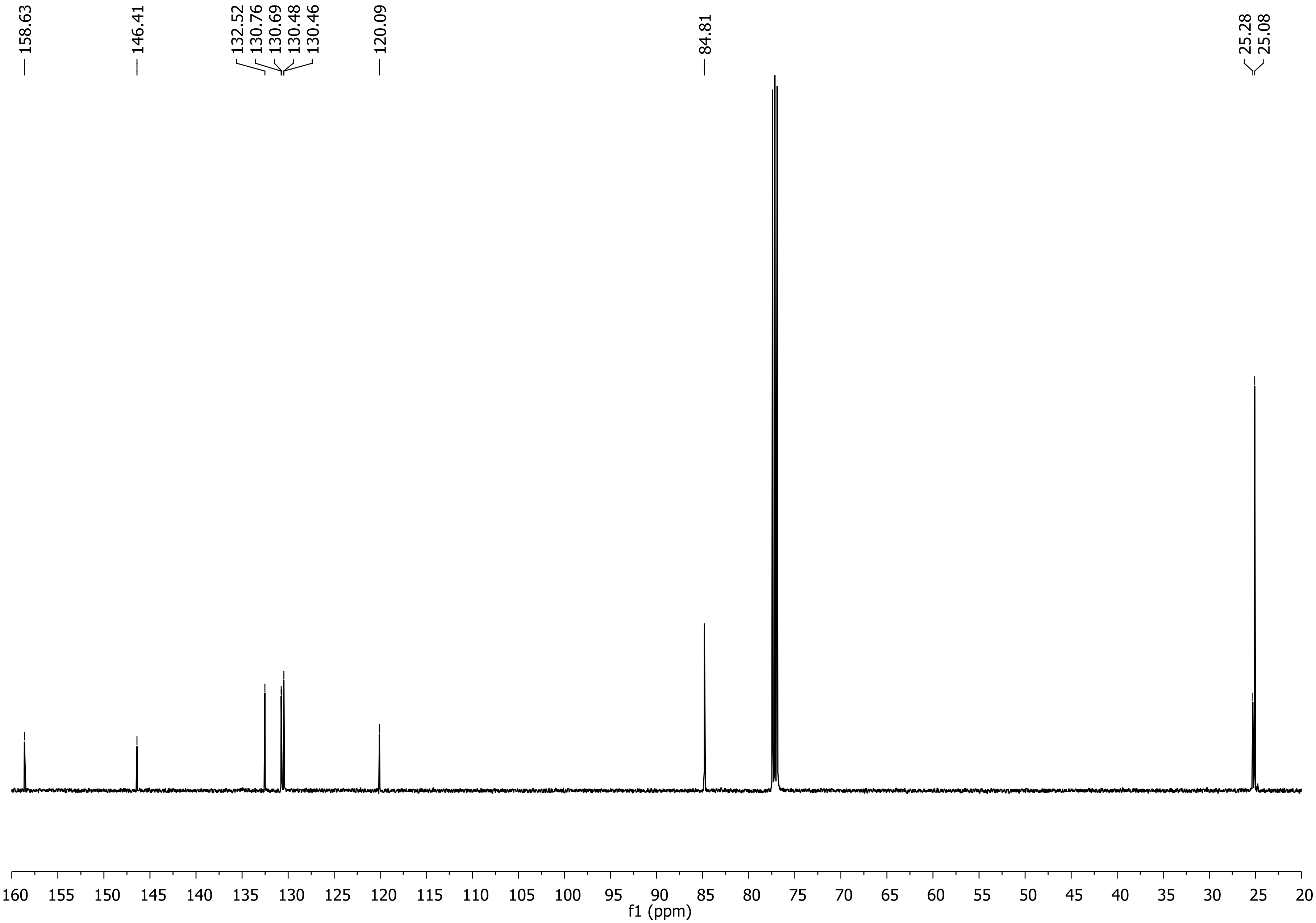
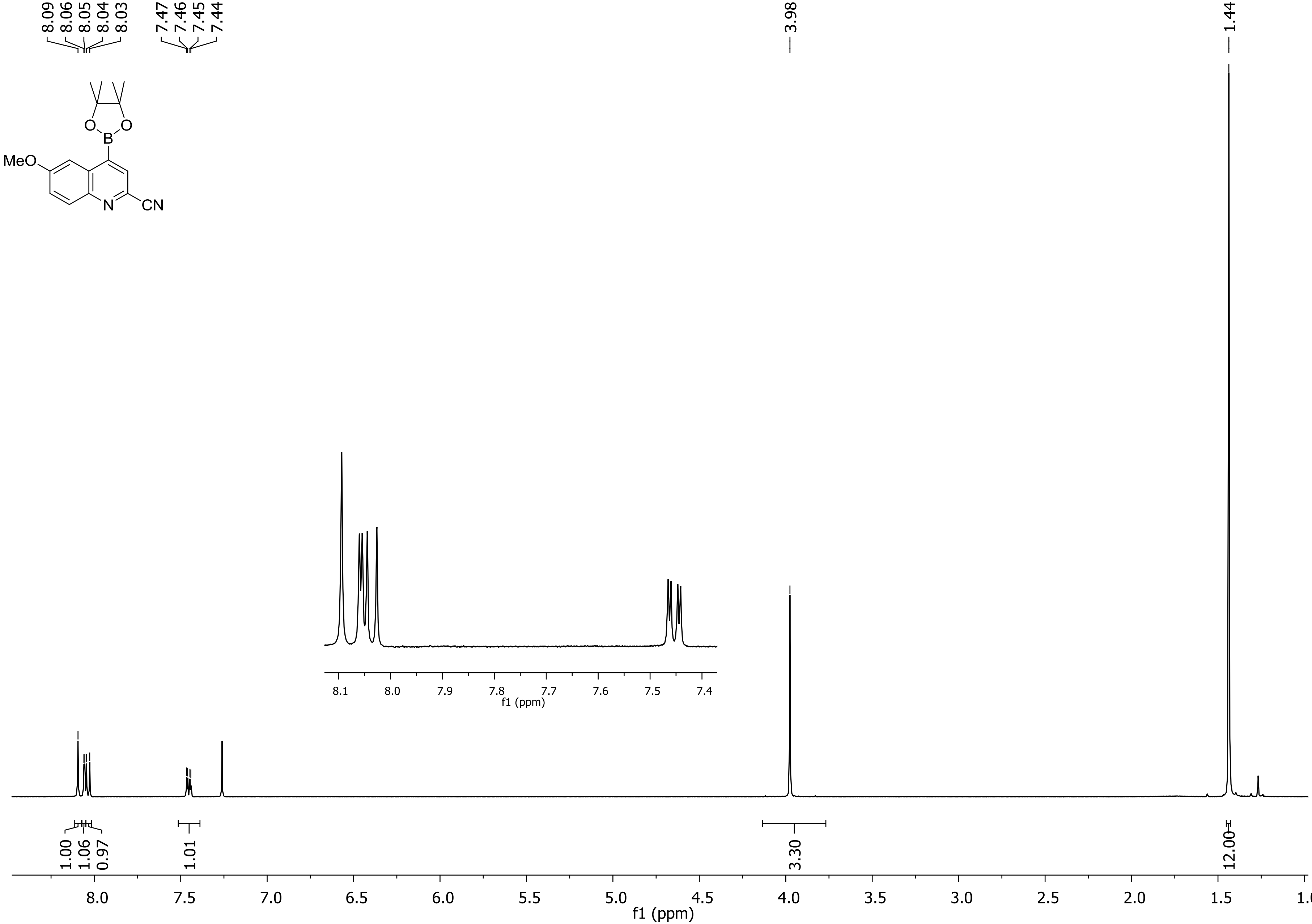
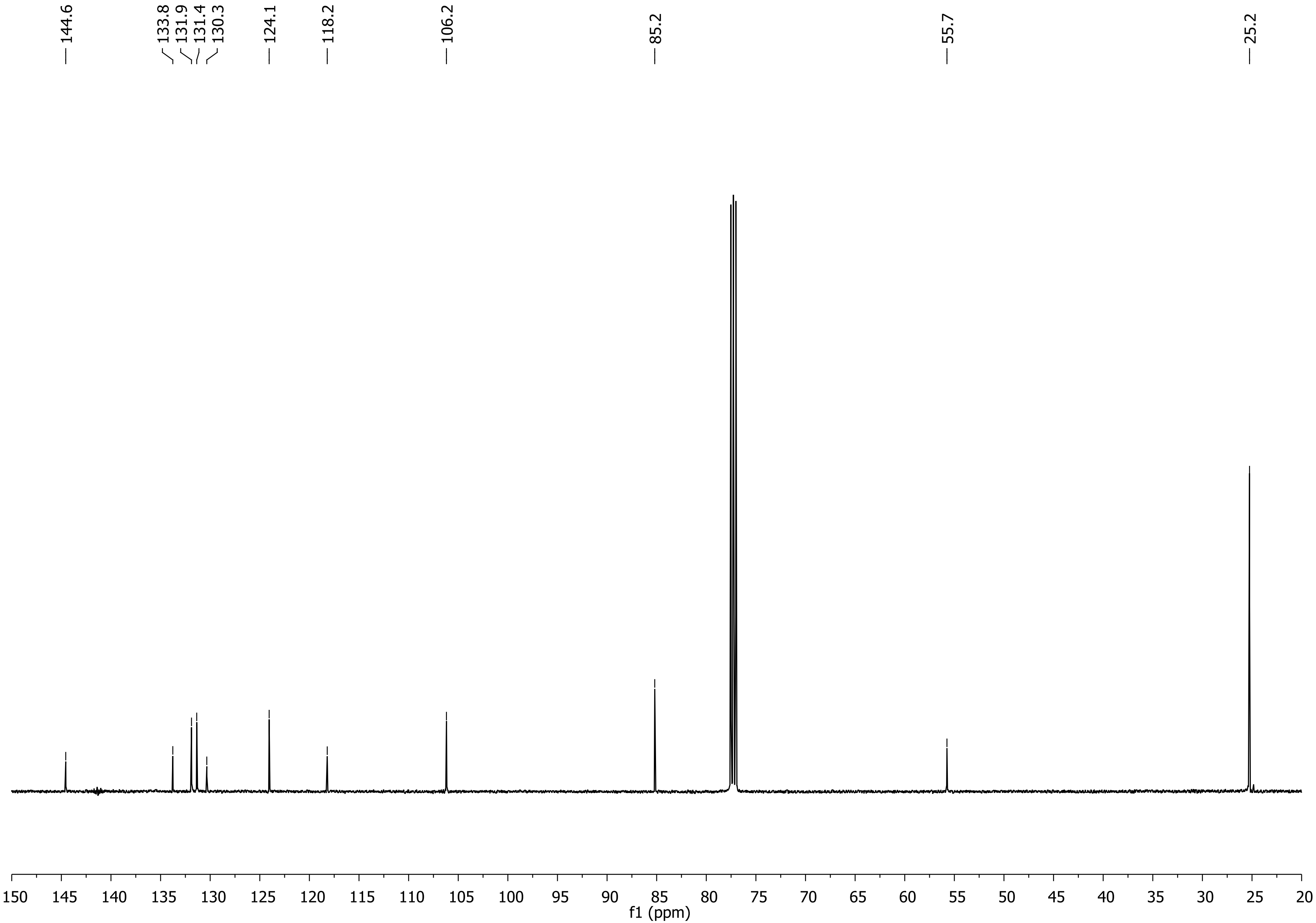


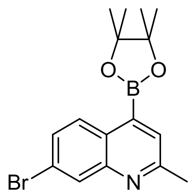
^{1}H NMR (500 MHz, $CDCl_3$), 11e

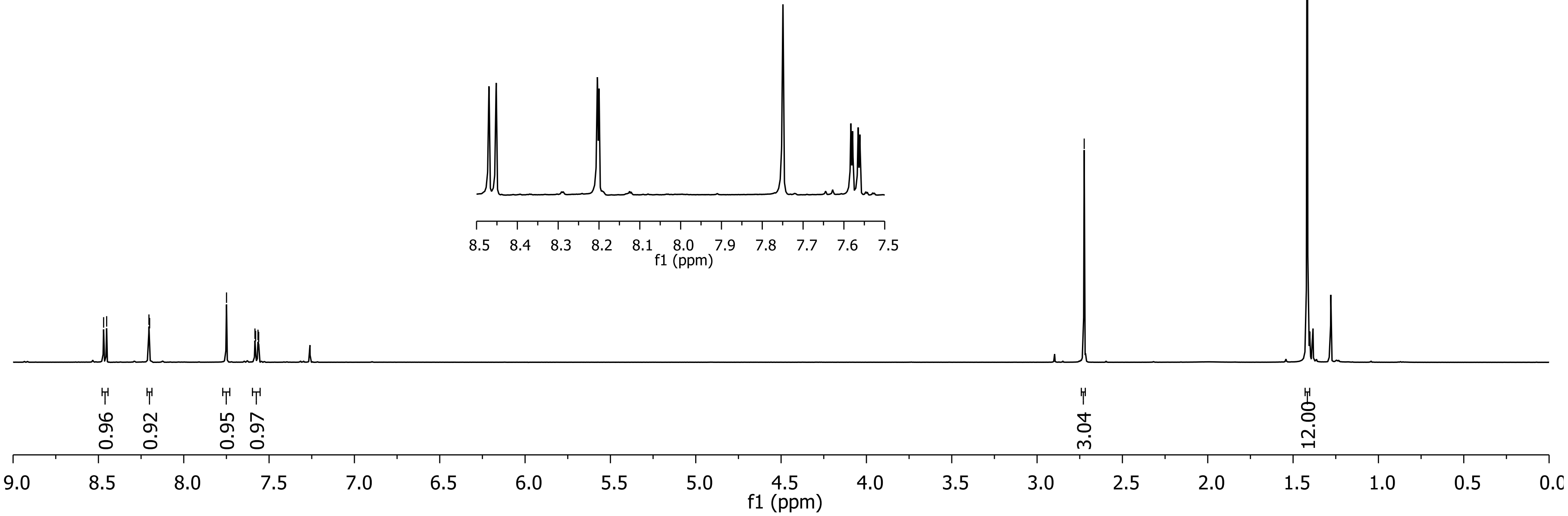


^{13}C NMR (126 MHz, $CDCl_3$), 11e

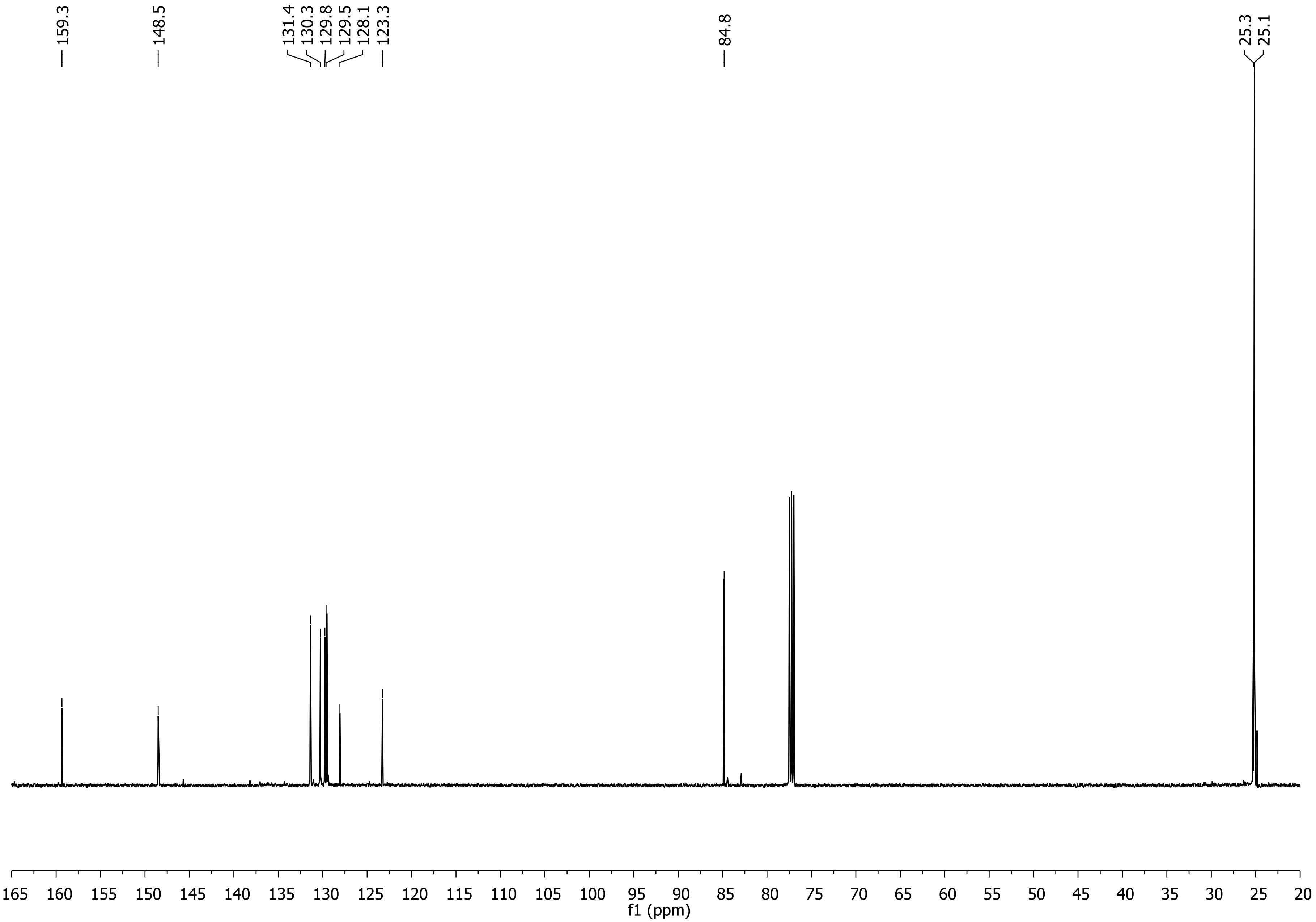


^{1}H NMR (500 MHz, $CDCl_3$), 13a

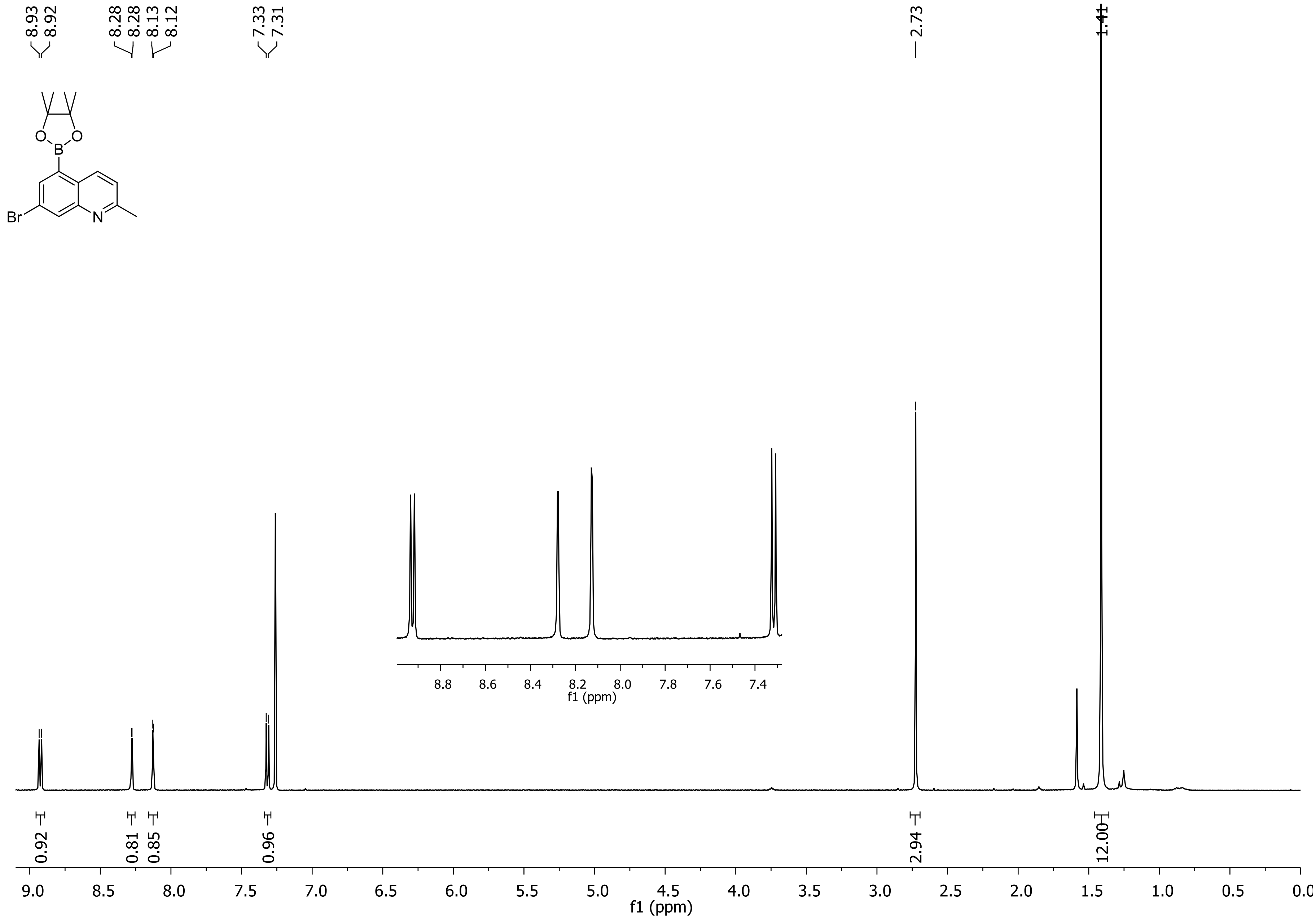




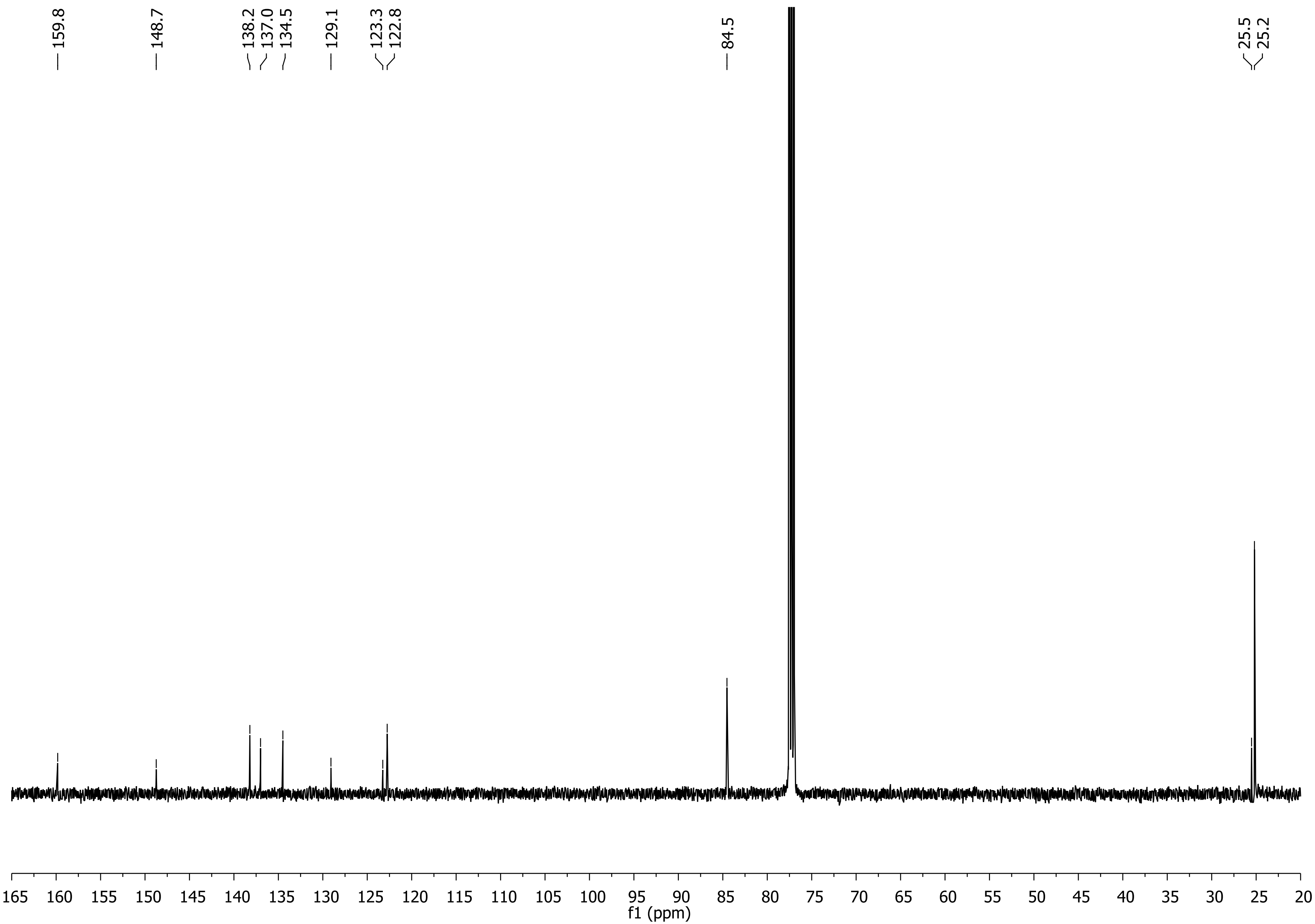
^{13}C NMR (126 MHz, $CDCl_3$), 13a



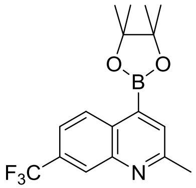
^{1}H NMR (500 MHz, $CDCl_3$), 14a

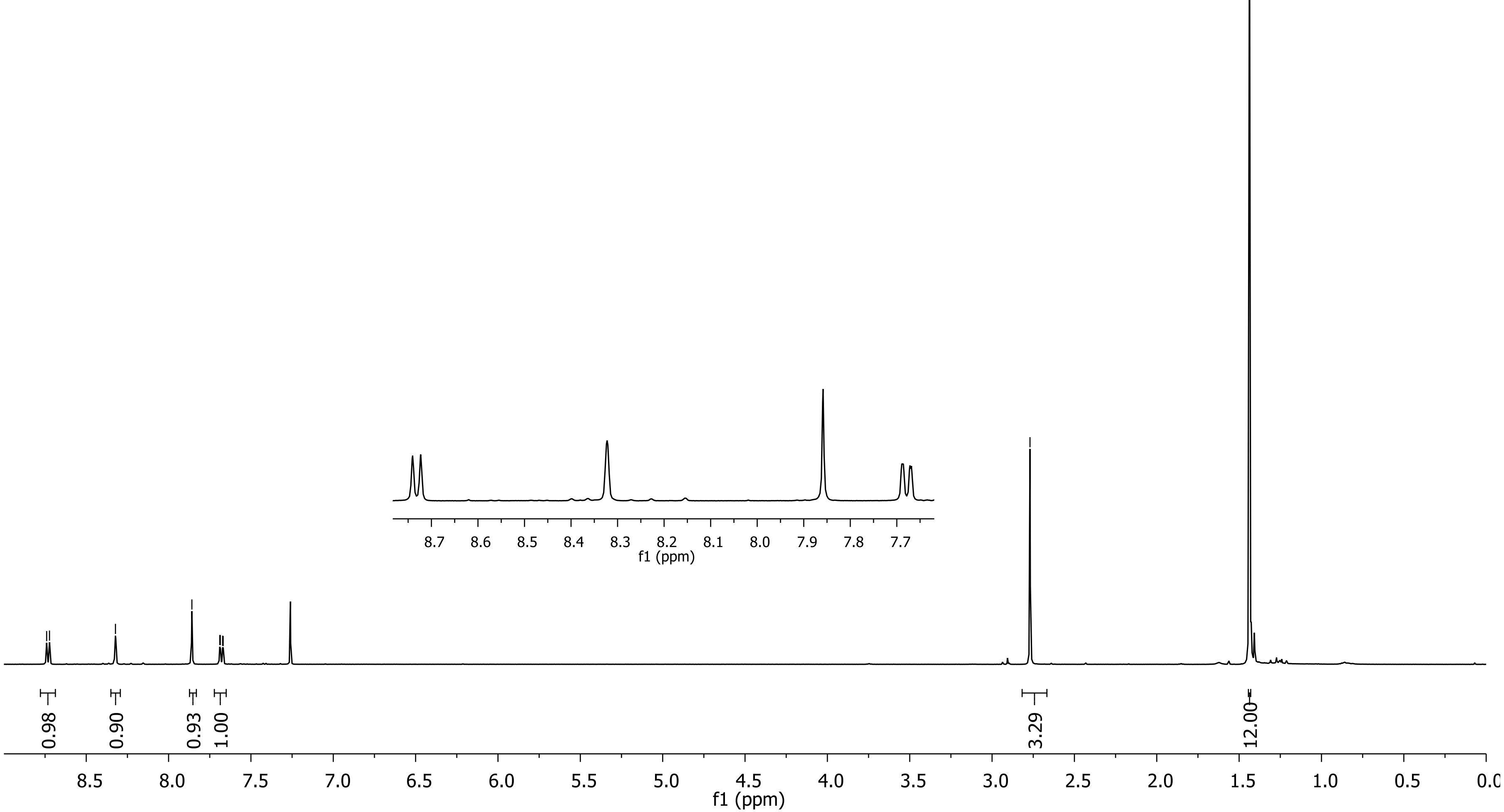


^{13}C NMR (126 MHz, $CDCl_3$), 14a

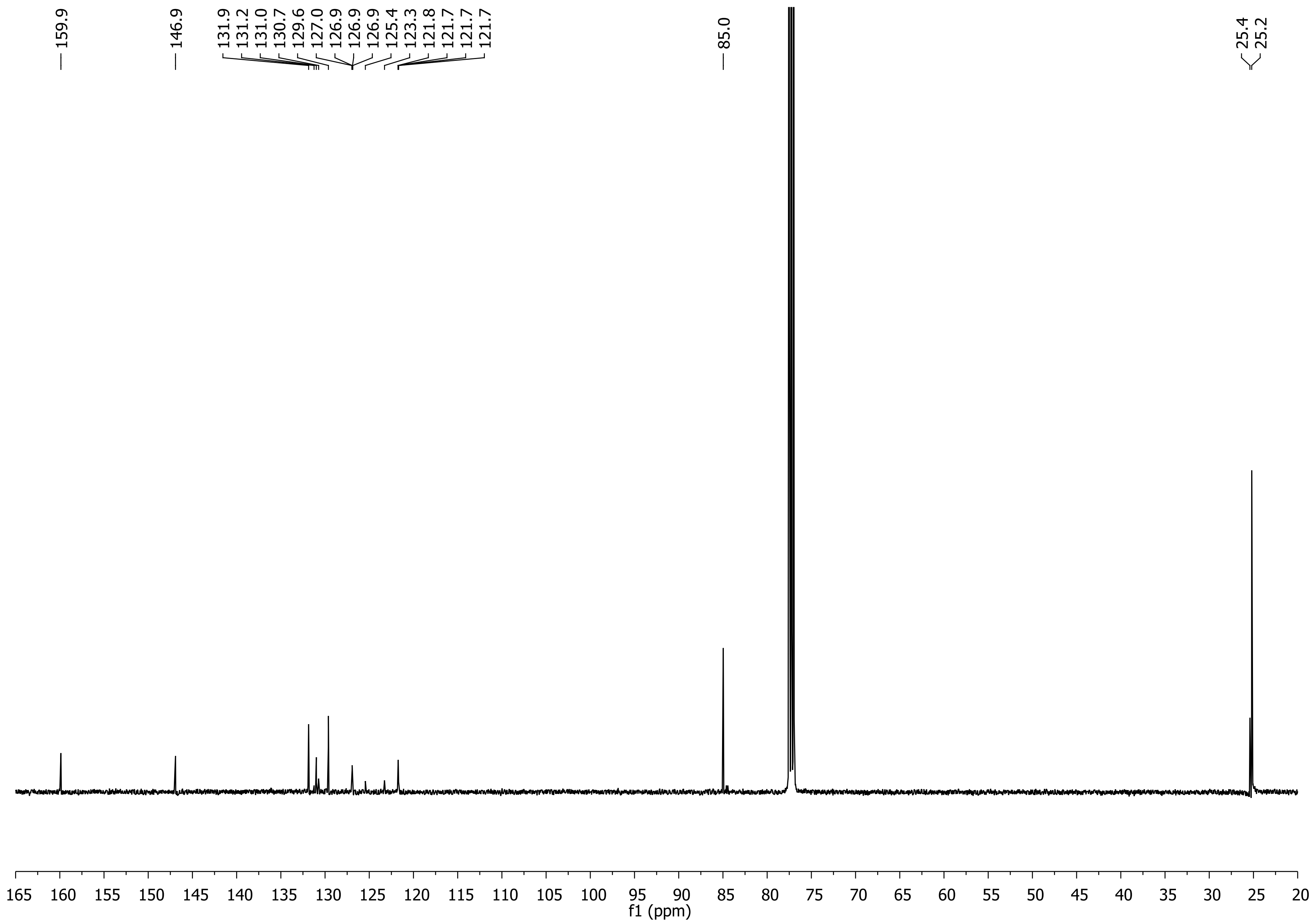


^{1}H NMR (500 MHz, $CDCl_3$), 13b

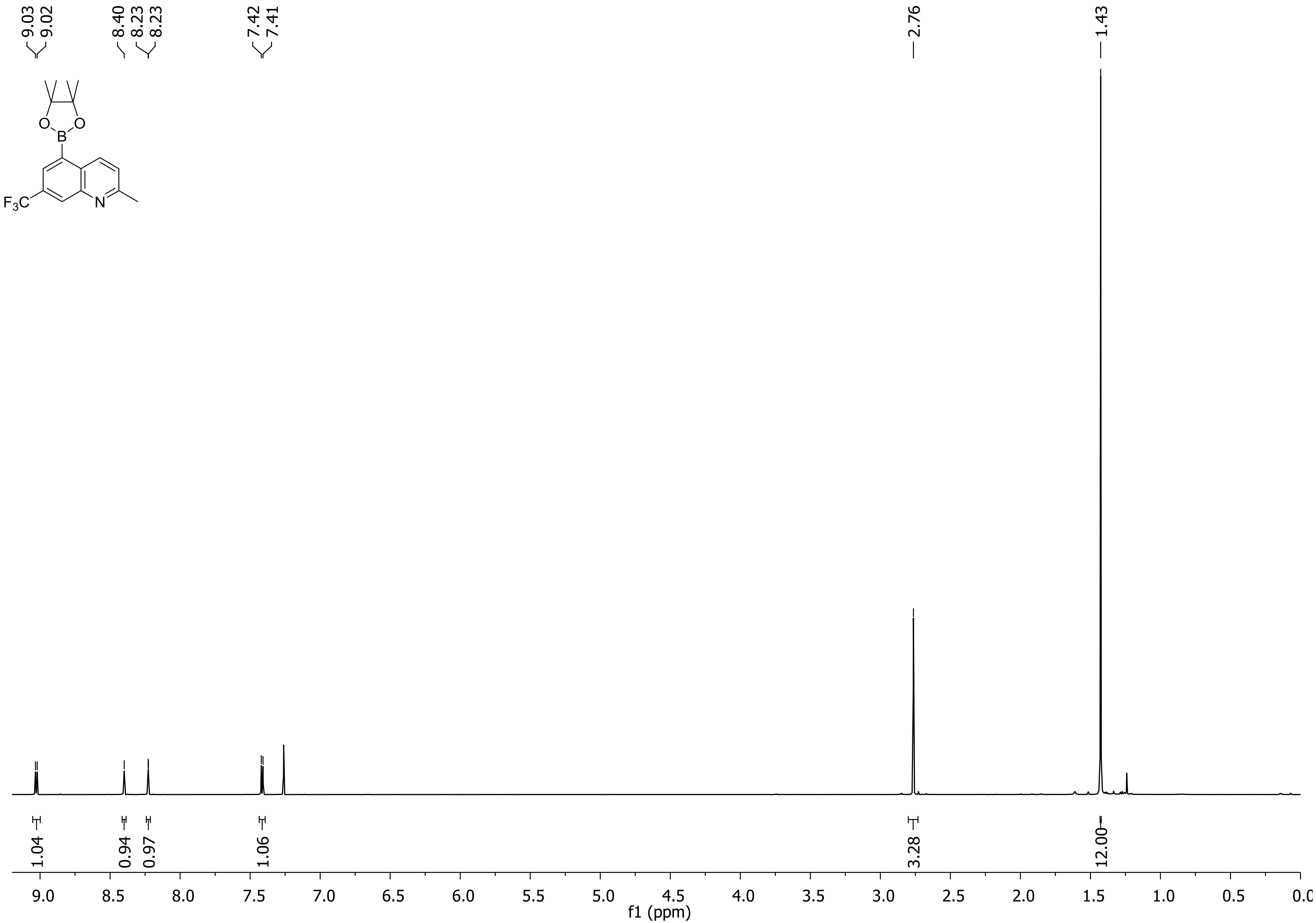




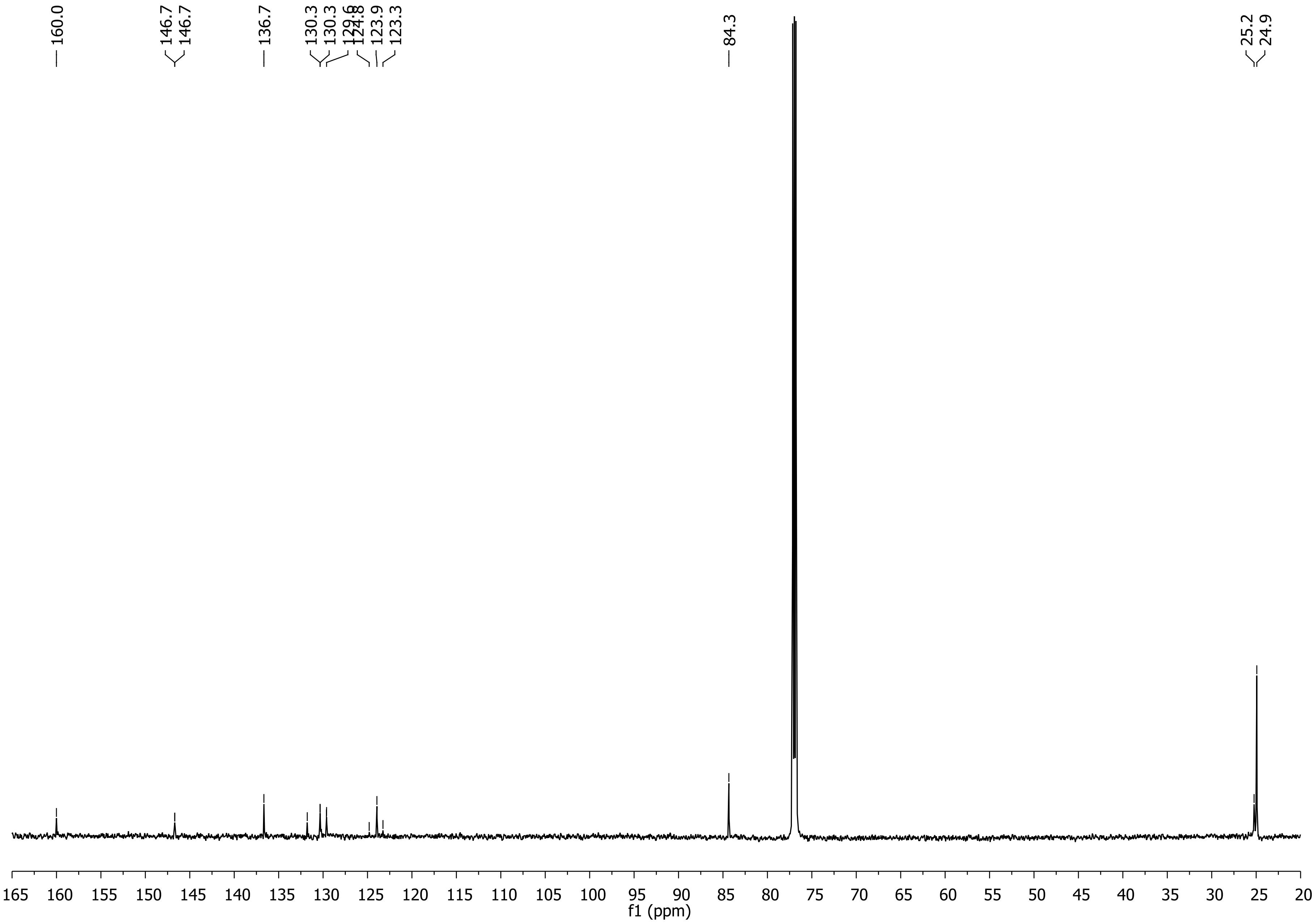
^{13}C NMR (126 MHz, $CDCl_3$), 13b



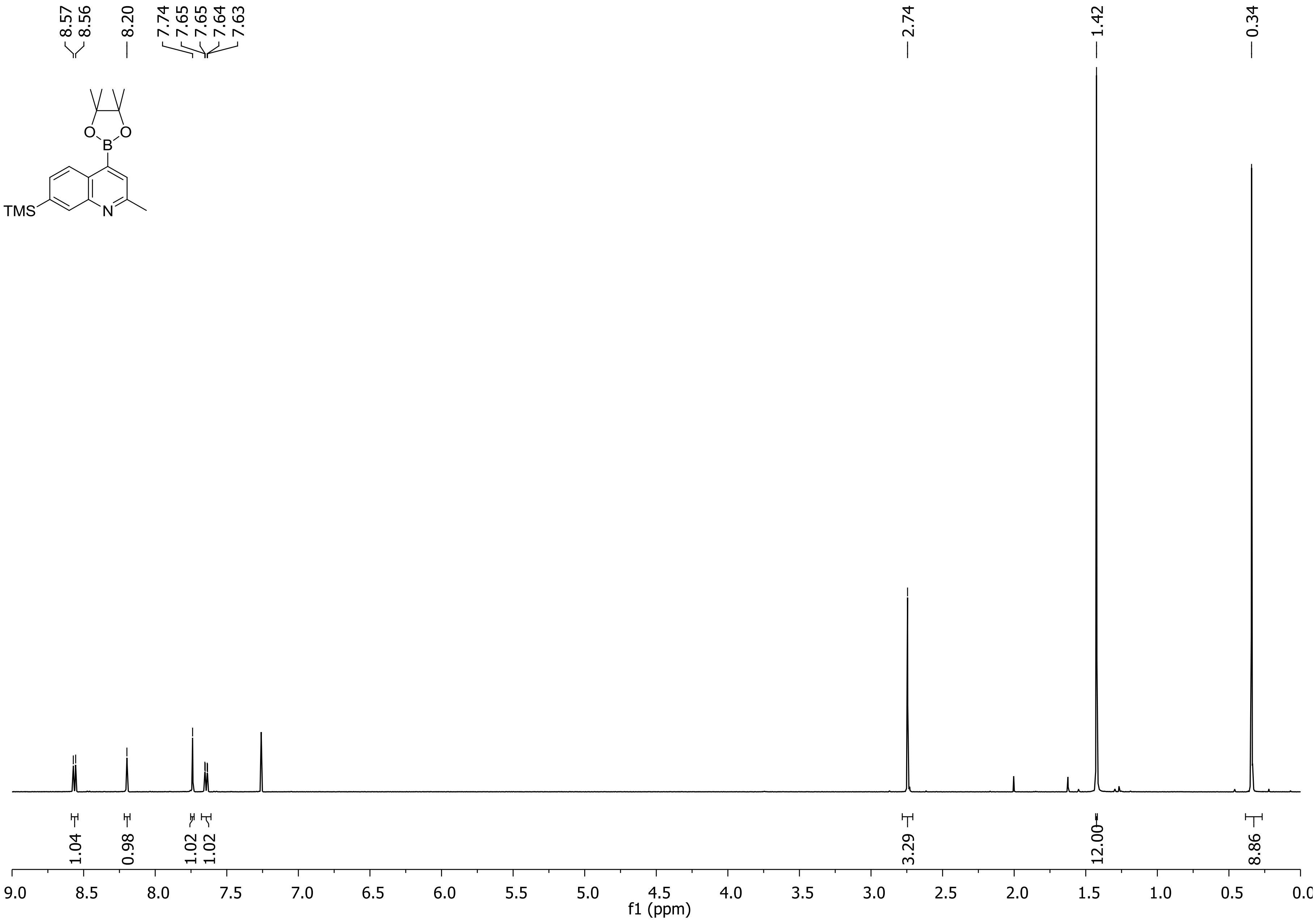
^{1}H NMR (700 MHz, $CDCl_3$), 14b



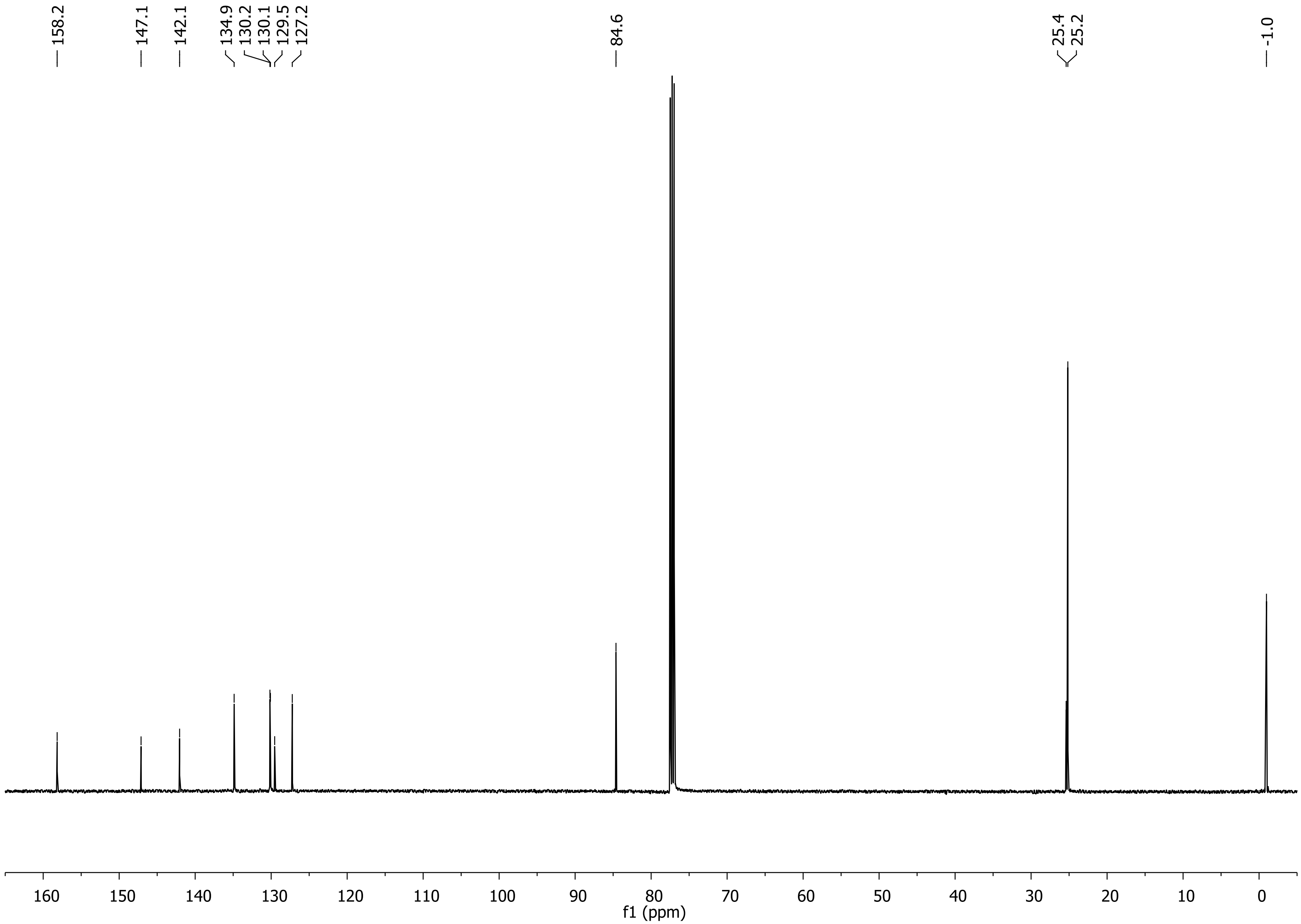
^{13}C NMR (126 MHz, $CDCl_3$), 14b



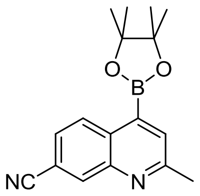
^{1}H NMR (500 MHz, $CDCl_3$), 13c

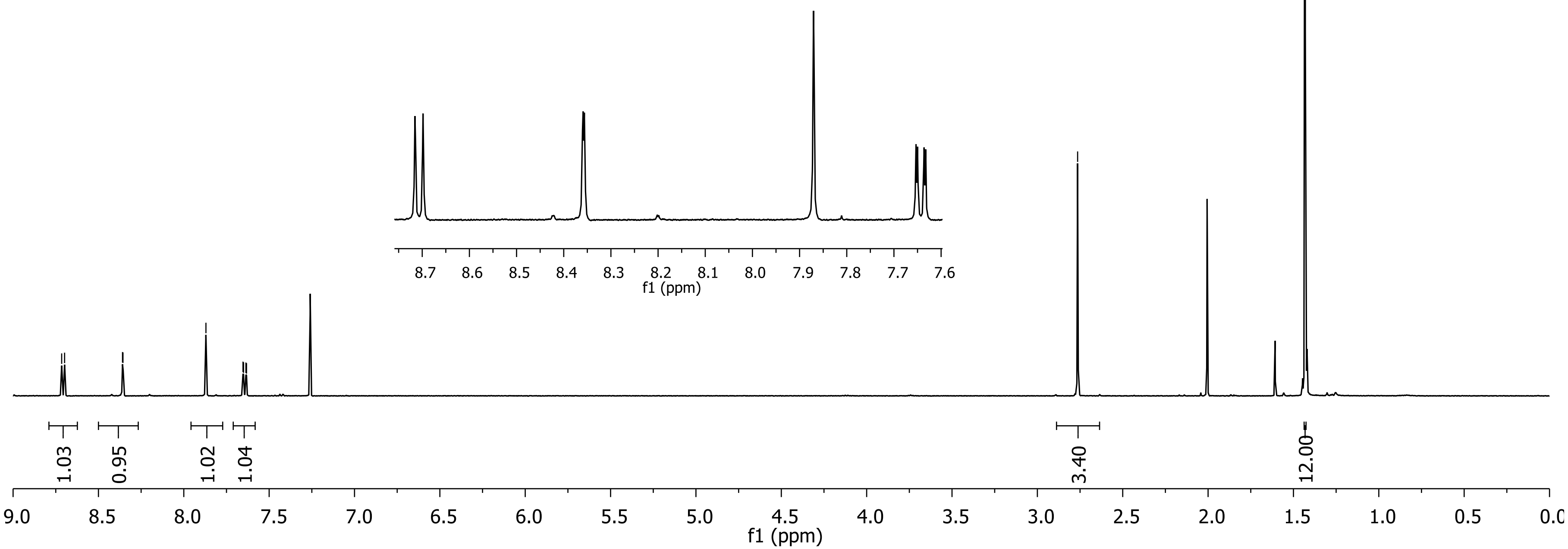


^{13}C NMR (126 MHz, $CDCl_3$), 13c

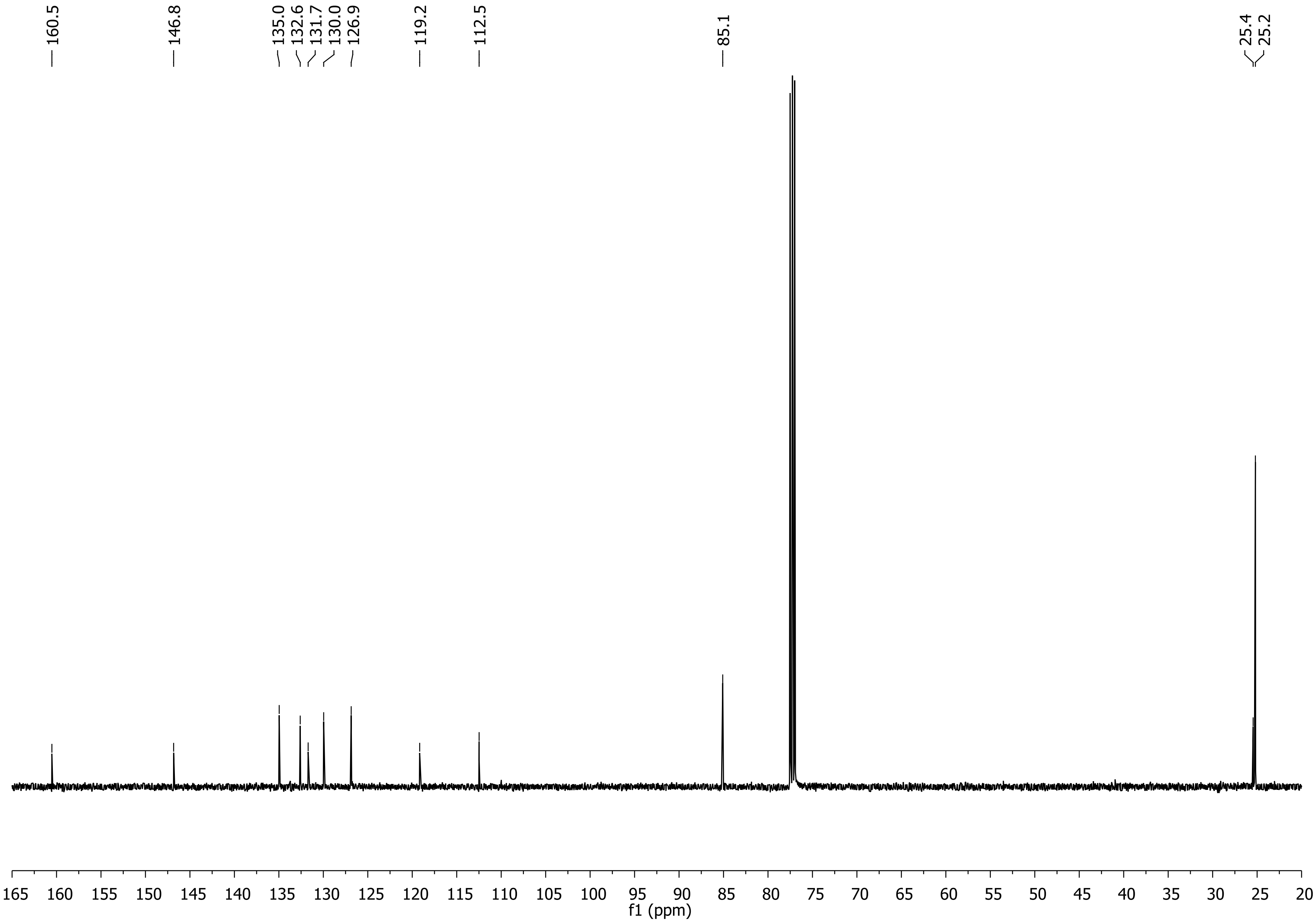


^{1}H NMR (500 MHz, $CDCl_3$), 13d

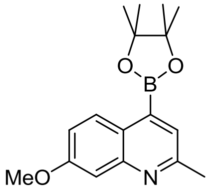


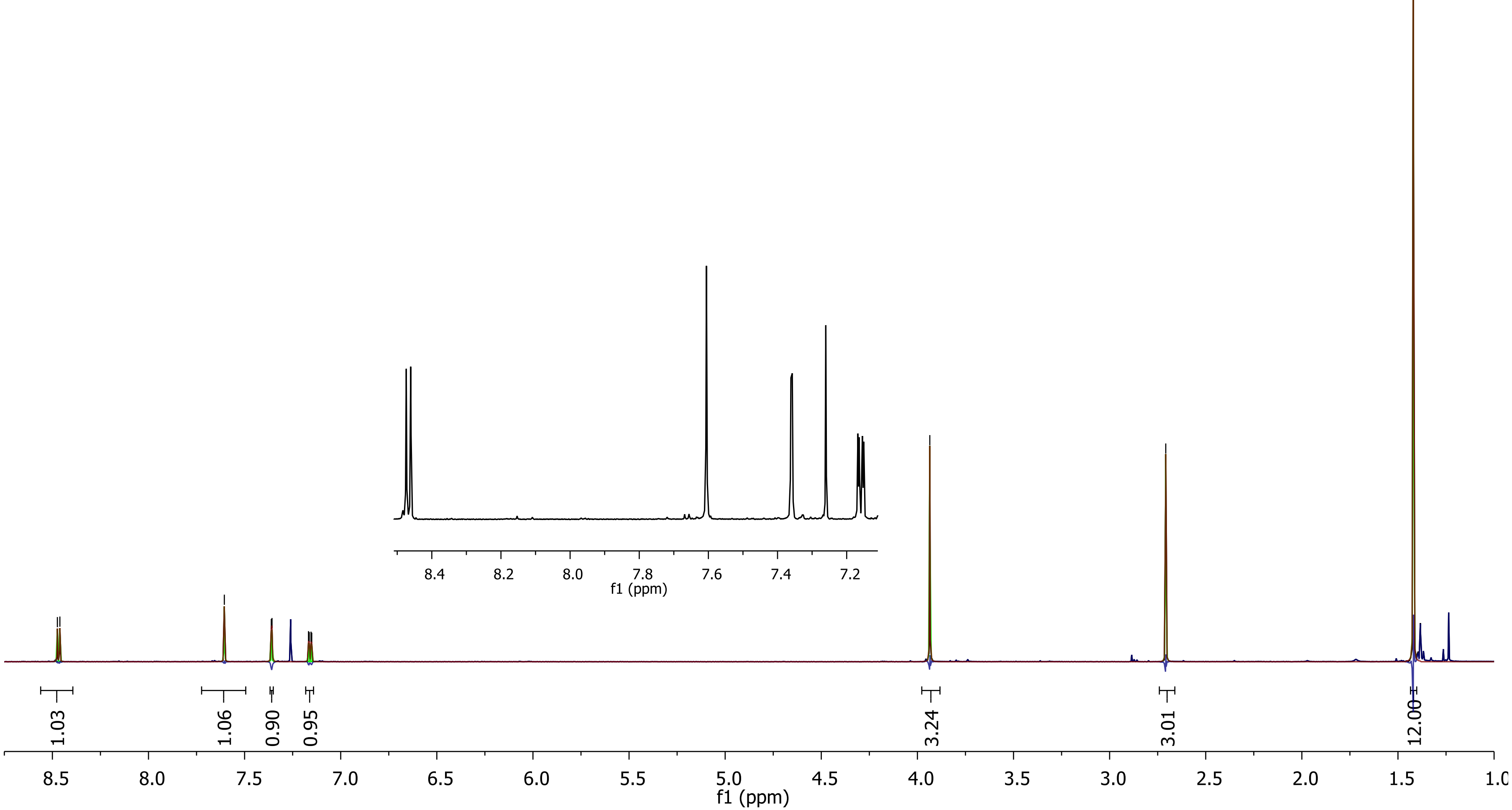


^{13}C NMR (126 MHz, $CDCl_3$), 13d

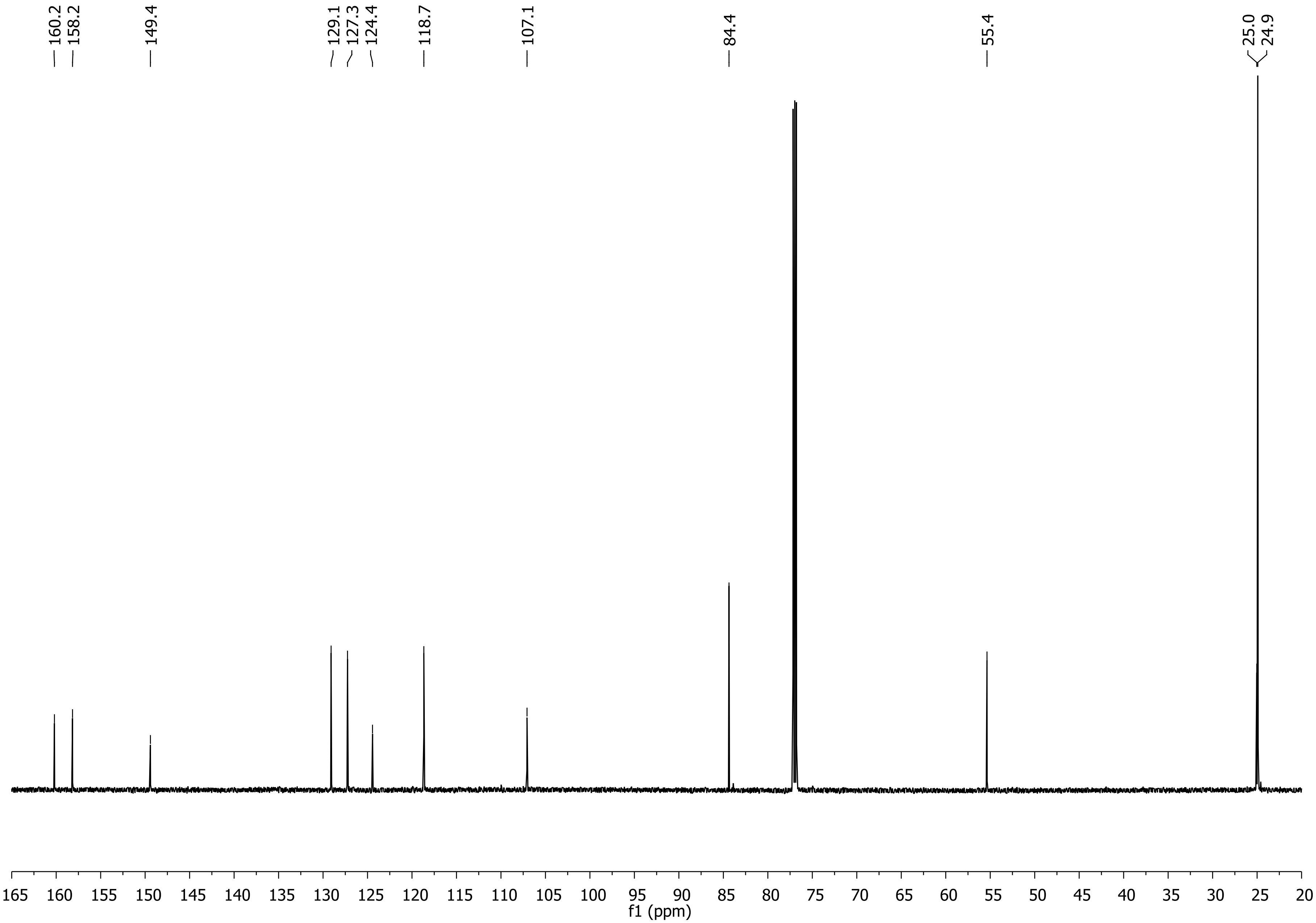


^{1}H NMR (700 MHz, $CDCl_3$), 13e

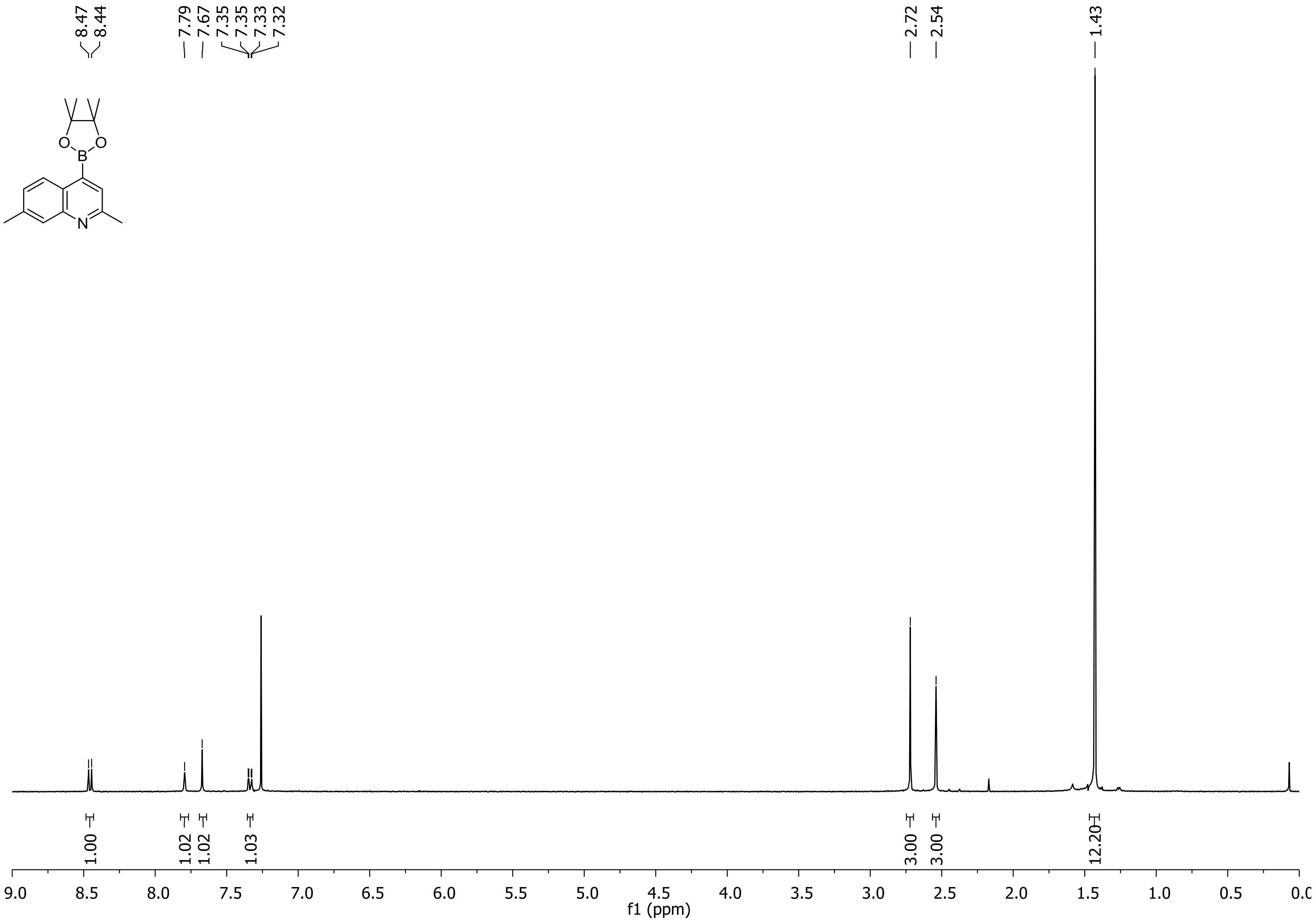




^{13}C NMR (176 MHz, $CDCl_3$), 13e



^{1}H NMR (400 MHz, $CDCl_3$), 13f



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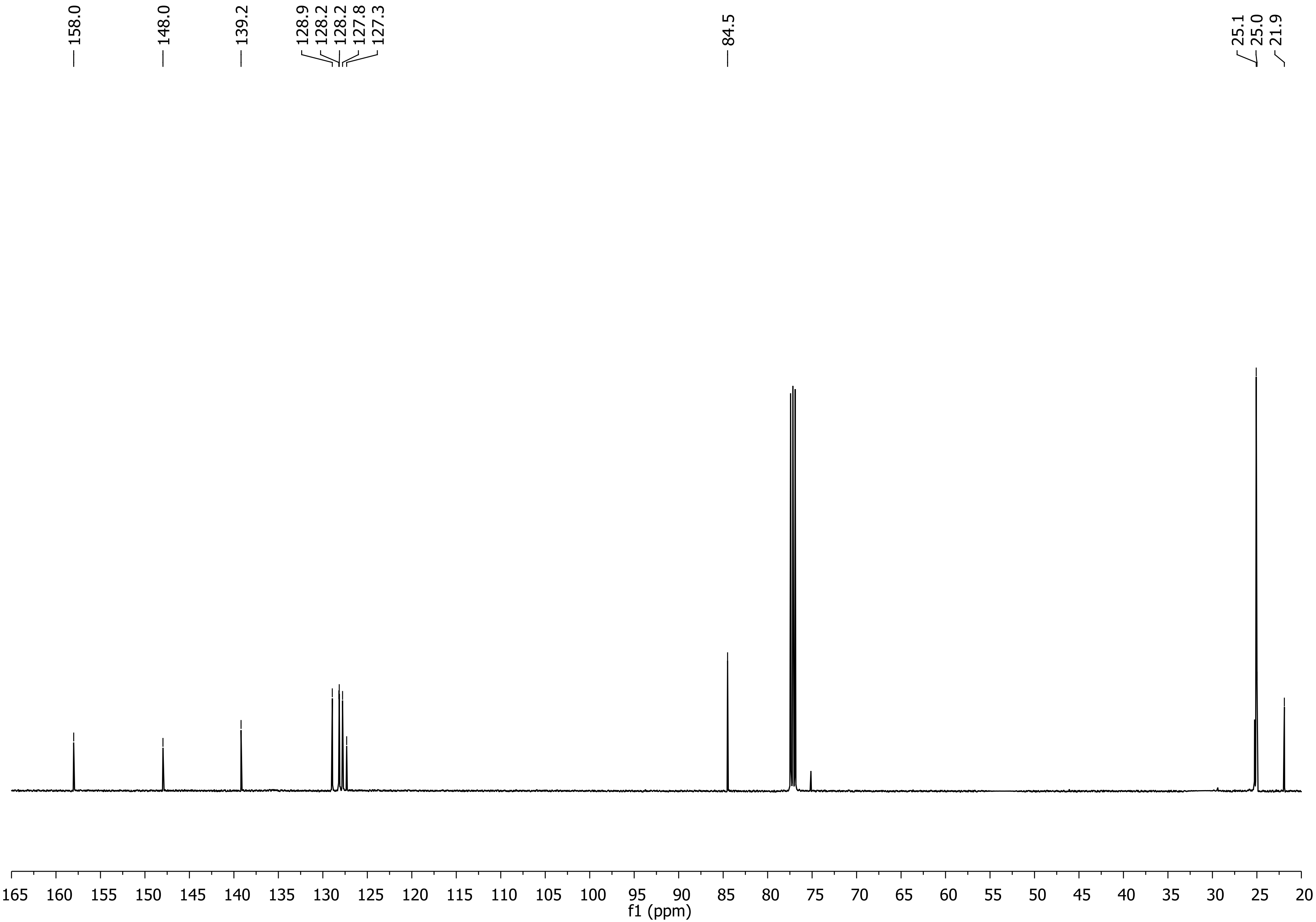
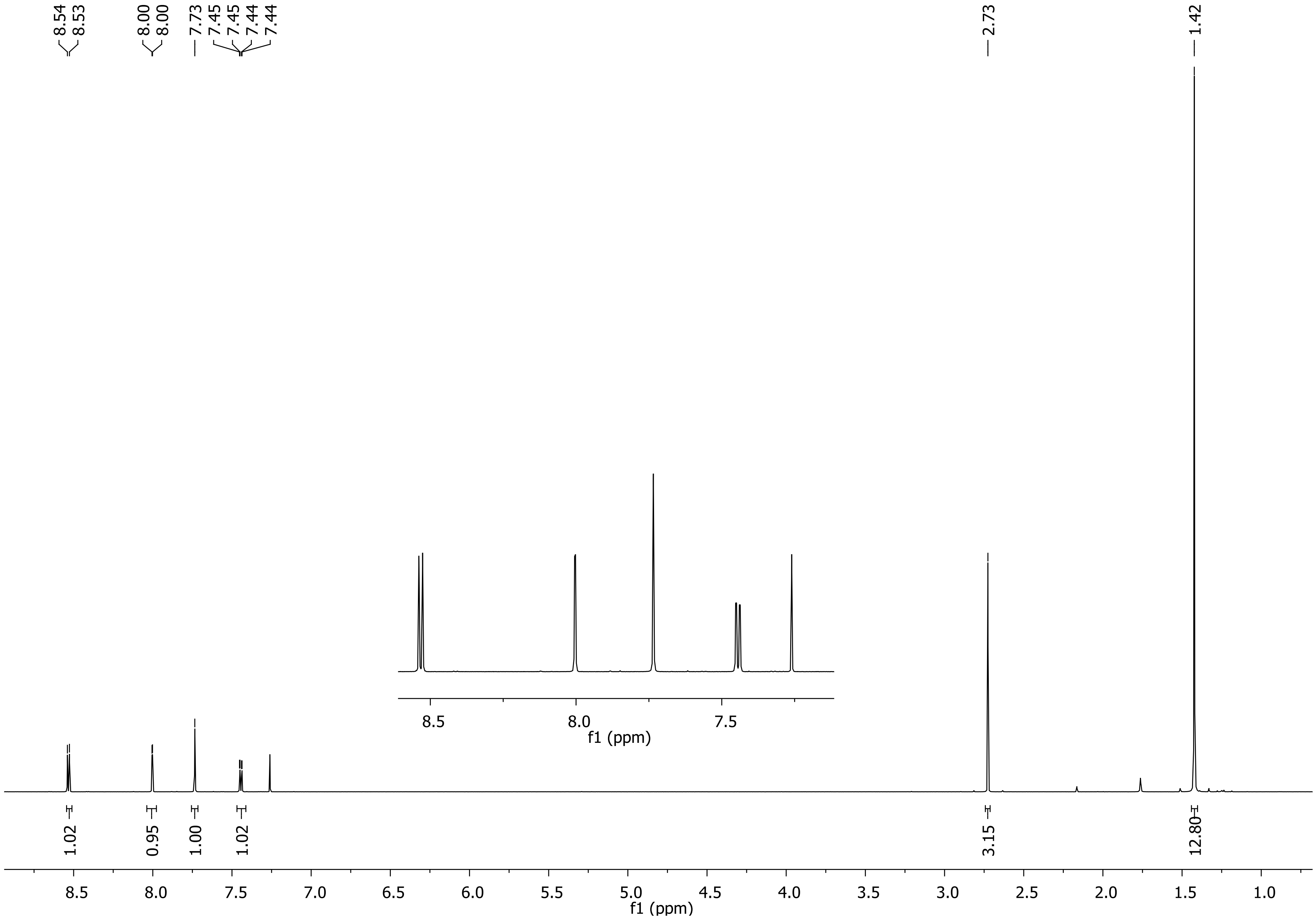
^{13}C NMR (176 MHz, $CDCl_3$), 13f

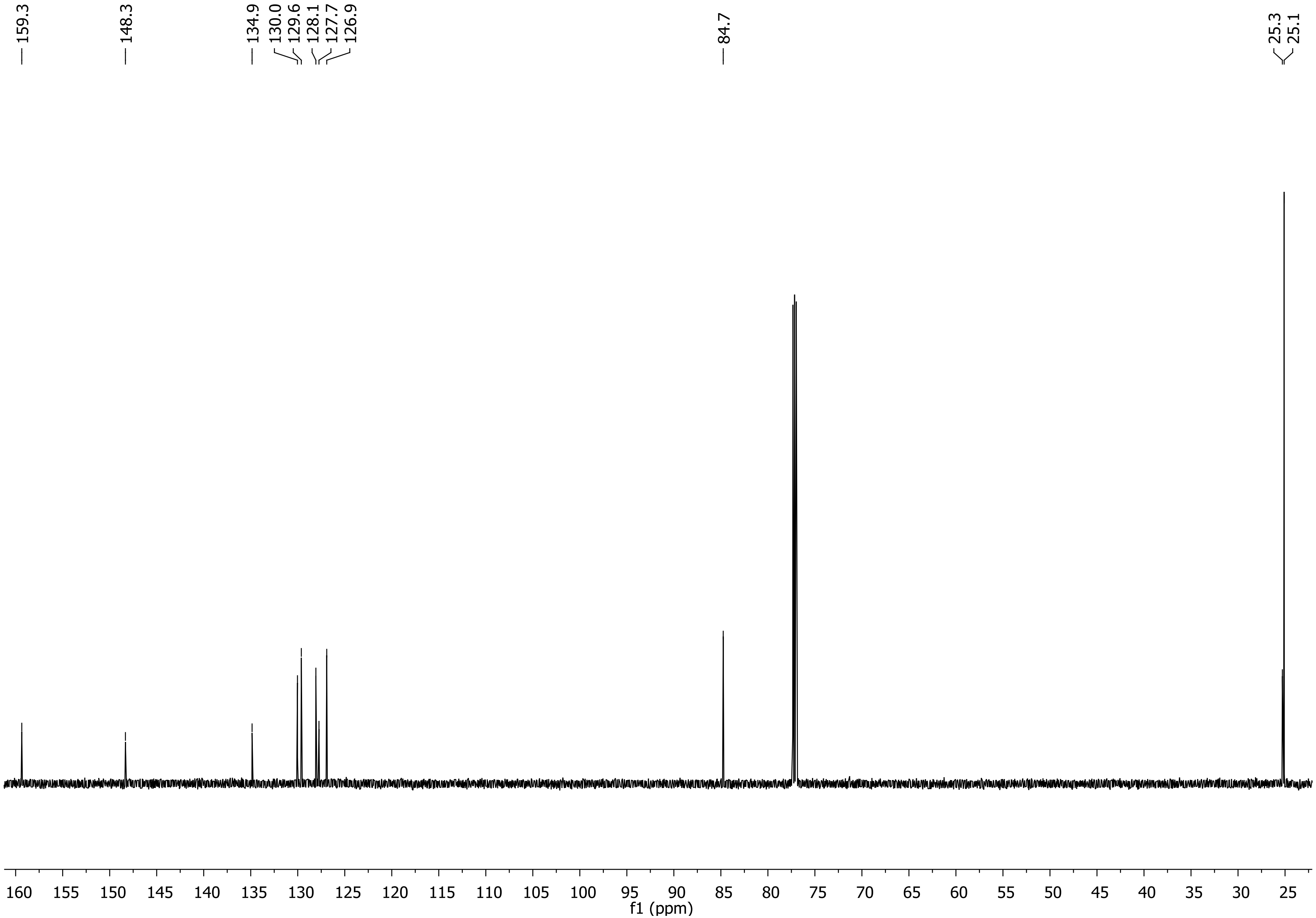


^{1}H NMR (700 MHz, $CDCl_3$), 13g

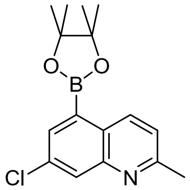


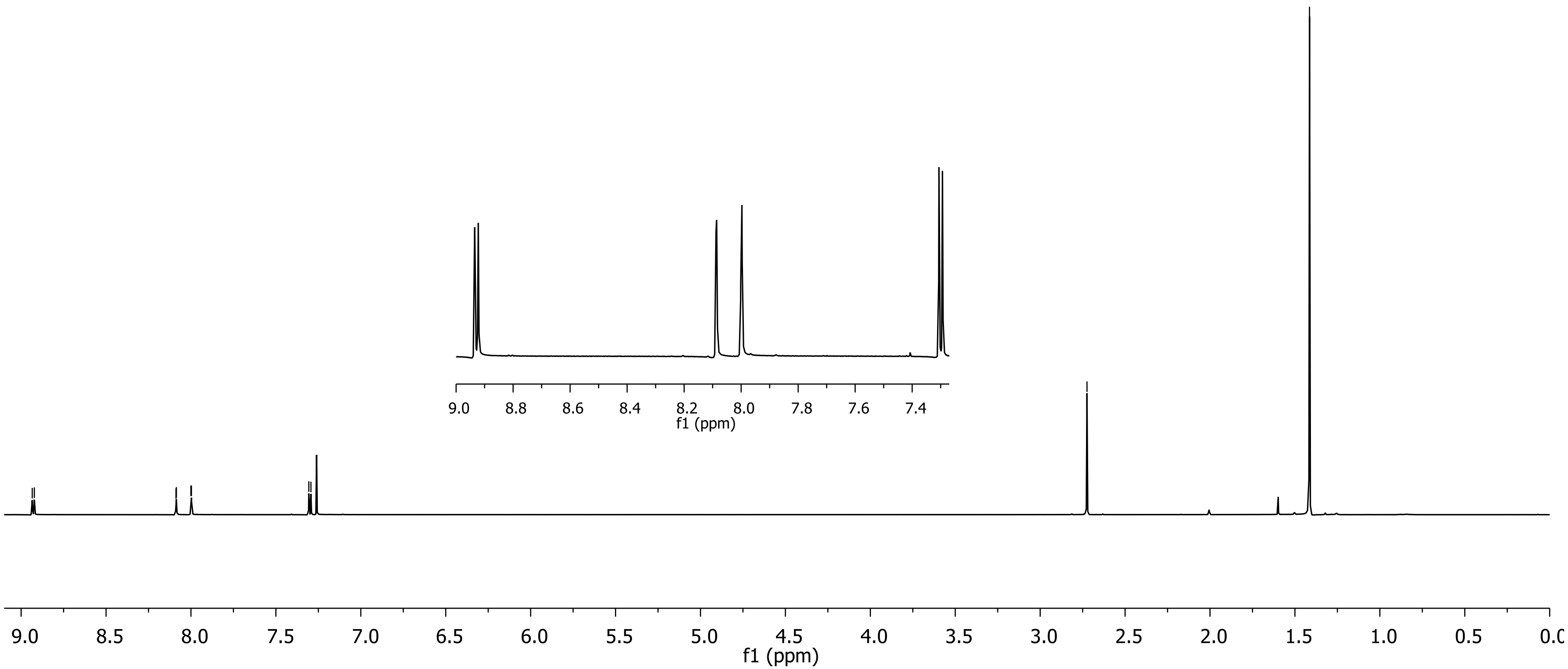
Electronic Supplementary Material (ESI) for Chemical Science

^{13}C NMR (176 MHz, $CDCl_3$), 13g

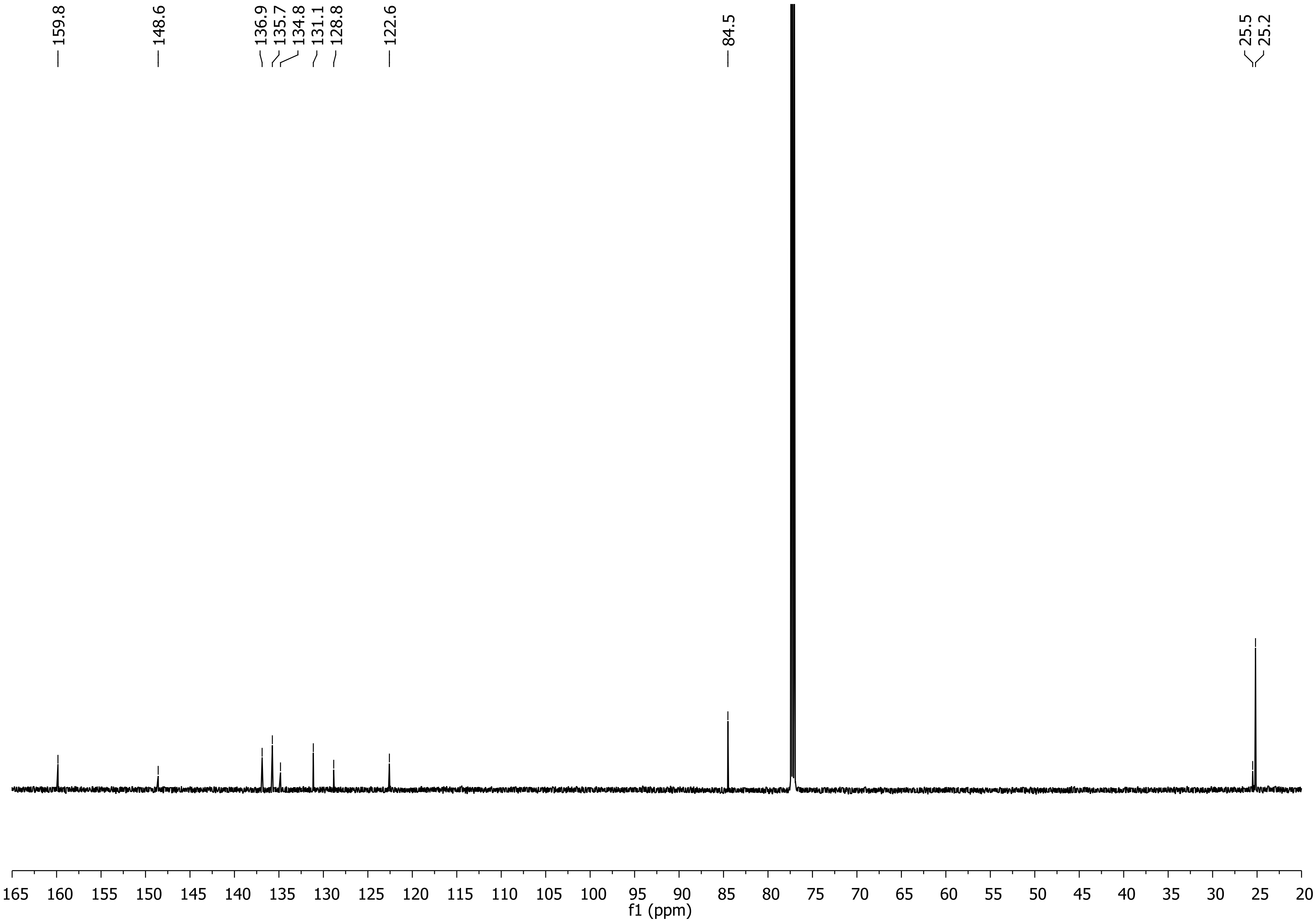


^{1}H NMR (700 MHz, $CDCl_3$), 14g

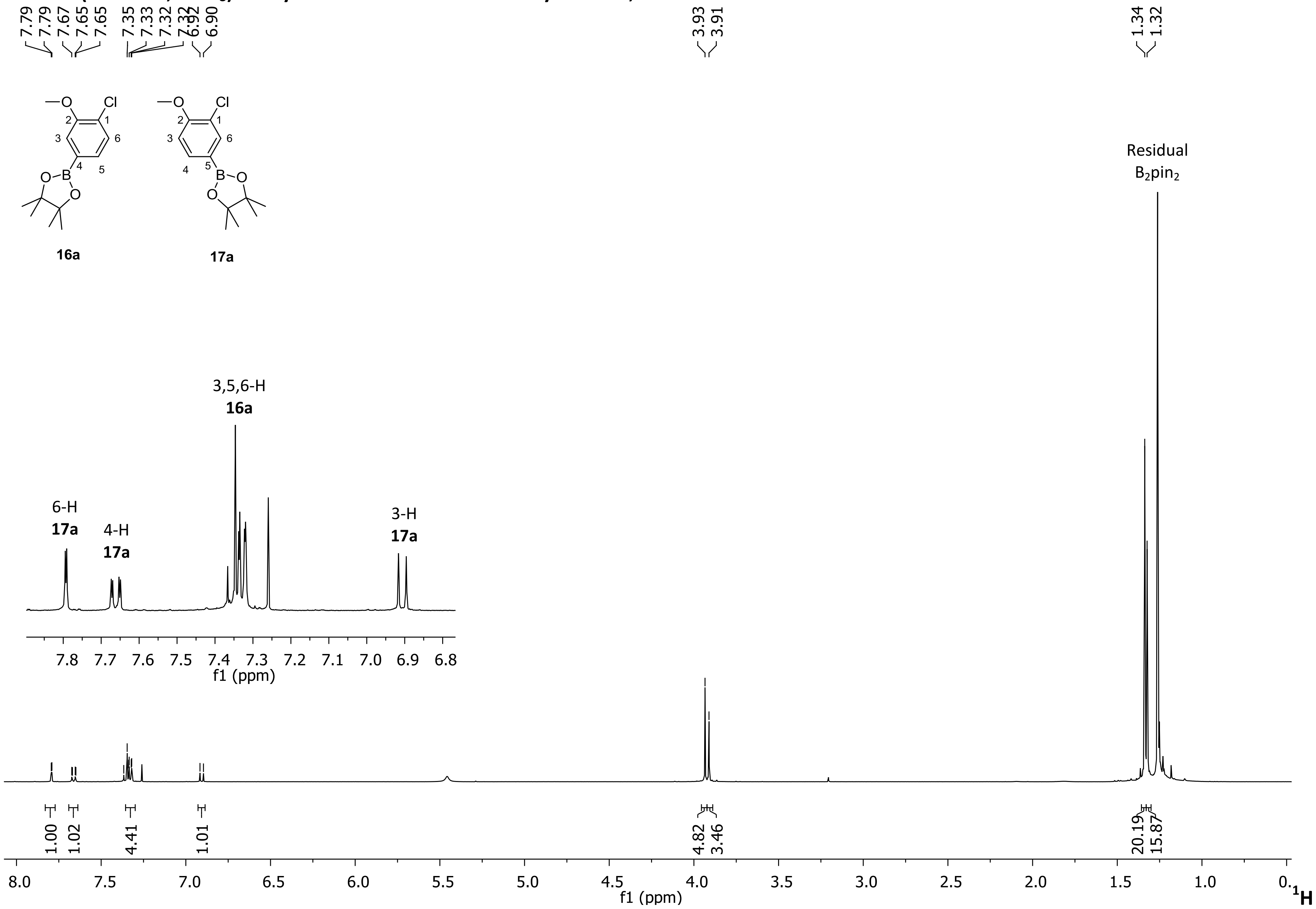




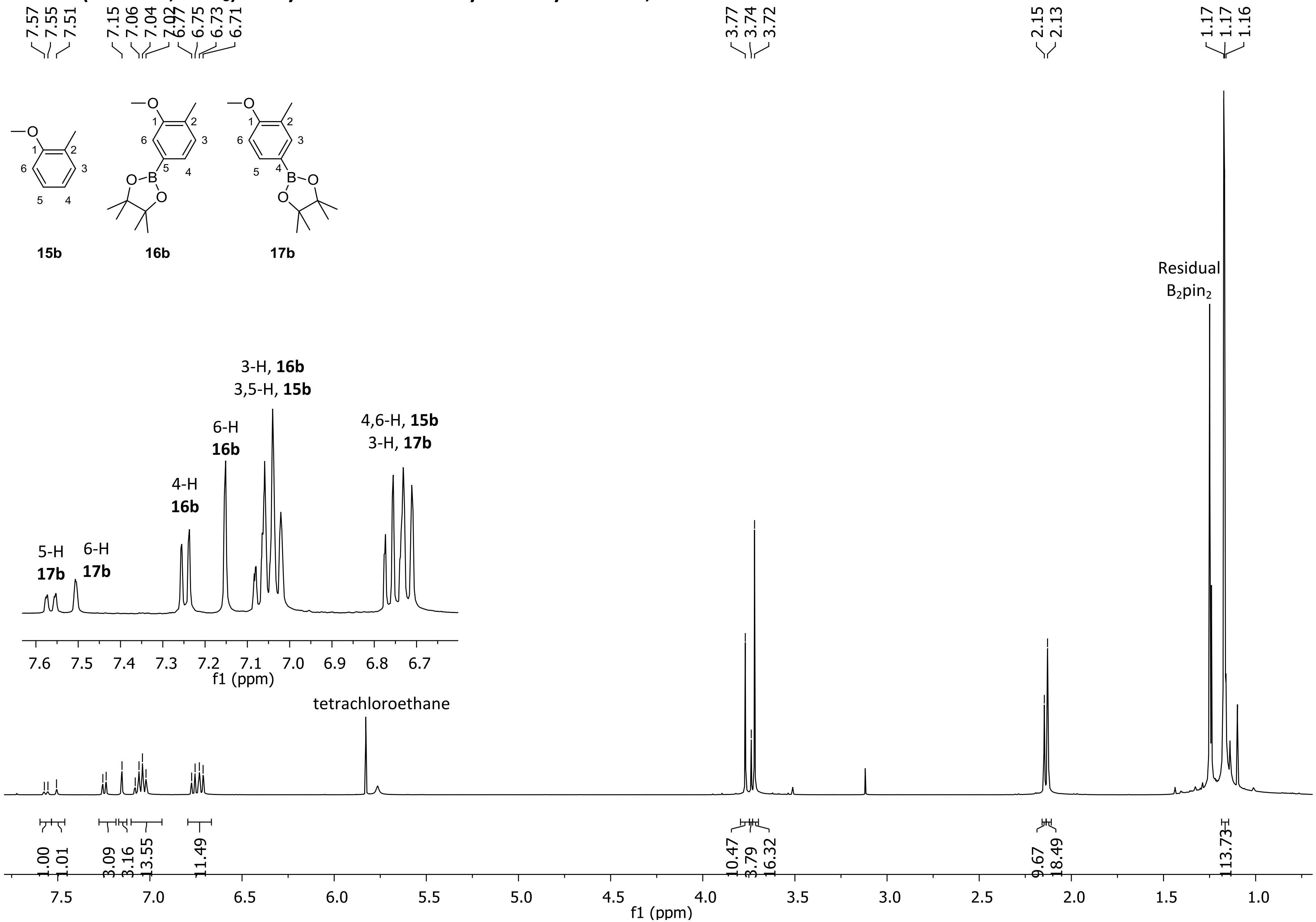
^{13}C NMR (176 MHz, $CDCl_3$), 14g



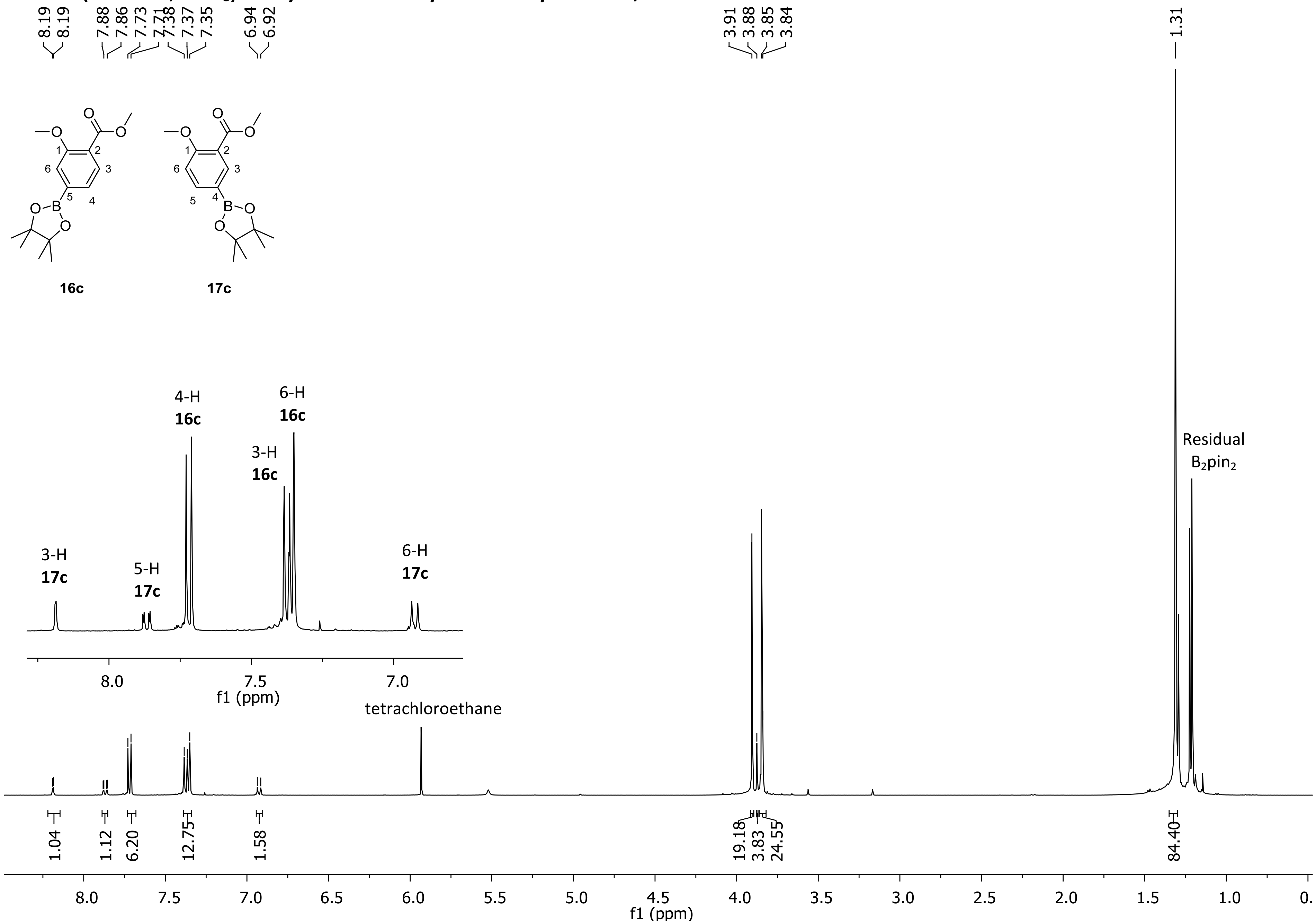
^{1}H NMR (400 MHz, $CDCl_3$) - Borylation of 1-chloro-2-methoxybenzene, 15a



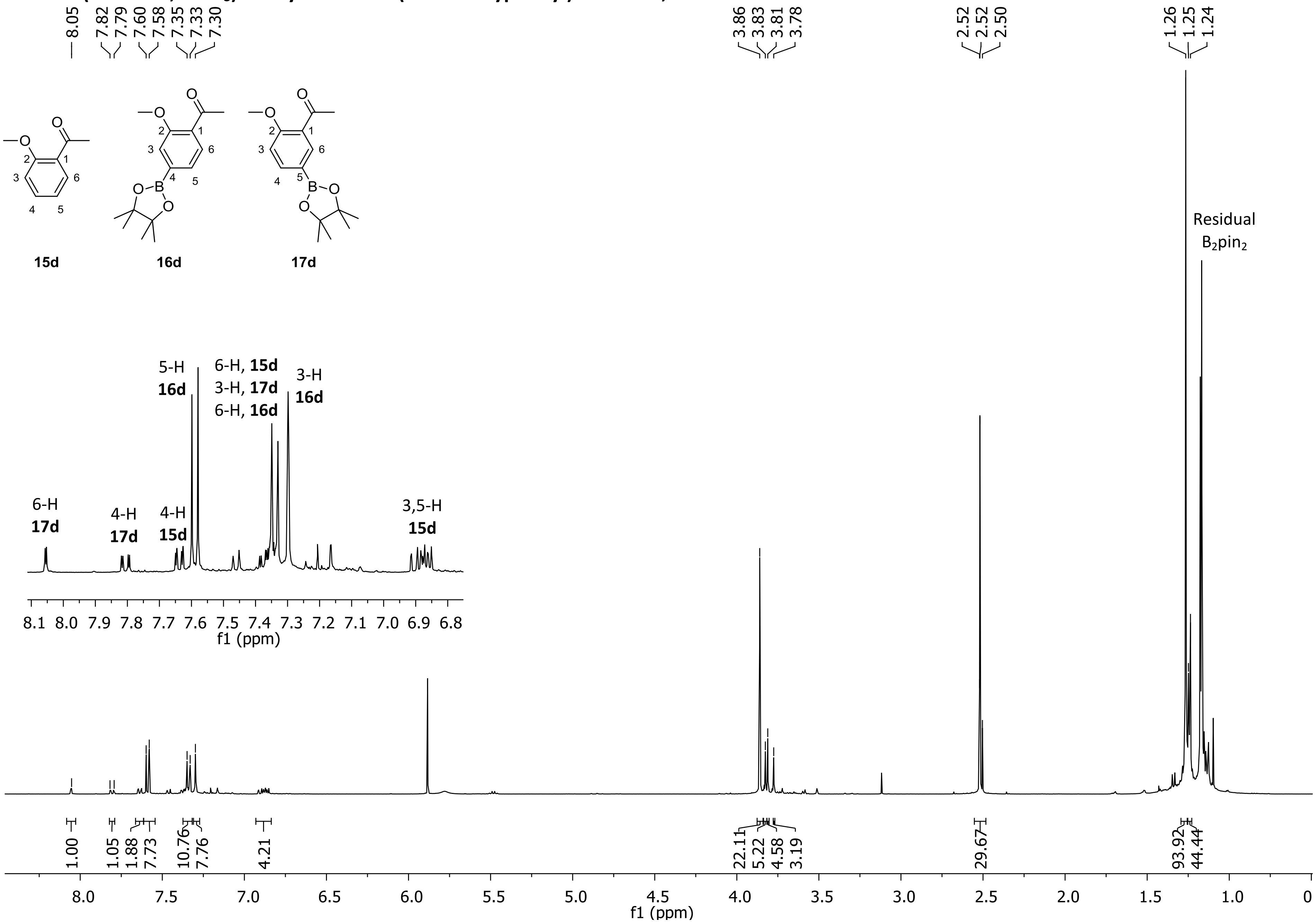
^{1}H NMR (400 MHz, $CDCl_3$) - Borylation of 1-methoxy-2-methylbenzene, 15b



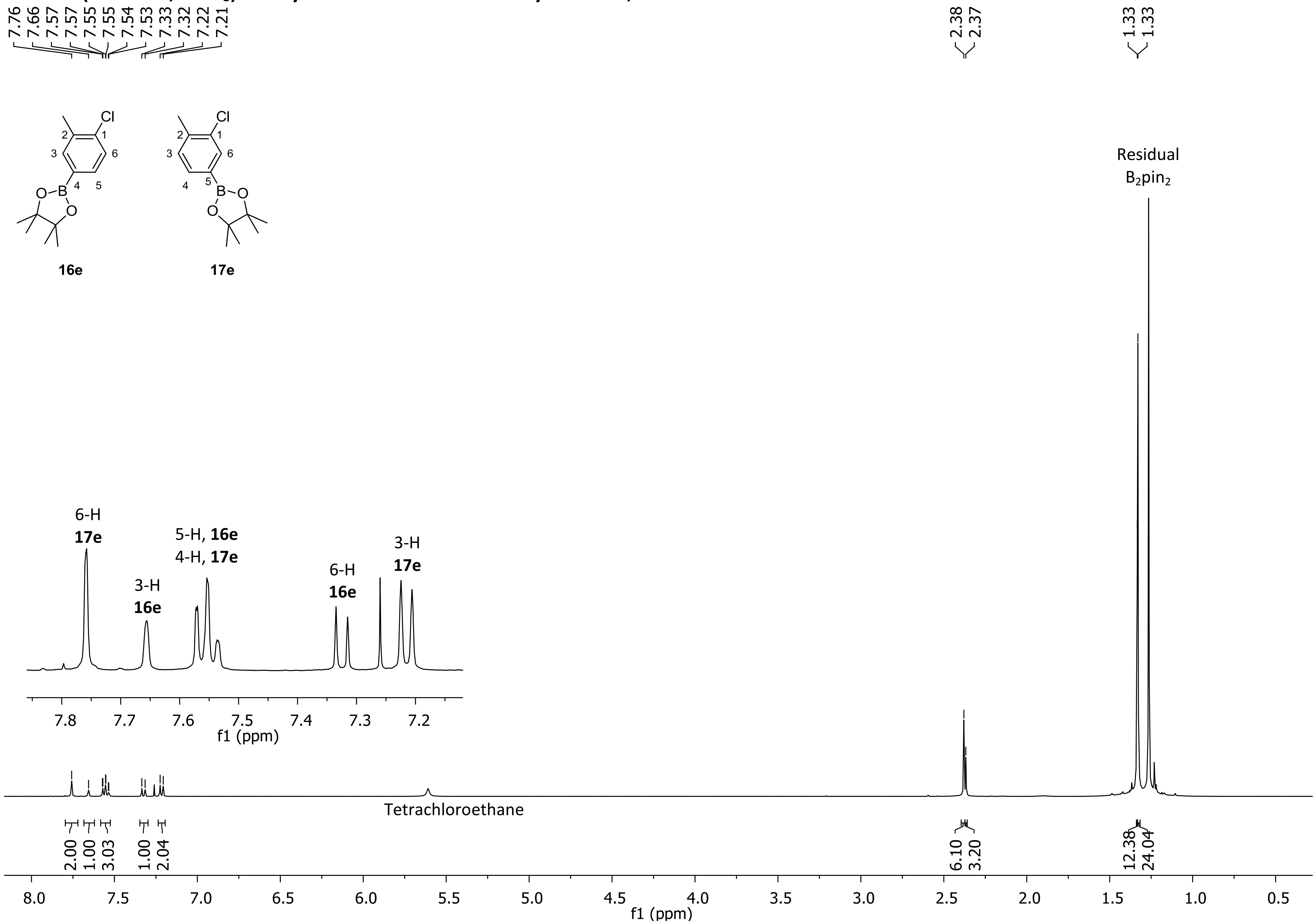
^1H NMR (400 MHz, $CDCl_3$) - Borylation of methyl 2-methoxybenzoate, 15c



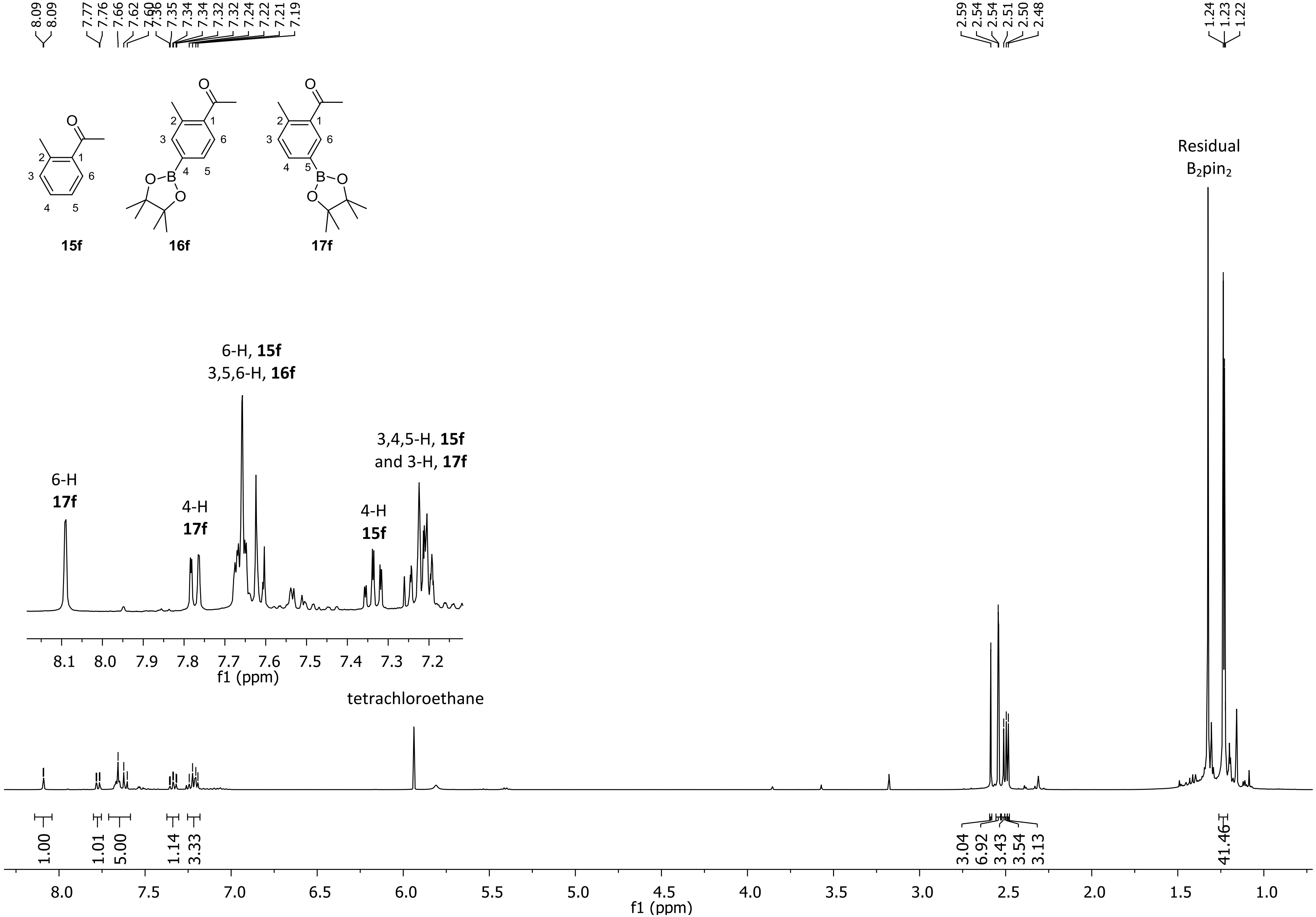
^{1}H NMR (400 MHz, $CDCl_3$) - Borylation of 1-(2-methoxyphenyl)ethanone, 15d



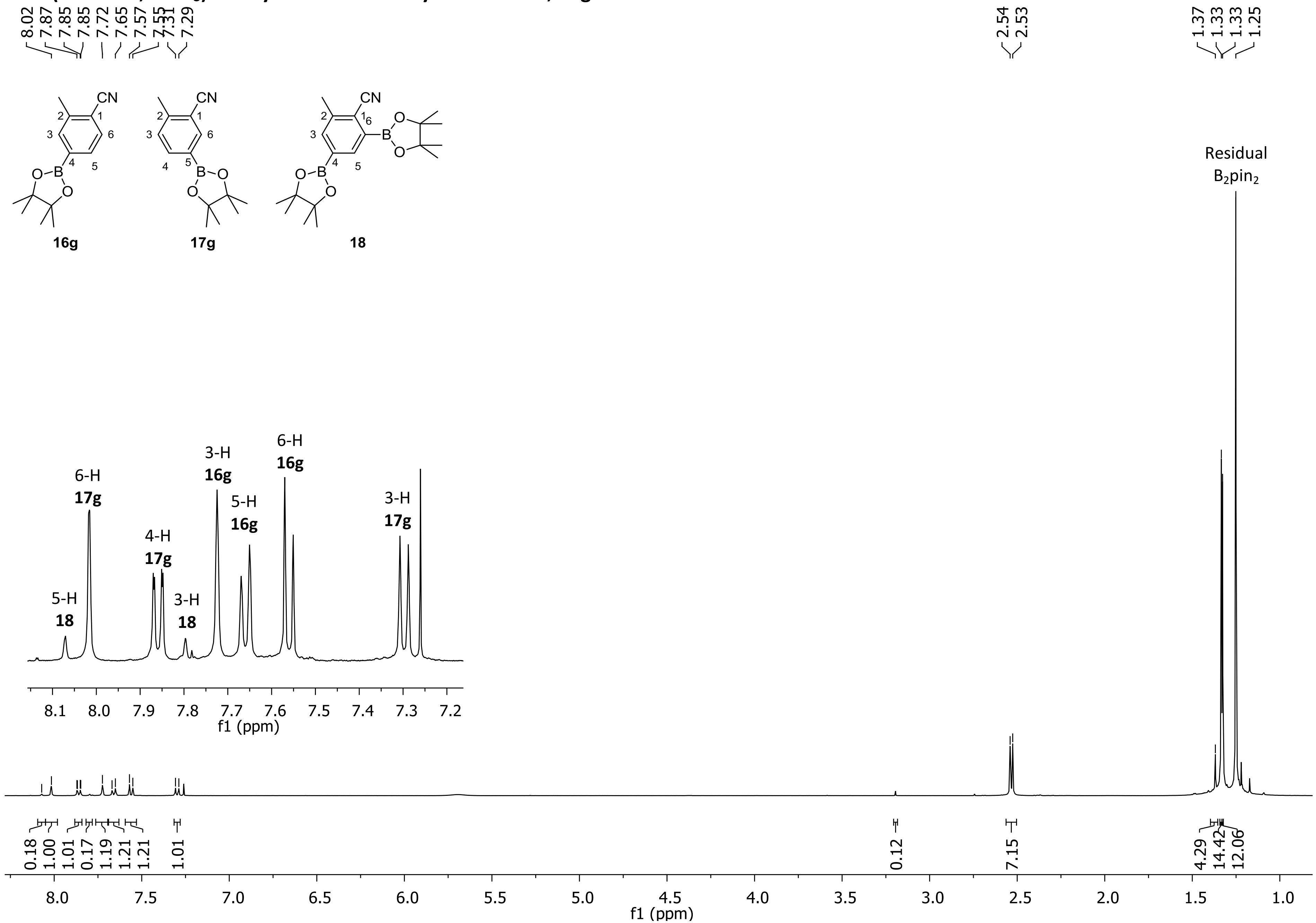
^{1}H NMR (400 MHz, $CDCl_3$) – Borylation of 1-chloro-2-methylbenzene, 15e



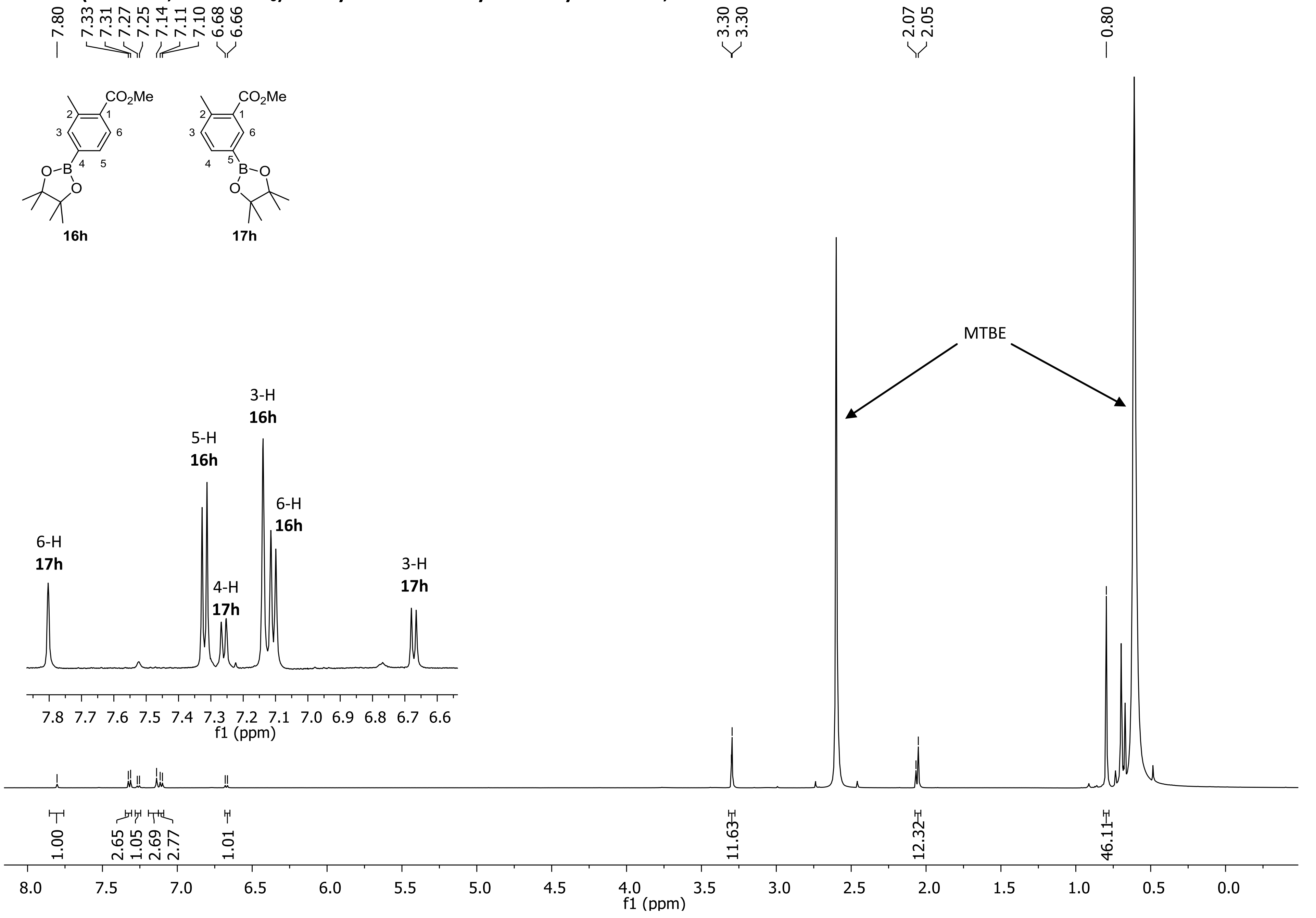
^{1}H NMR (400 MHz, $CDCl_3$) – Borylation of 1-(2-methylphenyl)ethanone, 15f



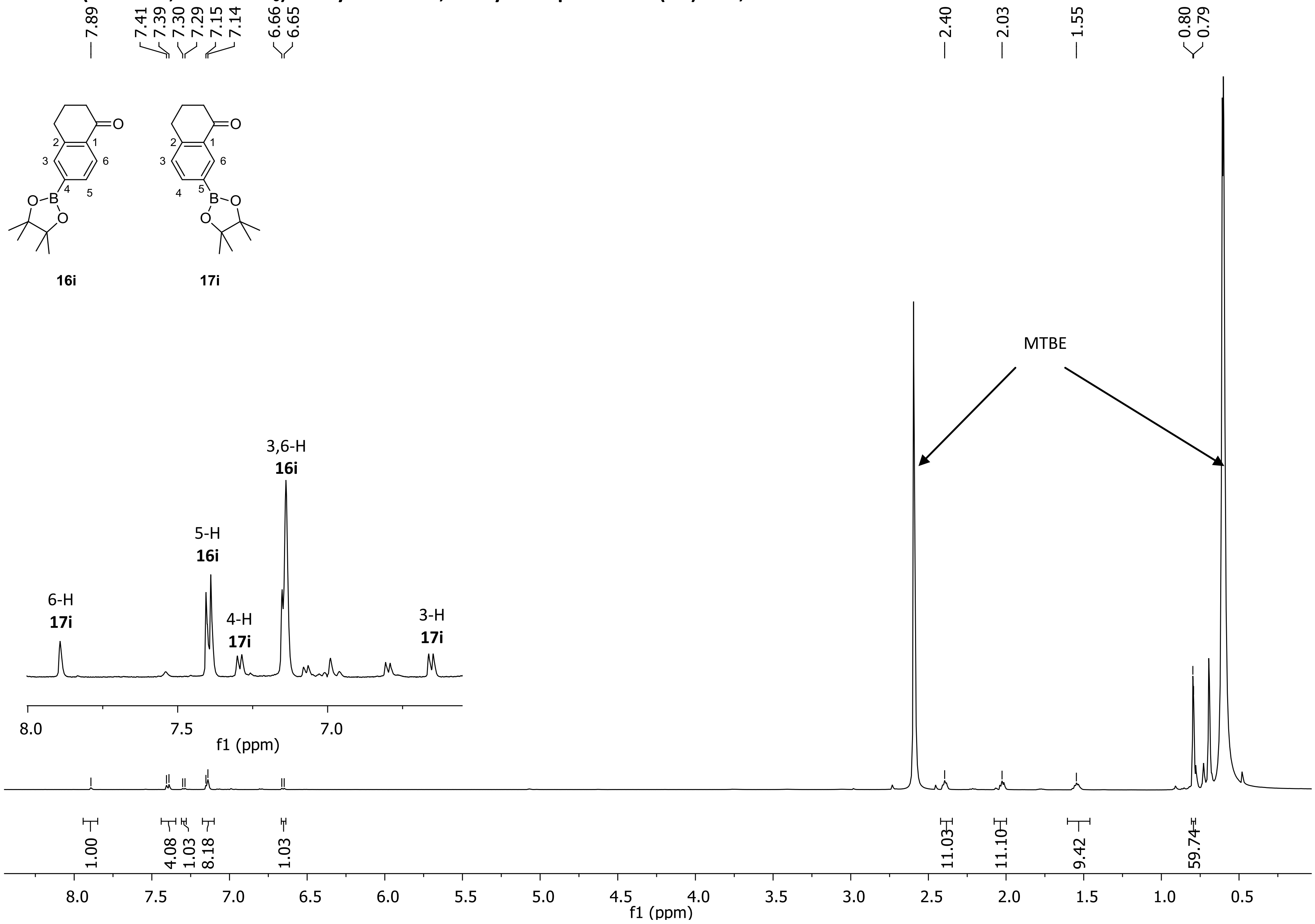
NMR (400 MHz, $CDCl_3$) – Borylation of 2-methylbenzonitrile, 15g



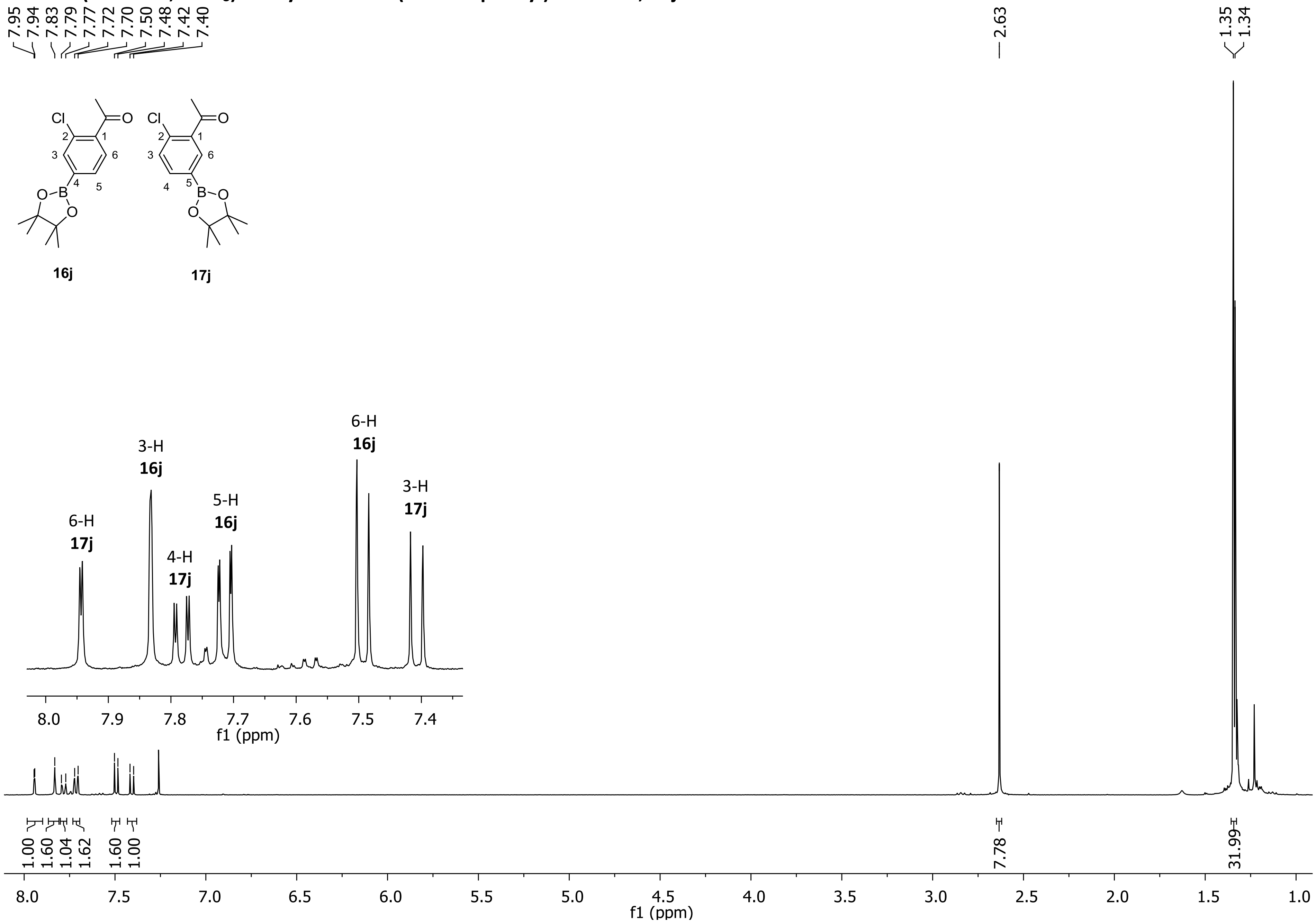
^{1}H NMR (400 MHz, acetone-d$_6$) – Borylation of methyl 2-methylbenzoate, 15h



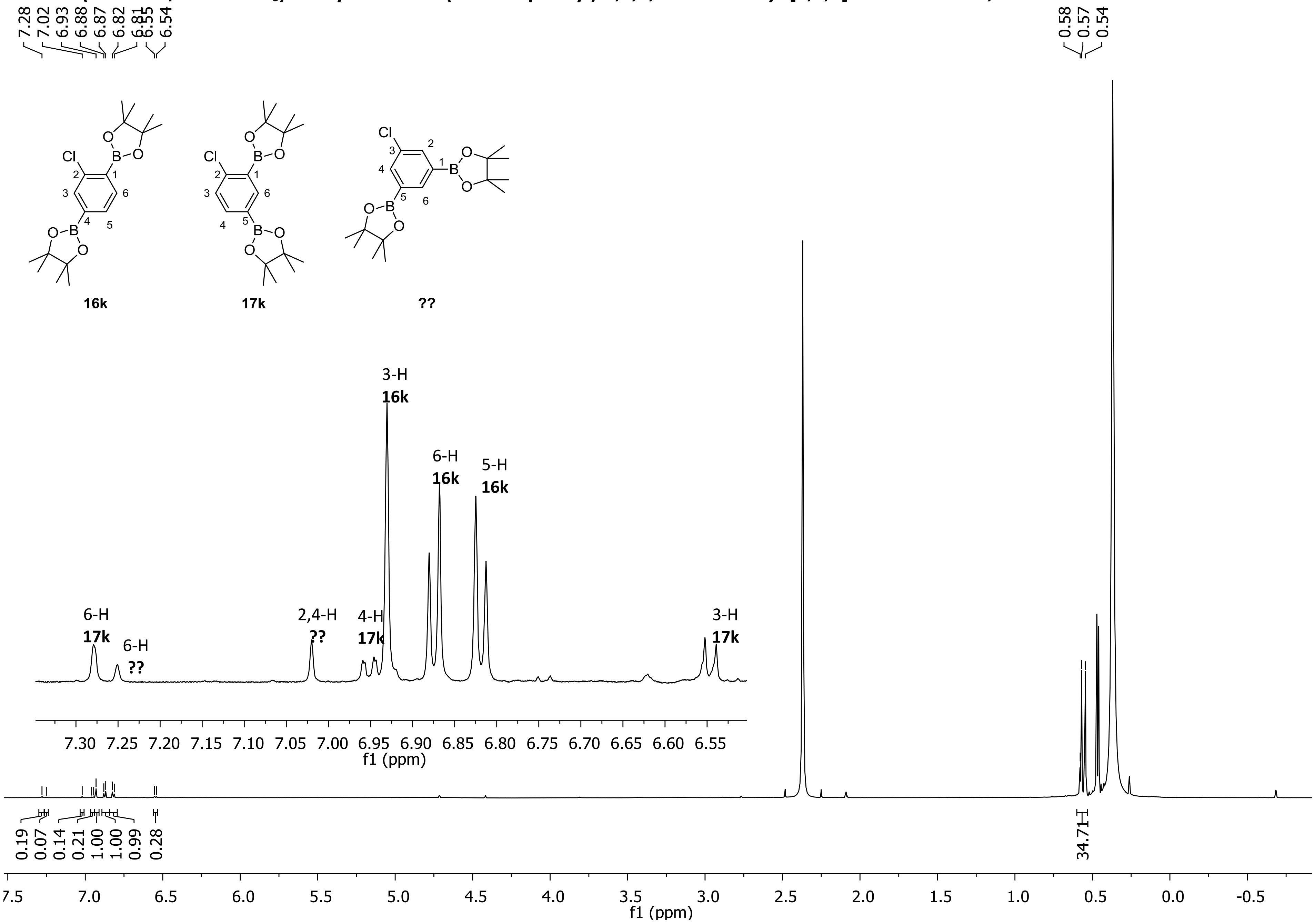
^{1}H NMR (400 MHz, acetone-d_6) - Borylation of 3,4-dihydronaphthalen-1(2*H*)-one, 15i



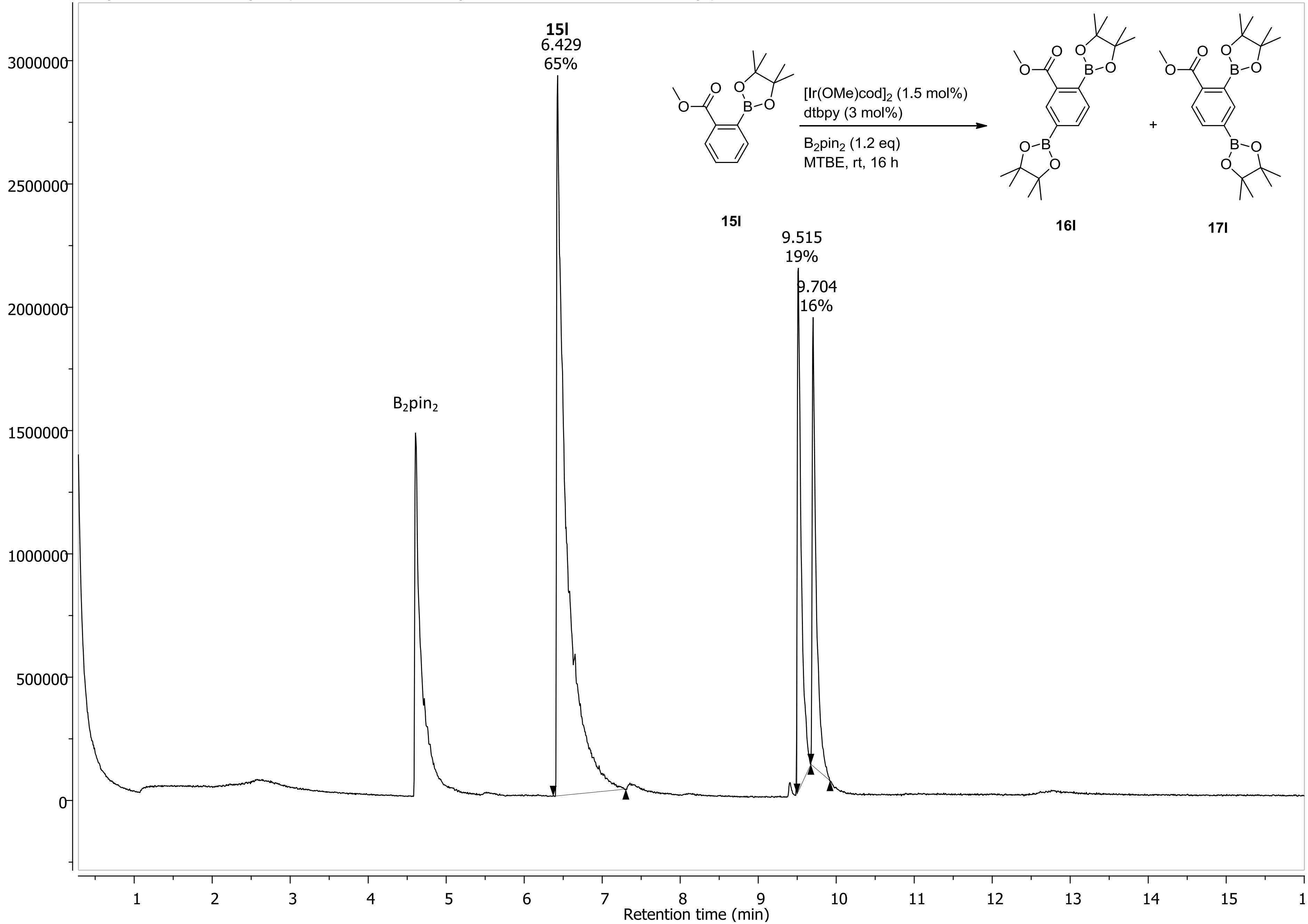
^{1}H NMR (400 MHz, $CDCl_3$) - Borylation of 1-(2-chlorophenyl)ethanone, 15j



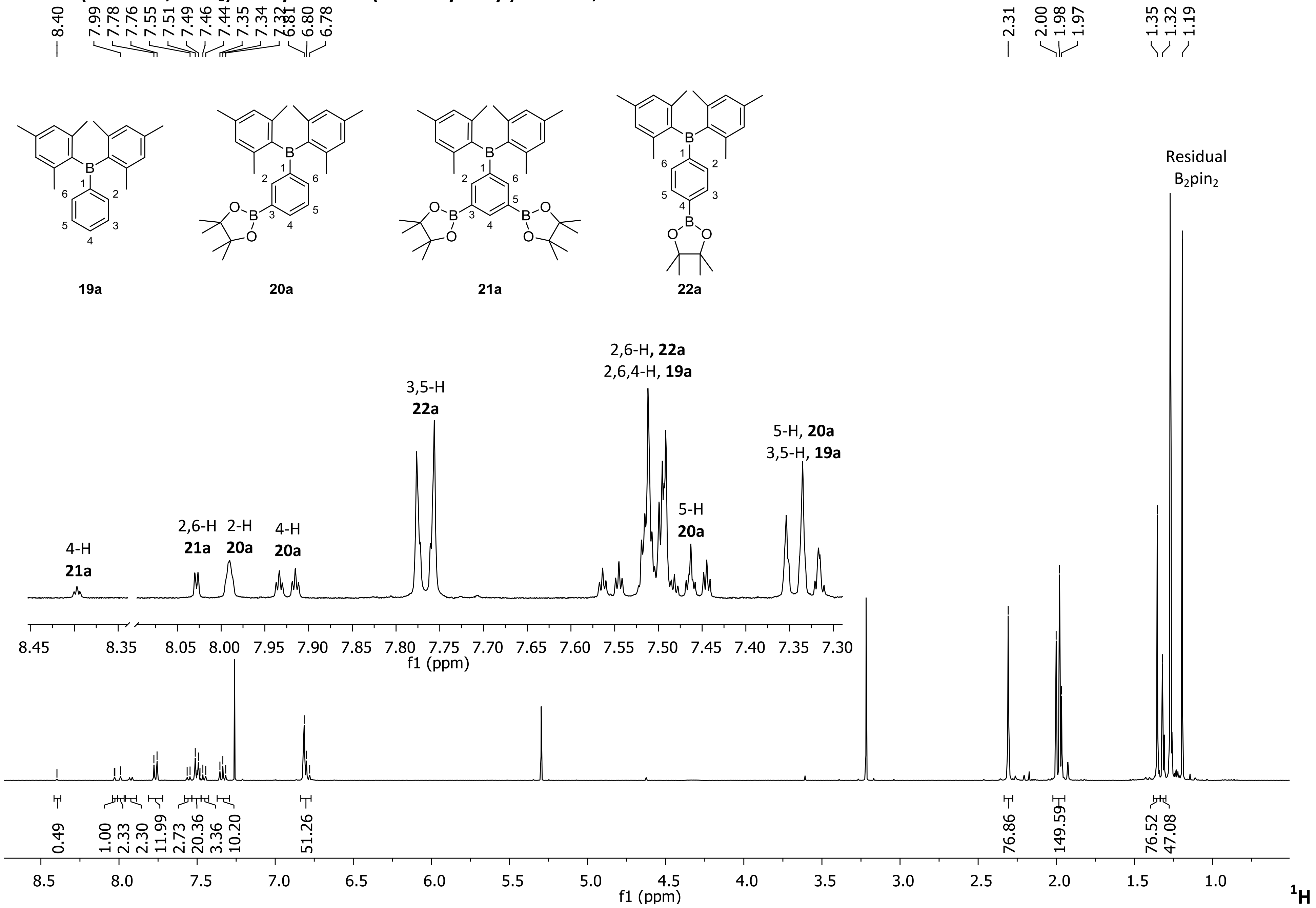
^{1}H NMR (600 MHz, acetone-d$_6$) - Borylation of 2-(2-chlorophenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane, 15k



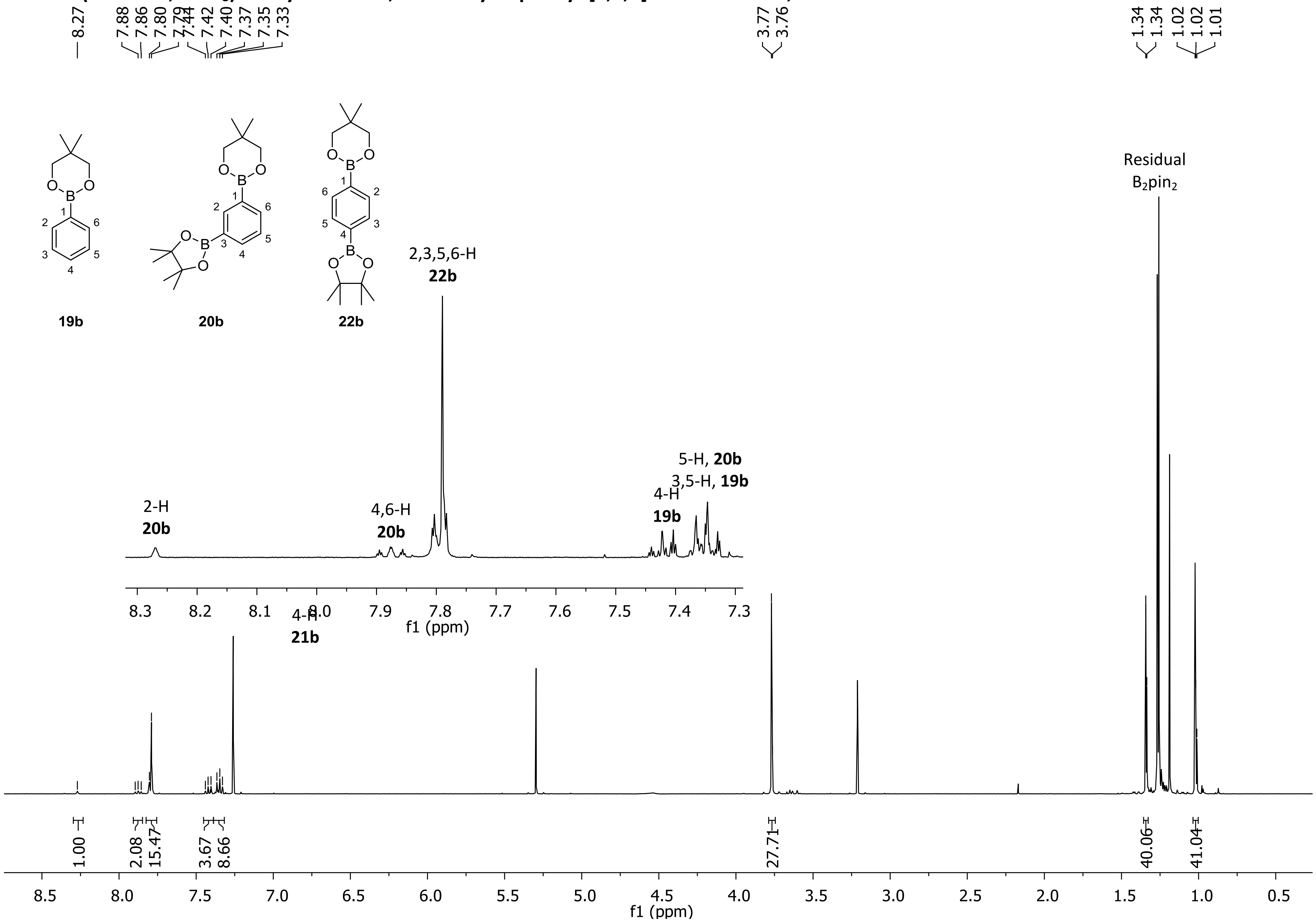
GC/MS - Borylation of methyl 2-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)benzoate, 15l



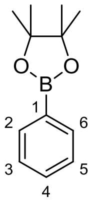
^{1}H NMR (400 MHz, $CDCl_3$) - Borylation of (Dimesitylboryl)benzene, 19a



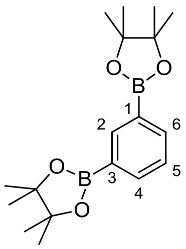
^{1}H NMR (400 MHz, $CDCl_3$) - Borylation of 5,5-dimethyl-2-phenyl-[1,3,2]-dioxaborinane, 19b



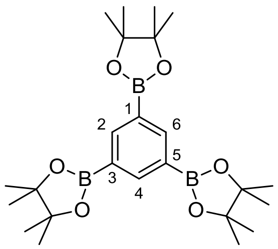
NMR (400 MHz, $CDCl_3$) - Borylation of 4,4,5,5-tetramethyl-2-phenyl-[1,3,2]-dioxaborolane, 19c



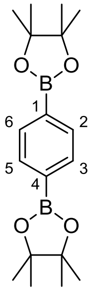
19c



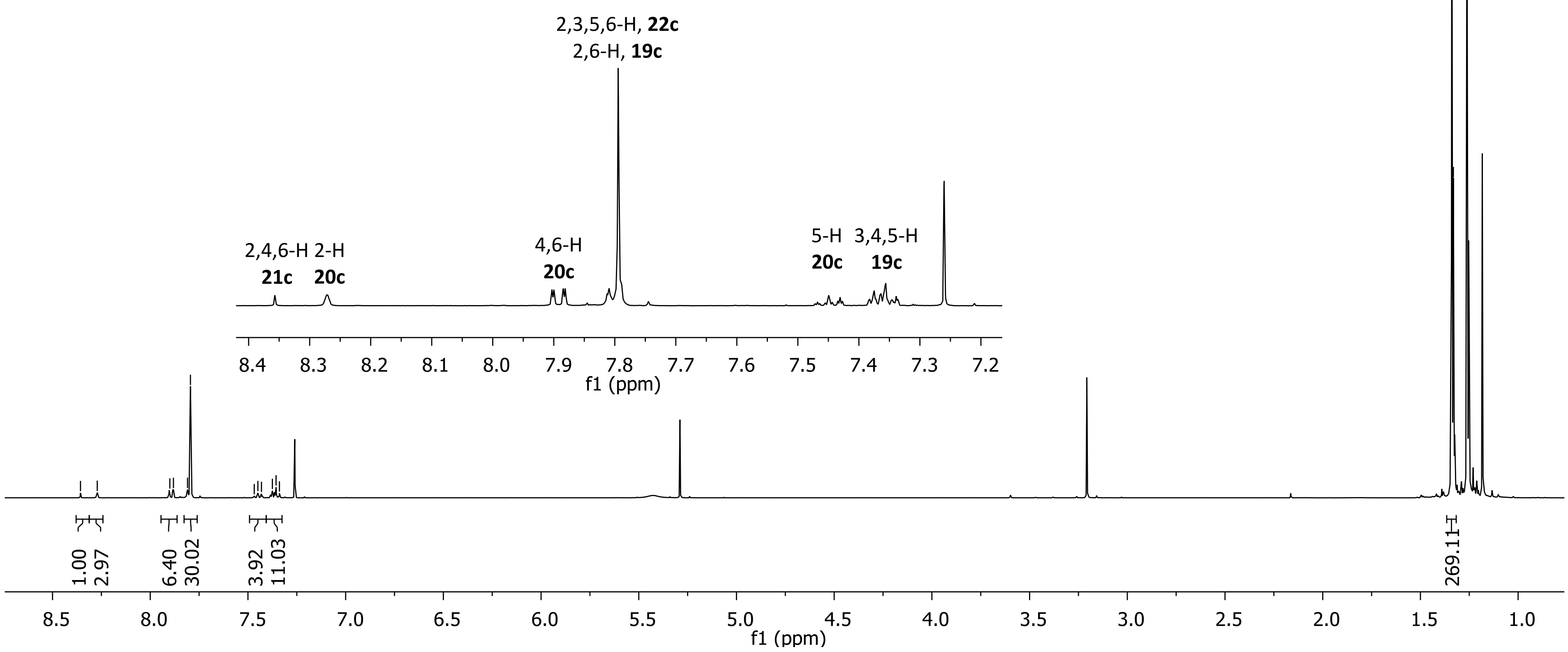
20c



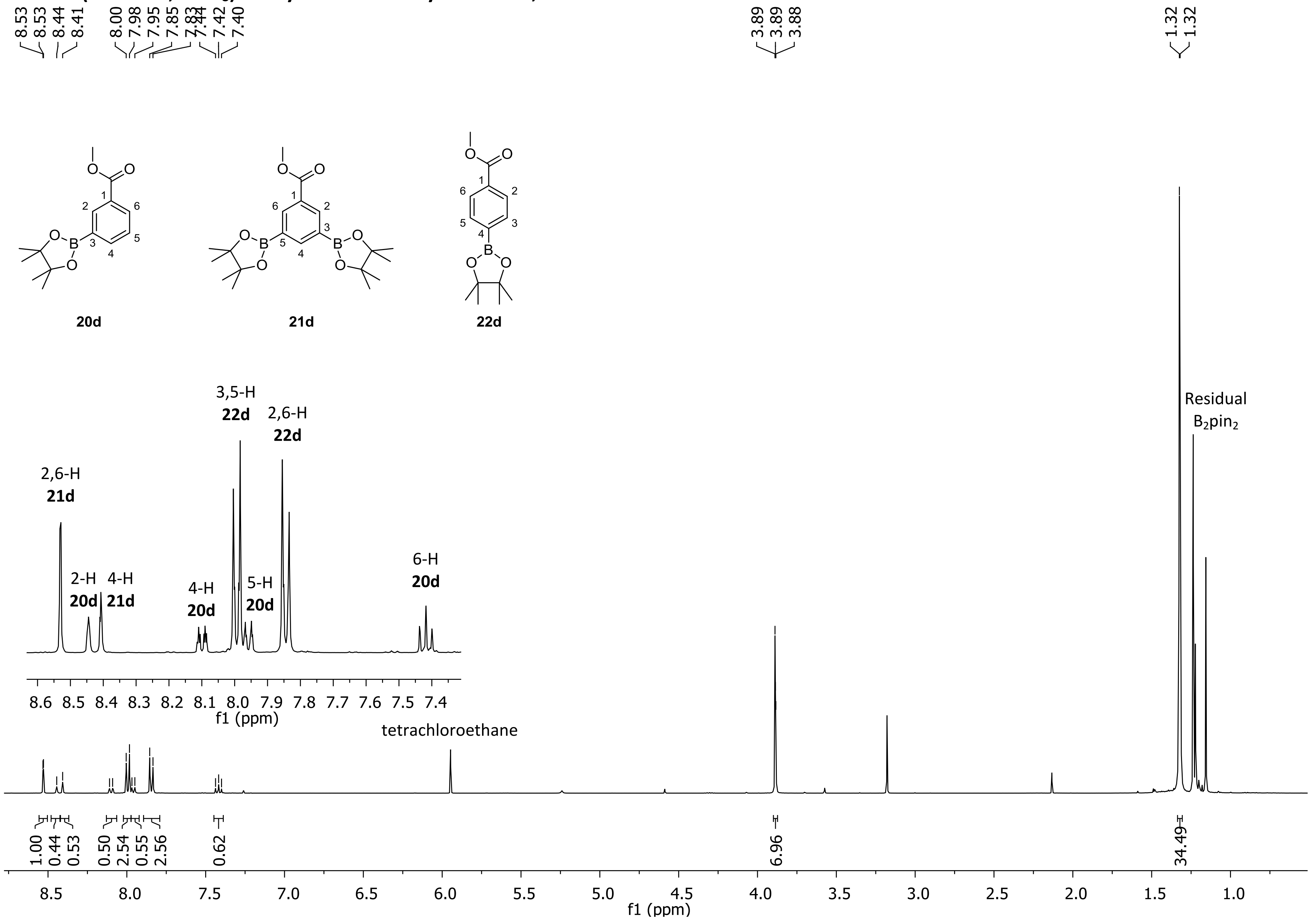
21c



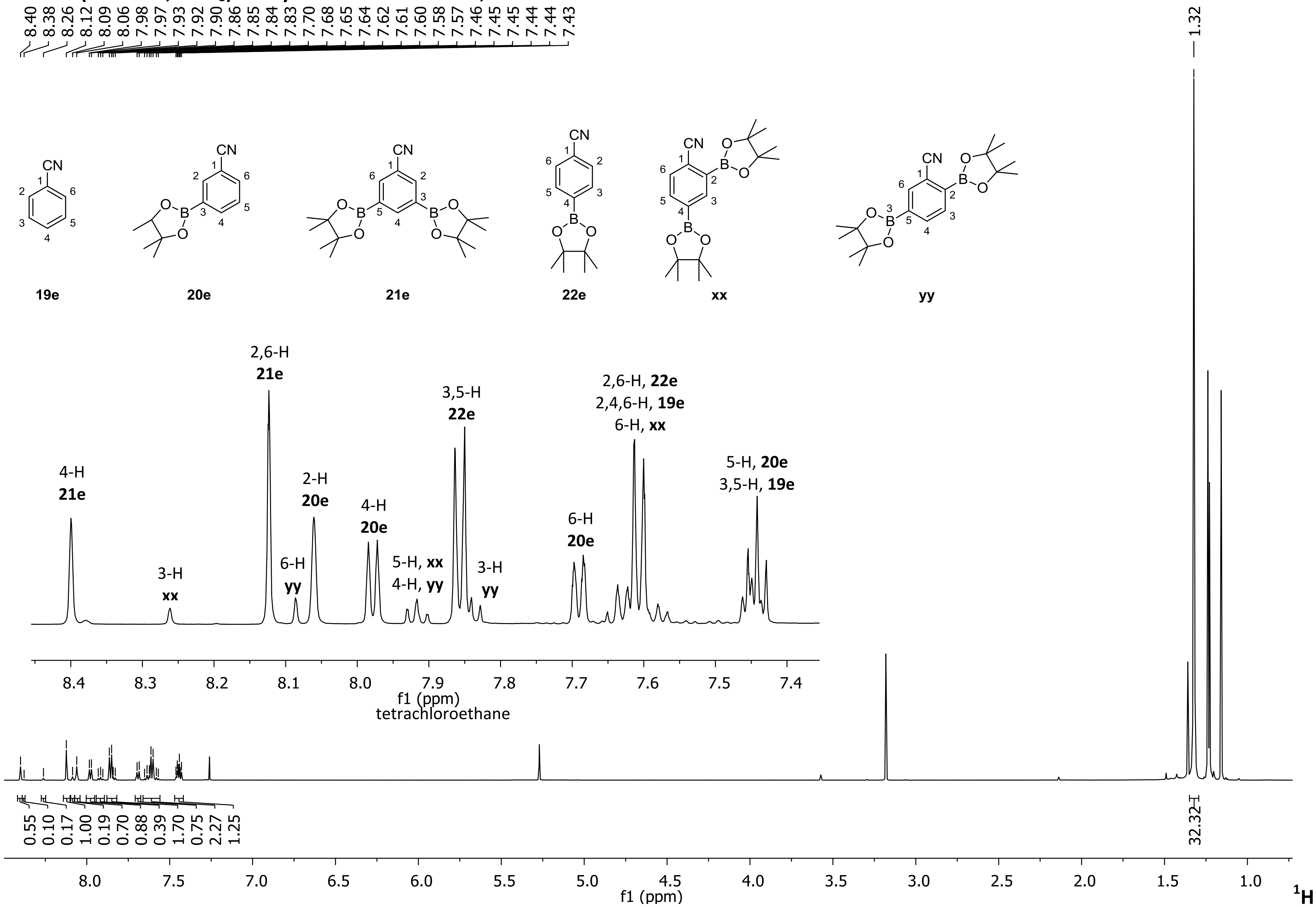
22c



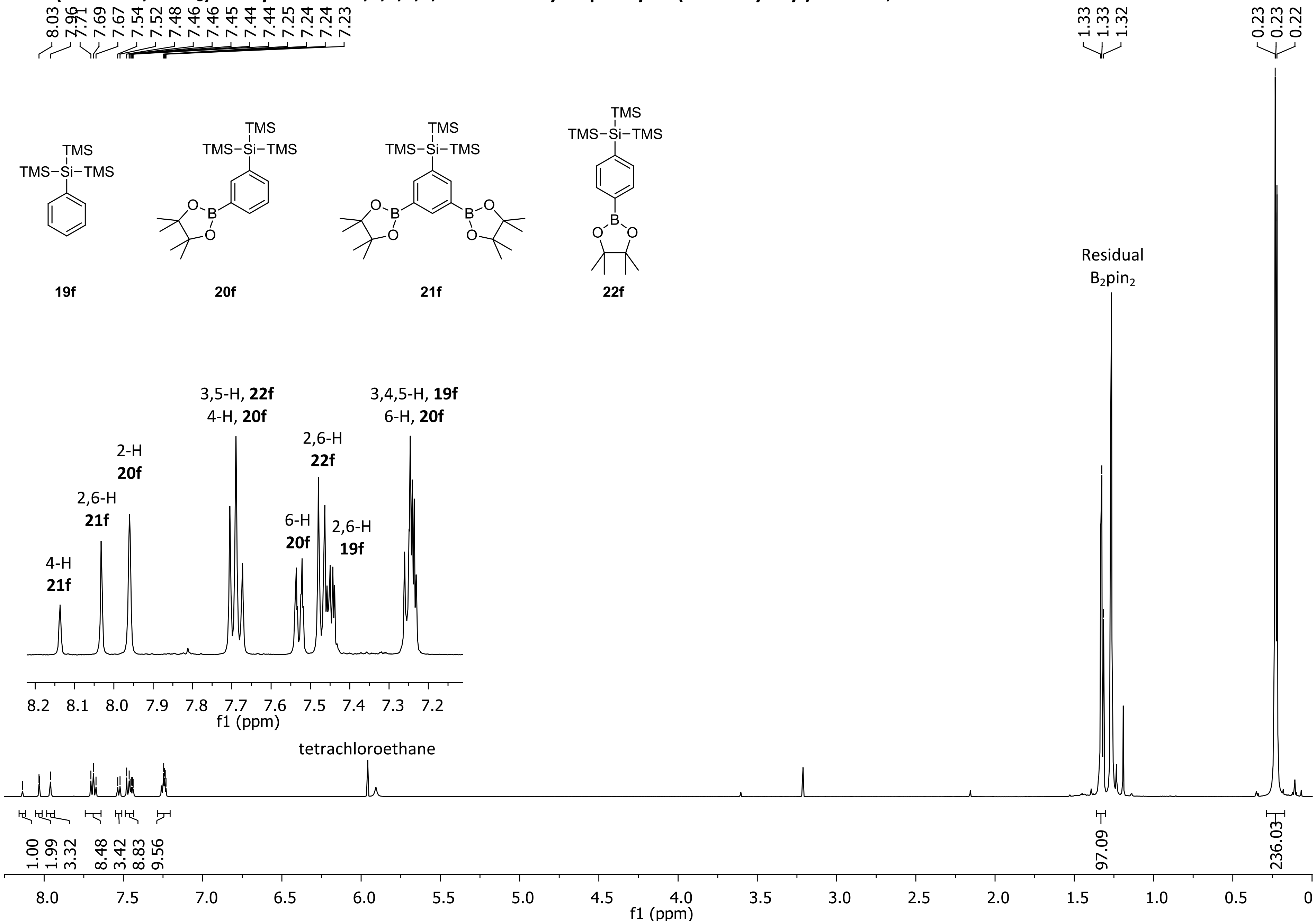
[1]H NMR (400 MHz, $CDCl_3$) - Borylation of methyl benzoate, 19d



^{1}H NMR (500 MHz, $CDCl_3$) - Borylation of benzonitrile, 19e



NMR (500 MHz, $CDCl_3$) - Borylation of 1,1,1,3,3,3-hexamethyl-2-phenyl-2-(trimethylsilyl)trisilane, 19f



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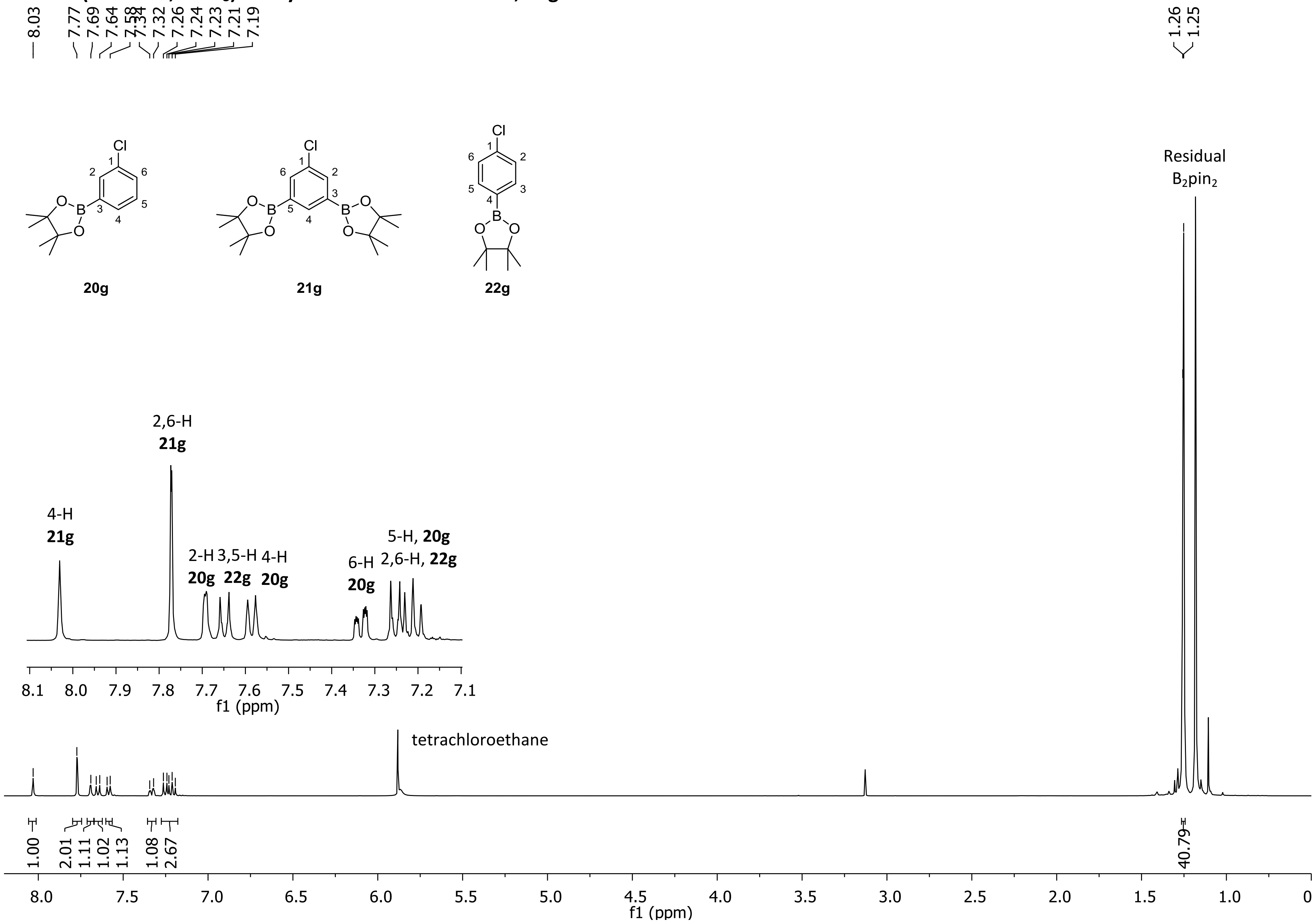
^{1}H NMR (400 MHz, $CDCl_3$) - **Borylation of chlorobenzene, 19g**



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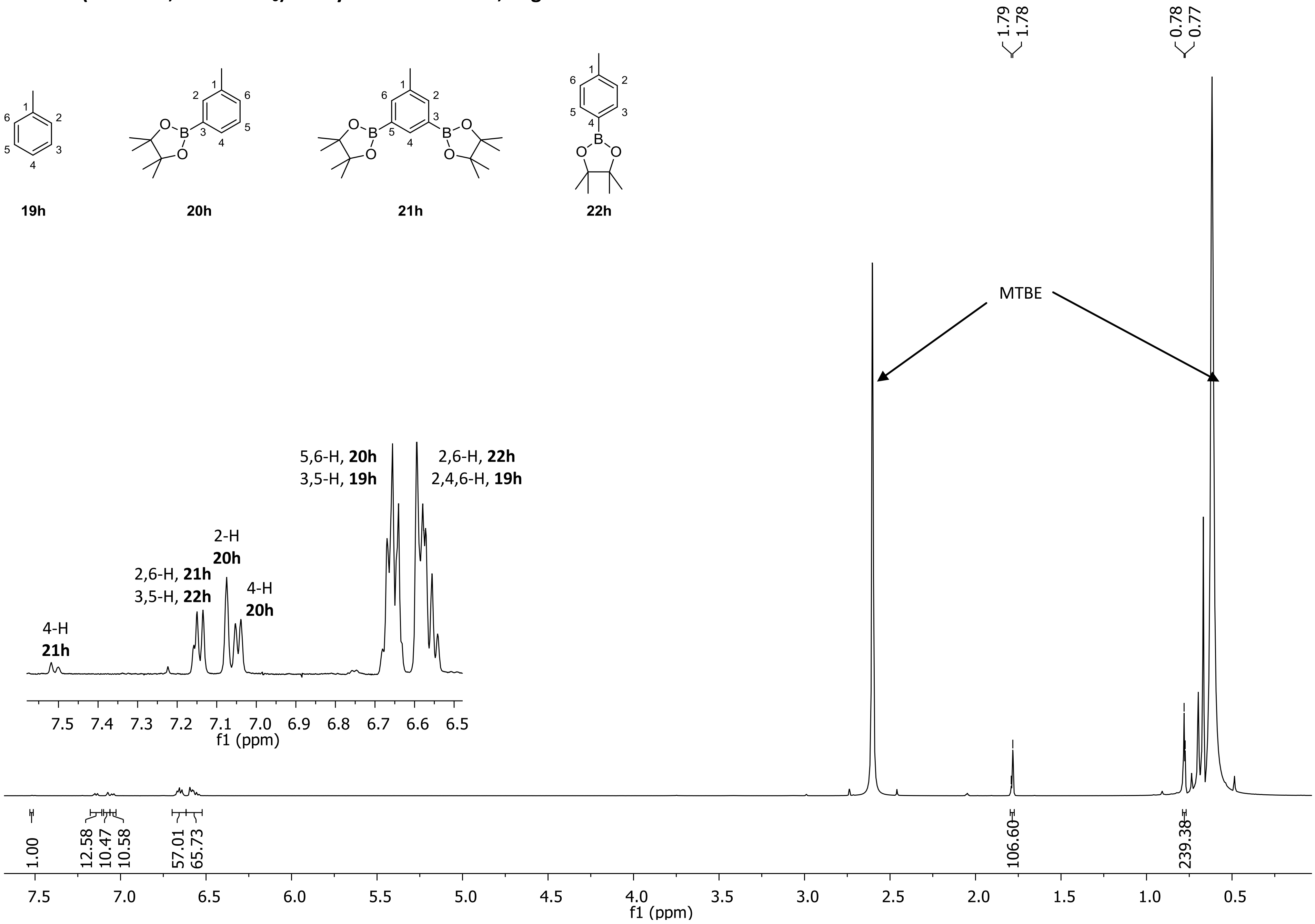
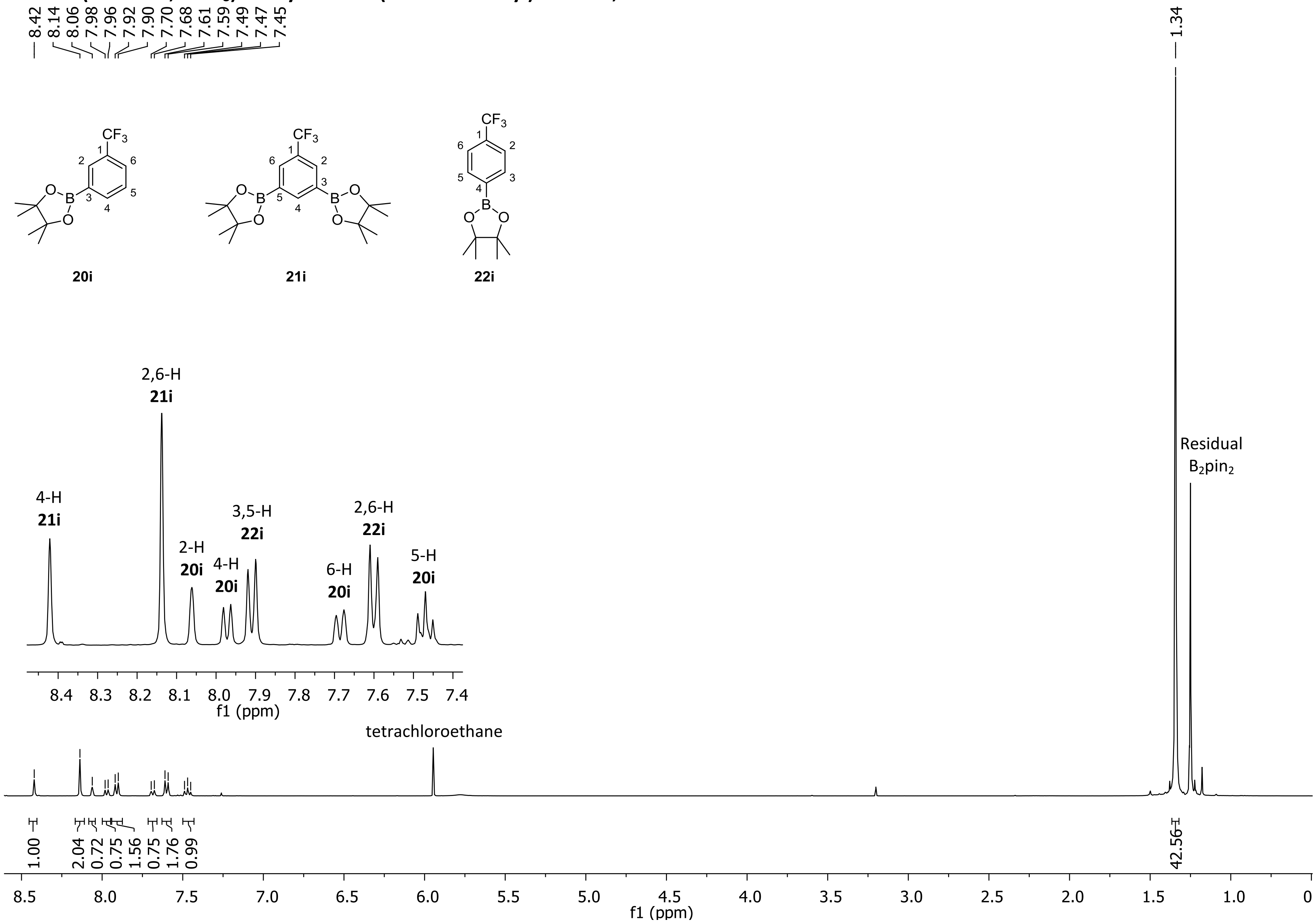
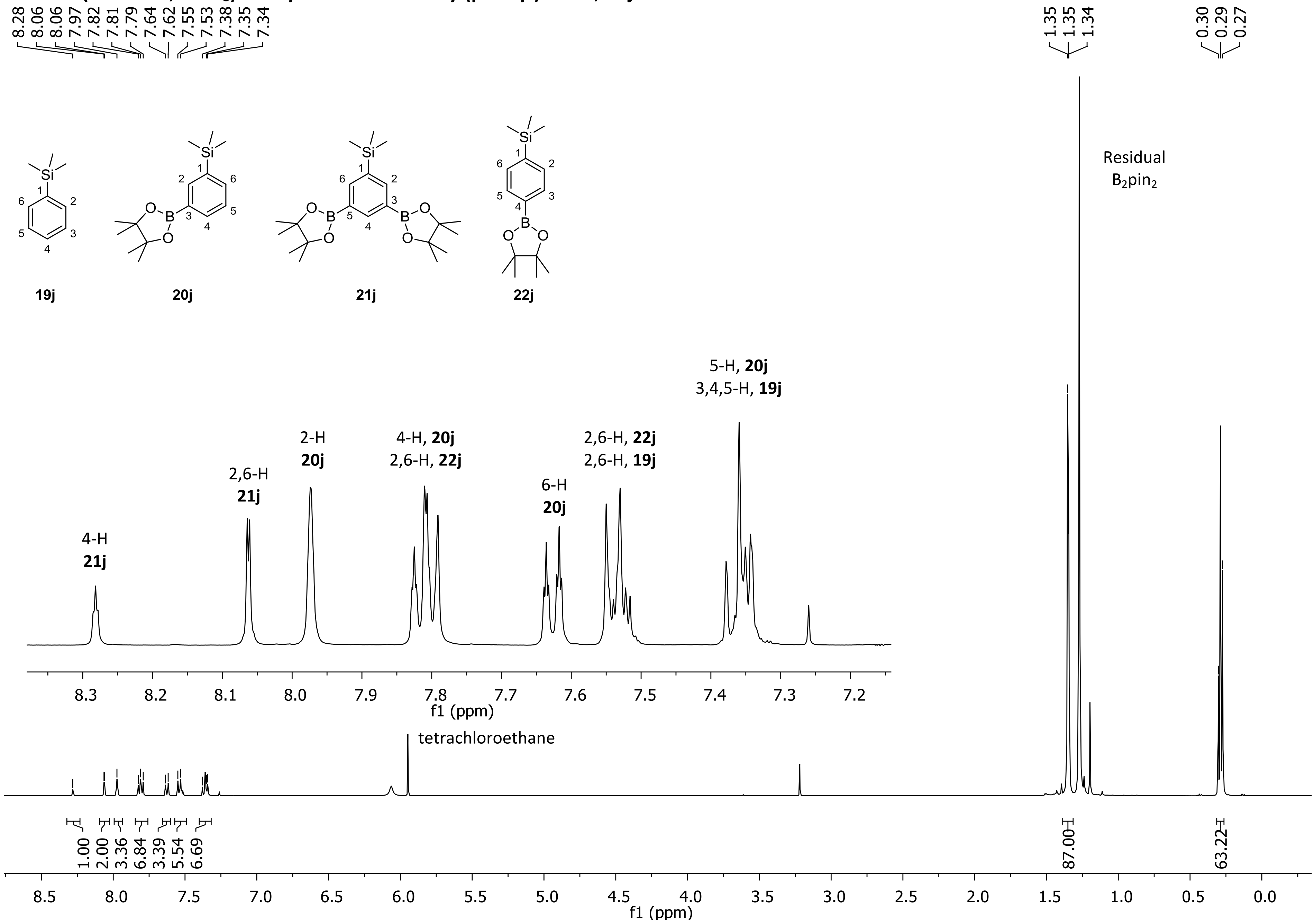
^{1}H NMR (500 MHz, acetone-d_6) - Borylation of toluene, 19g



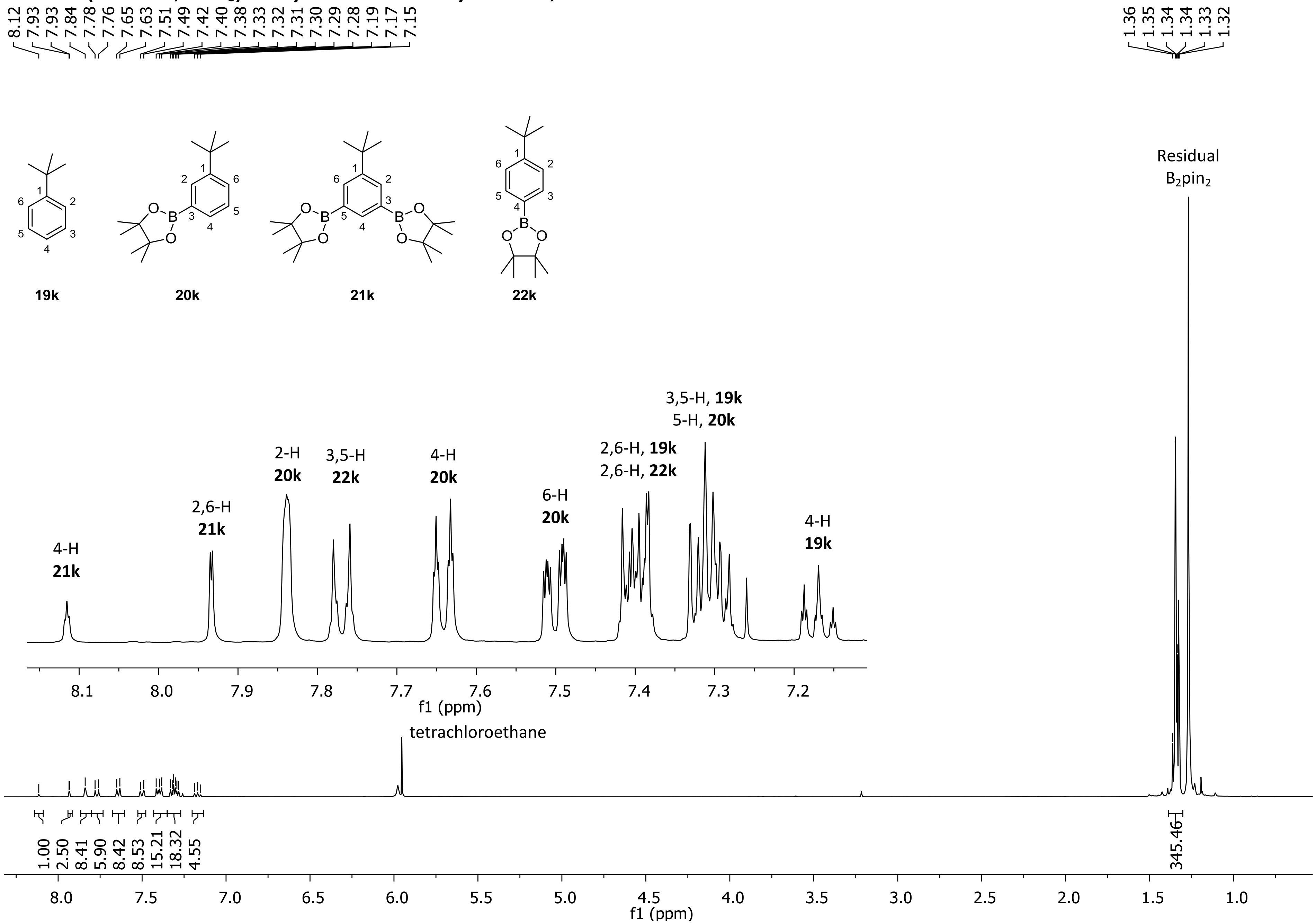
^{1}H NMR (500 MHz, $CDCl_3$) - Borylation of (trifluoromethyl)benzene, 19i



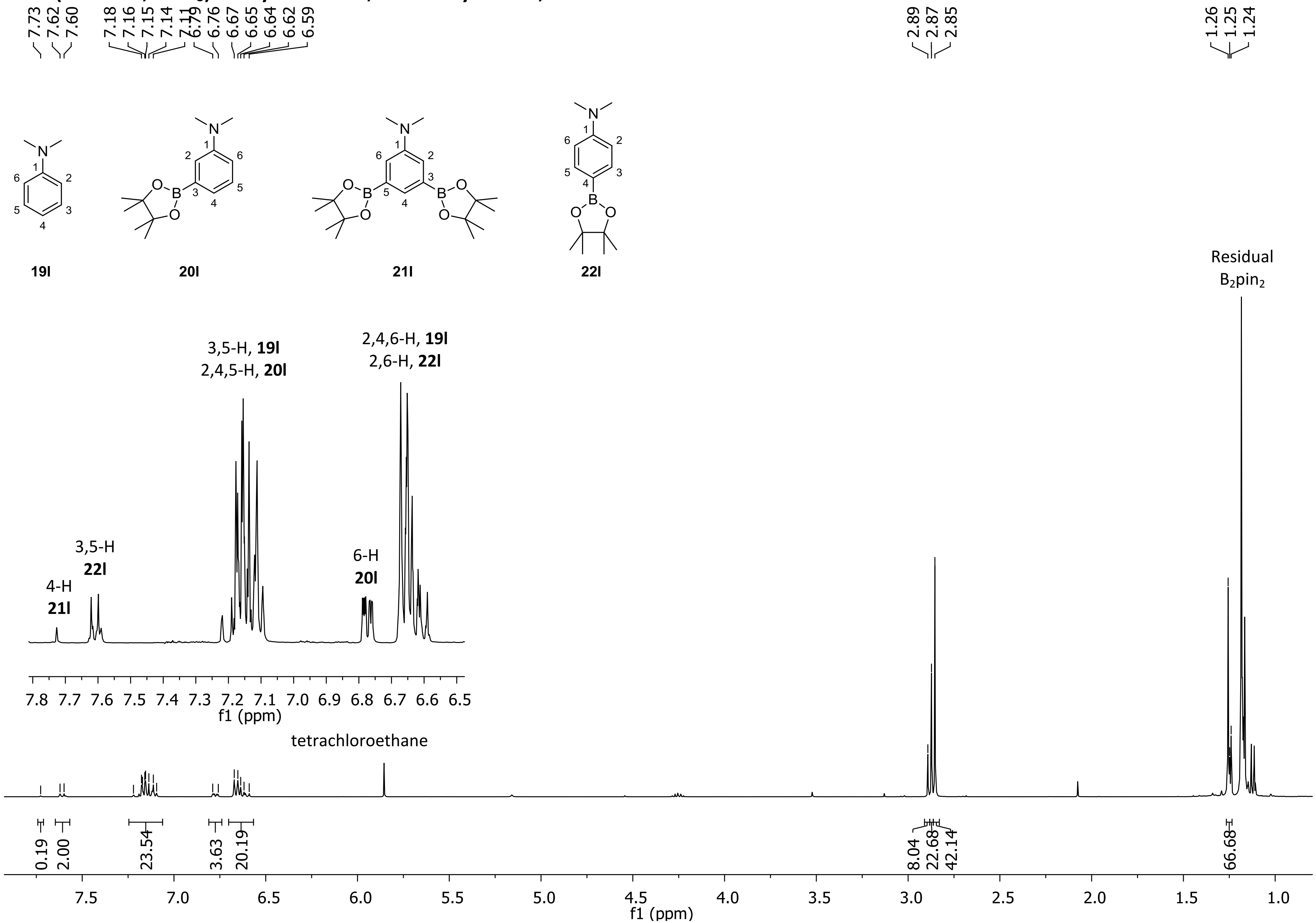
^{1}H NMR (400 MHz, $CDCl_3$) - Borylation of trimethyl(phenyl)silane, 19j



^{1}H NMR (400 MHz, $CDCl_3$) - Borylation of *tert*-butylbenzene, 19k



NMR (400 MHz, $CDCl_3$) - Borylation of N,N-dimethylaniline, 19l



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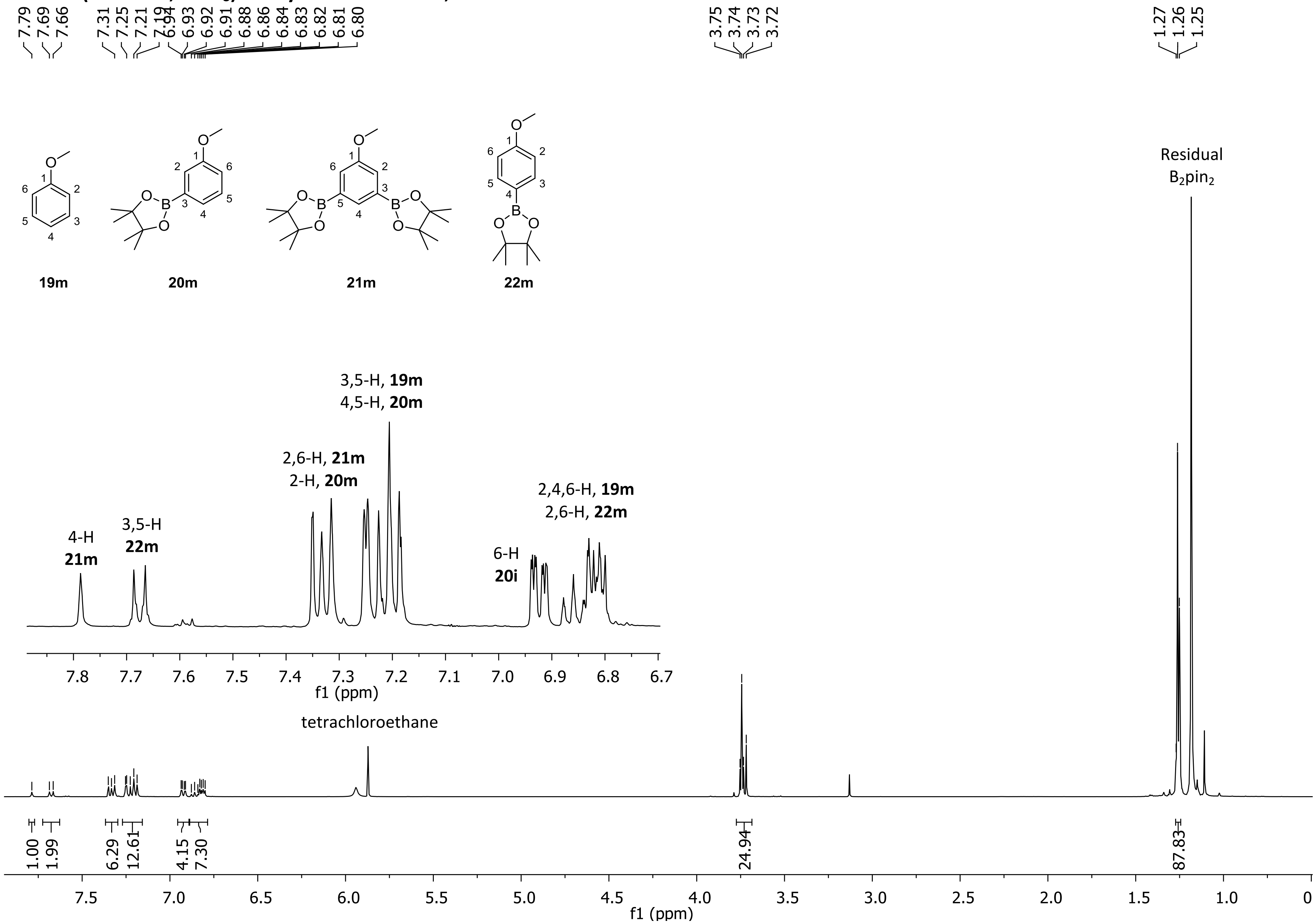
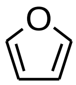
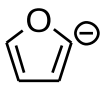
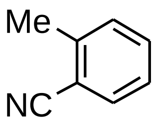
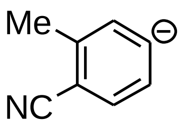
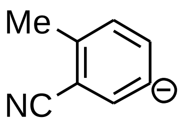
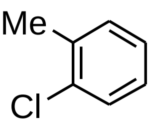
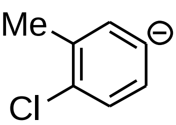
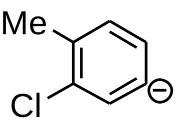
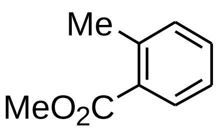
^{1}H NMR (400 MHz, $CDCl_3$) - Borylation of anisole, 19m



8.0 pKa Calculations

8.1 Table S5 - Electronic Energies, Thermal Correction to Gibbs Free Energies and Solvation Free Energies

Molecule	TCG	E	G(gas)=TCG+E	ΔG_{solv}(kcal/mol)
	0.043925	-230.1031818	-230.0592568	-2.35
	0.028617	-229.4671449	-229.4385279	-64.35
	0.094396	-363.9294711	-363.8350751	-3.32
	0.079339	-363.3010946	-363.2217556	-52.57
	0.078612	-363.2998986	-363.2212866	-53.49
	0.087421	-731.2842418	-731.1968208	-0.58
	0.071864	-730.641885	-730.570021	-55.03
	0.07167	-730.6450551	-730.5733851	-54.33
	0.135411	-499.6131694	-499.4777584	-1.02

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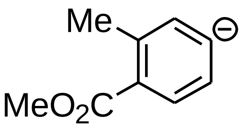
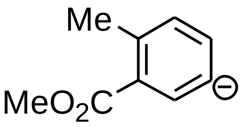
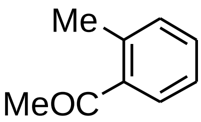
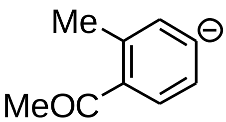
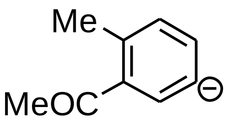
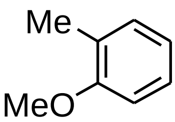
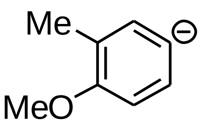
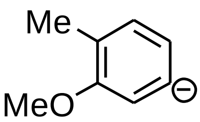
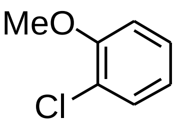
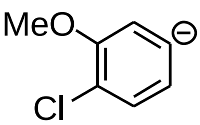
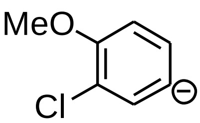
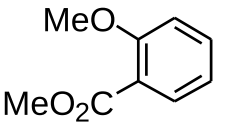
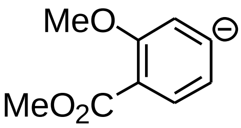
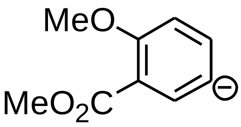
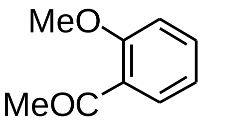
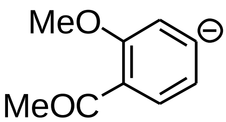
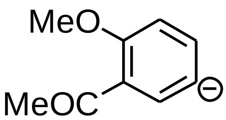
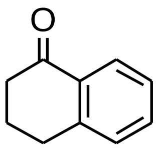
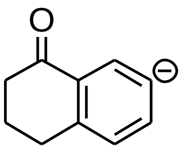
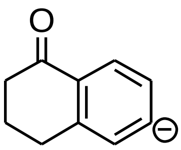
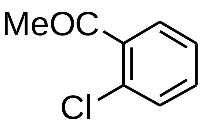
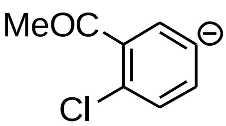
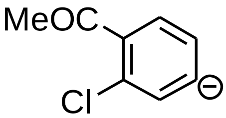
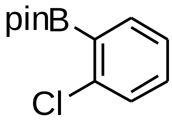
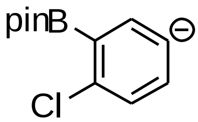
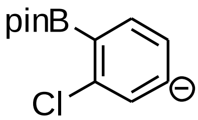
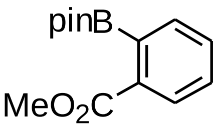
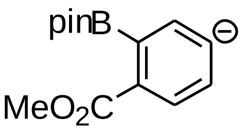
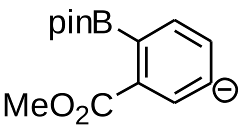
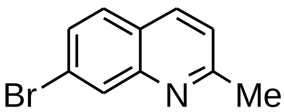
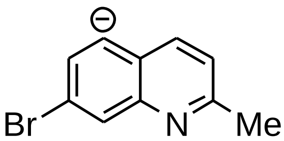
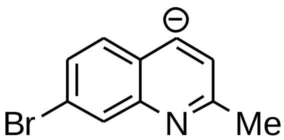
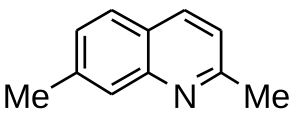
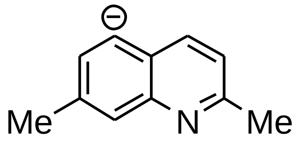
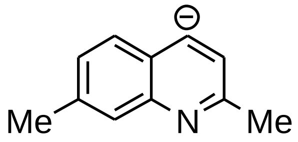
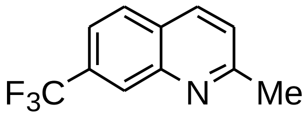
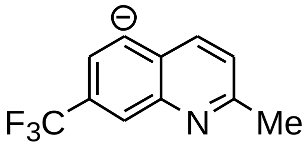
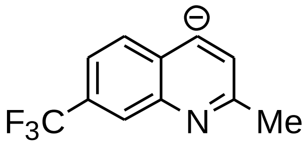
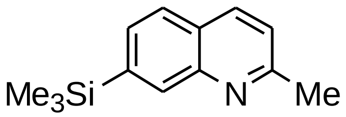
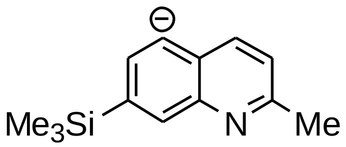
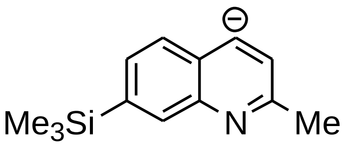
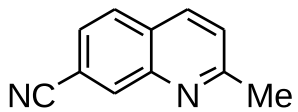
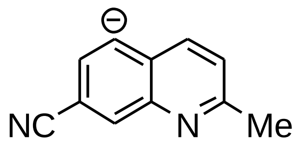
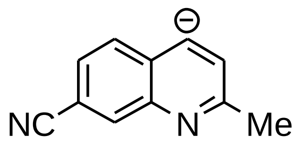
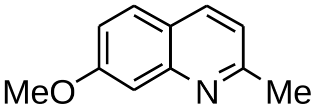
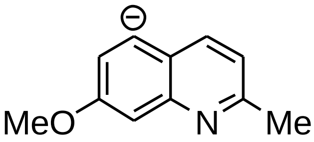
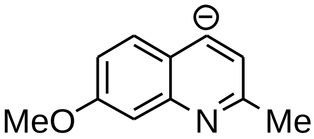
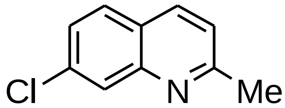
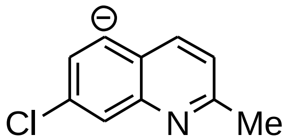
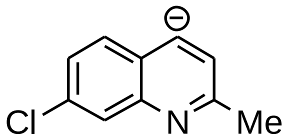
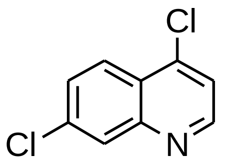
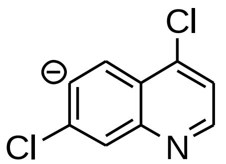
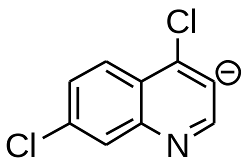
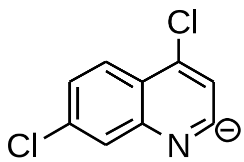
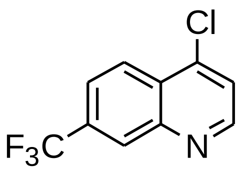
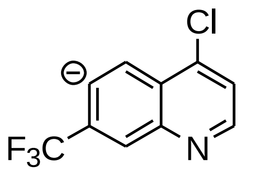
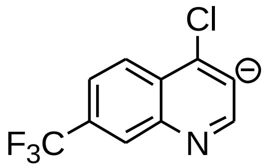
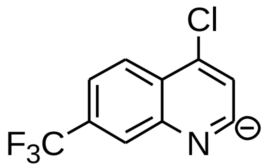
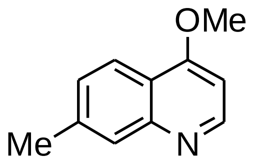
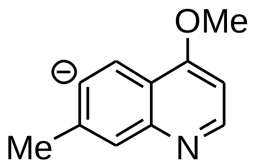
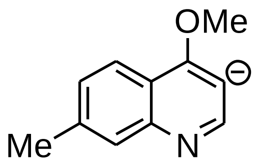
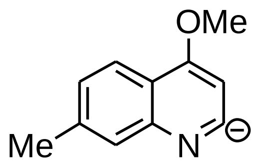
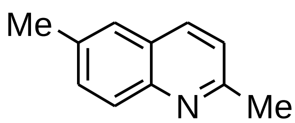
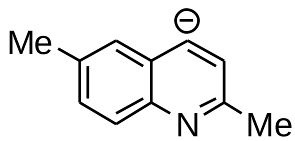
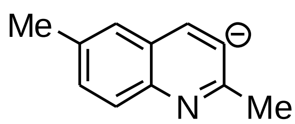
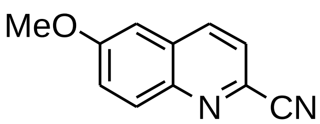
	0.120408	-498.9747251	-498.8543171	-54.3
	0.119885	-498.9706458	-498.8507608	-55.83
	0.132162	-424.3511293	-424.2189673	-1.69
	0.117166	-423.71567	-423.598504	-53.76
	0.116112	-423.7127063	-423.5965943	-54.62
	0.128488	-386.221046	-386.092558	-0.31
	0.11238	-385.5652747	-385.4528947	-59.93
	0.112486	-385.5681474	-385.4556614	-59.05
	0.090858	-806.5145608	-806.4237028	-2.57
	0.075198	-805.873653	-805.798455	-56.82
	0.074948	-805.8734032	-805.7984552	-56.83

	0.137663	-574.8426897	-574.7050267	-3.74
	0.123253	-574.2061827	-574.0829297	-56.87
	0.122779	-574.1994545	-574.0766755	-59.29
	0.133629	-499.5807817	-499.4471527	-4.55
	0.11981	-498.9466621	-498.8268521	-56.92
	0.118863	-498.9407524	-498.8218894	-58.36
	0.141998	-462.4748584	-462.3328604	-2.86
	0.125633	-461.8332084	-461.7075754	-57.66
	0.126898	-461.839283	-461.712385	-55.27
	0.093887	-844.6438603	-844.5499733	-2.55
	0.078448	-844.0142435	-843.9357955	-53.08

	0.077845	-844.0202292	-843.9423842	-50.81
	0.221125	-1102.77853	-1102.557405	3.77
	0.20508	-1102.13634	-1101.93126	-50.61
	0.205654	-1102.14296	-1101.937306	-49.12
	0.269426	-871.1095955	-870.8401695	3.41
	0.253823	-870.4711872	-870.2173642	-50.17
	0.253	-870.4689186	-870.2159186	-50.96
	0.116562	-3014.931905	-3014.815343	-3.03
	0.101185	-3014.311748	-3014.210563	-50.18
	0.101059	-3014.311169	-3014.21011	-50.23
	0.155215	-480.7217832	-480.5665682	-1.41

	0.139507	-480.0843048	-479.9447978	-54.53
	0.139544	-480.0904231	-479.9508791	-53.66
	0.12692	-778.5575277	-778.4306077	-1.66
	0.112834	-777.9356782	-777.8228442	-49.05
	0.112571	-777.9405829	-777.8280119	-47.36
	0.221054	-850.1410867	-849.9200327	4.27
	0.205581	-849.5071898	-849.3016088	-46.54
	0.205563	-849.5135096	-849.3079466	-45.49
	0.125674	-533.6620532	-533.5363792	-5.25
	0.110802	-533.0467284	-532.9359264	-50.54
	0.110502	-533.0503584	-532.9398564	-48.96

	0.159291	-555.9574044	-555.7981134	-2.57
	0.143846	-555.3218622	-555.1780162	-55.9
	0.14335	-555.3258282	-555.1824782	-54.78
	0.118017	-901.0177945	-900.8997775	-2.71
	0.102652	-900.3954125	-900.2927605	-50.84
	0.10226	-900.3962655	-900.2940055	-50.51
	0.081318	-1321.309512	-1321.228194	-3.14
	0.065561	-1320.695815	-1320.630254	-50.59
	0.065957	-1320.703509	-1320.637552	-48.59
	0.06466	-1320.684956	-1320.620296	-51.59
	0.090705	-1198.848459	-1198.757754	-2.1

	0.07661	-1198.233853	-1198.157243	-49.03
	0.078317	-1198.24763	-1198.169313	-45.59
	0.07697	-1198.228344	-1198.151374	-48.76
	0.159744	-555.9556434	-555.7958994	-3.06
	0.143875	-555.3132824	-555.1694074	-57.54
	0.143942	-555.3329563	-555.1890143	-52.16
	0.14311	-555.3080124	-555.1649024	-60.68
	0.155111	-480.7215334	-480.5664224	-1.42
	0.139427	-480.0900652	-479.9506382	-53.52
	0.139704	-480.086793	-479.947089	-53.56
	0.129903	-608.8914819	-608.7615789	-6.55

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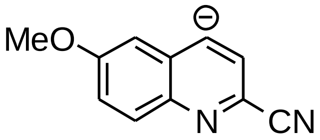
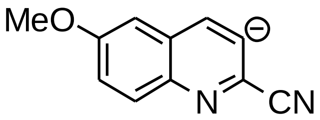
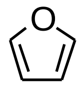
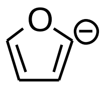
	0.11505	-608.2824471	-608.1673971	-50.43
	0.114834	-608.2796501	-608.1648161	-54.23

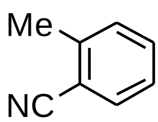
8.2 Table S6 - Cartesian Coordinates Optimized by Optimal Method



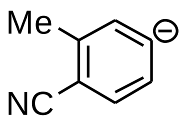
O	0.000151	-1.161037	0.000349
C	1.094995	-0.347333	0.000167
C	0.717811	0.960016	-0.000013
C	-0.718063	0.959833	-0.000060
C	-1.094903	-0.347615	0.000206
H	2.050259	-0.849771	0.000253
H	1.373472	1.819650	-0.000132
H	-1.373952	1.819294	-0.000214
H	-2.050042	-0.850293	0.000321



O	0.798691	-0.861140	-0.000193
C	1.009021	0.487236	0.000161
C	-0.183276	1.148571	-0.000083
C	-1.185427	0.114502	-0.000020
C	-0.616738	-1.162075	0.000169
H	2.040376	0.831902	0.000302
H	-0.311266	2.229784	-0.000127
H	-2.260120	0.298028	0.000002

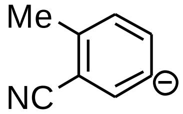


C	-0.718984	-1.273500	0.043906
C	0.671825	-1.278690	-0.002049
C	1.362943	-0.067280	-0.052925
C	0.665339	1.141948	-0.057746
C	-0.731017	1.179714	-0.012378
C	-1.417825	-0.055256	0.038907
H	-1.276128	-2.204193	0.083883
H	1.211157	-2.221142	0.001870
H	2.448882	-0.061634	-0.089008
H	1.214481	2.079090	-0.097559
C	-1.481873	2.487803	-0.017927
H	-2.157749	2.556603	-0.878513
H	-2.102993	2.595600	0.879116
H	-0.791332	3.334856	-0.058293
C	-2.851484	-0.071759	0.086769
N	-4.014628	-0.077938	0.125409



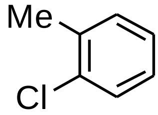
C	-0.718849	-1.268827	0.035538
C	0.672584	-1.242290	-0.021859
C	1.474197	-0.063896	-0.080872
C	0.661830	1.106996	-0.073895
C	-0.735549	1.167358	-0.018328
C	-1.447025	-0.058837	0.038136

H	-1.272974	-2.209275	0.079265
H	1.166204	-2.225002	-0.020063
H	1.158450	2.089397	-0.115953
C	-1.476224	2.486646	-0.017669
H	-2.161473	2.579292	-0.872184
H	-2.091291	2.617899	0.883889
H	-0.765351	3.320256	-0.064421
C	-2.870991	-0.081923	0.096711
N	-4.039643	-0.099081	0.143850

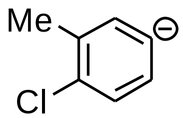


C	-0.687067	-1.267983	0.041230
C	0.723991	-1.384424	-0.003223
C	1.328924	-0.100577	-0.052136
C	0.652638	1.132213	-0.057227
C	-0.739942	1.193062	-0.012167
C	-1.416872	-0.049117	0.038209
H	-1.305202	-2.173948	0.082104
H	2.426878	-0.031117	-0.090314
H	1.211695	2.072870	-0.096927
C	-1.483437	2.508280	-0.016670
H	-2.165157	2.598574	-0.874278
H	-2.103314	2.639572	0.881635
H	-0.779262	3.348358	-0.061032

C	-2.847411	-0.075466	0.086354
N	-4.014856	-0.131241	0.125906

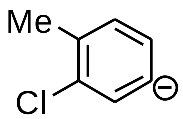


C	-0.297681	-1.545920	0.062331
C	1.095500	-1.545884	-0.000602
C	1.785201	-0.335586	-0.064570
C	1.078519	0.866536	-0.065241
C	-0.321682	0.903784	-0.003033
C	-0.982581	-0.332118	0.060343
H	-0.854352	-2.475709	0.112701
H	1.633524	-2.489612	0.000698
H	2.870366	-0.325211	-0.113842
H	1.619161	1.808558	-0.115180
C	-1.064985	2.215215	-0.005004
H	-1.751653	2.284892	-0.856673
H	-1.672301	2.332521	0.900050
H	-0.366429	3.055198	-0.059323
Cl	-2.746223	-0.374596	0.141210



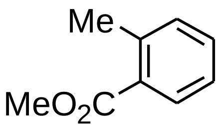
C	-0.297396	-1.542469	0.055369
C	1.104717	-1.504089	-0.026086

C	1.899778	-0.329439	-0.103674
C	1.081062	0.827556	-0.088268
C	-0.330420	0.889682	-0.009066
C	-0.993354	-0.337761	0.062424
H	-0.847490	-2.482513	0.112602
H	1.593025	-2.491014	-0.027215
H	1.559864	1.819544	-0.142765
C	-1.062642	2.210535	-0.003102
H	-1.761701	2.305612	-0.846307
H	-1.660238	2.353957	0.908511
H	-0.343081	3.036087	-0.067430
Cl	-2.802063	-0.387388	0.167556



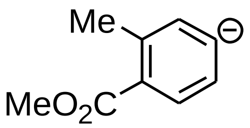
C	-0.262985	-1.554619	0.060119
C	1.153254	-1.636819	-0.001814
C	1.762174	-0.357341	-0.063530
C	1.078910	0.864072	-0.065277
C	-0.324067	0.910695	-0.002908
C	-0.945161	-0.340966	0.058694
H	-0.876639	-2.461863	0.112347
H	2.859273	-0.290355	-0.115243
H	1.621735	1.816151	-0.115375
C	-1.071411	2.220862	-0.004218

H	-1.760803	2.307468	-0.855615
H	-1.682973	2.353653	0.898993
H	-0.365059	3.059001	-0.057799
Cl	-2.798476	-0.361294	0.143494



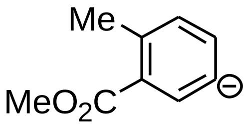
C	-1.338072	-1.046422	0.008569
C	0.049681	-1.131579	-0.007868
C	0.805001	0.040683	-0.029978
C	0.164972	1.278587	-0.035424
C	-1.231578	1.395523	-0.019266
C	-1.990468	0.198592	0.003277
H	-1.937194	-1.948782	0.025838
H	0.535761	-2.103062	-0.003454
H	1.890900	-0.005994	-0.043038
H	0.761228	2.187396	-0.052767
C	-1.840513	2.778123	-0.026881
H	-2.491288	2.929098	-0.893196
H	-2.469724	2.948087	0.851783
H	-1.049553	3.534847	-0.044877
C	-3.481226	0.239592	0.021808
O	-4.167430	1.244749	0.020420
O	-4.029937	-1.002348	0.041619
C	-5.463231	-1.035217	0.060918

H	-5.872886	-0.548595	-0.828491
H	-5.730295	-2.092589	0.076480
H	-5.849505	-0.528235	0.949392

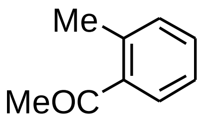


C	-1.332767	-1.053654	0.002531
C	0.055835	-1.104314	-0.017415
C	0.923180	0.029350	-0.041294
C	0.165731	1.235811	-0.041675
C	-1.228939	1.374761	-0.022171
C	-2.016146	0.186512	0.000758
H	-1.923185	-1.968598	0.019827
H	0.495177	-2.113172	-0.014084
H	0.712906	2.191704	-0.058990
C	-1.837955	2.761025	-0.025975
H	-2.492079	2.928455	-0.890279
H	-2.465863	2.944644	0.854346
H	-1.036563	3.511063	-0.044964
C	-3.475032	0.233889	0.021664
O	-4.203230	1.221851	0.023070
O	-4.056873	-1.027321	0.041883
C	-5.474552	-1.021770	0.062454
H	-5.890550	-0.525433	-0.822308
H	-5.777295	-2.073146	0.077317

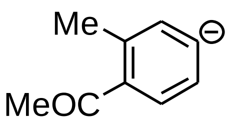
H	-5.864744	-0.507754	0.948856



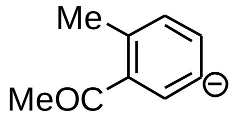
C	-1.302042	-1.058270	0.090913
C	0.102520	-1.252481	0.042996
C	0.764124	-0.000976	-0.037265
C	0.141765	1.259924	-0.042047
C	-1.246715	1.394071	-0.014073
C	-1.992824	0.183286	0.040543
H	-1.946562	-1.937114	0.185436
H	1.863492	0.021079	-0.110435
H	0.745586	2.172761	-0.089655
C	-1.861678	2.776180	-0.057065
H	-2.573811	2.894637	-0.882970
H	-2.428111	3.011685	0.852084
H	-1.070445	3.528805	-0.174635
C	-3.462399	0.233207	0.079382
O	-4.179181	1.215476	0.244865
O	-4.051928	-1.005198	-0.088395
C	-5.468230	-1.002735	-0.005971
H	-5.915944	-0.367242	-0.778974
H	-5.776612	-2.042201	-0.150551
H	-5.816240	-0.640650	0.968683



C	-1.237587	-1.084377	0.014268
C	0.152809	-1.110106	-0.014128
C	0.852675	0.094871	-0.044343
C	0.153748	1.300875	-0.045660
C	-1.246107	1.354253	-0.017464
C	-1.958200	0.124238	0.013339
H	-1.774199	-2.026542	0.037750
H	0.681585	-2.059023	-0.012665
H	1.939348	0.099181	-0.066882
H	0.707628	2.236171	-0.069289
C	-1.907980	2.711983	-0.021622
H	-2.572887	2.836266	-0.881307
H	-2.536641	2.859271	0.861404
H	-1.145709	3.497828	-0.047808
C	-3.455437	0.082637	0.044812
O	-4.133429	1.101215	0.045107
C	-4.157476	-1.271685	0.077473
H	-3.910194	-1.874590	-0.804060
H	-3.873038	-1.851258	0.963433
H	-5.233467	-1.091337	0.097670

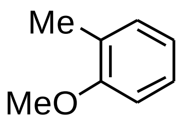


C	-1.241323	-1.077352	0.005988
C	0.147923	-1.075104	-0.028258
C	0.965946	0.093559	-0.062116
C	0.156082	1.266255	-0.055811
C	-1.242507	1.346644	-0.022187
C	-1.988155	0.127999	0.010366
H	-1.774463	-2.029481	0.030272
H	0.627381	-2.065660	-0.028524
H	0.663141	2.243870	-0.079720
C	-1.904166	2.707962	-0.021707
H	-2.574875	2.846148	-0.878053
H	-2.531640	2.866473	0.863424
H	-1.132383	3.488851	-0.049942
C	-3.451603	0.093167	0.046821
O	-4.181349	1.093171	0.053451
C	-4.158741	-1.274957	0.079876
H	-3.913884	-1.880107	-0.800988
H	-3.871522	-1.859097	0.962161
H	-5.236009	-1.091020	0.103657



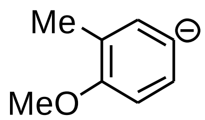
C	-1.209543	-1.081375	0.010159
C	0.200836	-1.227624	-0.018487
C	0.811321	0.052643	-0.046478

C	0.136633	1.286234	-0.046296
C	-1.255949	1.366371	-0.017397
C	-1.961349	0.127122	0.012183
H	-1.806147	-2.001187	0.033664
H	1.910844	0.122256	-0.070905
H	0.704971	2.222726	-0.069295
C	-1.916509	2.727296	-0.019157
H	-2.582904	2.869207	-0.878334
H	-2.546737	2.889141	0.863439
H	-1.146048	3.510541	-0.044138
C	-3.435931	0.093028	0.044008
O	-4.157848	1.097053	0.046946
C	-4.149823	-1.267771	0.076159
H	-3.901282	-1.873387	-0.802544
H	-3.862492	-1.852687	0.956984
H	-5.226479	-1.077922	0.097519



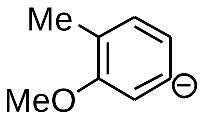
C	0.445723	-1.300875	0.240736
C	1.830247	-1.275642	0.042350
C	2.489063	-0.067605	-0.160010
C	1.752743	1.121957	-0.163566
C	0.372111	1.132147	0.030995
C	-0.276777	-0.104647	0.234989

H	-0.054428	-2.250035	0.396883
H	2.384725	-2.210419	0.048392
H	3.564074	-0.044023	-0.313989
H	2.262169	2.070077	-0.321500
C	-0.427713	2.410320	0.028383
H	-1.198667	2.397795	-0.751423
H	-0.952353	2.555536	0.980348
H	0.220898	3.274926	-0.142737
O	-1.631965	-0.024668	0.419038
C	-2.355789	-1.224454	0.629549
H	-3.399618	-0.927920	0.750654
H	-2.270307	-1.905190	-0.228083
H	-2.020308	-1.746184	1.535983



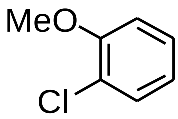
C	0.444300	-1.286768	0.207524
C	1.835581	-1.229692	-0.020662
C	2.597293	-0.056947	-0.246082
C	1.755760	1.088059	-0.211905
C	0.364896	1.123075	0.008126
C	-0.289256	-0.100212	0.220736
H	-0.049254	-2.246525	0.371167
H	2.339761	-2.210266	-0.015211
H	2.205202	2.083923	-0.371657

C	-0.418939	2.416066	0.020040
H	-1.206709	2.437946	-0.748160
H	-0.929368	2.590170	0.979388
H	0.252775	3.264951	-0.162589
O	-1.676856	-0.023505	0.436586
C	-2.354908	-1.229693	0.651409
H	-3.411550	-0.975209	0.798442
H	-2.271006	-1.918284	-0.205811
H	-1.990392	-1.764326	1.544334



C	0.487312	-1.290701	0.243825
C	1.898400	-1.374709	0.056740
C	2.466326	-0.087892	-0.142204
C	1.751430	1.117920	-0.156271
C	0.364221	1.143463	0.032966
C	-0.255035	-0.101955	0.235042
H	-0.071510	-2.221131	0.408293
H	3.552893	0.001629	-0.300803
H	2.265318	2.074496	-0.316748
C	-0.434524	2.424243	0.023421
H	-1.206995	2.432999	-0.760508
H	-0.968147	2.594836	0.970786
H	0.223846	3.286084	-0.147949

O	-1.649766	-0.021227	0.420180
C	-2.340127	-1.223790	0.628225
H	-3.398505	-0.960098	0.749703
H	-2.241119	-1.917668	-0.221448
H	-1.998978	-1.753393	1.531742



C	-1.063568	-0.490348	0.000847
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C	0.442295	1.845872	0.000139
C	-0.952497	1.920556	0.000144
C	-1.726339	0.752970	0.000470
H	0.801981	-1.534959	0.001112
H	2.169811	0.551164	0.000522
H	1.021330	2.765100	-0.000089
H	-1.435651	2.890846	-0.000083
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O	-3.083474	0.724955	0.000398
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H	-3.558731	2.551288	-0.895703
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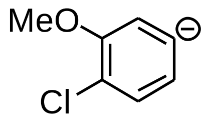

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C	-0.910203	1.901239	0.000155
C	-1.707804	0.741746	0.000499
H	0.808141	-1.544680	0.001152
H	2.155195	0.500119	0.000593
H	-1.454321	2.853491	-0.000360
Cl	-2.025194	-2.014522	0.001108
O	-3.098991	0.717961	0.000432
C	-3.762774	1.955992	0.000107
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H	-4.834789	1.727693	-0.000061
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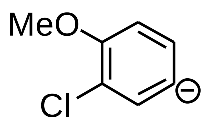

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C	-0.952044	1.905545	0.000094

C	-1.731724	0.743453	0.000420
H	0.772233	-1.557287	0.000868
H	0.986531	2.759535	-0.000274
H	-1.434792	2.884626	-0.000035
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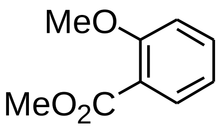

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H	2.074088	2.338100	0.000016
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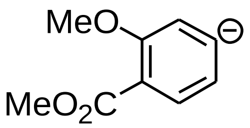

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C	-0.785788	0.410502	0.000801
H	-0.744357	-1.741636	0.001779
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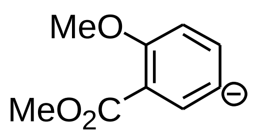

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C	0.117409	0.388524	-0.082624
H	1.019284	2.302781	-0.222058
H	-3.265104	2.260478	0.065266
H	-3.248017	-0.149601	0.021499
C	1.409764	-0.310573	-0.158427
O	1.648549	-1.436521	-0.569338
O	2.453442	0.488898	0.281726
C	3.739485	-0.091495	0.132746

H	4.448908	0.655260	0.501453
H	3.833373	-1.017096	0.712830
H	3.957122	-0.329885	-0.915238
O	-1.032261	-1.719316	0.018294
C	-2.240555	-2.426428	0.105848
H	-2.815415	-2.168518	1.010208
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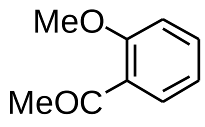

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C	0.055555	1.546435	-0.000020
C	-0.720903	0.350854	0.000131
H	-0.604065	-1.795201	0.000806
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H	3.184537	0.193050	0.000928
H	2.054272	2.368172	0.000180
C	-2.220054	0.363706	-0.000447
O	-2.876323	1.392673	-0.003699
O	-0.602804	2.726935	-0.000262
C	0.140165	3.936118	0.000472

H	0.768693	4.025505	0.895990
H	0.769096	4.026321	-0.894684
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C	-2.950810	-0.980014	0.003050
H	-2.702449	-1.579657	-0.880356
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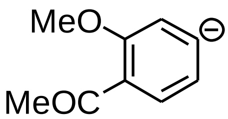

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C	0.062473	1.529128	0.000411
C	-0.750486	0.354913	0.001000
H	-0.609152	-1.803832	0.001812
H	1.790040	-1.932133	0.001488
H	2.016316	2.365336	-0.000269
C	-2.217461	0.371998	0.001217
O	-2.926165	1.381501	0.000900
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C	0.151356	3.919859	-0.000208
H	0.793161	4.006929	0.889612
H	0.792902	4.006789	-0.890233

H	-0.573582	4.741374	-0.000182
C	-2.952320	-0.985991	0.001913
H	-2.702294	-1.587635	-0.880161
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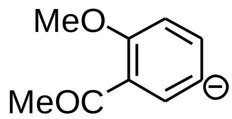

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C	1.429478	1.450602	-0.023276
C	0.039694	1.549118	-0.060721
C	-0.728492	0.352120	-0.083355
H	-0.633887	-1.773833	-0.158803
H	3.147193	0.217189	0.089242
H	2.040425	2.352166	0.001121
C	-2.204849	0.363956	-0.131702
O	-2.901438	1.354153	-0.360805
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C	0.134762	3.930923	0.054933
H	0.742664	3.957706	0.973754
H	0.812994	4.067515	-0.802869
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C	-2.943778	-0.965349	0.109390

H	-2.761538	-1.676593	-0.705235
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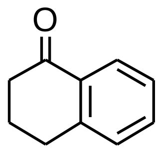

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C	2.402530	-0.017894	-0.885488
C	1.180022	0.467756	-1.331275
C	-1.272367	0.828489	-1.092660
C	-2.510074	0.646078	-0.222542
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C	-1.168356	-0.601131	1.502277
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H	1.375140	-1.431887	2.037658
H	3.418871	-1.091888	0.688218
H	3.300438	0.129075	-1.479298
H	1.089922	0.999734	-2.273118
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H	-3.328507	-0.683732	1.287605
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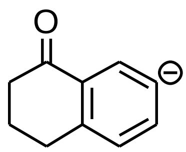

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H	1.357394	-1.454549	2.016906
H	3.380144	-1.114983	0.713735
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H	-1.286426	0.260072	2.234872
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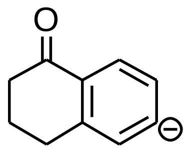

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C	2.382791	-0.096637	-0.884993
C	1.186237	0.439664	-1.342991
C	-1.257491	0.857509	-1.079955
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C	-2.438875	-0.613334	0.657169
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O	-1.374661	1.501540	-2.128743
H	1.294923	-1.515641	1.974599
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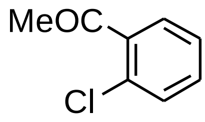

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C	0.837414	-1.615248	0.059410
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H	2.204829	1.981998	-0.197419
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H	0.425005	-2.617042	0.109903
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H	-2.429557	0.624864	1.010843
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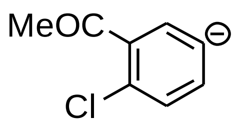

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H	2.331041	1.837184	0.094246
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H	0.320006	-2.660801	0.076471
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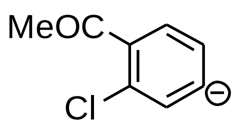

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C	2.281661	-1.366512	0.000410
C	0.919028	-1.623290	0.000002
C	-0.044761	-0.579565	-0.000074
H	2.192439	2.006389	0.000258

H	2.936079	-2.248820	0.000600
H	0.525299	-2.638621	-0.000112
Cl	-0.525592	2.230615	-0.000925
C	-1.463416	-1.011667	-0.000157
O	-1.759190	-2.210634	-0.002020
C	-2.625657	-0.021776	0.002426
H	-2.599225	0.632726	0.879054
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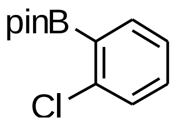

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C	2.348331	-0.856912	-0.109571
C	2.237280	0.700524	0.119815
C	3.309801	-1.587225	0.826114
H	3.288067	-2.660396	0.610552
H	4.337460	-1.234112	0.682617
H	3.036776	-1.448936	1.874632
C	2.634792	-1.242353	-1.566945
H	3.662603	-0.999176	-1.856227
H	2.491199	-2.321124	-1.682849
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C	2.492133	1.124435	1.572340
H	3.549399	1.029116	1.841621
H	2.197965	2.171490	1.691897
H	1.899882	0.526631	2.272262
C	3.065215	1.561553	-0.831949
H	2.884119	2.619645	-0.618440
H	4.136167	1.367510	-0.702099
H	2.801019	1.379966	-1.876101
C	-1.396721	-0.430481	0.025447
C	-1.862258	-1.760410	0.095533
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H	-1.123151	-2.554599	0.140784
C	-3.745657	0.276267	-0.022458
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H	-3.535794	-3.114676	0.161861
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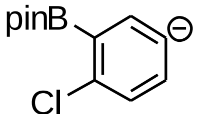

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H	-3.640101	-1.369963	1.619755
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C	3.758294	0.192653	0.049447
C	4.131102	-1.166726	0.041798

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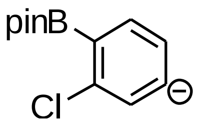

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C	-2.187921	0.710288	-0.102718
C	-3.315864	-1.545708	-0.827195
H	-3.298472	-2.624415	-0.636103
H	-4.337513	-1.185624	-0.651849
H	-3.065317	-1.389048	-1.879137
C	-2.587252	-1.248422	1.555656
H	-3.608978	-1.003761	1.870240
H	-2.443339	-2.329397	1.654210
H	-1.884051	-0.753793	2.232667
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H	-3.486986	1.080339	-1.838366
H	-2.111201	2.195612	-1.660421
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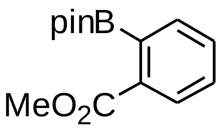

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H	3.601259	-1.557735	-1.481358
C	2.394599	1.678665	-1.133528

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H	3.082042	0.777780	2.679879
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H	-2.625853	-4.091692	-0.119927
H	-4.307734	-0.137183	0.024963
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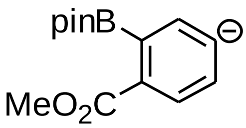

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H	4.553527	0.067411	-1.343388
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C	2.300719	1.736643	-1.060732
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H	2.089588	1.866817	-2.127801
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H	4.351059	-1.351306	0.878508
H	3.116861	-1.684162	2.114863
H	2.867098	-2.241602	0.456708
C	3.110846	1.010247	1.646048
H	3.089944	0.694318	2.695030

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C	-1.217762	-2.517184	-0.094202
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C	-3.558123	-2.284427	-0.056655
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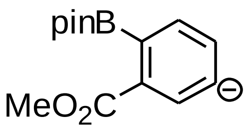

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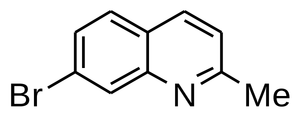

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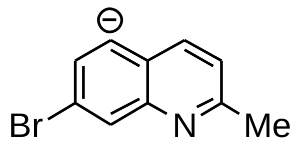

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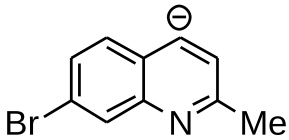

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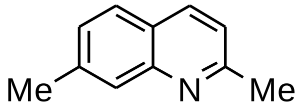

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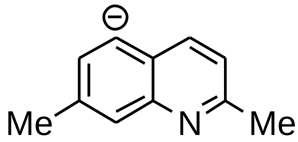

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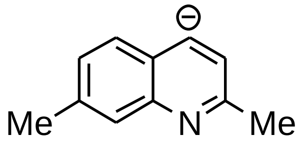

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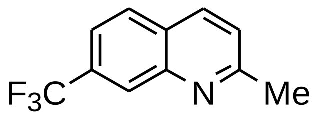

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Electronic Supplementary Material (ESI) for Chemical Science
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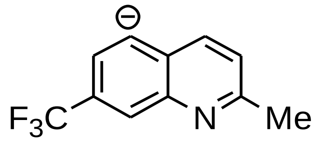

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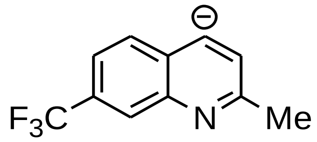

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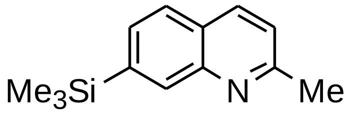

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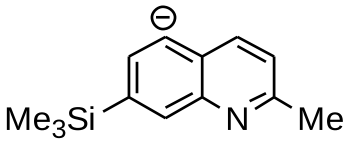

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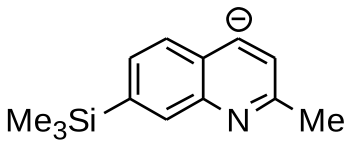

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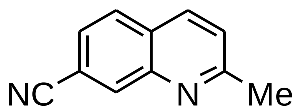

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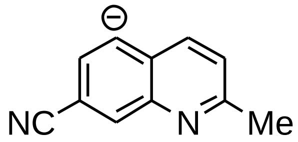

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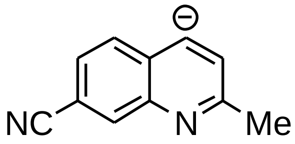

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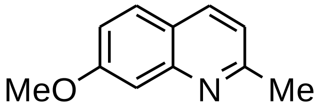

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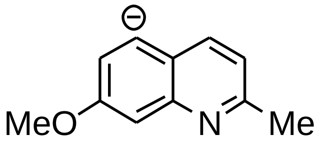

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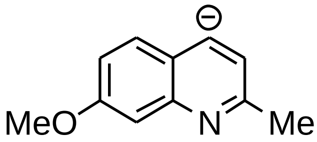

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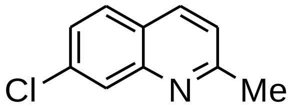

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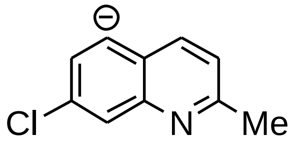

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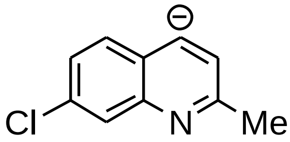

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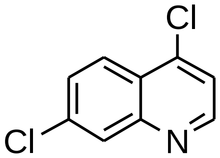

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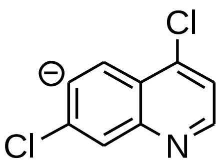

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C	-0.174505	2.218336	0.003613
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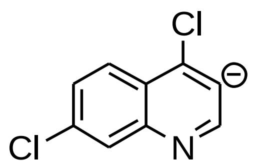

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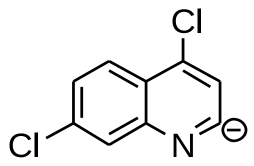

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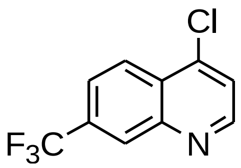

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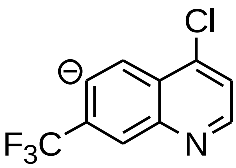

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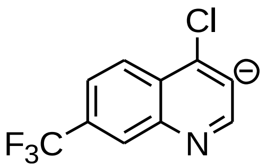

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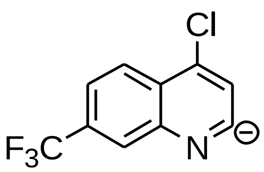

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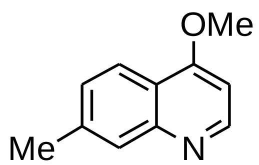

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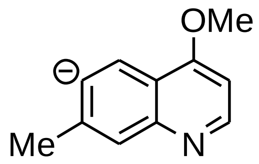

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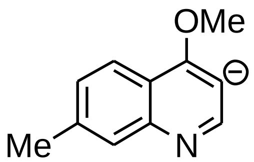

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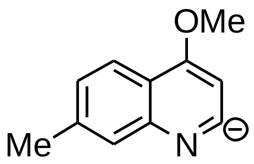

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O	-2.310663	-1.308047	0.000125
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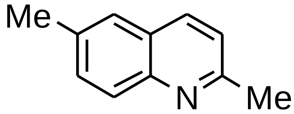

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H	4.499668	-0.032931	-0.880921
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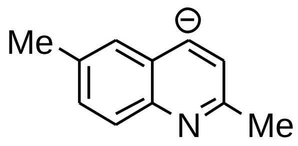

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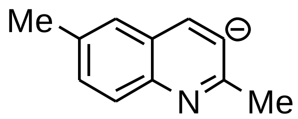

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H	4.483760	-0.018476	-0.881118
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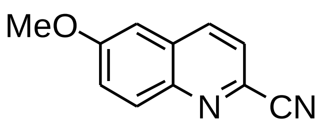
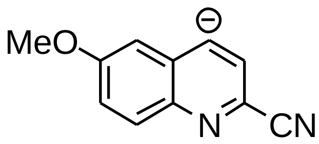
H	-4.455908	-0.096634	-0.876360
H	-3.992963	-1.588814	0.000561



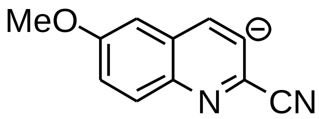
C	-4.553687	-0.790555	0.022537
C	-3.185180	-0.803908	0.018293
C	-2.448118	0.415463	0.004432
C	-3.169963	1.653802	-0.004915
C	-4.588700	1.646424	-0.000305
C	-5.269365	0.443146	0.013279
H	-5.131574	-1.709246	0.032978
H	-2.625389	-1.733383	0.025239
C	-2.403909	2.846460	-0.018635
H	-5.113770	2.595157	-0.007663
C	-1.031409	2.774889	-0.022328
C	-0.421205	1.491505	-0.012023
H	-2.908408	3.809452	-0.026181
H	-0.413150	3.666168	-0.032809
C	1.020122	1.403354	-0.016101
N	2.182239	1.372445	-0.019754

N	-1.093902	0.349309	0.000827
O	-6.619935	0.306807	0.018903
C	-7.416416	1.484230	0.010291
H	-7.234076	2.082294	-0.891659
H	-8.452681	1.143370	0.017424
H	-7.227714	2.099761	0.899118



C	-4.555305	-0.806123	0.022744
C	-3.181865	-0.815541	0.018234
C	-2.438677	0.401261	0.003502
C	-3.134818	1.658275	-0.006722
C	-4.562884	1.621017	-0.001510
C	-5.256199	0.429489	0.012761
H	-5.133317	-1.727077	0.033867
H	-2.625754	-1.750557	0.025693
C	-2.466704	2.942341	-0.021806
H	-5.053784	2.589166	-0.009631
C	-1.074564	2.762813	-0.024601
C	-0.444836	1.487918	-0.014022
H	-0.400645	3.626610	-0.035401
C	1.003159	1.417950	-0.017942
N	2.169093	1.426487	-0.021737
N	-1.079303	0.314207	-0.000055

O	-6.636145	0.306752	0.018792
C	-7.380977	1.503917	0.008810
H	-7.177304	2.106122	-0.888641
H	-8.435281	1.210642	0.015161
H	-7.171821	2.124423	0.892445

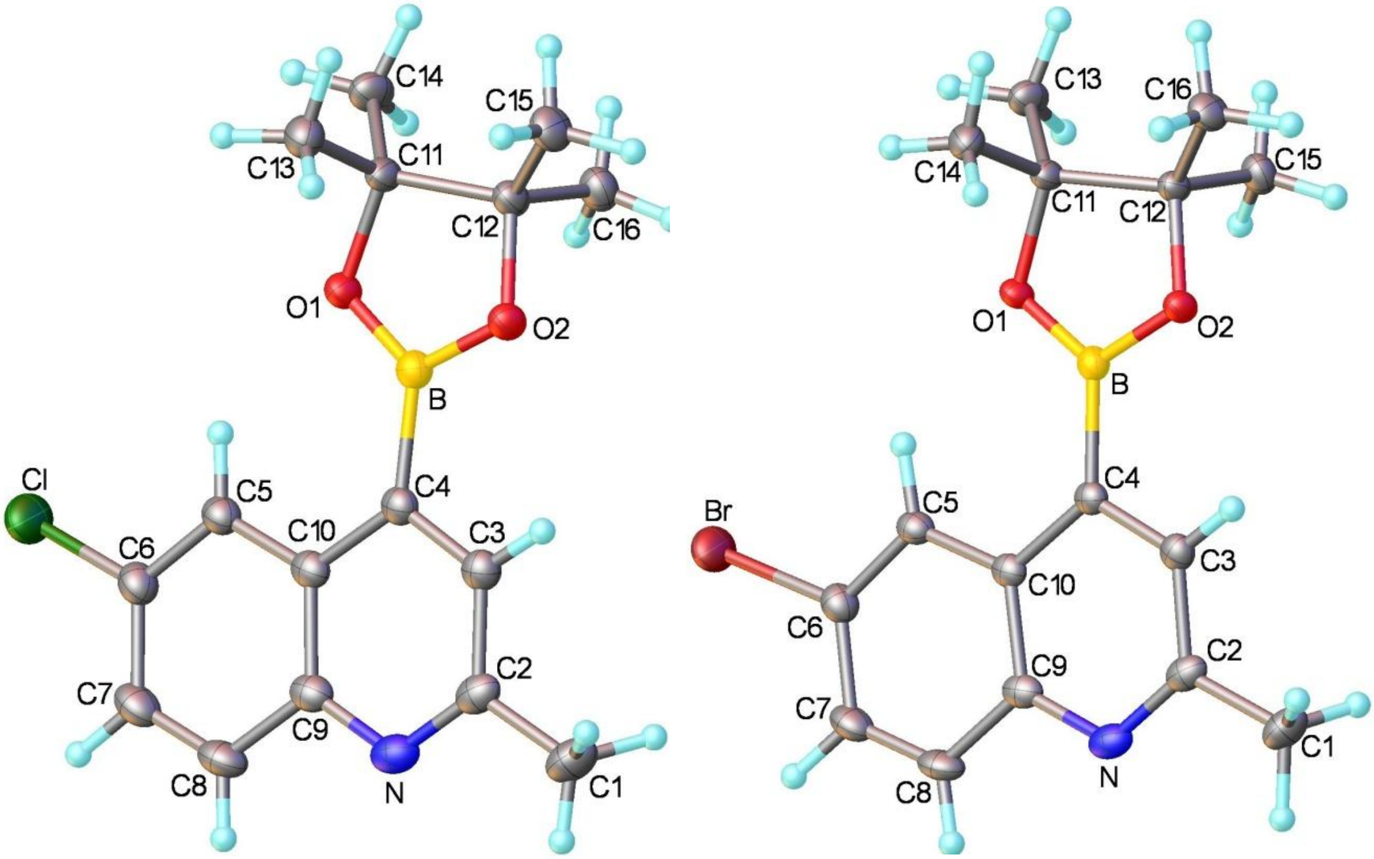


C	-4.557217	-0.807629	0.023635
C	-3.183507	-0.814971	0.018576
C	-2.438149	0.398078	0.002976
C	-3.147022	1.643739	-0.007597
C	-4.573821	1.624941	-0.002045
C	-5.259170	0.429307	0.013252
H	-5.136453	-1.726971	0.035446
H	-2.624294	-1.747222	0.026272
C	-2.370274	2.832971	-0.023188
H	-5.092881	2.579760	-0.010492
C	-0.971410	2.871575	-0.028748
C	-0.455892	1.528908	-0.016252
H	-2.945681	3.771320	-0.031108
C	0.998462	1.396760	-0.020207
N	2.161127	1.308058	-0.023484
N	-1.083183	0.341954	-0.001364
O	-6.636789	0.302821	0.019984

C	-7.392075	1.493109	0.010482
H	-7.195926	2.095922	-0.888475
H	-8.443415	1.190795	0.018347
H	-7.188369	2.115013	0.894646

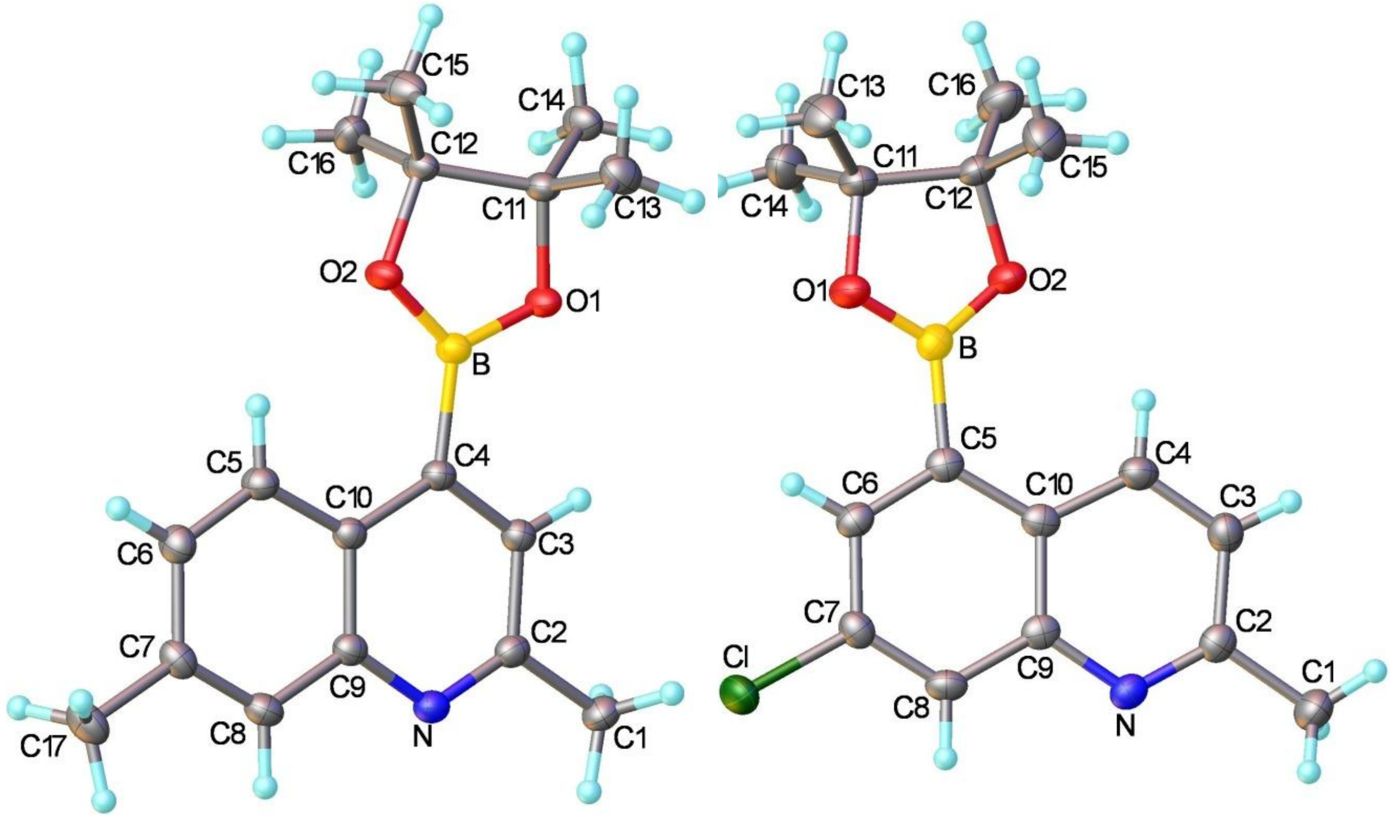
9.0 X-Ray Crystal Structures

9.1 Figure S1 - 2-methyl-6-chloro-4-Bpin-quinoline 11c and 2-methyl-6-bromo-4-Bpin-quinoline 11d



X-ray molecular structures of 2-methyl-6-chloro-4-Bpin-quinoline **11c** (left) and 2-methyl-6-bromo-4-Bpin-quinoline **11d** (right) at 120 K. Thermal ellipsoids are shown at the 50% probability level. Crystals of **11c** and **11d** are isotypic (isomorphous).

9.2 Figure S2 - 2,7-dimethyl-4-Bpin-quinoline 13f and 2-methyl-7-chloro-5-Bpin quinoline 14g



X-ray molecular structures of 2,7-dimethyl-4-Bpin-quinoline **13f** (left) and 2-methyl-7-chloro-5-Bpin quinoline (right) **14g** at 120 K. Thermal ellipsoids are shown at the 50% probability level.