Supporting Information

Three-Component Olefin Dicarbofunctionalization Enabled by Nickel/Photoredox Dual Catalysis

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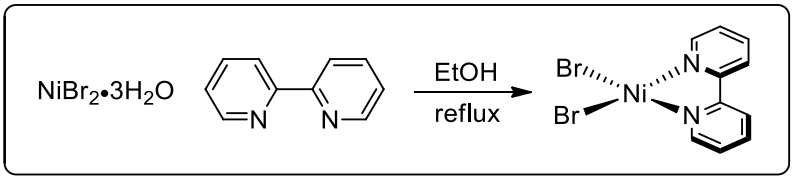
General Considerations: All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a 4- or 5-port dual-bank manifold. LED irradiation was accomplished using the LED reactor described in our previous report.[1] Tetrahydrofuran was dried using a solvent delivery system. All reagents were purchased and used as received from suppliers unless otherwise noted. Nickel pre-complexes were prepared as described here. The transition metal photocatalysts ($Ru(bpy)_3(PF_6)_2$ and $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$) were prepared in-house by the procedure outlined in our previous publications;[2] others were purchased from commercial sources. The organic photocatalysts 4CzIPN and Cl-4CzIPN were prepared in-house by the procedure outlined in our previous publication.[3] Aryl- and heteroaryl bromides were either purchased from commercial sources, prepared as previously reported,[4] or prepared as outlined here. Potassium alkyltrifluoroborates were either purchased from commercial sources or prepared by the methods outlined here. Solvents were purified with drying cartridges through a solvent delivery system. Reactions were monitored by GC/MS or TLC using silica gel F_{254} plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using EtOAc/hexanes, CH_2Cl_2/hexanes, or EtOAc with 1% MeOH/hexanes and visualized using permanganate stain, Seebach's stain,[5] CAM (Hanessian's) stain, and/or UV light. Silica plugs utilized flash silica gel (60 Å porosity, 32-63 μm). Flash chromatography was accomplished using an automated system (monitoring at 254 nm and 280 nm) with silica cartridges (60 Å porosity, 20-40 μm). Accurate mass measurement analyses were conducted using electron ionization (EI) or electrospray ionization (ESI). The signals were mass measured against an internal lock mass reference of perfluorotributylamine (PFTBA) for EI-GCMS, and leucine enkephalin for ESI-LCMS. The utilized software calibrates the instruments and reports measurements by use of neutral atomic masses. The mass of the electron is not included. IR spectra were recorded using either neat oil or solid products. Melting points (°C) are uncorrected. NMR spectra [^1H, $^{13}C\ \{^1H\}$, ^{11}B, $^{19}F\ \{^1H\}$] were obtained at 298 K. ^1H NMR (500.4 MHz) chemical shifts are referenced to residual, non-deuterated $CHCl_3$ (δ 7.26) in $CDCl_3$ and acetone-d_5 (δ 2.09) in acetone-d_6. $^{13}C\{^1H\}$ NMR (125.8 MHz) chemical shifts are reported relative to $CDCl_3$ (δ 77.3) and the carbonyl carbon of acetone (δ 205.9). ^{11}B NMR (128.4 MHz) chemical shifts are uncorrected. ^{19}F NMR spectra were referenced to hexafluorobenzene (δ –161.64 in $CDCl_3$ or –164.67 in acetone-d_6).[6] Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant J (Hz) and integration.

Preparation of Nickel Bromide Bipyridine [$NiBr_2$(bpy)]



A flask was charged with $NiBr_2$•$3H_2O$ (5.45 g, 20.0 mmol, 1.00 equiv) and 2,2′-bipyridine (3.28 g, 21.0 mmol, 1.05 equiv) and evacuated and purged with argon three times. Absolute EtOH (75 mL) was added, and the suspension was heated to a vigorous reflux for 24 h. During the refluxing period the color of the suspension changed from light brown to yellow/green. The resulting suspension was cooled to rt and filtered through a medium porosity fritted glass funnel and washed with Et_2O (3 × 150 mL). The resulting powder was dried under high vacuum at 50 °C for 24 h and stored in a desiccator. This complex is hygroscopic, and absorption of H_2O from the atmosphere is accompanied by a change in color (dull yellow/green to bright blue). We observed that the efficacy of the dicarbofunctionalization reaction was dependent upon the anhydrous nature of the nickel catalysts.[7]

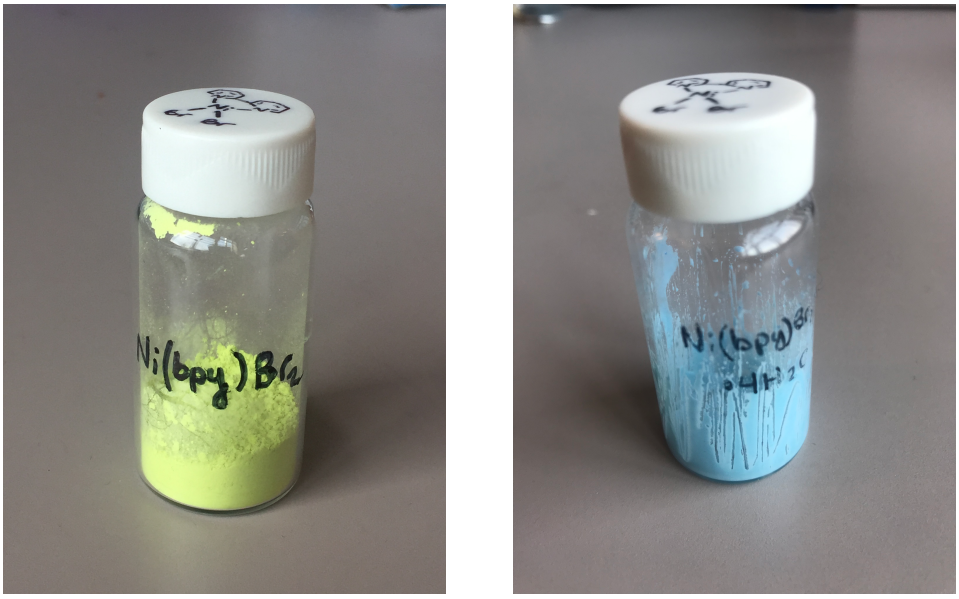
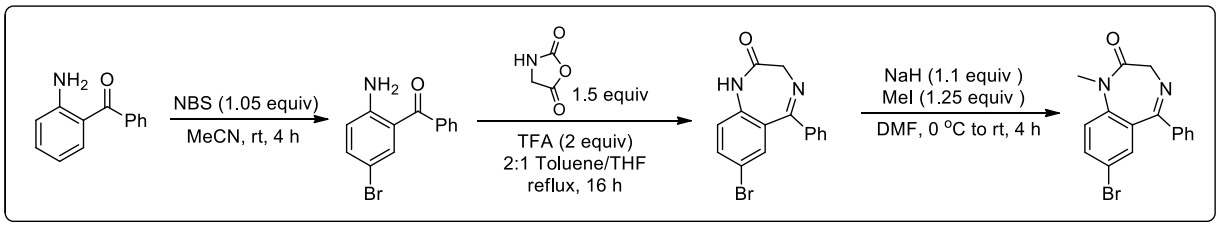


Figure S1. (Left) A sample of anhydrous Ni(bpy)Br_2 (Right) A sample of hydrated Ni(bpy)Br_2

Synthesis of Aryl and Heteroaryl Bromides

7-Bromo-1-methyl-5-phenyl-1*H*-benzo[*e*][1,4]diazepin-2(3*H*)-one



Bromination

To a 100 mL flask equipped with a stirrer bar was added 2-aminobenzophenone (0.510 g, 2.60 mmol, 1 equiv) followed by MeCN (30 mL). The flask was then cooled to 0 °C via an ice/water bath. After 10 min, NBS (0.483 g, 2.71 mmol, 1.05 equiv) was added to the reaction in five portions over the course of 50 min. The mixture was stirred at rt for 3 h. The solvent was then removed *in vacuo* by rotary evaporation. The resulting crude solid was taken up in a 1:1 Et_2O/EtOAc soln (30 mL). This soln was then washed with deionized H_2O (30 mL) followed by brine (30 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. The crude solid was recrystallized from hexanes/Et_2O (2:1) to yield (2-amino-5-bromophenyl)(phenyl)methanone as yellow needles (0.509 g, 71%). All data matched that reported in the literature.[8]

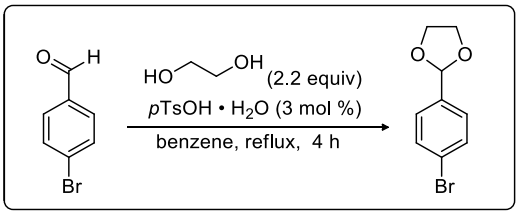
Condensation/Annulation

To a 100 mL flask equipped with a stirrer bar was added (2-amino-5-bromophenyl)(phenyl)methanone (1.11 g, 4.00 mmol, 1 equiv) dissolved in a 2:1 mixture of toluene and THF (60 mL). Oxazolidine-2,5-dione (0.505 g, 5.00 mmol, 1.25 equiv) was added in one portion followed by CF_3CO_2H (0.91 g, 0.61 mL, 8.0 mmol, 2 equiv). The reaction mixture was heated at reflux overnight. The reaction mixture was concentrated *in vacuo* by rotary evaporation. The resulting crude solid was taken up in EtOAc (30 mL) and washed with satd aq $NaHCO_3$ (30 mL). The layers were separated, and the aq layer was extracted with EtOAc (2 × 30 mL). The organic layer was washed with brine (100 mL) and dried (Na_2SO_4). The solvent was removed *in vacuo* by rotary evaporation to give the crude annulation product. The crude solid was purified *via* SiO_2 column chromatography to yield 7-bromo-5-phenyl-1H-benzo[*e*][1,4]diazepin-2(3*H*)-one as a crystalline, yellow solid (0.44 g, 35%). All data matched that reported in the literature.[9]

Methylation

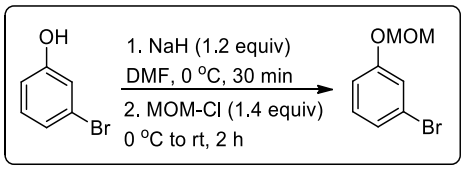
To a slurry of NaH (35 mg, 1.47 mmol, 1.1 equiv) in anhyd DMF (10 mL) cooled to 0 °C in an ice-water bath was added 7-bromo-5-phenyl-1H-benzo[e][1,4]diazepin-2(3H)-one (0.420 g, 1.33 mmol, 1 equiv) dissolved in 5 mL of anhyd DMF, which resulted in vigorous bubbling. The reaction mixture was stirred for 30 min, after which MeI was added dropwise, neat. The reaction was allowed to stir for 4 h while coming to rt. The reaction mixture was diluted with H_2O and EtOAc, and the layers were separated. The aq layer was extracted with EtOAc (3 × 15 mL). The organic layer was washed with brine, dried (Na_2SO_4), and concentrated *via* rotary evaporation. The crude solid was purified *via* silica gel chromatography to afford 7-bromo-1-methyl-5-phenyl-1H-benzo[e][1,4]diazepin-2(3H)-one as a powdery yellow solid (0.282 mg, 64%). All data matched that reported in the literature.[10]

2-(4-Bromophenyl)-1,3-dioxolane



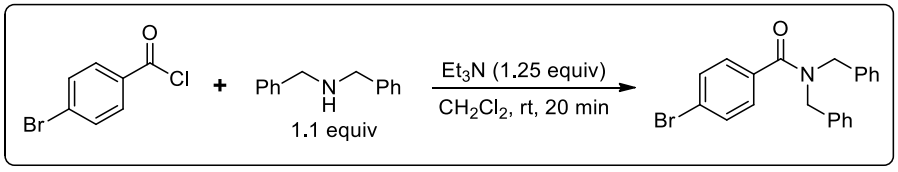
2-(4-Bromophenyl)-1,3-dioxolane was prepared *via* a modified literature procedure.[11] To a 50 mL round bottom flask equipped with a stirrer bar was added *p*-bromobenzaldehyde (0.485 g, 2.62 mmol, 1 equiv) followed by benzene (10 mL). The contents of the flask were stirred and, after 2 min, *p*-TsOH•H_2O (15.0 mg, 0.0789 mmol, 0.03 equiv) and ethylene glycol (0.358 g, 0.322 mL, 5.77 mmol, 2.2 equiv) were added. The flask was equipped with a Dean-Stark trap and heated at reflux for 4 h. After cooling to rt, the reaction mixture was diluted with EtOAc (20 mL) and transferred to a separatory funnel. The organic layer was washed with cold, deionized H_2O (30 mL). The organic layer was then washed with brine (30 mL) and dried (Na_2SO_4). The solvent was removed *in vacuo* by rotary evaporation to yield 2-(4-bromophenyl)-1,3-dioxolane as a colorless oil (0.585 g, 97%). All data matched that reported in the literature.[12]

1-Bromo-3-(methoxymethoxy)benzene



1-Bromo-3-(methoxymethoxy)benzene was prepared via a modified literature procedure.[13] To a 100 mL round bottom flask equipped with a stirrer bar was added NaH (0.230 g, 9.60 mmol, 1.2 equiv). The flask was sealed with a rubber septum and placed under an Ar atmosphere via an inlet needle. The flask was charged with anhyd DMF (24 mL) and then cooled to 0 °C in an ice-water bath. After 5 min, a soln of 3-bromophenol (1.38 g, 8.00 mmol, 1 equiv) in anhyd DMF (5 mL) was added to the flask. **CAUTION:** *Evolves H_2 gas*! The mixture was stirred for 30 min at 0 °C. After this time, a soln of MOM-Cl (0.902 g, 0.85 mL, 11.2 mmol, 1.4 equiv) in anhyd DMF (5 mL) was added dropwise. After complete addition, the ice bath was removed, and the reaction mixture was stirred at rt for 2 h. After this time, the reaction was carefully quenched with cold, deionized H_2O (20 mL). The contents of the flask were transferred to a separatory funnel and diluted with EtOAc (30 mL). The layers were separated, and the aq layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with deionized H_2O (60 mL), brine (100 mL), and dried (Na_2SO_4). The solvent was removed *in vacuo* by rotary evaporation to afford 1-bromo-3-(methoxymethoxy)benzene as a clear, colorless oil (1.51g, 87%). All data matched that reported in the literature.[14]

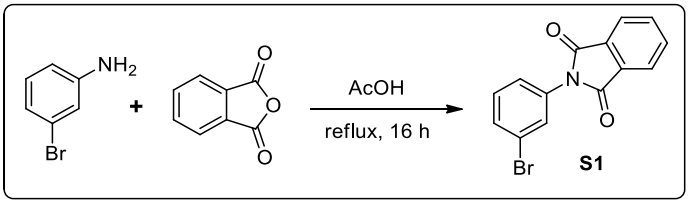
N,N-Dibenzyl-4-bromobenzamide



To a 150 mL round bottom flask equipped with a stirrer bar was added 4-bromobenzoyl chloride (2.20 g, 10.0 mmol, 1.00 equiv) followed by CH_2Cl_2 (30 mL). The flask was sealed with a rubber septum and placed under an Ar atmosphere *via* an inlet needle. The flask was charged with Et_3N (1.77 g, 2.44 mL, 17.5 mmol, 1.75 equiv) and was then cooled to 0 °C in an ice-water bath. After 5 min, Bn_2NH (2.96 g, 15.0 mmol, 1.50 equiv) was added dropwise to the flask. The mixture was stirred for 20 min at 0 °C. After this time, 2 M aq HCl (50 mL) was added to the flask. The contents of the flask were transferred to a separatory funnel and diluted with CH_2Cl_2 (30 mL). The layers were separated, and the aq layer was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were washed with 2 M HCl (2 × 50

mL), brine (100 mL), and dried (Na_2SO_4). The solvent was removed *in vacuo* by rotary evaporation to afford *N,N*-dibenzyl-4-bromobenzamide as an off-white solid (2.315 g, 91%). All data matched that reported in the literature.[15]

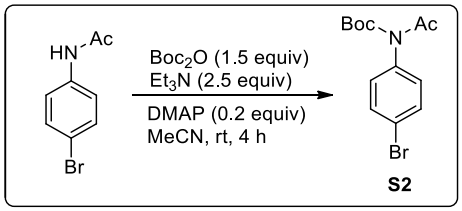
N-(3-Bromophenyl)phthalimide), S1



N-(3-Bromophenyl)phthalimide), **S1** was prepared *via* a modified literature procedure.[16] To a 100 mL round bottom flask equipped with a stirrer bar was added 3-bromoaniline (1.72 g, 10.0 mmol, 1 equiv) followed by AcOH (50 mL). The mixture was stirred for 2 min, and then phthalic anhydride (1.48 g, 10.0 mmol, 1 equiv) was added. The flask was equipped with a reflux condenser, and the reaction mixture was heated to reflux for 16 h. After this time, the reaction mixture was cooled to rt, and ice was added to the mixture, which caused the precipitation of a white powder. This solid was collected by vacuum filtration through a medium porosity fritted funnel and dried to yield *N*-(3-bromophenyl)phthalimide) as a white powder (2.65 g, 88 %) (mp = 162 – 163 ºC).

^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.97 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.66 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.36 - 7.45 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 167.0, 134.8, 133.1, 131.7, 131.3, 130.4, 129.7, 125.2, 124.1, 122.6. **FT-IR** (cm^{-1}, neat, ATR) 3012 (w), 1711 (vs), 1477 (m), 1376 (s), 1078 (m), 862 (m). **HRMS** (EI) calcd for $C_{14}H_8BrNO_2$ $[M]^+$: 300.9738, found: 300.9741.

tert-Butyl Acetyl(4-bromophenyl)carbamate, S2

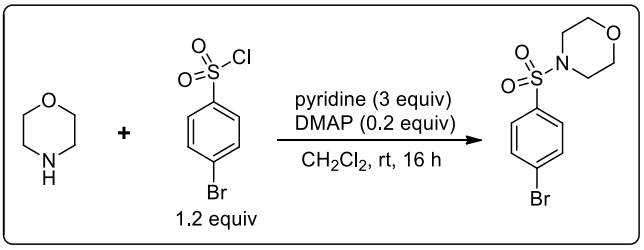


To a 150 mL round bottom flask equipped with a stirrer bar was added 4-bromoacetanilide (2.14 g, 10.0 mmol, 1.00 equiv) and DMAP (0.244 g, 2.00 mmol, 0.2 equiv). The flask was sealed with a rubber septum and placed under an Ar atmosphere *via* an inlet needle. The flask was charged with MeCN (35

mL) and Et_3N (3.5 mL, 25 mmol, 2.5 equiv). After stirring for 2 min, Boc_2O (3.27 g, 15.0 mmol, 1.5 equiv) was added *via* a syringe. The mixture was stirred for 4 h at rt. After this time, 1 M aq HCl (50 mL) was added to the flask. The contents of the flask were transferred to a separatory funnel and diluted with EtOAc (60 mL). The layers were separated, and the aq layer was extracted with EtOAc (2 × 30 mL). The combined organic layers were washed with 2 M HCl (2 × 50 mL), brine (100 mL), and dried (Na_2SO_4). The solvent was removed *in vacuo* by rotary evaporation to afford the crude Boc aniline. Further purification was accomplished by recrystallization from MeOH to afford *tert*-butyl acetyl(4-bromophenyl)carbamate, **S2,** as a white solid (2.307 g, 73%) (mp = 122-123 °C).

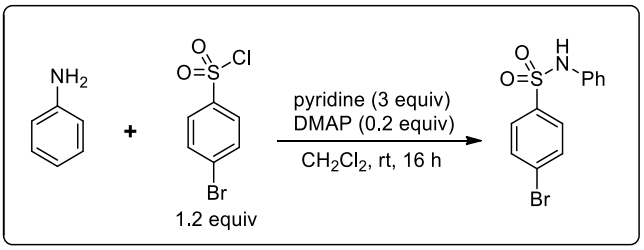
^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.52 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 2.59 (s, 3H), 1.39 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 173.0, 152.5, 138.1, 132.3, 130.1, 121.8, 83.8, 278.0, 26.6. **FT-IR** (cm^{-1}, neat, ATR) 2985 (vw), 1737 (s), 1704 (vs), 1367 (m), 1271 (s), 1257 (s), 845 (m). **HRMS** (EI) calcd for C_8H_7BrNO $[M\text{-}Boc]^+$: 212.9789, found: 212.9769.

4-((4-Bromophenyl)sulfonyl)morpholine)



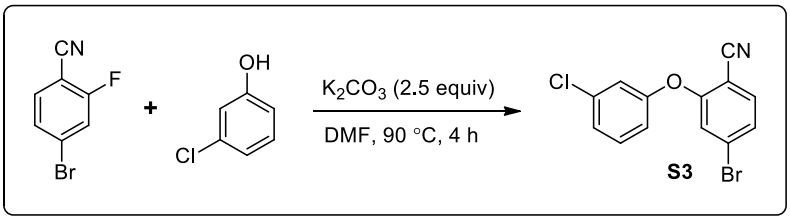
To a 150 mL round bottom flask equipped with a stirrer bar was added 4-bromobenzenesulfonyl chloride (6.13 g, 24.0 mmol, 1.2 equiv) and DMAP (0.489 g, 4.80 mmol, 0.2 equiv). The flask was sealed with a rubber septum and placed under an Ar atmosphere *via* an inlet needle. The flask was charged with CH_2Cl_2 (67 mL) and pyridine (4.83 mL, 60.0 mmol, 3 equiv) followed by morpholine (1.73 mL, 20.0 mmol, 1 equiv). The mixture was stirred overnight at rt. After this time, 1 M aq HCl (50 mL) was added to the flask. The contents of the flask were transferred to a separatory funnel and diluted with CH_2Cl_2 (25 mL). The layers were separated, and the aq layer was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were washed with 1 M HCl (2 × 50 mL), deionized H_2O (100 mL), brine (100 mL), and dried (Na_2SO_4). The solvent was removed *in vacuo* by rotary evaporation to afford the sulfonamide. Further purification was accomplished by recrystallization from CH_2Cl_2 at -20 °C to afford 4-((4-bromophenyl)sulfonyl)morpholine) as a white crystalline solid (4.96 g, 81%) (mp = 149-150 °C). All data matched that reported in the literature. [17]

4-Bromo-*N*-phenylbenzenesulfonamide



To a 150 mL round bottom flask equipped with a stirrer bar was added 4-bromobenzenesulfonyl chloride (1.66 g, 6.50 mmol, 1.3 equiv) and DMAP (0.122 g, 1.00 mmol, 0.2 equiv). The flask was sealed with a rubber septum and placed under an Ar atmosphere *via* an inlet needle. The flask was charged with CH_2Cl_2 (17 mL) and pyridine (1.21 mL, 15.0 mmol, 3 equiv) followed by aniline (0.456 mL, 5.00 mmol, 1 equiv). The mixture was stirred overnight at rt. After this time, 1 M aq HCl (50 mL) was added to the flask. The contents of the flask were transferred to a separatory funnel and diluted with CH_2Cl_2 (25 mL). The layers were separated, and the aq layer was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were washed with 1 M HCl (2 × 50 mL), deionized H_2O (100 mL), brine (100 mL), and dried (Na_2SO_4). The solvent was removed *in vacuo* by rotary evaporation to afford the sulfonamide. Further purification was accomplished by recrystallization from MeOH to afford 4-bromo-*N*-phenylbenzenesulfonamide as a white crystalline solid (1.34 g, 86%) (mp = 114-115 ºC). All data matched that reported in the literature.[18]

4-Bromo-2-(3-chlorophenoxy)benzonitrile, S3

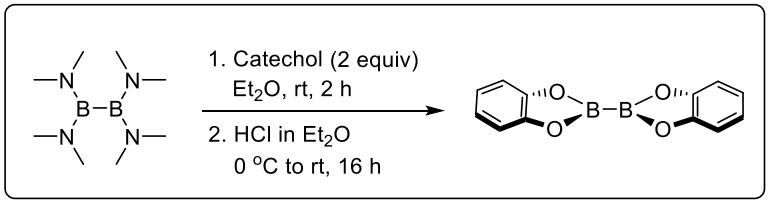


To a 100 mL round bottom flask equipped with a stir bar was added 4-bromo-2-fluorobenzonitrile (0.643 g, 3.21 mmol, 1.0 equiv) and potassium carbonate (1.11 g, 8.03 mmol, 2.5 equiv). The flask was capped with a septum and placed under an Ar atmosphere via an inlet needle. Anhydrous DMF (15 mL) was added to the flask via syringe followed by 3-chlorophenol (0.475 g, 3.69 mmol, 1.15 equiv). The reaction was then heated to 90 ºC for 4 hours. After cooling to room temperature the reaction was quenched with saturated aq NH_4Cl (30 mL) and the mixture was extracted with diethyl ether (3 X 25 mL). The combined organic extracts were washed with 2 M aq NaOH (2 × 25 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated via rotary evaporation. Further purification was accomplished by SiO_2 column

chromatography (hexanes to 93:7 hexanes/EtOAc) to yield the desired compound **S3** as a white solid (0.960 g, 97%) (mp = 88-90 ^{o}C)

^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.53 (d, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 8.2 Hz, 1H), 7.33 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.28 - 7.23 (m, 1H), 7.11 (t, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 1.4 Hz, 1H), 7.00 (dd, *J* = 8.2, 2.2 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 159.7, 155.4, 136.0, 135.0, 131.4, 129.0, 127.2, 126.2, 120.9, 120.9, 118.5, 115.3, 103.3. **FT-IR** (cm^{-1}, neat, ATR) 3092 (vw), 2232 (w), 1584 (m), 1471 (s), 1400 (m), 1234 (s), 923 (m), 853 (m). **HRMS** (EI) calcd for $C_{13}H_7BrClNO$ [M^+]: 306.9400, found: 306.9396.

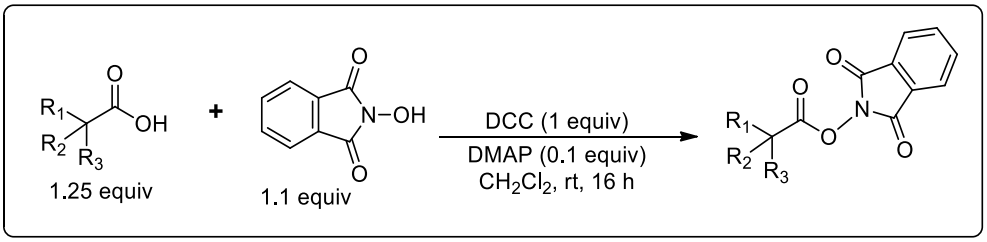
Synthesis of Bis(catecholato)diboron



Bis(catecholato)diboron was prepared according to a modified literature procedure.[19] A 500 mL, three-necked round bottom flask was equipped with large stirrer bar, two rubber septa, and an addition funnel capped with a rubber septum. The flask was equipped with an inlet needle, and the flask was evacuated and backfilled with Ar three times. The addition funnel was sealed off from the flask, equipped with an inlet needle, and backfilled with Ar. The funnel was charged with 200 mL of Et_2O. The Et_2O was degassed for 5 min, then added to the flask. Tetrakis(dimethylamido)diboron (6.00 g, 6.48 mL, 30.3 mmol, 1 equiv) was added *via* a syringe. The boron soln was allowed to drain into the flask, and then the addition funnel was sealed off from the flask. The funnel was then charged with a degassed soln of catechol (6.67 g, 60.6 mmol, 2.0 equiv) in anhyd Et_2O (50 mL). This soln was then added to the flask dropwise over 15 min. The soln became a thick, white slurry. After stirring for 2 h at rt, the reaction mixture was cooled to 0 ^{o}C in an ice-water bath, and the septum was removed from the addition funnel. To the addition funnel was added a degassed 1 M solution of HCl in Et_2O (150 mL, 151.5 mmol, 5 equiv), and this was added to the chilled flask, dropwise, over 20 min. The reaction mixture was allowed to warm to rt overnight. The reaction mixture was concentrated *in vacuo via* rotary evaporation to yield a crude, white solid. The solid was taken up in boiling toluene and filtered through a coarse fritted glass funnel to remove the diethylammonium chloride by-product. This was repeated two times. The filtrate was concentrated *via* rotary evaporation, and the crude solid was washed with cold MeCN (2 × 20 mL) to afford a fluffy white solid (5.1 g, 71%). All data matched that reported in the literature.[20]

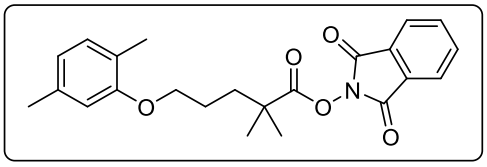
Synthesis of Organotrifluoroborates

General Procedure A1: Preparation of *N*-Hydroxyphthalimide Esters



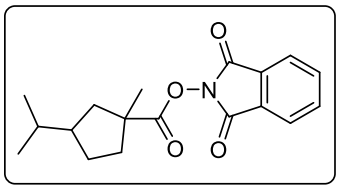
To an appropriately-sized round bottom flask equipped with a stirrer bar was added *N*-hydroxyphthalimide (1.1 equiv), DMAP (0.1 equiv), and the requisite carboxylic acid (1.25 equiv). The flask was sealed with a rubber septum and placed under an Ar atmosphere *via* an inlet needle. The flask was charged with CH_2Cl_2 (0.3 M), and the flask was cooled to 0 °C via an ice water bath. After 5 min, a soln of DCC (1 equiv) in CH_2Cl_2 (2 M) was added to the flask over 2 min. After complete addition, the ice-bath was removed, and the mixture was stirred overnight at rt. A voluminous precipitate was observed. After this time, the reaction mixture was filtered through a medium porosity fritted funnel (to remove the urea by-product). The filtrate was transferred to a separatory funnel and washed with satd aq Na_2CO_3, and the aq layer was extracted twice with CH_2Cl_2. The organic layer was washed with deionized H_2O, brine, and dried (Na_2SO_4). The solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by passing the crude material over a pad of silica, eluting with a proper ratio of hexane/EtOAc.

1,3-Dioxoisoindolin-2-yl 5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanoate, S4 (2.168 g, 47%) was



prepared from 5-(2,5-dimethylphenoxy)-2,2-dimethyl pentanoic acid (3.476 g, 13.89 mmol) according to **General Procedure A1.** The desired compound **S4** was obtained as a powdery white solid (mp = 74-75 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.89 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.2 Hz, 2H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.69 - 6.63 (m, 2H), 4.01 (t, *J* = 4.7 Hz, 2H), 2.33 - 2.29 (m, 3H), 2.21 - 2.17 (m, 3H), 1.98 - 1.92 (m, 4H), 1.45 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 157.3, 136.5, 130.4, 123.8, 120.6, 112.2, 83.1, 68.8, 37.4, 26.6, 25.0, 24.8, 21.5, 15.9. **FT-IR** (cm^{-1}, neat, ATR) 3001 (vw), 2950 (w), 1742 (vs), 1146 (s), 696 (m). **HRMS** (ESI) calcd for $C_{23}H_{25}NO_5$ $[M]^+$: 395.1733, found: 395.1740.

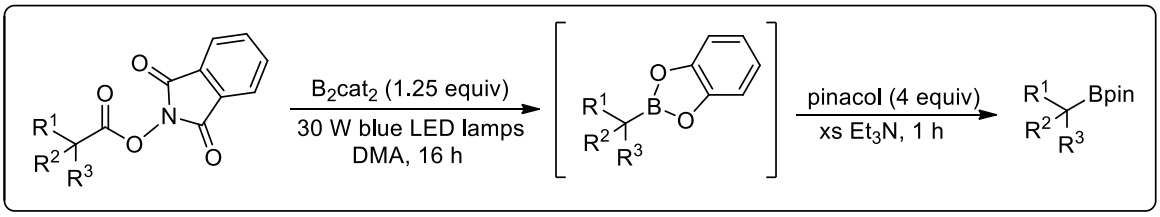
1,3-Dioxoisoindolin-2-yl 3-Isopropyl-1-methylcyclopentane Carboxylate, S5 (3.004 g, 97%) was



prepared from 3-isopropyl-1-methylcyclopentane-1-carboxylic acid (2.063 g, 10.00 mmol) according to **General Procedure A1.** The desired compound **S5** was obtained as a powdery white solid (mp = 74-75 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.88 (dd, *J* = 5.5, 3.1 Hz, 2 H), 7.78 (dd, *J* = 5.3, 3.2 Hz, 2 H), 2.45 (ddd, *J* = 13.0, 9.1, 3.5 Hz, 1 H), 2.05 - 1.96 (m, 1 H), 1.96 - 1.85 (m, 2 H), 1.81 - 1.70 (m, 1 H), 1.69 - 1.60 (m, 1 H), 1.51 - 1.41 (m, 5 H), 0.94 - 0.86 (m, 6 H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 174.8, 162.3, 134.8, 129.2, 124.0, 48.0, 47.1, 42.8, 38.1, 33.4, 30.7, 25.5, 21.7, 21.6 ppm. **FT-IR** (cm^{-1}, neat, ATR) 2958 (w), 1741 (vs), 696 (m). **HRMS** (EI) calcd for C_9H_{17} [M – CO_2phthalimide]: 125.1325, found: 125.1243 and $C_8H_5NO_2$ [phthalimide]: 147.0320, found: 147.0320.

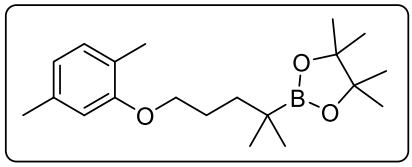
Synthesis of Pinacolboronate Esters from NHPI Esters

General Procedure A2: Synthesis of 3° Bpins via Decarboxylative Borylation of NHPI Esters



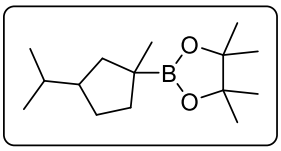
Pinacolboronate esters were prepared from NHPI redox-active esters *via* a modified literature procedure.[21] To an appropriately sized reaction vial equipped with a stirrer bar was added the NHPI ester (1 equiv) and B_2cat_2 (1.25 equiv). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum and placed under an inert atmosphere of argon. Thoroughly degassed DMA (0.1 M) was added, and the headspace of the vial was purged with Ar for 30 sec. The vial was sealed with Parafilm® and irradiated overnight with Kessil H150-Blue lamps using a previously described photoreactor.[22] After this time, the vial was removed from the reactor and was charged with a soln of pinacol (4 equiv) in Et_3N (25 equiv) and then stirred for 1 h. The contents of the vial were transferred to a separatory funnel and diluted with EtOAc and a 1:1 H_2O/satd NH_4Cl soln. The layers were separated, and the aq layer was extracted twice with EtOAc. The organic layer was washed with H_2O, brine, and dried (Na_2SO_4). The solvent was removed *in vacuo* by rotary evaporation to give the crude ester. Further purification was accomplished by rapid silica gel column chromatography to yield the desired boronic ester.

2-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, S6



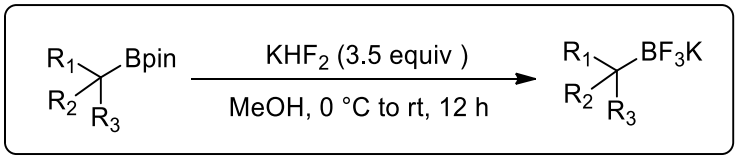
(combined yield: 0.822 g, 50%) was prepared from **S4** (0.198 g, 0.500 mmol) according to **General Procedure A2**. The reaction was carried out 10 times in parallel (5.00 mmol total). After 24 h of irradiation, the reactions were combined and converted into the corresponding pinacol boronate ester and purified together. The desired compound **S6** was obtained as a waxy, salmon-colored solid (mp = 57-59 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 6.99 (d, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 3.91 (t, *J* = 6.6 Hz, 2H), 2.30 (s, 3H), 2.18 (s, 3H), 1.74 (br s, 2H), 1.46 - 1.40 (m, 2H), 1.23 (s, 12H), 0.96 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 157.3, 136.5, 130.4, 123.8, 120.6, 112.2, 83.1, 68.8, 37.4, 26.6, 25.0, 24.8, 21.5, 15.9. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 34.3. **FT-IR** (cm^{-1}, neat, ATR) 2937 (w), 2863 (w), 1308 (m), 1265 (m), 1140 (s). **HRMS** (EI) calcd for $C_{20}H_{33}BO_3$ $[M]^+$: 332.2523, found: 332.2535.

2-(-3-Isopropyl-1-methylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, S7 (0.290 g, 23%) was



prepared from **S5** (1.577 g, 5.00 mmol) according to **General Procedure A2**. The desired compound **S7** was obtained as a pink-tinted oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 2.05 - 1.75 (m, 2H), 1.75 - 1.60 (m, 1H), 1.58 - 1.29 (m, 3H), 1.28 - 1.13 (m, 14H), 0.99 (d, *J* = 14.0 Hz, 3H), 0.87 (dd, *J* = 6.0, 4.6 Hz, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 83.0, 82.9, 48.7, 46.9, 43.0, 41.6, 36.9, 36.8, 34.3, 33.9, 31.3, 30.2, 24.8, 24.8, 24.3, 22.0, 21.9, 21.8, 21.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 34.7. **FT-IR** (cm^{-1}, neat, ATR) 2973 (m), 2945 (m), 1433 (w), 1364 (m), 1318 (m), 1204 (m). **HRMS** (EI) calcd for C_9H_{17} [M – Bpin; C_9H_{17}]: 125.1325, found: 125.1337.

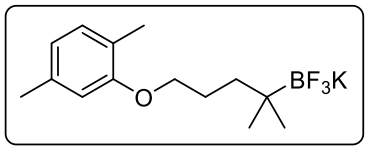
General Procedure A3: Conversion of Pinacolboronate Esters to Organotrifluoroborates



To an appropriately sized round bottom flask equipped with a stirrer bar was added the pinacolboronate ester (1 equiv). MeOH was added to the flask, and the soln was cooled to 0 °C in an ice-water bath. After cooling for 5 min, aq KHF_2 (3.5 equiv, 4.5 M) was added dropwise *via* an addition funnel. After complete addition, the ice-water bath was removed, and the reaction was allowed to stir at rt overnight. After this time, the solvent was removed *in vacuo via* rotary evaporation. The resulting crude solid was taken up in

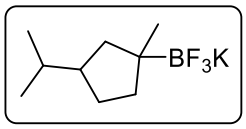
boiling acetone (three to five portions) and filtered through a fritted glass funnel to remove inorganic salts. The filtrate was concentrated *via* rotary evaporation, and the crude solid was washed with a 1:1 mixture of pentane/CH_2Cl_2 then CH_2Cl_2 to afford the pure organotrifluoroborate.

Potassium (5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)trifluoroborate, S8 (0.951 g, 93%) was



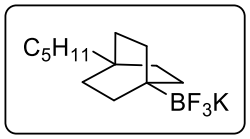
prepared from **S6** according to **General Procedure A3**. The desired compound **S8** was obtained as a crystalline, white solid (mp = 82-83 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 6.94 (d, *J* = 7.5 Hz, 1H), 6.70 (s, 1H), 6.58 (d, *J* = 7.5 Hz, 1H), 3.86 (t, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 2.12 (s, 3H), 1.88 - 1.78 (m, 2H), 1.30 - 1.23 (m, 2H), 0.73 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 157.3, 136.5, 130.4, 123.8, 120.6, 112.2, 83.1, 68.8, 37.4, 26.6, 25.0, 24.8, 21.5, 15.9. **^{19}F NMR** ($CDCl_3$, 471 MHz) δ - 151.00 (s, 3F).**^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 6.9. **FT-IR** (cm^{-1}, neat, ATR) 2948 (w), 2861 (vw), 1509 (m), 1263 (m), 1025 (s), 948 (m). **HRMS** (ESI) calcd for $C_{14}H_{21}BF_3O$ $[M\text{-}K^+]^+$: 277.1630, found: 273.1657.

Potassium (3-Isopropyl-1-methylcyclopentyl)trifluoroborate, S9 (0.290 g, 66%) was prepared from



S7 (0.480 g, 1.90 mmol) according to **General Procedure A3**. The desired compound **S9** was obtained as a powdery white solid (mp = 234-235 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ) δ ppm 1.94 (dd, *J* = 11.9, 7.9 Hz) and 0.54 (t, *J* = 10.8 Hz, 1H total), 1.69 (m, 2H), 1.53 (dt, *J* = 17.0, 8.2 Hz, 1H), 1.24 (m, 2H), 1.12 (m, 1H), 0.97 (m, 1H), 0.85 (m, 6H), 0.78 (d, *J* = 7.6 Hz, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 50.3, 48.2, 43.9, 42.6, 37.4, 37.2, 35.7, 35.0, 32.4, 31.9, 27.4, 26.0, 22.5, 22.4. **^{19}F NMR** ($CDCl_3$, 471 MHz) δ - 151.93 (s, 3F).**^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 5.6. **FT-IR** (cm^{-1}, neat, ATR) 2951 (m), 1465 (w), 1049 (w), 938 (s). **HRMS** (ESI) calcd for $C_9H_{17}BF_3$ $[M\text{-}K^+]^-$: 193.1375, found: 193.1369.

Potassium (4-Pentylbicyclo[2.2.2]octan-1-yl)trifluoroborate, S10 (0.730 g, 88%) was prepared from

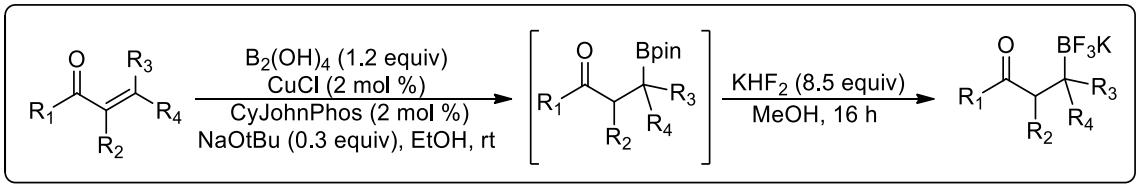


the corresponding NHPI ester (0.890 g, 2.91 mmol) according to **General Procedure A3**. The desired compound **S10** was obtained as a powdery white solid (mp = 255-257 °C). **^{1}H NMR** (acetone-d_6, 500 MHz) δ ppm 1.48 - 1.40 (m, 6H), 1.28 - 1.37 (m, 2H), 1.26 - 1.15 (m, 10H), 1.03 - 0.96 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (acetone-d_6, 125 MHz) δ ppm 43.9, 33.9, 32.9, 31.2, 28.4, 24.0, 23.4, 14.4, 0.5. **^{19}F NMR** ($CDCl_3$, 471 MHz) δ - 152.67 (s, 3F).**^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 4.6. **FT-IR** (cm^{-1}, neat, ATR) 2923 (m), 2854 (m), 1202 (m), 908 (s). **HRMS** (ESI) calcd for $C_{13}H_{23}BF_3$ $[M\text{-}K^+]^-$: 247.1845, found: 247.1866.

Potassium (1-Methylcyclohexyl)trifluoroborate, S11 (0.330 g, 39%) was prepared from the corresponding NHPI ester (0.935 g, 4.17 mmol) according to **General Procedure A2**. The desired compound **S11** was obtained as a powdery white solid (mp = 195-197 °C). **^{1}H NMR** (acetone-d_6, 500 MHz) δ ppm 1.58 - 1.50 (m, 2H), 1.49 - 1.37 (m, 5H), 1.32 - 1.23 (m, 1H), 1.09 – 1.02 (m, 2H), 0.76 (s, 3H). **^{13}C NMR** (acetone-d_6, 125 MHz) δ ppm 35.6, 28.6, 23.3, 22.9, 22.8, 22.7. **^{19}F NMR** ($CDCl_3$, 471 MHz) δ - 151.80 (s, 3F).**^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 6.4. **FT-IR** (cm^{-1}, neat, ATR) 3657 (m), 3541 (w), 2919 (m), 949 (s), 921 (s), 871 (m). **HRMS** (ESI) calcd for $C_7H_{13}BF_3$ $[M\text{-}K^+]^+$: 165.1062, found: 165.1078.

Synthesis of Pinacolboronate Esters from α,β-Unsaturated Carbonyl Compounds

General Procedure B: Two-Step/One-Pot Borylation/BF_3K Synthesis from Enones

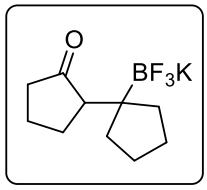


The following protocol is a modified literature procedure.[23] In an argon filled glovebox, CuCl (2 mol %), NaO*t*-Bu (30 mol %), CyJohnPhos (2 mol %), and $B_2(OH)_4$ (1.2 equiv) were added to the flask. The flask was sealed with a rubber septum and removed from the glovebox. Absolute EtOH (0.1 M) and the enone (1 equiv) were then added via a syringe. The reaction was allowed to stir at rt under Ar until the solution turned colorless (1–24 h), at which point the borylation was judged to be complete. The reaction mixture was filtered through a pad of Celite, and the pad was washed with EtOAc. The filtrate was concentrated *via* rotary evaporation, and the resultant crude Bpin was taken up in MeOH (0.1 M) and cooled to 0 °C in an ice-water bath. After 5 min, aqueous KHF_2 (8.5 equiv, 4.5 M) was added dropwise *via* an addition funnel. After complete addition, the ice bath was removed, and the reaction was allowed to stir overnight. After this time, the crude reaction mixture was concentrated *via* rotary evaporation. The crude solid was taken up in portions of boiling acetone and filtered through a coarse fritted glass funnel to remove inorganic byproducts. The filtrate was concentrated via rotary evaporation, and the crude solid was washed with a 1:1 mixture of pentane/CH_2Cl_2 then CH_2Cl_2 to afford pure organotrifluoroborate.

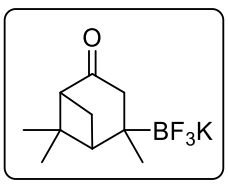
Potassium (1-Methyl-3-oxocyclopentyl)trifluoroborate,[24] S12 (0.717 g, 70%) was prepared according to **General Procedure B**. All data matched that recorded in the literature.

Potassium (2-Methyl-4-oxopentan-2-yl)trifluoroborate,[23] S13 (5.99 g, 83%) was prepared according to **General Procedure B**. All data matched that recorded in the literature.

Potassium (2'-Oxo-[1,1'-bi(cyclopentan)]-1-yl)trifluoroborate, S14 (0.690 g, 54%) was prepared according to **General Procedure B**. The desired compound **S14** was obtained as a crystalline, white solid (mp = 170-171 ºC). **^{1}H NMR** (acetone-d_6, 500 MHz) δ ppm 2.18 - 2.07 (m, 2H), 2.01 - 1.91 (m, 2H), 1.91 - 1.83 (m, 1H), 1.80 - 1.65 (m, 3H), 1.59 - 1.39 (m, 6H), 1.35 (dd, J = 11.5, 6.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 223.8, 56.8, 40.7, 35.9, 34.3, 29.3, 26.8, 26.1, 21.6 ppm. **^{19}F NMR** ($CDCl_3$, 471 MHz) δ - 143.10 (s, 3F).**^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 4.9, 4.4. **FT-IR** (cm^{-1}, neat, ATR) 2951 (w), 1593 (m), 1364 (m), 1318 (m), 1204 (m), 1140 (vs) **HRMS** (ESI) calcd for $C_{10}H_{15}BF_3O$ [M-K^+]$^-$: 21s9.1168, found: 219.1169.

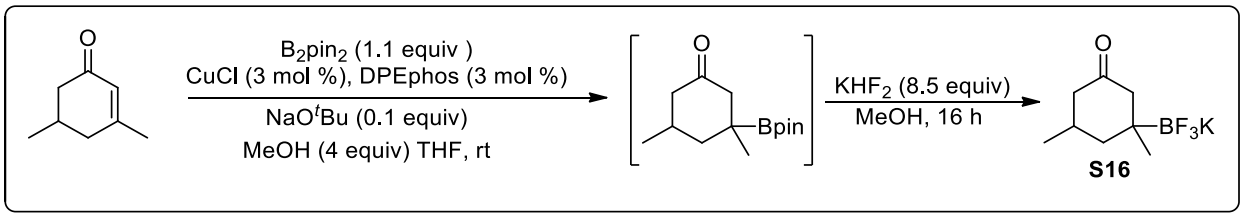


Potassium (2,6,6-Trimethyl-4-oxobicyclo[3.1.1]heptan-2-yl)trifluoroborate, S15 (1.340 g, 80%) was prepared according to **General Procedure B**. The desired compound **S15** was obtained as a crystalline, white solid (mp = 115-117 ºC). **^{1}H NMR** (acetone-d*6*, 500 MHz) δ ppm 2.75 and 2.71 (s, total 1H), 2.24 - 2.17 (m, 2H), 2.13 (d, J = 8.8 Hz, 1H), 2.09 – 2.05 (m, 1H), 1.81 and 1.77 (s, total 1H), 1.26 (s, 3H), 0.99 (s, 3H), 0.95 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 216.9, 58.9, 51.0, 45.0, 42.4, 27.6, 26.3, 25.6, 23.5 ppm **^{19}F NMR** ($CDCl_3$, 471 MHz) δ - 150.75 (s, 3F).**^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 4.8. **FT-IR** (cm^{-1}, neat, ATR) 2937 (w), 1690 (m), 1025 (m), 982 (s), 950 (m). **HRMS** (ESI) calcd for $C_{10}H_{15}BF_3O$ [M-K^+]$^+$: 219.1168, found: 219.1178.



Alternative Procedure for Borylation of Enones

Potassium (1,3-Dimethyl-5-oxocyclohexyl)trifluoroborate, S16

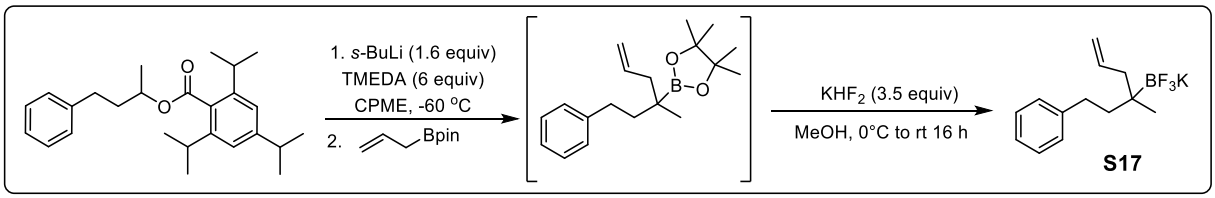


The following protocol is modified from a literature procedure.[25] To a 100 mL round bottom flask was added the enone (*if solid*) (1 equiv). The flask was carefully brought into the glovebox. CuCl (0.018 g, 0.18 mmol 0.03 equiv), DPEphos (0.097 g, 0.18 mmol, 0.03 equiv), and NaO*t*-Bu (0.058 g, 0.60 mmol, 0.01 equiv) were added to the flask. The flask was sealed with a rubber septum and removed from the glovebox. Anhyd THF (12 mL) was added to the flask, and the contents of the flask were stirred for ~30 min. After this time, the flask was charged with a soln of B_2pin_2 in THF (4 mL). After 10 min, the flask was charged with the enone (0.745 g, 6.00 mmol, 1 equiv) followed by MeOH (0.769 g, 0.97 mL, 24.0

mmol, 4 equiv) added via syringe. The reaction was allowed to stir at rt under Ar until TLC analysis confirmed reaction completion. The reaction mixture was filtered through a pad of Celite, and the pad was washed Et_2O (2 x 15 mL). The filtrate was concentrated via rotary evaporation, and the resultant crude Bpin was taken up in MeOH (0.1 M) and cooled to 0 °C in an ice-water bath. After 5 min, 4.5 M aq KHF_2 (11.3 mL, 0.051 mmol, 8.5 equiv) was added dropwise via an addition funnel. After complete addition, the ice bath was removed, and the reaction was allowed to stir overnight. After this time, the crude reaction mixture was concentrated via rotary evaporation. The crude solid was taken up in portions of boiling acetone (5 x 15 mL), and filtered through a coarse fritted glass funnel to remove inorganic byproducts. The filtrate was concentrated via rotary evaporation, and the crude solid was washed with a 1:1 mixture of pentane/CH_2Cl_2 (50 mL) then CH_2Cl_2 (20 mL) to afford pure organotrifluoroborate **S16** (0.141 g, 10% over two steps) as a crystalline, white solid (mp = 180-181 °C).

^{1}H NMR (acetone-d_6, 500 MHz) δ ppm 2.36 - 2.23 (m, 1H), 2.18 (d, J = 13.0 Hz, 1H), 1.86 (d, J = 12.2 Hz, 1H), 1.72 (t, J = 12.9 Hz, 1H), 1.56 (d, J = 13.0 Hz, 1H), 1.17 (s, 2H), 0.88 (d, J = 6.4 Hz, 3H), 0.78 (s, 3H). **^{13}C NMR** (acetone-d_6, 125 MHz) δ ppm 52.8, 50.2, 46.9, 31.4, 28.1, 25.3, 25.2, 23.7. **^{19}F NMR** (acetone-d_6, 471 MHz) δ -147.46 (s, 3F).**^{11}B NMR** (acetone-d_6, 128.4 MHz) δ 9.8, 9.4. **FT-IR** (cm^{-1}, neat, ATR) 2954 (w), 2922 (vw), 2866 (vw), 2820 (vw), 1701 9s), 1016 (s), 958 (s). **HRMS** (ESI) calcd for $C_8H_{13}BF_3O$ [M-K$^+$]$^+$: 193.1012, found: 193.0993.

Preparation of Alkene-containing Organotrifluoroborate, S17



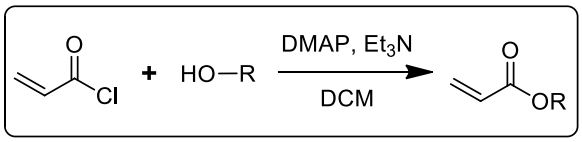
4,4,5,5-Tetramethyl-2-(3-methyl-1-phenylhex-5-en-3-yl)-1,3,2-dioxaborolane (**S17**) was prepared via known literature procedure.[26] After the lithiation/borylation reaction, the product was passed through a silica plug, eluting with Et_2O. After removal of the solvent, the crude product was converted to the corresponding organotrifluoroborate using **General Procedure A3**. The desired compound was obtained as a white crystalline solid (mp = 156-158 °C) (0.401 g, 36% yield).

^{1}H NMR (acetone-d_6, 500 MHz) δ ppm 7.21 - 7.16 (m, 2H), 7.16 - 7.11 (m, 2H), 7.08 - 7.03 (m, 1H), 6.14 - 6.03 (m, 1H), 4.85 (dt, J = 17.1, 1.4 Hz, 1H), 4.79 (dd, J = 10.1, 2.9 Hz, 1H), 2.68 - 2.56 (m, 2H), 2.14 - 2.07 (m, 1H), 1.99 (dd, J = 13.4, 7.7 Hz, 1H), 1.42 (t, J = 8.7 Hz, 2H), 0.79 - 0.72 (m, 3H). **^{13}C NMR** (acetone-d_6, 125 MHz) δ ppm 147.2, 141.6, 129.2, 128.7, 125.4, 113.1, 43.8, 42.3, 32.6, 23.3. **^{19}F**

NMR (acetone-d_6, 471 MHz) δ -148.42 (s, 3F).[11] **B NMR** (acetone-d_6, 128.4 MHz) δ 9.8. **FT-IR** 3063 (w), 2944 (m), 1495 (w), 937 (vs) (cm^{-1}, neat, ATR). **HRMS** (ESI) calcd for $C_{13}H_{17}BF_3$ $[M\text{-}K^+]^+$: 241.1375, found: 241.1377.

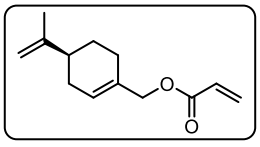
Synthesis of Non-Commercial Giese Acceptors

General Procedure C: Preparation of Acrylates



An appropriately sized flask equipped with a stir bar was charged with the desired alcohol (1 equiv), sealed with a rubber septum with inlet needle, and purged with Ar. The flask was then charged with anhydrous dichloromethane (0.3 M) and the flask was placed in an ice/water bath and allowed to cool to 0 °C. Acryloyl chloride (1.5 equiv) was added followed by DMAP (0.1 equiv). Triethylamine (2.5 equiv) was added dropwise and the solution darkened. The flask was stirred at 0 °C for five minutes after this addition and then the ice bath was removed. The contents of the flask were stirred at rt for two h. The reaction was then quenched with saturated aqueous NH_4Cl and the layers were separated. The aqueous layer was extracted with dichloromethane and the combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated *via* rotary evaporation. The resulting crude acylated product was purified via passage of the crude material over a pad of silica and/or vacuum distillation.

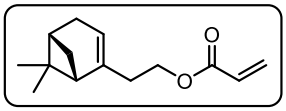
Pent-4-en-1-yl Acrylate,[27] **S18** (1.12 g, 81%) was prepared from 4-penten-1-ol (850 mg, 9.87 mmol) using **General Procedure C**. The desired acrylate **S18** was isolated as colorless liquid. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 6.40 (dd, *J*=17.4, 1.4 Hz, 1 H), 6.12 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.75 - 5.89 (m, 2H), 5.04 (dq, *J* = 17.2, 1.6 Hz, 1H), 4.99 (dq, *J* = 10.1, 1.1 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 2.15 (q, *J* = 7.3 Hz, 2H), 1.78 (dt, *J* = 13.6, 6.9 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 166.5, 137.7, 130.8, 128.9, 115.6, 64.2, 30.3, 28.1. **FT-IR** (cm^{-1}, neat, ATR) 2956 (w), 1723 (vs), 1407 (m), 1270 (s), 1184 (vs), 809 (s). **HRMS** (ESI) calcd for $C_8H_{12}O_2$ $[M]^+$: 140.0837, found: 140.0835.



(*S*)-(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl Acrylate, S19 (1.54 g, 75%) was prepared from (*S*)-perillyl alcohol (1.52 g, 10.0 mmol) using **General Procedure C**. The desired acrylate **S19** was isolated as a colorless liquid. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 6.42 (d, *J* = 17.2 Hz, 1H), 6.14 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.83 (d, *J* =

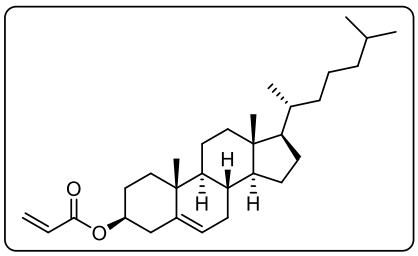
10.5 Hz, 1H), 5.78 (br. s, 1H), 4.72 (d, *J* = 8.4 Hz, 2H), 4.55 (s, 2H), 2.22 - 2.05 (m, 4H), 2.03 - 1.92 (m, 1H), 1.91 - 1.81 (m, 1H), 1.74 (s, 3H), 1.50 (tt, *J* = 12.0, 8.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 166.4 (s), 149.9 (s), 132.8 (s), 131.0 (s), 128.8 (s), 126.1 (s), 109.1 (s), 68.8 (s), 41.1 (s), 30.7 (s), 27.6 (s), 26.7 (s), 21.0 (s). **FT-IR** (cm^{-1}, neat, ATR) 2920 (w), 1724 (vs), 1405 (m), 1180 (vs), 808 (m). **HRMS** (ESI) calcd for $C_{13}H_{18}O_2$ $[M]^+$: 206.1307, found: 206.1321.

2-((1*S*,5*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl Acrylate, S20 (1.15 g, 87%) was prepared



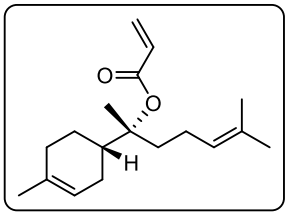
from 1-(S)-nopol (998 mg, 6.00 mmol) using **General Procedure C**. The desired acrylate **S20** was isolated as colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 6.38 (d, *J* = 17.2 Hz, 1H), 6.10 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.80 (d, *J* = 10.5 Hz, 1H), 5.31 (s, 1H), 4.10 - 4.24 (m, 2H), 2.30 - 2.41 (m, 3H), 2.22 (q, *J* = 17.2 Hz, 2H), 2.00 - 2.11 (m, 2H), 1.27 (s, 3H), 1.15 (d, *J* = 8.5 Hz, 1H), 0.82 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 166.5, 144.4, 130.7, 128.9, 119.2, 63.2, 46.0, 41.0, 38.3, 36.2, 31.9, 31.7, 26.6, 21.4. **FT-IR** (cm^{-1}, neat, ATR) 2915 (m), 1725 (vs), 1406 (m), 1183 (vs), 984 (m), 808 (m). **HRMS** (ESI) calcd for $C_{14}H_{20}O_2$ $[M]^+$: 220.1463 found: 220.1456.

Cholesteryl Acrylate,[28] **S21** (1.83 g, 69%) was prepared from cholesterol (2.32 g, 6.00 mmol) using



General Procedure C. The desired acrylate **S21** was isolated as white powdery solid (mp = 119-121 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 6.38 (dd, *J* = 17.4, 1.4 Hz, 1H), 6.10 (dd, *J* = 17.4, 10.4 Hz, 1H), 5.79 (dd, *J* = 10.5, 1.4 Hz, 1H), 5.39 (d, *J* = 4.7 Hz, 1H), 4.62 - 4.75 (m, 1H), 2.36 (d, *J* = 7.5 Hz, 2H), 1.78 - 2.08 (m, 5H), 1.41 - 1.69 (m, 7H), 1.21 - 1.40 (m, 4H), 1.05 - 1.21 (m, 7H), 1.03 (s, 3H), 0.90 - 1.02 (m, 6H), 0.87 (dd, *J* = 6.6, 2.1 Hz, 6H), 0.68 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 165.9, 139.9, 130.5, 129.4, 123.0, 74.4, 57.0, 56.5, 50.3, 42.6, 40.0, 39.8, 38.4, 37.3, 36.9, 36.5, 36.1, 32.2, 32.2 , 28.5, 28.3, 28.1, 24.6, 24.1, 23.1, 22.9, 21.3, 19.6, 19.0, 12.2. **FT-IR** (cm^{-1}, neat, ATR) 2934 (w), 1719 (s), 1409 (m), 1203 (vs), 984 (m), 804 (m). **HRMS** (ESI) calcd for $C_{30}H_{48}O_2$ $[M]^+$: 440.3654, found: 440.3650.

(*R*)-6-Methyl-2-((*S*)-4-methylcyclohex-3-en-1-yl)hept-5-en-2-yl Acrylate, S22 (890 mg, 32%) was



prepared from (-)-α-Bisabolol (2.250 g, 10.12 mmol) using **General Procedure C** with the following modifications: 1) $CHCl_3$ was used in place of dichloromethane as the solvent; 2) The reaction was heated to 55 °C for 16 hrs. The desired acrylate **S22** was isolated as a yellow-tinted, viscous oil. **^{1}H NMR**

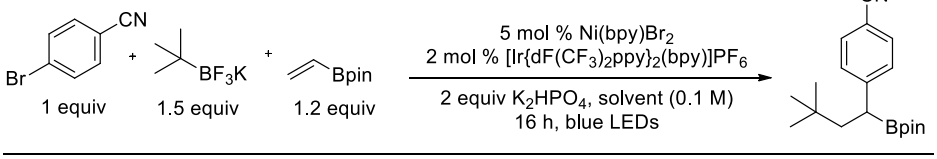
($CDCl_3$, 500 MHz) δ ppm 6.29 (dd, *J* = 17.4, 1.5 Hz, 1H), 6.05 (dd, *J* = 17.3, 10.3 Hz, 1H), 5.73 (dd, *J* = 10.4, 1.5 Hz, 1H), 5.32 - 5.40 (m, 1H), 5.04 - 5.14 (m, 1H), 2.25 (tdd, *J* = 11.7, 11.7, 5.0, 2.0 Hz, 1H), 1.76 - 2.10 (m, 9H), 1.66 (s, 3H), 1.64 (s, 3H), 1.58 (s, 3H), 1.44 (s, 3H), 1.34 (qd, *J* = 11.9, 5.3 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 165.6, 134.4, 131.9, 130.6, 129.6, 124.3, 120.5, 87.6, 40.8, 35.8, 31.2, 26.6, 26.0, 23.9, 23.6, 22.3, 20.8, 17.8. **FT-IR** (cm^{-1}, neat, ATR) 2926 (w), 1719 (vs), 1401 (m), 1203 (vs), 1046 (m), 809 (m). **HRMS** (ESI) calcd for $C_{15}H_{24}$ $[M - CH_2{=}CHCO_2H]^+$: 204.1878, found: 204.1866.

Optimization and Control Studies

General Optimization Procedure A: To a 4 mL reaction vial equipped with a stirrer bar was added 1-bromo-4-chlorobenzene (**1**) (19.1 mg, 0.1 mmol, 1 equiv), $^{t}BuBF_3K$ (**2**) (24.6 mg, 0.15 mmol, 1.5 equiv), the appropriate amount of K_2HPO_4 (1 or 2 equiv), the appropriate photocatalyst (0.002 mmol, 0.02 equiv for organometallic complexes or 0.005 mmol, 0.05 equiv for organic dyes), and anhyd Ni(bpy)Br_2 (0.005 mmol, 0.05 equiv). The vial was sealed with a cap containing a TFE-lined silicone septa and was evacuated and purged with argon three times via an inlet needle. The vial was then charged with the vinyl boronate (**3**) (20.6 mg, 0.12 mmol, 1.2 equiv) in anhyd, degassed THF (1 mL). After this, the cap was sealed with Parafilm®, and the vial was irradiated with blue LEDs for 16 h (470 nm, ~10 W, at a distance of ~4.5 cm). The temperature of the reaction was maintained at approximately 27 ºC via a fan. After 16 h, an aliquot of a solution of 4,4′-di-*tert*-butylbiphenyl in MeCN with a known concentration (20 mol % relative to the aryl halide) was added to each vial. Reaction progress was evaluated by GCMS to determine product-to-internal standard ratio (P/IS). These ratios were determined by comparing the values of the corrected peak areas of the desired product against 4,4′-di-*tert*-butylbiphenyl or 2,6-dimethylnaphthalene.

General Optimization Procedure B: To a 4 mL reaction vial equipped with a stirrer bar was added the appropriate aryl halide (0.1 mmol, 1 equiv), $^{t}BuBF_3K$ (**2**) (24.6 mg, 0.15 mmol, 1.5 equiv), the appropriate base (0.1 mmol, 1 equiv), the appropriate Ni source (0.005 mmol, 0.05 equiv), and $[Ir\{dF(CF_3)_2ppy\}_2(bpy)]PF_6$ (2.0 mg, 0.002 mmol, 0.02 equiv). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum, evacuated, and filled with argon three times. The vinyl boronate (**3**) and aryl bromides (if liquid) were dissolved in degassed THF and added to the reaction mixture. The vial was further sealed with Parafilm® and irradiated with blue LEDs (470 nm, ~10 W, at a distance of ~4.5 cm) for 16 h. Upon reaction completion, a 250 μL aliquot of the reaction mixture concentrated via rotary evaporation then re-dissolved in 250 μL of $CDCl_3$. The resulting soln was passed through a hydrophobic PTFE 0.2 μm syringe-driven filter unit and dispensed into an NMR tube. To the NMR tube was also added 250 μL of a stock soln of dimethyl fumarate (0.1 M in $CDCl_3$). NMR yields were calculated based on relative integrations of the alkenyl peak of dimethyl fumarate and the benzylic proton in the dicarbofunctionalized products.

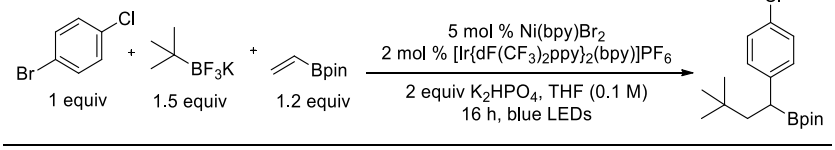
Table S1: Solvent Screen for Ni/Photoredox Dicarbofunctionalization[a]



solvent	P/IS
NMP	2.04
1,4-dioxane	3.31
THF	4.15
MeCN	0.19
DMA	3.30
DMSO	0.04
acetone	2.16
EtOAc	4.10

[a]Performed according to **General Optimization Procedure A**

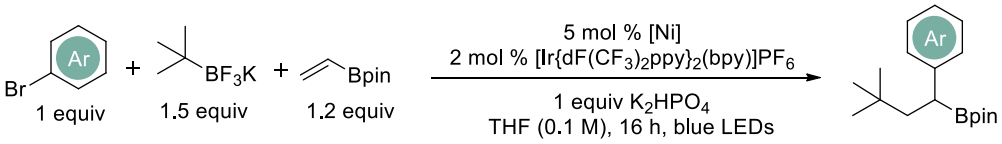
Table S2: Photocatalyst Screen for Ni/Photoredox Dicarbofunctionalization[a]

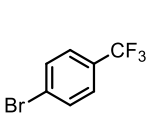


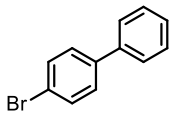
photocatalyst	P/IS
$[Ir\{dF(CF_3)_2ppy\}_2(bpy)]PF_6$	2.00
$[Ir\{dF(CF_3)_2ppy\}_2(dtbpy)]PF_6$	1.88
$[Ir\{ppy\}_2(dtbpy)]PF_6$	0.11
$[Ru(bpy)_3](PF_6)_2$	-
$[Ru(bpz)_3](PF_6)_2$	-
4-CzIPN	0.24
4-Cl-CzIPN	1.78

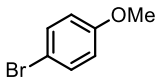
[a]Performed according to **General Optimization Procedure A**

Table S3: Nickel/Ligand Screen for Ni/Photoredox Dicarbofunctionalization[a]









[Ni]	NMR yield (%)	[Ni]	NMR yield (%)	[Ni]	NMR yield (%)
$Ni(dme)Br_2$	15	$Ni(dme)Br_2$	0	$Ni(dme)Br_2$	0
$Ni(dtbbpy)Br_2$	45	$Ni(dtbbpy)Br_2$	34	$Ni(dtbbpy)Br_2$	31
$Ni(Me\text{-}pyr)Br_2$	9	$Ni(Me\text{-}pyr)Br_2$	4	$Ni(Me\text{-}pyr)Br_2$	0
$Ni(acac)_2$	0	$Ni(acac)_2$	0	$Ni(acac)_2$	0
$Ni(TMHD)_2$	0	$Ni(TMHD)_2$	0	$Ni(TMHD)_2$	0
Ni(phthaloCN)	0	Ni(phthaloCN)	0	Ni(phthaloCN)	0
$Ni(phen)Br_2$	31	$Ni(phen)Br_2$	41	$Ni(phen)Br_2$	6
$Ni(imine)Br_2$	0	$Ni(imine)Br_2$	0	$Ni(imine)Br_2$	0
$Ni(bpy)Br_2$	55	$Ni(bpy)Br_2$	29	$Ni(bpy)Br_2$	19

[a]Performed according to **General Optimization Procedure B**

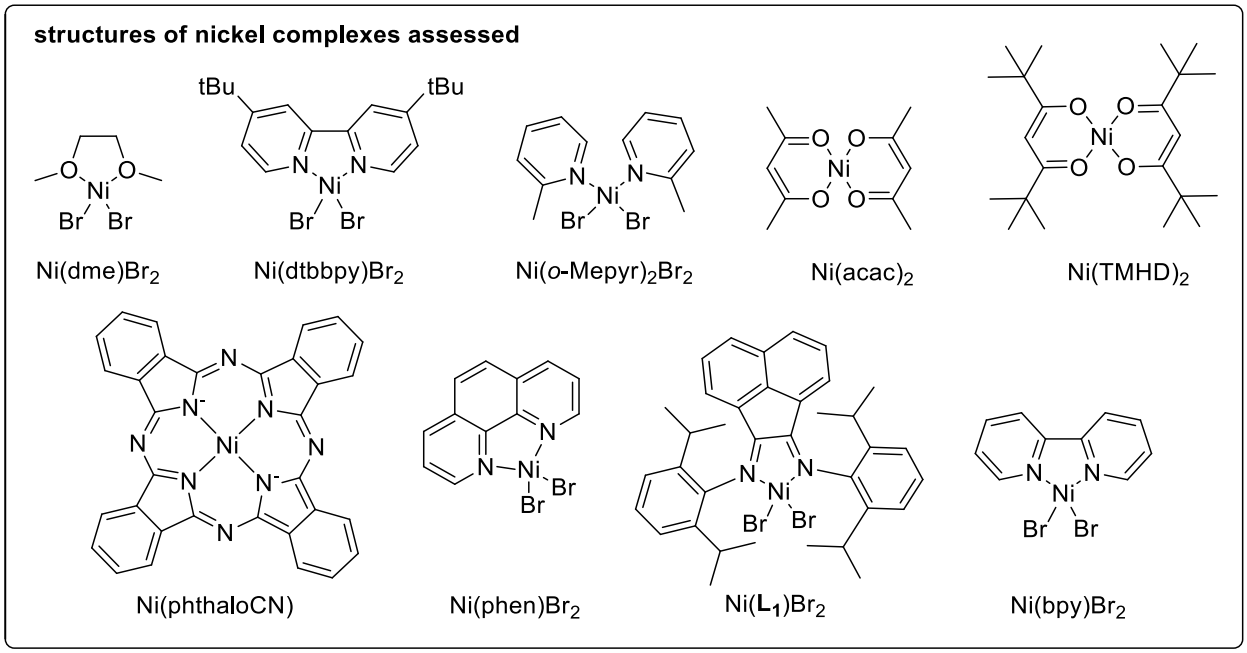
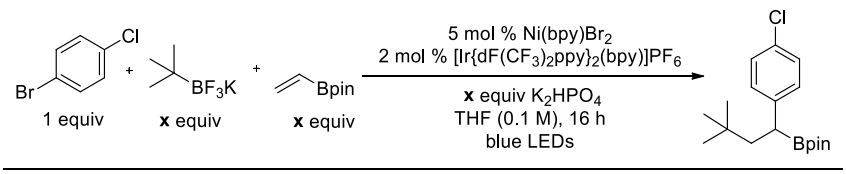


Table S4: Base Screen for Ni/Photoredox Dicarbofunctionalization[a]

base	NMR yield (%)
K_2HPO_4	63
KOAc	0
Cs_2CO_3	0
K_3PO_4	7
K_2CO_3	64[b]
$NaHCO_3$	75[b]

[a]Performed according to **General Optimization Procedure B** [b]Although slightly higher NMR yields were achieved for these entries, the formation of inseparable, undesired products was observed.

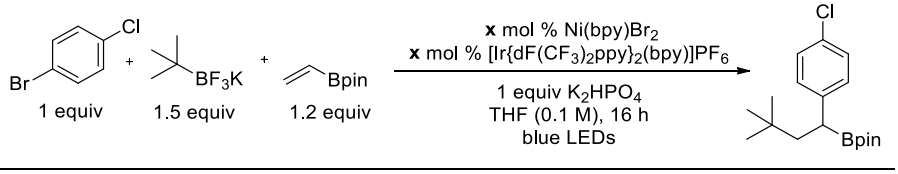
Table S5: Stoichiometry Variation for Ni/Photoredox Dicarbofunctionalization[a]



equiv vinyl Bpin	equiv $^tBuBF_3K$	equiv K_2HPO_4	NMR yield (%)
1.2	1.5	1	63
1.5	1.5	1	58
1.2	2	1	56
1.2	1.5	2	70
1.5	1.1	1	41

[a]Performed according to **General Optimization Procedure A**

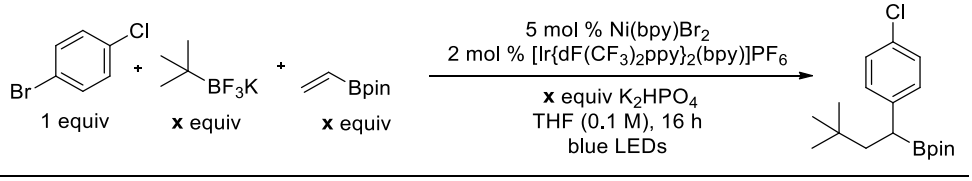
Table S6: Catalyst Loading Analysis for Ni/Photoredox Dicarbofunctionalization[a]



mol % Ir	mol % Ni	NMR yield (%)
2	5	63
5	10	66
3	3	58
5	3	59

[a]Performed according to **General Optimization Procedure A**

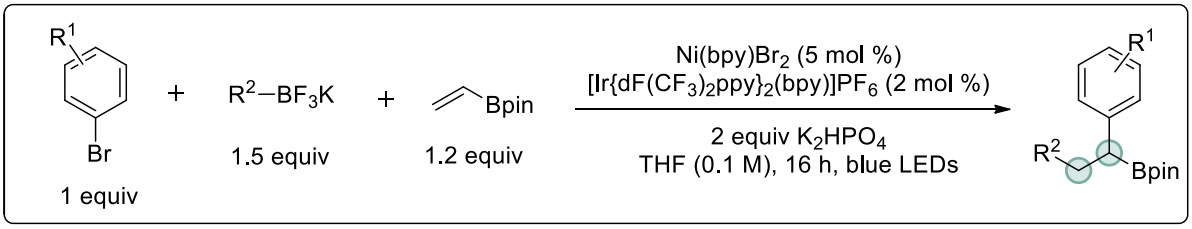
Table S7: Concentration Screen for Ni/Photoredox Dicarbofunctionalization[a]



conc. (M)	NMR yield (%)
0.05	67
0.075	61
0.1	70
0.175	63
0.25	39

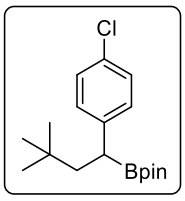
[a]Performed according to **General Optimization Procedure A**

General Procedure for Ni/Photoredox Dicarbofunctionalization (DCF)



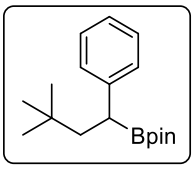
To an 8 mL reaction vial equipped with a stirrer bar was added organotrifluoroborate (0.75 mmol, 1.5 equiv), aryl halide (*if solid*) (0.5 mmol, 1 equiv), K_2HPO_4 (0.173 g, 1.0 mmol, 2 equiv), anhyd $NiBr_2$(bpy) (9.5 mg, 5 mol %), and [Ir{dF(CF_3)$_2$ppy}$_2$(bpy)]PF_6 (10 mg, 2 mol %). The reaction vessel was sealed with a cap containing a TFE-lined silicone septum, evacuated, and backfilled with argon three times. VinylBpin (0.093 g, 0.6 mmol, 1.2 equiv) and aryl bromides (*if liquid*) were dissolved in degassed THF (5 mL) and added to the reaction mixture. The vial was further sealed with Parafilm® and irradiated with blue LEDs (470 nm, ~10 W, at a distance of ~4.5 cm). The reaction was monitored by TLC. When the reaction was judged complete (typically 16-48 h), the crude reaction mixture was transferred to a round bottom flask and concentrated via rotary evaporation. Further purification was accomplished by passing the crude material through a pad of Celite®, eluting with either CH_2Cl_2 or EtOAc followed by SiO_2 column chromatography (hexanes/EtOAc or hexanes/CH_2Cl_2). In select cases, the crude product was passed through a small pad of SiO_2, eluting with either (hexanes/EtOAc or hexanes/CH_2Cl_2). In event that these methods did not provide the pure DCF prduct, further purification was accomplished by recrystallization from MeOH.

2-(1-(4-Chlorophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 4 (0.111 g, 69%)



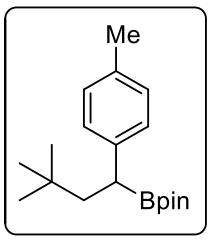
was prepared according to the general DCF procedure. The desired compound **4** was obtained as a crystalline, white solid (mp = 97-99 ºC).**^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.20 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 2.36 (dd, *J* = 9.7, 3.9 Hz, 1H), 1.98 (dd, *J* = 13.3, 9.7 Hz, 1H), 1.46 (dd, *J* = 13.3, 3.9z Hz, 1H), 1.14 (s, 12H), 0.89 (s, 9H) δ ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 143.7, 130.9, 129.8, 128.6, 83.6, 46.7, 31.7, 29.9, 24.9 (2C), 24.7 (2C) ppm.**^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.7. **FT-IR** (cm^{-1}, neat, ATR) 2953 (w), 1489 (w), 1365 (s), 1327 (s), 1140 (vs), 841 (w) **HRMS** (EI) calcd for $C_{18}H_{28}BClO_2$ $[M]^+$: 322.1871, found: 322.1862.

2-(3,3-Dimethyl-1-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 5 (0.090 g, 62%) was



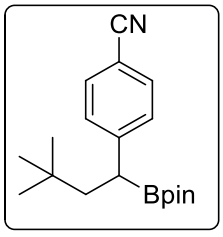
prepared according to the general DCF procedure. The desired compound **5** was obtained as a crystalline, white solid (mp = 80-82 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.23 (d, *J* = 4.1 Hz, 4H), 7.13 - 7.08 (m, 1H), 2.39 (dd, *J* = 9.9, 3.5 Hz, 3H), 2.02 (dd, *J* = 13.1, 10.1 Hz, 3H), 1.50 (dd, *J* = 13.3, 3.5 Hz, 3H), 1.14 (d, *J* = 2.7 Hz, 12H), 0.90 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 1445.1, 128.5, 128.4, 125.2, 83.5, 46.8, 31.6, 29.9, 24.8, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.8. **FT-IR** (cm^{-1}, neat, ATR) 2954 (w), 1365 (vs), 1349 (s), 1327 (s), 1143 (s), 702 (m). **HRMS** (EI) calcd for $C_{18}H_{29}BO_2$ $[M]^+$: 288.2261, found: 288.2253.

2-(3,3-Dimethyl-1-(*p*-tolyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 6 (0.099 g, 66%) was



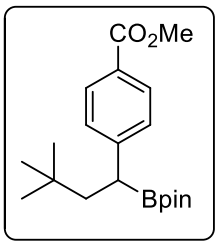
prepared according to the general DCF procedure. The desired compound **6** was obtained as a crystalline, white solid (mp = 93-94 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.12 (d, *J* = 7.8 Hz, 2H), 7.07 - 7.02 (m, 2H), 2.35 (dd, *J* = 10.1, 3.2 Hz, 1H), 2.29 (s, 3H), 2.01 (dd, *J* = 13.1, 10.2 Hz, 1H), 1.46 (dd, *J* = 13.3, 3.4 Hz, 1H), 1.15 (d, *J* = 3.1 Hz, 12H), 0.90 (s, 9H) . **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 142.0, 134.6, 129.3, 128.3, 83.4, 47.1, 31.6, 30.0, 24.9, 24.7, 21.3. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.8. **FT-IR** (cm^{-1}, neat, ATR) 2951 (w), 1364 (s), 1346 (s), 1323 (s), 1142 (vs). **HRMS** (EI) calcd for $C_{19}H_{31}BO_2$ $[M]^+$: 302.2417, found: 302.2410.

4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzonitrile, 7 (0.134 g, 86%)

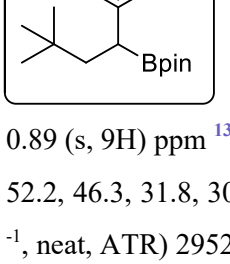


was prepared according to the general DCF procedure. The desired compound **7** was obtained as a crystalline, white solid (mp = 106-108 ºC).**^{1}H NMR** ($CDCl_3$, 500 MHz) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 2.47 (dd, *J* = 9.3, 4.3 Hz, 1H), 2.01 (dd, *J* = 13.4, 9.3 Hz, 1H), 1.49 (dd, *J* = 13.4, 4.3 Hz, 1H), 1.13 (s, 12H), 0.88 (s, 9H) ppm **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 151.4, 132.3, 129.2, 119.6, 109.0, 83.9 (2C), 46.2, 31.8, 29.9 (3C), 24.8 (2C), 24.7 (2C) ppm.**^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.7. **FT-IR** (cm^{-1}, neat, ATR) 2957 (w), 2225 (m), 1603 (w), 1365 (s), 1329 (s), 1138 (vs), 840 (m), 559 (w). **HRMS** (EI) calcd for $C_{19}H_{28}BNO_2$ $[M]^+$: 313.2213, found: 313.2225.

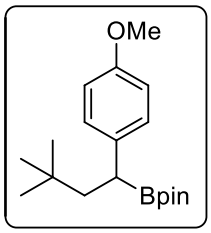
Methyl 4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzoate, 8 (0.114 g, 66%) was prepared according to the general DCF procedure *with the following modification:* The reaction was run for 48 h. The desired compound **8** was obtained as a crystalline, white solid (mp = 100-102 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 3.88 (s, 3H), 2.48 (dd, *J* = 9.4, 4.1 Hz, 1H), 2.03 (dd, *J* = 13.3, 9.4 Hz, 1H), 1.52 (dd, *J* = 13.4, 4.1 Hz, 1H), 1.13 (s, 12H), 0.89 (s, 9H) ppm **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 167.6, 151.1, 129.9 (2C), 128.4 (2C), 127.2, 83.7 (2C), 52.2, 46.3, 31.8, 30.0 (3C), 24.8 (2C), 24.7 (2C) ppm **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.5. **FT-IR** (cm $^{-1}$, neat, ATR) 2952 (w), 1718 (vs), 1365 (m), 1327 (m), 1282 (vs), 1140 (m), 1107 (w). **HRMS** (EI) calcd for $C_{20}H_{31}BO_4$ $[M]^+$: 346.2315, found: 346.2319.



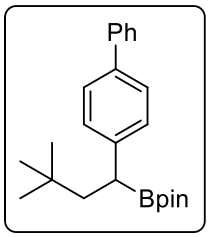
2-(3,3-Dimethyl-1-(4-(trifluoromethyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 9 (0.144 g, 81%) was prepared according to the general DCF procedure. The desired compound **9** was obtained as a crystalline, white solid (mp = 94-96 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.53 – 7.43 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.47 (dd, *J* = 9.6, 4.0 Hz, 1H), 2.03 (dd, *J* = 13.3, 9.6 Hz, 1H), 1.50 (dd, *J* = 13.3, 4.0 Hz, 1H), 1.14 (s, 12H), 0.90 (s, 9H) ppm **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 149.6, 128.7, 127.4 (q, $_{C\text{-}C\text{-}F}$ *J* = 31.9 Hz), 125.3 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ =3.6 Hz), 124.7 (q, $J_{C\text{-}F}$ = 272.5 Hz), 83.8, 46.6, 31.8, 29.9, 24.9, 24.7 **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.6. **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -115.17 (s, 1 F). **FT-IR** (cm^{-1}, neat, ATR) 2958 (vw), 1324 (s), 1123 (m), 906 (s), 729 (vs). **HRMS** (EI) calcd for $C_{19}H_{28}BF_3O_2$ $[M]^+$: 356.2134, found: 356.2143.



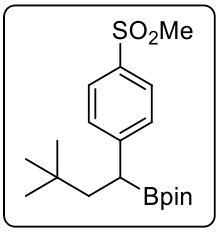
2-(1-(4-Methoxyphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 10 (0.085 g, 53%) was prepared according to the general DCF procedure *with the following modification:* $NiBr_2$(dtbbpy) was used as the Ni catalyst. The desired compound **10** was obtained as a crystalline, white solid (mp = 106-108 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.14 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 2H), 3.77 (s, 3H), 2.33 (d, *J* = 9.6 Hz, 1H), 1.98 (t, *J* = 13.1 Hz, 1H), 1.45 (d, *J* = 13.1 Hz, 1H), 1.14 (s, 12H), 0.89 (s, 9H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 157.5, 137.1, 129.3 (2C), 114.0 (2C), 83.4 (2C), 55.5, 47.1, 31.6, 30.0 (3C), 24.9 (2C), 24.7 (2C) ppm **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.8. **FT-IR** (cm^{-1}, neat, ATR) 2951 (m), 1508 (vs), 1366 (s), 1322 (s), 1246 (s), 1143 (vs). **HRMS** (EI) calcd for $C_{19}H_{31}BO_3$ $[M]^+$: 318.2366, found: 318.2352.



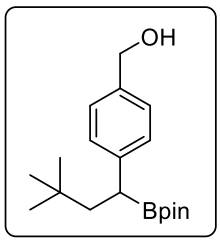
2-(1-([1,1'-Biphenyl]-4-yl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 11 (0.165 g, 91%) was prepared according to the general DCF procedure *with the following modification:* $NiBr_2$(phen) used as the Ni catalyst. The desired compound **11** was obtained as a crystalline, white solid (mp = 101-103 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.57 - 7.61 (m, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.28 - 7.33 (m, 3H), 2.44 (dd, *J* = 9.9, 3.7 Hz, 1H), 2.06 (dd, *J* = 13.3, 10.1 Hz, 1H), 1.53 (dd, *J* = 13.3, 3.7 Hz, 1H), 1.16 (d, *J* = 2.1 Hz, 12H), 0.92 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 144.3, 141.4, 138.0, 128.9, 128.8, 127.2, 127.1(4), 127.1(0), 83.6, 46.9, 31.7, 30.0, 24.9, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.1. **FT-IR** (cm^{-1}, neat, ATR) 2951 (w), 1365 (s), 1322 (s), 1141 (vs), 697 (m). **HRMS** (EI) calcd for $C_{24}H_{33}BO_2$ $[M]^+$: 364.2574, found: 364.2598.



2-(3,3-Dimethyl-1-(4-(methylsulfonyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 12 (0.146 g, 80%) was prepared according to the general DCF procedure. The desired compound **12** was obtained as a crystalline, white solid (mp = 143-145 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.80 (d, *J* = 7.3 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 3.03 (s, 3H), 2.51 (d, *J* = 9.0 Hz, 1H), 2.01 - 2.08 (m, 1H), 1.50 (d, *J* = 13.4 Hz, 1H), 1.14 (s, 12H), 0.90 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 152.4, 137.4, 129.3, 127.6, 84.0, 46.5, 44.9, 31.8, 29.9, 24.9, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.6. **FT-IR** (cm^{-1}, neat, ATR) 2952 (w), 1366 (w), 1318 (m), 1305 (s), 1139 (vs). **HRMS** (EI) calcd for $C_{19}H_{31}BO_4S$ $[M]^+$: 366.2036, found: 366.2032.



(4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)methanol, 13 (0.073 g, 58%) was prepared according to the general DCF procedure *with the following modification*: upon reaction completion, AcOH (3 equiv, 86 µL, 1.5 mmol) was added to the reaction, and the reaction was stirred for 5 minutes prior to chromatographic purification. The desired compound **13** was obtained as a dense, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.25 - 7.21 (m, 4H), 4.63 (s, 2H), 2.39 (dd, *J* = 9.9, 3.8 Hz, 1H), 2.01 (dd, *J* = 13.3, 9.9 Hz, 1H), 1.60 (br. s, 1H), 1.47 (dd, *J* = 13.4, 3.7 Hz, 1H), 1.14 (d, *J* = 3.1 Hz, 12H), 0.90 (s, 9H) **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 144.8, 137.8, 128.7, 127.5, 83.5, 65.6, 46.9, 31.7, 29.9, 24.9, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.4. **FT-IR** (cm^{-1}, neat, ATR) 3320 (br), 2951 (m), 1385 (m), 1293 (m), 1122 (s). **HRMS** (EI) calcd for $C_{18}H_{31}BO_3$ $[M]^+$: 318.2366, found: 318.2358.

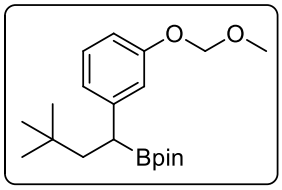


4-((4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)sulfonyl) Morpholine, 14 (0.210 g, 98%) was prepared according to the general DCF procedure. The desired compound **14** was obtained as a crystalline, white solid (mp = 219-221 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.61 (d, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 3.73 (br s, 4H), 2.97 (br s, 4H), 2.51 (d, *J* = 9.0 Hz, 1H), 2.04 (dd, *J* = 12.7, 10.2 Hz, 1H), 1.49 - 1.54 (m, 1H), 1.13 (s, 12H), 0.90 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 151.6, 131.7, 129.0, 128.2, 83.9, 66.4, 46.3, 46.2, 31.8, 29.9, 24.8, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.2. **FT-IR** (cm^{-1}, neat, ATR) 2978 (w), 2950 (w), 2862 (w), 1345 (s), 1165 (vs), 1140 (m), 1115 (m), 947 (m). **HRMS** (ESI) calcd for $C_{22}H_{37}BNO_5S$ $[M+H]^+$: 438.2469, found: 438.2486.

4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-*N*-phenylbenzenesulfonamide, 15 (0.190 g, 86%) was prepared according to the general DCF procedure. The desired compound **15** was obtained as a crystalline, white solid (mp = 149-151 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.61 (d, *J* = 7.9 Hz, 2H), 7.26 - 7.29 (m, 2H), 7.16 - 7.23 (m, 2H), 7.09 (d, *J* = 6.9 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.45 (s, 1H), 2.48 – 2.41 (m, 1H), 2.02 - 1.92 (m, 1H), 1.52 - 1.44 (m, 1H), 1.09 (s, 12H), 0.86 (s, 9H) **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 151.4, 136.8, 135.5, 129.5, 128.9, 127.6, 125.7, 122.2, 83.8, 45.9, 31.7, 29.9, 24.7, 24.6. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.7. **FT-IR** (cm^{-1}, neat, ATR) 3256 (w), 2954 (w), 1330 (m), 1157 (vs), 1140 (vs). **HRMS** (EI) calcd for $C_{24}H_{34}BNO_4S$ $[M]^+$: 443.2302, found: 443.2309.

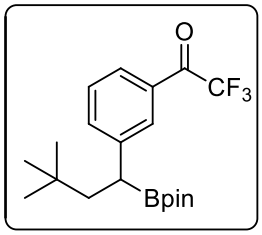
***tert*-Butyl Acetyl(4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl) carbamate, 16** (0.156 g, 70%) was prepared according to the general DCF procedure. The desired compound **16** was obtained as a crystalline, white solid (mp = 99-101 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.24 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 2 H), 2.52 (s, 3H), 2.43 (dd, *J* =9.8, 3.8 Hz, 1H), 2.00 (dd, *J* = 13.3, 9.9 Hz, 1 H), 1.54 (dd, *J* = 13.4, 4.0 Hz, 1H), 1.34 (s, 9H), 1.12 (s, 12H), 0.89 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 173.3, 153.2, 144.7, 136.2, 128.9, 128.0, 83.5, 83.0, 46.3, 31.7, 30.0, 28.1, 26.7, 24.8, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.3. **FT-IR** (cm^{-1}, neat, ATR) 2978 (w), 2951 (w), 1735 (s), 1709 (s), 1367 (s), 1270 (vs), 1254 (s), 1154 (vs), 1142 (vs), 1095 (s). **HRMS** (ESI) calcd for $C_{25}H_{40}BNO_5$ $[M+ Na]^+$: 268.2897, found: 268.2898.

2-(1-(3-(Methoxymethoxy)phenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 17



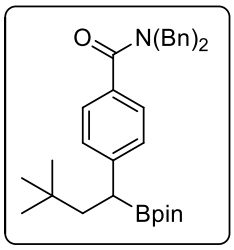
(0.098 g, 59%) was prepared according to the general DCF procedure. The desired compound **17** was obtained as a colorless, dense oil. ^{1}**H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.14 (t, *J* = 7.9 Hz, 1H), 6.92 (t, *J* = 1.8 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.77 - 6.81 (m, 1H), 5.15 (q, *J* = 6.2 Hz, 2H), 3.47 (s, 3H), 2.36 (dd, *J* = 10.0, 3.6 Hz, 1H), 2.00 (dd, *J* = 13.4, 10.0 Hz, 1H), 1.48 (dd, *J* = 13.4, 3.7 Hz, 1H), 1.15 (d, *J* = 3.1 Hz, 12H), 0.90 (s, 9H). ^{13}**C NMR** ($CDCl_3$, 125 MHz) δ ppm 157.5, 146.9, 129.4, 122.3, 116.6, 113.1, 94.8, 83.5, 56.2, 46.8, 31.6, 29.9, 24.9, 24.7. ^{11}**B NMR** ($CDCl_3$, 128.4 MHz) δ 32.3. **FT-IR** (cm^{-1}, neat, ATR) 2952 (m), 1366 (m), 1321 (m), 1147 (vs), 1020 (m). **HRMS** (EI) calcd for $C_{20}H_{33}BO_4$ $[M]^+$: 348.2472, found: 348.2482.

1-(3-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)-2,2,2-



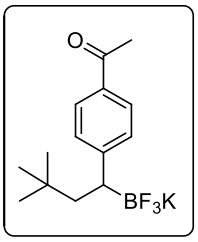
trifluoroethanone, 18 (0.184 g, 99%) was prepared according to the general DCF procedure. The desired compound **18** was obtained as a clear, colorless oil. ^{1}**H NMR** ($CDCl_3$, 500 MHz) δ 7.95 (s, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.58 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 2.49 (dd, *J* = 9.4, 3.9 Hz, 1H), 2.04 (dd, *J* = 13.4, 9.5 Hz, 1H), 1.49 (dd, *J* = 13.4, 4.0 Hz, 1H), 1.14 (s, 12H), 0.90 (s, 9H). ^{13}**C NMR** ($CDCl_3$, 125 MHz) δ 181.0 (q, $_{C\text{-}C\text{-}F}$ *J* = 35.4 Hz, C), 146.7, 136.0, 130.2, 130.0, 129.3, 127.3 (q, $_{C\text{-}C\text{-}C\text{-}F}$ *J* = 2.2 Hz, C), 117.0 (q, $_{C\text{-}F}$ *J* = 291.9 Hz, CF_3), 83.8, 46.8, 31.7, 29.9, 24.8, 24.7. ^{19}**F NMR** (CDCl3, 471 MHz) -71.14 (s, 3F).^{11}**B NMR** ($CDCl_3$, 128.4 MHz) δ 32.6. **FT-IR** (cm^{-1}, neat, ATR) 2959 (w), 1716 (m), 1365 (m), 1325 (m), 1199 (s), 1143 (vs), 966 (w), 734 (m). **HRMS** (EI) calcd for $C_{20}H_{29}BF_3O_3$ $[M+H]^+$: 385.2162, found: 385.2148.

***N,N*-Dibenzyl-4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzamide, 19**



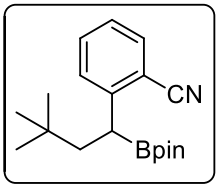
(0.191 g, 75%) was prepared according to the general DCF procedure. The desired compound **19** was obtained as a crystalline, white solid (mp = 115-116 ºC). ^{1}**H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.39 (d, *J* = 7.9 Hz, 2H), 7.26 - 7.37 (m, 8H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.13 (br s, 2H), 4.69 (br s, 2H), 4.41 (br s, 2H), 2.40 (dd, *J* = 9.7, 3.6 Hz, 1H), 1.99 (dd, *J* = 13.2, 9.8 Hz, 1H), 1.46 (dd, *J* = 13.4, 3.7 Hz, 1H), 1.12 (s, 12H), 0.88 (s, 9H). ^{13}**C NMR** ($CDCl_3$, 125 MHz) δ ppm 172.7, 147.2, 132.8, 128.9, 128.5, 128.4, 127.7, 127.2, 127.1, 83.5, 51.8, 47.1, 46.4, 31.5, 29.8, 24.7, 24.6. ^{11}**B NMR** ($CDCl_3$, 128.4 MHz) δ 33.3. **FT-IR** (cm^{-1}, neat, ATR) 2951 (w), 1635 (s), 1364 (s), 1324 (s), 1140 (vs), 699 (s). **HRMS** (EI) calcd for $C_{33}H_{42}BNO_3$ $[M]^+$: 511.3258, found: 511.3258.

Potassium (1-(4-Acetylphenyl)-3,3-dimethylbutyl)trifluoroborate, 20 (0.133 g, 88%) was prepared



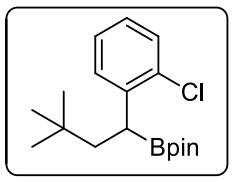
according to the general DCF procedure *with the following modification*: After filtration of the crude reaction through Celite, the solvent was removed, and the crude material was converted to the trifluoroborate following **GPA2**. The desired compound **20** was obtained as a crystalline yellow solid (mp = 152-153 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.69 (d, *J*=8.2 Hz, 2 H), 7.26 (d, *J*=8.1 Hz, 2 H), 2.46 (s, 3 H), 1.99 - 1.90 (m, 1 H), 1.84 - 1.71 (m, 2 H), 0.71 (s, 9 H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 205.9, 197.1, 161.1 , 132.6 , 129.0 , 127.7 , 45.8 , 32.8 , 30.5 , 26.1. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 4.13. **^{19}F NMR** ($CDCl_3$, 471 MHz) -146.0 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR) 2950 (w), 1669 (m), 1600 (m), 1361 (m), 1277 (m), 955 (s). **HRMS** (ESI) calcd for $C_{14}H_{19}BF_3O$ $[M\text{-}K^+]^-$: 271.1481, found: 271.1494.

2-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzonitrile, 21 (0.099 g, 63%)



was prepared according to the general DCF procedure *with the following modification:* The reaction was run for 48 h. The desired compound **21** was obtained as a crystalline, white solid (mp = 78-80 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.56 (d, *J* = 7.8 Hz, 1H), 7.39 - 7.48 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 2.87 (dd, *J* = 7.5, 5.5 Hz, 1H), 2.02 (dd, *J* = 13.5, 8.2 Hz, 1H), 1.54 (dd, *J* = 13.7, 5.3 Hz, 1H), 1.17 (d, *J* = 9.8 Hz, 12H), 0.90 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 149.8, 133.3, 132.6, 129.3, 125.7, 118.9, 112.7, 83.9, 46.8, 31.9, 29.2 - 30.2 (m), 24.9, 24.8. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.4. **FT-IR** (cm^{-1}, neat, ATR) 2955 (m), 2224 (w), 1356 (s), 1325 (s), 1319 (m), 1141 (vs). **HRMS** (EI) calcd for $C_{19}H_{28}BNO_2[M]^+$: 313.2213, found: 313.2217.

2-(1-(2-Chlorophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 22 (0.069 g,



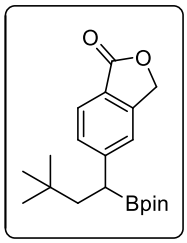
43%) was prepared according to the general DCF procedure *with the following modification:* The reaction was run for 48 h. The desired compound **22** was obtained as a crystalline, white solid (mp = 68-70 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.32 (dd, *J* = 15.0, 7.8 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 2.92 (dd, *J* = 7.3, 4.7 Hz, 1H), 1.97 (dd, *J* = 13.4, 8.5 Hz, 1H), 1.49 (dd, *J* = 13.4, 4.3 Hz, 1H), 1.18 (d, *J* = 8.4 Hz, 12H), 0.90 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 143.1, 133.9, 130.2, 129.7, 126.8, 126.4, 83.6, 46.4, 31.6 - 32.1 (m), 29.9, 24.9, 24.8. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.7. **FT-IR** (cm^{-1}, neat, ATR) 2952 (w), 1365 (s), 1321 (s), 1141 (vs). **HRMS** (EI) calcd for $C_{18}H_{28}BClO_2$ $[M]^+$: 322.1871, found: 322.1866.

2-(1-(3,5-di-*tert*-Butylphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 23 (0.110 g, 55%) was prepared according to the general DCF procedure *with the following modification:* The reaction was run for 48 h. The desired compound **23** was obtained as a crystalline, white solid (mp = 111-112 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.14 - 7.17 (m, 1H), 7.07 (d, *J* = 1.5 Hz, 2H), 2.38 (dd, *J* = 11.0, 2.4 Hz, 1H), 2.04 (dd, *J* = 13.0, 11.1 Hz, 1H), 1.49 (dd, *J* = 13.1, 2.6 Hz, 1H), 1.30 (s, 18H), 1.14 (d, *J* = 3.8 Hz, 12H), 0.92 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 150.5, 143.7, 122.9, 119.1, 83.3, 47.1, 35.1, 31.8, 31.6, 30.0, 25.0, 24.6. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.8. **FT-IR** (cm^{-1}, neat, ATR) 2953 (m), 2865 (s), 1362 (m), 11433 (s), 870 (w). **HRMS** (EI) calcd for $C_{26}H_{45}BO_2$ $[M]^+$: 400.3513, found: 400.3515.

2-(1-(3,5-Dimethoxyphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 24 (0.141 g, 81%) was prepared according to the general DCF procedure. The desired compound **24** was obtained as a crystalline, white solid (mp = 74-75 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 6.41 (s, 2H), 6.24 (s, 1H), 3.76 (s, 6H), 2.32 (dd, *J* = 9.8, 2.5 Hz, 1H), 1.98 (dd, *J* = 13.0, 10.3 Hz, 1H), 1.47 (dd, *J* = 13.3, 2.9 Hz, 1H), 1.16 (s, 12H), 0.90 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 160.9, 147.6, 106.4, 97.8, 83.6, 55.5, 46.9, 31.6, 29.9, 25.0, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.7. **FT-IR** (cm^{-1}, neat, ATR) 2951 (w), 1593 (m), 1364 (m), 1318 (m), 1204 (m), 1140 (vs) **HRMS** (EI) calcd for $C_{20}H_{33}BO_4$ $[M]^+$: 348.2472, found: 348.2471.

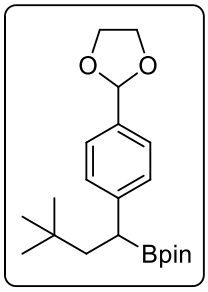
2-(3,3-Dimethyl-1-(4-(1-(trifluoromethyl)cyclopropyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 25 (0.091 g, 46%) was prepared according to the general DCF procedure. The desired compound **25** was obtained as clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.30 (d, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 2.38 (dd, *J* = 10.1, 2.6 Hz, 1H), 2.02 (dd, *J* = 12.7, 11.0 Hz, 1H), 1.45 (dd, *J* = 13.4, 2.9 Hz, 1H), 1.28 - 1.31 (m, 2H), 1.14 (s, 12H), 0.99 (br s, 2H), 0.90 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 145.3, 132.9, 131.3, 128.3, 126.8 (q, $J_{C\text{-}F}$ = 273.1 Hz, CF_3), 83.6, 46.9, 31.6, 29.9, 28.0 (q, $J_{C\text{-}C\text{-}F}$ = 33.2 Hz, C), 24.9 , 24.7, 9.9. **^{19}F NMR** ($CDCl_3$, 471 MHz) -70.11 (s, 3F).**^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.0. **FT-IR** (cm^{-1}, neat, ATR) 2954 (w), 1360 (m), 1324 (m), 1136 (vs), 1087 (m), 839 (w), 735 (w), 573 (m). **HRMS** (EI) calcd for $C_{22}H_{32}BF_3O_2$ $[M]^+$: 396.2447, found: 396.2446.

5-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)isobenzofuran-1(3H)-one, 26 (0.130 g, 76%) was prepared according to the general DCF procedure. The desired compound **26** was



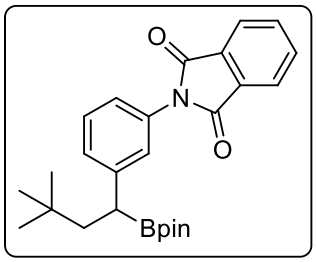
obtained as a crystalline, white solid (mp = 111-113 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.78 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.33 (s, 1H), 5.26 (s, 2H), 2.55 (dd, *J* = 9.3, 4.1 Hz, 1H), 2.06 (dd, *J* = 13.3, 9.3 Hz, 1H), 1.53 (dd, *J* = 13.4, 4.1 Hz, 1H), 1.14 (s, 12H), 0.90 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 171.6, 153.1, 147.4, 129.7, 125.7, 123.0, 121.6, 84.0, 69.8, 46.6, 31.8, 29.9, 24.8, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.7. **FT-IR** (cm^{-1}, neat, ATR) 2954 (w), 1768 (vs) 1352 (m) 1136 (m), 1035 (m). **HRMS** (EI) calcd for $C_{20}H_{29}BO_4$ $[M]^+$: 344.2159, found: 344.2168.

2-(1-(4-(1,3-Dioxolan-2-yl)phenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 27

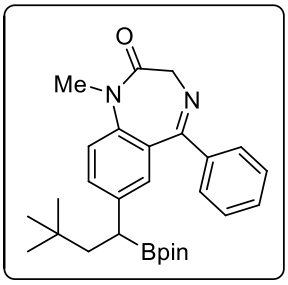


(0.106 g, 59%) was prepared according to the general DCF procedure. The desired compound **27** was obtained as a crystalline, white solid (mp = 88-90 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.34 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.75 (s, 1H), 4.11 - 4.16 (m, 2H), 4.00 - 4.04 (m, 2H), 2.40 (dd, *J* = 9.8, 3.7 Hz, 1H), 2.00 (dd, *J* = 13.4, 9.8 Hz, 1H), 1.48 (dd, *J* = 13.4, 3.7 Hz, 1H), 1.14 (d, *J* = 2.3 Hz, 12H), 0.89 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 146.5, 134.6, 128.5, 126.7, 104.3, 83.6, 65.5(7), 65.5(5), 46.9, 31.7, 29.9, 24.9, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.9. **FT-IR** (cm^{-1}, neat, ATR) 2952 (w), 1365 (s), 1322 (s), 1141 (vs) 1080 (s), 967 (m). **HRMS** (EI) calcd for $C_{21}H_{33}BO_4$ $[M]^+$: 360.2472, found: 360.2484.

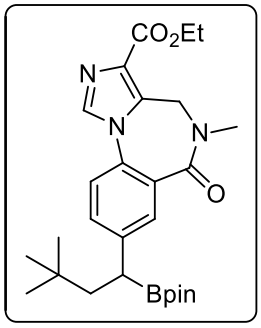
2-(3-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)isoindoline-1,3-dione, 28 (0.112 g, 52%) was prepared according to the general DCF procedure. The desired compound **28** was obtained as a crystalline, white solid (mp = 118-119 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.94 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.26 - 7.30 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 1H), 2.47 (dd, *J* = 10.0, 3.7 Hz, 1H), 2.02 (dd, *J* = 13.3, 10.1 Hz, 1H), 1.55 (dd, *J* = 13.3, 3.8 Hz, 1H), 1.17 (d, *J* = 3.7 Hz, 12H), 0.91 (s, 9H) . **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 167.6, 146.3, 134.5, 132.2, 131.8, 129.2, 128.4, 126.9, 123.9, 123.7, 83.7, 46.6, 31.7, 30.0, 24.8, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.6. **FT-IR** (cm^{-1}, neat, ATR) 2951 (w), 1721 (vs), 1371 (s), 1322 (m), 1141 (m), 717 (m). **HRMS** (EI) calcd for $C_{26}H_{32}BNO_4$ $[M]^+$: 433.2424, found: 433.2430.



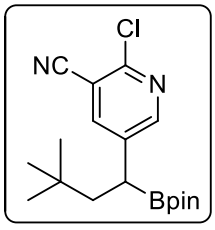
7-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-1-methyl-5-phenyl-1H-benzo[e][1,4]diazepin-2(3H)-one, 30 (0.175 g, 76%) was prepared according to the general DCF procedure. The desired compound **30** was obtained as a dense, yellow oil. Compound **30** rapidly decomposed upon standing neat but is stable in solution; ^{1}H NMR was therefore taken with residual chromatography solvent. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.61 (dd, *J* = 6.9, 4.8 Hz, 2H), 7.34 - 7.47 (m, 4H), 7.22 (dd, *J* = 8.5, 3.8 Hz, 1H), 7.14 (d, *J* = 1.8 Hz, 1H), 4.77 (dd, *J* = 10.6, 2.1 Hz, 1H), 3.76 (d, *J* = 10.7 Hz, 1H), 3.35 - 3.40 (m, 3H), 2.33 - 2.41 (m, 1H), 1.88 - 1.98 (m, 1H), 1.44 (ddd, *J* = 18.3, 13.5, 4.3 Hz, 1H), 1.09 - 1.16 (m, 12H), 0.86 (d, *J* = 10.7 Hz, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 143.4, 142.6, 136.3, 135.9, 134.9, 134.8, 132.6, 131.9, 129.5, 122.2, 84.1, 46.8, 45.8, 36.0, 31.9, 31.7, 30.4, 29.9, 29.8, 24.9, 24.8(4), 24.7(6). **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.3. **FT-IR** (cm^{-1}, neat, ATR) 2951 (w), 1680 (vs), 1321 (m), 1140 (m) 699 (w). **HRMS** (EI) calcd for $C_{28}H_{37}BN_2O_3$ $[M]^+$: 460.2897, found: 460.2884.



Ethyl 8-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-5-methyl-6-oxo-5,6-dihydro-4H-benzo[f]imidazo[1,5-a][1,4]diazepine-3-carboxylate, 31 (0.219 g, 88%) was prepared according to the general DCF procedure. The desired compound **31** was obtained as a crystalline, white solid (mp = 132-133 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.91 (br s, 1H), 7.85 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 5.23 – 5.03 (br s, 1H), 4.96 – 4.24 (m, 3H), 3.22 (s, 3H), 2.55 - 2.45 (m, 1H), 2.06 – 1.99 (m, 1H), 1.57 - 1.47 (m, 1H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.16 (s, 12H), 0.90 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 167.0, 163.5, 146.5, 135.9, 135.2, 132.8, 132.3, 129.6, 129.1, 128.7, 128.6, 121.9, 83.9, 61.2, 42.7, 36.0, 31.8, 29.9, 24.9, 24.7, 14.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.3. **FT-IR** (cm^{-1}, neat, ATR) 2952 (m), 1366 (m), 1321 (m), 1147 (vs), 1020 (m). **HRMS** (ESI) calcd for $C_{27}H_{39}BN_3O_5$ $[M+H]^+$: 496.2983, found: 496.2960.

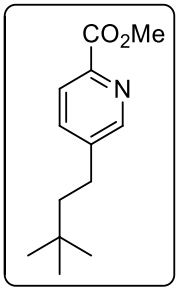


2-Chloro-5-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)nicotinonitrile, 32 (0.127g, 73%) was prepared according to the general DCF procedure. The desired compound **32** was obtained as a crystalline, white solid (mp = 76-78 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.42 (d, *J* = 2.3 Hz, 1H), 7.85 (d, *J* = 2.4 Hz, 1H), 2.44 (dd, *J* = 8.5, 4.7 Hz, 1H), 1.99 (dd, *J* = 13.5, 8.9 Hz, 1H), 1.43 (dd, *J* = 13.5, 4.8 Hz, 1H), 1.16 (d, *J* = 4.6 Hz, 12H), 0.89 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 153.0,

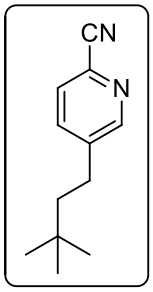


149.4, 142.0, 140.7, 115.3, 110.4, 84.4, 46.4, 312.0, 29.9, 24.9, 24.8. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.5. **FT-IR** (cm^{-1}, neat, ATR) 2950 (m), 12234 (w). 1355(s), 1352 (s), 1326 (s), 1139 (vs). **HRMS** (EI) calcd for $C_{18}H_{26}BClN_2O_2$ $[M]^+$: 348.1776, found: 348.1788.

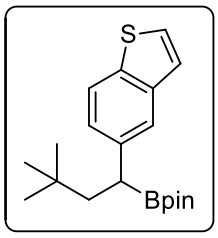
Methyl 5-(3,3-Dimethylbutyl)picolinate, 33 (0.046 g, 42%) was prepared according to the general DCF procedure. The desired compound **33** was obtained as a colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 8.54 (s, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.63 (dd, *J* = 8.0, 1.9 Hz, 1H), 3.98 (s, 3H), 2.59 - 2.67 (m, 2H), 1.45 - 1.53 (m, 2H), 0.96 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 166.1, 150.3, 145.8, 143.2, 136.8, 125.2, 53.0, 45.9, 30.9, 29.5, 28.8. **FT-IR** (cm^{-1}, neat, ATR) 2987 (m), 1721 (vs) 1378 (m) 1256 (m), 936 (w). **HRMS** (ESI) calcd for $C_{13}H_{20}NO_2$ $[M+H]^+$: 222.1494, found: 222.1497.



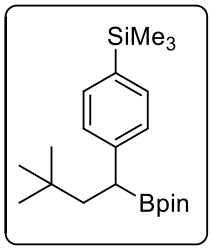
5-(3,3-Dimethylbutyl)picolinonitrile, 34 (0.074 g, 79%) was prepared according to the general DCF procedure. The desired compound **34** was obtained as a crystalline, white solid (mp = 65-67 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 8.54 (s, 1H), 7.59 - 7.65 (m, 2H), 2.61 - 2.69 (m, 2H), 1.45 - 1.53 (m, 2H), 0.98 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 151.7, 143.4, 136.7, 131.5, 128.4, 117.7, 45.8, 31.0, 29.5, 29.0. **FT-IR** (cm^{-1}, neat, ATR) 2955 (s), 2235 (w), 1470 (s) 1366 (m). **HRMS** (ESI) calcd for $C_{12}H_{16}N_2$ $[M]^+$: 188.1313, found: 188.1301.



2-(1-(Benzo[b]thiophen-5-yl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 35 (0.105 g, 61%) was prepared according to the general DCF procedure. The desired compound **35** was obtained as a powdery, white solid (mp = 143–144 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm7.74 (d, *J* = 8.4 Hz, 1H), 7.67 (s, 1H), 7.37 (d, *J* = 5.5 Hz, 1H), 7.24 (m, 2H), 2.50 (dd, *J* = 9.7, 3.3 Hz, 1H), 2.08 (dd, *J* = 12.5, 9.9 Hz, 1H), 1.55 (dd, *J* = 13.0, 3.1 Hz, 1H), 1.14 (d, *J* = 5.7 Hz, 12H), 0.92 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 141.3, 140.3, 136.9, 126.3, 125.6, 124.1, 123.0, 122.4, 83.5, 47.3, 31.7, 30.0, 24.9, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ ppm 33.0. **FT-IR** (cm^{-1}, neat, ATR) 2954 (w), 1361 (s), 1330 (s), 1137 (vs), 967 (m), 837 (m), 702 (s). **HRMS** (EI) calcd for $C_{20}H_{30}BO_2S$ $[M+H]^+$: 345.2060 found: 345.2066.

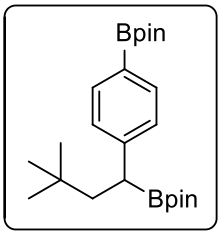


(4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)trimethylsilane, 36



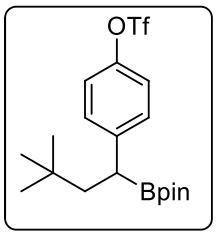
(0.162 g, 90%) was prepared according to the general DCF procedure. The desired compound **36** was obtained as a crystalline, white solid (mp = 89-90 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.38 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 2.37 (dd, *J* = 10.2, 3.1 Hz, 1H), 2.03 (dd, *J* = 13.3, 10.4 Hz, 1H), 1.47 (dd, *J* = 13.3, 3.2 Hz, 1H), 1.15 (d, *J* = 1.5 Hz, 12H), 0.90 (s, 9H), 0.23 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 145.8, 136.5, 133.6, 127.9, 83.5, 47.0, 31.6, 29.9, 24.9, 24.7, -0.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 21.2. **FT-IR** (cm^{-1}, neat, ATR) 2953 (w), 1364 (m), 1315 (m), 1247 (m), 1142 (s), 1107 (m), 835 (vs). **HRMS** (EI) calcd for $C_{21}H_{37}BO_2Si$ $[M]^+$: 360.2656, found: 360.2659.

2-(4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)-4,4,5,5-



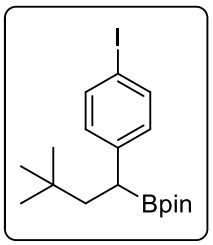
tetramethyl-1,3,2-dioxaborolane, 37 (0.144 g, 70%) was prepared according to the general DCF procedure. The desired compound **37** was obtained as a crystalline, white solid (mp = 137-139 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.68 (d, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 2.37 - 2.44 (m, 1H), 1.96 - 2.05 (m, 1H), 1.50 (dd, *J* = 13.3, 3.5 Hz, 1H), 1.33 (s, 12H), 1.13 (s, 12H), 0.89 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 148.8, 135.1, 128.0, 83.8, 83.6, 46.6, 31.7, 30.0, 25.2, 25.1, 24.9, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 31.4 (2 × B). **FT-IR** (cm^{-1}, neat, ATR) 2978 (x), 2952 (vw), 1607 (w), 1358 (vs), 1319 (m), 1142 (s). **HRMS** (EI) calcd for $C_{24}H_{40}B_2O_4$ $[M]^+$: 414.3113, found: 414.3102.

4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl



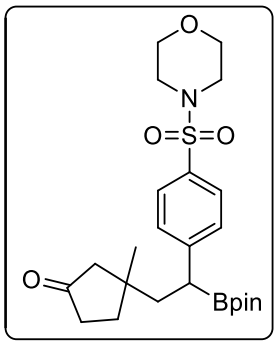
trifluoromethanesulfonate, 38 (0.140 g, 64%) was prepared according to the general DCF procedure. The desired compound **38** was obtained as a powdery, white solid (mp = 74–75 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.28 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 2.43 (dd, *J* = 13.2, 3.5 Hz, 1H), 2.00 (dd, *J* = 13.0, 12.3 Hz, 1H), 1.47 (dd, *J* = 13.3, 3.4 Hz, 1H), 1.13 (s, 12H), 0.89 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 147.5, 145.9, 130.0, 121.2, 119.0 (q, $_{C\text{-}F}J$ = 319.5 Hz, CF_3), 83.8, 46.6, 31.7, 29.9, 24.8, 24.7. **^{19}F NMR** ($CDCl_3$, 471 MHz) -72.80 (s, 3F).**^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.3. **FT-IR** (cm^{-1}, neat, ATR) 2977 (w), 1426 (m), 1202 (vs), 1134 (vs), 883 (s), 610 (s). **HRMS** (ESI) calcd for $C_{19}H_{28}BF_3O_5S$ $[M]^+$: 436.1703, found: 436.1711.

2-(1-(4-Iodophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 39 (0.132 g, 64%)

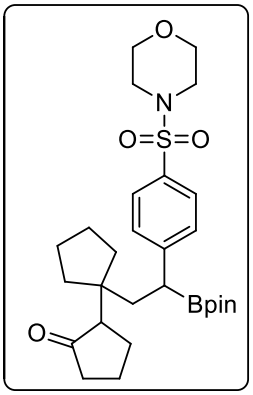


was prepared according to the general DCF procedure *with the following modifications:* 1,4-diiodobenze (0.165 g, 0.500 mmol) was used. The desired compound **39** was obtained as a white crystalline solid (mp = 120-121 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.54 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 2.33 (dd, *J* = 9.5, 3.7 Hz, 1H), 1.97 (dd, *J* = 13.2, 9.8 Hz, 1H), 1.45 (dd, *J* = 13.3, 3.8 Hz, 1H), 1.14 (s, 12 H), 0.88 (s, 9 H). **^{13}C NMR** ($CDCl_3$, 125 MHz) 145.0, 137.5, 130.6, 90.2, 83.7, 46.6, 31.7, 29.9, 24.9, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) 32.5. **FT-IR** (cm^{-1}, neat, ATR) 2955 (m), 1462 (m), 1380 (s), 1210 (s), 810 (m). **HRMS** (EI) calcd for $C_{18}H_{28}BIO_2$ [M^+]: 414.1227, found: 414.1216.

3-Methyl-3-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentanone, 40 (0.155 g, 65%) was prepared according to the general DCF procedure. The desired compound **40** was obtained as a crystalline, white solid (mp = 215-217 ºC). The diastereomeric ratio was 1.4:1 as determined by ^{1}H NMR analysis of the crude reaction. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.63 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 8.9 Hz, 2H), 3.78 - 3.68 (m, 4H), 3.00 – 2.95 (m, 4H), 2.58 - 2.47 (m, 1H), 2.34 - 2.20 (m, 3H), 2.15 - 1.67 (m, 5H), 1.14 (d, *J* = 1.7 Hz, 12H), 1.06 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 219.4, 219.3, 150.5, 150.4, 132.3, 132.2, 129.0, 128.4, 84.3, 84.2, 66.4, 52.8, 52.8, 46.3, 44.0, 43.9, 40.7, 36.9, 36.8, 35.7, 35.7, 30.0, 25.4, 25.3, 24.9, 24.8, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.3. **FT-IR** (cm^{-1}, neat, ATR) 2976 (w), 2915 (w), 2855 (w), 1741 (s), 1344 (s), 1164 (vs). **HRMS** (ESI) calcd for $C_{24}H_{37}BNO_6S$ [M+H]$^+$: 478.2435, found: 478.2422.



1'-(2-(4-(Morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-[1,1'-bi(cyclopentan)]-2-one, 41 (0.092 g, 35%) was prepared according to the general DCF procedure *with the following modification*: The reaction was run for 48 h. The desired compound **41** was obtained as a crystalline, white solid (mp = 141-143 ºC). The diastereomeric ratio was 2.2:1 as determined by ^{1}H NMR analysis of the crude reaction. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.61 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 3.77 - 3.69 (m, 4H), 3.01 - 2.93 (m, 4H), 2.49 – 2.41 (m, 1H), 2.36 - 2.12 (m, 3H), 2.12 - 1.88 (m, 4H), 1.81 - 1.31 (m, 10H), 1.14 (d, *J* = 2.0 Hz, 12H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 220.8, 220.6, 151.2, 131.9, 129.2, 129.1, 128.2, 128.2, 84.0, 66.4, 54.4, 54.2, 48.2, 48.2, 46.3, 41.0, 40.8, 39.1, 36.0, 35.5, 35.4, 34.7, 27.6, 27.0, 25.2, 25.1, 25.1, 25.0, 24.9, 24.8, 24.6, 20.5. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.2. **FT-IR** (cm^{-1}, neat,

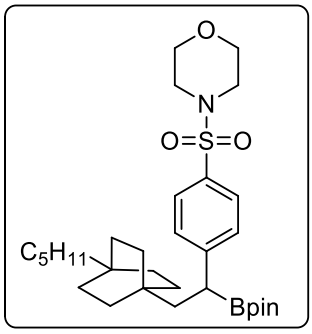


ATR) 2952 (m), 2870 (w), 1719 (s), 979 (m). **HRMS** (ESI) calcd for $C_{28}H_{43}BNO_6S$ $[M+H]^+$: 532.2904, found: 532.2888.

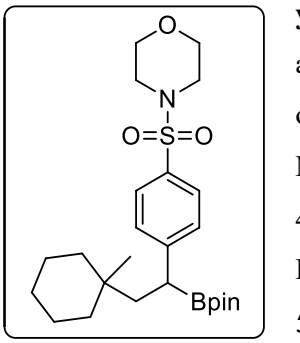
3,5-Dimethyl-3-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclohexanone, 42 (0.174 g, 69%) was prepared according to the general DCF procedure. The desired compound **42** was obtained as a crystalline, white solid (mp = 208-209 °C). The diastereomeric ratio was 5:3:1 determined by ^{1}H NMR analysis of the crude reaction. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.61 (d, *J* = 8.6 Hz, 2H), 7.37 (dd, *J* = 13.9, 8.2 Hz, 2H), 3.73 (t, *J* = 3.9 Hz, 4H), 3.00 - 2.94 (m, 4H), 2.72 - 2.40 (m, 1H), 2.37 - 2.26 (m, 1H), 2.21 - 1.82 (m, 5H), 1.79 - 1.55 (m, 2H), 1.55 - 1.31 (m, 1H), 1.13 (d, *J* = 7.2 Hz, 12H), 1.01 (t, *J* = 6.3 Hz, 3H), 0.96 - 0.87 (m, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 211.5, 211.4, 150.7, 150.6, 132.1, 129.3, 129.2, 129.1, 129.0, 128.4, 128.3, 128.3, 84.2, 84.1, 66.4, 66.4, 53.3, 53.0, 49.7, 49.4, 47.2, 46.4, 46.3, 46.3, 45.5, 40.2, 39.3, 39.2, 29.7, 29.1, 29.0, 24.9, 24.8, 24.8, 24.7, 24.6, 23.8, 22.8. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.0. **FT-IR** (cm^{-1}, neat, ATR) 2958 (m), 1710 (m), 1348 (s), 1153 (vs) **HRMS** (EI) calcd for $C_{26}H_{40}BNO_6S$ $[M]^+$: 505.2669, found: 505.2667.

4-(Adamantan-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl) morpholine, 43 (0.230 g, 89%) was prepared according to the general DCF procedure. The desired compound **43** was obtained as a crystalline, white solid (mp = 219-220 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.61 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 3.73 (t, *J* = 4.6 Hz, 4H), 2.97 (t, *J* = 4.3 Hz, 4H), 2.55 (dd, *J* = 9.6, 3.8 Hz, 1H), 1.97 - 1.85 (m, 4H), 1.72 – 1.58 (m, 6H), 1.55 – 1.40 (m, 6H), 1.38 (dd, *J* = 13.4, 3.8 Hz, 1H), 1.13 (d, *J* = 1.8 Hz, 12H) **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 151.8, 131.6, 129.1, 128.1, 83.9, 66.4, 46.9, 46.3, 42.9, 37.4, 33.6, 29.0, 24.8, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.8. **FT-IR** (cm^{-1}, neat, ATR) 2900 (m), 2847 (w), 1344 (m), 1163 (s), 1114 (m), 945 (m). **HRMS** (ESI) calcd for $C_{28}H_{43}BNO_5S$ $[M+H]^+$: 516.2955, found: 516.2964.

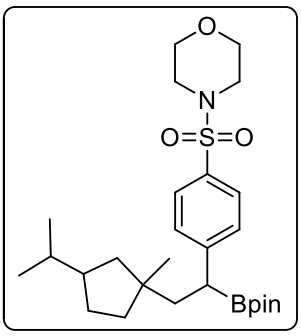
4-((4-(2-(4-Pentylbicyclo[2.2.2]octan-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine, **44** (0.220 g, 79%) was prepared according to the general DCF procedure *with the following modification:* The reaction was run for 48 h. The desired compound **44** was obtained as a crystalline, white solid (mp = 199-200 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 3.73 (t, *J* = 4.3 Hz, 4H), 3.00 - 2.92 (m, 4H), 2.49 (dd, *J* = 9.5, 3.7 Hz, 1H), 1.91 (dd, *J* = 13.4, 9.8 Hz, 1H), 1.43 - 1.35 (m, 4H), 1.35 - 1.24 (m, 12H), 1.20 - 1.15 (m, 3H), 1.13 (s, 12H), 1.04 - 0.99 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 151.7, 131.6, 129.0, 128.1, 83.9, 66.4, 46.3, 44.1, 42.0, 33.2, 32.1, 31.8, 31.5, 30.8, 24.8, 24.7, 23.6, 23.0, 14.4. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.6. **FT-IR** (cm^{-1}, neat, ATR) 2926 (m), 1454 (w), 1352 (s), 1165 (vs), 945 (m). **HRMS** (ESI) calcd for $C_{31}H_{51}BNO_5S$ $[M+H]^+$: 560.3581, found: 560.3568.



4-((4-(2-(1-Methylcyclohexyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine, 45 (0.155g, 65%) was prepared according to the general DCF procedure. The desired compound **45** was obtained as a crystalline, white solid (mp = 185-187 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.61 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 3.77 -3.69 (m, 4H), 3.03 - 2.92 (m, 4H), 2.52 (dd, *J* = 9.5, 3.7 Hz, 1H), 2.03 (dd, *J* = 13.4, 9.6 Hz, 1H), 1.55 (dd, *J* = 13.5, 3.9 Hz, 1H), 1.52 - 1.35 (m, 5H), 1.31 - 1.19 (m, 5H), 1.13 (d, *J* = 4.6 Hz, 12H), 0.88 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 151.9, 131.6, 129.1, 128.2, 83.9, 66.4, 46.3, 38.3, 38.2, 34.1, 26.7, 24.8, 24.6, 22.4, 22.3. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.8. **FT-IR** (cm^{-1}, neat, ATR) 2945 (m), 1455 (w), 1346 (s), 1169 (vs), 710 (vs). **HRMS** (ESI) calcd for $C_{25}H_{41}BNO_5S$ $[M+H]^+$: 478.2799, found: 478.2808.



4-((4-(2-(3-Isopropyl-1-methylcyclopentyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl) phenyl)sulfonyl) Morpholine, 46 (0.205 g, 81%) was prepared according to the general DCF procedure. The desired compound **46** was obtained as a crystalline, white solid (mp = 127-128 ºC). The diastereomeric ratio was 1.2:1.1:1.1:1 as determined by ^{1}H NMR analysis of the crude reaction. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.61 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 3.73 (t, *J* = 4.5 Hz, 4H), 3.02 - 2.91 (m, 4H), 2.54 - 2.46 (m, 1H), 2.18 – 2.06 (m, 1H), 1.82 - 1.18 (m, 9H), 1.14 (s, 12H), 0.98 - 0.92 (m, 3H), 0.87 –

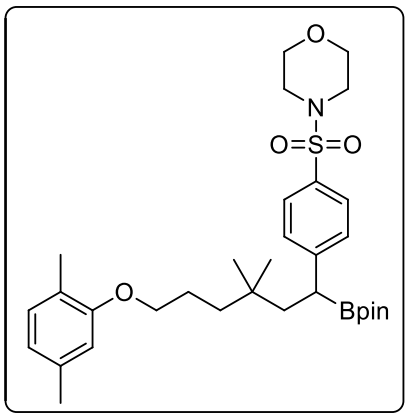


0.78 (m, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 151.8, 151.7, 151.6, 131.7, 129.1, 128.2, 128.1, 83.9, 66.4, 47.5, 47.5, 46.7, 46.4, 46.3, 45.9, 45.9, 45.6, 45.4, 45.2, 45.0, 44.7, 44.4, 43.4, 43.4, 43.0, 40.6, 39.8, 39.7, 39.2, 34.4, 34.4, 34.3, 34.2, 30.4, 30.1, 30.0, 29.8, 29.6, 28.3, 28.1, 26.8. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 34.0. **FT-IR** (cm^{-1}, neat, ATR) 2952 (m), 1366 (m), 1321 (m), 1147 (vs), 1020 (m). **HRMS** (EI) calcd for $C_{27}H_{44}BNO_5S$ $[M]^+$: 505.3033, found: 505.3027.

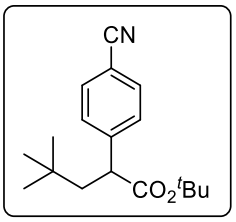
Ethyl 3,3-Dimethyl-5-(4-(morpholinosulfonyl)phenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate, 47 (0.172 g, 68%) was prepared according to the general DCF procedure. The desired compound **47** was obtained as a crystalline, white solid (mp = 92-94 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.62 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.73 (t, *J* = 4.7 Hz, 4H), 2.97 (t, *J* = 4.4 Hz, 4H), 2.53 (dd, *J* = 9.2, 4.1 Hz, 1H), 2.21 (d, *J* = 2.1 Hz, 2H), 2.12 (dd, *J* = 13.6, 9.3 Hz, 1H), 1.69 (dd, *J* = 13.6, 4.3 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 12H), 1.01 (d, *J* = 8.2 Hz, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 172.2, 151.0, 131.9, 129.1, 128.2, 84.0, 66.4, 60.2, 46.6, 46.3, 44.4, 34.6, 27.8, 27.4, 24.8, 24.7, 14.6. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.7. **FT-IR** (cm^{-1}, neat, ATR) 2986 (m), 1732 (s) 1360 (m) 1218 (vs) 903 (m). **HRMS** (ESI) calcd for $C_{25}H_{40}BNO_7S$ $[M+Na]^+$: 532.2521, found: 532.2548.

4,4-Dimethyl-6-(4-(morpholinosulfonyl)phenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one, 48 (0.186 g, 78%) was prepared according to the general DCF procedure. The desired compound **48** was obtained as a crystalline, white solid (mp = 133-135 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.62 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 3.76 - 3.70 (m, 4H), 3.01 - 2.93 (m, 4H), 2.49 (dd, *J* = 8.9, 4.7 Hz, 1H), 2.33 (d, *J* = 4.7 Hz, 2H), 2.11 – 2.05 (m, 4H), 1.75 (dd, *J* = 13.5, 4.7 Hz, 1H), 1.13 (s, 12H), 1.02 (s, 3H), 0.99 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 208.6, 151.0, 132.0, 129.1, 128.2, 84.1, 66.4, 54.4, 46.3, 44.3, 34.8, 32.8, 27.7, 27.4, 24.8, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.3. **FT-IR** (cm^{-1}, neat, ATR) 2975 (m), 1342 (s), 1152 (vs), 944 (s), 571 (m). **HRMS** (ESI) calcd for $C_{24}H_{39}BNO_6S$ $[M+H]^+$: 480.2591, found: 480.2583.

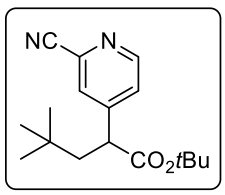
4-((4-(6-(2,5-Dimethylphenoxy)-3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl) phenyl)sulfonyl)morpholine, 49 (0.186 g, 64%) was prepared according to the general DCF procedure. The desired compound **49** was obtained as a crystalline, white solid (mp = 99-100 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.61 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 3.89 (t, *J* = 6.4 Hz, 2H), 3.73 (t, *J* = 4.6 Hz, 4H), 2.97 (t, *J* = 4.6 Hz, 4H), 2.51 (dd, *J* = 9.4, 3.7 Hz, 1H), 2.30 (s, 3H), 2.18 (s, 3H), 2.07 (dd, *J* = 13.4, 9.5 Hz, 1H), 1.72 (dd, *J* = 14.2, 7.6 Hz, 2H), 1.57 (dd, *J* = 13.5, 3.9 Hz, 1H), 1.40 (t, *J* = 8.5 Hz, 2H), 1.13 (s, 12H), 0.91 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 157.3, 151.6, 136.8, 131.8, 130.6, 129.1, 128.2, 123.8, 120.9, 84.0, 68.8, 66.4, 46.3, 44.4, 38.8, 34.0, 27.5, 27.4, 24.8, 24.7, 24.6, 21.7, 16.1. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.0. **FT-IR** (cm^{-1}, neat, ATR) 2956 (w), 2924 (w), 1351 (m), 1262 (m), 1165 (s), 945 (m). **HRMS** (EI) calcd for $C_{32}H_{48}BNO_6S$ $[M]^+$: 608.3295, found: 608.3204.



***tert*-Butyl 2-(4-Cyanophenyl)-4,4-dimethylpentanoate, 50** (0.068 g, 47%) was prepared according to the general DCF procedure *with the following modification: tert*-Butyl acrylate (0.077 g, 0.60 mmol, 1.2 equiv) was used in place of vinylBpin. The desired compound **50** was obtained as a crystalline, white solid (mp = 84-85 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.59 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 3.57 (dd, *J* = 8.9, 3.4 Hz, 1H), 2.26 (dd, *J* = 14.1, 9.0 Hz, 1H), 1.47 (dd, *J* = 13.9, 3.3 Hz, 1H), 1.37 (s, 9H), 0.90 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 172.9, 147.2, 132.6, 128.8, 119.1, 111.0, 81.4, 49.8, 47.2, 31.4, 29.7, 28.0. **FT-IR** (cm^{-1}, neat, ATR) 2954 (w), 2228 (w), 1722 (m), 1365 (m), 1141 (s), 839 (m), 564 (m). **HRMS** (EI) calcd for $C_{14}H_{25}NO_2$ $[M-C_4H_8]^+$: 231.1259, found: 231.1265.

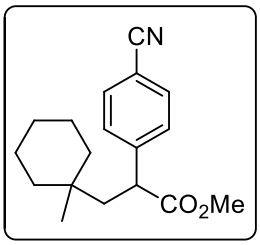


***tert*-Butyl 2-(2-Cyanopyridin-4-yl)-4,4-dimethylpentanoate**, **51** (0.82 g, 57%) was prepared according to the general DCF procedure *with the following modification*: *tert*-butyl acrylate (0.077 g, 0.60 mmol, 1.2 equiv) was used in place of vinylBpin. The desired compound **51** was obtained as a white solid (mp = 77 – 79 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 8.64 (d, *J* = 1.7 Hz, 1H), 7.80 (dd, *J* = 8.0, 2.2 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 3.62 (dd, *J* = 8.9, 4.0 Hz, 1H), 2.28 (dd, *J* = 14.0, 8.8 Hz, 1H), 1.48 (dd, *J* = 14.0, 4.0 Hz, 1H) 1.38 (s, 9H), 0.91 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 172.3, 151.2, 141.5, 136.1, 132.6, 128.6,



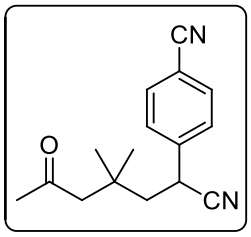
117.5, 82.1, 47.3, 31.5, 29.7, 28.1. **FT-IR** (cm^{-1}, neat, ATR) 2958 (m), 2236 (w), 1727 (s) 1368 (m), 1144 (vs), 857 (w). **HRMS** (EI) calcd for $C_{13}H_{15}N_2O_2$ $[M\text{-}t\text{Bu}]^+$: 232.1221, found: 232.1222.

Methyl 2-(4-Cyanophenyl)-3-(1-methylcyclohexyl)propanoate, 52 (0.129 g, 91%) was prepared



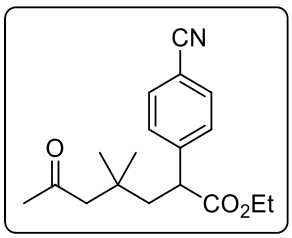
according to the general DCF procedure *with the following modification.* Methyl acrylate (0.057 g, 0.60 mmol, 1.2 equiv) was used in place of vinylBpin. The desired compound **52** was obtained as a colorless, dense oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.59 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 3.73 (dd, J = 8.7, 4.0 Hz, 1H), 3.65 (s, 3H), 2.29 (dd, J = 14.2, 8.7 Hz, 1H), 1.58 (dd, J = 14.1, 3.9 Hz, 1H), 1.48 - 1.36 (m, 5H), 1.28 - 1.21 (m, 4H), 1.21 - 1.14 (m, 1H), 0.85 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 174.6, 146.7, 132.7, 129.0, 119.0, 111.3, 52.6, 47.5, 38.1, 38.0, 33.8, 26.5, 22.1. **FT-IR** (cm^{-1}, neat, ATR) 2925 (m), 2229 (w), 1735 (s), 1210 (m), 1158 (s), 836 (w). **HRMS** (ESI) calcd for $C_{18}H_{23}NO_2$ $[M]^+$: 285.1729, found: 285.1736.

4-(1-Cyano-3,3-dimethyl-5-oxohexyl)benzonitrile 53 (0.113 g, 89%) was prepared according to the



general DCF procedure *with the following modification*: Acrylonitrile (0.039 g, 0.60 mmol, 1.2 equiv) was used in place of vinylBpin. The desired compound **53** was obtained as an off-white wax. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.68 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 3.92 (dd, J = 11.1, 3.4 Hz, 1H), 2.66 - 2.59 (m, 1H), 2.47 (d, J = 16.5 Hz, 1H), 2.22 - 2.12 (m, 4H), 1.89 (dd, J = 14.2, 3.4 Hz, 1H), 1.19 (s, 3H), 1.12 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 208.6, 151.0, 132.0, 129.1, 128.2, 84.1, 66.4, 54.4, 46.3, 44.3, 34.8, 32.8, 27.7, 27.4, 24.8, 24.7. **FT-IR** (cm^{-1}, neat, ATR) 2959 (m), 2230 (m), 1711 (s), 1325 (vs), 835 (s), 576 (s). **HRMS** (EI) calcd for $C_{16}H_{18}N_2O$ $[M]^+$: 254.1419, found: 254.1427.

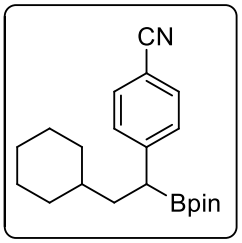
Ethyl 2-(4-Cyanophenyl)-4,4-dimethyl-6-oxoheptanoate, 54 (0.133 g, 88%) was prepared according to



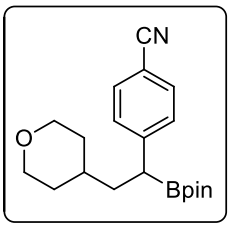
the general DCF procedure *with the following modification*. Ethyl acrylate (0.060 g, 0.60 mmol, 1.2 equiv) was used in place of vinylBpin. The desired compound **54** was obtained as a colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.59 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 4.17 - 4.02 (m, 2H), 3.69 (dd, J = 8.9, 4.0 Hz, 1H), 2.39 - 2.28 (m, 3H), 2.07 (s, 3H), 1.81 (dd, J = 14.1, 4.0 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H), 1.00 (s, 3H), 0.98 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 208.2, 173.7, 146.1, 132.7, 129.0, 119.0, 111.4, 61.6, 53.9, 48.4, 45.0, 34.2, 32.6, 27.7, 27.5,

14.3. **FT-IR** (cm^{-1}, neat, ATR) 2960 (m), 1728 (vs), 1366 (m), 1152 (vs), 1020 (m). **HRMS** (EI) calcd for $C_{18}H_{23}NO_3$ $[M]^+$: 301.1678, found: 301.1687.

4-(2-Cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl) Benzonitrile, 55 (0.068 g, 40%) was prepared according to the general DCF procedure *with the following modifications:* $NiBr_2$(phen) (10 mg, 0.05 mmol, 5 mol%) was used in place of $NiBr_2$(bpy). An excess of vinylBpin was used (0.231 g, 1.50 mmol, 3.0 equiv). The desired compound **55** was obtained as a crystalline, white solid (mp = 96-98 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 2.52 (t, *J* = 8.1 Hz, 1H), 1.77 - 1.55 (m, 7H), 1.27 - 1.03 (m, 16H), 0.93 - 0.80 (m, 2H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 150.1, 132.3, 129.3, 119.7, 109.1, 83.9, 39.6, 36.8, 33.9, 33.1, 26.8, 26.5, 26.5, 24.8, 24.8 ppm. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.1 **FT-IR** (cm^{-1}, neat, ATR) 2921 (s), 2226 (m), 1606 (m), 1380 (vs), 1140 (s), 851 (m) **HRMS** (EI) calcd for $C_{21}H_{30}BNO_2$ $[M^+]$: 339.2370, found: 339.2370.



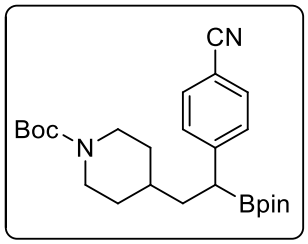
4-(3-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl) Benzonitrile, 56 (0.089 g, 57%) was prepared according to the General Procedure *with the following modifications:* $NiBr_2$(phen) (10 mg, 0.05 mmol, 5 mol %) was used in place of $NiBr_2$(bpy). An excess of vinylBpin was used (0.231 g, 1.50 mmol, 3.0 equiv). The desired compound **56** was obtained as a dense oil that solidified after standing overnight in a refrigerator (mp = 44-45 ºC). The diastereomeric ratio was 1.1:1 as determined by ^{1}H NMR analysis of the crude reaction. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 2.52 -2.48 (m, 1H), 1.91 - 1.69 (m, 1H), 1.62 – 1.42 (m, 1H), 1.41 - 1.23 (m, 2H), 1.20 - 1.13 (m, 13H), 0.87 - 0.79 (m, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 150.3, 150.0, 132.3, 129.3, 129.3, 119.6, 109.1, 83.9, 39.3, 38.6, 33.9, 33.3, 29.9, 29.3, 24.9, 24.8, 24.8, 19.7, 18.9, 11.5, 11.5 ppm. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 31.5 **FT-IR** (cm^{-1}, neat, ATR) 2961 (w), 2226 (w), 1462 (w), 1370 (s), 1326 (vs), 852 (m). **HRMS** (EI) calcd for $C_{19}H_{28}BNO_2$ $[M^+]$: 313.2213, found : 313.2220.



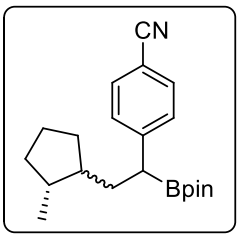
4-(2-(Tetrahydro-2H-pyran-4-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl) benzonitrile, 57 (0.092 g, 54%) was prepared according to the general DCF procedure *with the following modifications:* Ni(phen)Br_2 (10 mg, 0.05 mmol, 5 mol %) was used in place of Ni(bpy)Br_2. An excess of vinylBpin was used (0.231 g, 1.50 mmol, 3.0 equiv). The desired compound **57** was obtained as a colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.54 (d, *J*=8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.92 (td, *J* =

11.2, 2.6 Hz, 2H), 3.27 (tt, *J* = 11.9, 2.6 Hz, 2H), 2.52 (t, *J* = 8.1 Hz, 1H), 1.80-1.74 (m, 1H), 1.69 (dd, *J* = 8.5, 5.6 Hz, 1H), 1.62 (d, *J* = 13.0 Hz, 1H), 1.52 (d, *J* = 12.4 Hz, 1H), 1.39-1.32 (m, 1H), 1.30-1.23 (m, 2H), 1.18 (d, *J* = 4.7 Hz, 12H) **^{13}C NMR** ($CDCl_3$, 125 MHz) 149.5, 132.5, 129.3, 119.5, 109.4, 84.1, 68.2, 39.0, 34.2, 33.7, 32.8, 24.8. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.5. **FT-IR** (cm^{-1}, neat, ATR) 2977 (m), 2926 (m), 2226 (w), 1371 (m), 1324 (m), 1140 (s). **HRMS** (EI) calcd for $C_{20}H_{28}BNO_3$ [M^+]: 341.2162, found: 341.2172.

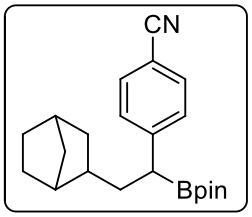
***tert*-Butyl-4-(2-(4-cyanophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)piperidine-1-carboxylate, 58** (0.112 g, 51%) was prepared according to the general DCF procedure *with the following modifications:* $Ni(phen)Br_2$ (10 mg, 0.05 mmol, 5 mol %) was used in place of $Ni(bpy)Br_2$. An excess of vinylBpin was used (0.231 g, 1.50 mmol, 3.0 equiv). The desired compound **58** was obtained as a colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.54 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 4.02 (br. s, 2H), 2.58 (br. s, 2H), 2.52 (t, *J* = 8.1 Hz, 1H), 1.79-1.72 (m, 1H), 1.71-1.62 (m, 2H), 1.58 (s, 1H), 1.44 (s, 9H), 1.17 (d, *J* = 4.9 Hz, 12H), 1.07 (t, *J* = 13.6 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) 155.1, 149.5, 132.5, 129.2, 119.5, 109.4, 84.1, 79.5, 38.6, 35.2, 28.7, 24.9. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.8. **FT-IR** (cm^{-1}, neat, ATR) 2977 (m), 2926 (m), 2226 (w), 1689 (vs), 1365 (s), 1165 (m), 1142 (m). **HRMS** (EI) calcd for $C_{20}H_{28}BN_2O_2$ [M^+ - Boc]: 339.2244, found: 339.2231.



4-(2-(2-Methylcyclopentyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl) Benzonitrile, 59 (0.090 g, 53%) was prepared according to the general DCF procedure *with the following modifications:* $Ni(phen)Br_2$ (10 mg, 0.05 mmol, 5 mol %) was used in place of $Ni(bpy)Br_2$. An excess of vinylBpin was used (0.231 g, 1.50 mmol, 3.0 equiv). The desired compound **59** was obtained as a colorless oil. The diastereomeric ratio was 1.5:1 as determined by ^{1}H NMR analysis of the crude reaction. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.53 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.44 (dd, *J* = 9.9, 5.8 Hz, 1H), 1.98 - 1.90 (m, 1H), 1.79 - 1.73 (m, 2H), 1.61 – 1.55 (m, 1H), 1.52 - 1.48 (m, 2H), 1.39 (pent, *J* = 7.5 Hz, 1H), 1.29 - 1.24 (m, 2H), 1.18 (m, 13H), 0.87 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz). 149.8, 132.4, 129.3, 119.6, 109.1, 83.9, 46.3, 40.8, 36.6, 35.0, 32.1, 24.9, 24.8, 23.6, 19.4. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 33.2. **FT-IR** (cm^{-1}, neat, ATR). 2987 (m), 2221 (w), 1390 (m), 1120 (m), 871 (m). **HRMS** (EI) calcd for $C_{24}H_{31}NO_2$ [M^+]: 365.2355, found: 365.2363.

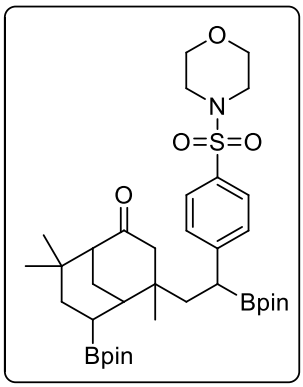


4-(2-(Bicyclo[2.2.1]heptan-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl) Benzonitrile,

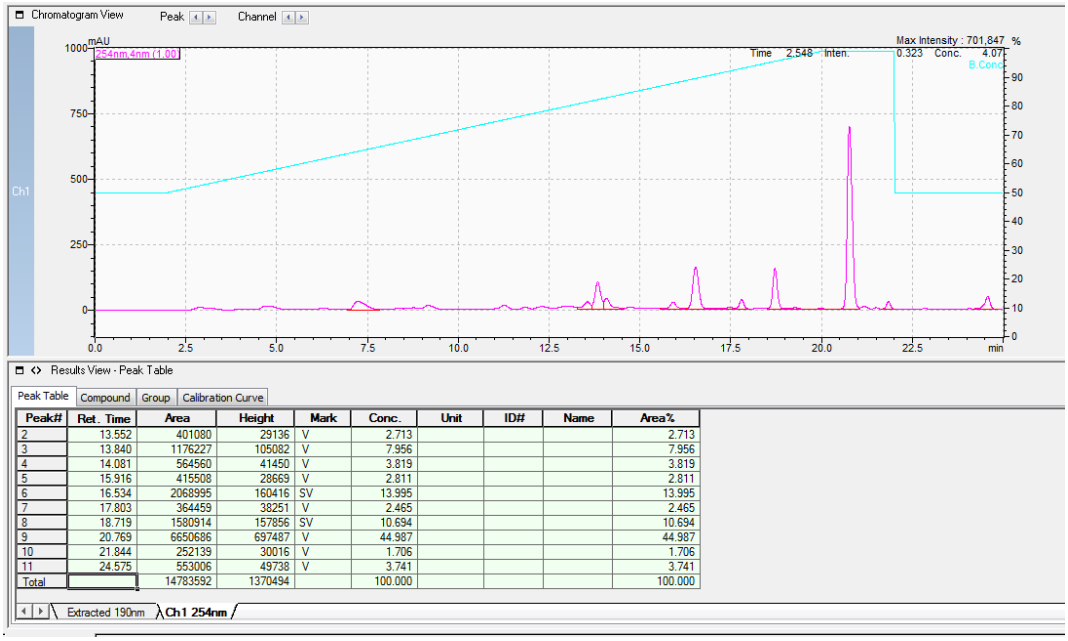


60 (0.087 g, 50%) was prepared according to the general DCF procedure *with the following modifications:* Ni(phen)Br_2 (10 mg, 0.05 mmol, 5 mol %) was used in place of Ni(bpy)Br_2. An excess of vinylBpin was used (0.231 g, 1.50 mmol, 3.0 equiv). The desired compound **60** was obtained as crystalline solid (mp = 69-71 °C). The diastereomeric ratio was 1.2:1 as determined by ^{1}H NMR analysis of the crude reaction. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.53 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.29 (dd, *J* = 8.2, 1.6 Hz, 2H), 2.43 (q, *J* = 7.3 Hz, 1H), 2.19 – 2.13 (m, 1H), 2.03 - 1.86 (m, 1H), 1.85 – 1.62 (m, 1H) 1.45 - 1.40 (m, 2H), 1.36 - 1.22 (m, 4H), 1.20 - 1.15 (m, 12H), 1.10 - 1.00 (m, 4H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 150.1, 149.9, 132.3, 129.5, 129.4, 119.7, 109.1, 83.9, 41.5, 41.4, 41.3, 40.9, 39.3, 39.0, 38.6, 38.0, 36.8, 35.6, 35.5, 30.3, 30.3, 29.0, 24.8. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 32.4. **FT-IR** (cm^{-1}, neat, ATR) 2947 (m), 2227 (w), 1353 (m), 1327 (m), 1142 (s), 850 (m). **HRMS** (EI) calcd for $C_{22}H_{30}BNO_2$ [M^+]: 351.2370, found: 351.2398.

4,8,8-Trimethyl-4-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[3.3.1]nonan-2-one, 61

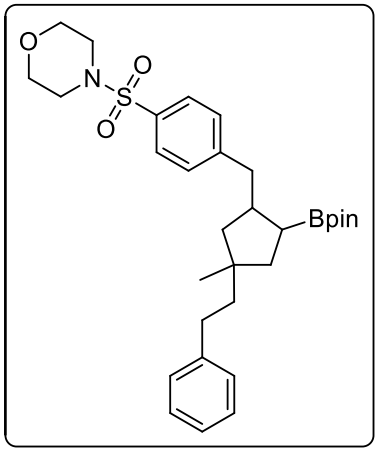


(0.137 g, 40%) was prepared according to the general DCF procedure *with the following modification*: 2.5 equiv of vinylboronic acid pinacol ester were used. The desired compound **61** was obtained as a crystalline, white solid (mp = 120-121 °C). The diastereomeric ratio was 5.8:1.8:1.3:1 as determined by HPLC analysis of the isolated material. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.60 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 3.76 - 3.71 (m, 4H), 3.00 - 2.94 (m, 4H), 2.48 (dd, *J* = 7.9, 4.7 Hz, 1H), 2.35 - 2.15 (m, 2H), 2.07 - 1.64 (m, 7H), 1.51 - 1.40 (m, 2H), 1.25 (d, *J* = 6.6 Hz, 12H), 1.13 (d, *J* = 4.3 Hz, 12H), 1.07 (s, 3H), 1.03 (s, 3H), 0.81 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 214.1, 150.9, 131.9, 129.2, 128.3, 84.1, 83.5, 66.4, 57.4, 55.0, 46.4, 44.6, 42.6, 35.6, 35.4, 31.6, 29.7, 29.6, 27.8, 27.0, 25.3, 25.2, 24.9, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 34.9. **FT-IR** (cm^{-1}, neat, ATR) 2978 (w), 1793 (s), 1361 (vs), 1143 (vs), 1138 (vs), 935 (m). **HRMS** (EI) calcd for $C_{36}H_{58}B_2NO_8S$ [M+H]$^+$: 686.4069, found: 686.3861.

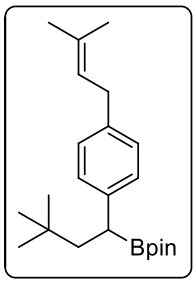


Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Name	Area%
2	13.552	401080	29136	V	2.713				2.713
3	13.840	1176227	105082	V	7.956				7.956
4	14.081	564560	41450	V	3.819				3.819
5	15.916	415508	28669	V	2.811				2.811
6	16.534	2068995	160416	SV	13.995				13.995
7	17.803	364459	38251	V	2.465				2.465
8	18.719	1580914	157856	SV	10.694				10.694
9	20.769	6650686	697487	V	44.987				44.987
10	21.844	252139	30016	V	1.706				1.706
11	24.575	553006	49738	V	3.741				3.741
Total		14783592	1370494		100.000				100.000

4-((4-((4-Methyl-4-phenethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)methyl) phenyl)sulfonyl) Morpholine, 62 (0.197 g, 71%) was prepared according to the general DCF procedure. The desired compound **62** was obtained as a crystalline, white solid (mp = 101-103 °C). The diastereomeric ratio was 2.5:1.5:1 as determined by ^{1}H NMR analysis of the crude reaction. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.64 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.29 - 7.22 (m, 2H), 7.20 - 7.12 (m, 3H), 3.77- 3.70 (m, 4H), 3.07 - 2.94 (m, 4H), 2.64 - 2.46 (m, 4H), 1.81 - 1.73 (m, 1H), 1.72 - 1.63 (m, 2H), 1.59 (dd, *J* = 11.9, 8.4 Hz, 1H), 1.55 (s, 2H), 1.53 - 1.47 (m, 1H), 1.29 - 1.23 (m, 13H), 1.14 and 0.98 (s, 3H total). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 148.8, 148.7, 143.8, 132.5, 129.8, 128.6, 128.6, 128.2, 125.8, 125.8, 83.4, 66.4, 46.6, 46.4, 46.3, 46.2, 44.0, 43.0, 42.8, 42.5, 42.1, 41.7, 41.3, 40.9, 40.6, 32.5, 31.8, 27.6, 26.0, 25.9, 25.3, 25.2. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) δ 34.1. **FT-IR** (cm^{-1}, neat, ATR) 2927 (w), 1371 (m), 1349 (s), 1165 (vs), 1113 (s), 942 (m). **HRMS** (EI) calcd for $C_{31}H_{44}BNO_5SNa$ $[M+Na]^+$: 576.2931, found: 576.2958.

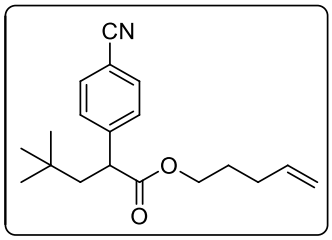


2-(3,3-Dimethyl-1-(4-(3-methylbut-2-en-1-yl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 63 (0.120 g, 66%) was prepared according to the general DCF procedure. The desired compound **63** was obtained as a colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.13 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 5.31 (dt, *J* = 7.3, 1.4 Hz, 2H), 3.28 (d, *J* = 7.2, 2H), 2.35 (dd, *J* = 10.2, 3.4 Hz, 1H), 2.01 (dd, *J* =



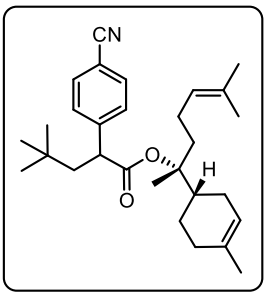
13.3, 10.2 Hz, 1H), 1.74 (s, 3H), 1.71 (s, 3H), 1.45 (dd, *J* = 13.4, 3.4 Hz, 1H), 1.15 (d, *J* = 2.4 Hz, 12H), 0.90 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) 142.4, 138.5, 132.4, 128.5, 128.4, 123.9, 83.4, 47.2, 34.2, 31.6, 29.9, 26.0, 24.9, 24.7, 18.1. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) 32.7. **FT-IR** (cm^{-1}, neat, ATR) 2953 (m), 1364 (s), 1318 (s), 1142 (vs), 863 (m). **HRMS** (EI) calcd for $C_{23}H_{37}BO_2$ [M^+]: 356.2887, found: 356.2908.

Pent-4-en-1-yl-2-(4-cyanophenyl)-4,4-dimethylpentanoate, 64 (0.122 g, 82%) was prepared according



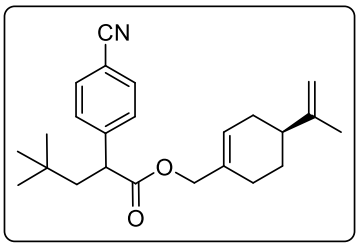
to the general DCF procedure *with the following modifications:* Pent-4-en-1-yl acrylate (0.084 g, 0.600 mmol) was used in place of vinylBpin. The desired compound **64** was obtained as a colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.59 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 5.77 - 5.66 (m, 1H), 4.95 (s, 1H), 4.93 (d, *J* = 4.7 Hz, 1H), 4.11 – 3.97 (m, 2H), 3.69 (dd, *J* = 8.9, 4.0 Hz, 1H), 2.29 (dd, *J* = 14.0, 9.0 Hz, 1H), 2.01 (q, *J* = 7.1 Hz, 2H), 1.70 - 1.62 (m, 2H), 1.54 (dd, *J* = 14.0, 4.0 Hz, 1H), 0.89 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) 173.9, 146.6, 137.4, 132.7, 129.0, 119.0, 115.7, 111.3, 64.9, 48.8, 47.4, 31.4, 30.2, 29.7, 27.9. **FT-IR** (cm^{-1}, neat, ATR) 2969 (m), 1486 (s), 1010 (s), 807 (s). **HRMS** (EI) calcd for $C_{19}H_{25}NO_2$ [M^+]: 299.1885, found: 299.1897.

(*R*)-6-Methyl-2-((*S*)-4-methylcyclohex-3-en-1-yl)hept-5-en-2-yl-2-(4-cyanophenyl)-4,4-dimethyl



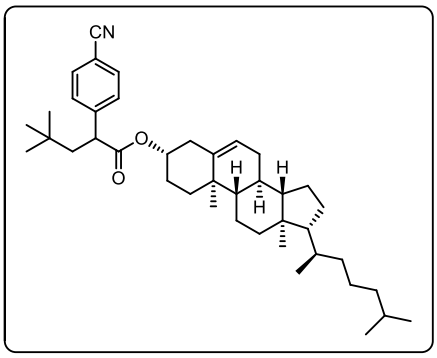
pentanoate, 65 (0.089 g, 41%) was prepared according to the general DCF procedure *with the following modifications:* (*S*)-6-methyl-2-((S)-4-methylcyclohex-3-en-1-yl)hept-5-en-2-ol (0.123 g, 0.600 mmol) was used in place of vinylBpin. The desired compound **65** was obtained as colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.59 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 5.33 - 5.23 (m, 1H), 4.99 – 4.89 (m, 1H), 3.60 (dd, *J* = 7.1, 4.0 Hz, 2H), 2.28 (dd, *J* = 13.9, 8.2 Hz, 1H), 2.08 - 1.86 (m, 4H), 1.80 - 1.71 (m, 4H), 1.67 - 1.61 (m, 8H), 1.57 - 1.51 (m, 2H), 1.50 - 1.41 (m, 3 H), 1.30 (d, *J*=19.5 Hz, 3 H), 0.89 (s, 9 H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 172.8, 172.6, 147.4, 147.4, 134.5, 134.3, 132.6, 132.0, 129.1, 124.1, 124.0, 120.4, 119.1, 111.1, 88.3, 50.0, 50.0, 46.8, 46.7, 40.8, 40.6, 35.8, 35.7, 31.4, 31.1, 29.8, 26.5, 26.4, 25.9, 25.9, 24.0, 23.8, 23.6, 22.1, 22.0, 20.6, 20.5, 17.8, 17.7. **FT-IR** (cm^{-1}, neat, ATR) 2958 (m), 2229 (w), 1726 (vs), 1210 (m), 1151 (vs), 835 (m). **HRMS** (EI) calcd for $C_{15}H_{24}$ [M^+ - $C_{14}H_{17}NO_2^+$]: 204.1878, found: 204.1883.

((*S*)-4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl-2-(4-cyanophenyl)-4,4-dimethylpentanoate, 66



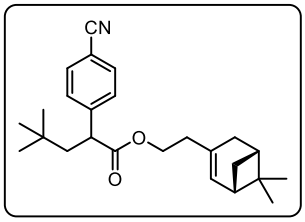
(0.089 g, 41%) was prepared according to the general DCF procedure *with the following modifications:* (*S*)-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl acrylate (0.124 g, 0.600 mmol) was used in place of vinylBpin. The desired compound **66** was obtained as colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.59 (d, *J* = 8.2 Hz, 2H), 7.44 (dd, *J* = 8.2, 1.4 Hz, 2H), 5.67 (br. s, 1H), 4.70 (d, *J* = 16.5 Hz, 2H), 4.49 - 4.36 (m, 2H), 3.71 (dd, *J* = 8.9, 4.0 Hz, 1H), 2.30 (dd, *J* = 14.0, 8.9 Hz, 1H), 2.16 – 2.05 (br. s, 2H), 1.97 – 1.88 (m, 3H), 1.83 - 1.75 (m, 1H), 1.72 (s, 3H), 1.55 (dd, *J* = 14.0, 4.0 Hz, 1H), 1.46 - 1.35 (m, 1H), 0.89 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 173.8, 173.8, 149.6, 146.5, 132.7, 132.4, 129.0, 126.7, 126.7, 119.0, 111.3, 109.1, 69.5, 48.8, 48.8, 47.4, 47.4, 40.9, 31.4, 30.7, 29.6, 27.4, 27.4, 26.6, 26.6, 21.0. **FT-IR** (cm^{-1}, neat, ATR) 2954 (m), 2229 (w), 1733 (s), 1147 (vs), 837 (m), 737 (vs). **HRMS** (EI) calcd for $C_{24}H_{31}NO_2$ [M^+]: 365.2355, found: 365.2363.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,



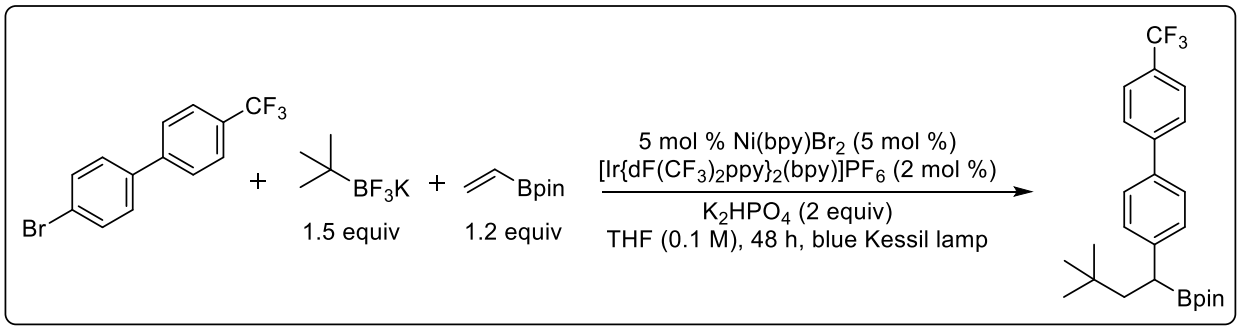
12,13,14,15,16,17-tetradecahydro-1H-cyclopenta [a]phenanthren-3-yl 2-(4-Cyanophenyl)-4,4-dimethylpentanoate, 67 (0.125 g, 42%) was prepared according to the general DCF procedure *with the following modifications:* cholesteryl acrylate (0.265 g, 0.600 mmol) was used in place of vinylBpin. The desired compound **67** was obtained as a white powdery solid (mp = 136-138 ºC). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.59 (dd, *J*=8.3, 1.8 Hz, 2H), 7.43 (d, *J*=7.9 Hz, 2H), 5.38 – 5.28 (m, 1H), 4.60 – 4.52 (m, 1H), 3.65 (dd, *J*=9.1, 3.6 Hz, 1H), 2.33 - 2.26 (m, 2H), 2.24 - 2.10 (m, 1H), 2.02 – 1.91 (m, 2H), 1.87 - 1.64 (m, 3H), 1.60 - 1.40 (m, 8H), 1.39 - 1.06 (m, 11H), 1.03 - 0.95 (m, 5H), 0.93 - 0.88 (m, 13H), 0.86 (dd, *J*=6.6, 2.1 Hz, 6H), 0.66 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 173.3, 146.8, 139.6, 139.6, 132.6, 128.9, 123.2, 123.1, 119.0, 111.2, 75.0, 56.9, 56.4, 50.3, 49.0, 47.5, 42.6, 40.0, 39.8, 38.1, 38.0, 37.2, 37.1, 36.8, 36.5, 36.0, 32.2, 32.1, 32.1, 32.1, 31.4, 29.7, 28.5, 28.3, 27.8, 27.7, 24.5, 24.1, 23.1, 22.8, 21.3, 19.6, 19.0, 12.1. **FT-IR** (cm^{-1}, neat, ATR) 2948 (s), 2229 (w), 1732 (s), 1467 (w), 1154 (m), 839 (vw). **HRMS** (EI) calcd for $C_{27}H_{44}$ [M - $C_{14}H_{17}NO_2^+$]: 368.3443, found: 368.3429.

2-((1*S*,5*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-3-yl)ethyl-2-(4-cyanophenyl)-4,4-

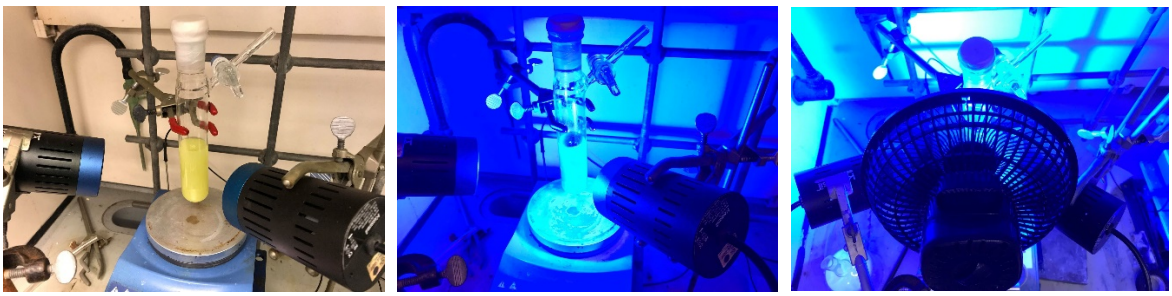


dimethylpentanoate, 68 (0.110 g, 58%) was prepared according to the general DCF procedure *with the following modifications:* 2-((1S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl acrylate (0.132 g, 0.600 mmol) was used in place of vinylBpin. The desired compound **68** was obtained as a colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.59 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 5.15 (dd, *J* = 19.0, 1.3 Hz, 1H), 4.12 – 4.05 (m, 1H), 4.05 – 3.98 (m, 1H), 3.67 (dd, *J* = 8.6, 4.2 Hz, 1H), 2.34 - 2.25 (m, 2H), 2.24 - 2.11 (m, 4H), 2.05 (br. s, 1H), 1.99 - 1.94 (m, 1H), 1.57 - 1.52 (m, 1H), 1.23 (s, 3H), 1.04 (dd, *J* = 17.2, 8.5 Hz, 1H), 0.88 (d, *J* = 0.9 Hz, 9H), 0.74 (d, *J* = 16.8 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) 173.9, 173.8, 146.6, 144.0, 132.7, 129.1, 119.2, 119.1, 119.0, 111.3, 63.6, 48.8, 47.4, 47.3, 45.9, 45.9, 40.9, 38.2, 38.2, 36.0, 31.9, 31.6, 31.4, 29.7, 26.5, 21.4, 21.3 **FT-IR** (cm^{-1}, neat, ATR) 2952 (w), 2914 (w), 2229 (w), 1732 (s), 1149 (vs), 837 (m). **HRMS** (EI) calcd for $C_{24}H_{31}NO_2$ [M^+]: 365.2355, found: 365.2363.

Procedure for Scale-up of Dicarbofunctionalization



To a 100 mL Schlenk tube (dimensions: height = 15 cm, diameter = 4 cm) equipped with a stirrer bar was added ^{t}BuBF$_3$K (1.230 g, 7.50 mmol, 1.5 equiv), 4-bromo-4′-(trifluoromethyl)-1,1′-biphenyl (1.506 g, 5.00 mmol, 1 equiv), K_2HPO_4 (1.742 g, 10.0 mmol, 2 equiv), anhyd $NiBr_2$(bpy) (0.094 g, 0.25 mmol, 5 mol %), and [Ir{dF(CF$_3$)$_2$ppy}$_2$(bpy)]PF$_6$ (0.101 g, 0.1 mmol, 2 mol %). The top of the vessel was sealed with a rubber septum, and the reaction was evacuated and backfilled with argon three times. The tube was charged with vinylboronic acid pinacol ester (0.924 g, 6.00 mmol, 1.2 equiv) dissolved in degassed THF (50 mL) via a syringe. The side-arm was closed, and the septum was sealed with Parafilm®. The tube was placed in front of two Kessil® H150 Blue lamps (24VDC, 1.5A, 30W) approximately 6 in away from the tube and irradiated for 48 h. The reaction was maintained at rt via air cooling by a clip fan. Below are pictures of the reaction set-up.



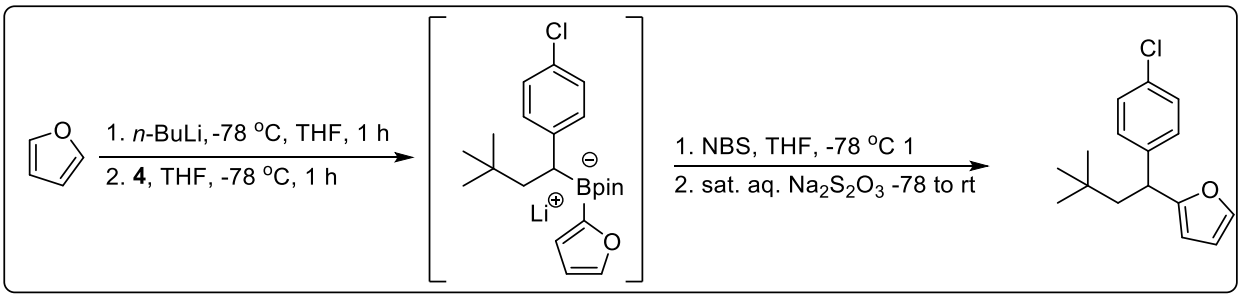
After confirmation that the reaction was complete by TLC, the crude reaction was filtered through a pad of Celite®, eluting with CH_2Cl_2. The filtrate was concentrated by rotary evaporation. The resulting light orange solid was recrystallized from MeOH to yield the desired cross-coupled product, **29** (1.863 g, 86%) as a white crystalline solid (mp = 118-120 ºC).

^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.67 (ABq, J_{AB} = 8.8 Hz, 4H), 7.49 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 2.45 (dd, J = 9.8, 3.6 Hz, 1H), 2.06 (dd, J = 13.3, 9.9 Hz, 1H), 1.50 - 1.56 (m, 1H), 1.16 (d, J = 1.7 Hz, 12H), 0.92 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 145.6, 145.0, 136.6, 129.1, 127.4, 125.9 (q, $J_{C\text{-}C\text{-}F}$ = 3.6 Hz, C), 124.7 (q, $J_{C\text{-}F}$ = 271.6 Hz, CF_3), 83.6, 46.9, 31.7, 30.0, 24.9, 24.8. **^{11}B NMR**

($CDCl_3$, 128.4 MHz) δ 33.1. **^{19}F NMR** ($CDCl_3$, 471 MHz) δ ppm -62.3 (3F). **FT-IR** (cm^{-1}, neat, ATR) 2950 (m) 1573 (w), 1310 (vs), 1132 (m) 1087 (m). **HRMS** (EI) calcd for $C_{25}H_{32}BF_3O_2$ $[M]^+$: 432.2447, found: 432.2455.

Functionalization of Bpin-Containing DCF Products

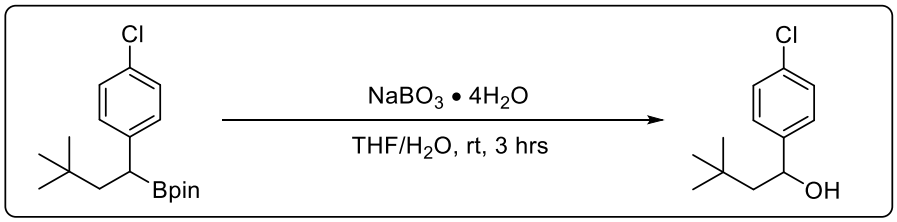
Homologation



2-(1-(4-Chlorophenyl)-3,3-dimethylbutyl)furan, 4a (0.055 g, 60%) was prepared from **4** according to a modified literature procedure.[29] A solution of furan (30.5 µL, 0.42 mmol, 1.2 equiv) in THF (2 mL, 0.2 M) was cooled to -78 °C and treated with *n*-BuLi (170 µL, 0.42 mmol, 1.2 equiv, 2.5 M in hexanes). After this time, the reaction mixture was charged with **4** (113 mg, 0.35 mmol, 1 equiv) in THF (1 mL, 0.35 M) dropwise. The mixture was stirred for one hour at -78 °C. After this time, the reaction mixture was charged with a solution of NBS (74.8 mg, 0.42 mmol, 1.2 equiv) and stirred at -78 °C for 1 h. Saturated $Na_2S_2O_3$ (1.5 mL) was added to the reaction mixture and stirred vigorously while warming to room temperature over an hour. The reaction mixture was transferred to a separatory funnel, diluted with Et_2O and H_2O, and layers separated. The aq layer was extracted twice with Et_2O. The combined organic layers were washed with deionized H_2O, dried (Na_2SO_4) and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (hexanes/EtOAc). The desired compound **4a** was obtained as a dense, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.21 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 6.23 – 6.21 (m, 1H), 5.97 (d, J = 2.9 Hz, 1H), 4.01 (t, J = 6.8 Hz, 1H), 2.12 (dd, J = 14.0, 7.5 Hz, 1H), 1.75 (dd, J = 14.0, 6.1 Hz, 1H), 0.79 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 158.3, 143.4, 141.4, 132.2, 129.4, 128.8, 110.5, 105.5, 48.6, 41.7, 31.4, 30.0. **FT-IR** (cm^{-1}, neat, ATR) 2954 (m), 1490 (m), 1091 (s), 1014 (s), 727 (m). **HRMS** (EI) calcd for $C_{16}H_{19}ClO$ $[M]^+$: 262.1124, found: 262.1131.

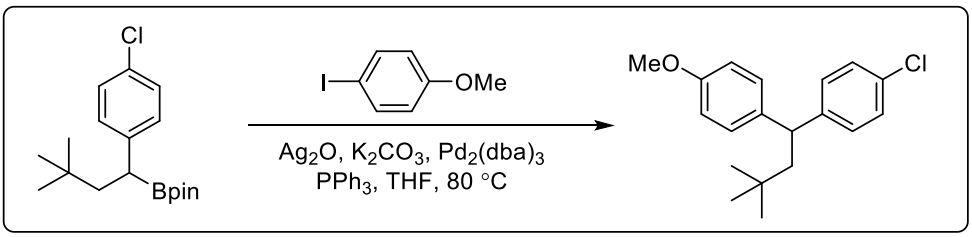
Oxidation



1-(4-Chlorophenyl)-3,3-dimethylbutan-1-ol, 4b (0.100 g, 94%) was prepared from **4** via the following procedure: A solution of **4** (0.161 g, 0.500 mmol) was dissolved in THF (4 mL) and deionized water (1 mL). Sodium perborate tetrahydrate (0.539 g, 3.50 mmol, 7.0 equiv) was then added in one portion and the reaction stirred for 4 h at rt. The reaction was then diluted with diethyl ether (5 mL) and water (5 mL) and the organic layer extracted. The aqueous layer was extracted with additional diethyl ether (5 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated via rotary evaporation. The resulting crude oil was purified by passing the crude material through a short pad of SiO_2, eluting with hexanes/EtOAc (4:1) to yield the desired compound, **4b**, as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.28 (q, J = 8.2 Hz, 4H), 4.80 (dd, J = 8.0, 2.5 Hz, 1H), 1.81 (br. s, 1H), 1.72 (dd, J = 14.5, 8.4 Hz, 1H), 1.55 (dd, J = 14.5, 3.2 Hz, 1H), 0.99 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 145.2, 133.2, 128.9, 127.4, 72.1, 53.3, 30.8, 30.4. **FT-IR** (cm^{-1}, neat, ATR) 3340 (br), 2926 (m), 1165 (m), 1142 (m), 942 (s). **HRMS** (EI) calcd for $C_{12}H_{17}ClO$ [M^+]: 212.0968, found: 212.0974.

Cross-Coupling



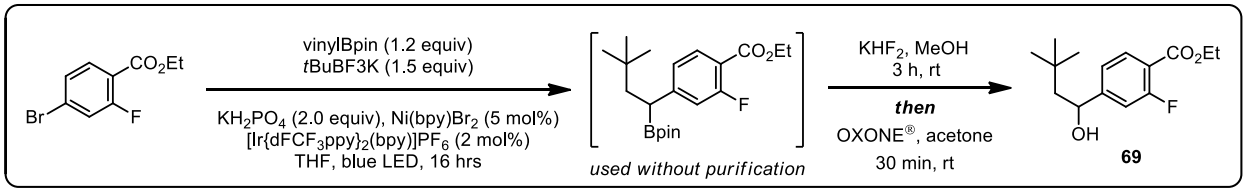
1-Chloro-4-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)benzene, 4c (0.074 g, 94%) was prepared from **4** via a modified literature procedure.[30] A two-dram vial, equipped with a stir bar, was charged with **4** (0.084 g, 0.259 mmol, 1.0 equiv), 4-iodoanisole (0.121 g, 0.519 mmol, 2.0 equiv), Ag_2O (0.090 g, 0.388 mmol, 1.5 equiv), K_2CO_3 (0.054 g, 0.388 mmol, 1.5 equiv), $Pd_2(dba)_3$ (0.012 g, 0.013 mmol, 5 mol %) and PPh_3 (0.027 g, 0.103 mmol, 40 mol %). The vial was placed under an Ar atmosphere via an inlet needle. Anhydrous THF (3 mL) was added via syringe and the reaction heated 80 ºC for 16 hours. The reaction was then cooled to room temperature and filtered through a pad of Celite® and concentrated via

rotary evaporation. The resulting crude oil was purified via flash silica chromatography (hexanes to 9:1 hexanes/EtOAc) to yield the desired compound, **4c**, as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.24 - 7.17 (m, 4H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 3.98 (t, *J* = 6.7 Hz, 1H), 3.76 (s, 3H), 2.03 (dd, *J* = 6.6, 4.7 Hz, 2H), 0.82 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 158.1, 146.0, 138.7, 131.7, 129.3, 128.8, 128.8, 114.2, 55.5, 49.8, 47.2, 31.8, 30.5. **FT-IR** (cm^{-1}, neat, ATR) 2951 (m), 1510 (s), 1247 (vs), 1035 (w), 823 (m). **HRMS** (EI) calcd for $C_{19}H_{23}ClO$ [M^+]: 302.1437, found: 302.1450.

Synthesis of an Intermediate to TK-666 and Related Derivatives

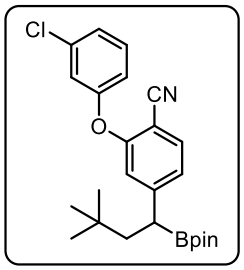
Synthesis of a TK-666 Intermediate via Ni/Photoredox DCF/Oxidation Protocol



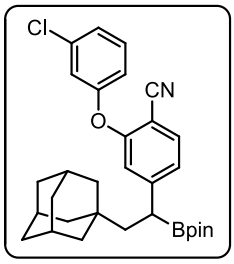
Ethyl 2-Fluoro-4-(1-hydroxy-3,3-dimethylbutyl)benzoate, 69 (0.102 g, 77%) was prepared via a three-step reaction sequence.[31] Ethyl 4-bromo-2-fluorobenzoate (0.124 g, 0.500 mmol) was subjected to standard conditions used in General DCF procedure *with the following modification*. After 16 hours of irradiation the crude material was passed through a fritted disk filter and washed with THF (5 mL). The crude solution was concentrated to ~5 mL total volume. The reaction flask was placed in an ice/water bath and saturated aqueous KHF_2 (0.44 mL, 2.0 mmol, 4.5 M) was added dropwise. After stirring for 3 hours, the reaction was evaporated to dryness and the crude material was extracted with three portions of boiling acetone (~5 mL each). The solution was concentrated to ~3 mL total volume. Oxone® (0.308 g, 0.500 mmol, 1.0 equiv) in water (2.5 mL) was added in one portion. After stirring at room temperature for 30 min, saturated aqueous NH_4Cl (5 mL) was added and the mixture was extracted twice with ethyl acetate (5 mL each). The combined organic extracts were dried over sodium sulfate, filtered and concentrated via rotary evaporation. The crude oil was purified via flash silica column chromatography (hexanes to 8:2 hexanes/EtOAc) to yield the desired compound, **69**, as a clear, colorless oil.

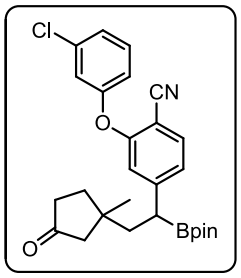
^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.86 (t, J = 8.1 Hz, 1H), 7.14 – 7.09 (m, 2H), 4.84 (d, J = 8.6 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 2.04 (br. s, 1H), 1.68 (dd, J = 14.6, 8.7 Hz, 1H), 1.53 (dd, J = 14.6, 3.0 Hz, 1H), 1.38 (t, J = 7.2 Hz, 3H), 1.00 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 164.6 (d, J = 3.7 Hz), 162.4 (d, J = 261 Hz), 154.4 (d, J = 8.2 Hz), 132.5, 121.3 (d, J = 3.6 Hz), 117.8 (d, J = 10.0 Hz), 114.3 (d, J = 23 Hz), 71.8, 61.5, 52.3, 30.9, 30.4, 14.5. **^{19}F NMR** ($CDCl_3$, 471 MHz) δ ppm -112.0. **FT-IR** (cm^{-1}, neat, ATR) 3456 (br), 2953 (m), 1711 (s), 1278 (vs), 1084 (vs), 775 (m). **HRMS** (EI) calcd for $C_{15}H_{21}FO_3$ [M^+]: 268.1465, found: 268.1475.

2-(3-Chlorophenoxy)-4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl) Benzonitrile, 70 (0.136 g, 62%) was prepared according to the general DCF procedure using aryl bromide **S3** (0.154 g, 0.5 mmol). The desired compound, **70**, was obtained as a colorless viscous oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.53 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 8.1 Hz, 1H), 7.16 (ddd, *J* = 7.0, 4.0, 2.6 Hz, 1H), 7.06 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.00 (t, *J*=2.1 Hz, 1 H), 6.94 (ddd, *J* = 8.2, 2.3, 0.8 Hz, 1H), 6.84 (d, *J* = 1.2 Hz, 1H), 2.40 (dd, *J* = 9.0, 4.6 Hz, 1H), 1.90 (dd, *J* = 13.4, 9.0 Hz, 1 H), 1.43 (dd, *J*=13.4, 4.6 Hz, 1H), 1.12 (d, *J*=5.5 Hz, 12H), 0.85 (s, 9H).^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm 158.6, 156.9, 153.9, 135.6, 133.9, 131.0, 124.9, 124.4, 119.7, 118.4, 117.7, 116.4, 101.6, 84.0, 46.0, 31.8, 29.9, 24.8, 24.7. ^{11}B NMR ($CDCl_3$, 128.4 MHz) 32.3. FT-IR (cm^{-1}, neat, ATR) 2891 (w), 2229 (w), 1239 (vs), 1138 (s), 1110 (m), 848 (m). HRMS (EI) calcd for $C_{25}H_{31}BClNO_3$ [M^+]: 439.2086, found: 439.2087.



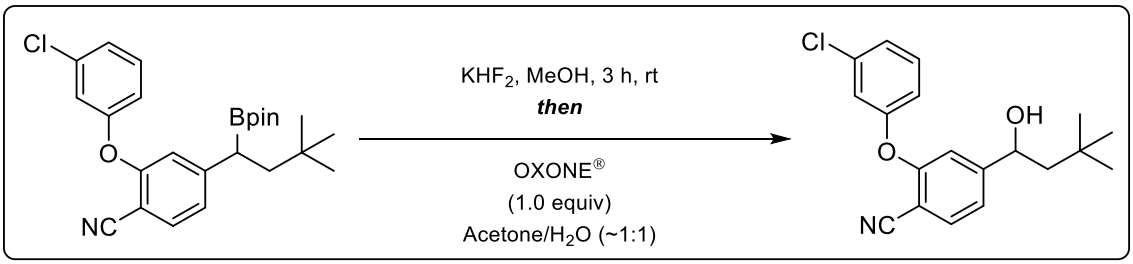
4-(2-(Adamantan-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2-(3-chloro phenoxy)benzonitrile, 71 (0.142 g, 55%) was prepared according to the general DCF procedure using aryl bromide **S3** (0.154 g, 0.5 mmol). The desired compound, **71**, was obtained as a white foam. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.53 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 8.1 Hz, 1H), 7.16 (ddd, *J* = 7.0, 4.0, 2.6 Hz, 1H), 7.06 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.00 (t, *J*=2.1 Hz, 1 H), 6.94 (ddd, *J* = 8.2, 2.3, 0.8 Hz, 1H), 6.84 (d, *J* = 1.2 Hz, 1H), 2.40 (dd, *J* = 9.0, 4.6 Hz, 1H), 1.90 (dd, *J* = 13.4, 9.0 Hz, 1 H), 1.43 (dd, *J*=13.4, 4.6 Hz, 1H), 1.12 (d, *J*=5.5 Hz, 12H), 0.85 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm 158.5, 157.0, 154.1, 135.6, 133.9, 131.0, 124.9, 124.5, 119.7, 118.6, 117.7, 116.4, 101.5, 84.0, 46.6, 42.9, 37.3, 33.7, 28.9, 24.8, 24.7. ^{11}B NMR ($CDCl_3$, 128.4 MHz) 33.2. FT-IR (cm^{-1}, neat, ATR) 2901 (m), 2846 (w), 2229 (w), 1358 (m), 1239 (vs), 1140 (s), 840 (m), 778 (w). HRMS (EI) calcd for $C_{31}H_{37}BClNO_3$ [M^+]: 517.2555, found: 517.2540.





2-(3-Chlorophenoxy)-4-(2-(1-methyl-3-oxocyclopentyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile, 72 (0.190 g, 79%) was prepared according to the general DCF procedure using aryl bromide **S3** (0.154 g, 0.5 mmol). The desired compound, **72**, was obtained as a yellow-tinted oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ ppm 7.55 (dd, *J* = 8.1, 3.2 Hz, 1H), 7.31 (t, *J* = 8.2 Hz, 1H), 7.17 (ddd, *J* = 7.9, 1.8, 0.8 Hz, 1H), 7.07 - 7.02 (m, 1H), 7.02 - 6.98 (m, 1H), 6.97 - 6.93 (m, 1H), 6.81 (dd, *J* = 12.2, 1.4 Hz, 1H), 2.40 (dd, *J* = 8.2, 5.6 Hz, 1H), 2.28 - 2.21 (m, 2 H), 2.14 – 2.09 (m, 1H), 2.08 - 2.00 (m, 1 H), 1.89 (d, *J* = 6.1 Hz, 1H), 1.79 - 1.73 (m, 1H), 1.69 - 1.64 (m, 2H), 1.13 (d, *J* = 3.2 Hz, 12 H), 1.00 (s, 3 H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 219.3, 158.8, 158.8, 156.7, 156.7, 152.8, 152.6, 135.6, 134.2, 131.1, 125.1, 124.2, 119.9, 119.8, 118.2, 118.1, 117.9, 117.8, 116.1, 101.9, 84.3, 84.3, 52.8, 52.7, 43.7, 40.7, 40.6, 36.9, 36.7, 35.7, 25.2, 24.9, 24.8, 24.7. **^{11}B NMR** ($CDCl_3$, 128.4 MHz) 33.4. **FT-IR** (cm^{-1}, neat, ATR) 2977 (w), 2229 (w), 1738 (m), 1371 (m), 1138 (vs), 849 (m). **HRMS** (EI) calcd for $C_{27}H_{31}BClNO_4$ [M^+]: 479.2035, found: 479.2041.

Synthesis of a TK-666 Derivative via Oxidation



2-(3-Chlorophenoxy)-4-(1-hydroxy-3,3-dimethylbutyl)benzonitrile, 70a (0.143 g, 71%) was prepared from 2-(3-chlorophenoxy)-4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzonitrile **68** (0.269 g, 0.611 mmol) in a two-step reaction sequence.[31] **70** was converted to the corresponding organotrifluoroborate using GPA3 (*see page S13*). The resulting solid (0.190 g, 0.453 mmol) was then dissolved in acetone (3 mL) and a solution Oxone® (0.278 g, 0.453 mmol, 1.0 equiv) in water (2.5 mL) was added in one portion. After stirring at room temperature for 30 min, saturated aqueous NH_4Cl (5 mL) was added and the mixture was extracted twice with ethyl acetate (5 mL each). The combined organic extracts were dried over

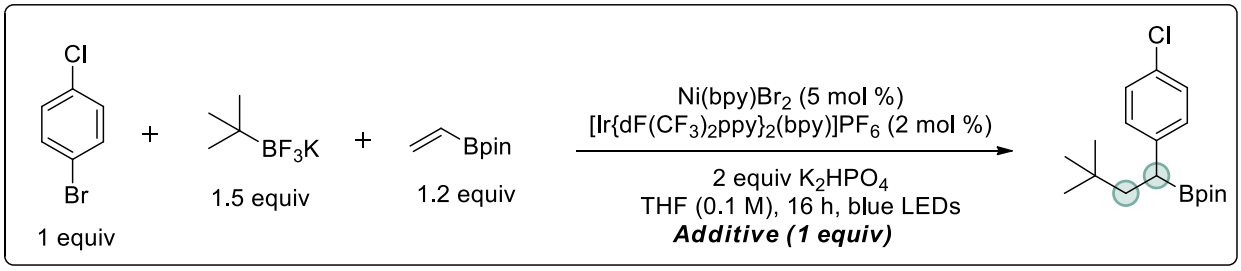
sodium sulfate, filtered and concentrated via rotary evaporation. The crude oil was purified via flash silica column chromatography to yield the desired compound, **68a**, as a clear, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.63 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 8.1 Hz, 1H), 7.19 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.14 (d, *J* = 7.9, 0.9 Hz, 1H), 7.06 (m, 1H), 6.96 (m, 2H), 4.86 - 4.77 (m, 1H), 1.80 (d, *J* = 3.4 Hz, 1H), 1.63 (dd, *J* = 14.6, 8.9 Hz, 1H), 1.48 (dd, *J* = 14.6, 2.4 Hz, 1H), 0.99 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ ppm 159.2, 156.5, 154.5, 135.7, 134.3, 131.2, 125.3, 121.4, 120.1, 117.9, 115.9, 115.4, 103.3, 72.0, 53.4, 31.0, 30.4. **FT-IR** (cm^{-1}, neat, ATR) 3436 (br w) 2952 (m), 2237 (w), 1566 (m), 1243 (vs), 1243 (s), 1109 (m), 871 (m), 678 (m). **HRMS** (EI) calcd for $C_{19}H_{20}ClNO_2$ [M^+]: 329.1183, found: 329.1190.

Limitations of the Method

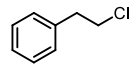
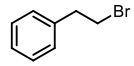
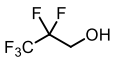
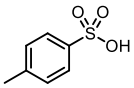
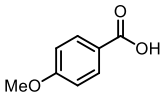
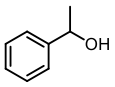
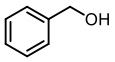
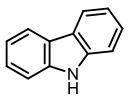
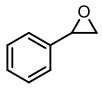
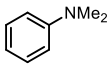
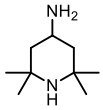
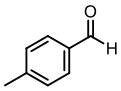
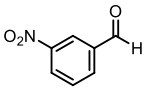
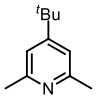
Robustness Screen for Ni/Photoredox Dicarbofunctionalization

Procedure for evaluation of reaction robustness:



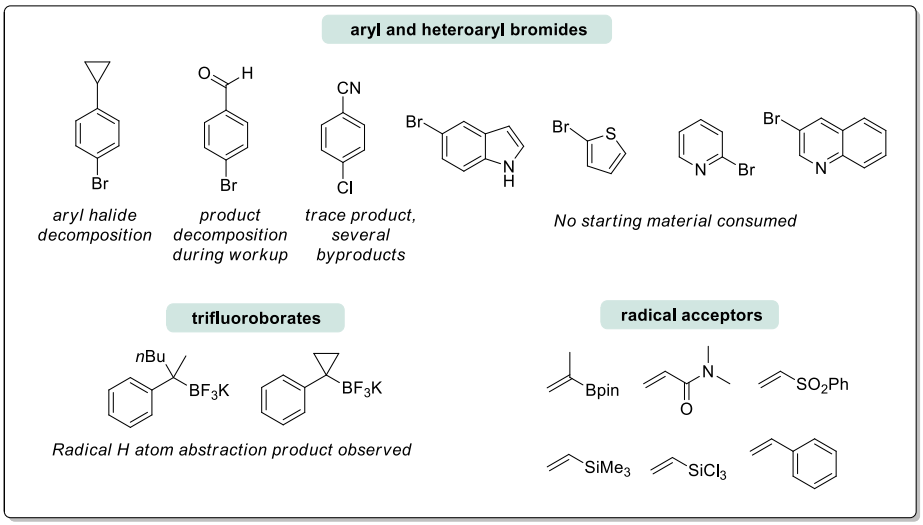
To a 4 mL reaction vial equipped with a stirrer bar was added 1-bromo-4-chlorobenzene (**1**) (19.1 mg, 0.1 mmol, 1 equiv), ^{t}BuBF$_3$K (**2**) (24.6 mg, 0.15 mmol, 1.5 equiv), and [Ir{dF(CF$_3$)$_2$ppy}$_2$(bpy)]PF$_6$ (2.0 mg, 0.002 mmol, 0.02 equiv), anhyd NiBr$_2$(bpy) (0.005 mmol, 0.05 equiv), K$_2$HPO$_4$ (34.8 mg, 0.2 mmol, 2 equiv), and, if solid, the additive of interest (0.1 mmol, 1 equiv). The vial was sealed with a cap containing a TFE-lined silicone septa and was evacuated and purged with argon three times via an inlet needle. The vial was then charged with the vinyl boronate (**3**) (20.6 mg, 0.12 mmol, 1.2 equiv), and, if liquid, the additive of interest (0.1 mmol, 1 equiv) in anhyd degassed THF (1 mL). After this, the cap was sealed with Parafilm®, and the vial was irradiated with blue LEDs for 16 h. The temperature of the reaction was maintained at approximately 27 ºC via a fan. After 16 h, an aliquot of a solution of 4,4′-di-*tert*-butylbiphenyl in MeCN with a known concentration (20 mol % relative to the aryl halide) was added to each vial and thoroughly mixed. A 250 µL aliquot was then removed from each vial, diluted with 500 µL of MeCN, and analyzed by UV/Vis absorption on a UPLC. Response factors for the starting material and product were determined (using NMR and HPLC). This value was used to calculate yield. The remaining additive was determined strictly using HPLC response factors.

Table S8: Ni/Photoredox DCF Robustness Screen Results[a]

Entry		Remaining Additive		Yield of Product		Remaining Aryl Bromide	
1		✓	100%	✓	96%	✓	4%
2		✓	92%	✓	93%	✓	7%
3		○	---[b]	✓	100%	✓	0%
4		✗	20%	✗	45%	✗	55%
5		✓	100%	✗	26%	✗	72%
6		✓	88%	✓	100%	✓	0%
7		✓	90%	✓	100%	✓	0%
8		✗	32%	✗	26%	✗	80%
9		−	60%	✗	0%	✗	98%
10		✓	100%	✗	0%	✓	10%
11		✓	100%	✗	3%	✗	97%
12		✓	100%	✗	0%	✗	83%
13		✓	100%	−	55%	−	45%
14		✓	91%	✓	95%	✓	5%
15		−	91%	✓	88%	✓	11%
16		✗	0%	✓	85%	✓	15%
17		✓	100%	✗	8%	✓	11%
18		○	---[b]	✗	26%	✗	74%
19		✓	81%	−	45%	−	55%
20		✓	100%	✗	2%	✗	91%
21		✓	100%	✗	4%	✗	89%
22		○	---[b]	✗	31%	−	58%
23		✓	100%	−	47%	−	53%
24		○	---[b]	✓	74%	✓	24%
25	NONE	○	---[b]	✓	93%	✓	7%

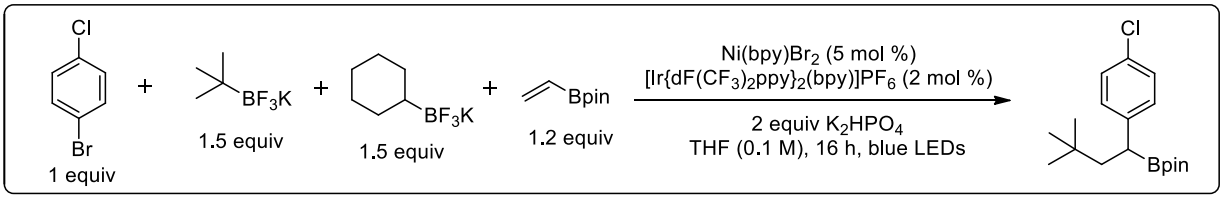
[a] General reaction conditions: 1-bromo-4-chlorobenzene (0.1 mmol, 1 equiv), $^{t}BuBF_3K$ (0.15 mmol, 1.5 equiv), and $[Ir\{dF(CF_3)_2ppy\}_2(bpy)]PF_6$ (0.002 mmol, 0.02 equiv), anhyd $Ni(bpy)Br_2$ (0.005 mmol, 0.05 equiv), K_2HPO_4 (0.2 mmol, 2 equiv), and the additive of interest (0.1 mmol, 1 equiv), VinylBpin (0.12 mmol, 1.2 equiv) THF (0.1 M), 16 h, irradiating with blue LED; Yield determined as described above. [b] Not determined, additive eluted with the solvent front on HPLC or was not UV active.

Failed examples for Ni/Photoredox Dicarbofunctionalization

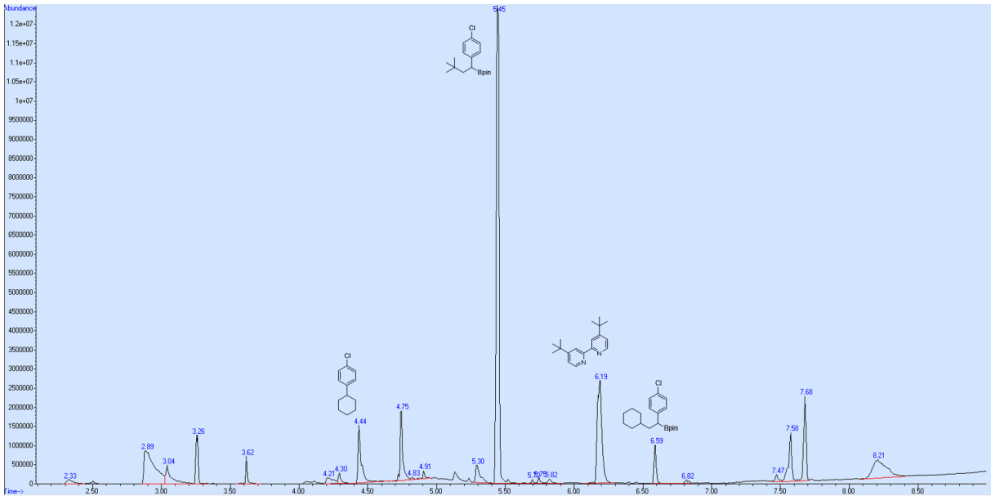


Mechanistic Experiments

Organotrifluoroborate Competition Experiment



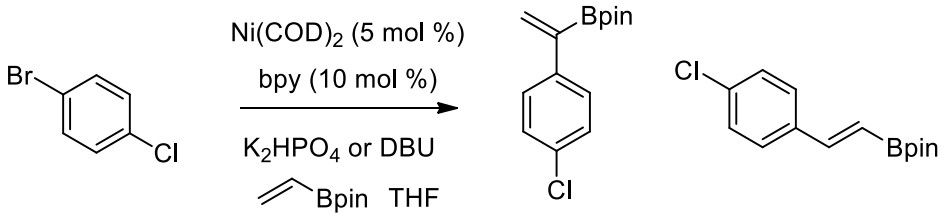
This experiment was carried out following General Procedure B *with the following modification*. Cyclohexyltrifluoroborate was added to the reaction (28.5 mg, 0.15 mmol, 1.5 equiv). The ratio of products was determined without the use of an internal standard.



GC/MS trace of competition experiment with labeled peaks of key products.

Control Reactions for Mechanistic Insight

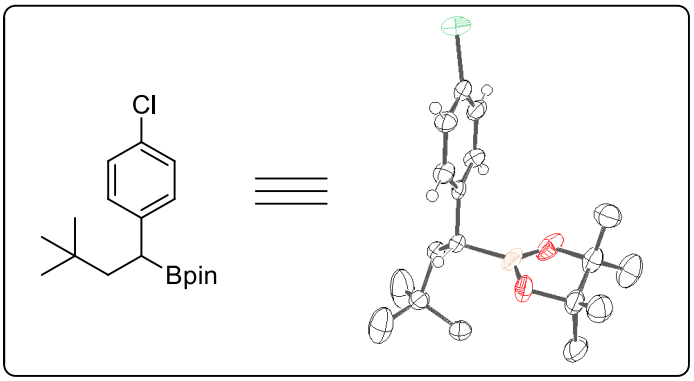
Experiments with a Ni^0 source in the absence of photocatalyst and radical precursor were performed to probe the possibility of Heck or Suzuki-type coupling reactivity. The crude reaction was filtered through a Celite® plug and analyzed by ^1H NMR. Results of this experiment provide further support for our proposed mechanism, as there was no consumption of vinylBpin under conditions similar to those in our original reaction.



neither product observed
no measurable amount of vinylBpin consumption

Crystallographic Data for Relevant Compounds

X-ray Structure Determination of Compound 4



Compound 9241, $C_{18}H_{28}O_2BCl$, crystallizes in the triclinic space group PT with a=9.2264(4)Å, b=9.8051(4)Å, c=12.0617(6)Å, α=112.120(2)°, β=103.086(2)°, γ=101.278(2)°, V=935.71(7)Å^3, Z=2, and d_{calc}=1.145 g/cm$_3$. X-ray intensity data were collected on a Bruker APEXII [1] CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073Å) at a temperature of 173K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. A total of 2724 frames were collected with a crystal to detector distance of 37.5 mm, rotation widths of 0.5° and exposures of 15 seconds:

scan type	2θ	ω	ϕ	χ	Frames
ϕ	-23.00	315.83	12.48	28.88	739
ω	-5.50	321.59	133.99	70.63	69
ϕ	-23.00	334.21	38.95	73.66	739
ϕ	24.50	7.41	12.48	28.88	739
ϕ	-25.50	323.22	190.42	83.36	438

Rotation frames were integrated using SAINT [2], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 22602 reflections were measured over the ranges $3.862 \leq 2\theta \leq 55.014°$, $-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-15 \leq l \leq 15$ yielding 4181 unique reflections (R_{int} = 0.0306). The intensity data were corrected for

Lorentz and polarization effects and for absorption using SADABS [3] (minimum and maximum transmission 0.6228, 0.7456). The structure was solved by direct methods – ShelXS-97 [4]. The CH_2-CH-PhCl substituent is disordered in two different orientations in a ratio of 55:45. Refinement was by full-matrix least squares based on F^2 using SHELXL-2017 [5]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0869P)^2 + 0.6032P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0613 and wR2=0.1682 for 3338 observed reflections for which $F > 4\sigma(F)$ and R1=0.0751 and wR2=0.1802 and GOF =1.030 for all 4181 unique, non-zero reflections and 263 variables. The maximum Δ/σ in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were +0.69 and -0.40 e/Å^3.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2. and 3. Anisotropic thermal parameters are in Table 4. Tables 5. and 6. list bond distances and bond angles. Figures 1. and 2. are ORTEP representations of the molecule with 50% probability thermal ellipsoids displayed.

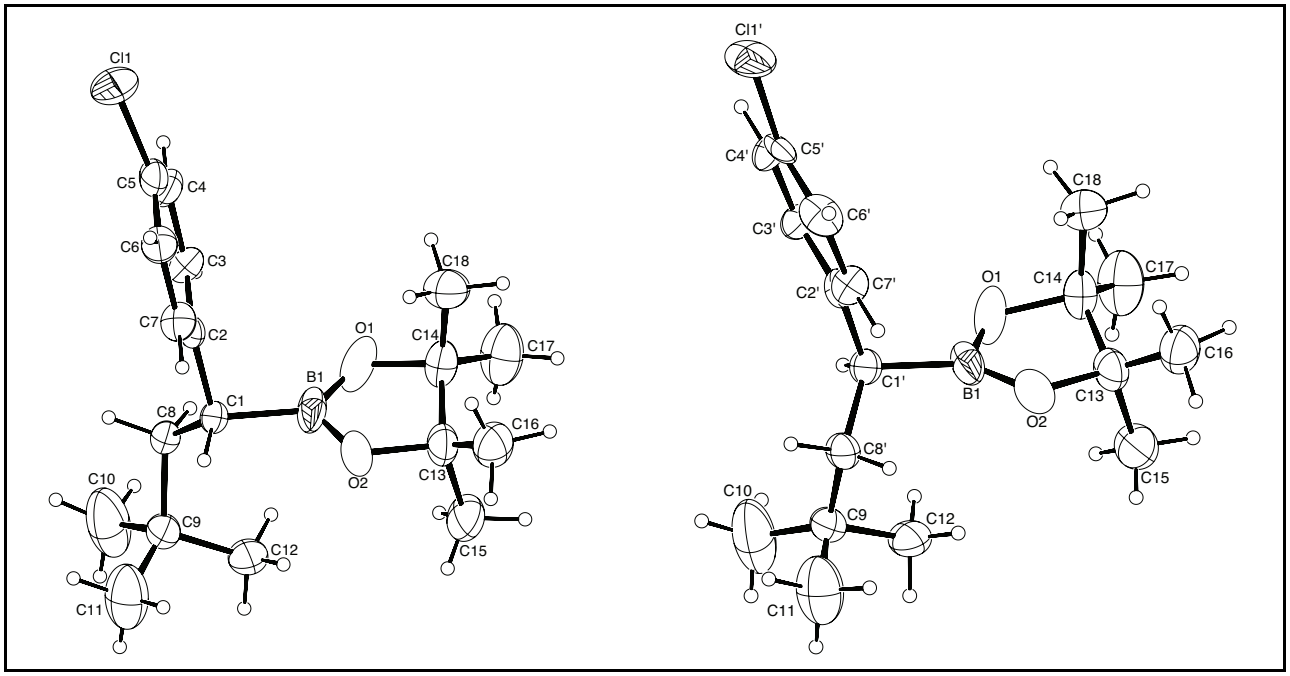


Figure 1. ORTEP drawing of the two disorder models with 50% thermal ellipsoids.

Table 1. Summary of Structure Determination of Compound 4

Empirical formula	$C_{18}H_{28}O_2BCl$
Formula weight	322.66
Temperature/K	173
Crystal system	triclinic
Space group	$P\bar{1}$
a	9.2264(4)Å
b	9.8051(4)Å
c	12.0617(6)Å
α	112.120(2)°
β	103.086(2)°
γ	101.278(2)°
Volume	935.71(7)Å^3
Z	2
d_{calc}	1.145 g/cm^3
μ	0.208 mm^{-1}
F(000)	348.0
Crystal size, mm	0.17 × 0.16 × 0.04
2θ range for data collection	3.862 - 55.014°
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	22602
Independent reflections	4181[R(int) = 0.0306]
Data/restraints/parameters	4181/108/263
Goodness-of-fit on F^2	1.030

Final R indexes [I>=2σ (I)]	R_1 = 0.0613, wR_2 = 0.1682
Final R indexes [all data]	R_1 = 0.0751, wR_2 = 0.1802
Largest diff. peak/hole	0.69/-0.40 eÅ^{-3}

Table 2 . Refined Positional Parameters for Compound 4

Atom	*x*	*y*	*z*	U(eq)
O1	0.79119(18)	0.9307(2)	0.33128(17)	0.0600(5)
O2	0.71082(19)	0.7671(2)	0.12189(19)	0.0563(5)
C1	0.9897(4)	0.7974(4)	0.2176(4)	0.0292(7)
C2	1.0967(7)	0.9542(6)	0.2380(4)	0.0254(11)
C3	1.1666(8)	1.0760(8)	0.3596(4)	0.0319(13)
C4	1.2613(11)	1.2174(8)	0.3777(7)	0.0387(15)
C5	1.2861(13)	1.2370(9)	0.2740(9)	0.041(2)
C6	1.2163(13)	1.1152(10)	0.1524(8)	0.0387(14)
C7	1.1216(10)	0.9738(8)	0.1343(4)	0.0340(11)
Cl1	1.4271(10)	1.4016(9)	0.2938(10)	0.0634(13)
C1'	1.0071(5)	0.8428(5)	0.2925(5)	0.0318(8)
C2'	1.1068(9)	0.9804(7)	0.2849(5)	0.0263(14)
C3'	1.1976(10)	1.1138(9)	0.3957(5)	0.0345(15)
C4'	1.2956(13)	1.2364(9)	0.3892(9)	0.039(2)
C5'	1.3027(16)	1.2256(11)	0.2720(11)	0.0308(17)
C6'	1.2119(15)	1.0922(12)	0.1613(8)	0.0416(19)
C7'	1.1139(11)	0.9696(9)	0.1677(5)	0.0321(16)
Cl1'	1.4132(10)	1.3842(10)	0.2694(12)	0.0627(16)

C8	1.0633(4)	0.7438(4)	0.3151(3)	0.0325(7)
C8'	1.0202(5)	0.6855(5)	0.2088(4)	0.0355(9)
C9	0.9905(2)	0.5664(2)	0.2721(2)	0.0461(5)
C10	1.0982(5)	0.5654(5)	0.3863(3)	0.1075(16)
C11	0.9945(4)	0.4367(5)	0.1561(3)	0.0801(10)
C12	0.8250(3)	0.5380(3)	0.2786(2)	0.0482(5)
C13	0.5719(2)	0.8042(3)	0.1468(2)	0.0442(5)
C14	0.6455(2)	0.9539(3)	0.2724(2)	0.0468(5)
C15	0.4752(3)	0.6702(3)	0.1613(4)	0.0716(9)
C16	0.4786(3)	0.8205(3)	0.0361(2)	0.0554(6)
C17	0.5543(3)	0.9833(4)	0.3620(3)	0.0700(8)
C18	0.6939(3)	1.0981(3)	0.2492(3)	0.0603(7)
B1	0.8288(3)	0.8350(3)	0.2337(4)	0.0557(8)

Table 3 . Positional Parameters for Hydrogens in Compound 4

Atom	*x*	*y*	*z*	U(eq)
H1	0.967821	0.716581	0.129717	0.035
H3	1.149623	1.062598	0.430209	0.038
H4	1.308807	1.300308	0.460528	0.046
H6	1.233199	1.12858	0.081771	0.046
H7	1.074053	0.890856	0.051446	0.041
H1'	1.030414	0.859065	0.382485	0.038
H3'	1.192784	1.121139	0.475489	0.041

H4'	1.357413	1.327282	0.4646	0.046
H6'	1.2167	1.084867	0.081452	0.05
H7'	1.05205	0.878706	0.092322	0.039
H8a	1.049085	0.802795	0.396687	0.039
H8b	1.177214	0.767554	0.329376	0.039
H8a'	1.125611	0.700025	0.200201	0.043
H8b'	0.941861	0.641493	0.123176	0.043
H10a	1.206662	0.595731	0.388054	0.161
H10b	1.070081	0.461088	0.381404	0.161
H10c	1.087674	0.638769	0.463718	0.161
H11a	0.918986	0.428162	0.080263	0.12
H11b	0.967126	0.339044	0.162883	0.12
H11c	1.099843	0.458633	0.149962	0.12
H12a	0.823641	0.621755	0.354759	0.072
H12b	0.791068	0.438868	0.281902	0.072
H12c	0.753916	0.535057	0.203214	0.072
H15a	0.462067	0.571887	0.090439	0.107
H15b	0.372267	0.68217	0.161281	0.107
H15c	0.529435	0.67057	0.241324	0.107
H16a	0.54651	0.893714	0.017973	0.083
H16b	0.392941	0.859039	0.056193	0.083
H16c	0.43521	0.719383	-0.038304	0.083
H17a	0.53561	0.897626	0.385484	0.105
H17b	0.453753	0.991159	0.32089	0.105
H17c	0.613573	1.080307	0.438253	0.105

H18a	0.76453	1.185663	0.328747	0.09
H18b	0.600291	1.12393	0.218088	0.09
H18c	0.747399	1.076229	0.185963	0.09

Table 4 . Refined Thermal Parameters (U's) for Compound 4

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0271(7)	0.0923(14)	0.0692(11)	0.0524(11)	0.0069(7)	0.0127(8)
O2	0.0417(9)	0.0551(10)	0.0920(13)	0.0368(9)	0.0388(9)	0.0283(7)
C1	0.0232(15)	0.0297(18)	0.0357(19)	0.0128(15)	0.0142(15)	0.0085(12)
C2	0.0238(16)	0.0295(19)	0.029(3)	0.013(2)	0.017(3)	0.0118(14)
C3	0.027(3)	0.038(4)	0.026(3)	0.013(2)	0.008(3)	0.003(2)
C4	0.023(4)	0.042(3)	0.043(3)	0.013(2)	0.012(2)	0.0060(19)
C5	0.029(3)	0.039(4)	0.066(4)	0.028(3)	0.026(3)	0.016(3)
C6	0.039(3)	0.039(3)	0.056(3)	0.033(2)	0.023(2)	0.014(2)
C7	0.036(2)	0.043(2)	0.035(3)	0.024(2)	0.019(2)	0.0125(17)
Cl1	0.0530(13)	0.0424(14)	0.094(2)	0.0328(13)	0.0308(11)	0.0004(9)
C1'	0.0253(19)	0.033(2)	0.040(2)	0.016(2)	0.0157(19)	0.0103(16)
C2'	0.022(2)	0.040(4)	0.028(4)	0.020(3)	0.016(3)	0.015(3)
C3'	0.029(4)	0.032(4)	0.038(4)	0.013(3)	0.009(3)	0.005(3)
C4'	0.022(5)	0.037(3)	0.054(3)	0.019(3)	0.014(3)	0.002(2)
C5'	0.028(3)	0.028(3)	0.059(4)	0.029(3)	0.028(3)	0.020(3)
C6'	0.053(4)	0.050(4)	0.045(3)	0.033(3)	0.029(3)	0.025(4)
C7'	0.033(3)	0.039(3)	0.026(3)	0.014(3)	0.016(3)	0.010(2)
Cl1'	0.057(3)	0.043(2)	0.118(5)	0.049(3)	0.054(3)	0.019(2)

C8	0.0251(15)	0.0318(17)	0.0410(19)	0.0164(14)	0.0105(13)	0.0090(12)
C8'	0.030(2)	0.035(2)	0.047(3)	0.0180(19)	0.0191(18)	0.0145(16)
C9	0.0342(10)	0.0346(11)	0.0728(15)	0.0273(10)	0.0160(10)	0.0123(8)
C10	0.083(2)	0.133(4)	0.0635(19)	-0.0003(19)	-0.0058(16)	0.068(2)
C11	0.0671(18)	0.120(3)	0.0595(16)	0.0324(17)	0.0301(14)	0.0461(19)
C12	0.0435(12)	0.0365(11)	0.0699(15)	0.0269(10)	0.0245(11)	0.0095(9)
C13	0.0326(10)	0.0506(12)	0.0611(13)	0.0295(10)	0.0224(9)	0.0191(9)
C14	0.0320(10)	0.0632(14)	0.0462(12)	0.0242(10)	0.0116(9)	0.0182(9)
C15	0.0425(13)	0.0619(17)	0.133(3)	0.0590(18)	0.0405(16)	0.0183(11)
C16	0.0454(13)	0.0596(15)	0.0482(13)	0.0149(11)	0.0077(10)	0.0167(11)
C17	0.0581(16)	0.109(3)	0.0523(14)	0.0350(15)	0.0295(12)	0.0338(16)
C18	0.0568(15)	0.0439(14)	0.0719(17)	0.0244(12)	0.0122(13)	0.0114(11)
B1	0.0276(11)	0.0587(16)	0.115(2)	0.0650(18)	0.0319(14)	0.0193(11)

Table 5 . Bond Distances in Compound 4, Å

O1-C14	1.473(3)	O1-B1	1.366(4)	O2-C13	1.463(2)
O2-B1	1.350(4)	C1-C2	1.553(6)	C1-C8	1.538(5)
C1-B1	1.633(4)	C2-C3	1.3950	C2-C7	1.3950
C3-C4	1.3950	C4-C5	1.3952	C5-C6	1.3949
C5-Cl1	1.761(10)	C6-C7	1.3950	C1'-C2'	1.523(7)
C1'-C8'	1.539(6)	C1'-B1	1.611(5)	C2'-C3'	1.3950
C2'-C7'	1.3951	C3'-C4'	1.3950	C4'-C5'	1.3948
C5'-C6'	1.3950	C5'-Cl1'	1.700(11)	C6'-C7'	1.3951

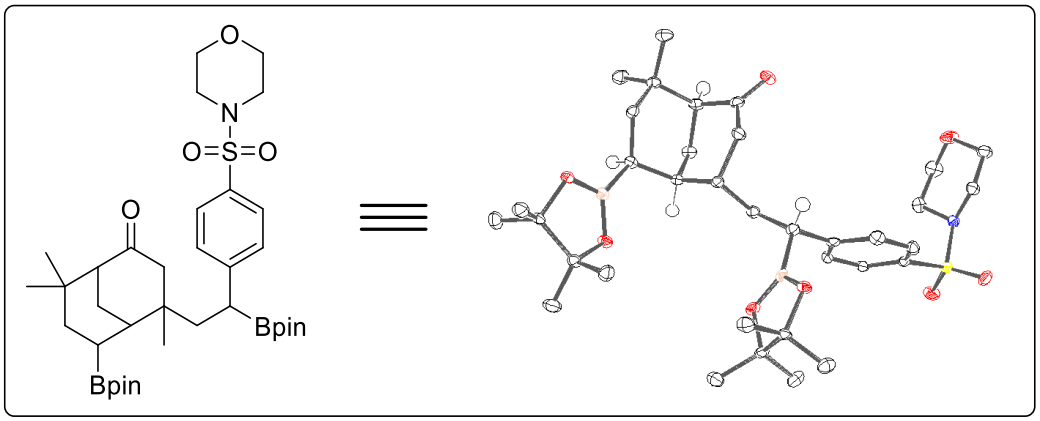
C8-C9	1.566(4)	C8'-C9	1.632(5)	C9-C10	1.510(4)
C9-C11	1.509(4)	C9-C12	1.522(3)	C13-C14	1.543(3)
C13-C15	1.528(3)	C13-C16	1.498(3)	C14-C17	1.493(3)
C14-C18	1.544(4)				

Table 6 . Bond Angles in Compound 4, °

B1-O1-C14	106.11(18)	B1-O2-C13	107.7(2)	C2-C1-B1	103.3(3)
C8-C1-C2	111.7(3)	C8-C1-B1	111.9(3)	C3-C2-C1	120.0(3)
C3-C2-C7	120.0	C7-C2-C1	120.0(3)	C2-C3-C4	120.0
C3-C4-C5	120.0	C4-C5-Cl1	121.6(6)	C6-C5-C4	120.0
C6-C5-Cl1	117.7(6)	C5-C6-C7	120.0	C6-C7-C2	120.0
C2'-C1'-C8'	114.1(4)	C2'-C1'-B1	104.9(4)	C8'-C1'-B1	105.4(4)
C3'-C2'-C1'	120.0(4)	C3'-C2'-C7'	120.0	C7'-C2'-C1'	119.9(4)
C2'-C3'-C4'	120.0	C5'-C4'-C3'	120.0	C4'-C5'-C6'	120.0
C4'-C5'-Cl1'	117.7(7)	C6'-C5'-Cl1'	122.1(7)	C5'-C6'-C7'	120.0
C2'-C7'-C6'	120.0	C1-C8-C9	112.9(3)	C1'-C8'-C9	110.0(3)
C10-C9-C8	94.8(3)	C10-C9-C8'	128.7(3)	C10-C9-C12	109.1(3)
C11-C9-C8	125.9(3)	C11-C9-C8'	90.1(3)	C11-C9-C10	107.2(2)
C11-C9-C12	109.9(2)	C12-C9-C8	108.2(2)	C12-C9-C8'	109.3(2)
O2-C13-C14	101.70(17)	O2-C13-C15	107.94(19)	O2-C13-C16	108.56(19)
C15-C13-C14	112.6(2)	C16-C13-C14	115.6(2)	C16-C13-C15	109.8(2)
O1-C14-C13	101.83(18)	O1-C14-C17	109.14(19)	O1-C14-C18	106.91(19)
C17-C14-C13	117.2(2)	C17-C14-C18	109.5(2)	C18-C14-C13	111.58(19)
O1-B1-C1	134.6(3)	O1-B1-C1'	106.6(3)	O2-B1-O1	113.10(19)
O2-B1-C1	112.0(3)	O2-B1-C1'	140.3(3)		

This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys.

X-ray Structure Determination of Compound 55



Compound **X**, $C_{37}H_{59}B_2Cl_2NO_8S$, crystallizes in the triclinic space group P$\bar{1}$ with a=11.9599(6)Å, b=13.0727(6)Å, c=14.6426(7)Å, α=106.075(2)°, β=108.081(2)°, γ=102.136(2)°, V=1978.23(17)Å^3, Z=2, and d_{calc}=1.293 g/cm$_3$. X-ray intensity data were collected on a [1] CMOS area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073Å) at a temperature of 100K. Preliminary indexing was performed from a series of twenty-four 0.5° rotation frames with exposures of 10 seconds. A total of 2460 frames were collected with a crystal to detector distance of 33.0 mm, rotation widths of 0.5° and exposures of 5 seconds:

scan type	2θ	ω	φ	χ	Frames
ω	3.18	196.87	216.00	54.72	304
ω	-46.78	146.91	259.43	54.72	304
ω	3.18	196.87	288.00	54.72	304
ϕ	3.18	349.56	0.00	54.72	720
ω	3.18	196.87	0.00	54.72	304
ω	3.18	196.87	144.00	54.72	304
ω	3.18	196.87	72.00	54.72	220

Rotation frames were integrated using SAINT, producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 81673 reflections were measured over the ranges $5.798 \leq 2\theta \leq 50.866°$, $-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-17 \leq l \leq 17$ yielding 7288 unique reflections (R_{int} = 0.0625). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS (minimum and maximum transmission 0.7205, 0.7452). The structure was solved by direct methods - ShelXT. Refinement was by

full-matrix least squares based on F^2 using SHELXL-2018. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0294P)^2 + 1.6812P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0374 and wR2=0.0799 for 6117 observed reflections for which $F > 4\sigma(F)$ and R1=0.0489 and wR2=0.0856 and GOF =1.037 for all 7288 unique, non-zero reflections and 471 variables. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.39 and -0.34 e/Å^3.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2. and 3. Anisotropic thermal parameters are in Table 4. Tables 5. and 6. list bond distances and bond angles. Figure 1. is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

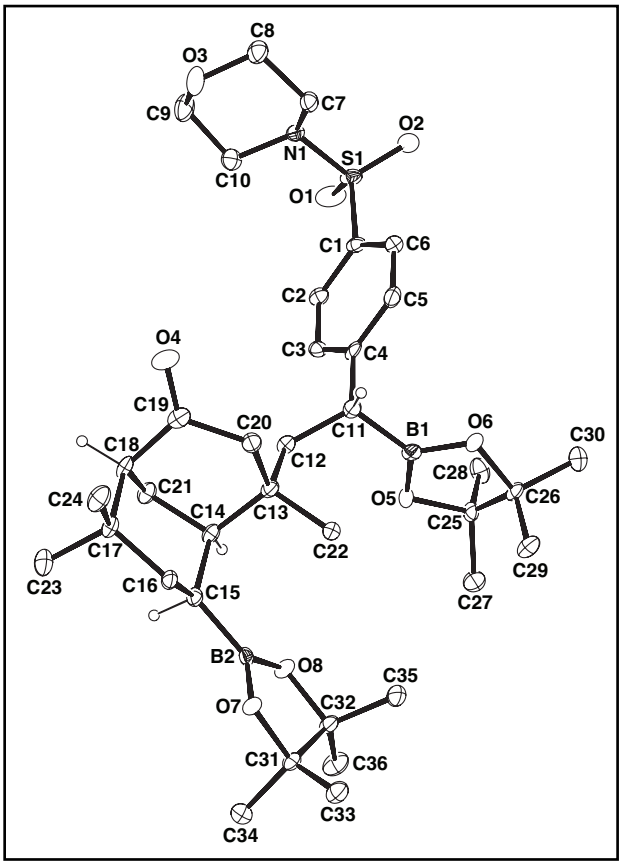


Figure 1. ORTEP drawing of the title compound with 50% thermal ellipsoids.

Table 1. Summary of Structure Determination of Compound 55

Empirical formula	$C_{37}H_{59}B_2Cl_2NO_8S$
Formula weight	770.43
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a	11.9599(6)Å
b	13.0727(6)Å
c	14.6426(7)Å
α	106.075(2)°
β	108.081(2)°
γ	102.136(2)°
Volume	1978.23(17)Å^3
Z	2
d_{calc}	1.293 g/cm^3
μ	0.267 mm^{-1}
F(000)	824.0
Crystal size, mm	0.25 × 0.12 × 0.1
2θ range for data collection	5.798 - 50.866°
Index ranges	$-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-17 \leq l \leq 17$
Reflections collected	81673
Independent reflections	7288[R(int) = 0.0625]
Data/restraints/parameters	7288/0/471
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.0799
Final R indexes [all data]	R_1 = 0.0489, wR_2 = 0.0856
Largest diff. peak/hole	0.39/-0.34 eÅ^{-3}

Table 2 . Refined Positional Parameters for Compound 55

Atom	*x*	*y*	*z*	U(eq)
Cl1	0.94031(5)	0.81099(5)	0.32619(4)	0.03656(14)
Cl2	0.68381(4)	0.66348(4)	0.21230(4)	0.02620(12)
S1	0.41138(4)	0.87086(4)	0.07484(4)	0.01827(11)
O1	0.38549(13)	0.95070(11)	0.14791(12)	0.0278(3)
O2	0.34689(12)	0.84223(12)	-0.03382(11)	0.0258(3)
O3	0.81562(12)	0.94695(12)	0.15394(10)	0.0265(3)
O4	0.80335(12)	0.46697(11)	0.29010(11)	0.0253(3)
O5	0.17240(11)	0.39448(10)	0.19654(9)	0.0160(3)
O6	0.15777(11)	0.30999(10)	0.03214(9)	0.0152(3)
O7	0.43926(10)	0.09969(10)	0.43196(9)	0.0155(3)
O8	0.33107(11)	0.22382(10)	0.42726(9)	0.0162(3)
N1	0.56015(13)	0.91989(12)	0.10064(11)	0.0154(3)
C1	0.38864(15)	0.74484(15)	0.09907(14)	0.0150(4)
C2	0.40063(16)	0.74860(15)	0.19751(14)	0.0157(4)
C3	0.39434(16)	0.65121(15)	0.21907(14)	0.0164(4)
C4	0.37941(15)	0.55034(14)	0.14392(14)	0.0147(4)
C5	0.36460(16)	0.54883(15)	0.04539(14)	0.0182(4)
C6	0.36832(16)	0.64428(15)	0.02211(14)	0.0179(4)
C7	0.60402(16)	0.85434(15)	0.02822(14)	0.0181(4)
C8	0.73515(17)	0.92033(17)	0.05001(15)	0.0222(4)
C9	0.77454(19)	1.01564(17)	0.22136(16)	0.0276(5)
C10	0.64530(17)	0.95443(15)	0.20923(14)	0.0199(4)
C11	0.37627(16)	0.44256(14)	0.16563(14)	0.0153(4)
C12	0.45688(16)	0.46474(14)	0.27807(13)	0.0148(4)
C13	0.49866(15)	0.36513(14)	0.29737(14)	0.0141(4)
C14	0.54755(15)	0.39454(14)	0.41600(13)	0.0135(4)
C15	0.56325(15)	0.29844(14)	0.45573(13)	0.0136(4)
C16	0.66347(15)	0.25329(14)	0.43241(14)	0.0145(4)
C17	0.78885(15)	0.34564(14)	0.46783(14)	0.0149(4)
C18	0.77081(15)	0.44890(14)	0.43874(14)	0.0159(4)
C19	0.73226(16)	0.42661(15)	0.32480(15)	0.0172(4)
C20	0.60074(16)	0.35258(15)	0.25463(14)	0.0170(4)
C21	0.67286(16)	0.49039(14)	0.47152(14)	0.0164(4)
C22	0.38814(16)	0.25571(14)	0.23958(13)	0.0148(4)
C23	0.85718(17)	0.38588(17)	0.58548(15)	0.0231(4)
C24	0.87000(17)	0.29592(16)	0.41816(15)	0.0215(4)
C25	0.03859(15)	0.34959(15)	0.13160(13)	0.0151(4)
C26	0.03326(15)	0.26468(15)	0.03007(14)	0.0150(4)
C27	-0.02948(17)	0.29815(17)	0.18810(15)	0.0225(4)
C28	0.00109(18)	0.45001(16)	0.11746(15)	0.0219(4)
C29	0.01794(17)	0.14607(15)	0.02942(15)	0.0206(4)
C30	-0.06064(17)	0.26030(16)	-0.06956(14)	0.0211(4)

C31	0.32204(15)	0.04560(15)	0.43703(14)	0.0152(4)
C32	0.23873(16)	0.11535(15)	0.40015(14)	0.0160(4)
C33	0.27799(17)	-0.07765(15)	0.36878(15)	0.0194(4)
C34	0.35093(18)	0.05836(17)	0.54898(14)	0.0223(4)
C35	0.16604(17)	0.06829(16)	0.28360(15)	0.0216(4)
C36	0.15272(18)	0.13660(17)	0.45496(16)	0.0245(4)
C37	0.83790(18)	0.68845(18)	0.22022(17)	0.0289(5)
B1	0.23299(18)	0.37867(16)	0.13167(16)	0.0149(4)
B2	0.44155(18)	0.20522(17)	0.43478(15)	0.0137(4)

Table 3 . Positional Parameters for Hydrogens in Compound 55

Atom	*x*	*y*	*z*	U(eq)
H2	0.413016	0.817206	0.249541	0.019
H3	0.400256	0.653026	0.285751	0.02
H5	0.351629	0.480325	-0.007048	0.022
H6	0.357112	0.641432	-0.045789	0.022
H7a	0.549075	0.838966	-0.043746	0.022
H7b	0.601831	0.781417	0.036544	0.022
H8a	0.765857	0.875709	0.002659	0.027
H8b	0.735685	0.990746	0.036918	0.027
H9a	0.774246	1.084902	0.206295	0.033
H9b	0.83313	1.038049	0.293709	0.033
H10a	0.645682	0.887436	0.228228	0.024
H10b	0.617558	1.004565	0.255293	0.024
H11	0.408013	0.396037	0.119457	0.018
H12a	0.409853	0.485714	0.321213	0.018
H12b	0.532107	0.530222	0.301859	0.018
H14	0.486593	0.423641	0.439904	0.016
H15	0.600591	0.337206	0.532593	0.016
H16a	0.632819	0.211887	0.357033	0.017
H16b	0.677309	0.199113	0.466932	0.017
H18	0.851938	0.511551	0.476404	0.019
H20a	0.598707	0.273224	0.236408	0.02
H20b	0.57869	0.3679	0.189902	0.02
H21a	0.698839	0.513207	0.547288	0.02
H21b	0.664624	0.556498	0.452924	0.02
H22a	0.414322	0.19352	0.253569	0.022
H22b	0.358457	0.240036	0.165183	0.022
H22c	0.320969	0.263607	0.26303	0.022
H23a	0.867406	0.321437	0.604932	0.035
H23b	0.808679	0.42113	0.619423	0.035
H23c	0.939093	0.44077	0.6072	0.035

H24a	0.949962	0.354028	0.440685	0.032
H24b	0.827953	0.268624	0.342781	0.032
H24c	0.884131	0.233227	0.439163	0.032
H27a	0.005126	0.241538	0.206386	0.034
H27b	-0.118002	0.262468	0.143341	0.034
H27c	-0.019581	0.357172	0.251121	0.034
H28a	0.019197	0.505739	0.185141	0.033
H28b	-0.088118	0.425168	0.075097	0.033
H28c	0.047989	0.483919	0.08301	0.033
H29a	0.025816	0.099847	-0.032098	0.031
H29b	-0.064257	0.113279	0.028379	0.031
H29c	0.082395	0.148581	0.091545	0.031
H30a	-0.043479	0.33541	-0.073214	0.032
H30b	-0.144661	0.235126	-0.071174	0.032
H30c	-0.054444	0.207523	-0.128623	0.032
H33a	0.27253	-0.084229	0.299093	0.029
H33b	0.195893	-0.114918	0.365497	0.029
H33c	0.337061	-0.113487	0.397599	0.029
H34a	0.415962	0.025452	0.571758	0.033
H34b	0.275688	0.019466	0.555174	0.033
H34c	0.37978	0.138392	0.592229	0.033
H35a	0.131419	0.123883	0.263046	0.032
H35b	0.098277	-0.000863	0.264007	0.032
H35c	0.221649	0.051586	0.248756	0.032
H36a	0.201903	0.177715	0.529069	0.037
H36b	0.095488	0.064549	0.444207	0.037
H36c	0.105066	0.181291	0.427095	0.037
H37A	0.86455	0.623249	0.227099	0.035
H37B	0.841362	0.696306	0.155729	0.035

Table 4 . Refined Thermal Parameters (U's) for Compound 55

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	0.0188(3)	0.0411(3)	0.0360(3)	0.0077(3)	0.0057(2)	-0.0006(2)
Cl2	0.0139(2)	0.0289(3)	0.0354(3)	0.0130(2)	0.0098(2)	0.00451(19)
S1	0.0154(2)	0.0204(2)	0.0276(3)	0.0166(2)	0.0107(2)	0.00872(18)
O1	0.0315(8)	0.0249(7)	0.0468(9)	0.0218(7)	0.0265(7)	0.0193(6)
O2	0.0157(7)	0.0349(8)	0.0309(8)	0.0242(7)	0.0046(6)	0.0066(6)
O3	0.0140(7)	0.0306(8)	0.0241(7)	0.0025(6)	0.0013(6)	0.0055(6)
O4	0.0188(7)	0.0303(8)	0.0355(8)	0.0182(7)	0.0170(6)	0.0074(6)
O5	0.0104(6)	0.0179(6)	0.0151(6)	0.0055(5)	0.0006(5)	0.0026(5)
O6	0.0100(6)	0.0151(6)	0.0182(7)	0.0053(5)	0.0052(5)	0.0014(5)
O7	0.0096(6)	0.0172(6)	0.0209(7)	0.0096(5)	0.0061(5)	0.0027(5)
O8	0.0129(6)	0.0129(6)	0.0222(7)	0.0060(5)	0.0078(5)	0.0023(5)
N1	0.0143(7)	0.0158(8)	0.0171(8)	0.0080(6)	0.0065(6)	0.0040(6)
C1	0.0110(8)	0.0170(9)	0.0220(10)	0.0126(8)	0.0074(7)	0.0058(7)
C2	0.0131(9)	0.0164(9)	0.0201(10)	0.0072(8)	0.0085(8)	0.0058(7)
C3	0.0125(8)	0.0226(10)	0.0171(9)	0.0113(8)	0.0068(7)	0.0051(7)
C4	0.0047(8)	0.0154(9)	0.0221(10)	0.0079(8)	0.0035(7)	0.0012(7)
C5	0.0139(9)	0.0160(9)	0.0177(9)	0.0031(8)	0.0030(8)	0.0003(7)
C6	0.0146(9)	0.0215(10)	0.0161(9)	0.0084(8)	0.0051(8)	0.0022(7)
C7	0.0161(9)	0.0205(9)	0.0144(9)	0.0036(8)	0.0056(8)	0.0039(8)
C8	0.0157(9)	0.0269(10)	0.0225(10)	0.0070(8)	0.0080(8)	0.0061(8)
C9	0.0237(11)	0.0223(10)	0.0223(11)	-0.0018(9)	0.0038(9)	0.0005(8)
C10	0.0241(10)	0.0155(9)	0.0163(9)	0.0025(8)	0.0073(8)	0.0043(8)
C11	0.0136(9)	0.0140(9)	0.0171(9)	0.0057(7)	0.0052(7)	0.0036(7)
C12	0.0127(8)	0.0133(9)	0.0171(9)	0.0050(7)	0.0058(7)	0.0030(7)
C13	0.0102(8)	0.0134(9)	0.0190(9)	0.0078(7)	0.0051(7)	0.0030(7)
C14	0.0102(8)	0.0115(8)	0.0175(9)	0.0029(7)	0.0061(7)	0.0033(7)
C15	0.0122(8)	0.0153(9)	0.0107(8)	0.0027(7)	0.0039(7)	0.0027(7)
C16	0.0104(8)	0.0140(9)	0.0162(9)	0.0066(7)	0.0016(7)	0.0025(7)
C17	0.0091(8)	0.0146(9)	0.0176(9)	0.0040(7)	0.0037(7)	0.0021(7)
C18	0.0086(8)	0.0124(9)	0.0205(10)	0.0021(7)	0.0035(7)	-0.0001(7)
C19	0.0146(9)	0.0144(9)	0.0268(10)	0.0097(8)	0.0100(8)	0.0075(7)
C20	0.0134(9)	0.0226(10)	0.0156(9)	0.0072(8)	0.0068(7)	0.0053(7)
C21	0.0145(9)	0.0117(9)	0.0192(9)	0.0024(7)	0.0056(8)	0.0028(7)
C22	0.0132(9)	0.0151(9)	0.0145(9)	0.0062(7)	0.0040(7)	0.0028(7)
C23	0.0139(9)	0.0268(11)	0.0219(10)	0.0068(8)	0.0018(8)	0.0046(8)
C24	0.0134(9)	0.0194(10)	0.0303(11)	0.0069(8)	0.0084(8)	0.0057(8)
C25	0.0093(8)	0.0176(9)	0.0162(9)	0.0065(7)	0.0019(7)	0.0047(7)
C26	0.0076(8)	0.0156(9)	0.0203(9)	0.0066(7)	0.0051(7)	0.0016(7)
C27	0.0174(10)	0.0276(11)	0.0242(10)	0.0106(9)	0.0105(8)	0.0057(8)
C28	0.0238(10)	0.0225(10)	0.0178(10)	0.0056(8)	0.0039(8)	0.0128(8)
C29	0.0163(9)	0.0145(9)	0.0293(11)	0.0078(8)	0.0087(8)	0.0029(7)
C30	0.0168(9)	0.0233(10)	0.0181(10)	0.0052(8)	0.0027(8)	0.0064(8)

C31	0.0091(8)	0.0188(9)	0.0185(9)	0.0085(8)	0.0063(7)	0.0024(7)
C32	0.0115(8)	0.0145(9)	0.0211(10)	0.0071(8)	0.0064(7)	0.0017(7)
C33	0.0153(9)	0.0180(9)	0.0244(10)	0.0082(8)	0.0077(8)	0.0040(7)
C34	0.0209(10)	0.0261(10)	0.0184(10)	0.0110(8)	0.0060(8)	0.0036(8)
C35	0.0138(9)	0.0231(10)	0.0241(10)	0.0123(8)	0.0019(8)	0.0023(8)
C36	0.0176(10)	0.0255(11)	0.0349(12)	0.0117(9)	0.0151(9)	0.0077(8)
C37	0.0165(10)	0.0339(12)	0.0322(12)	0.0064(10)	0.0124(9)	0.0039(9)
B1	0.0149(10)	0.0118(9)	0.0213(11)	0.0111(8)	0.0056(9)	0.0062(8)
B2	0.0114(9)	0.0184(10)	0.0075(9)	0.0033(8)	0.0021(8)	0.0023(8)

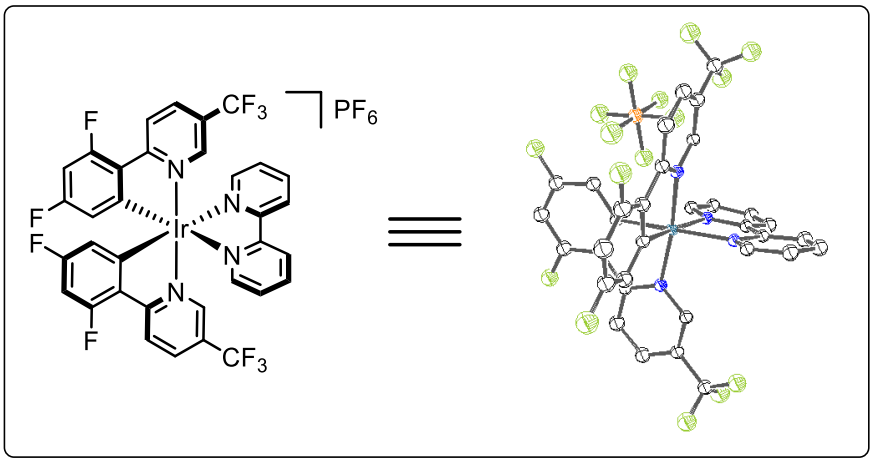
Table 5 . Bond Distances in Compound 55, Å

Cl1-C37	1.759(2)	Cl2-C37	1.7635(19)	S1-O1	1.4328(14)
S1-O2	1.4330(14)	S1-N1	1.6397(15)	S1-C1	1.7632(17)
O3-C8	1.421(2)	O3-C9	1.421(2)	O4-C19	1.220(2)
O5-C25	1.470(2)	O5-B1	1.361(2)	O6-C26	1.470(2)
O6-B1	1.364(2)	O7-C31	1.465(2)	O7-B2	1.363(2)
O8-C32	1.465(2)	O8-B2	1.370(2)	N1-C7	1.472(2)
N1-C10	1.474(2)	C1-C2	1.389(2)	C1-C6	1.390(3)
C2-C3	1.387(2)	C3-C4	1.399(3)	C4-C5	1.392(3)
C4-C11	1.523(2)	C5-C6	1.377(3)	C7-C8	1.508(2)
C9-C10	1.514(3)	C11-C12	1.535(2)	C11-B1	1.588(3)
C12-C13	1.554(2)	C13-C14	1.553(2)	C13-C20	1.553(2)
C13-C22	1.533(2)	C14-C15	1.545(2)	C14-C21	1.539(2)
C15-C16	1.530(2)	C15-B2	1.571(2)	C16-C17	1.544(2)
C17-C18	1.560(2)	C17-C23	1.535(3)	C17-C24	1.528(2)
C18-C19	1.509(3)	C18-C21	1.539(2)	C19-C20	1.508(2)
C25-C26	1.563(2)	C25-C27	1.515(2)	C25-C28	1.519(2)
C26-C29	1.520(2)	C26-C30	1.517(2)	C31-C32	1.561(2)
C31-C33	1.516(2)	C31-C34	1.519(2)	C32-C35	1.523(3)
C32-C36	1.513(2)				

Table 6 . Bond Angles in Compound 55, °

O1-S1-O2	120.28(9)	O1-S1-N1	106.83(8)	O1-S1-C1	108.30(8)
O2-S1-N1	106.79(8)	O2-S1-C1	107.63(8)	N1-S1-C1	106.22(8)
C9-O3-C8	109.07(14)	B1-O5-C25	106.91(13)	B1-O6-C26	107.23(13)
B2-O7-C31	107.57(13)	B2-O8-C32	107.51(13)	C7-N1-S1	115.41(12)
C7-N1-C10	112.18(14)	C10-N1-S1	116.25(12)	C2-C1-S1	119.40(14)
C2-C1-C6	120.58(16)	C6-C1-S1	119.84(13)	C3-C2-C1	119.35(17)
C2-C3-C4	120.87(16)	C3-C4-C11	122.43(16)	C5-C4-C3	118.27(16)
C5-C4-C11	119.29(16)	C6-C5-C4	121.58(17)	C5-C6-C1	119.26(17)
N1-C7-C8	109.10(15)	O3-C8-C7	111.21(15)	O3-C9-C10	111.39(15)
N1-C10-C9	108.45(15)	C4-C11-C12	112.83(14)	C4-C11-B1	104.65(13)
C12-C11-B1	114.08(14)	C11-C12-C13	115.69(14)	C14-C13-C12	106.31(14)
C20-C13-C12	108.75(14)	C20-C13-C14	112.27(14)	C22-C13-C12	109.76(14)
C22-C13-C14	111.33(14)	C22-C13-C20	108.38(14)	C15-C14-C13	117.60(14)
C21-C14-C13	110.85(14)	C21-C14-C15	107.39(14)	C14-C15-B2	117.29(14)
C16-C15-C14	112.05(14)	C16-C15-B2	114.57(14)	C15-C16-C17	113.82(14)
C16-C17-C18	111.83(14)	C23-C17-C16	109.63(14)	C23-C17-C18	108.67(14)
C24-C17-C16	109.07(14)	C24-C17-C18	109.79(14)	C24-C17-C23	107.77(15)
C19-C18-C17	113.82(14)	C19-C18-C21	107.20(14)	C21-C18-C17	111.99(14)
O4-C19-C18	122.00(16)	O4-C19-C20	120.80(17)	C20-C19-C18	117.19(15)
C19-C20-C13	116.80(15)	C14-C21-C18	108.83(14)	O5-C25-C26	102.43(13)
O5-C25-C27	108.64(14)	O5-C25-C28	105.78(14)	C27-C25-C26	115.31(15)
C27-C25-C28	110.45(15)	C28-C25-C26	113.37(14)	O6-C26-C25	102.54(13)
O6-C26-C29	107.25(13)	O6-C26-C30	107.44(14)	C29-C26-C25	113.77(15)
C30-C26-C25	115.53(14)	C30-C26-C29	109.58(15)	O7-C31-C32	102.53(13)
O7-C31-C33	107.42(14)	O7-C31-C34	106.78(14)	C33-C31-C32	115.73(15)
C33-C31-C34	110.36(15)	C34-C31-C32	113.17(15)	O8-C32-C31	102.20(13)
O8-C32-C35	107.69(14)	O8-C32-C36	107.74(14)	C35-C32-C31	113.04(15)
C36-C32-C31	115.46(15)	C36-C32-C35	110.02(15)	Cl1-C37-Cl2	111.41(11)
O5-B1-O6	114.12(16)	O5-B1-C11	123.28(17)	O6-B1-C11	122.39(16)
O7-B2-O8	113.14(15)	O7-B2-C15	122.56(16)	O8-B2-C15	124.04(16)

X-ray Structure Determination of Compound S15



Compound S15, $C_{77}H_{54}F_{32}Ir_2N_8O_3P_2$, crystallizes in the triclinic space group PT with a=11.4834(8)Å, b=13.1501(9)Å, c=14.4544(10)Å, α=72.640(2)°, β=89.929(2)°, γ=77.252(2)°, V=2027.1(2)Å^3, Z=1, and d_{calc}=1.797 g/cm$_3$. X-ray intensity data were collected on a Bruker D8QUEST [1] CMOS area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073Å) at a temperature of 100K. Preliminary indexing was performed from a series of twenty-four 0.5° rotation frames with exposures of 10 seconds. A total of 2448 frames were collected with a crystal to detector distance of 60.0 mm, rotation widths of 0.5° and exposures of 4 seconds:

scan type	2θ	ω	ϕ	χ	Frames
ω	22.35	190.09	255.00	54.72	408
ω	22.35	190.09	0.00	54.72	408
ω	22.35	190.09	153.00	54.72	408
ω	22.35	190.09	51.00	54.72	408
ω	22.35	190.09	306.00	54.72	408
ω	22.35	190.09	204.00	54.72	408

Rotation frames were integrated using SAINT [2], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 51347 reflections were measured over the ranges $5.84 \leq 2\theta \leq 55.174°$, $-14 \leq h \leq 14$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$ yielding 9324 unique reflections ($R_{int} = 0.0356$). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS [3] (minimum and maximum transmission 0.7456, 0.6399). The structure was solved by direct methods - ShelXT [4]. Refinement was by full-matrix least squares based on F^2 using SHELXL-2017 [5]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2) + (0.0001P)^2 + 28.5043P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0478 and wR2=0.1216 for 8590 observed reflections for which $F > 4\sigma(F)$ and R1=0.0532 and wR2=0.1246 and GOF =1.275 for all 9324 unique, non-zero reflections and 565 variables. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +3.98 and -2.21 e/Å^3.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2. and 3. Anisotropic thermal parameters are in Table 4. Tables 5. and 6. list bond distances and bond angles. Figure 1. is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

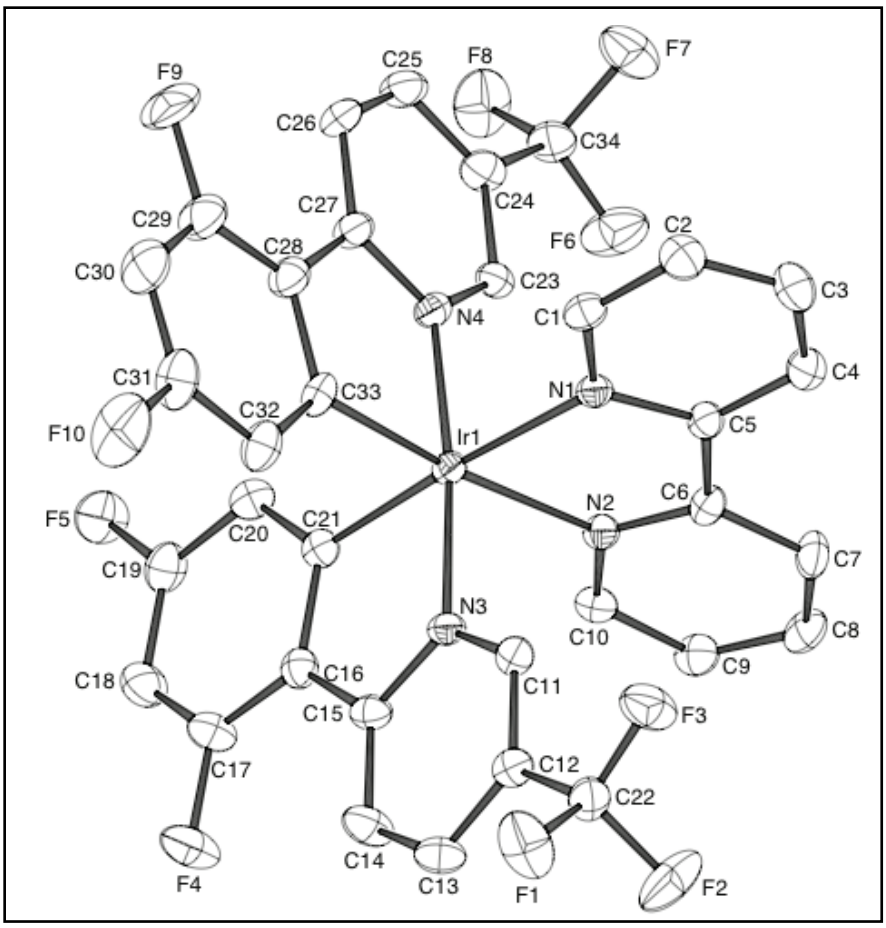


Figure 1. ORTEP drawing of the title compound (**S15**) with 50% thermal ellipsoids.

Table 1. Summary of Structure Determination of Compound S15

Empirical formula	$C_{77}H_{54}F_{32}Ir_2N_8O_3P_2$
Formula weight	2193.62
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a	11.4834(8)Å
b	13.1501(9)Å
c	14.4544(10)Å
α	72.640(2)°
β	89.929(2)°
γ	77.252(2)°
Volume	2027.1(2)$Å^3$
Z	1
d_{calc}	1.797 g/cm^3
μ	3.445 mm^{-1}
F(000)	1068.0
Crystal size, mm	0.3 × 0.25 × 0.2
2θ range for data collection	5.84 - 55.174°
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18
Reflections collected	51347
Independent reflections	9324[R(int) = 0.0356]
Data/restraints/parameters	9324/0/565
Goodness-of-fit on F^2	1.275

Final R indexes [I>=2σ (I)]	R_1 = 0.0478, wR_2 = 0.1216
Final R indexes [all data]	R_1 = 0.0532, wR_2 = 0.1246
Largest diff. peak/hole	3.98/-2.21 eÅ^{-3}

Table 2 . Refined Positional Parameters for Compound S15

Atom	*x*	*y*	*z*	U(eq)
Ir1	0.26250(2)	0.31756(2)	0.29199(2)	0.01566(8)
N1	0.1275(5)	0.4409(4)	0.3219(4)	0.0171(11)
N2	0.3475(5)	0.3593(4)	0.4025(4)	0.0172(11)
N3	0.2339(5)	0.1857(4)	0.4001(4)	0.0174(11)
N4	0.2969(5)	0.4376(5)	0.1760(4)	0.0183(11)
C1	0.0207(6)	0.4856(6)	0.2725(5)	0.0206(13)
C2	-0.0598(7)	0.5714(6)	0.2898(6)	0.0263(15)
C3	-0.0299(7)	0.6121(6)	0.3621(6)	0.0275(15)
C4	0.0793(7)	0.5670(6)	0.4142(5)	0.0261(15)
C5	0.1571(6)	0.4812(5)	0.3936(5)	0.0178(12)
C6	0.2774(6)	0.4297(6)	0.4420(5)	0.0188(13)
C7	0.3174(7)	0.4518(6)	0.5234(5)	0.0247(15)
C8	0.4344(7)	0.4019(6)	0.5617(5)	0.0254(15)
C9	0.5076(6)	0.3331(6)	0.5193(5)	0.0233(14)
C10	0.4611(6)	0.3130(5)	0.4399(5)	0.0199(13)
C11	0.1421(6)	0.1901(6)	0.4582(5)	0.0189(13)
C12	0.1313(6)	0.0996(6)	0.5328(5)	0.0205(13)
C13	0.2147(7)	0.0011(6)	0.5493(5)	0.0267(15)

C14	0.3058(7)	-0.0038(6)	0.4877(6)	0.0280(16)
C15	0.3161(6)	0.0888(5)	0.4126(5)	0.0197(13)
C16	0.4063(6)	0.0956(6)	0.3416(5)	0.0198(13)
C17	0.4972(7)	0.0088(6)	0.3344(6)	0.0262(15)
C18	0.5776(7)	0.0189(6)	0.2636(6)	0.0296(16)
C19	0.5643(7)	0.1217(6)	0.1971(5)	0.0269(15)
C20	0.4772(6)	0.2117(6)	0.2005(5)	0.0229(14)
C21	0.3961(6)	0.2003(5)	0.2728(5)	0.0179(13)
C22	0.0304(7)	0.1043(6)	0.5984(5)	0.0247(15)
C23	0.3708(6)	0.5035(5)	0.1808(5)	0.0185(13)
C24	0.3892(6)	0.5856(6)	0.1008(5)	0.0240(14)
C25	0.3301(7)	0.6002(6)	0.0119(5)	0.0276(16)
C26	0.2560(7)	0.5347(6)	0.0060(5)	0.0281(16)
C27	0.2395(6)	0.4507(6)	0.0884(5)	0.0218(14)
C28	0.1688(6)	0.3705(6)	0.0935(5)	0.0236(14)
C29	0.1037(7)	0.3632(7)	0.0160(6)	0.0317(17)
C30	0.0374(8)	0.2854(7)	0.0262(6)	0.0363(19)
C31	0.0379(7)	0.2135(7)	0.1169(6)	0.0321(17)
C32	0.1024(6)	0.2142(7)	0.1975(5)	0.0259(15)
C33	0.1675(6)	0.2936(6)	0.1866(5)	0.0198(13)
C34	0.4720(7)	0.6556(6)	0.1088(5)	0.0283(16)
F1	-0.0292(5)	0.0269(4)	0.6026(4)	0.0431(13)
F2	0.0701(5)	0.0883(5)	0.6898(3)	0.0496(14)
F3	-0.0489(4)	0.1993(4)	0.5720(4)	0.0368(11)
F4	0.5108(4)	-0.0922(4)	0.3994(4)	0.0371(11)

F5	0.6415(4)	0.1359(4)	0.1265(3)	0.0364(11)
F6	0.5293(5)	0.6254(4)	0.1952(4)	0.0460(14)
F7	0.4118(5)	0.7609(4)	0.0914(4)	0.0426(12)
F8	0.5538(5)	0.6580(5)	0.0429(4)	0.0461(13)
F9	0.1034(5)	0.4333(4)	-0.0737(3)	0.0469(14)
F10	-0.0253(5)	0.1358(5)	0.1278(4)	0.0518(15)
P1	0.77550(19)	0.31570(17)	0.32440(16)	0.0305(4)
F11	0.8192(5)	0.3849(5)	0.2261(3)	0.0437(13)
F12	0.7328(5)	0.2459(4)	0.4247(4)	0.0456(14)
F13	0.6987(6)	0.2663(6)	0.2669(5)	0.069(2)
F14	0.6653(5)	0.4150(4)	0.3203(4)	0.0479(13)
F15	0.8536(5)	0.3643(4)	0.3859(3)	0.0381(11)
F16	0.8895(5)	0.2168(4)	0.3348(5)	0.0487(14)
O1	0.7801(13)	0.8238(9)	0.1611(8)	0.069(5)
C35	0.7656(8)	0.8889(7)	0.0805(8)	0.033(4)
C36	0.6670(15)	0.8953(16)	0.0086(12)	0.071(7)
C37	0.8450(13)	0.9682(11)	0.0463(10)	0.039(4)
O2	0.2962(6)	0.6794(5)	0.3083(4)	0.0505(17)
C38	0.2373(4)	0.7644(4)	0.2545(3)	0.043(2)
C39	0.2561(9)	0.8740(5)	0.2555(7)	0.056(3)
C40	0.1410(7)	0.7666(7)	0.1826(6)	0.055(3)

Table 3 . Positional Parameters for Hydrogens in Compound S15

Atom	*x*	*y*	*z*	U(eq)
H1	-0.00046	0.456881	0.223479	0.027
H2	-0.134372	0.602102	0.252718	0.035
H3	-0.084309	0.670751	0.375803	0.037
H4	0.100973	0.594508	0.463765	0.035
H7	0.266238	0.499603	0.55189	0.033
H8	0.463816	0.415333	0.617337	0.034
H9	0.58824	0.300296	0.543839	0.031
H10	0.510828	0.264816	0.410873	0.026
H11	0.083844	0.256949	0.447473	0.025
H13	0.209031	-0.061318	0.601553	0.036
H14	0.362533	-0.071133	0.496444	0.037
H18	0.638926	-0.041478	0.260573	0.039
H20	0.472641	0.281081	0.153687	0.03
H23	0.41132	0.492819	0.241415	0.025
H25	0.341628	0.65592	-0.044317	0.037
H26	0.214822	0.545663	-0.054348	0.037
H30	-0.007001	0.28184	-0.027782	0.048
H32	0.102	0.161544	0.258954	0.034
H36a	0.670089	0.952804	-0.052137	0.106
H36b	0.6776	0.824803	-0.004163	0.106
H36c	0.589307	0.912393	0.035518	0.106
H37a	0.818984	1.013759	-0.020671	0.058

H37b	0.839731	1.014914	0.088438	0.058
H37c	0.928017	0.927322	0.048756	0.058
H39a	0.200064	0.932546	0.206857	0.084
H39b	0.242181	0.882361	0.32	0.084
H39c	0.338412	0.878434	0.240213	0.084
H40a	0.103733	0.842706	0.145891	0.083
H40b	0.176385	0.727324	0.137668	0.083
H40c	0.080158	0.731254	0.217457	0.083

Table 4 . Refined Thermal Parameters (U's) for Compound S15

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir1	0.01686(12)	0.01657(12)	0.01365(12)	-0.00384(9)	0.00014(8)	-0.00511(9)
N1	0.020(3)	0.016(3)	0.015(3)	-0.003(2)	0.000(2)	-0.005(2)
N2	0.019(3)	0.017(3)	0.017(3)	-0.005(2)	-0.002(2)	-0.007(2)
N3	0.021(3)	0.016(3)	0.015(3)	-0.002(2)	-0.001(2)	-0.006(2)
N4	0.018(3)	0.020(3)	0.015(3)	-0.004(2)	0.001(2)	-0.002(2)
C1	0.019(3)	0.024(3)	0.018(3)	-0.003(3)	0.001(2)	-0.007(3)
C2	0.021(3)	0.027(4)	0.030(4)	-0.009(3)	-0.002(3)	-0.004(3)
C3	0.024(4)	0.024(4)	0.035(4)	-0.013(3)	0.003(3)	-0.002(3)
C4	0.031(4)	0.023(3)	0.024(4)	-0.009(3)	-0.005(3)	-0.004(3)
C5	0.019(3)	0.018(3)	0.018(3)	-0.006(2)	0.001(2)	-0.006(2)
C6	0.020(3)	0.023(3)	0.016(3)	-0.007(3)	0.003(2)	-0.009(3)
C7	0.027(4)	0.028(4)	0.024(3)	-0.016(3)	-0.001(3)	-0.006(3)
C8	0.026(4)	0.033(4)	0.019(3)	-0.009(3)	-0.005(3)	-0.010(3)

C9	0.022(3)	0.025(3)	0.024(3)	-0.006(3)	-0.004(3)	-0.009(3)
C10	0.018(3)	0.018(3)	0.022(3)	-0.003(3)	-0.001(3)	-0.004(2)
C11	0.019(3)	0.020(3)	0.019(3)	-0.006(3)	0.003(2)	-0.008(3)
C12	0.021(3)	0.022(3)	0.019(3)	-0.005(3)	0.000(3)	-0.008(3)
C13	0.030(4)	0.021(3)	0.025(4)	0.002(3)	0.003(3)	-0.009(3)
C14	0.027(4)	0.018(3)	0.034(4)	-0.001(3)	0.006(3)	-0.005(3)
C15	0.019(3)	0.019(3)	0.019(3)	-0.002(3)	-0.002(3)	-0.005(3)
C16	0.018(3)	0.022(3)	0.020(3)	-0.008(3)	0.000(3)	-0.004(3)
C17	0.026(4)	0.019(3)	0.030(4)	-0.002(3)	0.002(3)	-0.006(3)
C18	0.028(4)	0.024(4)	0.032(4)	-0.008(3)	0.003(3)	0.002(3)
C19	0.025(4)	0.034(4)	0.025(4)	-0.013(3)	0.009(3)	-0.009(3)
C20	0.021(3)	0.026(4)	0.021(3)	-0.005(3)	0.001(3)	-0.007(3)
C21	0.017(3)	0.020(3)	0.020(3)	-0.007(3)	0.000(2)	-0.008(2)
C22	0.030(4)	0.024(3)	0.022(3)	-0.007(3)	0.009(3)	-0.012(3)
C23	0.019(3)	0.016(3)	0.020(3)	-0.004(2)	0.004(2)	-0.003(2)
C24	0.023(3)	0.023(3)	0.024(3)	-0.004(3)	0.009(3)	-0.007(3)
C25	0.033(4)	0.025(4)	0.019(3)	0.000(3)	0.005(3)	-0.005(3)
C26	0.040(4)	0.028(4)	0.013(3)	-0.004(3)	0.000(3)	-0.003(3)
C27	0.025(3)	0.023(3)	0.015(3)	-0.004(3)	0.001(3)	-0.004(3)
C28	0.022(3)	0.027(4)	0.019(3)	-0.007(3)	-0.002(3)	-0.002(3)
C29	0.032(4)	0.037(4)	0.023(4)	-0.008(3)	-0.007(3)	-0.005(3)
C30	0.036(4)	0.044(5)	0.033(4)	-0.017(4)	-0.011(3)	-0.009(4)
C31	0.027(4)	0.045(5)	0.036(4)	-0.023(4)	0.002(3)	-0.018(3)
C32	0.021(3)	0.036(4)	0.024(4)	-0.015(3)	0.002(3)	-0.009(3)
C33	0.016(3)	0.030(4)	0.016(3)	-0.011(3)	0.002(2)	-0.005(3)

C34	0.037(4)	0.023(4)	0.024(4)	-0.001(3)	0.010(3)	-0.013(3)
F1	0.041(3)	0.038(3)	0.063(3)	-0.022(3)	0.027(3)	-0.025(2)
F2	0.042(3)	0.083(4)	0.020(2)	-0.013(3)	0.007(2)	-0.009(3)
F3	0.038(3)	0.026(2)	0.040(3)	-0.002(2)	0.014(2)	-0.003(2)
F4	0.036(3)	0.021(2)	0.044(3)	0.001(2)	0.010(2)	-0.0005(19)
F5	0.032(2)	0.039(3)	0.034(3)	-0.009(2)	0.017(2)	-0.003(2)
F6	0.059(3)	0.046(3)	0.033(3)	0.003(2)	-0.007(2)	-0.033(3)
F7	0.048(3)	0.024(2)	0.054(3)	-0.007(2)	0.008(3)	-0.012(2)
F8	0.044(3)	0.056(3)	0.049(3)	-0.022(3)	0.025(3)	-0.026(3)
F9	0.068(4)	0.049(3)	0.020(2)	-0.002(2)	-0.017(2)	-0.018(3)
F10	0.054(3)	0.073(4)	0.049(3)	-0.029(3)	0.000(3)	-0.044(3)
P1	0.0302(10)	0.030(1)	0.0373(11)	-0.0130(9)	0.0097(9)	-0.0157(8)
F11	0.047(3)	0.067(4)	0.024(2)	-0.010(2)	0.001(2)	-0.033(3)
F12	0.042(3)	0.029(3)	0.059(3)	-0.003(2)	0.028(3)	-0.008(2)
F13	0.058(4)	0.096(5)	0.089(5)	-0.059(4)	0.012(4)	-0.049(4)
F14	0.046(3)	0.037(3)	0.049(3)	-0.003(2)	0.001(3)	0.000(2)
F15	0.052(3)	0.040(3)	0.025(2)	-0.008(2)	0.000(2)	-0.020(2)
F16	0.039(3)	0.043(3)	0.070(4)	-0.024(3)	0.023(3)	-0.014(2)
O1	0.097(13)	0.028(7)	0.072(11)	-0.007(7)	0.034(10)	-0.005(8)
C35	0.027(8)	0.025(8)	0.047(10)	-0.022(7)	0.010(7)	0.008(6)
C36	0.048(13)	0.055(14)	0.12(2)	-0.027(14)	0.011(14)	-0.029(11)
C37	0.043(10)	0.036(9)	0.043(10)	-0.018(8)	0.017(8)	-0.014(8)
O2	0.054(4)	0.058(4)	0.041(4)	-0.010(3)	-0.002(3)	-0.020(4)
C38	0.035(5)	0.057(6)	0.040(5)	-0.018(5)	0.002(4)	-0.010(4)
C39	0.064(7)	0.055(6)	0.058(7)	-0.028(5)	0.005(5)	-0.018(5)

C40	0.043(6)	0.072(8)	0.050(6)	-0.020(5)	-0.002(5)	-0.010(5)

Table 5 . Bond Distances in Compound S15, Å

Ir1-N1	2.127(6)	Ir1-N2	2.138(5)	Ir1-N3	2.047(5)
Ir1-N4	2.038(6)	Ir1-C21	2.005(7)	Ir1-C33	2.013(7)
N1-C1	1.339(8)	N1-C5	1.371(8)	N2-C6	1.347(9)
N2-C10	1.349(8)	N3-C11	1.349(9)	N3-C15	1.371(9)
N4-C23	1.356(9)	N4-C27	1.374(8)	C1-C2	1.378(10)
C2-C3	1.383(10)	C3-C4	1.378(10)	C4-C5	1.383(10)
C5-C6	1.471(9)	C6-C7	1.394(9)	C7-C8	1.392(10)
C8-C9	1.377(11)	C9-C10	1.384(9)	C11-C12	1.376(9)
C12-C13	1.386(10)	C12-C22	1.499(10)	C13-C14	1.376(10)
C14-C15	1.396(9)	C15-C16	1.456(9)	C16-C17	1.395(10)
C16-C21	1.418(9)	C17-C18	1.374(11)	C17-F4	1.355(8)
C18-C19	1.381(11)	C19-C20	1.384(10)	C19-F5	1.349(8)
C20-C21	1.396(9)	C22-F1	1.333(8)	C22-F2	1.338(9)
C22-F3	1.323(9)	C23-C24	1.379(9)	C24-C25	1.394(10)
C24-C34	1.489(10)	C25-C26	1.356(11)	C26-C27	1.407(10)
C27-C28	1.451(10)	C28-C29	1.386(10)	C28-C33	1.424(10)
C29-C30	1.380(12)	C29-F9	1.348(9)	C30-C31	1.367(12)
C31-C32	1.386(10)	C31-F10	1.352(9)	C32-C33	1.385(10)
C34-F6	1.319(9)	C34-F7	1.353(9)	C34-F8	1.335(9)
P1-F11	1.589(5)	P1-F12	1.609(5)	P1-F13	1.571(6)

P1-F14	1.592(6)	P1-F15	1.612(5)	P1-F16	1.600(6)
O1-C35	1.2079	C35-C36	1.5088	C35-C37	1.5087
O2-C38	1.2078	C38-C39	1.5088	C38-C40	1.5088

Table 6 . Bond Angles in Compound S15, °

N1-Ir1-N2	76.4(2)	N3-Ir1-N1	98.2(2)	N3-Ir1-N2	86.8(2)
N4-Ir1-N1	87.1(2)	N4-Ir1-N2	97.4(2)	N4-Ir1-N3	173.9(2)
C21-Ir1-N1	175.9(2)	C21-Ir1-N2	99.6(2)	C21-Ir1-N3	80.4(2)
C21-Ir1-N4	94.6(2)	C21-Ir1-C33	86.8(3)	C33-Ir1-N1	97.2(2)
C33-Ir1-N2	173.4(3)	C33-Ir1-N3	95.5(3)	C33-Ir1-N4	80.7(3)
C1-N1-Ir1	125.1(5)	C1-N1-C5	118.5(6)	C5-N1-Ir1	116.3(4)
C6-N2-Ir1	116.1(4)	C6-N2-C10	119.2(6)	C10-N2-Ir1	124.4(5)
C11-N3-Ir1	124.1(5)	C11-N3-C15	120.0(6)	C15-N3-Ir1	115.9(4)
C23-N4-Ir1	124.2(4)	C23-N4-C27	119.5(6)	C27-N4-Ir1	116.3(5)
N1-C1-C2	122.7(7)	C1-C2-C3	118.7(7)	C4-C3-C2	119.5(7)
C3-C4-C5	119.4(7)	N1-C5-C4	121.1(6)	N1-C5-C6	114.9(6)
C4-C5-C6	124.0(6)	N2-C6-C5	115.7(6)	N2-C6-C7	121.6(6)
C7-C6-C5	122.7(6)	C8-C7-C6	118.3(7)	C9-C8-C7	120.1(6)
C8-C9-C10	118.5(7)	N2-C10-C9	122.2(7)	N3-C11-C12	121.2(6)
C11-C12-C13	120.3(7)	C11-C12-C22	121.5(6)	C13-C12-C22	118.2(6)
C14-C13-C12	118.2(7)	C13-C14-C15	120.9(7)	N3-C15-C14	119.4(6)
N3-C15-C16	113.6(6)	C14-C15-C16	127.0(6)	C17-C16-C15	125.9(6)
C17-C16-C21	118.7(6)	C21-C16-C15	115.5(6)	C18-C17-C16	123.5(7)

F4-C17-C16	120.5(7)	F4-C17-C18	115.9(7)	C17-C18-C19	116.3(7)
C18-C19-C20	123.3(7)	F5-C19-C18	118.5(7)	F5-C19-C20	118.2(7)
C19-C20-C21	119.8(7)	C16-C21-Ir1	114.5(5)	C20-C21-Ir1	127.1(5)
C20-C21-C16	118.4(6)	F1-C22-C12	112.1(6)	F1-C22-F2	106.1(6)
F2-C22-C12	111.4(6)	F3-C22-C12	113.3(6)	F3-C22-F1	107.1(6)
F3-C22-F2	106.4(6)	N4-C23-C24	122.3(6)	C23-C24-C25	118.5(7)
C23-C24-C34	120.7(7)	C25-C24-C34	120.8(6)	C26-C25-C24	119.8(7)
C25-C26-C27	120.7(7)	N4-C27-C26	119.1(7)	N4-C27-C28	113.2(6)
C26-C27-C28	127.7(7)	C29-C28-C27	125.5(7)	C29-C28-C33	118.2(7)
C33-C28-C27	116.3(6)	C30-C29-C28	122.5(8)	F9-C29-C28	120.4(7)
F9-C29-C30	117.1(7)	C31-C30-C29	117.4(7)	C30-C31-C32	123.5(7)
F10-C31-C30	118.2(7)	F10-C31-C32	118.3(8)	C33-C32-C31	118.5(7)
C28-C33-Ir1	113.4(5)	C32-C33-Ir1	126.7(5)	C32-C33-C28	119.9(6)
F6-C34-C24	113.6(6)	F6-C34-F7	106.7(7)	F6-C34-F8	107.8(7)
F7-C34-C24	110.9(7)	F8-C34-C24	112.0(6)	F8-C34-F7	105.4(6)
F11-P1-F12	179.2(3)	F11-P1-F14	90.9(3)	F11-P1-F15	90.2(3)
F11-P1-F16	90.7(3)	F12-P1-F15	89.0(3)	F13-P1-F11	91.2(3)
F13-P1-F12	89.6(4)	F13-P1-F14	91.5(4)	F13-P1-F15	178.5(4)
F13-P1-F16	91.7(4)	F14-P1-F12	89.3(3)	F14-P1-F15	88.7(3)
F14-P1-F16	176.3(3)	F16-P1-F12	89.0(3)	F16-P1-F15	88.0(3)
O1-C35-C36	121.8	O1-C35-C37	121.8	C37-C35-C36	116.3
O2-C38-C39	121.8	O2-C38-C40	121.8	C40-C38-C39	116.3

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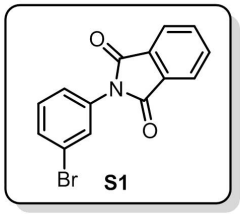
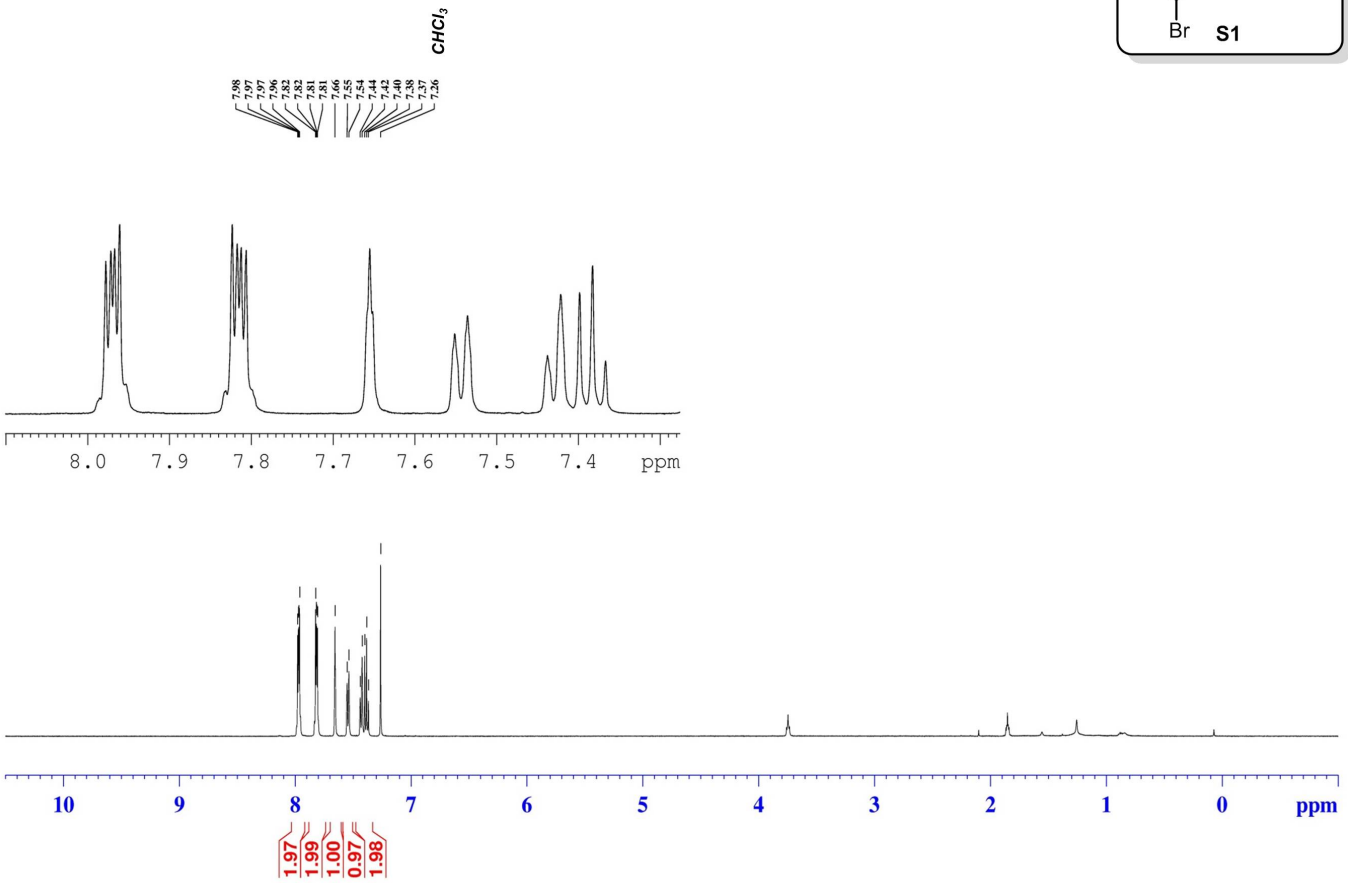
Spectra of Synthesized Compounds

***N*-(3-bromophenyl)phthalimide)**
500 MHz, $CDCl_3$

^{1}H NMR

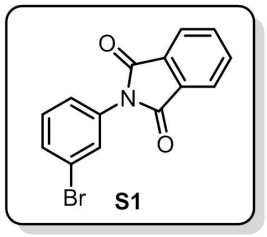


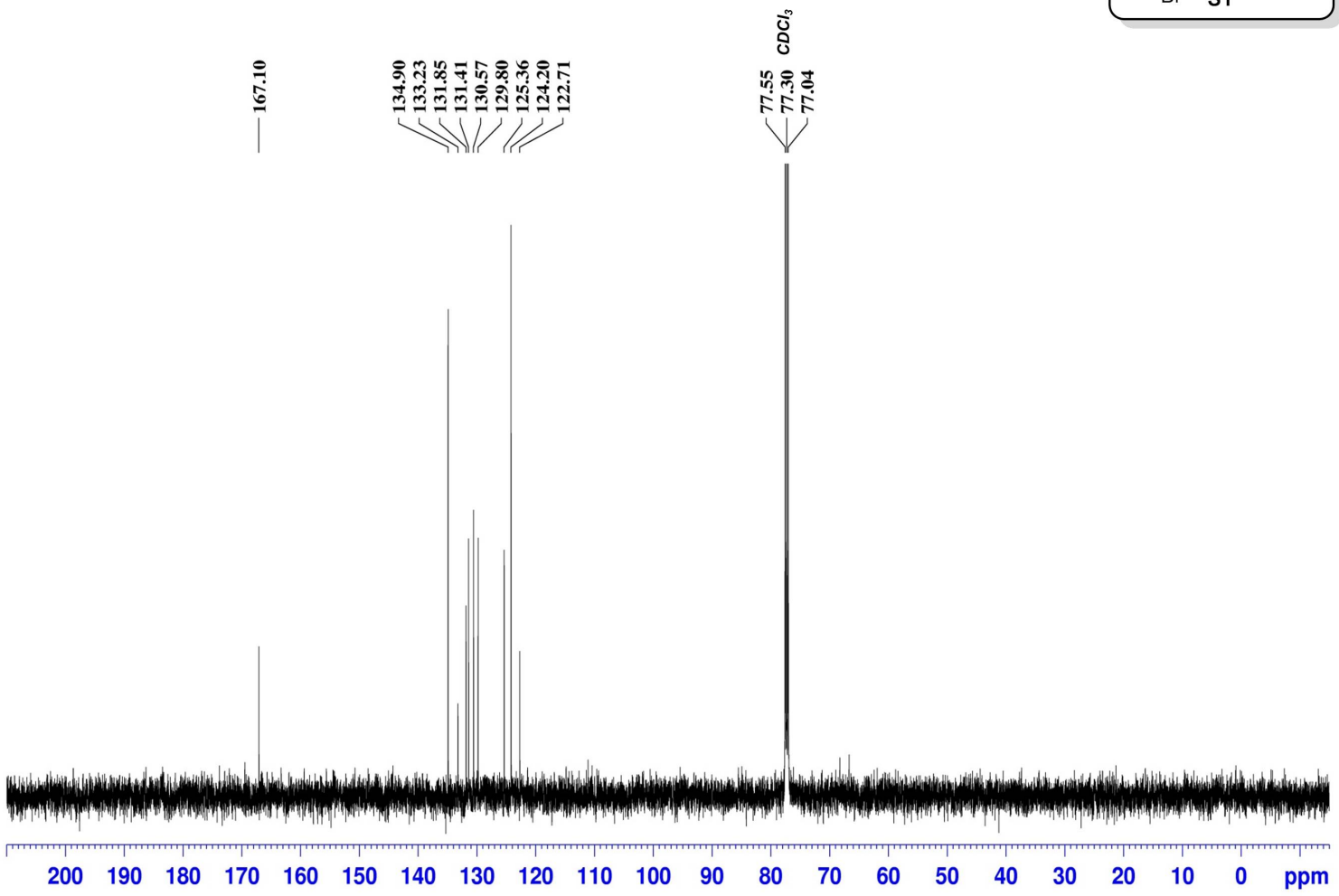
S1



N-(3-Bromophenyl)phthalimide)
125 MHz, $CDCl_3$

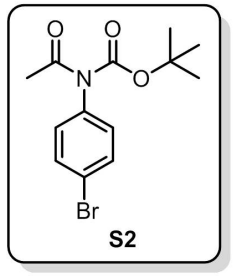
^{13}C NMR

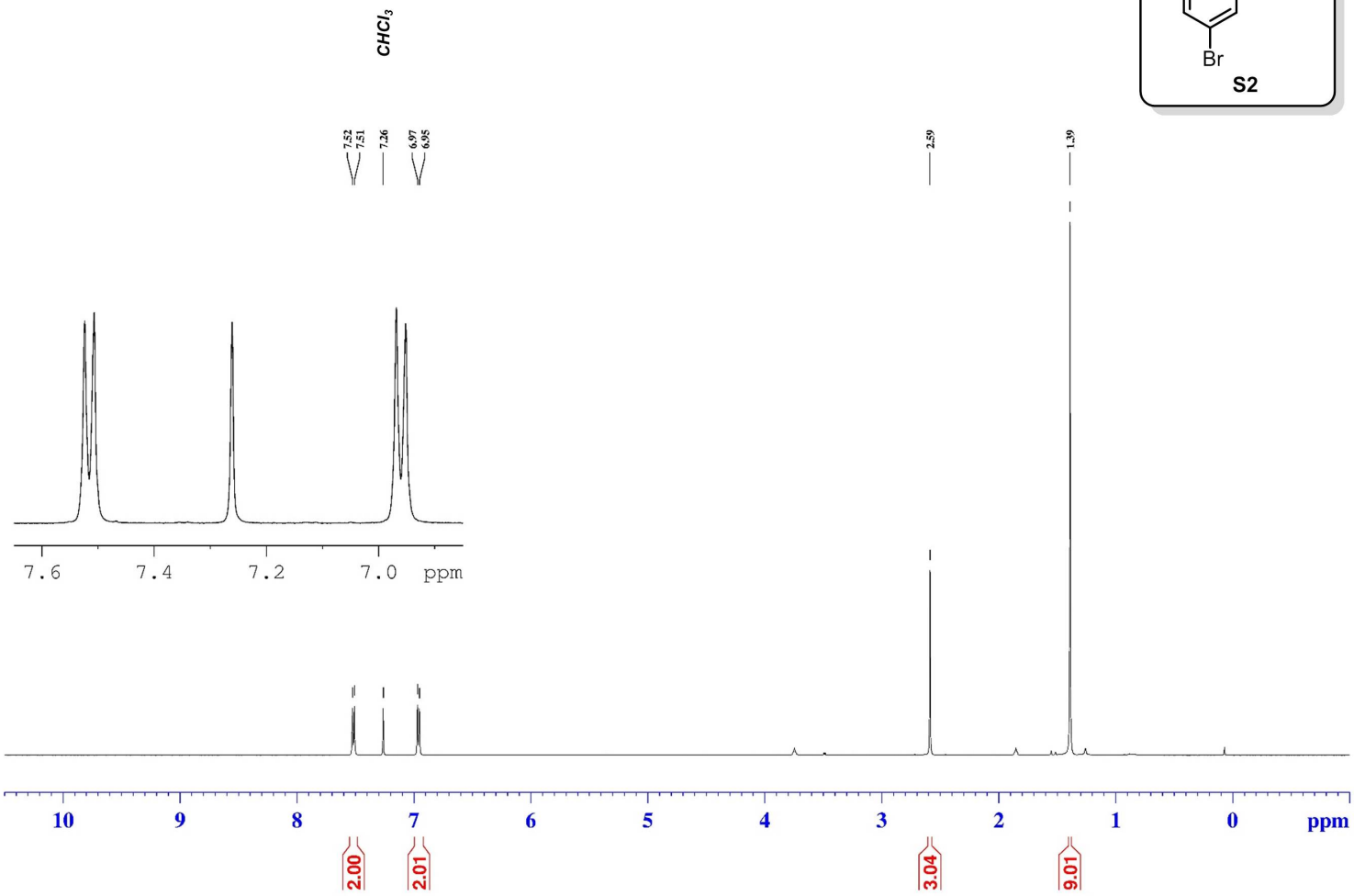




tert-butyl acetyl(4-bromophenyl)carbamate
500 MHz, $CDCl_3$

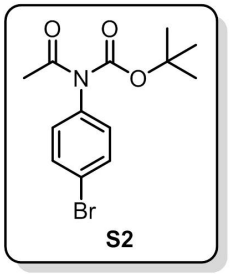
^1H NMR

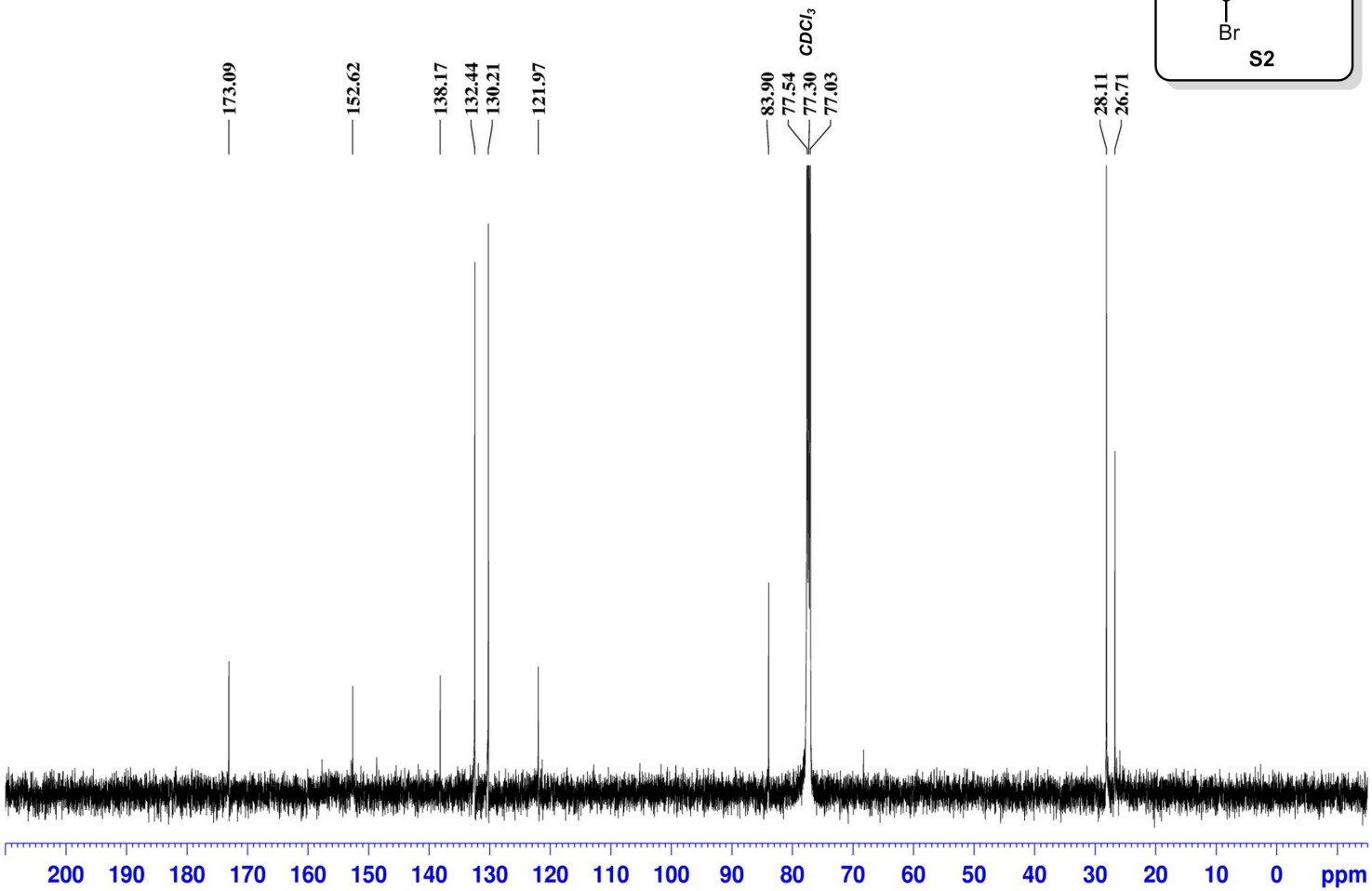




Tert-butyl acetyl(4-bromophenyl)carbamate
125 MHz, $CDCl_3$

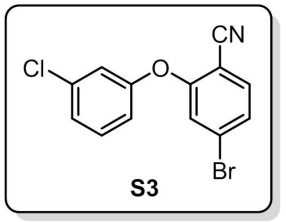
^{13}C NMR



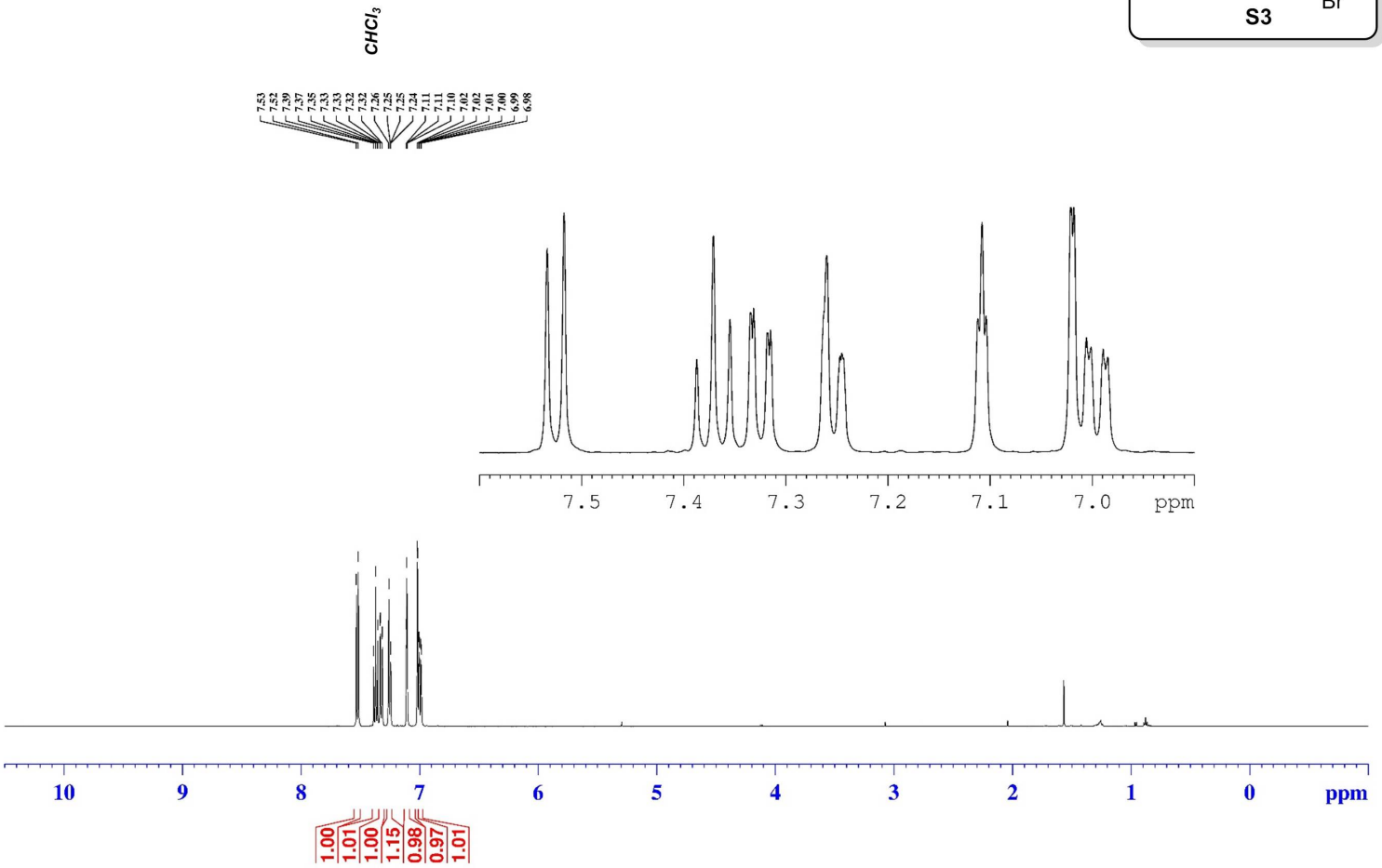


4-bromo-2-(3-chlorophenoxy)benzonitrile
500 MHz, $CDCl_3$

^{1}H NMR

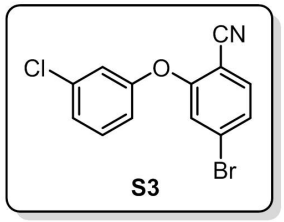


S3

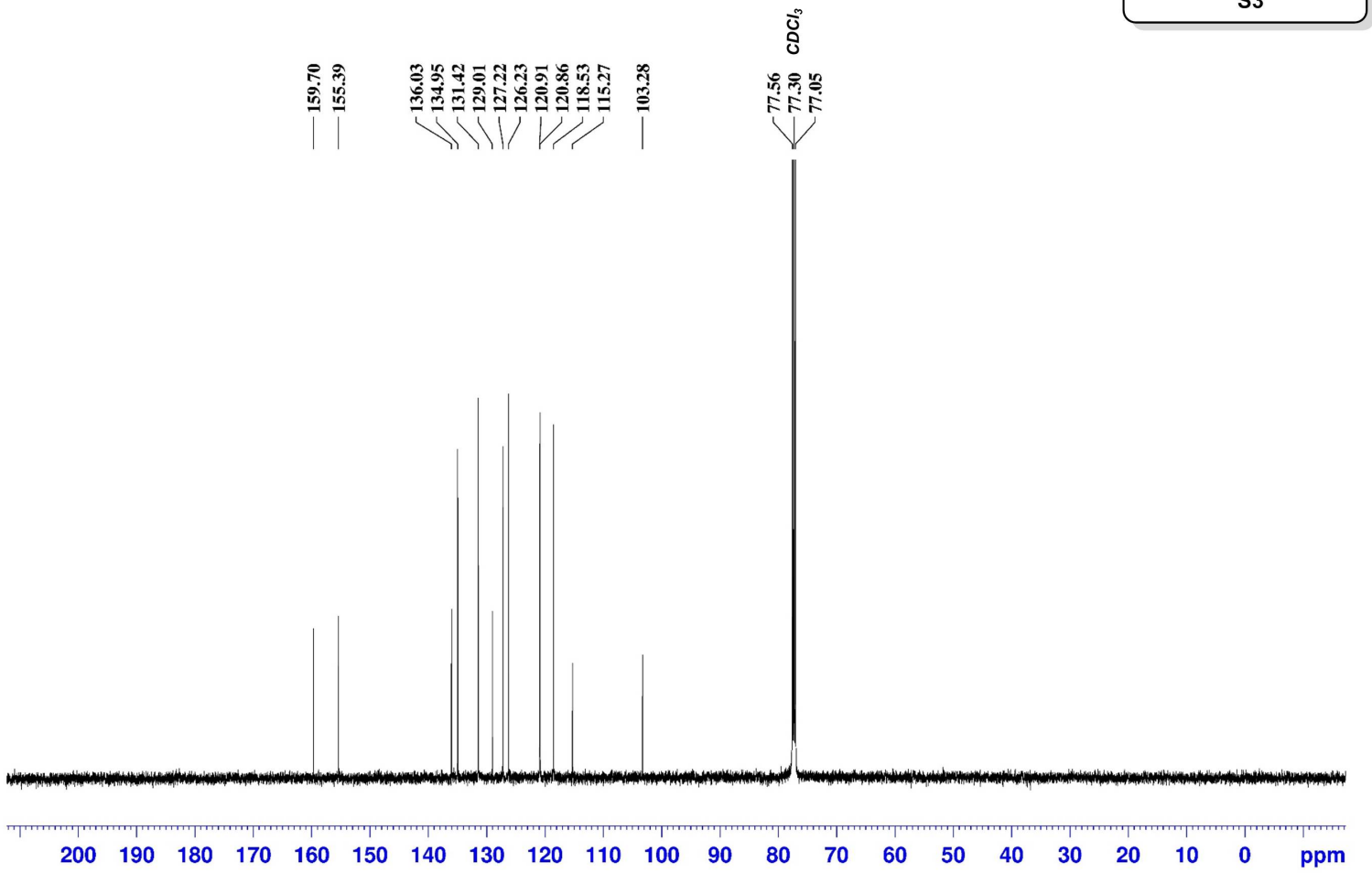


4-bromo-2-(3-chlorophenoxy)benzonitrile
125 MHz, $CDCl_3$

^{13}C NMR

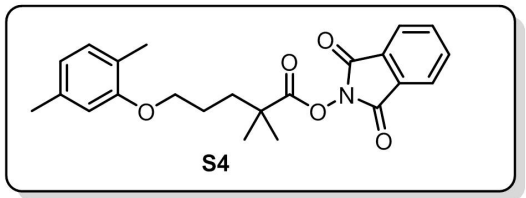


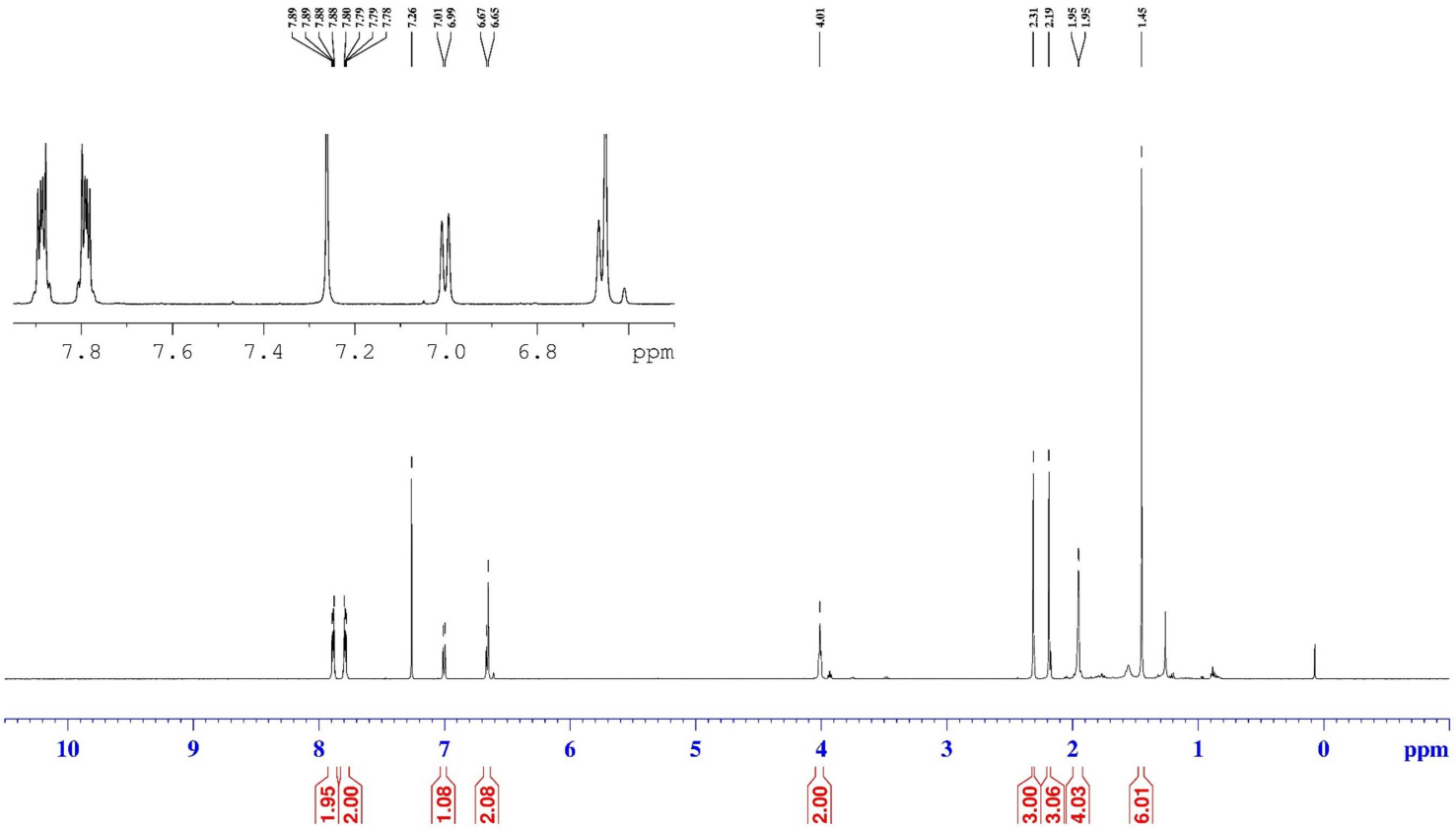
S3



1,3-dioxoisoindolin-2-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate
500 MHz, $CDCl_3$

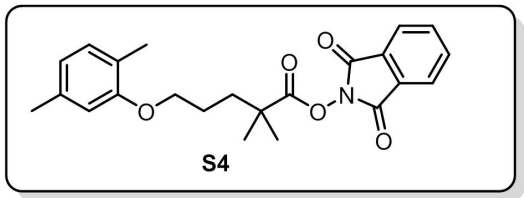
^{1}H NMR

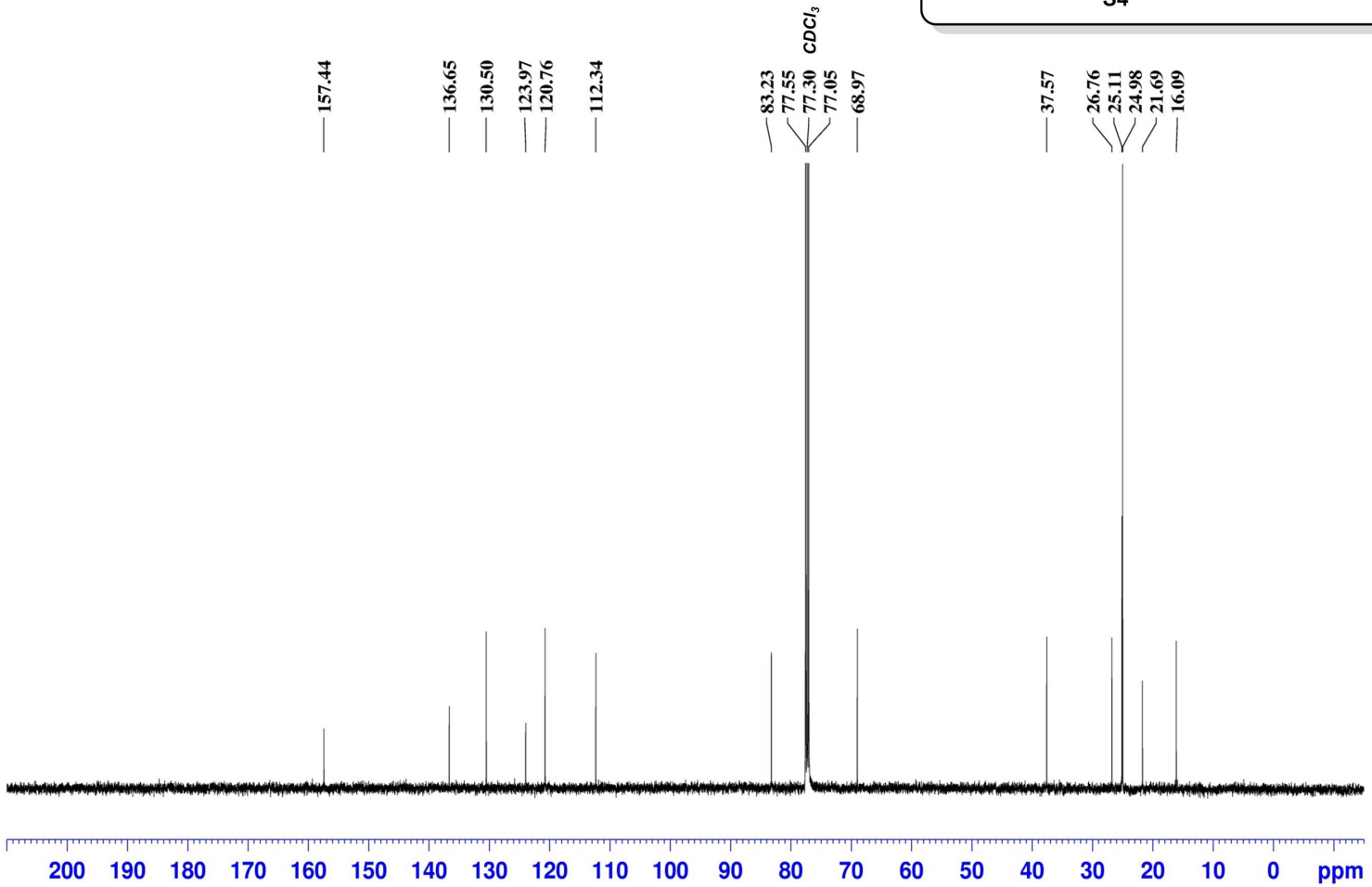




1,3-Dioxoisoindolin-2-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate
125 MHz, $CDCl_3$

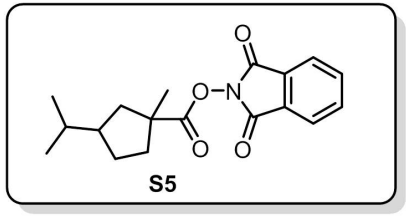
^{13}C NMR



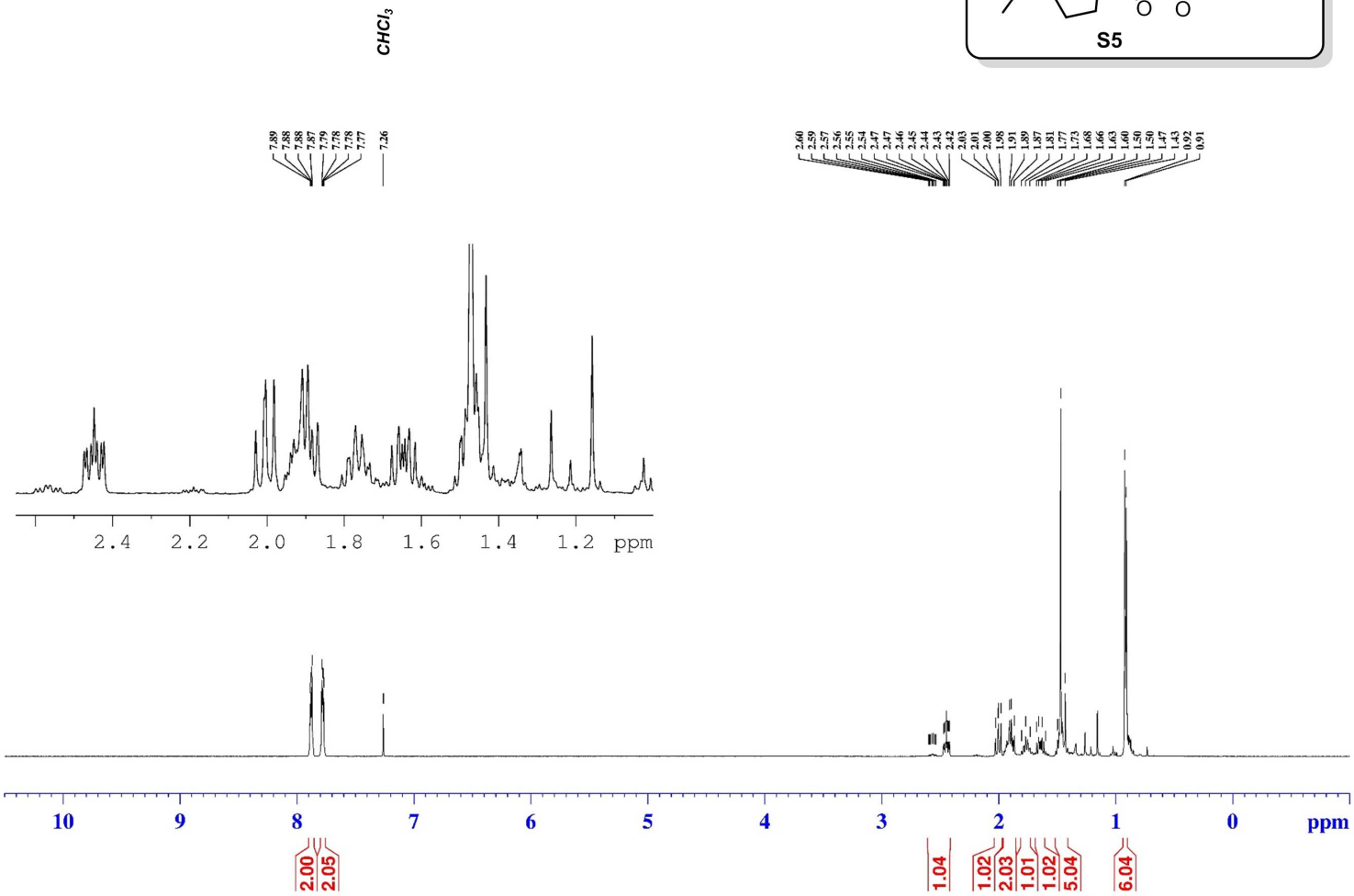


(3*R*)-1,3-dioxoisoindolin-2-yl 3-isopropyl-1-methylcyclopentanecarboxylate ***^{1}H NMR***

500 MHz, $CDCl_3$

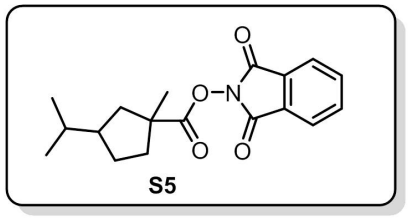


S5

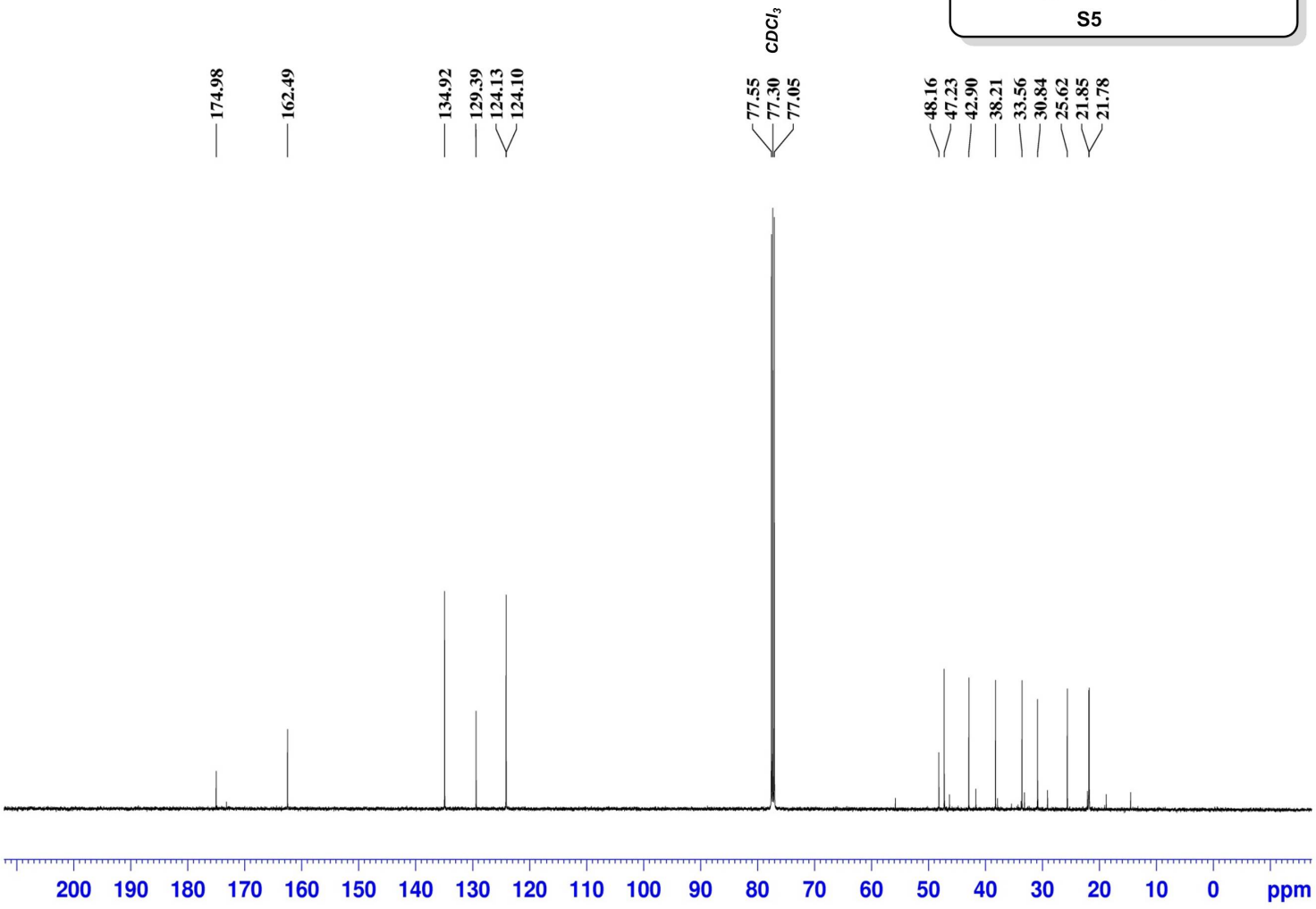


1,3-Dioxoisoindolin-2-yl 3-isopropyl-1-methylcyclopentanecarboxylate
125 MHz, $CDCl_3$

^{13}C NMR

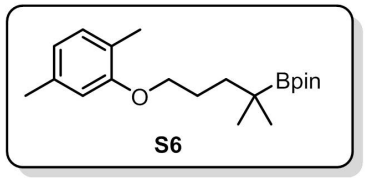


S5

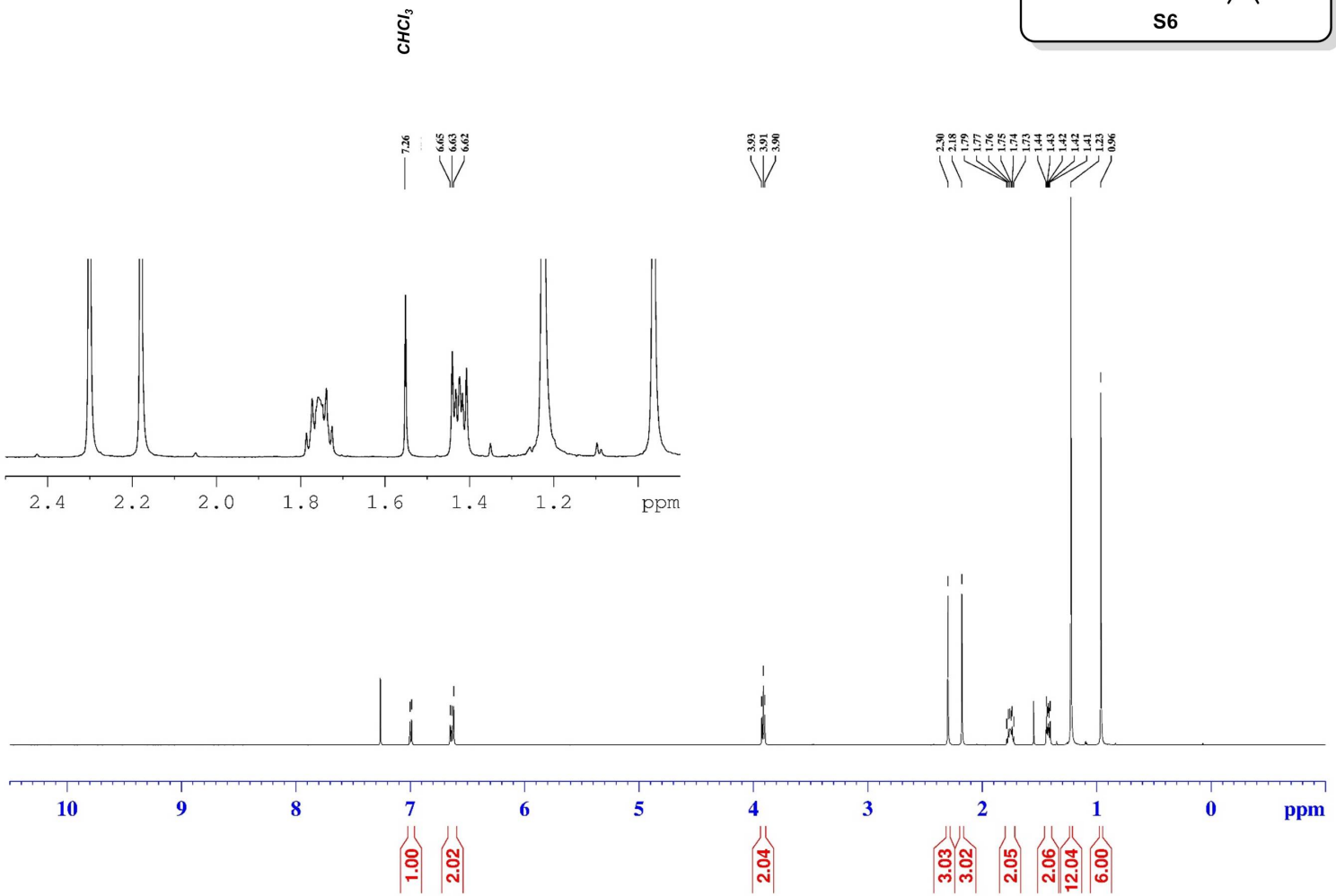


^1H NMR

2-(5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

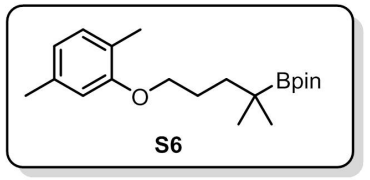


S6

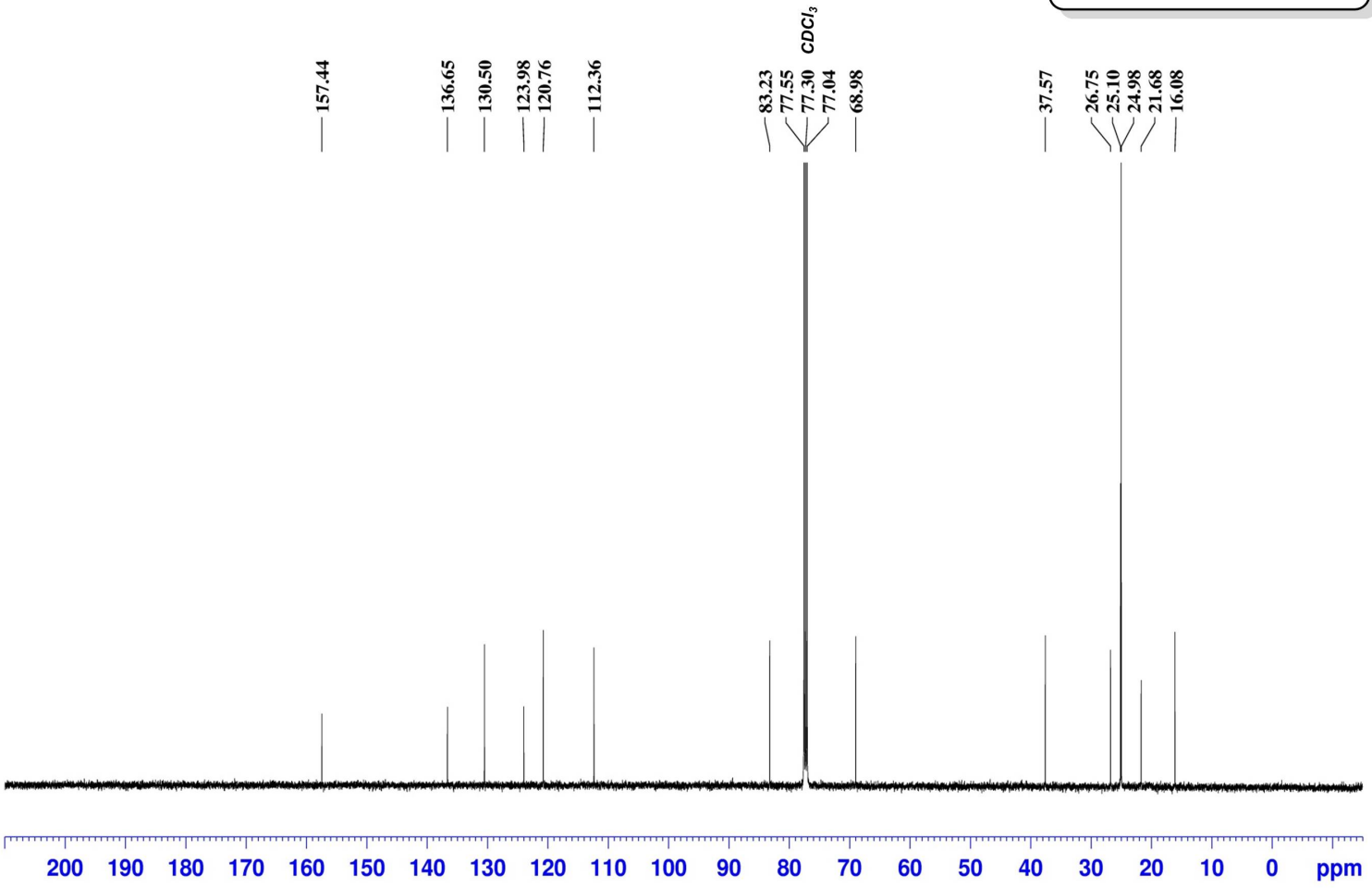


^{13}C NMR

2-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$

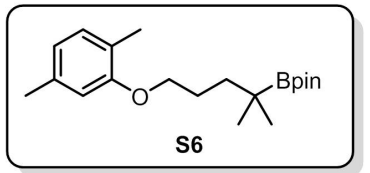


S6

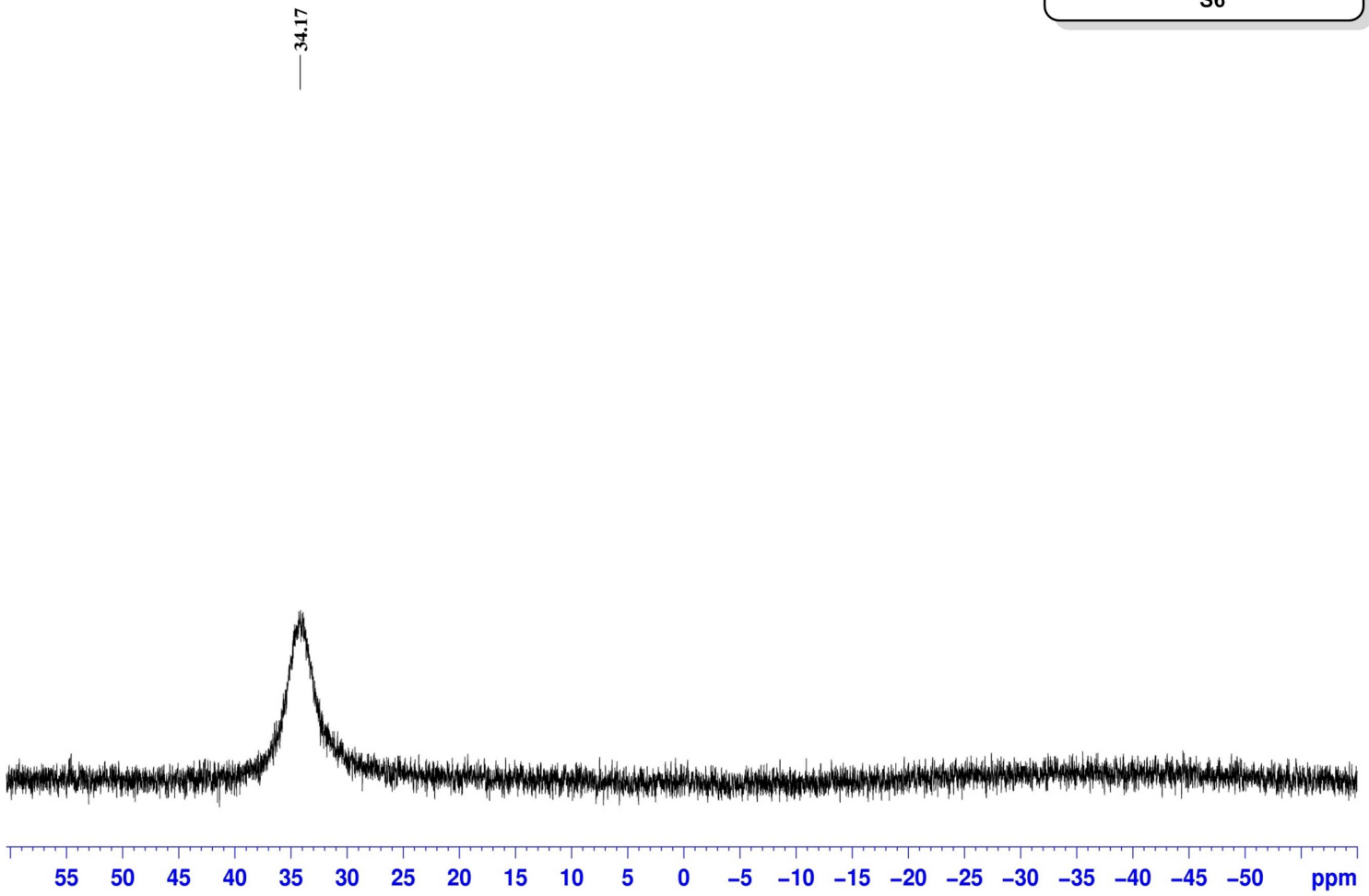


^{11}B NMR

2-(5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$

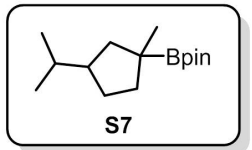


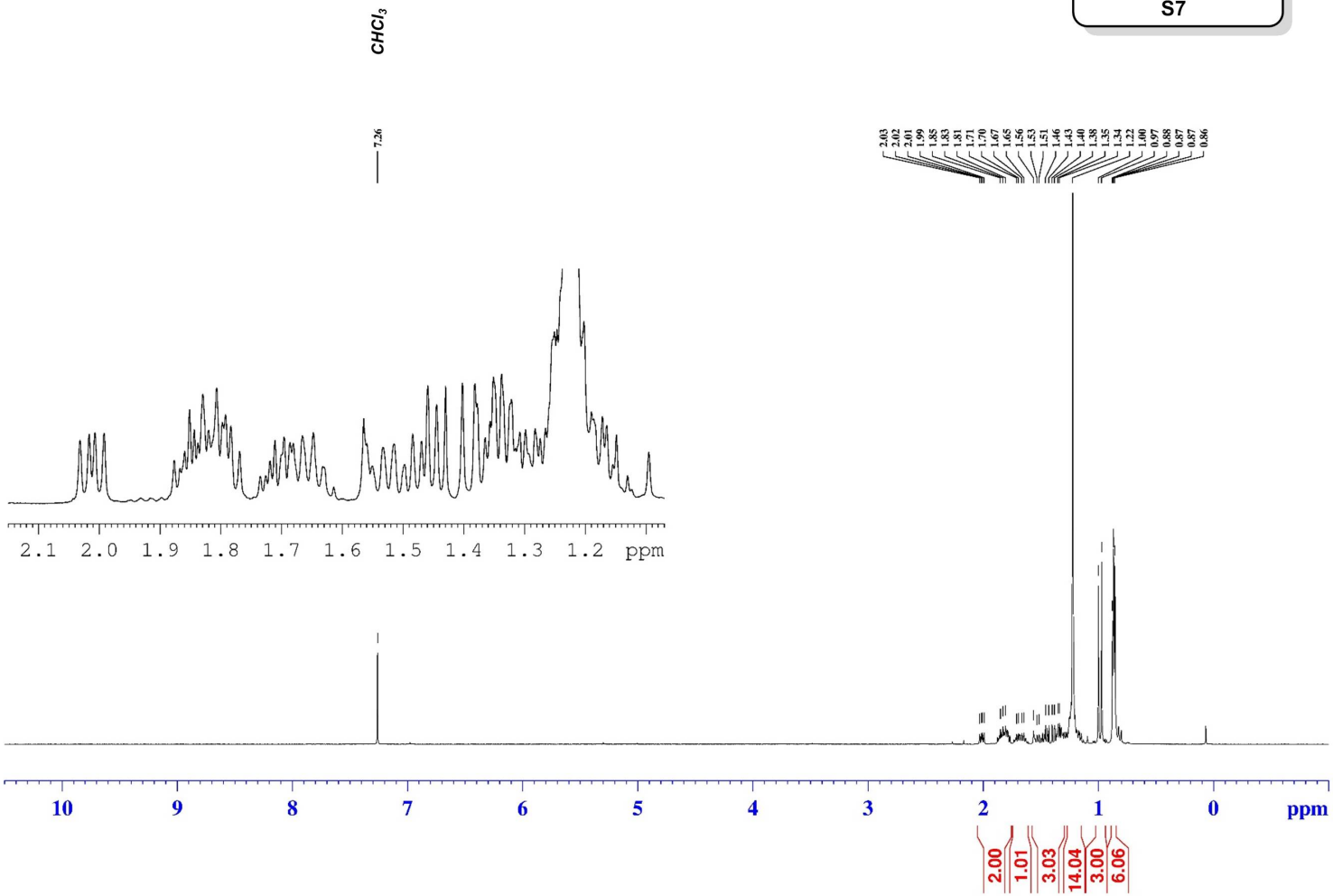
S6



^1H NMR

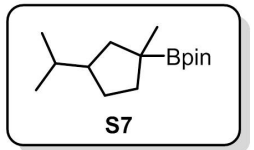
2-((3R)-3-isopropyl-1-methylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

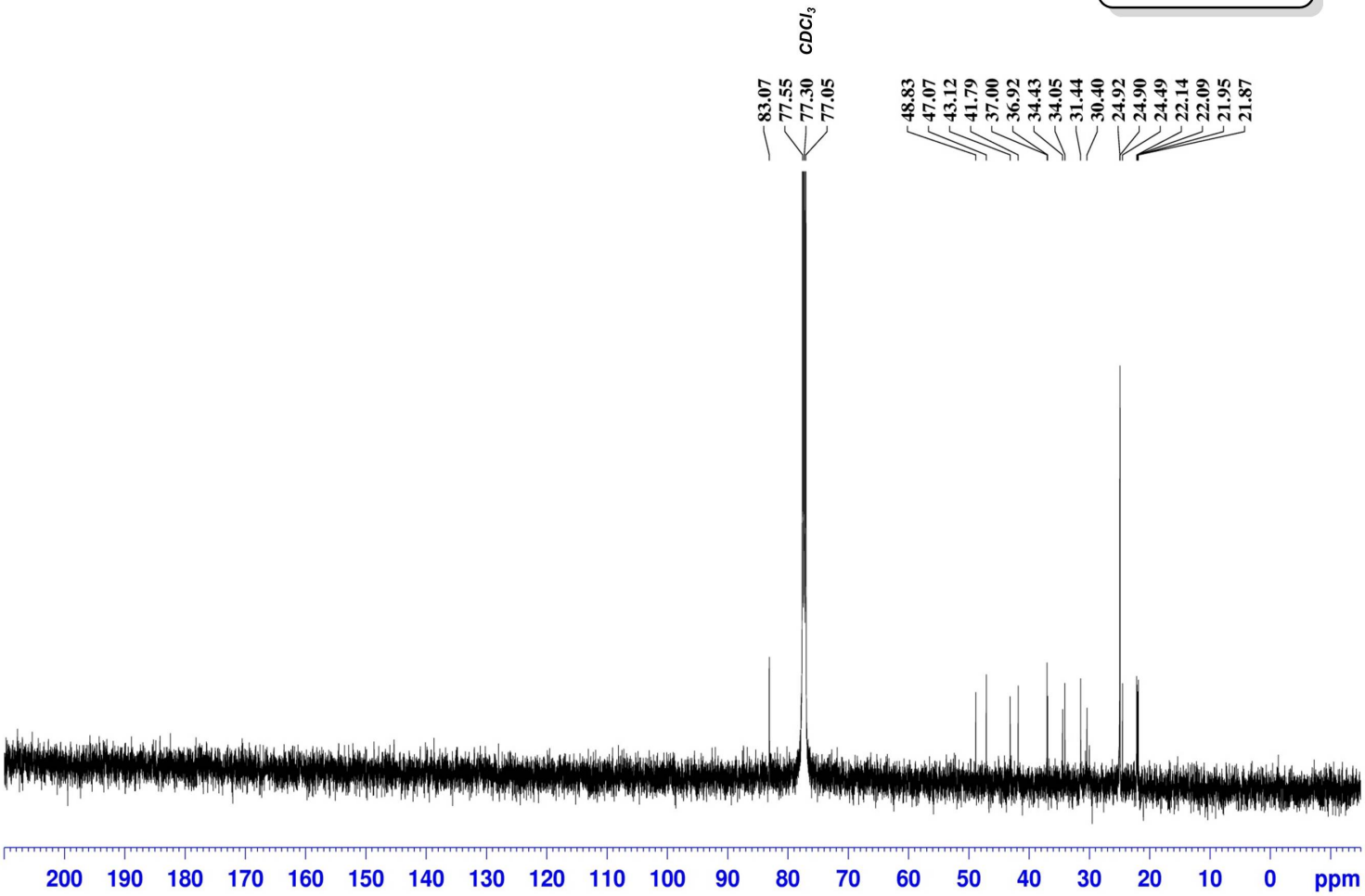




^{13}C NMR

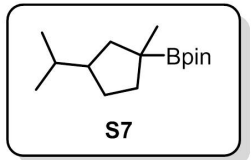
2-(3-Isopropyl-1-methylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$



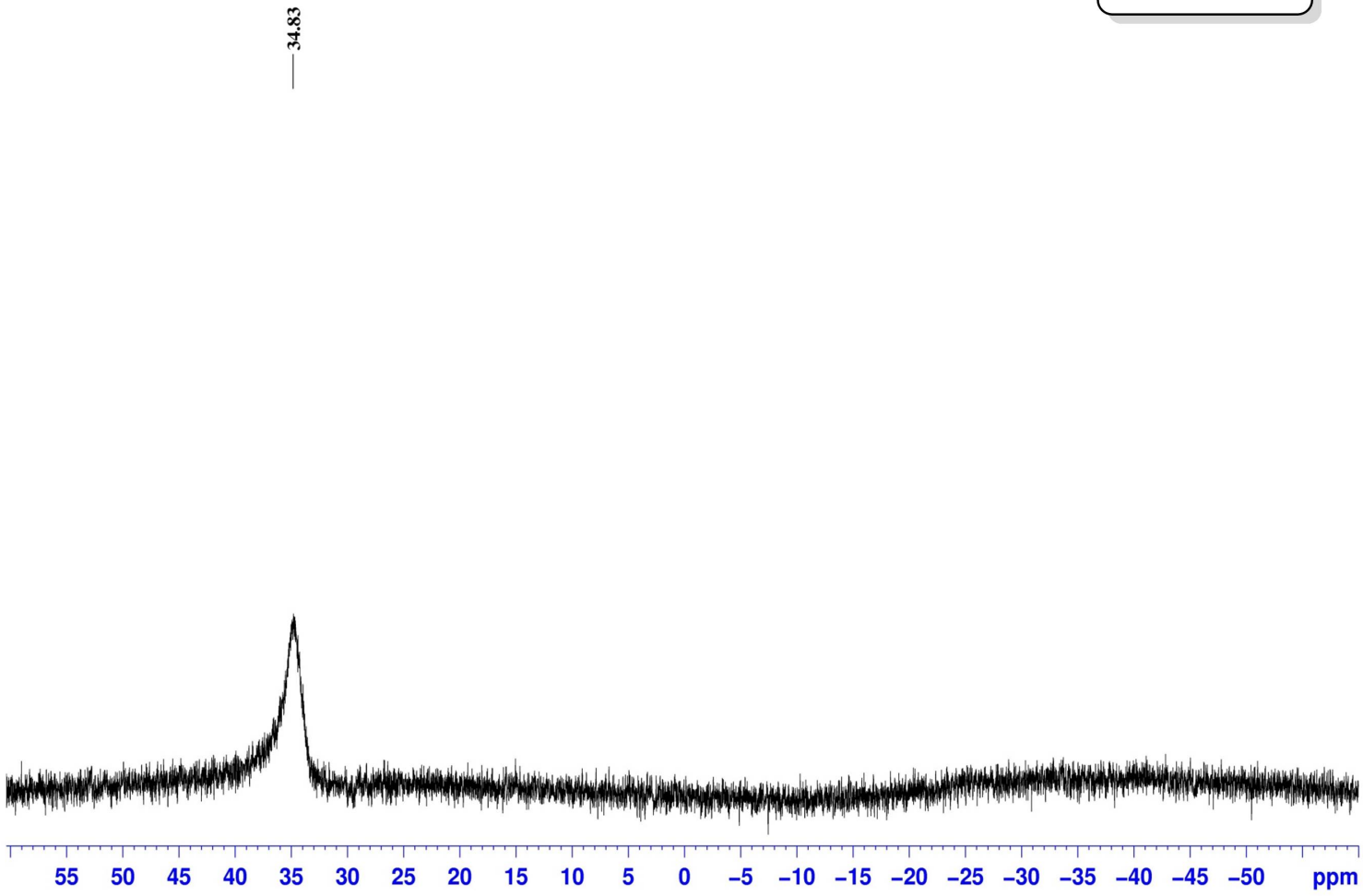


^{11}B NMR

2-((3R)-3-isopropyl-1-methylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$

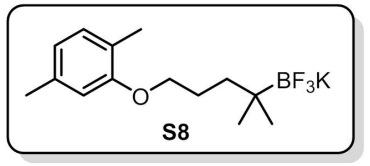


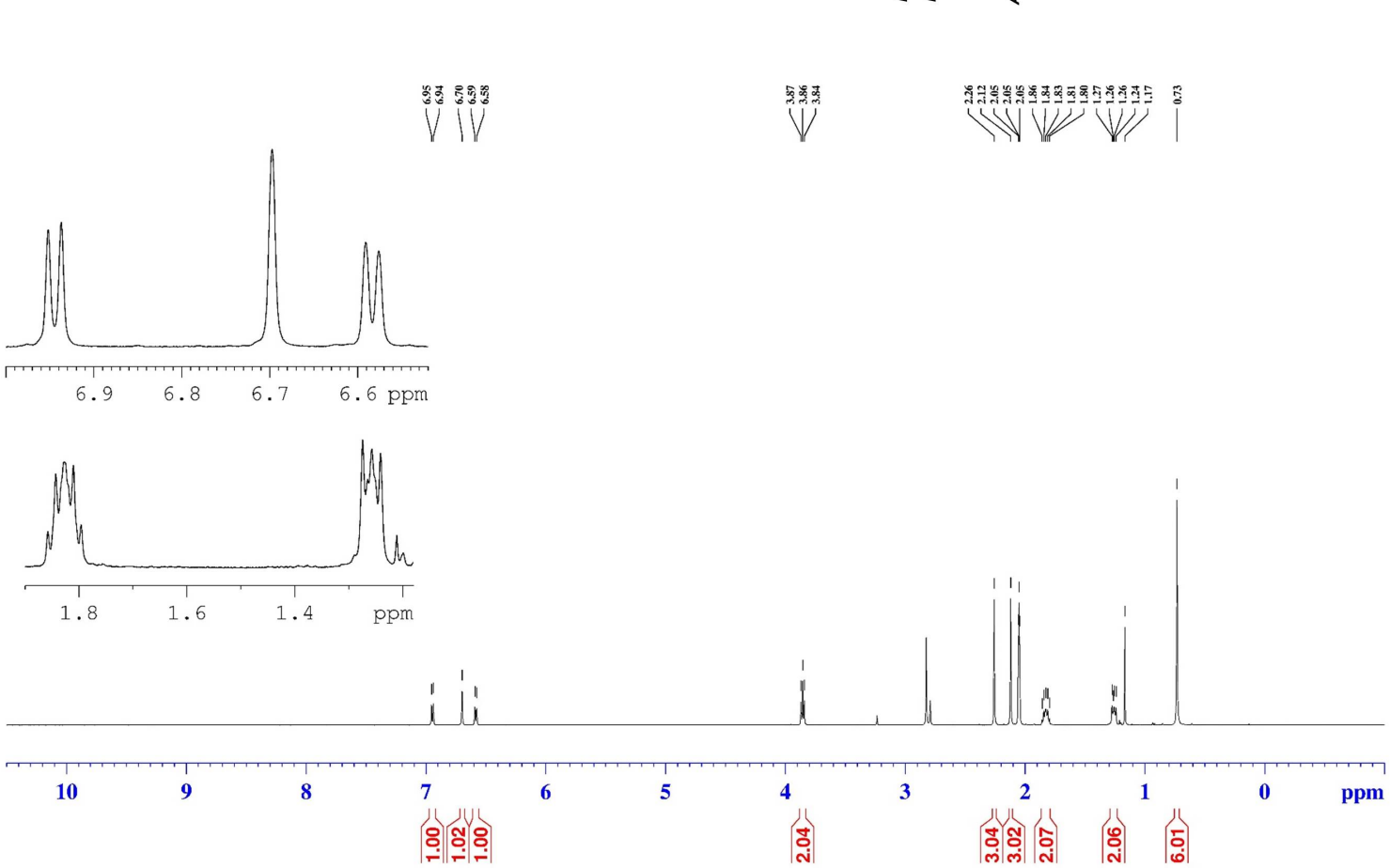
S7



Potassium (5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)trifluoroborate
500 MHz, Acetone-d_6

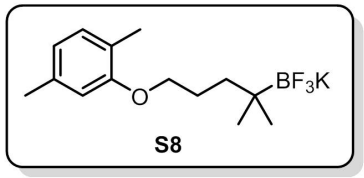
^1H NMR



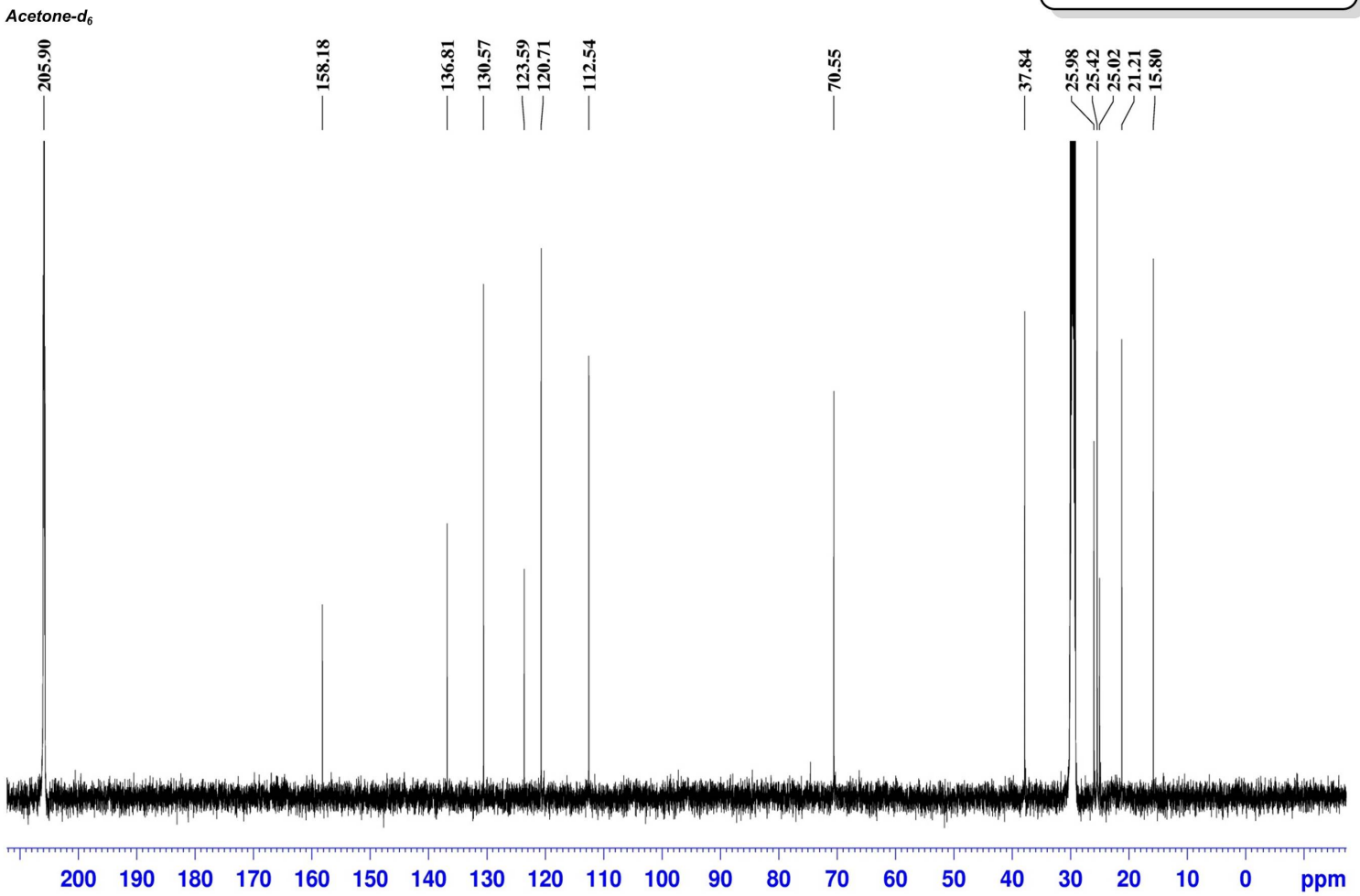


^{13}C NMR

Potassium (5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)trifluoroborate
125 MHz, Acetone-d_6

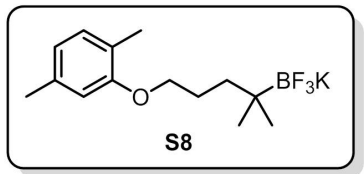


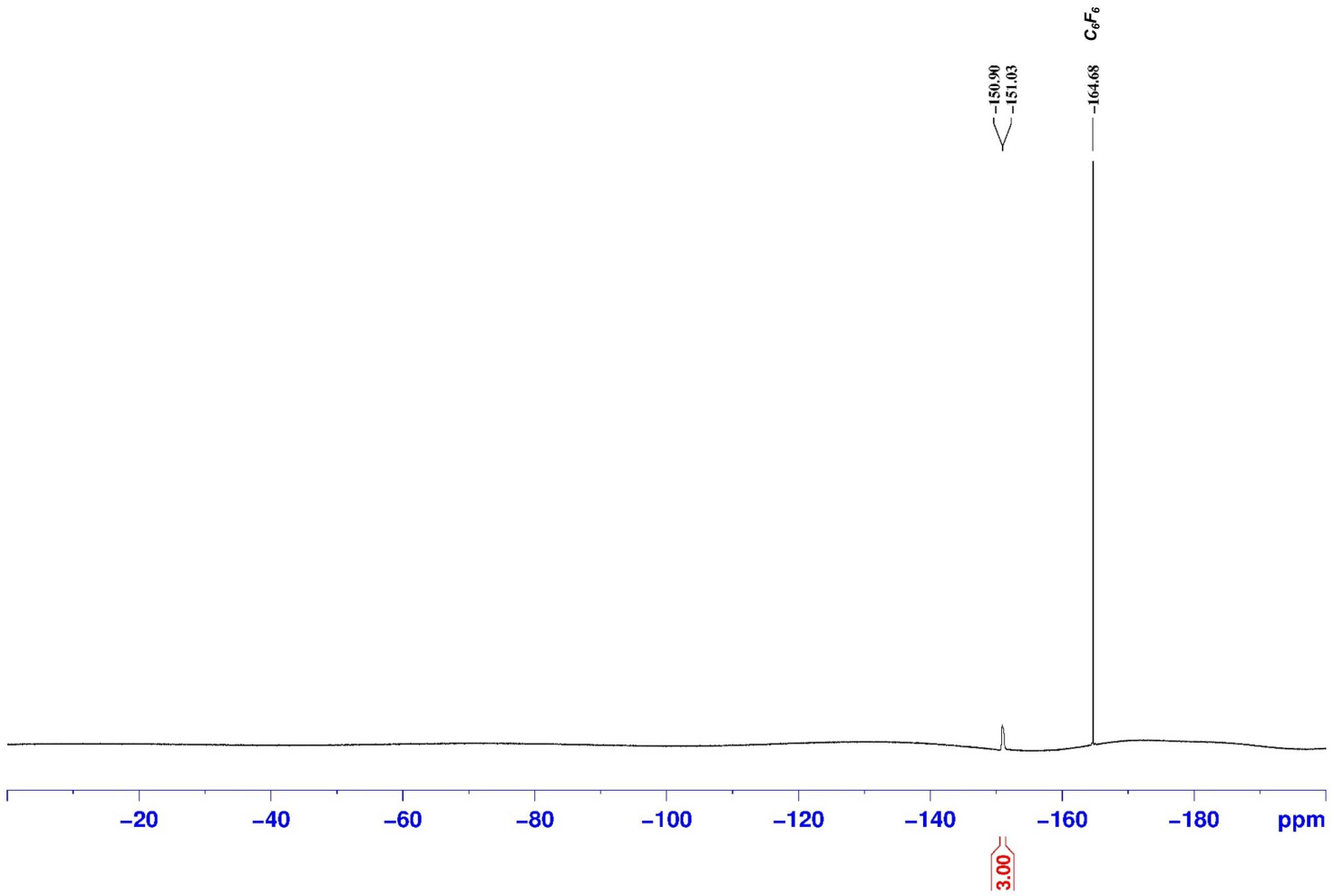
S8



^{19}F NMR

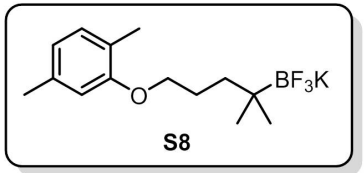
Potassium (5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)trifluoroborate
471 MHz, Acetone-d_6



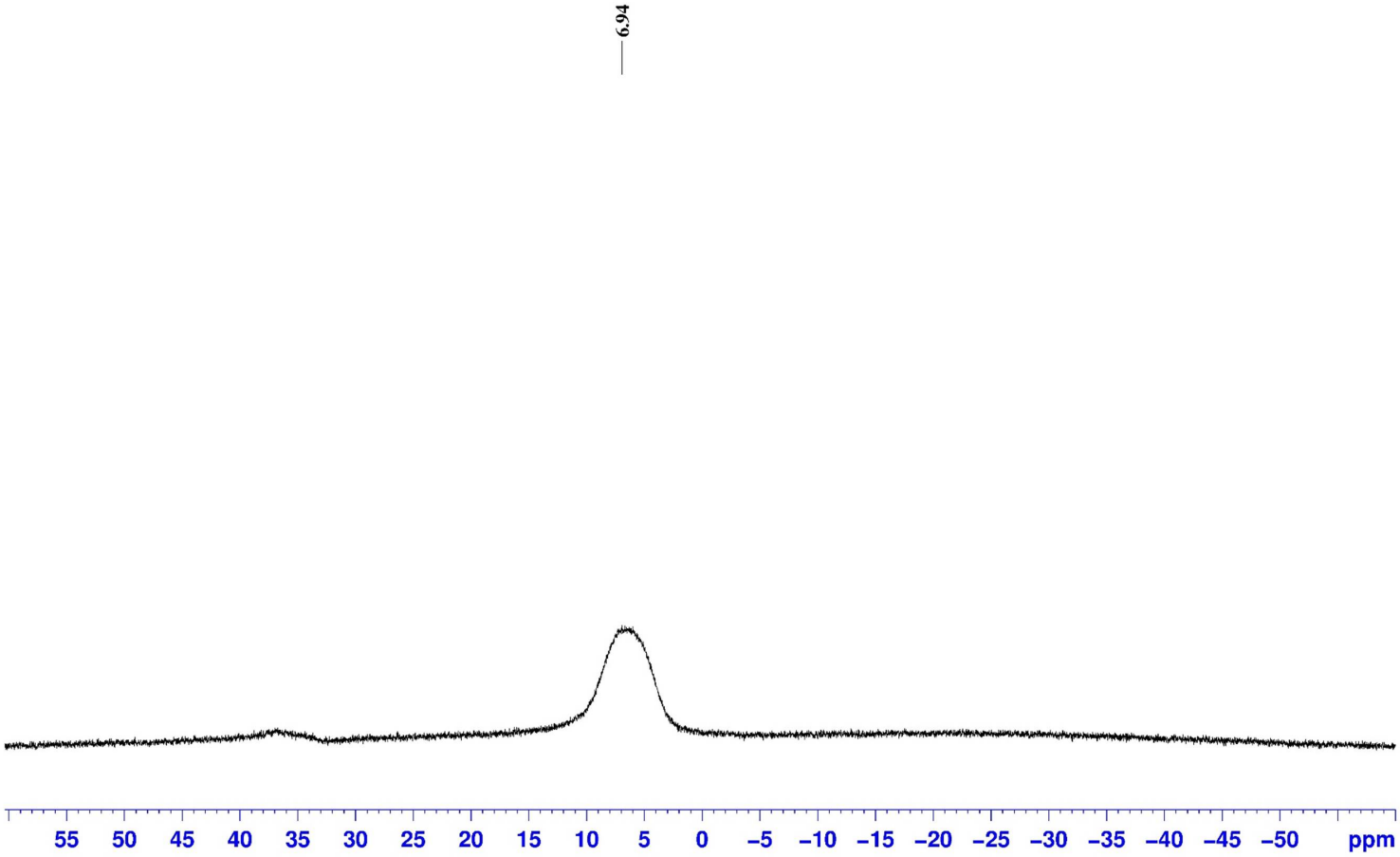


^{11}B NMR

Potassium (5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)trifluoroborate
128 MHz, Acetone-d_6

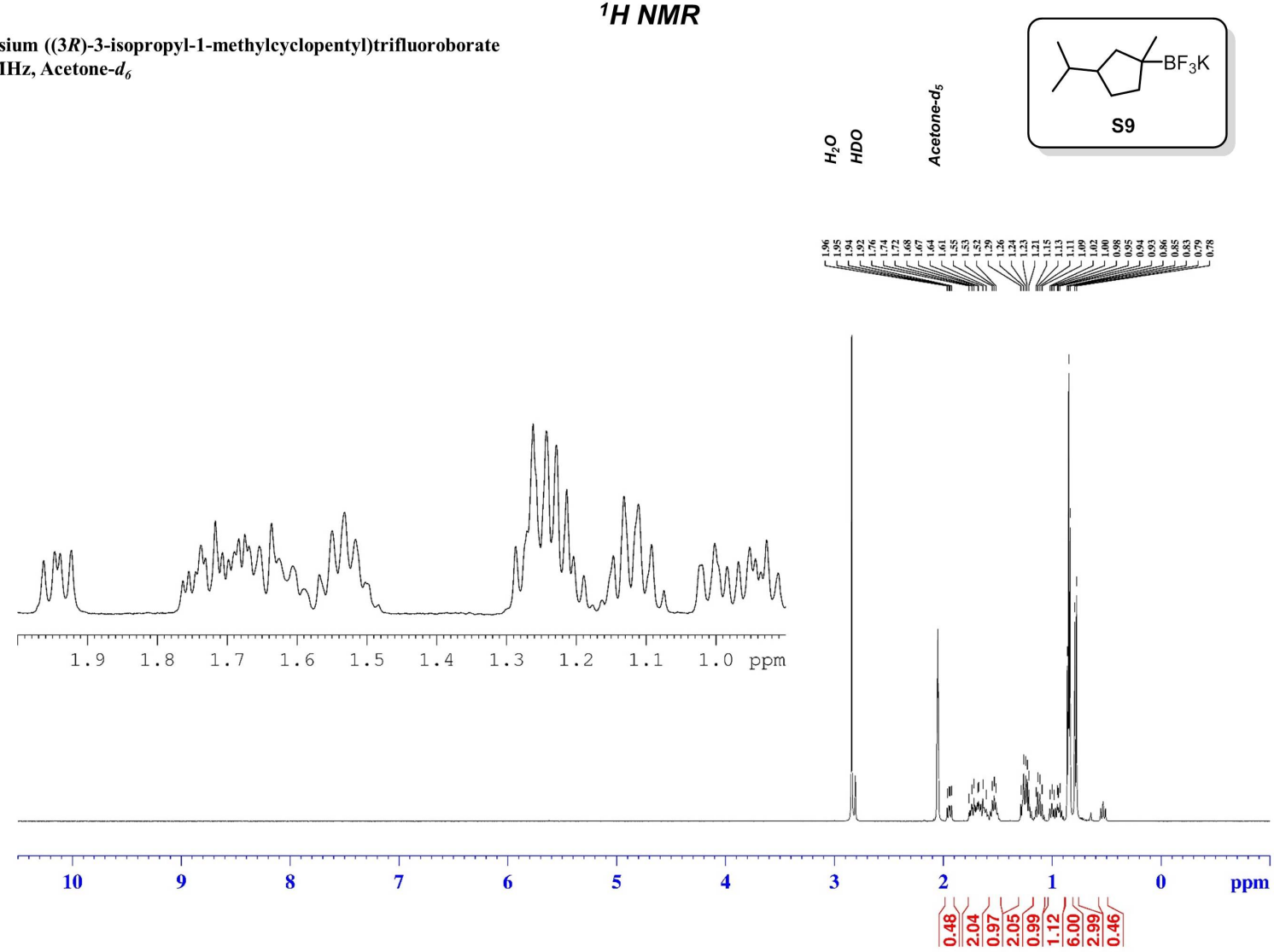


S8



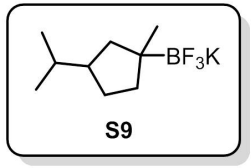
Potassium ((3*R*)-3-isopropyl-1-methylcyclopentyl)trifluoroborate
500 MHz, Acetone-d_6

^1H NMR

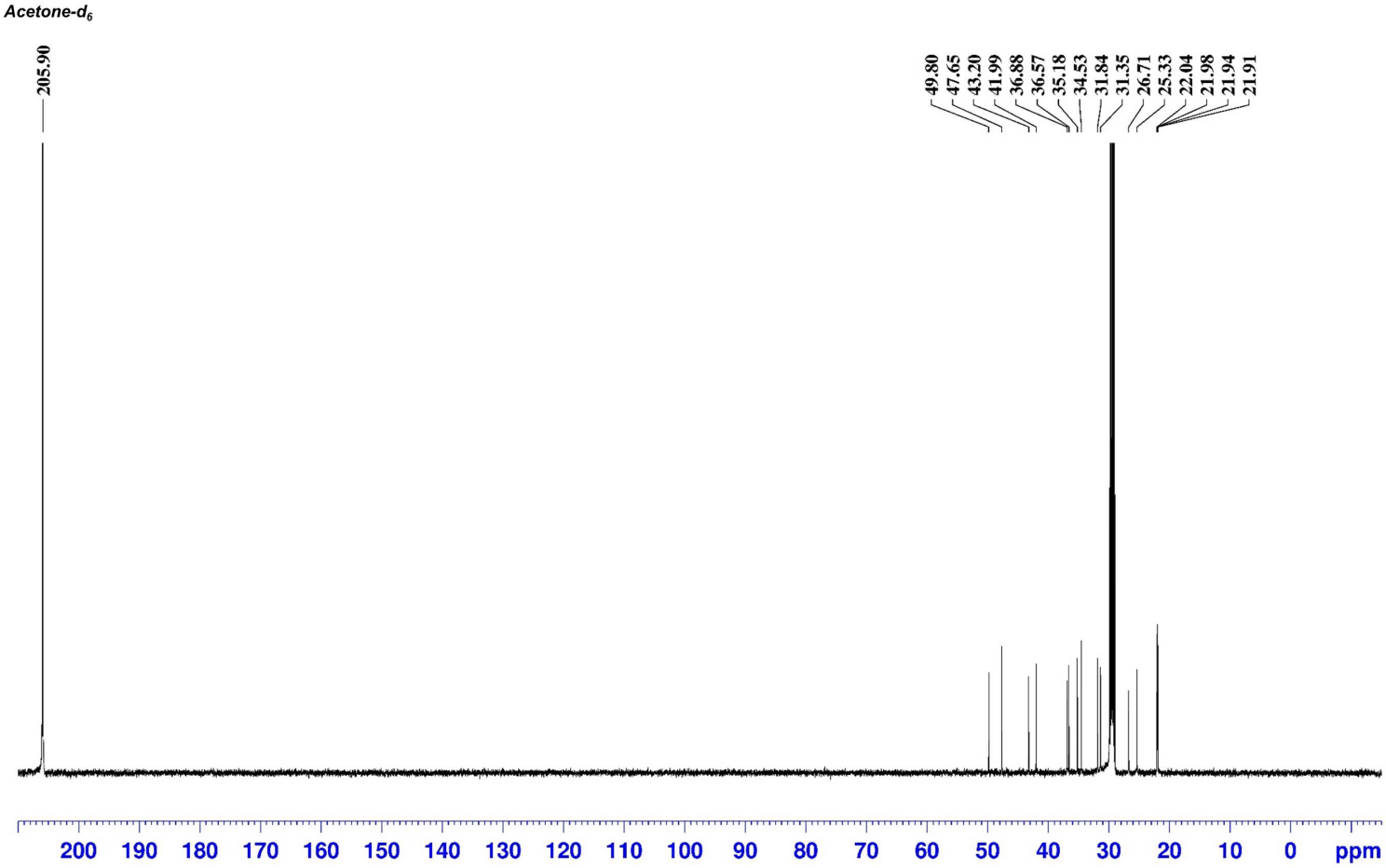


^{13}C NMR

Potassium (3-isopropyl-1-methylcyclopentyl)trifluoroborate
125 MHz, Acetone-d_6

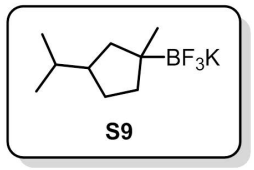


S9

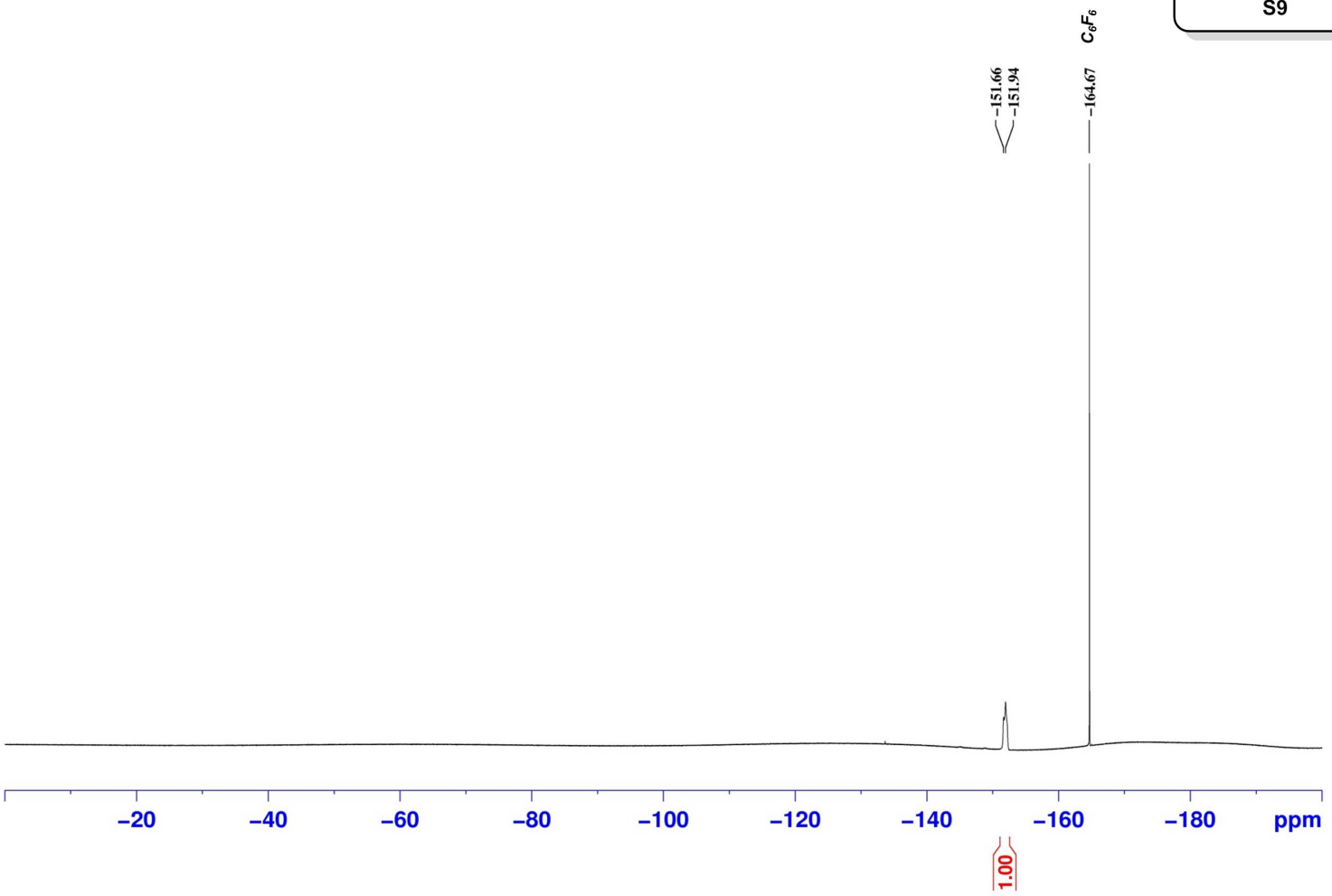


^{19}F NMR

Potassium ((3*R*)-3-isopropyl-1-methylcyclopentyl)trifluoroborate
471 MHz, Acetone-d_6

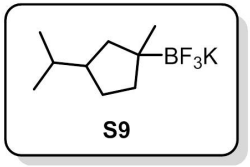


S9

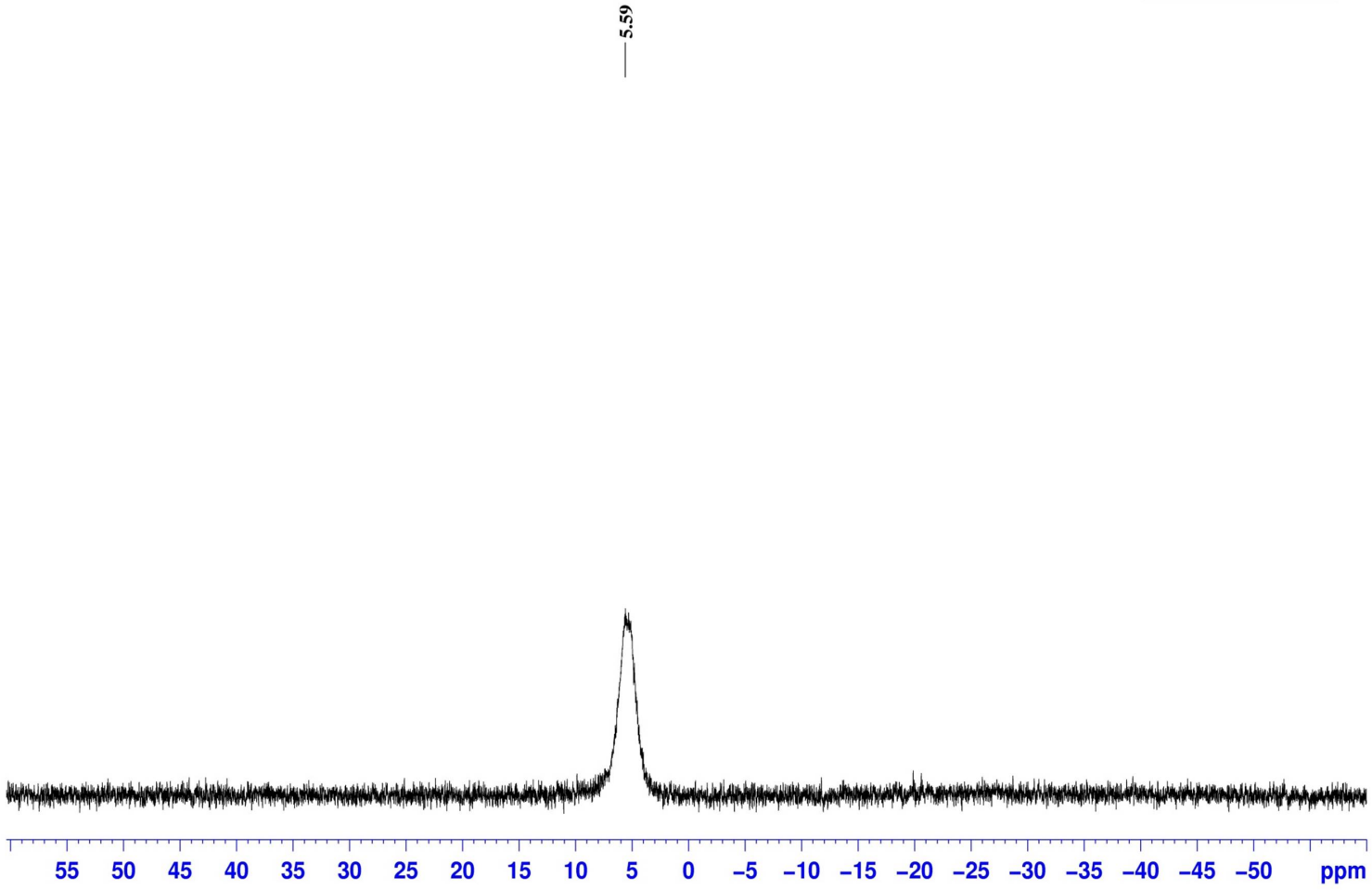


Potassium ((3*R*)-3-isopropyl-1-methylcyclopentyl)trifluoroborate
128 MHz, Acetone-d_6

^{11}B NMR

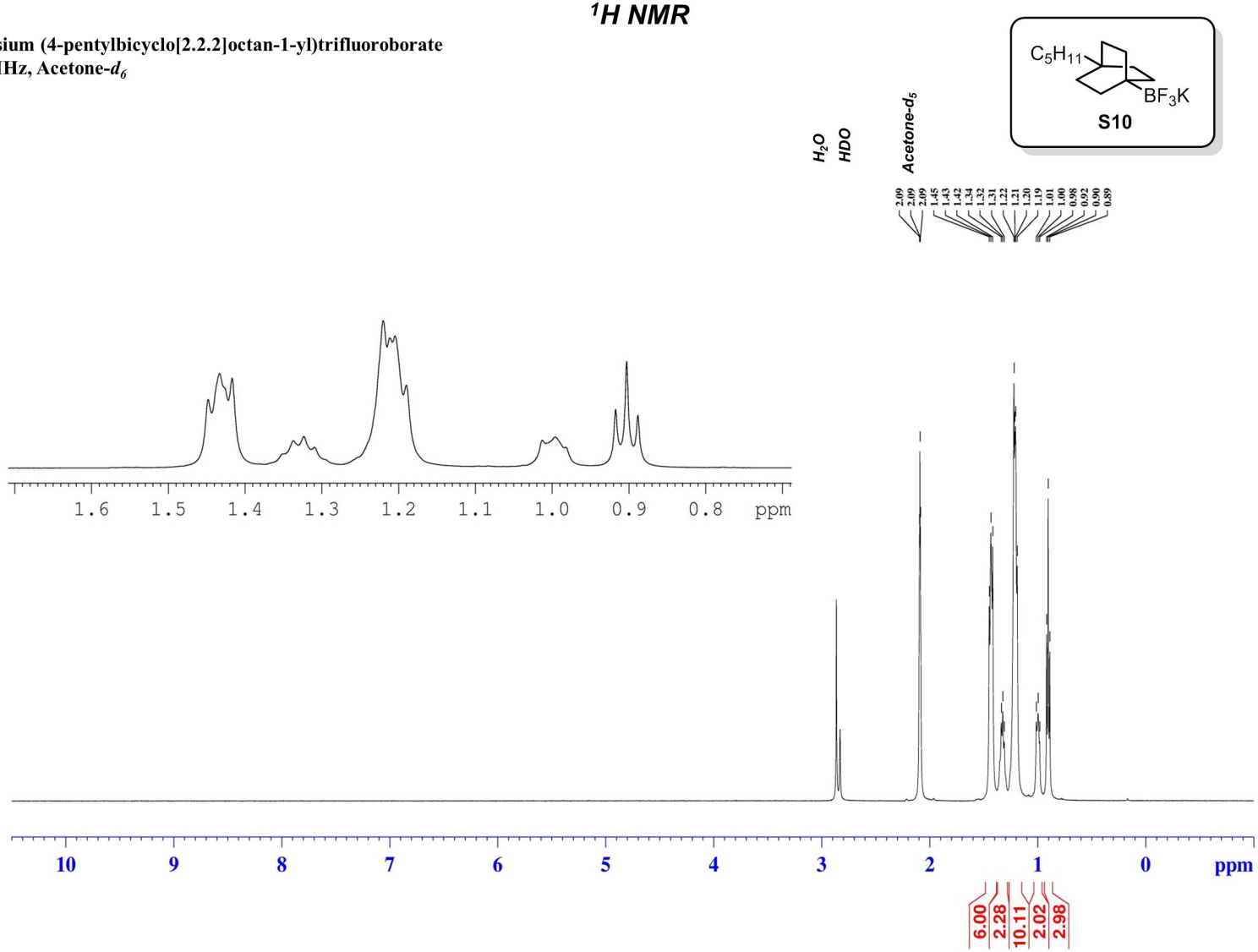


S9



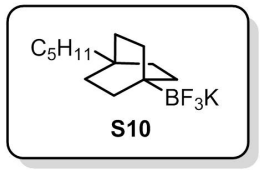
^1H NMR

Potassium (4-pentylbicyclo[2.2.2]octan-1-yl)trifluoroborate
500 MHz, Acetone-d_6

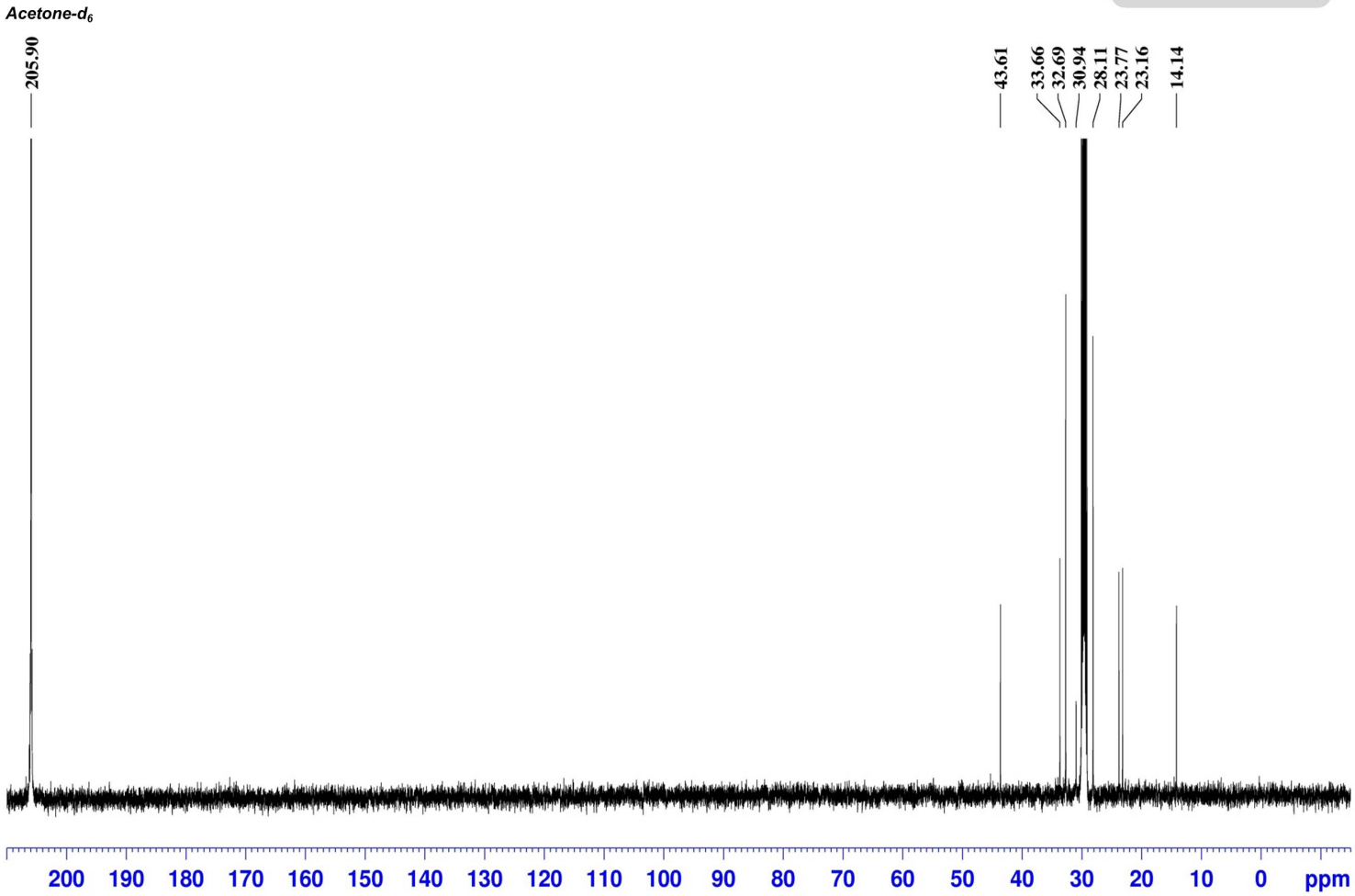


^{13}C NMR

Potassium (4-pentylbicyclo[2.2.2]octan-1-yl)trifluoroborate
125 MHz, Acetone-d_6

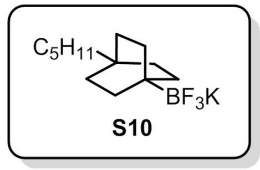


S10

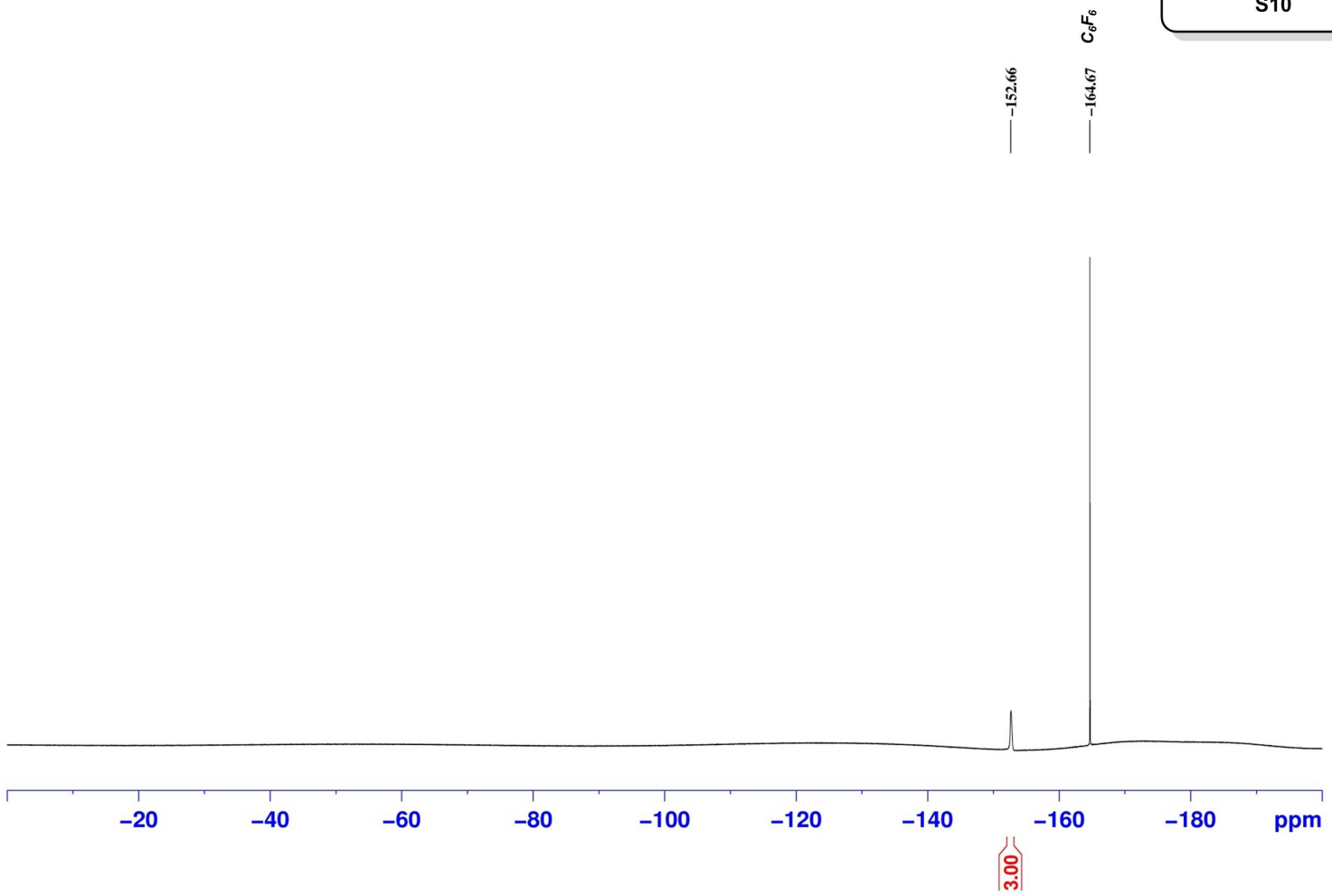


^{19}F NMR

Potassium (4-pentylbicyclo[2.2.2]octan-1-yl)trifluoroborate
471 MHz, Acetone-d_6

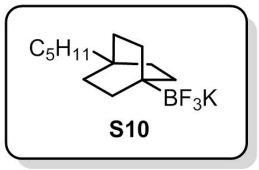


S10

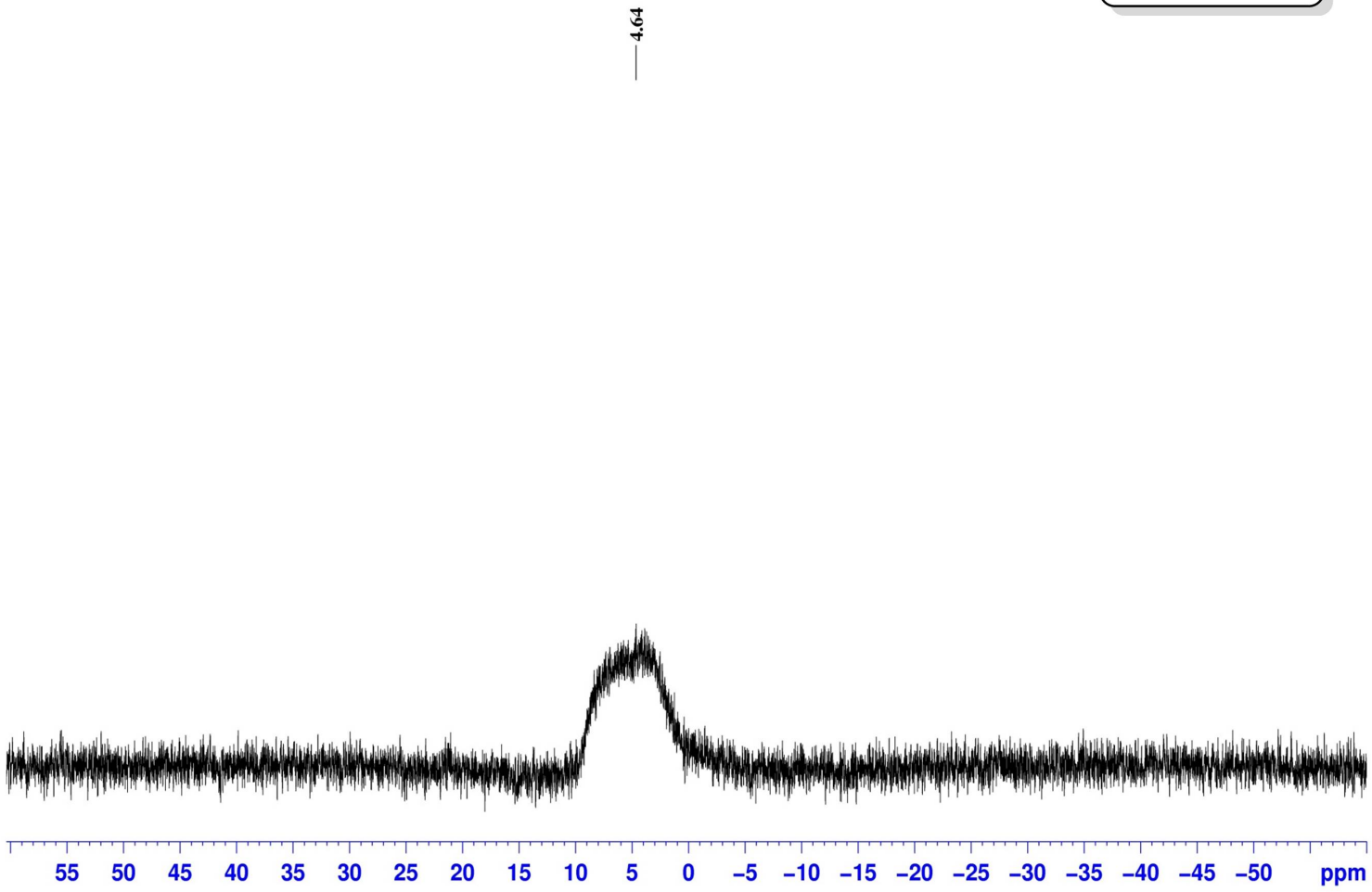


Potassium (4-pentylbicyclo[2.2.2]octan-1-yl)trifluoroborate
128 MHz, Acetone-d_6

^{11}B NMR

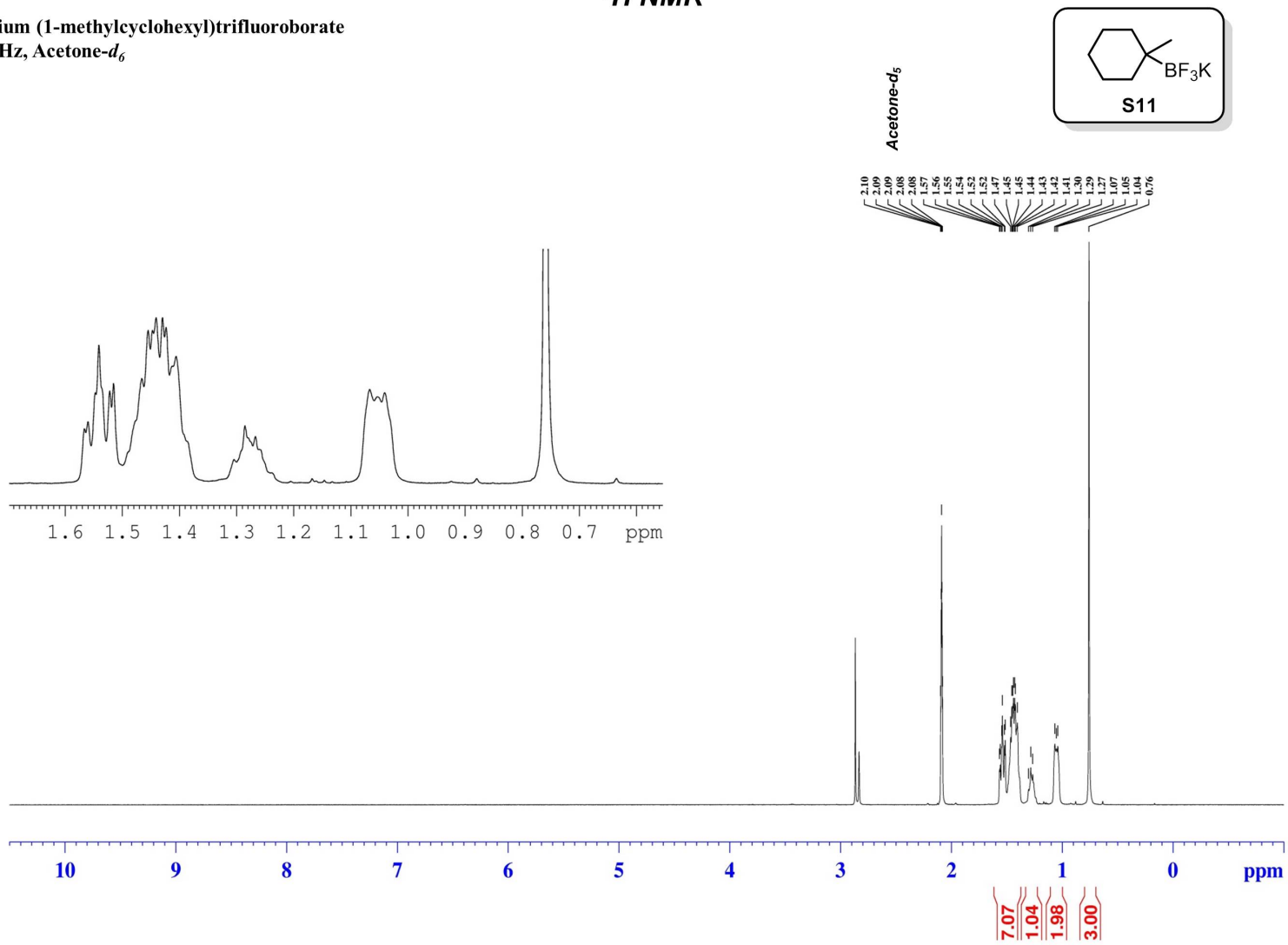


S10



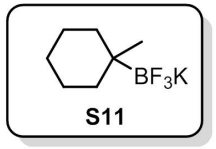
^1H NMR

Potassium (1-methylcyclohexyl)trifluoroborate
500 MHz, Acetone-d_6

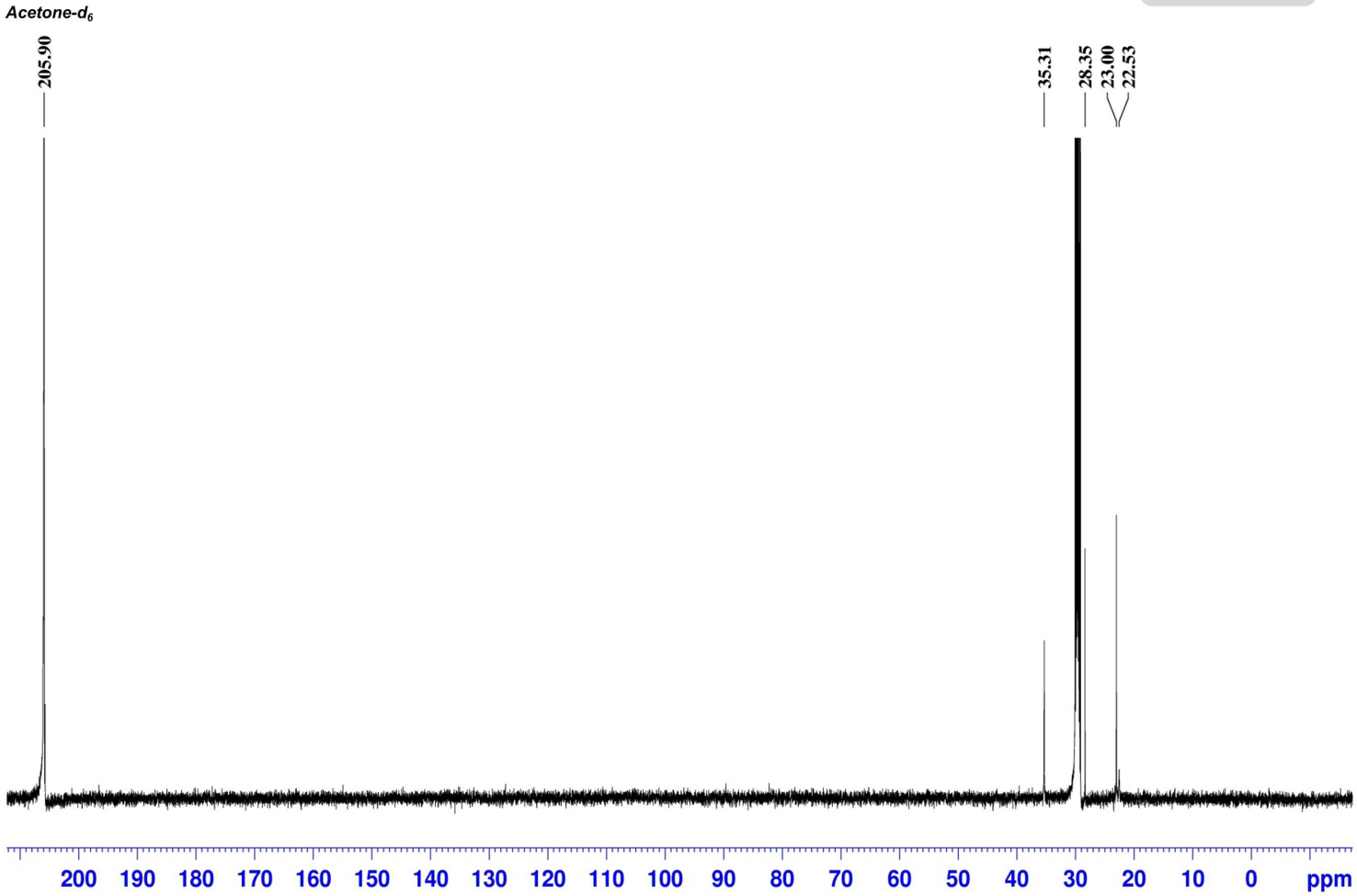


Potassium (1-methylcyclohexyl)trifluoroborate
125 MHz, Acetone-d_6

^{13}C NMR

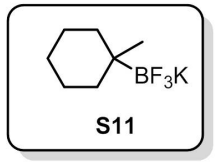


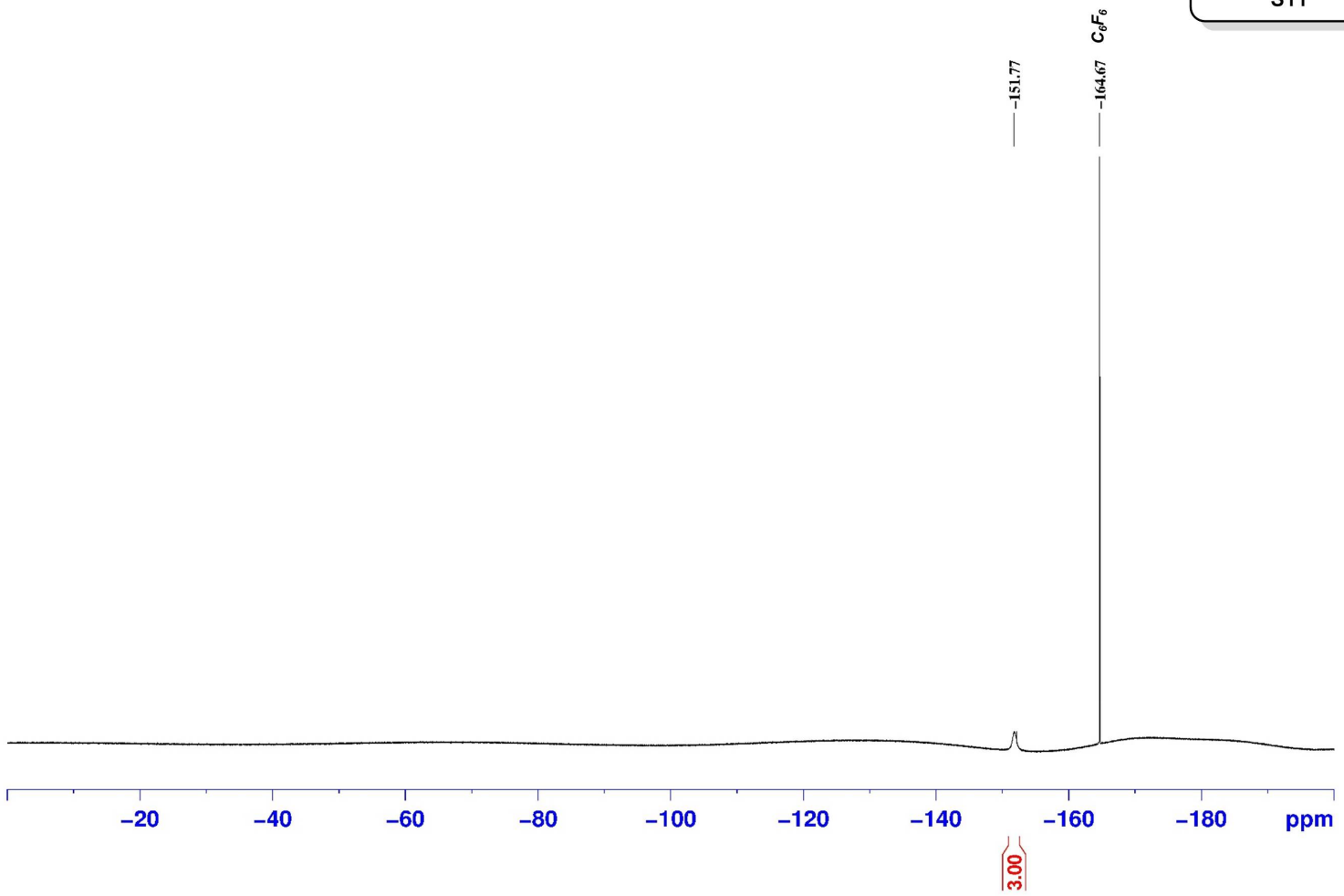
S11



^{19}F NMR

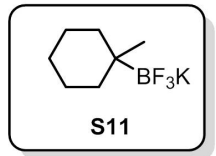
Potassium (1-methylcyclohexyl)trifluoroborate
471 MHz, Acetone-d_6



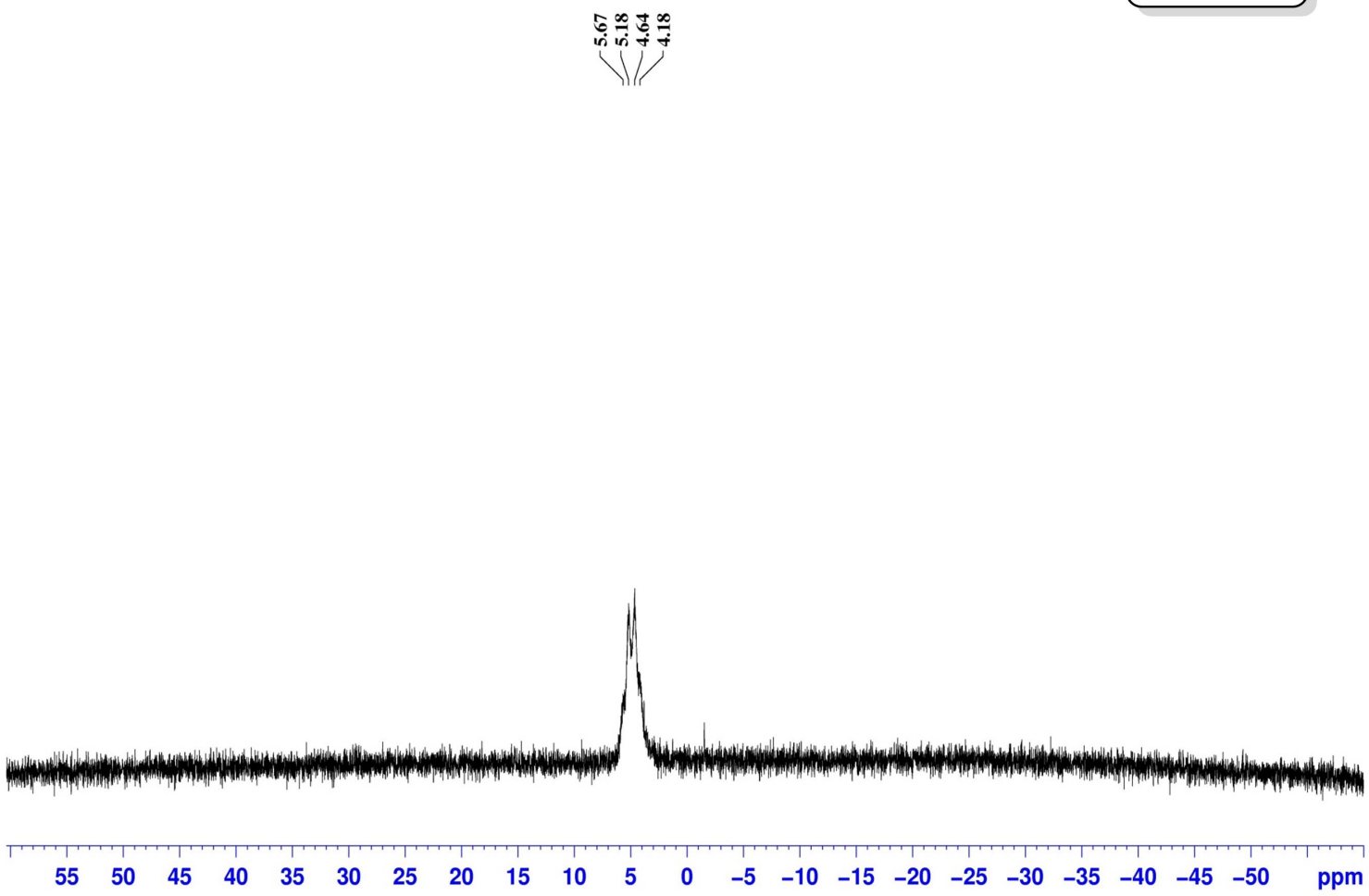


Potassium (1-methylcyclohexyl)trifluoroborate
128 MHz, Acetone-d_6

^{11}B NMR

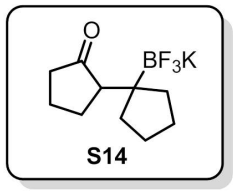


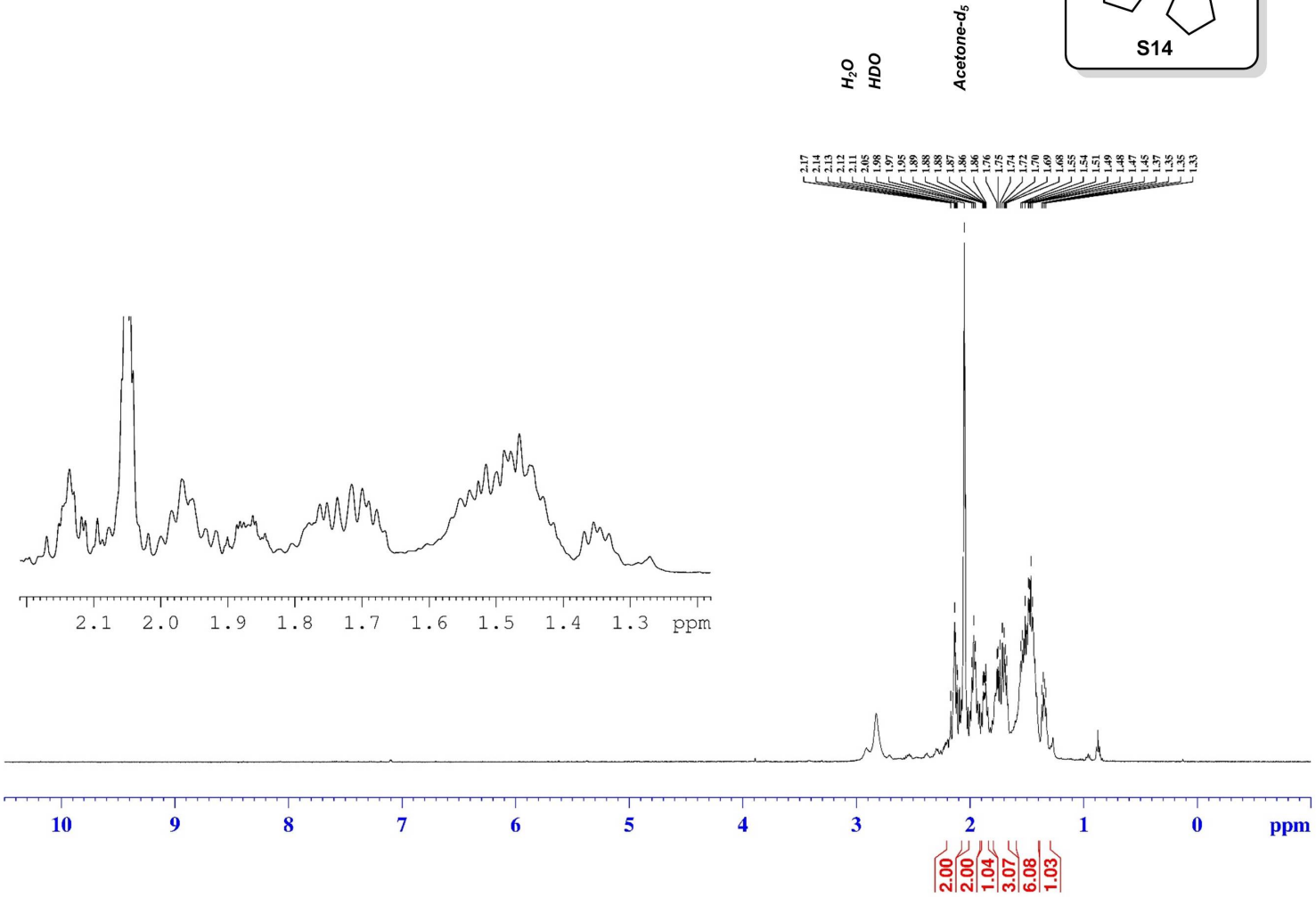
S11



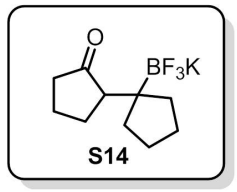
Potassium (2′-oxo-[1,1'-bi(cyclopentan)]-1-yl) trifluoroborate
500 MHz, Acetone-d_6

^1H NMR

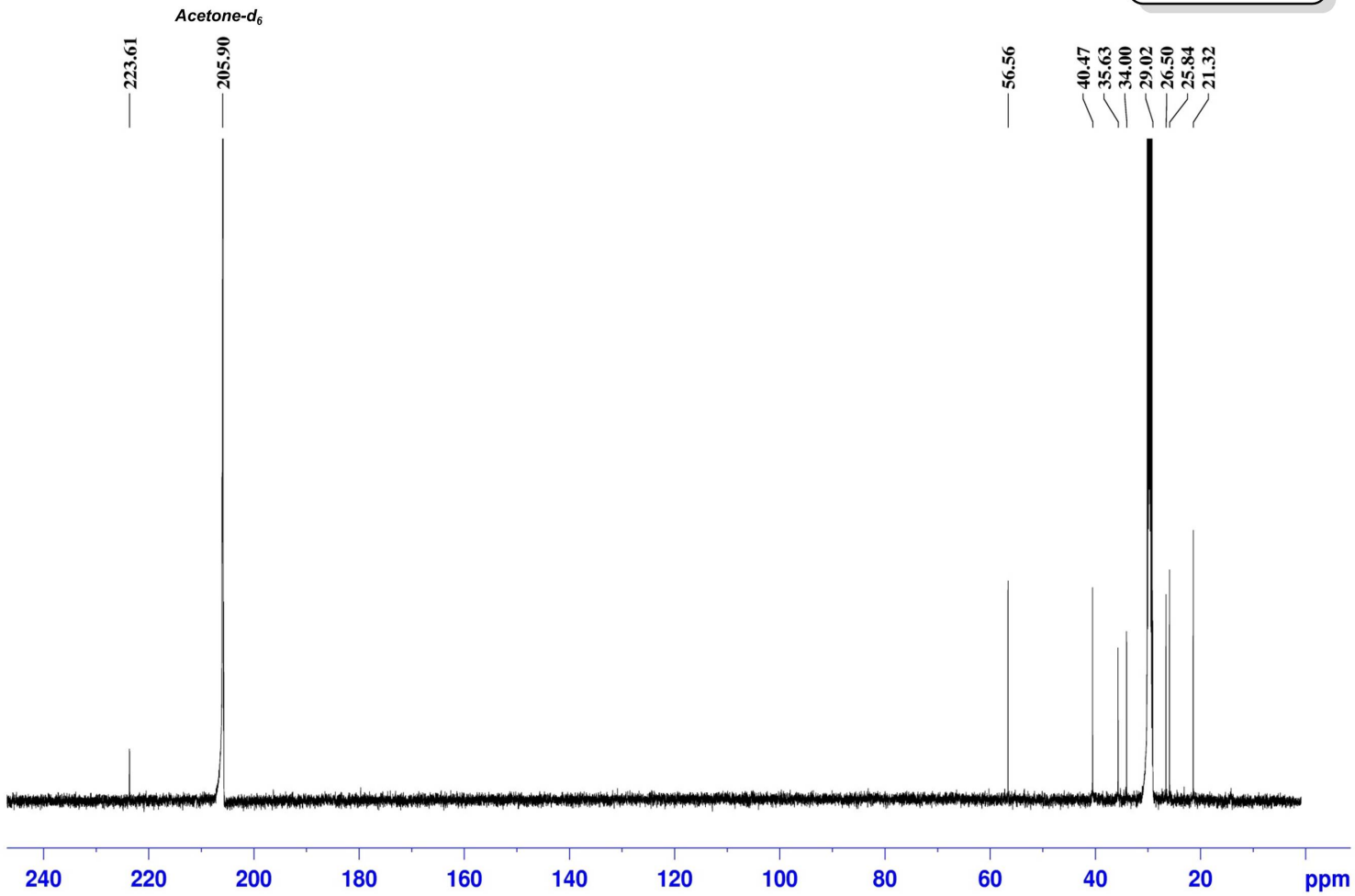




^{13}C NMR

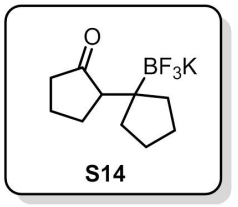


Potassium (2′-oxo-[1,1'-bi(cyclopentan)]-1-yl) trifluoroborate
125 MHz, Acetone-d_6

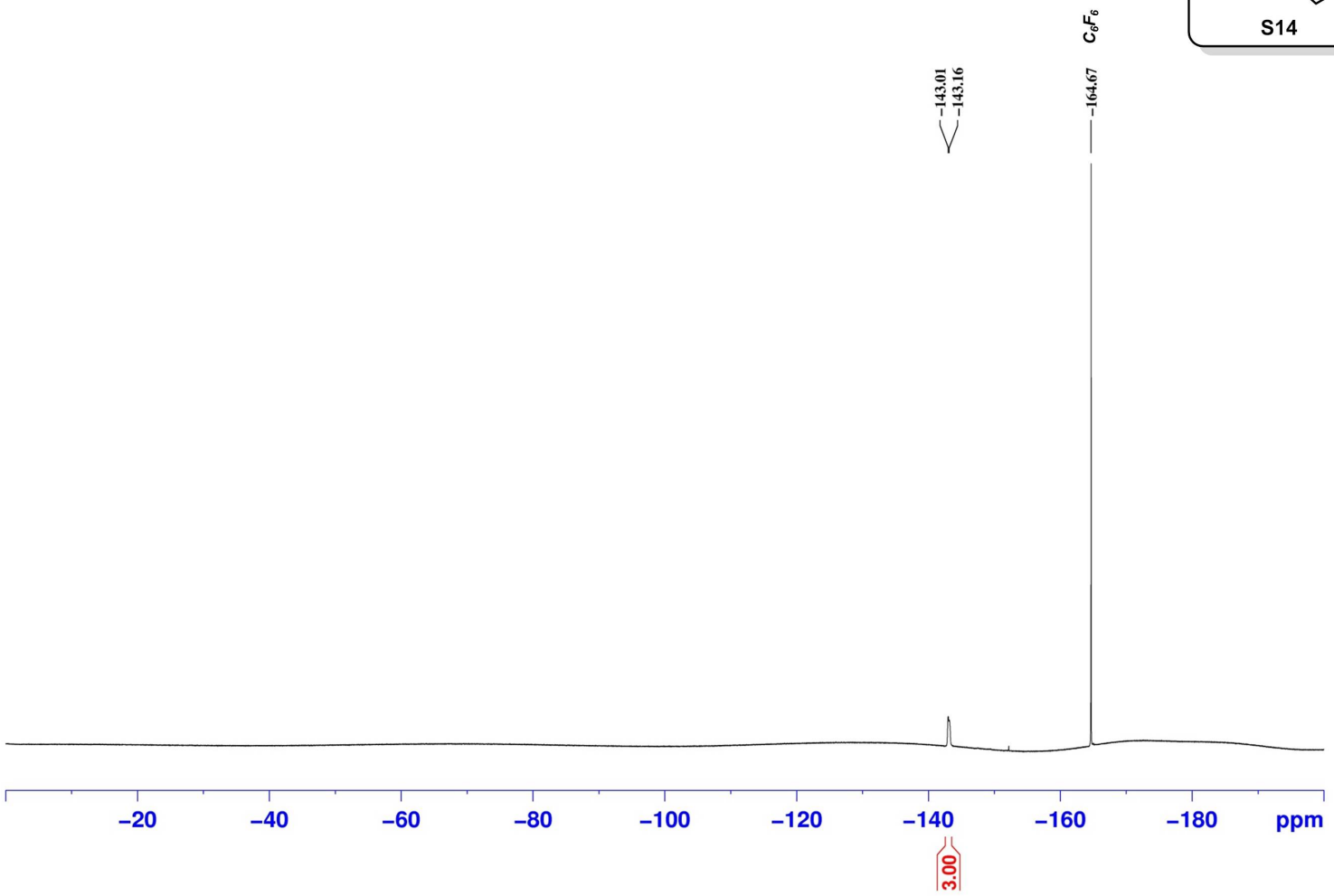


^{19}F NMR

Potassium (2′-oxo-[1,1'-bi(cyclopentan)]-1-yl) trifluoroborate
471 MHz, Acetone-d_6

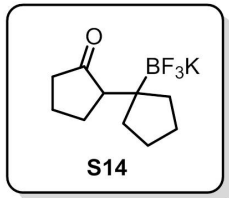


S14

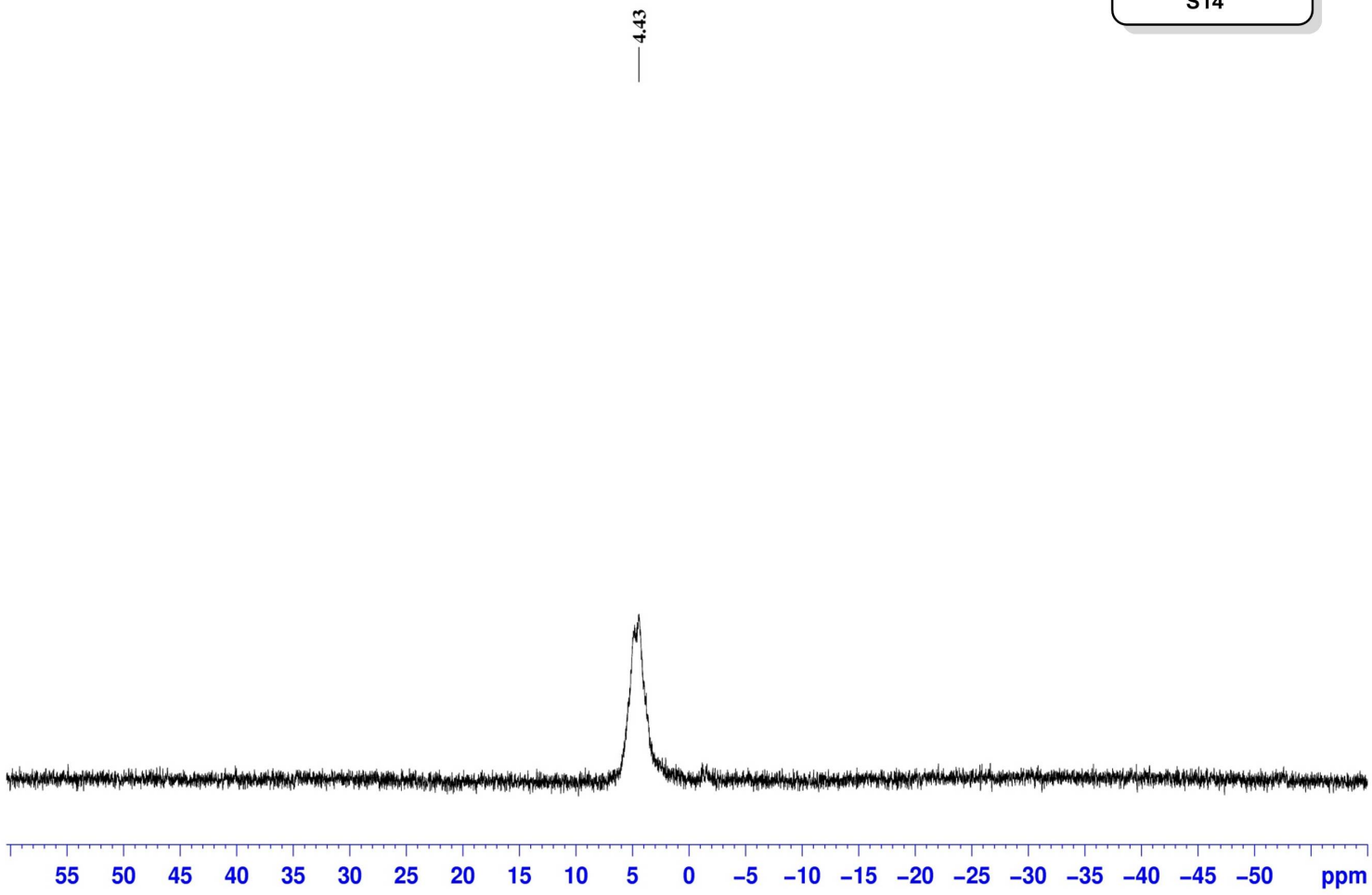


Potassium (2′-oxo-[1,1'-bi(cyclopentan)]-1-yl) trifluoroborate
128 MHz, Acetone-d_6

^{11}B NMR

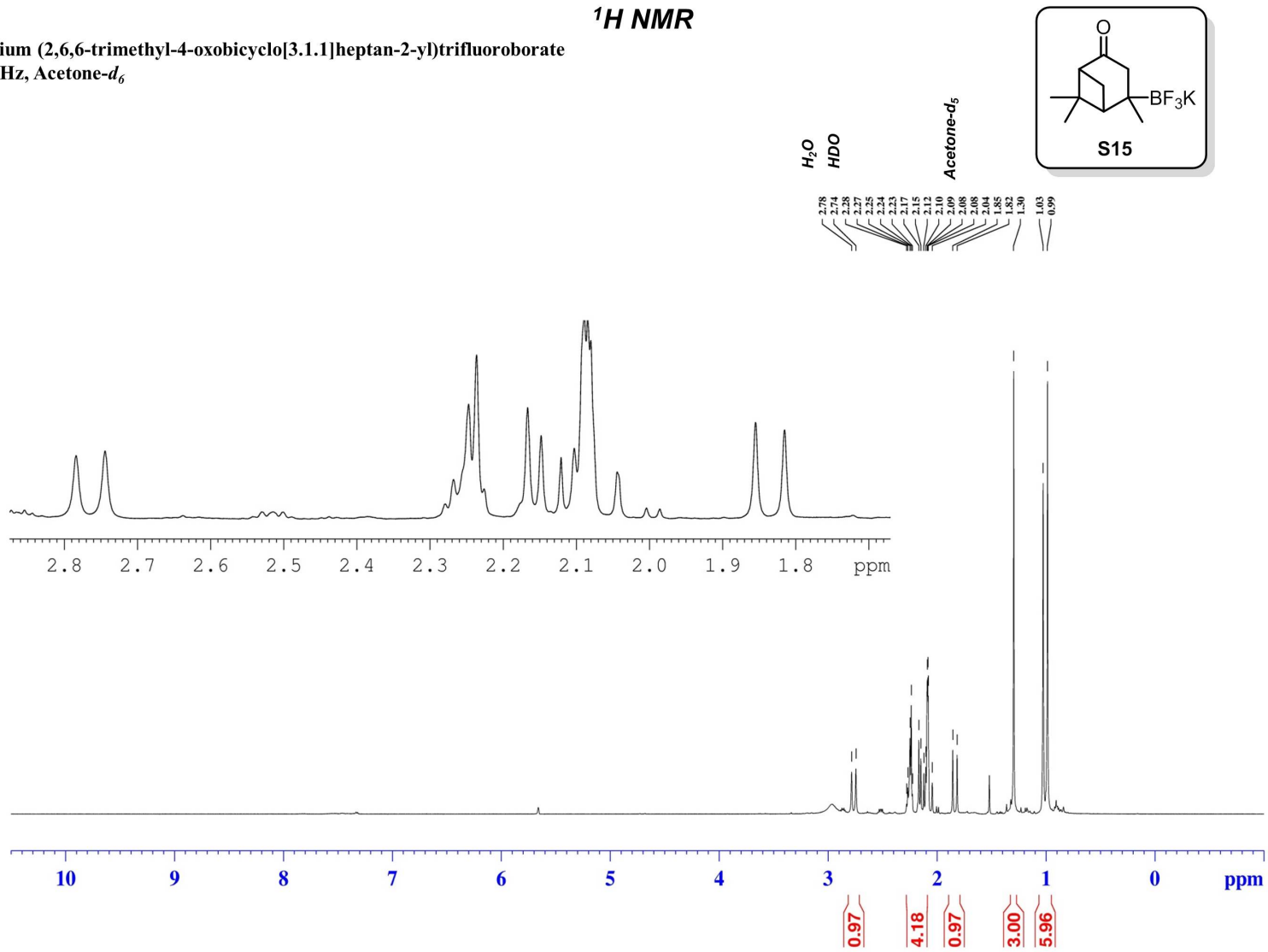


S14



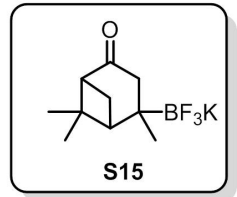
Potassium (2,6,6-trimethyl-4-oxobicyclo[3.1.1]heptan-2-yl)trifluoroborate
500 MHz, Acetone-d_6

^1H NMR

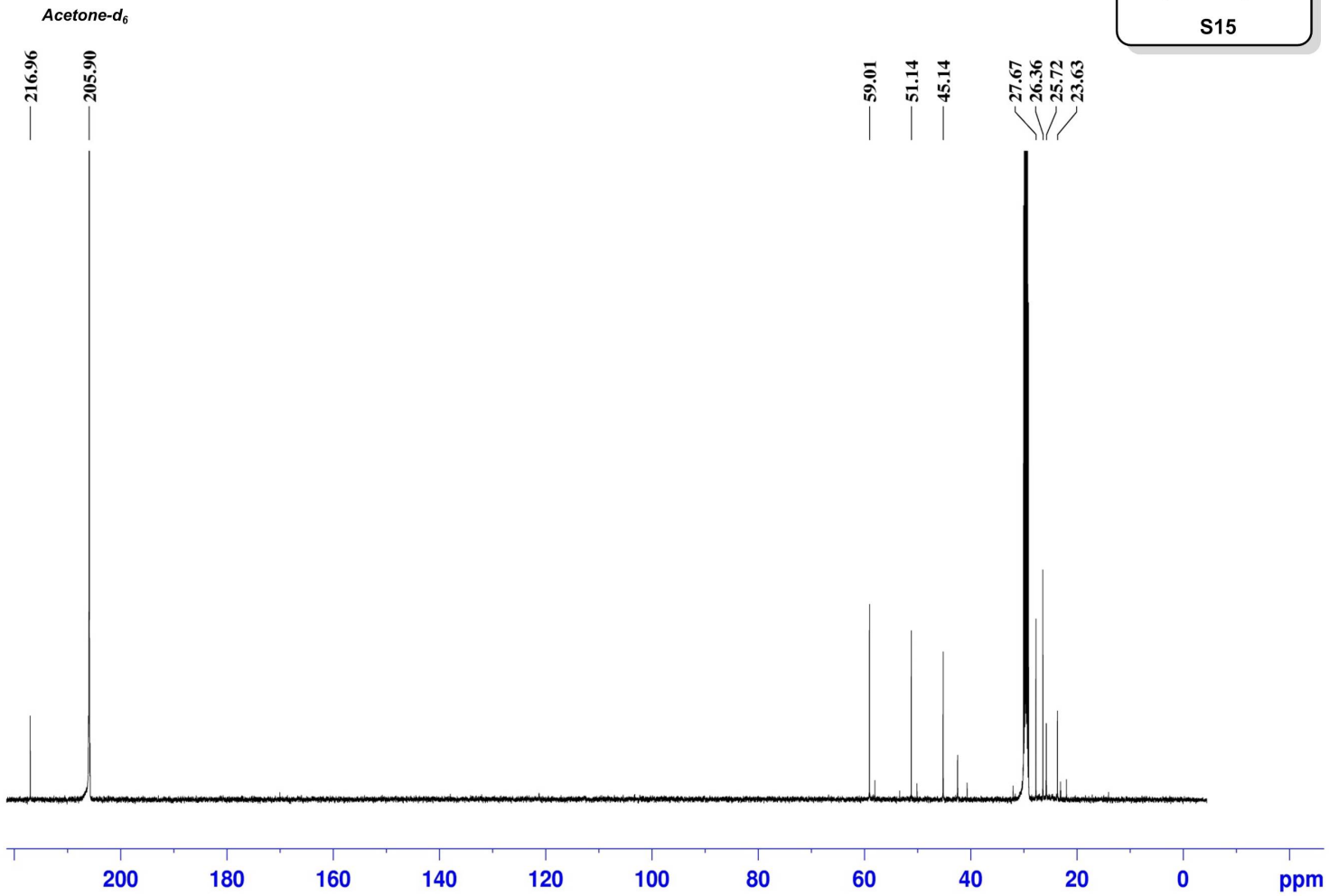


^{13}C NMR

Potassium (2,6,6-trimethyl-4-oxobicyclo[3.1.1]heptan-2-yl)trifluoroborate
125 MHz, Acetone-d_6

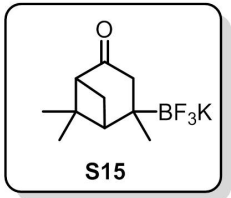


S15

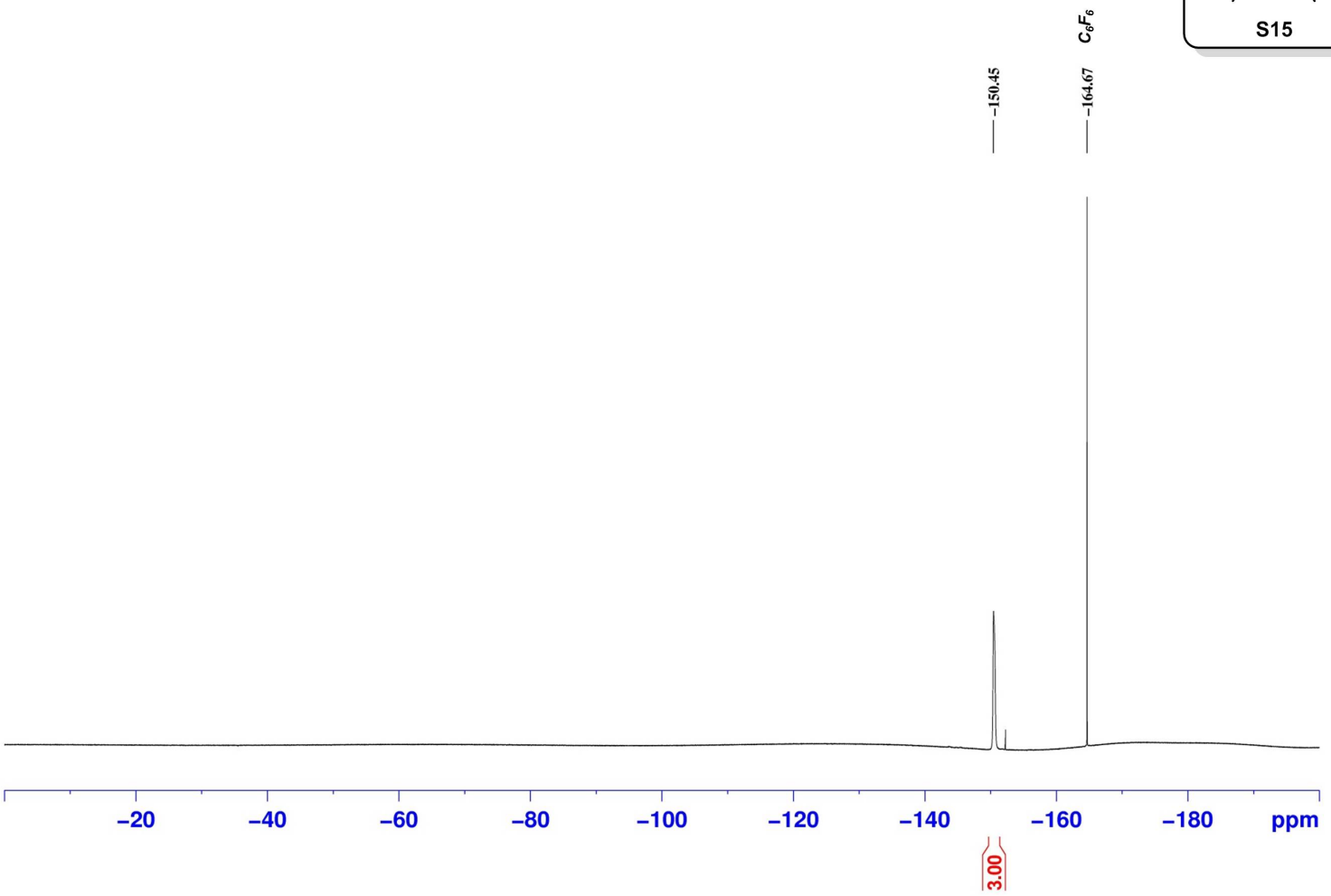


^{19}F NMR

Potassium (2,6,6-trimethyl-4-oxobicyclo[3.1.1]heptan-2-yl)trifluoroborate
471 MHz, Acetone-d_6

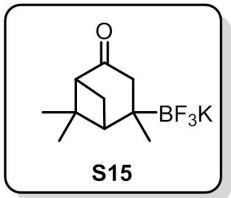


S15

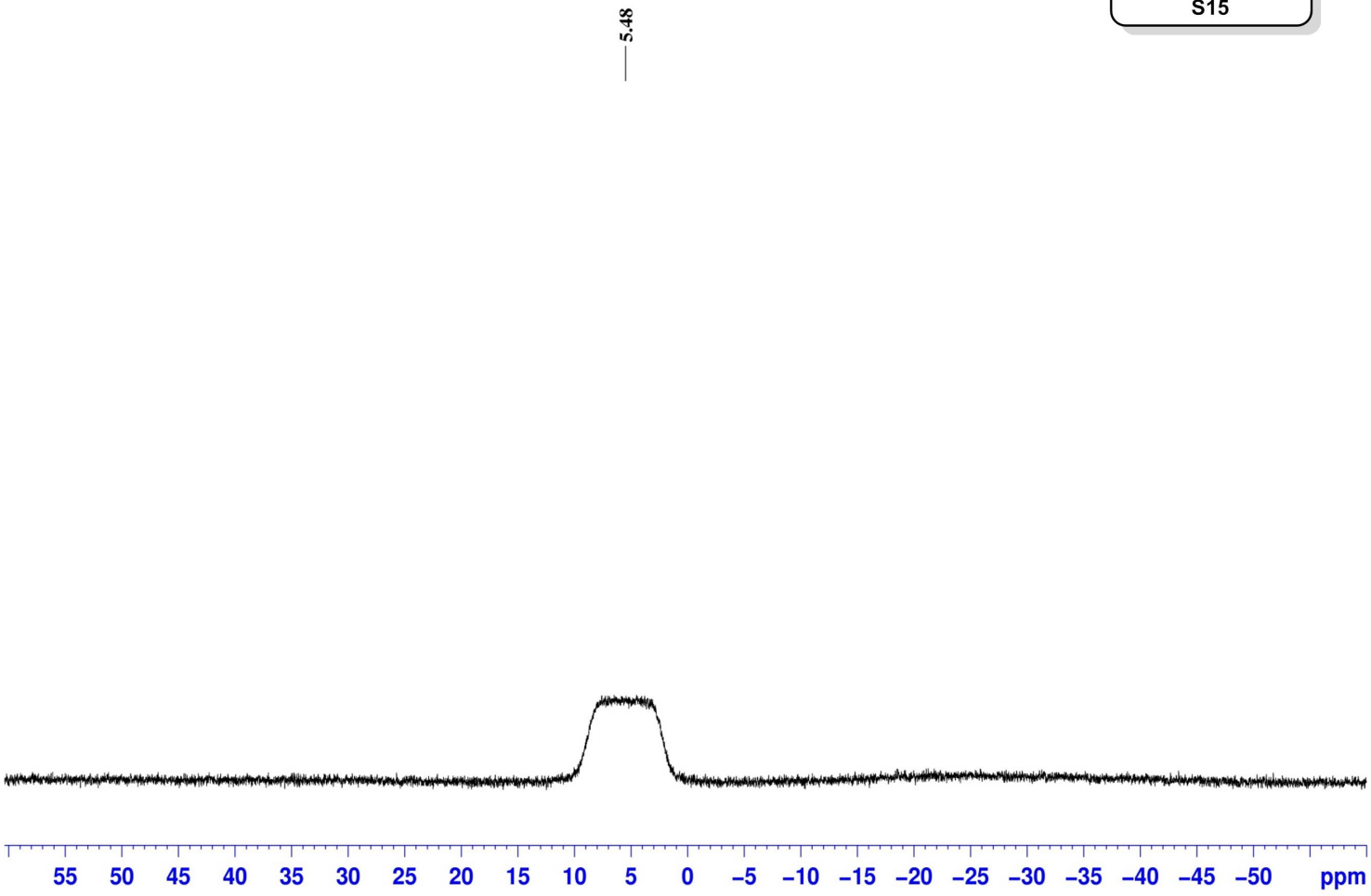


^{11}B NMR

Potassium (2,6,6-trimethyl-4-oxobicyclo[3.1.1]heptan-2-yl)trifluoroborate
128 MHz, Acetone-d_6

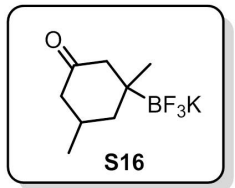


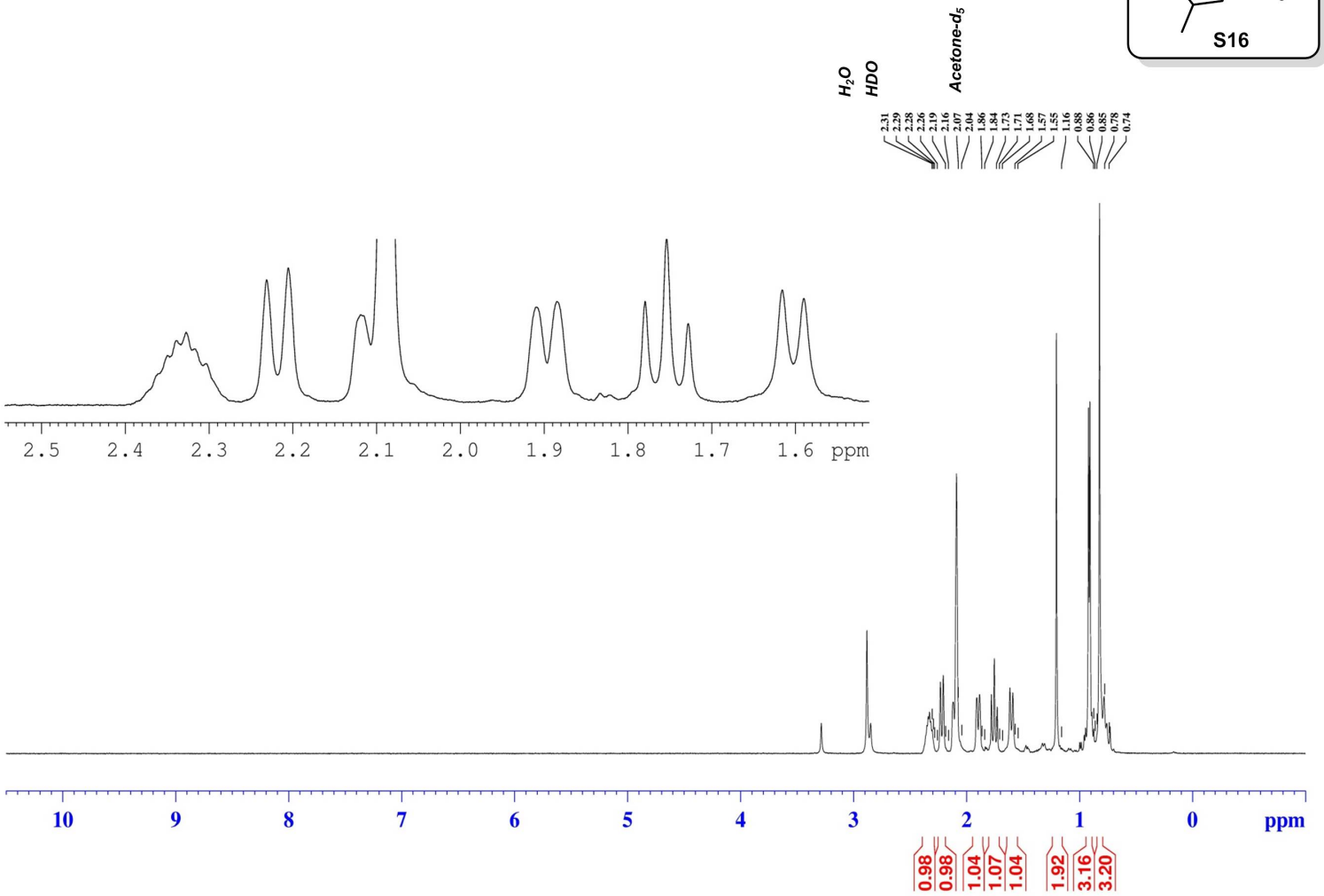
S15



Potassium (1,3-dimethyl-5-oxocyclohexyl)trifluoroborate
500 MHz, Acetone-d_6

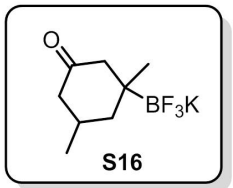
^1H NMR



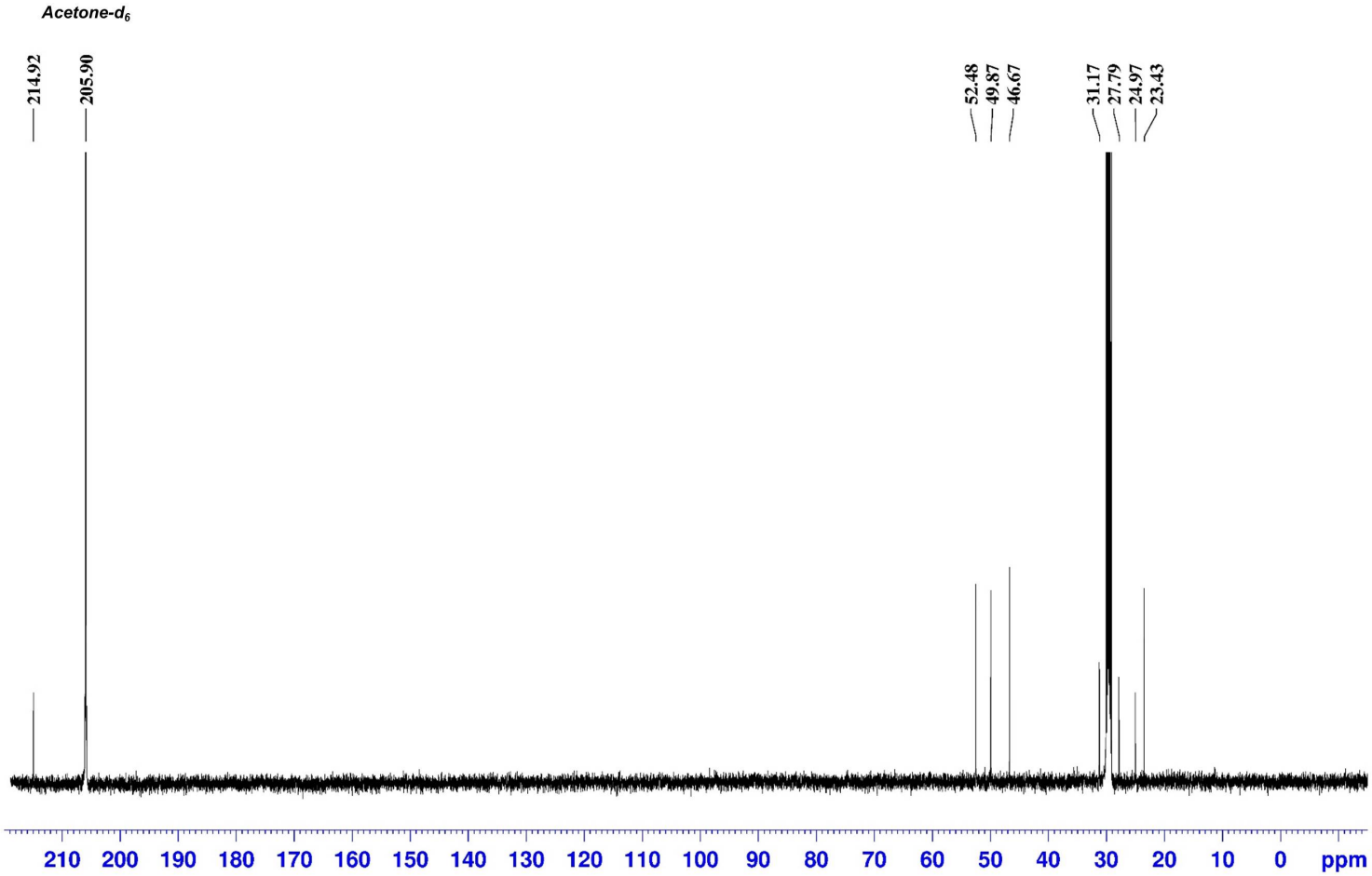


^{13}C NMR

Potassium (1,3-dimethyl-5-oxocyclohexyl)trifluoroborate
125 MHz, Acetone-d_6

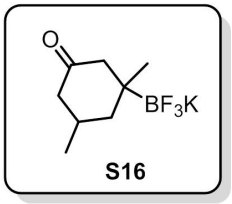


S16

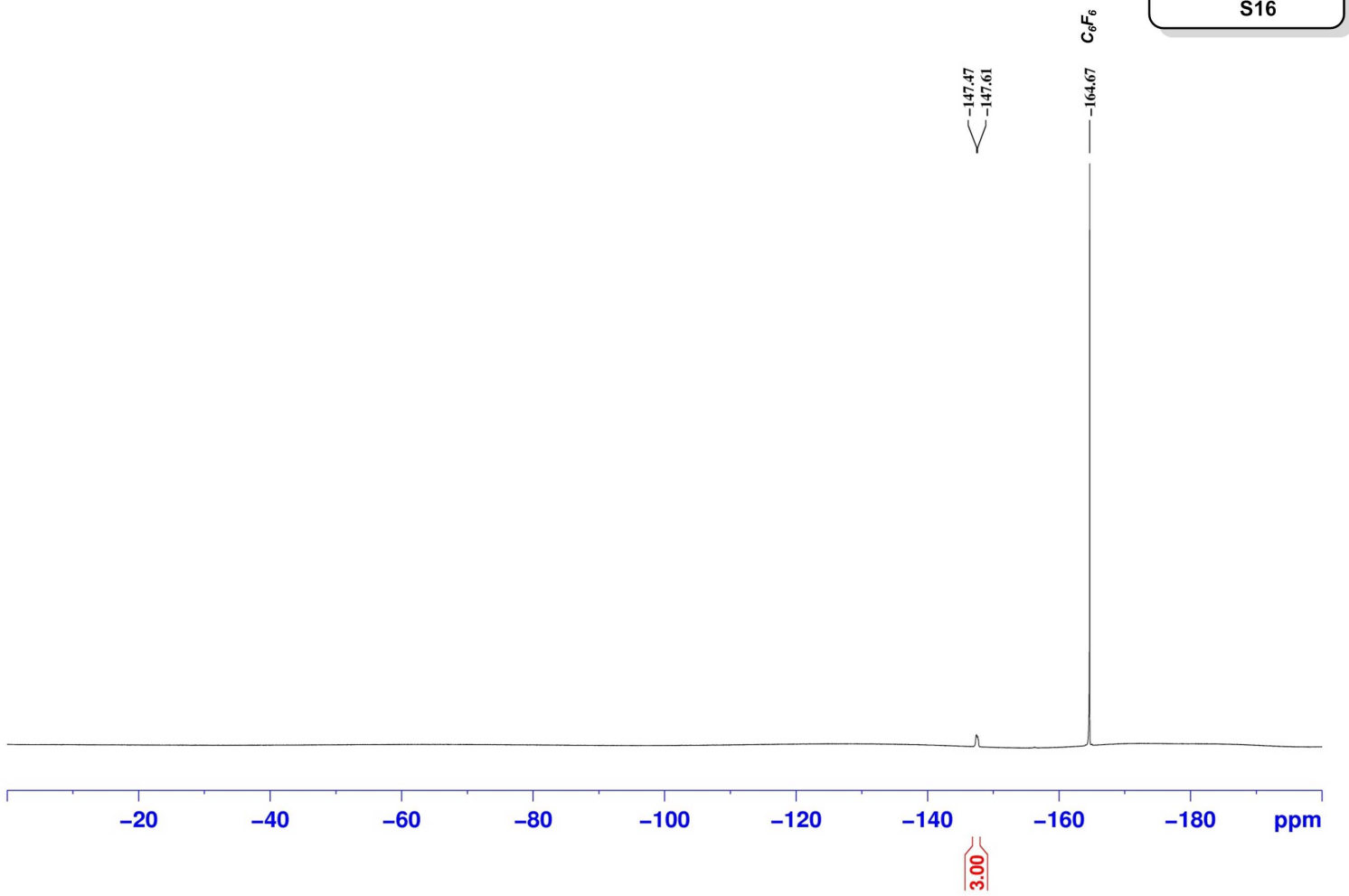


Potassium (1,3-dimethyl-5-oxocyclohexyl)trifluoroborate
471 MHz, Acetone-d_6

^{19}F NMR

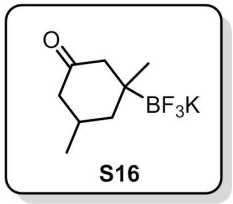


S16

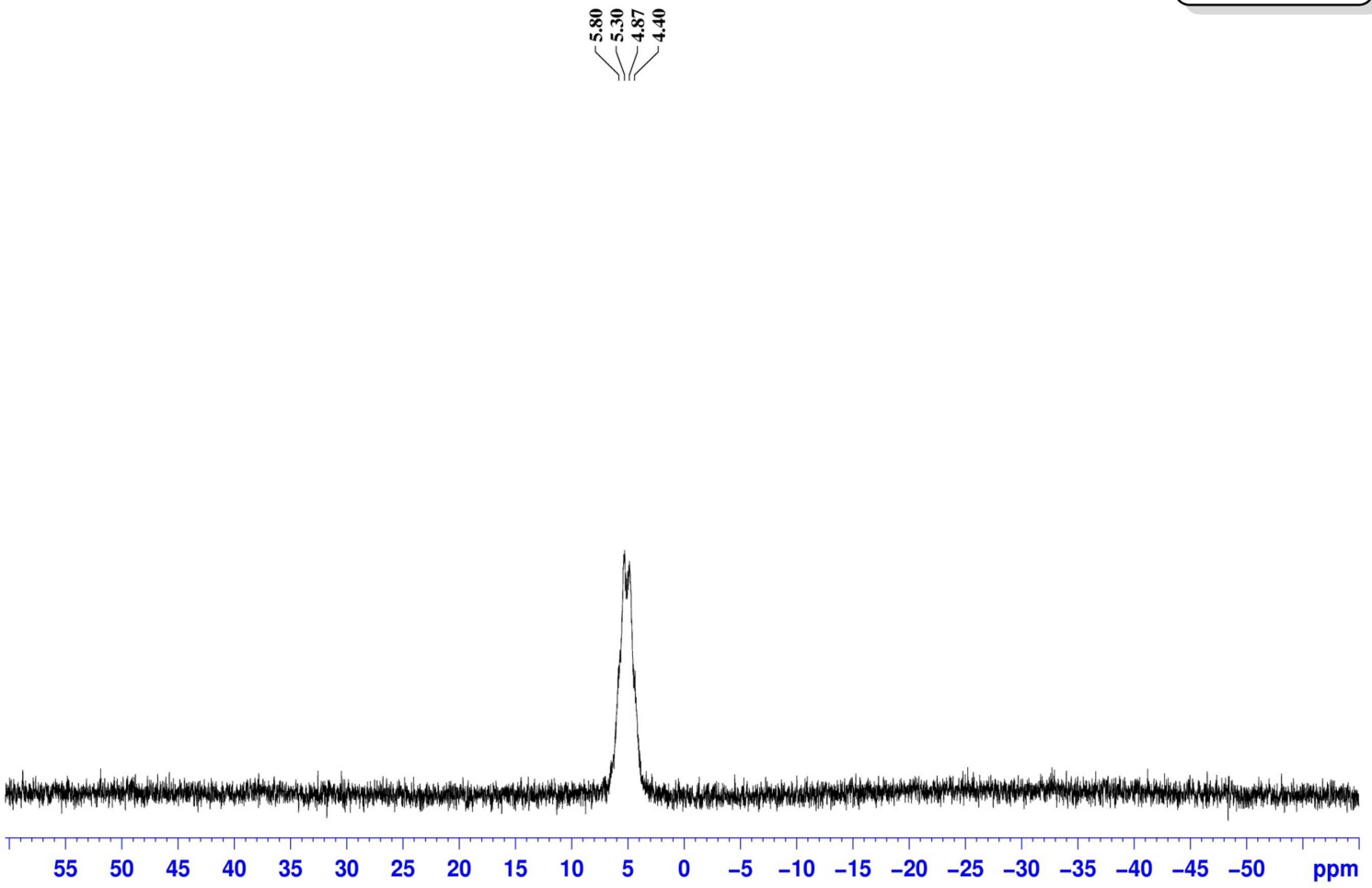


Potassium (1,3-dimethyl-5-oxocyclohexyl)trifluoroborate
128 MHz, Acetone-d_6

^{11}B NMR

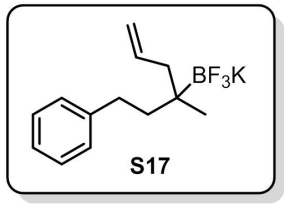


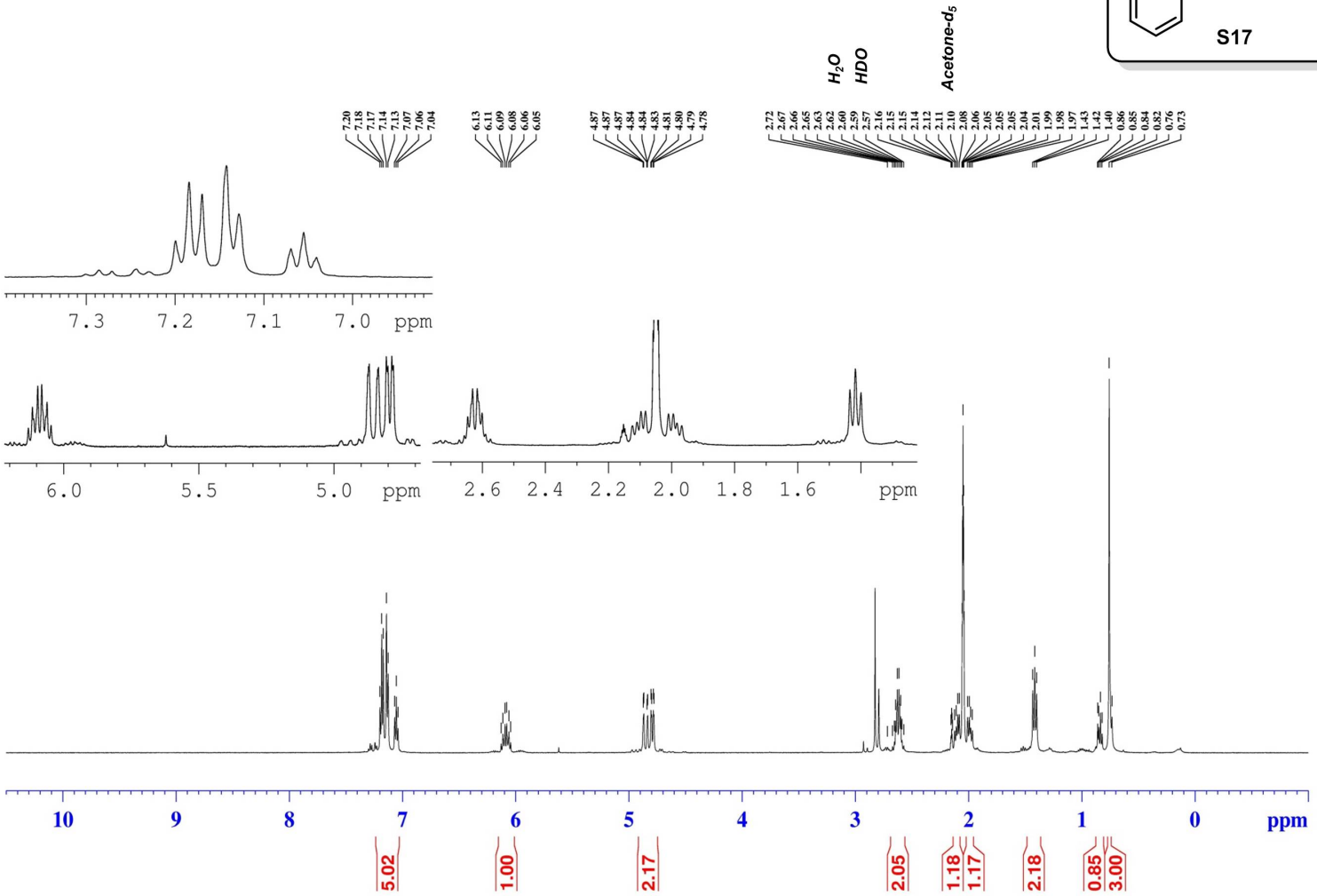
S16



Potassium (1,3-dimethyl-5-oxocyclohexyl)trifluoroborate
500 MHz, Acetone-d_6

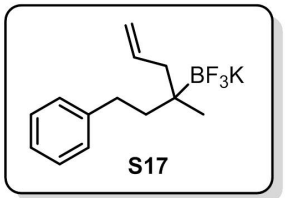
^1H NMR



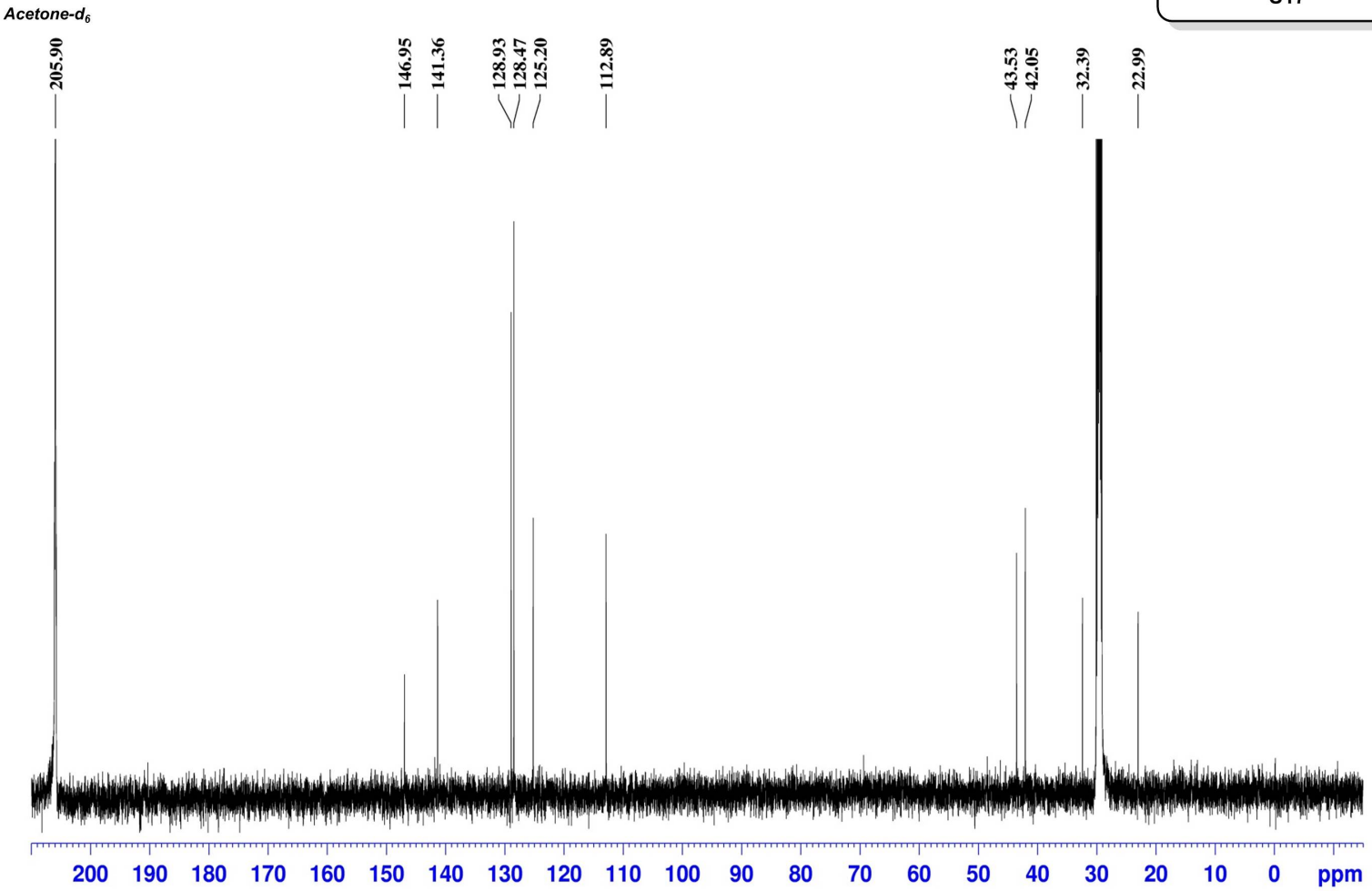


^{13}C NMR

Potassium (1,3-dimethyl-5-oxocyclohexyl)trifluoroborate
125 MHz, Acetone-d_6

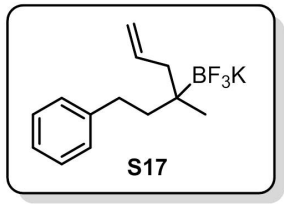


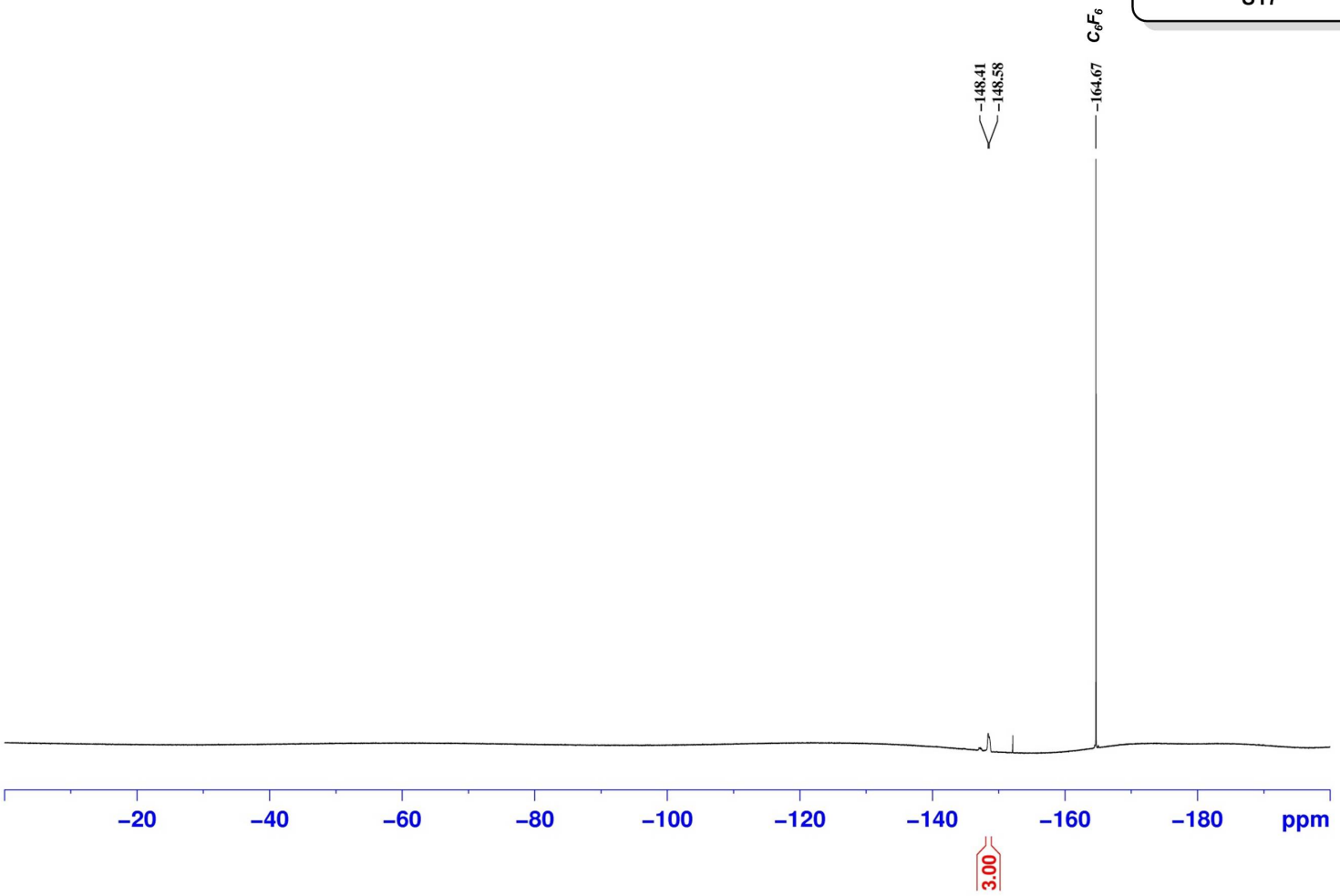
S17



Potassium (1,3-dimethyl-5-oxocyclohexyl)trifluoroborate
471 MHz, Acetone-d_6

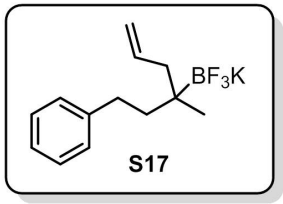
^{19}F NMR

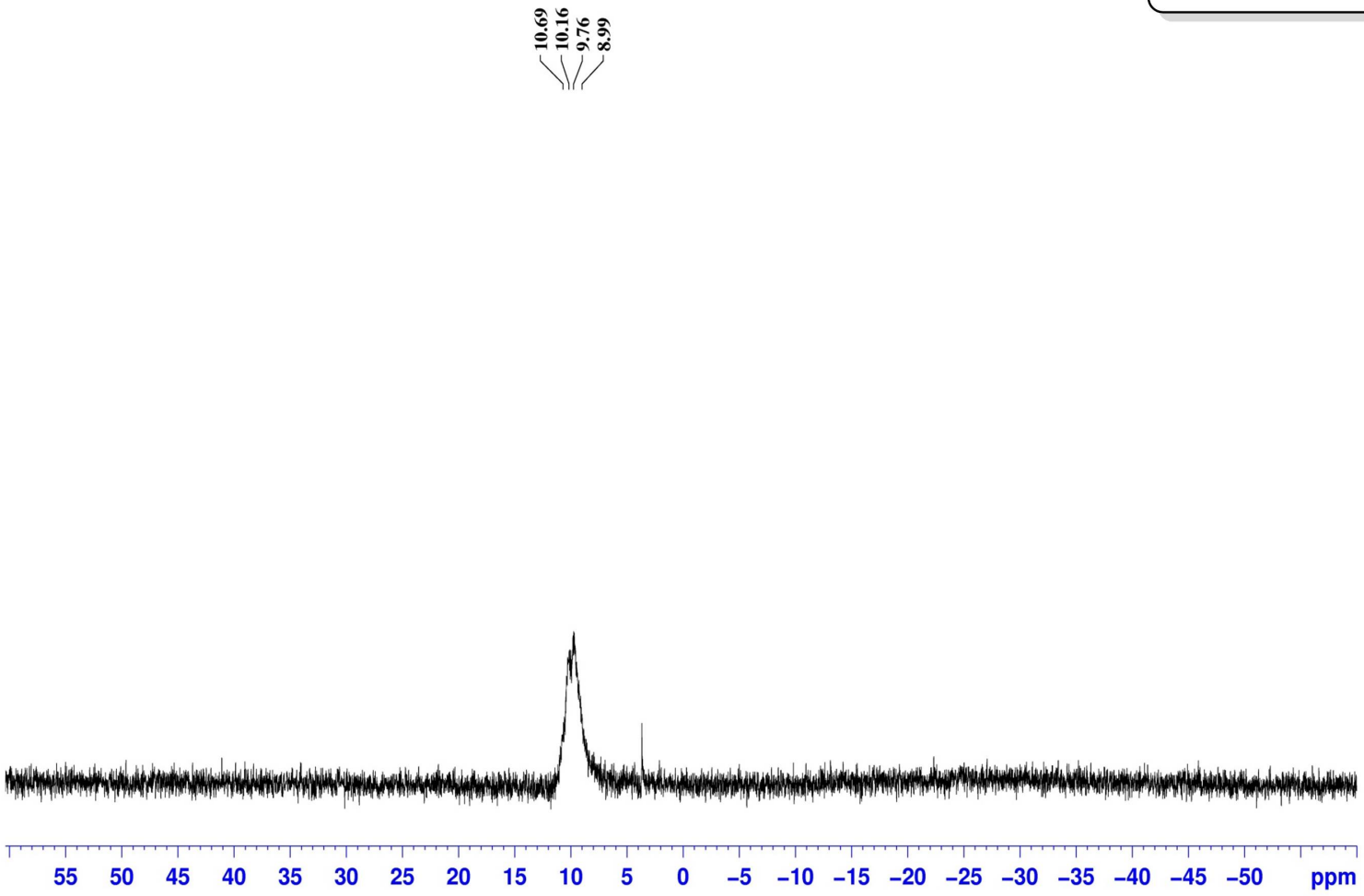




Potassium (1,3-dimethyl-5-oxocyclohexyl)trifluoroborate
128 MHz, Acetone-d_6

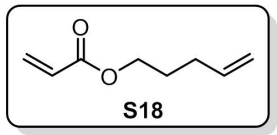
^{11}B NMR

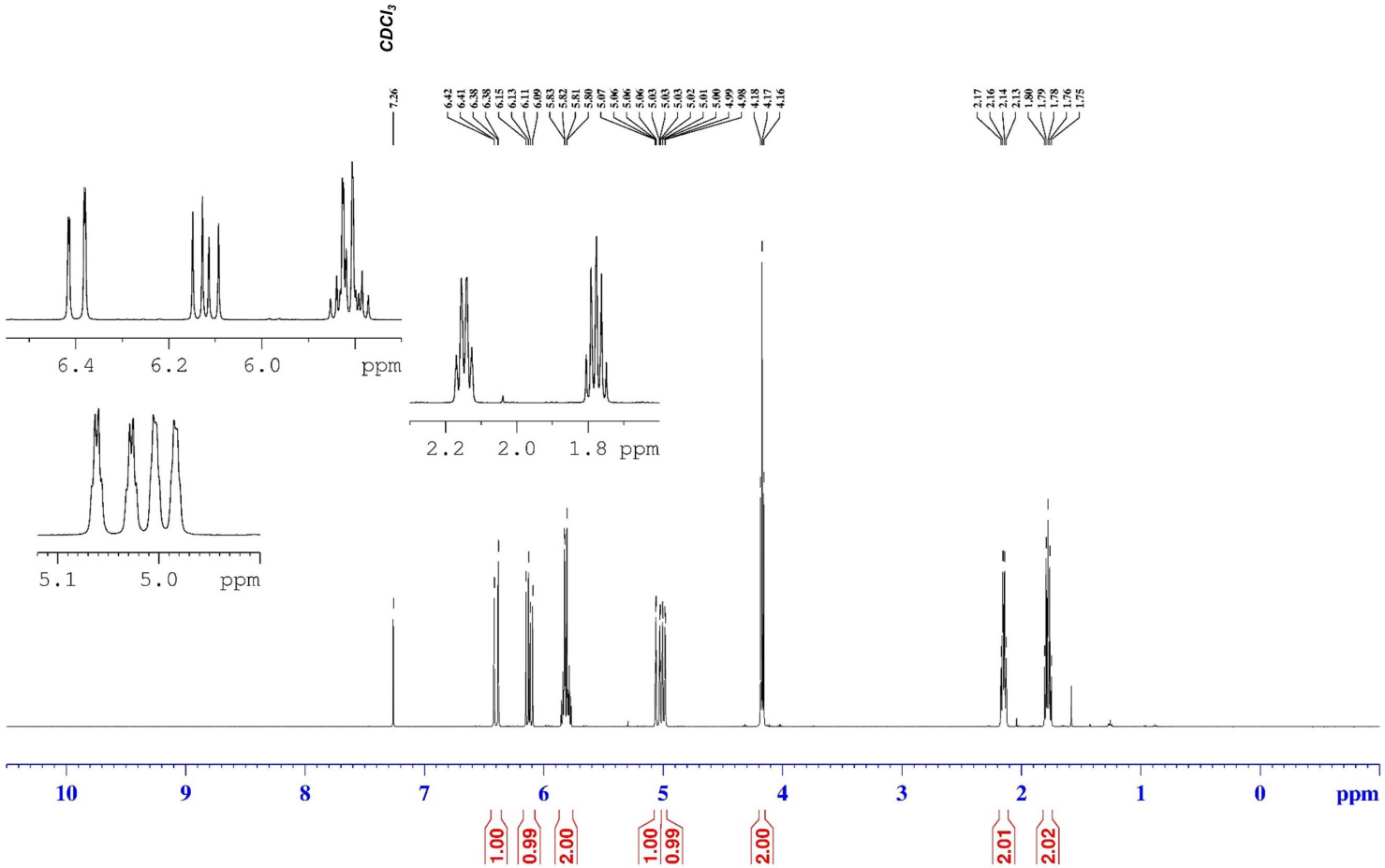




Pent-4-en-1-yl acrylate
500 MHz, $CDCl_3$

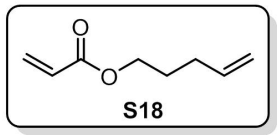
^1H NMR

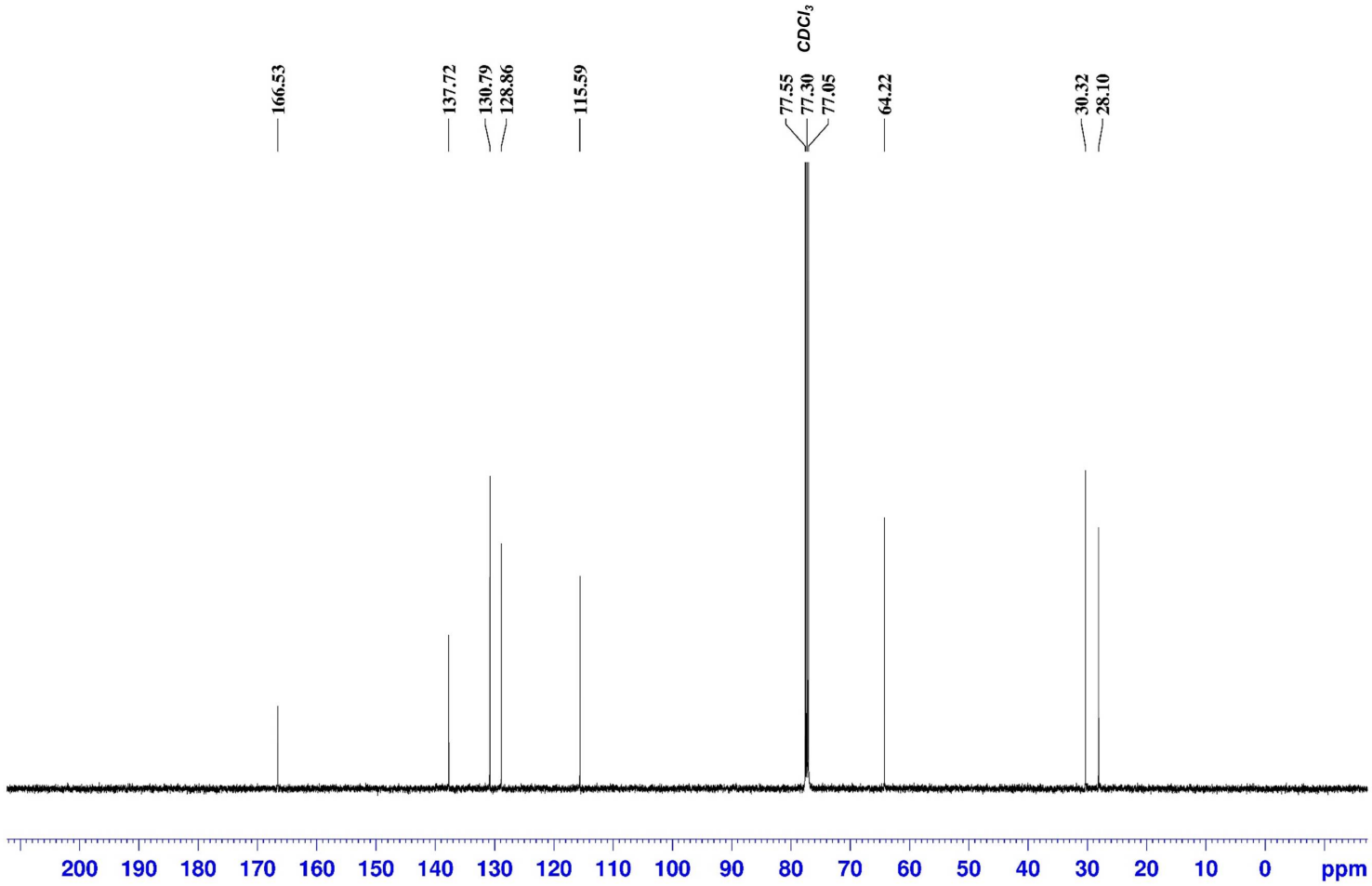




Pent-4-en-1-yl acrylate
125 MHz, $CDCl_3$

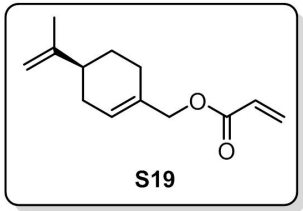
^1H NMR

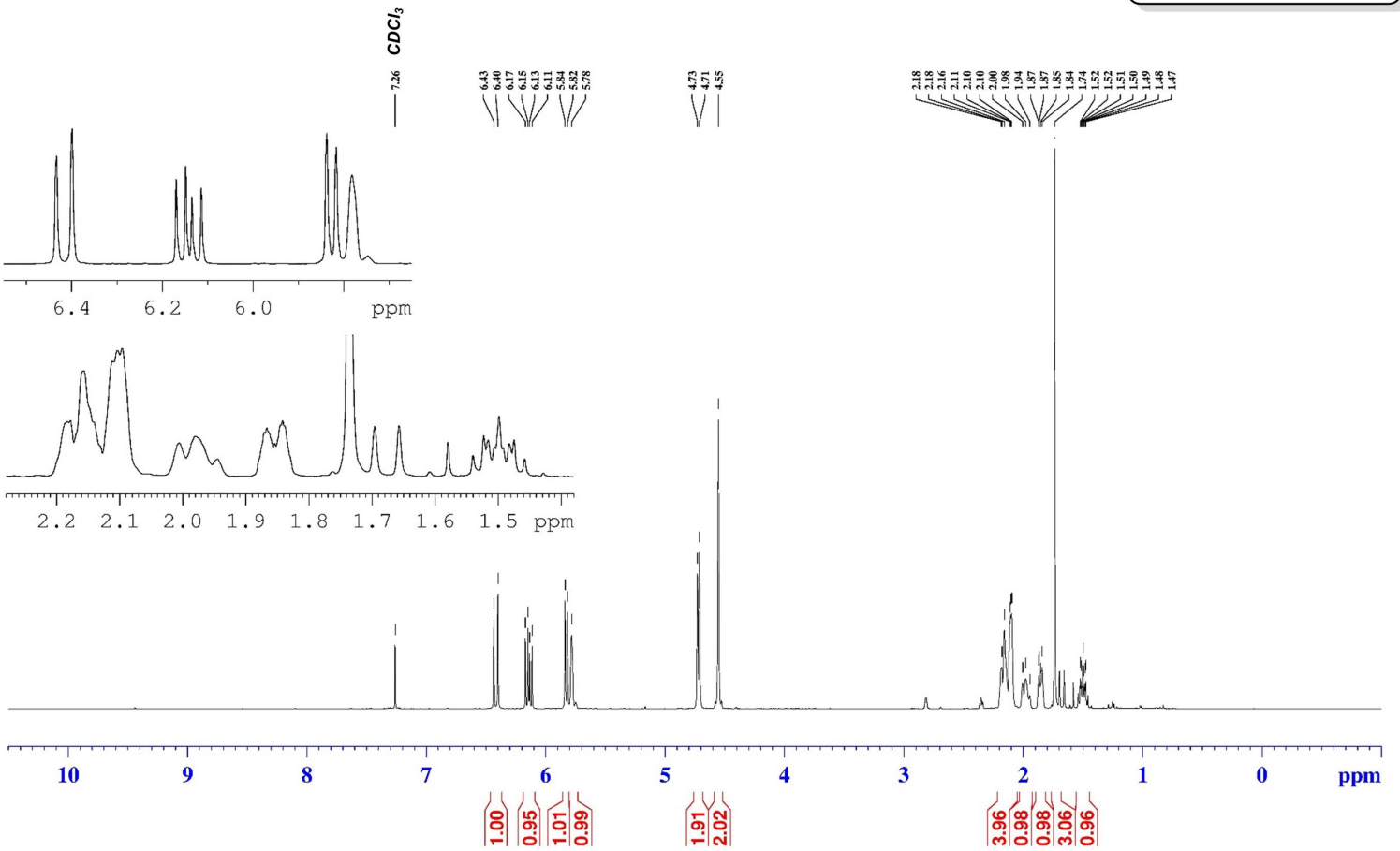




^1H NMR

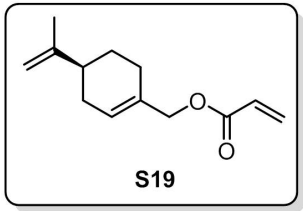
(*S*)-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl acrylate
500 MHz, $CDCl_3$

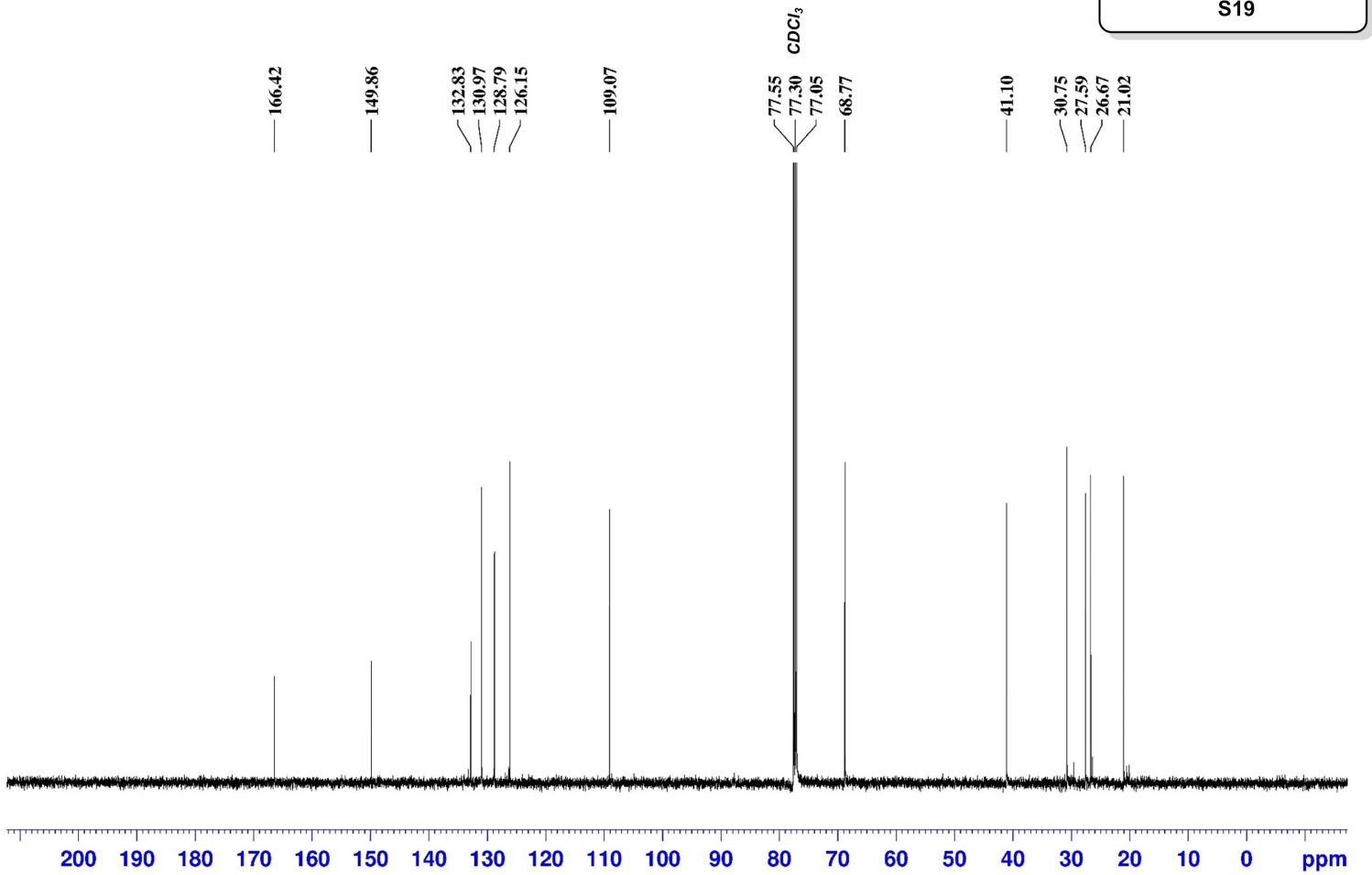




^1H NMR

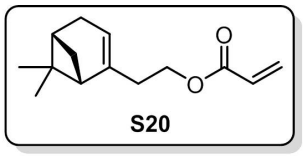
(*S*)-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl acrylate
125 MHz, $CDCl_3$

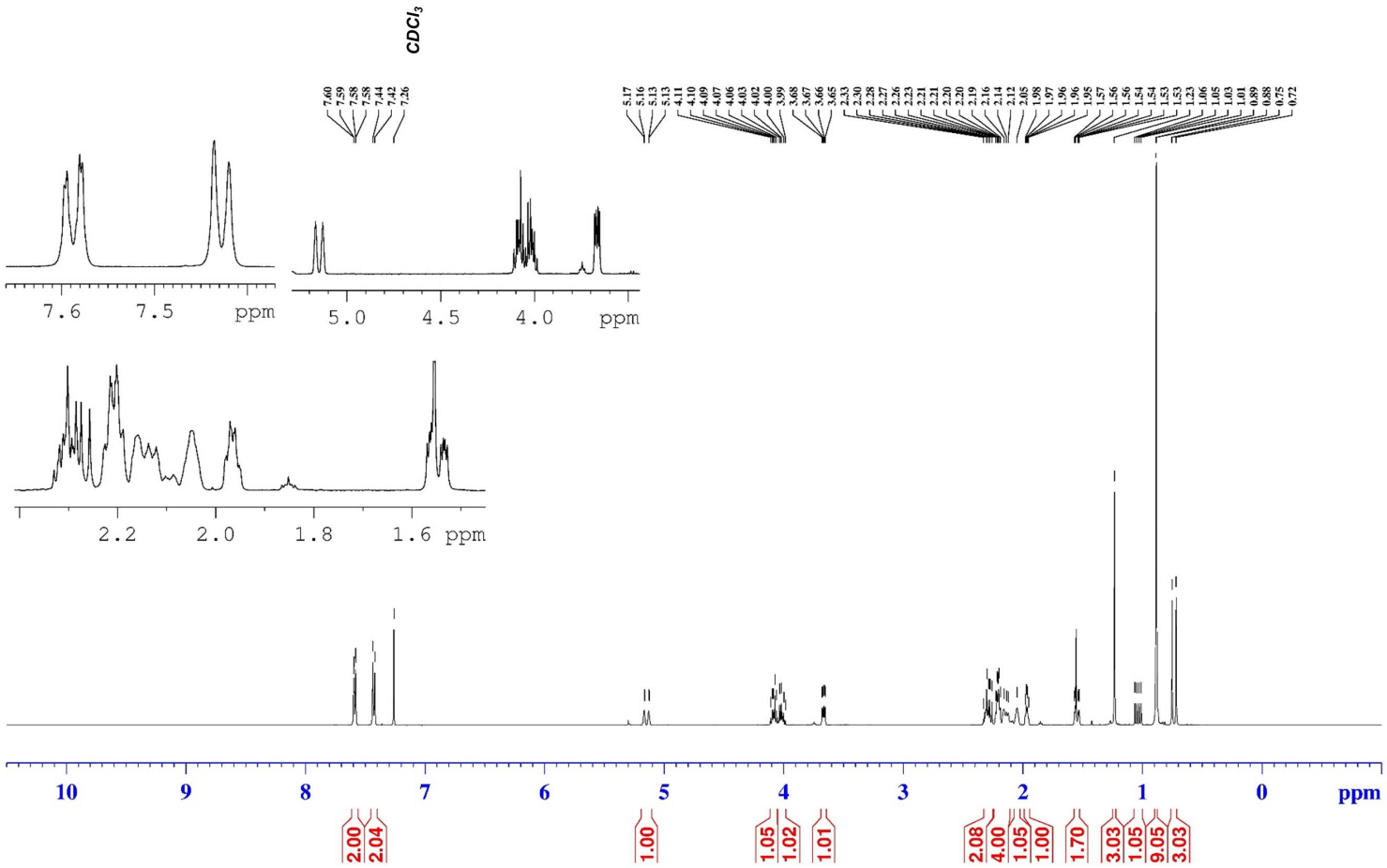




^1H NMR

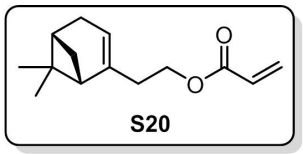
2-((*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl acrylate
500 MHz, $CDCl_3$

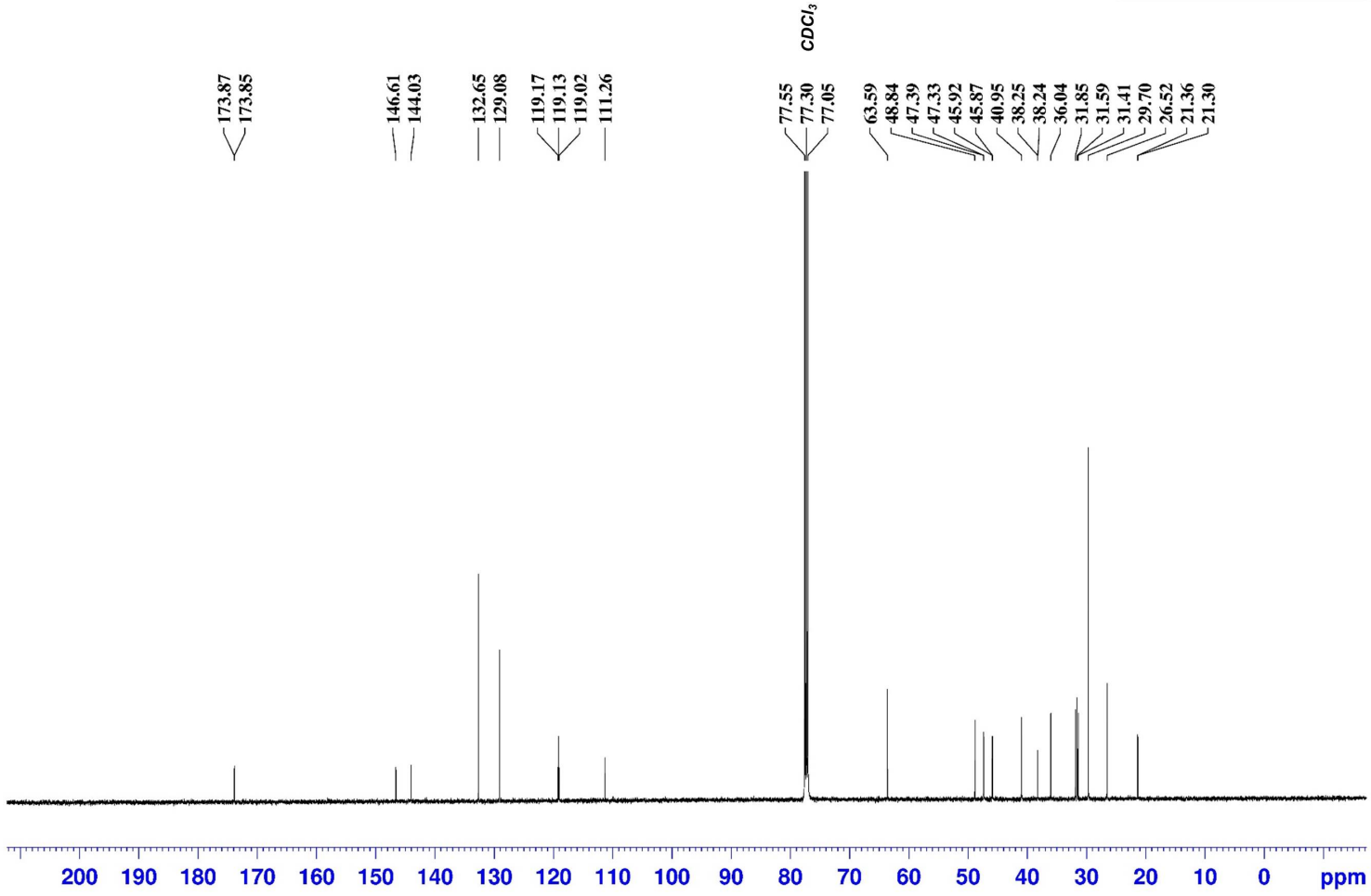




^1H NMR

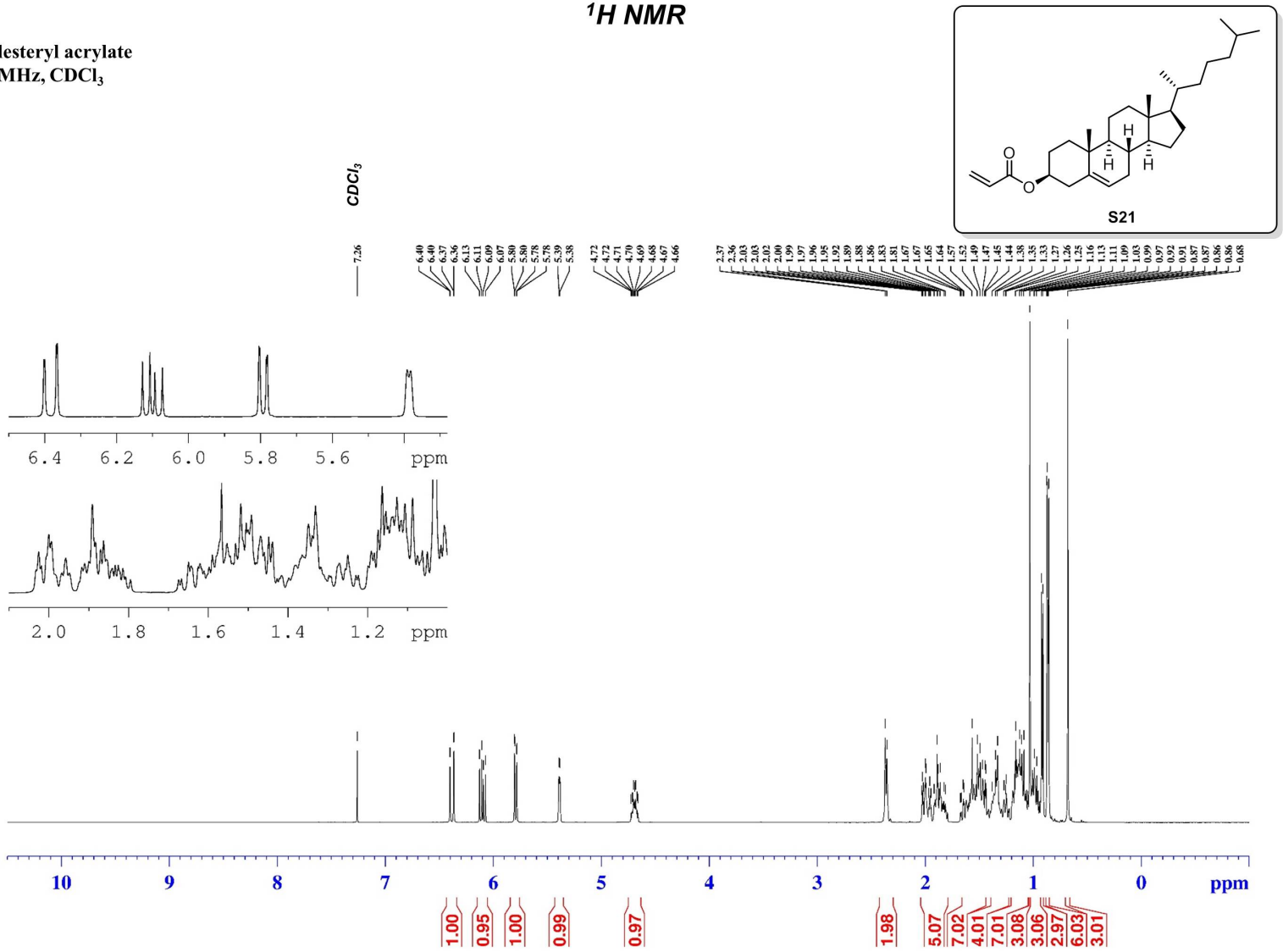
2-((*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl acrylate
125 MHz, $CDCl_3$





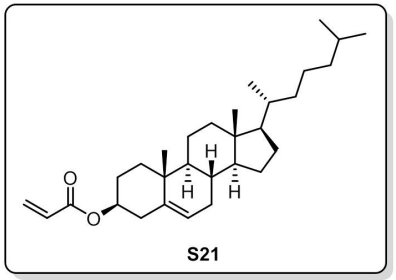
Cholesteryl acrylate
500 MHz, $CDCl_3$

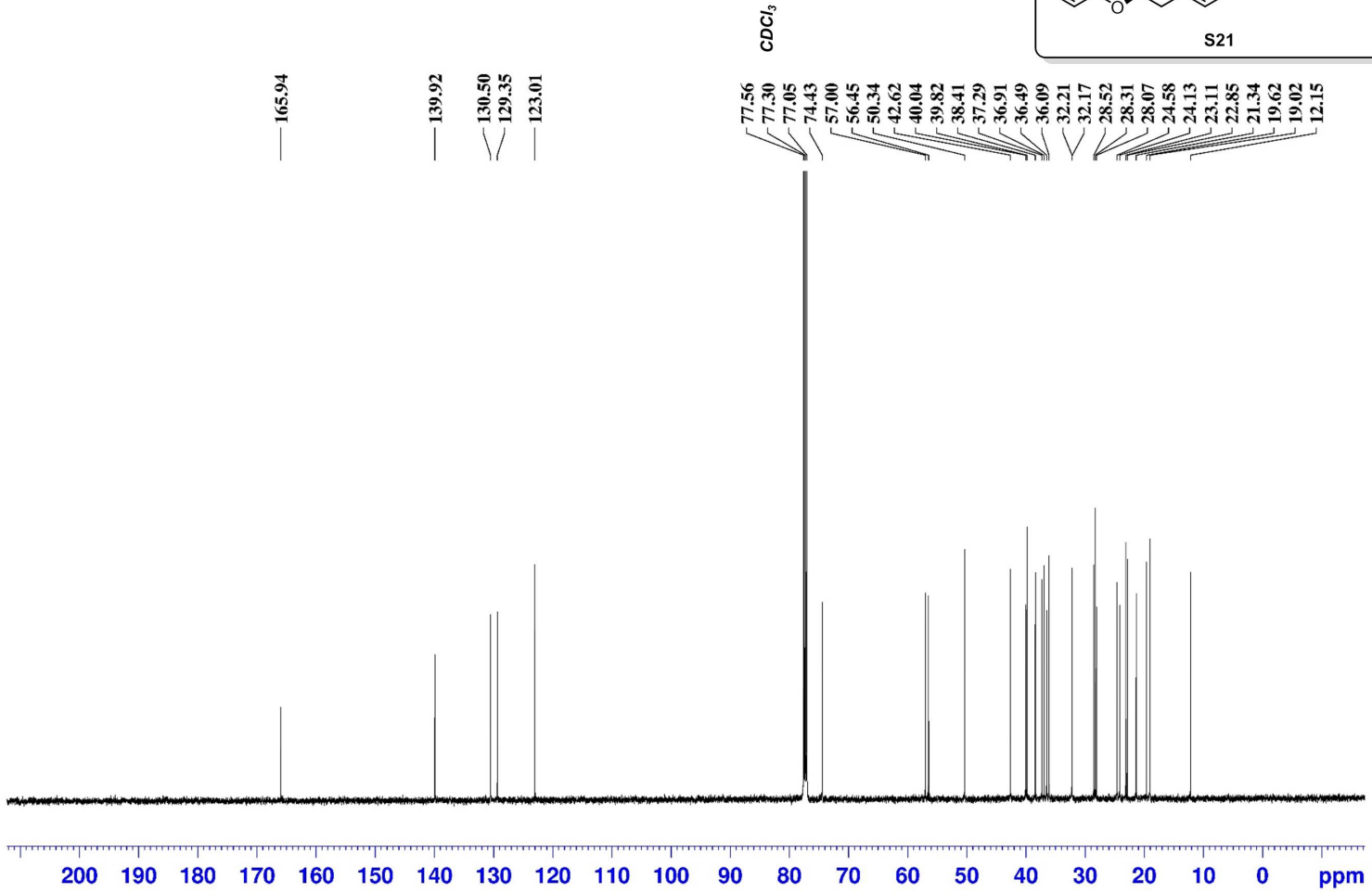
^1H NMR



Cholesteryl acrylate
125 MHz, $CDCl_3$

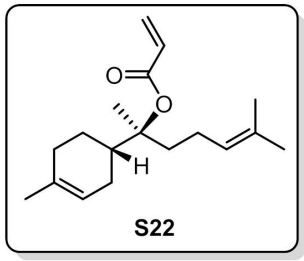
^1H NMR



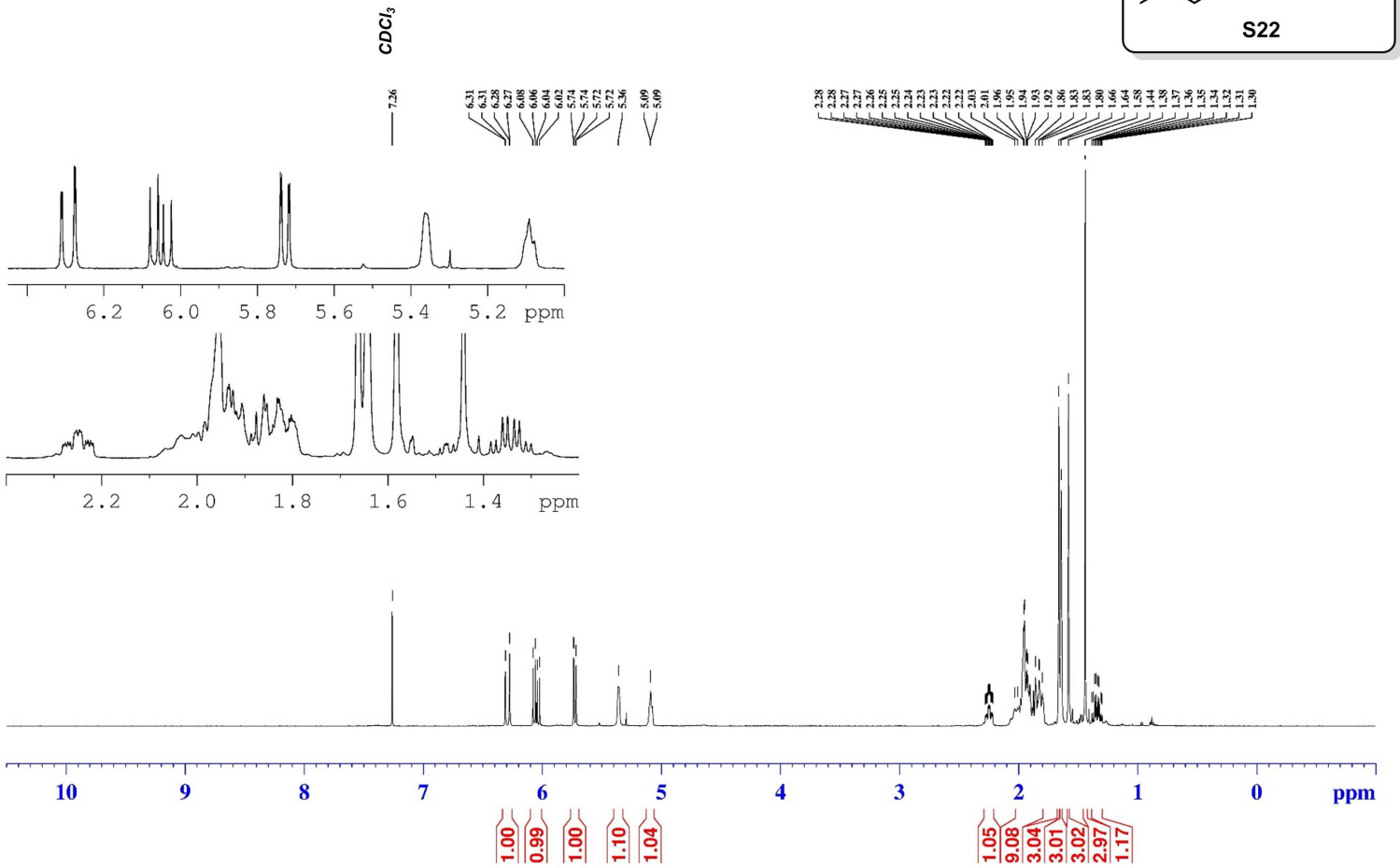


^{1}H NMR

(*S*)-6-methyl-2-((*S*)-4-methylcyclohex-3-en-1-yl)hept-5-en-2-yl acrylate
500 MHz, $CDCl_3$

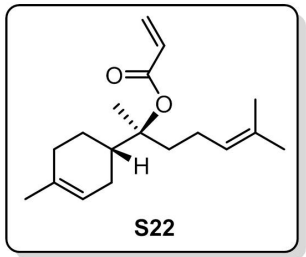


S22

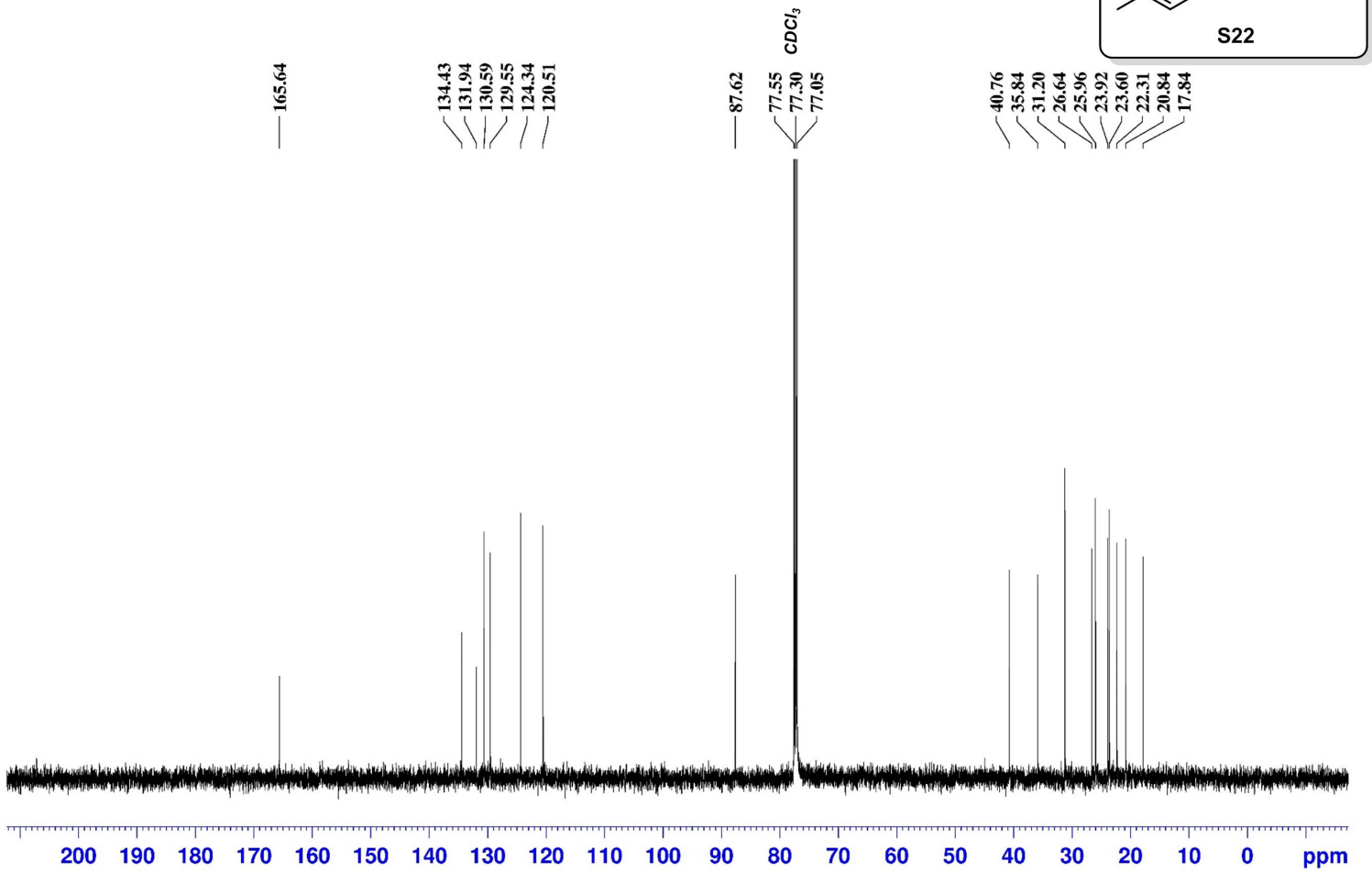


^1H NMR

(*S*)-6-methyl-2-((*S*)-4-methylcyclohex-3-en-1-yl)hept-5-en-2-yl acrylate
125 MHz, $CDCl_3$

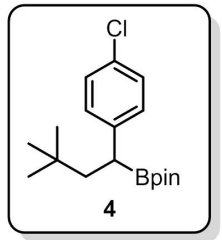


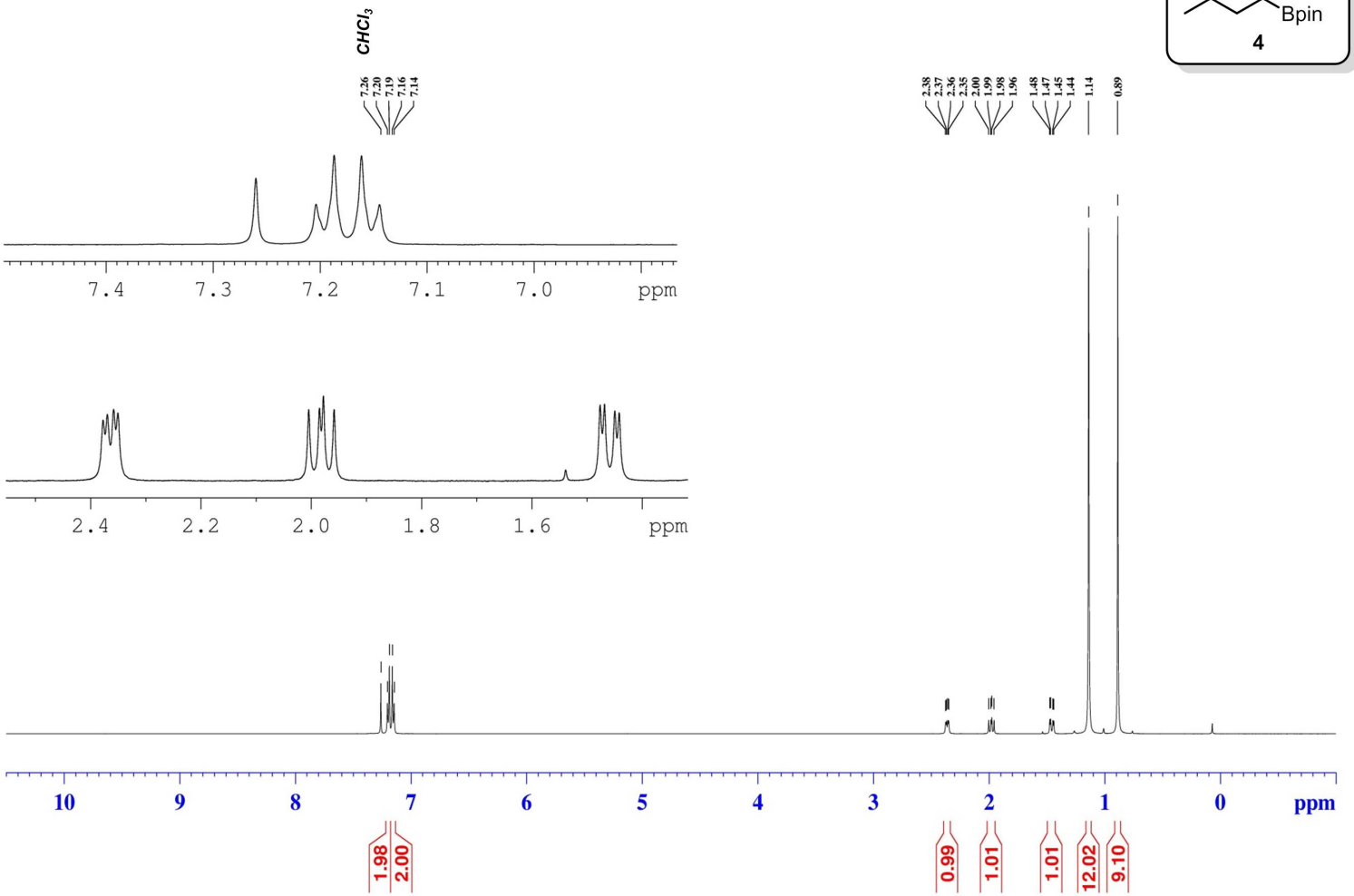
S22



^1H NMR

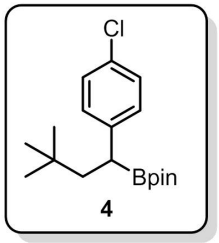
2-(1-(4-chlorophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

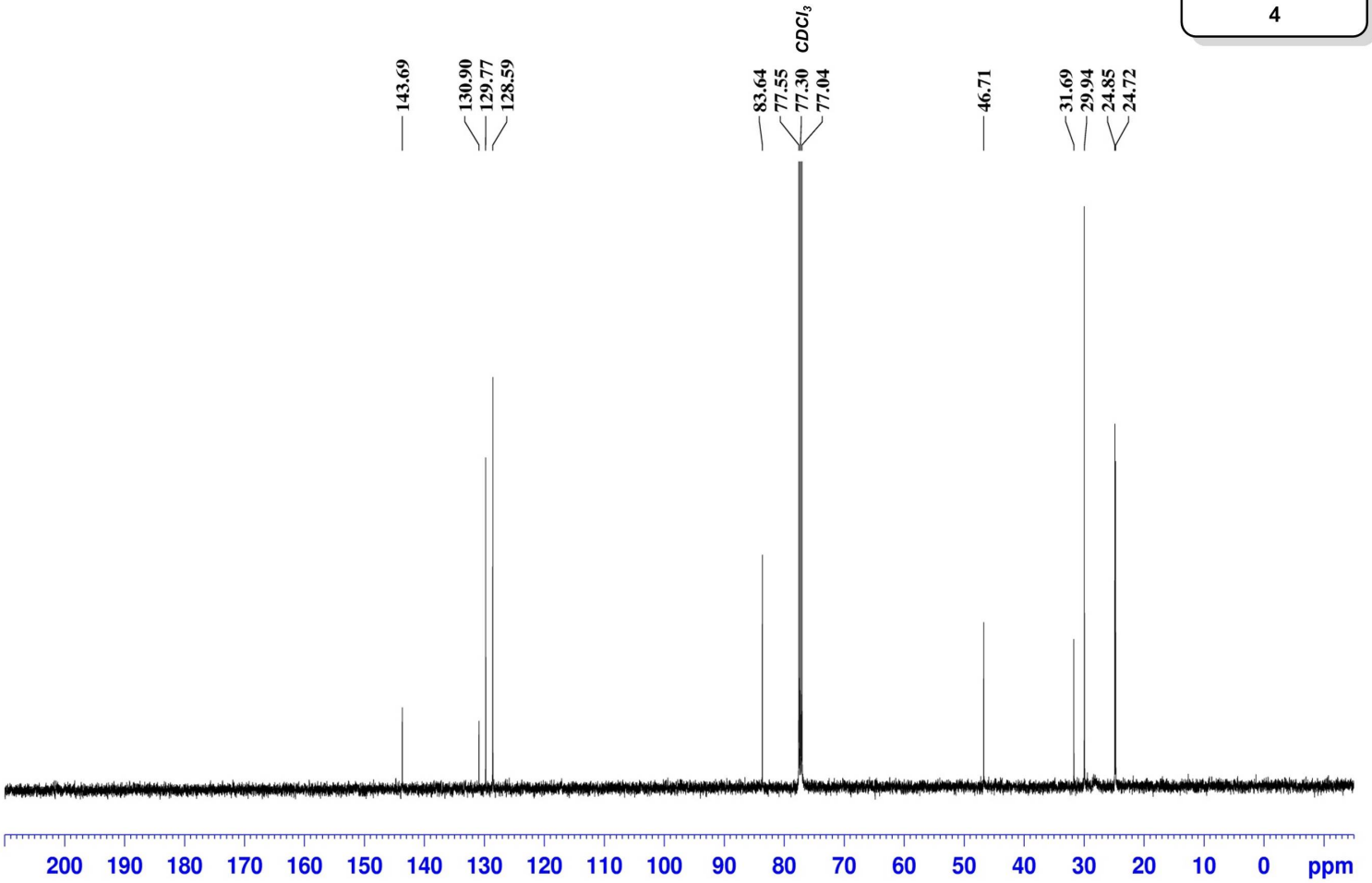




^{13}C NMR

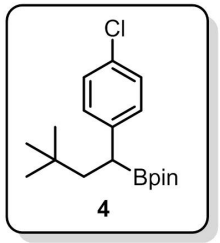
2-(1-(4-Chlorophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$

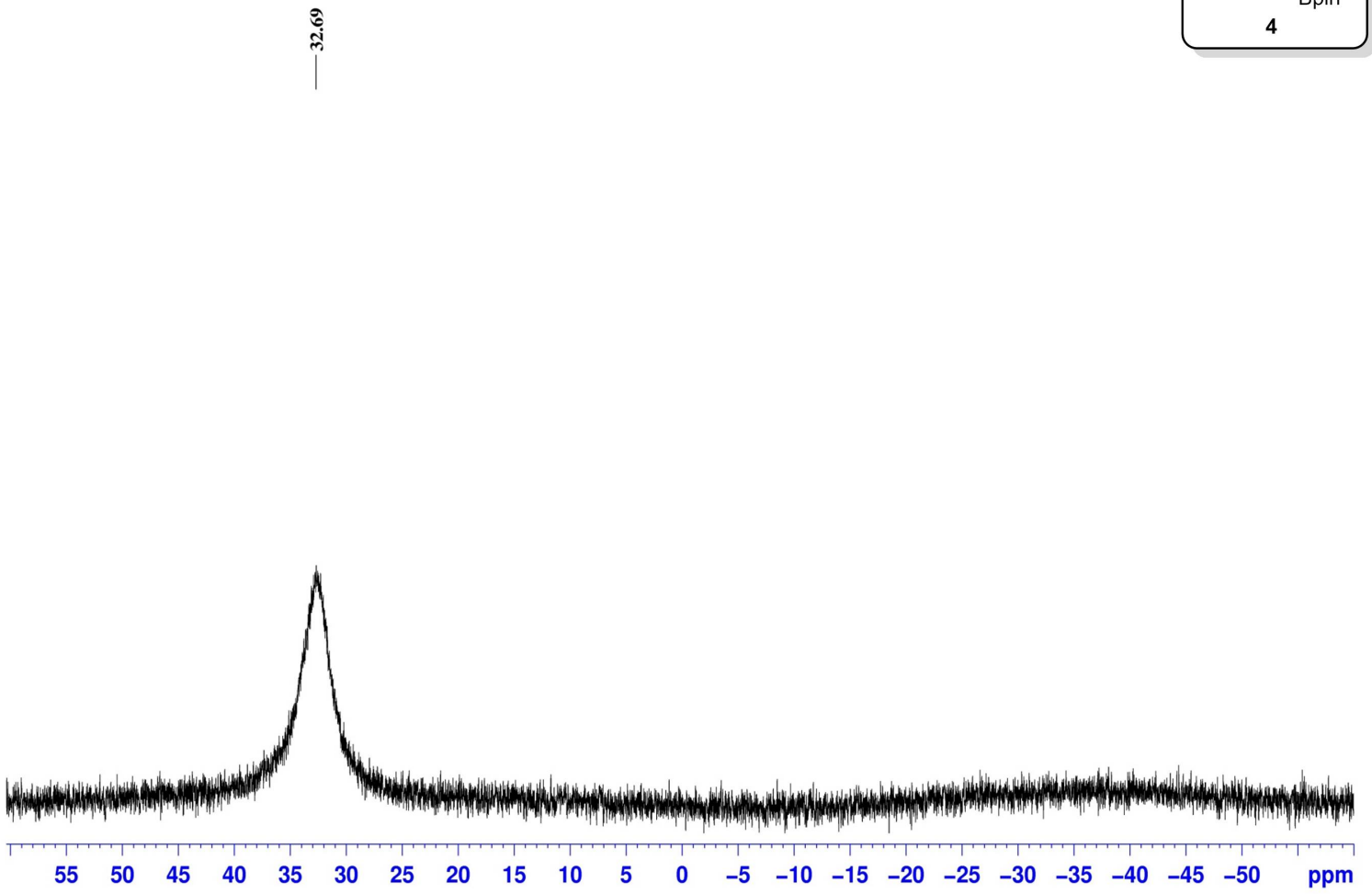




^{11}B NMR

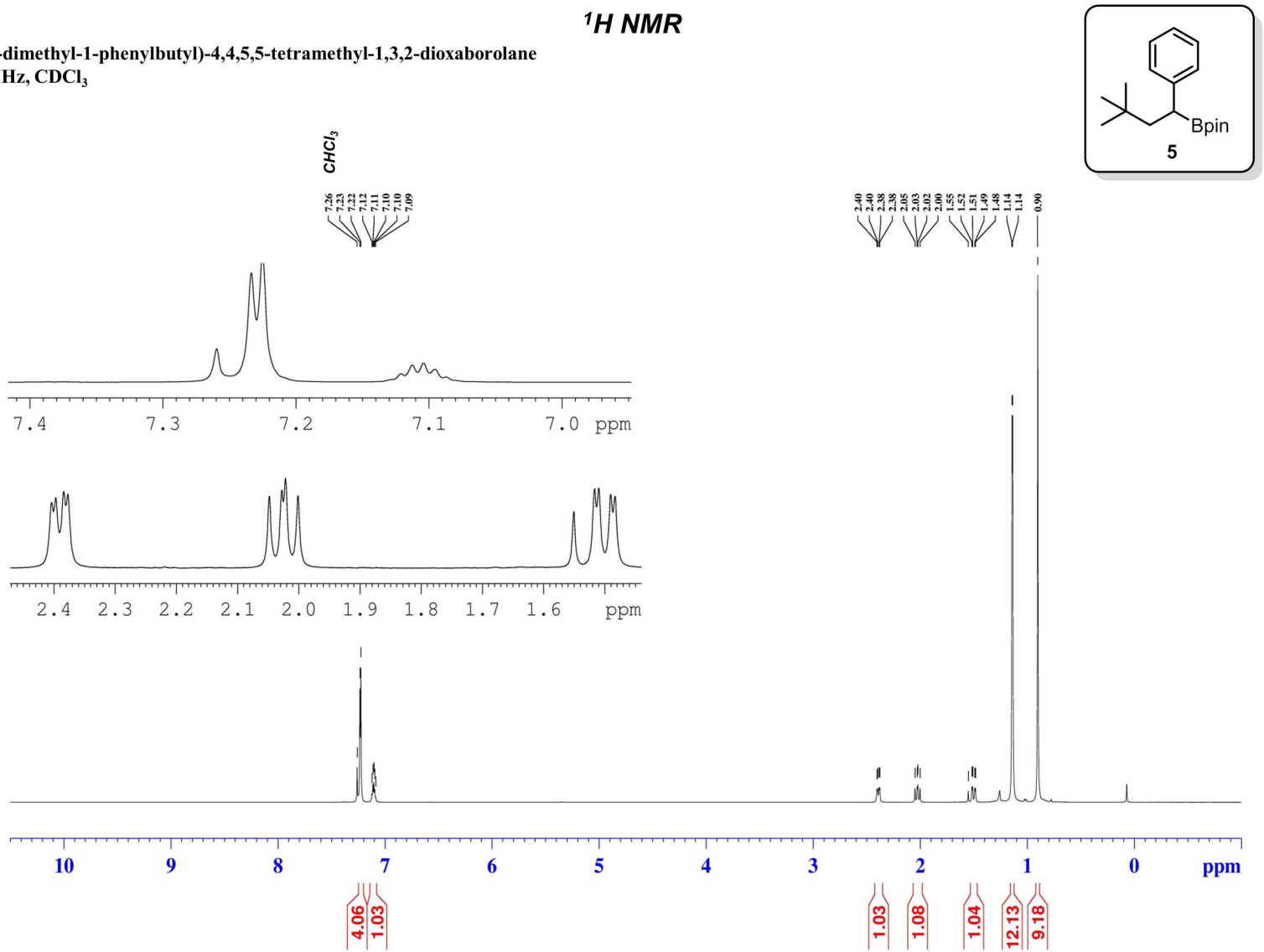
2-(1-(4-chlorophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$





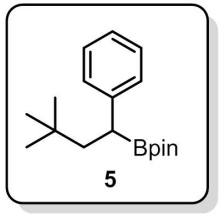
^1H NMR

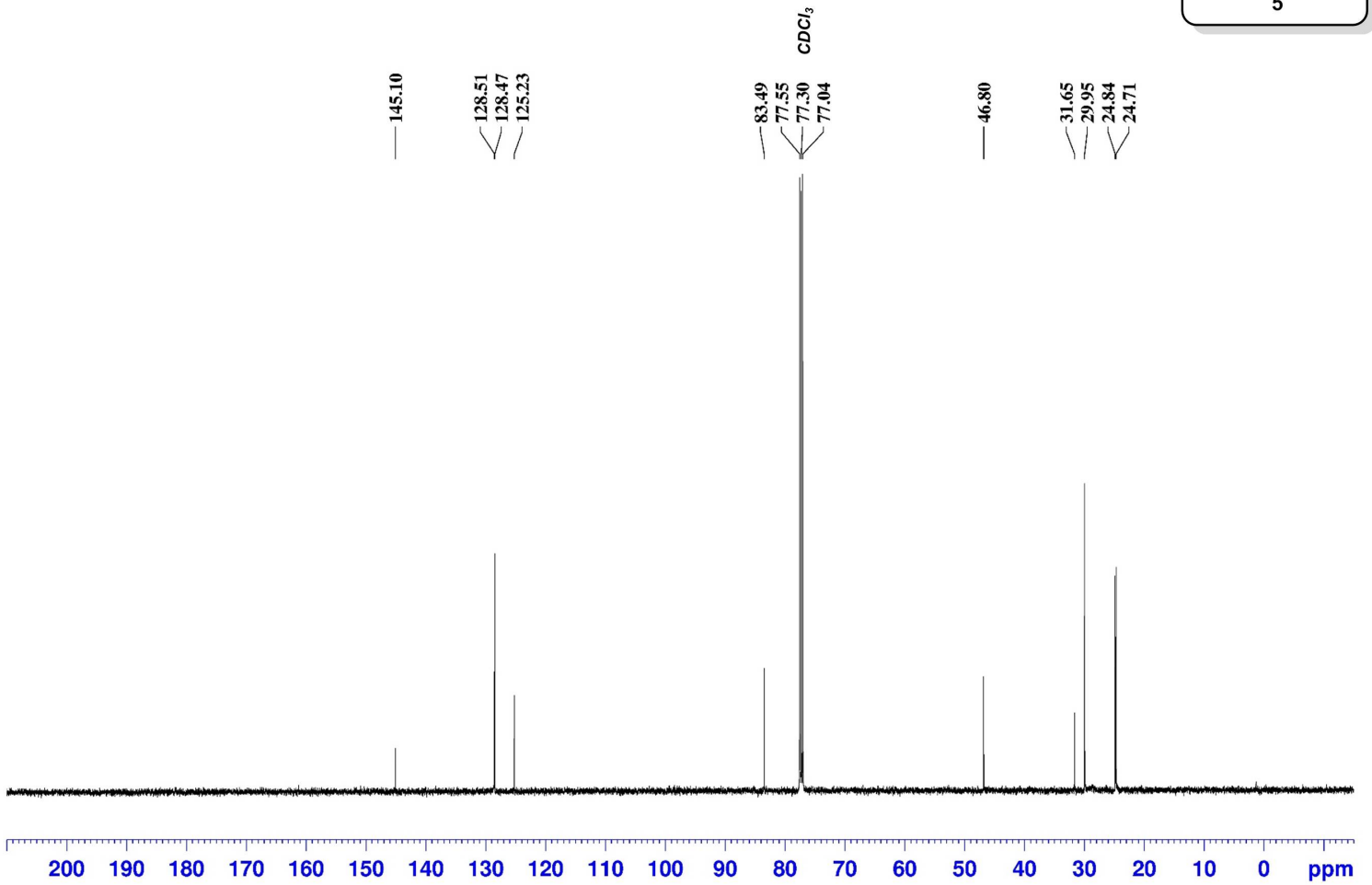
2-(3,3-dimethyl-1-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$



^{13}C NMR

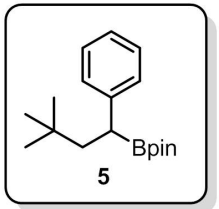
2-(3,3-Dimethyl-1-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$

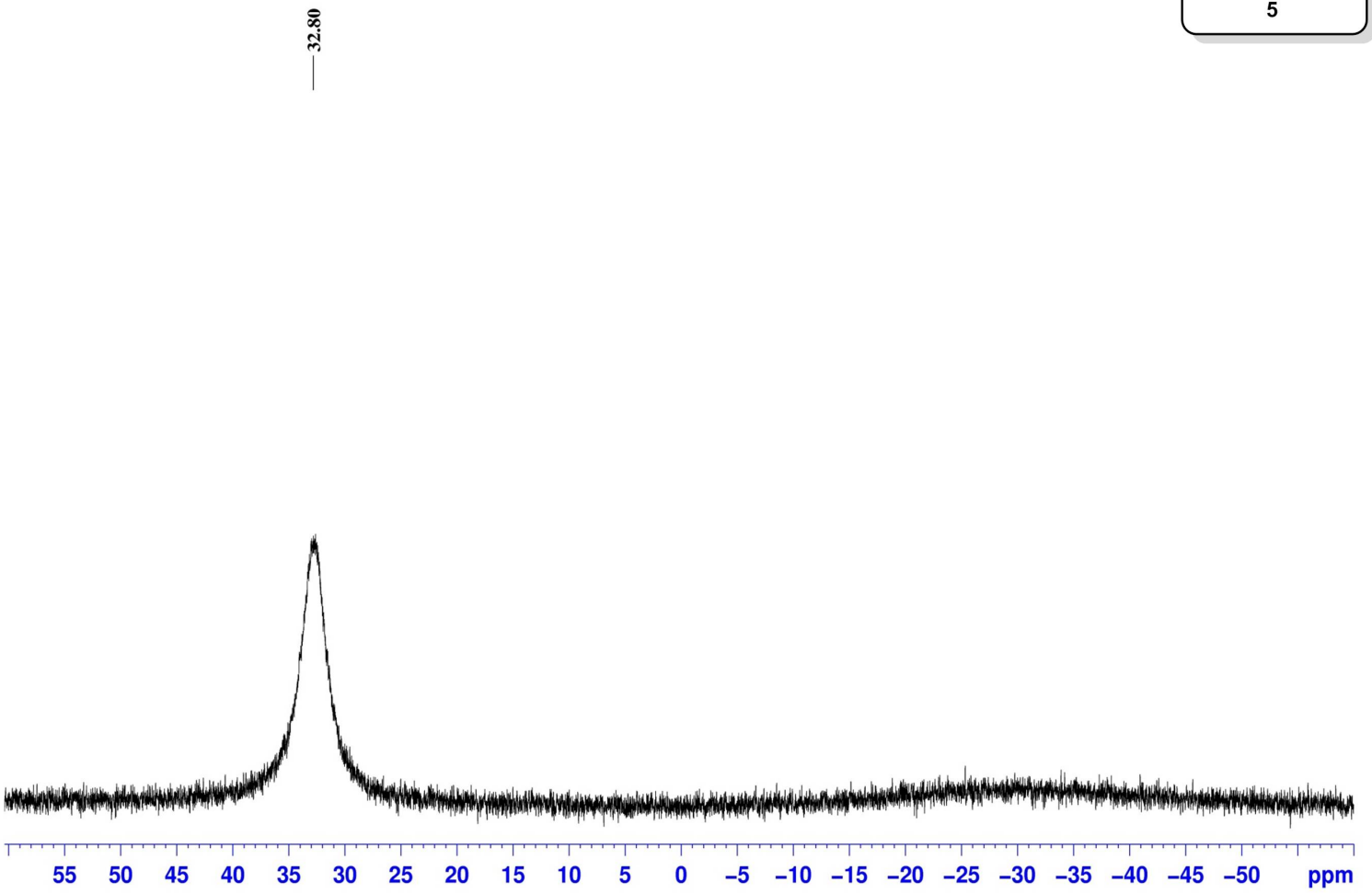




^{11}B NMR

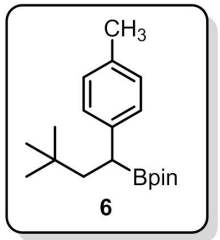
2-(3,3-dimethyl-1-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$

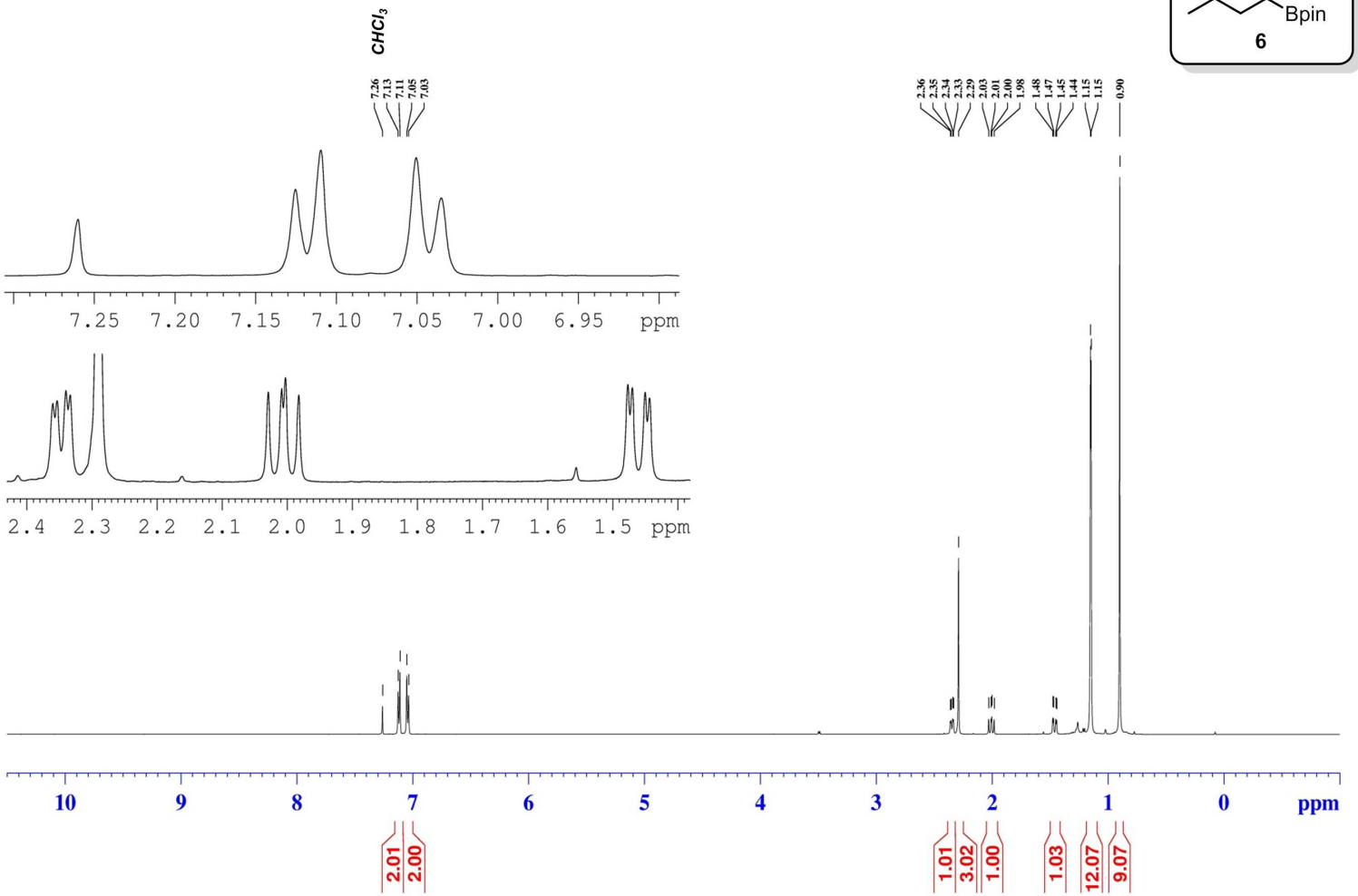




^1H NMR

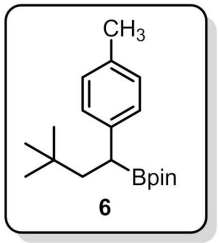
2-(3,3-dimethyl-1-(p-tolyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

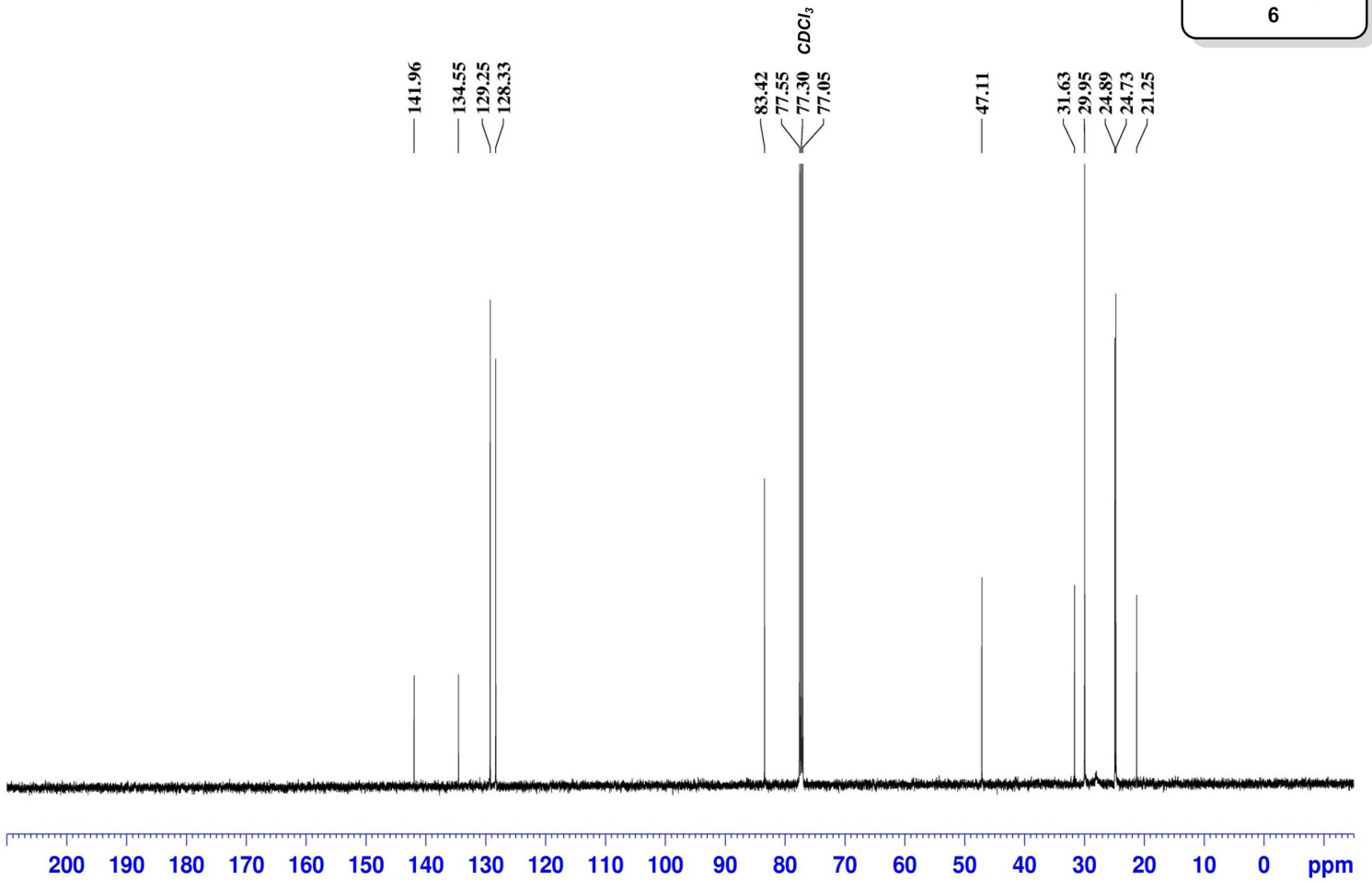




^{13}C NMR

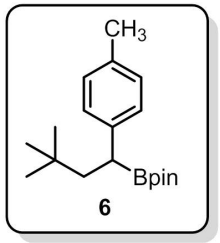
2-(3,3-Dimethyl-1-(p-tolyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$

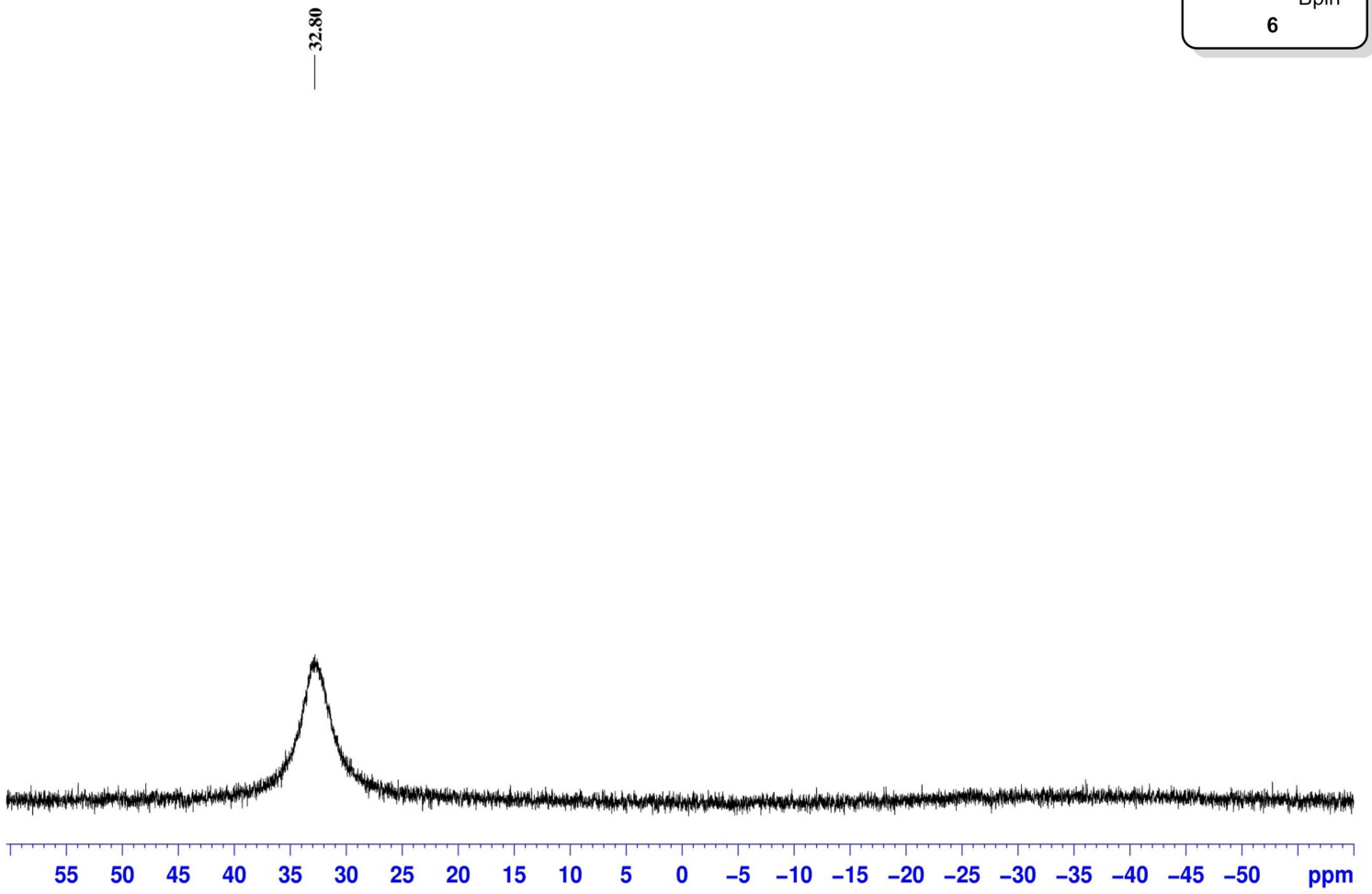




^{11}B NMR

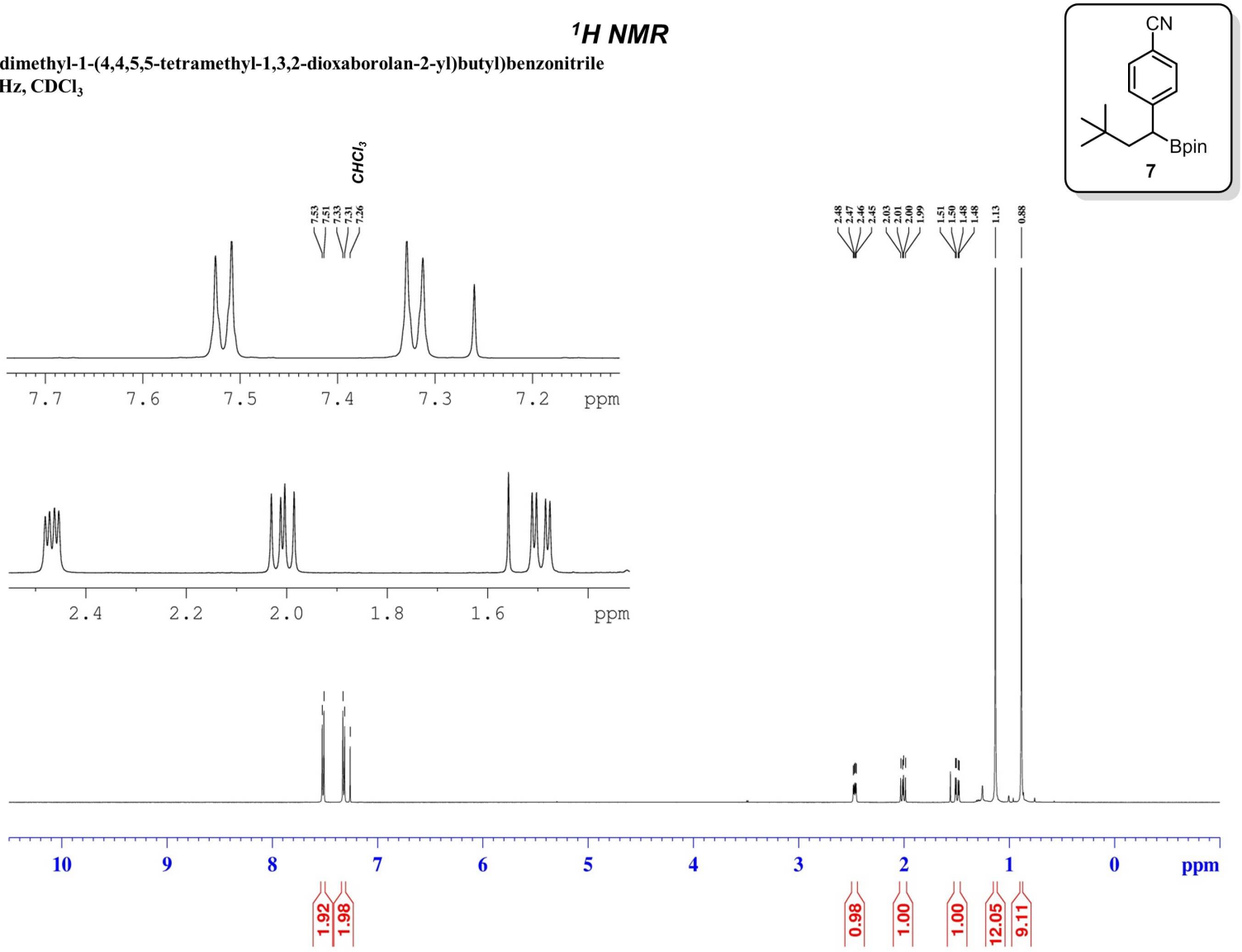
2-(3,3-dimethyl-1-(p-tolyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$





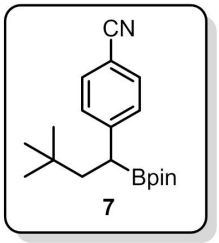
^1H NMR

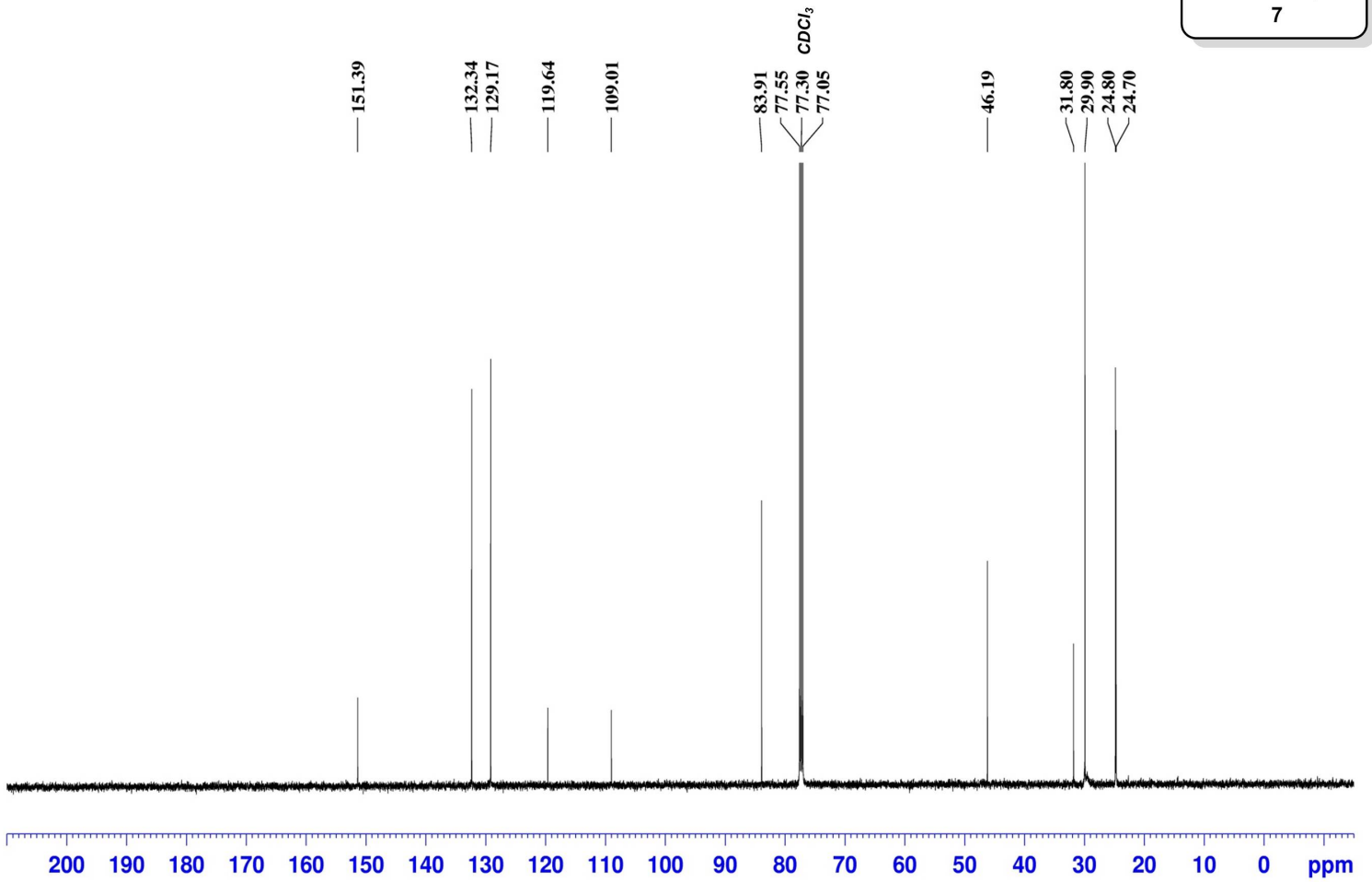
4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzonitrile
500 MHz, $CDCl_3$



^{13}C NMR

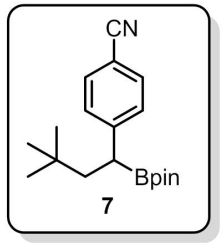
4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzonitrile
125 MHz, $CDCl_3$

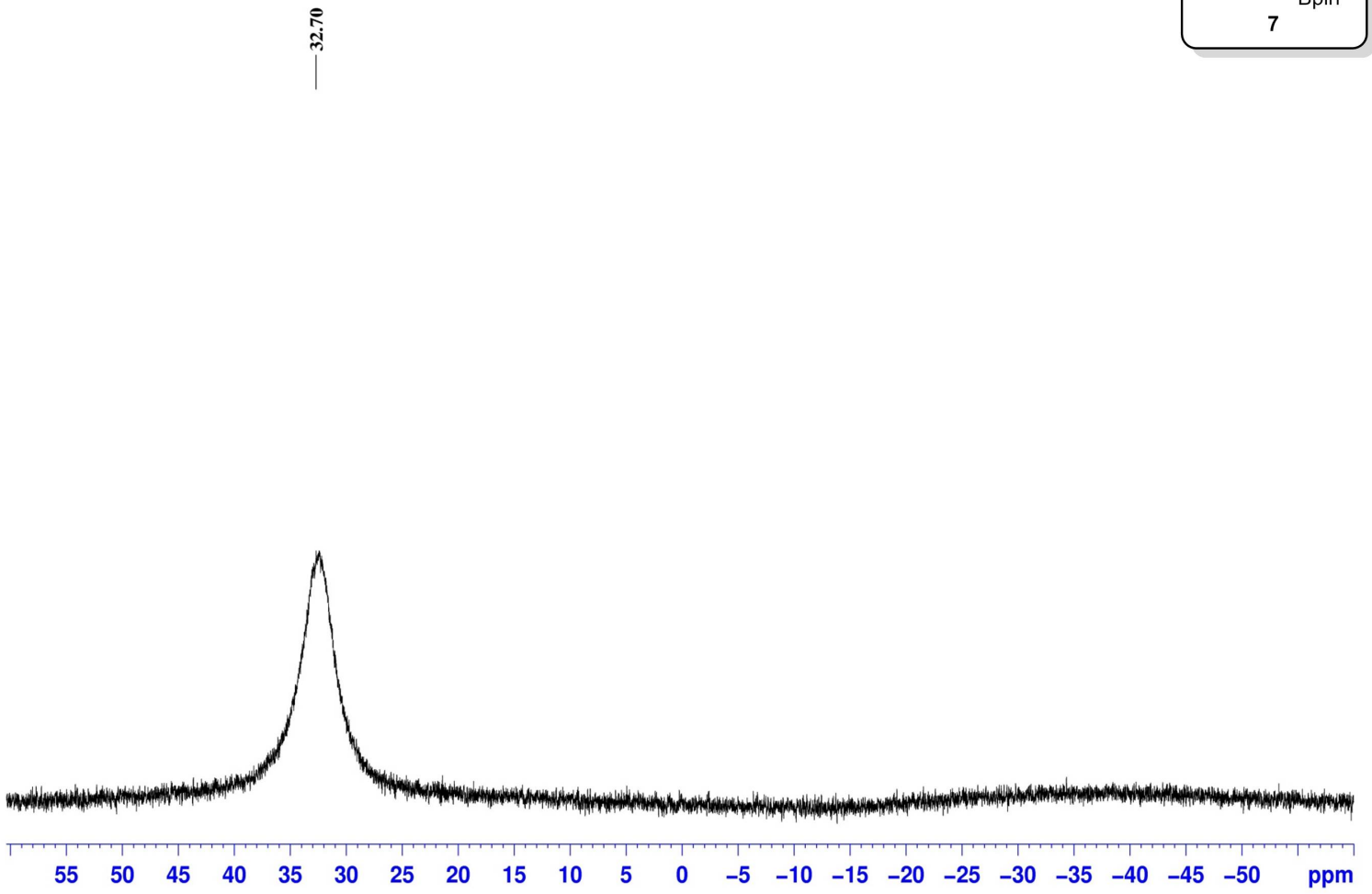




^{11}B NMR

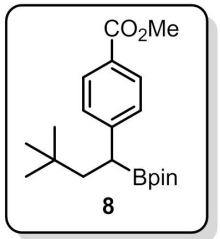
4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzonitrile
128 MHz, $CDCl_3$

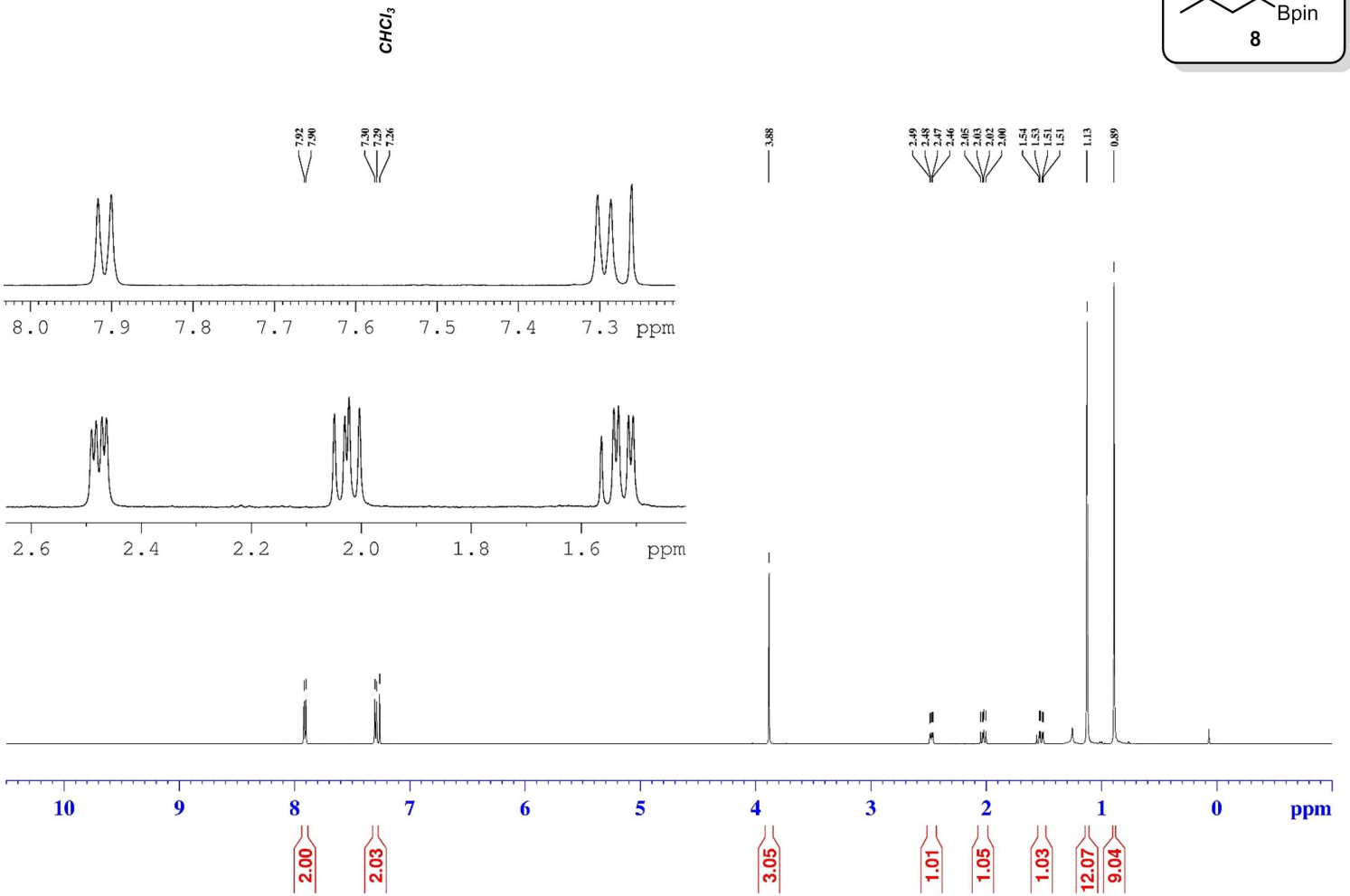




^1H NMR

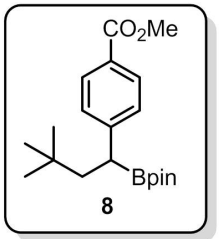
methyl 4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzoate
500 MHz, $CDCl_3$

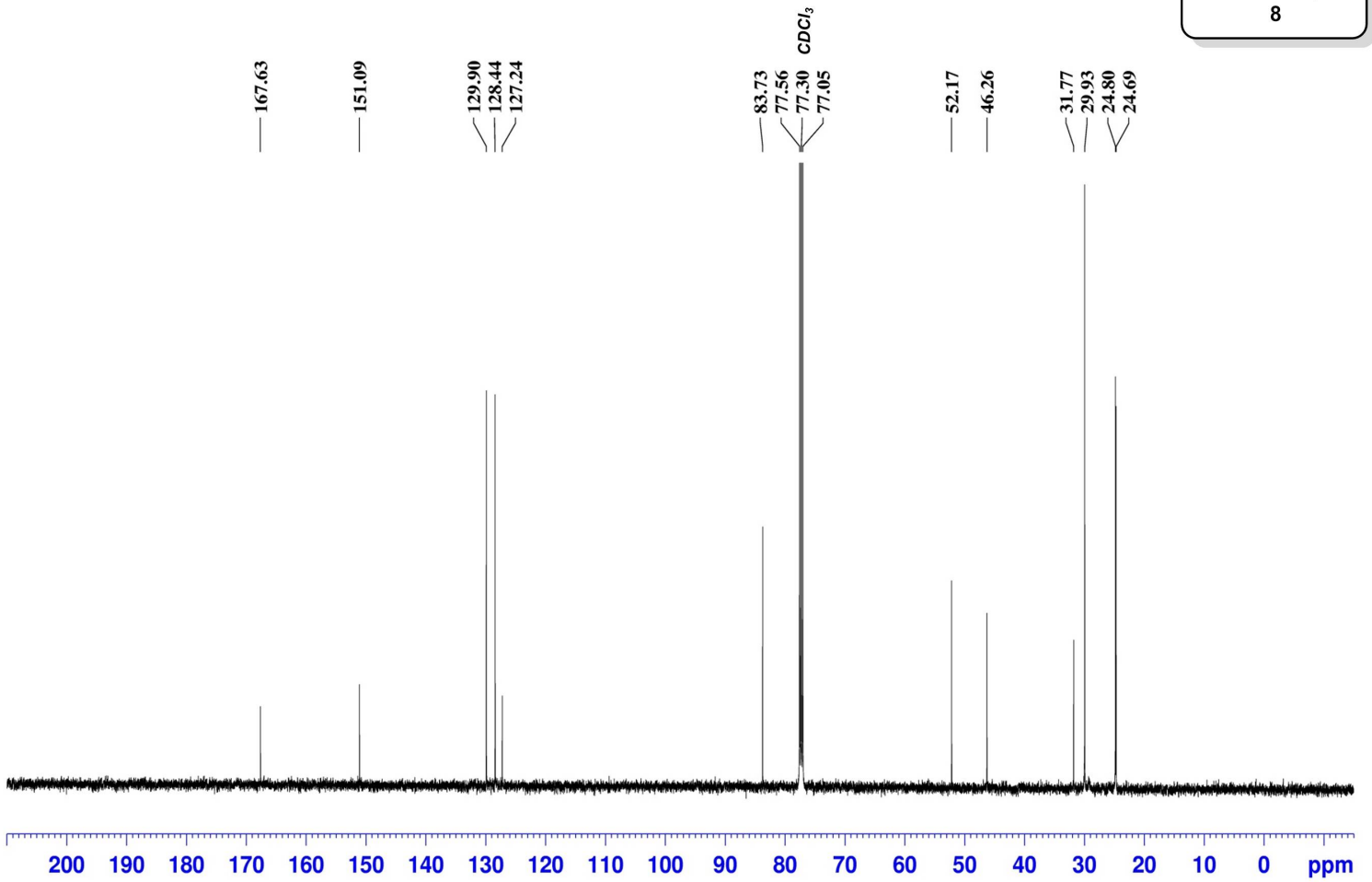




^{13}C NMR

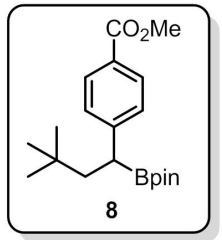
Methyl 4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzoate
125 MHz, $CDCl_3$

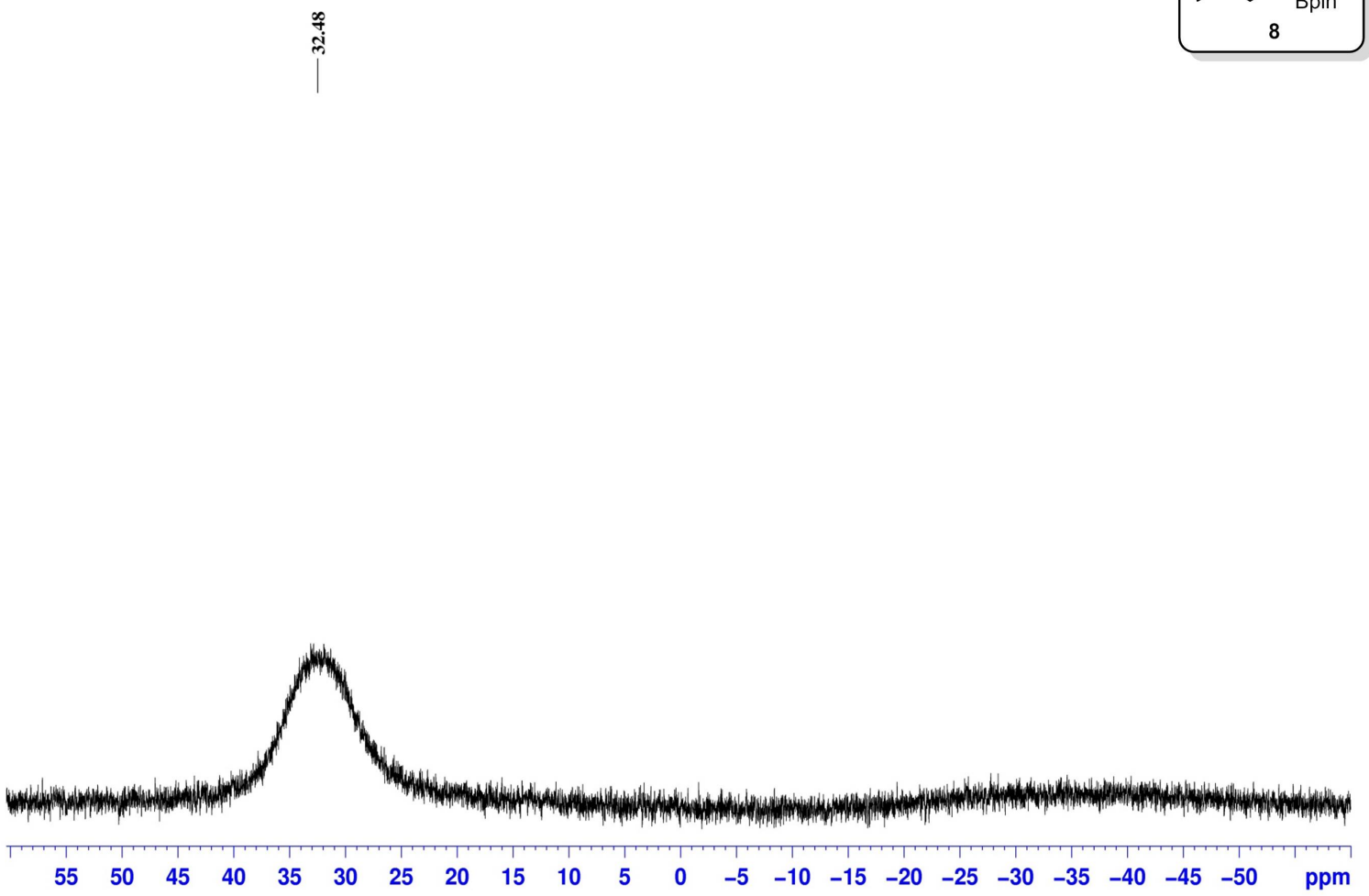




^{11}B NMR

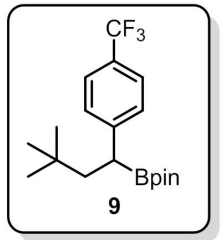
methyl 4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzoate
128 MHz, $CDCl_3$

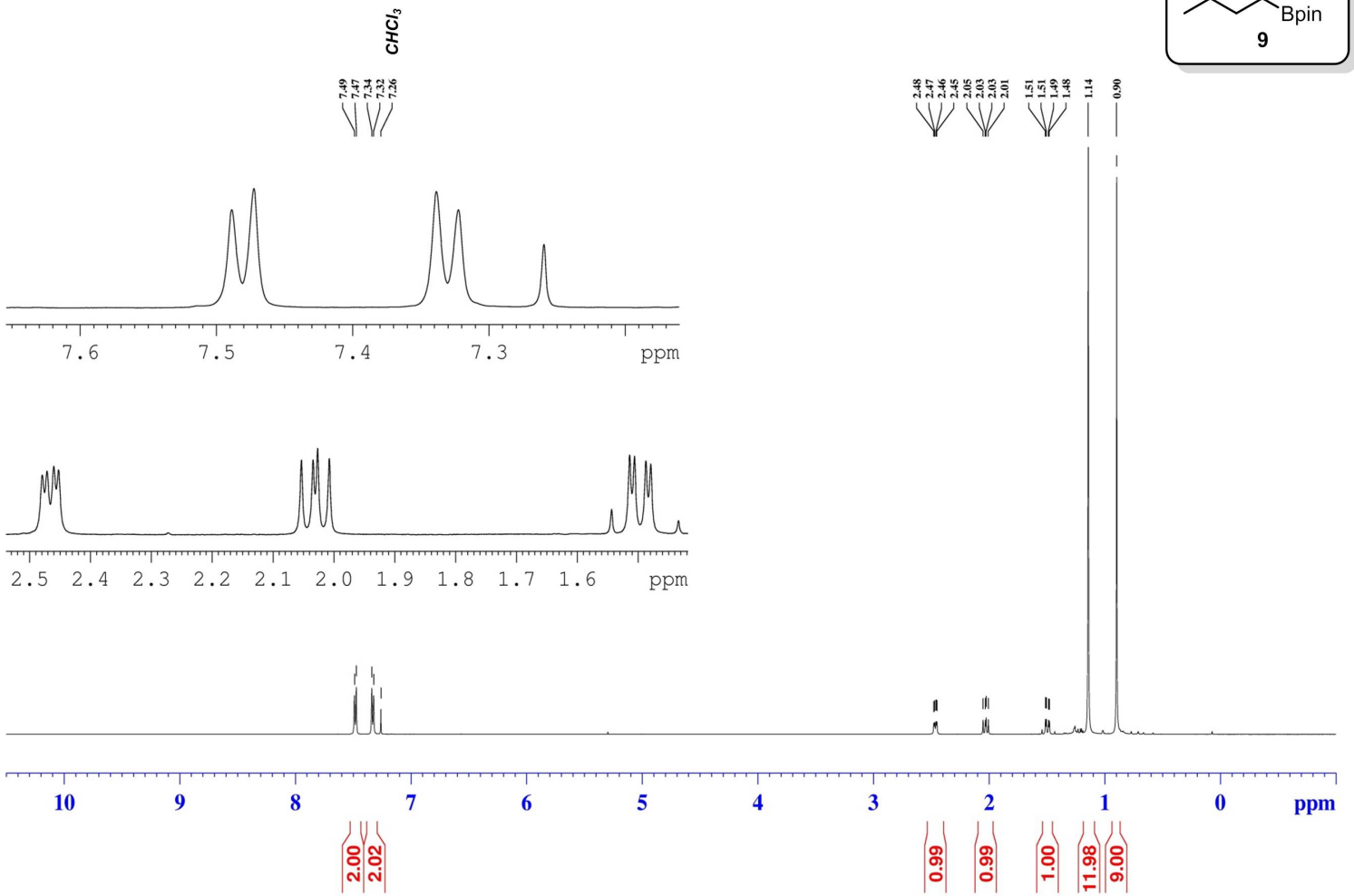




^1H NMR

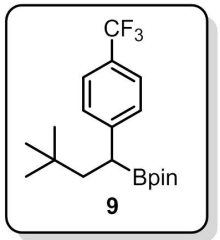
2-(3,3-dimethyl-1-(4-(trifluoromethyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

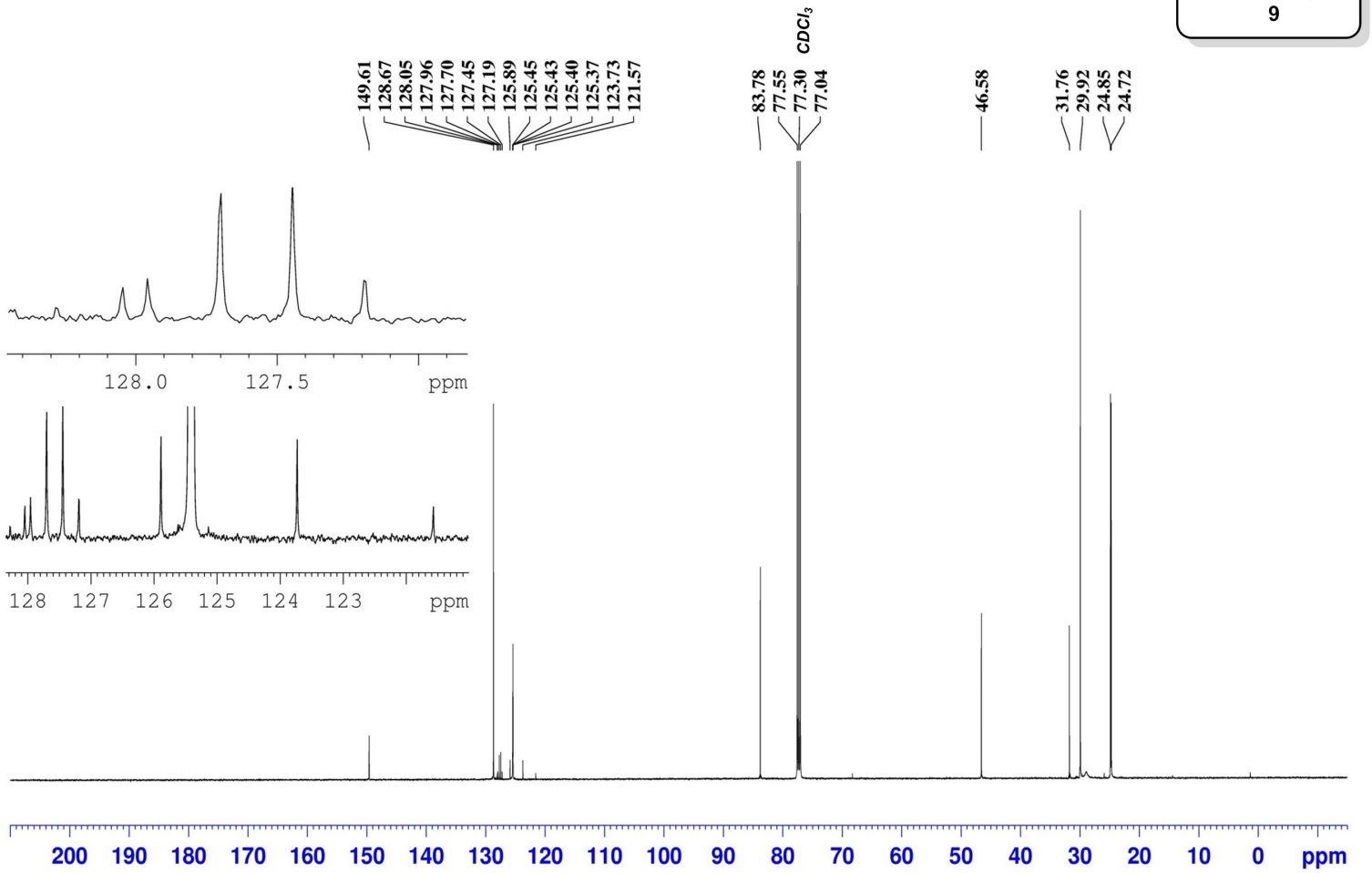




^{13}C NMR

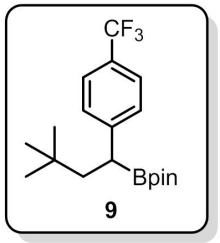
2-(3,3-Dimethyl-1-(4-(trifluoromethyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$

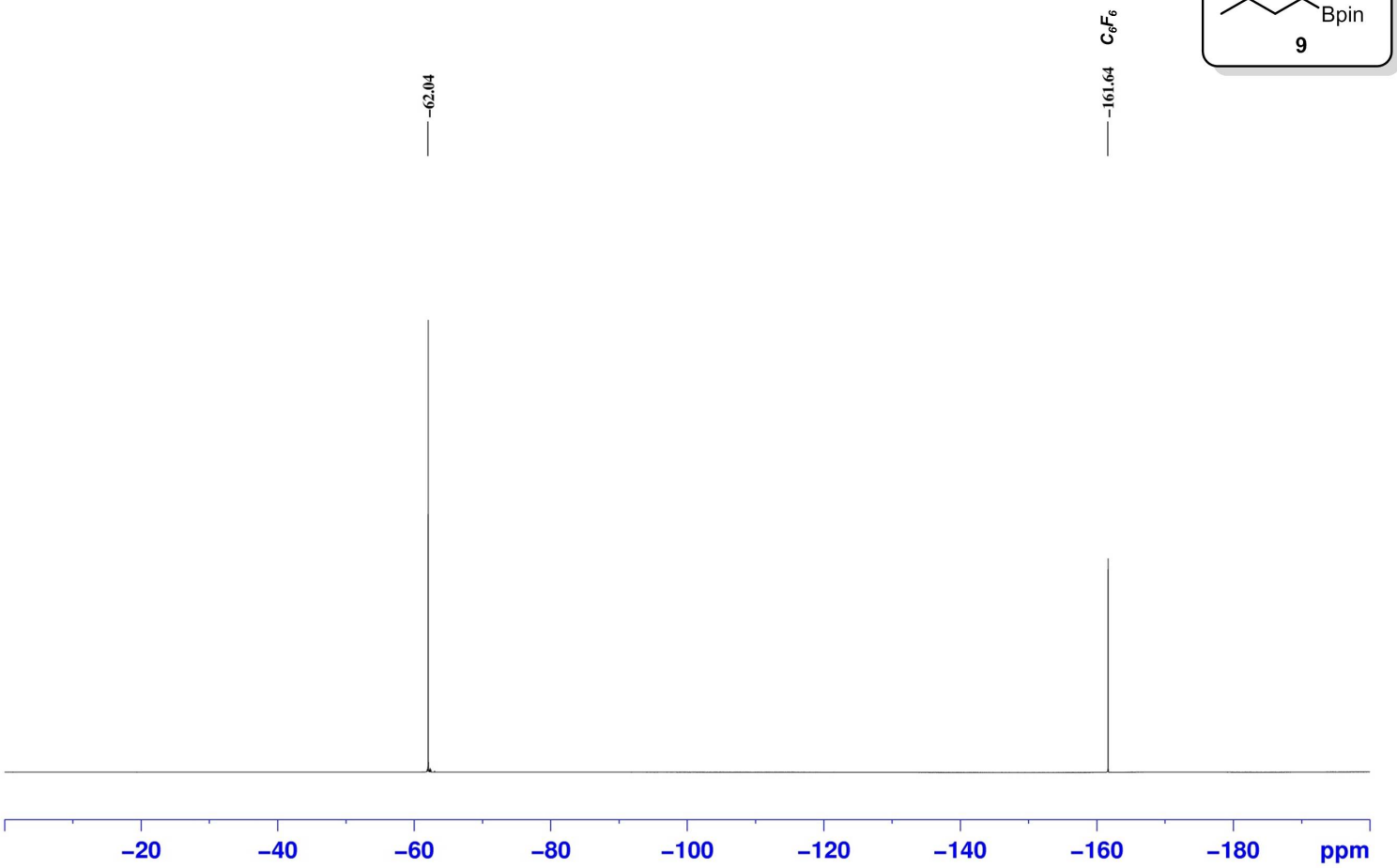




^{19}F NMR

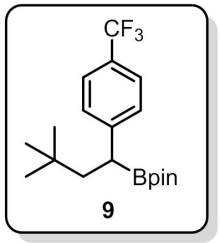
2-(3,3-dimethyl-1-(4-(trifluoromethyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
471 MHz, $CDCl_3$

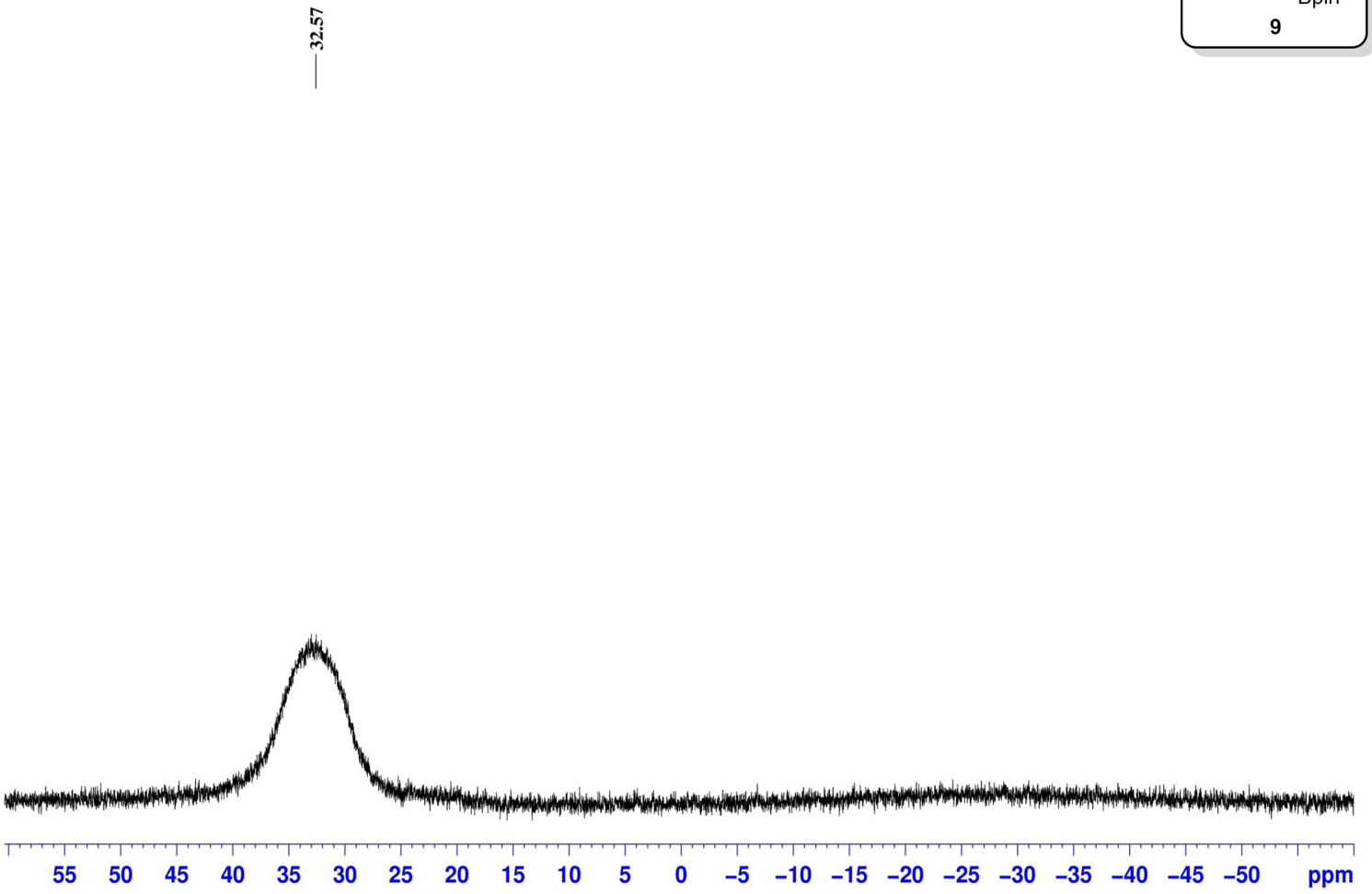




^{11}B NMR

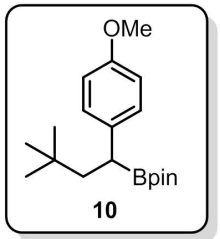
2-(3,3-dimethyl-1-(4-(trifluoromethyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$

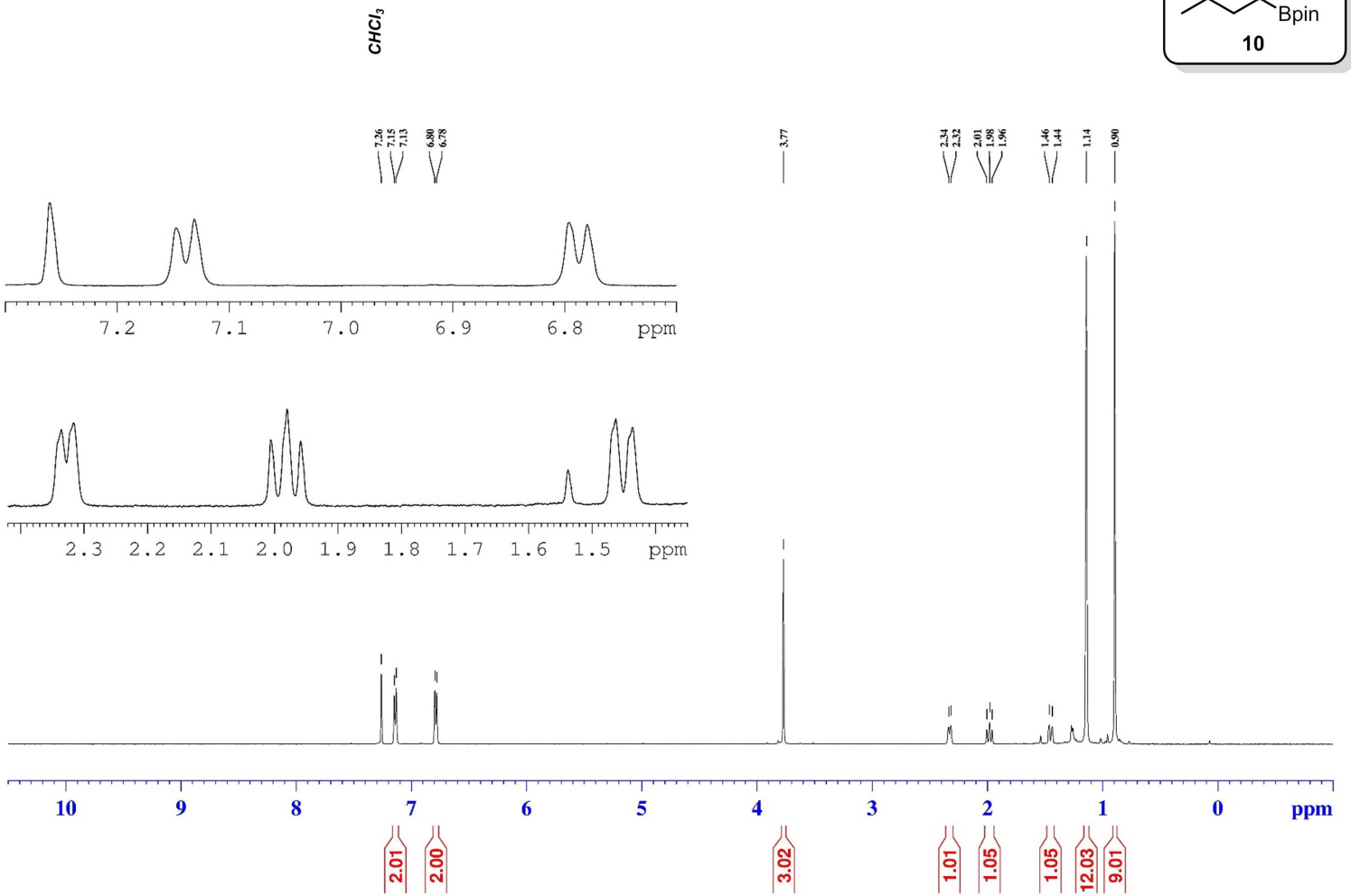




^1H NMR

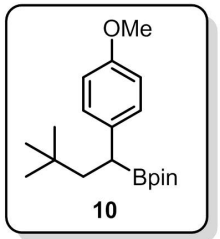
2-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

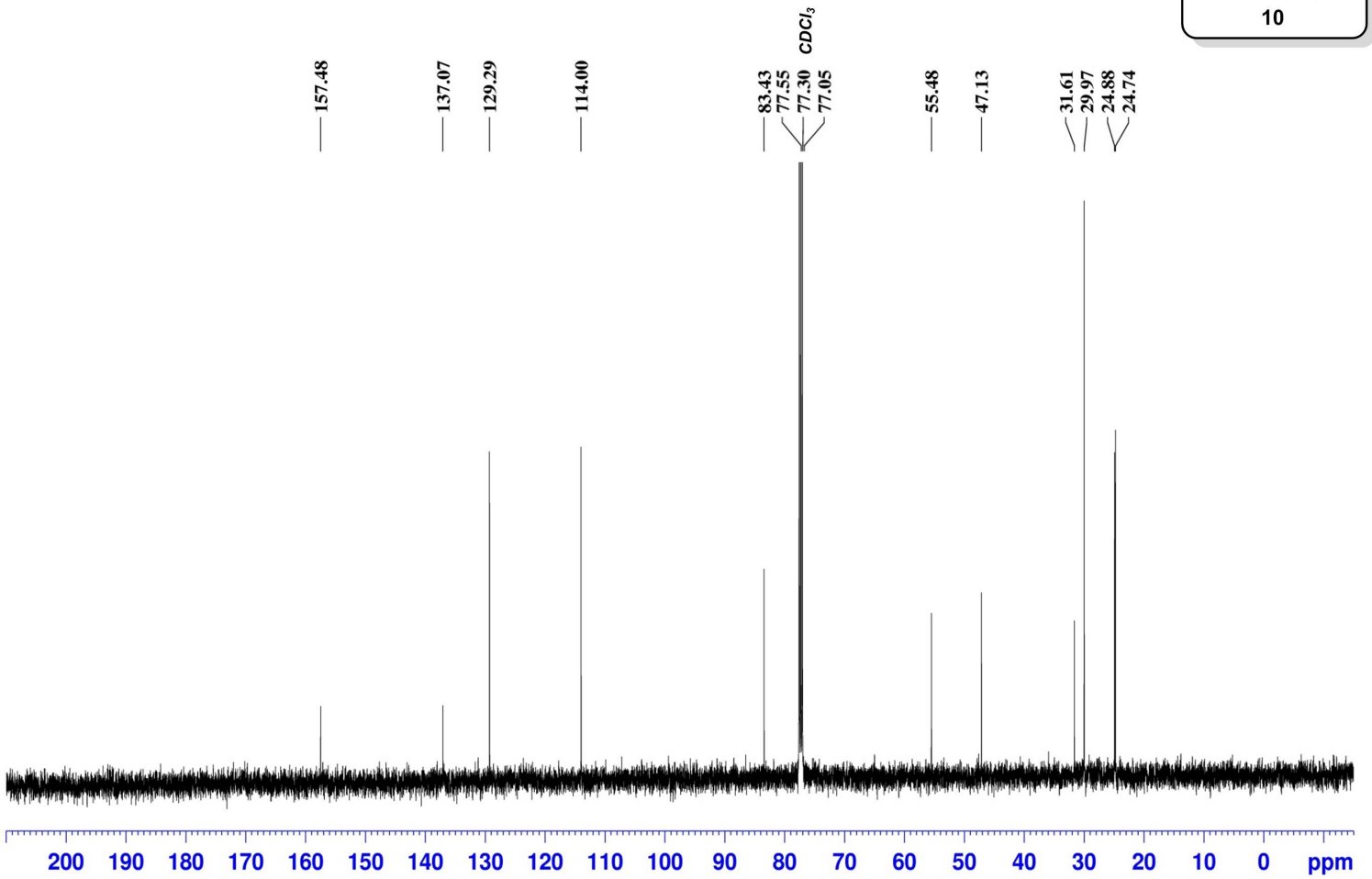




^{13}C NMR

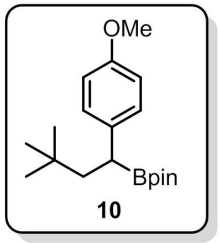
2-(1-(4-Methoxyphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$





^{11}B NMR

2-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$



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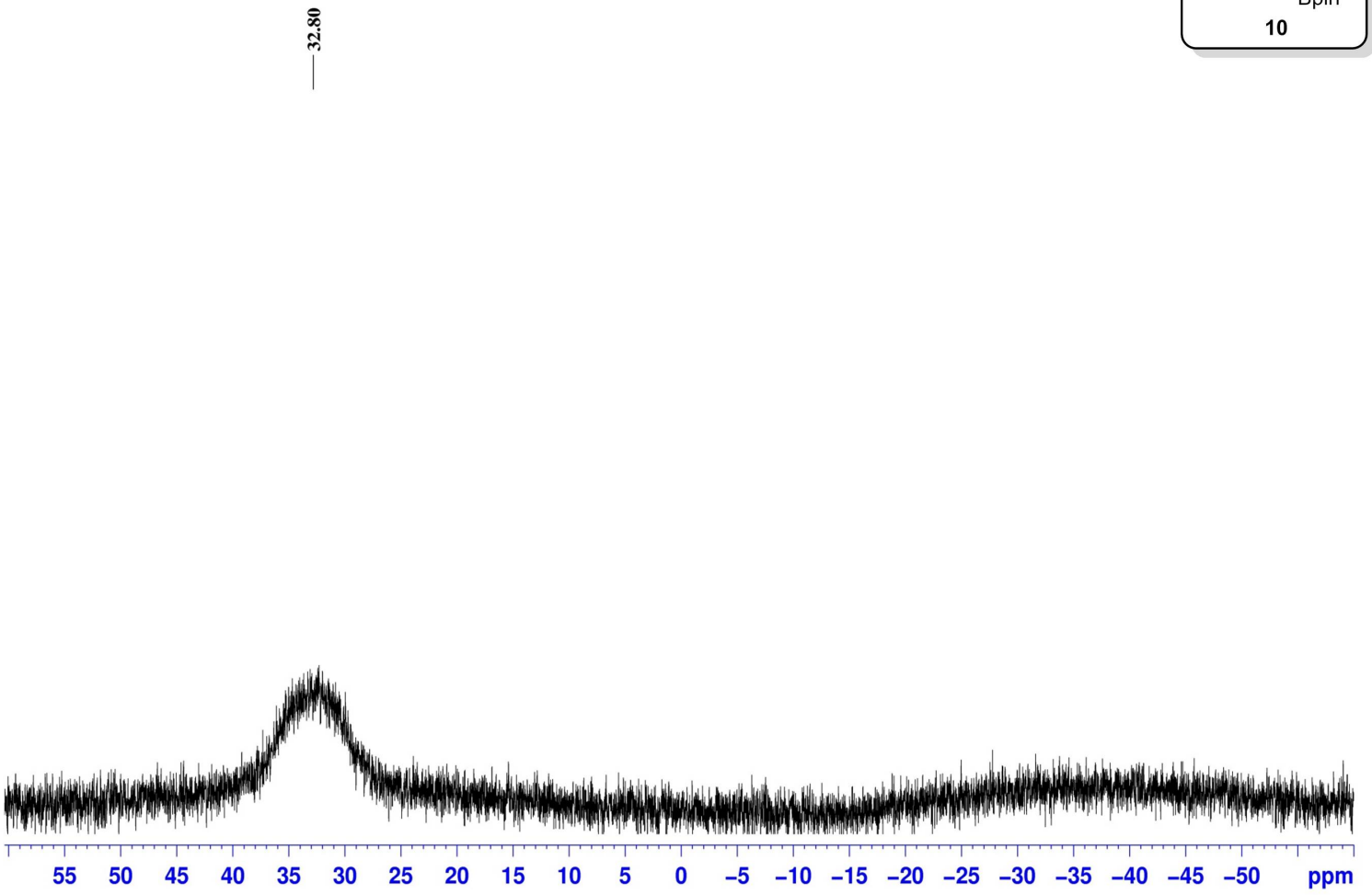
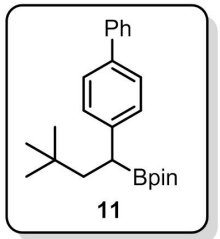
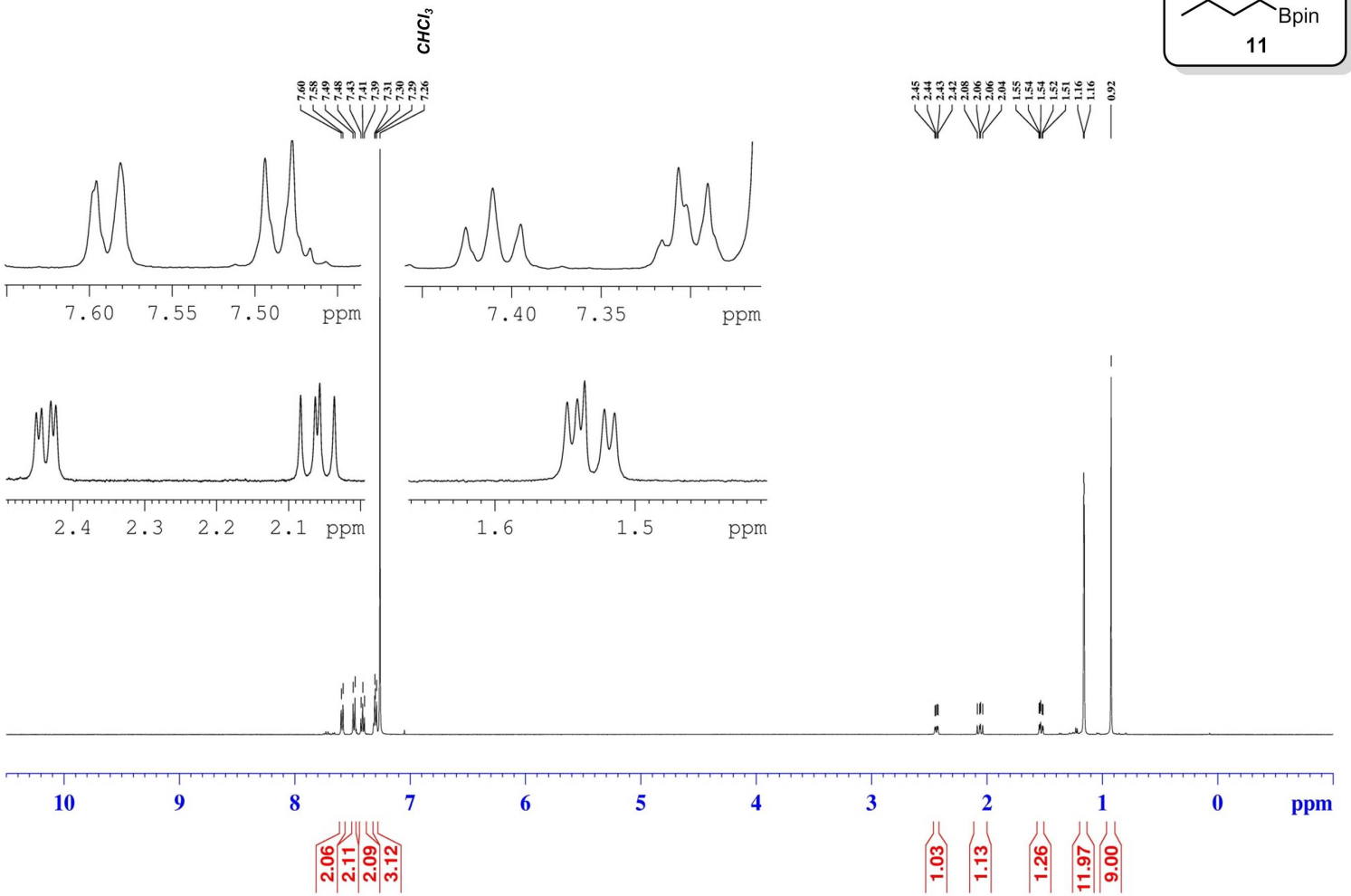


^1H NMR

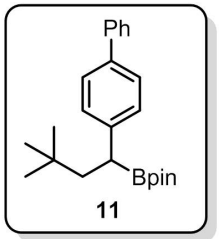
2-(1-([1,1'-biphenyl]-4-yl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

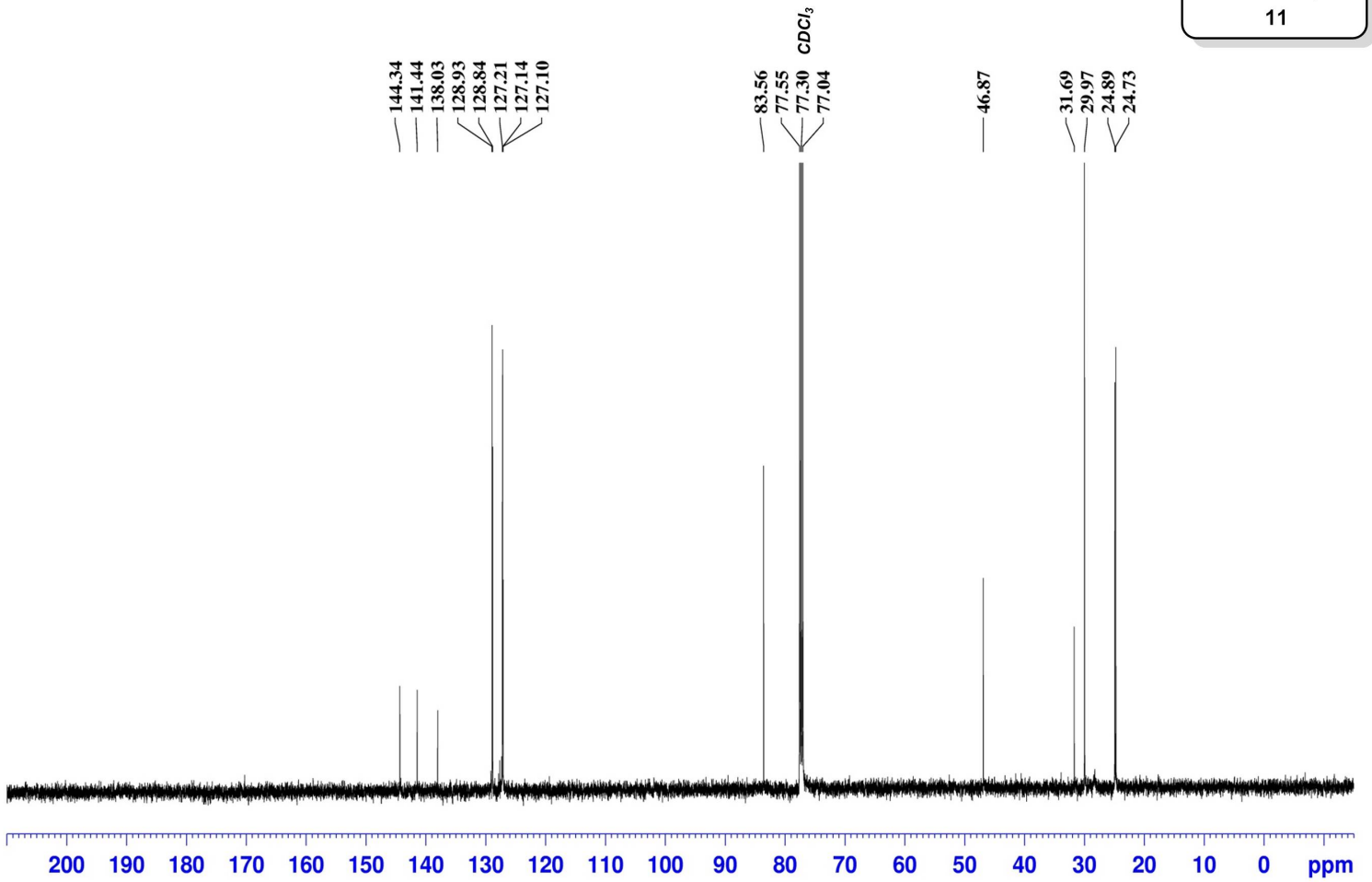




^{13}C NMR

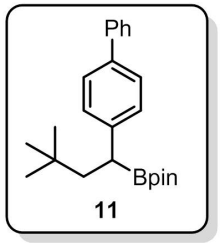
2-(1-([1,1'-Biphenyl]-4-yl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$

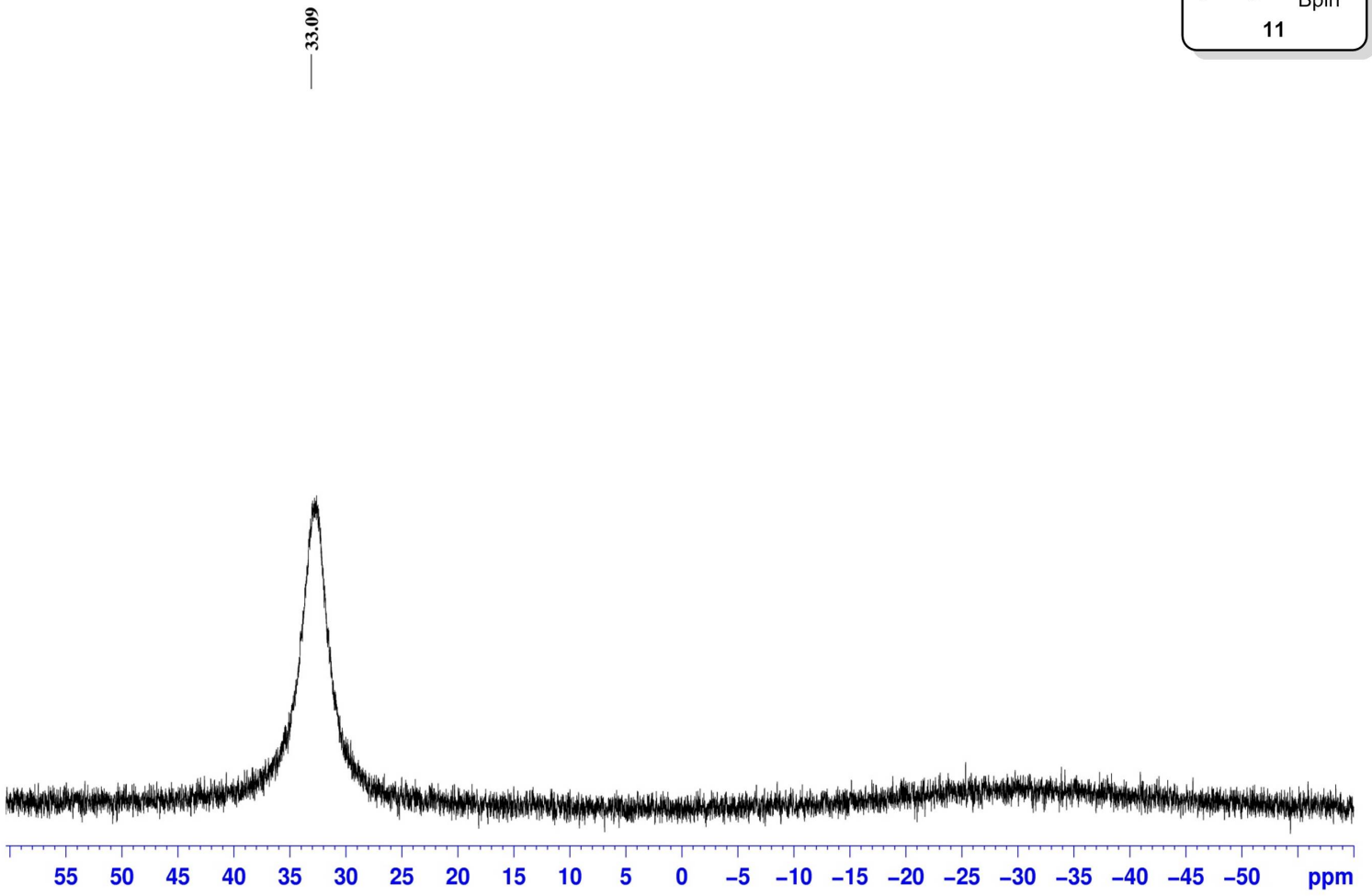




^{11}B NMR

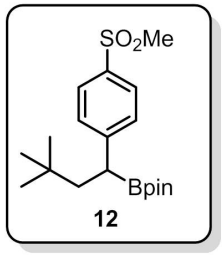
2-(1-([1,1'-biphenyl]-4-yl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$

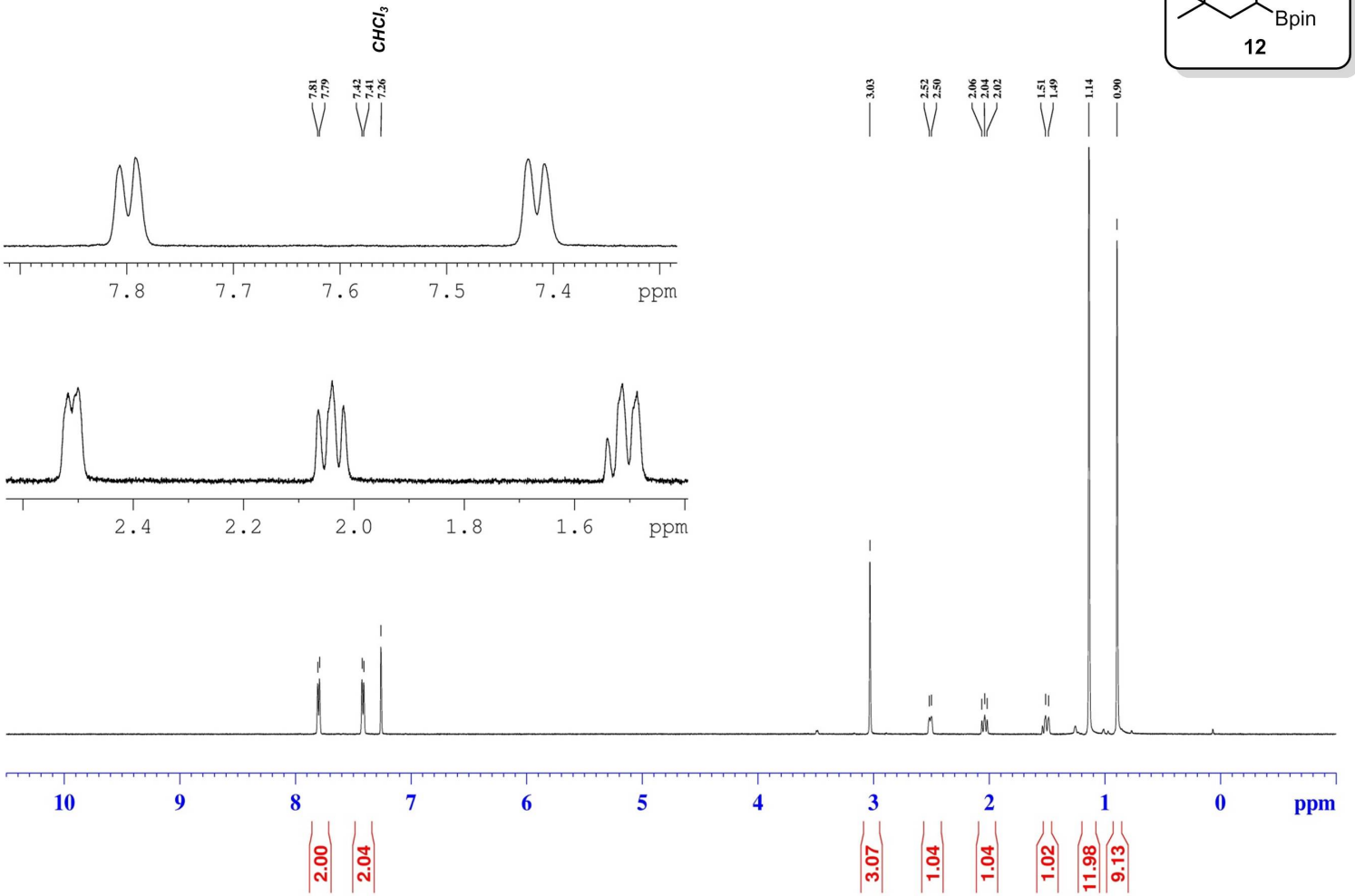




^1H NMR

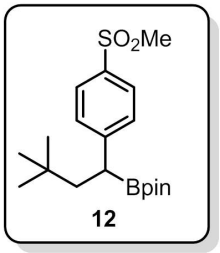
2-(3,3-dimethyl-1-(4-(methylsulfonyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

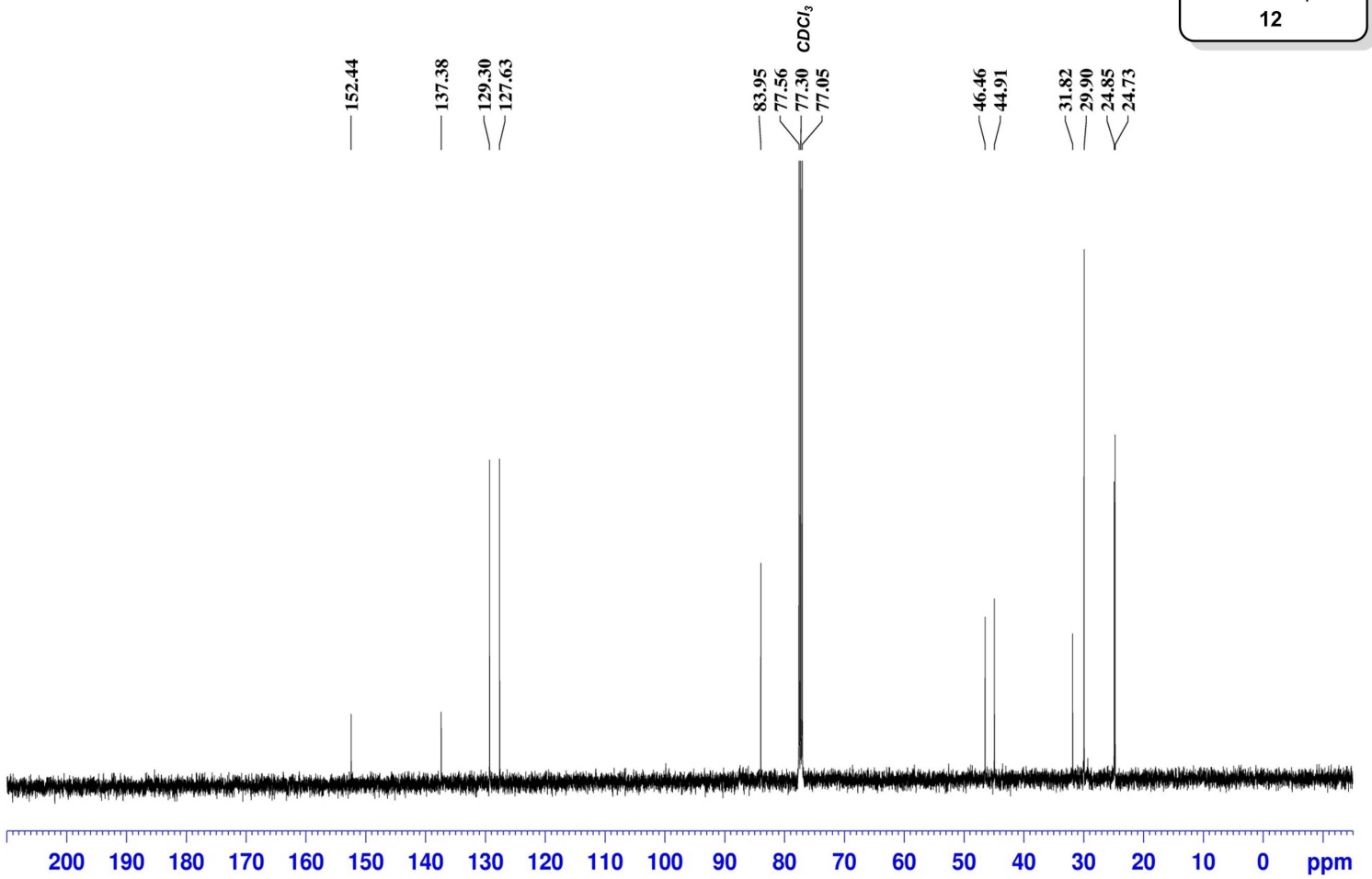




^{13}C NMR

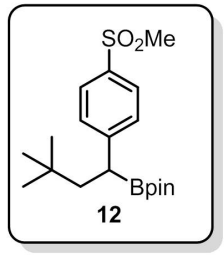
2-(3,3-Dimethyl-1-(4-(methylsulfonyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$

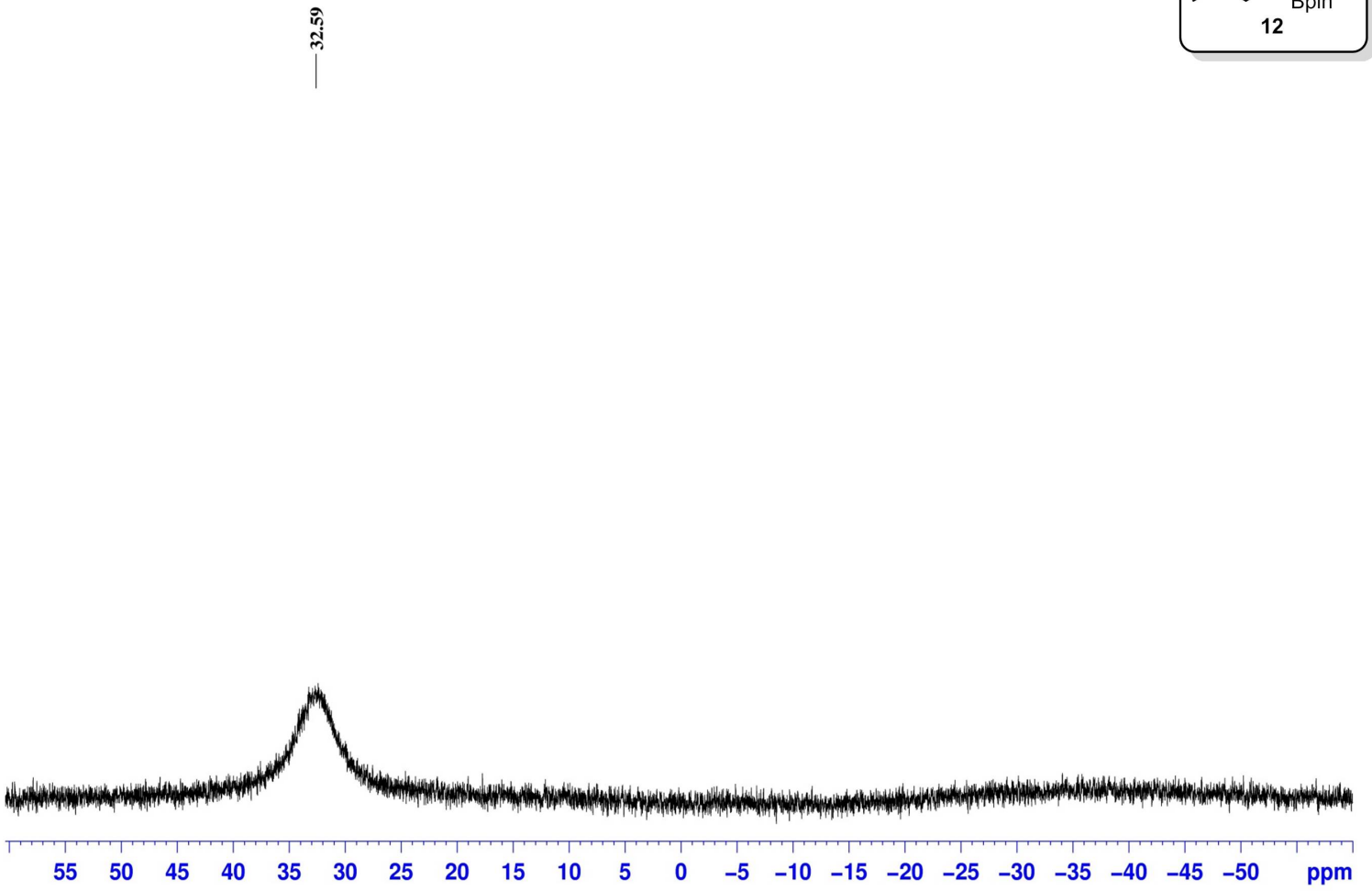




^{11}B NMR

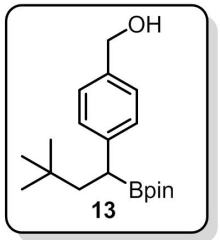
2-(3,3-dimethyl-1-(4-(methylsulfonyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$

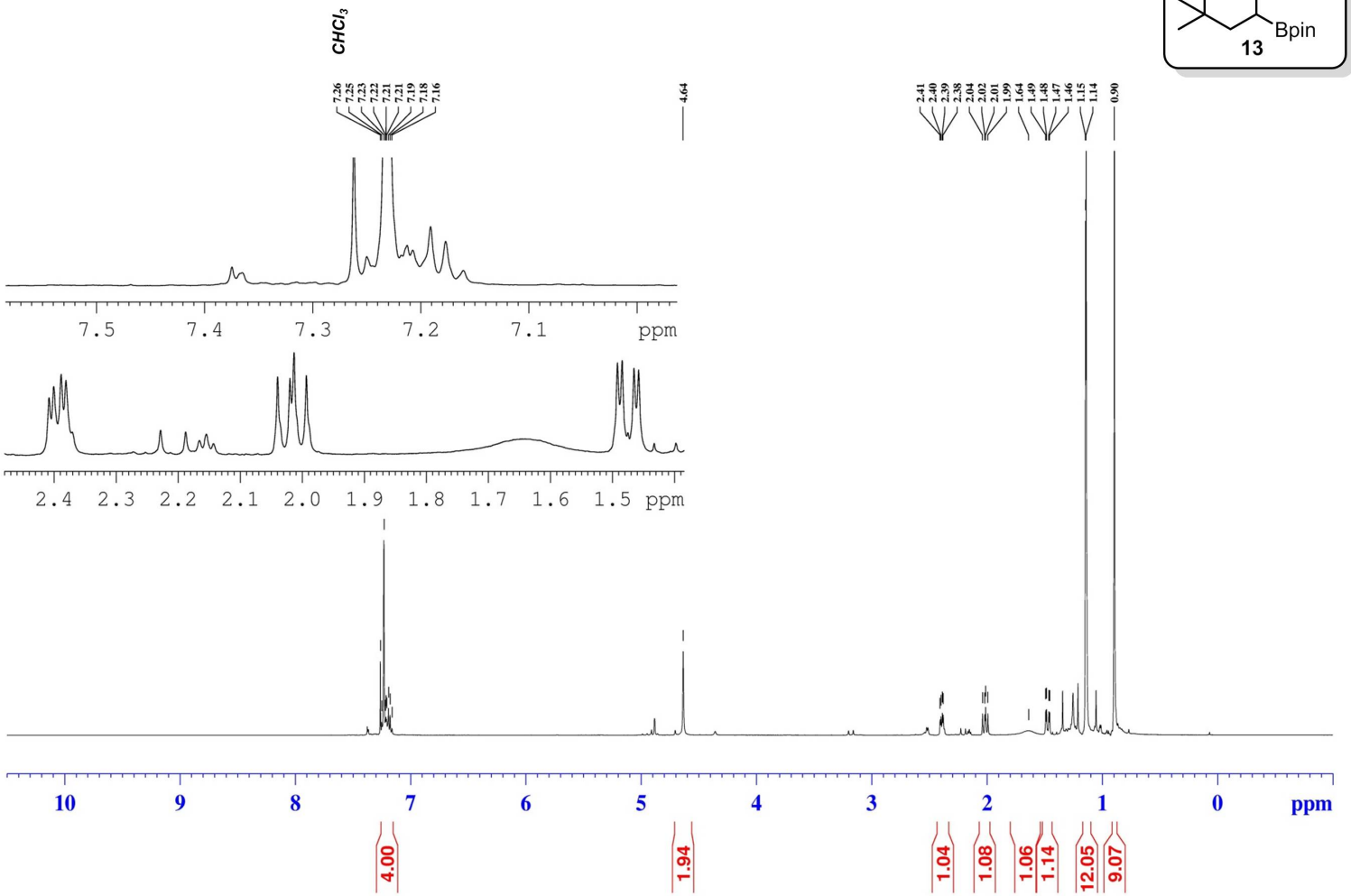




^1H NMR

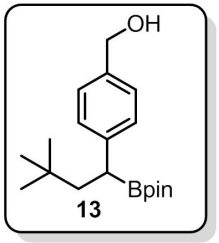
(4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)methanol
500 MHz, $CDCl_3$

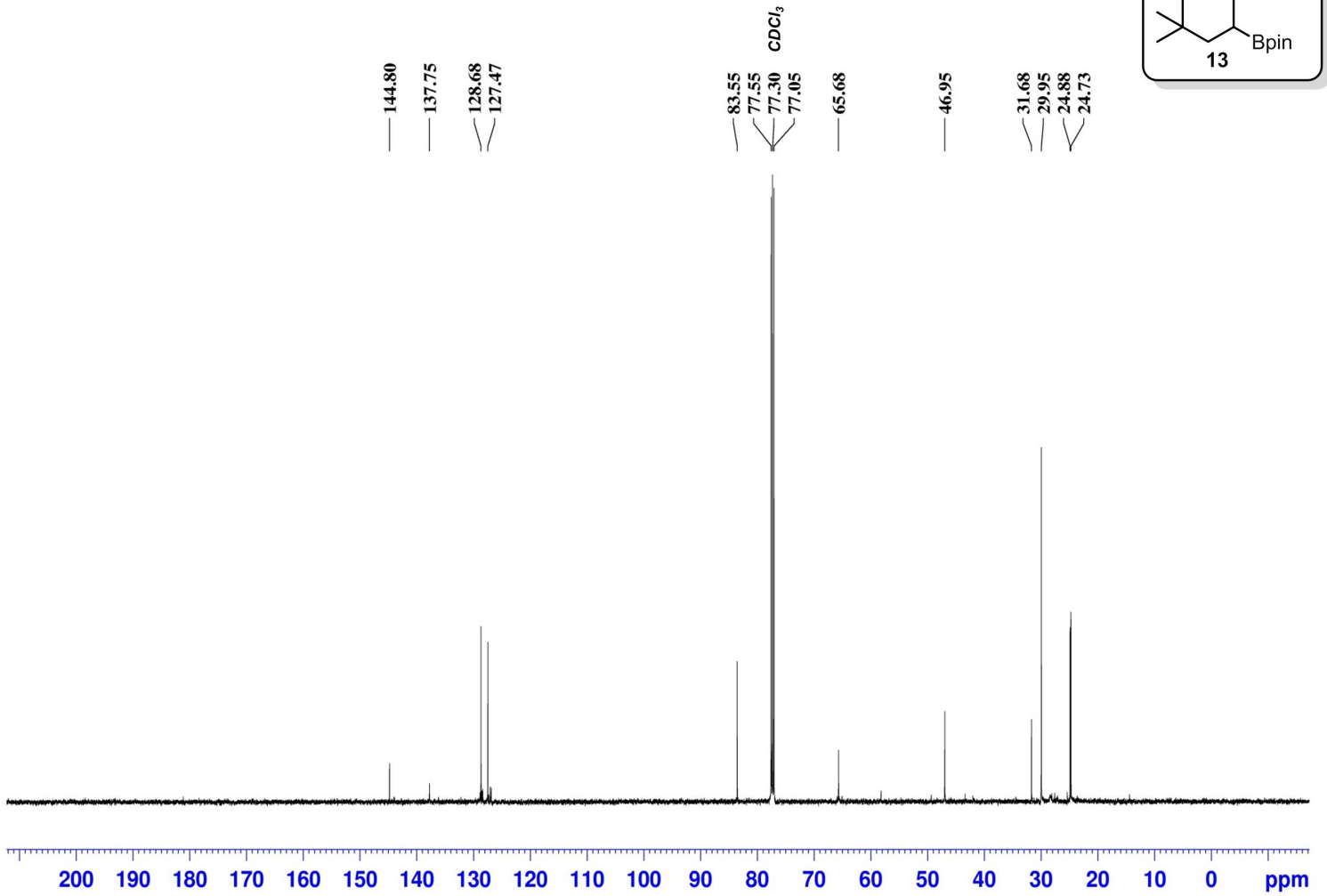




^{13}C NMR

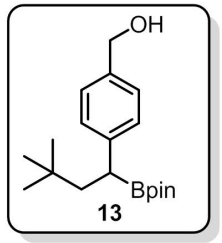
(4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)methanol
125 MHz, $CDCl_3$

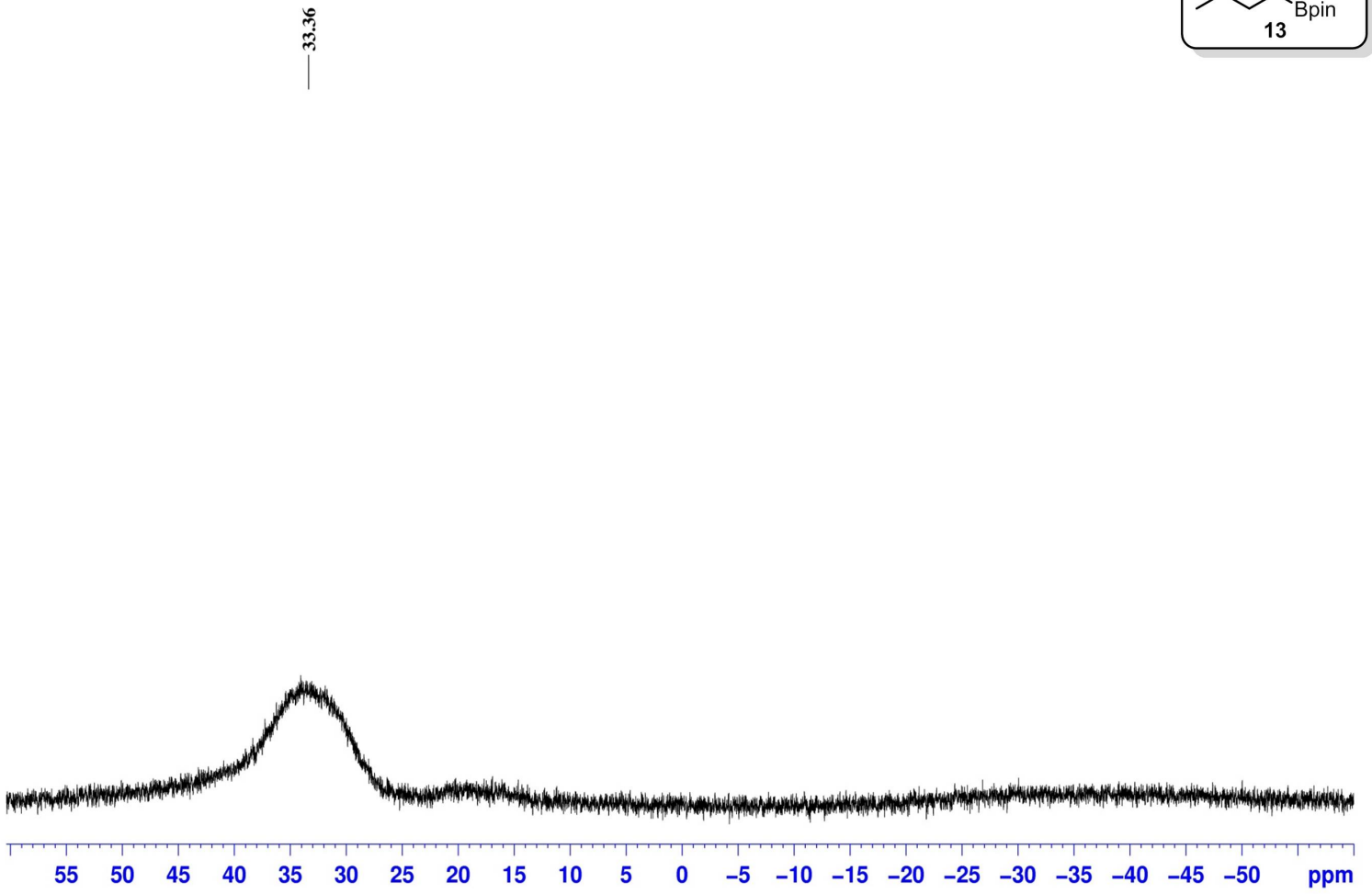




^{11}B NMR

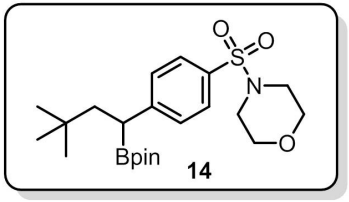
(4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)methanol
128 MHz, $CDCl_3$

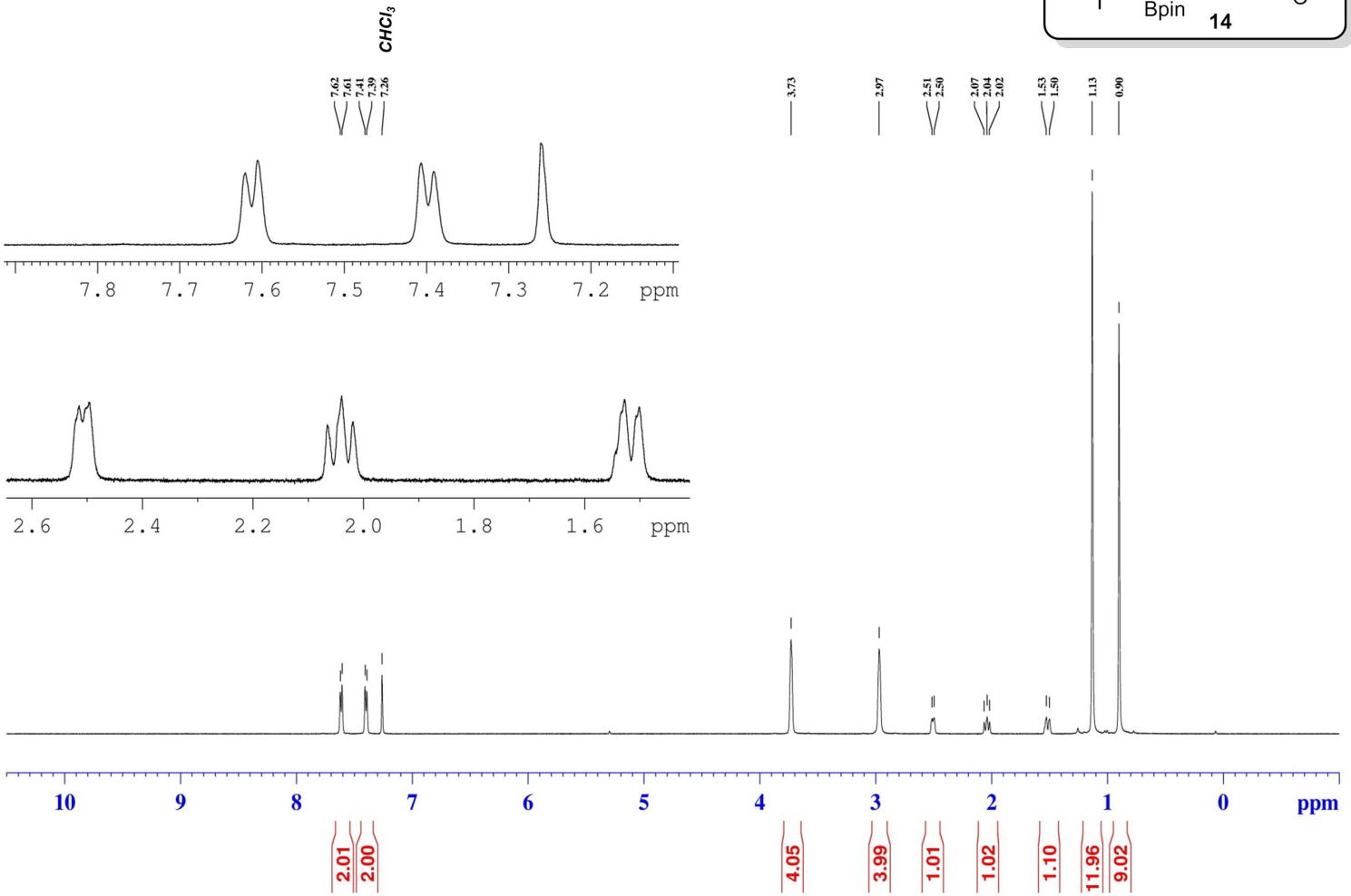




^1H NMR

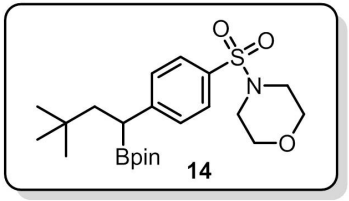
4-((4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)sulfonyl)morpholine
500 MHz, $CDCl_3$





^{13}C NMR

4-((4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)sulfonyl)morpholine
125 MHz, $CDCl_3$



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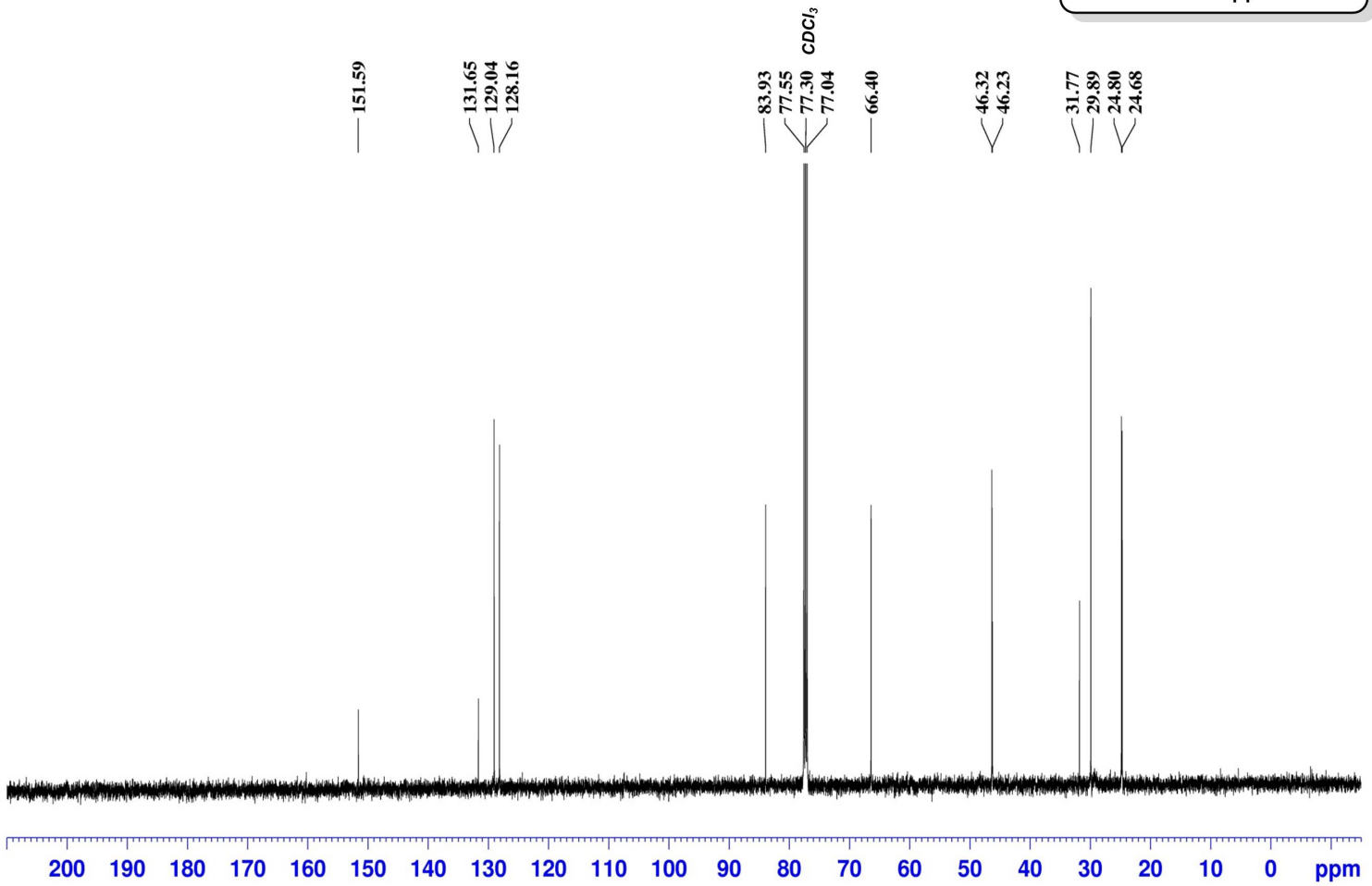
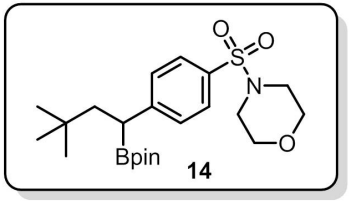


^{11}B NMR

4-((4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)sulfonyl)morpholine
128 MHz, $CDCl_3$



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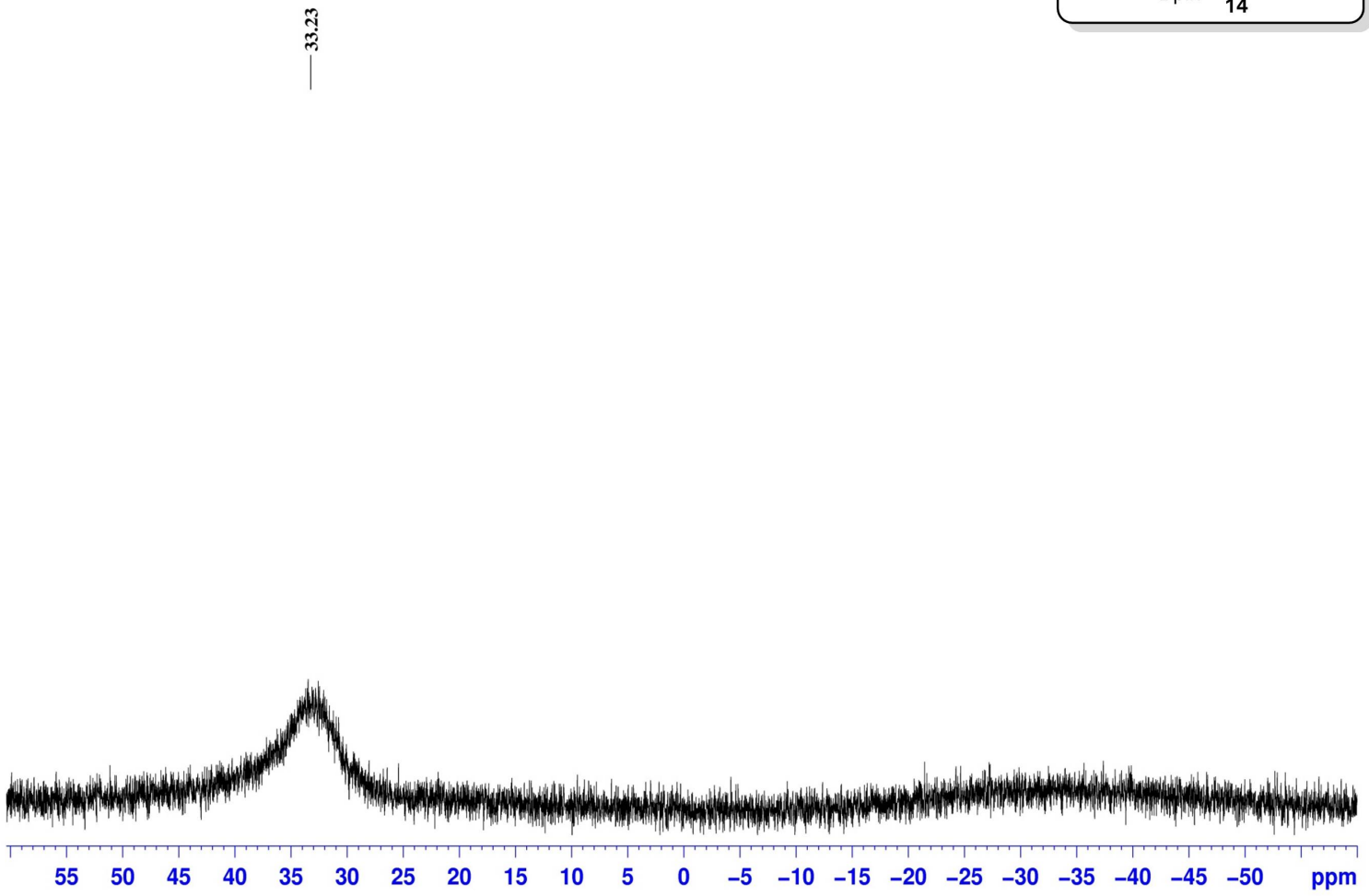
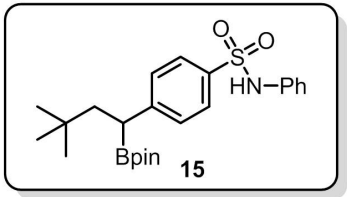
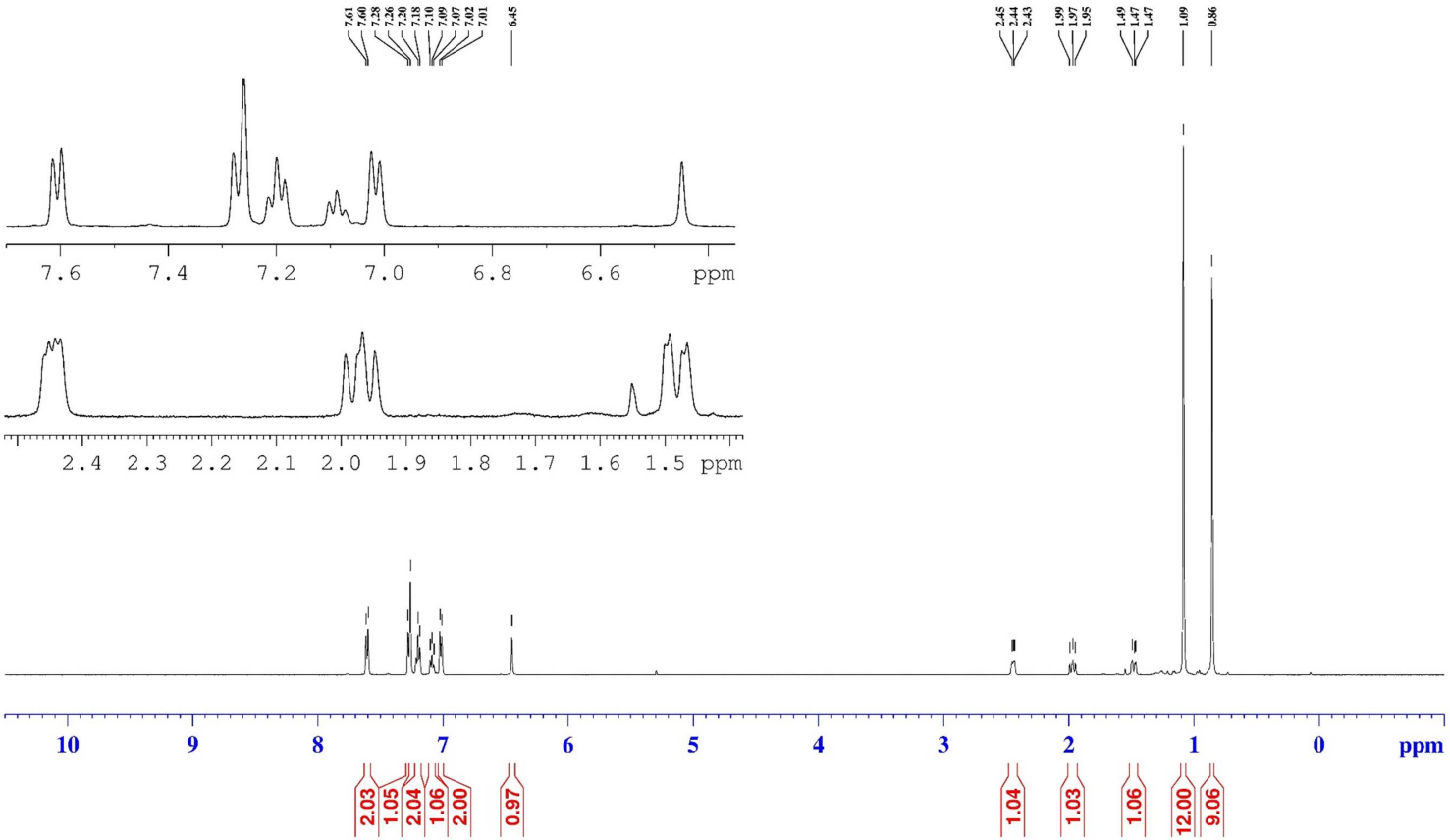


^1H NMR

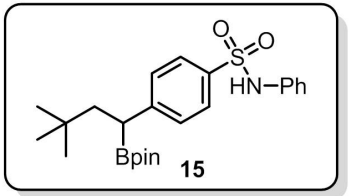
4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-N-phenylbenzenesulfonamide
500 MHz, $CDCl_3$

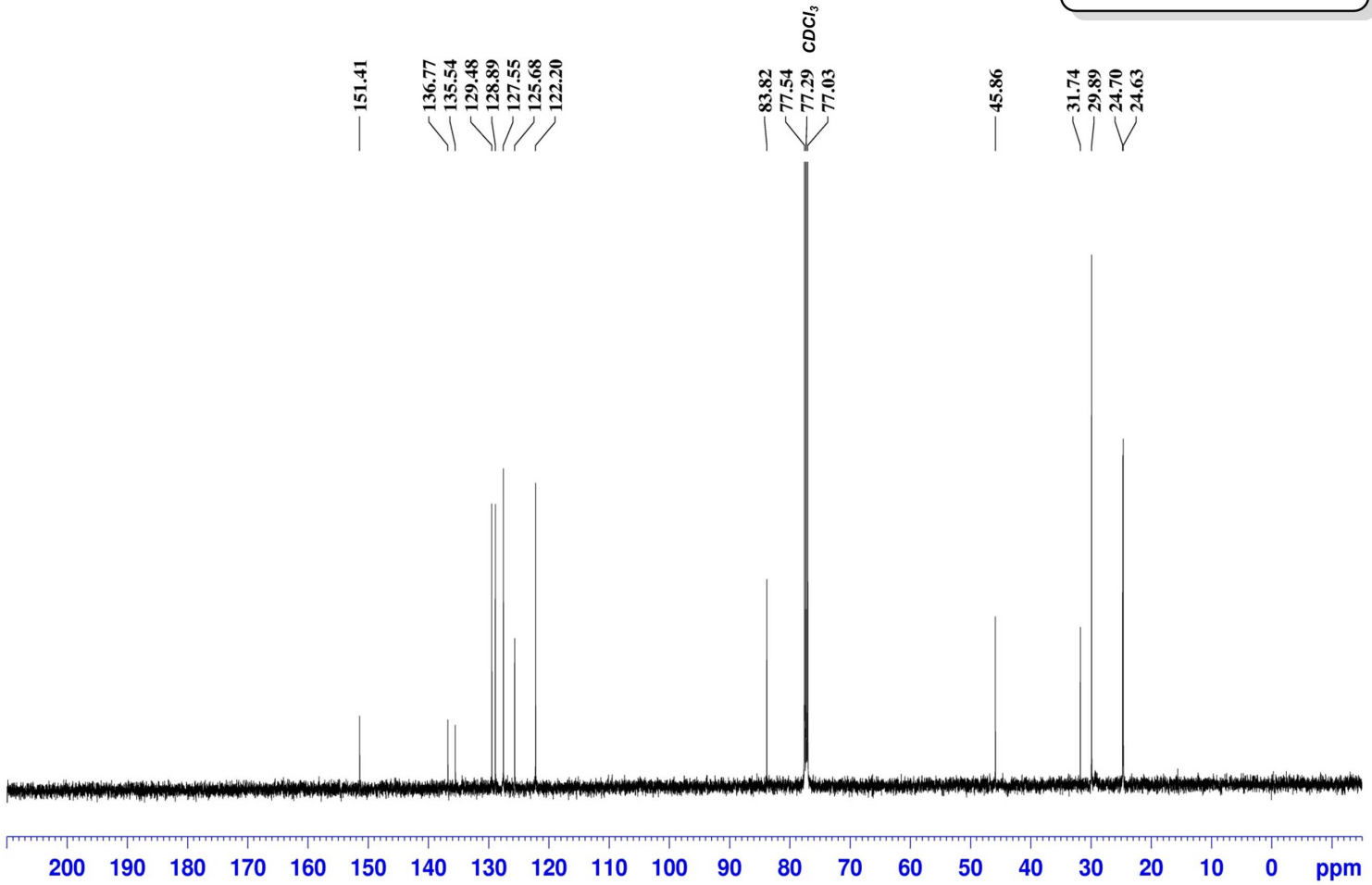




^{13}C NMR

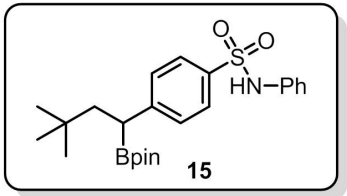
4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-N-phenylbenzenesulfonamide
125 MHz, $CDCl_3$





^{11}B NMR

4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-N-phenylbenzenesulfonamide
128 MHz, $CDCl_3$



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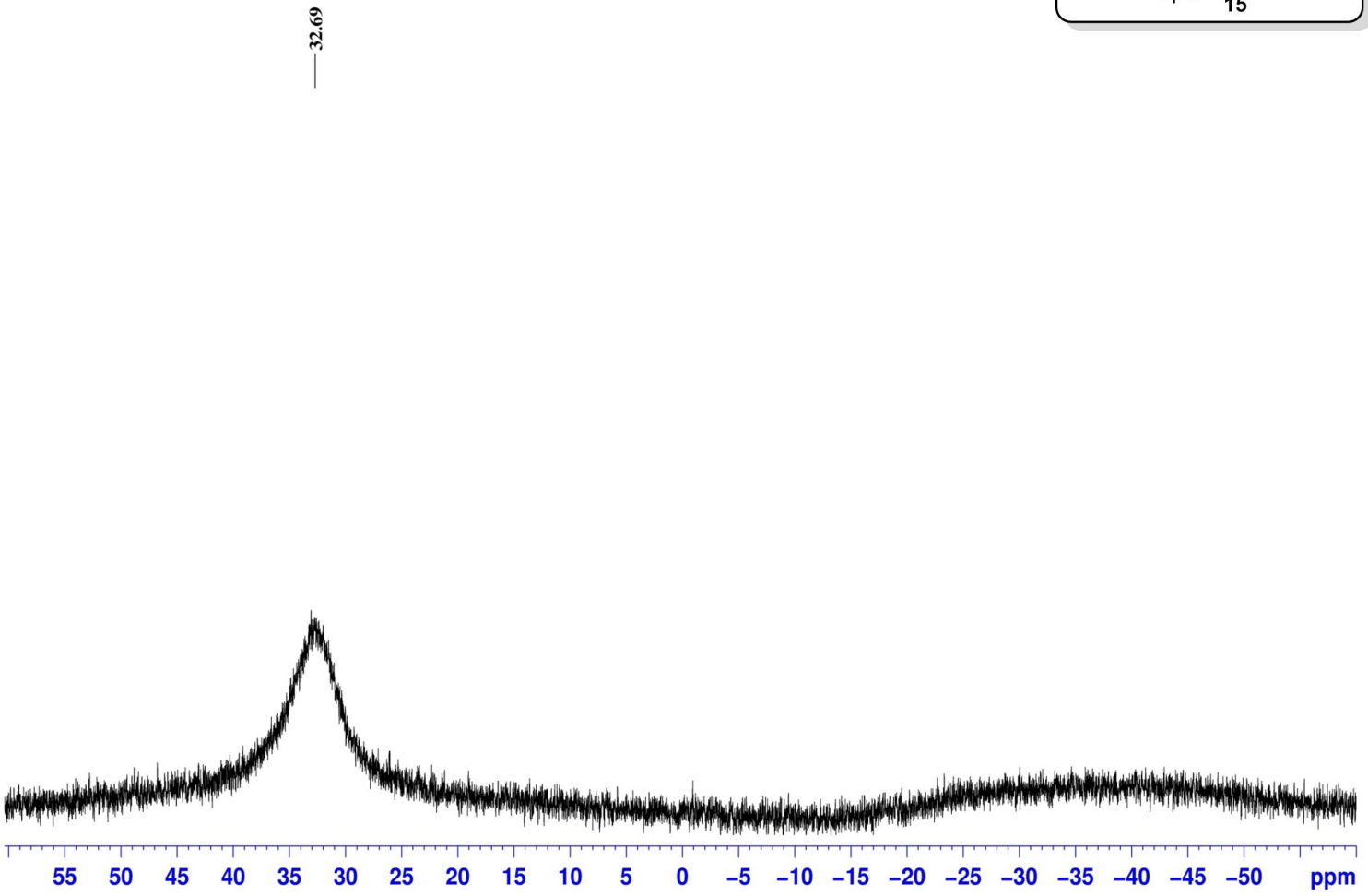
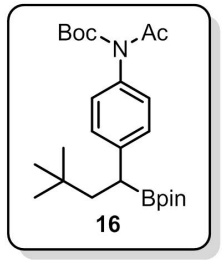
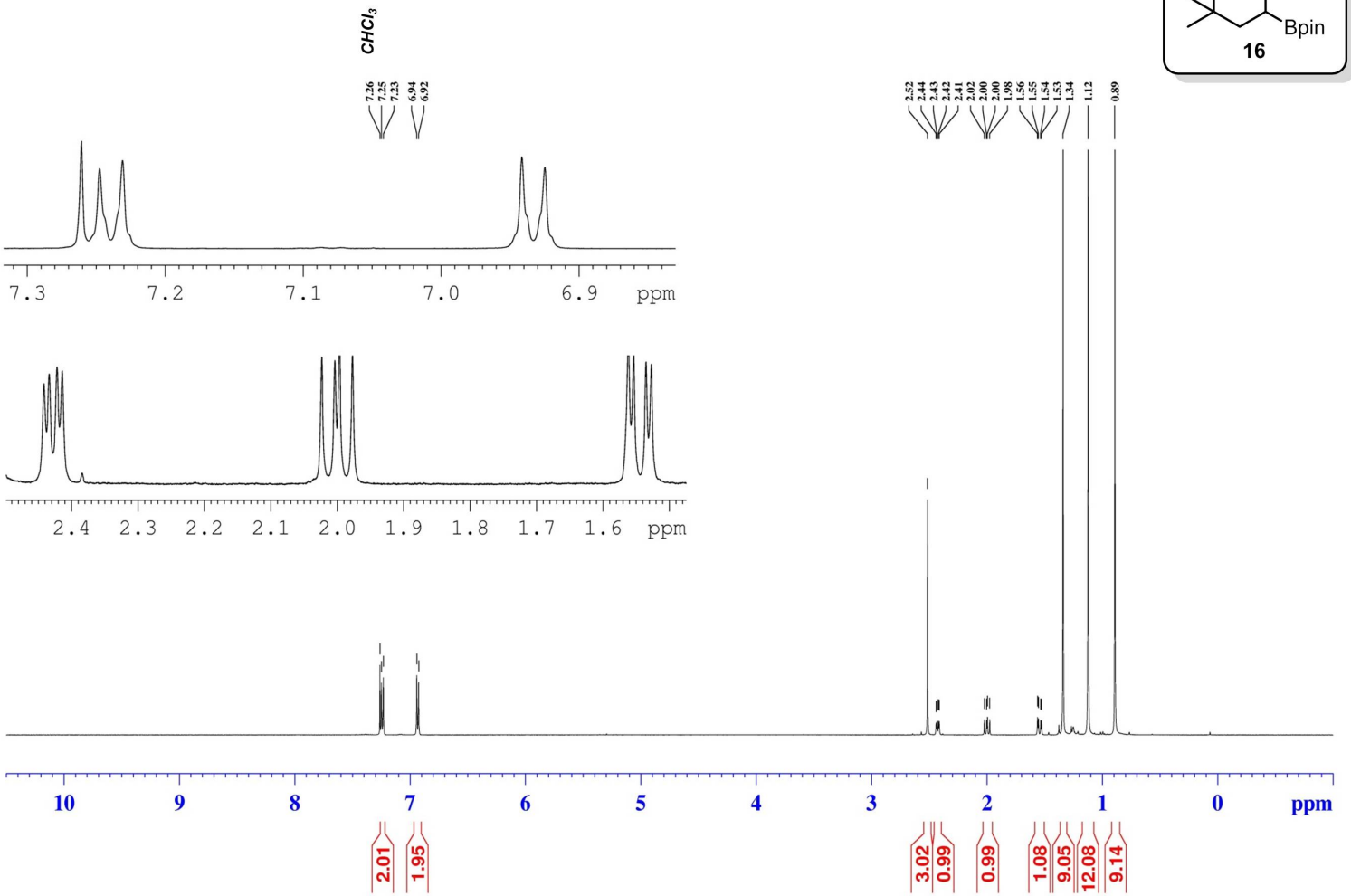


^1H NMR

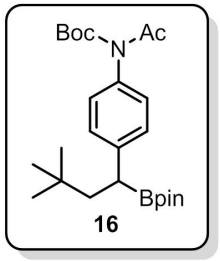
tert-butyl acetyl(4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)carbamate
500 MHz, $CDCl_3$

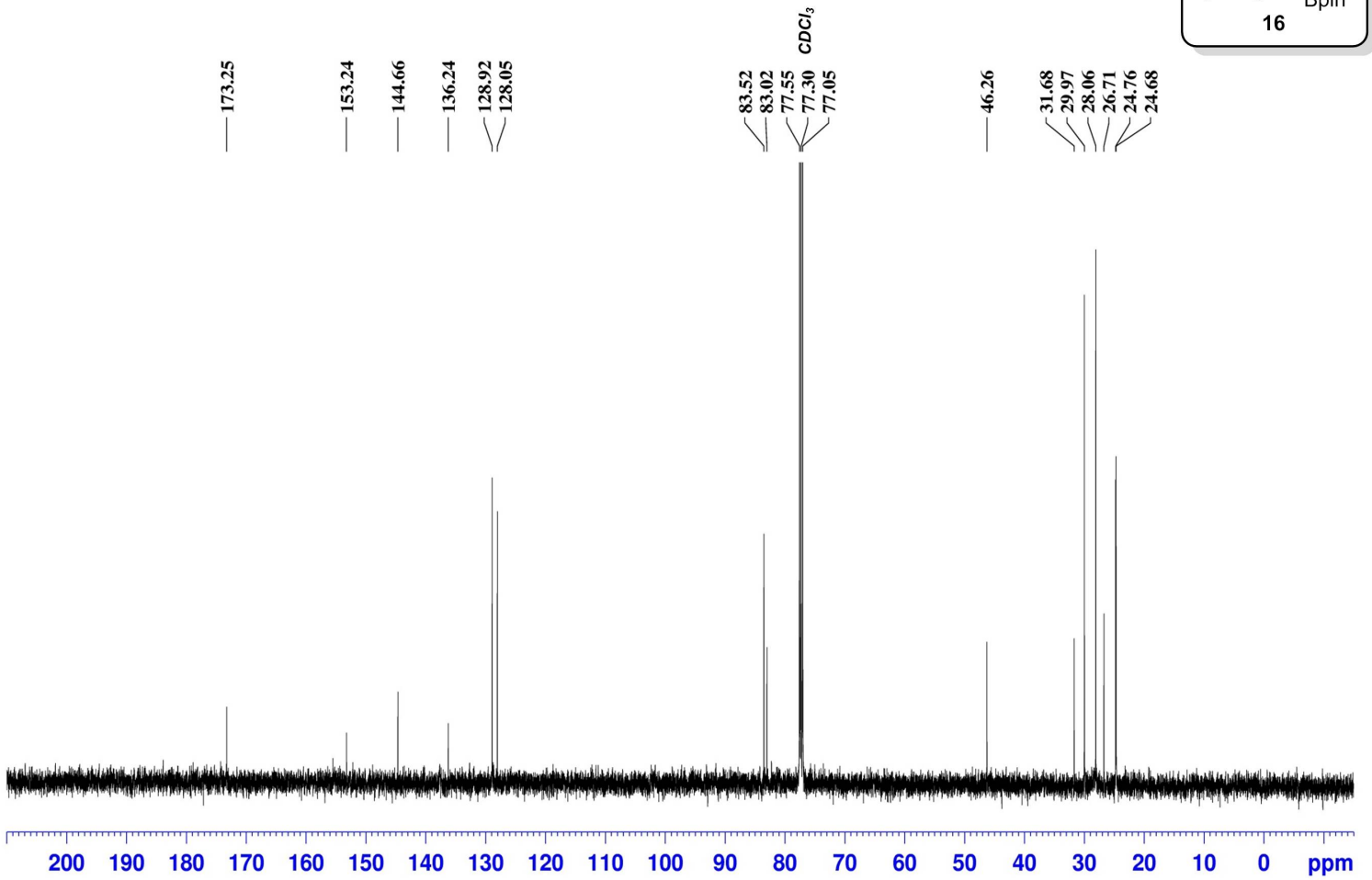




^{13}C NMR

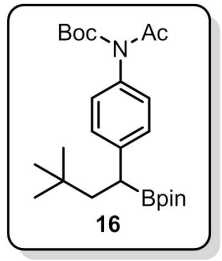
***Tert*-butyl acetyl(4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)carbamate**
125 MHz, $CDCl_3$





^{11}B NMR

***tert*-butyl acetyl(4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)carbamate**
128 MHz, $CDCl_3$



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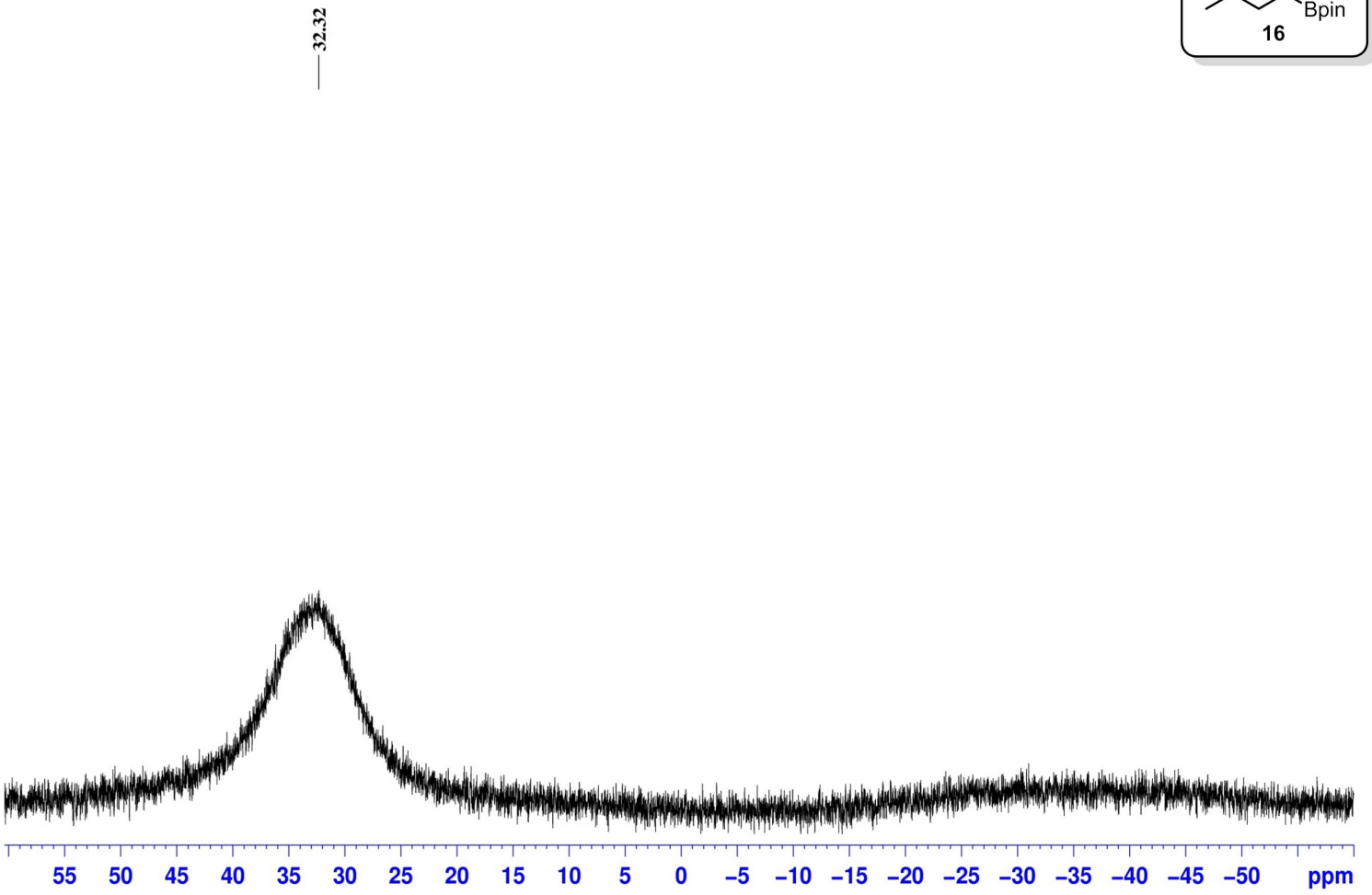
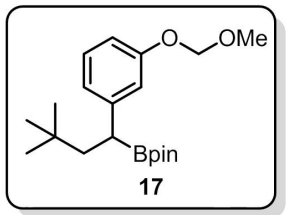
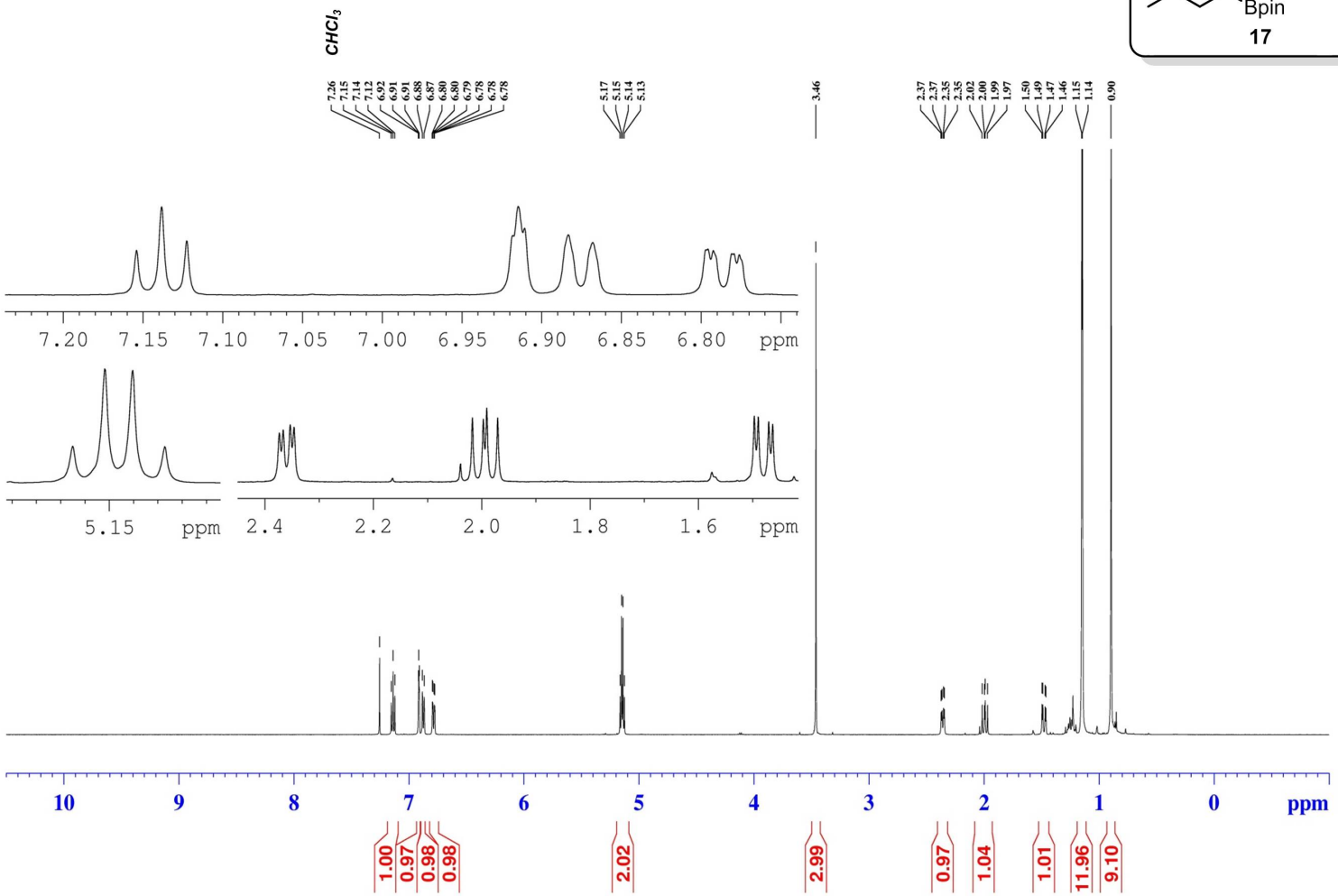


^1H NMR

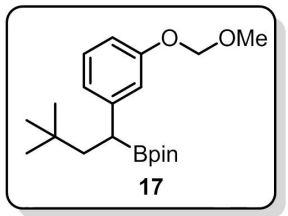
2-(1-(4-(1,3-dioxolan-2-yl)phenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

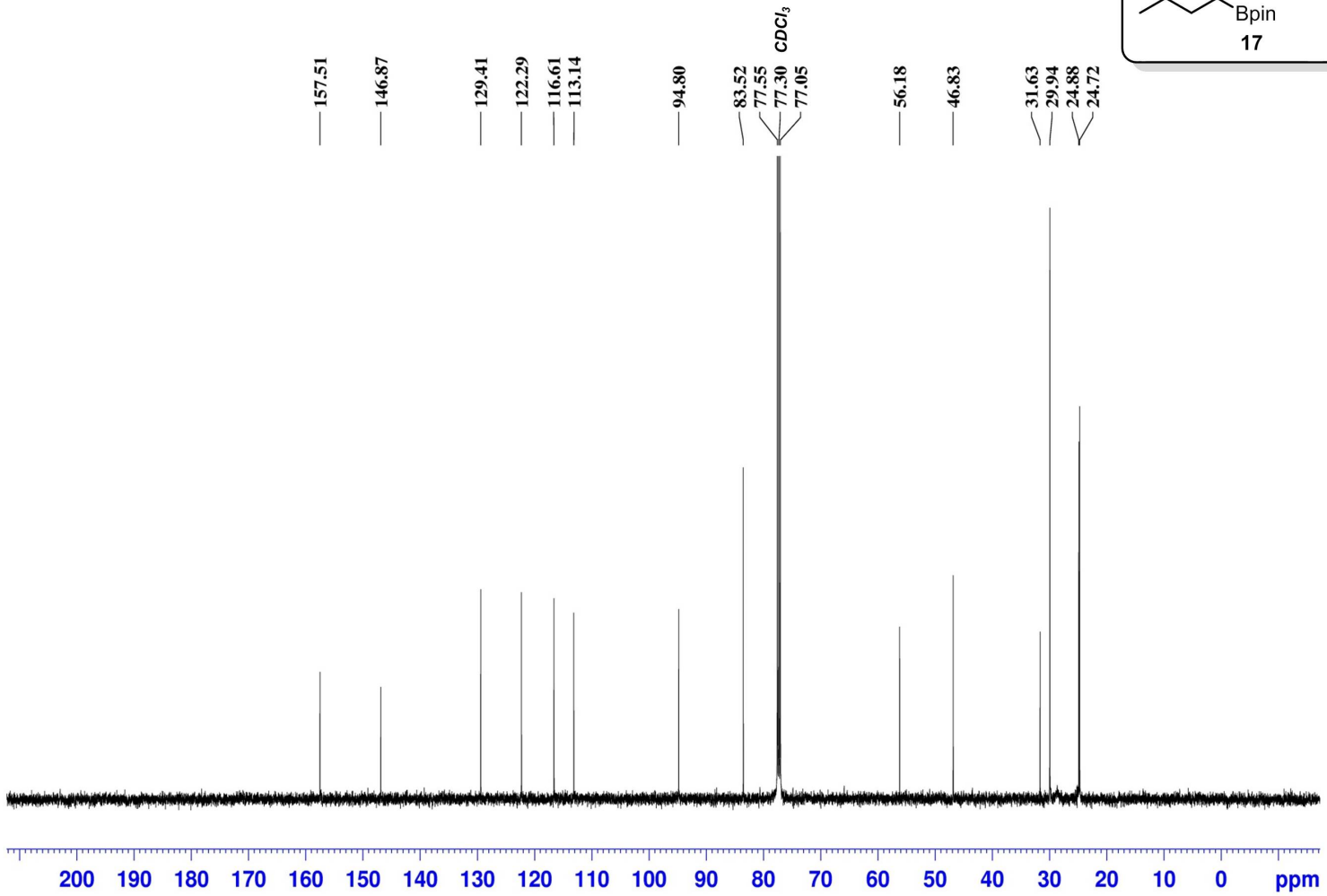




^{13}C NMR

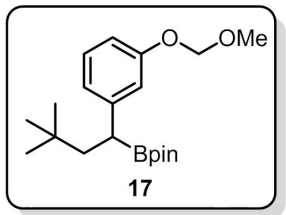
2-(1-(4-(1,3-Dioxolan-2-yl)phenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$





^{11}B NMR

2-(1-(4-(1,3-dioxolan-2-yl)phenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$



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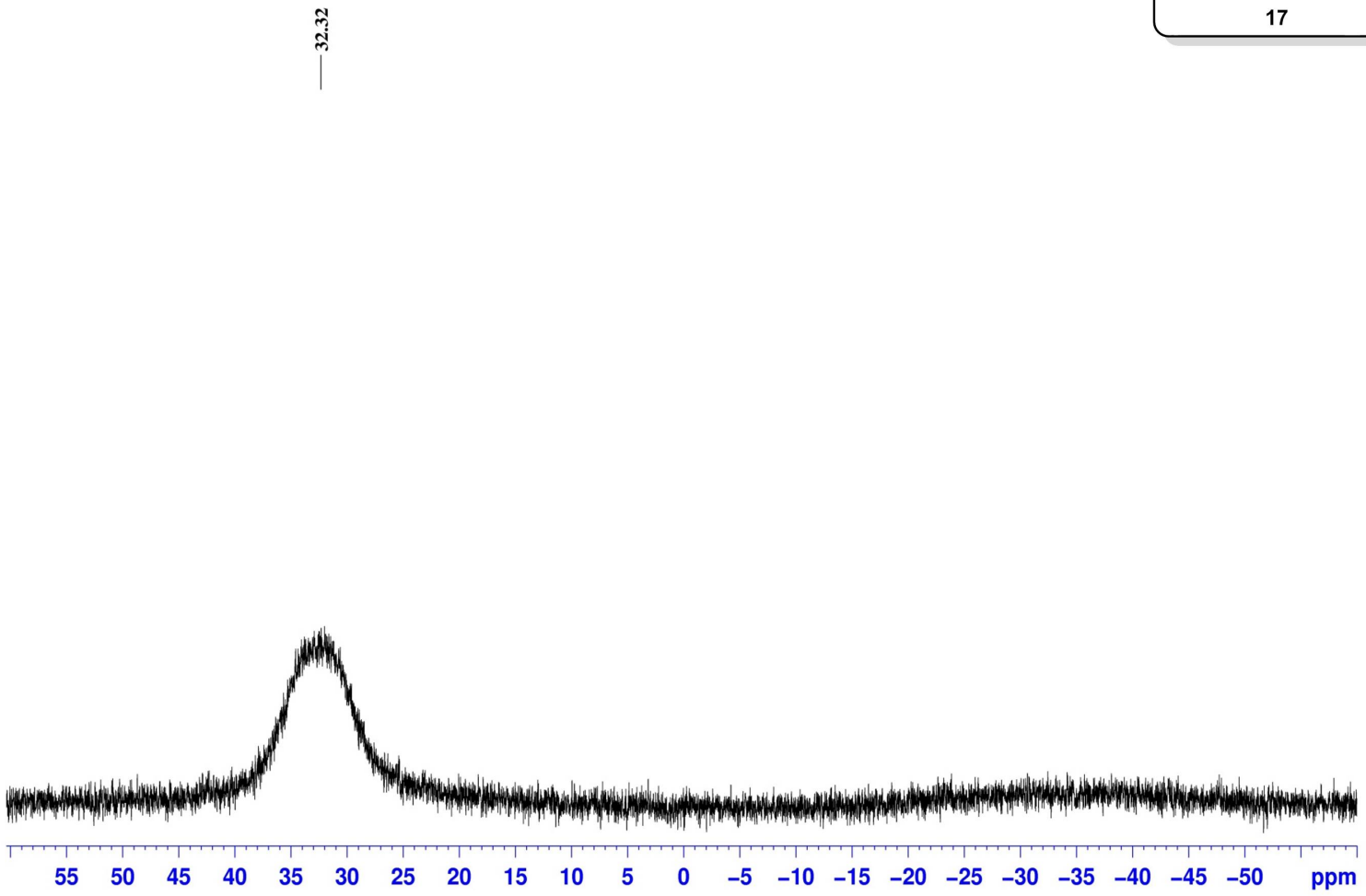
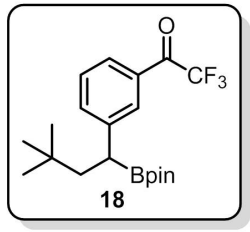
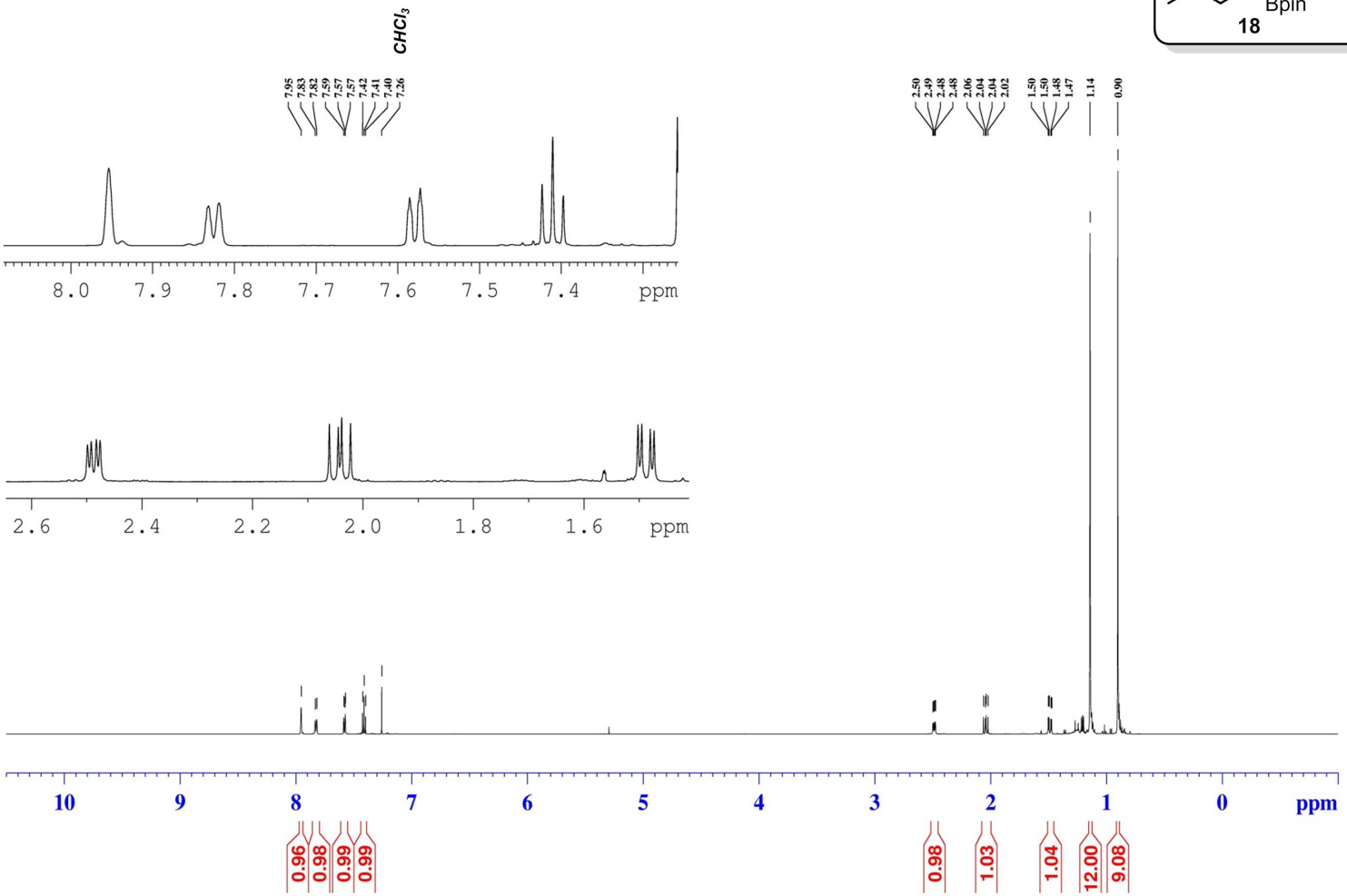


^1H NMR

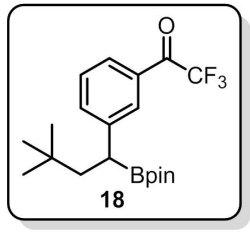
1-(3-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)-2,2,2-trifluoroethanone
500 MHz, $CDCl_3$

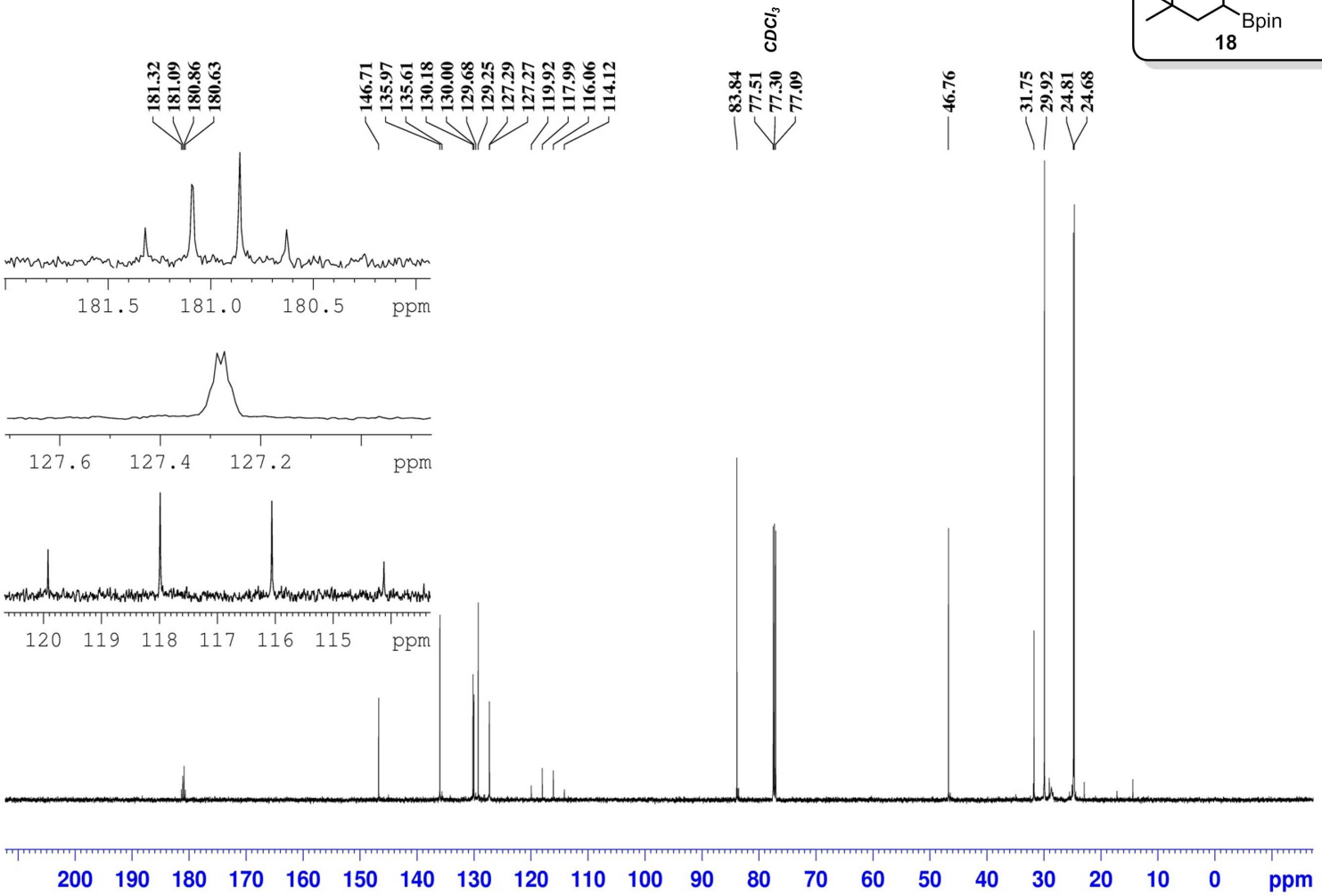




^{13}C NMR

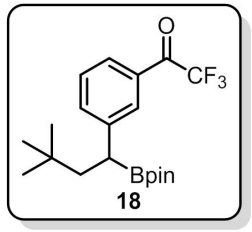
1-(3-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)-2,2,2-trifluoroethanone
125 MHz, $CDCl_3$

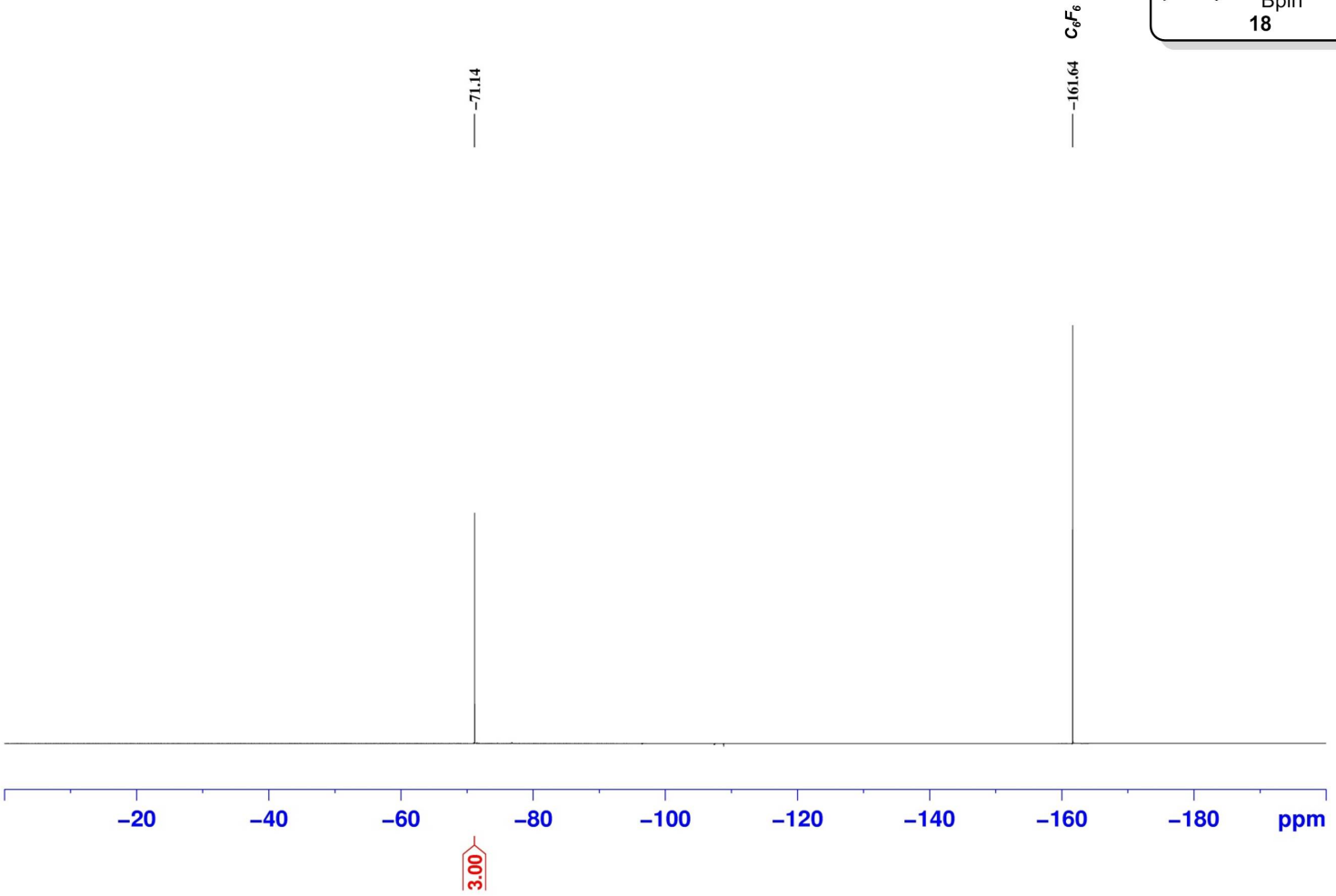




^{19}F NMR

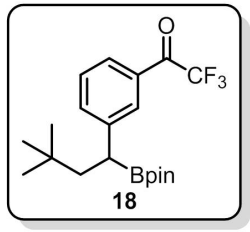
1-(3-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)-2,2,2-trifluoroethanone
471 MHz, $CDCl_3$

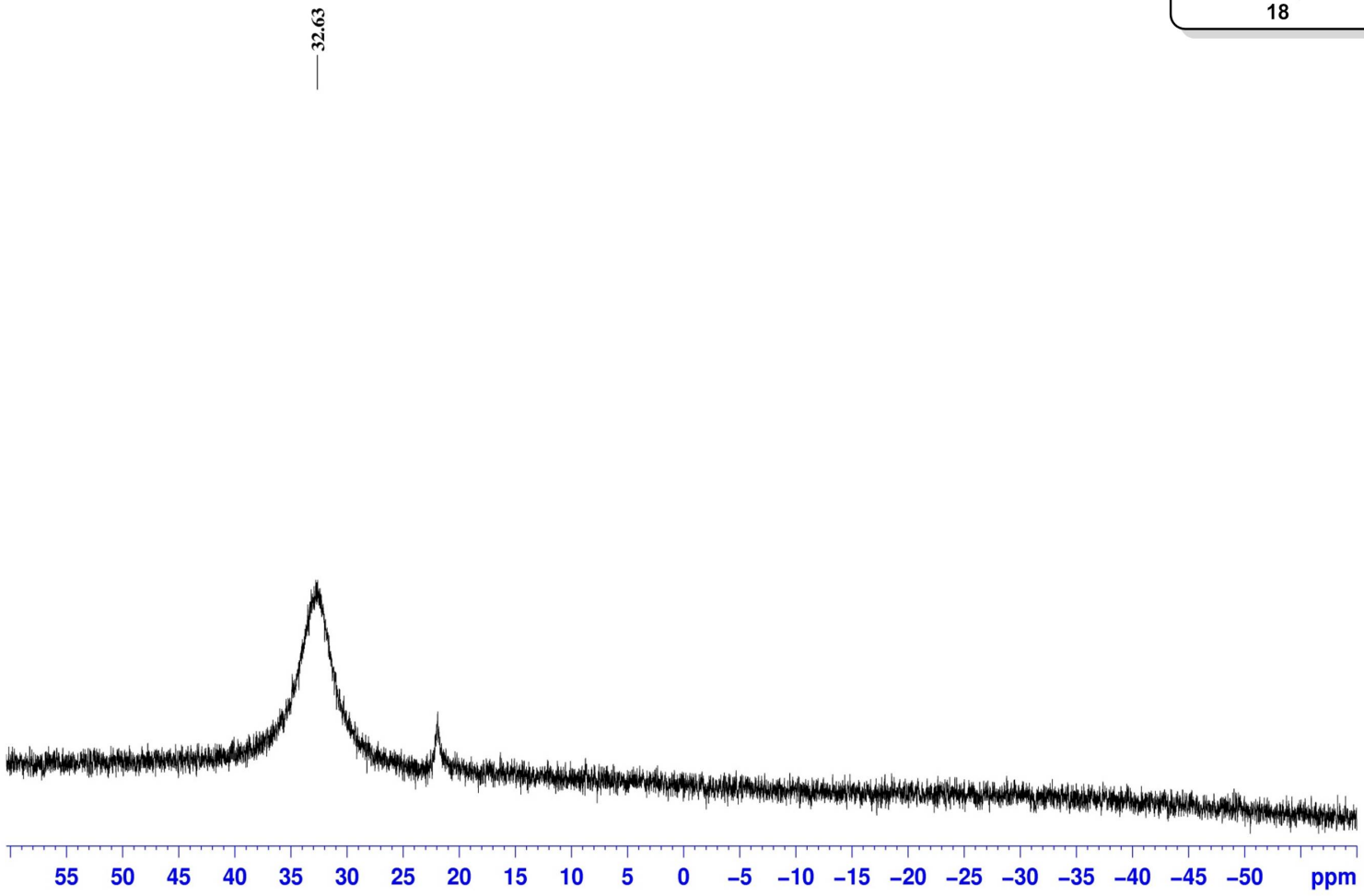




^{11}B NMR

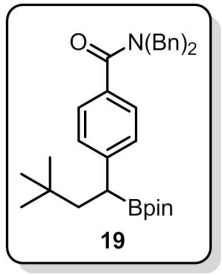
1-(3-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)-2,2,2-trifluoroethanone
128 MHz, $CDCl_3$

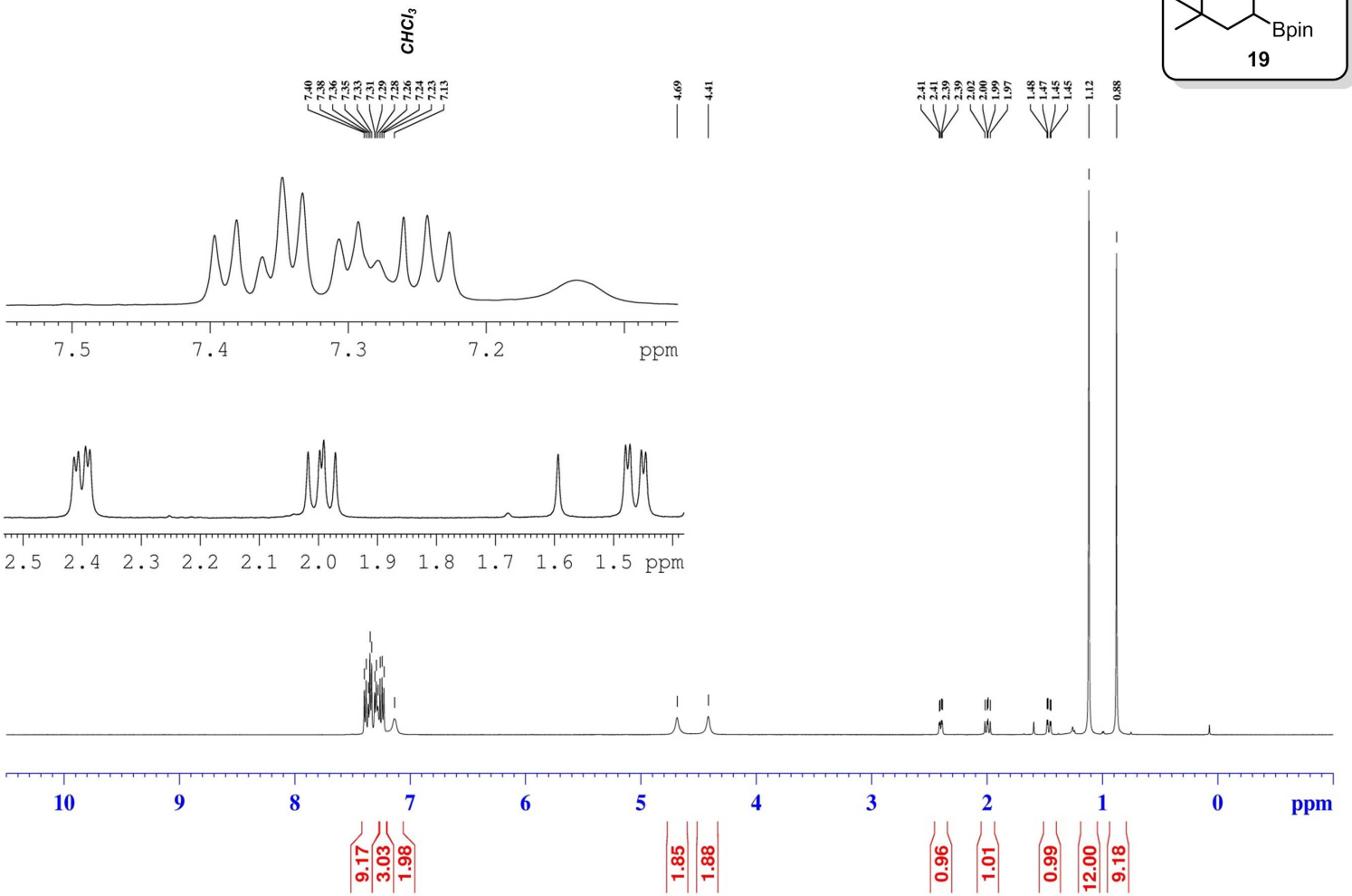




^1H NMR

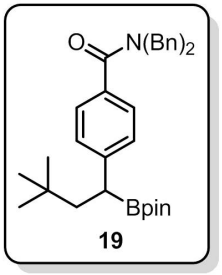
***N,N*-dibenzyl-4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzamide**
500 MHz, $CDCl_3$

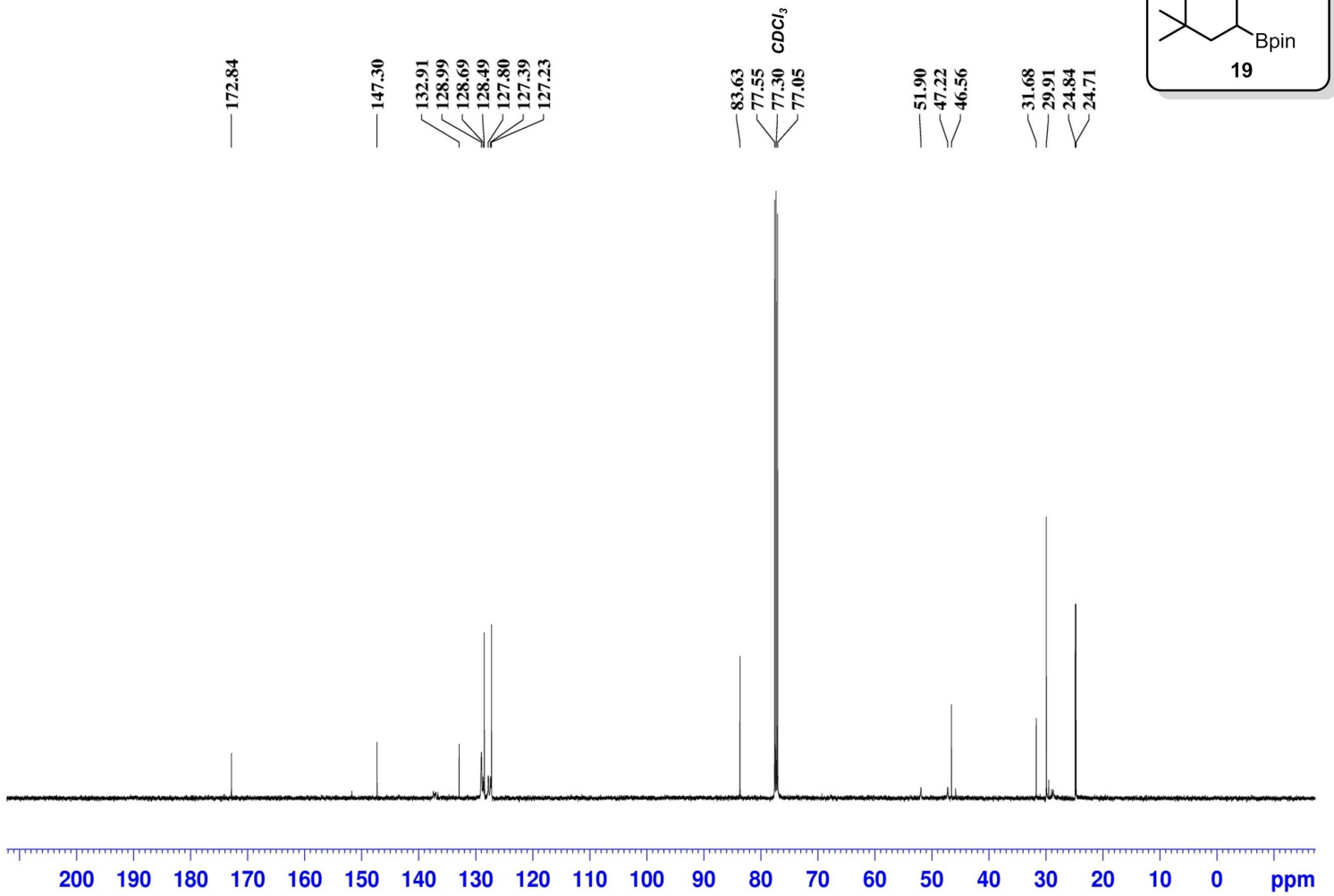




^{13}C NMR

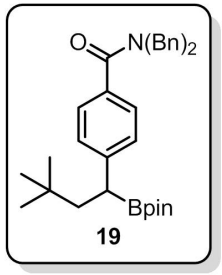
_N,N_-Dibenzyl-4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzamide
125 MHz, $CDCl_3$

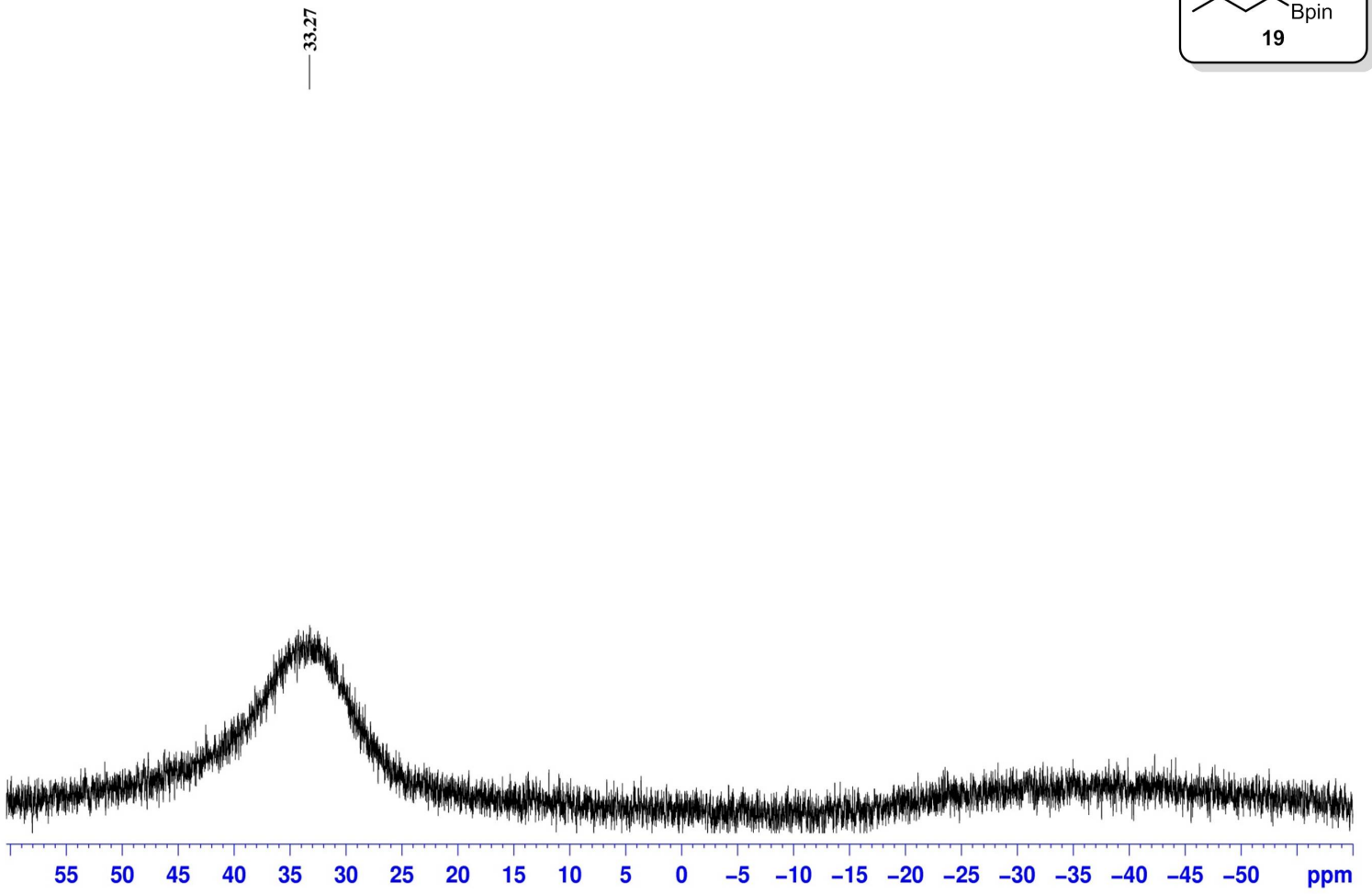




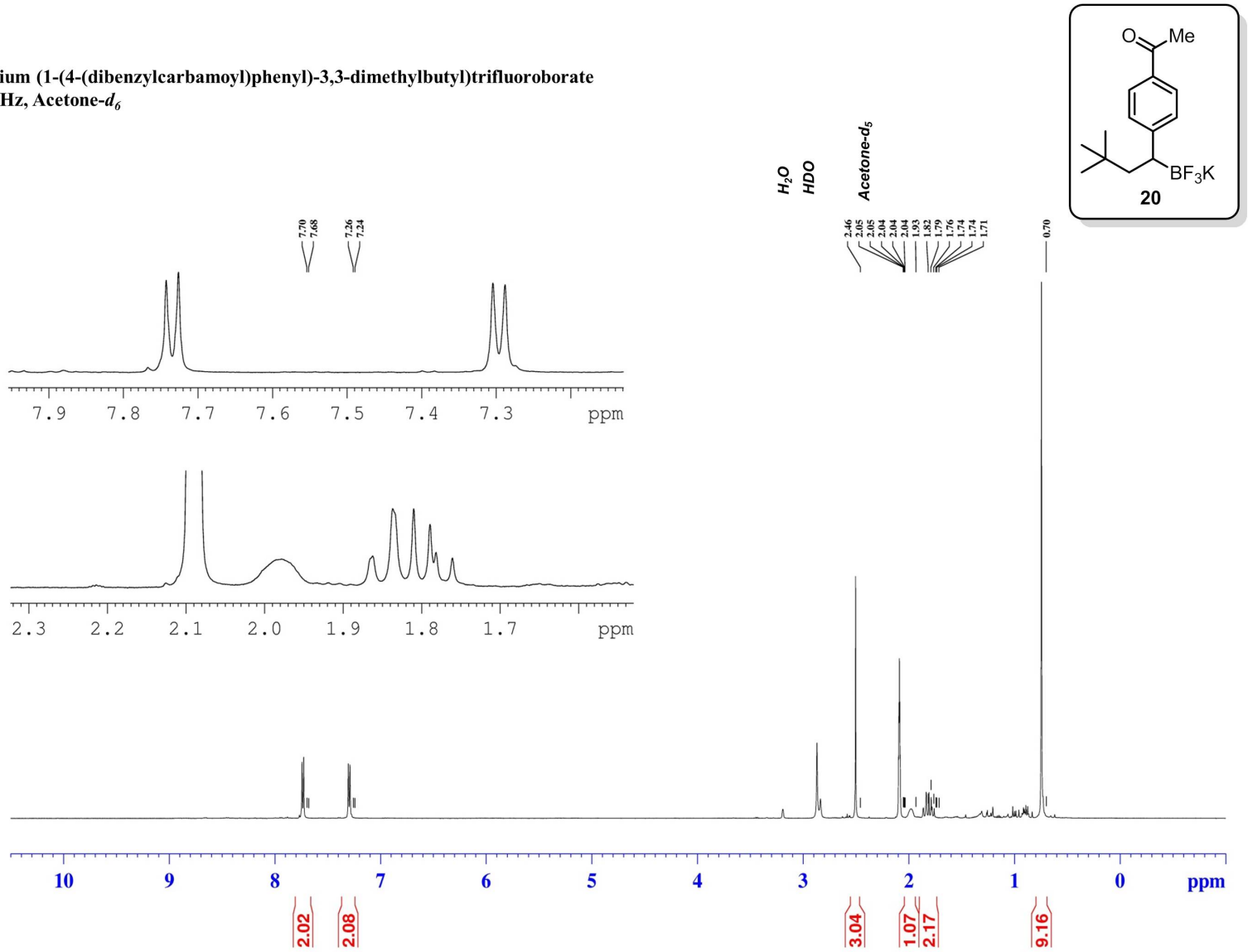
^{11}B NMR

N,N-dibenzyl-4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzamide
128 MHz, $CDCl_3$



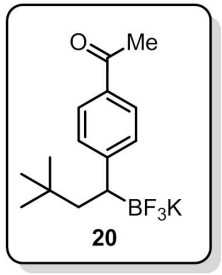


Potassium (1-(4-(dibenzylcarbamoyl)phenyl)-3,3-dimethylbutyl)trifluoroborate
500 MHz, Acetone-d_6



^{13}C NMR

Potassium (1-(4-(dibenzylcarbamoyl)phenyl)-3,3-dimethylbutyl)trifluoroborate
125 MHz, Acetone-d_6



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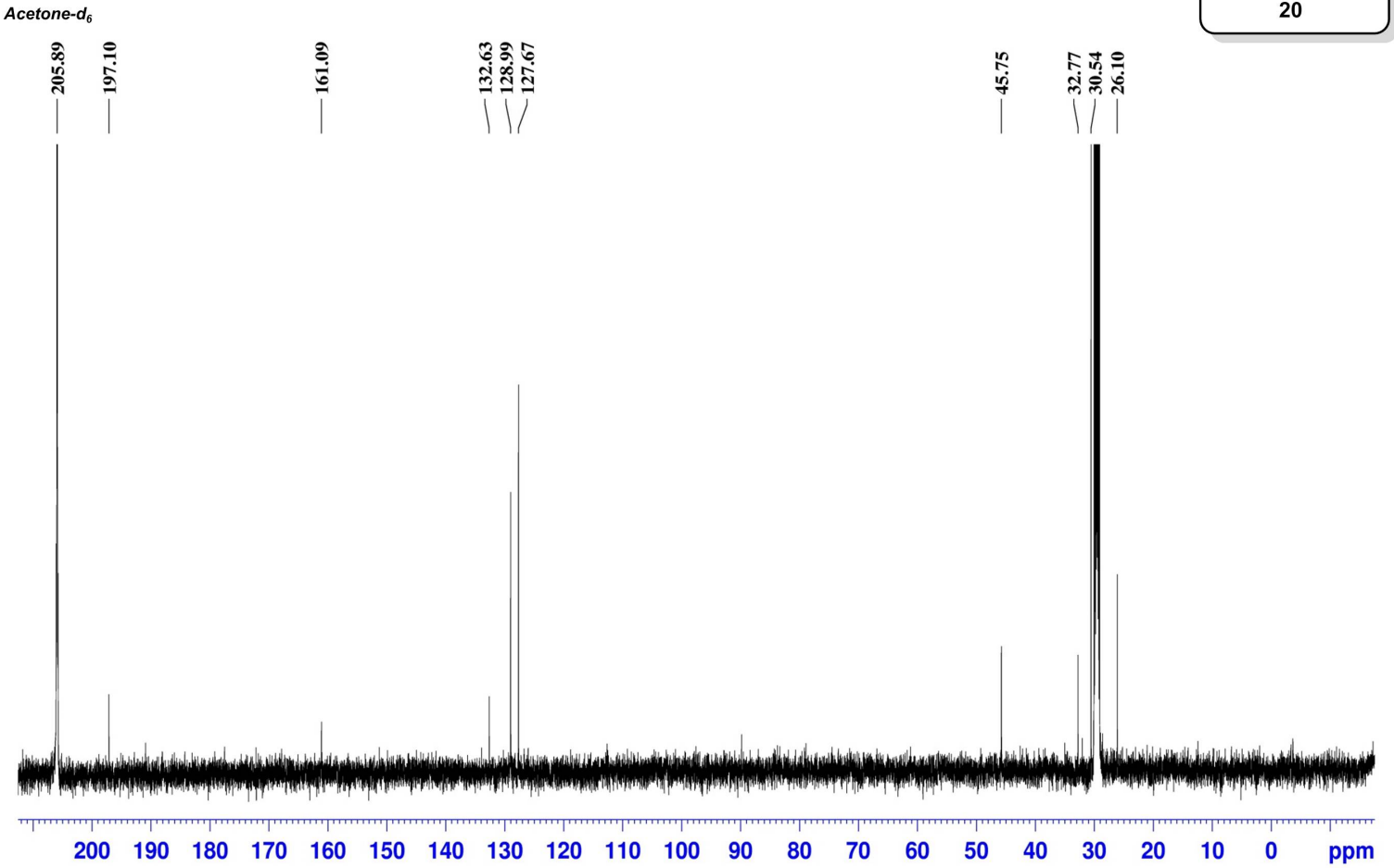
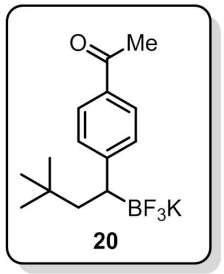
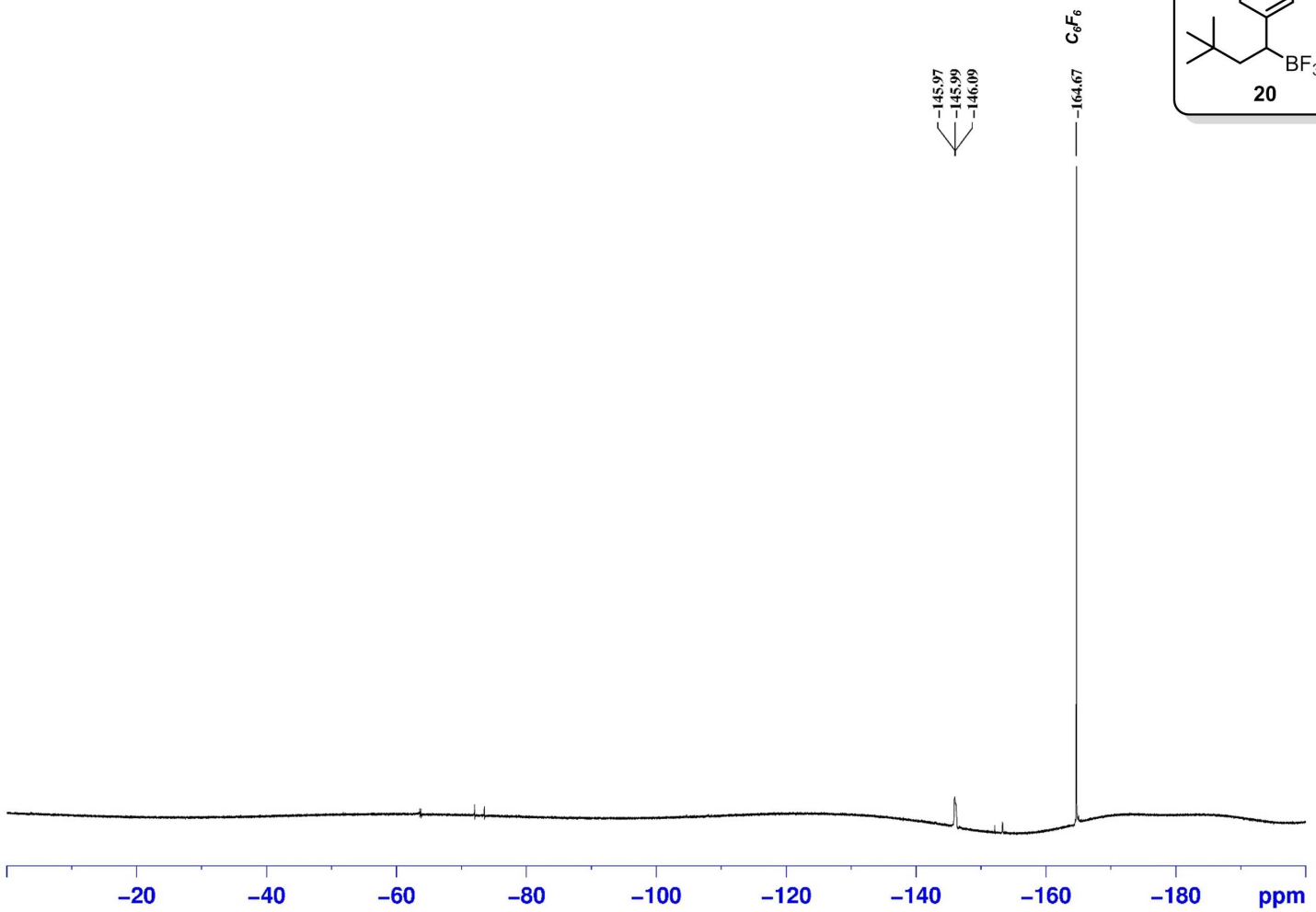


^{19}F NMR

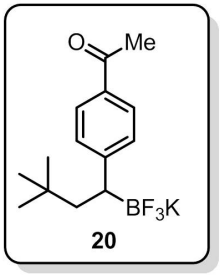
Potassium (1-(4-(dibenzylcarbamoyl)phenyl)-3,3-dimethylbutyl)trifluoroborate
471 MHz, Acetone-d_6

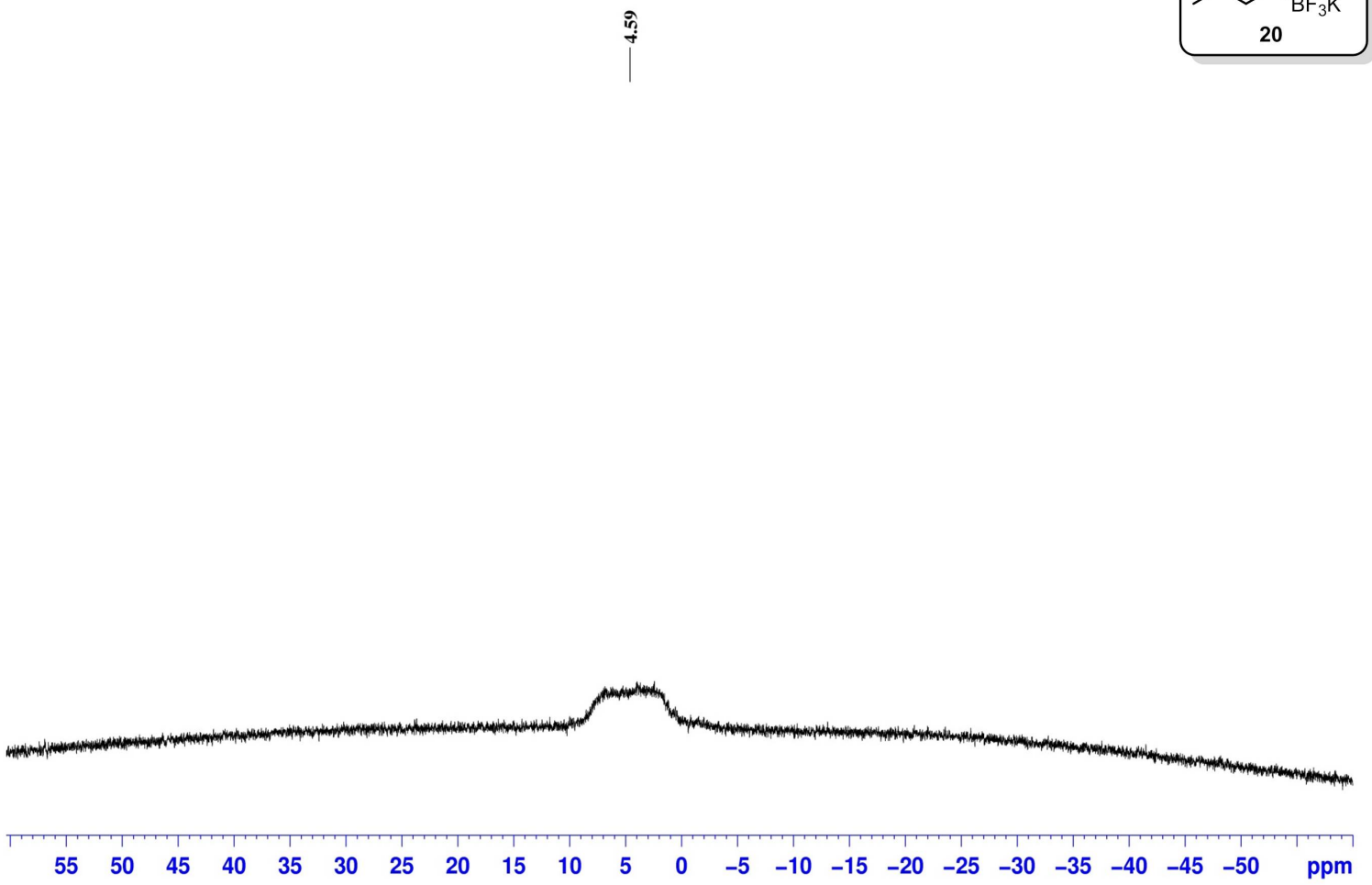




^{11}B NMR

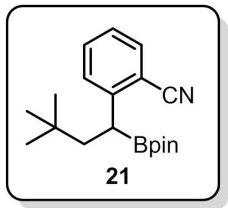
Potassium (1-(4-(dibenzylcarbamoyl)phenyl)-3,3-dimethylbutyl)trifluoroborate
128 MHz, Acetone-d_6

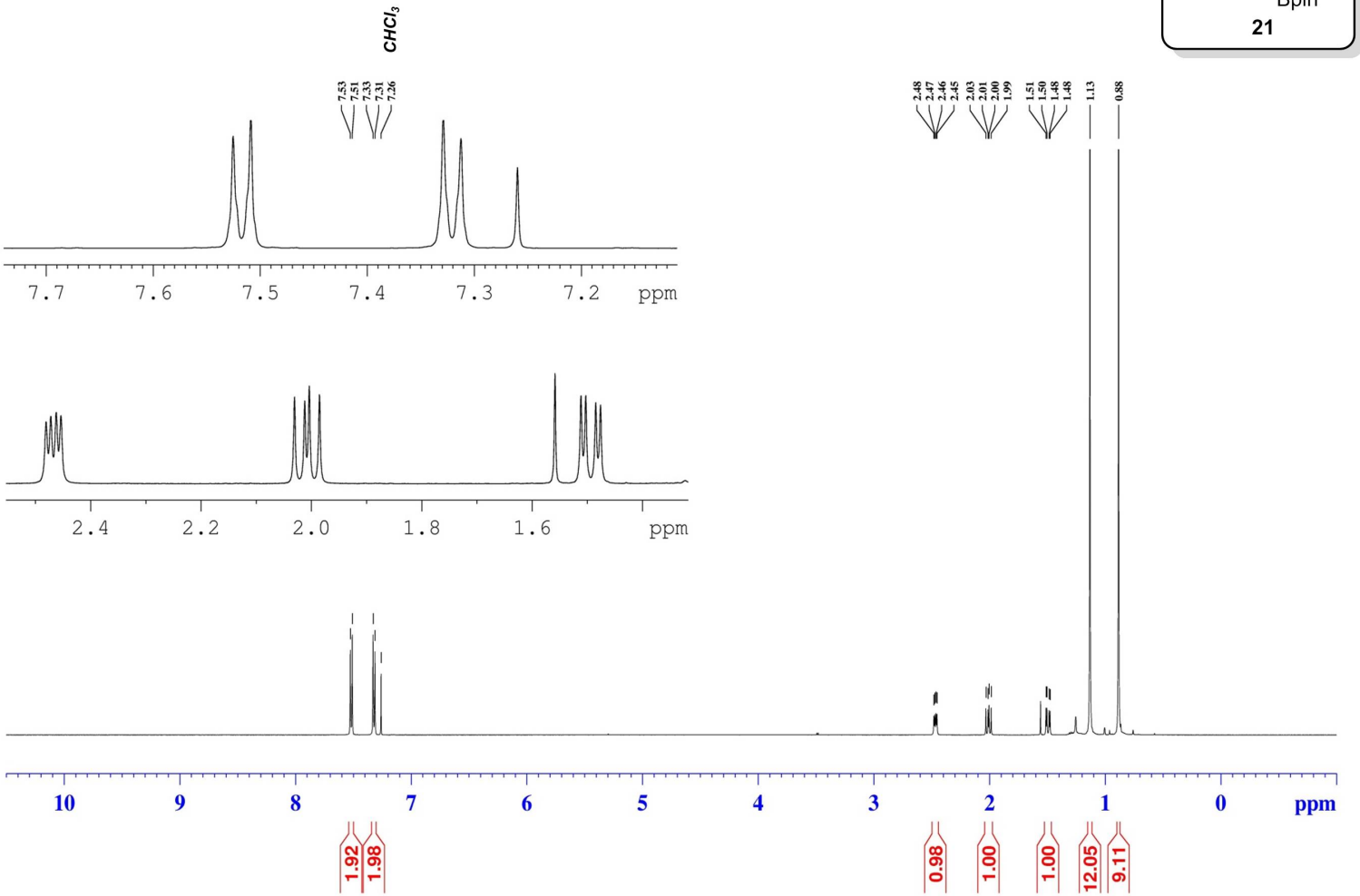




^1H NMR

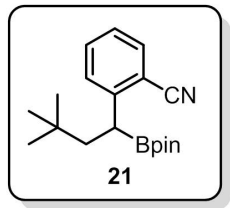
2-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzonitrile
500 MHz, $CDCl_3$

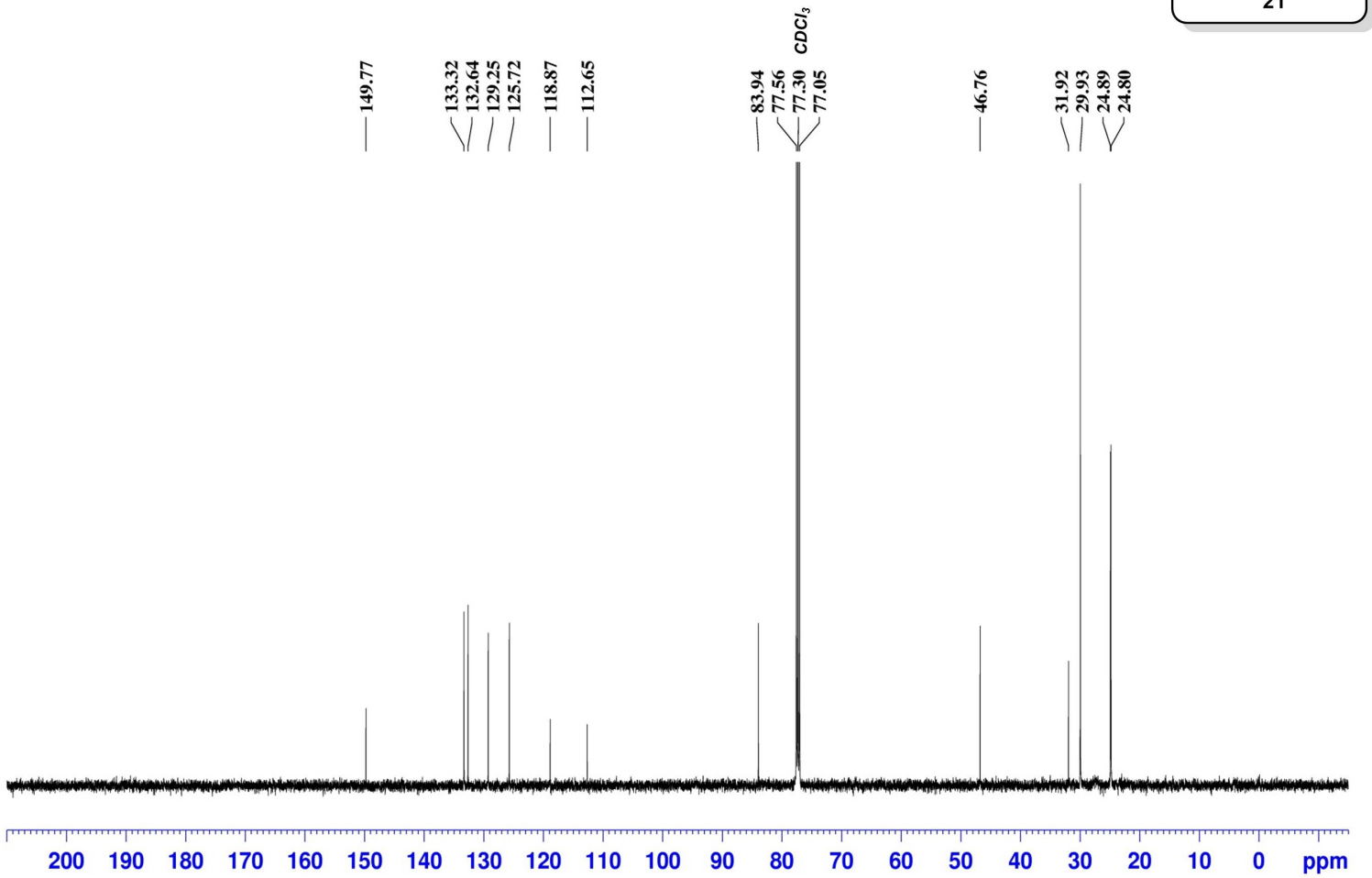




^{13}C NMR

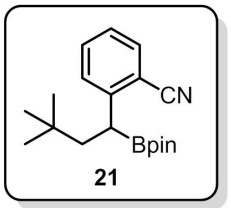
2-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzonitrile
125 MHz, $CDCl_3$





^{11}B NMR

2-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzonitrile
128 MHz, $CDCl_3$



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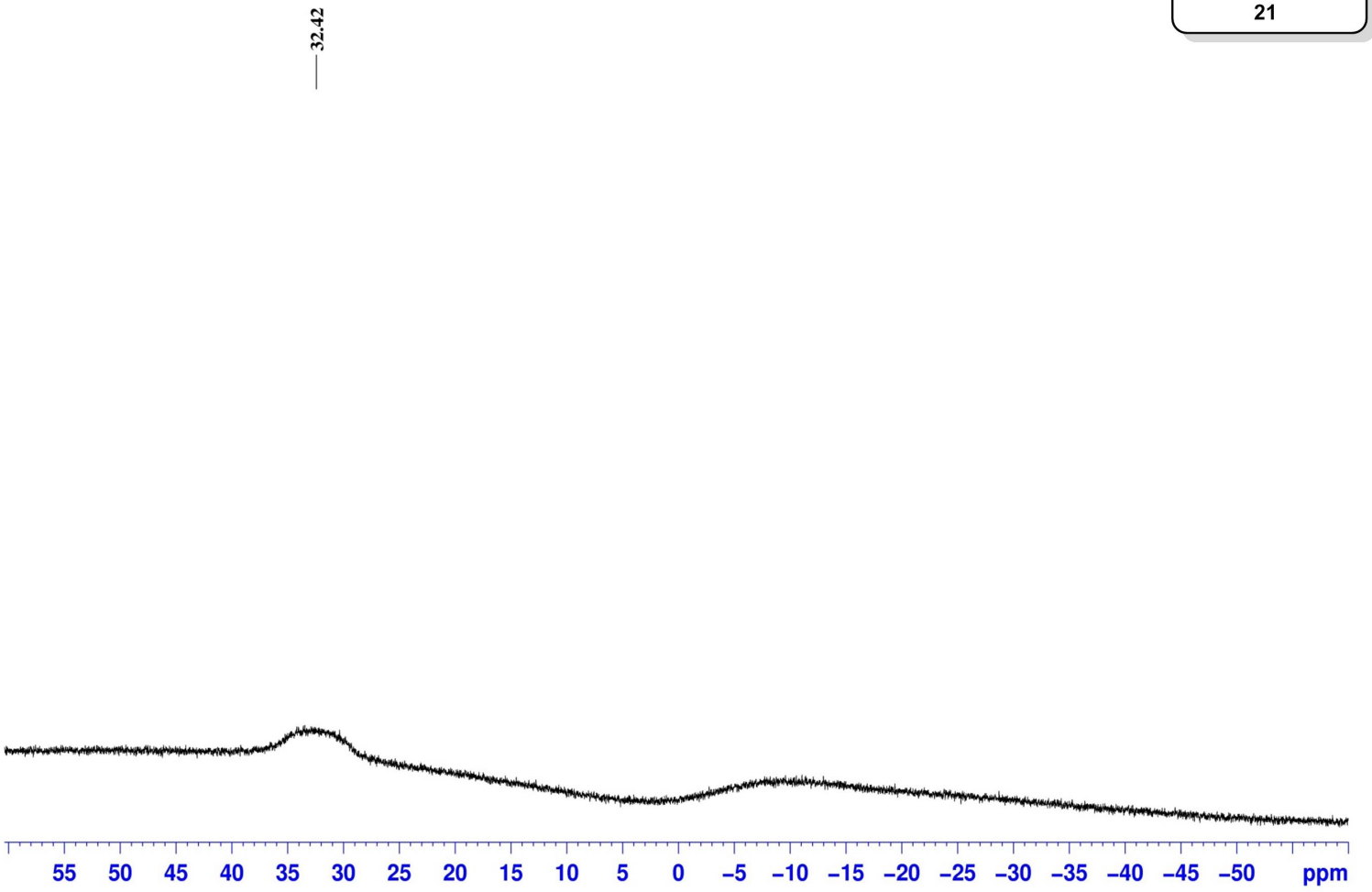
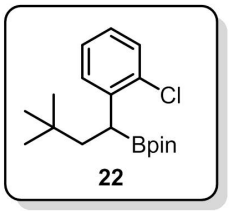
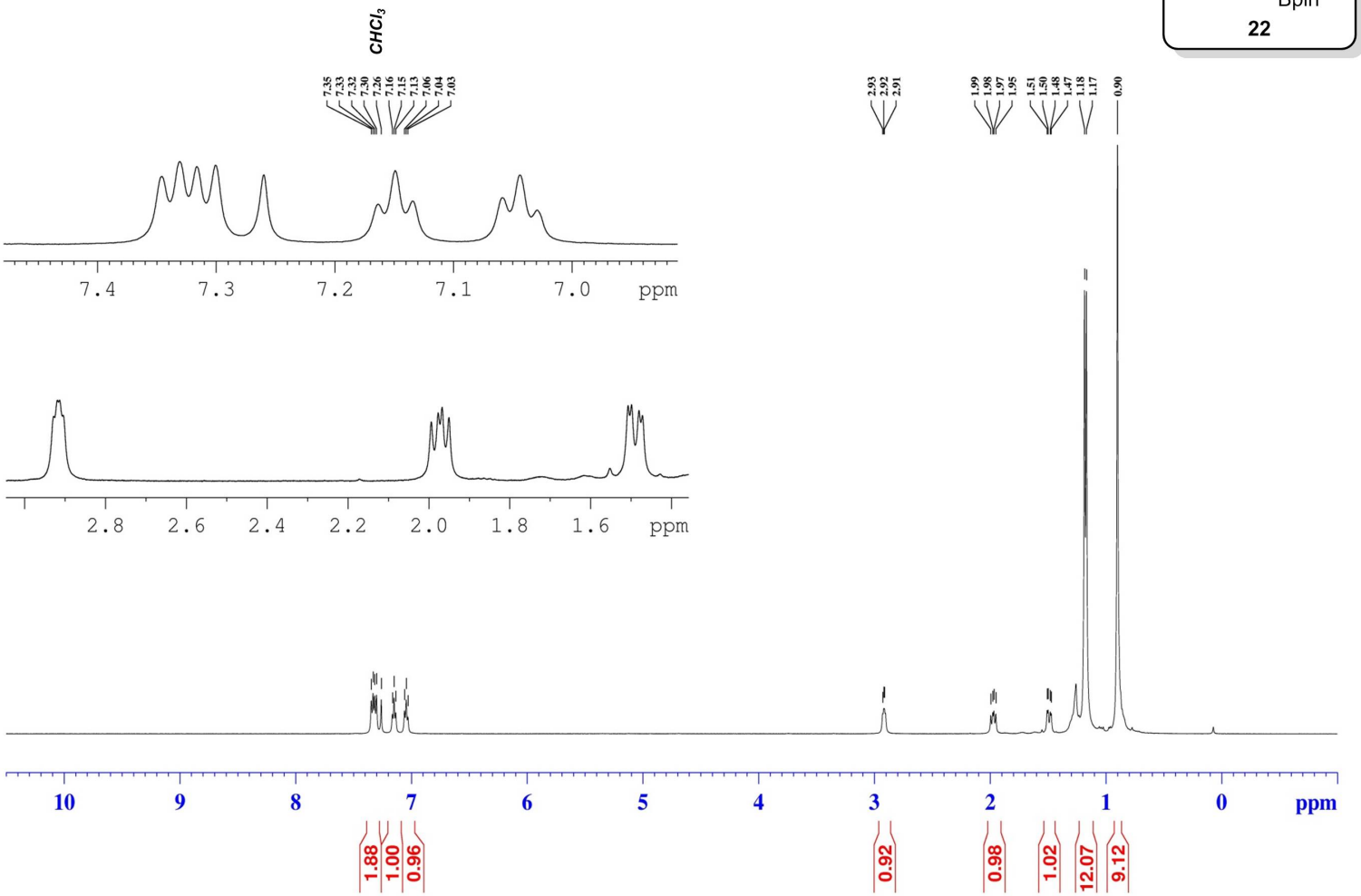


^1H NMR

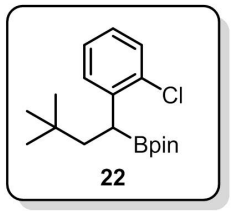
2-(1-(2-chlorophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

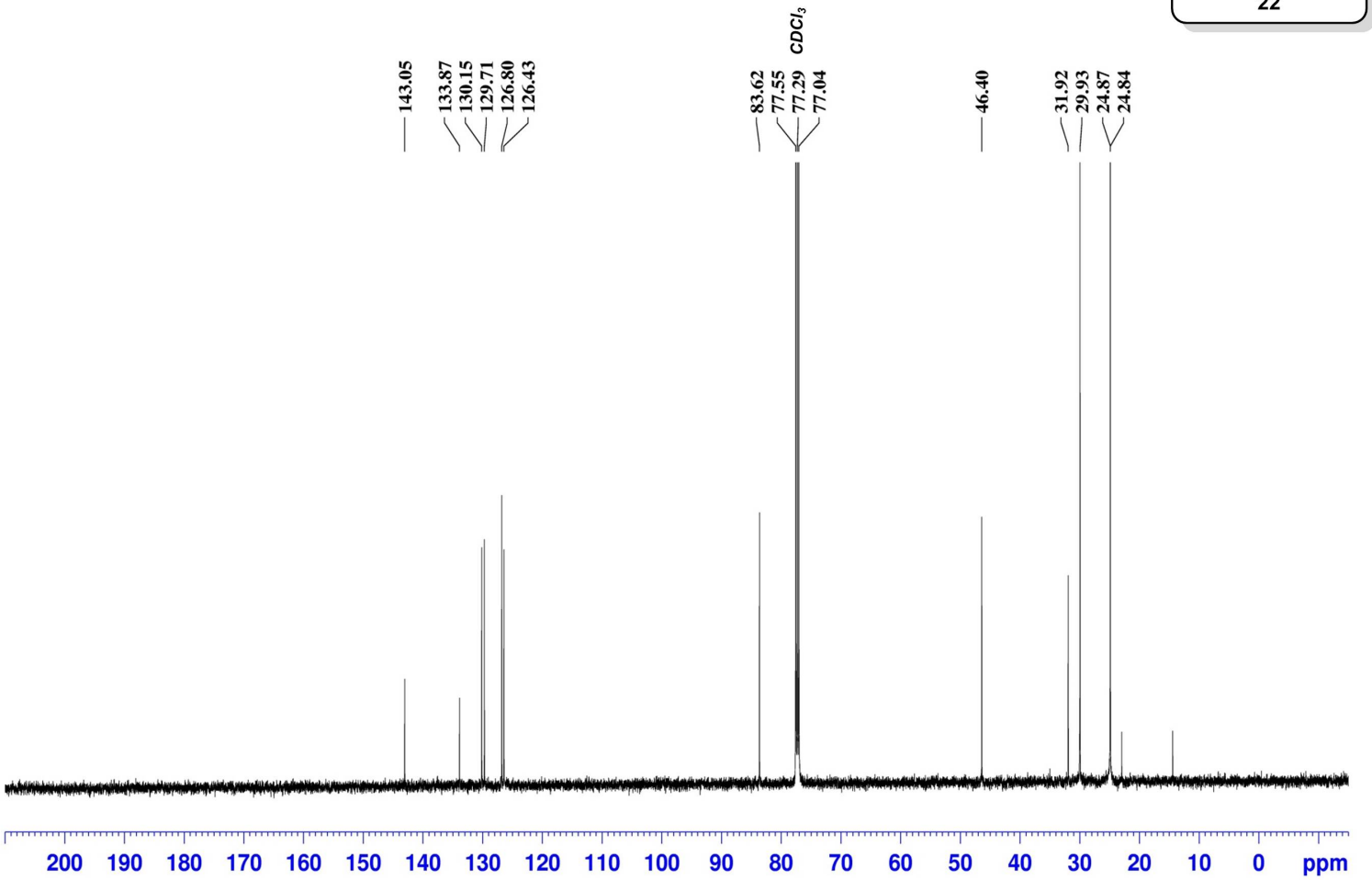




^{13}C NMR

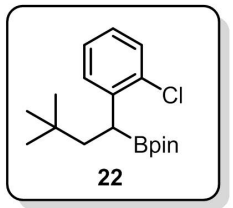
2-(1-(2-Chlorophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$





^{11}B NMR

2-(1-(2-chlorophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$



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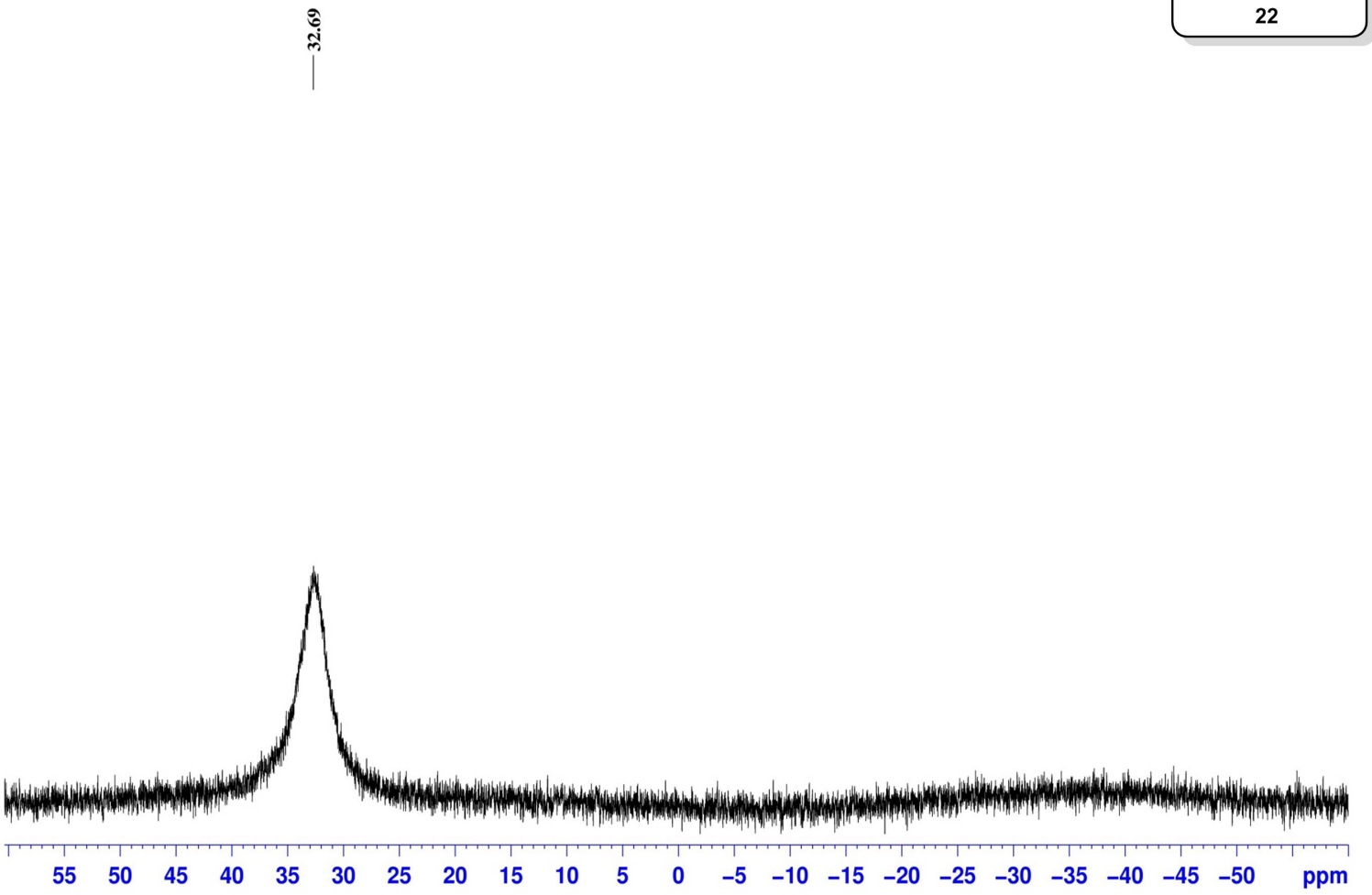
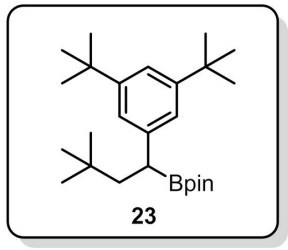
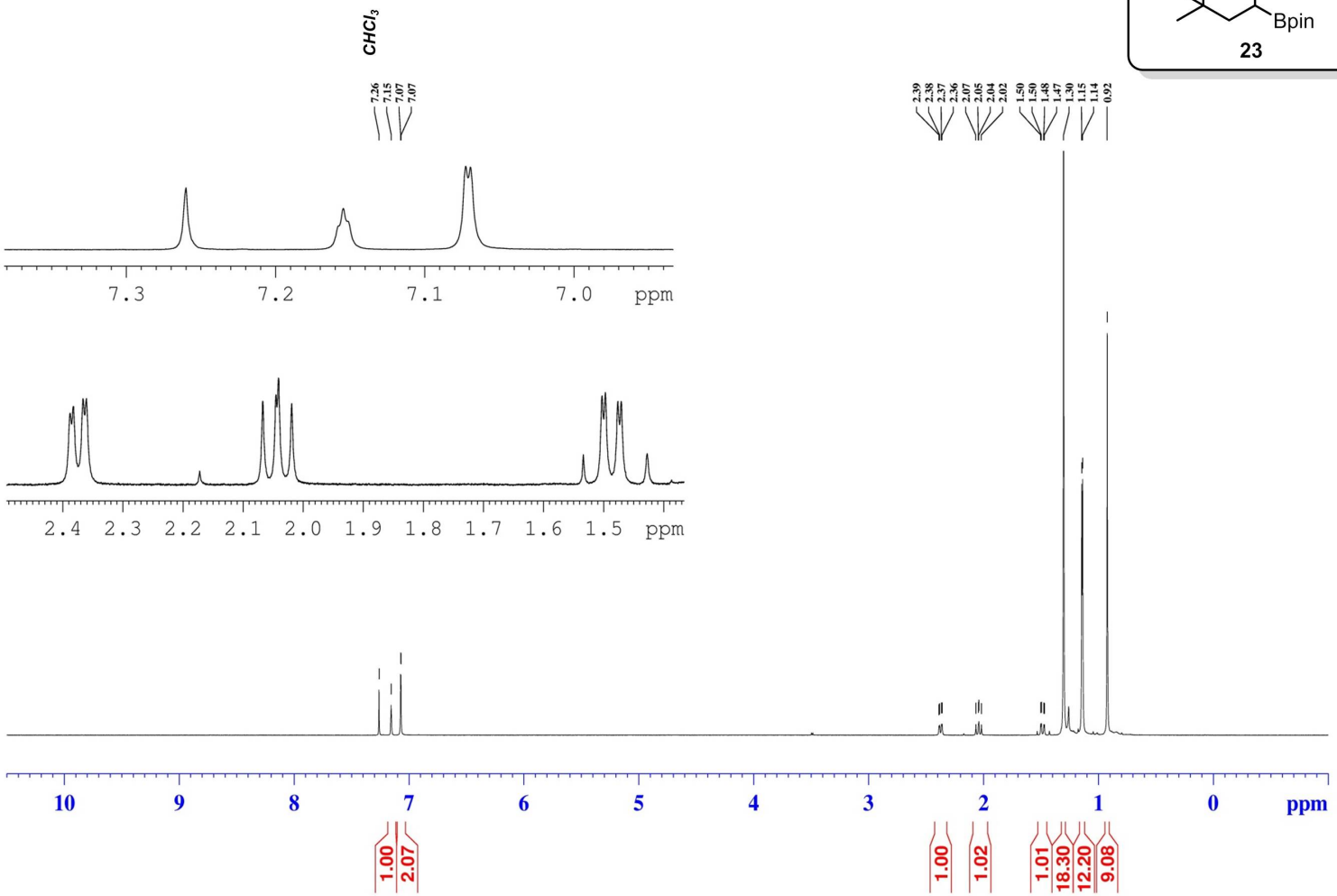


^1H NMR

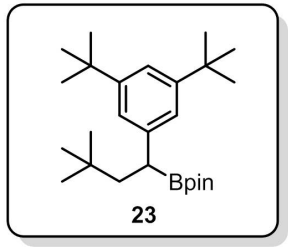
2-(1-(3,5-di-tert-butylphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$





^{13}C NMR

2-(1-(3,5-Di-tert-butylphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$



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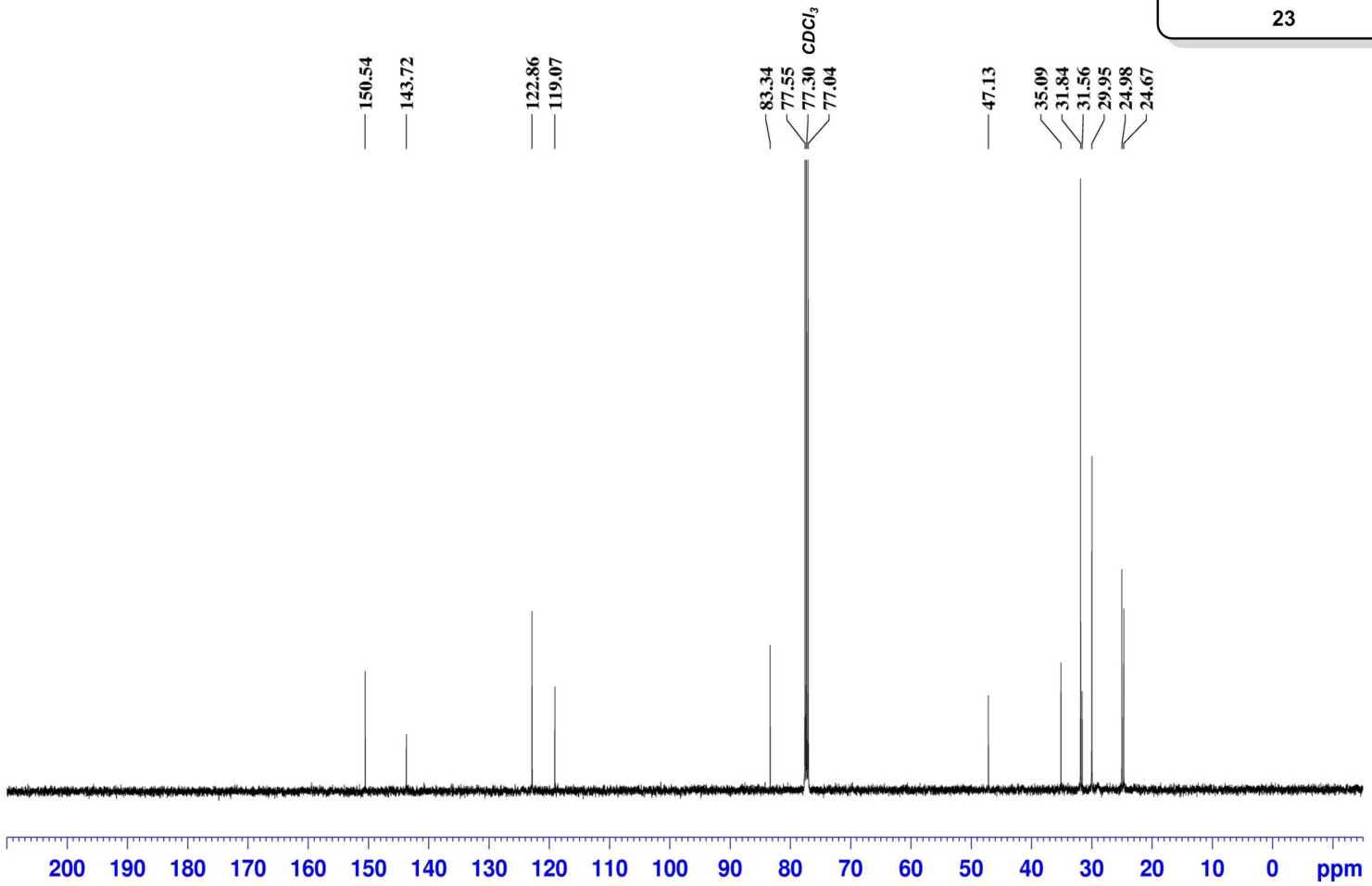
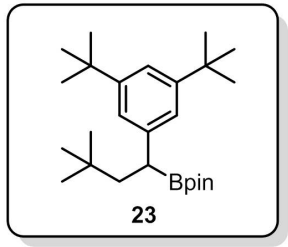


^{11}B NMR

2-(1-(3,5-di-tert-butylphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$



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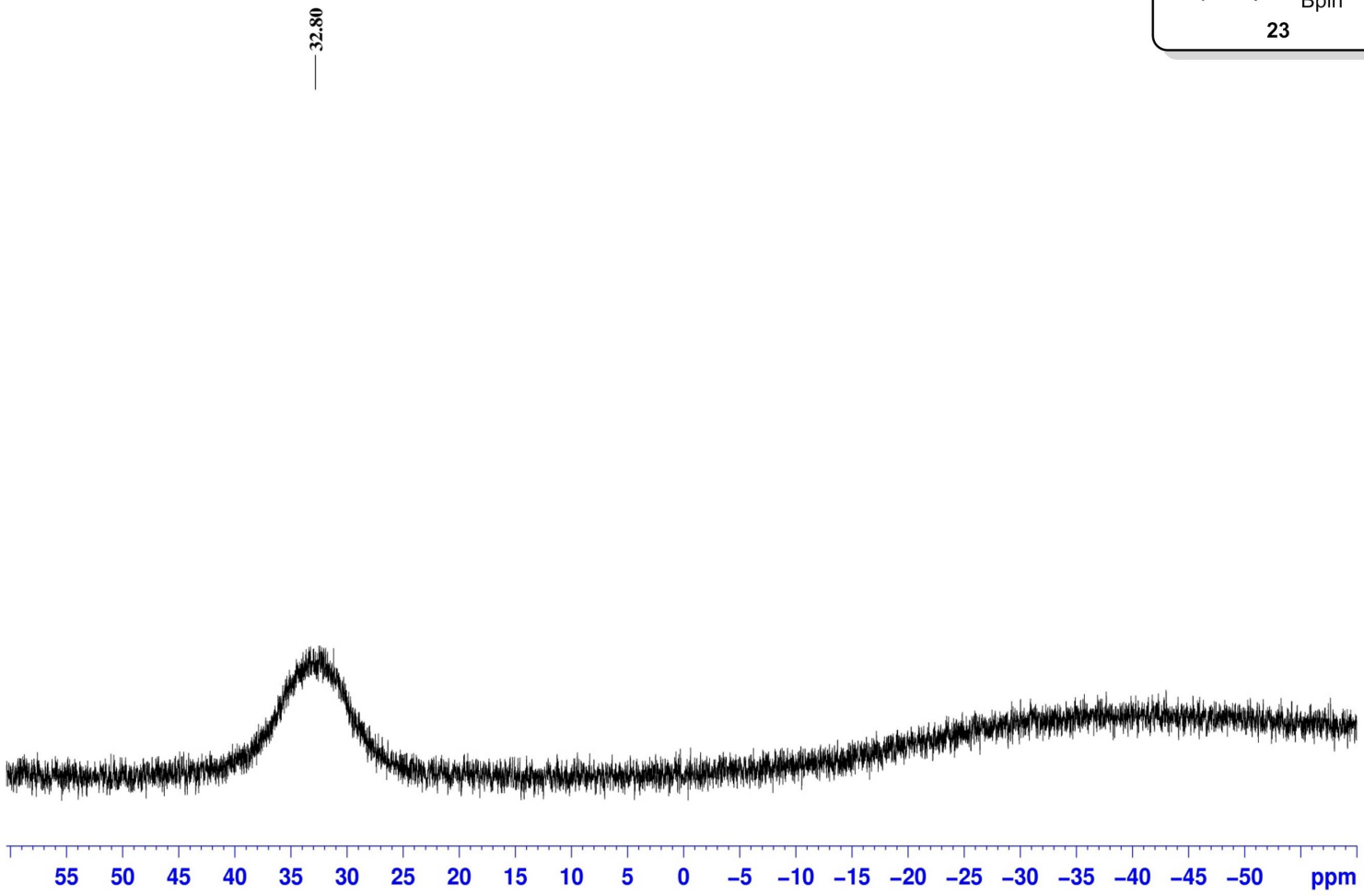
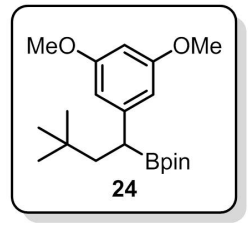
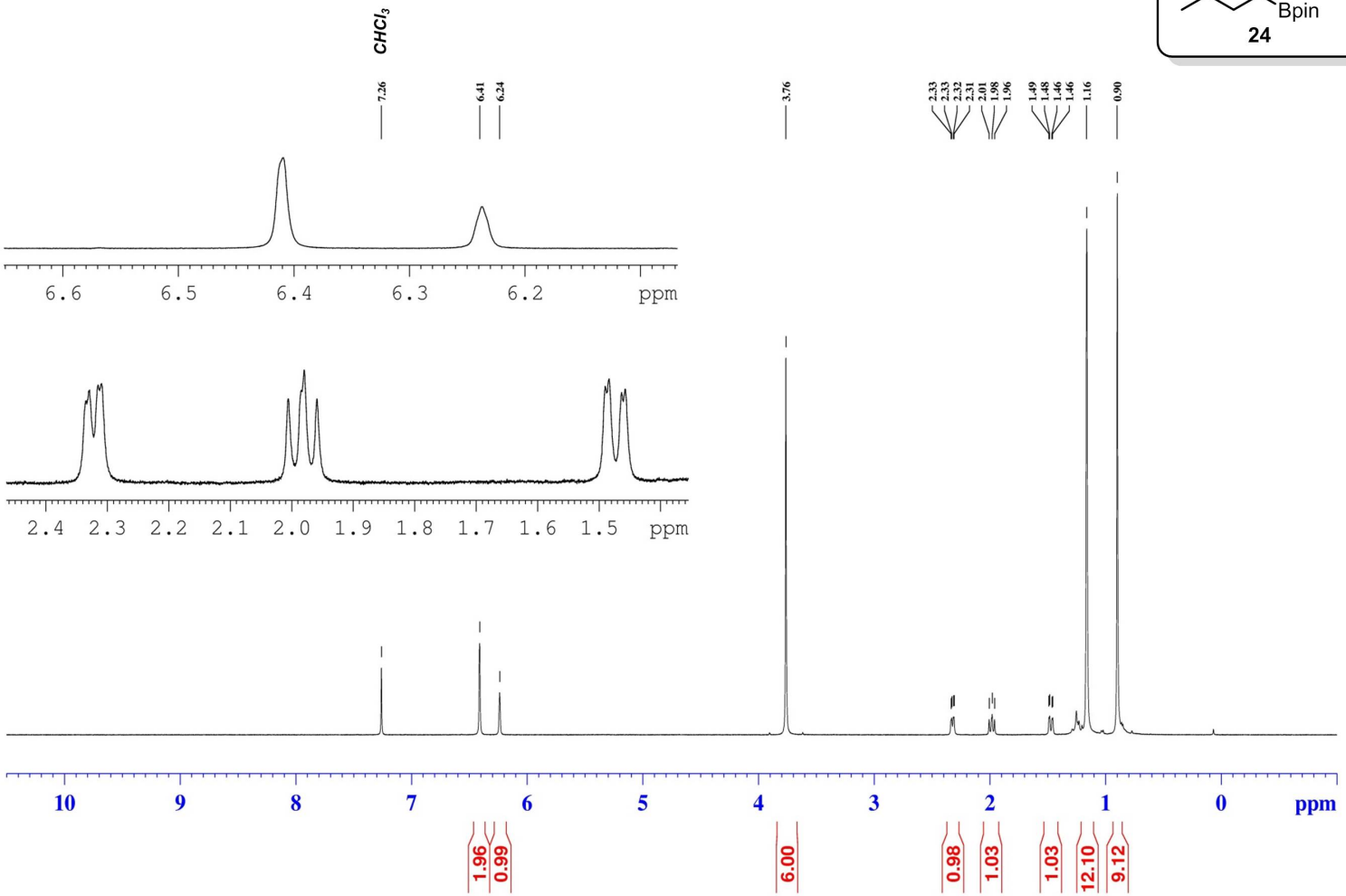


^1H NMR

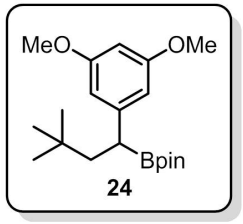
2-(1-(3,5-dimethoxyphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

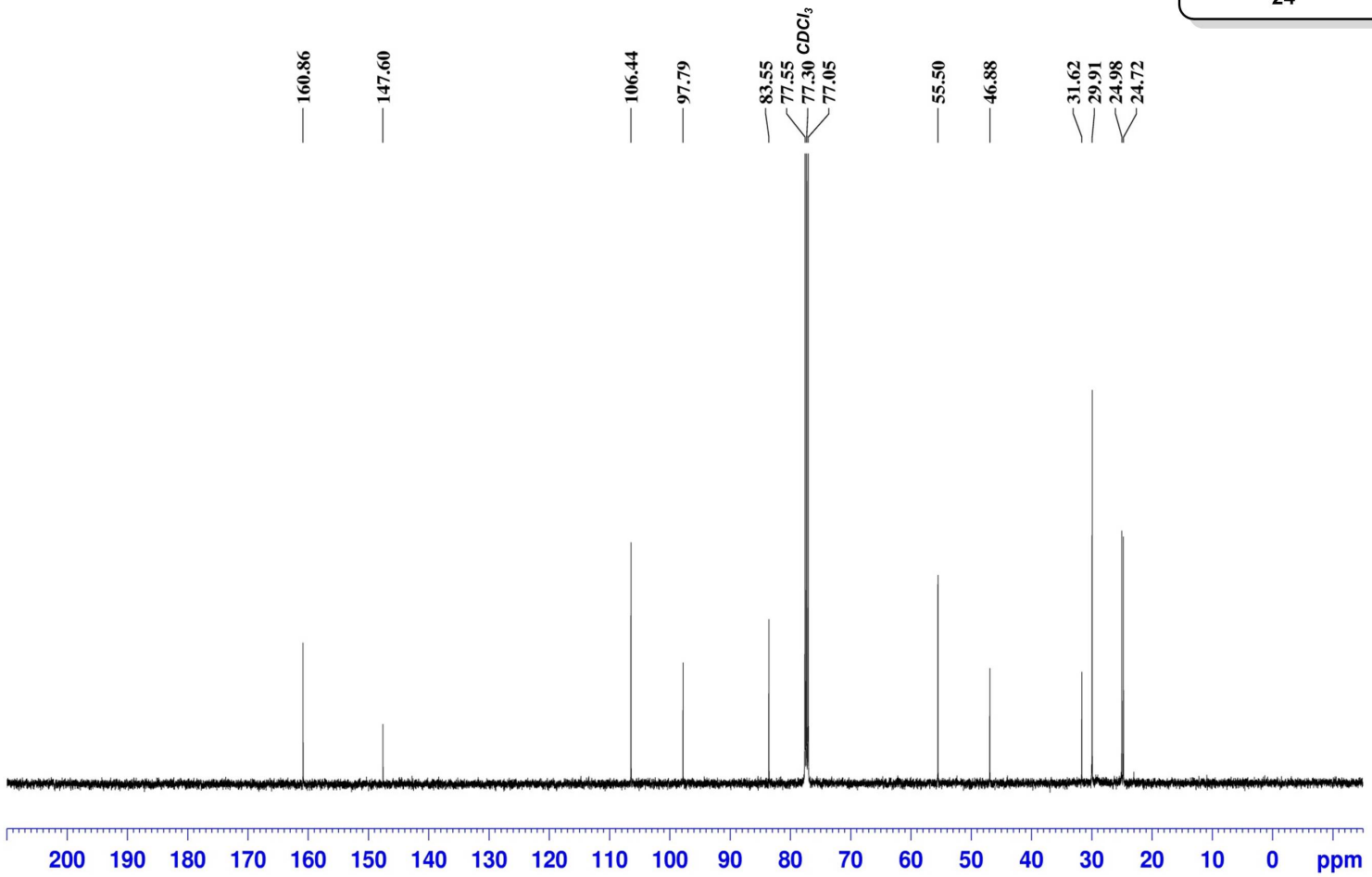




^{13}C NMR

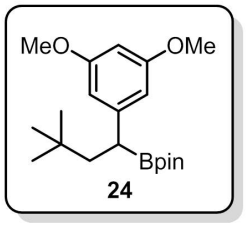
2-(1-(3,5-Dimethoxyphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$





^{11}B NMR

2-(1-(3,5-dimethoxyphenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$



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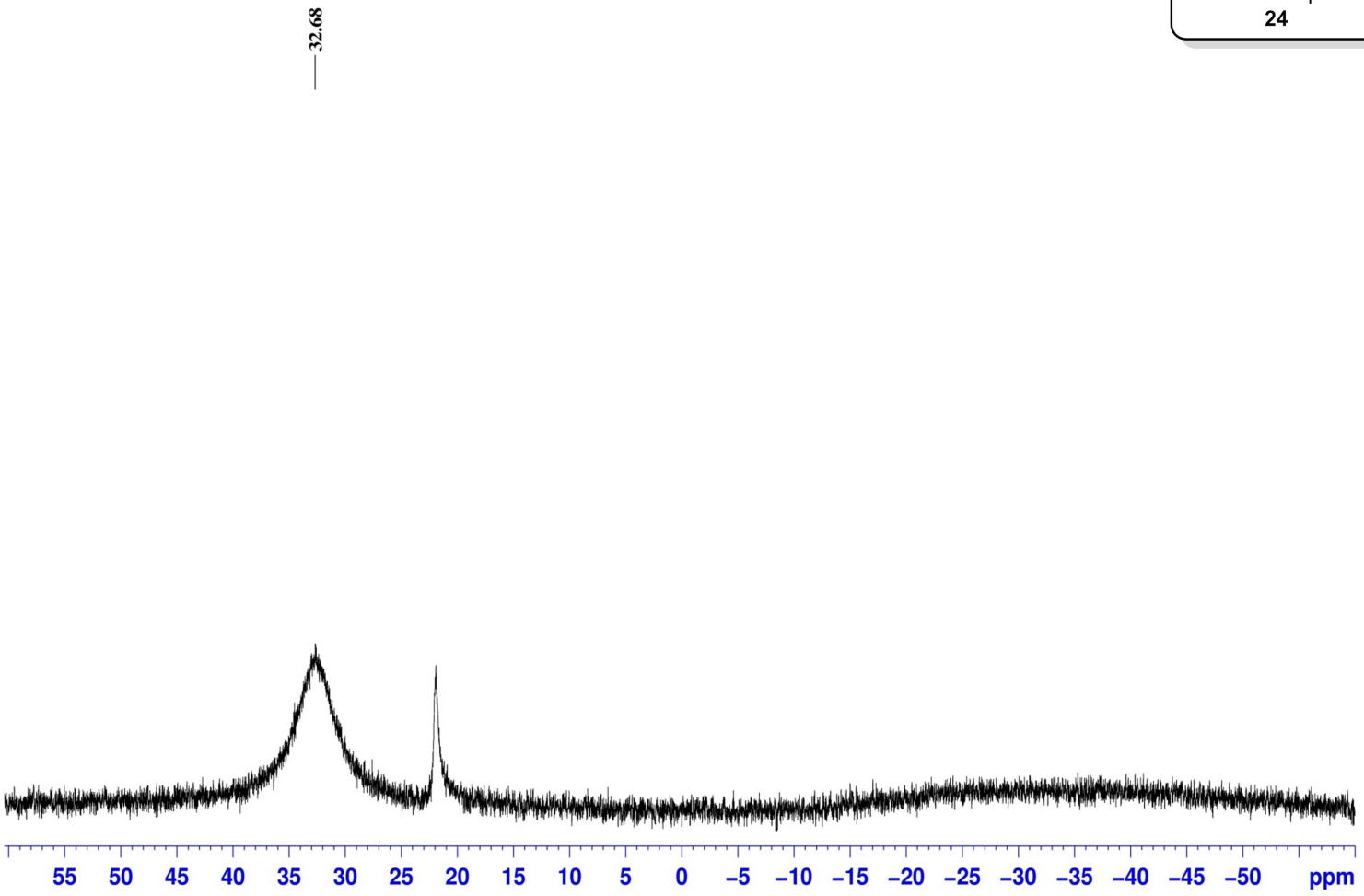
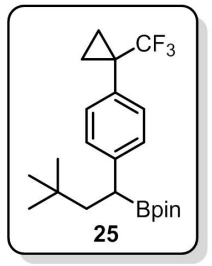
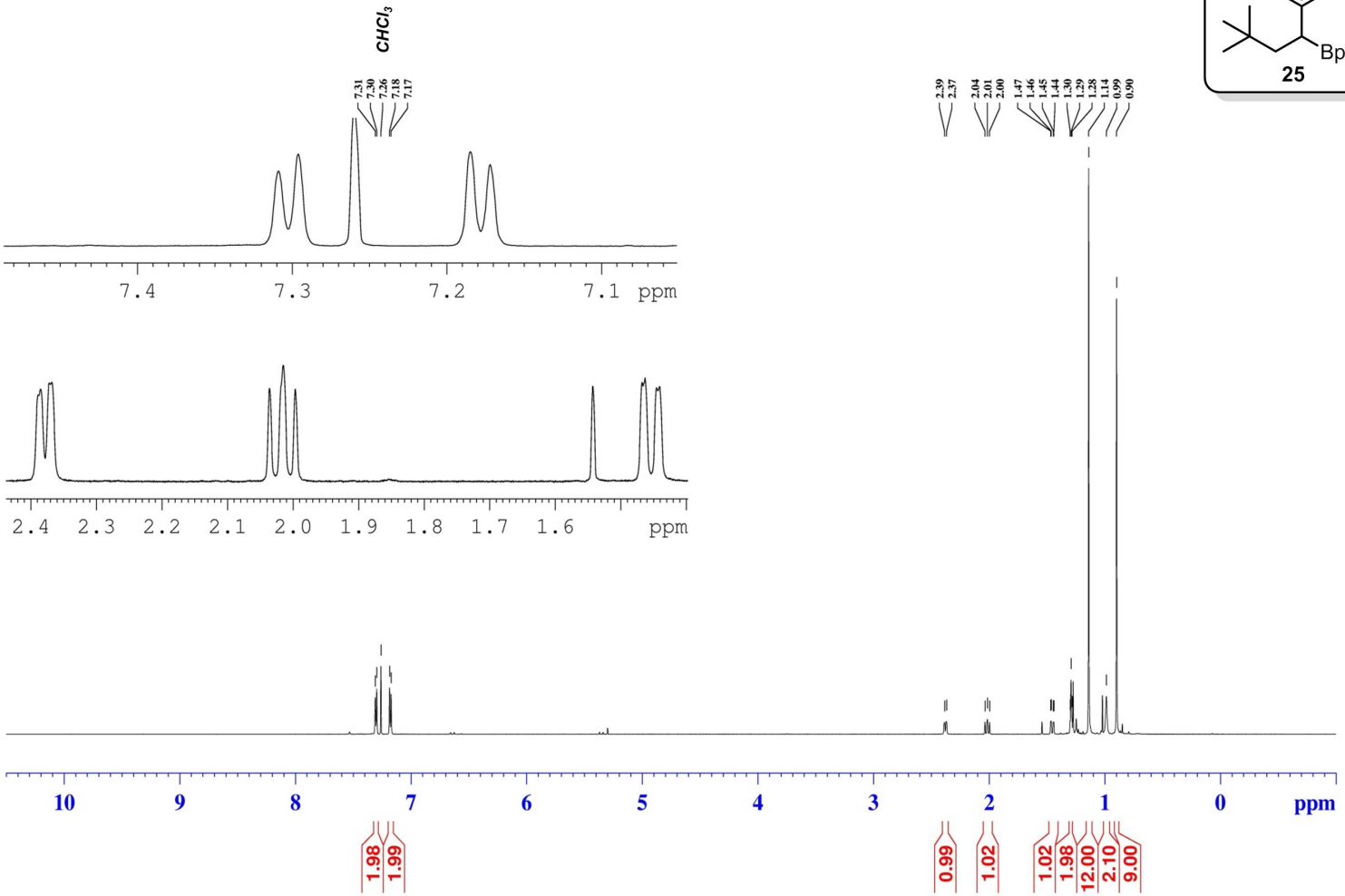


^1H NMR

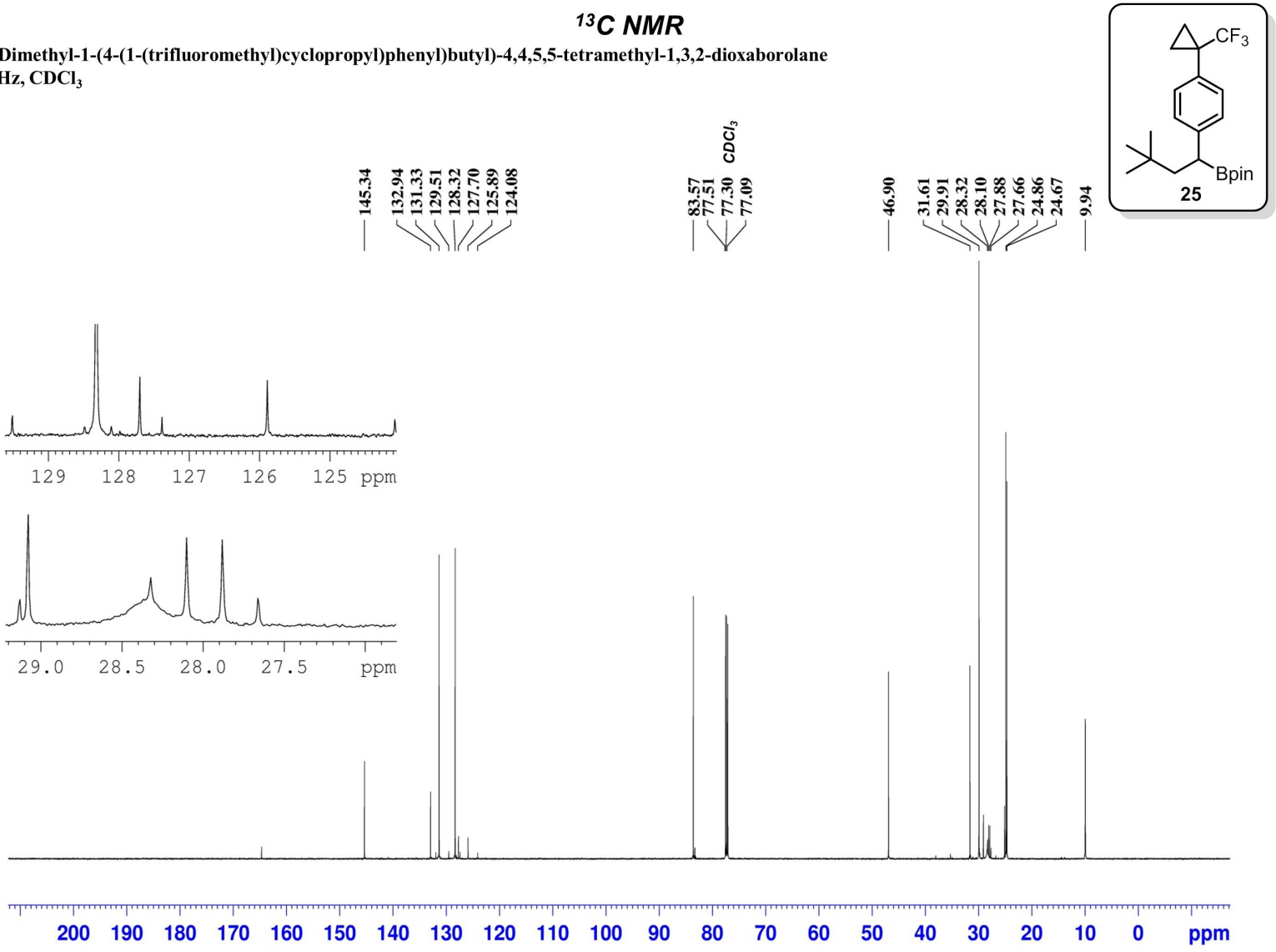
2-(3,3-dimethyl-1-(4-(1-(trifluoromethyl)cyclopropyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$





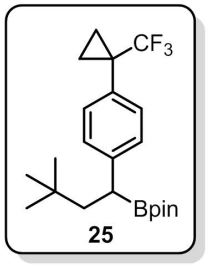
^{13}C NMR

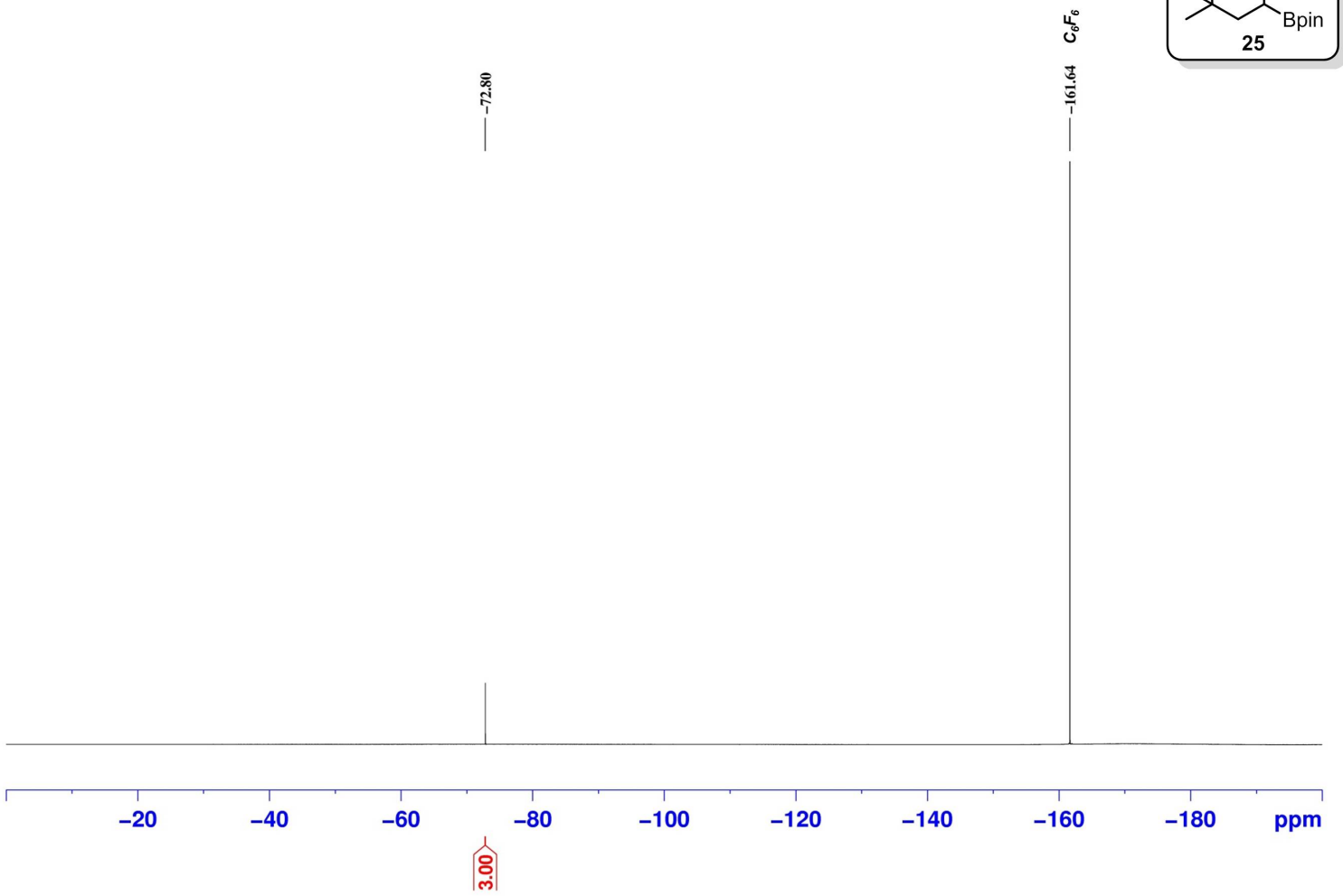
2-(3,3-Dimethyl-1-(4-(1-(trifluoromethyl)cyclopropyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$



^{19}F NMR

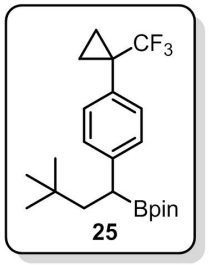
2-(3,3-dimethyl-1-(4-(1-(trifluoromethyl)cyclopropyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
471 MHz, $CDCl_3$

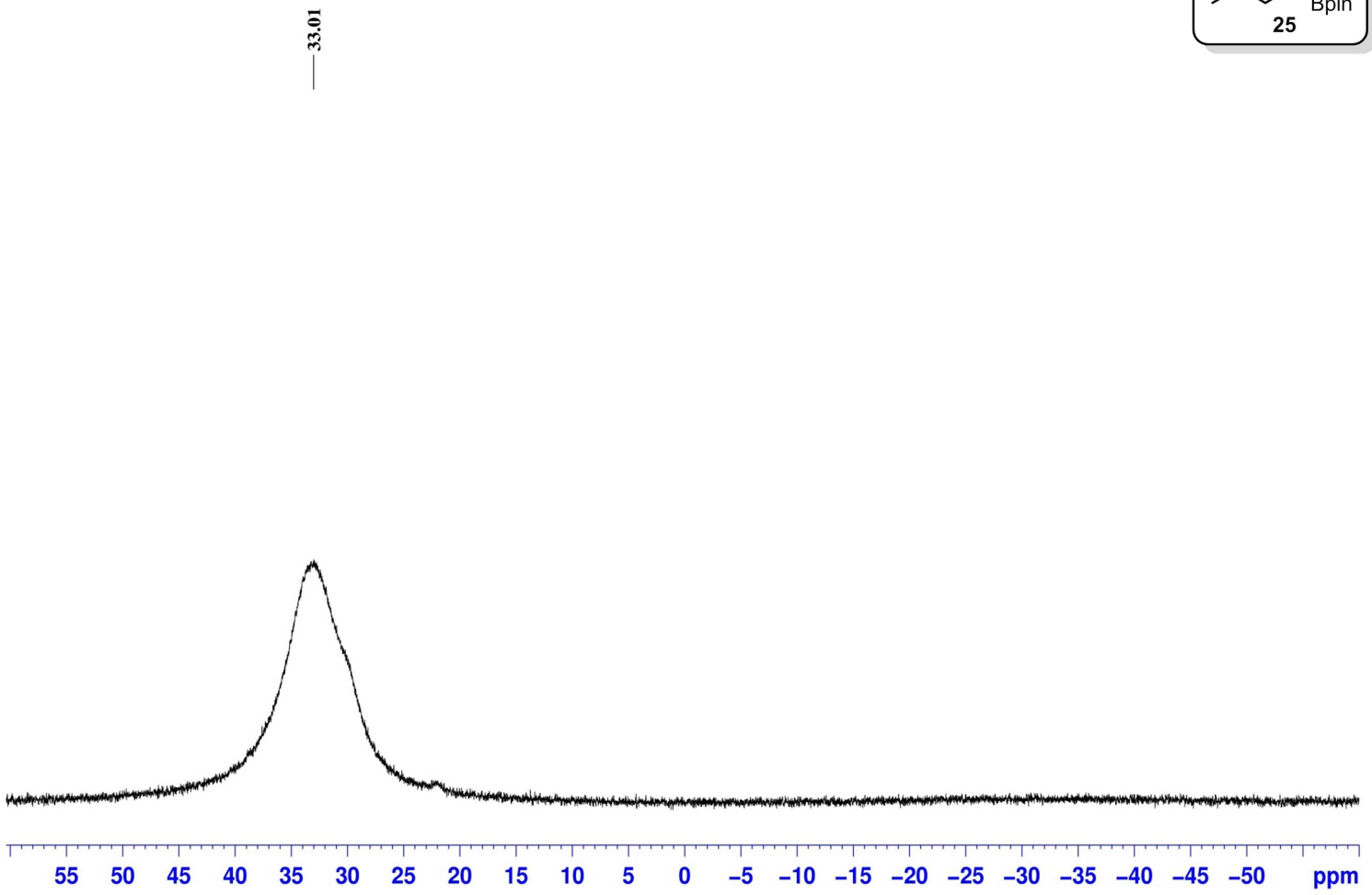




^{11}B NMR

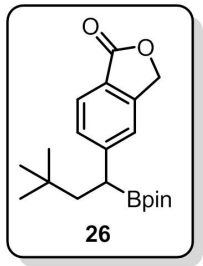
2-(3,3-dimethyl-1-(4-(1-(trifluoromethyl)cyclopropyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$





^1H NMR

5-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)isobenzofuran-1(3H)-one
500 MHz, $CDCl_3$



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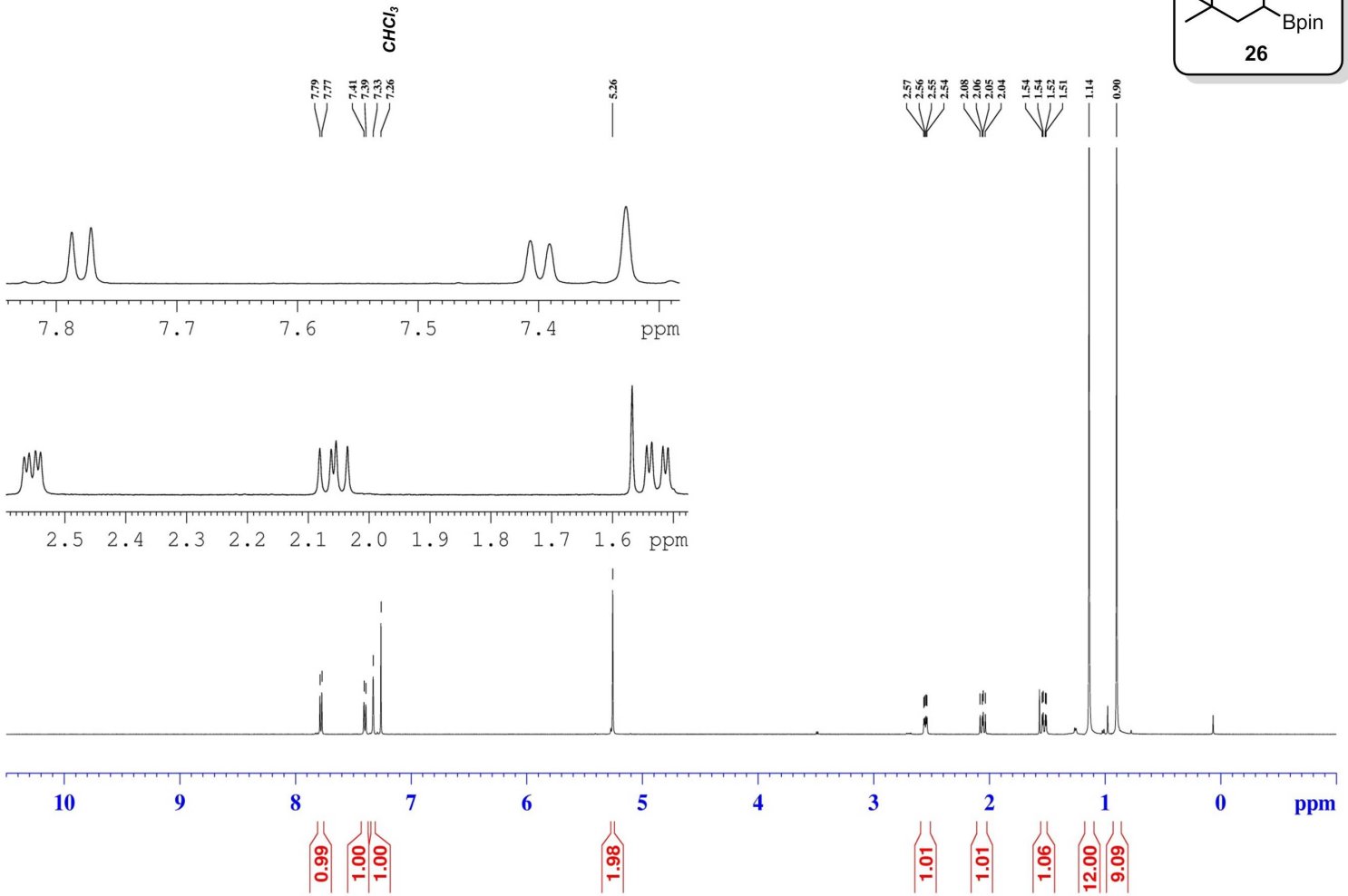
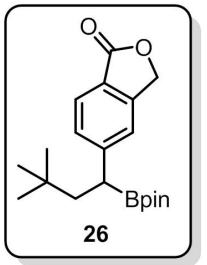


^{13}C NMR

5-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)isobenzofuran-1(3H)-one
125 MHz, $CDCl_3$



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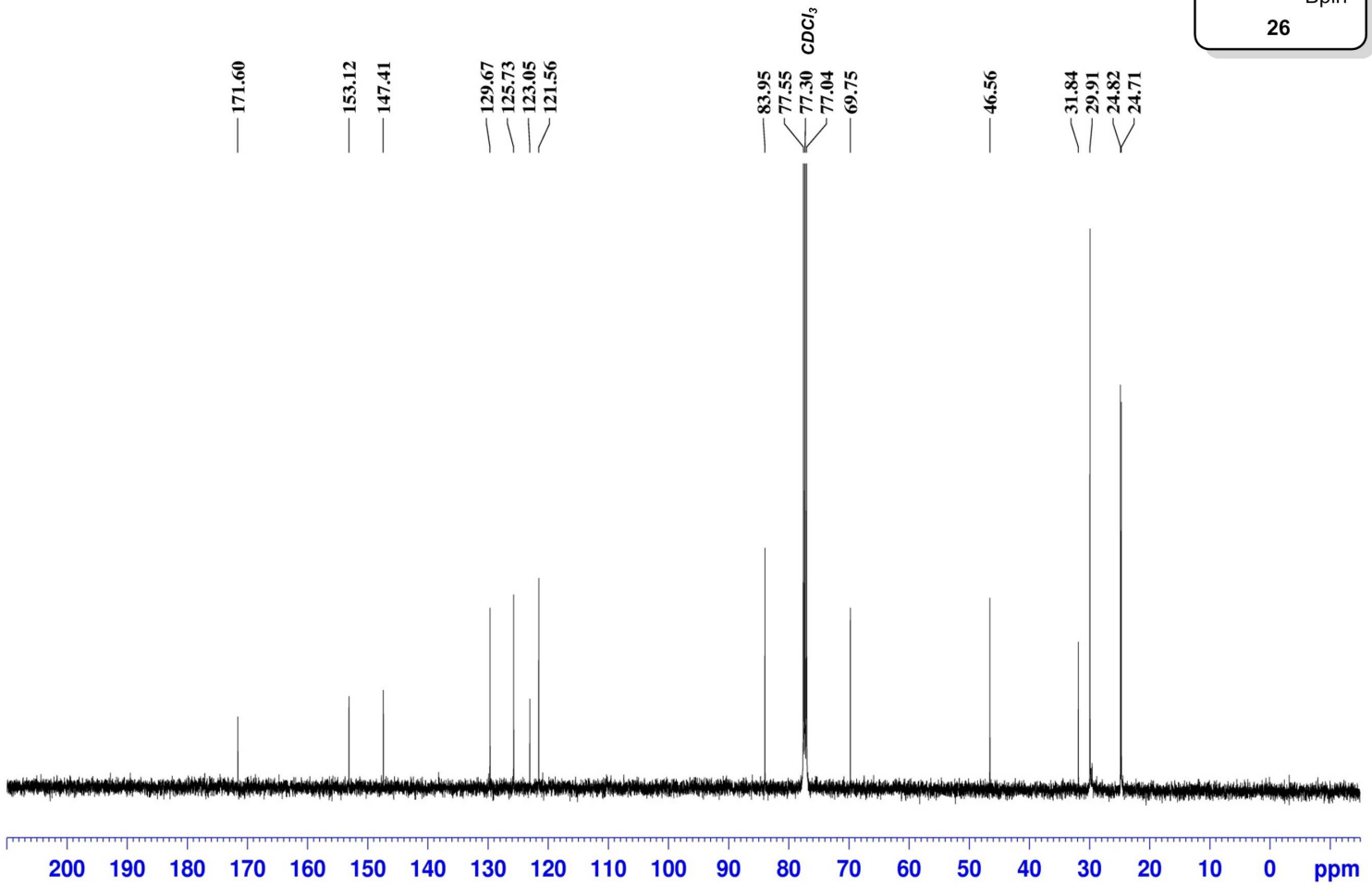
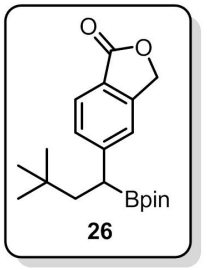


^{11}B NMR

5-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)isobenzofuran-1(3H)-one
128 MHz, $CDCl_3$



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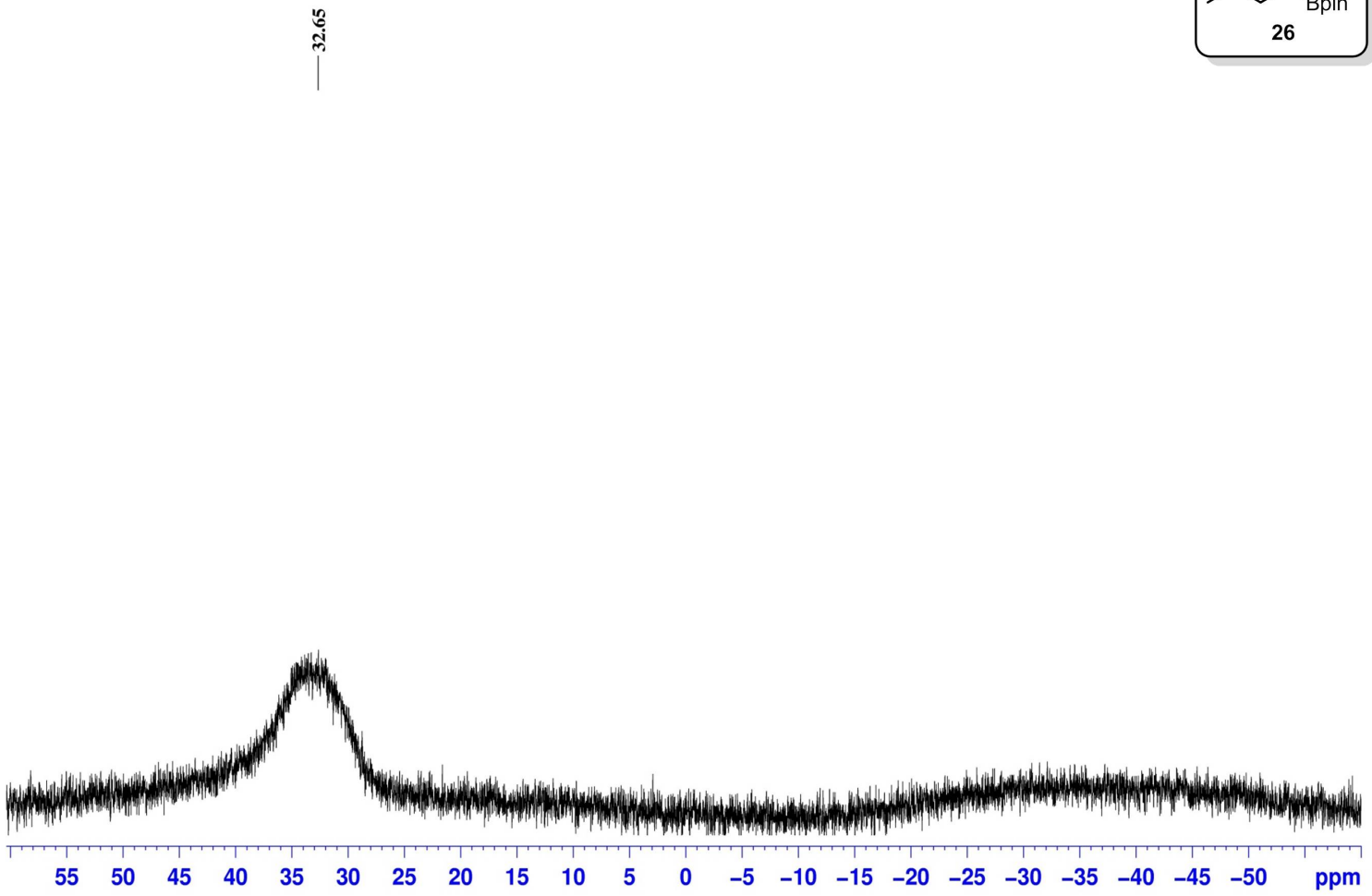
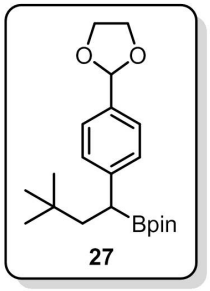
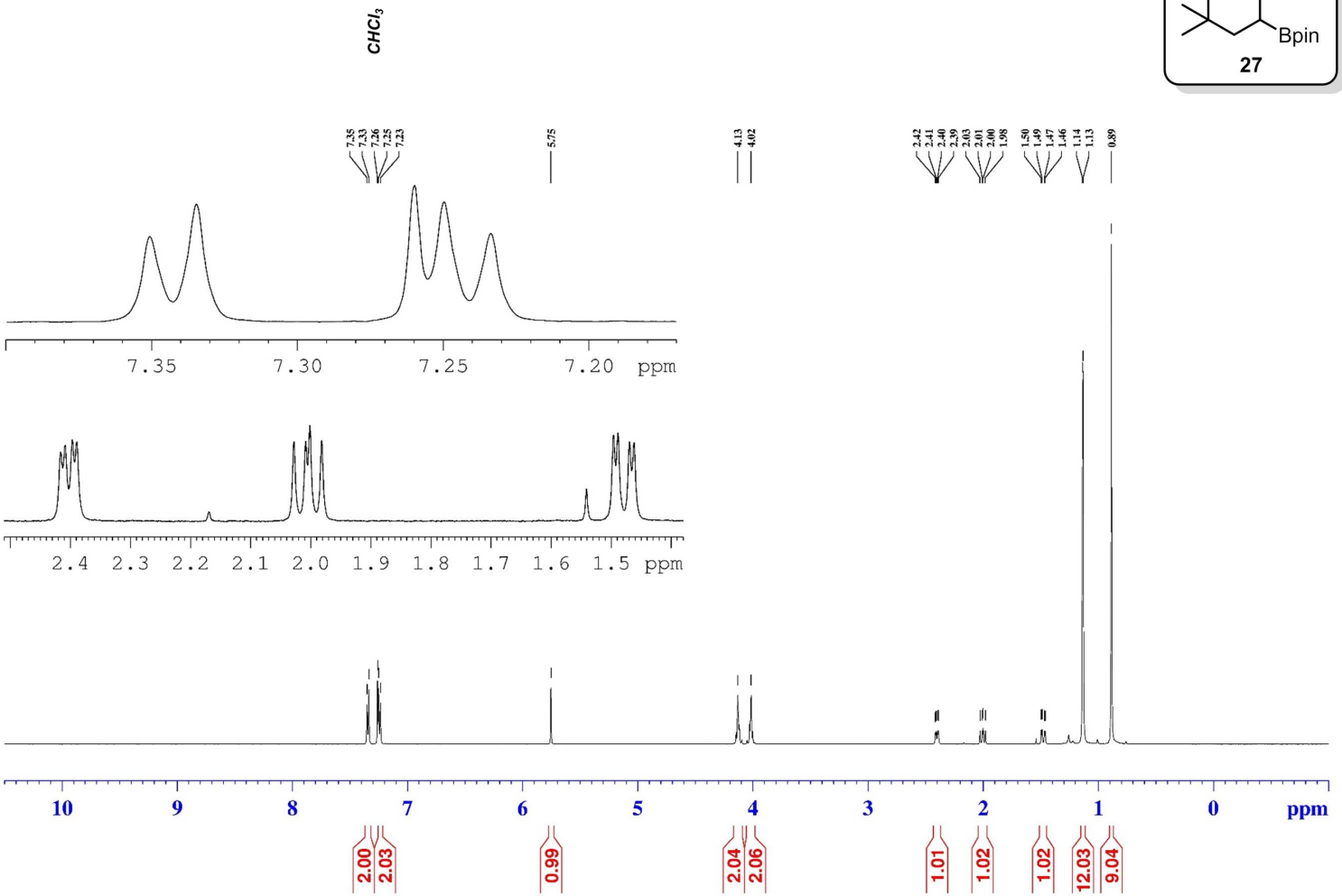


^1H NMR

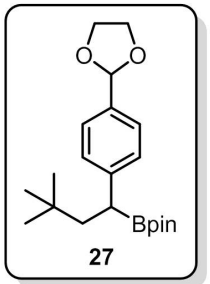
2-(1-(4-(1,3-dioxolan-2-yl)phenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

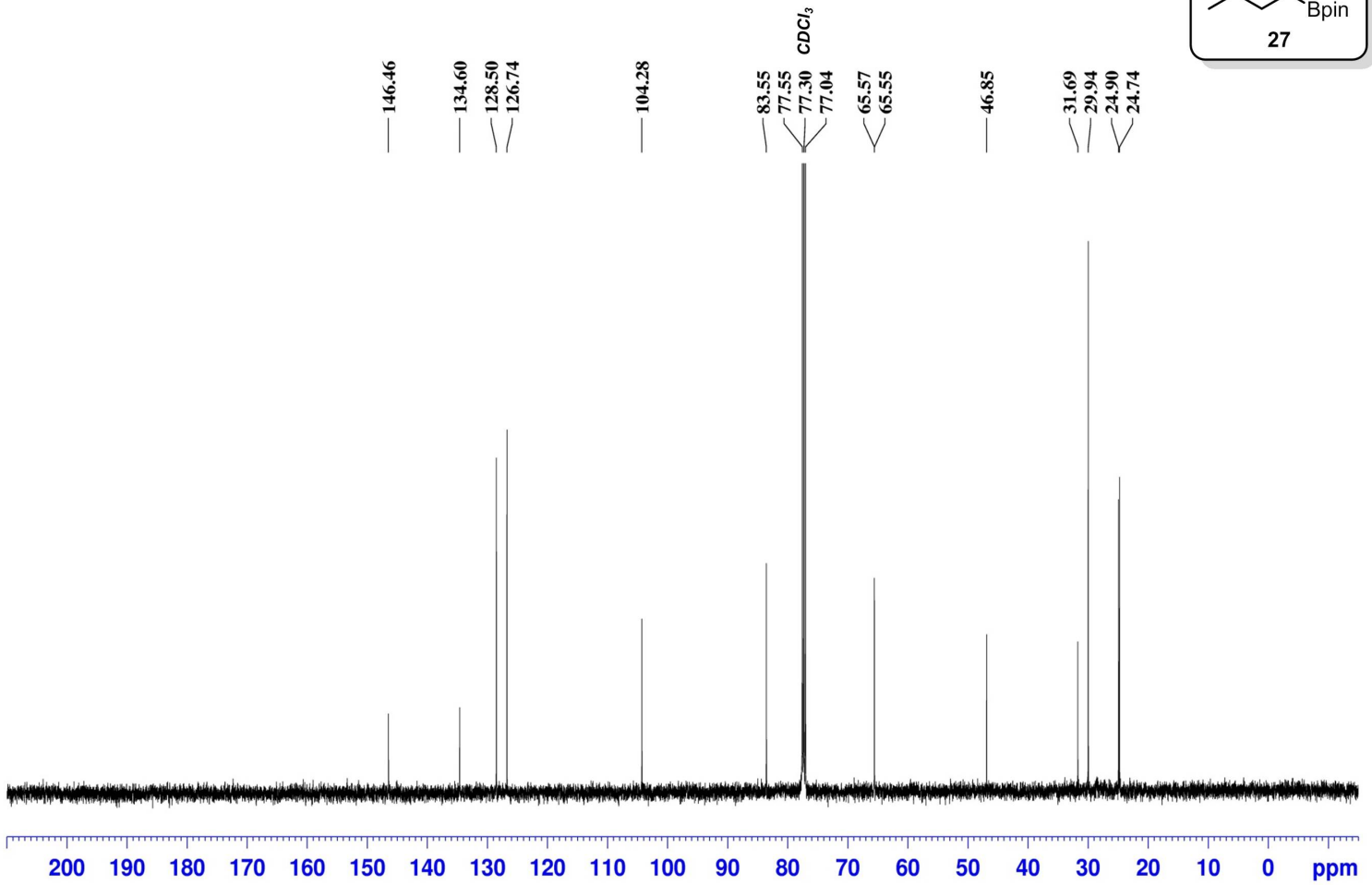




^{13}C NMR

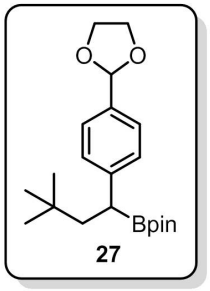
2-(1-(4-(1,3-Dioxolan-2-yl)phenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$





^{11}B NMR

2-(1-(4-(1,3-dioxolan-2-yl)phenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$



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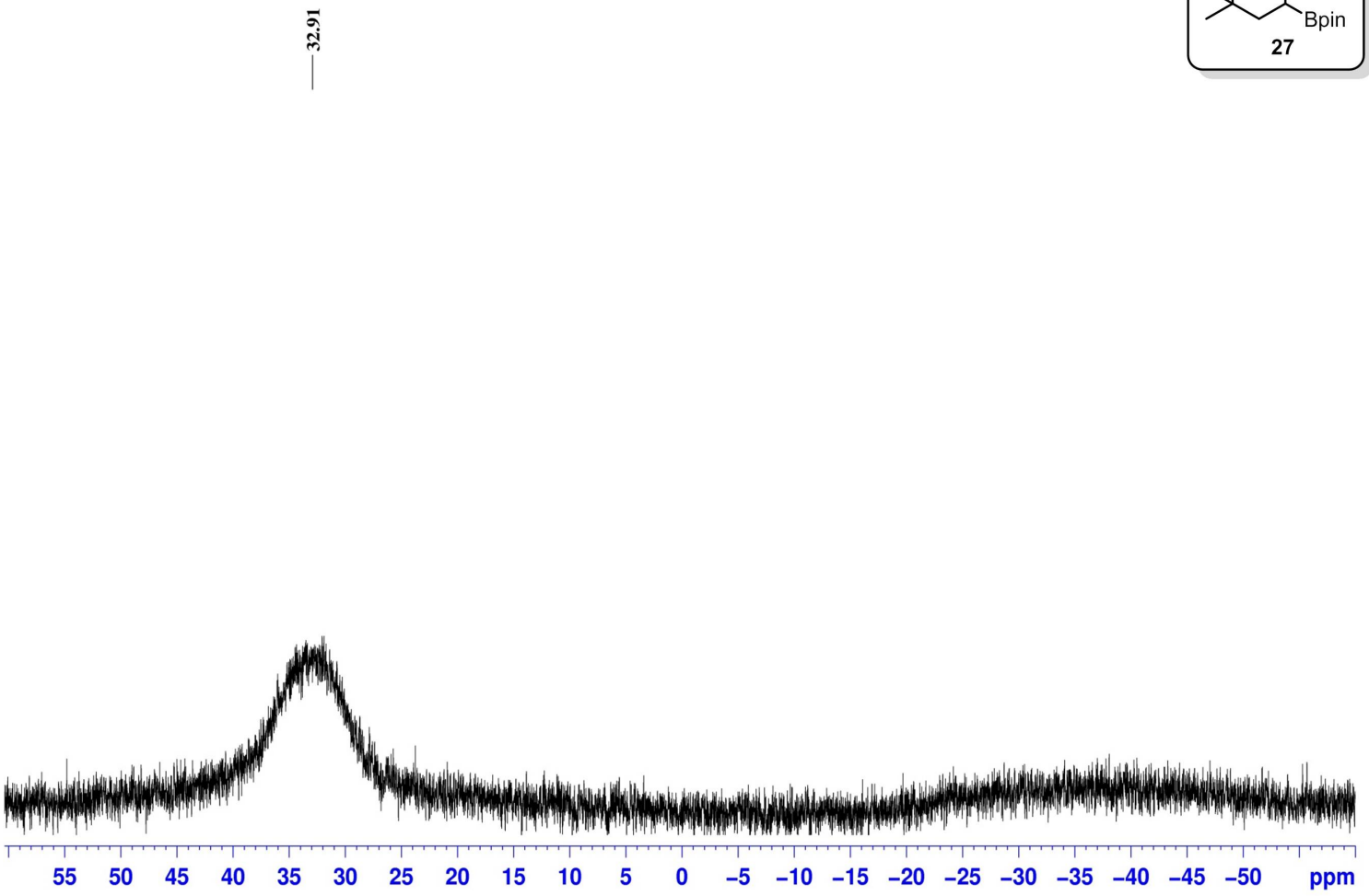
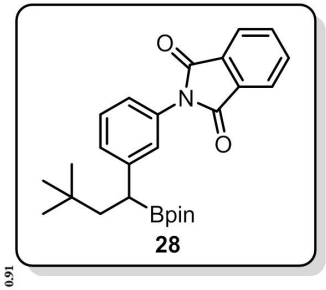


^1H NMR

2-(3-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)isoindoline-1,3-dione
500 MHz, $CDCl_3$



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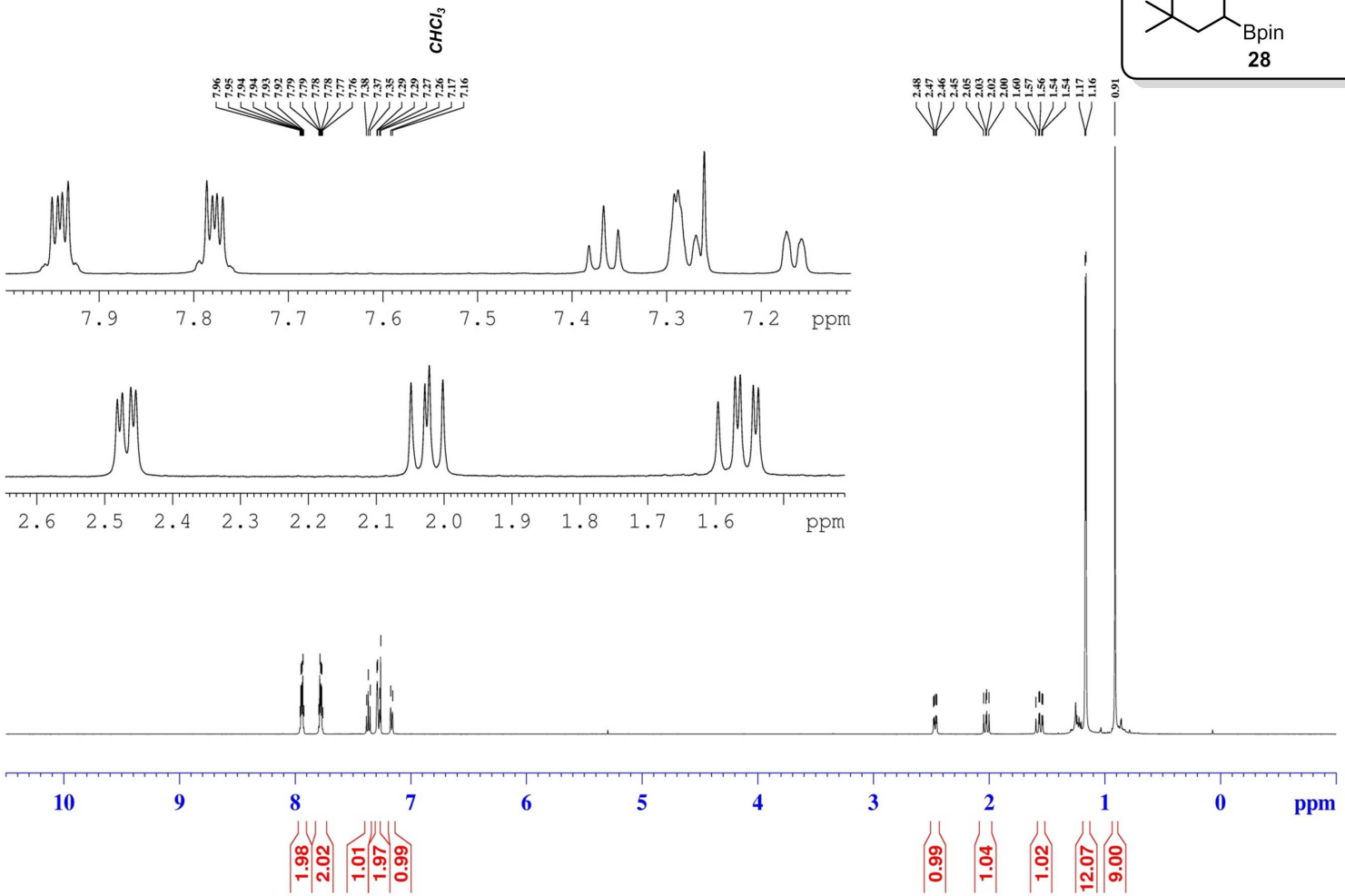
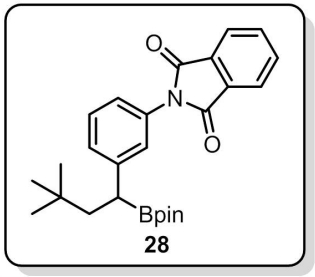


^{13}C NMR

2-(3-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)isoindoline-1,3-dione
125 MHz, $CDCl_3$



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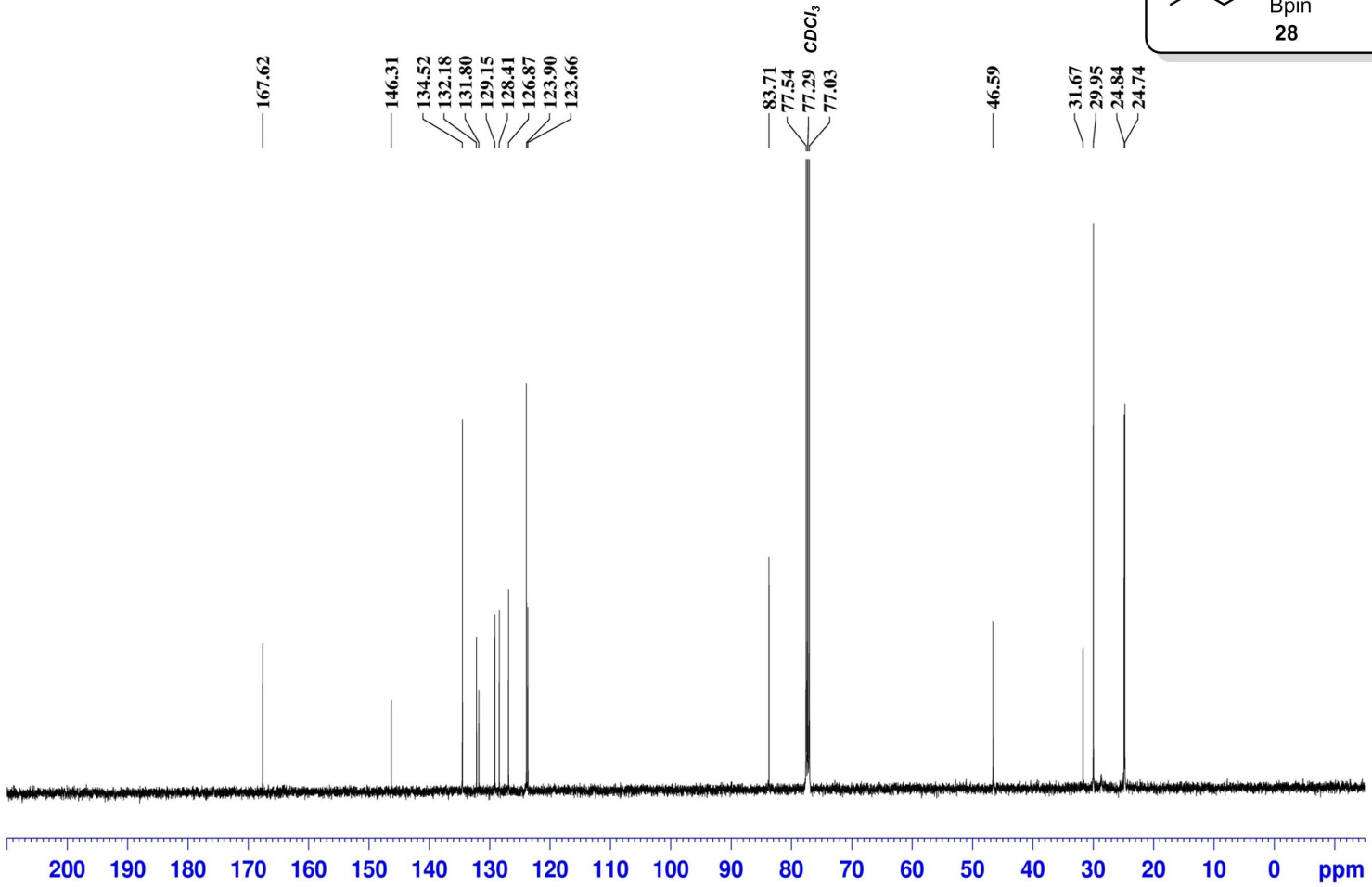
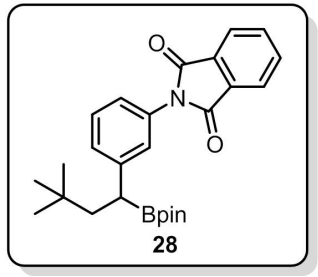


^{11}B NMR

2-(3-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)isoindoline-1,3-dione
128 MHz, $CDCl_3$



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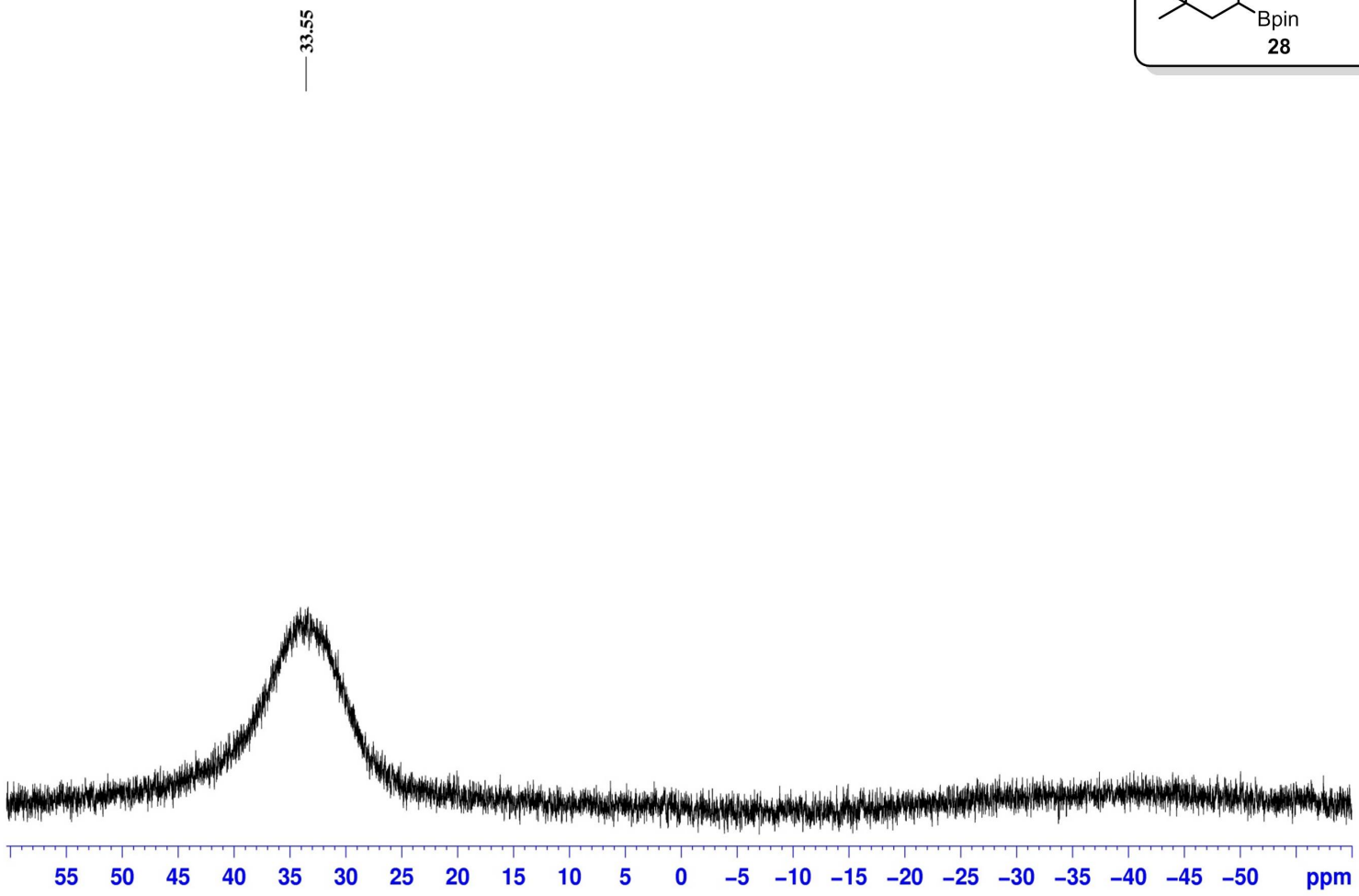
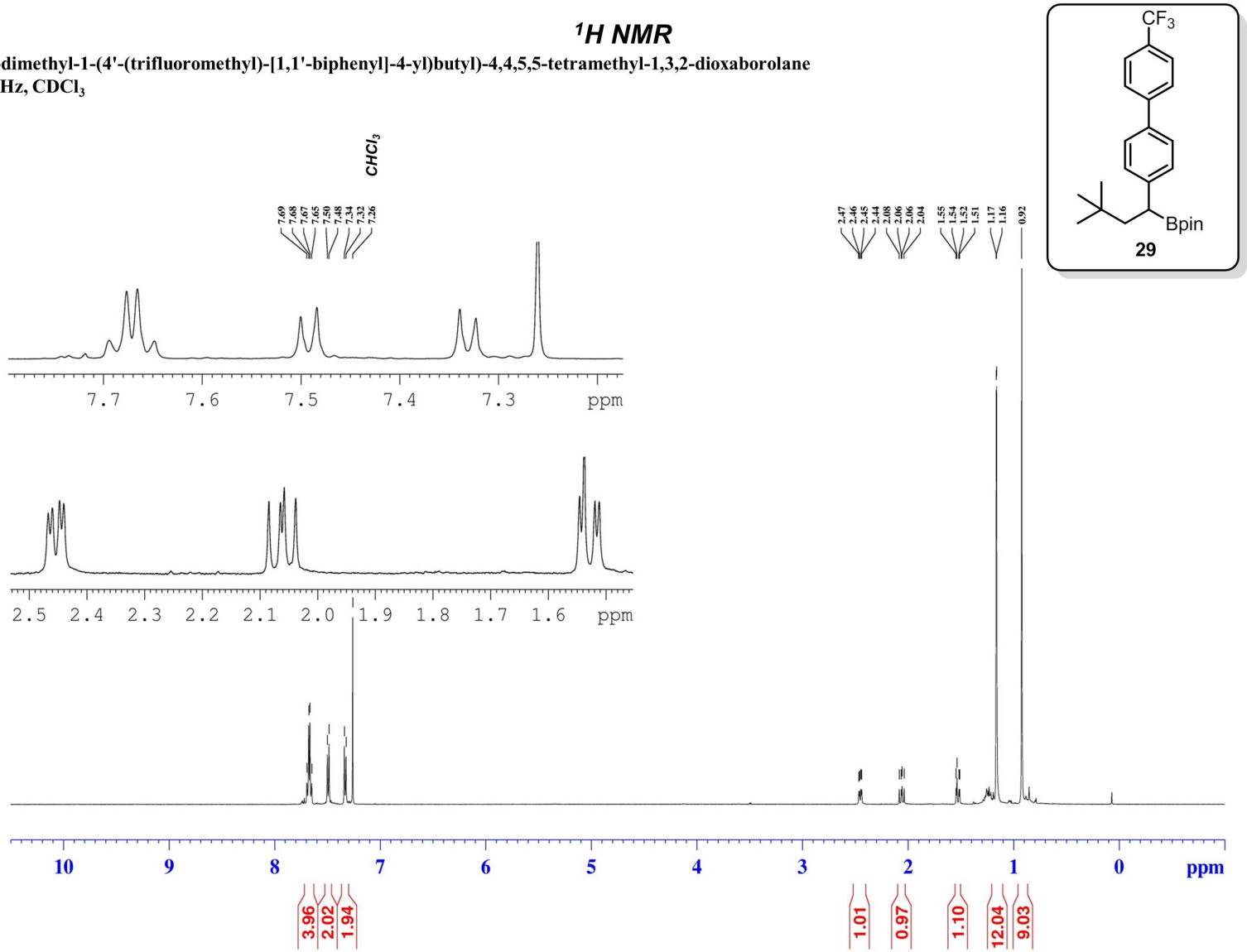


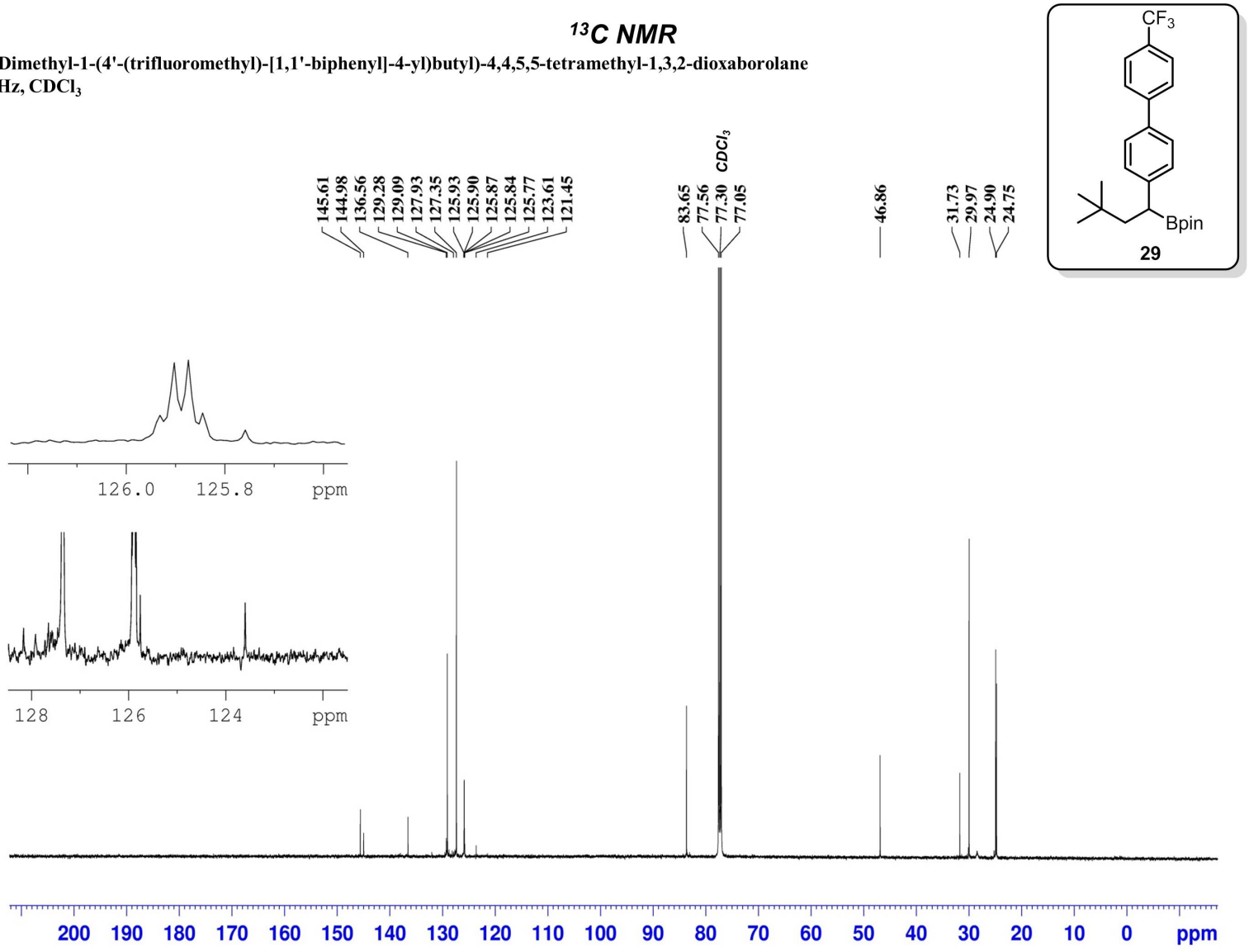
^1H NMR

2-(3,3-dimethyl-1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$



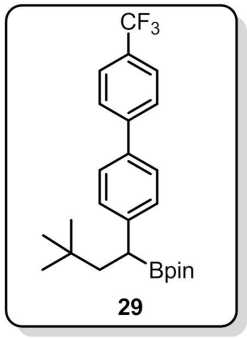
^{13}C NMR

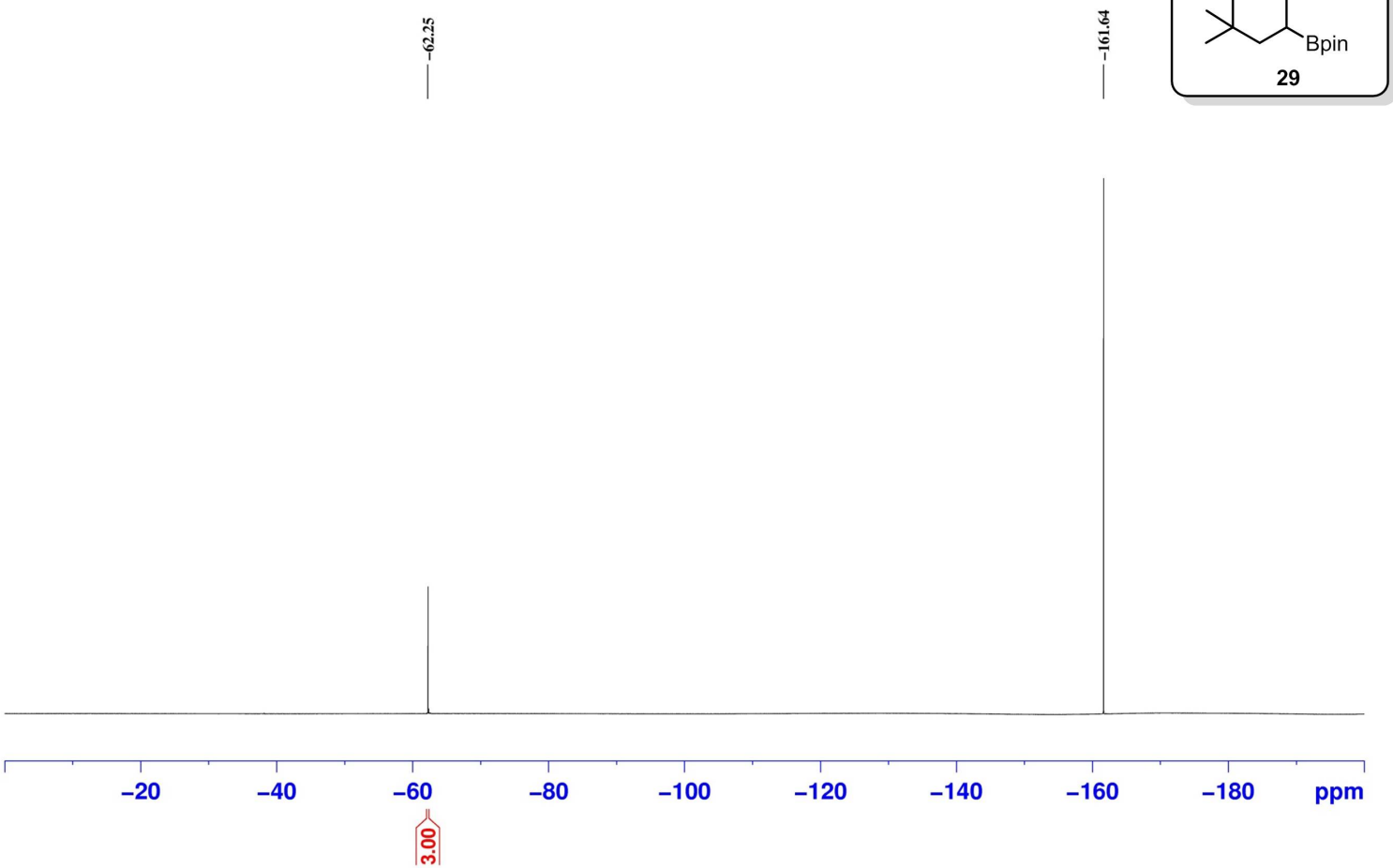
2-(3,3-Dimethyl-1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$



^{19}F NMR

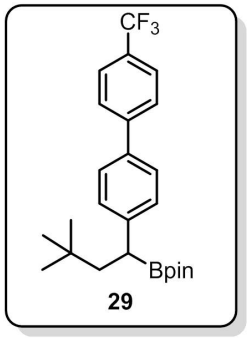
2-(3,3-dimethyl-1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
471 MHz, $CDCl_3$





^{11}B NMR

2-(3,3-dimethyl-1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$



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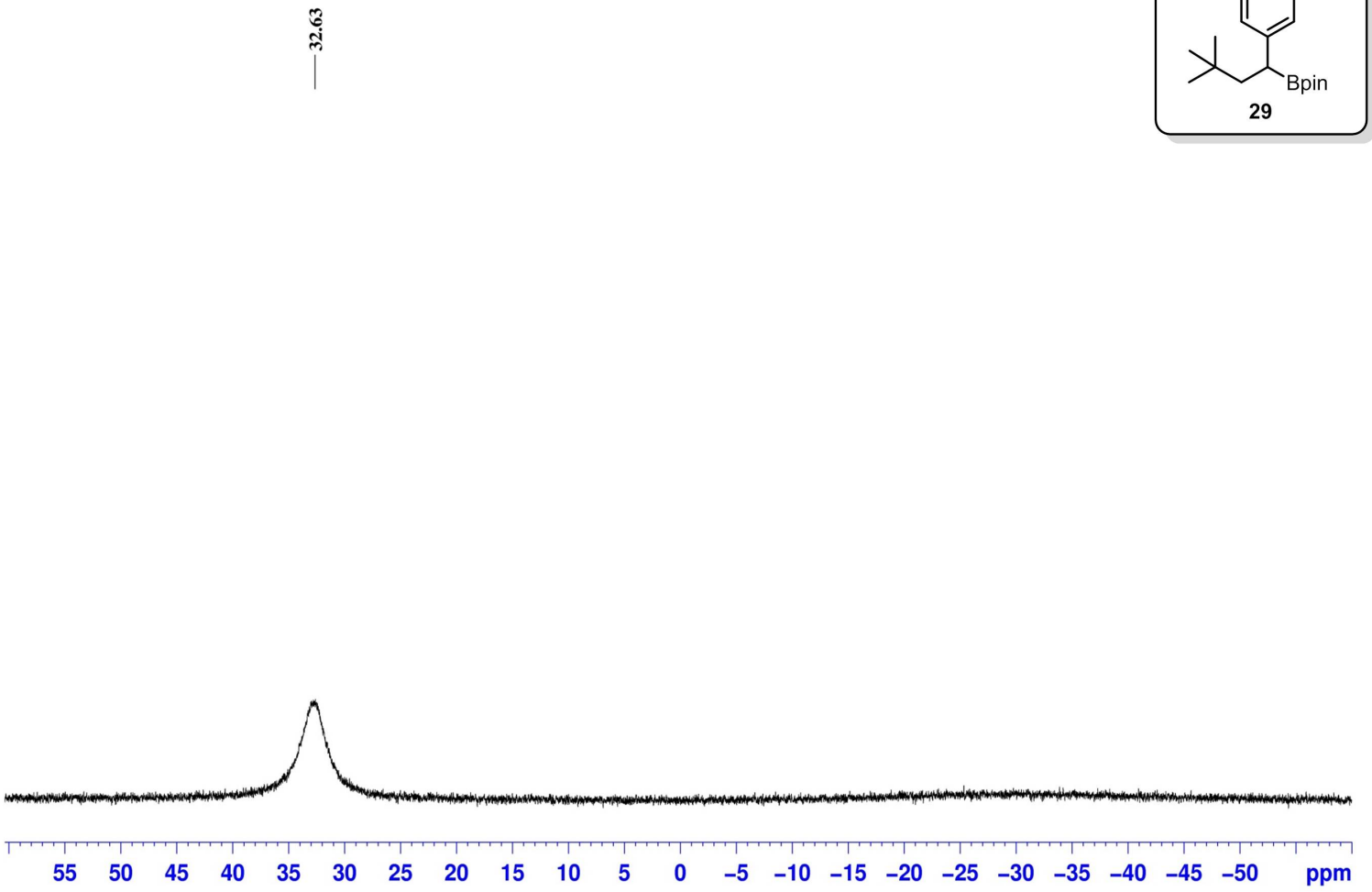
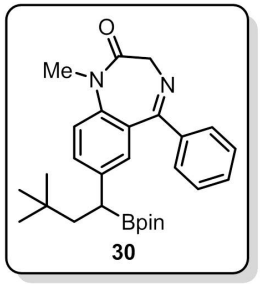
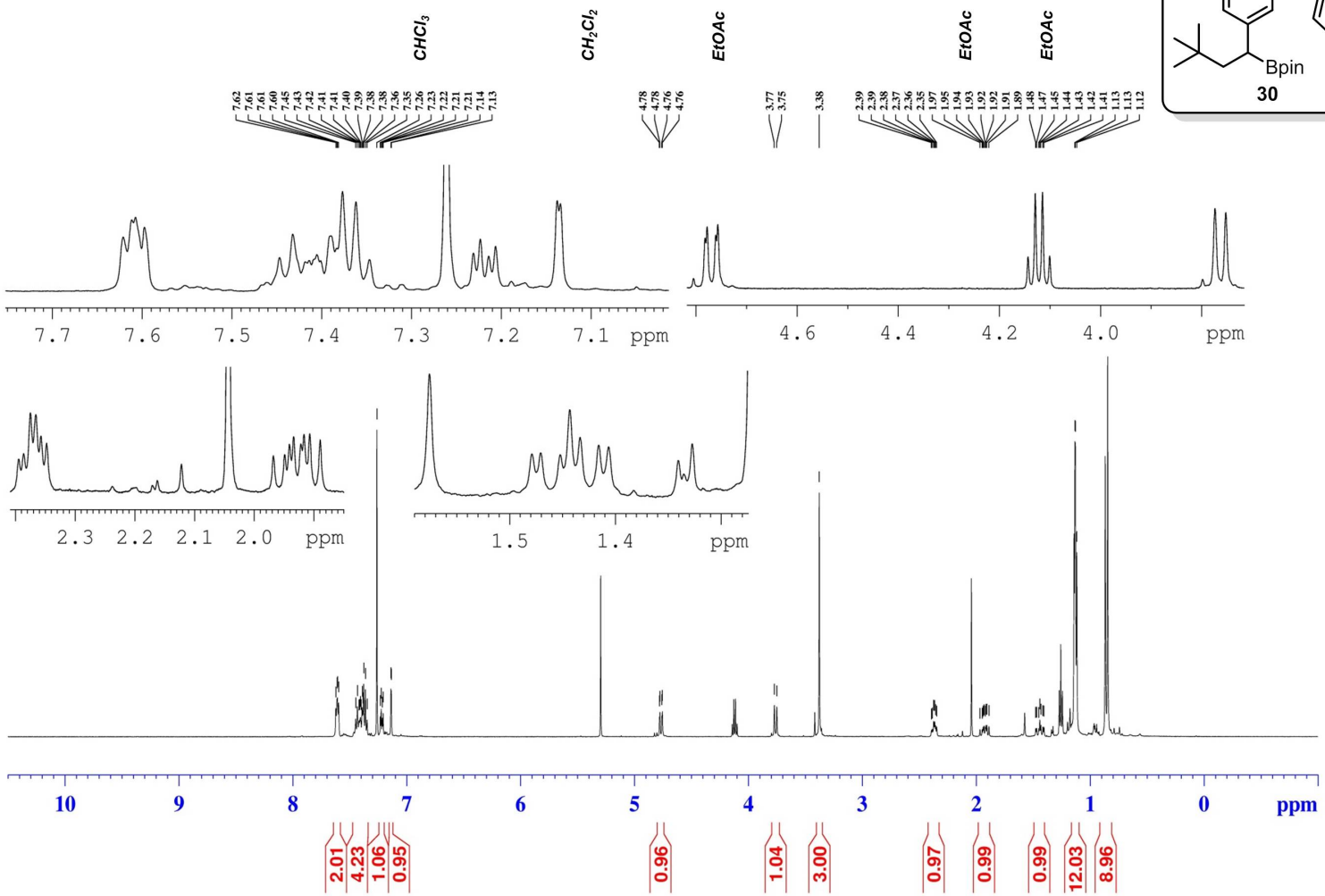


^1H NMR

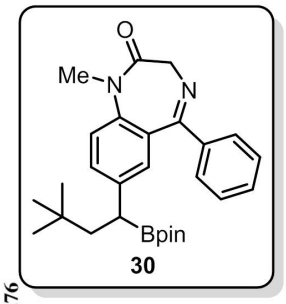
7-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-1-methyl-5-phenyl-1H-benzo[e][1,4]diazepin-2(3H)-one
500 MHz, $CDCl_3$





^{13}C NMR

7-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-1-methyl-5-phenyl-1H-benzo[e][1,4]diazepin-2(3H)-one
125 MHz, $CDCl_3$



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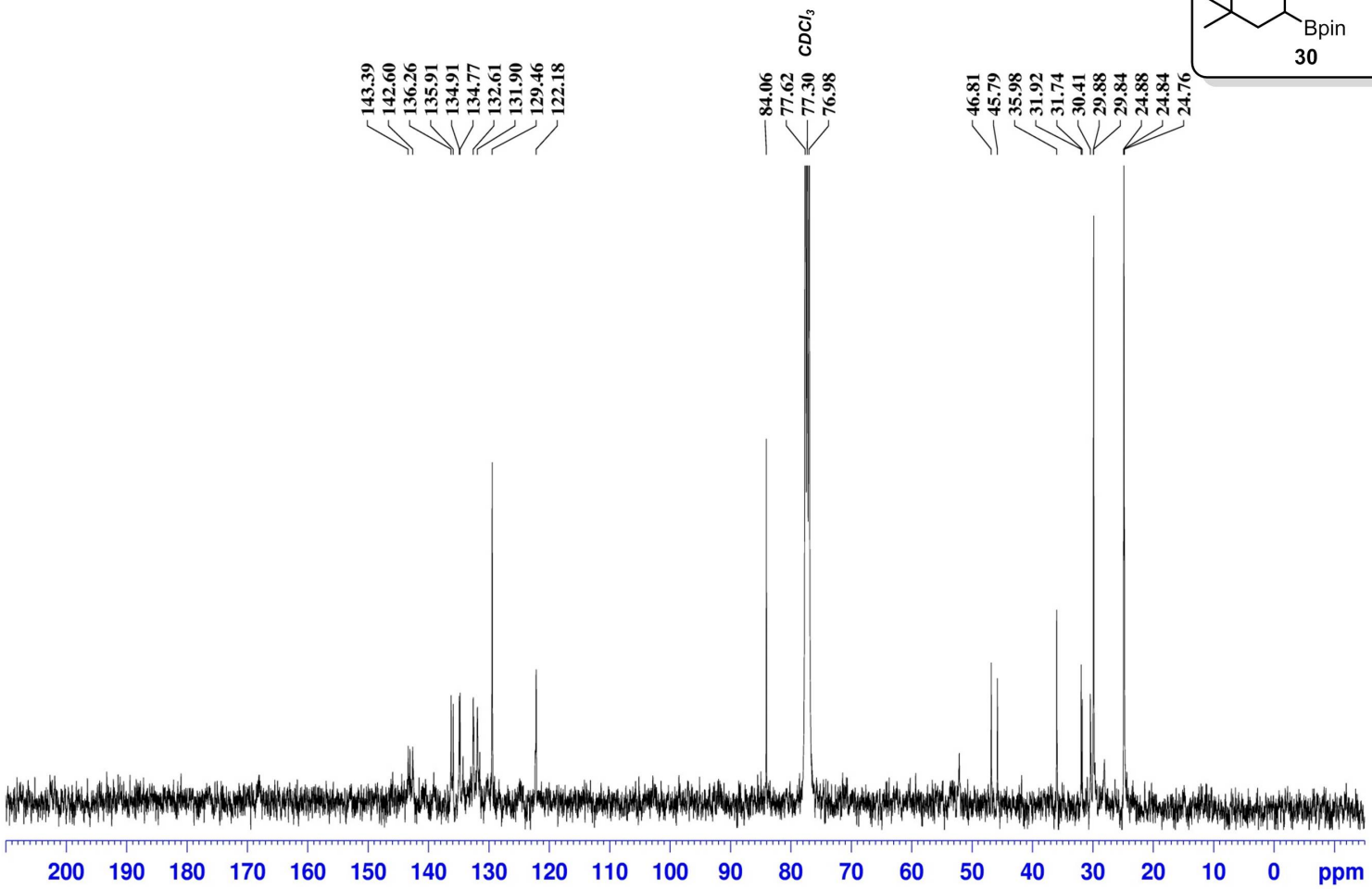
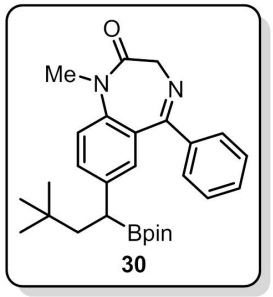


^{11}B NMR

7-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-1-methyl-5-phenyl-1H-benzo[e][1,4]diazepin-2(3H)-one
128 MHz, $CDCl_3$



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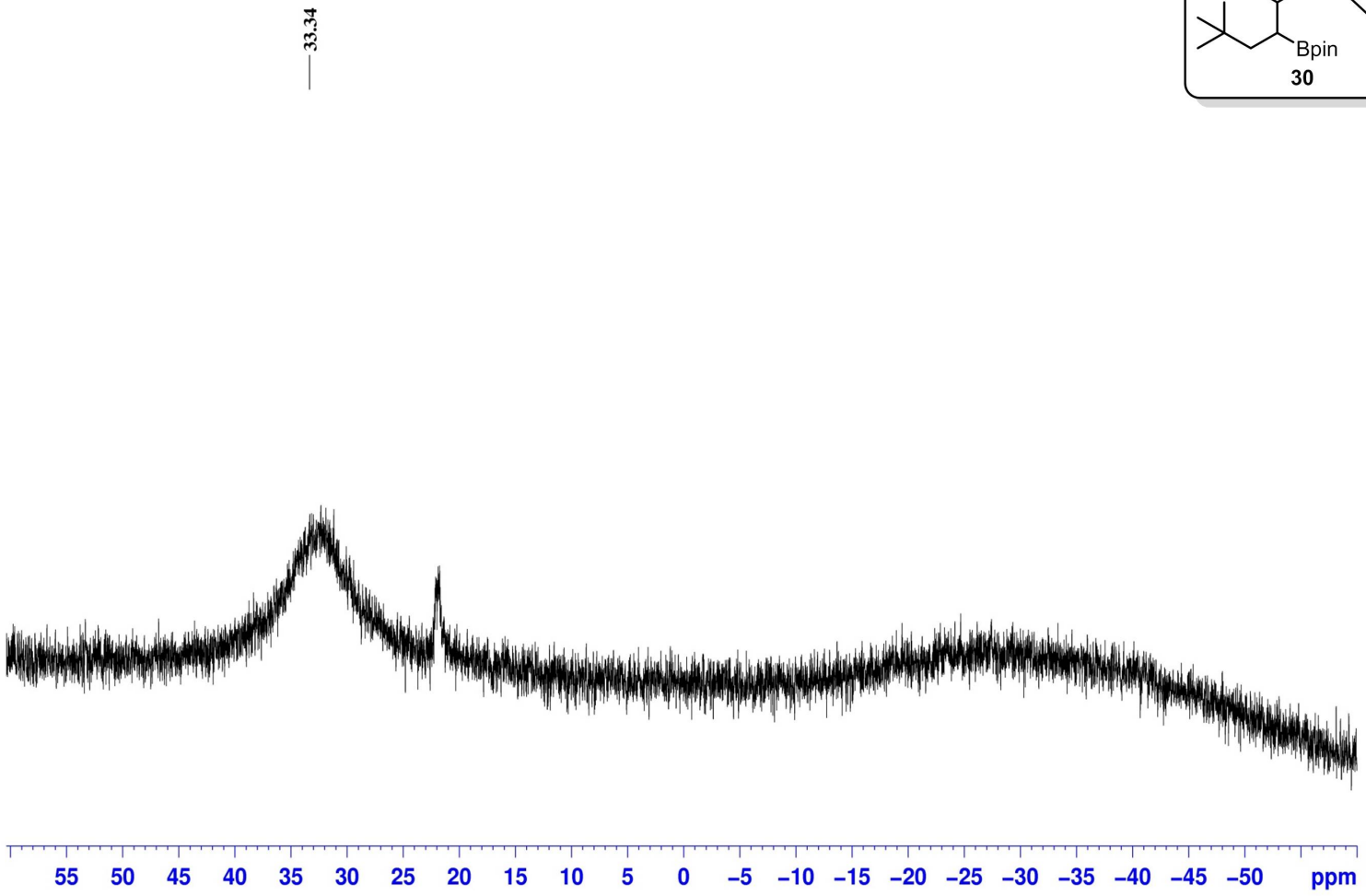
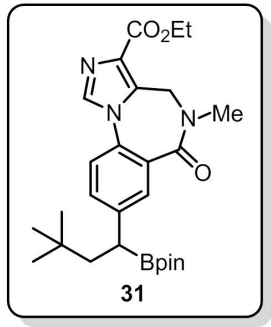


^1H NMR

ethyl 8-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-5-methyl-6-oxo-5,6-dihydro-4H-benzo[f]imidazo[1,5-a][1,4]diazepine-3-carboxylate
500 MHz, $CDCl_3$



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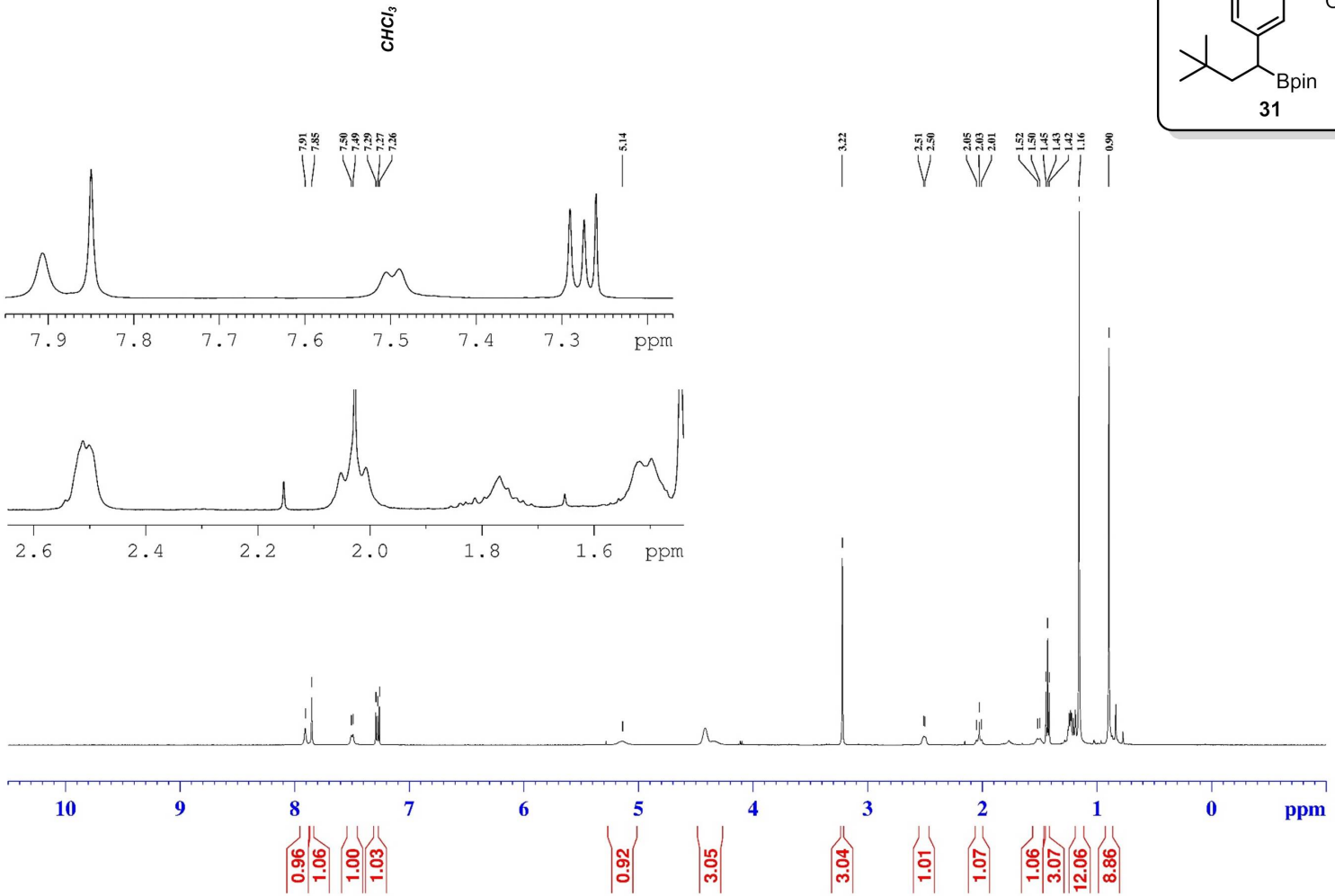
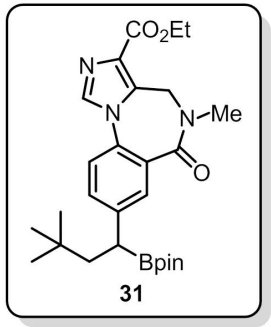


^{13}C NMR

Ethyl 8-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-5-methyl-6-oxo-5,6-dihydro-4H-benzo[f]imidazo[1,5-a][1,4]diazepine-3-carboxylate
125 MHz, $CDCl_3$



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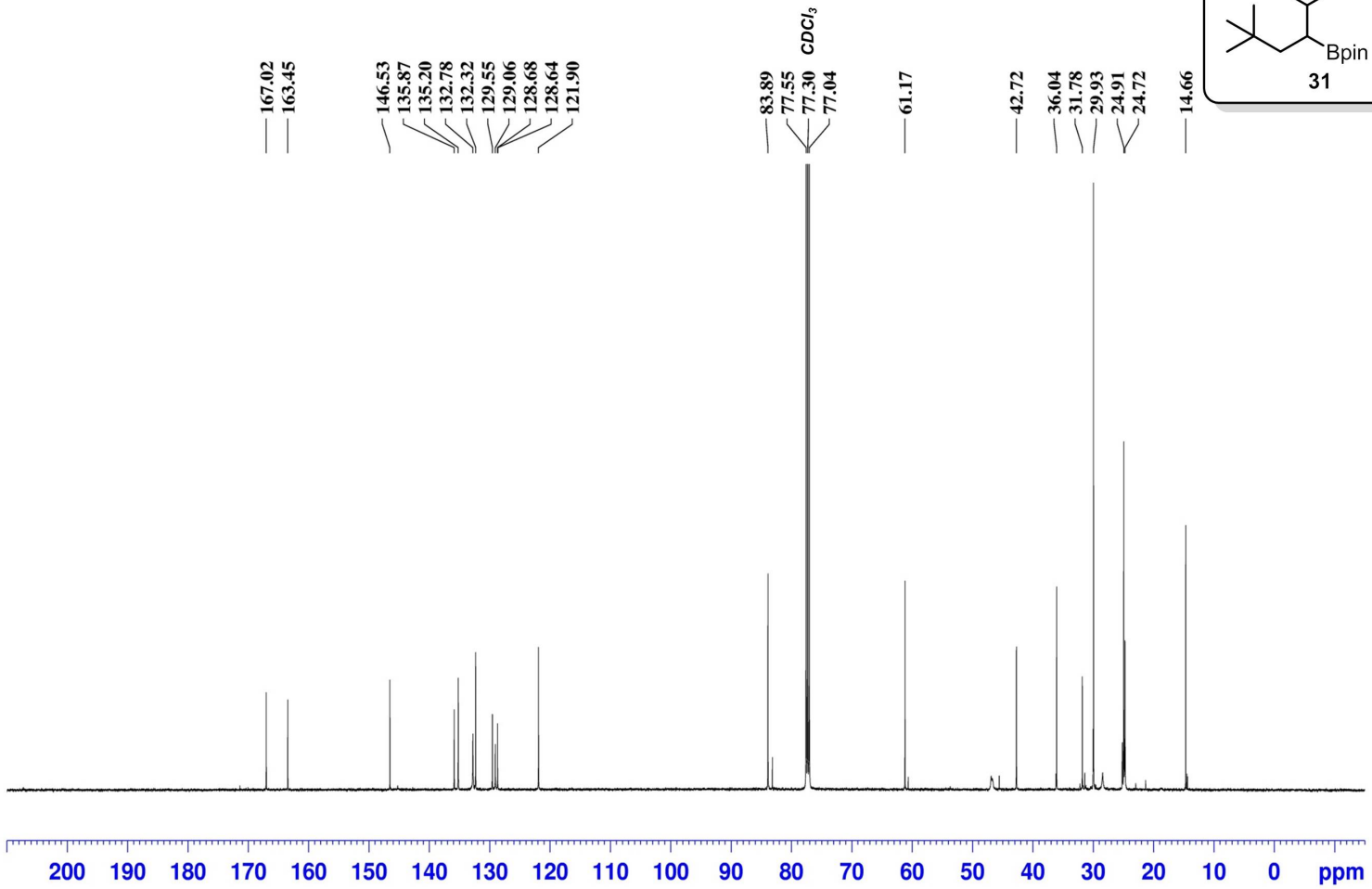
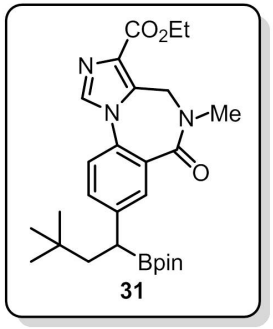


^{11}B NMR

ethyl 8-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-5-methyl-6-oxo-5,6-dihydro-4H-benzo[f]imidazo[1,5-a][1,4]diazepine-3-carboxylate
128 MHz, $CDCl_3$



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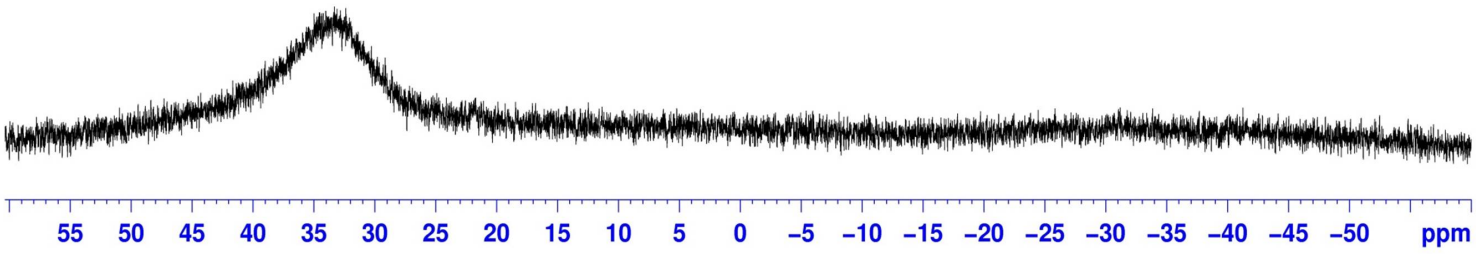
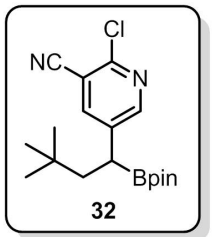
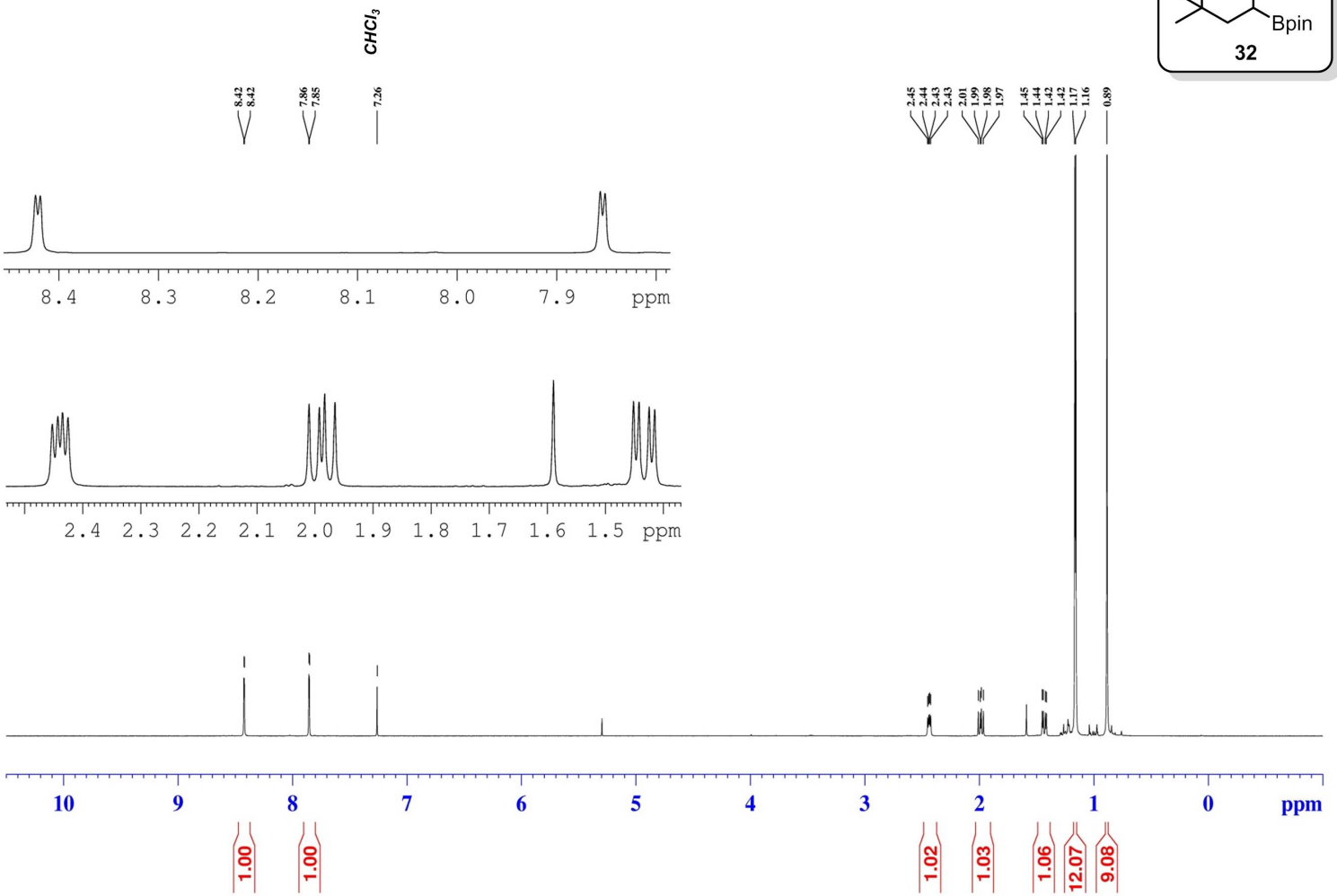
33.31



^1H NMR

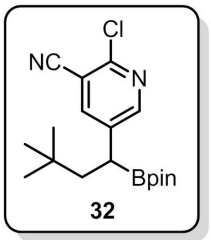
2-chloro-5-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)nicotinonitrile
500 MHz, $CDCl_3$

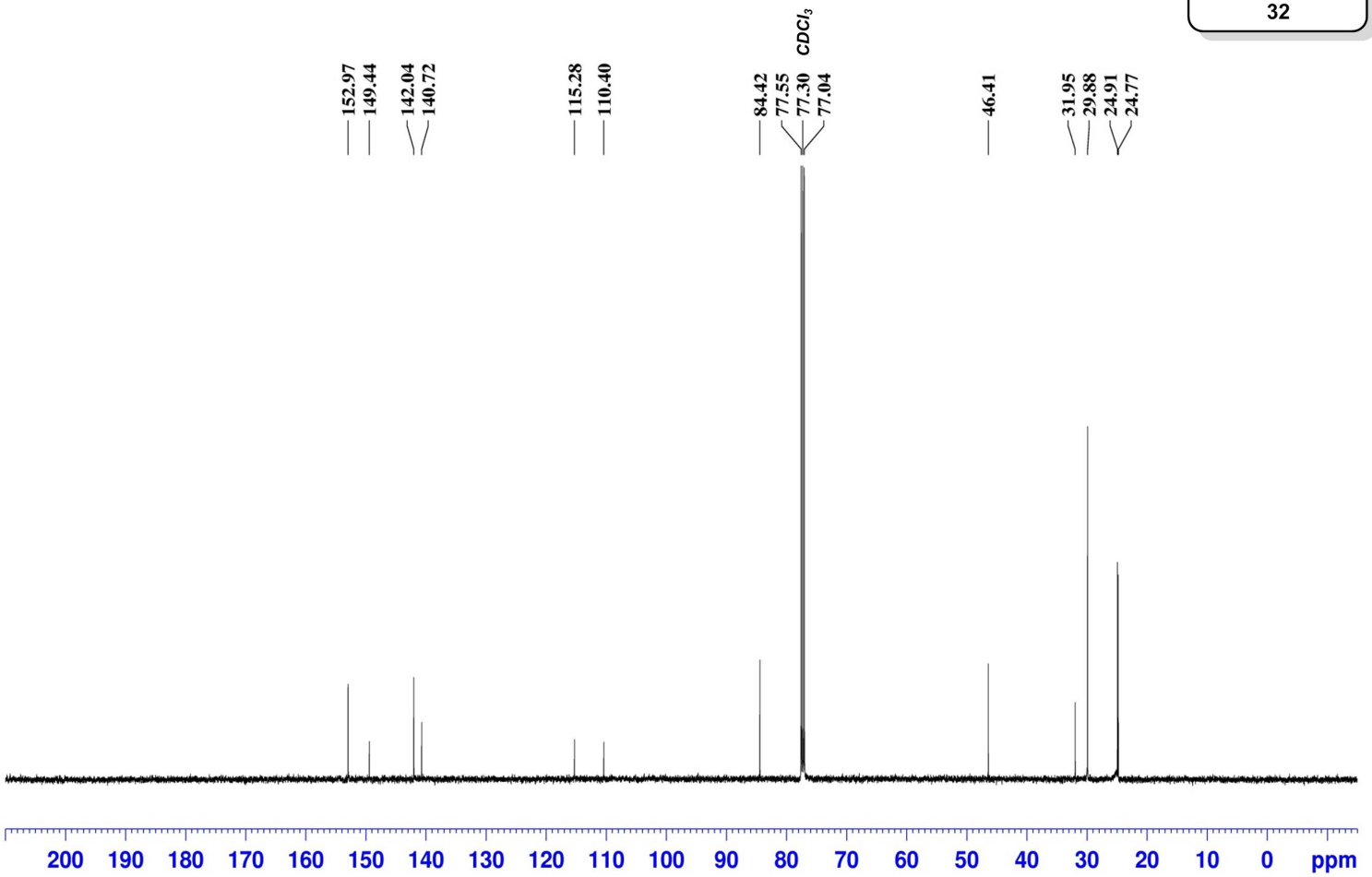




^{13}C NMR

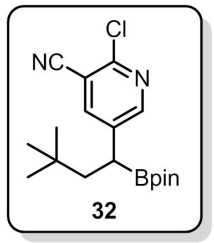
2-Chloro-5-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)nicotinonitrile
125 MHz, $CDCl_3$

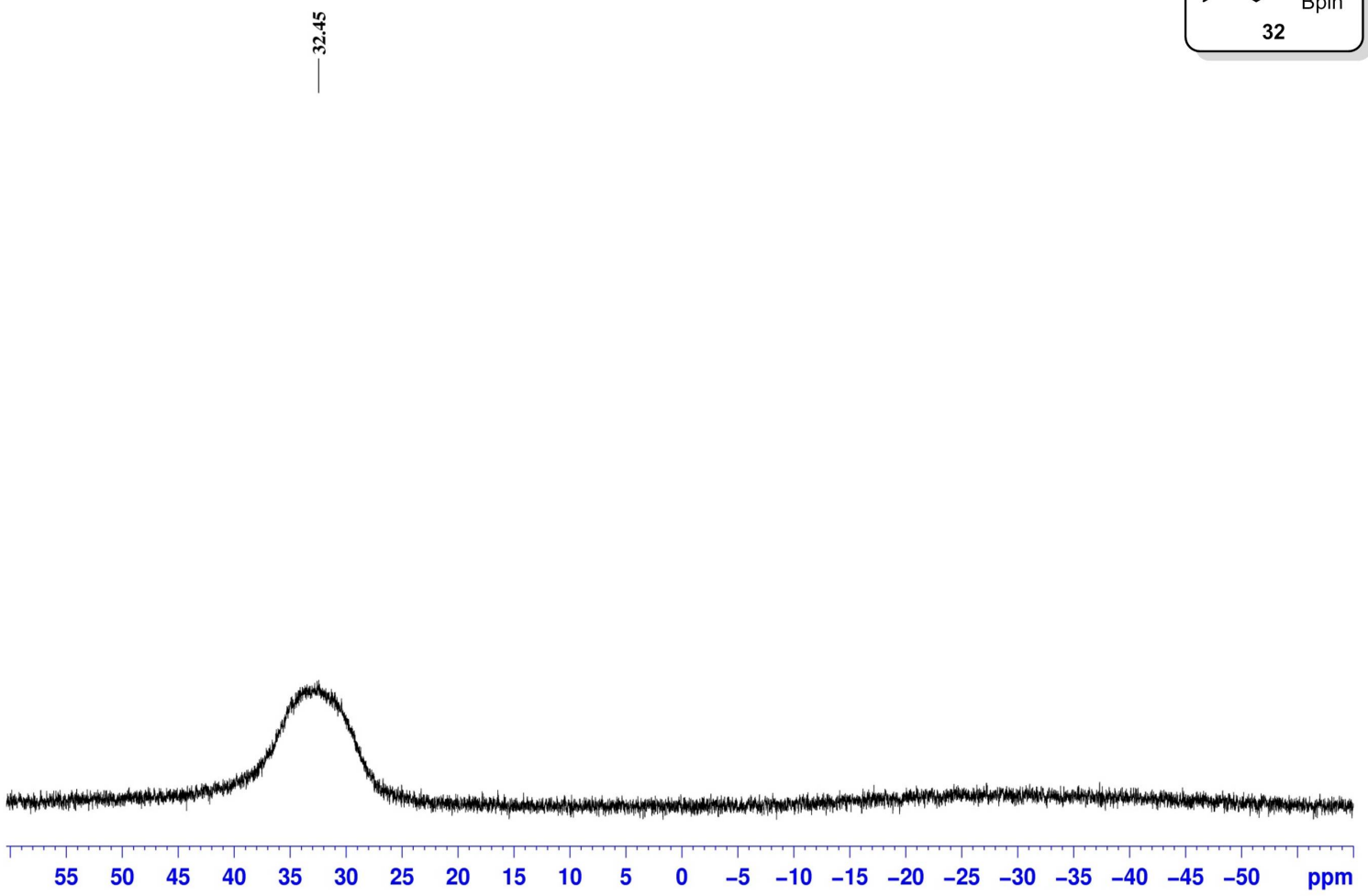




^{11}B NMR

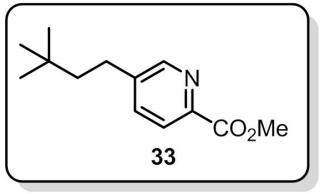
2-chloro-5-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)nicotinonitrile
128 MHz, $CDCl_3$





methyl 5-(3,3-dimethylbutyl)picolinate
500 MHz, $CDCl_3$

^1H NMR



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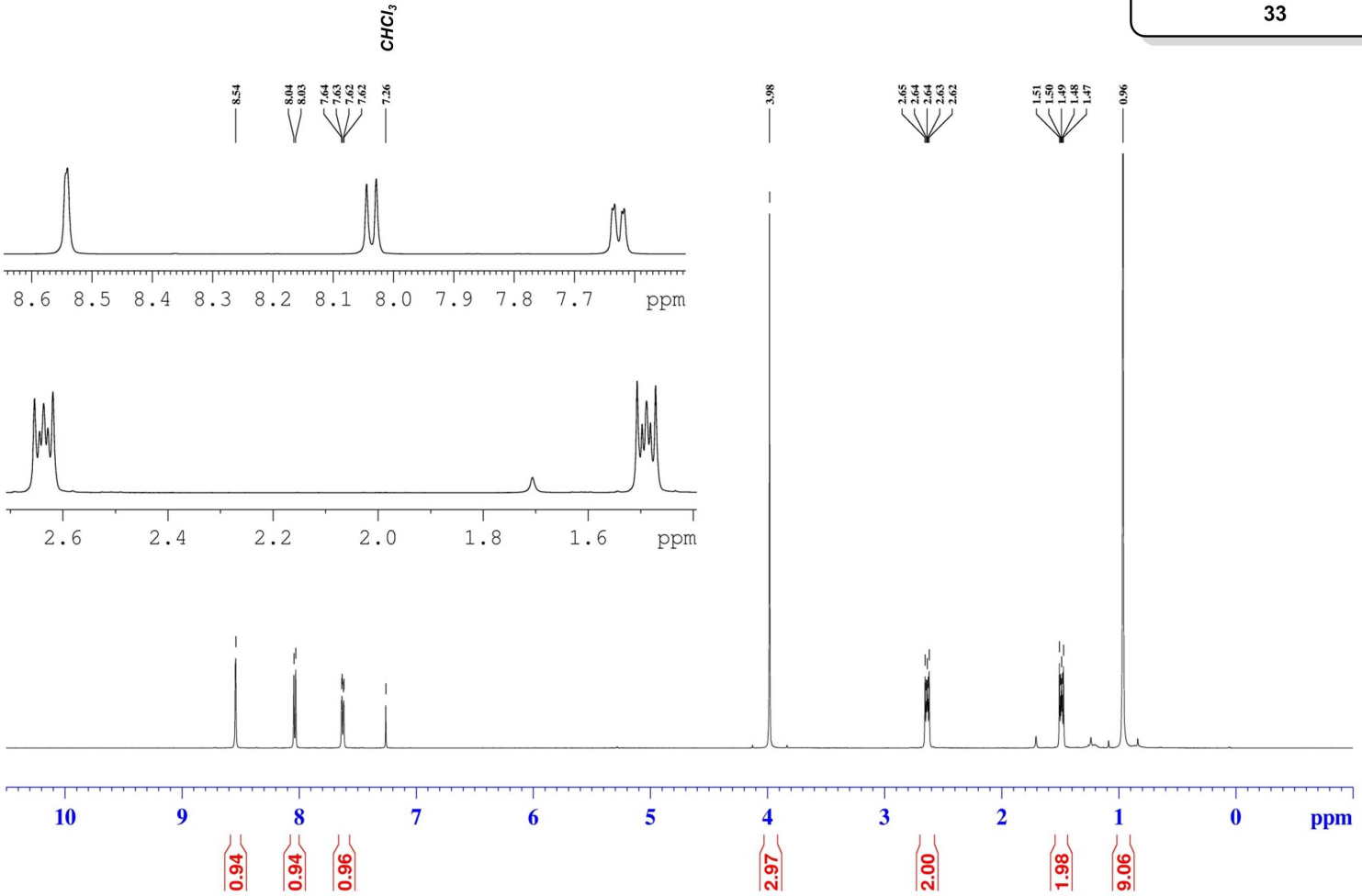
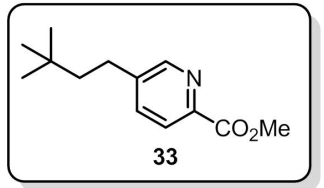


Methyl 5-(3,3-dimethylbutyl)picolinate
125 MHz, $CDCl_3$

^{13}C NMR



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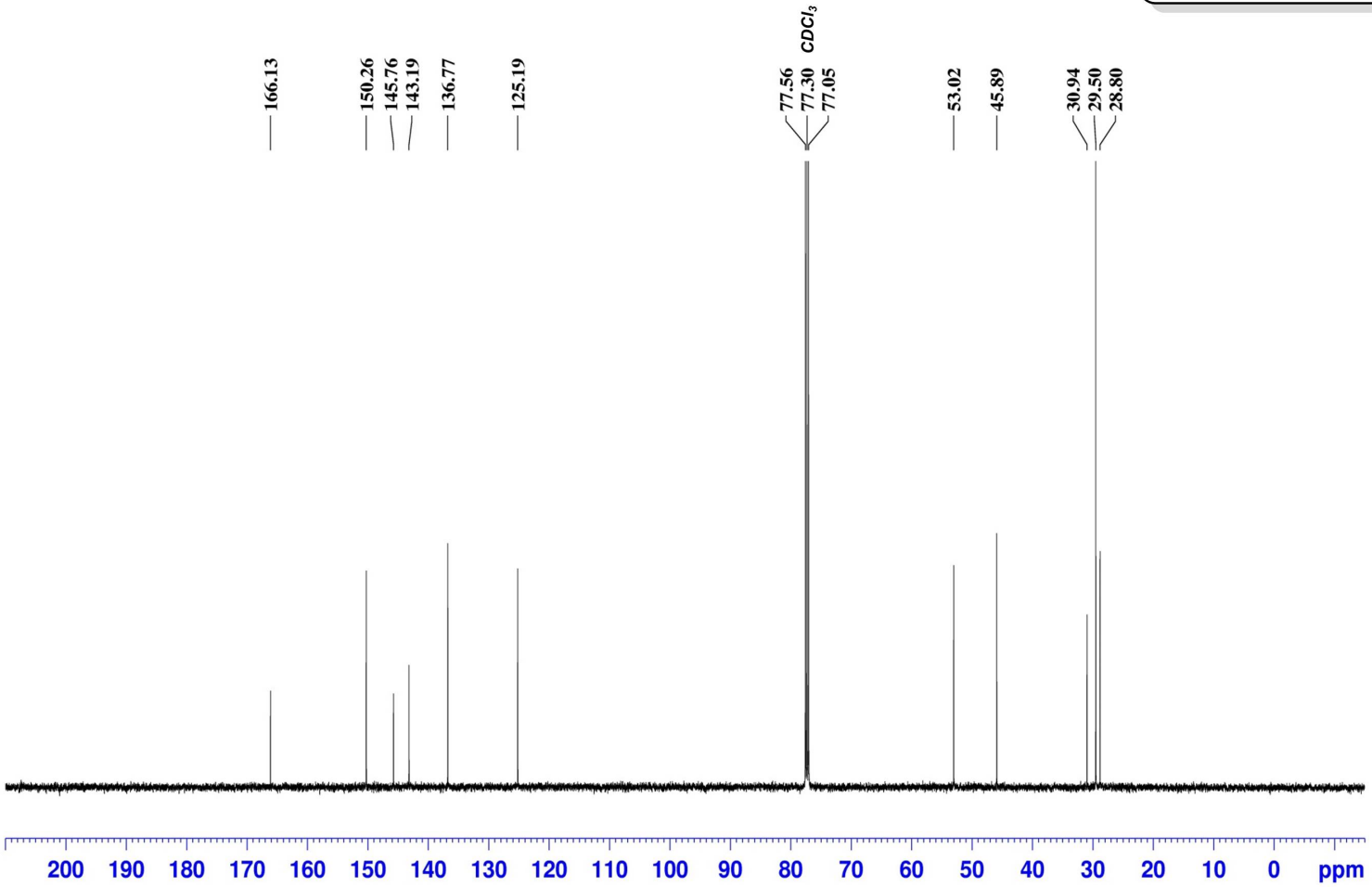
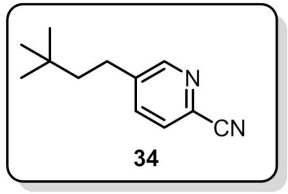
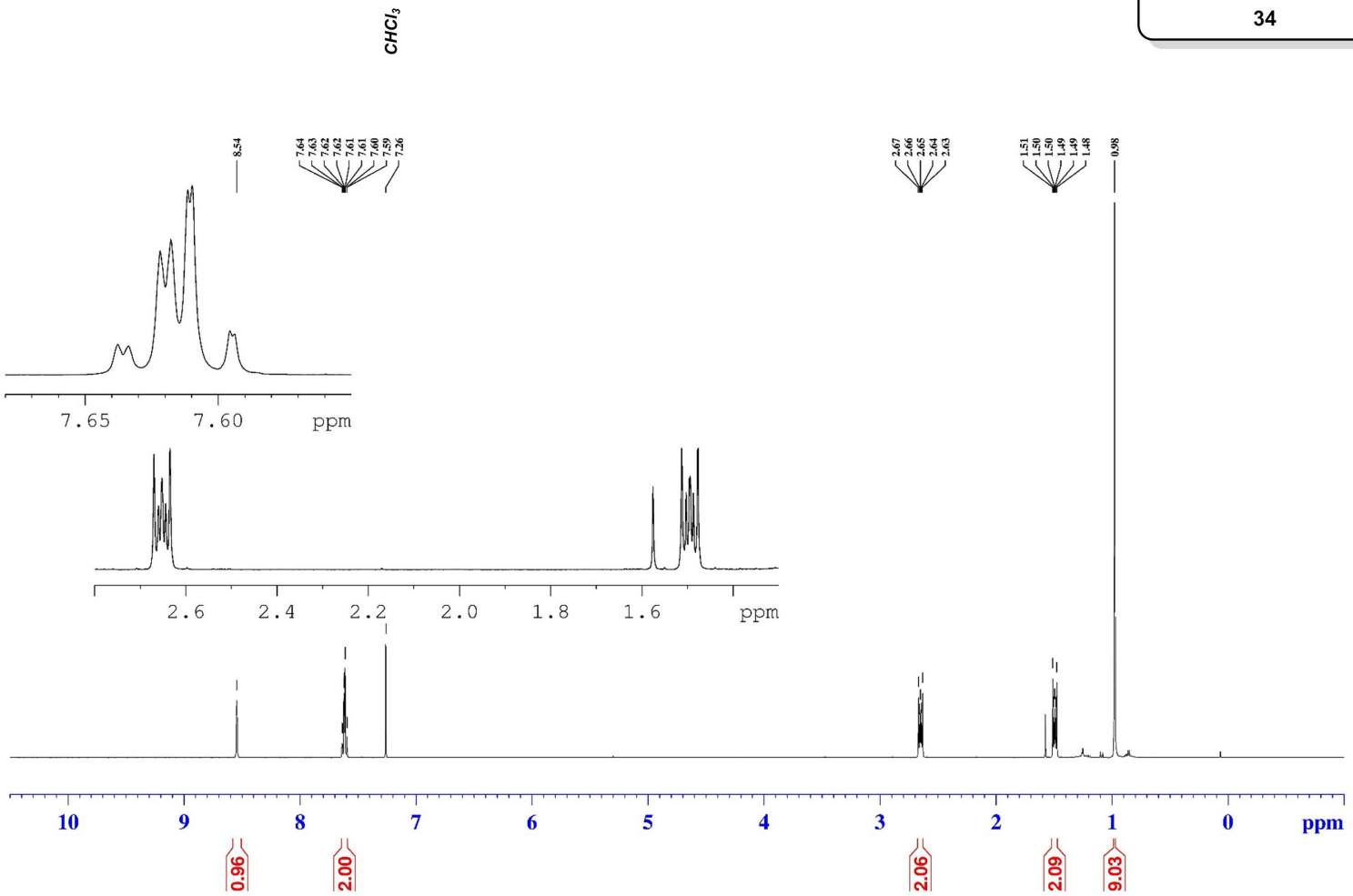


5-(3,3-dimethylbutyl)picolinonitrile
500 MHz, $CDCl_3$

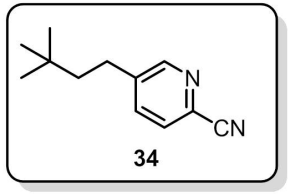
^{1}H NMR

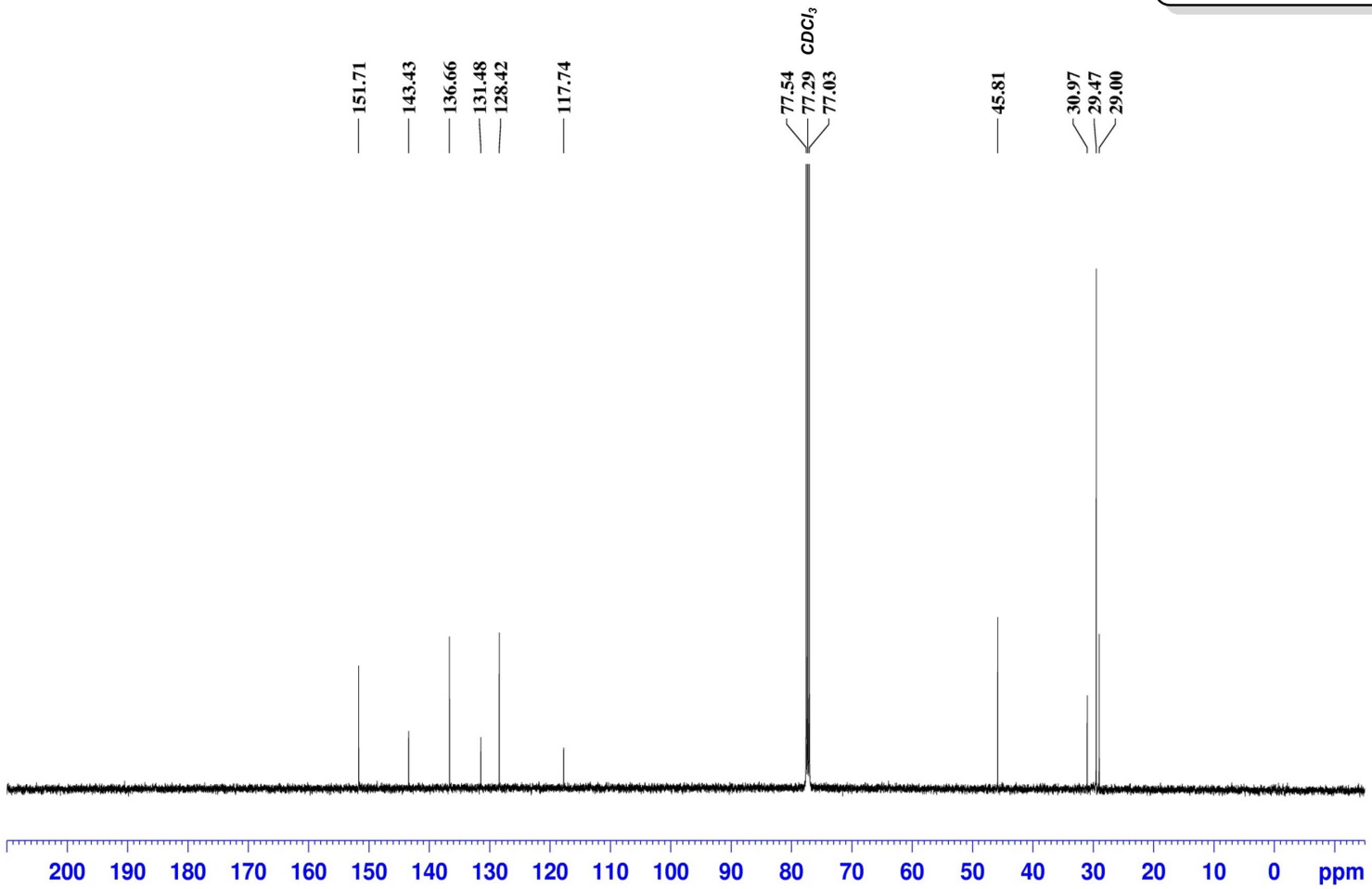




5-(3,3-Dimethylbutyl)picolinonitrile
125 MHz, $CDCl_3$

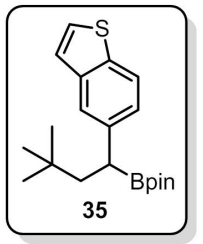
^{13}C NMR

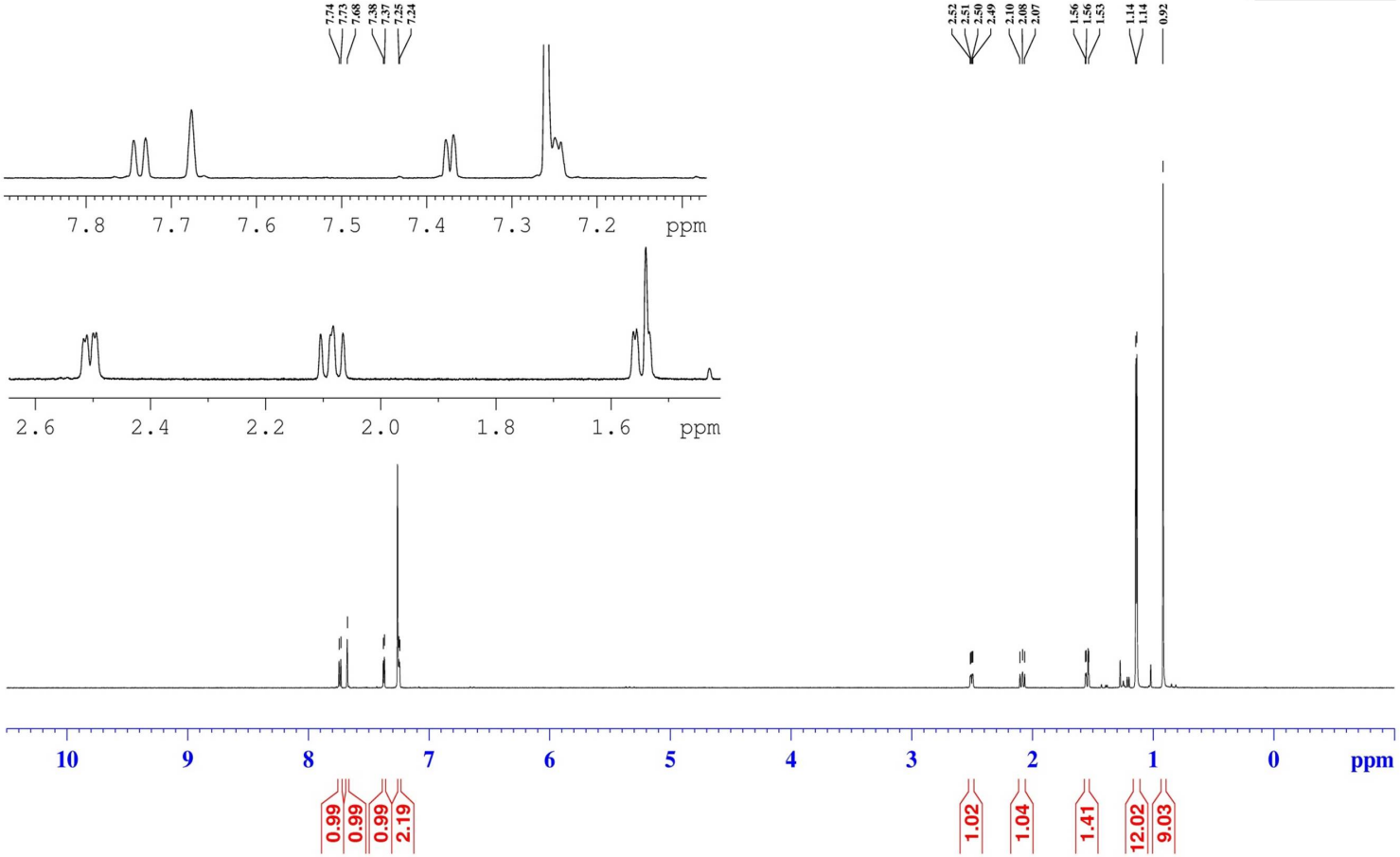




^{1}H NMR

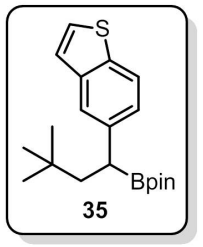
2-(1-(benzo[b]thiophen-5-yl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

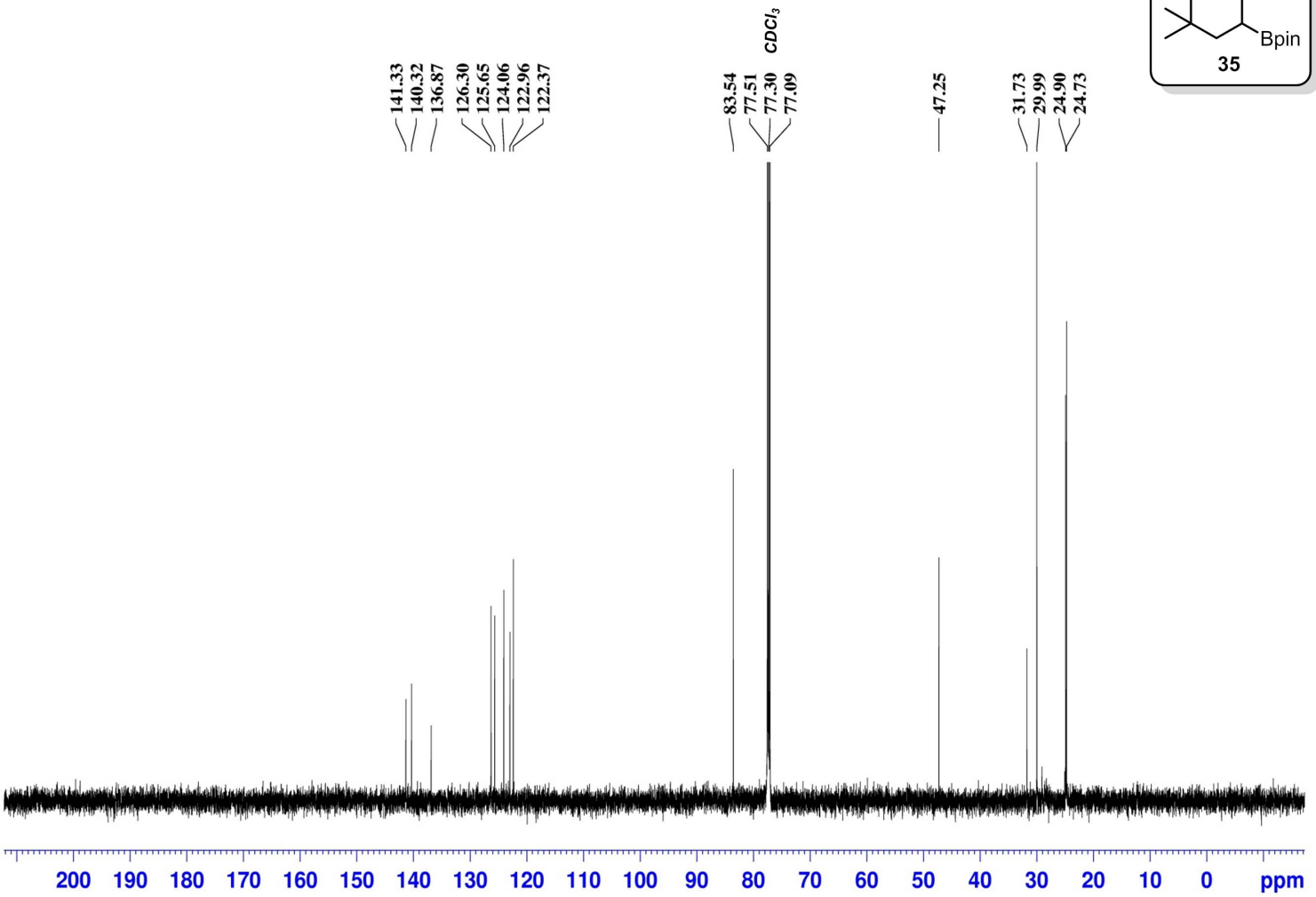




^{13}C NMR

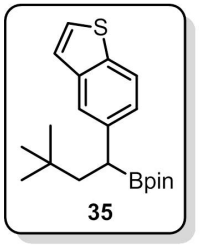
2-(1-(Benzo[b]thiophen-5-yl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$





^{11}B NMR

2-(1-(benzo[b]thiophen-5-yl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$



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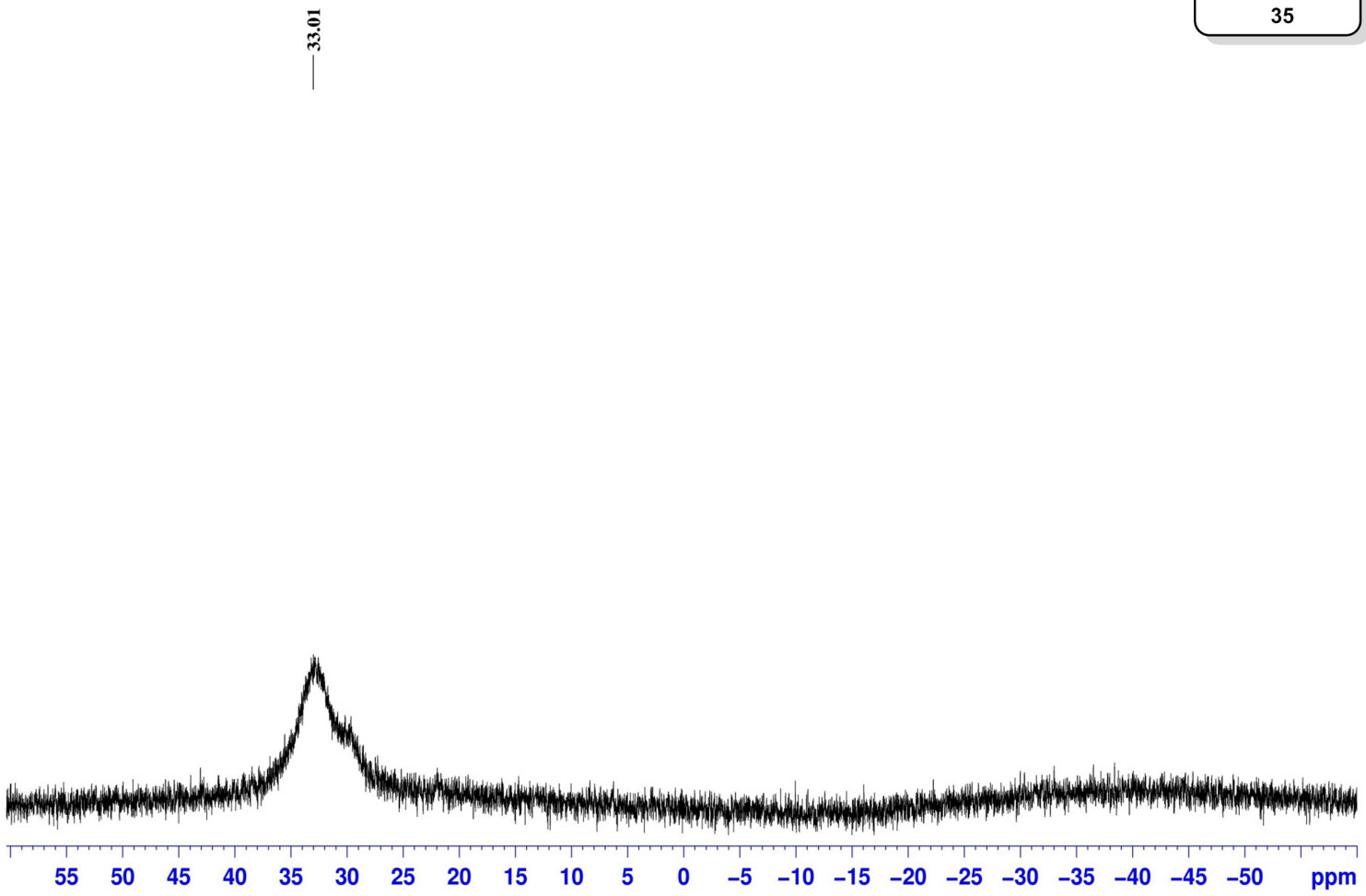
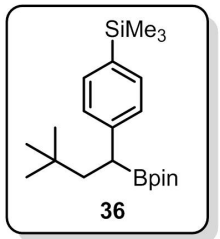
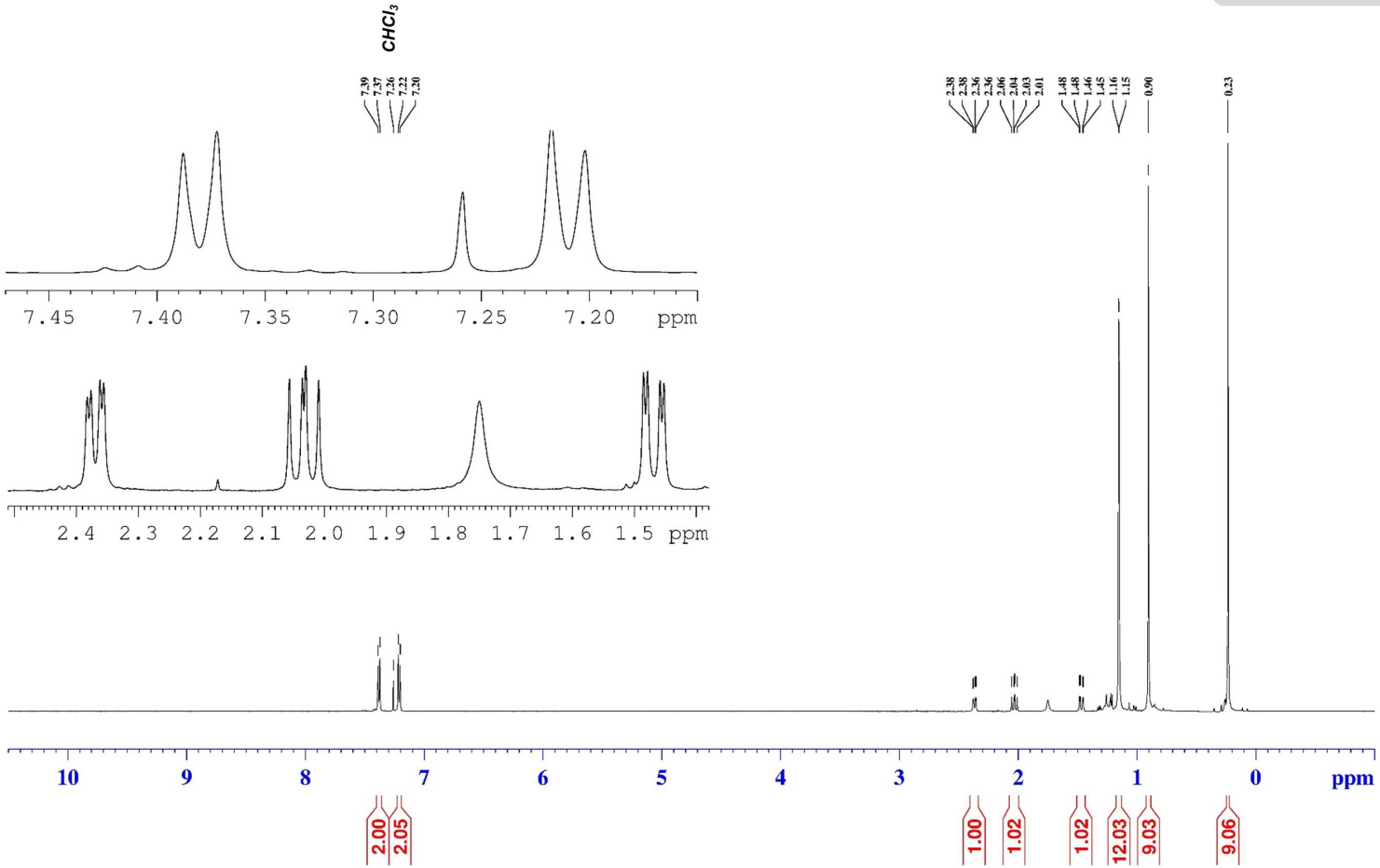


^1H NMR

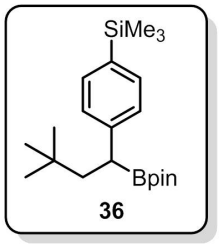
4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)trimethylsilane
500 MHz, $CDCl_3$

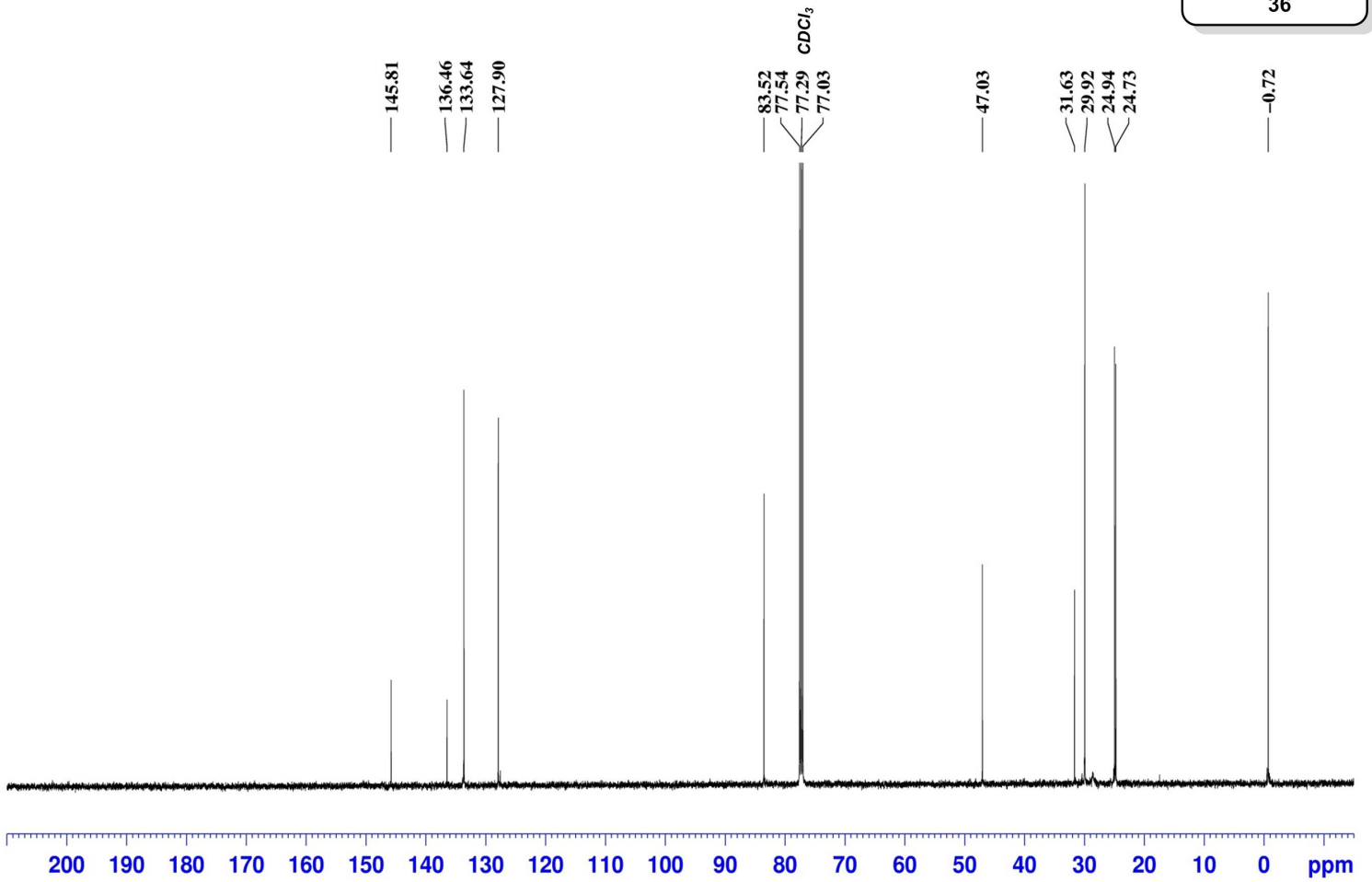




^{13}C NMR

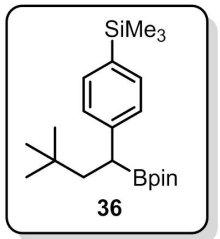
4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)trimethylsilane
125 MHz, $CDCl_3$





^{11}B NMR

4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)trimethylsilane
128 MHz, $CDCl_3$



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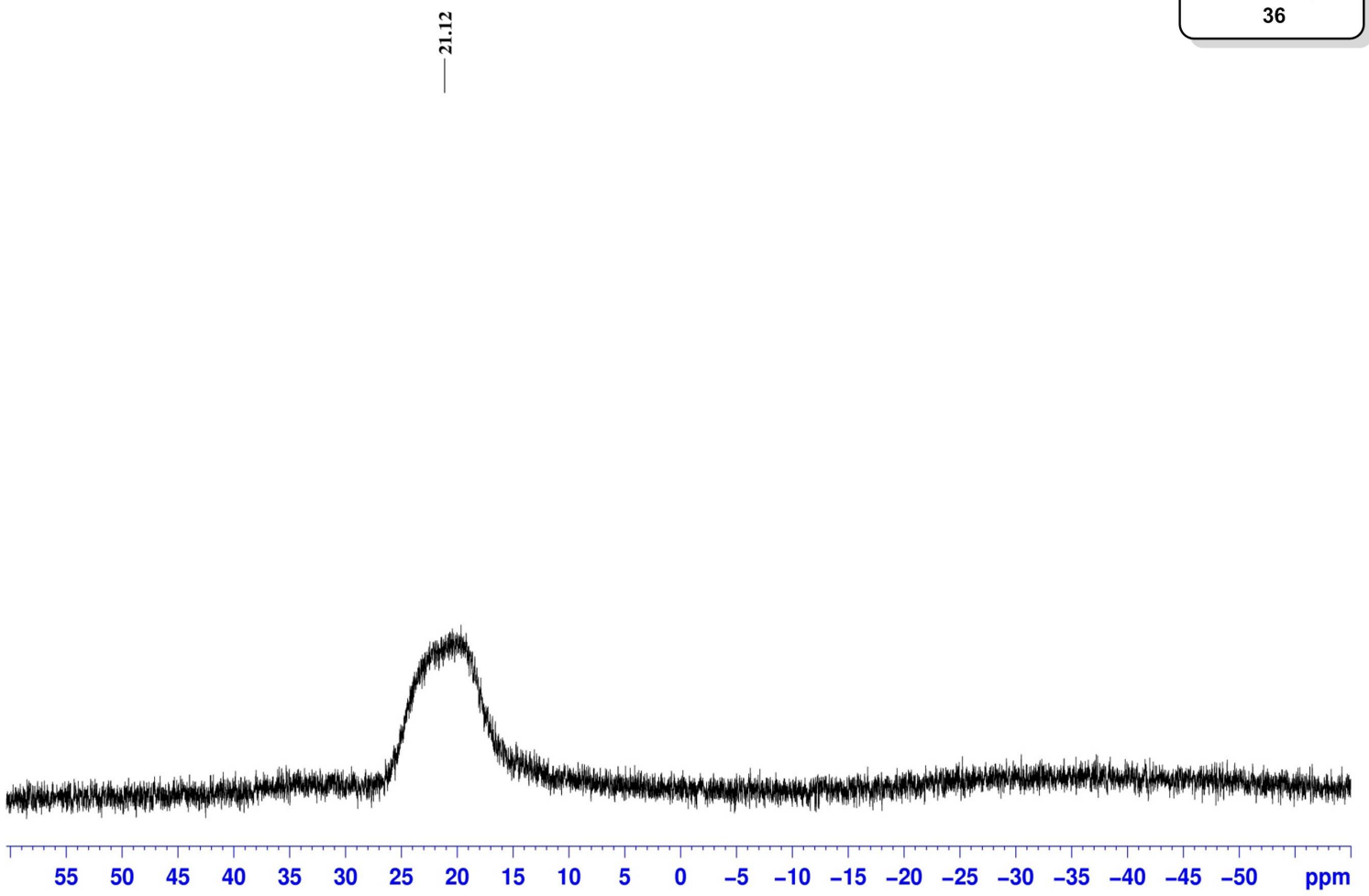
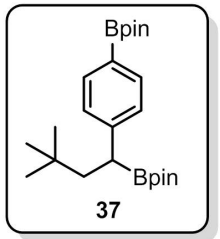
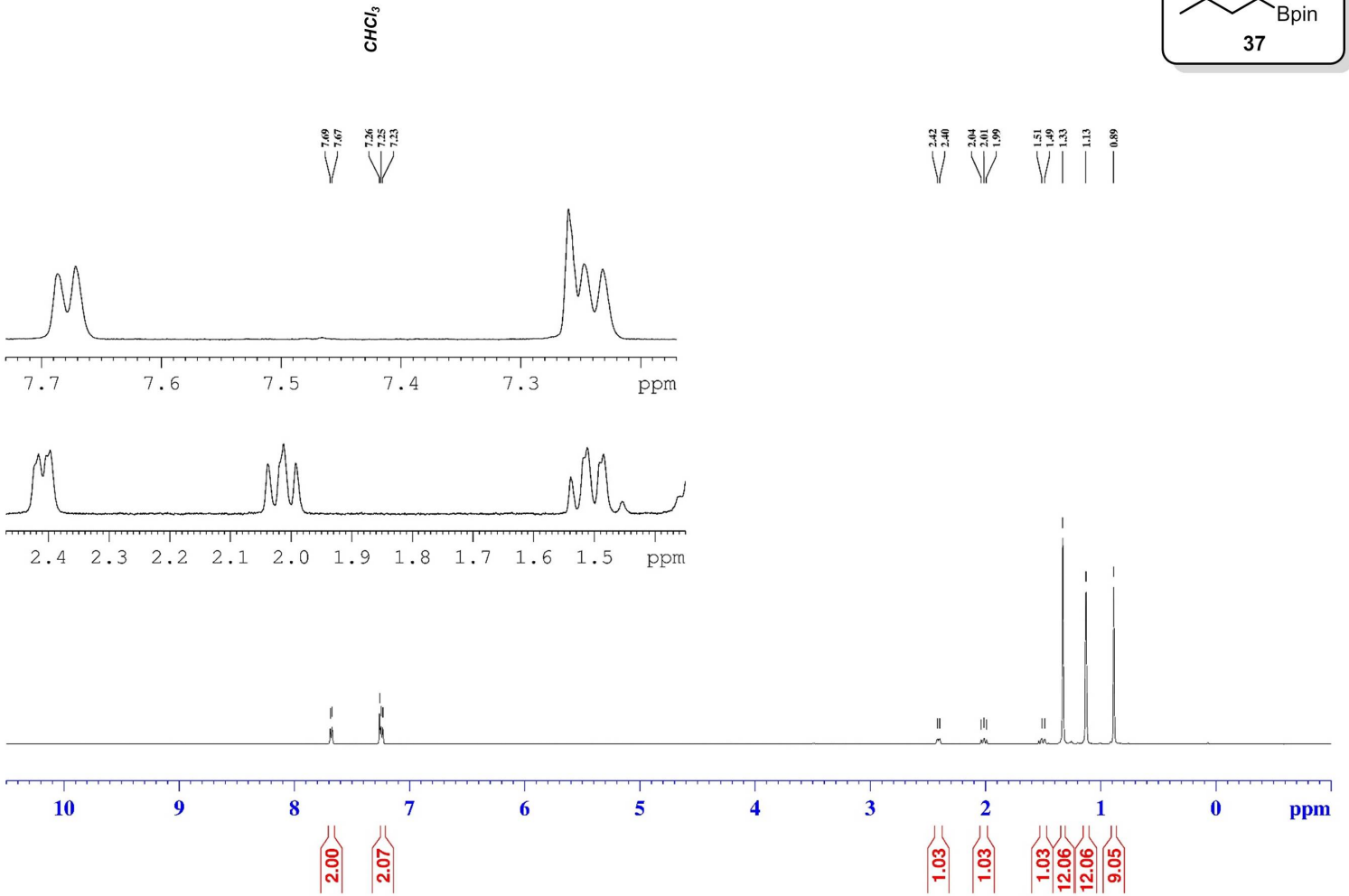


^1H NMR

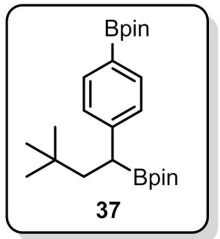
2-(4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

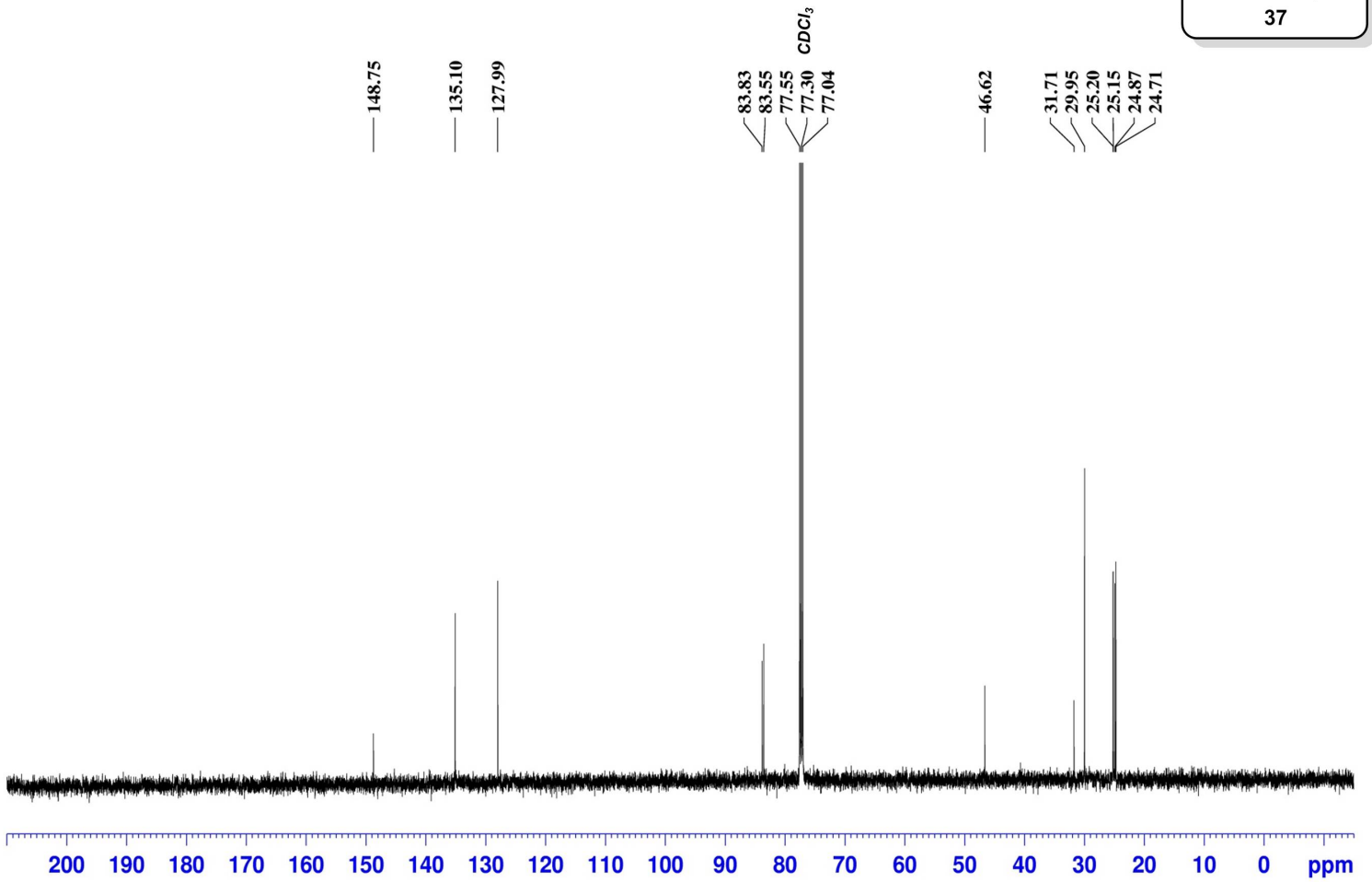




^{13}C NMR

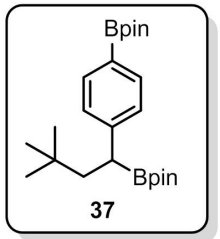
2-(4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$





^{11}B NMR

2-(4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$



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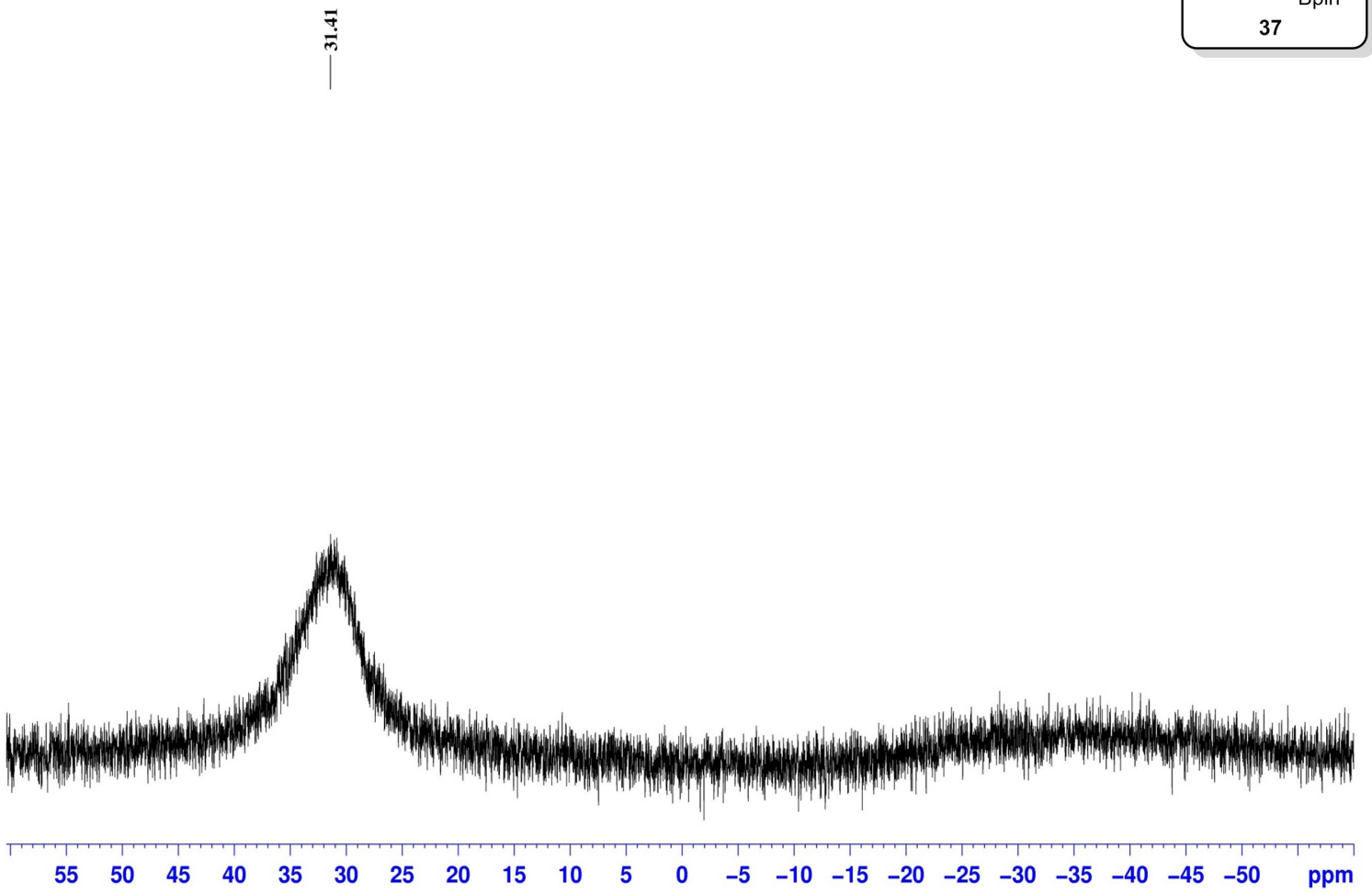
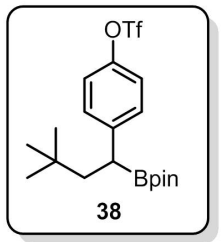
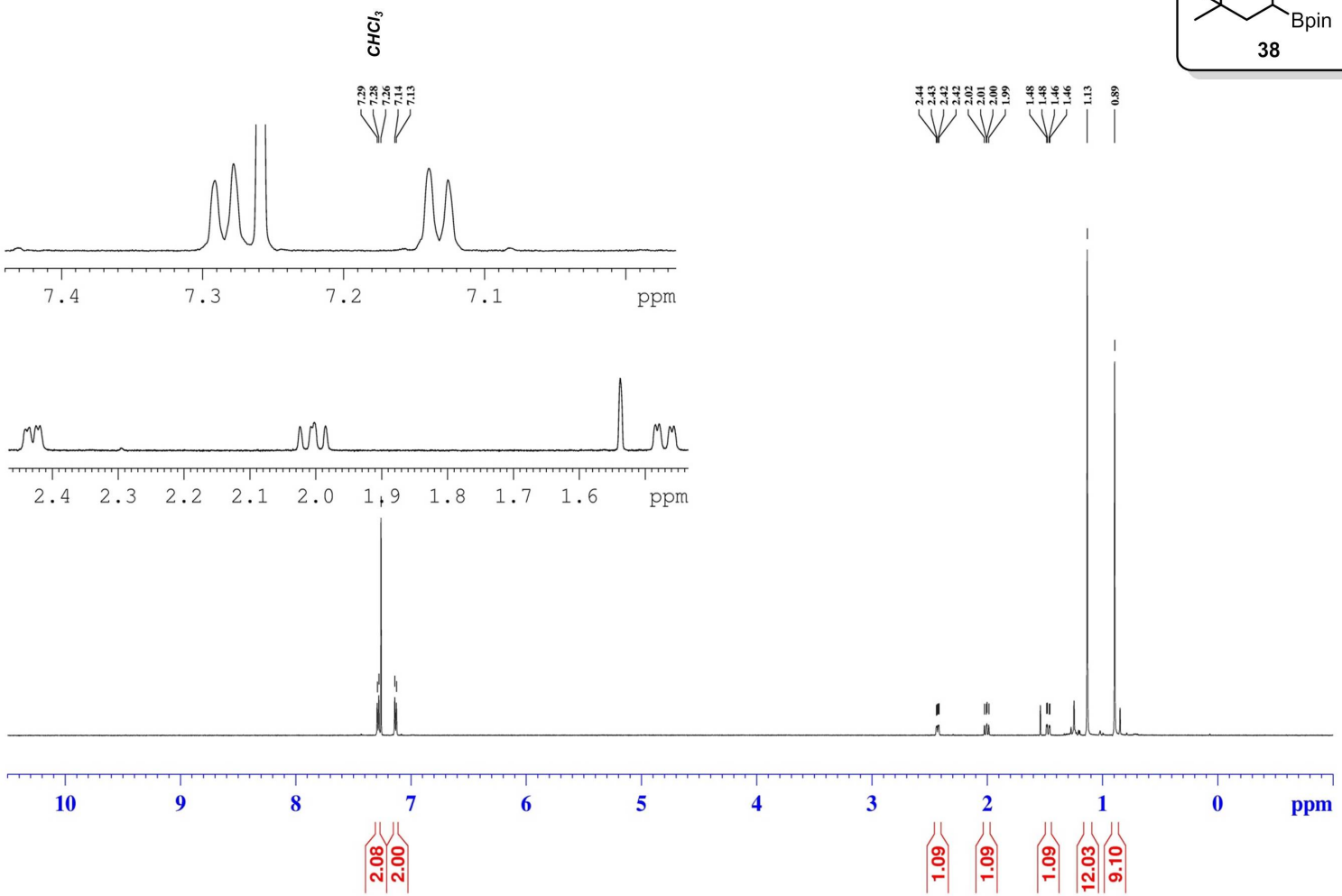


^1H NMR

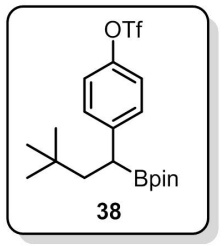
4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl trifluoromethanesulfonate
500 MHz, $CDCl_3$

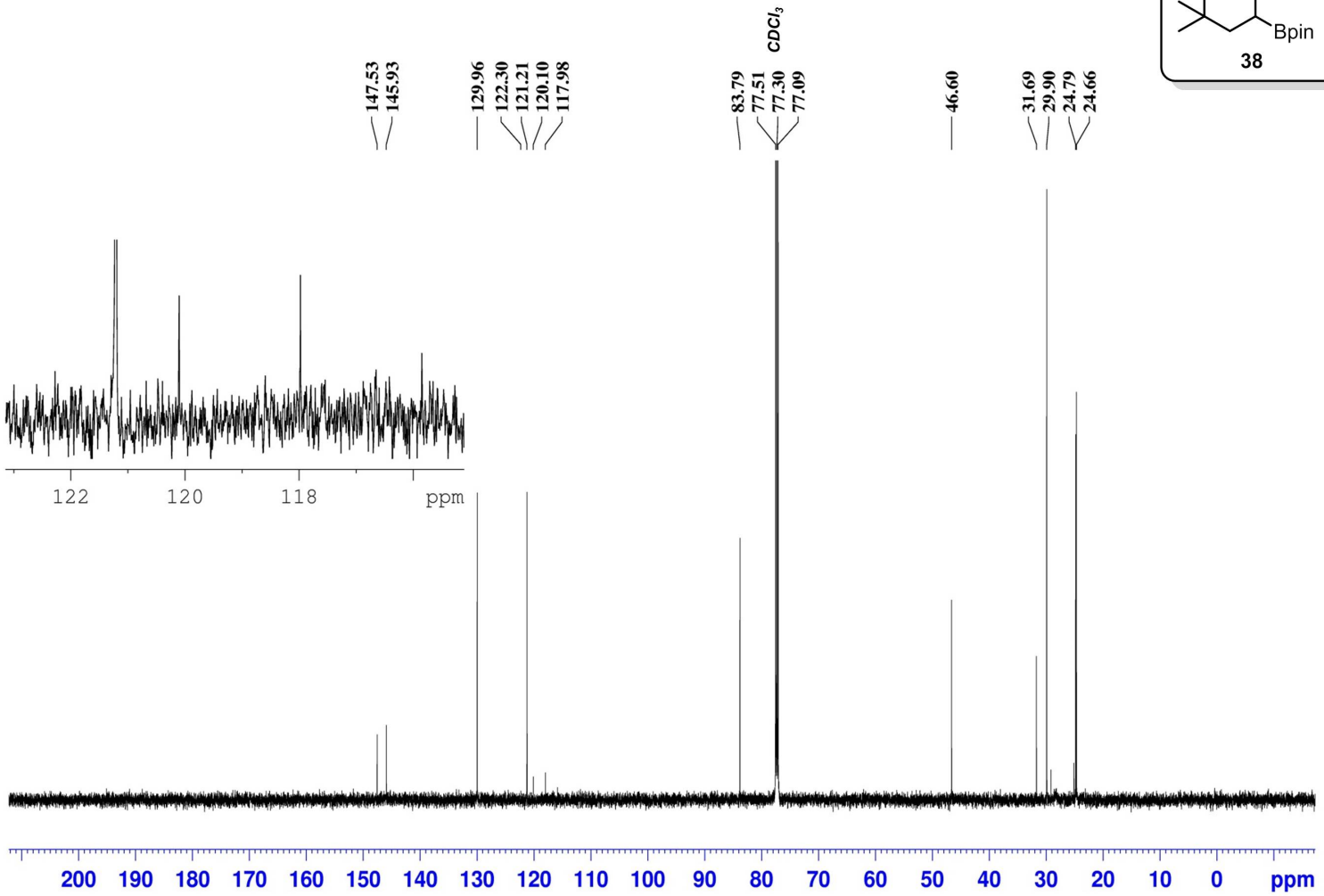




^{13}C NMR

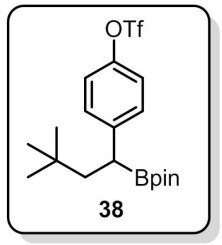
4-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl trifluoromethanesulfonate
125 MHz, $CDCl_3$

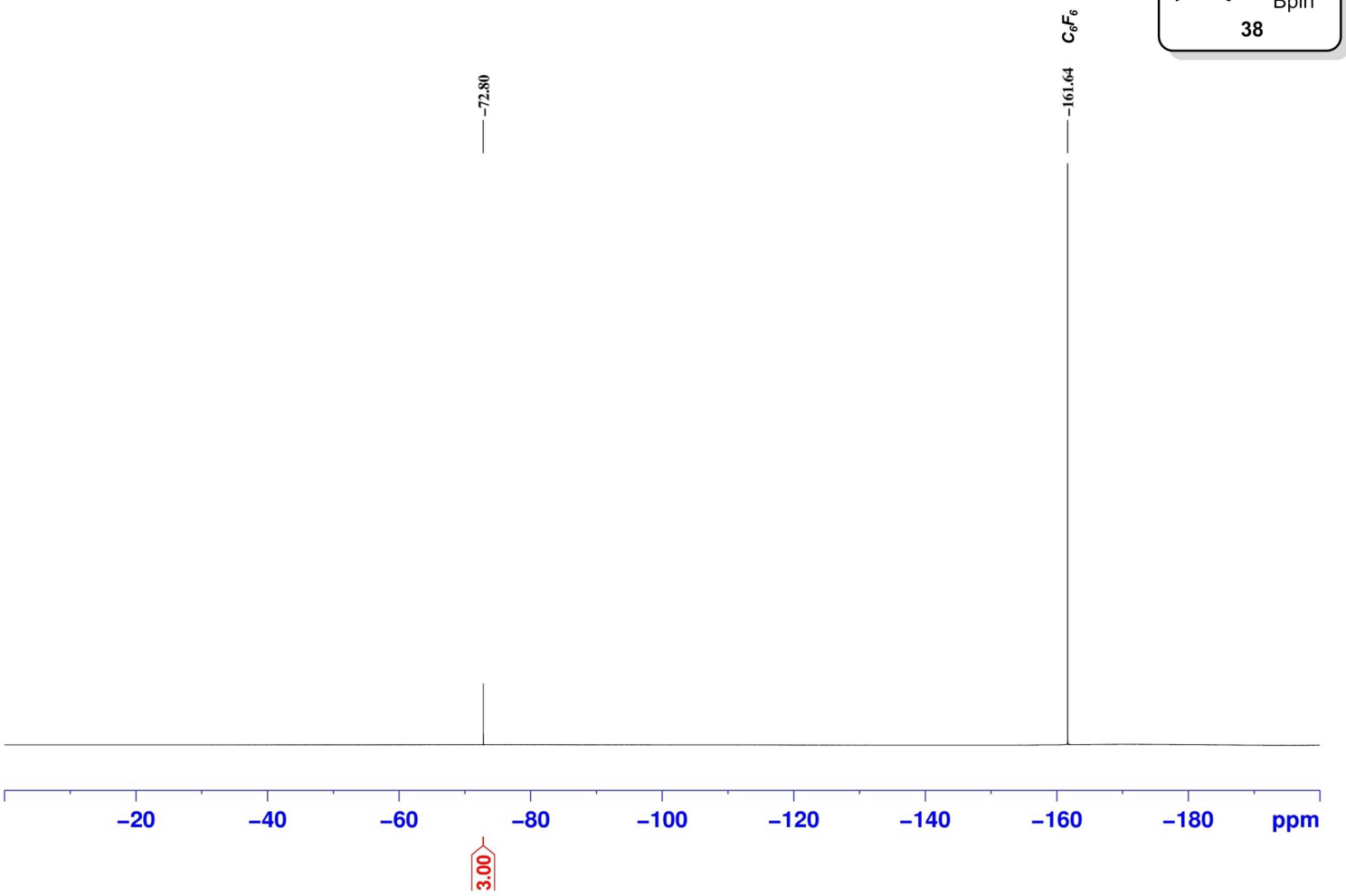




^{19}F NMR

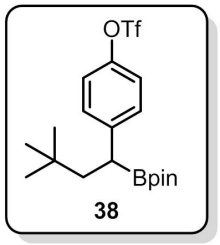
4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl trifluoromethanesulfonate
471 MHz, $CDCl_3$





^{11}B NMR

4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)phenyl trifluoromethanesulfonate
128 MHz, $CDCl_3$



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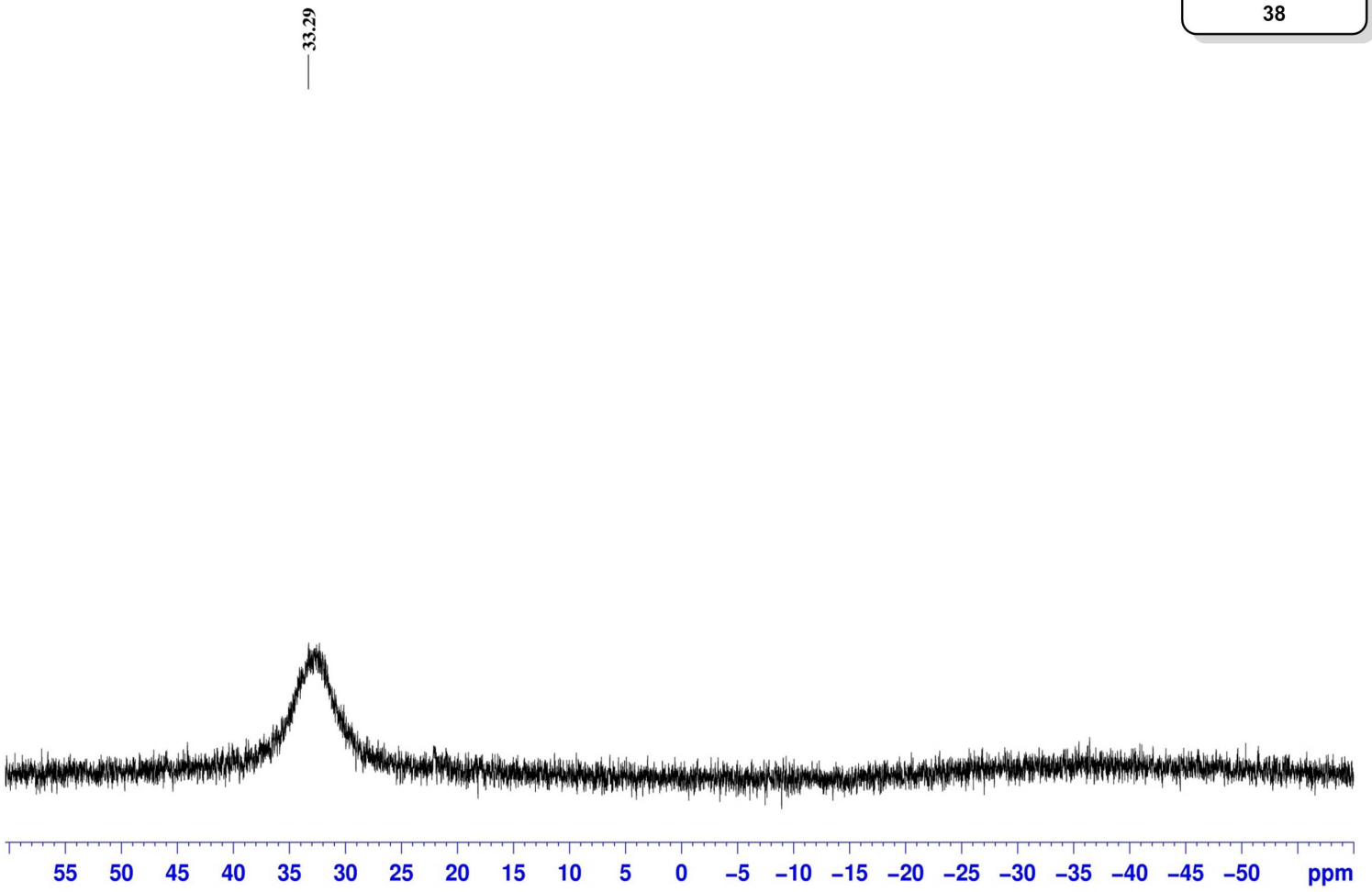
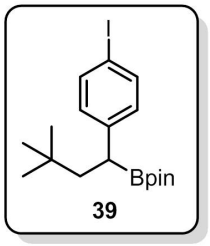
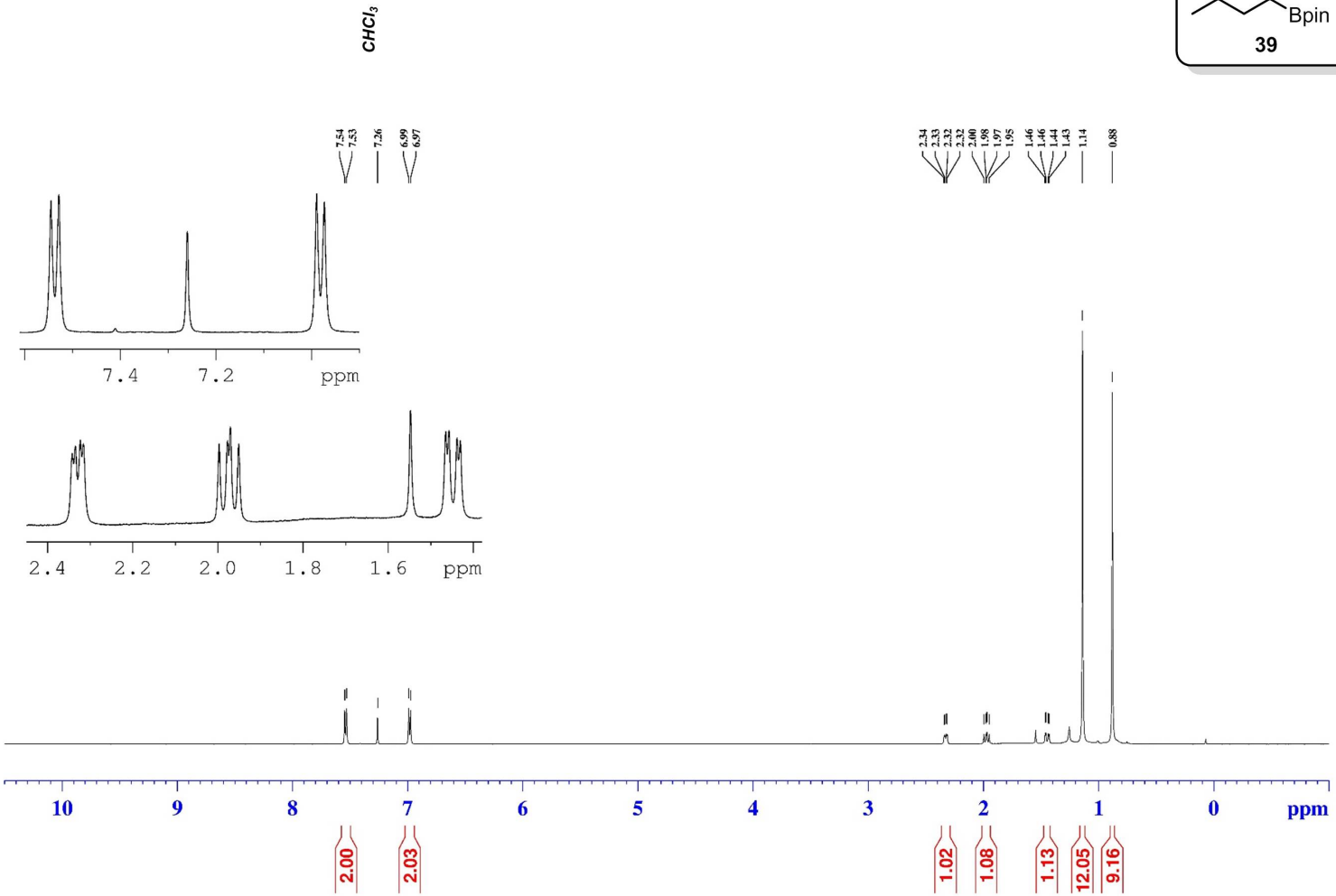


^1H NMR

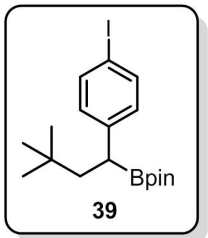
2-(1-(4-iodophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

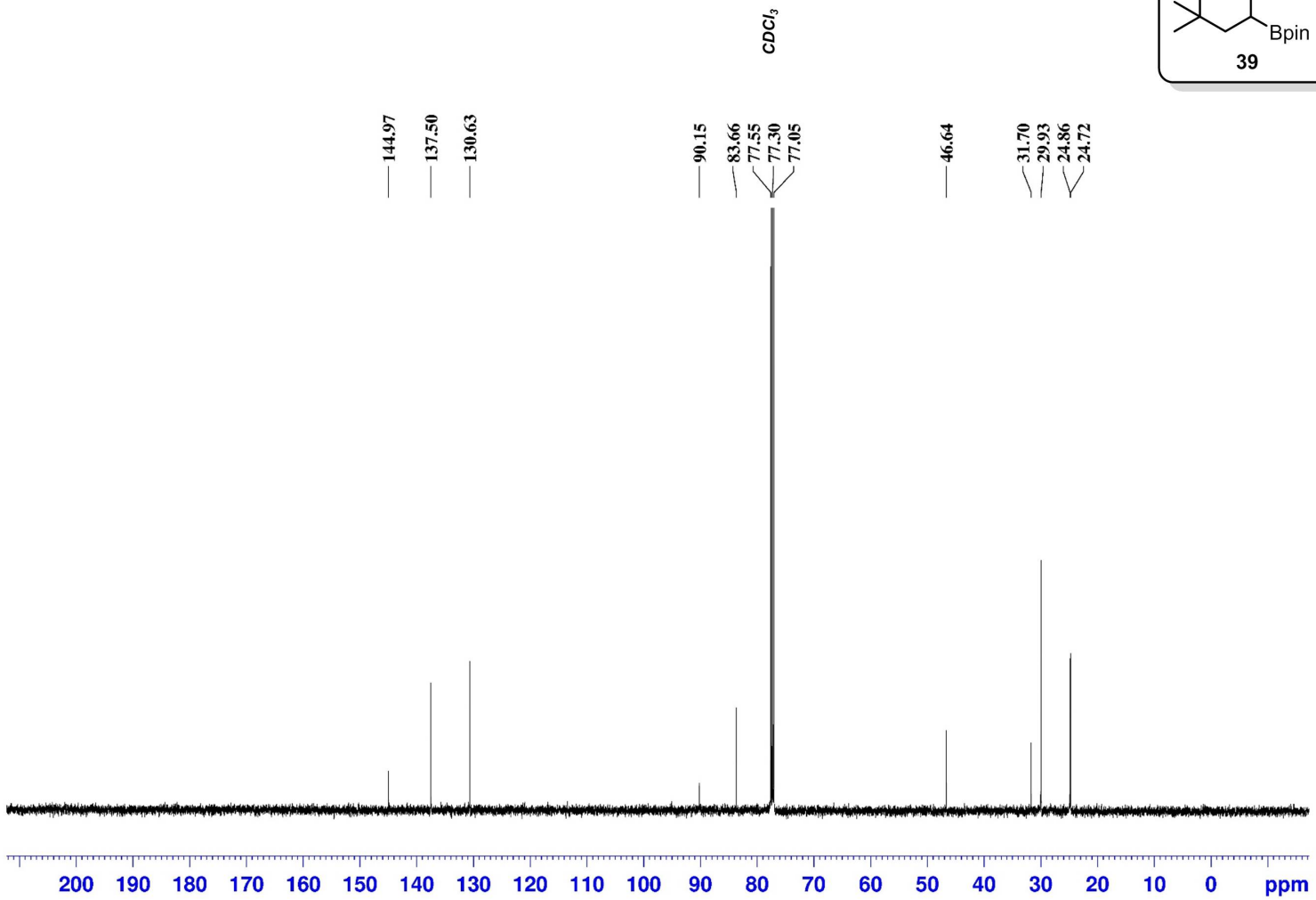




^{13}C NMR

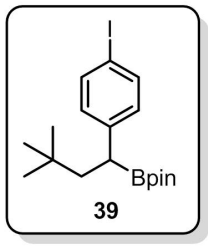
2-(1-(4-iodophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
125 MHz, $CDCl_3$





^{11}B NMR

2-(1-(4-iodophenyl)-3,3-dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
128 MHz, $CDCl_3$



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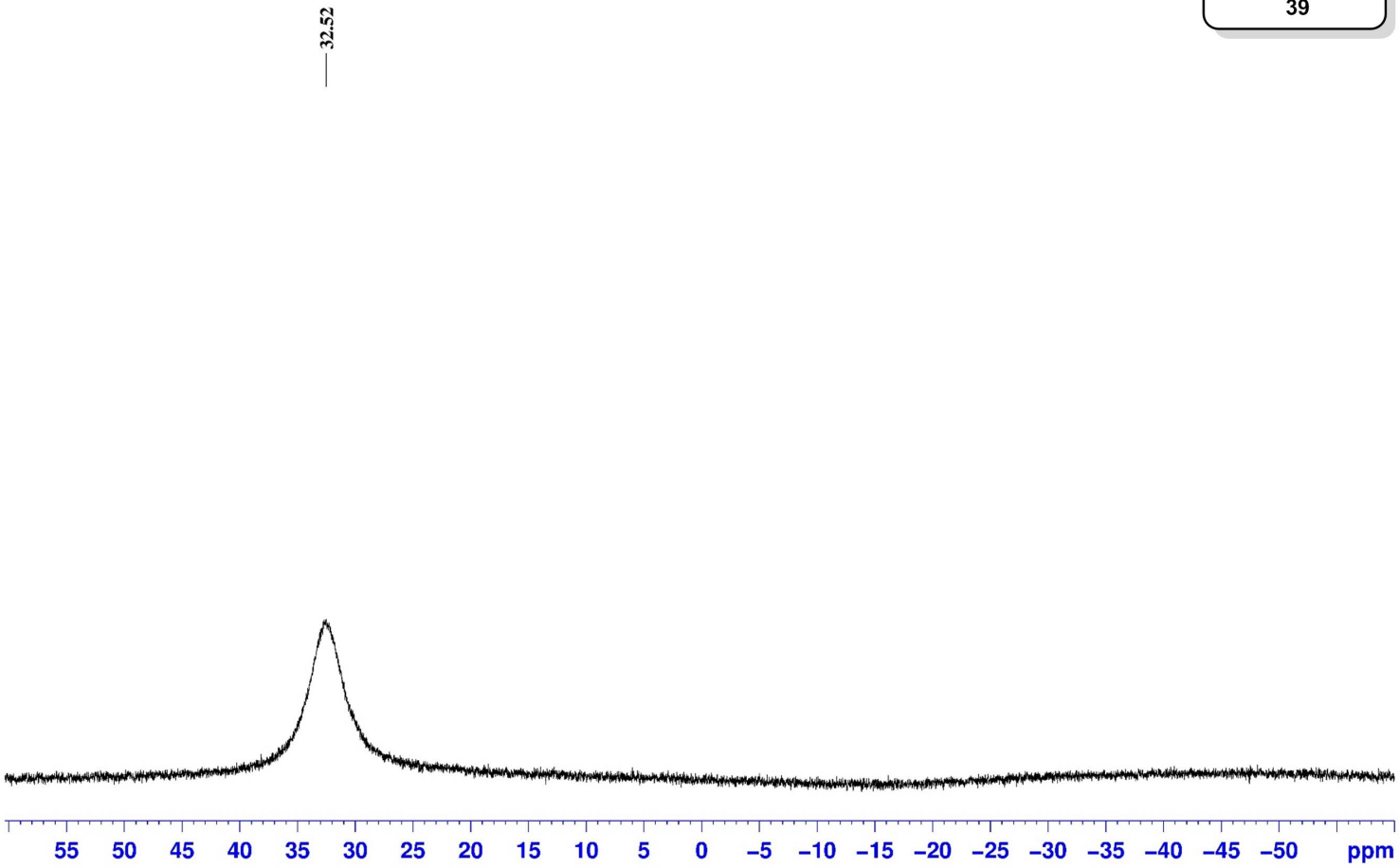
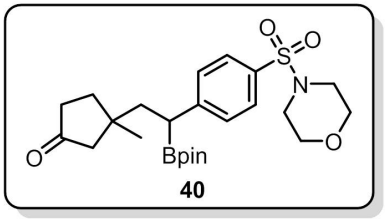
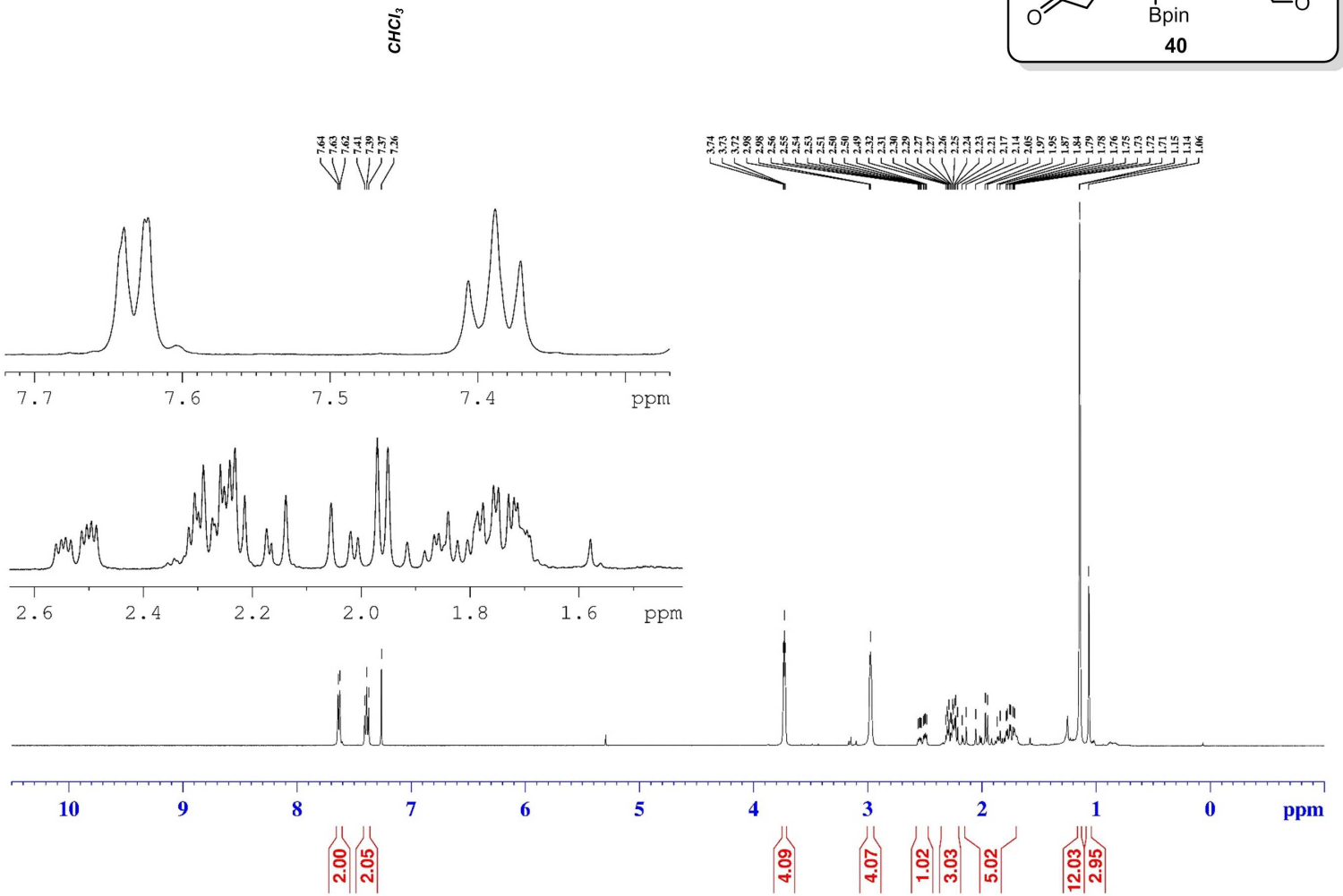


^1H NMR

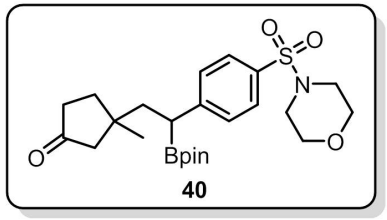
3-methyl-3-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentanone
500 MHz, $CDCl_3$





^{13}C NMR

3-Methyl-3-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentanone
125 MHz, $CDCl_3$



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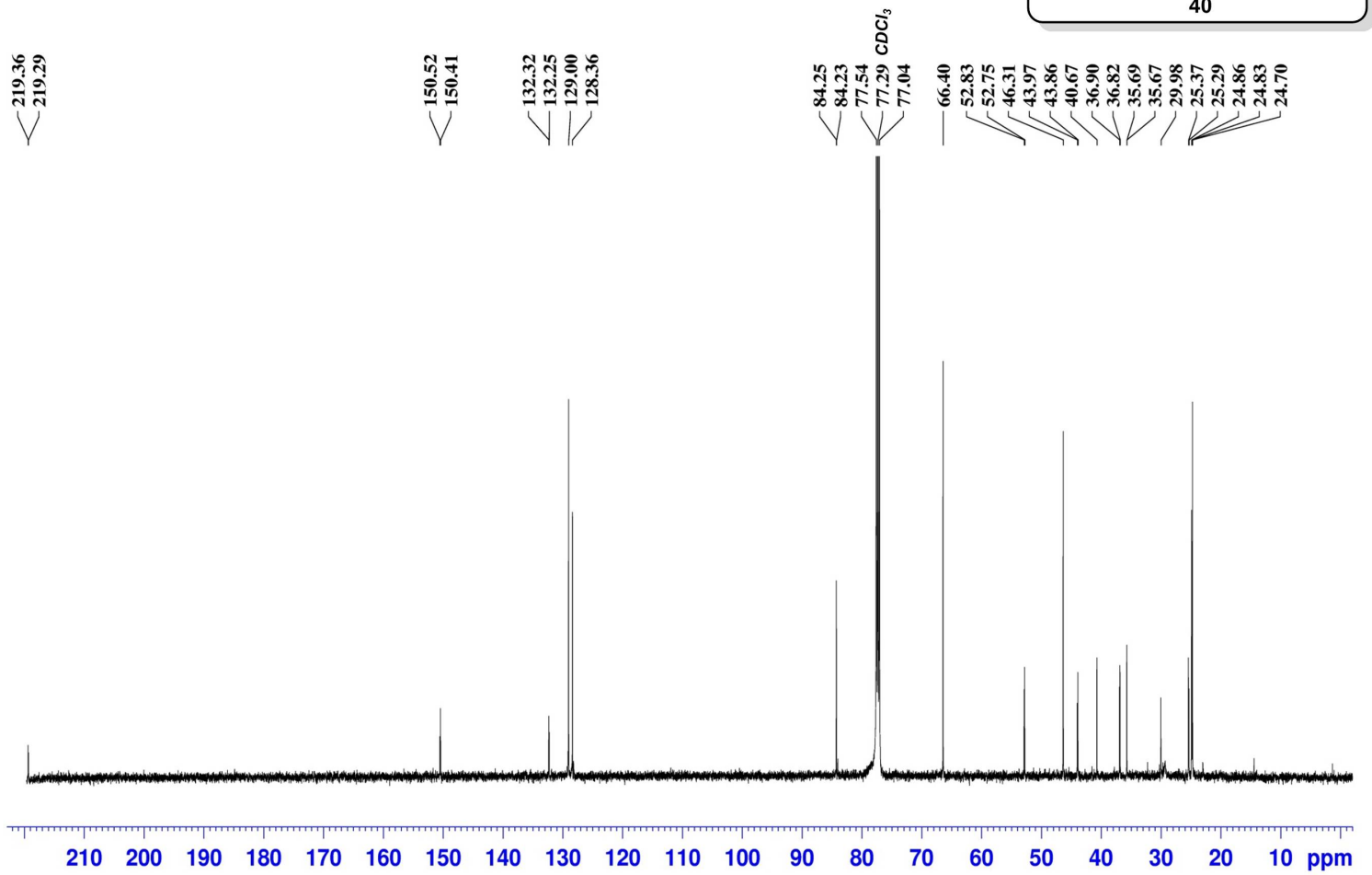
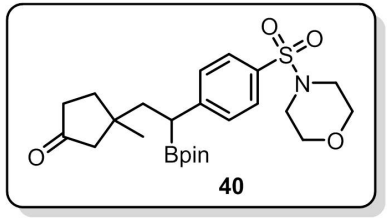


^{11}B NMR

3-methyl-3-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentanone
128 MHz, $CDCl_3$



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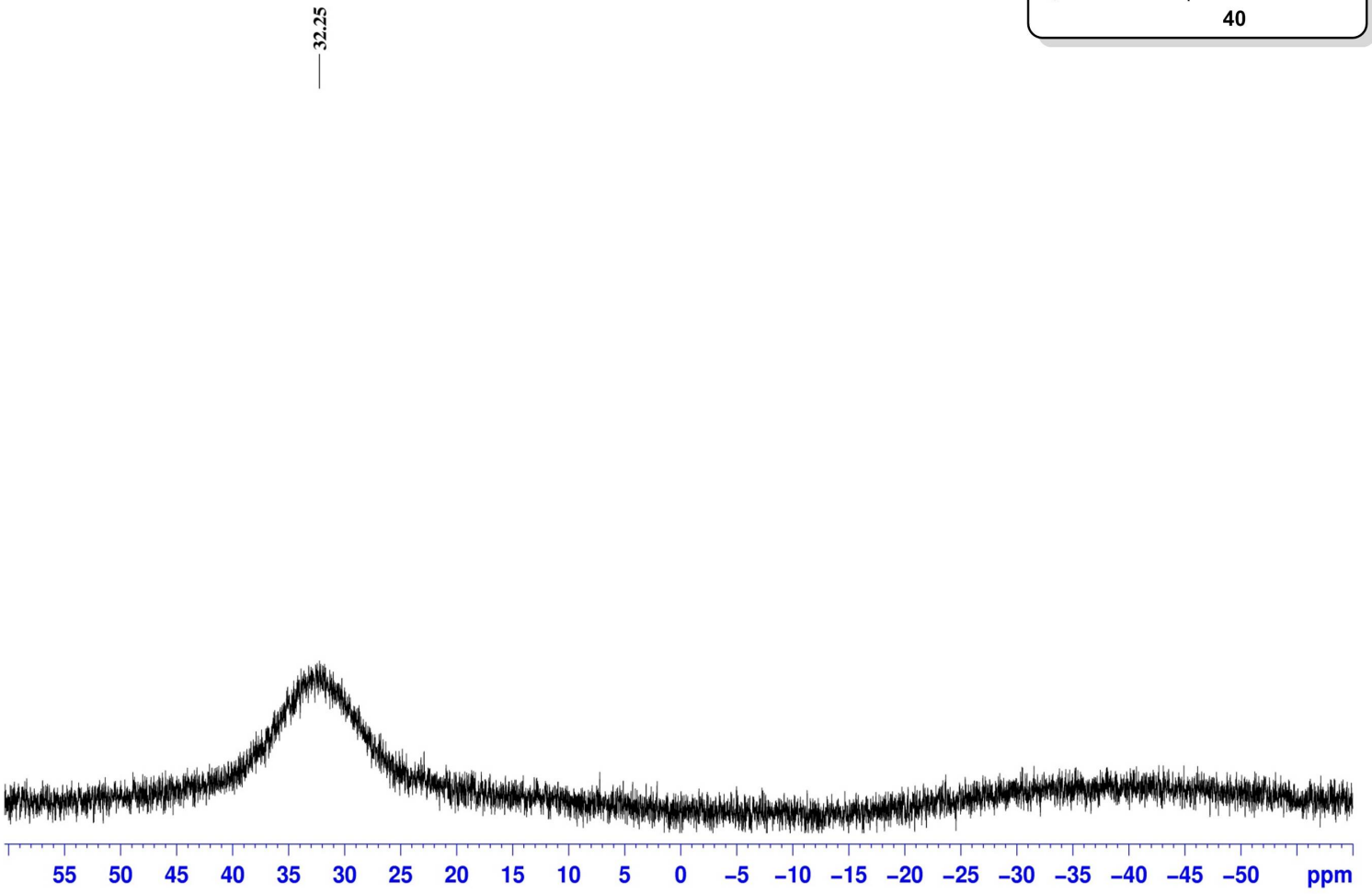
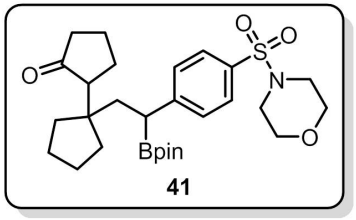
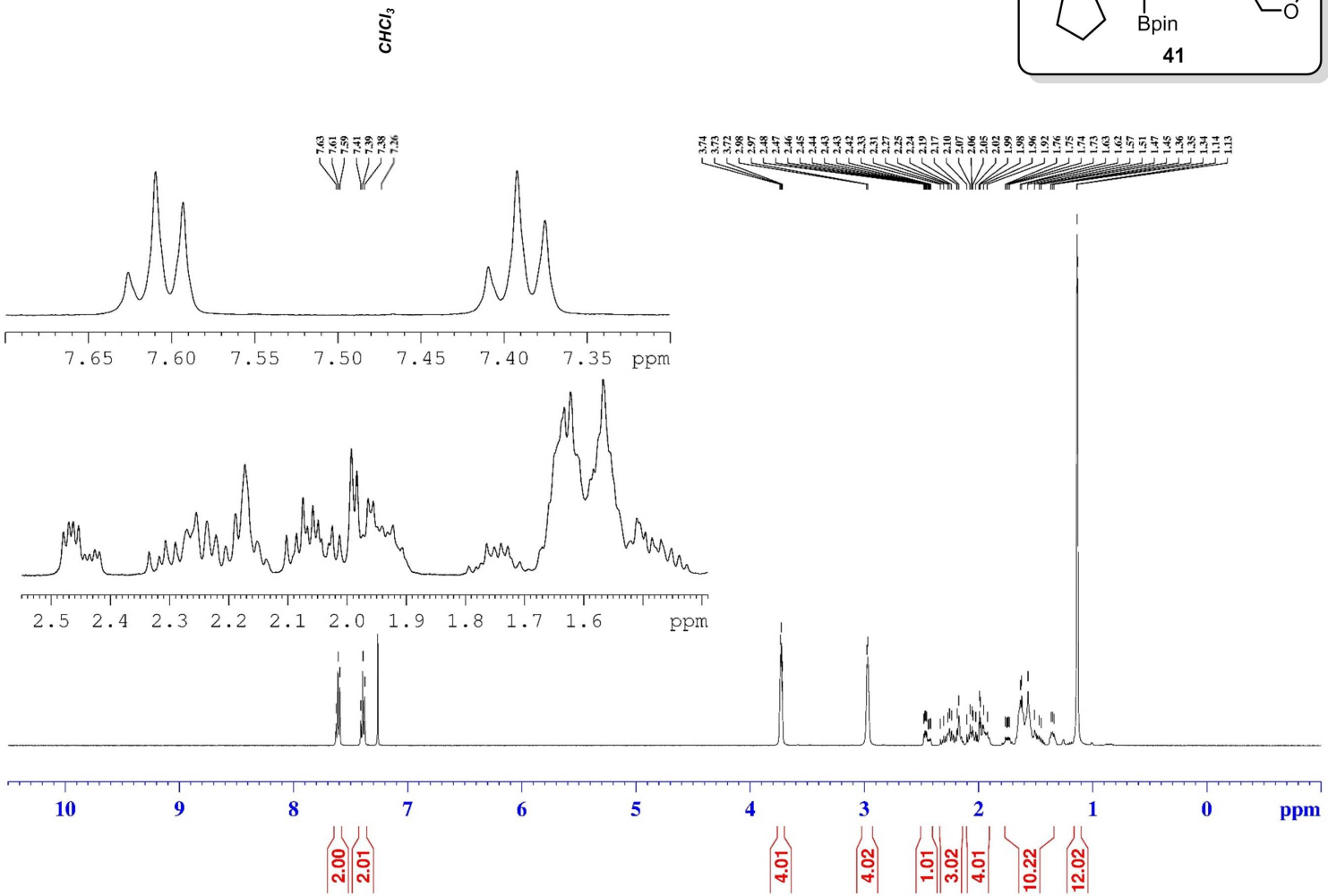


^1H NMR

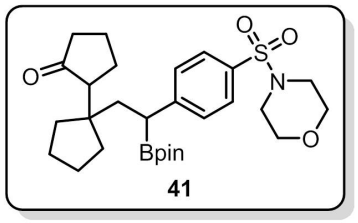
1'-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-[1,1'-bi(cyclopentan)]-2-one
500 MHz, $CDCl_3$





^{13}C NMR

1'-(2-(4-(Morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-[1,1'-bi(cyclopentan)]-2-one
125 MHz, $CDCl_3$



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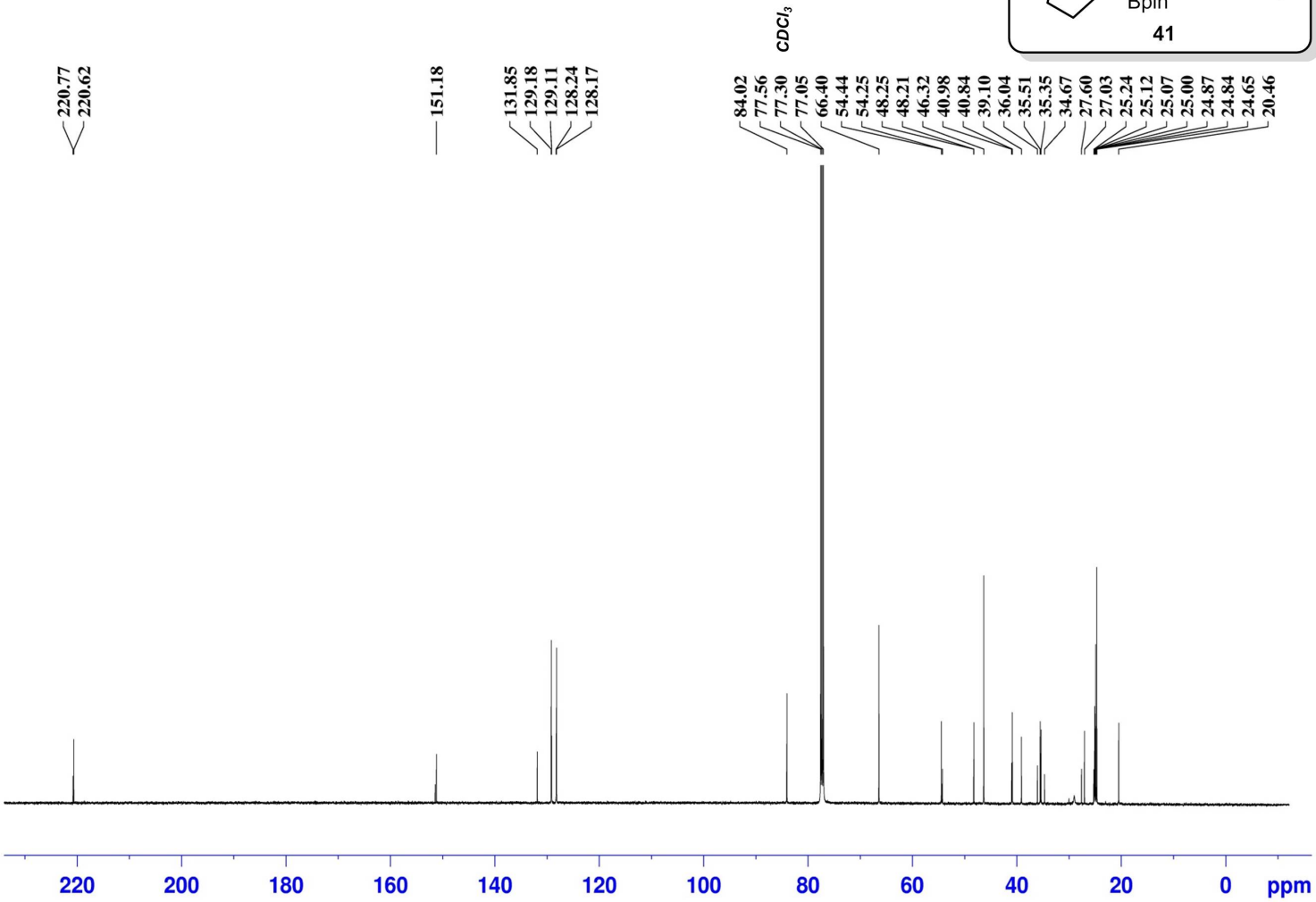
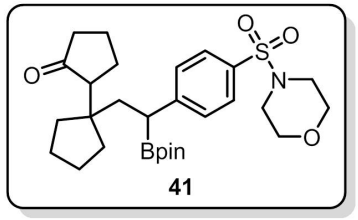


^{11}B NMR

1'-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-[1,1'-bi(cyclopentan)]-2-one
128 MHz, $CDCl_3$



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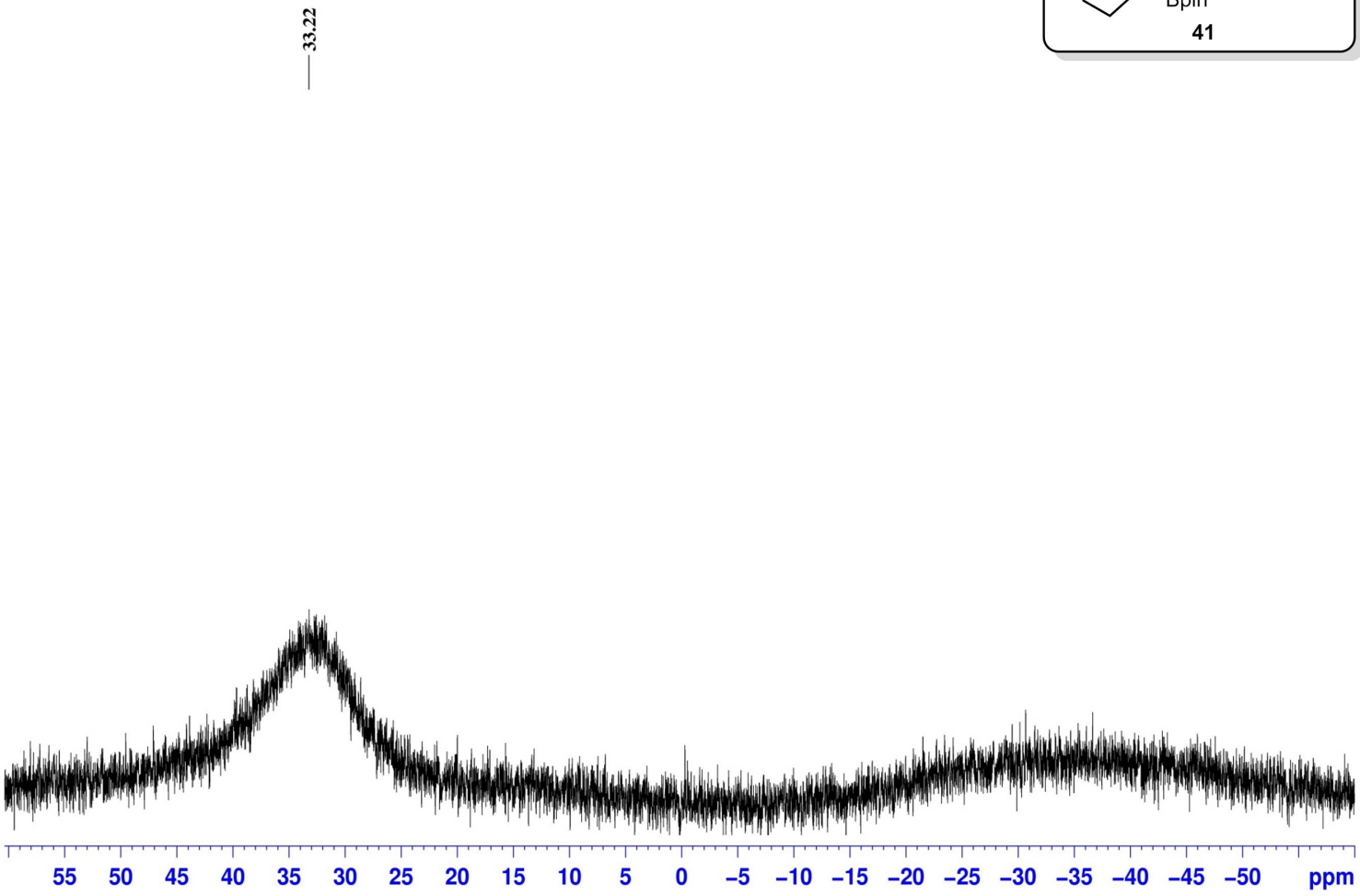
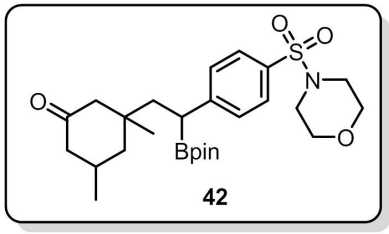
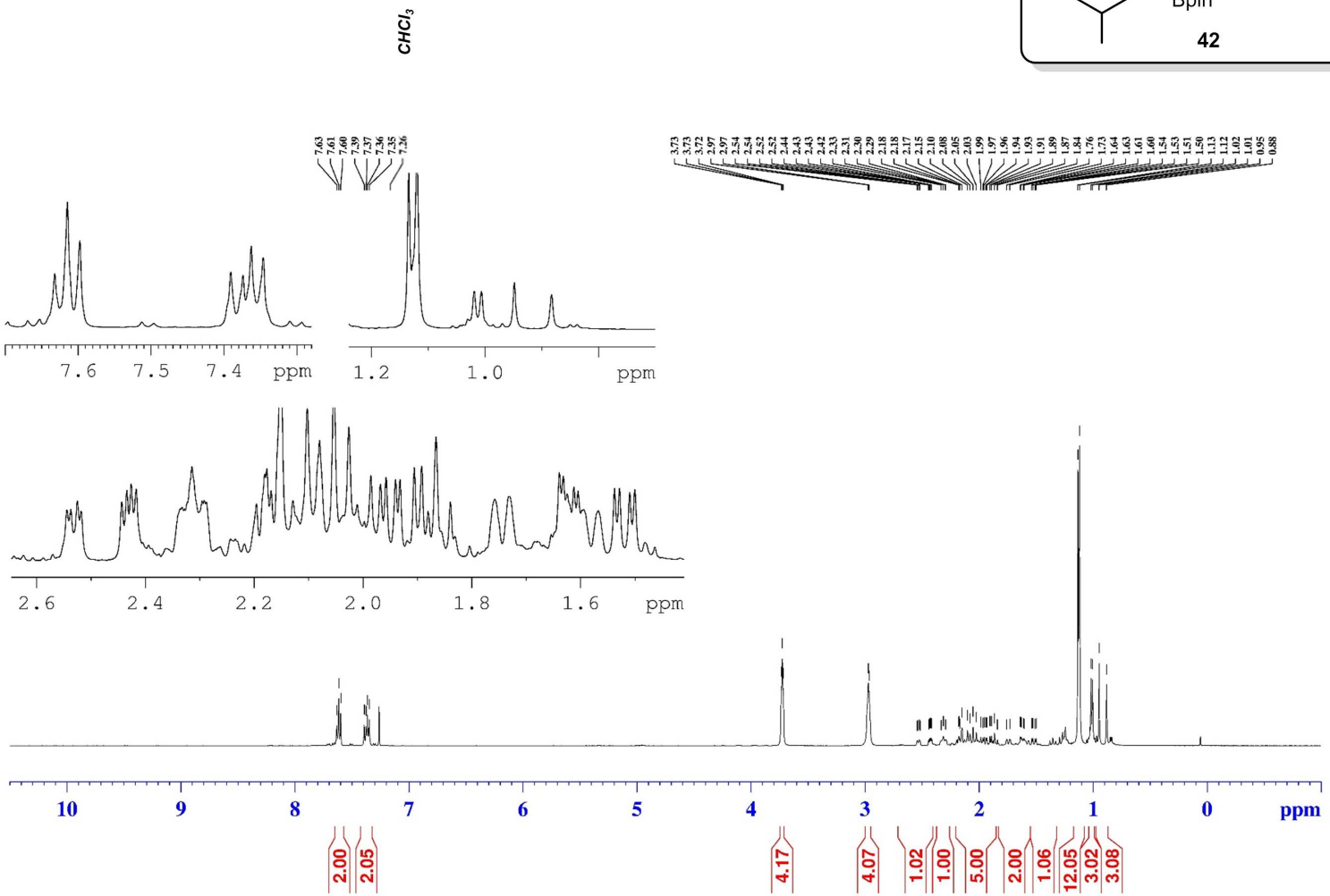


^1H NMR

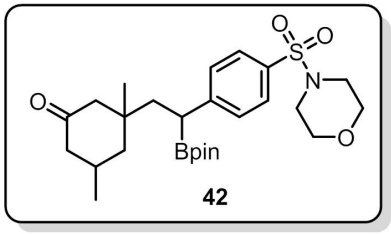
3,5-dimethyl-3-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclohexanone
500 MHz, $CDCl_3$





^{13}C NMR

3,5-Dimethyl-3-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclohexanone
125 MHz, $CDCl_3$



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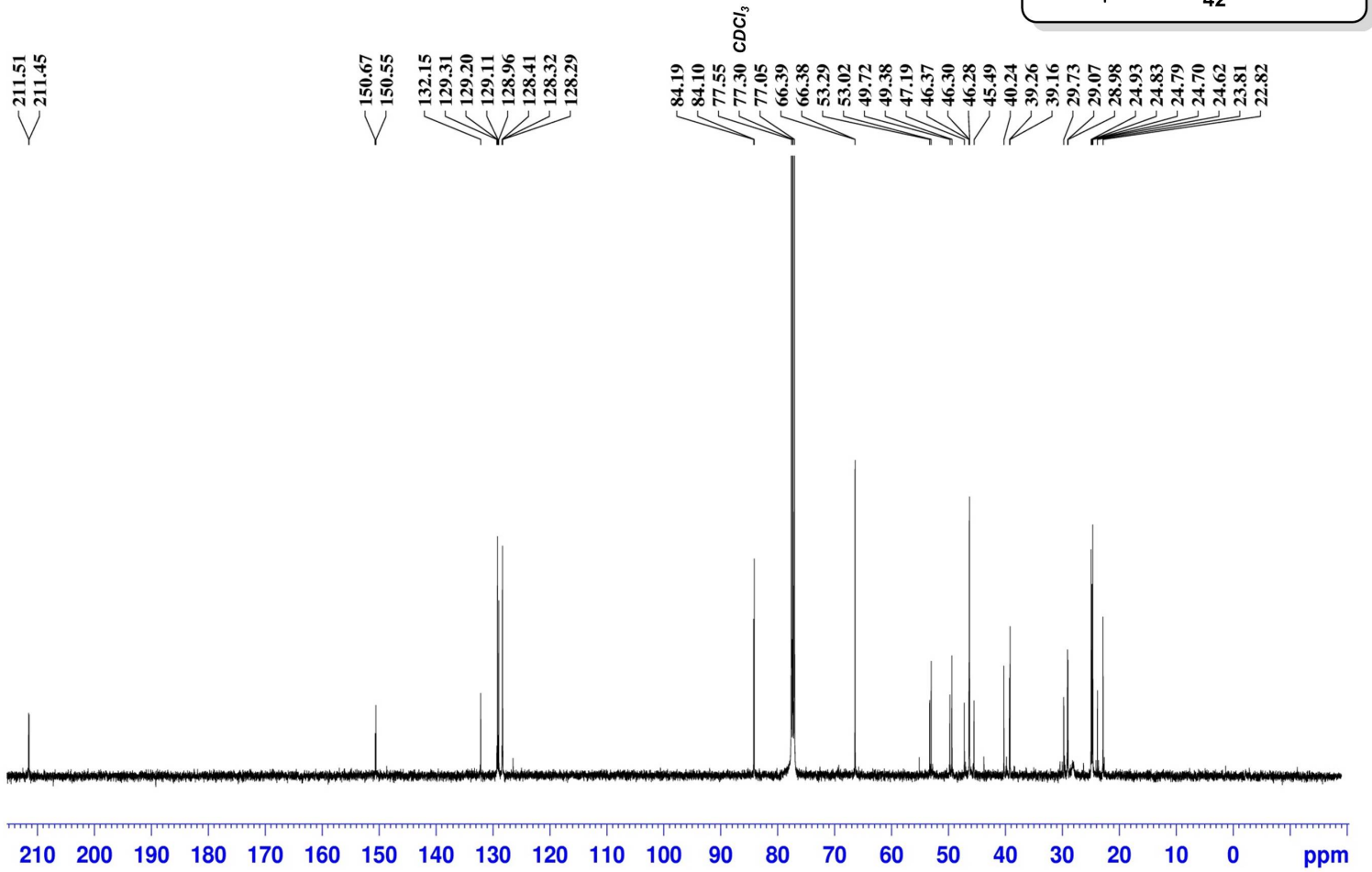
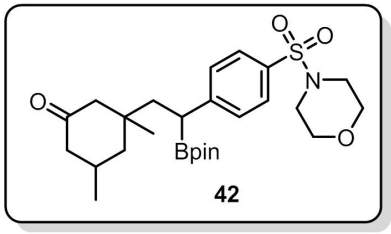


^{11}B NMR

3,5-dimethyl-3-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclohexanone
128 MHz, $CDCl_3$



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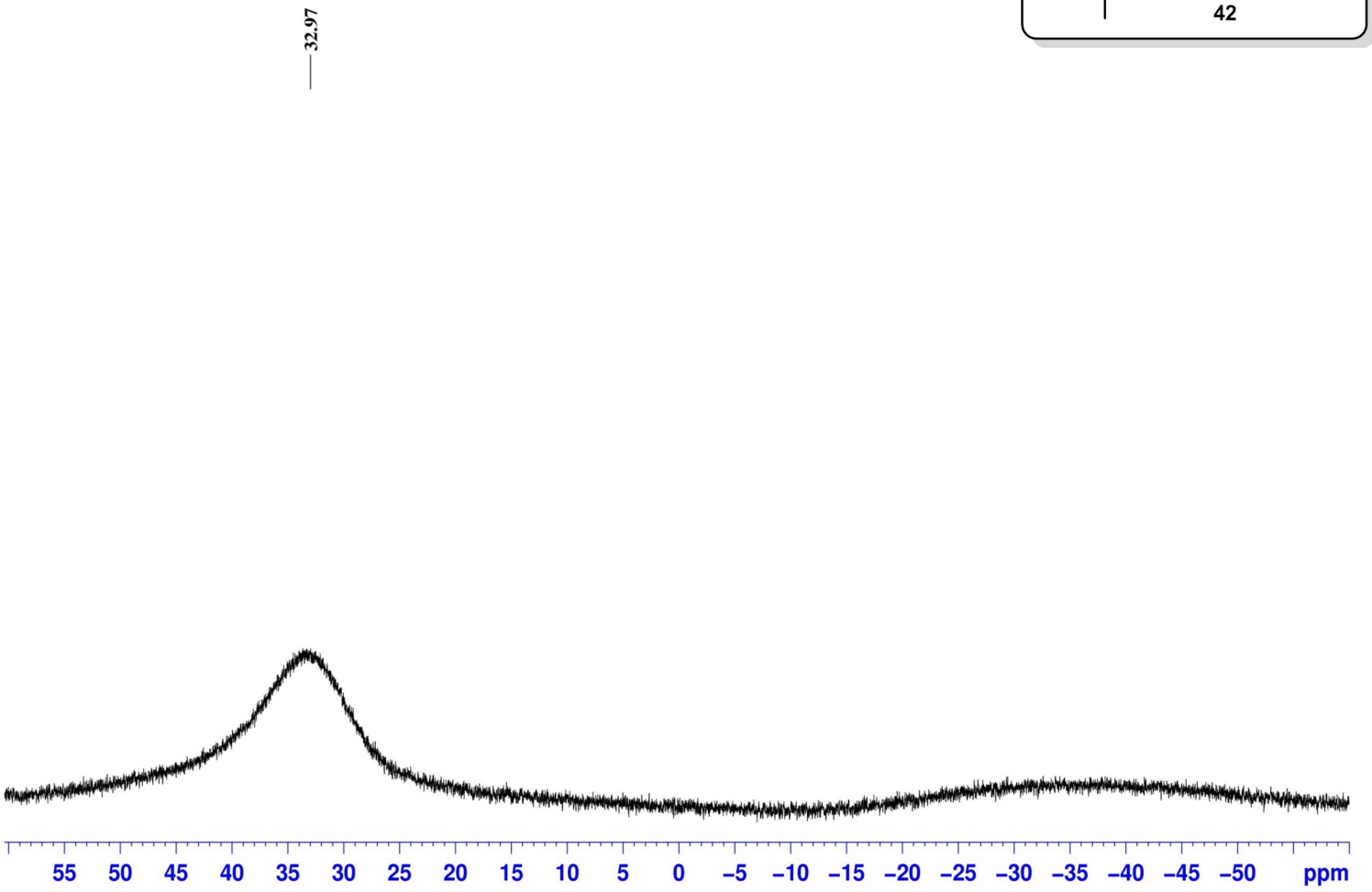
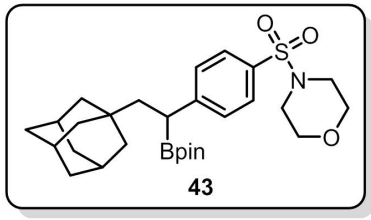


^1H NMR

4-((4-(2-((3r,5r,7r)-adamantan-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine
500 MHz, $CDCl_3$



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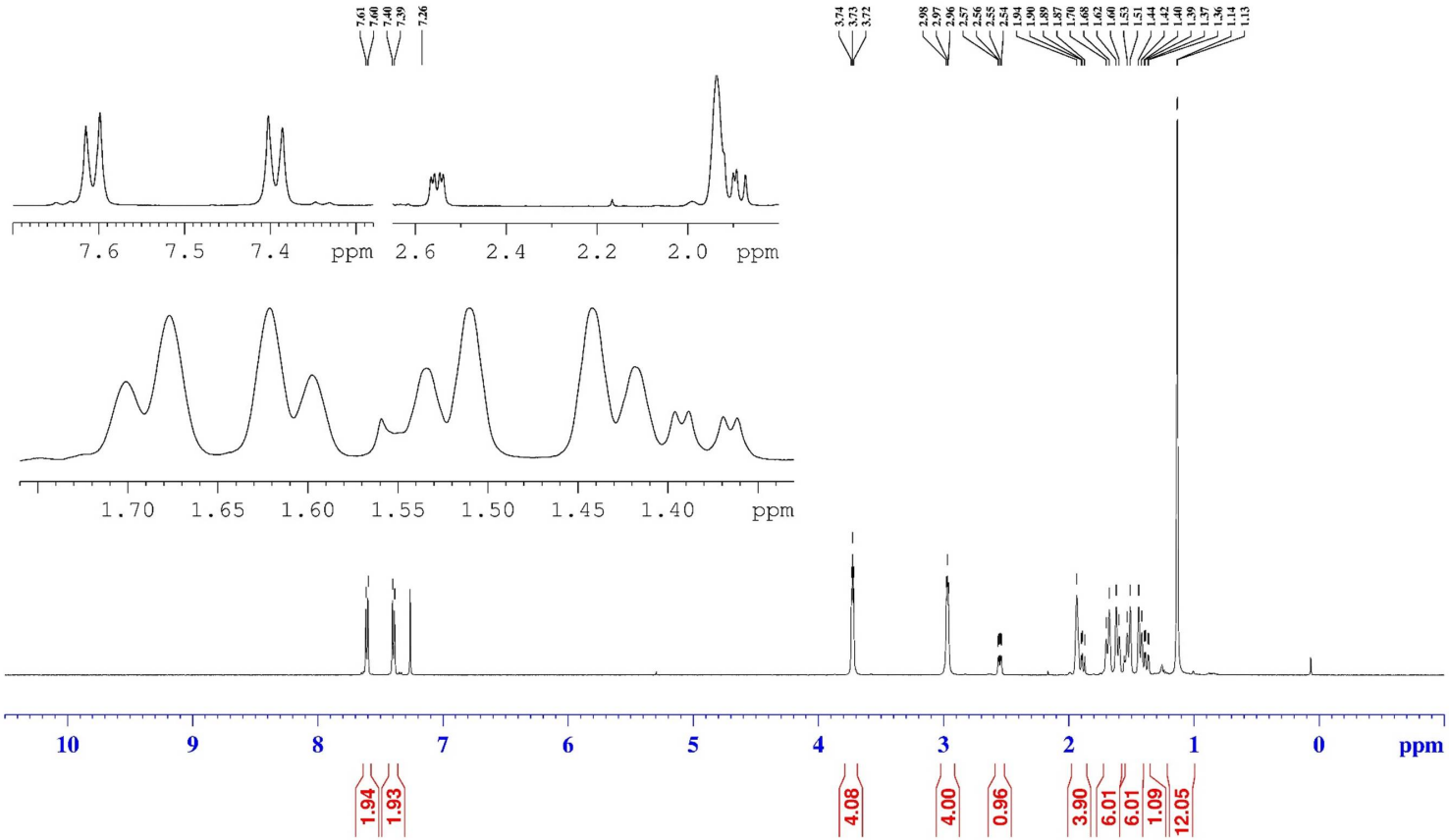
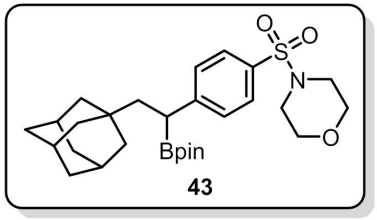


^{13}C NMR

4-((4-(2-Adamantan-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine
125 MHz, $CDCl_3$



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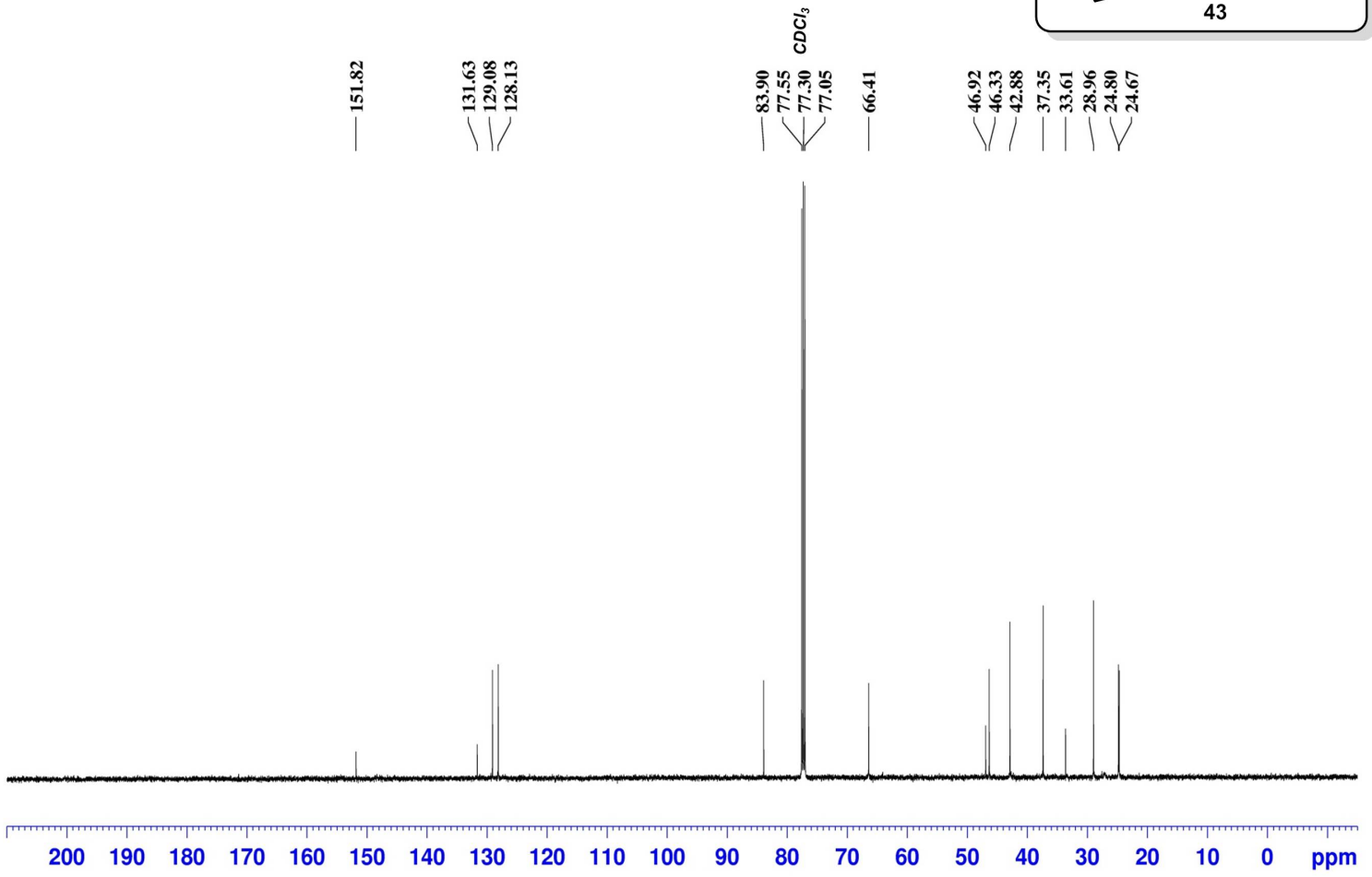
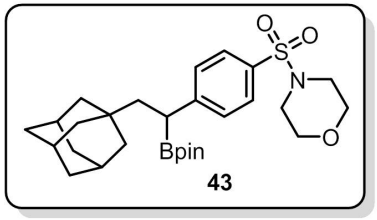


^{11}B NMR

4-((4-(2-((3r,5r,7r)-adamantan-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine
128 MHz, $CDCl_3$



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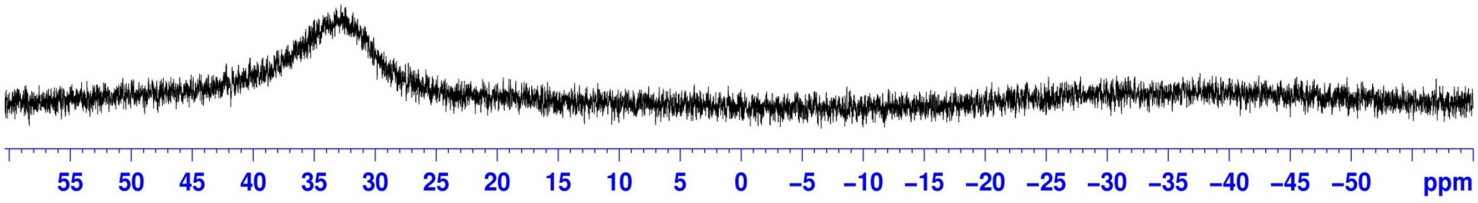
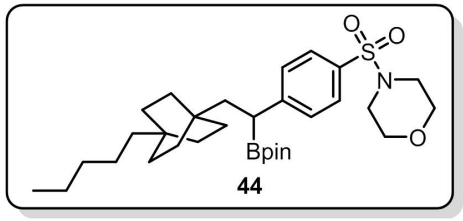
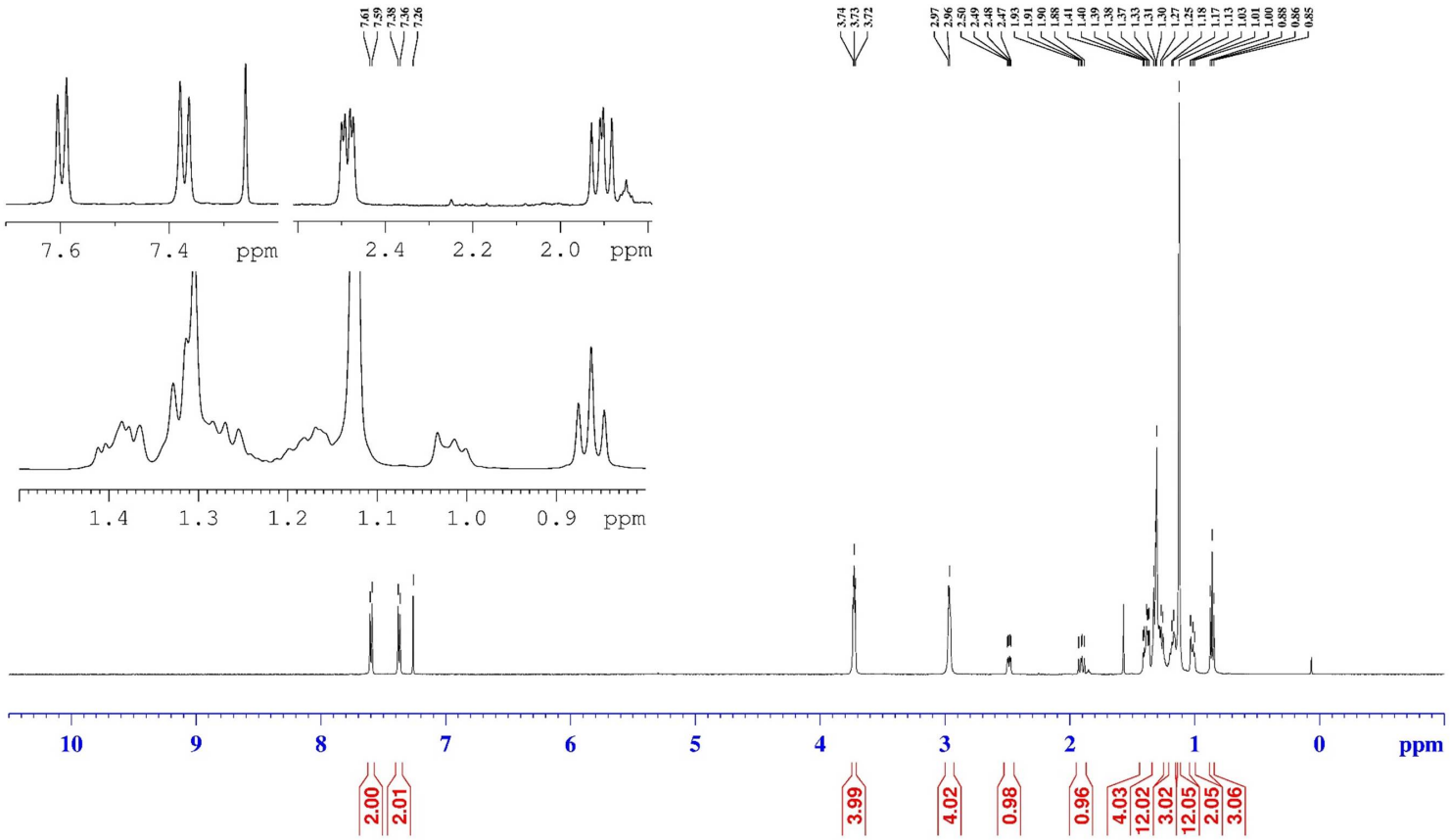


^1H NMR

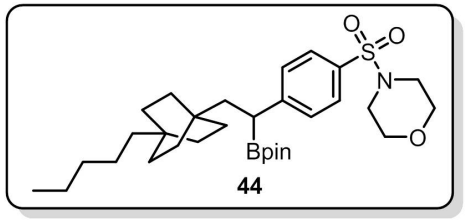
4-((4-(2-(4-pentylbicyclo[2.2.2]octan-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine
500 MHz, $CDCl_3$





^{13}C NMR

4-((4-(2-(4-Pentylbicyclo[2.2.2]octan-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine
125 MHz, $CDCl_3$



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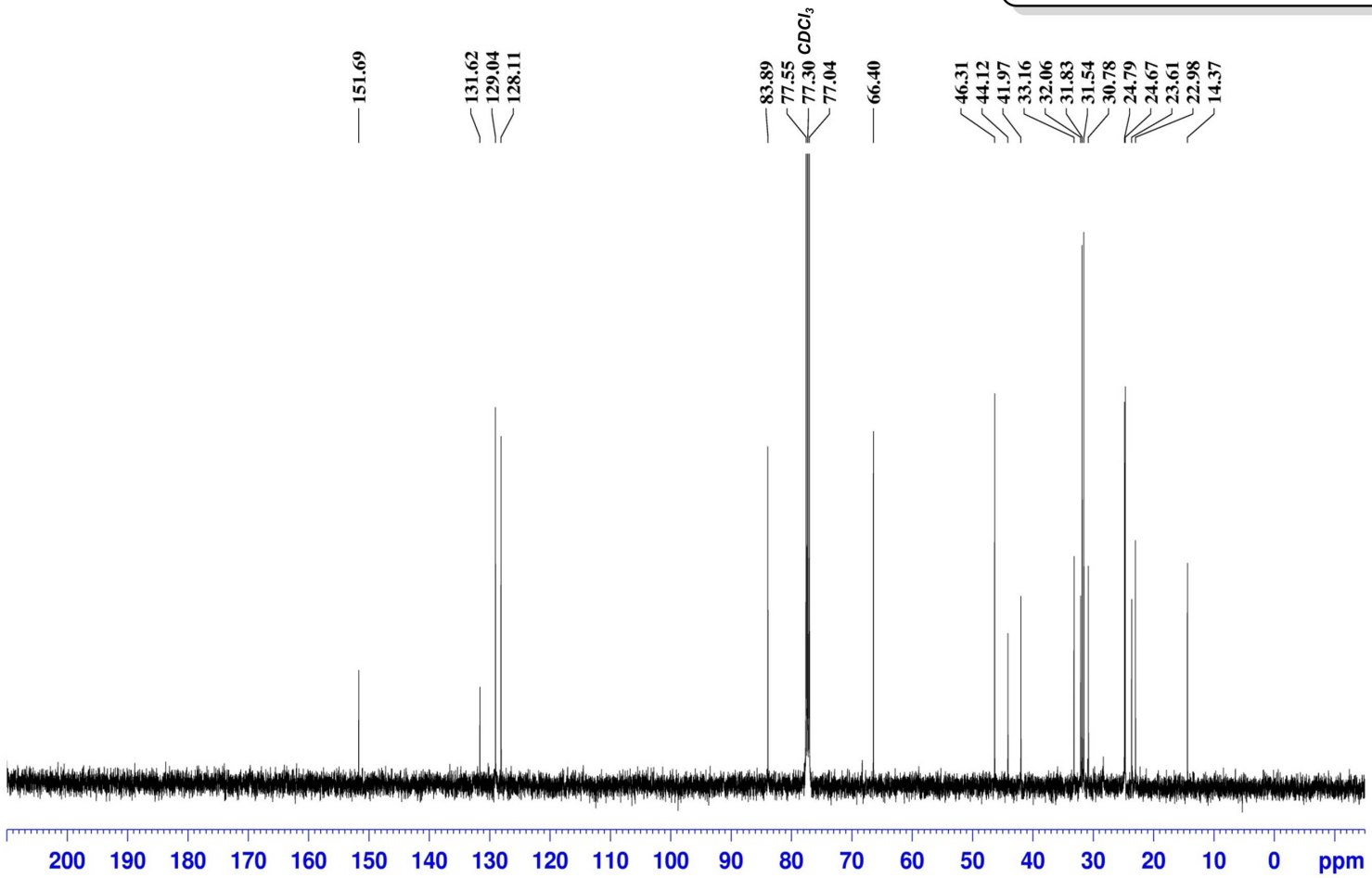
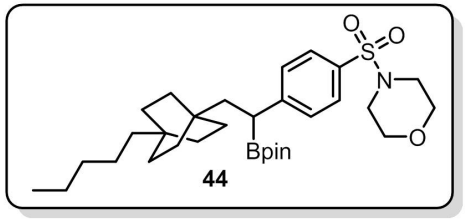


^{11}B NMR

4-((4-(2-(4-pentylbicyclo[2.2.2]octan-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine
128 MHz, $CDCl_3$



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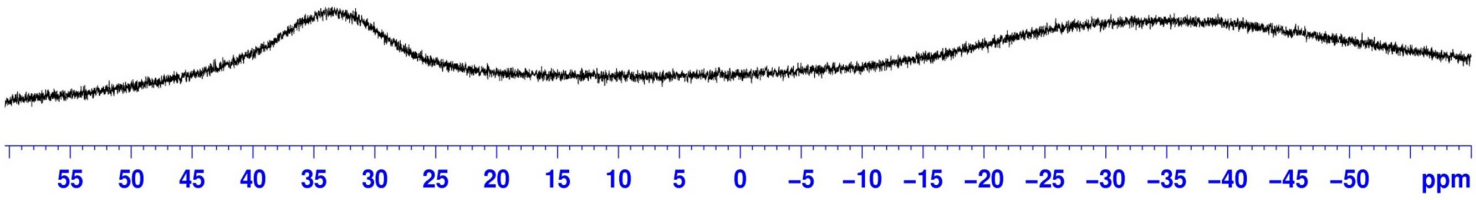
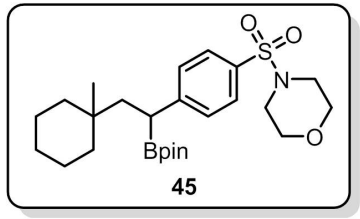
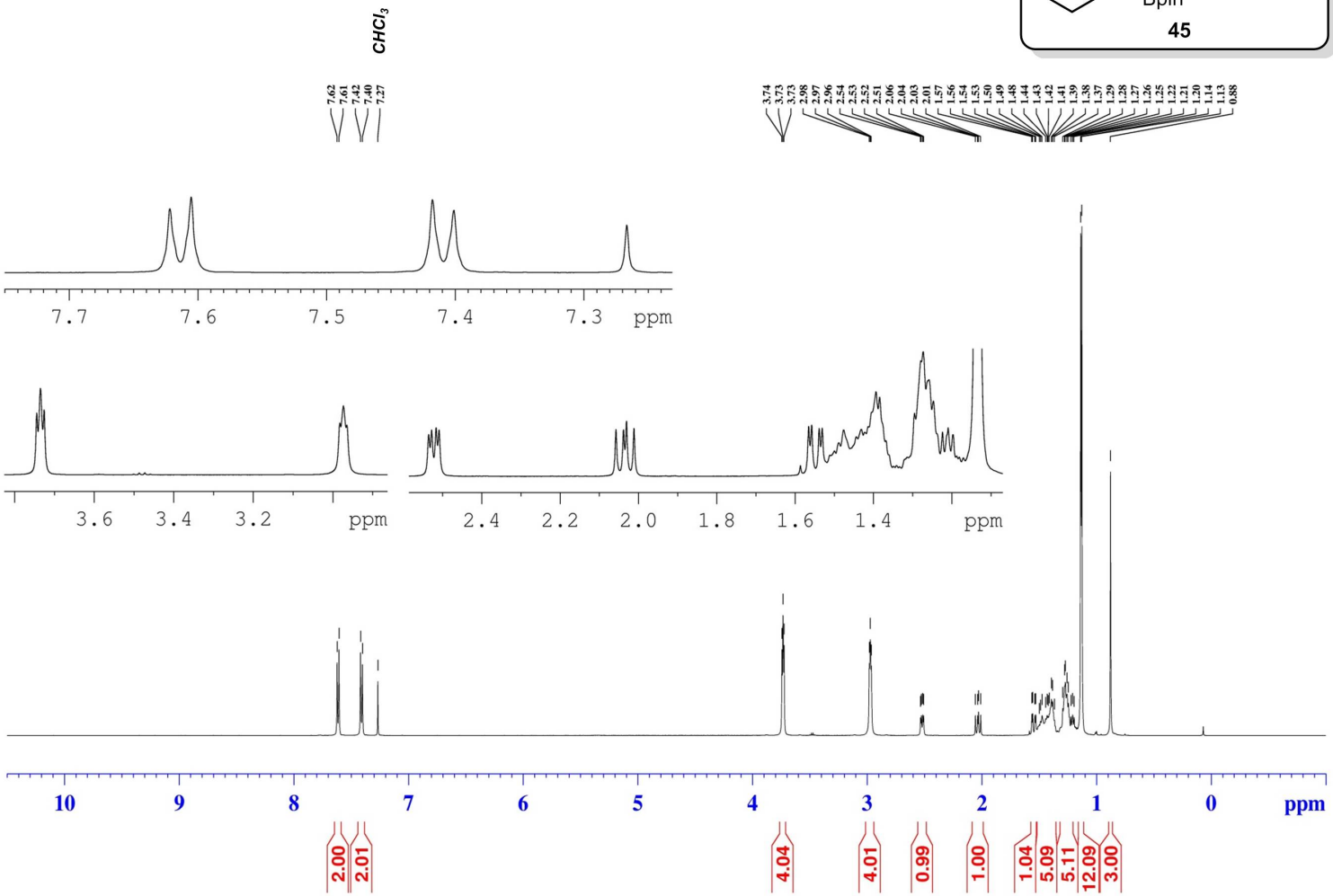


^1H NMR

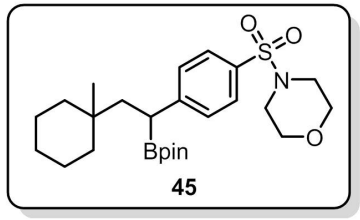
4-((4-(2-(1-methylcyclohexyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine
500 MHz, $CDCl_3$





^{13}C NMR

4-((4-(2-(1-Methylcyclohexyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine
125 MHz, $CDCl_3$



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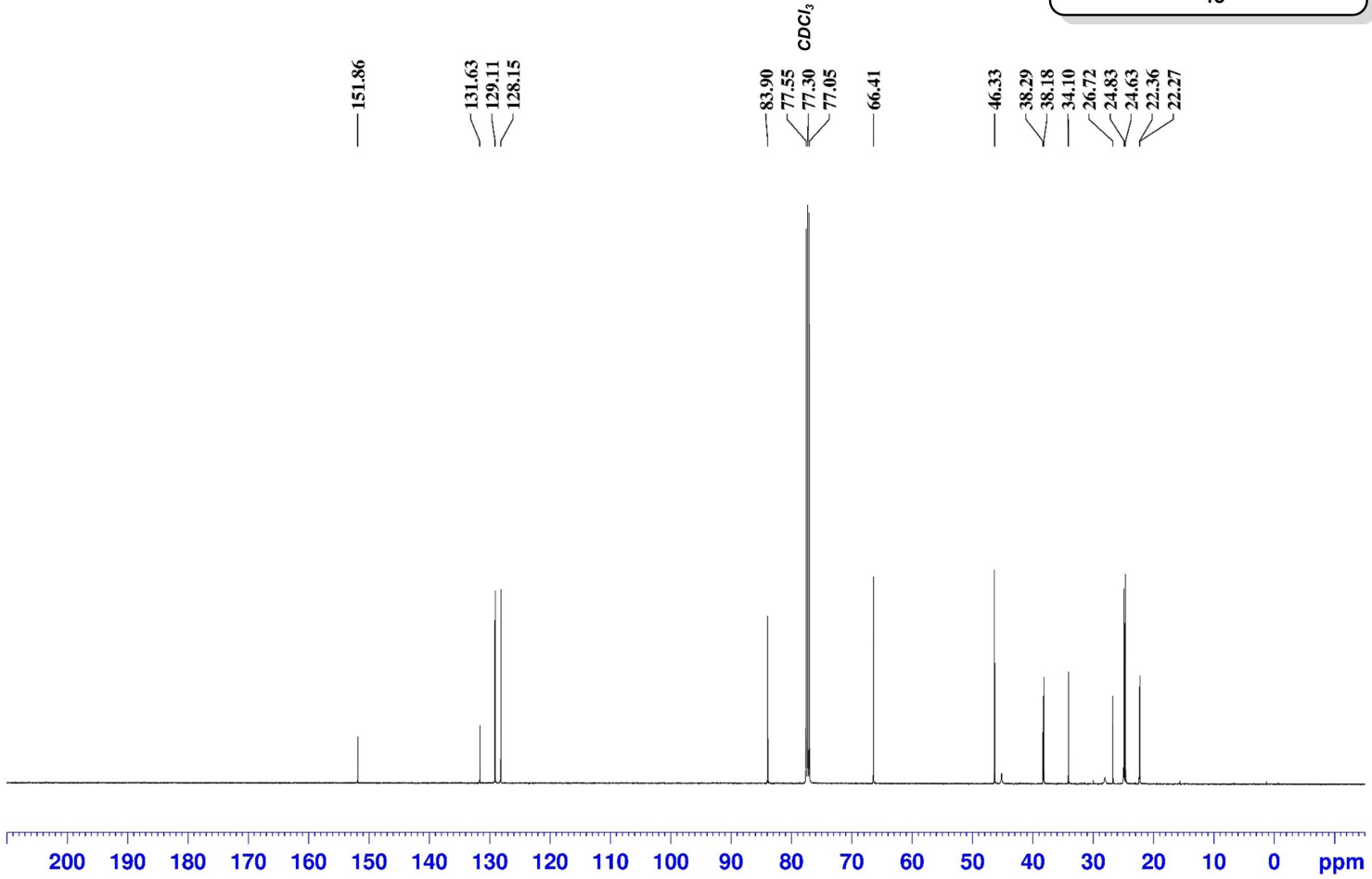
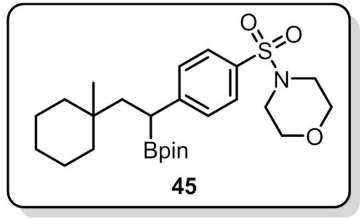


^{11}B NMR

4-((4-(2-(1-methylcyclohexyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine
128 MHz, $CDCl_3$



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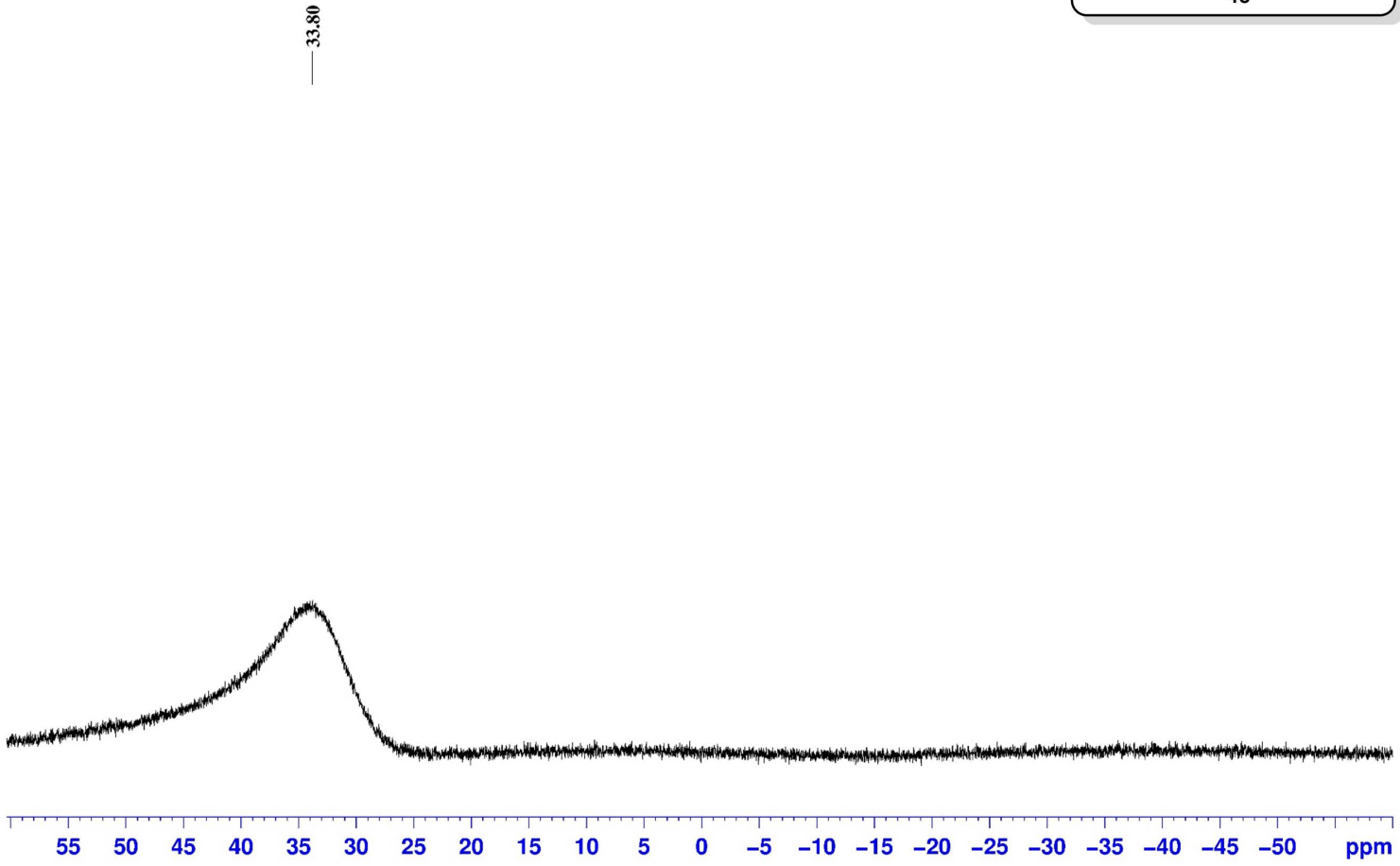
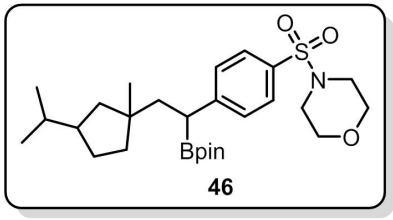


^1H NMR

4-((4-(2-((3*R*)-3-isopropyl-1-methylcyclopentyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine
500 MHz, $CDCl_3$



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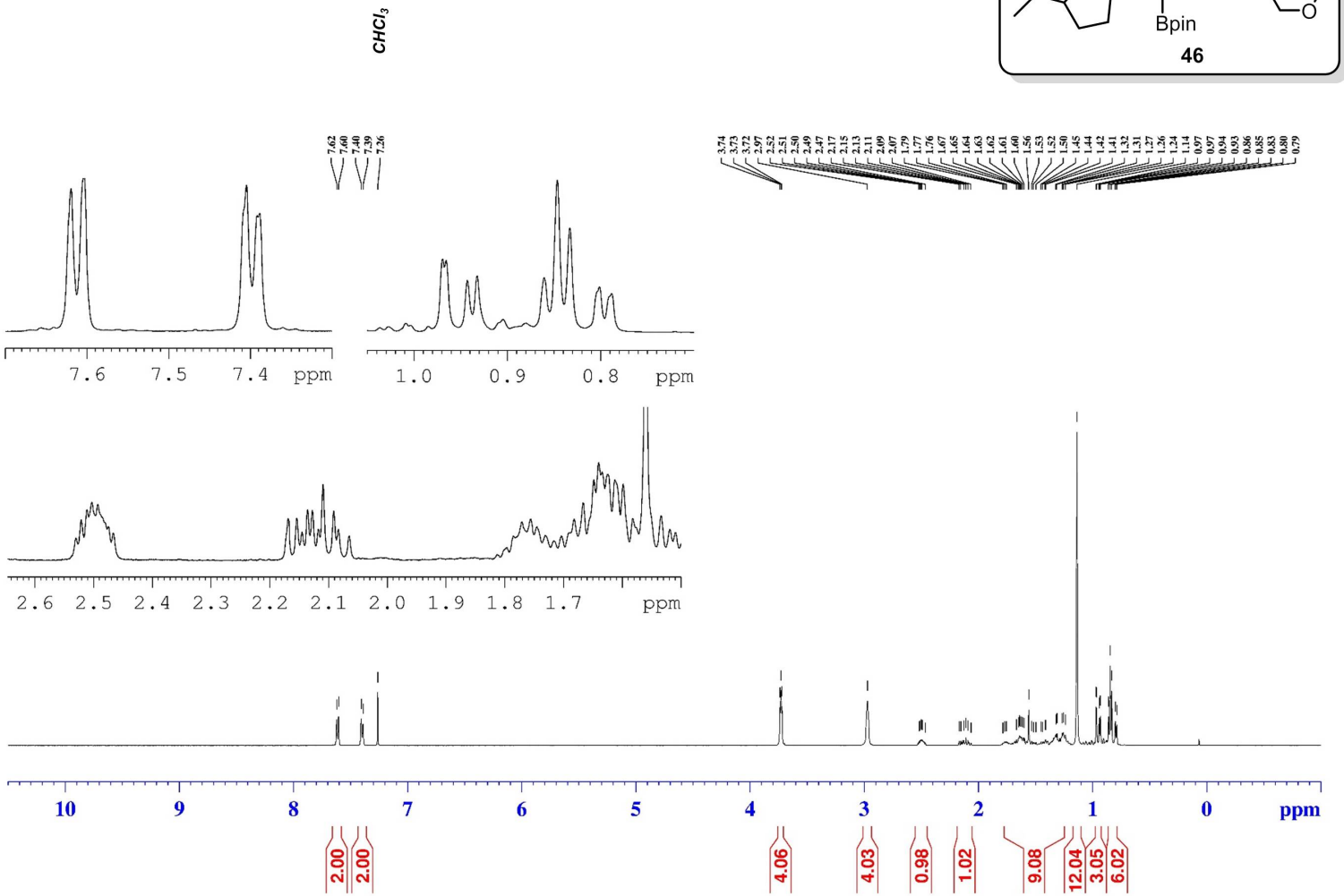
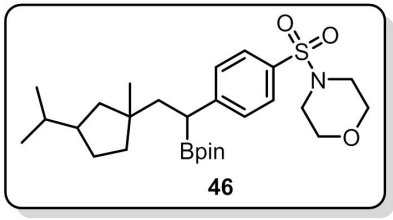
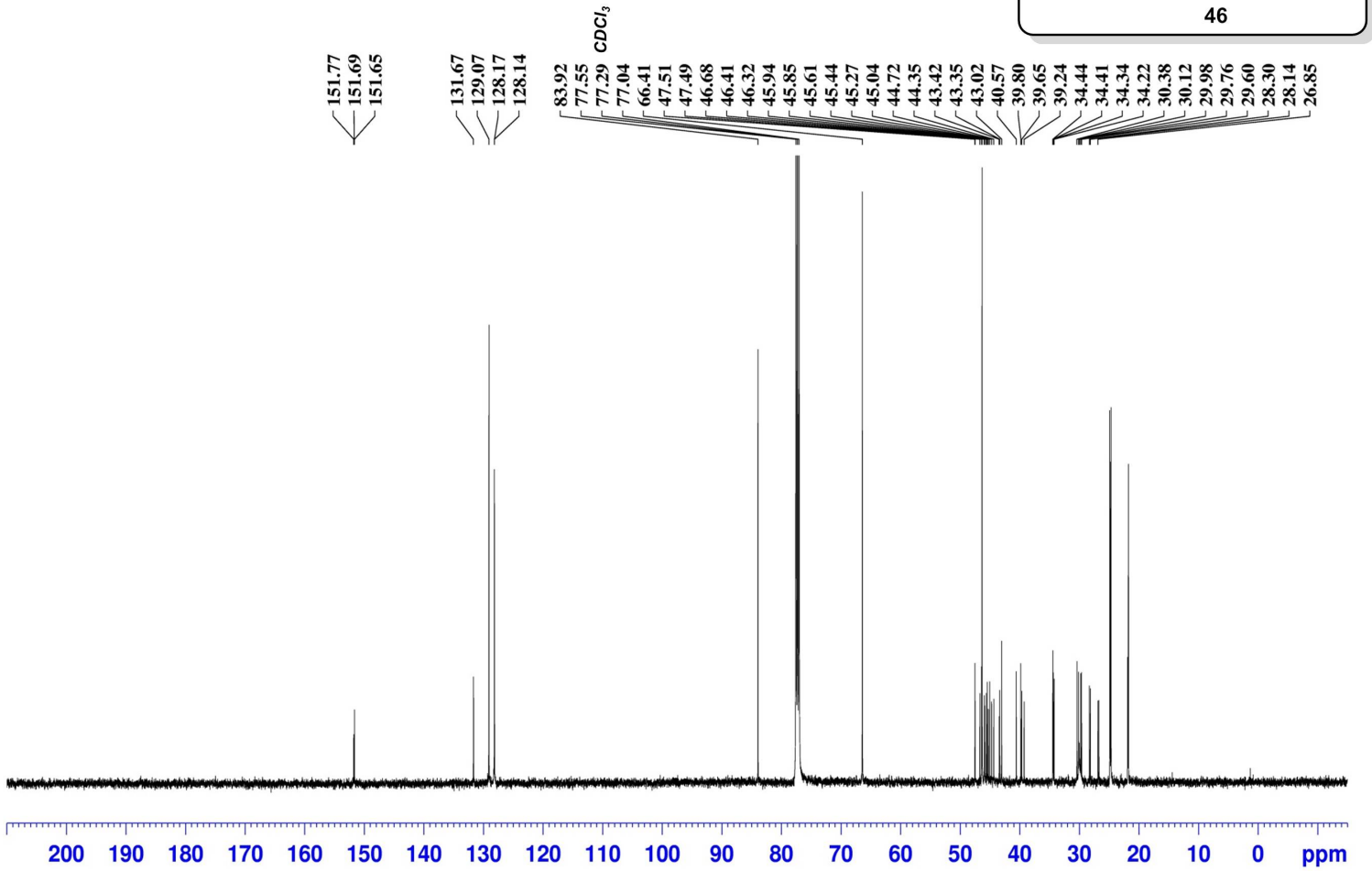


^{13}C NMR

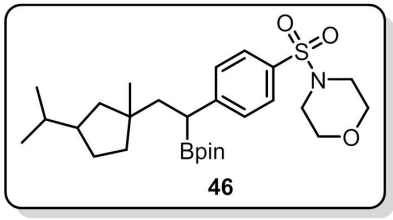
4-((4-(2-(-3-Isopropyl-1-methylcyclopentyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine
125 MHz, $CDCl_3$





^{11}B NMR

4-((4-(2-((3*R*)-3-isopropyl-1-methylcyclopentyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)morpholine
128 MHz, $CDCl_3$



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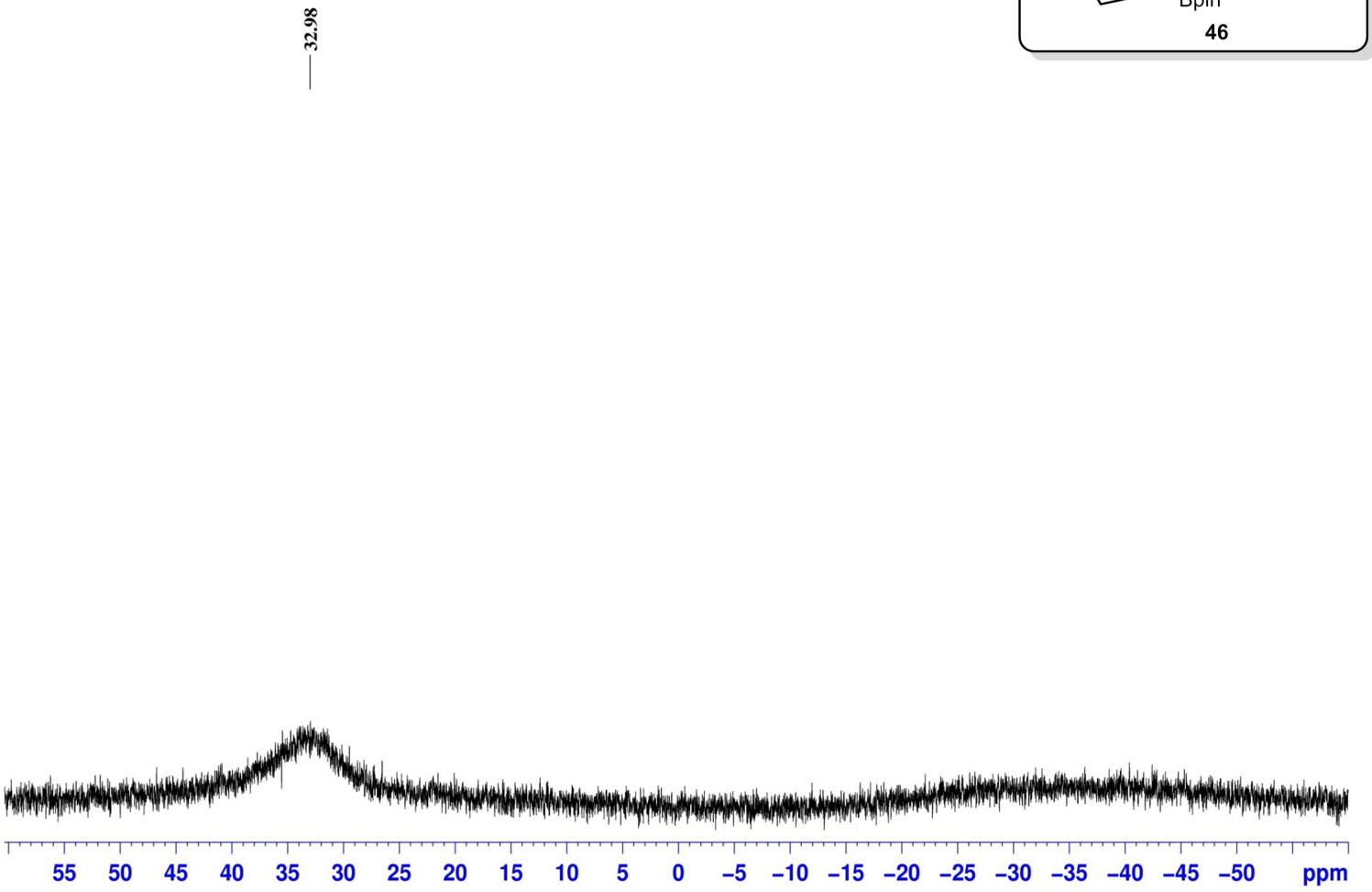
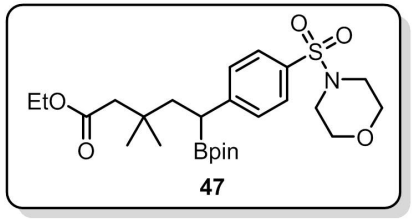


^1H NMR

ethyl 3,3-dimethyl-5-(4-(morpholinosulfonyl)phenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate
500 MHz, $CDCl_3$



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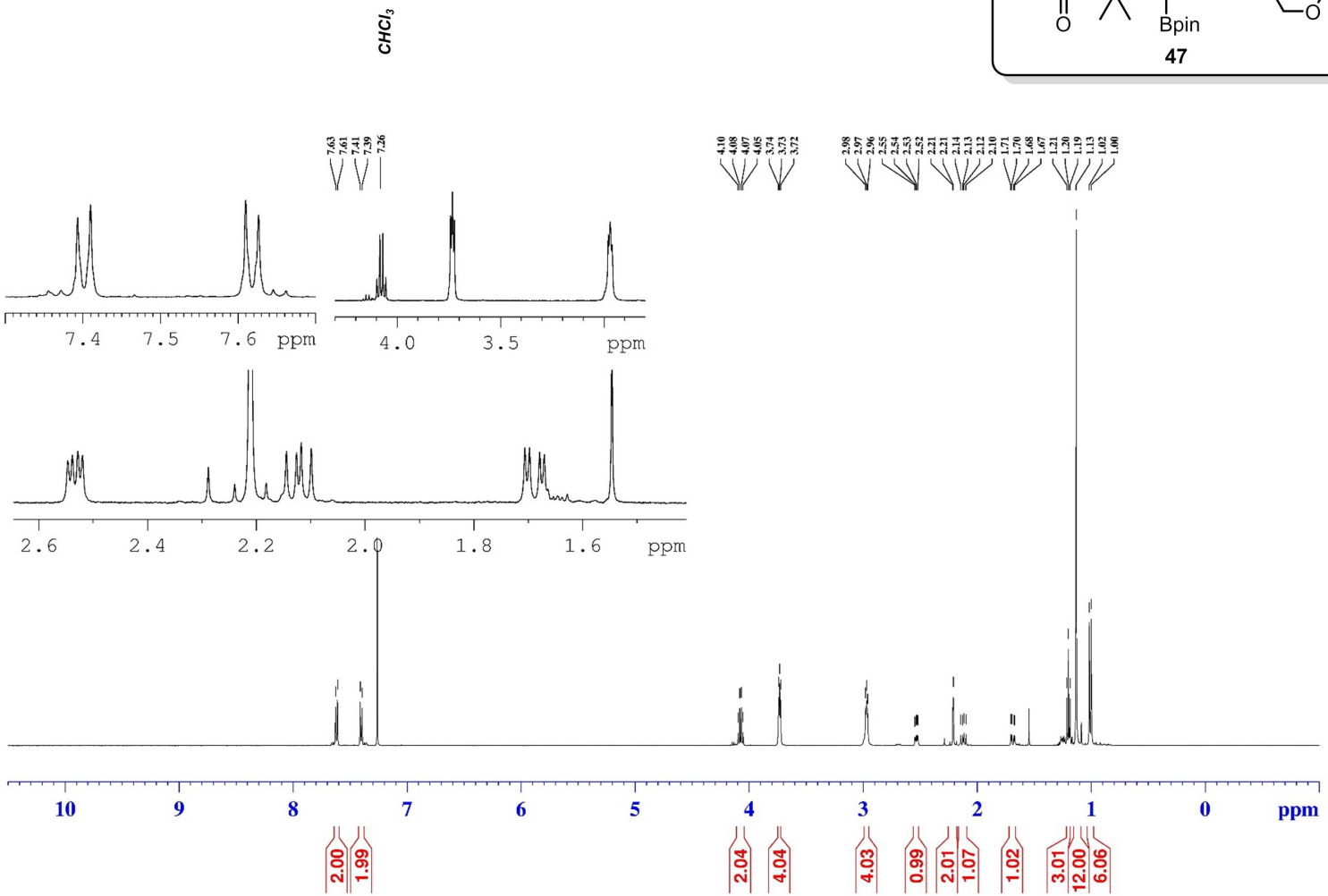
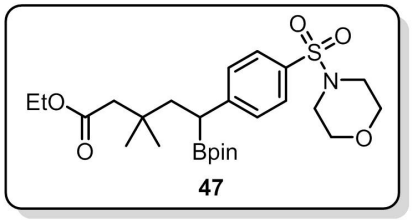


^{13}C NMR

Ethyl 3,3-dimethyl-5-(4-(morpholinosulfonyl)phenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate
125 MHz, $CDCl_3$



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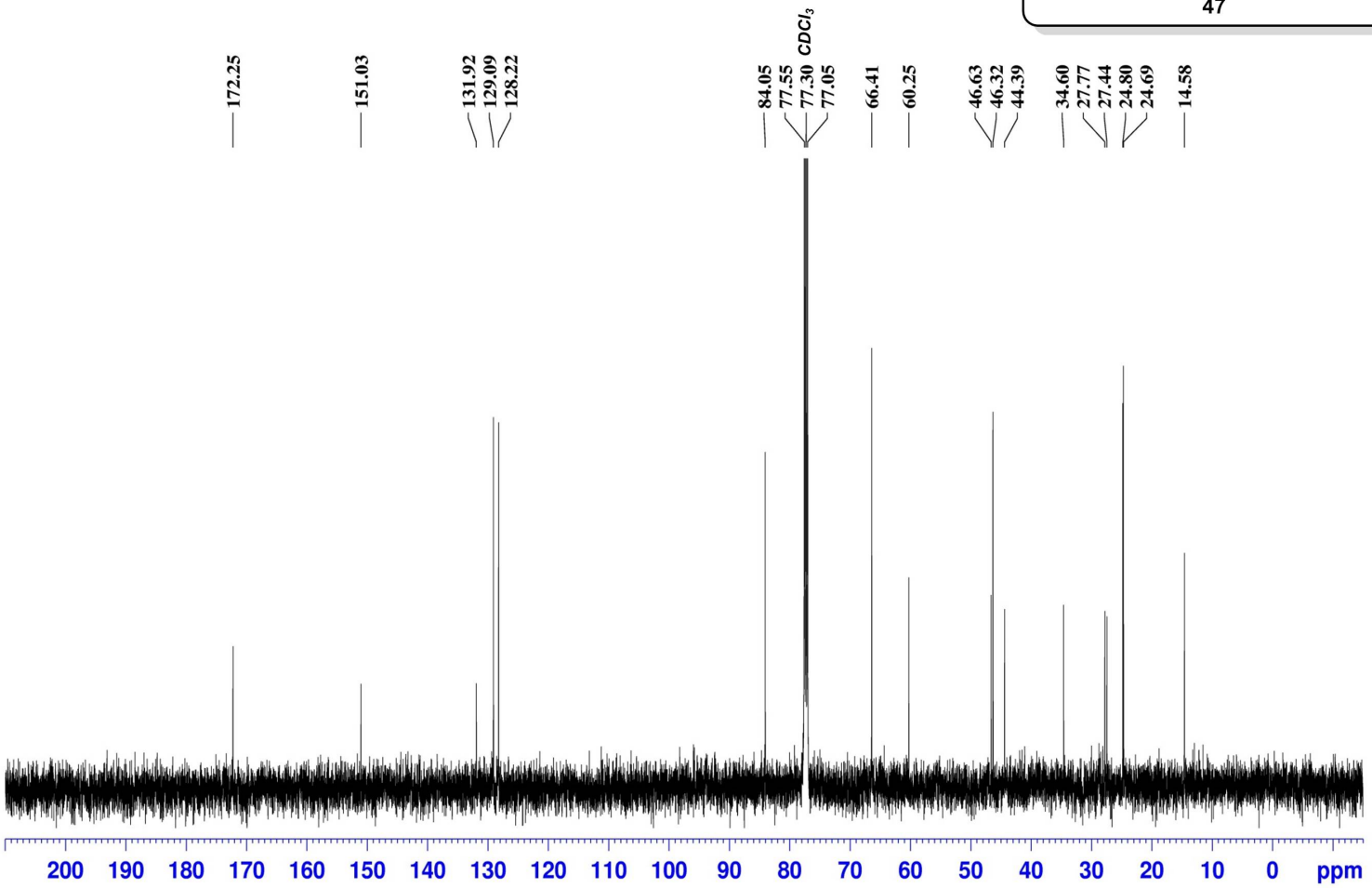
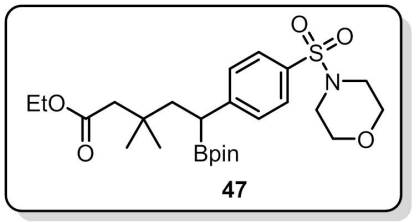


^{11}B NMR

ethyl 3,3-dimethyl-5-(4-(morpholinosulfonyl)phenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate
128 MHz, $CDCl_3$



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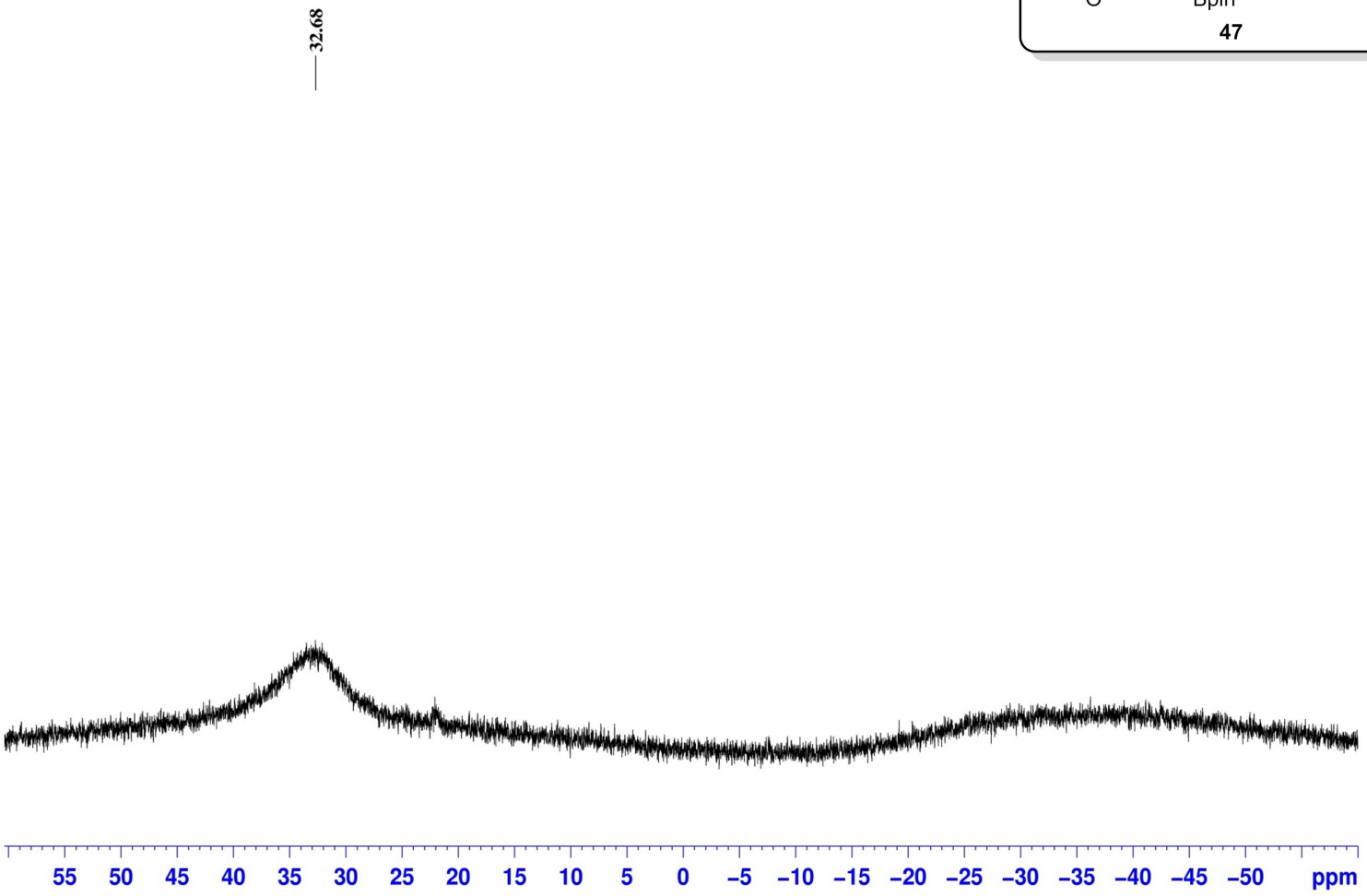
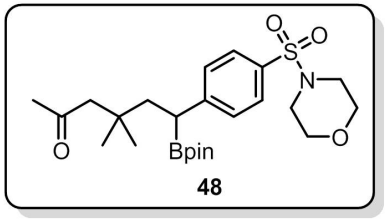


^1H NMR

4,4-dimethyl-6-(4-(morpholinosulfonyl)phenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one
500 MHz, $CDCl_3$



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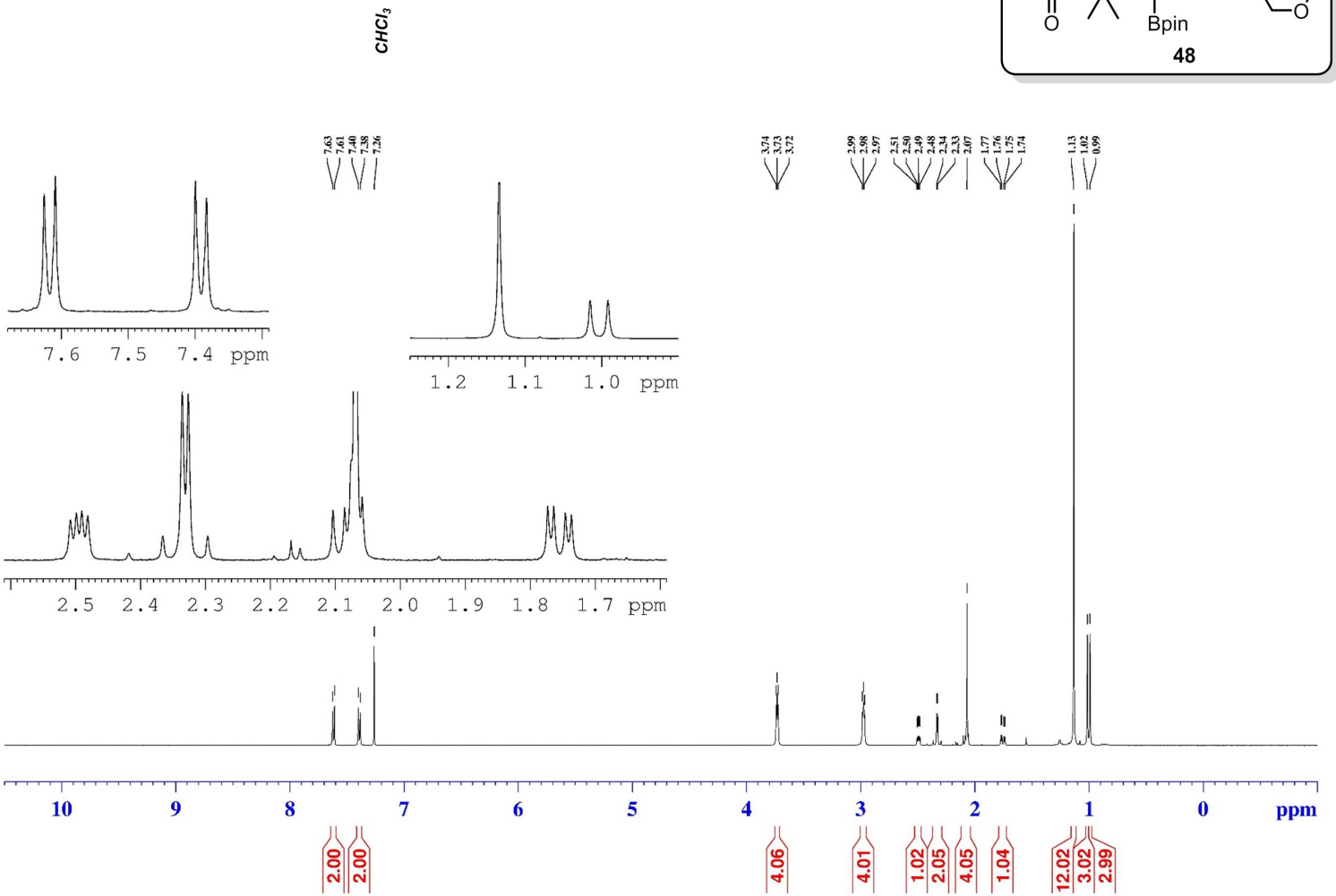
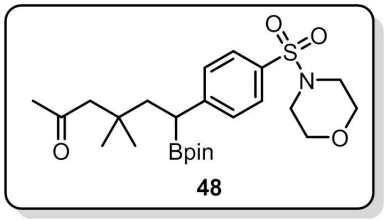


^{13}C NMR

4,4-Dimethyl-6-(4-(morpholinosulfonyl)phenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one
125 MHz, $CDCl_3$



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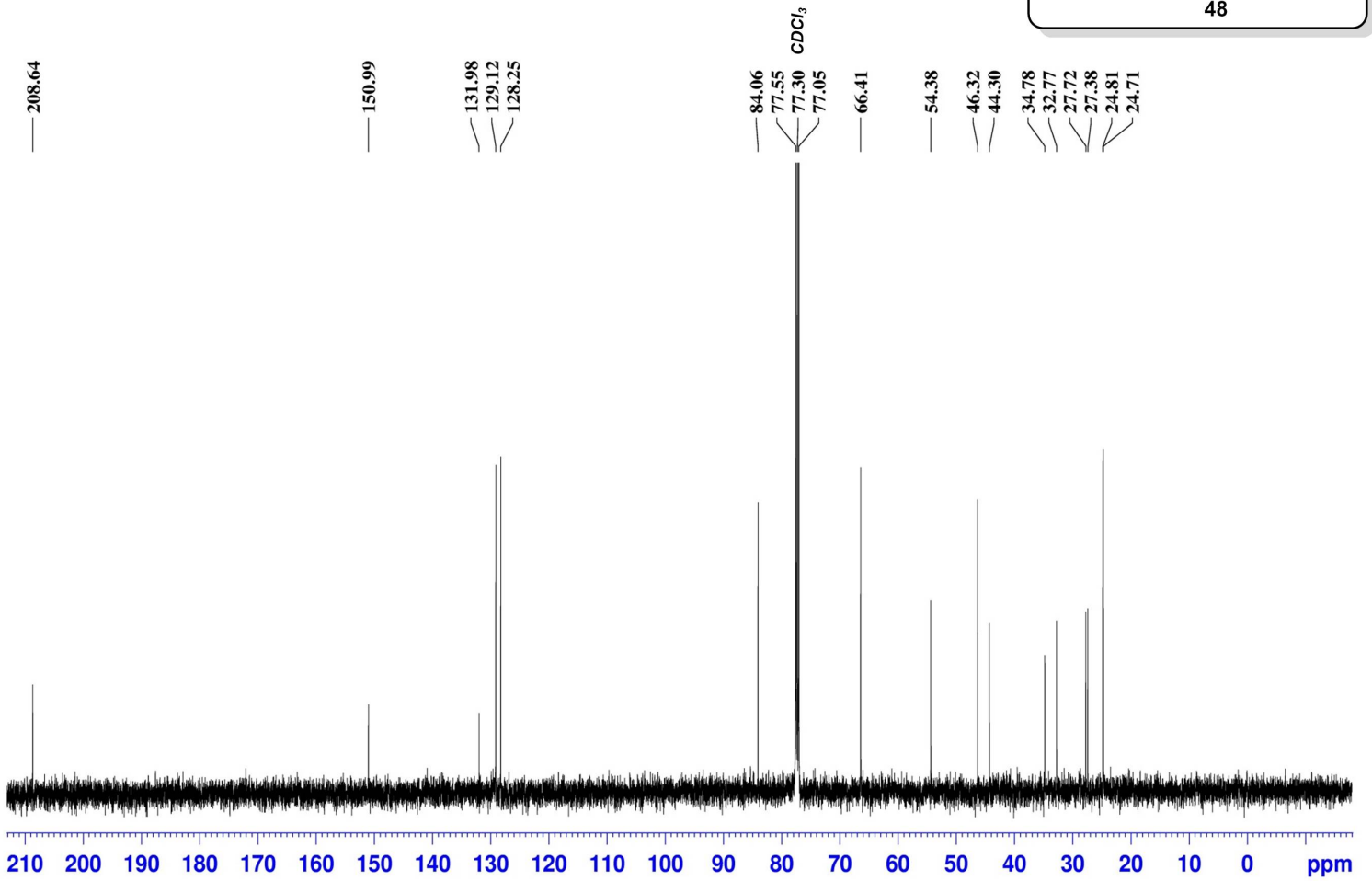
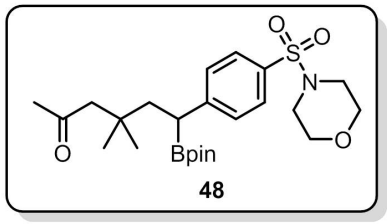


^{11}B NMR

4,4-dimethyl-6-(4-(morpholinosulfonyl)phenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one
128 MHz, $CDCl_3$



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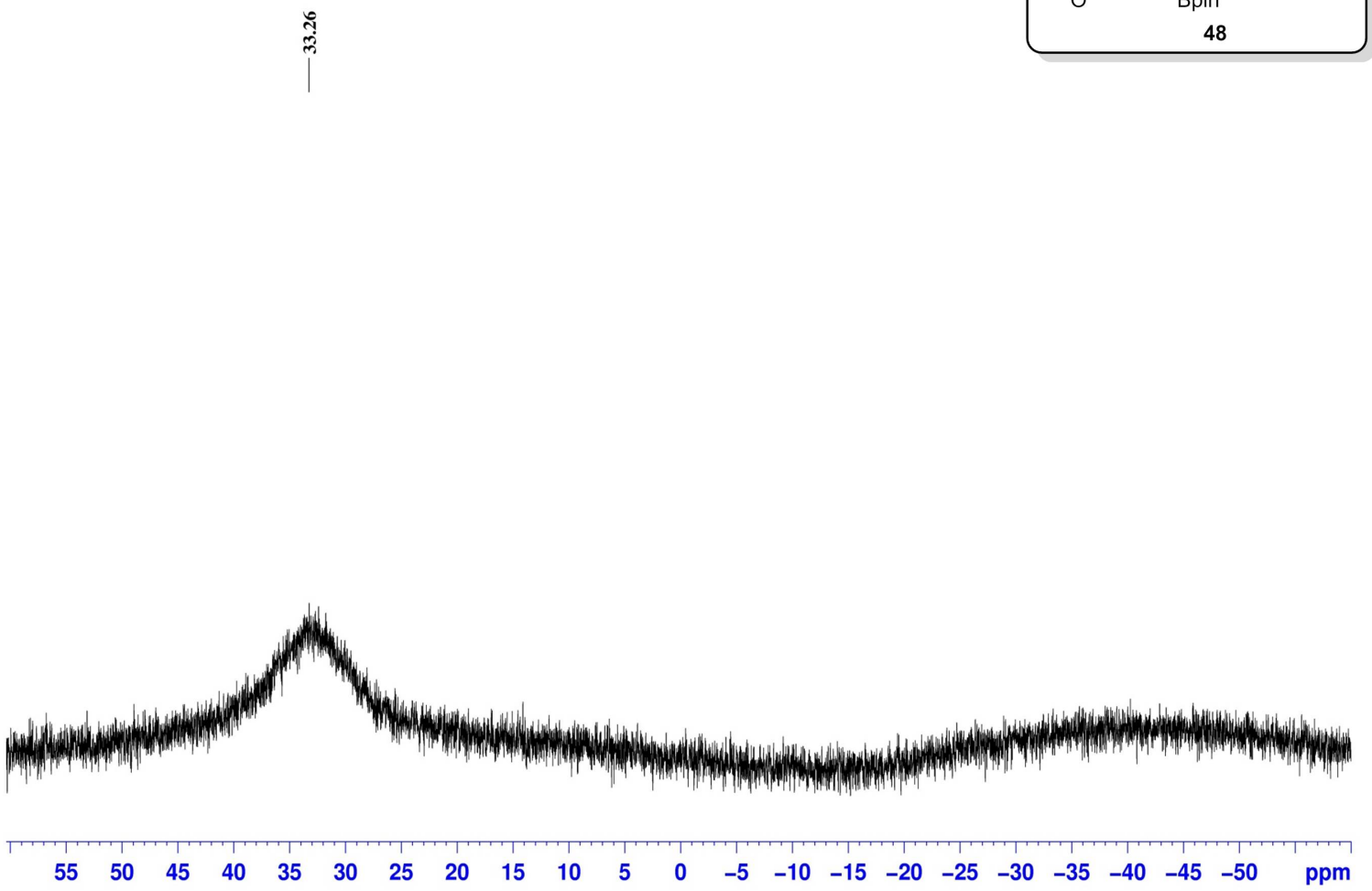
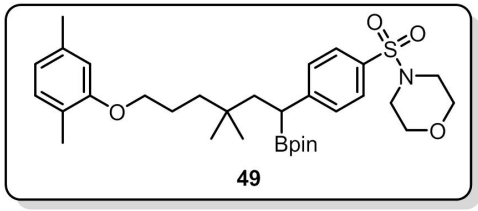
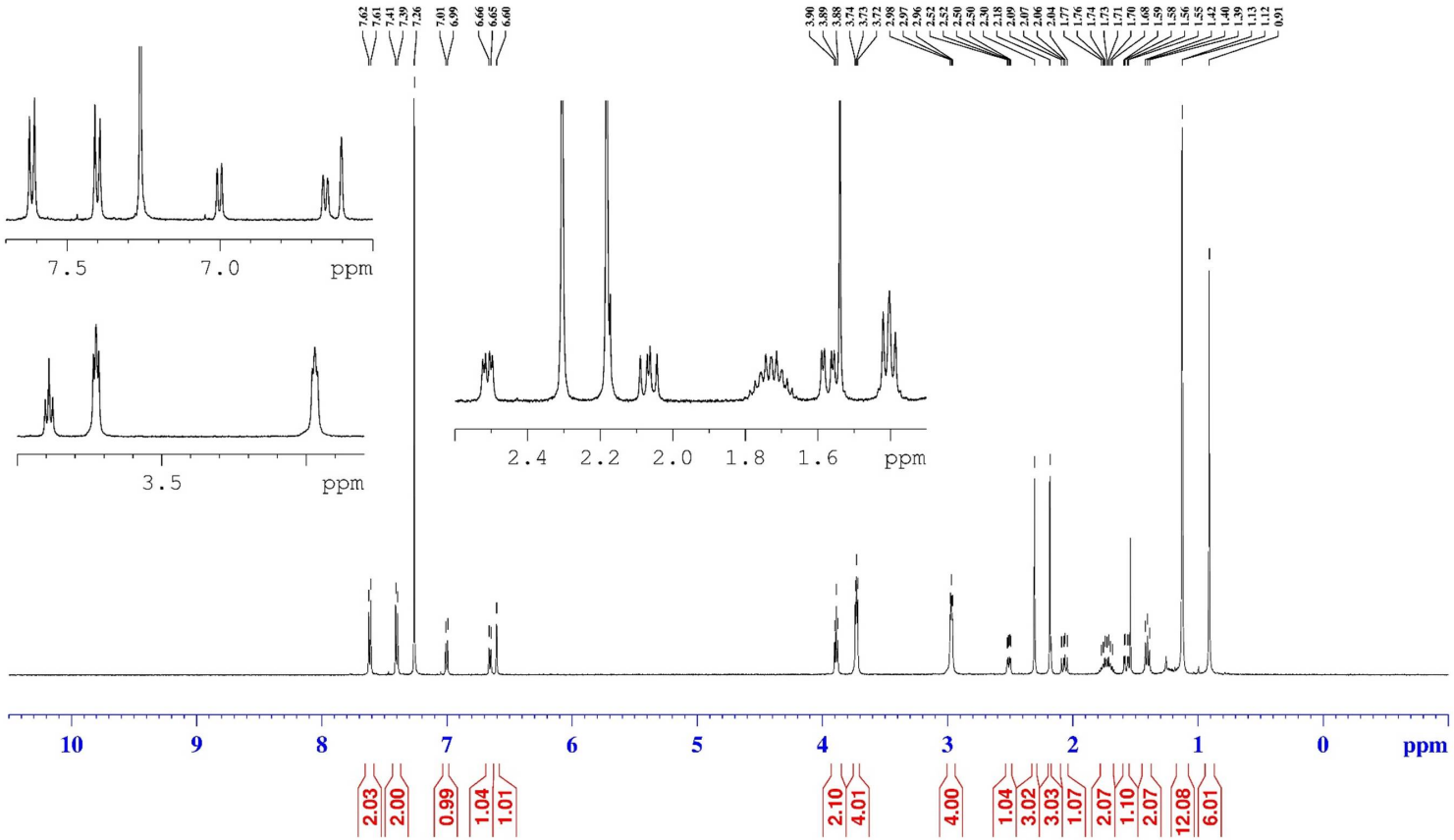


^1H NMR

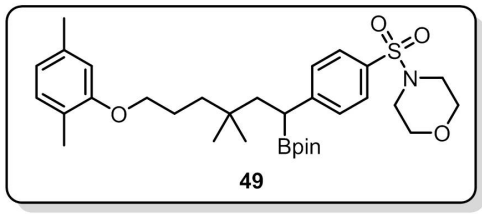
4-((4-(6-(2,5-dimethylphenoxy)-3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)phenyl)sulfonyl)morpholine
500 MHz, $CDCl_3$





^{13}C NMR

4-((4-(6-(2,5-Dimethylphenoxy)-3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)phenyl)sulfonyl)morpholine
125 MHz, $CDCl_3$



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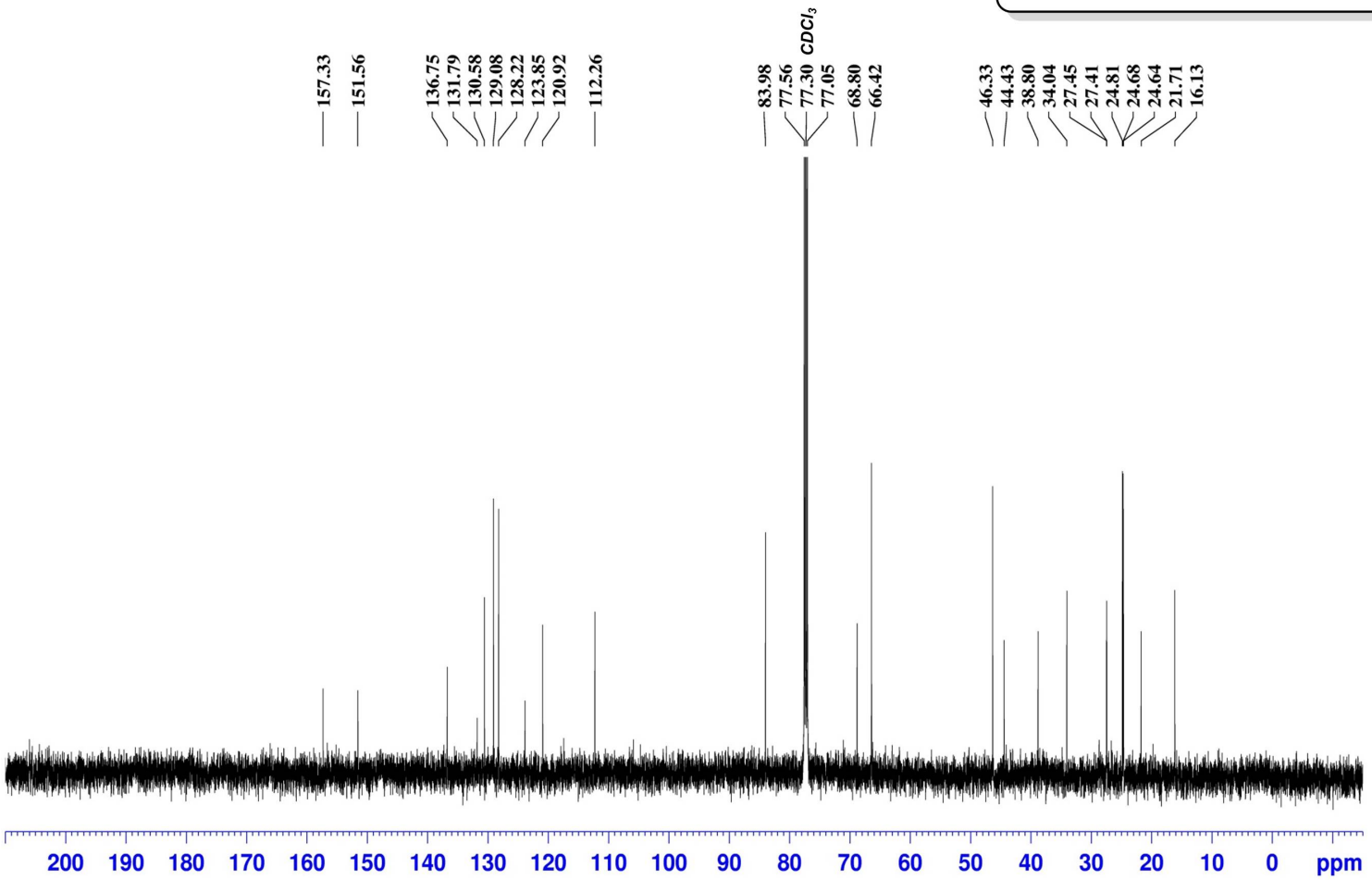
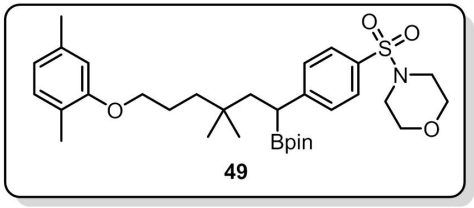


^{11}B NMR

4-((4-(6-(2,5-dimethylphenoxy)-3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)phenyl)sulfonyl)morpholine
128 MHz, $CDCl_3$



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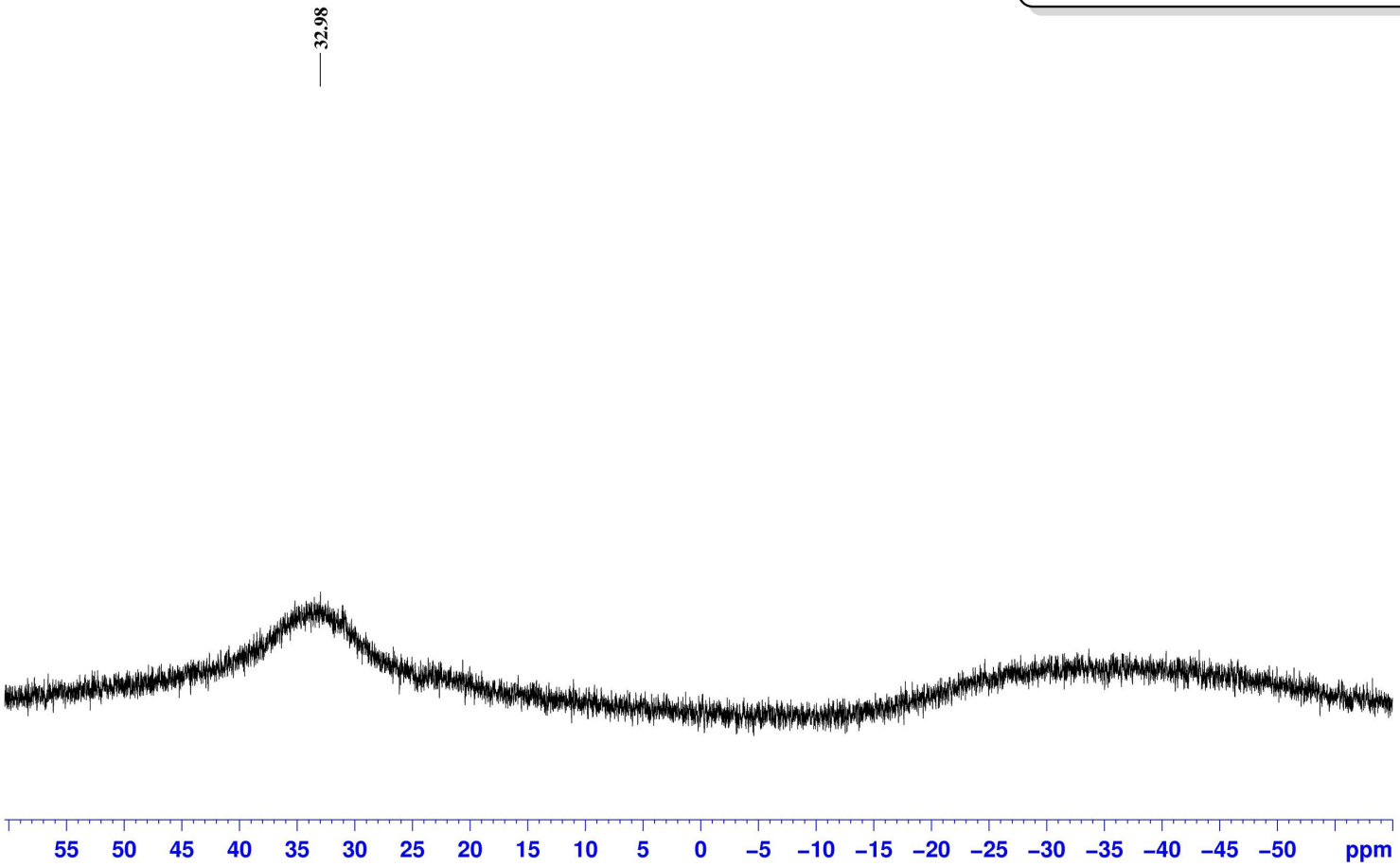
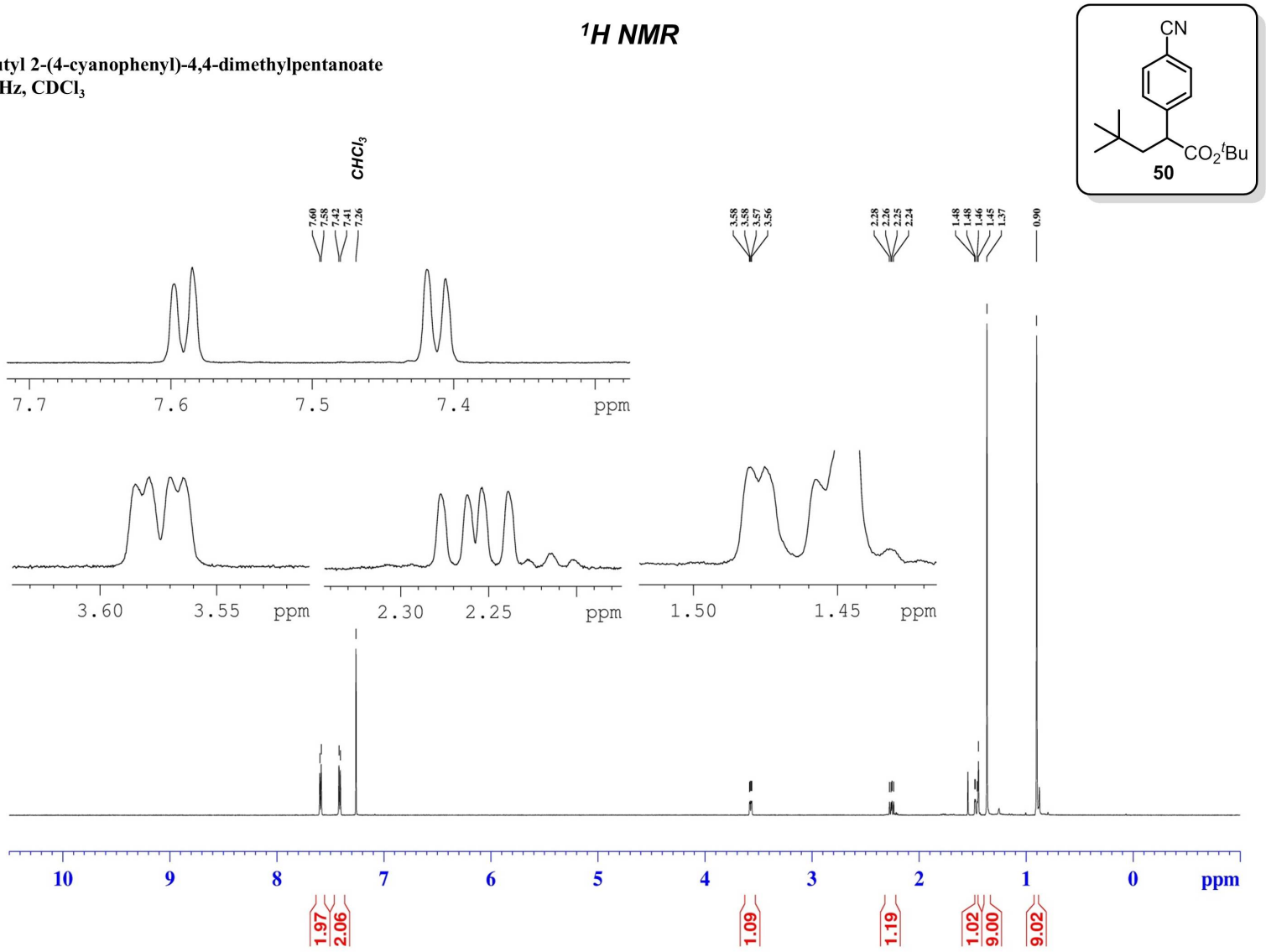


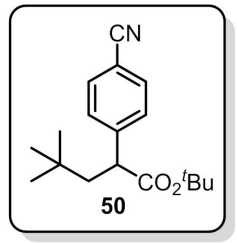
^1H NMR

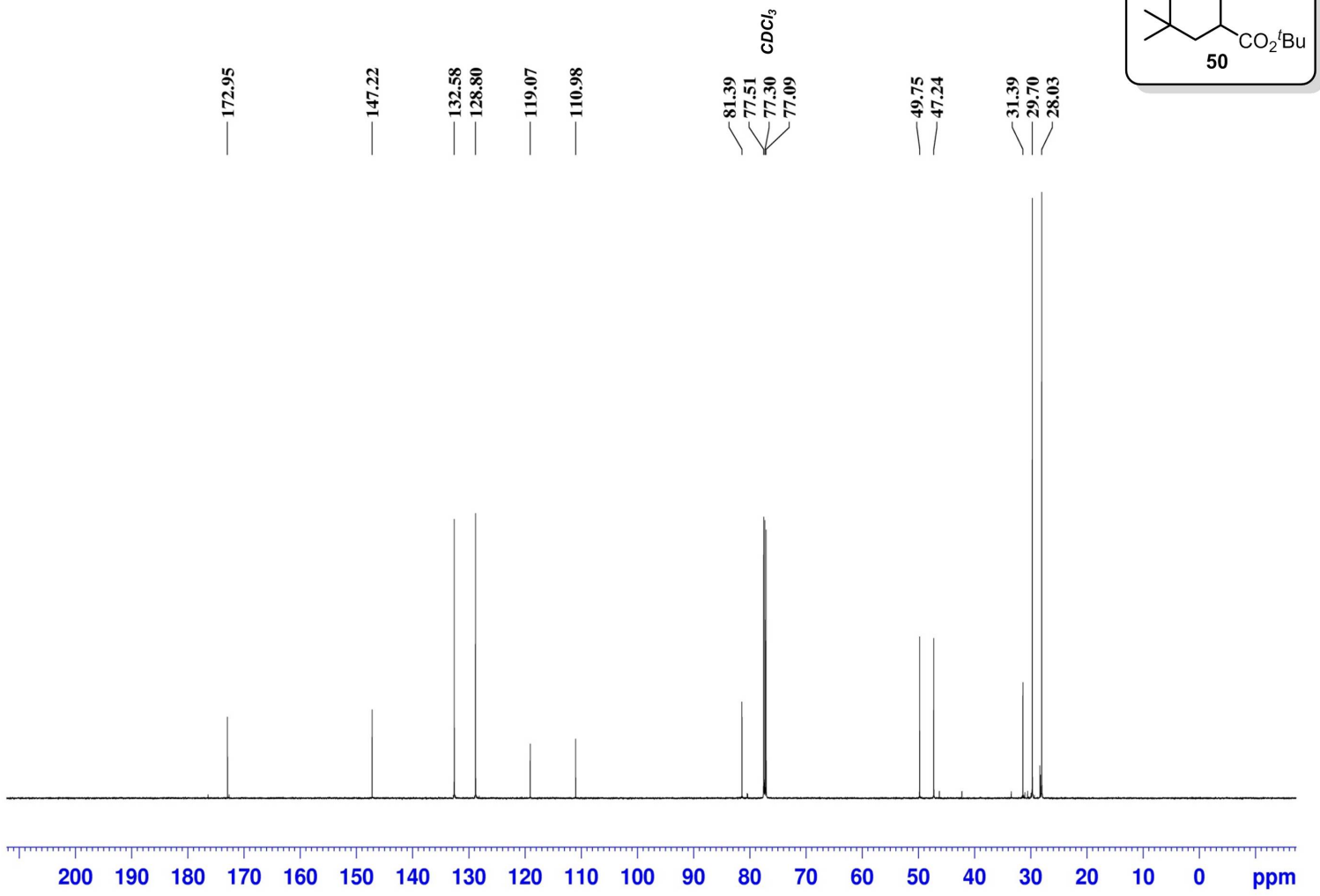
tert-butyl 2-(4-cyanophenyl)-4,4-dimethylpentanoate
125 MHz, $CDCl_3$



^{13}C NMR

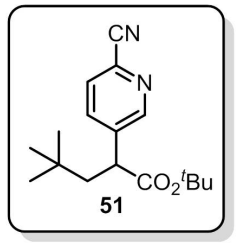
Tert-butyl 2-(4-cyanophenyl)-4,4-dimethylpentanoate
125 MHz, $CDCl_3$

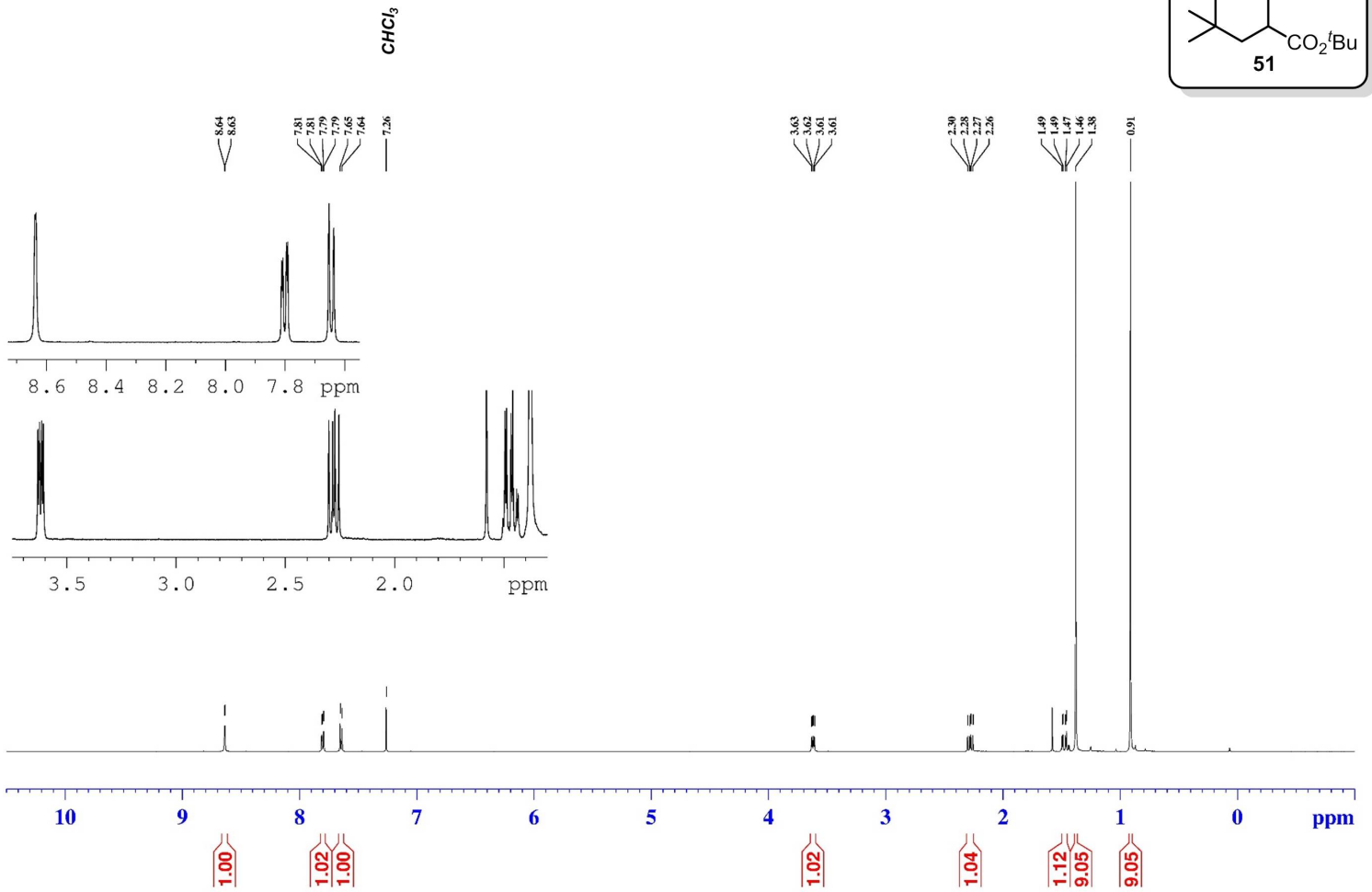




^1H NMR

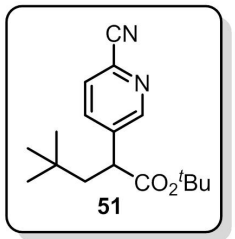
tert-Butyl 2-(6-cyanopyridin-3-yl)-4,4-dimethylpentanoate
125 MHz, $CDCl_3$

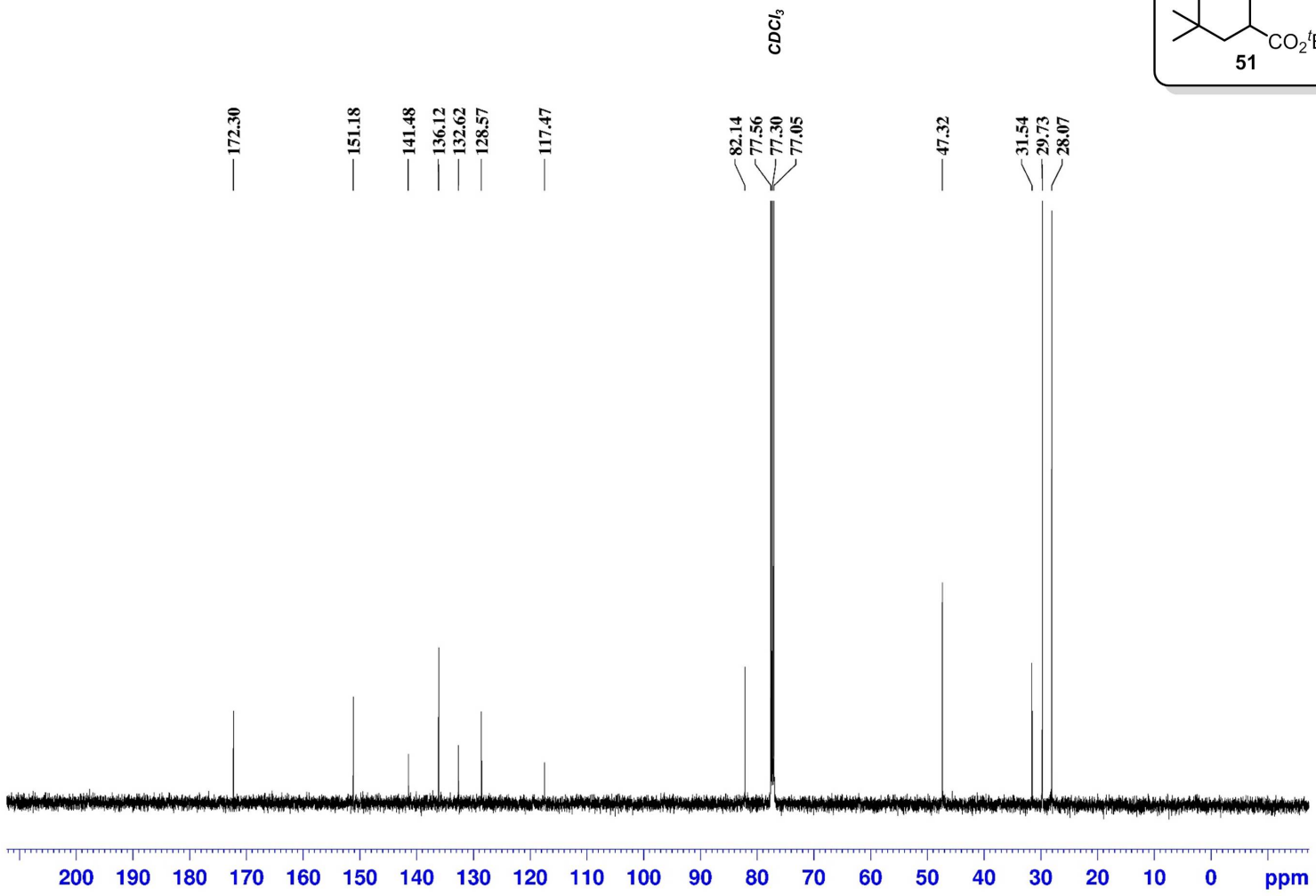




^{13}C NMR

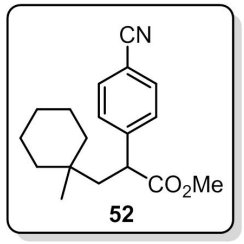
tert-Butyl 2-(6-cyanopyridin-3-yl)-4,4-dimethylpentanoate
125 MHz, $CDCl_3$

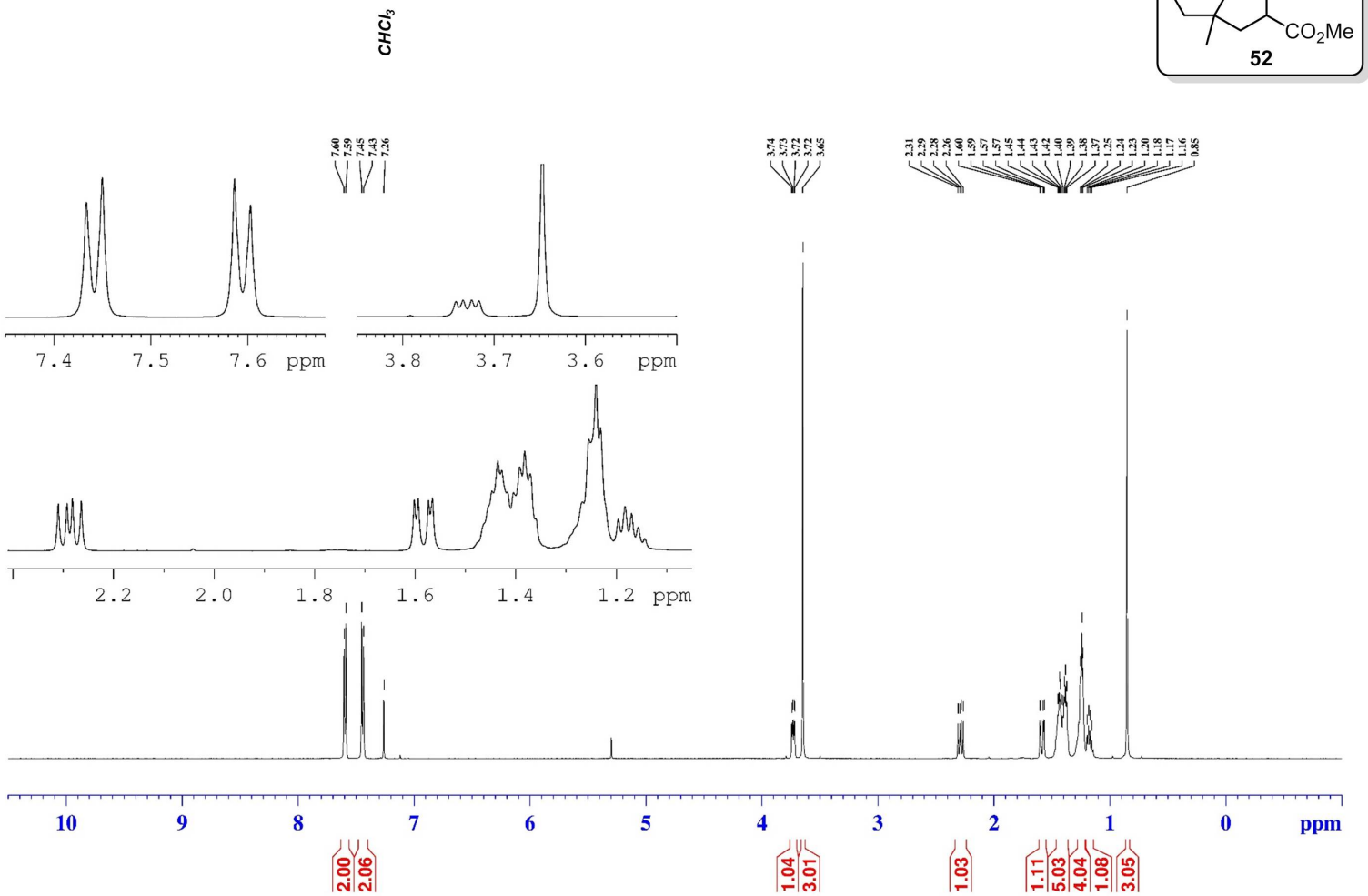




^1H NMR

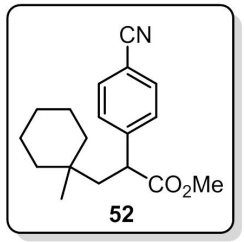
tert-butyl 2-(4-cyanophenyl)-4,4-dimethylpentanoate
125 MHz, $CDCl_3$



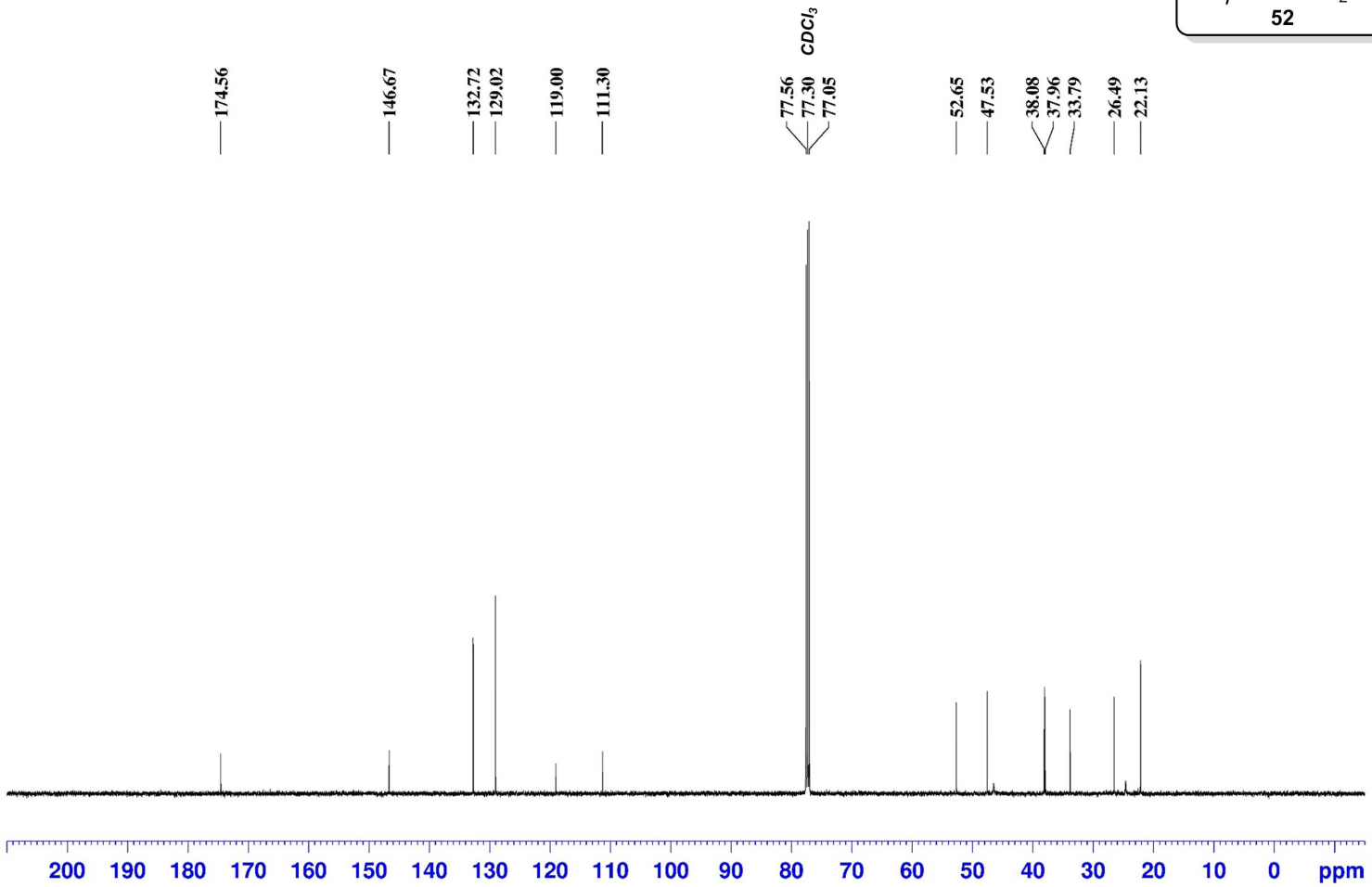


Methyl 2-(4-cyanophenyl)-3-cyclohexylpropanoate
125 MHz, $CDCl_3$

^{13}C NMR

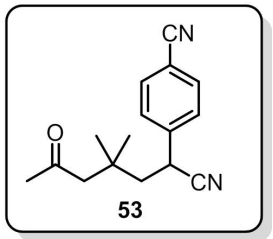


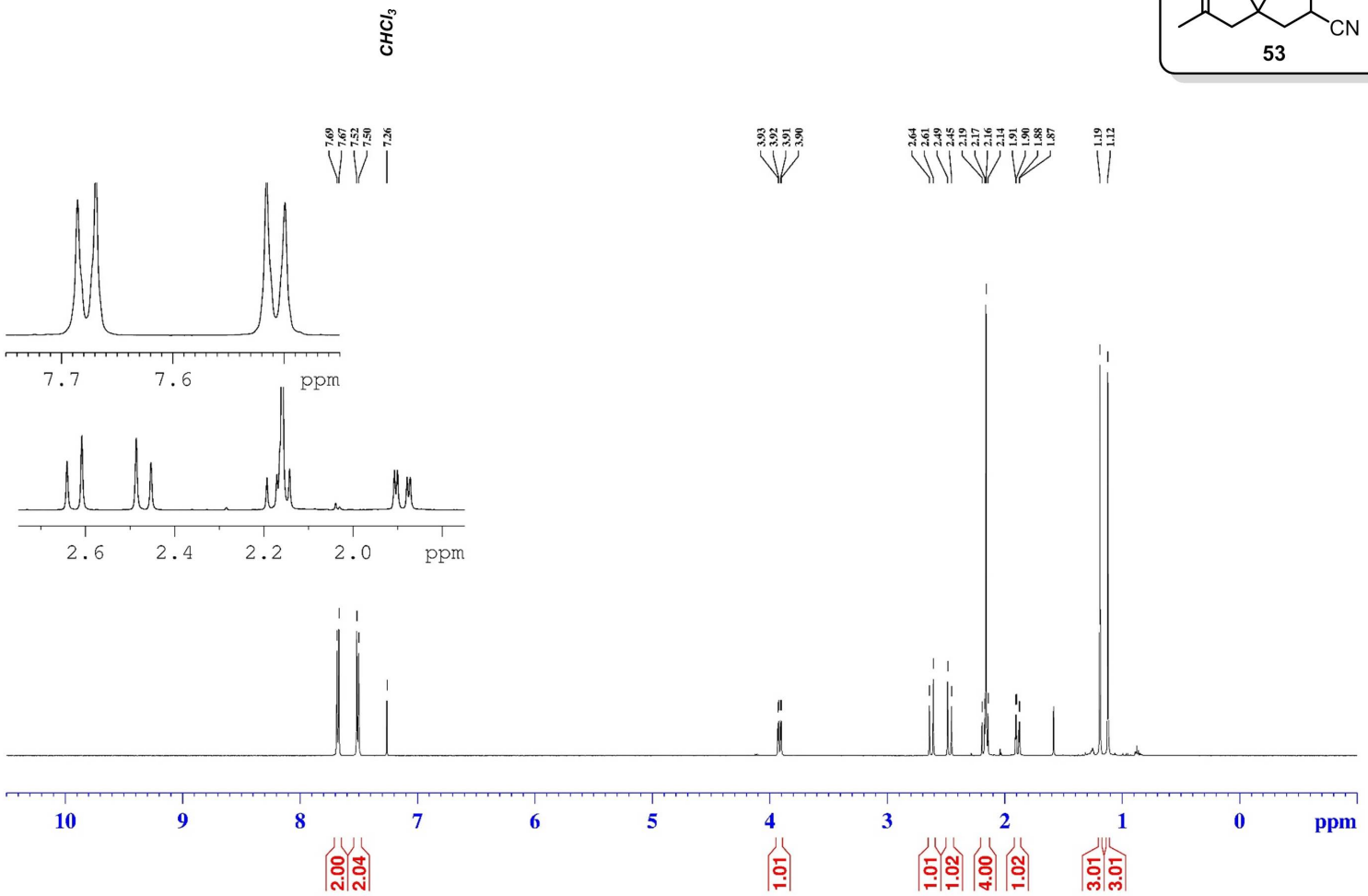
52



4-(1-cyano-3,3-dimethyl-5-oxohexyl)benzonitrile
500 MHz, $CDCl_3$

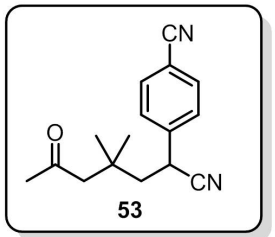
^{1}H NMR





4-(1-Cyano-3,3-dimethyl-5-oxohexyl)benzonitrile
125 MHz, $CDCl_3$

^{13}C NMR



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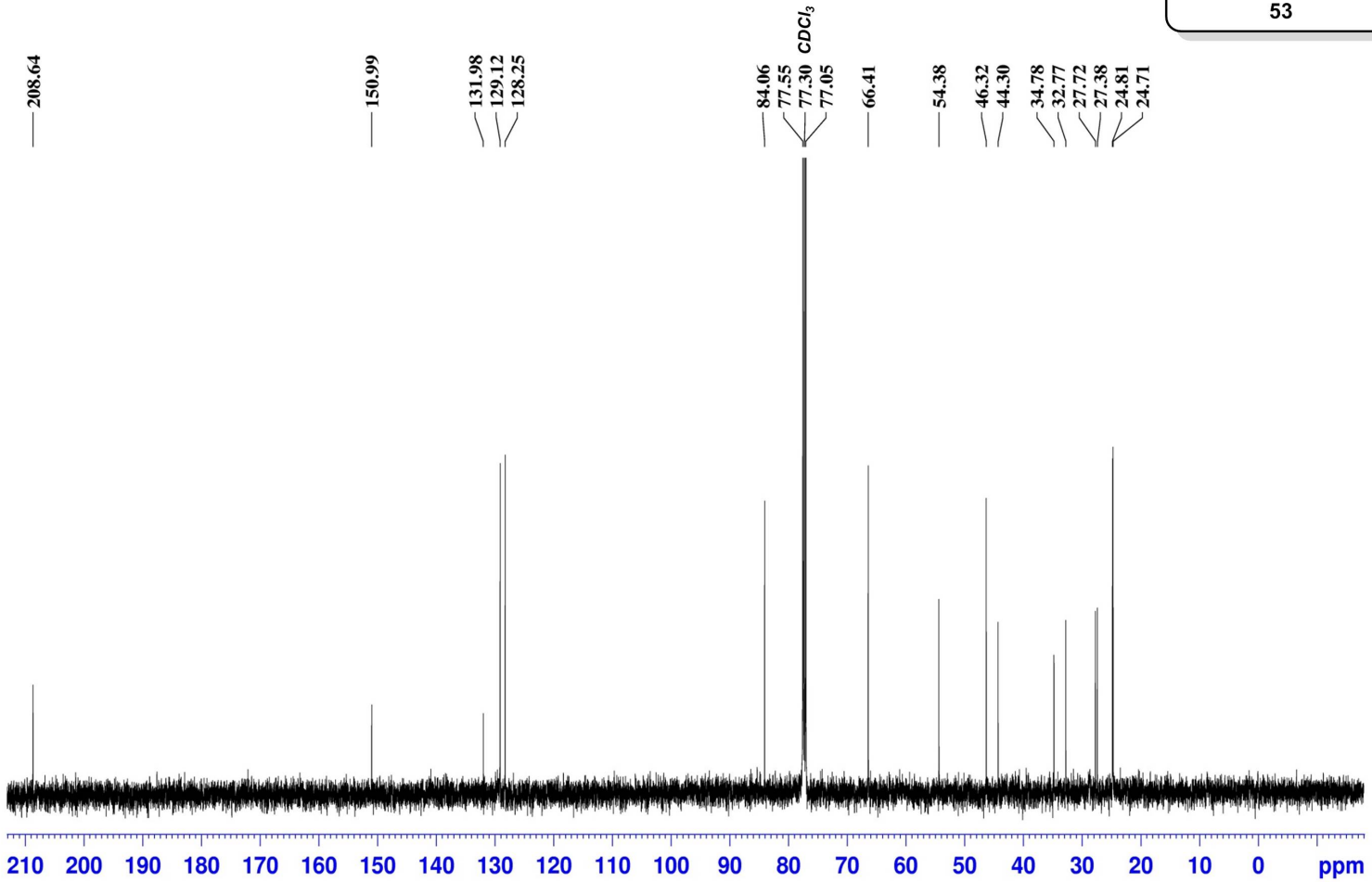
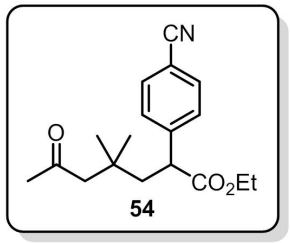
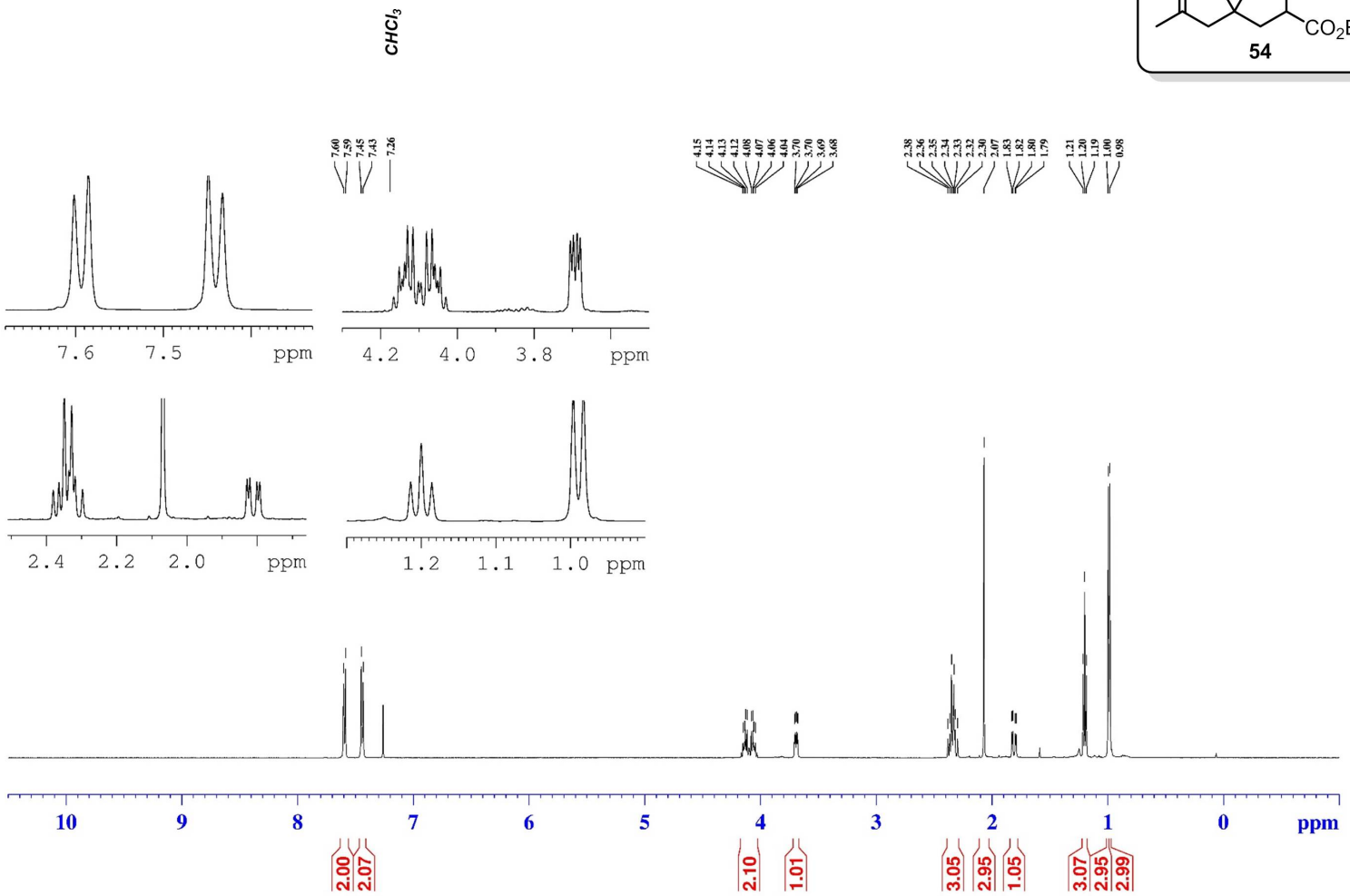


^1H NMR

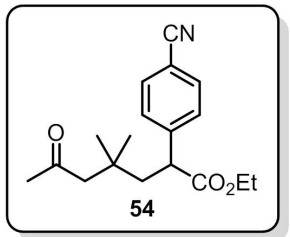
ethyl 2-(4-cyanophenyl)-4,4-dimethyl-6-oxoheptanoate
500 MHz, $CDCl_3$





Ethyl 2-(4-cyanophenyl)-4,4-dimethyl-6-oxoheptanoate
125 MHz, $CDCl_3$

^{13}C NMR



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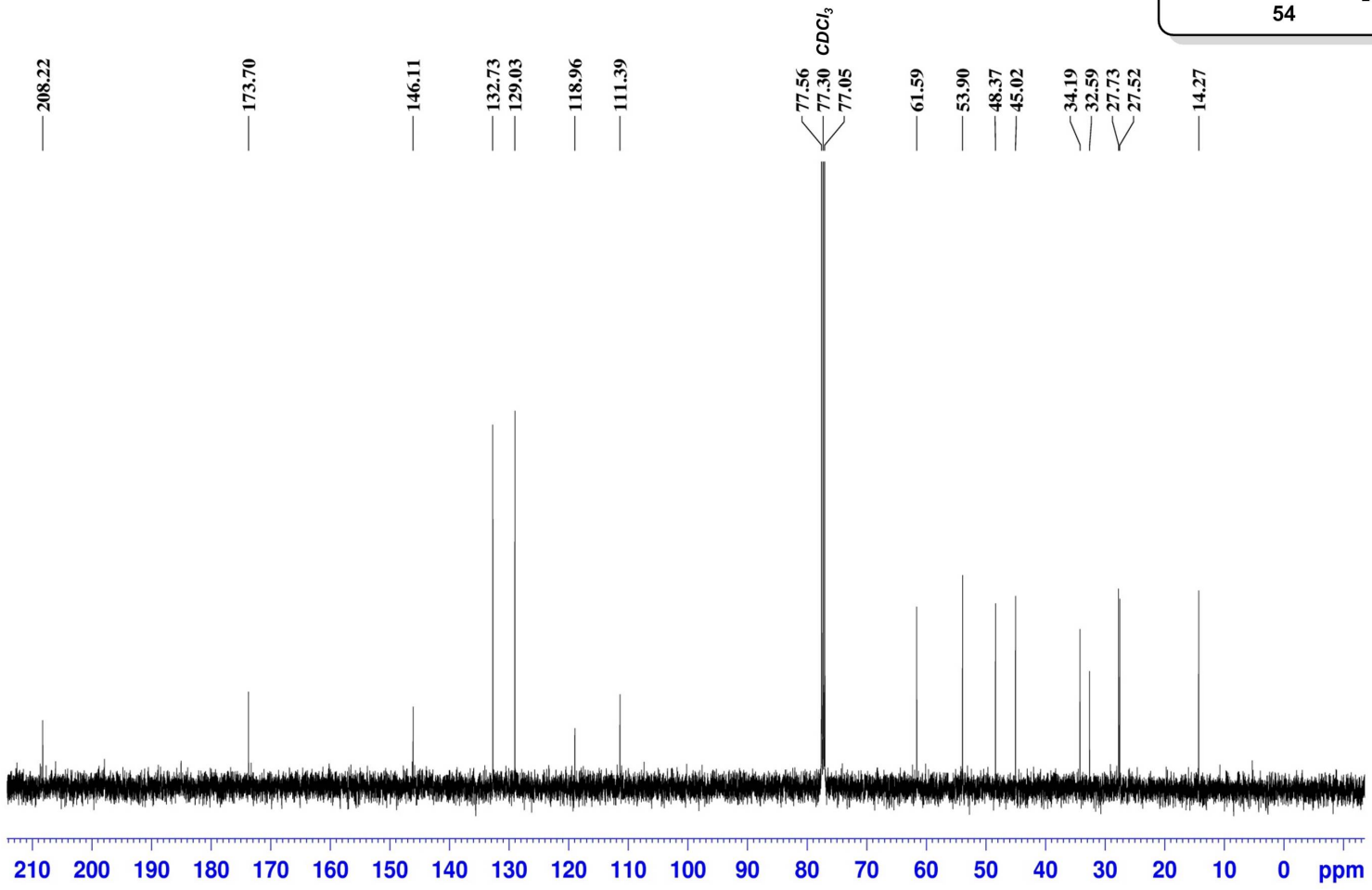
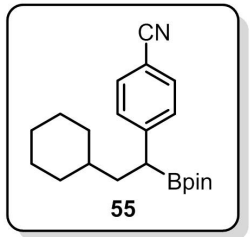
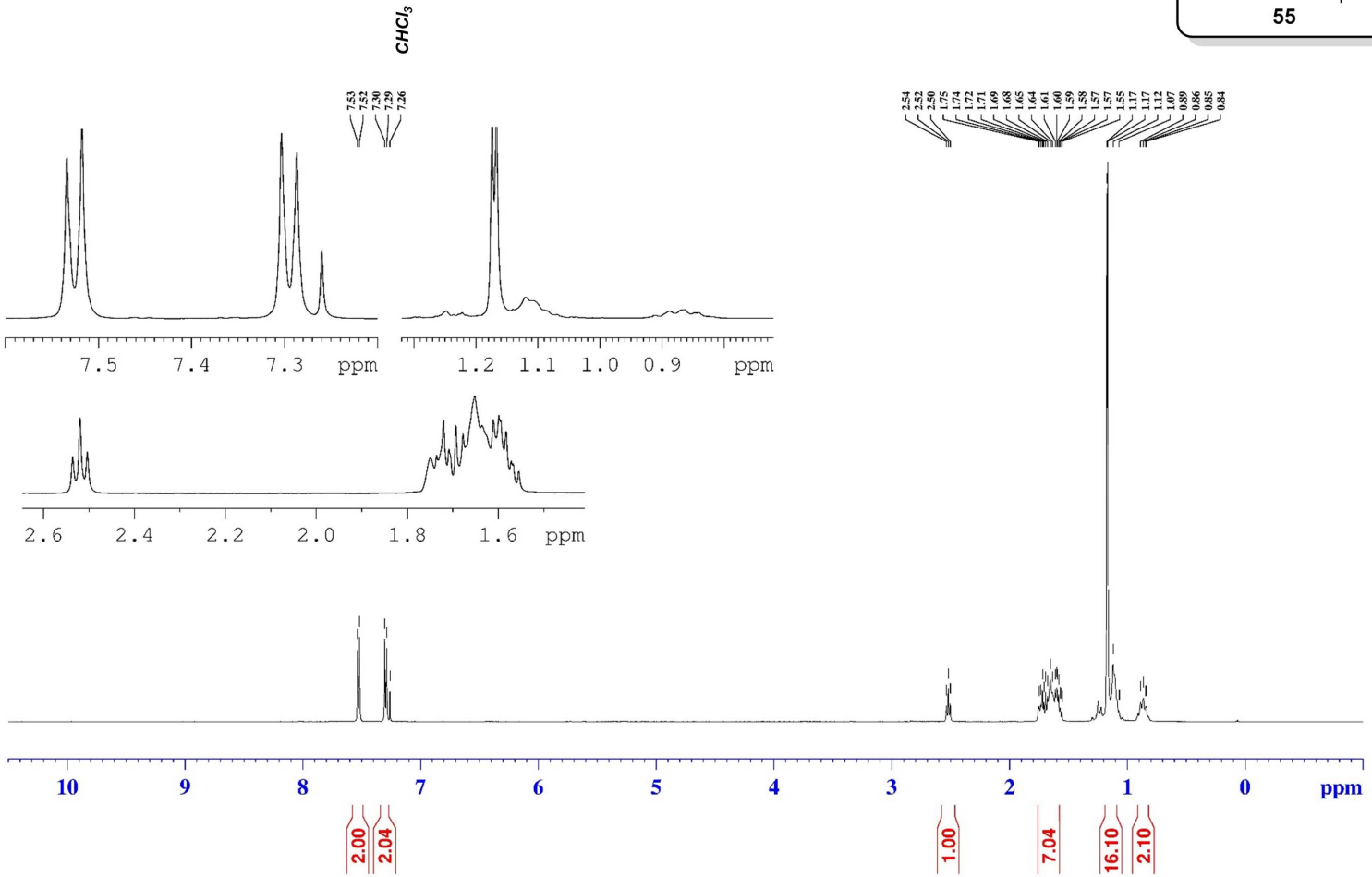


^1H NMR

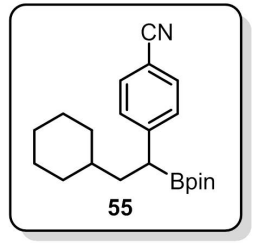
4-(2-cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile
500 MHz, $CDCl_3$

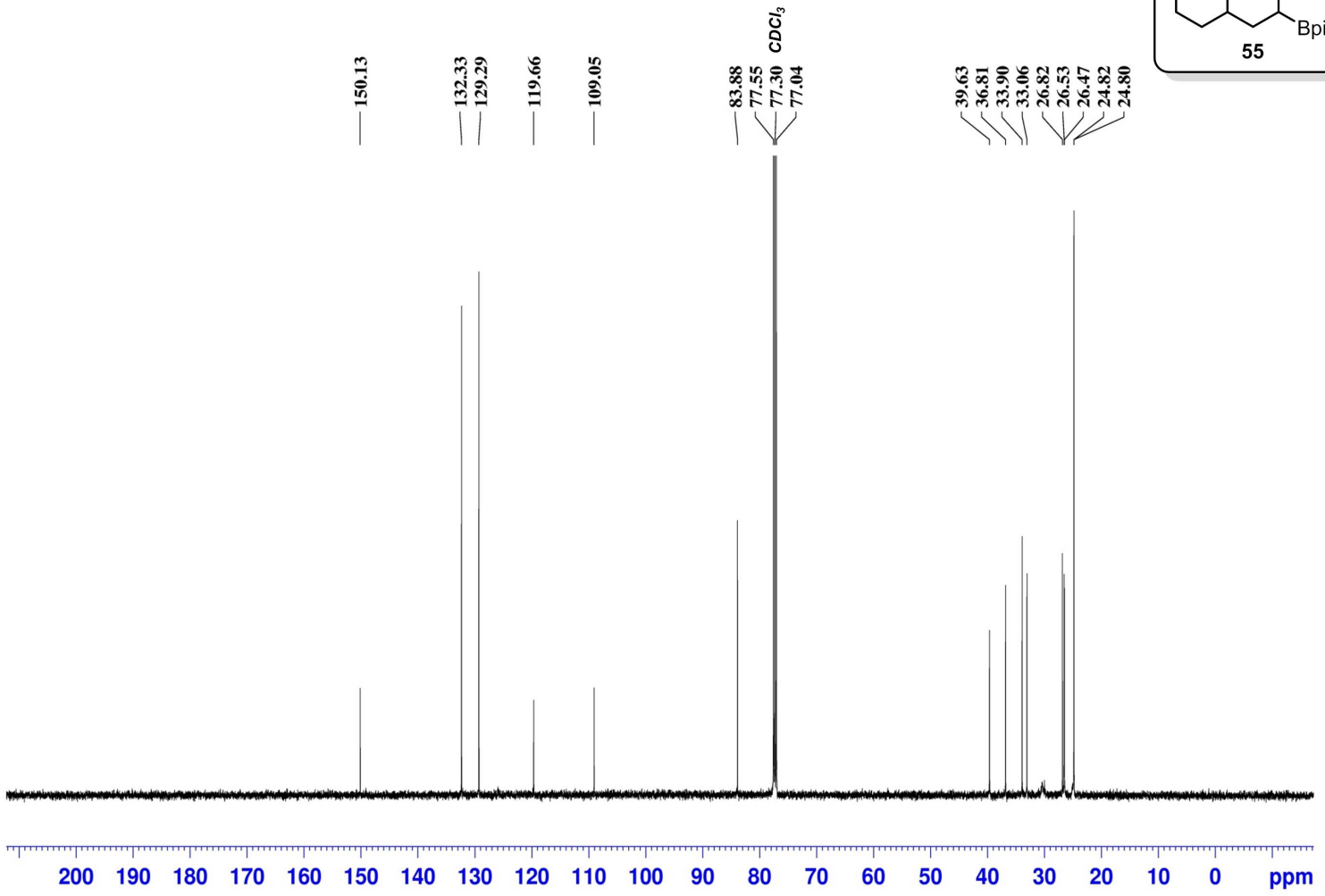




^{13}C NMR

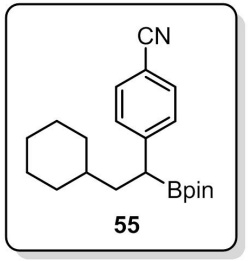
4-(2-Cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl) benzonitrile
125 MHz, $CDCl_3$

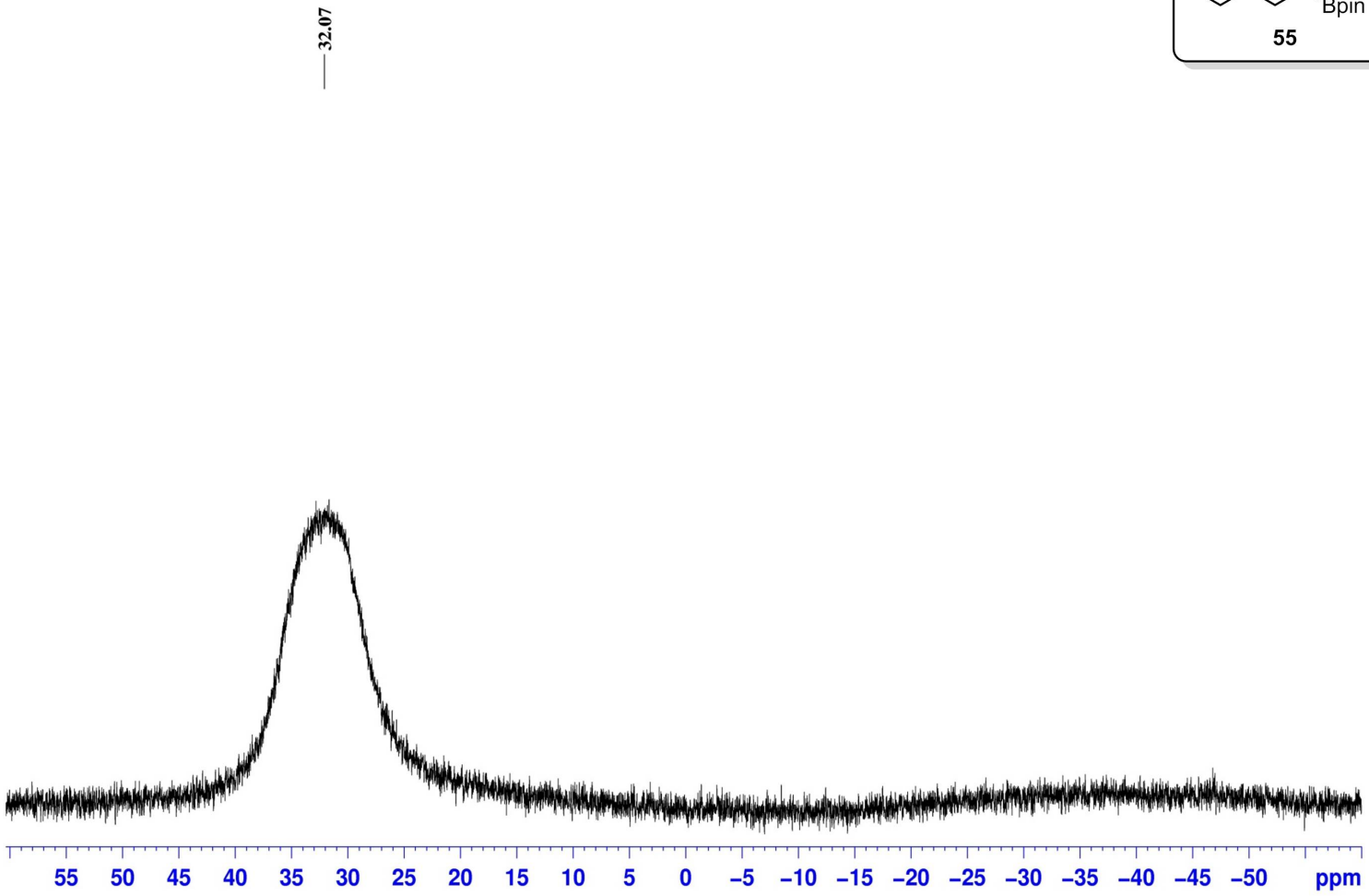




^{11}B NMR

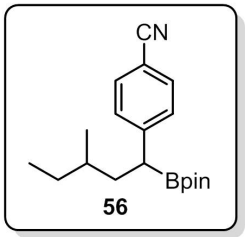
4-(2-cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl) benzonitrile
128 MHz, $CDCl_3$

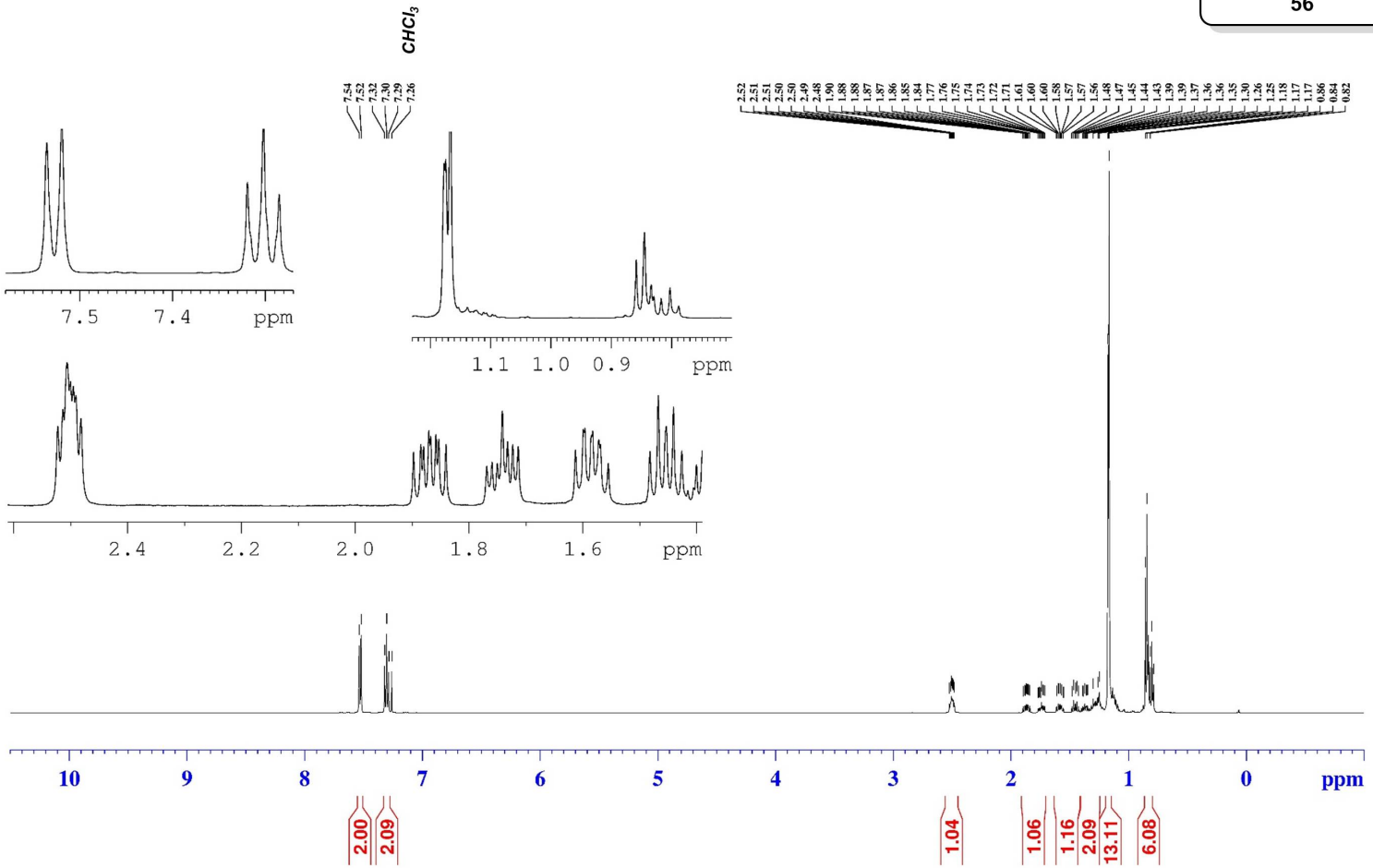




^1H NMR

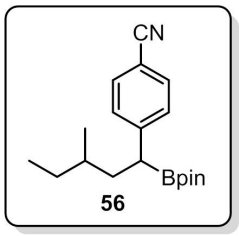
4-(3-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzonitrile
500 MHz, $CDCl_3$

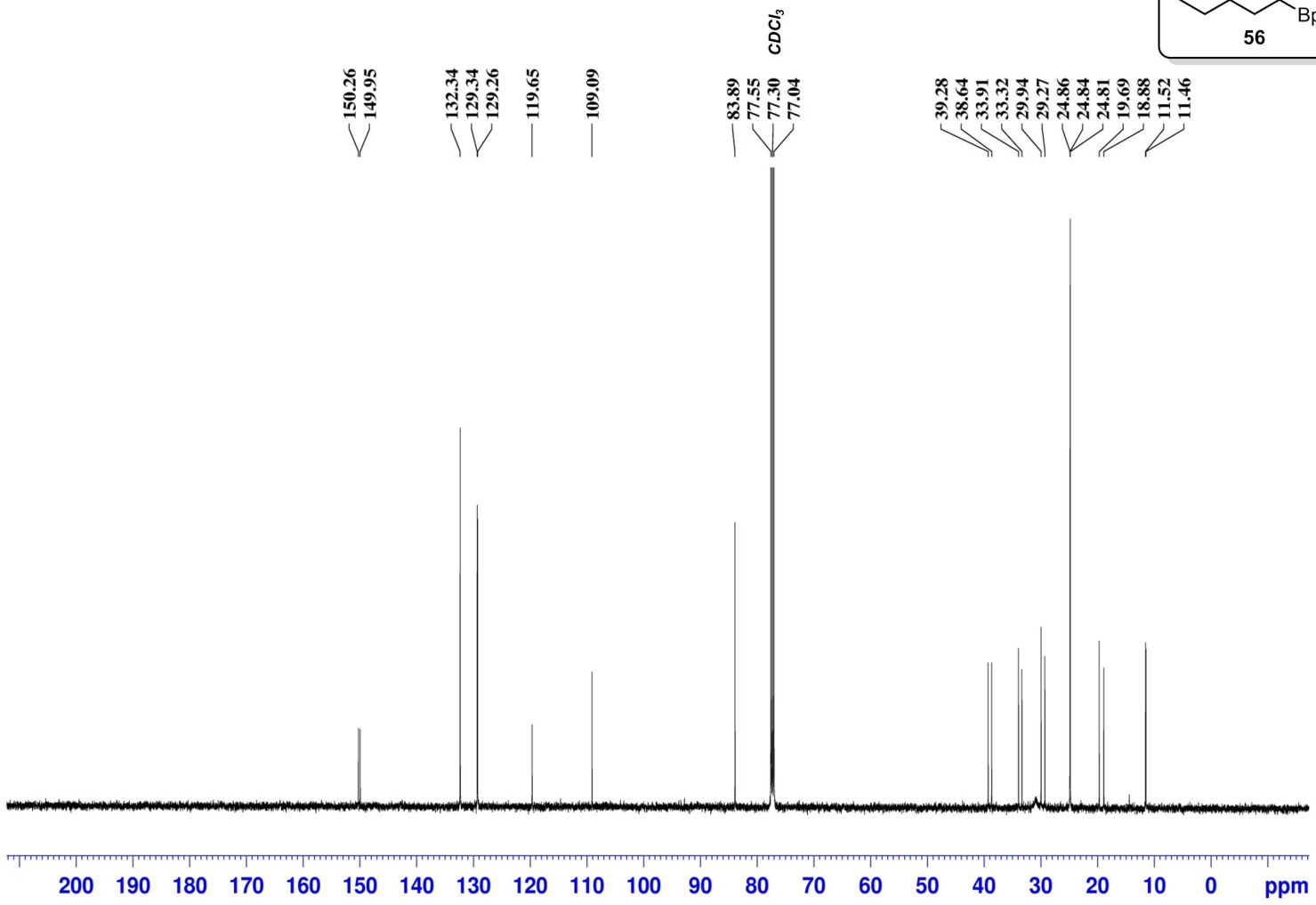




^{13}C NMR

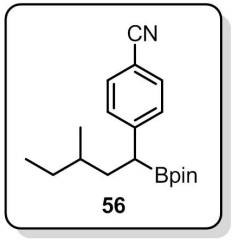
4-(3-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl) benzonitrile,
125 MHz,, $CDCl_3$





^{11}B NMR

4-(3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl) benzonitrile,
500 MHz, $CDCl_3$



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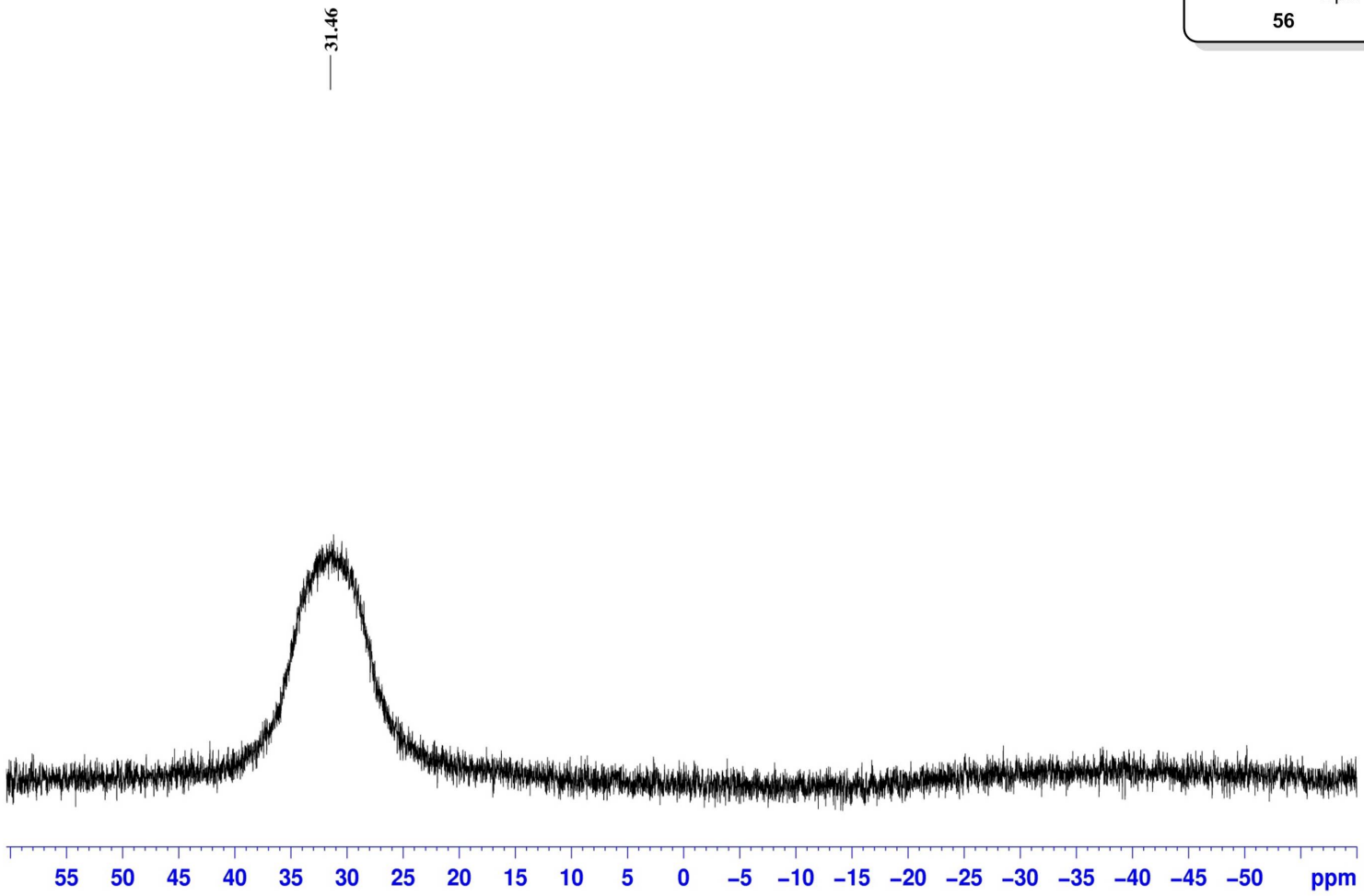
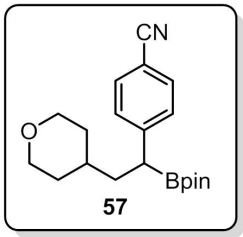
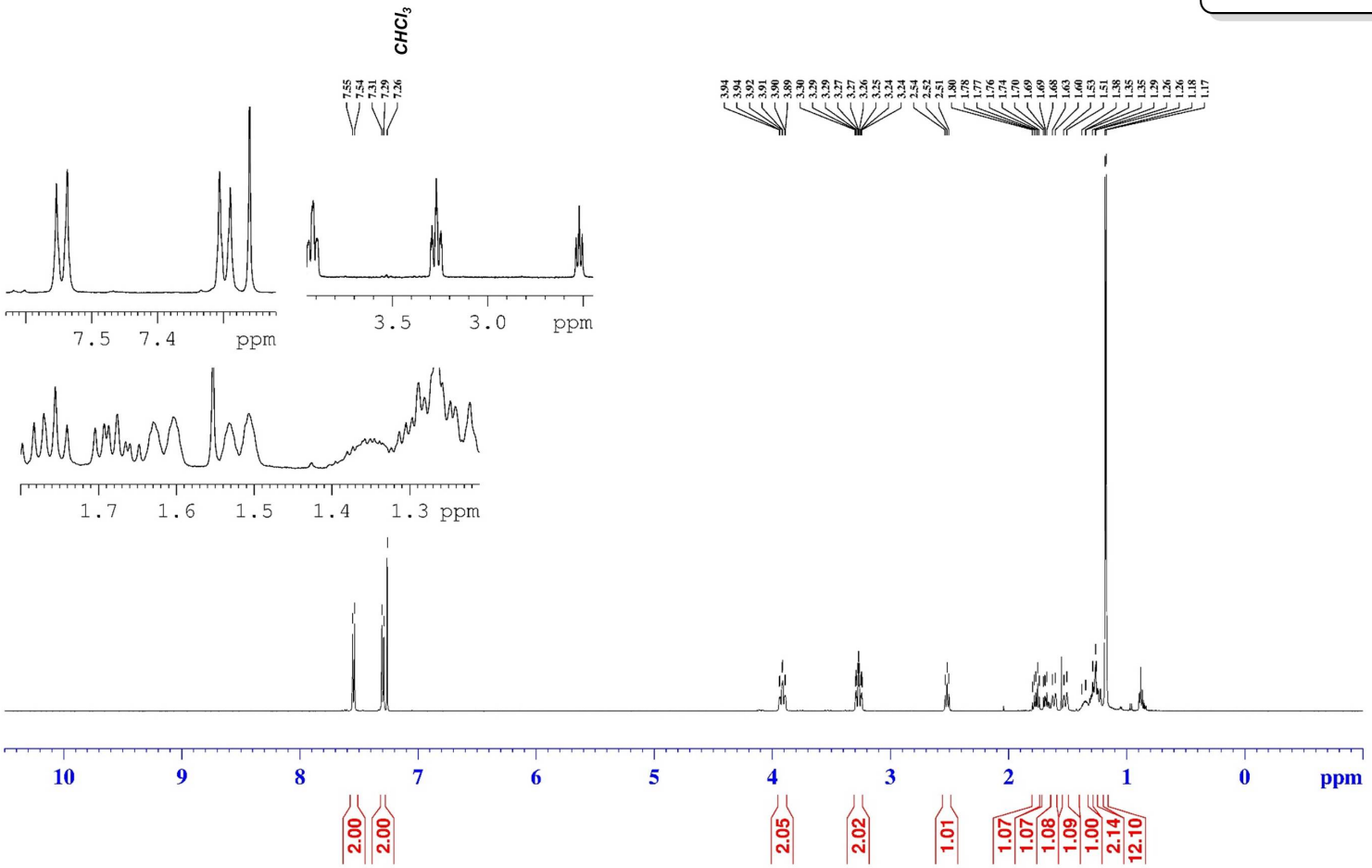


^1H NMR

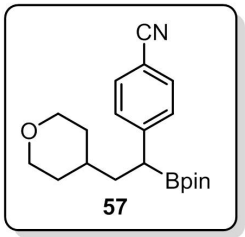


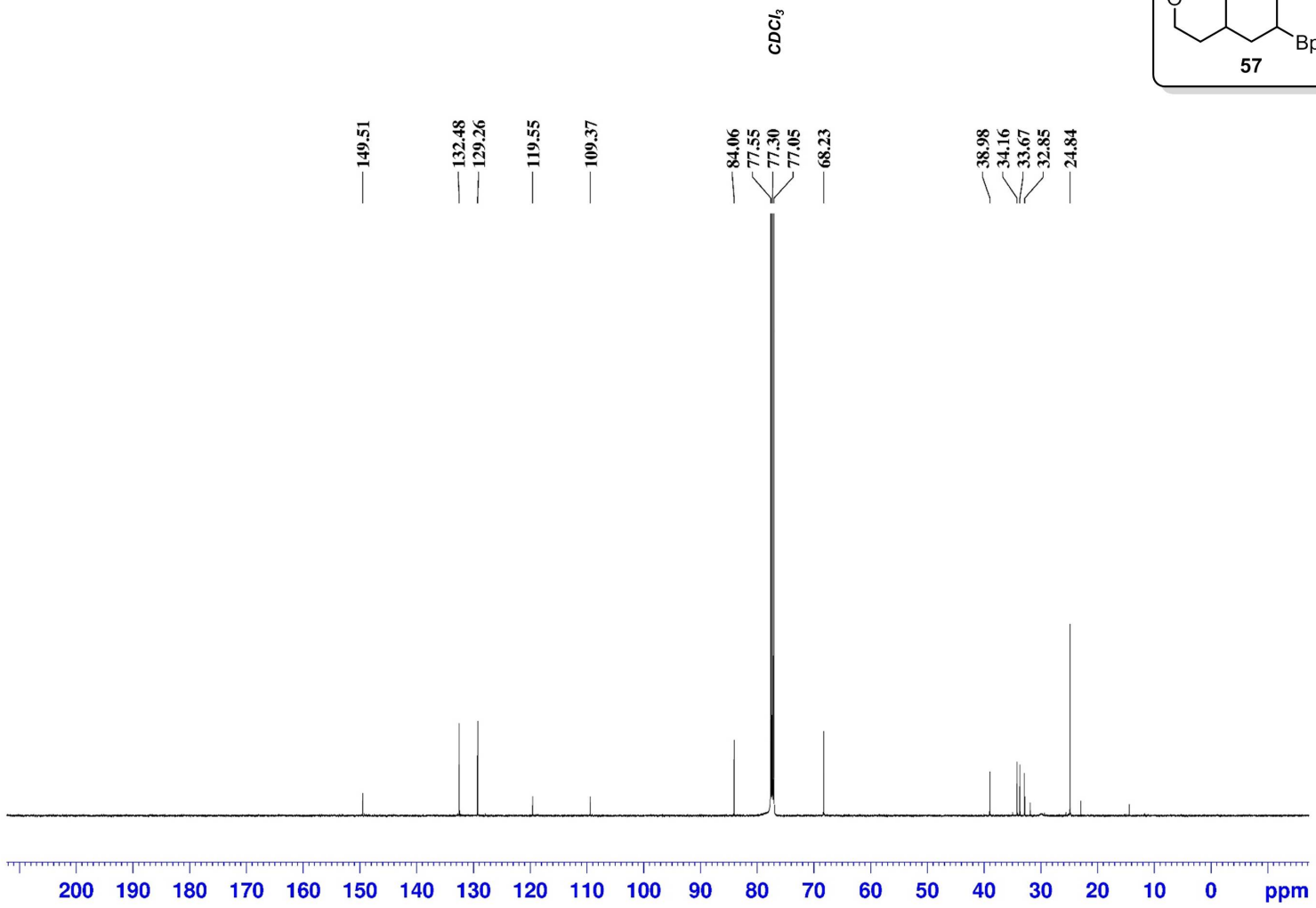
4-(2-(tetrahydro-2H-pyran-4-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile
500 MHz, $CDCl_3$



^{13}C NMR

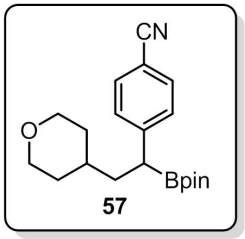
4-(2-(tetrahydro-2H-pyran-4-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile, 125 MHz,, $CDCl_3$





^{11}B NMR

4-(2-(tetrahydro-2H-pyran-4-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile, 500 MHz, $CDCl_3$



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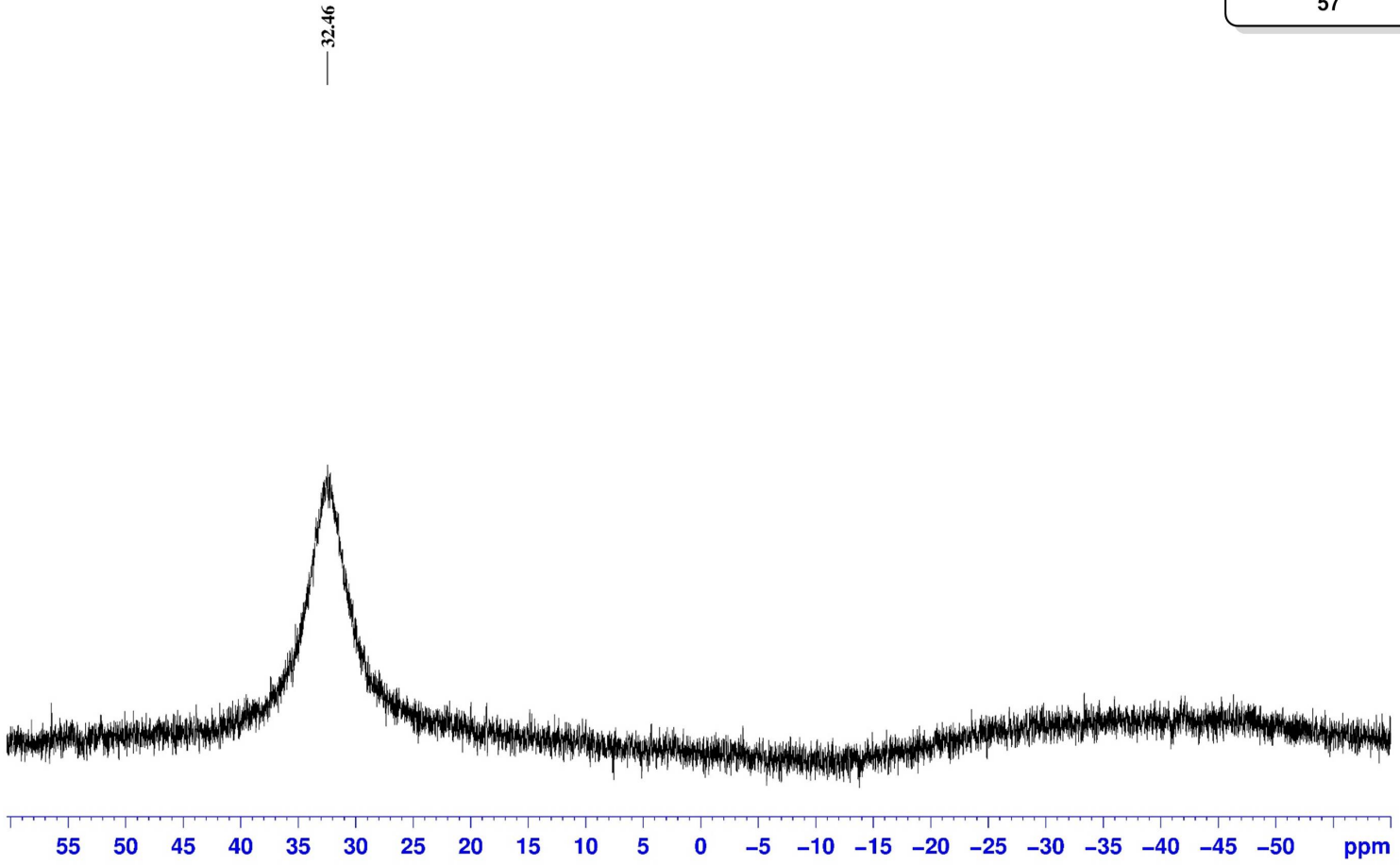
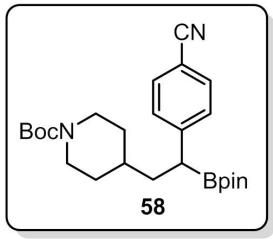
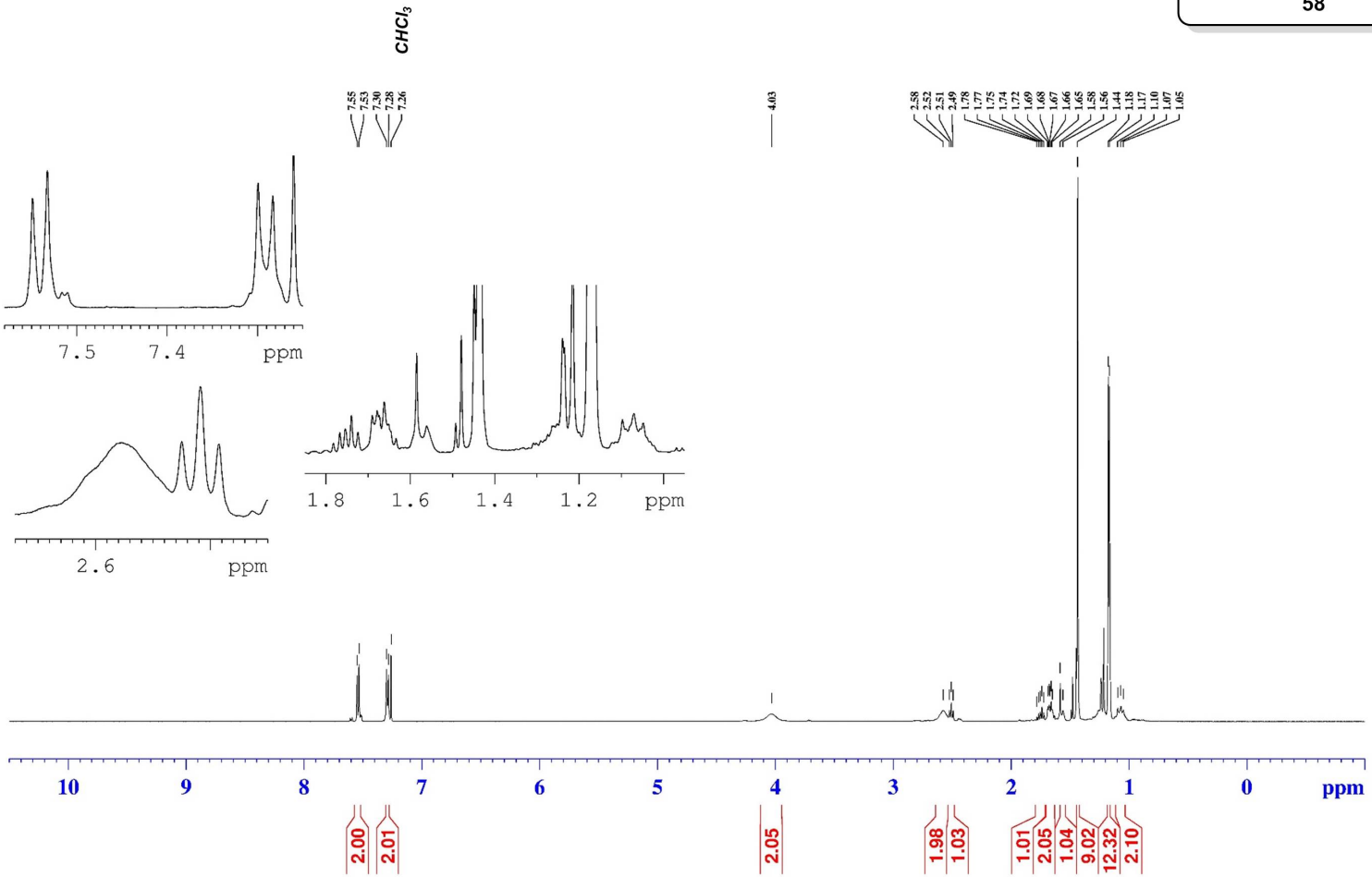


^1H NMR

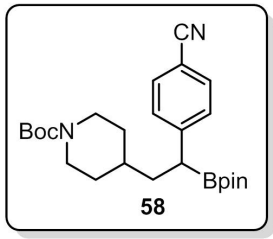


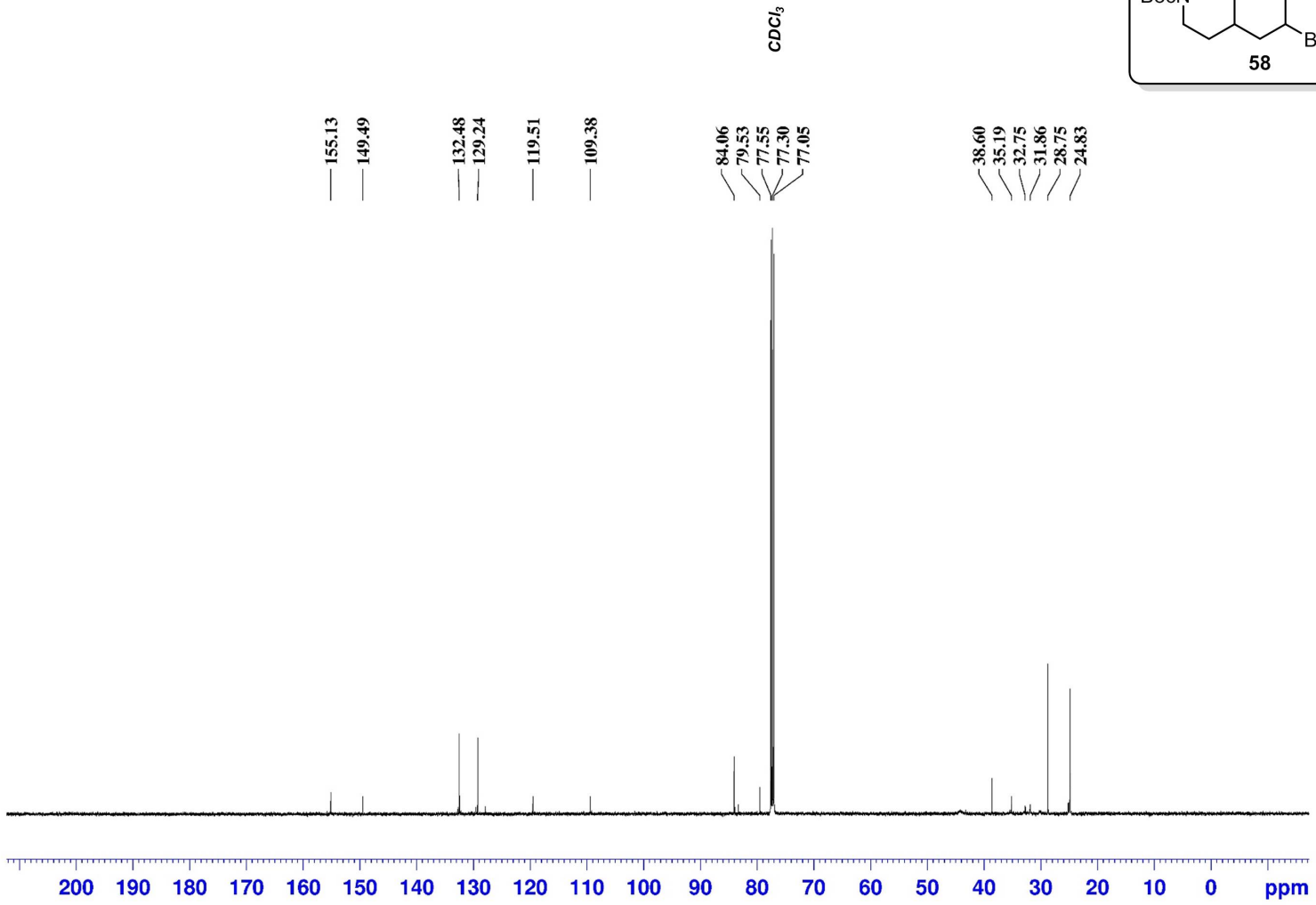
***Tert*-butyl 4-(2-(4-cyanophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)piperi dine-1-carboxylate**
500 MHz, $CDCl_3$



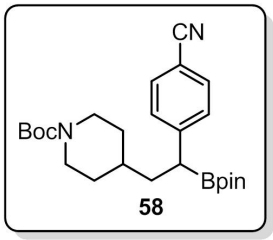
^{13}C NMR

***Tert*-butyl 4-(2-(4-cyanophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)piperi dine-1-carboxylate, 125 MHz,, $CDCl_3$**

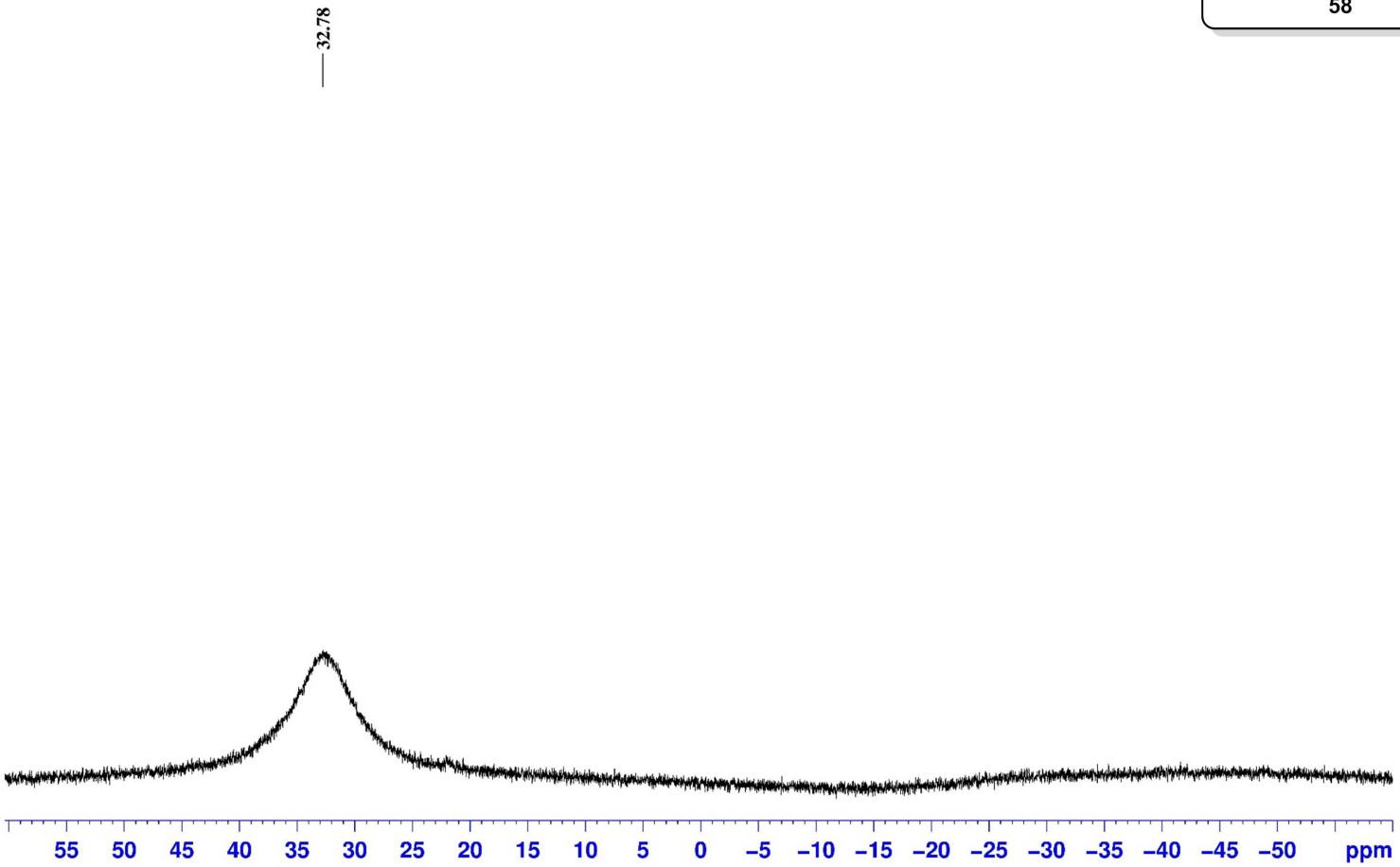




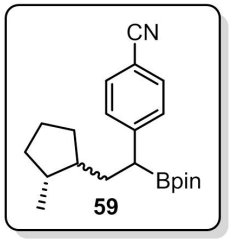
^{11}B NMR



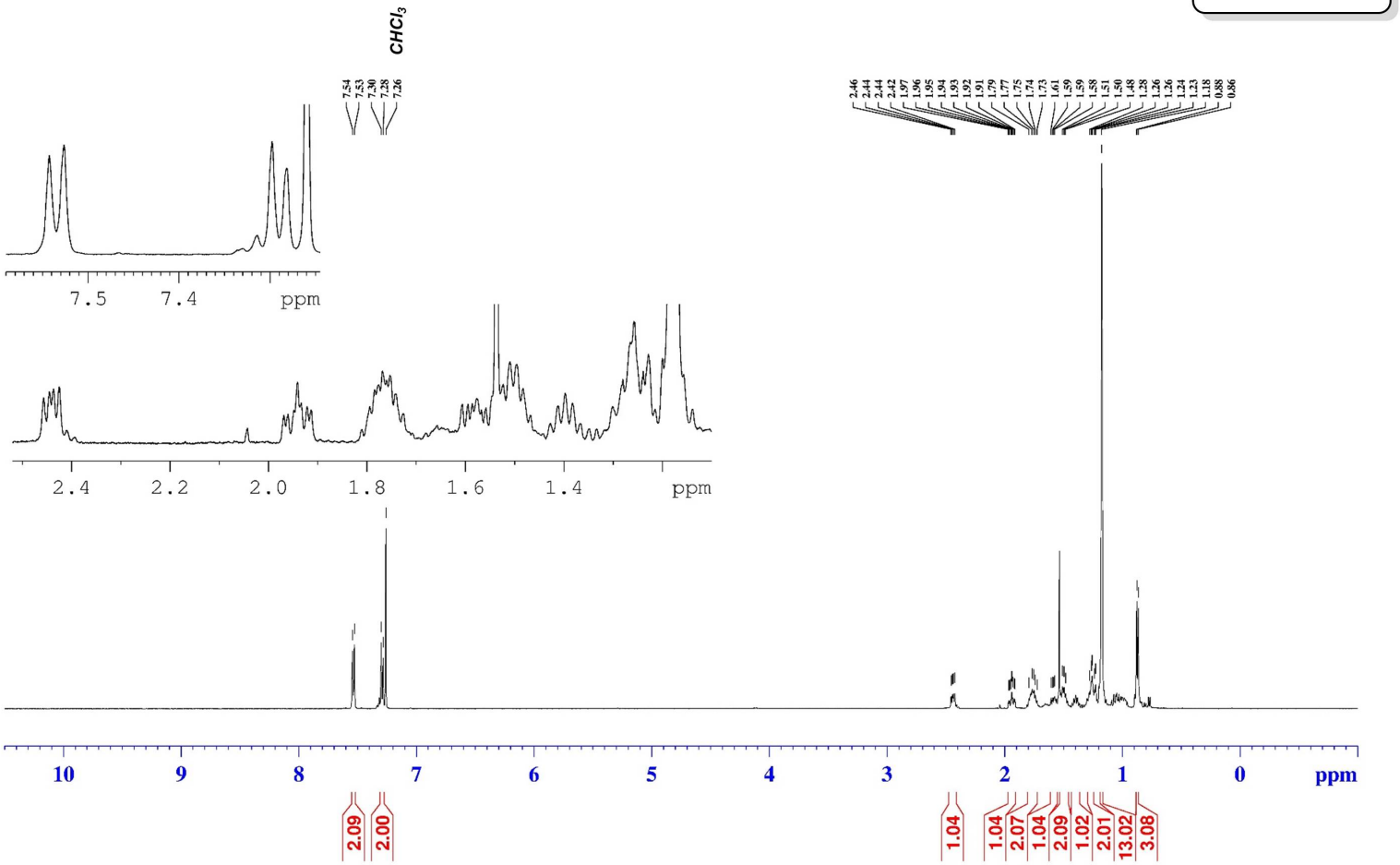
***Tert*-butyl 4-(2-(4-cyanophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)piperi dine-1-carboxylate, 500 MHz, $CDCl_3$**



^{1}H NMR

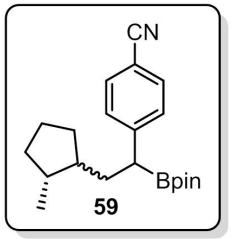


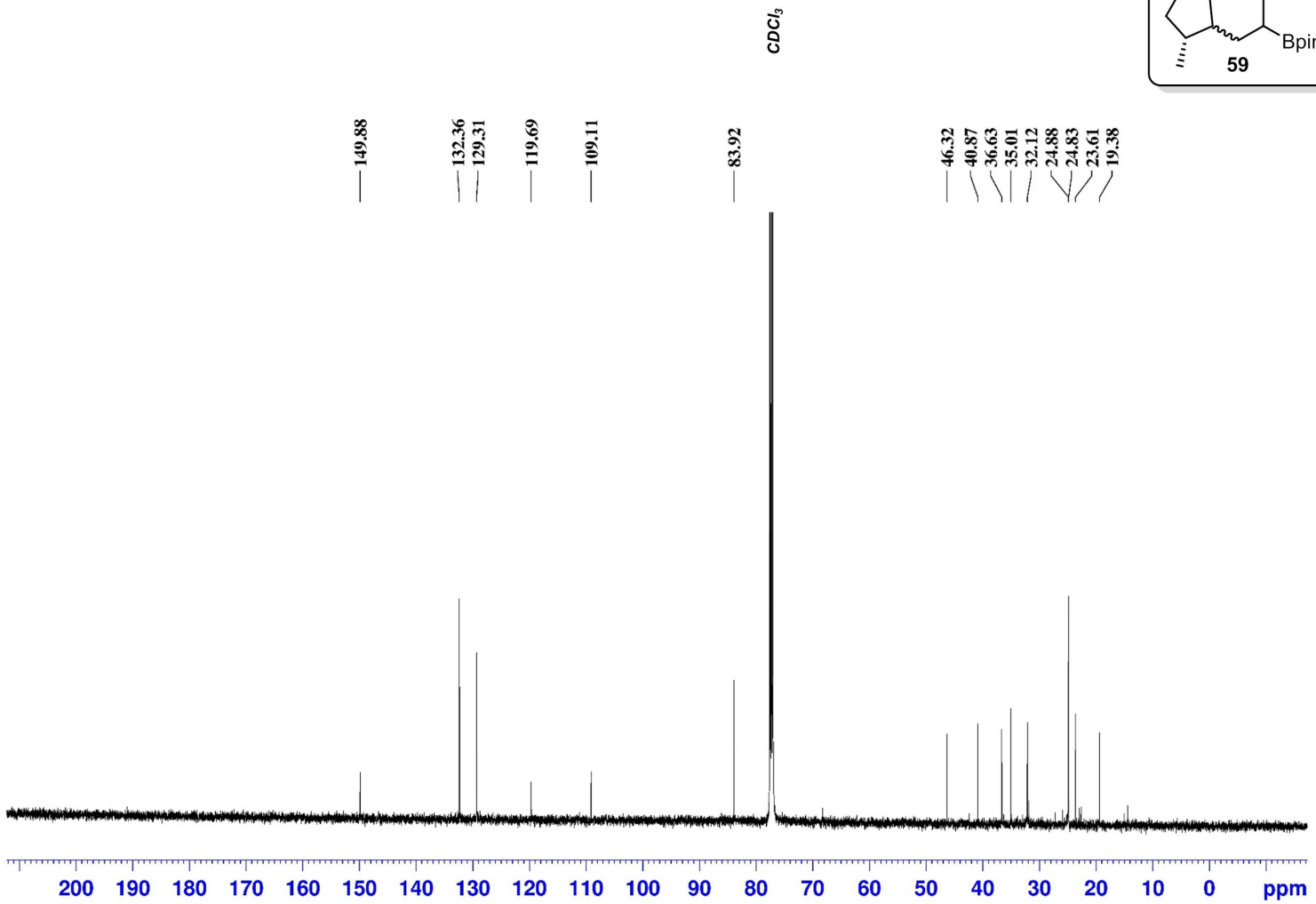
4-(2-(2-methylcyclopentyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile
500 MHz, $CDCl_3$



^{13}C NMR

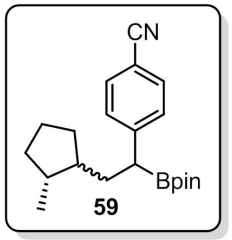
4-(2-(2-methylcyclopentyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile, 125 MHz,, $CDCl_3$





^{11}B NMR

4-(2-(2-methylcyclopentyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile, 500 MHz, $CDCl_3$



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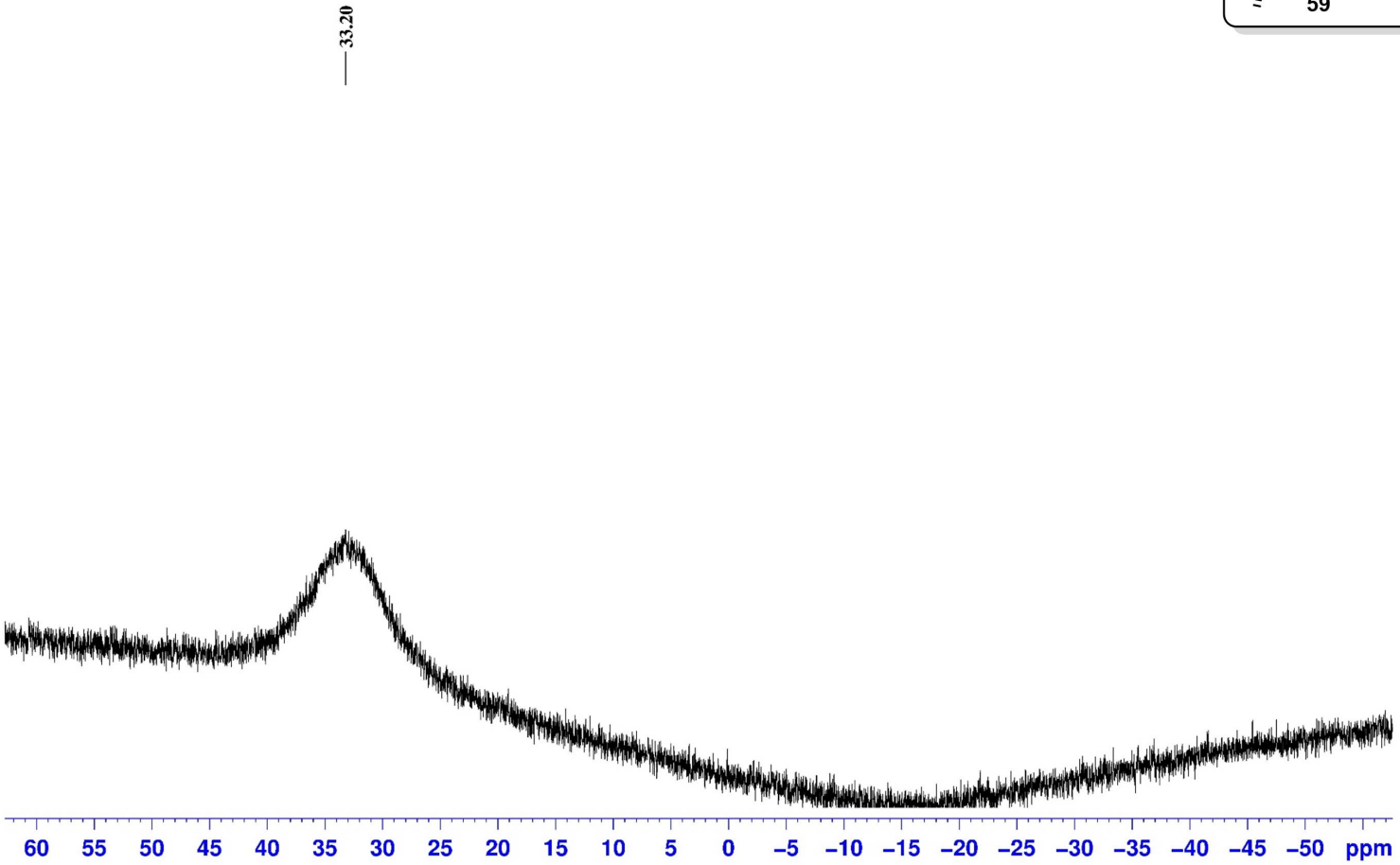
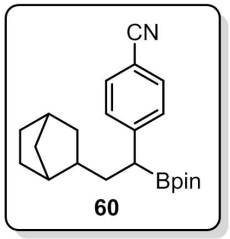
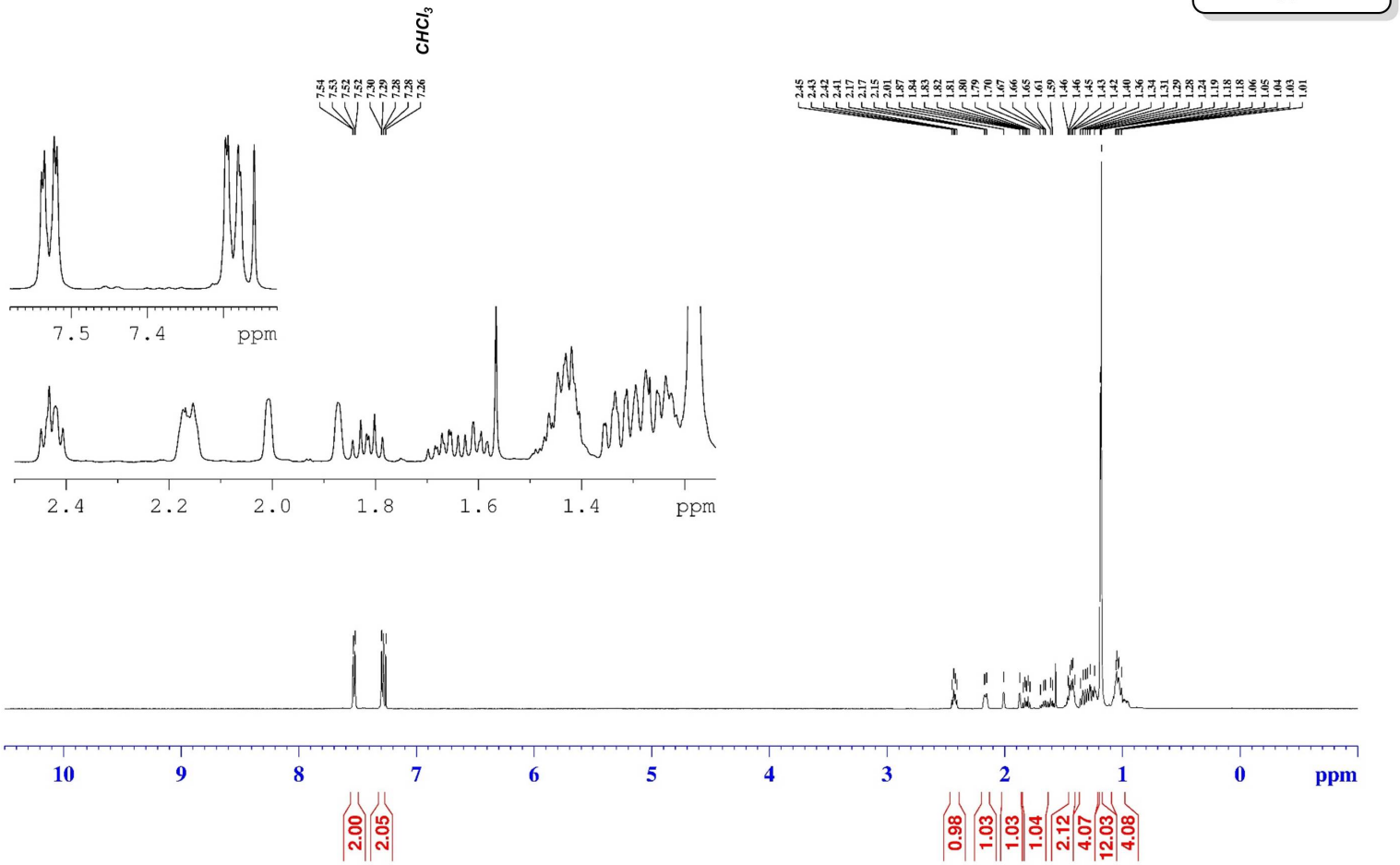


^1H NMR

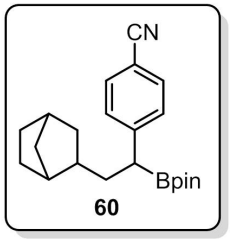


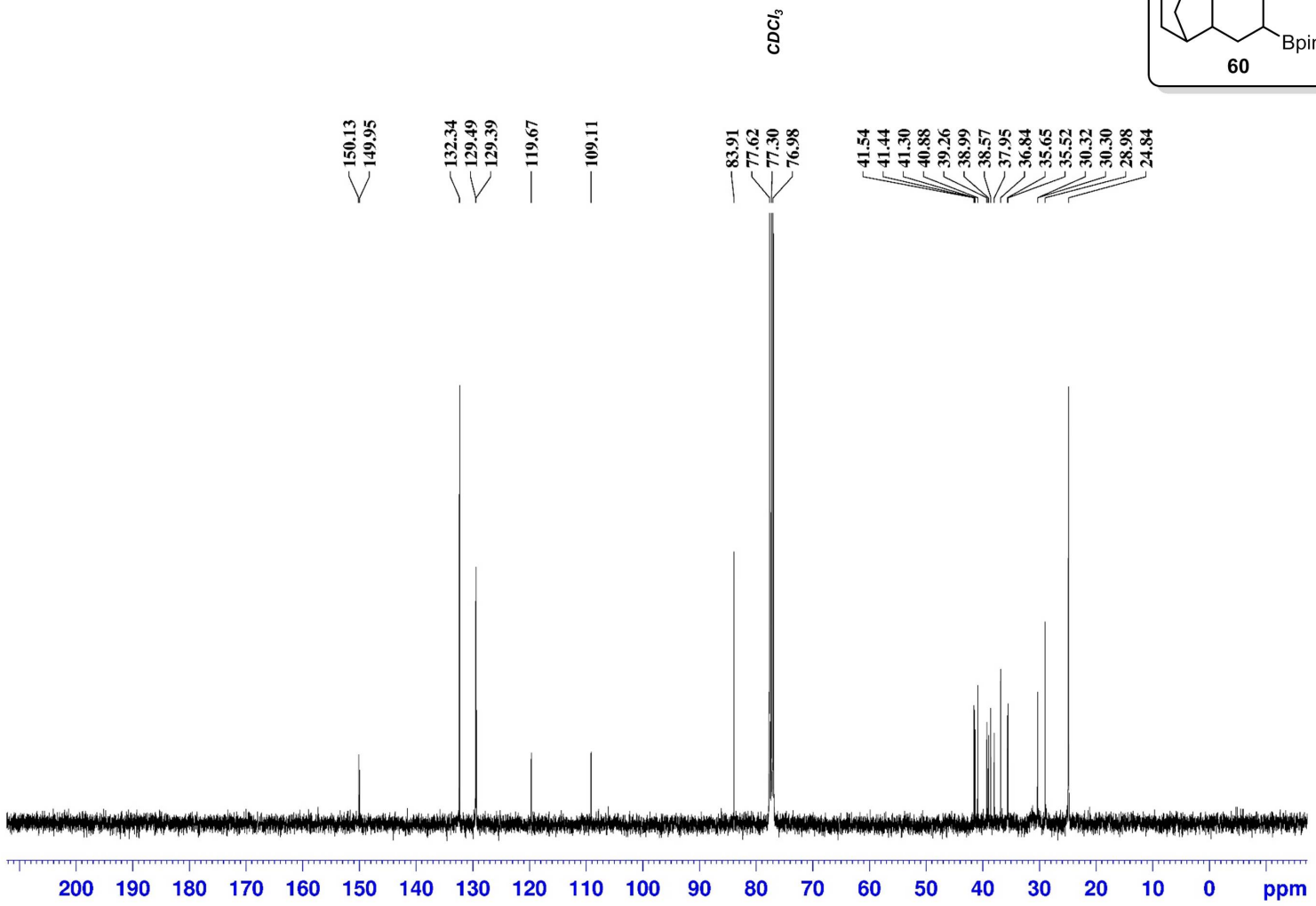
4-(2-(bicyclo[2.2.1]heptan-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile
500 MHz, $CDCl_3$



^{13}C NMR

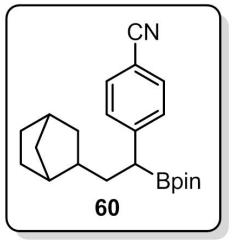
4-(2-(bicyclo[2.2.1]heptan-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile, 125 MHz,, $CDCl_3$





^{11}B NMR

4-(2-(bicyclo[2.2.1]heptan-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile, 500 MHz, $CDCl_3$



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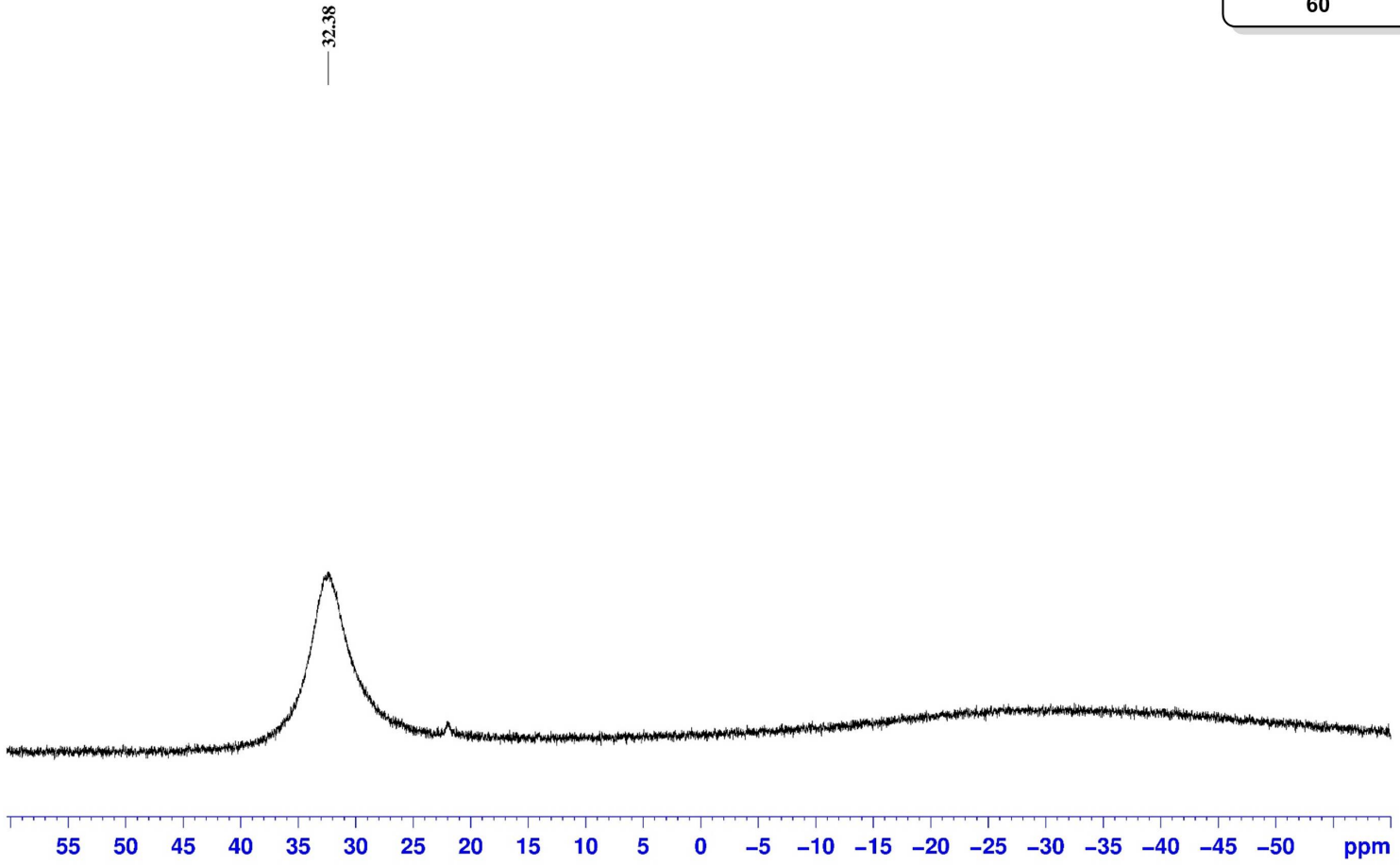
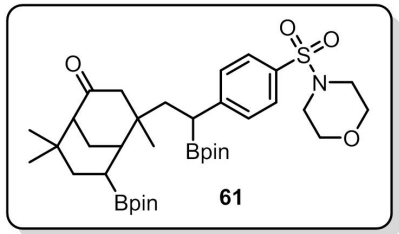


^1H NMR

4,8,8-trimethyl-4-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[3.3.1]nonan-2-one
500 MHz, $CDCl_3$



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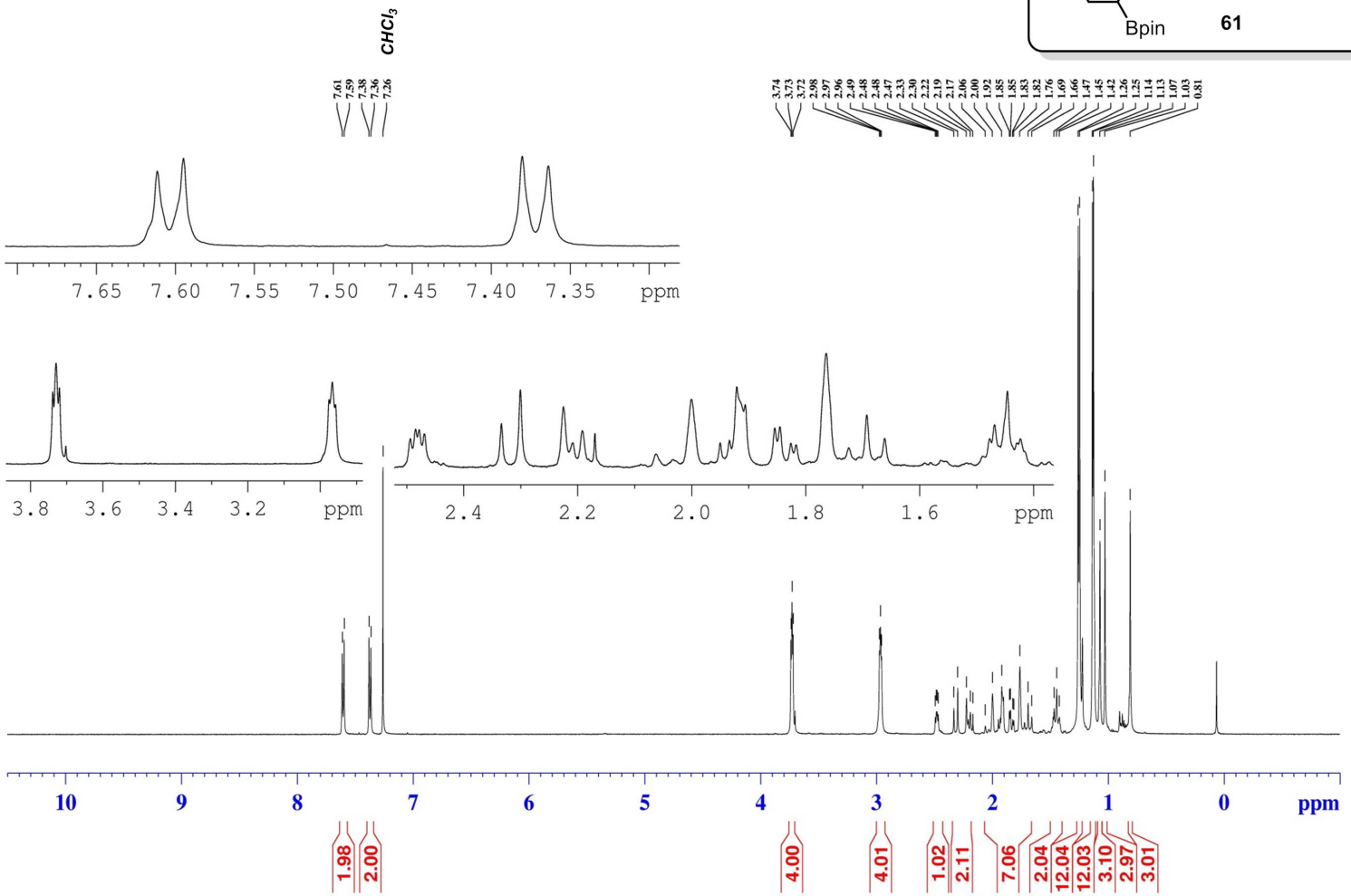
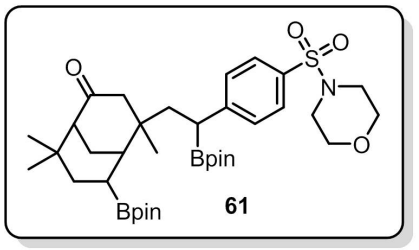


^{13}C NMR

4,8,8-Trimethyl-4-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[3.3.1]nonan-2-one
125 MHz, $CDCl_3$



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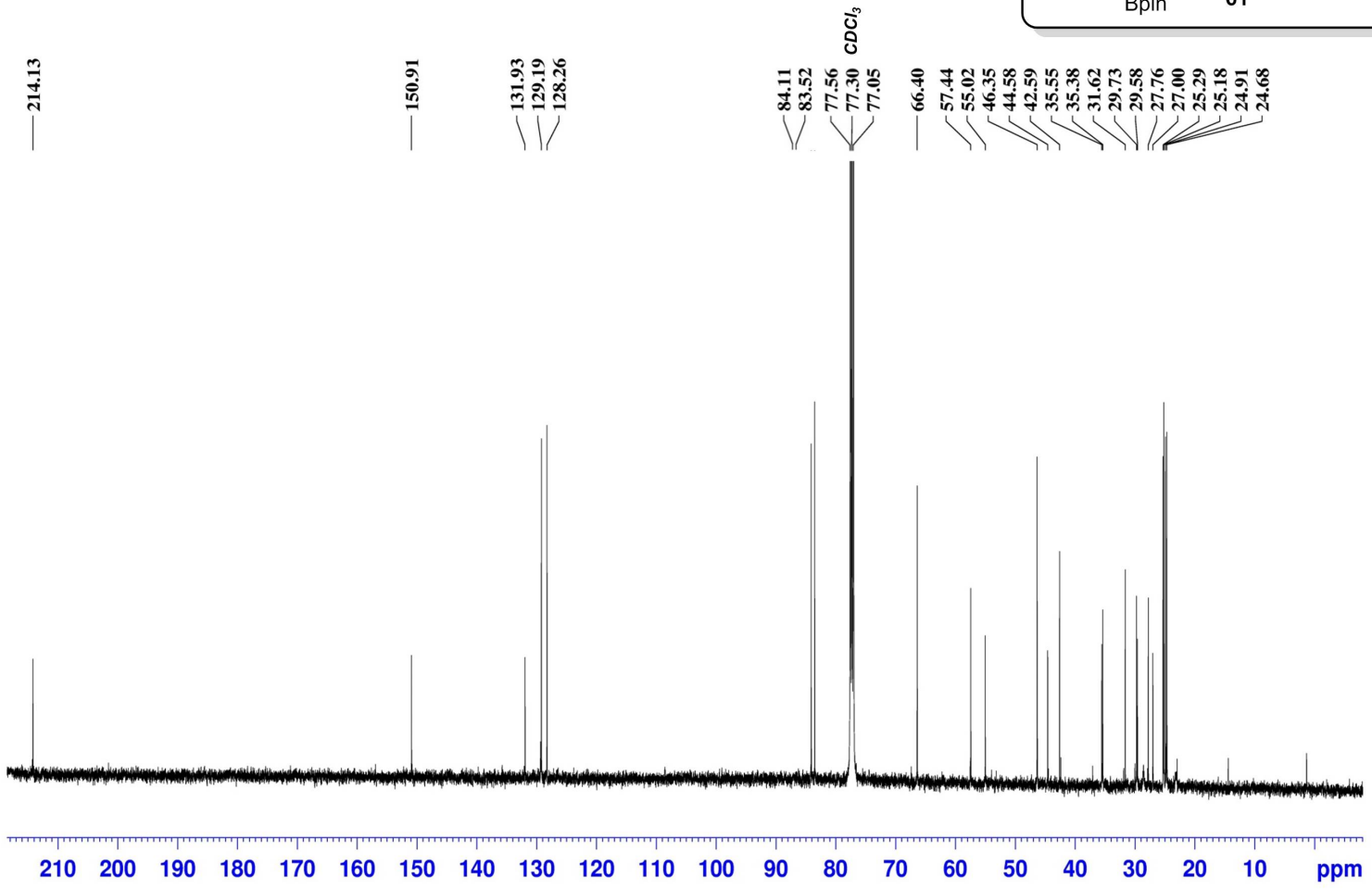
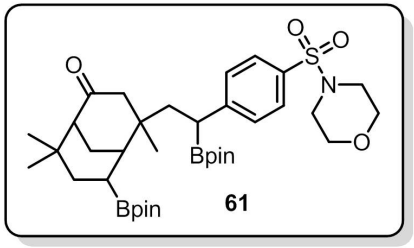


^{11}B NMR

4,8,8-trimethyl-4-(2-(4-(morpholinosulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[3.3.1]nonan-2-one
128 MHz, $CDCl_3$



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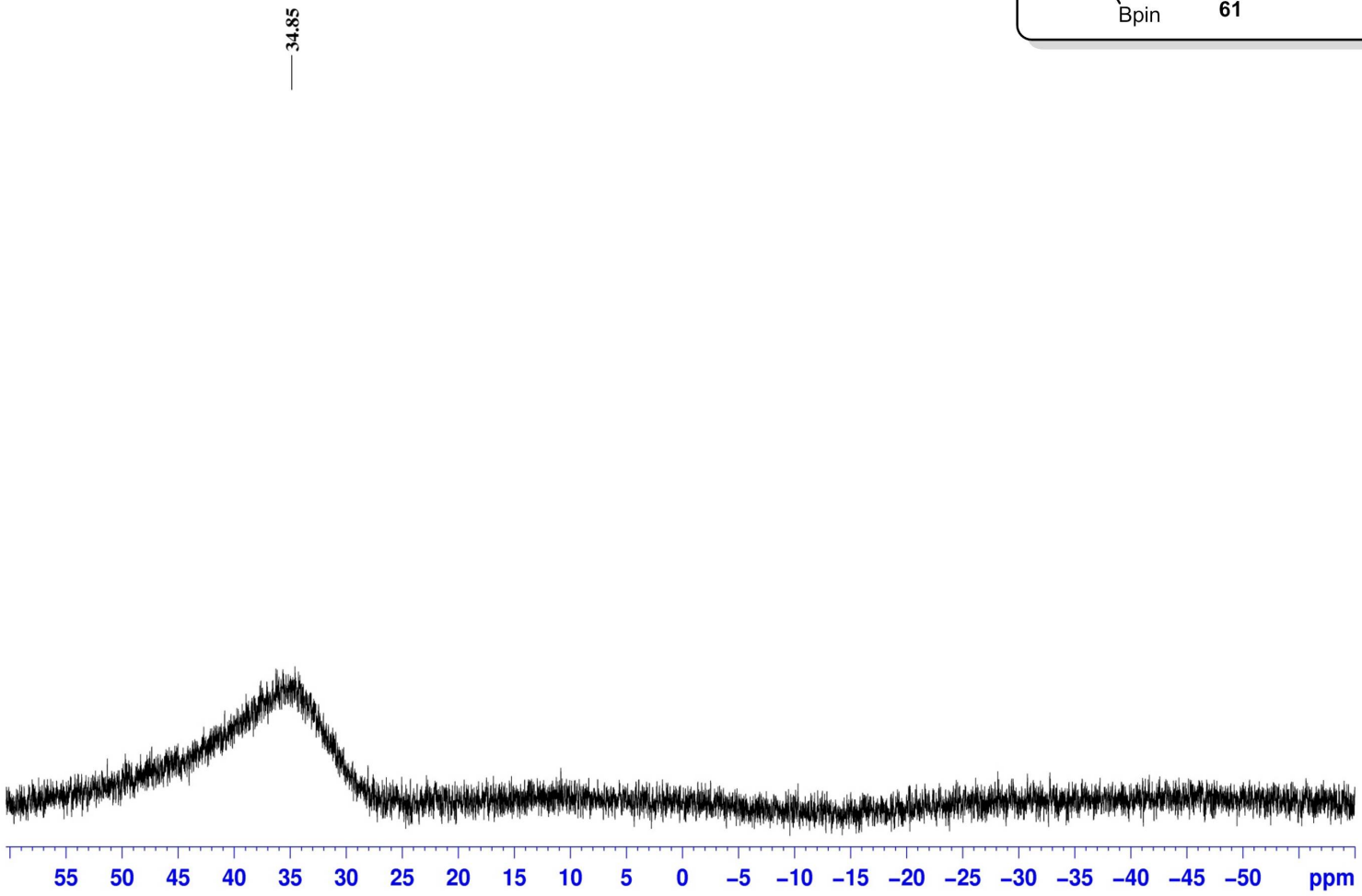
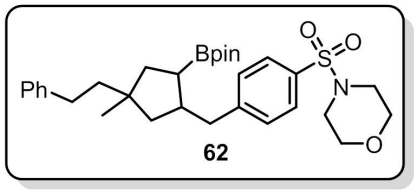


^1H NMR

4-((4-((4-methyl-4-phenethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)methyl)phenyl)sulfonyl)morpholine
500 MHz, $CDCl_3$



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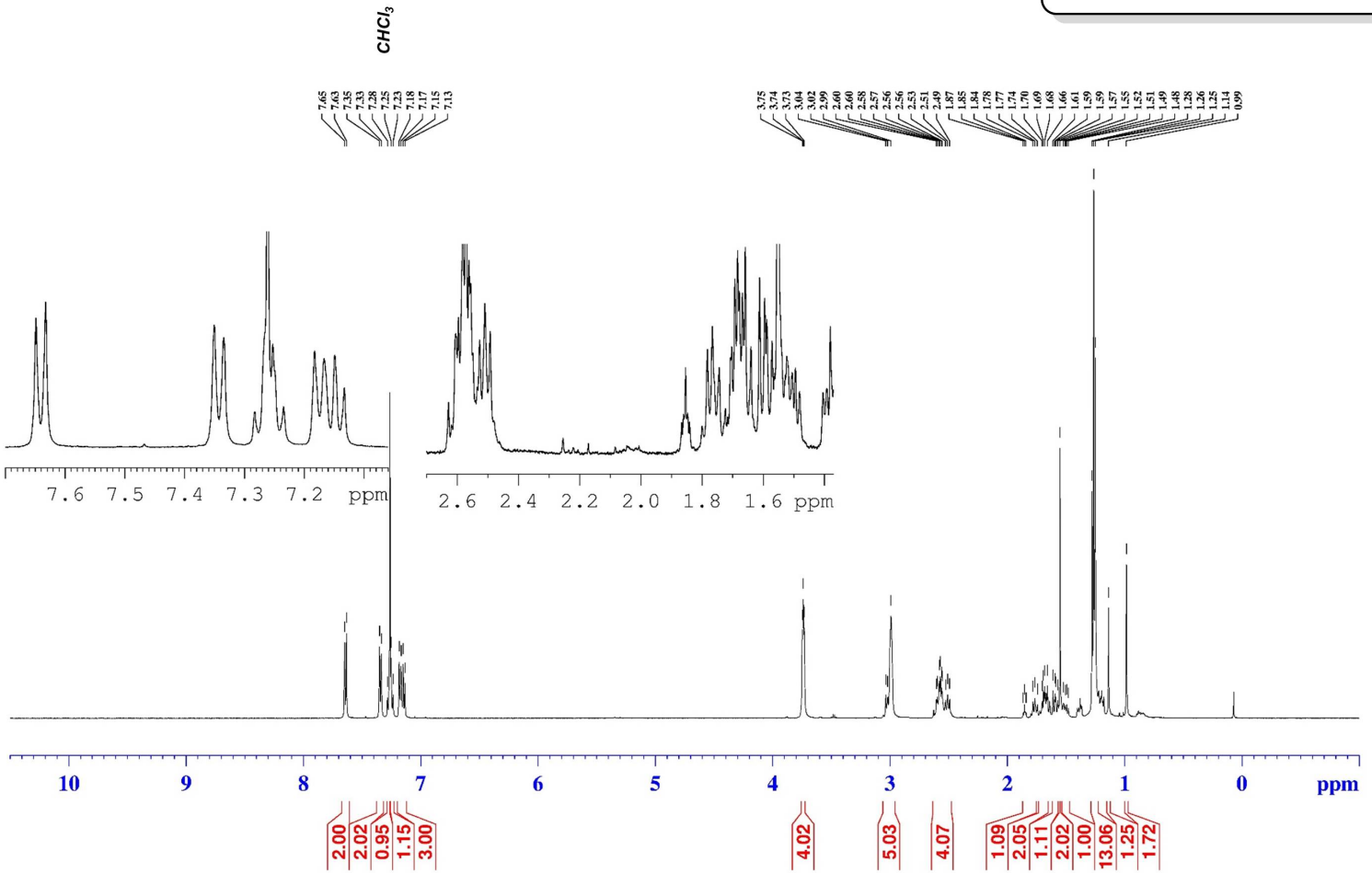
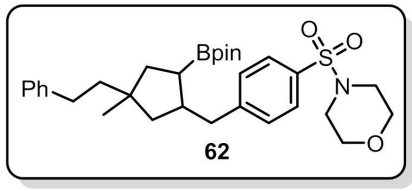


^{13}C NMR

4-((4-((4-Methyl-4-phenethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)methyl)phenyl)sulfonyl)morpholine
125 MHz, $CDCl_3$



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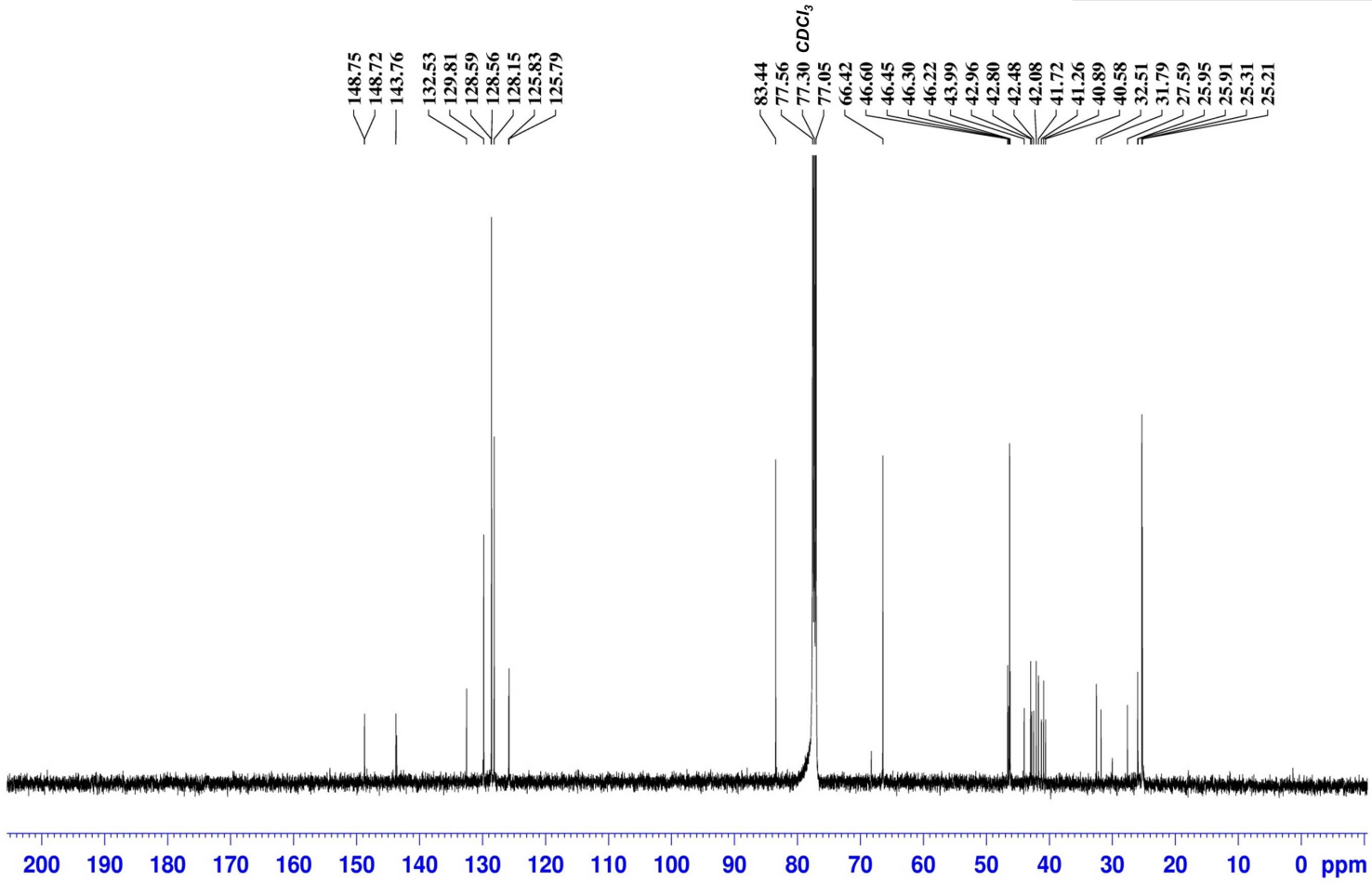
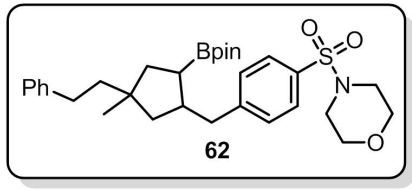


^{11}B NMR

4-((4-((4-methyl-4-phenethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)methyl)phenyl)sulfonyl)morpholine
128 MHz, $CDCl_3$



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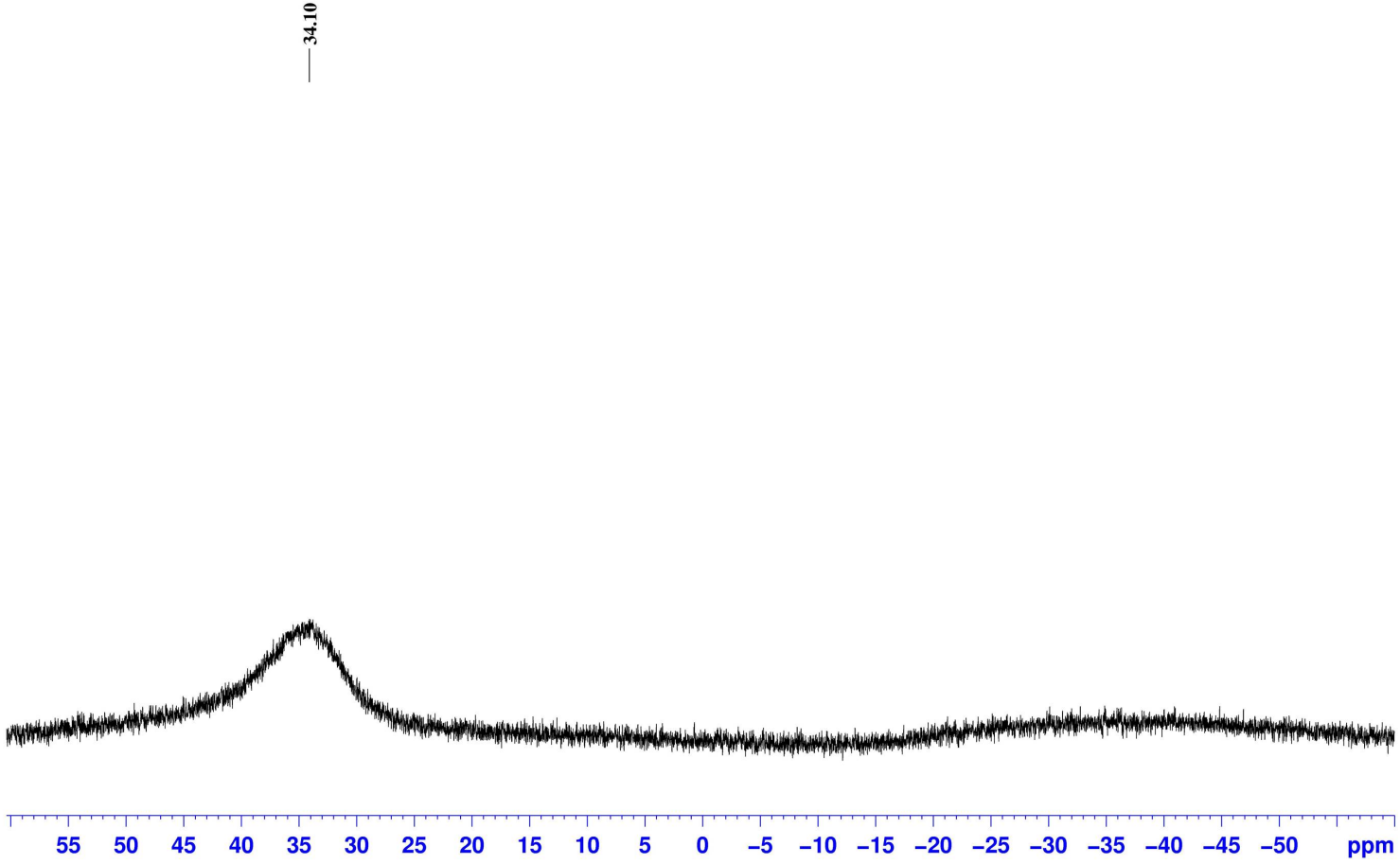
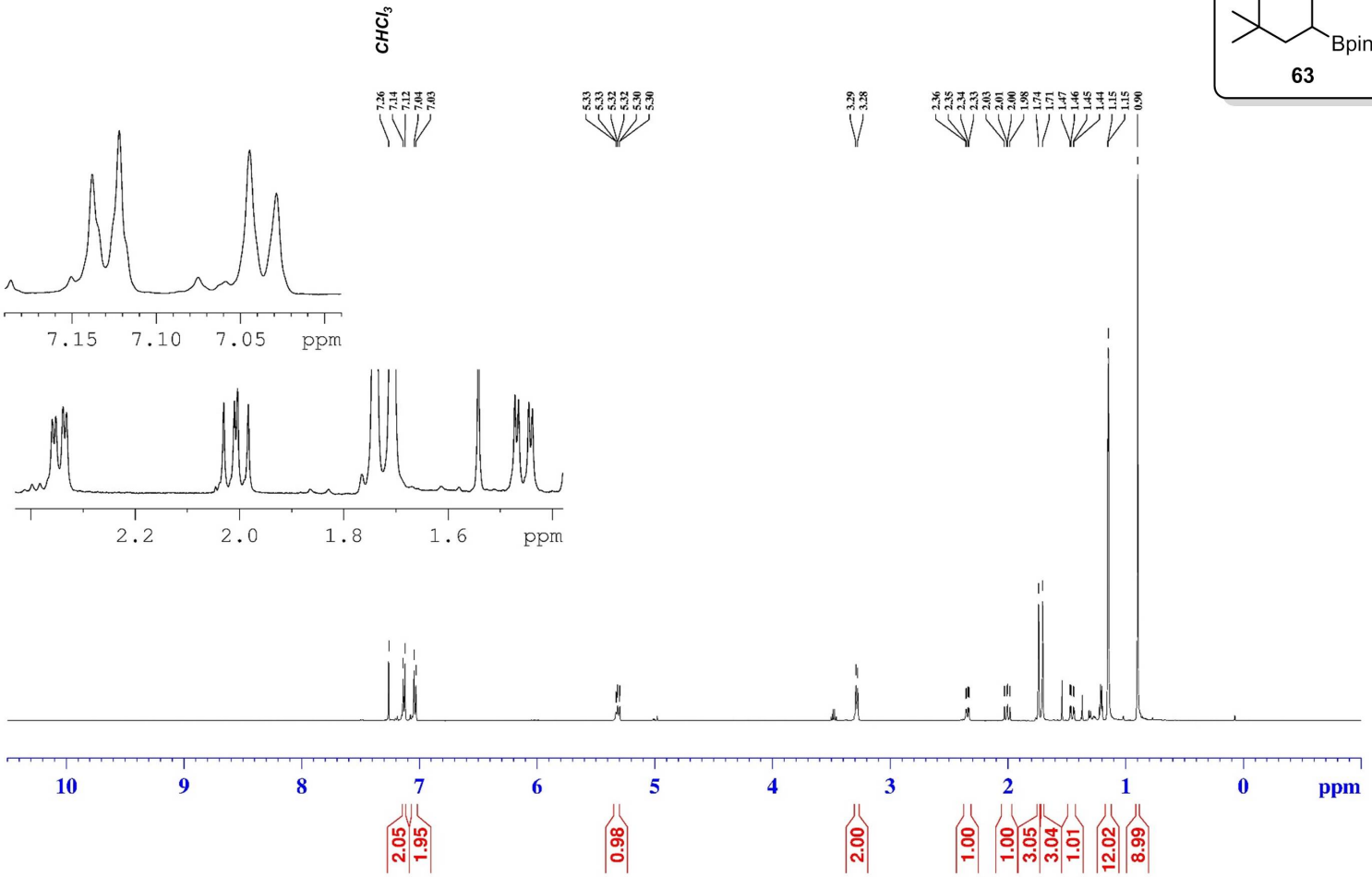
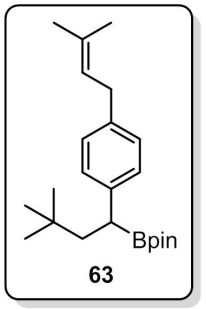


^1H NMR

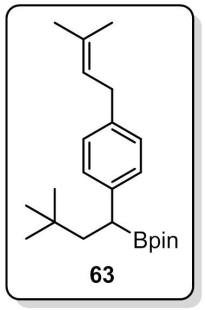
2-(3,3-dimethyl-1-(4-(3-methylbut-2-en-1-yl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
500 MHz, $CDCl_3$

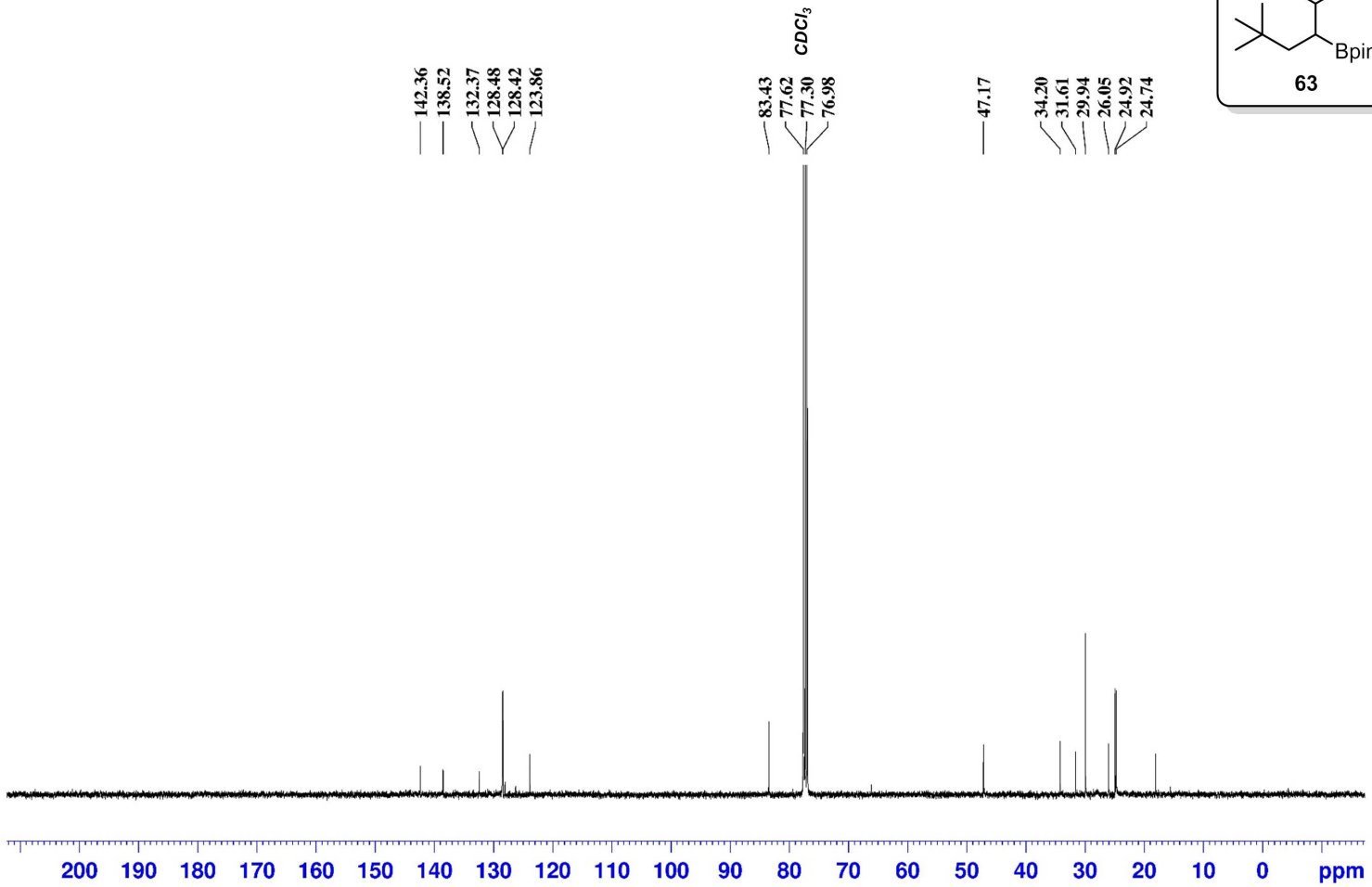




^{13}C NMR

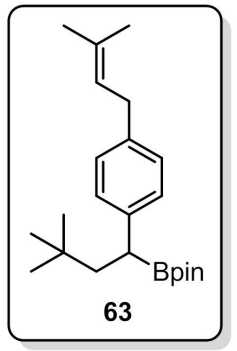
2-(3,3-dimethyl-1-(4-(3-methylbut-2-en-1-yl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 125 MHz, $CDCl_3$





^{11}B NMR

2-(3,3-dimethyl-1-(4-(3-methylbut-2-en-1-yl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 128 MHz, $CDCl_3$



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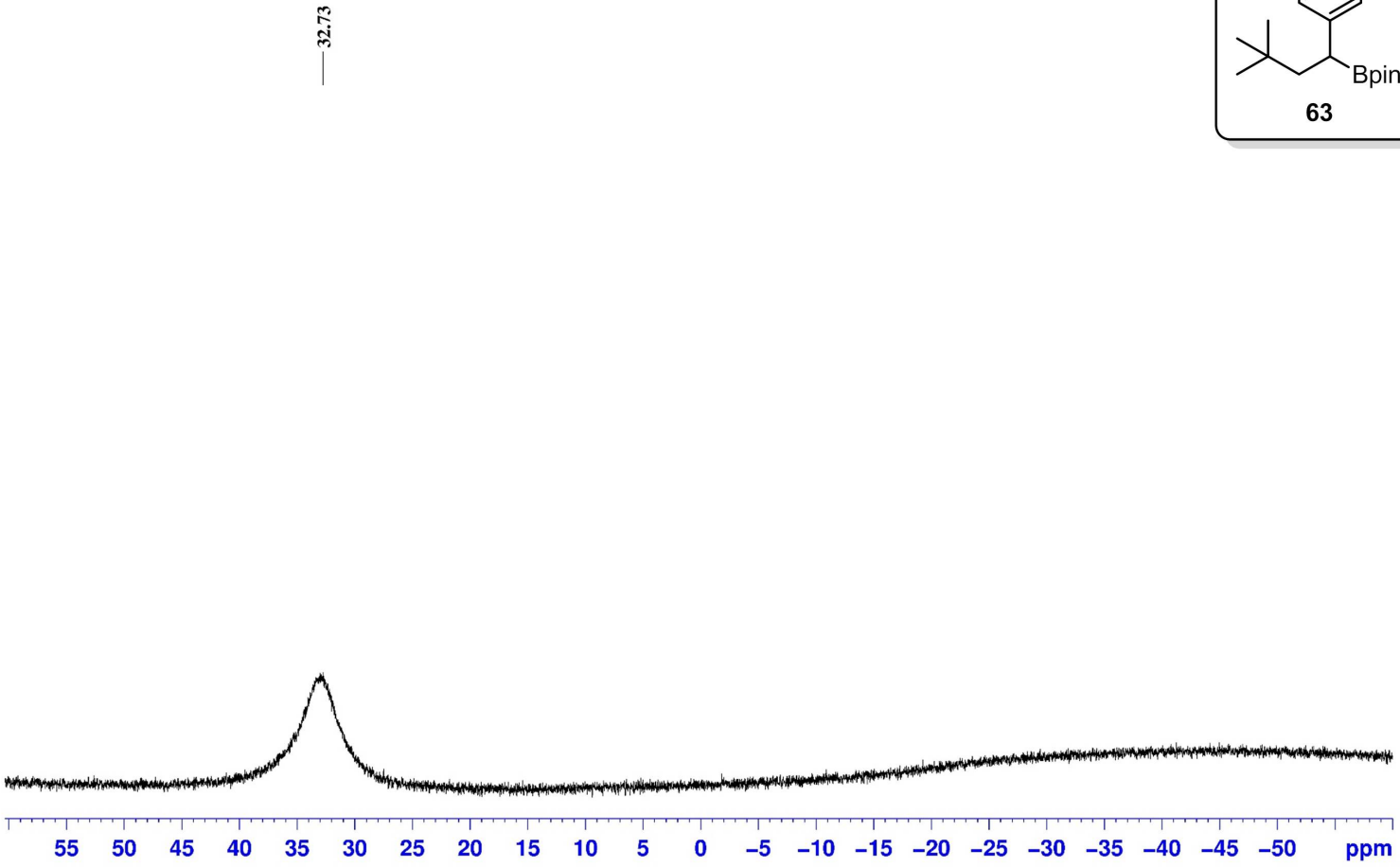
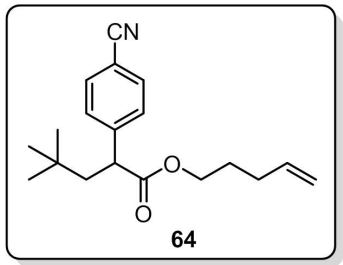
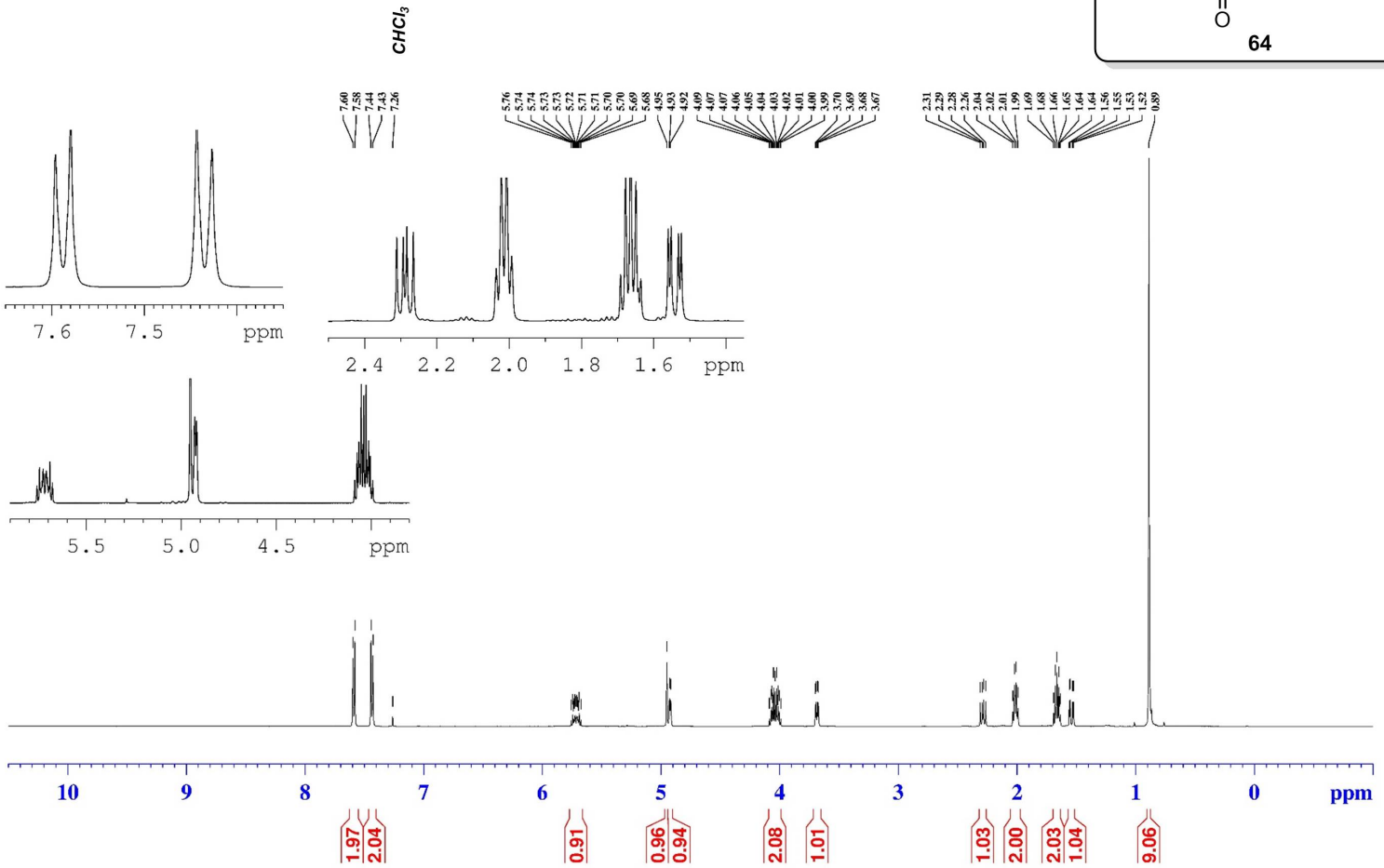


^1H NMR

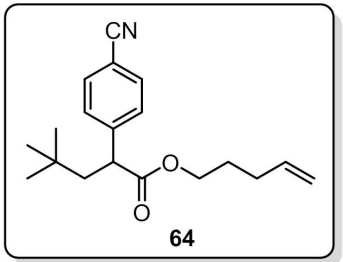
Pent-4-en-1-yl 2-(4-cyanophenyl)-4,4-dimethylpentanoate
500 MHz, $CDCl_3$

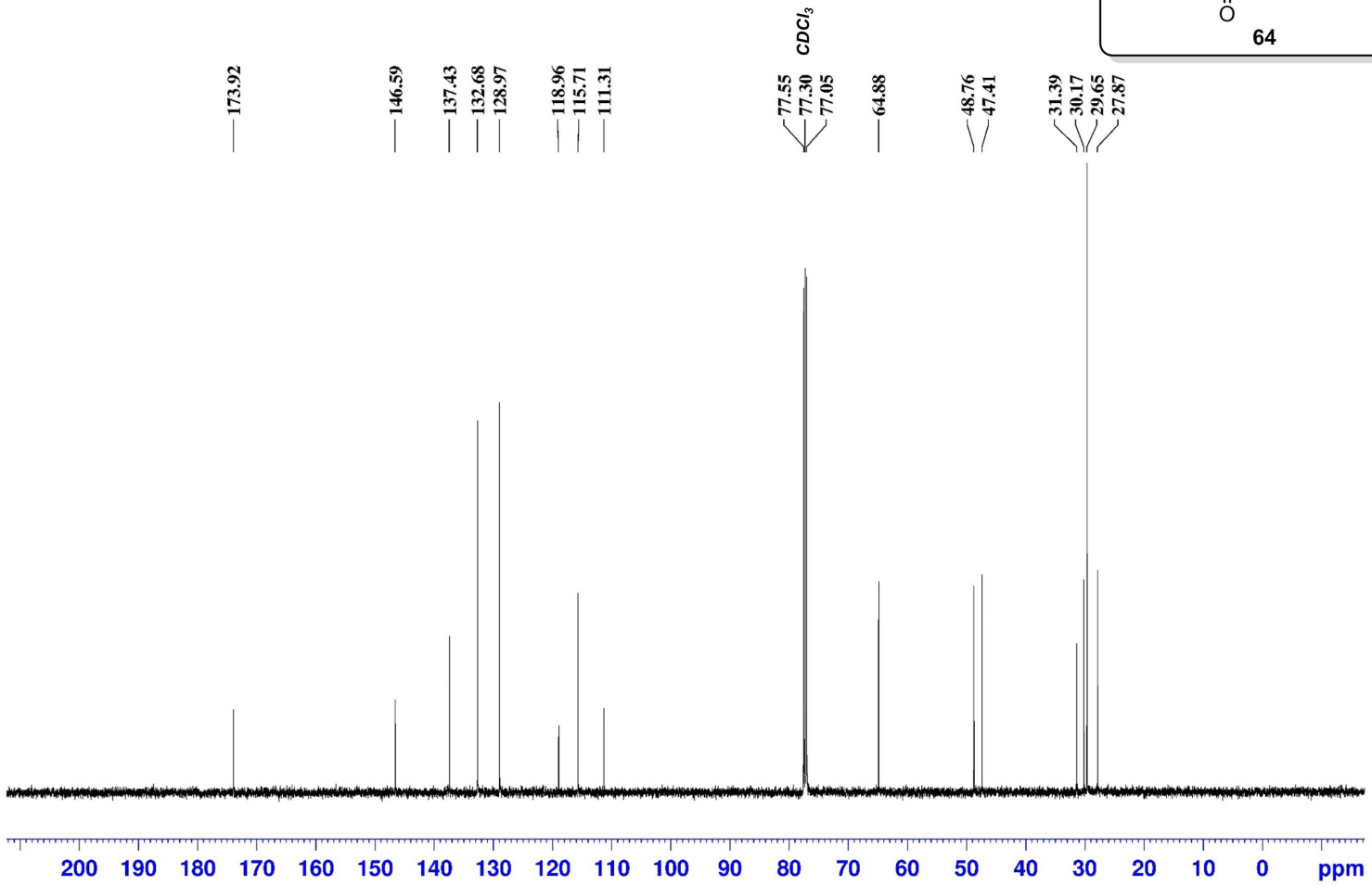




Pent-4-en-1-yl 2-(4-cyanophenyl)-4,4-dimethylpentanoate,
125 MHz, $CDCl_3$

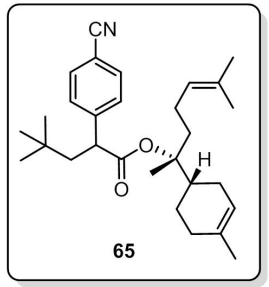
^{13}C NMR

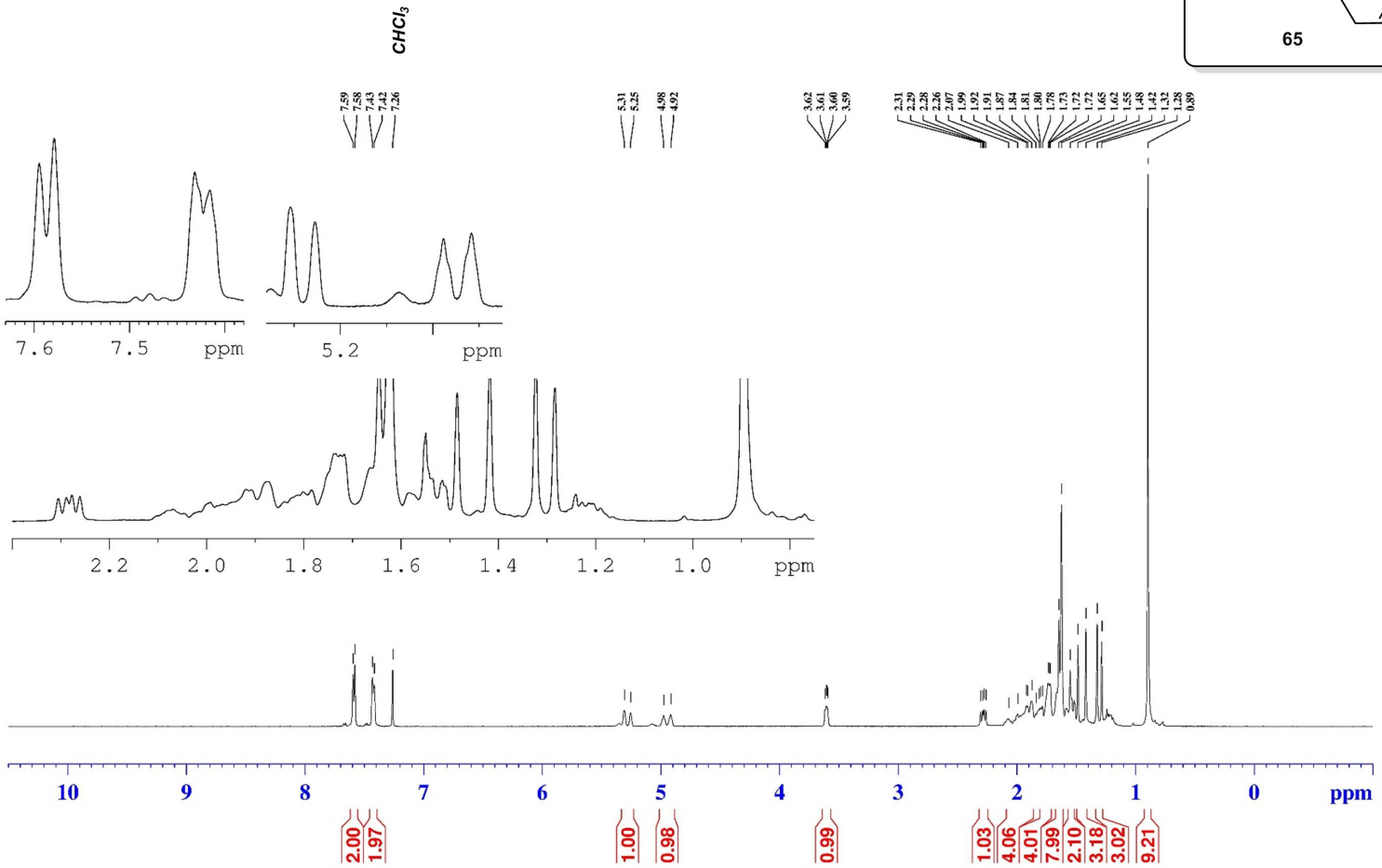




^{1}H NMR

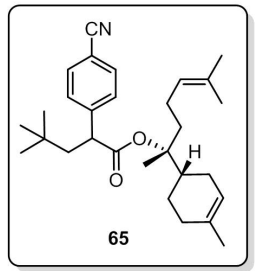
(*S*)-6-methyl-2-((*S*)-4-methylcyclohex-3-en-1-yl)hept-5-en-2-yl 2-(4-cyanophenyl)-4,4-dimethylpentanoate
500 MHz, $CDCl_3$

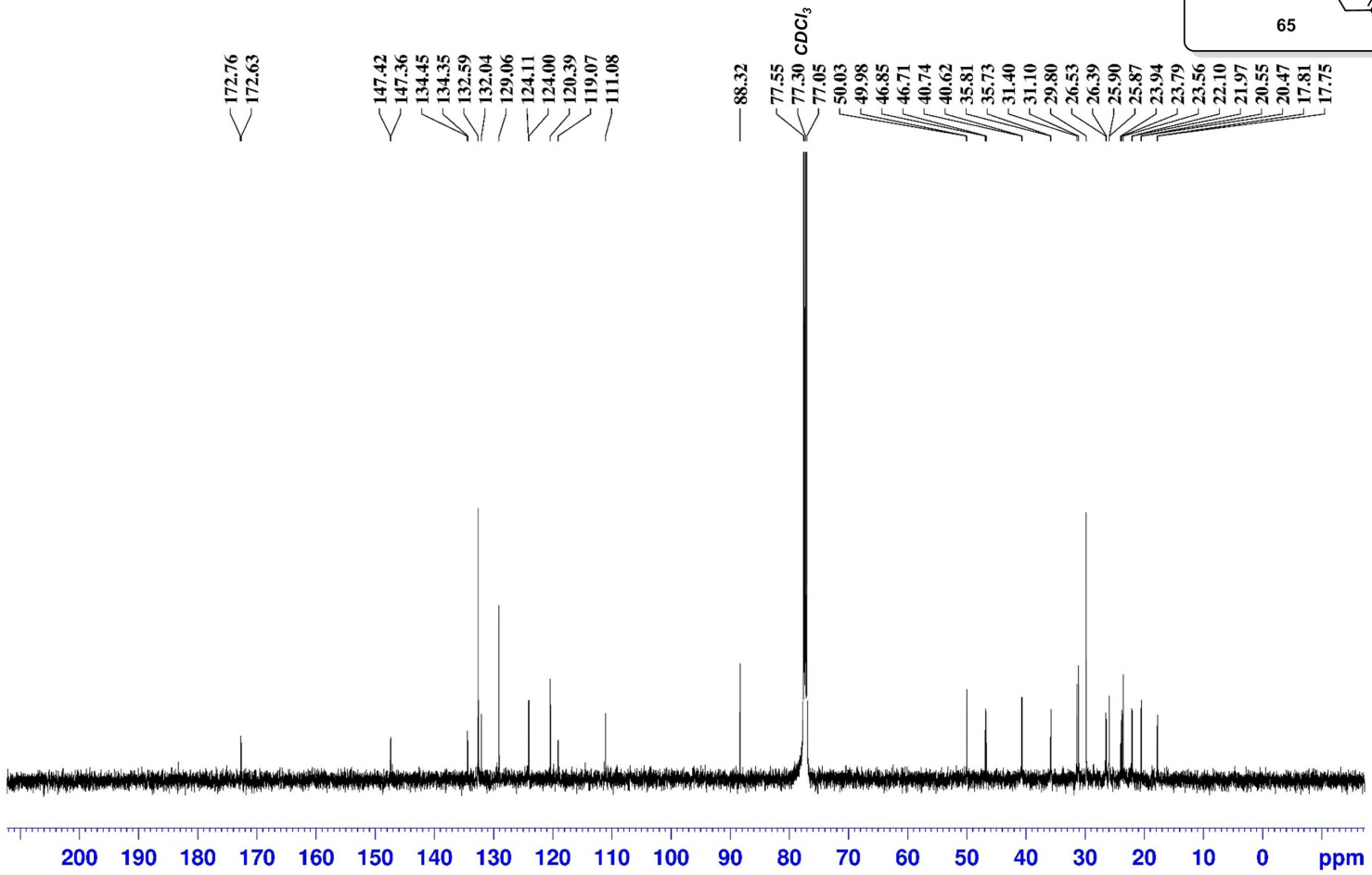




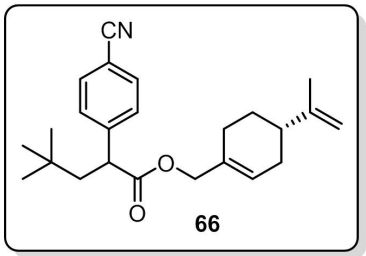
^{13}C NMR

(*S*)-6-methyl-2-((*S*)-4-methylcyclohex-3-en-1-yl)hept-5-en-2-yl 2-(4-cyanophenyl)-4,4-dimethylpentanoate, 125 MHz, $CDCl_3$

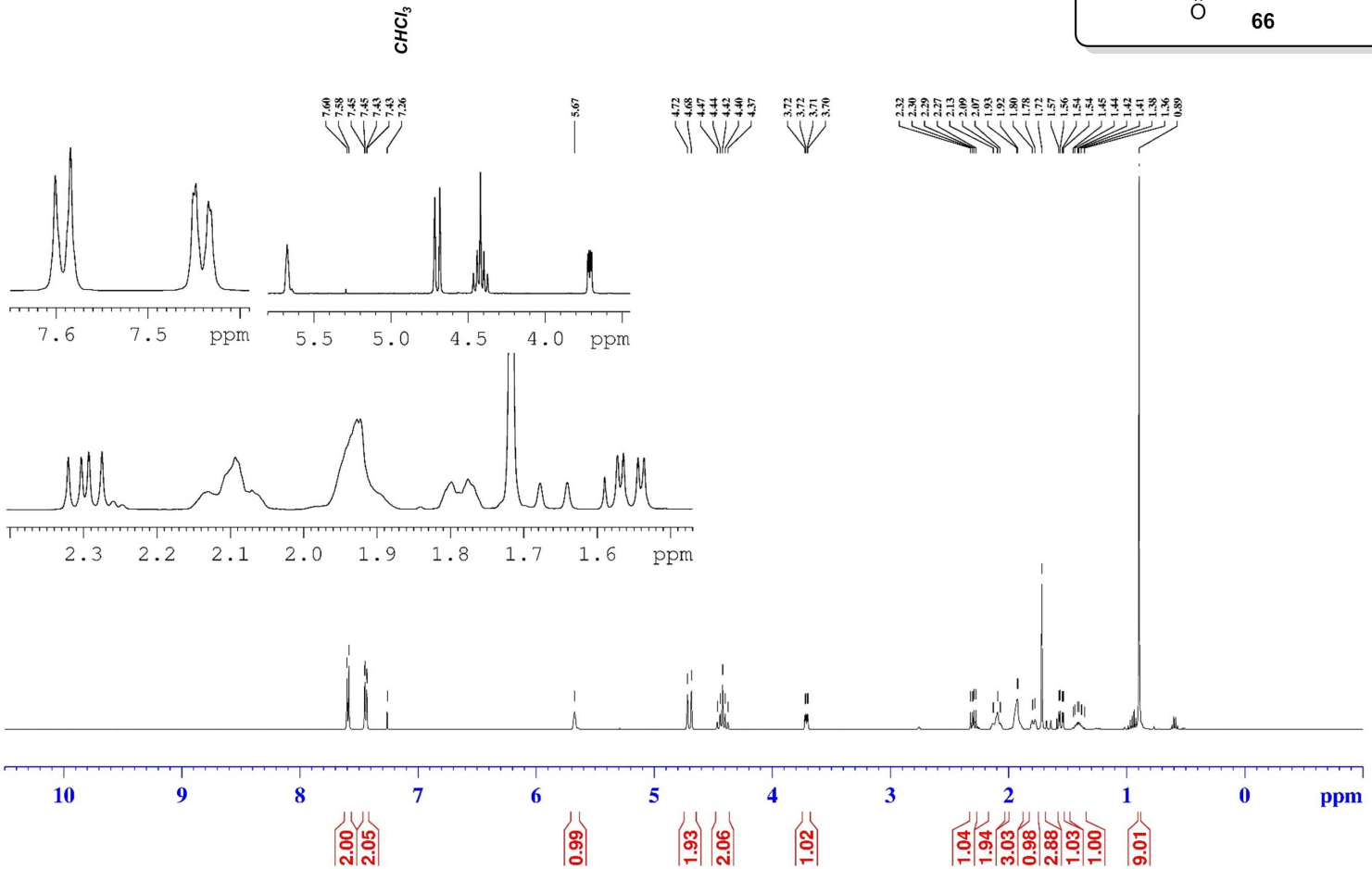




^1H NMR

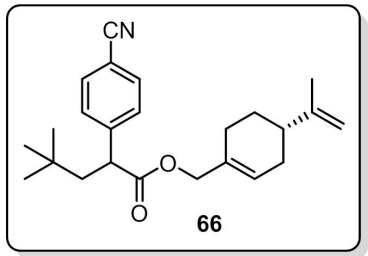


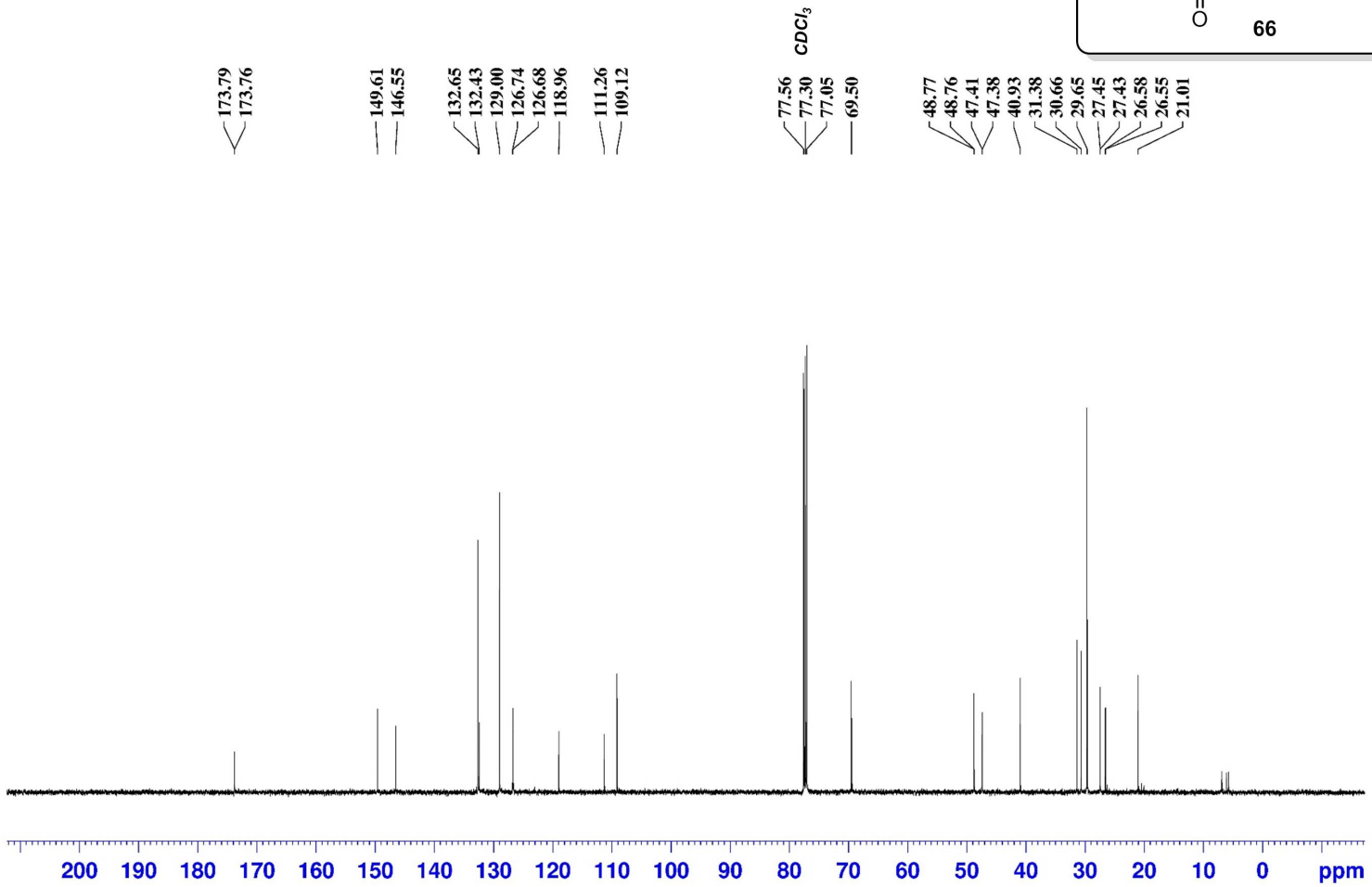
((*S*)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 2-(4-cyanophenyl)-4,4-dimethylpentanoate
500 MHz, $CDCl_3$



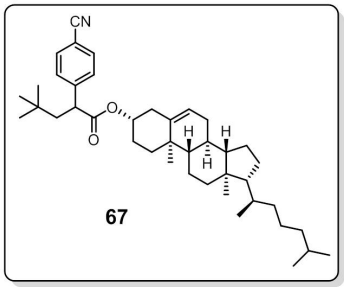
^{13}C NMR

((*S*)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 2-(4-cyanophenyl)-4,4-dimethylpentanoate, 125 MHz, $CDCl_3$

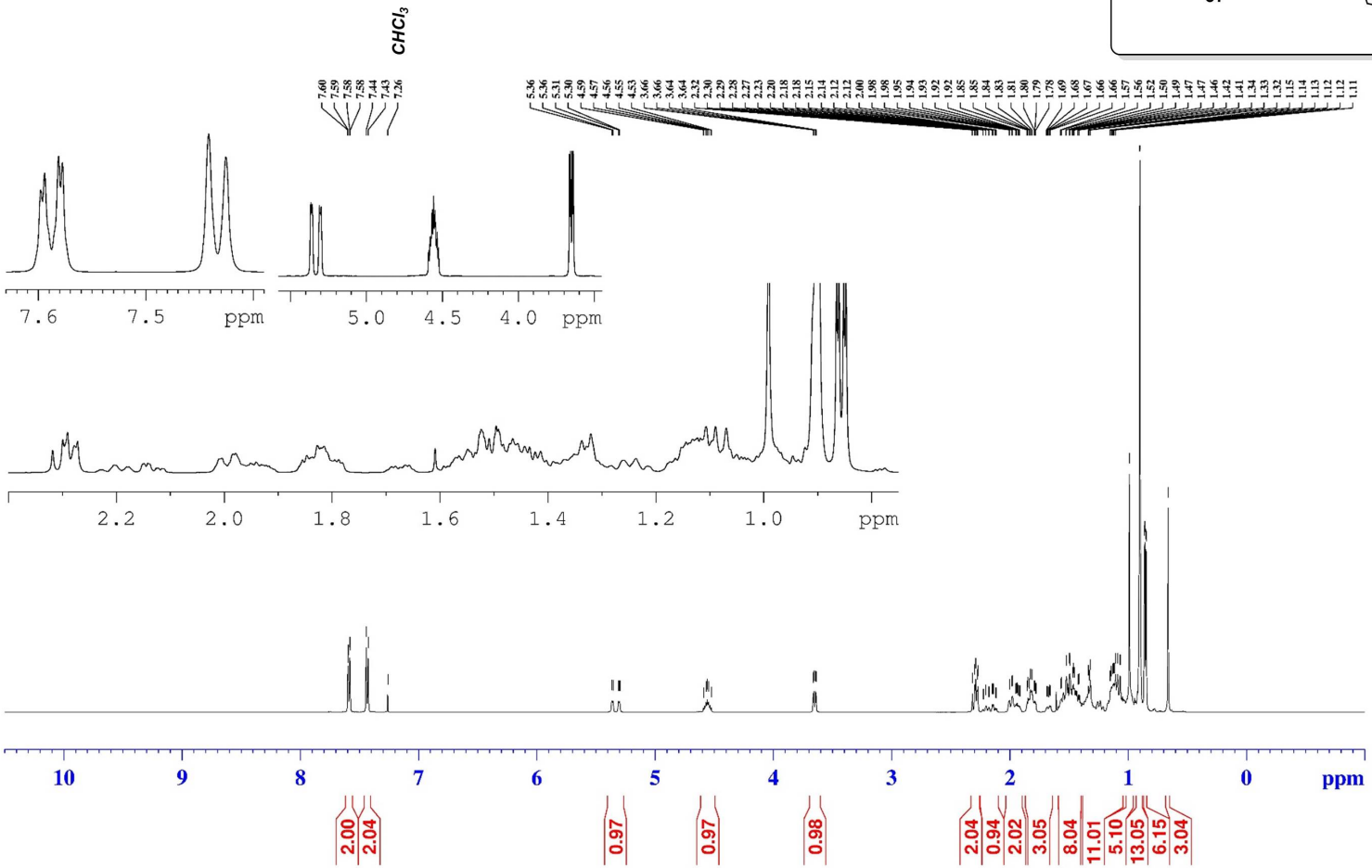




^{1}H NMR

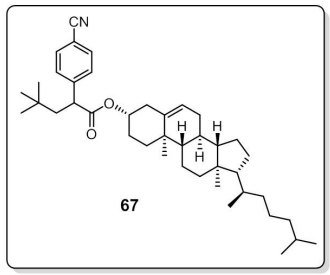


(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11, 12,13,14,15,16,17-tetradecahydro-1H-cyclopenta [a]phenanthren-3-yl 2-(4-cyanophenyl)-4,4-dimethyl pentanoate
500 MHz, $CDCl_3$



^{13}C NMR

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11, 12,13,14,15,16,17-tetradecahydro-1H-cyclopenta [a]phenanthren-3-yl 2-(4-cyanophenyl)-4,4-dimethyl pentanoate,
125 MHz, $CDCl_3$



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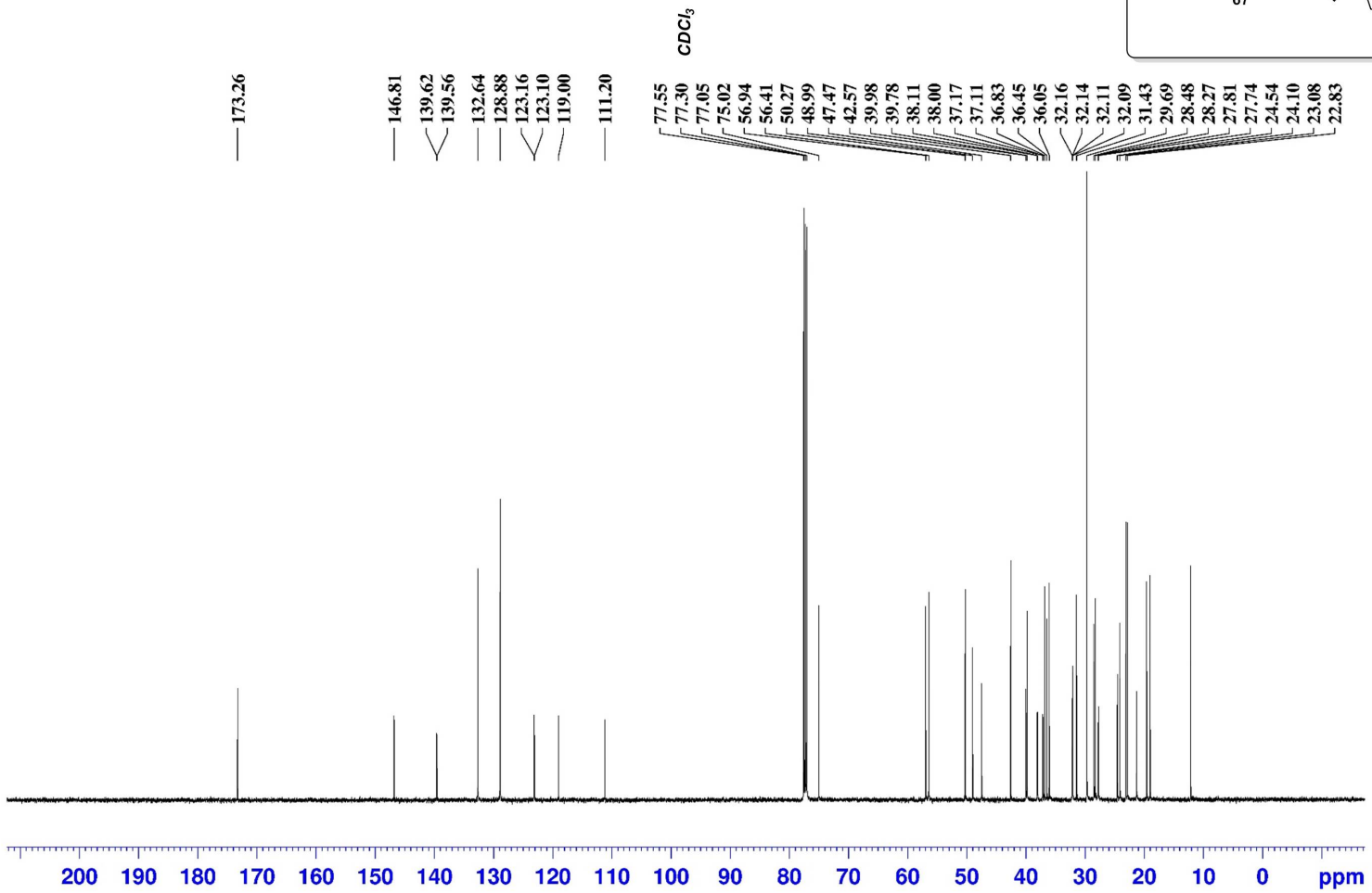
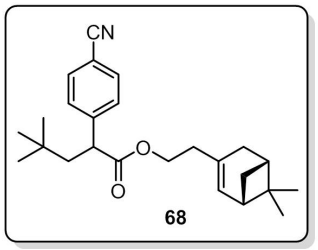
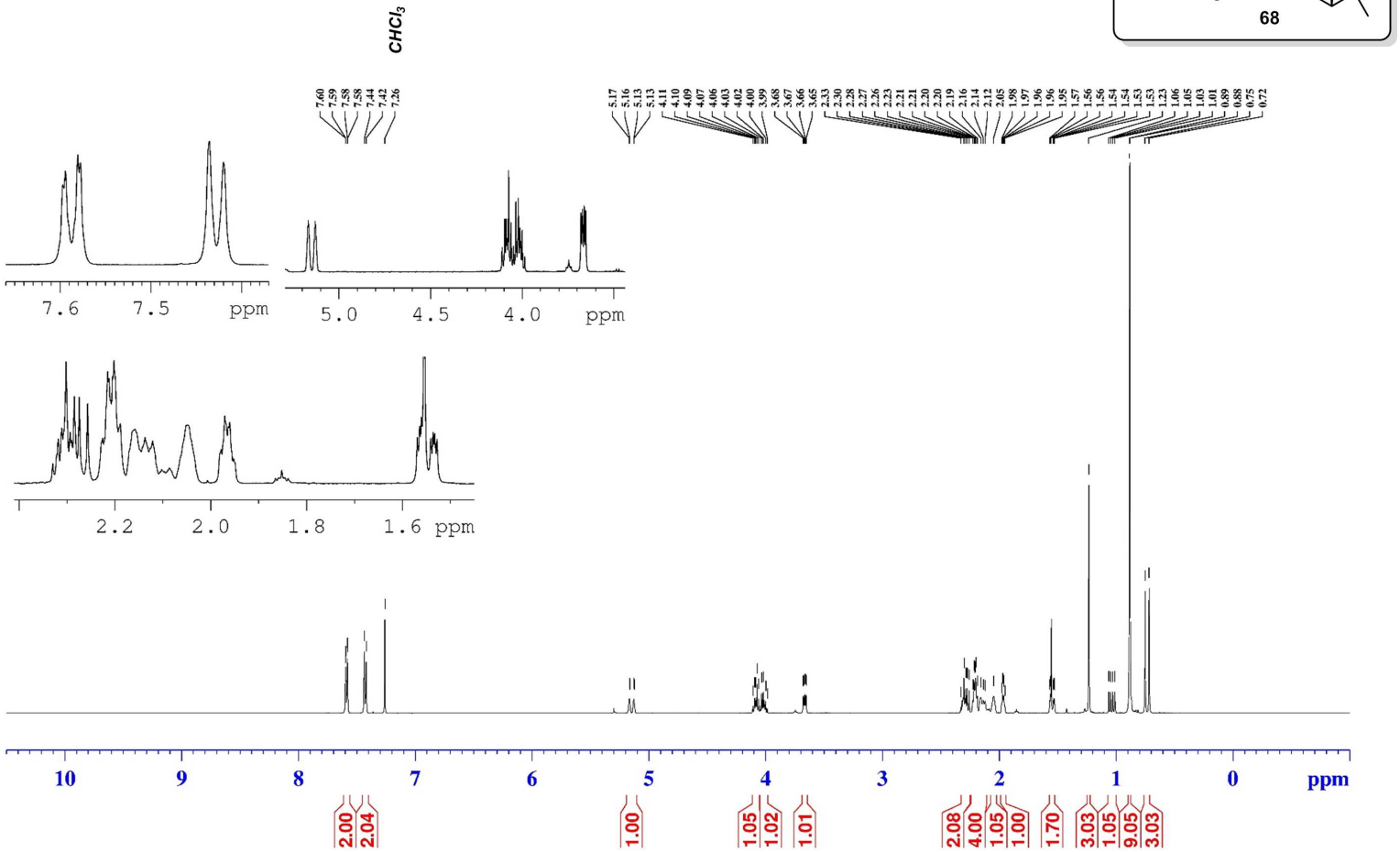


^1H NMR

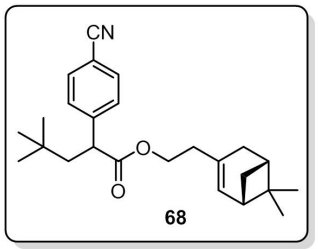


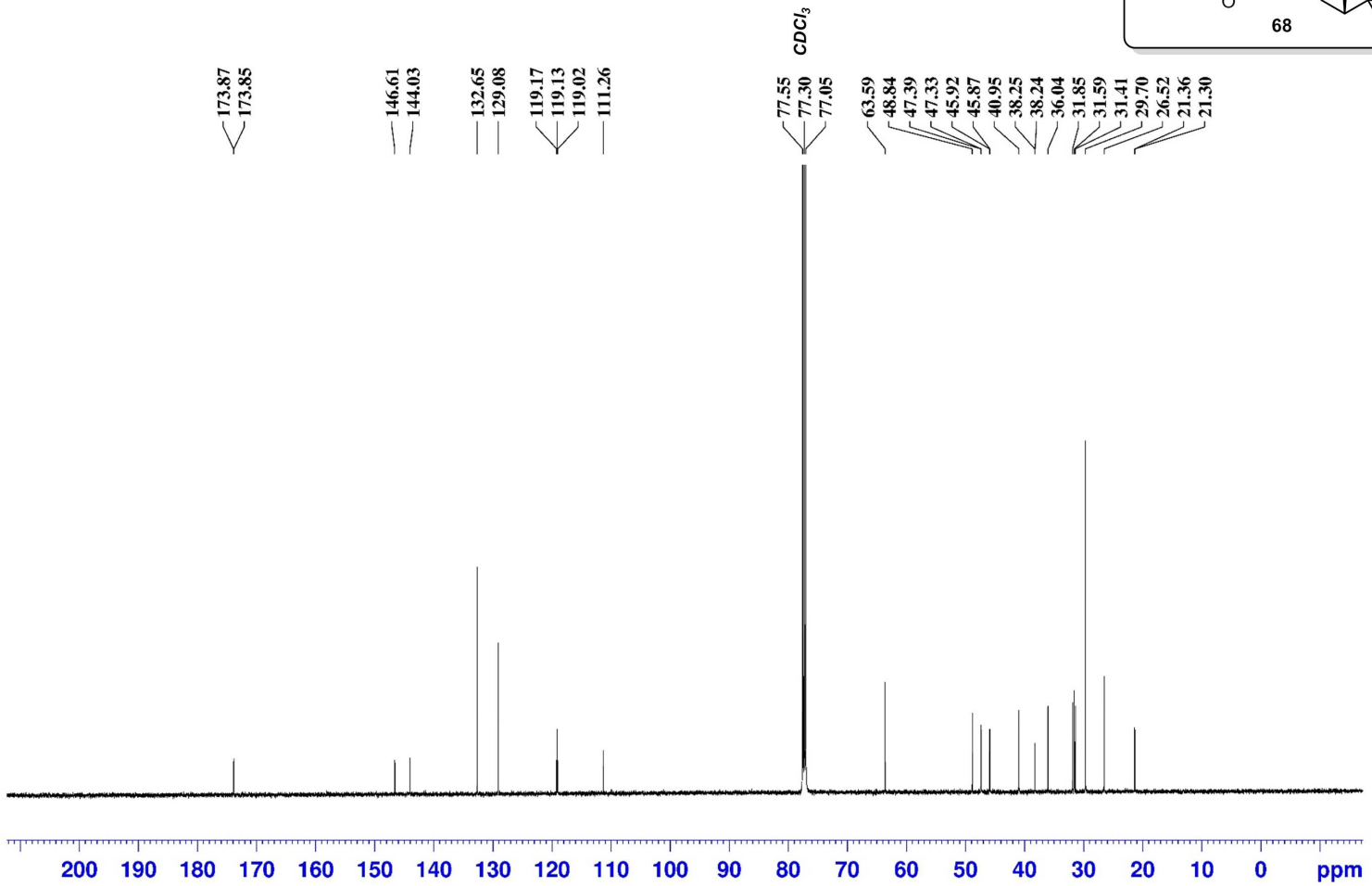
2-((1*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-3-yl)ethyl 2-(4-cyanophenyl)-4,4-dimethyl pentanoate
500 MHz, $CDCl_3$



^{13}C NMR

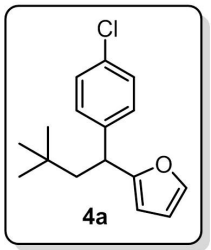
2-((1*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-3-yl)ethyl 2-(4-cyanophenyl)-4,4-dimethyl pentanoate
125 MHz, $CDCl_3$

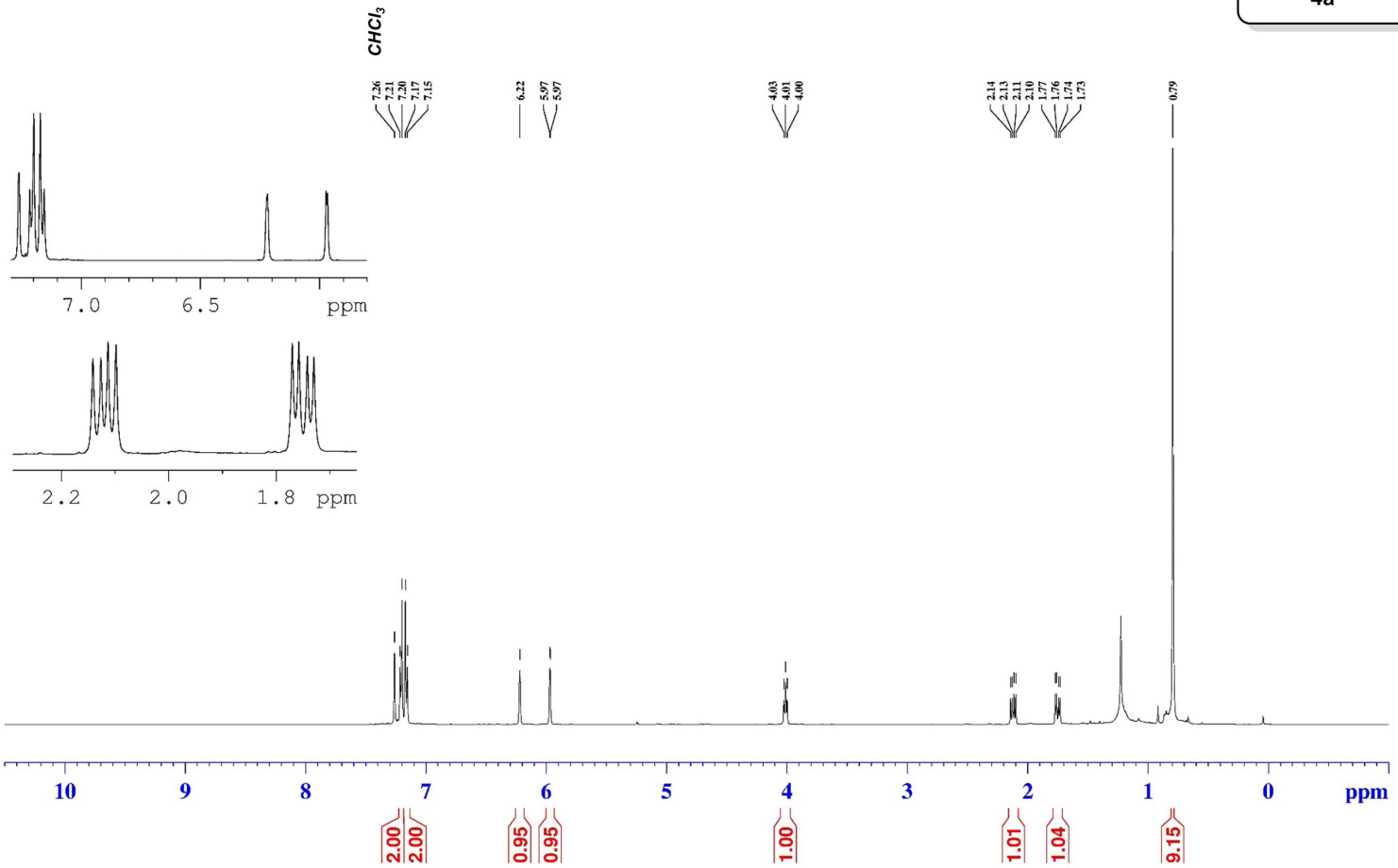




^1H NMR

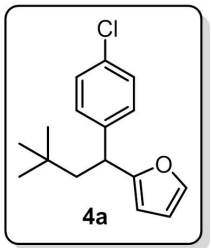
2-(1-(4-chlorophenyl)-3,3-dimethylbutyl)furan
500 MHz, $CDCl_3$

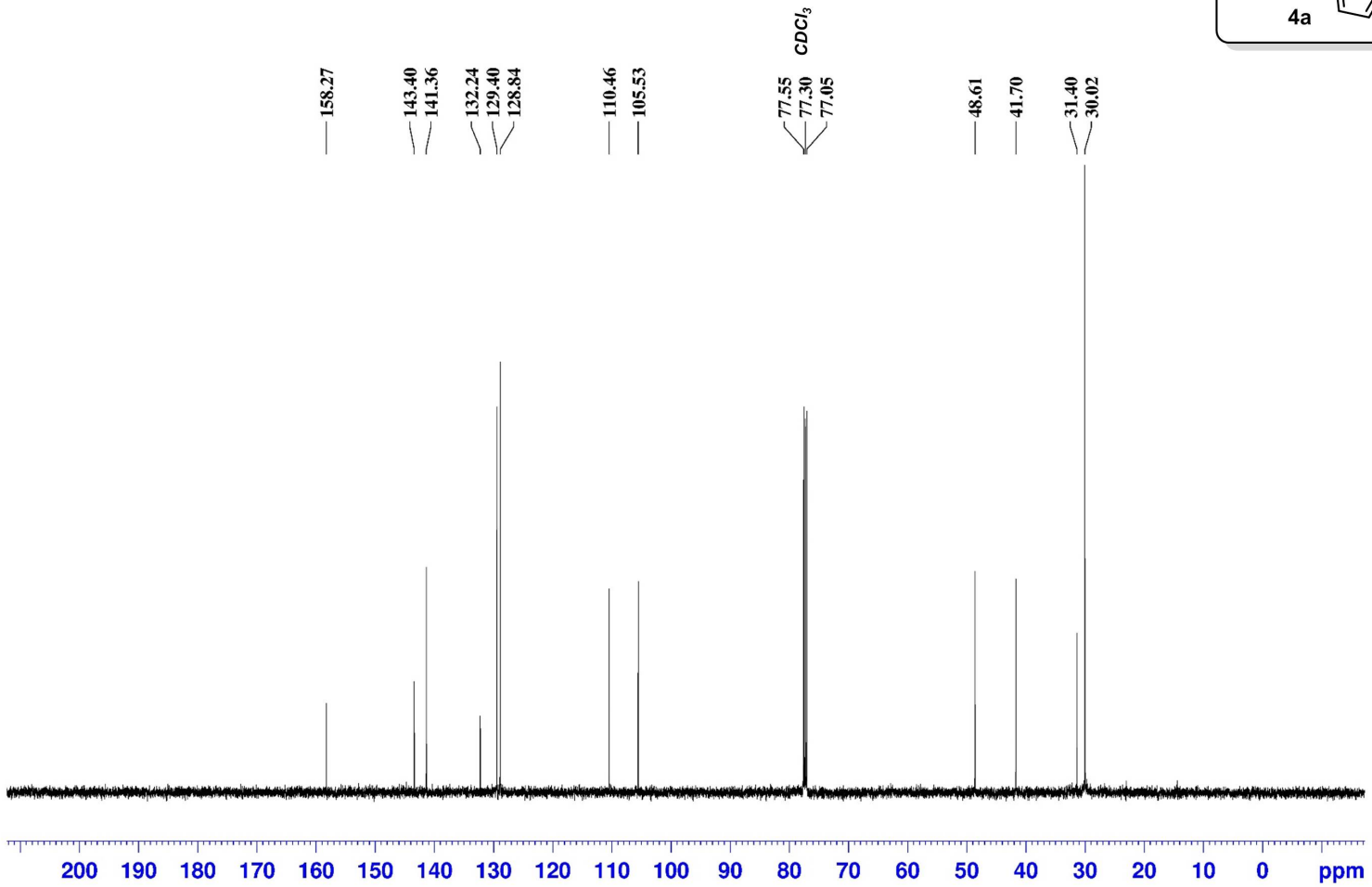




2-(1-(4-chlorophenyl)-3,3-dimethylbutyl)furan,
125 MHz, $CDCl_3$

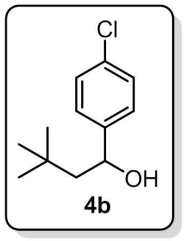
^{13}C NMR

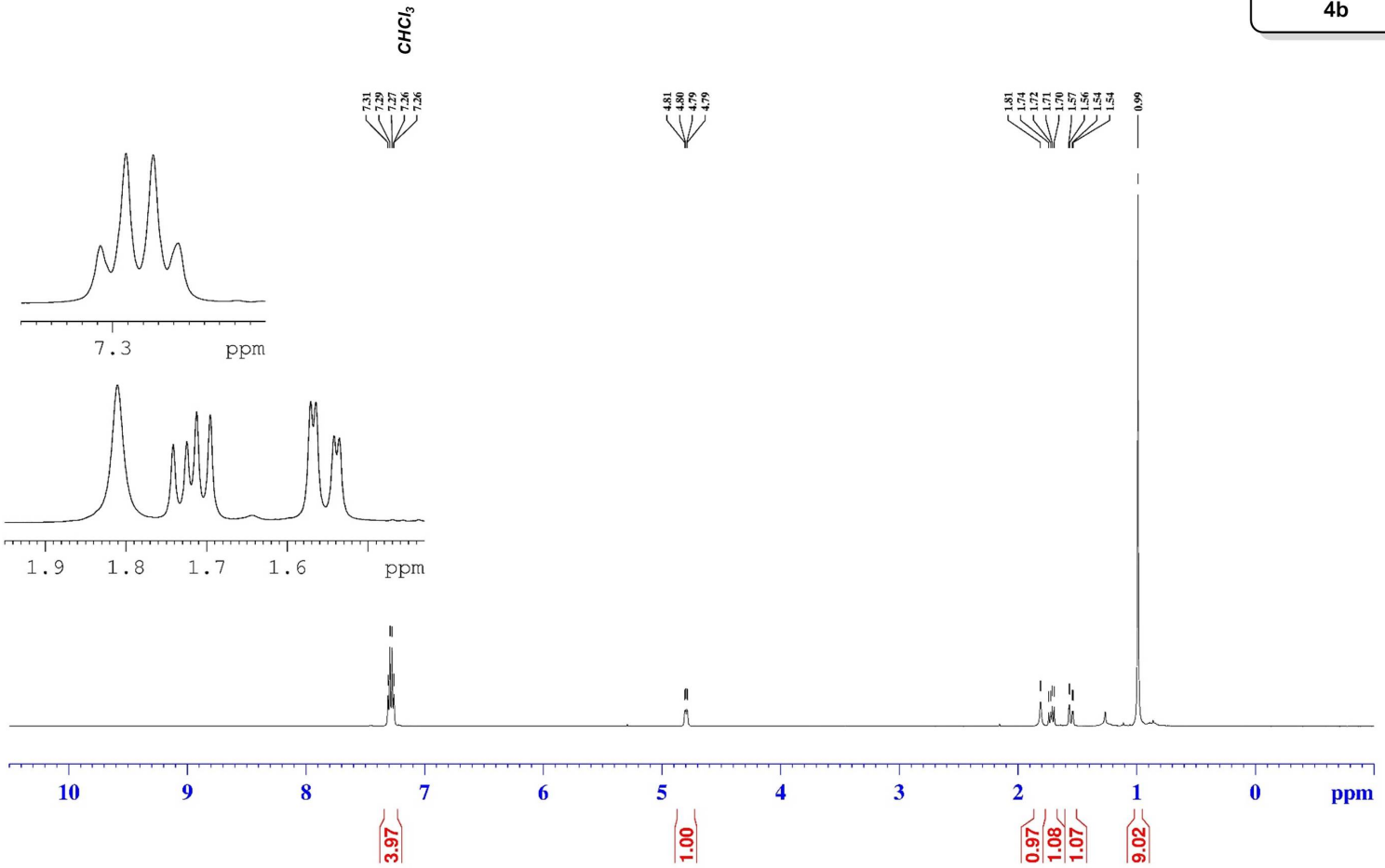




^1H NMR

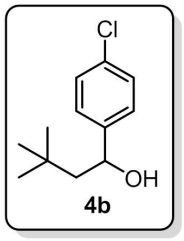
1-(4-chlorophenyl)-3,3-dimethylbutan-1-ol
500 MHz, $CDCl_3$

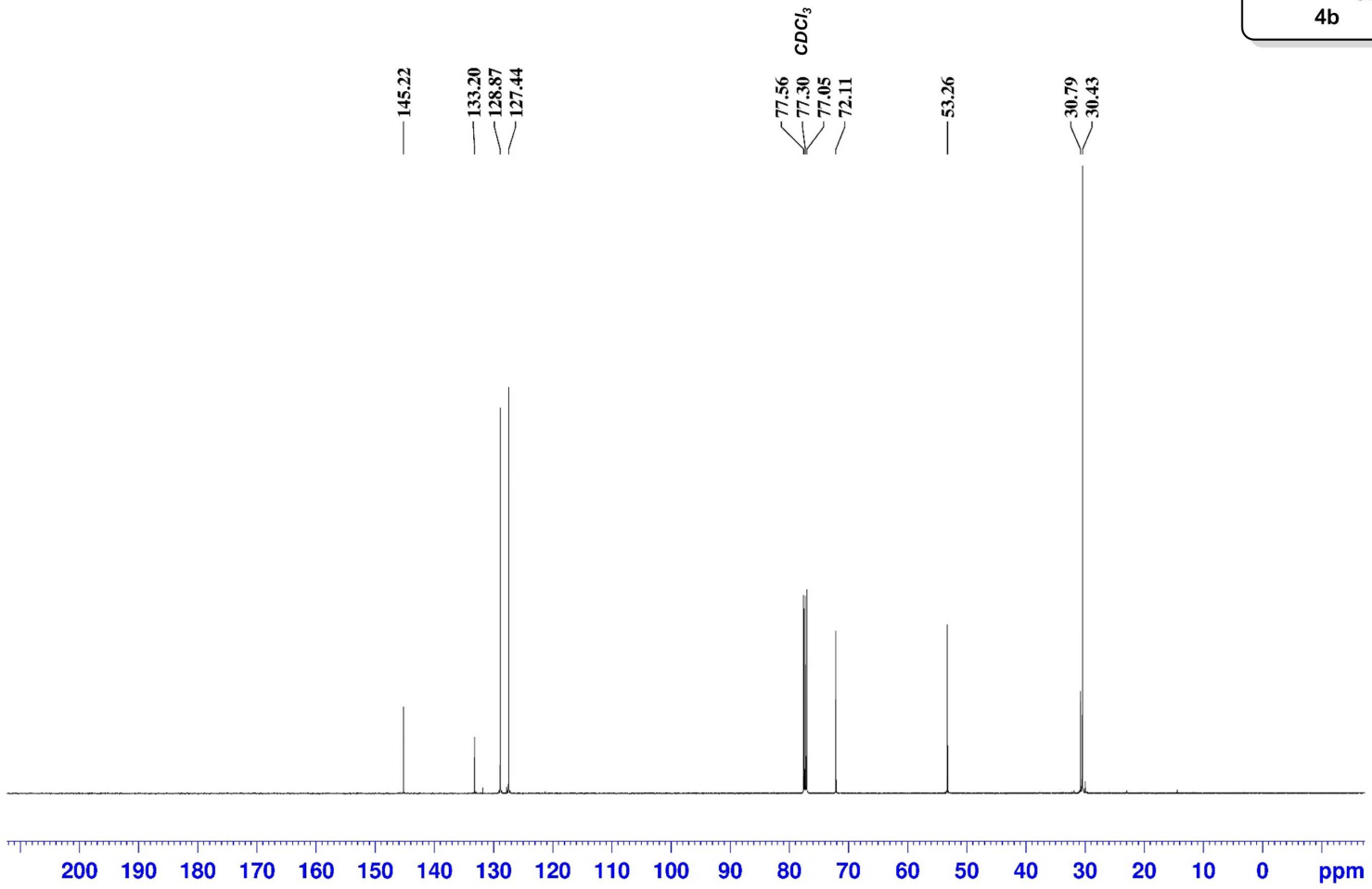




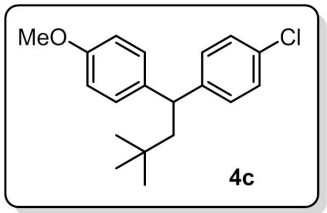
1-(4-chlorophenyl)-3,3-dimethylbutan-1-ol,
125 MHz, $CDCl_3$

^{13}C NMR

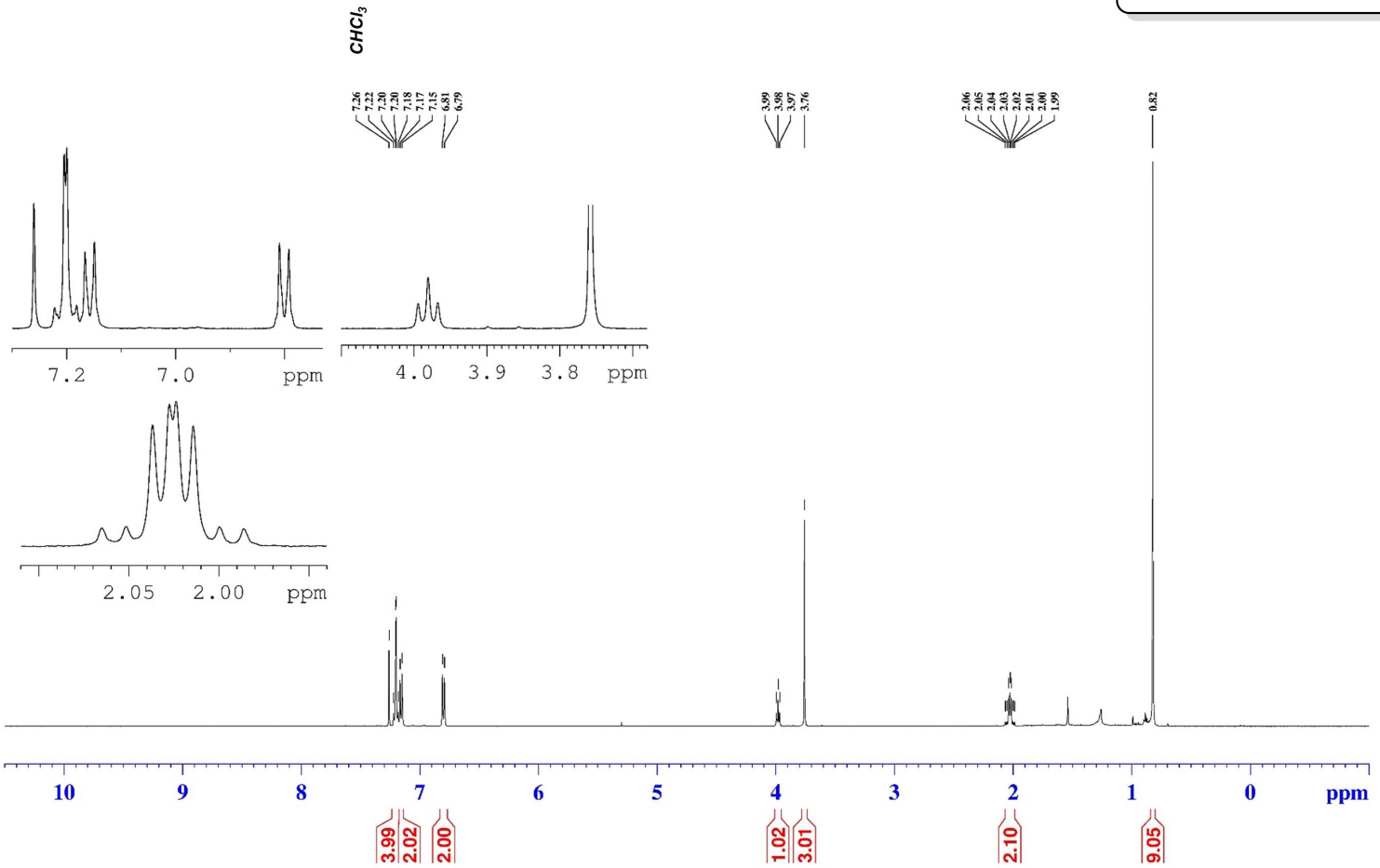




^1H NMR

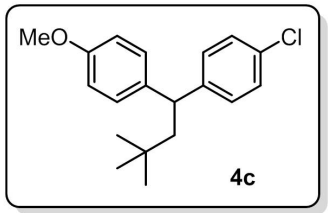


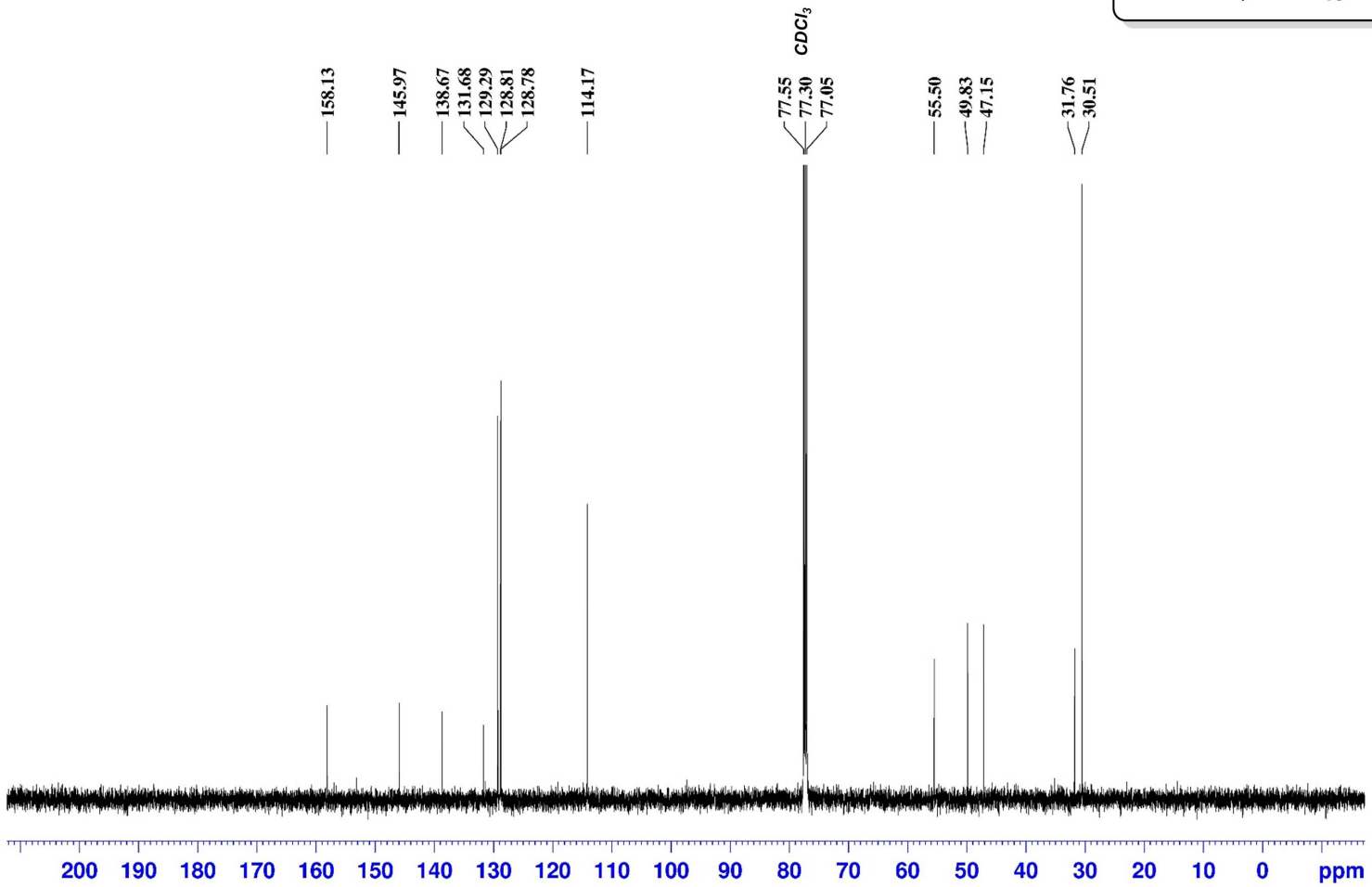
1-chloro-4-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)benzene
500 MHz, $CDCl_3$



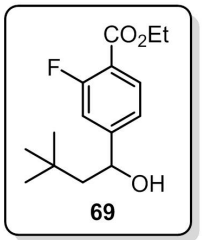
1-chloro-4-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)benzene,
125 MHz, $CDCl_3$

^{13}C NMR

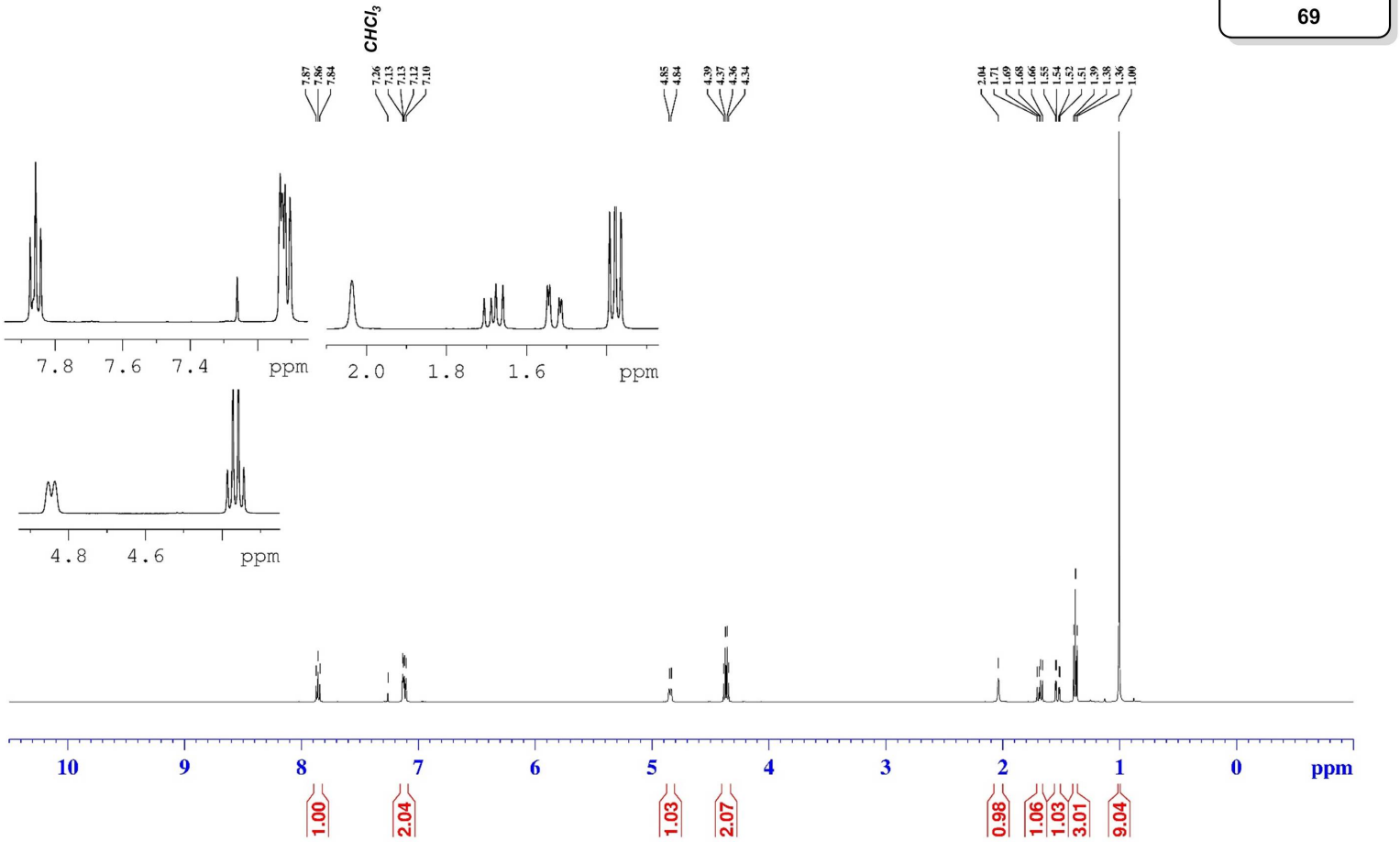




^{1}H NMR

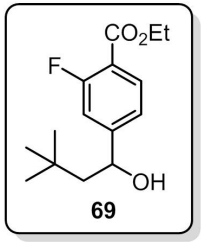


Ethyl 2-fluoro-4-(1-hydroxy-3,3-dimethylbutyl)benzoate
500 MHz, $CDCl_3$



^{13}C NMR

Ethyl 2-fluoro-4-(1-hydroxy-3,3-dimethylbutyl)benzoate,
125 MHz, $CDCl_3$



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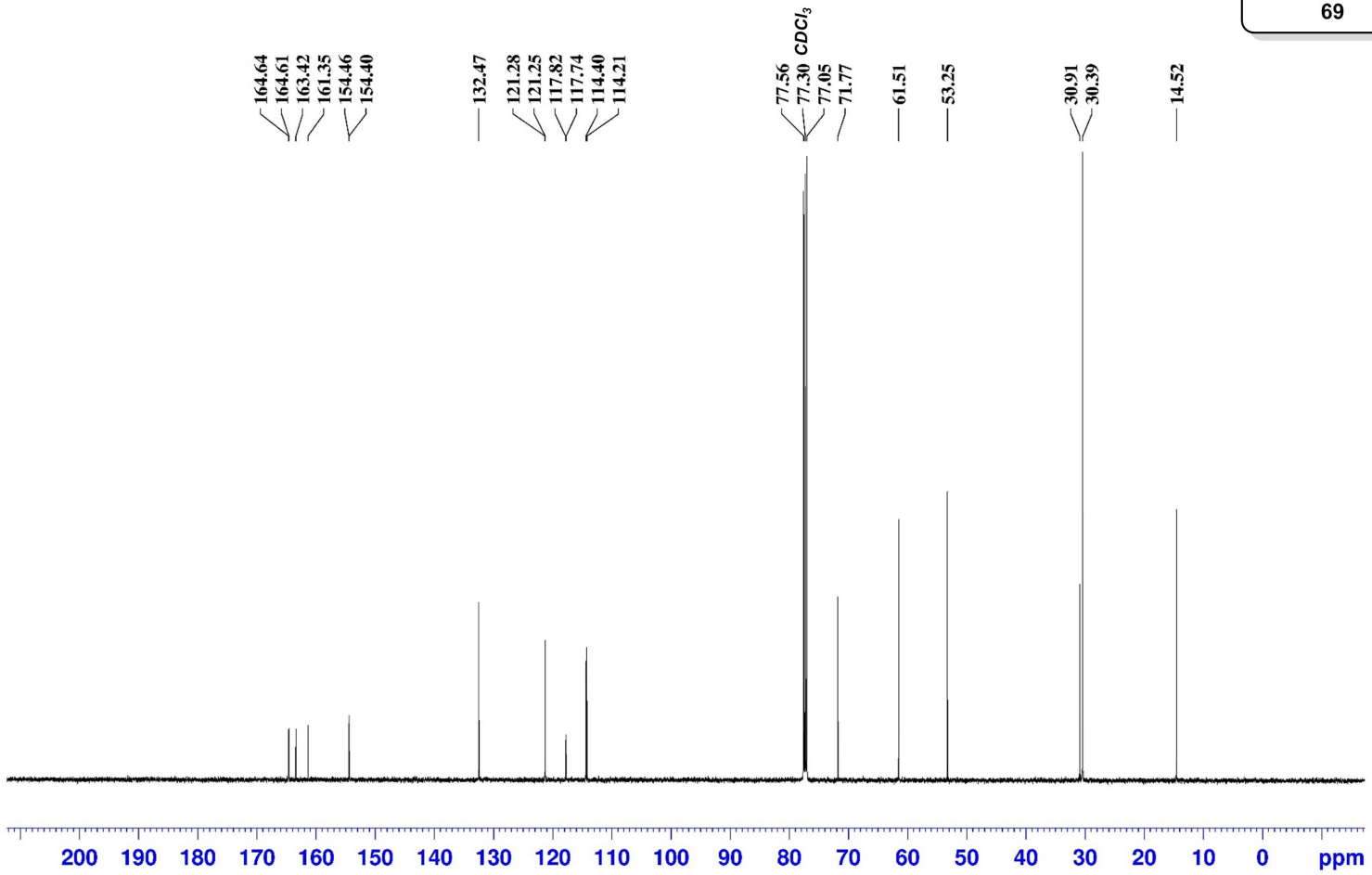
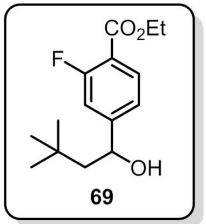
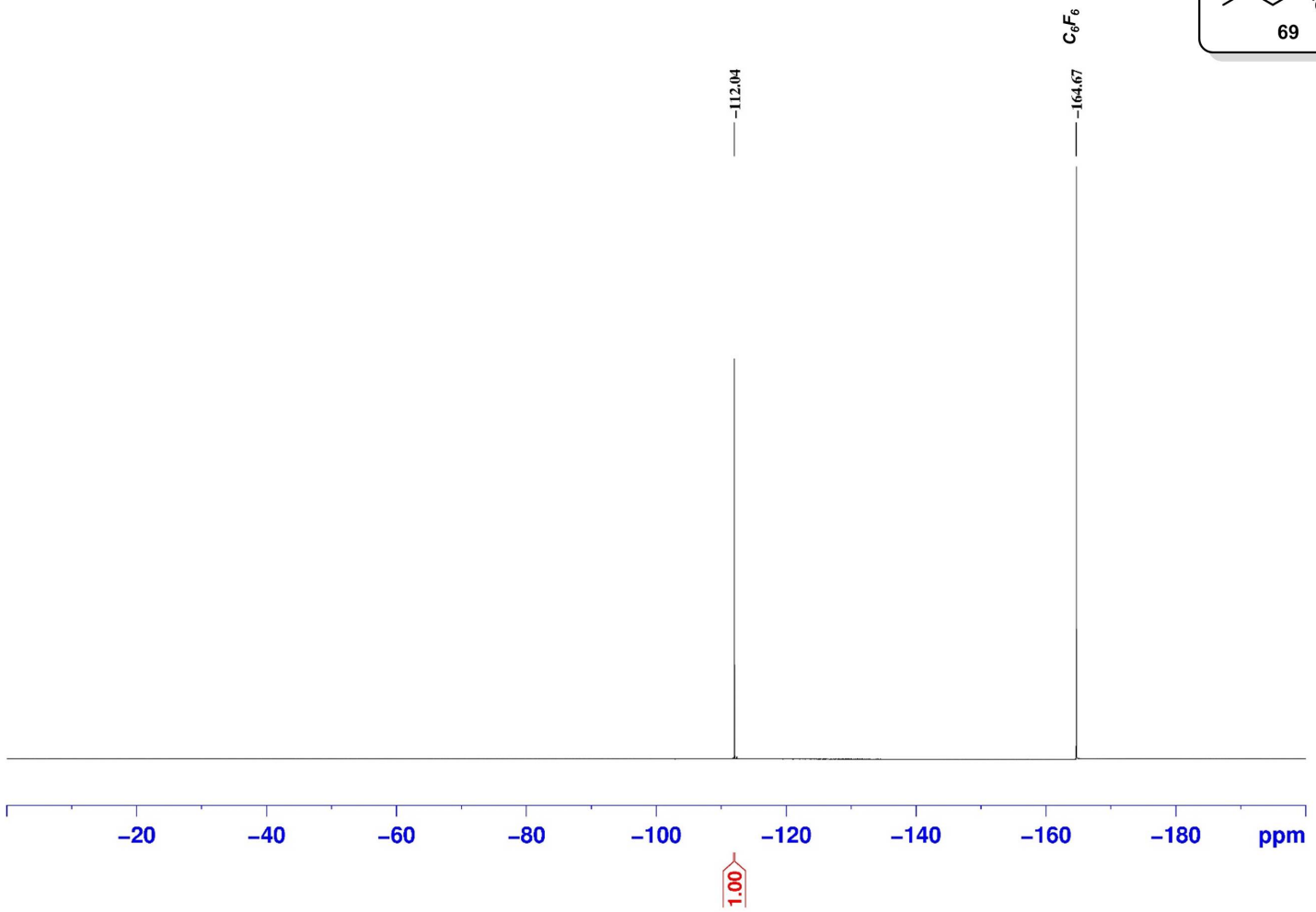


Ethyl 2-fluoro-4-(1-hydroxy-3,3-dimethylbutyl)benzoate
471 MHz, $CDCl_3$

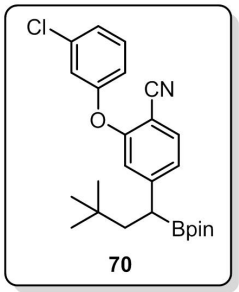
^{19}F NMR





^{1}H NMR

2-(3-chlorophenoxy)-4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzonitrile
500 MHz, $CDCl_3$



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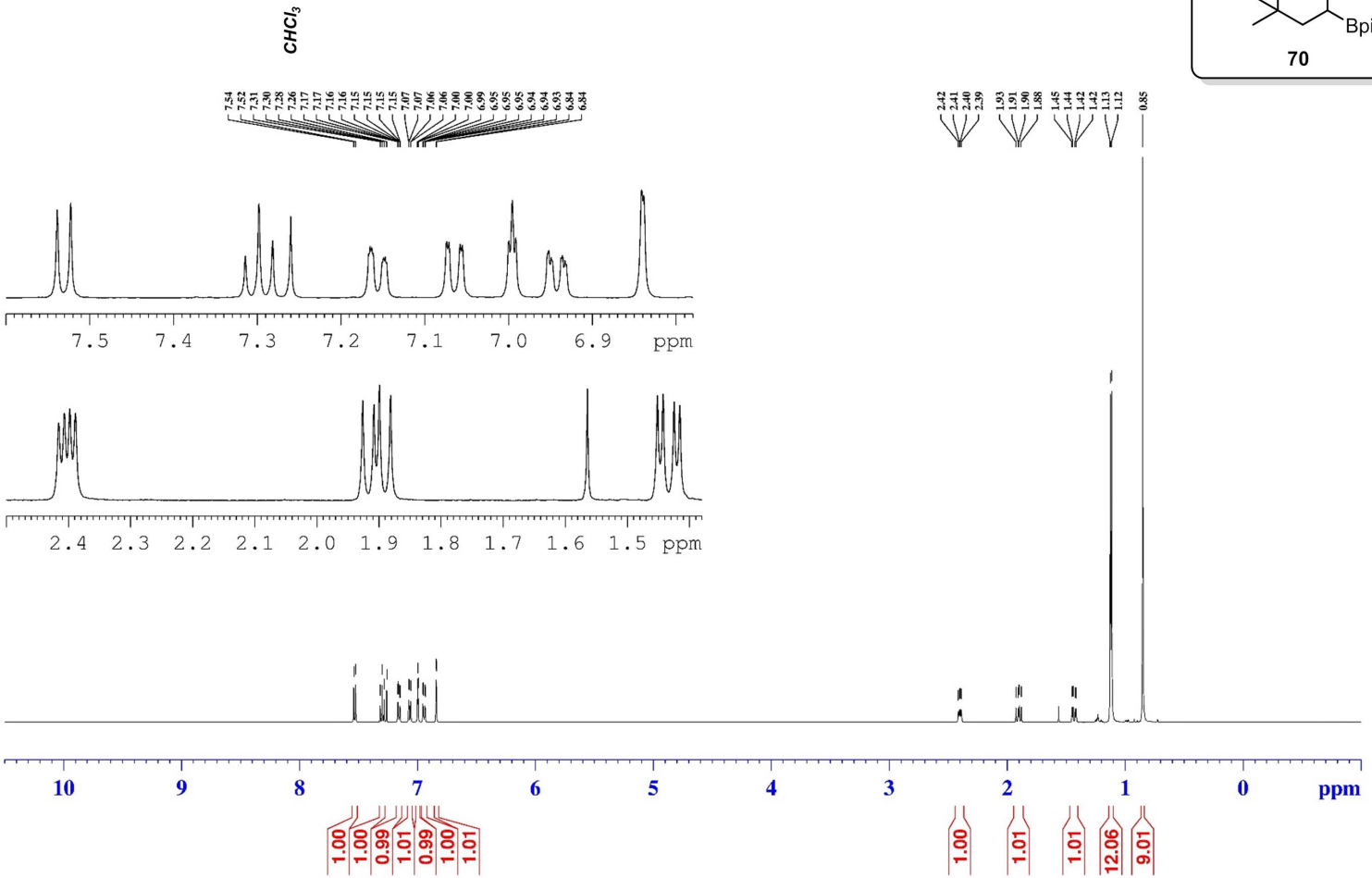
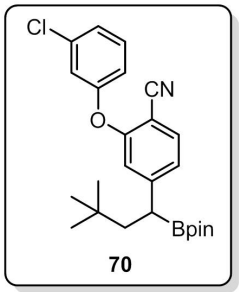


^{13}C NMR

2-(3-chlorophenoxy)-4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzonitrile, 125 MHz, $CDCl_3$



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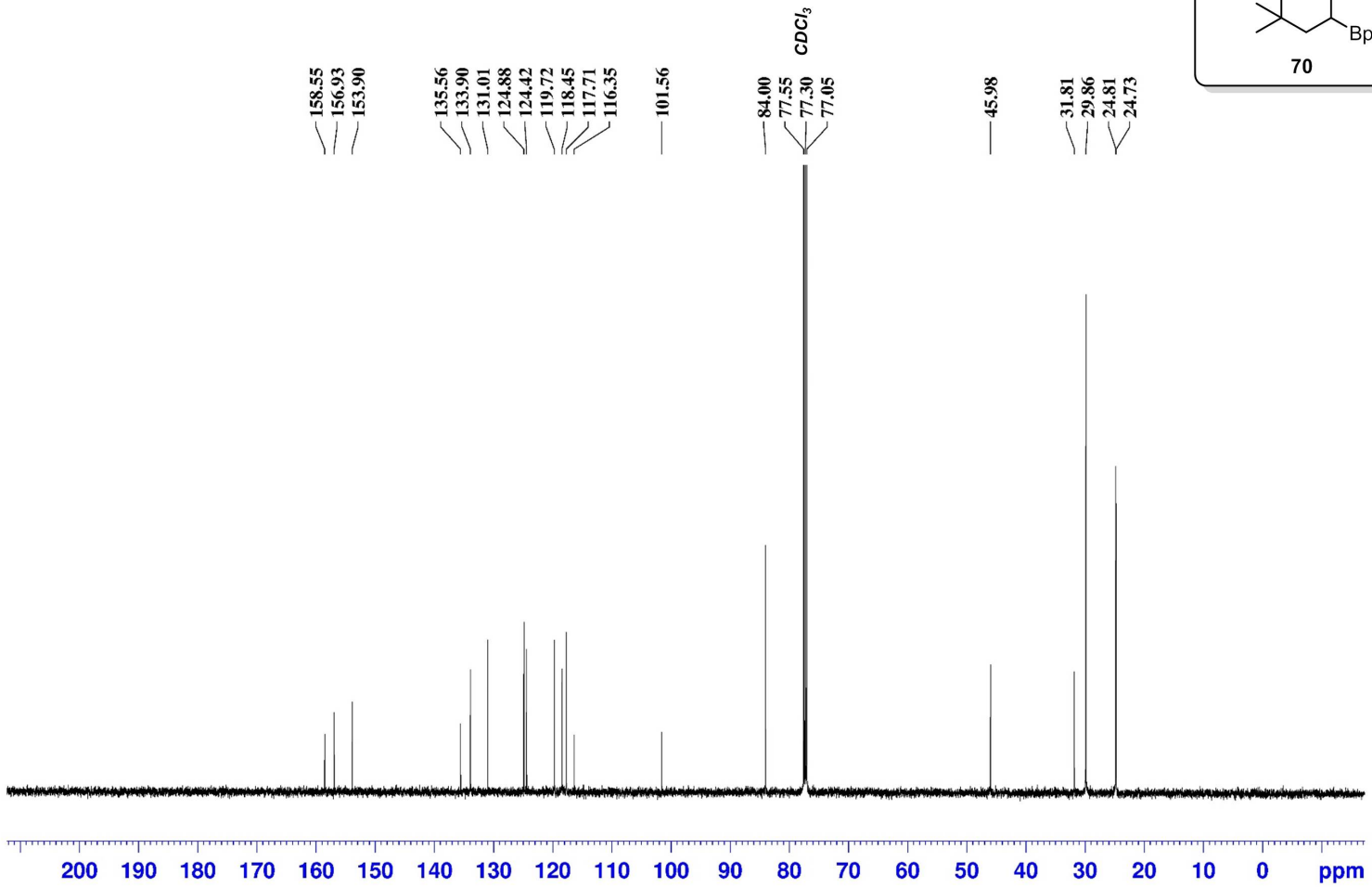
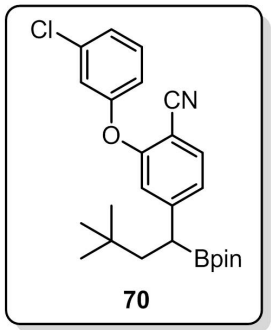


^{11}B NMR

2-(3-chlorophenoxy)-4-(3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzonitrile, 128 MHz, $CDCl_3$



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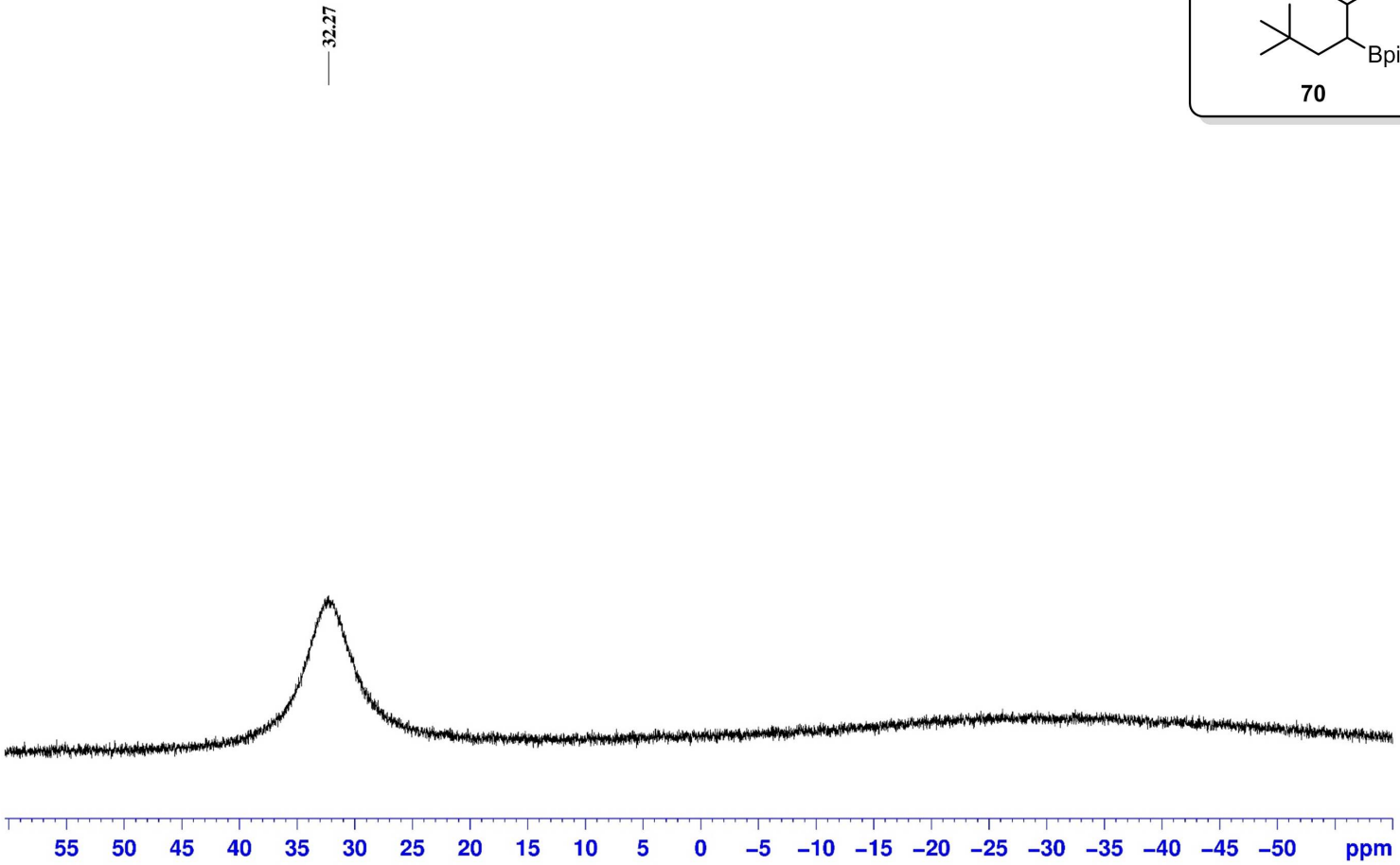
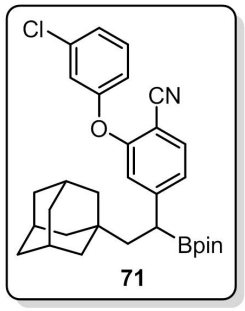
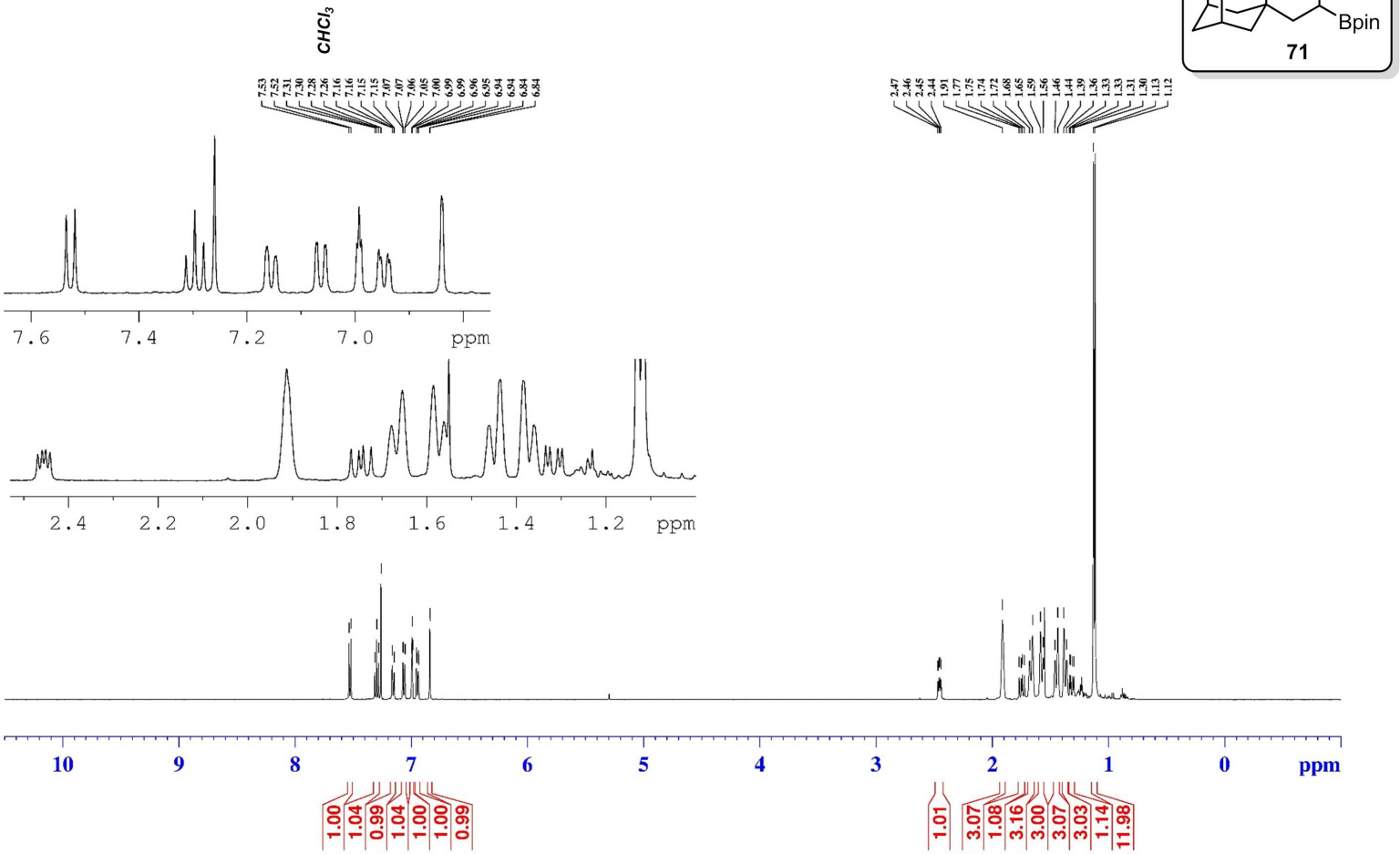


^{1}H NMR

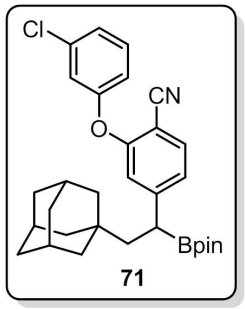


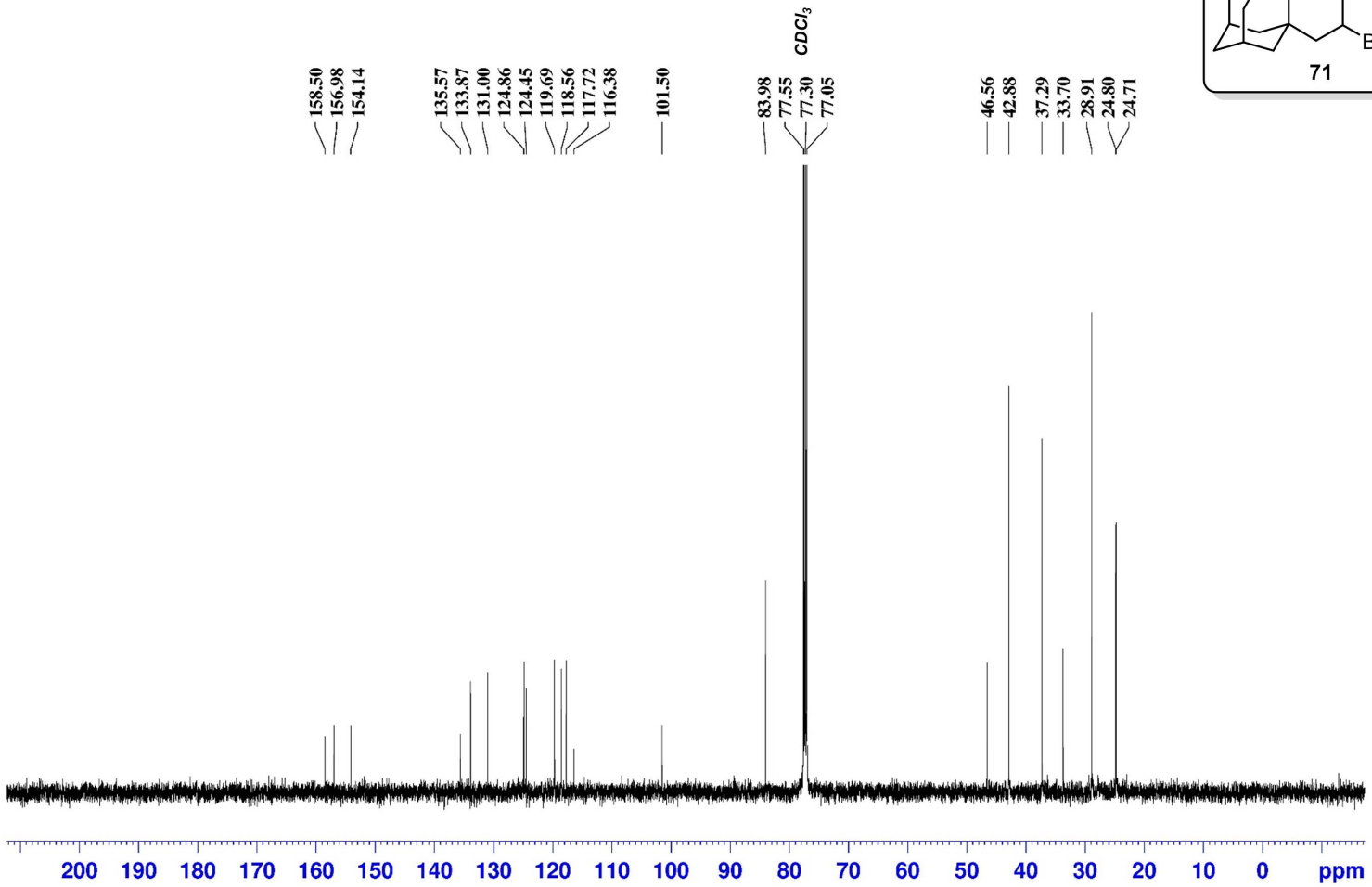
4-(2-(adamantan-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2-(3-chloro phenoxy)benzonitrile
500 MHz, $CDCl_3$



^{13}C NMR

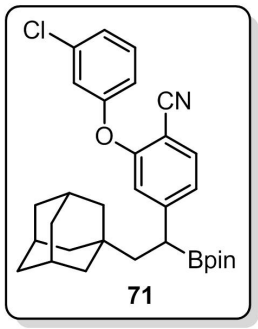
4-(2-(adamantan-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2-(3-chloro phenoxy)benzonitrile, 125 MHz, $CDCl_3$





^{11}B NMR

4-(2-(adamantan-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2-(3-chloro phenoxy)benzonitrile, 128 MHz, $CDCl_3$



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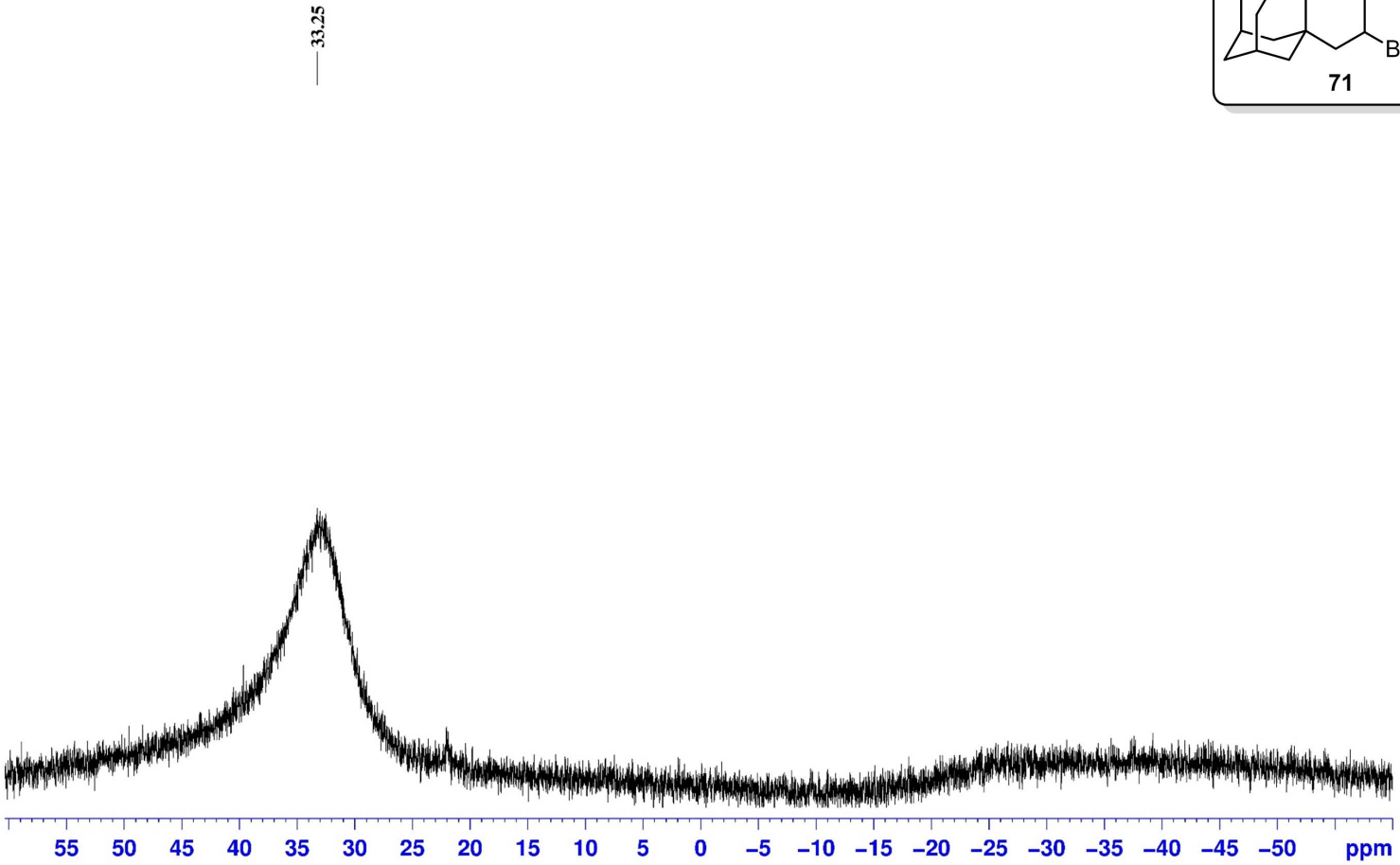
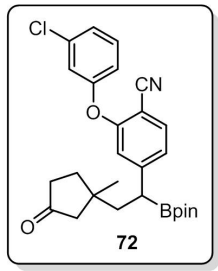
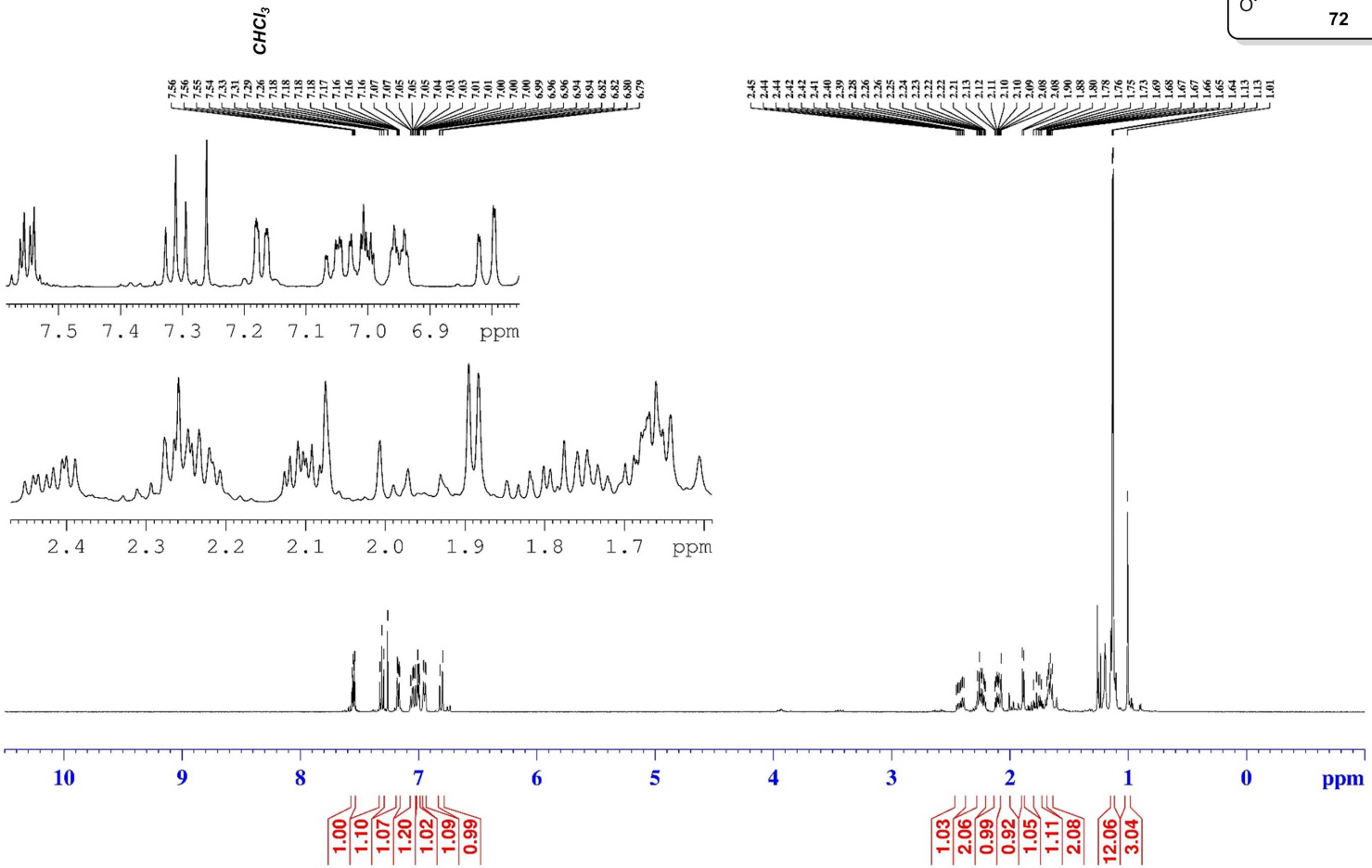


^1H NMR

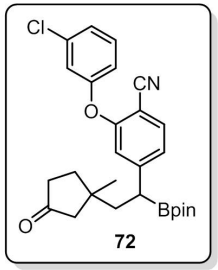


2-(3-chlorophenoxy)-4-(2-(1-methyl-3-oxocyclopentyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile
500 MHz, $CDCl_3$



^{13}C NMR

2-(3-chlorophenoxy)-4-(2-(1-methyl-3-oxocyclopentyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile, 125 MHz, $CDCl_3$



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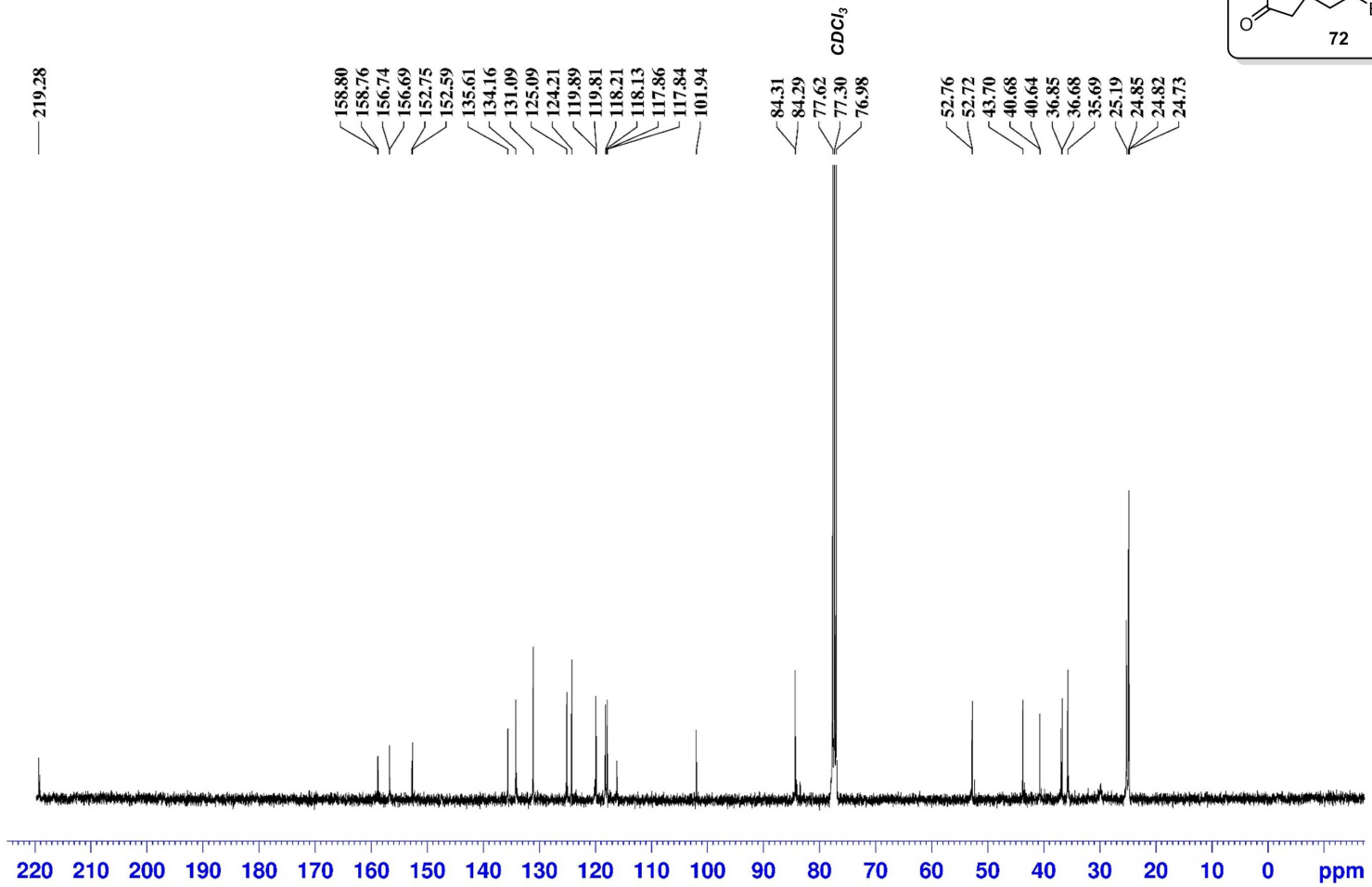
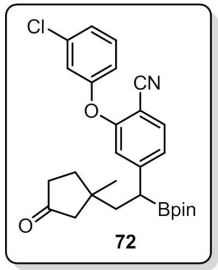
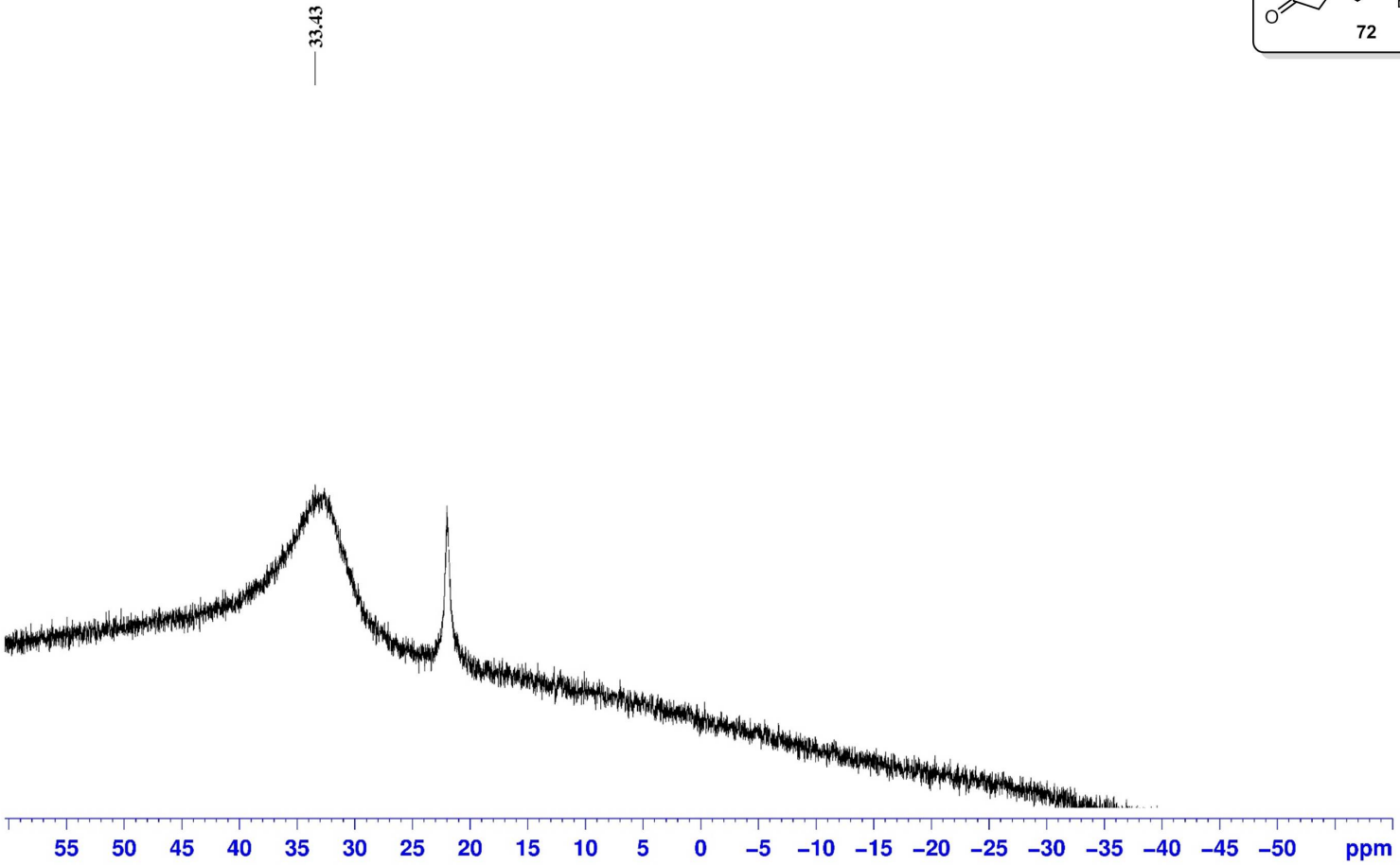


^{11}B NMR

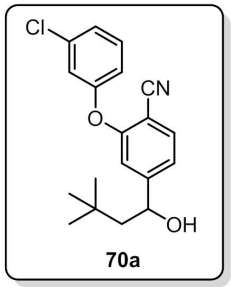


2-(3-chlorophenoxy)-4-(2-(1-methyl-3-oxocyclopentyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile, 128 MHz, $CDCl_3$



^{1}H NMR

2-(3-chlorophenoxy)-4-(1-hydroxy-3,3-dimethylbutyl)benzonitrile
500 MHz, $CDCl_3$



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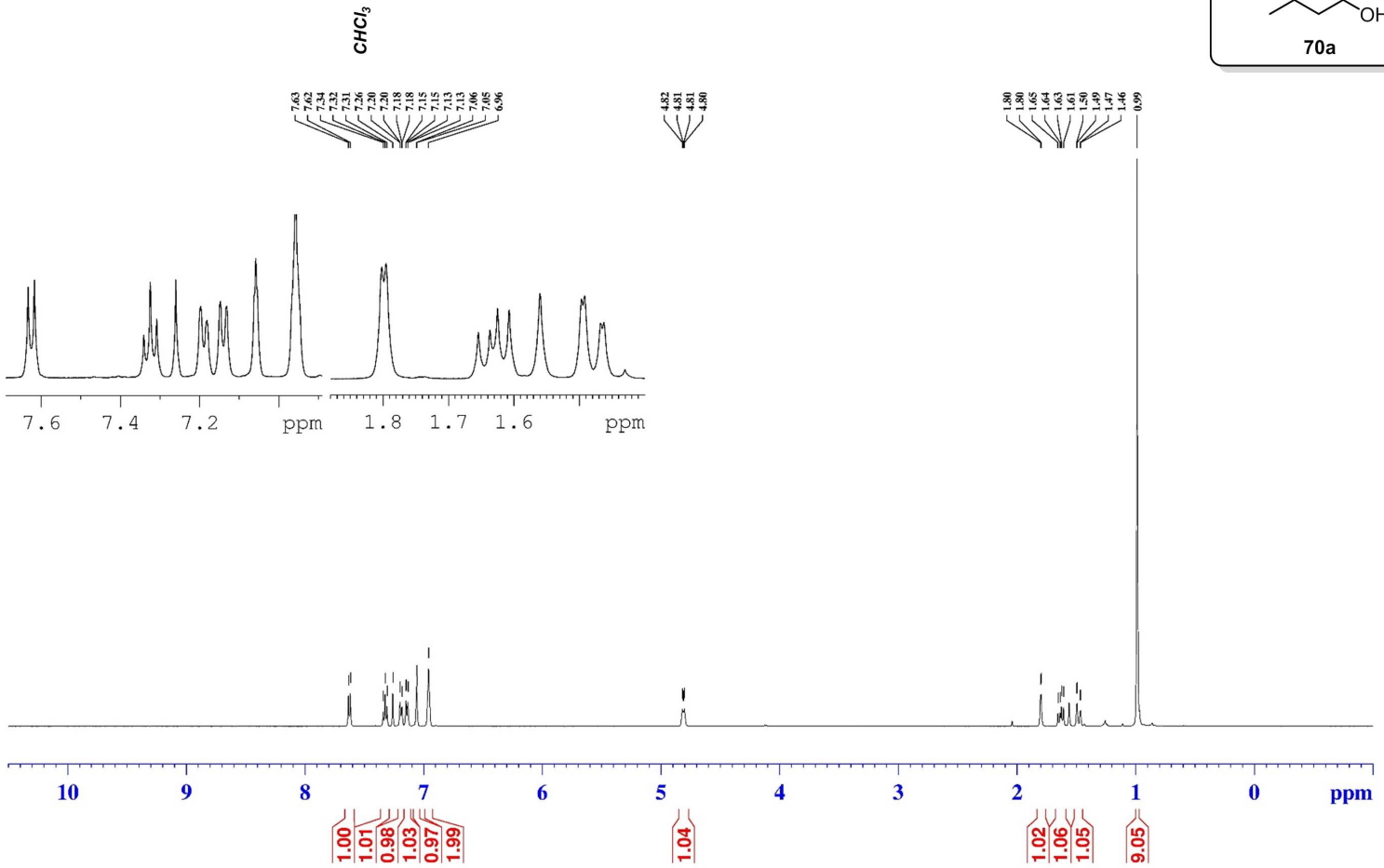
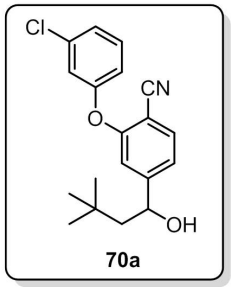


^{13}C NMR

2-(3-chlorophenoxy)-4-(1-hydroxy-3,3-dimethylbutyl)benzonitrile,
125 MHz, $CDCl_3$



70a