Supporting Information For:

Asymmetric Catalytic Hydroboration of Enol Carbamates Enables an Enantioselective Matteson Homologation

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Supplemental Material

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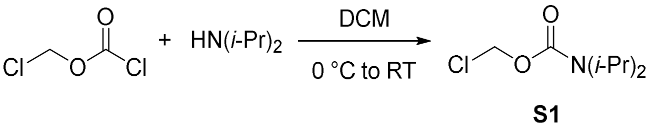
General Methods

All commercially available reagents were used as received unless otherwise stated. $[Rh(cod)_2]OTf$ (CAS No. 99326-34-8, Catalog No. 45-0110), ligand **L6b** (CAS No. 1221746-66-2, Catalog No. 26-1269) and 1,1′-bis(diisopropylphosphino)ferrocene (CAS No. 97239-80-0, Catalog No. 26-0275) were purchased from Strem Chemicals Inc. and stored in freezer under inert atmosphere. HBpin (CAS No. 25015-63-8, Catalog No. T2572) was purchased from TCI America, purified via distillation, and stored in a N_2-filled glovebox. All other reagents were purchased from various commercial sources (Sigma-Aldrich, Alfa Aesar, Matrix Scientific, Frontier Scientific, Combi-Blocks, TCI America, Oakwood Chemical). Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and Sigma-Aldrich. All reactions were conducted in oven- or flame-dried glassware under atmosphere of argon. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were purified by passing the degassed solvents through two activated alumina columns and were stored under inert atmosphere prior to use.

All NMR experiments were recorded on Bruker Ascend-600, Varian Inova-400 and Bruker Ascend-400 spectrometers. Data for ^1H and ^{13}C NMR spectra are reported as follows: chemical shift (δ, ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublets of doublets, dt = doublet of triplets, hept = heptet, m = multiplet), and coupling constant (Hz). The 7.26 resonance of residual $CHCl_3$ for ^1H spectra and the 77.23 ppm resonance of $CDCl_3$ for ^{13}C spectra were used as internal references. Silica gel flash chromatography purifications were performed using 40–63-micron flash silica gel purchased from Sorbtech Technologies. Reversed-phase flash chromatography was performed using Teledyne Isco RediSep Gold® C18 Reversed Phase columns on a Teledyne Isco CombiFlash® Rf 200 instrument. Thin layer chromatography (TLC) was performed on silica gel 60 F254 pre-coated glass plates (0.25 mm) purchased from E. Merck. Visualization of TLC plates was performed using ultraviolet light (254 nm) or $KMnO_4$ stain and heat as developing agents. Enantiomeric excess was measured on a Shimadzu Prominence HPLC with the column and solvent system indicated with each characterized compound. Mass spectra were acquired on an Agilent technologies 1200 series LC/MS using indicated ionization methods.

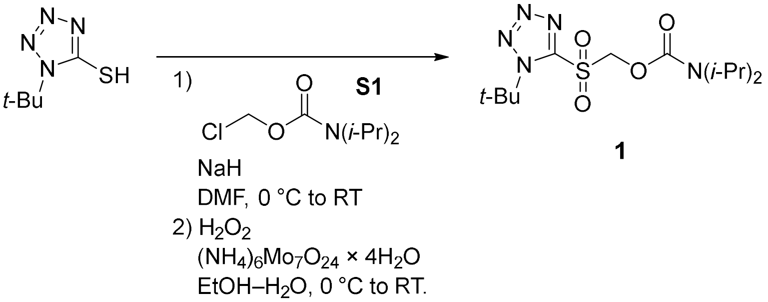
Synthesis of Substrates

Synthesis of Julia Reagent



Chloromethyl diisopropylcarbamate (S1).

At 0 °C and under argon, solution of diisopropylamine (10.0 mL, 7.22 g, 71.5 mmol, 2.50 equiv) in anhydrous DCM (10 mL) was added dropwise to a solution of chloromethyl chloroformate (2.50 mL, 3.68 g, 28.5 mmol, 1.00 equiv) in anhydrous DCM (40 mL). The mixture was stirred at ambient temperature overnight. The reaction was diluted with DCM (75 mL), and the resulting solution was washed with 1N HCl (15 mL), sat. aq. $NaHCO_3$ (15 mL) and water (15 mL), dried over Na_2SO_4, filtered and concentrated to afford 4.91 g (89%) of the title compound as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.82 (s, 2H), 4.06 (br s, 1H), 3.82 (br s, 1H), 1.24 (d, J = 6.8 Hz, 12H). Spectral data is consistent with previously reported results.[1]



((1-(*tert*-Butyl)-1*H*-tetrazol-5-yl)sulfonyl)methyl diisopropylcarbamate (1).

Step 1. 1-(*tert*-Butyl)-1*H*-tetrazole-5-thiol[2] (2.00 g, 12.7 mmol, 1.00 equiv) was dissolved in anhydrous DMF (60 mL) under argon. At 0 °C, sodium hydride (0.556 g of 60% dispersion in mineral oil, 0.334 g, 13.9 mmol, 1.10 equiv) was added, and the mixture was stirred with ice bath cooling for 15 min. Then a solution of **S1** (2.62 g, 13.5 mmol, 1.06 equiv) in anhydrous DMF (2.5 mL) was added dropwise at 0 °C, and the mixture was stirred under argon at ambient temperature overnight. Sat. aq. NH_4Cl (30 mL) was carefully added to quench the reaction, followed by water (10 mL). The product was extracted with EtOAc (3 × 60 mL). Combined organic layers were washed with water (5 × 50 mL) and brine (50 mL), dried over Na_2SO_4, filtered and concentrated. The resulting crude sulfide (pale-yellow oil that solidifies to form a beige solid) was used for the next step without further purification.

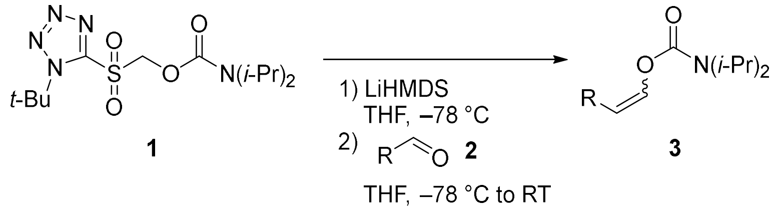
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (s, 2H), 4.06 (br hept, 1H), 3.72 (br hept, 1H), 1.71 (s, 9H), 1.21 (d, J = 6.6 Hz, 6H), 1.12 (d, J = 6.6 Hz, 6H). Step 2. At 0 °C, 30% aq. H_2O_2 (21 mL) was added dropwise to a solution of the sulfide (12.7 mmol, 1.00 equiv) in abs. EtOH (60 mL), followed by ammonium heptamolybdate tetrahydrate (7.03 g, 5.69 mmol, 0.45 equiv), and the mixture was stirred at ambient temperature overnight. At 0 °C, sat. aq. $Na_2S_2O_3$ (30 mL) was carefully added to quench the reaction, and the mixture was filtered through a silica gel pad (80 mL of EtOAc was used for additional washing). The filtrate was concentrated under vacuum, and the product was extracted from the resulting aqueous mixture with EtOAc (4 × 70 mL). Combined organic layers were washed with sat. aq. $Na_2S_2O_3$ (30 mL) and brine (30 mL), dried over Na_2SO_4, filtered and concentrated. The residue was vacuum-dried at 50 °C to afford 3.78 g (86% over two steps) of the Julia reagent **1** as a white solid which was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (s, 2H), 4.04 (hept, *J* = 6.8 Hz, 1H), 3.75 (hept, *J* = 6.8 Hz, 1H), 1.85 (s, 9H), 1.22 (d, *J* = 6.8 Hz, 6H), 1.10 (d, *J* = 6.8 Hz, 6H).

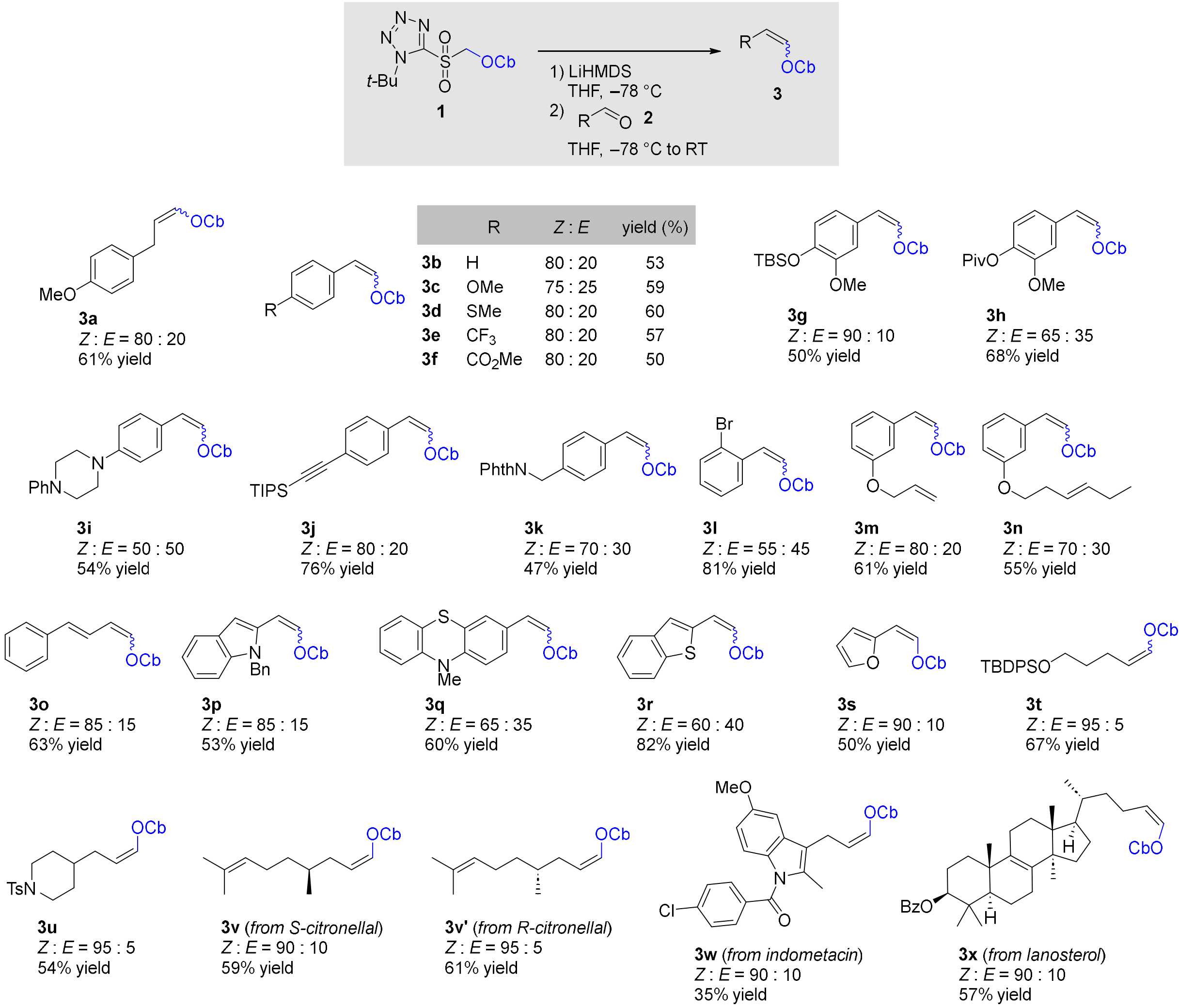
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 152.3, 77.7, 65.5, 47.6, 46.2, 29.6, 21.1, 20.2.

ESI MS calcd for $C_{13}H_{26}N_5O_4S^+$ $[M+H]^+$ 348.17, found 348.1.

General Procedure A for Julia olefination

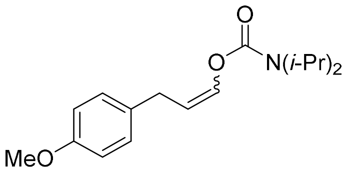


The following manipulations were carried out under argon. Sulfone **1** (0.631 g, 1.82 mmol, 1.50 equiv) was dissolved in anhydrous THF (12 mL), and the solution was cooled to –78 °C. LiHMDS (2.1 mL of 1.0 M in THF, 2.1 mmol, 1.7 equiv) was added dropwise, maintaining the temperature below –60 °C. The mixture was stirred with dry ice/acetone cooling for 40 min. Then a solution of aldehyde **2** (1.21 mmol, 1.00 equiv) in anhydrous THF (1.6 mL) was added dropwise, maintaining the temperature below –60 °C, and the mixture was stirred at ambient temperature overnight. Methanol (1 mL) was added to quench the reaction, and the volatiles were removed under vacuum. Subsequent flash chromatography afforded the desired enol carbamate **3**.



	R	Z : E	yield (%)
3b	H	80 : 20	53
3c	OMe	75 : 25	59
3d	SMe	80 : 20	60
3e	CF_3	80 : 20	57
3f	CO_2Me	80 : 20	50

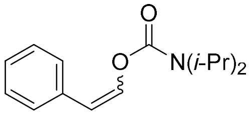
Scheme S1. Scope of Julia Olefination to Access Enol Carbamates. All reactions were run in THF (0.1 M) using Julia reagent **1** (1.5 equiv), LiHMDS (1.7 equiv) and aldehyde **2** (1.0 equiv). Yields are given for isolated products. *Z* : *E* ratios were determined by ^{1}H NMR.



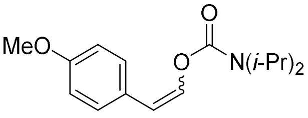
3-(4-Methoxyphenyl)prop-1-en-1-yl diisopropylcarbamate (3a).

General procedure A was followed on a 0.602 g (4.01 mmol) scale of 2-(4-methoxyphenyl)acetaldehyde **2a** (prepared by oxidation of 4-methoxyphenethyl alcohol with IBX according to the literature procedure[3]), which after flash chromatography on silica gel (eluting with hexanes/Et_2O = 90:10) afforded 0.714 g (61%) of the product as a yellow oil (*Z* : *E* = 80 : 20).

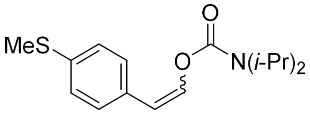
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.09 (m, 3H, *Z* + 3H, *E*), 6.89 – 6.79 (m, 2H, *Z* + 2H, *E*), 5.43 (dt, *J* = 12.4, 7.5 Hz, 1H, *E*), 4.91 (td, *J* = 7.5, 6.4 Hz, 1H, *Z*), 4.11 (br s, 1H, *Z* + 1H, *E*), 3.81 (br s, 1H, *Z* + 1H, *E*), 3.79 (s, 3H, *Z* + 3H, *E*), 3.46 (dd, *J* = 7.5, 1.7 Hz, 2H, *Z*), 3.27 (dd, *J* = 7.4, 1.7 Hz, 2H, *E*), 1.30 – 1.19 (br m, 12H, *Z* + 12H, *E*).
^{13}C NMR (151 MHz, $CDCl_3$) δ 158.05, 153.05, 137.26, 135.63, 132.65, 132.57, 129.48, 129.31, 113.97, 111.35, 109.82, 55.41, 46.98, 45.82, 33.02, 30.46, 21.70, 20.51.
ESI MS calcd for $C_{17}H_{26}NO_3^+$ [M+H]$^+$ 292.19, found 292.2.



Styryl diisopropylcarbamate (3b).
General procedure A was followed on a 0.123 g (1.16 mmol) scale of benzaldehyde **2b**, which after flash chromatography on silica gel (eluting with hexanes/EtOAc = 95:5) afforded 0.153 g (53%) of the product as a pale-yellow oil (*Z* : *E* = 80 : 20).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 12.8 Hz, 1H, *E*), 7.56 – 7.49 (m, 2H, *Z*), 7.37 – 7.15 (m, 4H, *Z* + 5H, *E*), 6.29 (d, *J* = 12.9 Hz, 1H, *E*), 5.63 (d, *J* = 7.3 Hz, 1H, *Z*), 4.27 (br s, 1H, *Z*), 4.08 (br s, 1H, *E*), 3.88 (br s, 1H, *E*), 3.78 (br s, 1H, *Z*), 1.39 – 1.21 (br m, 12H, *Z* + 12H, *E*).
^{13}C NMR (151 MHz, $CDCl_3$) δ 152.82, 151.80, 137.83, 135.55, 135.13, 134.81, 128.76, 128.37, 126.87, 126.83, 126.00, 112.57, 109.55, 62.59, 47.19, 46.98, 46.17, 46.04, 21.79, 21.13, 20.61.
ESI MS calcd for $C_{15}H_{22}NO_2^+$ [M+H]$^+$ 248.16, found 248.1.



4-Methoxystyryl diisopropylcarbamate (3c).
General procedure A was followed on a 0.150 g (1.10 mmol) scale of 4-methoxybenzaldehyde **2c**, which after flash chromatography on silica gel (eluting with hexanes/Et_2O = 90:10) afforded 0.180 g (59%) of the product as a white solid (*Z* : *E* = 75 : 25).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 12.8 Hz, 1H, *E*), 7.51 – 7.43 (m, 2H, *Z*), 7.28 – 7.21 (m, 2H, *E*), 7.16 (d, *J* = 7.3 Hz, 1H, *Z*), 6.91 – 6.83 (m, 2H, *Z*), 6.86 – 6.80 (m, 2H, *E*), 6.25 (d, *J* = 12.8 Hz, 1H, *E*), 5.57 (d, *J* = 7.3 Hz, 1H, *Z*), 4.27 (br s, 1H, *Z*), 4.08 (br s, 1H, *E*), 3.87 (br s, 1H, *E*), 3.82 (s, 3H, *Z*), 3.80 (s, 3H, *E*), 3.77 (br s, 1H, *Z*), 1.41 – 1.17 (br m, 12H, *Z* + 12H, *E*).
^{13}C NMR (151 MHz, $CDCl_3$) δ 158.71, 158.42, 136.43, 134.17, 129.97, 127.62, 127.51, 127.12, 114.23, 113.78, 112.22, 109.16, 55.42, 55.40, 47.15, 46.12, 21.15, 20.64.
ESI MS calcd for $C_{16}H_{24}NO_3^+$ [M+H]$^+$ 278.18, found 278.2.



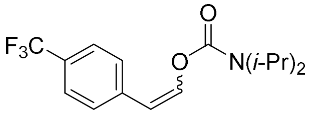
4-(Methylthio)styryl diisopropylcarbamate (3d).

General procedure A was followed on a 0.200 g (1.32 mmol) scale of 4-(methylthio)benzaldehyde **2d**, which after flash chromatography on silica gel (eluting with hexanes/Et_2O = 90:10) afforded 0.232 g (60%) of the product as a yellow solid (*Z* : *E* = 80 : 20).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 12.9 Hz, 1H, *E*), 7.49 – 7.41 (m, 2H, *Z*), 7.25 – 7.15 (m, 3H, *Z* + 4H, *E*), 6.25 (d, *J* = 12.8 Hz, 1H, *E*), 5.57 (d, *J* = 7.3 Hz, 1H, *Z*), 4.26 (br s, 1H, *Z*), 4.08 (br s, 1H, *E*), 3.87 (br s, 1H, *E*), 3.77 (br s, 1H, *Z*), 2.49 (s, 3H, *Z*), 2.48 (s, 3H, *E*), 1.42 – 1.16 (br m, 12H, *Z* + 12H, *E*).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.73, 137.55, 136.81, 136.72, 135.37, 132.12, 131.76, 129.14, 127.09, 126.50, 126.40, 112.06, 108.98, 47.24, 46.19, 21.16, 20.61, 16.14, 15.99.

ESI MS calcd for $C_{16}H_{24}NO_2S^+$ $[M+H]^+$ 294.15, found 294.1.



4-(Trifluoromethyl)styryl diisopropylcarbamate (3e).

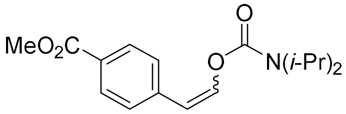
General procedure A was followed on a 0.200 g (1.15 mmol) scale of 4-(trifluoromethyl)benzaldehyde **2e**, which after flash chromatography on silica gel (eluting with hexanes/DCM = 50:50) afforded 0.206 g (57%) of the product as a yellow solid (*Z* : *E* = 80 : 20).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 12.9 Hz, 1H, *E*), 7.66 – 7.60 (m, 2H, *Z*), 7.59 – 7.55 (m, 2H, *Z*), 7.57 – 7.50 (m, 2H, *E*), 7.44 – 7.37 (m, 2H, *E*), 7.34 (d, *J* = 7.3 Hz, 1H, *Z*), 6.30 (d, *J* = 12.9 Hz, 1H, *E*), 5.65 (d, *J* = 7.4 Hz, 1H, *Z*), 4.24 (br s, 1H, *Z*), 4.08 (br s, 1H, *E*), 3.90 (br s, 1H, *E*), 3.78 (br s, 1H, *Z*), 1.43 – 1.16 (br m, 12H, *Z* + 12H, *E*).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.52, 139.60, 138.42, 137.35, 128.79, 128.45, 126.01, 125.73 (q, *J* = 3.9 Hz), 125.30 (q, *J* = 3.9 Hz), 123.45, 111.29, 108.17, 47.33, 46.36, 32.08, 30.07, 29.86, 21.79, 21.15, 20.57.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.47.

ESI MS calcd for $C_{16}H_{21}F_3NO_2^+$ $[M+H]^+$ 316.15, found 316.1.



Methyl 4-(2-((diisopropylcarbamoyl)oxy)vinyl)benzoate (3f).

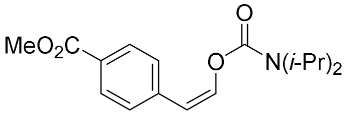
General procedure A was followed on a 0.202 g (1.23 mmol) scale of methyl 4-formylbenzoate **2f**, which after flash chromatography on silica gel (eluting with hexanes/Et_2O = 90:10) afforded 0.189 g (50%) of the product as a white solid (*Z* : *E* = 80 : 20).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 2H, *Z*), 7.96 (d, *J* = 12.9 Hz, 1H, *E*), 7.96 (m, 2H, *E*), 7.61 – 7.56 (m, 2H, *Z*), 7.39 – 7.35 (m, 2H, *E*), 7.35 (d, *J* = 7.3 Hz, 1H, *Z*), 6.31 (d, *J* = 12.9 Hz, 1H, *E*), 5.66 (d, *J* = 7.3 Hz, 1H, *Z*), 4.27 (br s, 1H, *Z*), 4.08 (br s, 1H, *E*), 3.92 (s, 3H, *Z*), 3.90 (s, 3H, *E*), 3.90 (br s, 1H, *E*), 3.78 (br s, 1H, *Z*), 1.41 – 1.20 (br m, 12H, *Z* + br m, 12H, *E*).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.09, 151.40, 140.12, 139.73, 139.56, 137.36, 130.15, 129.72, 128.55, 128.13, 125.73, 111.71, 108.58, 52.23, 52.18, 47.37, 46.30, 21.81, 21.14, 20.57.

ESI MS calcd for $C_{17}H_{24}NO_4^+$ $[M+H]^+$ 306.17, found 306.1.

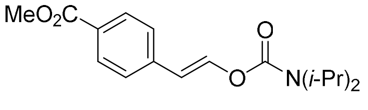
The *Z* and *E* isomers of **3f** were separated by flash chromatography on silica gel (eluting with DCM).



Methyl (*Z*)-4-(2-((diisopropylcarbamoyl)oxy)vinyl)benzoate (3f-*Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 2H, *Z*), 7.62 – 7.55 (m, 2H, *Z*), 7.35 (d, *J* = 7.3 Hz, 1H, *Z*), 5.66 (d, *J* = 7.4 Hz, 1H, *Z*), 4.27 (br s, 1H, *Z*), 3.92 (s, 3H, *Z*), 3.78 (br s, 1H, *Z*), 1.38 – 1.31 (br m, 6H, *Z*), 1.30 – 1.25 (br m, 6H, *Z*).

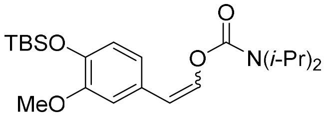
^{13}C NMR (151 MHz, $CDCl_3$) δ 167.09, 151.40, 139.56, 137.37, 129.72, 128.55, 128.13, 108.58, 52.23, 47.36, 46.30, 21.14, 20.57.



Methyl (*E*)-4-(2-((diisopropylcarbamoyl)oxy)vinyl)benzoate (3f-*E*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.94 (m, 2H, *E*), 7.96 (d, *J* = 13.1 Hz, 1H, *E*), 7.40 – 7.32 (m, 2H, *E*), 6.31 (d, *J* = 12.8 Hz, 1H, *E*), 4.08 (br s, 1H, *E*), 3.92 (br s, 1H, *E*), 3.90 (s, 3H, *E*), 1.28 (br d, *J* = 6.5 Hz, 12H, *E*).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.06, 152.48, 140.12, 139.73, 130.15, 128.32, 125.73, 111.71, 52.18, 47.13, 46.18, 21.78, 20.49.



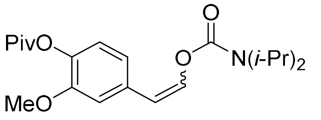
4-((*tert*-Butyldimethylsilyl)oxy)-3-methoxystyryl diisopropylcarbamate (3g).

General procedure A was followed on a 0.300 g (1.04 mmol) scale of TBS-protected vanillin **2g** (prepared from vanillin according to the literature procedure[4]), which after flash chromatography on silica gel (eluting with hexanes/Et_2O = 90:10) afforded 0.212 g (50%) of the product as a colorless oil (*Z* : *E* = 90 : 10).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 12.8 Hz, 1H, *E*), 7.17 (d, *J* = 7.4 Hz, 1H, *Z*), 7.06 (d, *J* = 2.0 Hz, 1H, *Z*), 6.98 (dd, *J* = 8.2, 2.0 Hz, 1H, *Z*), 6.83 (d, *J* = 1.8 Hz, 1H, *E*), 6.80 (d, *J* = 8.2 Hz, 1H, *Z*), 6.77 (d, *J* = 8.4 Hz, 1H, *E*), 6.74 (dd, *J* = 8.3, 1.8 Hz, 1H, *E*), 6.24 (d, *J* = 12.8 Hz, 1H, *E*), 5.54 (d, *J* = 7.4 Hz, 1H, *Z*), 4.34 (br s, 1H, *Z*), 4.08 (br s, 1H, *E*), 3.87 (br s, 1H, *E*), 3.80 (s, 3H, *Z*), 3.79 (s, 3H, *E*), 3.73 (br s, 1H, *Z*), 1.45 – 1.10 (br m, 12H, *Z* + 12H, *E*), 0.99 (s, 9H, *Z*), 0.99 (s, 9H, *E*), 0.15 (s, 6H, *Z*), 0.15 (s, 6H, *E*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.74, 151.13, 150.70, 144.18, 136.56, 134.22, 128.66, 121.88, 121.09, 120.83, 119.25, 112.76, 112.70, 109.46, 109.11, 55.54, 47.18, 46.03, 25.85, 21.10, 18.58, -4.52.

ESI MS calcd for $C_{22}H_{38}NO_4Si^+$ $[M+H]^+$ 408.26, found 408.2.



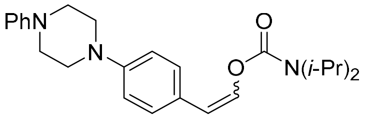
4-(2-((Diisopropylcarbamoyl)oxy)vinyl)-2-methoxyphenyl pivalate (3h).

General procedure A was followed on a 0.300 g (1.27 mmol) scale of pivaloyl-protected vanillin **2h** (prepared from vanillin according to the literature procedure[5]), which after flash chromatography on C18 silica gel (gradient elution: water–acetonitrile 90:10 → acetonitrile) afforded 0.325 g (68%) of the product as a yellow oil (*Z* : *E* = 65 : 35).

¹H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 12.8 Hz, 1H, *E*), 7.25 (d, *J* = 7.5 Hz, 1H, *Z*), 7.14 – 7.07 (m, 2H, *Z*), 6.95 (d, *J* = 8.0 Hz, 1H, *Z*), 6.93 – 6.88 (m, 2H, *E*), 6.85 (dd, *J* = 8.2, 1.8 Hz, 1H, *E*), 6.27 (d, *J* = 12.8 Hz, 1H, *E*), 5.57 (d, *J* = 7.4 Hz, 1H, *Z*), 4.33 (br s, 1H, *Z*), 4.06 (br s, 1H, *E*), 3.90 (br s, 1H, *E*), 3.80 (s, 3H, *Z* + 3H, *E*), 3.73 (br s, 1H, *Z*), 1.36 (s, 9H, *Z* + 9H, *E*), 1.31 – 1.16 (br m, 12H, *Z* + 12H, *E*).

¹³C NMR (151 MHz, $CDCl_3$) δ 176.89, 152.75, 151.53, 151.36, 151.01, 139.24, 139.06, 137.78, 135.42, 133.81, 133.48, 122.91, 122.57, 121.49, 118.91, 112.87, 112.24, 109.39, 108.93, 56.03, 56.00, 47.27, 46.99, 46.11, 39.21, 39.19, 27.36, 21.76, 21.15, 20.55, 20.51.

ESI MS calcd for $C_{21}H_{32}NO_5^+$ $[M+H]^+$ 378.23, found 378.2.



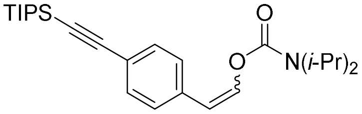
4-(4-Phenylpiperazin-1-yl)styryl diisopropylcarbamate (3i).

General procedure A was followed on a 0.200 g (0.750 mmol) scale of 4-(4-phenylpiperazin-1-yl)benzaldehyde **2i** (prepared from 4-fluorobenzaldehyde and 1-phenylpiperazine according to the literature procedure[6]), which after flash chromatography on C18 silica gel (gradient elution: water–acetonitrile 90:10 → acetonitrile) afforded 0.164 g (54%) of the product as a pink solid (*Z* : *E* = 50 : 50).

¹H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 12.8 Hz, 1H, *E*), 7.54 – 7.44 (m, 2H, *Z*), 7.36 – 7.22 (m, 3H, *Z* + 3H, *E*), 7.16 (d, *J* = 7.3 Hz, 1H, *E*), 7.03 – 6.86 (m, 5H, *Z* + 5H, *E*), 6.25 (d, *J* = 12.8 Hz, 1H, *E*), 5.56 (d, *J* = 7.3 Hz, 1H, *Z*), 4.30 (br s, 1H, *Z*), 4.08 (br s, 1H, *E*), 3.89 (br s, 1H, *E*), 3.77 (br s, 1H, *Z*), 3.41 – 3.28 (m, 8H, *Z* + 8H, *E*), 1.48 – 1.07 (br m, 12H, *Z* + 12H, *E*).

¹³C NMR (151 MHz, $CDCl_3$) δ 153.02, 151.94, 151.34, 150.13, 149.85, 136.21, 133.96, 129.71, 129.34, 129.32, 126.89, 126.75, 126.60, 120.28, 120.22, 116.51, 116.49, 115.92, 112.31, 109.26, 49.50, 49.40, 49.28, 47.18, 46.89, 46.03, 21.78, 21.17, 20.63, 20.55.

ESI MS calcd for $C_{25}H_{34}N_3O_2^+$ $[M+H]^+$ 408.26, found 408.2.



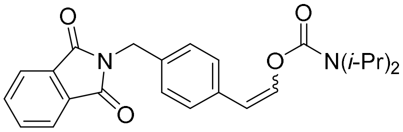
4-((Triisopropylsilyl)ethynyl)styryl diisopropylcarbamate (3j).

General procedure A was followed on a 0.304 g (1.06 mmol) scale of 4-((triisopropylsilyl)ethynyl)benzaldehyde **2j** (prepared from 4-bromobenzaldehyde and ethynyltriisopropylsilane according to the literature procedure[7]), which after flash chromatography on silica gel (eluting with hexanes/Et_2O = 90:10) afforded 0.346 g (76%) of the product as a dark-orange oil (*Z* : *E* = 80 : 20).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 12.8 Hz, 1H, *E*), 7.48 – 7.41 (m, 4H, *Z*), 7.43 – 7.36 (m, 2H, *E*), 7.28 – 7.21 (m, 2H, *E*), 7.27 (d, *J* = 7.3 Hz, 1H, *Z*), 6.26 (d, *J* = 12.8 Hz, 1H, *E*), 5.59 (d, *J* = 7.3 Hz, 1H, *Z*), 4.26 (br s, 1H, *Z*), 4.06 (br s, 1H, *E*), 3.90 (br s, 1H, *E*), 3.77 (br s, 1H, *Z*), 1.39 – 1.21 (br m, 15H, *Z* + 15H, *E*), 1.13 (s, 18H, *Z*), 1.12 (s, 18H, *E*).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.63, 151.56, 138.52, 136.17, 135.29, 134.90, 132.46, 132.05, 128.46, 125.67, 121.80, 121.71, 112.10, 108.94, 107.29, 107.27, 91.00, 47.29, 46.20, 21.13, 20.58, 18.82, 18.78, 11.46.

ESI MS calcd for $C_{26}H_{42}NO_2Si^+$ $[M+H]^+$ 428.30, found 428.3.



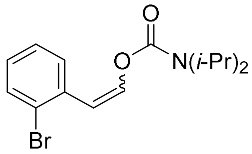
4-((1,3-Dioxoisoindolin-2-yl)methyl)styryl diisopropylcarbamate (3k).

General procedure A was followed on a 0.238 g (0.896 mmol) scale of 4-((1,3-dioxoisoindolin-2-yl)methyl)benzaldehyde **2k** (prepared from 4-(bromomethyl)benzaldehyde and potassium phthalimide according to the literature procedure[8]), which after flash chromatography on C18 silica gel (gradient elution: water–acetonitrile 90:10 → acetonitrile) afforded 0.170 g (47%) of the product as an off-white solid (*Z* : *E* = 70 : 30).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H, *E*), 7.85 – 7.82 (m, 2H, *Z*), 7.81 (d, *J* = 12.8 Hz, 1H, *E*), 7.79 – 7.72 (m, 2H, *E*), 7.72 – 7.68 (m, 2H, *Z*), 7.50 – 7.45 (m, 2H, *Z*), 7.42 – 7.37 (m, 2H, *Z*), 7.39 – 7.32 (m, 2H, *E*), 7.29 – 7.22 (m, 2H, *E*), 7.22 (d, *J* = 7.3 Hz, 1H, *Z*), 6.24 (d, *J* = 12.8 Hz, 1H, *E*), 5.56 (d, *J* = 7.4 Hz, 1H, *Z*), 4.82 (s, 2H, *Z*), 4.81 (s, 2H, *E*), 4.26 (br s, 1H, *Z*), 4.06 (br s, 1H, *E*), 3.88 (br s, 1H, *E*), 3.75 (br s, 1H, *Z*), 1.32 (br s, 12H, *E*), 1.26 (br d, *J* = 6.8 Hz, 12H, *Z*).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.20, 167.94, 152.71, 151.63, 138.01, 135.74, 134.87, 134.79, 134.78, 134.47, 134.45, 134.14, 134.11, 132.75, 132.25, 132.24, 129.12, 128.97, 128.84, 126.22, 123.73, 123.48, 112.06, 108.94, 47.28, 46.10, 41.50, 41.44, 21.75, 21.11, 20.58, 20.49.

ESI MS calcd for $C_{24}H_{27}N_2O_4^+$ $[M+H]^+$ 407.20, found 407.1.



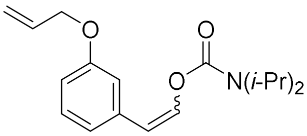
2-Bromostyryl diisopropylcarbamate (3l).

General procedure A was followed on a 0.224 g (1.21 mmol) scale of 2-bromobenzaldehyde **2l**, which after flash chromatography on silica gel (eluting with hexanes/Et$_2$O = 90:10) afforded 0.321 g (81%) of the product as a pale-yellow oil (*Z* : *E* = 55 : 45).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, *J* = 12.8 Hz, 1H, *E*), 7.74 (dd, *J* = 7.8, 1.7 Hz, 1H, *Z*), 7.57 (dd, *J* = 8.0, 1.3 Hz, 1H, *E*), 7.54 (dd, *J* = 8.0, 1.3 Hz, 1H, *E*), 7.48 (dd, J = 7.8, 1.7 Hz, 1H, *Z*), 7.36 (d, *J* = 7.3 Hz, 1H, *Z*), 7.26 (dd, *J* = 7.9, 1.3 Hz, 1H, *Z*), 7.23 (dd, *J* = 7.9, 1.3 Hz, 1H, *Z*), 7.11 – 7.04 (m, 2H, *E*), 6.61 (d, *J* = 12.7 Hz, 1H, *E*), 5.91 (d, *J* = 7.3 Hz, 1H, *Z*), 4.10 – 3.76 (br m, 2H, *Z* + 2H, *E*), 1.37 – 1.07 (br m, 12H, *Z* + 12H, *E*).

^{13}C NMR (151 MHz, CDCl$_3$) δ 152.47, 151.81, 139.44, 136.81, 135.13, 134.62, 133.07, 132.79, 130.83, 128.33, 128.30, 127.67, 126.92, 126.60, 123.67, 123.37, 111.62, 108.47, 46.92, 46.78, 46.51, 46.27, 21.73, 21.21, 20.51.

ESI MS calcd for $C_{15}H_{21}BrNO_2^+$ $[M+H]^+$ 326.08, found 326.1.



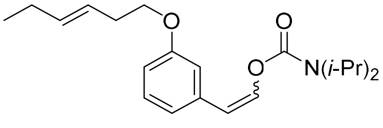
3-(Allyloxy)styryl diisopropylcarbamate (3m).

General procedure A was followed on a 0.259 g (1.60 mmol) scale of 3-(allyloxy)benzaldehyde **2m** (prepared from 3-hydroxybenzaldehyde according to the literature procedure[9]), which after flash chromatography on silica gel (eluting with hexanes/Et$_2$O = 90:10) afforded 0.294 g (61%) of the product as a yellow oil (*Z* : *E* = 80 : 20).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, *J* = 12.8 Hz, 1H, *E*), 7.25 (d, *J* = 7.6 Hz, 1H, *Z*), 7.23 (t, *J* = 7.9 Hz, 1H, *Z*), 7.19 (t, *J* = 8.0 Hz, 1H, *E*), 7.14 (dd, *J* = 2.6, 1.6 Hz, 1H, *Z*), 7.10 (dt, *J* = 7.6, 1.3 Hz, 1H, *Z*), 6.91 (dt, *J* = 7.6, 1.3 Hz, 1H, *E*), 6.87 (t, *J* = 2.0 Hz, 1H, *E*), 6.79 (ddd, *J* = 8.3, 2.6, 1.1 Hz, 1H, *Z*), 6.77 (ddd, *J* = 8.1, 2.6, 1.0 Hz, 1H, *E*), 6.26 (d, *J* = 12.8 Hz, 1H, *E*), 6.06 (ddt, *J* = 17.1, 10.5, 5.2 Hz, 1H, *Z*), 5.59 (d, *J* = 7.3 Hz, 1H, *Z* + 1H, *E*), 5.41 (dq, *J* = 17.3, 1.7 Hz, 1H, *Z* + 1H, *E*), 5.28 (ddq, *J* = 10.5, 2.9, 1.5 Hz, 1H, *Z* + 1H, *E*), 4.53 (dq, *J* = 5.2, 1.9 Hz, 2H, *Z* + 2H, *E*), 4.33 (br s, 1H, *Z*), 4.07 (br s, 1H, *E*), 3.89 (br s, 1H, *E*), 3.74 (br s, 1H, *Z*), 1.47 – 1.11 (br m, 12H, *Z* + 12H, *E*).

^{13}C NMR (151 MHz, CDCl$_3$) δ 158.93, 158.65, 152.73, 151.59, 138.04, 136.53, 136.09, 135.68, 133.39, 133.38, 129.70, 129.27, 121.62, 118.86, 117.74, 117.55, 115.14, 113.49, 113.25, 112.46, 111.93, 109.32, 68.84, 68.80, 47.29, 47.10, 46.05, 21.75, 21.11, 20.58, 20.49.

ESI MS calcd for $C_{18}H_{26}NO_3^+$ $[M+H]^+$ 304.19, found 304.4.



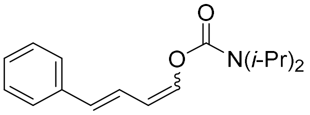
3-(((*E*)-Hex-3-en-1-yl)oxy)styryl diisopropylcarbamate (3n).

General procedure A was followed on a 0.249 g (1.22 mmol) scale of (*E*)-3-(hex-3-en-1-yloxy)benzaldehyde **2n** (prepared from 3-hydroxybenzaldehyde and (*E*)-hex-3-en-1-ol according to the literature procedure[10]), which after flash chromatography on silica gel (eluting with hexanes/Et_2O = 90:10) afforded 0.558 g (55%) of the product as a colorless oil (*Z* : *E* = 70 : 30).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 12.8 Hz, 1H, *E*), 7.25 (d, *J* = 7.4 Hz, 1H, *Z*), 7.18 (t, *J* = 7.9 Hz, 1H, *E*), 7.22 (t, *J* = 8.0 Hz, 1H, *Z*), 7.14 (dd, *J* = 2.6, 1.6 Hz, 1H, *Z*), 7.06 (dt, *J* = 7.7, 1.3 Hz, 1H, *Z*), 6.89 (dt, *J* = 7.7, 1.3 Hz, 1H, *E*), 6.86 (dd, *J* = 2.4, 1.7 Hz, 1H, *E*), 6.77 (ddd, *J* = 8.4, 2.6, 1.1 Hz, 1H, *Z*), 6.74 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 1H, *E*), 6.25 (d, *J* = 12.8 Hz, 1H, *E*), 5.67 – 5.55 (m, 1H, *Z* + 1H, *E*), 5.58 (d, *J* = 7.5 Hz, 1H, *Z*), 5.54 – 5.41 (m, 1H, *Z* + 1H, *E*), 4.34 (br s, 1H, *Z*), 4.07 (br s, 1H, *E*), 3.95 (t, *J* = 6.9 Hz, 2H, *E*), 3.95 (t, *J* = 6.9 Hz, 2H, *Z*), 3.89 (br s, 1H, *E*), 3.73 (br s, 1H, *Z*), 2.47 (qq, *J* = 6.7, 1.2 Hz, 2H, *Z* + 2H, *E*), 2.12 – 1.97 (m, 2H, *Z* + 2H, *E*), 1.48 – 1.15 (br m, 12H, *Z* + 12H, *E*), 0.99 (t, *J* = 7.5 Hz, 3H, *E*), 0.98 (t, *J* = 7.5 Hz, 3H, *Z*).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.34, 159.07, 152.78, 151.60, 138.00, 136.48, 136.04, 135.59, 135.01, 129.68, 129.25, 124.59, 124.50, 121.43, 118.70, 114.85, 113.43, 113.21, 112.54, 111.67, 109.40, 67.92, 67.89, 47.32, 47.04, 46.05, 32.81, 32.67, 25.81, 25.79, 21.77, 21.12, 20.60, 20.51, 13.87, 13.85.

ESI MS calcd for $C_{21}H_{32}NO_3^+$ $[M+H]^+$ 346.24, found 346.4.



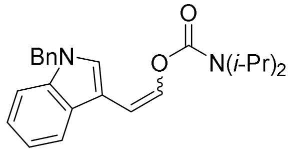
(3*E*)-4-Phenylbuta-1,3-dien-1-yl diisopropylcarbamate (3o).

General procedure A was followed on a 0.200 g (1.52 mmol) scale of cinnamaldehyde **2o**, which after flash chromatography on silica gel (eluting with hexanes/Et_2O = 90:10) afforded 0.261 g (63%) of the product as a yellow oil (*Z* : *E* = 85 : 15).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 12.3 Hz, 1H, *E*), 7.43 – 7.28 (m, 4H, *Z* + 4H, *E*), 7.26 – 7.18 (m, 1H, *Z* + 1H, *E*), 7.14 (dd, *J* = 6.4, 1.0 Hz, 1H, *Z*), 7.13 (ddd, *J* = 15.9, 11.0, 1.1 Hz, 1H, *Z*), 6.73 (dd, *J* = 15.6, 11.0 Hz, 1H, *E*), 6.54 (d, *J* = 15.9 Hz, 1H, *Z*), 6.48 (d, *J* = 15.7 Hz, 1H, *E*), 6.13 (dd, *J* = 12.2, 10.9 Hz, 1H, *E*), 5.58 (dd, *J* = 11.0, 6.4 Hz, 1H, *Z*), 4.38 – 3.57 (br m, 2H, *Z* + 2H, *E*), 1.49 – 1.10 (br m, 12H, *Z* + 12H, *E*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.22, 140.17, 137.28, 135.77, 130.92, 130.21, 128.46, 128.40, 127.26, 126.93, 126.06, 125.80, 124.36, 121.50, 113.09, 110.29, 46.90, 45.64, 21.50, 20.17.

ESI MS calcd for $C_{17}H_{24}NO_2^+$ $[M+H]^+$ 274.18, found 274.2.



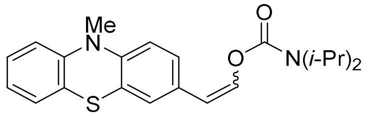
2-(1-Benzyl-1*H*-indol-3-yl)vinyl diisopropylcarbamate (3p).

General procedure A was followed on a 0.229 g (0.904 mmol) scale of 1-benzyl-1*H*-indole-3-carbaldehyde **2p** (prepared from indole-3-carbaldehyde according to the literature procedure[11]), which after flash chromatography on silica gel (eluting with hexanes/Et_2O = 90:10) afforded 0.181 g (53%) of the product as a brown oil (*Z* : *E* = 85 : 15).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 12.8 Hz, 1H, *E*), 7.80 (ddd, *J* = 7.6, 1.5, 0.8 Hz, 1H, *E*), 7.70 (ddd, *J* = 7.7, 1.4, 0.8 Hz, 1H, *Z*), 7.46 (s, 1H, *Z*), 7.34 – 7.09 (m, 8H, *Z* + 9H, *E*), 7.24 (d, *J* = 6.9 Hz, 1H, *Z*), 6.48 (dd, *J* = 12.9, 0.6 Hz, 1H, *E*), 5.95 (dd, *J* = 6.9, 0.7 Hz, 1H, *Z*), 5.31 (s, 2H, *Z*), 5.28 (s, 2H, *E*), 4.23 (br s, 1H, *Z*), 4.08 (br s, 1H, *E*), 3.91 (br s, 1H, *E*), 3.68 (br s, 1H, *Z*), 1.41 – 1.02 (br m, 12H, *Z* + 12H, *E*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.87, 137.40, 136.17, 135.54, 133.18, 128.94, 128.92, 127.89, 127.81, 127.57, 127.48, 127.10, 127.00, 126.77, 126.40, 126.16, 122.31, 120.41, 119.98, 119.85, 119.15, 109.94, 109.85, 109.63, 105.45, 100.83, 50.21, 50.11, 47.19, 45.93, 20.76.

ESI MS calcd for $C_{24}H_{29}N_2O_2^+$ $[M+H]^+$ 377.22, found 377.2.



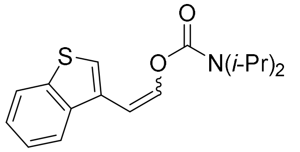
2-(10-Methyl-10*H*-phenothiazin-3-yl)vinyl diisopropylcarbamate (3q).

General procedure A was followed on a 0.155 g (0.642 mmol) scale of 10-methyl-10*H*-phenothiazine-3-carbaldehyde **2q** (prepared from 10-methylphenothiazine according to the literature procedure[12]), which after flash chromatography on C18 silica gel (gradient elution: water–acetonitrile 90:10 → acetonitrile) afforded 0.148 g (60%) of the product as a dark-orange solid (*Z* : *E* = 65 : 35).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 12.8 Hz, 1H, *E*), 7.49 (d, *J* = 2.0 Hz, 1H, *Z*), 7.21 (dd, *J* = 8.4, 2.0 Hz, 1H, *Z*), 7.19 – 7.06 (m, 2H, *Z* + 4H, *E*), 7.18 (d, *J* = 7.2 Hz, 1H, *Z*), 6.93 (dt, *J* = 7.6, 1.5 Hz, 1H, *Z*), 6.91 (dt, *J* = 7.5, 1.5 Hz, 1H, *E*), 6.80 (dd, *J* = 8.1, 1.1 Hz, 1H, *Z*), 6.79 (dd, *J* = 8.1, 1.1 Hz, 1H, *E*), 6.74 (d, *J* = 8.4 Hz, 1H, *Z*), 6.72 (d, *J* = 9.3 Hz, 1H, *E*), 6.19 (d, *J* = 12.8 Hz, 1H, *E*), 5.51 (d, *J* = 7.3 Hz, 1H, *Z*), 4.32 (br s, 1H, *Z*), 4.07 (br s, 1H, *E*), 3.88 (br s, 1H, *E*), 3.77 (br s, 1H, *Z*), 3.37 (s, 3H, *Z*), 3.35 (s, 3H, *E*), 1.33 (br s, 12H, *Z*), 1.27 (br d, *J* = 6.9 Hz, 12H, *E*).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.80, 151.66, 145.72, 145.66, 144.56, 144.33, 136.80, 134.67, 129.56, 129.33, 128.01, 127.54, 127.27, 127.23, 127.16, 125.02, 124.53, 123.75, 123.23, 123.18, 123.14, 122.55, 122.51, 114.25, 114.15, 114.10, 113.80, 111.50, 108.43, 47.33, 46.92, 46.06, 35.40, 21.75, 21.21, 20.61, 20.49.

ESI MS calcd for $C_{22}H_{27}N_2O_2S^+$ $[M+H]^+$ 383.18, found 383.2.



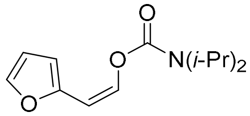
2-(Benzo[*b*]thiophen-3-yl)vinyl diisopropylcarbamate (3r).

General procedure A was followed on a 0.220 g (1.36 mmol) scale of benzo[*b*]thiophene-3-carbaldehyde **2r**, which after flash chromatography on silica gel (eluting with hexanes/Et_2O = 90:10) afforded 0.337 g (82%) of the product as a dark-green oil (*Z* : *E* = 60 : 40).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 12.9 Hz, 1H, *E*), 7.88 – 7.84 (m, 2H, *Z*), 7.82 (dd, *J* = 7.4, 1.5 Hz, 1H, *Z*), 7.67 (s, 1H, *Z*), 7.44 (d, *J* = 7.1 Hz, 1H, *Z*), 7.45 – 7.32 (m, 1H, *Z* + 4H, *E*), 7.33 (s, 1H, *E*), 6.55 (dd, *J* = 12.8, 0.9 Hz, 1H, *E*), 5.96 (d, *J* = 7.0 Hz, 1H, *Z*), 4.24 (br s, 1H, *Z*), 4.07 (br s, 1H, *E*), 3.96 (br s, 1H, *E*), 3.79 (br s, 1H, *Z*), 1.31 (br s, 12H, *Z*), 1.25 (br s, 12H, *E*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.70, 151.72, 140.47, 139.45, 138.73, 138.50, 137.94, 136.76, 130.71, 129.34, 124.56, 124.30, 123.89, 123.01, 122.78, 122.20, 121.87, 120.80, 105.41, 101.33, 47.09, 46.25, 21.80, 21.12, 20.59.

ESI MS calcd for $C_{17}H_{22}NO_2S^+$ $[M+H]^+$ 304.14, found 304.1.



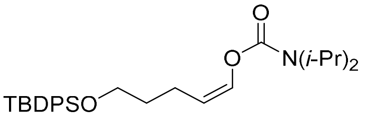
(*Z*)-2-(Furan-2-yl)vinyl diisopropylcarbamate (3s).

General procedure A was followed on a 0.150 g (1.56 mmol) scale of furfural **2s**, which after flash chromatography on silica gel (eluting with hexanes/Et_2O = 90:10) afforded 0.187 g (50%) of the product as a dark-brown oil (*Z* : *E* = 90 : 10).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 12.7 Hz, 1H, *E*), 7.35 (dd, *J* = 1.9, 0.9 Hz, 1H, *Z*), 7.30 (d, *J* = 1.9 Hz, 1H, *E*), 7.21 (d, *J* = 7.3 Hz, 1H, *Z*), 6.43 (dd, *J* = 3.5, 0.9 Hz, 1H, *Z*), 6.42 (dd, *J* = 3.4, 1.7 Hz, 1H, *Z*), 6.34 (dd, *J* = 3.3, 1.9 Hz, 1H, *E*), 6.15 (d, *J* = 3.2 Hz, 1H, *E*), 6.13 (d, *J* = 12.7 Hz, 1H, *E*), 5.63 (d, *J* = 7.3 Hz, 1H, *Z*), 4.28 (br s, 1H, *Z*), 4.09 (br s, 1H, *E*), 3.84 (br s, 1H, *Z* + br s, 1H, *E*), 1.33 (br m, 6H, *Z*), 1.31 (br m, 6H, *Z*), 1.27 (br m, 6H, *E*), 1.25 (br m, 6H, *E*).

^{13}C NMR only z (101 MHz, $CDCl_3$) δ 151.68, 150.20, 141.18, 133.94, 111.41, 108.57, 99.33, 47.01, 46.36, 21.05, 20.56.

ESI MS calcd for $C_{13}H_{20}NO_3^+$ $[M+H]^+$ 238.14, found 238.2.



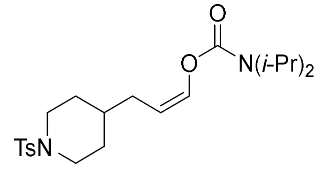
(*Z*)-5-((*tert*-Butyldiphenylsilyl)oxy)pent-1-en-1-yl diisopropylcarbamate (3t).

General procedure A was followed on a 0.310 g (0.949 mmol) scale of 4-((*tert*-butyldiphenylsilyl)oxy)butanal **2t** (prepared from butane-1,4-diol according to the literature procedure[13]), which after flash chromatography on silica gel (eluting with hexanes/Et$_2$O = 90:10) afforded 0.297 g (67%) of the product as a colorless oil (*Z* : *E* = 95 : 5).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 – 7.57 (m, 4H, *Z*), 7.46 – 7.31 (m, 6H, *Z*), 6.99 (dt, *J* = 6.5, 1.6 Hz, 1H, *Z*), 4.69 (td, *J* = 7.3, 6.4 Hz, 1H, *Z*), 4.10 (br s, 1H, *Z*), 3.77 (br s, 1H, *Z*), 3.68 (t, *J* = 6.3 Hz, 2H, *Z*), 2.27 (qd, *J* = 7.5, 1.6 Hz, 2H, *Z*), 1.67 (pd, *J* = 7.5, 6.3, 1.6 Hz, 2H, *Z*), 1.23 (br d, *J* = 6.8 Hz, 12H, *Z*), 1.04 (s, 9H, *Z*).

^{13}C NMR (151 MHz, CDCl$_3$) δ 153.15, 135.69, 135.29, 134.09, 129.67, 127.73, 110.54, 63.63, 46.89, 45.71, 32.56, 26.98, 21.71, 21.66, 20.52, 19.34.

ESI MS calcd for $C_{28}H_{42}NO_3Si^+$ [M+H]$^+$ 468.29, found 468.4.



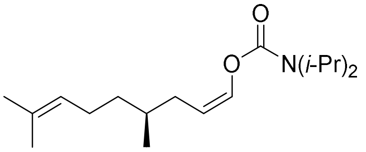
(*Z*)-3-(1-Tosylpiperidin-4-yl)prop-1-en-1-yl diisopropylcarbamate (3u).

General procedure A was followed on a 0.300 g (1.07 mmol) scale of 2-(1-tosylpiperidin-4-yl)acetaldehyde **2u** (prepared from 4-piperidineethanol according to the literature procedure[14]), which after flash chromatography on silica gel (eluting with hexanes/Et$_2$O = 80:20) afforded 0.244 g (54%) of the product as a colorless oil (*Z* : *E* = 95 : 5).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 – 7.56 (m, 2H, *Z*), 7.35 – 7.25 (m, 2H, *Z*), 7.01 (dt, *J* = 6.5, 1.4 Hz, 1H, *Z*), 4.62 (td, *J* = 7.7, 6.4 Hz, 1H, *Z*), 4.09 (br s, 1H, *Z*), 3.76 (dt, *J* = 11.6, 2.5 Hz, 2H, *Z*), 3.72 (br s, 1H, *Z*), 2.42 (s, 3H, *Z*), 2.19 (td, *J* = 11.7, 2.5 Hz, 2H, *Z*), 2.06 (ddd, *J* = 7.8, 6.6, 1.5 Hz, 2H, *Z*), 1.80 – 1.68 (m, 2H, *Z*), 1.31 (qd, *J* = 12.7, 12.2, 4.1 Hz, 2H, *Z*), 1.31 – 1.13 (br m, 13H, *Z*).

^{13}C NMR (101 MHz, CDCl$_3$) δ 153.03, 143.48, 136.41, 133.25, 129.67, 127.83, 108.10, 46.88, 46.60, 45.75, 35.73, 31.56, 31.45, 27.80, 21.63, 20.49.

ESI MS calcd for $C_{22}H_{35}N_2O_4S^+$ [M+H]$^+$ 423.23, found 423.4.



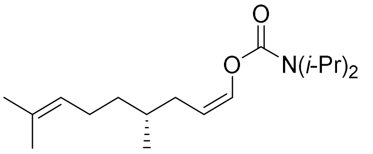
(*S*,*Z*)-4,8-Dimethylnona-1,7-dien-1-yl diisopropylcarbamate (3v).

General procedure A was followed on a 0.177 g (1.15 mmol) scale of (*S*)-citronellal **2v**, which after flash chromatography on silica gel (eluting with hexanes/Et$_2$O = 96:4) afforded 0.202 g (59%) of the product as a pale-yellow oil (*Z* : *E* = 90 : 10).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.03 (dt, *J* = 6.5, 1.5 Hz, 1H, *Z*), 5.09 (thept, *J* = 7.1, 1.3 Hz, 1H, *Z*), 4.73 (td, *J* = 7.6, 6.5 Hz, 1H, *Z*), 4.11 (br s, 1H, *Z*), 3.80 (br s, 1H, *Z*), 2.16 (dddd, *J* = 14.5, 7.3, 5.6, 1.6 Hz, 1H, *Z*), 2.08 – 1.88 (m, 3H, *Z*), 1.68 (q, *J* = 1.3 Hz, 3H, *Z*), 1.60 (q, *J* = 1.3 Hz, 3H, *Z*), 1.57 – 1.45 (m, 1H, *Z*), 1.37 (dddd, *J* = 13.4, 9.4, 6.6, 5.5 Hz, 1H, *Z*), 1.32 – 1.17 (br m, 12H, *Z*), 1.17 (dddd, *J* = 13.6, 9.3, 7.9, 6.2 Hz, 1H, *Z*), 0.90 (d, *J* = 6.6 Hz, 3H, *Z*).

^{13}C NMR (101 MHz, CDCl$_3$) δ 153.25, 135.75, 131.30, 124.93, 109.56, 46.89, 45.76, 36.93, 33.00, 32.32, 25.85, 25.78, 21.63, 20.55, 19.59, 17.76.

ESI MS calcd for $C_{18}H_{33}KNO_2^+$ [M+K]$^+$ 334.21, found 334.2.



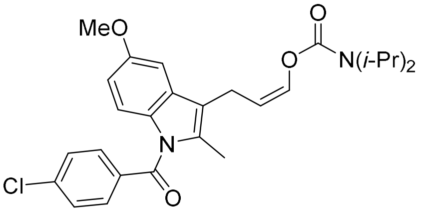
(*R*,*Z*)-4,8-Dimethylnona-1,7-dien-1-yl diisopropylcarbamate (3v').

General procedure A was followed on a 0.197 g (1.28 mmol) scale of (*R*)-citronellal **2v'**, which after flash chromatography on silica gel (eluting with hexanes/Et$_2$O = 96:4) afforded 0.230 g (61%) of the product as a pale-yellow oil (*Z* : *E* = 95 : 5).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.03 (dt, *J* = 6.5, 1.5 Hz, 1H, *Z*), 5.09 (thept, *J* = 7.1, 1.3 Hz, 1H, *Z*), 4.73 (td, *J* = 7.6, 6.5 Hz, 1H, *Z*), 4.11 (br s, 1H, *Z*), 3.80 (br s, 1H, *Z*), 2.16 (dddd, *J* = 14.5, 7.3, 5.7, 1.6 Hz, 1H, *Z*), 2.07 – 1.90 (m, 3H, *Z*), 1.68 (q, *J* = 1.3 Hz, 3H, *Z*), 1.60 (q, *J* = 1.3 Hz, 3H, *Z*), 1.57 – 1.44 (m, 1H, *Z*), 1.37 (dddd, *J* = 13.4, 9.5, 6.6, 5.5 Hz, 1H, *Z*), 1.32 – 1.17 (br m, 12H, *Z*), 1.17 (dddd, *J* = 13.6, 9.3, 7.9, 6.2 Hz, 1H, *Z*), 0.90 (d, *J* = 6.7 Hz, 3H, *Z*).

^{13}C NMR (101 MHz, CDCl$_3$) δ 153.24, 135.74, 131.28, 124.91, 109.54, 46.87, 45.75, 36.92, 32.99, 32.31, 25.83, 25.77, 21.62, 20.54, 19.57, 17.74.

ESI MS calcd for $C_{18}H_{33}NNaO_2^+$ [M+Na]$^+$ 318.24, found 318.2.



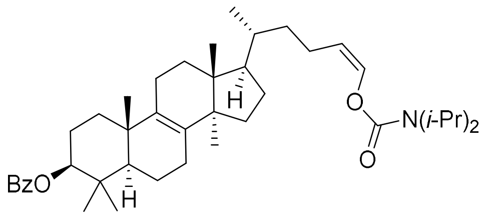
(*Z*)-3-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)prop-1-en-1-yl diisopropylcarbamate (3w).

General procedure A was followed on a 0.560 g (1.64 mmol) scale of 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetaldehyde **2w** (prepared from indomethacin according to the literature procedure[15]), which after flash chromatography on C18 silica gel (gradient elution: water–acetonitrile 90:10 → acetonitrile) afforded 0.279 g (35%) of the product as a dark-orange solid (*Z* : *E* = 90 : 10).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.69 – 7.60 (m, 2H, *Z*), 7.50 – 7.42 (m, 2H, *Z*), 7.13 (dt, *J* = 6.4, 1.8 Hz, 1H, *Z*), 6.94 (d, *J* = 2.5 Hz, 1H, *Z*), 6.88 (d, *J* = 9.0 Hz, 1H, *Z*), 6.66 (dd, *J* = 9.0, 2.6 Hz, 1H, *Z*), 4.82 (q, *J* = 7.0 Hz, 1H, *Z*), 4.07 (br s, 1H, *Z*), 3.97 (br s, 1H, *Z*), 3.81 (s, 3H, *Z*), 3.54 (dd, *J* = 7.1, 1.9 Hz, 2H, *Z*), 2.35 (s, 3H, *Z*), 1.44 – 1.17 (br m, 12H, *Z*).

^{13}C NMR (151 MHz, CDCl$_3$) δ 168.46, 156.01, 152.80, 139.20, 135.73, 134.30, 134.21, 131.25, 131.08, 129.23, 122.98, 118.04, 115.11, 111.44, 108.51, 101.55, 55.79, 46.95, 46.08, 21.76, 20.55, 20.27, 13.40.

ESI MS calcd for $C_{27}H_{32}ClN_2O_4^+$ [M+H]$^+$ 483.20, found 483.4.



(3*S*,5*R*,10*S*,13*R*,14*R*,17*R*)-17-((*R*,*Z*)-6-((Diisopropylcarbamoyl)oxy)hex-5-en-2-yl)-4,4,10,13,14-pentamethyl-2,3,4,5,6,7,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl benzoate (3x).

General procedure A was followed on a 0.362 g (0.717 mmol) scale of aldehyde **2x** (prepared from lanosterol according to the literature procedures[16,17]), which after flash chromatography on silica gel (eluting with hexanes/Et$_2$O = 80:20) afforded 0.263 g (57%) of the product as an off-white solid (*Z* : *E* = 90 : 10).

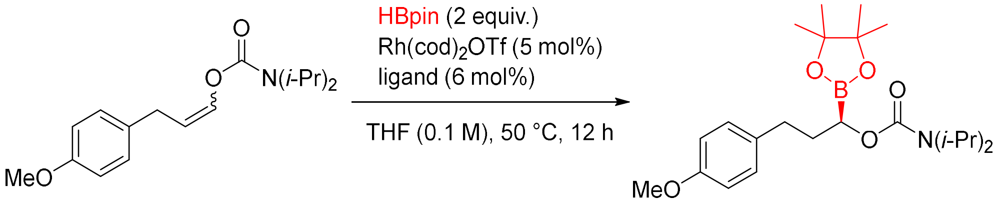
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.09 – 8.01 (m, 2H, *Z*), 7.60 – 7.50 (m, 1H, *Z*), 7.49 – 7.40 (m, 2H, *Z*), 6.98 (dt, *J* = 6.4, 1.5 Hz, 1H, *Z*), 4.75 (dd, *J* = 11.5, 4.4 Hz, 1H, *Z*), 4.71 (dd, *J* = 7.5, 6.4 Hz, 1H, *Z*), 4.11 (br s, 1H, *Z*), 3.82 (br s, 1H, *Z*), 2.32 – 2.15 (m, 1H, *Z*), 2.13 – 1.98 (m, 6H, *Z*), 2.01 – 1.06 (m, 28H, *Z*), 1.05 (s, 3H, *Z*), 1.05 (s, 3H, *Z*), 0.96 (s, 3H, *Z*), 0.93 (d, *J* = 6.3 Hz, 3H, *Z*), 0.89 (s, 3H, *Z*), 0.70 (s, 3H, *Z*).

^{13}C NMR (151 MHz, CDCl$_3$) δ 166.44, 153.27, 134.94, 134.63, 134.38, 132.85, 131.13, 129.67, 128.46, 111.61, 81.69, 50.70, 50.45, 49.97, 46.90, 45.73, 44.64, 38.35, 37.08, 36.27, 36.12, 35.41, 31.10, 30.96, 28.37, 28.23, 26.52, 24.40, 24.38, 22.03, 21.70, 21.17, 20.54, 19.36, 18.69, 18.29, 16.97, 15.91.

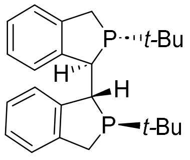
ESI MS calcd for $C_{42}H_{64}NO_4^+$ $[M+H]^+$ 646.48, found 646.6.

Optimization of Asymmetric Hydroboration

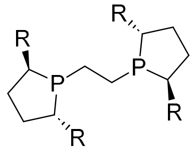
Table S1. Screening of chiral ligands in the asymmetric hydroboration[a]



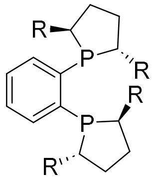
3a, Z : E = 80 : 20 **4a**



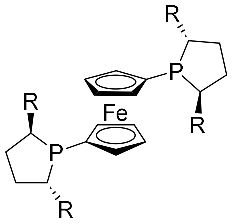
Duanphos **L1**



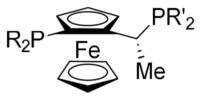
BPE **L2**



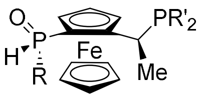
Duphos **L3**



Ferrocelane **L4**



Josiphos **L5**



JoSPOphos **L6**

Entry	Ligand	R	R'	Yield (%)[b]	ee (%)[c]
1	**L1**	–	–	(trace)	7
2	**L2a**	Me	–	0	–
3	**L2b**	Et	–	13	34
4	**L2c**	*i*-Pr	–	0	–
5	**L2d**	Ph	–	0	–
6	**L4a**	Me	–	21	n.d.
7	**L4b**	Et	–	18	n.d.
8	**L4c**	*i*-Pr	–	0	–
9	**L3a**	Me	–	47	49
10	**L3b**	Et	–	52	65
11	**L3c**	*i*-Pr	–	0	–
12	**L5a**	Ph	Cy	(trace)	n.d.
13	**L5b**	Ph	*t*-Bu	69	10
14	**L5c**	Cy	Cy	35	3
15	**L5d**	Cy	Ph	(trace)	n.d.
16	**L5e**	Ph	3,5-Me$_2$C$_6$H$_3$	0	–
17	**L5f**	3,5-(CF$_3$)$_2$C$_6$H$_3$	Cy	0	–
18	**L5g**	4-MeO-3,5-Me$_2$C$_6$H$_2$	Cy	64	66
19	**L5h**	3,5-(CF$_3$)$_2$C$_6$H$_3$	3,5-Me$_2$C$_6$H$_3$	0	–
20	**L5i**	Cy	*t*-Bu	0	–
21	**L6a**	*t*-Bu	Ph	0	–
22	**L6b**	Ph	*t*-Bu	50	91

[a] Reactions were run on a 0.07 mmol scale; starting material, reagents and solvent were mixed in a N$_2$-filled glove box. [b] Yields were determined by ^{1}H NMR using triphenylmethane as an internal standard. [c] Enantiomeric excess (ee) values were determined by HPLC on chiral media.

General Procedure B for Table S1

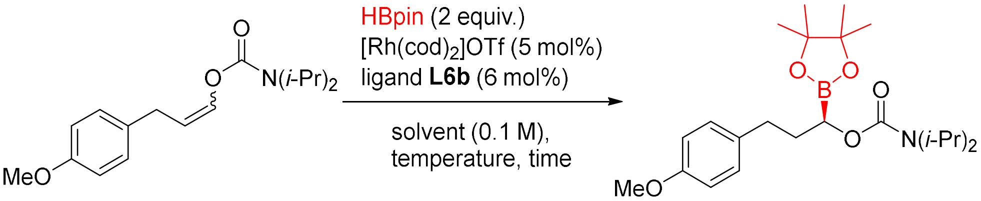
Substrate **3a** (126 mg, 432 µmol, 1.00 equiv) and triphenylmethane (106 mg, 432 µmol, 1.00 equiv) were weighed in a 2-dram screw-cap vial, which was then transferred into a N_2-filled glove box.

The following manipulations were carried out inside a glove box. Six different ligands (2–6 µmol) were weighed in six 1-dram screw-cap vials equipped with stir bars. $[Rh(cod)_2]OTf$ (10 mg, 21 µmol, 5 mol%) was weighed in a separate 2-dram screw-cap vial and then dissolved in THF (3.92 mL). Catalyst solution was transferred to the vial containing substrate **3a** and triphenylmethane (additional 0.40-mL portion of THF was used for rinsing). Six aliquots of this solution were added to each of the six vials with ligands (volume of each aliquot was calculated individually for each reaction based on the exact weight of the ligand, so that the amount of ligand in the resulting mixture was 6 mol% relative to **3a**). An additional 0.05-mL aliquot was transferred to a separate vial and then used for "zero point" ^1H NMR. HBpin (2.0 equiv) was then added to each reaction vial. All mixtures were briefly stirred, and the reaction vials were sealed with Teflon screw caps.

Reaction mixtures were removed from the glove box and stirred at 50 °C for 12 h. Ca. 0.05-mL aliquots were taken and used for ^1H NMR analysis to determine product yields. If product yield was greater than 20%, the mixture was concentrated, and the product was purified by flash column chromatography on silica gel (hexanes/EtOAc = 70:30). The purified product was analyzed by chiral HPLC (CHIRALCEL® OZ-3, 0.75% IPA in hexane, 1.0 mL/min, 220 nm).

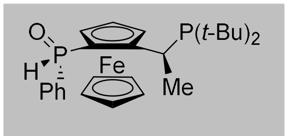
Racemic sample was obtained by running the reaction using 1,1′-bis(diisopropylphosphino)ferrocene (DiPrPF)[18] instead of **L6b** as a ligand.

Table S2. Optimization of reaction conditions[a]



3a, Z : E = 80 : 20

4a



L6b

Entry	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]	ee (%)[c]
1	THF	50	12	50	91
2[d]	THF	50	12	30	n.d.
3	PhMe	50	12	43	87
4	xylenes	50	12	28	81
5	Et_2O	35	12	10	n.d.
6	CH_2Cl_2	40	12	12	n.d.
7	DCE	50	12	46	94
8	dioxane	50	12	0	–
9	MeCN	50	12	0	–
10	MeTHF	50	12	36	91
11	DMF	50	12	0	–
12	$PhCF_3$	50	12	81	85
13[e]	$PhCF_3$	50	12	80[f]	78
14[g]	$PhCF_3$	50	12	0	–
15[h]	$PhCF_3$	50	12	77	70
16	$PhCF_3$	35	12	59	95
17[e]	**$PhCF_3$**	**35**	**18**	**65**[f]	**97**
18	$PhCF_3$	35	24	85	83
19	$PhCF_3$	rt	24	50	n.d.
20	$PhCF_3$	rt	48	68	93
21[e]	**$PhCF_3$**	**rt**	**48**	**67**[f]	**98**

[a] Reactions were run on a 0.05 mmol scale; starting material, reagents and solvent were mixed in a N_2-filled glove box. [b] Yields were determined by ^1H NMR using triphenylmethane as an internal standard. [c] Enantiomeric excess (ee) values were determined by HPLC on chiral media. [d] $[Rh(cod)Cl]_2$ (5 mol%) was used as a catalyst, with AgOTf (6 mol%) as an additive. [e] Reaction was run on a 0.35 mmol scale. [f] Isolated yield. [g] No glove box was used. [h] Starting material with Z : E = 55 : 45 was used.

General Procedure C for Table S2 (0.05 mmol scale reactions)

Substrate **3a** (21 mg, 72 μmol) and triphenylmethane (17 mg, 70 μmol) were weighed in a 2-dram screw-cap vial, which was then transferred into a N_2-filled glove box.

The following manipulations were carried out inside a glove box. Ligand **L6b** (1.5 mg, 3.1 μmol, 6 mol%) was weighed in a 1-dram screw-cap vial. Substrate **3a** and triphenylmethane were dissolved in a solvent (0.72 mL). It was assumed that the resulting solution was 0.10 M with respect to the substrate **3a**. 0.51 mL of this solution was transferred to the vial with ligand (the remaining portion was used for "zero point" ^{1}H NMR). [Rh(cod)$_2$]OTf (1.2 mg, 2.6 μmol, 5 mol%) was weighed in a 1-dram screw-cap vial equipped with a stir bar. The solution of substrate **3a**, triphenylmethane and ligand **L6b** was transferred to the vial with catalyst. HBpin (15 μL, 13 mg, 0.10 mmol, 2.0 equiv) was then added, and the mixture was briefly stirred. The reaction vial was sealed with Teflon screw cap.

Reaction mixture was removed from the glove box and stirred at the required temperature for the required period of time (in accordance with Table S2). Ca. 0.05-mL aliquot was taken and used for ^{1}H NMR analysis to determine product yield. If product yield was greater than 20%, the mixture was concentrated, and the product was purified by flash column chromatography on silica gel (hexanes/EtOAc = 70:30). The purified product was analyzed by chiral HPLC (CHIRALCEL® OZ-3, 0.75% IPA in hexane, 1.0 mL/min, 220 nm).

General Procedure D for Table S2 (0.35 mmol scale reactions)

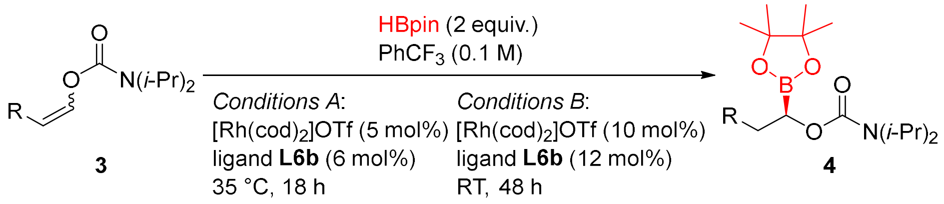
Substrate **3a** (100 mg, 0.350 mmol, 1.00 equiv) was weighed in a 2-dram screw-cap vial, which was then transferred into a N_2-filled glove box.

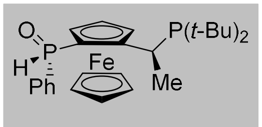
The following manipulations were carried out inside a glove box. Ligand **L6b** (10 mg, 21 μmol, 6 mol%) was weighed in a 1-dram screw-cap vial; [Rh(cod)$_2$]OTf (8.2 mg, 18 μmol, 5 mol%) was weighed in a separate 2-dram screw-cap vial equipped with a stir bar. Substrate **3a** was dissolved in $PhCF_3$ (3.00 mL), and the resulting solution was transferred to the vial with ligand (additional 0.50-mL portion of $PhCF_3$ was used for rinsing). The solution of substrate **3a** and ligand **L6b** was then transferred to the vial with catalyst. HBpin (102 μL, 90 mg, 0.70 mmol, 2.0 equiv) was then added, and the mixture was briefly stirred. The reaction vial was sealed with Teflon screw cap.

Reaction mixture was removed from the glove box and stirred at the required temperature for the required period of time (in accordance with Table S2). The mixture was concentrated, and the product was purified by flash column chromatography on silica gel (hexanes/EtOAc = 70:30). The purified product was analyzed by chiral HPLC (CHIRALCEL® OZ-3, 0.75% IPA in hexane, 1.0 mL/min, 220 nm).

Scope of Asymmetric Hydroboration

General Procedure E for asymmetric hydroboration





L6b

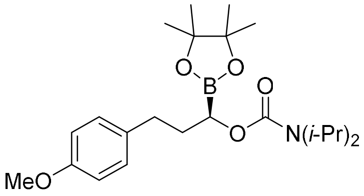
Enol carbamate **3** (0.50 mmol, 1.0 equiv) was weighed in a 2-dram screw-cap vial, which was then transferred into a N_2-filled glove box.

The following manipulations were carried out inside a glove box. Ligand **L6b** (14–28 mg, 30–60 µmol, 6–12 mol%) was weighed in a 1-dram screw-cap vial; $[Rh(cod)_2]OTf$ (12–24 mg, 25–50 µmol, 5–10 mol%) was weighed in a separate 20-mL screw-cap vial equipped with a stir bar. Substrate **3** was dissolved in $PhCF_3$ (4.0 mL), and the resulting solution was transferred to the vial with ligand (additional 1.0-mL portion of $PhCF_3$ was used for rinsing). The solution of substrate **3** and ligand **L6b** was then transferred to the vial with catalyst. HBpin (0.15 µL, 0.13 g, 1.0 mmol, 2.0 equiv) was then added, and the mixture was briefly stirred. The reaction vial was sealed with Teflon screw cap.

Reaction mixture was removed from the glove box and stirred at 35 °C (*Conditions A*) or at room temperature (*Conditions B*) with the reaction progress monitored by ^1H NMR (aliquots for analysis were withdrawn inside a glove box). Generally, hydroboration is complete in 18 h at 35 °C and in 48 h at room temperature.

The mixture was concentrated, and pinacol was removed by transferring the crude product into a 250-mL round-bottom flask, dissolving in MeOH (2 mL), adding water (0.4–0.8 mL) until the solution becomes cloudy, and concentrating on a rotavap. After 6–9 azeotropic evaporation cycles pinacol is removed (as indicated by absence of the 1.24 ppm peak in ^1H NMR).[19] Subsequent flash chromatography afforded the desired enantioenriched hydroboration product **4**.

Racemic product samples were obtained by following the same procedure using 1,1′-bis(diisopropylphosphino)ferrocene (DiPrPF) instead of **L6b** as a ligand.



(*R*)-3-(4-Methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl diisopropylcarbamate (4a). General procedure E was followed on a 102 mg (0.350 mmol) scale of **3a** with 6 mol% of **L6b** and 5 mol% of the catalyst at room temperature (the reaction was complete in 48 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 70:30) afforded 98 mg (67%) of the product as a pale-yellow oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.16 – 7.07 (m, 2H), 6.87 – 6.77 (m, 2H), 4.07 (hept, *J* = 6.9 Hz, 1H), 3.82 (dd, *J* = 10.6, 3.9 Hz, 1H), 3.78 (s, 3H), 3.76 (hept, *J* = 6.9 Hz, 1H), 2.79 (ddd, *J* = 14.7, 9.9, 5.3 Hz, 1H), 2.65 (ddd, *J* = 13.8, 9.4, 6.6 Hz, 1H), 2.03 – 1.93 (m, 1H), 1.92 – 1.80 (m, 1H), 1.28 – 1.20 (m, 12H), 1.17 (s, 12H).

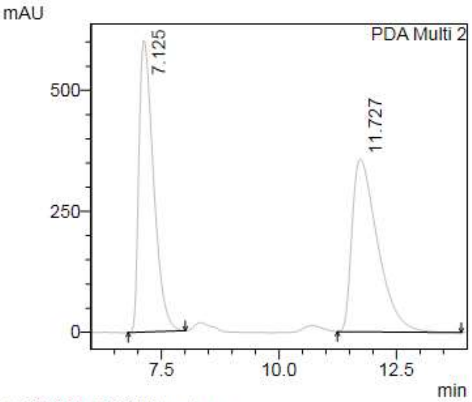
^{13}C NMR (101 MHz, CDCl$_3$) δ 162.77, 157.66, 134.60, 129.42, 113.70, 79.74, 55.26, 48.44, 46.61, 33.61, 33.35, 25.30, 24.96, 20.62, 20.61, 20.35, 20.26 (the carbon attached to boron was not observed due to quadrupolar relaxation[20]).

^{11}B NMR (128 MHz, CDCl$_3$) δ 12.86.

ESI MS calcd for $C_{23}H_{39}BNO_5^+$ $[M+H]^+$ 420.29, found 420.2.

Chiral HPLC CHIRALCEL® OZ-3, 0.75% IPA in hexane, 1.0 mL/min, 220 nm: 98% ee

Racemic Material



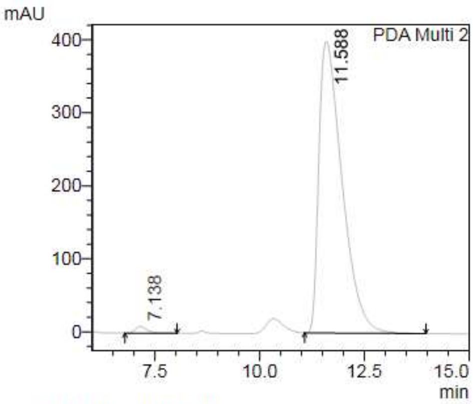
1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.125	13029627	49.036
2	11.727	13541857	50.964
Total		26571484	100.000

Enantioenriched Material



1 PDA Multi 2/220nm 4nm

PeakTable

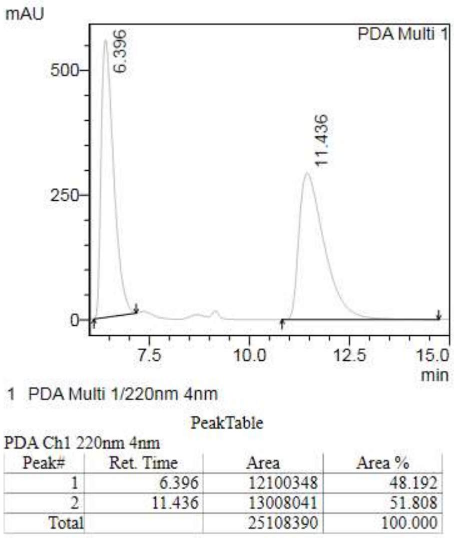
PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.138	186856	1.199
2	11.588	15394461	98.801
Total		15581317	100.000

The same reaction was run on a 284 mg (0.974 mmol) scale of **3a** (complete in 57 h), and it afforded 231 mg (57%) of the product with identical spectral data.

Chiral HPLC CHIRALCEL® OZ-3, 0.75% IPA in hexane, 1.0 mL/min, 220 nm: 92% ee

Racemic Material



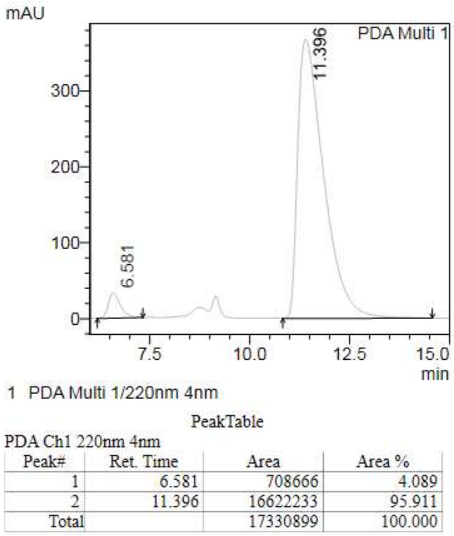
1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.396	12100348	48.192
2	11.436	13008041	51.808
Total		25108390	100.000

Enantioenriched Material



1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.581	708666	4.089
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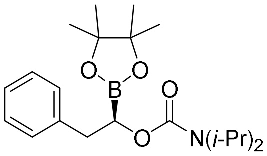
Total		17330899	100.000



(*R*)-2-Phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl diisopropylcarbamate (4b).

General procedure E was followed on a 76 mg (0.31 mmol) scale of **3b** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 70:30) afforded 70 mg (60%) of the product as a pale-yellow oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.23 (m, 4H), 7.22 – 7.14 (m, 1H), 4.10 (dd, *J* = 8.6, 6.6 Hz, 1H), 4.04 (hept, *J* = 6.8 Hz, 1H), 3.72 (hept, *J* = 6.8 Hz, 1H), 3.02 – 2.90 (m, 2H), 1.25 (d, *J* = 7.0 Hz, 6H), 1.20 (s, 6H), 1.19 (s, 6H), 1.08 (d, *J* = 6.9 Hz, 6H).

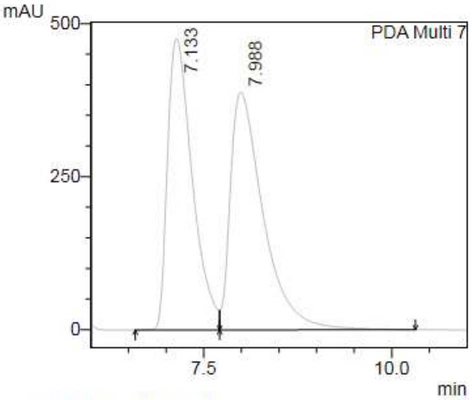
^{13}C NMR (151 MHz, CDCl$_3$) δ 162.83, 141.25, 128.92, 128.23, 125.82, 79.96, 48.48, 46.79, 37.91, 25.30, 25.01, 20.55, 20.48, 20.42, 20.35 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 12.50.

ESI MS calcd for $C_{21}H_{35}BNO_4^+$ [M+H]$^+$ 376.27, found 376.2.

Chiral HPLC CHIRALCEL® OZ-3, 0.4% IPA in hexane, 1.0 mL/min, 200 nm: 91% ee

Racemic Material



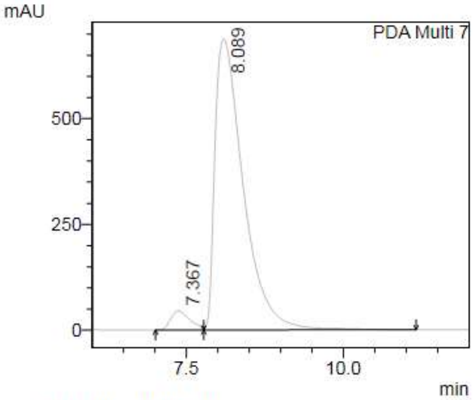
1 PDA Multi 7/200nm 4nm

PeakTable

PDA Ch7 200nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.133	10919759	48.002
2	7.988	11828675	51.998
Total		22748434	100.000

Enantioenriched Material

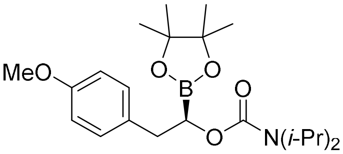


1 PDA Multi 7/200nm 4nm

PeakTable

PDA Ch7 200nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.367	974742	4.321
2	8.089	21582766	95.679
Total		22557507	100.000



(*R*)-2-(4-Methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl diisopropylcarbamate (4c). General procedure E was followed on an 88 mg (0.32 mmol) scale of **3c** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 70:30) afforded 83 mg (64%) of the product as a pale-yellow oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.20 – 7.14 (m, 2H), 6.86 – 6.79 (m, 2H), 4.08 – 3.98 (m, 2H), 3.78 (s, 3H), 3.73 (hept, J = 6.8 Hz, 1H), 2.97 – 2.84 (m, 2H), 1.25 (d, J = 6.8 Hz, 6H), 1.20 (s, 6H), 1.18 (s, 6H), 1.09 (d, J = 6.8 Hz, 6H).

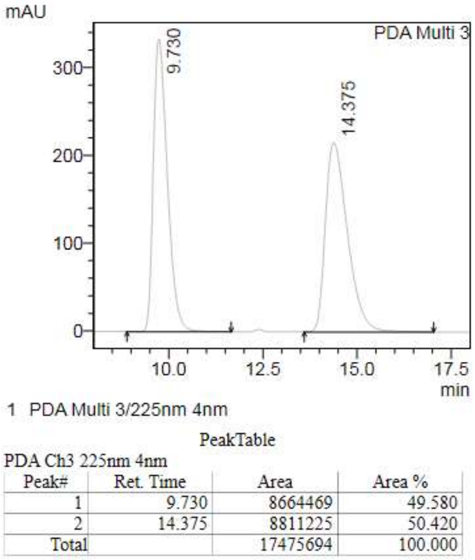
^{13}C NMR (151 MHz, CDCl$_3$) δ 162.85, 157.82, 133.32, 129.82, 113.65, 79.96, 55.35, 48.45, 46.82, 36.99, 25.31, 25.02, 20.58, 20.52, 20.44, 20.37 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 12.66.

ESI MS calcd for $C_{22}H_{37}BNO_5^+$ $[M+H]^+$ 406.28, found 406.3.

Chiral HPLC CHIRALCEL® OZ-3, 1.0% IPA in hexane, 1.0 mL/min, 225 nm: 91% ee

Racemic Material



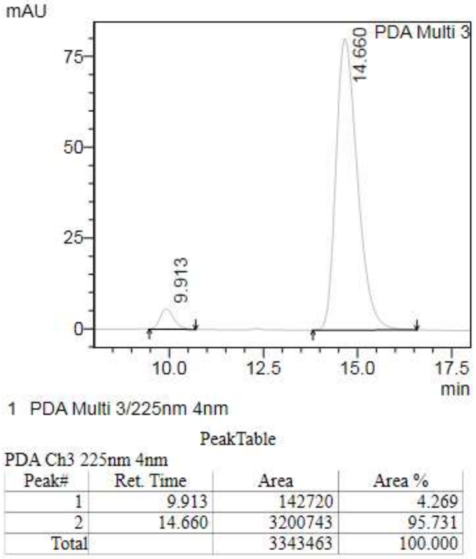
1 PDA Multi 3/225nm 4nm

PeakTable

PDA Ch3 225nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.730	8664469	49.580
2	14.375	8811225	50.420
Total		17475694	100.000

Enantioenriched Material

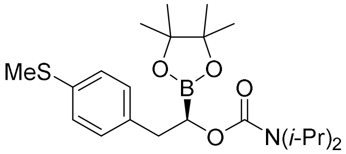


1 PDA Multi 3/225nm 4nm

PeakTable

PDA Ch3 225nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.913	142720	4.269
2	14.660	3200743	95.731
Total		3343463	100.000



(*R*)-2-(4-(Methylthio)phenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl diisopropylcarbamate (4d). General procedure E was followed on a 104 mg (0.354 mmol) scale of **3d** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 70:30) afforded 95 mg (64%) of the product as a beige solid. Absolute stereochemistry was assigned by X-ray crystallography.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.14 (m, 4H), 4.11 – 3.98 (m, 2H), 3.73 (hept, *J* = 6.8 Hz, 1H), 2.99 – 2.85 (m, 2H), 2.47 (s, 3H), 1.25 (d, *J* = 6.6 Hz, 6H), 1.20 (s, 6H), 1.19 (s, 6H), 1.09 (d, *J* = 6.8 Hz, 6H).

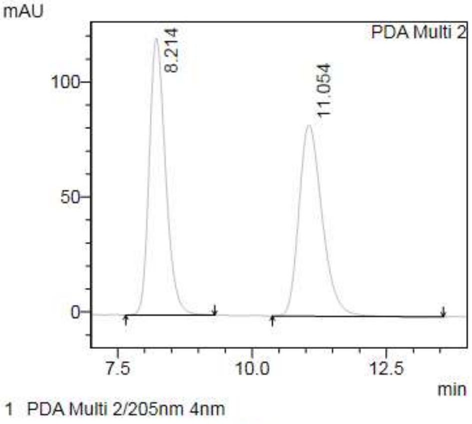
^{13}**C NMR** (151 MHz, $CDCl_3$) δ 162.80, 138.45, 135.19, 129.48, 127.06, 79.99, 48.48, 46.86, 37.39, 25.32, 25.02, 20.58, 20.52, 20.43, 20.36, 16.46 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}**B NMR** (128 MHz, $CDCl_3$) δ 12.54.

ESI MS calcd for $C_{22}H_{37}BNO_4S^+$ $[M+H]^+$ 422.25, found 422.2.

Chiral HPLC CHIRALCEL® OZ-3, 1.0% IPA in hexane, 1.0 mL/min, 205 nm: 95% ee

Racemic Material

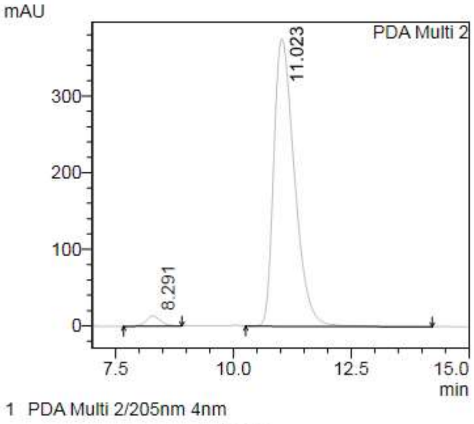


PeakTable

PDA Ch2 205nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.214	2548146	50.518
2	11.054	2495867	49.482
Total		5044013	100.000

Enantioenriched Material



PeakTable

PDA Ch2 205nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.291	295226	2.503
2	11.023	11501873	97.497
Total		11797100	100.000

X-ray crystallography. Crystals grew as clusters of large, colorless prisms by slow evaporation from hexane/EtOAc 70:30. The data crystal was cut from a larger crystal and had approximate dimensions: 0.43 × 0.22 × 0.11 mm. The data were collected on a Rigaku Oxford Diffraction HyPix6000E Dual Source diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418 Å) with collimating mirror monochromators. A total of 4455 frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 4 seconds per frame for frames collected with a detector offset of ±48.2° and 16 seconds per frame with frames collected with a detector offset of 107.8°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S3. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.41.115a.[21] The structure was solved by direct methods using SHELXT[22] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-hydrogen atoms using SHELXL-2018/3.[23] Structure analysis was aided by use of the programs PLATON[24] and OLEX2.[25] The hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to $1.2\times U_{eq}$ of the attached atom ($1.5\times U_{eq}$ for methyl hydrogen atoms). The absolute configuration was determined using the method of Flack[26] and confirmed using the Hooft y-parameter method, which resulted in a Hooft y-parameter of 0.01(1).[27]

The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized, where $w = 1/[(\sigma(F_O))^2 + (0.0715\times P)^2 + (1.6689\times P)]$ and $P = (|F_O|^2 + 2|F_C|^2)/3$. $R_W(F^2)$ refined to 0.131, with R(F) = 0.0484 and a goodness of fit S = 1.04. Definitions used for calculating R(F), $R_W(F^2)$ and the goodness of fit S are given below.[28] The data were checked for secondary extinction effects, but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[29] All figures were generated using SHELXTL/PC.[30] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found below. The structure was deposited with the Cambridge Crystallographic Database (CCDC: 226136).

Table S3. Crystal data and structure refinement for 4d

Empirical formula	$C_{22}H_{36}BNO_4S$	
Formula weight	421.39	
Temperature	100.02(13) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 6.45491(9) Å	α = 90°
	b = 23.0622(3) Å	β = 98.2351(13)°
	c = 15.8936(2) Å	γ = 90°
Volume	2341.59(6) $Å^3$	
Z	4	
Density (calculated)	1.195 Mg/m^3	
Absorption coefficient	1.435 mm^{-1}	
F(000)	912	
Crystal size	0.428 × 0.22 × 0.111 mm^3	
Theta range for data collection	2.809 to 77.263°	
Index ranges	$-8 \leq h \leq 8, -28 \leq k \leq 28, -19 \leq l \leq 15$	
Reflections collected	31964	
Independent reflections	9354 [R(int) = 0.0380]	
Completeness to theta = 67.684°	99.9%	
Absorption correction	Gaussian and multi-scan	
Max. and min. transmission	1.000 and 0.373	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9354 / 1 / 541	
Goodness-of-fit on F^2	1.038	
Final R indices [I > 2sigma(I)]	R1 = 0.0484, wR2 = 0.1298	
R indices (all data)	R1 = 0.0495, wR2 = 0.1306	
Absolute structure parameter	0.005(13)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.680 and –0.302 e.$Å^{-3}$	

Table S4. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for 4d; U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
S1	2175(2)	6730(1)	4042(1)	41(1)
O1	8747(4)	4381(1)	4567(1)	23(1)
O2	11070(4)	3718(1)	5093(2)	26(1)
O3	9364(4)	3535(1)	6375(2)	22(1)
O4	12192(4)	4163(1)	6515(2)	24(1)
N1	10203(5)	3789(1)	3663(2)	24(1)
C1	10021(5)	3952(2)	4449(2)	21(1)
C2	8998(5)	4518(2)	5501(2)	21(1)
C3	6838(5)	4639(2)	5729(2)	22(1)
C4	5754(5)	5164(2)	5282(2)	21(1)
C5	3715(6)	5124(2)	4879(2)	24(1)
C6	2644(6)	5604(2)	4523(2)	27(1)
C7	3633(6)	6143(2)	4544(2)	26(1)
C8	5692(6)	6187(2)	4927(2)	28(1)
C9	6734(6)	5701(2)	5296(2)	26(1)
C10	10957(6)	3294(2)	7002(2)	31(1)
C11	12285(7)	3835(2)	7296(2)	32(1)
C12	9027(6)	4095(2)	2925(2)	29(1)
C13	10480(8)	4488(2)	2511(3)	38(1)
C14	7861(7)	3668(2)	2291(2)	42(1)
C15	11753(6)	3333(2)	3519(2)	29(1)

C16	11114(7)	2742(2)	3836(3)	35(1)
C17	13976(6)	3501(2)	3875(3)	36(1)
C18	3359(7)	7356(2)	4585(3)	33(1)
C19	9954(7)	2980(2)	7661(3)	34(1)
C20	12283(7)	2852(2)	6567(3)	33(1)
C21	11233(8)	4191(2)	7938(3)	38(1)
C22	14542(6)	3742(2)	7647(3)	35(1)
B1	10354(6)	3990(2)	5975(2)	20(1)
S2	13076(2)	3233(1)	886(1)	38(1)
O5	6684(4)	5631(1)	389(1)	23(1)
O6	4271(4)	6279(1)	-117(1)	25(1)
O7	5502(4)	6488(1)	-1505(2)	23(1)
O8	3170(4)	5732(1)	-1439(1)	22(1)
N2	4982(5)	6141(1)	1307(2)	23(1)
C23	5281(5)	6023(2)	517(2)	21(1)
C24	6884(5)	5621(2)	-542(2)	21(1)
C25	6824(6)	5000(2)	-829(2)	24(1)
C26	8380(6)	4581(2)	-351(2)	22(1)
C27	10479(6)	4725(2)	-93(2)	25(1)
C28	11880(6)	4309(2)	280(2)	26(1)
C29	11229(6)	3747(2)	407(2)	25(1)
C30	9113(6)	3604(2)	163(2)	27(1)
C31	7742(6)	4022(2)	-204(2)	26(1)
C32	3670(6)	6612(2)	-2109(2)	24(1)
C33	2674(6)	6000(2)	-2264(2)	23(1)
C34	6163(6)	5826(2)	2037(2)	28(1)

C35	4734(8)	5409(2)	2413(3)	42(1)
C36	7228(7)	6245(2)	2706(2)	39(1)
C37	3369(6)	6576(2)	1463(2)	27(1)
C38	1164(6)	6390(2)	1072(3)	36(1)
C39	3924(7)	7180(2)	1190(3)	33(1)
C40	12040(7)	2560(2)	436(3)	38(1)
C41	2267(6)	7028(2)	-1696(2)	29(1)
C42	4377(7)	6896(2)	-2883(3)	35(1)
C43	3714(6)	5651(2)	-2905(2)	31(1)
C44	312(6)	5999(2)	-2517(2)	33(1)
B2	4954(6)	6018(2)	-1002(2)	20(1)

Table S5. Bond lengths [Å] for 4d

S1-C7	1.773(4)	N1-C12	1.482(5)	C5-C6	1.383(5)
S1-C18	1.795(4)	N1-C15	1.492(5)	C6-H6	0.9500
O1-C1	1.318(4)	C2-H2	1.0000	C6-C7	1.395(5)
O1-C2	1.503(4)	C2-C3	1.516(5)	C7-C8	1.384(5)
O2-C1	1.264(4)	C2-B1	1.619(5)	C8-H8	0.9500
O2-B1	1.662(4)	C3-H3A	0.9900	C8-C9	1.393(5)
O3-C10	1.438(4)	C3-H3B	0.9900	C9-H9	0.9500
O3-B1	1.426(5)	C3-C4	1.521(5)	C10-C11	1.549(6)
O4-C11	1.448(4)	C4-C5	1.382(5)	C10-C19	1.494(5)
O4-B1	1.418(4)	C4-C9	1.390(5)	C10-C20	1.554(6)
N1-C1	1.327(4)	C5-H5	0.9500	C11-C21	1.541(6)
C12-C13	1.519(6)	O5-C23	1.316(4)	C35-H35B	0.9800
C11-C22	1.499(6)	O5-C24	1.504(4)	C35-H35C	0.9800
C12-H12	1.0000	O6-C23	1.266(4)	C36-H36A	0.9800
C12-C14	1.527(6)	O6-B2	1.646(4)	C36-H36B	0.9800
C13-H13A	0.9800	O7-C32	1.441(4)	C36-H36C	0.9800
C13-H13B	0.9800	O7-B2	1.422(5)	C37-H37	1.0000

C13-H13C	0.9800	O8-C33	1.444(4)	C37-C38	1.530(5)
C14-H14A	0.9800	O8-B2	1.419(4)	C37-C39	1.517(6)
C14-H14B	0.9800	N2-C23	1.325(4)	C38-H38A	0.9800
C14-H14C	0.9800	N2-C34	1.484(5)	C38-H38B	0.9800
C15-H15	1.0000	N2-C37	1.492(5)	C38-H38C	0.9800
C15-C16	1.529(6)	C24-H24	1.0000	C39-H39A	0.9800
C15-C17	1.516(6)	C24-C25	1.503(5)	C39-H39B	0.9800
C16-H16A	0.9800	C24-B2	1.632(5)	C39-H39C	0.9800
C16-H16B	0.9800	C25-H25A	0.9900	C40-H40A	0.9800
C16-H16C	0.9800	C25-H25B	0.9900	C40-H40B	0.9800
C17-H17A	0.9800	C25-C26	1.517(5)	C40-H40C	0.9800
C17-H17B	0.9800	C26-C27	1.398(5)	C41-H41A	0.9800
C17-H17C	0.9800	C26-C31	1.384(5)	C41-H41B	0.9800
C18-H18A	0.9800	C27-H27	0.9500	C41-H41C	0.9800
C18-H18B	0.9800	C27-C28	1.391(5)	C42-H42A	0.9800
C18-H18C	0.9800	C28-H28	0.9500	C42-H42B	0.9800
C19-H19A	0.9800	C28-C29	1.387(5)	C42-H42C	0.9800
C19-H19B	0.9800	C29-C30	1.405(5)	C43-H43A	0.9800
C19-H19C	0.9800	C30-H30	0.9500	C43-H43B	0.9800
C20-H20A	0.9800	C30-C31	1.381(5)	C43-H43C	0.9800
C20-H20B	0.9800	C31-H31	0.9500	C44-H44A	0.9800
C20-H20C	0.9800	C32-C33	1.557(5)	C44-H44B	0.9800
C21-H21A	0.9800	C32-C41	1.530(5)	C44-H44C	0.9800
C21-H21B	0.9800	C32-C42	1.519(5)		
C21-H21C	0.9800	C33-C43	1.526(5)		
C22-H22A	0.9800	C33-C44	1.520(5)		
C22-H22B	0.9800	C34-H34	1.0000		
C22-H22C	0.9800	C34-C35	1.513(6)		
S2-C29	1.773(4)	C34-C36	1.526(6)		
S2-C40	1.797(4)	C35-H35A	0.9800		

Table S6. Bond angles [°] for 4d

C7-S1-C18	103.67(18)	C8-C7-C6	118.9(3)	H14A-C14-H14B	109.5
C1-O1-C2	108.4(2)	C7-C8-H8	120.0	H14A-C14-H14C	109.5
C1-O2-B1	109.8(3)	C7-C8-C9	120.1(3)	H14B-C14-H14C	109.5
B1-O3-C10	105.8(3)	C9-C8-H8	120.0	N1-C15-H15	106.6
B1-O4-C11	107.5(3)	C4-C9-C8	121.3(3)	N1-C15-C16	111.0(3)
C1-N1-C12	120.4(3)	C4-C9-H9	119.4	N1-C15-C17	112.5(3)
C1-N1-C15	119.7(3)	C8-C9-H9	119.4	C16-C15-H15	106.6
C12-N1-C15	119.6(3)	O3-C10-C11	102.0(3)	C17-C15-H15	106.6
O1-C1-N1	119.2(3)	O3-C10-C19	109.5(3)	C17-C15-C16	113.0(4)
O2-C1-O1	118.6(3)	O3-C10-C20	109.2(3)	C15-C16-H16A	109.5
O2-C1-N1	122.1(3)	C11-C10-C20	110.3(3)	C15-C16-H16B	109.5
O1-C2-H2	108.0	C19-C10-C11	117.1(3)	C15-C16-H16C	109.5
O1-C2-C3	107.5(3)	C19-C10-C20	108.5(3)	H16A-C16-H16B	109.5
O1-C2-B1	106.1(3)	O4-C11-C10	102.1(3)	H16A-C16-H16C	109.5
C3-C2-H2	108.0	O4-C11-C21	108.8(3)	H16B-C16-H16C	109.5
C3-C2-B1	118.8(3)	O4-C11-C22	108.2(3)	C15-C17-H17A	109.5
B1-C2-H2	108.0	C21-C11-C10	110.6(3)	C15-C17-H17B	109.5
C2-C3-H3A	108.7	C22-C11-C10	117.5(4)	C15-C17-H17C	109.5
C2-C3-H3B	108.7	C22-C11-C21	109.1(3)	H17A-C17-H17B	109.5
C2-C3-C4	114.4(3)	N1-C12-H12	107.6	H17A-C17-H17C	109.5
H3A-C3-H3B	107.6	N1-C12-C13	110.4(3)	H17B-C17-H17C	109.5
C4-C3-H3A	108.7	N1-C12-C14	111.3(3)	S1-C18-H18A	109.5
C4-C3-H3B	108.7	C13-C12-H12	107.6	S1-C18-H18B	109.5
C5-C4-C3	120.5(3)	C13-C12-C14	112.1(3)	S1-C18-H18C	109.5
C5-C4-C9	117.9(3)	C14-C12-H12	107.6	H18A-C18-H18B	109.5
C9-C4-C3	121.6(3)	C12-C13-H13A	109.5	H18A-C18-H18C	109.5
C4-C5-H5	119.2	C12-C13-H13B	109.5	H18B-C18-H18C	109.5
C4-C5-C6	121.5(3)	C12-C13-H13C	109.5	C10-C19-H19A	109.5
C6-C5-H5	119.2	H13A-C13-H13B	109.5	C10-C19-H19B	109.5
C5-C6-H6	119.9	H13A-C13-H13C	109.5	C10-C19-H19C	109.5
C5-C6-C7	120.2(3)	H13B-C13-H13C	109.5	H19A-C19-H19B	109.5
C7-C6-H6	119.9	C12-C14-H14A	109.5	H19A-C19-H19C	109.5
C6-C7-S1	117.3(3)	C12-C14-H14B	109.5	H19B-C19-H19C	109.5
C8-C7-S1	123.8(3)	C12-C14-H14C	109.5	C10-C20-H20A	109.5
C10-C20-H20B	109.5	C25-C24-O5	108.1(3)	O8-C33-C44	108.9(3)
C10-C20-H20C	109.5	C25-C24-H24	109.6	C43-C33-C32	111.8(3)

H20A-C20-H20B	109.5	C25-C24-B2	114.4(3)	C44-C33-C32	114.8(3)
H20A-C20-H20C	109.5	B2-C24-H24	109.6	C44-C33-C43	110.1(3)
H20B-C20-H20C	109.5	C24-C25-H25A	107.8	N2-C34-H34	107.9
C11-C21-H21A	109.5	C24-C25-H25B	107.8	N2-C34-C35	110.2(3)
C11-C21-H21B	109.5	C24-C25-C26	118.0(3)	N2-C34-C36	111.3(3)
C11-C21-H21C	109.5	H25A-C25-H25B	107.2	C35-C34-H34	107.9
H21A-C21-H21B	109.5	C26-C25-H25A	107.8	C35-C34-C36	111.5(3)
H21A-C21-H21C	109.5	C26-C25-H25B	107.8	C36-C34-H34	107.9
H21B-C21-H21C	109.5	C27-C26-C25	122.7(3)	C34-C35-H35A	109.5
C11-C22-H22A	109.5	C31-C26-C25	119.1(3)	C34-C35-H35B	109.5
C11-C22-H22B	109.5	C31-C26-C27	118.1(3)	C34-C35-H35C	109.5
C11-C22-H22C	109.5	C26-C27-H27	119.8	H35A-C35-H35B	109.5
H22A-C22-H22B	109.5	C28-C27-C26	120.3(3)	H35A-C35-H35C	109.5
H22A-C22-H22C	109.5	C28-C27-H27	119.8	H35B-C35-H35C	109.5
H22B-C22-H22C	109.5	C27-C28-H28	119.5	C34-C36-H36A	109.5
O3-B1-O2	107.0(3)	C29-C28-C27	121.0(3)	C34-C36-H36B	109.5
O3-B1-C2	120.9(3)	C29-C28-H28	119.5	C34-C36-H36C	109.5
O4-B1-O2	107.9(3)	C28-C29-S2	119.2(3)	H36A-C36-H36B	109.5
O4-B1-O3	109.1(3)	C28-C29-C30	118.8(3)	H36A-C36-H36C	109.5
O4-B1-C2	114.8(3)	C30-C29-S2	121.9(3)	H36B-C36-H36C	109.5
C2-B1-O2	95.1(2)	C29-C30-H30	120.3	N2-C37-H37	106.7
C29-S2-C40	102.54(19)	C31-C30-C29	119.4(3)	N2-C37-C38	112.0(3)
C23-O5-C24	108.7(3)	C31-C30-H30	120.3	N2-C37-C39	111.7(3)
C23-O6-B2	109.9(3)	C26-C31-H31	118.9	C38-C37-H37	106.7
B2-O7-C32	106.3(3)	C30-C31-C26	122.3(4)	C39-C37-H37	106.7
B2-O8-C33	107.7(3)	C30-C31-H31	118.9	C39-C37-C38	112.6(3)
C23-N2-C34	120.8(3)	O7-C32-C33	101.9(3)	C37-C38-H38A	109.5
C23-N2-C37	119.7(3)	O7-C32-C41	108.5(3)	C37-C38-H38B	109.5
C34-N2-C37	119.5(3)	O7-C32-C42	108.2(3)	C37-C38-H38C	109.5
O5-C23-N2	119.0(3)	C41-C32-C33	112.3(3)	H38A-C38-H38B	109.5
O6-C23-O5	119.0(3)	C42-C32-C33	115.3(3)	H38A-C38-H38C	109.5
O6-C23-N2	122.0(3)	C42-C32-C41	110.1(3)	H38B-C38-H38C	109.5
O5-C24-H24	109.6	O8-C33-C32	102.2(3)	C37-C39-H39A	109.5
O5-C24-B2	105.4(2)	O8-C33-C43	108.6(3)	C37-C39-H39B	109.5
C37-C39-H39C	109.5	O8-B2-O6	106.9(3)	C24-B2-O6	95.9(2)
H39A-C39-H39B	109.5	O8-B2-O7	109.2(3)	H39B-C39-H39C	109.5
H39A-C39-H39C	109.5	O8-B2-C24	118.2(3)	S2-C40-H40A	109.5

S2-C40-H40B	109.5
S2-C40-H40C	109.5
H40A-C40-H40B	109.5
H40A-C40-H40C	109.5
H40B-C40-H40C	109.5
C32-C41-H41A	109.5
C32-C41-H41B	109.5
C32-C41-H41C	109.5
H41A-C41-H41B	109.5
H41A-C41-H41C	109.5
H41B-C41-H41C	109.5
C32-C42-H42A	109.5
C32-C42-H42B	109.5
C32-C42-H42C	109.5
H42A-C42-H42B	109.5
H42A-C42-H42C	109.5
H42B-C42-H42C	109.5
C33-C43-H43A	109.5
C33-C43-H43B	109.5
C33-C43-H43C	109.5
H43A-C43-H43B	109.5
H43A-C43-H43C	109.5
H43B-C43-H43C	109.5
C33-C44-H44A	109.5
C33-C44-H44B	109.5
C33-C44-H44C	109.5
H44A-C44-H44B	109.5
H44A-C44-H44C	109.5
H44B-C44-H44C	109.5
O7-B2-O6	108.6(3)
O7-B2-C24	116.4(3)

Table S7. Anisotropic displacement parameters (Å^2 × 10^3) for 4d; the anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S1	51(1)	24(1)	41(1)	0(1)	-21(1)	7(1)
O1	30(1)	26(1)	12(1)	-1(1)	3(1)	5(1)
O2	36(1)	27(1)	15(1)	-2(1)	4(1)	8(1)
O3	21(1)	23(1)	21(1)	2(1)	0(1)	1(1)
O4	29(1)	24(1)	18(1)	4(1)	-1(1)	-6(1)
N1	32(2)	25(2)	14(1)	-2(1)	4(1)	-2(1)
C1	26(2)	21(2)	16(2)	-3(1)	4(1)	-4(1)
C2	31(2)	20(2)	12(1)	-3(1)	4(1)	0(1)
C3	29(2)	21(2)	17(1)	2(1)	7(1)	4(1)
C4	29(2)	21(2)	14(1)	-2(1)	6(1)	3(1)
C5	30(2)	23(2)	22(2)	-3(1)	6(1)	-1(1)
C6	30(2)	28(2)	21(2)	-3(1)	0(1)	0(1)
C7	36(2)	22(2)	16(2)	1(1)	-4(1)	7(1)
C8	35(2)	21(2)	27(2)	-1(1)	-2(2)	-3(1)
C9	31(2)	26(2)	21(2)	-2(1)	-2(1)	3(2)
C10	30(2)	33(2)	28(2)	9(2)	-2(1)	-1(2)
C11	38(2)	31(2)	24(2)	6(2)	-3(2)	-5(2)
C12	35(2)	37(2)	14(2)	-1(1)	0(1)	0(2)
C13	56(3)	34(2)	25(2)	2(2)	10(2)	-6(2)
C14	48(2)	60(3)	16(2)	-5(2)	-1(2)	-19(2)
C15	38(2)	30(2)	20(2)	-8(1)	12(1)	-1(2)

C16	47(2)	28(2)	31(2)	-9(2)	13(2)	-2(2)
C17	35(2)	37(2)	40(2)	-7(2)	16(2)	2(2)
C18	38(2)	24(2)	37(2)	3(2)	-1(2)	1(2)
C19	41(2)	33(2)	28(2)	8(2)	1(2)	-6(2)
C20	38(2)	28(2)	34(2)	0(2)	1(2)	1(2)
C21	55(3)	36(2)	25(2)	-3(2)	6(2)	2(2)
C22	35(2)	41(2)	28(2)	6(2)	-5(2)	-4(2)
B1	27(2)	19(2)	15(2)	-3(1)	6(1)	-1(1)
S2	42(1)	28(1)	37(1)	3(1)	-13(1)	7(1)
O5	30(1)	24(1)	14(1)	-2(1)	3(1)	4(1)
O6	34(1)	26(1)	14(1)	-4(1)	1(1)	8(1)
O7	30(1)	20(1)	19(1)	-1(1)	2(1)	-1(1)
O8	29(1)	20(1)	16(1)	2(1)	1(1)	-1(1)
N2	27(2)	28(2)	14(1)	-4(1)	2(1)	-2(1)
C23	25(2)	20(2)	16(2)	-3(1)	2(1)	-2(1)
C24	28(2)	24(2)	12(1)	-1(1)	3(1)	1(1)
C25	32(2)	22(2)	18(2)	-2(1)	-2(1)	5(1)
C26	31(2)	23(2)	12(1)	-4(1)	1(1)	4(1)
C27	34(2)	21(2)	21(2)	-2(1)	4(1)	-1(1)
C28	30(2)	29(2)	18(2)	-3(1)	1(1)	0(1)
C29	35(2)	24(2)	15(2)	1(1)	-1(1)	7(1)
C30	35(2)	24(2)	21(2)	0(1)	0(1)	0(1)
C31	31(2)	27(2)	19(2)	-2(1)	0(1)	2(1)
C32	33(2)	23(2)	17(2)	5(1)	4(1)	5(1)
C33	31(2)	23(2)	15(2)	1(1)	0(1)	2(1)
C34	34(2)	34(2)	15(2)	1(1)	1(1)	1(2)

C35	61(3)	35(2)	30(2)	5(2)	10(2)	-7(2)
C36	43(2)	54(3)	18(2)	-2(2)	-2(2)	-7(2)
C37	29(2)	33(2)	20(2)	-8(1)	5(1)	-1(2)
C38	28(2)	47(3)	32(2)	-6(2)	8(2)	0(2)
C39	44(2)	28(2)	29(2)	-8(2)	10(2)	2(2)
C40	38(2)	23(2)	51(3)	6(2)	1(2)	3(2)
C41	39(2)	27(2)	22(2)	1(1)	5(1)	10(2)
C42	47(2)	31(2)	29(2)	11(2)	13(2)	6(2)
C43	42(2)	32(2)	18(2)	-4(2)	5(2)	4(2)
C44	33(2)	36(2)	27(2)	1(2)	-4(2)	4(2)
B2	27(2)	18(2)	16(2)	-3(1)	4(1)	2(1)

Table S8. Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3) for 4d

	x	y	z	U(eq)
H2	9846	4881	5599	25
H3A	6960	4699	6351	26
H3B	5948	4294	5585	26
H5	3033	4758	4845	29
H6	1230	5567	4264	32
H8	6395	6550	4938	34
H9	8143	5737	5562	32
H12	7959	4347	3142	35
H13A	11086	4780	2922	57

H13B	9688	4681	2018	57
H13C	11604	4256	2327	57
H14A	8874	3434	2036	63
H14B	6976	3883	1844	63
H14C	6985	3414	2587	63
H15	11706	3297	2889	34
H16A	12053	2443	3671	52
H16B	9672	2655	3584	52
H16C	11206	2751	4457	52
H17A	14128	3507	4498	55
H17B	14284	3887	3667	55
H17C	14953	3218	3692	55
H18A	2585	7705	4374	50
H18B	4814	7389	4481	50
H18C	3323	7316	5197	50
H19A	9016	3245	7908	52
H19B	11039	2840	8110	52
H19C	9149	2651	7399	52
H20A	11351	2572	6239	50
H20B	13238	2647	7003	50
H20C	13095	3059	6186	50
H21A	11836	4582	7986	58
H21B	11469	4001	8495	58
H21C	9726	4217	7742	58
H22A	14643	3470	8124	53
H22B	15177	4113	7844	53

H22C	15281	3583	7201	53
H24	8247	5800	-631	25
H25A	7031	4994	-1434	29
H25B	5400	4849	-800	29
H27	10952	5108	-173	30
H28	13304	4412	450	31
H30	8629	3222	250	32
H31	6310	3923	-360	31
H34	7280	5593	1818	33
H35A	3589	5626	2610	63
H35B	5532	5203	2893	63
H35C	4156	5128	1979	63
H36A	8051	6528	2434	58
H36B	8154	6028	3137	58
H36C	6163	6448	2975	58
H37	3375	6591	2092	32
H38A	1037	6413	451	53
H38B	133	6648	1273	53
H38C	911	5991	1241	53
H39A	5347	7277	1454	50
H39B	2935	7461	1370	50
H39C	3847	7192	570	50
H40A	11859	2585	-185	57
H40B	10683	2483	623	57
H40C	13012	2244	627	57
H41A	1035	7127	-2106	44

H41B	3049	7382	-1518	44
H41C	1817	6841	-1199	44
H42A	5436	6651	-3093	52
H42B	4978	7277	-2725	52
H42C	3174	6941	-3330	52
H43A	5235	5657	-2740	46
H43B	3360	5823	-3472	46
H43C	3213	5250	-2916	46
H44A	-53	6225	-3039	49
H44B	-354	6171	-2060	49
H44C	-180	5599	-2615	49

Table S9. Torsion angles [°] for 4d

S1-C7-C8-C9	-179.0(3)	C1-O1-C2-C3	-139.9(3)
O1-C2-C3-C4	-62.9(4)	C1-O1-C2-B1	-11.8(3)
O1-C2-B1-O2	12.8(3)	C1-O2-B1-O3	113.1(3)
O1-C2-B1-O3	-100.5(3)	C1-O2-B1-O4	-129.5(3)
O1-C2-B1-O4	125.2(3)	C1-O2-B1-C2	-11.4(3)
O3-C10-C11-O4	-35.6(4)	C1-N1-C12-C13	104.8(4)
O3-C10-C11-C21	80.0(4)	C1-N1-C12-C14	-130.2(4)
O3-C10-C11-C22	-153.8(3)	C1-N1-C15-C16	68.2(4)
C1-N1-C15-C17	-59.5(4)	C20-C10-C11-O4	80.3(4)
C2-O1-C1-O2	4.1(4)	C20-C10-C11-C21	-164.1(3)
C2-O1-C1-N1	-174.2(3)	C20-C10-C11-C22	-37.9(5)
C2-C3-C4-C5	131.0(3)	B1-O2-C1-O1	5.6(4)
C2-C3-C4-C9	-51.8(4)	B1-O2-C1-N1	-176.2(3)
C3-C2-B1-O2	133.9(3)	B1-O3-C10-C11	33.9(4)
C3-C2-B1-O3	20.6(5)	B1-O3-C10-C19	158.6(3)
C3-C2-B1-O4	-113.7(3)	B1-O3-C10-C20	-82.7(3)
C3-C4-C5-C6	175.2(3)	B1-O4-C11-C10	24.2(4)

C3-C4-C9-C8	-176.4(3)
C4-C5-C6-C7	1.8(5)
C5-C4-C9-C8	0.9(5)
C5-C6-C7-S1	178.0(3)
C5-C6-C7-C8	-0.2(5)
C6-C7-C8-C9	-1.0(6)
C7-C8-C9-C4	0.6(6)
C9-C4-C5-C6	-2.2(5)
C10-O3-B1-O2	96.3(3)
C10-O3-B1-O4	-20.2(4)
C10-O3-B1-C2	-156.7(3)
C11-O4-B1-O2	-119.8(3)
C11-O4-B1-O3	-3.9(4)
C11-O4-B1-C2	135.6(3)
C12-N1-C1-O1	1.4(5)
C12-N1-C1-O2	-176.8(3)
C12-N1-C15-C16	-117.6(4)
C12-N1-C15-C17	114.7(4)
C15-N1-C1-O1	175.6(3)
C15-N1-C1-O2	-2.7(5)
C15-N1-C12-C13	-69.4(4)
C15-N1-C12-C14	55.7(5)
C18-S1-C7-C6	154.7(3)
C18-S1-C7-C8	-27.2(4)
C19-C10-C11-O4	-155.1(3)
C19-C10-C11-C21	-39.5(5)
C19-C10-C11-C22	86.7(5)
C25-C26-C27-C28	-174.6(3)
C25-C26-C31-C30	174.5(3)
C26-C27-C28-C29	-0.3(5)
C27-C26-C31-C30	-1.9(5)
C27-C28-C29-S2	-179.9(3)
C27-C28-C29-C30	-0.9(5)
C28-C29-C30-C31	0.7(5)
C29-C30-C31-C26	0.7(5)
C31-C26-C27-C28	1.7(5)
C32-O7-B2-O6	-97.1(3)
B1-O4-C11-C21	-92.8(4)
B1-O4-C11-C22	148.8(3)
B1-C2-C3-C4	176.8(3)
S2-C29-C30-C31	179.7(3)
O5-C24-C25-C26	-54.8(4)
O5-C24-B2-O6	10.2(3)
O5-C24-B2-O7	124.4(3)
O5-C24-B2-O8	-102.5(3)
O7-C32-C33-O8	34.5(3)
O7-C32-C33-C43	-81.6(3)
O7-C32-C33-C44	152.2(3)
C23-O5-C24-C25	-133.0(3)
C23-O5-C24-B2	-10.3(3)
C23-O6-B2-O7	-128.5(3)
C23-O6-B2-O8	113.8(3)
C23-O6-B2-C24	-8.1(3)
C23-N2-C34-C35	-107.8(4)
C23-N2-C34-C36	127.9(4)
C23-N2-C37-C38	62.2(4)
C23-N2-C37-C39	-65.2(4)
C24-O5-C23-O6	5.3(4)
C24-O5-C23-N2	-174.2(3)
C24-C25-C26-C27	-42.2(5)
C24-C25-C26-C31	141.6(3)
C25-C24-B2-O6	128.7(3)
C25-C24-B2-O7	-117.1(3)
C25-C24-B2-O8	16.0(4)
B2-O8-C33-C32	-23.8(3)
B2-O8-C33-C43	94.5(3)
B2-O8-C33-C44	-145.7(3)
B2-C24-C25-C26	-171.8(3)
C32-O7-B2-O8	19.1(3)
C32-O7-B2-C24	156.2(3)
C33-O8-B2-O6	121.7(3)
C33-O8-B2-O7	4.3(4)
C33-O8-B2-C24	-131.8(3)
C34-N2-C23-O5	-1.7(5)

C34-N2-C23-O6	178.9(3)
C34-N2-C37-C38	-114.9(4)
C34-N2-C37-C39	117.7(4)
C37-N2-C23-O5	-178.8(3)
C37-N2-C23-O6	1.8(5)
C37-N2-C34-C35	69.3(4)
C37-N2-C34-C36	-55.0(4)
C40-S2-C29-C28	-151.3(3)
C40-S2-C29-C30	29.8(4)
C41-C32-C33-O8	-81.4(3)
C41-C32-C33-C43	162.5(3)
C41-C32-C33-C44	36.2(4)
C42-C32-C33-O8	151.4(3)
C42-C32-C33-C43	35.3(4)
C42-C32-C33-C44	-91.0(4)
B2-O6-C23-O5	2.5(4)
B2-O6-C23-N2	-178.1(3)
B2-O7-C32-C33	-32.6(3)
B2-O7-C32-C41	86.0(3)
B2-O7-C32-C42	-154.5(3)

Figure S1. View of molecule 1 in 4d showing the atom labeling scheme; displacement ellipsoids are scaled to the 50% probability level

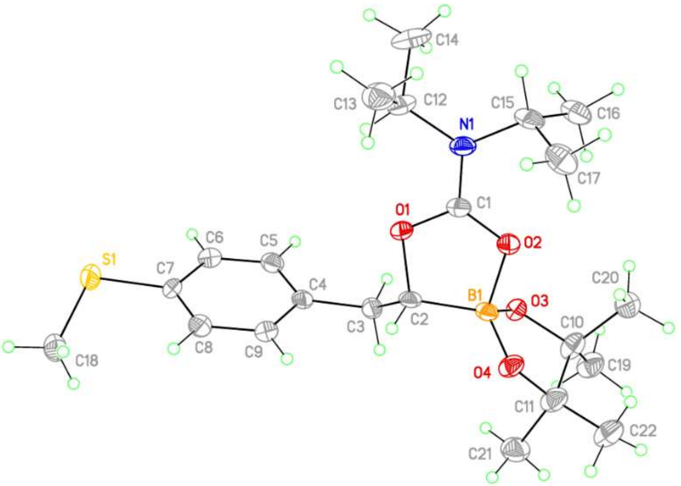
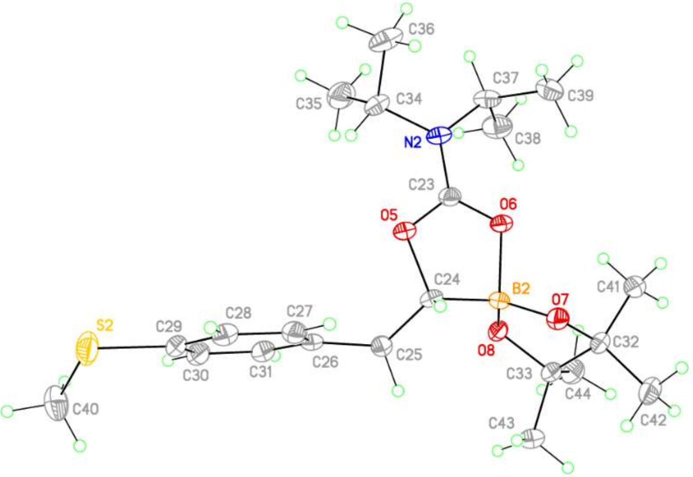
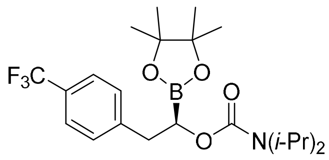


Figure S2. View of molecule 2 in 4d showing the atom labeling scheme; displacement ellipsoids are scaled to the 50% probability level





(*R*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethyl)phenyl)ethyl diisopropylcarbamate (4e). General procedure E was followed on a 101 mg (0.320 mmol) scale of **3e** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 70:30) afforded 81 mg (57%) of the product as a beige solid. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 2H), 7.42 – 7.33 (m, 2H), 4.09 (dd, *J* = 10.3, 4.9 Hz, 1H), 4.04 (hept, *J* = 6.8 Hz, 1H), 3.72 (hept, *J* = 6.8 Hz, 1H), 3.09 – 2.93 (m, 2H), 1.25 (d, *J* = 7.0 Hz, 6H), 1.20 (s, 6H), 1.19 (s, 6H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.07 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.73, 145.43, 129.23, 128.28 (q, *J* = 31.8 Hz), 125.19 (q, *J* = 3.8 Hz), 124.55 (q, *J* = 271.2 Hz), 80.11, 48.62, 46.90, 37.79, 25.32, 25.01, 20.54, 20.49, 20.40, 20.34 (the carbon attached to boron was not observed due to quadrupolar relaxation).

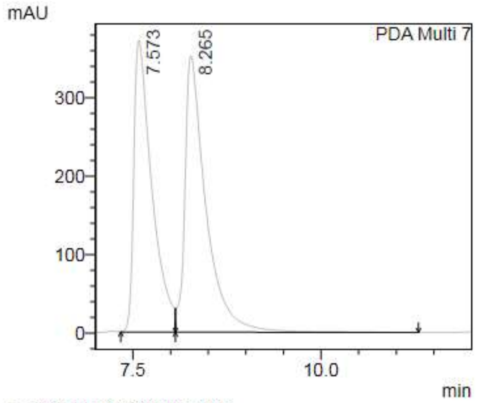
^{11}B NMR (128 MHz, $CDCl_3$) δ 12.58.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.26.

ESI MS calcd for $C_{22}H_{34}BF_3NO_4^+$ $[M+H]^+$ 444.25, found 444.2.

Chiral HPLC CHIRALPAK® IA, 0.75% IPA in hexane, 1.0 mL/min, 210 nm: 93% ee

Racemic Material



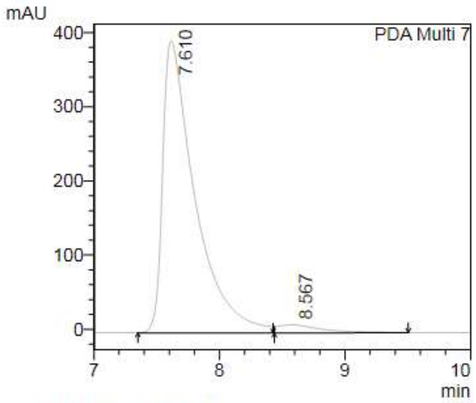
1 PDA Multi 7/210nm 4nm

PeakTable

PDA Ch7 210nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.573	6203627	47.626
2	8.265	6822038	52.374
Total		13025666	100.000

Enantioenriched Material



1 PDA Multi 7/210nm 4nm

PeakTable

PDA Ch7 210nm 4nm

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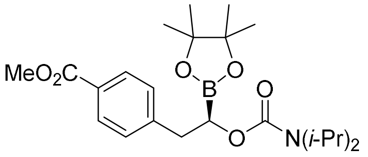


Methyl (*R*)-4-(2-((diisopropylcarbamoyl)oxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (4f). General procedure E was followed on a 66 mg (0.22 mmol) scale of **3f** with 12 mol% of **L6b** and 10 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 60:40) afforded 42 mg (44%) of the product as a yellow oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.36 – 7.29 (m, 2H), 4.10 (dd, *J* = 10.2, 5.2 Hz, 1H), 4.06 (hept, *J* = 6.8 Hz, 1H), 3.90 (s, 3H), 3.69 (hept, *J* = 6.8 Hz, 1H), 3.09 – 2.93 (m, 2H), 1.24 (d, *J* = 6.8 Hz, 6H), 1.20 (s, 6H), 1.19 (s, 6H), 1.06 (d, *J* = 6.9 Hz, 6H).

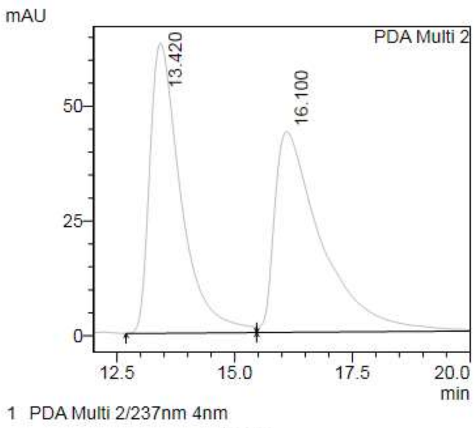
^{13}C NMR (151 MHz, $CDCl_3$) δ 167.43, 162.79, 146.98, 129.68, 128.99, 127.92, 80.09, 52.12, 48.68, 46.84, 38.04, 25.36, 25.04, 20.59, 20.53, 20.42, 20.35 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ 12.59.

ESI MS calcd for $C_{23}H_{37}BNO_6^+$ $[M+H]^+$ 434.27, found 434.2.

Chiral HPLC CHIRALCEL® OD-H, 0.6% IPA in hexane, 1.0 mL/min, 237 nm: 88% ee

Racemic Material

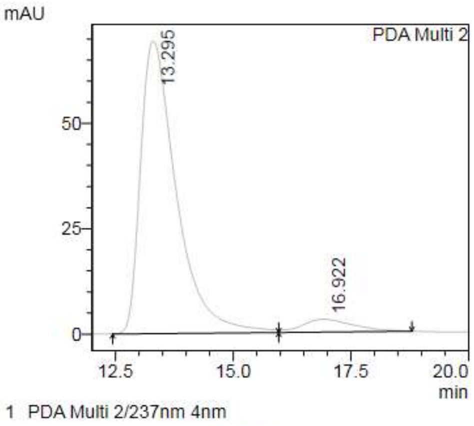


PeakTable

PDA Ch2 237nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.420	2916368	48.945
2	16.100	3042049	51.055
Total		5958417	100.000

Enantioenriched Material



PeakTable

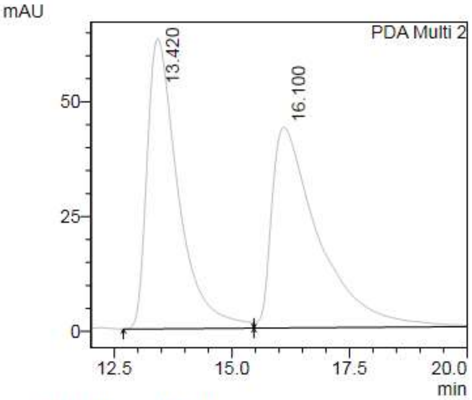
PDA Ch2 237nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.295	3678917	94.037
2	16.922	233288	5.963
Total		3912205	100.000

The same reaction was run on a 17 mg (0.056 mmol) scale of **3f-*Z***, and it afforded 12 mg (50%) of the product with identical spectral data.

Chiral HPLC CHIRALCEL® OD-H, 0.6% IPA in hexane, 1.0 mL/min, 237 nm: 96% ee

Racemic Material



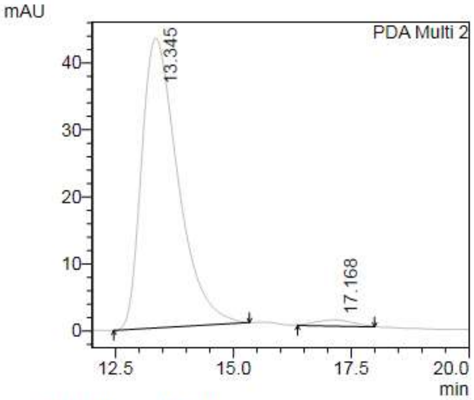
1 PDA Multi 2/237nm 4nm

PeakTable

PDA Ch2 237nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.420	2916368	48.945
2	16.100	3042049	51.055
Total		5958417	100.000

Enantioenriched Material

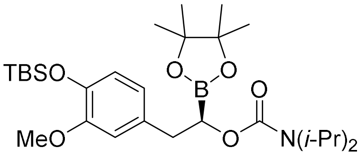


1 PDA Multi 2/237nm 4nm

PeakTable

PDA Ch2 237nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.345	2324433	97.865
2	17.168	50699	2.135
Total		2375133	100.000



(*R*)-2-(4-((*tert*-Butyldimethylsilyl)oxy)-3-methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl diisopropylcarbamate (4g).

General procedure E was followed on a 103 mg (0.253 mmol) scale of **3g** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 70:30) afforded 60 mg (44%) of the product as a pale-yellow oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.78 (d, *J* = 2.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.69 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.09 (hept, *J* = 7.0 Hz, 1H), 4.08 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.76 (s, 3H), 3.66 (hept, *J* = 6.9 Hz, 1H), 2.94 – 2.86 (m, 2H), 1.23 (d, *J* = 6.8 Hz, 6H), 1.19 (s, 6H), 1.17 (s, 6H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.98 (s, 9H), 0.12 (s, 6H).

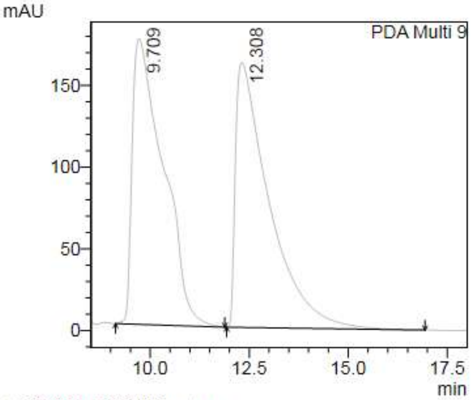
^{13}C NMR (151 MHz, CDCl$_3$) δ 162.92, 150.67, 143.01, 134.63, 121.11, 120.70, 112.83, 80.00, 55.48, 48.70, 46.66, 37.49, 25.90, 25.35, 25.05, 20.60, 20.57, 20.40, 20.34, 18.60, -4.57 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 12.73.

ESI MS calcd for $C_{28}H_{51}BNO_6Si^+$ $[M+H]^+$ 536.36, found 536.3.

Chiral HPLC CHIRALCEL® OD-H, 0.3% IPA in hexane, 1.0 mL/min, 205 nm: 83% ee

Racemic Material



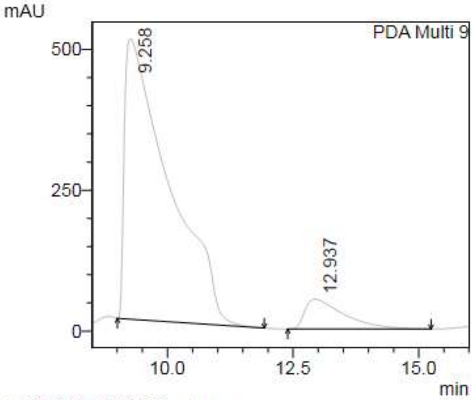
1 PDA Multi 9/205nm 4nm

PeakTable

PDA Ch9 205nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.709	9543777	49.907
2	12.308	9579320	50.093
Total		19123097	100.000

Enantioenriched Material

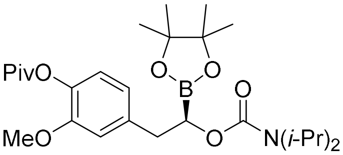


1 PDA Multi 9/205nm 4nm

PeakTable

PDA Ch9 205nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.258	30597085	91.387
2	12.937	2883866	8.613
Total		33480951	100.000



(*R*)-4-(2-((Diisopropylcarbamoyl)oxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2-methoxyphenyl pivalate (4h).

General procedure E was followed on a 115 mg (0.305 mmol) scale of **3h** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 60:40) afforded 50 mg (33%) of the product as a pale-yellow oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.89 (d, *J* = 8.1 Hz, 1H), 6.88 (d, *J* = 1.7 Hz, 1H), 6.81 (dd, *J* = 8.0, 1.8 Hz, 1H), 4.10 (dd, *J* = 9.2, 5.8 Hz, 1H), 4.03 (hept, *J* = 6.9 Hz, 1H), 3.77 (s, 3H), 3.73 (hept, *J* = 6.9 Hz, 1H), 3.02 – 2.86 (m, 2H), 1.36 (s, 9H), 1.25 (d, *J* = 6.8 Hz, 6H), 1.21 (s, 6H), 1.20 (s, 6H), 1.10 (d, *J* = 6.8 Hz, 6H).

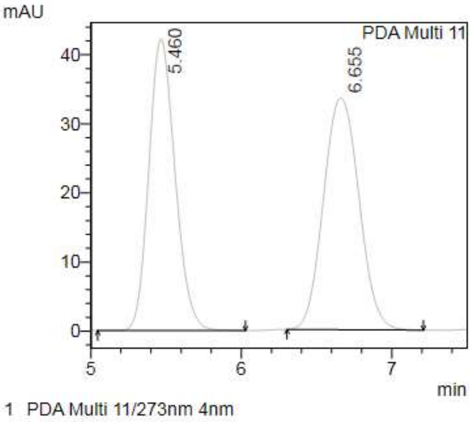
^{13}C NMR (151 MHz, CDCl$_3$) δ 177.00, 162.83, 150.92, 139.87, 138.36, 122.28, 121.06, 113.05, 80.10, 55.97, 48.53, 46.92, 39.17, 37.84, 27.38, 25.37, 25.03, 20.59, 20.56, 20.45, 20.40 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 12.68.

ESI MS calcd for $C_{27}H_{45}BNO_7^+$ [M+H]$^+$ 506.33, found 506.4.

Chiral HPLC CHIRALPAK® AD-H, 2.5% IPA in hexane, 1.3 mL/min, 273 nm: 95% ee

Racemic Material

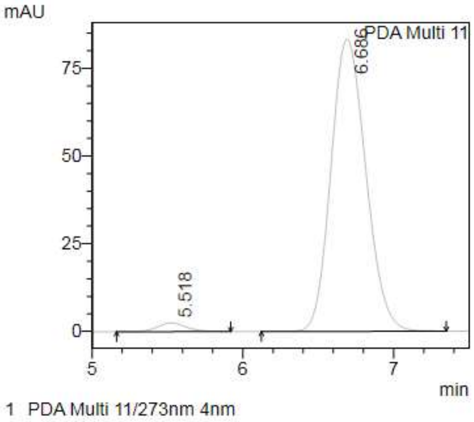


PeakTable

PDA Ch11 273nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.460	512915	48.202
2	6.655	551179	51.798
Total		1064093	100.000

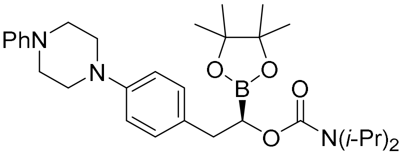
Enantioenriched Material



PeakTable

PDA Ch11 273nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.518	34179	2.485
2	6.686	1340998	97.515
Total		1375177	100.000



(*R*)-2-(4-(4-Phenylpiperazin-1-yl)phenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl diisopropylcarbamate (4i).

General procedure E was followed on a 119 mg (0.292 mmol) scale of **3i** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 60:40) afforded 66 mg (42%) of the product as a beige solid. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.29 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.21 – 7.16 (m, 2H), 7.02 – 6.96 (m, 2H), 6.95 – 6.91 (m, 2H), 6.89 (tt, *J* = 7.3, 1.0 Hz, 1H), 4.06 (dd, *J* = 9.8, 5.3 Hz, 1H), 4.03 (hept, *J* = 6.8 Hz, 1H), 3.75 (hept, *J* = 6.8 Hz, 1H), 3.37 – 3.28 (m, 8H), 2.94 – 2.84 (m, 2H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.20 (s, 6H), 1.18 (s, 6H), 1.10 (d, *J* = 6.8 Hz, 6H).

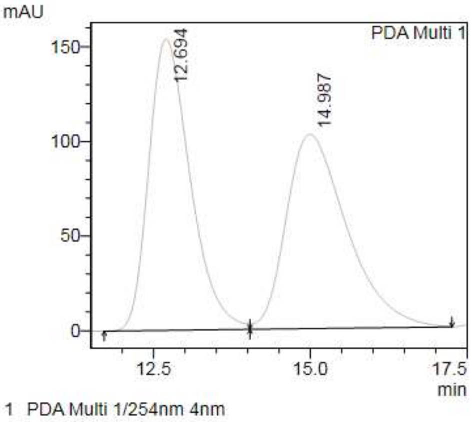
^{13}C NMR (101 MHz, CDCl$_3$) δ 162.75, 151.30, 149.41, 132.98, 129.50, 129.18, 120.01, 116.48, 116.32, 79.85, 49.91, 49.46, 48.30, 46.76, 36.91, 25.22, 24.95, 20.51, 20.45, 20.36, 20.30 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 12.88.

ESI MS calcd for $C_{31}H_{47}BN_3O_4^+$ $[M+H]^+$ 536.37, found 536.3.

Chiral HPLC CHIRALCEL® OZ-3, 1.5% IPA in hexane, 1.0 mL/min, 254 nm: 93% ee

Racemic Material

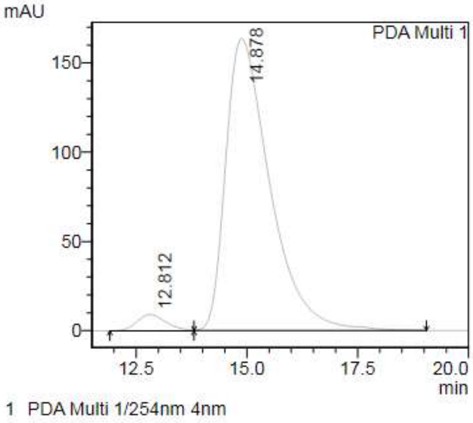


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.694	7068501	50.506
2	14.987	6926835	49.494
Total		13995336	100.000

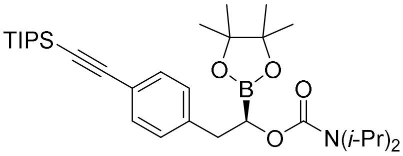
Enantioenriched Material



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.812	419424	3.555
2	14.878	11377262	96.445
Total		11796685	100.000



(*R*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-((triisopropylsilyl)ethynyl)phenyl)ethyl diisopropylcarbamate (4j).

General procedure E was followed on a 148 mg (0.346 mmol) scale of **3j** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 70:30) afforded 85 mg (44%) of the product as a pale-yellow oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.36 (m, 2H), 7.23 – 7.15 (m, 2H), 4.05 (dd, *J* = 9.0, 6.2 Hz, 1H), 4.01 (hept, *J* = 6.8 Hz, 1H), 3.72 (hept, *J* = 6.8 Hz, 1H), 2.98 – 2.90 (m, 2H), 1.25 (d, *J* = 6.8 Hz, 6H), 1.20 (s, 6H), 1.19 (s, 6H), 1.12 (s, 21H), 1.09 (d, *J* = 6.8 Hz, 6H).

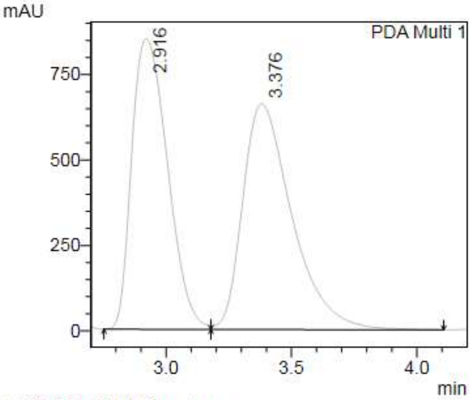
^{13}C NMR (151 MHz, CDCl$_3$) δ 162.81, 141.97, 132.05, 128.78, 120.99, 107.53, 89.70, 80.03, 48.53, 46.91, 37.97, 25.38, 25.05, 20.60, 20.55, 20.46, 20.39, 18.82, 11.47 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 12.33.

ESI MS calcd for $C_{32}H_{55}BNO_4Si^+$ [M+H]$^+$ 556.40, found 556.6.

Chiral HPLC CHIRALPAK® AD-H, 1.0% IPA in hexane, 1.5 mL/min, 254 nm: 96% ee

Racemic Material

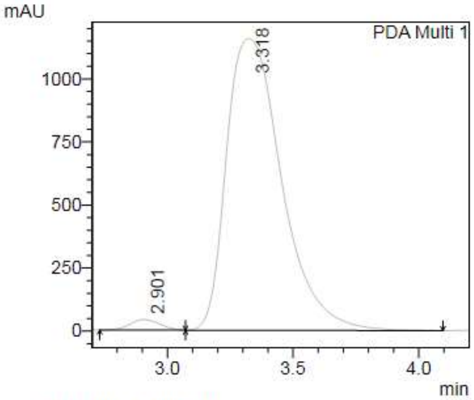


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	2.916	8466582	48.381
2	3.376	9033137	51.619
Total		17499719	100.000

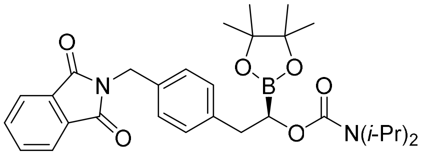
Enantioenriched Material



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	2.901	346965	1.924
2	3.318	17691094	98.076
Total		18038059	100.000



(*R*)-2-(4-((1,3-Dioxoisoindolin-2-yl)methyl)phenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl diisopropylcarbamate (4k).

General procedure E was followed on a 101 mg (0.248 mmol) scale of **3k** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 60:40) afforded 63 mg (47%) of the product as a beige solid. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 – 7.78 (m, 2H), 7.72 – 7.65 (m, 2H), 7.37 – 7.30 (m, 2H), 7.23 – 7.16 (m, 2H), 4.81 (s, 2H), 4.03 (dd, *J* = 9.8, 5.2 Hz, 1H), 3.98 (hept, *J* = 6.8 Hz, 1H), 3.73 (hept, *J* = 6.8 Hz, 1H), 2.98 – 2.84 (m, 2H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H), 1.17 (s, 6H), 1.16 (s, 6H), 1.06 (d, *J* = 6.8 Hz, 3H), 1.05 (d, *J* = 6.9 Hz, 3H).

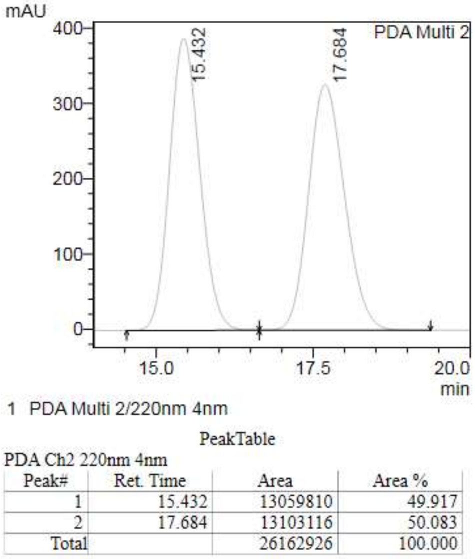
^{13}C NMR (101 MHz, CDCl$_3$) δ 168.07, 162.64, 140.88, 133.94, 133.81, 132.19, 129.11, 128.44, 123.29, 79.86, 48.25, 46.82, 41.39, 37.46, 25.18, 24.91, 20.43, 20.39, 20.33, 20.27 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 12.43.

ESI MS calcd for $C_{30}H_{40}BN_2O_6^+$ $[M+H]^+$ 535.30, found 535.4.

Chiral HPLC CHIRALPAK® AD-H, 5.0% IPA in hexane, 1.3 mL/min, 220 nm: 95% ee

Racemic Material



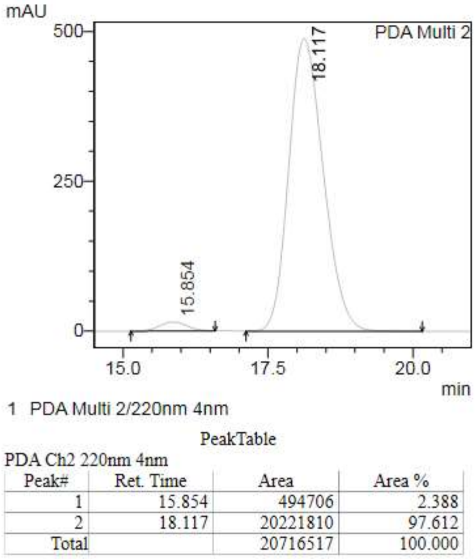
1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.432	13059810	49.917
2	17.684	13103116	50.083
Total		26162926	100.000

Enantioenriched Material

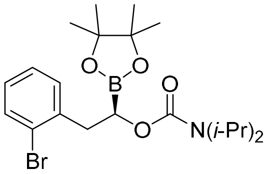


1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.854	494706	2.388
2	18.117	20221810	97.612
Total		20716517	100.000



(*R*)-2-(2-Bromophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl diisopropylcarbamate (4l).

General procedure E was followed on a 121 mg (0.371 mmol) scale of **3l** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 70:30) afforded 70 mg (42%) of the product as a pale-yellow oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.28 (dd, *J* = 6.9, 1.8 Hz, 1H), 7.21 (td, *J* = 7.4, 1.3 Hz, 1H), 7.06 (td, *J* = 7.6, 1.8 Hz, 1H), 4.17 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.98 (hept, *J* = 6.8 Hz, 1H), 3.81 (hept, *J* = 6.8 Hz, 1H), 3.13 (dd, *J* = 15.6, 3.2 Hz, 1H), 3.03 (dd, *J* = 15.5, 11.4 Hz, 1H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.22 (s, 6H), 1.21 (s, 6H), 1.11 (d, *J* = 6.8 Hz, 6H).

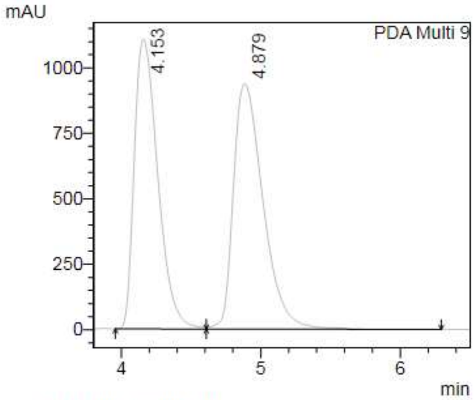
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.80, 140.57, 132.87, 131.22, 127.69, 127.13, 124.75, 80.03, 48.28, 47.05, 38.39, 25.26, 25.00, 20.59, 20.58, 20.54, 20.41 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ 12.59.

ESI MS calcd for $C_{21}H_{34}BBrNO_4^+$ $[M+H]^+$ 454.18, found 454.1.

Chiral HPLC CHIRALCEL® OZ-3, 1.0% IPA in hexane, 1.0 mL/min, 205 nm: 81% ee

Racemic Material



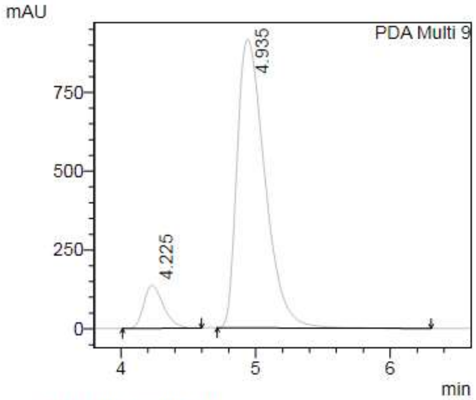
1 PDA Multi 9/205nm 4nm

PeakTable

PDA Ch9 205nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.153	12991543	48.366
2	4.879	13869533	51.634
Total		26861076	100.000

Enantioenriched Material

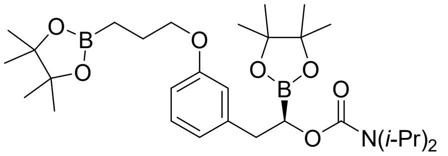


1 PDA Multi 9/205nm 4nm

PeakTable

PDA Ch9 205nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.225	1401215	9.633
2	4.935	13144283	90.367
Total		14545497	100.000



(*R*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)phenyl)ethyl diisopropylcarbamate (4m).

General procedure E was followed on a 106 mg (0.349 mmol) scale of **3m** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 70:30) afforded 84 mg (43%) of the product as a pale-yellow oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.16 (t, *J* = 8.1 Hz, 1H), 6.85 – 6.79 (m, 2H), 6.72 (ddd, *J* = 8.2, 2.4, 1.2 Hz, 1H), 4.09 (dd, *J* = 8.3, 6.7 Hz, 1H), 4.02 (hept, *J* = 6.8 Hz, 1H), 3.91 (td, *J* = 6.8, 1.0 Hz, 2H), 3.74 (hept, *J* = 6.8 Hz, 1H), 2.95 – 2.86 (m, 2H), 1.87 (p, *J* = 7.0 Hz, 2H), 1.27 – 1.23 (m, 18H), 1.20 (s, 6H), 1.19 (s, 6H), 1.10 (d, *J* = 6.8 Hz, 6H), 0.90 (t, *J* = 7.9 Hz, 2H).

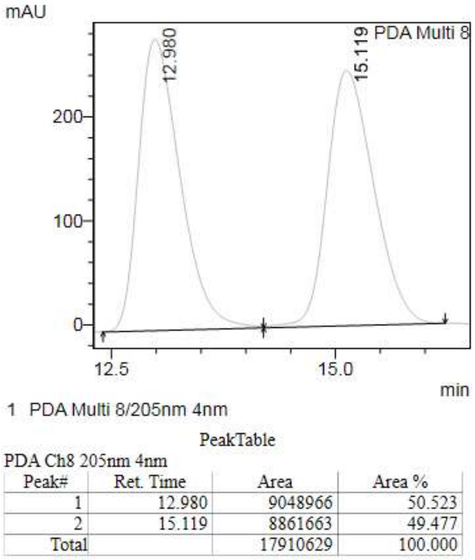
^{13}C NMR (151 MHz, CDCl$_3$) δ 162.85, 159.22, 142.87, 129.08, 121.12, 115.03, 112.23, 83.21, 79.97, 69.61, 48.45, 46.87, 38.05, 25.34, 25.04, 24.97, 24.85, 23.96, 20.61, 20.54, 20.46, 20.40 (the carbons attached to borons were not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 33.95, 12.48.

ESI MS calcd for $C_{30}H_{51}B_2NNaO_7^+$ $[M+Na]^+$ 582.37, found 582.3.

Chiral HPLC CHIRALPAK® AD-H, 0.75% IPA in hexane, 1.2 mL/min, 205 nm: 95% ee

Racemic Material

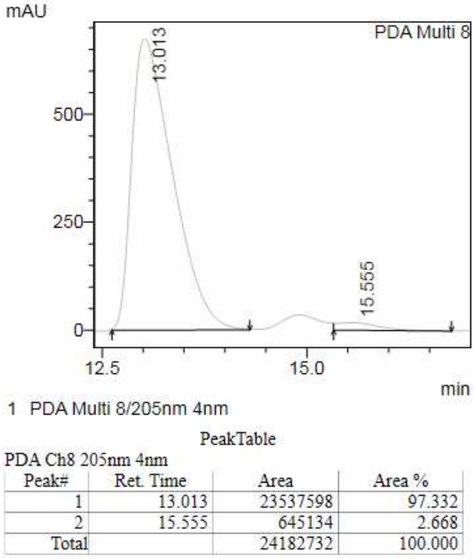


PeakTable

PDA Ch8 205nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.980	9048966	50.523
2	15.119	8861663	49.477
Total		17910629	100.000

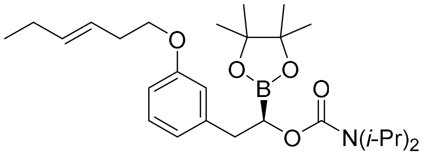
Enantioenriched Material



PeakTable

PDA Ch8 205nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.013	23537598	97.332
2	15.555	645134	2.668
Total		24182732	100.000



(*R*,*E*)-2-(3-(Hex-3-en-1-yloxy)phenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl diisopropylcarbamate (4n).

General procedure E was followed on a 102 mg (0.295 mmol) scale of **3n** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with DCM/Et_2O = 95:5) afforded 42 mg (30%) of the product as a colorless oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 8.0 Hz, 1H), 6.86 – 6.80 (m, 2H), 6.73 (dd, *J* = 7.5, 2.5 Hz, 1H), 5.60 (dt, *J* = 15.5, 6.2 Hz, 1H), 5.47 (dt, *J* = 15.3, 6.8 Hz, 1H), 4.09 (dd, *J* = 8.6, 6.5 Hz, 1H), 4.02 (hept, *J* = 6.7 Hz, 1H), 3.94 (td, *J* = 7.0, 1.8 Hz, 2H), 3.75 (hept, *J* = 7.0 Hz, 1H), 2.95 – 2.89 (m, 2H), 2.46 (q, *J* = 6.8 Hz, 2H), 2.03 (p, *J* = 7.4 Hz, 2H), 1.25 (d, *J* = 6.8 Hz, 6H), 1.20 (s, 6H), 1.19 (s, 6H), 1.10 (d, *J* = 6.8 Hz, 6H), 0.98 (t, *J* = 7.4 Hz, 3H).

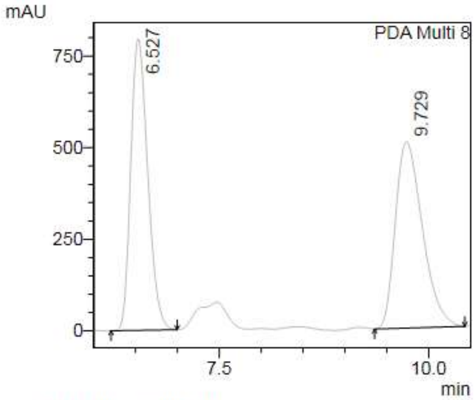
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.85, 159.04, 142.92, 134.89, 129.14, 124.62, 121.35, 115.01, 112.29, 79.99, 67.84, 48.47, 46.88, 38.04, 32.68, 25.81, 25.34, 25.04, 20.60, 20.54, 20.46, 20.40, 13.89 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ 12.92.

ESI MS calcd for $C_{27}H_{45}BNO_5^+$ $[M+H]^+$ 474.34, found 474.6.

Chiral HPLC CHIRALPAK® AD-H, 1.0% IPA in hexane, 1.3 mL/min, 205 nm: 90% ee

Racemic Material



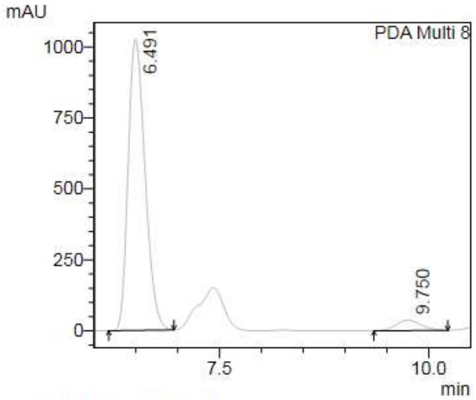
1 PDA Multi 8/205nm 4nm

PeakTable

PDA Ch8 205nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.527	11217049	49.581
2	9.729	11406566	50.419
Total		22623615	100.000

Enantioenriched Material

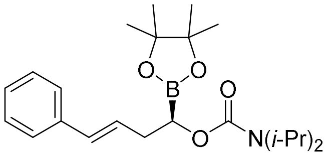


1 PDA Multi 8/205nm 4nm

PeakTable

PDA Ch8 205nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.491	14396199	95.034
2	9.750	752281	4.966
Total		15148480	100.000



(*R*,*E*)-4-Phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl diisopropylcarbamate (4o). General procedure E was followed on a 100 mg (0.366 mmol) scale of **3o** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 75:25) afforded 90 mg (61%) of the product as a pale-yellow oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.32 (m, 2H), 7.31 – 7.26 (m, 2H), 7.23 – 7.14 (m, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.34 (dt, *J* = 15.8, 6.5 Hz, 1H), 4.08 (hept, *J* = 6.8 Hz, 1H), 3.92 (dd, *J* = 9.9, 4.7 Hz, 1H), 3.78 (hept, *J* = 6.8 Hz, 1H), 2.64 – 2.47 (m, 2H), 1.24 (d, *J* = 6.8 Hz, 6H), 1.20 (s, 12H), 1.19 (d, *J* = 6.7 Hz, 3H), 1.18 (d, *J* = 6.7 Hz, 3H).

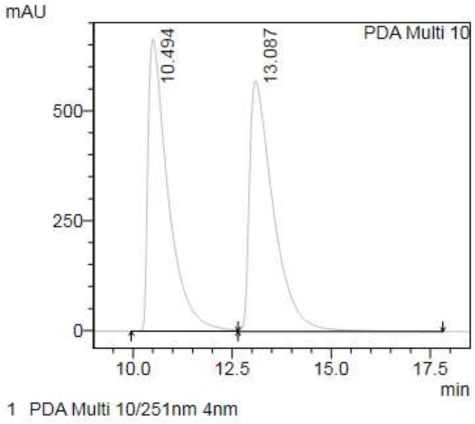
^{13}C NMR (151 MHz, CDCl$_3$) δ 162.92, 138.08, 131.11, 129.50, 128.56, 126.91, 126.12, 79.97, 48.64, 46.81, 35.58, 25.41, 25.02, 20.71, 20.58, 20.42, 20.34 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 12.98.

ESI MS calcd for $C_{23}H_{37}BNO_4^+$ $[M+H]^+$ 402.28, found 402.2.

Chiral HPLC CHIRALCEL® OD-H, 0.5% IPA in hexane, 1.0 mL/min, 251 nm: 92% ee

Racemic Material

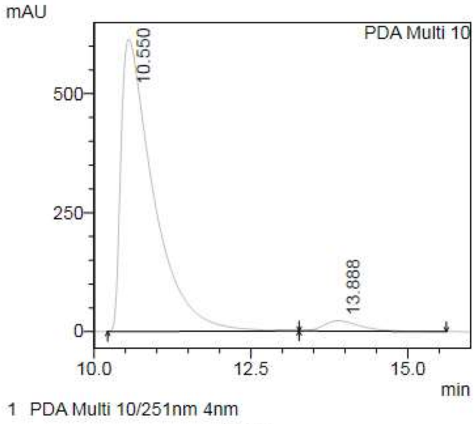


PeakTable

PDA Ch10 251nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.494	23372091	49.486
2	13.087	23857671	50.514
Total		47229762	100.000

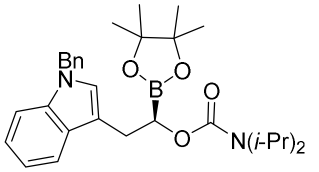
Enantioenriched Material



PeakTable

PDA Ch10 251nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.550	22129141	96.231
2	13.888	866640	3.769
Total		22995781	100.000



(*R*)-2-(1-Benzyl-1*H*-indol-3-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl diisopropylcarbamate (4p). General procedure E was followed on an 87 mg (0.23 mmol) scale of **3p** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 70:30) afforded 57 mg (49%) of the product as a dark-orange oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.32 – 7.19 (m, 4H), 7.16 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.14 – 7.04 (m, 3H), 6.97 (s, 1H), 5.28 (s, 2H), 4.26 – 4.16 (m, 1H), 4.00 (hept, *J* = 6.8 Hz, 1H), 3.73 (hept, *J* = 6.9 Hz, 1H), 3.17 – 3.04 (m, 2H), 1.31 – 1.16 (m, 18H), 1.06 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H).

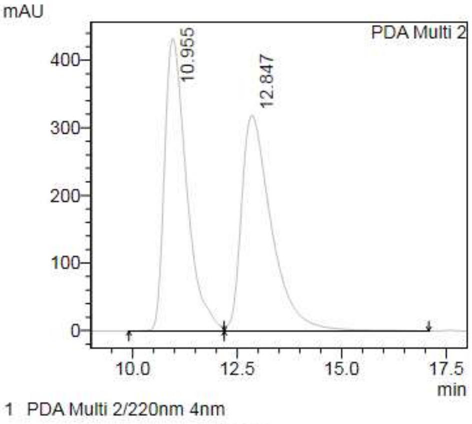
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.78, 137.92, 136.62, 128.65, 128.46, 127.44, 126.86, 125.91, 121.50, 119.43, 118.69, 114.78, 109.38, 79.83, 49.80, 48.17, 46.76, 27.34, 25.23, 24.95, 20.46, 20.38, 20.34, 20.30 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ 12.64.

ESI MS calcd for $C_{30}H_{42}BN_2O_4^+$ $[M+H]^+$ 505.32, found 505.4.

Chiral HPLC CHIRALCEL® OZ-3, 1.0% IPA in hexane, 1.0 mL/min, 220 nm: 93% ee

Racemic Material

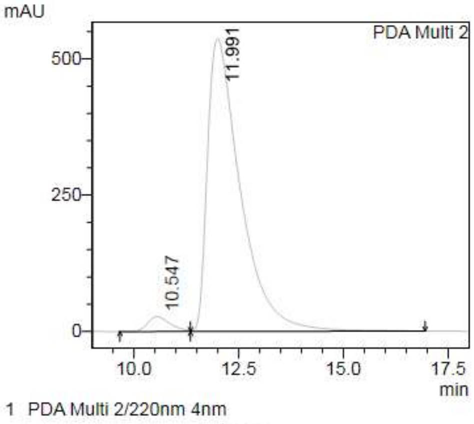


PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.955	15846827	49.807
2	12.847	15969389	50.193
Total		31816216	100.000

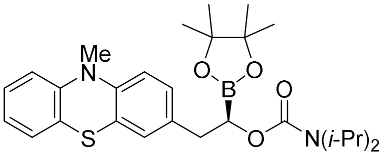
Enantioenriched Material



PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.547	1033922	3.394
2	11.991	29431593	96.606
Total		30465515	100.000



(*R*)-2-(10-Methyl-10*H*-phenothiazin-3-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl diisopropylcarbamate (4q).

General procedure E was followed on an 85 mg (0.22 mmol) scale of **3q** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 60:40) afforded 58 mg (52%) of the product as a brown solid. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (600 MHz, CD_3CN) δ 7.20 (ddd, *J* = 8.7, 7.4, 1.5 Hz, 1H), 7.13 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.11 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 3.89 (hept, *J* = 6.8 Hz, 1H), 3.86 (hept, *J* = 6.8 Hz, 1H), 3.80 (dd, *J* = 10.1, 4.7 Hz, 1H), 3.32 (s, 3H), 2.84 – 2.67 (m, 2H), 1.23 (d, *J* = 6.8 Hz, 6H), 1.13 – 1.10 (m, 6H), 1.11 (s, 6H), 1.08 (s, 6H).

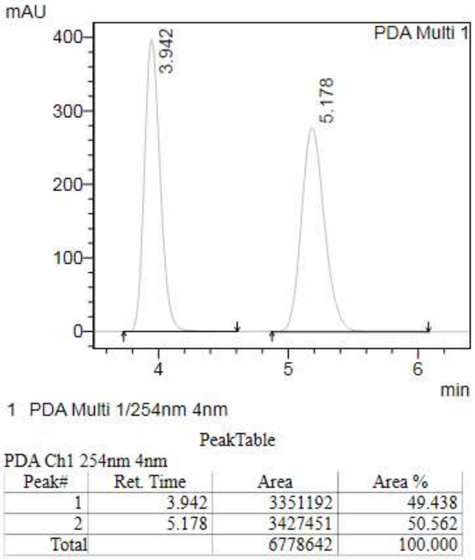
^{13}C NMR (151 MHz, CD_3CN) δ 162.88, 146.95, 144.72, 136.27, 129.24, 128.60, 128.53, 127.79, 123.75, 123.34, 123.23, 115.23, 115.11, 80.63, 48.37, 37.49, 35.76, 25.60, 25.37, 25.13, 20.55, 20.51, 20.49, 20.42 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ 12.53.

ESI MS calcd for $C_{28}H_{40}BN_2O_4S^+$ $[M+H]^+$ 511.28, found 511.4.

Chiral HPLC CHIRALPAK® AD-H, 10% IPA in hexane, 1.3 mL/min, 254 nm: 91% ee

Racemic Material

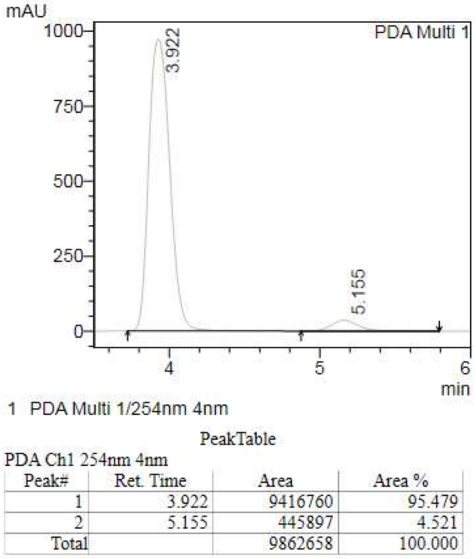


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	3.942	3351192	49.438
2	5.178	3427451	50.562
Total		6778642	100.000

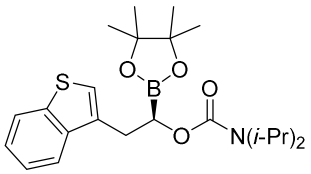
Enantioenriched Material



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	3.922	9416760	95.479
2	5.155	445897	4.521
Total		9862658	100.000



(*R*)-2-(Benzo[*b*]thiophen-3-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl diisopropylcarbamate (4r). General procedure E was followed on a 113 mg (0.372 mmol) scale of **3r** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 70:30) afforded 101 mg (63%) of the product as a beige solid. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.79 (dd, *J* = 7.2, 1.7 Hz, 1H), 7.35 (pd, *J* = 7.1, 1.3 Hz, 2H), 7.21 (s, 1H), 4.26 (dd, *J* = 9.6, 5.0 Hz, 1H), 4.02 (hept, *J* = 6.8 Hz, 1H), 3.76 (hept, *J* = 6.9 Hz, 1H), 3.26 – 3.12 (m, 2H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.26 (d, *J* = 6.7 Hz, 3H), 1.22 (s, 6H), 1.22 (s, 6H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.07 (d, *J* = 6.8 Hz, 3H).

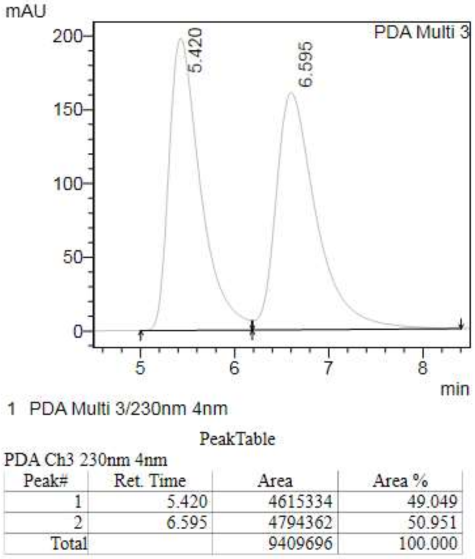
^{13}C NMR (151 MHz, CDCl$_3$) δ 162.82, 140.48, 139.39, 135.64, 124.19, 123.86, 122.88, 122.05, 121.88, 80.11, 48.45, 47.04, 30.77, 25.35, 25.04, 20.63, 20.51, 20.49, 20.41 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 12.68.

ESI MS calcd for $C_{23}H_{35}BNO_4S^+$ $[M+H]^+$ 432.24, found 432.4.

Chiral HPLC CHIRALCEL® OZ-3, 0.45% IPA in hexane, 1.25 mL/min, 230 nm: 95% ee

Racemic Material



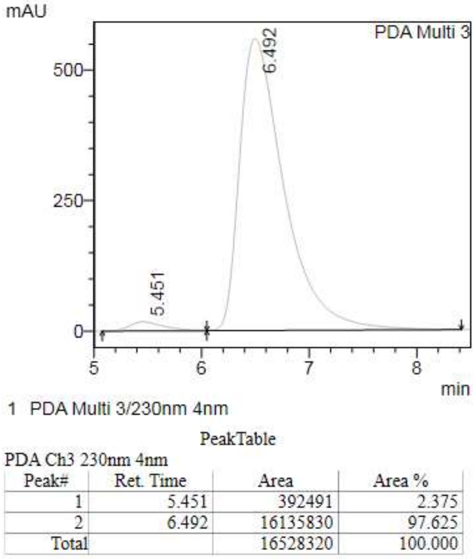
1 PDA Multi 3/230nm 4nm

PeakTable

PDA Ch3 230nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.420	4615334	49.049
2	6.595	4794362	50.951
Total		9409696	100.000

Enantioenriched Material

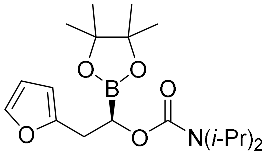


1 PDA Multi 3/230nm 4nm

PeakTable

PDA Ch3 230nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.451	392491	2.375
2	6.492	16135830	97.625
Total		16528320	100.000



(*R*)-2-(Furan-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl diisopropylcarbamate (4s).

General procedure E was followed on a 94 mg (0.40 mmol) scale of **3s** with 6 mol% of **L6b** and 5 mol% of the catalyst at 35 °C (the reaction was complete in 18 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 70:30) afforded 88 mg (61%) of the product as a brown oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.28 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.06 (dt, *J* = 3.1, 0.9 Hz, 1H), 4.16 – 4.05 (m, 2H), 3.72 (hept, *J* = 6.9 Hz, 1H), 2.99 (ddd, *J* = 16.7, 11.0, 0.8 Hz, 1H), 2.91 (ddd, *J* = 16.7, 3.9, 1.0 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 6H), 1.18 (s, 12H), 1.16 (d, *J* = 6.8 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 3H).

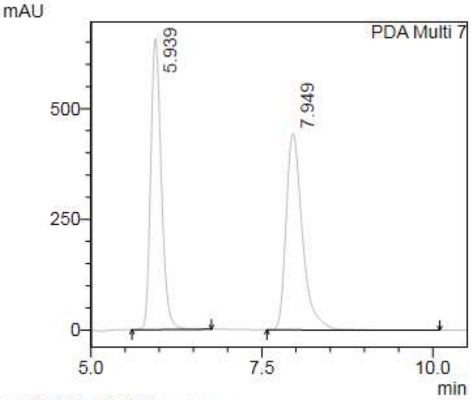
^{13}C NMR (151 MHz, CDCl$_3$) δ 162.93, 155.39, 140.93, 110.21, 105.53, 80.03, 48.80, 46.79, 30.55, 25.31, 24.96, 20.66, 20.47, 20.39, 20.30 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 12.57.

ESI MS calcd for $C_{19}H_{33}BNO_5^+$ [M+H]$^+$ 366.24, found 366.2.

Chiral HPLC CHIRALCEL® OD-H, 0.8% IPA in hexane, 1.0 mL/min, 210 nm: 92% ee

Racemic Material



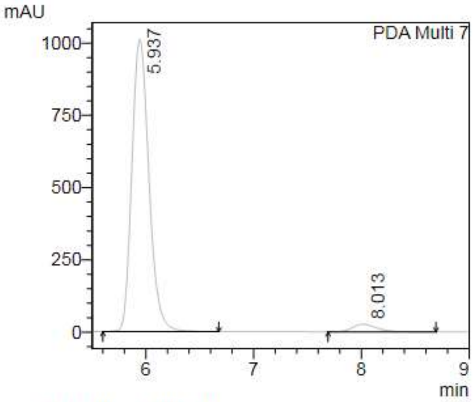
1 PDA Multi 7/210nm 4nm

PeakTable

PDA Ch7 210nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.939	7095025	49.088
2	7.949	7358710	50.912
Total		14453735	100.000

Enantioenriched Material

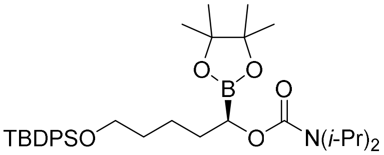


1 PDA Multi 7/210nm 4nm

PeakTable

PDA Ch7 210nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.937	11158054	96.240
2	8.013	435885	3.760
Total		11593939	100.000



(*R*)-5-((*tert*-Butyldiphenylsilyl)oxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl diisopropylcarbamate (4t).

General procedure E was followed on a 100 mg (0.214 mmol) scale of **3t** with 11 mol% of **L6b** and 10 mol% of the catalyst at room temperature (the reaction was complete in 48 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 70:30) afforded 71 mg (56%) of the product as a colorless oil. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.70 – 7.62 (m, 4H), 7.45 – 7.32 (m, 6H), 4.07 (hept, *J* = 6.8 Hz, 1H), 3.83 – 3.72 (m, 2H), 3.67 (t, *J* = 5.9 Hz, 2H), 1.75 – 1.52 (m, 6H), 1.24 (d, *J* = 6.8 Hz, 6H), 1.19 (d, *J* = 6.9 Hz, 6H), 1.18 (s, 6H), 1.17 (s, 6H), 1.03 (s, 9H).

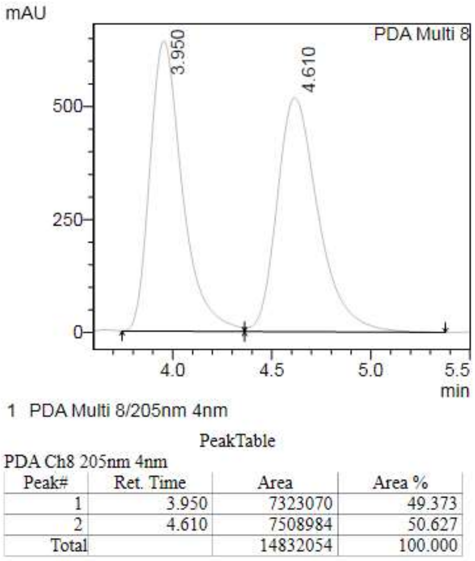
^{13}C NMR (151 MHz, CDCl$_3$) δ 162.94, 135.70, 134.28, 129.60, 127.70, 79.82, 64.14, 48.52, 46.68, 32.76, 31.47, 29.85, 26.99, 25.38, 25.07, 24.46, 20.74, 20.45, 20.39, 19.35 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 13.00.

ESI MS calcd for $C_{34}H_{55}BNO_5Si^+$ [M+H]$^+$ 596.39, found 596.6.

Chiral HPLC CHIRALCEL® OZ-3, 0.4% IPA in hexane, 1.0 mL/min, 205 nm: 97% ee

Racemic Material

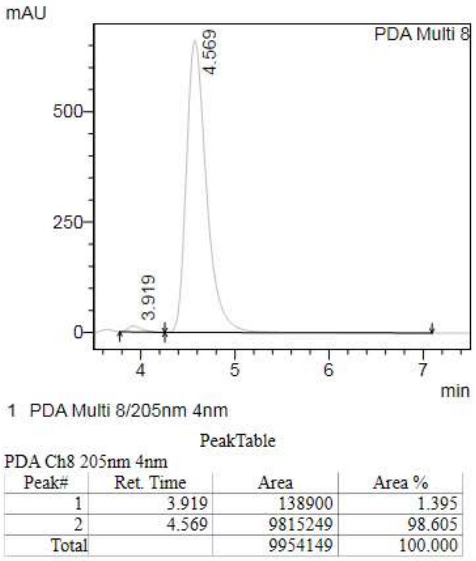


PeakTable

PDA Ch8 205nm 4nm

Peak#	Ret. Time	Area	Area %
1	3.950	7323070	49.373
2	4.610	7508984	50.627
Total		14832054	100.000

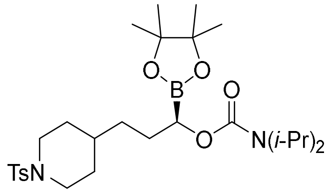
Enantioenriched Material



PeakTable

PDA Ch8 205nm 4nm

Peak#	Ret. Time	Area	Area %
1	3.919	138900	1.395
2	4.569	9815249	98.605
Total		9954149	100.000



(*R*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(1-tosylpiperidin-4-yl)propyl diisopropylcarbamate (4u). General procedure E was followed on a 151 mg (0.357 mmol) scale of **3u** with 12 mol% of **L6b** and 10 mol% of the catalyst at room temperature (the reaction was complete in 48 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 60:40) afforded 59 mg (30%) of the product as a white solid. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.34 – 7.28 (m, 2H), 4.05 (hept, *J* = 6.7 Hz, 1H), 3.78 (hept, *J* = 6.8 Hz, 1H), 3.78 – 3.70 (m, 2H), 3.69 (dd, *J* = 10.1, 4.3 Hz, 1H), 2.43 (s, 3H), 2.20 (t, *J* = 11.6 Hz, 2H), 1.74 (t, *J* = 13.7 Hz, 2H), 1.46 – 1.25 (m, 3H), 1.23 (d, *J* = 7.0 Hz, 6H), 1.19 (d, *J* = 6.9 Hz, 6H), 1.16 (s, 6H), 1.15 (s, 6H).

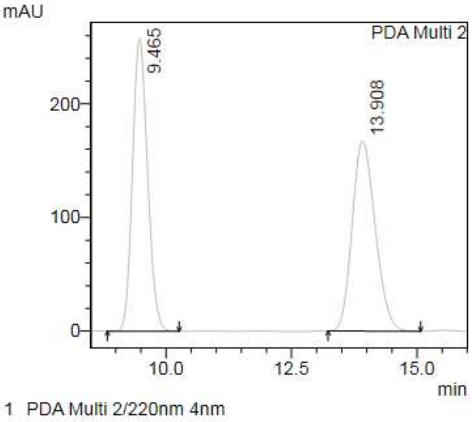
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.84, 143.44, 133.20, 129.67, 127.87, 79.87, 48.60, 46.74, 46.66, 46.63, 35.27, 34.42, 31.88, 31.50, 28.82, 25.40, 25.02, 21.67, 20.73, 20.69, 20.43, 20.36 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ 12.98.

ESI MS calcd for $C_{28}H_{48}BN_2O_6S^+$ $[M+H]^+$ 551.33, found 551.4.

Chiral HPLC CHIRALPAK® AD-H, 7.0% IPA in hexane, 1.3 mL/min, 220 nm: 96% ee

Racemic Material

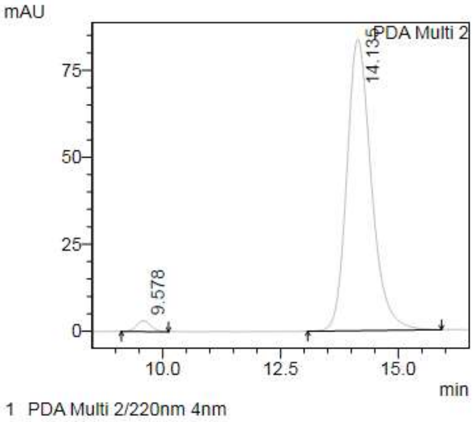


PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.465	5382801	50.121
2	13.908	5356848	49.879
Total		10739650	100.000

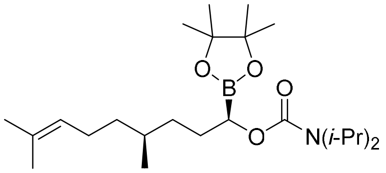
Enantioenriched Material



PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.578	65829	2.122
2	14.135	3036542	97.878
Total		3102371	100.000



(1*R*,4*S*)-4,8-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)non-7-en-1-yl diisopropylcarbamate (4v). General procedure E was followed on an 89 mg (0.30 mmol) scale of **3v** with 12 mol% of **L6b** and 10 mol% of the catalyst at room temperature (the reaction was complete in 48 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 80:20) afforded 81 mg (63%) of the product as a colorless oil. Absolute stereochemistry was assigned by analogy to **4d**.

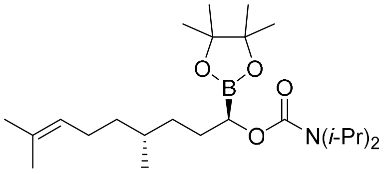
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (ddq, *J* = 8.5, 5.6, 1.3 Hz, 1H), 4.07 (hept, *J* = 6.8 Hz, 1H), 3.80 (hept, *J* = 6.8 Hz, 1H), 3.74 (dd, *J* = 9.3, 5.1 Hz, 1H), 1.95 (dh, *J* = 14.1, 7.4 Hz, 2H), 1.67 (d, *J* = 1.3 Hz, 3H), 1.67 – 1.08 (m, 7H), 1.59 (s, 3H), 1.24 (d, *J* = 7.2 Hz, 6H), 1.21 (d, *J* = 6.8 Hz, 6H), 1.18 (s, 12H), 0.89 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.94, 131.07, 125.21, 79.84, 48.52, 46.67, 37.00, 35.30, 32.62, 29.09, 25.87, 25.68, 25.40, 25.07, 20.75, 20.70, 20.45, 20.39, 19.87, 17.77 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ 12.59.

ESI MS calcd for $C_{24}H_{47}BNO_4^+$ $[M+H]^+$ 424.36, found 424.3.

Chiral HPLC was not performed due to lack of suitable chromophores; enantiopurity was determined by ^{13}C NMR (see page S194).



(1*R*,4*R*)-4,8-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)non-7-en-1-yl diisopropylcarbamate (4v').

General procedure E was followed on a 100 mg (0.338 mmol) scale of **3v'** with 12 mol% of **L6b** and 10 mol% of the catalyst at room temperature (the reaction was complete in 48 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 80:20) afforded 54 mg (38%) of the product as a pale-yellow oil. Absolute stereochemistry was assigned by analogy to **4d**.

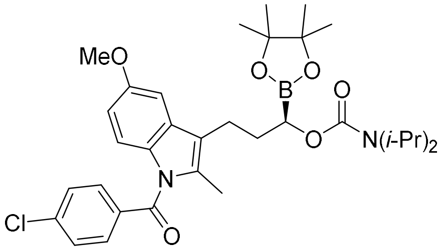
^{1}H NMR (400 MHz, CDCl$_3$) δ 5.09 (ddq, *J* = 8.5, 5.6, 1.5 Hz, 1H), 4.08 (hept, *J* = 6.3 Hz, 1H), 3.80 (hept, *J* = 6.9 Hz, 1H), 3.76 (dd, *J* = 10.7, 4.0 Hz, 1H), 2.07 – 1.89 (m, 2H), 1.73 – 1.12 (m, 7H), 1.67 (d, *J* = 1.4 Hz, 3H), 1.59 (d, *J* = 1.4 Hz, 3H), 1.24 (d, *J* = 6.8 Hz, 6H), 1.21 (d, *J* = 6.8 Hz, 6H), 1.18 (s, 12H), 0.87 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 162.89, 131.00, 125.11, 79.72, 48.46, 46.59, 37.39, 35.06, 32.34, 28.99, 25.79, 25.69, 25.32, 24.99, 20.68, 20.63, 20.38, 20.31, 19.60, 17.70 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 12.59.

ESI MS calcd for $C_{24}H_{47}BNO_4^+$ $[M+H]^+$ 424.36, found 424.3.

Chiral HPLC was not performed due to lack of suitable chromophores; enantiopurity was determined by ^{13}C NMR (see page S198).



(*R*)-3-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl diisopropylcarbamate (4w).

General procedure E was followed on a 67 mg (0.14 mmol) scale of **3w** with 11 mol% of **L6b** and 10 mol% of the catalyst at room temperature (the reaction was complete in 14 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 60:40) afforded 35 mg (41%) of the product as a yellow solid. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.69 – 7.64 (m, 2H), 7.52 – 7.46 (m, 2H), 6.99 – 6.95 (m, 2H), 6.67 (dd, *J* = 8.9, 2.6 Hz, 1H), 4.10 (hept, *J* = 6.8 Hz, 1H), 3.91 (dd, *J* = 9.6, 4.2 Hz, 1H), 3.85 (s, 3H), 3.76 (hept, *J* = 6.9 Hz, 1H), 2.88 (ddd, *J* = 14.6, 9.0, 5.9 Hz, 1H), 2.79 (dt, *J* = 14.5, 7.8 Hz, 1H), 2.32 (s, 3H), 2.04 – 1.94 (m, 2H), 1.28 (d, *J* = 6.8 Hz, 6H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 7.1 Hz, 3H), 1.20 (s, 6H), 1.20 (s, 6H).

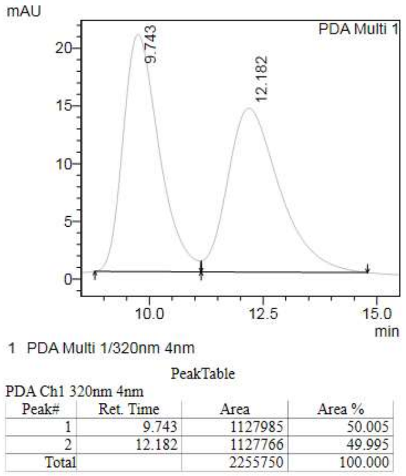
^{13}C NMR (101 MHz, CDCl$_3$) δ 168.39, 162.86, 156.06, 138.96, 134.54, 133.96, 131.48, 131.20, 131.15, 129.15, 120.08, 115.09, 111.25, 101.62, 79.92, 55.86, 48.58, 46.79, 31.71, 25.47, 25.03, 22.47, 20.67, 20.67, 20.47, 20.38, 13.49 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) 12.78.

ESI MS calcd for $C_{33}H_{45}BClN_2O_6^+$ $[M+H]^+$ 611.31, found 611.5.

Chiral HPLC CHIRALCEL® OZ-3, 3.0% IPA in hexane, 1.0 mL/min, 320 nm: 94% ee

Racemic Material

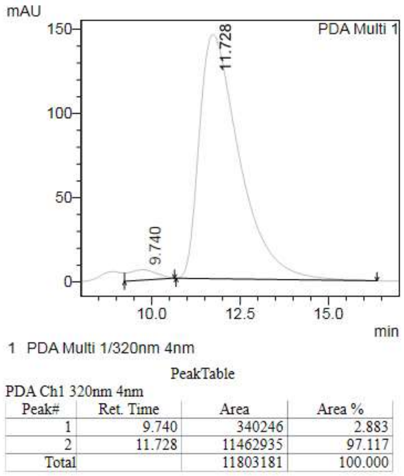


PeakTable

PDA Ch1 320nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.743	1127985	50.005
2	12.182	1127766	49.995
Total		2255750	100.000

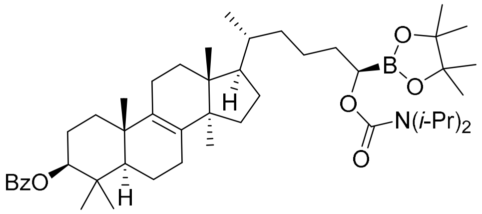
Enantioenriched Material



PeakTable

PDA Ch1 320nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.740	340246	2.883
2	11.728	11462935	97.117
Total		11803181	100.000



(3*S*,5*R*,10*S*,13*R*,14*R*,17*R*)-17-((2*R*,6*R*)-6-((Diisopropylcarbamoyl)oxy)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)-4,4,10,13,14-pentamethyl-2,3,4,5,6,7,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl benzoate (4x).

General procedure E was followed on a 109 mg (0.169 mmol) scale of **3x** with 12 mol% of **L6b** and 10 mol% of the catalyst at room temperature (the reaction was complete in 48 h). Flash chromatography on silica gel (eluting with hexanes/EtOAc = 80:20) afforded 60 mg (46%) of the product as a white solid. Absolute stereochemistry was assigned by analogy to **4d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, J = 7.3 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 4.68 (dd, J = 11.6, 4.4 Hz, 1H), 4.02 (hept, J = 6.8 Hz, 1H), 3.78 – 3.65 (m, 2H), 2.06 – 1.91 (m, 3H), 1.89 – 1.03 (m, 22H), 1.20 – 1.13 (m, 12H), 1.11 (s, 12H), 0.98 (s, 3H), 0.98 (s, 3H), 0.89 (s, 3H), 0.84 (d, J = 6.4 Hz, 3H), 0.82 (s, 3H), 0.63 (s, 3H).

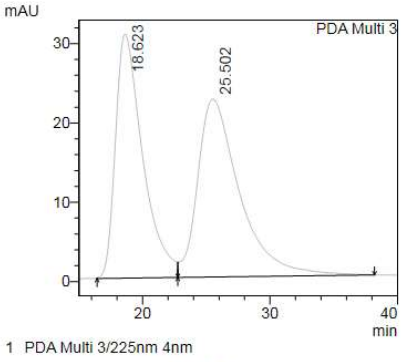
^{13}C NMR (151 MHz, CDCl$_3$) δ 166.47, 162.96, 134.69, 134.35, 132.86, 131.14, 129.67, 128.46, 81.73, 79.81, 50.71, 50.38, 49.95, 48.57, 46.64, 44.57, 43.17, 38.36, 37.08, 36.42, 36.26, 35.41, 32.17, 31.09, 30.98, 28.27, 28.23, 26.52, 25.42, 25.09, 24.48, 24.39, 21.18, 20.78, 20.71, 20.46, 20.39, 19.36, 18.94, 18.29, 16.97, 15.91 (the carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, CDCl$_3$) δ 13.25.

ESI MS calcd for $C_{48}H_{77}BNO_6^+$ [M+H]$^+$ 774.58, found 774.4.

Chiral HPLC CHIRALCEL® OZ-3, 0.35% IPA in hexane, 1.2 mL/min, 225 nm: 97:3 dr

Racemic Material

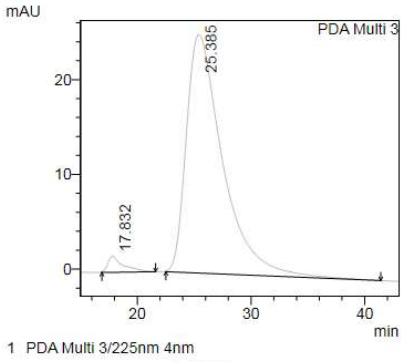


PeakTable

PDA Ch3 225nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.623	4577808	47.068
2	25.502	5148240	52.932
Total		9726048	100.000

Enantioenriched Material



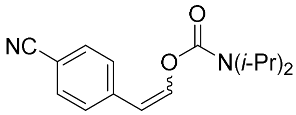
PeakTable

PDA Ch3 225nm 4nm

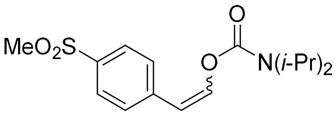
Peak#	Ret. Time	Area	Area %
1	17.832	160451	2.796
2	25.385	5578088	97.204
Total		5738539	100.000

Limitations of Asymmetric Hydroboration

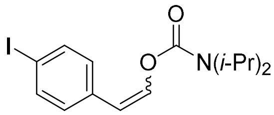
Figure S3. Substrates that failed to yield the desired hydroboration products



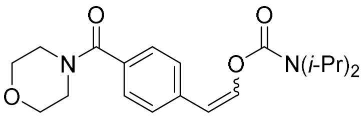
slow hydrogenation



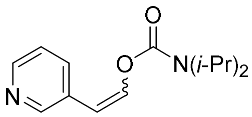
hydrogenation



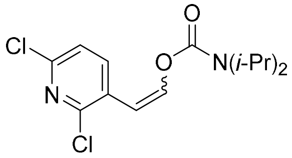
slow reaction



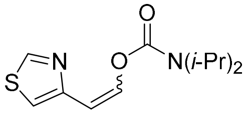
slow hydrogenation



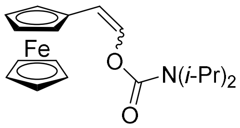
slow hydrogenation



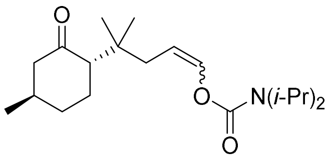
slow hydrogenation



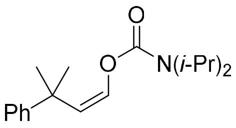
no reaction



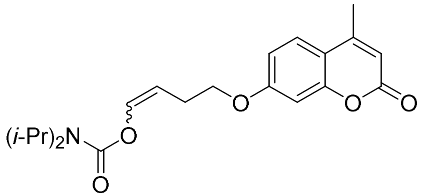
slow hydrogenation



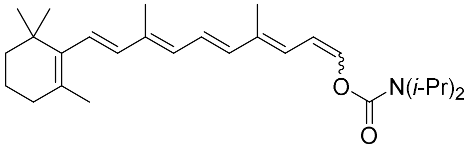
messy



slow hydrogenation



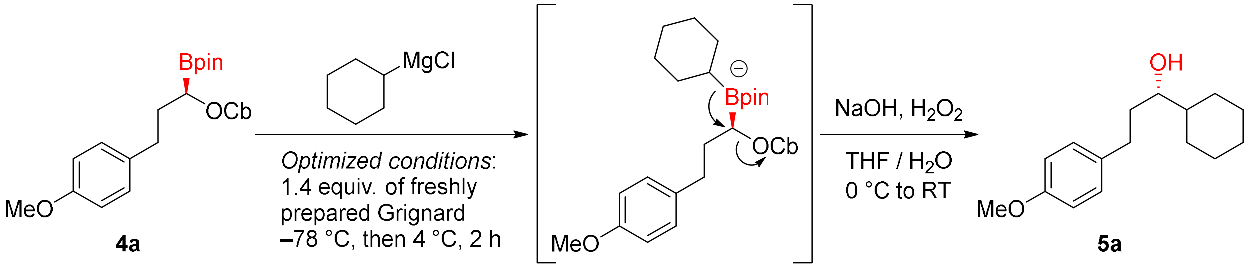
slow reaction



messy

Reactions of Hydroboration Products with Grignard Reagents

Table S10. Optimization of enantioselectivity of 1,2-metalate rearrangement



Entry	Deviation from optimized conditions	es (%)[a]	Yield (%)
1	None	97	71
2	Commercial Grignard instead of freshly prepared Grignard	89–96	57–73
3	THF instead of Et_2O	–	(messy)
4	RT instead of [–78 °C, then 4 °C]	85	75
5	4.8 equiv of Grignard instead of 1.4 equiv	94	67

[a] Enantioselectivity (es) is defined as ee of the product divided by ee of the starting material.

General Procedure F for the preparation of Grignard reagents

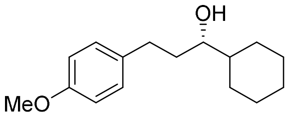
All manipulations were carried out under argon. Halide (10.0 mmol, 1.00 equiv) was dissolved in anhydrous Et_2O (5.0 mL), and a 0.5-mL portion of the resulting solution was added to dried Mg turnings (0.360 g, 15.0 mmol, 1.50 equiv). Iodine (cat.) was added, and the mixture was heated at 35 °C until discoloration. The remaining portion of the halide solution in Et_2O was added, and the mixture was stirred at reflux for 1 h. The concentration of the resulting Grignard reagent was determined by iodometric titration.[31]

General Procedure G for Table S10 (entry 1)

At –78 °C and under argon, freshly prepared Grignard (according to General Procedure F; 0.14 mmol, 1.4 equiv) was added dropwise (over 2 min) to a solution of hydroboration product (0.10 mmol, 1.0 equiv) in anhydrous Et_2O (1.0 mL). The mixture was stirred under argon in a cold room (4 °C) for 2 h. After that, insoluble solids were removed by filtration through a Pasteur pipette with a silica gel plug (ca. 1 mL of silica gel was used; additional 2-mL portion of Et_2O was used for washing), and the filtrate was concentrated under vacuum.

The crude secondary boronate was then redissolved in THF (1.0 mL), and the solution was cooled to 0 °C and treated with 3M NaOH (0.17 mL) and 30% aq. H_2O_2 (0.17 mL). The mixture was stirred at ambient temperature for 2 h. At 0 °C, sat. aq. $Na_2S_2O_3$ (1 mL) was carefully added to quench the reaction, and the product was extracted with EtOAc (3 × 2 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated. Subsequent flash chromatography afforded the desired secondary alcohol.

Racemic product samples were obtained by following the same procedure using racemic boronates as starting materials.



(*S*)-1-Cyclohexyl-3-(4-methoxyphenyl)propan-1-ol (5a).

General procedure G was followed on a 35 mg (0.083 mmol) scale of **4a** (98% ee) with cyclohexylMgCl, which after flash chromatography on silica gel (eluting with hexanes/EtOAc = 85:15) afforded 15 mg (71%) of the product as a white solid. Absolute stereochemistry was assigned by analogy to **5d**.

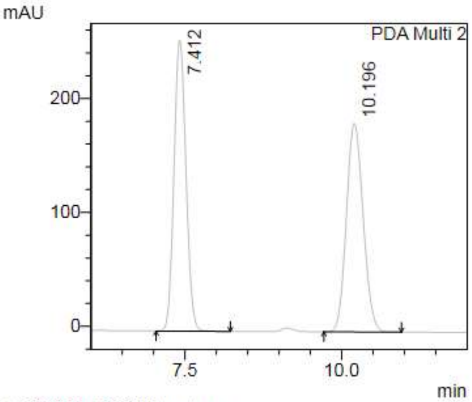
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 – 7.08 (m, 2H), 6.88 – 6.79 (m, 2H), 3.79 (s, 3H), 3.38 (ddd, *J* = 8.9, 5.4, 3.2 Hz, 1H), 2.77 (ddd, *J* = 13.8, 9.9, 5.4 Hz, 1H), 2.59 (ddd, *J* = 13.8, 9.7, 6.7 Hz, 1H), 1.88 – 1.58 (m, 6H), 1.42 – 0.91 (m, 7H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 157.83, 134.53, 129.43, 113.92, 75.72, 55.39, 43.90, 36.26, 31.56, 29.30, 27.91, 26.65, 26.46, 26.32.

ESI MS calcd for $C_{16}H_{23}O^+$ [M–OH]$^+$ 231.17, found 231.2.

Chiral HPLC CHIRALCEL® OD-H, 3.5% IPA in hexane, 1.5 mL/min, 220 nm: 95% ee, 97% es

Racemic Material



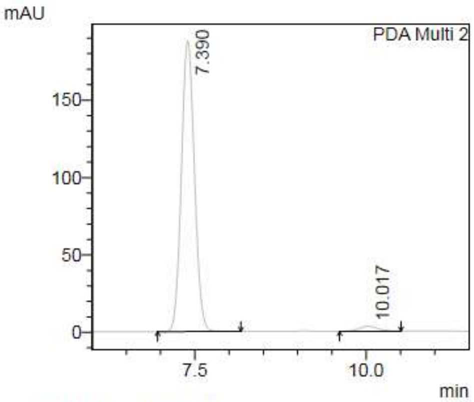
1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.412	3395824	49.846
2	10.196	3416777	50.154
Total		6812601	100.000

Enantioenriched Material

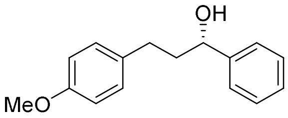


1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.390	2494412	97.591
2	10.017	61573	2.409
Total		2555984	100.000



(*S*)-3-(4-Methoxyphenyl)-1-phenylpropan-1-ol (5b).

General procedure G was followed on a 43 mg (0.10 mmol) scale of **4a** (98% ee) with PhMgBr, which after flash chromatography on silica gel (eluting with hexanes/EtOAc = 85:15) afforded 12 mg (50%) of the product as a colorless oil. Absolute stereochemistry was assigned by analogy to **5d**.

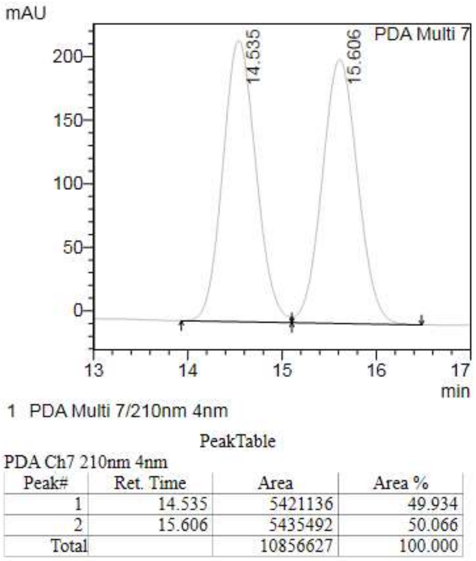
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 (d, *J* = 4.1 Hz, 4H), 7.24 – 7.15 (m, 1H), 7.07 – 6.98 (m, 2H), 6.80 – 6.70 (m, 2H), 4.59 (dd, *J* = 7.9, 5.3 Hz, 1H), 3.70 (s, 3H), 2.61 (ddd, *J* = 13.7, 9.5, 5.8 Hz, 1H), 2.53 (ddd, *J* = 14.0, 9.7, 7.1 Hz, 1H), 2.02 (dddd, *J* = 13.8, 9.3, 7.8, 5.9 Hz, 1H), 1.91 (dddd, *J* = 13.7, 9.5, 6.7, 5.3 Hz, 1H), 1.79 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.90, 144.74, 133.91, 129.45, 128.64, 127.76, 126.06, 113.93, 73.99, 55.39, 40.82, 31.26.

ESI MS calcd for $C_{16}H_{17}O^+$ $[M–OH]^+$ 225.13, found 225.4.

Chiral HPLC CHIRALCEL® OD-H, 5.0% IPA in hexane, 1.25 mL/min, 210 nm: 94% ee, 96% es

Racemic Material

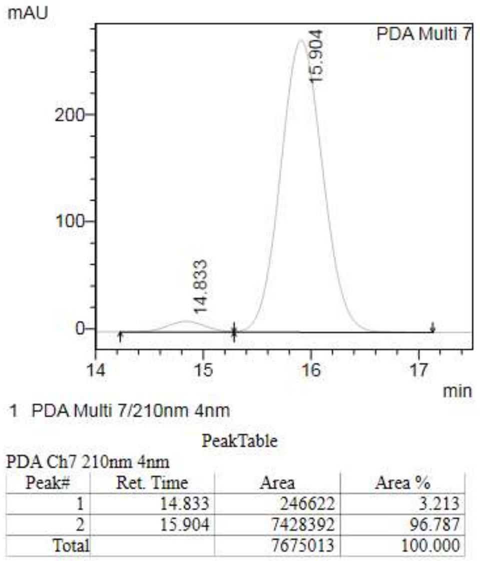


PeakTable

PDA Ch7 210nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.535	5421136	49.934
2	15.606	5435492	50.066
Total		10856627	100.000

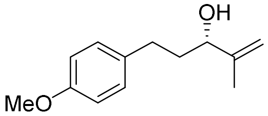
Enantioenriched Material



PeakTable

PDA Ch7 210nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.833	246622	3.213
2	15.904	7428392	96.787
Total		7675013	100.000



(*S*)-5-(4-Methoxyphenyl)-2-methylpent-1-en-3-ol (5c).

General procedure G was followed on a 34 mg (0.081 mmol) scale of **4a** (92% ee) with isopropenylMgBr, which after flash chromatography on silica gel (eluting with hexanes/EtOAc = 85:15) afforded 11 mg (65%) of the product as a colorless oil. Absolute stereochemistry was assigned by analogy to **5d**.

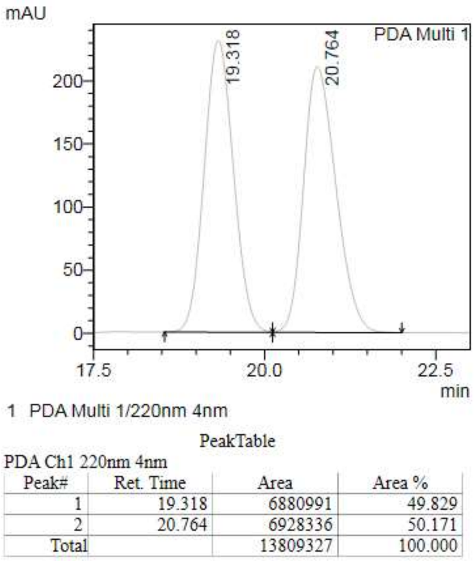
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.05 (m, 2H), 6.89 – 6.79 (m, 2H), 4.96 (dp, *J* = 1.9, 0.9 Hz, 1H), 4.86 (p, *J* = 1.6 Hz, 1H), 4.08 (q, *J* = 7.1, 3.9 Hz, 1H), 3.79 (s, 3H), 2.67 (ddd, *J* = 15.6, 8.9, 6.9 Hz, 1H), 2.58 (ddd, *J* = 13.9, 9.0, 7.1 Hz, 1H), 1.92 – 1.75 (m, 2H), 1.74 (s, 3H), 1.47 (d, *J* = 3.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.90, 147.58, 134.13, 129.47, 113.93, 111.35, 75.39, 55.41, 36.93, 31.10, 17.77.

ESI MS calcd for $C_{13}H_{17}O^+$ $[M–OH]^+$ 189.13, found 189.2.

Chiral HPLC CHIRALCEL® OD-H, 1.5% IPA in hexane, 1.5 mL/min, 220 nm: 88% ee, 96% es

Racemic Material

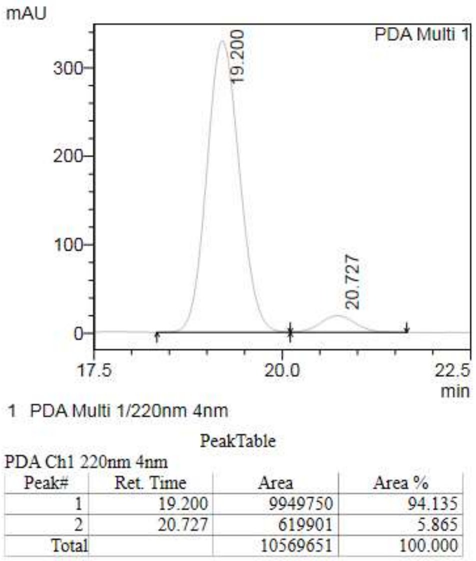


PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.318	6880991	49.829
2	20.764	6928336	50.171
Total		13809327	100.000

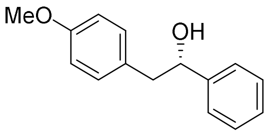
Enantioenriched Material



PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.200	9949750	94.135
2	20.727	619901	5.865
Total		10569651	100.000



(*S*)-2-(4-Methoxyphenyl)-1-phenylethan-1-ol (5d).

General procedure G was followed on a 50 mg (0.12 mmol) scale of **4c** (91% ee) with PhMgBr, which after flash chromatography on silica gel (eluting with hexanes/EtOAc = 85:15) afforded 13 mg (48%) of the product as a colorless oil. Absolute stereochemistry was assigned by comparing the order of elution of each enantiomer on OD-H column with the literature results.[32]

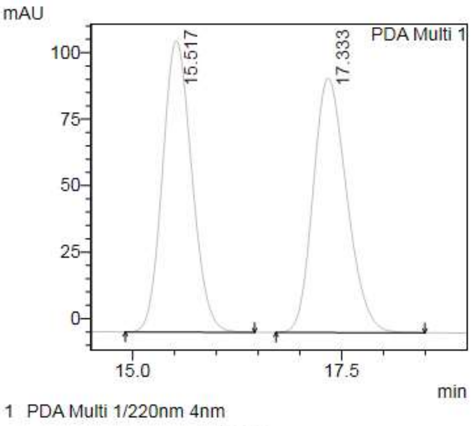
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.27 (m, 5H), 7.14 – 7.08 (m, 2H), 6.88 – 6.80 (m, 2H), 4.86 (ddd, *J* = 8.1, 4.8, 2.9 Hz, 1H), 3.80 (s, 3H), 3.00 (dd, *J* = 13.8, 4.8 Hz, 1H), 2.93 (dd, *J* = 13.8, 8.5 Hz, 1H), 1.91 (d, *J* = 3.0 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 158.50, 143.96, 130.62, 130.07, 128.53, 127.71, 126.04, 114.06, 75.56, 55.39, 45.32.

ESI MS calcd for $C_{15}H_{15}O^+$ [M–OH]$^+$ 211.11, found 211.2.

Chiral HPLC CHIRALCEL® OD-H, 3.0% IPA in hexane, 1.3 mL/min, 220 nm: 89% ee, 98% es

Racemic Material

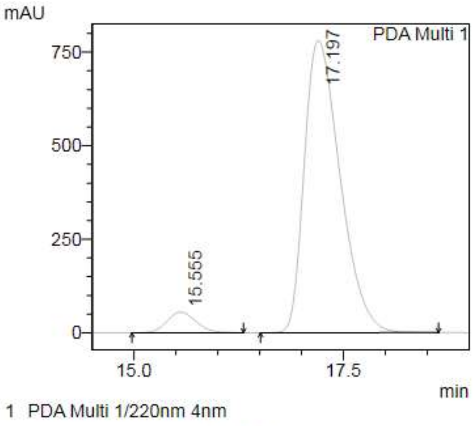


PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.517	2674004	49.928
2	17.333	2681738	50.072
Total		5355742	100.000

Enantioenriched Material



PeakTable

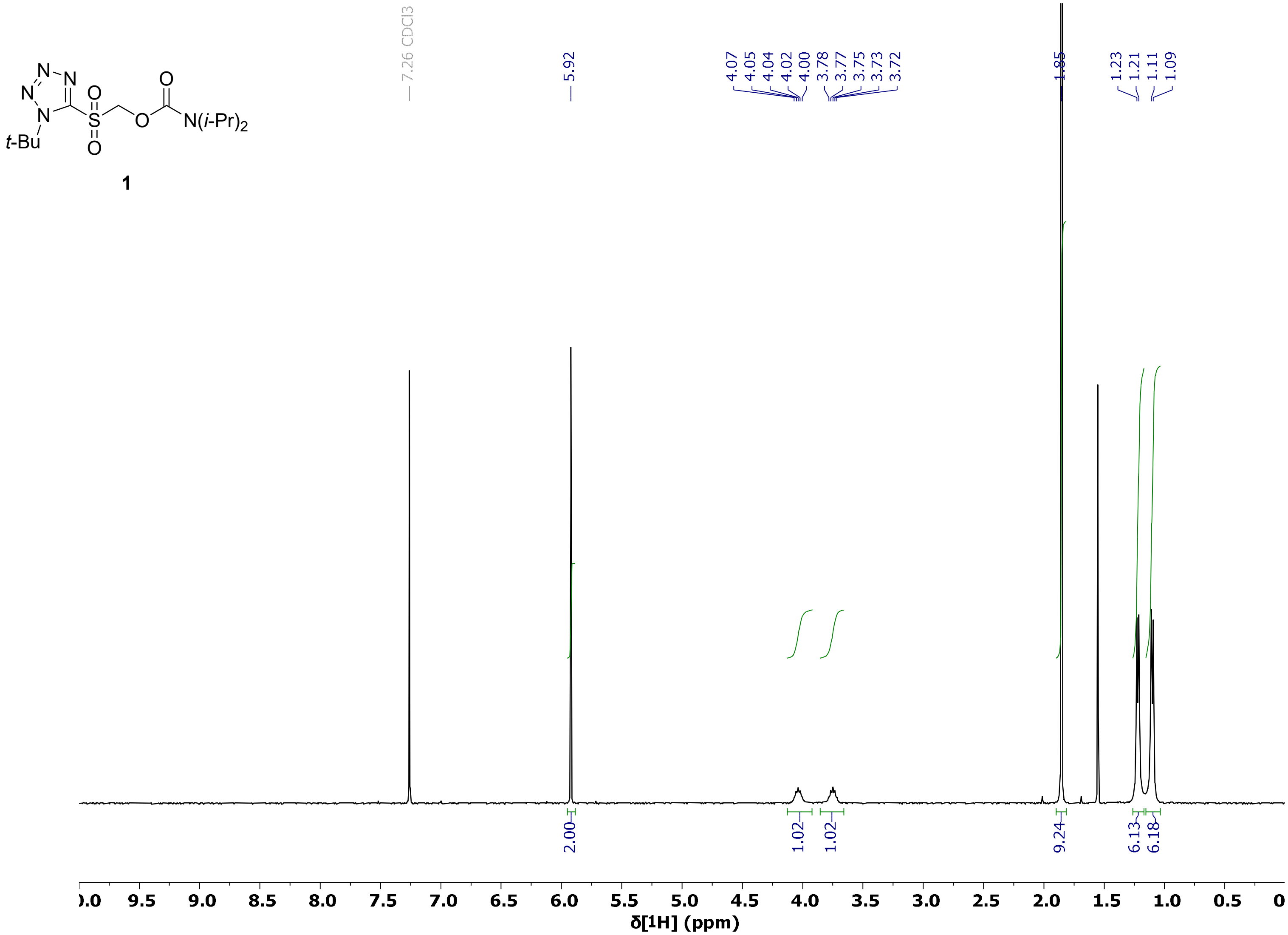
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.555	1334536	5.439
2	17.197	23203372	94.561
Total		24537908	100.000

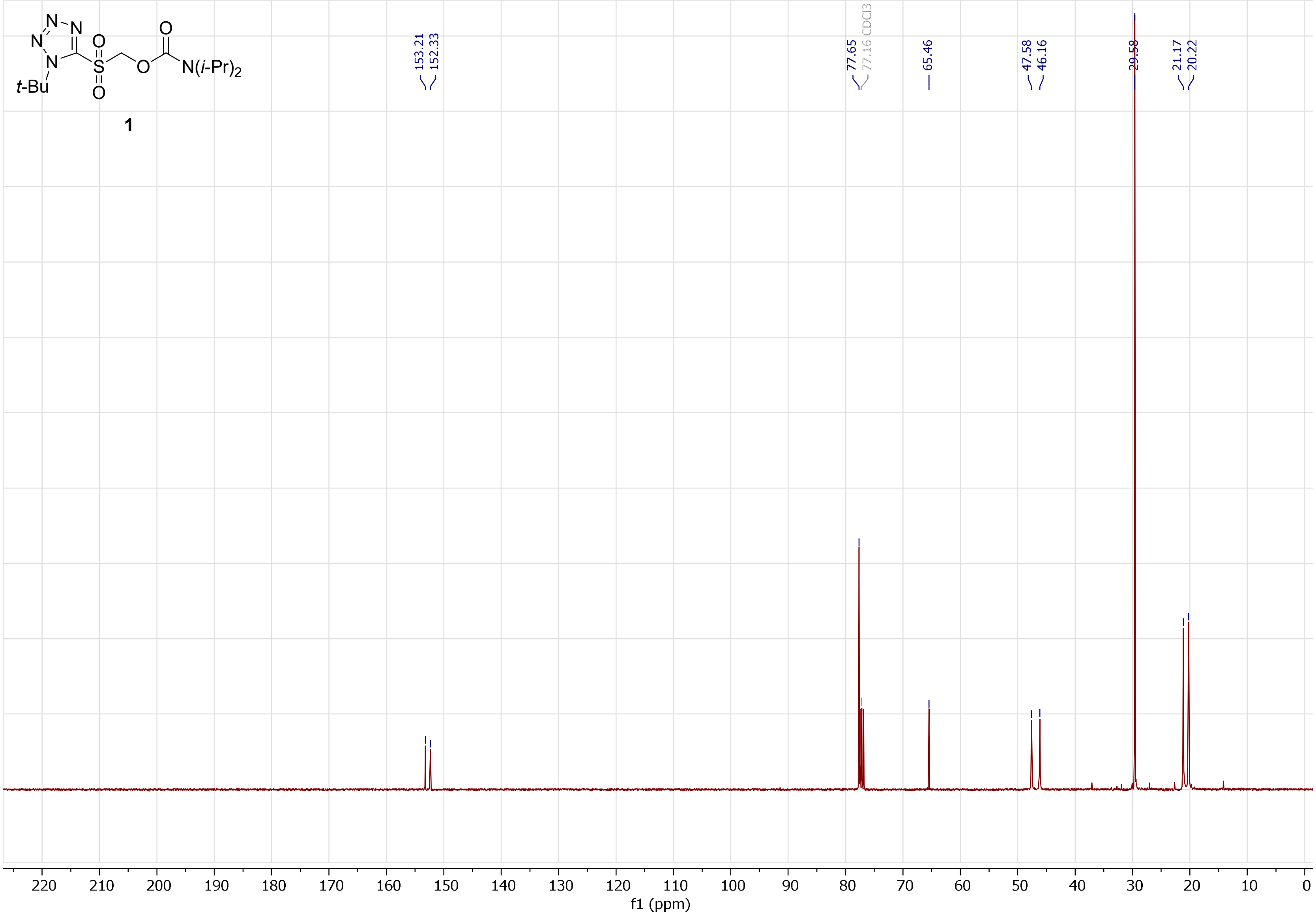
NMR Spectra

¹H NMR (400 MHz, $CDCl_3$)

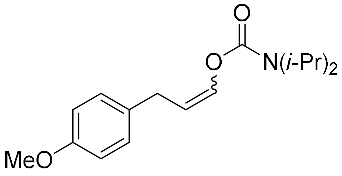
1



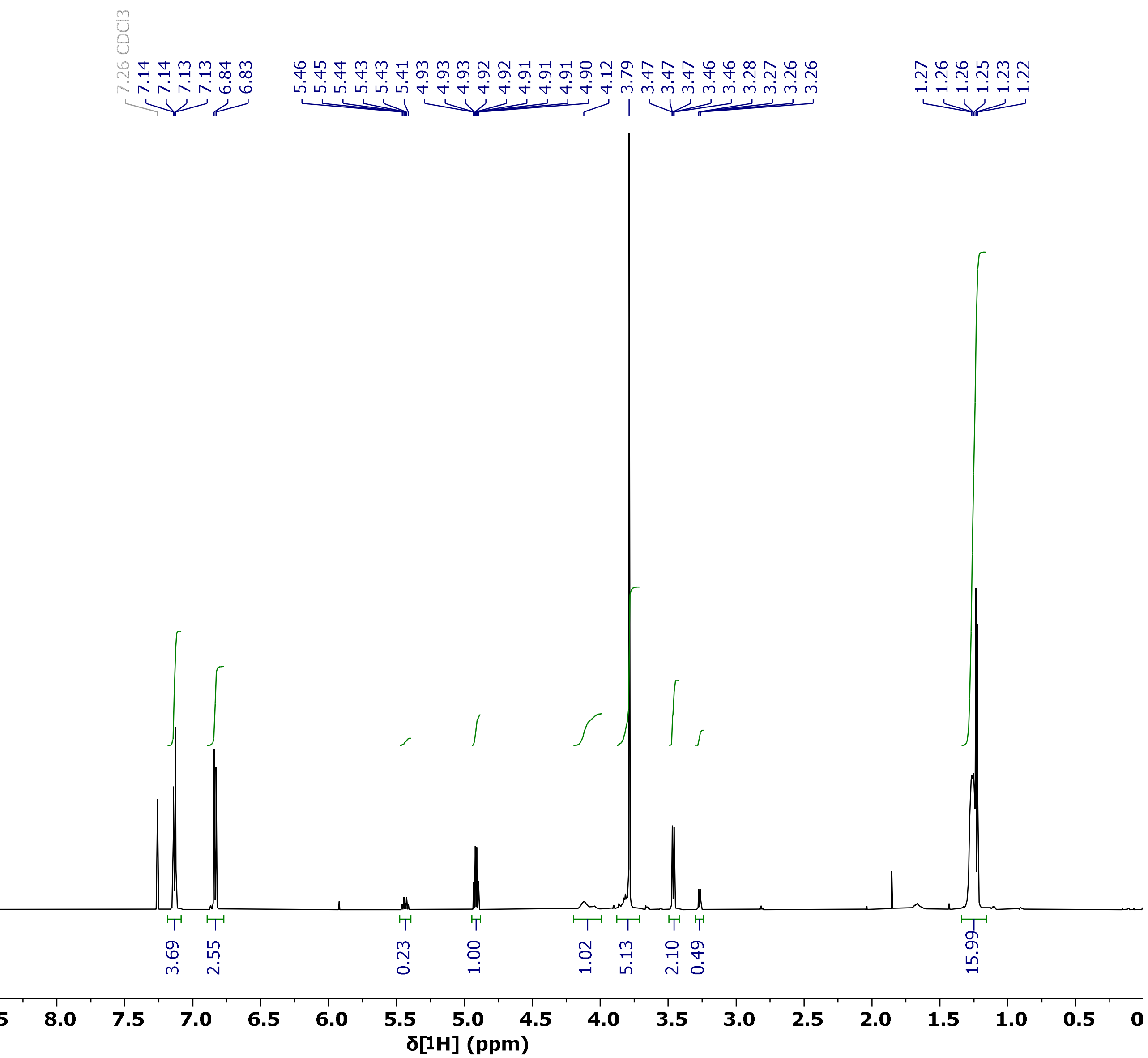
^{13}C NMR (101 MHz, $CDCl_3$)



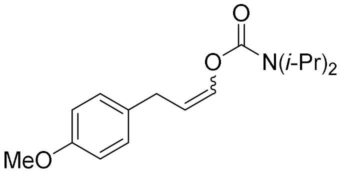
^{1}H NMR (400 MHz, $CDCl_3$)



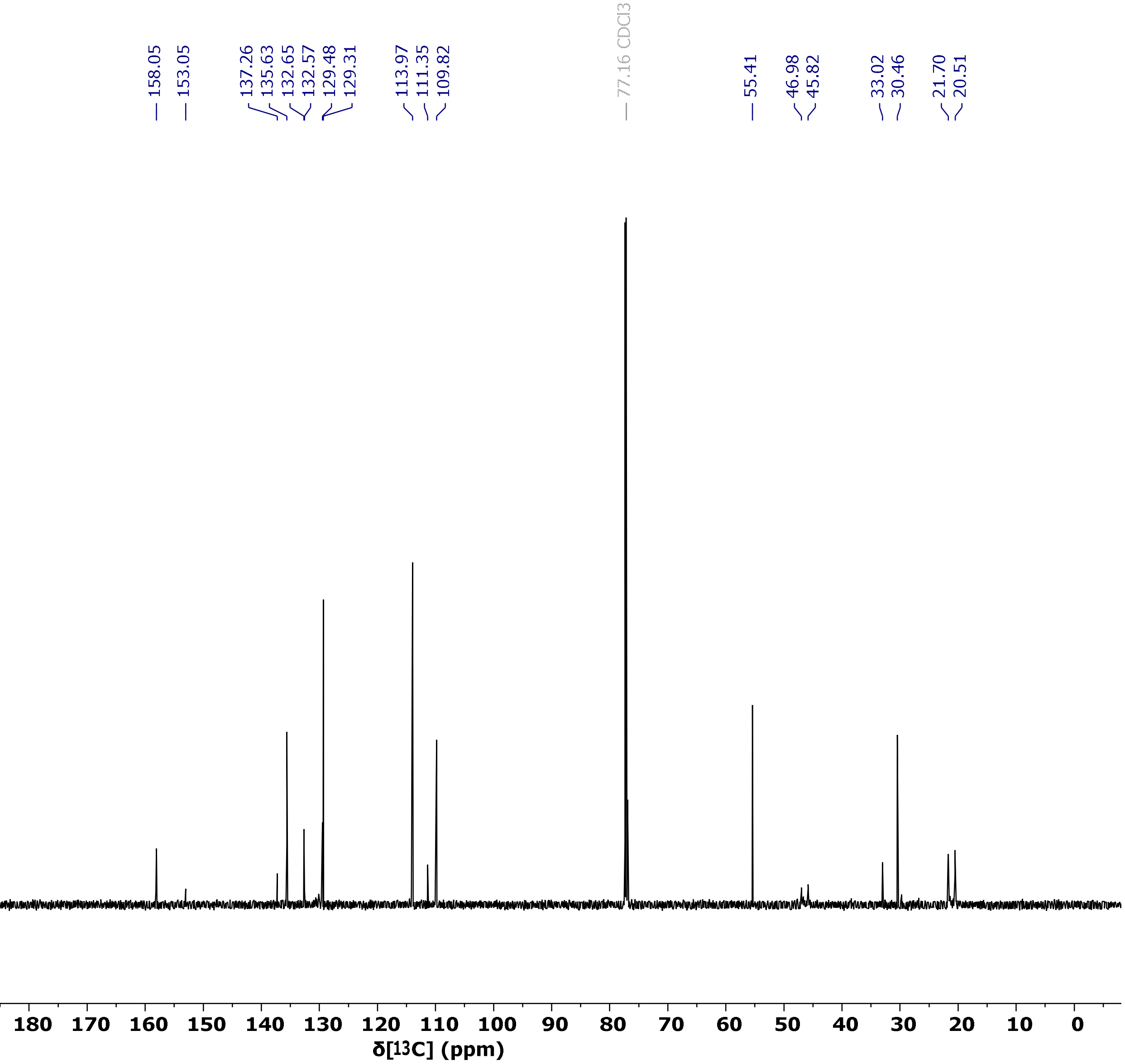
3a, *Z* : *E* = 80 : 20



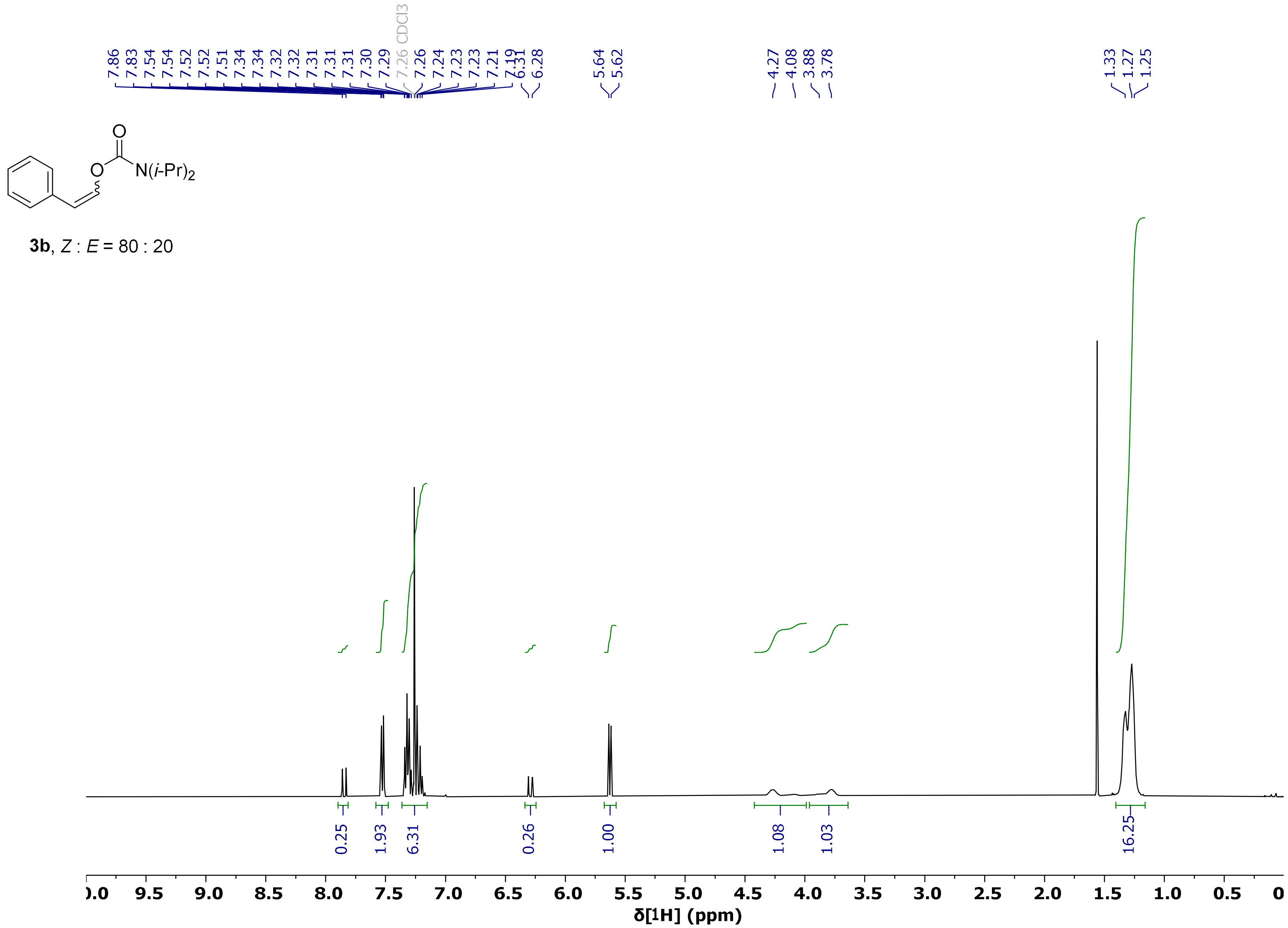
^{13}C NMR (151 MHz, $CDCl_3$)



3a, *Z* : *E* = 80 : 20

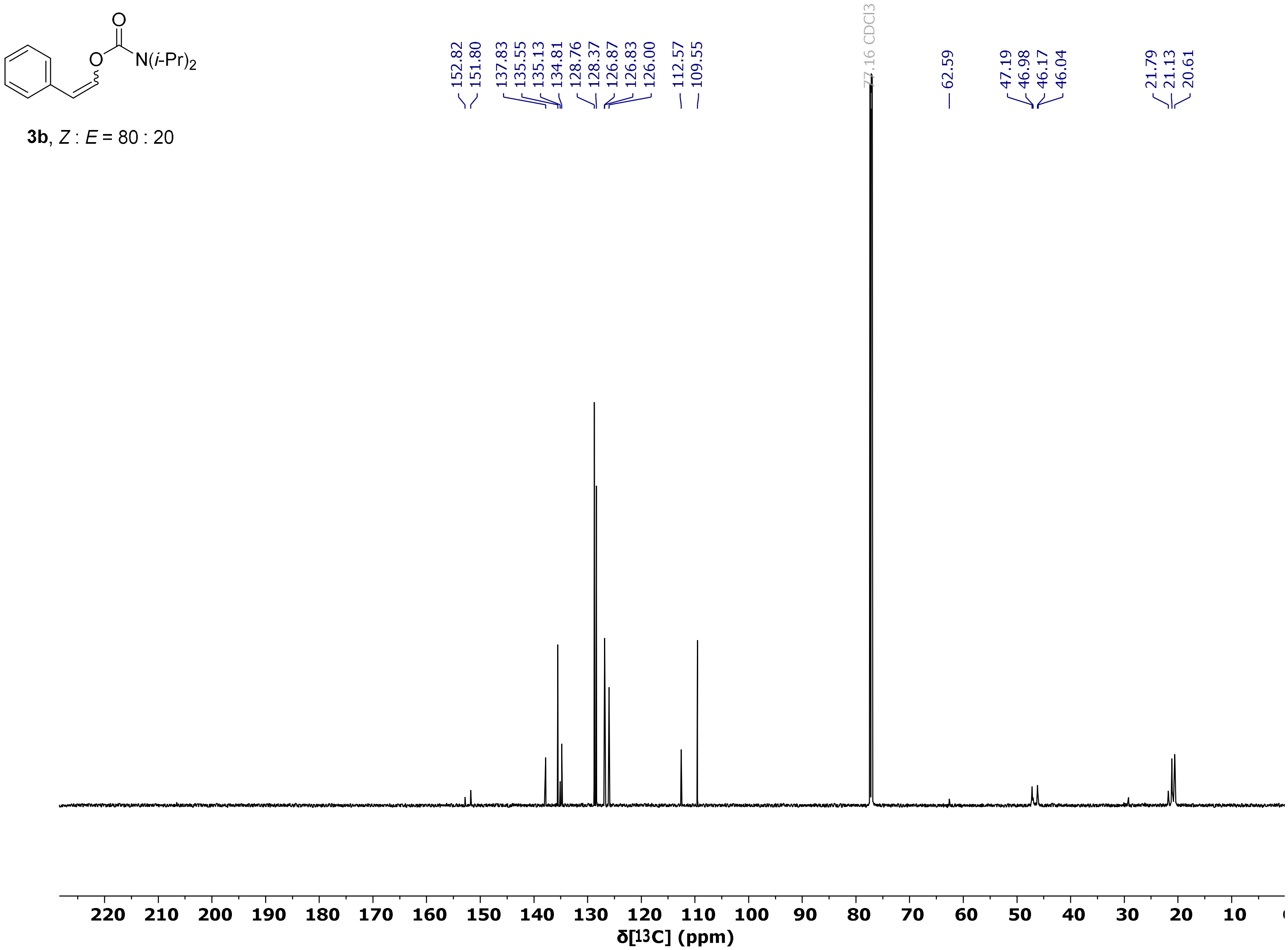


^{1}H NMR (400 MHz, $CDCl_3$)



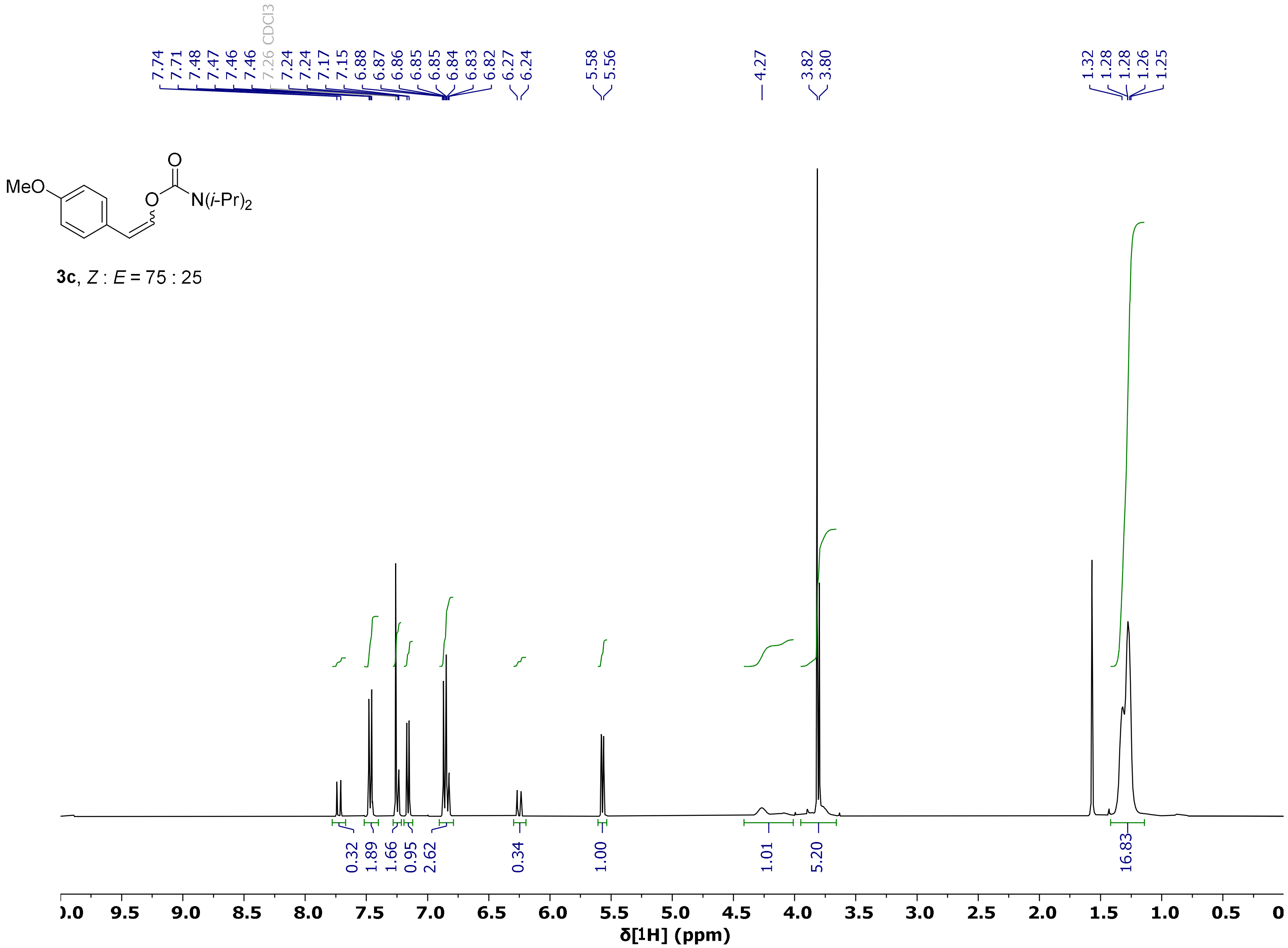
3b, *Z* : *E* = 80 : 20

^{13}C NMR (151 MHz, CDCl$_3$)



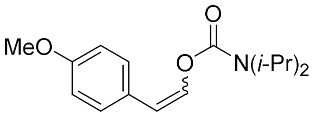
3b, *Z* : *E* = 80 : 20

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

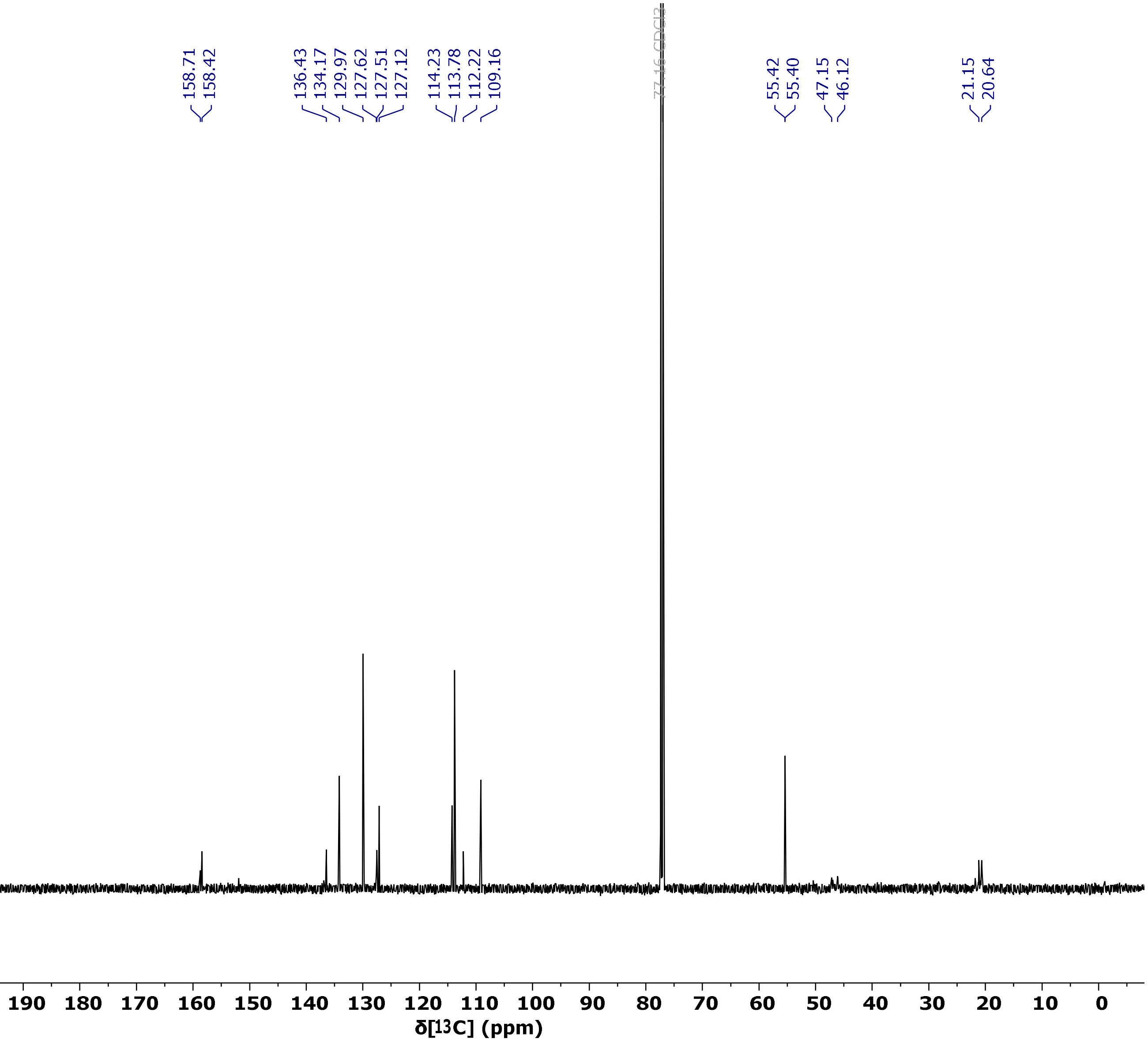


3c, *Z* : *E* = 75 : 25

^{13}**C NMR** (151 MHz, CDCl$_3$)

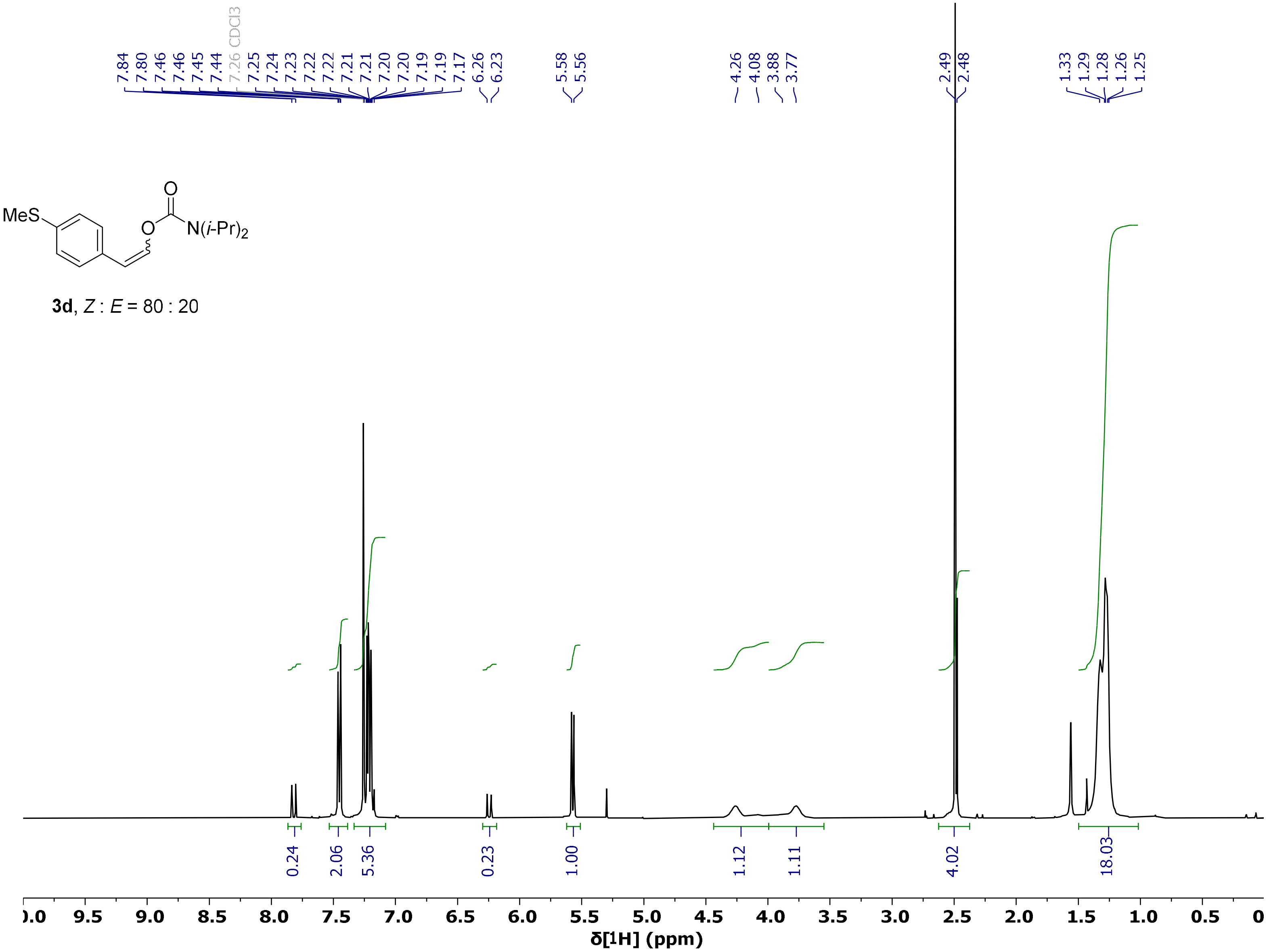


3c, *Z* : *E* = 75 : 25

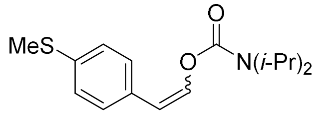


^{1}H NMR (400 MHz, $CDCl_3$)

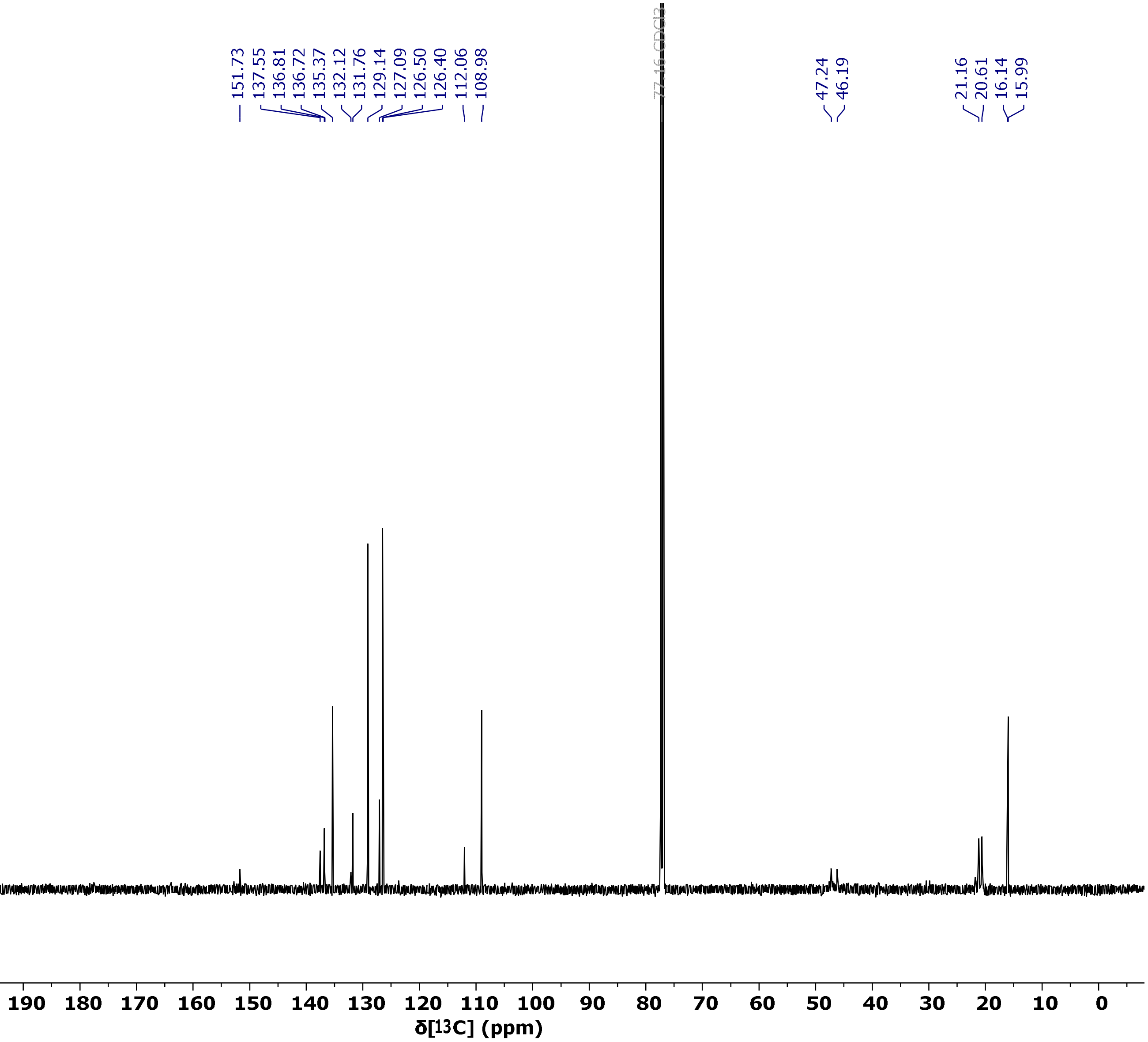
3d, *Z* : *E* = 80 : 20



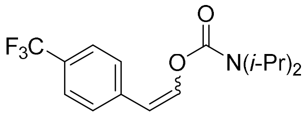
^{13}C NMR (151 MHz, $CDCl_3$)



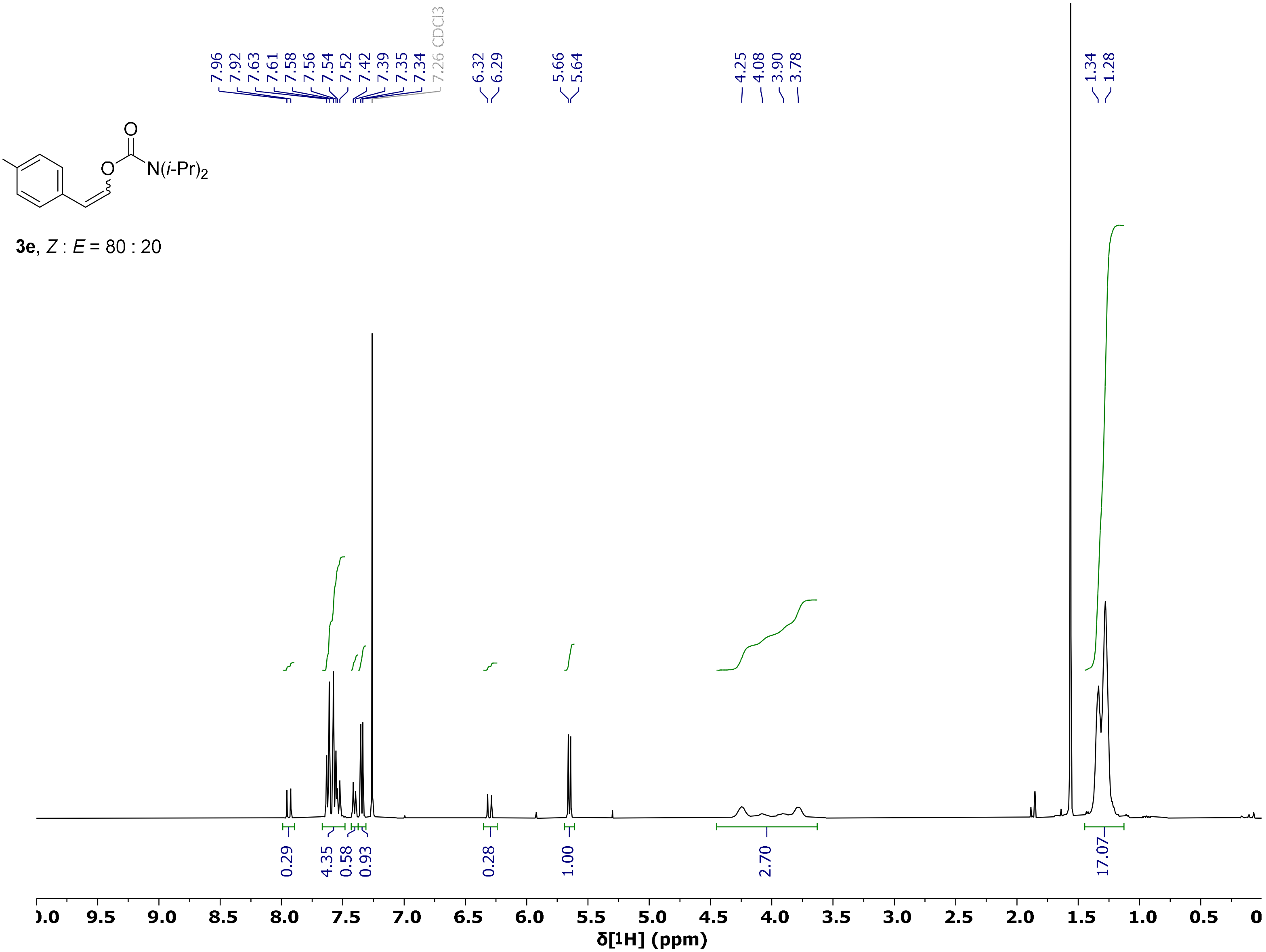
3d, *Z* : *E* = 80 : 20



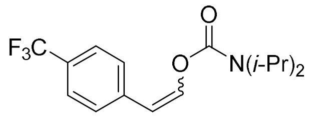
^{1}H NMR (400 MHz, $CDCl_3$)



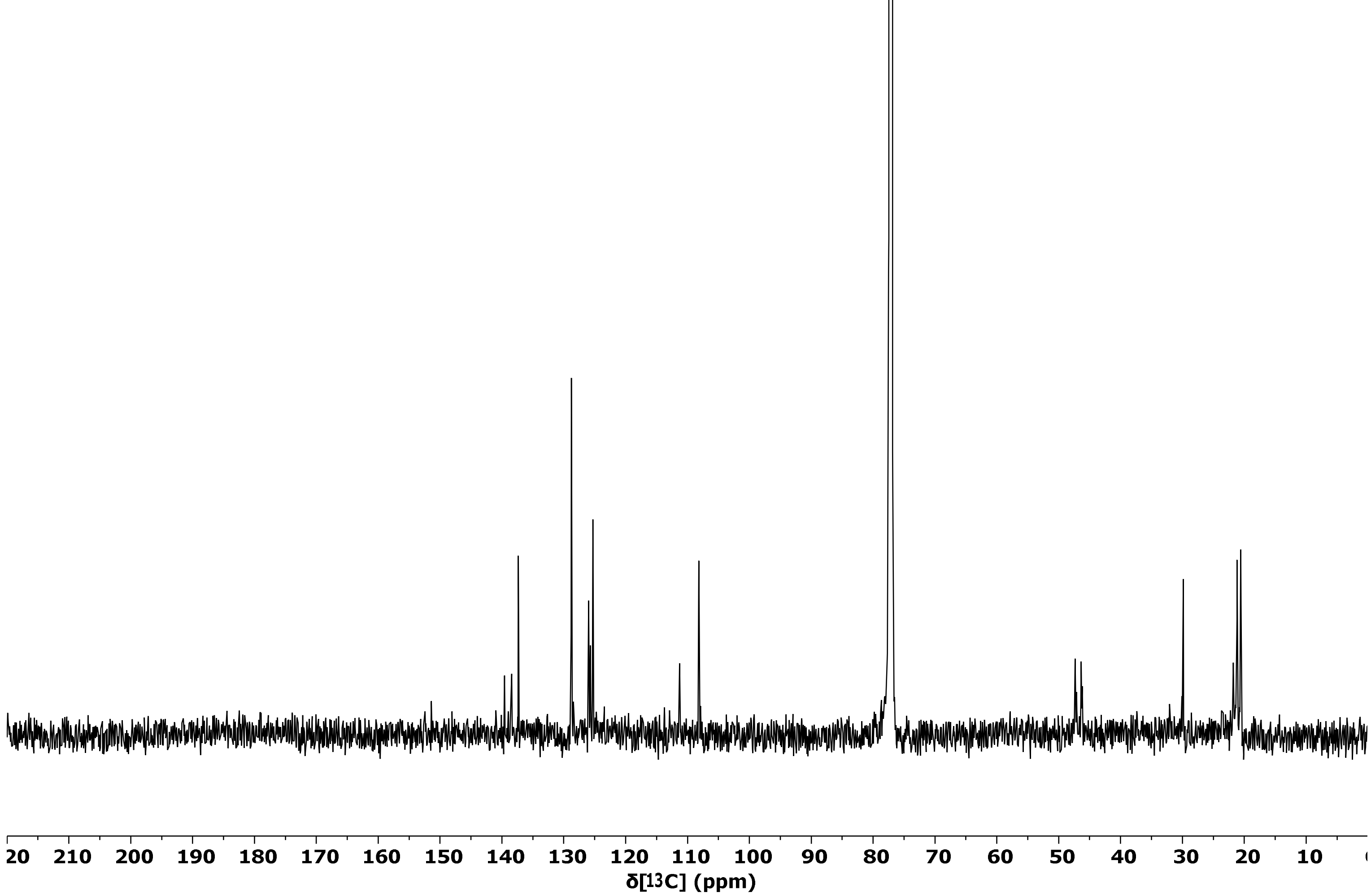
3e, *Z* : *E* = 80 : 20



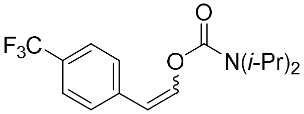
^{13}C NMR (151 MHz, $CDCl_3$)



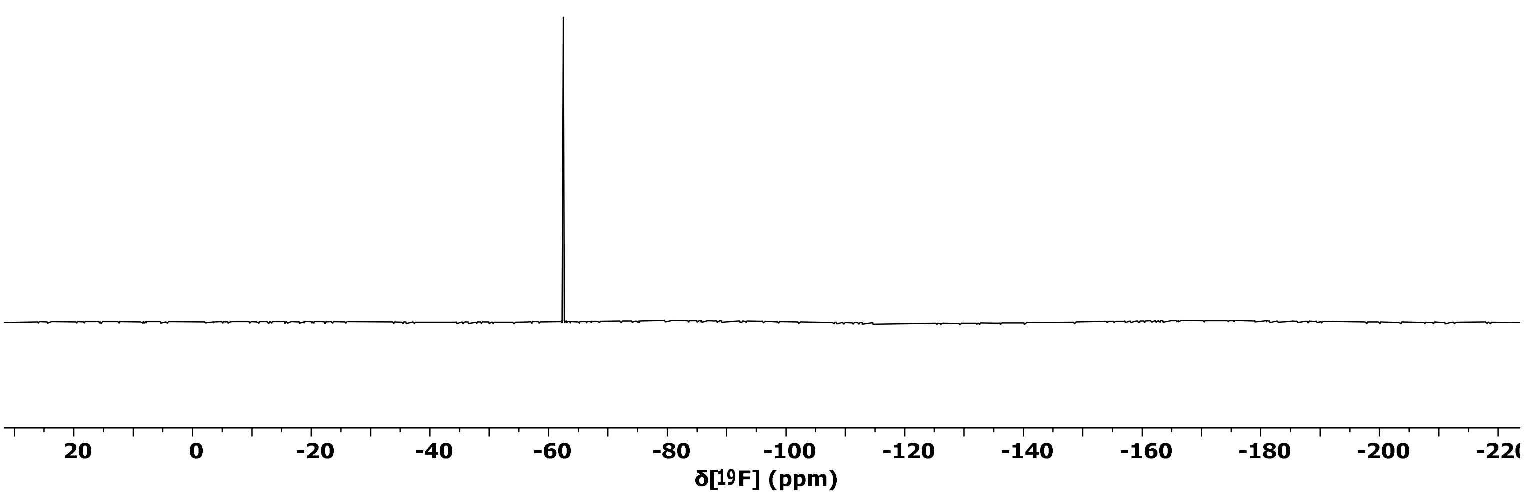
3e, *Z* : *E* = 80 : 20



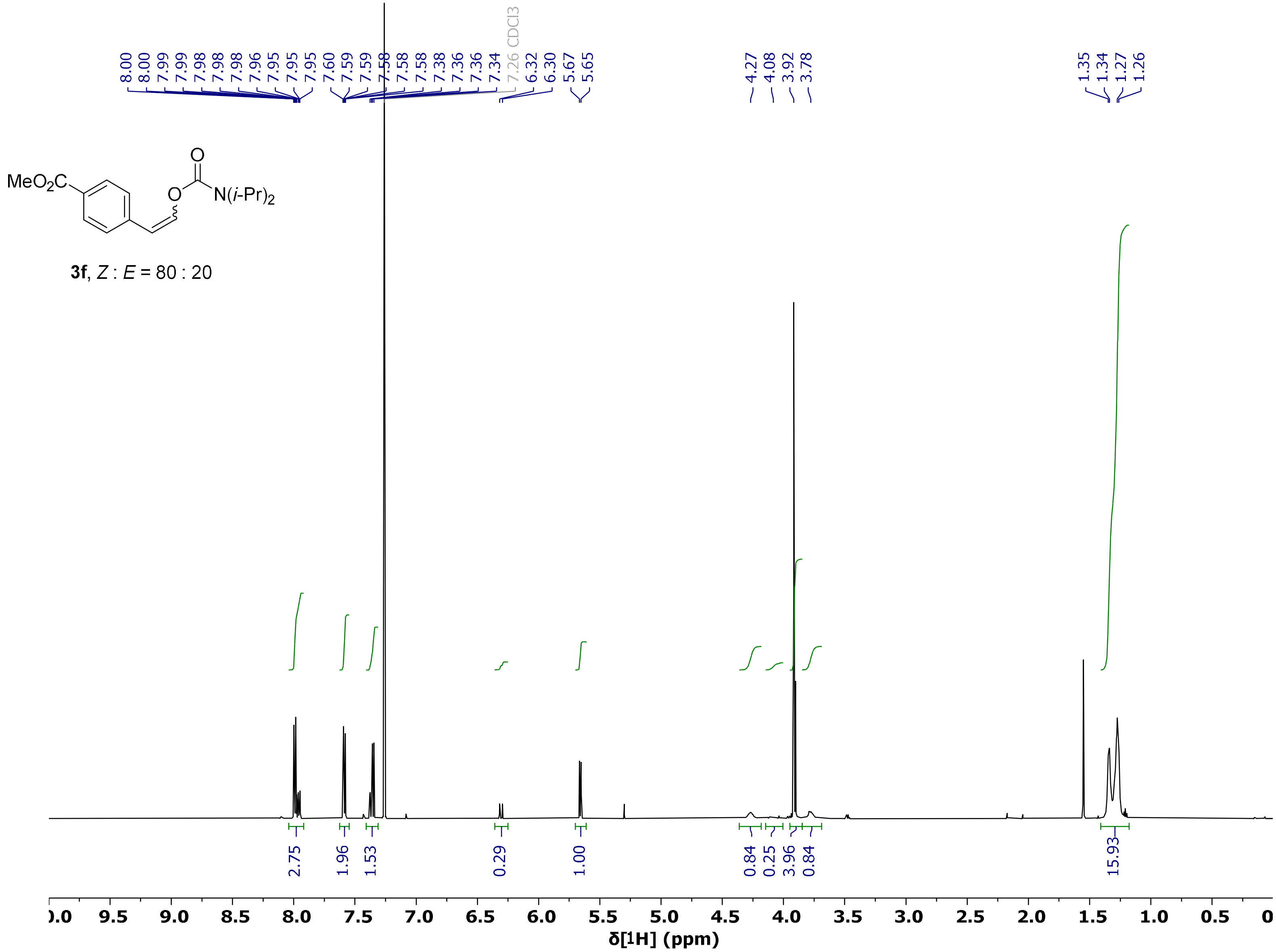
^{19}F NMR (376 MHz, $CDCl_3$)



3e, *Z* : *E* = 80 : 20

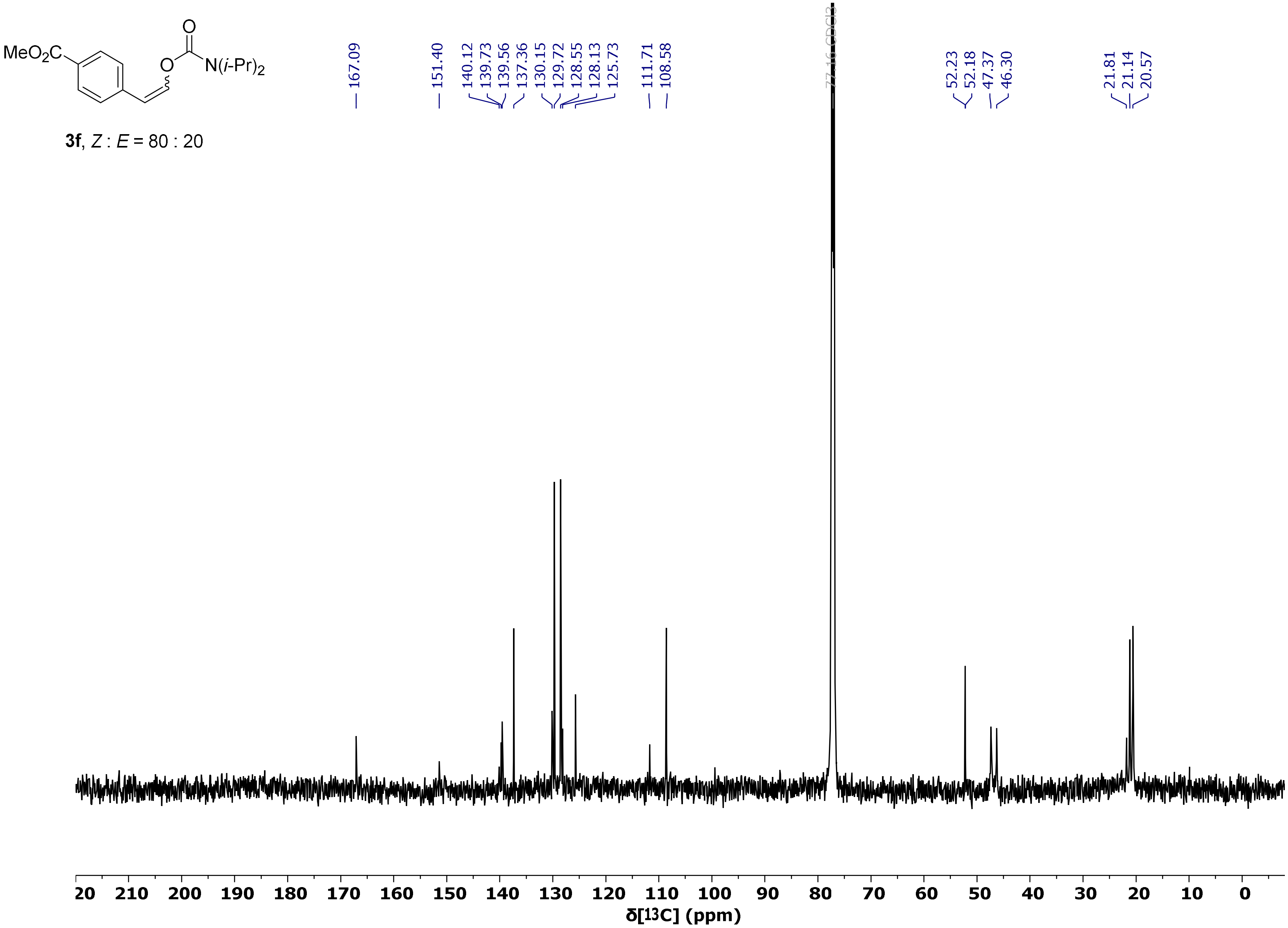


^{1}**H NMR** (400 MHz, CDCl$_3$)



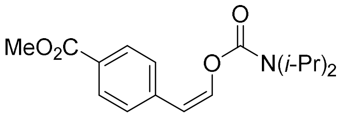
3f, *Z* : *E* = 80 : 20

^{13}**C NMR** (151 MHz, $CDCl_3$)

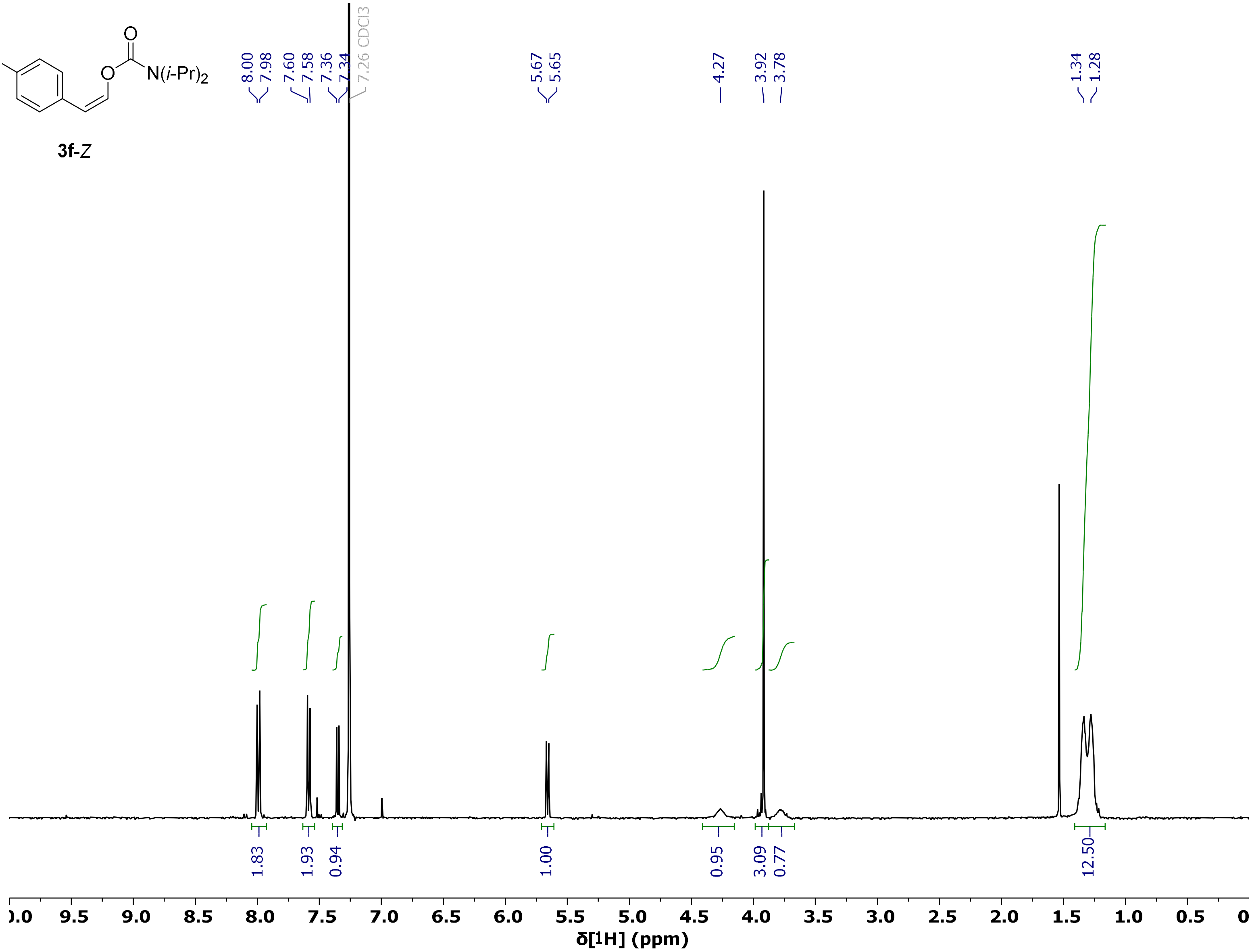


3f, *Z* : *E* = 80 : 20

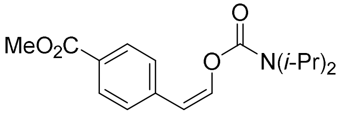
^{1}**H NMR** (400 MHz, $CDCl_3$)



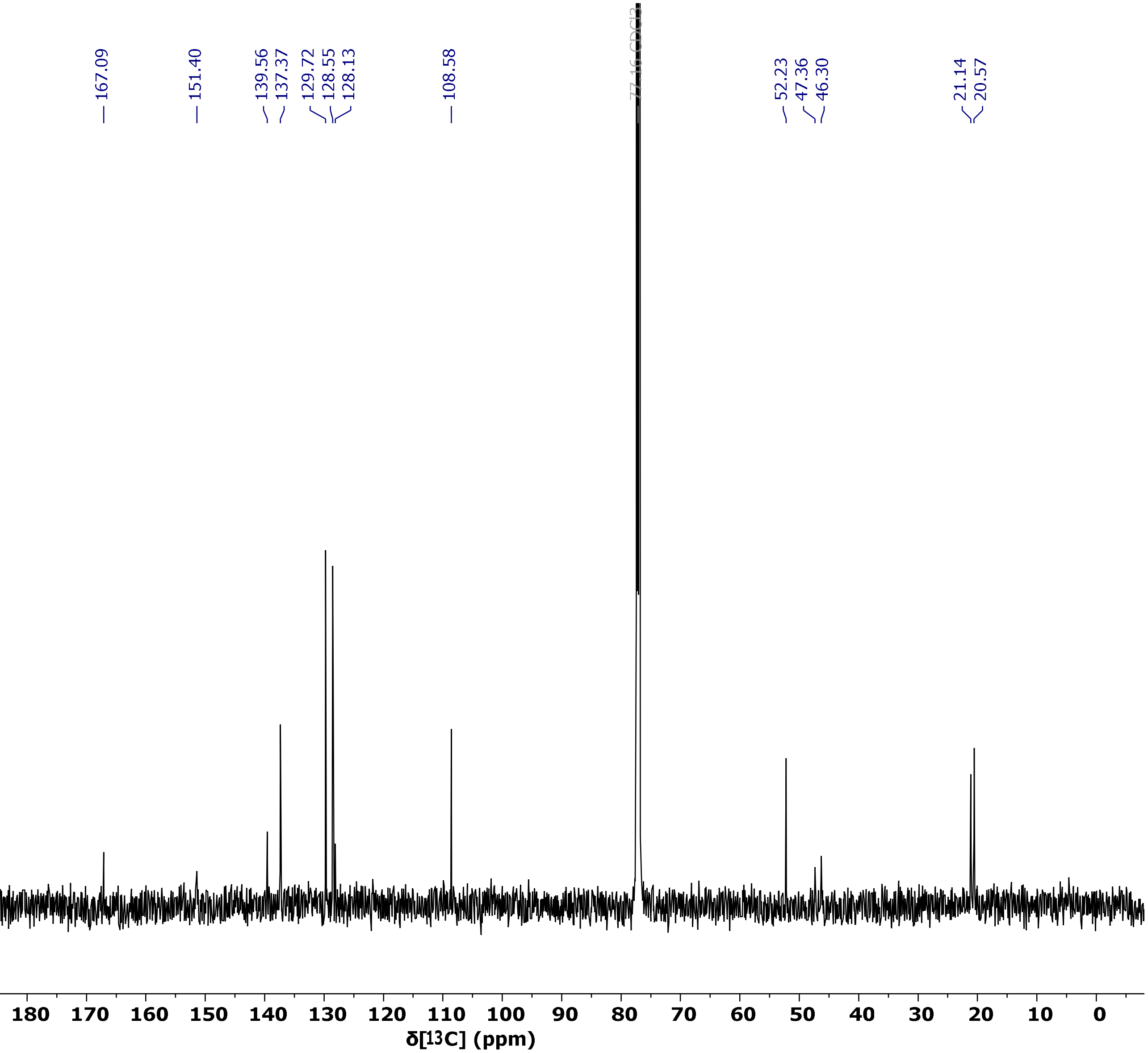
3f-*Z*



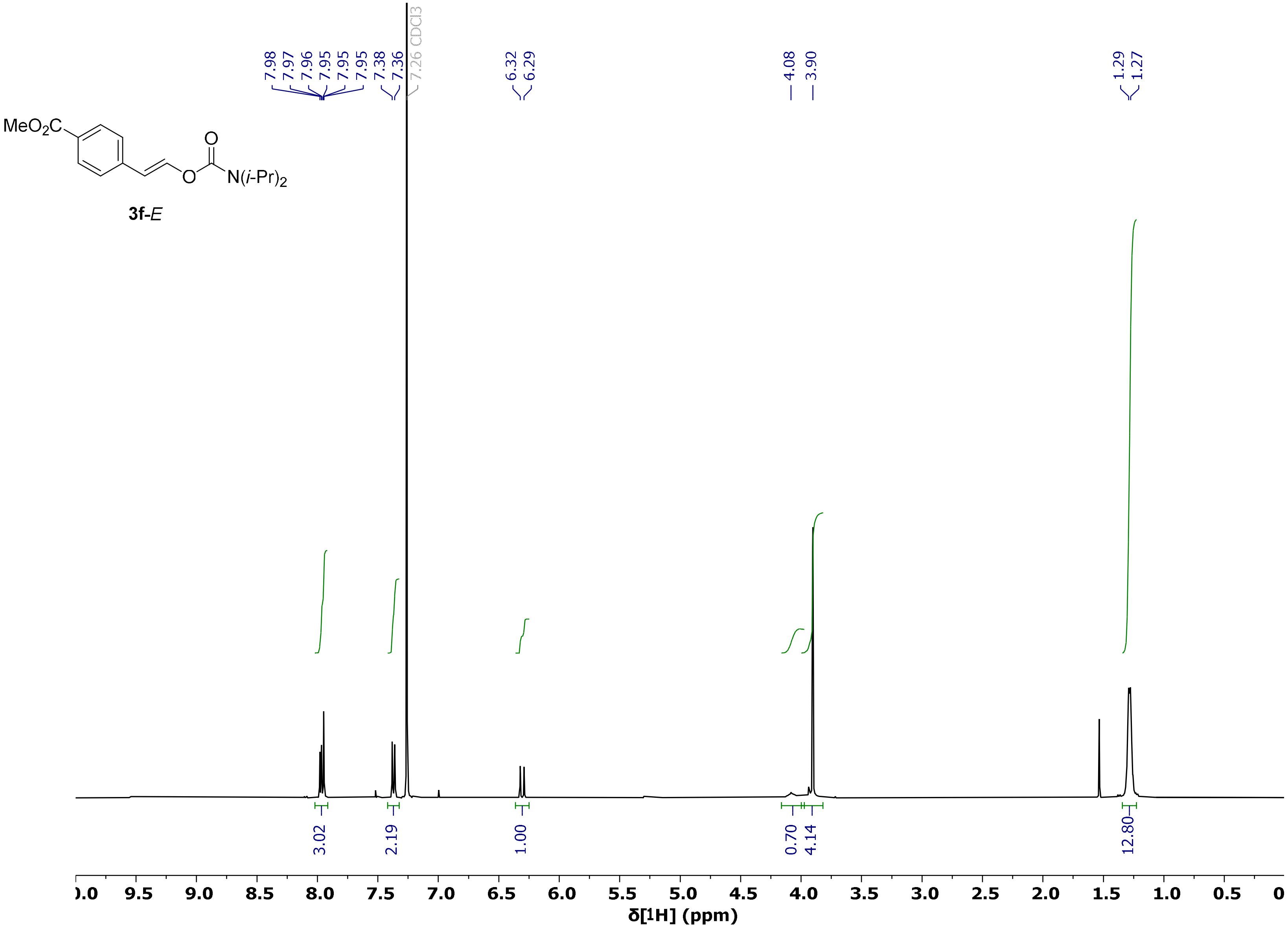
^{13}**C NMR** (151 MHz, $CDCl_3$)



3f-*Z*

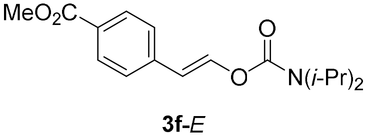


^{1}H NMR (600 MHz, $CDCl_3$)

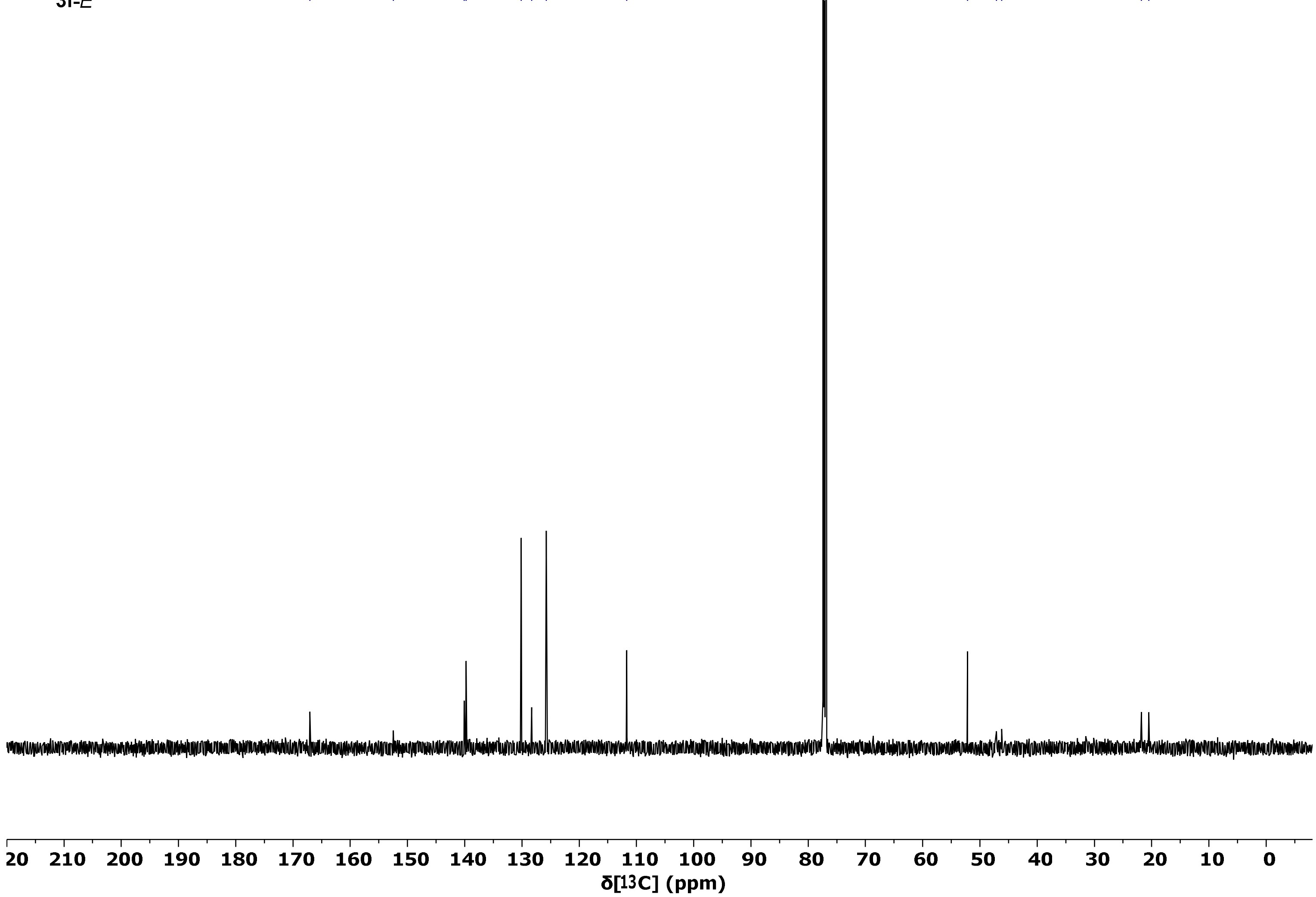


3f-*E*

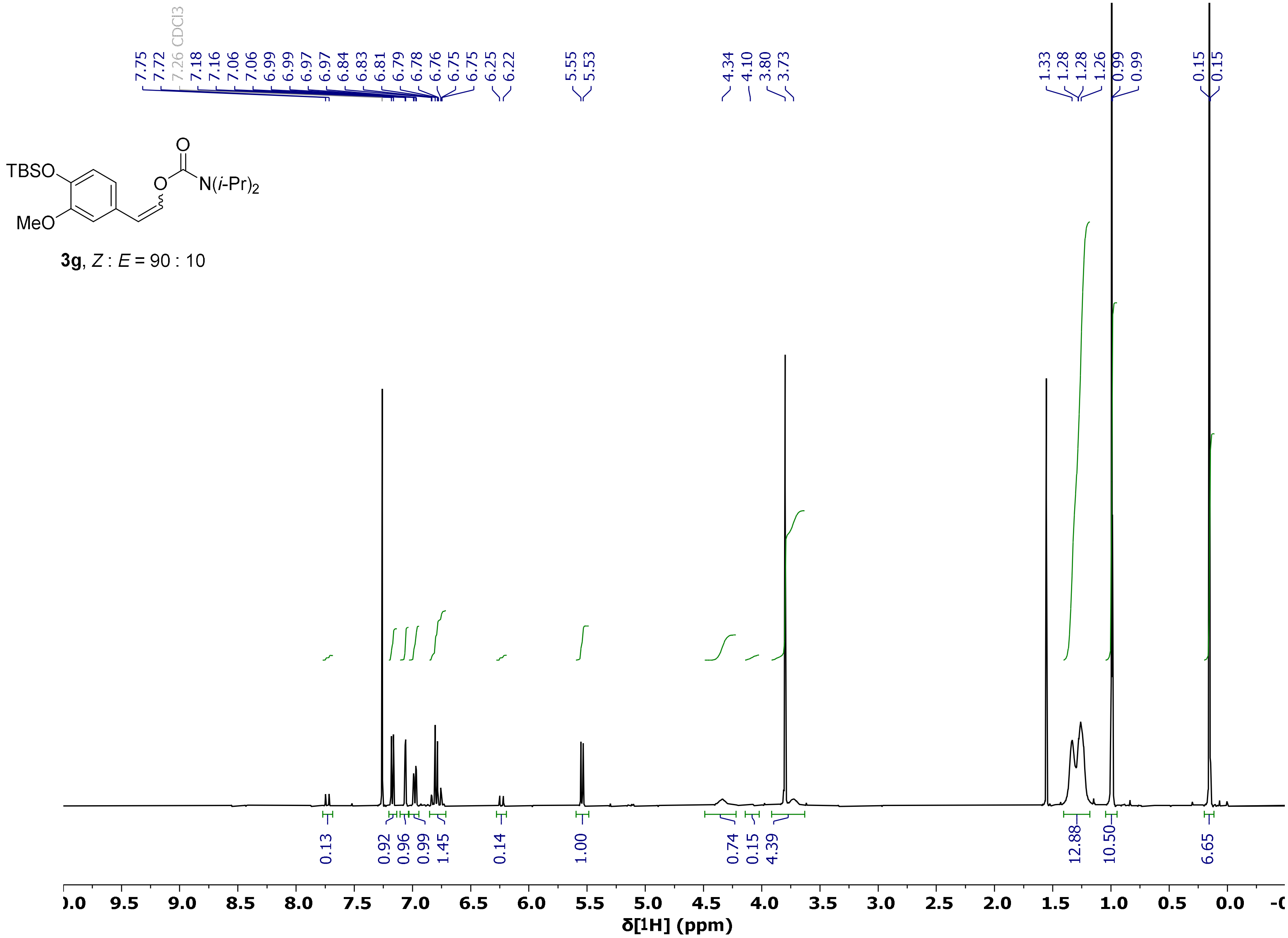
^{13}**C NMR** (151 MHz, $CDCl_3$)



3f-*E*

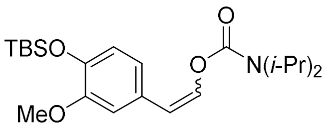


^{1}**H NMR** (400 MHz, CDCl$_3$)

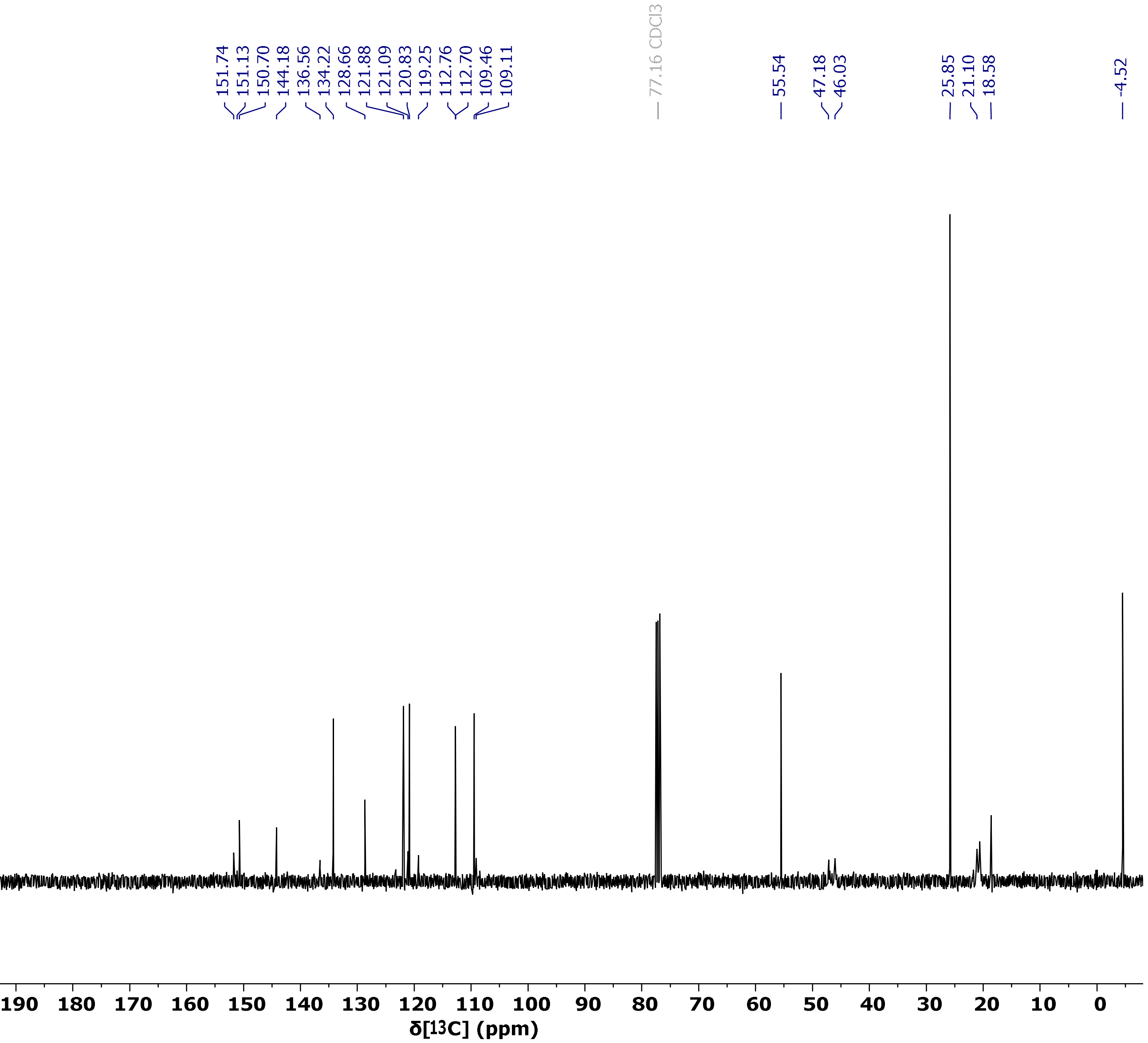


3g, *Z* : *E* = 90 : 10

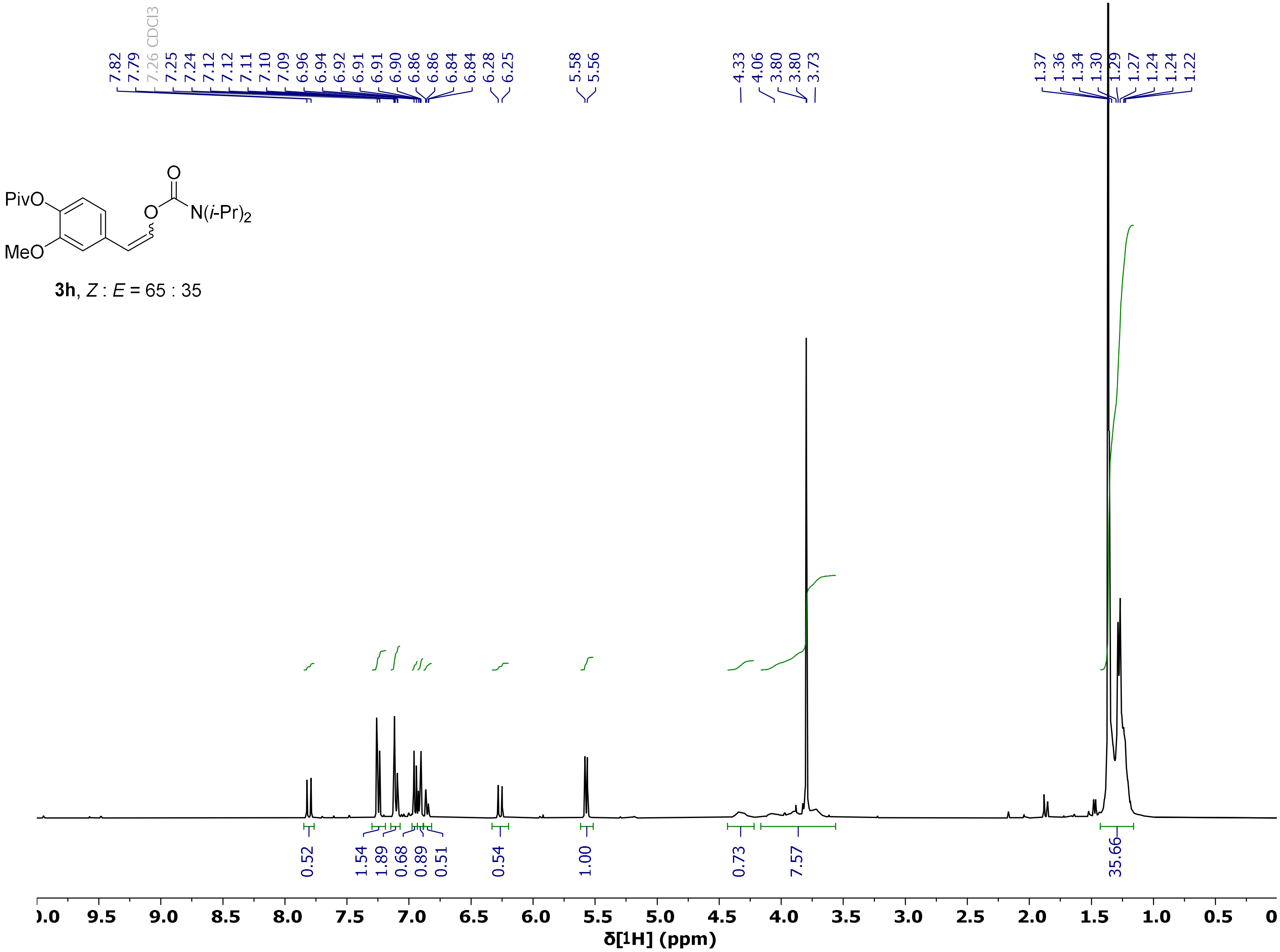
^{13}C NMR (101 MHz, CDCl$_3$)



3g, *Z* : *E* = 90 : 10

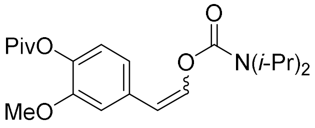


^{1}H NMR (400 MHz, $CDCl_3$)

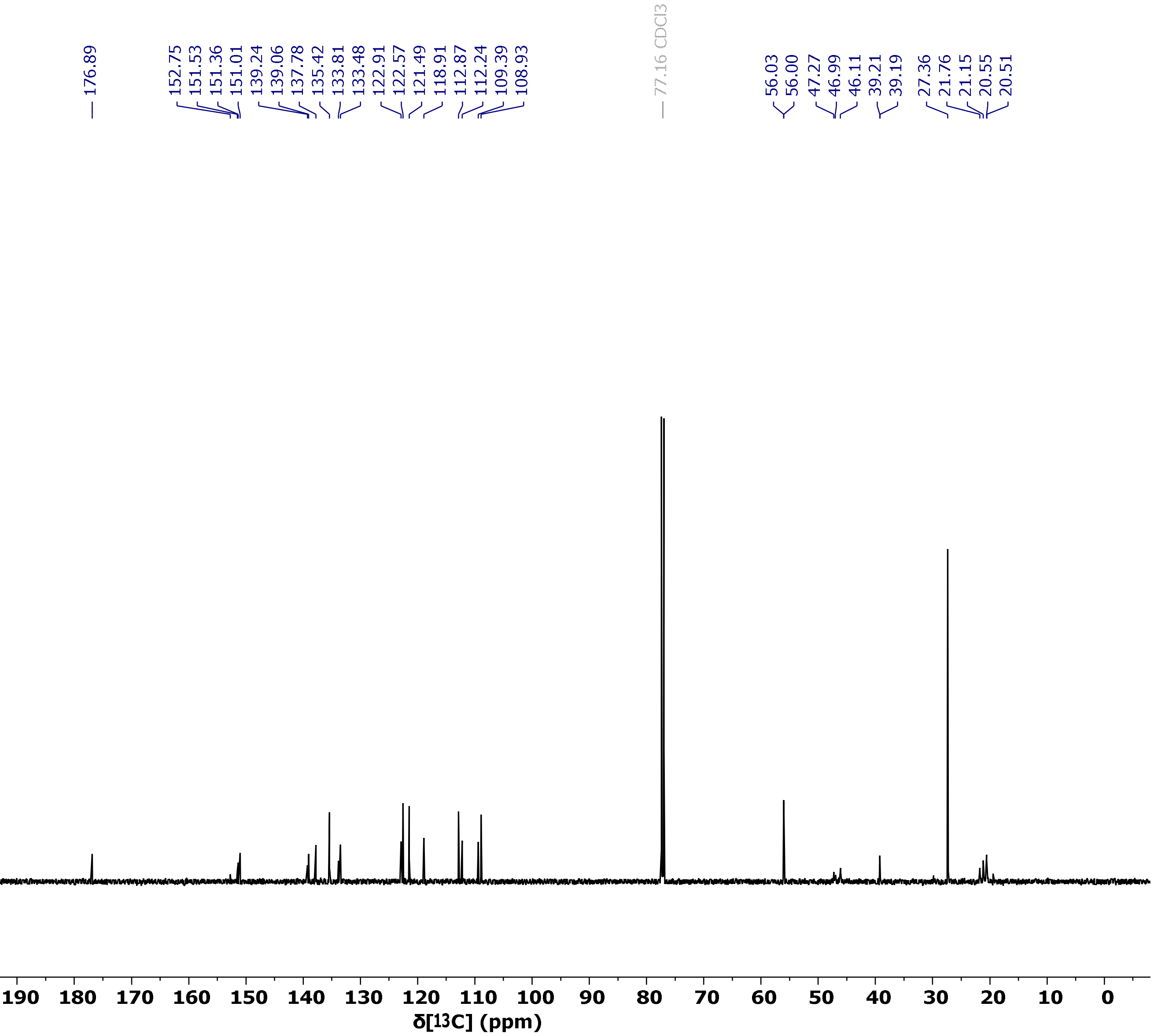


3h, *Z* : *E* = 65 : 35

^{13}C NMR (151 MHz, $CDCl_3$)

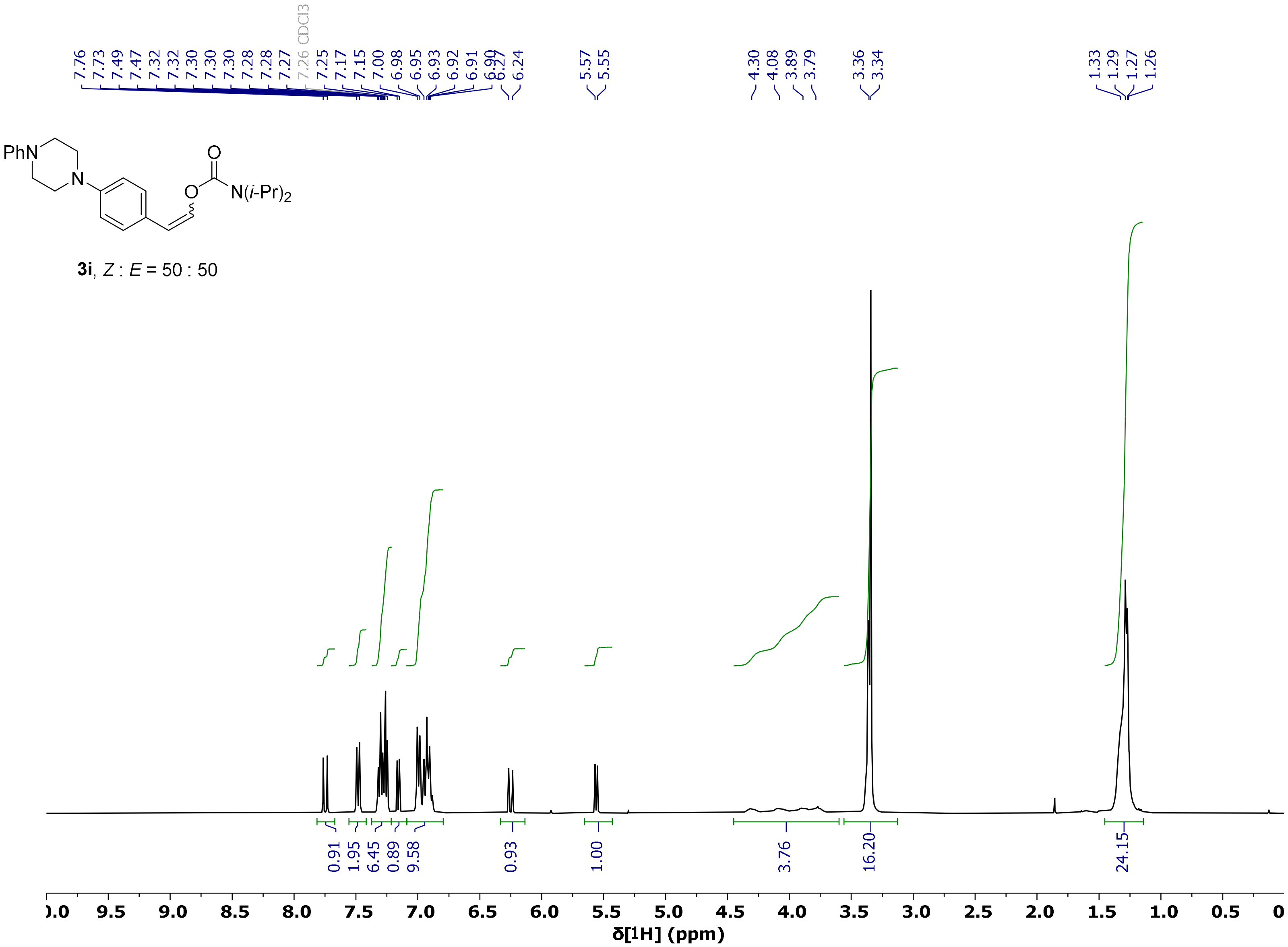


3h, *Z* : *E* = 65 : 35

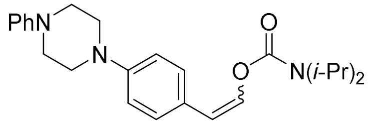


^{1}H NMR (400 MHz, CDCl$_3$)

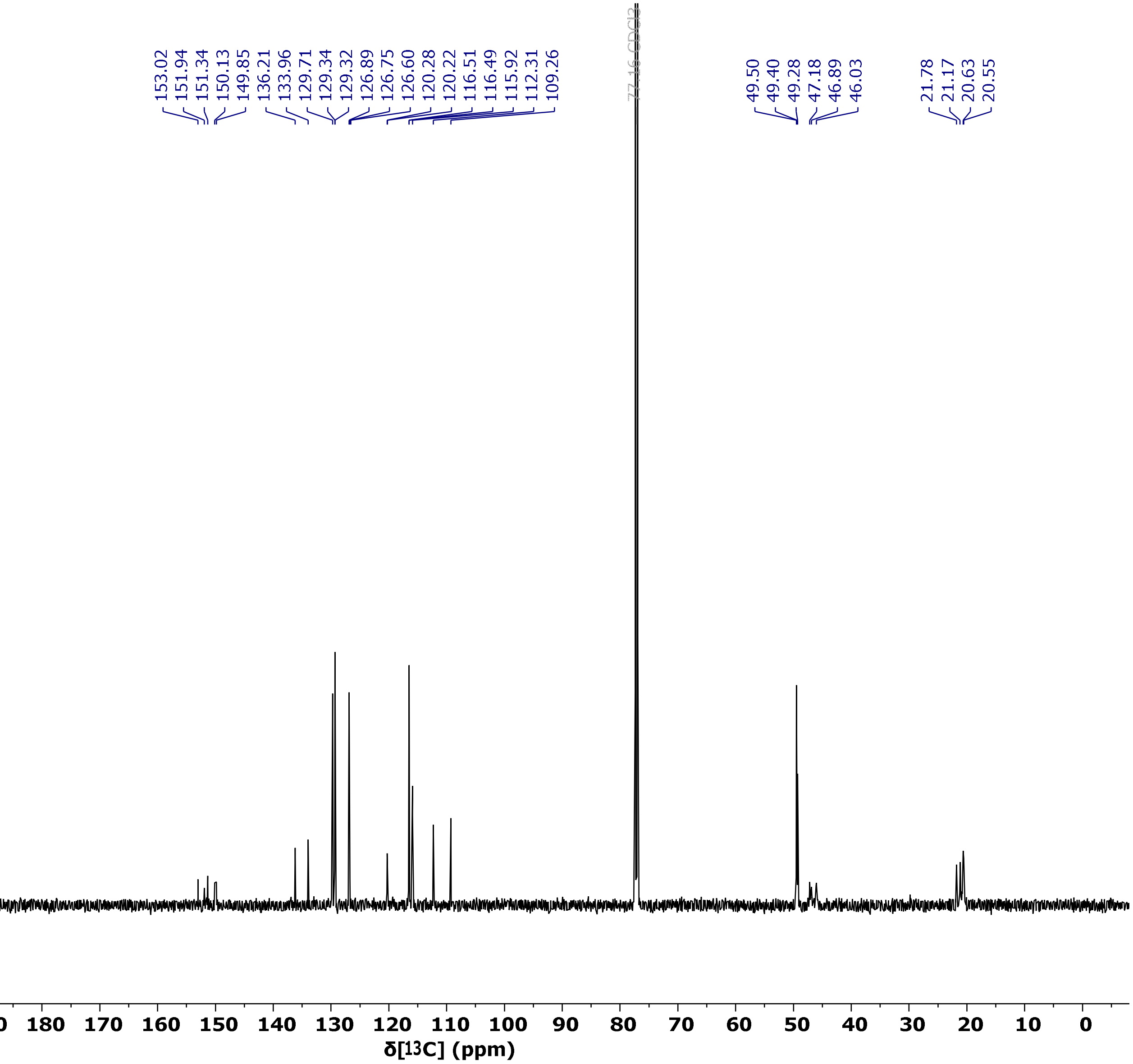
3i, *Z* : *E* = 50 : 50



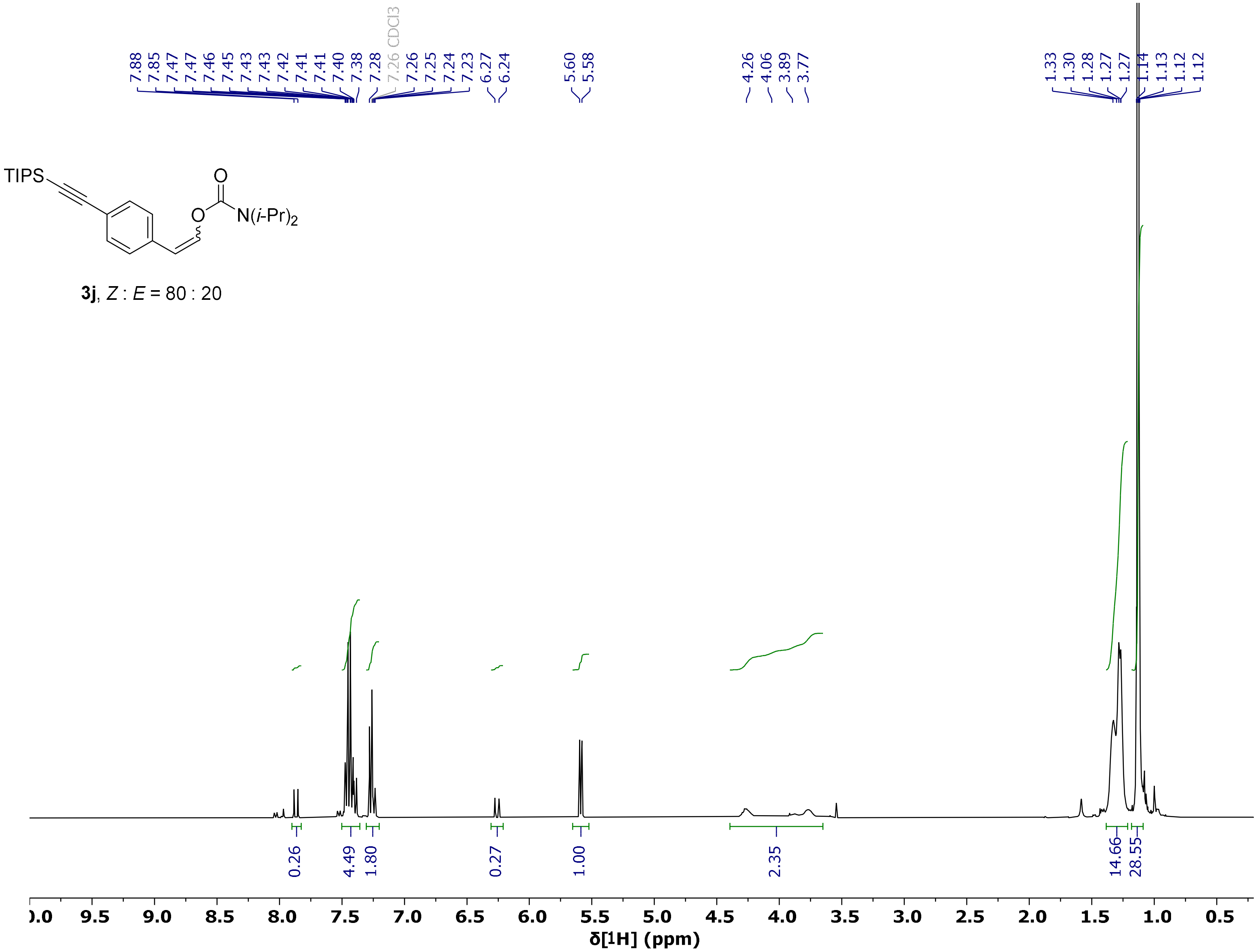
^{13}C NMR (151 MHz, $CDCl_3$)



3i, *Z* : *E* = 50 : 50

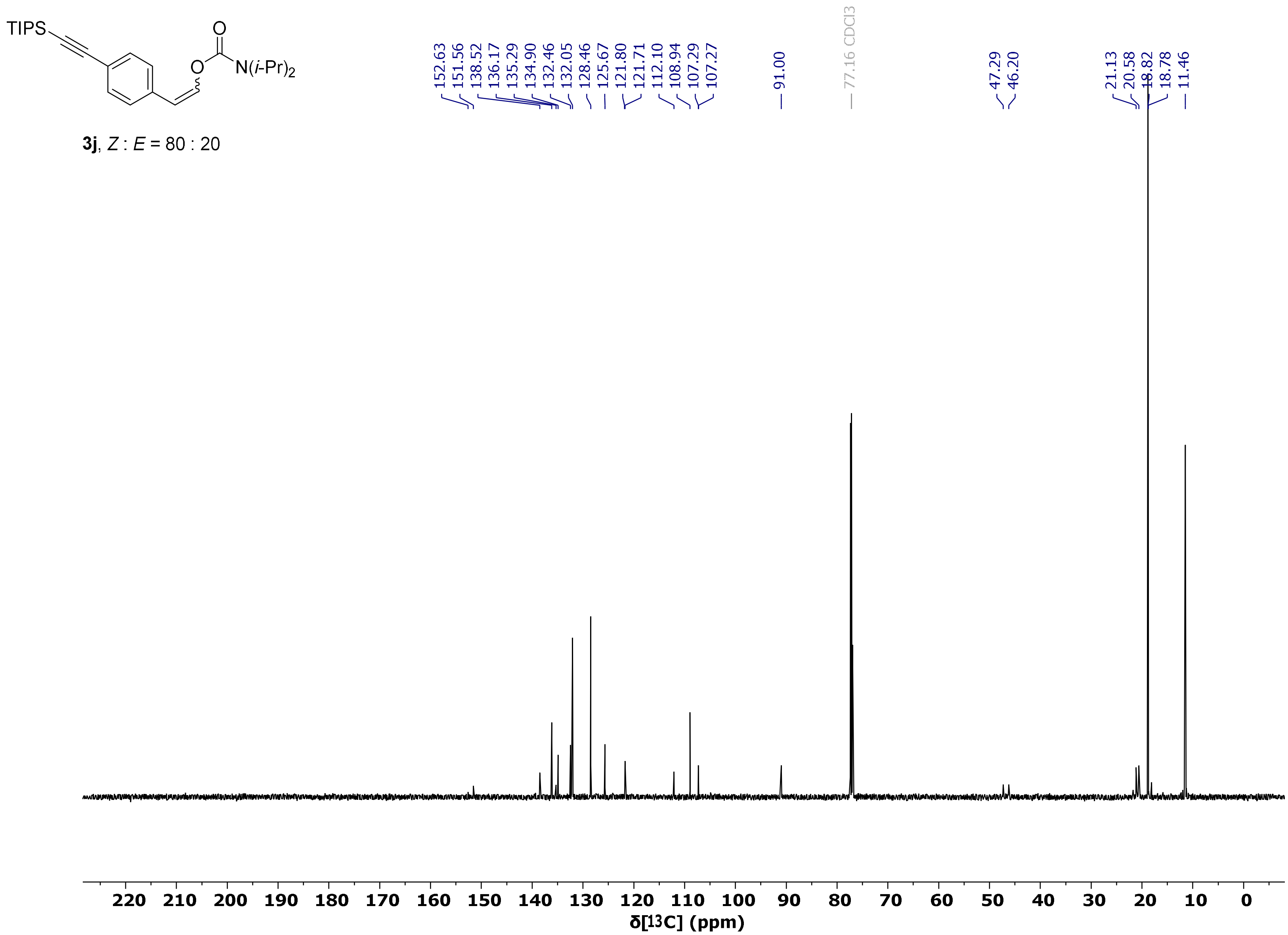


^{1}H NMR (400 MHz, $CDCl_3$)

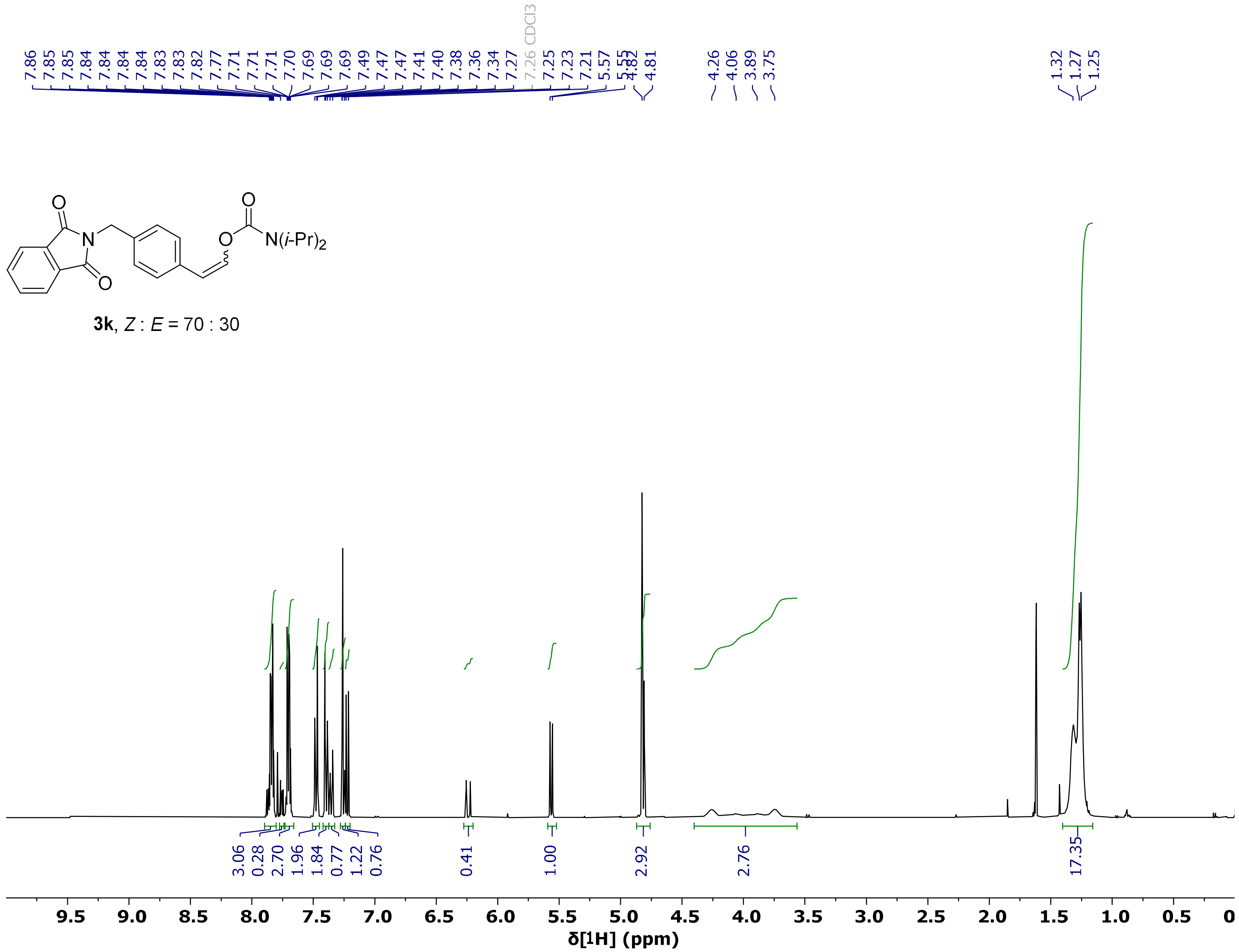


3j, *Z* : *E* = 80 : 20

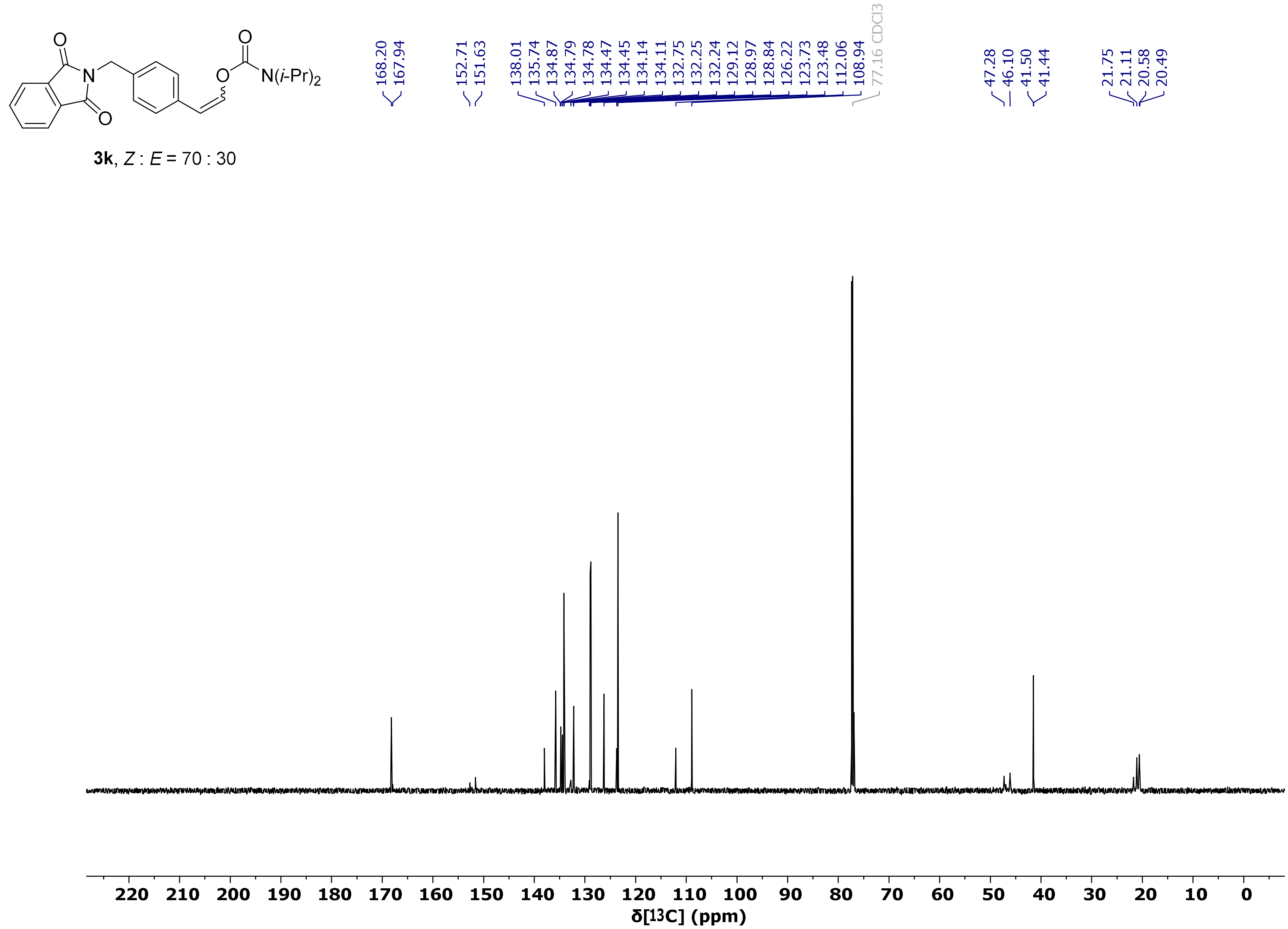
^{13}C NMR (151 MHz, $CDCl_3$)


3j, *Z* : *E* = 80 : 20

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

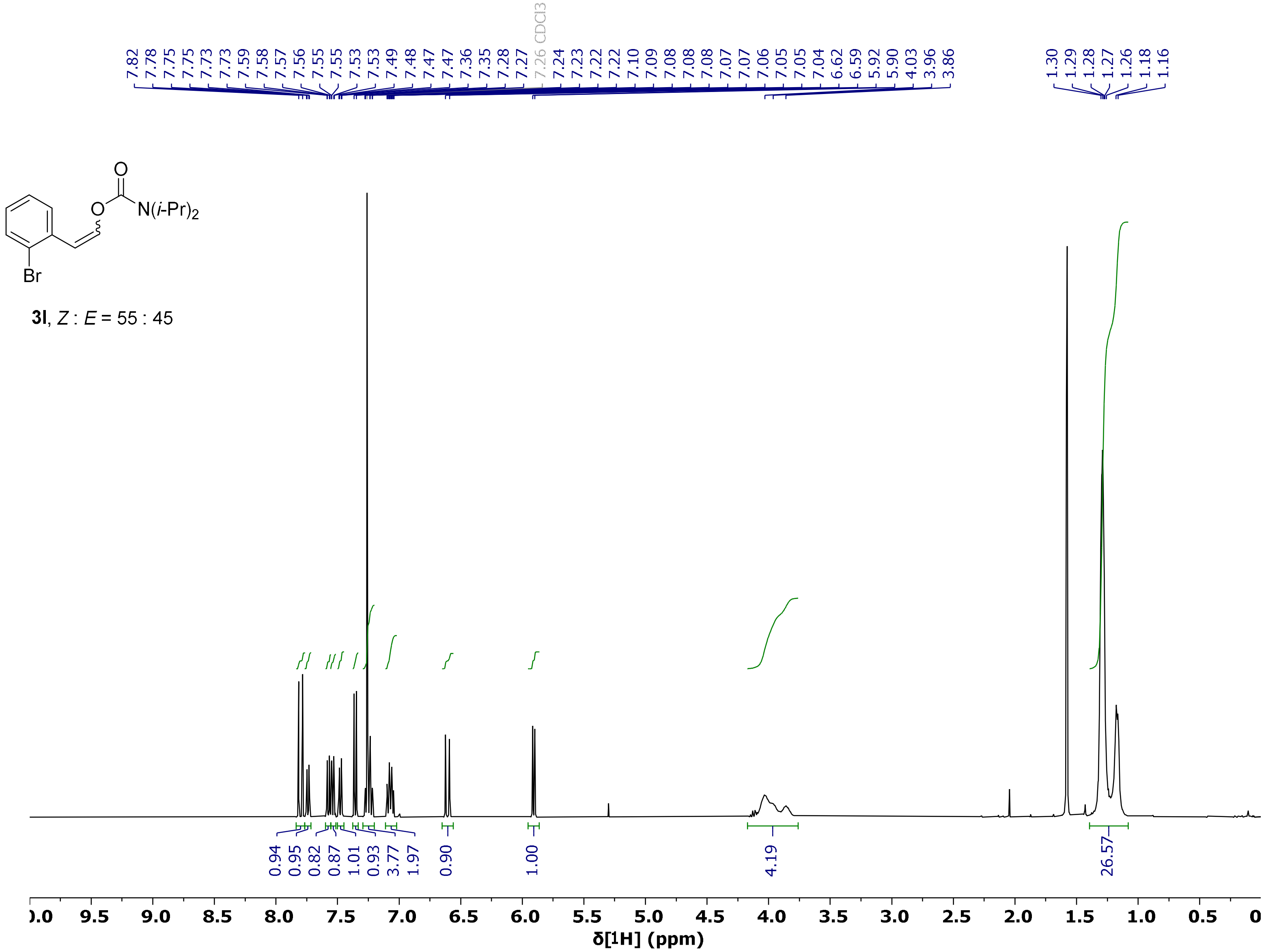


^{13}C NMR (151 MHz, $CDCl_3$)



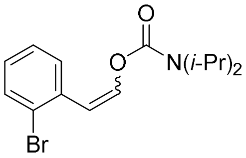
3k, *Z* : *E* = 70 : 30

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

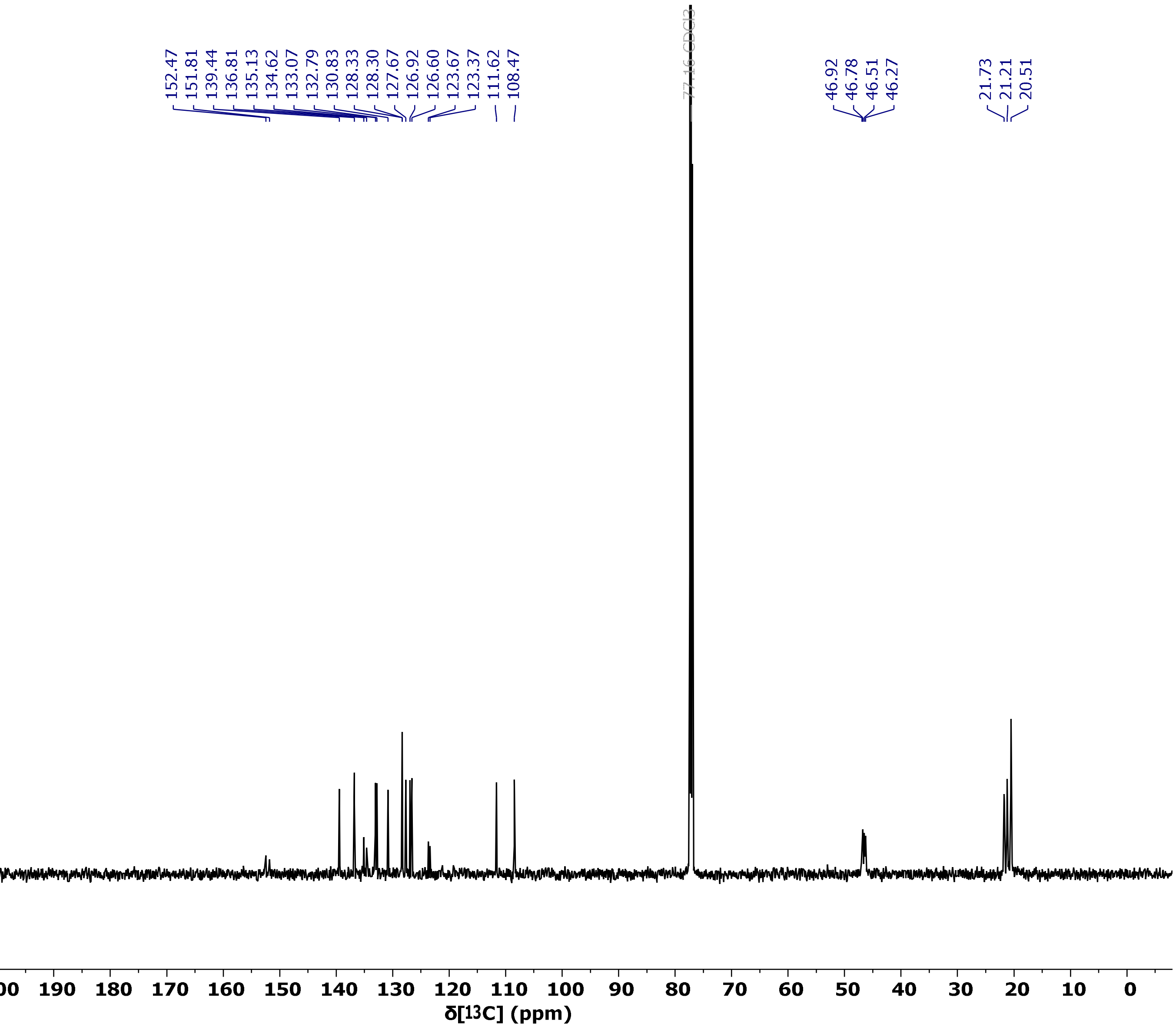


3l, *Z* : *E* = 55 : 45

^{13}C NMR (151 MHz, CDCl$_3$)

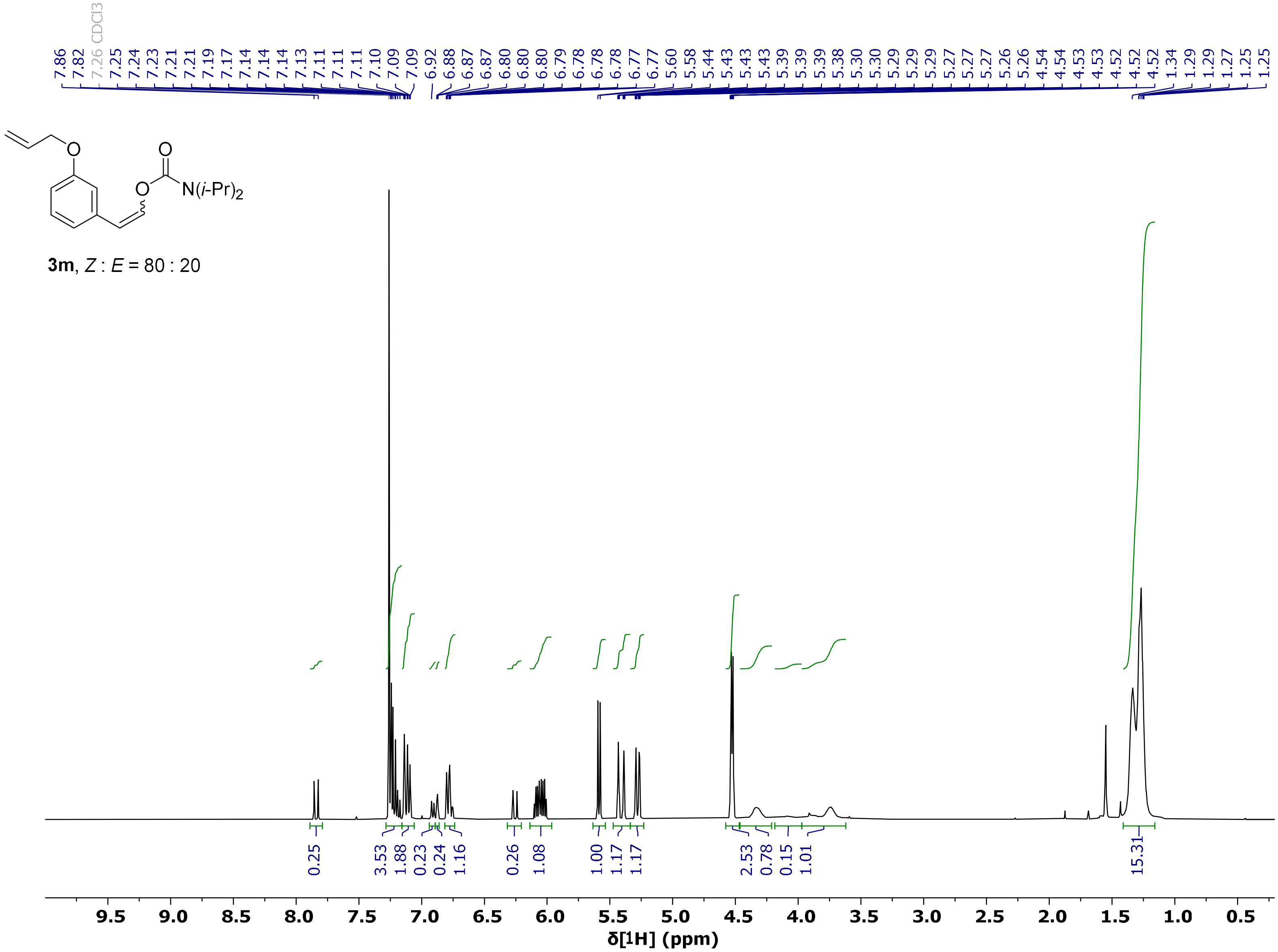


3l, *Z* : *E* = 55 : 45

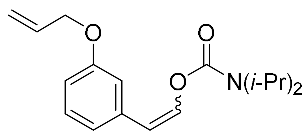


¹H NMR (400 MHz, $CDCl_3$)

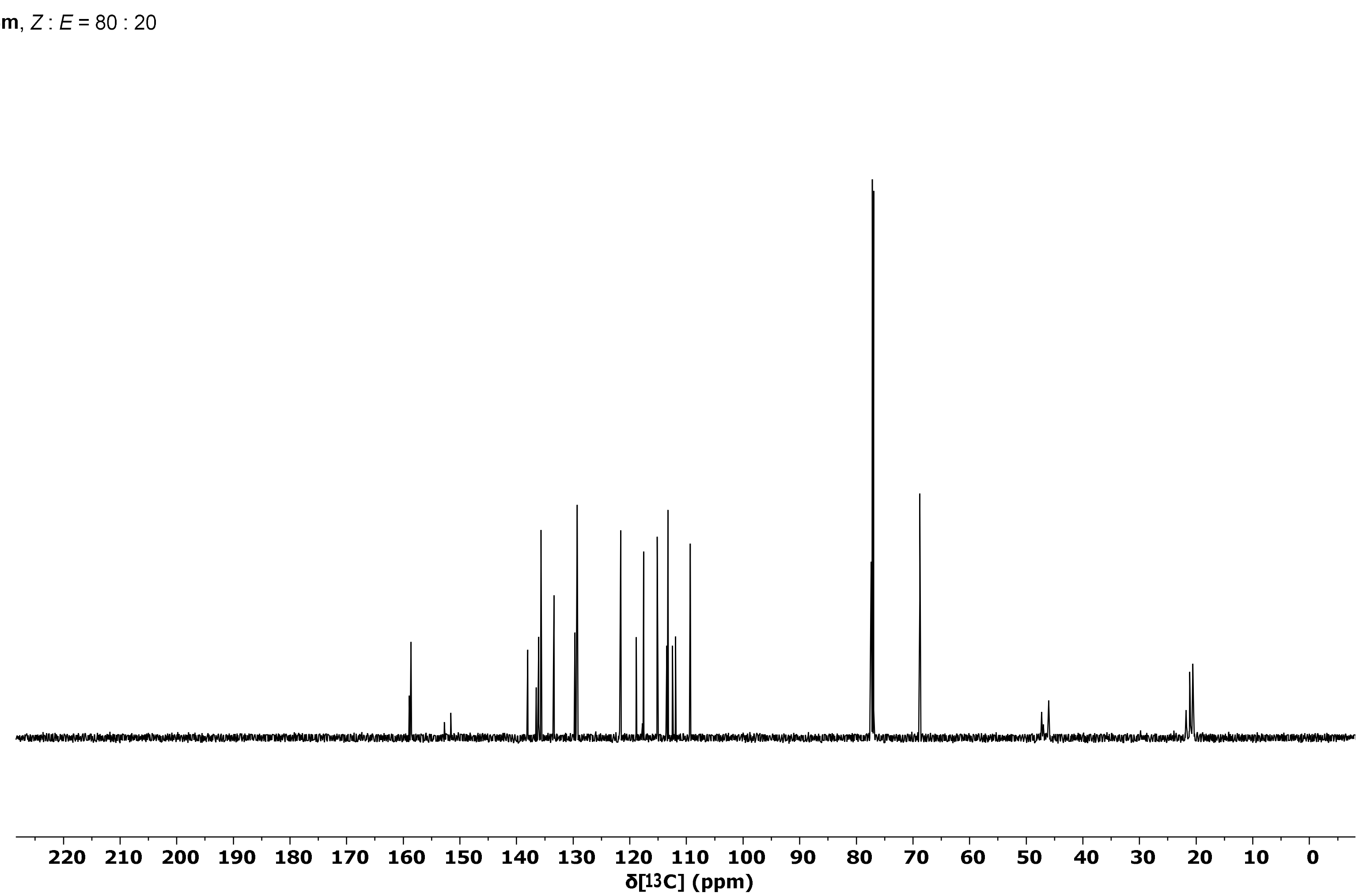
3m, *Z* : *E* = 80 : 20



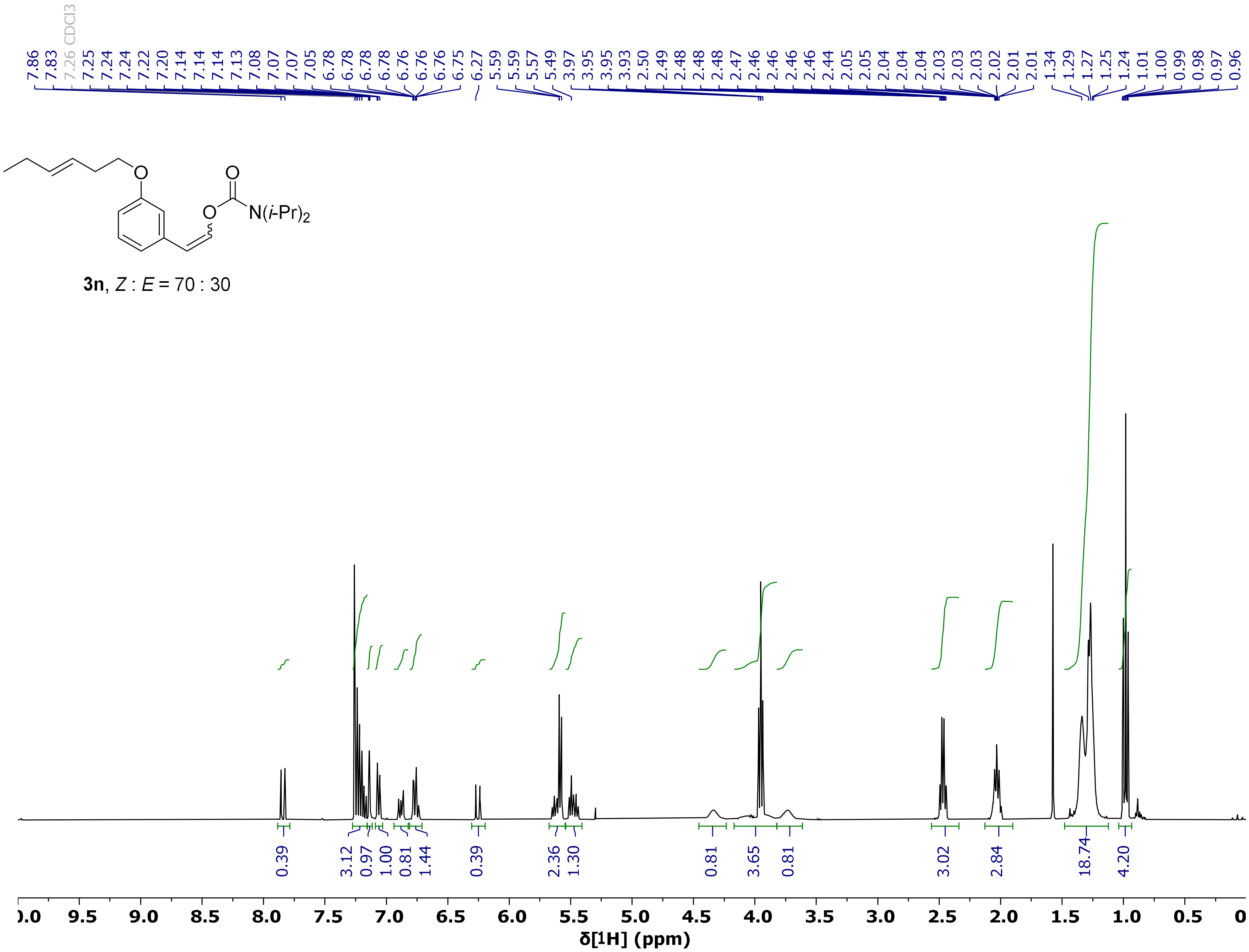
^{13}C NMR (151 MHz, $CDCl_3$)



3m, *Z* : *E* = 80 : 20

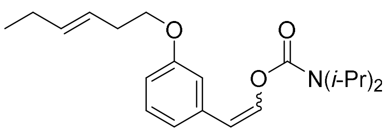


^{1}H NMR (400 MHz, $CDCl_3$)

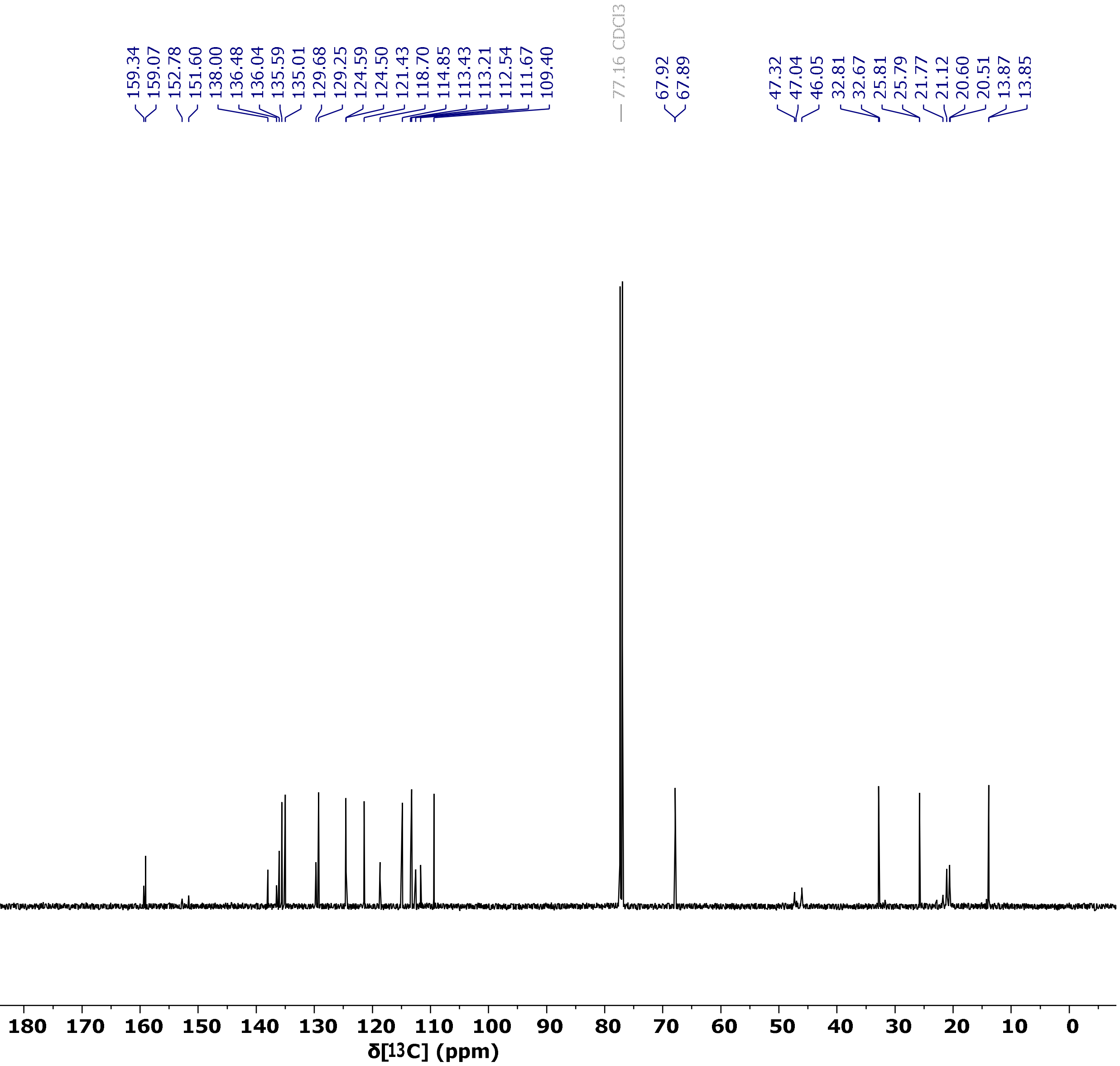


3n, *Z* : *E* = 70 : 30

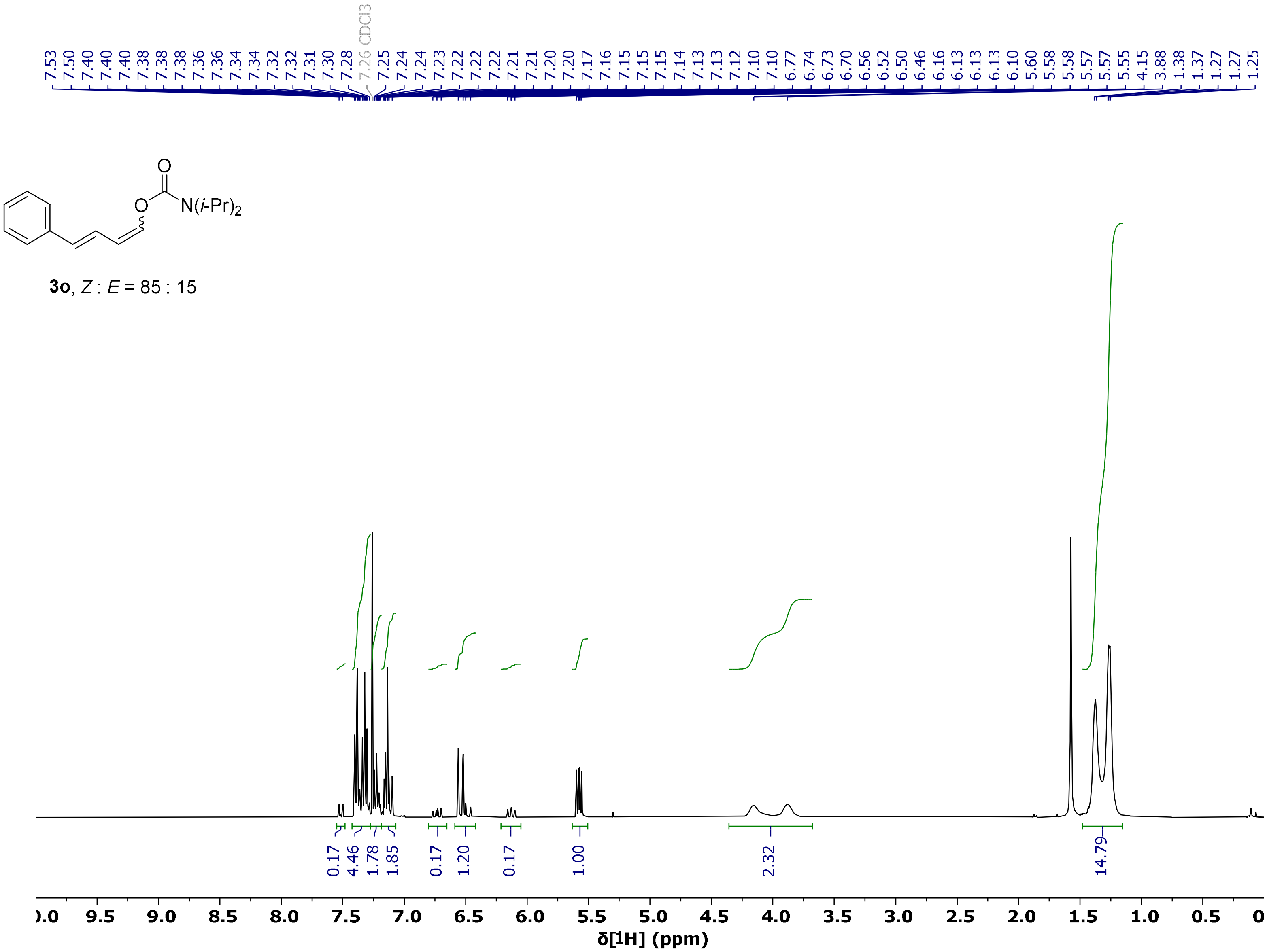
^{13}**C NMR** (151 MHz, $CDCl_3$)



3n, *Z* : *E* = 70 : 30

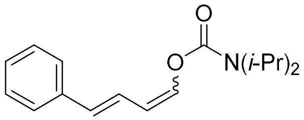


^{1}H NMR (400 MHz, $CDCl_3$)

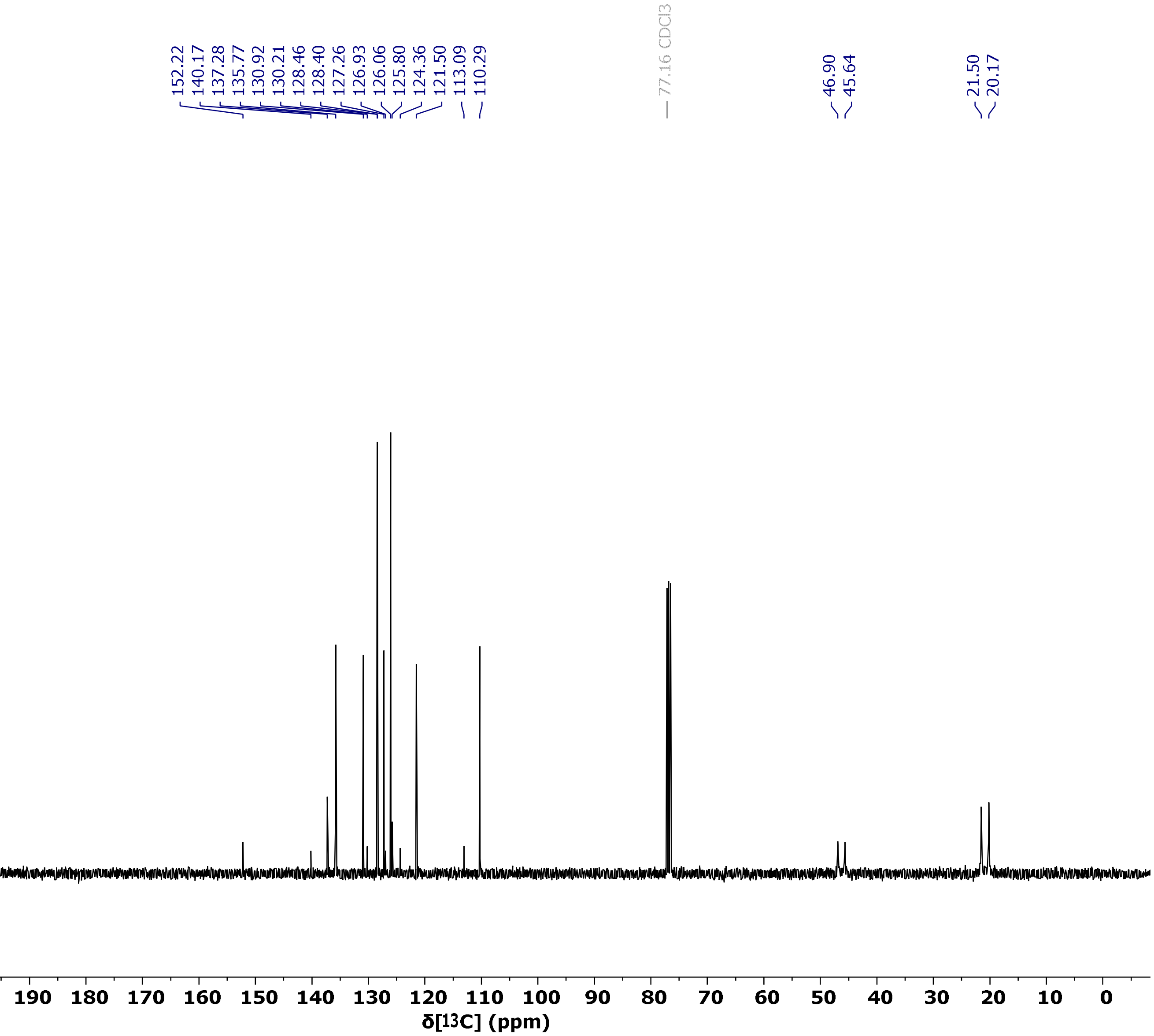


3o, *Z* : *E* = 85 : 15

^{13}C NMR (101 MHz, CDCl$_3$)

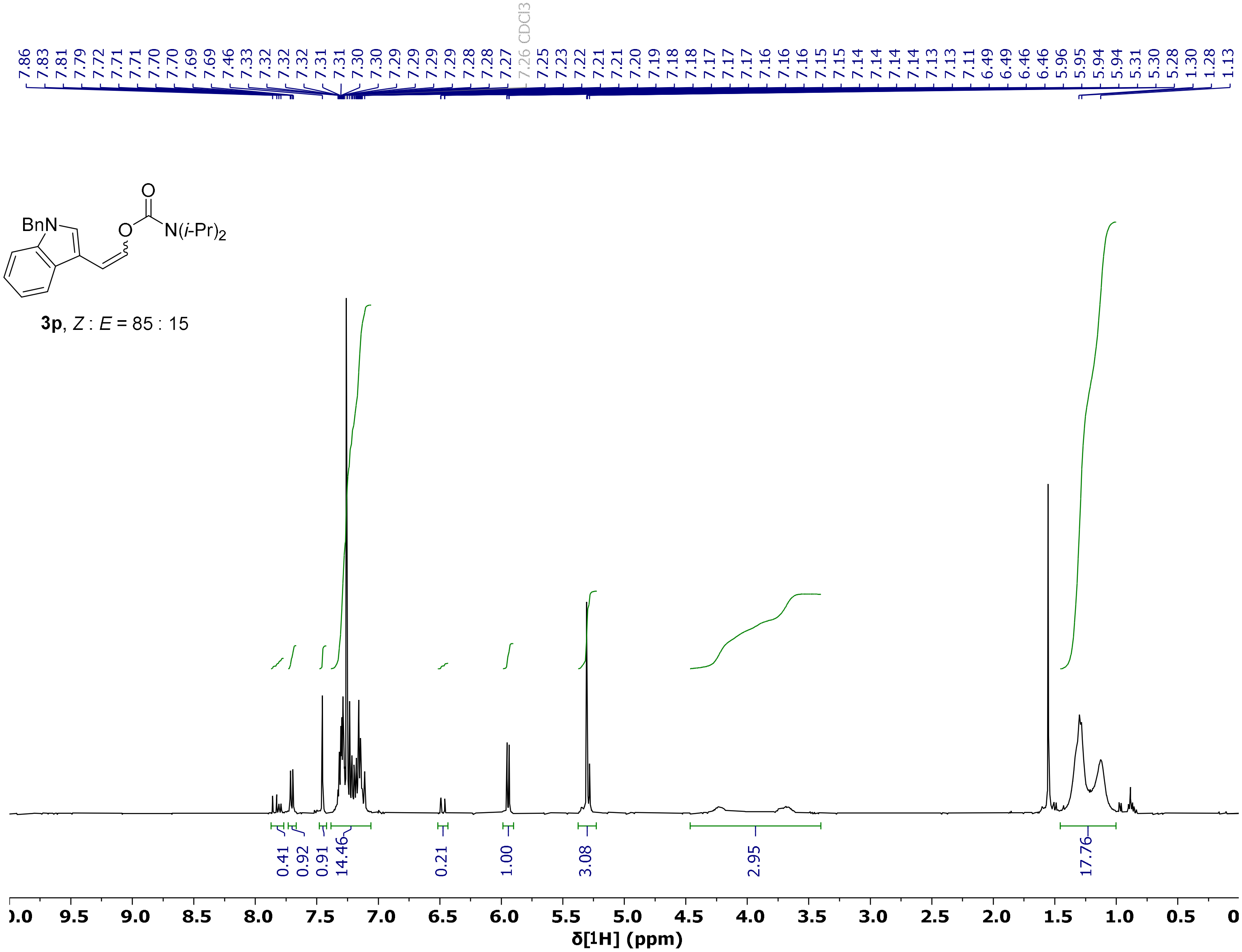


3o, *Z* : *E* = 85 : 15

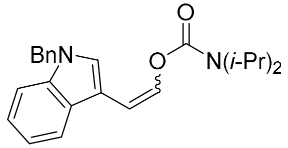


^{1}H NMR (400 MHz, $CDCl_3$)

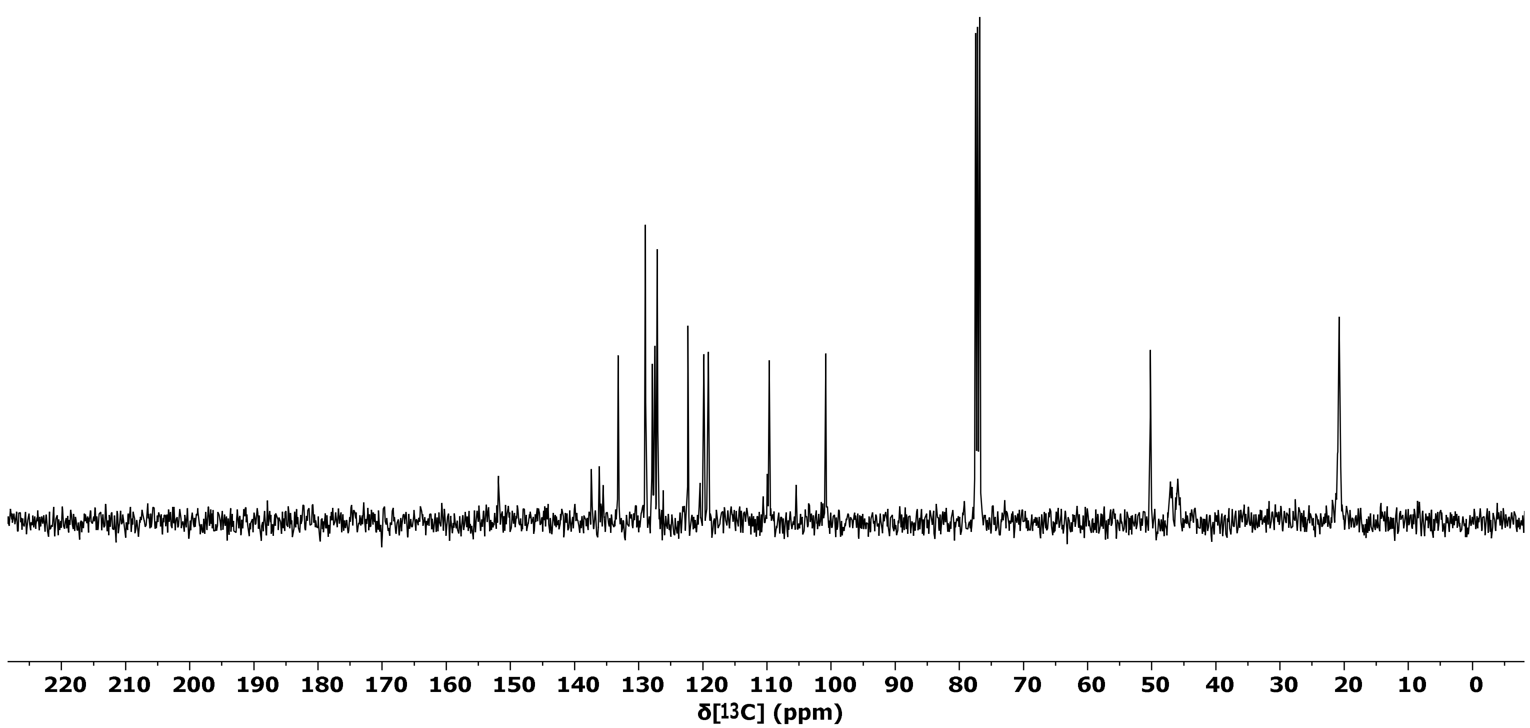
3p, *Z* : *E* = 85 : 15



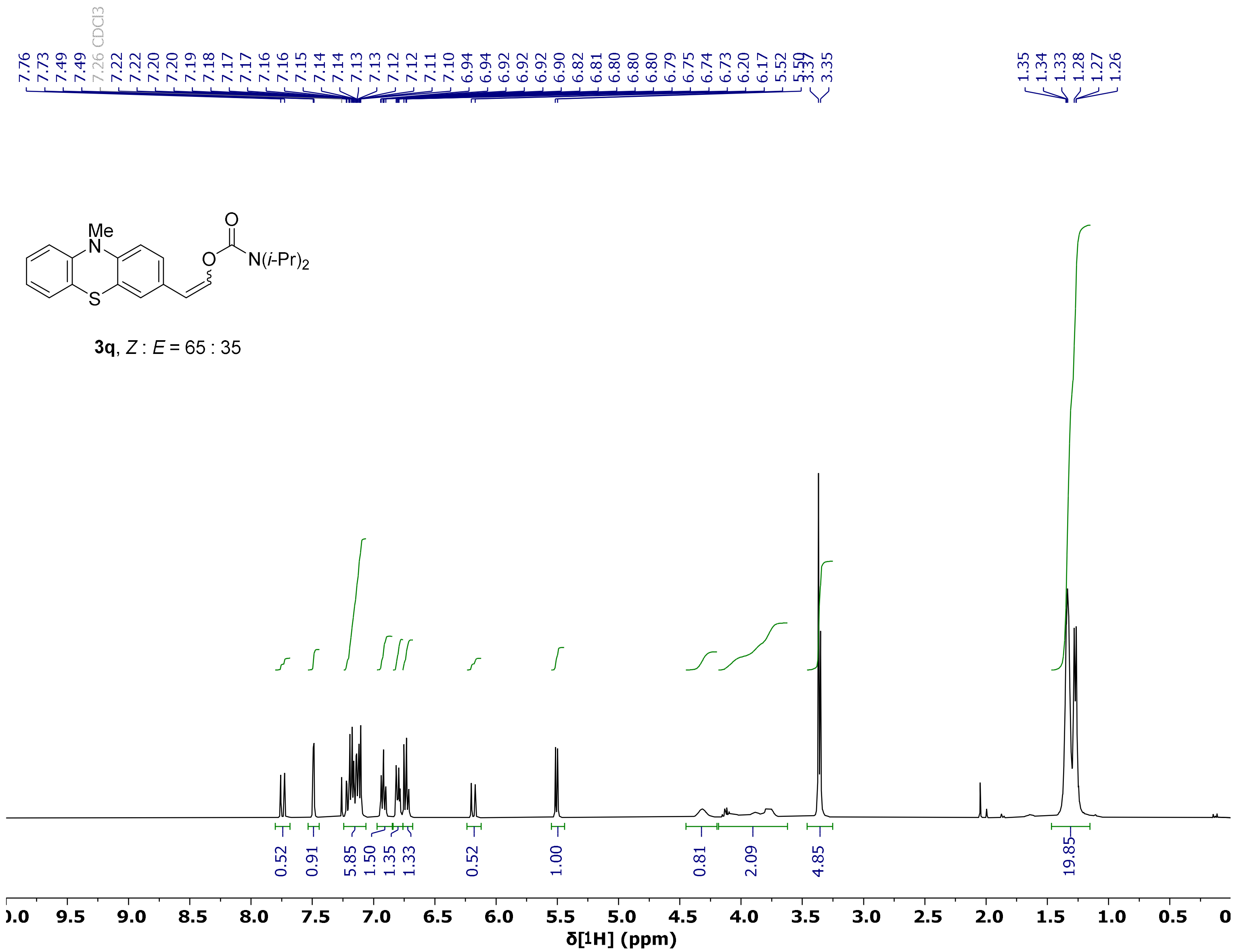
^{13}C NMR (101 MHz, CDCl$_3$)



3p, *Z* : *E* = 85 : 15

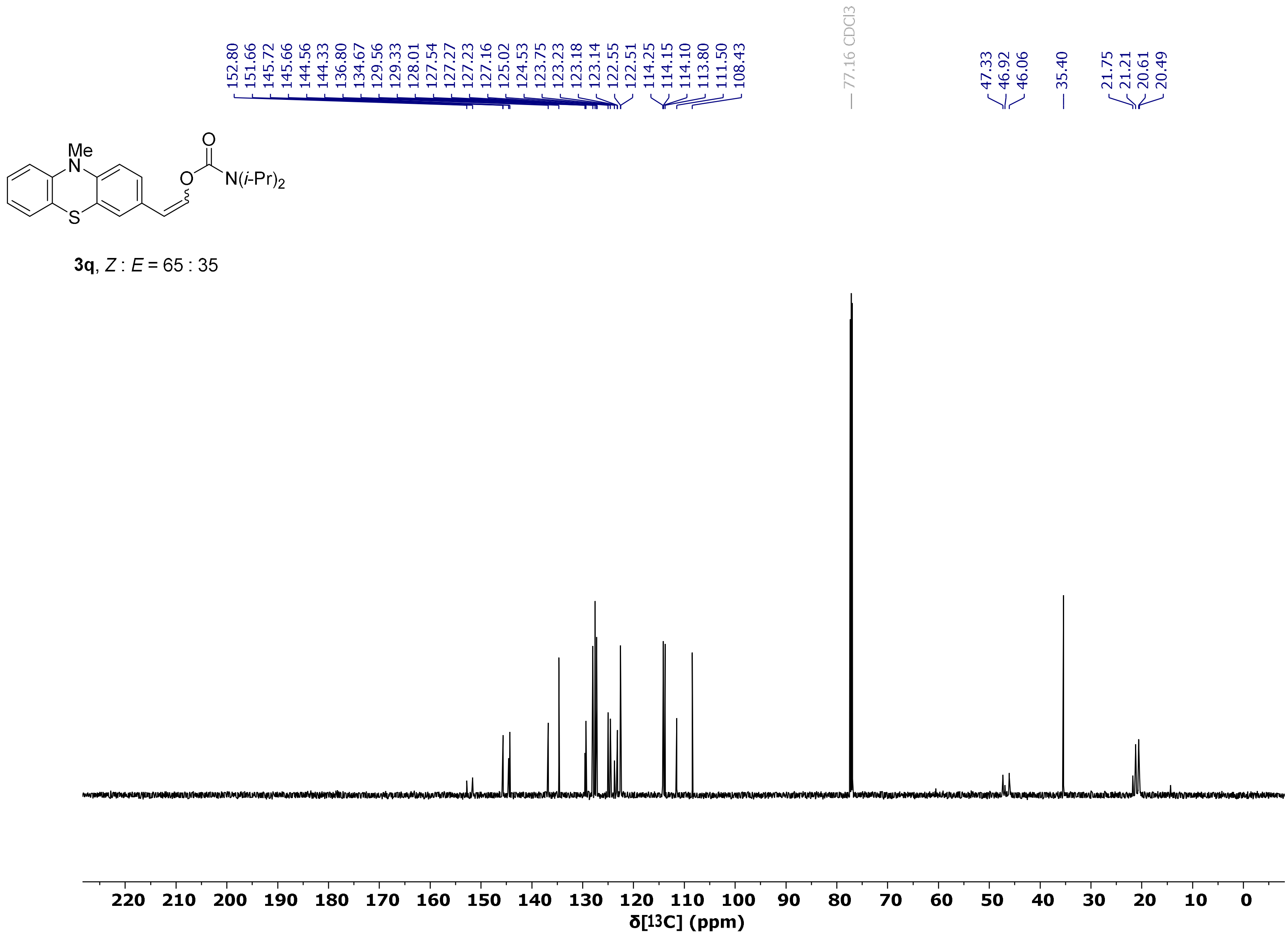


^{1}H NMR (400 MHz, $CDCl_3$)



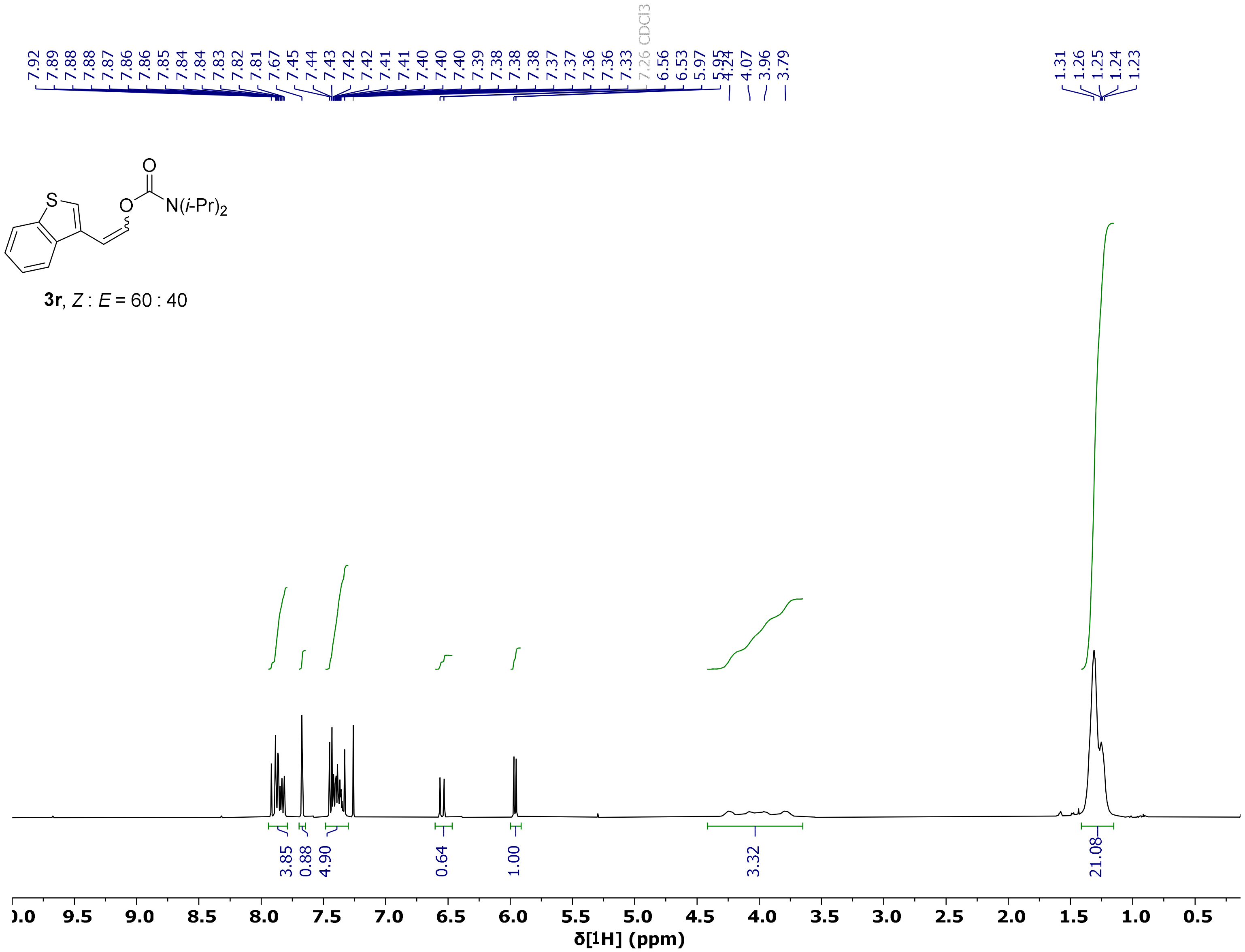
3q, *Z* : *E* = 65 : 35

^{13}C NMR (151 MHz, $CDCl_3$)



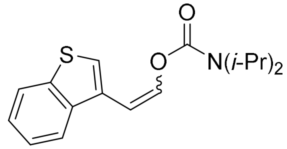
3q, *Z* : *E* = 65 : 35

^{1}H NMR (400 MHz, CDCl$_3$)

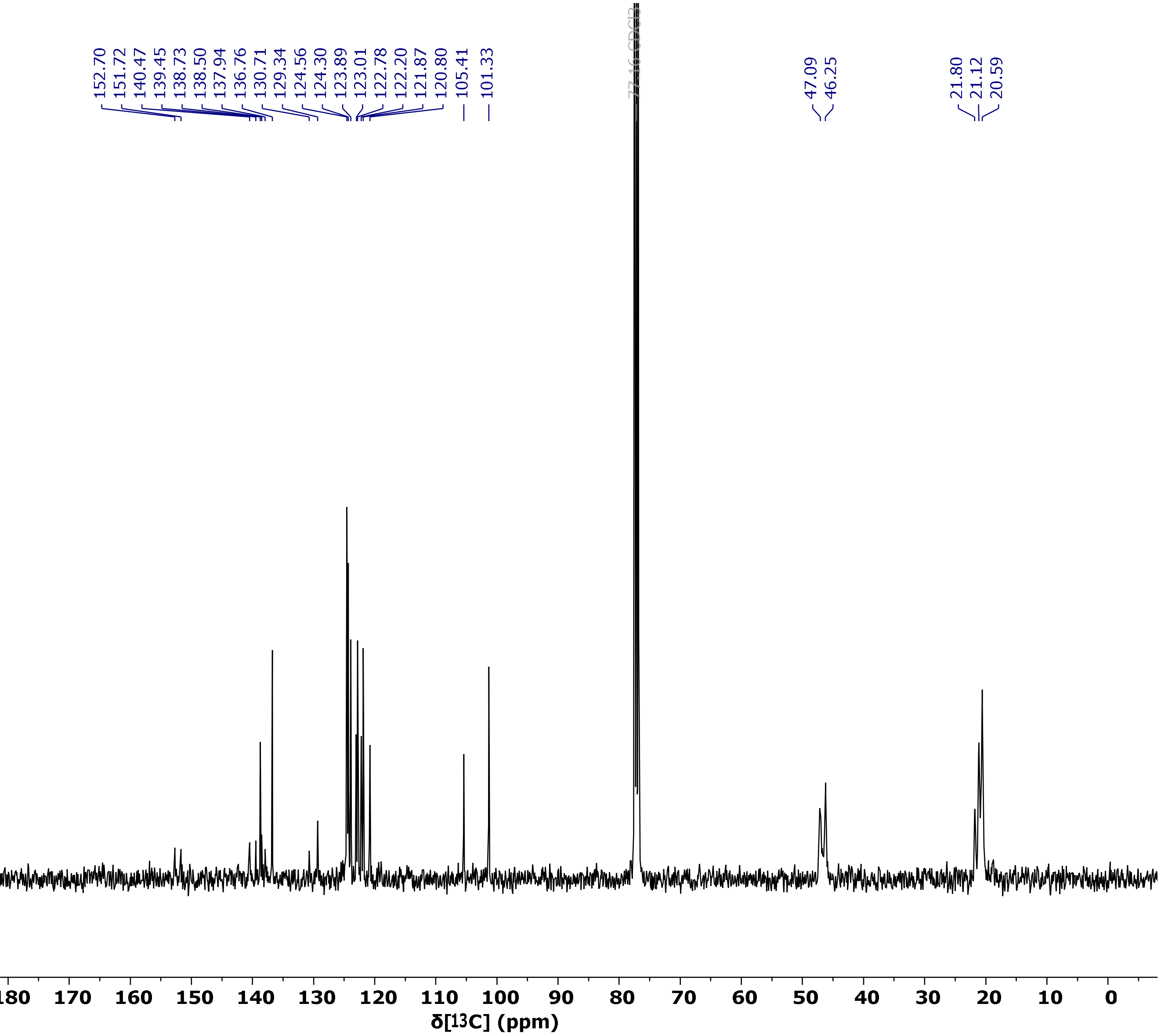


3r, *Z* : *E* = 60 : 40

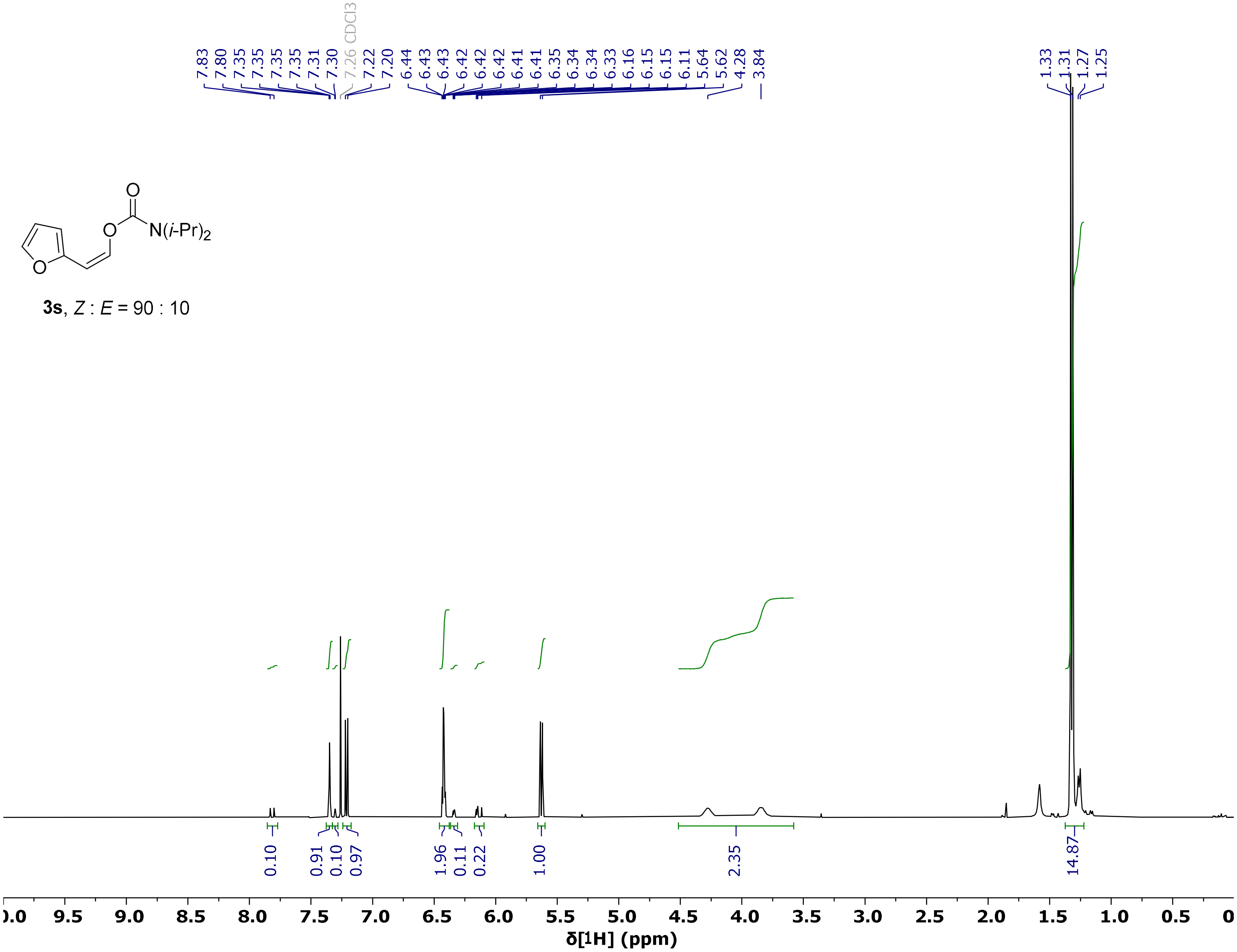
¹³C NMR (101 MHz, $CDCl_3$)



3r, *Z* : *E* = 60 : 40

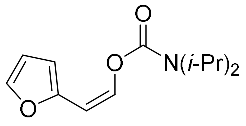


^{1}H NMR (400 MHz, $CDCl_3$)

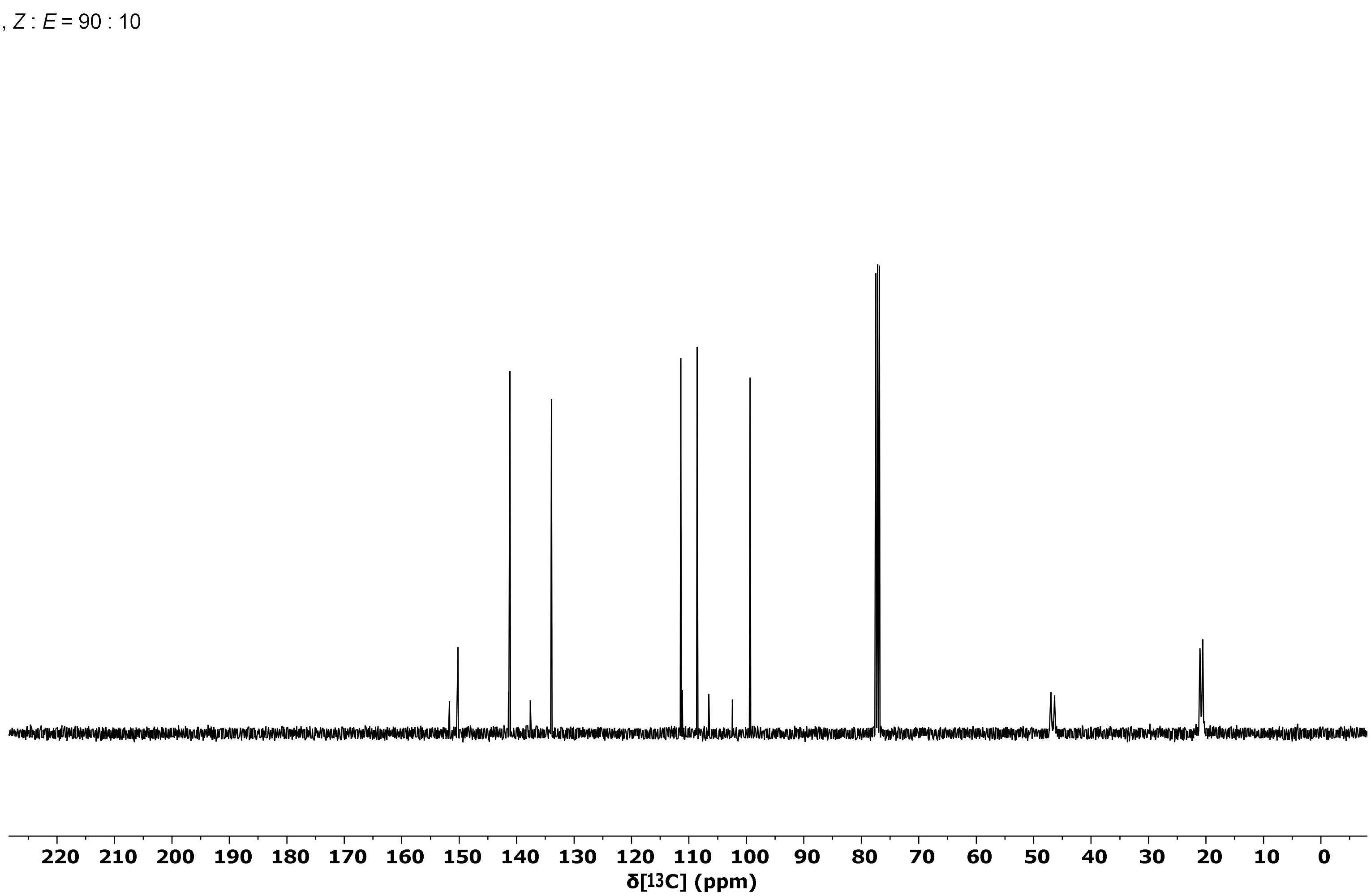


3s, *Z* : *E* = 90 : 10

^{13}C NMR (101 MHz, $CDCl_3$)

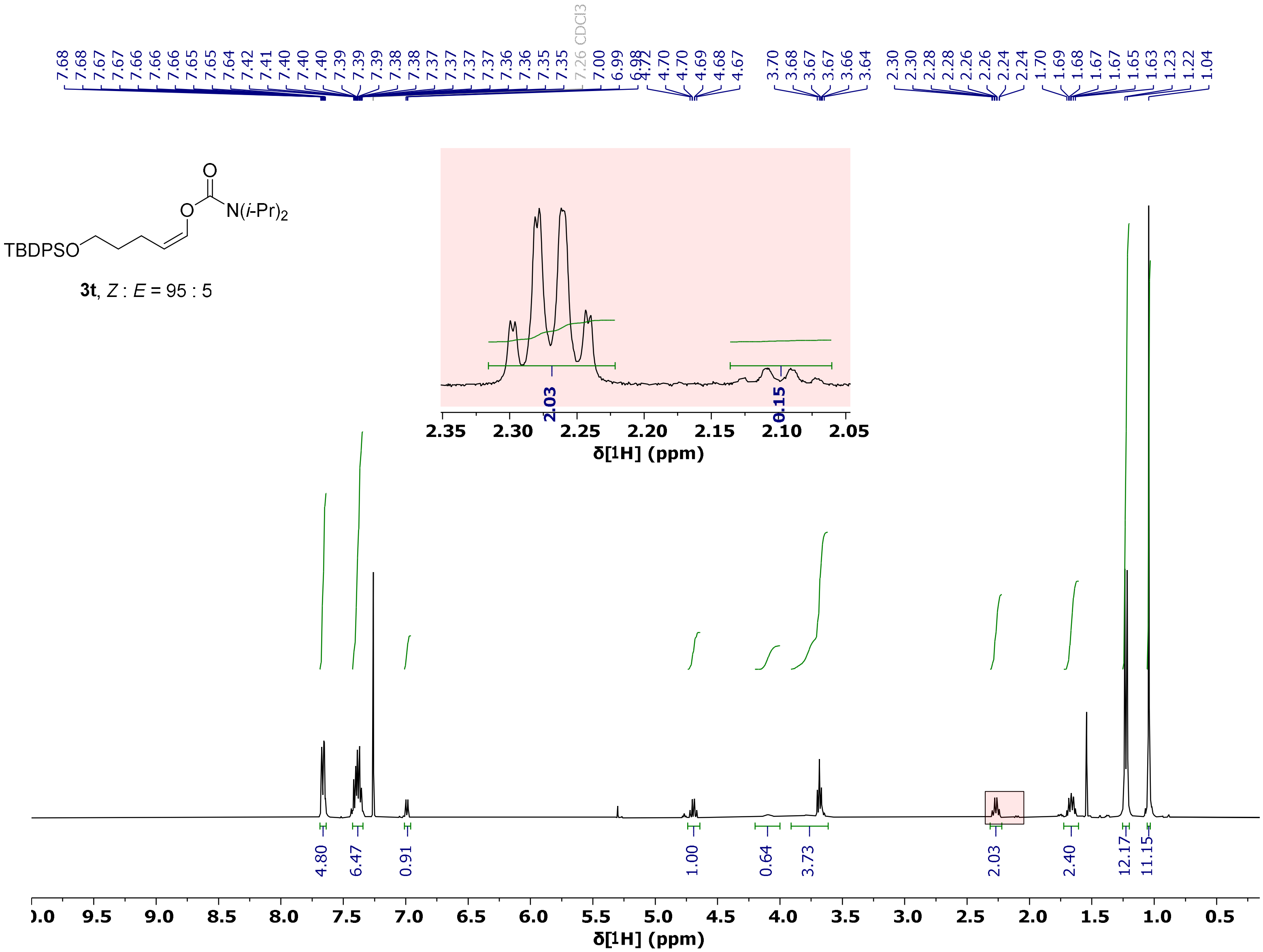


3s, *Z* : *E* = 90 : 10

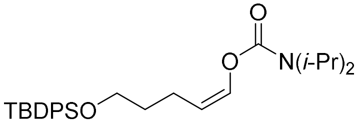


^{1}H NMR (400 MHz, $CDCl_3$)

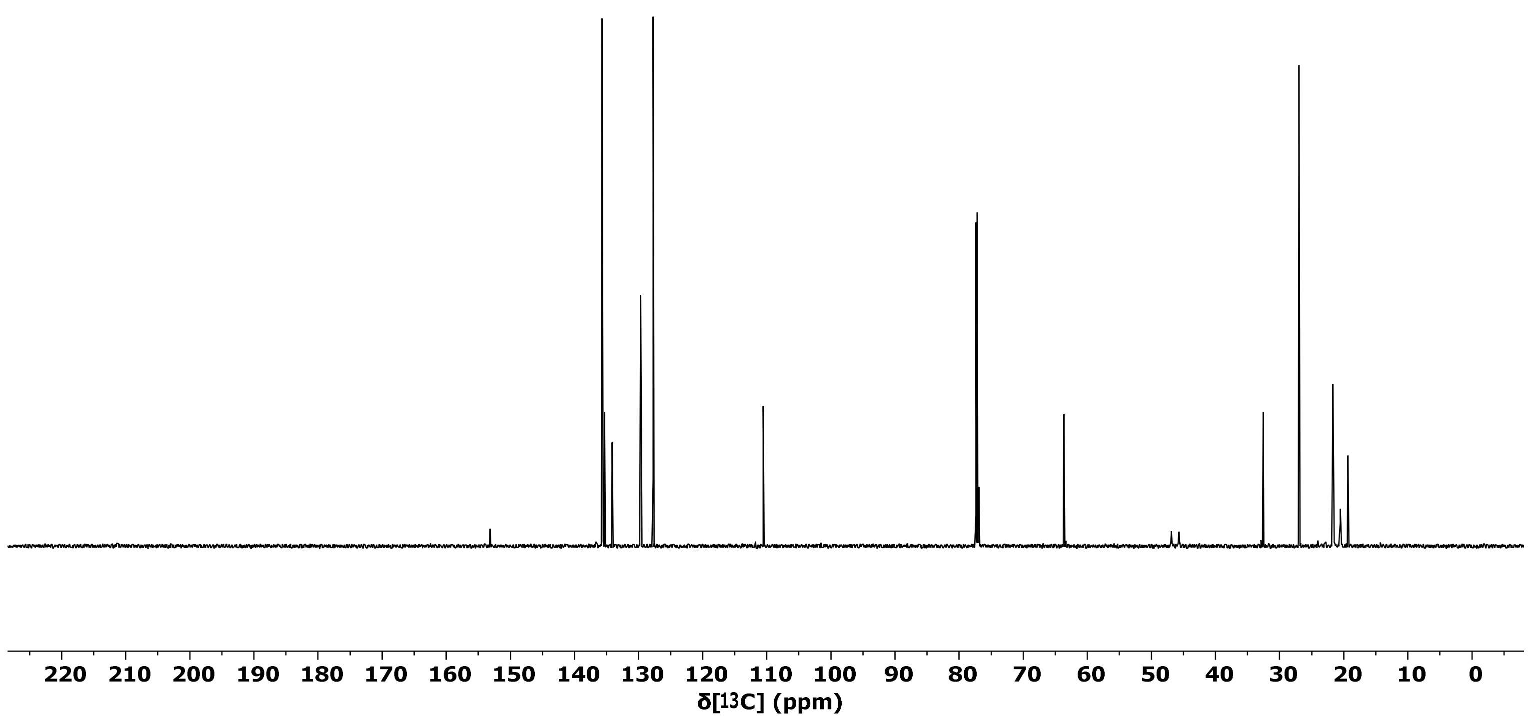
3t, *Z* : *E* = 95 : 5



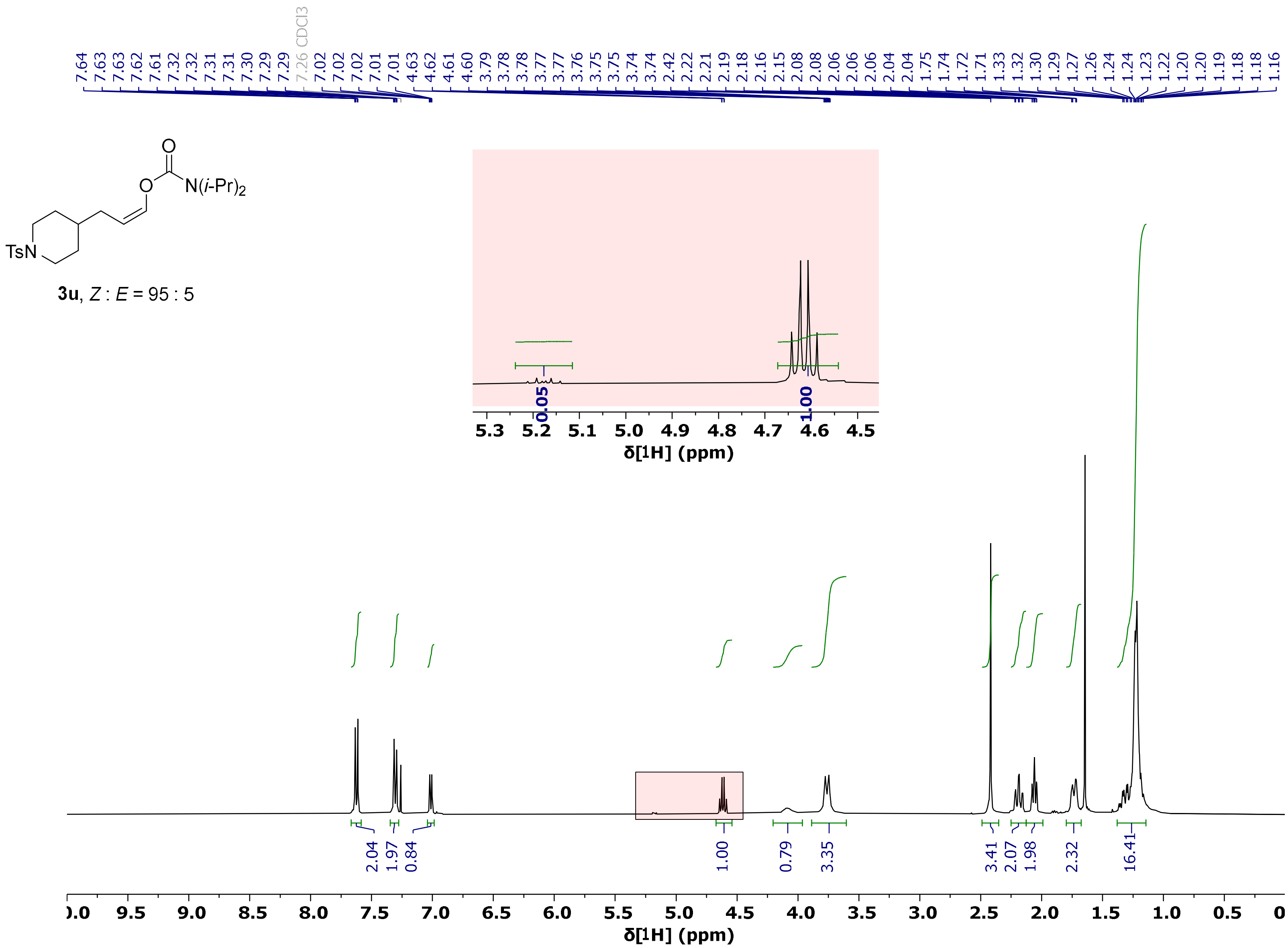
^{13}C NMR (151 MHz, $CDCl_3$)



3t, *Z* : *E* = 95 : 5

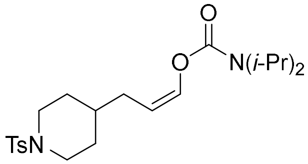


^{1}H NMR (400 MHz, CDCl$_3$)

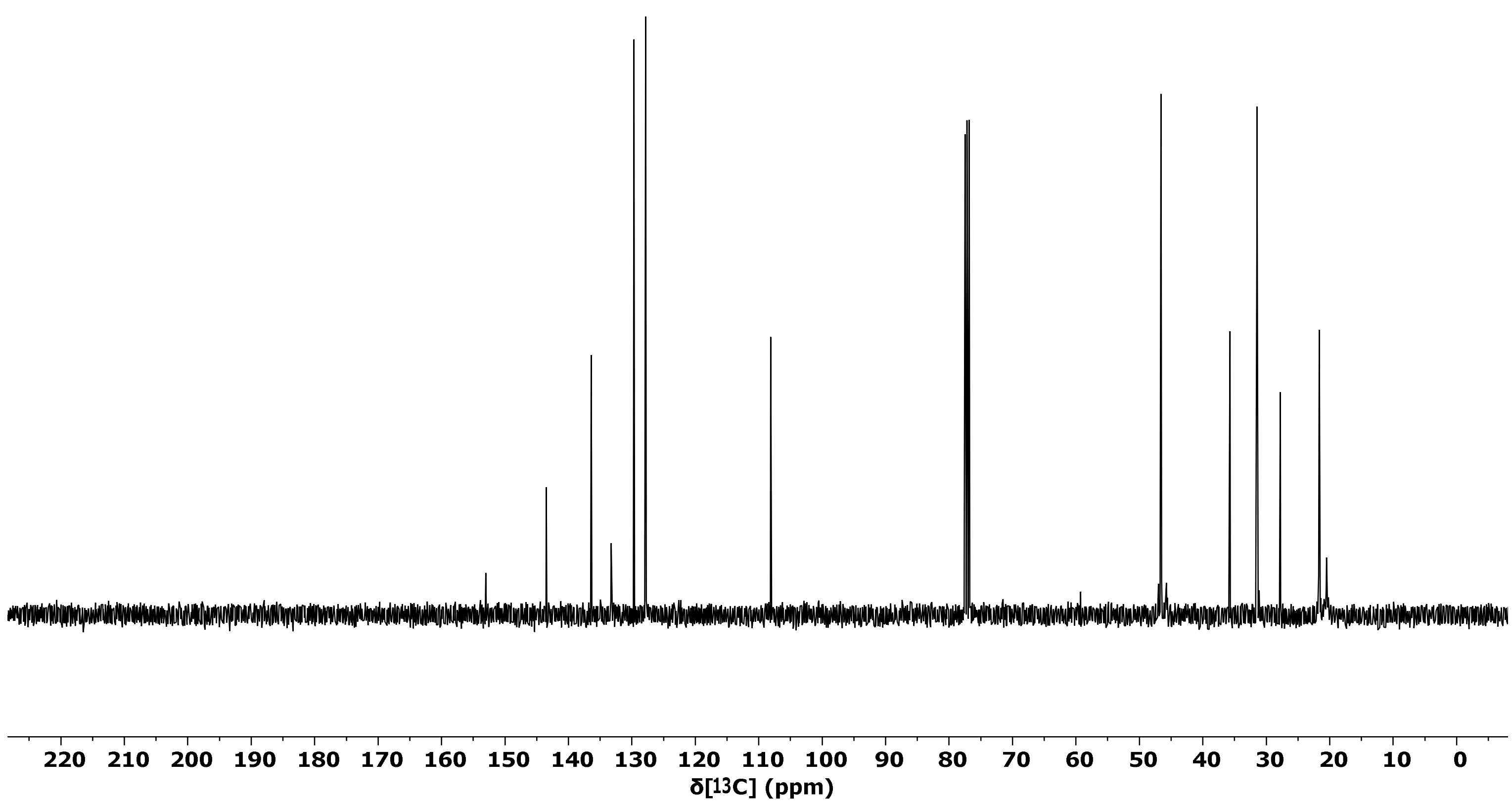


3u, *Z* : *E* = 95 : 5

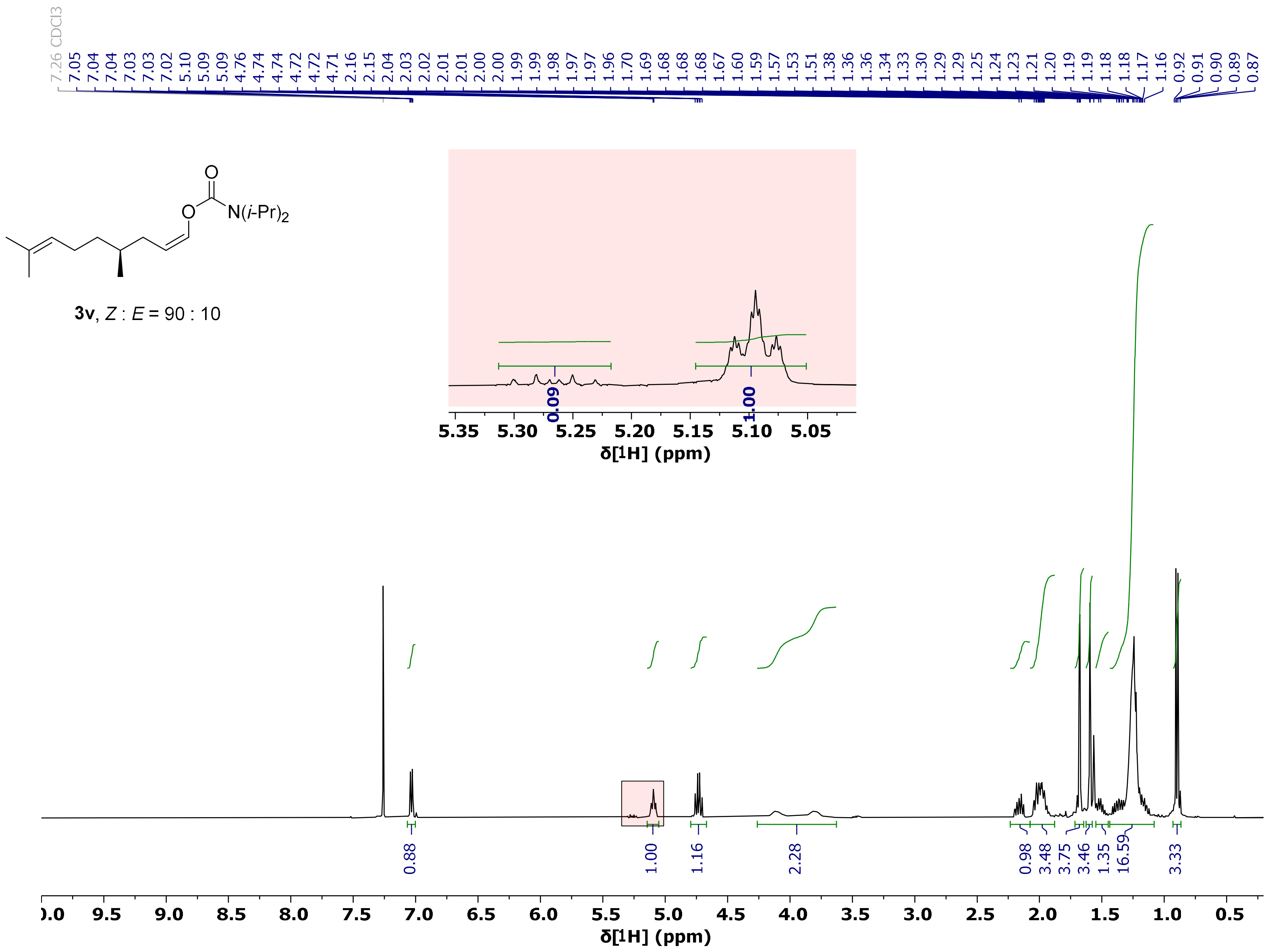
^{13}C NMR (101 MHz, $CDCl_3$)



3u, *Z* : *E* = 95 : 5

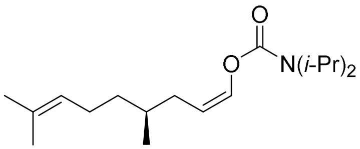


^{1}H NMR (400 MHz, $CDCl_3$)

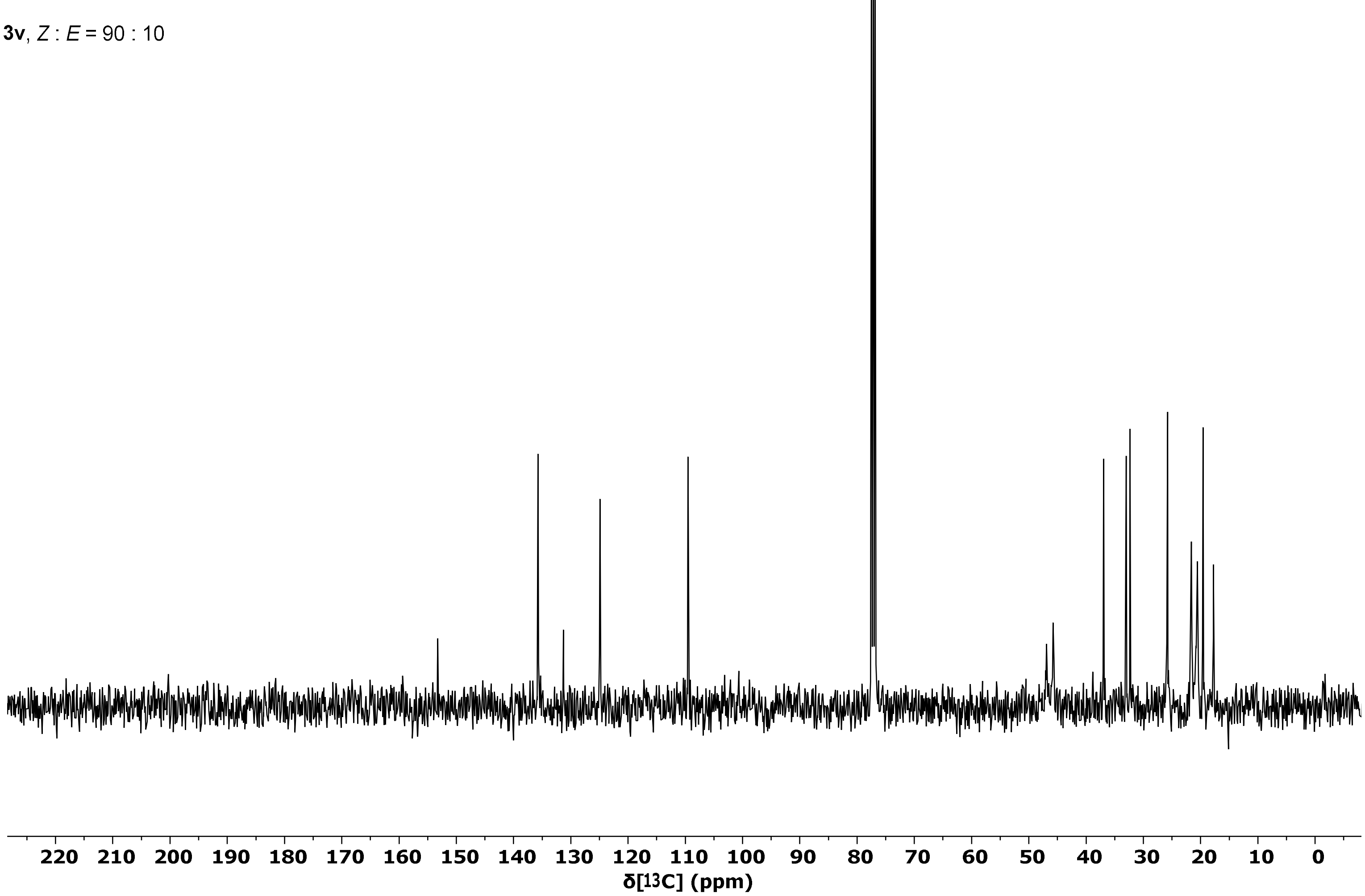


3v, *Z* : *E* = 90 : 10

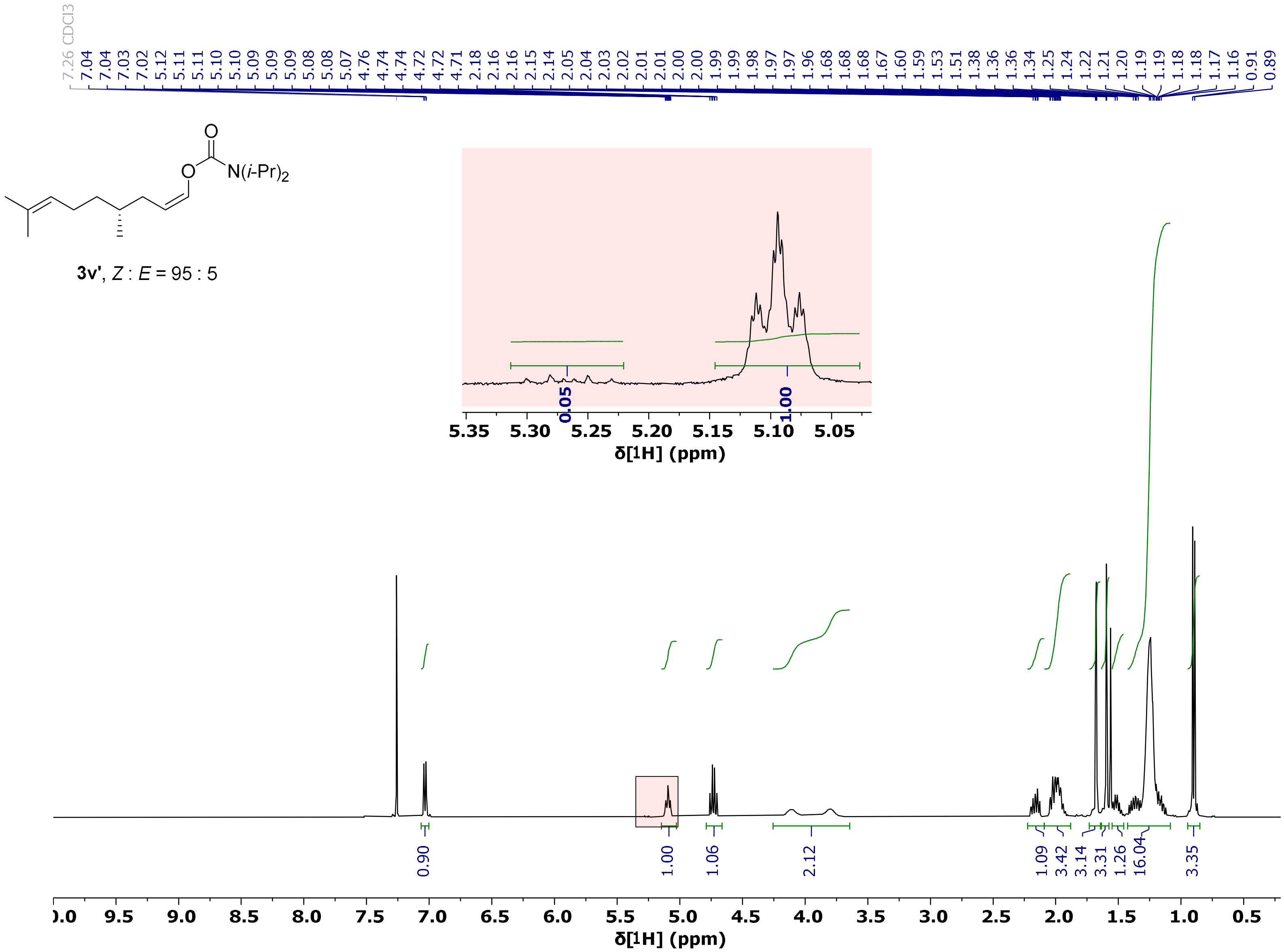
^{13}C NMR (101 MHz, $CDCl_3$)



3v, *Z* : *E* = 90 : 10

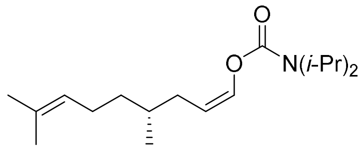


¹H NMR (400 MHz, $CDCl_3$)

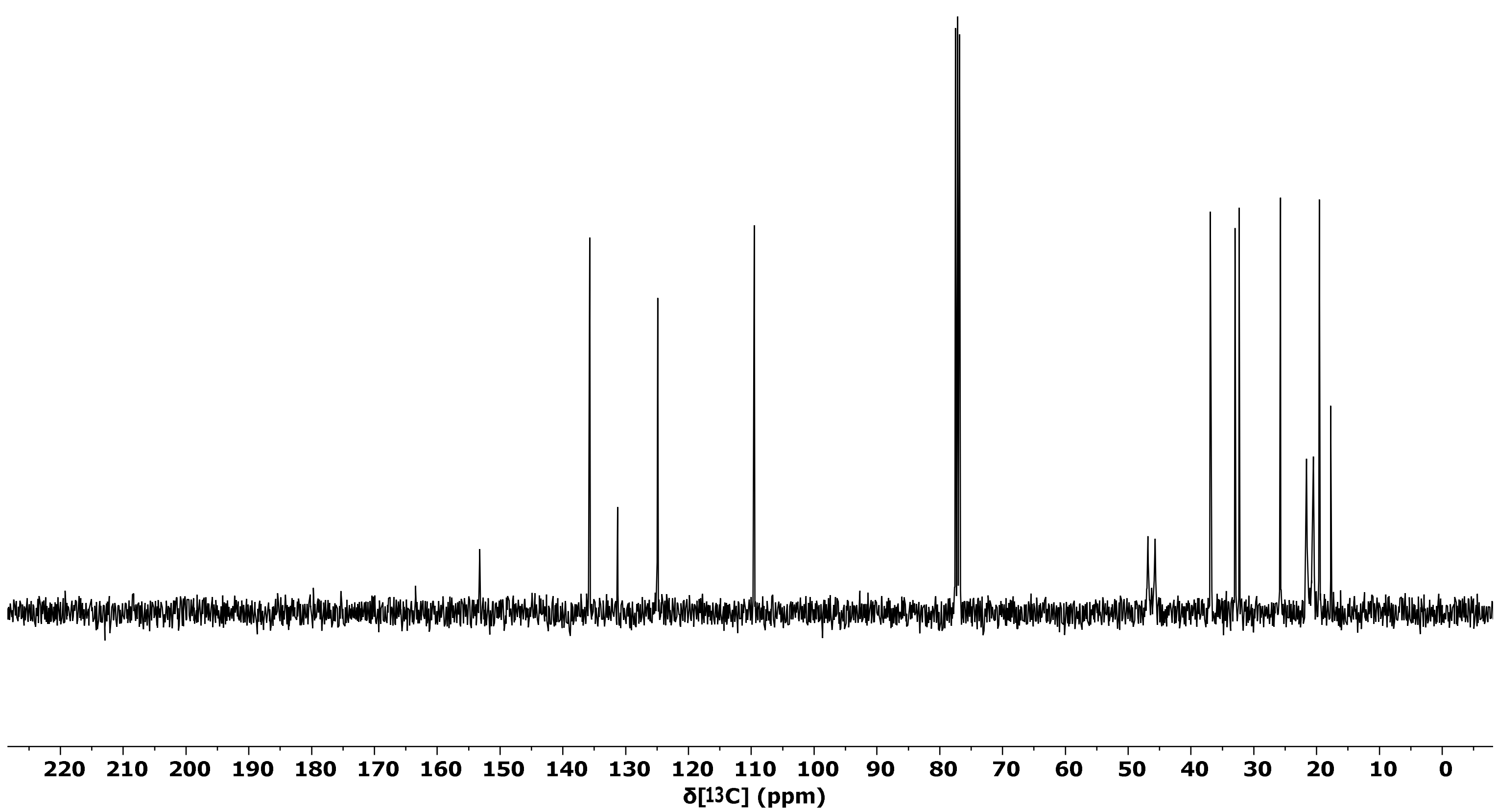


3v', *Z* : *E* = 95 : 5

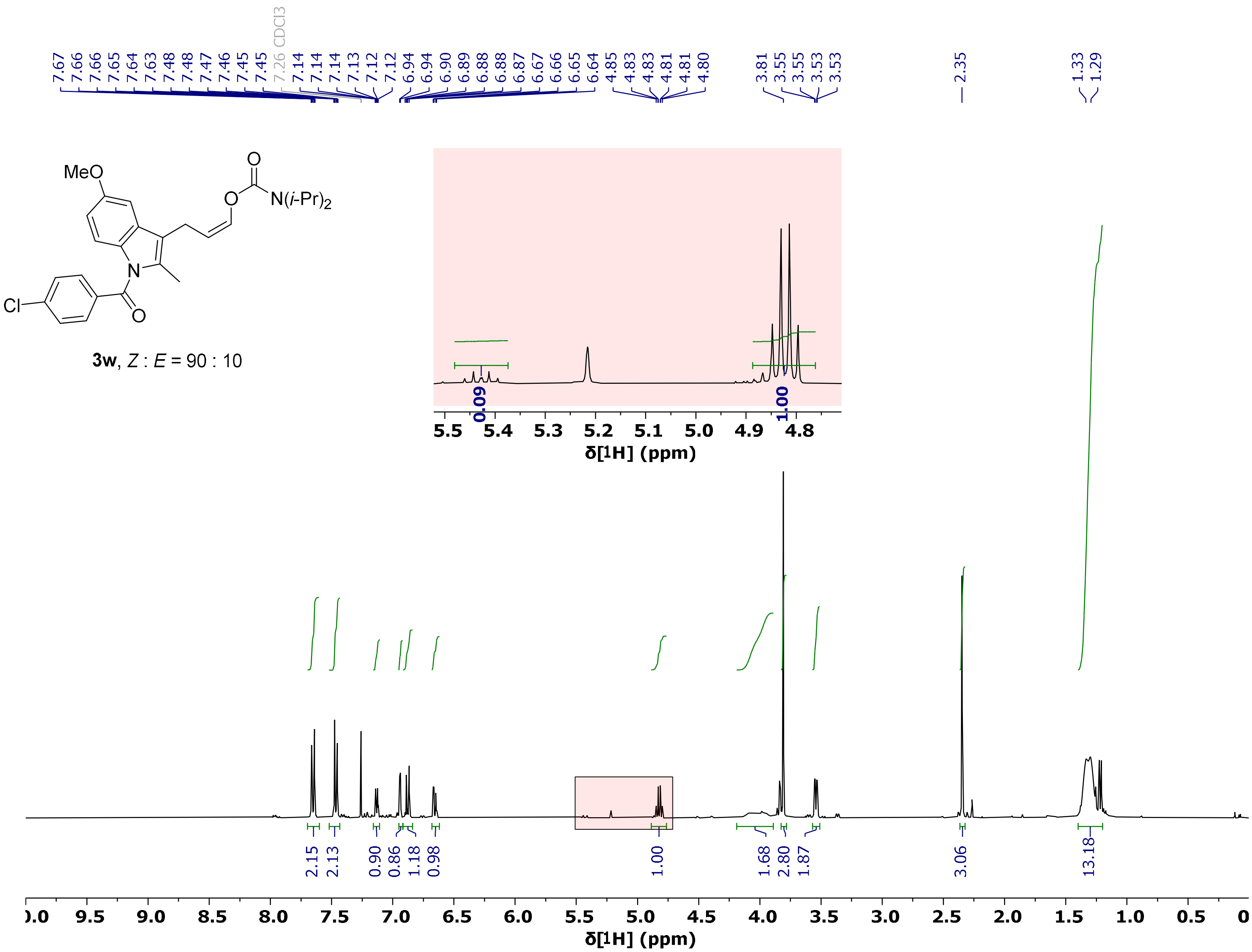
^{13}C NMR (101 MHz, CDCl$_3$)



3v', *Z* : *E* = 95 : 5

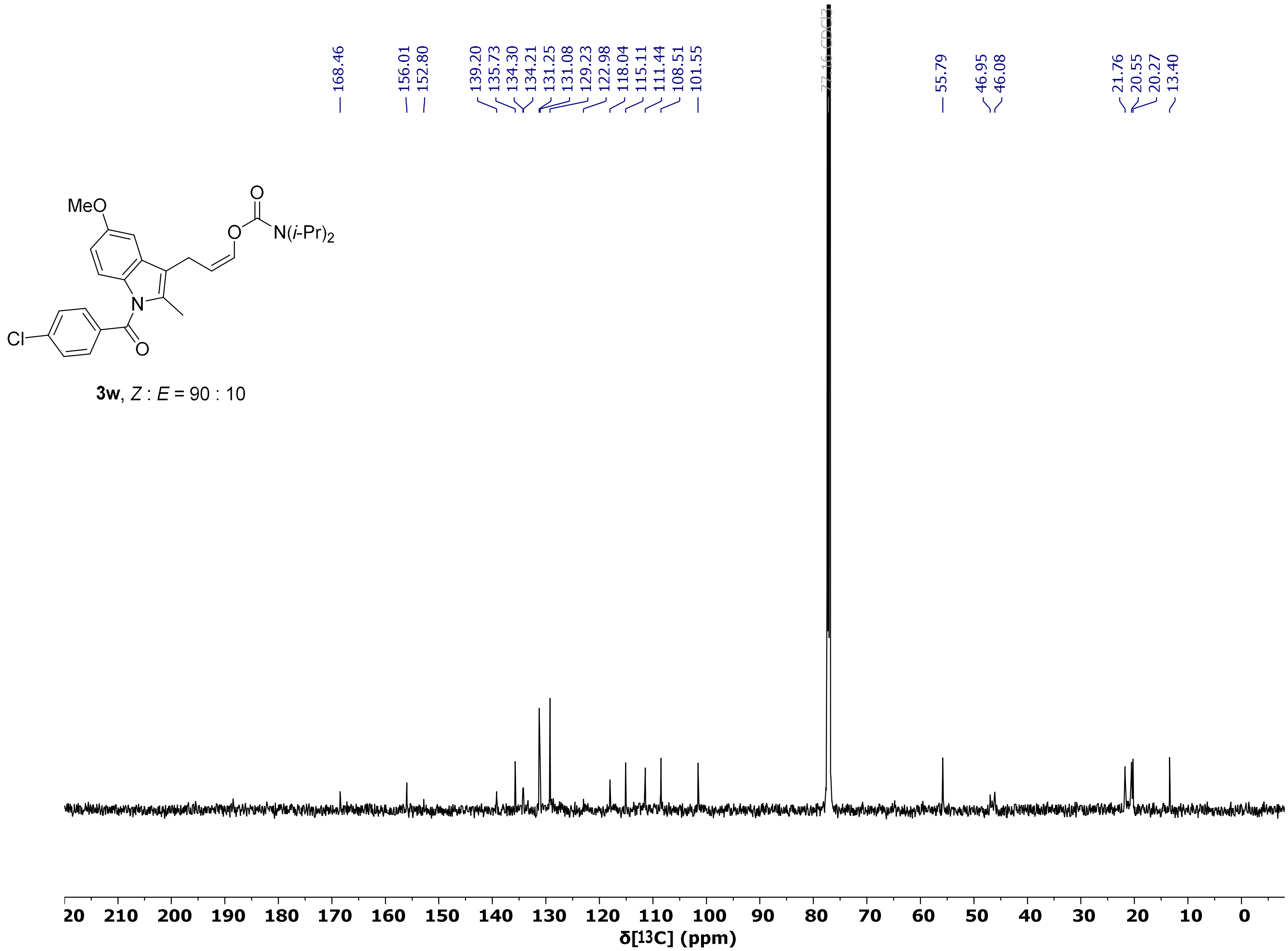


^{1}H NMR (400 MHz, $CDCl_3$)



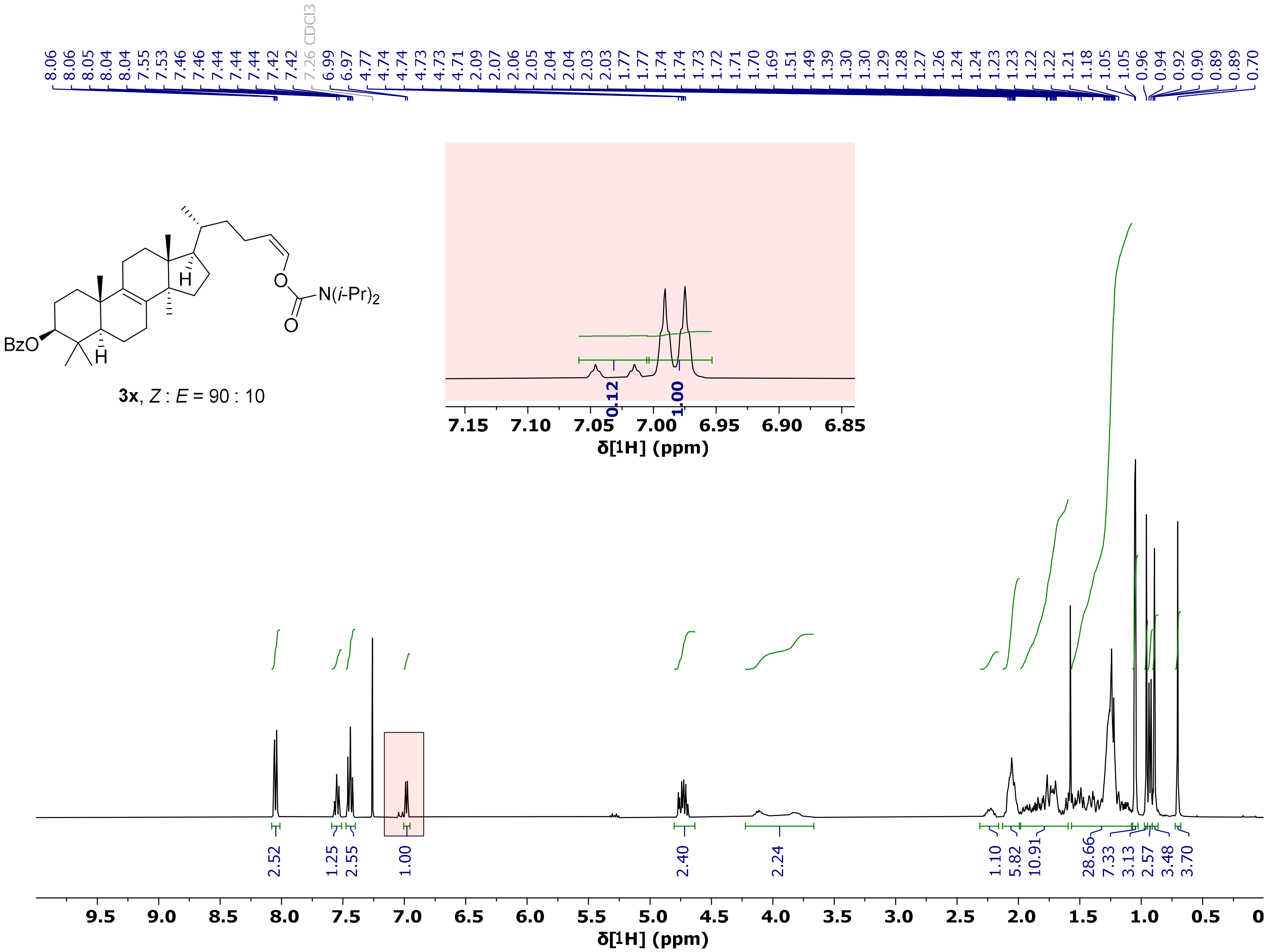
3w, *Z* : *E* = 90 : 10

^{13}C NMR (151 MHz, $CDCl_3$)



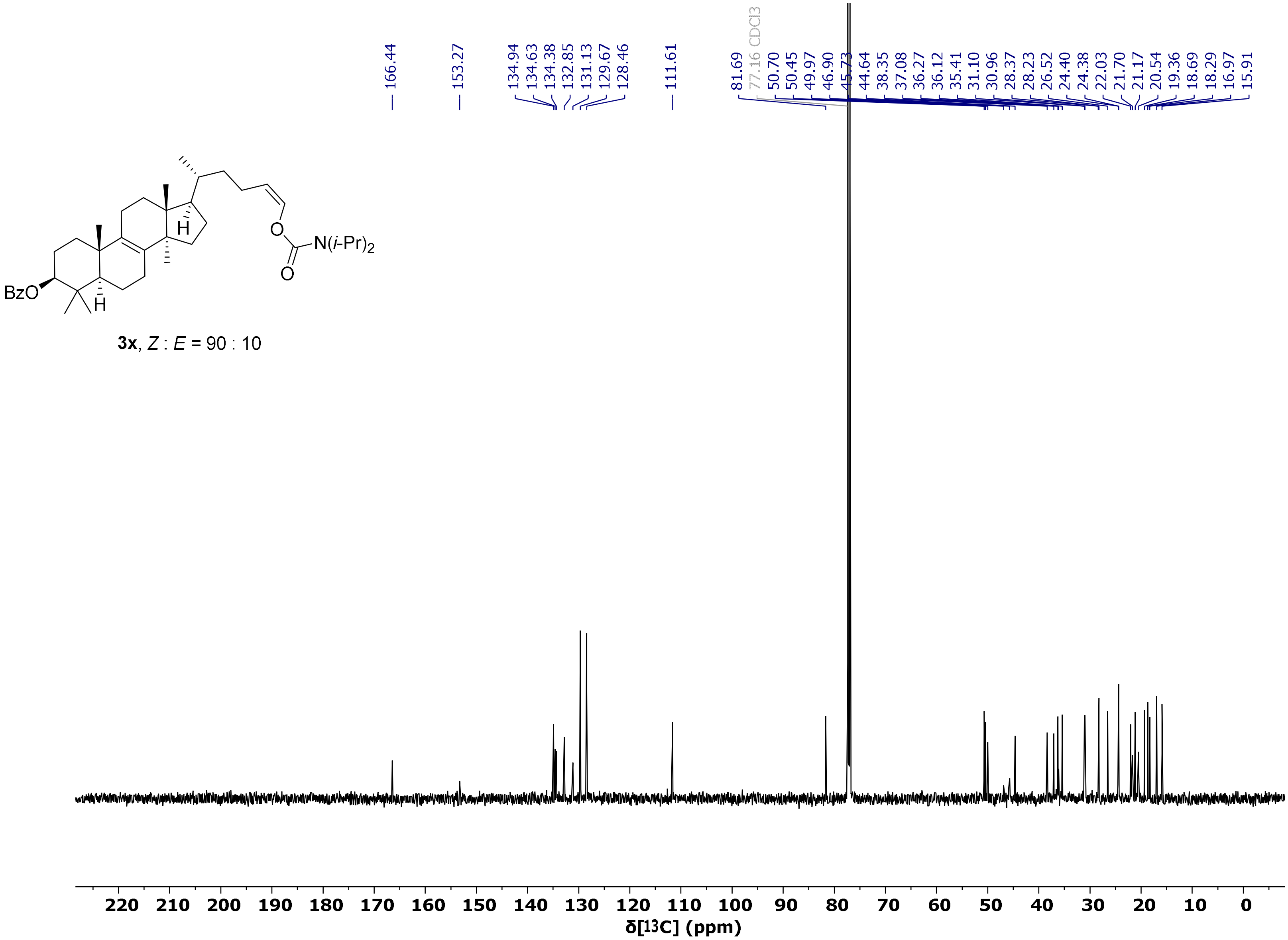
3w, *Z* : *E* = 90 : 10

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



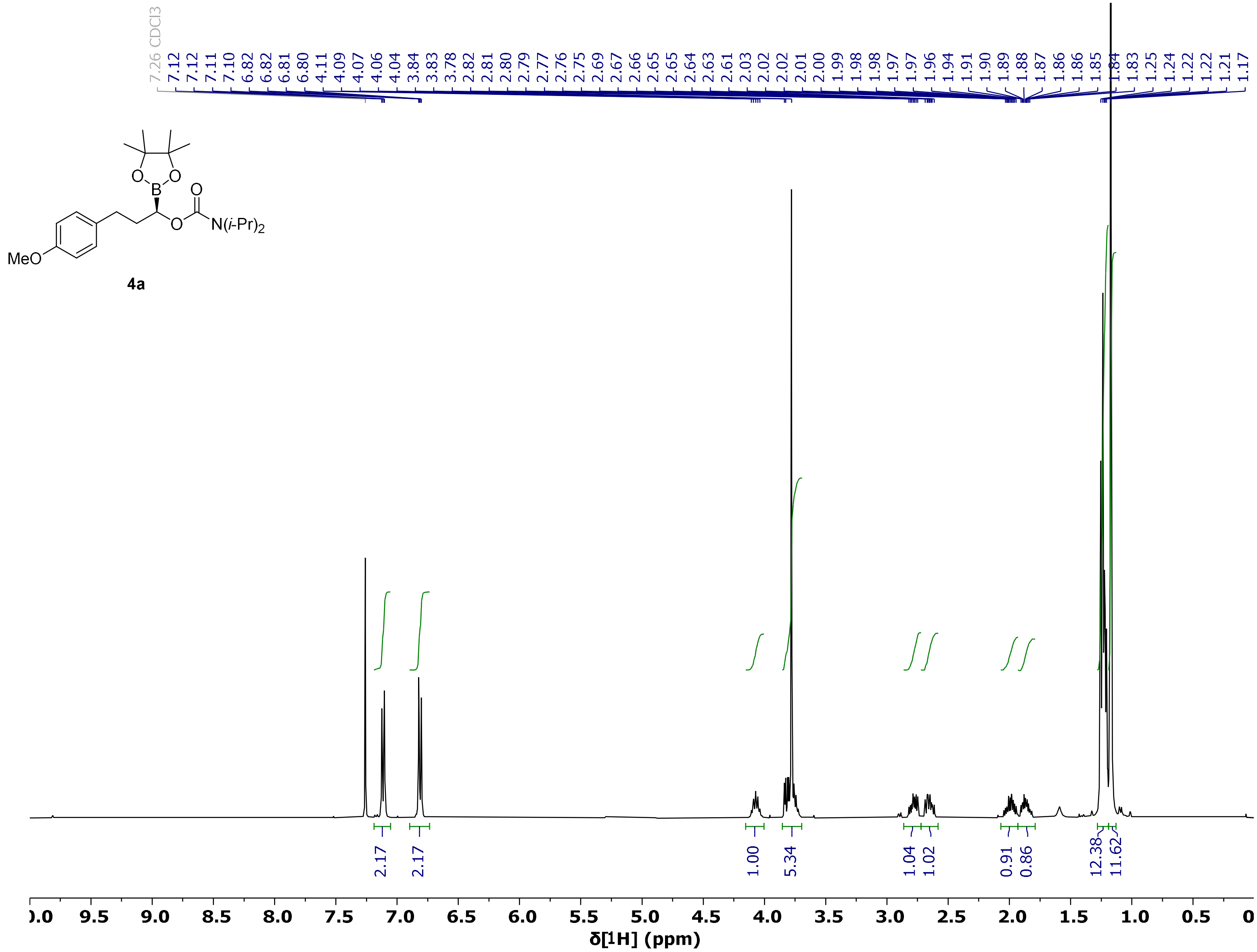
3x, *Z* : *E* = 90 : 10

^{13}C NMR (151 MHz, $CDCl_3$)



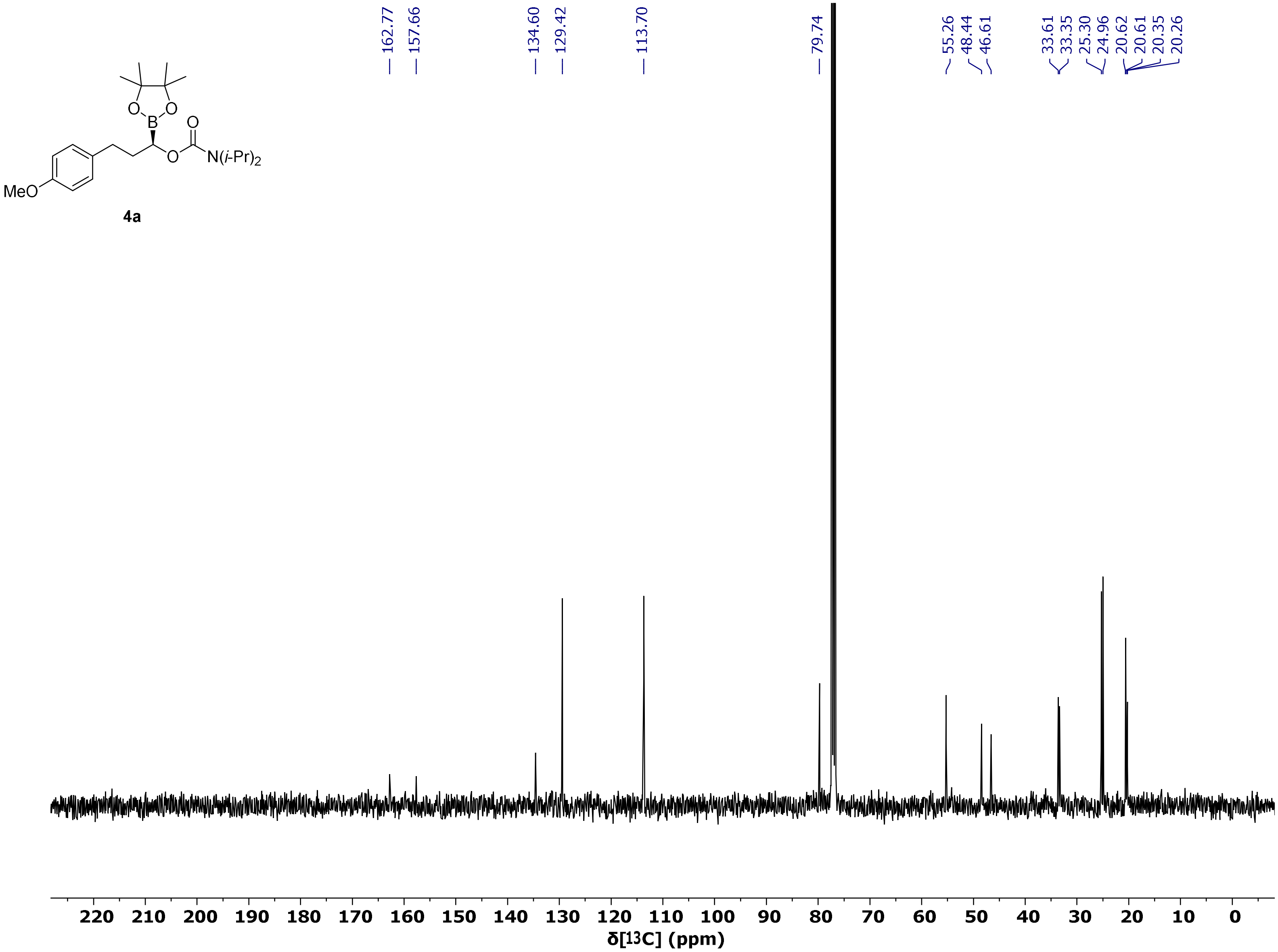
3x, *Z* : *E* = 90 : 10

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



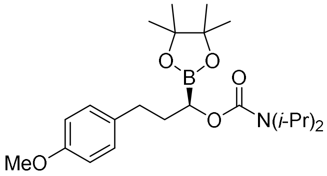
4a

^{13}C NMR (101 MHz, CDCl$_3$)

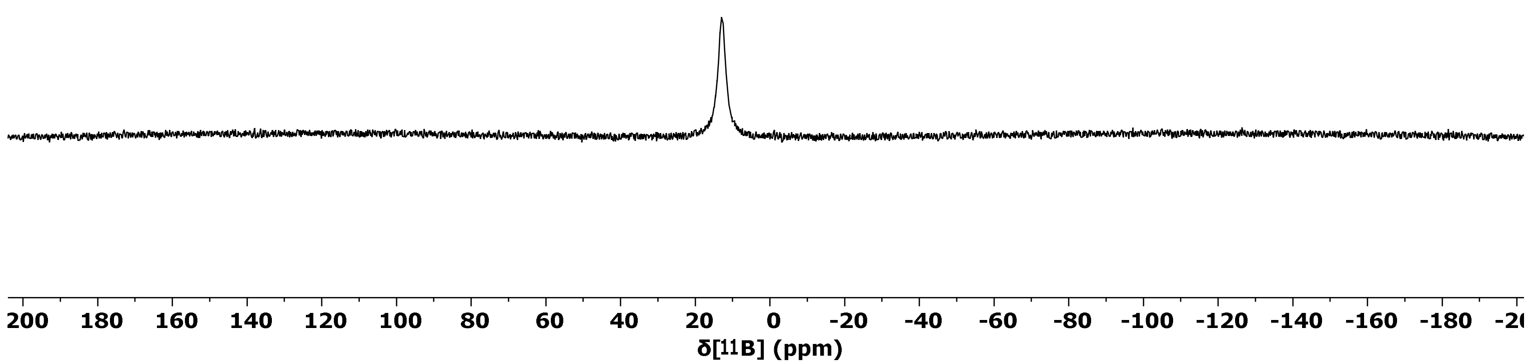


4a

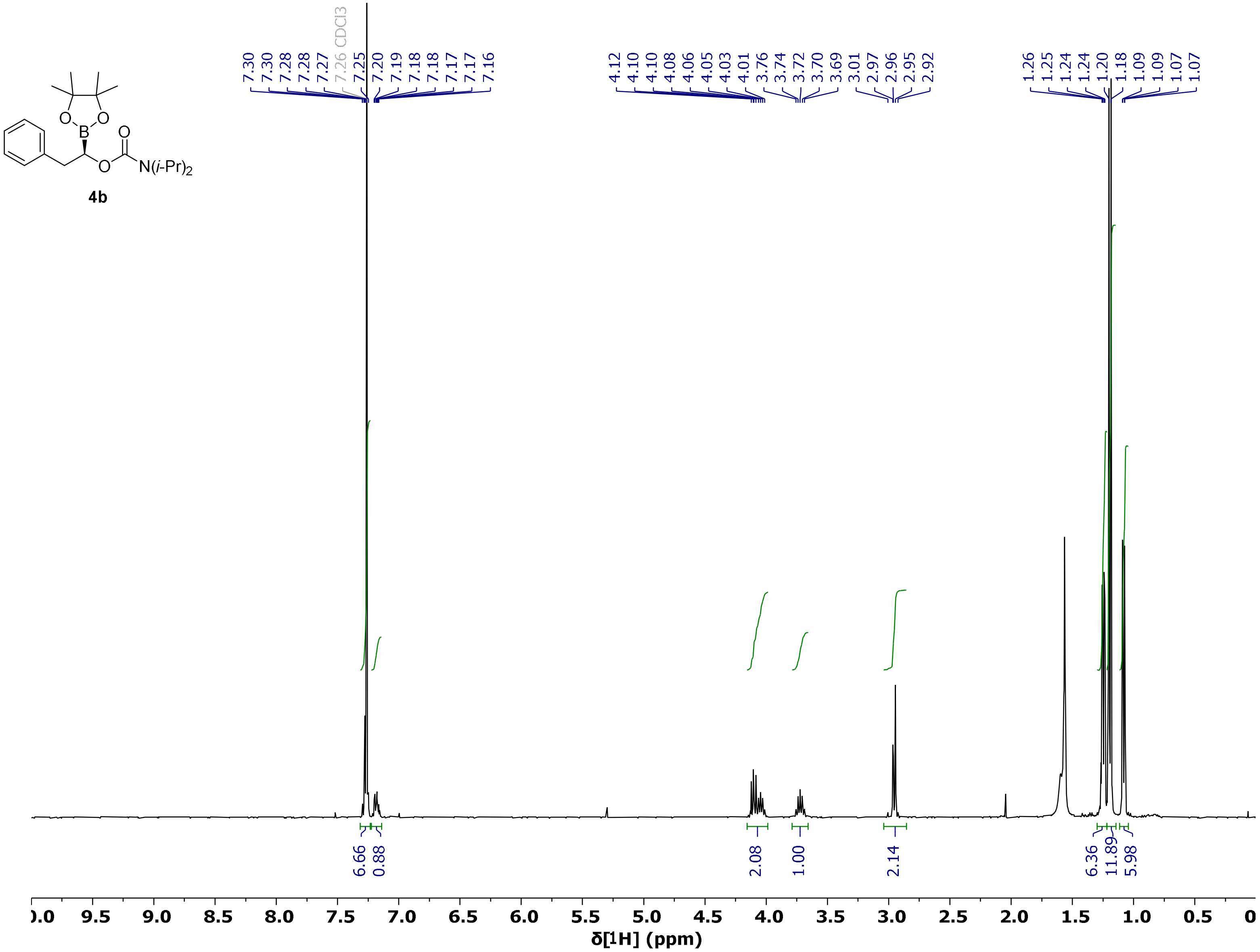
^{11}B NMR (128 MHz, $CDCl_3$)



4a

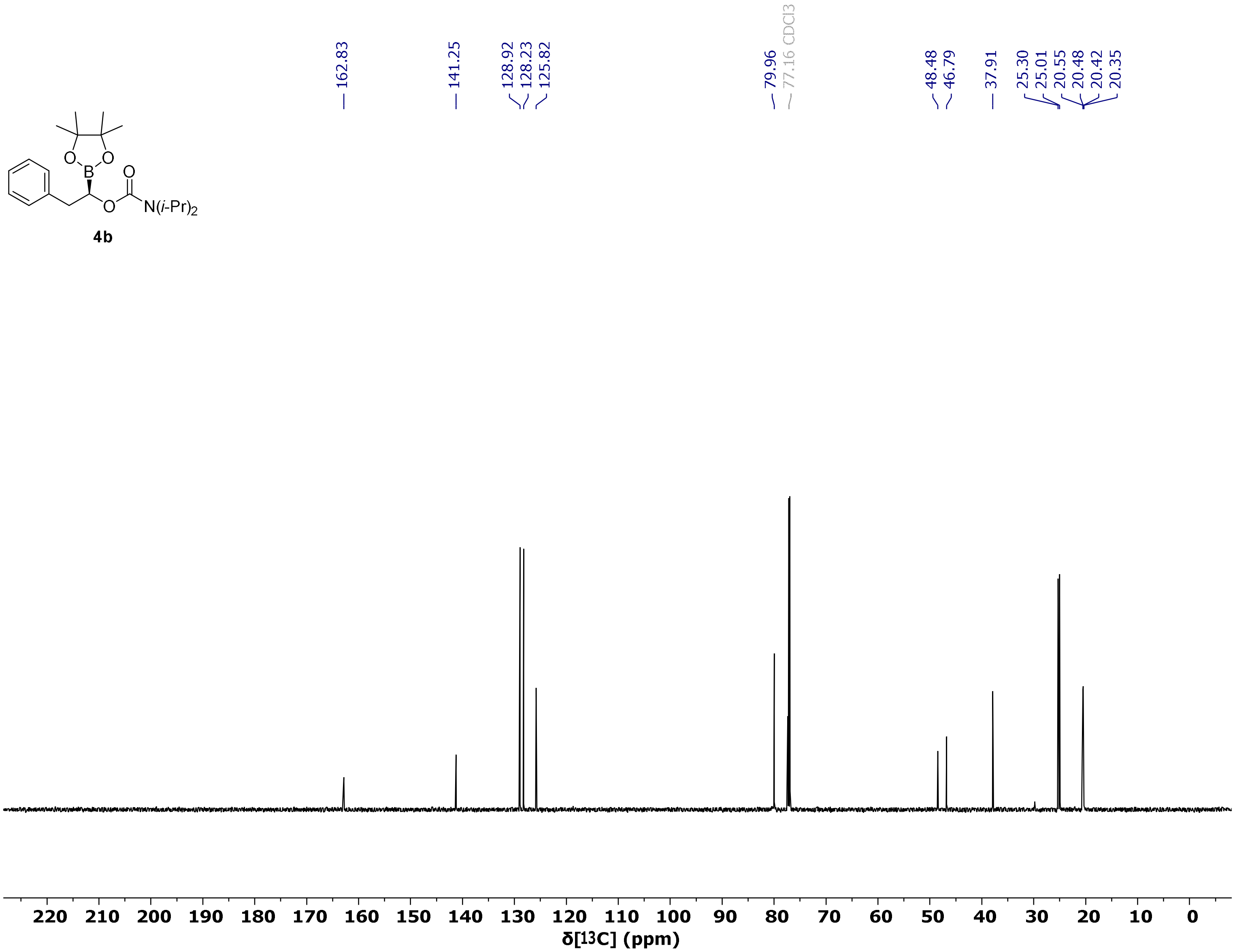


^{1}H NMR (400 MHz, $CDCl_3$)



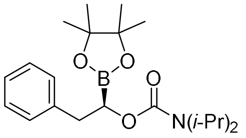
4b

^{13}C NMR (151 MHz, $CDCl_3$)

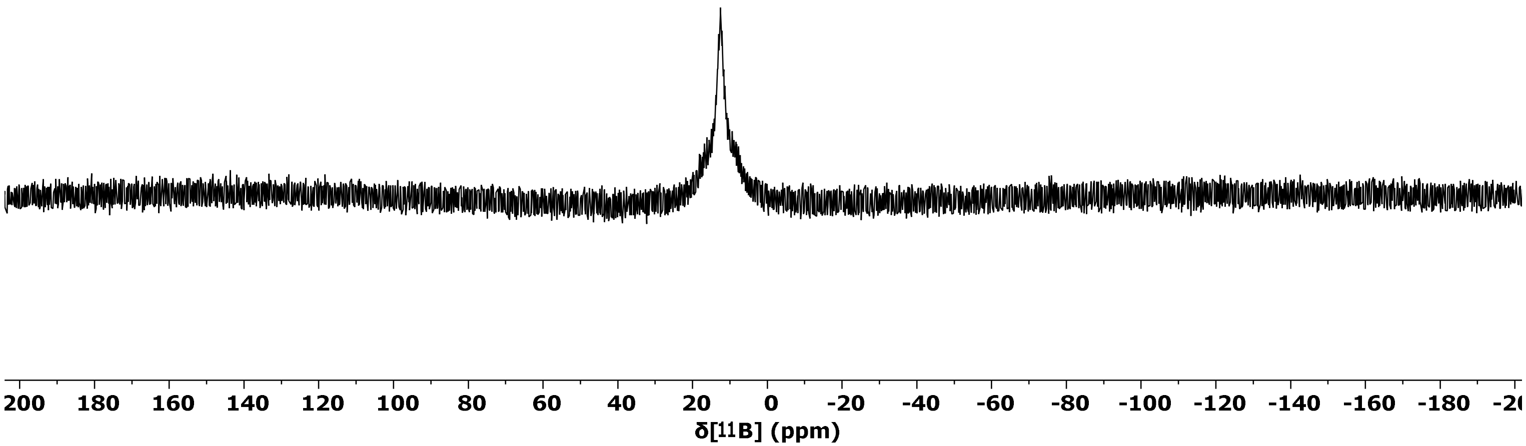


4b

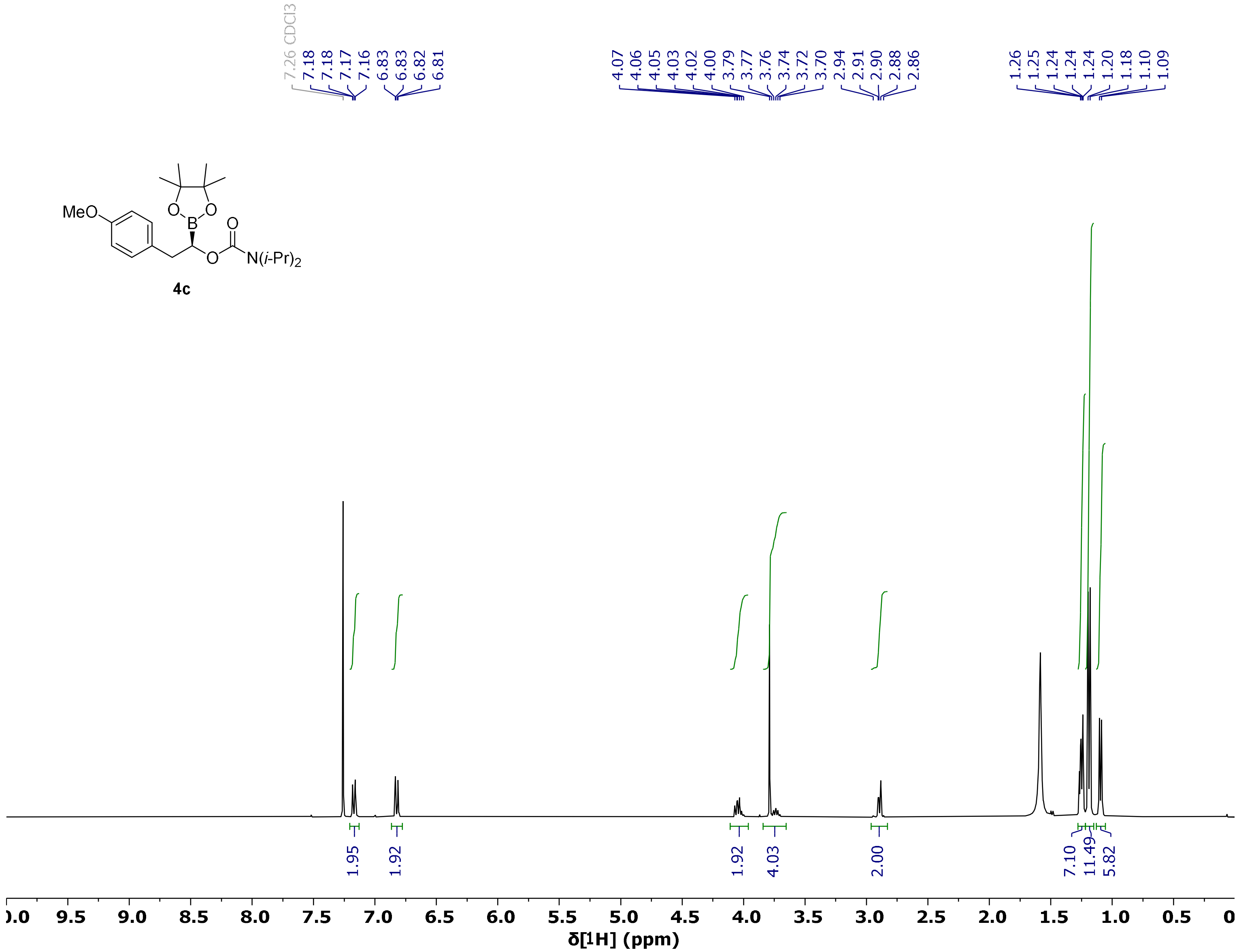
^{11}B NMR (128 MHz, $CDCl_3$)



4b

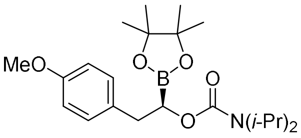


^{1}H NMR (400 MHz, $CDCl_3$)

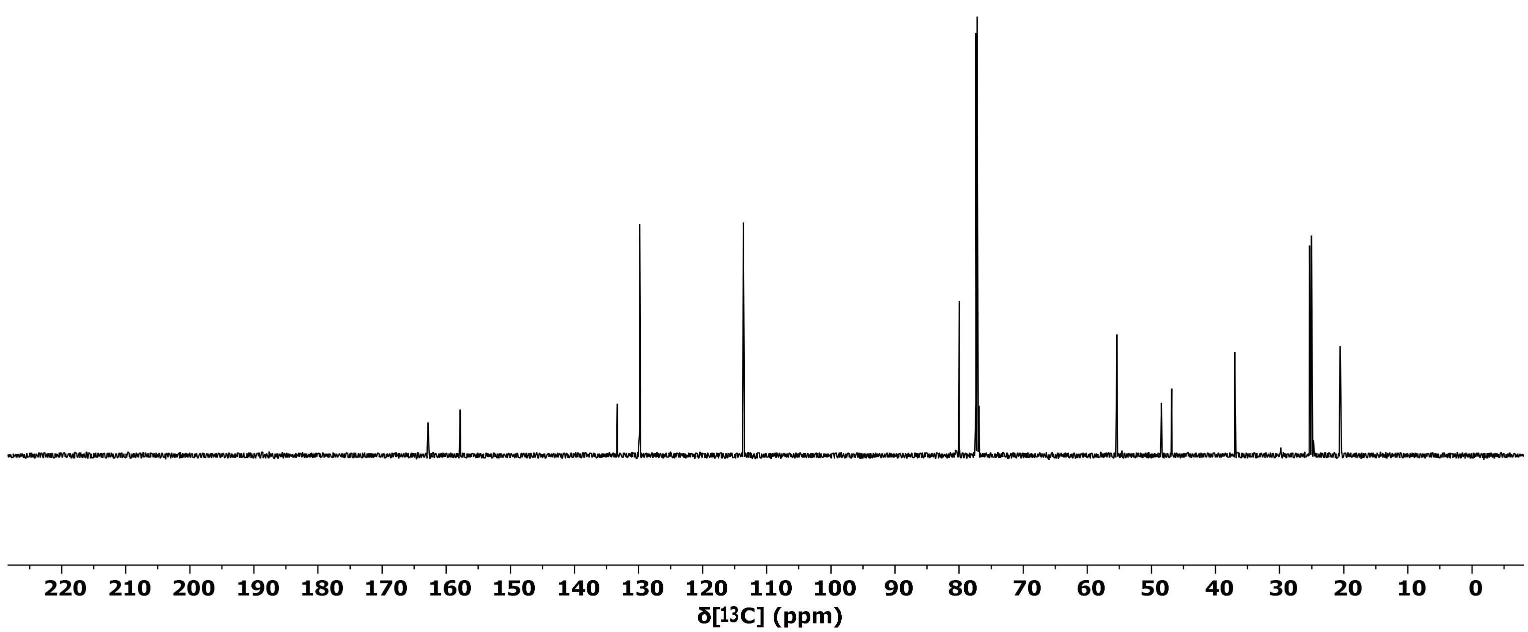


4c

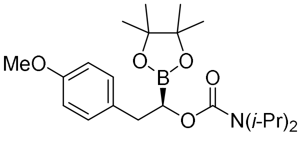
^{13}C NMR (151 MHz, CDCl$_3$)



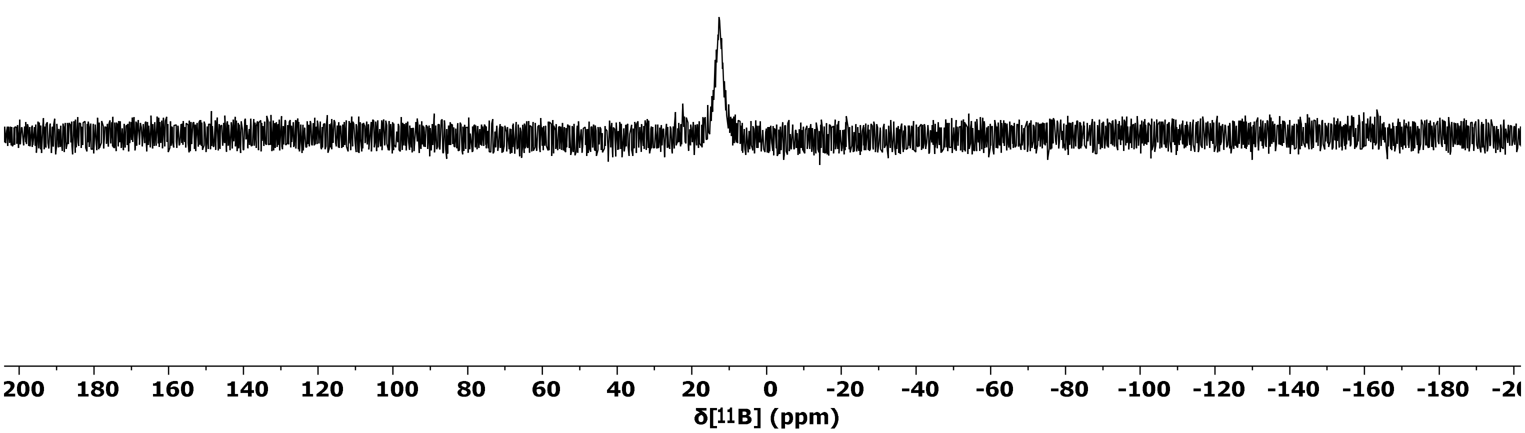
4c



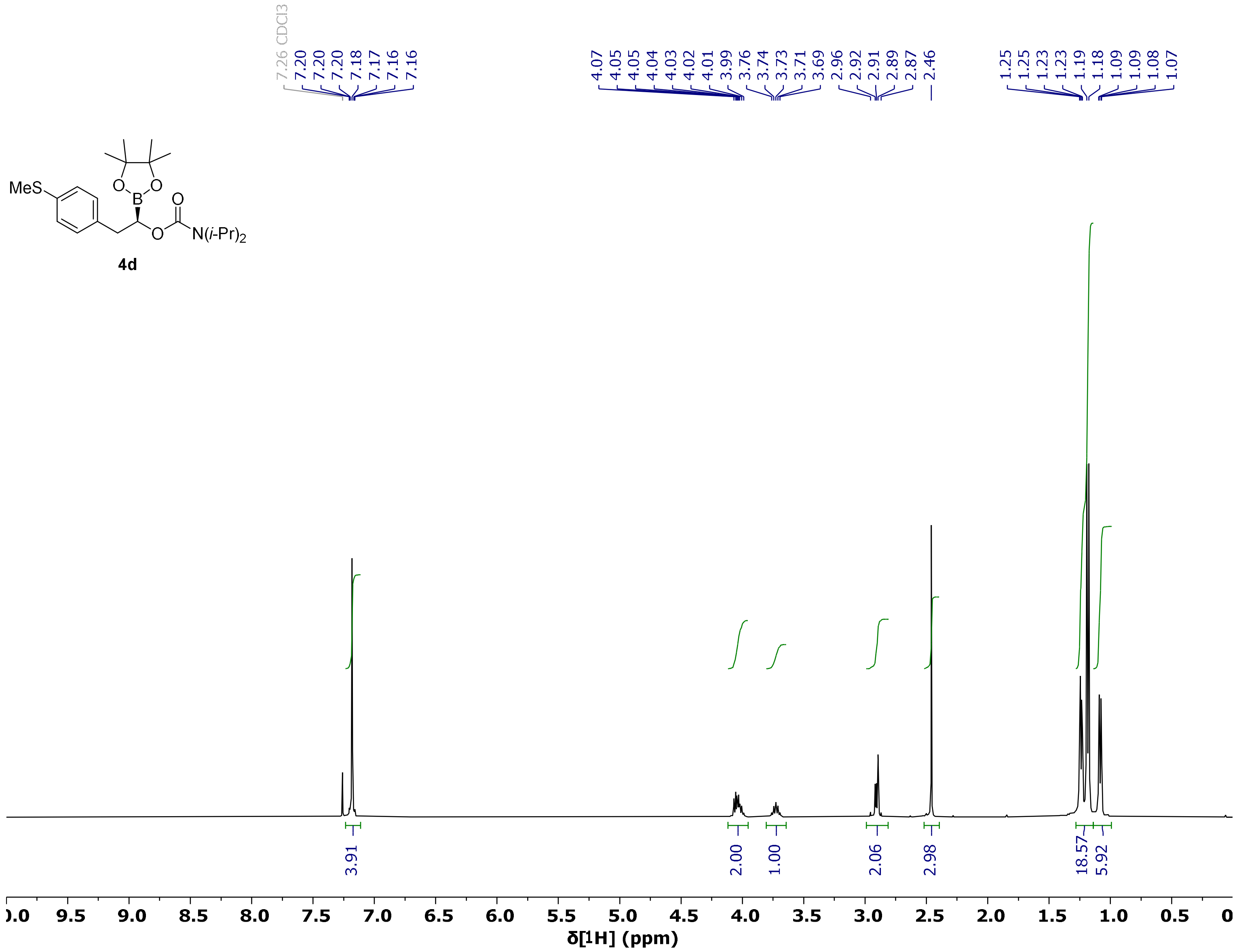
^{11}B NMR (128 MHz, $CDCl_3$)



4c

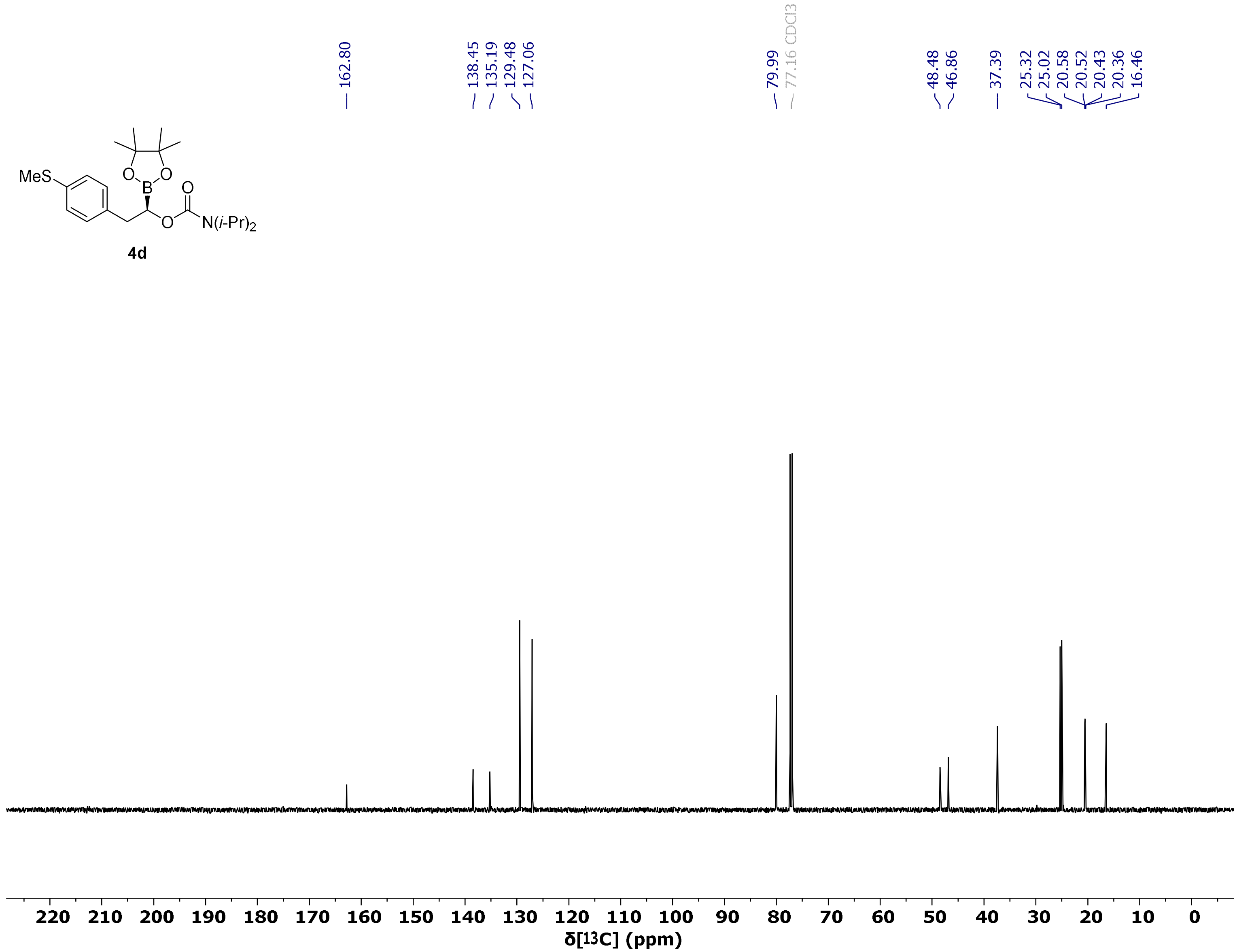


^{1}H NMR (400 MHz, $CDCl_3$)



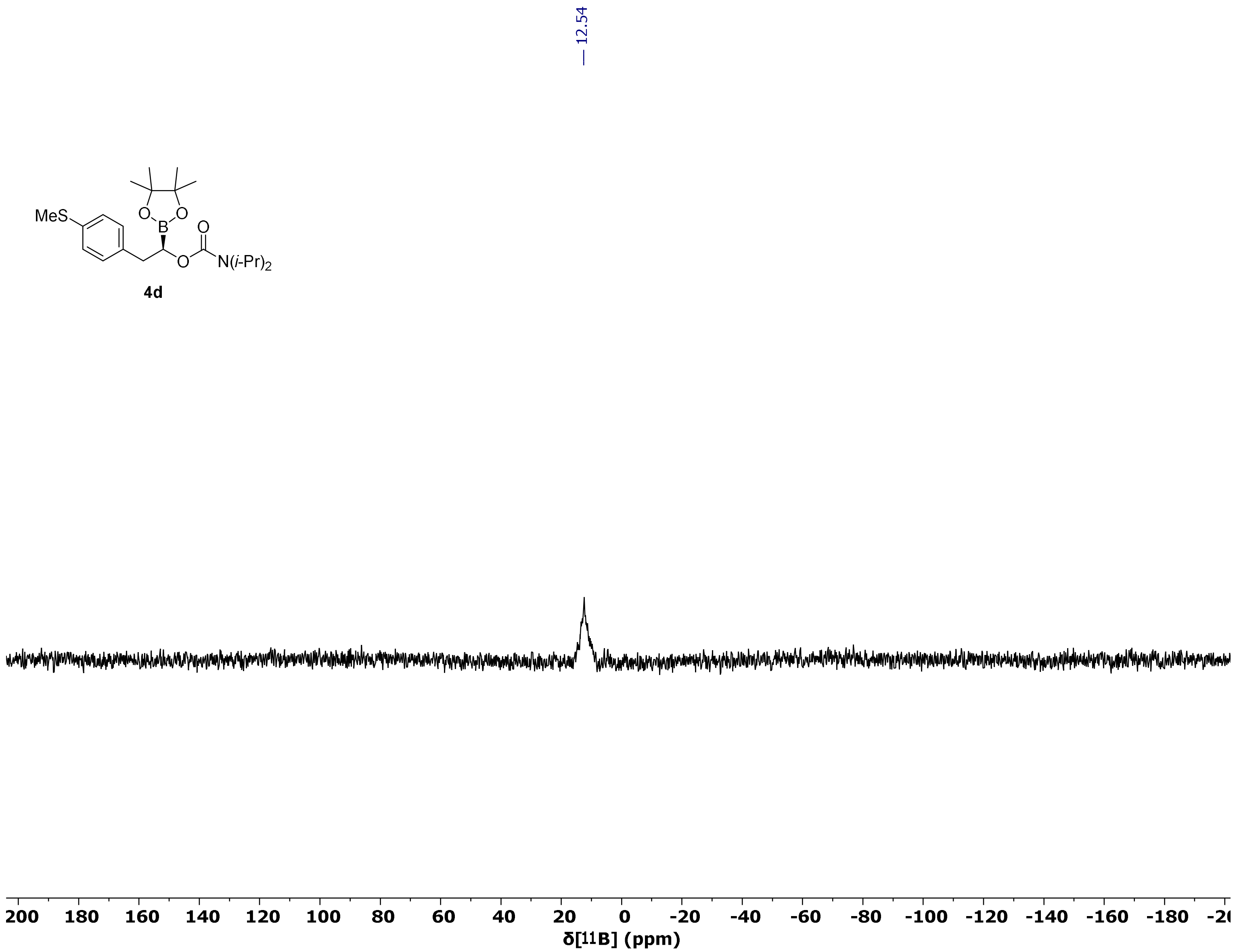
4d

^{13}C NMR (151 MHz, CDCl$_3$)



4d

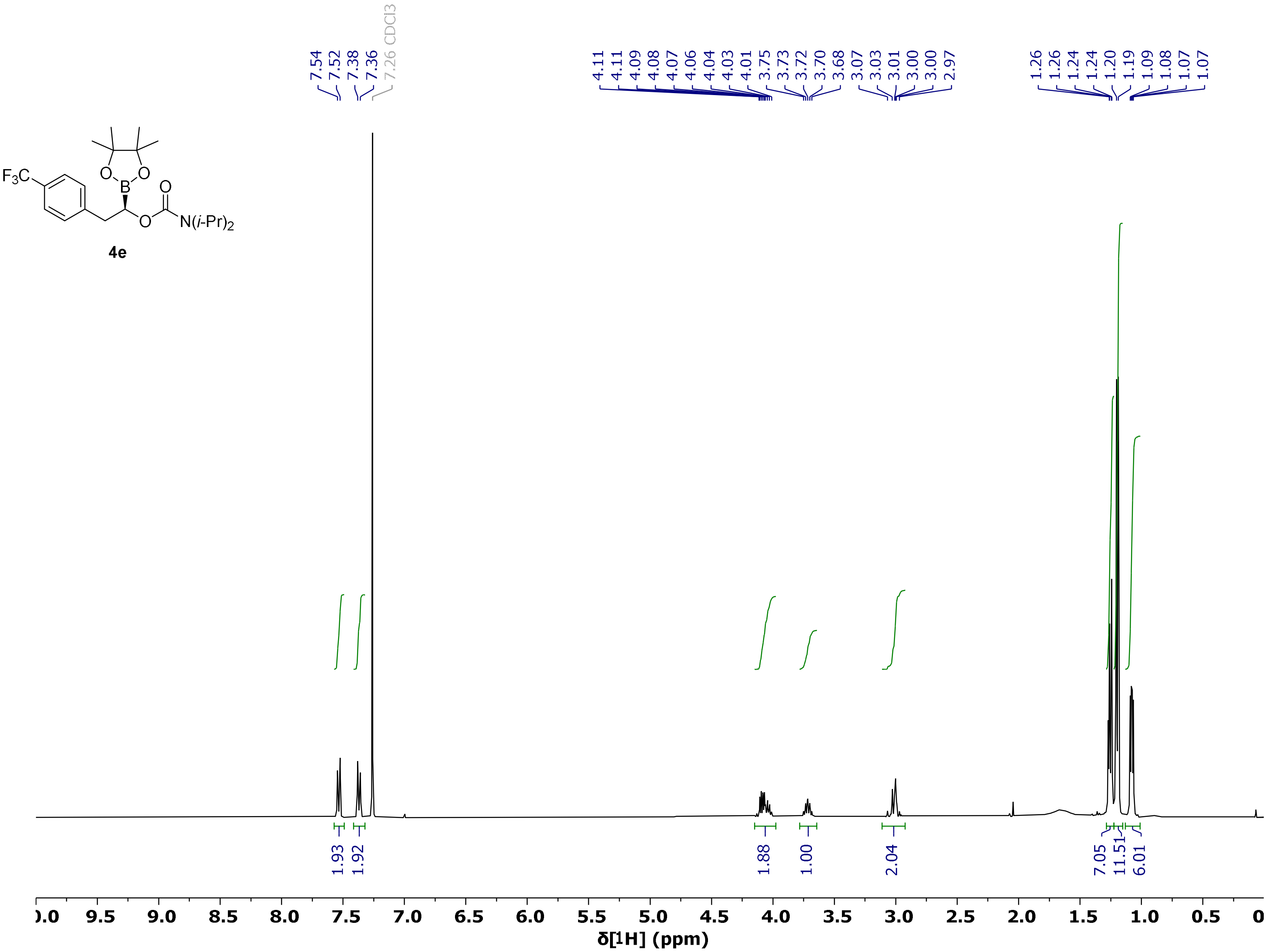
^{11}B NMR (128 MHz, $CDCl_3$)



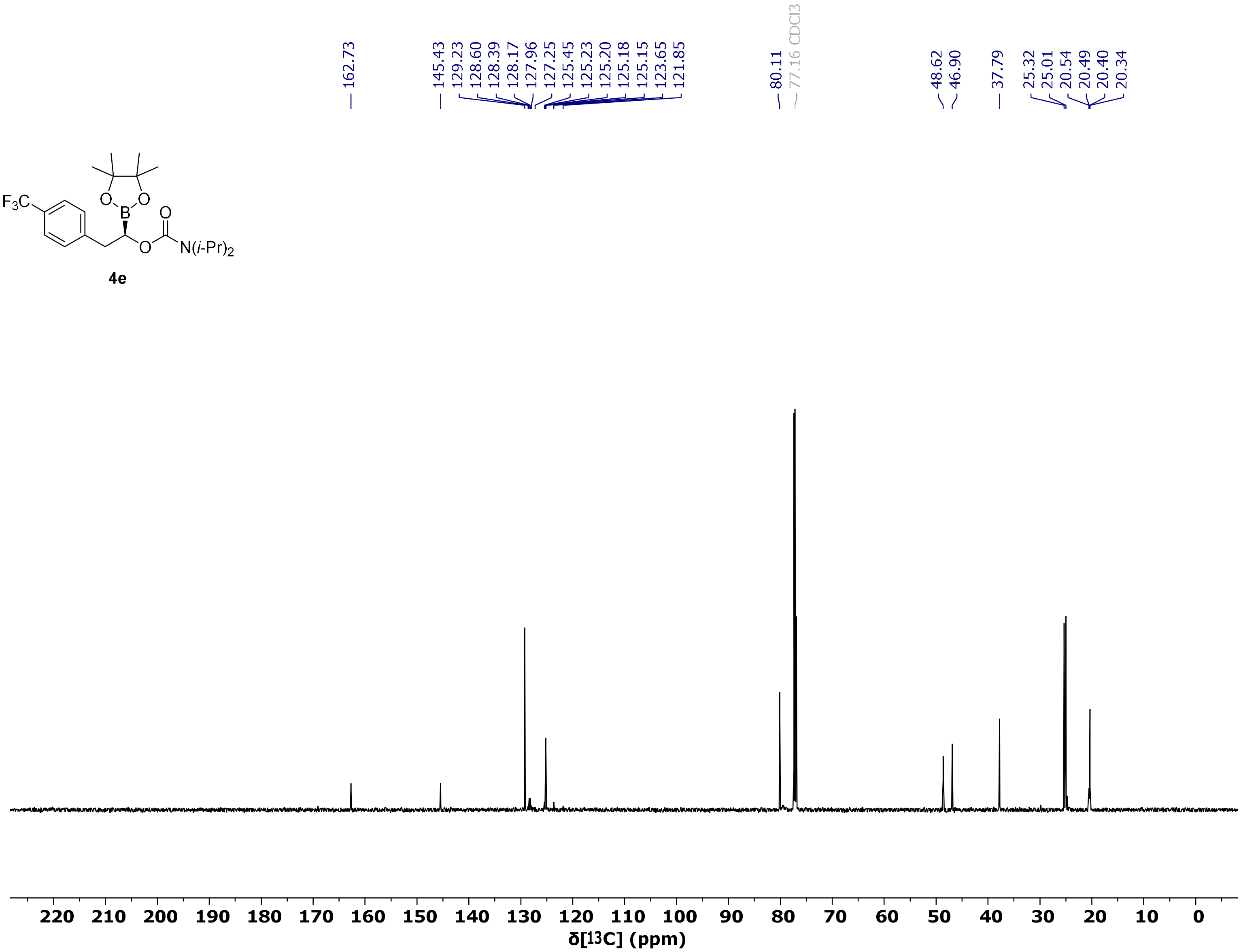
4d

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

4e

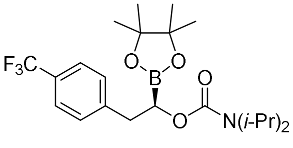


^{13}C NMR (151 MHz, $CDCl_3$)

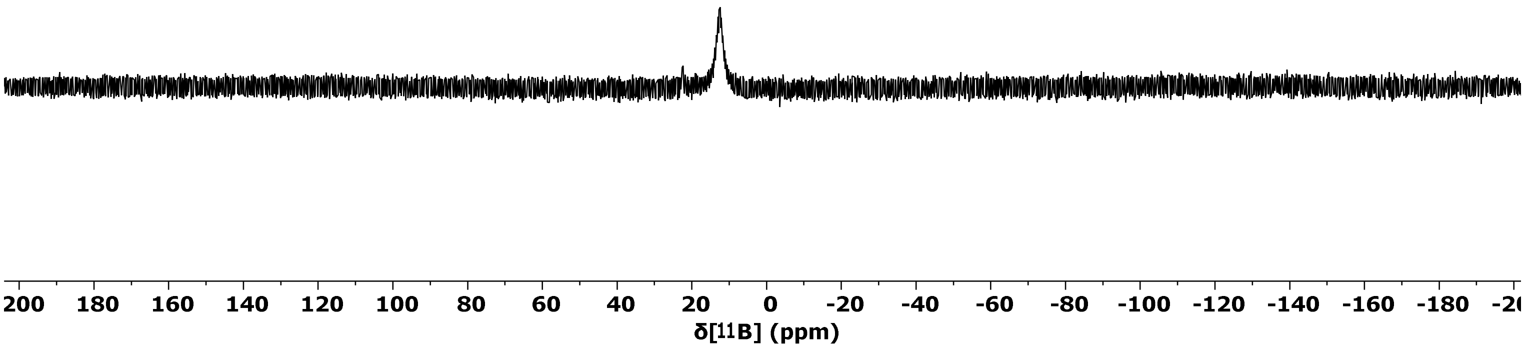


4e

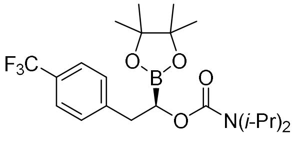
^{11}B NMR (128 MHz, $CDCl_3$)



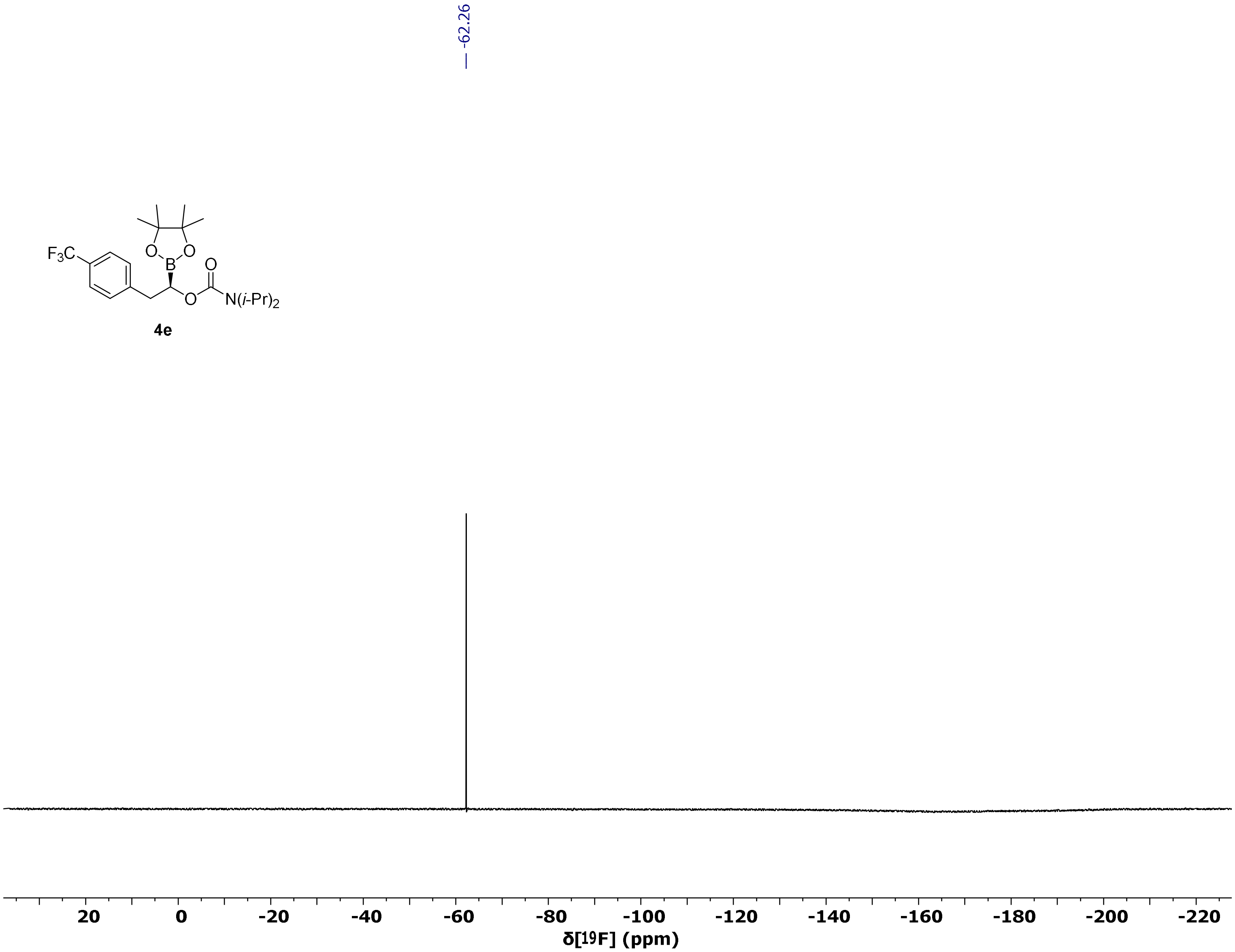
4e



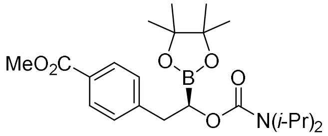
^{19}F NMR (376 MHz, $CDCl_3$)



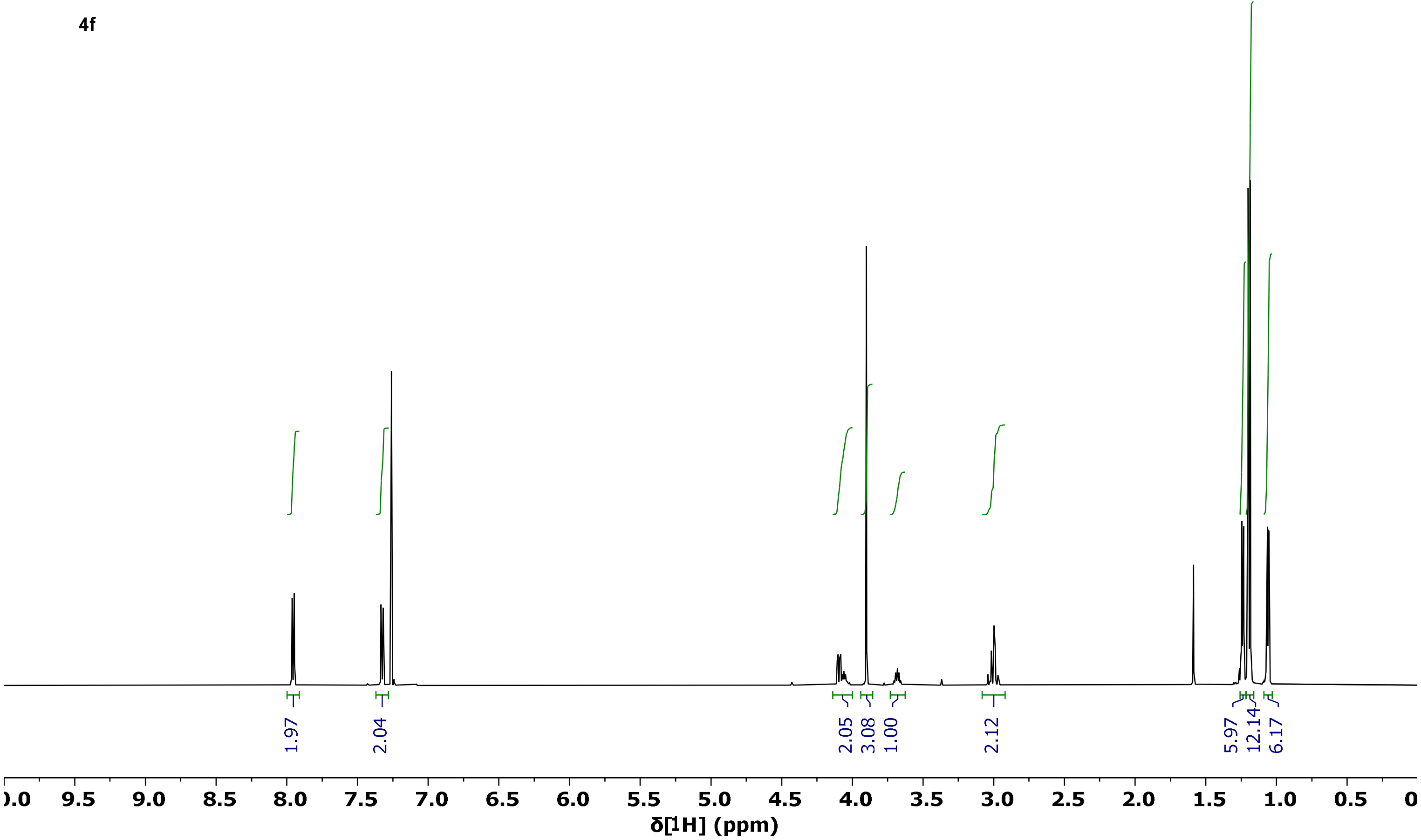
4e



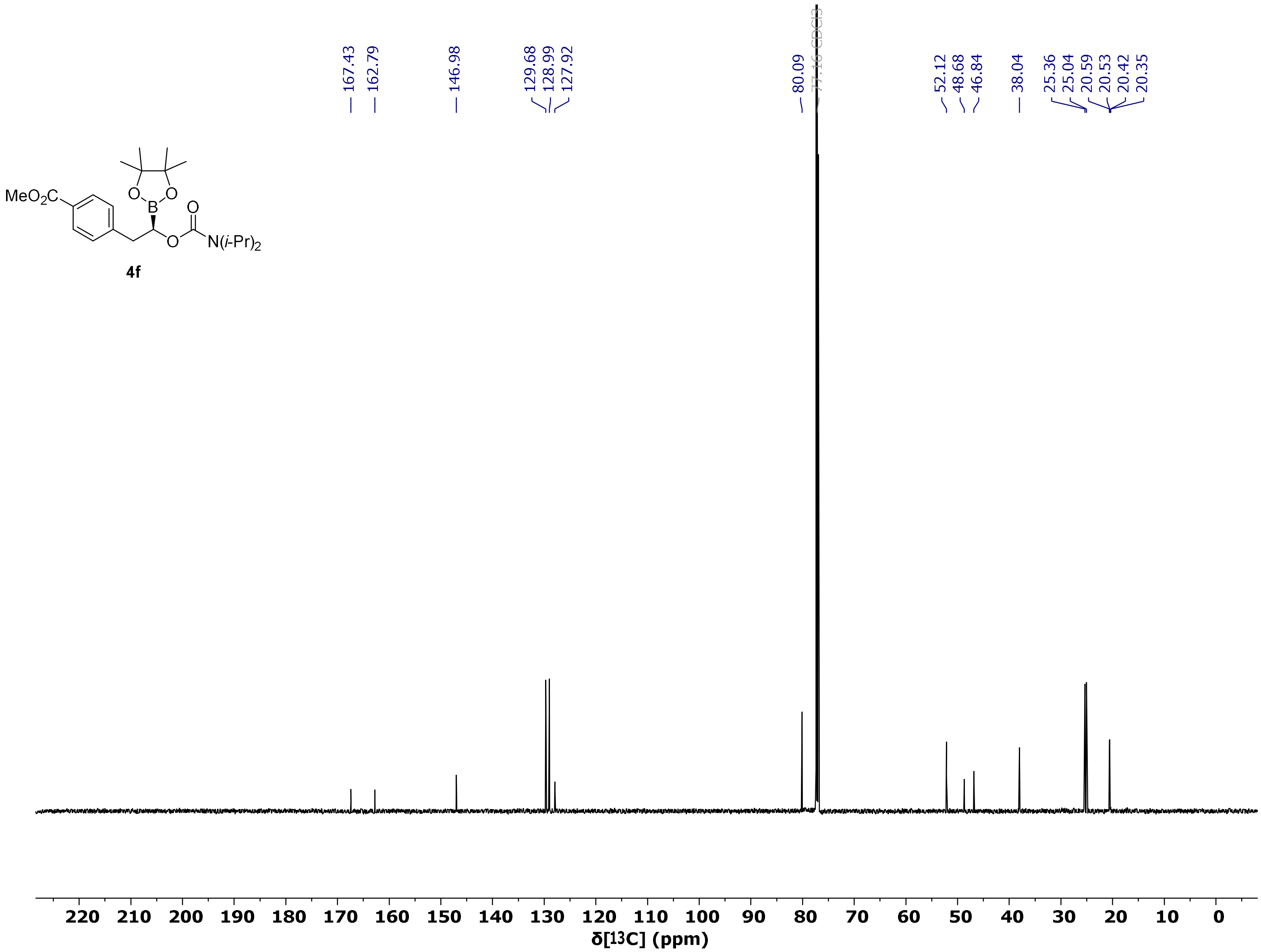
^{1}H NMR (400 MHz, CDCl$_3$)



4f

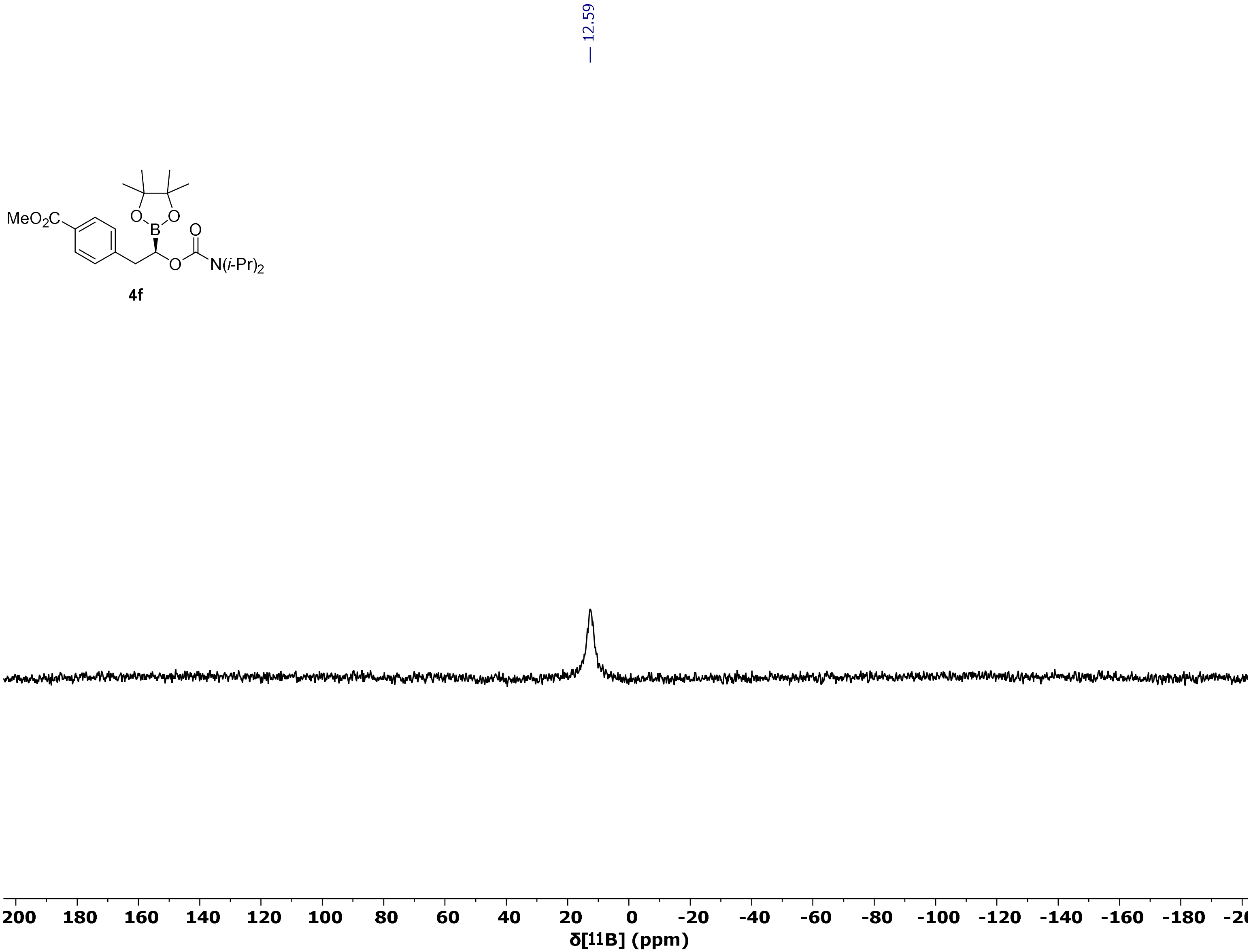


^{13}C NMR (151 MHz, $CDCl_3$)



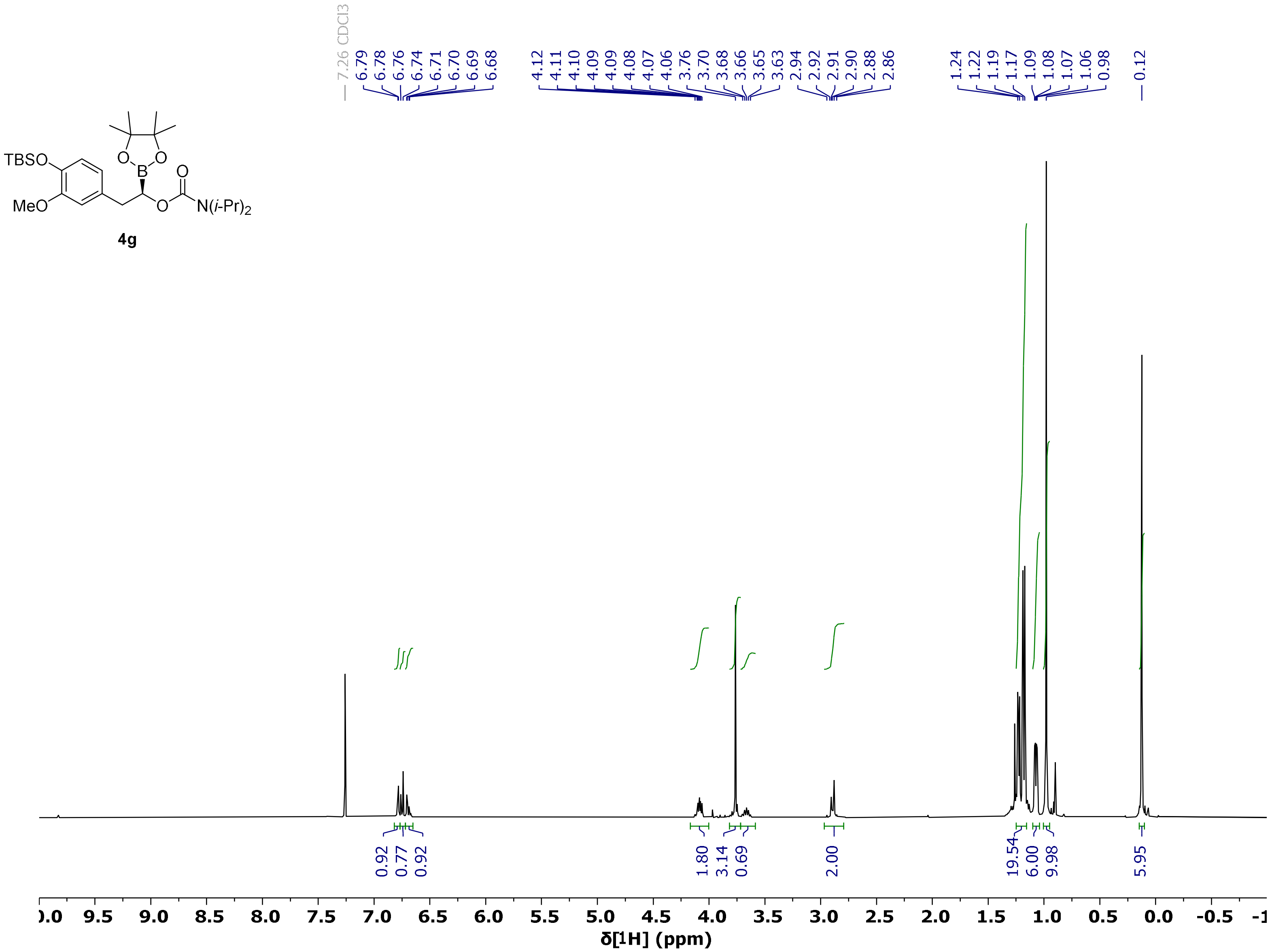
4f

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



4f

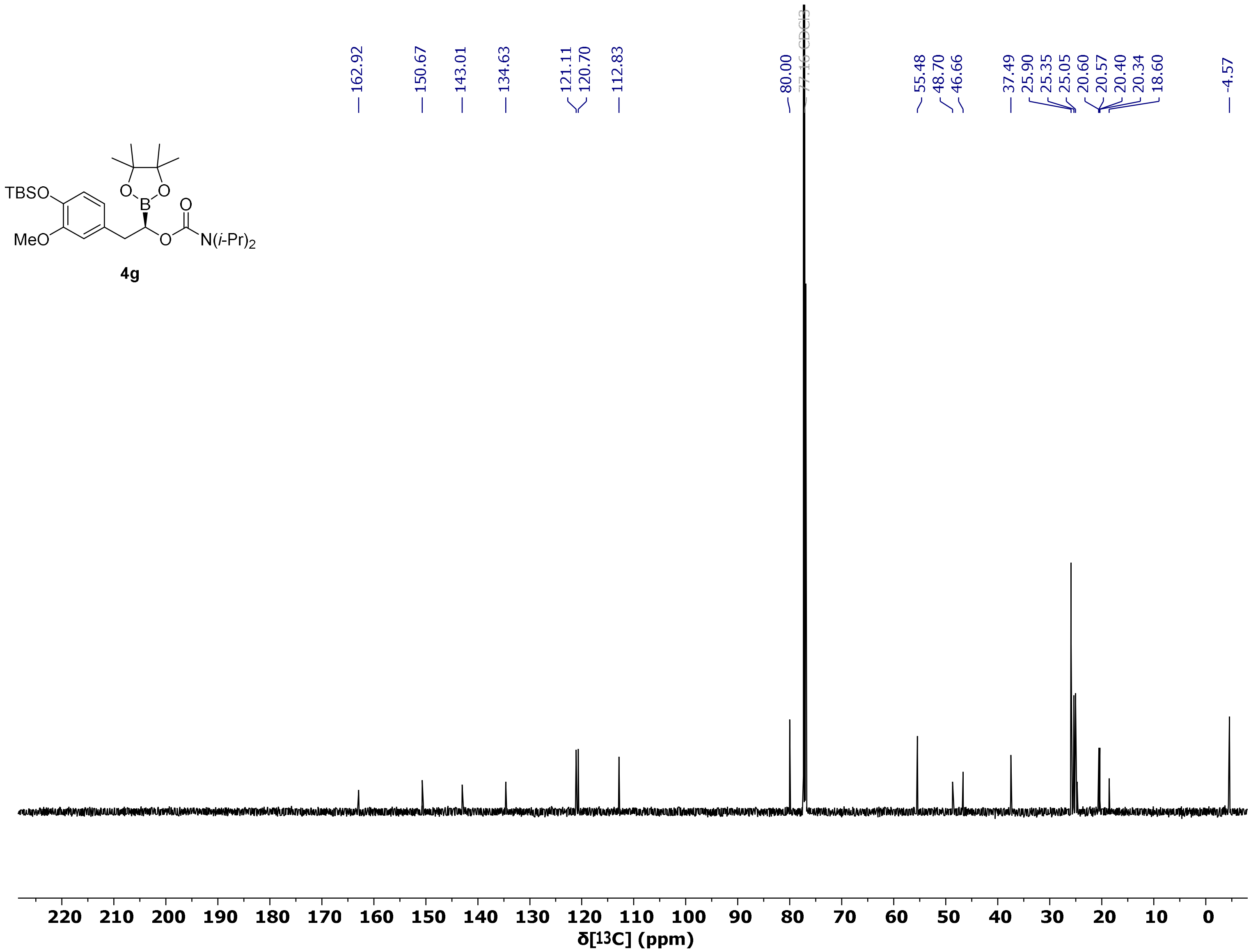
^{1}**H NMR** (400 MHz, CDCl$_3$)



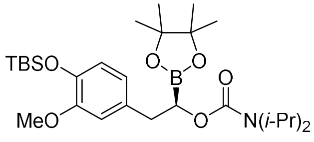
4g

^{13}**C NMR** (151 MHz, $CDCl_3$)

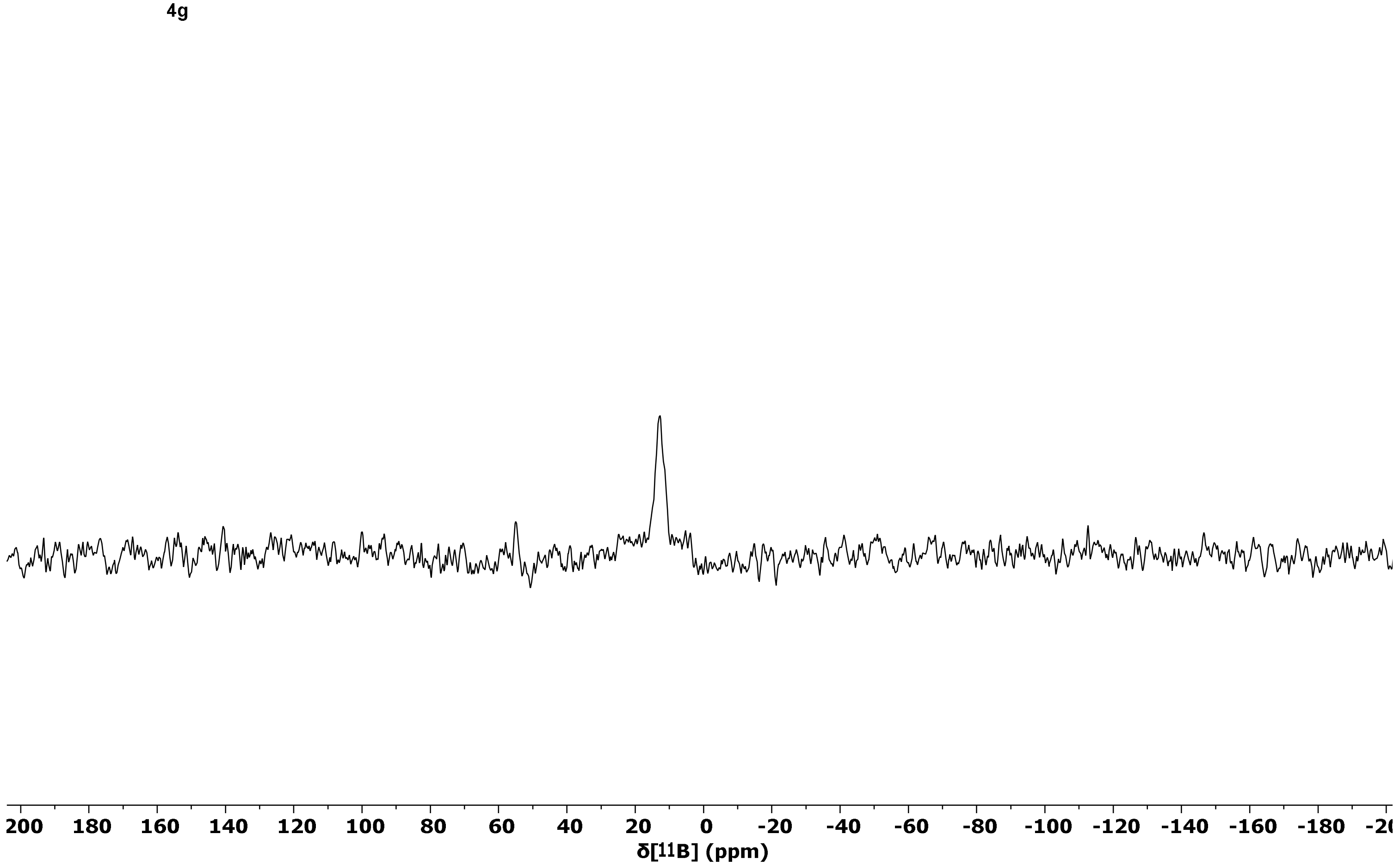
4g



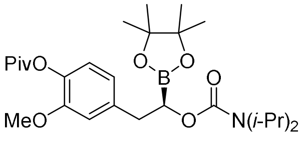
^{11}**B NMR** (128 MHz, $CDCl_3$)



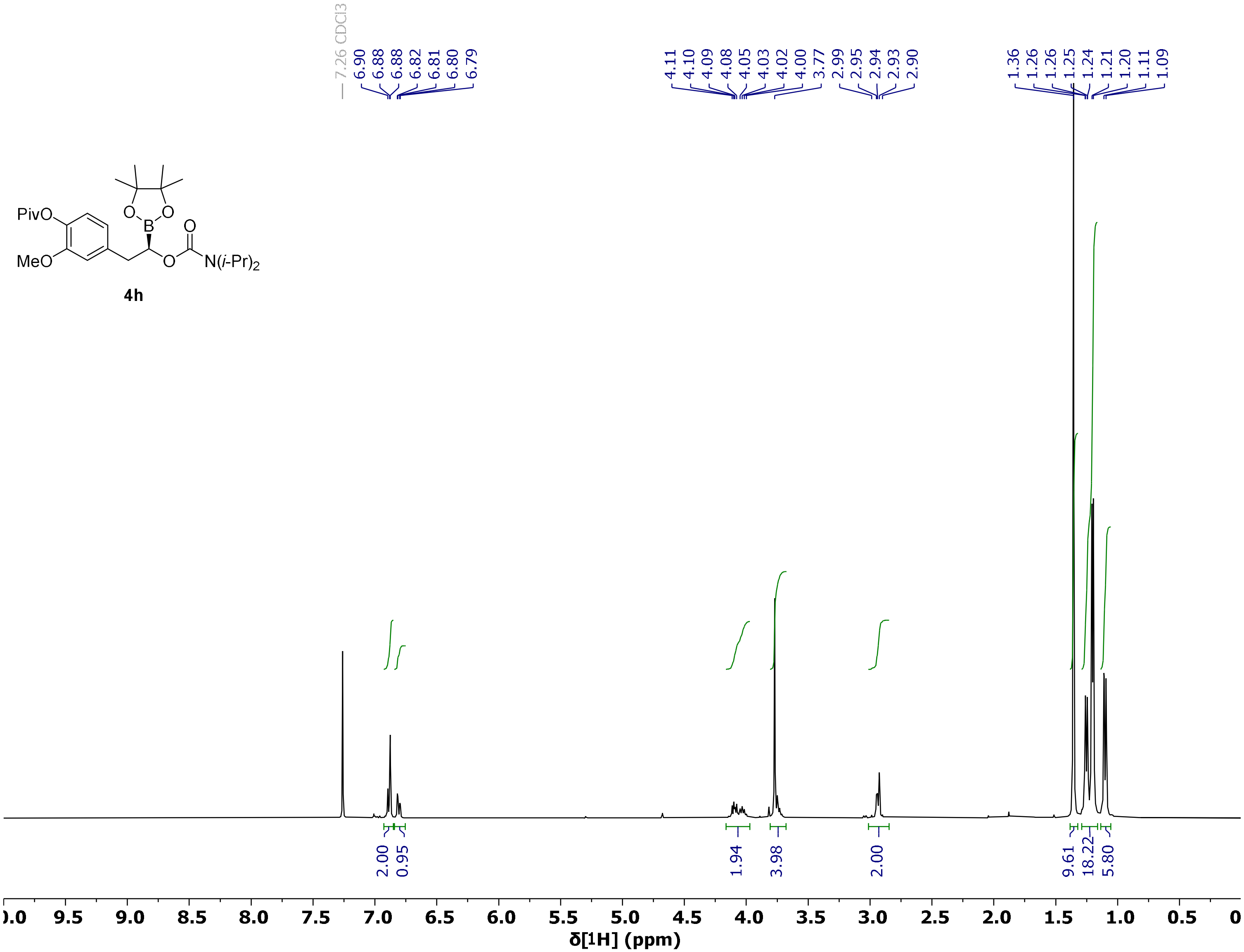
4g



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

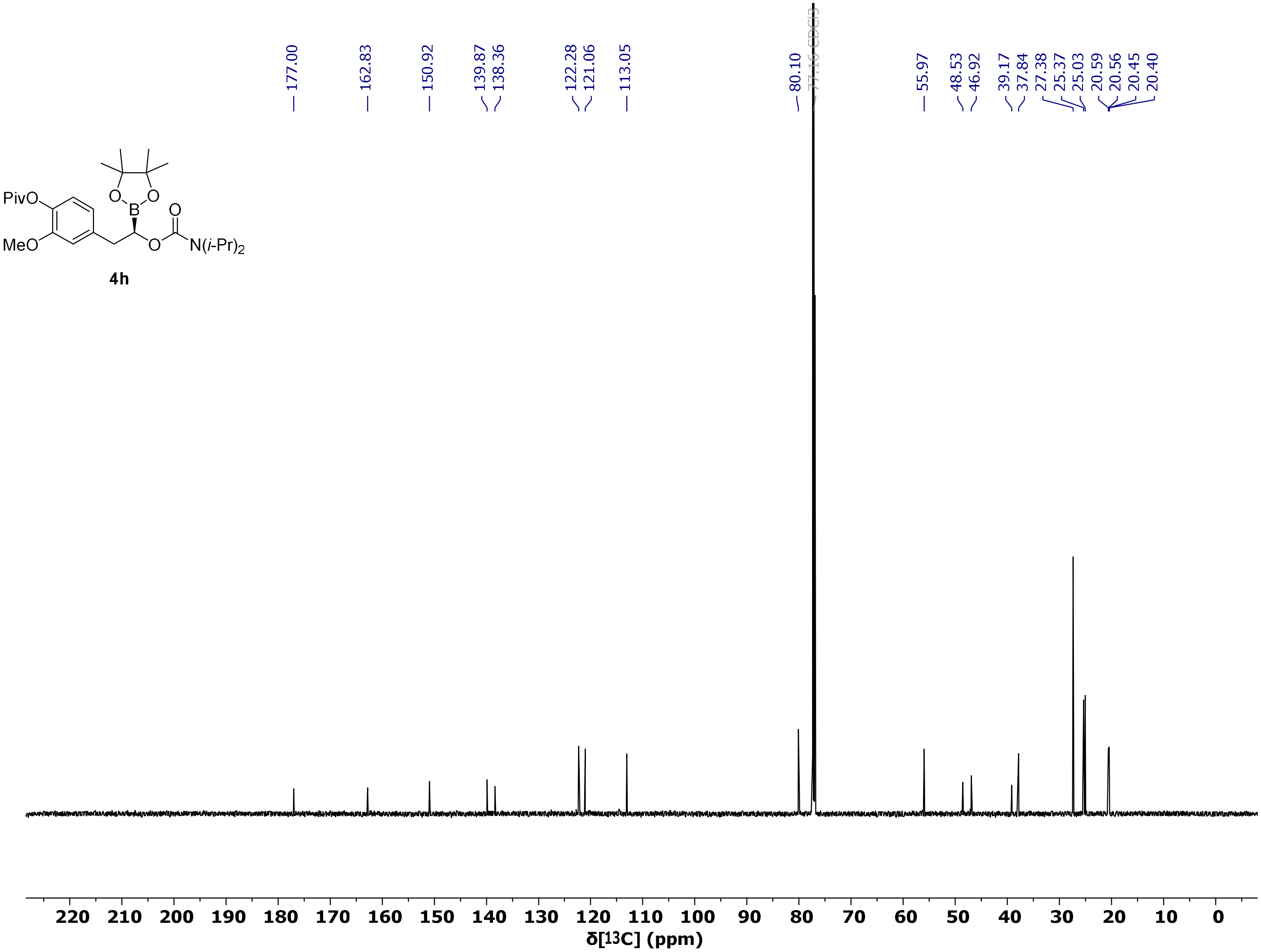


4h

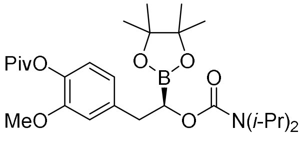


^{13}**C NMR** (151 MHz, $CDCl_3$)

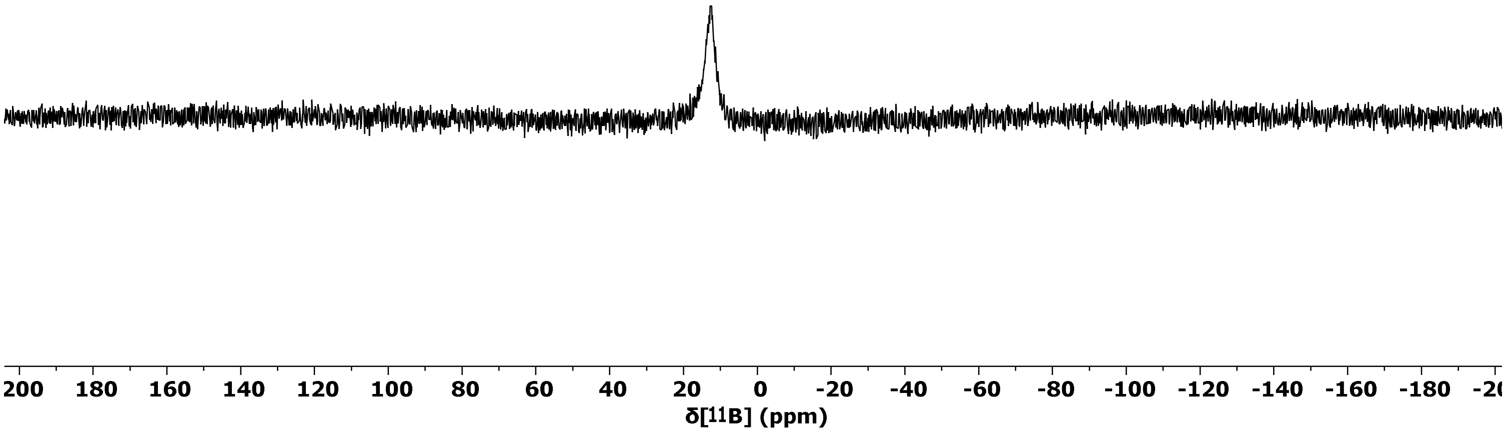
4h



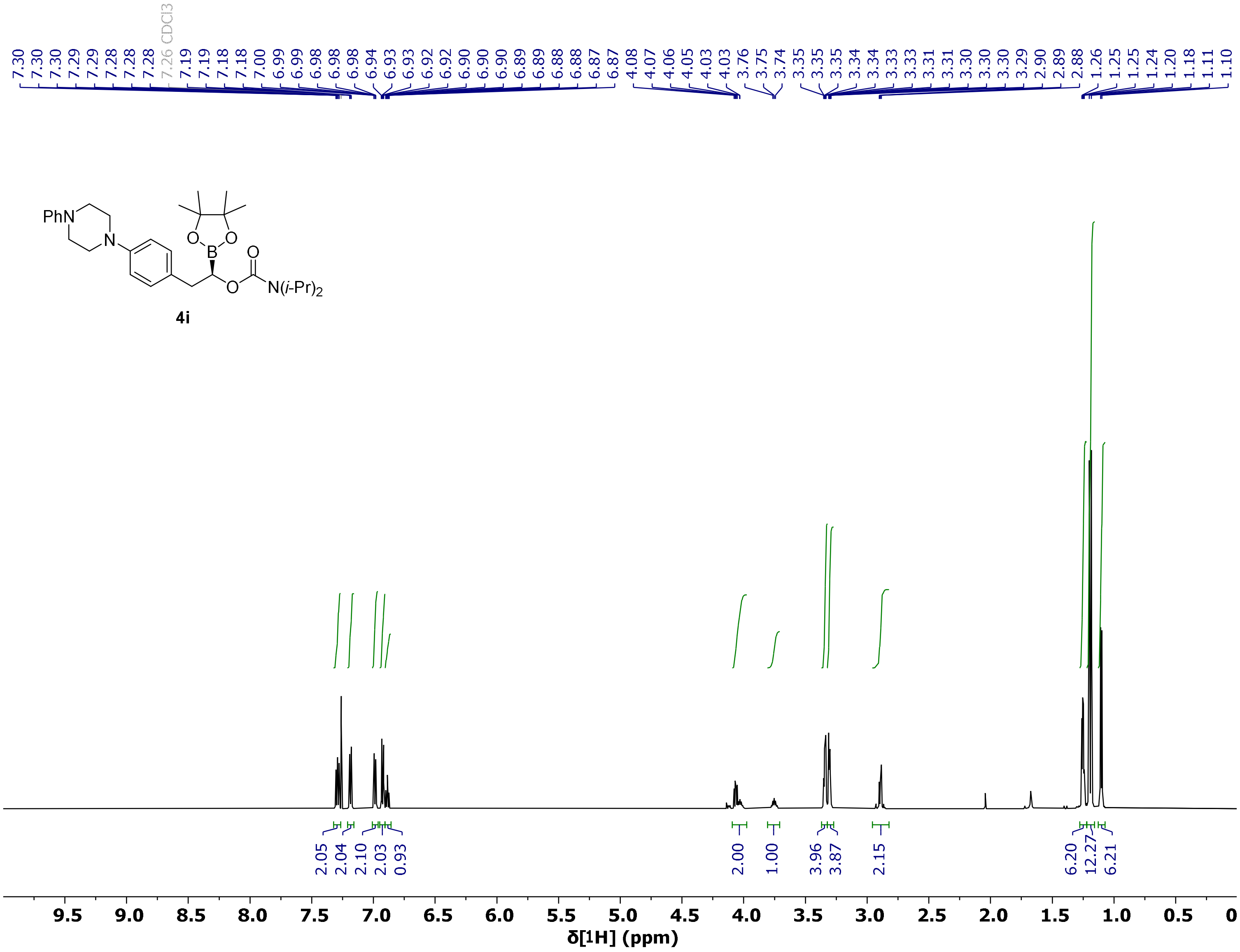
^{11}B NMR (128 MHz, CDCl$_3$)



4h

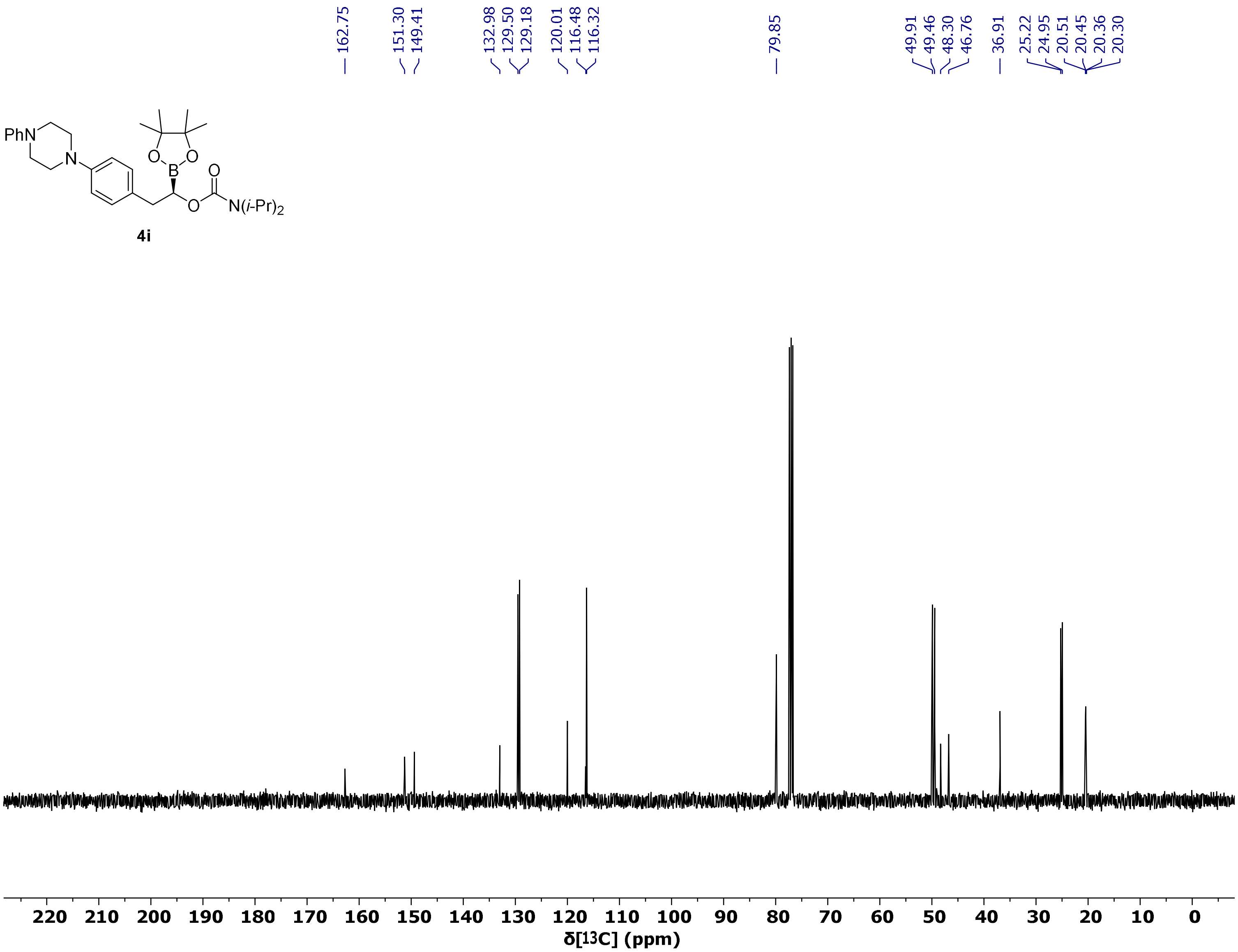


^{1}H NMR (600 MHz, $CDCl_3$)



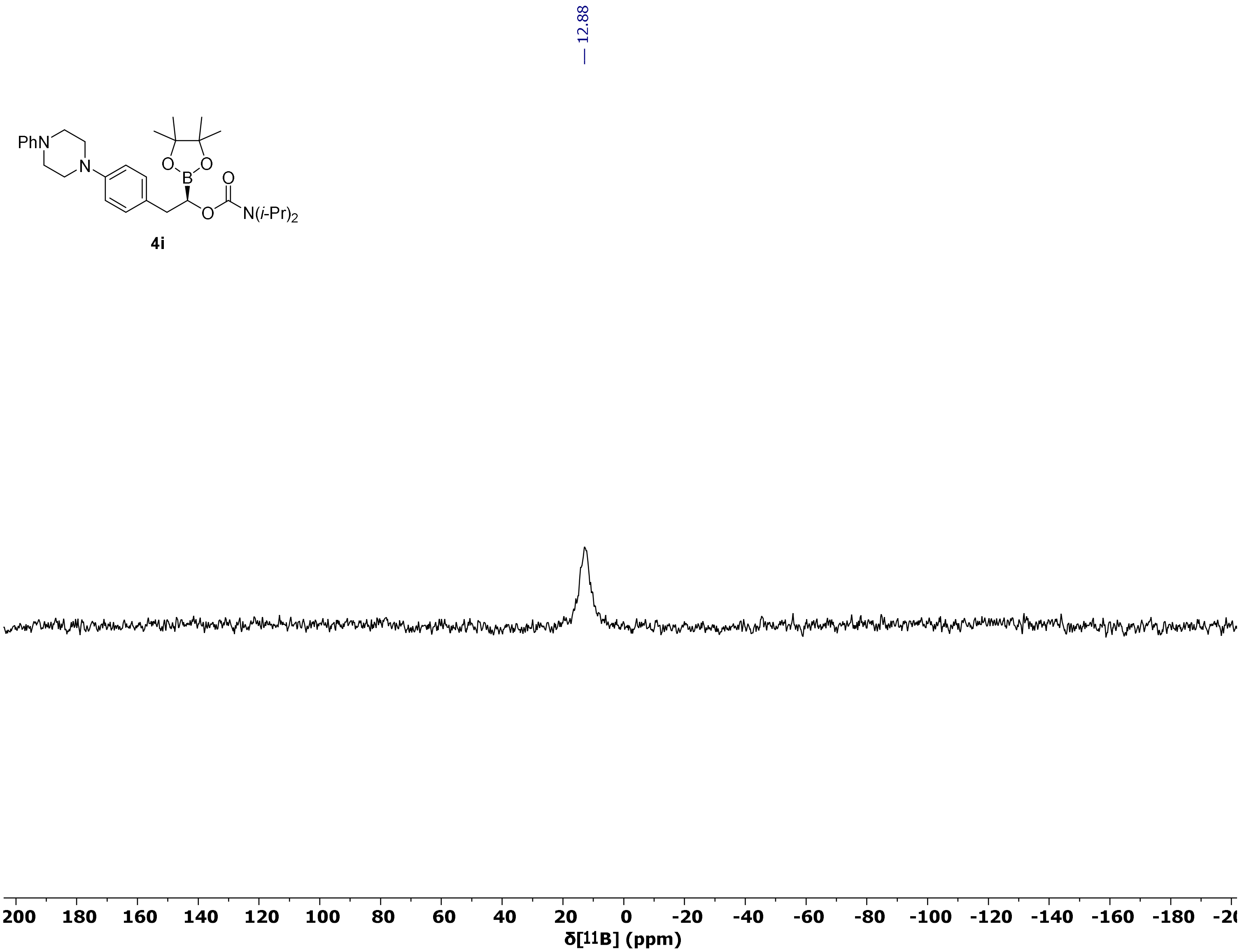
4i

^{13}C NMR (101 MHz, CDCl$_3$)



4i

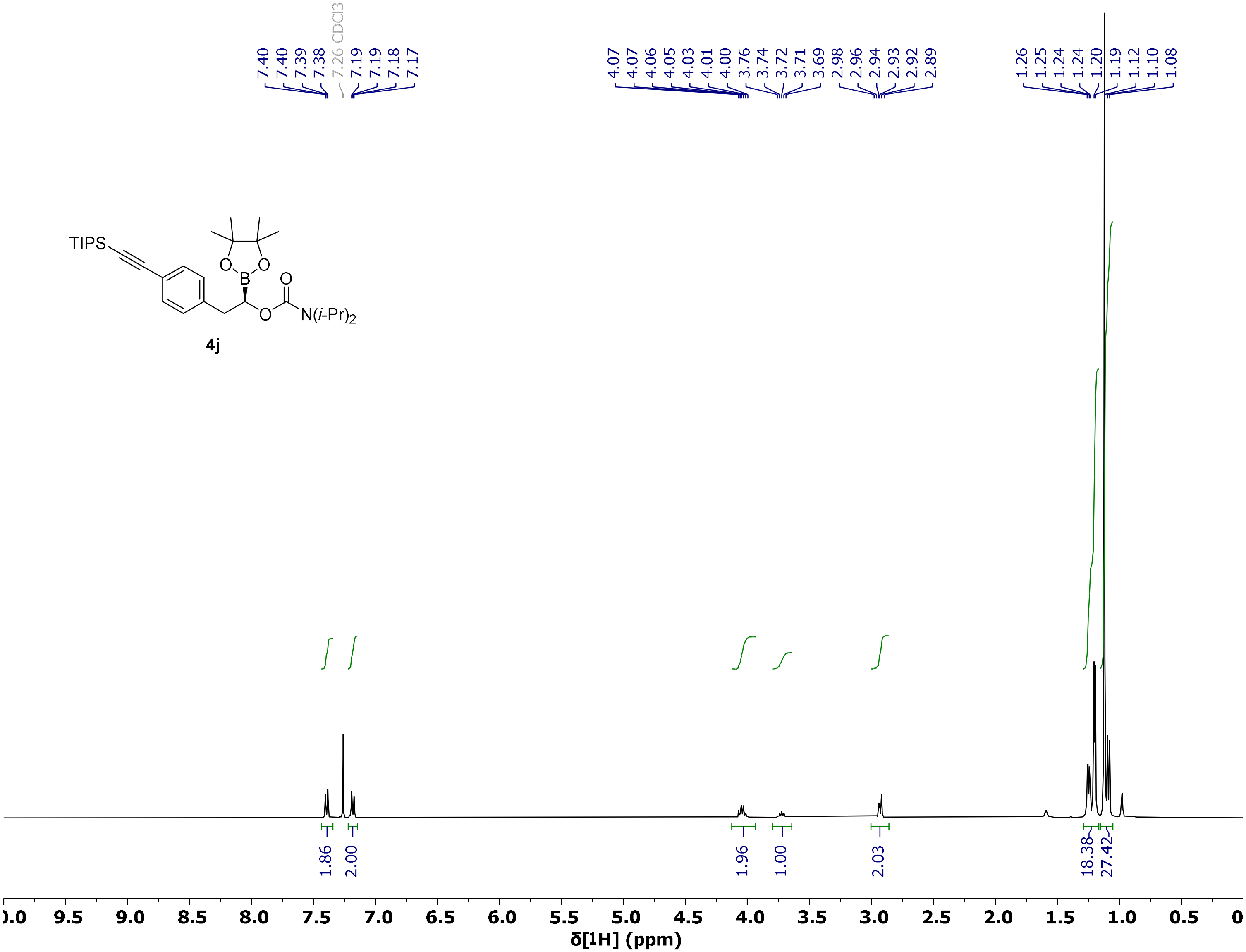
^{11}B NMR (128 MHz, $CDCl_3$)



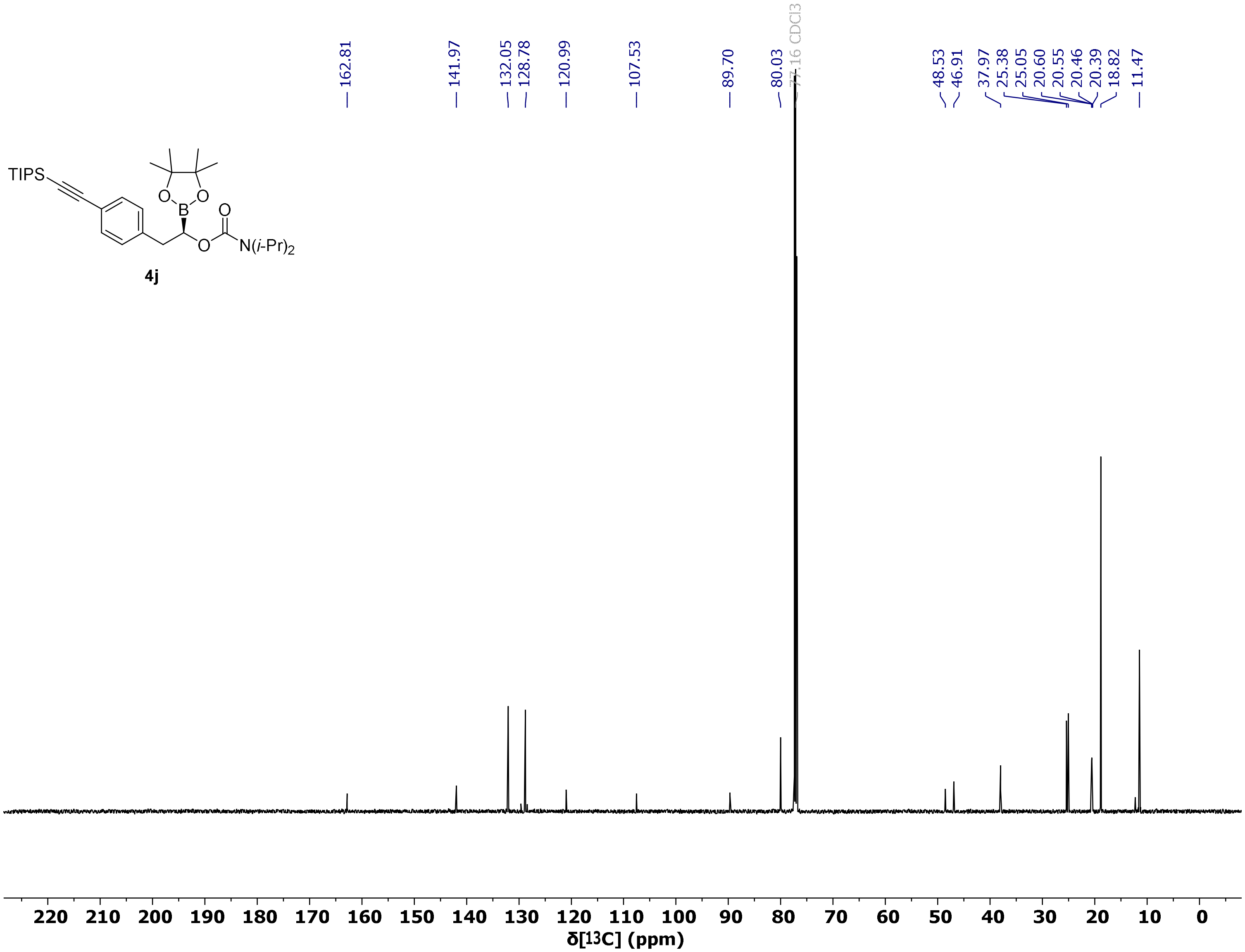
4i

^{1}H NMR (400 MHz, CDCl$_3$)

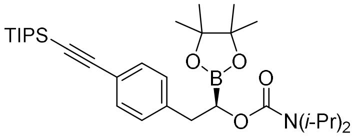
4j



^{13}C NMR (151 MHz, $CDCl_3$)



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



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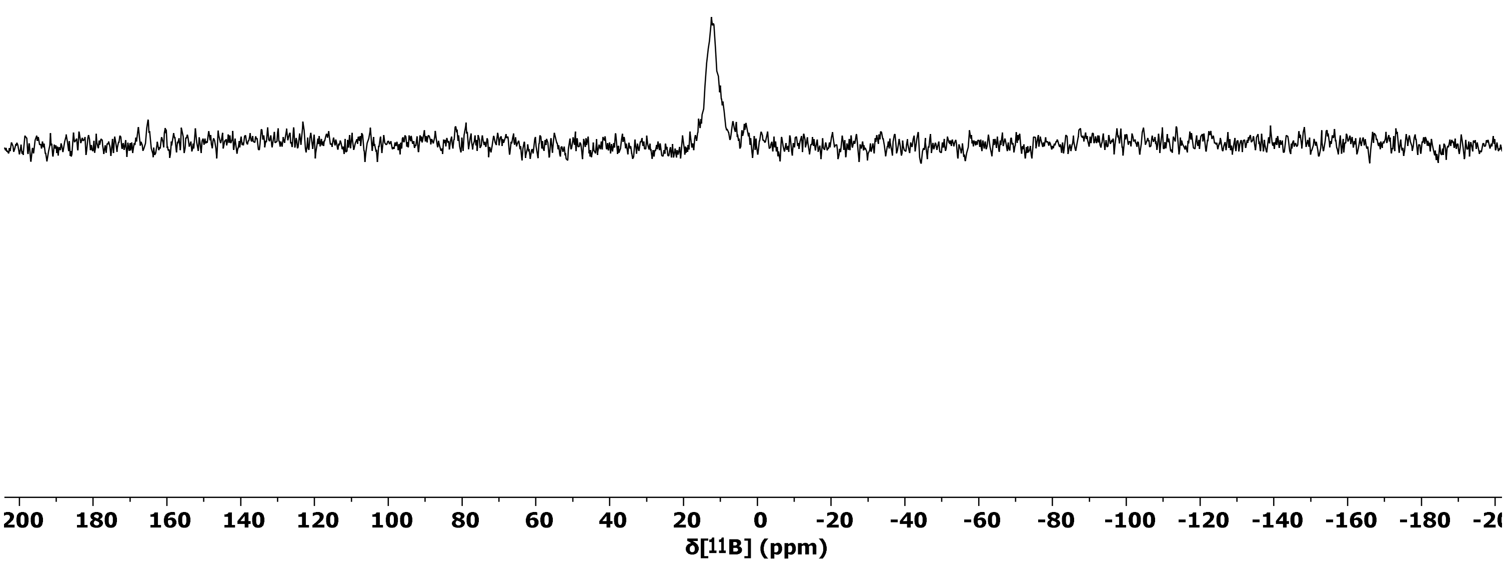
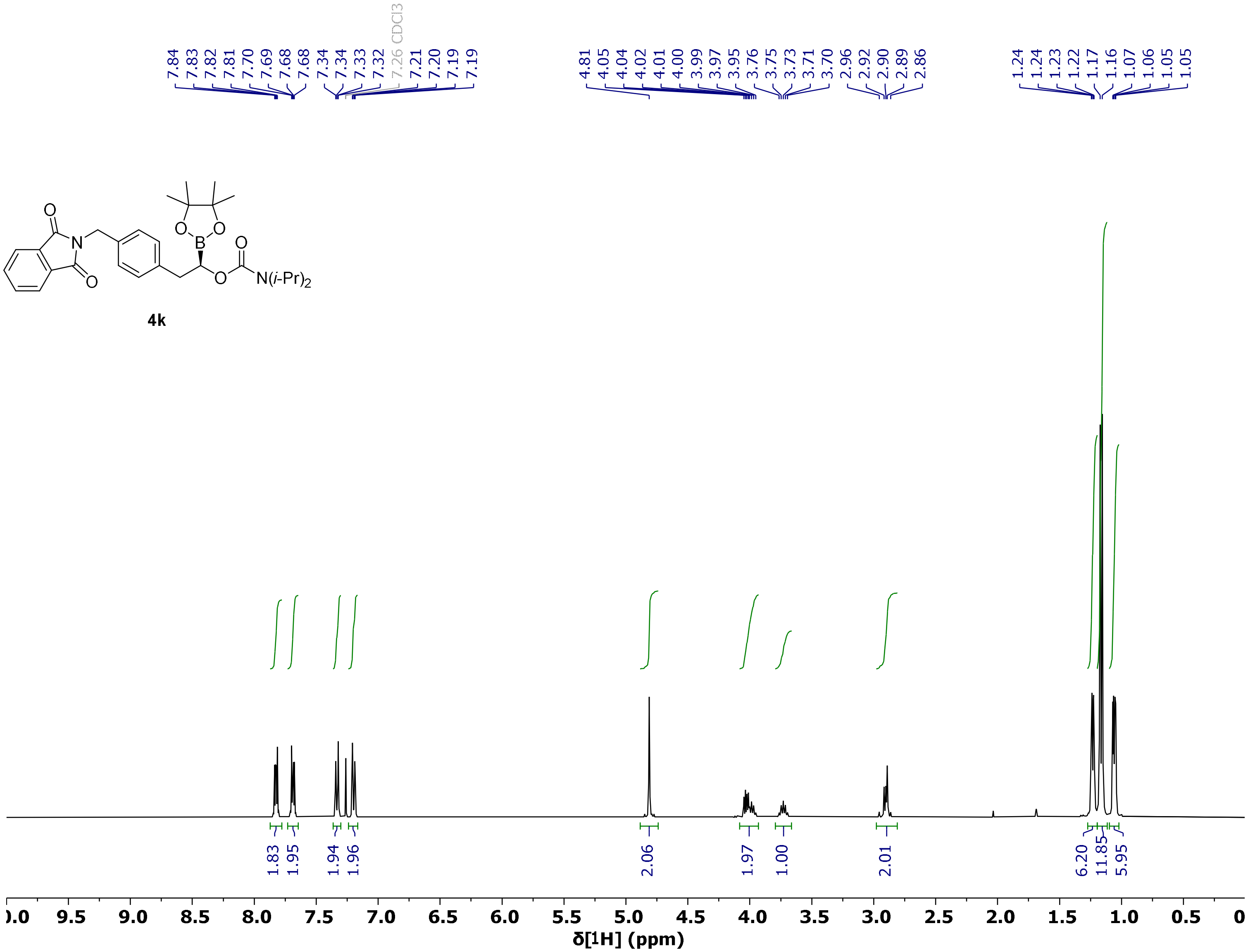
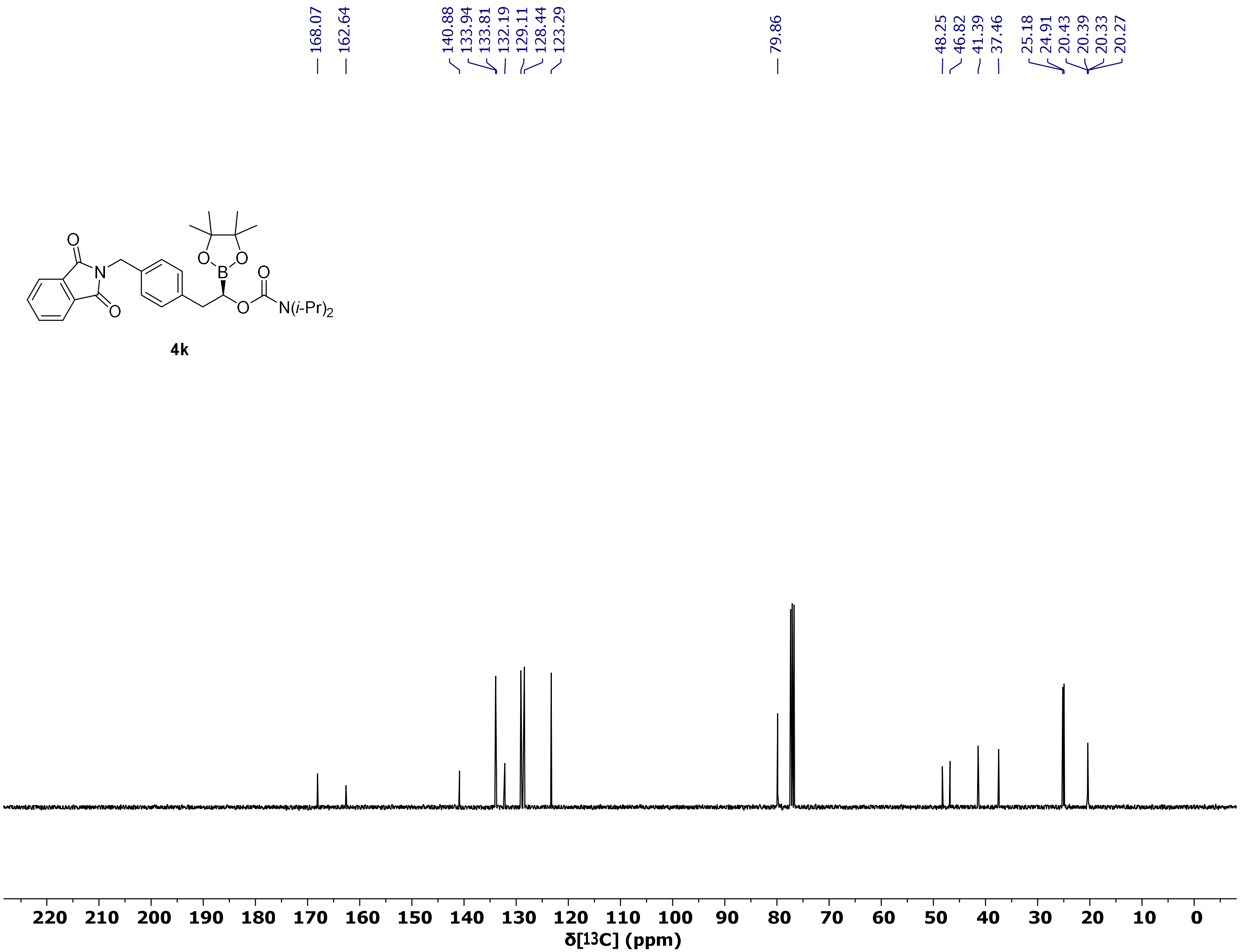


^{1}H NMR (400 MHz, $CDCl_3$)

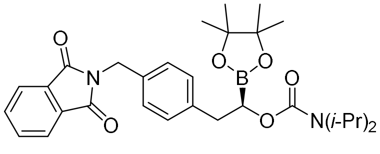
4k



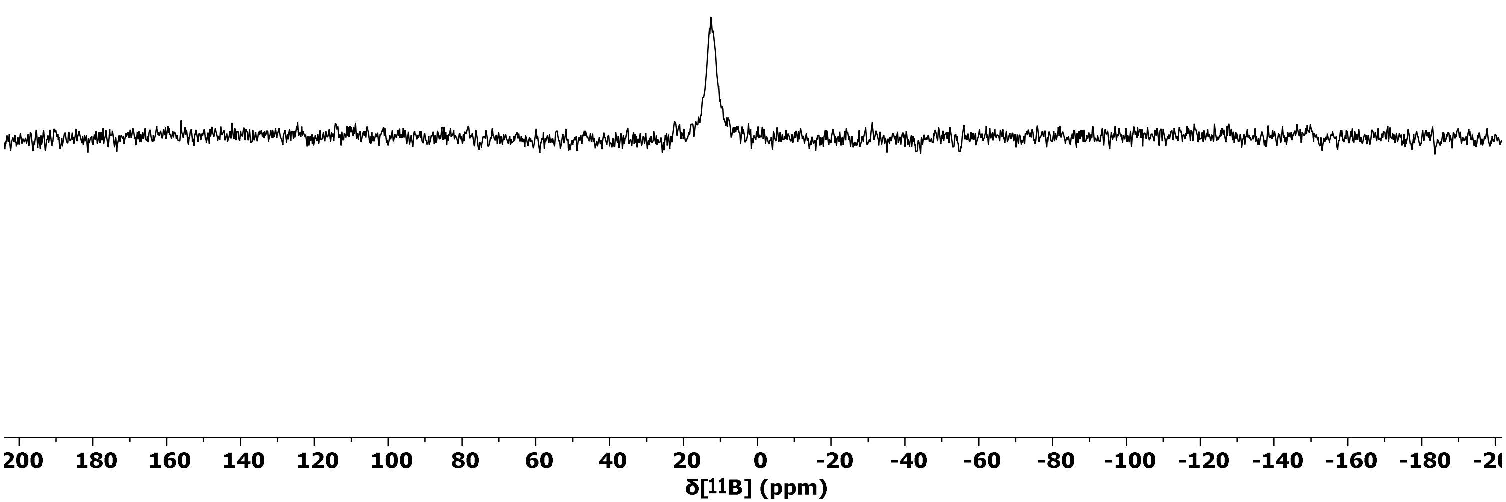
^{13}C NMR (101 MHz, CDCl$_3$)



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

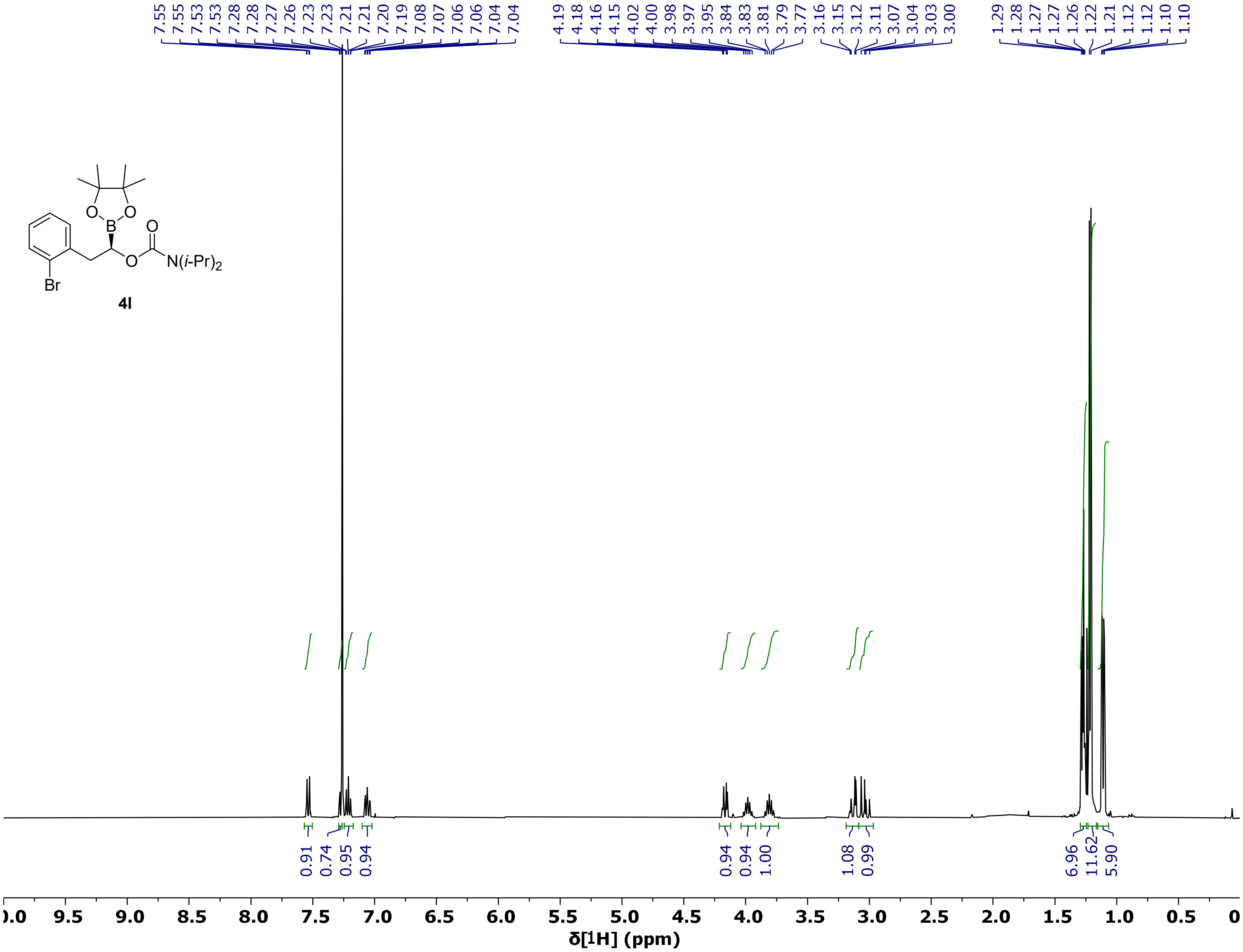


4k

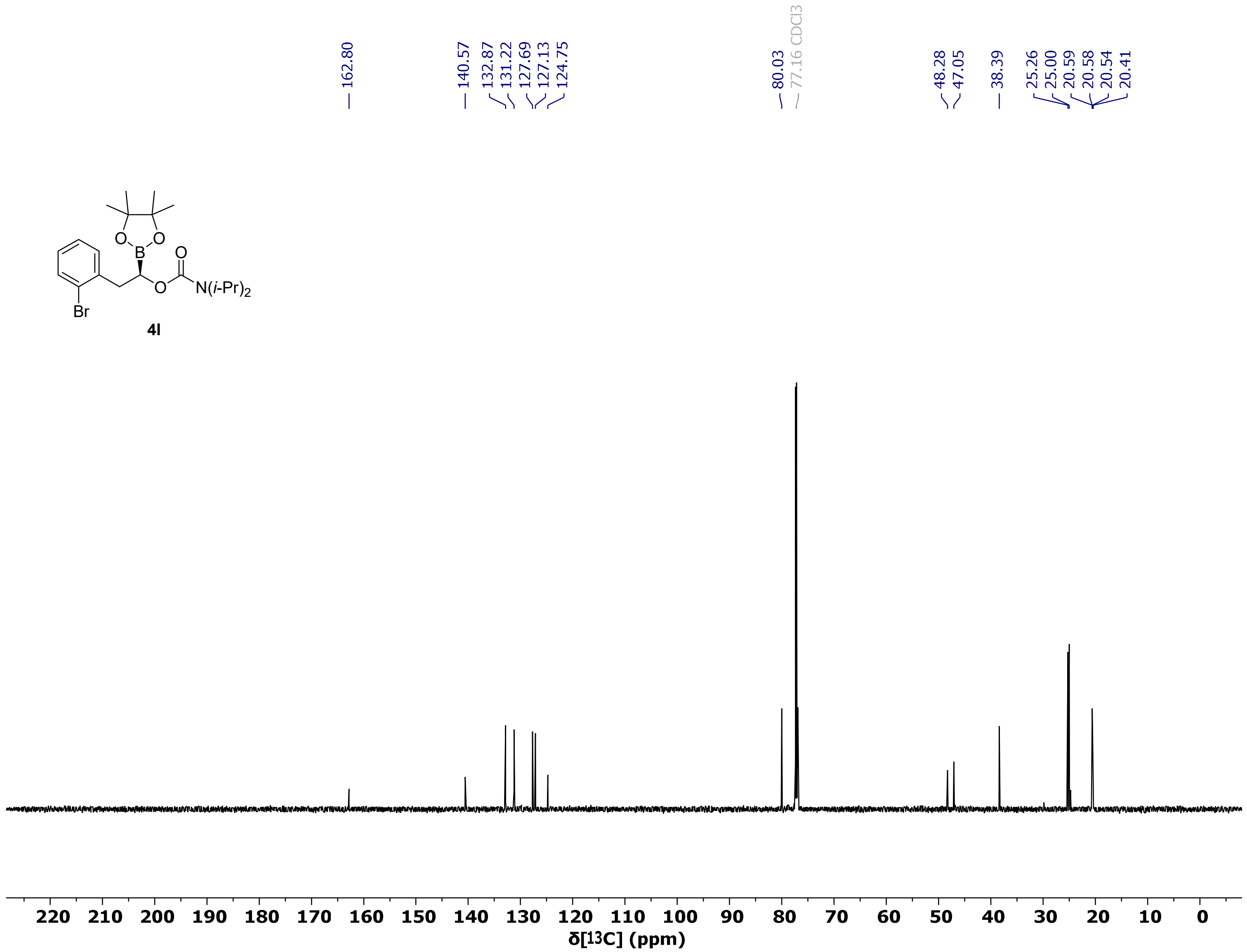


^{1}H NMR (400 MHz, $CDCl_3$)

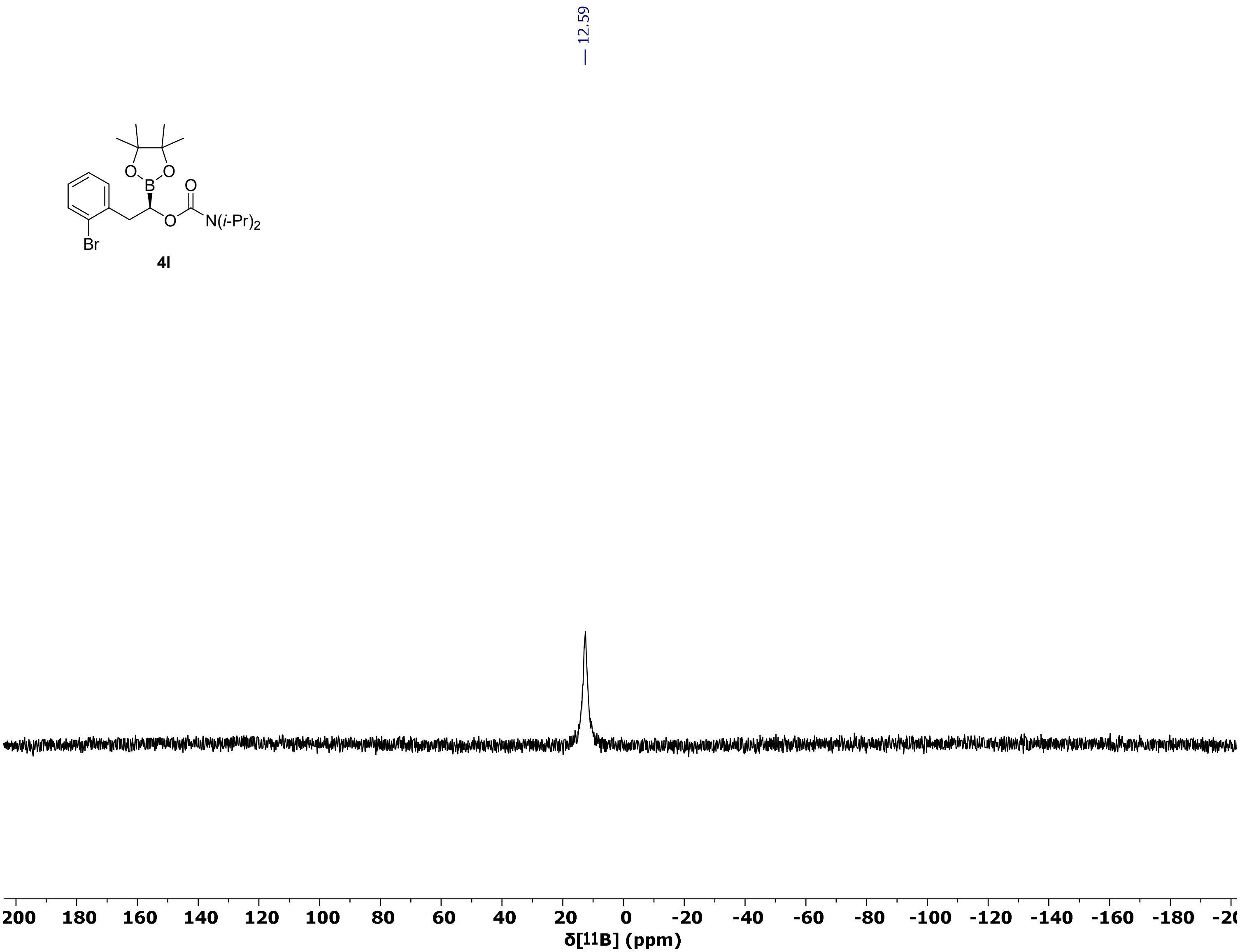
4l



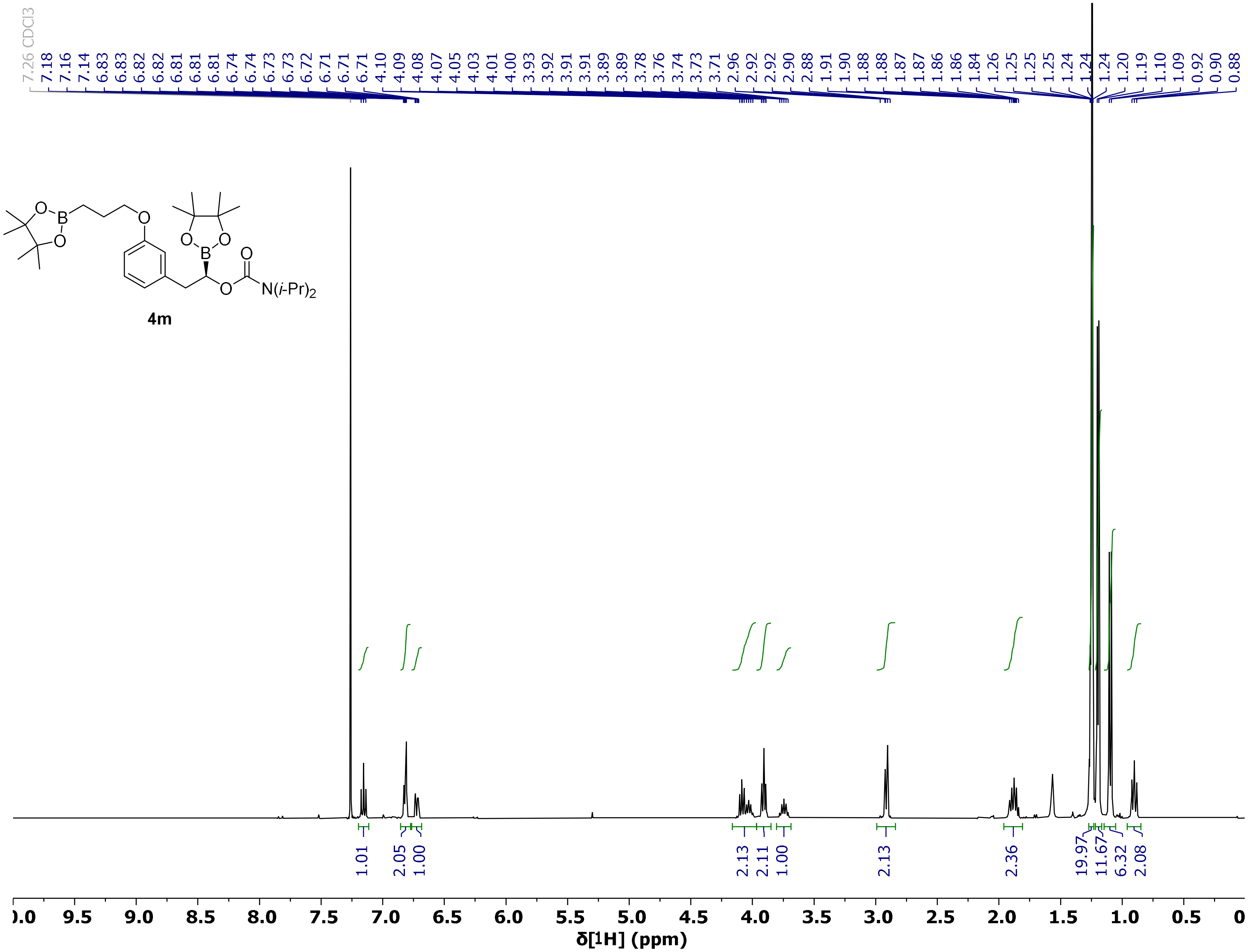
^{13}C NMR (151 MHz, $CDCl_3$)



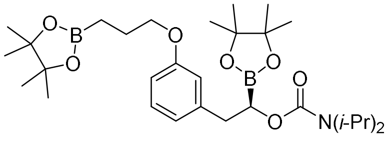
^{11}B NMR (128 MHz, $CDCl_3$)



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



^{13}C NMR (151 MHz, $CDCl_3$)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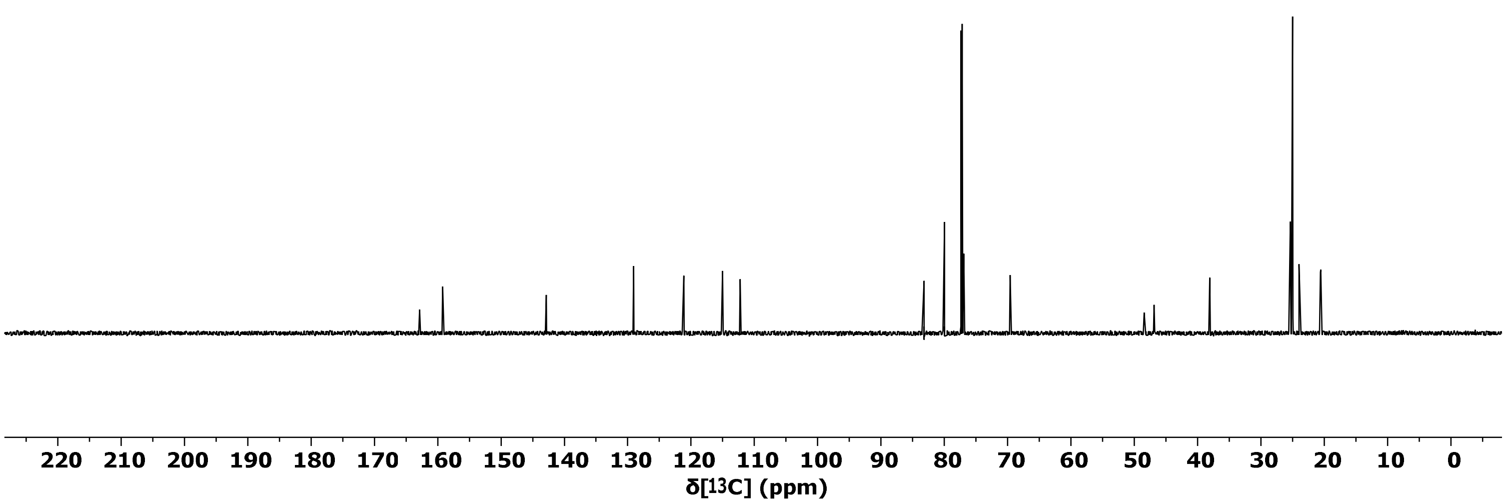
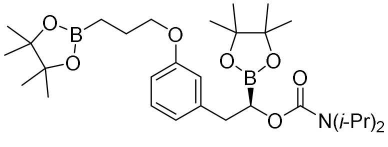


^{11}**B NMR** (128 MHz, $CDCl_3$)



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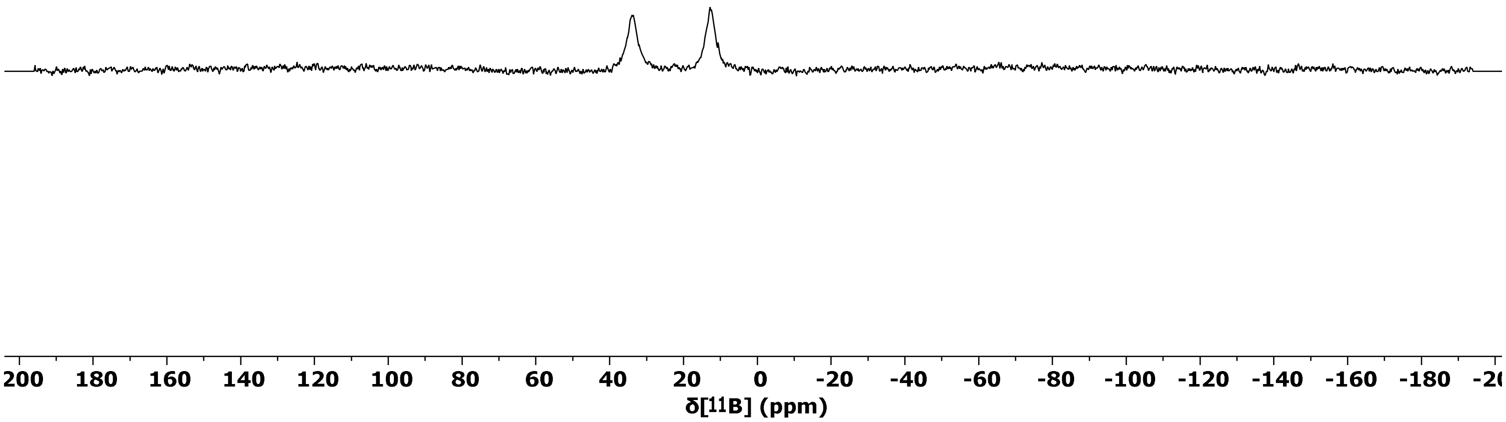
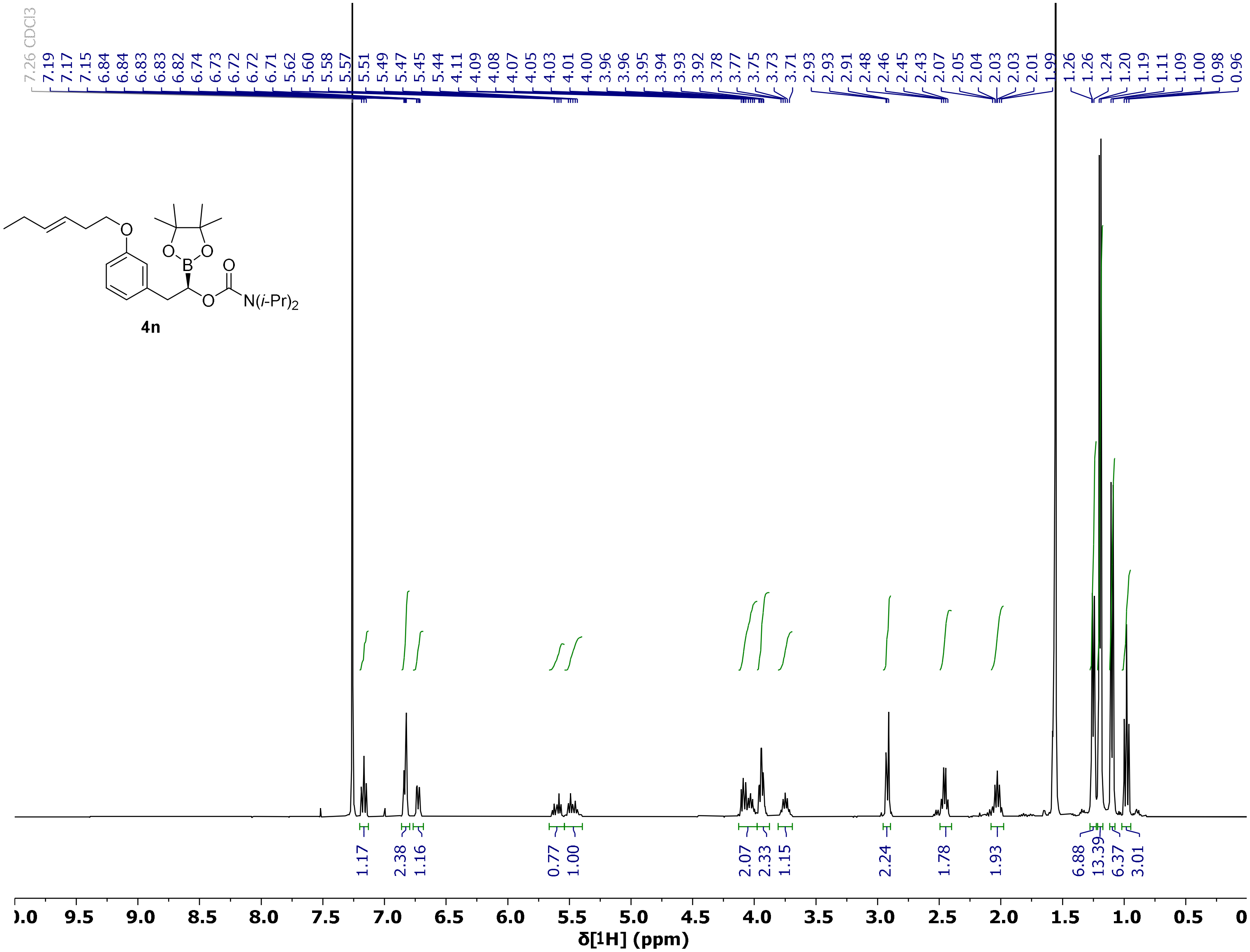
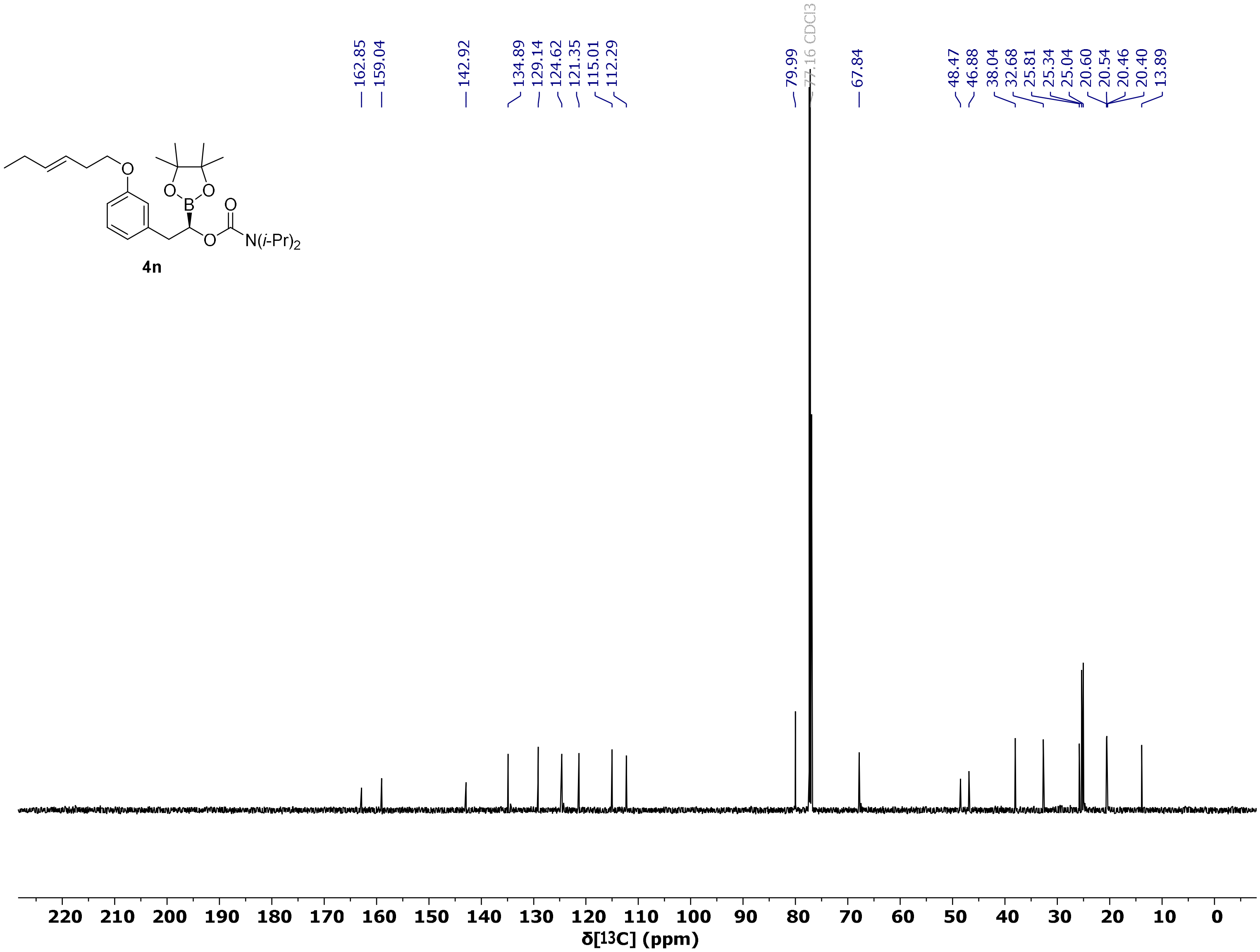


^{1}H NMR (400 MHz, CDCl$_3$)

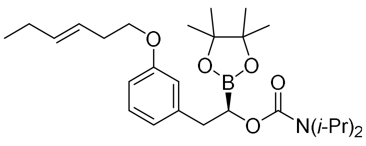


^{13}C NMR (151 MHz, $CDCl_3$)



4n

^{11}B NMR (128 MHz, CDCl$_3$)



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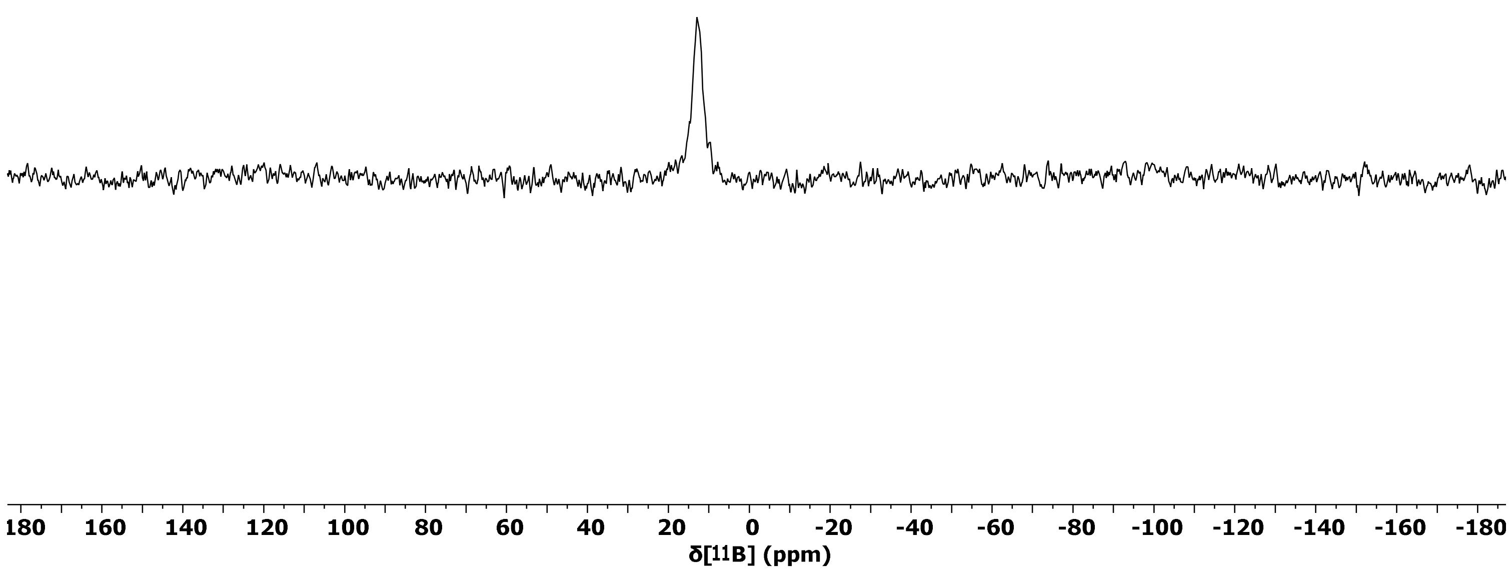
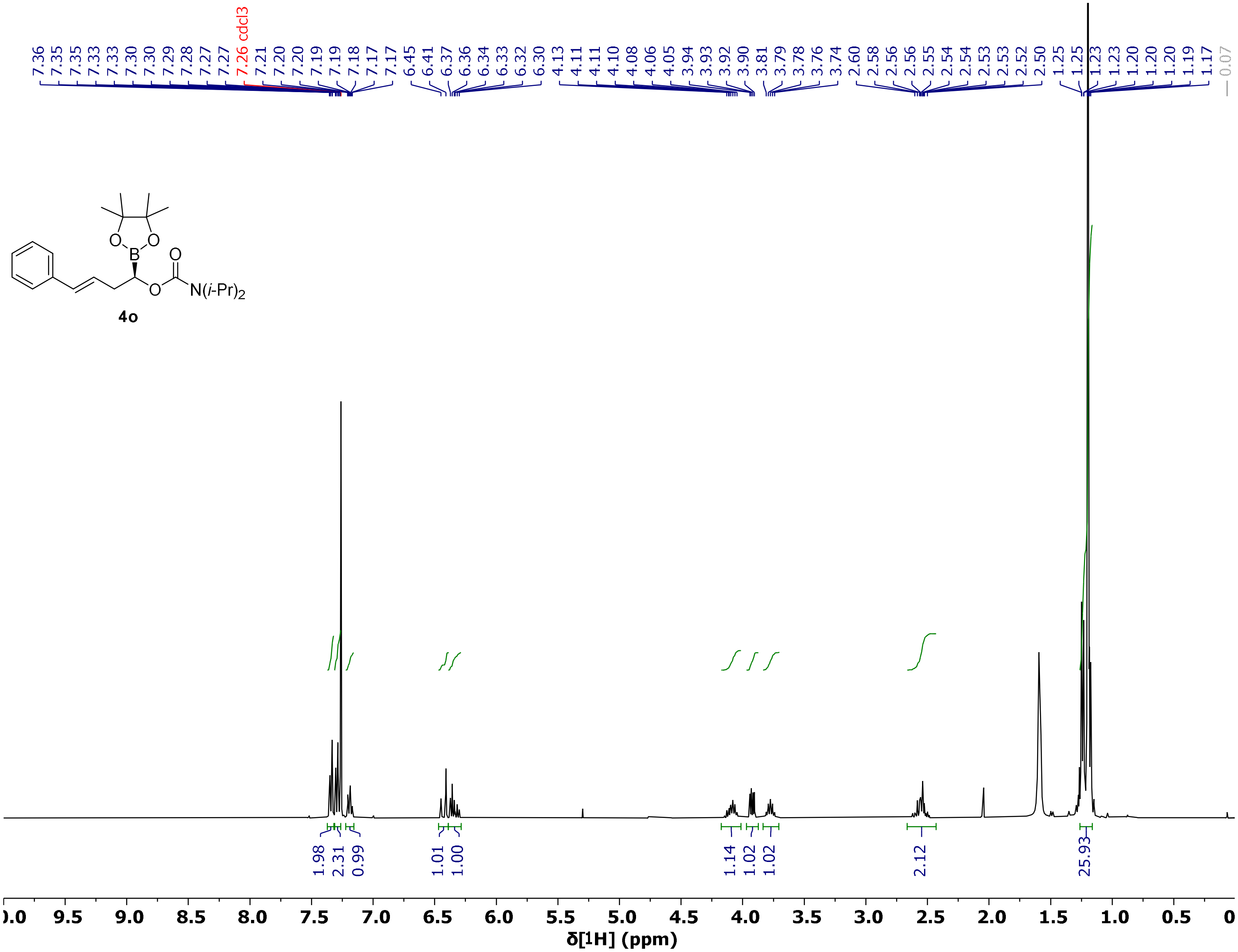
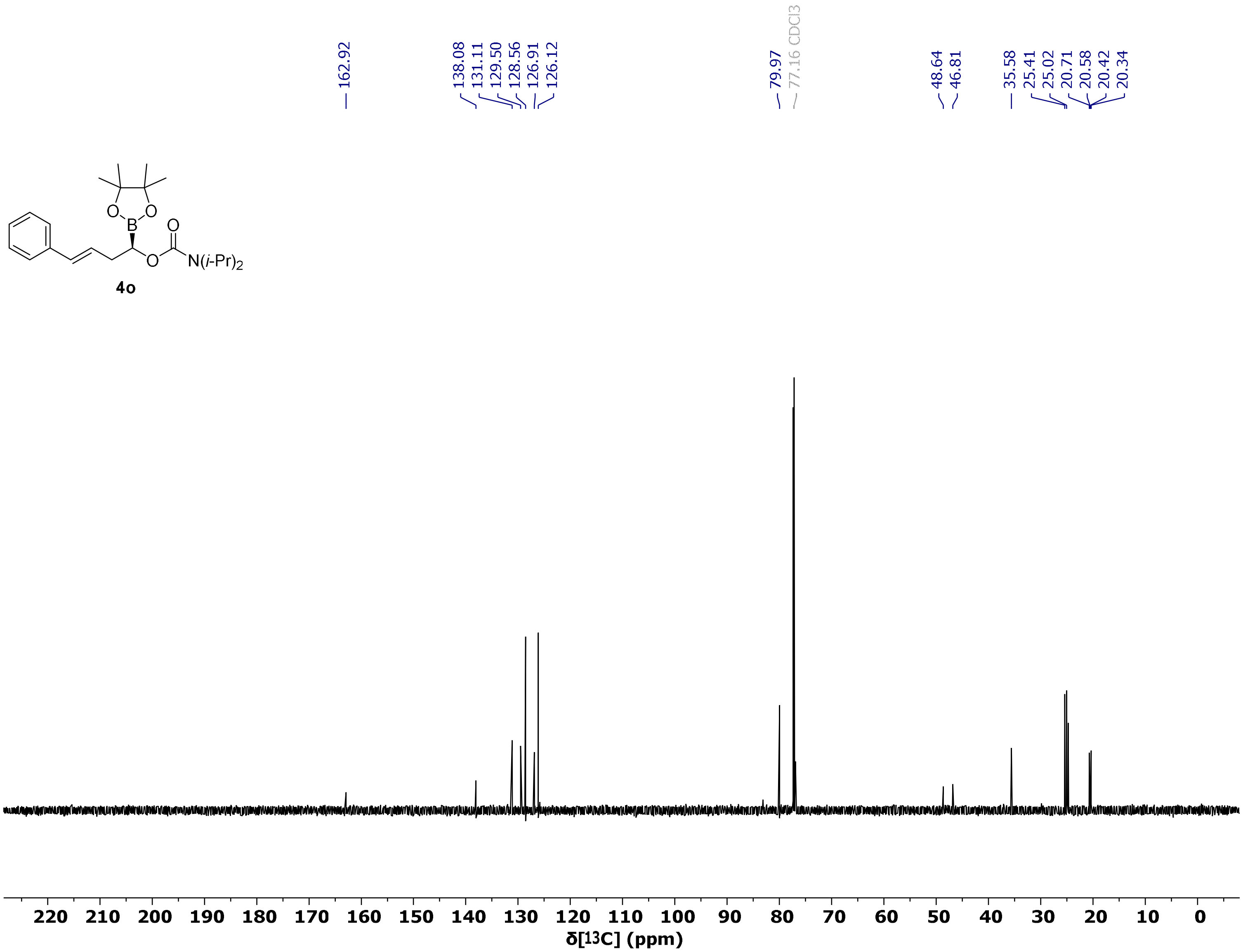


^{1}H NMR (400 MHz, $CDCl_3$)



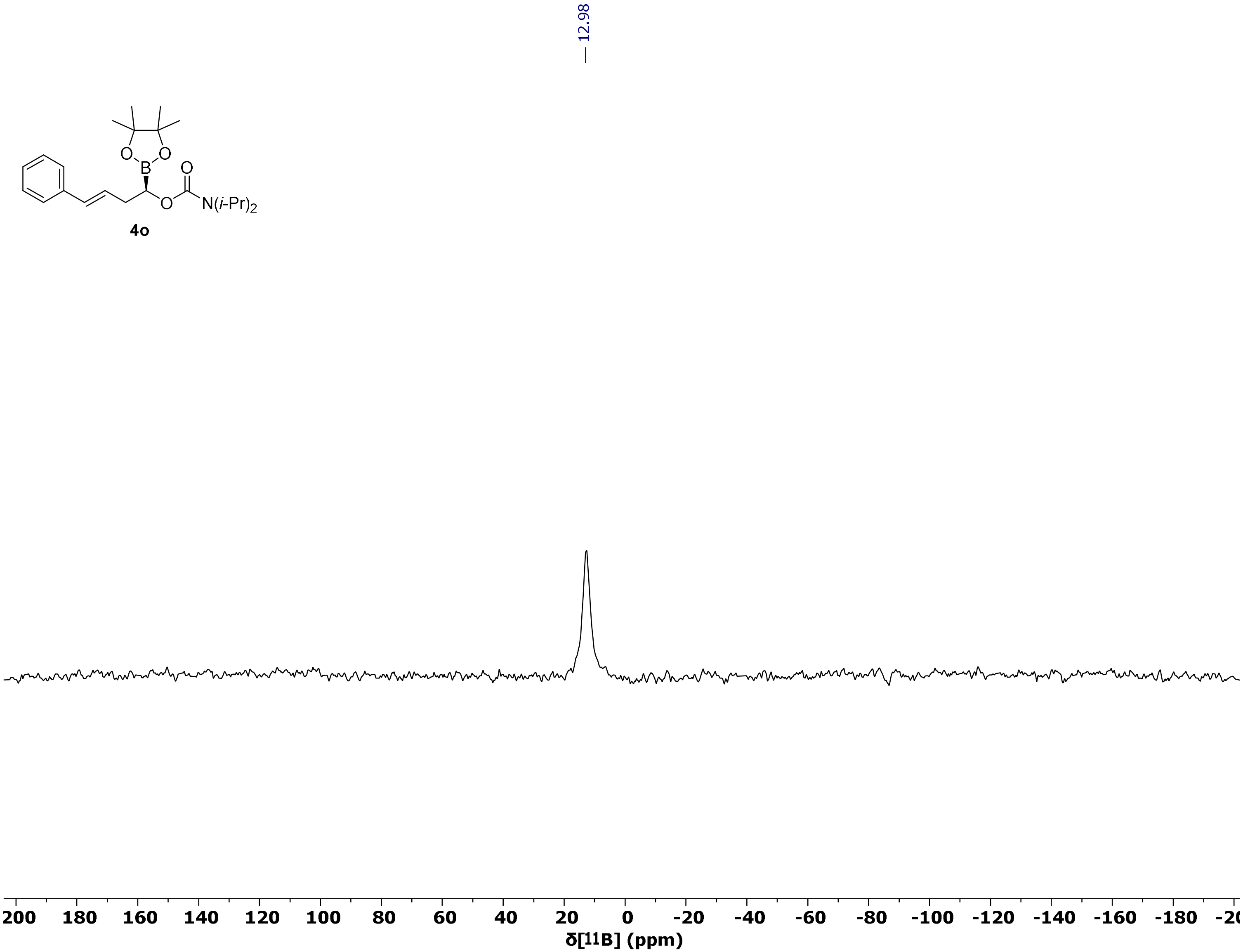
^{13}C NMR (151 MHz, $CDCl_3$)



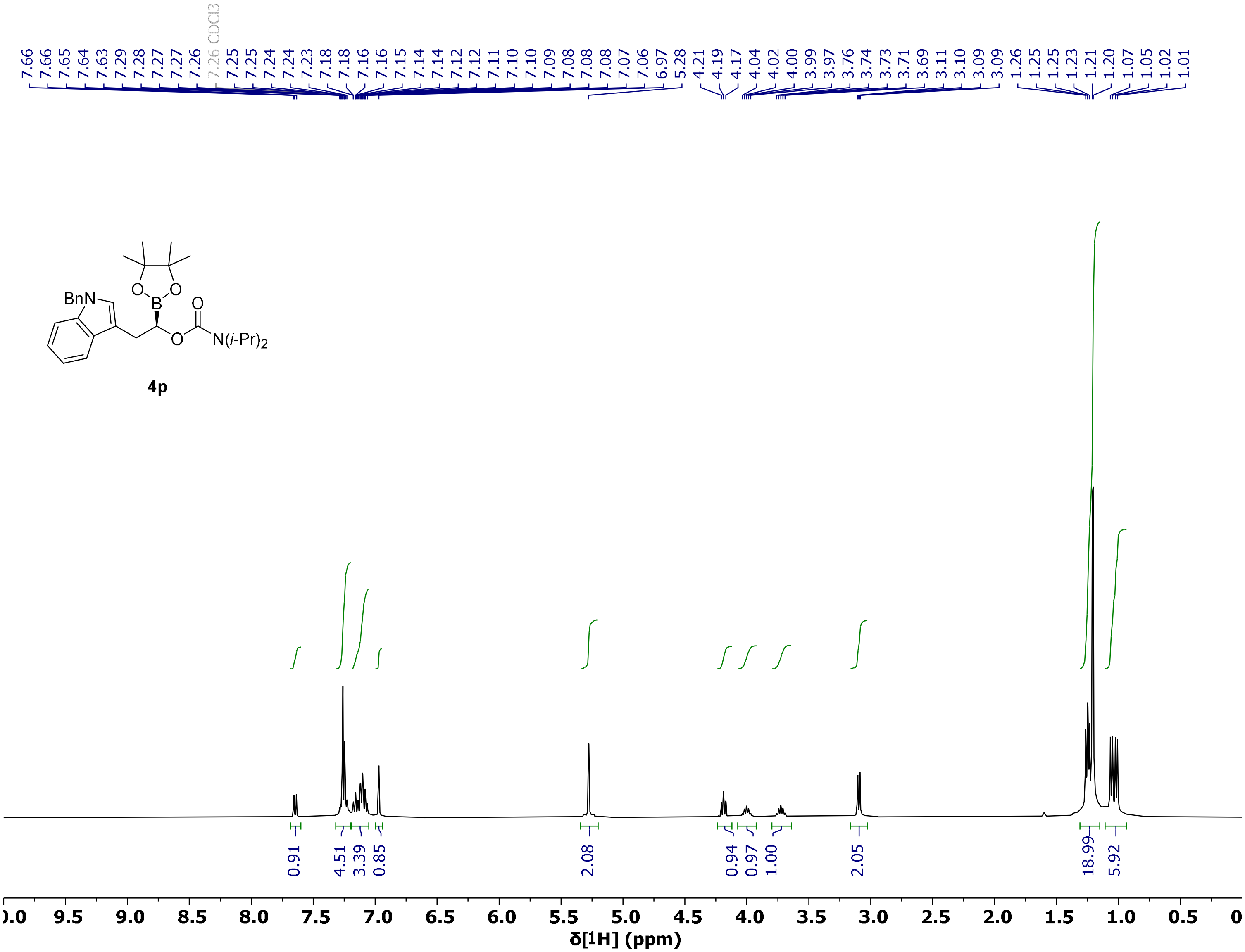
4o

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

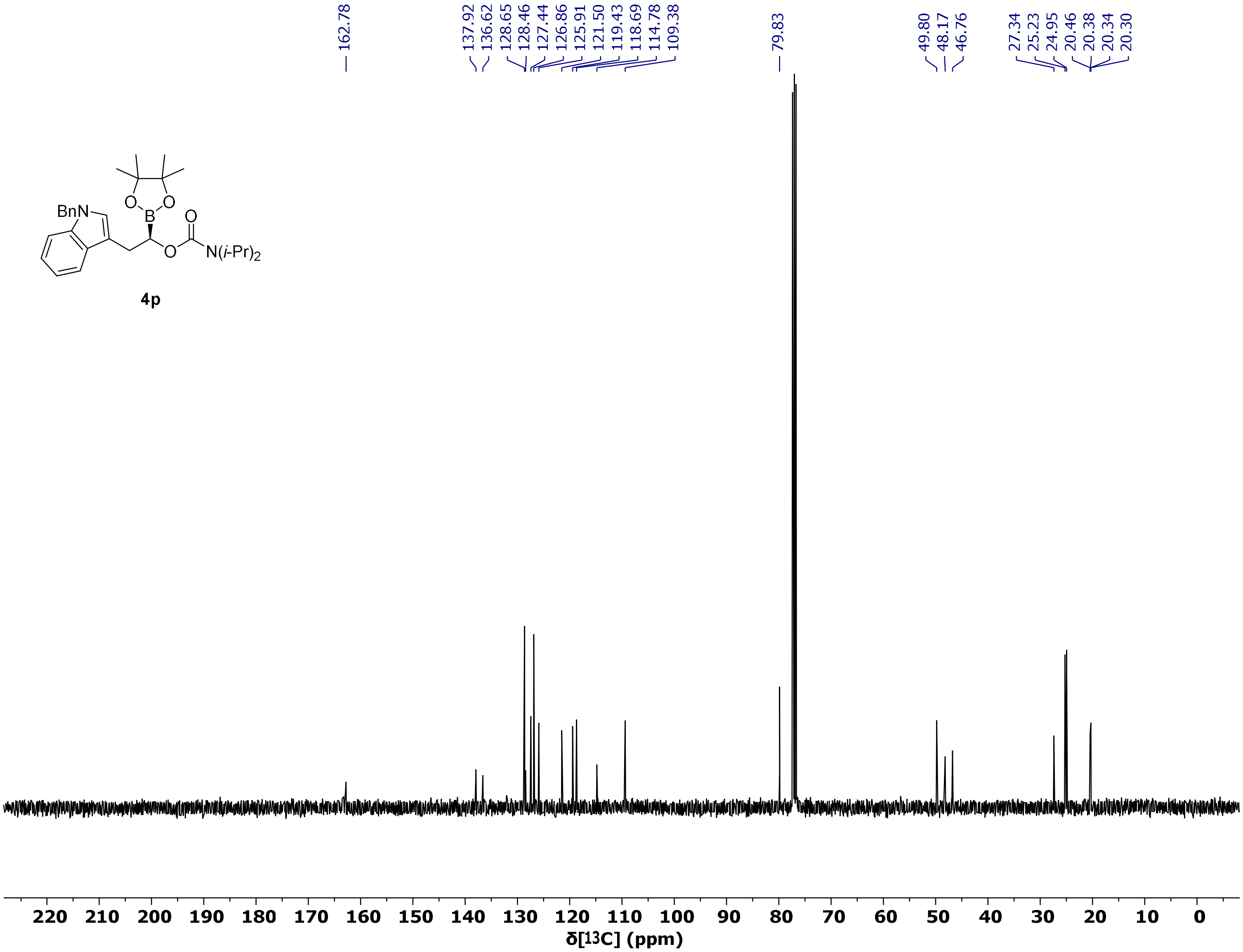
4o



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

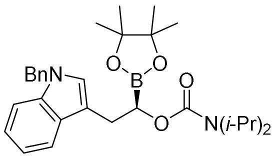


^{13}**C NMR** (101 MHz, $CDCl_3$)

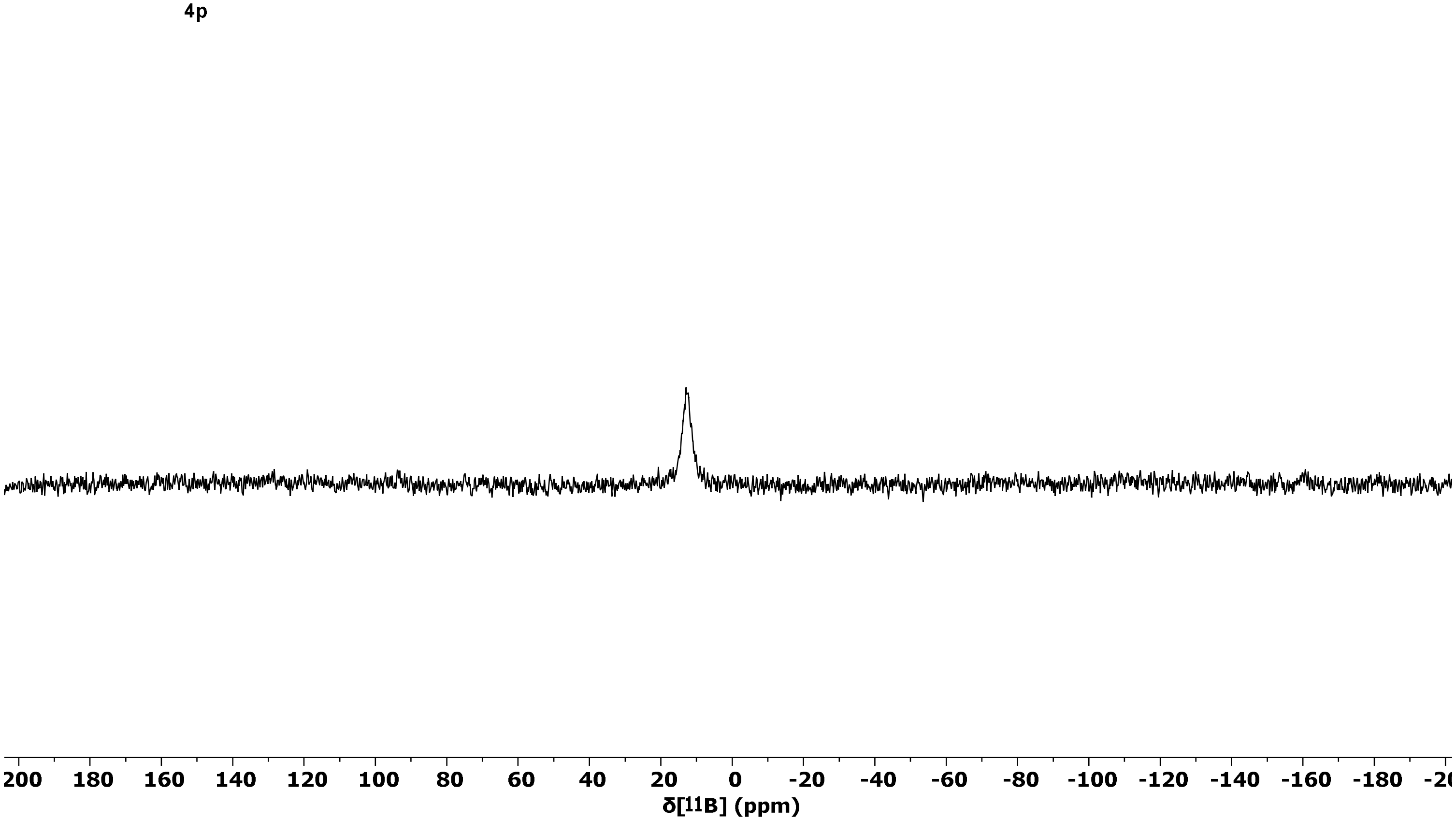


4p

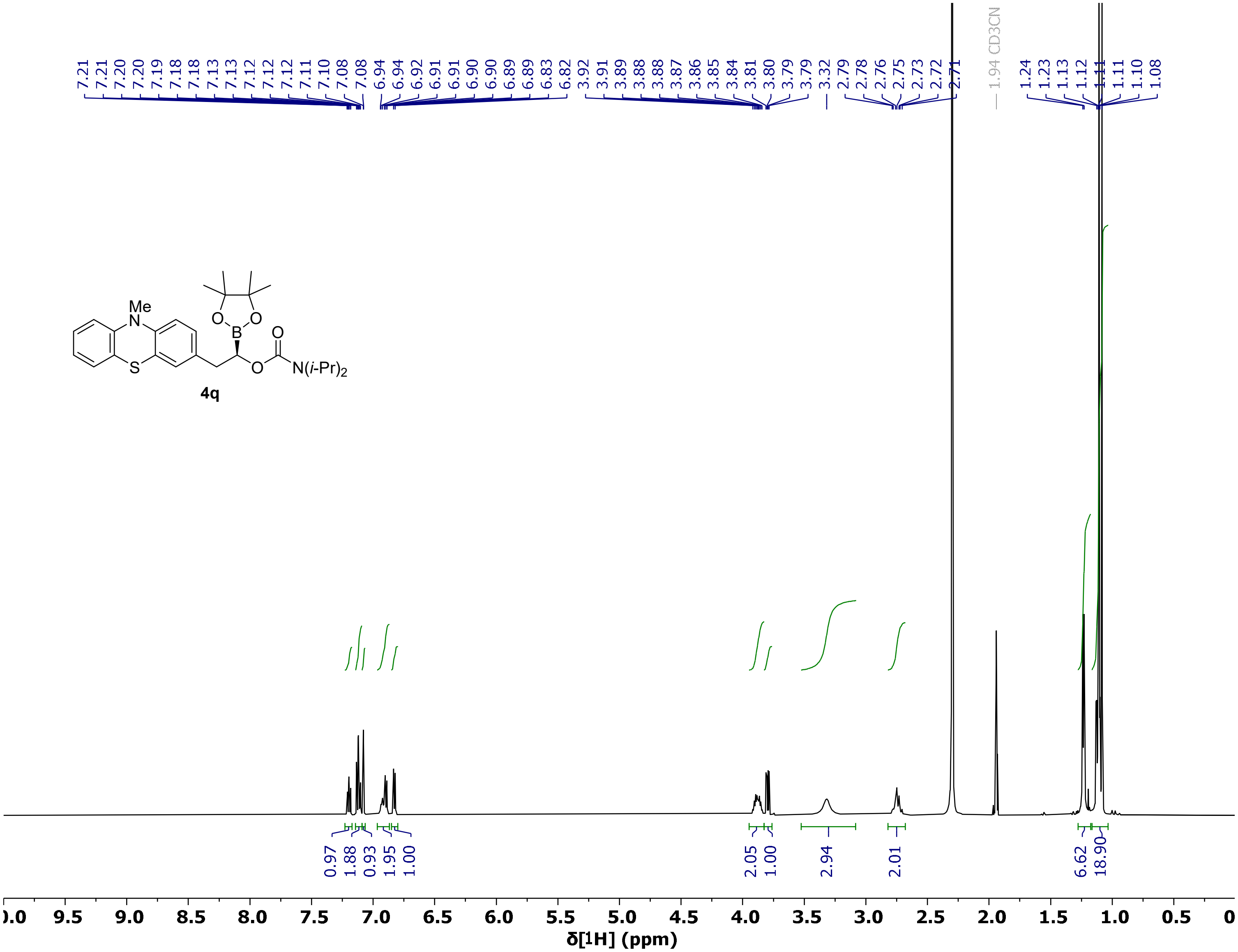
^{11}B NMR (128 MHz, $CDCl_3$)



4p

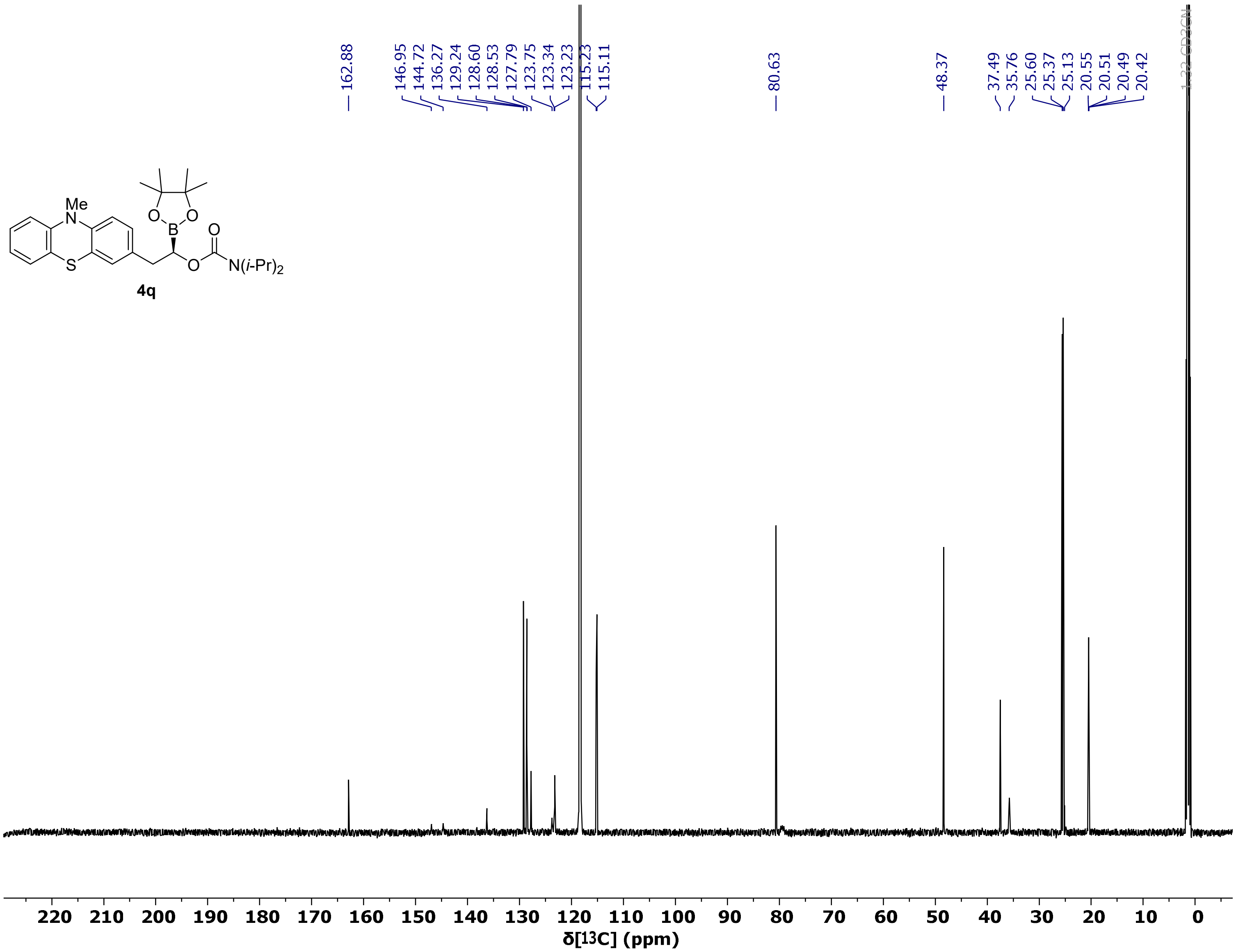


^{1}H NMR (600 MHz, CD_3CN)

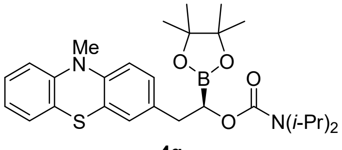


4q

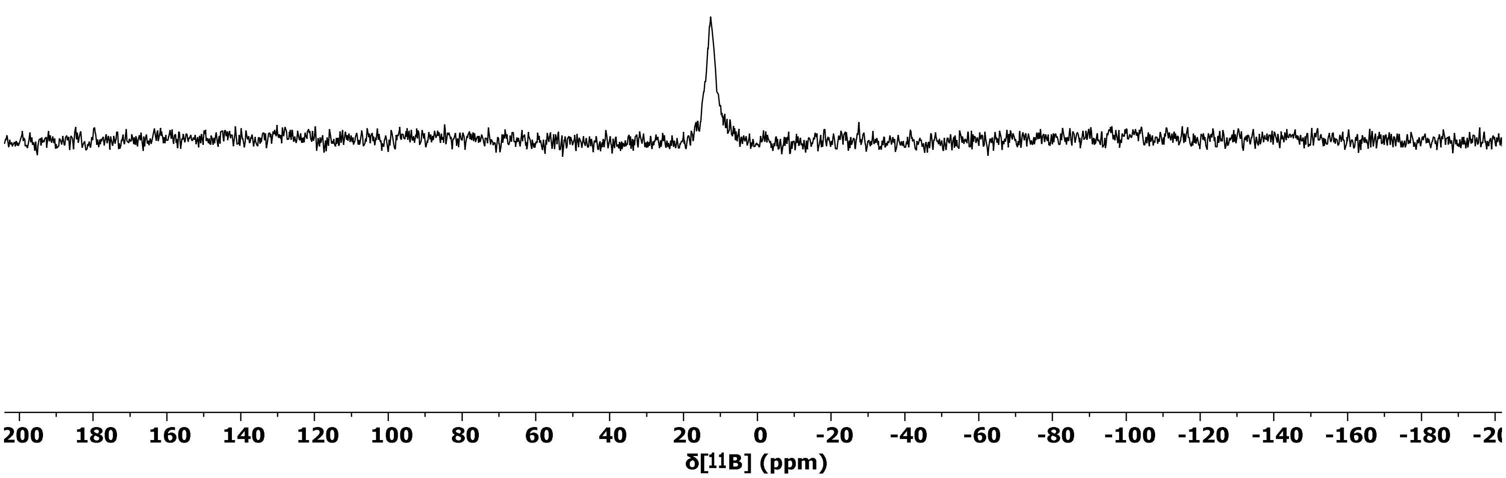
^{13}C NMR (151 MHz, CD_3CN)



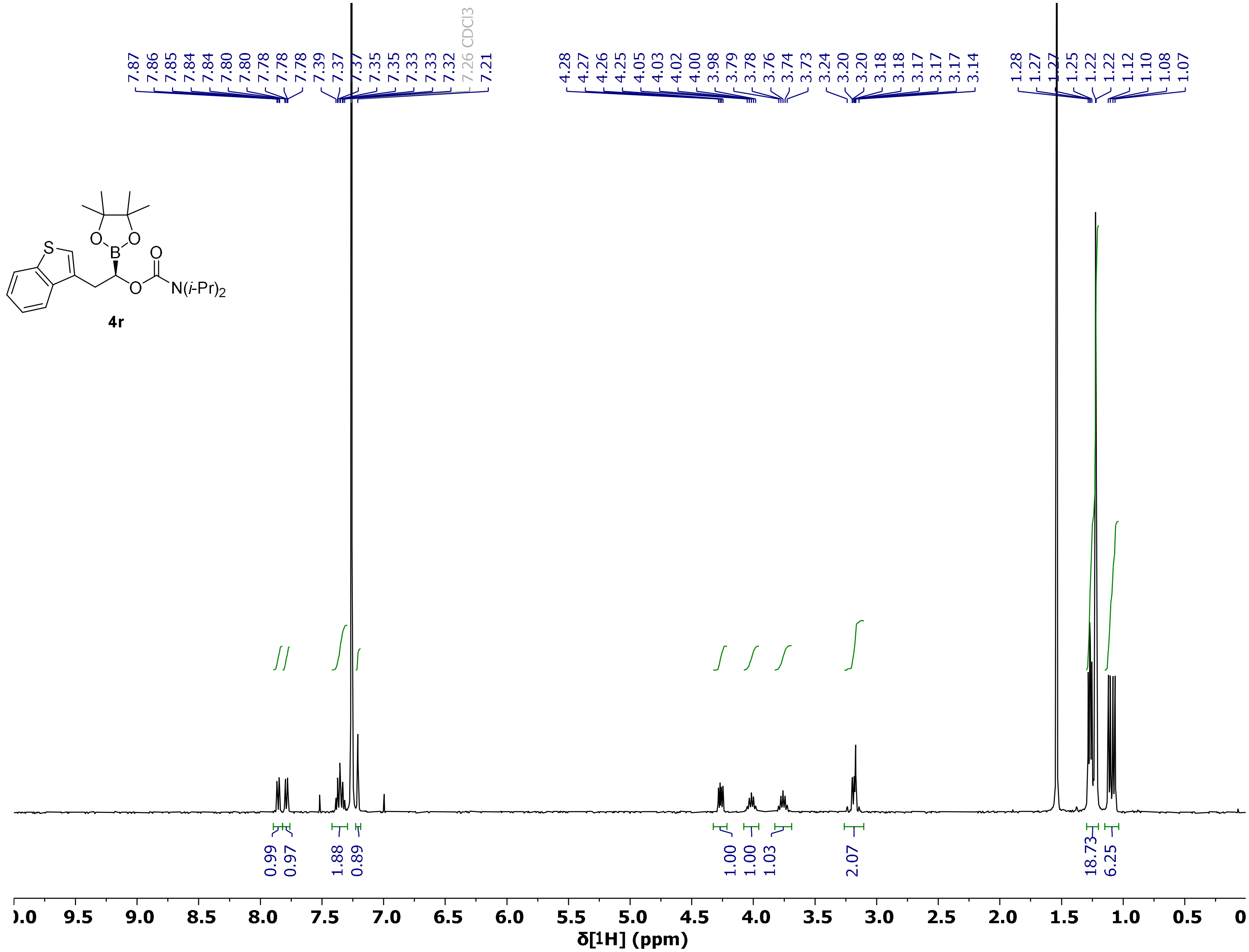
^{11}B NMR (128 MHz, $CDCl_3$)



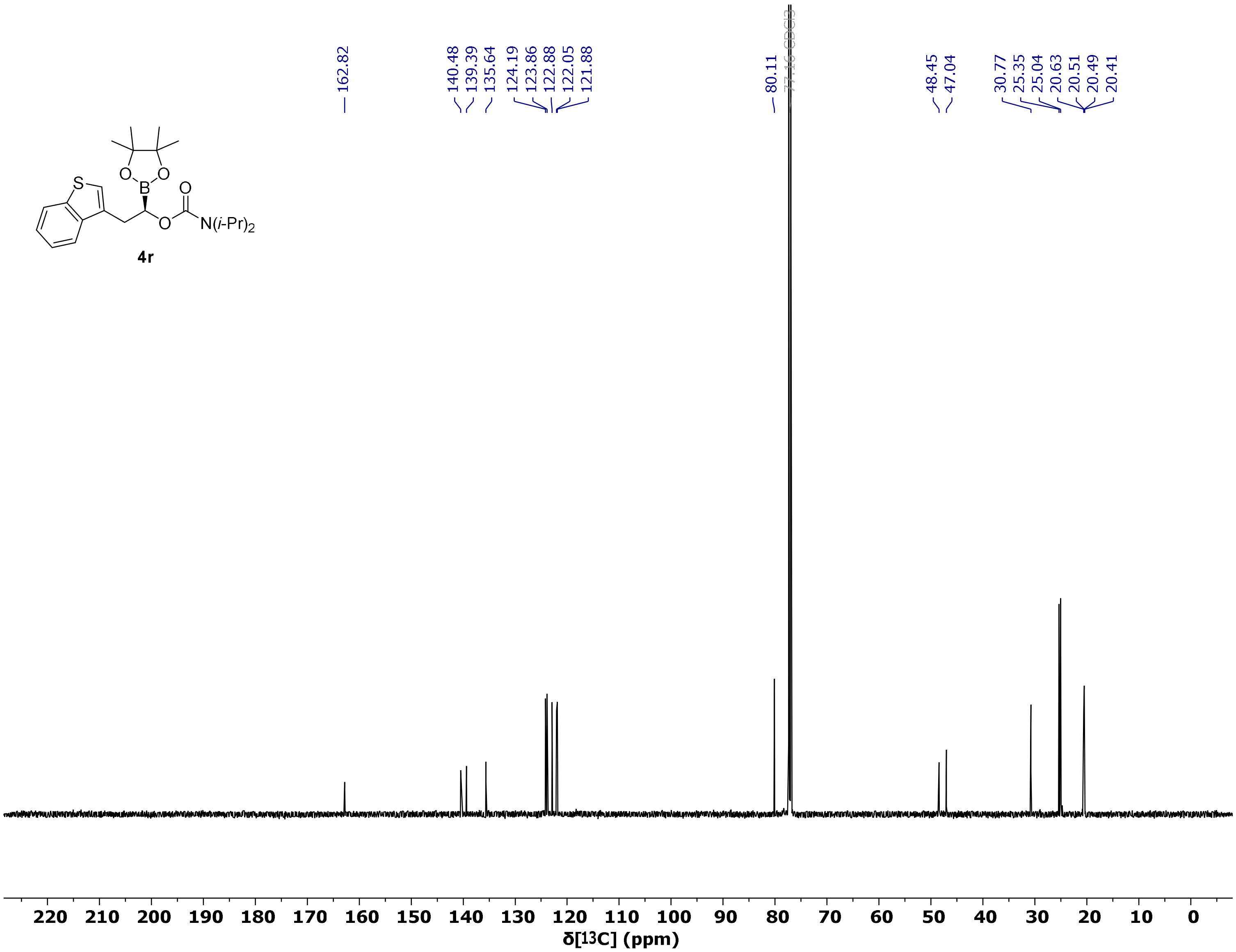
4q



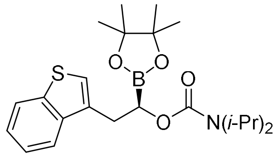
¹H NMR (400 MHz, $CDCl_3$)

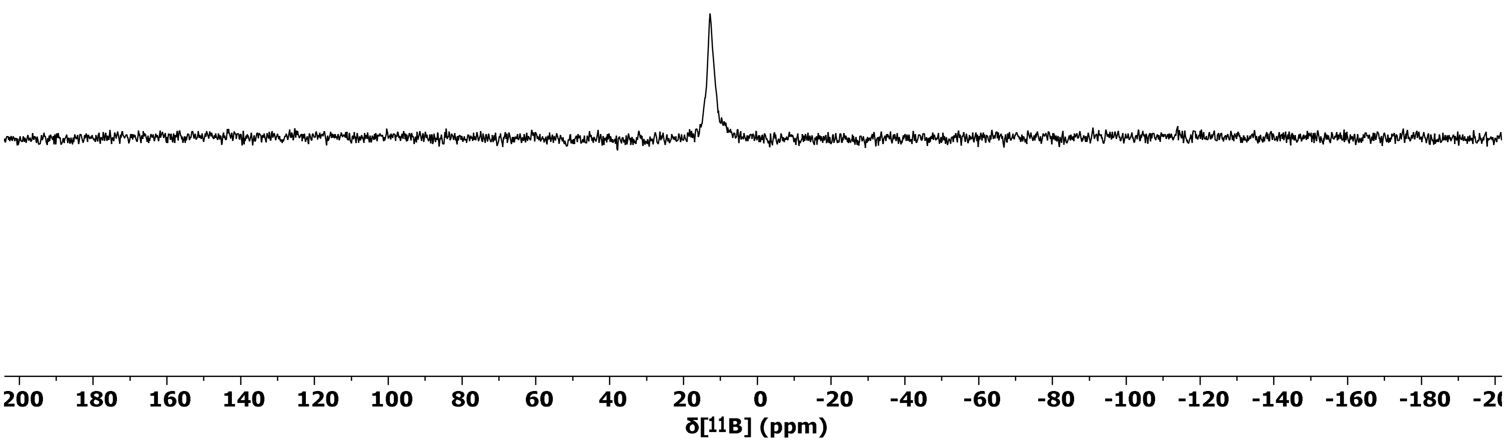


^{13}**C NMR** (151 MHz, CDCl$_3$)



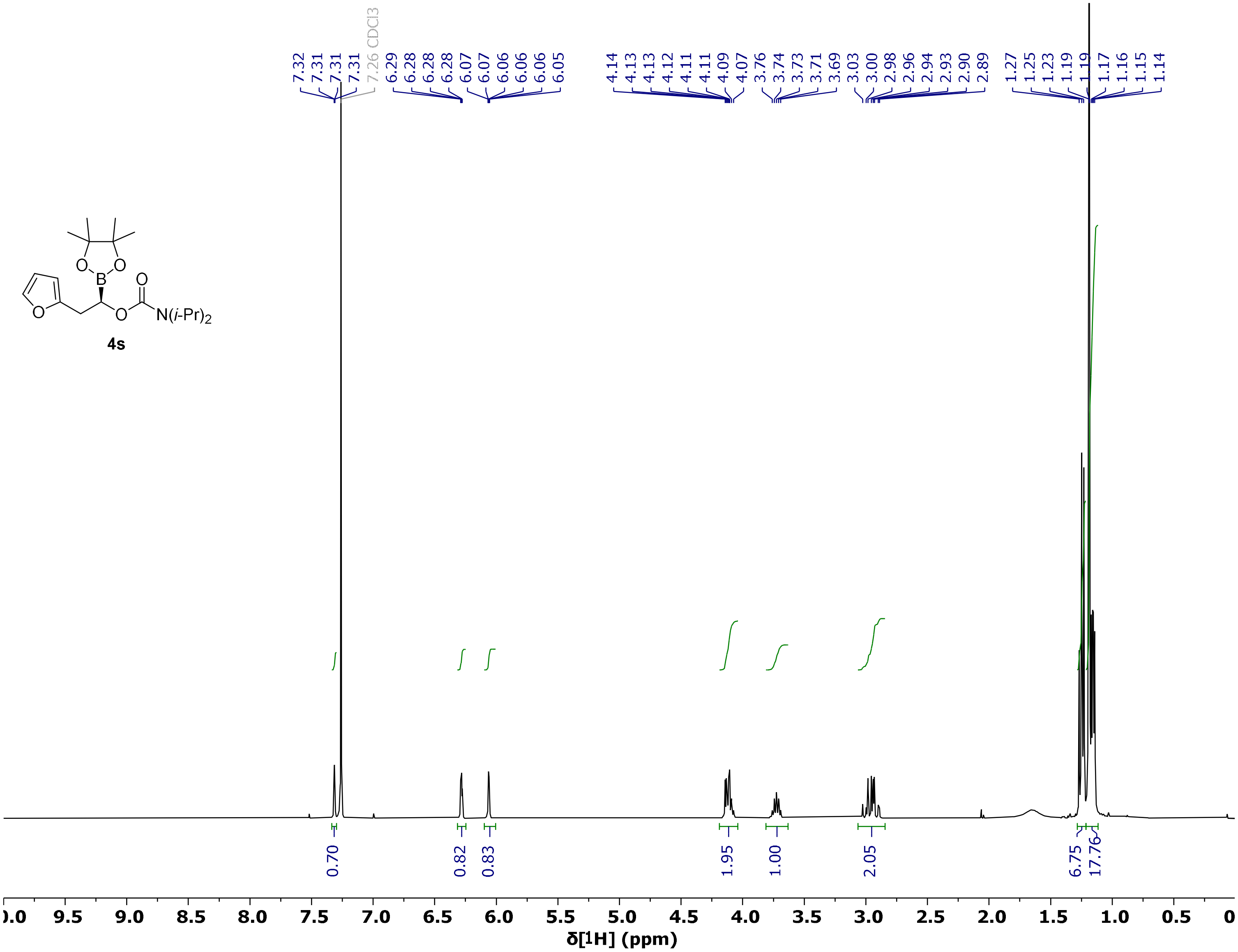
^{11}**B NMR** (128 MHz, $CDCl_3$)


4r



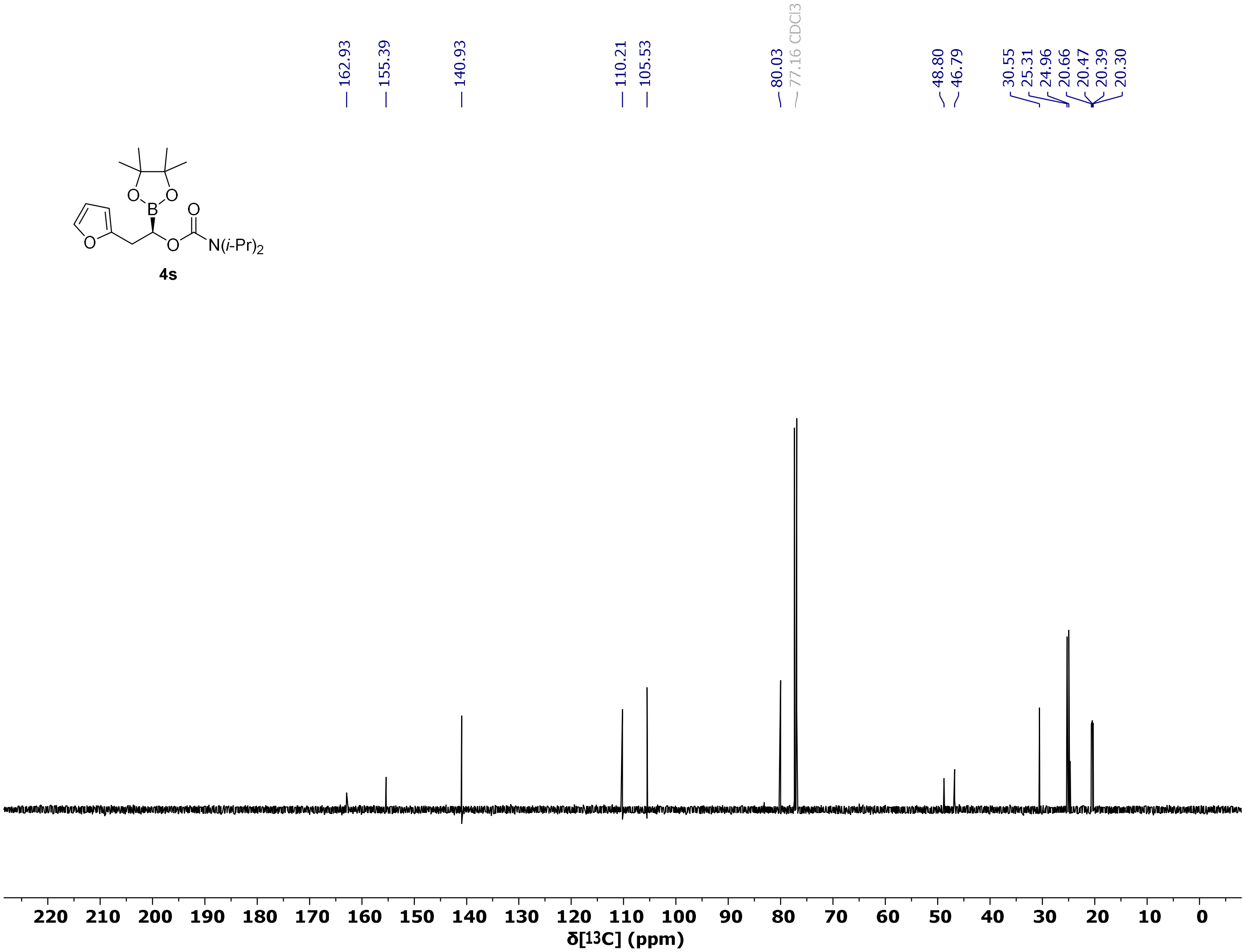
^{1}H NMR (400 MHz, $CDCl_3$)

4s

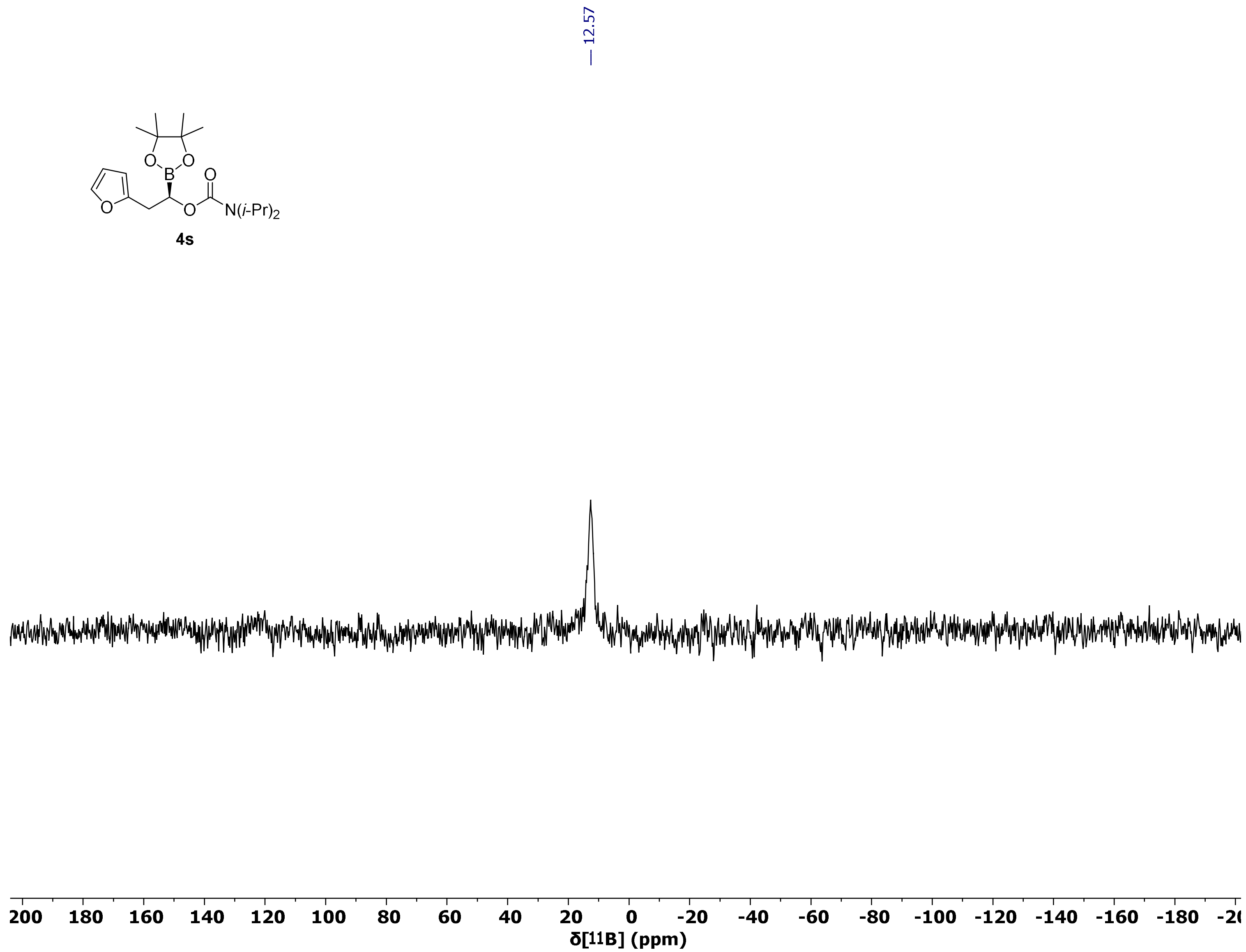


^{13}**C NMR** (151 MHz, CDCl$_3$)

4s



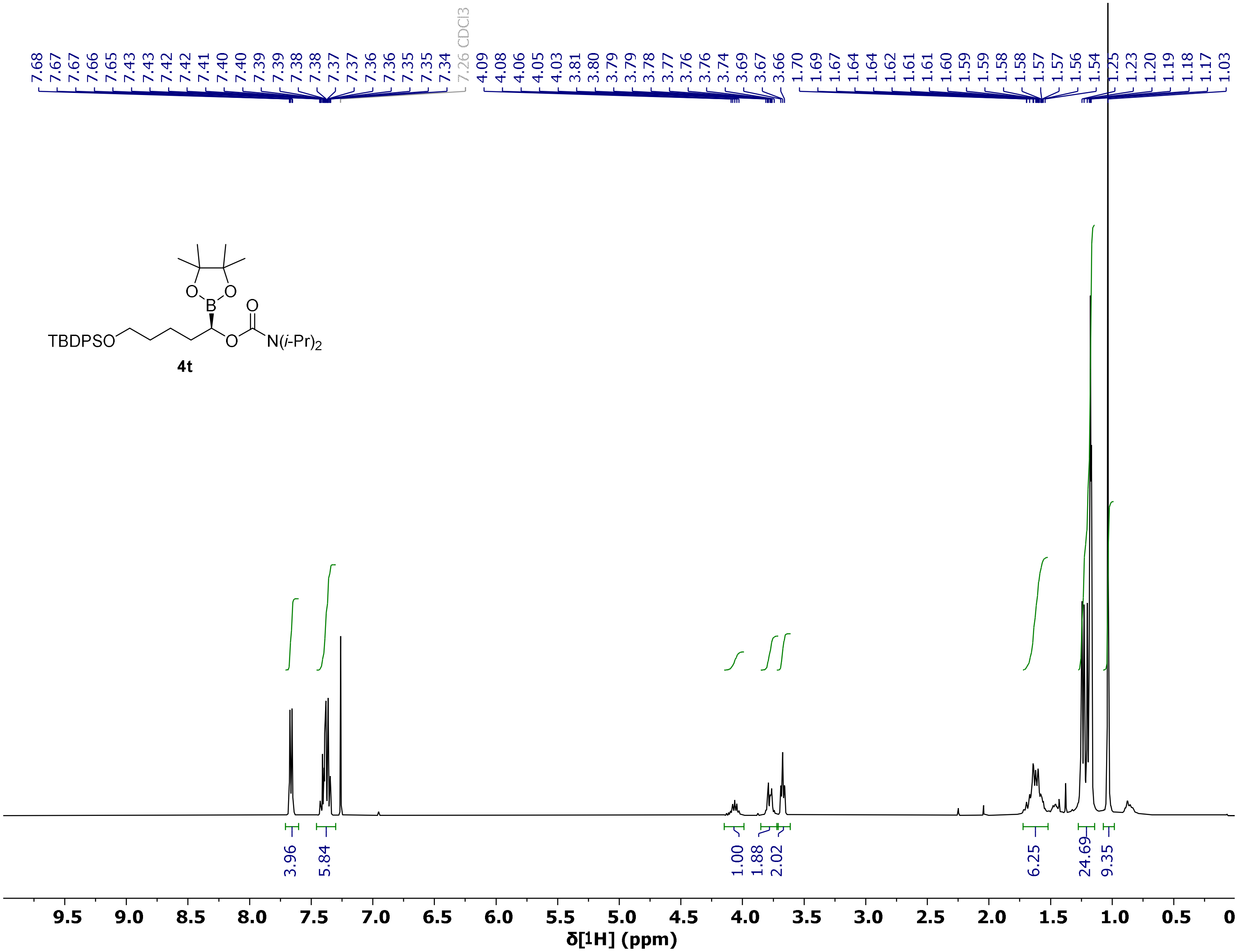
^{11}B NMR (128 MHz, $CDCl_3$)



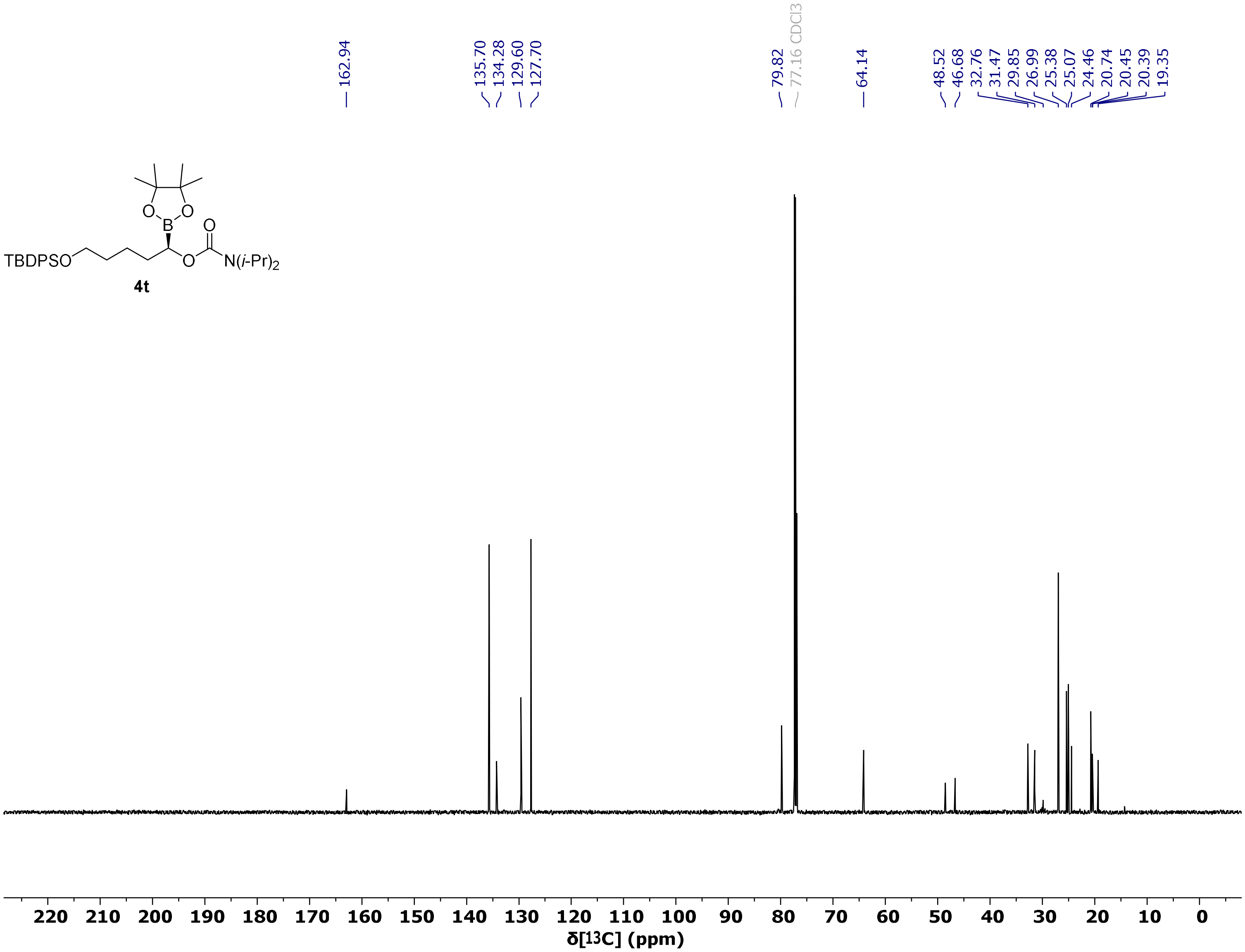
4s

^{1}**H NMR** (400 MHz, CDCl$_3$)

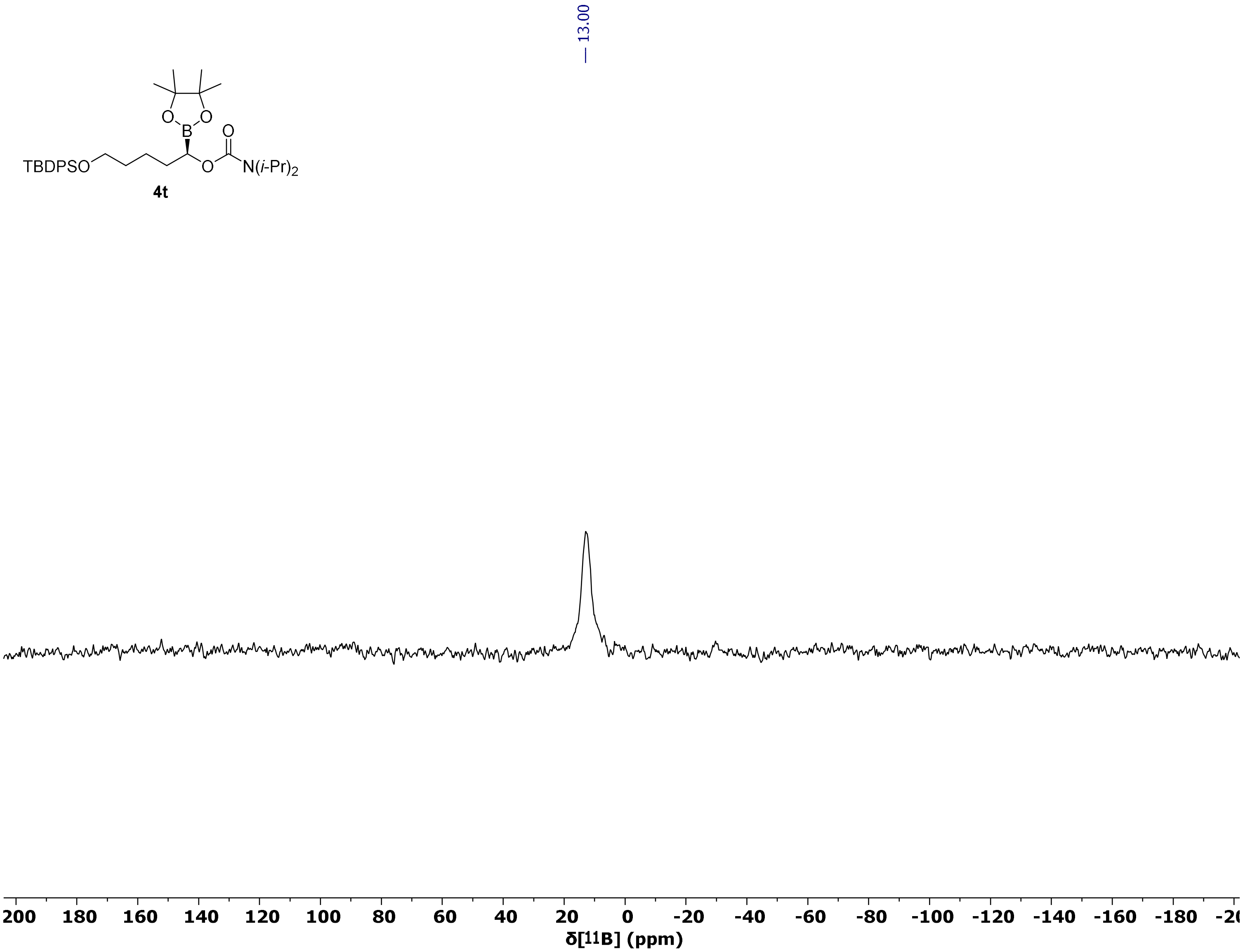
4t



^{13}**C NMR** (151 MHz, $CDCl_3$)

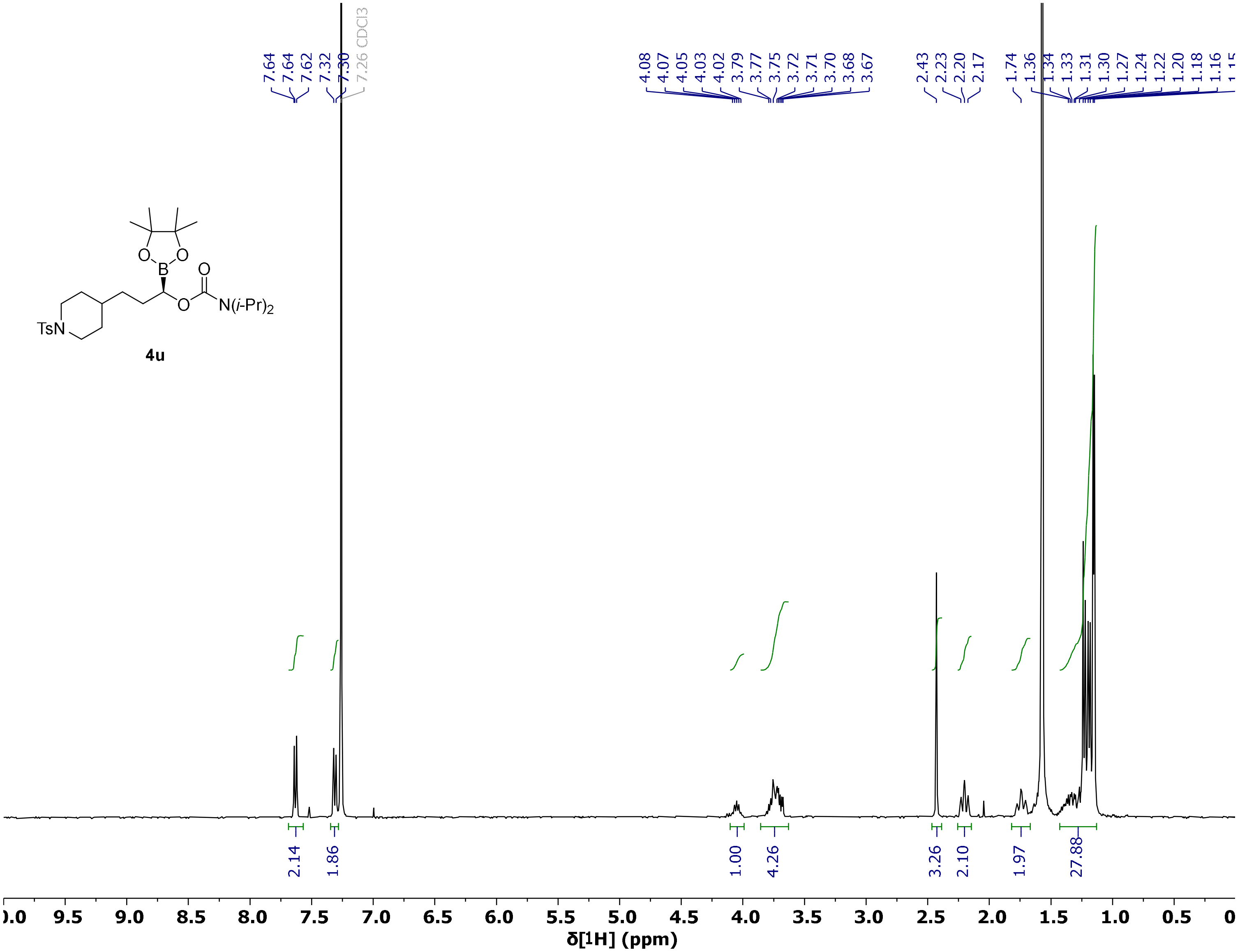


^{11}B NMR (128 MHz, $CDCl_3$)



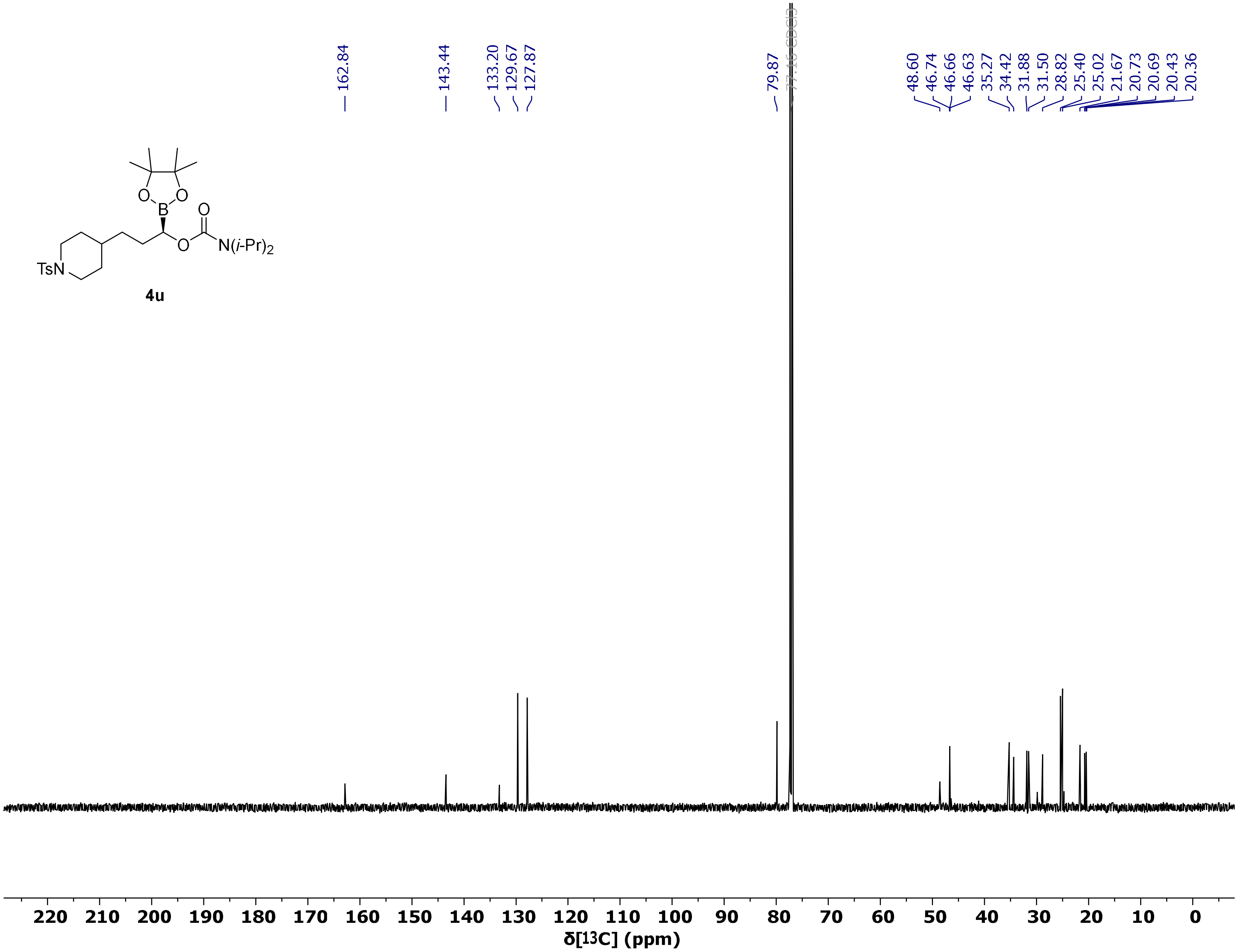
4t

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

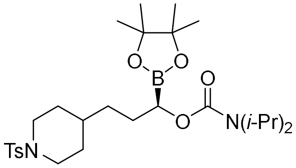


4u

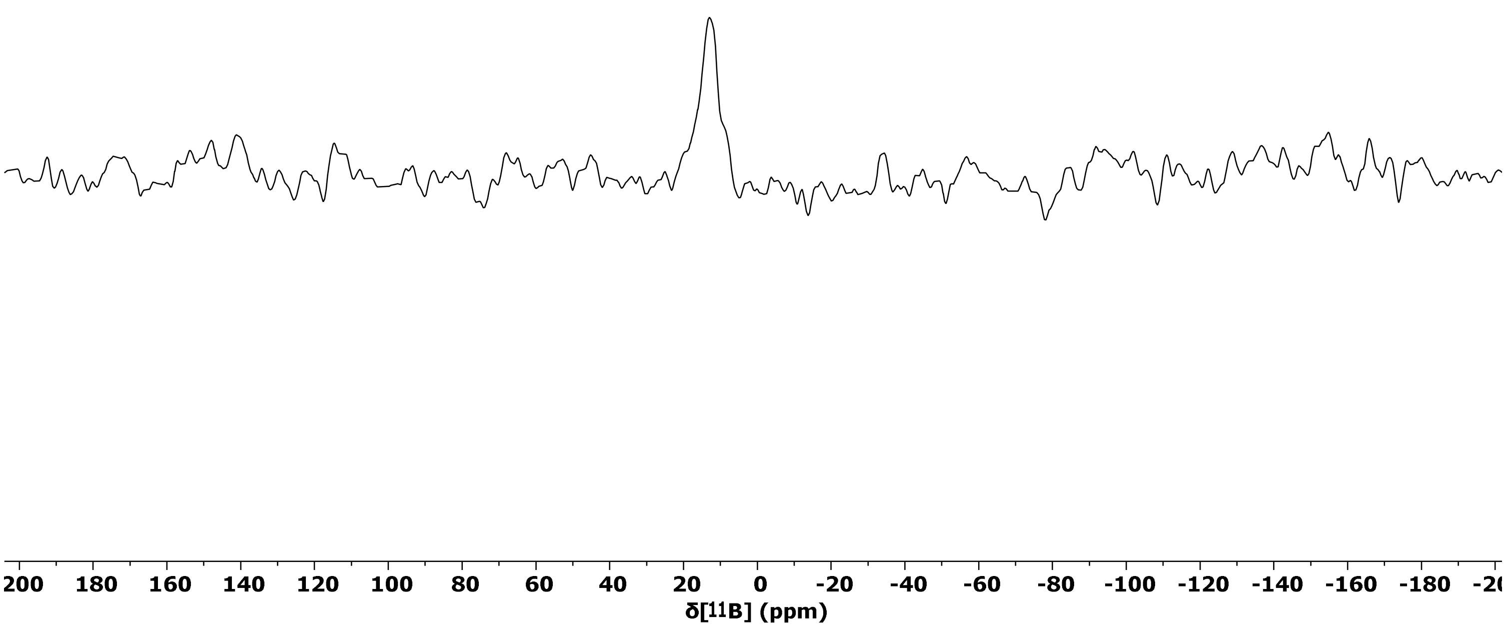
^{13}C NMR (151 MHz, CDCl$_3$)



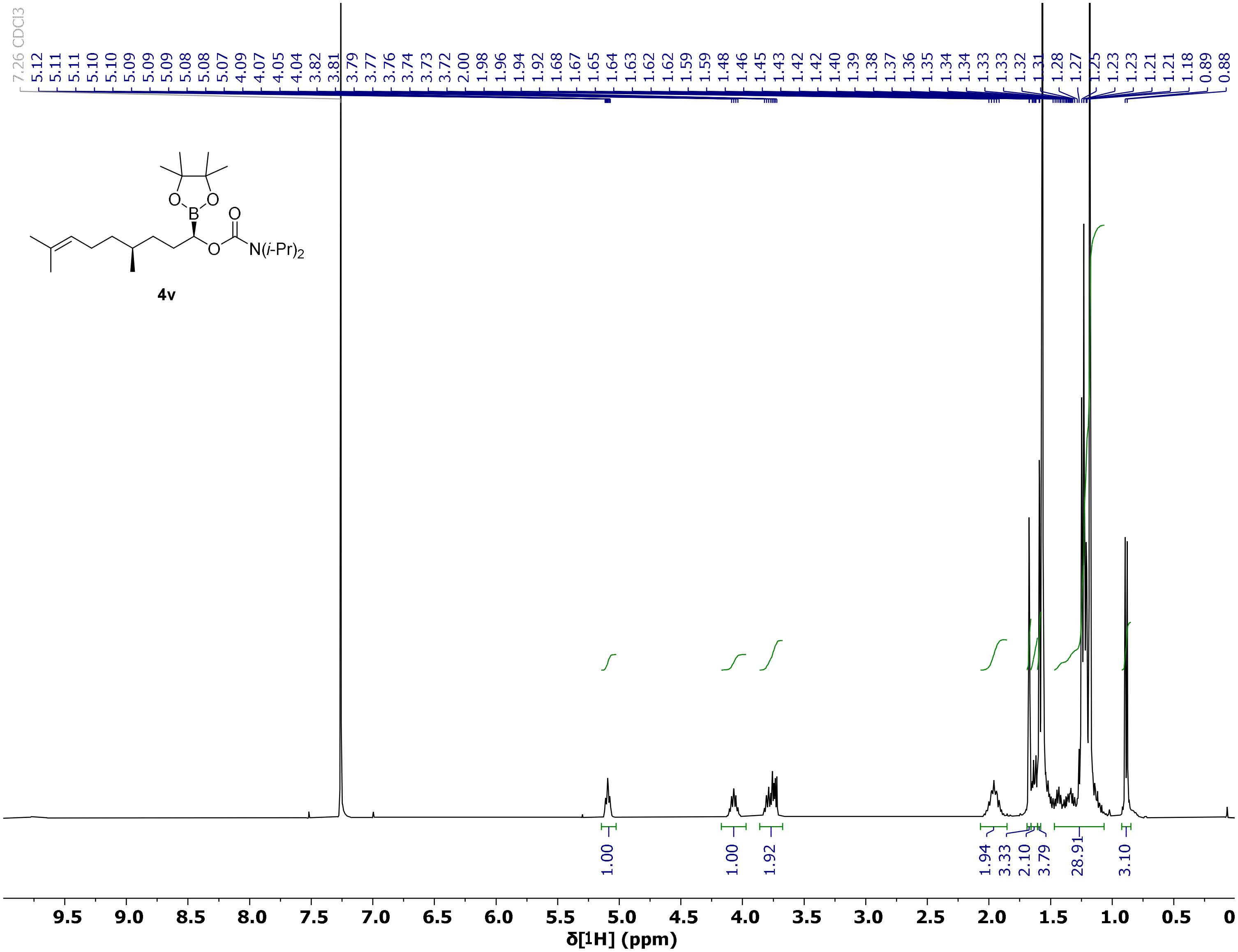
^{11}B NMR (128 MHz, $CDCl_3$)



4u

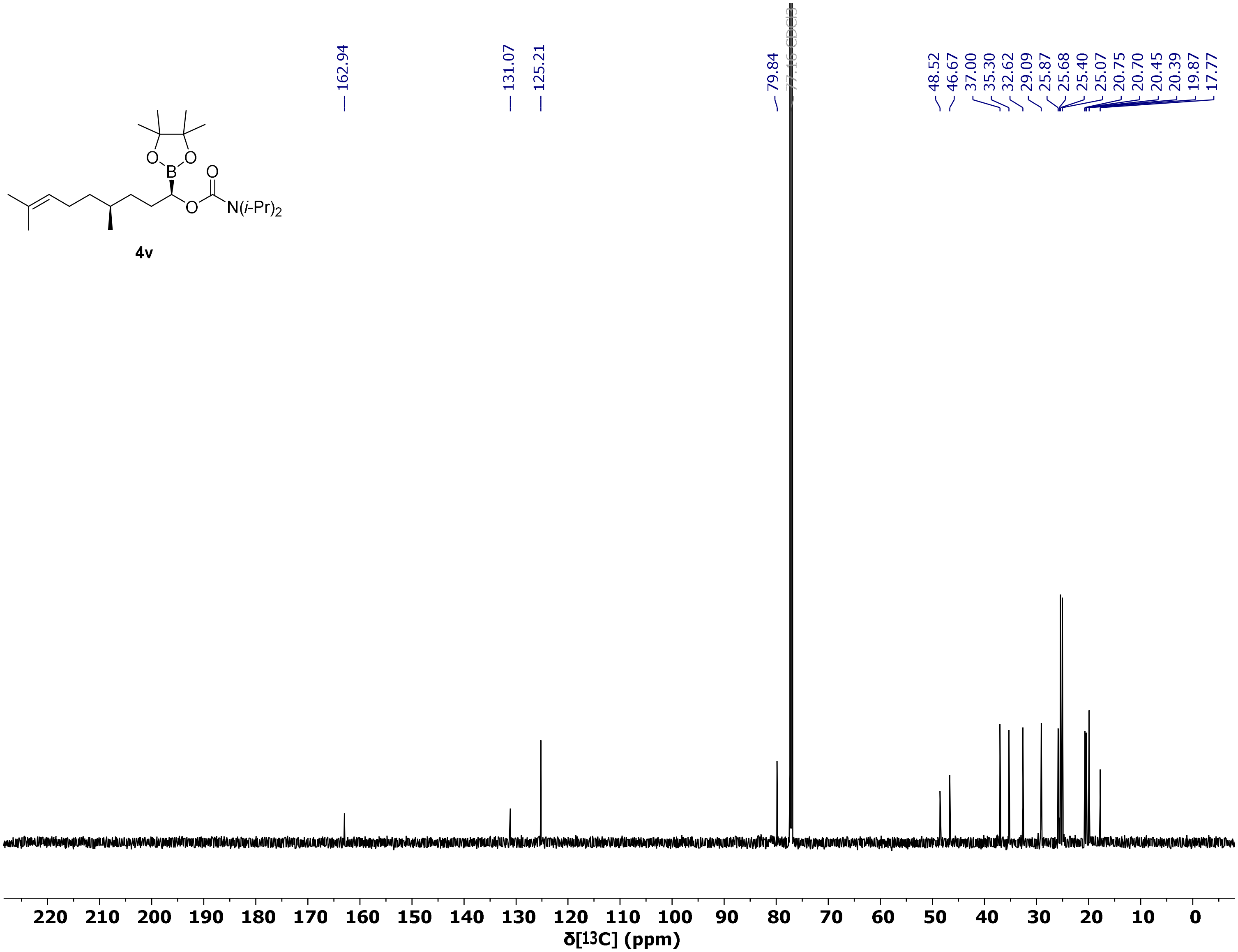


^{1}H NMR (400 MHz, $CDCl_3$)

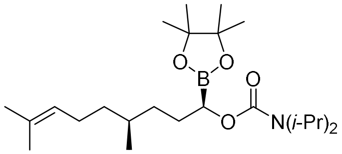


4v

^{13}C NMR (151 MHz, $CDCl_3$)

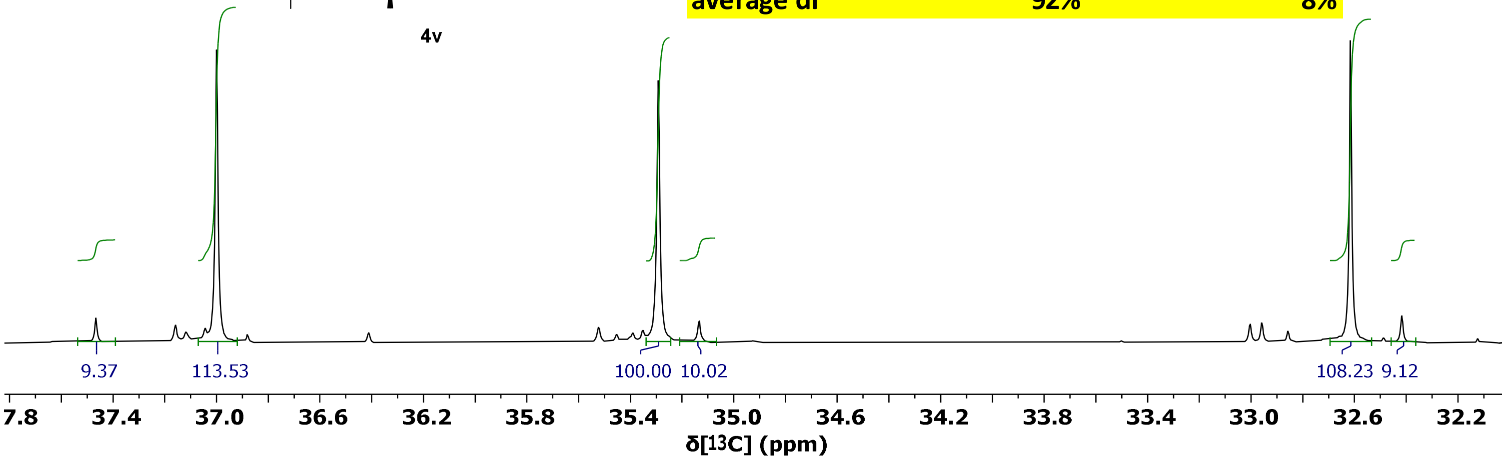


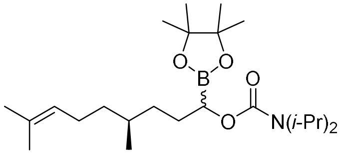
^{13}C NMR (151 MHz, CDCl$_3$)



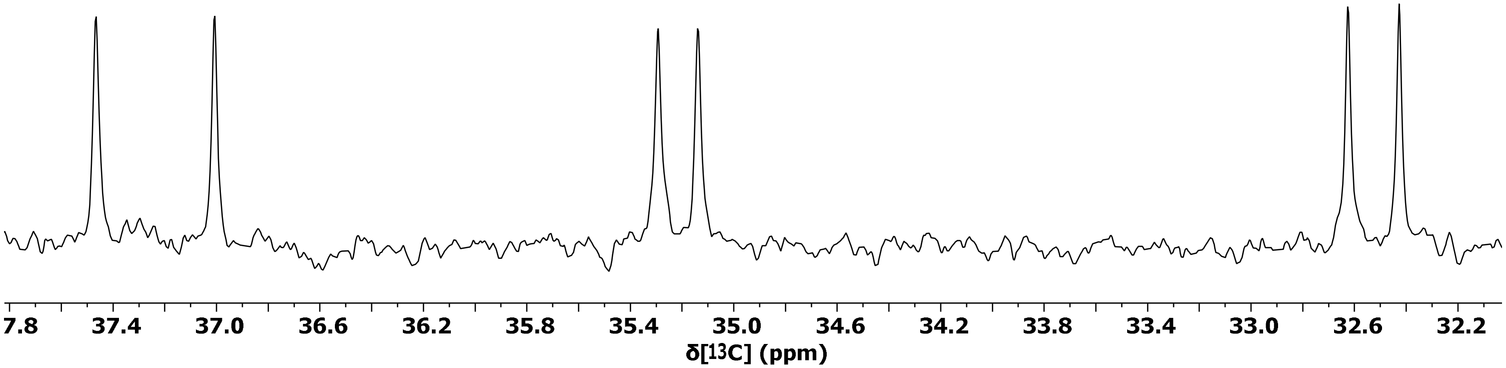
4v

	major	major %	minor	minor %
	113.53	92%	9.37	8%
	100	91%	10.02	9%
	108.23	92%	9.12	8%
average dr		**92%**		**8%**

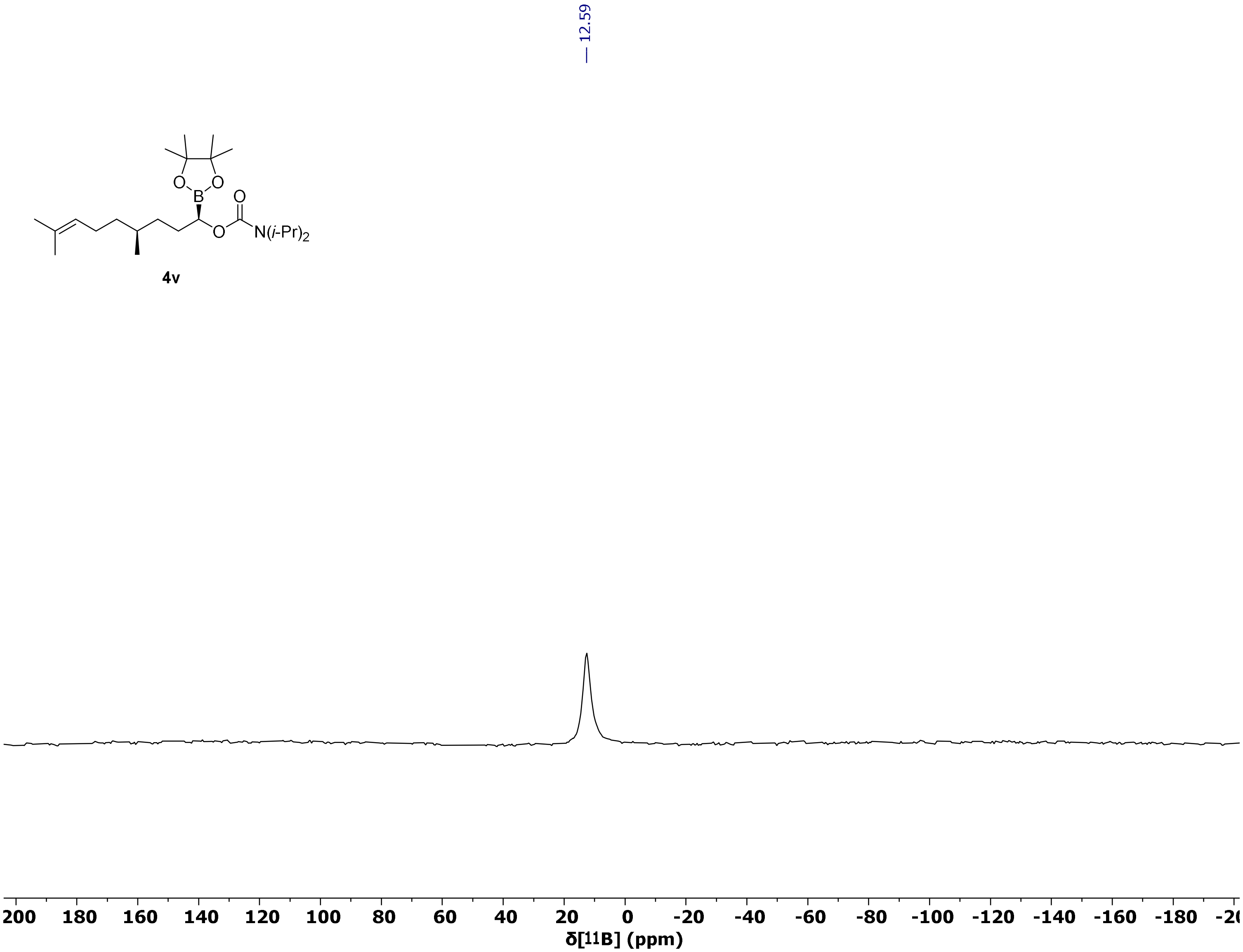




4v-*rac*

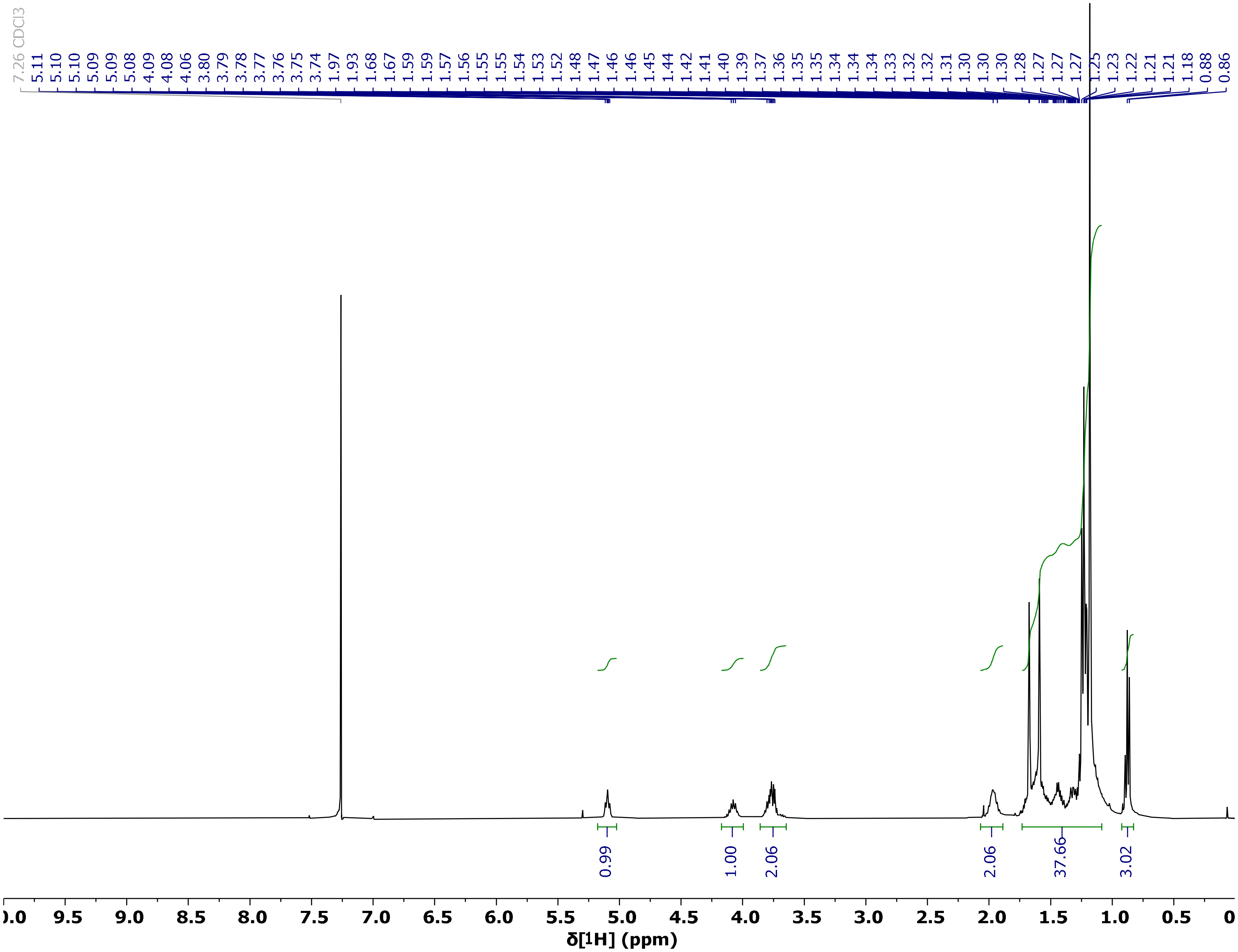


^{11}B NMR (128 MHz, $CDCl_3$)

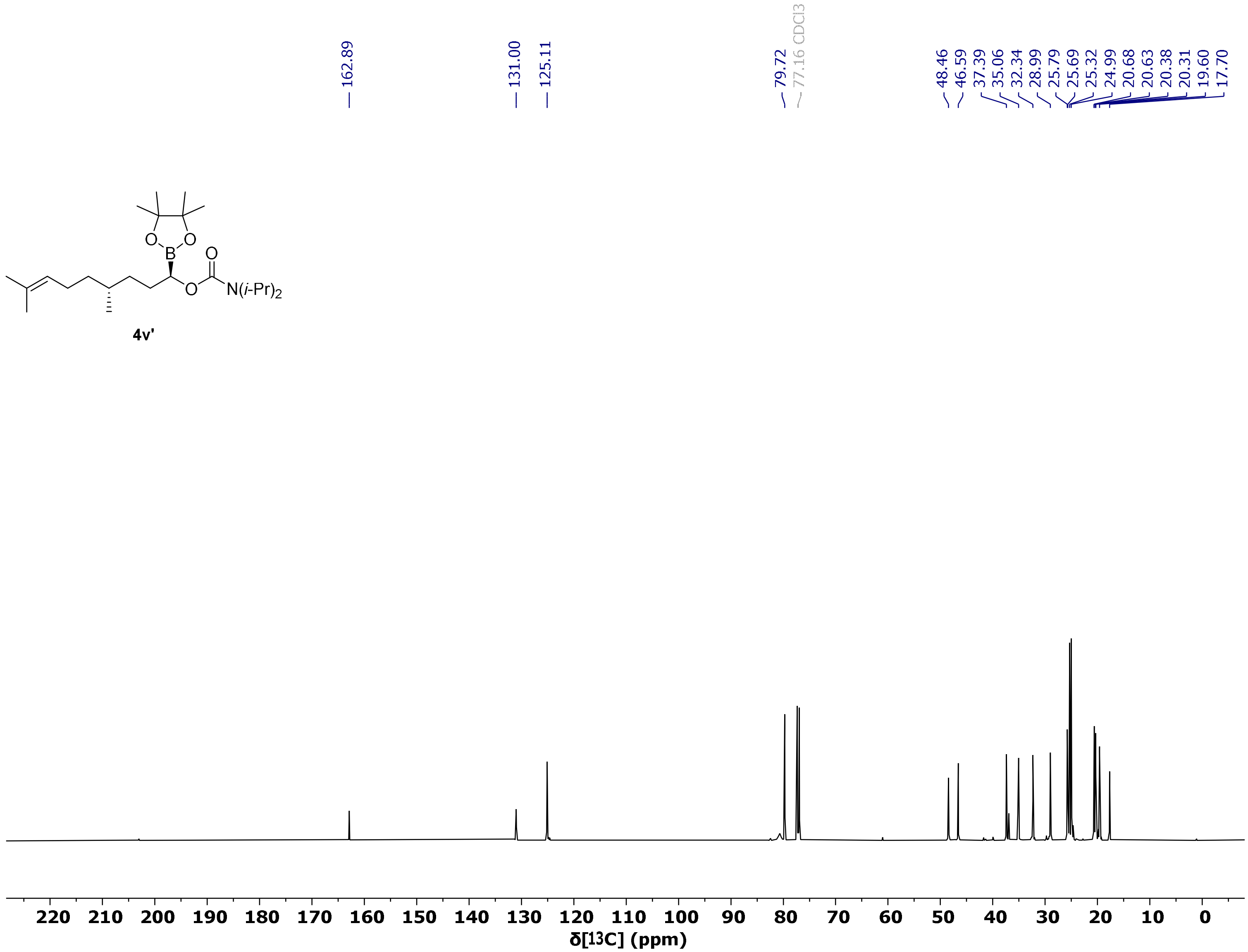


4v

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

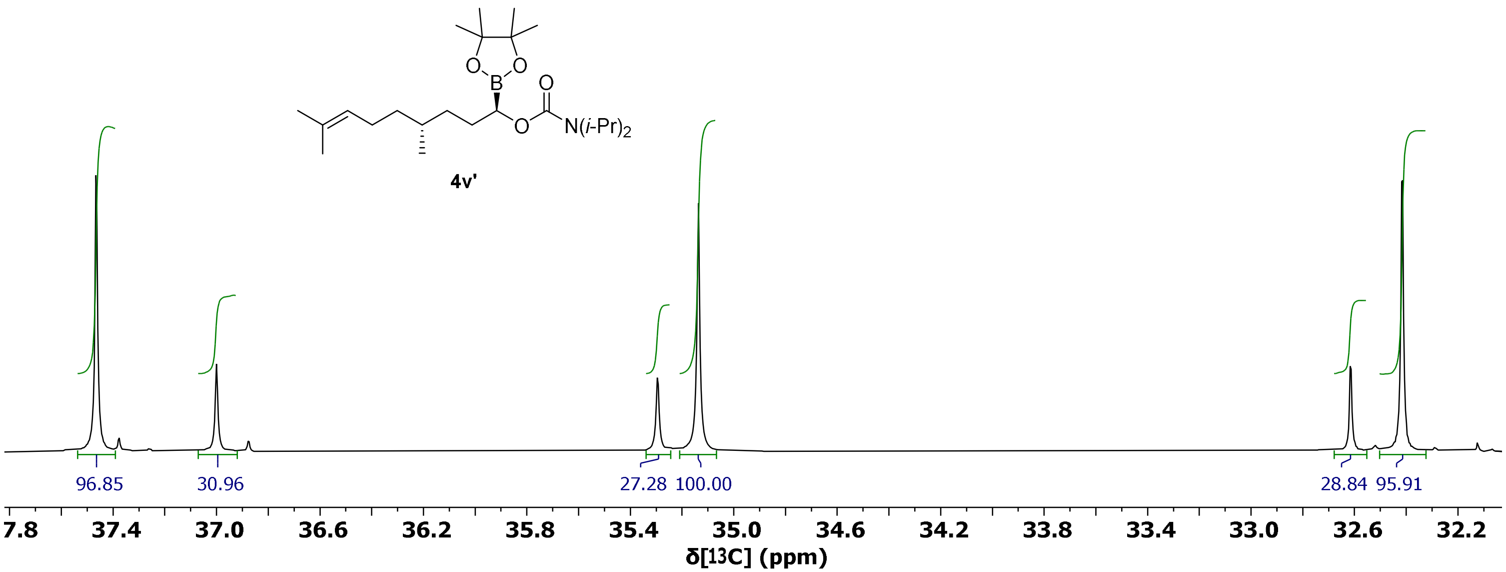


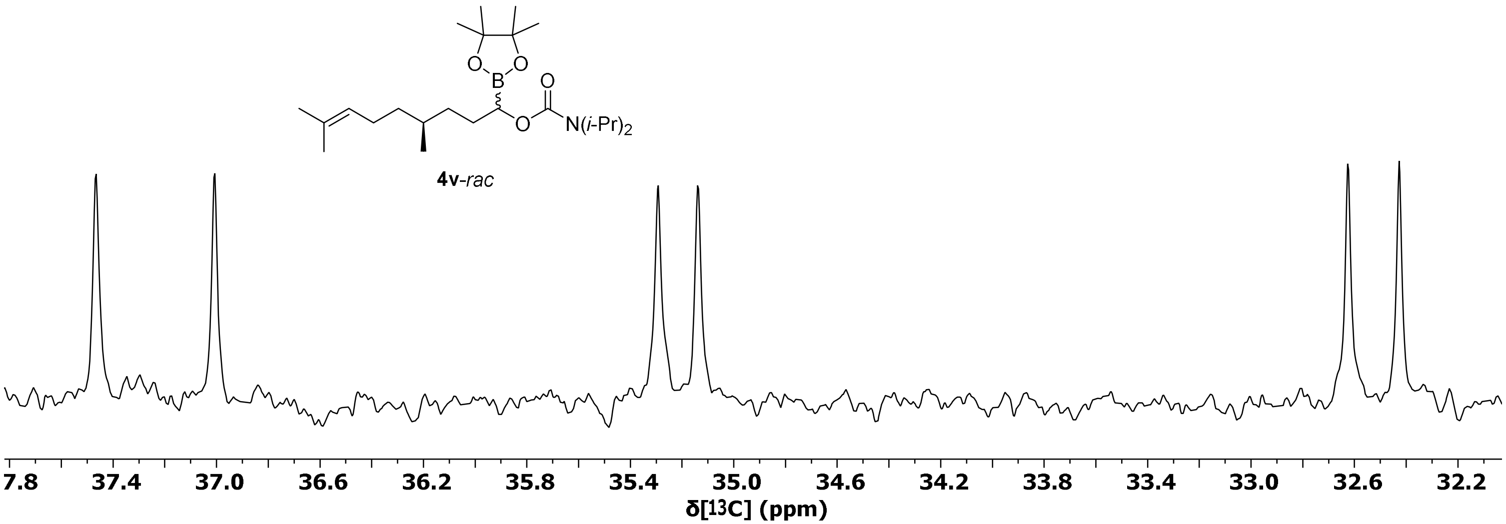
^{13}C NMR (151 MHz, $CDCl_3$)



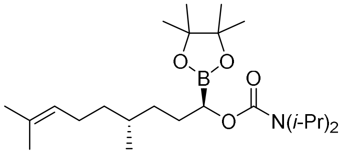
^{13}C NMR (151 MHz, $CDCl_3$)

	major	major %	minor	minor %
	96.85	76%	30.96	24%
	100	79%	27.28	21%
	95.91	77%	28.84	23%
average dr		**77%**		**23%**

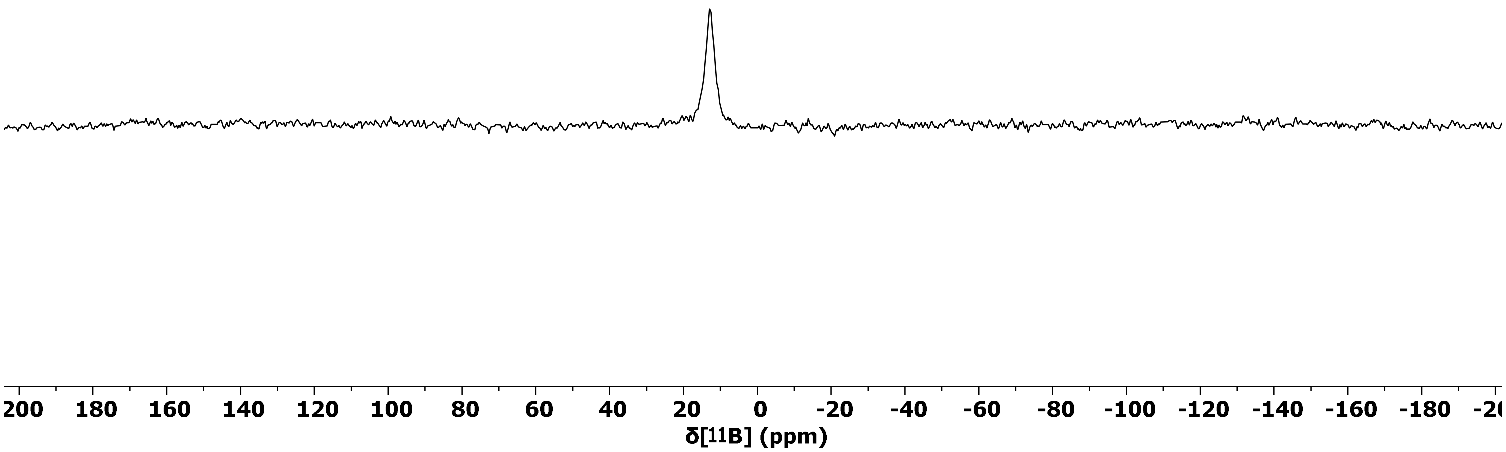




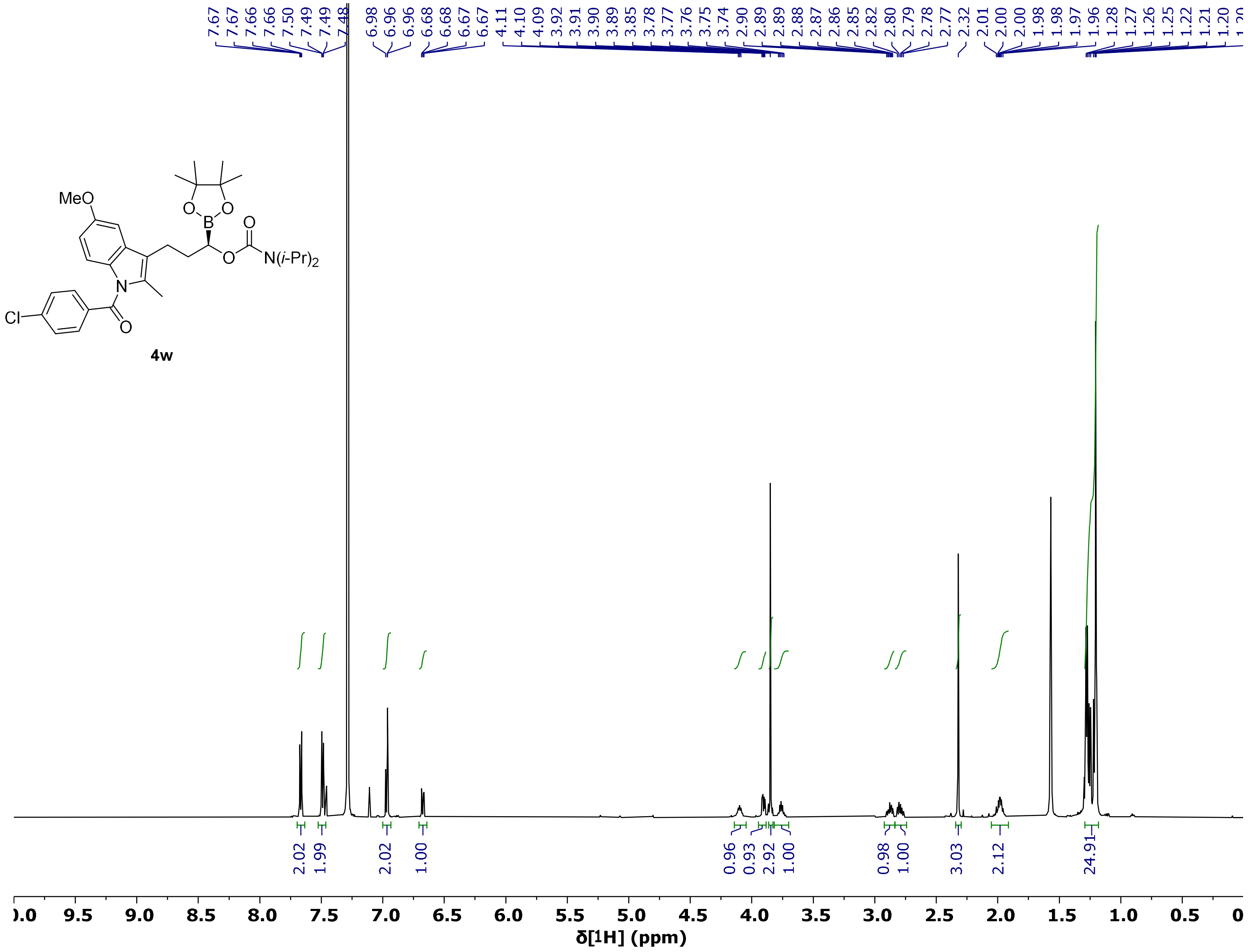
^{11}**B NMR** (128 MHz, CDCl$_3$)



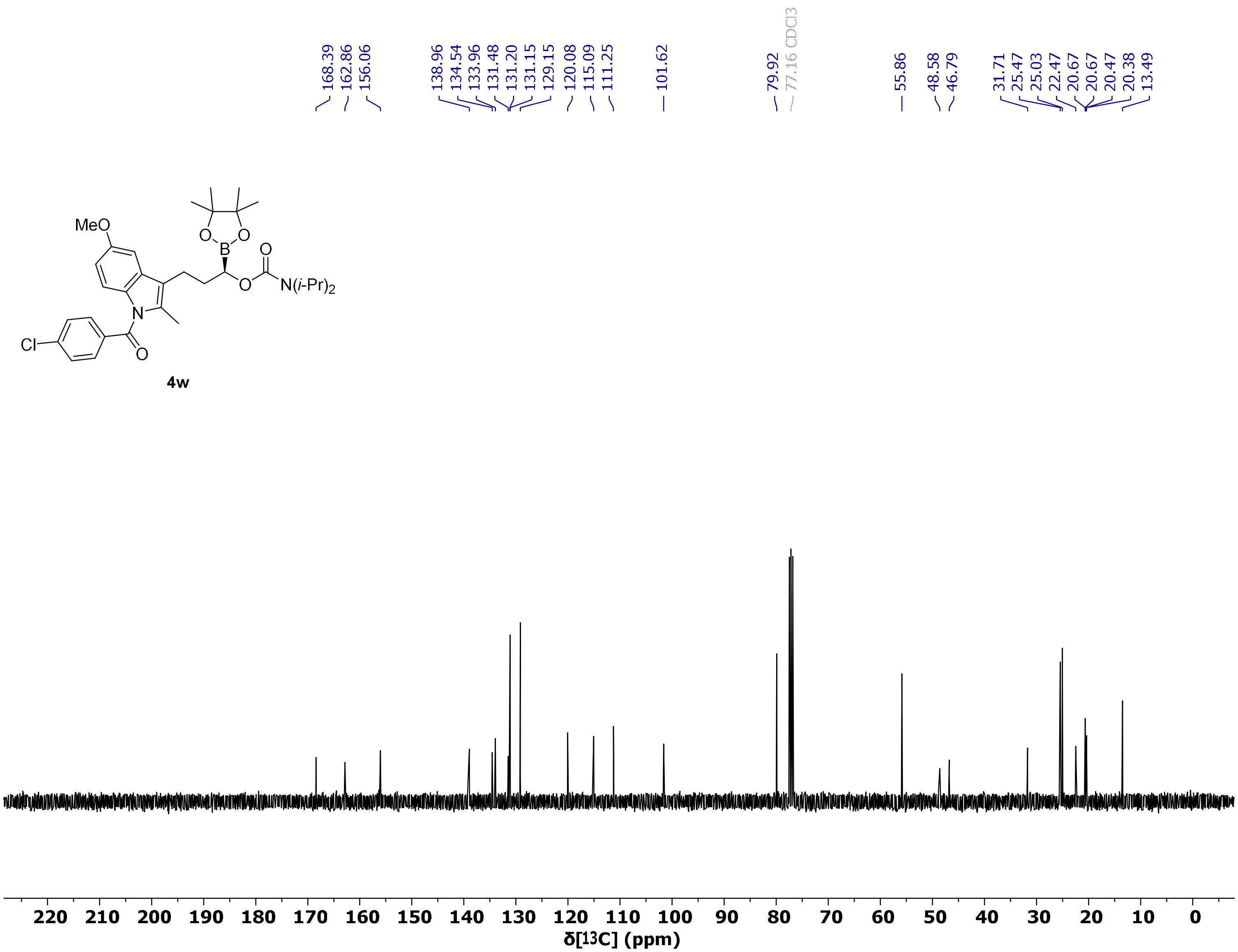
4v'



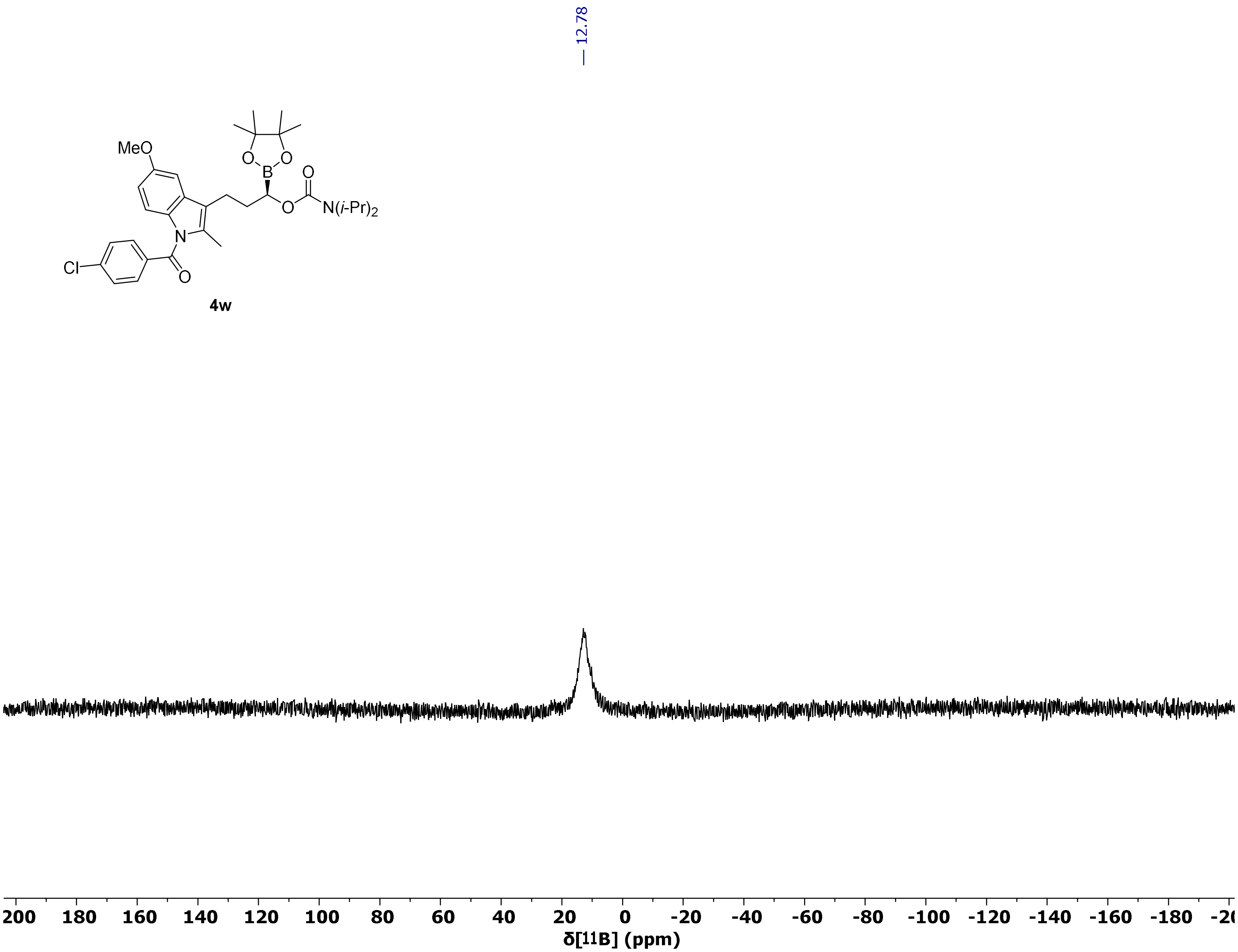
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

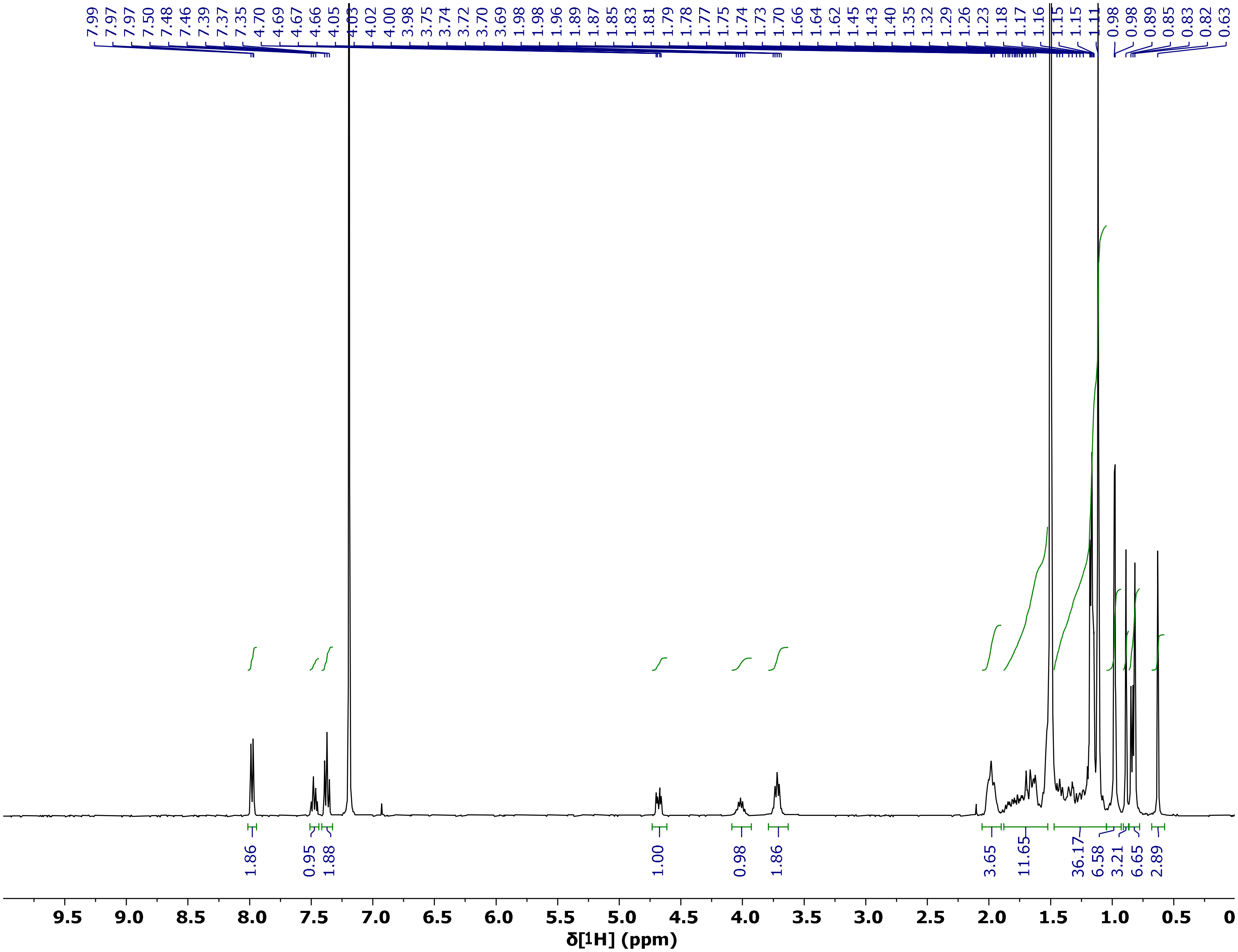


^{11}**B NMR** (128 MHz, CDCl$_3$)

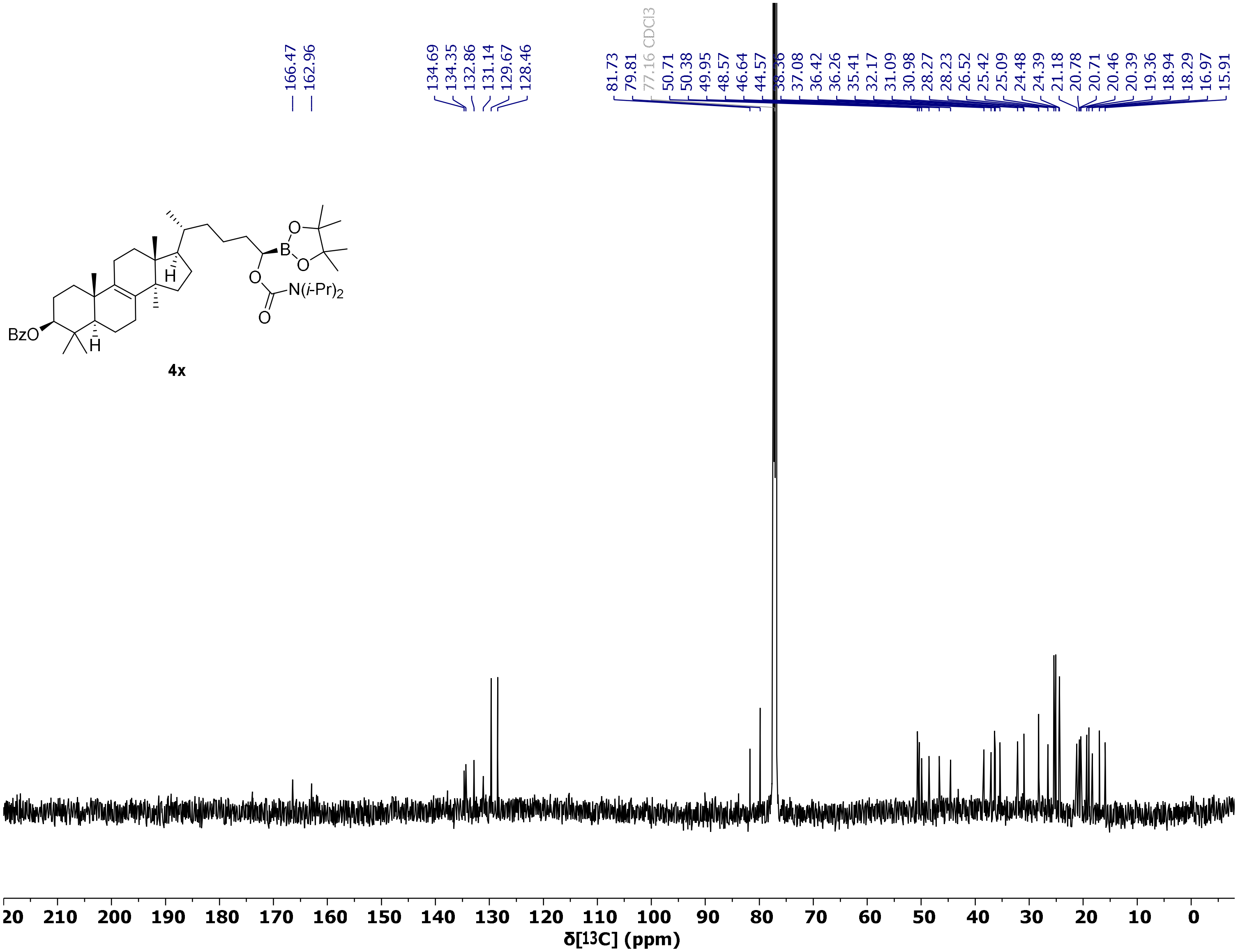


4w

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

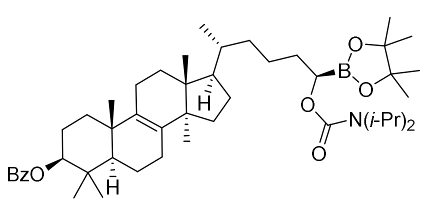


^{13}C NMR (151 MHz, $CDCl_3$)

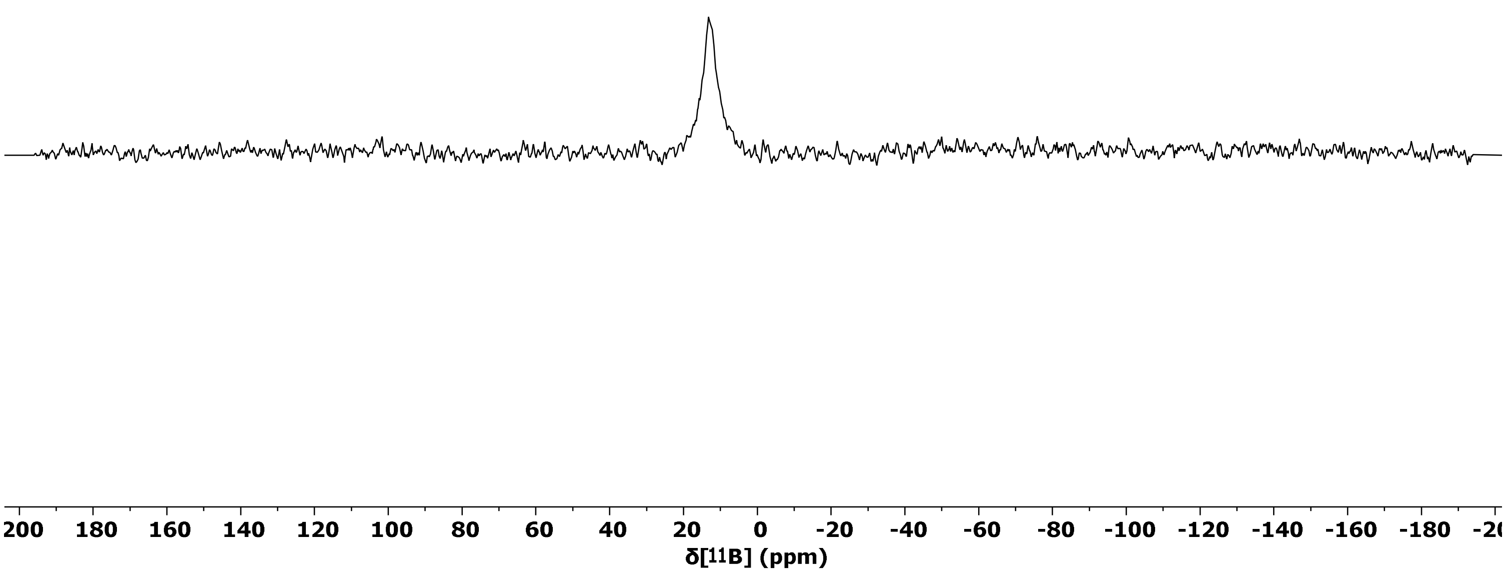


4x

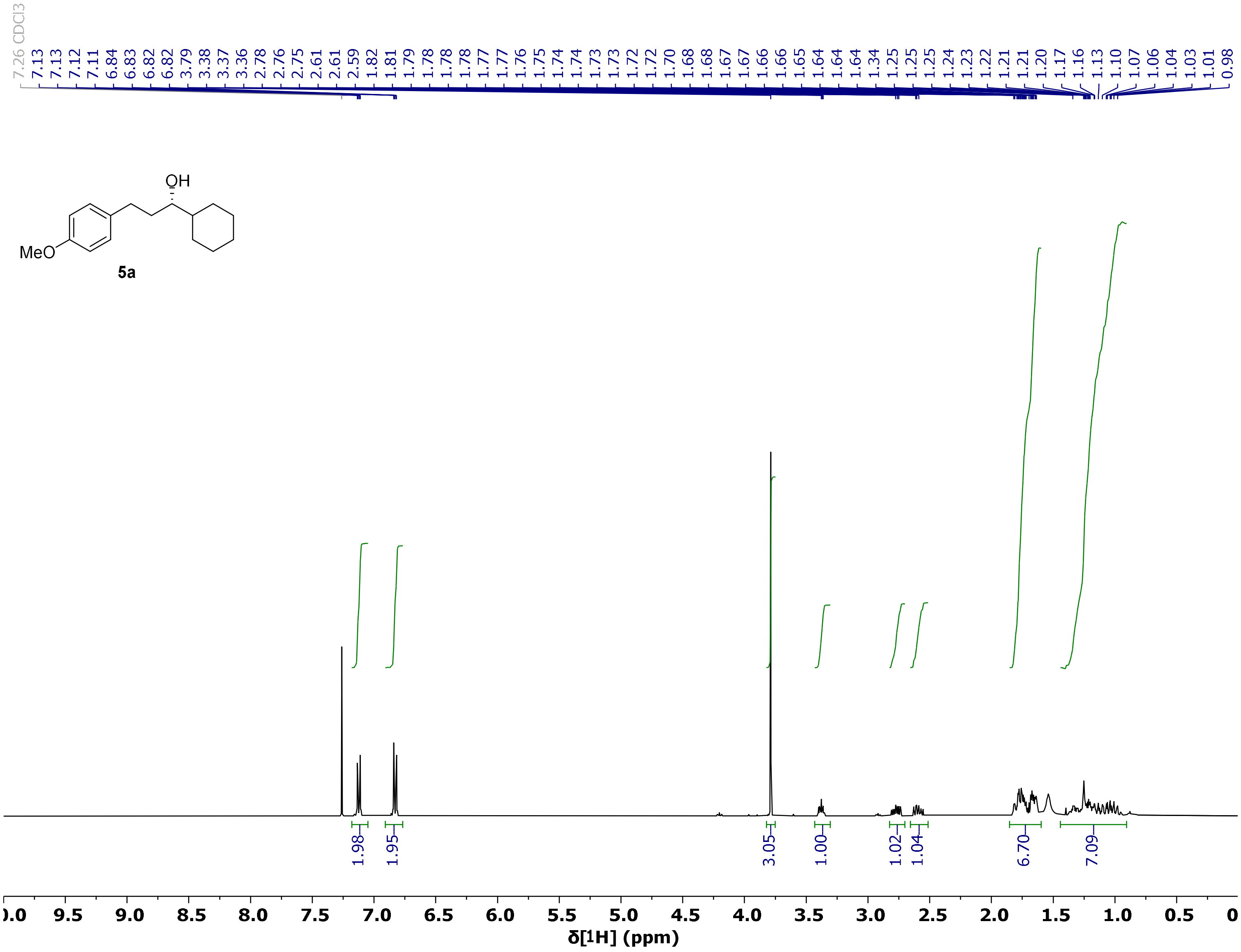
^{11}B NMR (128 MHz, CDCl$_3$)



4x



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



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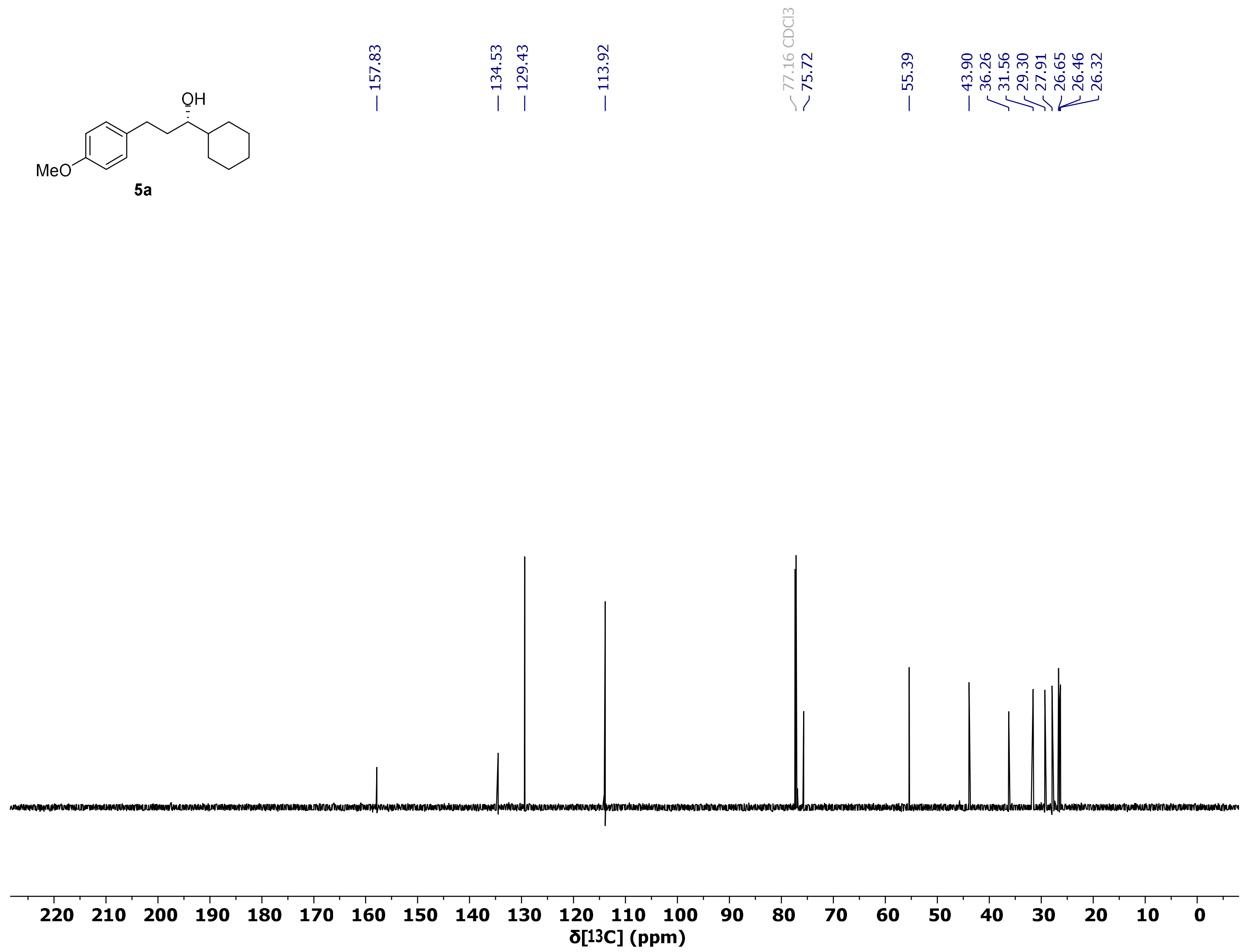
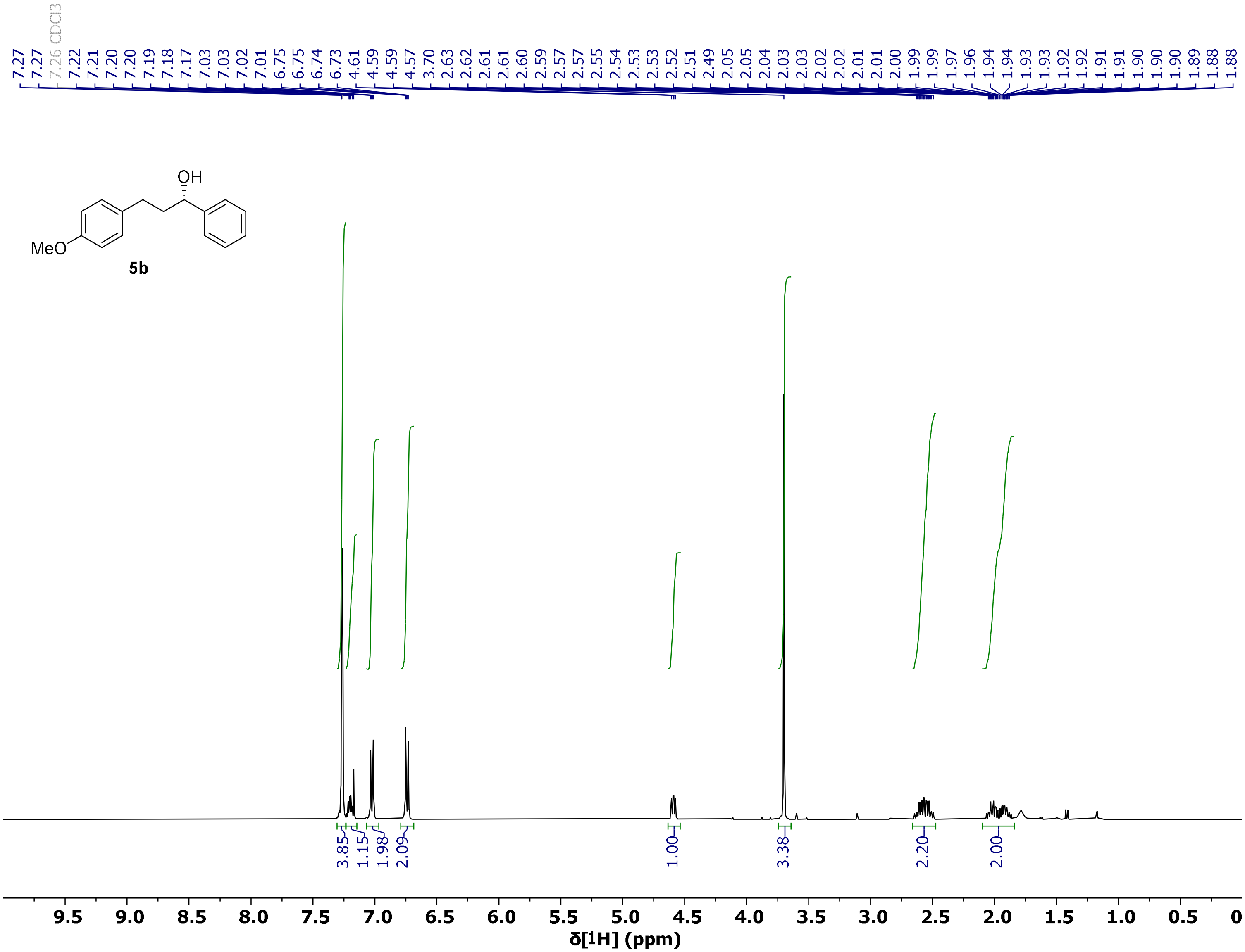


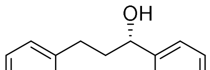
5a

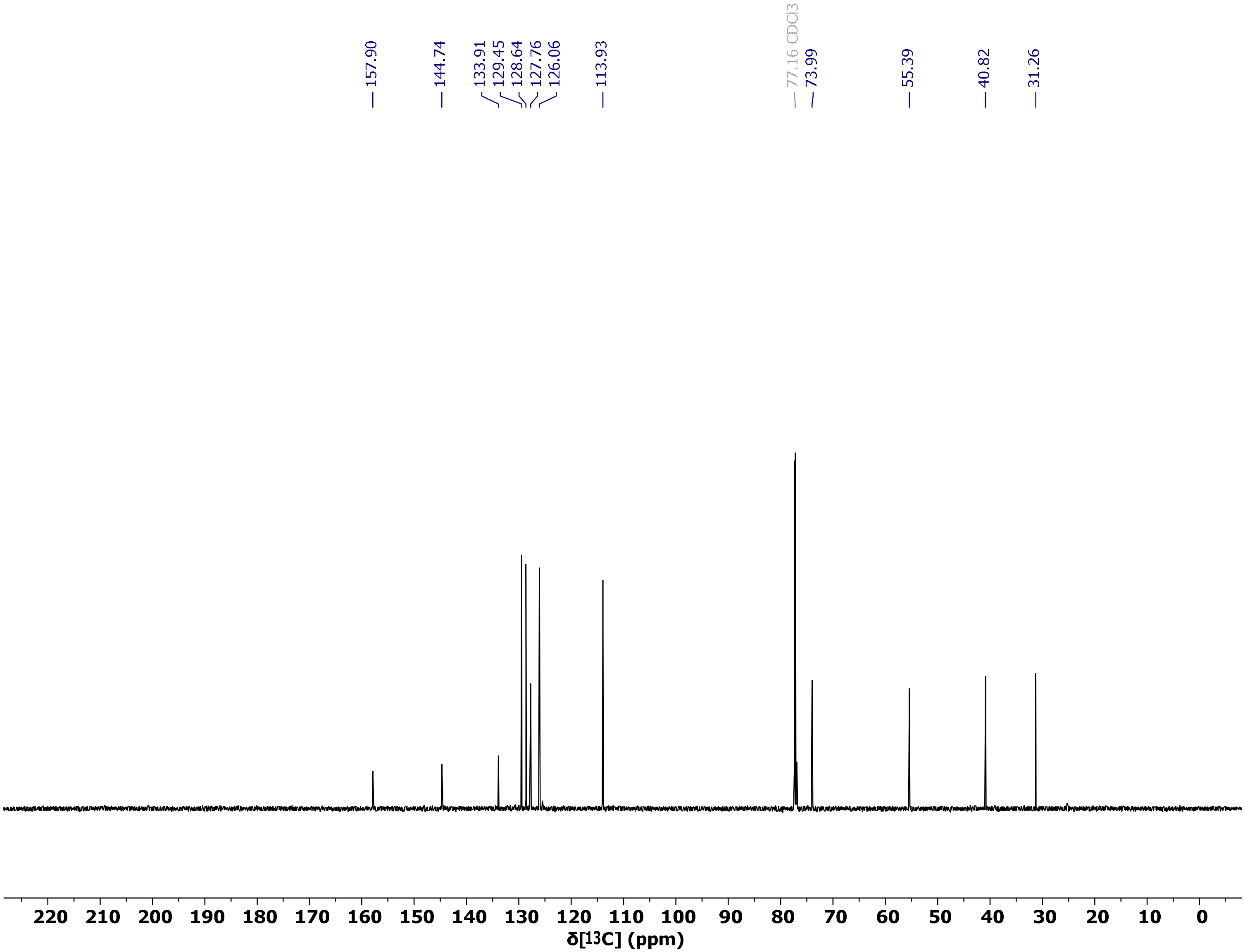
^{1}**H NMR** (400 MHz, $CDCl_3$)



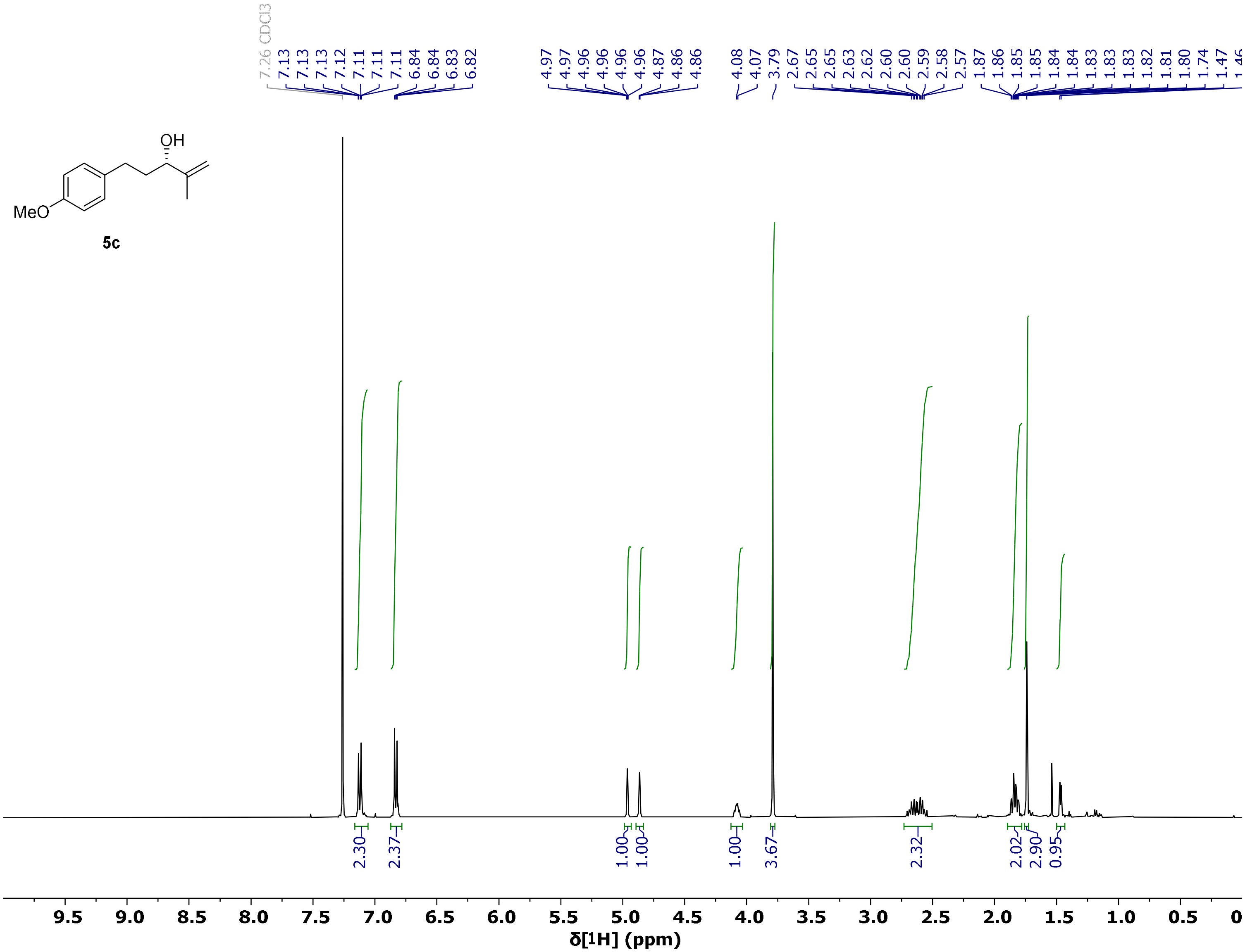
5b

^{13}C NMR (151 MHz, $CDCl_3$)

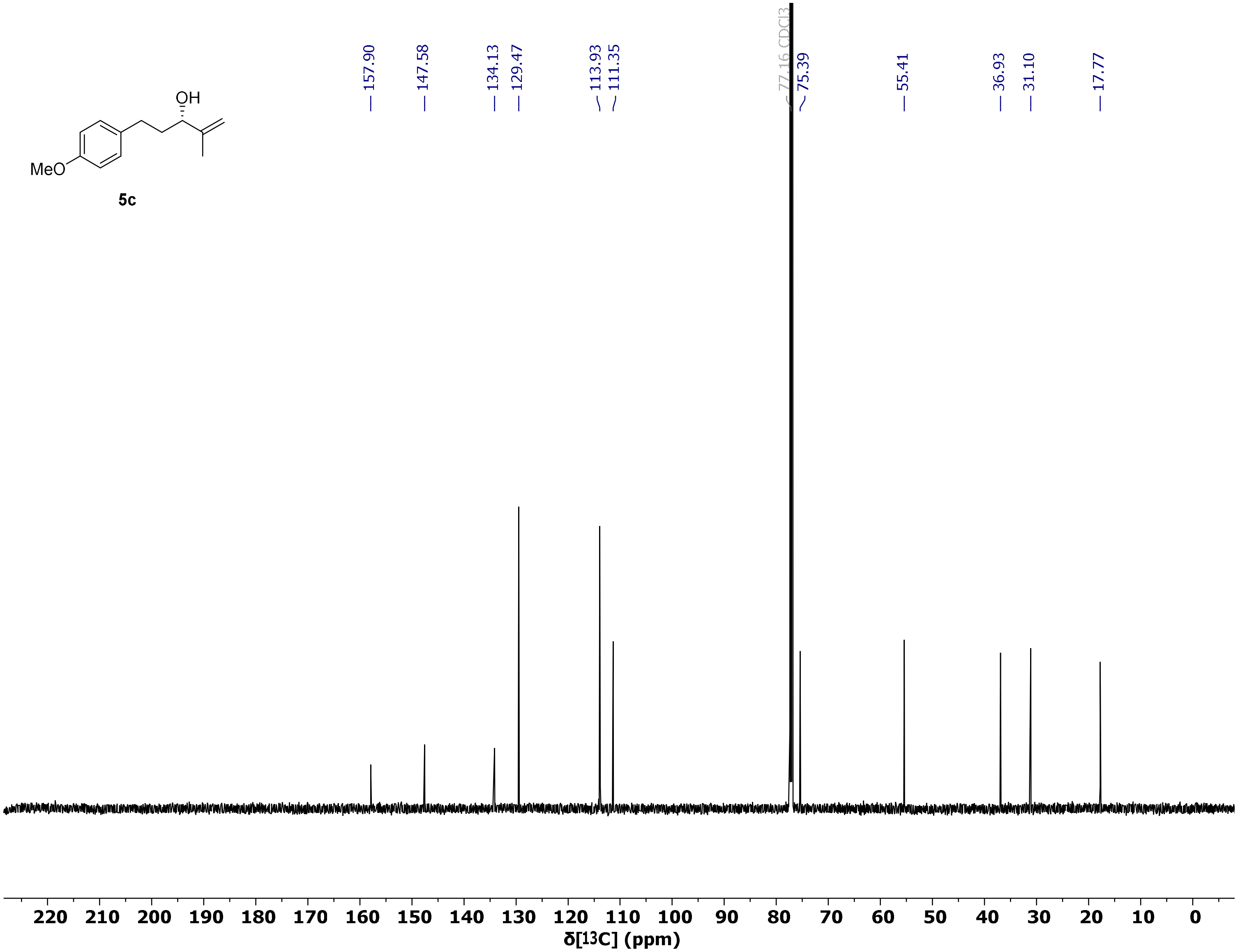




^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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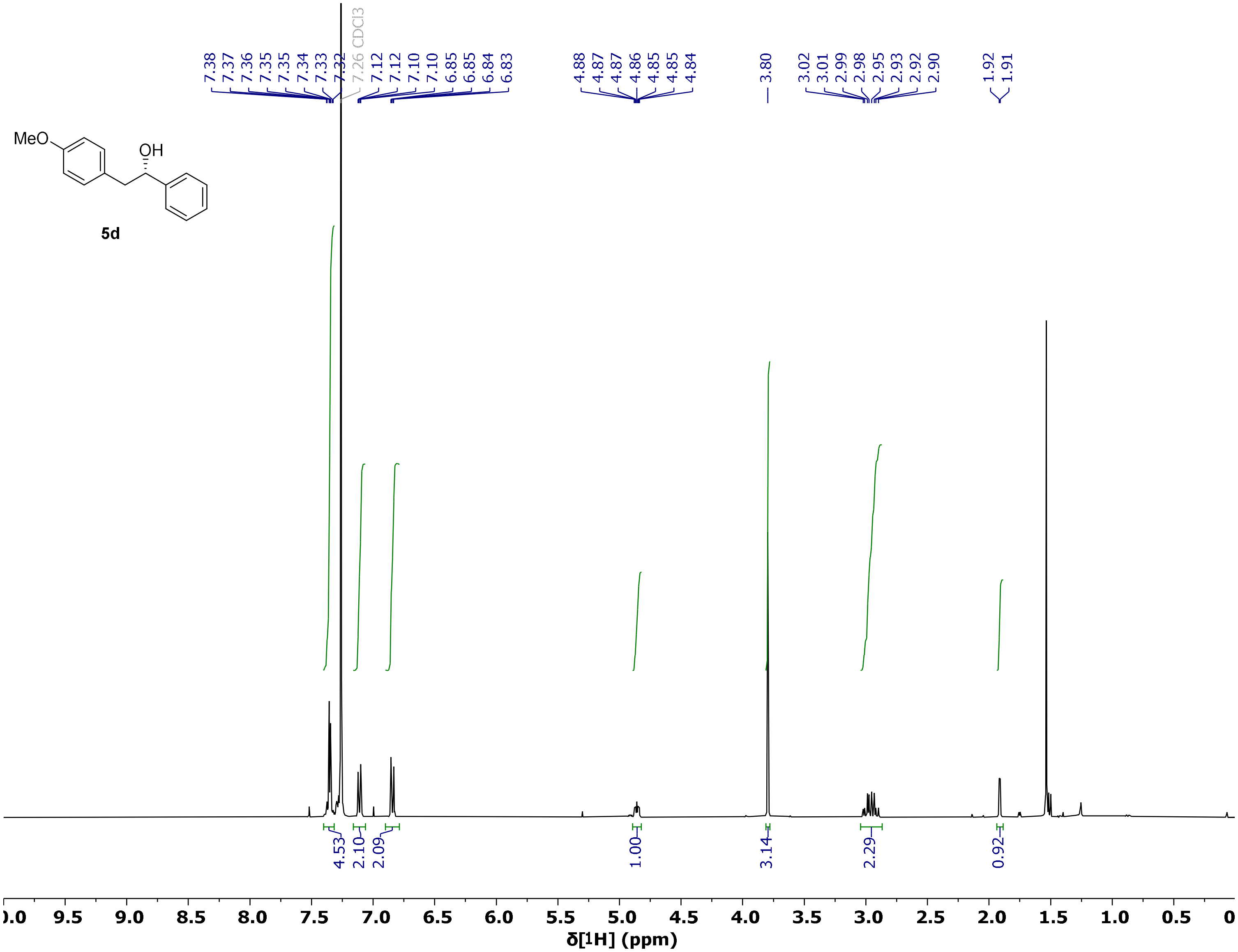

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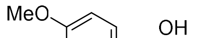

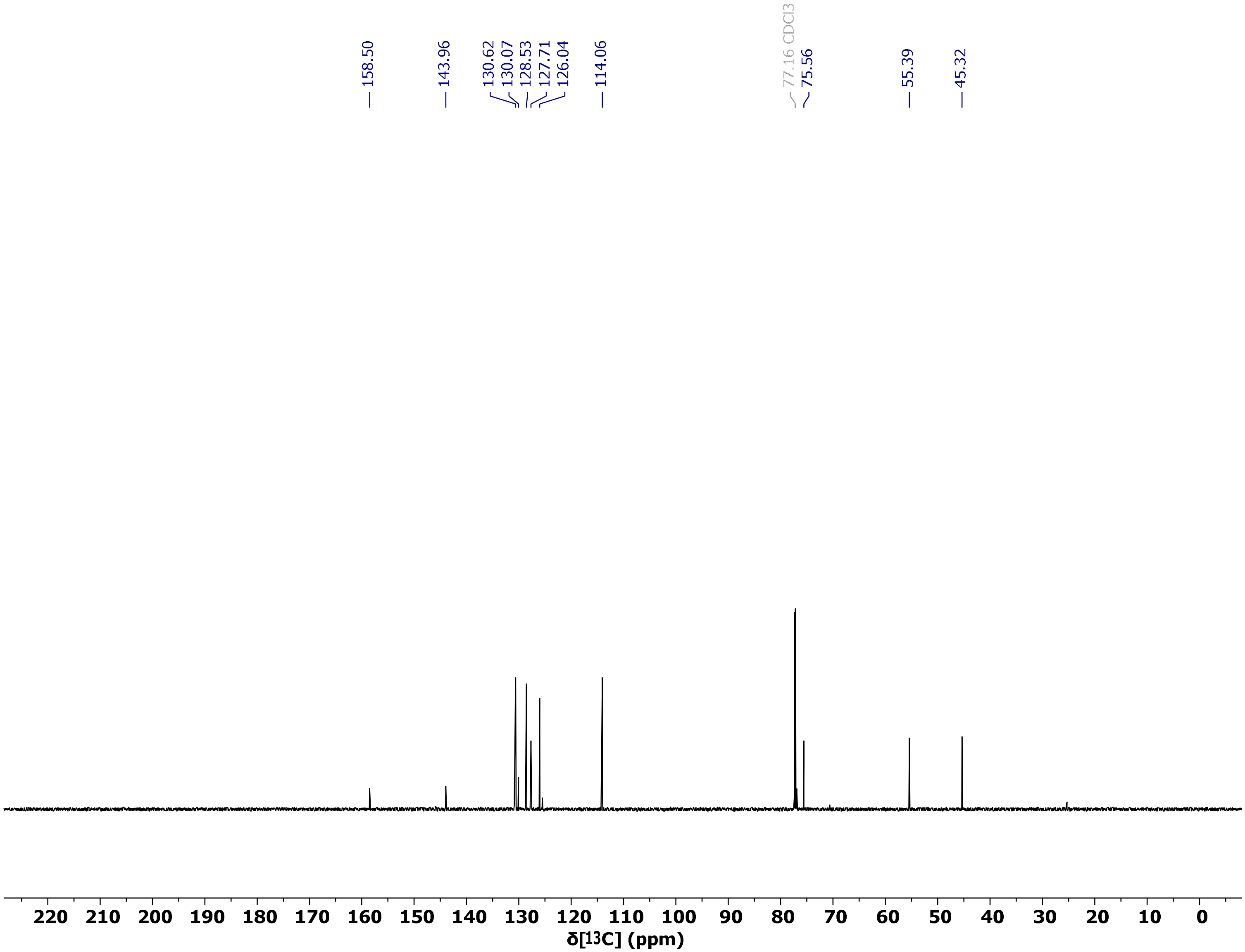

158.50
143.96
130.62
130.07
128.53
127.71
126.04
114.06
77.16 CDCl3
75.56
55.39
45.32
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ[13C] (ppm)

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[28] $R_W(F^2) = \{\Sigma w(|F_O|^2 - |F_C|^2)^2/\Sigma w(|F_O|)^4\}^{1/2}$, where w is the weight given each reflection

$R(F) = \Sigma(|F_O| - |F_C|)/\Sigma|F_O|\}$ for reflections with $F_O > 4(\sigma(F_O))$

$S = [\Sigma w(|F_O|^2 - |F_C|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters

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