Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Accessing alkyl boronic esters via visible light-mediated decarboxylative addition reactions of redox active esters

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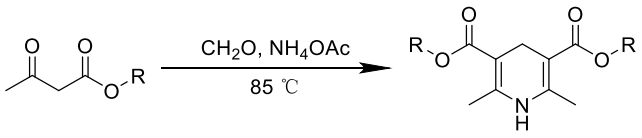
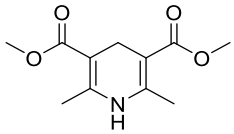
1. General information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon using standard Schlenk techniques at room temperature (r.t.). All reagents and solvents were obtained from commercial sources and were purified according to standard procedures before use. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished by flash chromatography on silica gel. The product spots on the thin layer chromatography (TLC) was identified/visualized by fluorescence quenching or by potassium permanganate, phosphomolybdic acid or dinitrophenylhydrazine staining. ^{1}H and ^{11}B NMR spectra were recorded on a Bruker Avance 400 (400 MHz and 128 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker Avance 400 or a Bruker Avance 600 spectrometer operating at 101 MHz or 151MHz. Chemical shifts are referenced to residual undeuterated solvent (note: $CDCl_3$ referenced at 7.26 and 77.00 ppm respectively, CD_2Cl_2 at 5.32 ^{1}H NMR, at 53.84 ppm ^{13}C NMR). Chemical shifts (δ) and coupling constants (*J*) are given in parts per million (ppm) and Hertz (Hz) respectively. The abbreviations of multiplicities: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, tt = triplet of triplets, br. = broad, m = multiplet or unresolved, etc. High resolution mass spectra (HRMS) were recorded on Waters Micromass GCT Premier (EI) and Exactive Plus LC-MS (ESI) mass spectrometers. Gas Chromatography (GC) measurements were performed on a GCMS-QP2010SE from SHIMADZU.

General procedure for synthesis of Hantzsch ester analogues



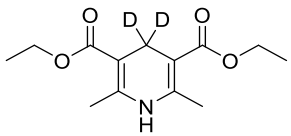
Methyl Hantzsch ester and deuterated ethyl Hantzsch ester were synthesized according to the reported procedure.[1] An oven-dried round bottom flask was charged with paraformaldehyde (1 equiv.), ester (4 equiv.), ammonium acetate (2 equiv.) and water (0.4 – 0.5 M), then the resulting mixture was stirred at 85 °C until the reaction was complete. After about 3 hours, the reaction mixture was allowed to cool down to room temperature. The reaction mixture was filtered and sequentially washed with water and EtOAc. The precipitate was dried in vacuo to get the desired product.



Dimethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (HE-1)

Following the general method, the reaction of paraformaldehyde (0.4 g, 12.48 mmol) and methyl acetoacetate (5.4 mL, 49.92 mmol) afforded methyl Hantzsch ester as a yellow solid (1.9 g, 69% yield). Spectral data are in accordance with those reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.15 (br. s, 1H), 3.70 (s, 6H), 3.27 (s, 2H), 2.19 (s, 6H) ppm.



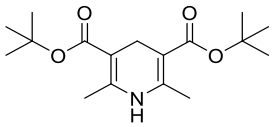
Diethyl 2,6-diethyl-1,4-dihydropyridine-3, 5-dicarboxylate-4,4-d_2 (D_2-HE)

Following the general method, the reaction of deuterated D_2-paraformaldehyde (0.1 g, 3.12 mmol) and ethyl acetoacetate (1.6 mL, 12.48 mmol) afforded deuterated ethyl Hantzsch ester as a yellow solid (0.6 g, 75% yield). Spectral data are in accordance with those reported in the

literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.24 (br. s, 1H), 4.16 (q, *J* = 7.1 Hz, 4H), 2.18 (s, 6H), 1.27 (t, *J* = 6.8Hz, 6H) ppm.

The *t*-Butyl Hantzsch ester was synthesized according to the reported procedure.[4] An oven dried round Schlenk flask was charged with paraformaldehyde (1 equiv.), ester (2 equiv.) and ammonium acetate (1.5 equiv.), then the mixture was stirred at 85 °C under argon atmosphere. After 30 min, some cold water was added to the solid crude product. The precipitate was filtered and recrystallized from methanol to get the desired product.

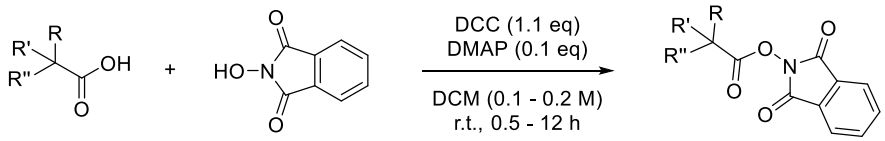


Di-*tert*-butyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (HE-3)

Following the general method, the reaction of paraformaldehyde (0.15 g, 4.99 mmol) and *tert*-butyl-acetoacetate (1.6 mL, 9.98 mmol) afforded *t*-Butyl Hantzsch ester as a yellow solid (0.72 g, 47% yield). Spectral data are in accordance with those reported in the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.98 (br. s, 1H), 3.14 (s, 2H), 2.14 (s, 6H), 1.47 (s, 18H) ppm.

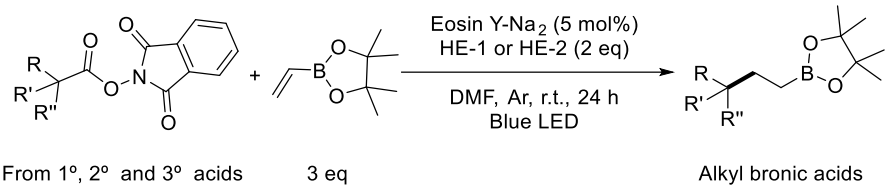
General procedure for synthesis of NHPI redox-active esters



NHPI redox-active esters were prepared according to the known procedures.[5] In a round bottom flask equipped with a stir bar was charged with carboxylic acid (1.0 equiv.), *N*-hydroxyphthalimide (1.1 equiv.), and DMAP (0.1 equiv.). Dichloromethane (DCM) was added (0.1 – 0.2 M), and the mixture was stirred vigorously followed by DCC (1.1 equiv.). The mixture was then allowed to stir for 0.5 – 12 hours until the acid was completely consumed (checked by TLC). The mixture was filtered through thin pads of Celite or silica

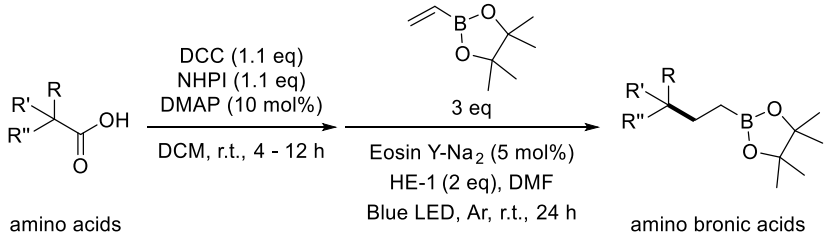
gel, and then rinsed with DCM. The filtrate was collected, and the solvent was removed under reduced pressure. Purification of the resulting residue by column chromatography or recrystallization afforded the corresponding NHPI redox-active ester products.[5-13]

General procedure A for the decarboxylative borylation of redox-active ester



Under argon, to an oven-dried Schlenk tube (10 mL) equipped with a stir bar, was added NHPI redox-active ester (0.2 mmol, 1 equiv.), Eosin Y-Na_2 (6.9 mg, 0.01 mmol, 0.05 equiv.), and HE-1 or HE-2 (0.4 mmol, 2 equiv.), followed by the addition of dry DMF (2 mL) and vinyl boronic acid pinacol ester (102 μL, 0.6 mmol, 3 equiv.). The reaction mixture was then degassed by three freeze-pump-thaw cycles. The Schlenk tube was then backfilled with argon. The reaction mixture was stirred at room temperature for 24 hours under the irradiation of 2 × 18W blue LED bulbs (at approximately 3 cm away from the light sources, ca. 25 °C). The resulting mixture was dissolved in EtOAc (12 mL for 0.2 mmol scale) and washed with saturated NaCl (3 × 12 mL for 0.2 mmol scale). The combined aqueous layers were extracted with EtOAc (12 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered before removal of the solvent by rotavapor. The product was purified by flash chromatography (SiO_2, PE：EA = 32：1 to 5：1) to give the corresponding pure product.

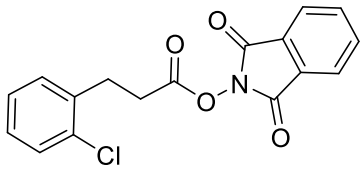
General procedure B: the one-opt procedure for the synthesis of amino boronic ester



To a 10-mL oven-dried round bottom flask was charged with amino acid (0.3 mmol, 1.0

equiv.), *N*-hydroxyphthalimid (53.8 mg, 0.33 mmol, 1.1 equiv.) and DMAP (3.7 mg, 0.03 mmol, 0.1 equiv.). Dichloromethane was added (3 mL, 0.1 M), and the mixture was stirred vigorously. DCC (68.1 mg, 0.33 mmol, 1.1 equiv.) was then added and the mixture allowed to stir until the acid was completely consumed (determined by TLC). The crude reaction mixture was concentrated under reduced pressure. The residue was dissolved in DMF (3 mL), and transferred into an oven-dried Schlenk tube (10 mL) under argon. Eosin Y-Na_2 (10.4 mg, 0.015 mmol, 0.05 equiv.), HE-1 (135.1 mg, 0.6 mmol, 2 equiv.), and vinyl boronic acid pinacol ester (153 μL, 0.9 mmol, 3 equiv.) were added. The reaction mixture was then degassed by three freeze-pump-thaw cycles, and backfilled with argon. The reaction mixture was stirred at room temperature for 24 h under the irradiation of 2 × 18W blue LED bulbs (at approximately 3 cm away from the light sources, ca. 25 °C). The resulting mixture was dissolved in EtOAc (18 mL for 0.3 mmol scale) and washed with saturated NaCl (3 × 18 mL for 0.3 mmol scale). The combined aqueous layers were extracted with EtOAc (18 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered before removal of the solvent by rotavapor. The product was purified by flash chromatography (SiO_2, PE：EA = 18：1 to 3：1) to give the corresponding pure product.

2. Characterizations of redox-active esters and products



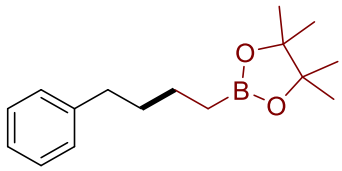
6s

Compound **6s**: 91% yield, white solids.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.87 (m, 2H), 7.79 – 7.77 (m, 2H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.18 (m, 2H), 3.21 (t, *J* = 7.7 Hz, 2H), 3.01 (t, *J* = 7.7 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.7, 161.8, 136.7, 134.7, 133.9, 130.6, 129.6, 128.8, 128.3, 127.1, 123.9, 30.7, 28.6 ppm;

HRMS (ESI+): $[M+Na]^+$ Calc. for $C_{17}H_{12}ClNO_4$: 334.0686; found: 334.0686.

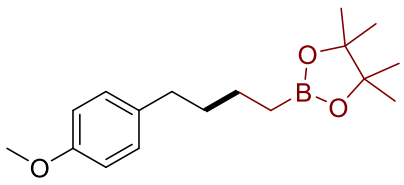


3[14]

Compound **3**: 81% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.24 (m, 2H), 7.18 – 7.14 (m, 3H), 2.61 (t, *J* = 7.5 Hz, 2H), 1.67 – 1.59 (m, 2H), 1.51 – 1.43 (m, 2H), 1.24 (s, 12H), 0.81 (t, *J* = 7.8 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.0, 128.4, 128.2, 125.5, 82.9, 35.8, 34.2, 24.8, 23.8 11.3 (br., C–B) ppm.

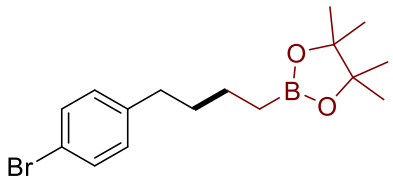


4[15]

Compound **4**: 56% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 7.9 Hz, 2H), 3.78 (s, 3H), 2.61 – 2.53 (m, 2H), 1.63 – 1.56 (m, 2H), 1.49 –1.42 (m, 2H), 1.24 (s, 12H), 0.81 (t, *J* = 7.8 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.5, 135.0, 129.2, 113.6, 82.9, 55.2, 34.8, 34.4, 24.8, 23.7, 11.0 (br., C–B) ppm.

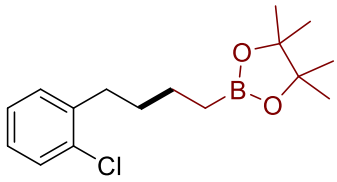


5[16]

Compound **5**: 59% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.0 Hz, 2H), 7.04 (d, *J* = 7.3 Hz, 2H), 2.55 (t, *J* = 7.5 Hz, 2H), 1.63 – 1.55 (m, 2H), 1.48 – 1.40 (m, 2H), 1.24 (s, 12H), 0.80 (t, *J* = 7.7 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.8, 131.2, 130.2, 119.2, 82.9, 35.1, 33.9, 24.8, 23.6, 11.1 (br., C–B) ppm.



6

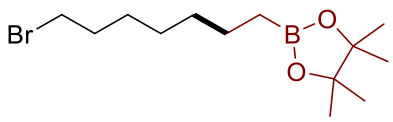
Compound **6**: 58% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.7 Hz, 1H), 7.21 – 7.08 (m, 3H), 2.71 (t, *J* = 7.6 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.54 – 1.47 (m, 2H), 1.24 (s, 12H), 0.83 (t, *J* = 7.8 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.4, 133.9, 130.3, 129.3, 127.0, 126.6, 82.9, 33.5, 32.4, 24.8, 23.9, 10.9 (br., C–B) ppm;

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.2 (br. s, 1B) ppm;

HRMS (ESI+): Calcd. for $C_{16}H_{25}BClO_2$ $[M+H]^+$: 295.1631; found: 295.1630.



7

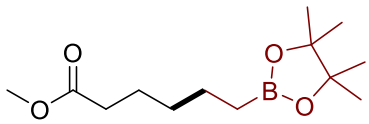
Compound **7**: 62% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.39 (t, *J* = 6.8 Hz, 2H), 1.87 – 1.79 (m, 2H), 1.40 – 1.38 (m, 4H), 1.33 – 1.29 (m, 4H), 1.24 (s, 12H), 0.76 (t, *J* = 7.7 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 82.9, 34.0, 32.8, 32.1, 28.5, 28.1, 24.8, 23.9 ppm. The signal of α-B-carbon was not detected due to the boron quadrupole;

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.3 (br. s, 1B) ppm;

HRMS (ESI+): Calcd. for $C_{13}H_{26}BBrNaO_2$$[M+Na]^+$: 327.1101; found: 327.1101.

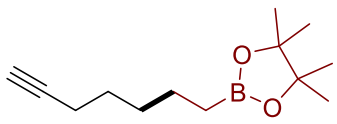


8[17]

Compound **8**: 51% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.65 (s, 3H), 2.29 (t, *J* = 7.4 Hz, 2H), 1.66 – 1.57 (m, 2H), 1.46 – 1.38 (m, 2H), 1.35 – 1.25 (m, 2H), 1.23 (s, 12H), 0.77 (t, *J* = 7.6 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.3, 82.9, 51.4, 34.1, 31.8, 24.82, 24.80, 23.6 ppm. The signal of α-B-carbon was not detected due to the boron quadrupole.

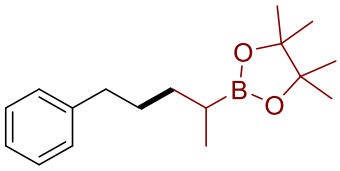


9[18]

Compound **9**: 61% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.19 – 2.15 (m, 2H), 1.94 – 1.90 (m, 1H), 1.56 – 1.49 (m, 2H), 1.44 – 1.35 (m, 4H), 1.24 (s, 12H), 0.78 (t, *J* = 7.0 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 84.8, 82.9, 68.0, 31.5, 28.3, 24.8, 23.5, 18.3 ppm. The signal of α-B-carbon was not detected due to the boron quadrupole.



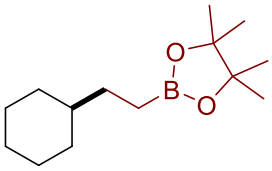
10[21]

Compound **10**: 52% yield (According to General procedure A with isopropenylboronic acid pinacol ester (3 equiv.)), colorless oil.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.25 (t, *J* = 7.3 Hz, 2H), 7.20 – 7.12 (m, 3H), 2.58 (t, *J* = 7.9 Hz, 2H), 1.67 – 1.57 (m, 2H), 1.49 – 1.40 (m, 1H), 1.36 – 1.28 (m, 1H), 1.20 (s, 12H), 1.03 – 0.95 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H) ppm;

^{13}C NMR (101 MHz, CD_2Cl_2): δ 143.5, 128.8, 128.5, 125.9, 83.2, 36.5, 33.4, 31.2, 25.0, 24.9, 15.7 ppm. The signal of α-B-carbon was not detected due to the boron quadrupole;

^{11}B NMR (128 MHz, CD_2Cl_2): δ 34.3 (br. s, 1B) ppm.

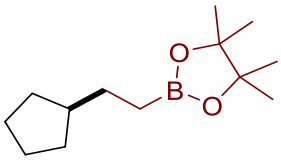


12[19]

Compound **12**: 85% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 – 1.60 (m, 5H), 1.31 – 1.26 (m, 2H), 1.24 (s, 12H), 1.23 – 1.02 (m, 4H), 0.87 – 0.82 (m, 2H), 0.77 – 0.73 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 39.9, 33.0, 31.4, 26.8, 26.8, 24.8 ppm. The signal of α-B-carbon was not detected due to the boron quadrupole.

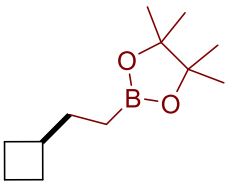


13[19]

Compound **13**: 65% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.76 – 1.65 (m, 3H), 1.62 – 1.45 (m, 4H), 1.43 – 1.37 (m, 2H), 1.24 (s, 12H), 1.11 – 1.03 (m, 2H), 0.77 (t, *J* = 8.2 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 42.6, 32.3, 30.2, 25.2, 24.8 ppm. The signal of α-B-carbon was not detected due to the boron quadrupole.



14

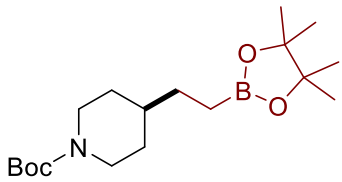
Compound **14**: 62% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22 – 2.15 (m, 1H), 2.04 – 1.96 (m, 2H), 1.83 – 1.74 (m, 2H), 1.61 – 1.53 (m, 2H), 1.50 – 1.44 (m, 2H), 1.24 (s, 12H), 0.68 – 0.64 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 38.3, 31.0, 27.9, 24.8, 18.1, 8.2 (br., C–B) ppm;

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.2 (br. s, 1B) ppm;

HRMS (ESI+): Calcd. for $C_{12}H_{24}BO_2$ $[M+H]^+$: 211.1864; found: 211.1864.



15

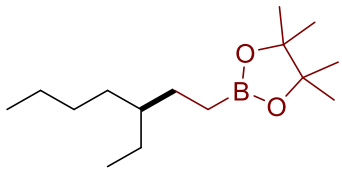
Compound **15**: 72% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.05 (br., 2H), 2.64 (t, *J* = 12.7 Hz, 2H), 1.65 – 1.58 (m, 3H), 1.44 (s, 9H), 1.39 – 1.31 (m, 2H), 1.24 (s, 12H), 1.10 – 0.96 (m, 2H), 0.76 (t, *J* = 8.0 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.0, 83.0, 79.1, 44.3 (br.), 38.2, 31.8, 30.5, 28.5, 24.8 ppm. The signal of α-B-carbon was not detected due to the boron quadrupole;

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.5 (br. s, 1B) ppm;

HRMS (ESI+): Calcd. for $C_{18}H_{34}BNNaO_4[M+Na]^+$: 362.2473; found: 362.2473.



16

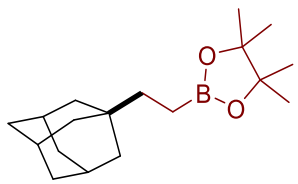
Compound **16**: 75% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 – 1.32 (m, 2H), 1.28 – 1.14 (m, 9H), 1.24 (s, 12H), 0.87 (t, *J* = 6.2 Hz, 3H), 0.82 (t, *J* = 6.9 Hz, 3H), 0.74 – 0.70 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 40.9, 32.4, 29.0, 27.1, 25.4, 24.8, 23.1, 14.1, 10.9, 7.9 (br., C–B) ppm;

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.3 (br. s, 1B) ppm;

HRMS (ESI+): Calcd. for $C_{15}H_{32}BO_2$ $[M+H]^+$: 255.2490; found: 255.2489.

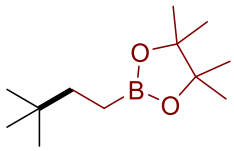


17[19]

Compound **17**: 73% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.92 (s, 3H), 1.68 (d, *J* = 11.5 Hz, 3H), 1.60 (d, *J* = 11.7 Hz, 3H), 1.42 (s, 6H), 1.24 (s, 12H), 1.19 – 1.14 (m, 2H), 0.70 – 0.65 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 41.9, 38.1, 37.3, 32.6, 28.8, 24.8, 3.4 (br., C–B) ppm.

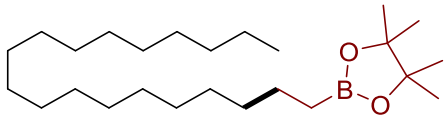


18[20]

Compound **18**: 65% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 – 1.27 (m, 2H), 1.24 (s, 12H), 0.84 (s, 9H), 0.71 (t, *J* = 8.0 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 82.9, 37.7, 30.8, 28.9, 24.8, 5.7 (br., C–B) ppm.



19

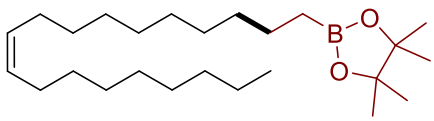
Compound **19**: 76% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 – 1.35 (m, 2H), 1.31 – 1.25 (m, 32H), 1.24 (s, 12H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.76 (t, *J* = 7.8 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 32.4, 31.9, 29.70 – 29.65 (10C), 29.6, 29.42, 29.36, 24.8, 24.0, 22.7, 14.1 ppm. The signal of α-B-carbon was not detected due to the boron quadrupole;

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.2 (br. s, 1B) ppm;

HRMS (ESI+): Calcd. for $C_{25}H_{52}BO_2$ $[M+H]^+$: 395.4055; found: 395.4053.



20

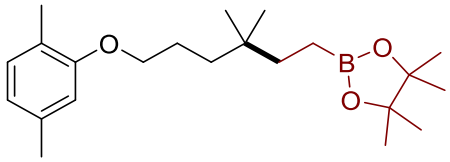
Compound **20**: 66% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.38 – 5.31 (m, 2H), 2.03 – 1.98 (m, 4H), 1.43 – 1.25 (m, 26H), 1.24 (s, 12H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.76 (t, *J* = 7.6 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 129.92, 129.88, 82.8, 32.4, 31.9, 29.80 (2C), 29.77, 29.69, 29.55 (2C), 29.52, 29.4, 29.3, 27.2 (2C), 24.8, 24.0, 22.7, 14.1 ppm. The signal of α-B-carbon was not detected due to the boron quadrupole;

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.0 (br. s, 1B) ppm;

HRMS (ESI+): Calcd. for $C_{25}H_{50}BO_2$ $[M+H]^+$: 393.3898; found: 393.3898.

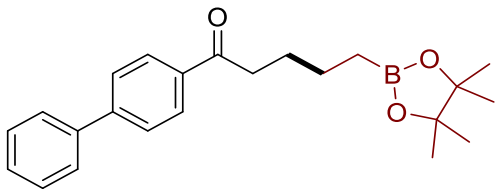


21[19]

Compound **21**: 72% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (d, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.4 Hz, 1H), 6.62 (s, 1H), 3.90 (t, *J* = 6.4 Hz, 2H), 2.31 (s, 3H), 2.18 (s, 3H), 1.78 – 1.71 (m, 2H), 1.38 – 1.32 (m, 4H), 1.26 (s, 12H), 0.87 (s, 6H), 0.74 – 0.70 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.1, 136.4, 130.2, 123.6, 120.5, 112.0, 82.9, 68.7, 37.5, 35.5, 33.0, 26.6, 24.8, 24.3, 21.4, 15.8, 5.2 (br., C–B) ppm.



22

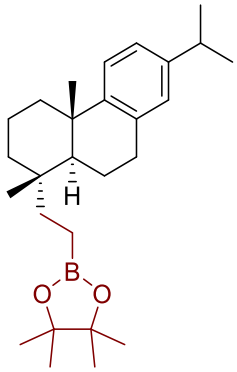
Compound **22**: 48% yield (According to General procedure A), white semi-solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.43 – 7.34 (m, 1H), 3.00 (t, *J* = 7.4 Hz, 2H), 1.82 – 1.72 (m, 2H), 1.57 – 1.50 (m, 2H), 1.24 (s, 12H), 0.90 – 0.80 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.2, 145.5, 140.0, 135.8, 128.9, 128.7, 128.1, 127.3, 127.2, 83.0, 38.6, 27.1, 24.8, 23.9 ppm. The signal of α-B-carbon was not detected due to the boron quadrupole;

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.5 (br. s, 1B) ppm;

HRMS (ESI+): Calcd. for $C_{23}H_{29}BNaO_3$ $[M+Na]^+$: 387.2102; found: 387.2101.

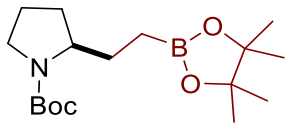


23[19]

Compound **23**: 67% yield (According to General procedure A), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.88 (s, 1H), 2.91 – 2.78 (m, 3H), 2.26 (d, *J* = 11.9 Hz, 1H), 1.84 – 1.76 (m, 1H), 1.73 – 1.68 (m, 1H), 1.65 – 1.55 (m, 2H), 1.45 (s, 1H), 1.42 – 1.33 (m, 4H), 1.25 – 1.21 (m, 10H), 1.24 (s, 12H), 0.90 (s, 3H), 0.72 – 0.59 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.8, 145.3, 135.0, 126.8, 124.3, 123.7, 82.8, 47.0, 38.7, 37.7, 37.5, 36.4, 35.9, 33.4, 30.4, 25.3, 24.8, 23.98, 23.96, 20.4, 19.0, 18.5, 4.3 (br., C–B) ppm.

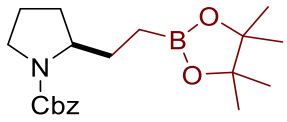


24[19]

Compound **24**: 82% yield (According to General procedure A), 78% yield (According to General procedure B), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 – 3.59 (m, 1H), 3.48 – 3.21 (m, 2H), 1.94 – 1.64 (m, 5H), 1.45 (s, 9H), 1.39 – 1.29 (m, 1H), 1.23 (s, 12H), 0.73 – 0.68 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.7, 83.0, 78.8, 59.1, 46.3, 29.7, 28.6, 28.3, 24.81, 24.78, 23.3, 7.6 (br., C–B) ppm.

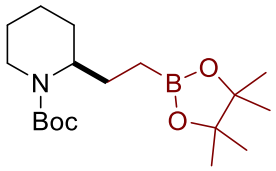


25[19]

Compound **23**: 56% yield (According to General procedure B), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.26 (m, 5H), 5.14 – 5.08 (m, 2H), 3.86 – 3.74 (br. s, 1H), 3.51 – 3.30 (m, 2H), 1.97 – 1.62 (m, 5H), 1.47 – 1.38 (m, 1H), 1.22 (s, 12H), 0.76 – 0.64 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.1 + 154.8 (rotameric peaks), 137.2, 128.3, 127.7, 83.0, 66.4 + 66.3 (rotameric peaks), 59.7 + 59.0 (rotameric peaks), 46.6 + 46.2 (rotameric peaks), 29.9 + 29.1 (rotameric peaks), 28.5 + 27.8 (rotameric peaks), 24.8, 24.7, 23.6 + 23.0 (rotameric peaks), 7.6 (br., C–B) ppm.

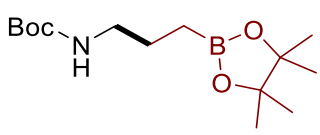


26[19]

Compound **26**: 24% yield (According to General procedure B), colorless oil. (The low isolated yield is due to the difficult separation from the pyridine by-product of Hantzsch ester by chromatography.)

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.11 (s, 1H), 3.94 (d, *J* = 13.5 Hz, 1H), 2.76 (t, *J* = 12.8 Hz, 1H), 1.82 – 1.71 (m, 1H), 1.60 – 1.48 (m, 6H), 1.44 (s, 9H), 1.40 – 1.30 (m, 1H), 1.24 (s, 12H), 0.70 (t, *J* = 8.3 Hz, 2H) ppm;

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.2, 83.0, 78.9, 52.5 (br.), 38.6 (br.), 28.5, 28.0 (br.), 25.7, 24.8, 23.9, 19.0, 8.0 (br., C–B) ppm.

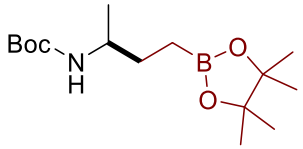


27[19]

Compound **27**: 48% yield (According to General procedure B), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.72 + 4.35 (2 × br. s, 1H), 3.12 – 3.07 (m, 2H), 1.65 – 1.57 (m, 2H), 1.43 (s, 9H), 1.24 (s, 12H), 0.79 (t, *J* = 7.6 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.0, 83.2, 78.8, 42.6, 28.4, 24.8, 24.1, 8.4 (br., C–B) ppm.

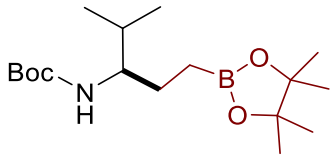


28[19]

Compound **28**: 73% yield (According to General procedure B), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.5 (br. s, 1H), 3.62 – 3.43 (br. m, 1H), 1.59 – 1.45 (m, 2H), 1.42 (s, 9H), 1.24 (s, 12H), 1.09 (d, *J* = 6.1 Hz, 3H), 0.79 (t, *J* = 7.6 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.5, 83.1, 78.7, 48.4, 30.9, 28.4, 24.9, 24.8, 21.2, 7.8 (br., C–B) ppm.

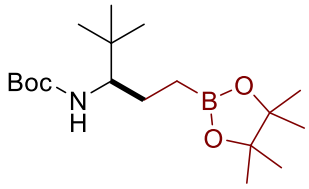


29[19]

Compound **29**: 65% yield (According to General procedure B), white waxy semi-solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.39 (d, *J* = 9.4 Hz, 1H) + 4.04 (br. s, 1H), 3.33 (tt, *J* = 9.5, 4.6 Hz, 1H) + 3.22 (br. s, 1H), 1.80 – 1.67 (m, 1H), 1.67 – 1.54 (m, 1H), 1.42 (s, 9H), 1.38 – 1.28 (m, 1H), 1.24 (s, 12H), 0.93 – 0.83 (m, 6H), 0.83 – 0.74 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.0, 83.1, 78.6, 57.6, 32.1, 28.4, 25.9, 25.0, 24.8, 19.0, 17.8 ppm. The signal of α-B-carbon was not detected due to the boron quadrupole.

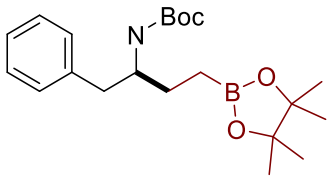


30[19]

Compound **30**: 61% yield (According to General procedure B), white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (85:15 ratio of rotamers) 4.24 (d, *J* = 10.1 Hz, 0.85H), 3.97 (d, *J* = 10.3 Hz, 0.15H), 3.25 (t, *J* = 10.9 Hz, 0.85H), 3.09 (t, *J* = 10.4 Hz, 0.15H), 1.77 – 1.69 (m, 1H), 1.44 (s, 1.35H), 1.42 (s, 7.65H), 1.25 (s, 12H), 1.17 – 1.09 (m, 1H), 0.87 (s, 9H), 0.78 – 0.71 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.3, 83.0, 78.5, 61.1, 35.0, 28.4, 26.4, 24.9, 24.8, 24.1 ppm. The signal of α-B-carbon was not detected due to the boron quadrupole.

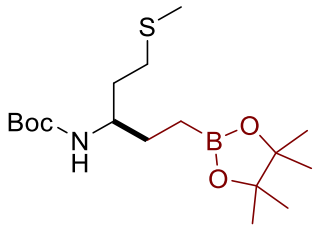


31[19]

Compound **31**: 59% yield (According to General procedure B), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.23 (m, 2H), 7.22 – 7.12 (m, 3H), 4.61 (d, *J* = 8.4 Hz, 1H), 3.70 (s, 1H), 2.88 – 2.80 (m, 1H), 2.70 – 2.65 (m, 1H), 1.67 – 1.59 (m, 1H), 1.44 – 1.30 (m, 1H), 1.39 (s, 9H), 1.23 (s, 12H), 0.80 (t, *J* = 7.3 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.5, 138.6, 129.5, 128.2, 126.0, 83.1, 78.8, 53.7, 41.5, 28.4, 27.7, 24.9, 24.7, 7.8 (br., C–B) ppm.

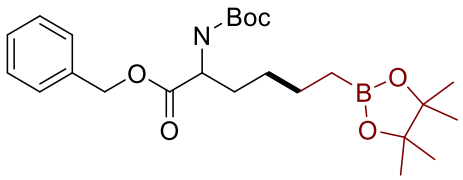


32[19]

Compound **32**: 69% yield (According to General procedure B), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.51 (d, *J* = 7.5 Hz, 1H), 3.55 (s, 1H), 2.55 – 2.39 (m, 2H), 2.08 (s, 3H), 1.79 – 1.70 (m, 1H), 1.66 – 1.57 (m, 2H), 1.50 – 1.40 (m, 1H), 1.41 (s, 9H) 1.23 (s, 12H), 0.83 – 0.77 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.7, 83.2, 78.9, 52.0, 35.3, 30.7, 29.0, 28.4, 24.9, 24.7, 15.5, 7.4 (br., C–B) ppm.



33

Compound **33**: 52% yield (According to General procedure B), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.30 (m, 5H), 5.20 – 5.08 (m, 2H), 5.00 (d, *J* = 8.5 Hz, 1H), 4.34 – 4.28 (m, 1H), 1.78 (s, 1H), 1.70 – 1.55 (m, 2H), 1.43 (s, 9H), 1.39 – 1.29 (m, 3H), 1.23 (s, 12H), 0.73 (t, *J* = 7.5 Hz, 2H) ppm;

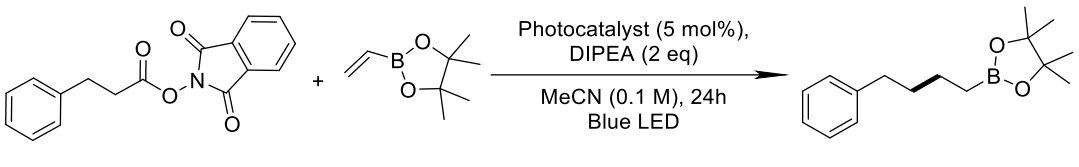
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.9, 155.4, 135.5, 128.6, 128.3, 128.2, 83.0, 79.7, 66.9, 53.6, 32.3, 28.3, 27.8, 24.8, 23.6, 11.1 (br., C–B) ppm;

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.1 (br. s, 1B) ppm;

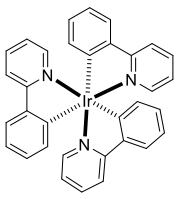
HRMS (ESI+): Calc. for $C_{24}H_{28}BNNaO_6[M+Na]^+$: 470.2684; found: 470.2684.

3. Reaction development

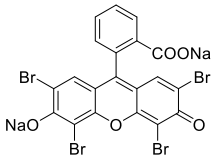
Table S1: Screening of photocatalyst.[a]



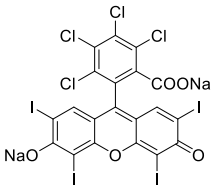
1 2 3



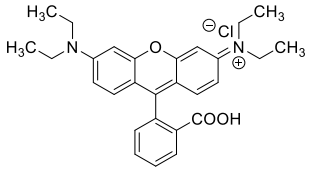
fac-Ir(ppy)$_3$



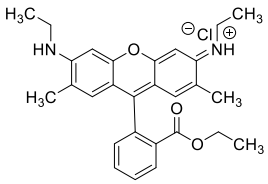
EosinY-Na$_2$



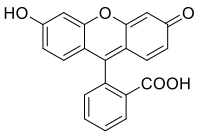
Acid Red 94



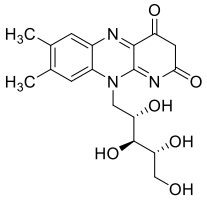
Rhodamine B



Rhodamine 6G



Fluorescein

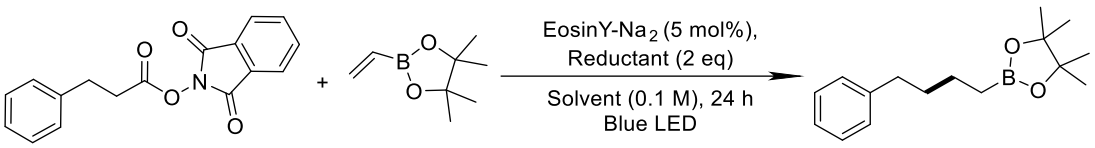


Riboflavin

Entry	Photocatalyst	Yield (%)
1	*fac*-Ir(ppy)$_3$	11
2	Eosin Y-Na$_2$	12
3	Acid Red 94	11
4	Rhodamine B	<2
5	Rhodamine 6G	<2
6	Fluorescein	6
7	Riboflavin	<2

[a]Reaction condition: on 0.05 mmol scale, vinyl boronic acid pinacol ester **2** (3 eq), photocatalyst (5 mol%), in MeCN (0.5 mL) at room temperature, under the irradiation of 2 × 18W blue LED bulbs, yields were determined by GC-MS using methoxybenzine as an internal standard.

Table S2: Screening of solvent and reductant.[a]

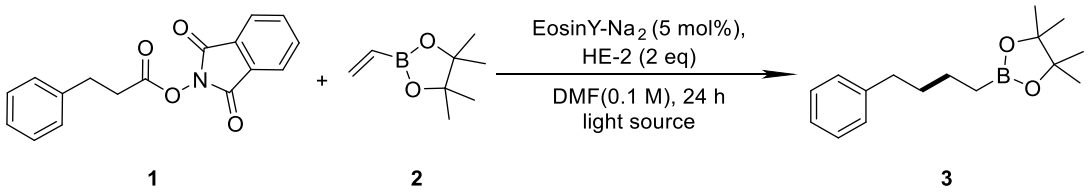


1 2 3

Entry	Solvents	Reductant	Yield (%)
1	MeCN	DIPEA	12
2	MeCN	HE-2/DIPEA (1:1)	31
3	MeCN	HE-2	40
4	DMF	HE-2	70
5	DMA	HE-2	60
6	DCM	HE-2	14
7	*Tert*-Butanol	HE-2	39
8	Dimethoxyehane	HE-2	49
9	DMF	DIPEA	12
10	DMF (0.45 ml) + H_2O (0.05 ml)	HE-2	44
11	DMF (0.4 ml) + H_2O (0.1 ml)	HE-2	37
12[b]	DMF	HE-2	38
13	DMF	HE-2 (1 eq)	49
14	DMF	HE-2 (1.5 eq)	58

[a]Reaction condition: on 0.05 mmol scale, vinyl boronic acid pinacol ester **2** (3 eq), Eosin Y-Na_2 (5 mol%), in Solvent (0.5 mL) at room temperature, under the irradiation of 2 × 18W blue LED bulbs, yields were determined by GC-MS using methoxybenzine as an internal standard. [b]Without degassing.

Table S3: Screening of light source and component ratio.[a]

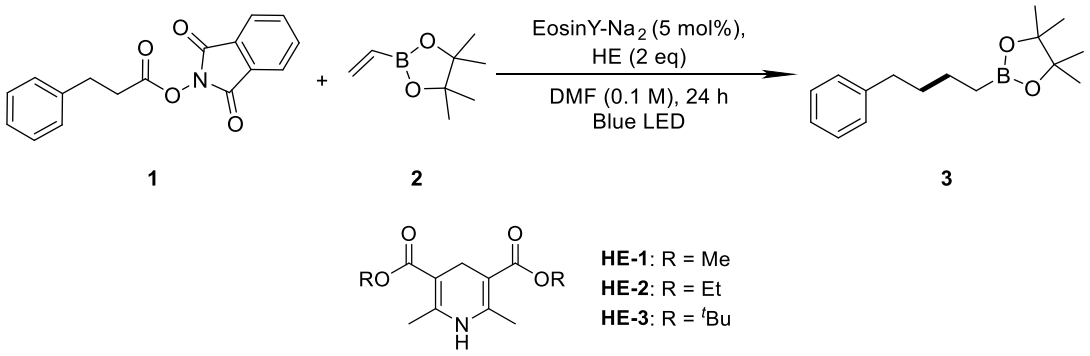


1 **2** **3**

Entry	Light Source	Yield (%)
1	15W blue LED bulb	64
2	18W blue LED bulb	70
3	24W blue photo-reactor	54
4	72W blue Photo-reactor	44
5[b]	18W blue LED bulb	51
6[c]	18W blue LED bulb	70
7[d]	18W blue LED bulb	56
8[e]	18W blue LED bulb	43

[a]Reaction condition: on 0.05 mmol scale, vinyl boronic acid pinacol ester **2** (3 eq), Eosin Y-Na_2 (5 mol%), in DMF (0.5 mL) at room temperature, under the irradiation of blue LED, yields were determined by GC-MS using methoxybenzine as an internal standard. [b]With 2 equivalent of **2**. [c]With 5 equivalent of **2**. [d]Using 2.5 mol% of Eosin Y-Na_2. [e]Using 10 mol% of Eosin Y-Na_2.

Table S4: Screening of Hantzsch ester analogue and control experiments.[a]



Entry	Reductant	Yield (%)
1	HE-1	83
2	HE-2	70
3	HE-3	62
5[b]	HE-1	28
6[c]	HE-1	NP
7	/	NP

[a]Reaction condition: on 0.05 mmol scale, vinyl boronic acid pinacol ester **2** (3 eq), Eosin Y-Na_2 (5 mol%), in DMF (0.5 mL) at room temperature, under the irradiation of 2 × 18W blue LED bulbs, yields were determined by GC-MS using methoxybenzine as an internal standard. [b]Without Eosin Y-Na_2. [c]In dark. NP = no product was observed.

4. Mechanistic study

Fluorescence quenching experiments

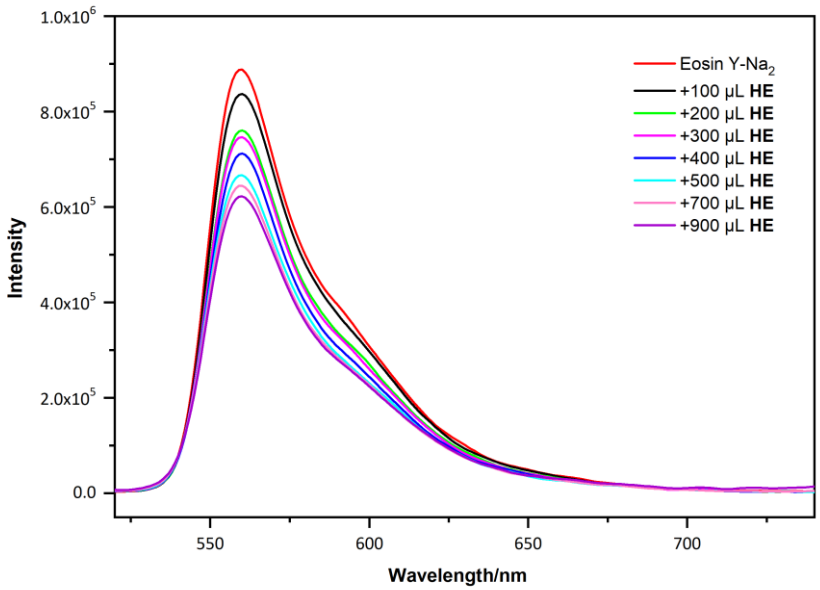


Figure S1. Fluorescence quenching of Eosin Y-Na_2 (30 µM in DMF) upon titration with Hantzsch ester (**HE**) (100 mM in DMF).

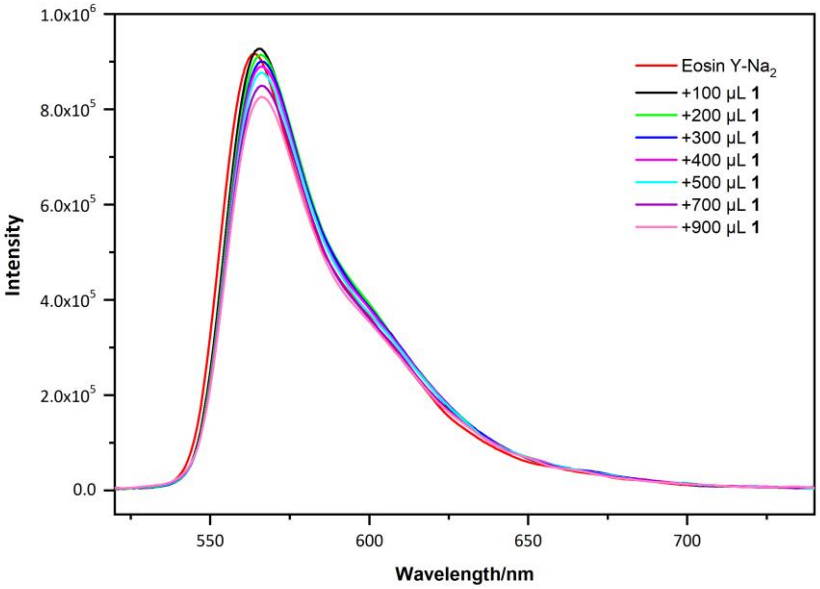
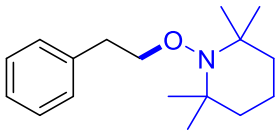


Figure S2. Fluorescence response of Eosin Y-Na_2 (30 µM in DMF) upon successive addition of redox-active ester **1** (100 mM in DMF).

TEMPO trapping experiment

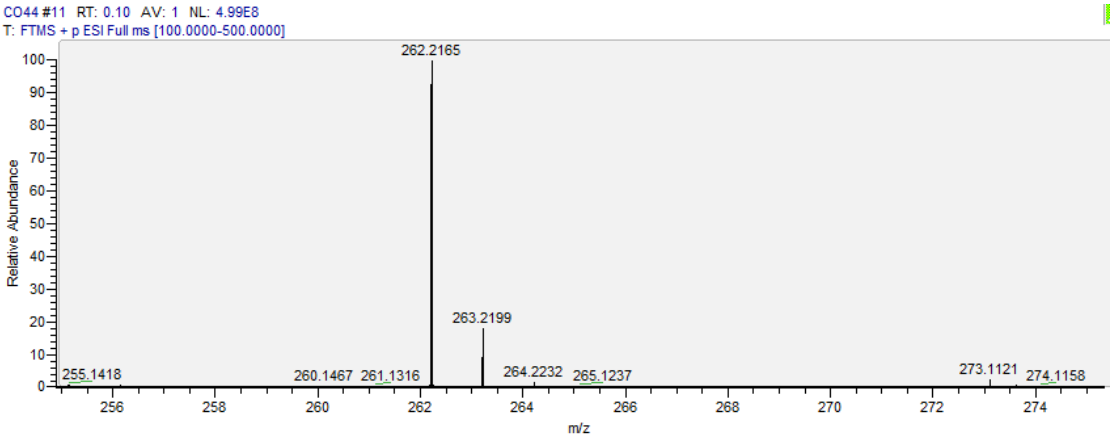
To an oven-dried Schlenk tube (10 mL) equipped with stir bar were added NHPI redox-active ester **1** (29.5 mg, 0.1 mmol, 1.0 equiv.), Eosin Y-Na_2 (3.5 mg, 0.005 mmol, 0.05 equiv.), HE-2 (50.6 mg, 0.2 mmol, 2.0 equiv.), TEMPO (31.3 mg, 0.2 mmol, 2.0 equiv.). After addition of dry DMF (1 mL), vinyl boronic acid pinacol ester (51 μL, 0.3 mmol, 3.0 equiv.) was added via syringe. The reaction mixture was degassed with three freeze-pump-thaw cycles. The reaction mixture was stirred and irradiated with 2 × 18W blue LED bulbs at room temperature for 24 hours (at approximately 3 cm away from the light sources, ca. 25 °C). Then a sample of the reaction mixture was submitted to HRMS analysis, which indicated the phenylethyl radical formed after decarboxylation and was trapped by TEMPO.



Chemical Formula: $C_{17}H_{27}NO$

$C_{17}H_{28}NO[M+H]^+$

m/z: 261.2165 (100.0%), 263.2199

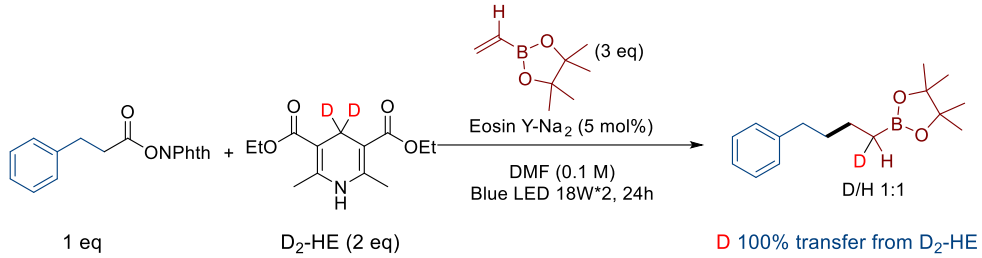


HRMS (ESI+): $C_{17}H_{28}NO[M+H]^+$ Calcd. for $C_{17}H_{28}NO$: 262.2165; found: 262.2165.

Figure S3. HRMS spectra for the TEMPO trapping reaction

Isotope-labeling experiment 1

Following the General procedure A with NHPI redox-active ester **1** (59.1 mg, 0.2 mmol, 1 equiv.), Eosin Y-Na_2 (6.9 mg, 0.01 mmol, 0.05 equiv.), deuterated ethyl Hantzsch ester (102.1 mg, 0.4 mmol, 2 equiv.), vinyl boronic acid pinacol ester (102 μL, 0.6 mmol, 3 equiv.) and dry DMF (2 mL), which was irradiated with 2 × 18W blue LED bulbs for 24 hours. Purification by flash column chromatography (hexanes∶EtOAc = 15∶1) afforded the deuterated product as a colorless oil.



From the **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28 – 7.24 (m, 2H), 7.18 – 7.14 (m, 3H), 2.60 (t, *J* = 7.5 Hz, 2H), 1.67 – 1.59 (m, 2H), 1.49 – 1.43 (m, 2H), 1.24 (s, 12H), 0.81 (t, *J* = 8.0 Hz, 1H) ppm; **^{11}B NMR** (128 MHz, $CDCl_3$): δ 34.5 (br. s, 1B) ppm, we could see the interatration of the H_2C-Bpin (δ 0.79-0.83 ppm) is only 1 proton, which meaned that the other proton was deuterium, coming from the deuterated Hantzsch ester.

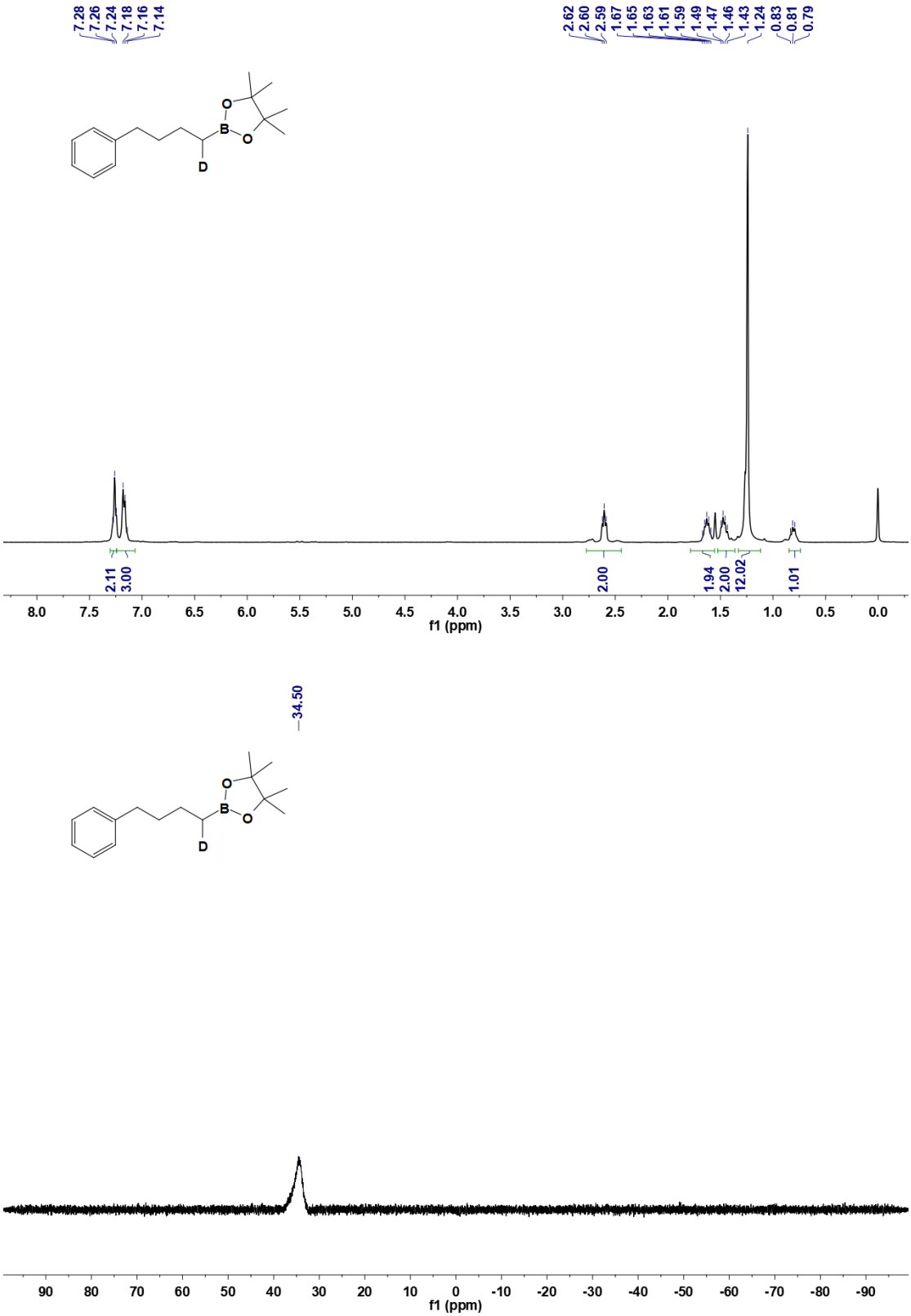
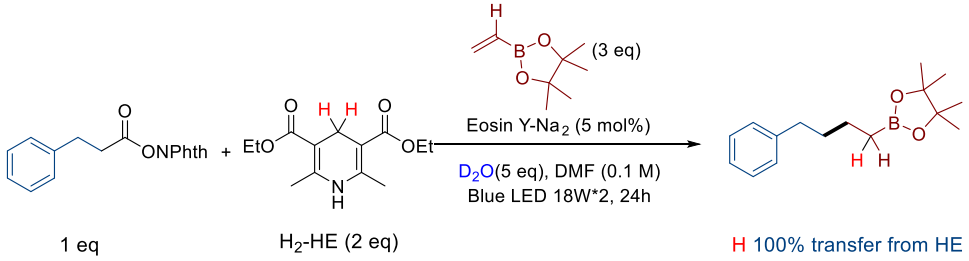


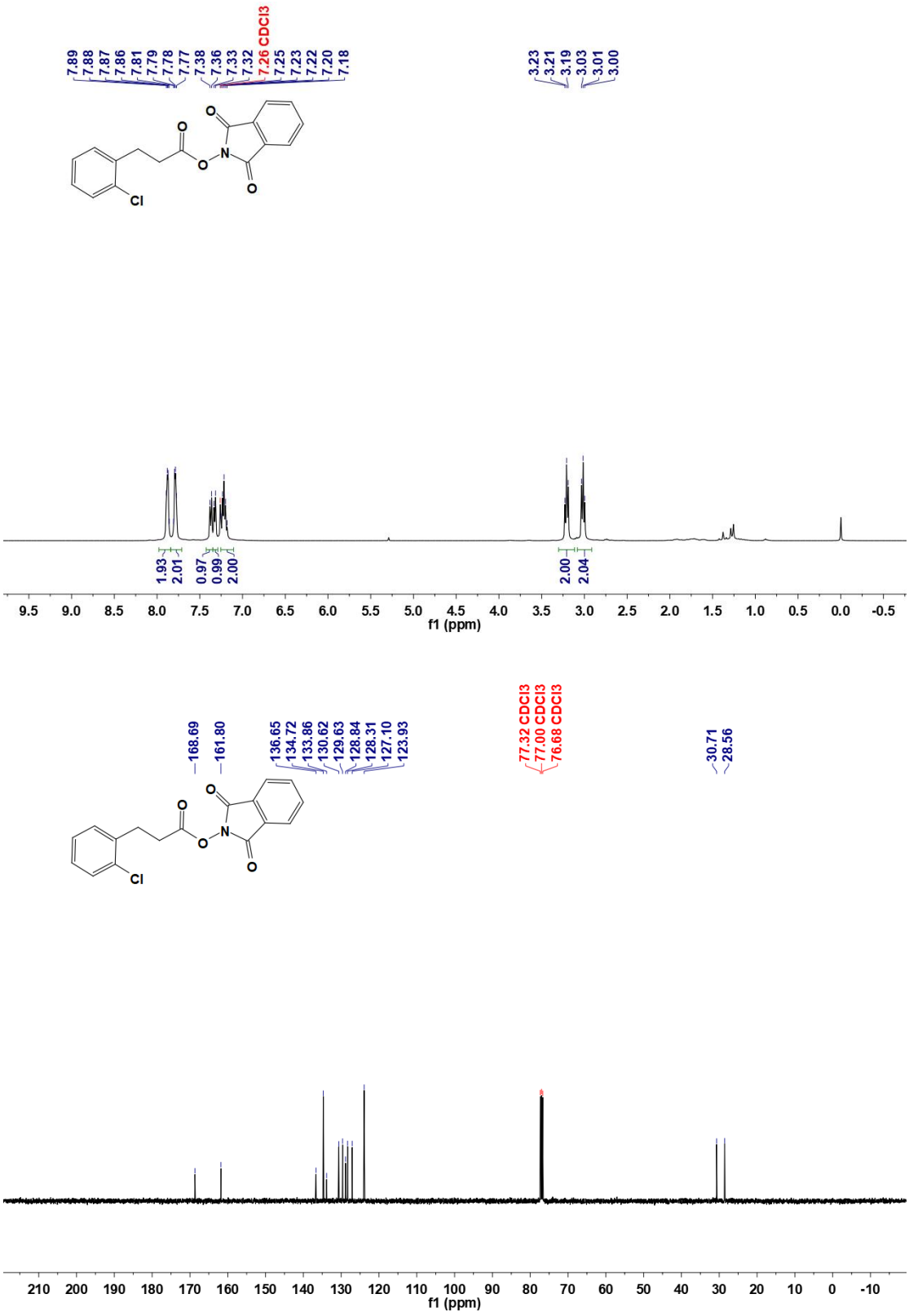
Figure S4. ^{1}H and ^{11}B NMR spectra of the deuterium-labeled product

Isotope-labeling experiment 2

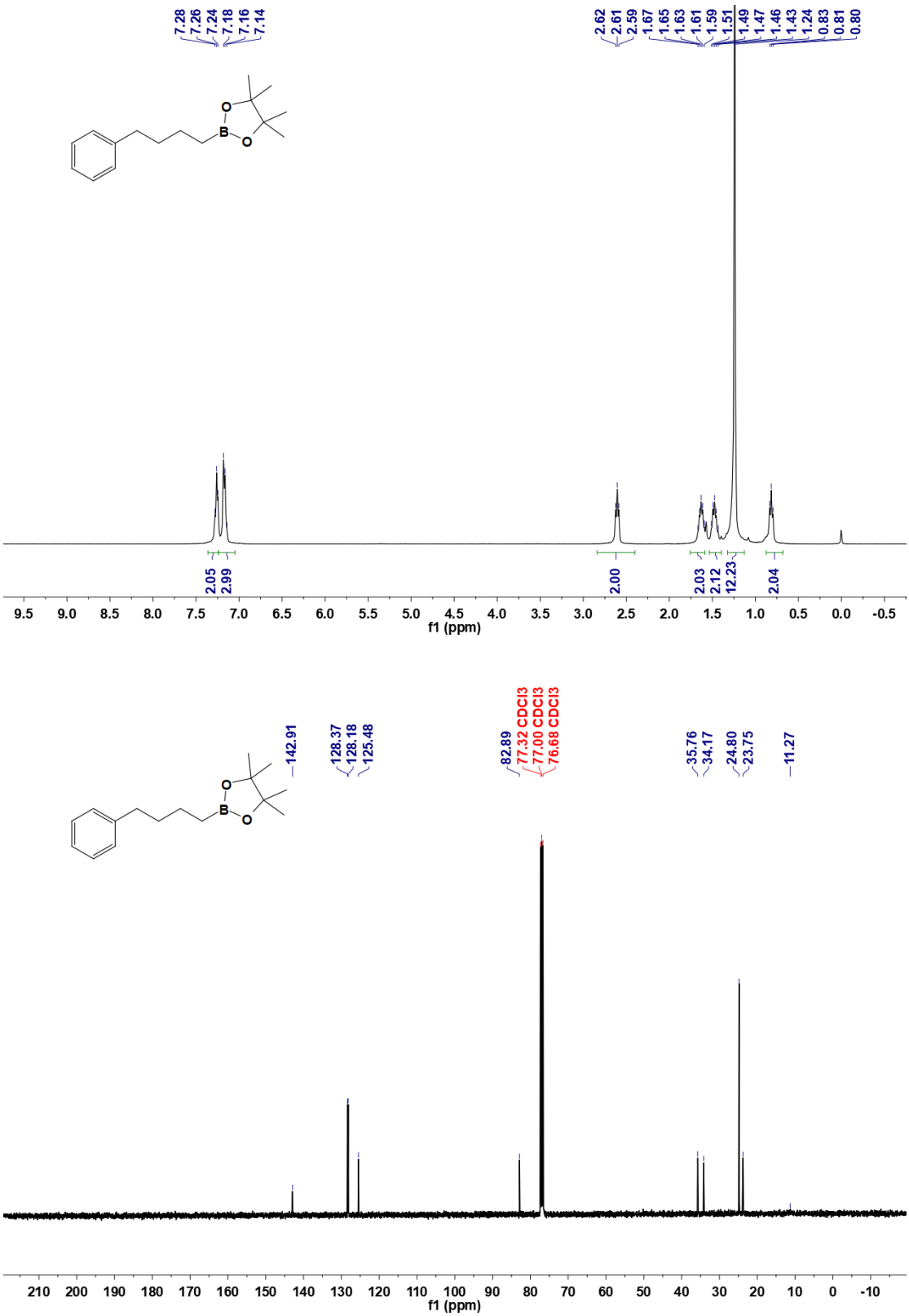
Under argon, to an oven-dried Schlenk tube (10 mL) equipped with stir bar were added NHPI redox-active ester **1** (59.1 mg, 0.2 mmol, 1.0 equiv.), Eosin Y-Na_2 (6.9 mg, 0.01 mmol, 0.05 equiv.), HE-2 (101.2 mg, 0.4 mmol, 2.0 equiv.), D_2O (18 μL, 1.0 mmol, 5.0 equiv.). After addition of dry DMF (1 mL), vinyl boronic acid pinacol ester (102 μL, 0.60 mmol, 3.0 equiv.) was added via syringe. The reaction mixture was then degassed by three freeze-pump-thaw cycles. The Schlenk tube was then backfilled with argon. The reaction mixture was stirred at room temperature for 24 hours under the irradiation of 2 × 18W blue LED bulbs (at approximately 3 cm away from the light sources, ca. 25 °C). The resulting mixture was dissolved in EtOAc (12 mL for 0.2mmol scale) and washed with saturated NaCl (3 ×12 mL for 0.2mmol scale). The combined aqueous layers were extracted with EtOAc (12 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered before removal of the solvent by rotavapor. The product was formed with 100% H-incorporation α to the boronic ester group, as determined by ^1H NMR. It showed that no intermediate α-boryl anion was formed. Therefore, this result further demonstrated the formation of an intermediate α-boryl radical.



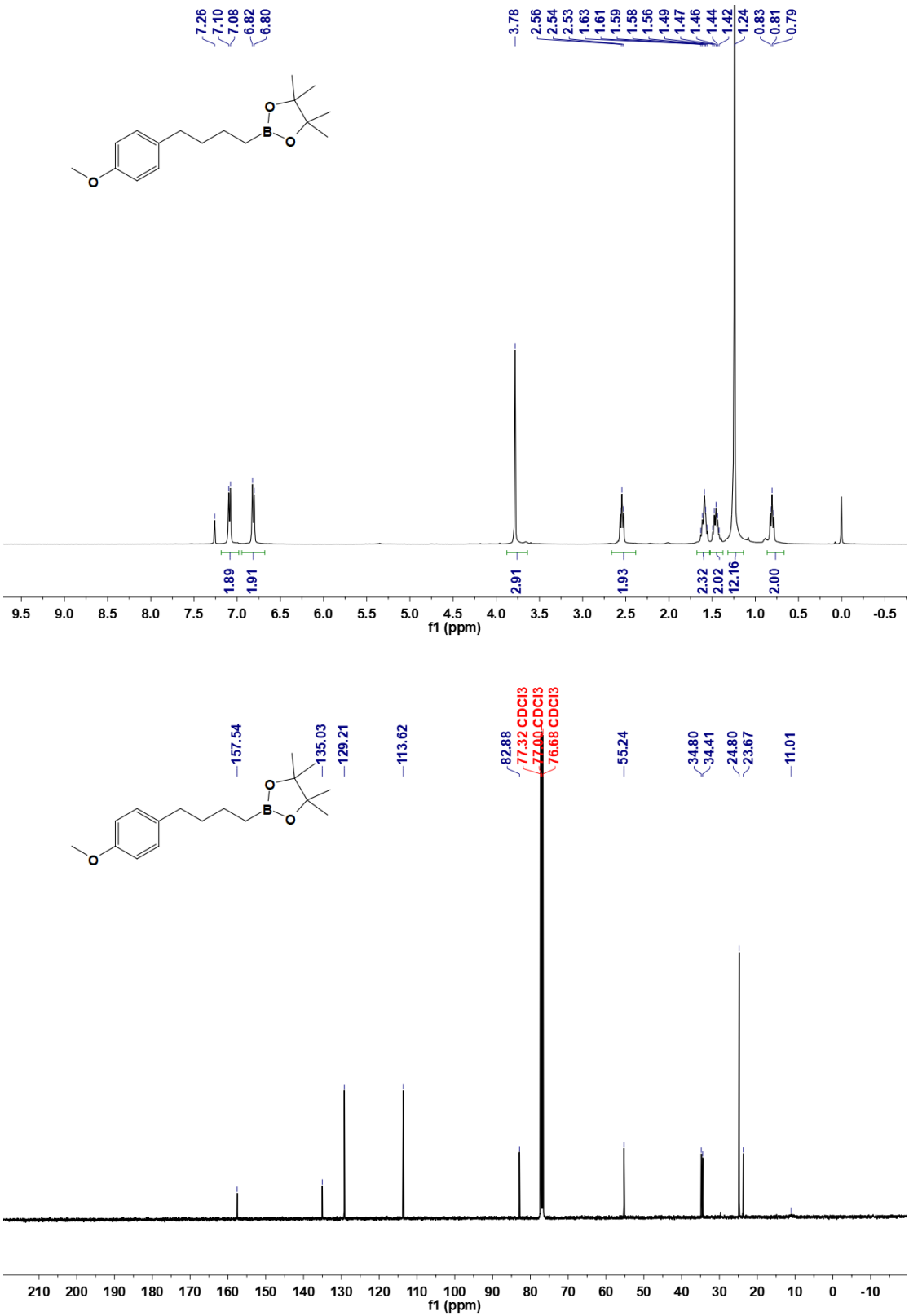
5. NMR spectra



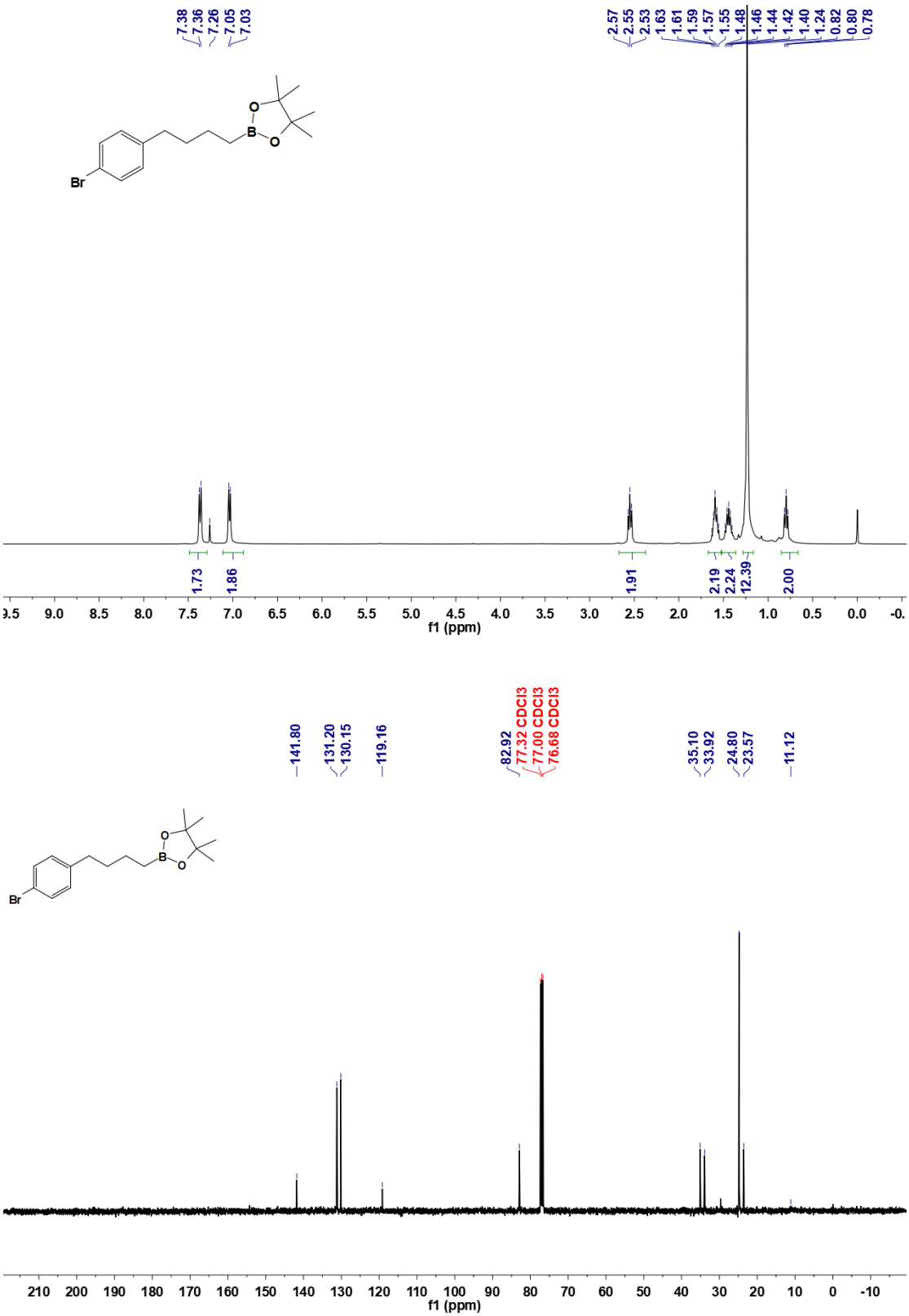
^{1}H and ^{13}C NMR spectra for compound **6s**



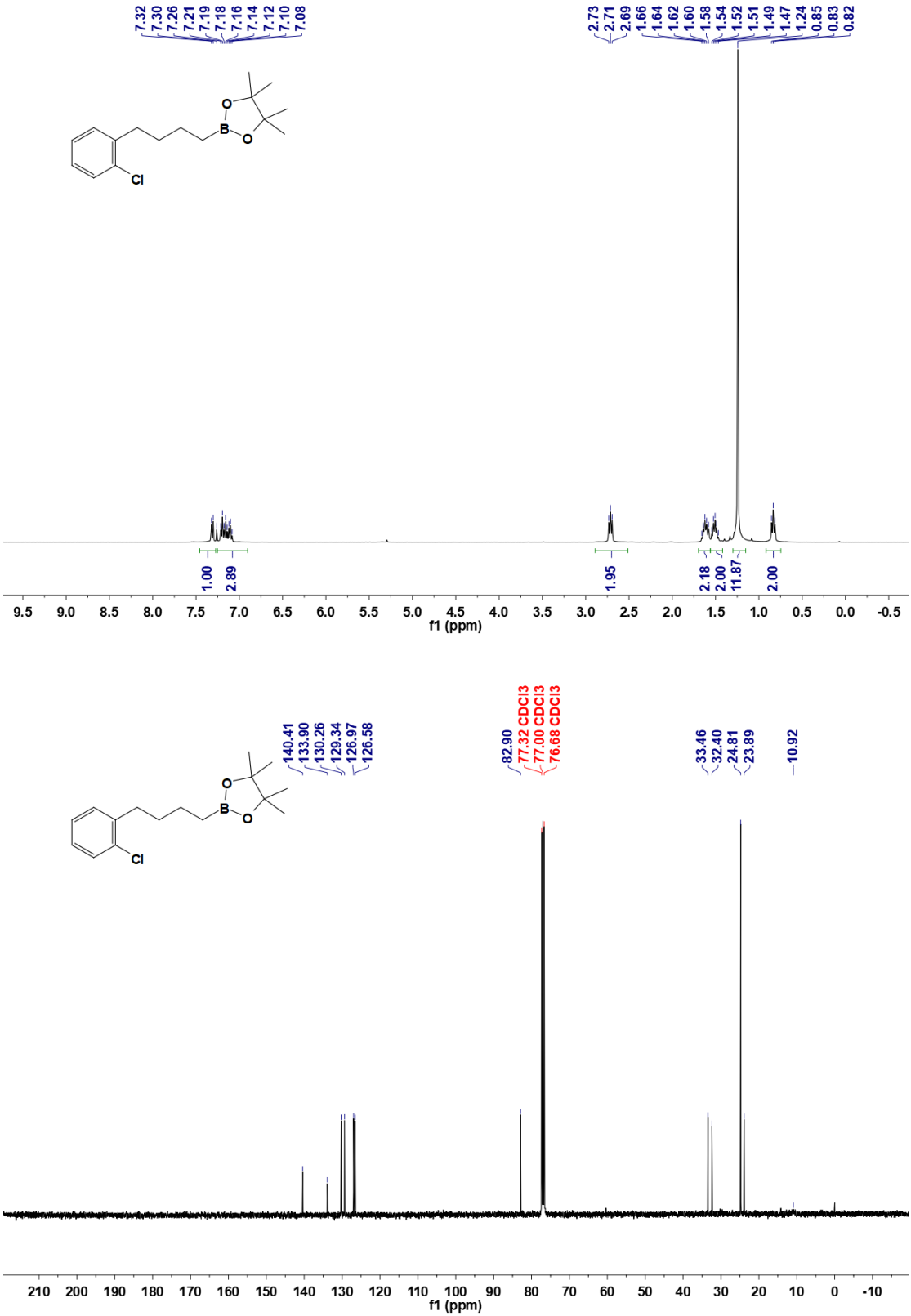
^{1}H and ^{13}C NMR spectra for compound **3**



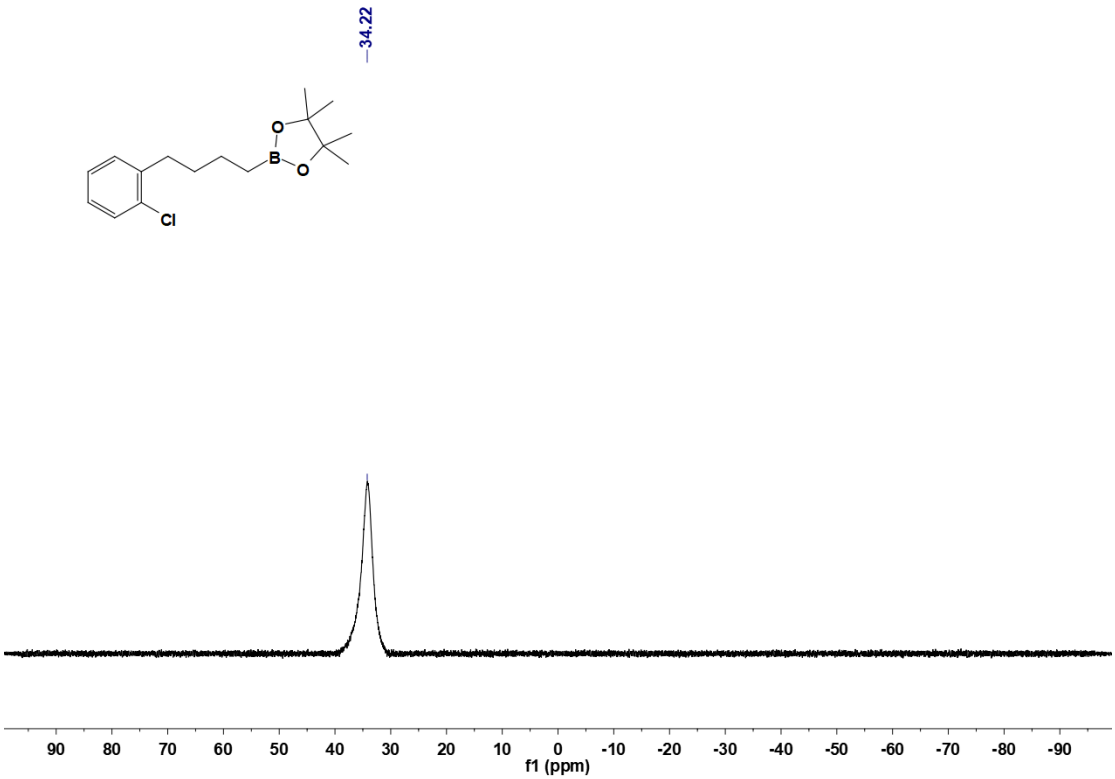
^{1}H and ^{13}C NMR spectra for compound **4**



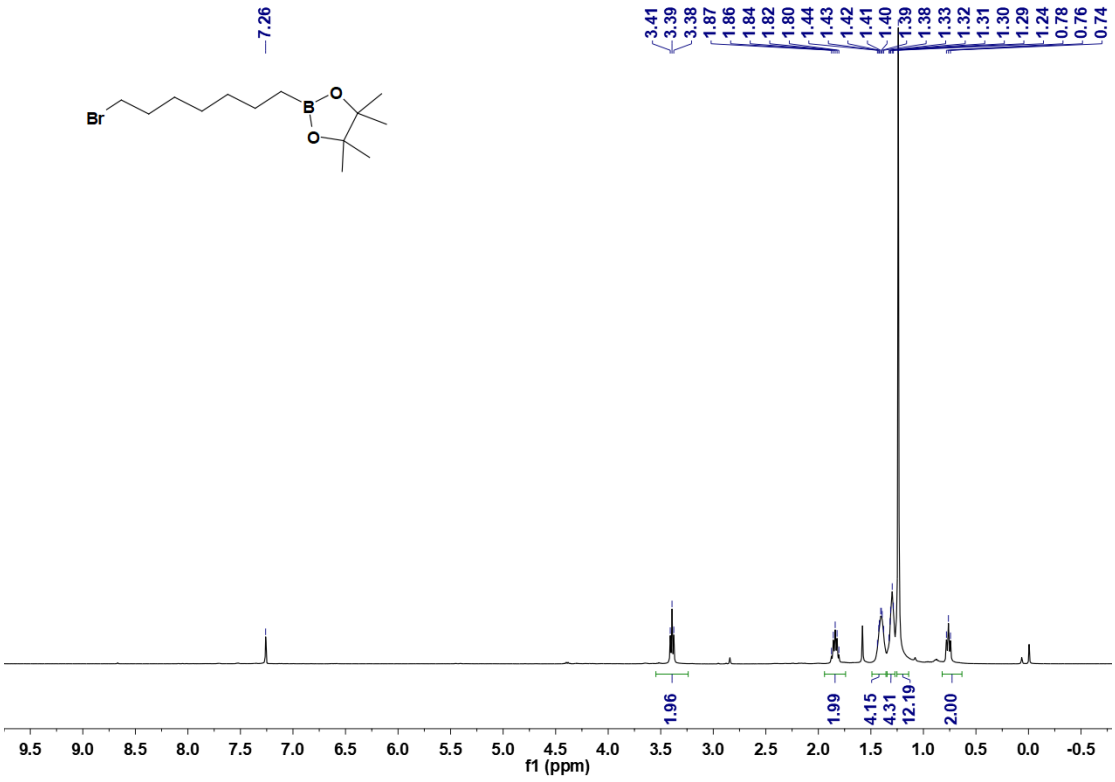
^{1}H and ^{13}C NMR spectra for compound **5**

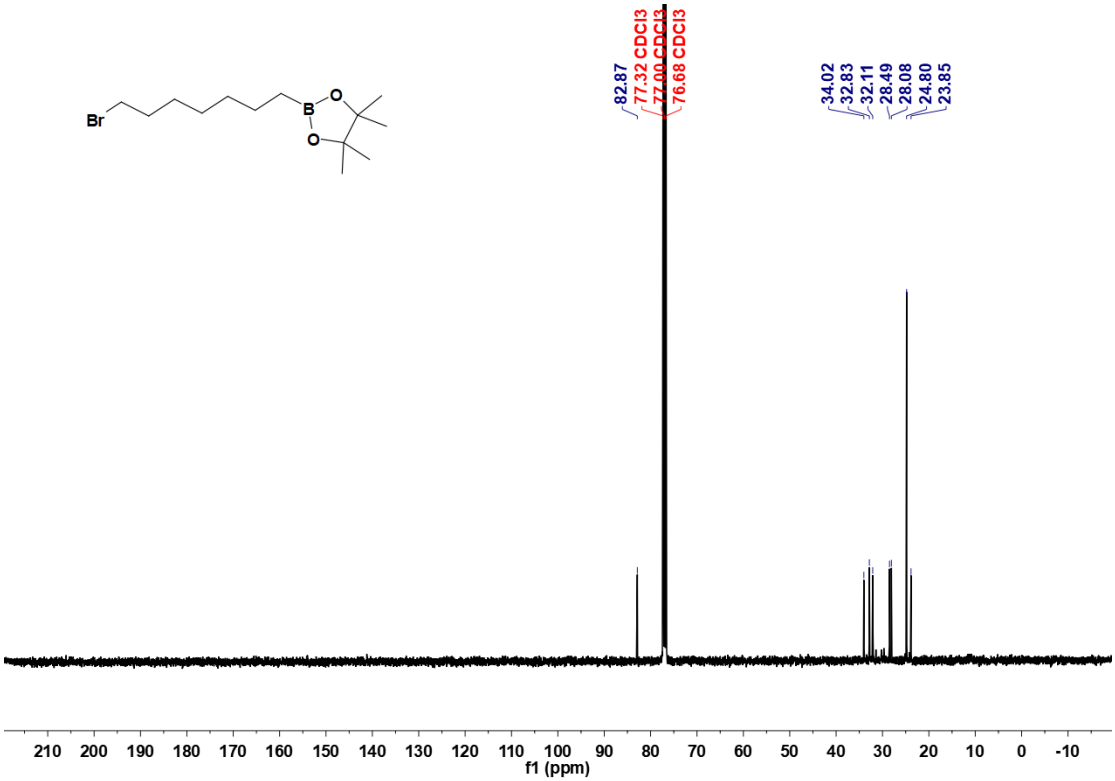


^{1}H and ^{13}C NMR spectra for compound **6**

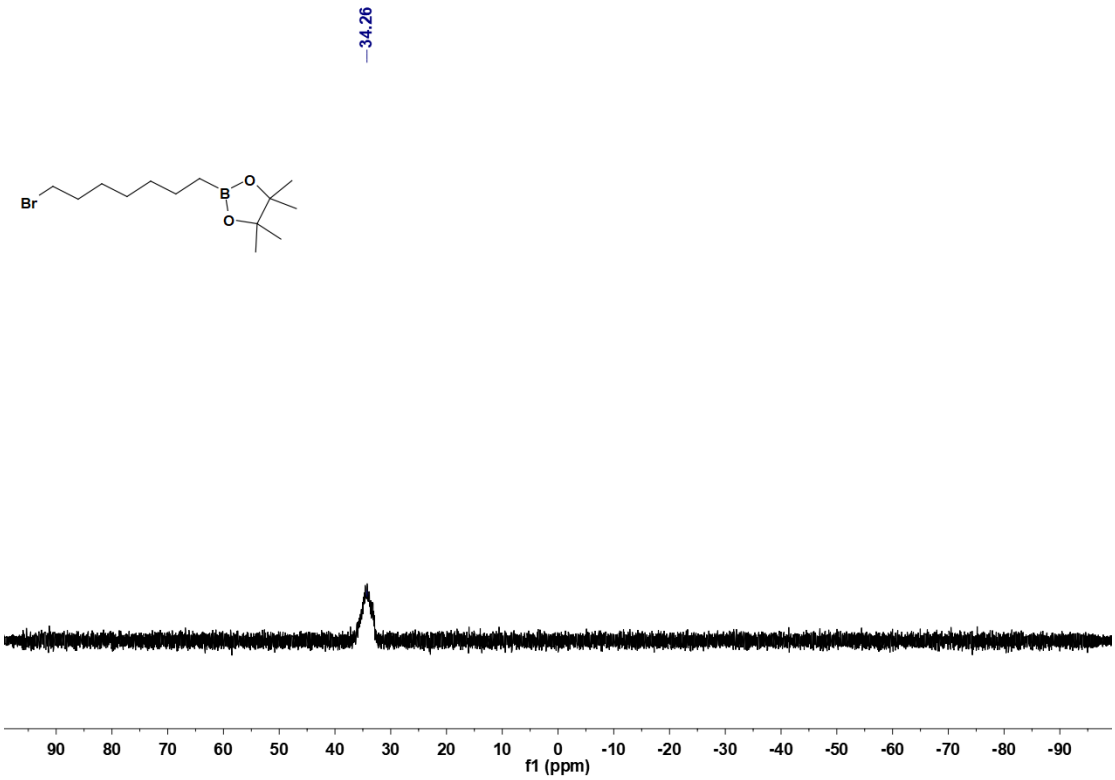


^{11}B NMR spectra for compound **6**

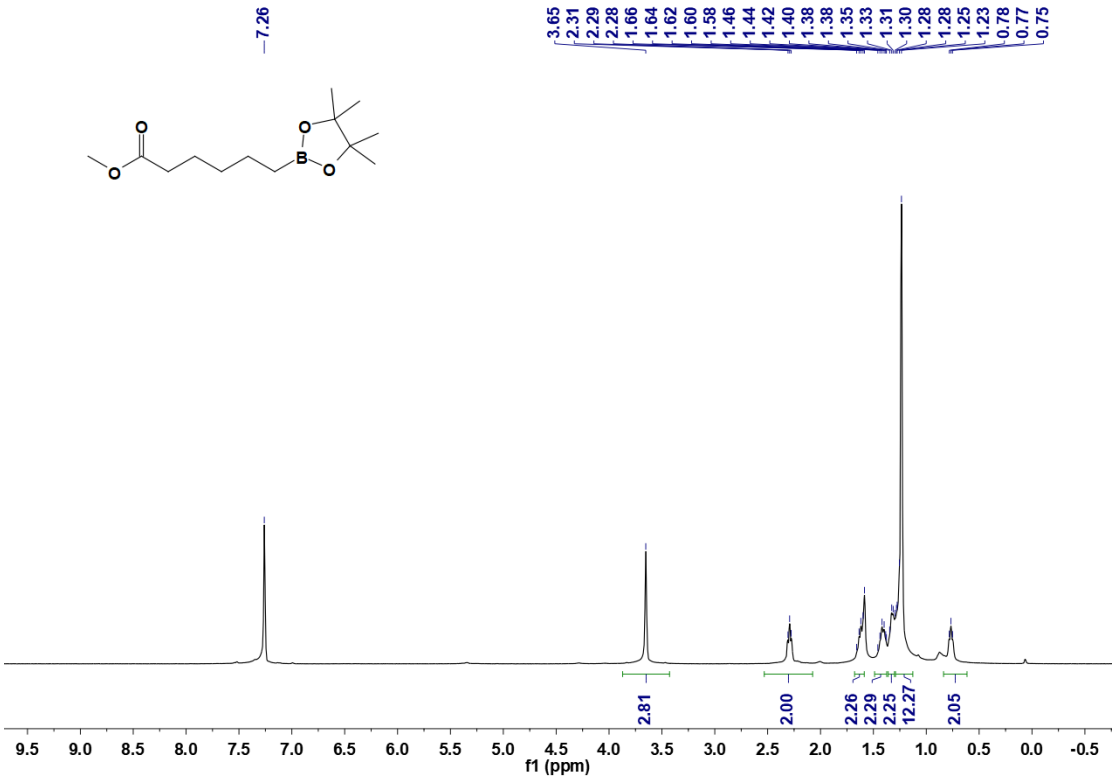


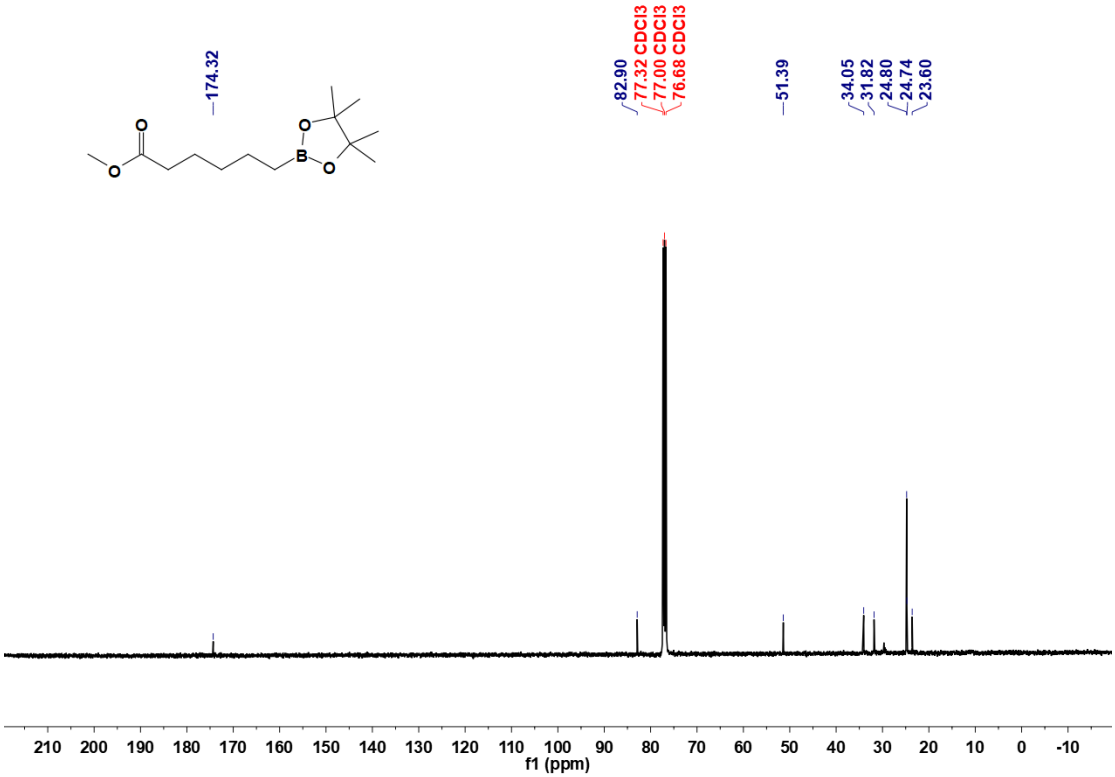


^{1}H and ^{13}C NMR spectra for compound **7**

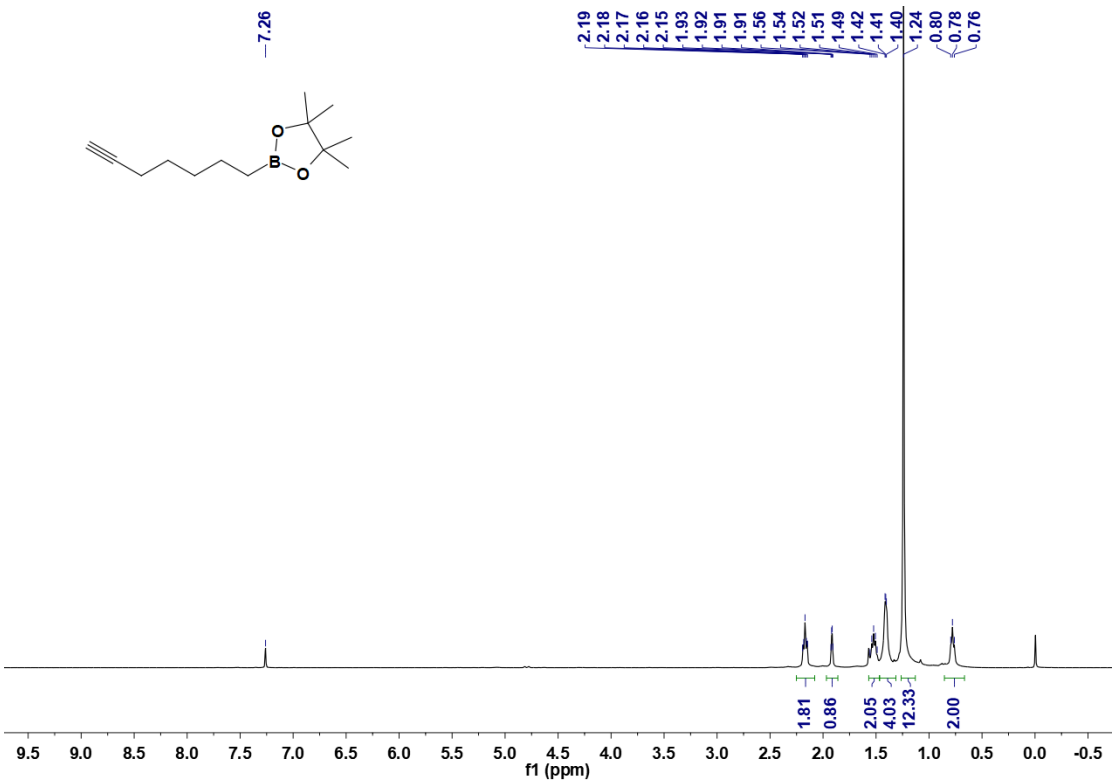


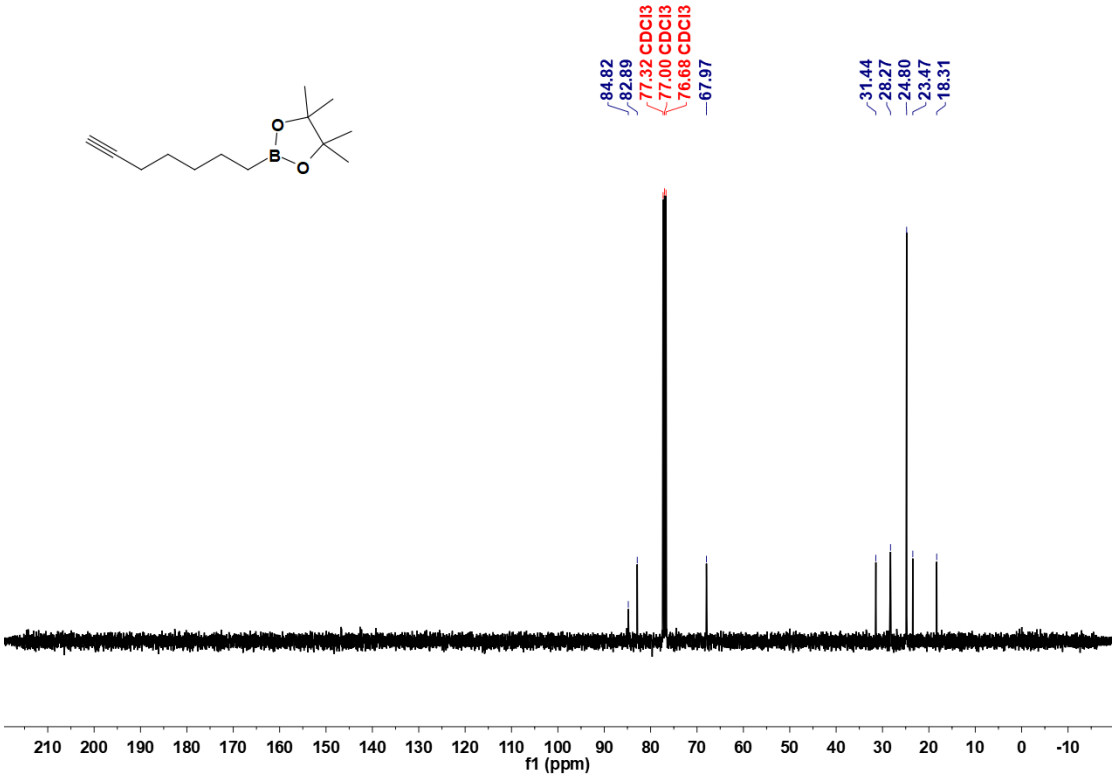
^{11}B NMR spectra for compound **7**



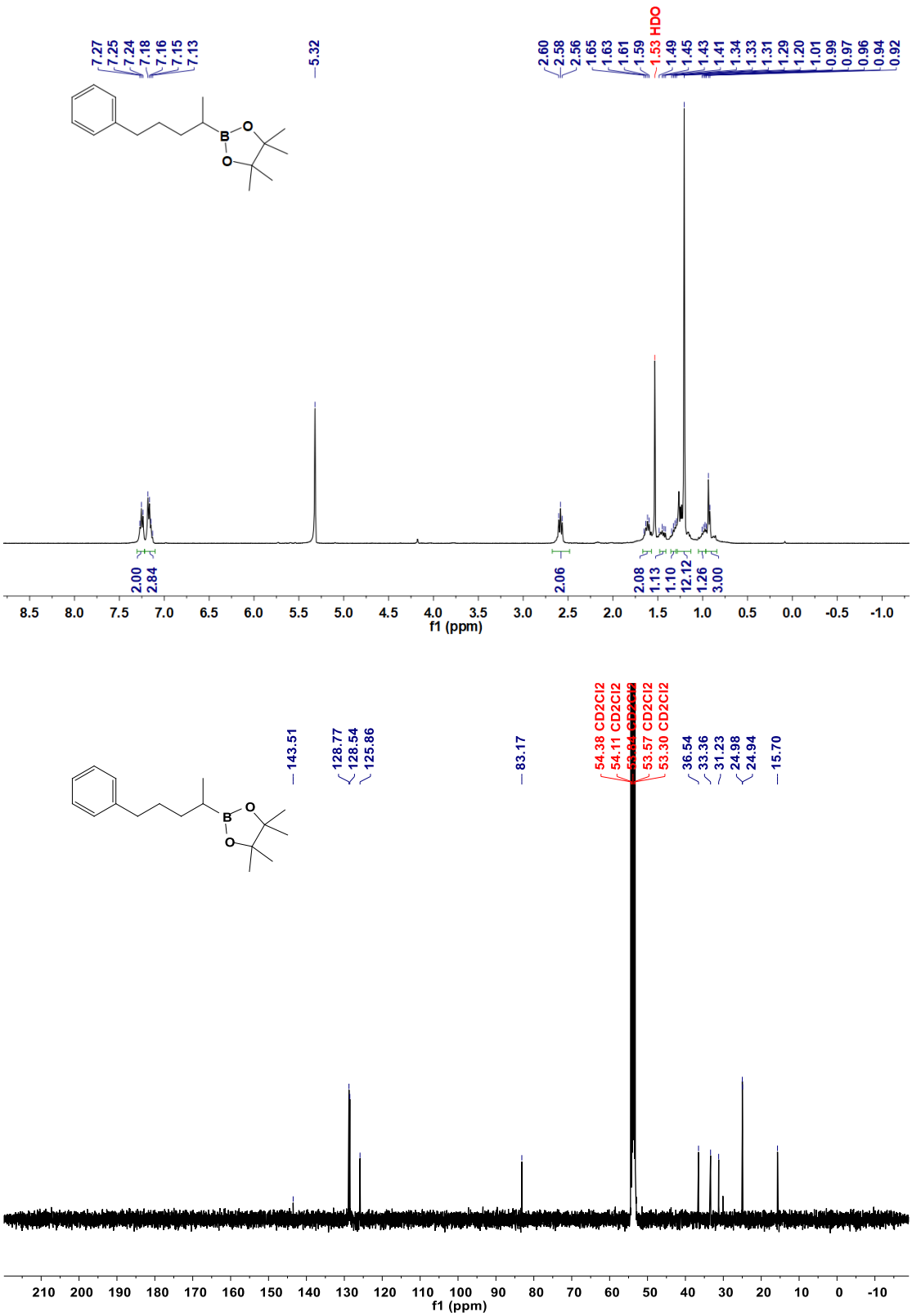


^{1}H and ^{13}C NMR spectra for compound **8**

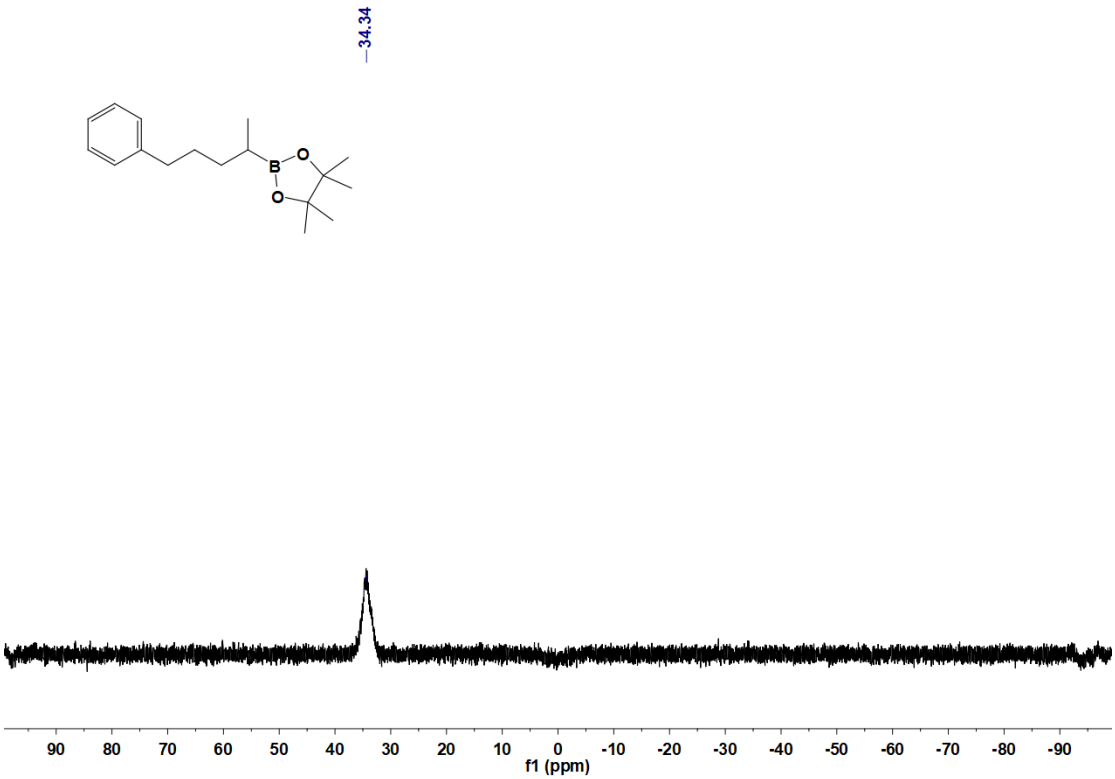




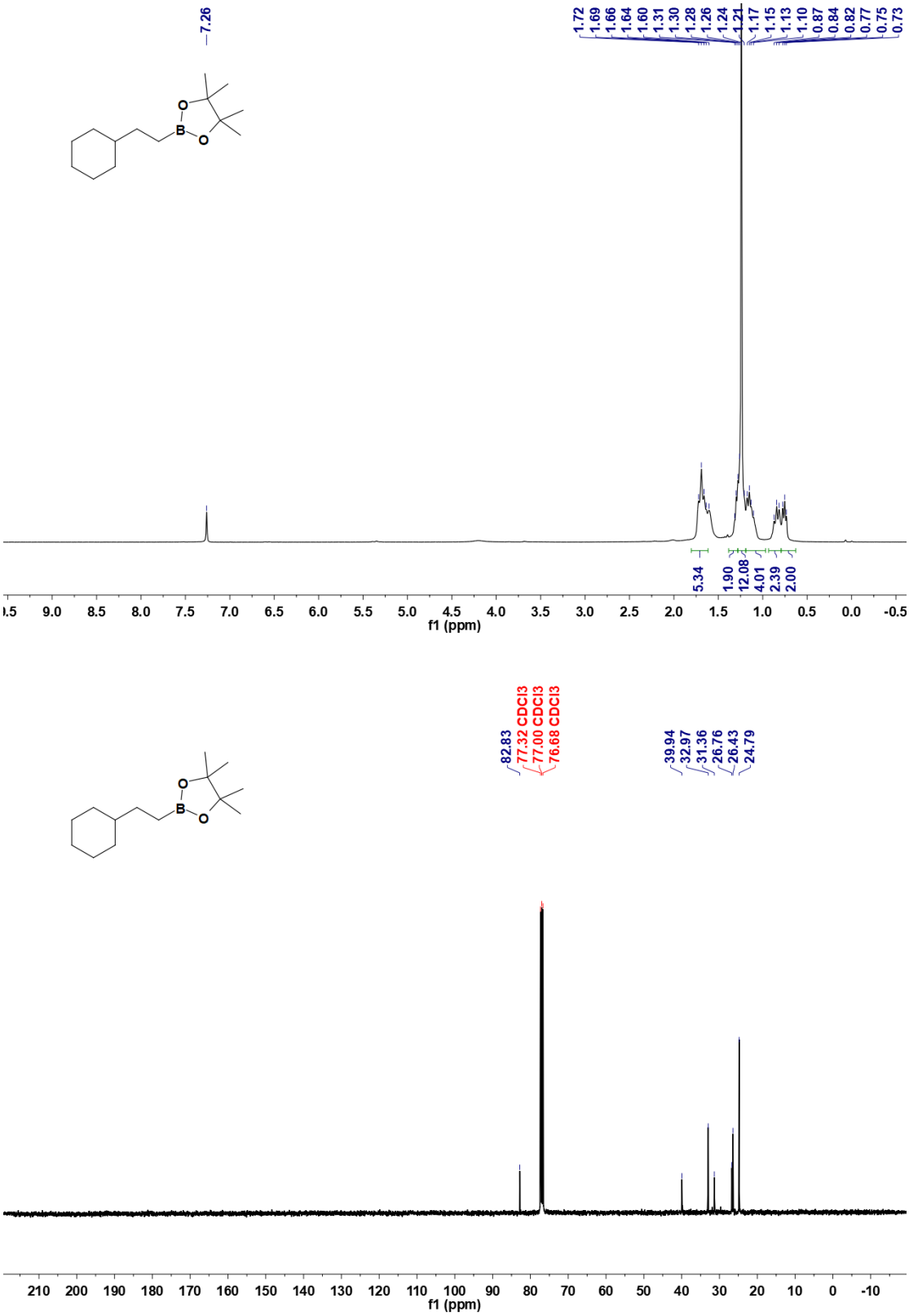
^{1}H and ^{13}C NMR spectra for compound **9**



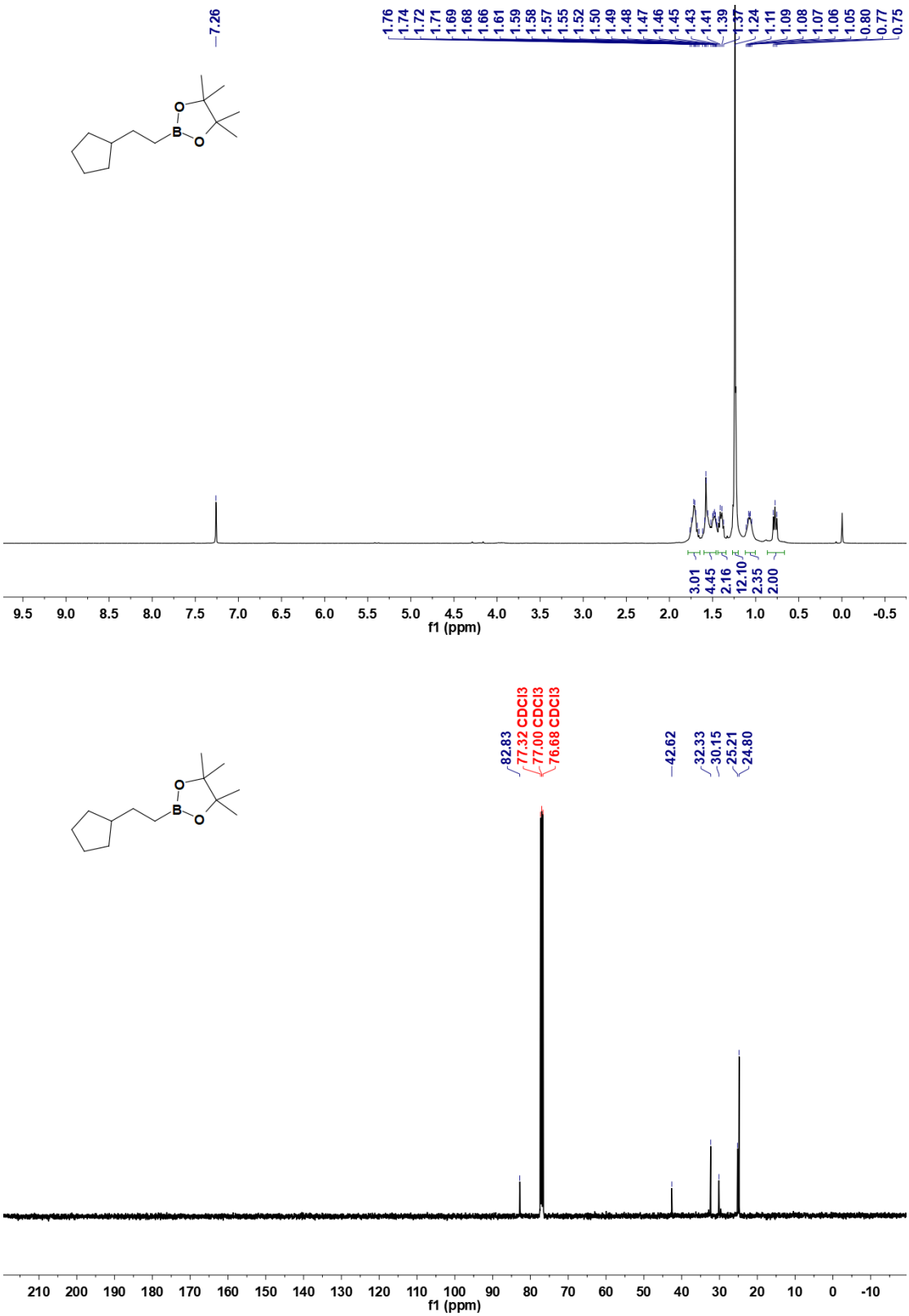
^{1}H and ^{13}C NMR spectra for compound **10**



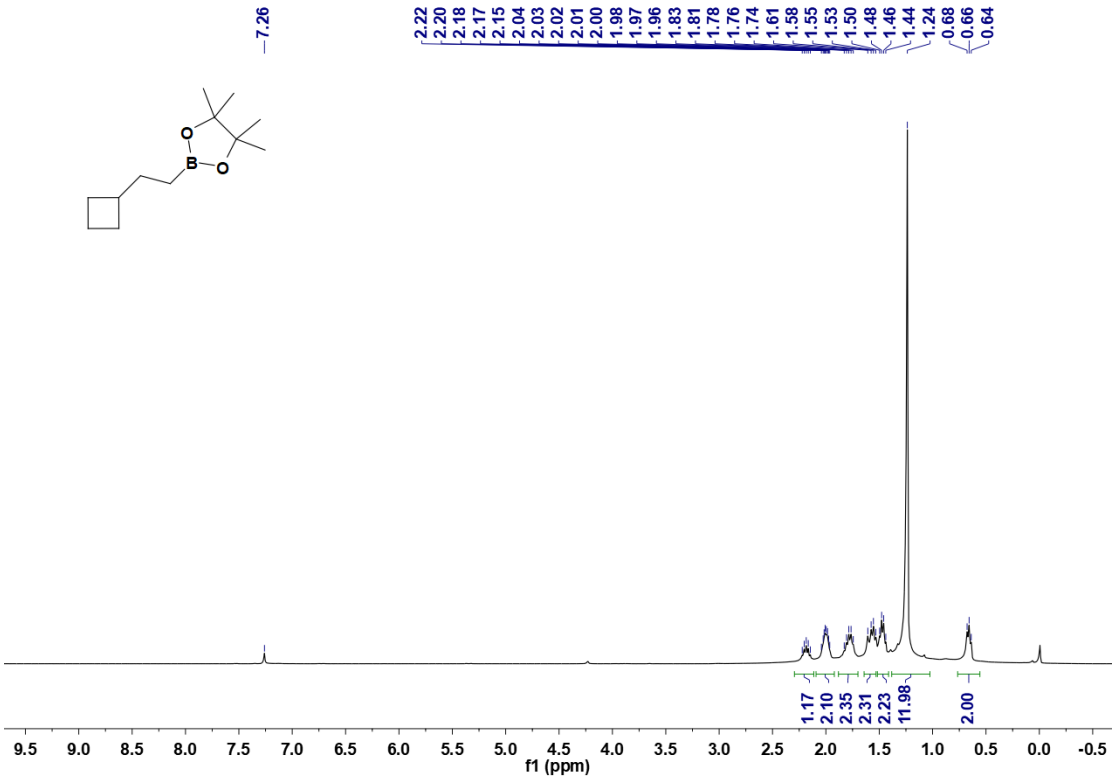
^{11}B NMR spectra for compound **10**

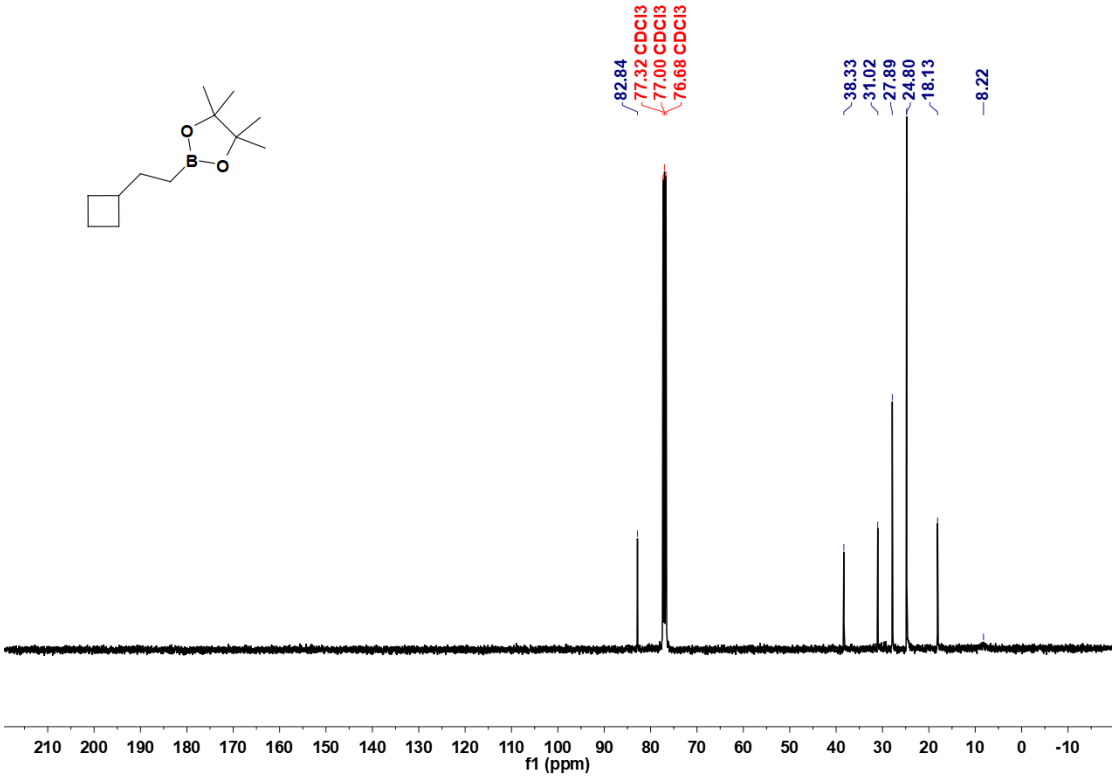


^{1}H and ^{13}C NMR spectra for compound **12**

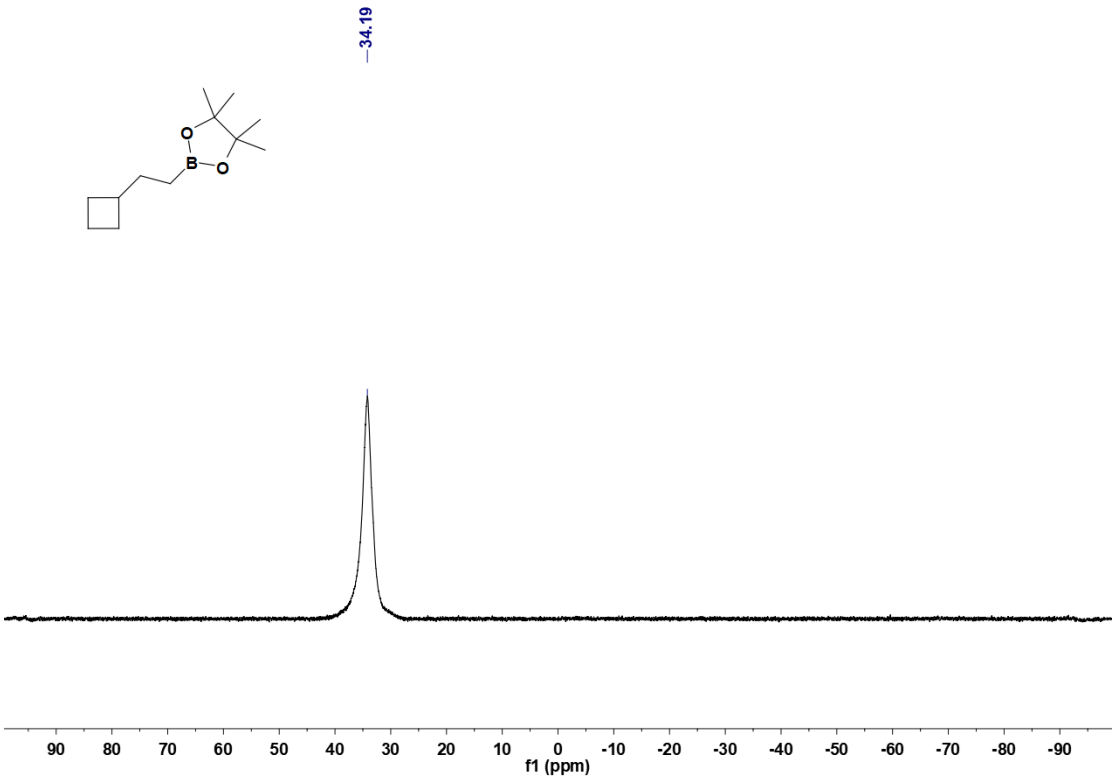


^{1}H and ^{13}C NMR spectra for compound **13**

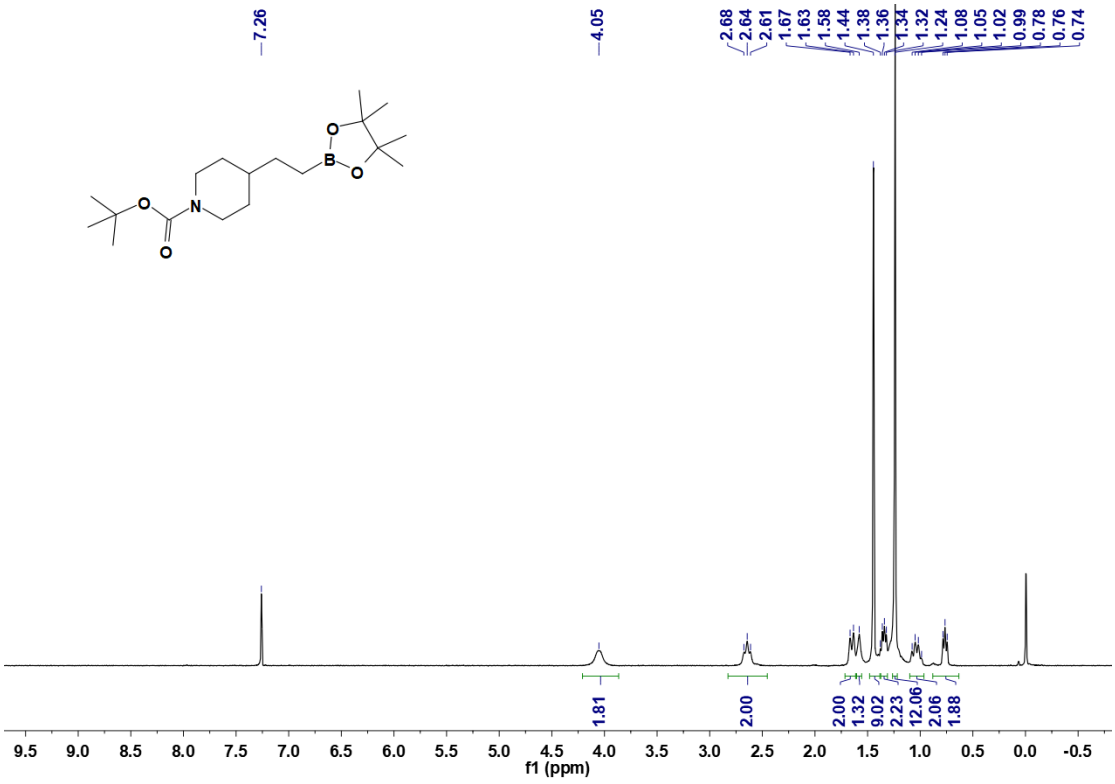


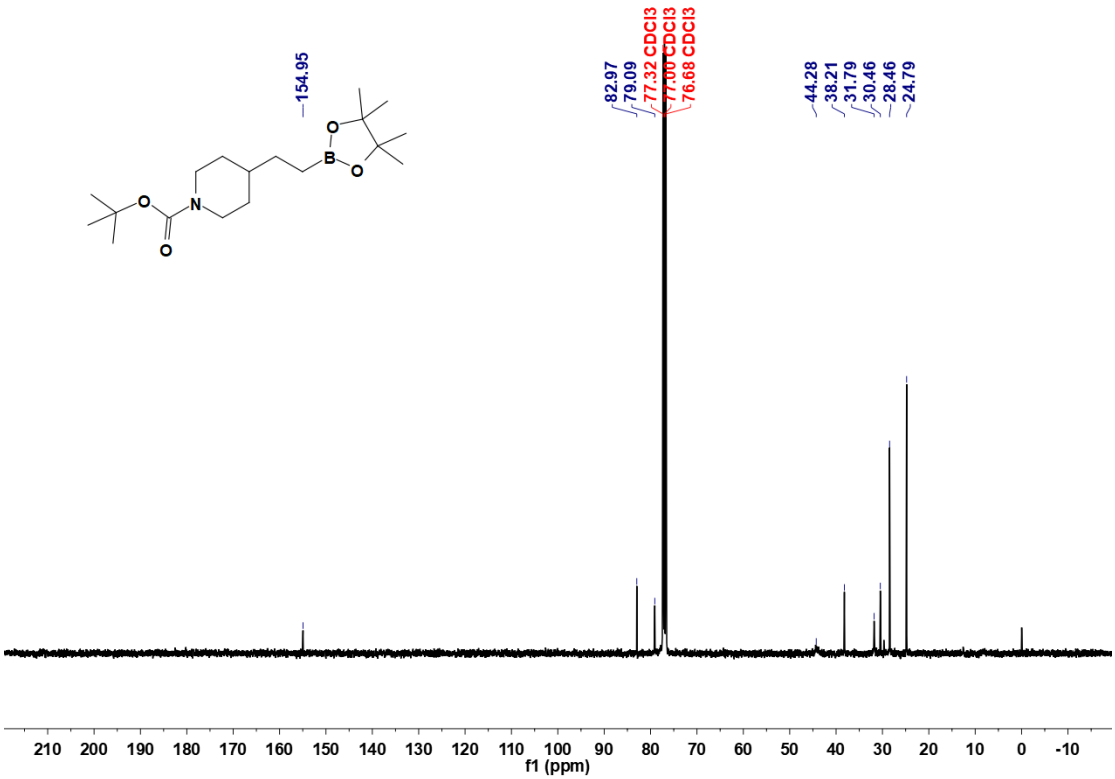


^{1}H and ^{13}C NMR spectra for compound **14**

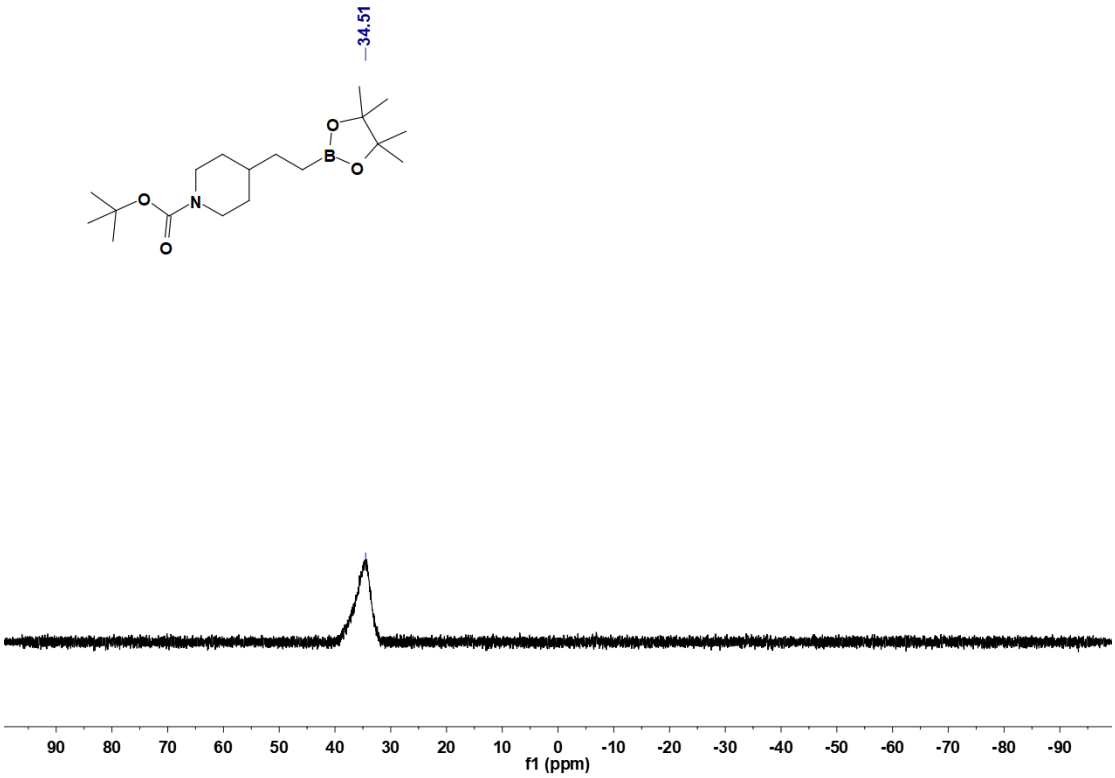


^{11}B NMR spectra for compound **14**

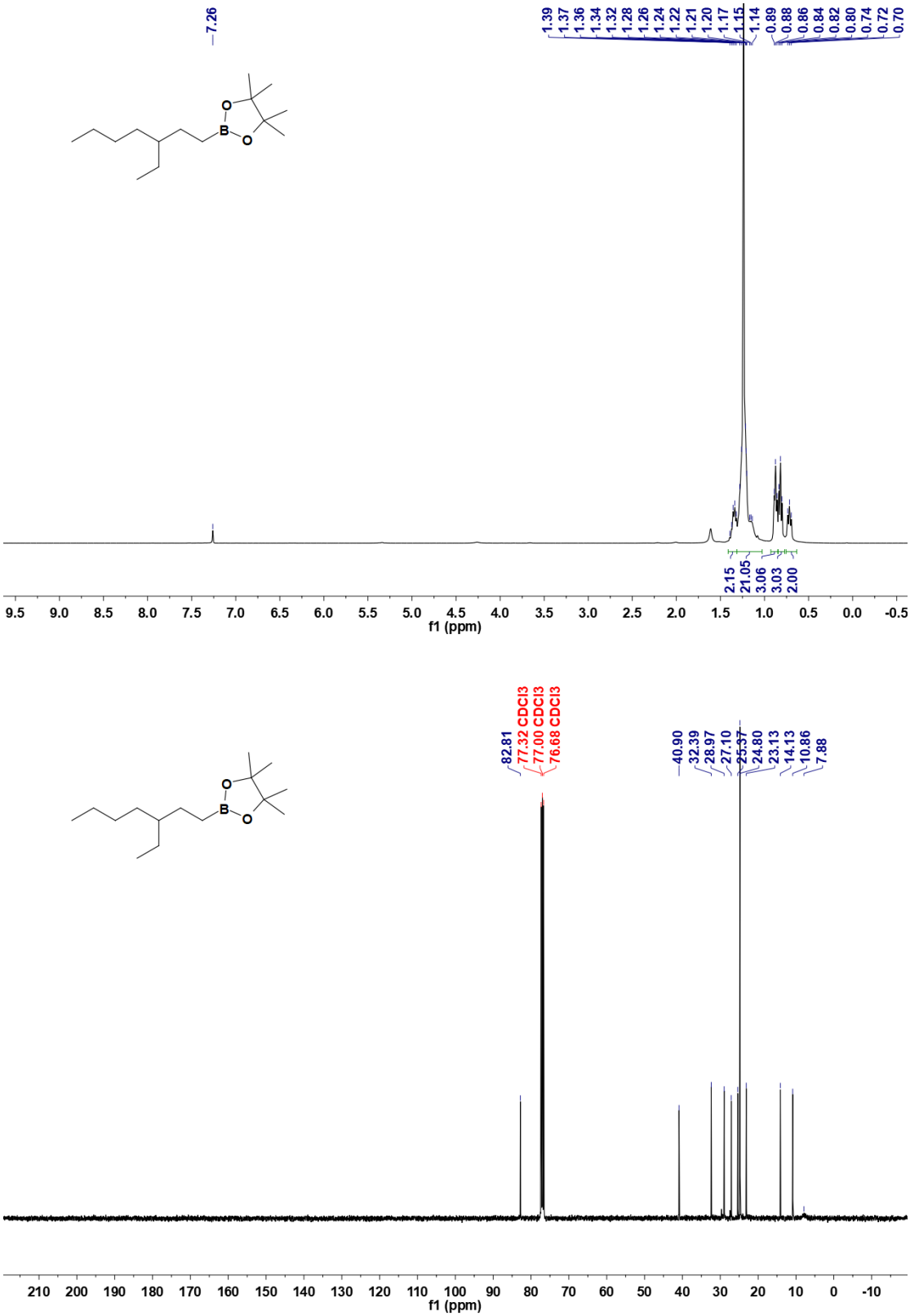




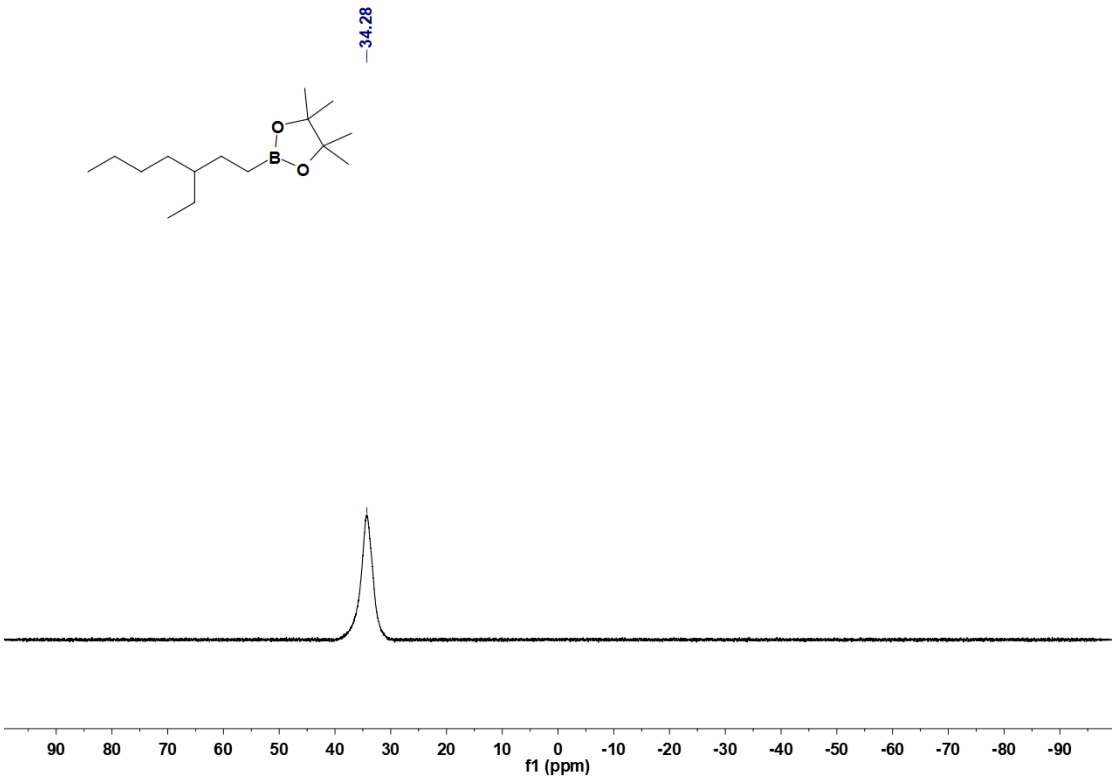
^{1}H and ^{13}C NMR spectra for compound **15**



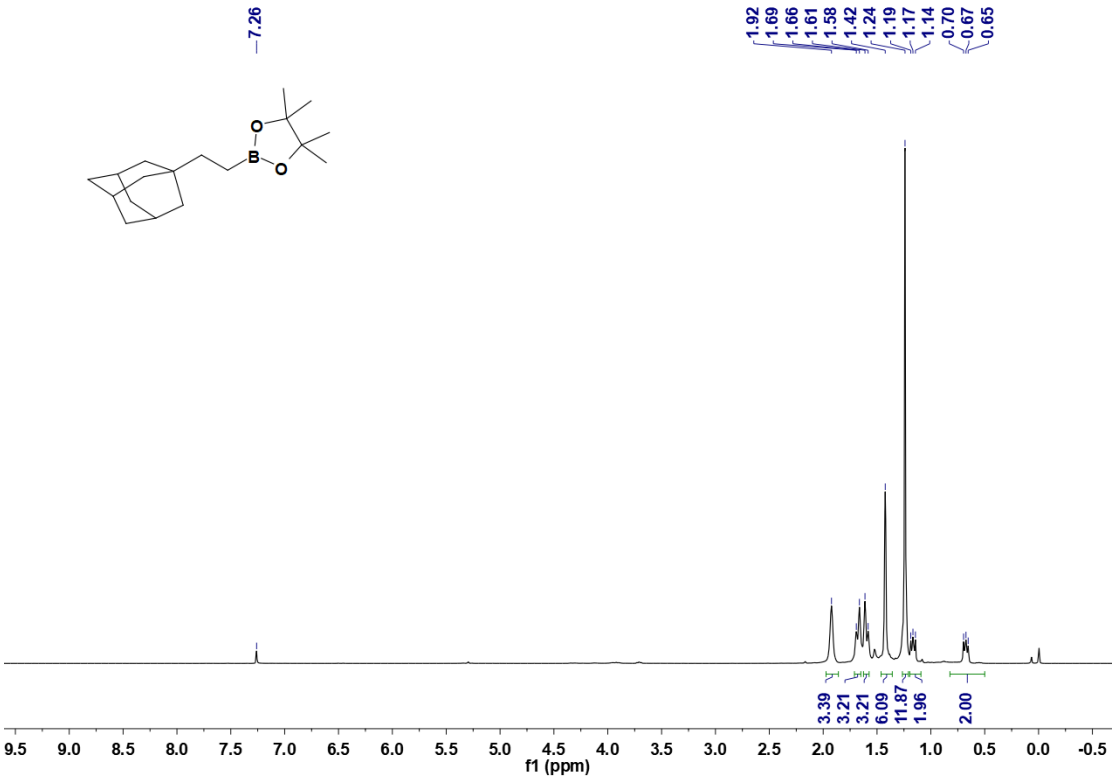
^{11}B NMR spectra for compound **15**

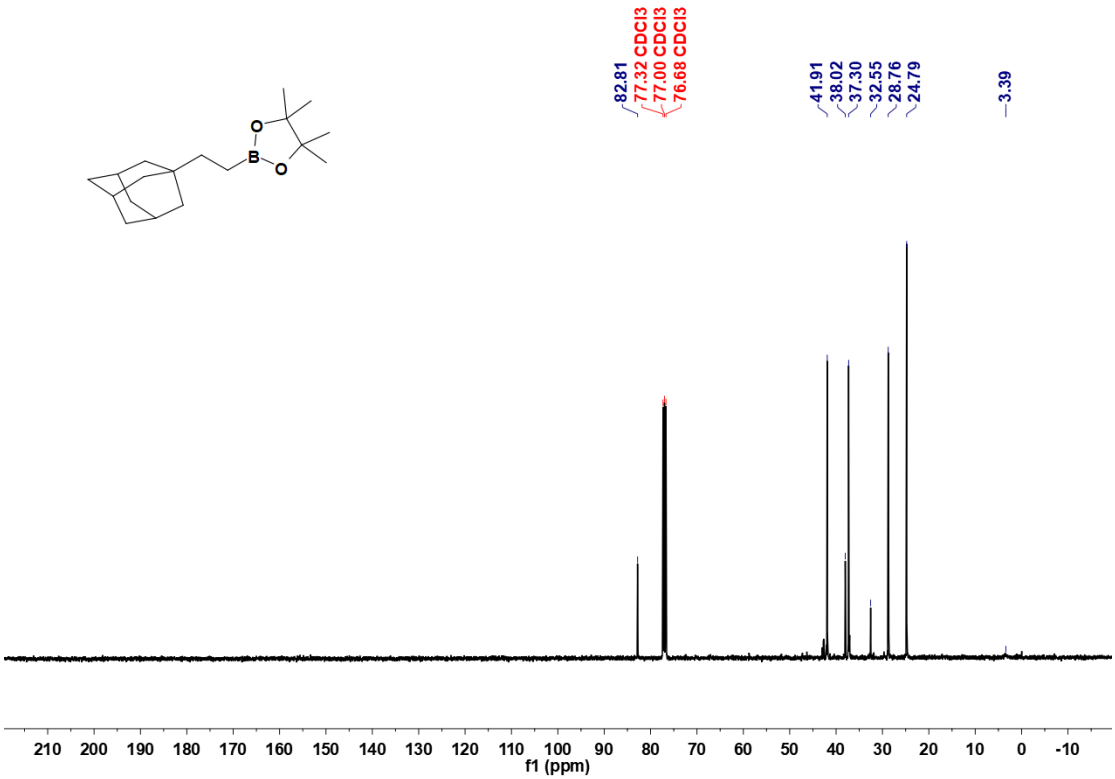


^{1}H and ^{13}C NMR spectra for compound **16**

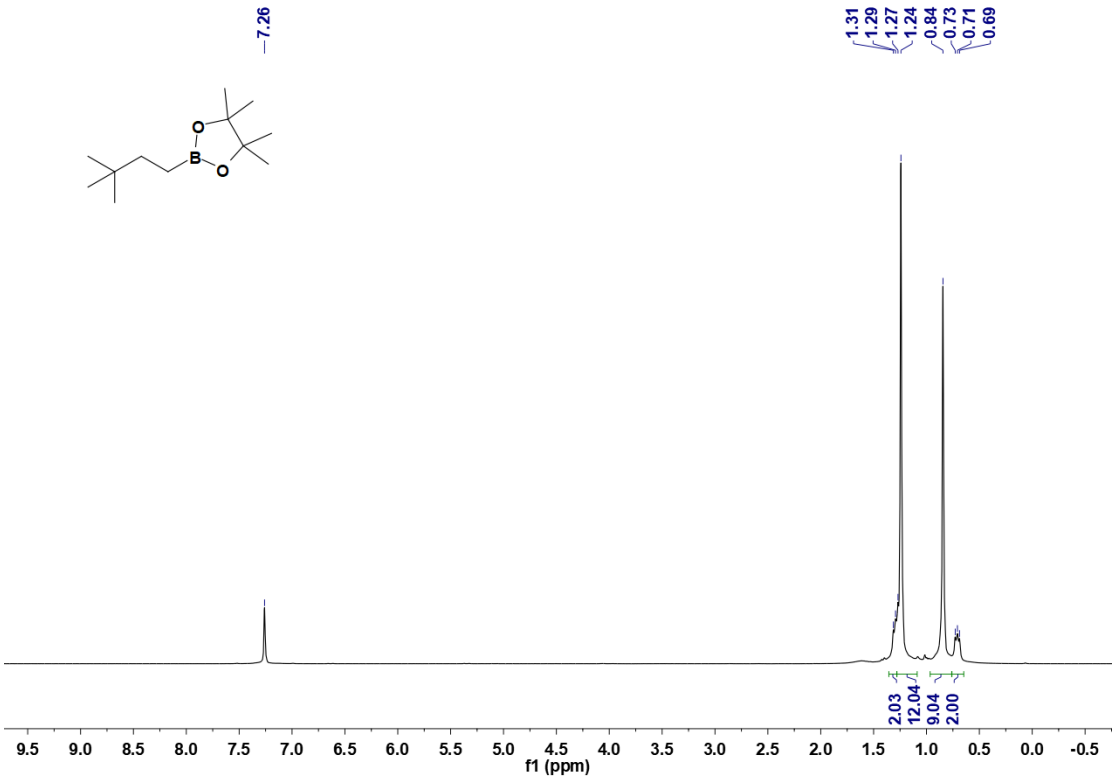


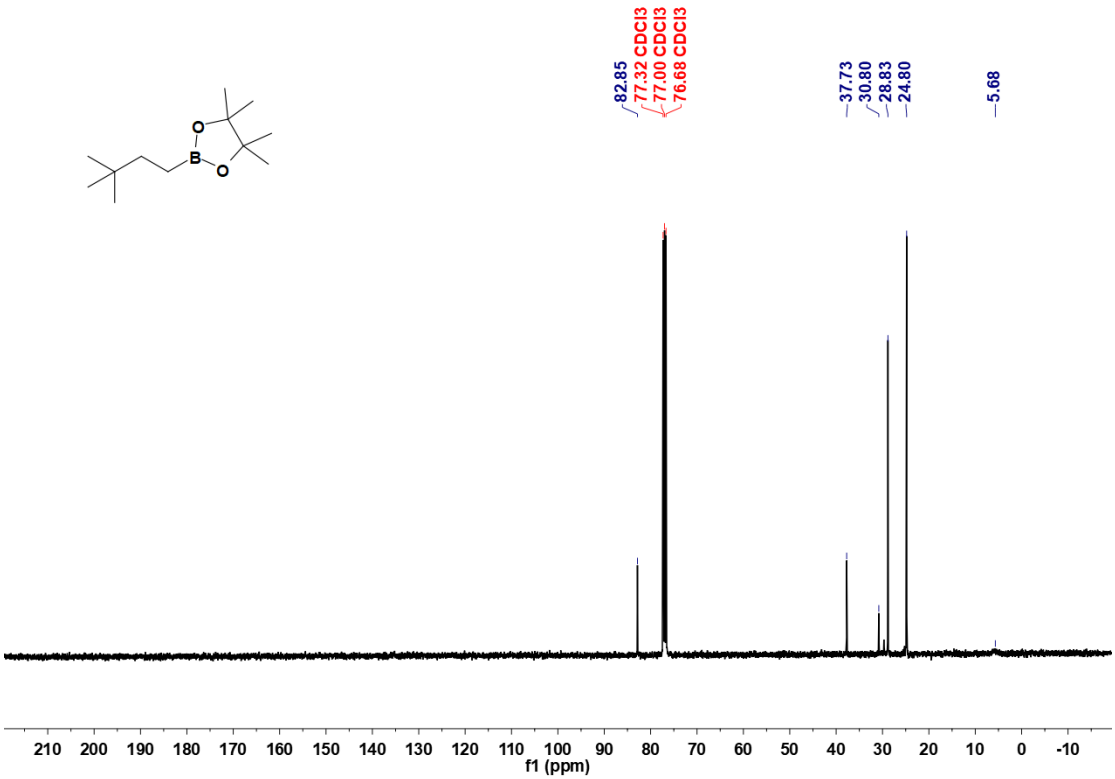
^{11}B NMR spectra for compound **16**



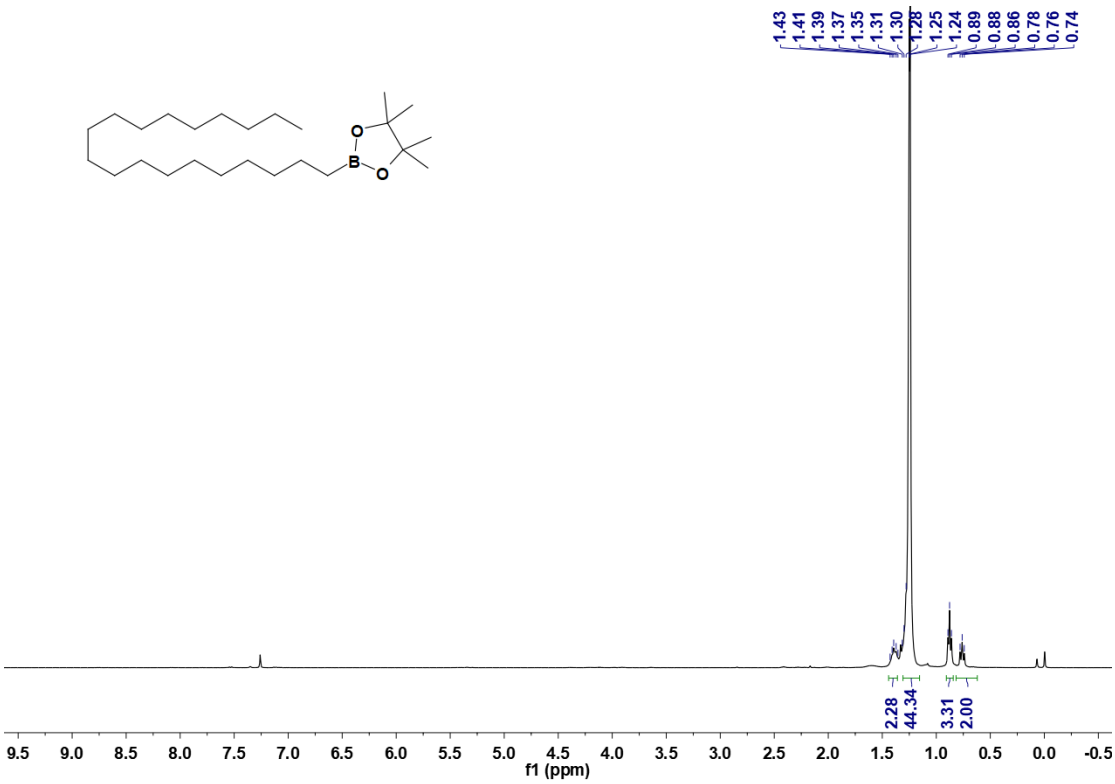


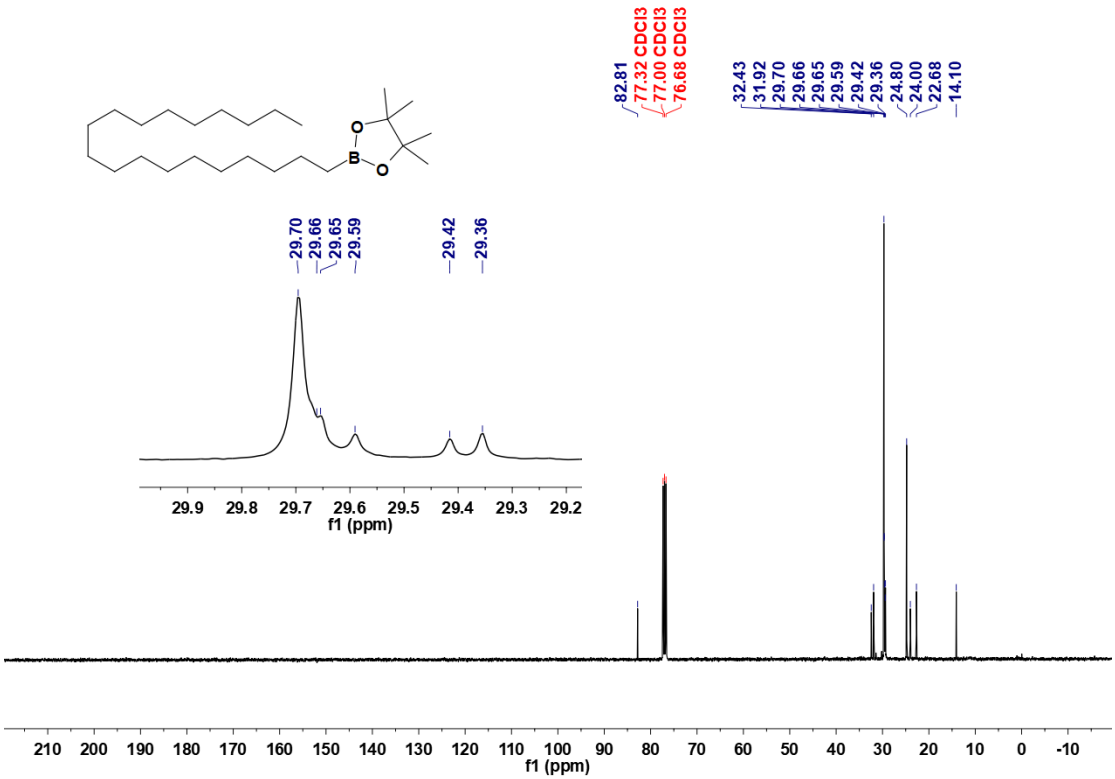
^{1}H and ^{13}C NMR spectra for compound **17**



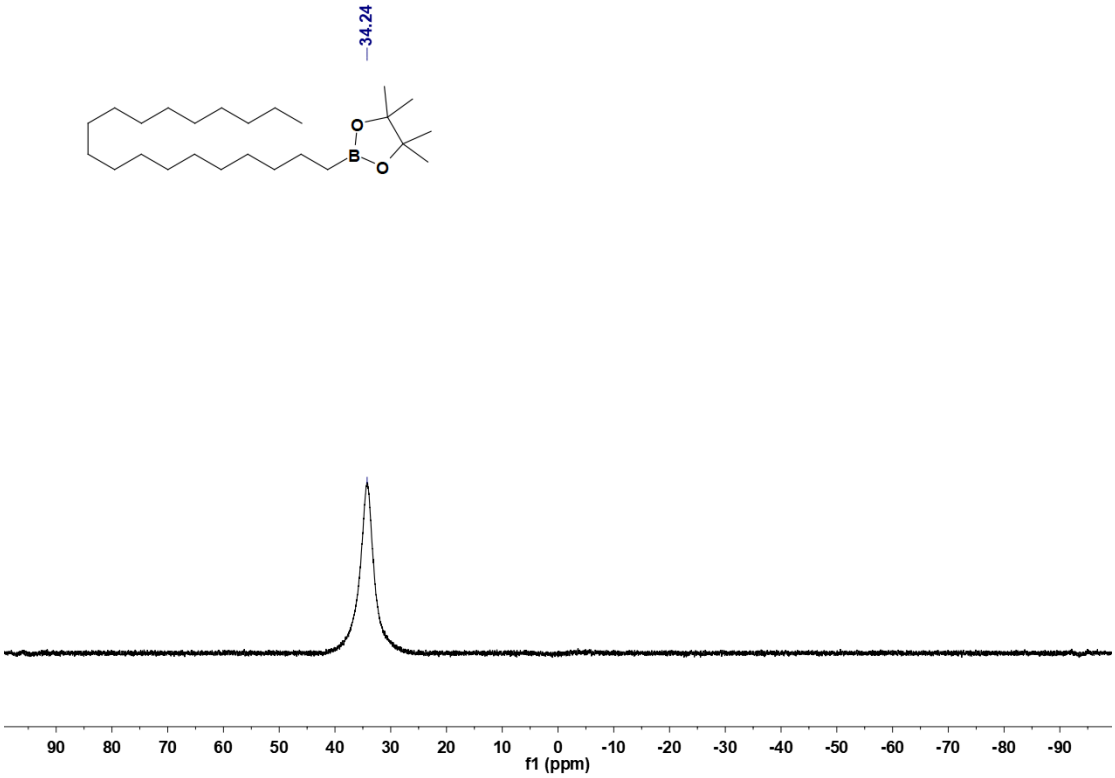


^{1}H and ^{13}C NMR spectra for compound **18**

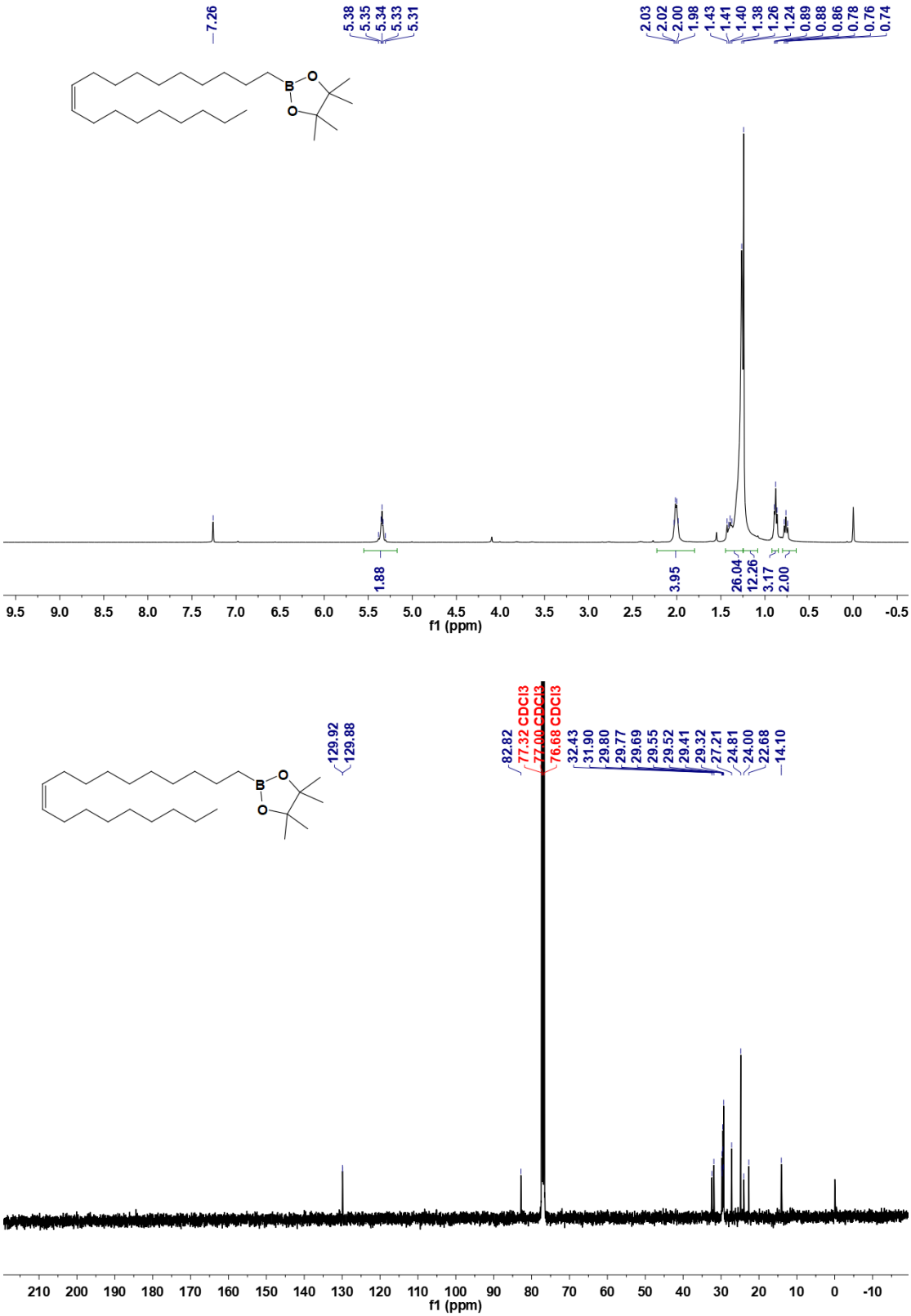




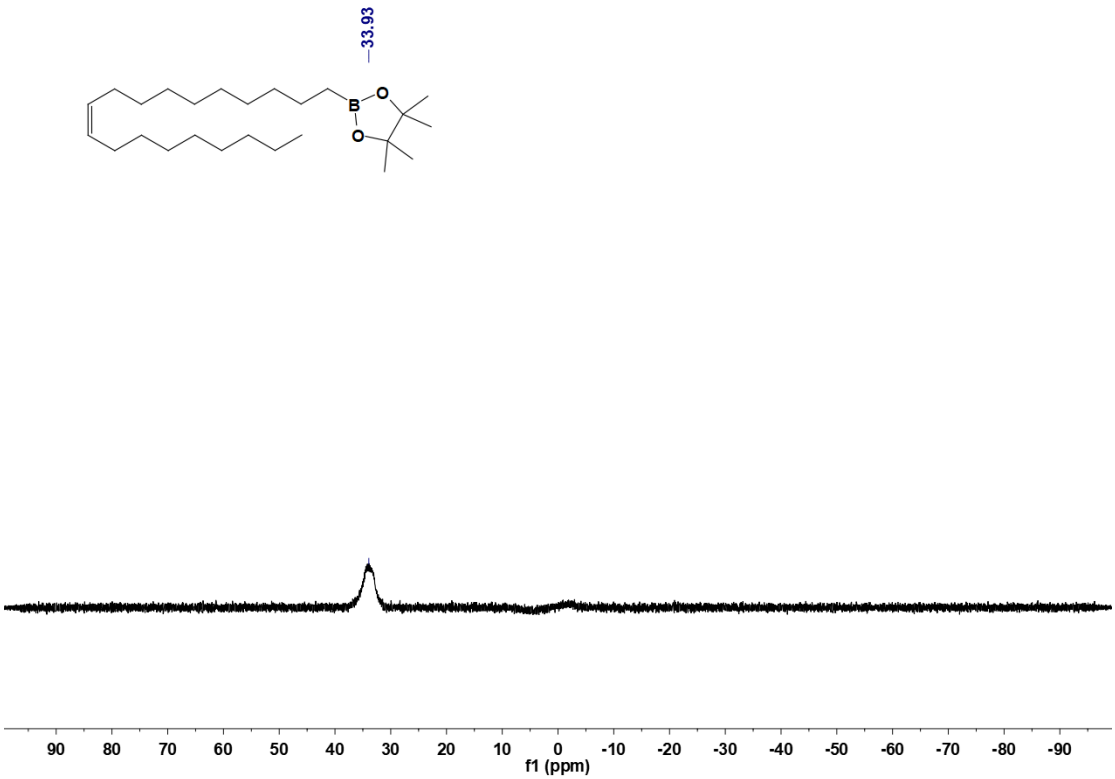
^{1}H and ^{13}C NMR spectra for compound **19**



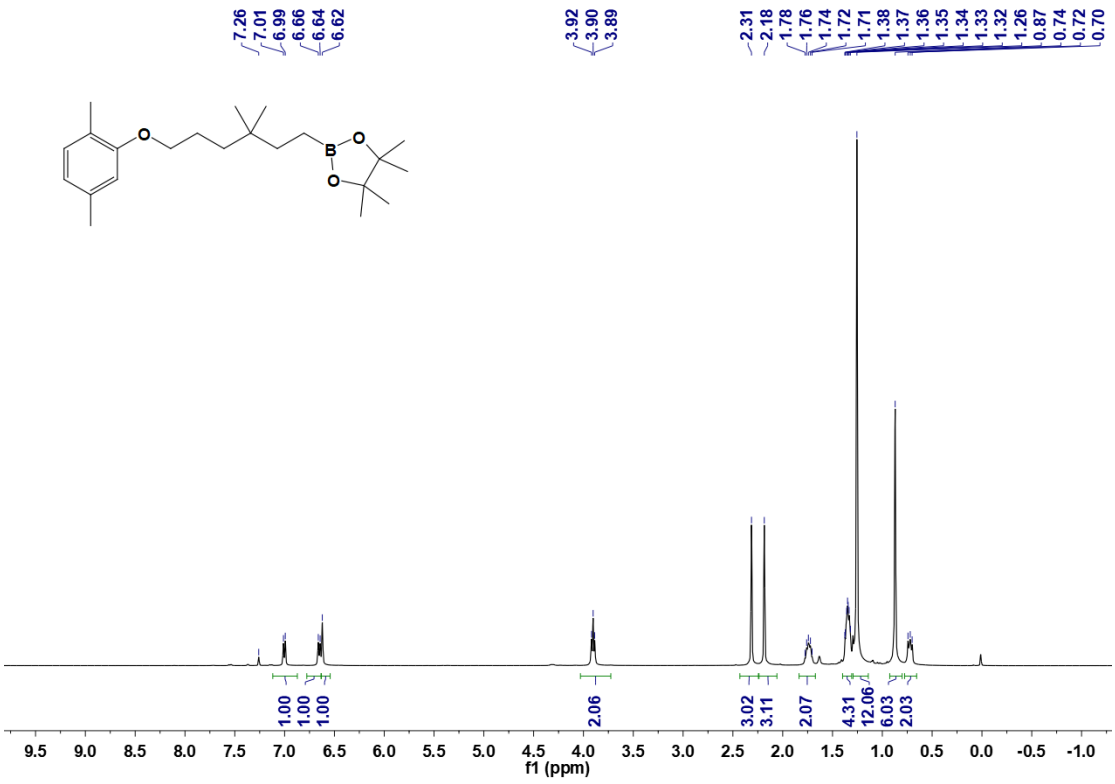
^{11}B NMR spectra for compound **19**

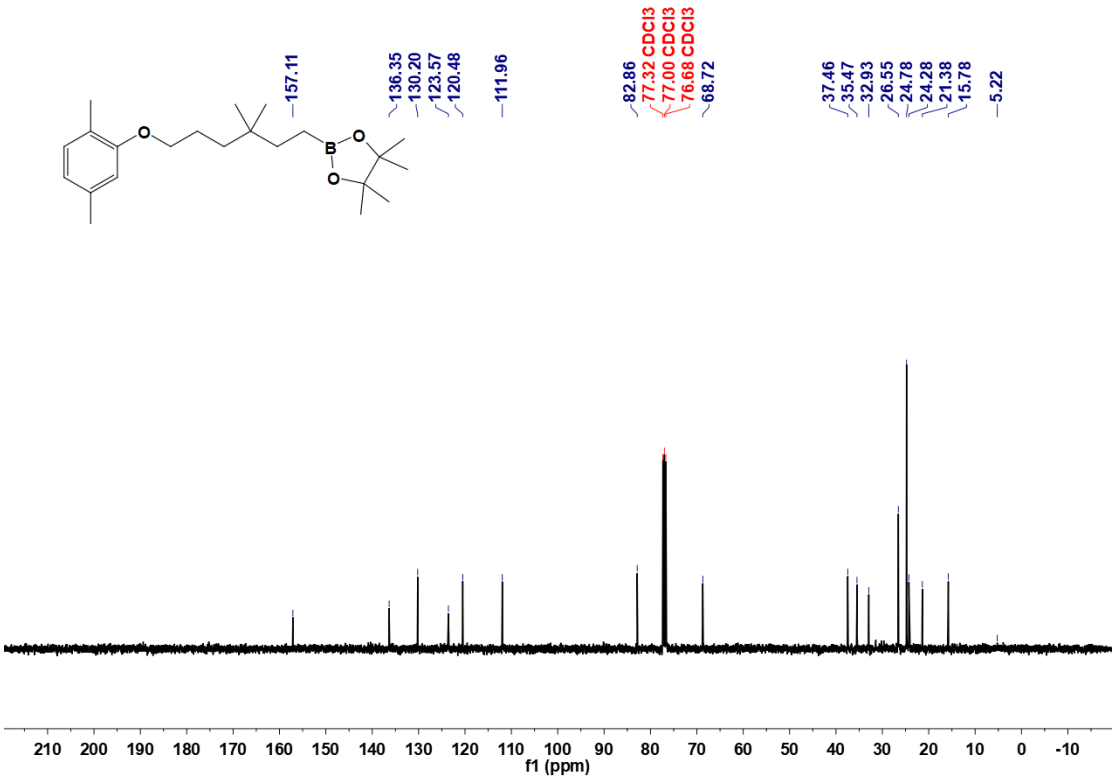


^{1}H and ^{13}C NMR spectra for compound **20**

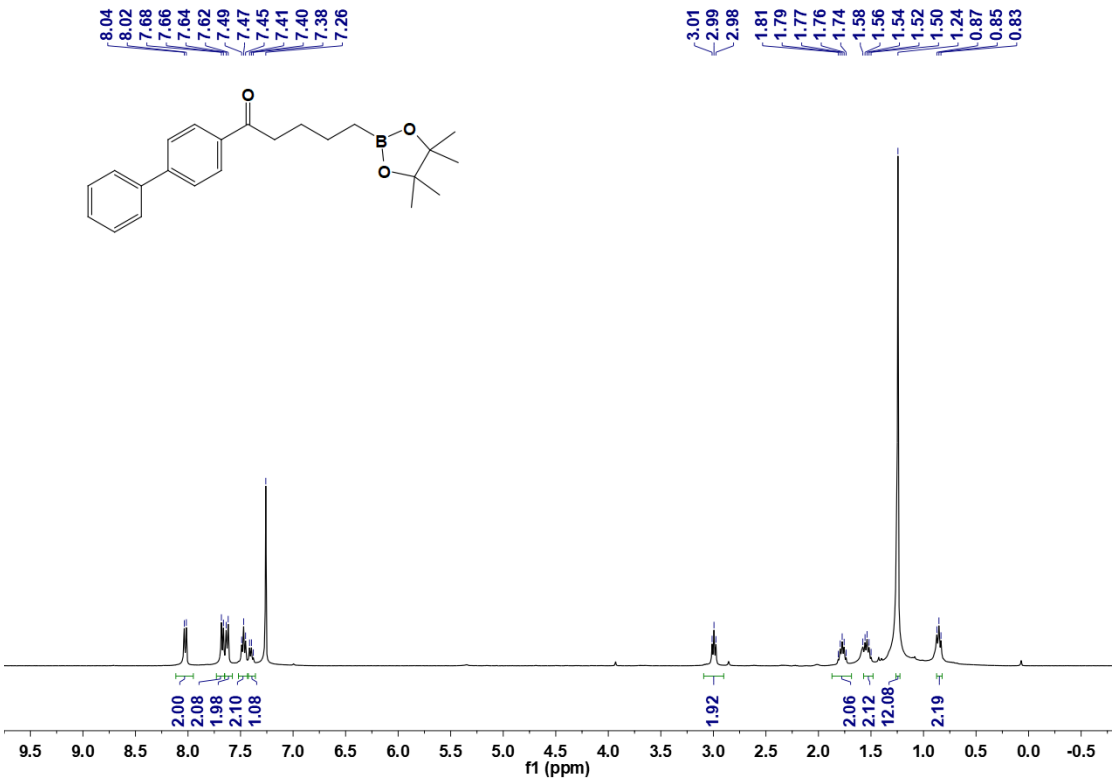


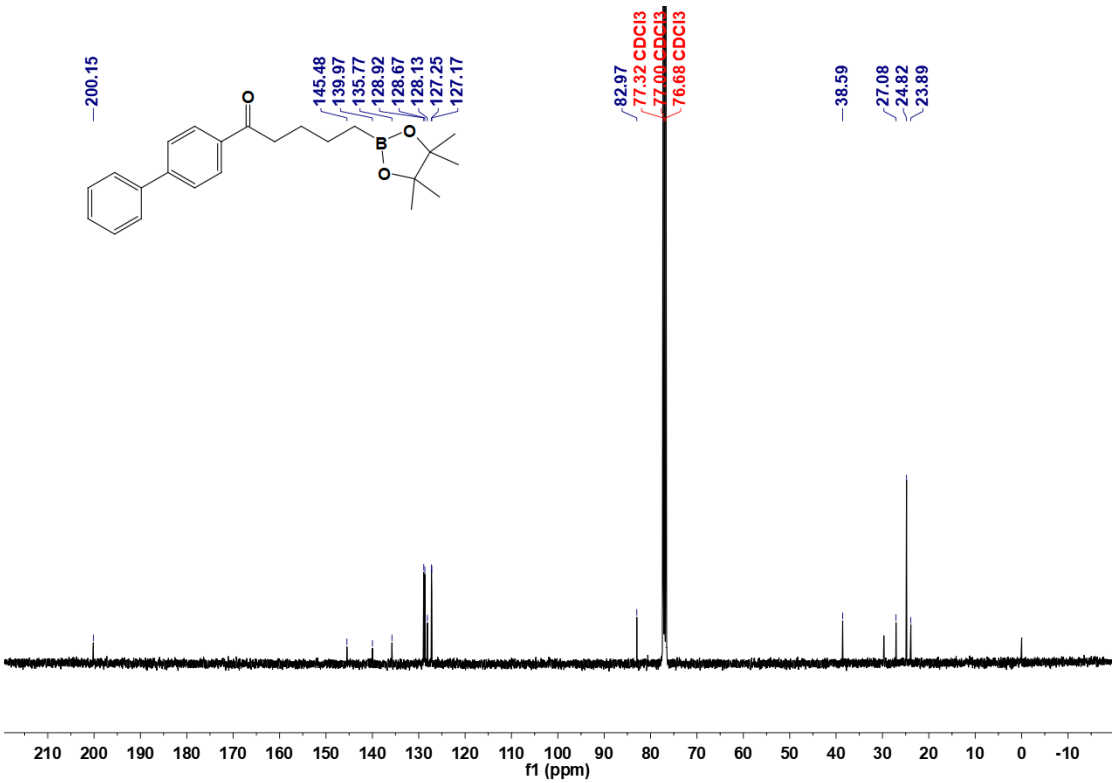
^{11}B NMR spectra for compound **20**



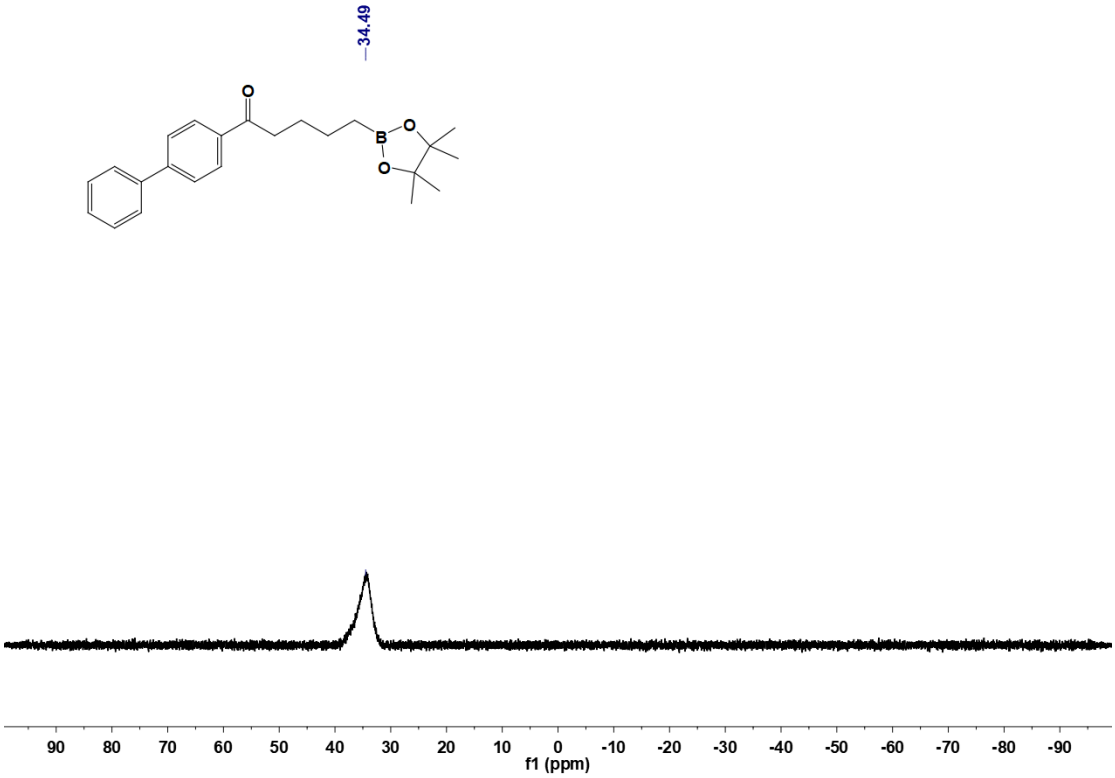


^{1}H and ^{13}C NMR spectra for compound **21**

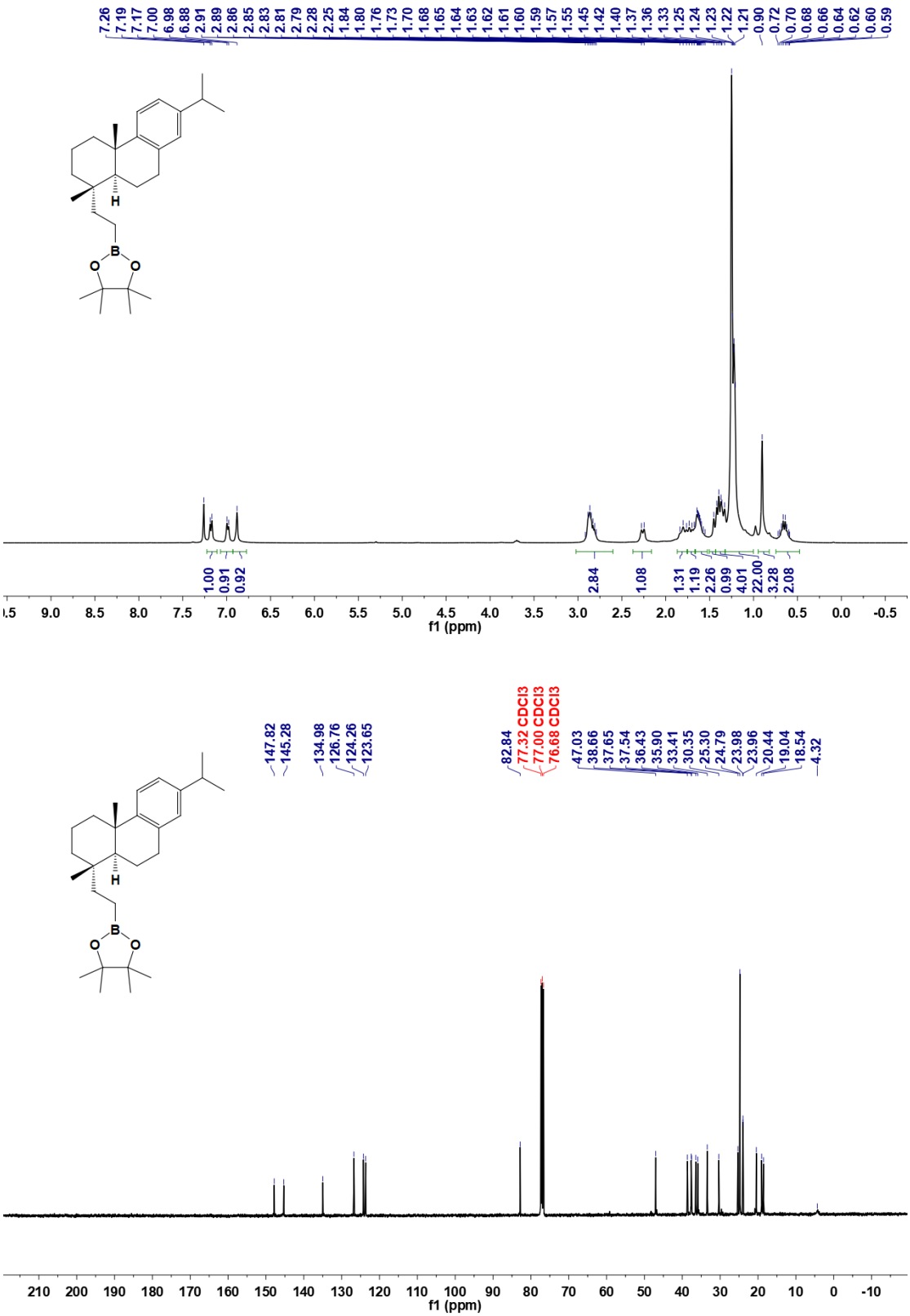




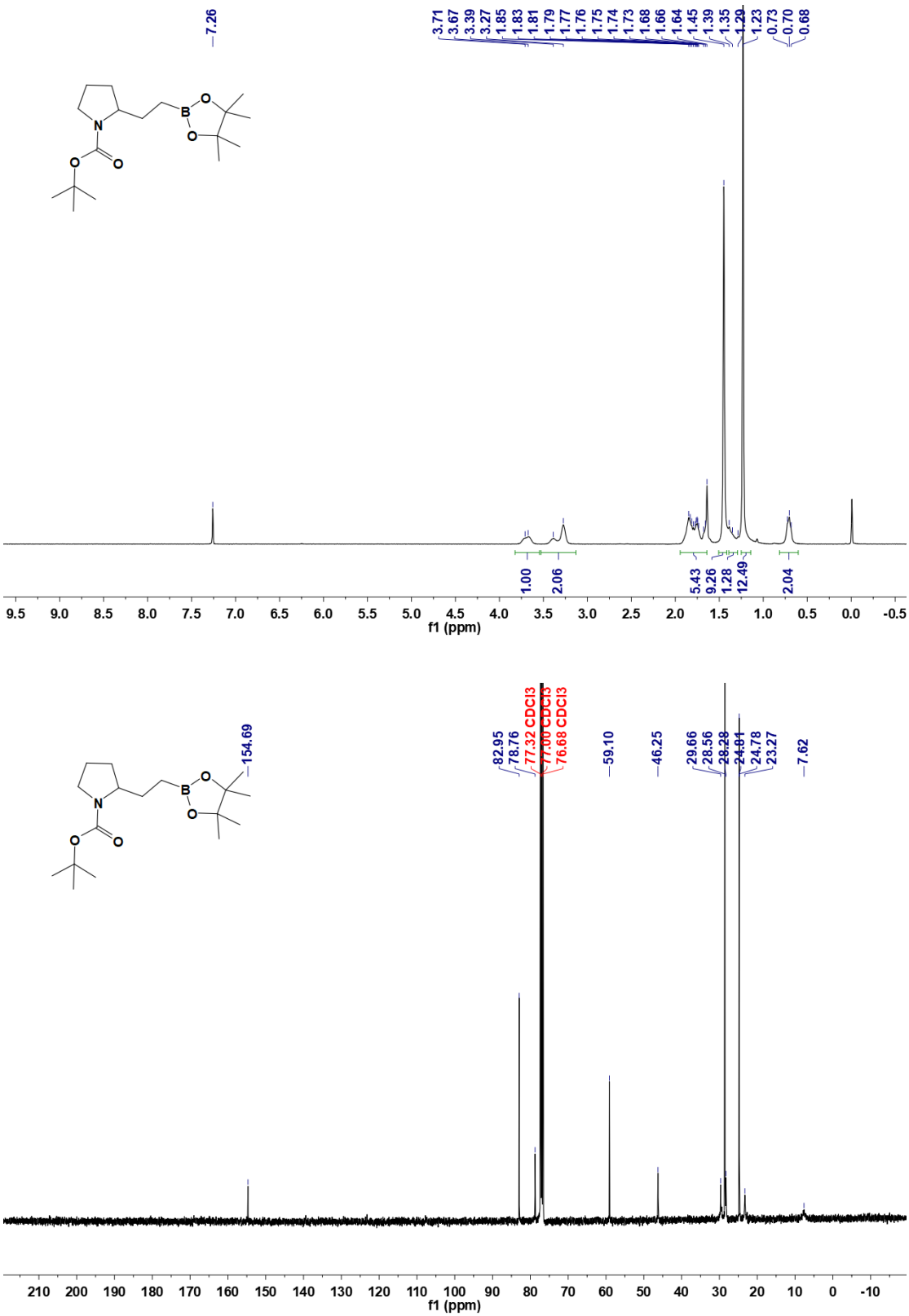
^{1}H and ^{13}C NMR spectra for compound **22**



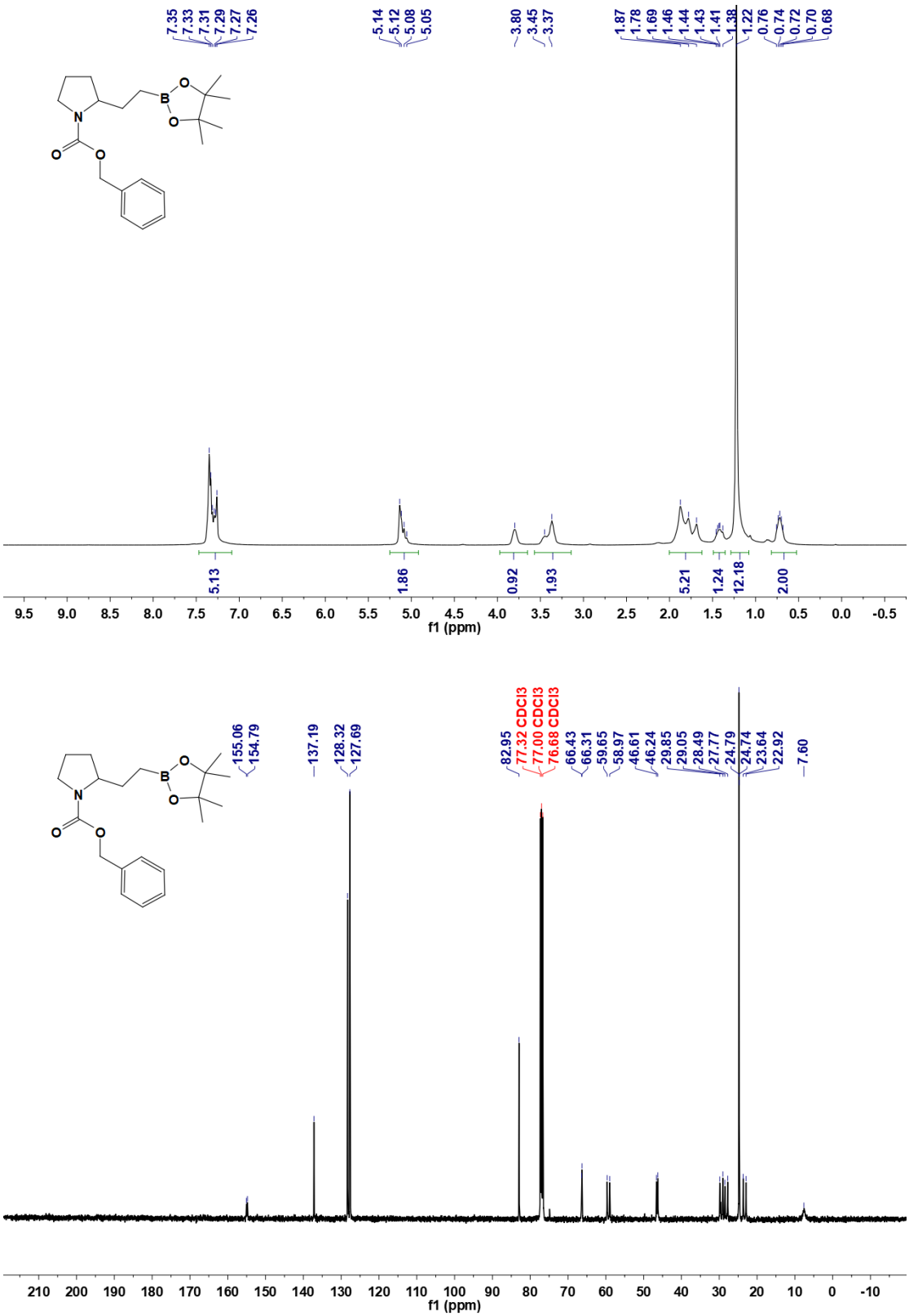
^{11}B NMR spectra for compound **22**



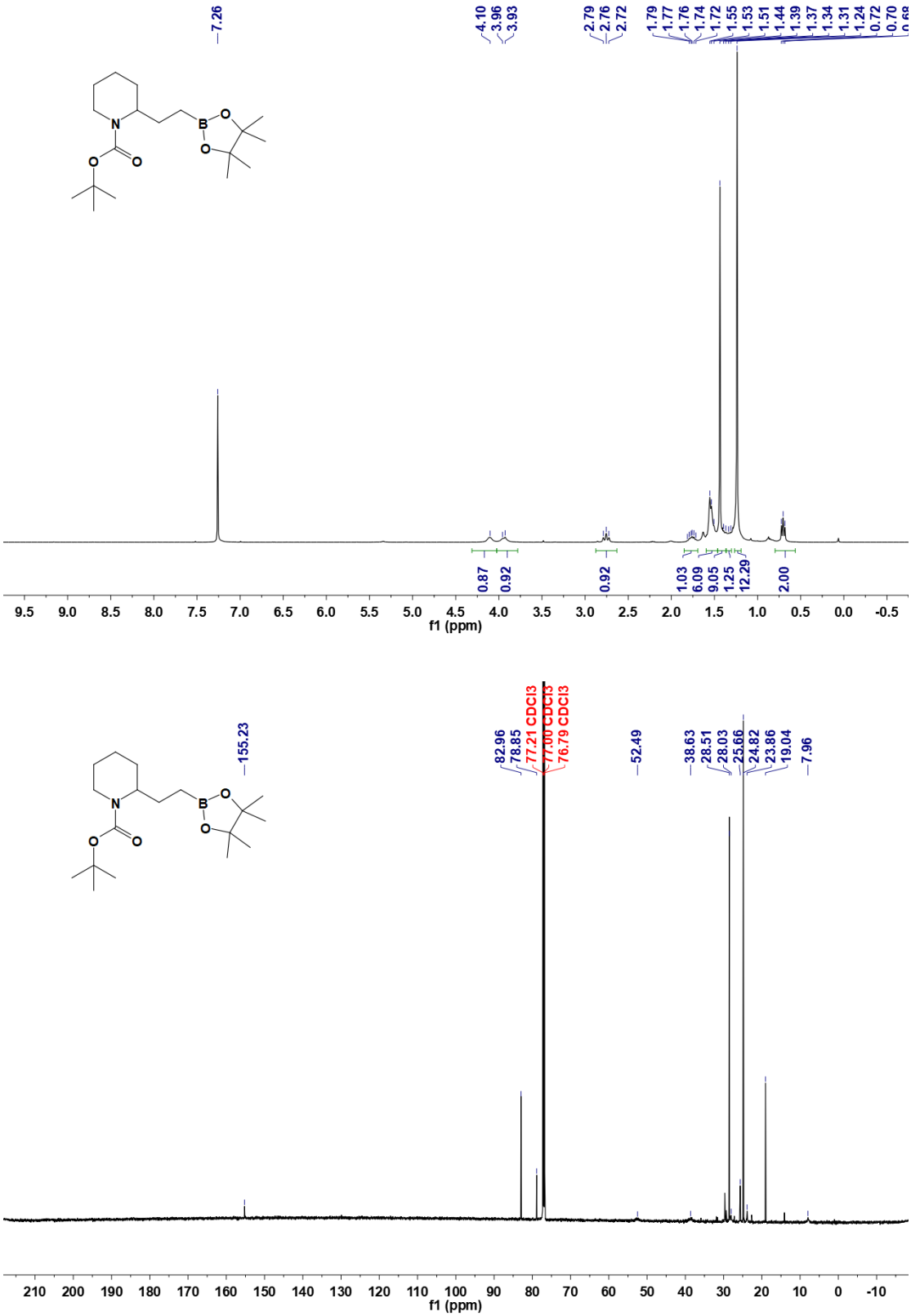
^{1}H and ^{13}C NMR spectra for compound **23**



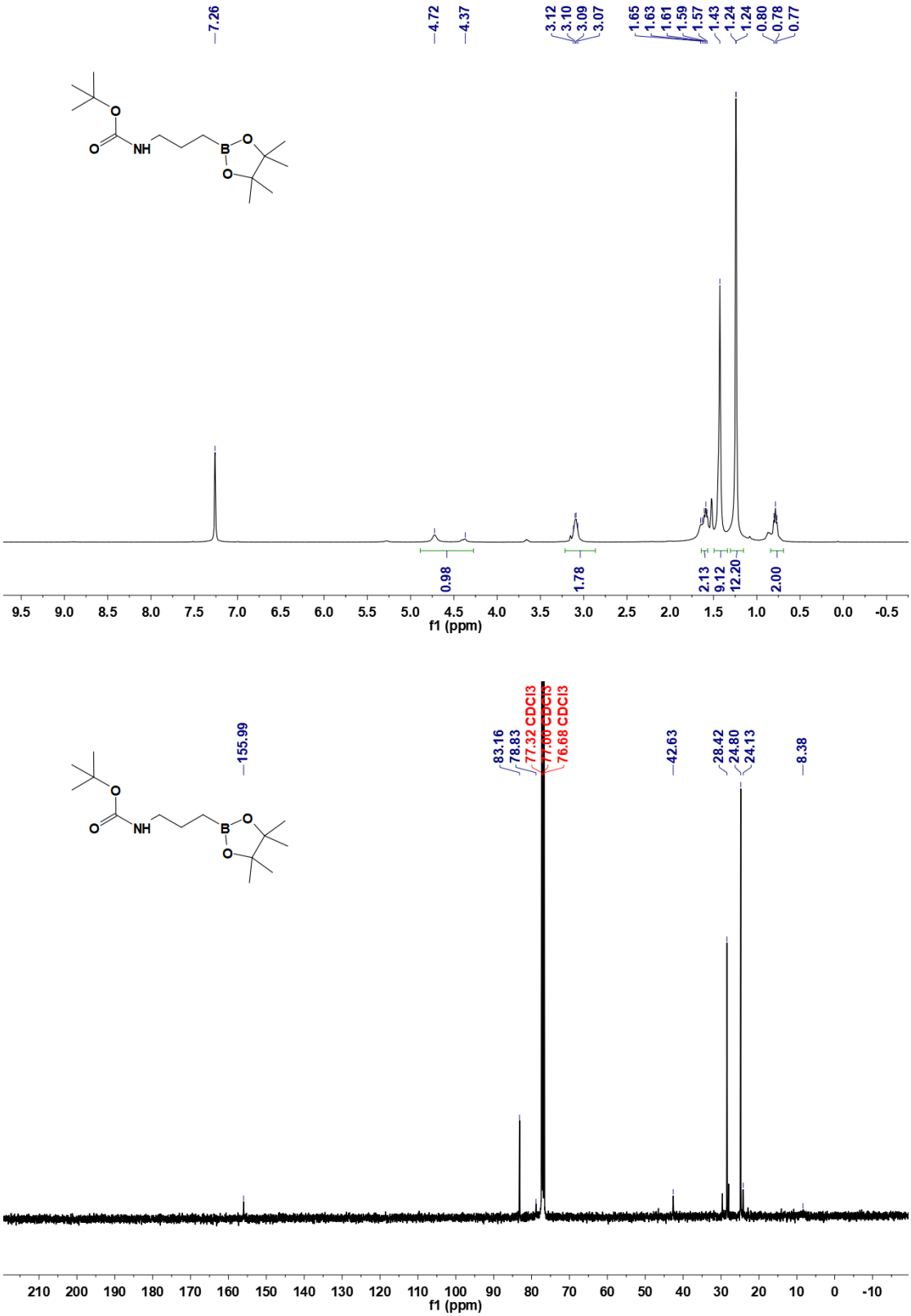
^{1}H and ^{13}C NMR spectra for compound **24**



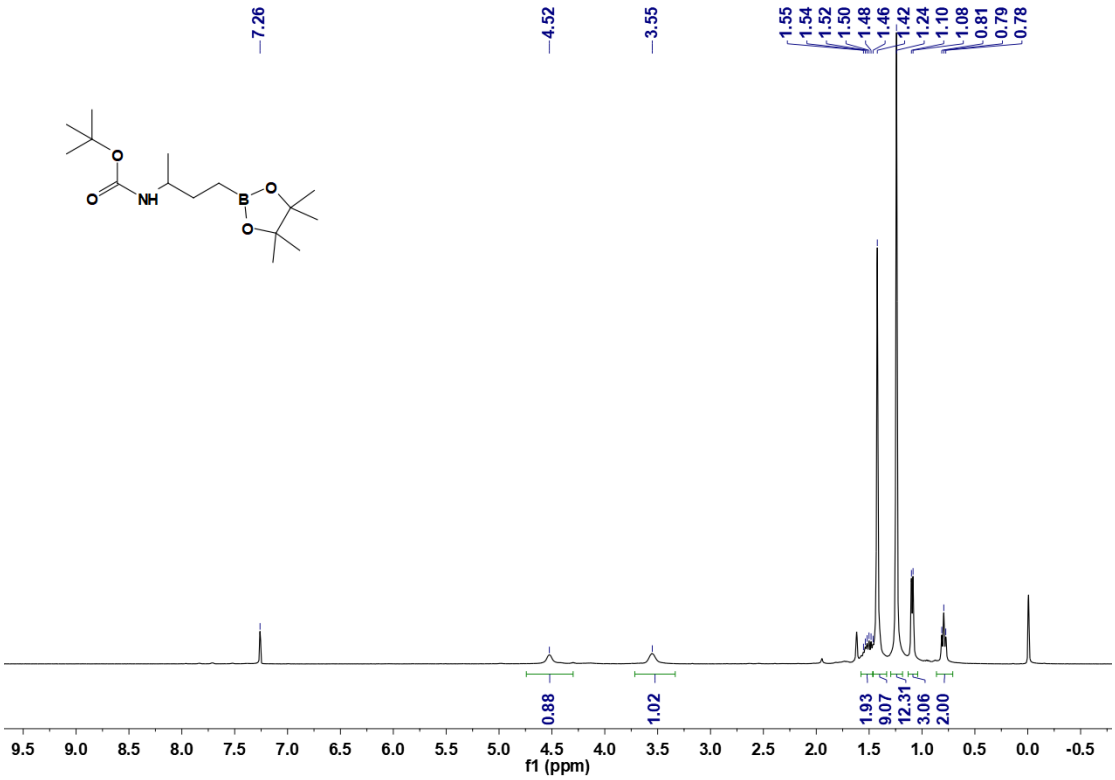
^{1}H and ^{13}C NMR spectra for compound **25**

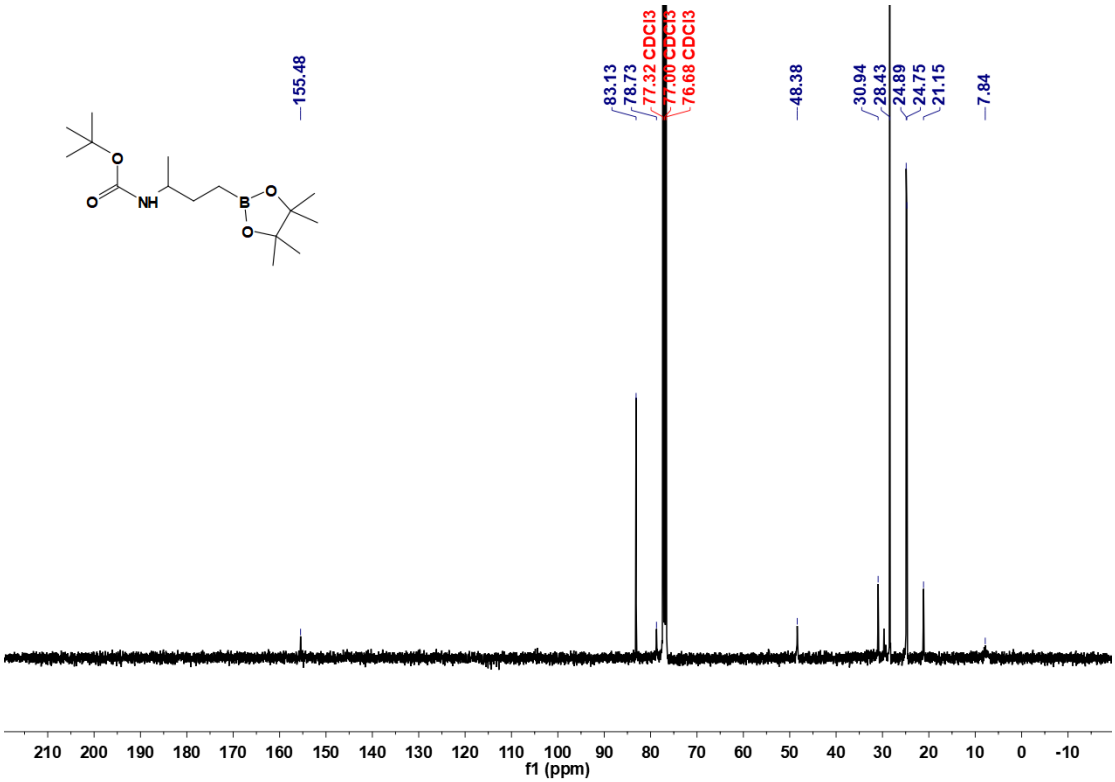


^{1}H and ^{13}C NMR spectra for compound **26**

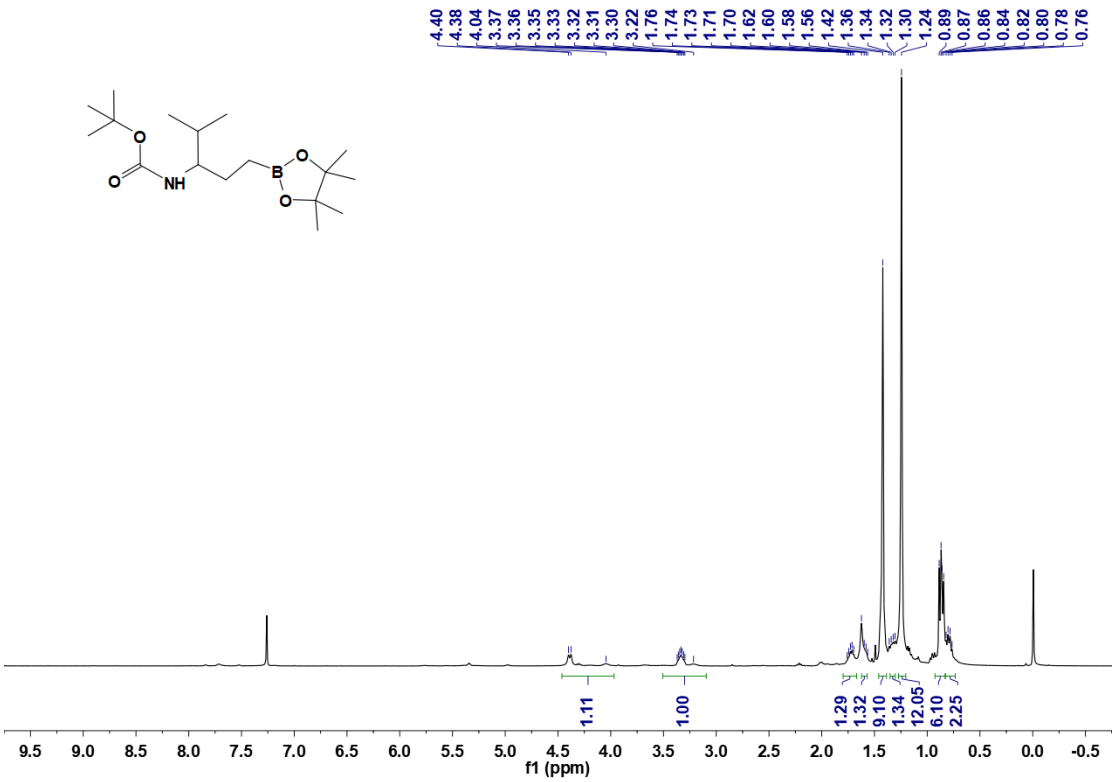


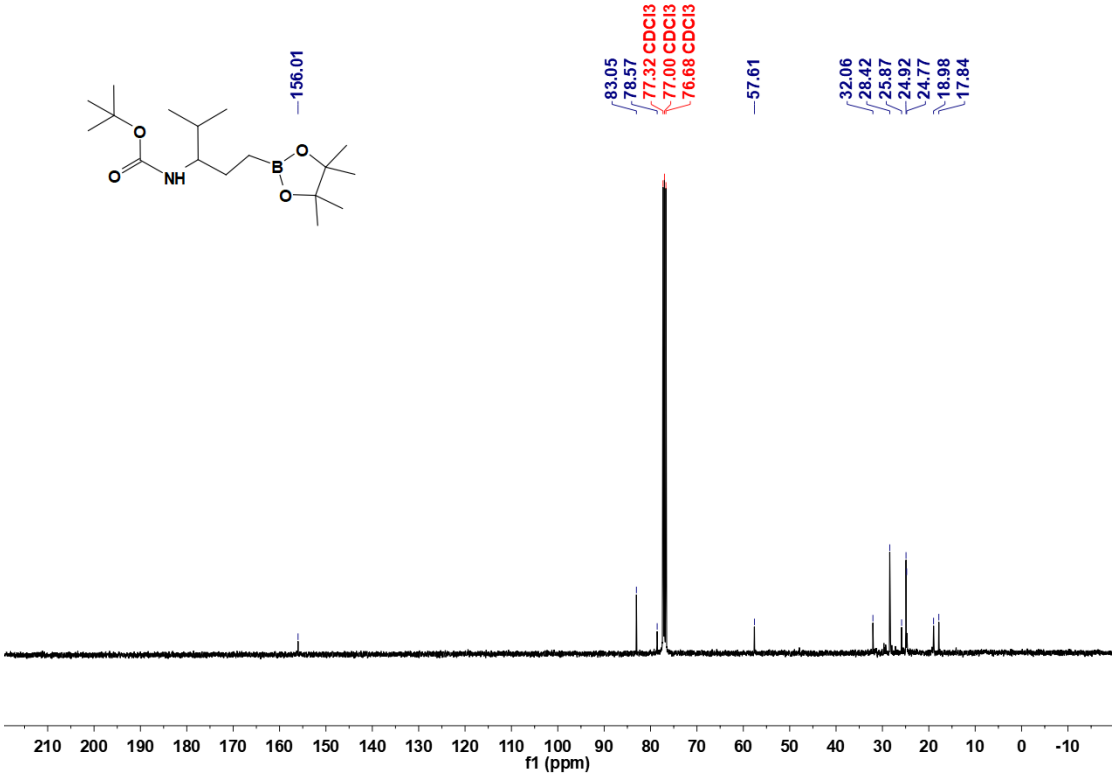
^{1}H and ^{13}C NMR spectra for compound **27**



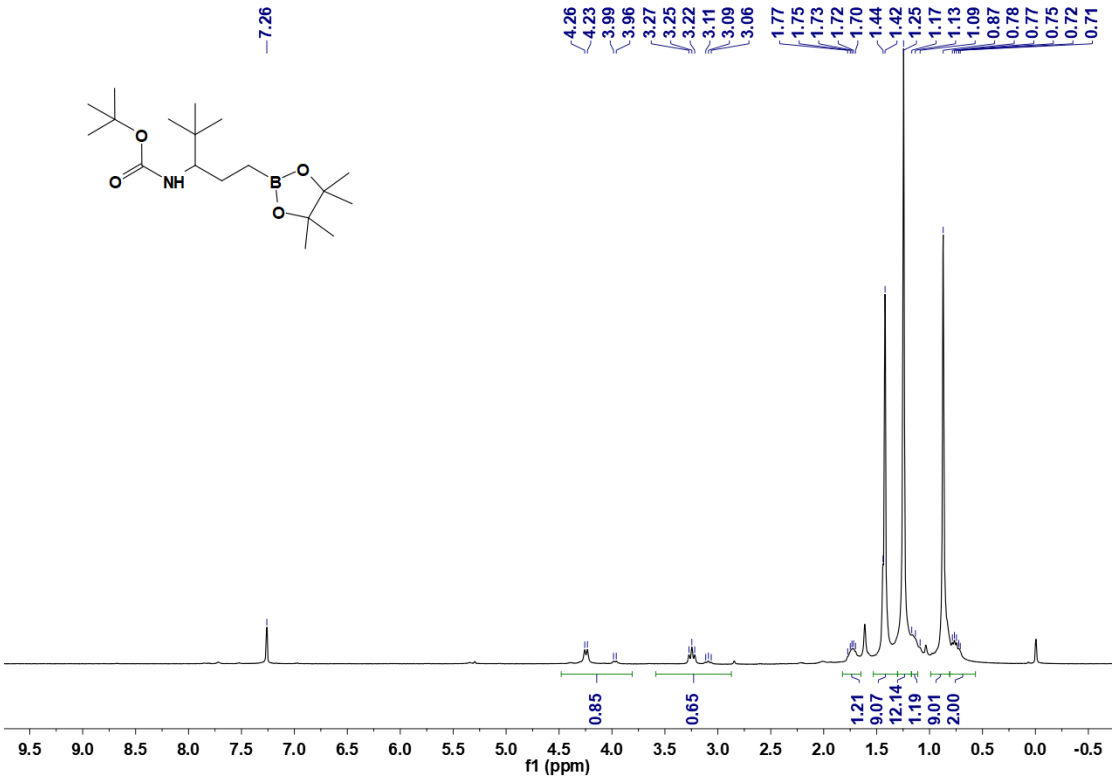


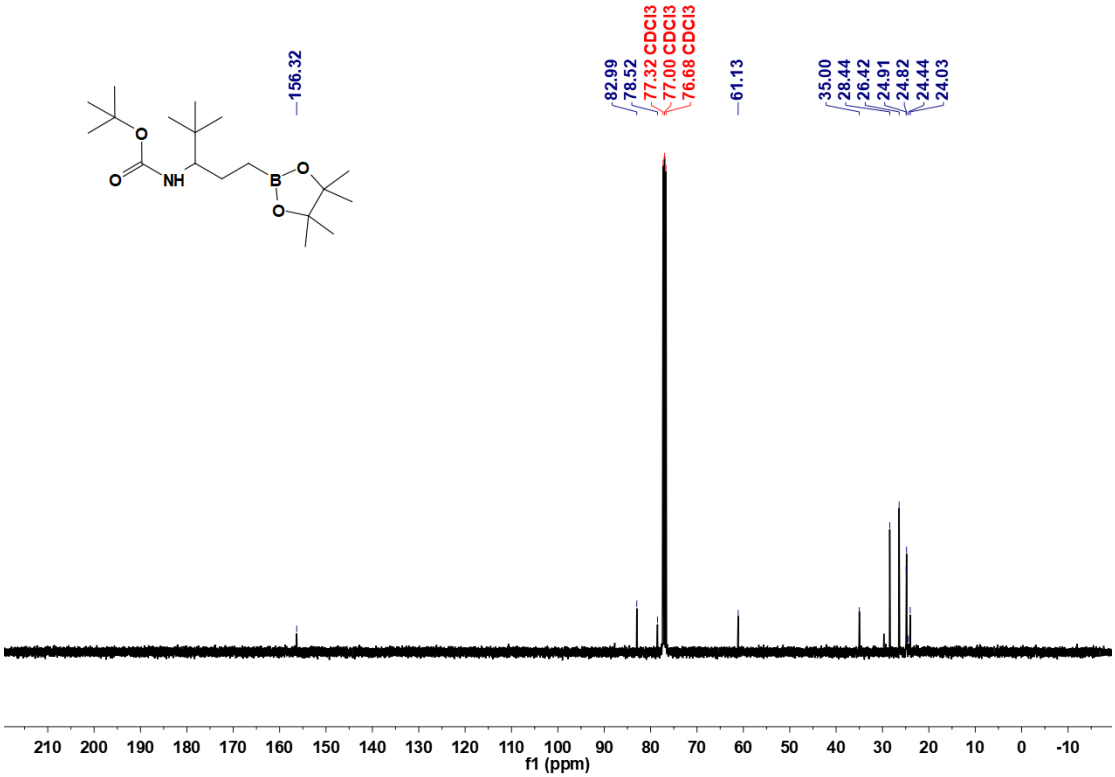
^{1}H and ^{13}C NMR spectra for compound **28**



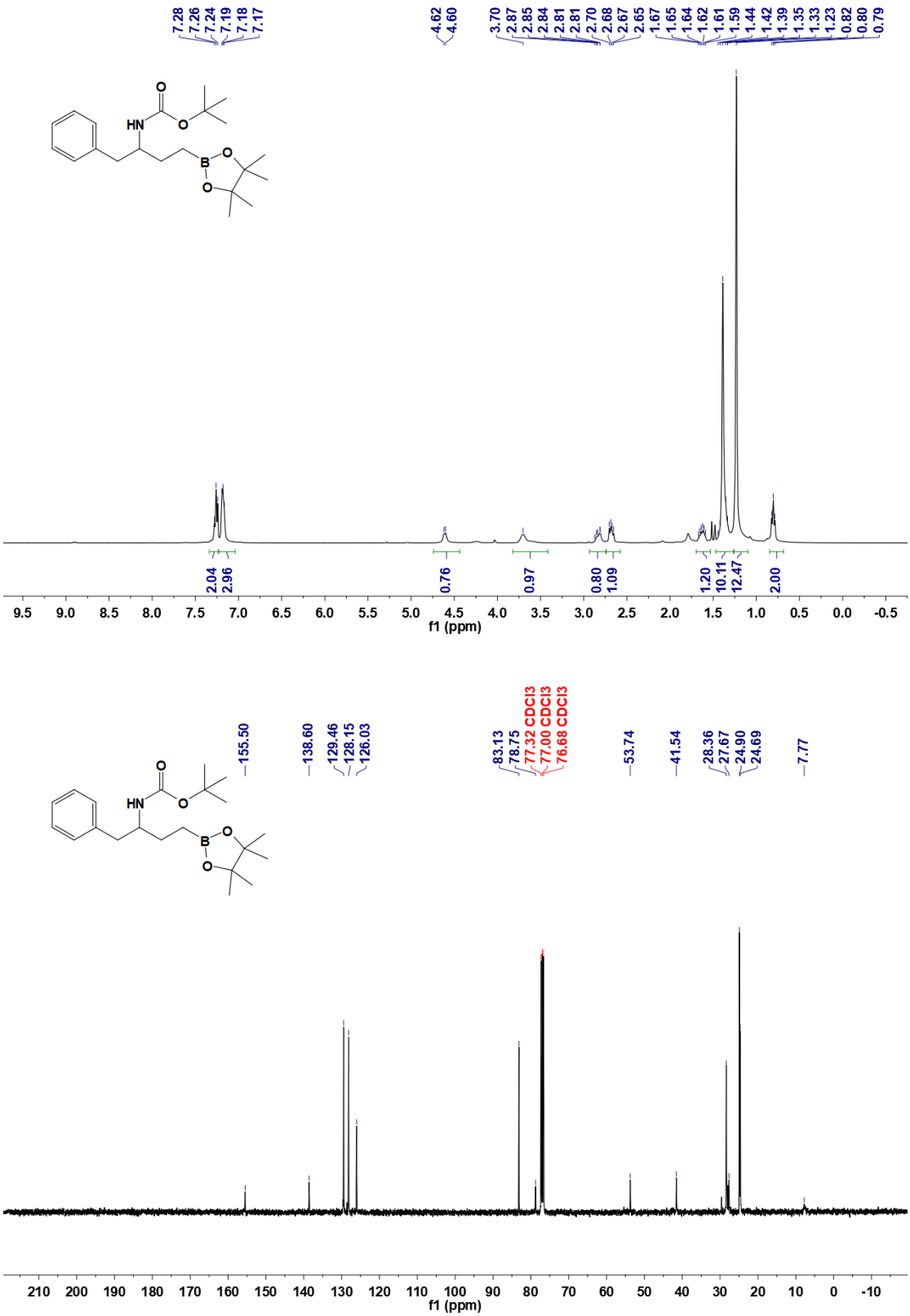


^{1}H and ^{13}C NMR spectra for compound **29**

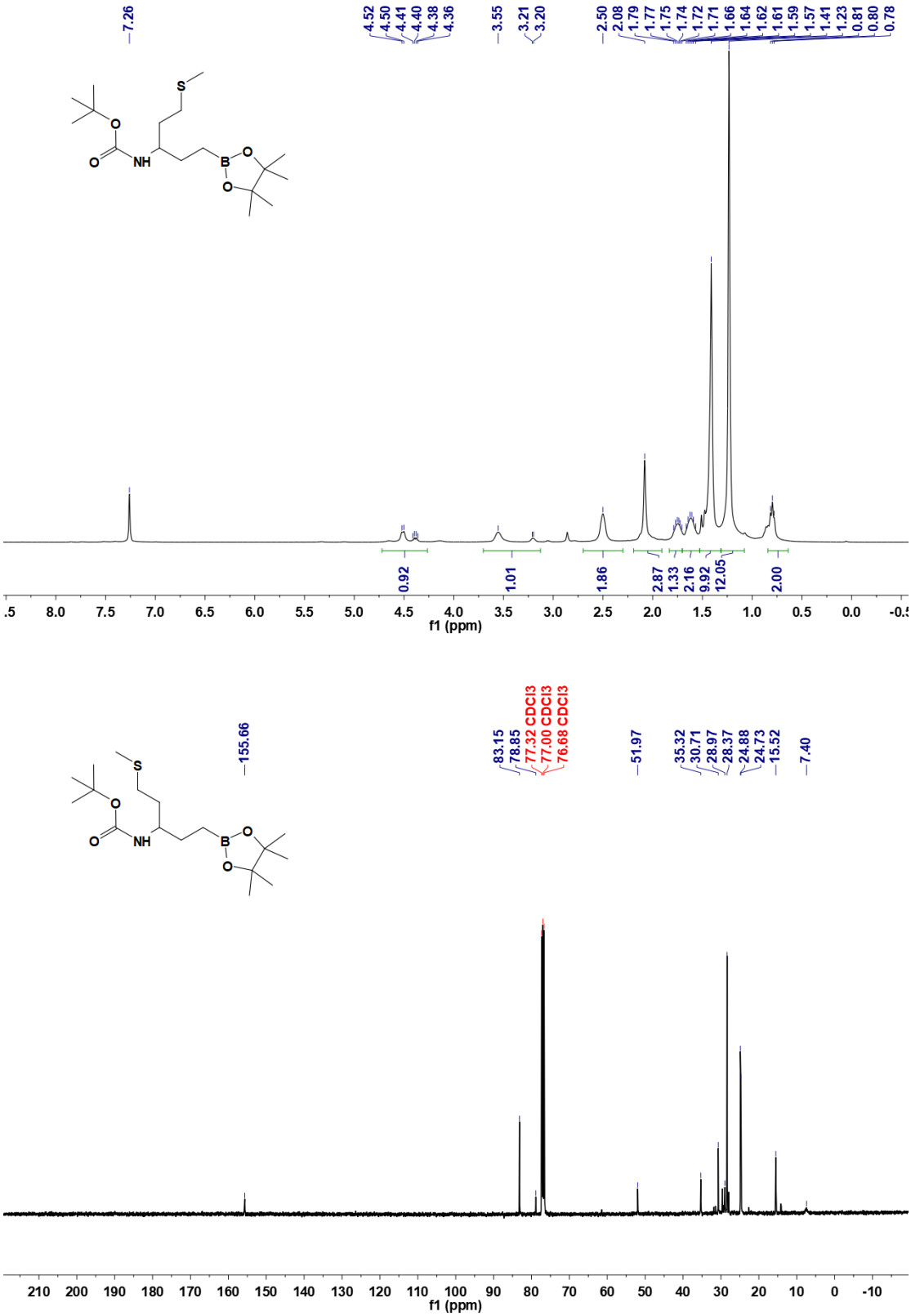




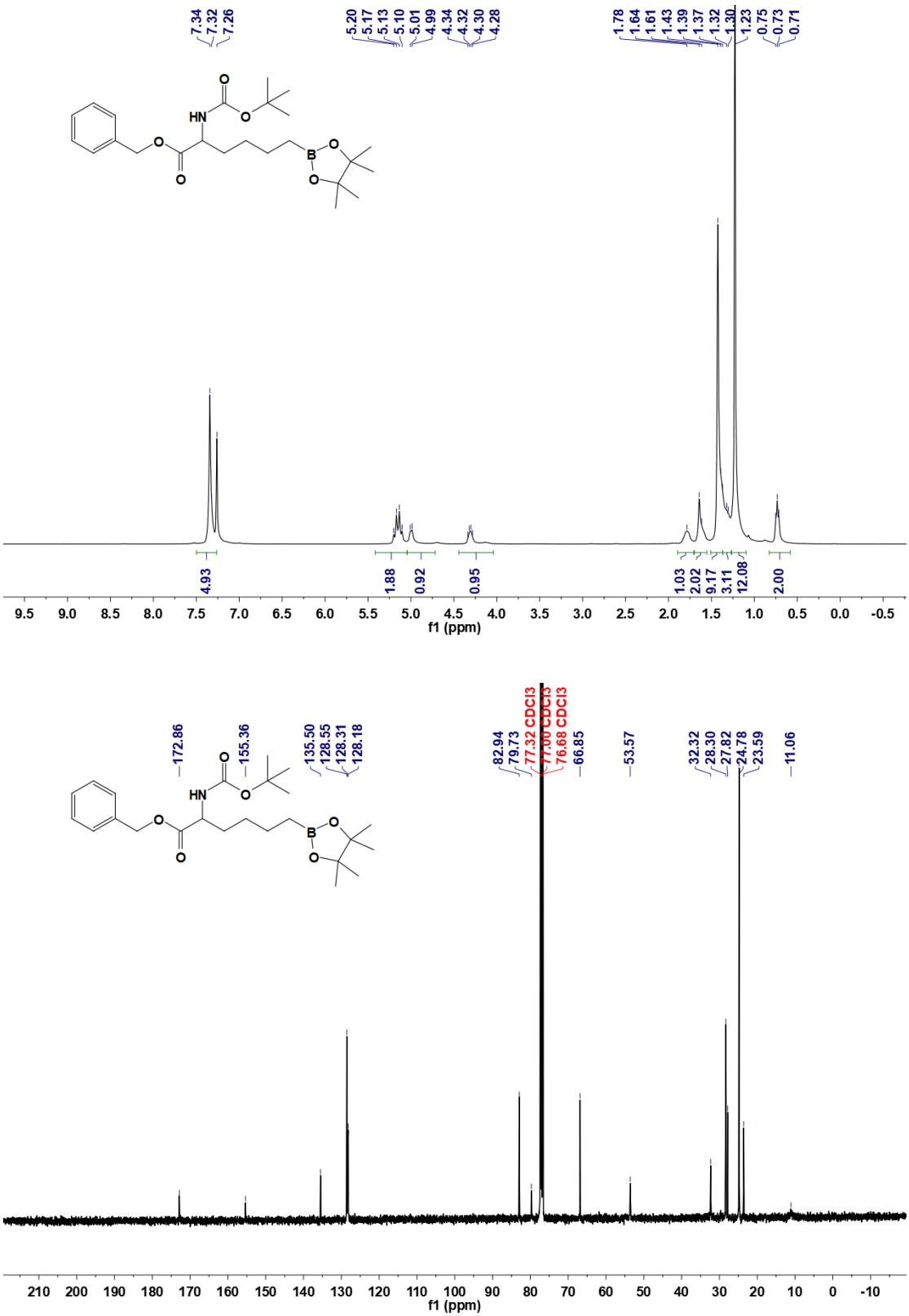
^{1}H and ^{13}C NMR spectra for compound **30**



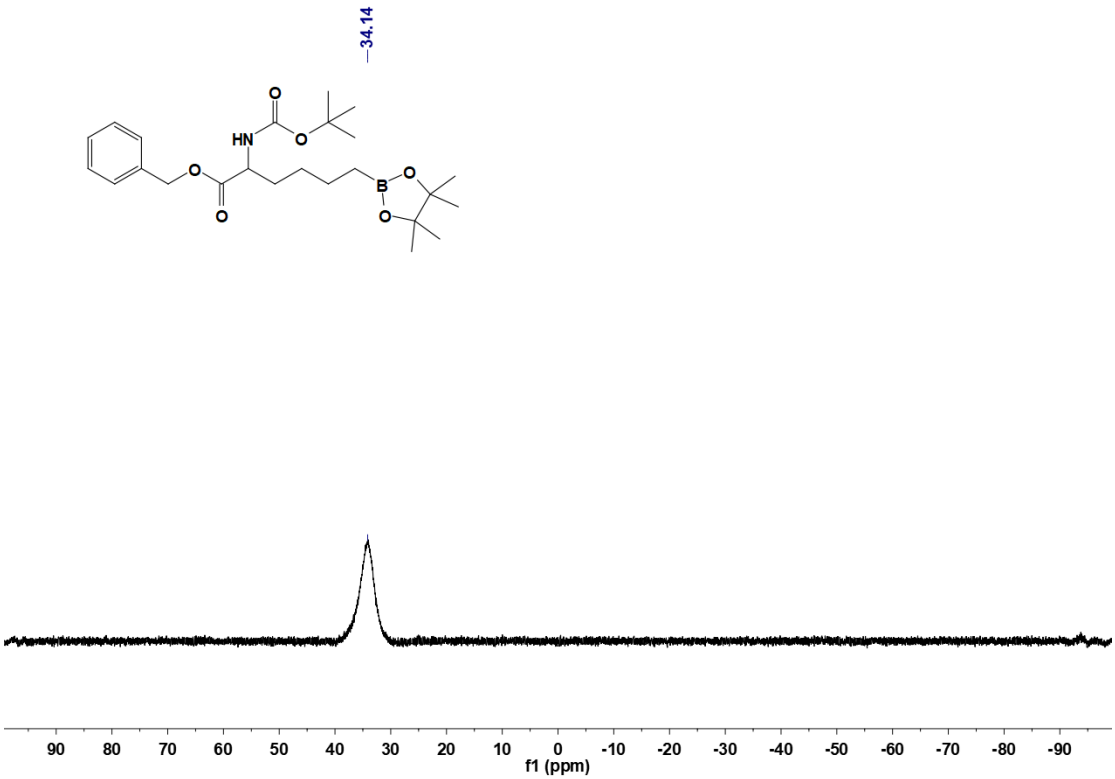
^{1}H and ^{13}C NMR spectra for compound **31**



^{1}H and ^{13}C NMR spectra for compound **32**



^{1}H and ^{13}C NMR spectra for compound **33**



^{11}B NMR spectra for compound **33**

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