Electrochemical Telescoped Synthesis of Alkyl Pinacol Boranes

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Supporting Information

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1. General Experimental Information

For preparative experiments, all reactions were carried out under an inert argon atmosphere with dry solvents under anhydrous conditions unless otherwise stated. Reagents were either purchased of the highest commercial quality and used without further purification, unless otherwise stated or donated by our industrial collaborators. Yields refer to chromatographically (GC-FID with internal standard homogeneous material, or isolated yields unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60F254), using UV light as the visualizing agent and/or CAM as a developing agent.

The

Purifications were done using Biotage Isolera One chromatography with Biotage Sfär Silica D column. GC-FID analysis was performed on a Shimadzu GC FID 230 with a flame ionization detector (FID), using an RTX-5MS Cap. column (30 m × 0.25 mm ID × 0.25 μm) and helium as carrier gas (40 cm/sec-1 linear velocity). The injector temperature was set to 280 °C. After 1 min at 50 °C, the temperature was increased by 25 °C/min to 300 °C and kept constant at 300 °C for 4 min. FID was used for detection, and the detector gases used for flame ionization were hydrogen and synthetic air (5.0 quality). GC-MS analysis was performed using a Shimadzu GCMS-QP2010 SE, using an RTX-5MS column (30 m × 0.25 mm × 0.25 μm) and helium as carrier gas (40 cm/sec linear velocity). The injector temperature was set to 280 °C. After 1 min at 50 °C, the oven temperature was increased by 25 °C/min to 300 °C and then kept at 300 °C for 3 min. The mass detector was a quadrupole with pre-rods and electron impact ionization. The following settings were used in the detector: ion source temperature 200 °C, interface temperature 310 °C, solvent cut time 2 min 30 sec, acquisition mode scan, mass range m/z = 50 till m/z = 400. 1H NMR spectra were recorded on a 300 MHz instrument. 13C NMR at 75 MHz. 19F NMR at 282 MHz. Chemical shifts (δ) are expressed in ppm downfield from TMS as internal standard. The letters s, d, t, q, and m are used to indicate singlet, doublet, triplet, quadruplet, and multiplet, respectively.

Electrolysis cells:

Reactions were carried out in an in-house built flow electrolysis cell.[1] The electrode separators with a thickness between 0.3-0.1 mm had a flow channel with an active surface area of 6.4 cm^2.
Graphite electrodes: IG-63 from GTD Graphit Technologie GmbH.

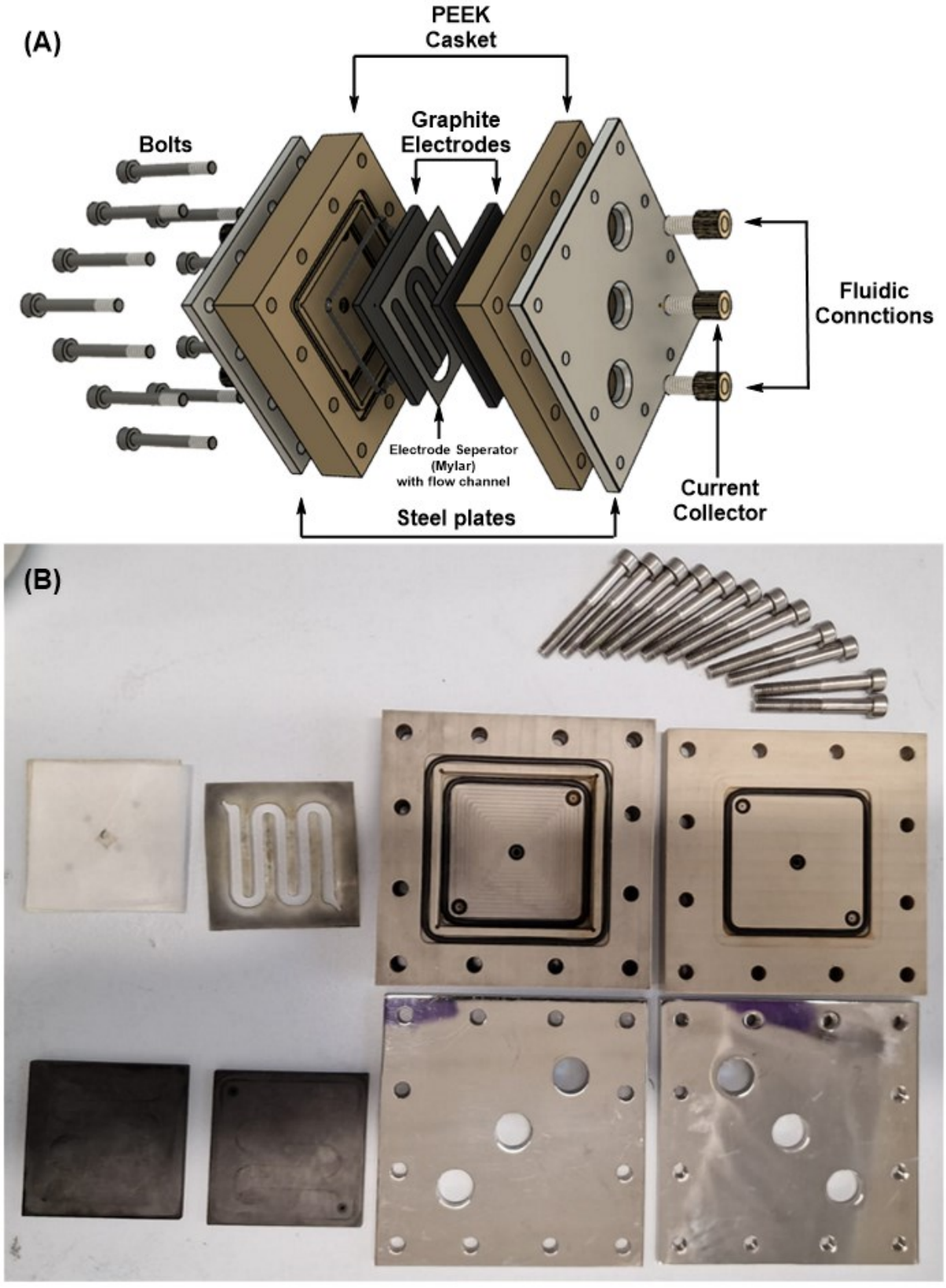
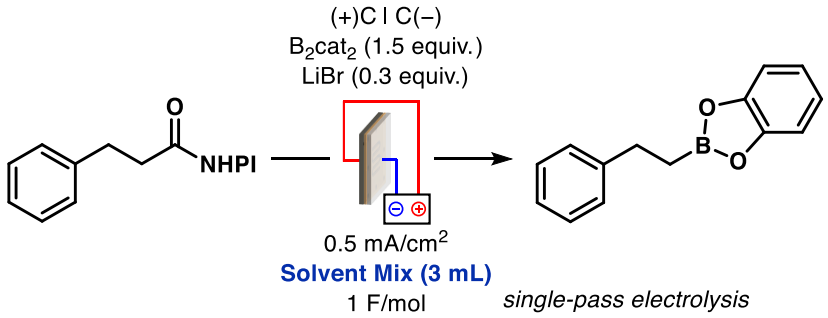


Figure S1. (A) exploded view & (B) disassembled flow plate reactor

2. Single Pass optimisation

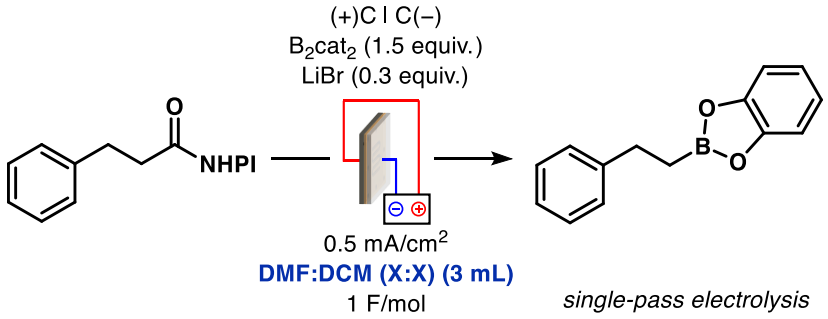
All optimisation experiments were carried out with a 0.2 M reaction solution in our *in-house*, parallel plate reactor shown in Figure S1. The crude reaction mixture was analysed via GC-FID with dodecane as an internal standard. Samples were taken at 1 F/mol.
Owing to the single-pass nature of the reaction, the electrochemical parameters were restricted in terms of reaction time as well as current density. Nevertheless, adjustment of these parameters was achieved by modification of the gasket (see Table S5-S6).

Table S1: Solvent Optimisation. [a]Dodecane used as internal standard



Entry	Solvent Mix 1:1	GC-FID A_P/A_{IS} [%][a]
1	**DCM:DMF**	**53**
2	DCM:DMAc	51
3	DCM:NMP	56
4	DCM:Sulfolane	31

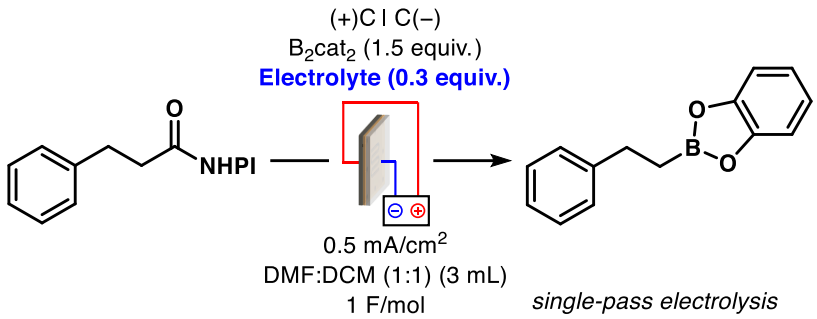
Table S2: Solvent Ratio Optimisation. [a]Dodecane used as internal standard



Entry	DMF:DCM ratio	GC-FID A_P/A_{IS} [%][a]
1	1:9	54
2	1:3	58
3	1:2	47
4*	**1:1**	**53**
5*	2:1	55
6*	3:1	51

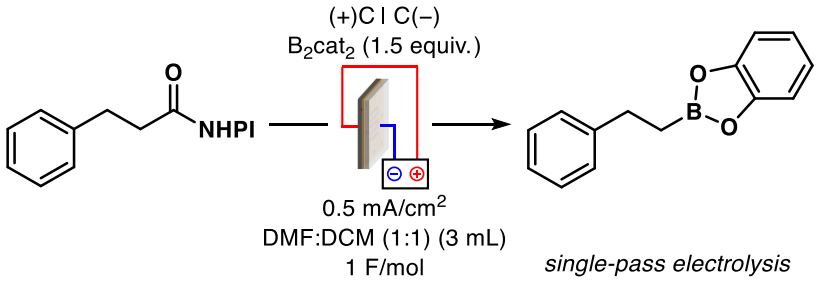
*Solution was only homogeneous in entry 4-6.

Table S3: Supporting Electrolytes. [a]Dodecane used as internal standard

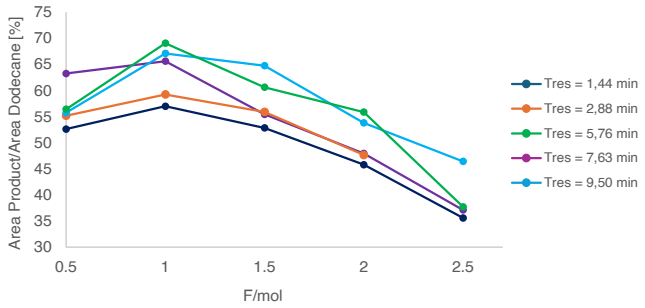


Entry	Supporting electrolyte	GC-FID A_P/A_{IS} [%][a]
1	**None**	**57**
2	LiBr	53
3	NBu_4PF_6	52
4	NBu_4BF_4	50
5	Et_4NBr	55
6	Et_4NI	55
7	Et_4NCl	61
8	$ZnBr_2$	52

Table S4: Residence Time Optimisation. [a]Dodecane used as internal standard



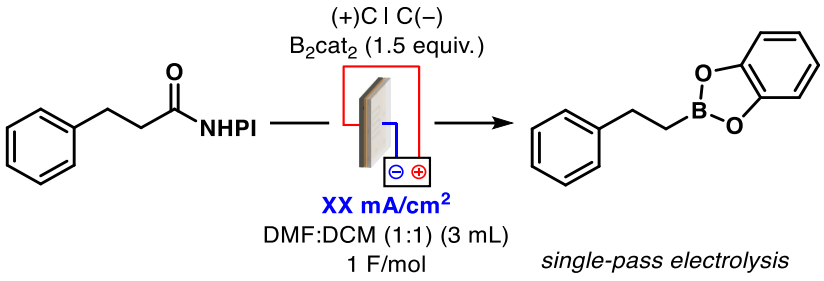
Entry	t_{res} [min]	GC-FID A_P/A_{IS} [%][a]
1	1.44	57
2	2.88	59
3	**5.76**	**69**
4	7.63	66
5	9.5	67



Graph S1. Impact of charge with residence time

Table S5: Flow Channels with Different Surface Areas (picture of the gaskets used below).

[a]Dodecane used as internal standard



Entry	Channel Surface Area	GC-FID A_P/A_{IS} [%][a]
1	**6.4 cm^2**	**69**
2	10.2 cm^2	56

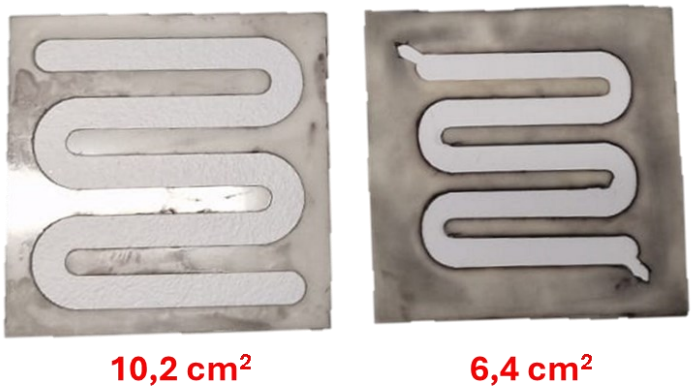
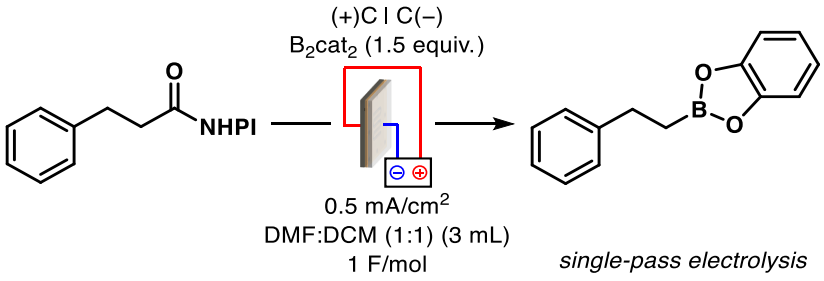


Table S6: Interelectrode Gap. [a]Dodecane used as internal standard

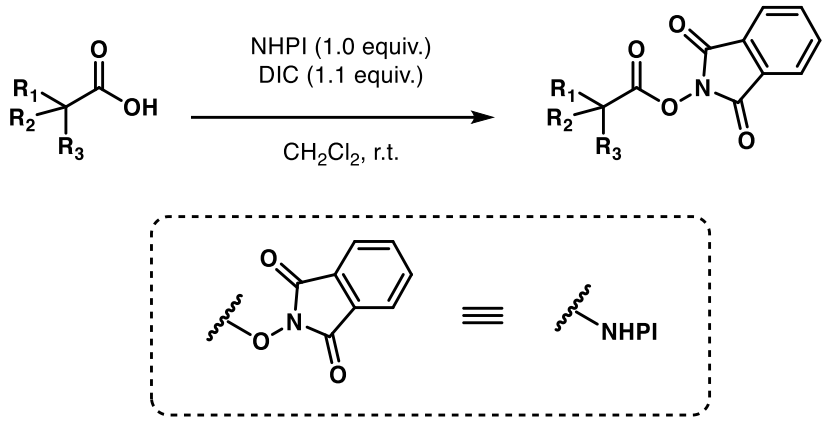


Entry	Interelectrode Gap	GC-FID A_P/A_{IS} [%][a]
1	0.3 mm	69
2	**0.1 mm**	**78**

The subsequent step was not systematically optimized owing to the excess of pinacol and triethylamine. Preliminary attempts to modify reaction temperature led to similar results, indicating the robustness of this process. In all cases, complete conversion of the catecholborane has been observed via GC analysis.

3. Synthetic Procedures and Characterisations

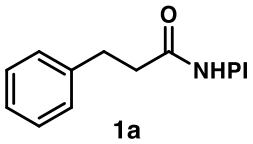
General Procedure 1: Starting Materials



Following the literature procedure, to a suspension of the carboxylic acid (1.0 equiv.) and *N*-hydroxy phthalimide (1.0 equiv.), in anhydrous CH_2Cl_2 (0.3 M with respect to the carboxylic acid), *N,N′*-diisopropylcarbodiimide (DIC, 1.1 equiv.) was added via syringe under Ar. The reaction mixture was stirred until complete (monitored by TLC, typically 0.5 h – 3 h). Upon completion, the mixture was filtered to remove the majority of the urea by-product then concentrated and was directly purified via silica gel column chromatography to afford the activated ester.

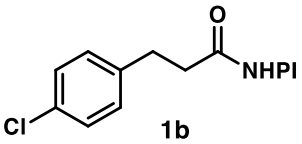
Previously reported NHPI esters used in this study are shown in Figure S2. Characterisation data for these RAEs was in agreement with the literature.[2–14]

Primary



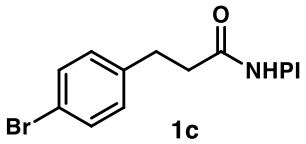
1a

CAS: 84379-71-5



1b

CAS: 2248410-58-2



1c

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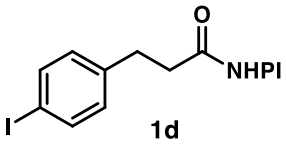

1d

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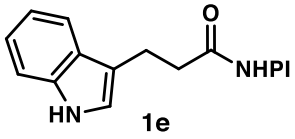

1e

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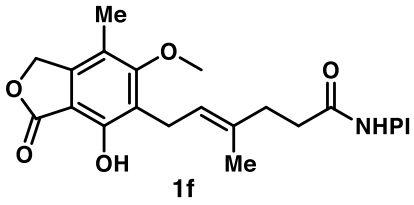
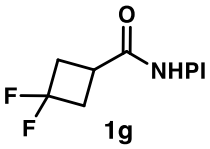


1f

CAS: 2173129-29-6

Secondary



1g

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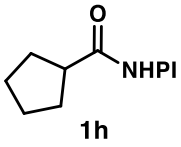
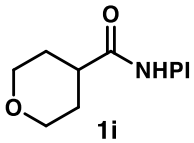


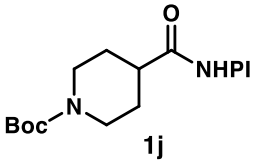
1h

CAS: 946513-95-7



1i

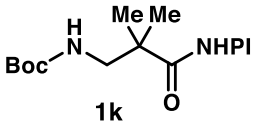
CAS: 1872262-74-2



1j

CAS: 1872262-73-1

Tertiary

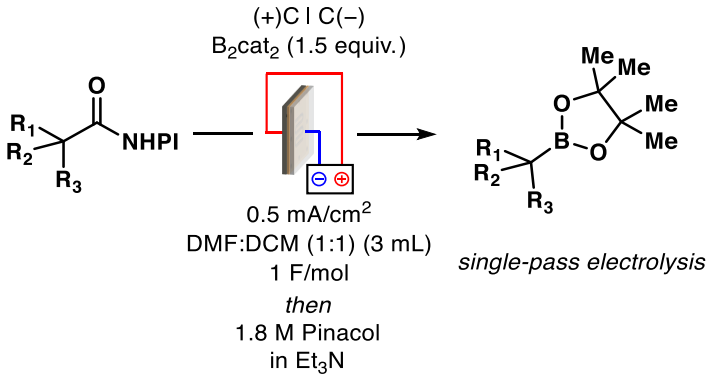


1k

CAS: 2248352-59-0

Figure S2: Redox active esters known to literature

General Procedure 2: Product synthesis



1.2 mmol of the corresponding redox active ester (**1**) were dissolved together with 1.5 equiv. (428 mg) of B_2cat_2 (**2**) in 6 mL of a 1:1 mixture dry DMF:DCM and loaded into a Harvard PHD ULTRA syringe pump equipped with a 6 mL Syringe. The flow rate was set to 11 µL/min, and the pump was connected to the reactor shown in figure S1 via 1/16-inch tubing. The Outlet of the parallel plate reactor was connected to a waste reservoir. The piston of the syringe was pushed in manually until reaction mixture was observed at the reactor outlet. The Parallel plate reactor was connected to a power supply (BK Precision 1739 DC Power Supply), set to a constant current of 3.5 mA (0.55 mA/cm^2). After an initial equilibration time of 30 minutes the outlet of the parallel plate reactor was connected to a T-piece mixer together with a second Harvard PHD ULTRA syringe pump equipped with a 6 mL syringe containing 1.33 mL of 1.8 M pinacol stock solution in dry Et_3N. The combined reaction stream was pumped through a 250 µL coil reactor at RT and collected into a vial under argon atmosphere. After collection of 3 mL of reaction mixture (corresponding to 0.6 mmol substrate, 4:32 h), the mixture was poured into a separatory funnel containing 10 mL saturated NH_4Cl, 10 mL H_2O and 30 mL EtOAc and extracted. The aqueous phase was extracted 3 additional times with 30 mL of EtOAc and the combined organic layer was dried over $MgSO_4$ and stripped *in vacuo*. The obtained crude product was purified by Biotage to obtain the final product.

Setup Picture:

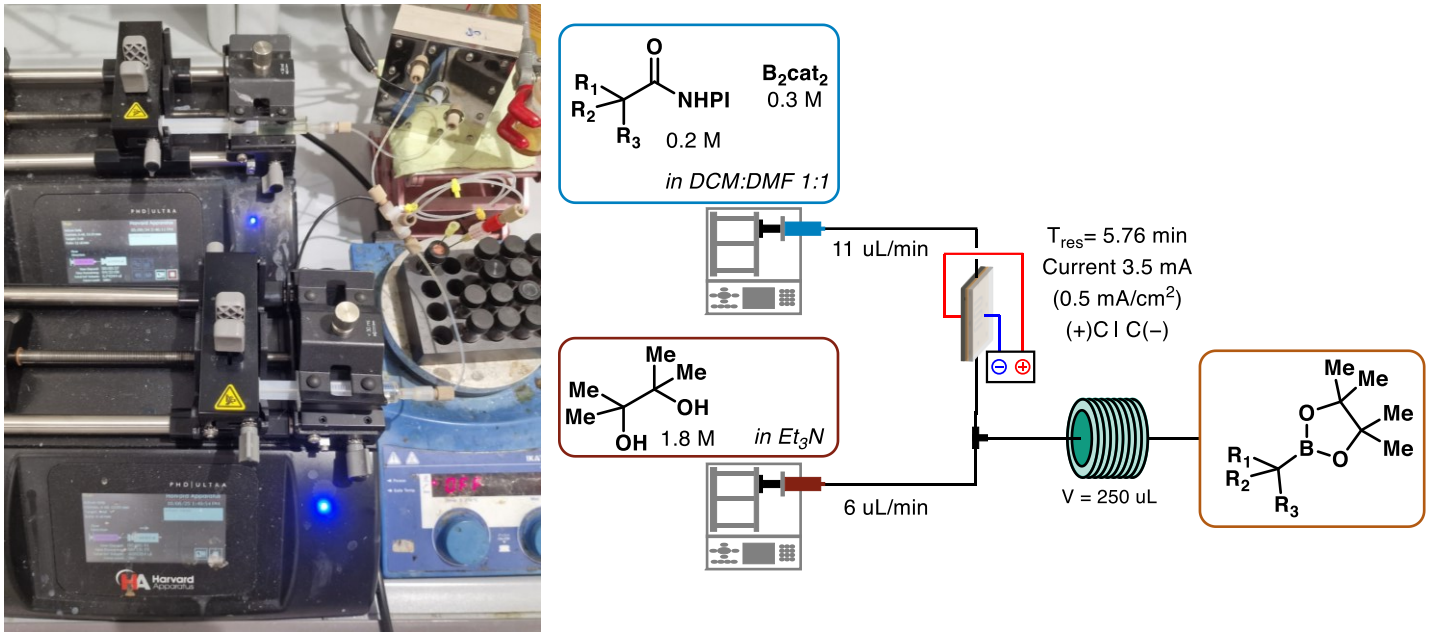
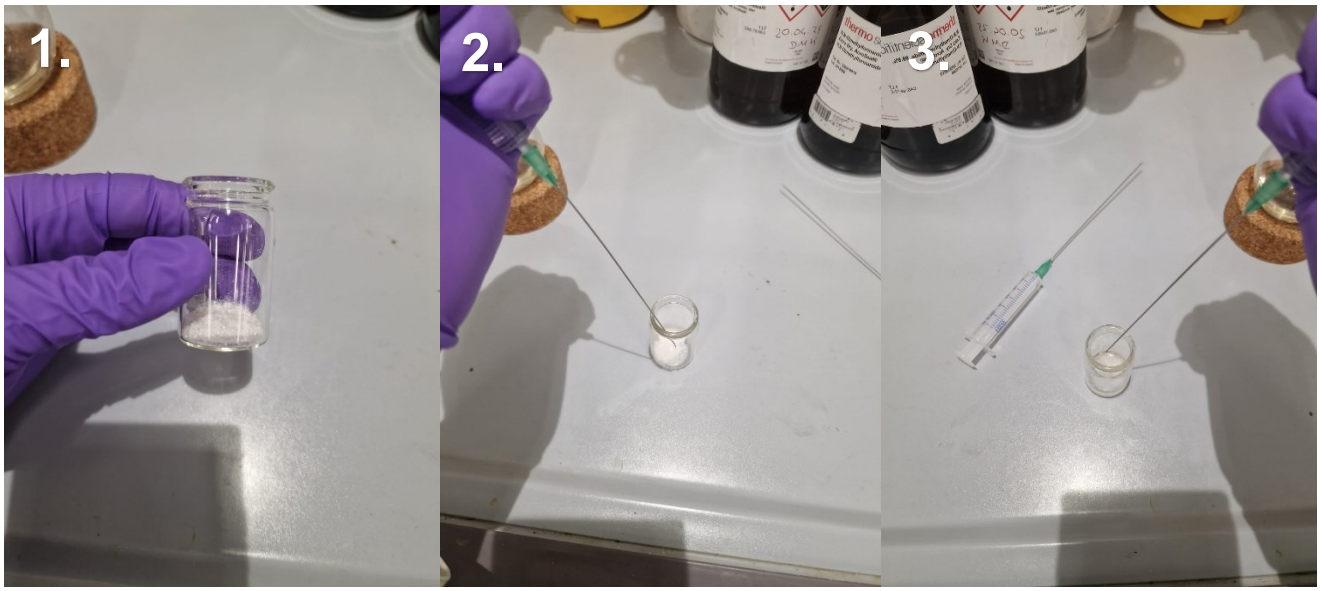
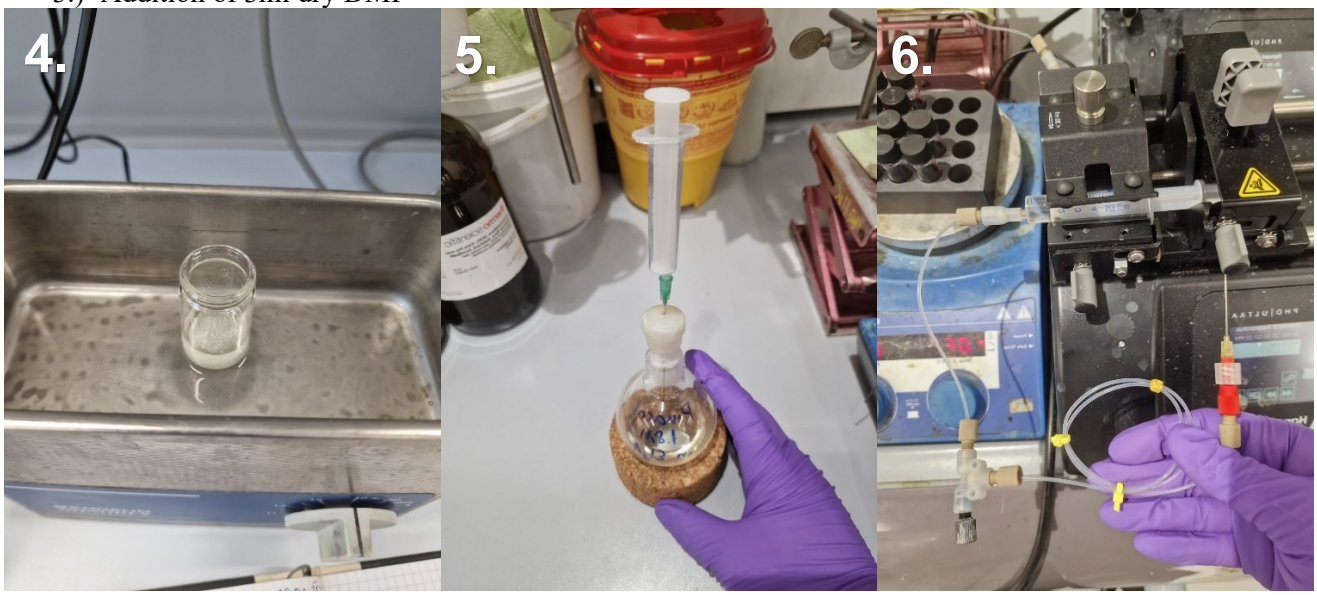


Figure S2. Left: Setup. Right: Scheme

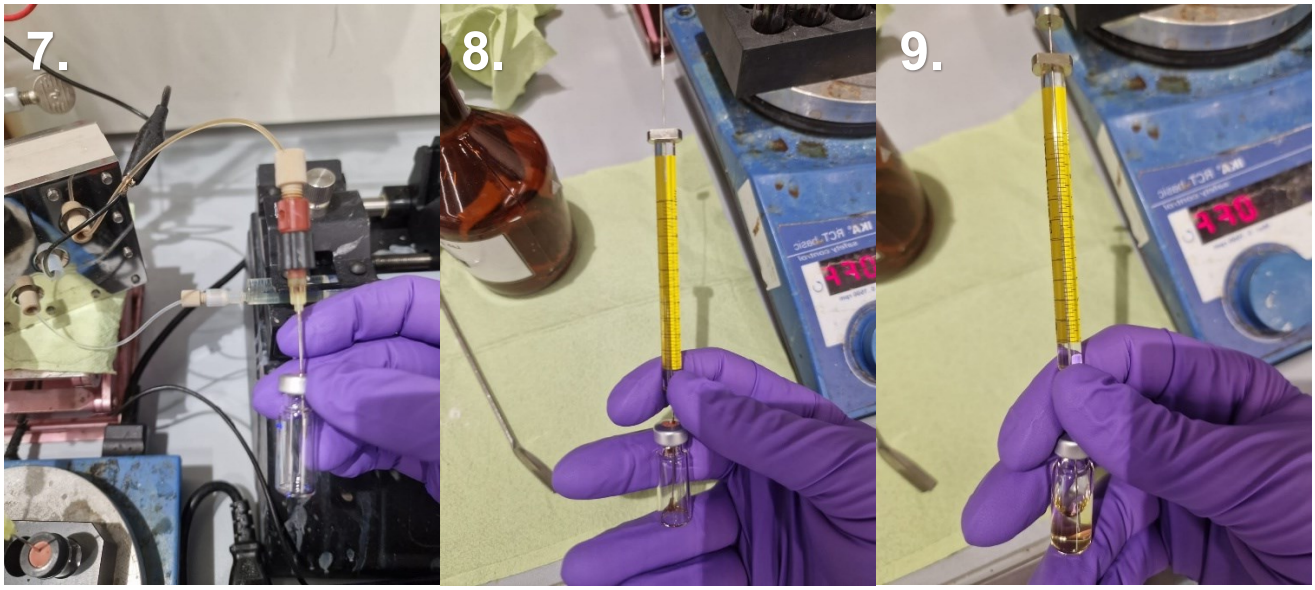
2.3 Visual Guide



1.) Redox active Ester and 2,2′-Bi-1,3,2-benzodioxaborol are weight into a oven dried glass vial
2.) Addition of 3 ml dry DCM
3.) Addition of 3ml dry DMF



4.) Dissolving vial ultrasonic bath
5.) Syringe is filled with 1.8M stock solution of pinacol in dry triethylamine
6.) Syringe with pinacol stock is loaded into a Harvard syringe pump (flow rate 6 uL/min) and tubing with a T piece equipped with a blind pin and 250 uL coil reactor is attached

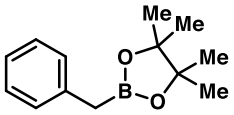


7.) Dissolved mixture from step 4 is loaded into a second Harvard syringe pump and set do a flow rate of 11 uL. It is pumped through the parallel plate reactor described in Figure S1. After applying current for 30 min steady state is reached and sample is taken from the reactor end.
8.) A defined amount of the taken sample (10 uL) is taken
9.) And injected into 1 ml of stock solution of dodecane in EtOAc.

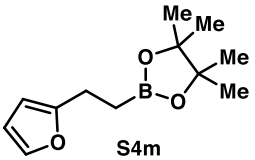
10.) Reactor outlet is connected to T piece to the position with the blind pin after reaching steady state
11.) Reaction mixture is collected in collection vial

4. Reaction Limitations

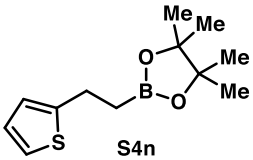
Several scope entries revealed issues in product purification and/or stability issues. Aside from benzylic compounds, for which the desired reactivity was not observed, heteroarenes such as furan, thiophene, and pyridine showed the product formation in the reaction crude. Nevertheless, the characterization of the final product for compounds **S4m-S4p** could not be executed due to instability either on deactivated silica or right after the purification.



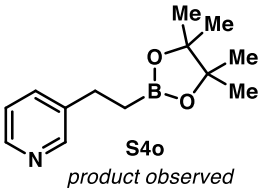
S4l
no product observed



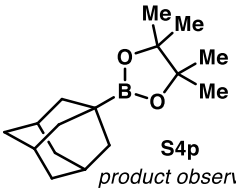
S4m
product observed in the crude - unstable



S4n
product observed in the crude - unstable



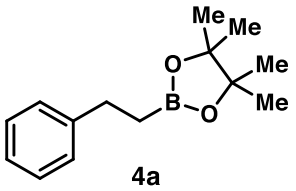
S4o
product observed in the crude - decomposed in purification



S4p
product observed in the crude - decomposed in purification

5. Characterization of Products

Compound 4a



4a

Following the General Procedure 2 with **RAE 1a** (354 mg, 1.2 mmol, 1.0 equiv.), 2,2′-Bi-1,3,2-benzodioxaborol (428 mg, 1.8 mmol, 1.5 equiv.) in DCM:DMF 1:1 (6.0 mL) for 1.0 F/mol and addition of 1.33 mL pinacol 1.8 M in triethylamine (4 equiv.), 3 mL reaction mixture where collected after reaching steady state and afforded 70 mg (50%) of the title compound as a colorless liquid after purification by column chromatography(Gradient elution from 8% EtOAc to 66% EtOAc in petrolether).

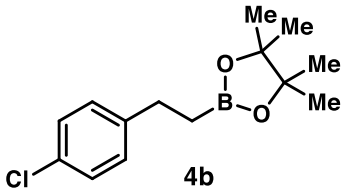
Physical Appearance: colorless liquid

TLC: PE:EtOAc 2:1, after staining with CAM: **R_F= 0.54**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.13 (m, 5H), 3.07 – 2.55 (t, 2H), 1.26 (s, 12H), 1.22 – 1.14 (t, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.5, 128.3, 128.1, 125.6, 83.2, 30.1, 24.9. The carbon attached to boron could not be observed due to quadrupolar relaxation.

Compound 4b



4b

Following the General Procedure 2 with **RAE 1b** (395 mg, 1.2 mmol, 1.0 equiv.), 2,2′-Bi-1,3,2-benzodioxaborol (428 mg, 1.8 mmol, 1.5 equiv.) in DCM:DMF 1:1 (6.0 mL) for 1.0 F/mol and addition of 1.33 mL pinacol 1.8 M in triethylamine (4 equiv.), 3 mL reaction mixture where collected after reaching steady state and afforded 39 mg (24%) of the title compound as a colorless liquid after purification by column chromatography(Gradient elution from 8% EtOAc to 66% EtOAc in petrolether).

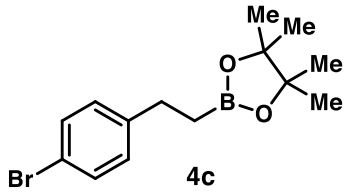
Physical Appearance: colorless liquid

TLC: PE:EtOAc 2:1, after staining with CAM: **R_F=0.62**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 2H), 7.17 – 7.09 (m, 2H), 2.78 – 2.65 (t, 2H), 1.21 (s, 12H), 1.11 (t, *J* = 8.7, 7.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 131.3, 129.5, 128.4, 83.3, 29.5, 24.9. The carbon attached to boron could not be observed due to quadrupolar relaxation.

Compound 4c



4c

Following the General Procedure 2 with **RAE 1c** (449 mg, 1.2 mmol, 1.0 equiv.), 2,2′-Bi-1,3,2-benzodioxaborol (428 mg, 1.8 mmol, 1.5 equiv.) in DCM:DMF 1:1 (6.0 mL) for 1.0 F/mol and addition of 1.33 mL pinacol 1.8 M in triethylamine (4 equiv.), 3 mL reaction mixture where collected after reaching steady state and afforded 97 mg (52%) of the title compound as a colorless liquid after purification by column chromatography(Gradient elution from 8% EtOAc to 66% EtOAc in petrolether).

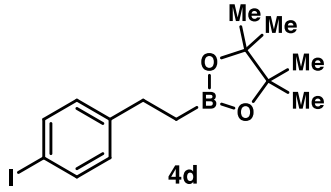
Physical Appearance: colorless liquid

TLC: PE:EtOAc 2:1, after staining with CAM: **R_F=0.5**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 2H), 7.15 – 7.03 (m, 2H), 2.78 – 2.61 (t, 2H), 1.21 (s, 12H), 1.11 (t, *J* = 8.7, 7.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.35, 131.19, 129.83, 119.19, 83.19, 29.40, 24.82. The carbon attached to boron could not be observed due to quadrupolar relaxation.

Compound 4d



4d

Following the General Procedure 2 with **RAE 1d** (504 mg, 1.2 mmol, 1.0 equiv.), 2,2′-Bi-1,3,2-benzodioxaborol (428 mg, 1.8 mmol, 1.5 equiv.) in DCM:DMF 1:1 (6.0 mL) for 1.0 F/mol and addition of 1.33 mL pinacol 1.8 M in triethylamine (4 equiv.), 3 mL reaction mixture where collected after reaching steady state and afforded 46 mg (21%) of the title compound as a colorless liquid after purification by column chromatography(Gradient elution from 8% EtOAc to 66% EtOAc in petrolether).

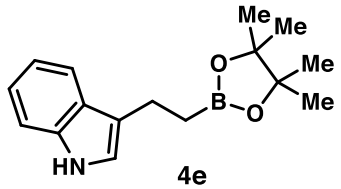
Physical Appearance: colorless liquid

TLC: PE:EtOAc 2:1, after staining with CAM: **R_F=0.54**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 2H), 7.17 – 7.10 (m, 2H), 2.84 – 2.58 (t, 2H), 1.21 (s, 12H), 1.11 (t, *J* = 8.7, 7.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 131.3, 129.5, 128.4, 83.3, 29.5, 24.9. The carbon attached to boron could not be observed due to quadrupolar relaxation.

Compound 4e



4e

Following the General Procedure 2 with **RAE 1e** (504 mg, 1.2 mmol, 1.0 equiv.), 2,2′-Bi-1,3,2-benzodioxaborol (428 mg, 1.8 mmol, 1.5 equiv.) in DCM:DMF 1:1 (6.0 mL) for 1.0 F/mol and addition of 1.33 mL pinacol 1.8 M in triethylamine (4 equiv.), 3 mL reaction mixture where collected after reaching steady state and afforded 46 mg (21%) of the title compound as a colorless liquid after purification by column chromatography(Gradient elution from 8% EtOAc to 66% EtOAc in petrolether).

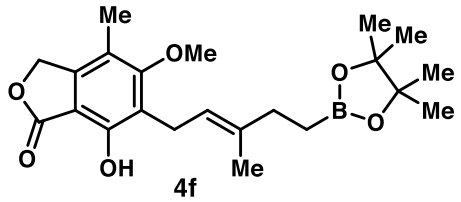
Physical Appearance: colorless liquid

TLC: PE:EtOAc 2:1, after staining with CAM: **R_F=0.51**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.72 – 7.57 (m, 1H), 7.38 – 7.30 (m, 1H), 7.14 (dddd, *J* = 22.8, 8.1, 7.0, 1.2 Hz, 2H), 7.02 – 6.92 (m, 1H), 2.96 – 2.82 (m, 2H), 1.29 (d, *J* = 8.2 Hz, 2H), 1.24 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 136.5, 127.6, 121.9, 120.8, 119.3, 119.2, 119.1, 111.0, 83.2, 24.9, 19.5. The carbon attached to boron could not be observed due to quadrupolar relaxation.

Compound 4f



4f

Following the General Procedure 2 with **RAE 1f** (384 mg, 1.2 mmol, 1.0 equiv.), 2,2′-Bi-1,3,2-benzodioxaborol (428 mg, 1.8 mmol, 1.5 equiv.) in DCM:DMF 1:1 (6.0 mL) for 1.0 F/mol and addition of 1.33 mL pinacol 1.8 M in triethylamine (4 equiv.), 3 mL reaction mixture where collected after reaching steady state and afforded 38 mg (16%) of the title compound as a colorless liquid after purification by column chromatography(Gradient elution from 8% EtOAc to 66% EtOAc in petrolether).

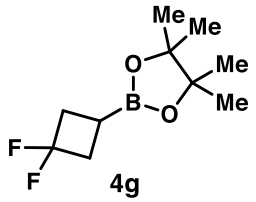
Physical Appearance: colorless liquid

TLC: PE:EtOAc 3:1, after staining with CAM: **R_F=0.5**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (s, 1H), 5.19 (s, 3H), 3.75 (s, 3H), 3.38 (d, *J* = 6.9 Hz, 2H), 2.14k (s, 3H), 2.09 (t, *J* = 8.0 Hz, 2H), 1.78 (d, *J* = 1.3 Hz, 3H), 1.18 (s, 12H), 0.87 (t, 2H).

^{13}C NMR (75 MHz, $CDCl_3$). δ 173.1, 163.9, 153.9, 143.9, 137.9, 122.8, 120.6, 116.8, 106.4, 83.1, 70.2, 61.1, 33.6, 24.9, 22.7, 16.3, 11.7. The carbon attached to boron could not be observed due to quadrupolar relaxation.

Compound 4g



4g

Following the General Procedure 2 with **RAE 1g** (337 mg, 1.2 mmol, 1.0 equiv.), 2,2′-Bi-1,3,2-benzodioxaborol (428 mg, 1.8 mmol, 1.5 equiv.) in DCM:DMF 1:1 (6.0 mL) for 1.0 F/mol and addition of 1.33 mL pinacol 1.8 M in triethylamine (4 equiv.), 3 mL reaction mixture where collected after reaching steady state and afforded 64 mg (49%) of the title compound as a colorless liquid after purification by column chromatography(Gradient elution from 8% EtOAc to 66% EtOAc in petrolether). NMR data for this compound had to be recorded immediately after synthesis and purification since the neat compound is sensitive to air and/or moisture.

Physical Appearance: colorless liquid that turns black after prolonged exposure to air and/or moisture.

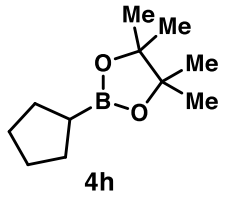
TLC: PE:EtOAc 2:1, after staining with CAM: **R_F=0.55**

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.69 – 2.44 (m, 4H), 1.65 – 1.52 (m, 1H), 1.25 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 83.8, 36.8 (t, *J* = 22.8 Hz), 24.70. The carbon attached to boron could not be observed due to quadrupolar relaxation.

^{19}F NMR (282 MHz, $CDCl_3$) δ -83.30 (dtt, *J* = 187.3, 11.8, 8.3 Hz), -94.78 (dp, *J* = 187.3, 15.5 Hz).

Compound 4h



4h

Following the General Procedure 2 with **RAE 1h** (311 mg, 1.2 mmol, 1.0 equiv.), 2,2′-Bi-1,3,2-benzodioxaborol (428 mg, 1.8 mmol, 1.5 equiv.) in DCM:DMF 1:1 (6.0 mL) for 1.0 F/mol and addition of 1.33 mL pinacol 1.8 M in triethylamine (4 equiv.), 3 mL reaction mixture where collected after reaching steady state and afforded 46 mg (39%) of the title compound as a colorless liquid after purification by column chromatography(Gradient elution from 8% EtOAc to 66% EtOAc in petrolether).

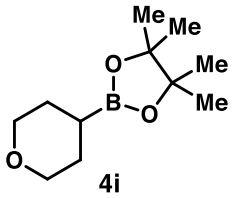
Physical Appearance: colorless liquid

TLC: PE:EtOAc 2:1, after staining with CAM: **R_F=0.6**

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.80 – 1.57 (m, 2H), 1.55 – 1.46 (m, 6H), 1.26 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 82.9, 28.7, 27.0, 24.9. The carbon attached to boron could not be observed due to quadrupolar relaxation.

Compound 4i



4i

Following the General Procedure 2 with **RAE 1i** (330 mg, 1.2 mmol, 1.0 equiv.), 2,2′-Bi-1,3,2-benzodioxaborol (428 mg, 1.8 mmol, 1.5 equiv.) in DCM:DMF 1:1 (6.0 mL) for 1.0 F/mol and addition of 1.33 mL pinacol 1.8 M in triethylamine (4 equiv.), 3 mL reaction mixture where collected after reaching steady state and afforded 50 mg (39%) of the title compound as a colorless liquid after purification by column chromatography(Gradient elution from 8% EtOAc to 66% EtOAc in petrolether).

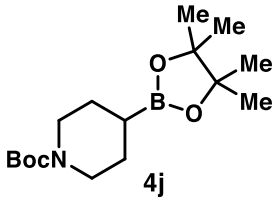
Physical Appearance: colorless liquid

TLC: PE:EtOAc 2:1, after staining with CAM: **R_F=0.56**

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.82 (dt, *J* = 11.2, 3.9 Hz, 2H), 3.55 – 3.35 (m, 2H), 1.68 – 1.56 (m, 4H), 1.24 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 83.3, 69.0, 27.8, 24.9. The carbon attached to boron could not be observed due to quadrupolar relaxation.

Compound 4j



4j

Following the General Procedure 2 with **RAE 1j** (449 mg, 1.2 mmol, 1.0 equiv.), 2,2′-Bi-1,3,2-benzodioxaborol (428 mg, 1.8 mmol, 1.5 equiv.) in DCM:DMF 1:1 (6.0 mL) for 1.0 F/mol and addition of 1.33 mL pinacol 1.8 M in triethylamine (4 equiv.), 3 mL reaction mixture where collected after reaching steady state and afforded 94 mg (50%) of the title compound as a colorless liquid after purification by column chromatography(Gradient elution from 8% EtOAc to 66% EtOAc in petrolether).

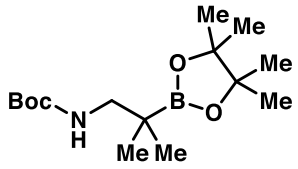
Physical Appearance: colorless liquid

TLC: PE:EtOAc 2:1, after staining with CAM: **R_F=0.44**

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (d, *J* = 12.9 Hz, 2H), 2.91 (ddd, *J* = 13.3, 10.1, 3.2 Hz, 2H), 1.62 (dt, *J* = 8.0, 5.1 Hz, 1H), 1.62 (dt, *J* = 10.1, 4.2 Hz, 2H), 1.43 (s, 9H), 1.22 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0, 83.3, 79.2, 28.6, 27.1, 24.9. The carbon attached to boron could not be observed due to quadrupolar relaxation.

Compound 4k



4k

Following the General Procedure 2 with **RAE 1k** (434 mg, 1.2 mmol, 1.0 equiv.), 2,2′-Bi-1,3,2-benzodioxaborol (428 mg, 1.8 mmol, 1.5 equiv.) in DCM:DMF 1:1 (6.0 mL) for 1.0 F/mol and addition of 1.33 mL pinacol 1.8 M in triethylamine (4 equiv.), 3 mL reaction mixture where collected after reaching steady state and afforded 38 mg (clean) + 48 mg (mixture with pinacol) (48% total yield) of the title compound as a colorless liquid after purification by column chromatography with silica that was deactivated with 20 w% H_2O prior to elution (Gradient elution from 8% EtOAc to 66% EtOAc in petrolether).

Physical Appearance: colorless liquid

TLC: PE:EtOAc 2:1, after staining with CAM: **R_F= 0.65**

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.90 – 4.74 (m, 1H), 3.65 (d, *J* = 6.3 Hz, 1H), 2.99 (d, *J* = 6.2 Hz, 2H), 1.42 (t, *J* = 4.2 Hz, 9H), 1.21 (s, 12H), 0.91 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 83.4, 78.7, 49.6, 28.44, 28.6, 28.5, 27.0, 24.8, 22.5. The carbon attached to boron could not be observed due to quadrupolar relaxation.

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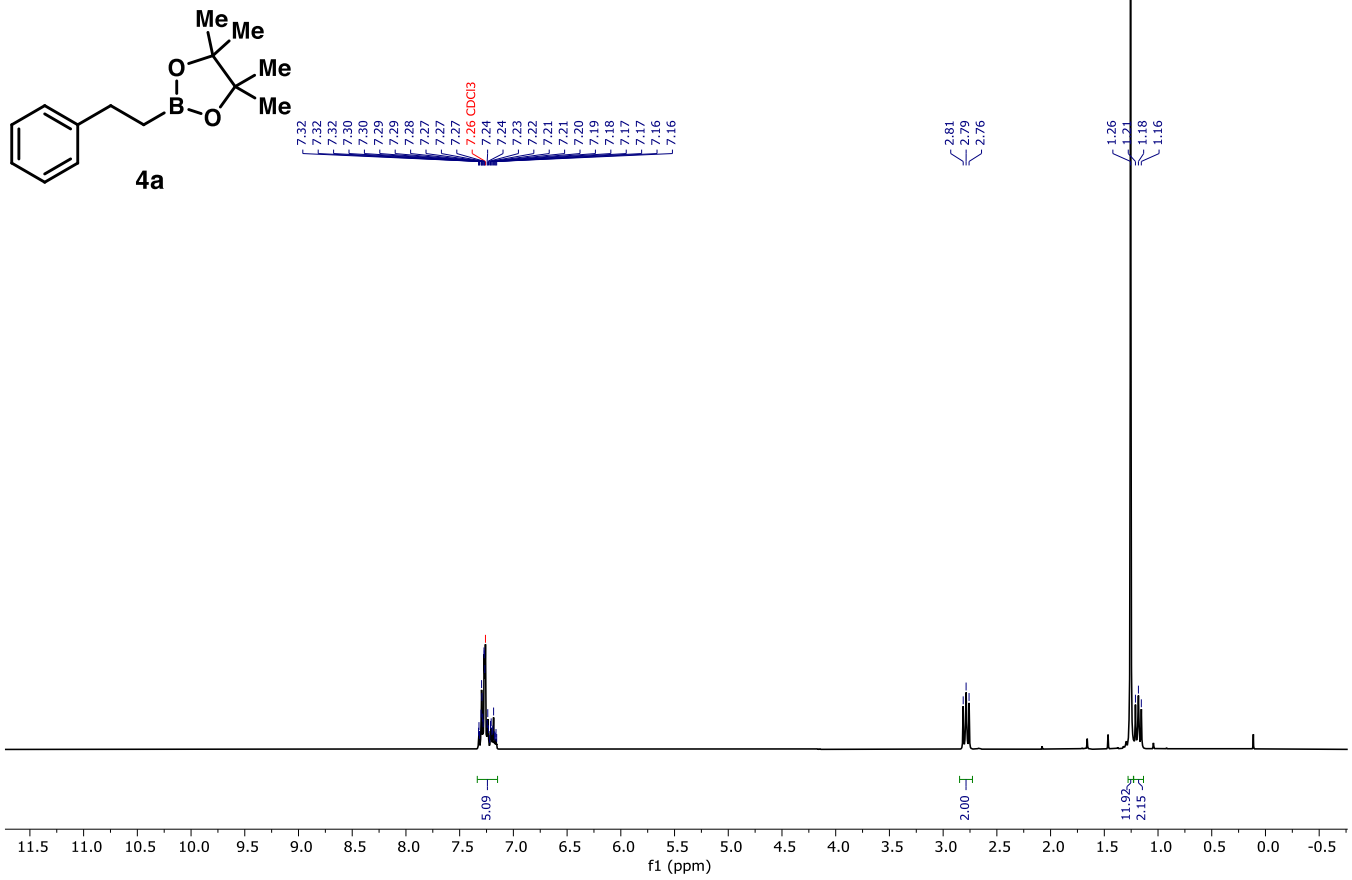
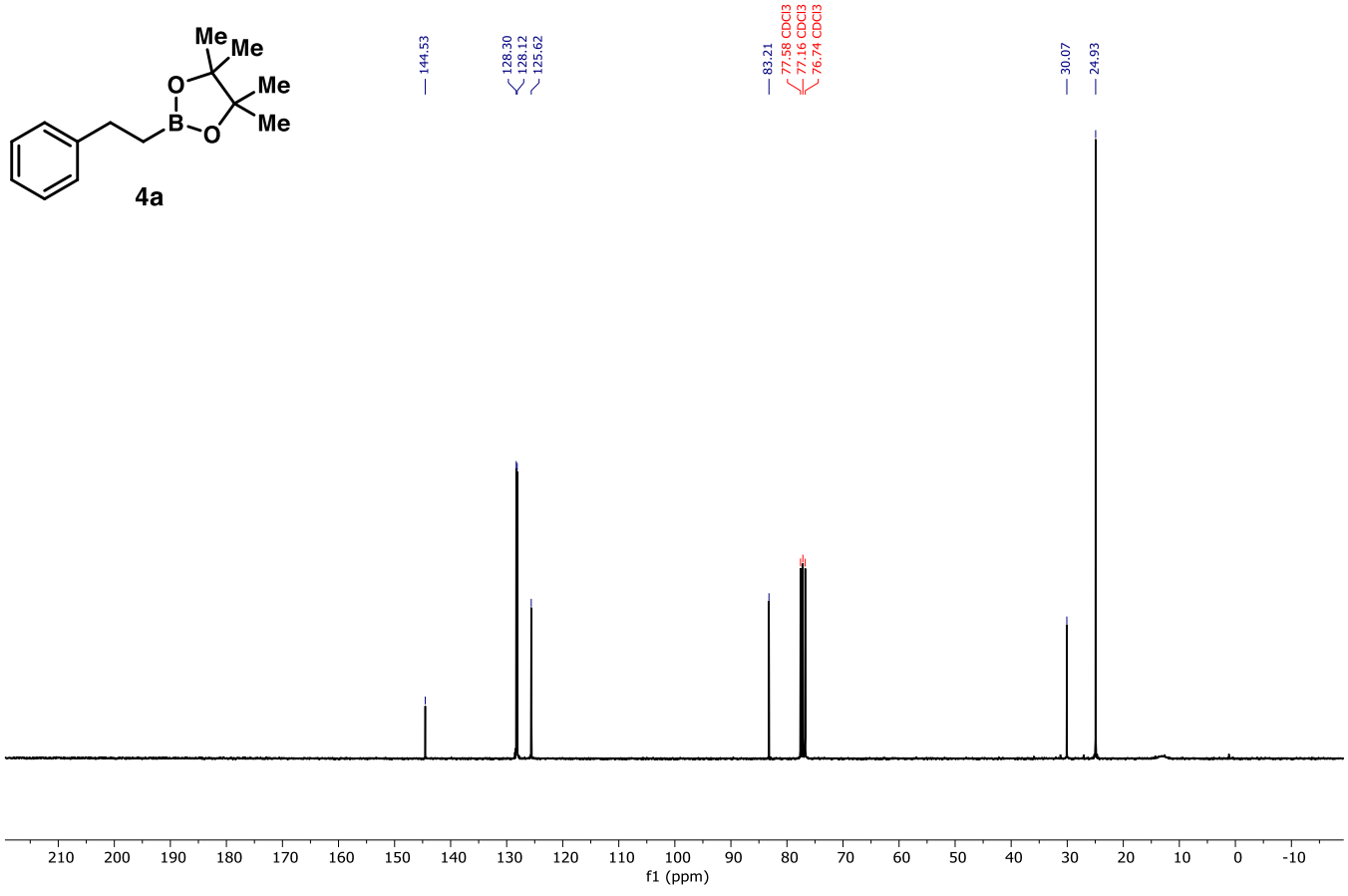
7. NMR Spectra

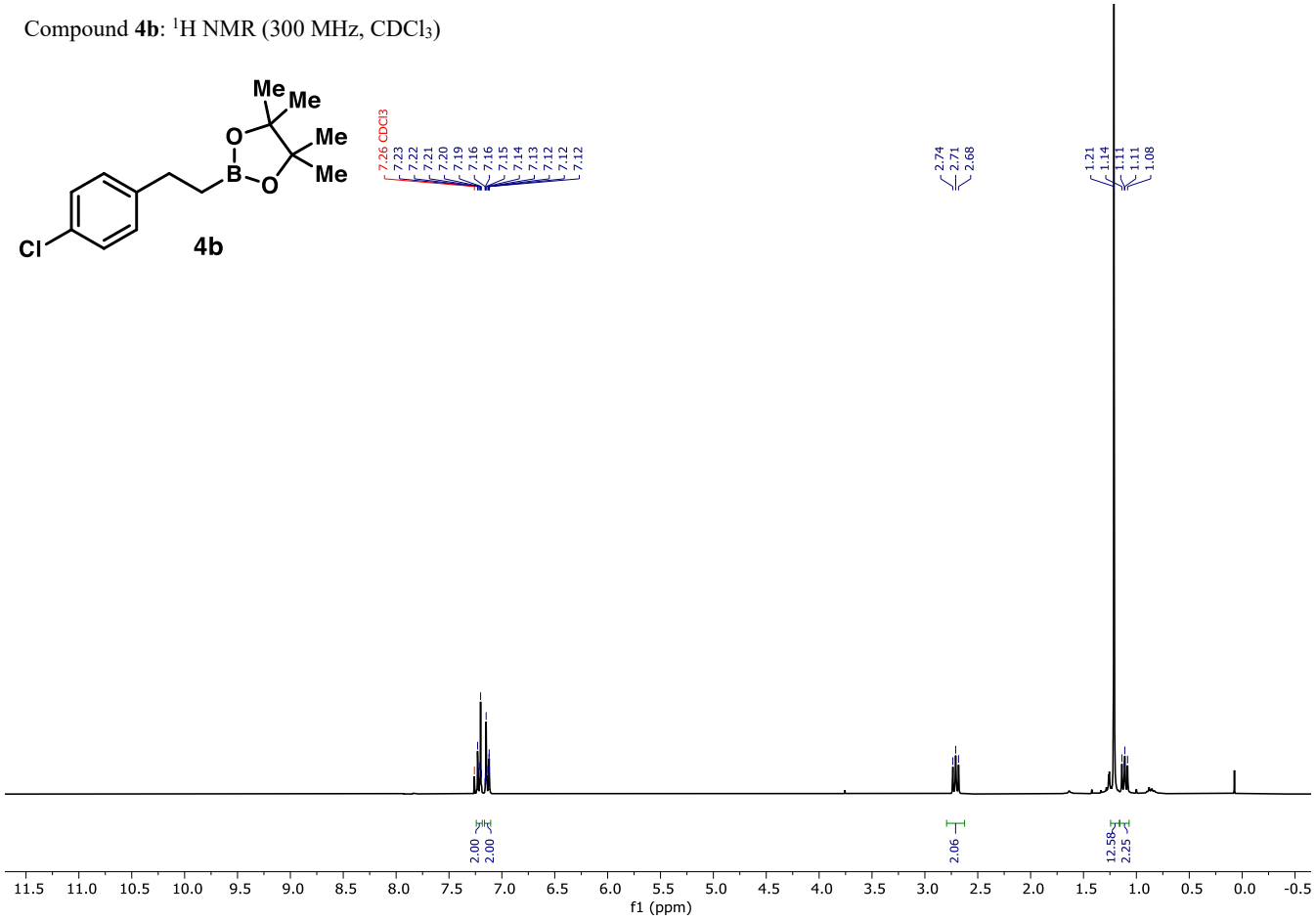
Compound **4a**: ^{1}H NMR (300 MHz, $CDCl_3$)



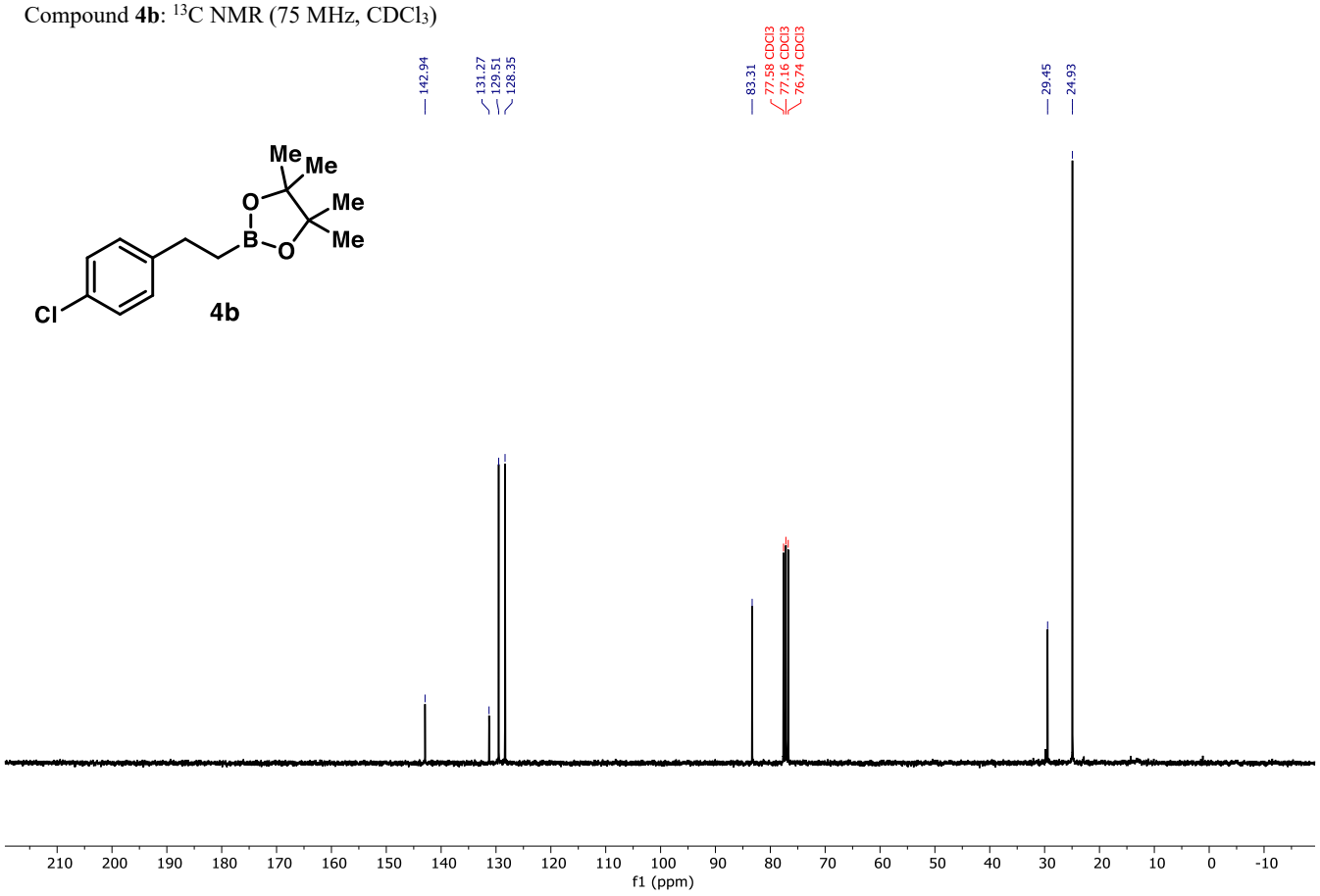
Compound **4a**: ^{13}C NMR (75 MHz, $CDCl_3$)



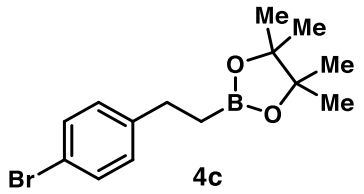
Compound **4b**: ^{1}H NMR (300 MHz, $CDCl_3$)



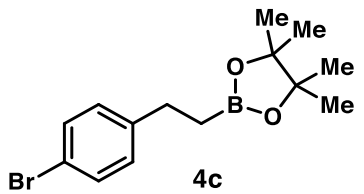
Compound **4b**: ^{13}C NMR (75 MHz, $CDCl_3$)



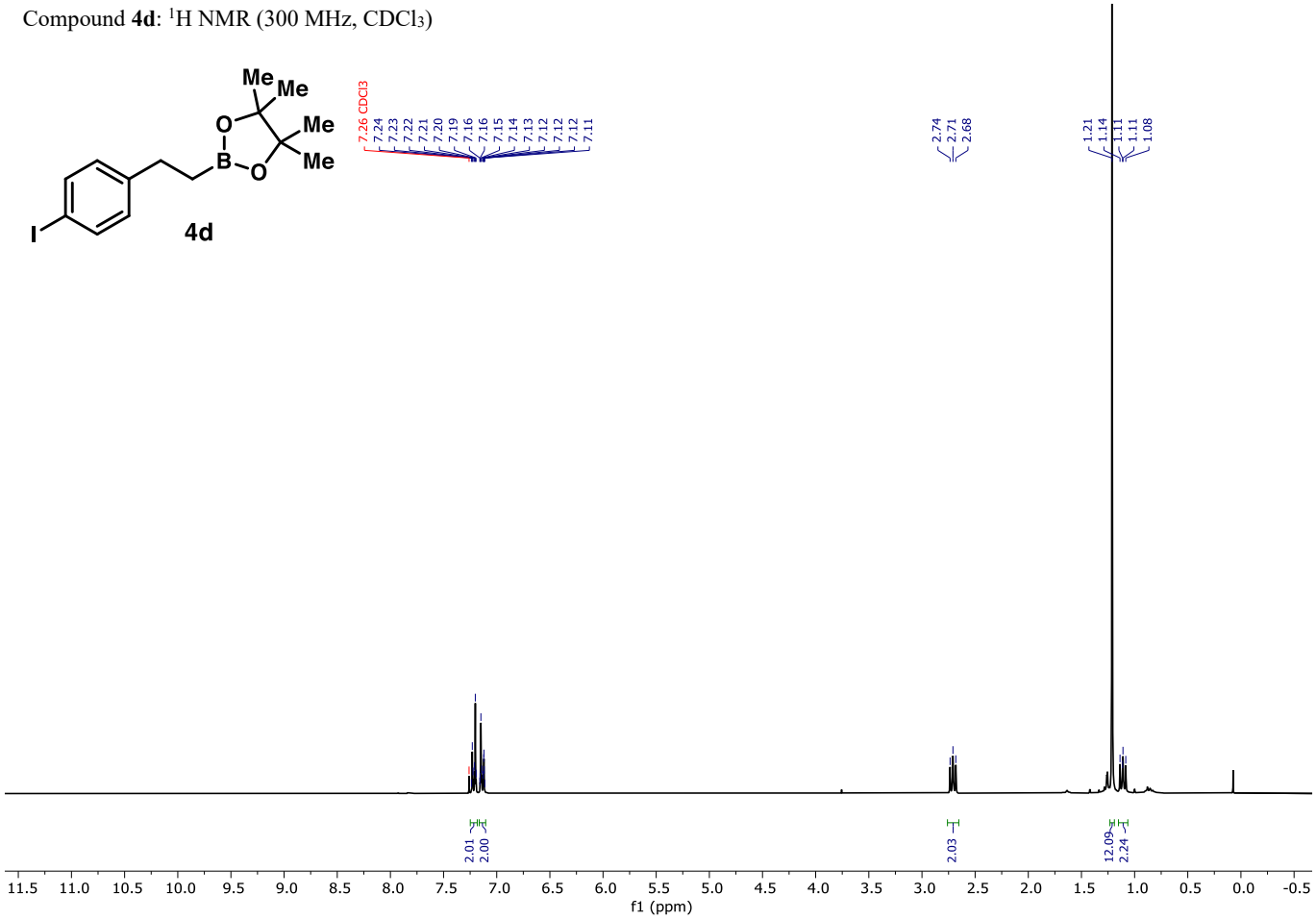
Compound **4c**: ^{1}H NMR (300 MHz, $CDCl_3$)



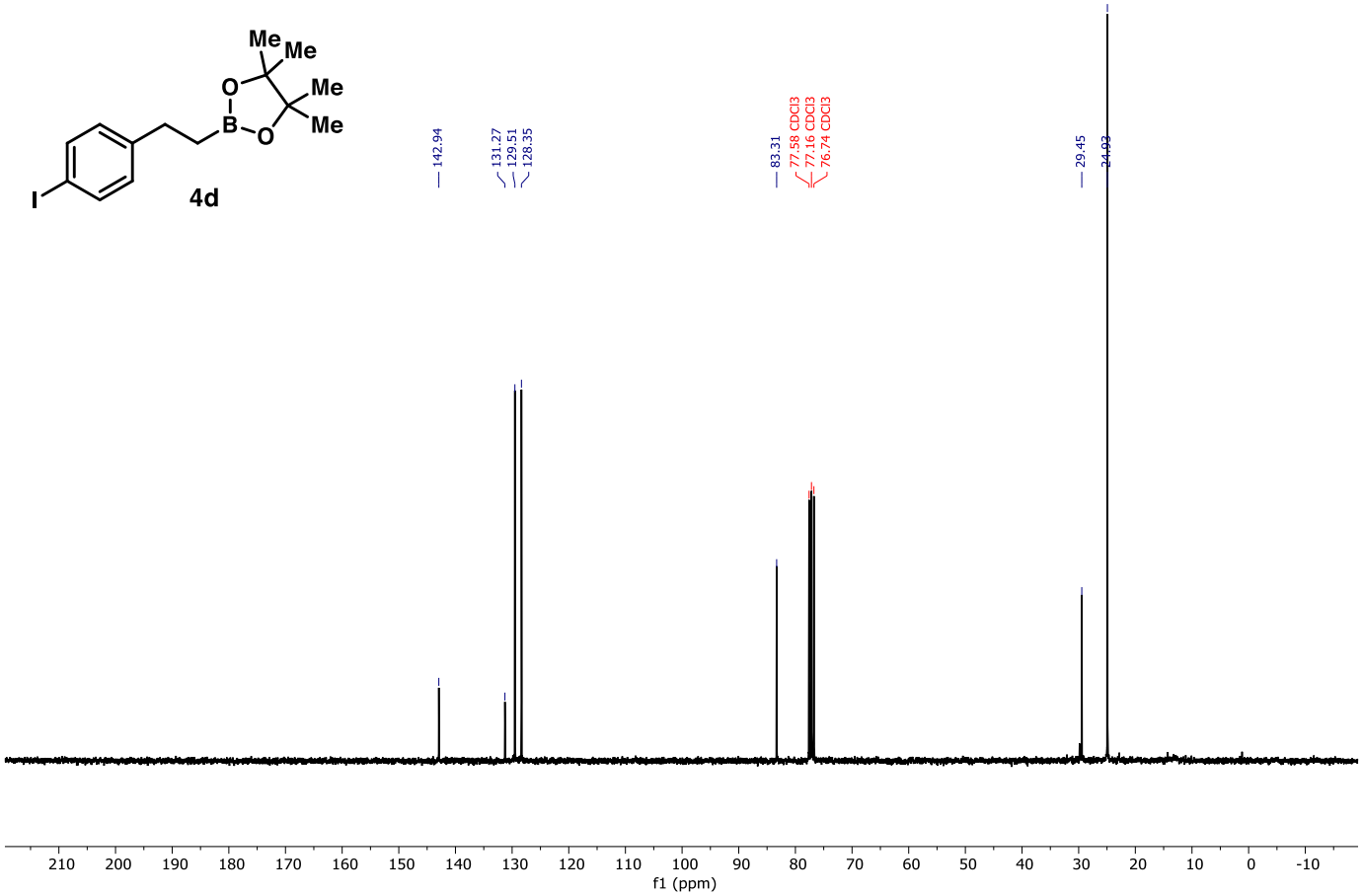
Compound **4c**: ^{13}C NMR (75 MHz, $CDCl_3$)



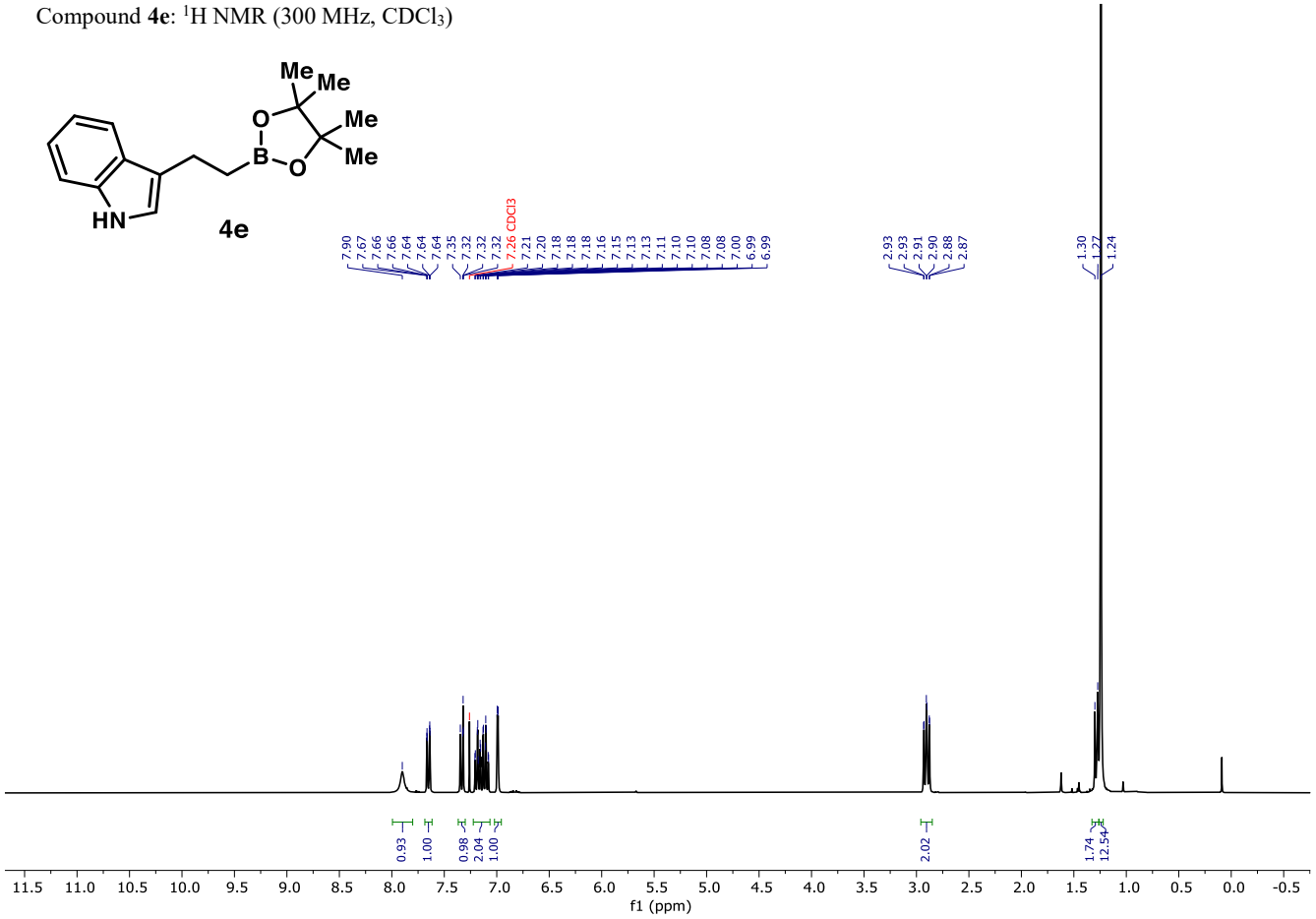
Compound **4d**: ^{1}H NMR (300 MHz, $CDCl_3$)



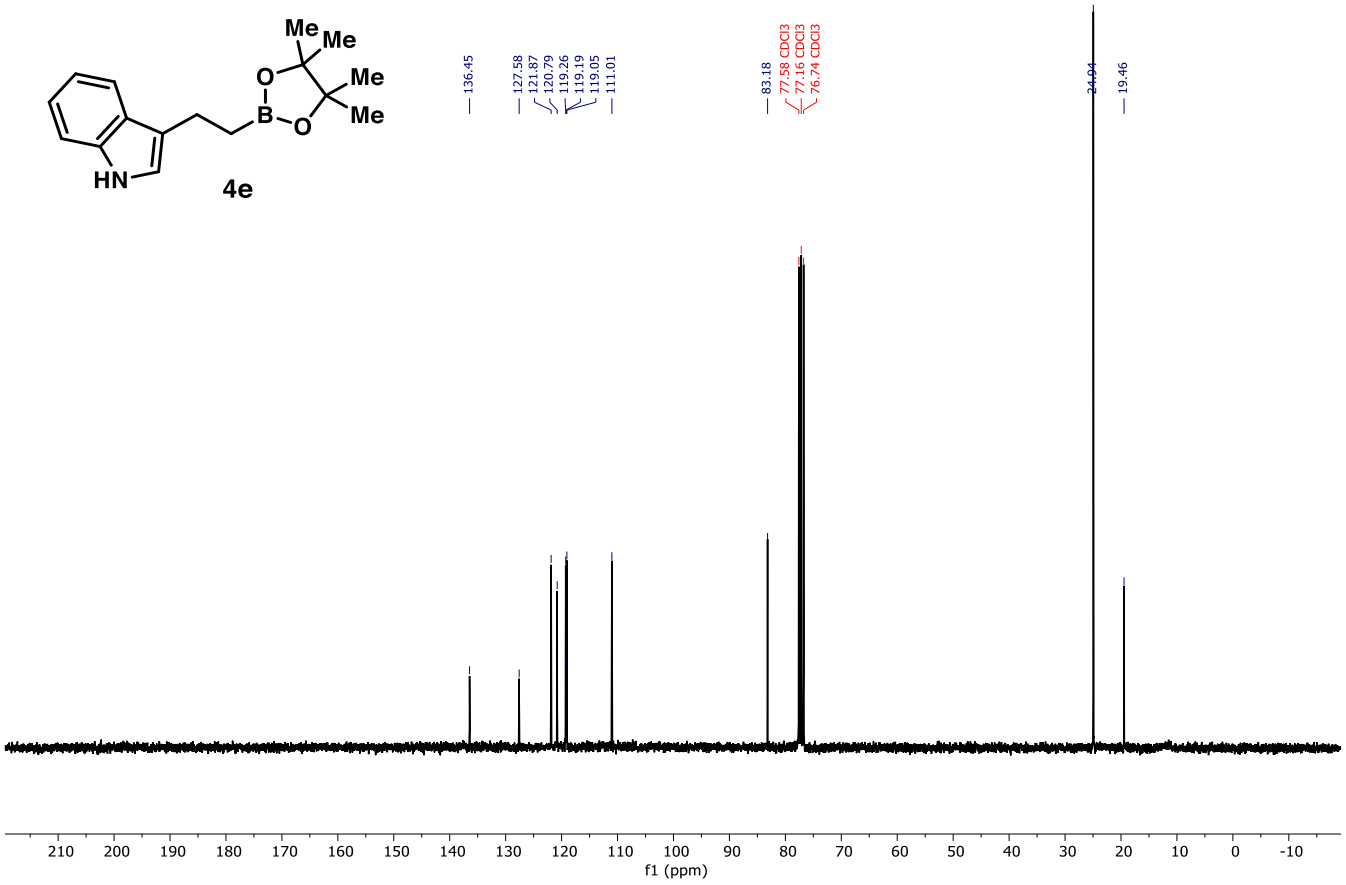
Compound **4d**: ^{13}C NMR (75 MHz, $CDCl_3$)



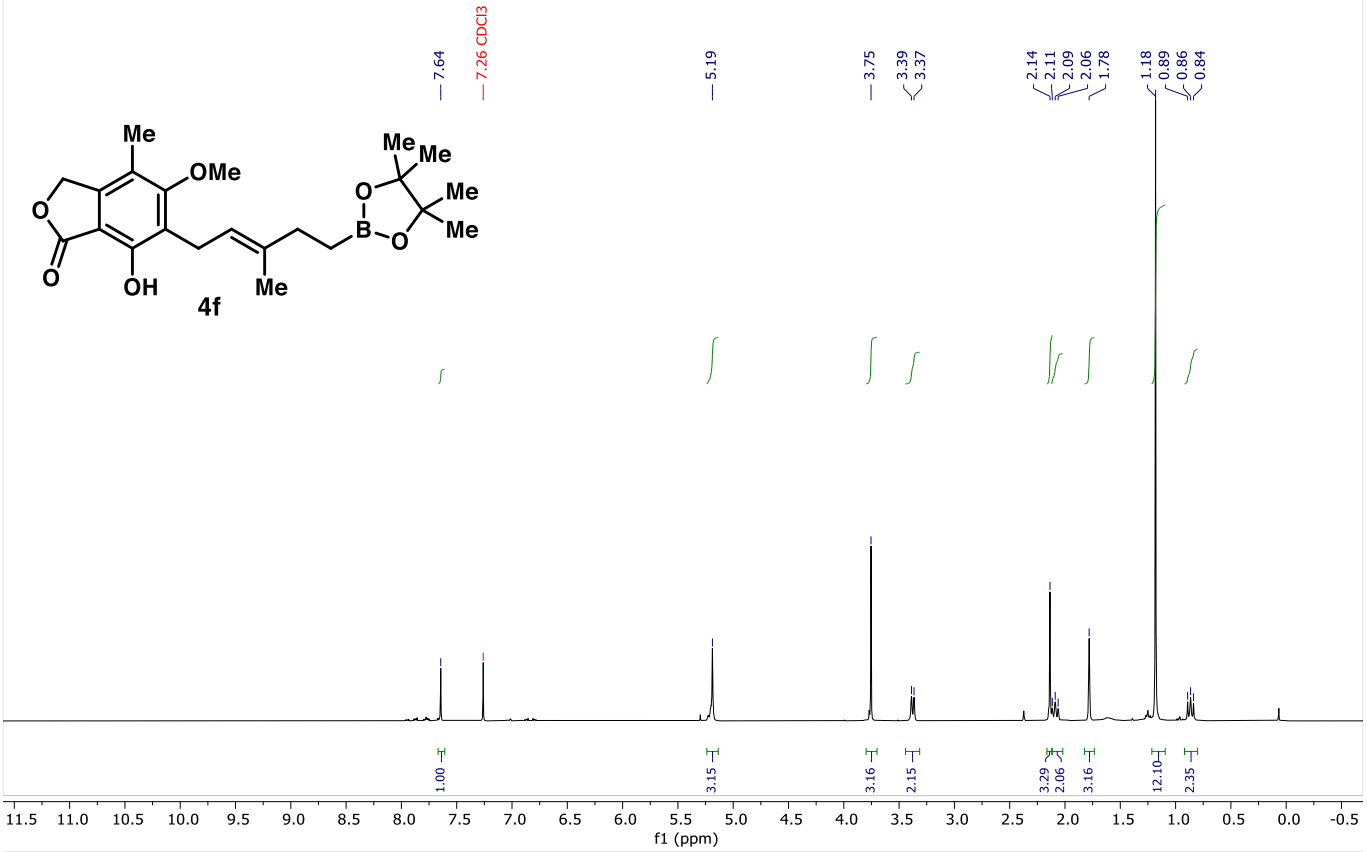
Compound **4e**: ^{1}H NMR (300 MHz, $CDCl_3$)



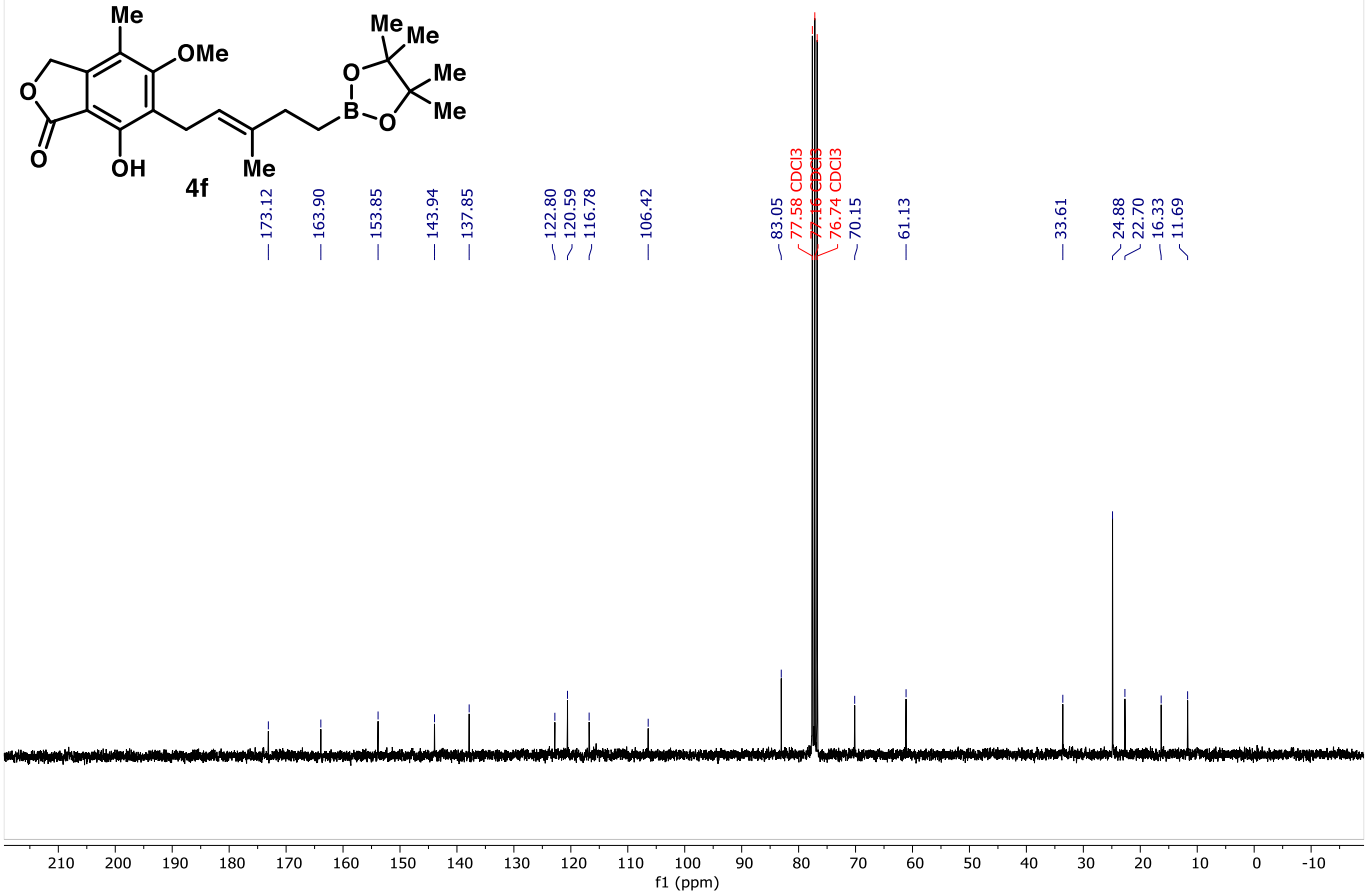
Compound **4e**: ^{13}C NMR (75 MHz, $CDCl_3$)



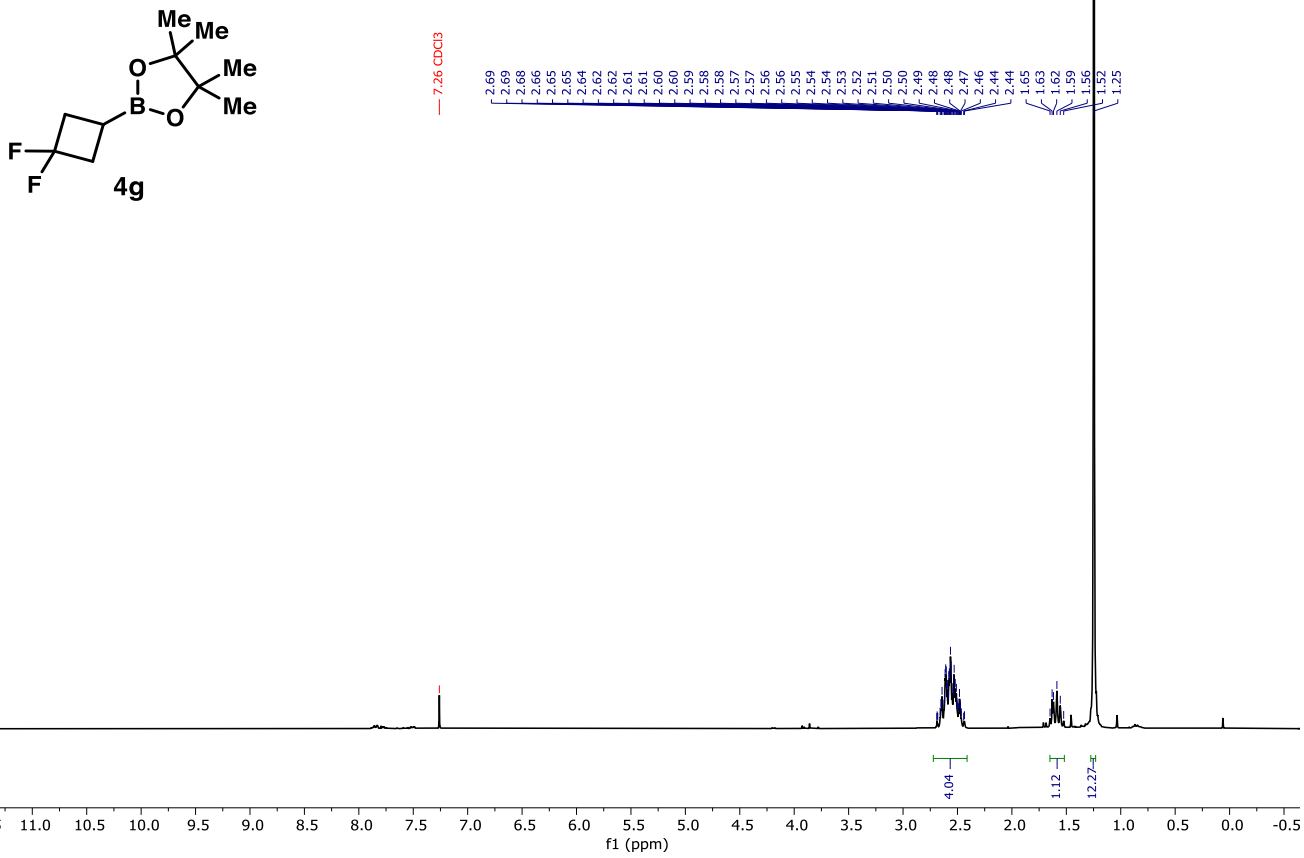
Compound **4f**: ^{1}H NMR (300 MHz, $CDCl_3$)



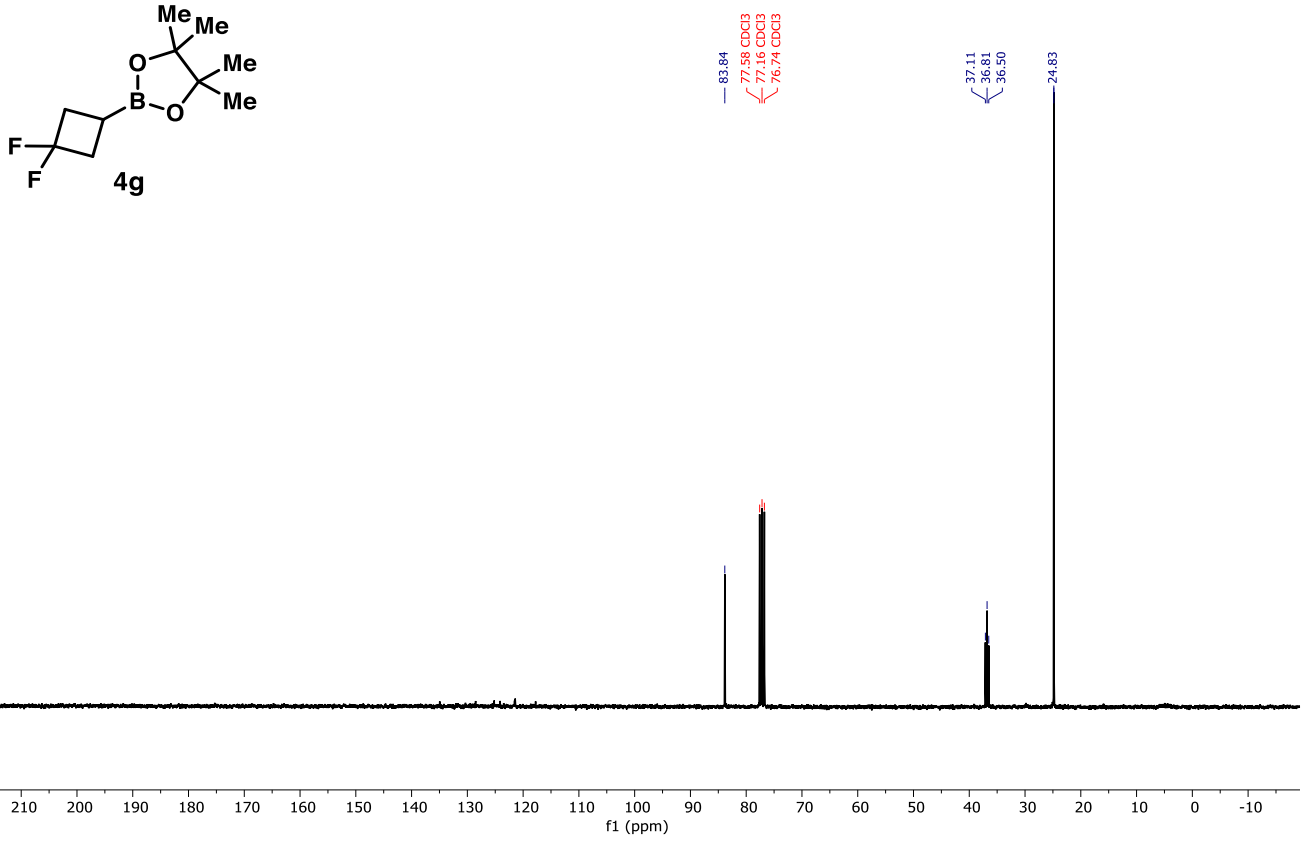
Compound **4f**: ^{13}C NMR (75 MHz, $CDCl_3$)



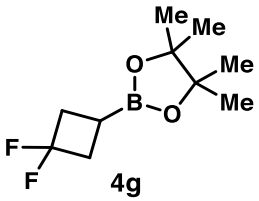
Compound **4g**: ^{1}H NMR (300 MHz, $CDCl_3$)



Compound **4g**: ^{13}C NMR (75 MHz, $CDCl_3$)

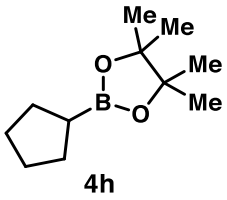


Compound **4g**: ^{19}F NMR (282 MHz, $CDCl_3$)



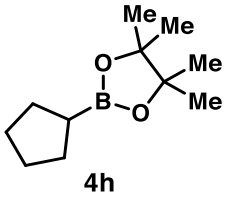
4g

Compound **4h**: ^{1}H NMR (300 MHz, $CDCl_3$)



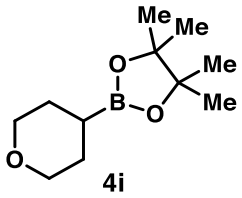
4h

Compound **4h**: ^{13}C NMR (101 MHz, $CDCl_3$)



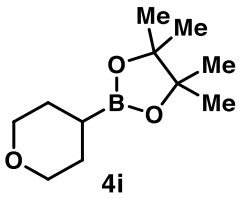
4h

Compound **4i**: ^{1}H NMR (300 MHz, $CDCl_3$)



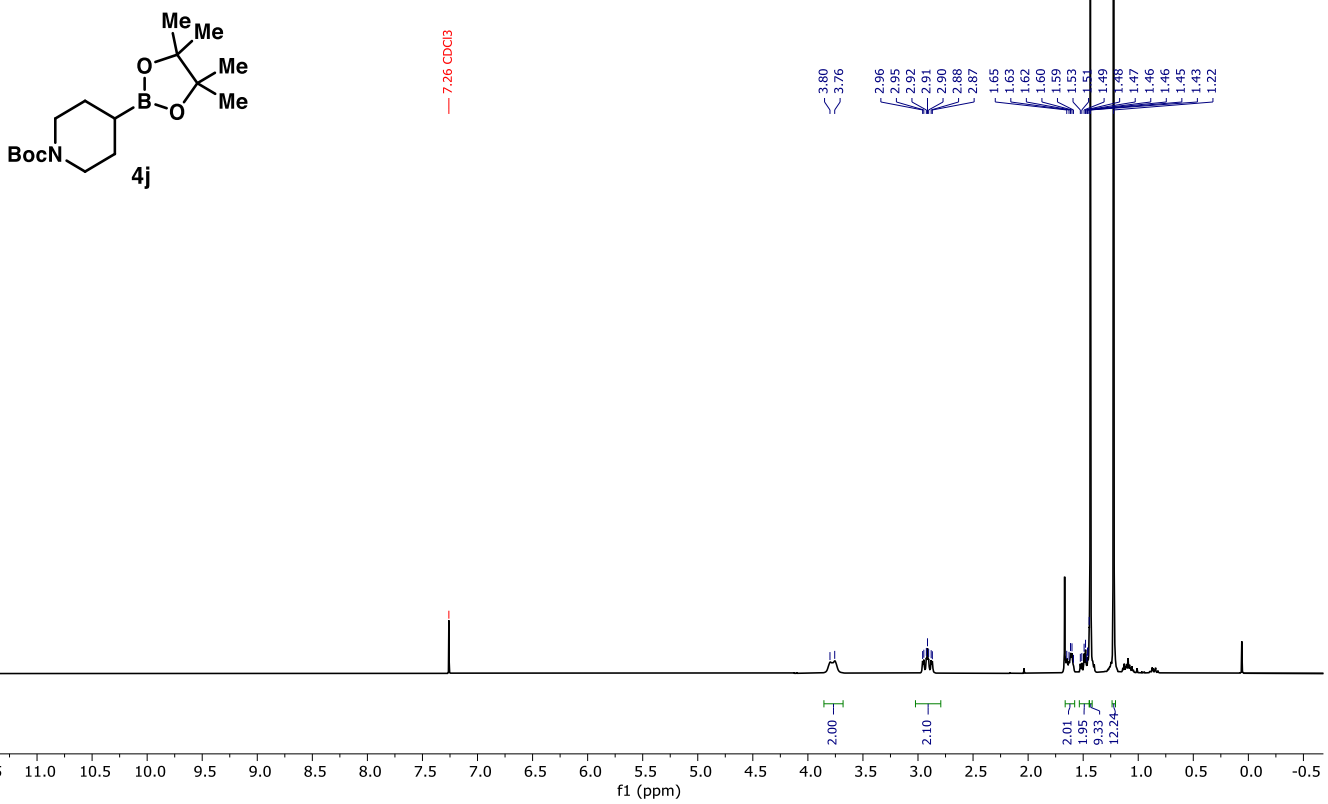
4i

Compound **4i**: ^{13}C NMR (75 MHz, $CDCl_3$)

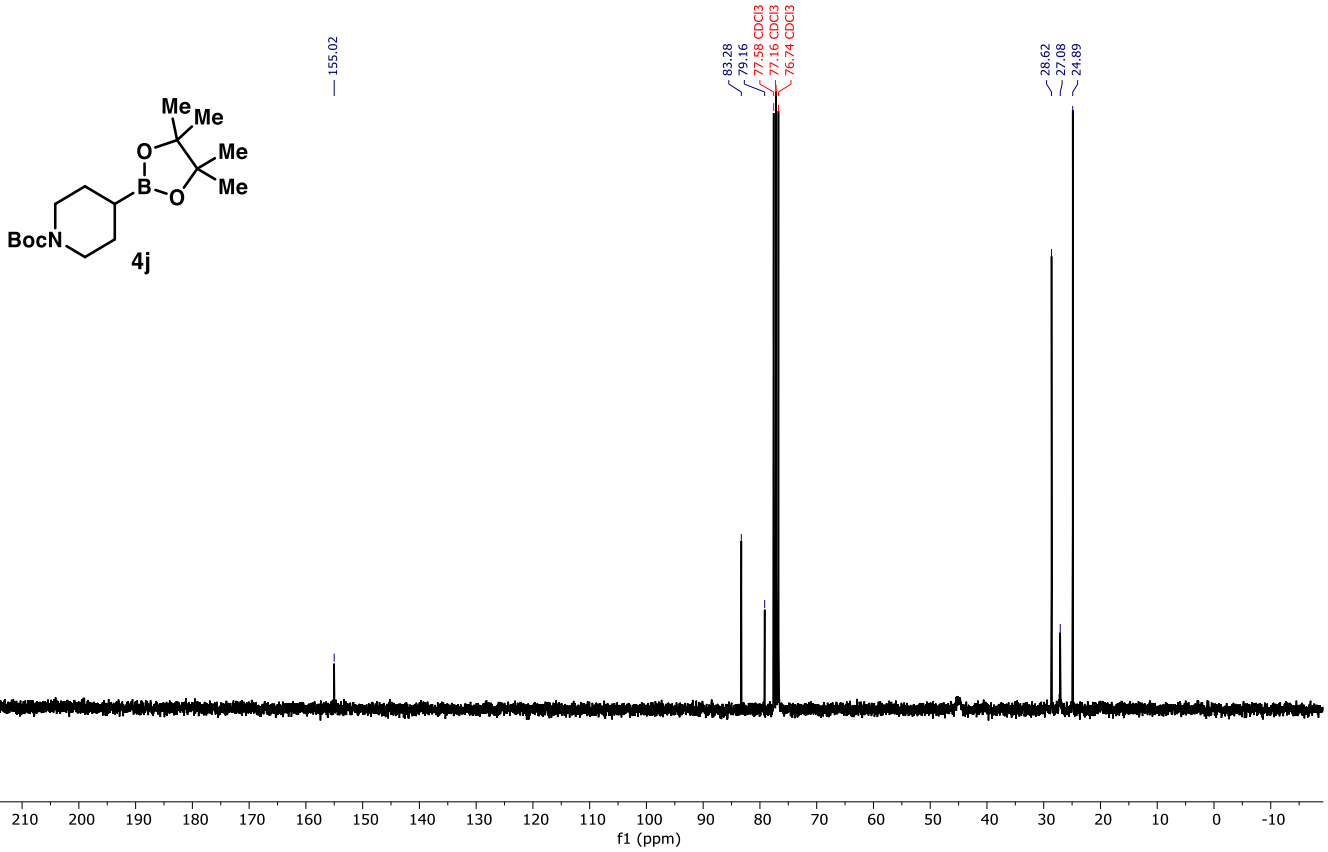


4i

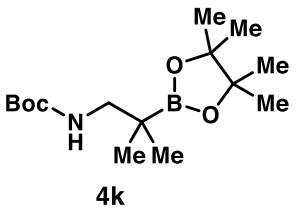
Compound **4j**: ^{1}H NMR (300 MHz, $CDCl_3$)



Compound **4j**: ^{13}C NMR (75 MHz, $CDCl_3$)

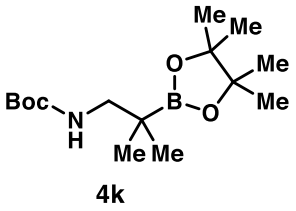


Compound **4k**: ^{1}H NMR (300 MHz, $CDCl_3$)



4k

Compound **4k**: ^{13}C NMR (75 MHz, $CDCl_3$)



4k