

Electronic supplementary information for the article

Synthesis of chiral boranes via asymmetric insertion of carbenes into B-H bonds catalyzed by the rhodium(I) diene complex

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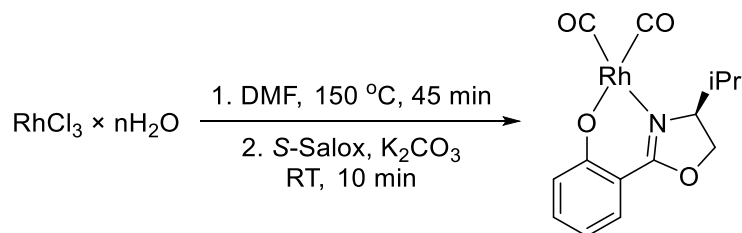
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General information

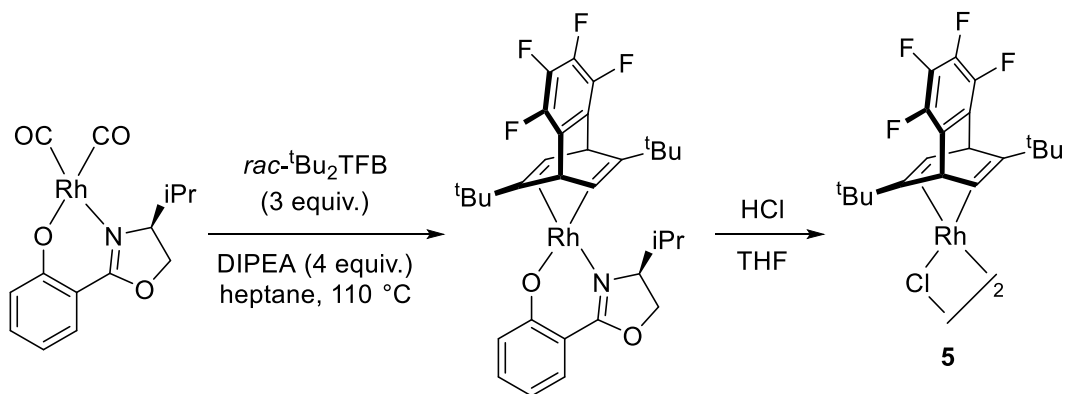
All reactions were carried out under argon, while isolation of products was conducted in air. The solvents used for the reactions were purified using MBraun Solvent Purification System and were stored under argon. Other solvents were purchased from the local suppliers and used as received. All reagents were obtained from commercial sources (Aldrich, TCI, Macklin) and used without further purification. Starting 1,3-dimethyl-imidazolyl-2-ylidene borane¹ and 1,3-isopropyl-imidazolyl-2-ylidene borane² were synthesized from NaBH₄ and imidazolium halides according to the literatures protocols. Starting aryl diazoesters were synthesized either by the diazo-transfer reaction³ or by the Pd-catalyzed coupling⁴ of methyl diazoacetate with aryl halides following the literature protocols. Starting compound **2a** was synthesized from 1,3-dimethyl-imidazolyl-2-ylidene borane and ethyldiazoacetate according to literature protocol.⁵ Macherey-Nagel silica gel 60 (230–400 mesh) was used for column chromatography. For thin layer chromatography (TLC) analysis either Macherey-Nagel POLYGRAM SIL G/UV₂₅₄ pre-coated polyester TLC plates (0.2 mm) or Sorbfil TLC-A-UV plates (0.09-0.12 mm) were used. NMR spectra were measured using Bruker Avance 300, Bruker Avance 400, or Varian Inova 400 spectrometer. Chemical shifts (δ) are given in ppm relative to TMS (¹H and ¹³C), BF₃·Et₂O (¹¹B) or CCl₃ (¹⁹F), coupling constants (*J*) are given in Hz. High-resolution mass spectra were recorded on SCIEX TripleTOF 5600+ instrument using electrospray ionization (ESI). Interface capillary voltage was set to 5500 V in a positive ion mode and to 4500 V in a negative mode with mass range from *m/z* 100 to 3000 Da; external or internal calibration was done with the Electrospray Calibrant Solution (Fluka). Enantiomeric excess values of the insertion products were measured using Shimadzu HPLC equipped with Daicel Chiralpak IB-3 and IH-3 columns (4.6 × 150 mm) and diode array detector; flow rate 1 mL/min was adjusted in all experiments, except for minor diastereomer in experiment **4o**, where flow rate was 0.5 mL/min.

Synthesis of the catalyst 5



The synthesis of (S-Salox)Rh(CO)₂ was carried out following the literature procedure.⁶ A Schlenk tube (15 ml) was charged with RhCl₃ × nH₂O (36% Rh content, 143 mg, 0.52 mmol), evacuated and backfilled with argon 3 times and then dry DMF (3 ml) was added. The tube was immersed in a pre-heated oil bath (155 °C) and stirred for 45 minutes. The solution quickly turned from dark red to yellow, indicating the formation of [(CO)₂RhCl]_x species. The resulting mixture was cooled to ambient temperature, S-Salox⁷ (102 mg, 0.5 mmol) and K₂CO₃ (207 mg, 1.5 mmol) were added maintaining the argon stream. The solution was stirred for 15 minutes and water (7 ml) was added, which results in formation of yellow solid product and dark brown-green solution (the color possibly originates from oxidation of the residual Salox anion). The mixture was opened to air and extracted with Et₂O (4 ml × 4). Once the organic washings became nearly colorless, they were combined and dried over Na₂SO₄. After drying, the solution was filtered to remove both sodium sulfate and any solid impurities. The solvent was evaporated on rotary evaporator and the resulting orange oil was dried at 60 °C to remove residual DMF. The crude product was dissolved in a mixture PE/EA/NEt₃ 100:10:1 and passed through a short pad (3 cm) of silica gel (small amount of orange impurities remain at the top layer). Yellow fraction was collected, evaporated and dried to give the product as yellow oil which slowly solidifies. It is rather stable in air both in solution and the solid state, but inert atmosphere is recommended for long storage (months). Yield 155-165 mg (85-90%).

¹H NMR (400 MHz, CDCl₃): δ = 7.67 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.35 (ddd, *J* = 8.7, 6.8, 1.9 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.69 – 6.61 (m, 1H), 4.52 – 4.38 (m, 2H), 4.33 (dt, *J* = 8.9, 3.7 Hz, 1H), 2.39 (heptd, *J* = 6.9, 3.4 Hz, 1H), 1.01 (d, *J* = 7.0 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H). Analytical data are consistent with the previously reported.⁸



A Schlenk tube (15 ml) was charged with (S-Salox)Rh(CO)₂ (75 mg, 0.2 mmol) and racemic diene⁸ *t*Bu₂TfB (200 mg, 0.6 mmol). The tube was evacuated and backfilled with argon 3 times, and then pure heptane (4 ml) and diisopropylethylamine (150 μL) were added. The tube was equipped with reflux condenser and gas bubbler and flushed with argon stream. Then it was immersed in a pre-heated oil bath (125 °C) and the mixture was refluxed with stirring for 50 hours with occasional flashing of gas phase with argon stream. It is important to maintain efficient reflux and to remove CO from gas phase, otherwise the reaction proceeds very slowly and may take two additional days. The conversion of starting complex (S-Salox)Rh(CO)₂ should be established by TLC analysis in PE/Et₃N 30:1 mixture; the starting complex has R_f = 0.57, the product has R_f = 0.71, the starting diene has R_f = 1. Before the analysis the TLC plate should be developed in the same mixture in order to deactivate the acidic silica gel. After the reaction completion, the mixture was opened to air and evaporated. At this point it is important to fully separate the

intermediate complex (S-Salox)Rh(*R,R*-^tBu₂TFB) from free diene in order to avoid racemization after the reaction with HCl. This can be done either by crystallization or by chromatography. For crystallization, dissolve most of the solid residue in hexane (5 ml), evaporate it to ca. 1.5 ml and put the flask in the fridge for 10 min to crystallize the product. Remove the mother liquid from yellow crystals and repeat this procedure again. Free ^tBu₂TFB is usually absent in after the second crystallization (should be checked by TLC). A more reliable, but slower procedure involves chromatography. A portion of silica gel was deactivated by soaking in PE:Et₃N 100:1 for 10 min, and then a short column was packed with this silica gel (1×15 cm). The mixture was subjected to this column, first free diene was eluted with PE:Et₃N 100:1 and then the product was eluted with PE:Et₃N 30:1. The yellow band was collected and evaporated to dryness to give the intermediate complex (S-Salox)Rh(*R,R*-^tBu₂TFB) (115 mg, 89% yield). It was dissolved in acetone (3 ml), concentrated aqueous HCl (200 μL, ca. 10 equiv.) was added, and the solution was stirred for 10 min. The mixture was evaporated to dryness and the residue was washed with cold methanol (1 ml x 3) to remove S-Salox. Drying in vacuum gives pure catalyst (*R,R*-^tBu₂TFB)RhCl₂ (**5**) as yellow powder. Yield 71 mg, 75%.

In case of a large scale synthesis it is reasonable to regenerate the excess of ^tBu₂TFB (from mother liquid during crystallization) and S-Salox (from methanol washings during the final stage).

¹H NMR (400 MHz, CDCl₃): δ = 5.43 (d, *J* = 6.0 Hz, 4H), 3.26 (d, *J* = 5.9 Hz, 4H), 1.14 (s, 36H).

¹⁹F NMR (376.5 MHz, CDCl₃): δ = -146.2 (d, *J* = 21.4 Hz, 4F), -159.1 (d, *J* = 21.4 Hz, 4F).

Analytical data are consistent with the previously reported.⁸

Enantiomeric purity ratio of the catalyst **5** was measured via chiral GC analysis of the replaced diene ligand. For this a sample of **5** (1 mg) was mixed with an excess of tBuNC (20 μL) in hexane (1 ml). The solution was filtered through a short layer of silica gel to remove insoluble rhodium species. The solvent was evaporated and the residue was dried in vacuum for several minutes to remove most of the isonitrile. The *ee* value of the remaining ligand ^tBu₂TFB was determined by Chromatec Crystal 5000.2 gas chromatograph equipped with Chiraldex B-PM capillary column (30 m x 0.25 mm, d_f 0.12 μm) and FID detector. Injection temperature 250 °C, column temperature 110 °C, detector temperature 250 °C; flow 55 cm/s He carrier gas). *t*_R = 92.86 min for *S,S*-^tBu₂TFB, *t*_R = 93.96 min for *R,R*-^tBu₂TFB.

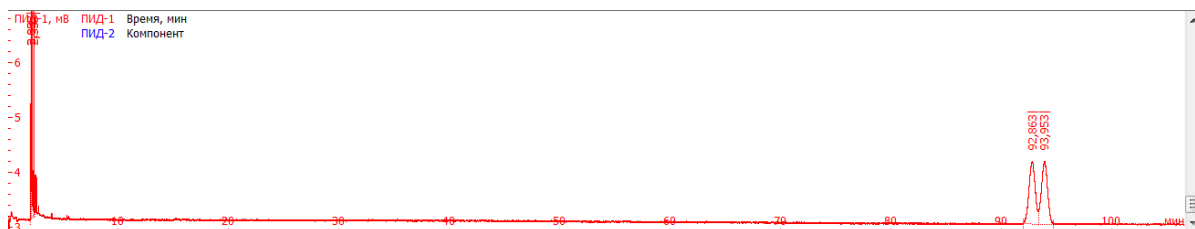


Figure S1. Racemic ^tBu₂TFB ligand.

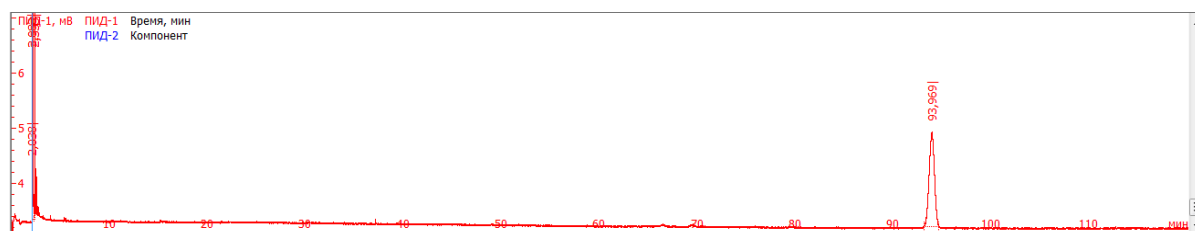
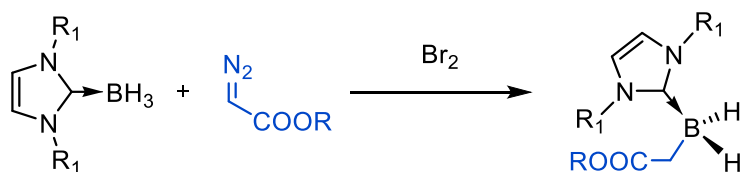


Figure S2. Chiral ^tBu₂TFB ligand obtained from the catalyst **5**.

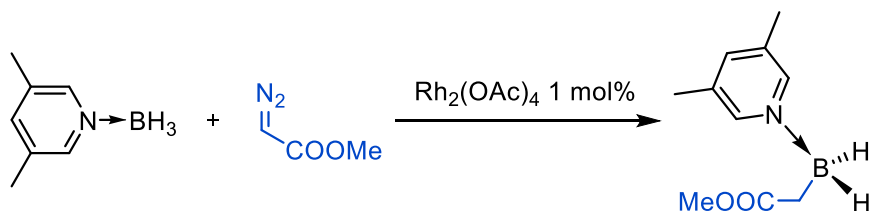
Synthesis of the starting prochiral boranes

General procedure (GP1) for the synthesis of NHC-boryl esters (2a–c,e)



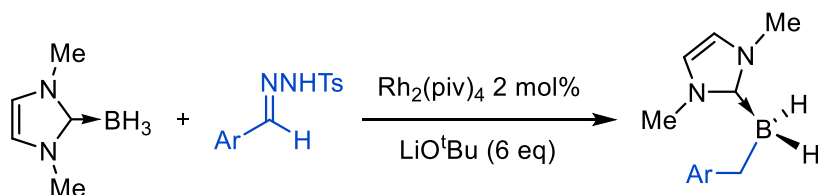
The synthesis was carried out by the modified literature procedure.⁵ In a 50 ml Schlenk flask adduct NHC-BH₃ (1.0–1.3 equiv) was dissolved in dichloromethane (1.0 M). Bromine (0.05 – 0.1 equiv) was added at 0 °C and the solution was stirred until it became colorless (5 – 10 min). Then corresponding diazoacetate (1.0–1.3 equiv) was then added dropwise, vigorous gas evolution was observed. The mixture was stirred at room temperature, until a small spot of the double carbene insertion product appeared on TLC plate. The crude mixture was concentrated under vacuum and the residue was purified by flash chromatography (ethyl acetate:n-hexane = 3:1).

Synthesis 3,5-dimethylpyridine-boryl ester (2d)



The synthesis was carried out by the modified literature procedure.⁹ 3,5-dimethylpyridine-borane (60.5 mg, 0.5 mmol, 1.0 equiv) and Rh₂(OAc)₄ (2.2 mg, 0.005 mmol, 1 mol %) were dissolved in dry CH₂Cl₂ (2.5 mL) under argon. A solution of methyl diazoacetate (60.0 mg, 0.6 mmol, 1.2 equiv) in CH₂Cl₂ (2.5 mL) was added dropwise via syringe pump over a period of 2 h. The resulting mixture was stirred at room temperature overnight. The progress was monitored by TLC, and the reaction was stopped when the spot of the double carbene insertion product appeared. The reaction mixture was evaporated in vacuum and the residue was purified by flash chromatography (ethyl acetate:n-hexane = 2:1) to give product **2d** as white solid. Yield 35 mg (36%).

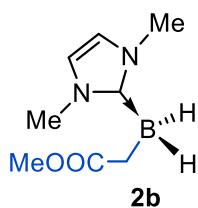
General procedure (GP2) for the synthesis of ArCH₂-NHC-borane (2f, 2g)



The synthesis was carried out by the modified literature procedure.¹⁰ In a Schlenk flask adduct NHC-BH₃ (2.0 equiv), corresponding tosylhydrazone (1.0 equiv), Rh₂(piv)₄ (2 mol %) and LiO^tBu (6.0 equiv) was dissolved in DCE (0.067 M). The resulting mixture was stirred at 55 °C overnight. Then the solution was evaporated under vacuum and the residue was purified by flash chromatography (n-hexane: ethyl acetate = 2:1) on silica gel to give products **2f** and **2g**. The resulting substances were stored in an argon atmosphere at –20 °C to avoid decomposition.

Analytical data of the starting prochiral boranes

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxoethyl)dihydroborate (2b)



The reaction was performed according to **GP1** using $\text{ImNMe}_2\text{-BH}_3$ (10.6 mmol, 1.165 g, 1.0 equiv), Br_2 (0.53 mmol, 27.3 μl , 0.05 equiv) and methyl diazoacetate (13.78 mmol, 1.378 g, 1.3 equiv) for 8 hours at room temperature. White solid. Yield 71% (1.378 g). $R_f = 0.4$ (EA:PE=5:1).

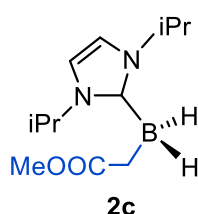
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.82 (s, 2H, NHC), 3.73 (s, 6H, NMe), 3.48 (s, 3H, COOMe), 2.0–1.4 (br q, $J = 88.7$ Hz, 2H, BH_2), 1.60 (br s, 2H, CH_2).

$^{11}\text{B NMR}$ (128 MHz, CDCl_3): δ -28.3.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 181.4 ($\underline{\text{COOMe}}$), 120.5 (NHC), 50.6 ($\underline{\text{COOMe}}$), 35.9 (NMe), 24.3 (q, $J_{\text{C-B}} = 31$ Hz, CH_2). Signal of NHC carbon connected to boron atom was not observed due to low intensity caused by quadrupole splitting.

HRMS: calculated for $\text{C}_8\text{H}_{15}\text{BN}_2\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 205.1119, found: 205.1114.

(1,3-diisopropyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxoethyl)dihydroborate (2c)



The reaction was performed according to **GP1** using $\text{ImNiPr}_2\text{-BH}_3$ (1.57 mmol, 260 mg, 1.0 equiv), Br_2 (0.078 mmol, 4 μl , 0.05 equiv) and methyl diazoacetate (2.035 mmol, 203.5 mg, 1.3 equiv) for 36 hours at room temperature. White solid. Yield 35% (130 mg). $R_f = 0.73$ (EA:PE=5:1).

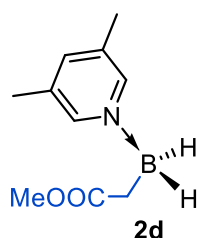
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.95 (s, 2H, NHC), 5.10 (st appears as q, $J = 6.7$ Hz, 2H, CH^{iPr}), 3.52 (s, 3H, COOMe), 2.0–1.5 (br q, 2H, BH_2), 1.61 (b s, 2H, CH_2), 1.40 (d, $J = 6.7$ Hz, 12H, CH_3^{iPr}).

$^{11}\text{B NMR}$ (128 MHz, CDCl_3): δ -28.18.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 181.1 ($\underline{\text{COOMe}}$), 115.7 (NHC), 50.6 ($\underline{\text{COOMe}}$), 49.3 ($\underline{\text{NCH}^{\text{iPr}}}$), 25.7 (br m, CH_2), 23.3 (Me^{iPr}). Signal of NHC carbon connected to boron atom was not observed due to low intensity caused by quadrupole splitting.

HRMS: calculated for $\text{C}_{12}\text{H}_{23}\text{BN}_2\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 261.1745, found: 261.1750

(3,5-dimethyl-pyridin-1-yl)(2-methoxy-2-oxoethyl)dihydroborate (2d)



$R_f = 0.75$ (EA:PE=5:1).

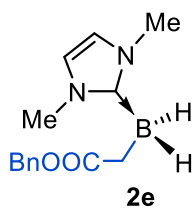
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.20 (s, 2H, Py), 7.57 (s, 1H, Py), 3.50 (s, 3H, COOMe), 2.38 (s, 6H, NMe), 1.80 (br s, 2H, CH_2).

$^{11}\text{B NMR}$ (128 MHz, CDCl_3): δ -6.09.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 179.9 ($\underline{\text{COOMe}}$), 144.6, 141.3, 135.4, 50.7 ($\underline{\text{COOMe}}$), 29.7 (br m, CH_2), 18.5 (Me^{Py}).

HRMS: calculated for $\text{C}_{10}\text{H}_{16}\text{BNNaO}_2^+$ $[\text{M}+\text{Na}]^+$: 216.1166, found: 216.1165.

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-benzyloxy-2-oxoethyl)dihydroborate (2e)



The reaction was performed according to **GP1** using $\text{ImNMe}_2\text{-BH}_3$ (1.3 mmol, 143 mg, 1.3 equiv), Br_2 (0.13 mmol, 6.7 μl , 0.1 equiv) and benzyl diazoacetate (1 mmol, 176 mg, 1 equiv). White solid. Yield 57% (147 mg). $R_f = 0.64$ (EA:PE=5:1).

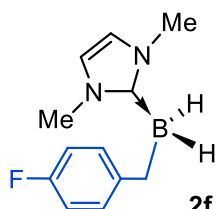
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.30 (m, 5H, Ph), 6.73 (s, 2H, NHC), 4.96 (s, 2H, CH_2Ph), 3.63 (s, 6H, NMe), 2.00–1.2 (br q, $J_{\text{H-B}} = 86$ Hz, 4H, BH_2), 1.68 (br s, CH_2 overlaps with BH_2).

$^{11}\text{B NMR}$ (128 MHz, CDCl_3): δ -28.3.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 180.7 (COOBn), 137.5, 128.3, 128.0, 127.6, 120.4, 64.7 (CH_2Ph), 35.8 (NMe), 24.5 (q, $J_{\text{C-B}} = 30$ Hz, CH_2). Signal of NHC carbon connected to boron atom was not observed due to low intensity caused by quadrupole splitting.

HRMS: calculated for $\text{C}_{14}\text{H}_{19}\text{BN}_2\text{O}_2\text{Na}$ [$\text{M}+\text{Na}$] $^+$: 281.1432, found: 281.1437

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(p-fluorobenzyl)dihydroborate (2f)



The reaction was performed according to **GP2** using $\text{ImNMe}_2\text{-BH}_3$ (1 mmol, 110 mg, 2.0 equiv), 4-fluorobenzaldehyde tosylhydrazone (0.5 mmol, 146 mg, 1.0 equiv), $\text{Rh}_2(\text{piv})_4$ (0.01 mmol, 6.1 mg, 2 mol %) and LiO^tBu (3 mmol, 240 mg, 6.0 equiv). White solid at -20 °C. Yield 61% (100 mg).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.75–6.70 (m, 6H, Ph+NHC), 3.46 (s, 6H, NMe), 2.0–1.5 (br m, 2H, BH_2), 1.90 (br s, CH_2).

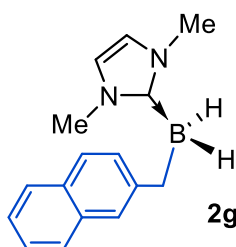
$^{11}\text{B NMR}$ (128 MHz, CDCl_3): δ -25.70.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -123.23.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.7, 128.3 ($J_{\text{C-F}} = 7$ Hz), 120.2, 114.2 ($J_{\text{C-F}} = 20$ Hz), 35.7 (NMe). Signal of NHC and CH_2 carbon atoms connected to boron atom were not observed due to low intensity caused by quadrupole splitting. We could not obtain better spectrum due to low stability of the compound.

HRMS: calculated for $[\text{C}_{12}\text{H}_{15}\text{BFN}_2, \text{M-H}]^+$: 217.1307, found: 217.1310.

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(naphthalen-2-yl-methyl)dihydroborate (2g)



The reaction was performed according to **GP2** using $\text{ImNMe}_2\text{-BH}_3$ (1.5 mmol, 165 mg, 2.0 equiv), 2-naphthaldehyde tosylhydrazone (0.75 mmol, 243 mg, 1.0 equiv), $\text{Rh}_2(\text{piv})_4$ (0.015 mmol, 9.2 mg, 2 mol %) and LiO^tBu (4.5 mmol, 360 mg, 6.0 equiv). White solid at -20 °C. Yield 61% (115 mg).

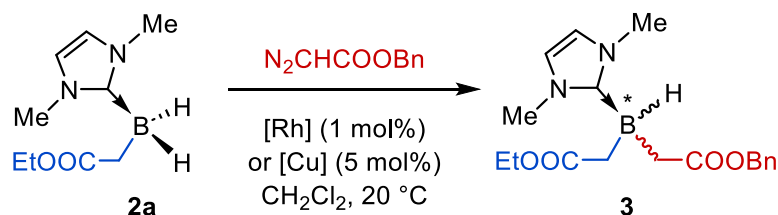
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.70 (d, 2H, $J = 7.7$ Hz, Ar), 7.59–7.51 (m, 2H, Ar), 7.36–7.23 (m, 2H, Ar), 7.13–7.05 (m, 2H, Ar), 6.69 (s, 2H, NHC), 3.37 (s, 6H, N-Me), 2.12 (br s, 2H, CH_2), 1.91–1.35 (m, 2H, BH_2).

$^{11}\text{B NMR}$ (128 MHz, CDCl_3): δ -25.70.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 149.8, 134.2, 130.4, 128.5, 127.5, 126.8, 126.7, 125.2, 125.1, 123.4, 123.3, 120.1, 35.6, 28.0 (br m, CH_2B). The signal of NHC carbon atom connected to boron atom was not observed due to low intensity caused by quadrupole splitting.

HRMS: calculated for $[\text{C}_{16}\text{H}_{18}\text{BN}_2, \text{M-H}]^+$: 249.1558, found: 249.1566.

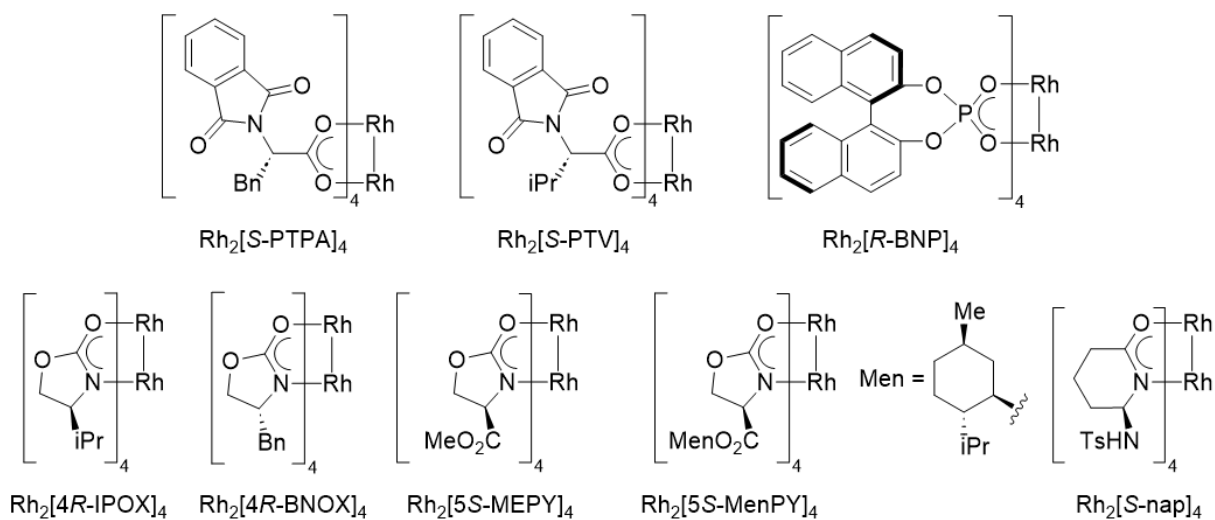
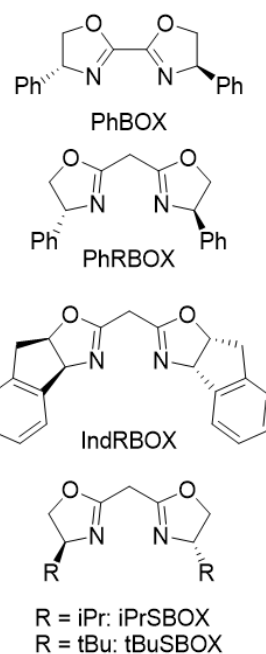
Catalyst screening for the insertion of benzyldiazoacetate into the prochiral borane **2a**



A catalyst (1 mol% [Rh] or 5 mol% [Cu]) was placed in a 10 ml Schlenk flask. The flask was evacuated and backfilled with argon, then the borane **2a** (20 mg, 0.1 mmol) and DCM (1 mL) were added. To the resulting solution benzyldiazoacetate (35 mg, 0.2 mmol) was added at once. The resulting mixture was stirred until full consumption of the starting diazo (typically 5 min for [Rh], 1 hour for [Cu]). The solvent was removed in vacuum, and the yield was determined via ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. The product was then purified by flash chromatography and analyzed by chiral HPLC.

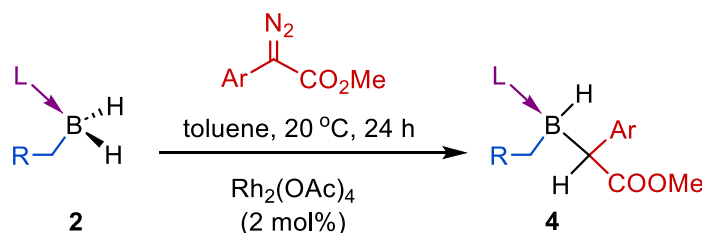
Table S1. Results of the catalyst screening.

entry	catalyst	yield (%)	ee (%)
1	$[\text{Cu}(\text{MeCN})_4]\text{PF}_6 + \text{PhBOX}$	53	0
2	$[\text{Cu}(\text{MeCN})_4]\text{PF}_6 + \text{PhRBOX}$	92	0
3	$[\text{Cu}(\text{MeCN})_4]\text{PF}_6 + \text{IndRBOX}$	73	0
4	$[\text{Cu}(\text{MeCN})_4]\text{PF}_6 + \text{iPrSBOX}$	81	0
5	$[\text{Cu}(\text{MeCN})_4]\text{PF}_6 + \text{tBuSBOX}$	82	5
6	$[\text{Cu}(\text{MeCN})_4]\text{PF}_6 + R\text{-BINAP}$	0	-
7	$\text{Rh}_2[\text{S-PTPA}]_4$	18	0
8	$\text{Rh}_2[\text{S-PTV}]_4$	19	0
9	$\text{Rh}_2[R\text{-BNP}]_4$	18	0
10	$\text{Rh}_2[4R\text{-IPOX}]_4$	70	11
11	$\text{Rh}_2[5S\text{-MEPY}]_4$	74	15
12	$\text{Rh}_2[5S\text{-MenPY}]_4$	32	17
13	$\text{Rh}_2[4R\text{-BNOX}]_4$	47	12
14	$\text{Rh}_2[\text{S-nap}]_4$	>95	0
15	$[(\text{COD})\text{RhCl}]_2 + R\text{-BINAP}$	0	-



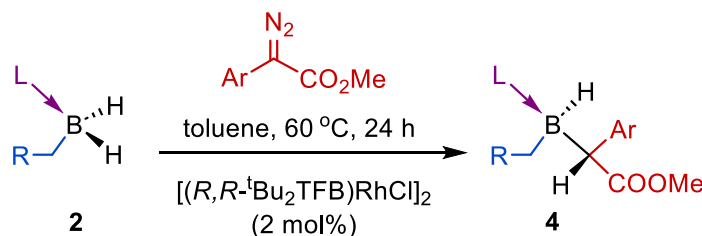
Synthesis of the insertion products **4**

General procedure for synthesis of the racemic products **4** using of $\text{Rh}_2(\text{OAc})_4$ catalyst.



The starting borane **2** (0.1 mmol, 1 equiv.), the diazo compound (0.15 mmol, 1.5 equiv.), and toluene (0.3 mL) were placed in a 0.5 mL vial. Mixture was bubbled with the argon stream for 3 minutes and then $\text{Rh}_2(\text{OAc})_4$ (1 mg, 2 μmol , 2 mol%) was added under argon. The resulting mixture was stirred at room temperature overnight (typically) until no more NHC-borane was present according to TLC. The solvent was evaporated in vacuum and mixture was purified by flash chromatography. In some cases, the crude mixture was directly transferred onto the TLC plate for preparative thin-layer chromatography.

General procedure for synthesis of the chiral products **4** using of the catalyst $[(R,R\text{-}^t\text{Bu}_2\text{TfB})\text{RhCl}]_2$.



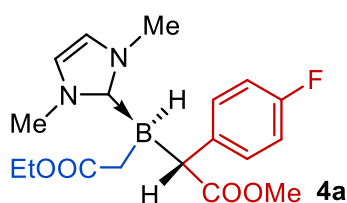
The starting borane **2** (0.1 mmol, 1 equiv.), the diazo compound (0.15 mmol, 1.5 equiv.), the catalyst $[(R,R\text{-}^t\text{Bu}_2\text{TfB})\text{RhCl}]_2$ (2 mg, 2 μmol , 2 mol%), and toluene (0.3 mL) were placed in a 0.5 mL vial. Mixture was bubbled with the argon stream for 3 minutes and then stirred at 60 °C for 24h (unless otherwise noted) until no more NHC-borane was present according to TLC. The solvent was evaporated in vacuum and mixture was purified by flash chromatography. In some cases, the crude mixture was directly transferred onto the TLC plate for preparative thin-layer chromatography.

Scaled-up synthesis of **4b**

In a 50 ml Schlenk flask equipped with PTFE coated magnetic stir bar the starting borane **2b** (2 mmol, 364 mg, 1 equiv.) and the catalyst $[(R,R\text{-}^t\text{Bu}_2\text{TfB})\text{RhCl}]_2$ (38.1 mg, 0.04 mmol, 2 mol%) were placed. The flask was subjected to a vacuum and refilled with argon three times. 12 ml of dry toluene and methyl phenyldiazoacetate (528 mg, 3 mmol, 1.5 equiv.) were added. The resulting mixture stirred at 60 °C for 24h until no more **2b** was present according to TLC. The solvent was evaporated in vacuum and the solid residue was purified by flash chromatography (ethyl acetate:n-hexane = 5:1) to give two diastereomeric products as colorless oils which slowly become white solids upon standing. Yield of major diastereomer was 409 mg (62%), yield of the minor diastereomer was 146 mg (22%).

Characterization of chiral borane products

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxoethyl)(2-methoxy-2-oxo-1-(4-fluorophenyl)ethyl)hydroborate (**4a**)



The reaction was performed using 0.1 mmol **2a**. Reaction time 24h. Purification by flash chromatography, n-hexane:EA = 2:1 -> 1:2. Minor diastereomer was not isolated. Analytical R_f = 0.55 (EA:PE=5:1).

Yield of the major diastereomer using the catalyst **5**: 23.8 mg (65%), *ee* 93%.

Analytical data are given for the major diastereomer.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.16 (dd, J = 8.6, 5.7 Hz, 2H, Ar), 6.77 (t, J = 8.9 Hz, 2H, Ar), 6.67 (s, 2H, NHC), 3.86 (qd, J = 7.1, 2.4 Hz, 2H, $\text{COOCH}_2\text{CH}_3$), 3.63 (s, 3H, COOMe), 3.51 (s, 6H, NMe), 3.21 (d, J = 5.1 Hz, 1H, CH), 2.2 – 1.6 (m, 3H, CH_2 + BH), 1.02 (t, J = 7.1 Hz, 3H, $\text{COOCH}_2\text{CH}_3$).

$^{11}\text{B NMR}$ (128 MHz, CDCl_3): δ -16.41.

$^{19}\text{F NMR}$ (282 MHz, CDCl_3): δ -119.88.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 179.4 ($\underline{\text{C}}\text{OOR}$), 178.7 ($\underline{\text{C}}\text{OOR}$), 161.7, 159.3, 139.8, 128.8 (d, $J_{\text{C-F}}$ = 7.3 Hz), 121.1, 114.22 (d, $J_{\text{C-F}}$ = 20.6 Hz), 58.87 ($\text{COOCH}_2\text{CH}_3$), 50.97 (COOMe), 36.55 (NMe), 14.50 ($\text{COOCH}_2\text{CH}_3$). Signals of carbon atoms connected to boron were not observed apparently due to quadrupolar coupling.

Chiral HPLC conditions for **major isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 80/20, t_R = 6.5 min for first peak, t_R = 8.4 min for second peak.

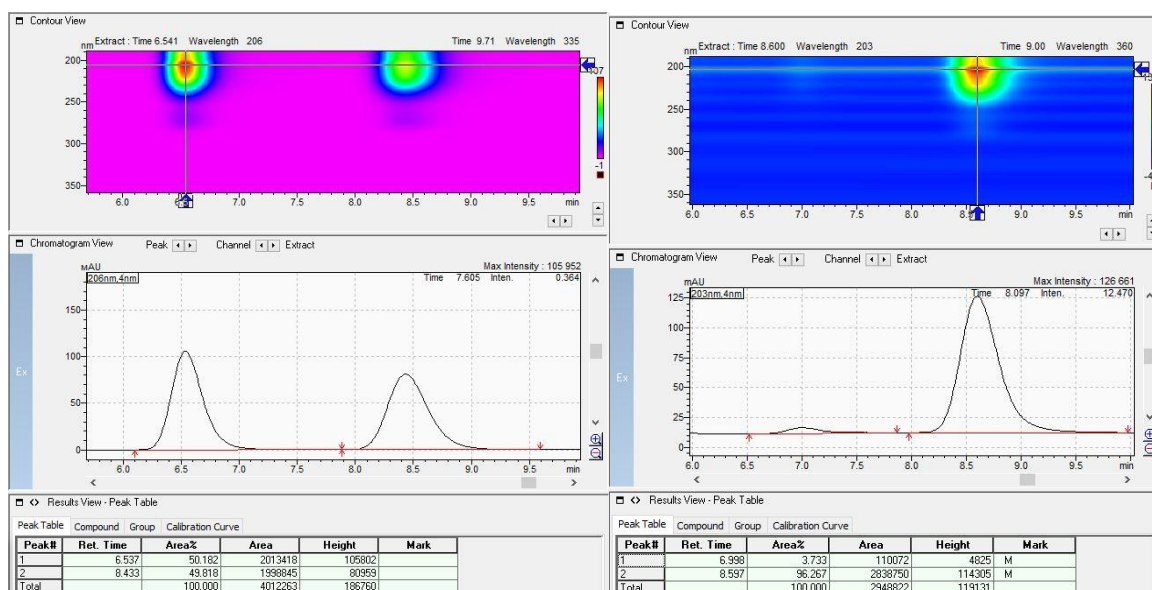
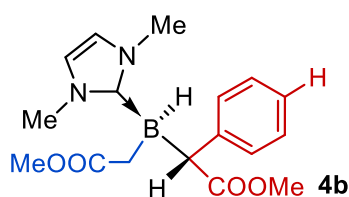


Figure S3. Chiral HPLC of the major diastereomer of **4a**: racemic (left) and chiral product (right).

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxoethyl)(2-methoxy-2-oxo-1-phenylethyl)hydroborate (4b)



Reaction time 24h. Purification by flash chromatography, EA:n-hexane = 5:1. Analytical R_f = 0.46 and 0.31 (EA:PE=5:1).

Yields of the diastereomers using catalyst $Rh_2(OAc)_4$: 17 mg (52%) and 11 mg (33%). dr \approx 3:2.

Yields of the diastereomers using the catalyst **5**: 22 mg (67%), ee 89%, and 6 mg (18%), ee 89%. dr \approx 3:1.

Analytical data are given for the major diastereomer. NMR spectra of the second diastereomer are similar, but broad due to the previously reported slow rotation around B-NHC bond.¹¹

¹H NMR (400 MHz, CDCl₃): δ 7.18 (m, 2H, Ph), 7.08 (m, 2H, Ph), 6.98 (m, 1H, Ph), 6.65 (s, 2H, NHC), 3.63 (s, 3H, COOMe), 3.46 (s, 6H, NMe), 3.43 (s, 3H, COOMe), 3.23 (br s, 1H, CH), 1.9–1.7 (m, 3H, CH₂ + BH).

¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -16.5 (s).

¹³C NMR (101 MHz, CDCl₃): δ 180.1 (C=O), 178.7 (C=O), 144.0, 127.7, 127.6, 124.4, 121.2, 51.0 (COOMe), 50.8 (COOMe), 36.5 (NMe). Signals of carbon atoms connected to boron were not observed apparently due to quadrupolar coupling.

HRMS: calculated for C₁₇H₂₄BN₂O₄⁺, [M+H]⁺: 331.1824, found: 331.1835.

Chiral HPLC conditions for **major isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 80/20, t_R = 6.5 min for first peak, t_R = 8.8 min for second peak. Chiral HPLC conditions for **minor isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 80/20, t_R = 5.4 min for first peak, t_R = 6.1 min for second peak.

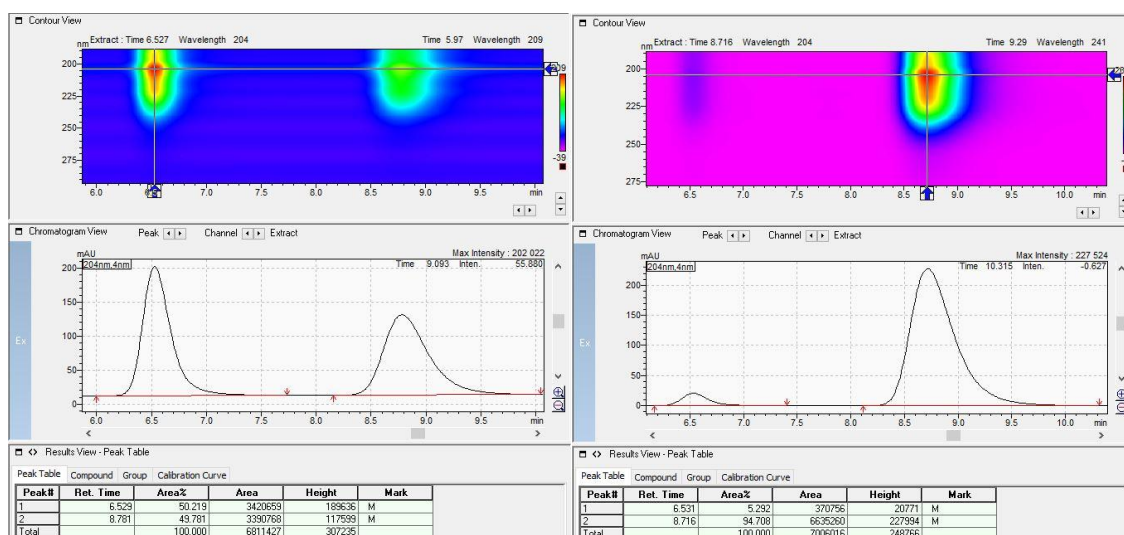


Figure S4. Chiral HPLC of the major diastereomer of **4b**: racemic sample (left) and chiral product (right).

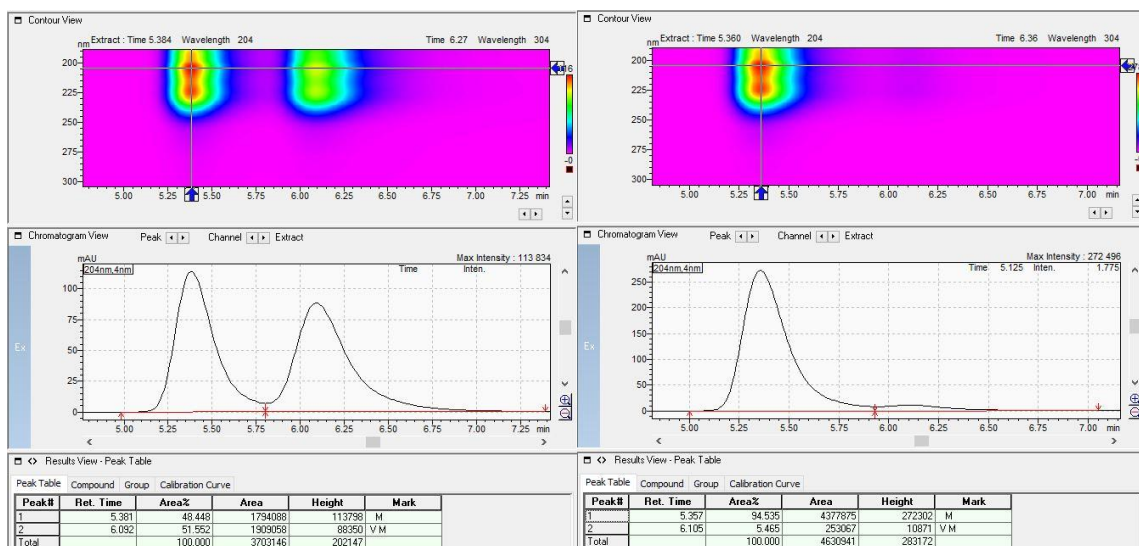
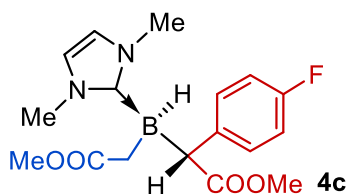


Figure S5. Chiral HPLC of the minor diastereomer of **4b**: racemic sample (left) and chiral product (right).

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxoethyl)(2-methoxy-2-oxo-1-(4-fluorophenyl)ethyl)hydroborate (4c)



Reaction time 24h. Purification by flash chromatography, EA:n-hexane = 5:1. Analytical R_f = 0.43 and 0.31 (EA:PE=5:1).

Yields of the diastereomers using catalyst $Rh_2(OAc)_4$: 18 mg (52%) and 16 mg (46%). dr \approx 1:1.

Yields of the diastereomers using the catalyst **5**: 26 mg (75%), ee 89% and 5 mg (14%), ee 94%. dr \approx 5:1.

Analytical data are given for the major diastereomer. NMR spectra of the second diastereomer are similar, but broad due to the previously reported slow rotation around B-NHC bond.¹¹

1H NMR (400 MHz, $CDCl_3$): δ 7.16 (m, 2H, Ar), 6.78 (m, 2H, Ar), 6.67 (s, 2H, NHC), 3.63 (s, 3H, COOMe), 3.51 (s, 6H, NMe), 3.43 (s, 3H, COOMe), 3.21 (br s, 1H, CH), 1.9–1.7 (m, 3H, CH_2 + BH).

$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -16.5 (s). ^{19}F NMR (282 MHz, $CDCl_3$): δ -119.8 (s).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.9 (COOMe), 178.69 (COOMe), 161.66, 139.68, 128.9 (J_{C-F} = 7.2 Hz), 121.26, 114.2 (J_{C-F} = 20.6 Hz), 51.0 (COOMe), 50.8 (COOMe), 36.5 (NMe). Signals of carbon atoms connected to boron were not observed apparently due to quadrupolar coupling. Signal of quaternary carbon connected to fluorine is not observed because of low intensity.

HRMS: calculated for $C_{17}H_{23}BFN_2O_4^+$ $[M+H]^+$: 349.1729, found: 349.1738.

Chiral HPLC conditions for **major isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 90/10, t_R = 18.1 min for first peak, t_R = 25.7 min for second peak. Chiral HPLC conditions for **minor isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 90/10, t_R = 12.9 min for first peak, t_R = 15.3 min for second peak.

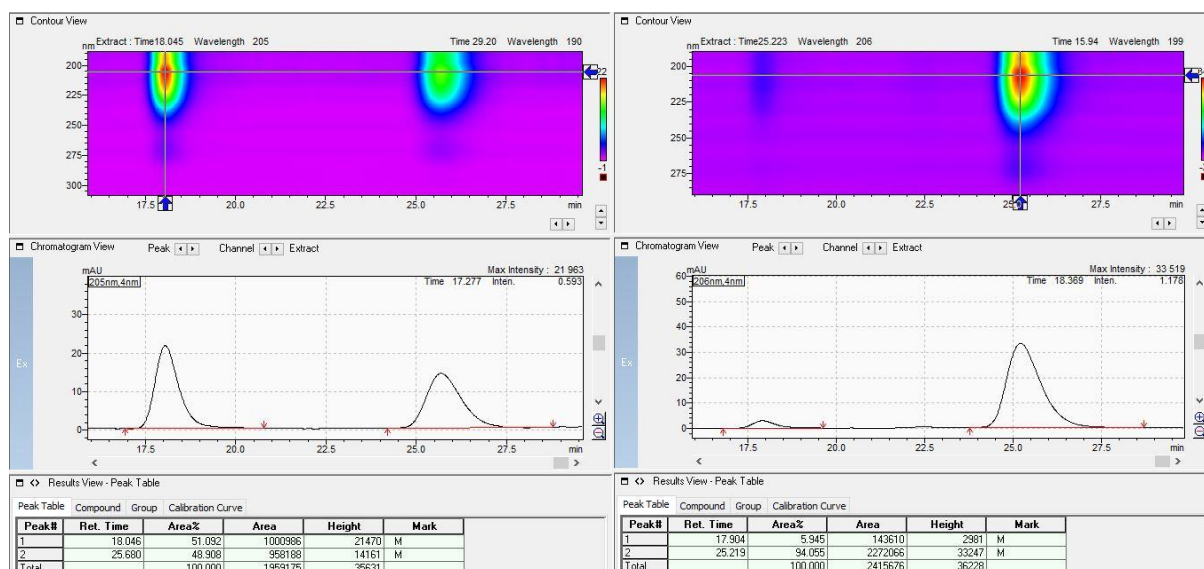


Figure S6. Chiral HPLC of the major diastereomer of **4c**: racemic sample (left) and chiral product (right).

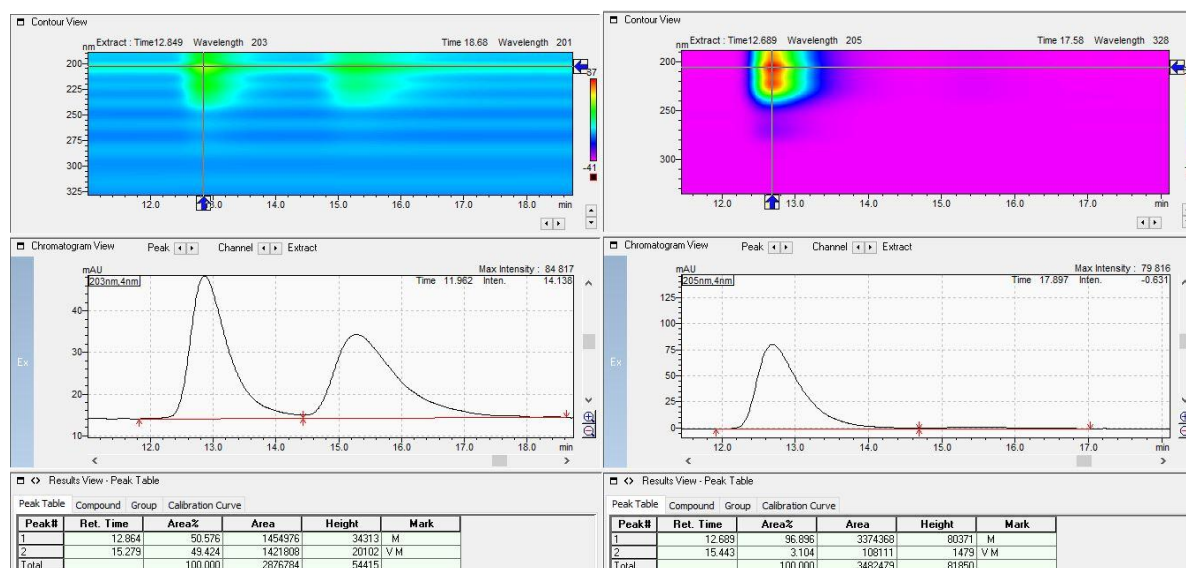
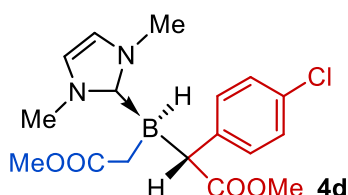


Figure S7. Chiral HPLC of the minor diastereomer of **4c**: racemic sample (left) and chiral product (right).

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxoethyl)(2-methoxy-2-oxo-1-(4-chlorophenyl)ethyl)hydroborate (4d)



Synthesis was conducted on 0.08 mmol scale. Reaction time 24h. Purification by flash chromatography, EA:n-hexane = 5:1. Analytical R_f = 0.46 and 0.32 (EA:PE=5:1).

Yields of the diastereomers using catalyst $Rh_2(OAc)_4$: 14 mg (38%) and 15 mg (41%). dr \approx 1:1.

Yields of the diastereomers using the catalyst **5**: 20 mg (55%), *ee* 93% and 8 mg (22%), *ee* 93%. dr \approx 5:2.

Analytical data are given for the major diastereomer. NMR spectra of the second diastereomer are similar, but broad due to the previously reported slow rotation around B-NHC bond.¹¹

1H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, J = 8.2 Hz, 2H, Ar), 7.05 (d, J = 8.2 Hz, 2H, Ar), 6.68 (s, 2H, NHC), 3.64 (s, 3H, COOMe), 3.51 (s, 6H, NMe), 3.43 (s, 3H, COOMe), 3.20 (br s, 1H, CH), 1.9–1.65 (m, 3H, CH_2 + BH).

^{11}B NMR (128 MHz, $CDCl_3$): δ -16.5 (s)

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.9 ($\underline{C}OOMe$), 178.4 ($\underline{C}OOMe$), 142.7, 129.9, 129.1, 127.6, 121.3, 51.0 ($\underline{C}OOMe$), 50.8 ($\underline{C}OOMe$), 36.6 (NMe). Signals of carbon atoms connected to boron were not observed apparently due to quadrupolar coupling.

HRMS: calculated for $C_{17}H_{23}BClN_2O_4^+$ $[M+H]^+$: 365.1434, found: 365.1442.

Chiral HPLC conditions for **major isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 80/20, t_R = 7 min for first peak, t_R = 10.4 min for second peak. Chiral HPLC conditions for **minor isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 90/10, t_R = 12.1 min for first peak, t_R = 14.0 min for second peak.

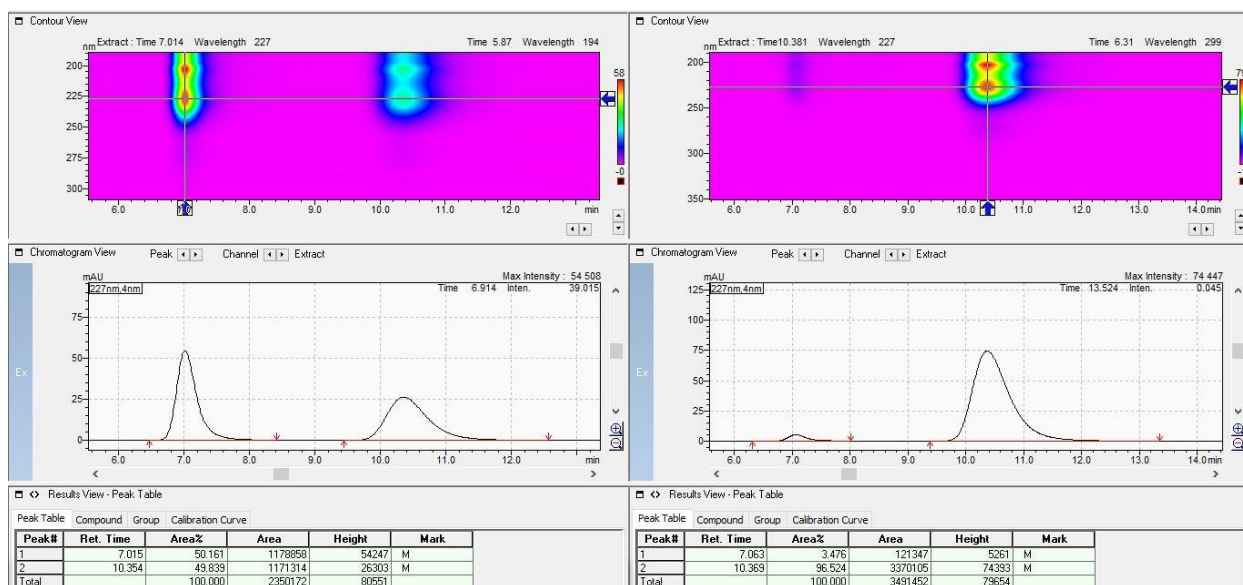


Figure S8. Chiral HPLC of the major diastereomer of **4d**: racemic sample (left) and chiral product (right).

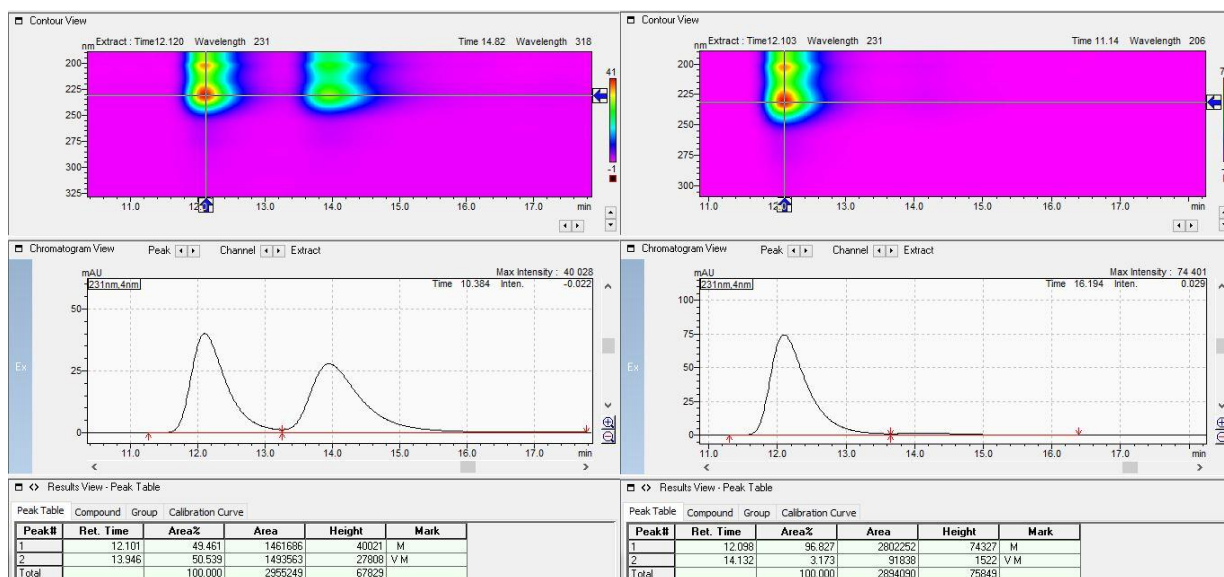
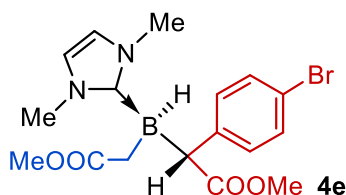


Figure S9. Chiral HPLC of the minor diastereomer of **4d**: racemic sample (left) and chiral product (right).

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxoethyl)(2-methoxy-2-oxo-1-(4-bromophenyl)ethyl)hydroborate (4e and 4e')



Reaction time 24h. Purification by flash chromatography, EA:n-hexane = 5:1. Analytical R_f = 0.47 and 0.26 (EA:PE=5:1).

Yields of the diastereomers using catalyst $Rh_2(OAc)_4$: 19 mg (46%) and 11 mg (27%). dr \approx 2:1.

Yields of the diastereomers using the catalyst **5**: 27 mg (66%), *ee* 93% and 6 mg (15%), *ee* 92%. dr \approx 5:2.

Analytical data for the major diastereomer **4e**.

1H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J = 8.4 Hz, 2H, Ar), 7.09 (d, J = 8.4 Hz, 2H, Ar), 6.68 (s, 2H, NHC), 3.63 (s, 3H, COOMe), 3.50 (s, 6H, NMe), 3.43 (s, 3H, COOMe), 3.20 (br d, 1H, J = 5.0 Hz, CH), 1.8–1.65 (m, 3H, CH_2 + BH).

$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -16.5 (s)

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.9 (COOMe), 179.7 (COOMe), 143.2, 130.6, 129.5, 121.3, 117.9, 51.1 (COOMe), 50.8 (COOMe), 36.6 (NMe). Signals of carbon atoms connected to boron were not observed apparently due to quadrupolar coupling.

HRMS: calculated for $C_{17}H_{23}BBRn_2O_4^+$, $[M+H]^+$: 409.0929, found 409.0930.

Chiral HPLC conditions for **major isomer 4e**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 80/20, t_R = 7.2 min for first peak, t_R = 10.5 min for second peak.

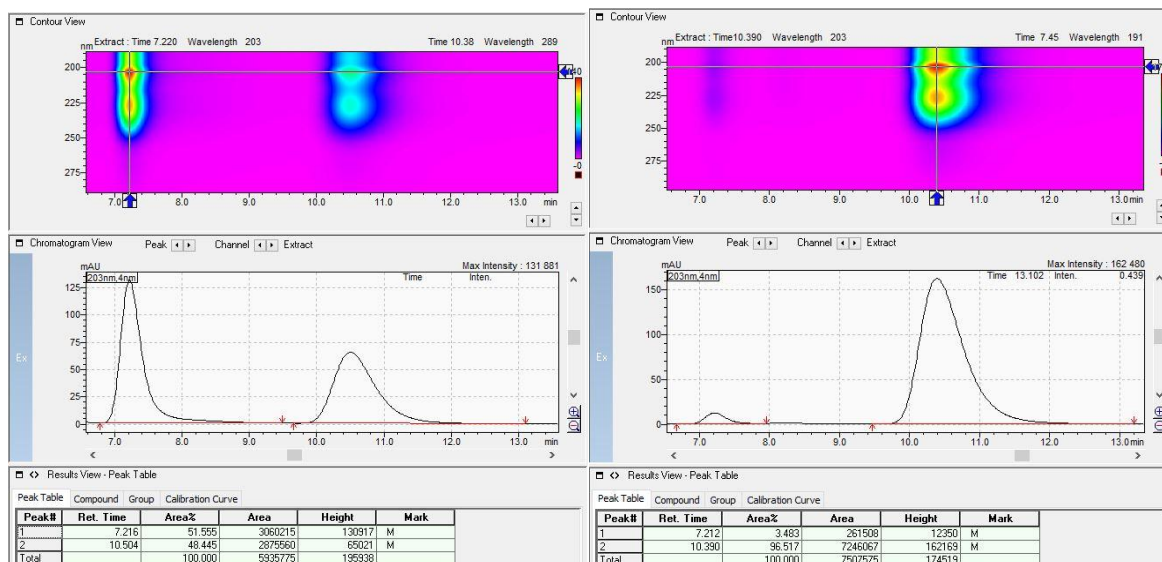
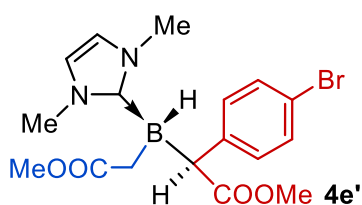


Figure S10. Chiral HPLC of the major diastereomer **4e**: racemic sample (left) and chiral product (right).



Analytical data for the minor diastereomer **4e'**.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.32 (d, 2H, $J = 8.4$ Hz, Ar), 7.24 (d, 2H, $J = 8.4$ Hz, Ar), 6.82 (s, 2H, NHC), 3.74 (br s, 6H, N-Me), 3.36 (s, 3H, COOMe), 3.35 (s, 3H, COOMe), 3.18 (m, 1H, CH), 1.8 – 1.4 (m, 3H, $\text{CH}_2 + \text{BH}$).

$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ -16.6 (s)

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 142.4, 130.7, 130.5, 121.4, 50.9 (COOMe), 50.7 (COOMe), 36.9 (NMe). Signals of ester carbon atoms as well as carbons connected to boron were not observed apparently due to low intensity.

Chiral HPLC conditions for **minor isomer 4e'**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/*i*PrOH = 90/10, $t_R = 12.7$ min for first peak, $t_R = 14.2$ min for second peak.

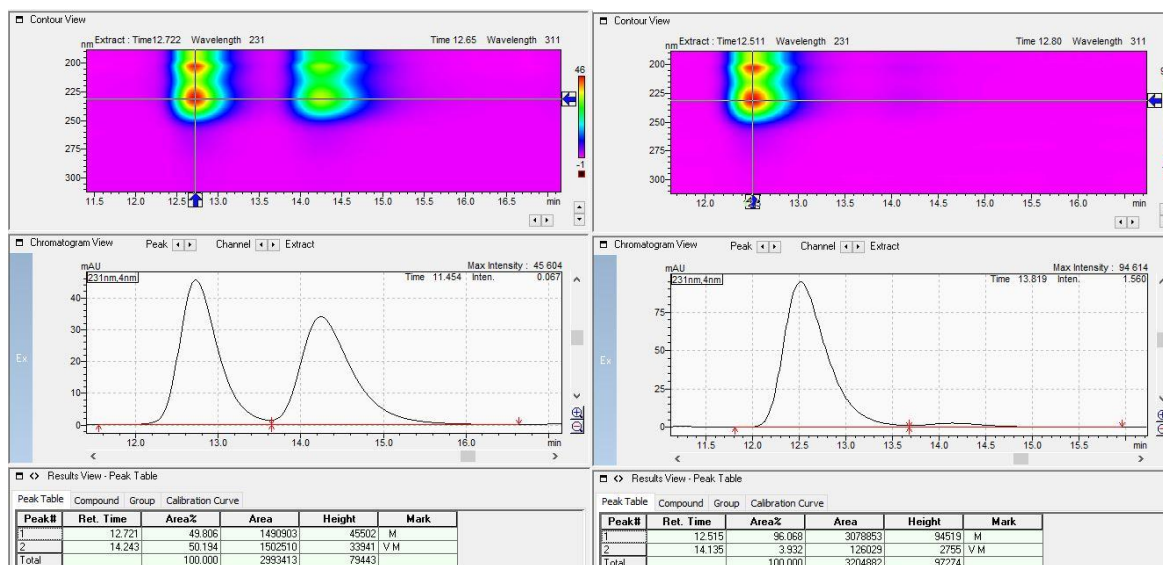
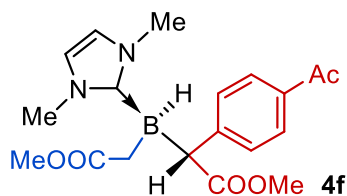


Figure S11. Chiral HPLC of the minor diastereomer **4e'**: racemic sample (left) and chiral product (right).

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxoethyl)(1-(4-acetylphenyl)-2-methoxy-2-oxoethyl)hydroborate (4f)



Reaction time 24h. Purification by flash chromatography, EA:DCM = 1:1. We could not separate diastereomers. Analytical $R_f = 0.36$ (EA:PE=5:1).

Yield using catalyst $Rh_2(OAc)_4$: 29 mg (78%)

Yield using the catalyst **5**: 28 mg (75%), *ee* 88% (for the major diastereomer), *dr* \approx 4:1.

Analytical data is given for a mixture of diastereomers.

1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, $J = 8.3$ Hz, 2H, Ar_{minor}), 7.70 (d, $J = 8.3$ Hz, 2H, Ar_{major}), 7.44 (d, $J = 8.3$ Hz, 2H, Ar_{minor}), 7.31 (d, $J = 8.3$ Hz, 2H, Ar_{major}), 6.83 (s, 2H, NHC_{minor}), 6.67 (s, 2H, NHC_{major}), 3.65 (s, 3H, $COOMe_{major}$), 3.48 (s, 6H, NMe_{major}), 3.43 (s, 3H, $COOMe_{major}$), 3.39 (s, 3H, $COOMe_{minor}$), 3.34 (m, 3H, $COOMe_{minor} + 1H, CH$), 3.32 (br s, 1H, CH), 2.56 (s, 3H, Ac_{minor}), 2.52 (s, 3H, Ac_{major}), 1.90 – 1.7 (m, 2H, CH_{2major}), 1.65 – 1.50 (m, 2H, CH_{2minor}).

^{11}B NMR (128 MHz, $CDCl_3$): δ -16.3 (br s)

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.7 (\underline{COOMe}), 177.8 (\underline{COOMe}), 150.7, 133.7, 128.7, 128.0, 127.9, 127.7, 121.5, 121.4, 112.3, 112.0, 51.0 (\underline{COOMe}), 50.8 (\underline{COOMe}), 36.9 (NMe_{minor}), 36.6 (NMe_{major}), 26.6 (Ac). Signals of carbon atoms connected to boron were not observed apparently due to quadrupolar coupling.

HRMS: calculated for $C_{19}H_{26}BN_2O_5$, $[M+H]^+$: 373.1929, found: 373.1936.

Chiral HPLC conditions for **major isomer** in the mixture: Chiralpak IH-3 (4.6 \times 150 mm), heptane/*i*PrOH = 80/20, $t_R = 11.9$ min for first peak, $t_R = 14.6$ min for second peak. The minor isomer was not separated and analyzed.

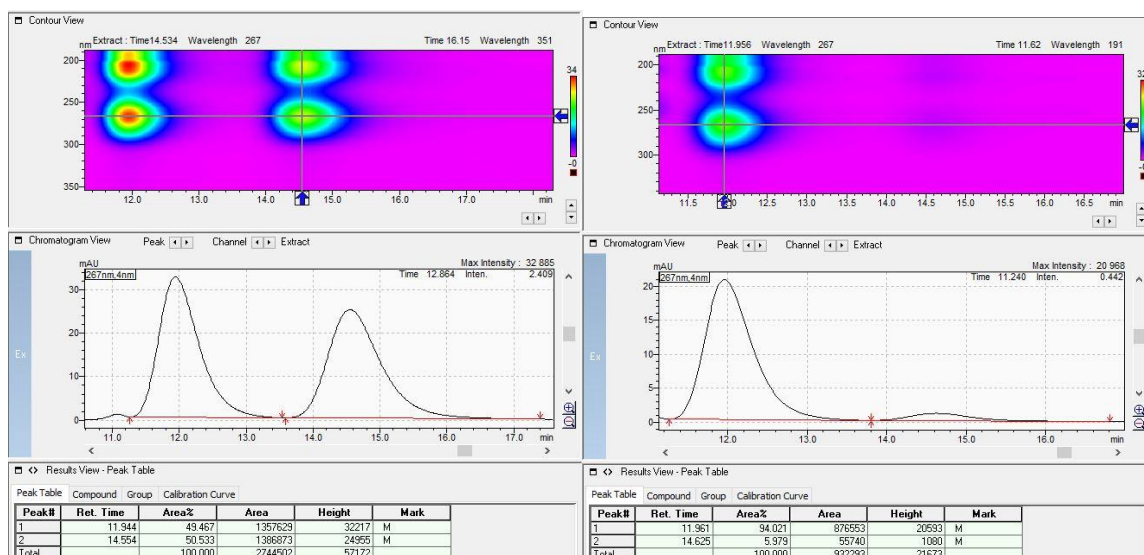
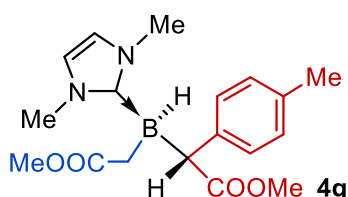


Figure S12. Chiral HPLC of the major diastereomer of **4f**: racemic sample (left) and chiral product (right).

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxoethyl)(2-methoxy-2-oxo-1-*p*-tolylethyl)hydroborate (4g**)**



Synthesis was conducted on a small scale (0.05 mmol). Reaction time 24h. Purification by flash chromatography, EA:n-hexane = 5:1. Analytical R_f = 0.56 and 0.28 (EA:PE=5:1).

Yields of the diastereomers using catalyst $Rh_2(OAc)_4$: 9 mg (49%) and 8 mg (44%). dr \approx 1:1.

Yields of the diastereomers using the catalyst **5**: 12 mg (66%), ee 94% and 4 mg (22%), ee 95%. dr \approx 3:1.

Analytical data are given for the major diastereomer. NMR spectra of the second diastereomer are similar, but broad due to the previously reported slow rotation around B-NHC bond.¹¹

1H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, 2H, J = 7.8 Hz, Ar), 6.89 (d, 2H, J = 7.8 Hz, Ar), 6.65 (s, 2H, NHC), 3.62 (s, 3H, COOMe), 3.48 (s, 6H, NMe), 3.43 (s, 3H, COOMe), 3.18 (br s, 1H, CH), 2.21 (s, 3H, Me^{Ar}), 1.9–1.7 (br m, 3H, CH₂ + BH).

$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -16.7 (s).

^{13}C NMR (101 MHz, $CDCl_3$): δ 180.1 (COOMe), 178.9 (COOMe), 140.8, 133.6, 128.3, 127.7, 121.2, 50.9 (COOMe), 50.7 (COOMe), 36.6 (NMe), 21.00 (Me). Signals of carbon atoms connected to boron were not observed apparently due to quadrupolar coupling.

HRMS: calculated for $C_{18}H_{26}BN_2O_4$ [M+H]⁺: 345.1980, found: 345.1988.

Chiral HPLC conditions for **major isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 80/20, t_R = 5.6 min for first peak, t_R = 6.6 min for second peak. Chiral HPLC conditions for **minor isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 90/10, t_R = 10.2 min for first peak, t_R = 11.5 min for second peak.

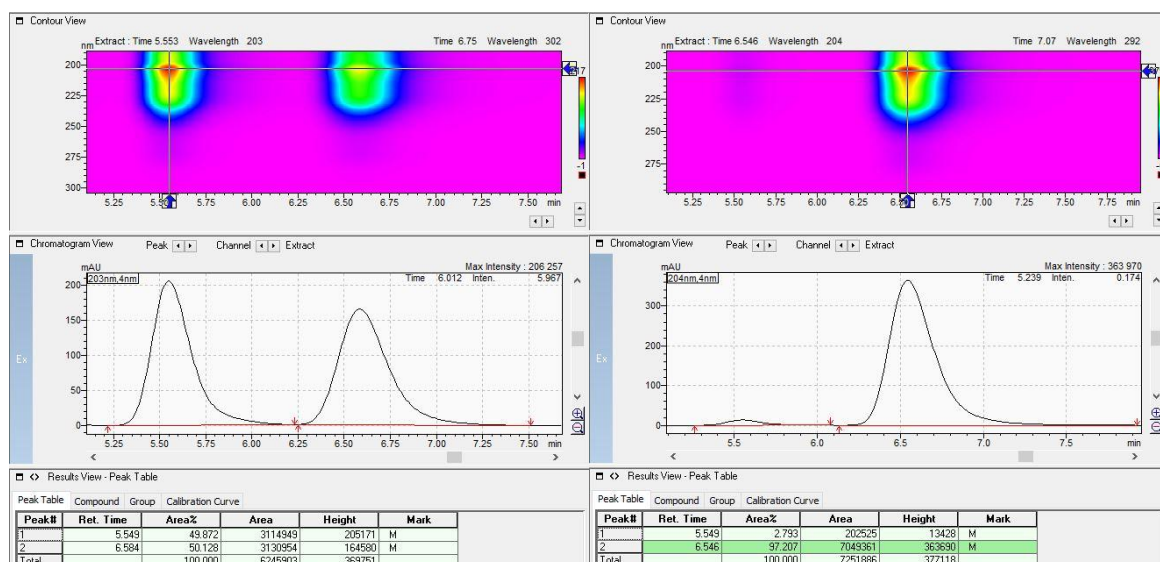


Figure S13. Chiral HPLC of the major diastereomer of **4g**: racemic sample (left) and chiral product (right).

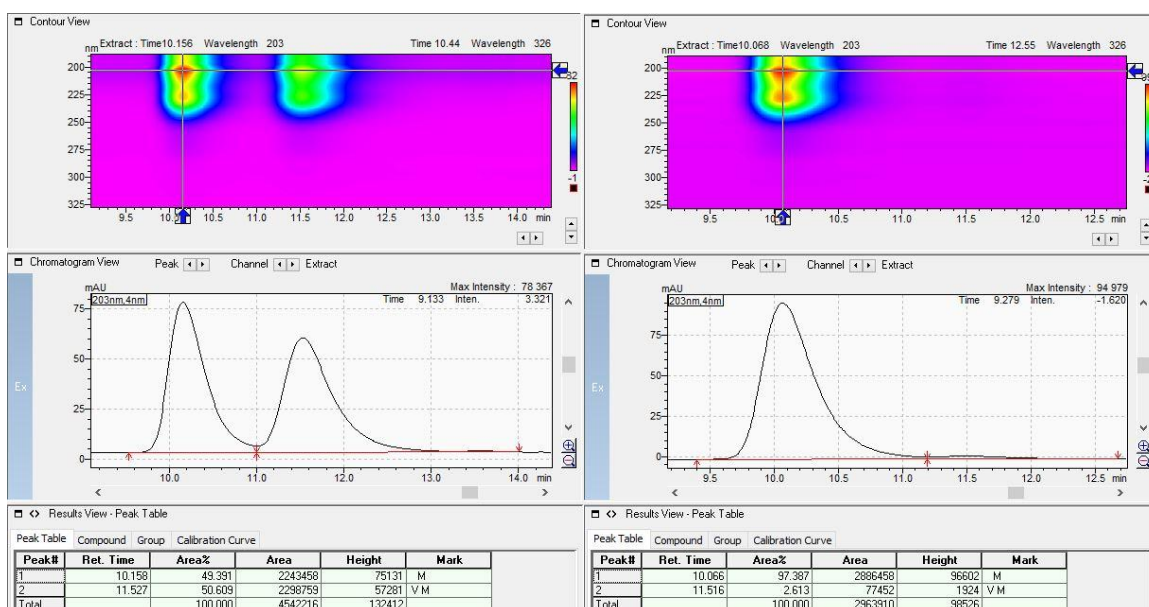
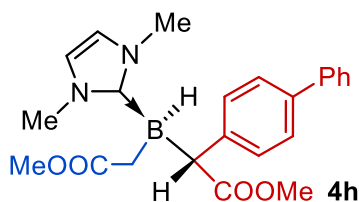


Figure S14. Chiral HPLC of the minor diastereomer of **4g**: racemic sample (left) and chiral product (right).

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxoethyl)(2-methoxy-2-oxo-1-([1,1'-biphenyl]-4-yl)ethyl)hydroborate (4h)



Reaction time 24h. Purification by preparative thin-layer chromatography, EA:DCM = 1:1. Analytical R_f = 0.5 and 0.3 (EA:PE=5:1).

Yields of the diastereomers using catalyst $Rh_2(OAc)_4$: 11 mg (27%) and 19 mg (47%). dr \approx 1:2.

Yields of the diastereomers using the catalyst **5**: 25 mg (62%), ee 94% and 10 mg (25%), ee 92%. dr \approx 5:2.

Analytical data are given for the major diastereomer. NMR spectra of the second diastereomer are similar, but broad due to the previously reported slow rotation around B-NHC bond.¹¹

¹H NMR (400 MHz, CDCl₃): δ 7.53 (d, 2H, J = 7.5 Hz, Ar), 7.45 – 7.30 (m, 4H, Ar), 7.30–7.25 (m, 3H, Ar + residual CHCl₃), 6.66 (s, 2H, NHC), 3.66 (s, 3H, COOMe), 3.50 (s, 6H, NMe), 3.45 (s, 3H, COOMe), 3.29 (br s, 1H, CH), 1.9–1.6 (m, 3H, CH₂ + BH).

¹¹B NMR (128 MHz, CDCl₃): δ -16.5 (s).

¹³C NMR (101 MHz, CDCl₃): δ 180.0 (COOMe), 178.7 (COOMe), 143.3, 141.3, 137.1, 128.8, 128.1, 126.9, 126.8, 126.2, 121.2, 51.0 (COOMe), 50.8 (COOMe), 36.6 (NMe). Signals of carbon atoms connected to boron were not observed apparently due to quadrupolar coupling.

HRMS: calculated for C₂₃H₂₈BN₂O₄⁺ [M+H]⁺: 407.2137, found 407.2145.

Chiral HPLC conditions for **major isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 80/20, t_R = 8.8 min for first peak, t_R = 10 min for second peak. Chiral HPLC conditions for **minor isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 80/20, t_R = 6.7 min for first peak, t_R = 8 min for second peak.

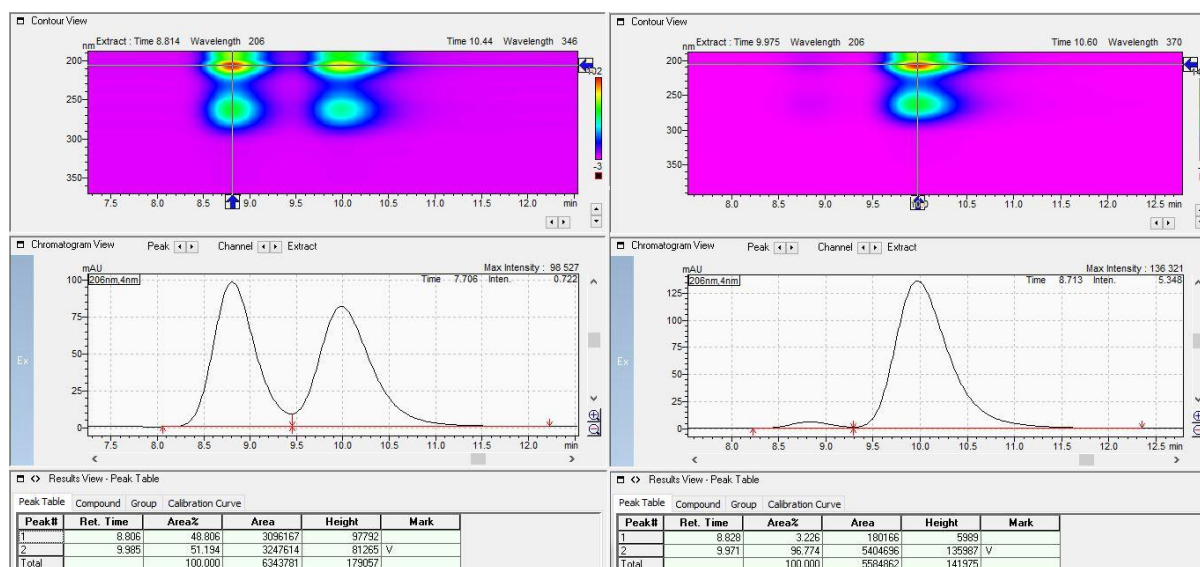


Figure S15. Chiral HPLC of the major diastereomer of **4h**: racemic sample (left) and chiral product (right).

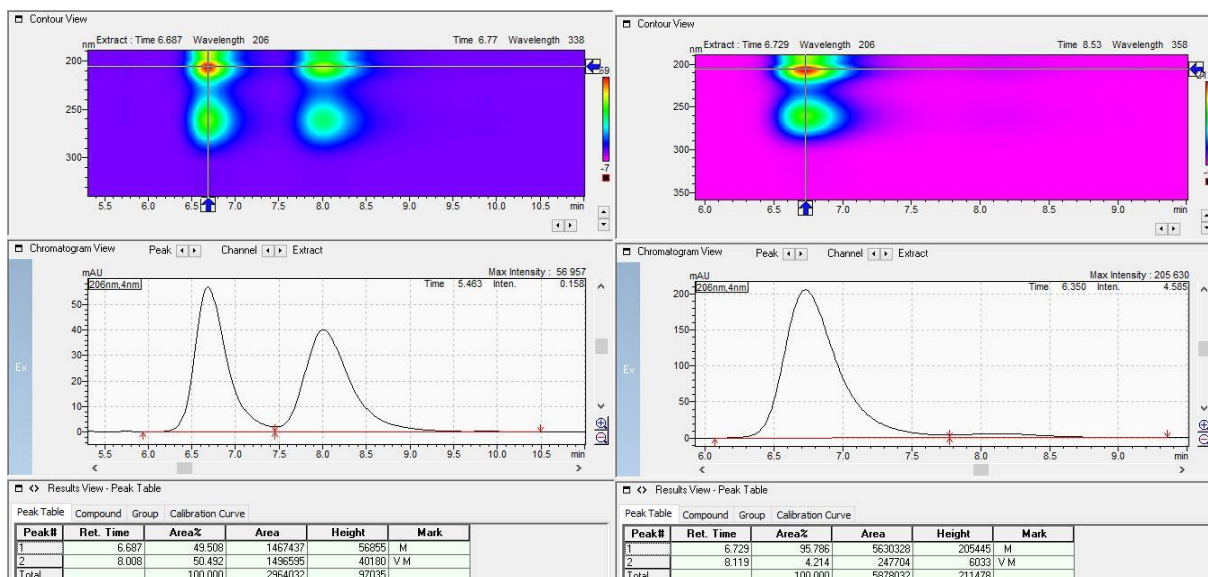
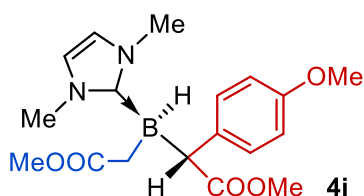


Figure S16. Chiral HPLC of the minor diastereomer of **4h**: racemic sample (left) and chiral product (right).

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxoethyl)(2-methoxy-2-oxo-1-(4-methoxyphenyl)ethyl)hydroborate (4i)



Reaction time 24h. Purification by preparative thin-layer chromatography, EA:n-hexane = 5:1. Analytical R_f = 0.4 and 0.31 (EA:PE=5:1).

Yields of the diastereomers using catalyst $Rh_2(OAc)_4$: 11 mg (31%) and 5 mg (14%). dr \approx 2:1.

Yields of the diastereomers using the catalyst **5**: 12 mg (33%), ee 93% and 3 mg (8%), ee 96%. dr \approx 4:1.

Analytical data are given for the major diastereomer. NMR spectra of the second diastereomer are similar, but broad due to the previously reported slow rotation around B-NHC bond.¹¹

1H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, 2H, J = 8.2 Hz, Ar), 6.70–6.60 (m, 4H, Ar + NHC), 3.71 (s, 3H, OMe), 3.63 (s, 3H, COOMe), 3.50 (s, 6H, NMe), 3.43 (s, 3H, COOMe), 3.17 (br s, 1H, CH), 1.90–1.6 (m, 3H, CH_2 + BH).

^{11}B NMR (128 MHz, $CDCl_3$): δ -16.7 (s).

^{13}C NMR (101 MHz, $CDCl_3$): δ 180.1 (\underline{C}_{COOMe}), 156.9 (\underline{C}_{Ar-OMe}), 136.2, 128.7, 121.2, 113.2, 55.4 (OMe), 50.9 (COOMe), 50.7 (COOMe), 36.5 (NMe). Signals of carbon atoms connected to boron were not observed apparently due to quadrupolar coupling. The second signal of \underline{C}_{COOMe} group were not observed apparently due to its low intensity.

HRMS: calculated for $C_{18}H_{26}BN_2O_5^+$ [$M+H$] $^+$: 361.1929, found 361.1937.

Chiral HPLC conditions for **major isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 80/20, t_R = 9.8 min for first peak, t_R = 11.5 min for second peak. Chiral HPLC conditions for **minor isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 80/20, t_R = 7.1 min for first peak, t_R = 8.3 min for second peak.

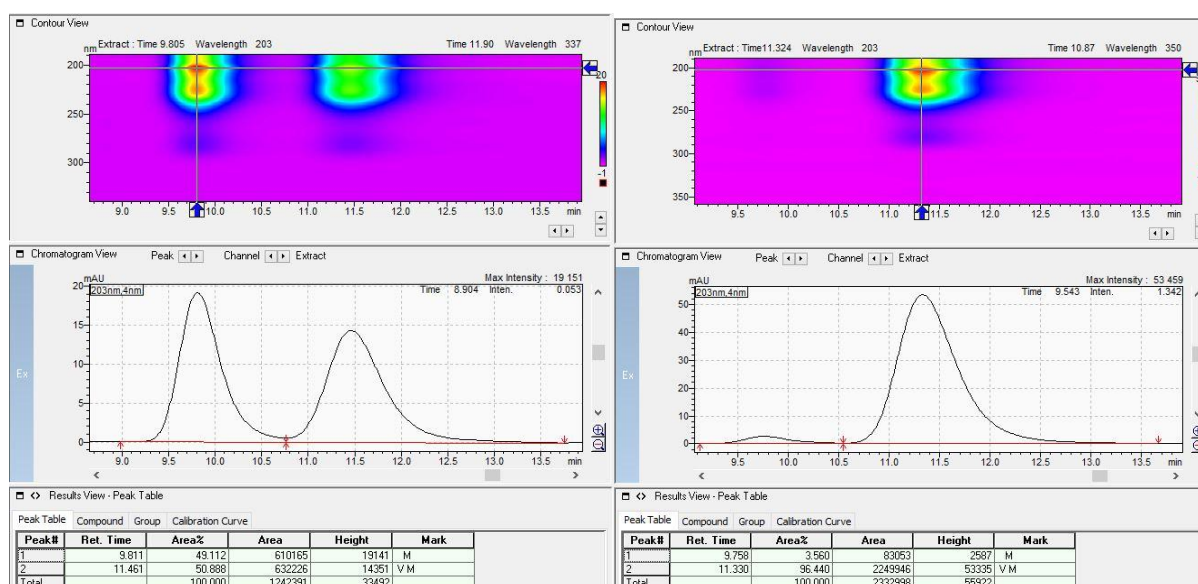


Figure S17. Chiral HPLC of the major diastereomer of **4i**: racemic sample (left) and chiral product (right).

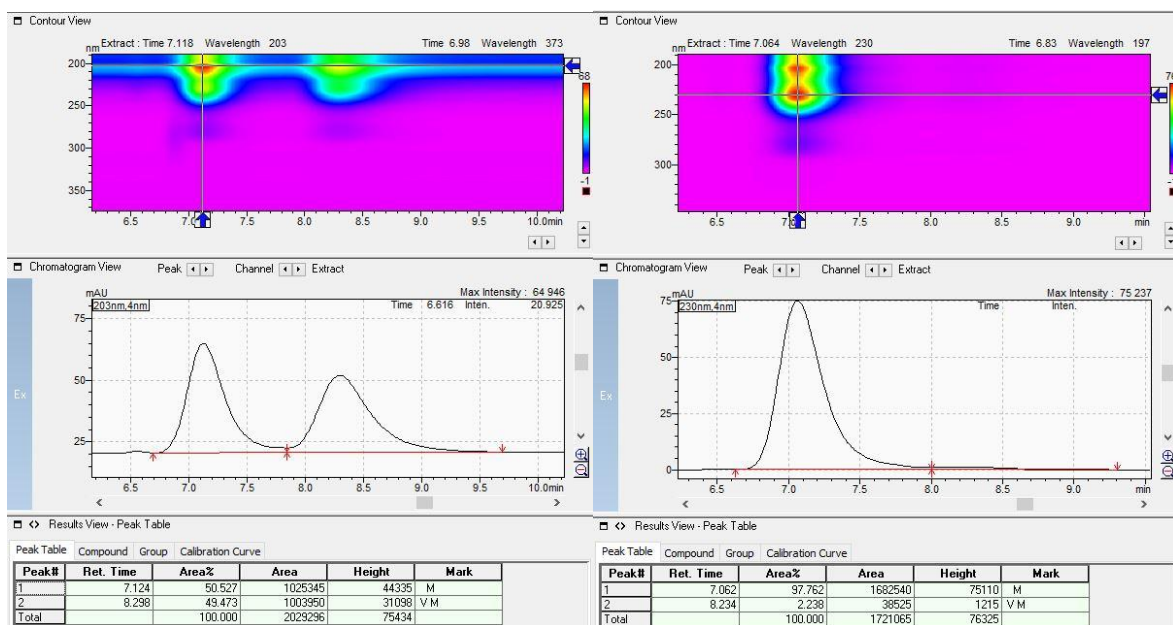
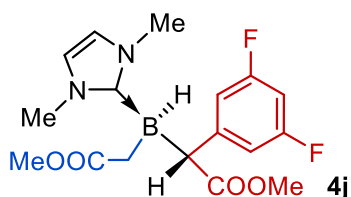


Figure S18. Chiral HPLC of the minor diastereomer of **4i**: racemic sample (left) and chiral product (right).

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxoethyl)(2-methoxy-2-oxo-1-(3,5-difluorophenyl)ethyl)hydroborate (4j)



The reaction using the catalyst $\text{Rh}_2(\text{OAc})_4$ is complete after 24h at RT. On the other hand, the reaction with the catalyst **5** does not reach completion even after 72h at 60 °C. However, it is much more selective and gives only one diastereomer. Purification was accomplished by flash chromatography, EA:DCM = 1:1. Analytical R_f = 0.58 and 0.5 (EA:PE=5:1).

Yields of the diastereomers using catalyst $\text{Rh}_2(\text{OAc})_4$: 19 mg (52%) and 13 mg (36%). dr \approx 3:2.

Yields of the only diastereomer using the catalyst **5**: 16 mg (44%), ee 92%, dr > 10:1.

Analytical data are given for the major diastereomer. NMR spectra of the second diastereomer are similar, but broad due to the previously reported slow rotation around B-NHC bond.¹¹

¹H NMR (400 MHz, CDCl_3): δ 6.77 (d, 2H, 4J = 8.0 Hz, Ar), 6.73 (s, 2H, NHC), 6.44 (t, 4J = 8.0, 1H, Ar), 3.65 (s, 3H, COOMe), 3.55 (s, 6H, NMe), 3.43 (s, 3H, COOMe), 3.22 (br s, 1H, CH), 1.9–1.6 (m, 3H, CH_2 + BH).

¹¹B{¹H} NMR (128 MHz, CDCl_3): δ -16.5 (s). ¹⁹F NMR (282 MHz, CDCl_3): δ -112.0 (s).

¹³C NMR (101 MHz, CDCl_3): δ 179.5 (COOMe), 177.5 (COOMe), 163.6 and 161.1 (m, C-F), 121.3 (NHC), 110.1 (d, $J_{\text{C-F}}$ = 24.4 Hz, ortho-Ar), 99.4 (t, $J_{\text{C-F}}$ = 25.3 Hz, para-Ar), 51.0 (COOMe), 50.6 (COOMe), 36.4 (NMe). Signals of carbon atoms connected to boron were not observed apparently due to quadrupolar coupling. One signal of aromatic quaternary carbon was not observed apparently due to its low intensity.

HRMS: calculated for $\text{C}_{17}\text{H}_{22}\text{BF}_2\text{N}_2\text{O}_4^+$ [M+H]⁺: 367.1635, found: 367.1641.

Chiral HPLC conditions for **major isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 80/20, t_R = 6.6 min for first peak, t_R = 8.9 min for second peak.

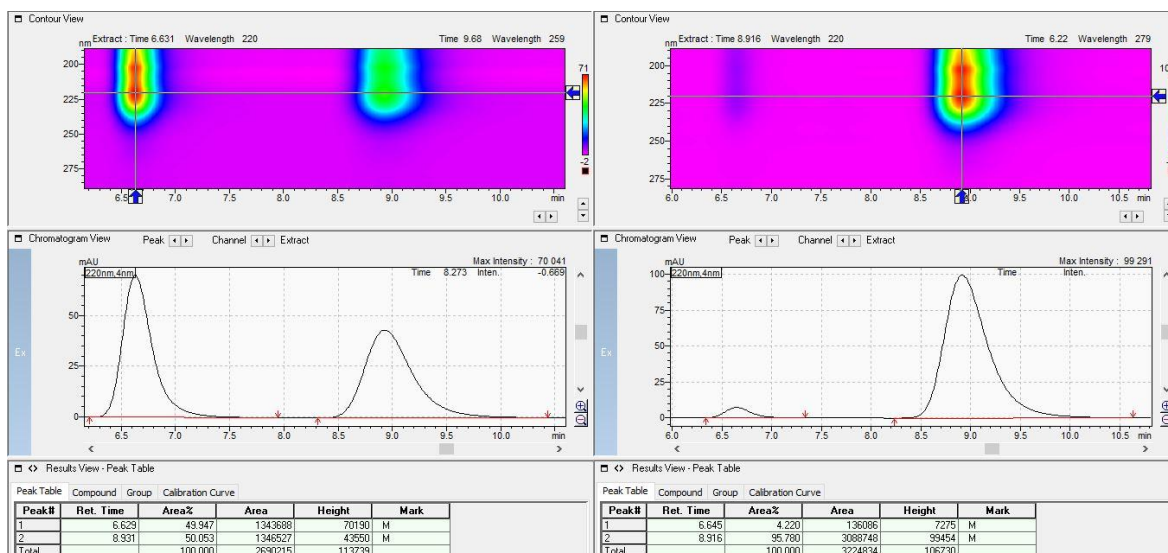
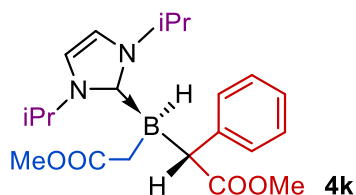


Figure S19. Chiral HPLC of **4j**: racemic sample (left) and chiral product (right).

(1,3-diisopropyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxoethyl)(2-methoxy-2-oxo-1-phenylethyl)hydroborate (4k)



Reaction time 48h. Purification by flash chromatography, DCM:EtOAc = 20:1. Major isomer is eluted in the second fraction. Analytical R_f = 0.51 and 0.38 (PE:EA=2:1).

Yields of the diastereomers using catalyst $\text{Rh}_2(\text{OAc})_4$: 18 mg (47%) and 17 mg (44%). dr \approx 1:1.

Yields of the diastereomers using the catalyst **5**: 25 mg (65%), *ee* 97% and 5 mg (13%), *ee* 90%. dr \approx 5:1.

Analytical data are given for the major diastereomer. NMR spectra of the second diastereomer are similar, but broad due to the previously reported slow rotation around B-NHC bond.¹¹ Noteworthy ^1H NMR spectrum suggests that such rotation is completely blocked for the major diastereomer.

^1H NMR (400 MHz, CDCl_3): δ 7.27 (m, 2H, Ar + residual CHCl_3), 7.06 (t, J = 7.6 Hz, 2H, Ar), 6.94 (t, J = 7.6 Hz, 1H, Ar), 6.90 (s, 1H, NHC), 6.76 (s, 1H, NHC), 5.03 (appears as q, J = 6.5 Hz, 1H, CH^{iPr}), 4.93 (appears as q, J = 6.5 Hz, 1H, CH^{iPr}), 3.66 (s, 3H, COOMe), 3.40 (s, 3H, COOMe), 3.14 (br d, J = 8.1 Hz, 1H, CH), 1.80 (m, 2H, CH_2), 1.59 (d, J = 6.5 Hz, 3H, iPr), 1.53 (d, J = 6.5 Hz, 3H, iPr), 1.13 (d, J = 6.5 Hz, 3H, iPr), 0.78 (d, J = 6.5 Hz, 3H, iPr).

^{11}B NMR (128 MHz, CDCl_3): δ -16.56 (s).

^{13}C NMR (101 MHz, CDCl_3): δ 179.8 ($\underline{\text{C}}\text{OOMe}$), 178.2 ($\underline{\text{C}}\text{OOMe}$), 144.4, 128.3, 127.6, 124.4, 116.4, 116.2, 50.9, 50.5, 49.7, 49.3, 23.8, 23.6, 22.1. Signals of carbon atoms connected to boron were not observed apparently due to quadrupolar coupling.

HRMS: calculated for $\text{C}_{21}\text{H}_{32}\text{BN}_2\text{O}_4^+$, $[\text{M}+\text{H}]^+$: 387.2450, found 387.2452

Chiral HPLC conditions for **major isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 95/5, t_R = 8.9 min for first peak, t_R = 10.6 min for second peak. Chiral HPLC conditions for **minor isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 95/5, t_R = 6.95 min for first peak, t_R = 10.95 min for second peak.

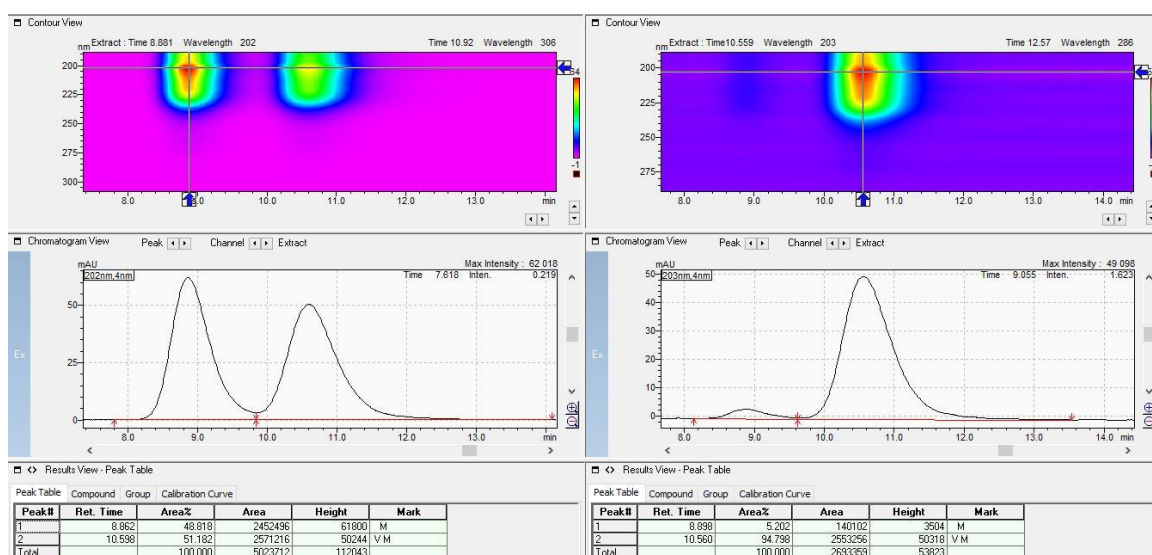


Figure S20. Chiral HPLC of the major diastereomer of **4k**: racemic sample (left) and chiral product (right).

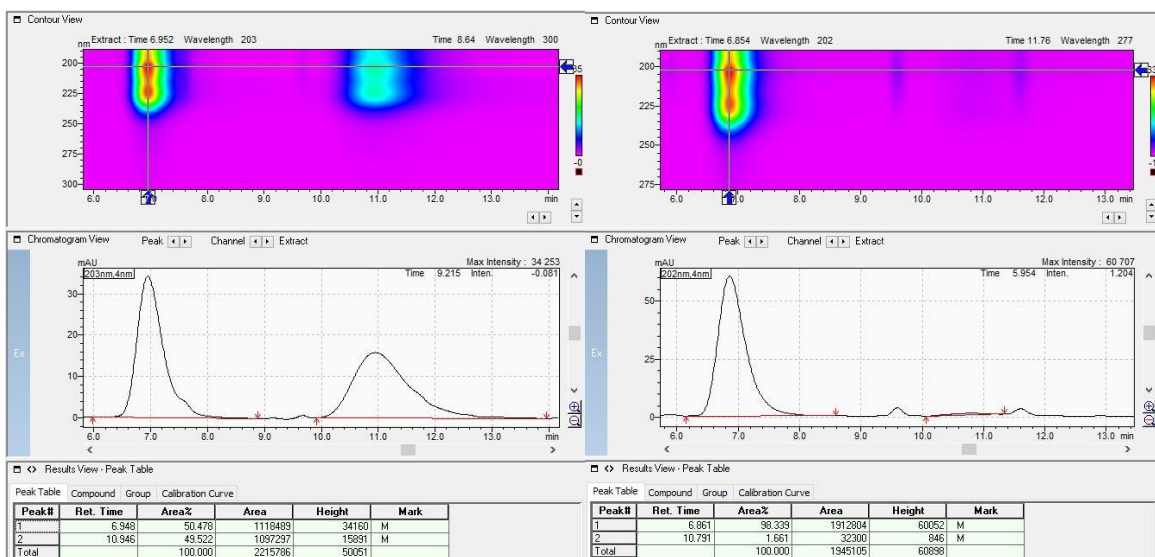
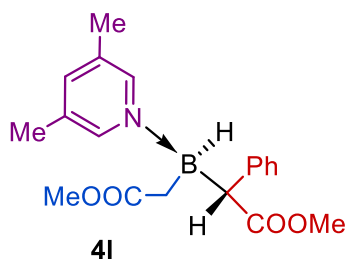


Figure S21. Chiral HPLC of the minor diastereomer of **4k**: racemic sample (left) and chiral product (right).

(3,5-dimethyl-pyridin-1-yl)(2-methoxy-2-oxoethyl)(2-methoxy-2-oxo-1-phenylethyl)hydroborate (4l)



Reaction time 24h. Purification by flash chromatography, EA:n-hexane = 5:2. We could not separate the diastereomers. Analytical R_f = 0.73 (EA:PE=5:1).

Yields of the diastereomers using catalyst $Rh_2(OAc)_4$: 13 mg (49%), dr \approx 1:1.

Yields of the diastereomers using the catalyst **5**: 11 mg (45%), dr \approx 1:1, *ee* 25% for first diastereomer, *ee* 33% for second diastereomer.

Analytical data are given for the mixture of diastereomers.

1H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 2H, Py), 7.70 (s, 2H, Py), 7.59 (s, 1H, Py), 7.51 (s, 1H, Py), 7.20–7.13 (m, 4H, Ph), 7.11–6.98 (m, 6H, Ph), 3.63 (s, 3H, COOMe), 3.45 (s, 3H, COOMe), 3.44 (s, 3H, COOMe), 3.37 (s, 3H, COOMe), 3.29 (d, J = 5.6 Hz, 1H, CH), 3.20 (d, J = 4.0 Hz, 1H, CH), 2.34 (s, 6H, Me^{Py}), 2.25 (s, 6H, Me^{Py}), 1.95 (dd, J = 12.0, 3.4 Hz, 1H, CH₂), 1.83 (dd, J = 12.0, 3.4 Hz, 1H, CH₂), 1.77 (dd, J = 12.0, 8.0 Hz, 1H, CH₂), 1.69 (dd, J = 12.0, 8.0 Hz, 1H, CH₂).

$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ 0.0 (s).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.7 (COOMe), 178.6 (COOMe), 144.3, 144.1, 142.2, 142.0, 134.9, 134.7, 128.3, 128.1, 127.8, 127.6, 124.8, 124.7, 51.0 (COOMe), 50.8 (COOMe), 18.5 (Me), 18.4 (Me). Signals of quaternary carbon atoms as well as carbons connected to boron were not observed because of too low intensity.

HRMS: calculated for $C_{19}H_{25}BNO_4^+$ [M+H]: 342.1871, found: 342.1879.

Chiral HPLC was carried out for the mixture of diastereomers using Chiralpak IH-3 (4.6 \times 150 mm), heptane/*i*PrOH = 98/2. Retention times for enantiomers of the first diastereomer are t_R = 21 and 24.6 min; for enantiomers of the second diastereomer are t_R = 34.1 and 36.3 min.

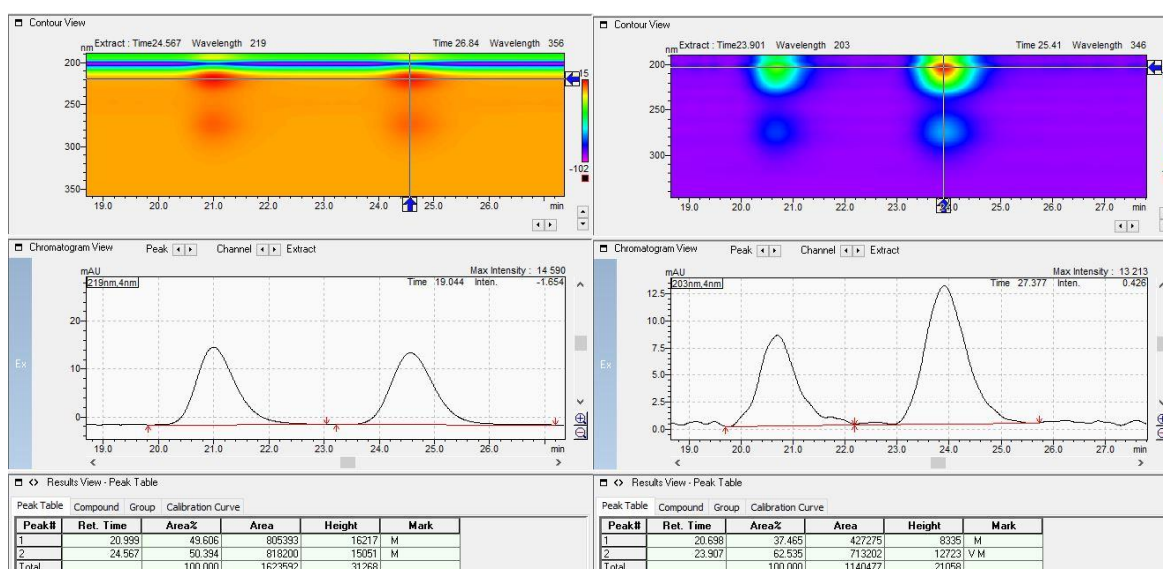


Figure S22. Chiral HPLC of the first diastereomer of **4l**: racemic sample (left) and chiral product (right).

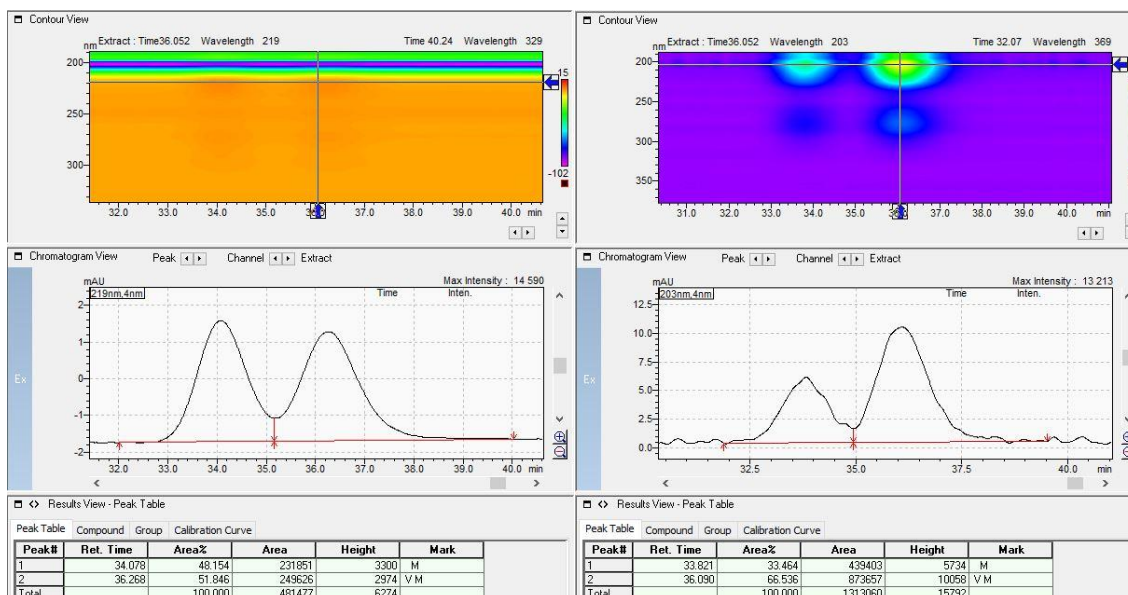
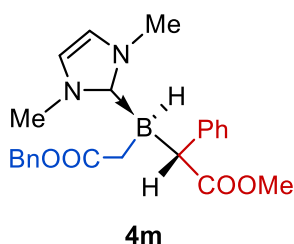


Figure S23. Chiral HPLC of the second diastereomer of **4I**: racemic sample (left) and chiral product (right).

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-benzyloxy-2-oxoethyl)(2-methoxy-2-oxo-1-phenylethyl)hydroborate (4m)



Reaction time 24h. Purification by preparative thin-layer chromatography, EA:DCM = 1:1. Analytical R_f = 0.61 and 0.51 (EA:PE=5:1).

Yields of the diastereomers using catalyst $Rh_2(OAc)_4$: 15 mg (37%) and 20 mg (49%). dr \approx 3:4.

Yields of the diastereomers using the catalyst **5**: 26 mg (64%), *ee* 95% and 12 mg (30%), *ee* 94%. dr \approx 2:1.

Analytical data are given for the major diastereomer. NMR spectra of the second diastereomer are similar, but broad due to the previously reported slow rotation around B-NHC bond.¹¹

¹H NMR (400 MHz, CDCl₃): δ 7.33–6.90 (m, 10H, 2Ph + residual CHCl₃), 6.53 (s, 2H, NHC), 4.87 (m, 2H, CH₂Ph), 3.64 (s, 3H, COOMe), 3.35 (s, 6H, NMe), 3.21 (br s, 1H, CH), 2.0–1.6 (m, 3H, CH₂+BH).

¹¹B NMR (128 MHz, CDCl₃): δ -16.5 (s).

¹³C NMR (101 MHz, CDCl₃): δ 179.2 + 178.6 (COOMe and COOBn), 144.0, 137.5, 128.3, 127.7, 127.6, 127.6, 124.3, 121.0, 64.8 (CH₂Ph), 50.9 (COOMe), 48.5 (C–B), 36.4 (NMe), 27.8 (C–B). Signals of carbons connected to boron atom are broad due to quadrupole splitting.

HRMS: calculated for C₂₉H₂₈BN₂O₄⁺ [M–Me]⁺: 407.2137, found: 407.2139.

Chiral HPLC conditions for **major isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 80/20, t_R = 7 min for first peak, t_R = 11.1 min for second peak. Chiral HPLC conditions for **minor isomer**: Chiralpak IH-3 (4.6 \times 150 mm), heptane/iPrOH = 80/20, t_R = 6.4 min for first peak, t_R = 8.3 min for second peak.

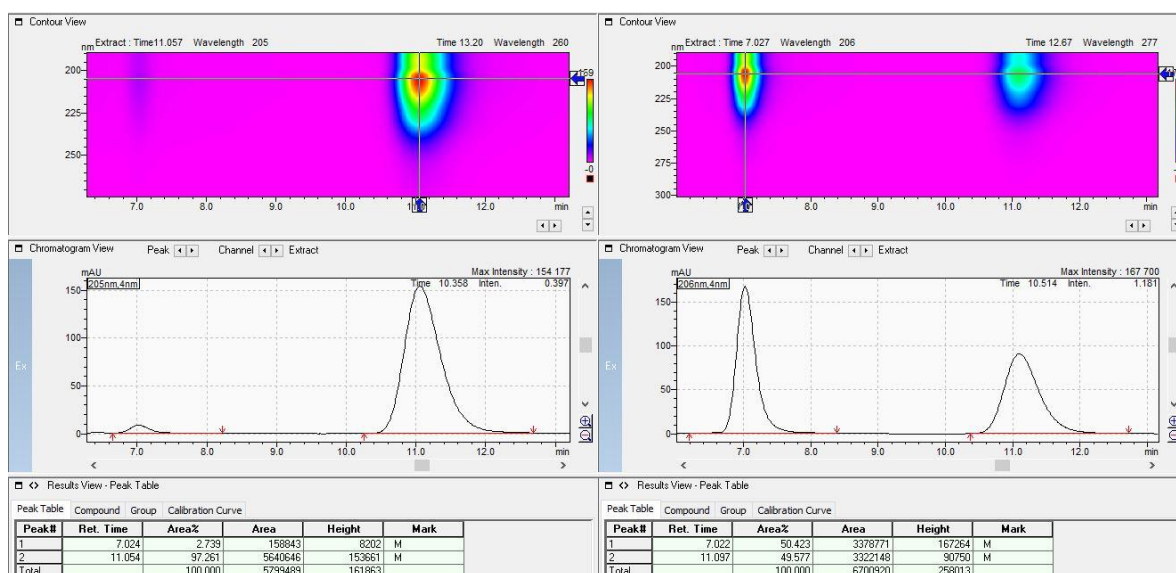


Figure S24. Chiral HPLC of the major diastereomer of **4m**: racemate (left) and chiral product (right).

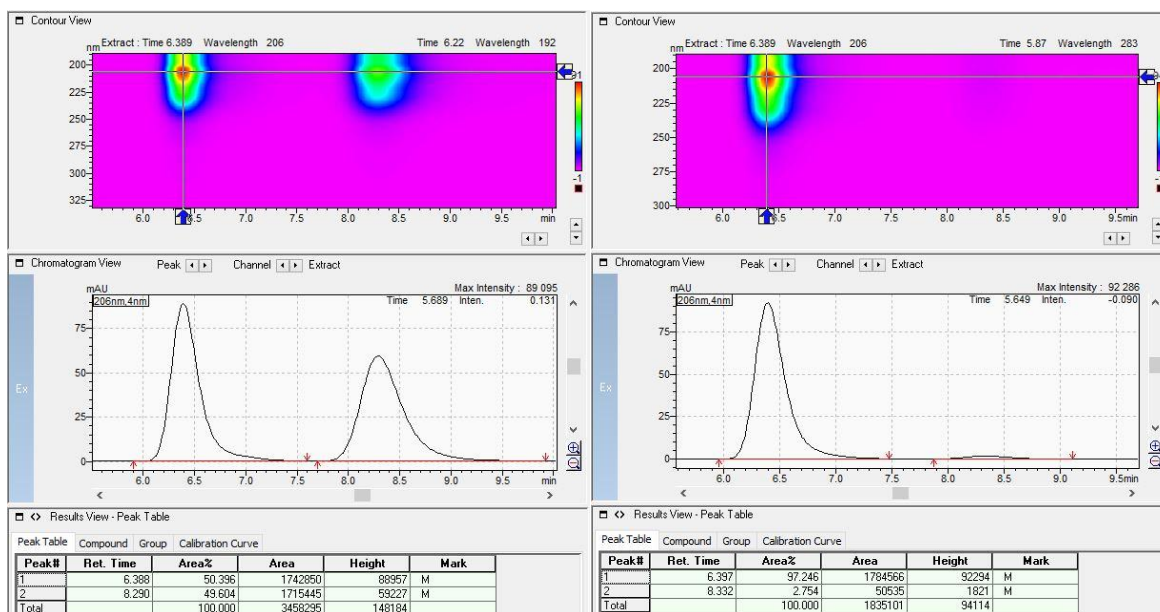
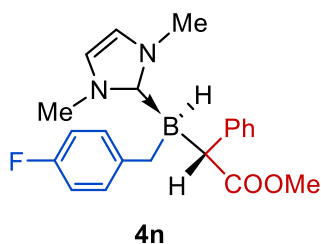


Figure S25. Chiral HPLC of the minor diastereomer of **4m**: racemate (left) and chiral product (right).

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(*p*-fluorobenzyl)(2-methoxy-2-oxo-1-phenylethyl)hydroborate (4n)



Reaction time 24h. Purification by preparative thin-layer chromatography, EA:n-hexane = 5:1. Analytical R_f = 0.85 and 0.73 (EA:PE=5:1).

Unstable! Requires storage under nitrogen at -20 °C.

Yields of the diastereomers using catalyst $Rh_2(OAc)_4$: 10 mg (27%) and 6 mg (16%). dr \approx 2:1.

Yields of the diastereomers using the catalyst **5**: 10 mg (27%), *ee* 86% and 5 mg (14%), *ee* 78%. dr \approx 2:1.

Spectral data given for the major diastereomer. The product slowly decomposed in solution, which complicated complete characterization (in particular measurement of ^{13}C NMR spectra).

1H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, J = 7.5 Hz, 2H, Ph), 7.07 (t, J = 7.5 Hz, 2H, Ph), 6.95 (m, 1H, Ph), 6.86 (m, 2H, Ar), 6.71 (m, 2H, Ar), 6.52 (s, 2H, NHC), 3.67 (s, 3H, COOMe), 3.41 (br s, 6H, NMe, broad due to slow rotation), 3.30 (br s, 1H, CH), 2.13 (m, 1H, CH_2), 1.95 (m, 1H, CH_2), 1.62 (BH + residual H_2O).

$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -14.2.

^{19}F NMR (282 MHz, $CDCl_3$): δ -122.43.

^{13}C NMR (101 MHz, $CDCl_3$): δ 128.9, 128.8, 127.7, 127.6, 124.2, 120.8, 114.2, 114.0, 50.9 (COOMe). Some signals are not observed due to their low intensity and low sample concentration. It was not possible to reliably assign C-F coupling constants.

HRMS: calculated for $C_{21}H_{24}BFN_2NaO_2^+$ [$M+Na$] $^+$ 389.1807, found 389.1811

Chiral HPLC conditions for **major isomer**: Chiralpak IB-3 (4.6 \times 150 mm), heptane/*i*PrOH = 90/10, t_R = 8.7 min for first peak, t_R = 10.7 min for second peak. Chiral HPLC conditions for **minor isomer**: Chiralpak IB-3 (4.6 \times 150 mm), heptane/*i*PrOH = 90/10, t_R = 28.9 min for first peak, t_R = 31.1 min for second peak.

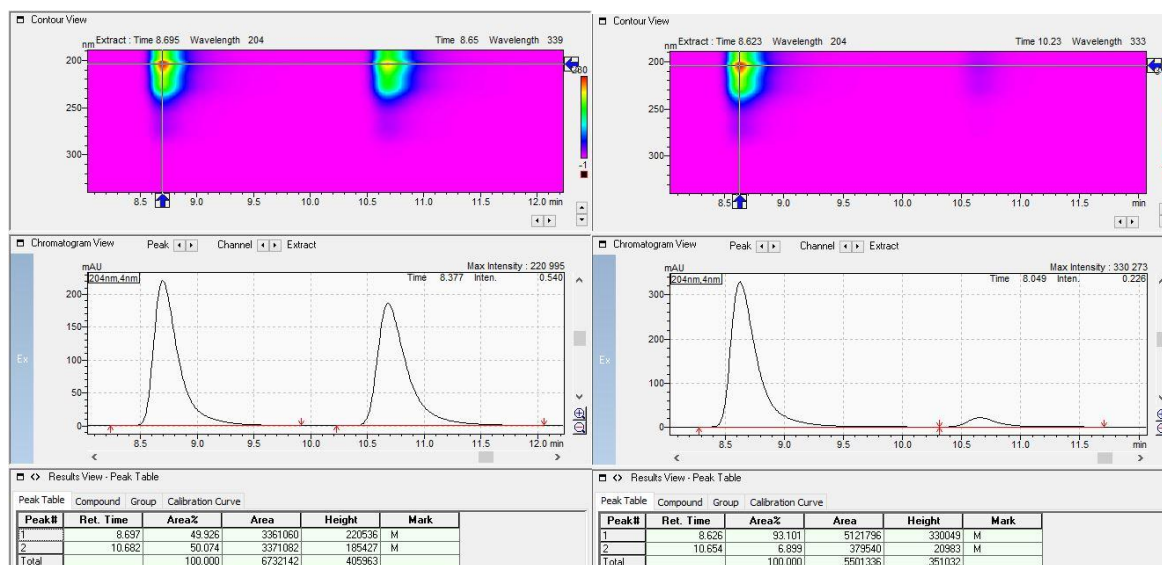


Figure S26. Chiral HPLC of the major diastereomer of **4n**: racemate (left) and chiral product (right).

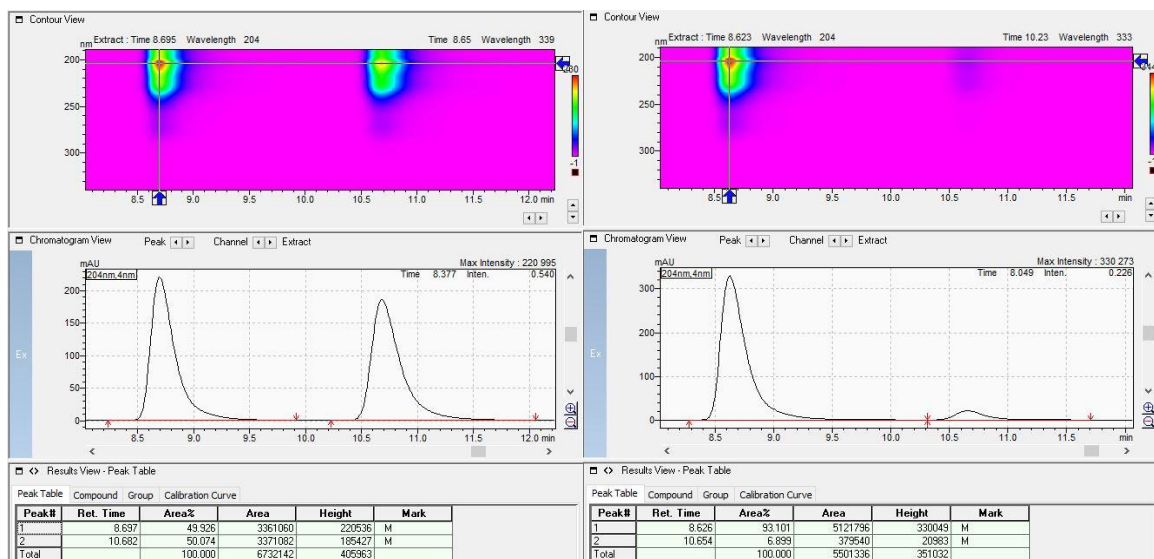
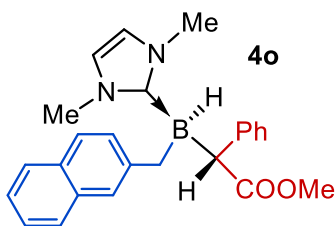


Figure S27. Chiral HPLC of the minor diastereomer of **4n**: racemate (left) and chiral product (right).

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(naphthalen-2-yl-methyl)(2-methoxy-2-oxo-1-phenyl)ethyl)hydroborate (4o)



Reaction time 24h. Purification by preparative thin-layer chromatography, EA:n-hexane = 3:1. Analytical R_f = 0.76 and 0.66 (EA:PE=5:1).

Unstable! Requires storage under nitrogen at -20 °C.

Yields of the diastereomers using catalyst $Rh_2(OAc)_4$: 18 mg (45%) and 15 mg (38%), dr \approx 1:1.

Yields of the diastereomers using the catalyst **5**: 15 mg (38%), *ee* 93% and 8 mg (20%), *ee* 92%, dr \approx 2:1.

Spectral data given for the major diastereomer. The product slowly decomposed in solution, which complicated complete characterization (in particular measurement of ^{13}C NMR spectra).

1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, 1H, J = 7.8 Hz, Ar), 7.58 – 7.51 (m, 2H, Ar), 7.33 – 7.20 (m, 7H, Ar), 7.08 (t, 2H, J = 7.5 Hz, Ar), 6.96 (t, 1H, J = 7.3 Hz, Ar), 6.45 (s, 2H, NHC), 3.70 (s, 3H, COOMe), 3.66 – 3.0 (br s, 6H, NMe, broad due to slow rotation along NHC-B bond¹¹), 3.37 (br d, 1H, J = 6.6 Hz, CH), 2.37 (m, 1H, CH_2), 2.17 (m, 1H, CH_2) 1.3–1.8 (br d, BH).

^{11}B NMR (128 MHz, $CDCl_3$): δ -14.14 (s)

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.35 (COOMe), 147.3, 144.8, 134.0, 128.6, 127.9, 127.6, 127.5, 126.9, 126.8, 125.2, 124.3, 124.2, 123.6, 120.8, 50.9 (COOMe), 36.2 (NMe). Signals of carbons connected to boron atom are not observed due to quadrupole splitting.

HRMS: calculated for $C_{25}H_{27}BN_2NaO_2^+ [M+Na]^+$ 421.2058, found 421.2064

Chiral HPLC conditions for **major isomer**: Chiralpak IB-3 (4.6 \times 150 mm), heptane/iPrOH = 90/10, t_R = 9.5 min for first peak, t_R = 11.1 min for second peak. Chiral HPLC conditions for **minor isomer**: Chiralpak IB-3 (4.6 \times 150 mm), heptane/iPrOH = 90/10, t_R = 8.9 min for first peak, t_R = 9.8 min for second peak.

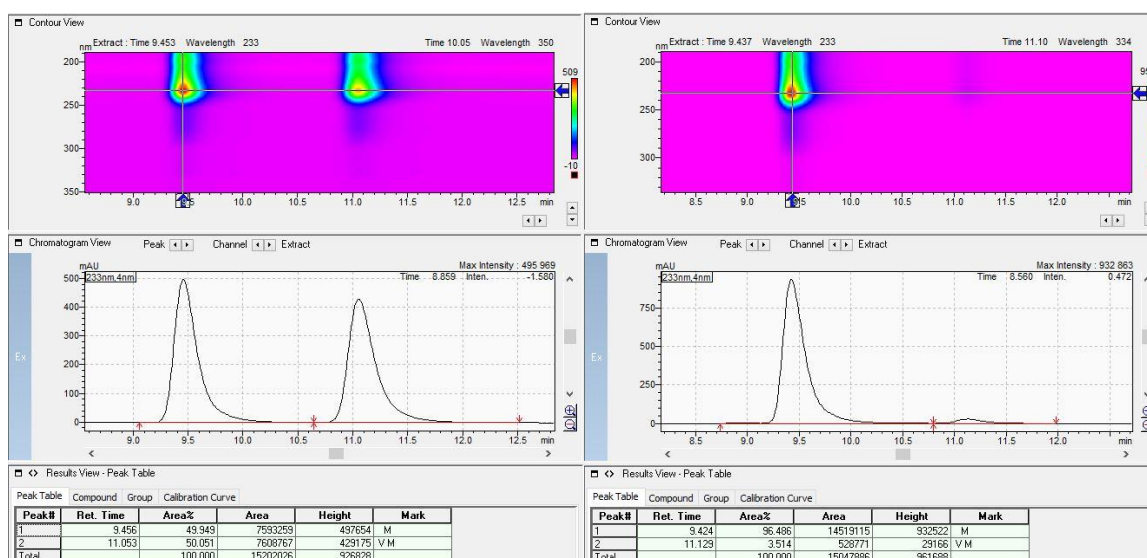


Figure S28. Chiral HPLC of the major diastereomer of **4o**: racemate (left) and chiral product (right).

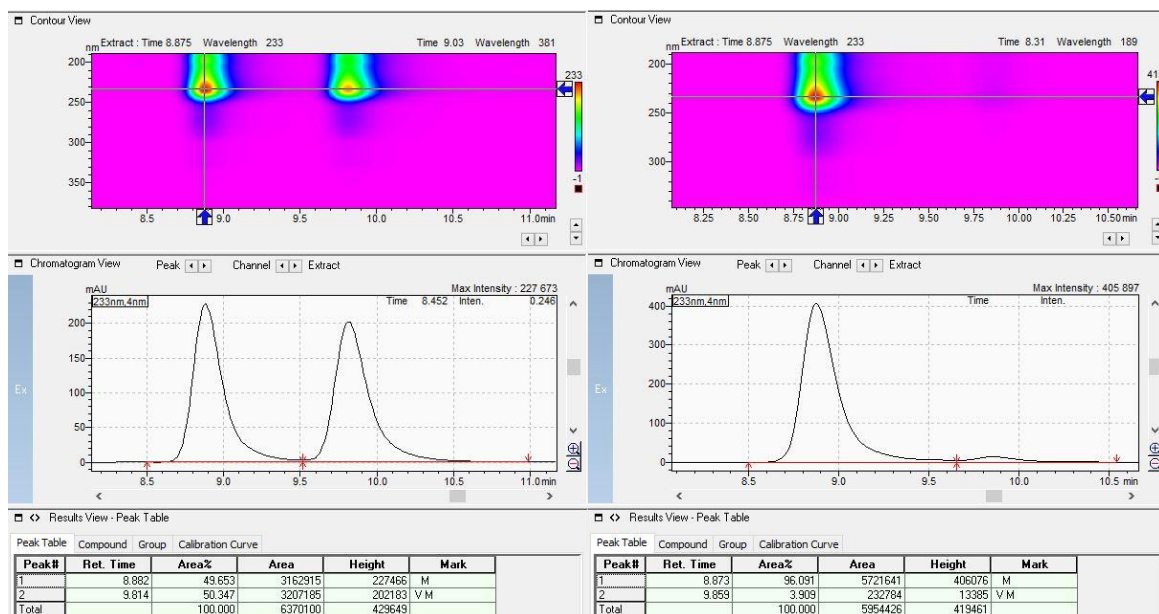


Figure S29. Chiral HPLC of the minor diastereomer of **4o**: racemate (left) and chiral product (right).

X-ray diffraction studies

X-ray diffraction data for **4e** were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutter-less ω -scan technique), using graphite monochromatized Cu K α -radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program (Version 1.171.41.106a, Rigaku Oxford Diffraction, 2021). The structure was solved by direct methods using SHELXT¹² and refined on F2 using SHELXL-2018 in the OLEX2 program.¹³ All non-hydrogen atoms were refined with individual anisotropic displacement parameters. Hydrogen atom of BH group was found in difference Fourier synthesis while positions of other hydrogens were calculated, and they all were refined in the isotropic approximation within the riding model. The refinement of the structure was somewhat problematic because of poor quality of the crystals, which were very difficult to grow. Nevertheless, the Flack parameter was equal to 0.02(2), indicating the correct assignment of absolute configuration. The crystal data and structure refinement parameters are given in Table S2. CCDC 2356996 contains the supplementary crystallographic data for **4e**.

Table S2. Crystal data and structure refinement parameters for **4e**.

Empirical formula	C ₁₇ H ₂₂ BBrN ₂ O ₄
Formula weight	409.08
Temperature	100.15 K
Wavelength	1.54184 Å
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	a = 8.2775(3) Å, α = 90°.
	b = 8.4391(4) Å, β = 90°.
	c = 27.6673(14) Å, γ = 90°.
Volume	1932.69(15) Å ³
Z	4
Density (calculated)	1.406 g/cm ³
Absorption coefficient	3.093 mm ⁻¹
F(000)	840
Crystal size	0.17 x 0.05 x 0.03 mm
Theta range for data collection	5.480 to 79.565°.
Index ranges	-9<=h<=8, -10<=k<=10, -33<=l<=35
Reflections collected	10888
Independent reflections	3771 [R(int) = 0.0754]
Observed reflections	3276
Completeness to theta = 67.684°	96.1 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.717
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3771 / 0 / 230
Goodness-of-fit on F2	1.128
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0842, wR2 = 0.2029
R indices (all data)	R1 = 0.0933, wR2 = 0.2076
Flack parameter	0.02(2)
Extinction coefficient	n/a
Largest diff. peak and hole	1.690 and -0.822 e.E ⁻³

NMR Spectra

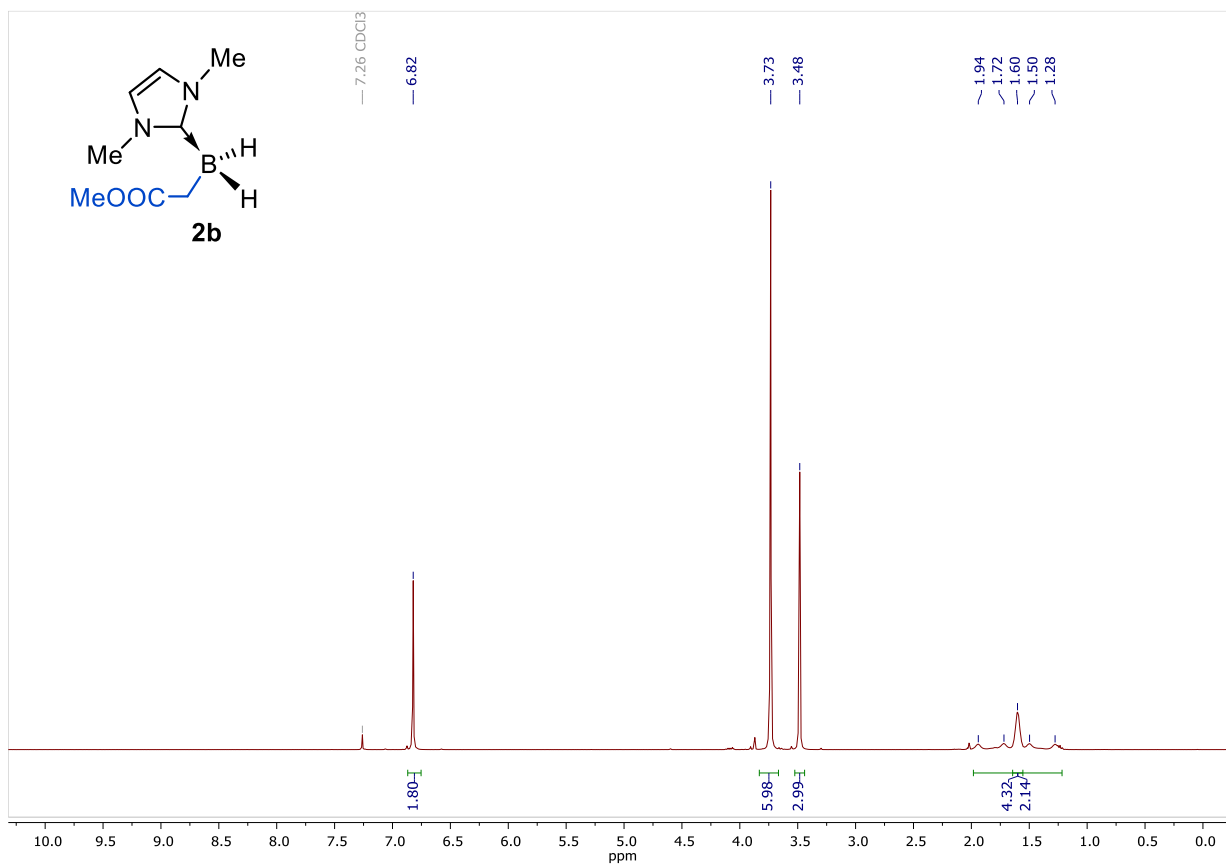


Figure S30. ¹H NMR spectrum of **2b** in CDCl₃.

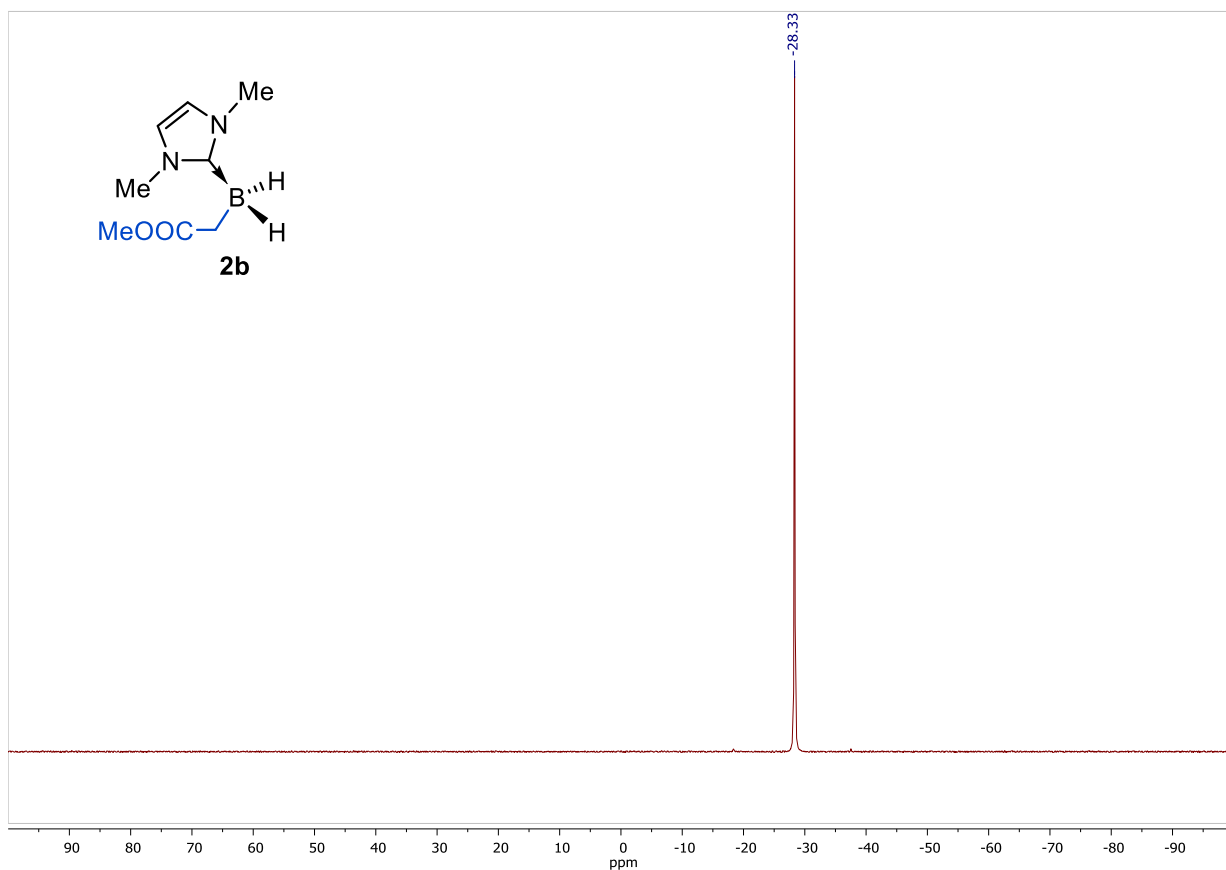


Figure S31. ¹¹B{¹H} NMR spectrum of **2b** in CDCl₃.

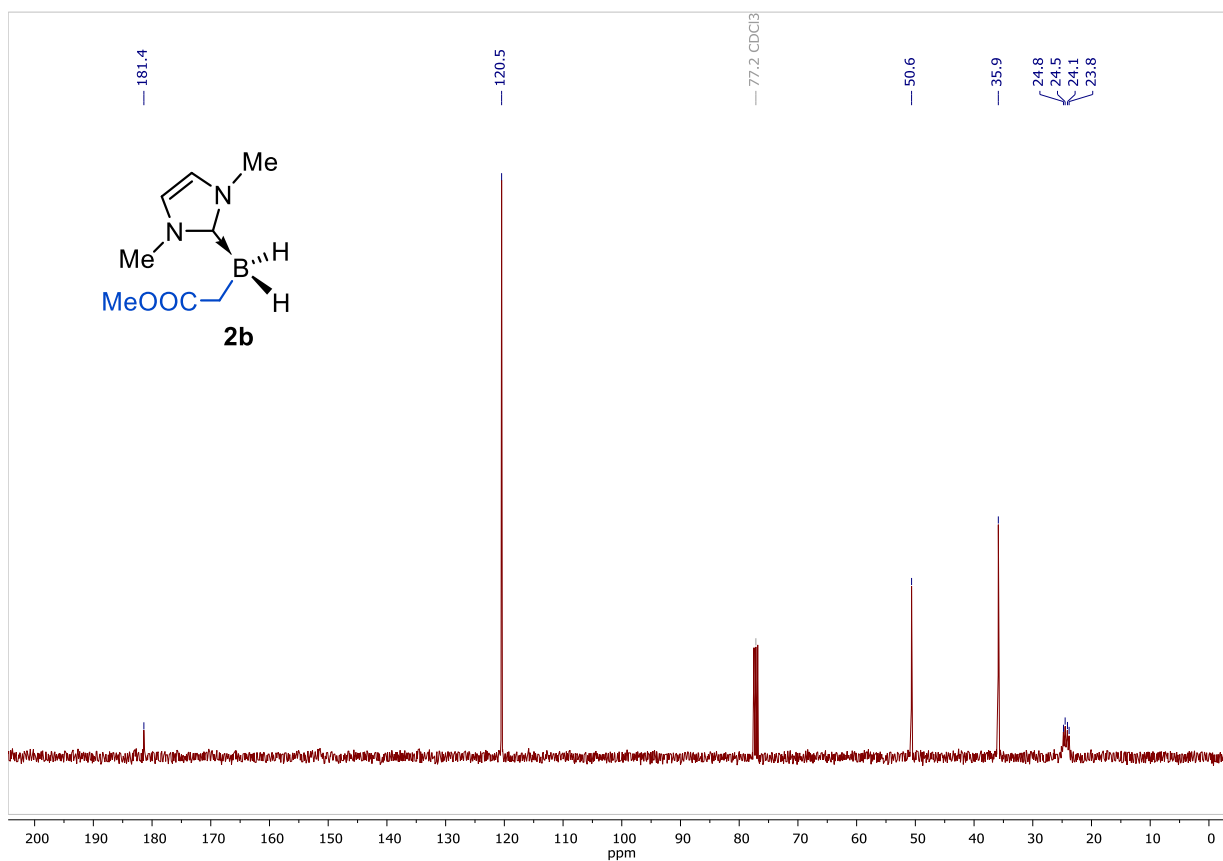


Figure S32. ^{13}C NMR spectrum of **2b** in CDCl_3 .

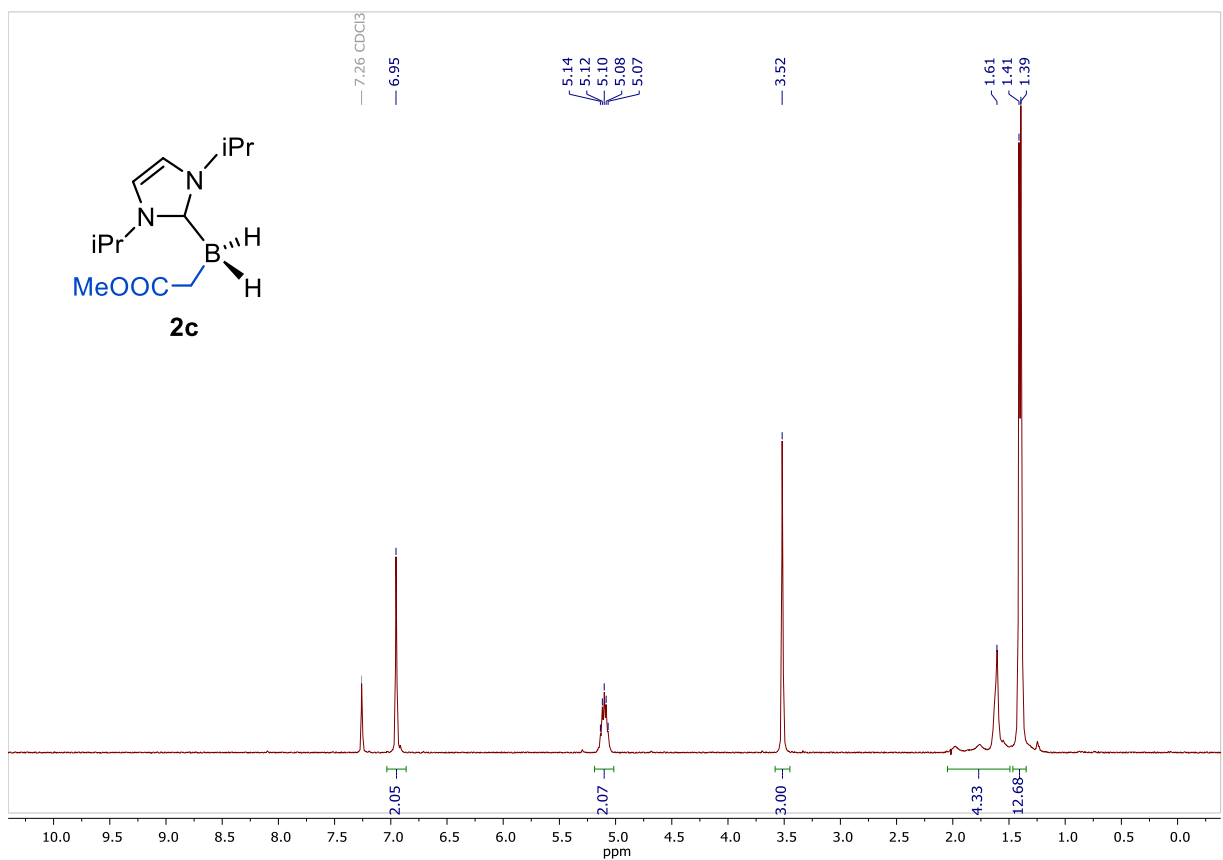


Figure S33. ^1H NMR spectrum of **2c** in CDCl_3 .

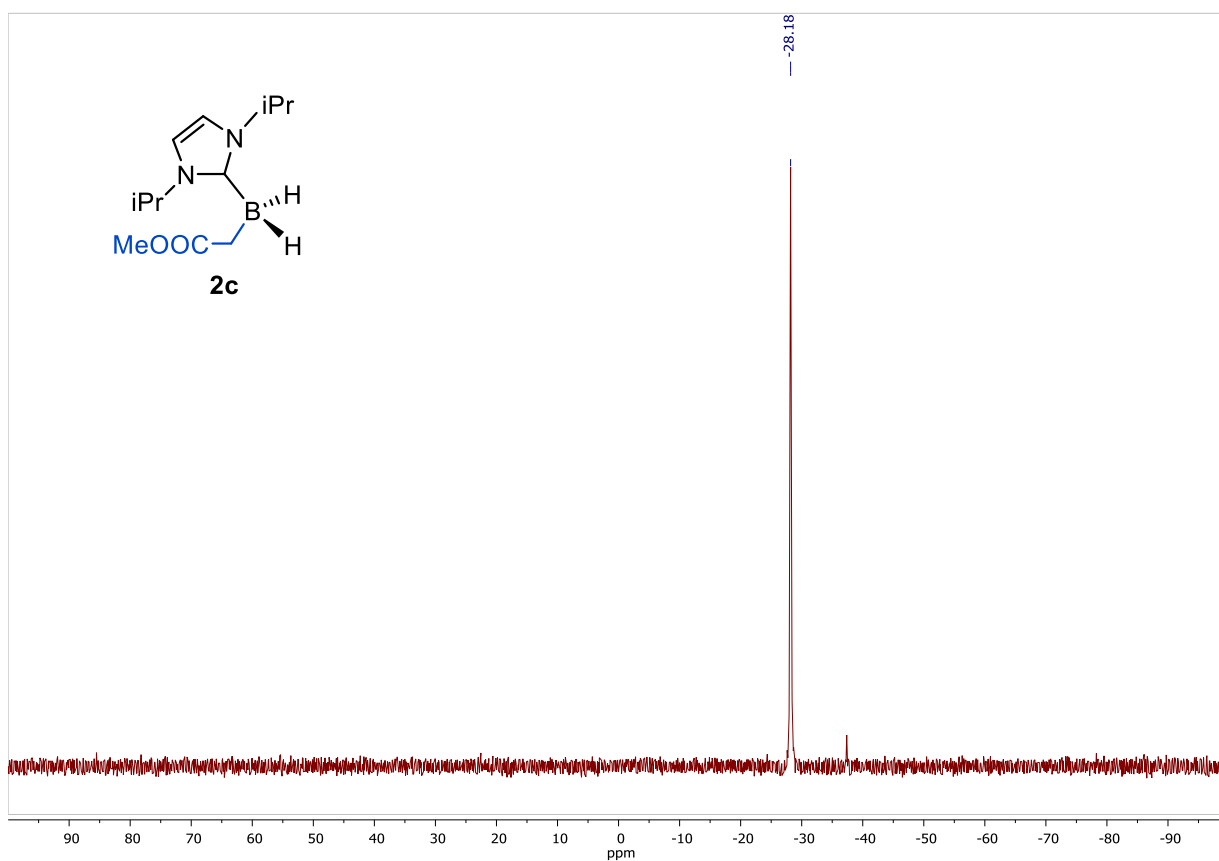


Figure S34. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **2c** in CDCl_3 .

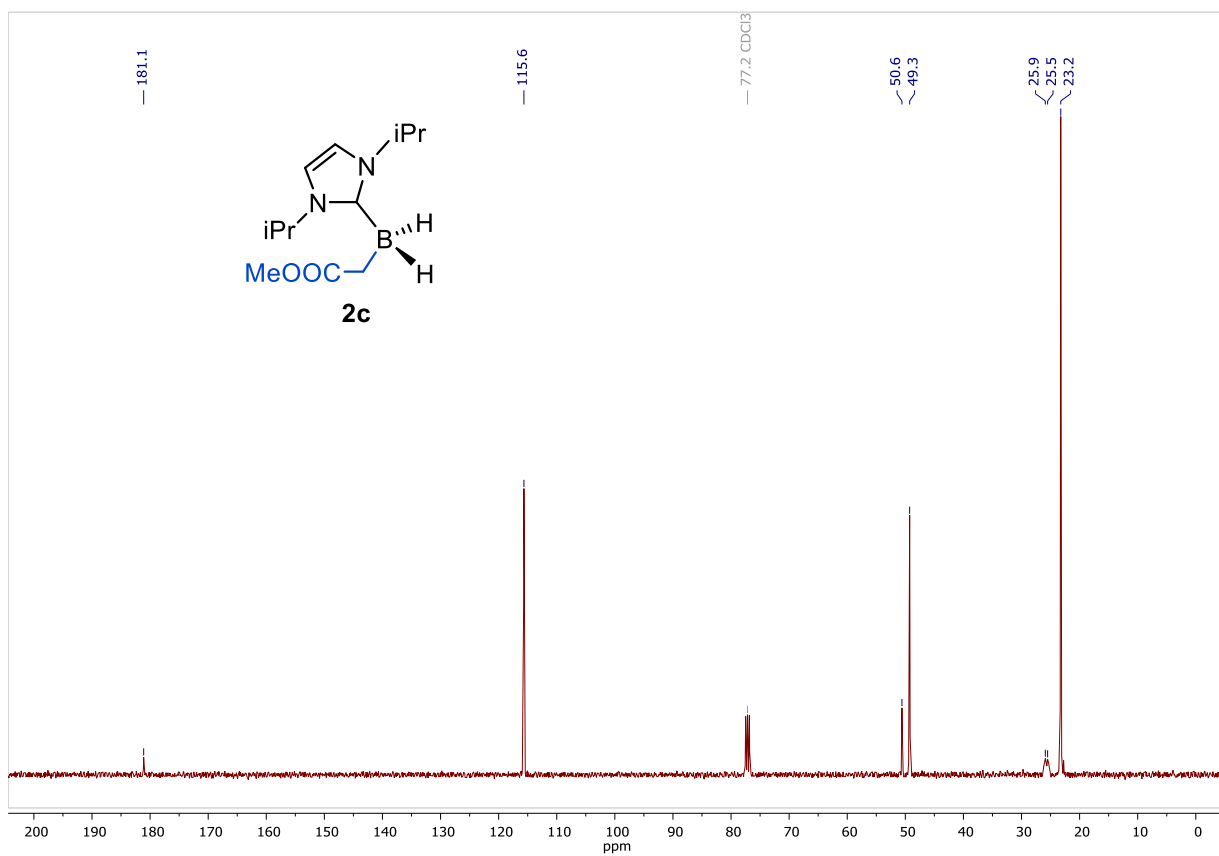


Figure S35. ^{13}C NMR spectrum of **2c** in CDCl_3 .

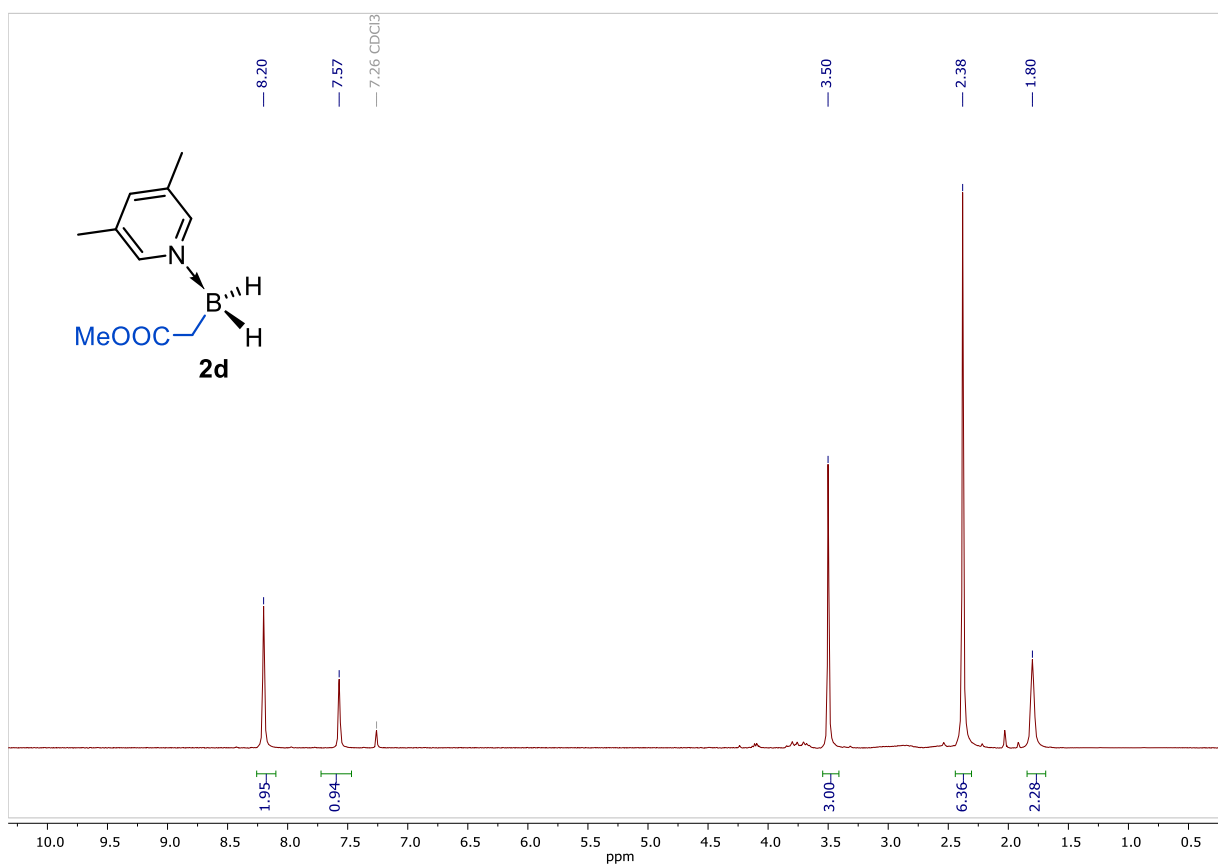


Figure S36. ¹H NMR spectrum of **2d** in CDCl₃.

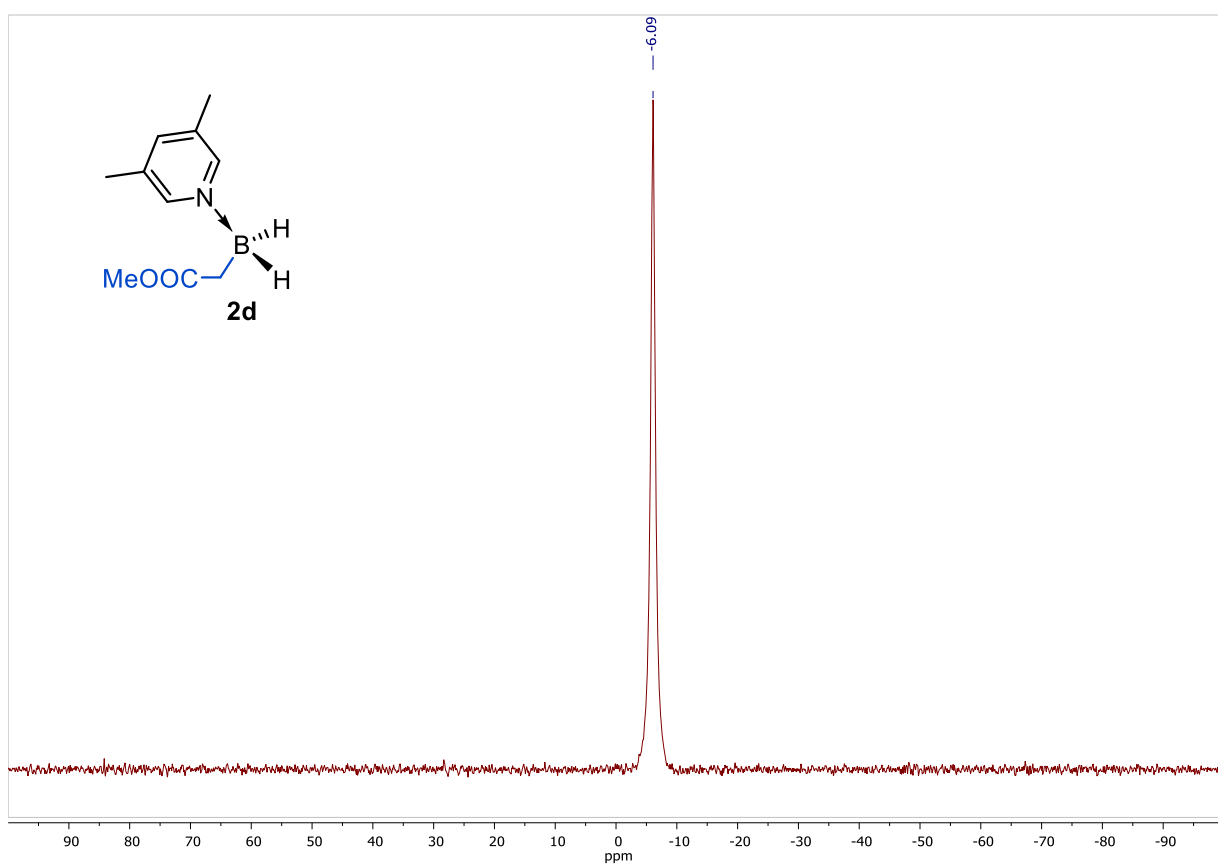


Figure S37. ¹¹B{¹H} NMR spectrum of **2d** in CDCl₃.

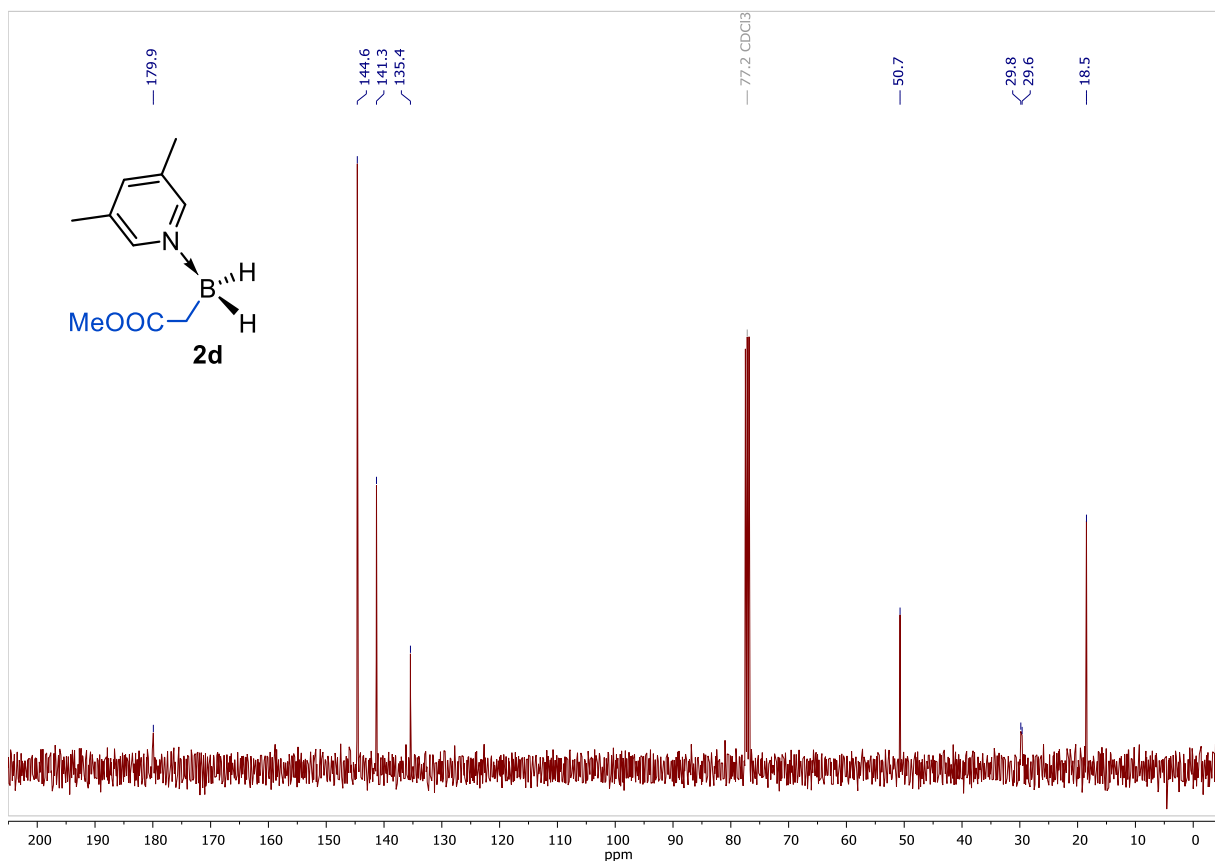


Figure S38. ¹³C NMR spectrum of **2d** in CDCl₃.

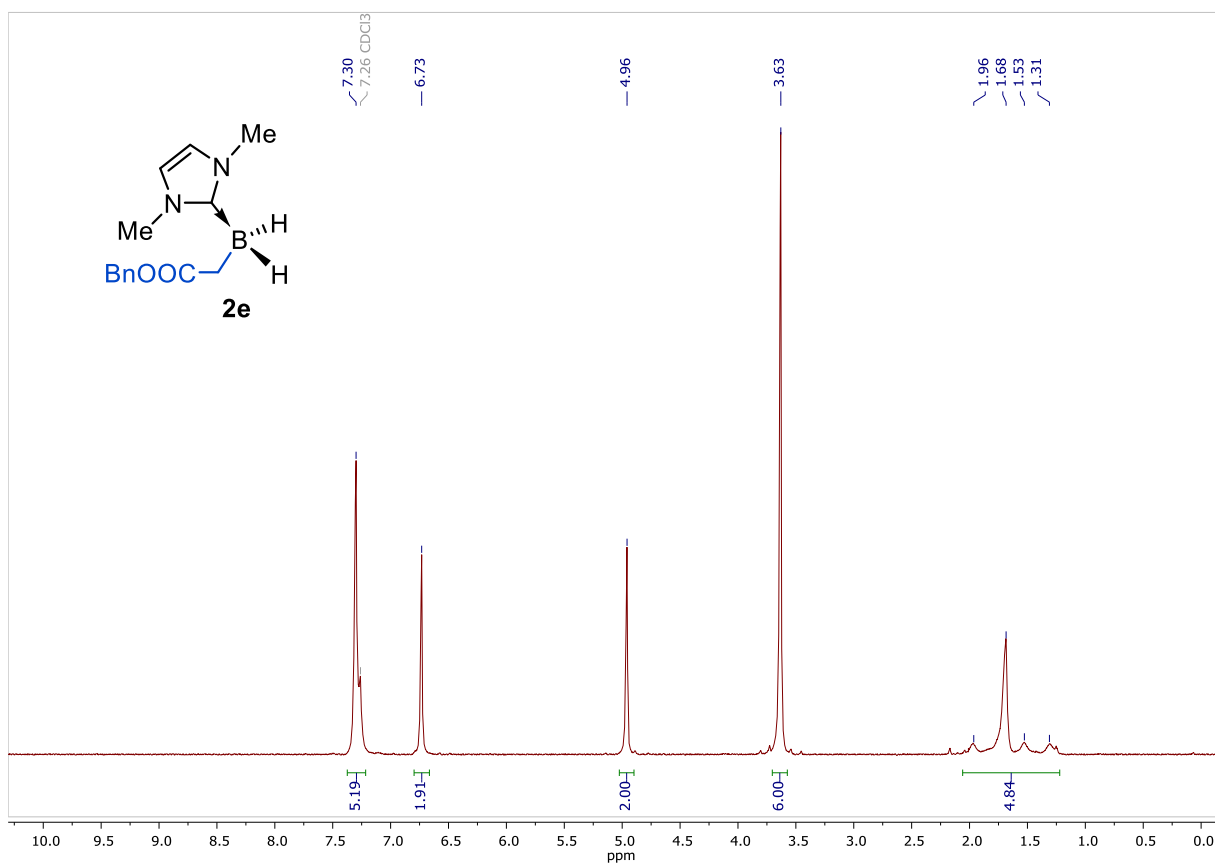


Figure S39. ¹H NMR spectrum of **2e** in CDCl₃.

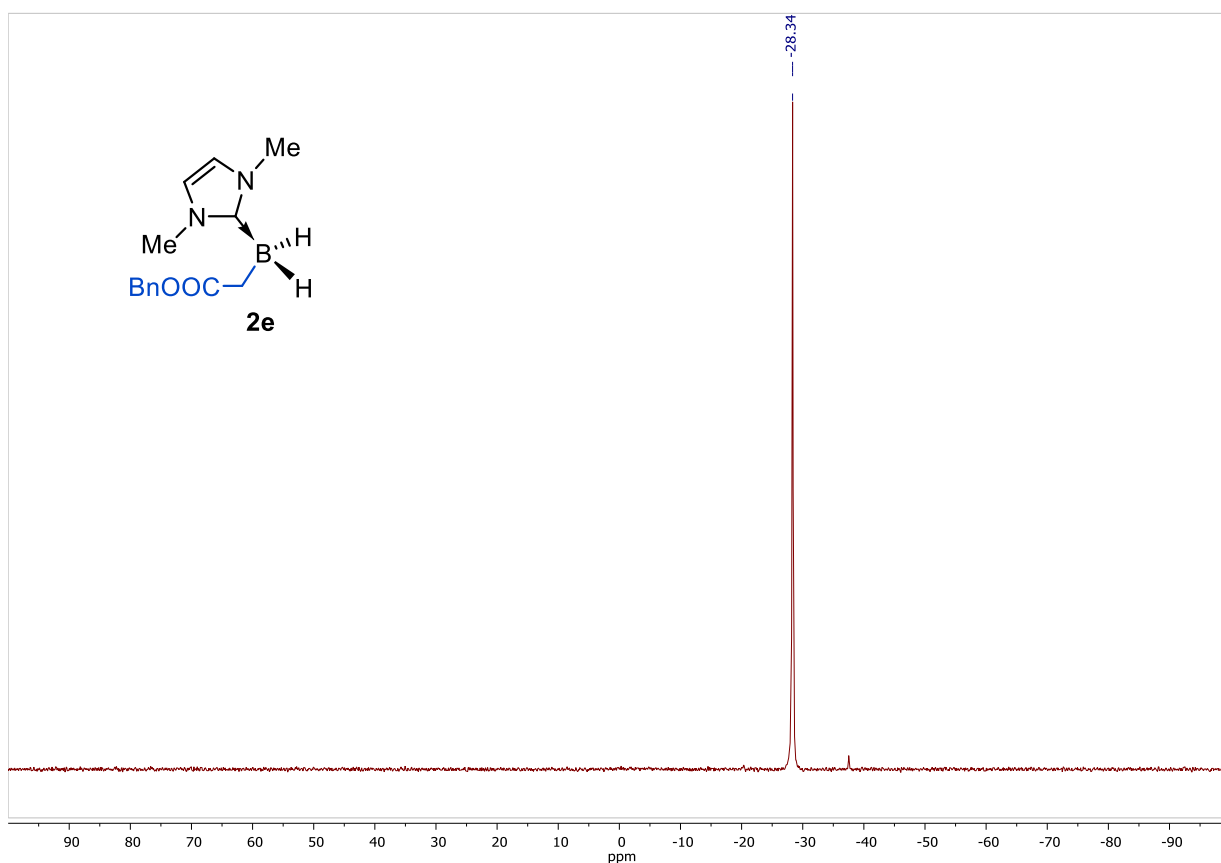


Figure S40. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **2e** in CDCl_3 .

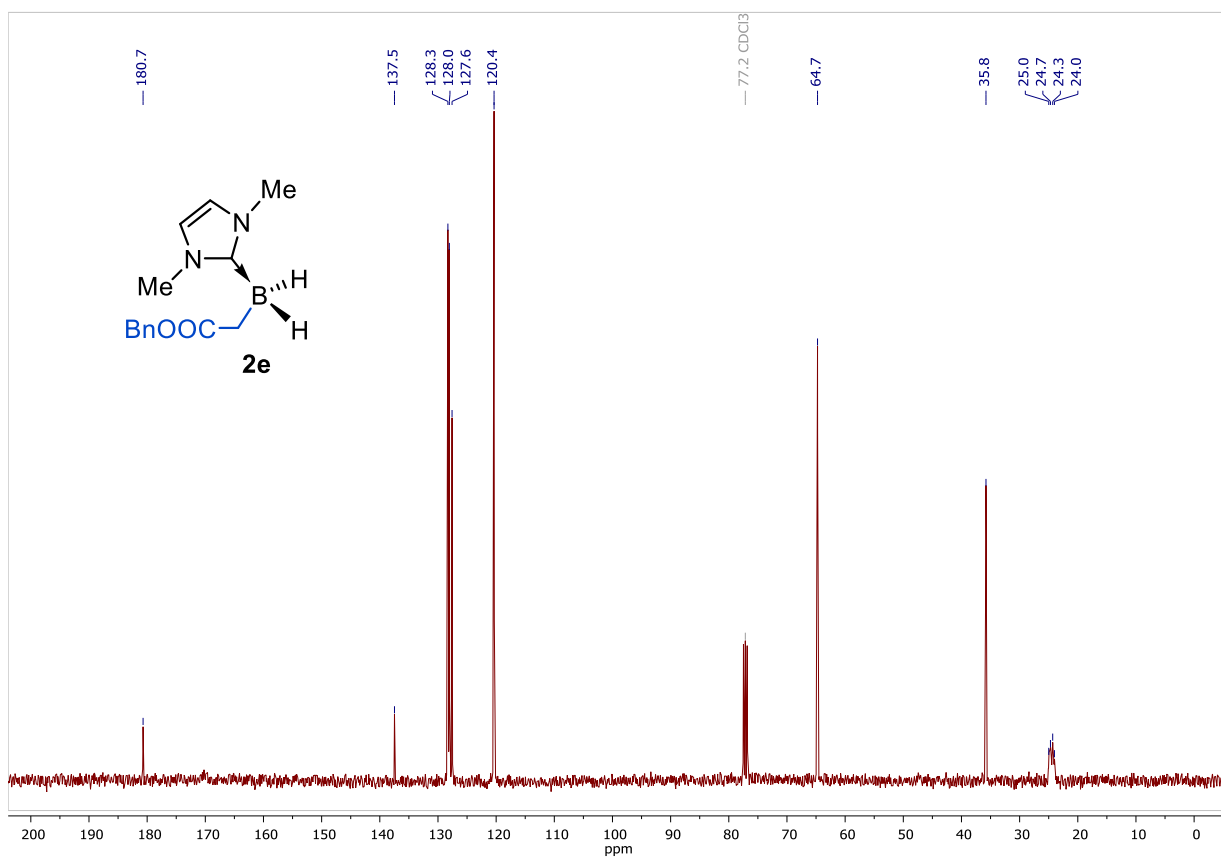


Figure S41. ^{13}C NMR spectrum of **2e** in CDCl_3 .

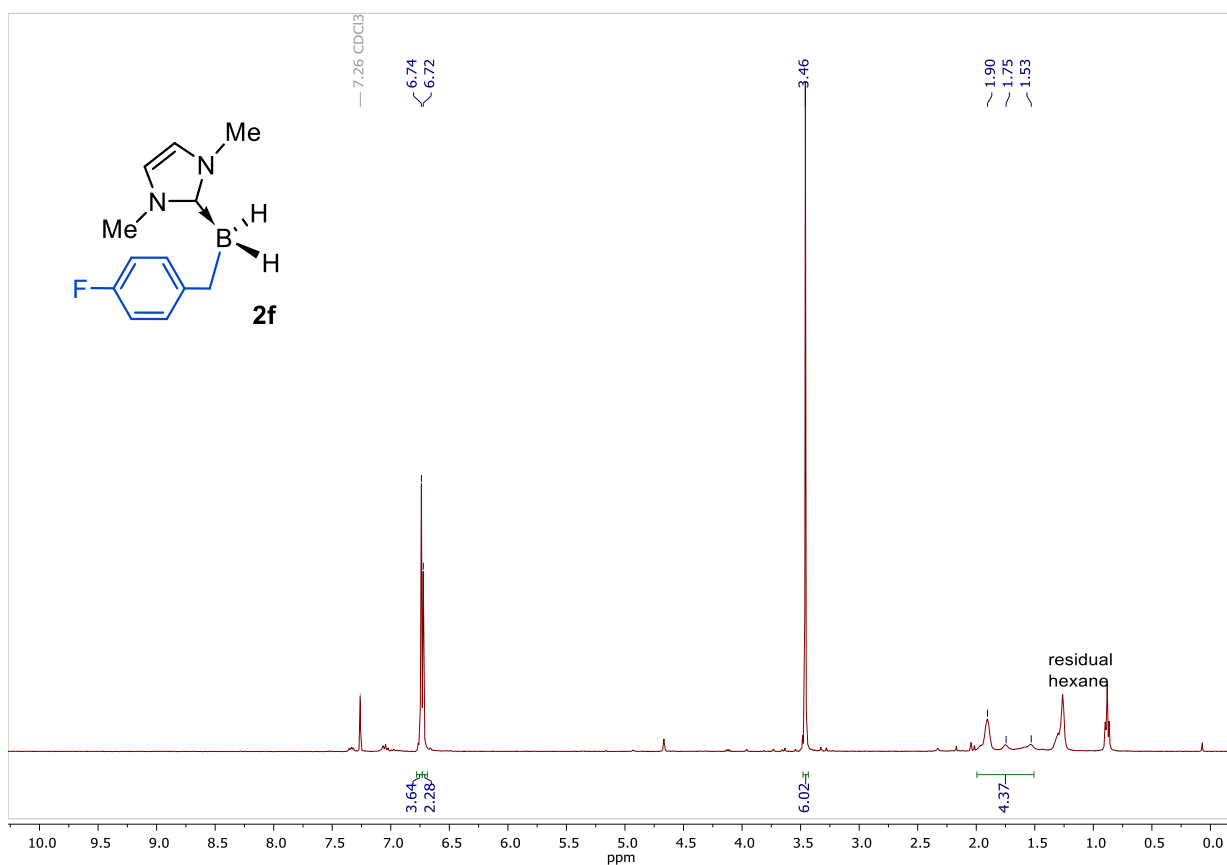


Figure S42. ^1H NMR spectrum of **2f** in CDCl_3 .

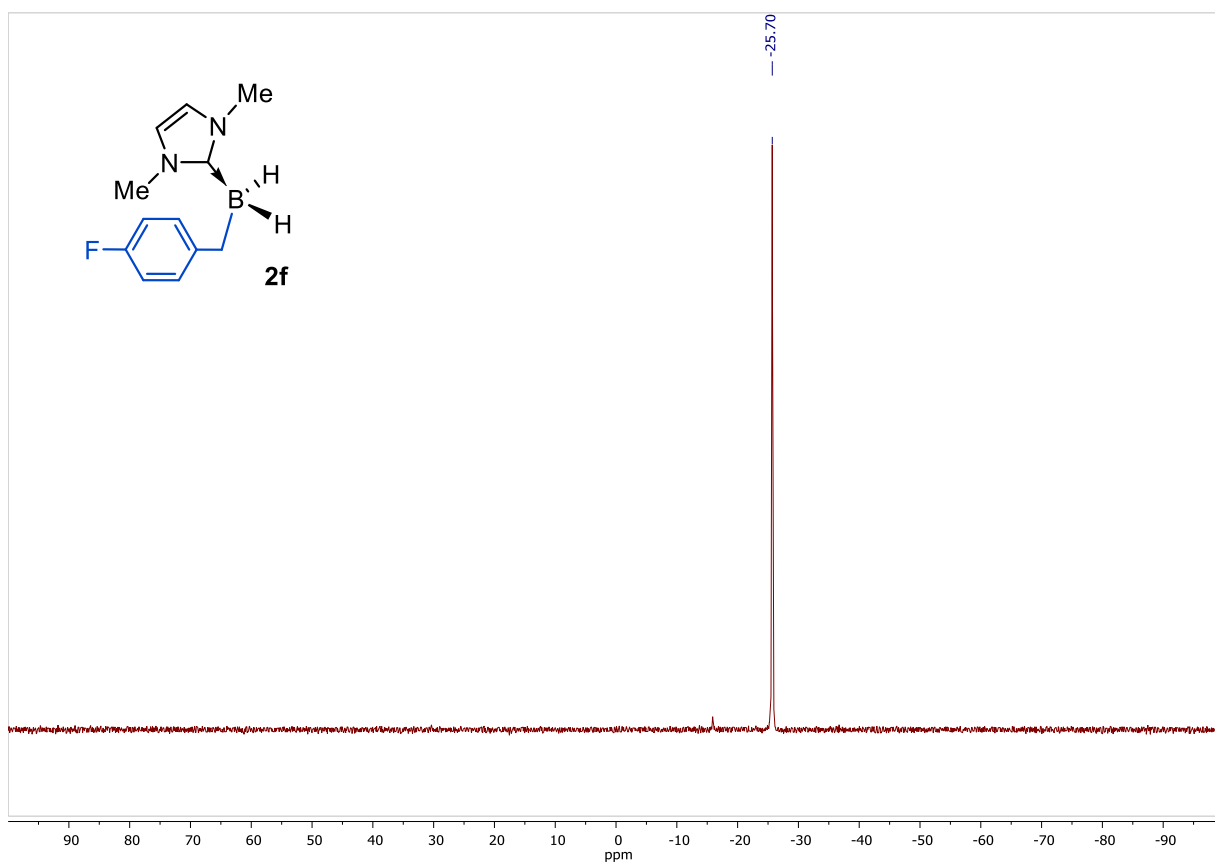


Figure S43. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **2f** in CDCl_3 .

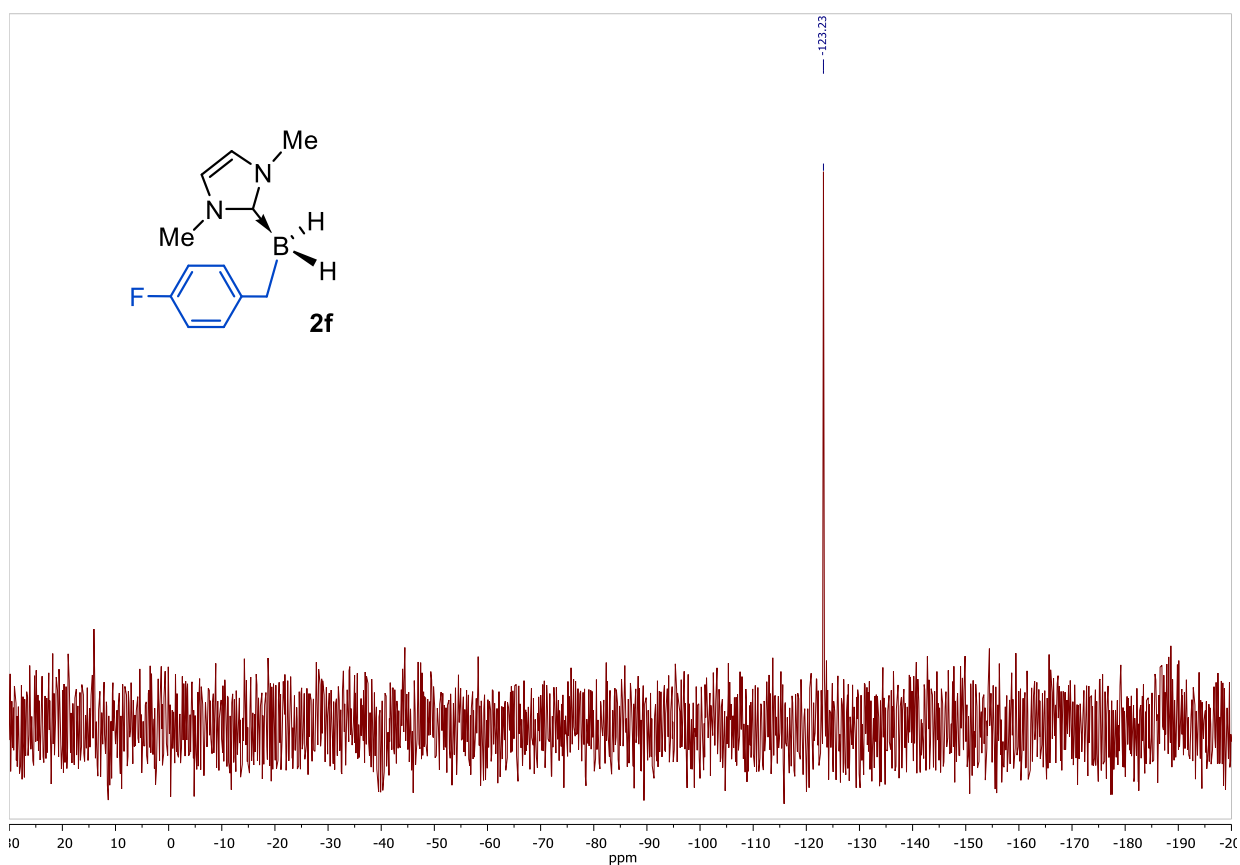


Figure S44. ¹⁹F NMR spectrum of **2f** in CDCl₃.

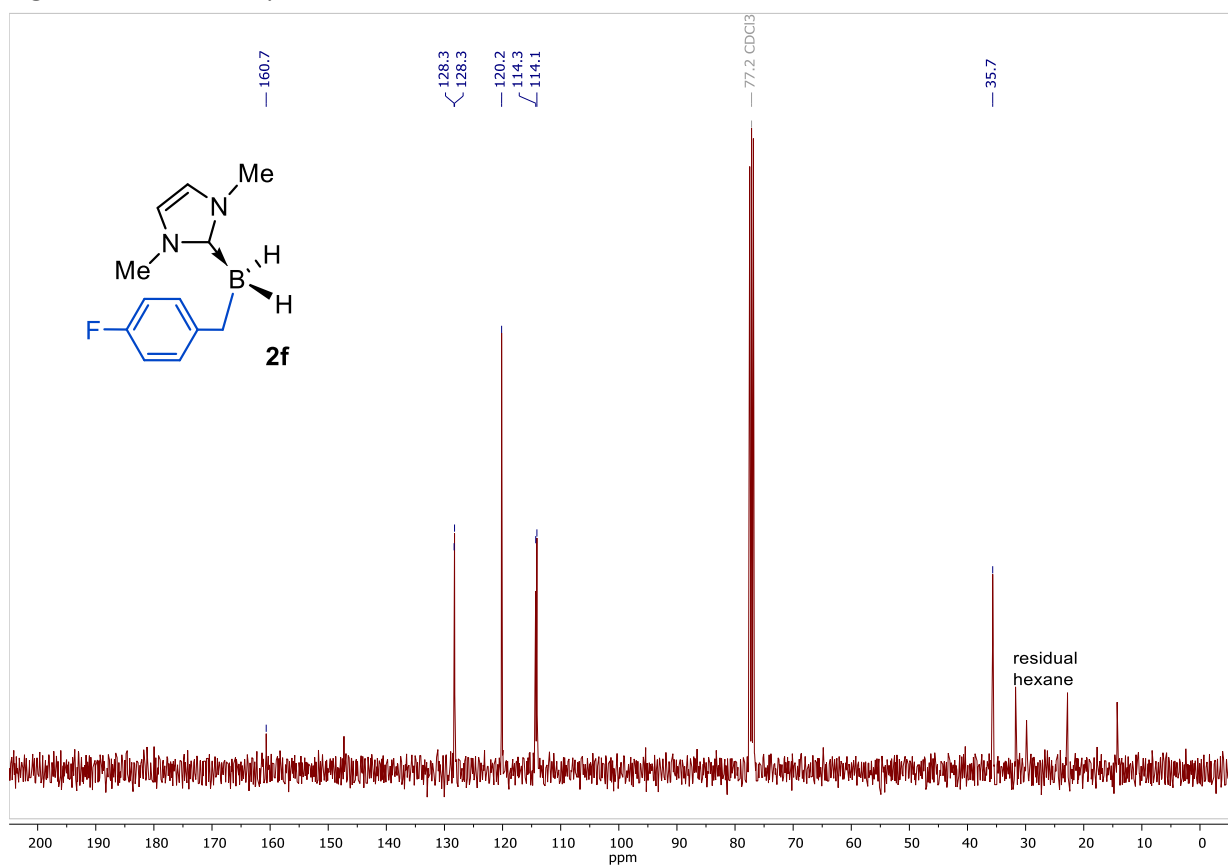


Figure S45. ¹³C NMR spectrum of **2f** in CDCl₃.

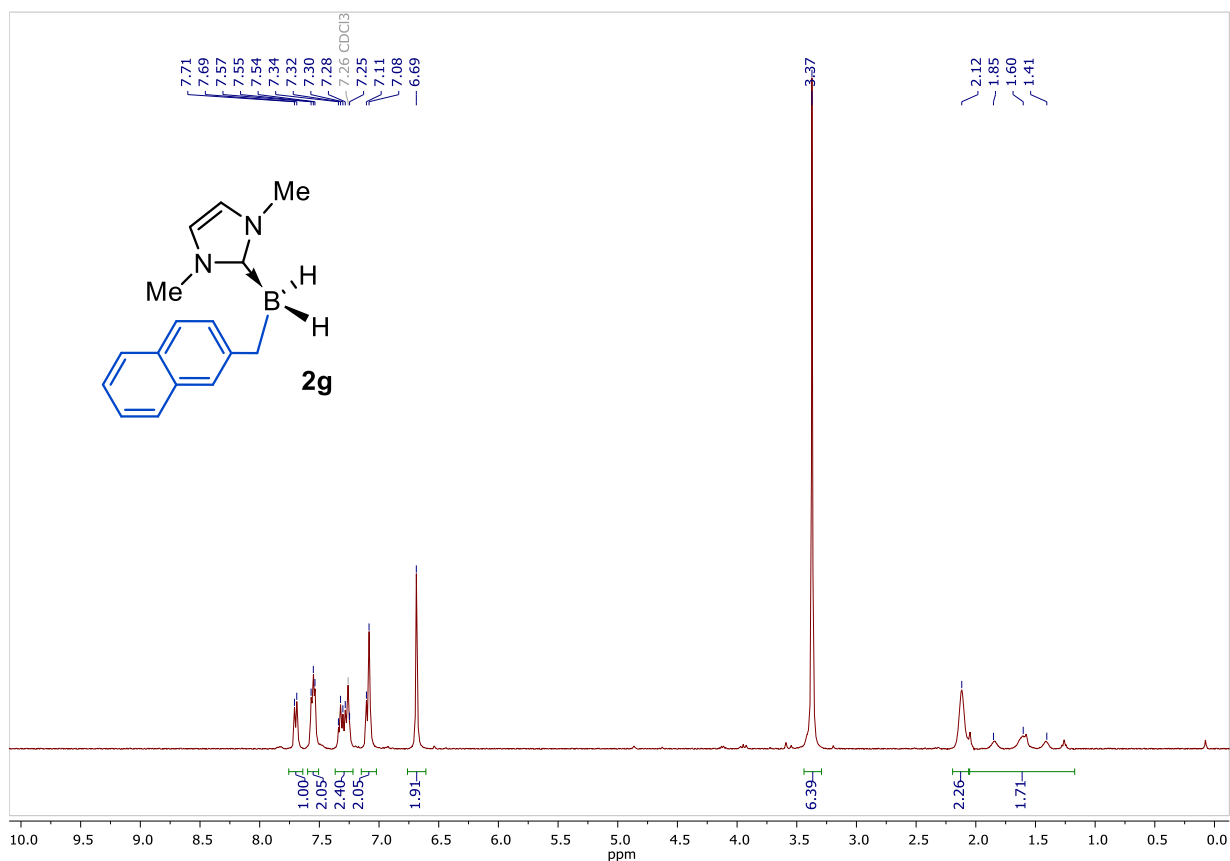


Figure S46. ¹H NMR spectrum of **2g** in CDCl₃.

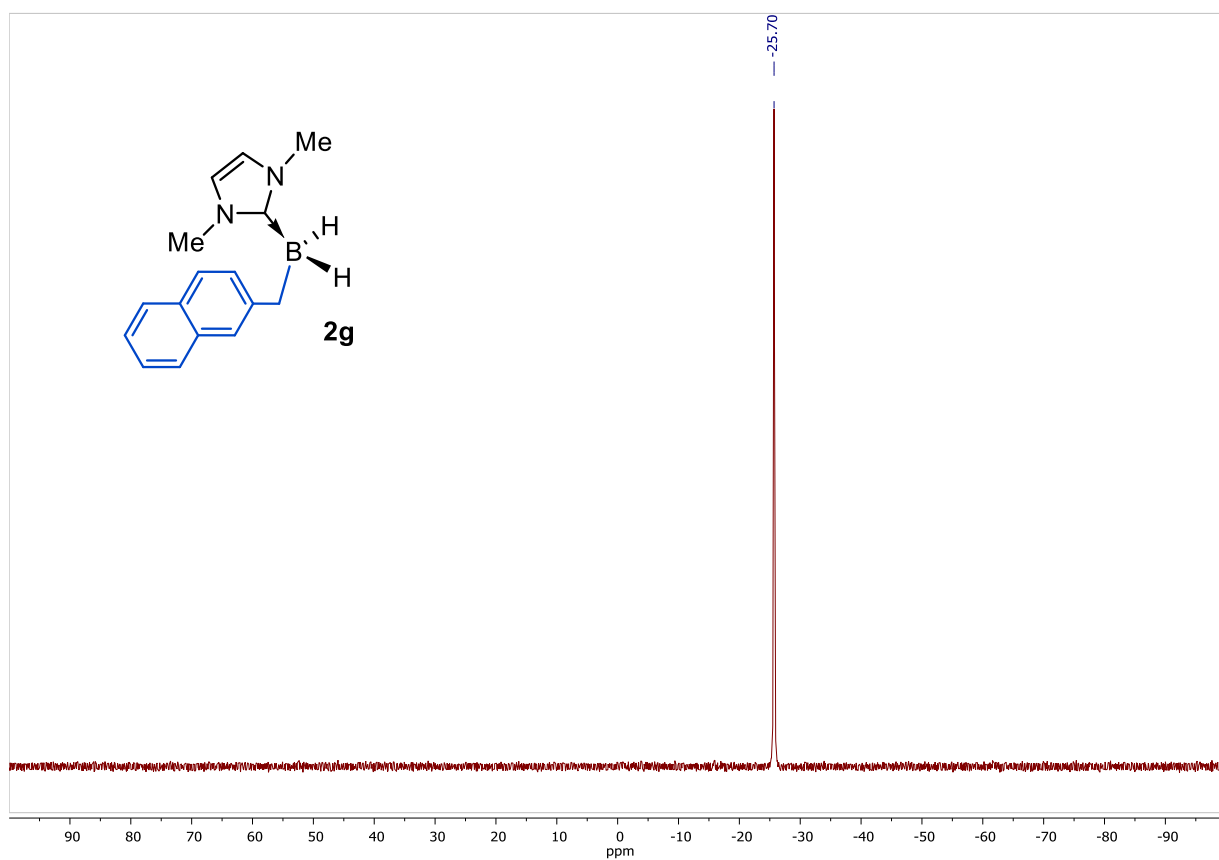


Figure S47. ¹¹B{¹H} NMR spectrum of **2g** in CDCl₃.

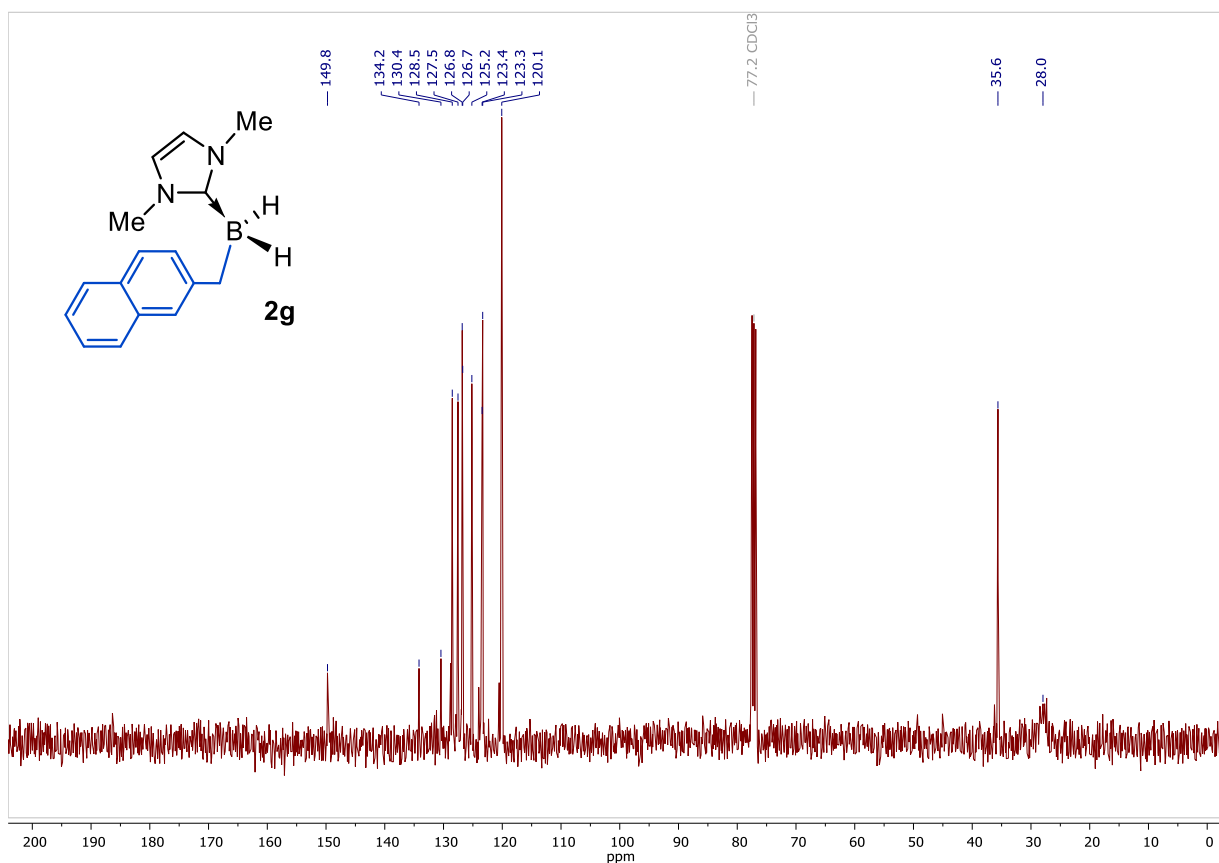


Figure S48. ^{13}C NMR spectrum of **2g** in CDCl_3 .

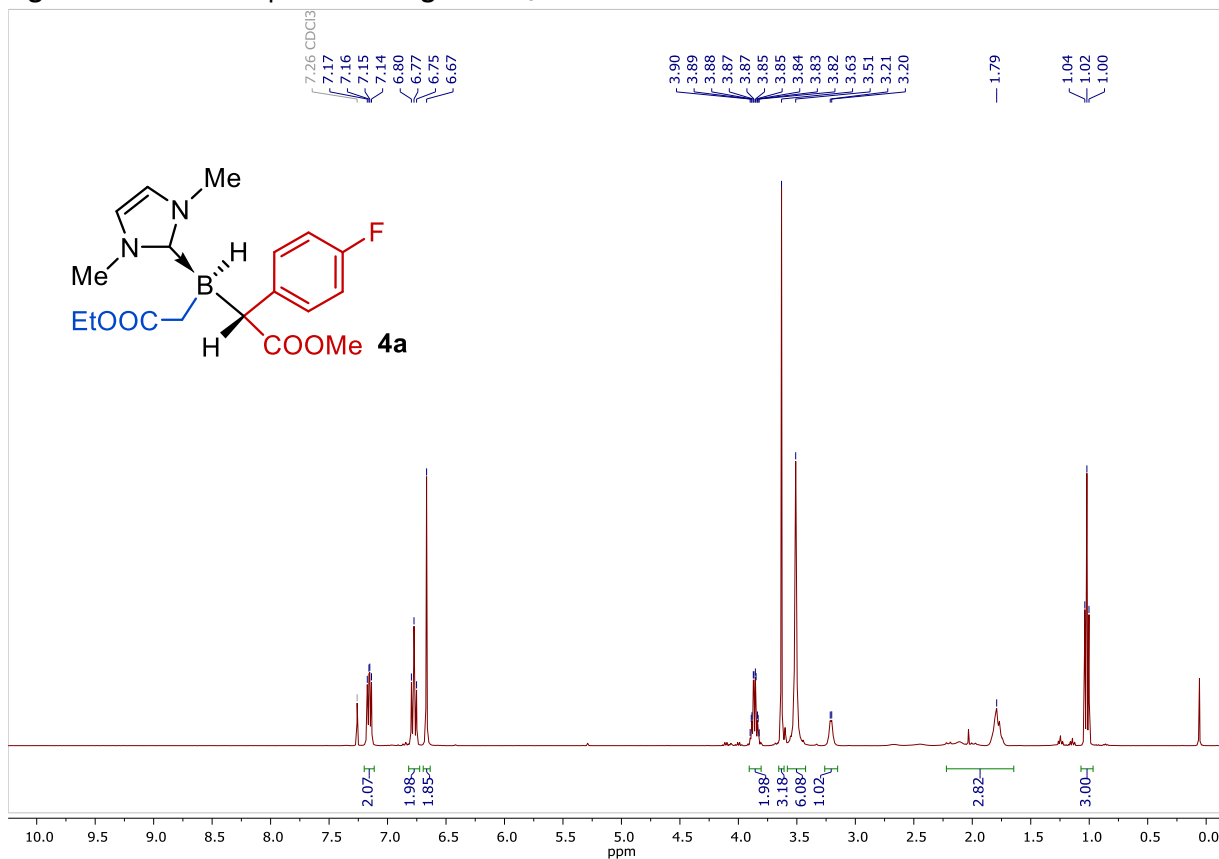


Figure S49. ^1H NMR spectrum of **4a** in CDCl_3 .

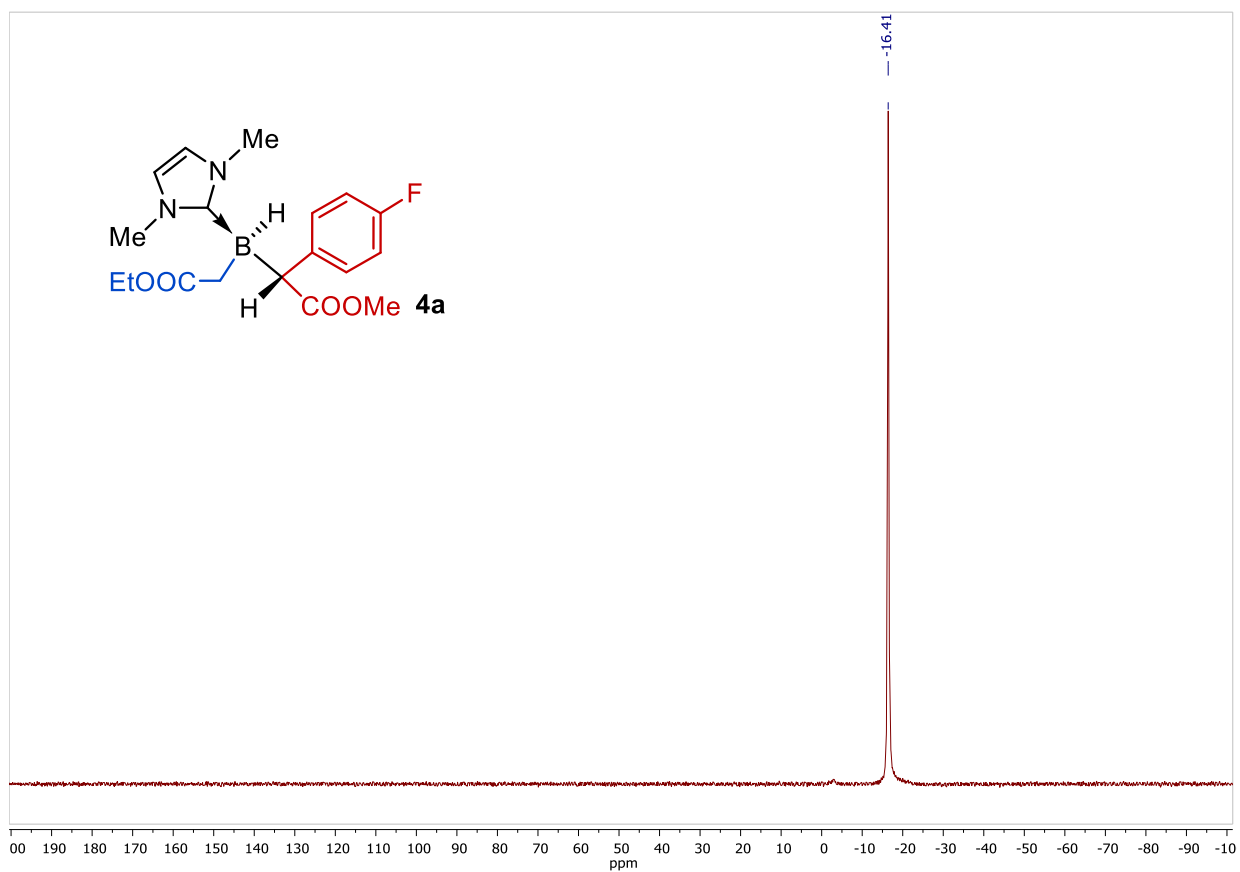


Figure S50. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4a** in CDCl_3 .

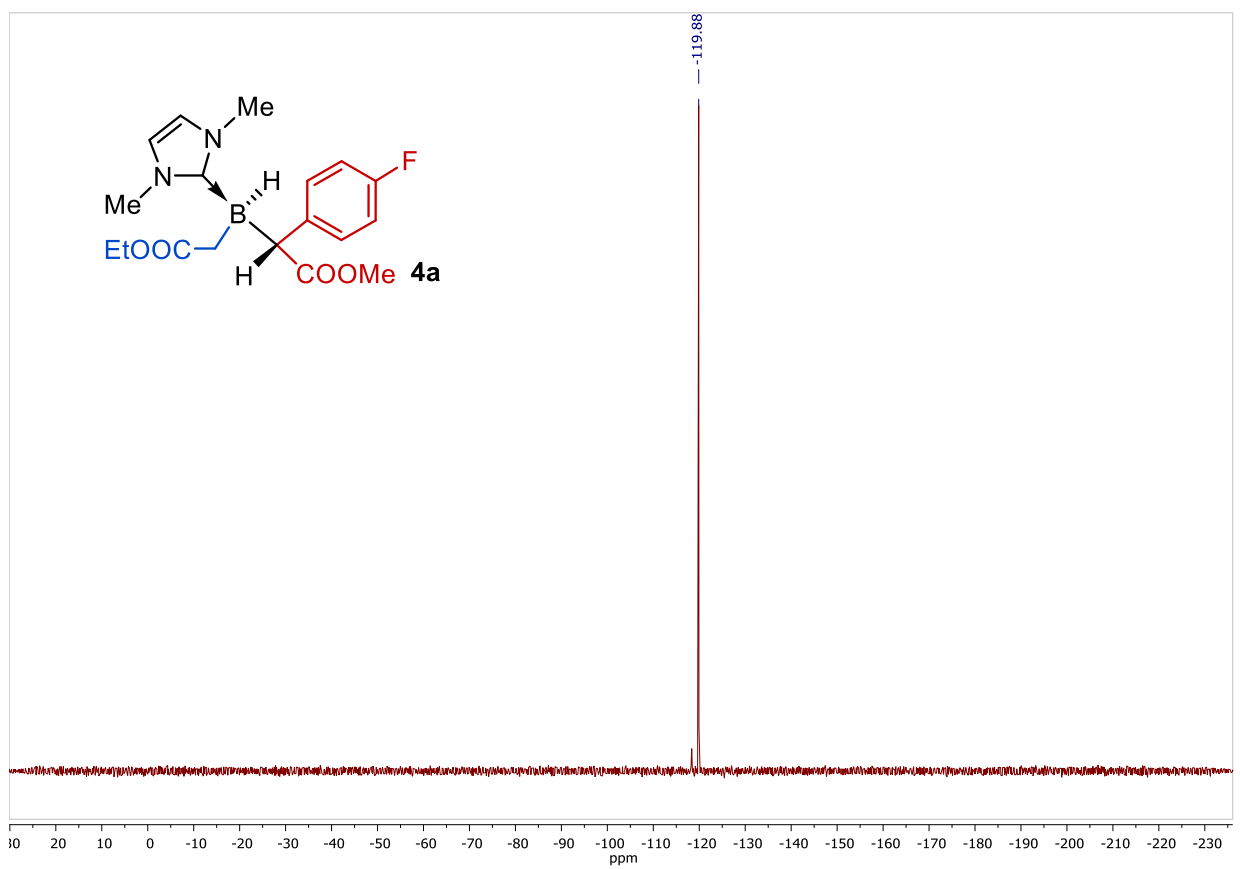


Figure S51. ^{19}F NMR spectrum of **4a** in CDCl_3 .

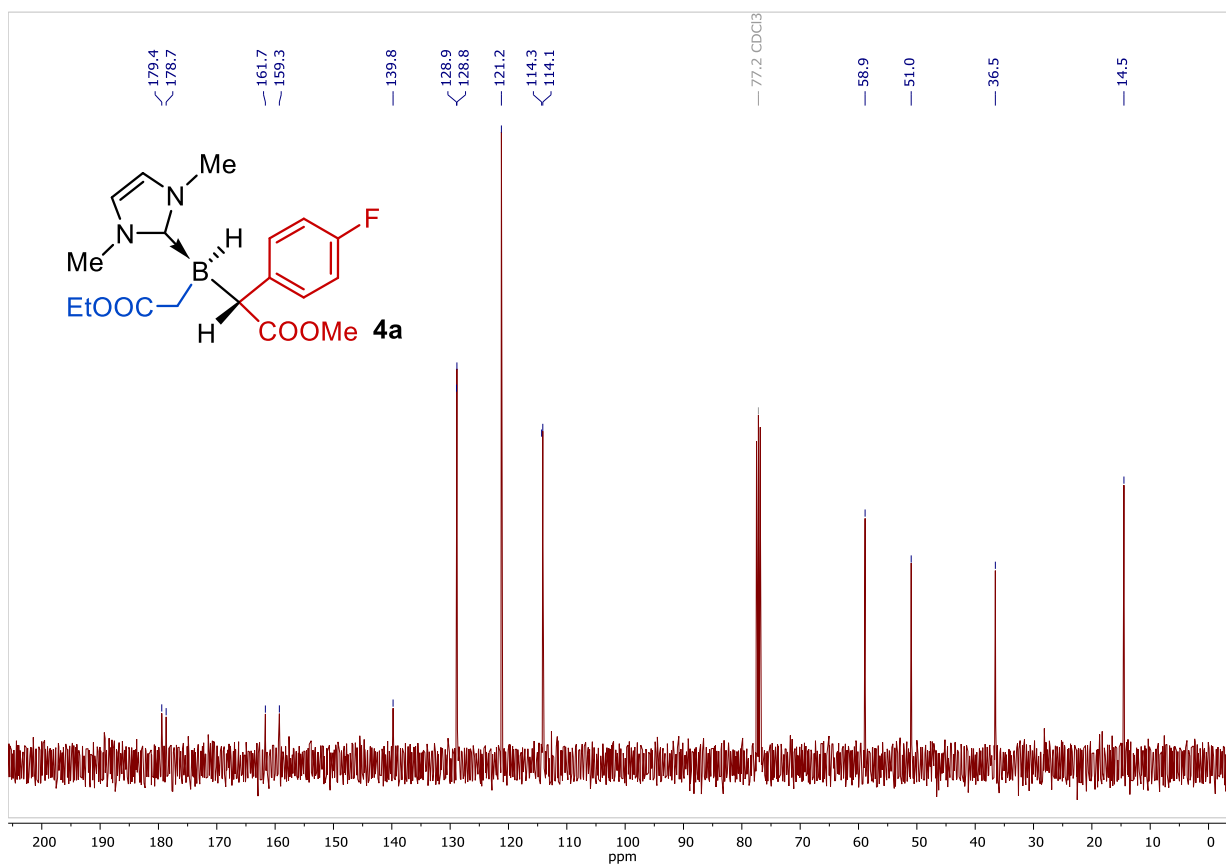


Figure S52. ^{13}C NMR spectrum of **4a** in CDCl_3 .

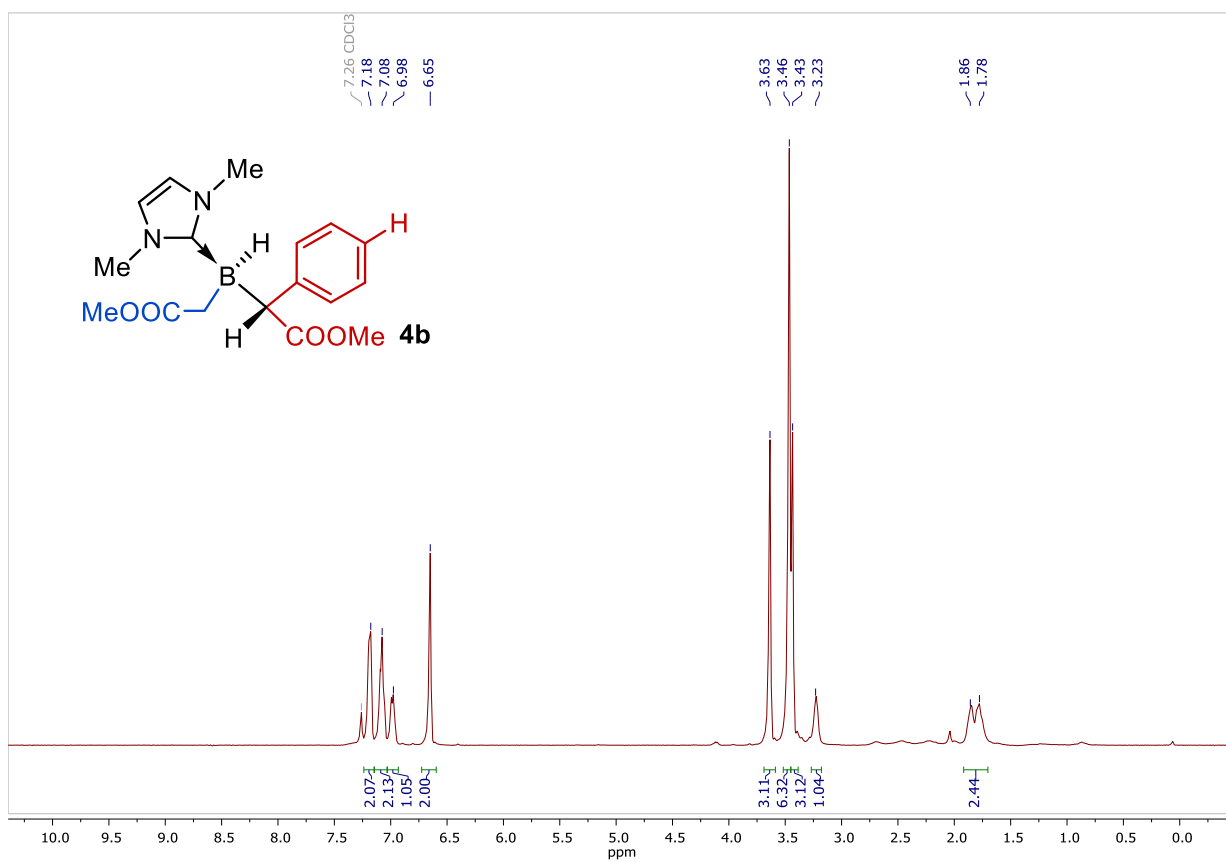


Figure S53. ^1H NMR spectrum of **4b** in CDCl_3 .

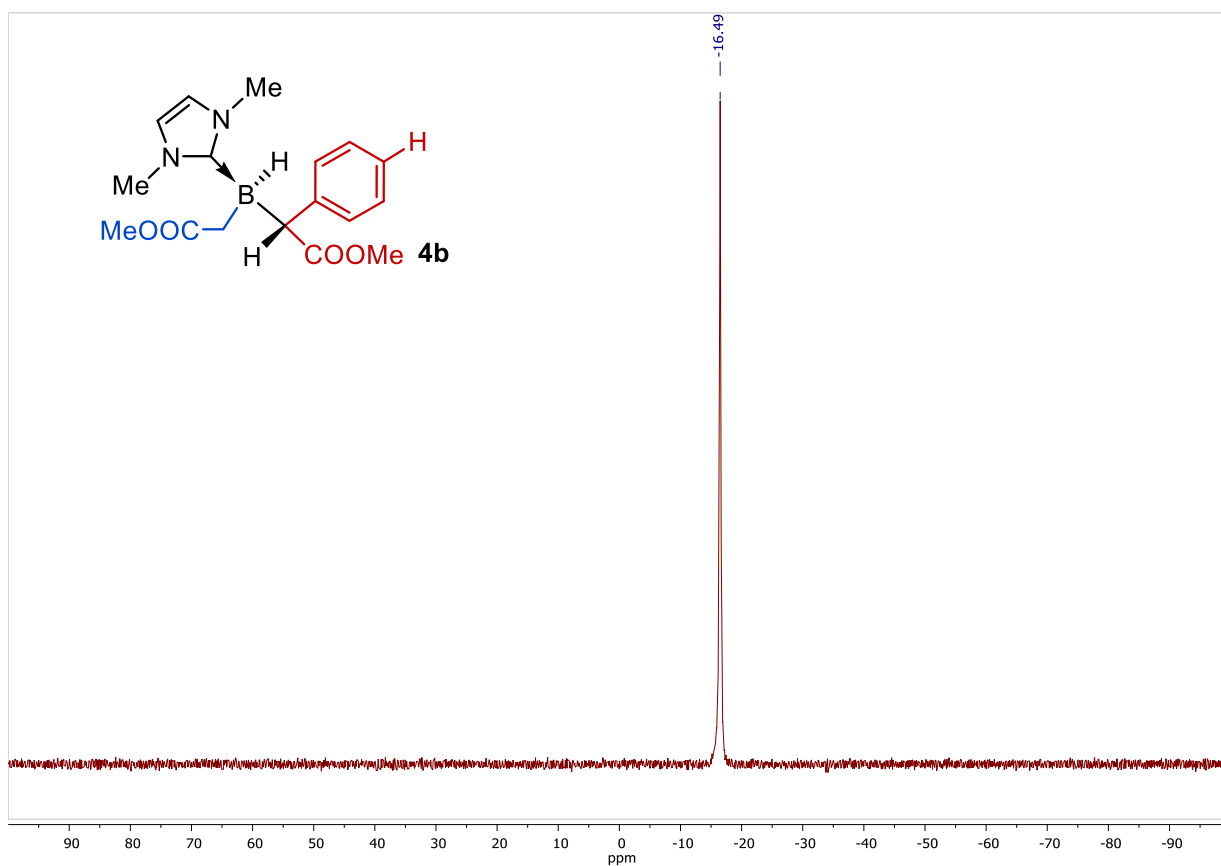


Figure S54. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4b** in CDCl_3 .

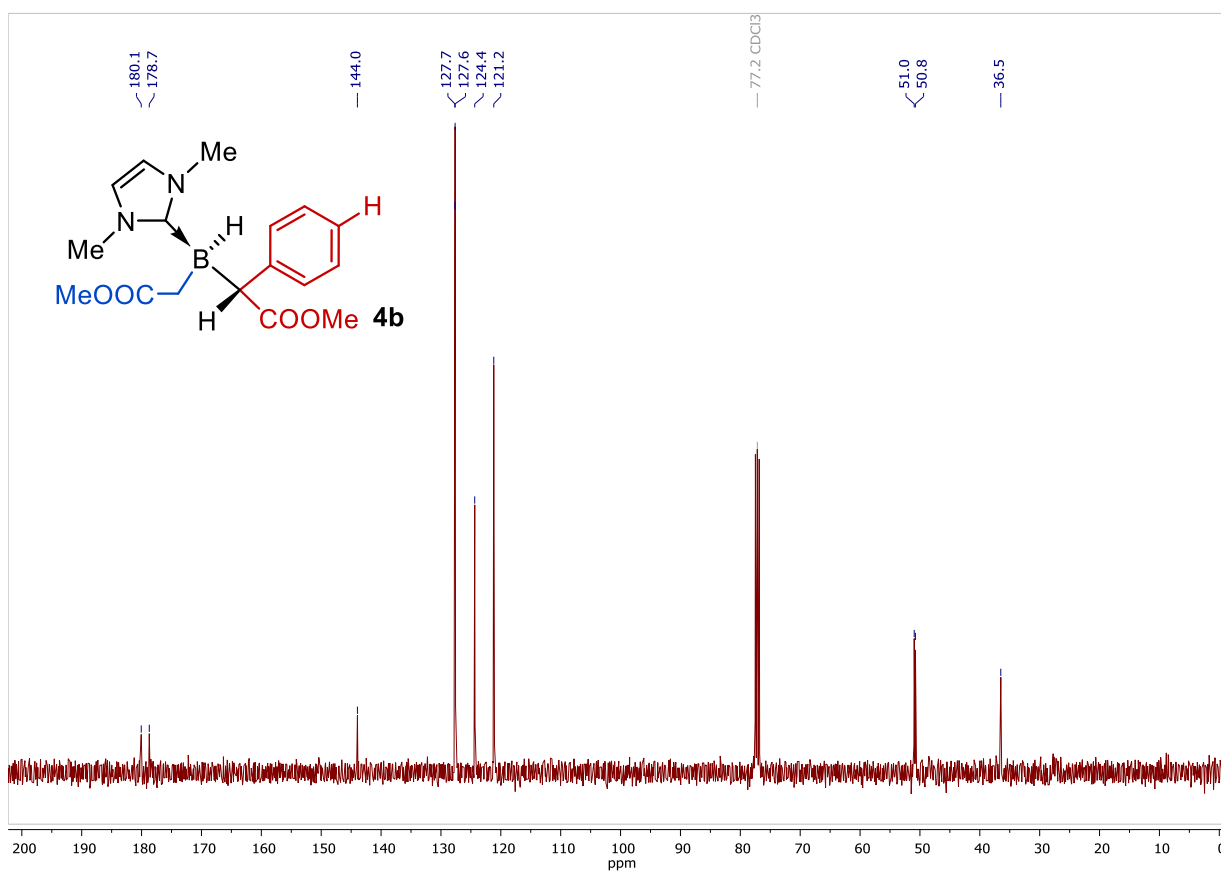


Figure S55. ^{13}C NMR spectrum of **4b** in CDCl_3 .

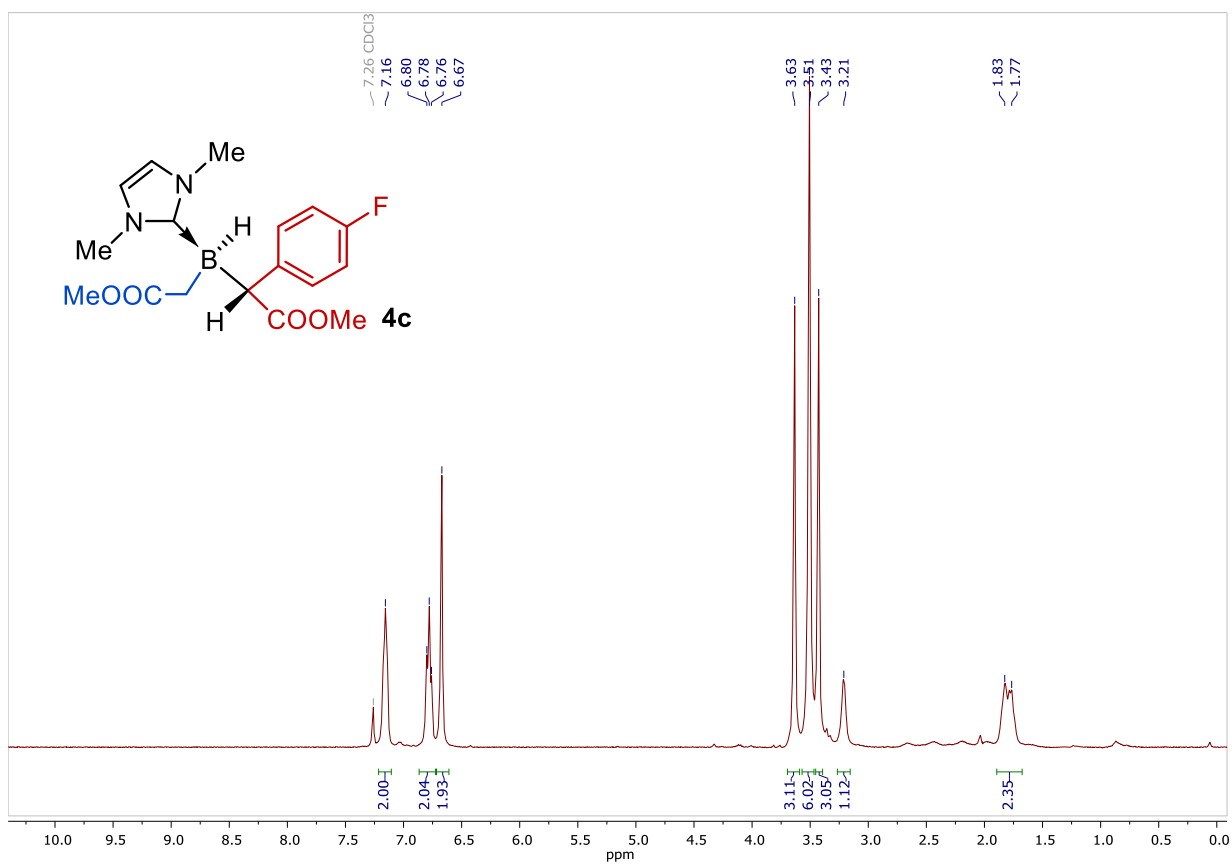


Figure S56. ^1H NMR spectrum of **4c** in CDCl_3 .

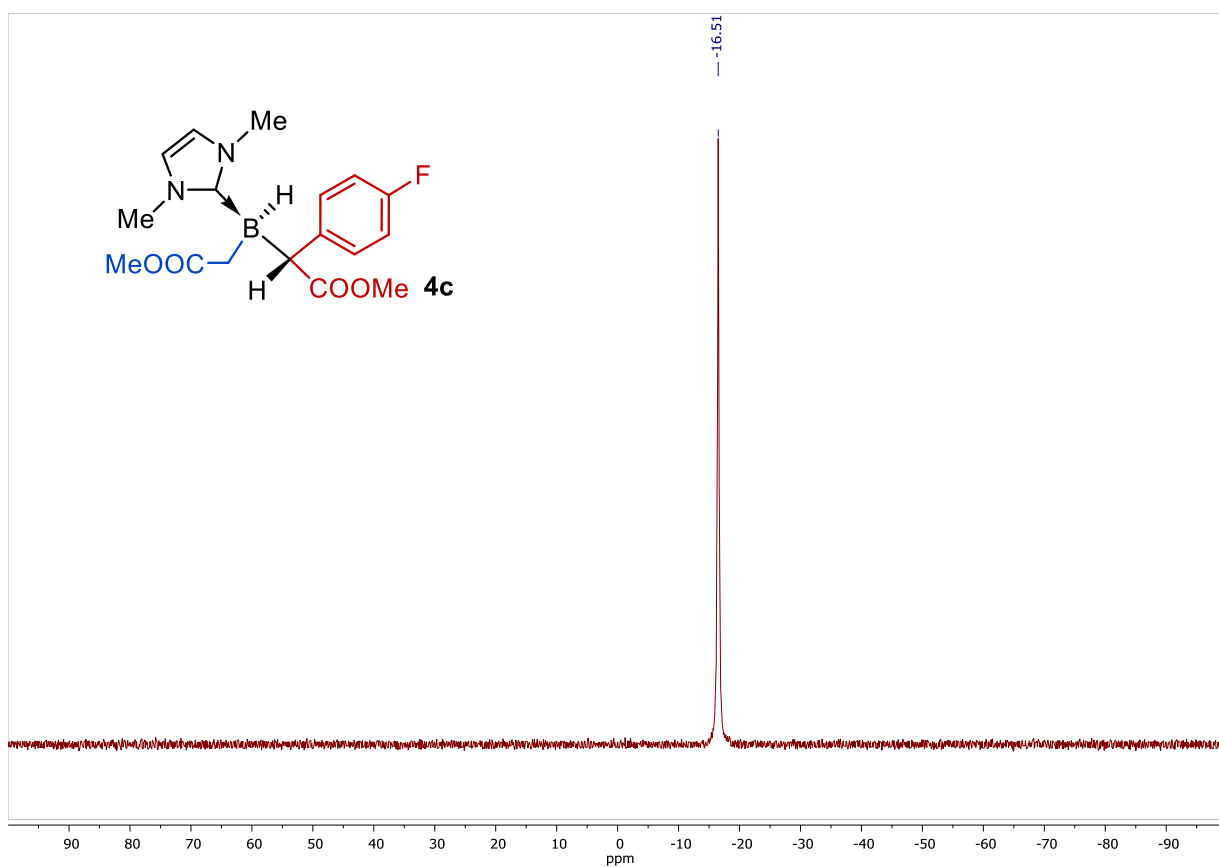


Figure S57. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4c** in CDCl_3 .

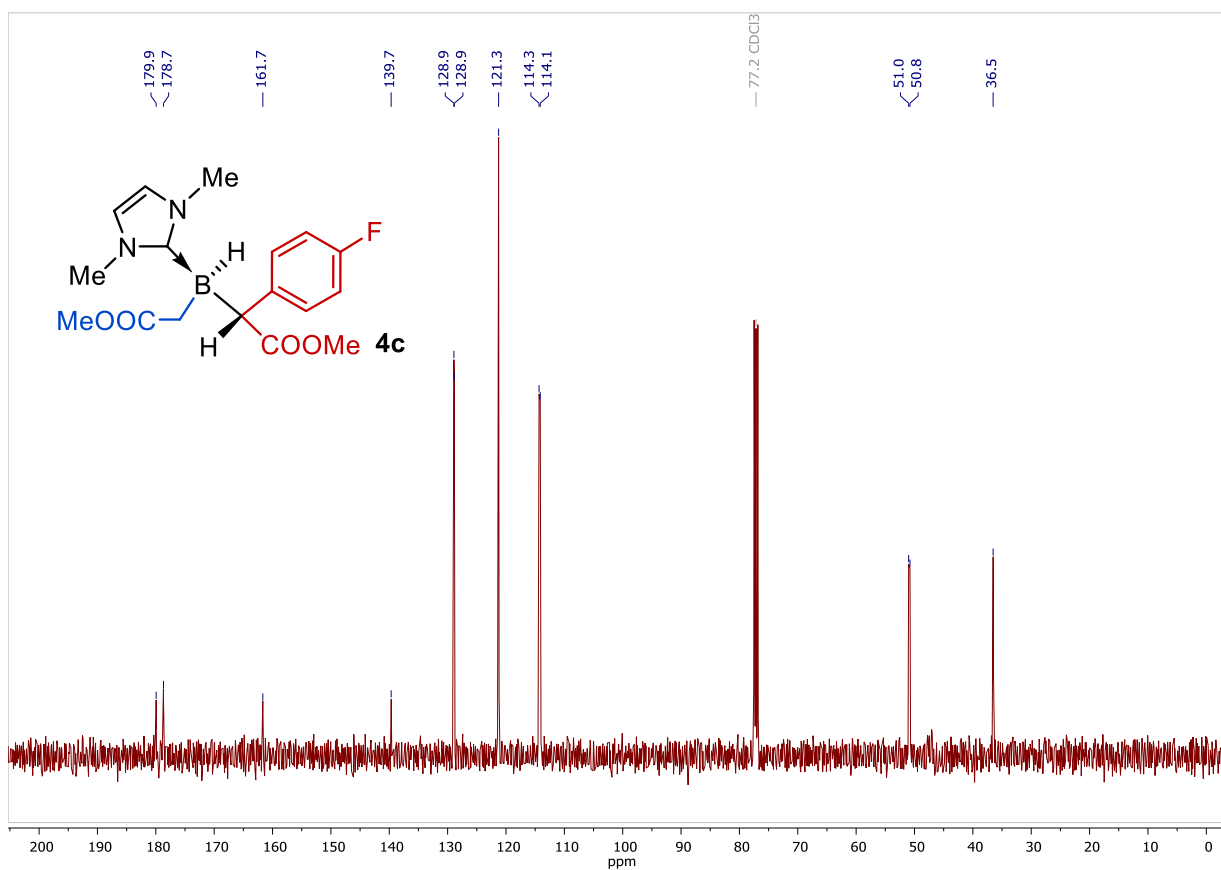


Figure S58. ¹³C NMR spectrum of **4c** in CDCl₃.

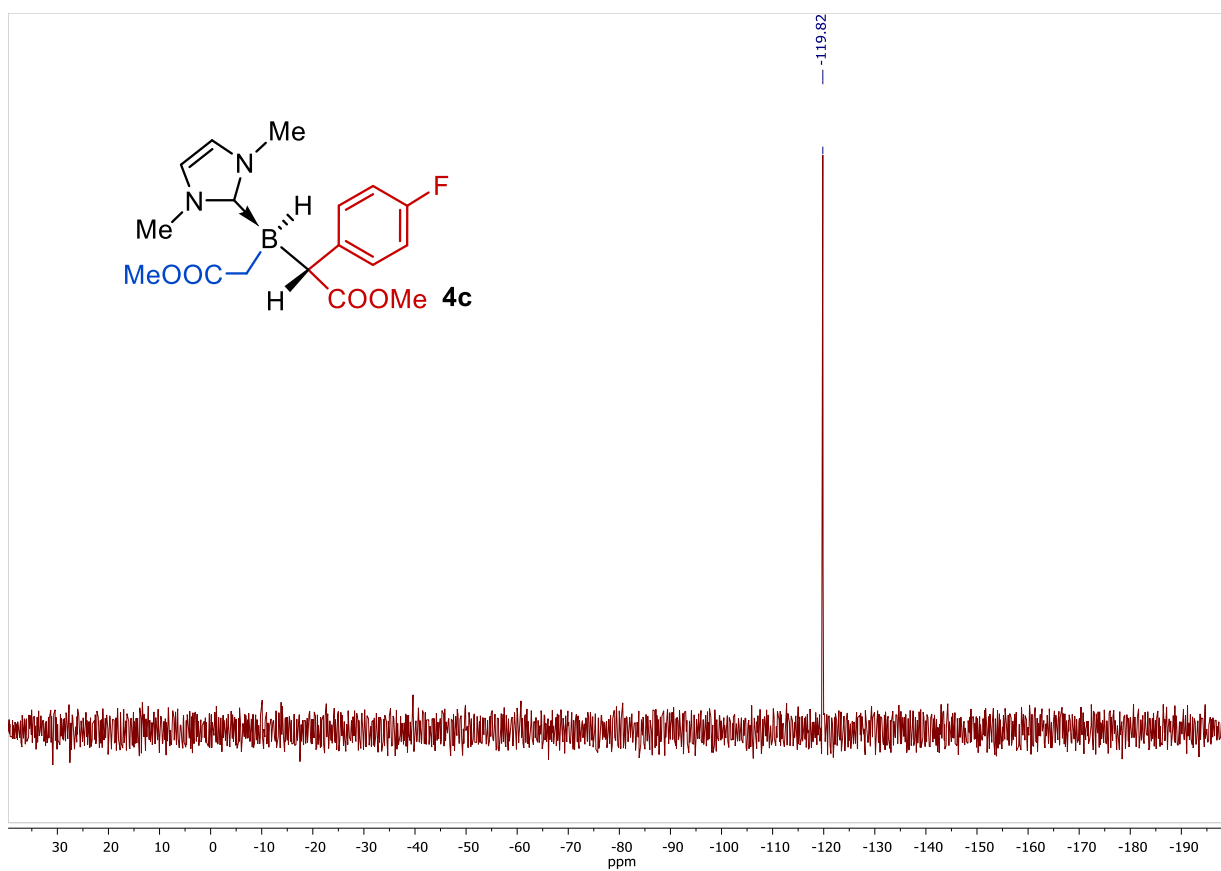


Figure S59. ¹⁹F NMR spectrum of **4c** in CDCl₃.

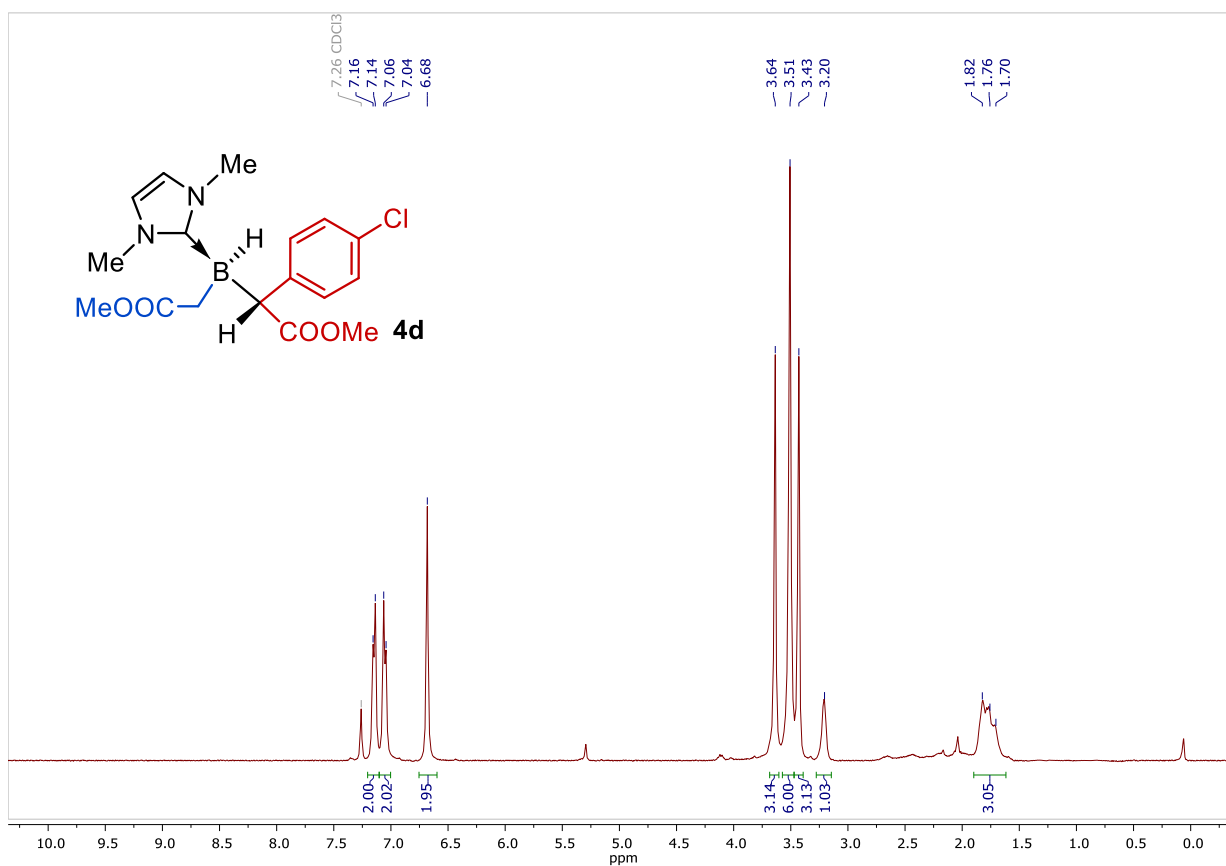


Figure S60. ^1H NMR spectrum of **4d** in CDCl_3 .

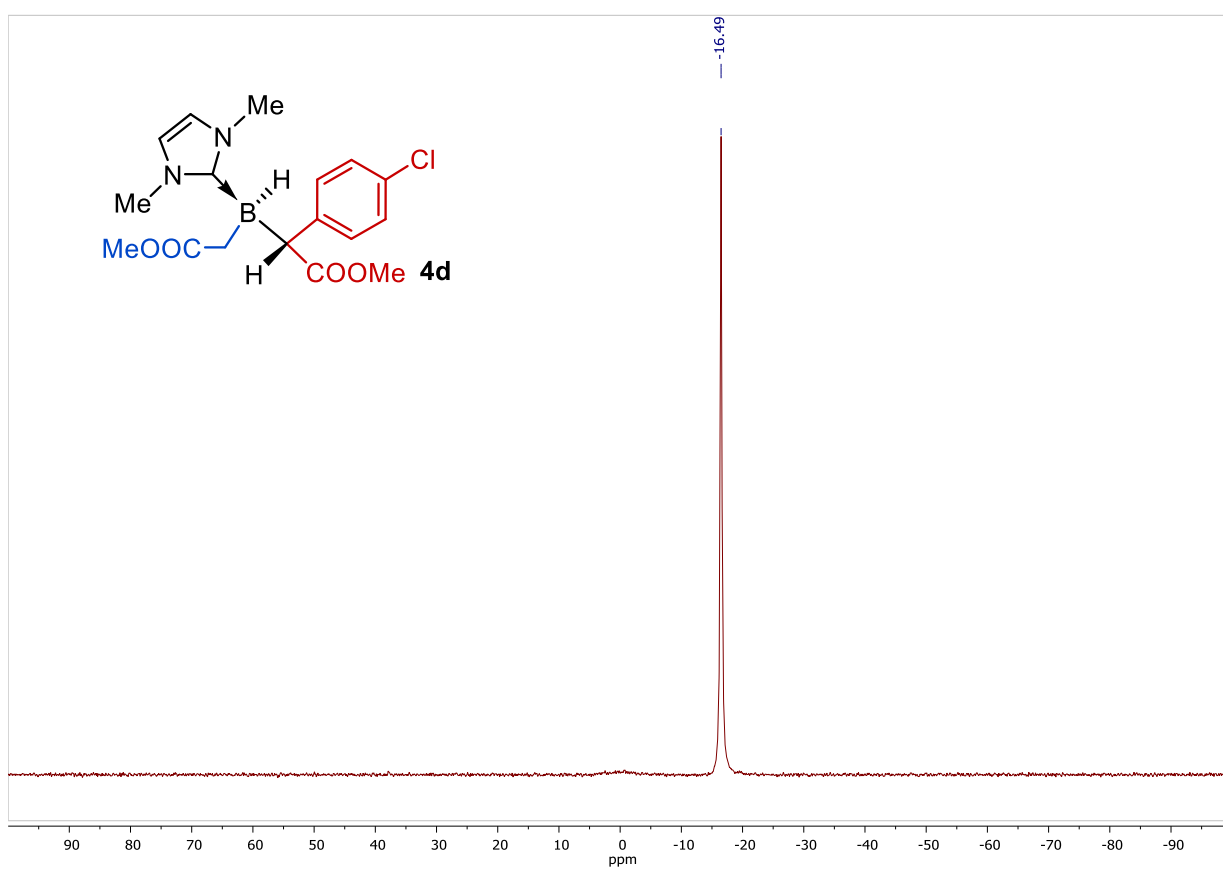


Figure S61. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4d** in CDCl_3 .

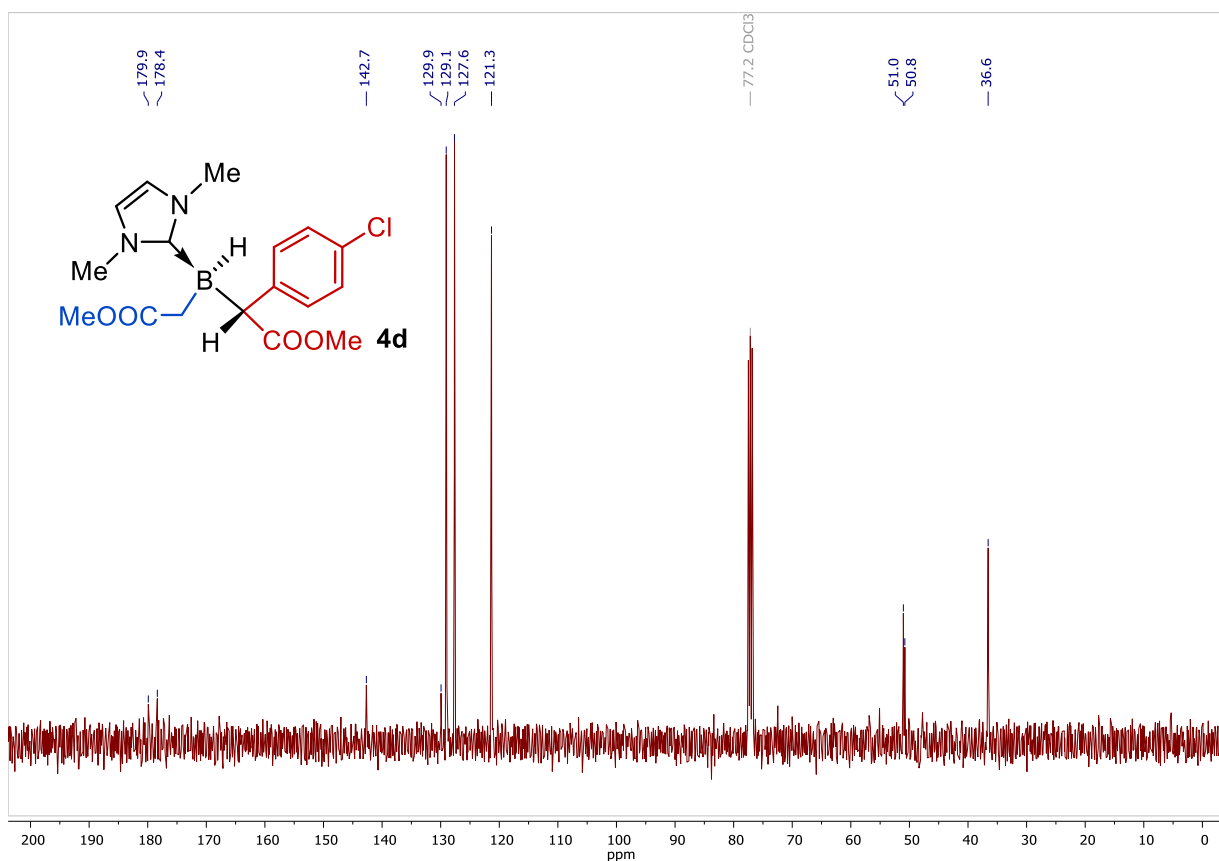


Figure S62. ^{13}C NMR spectrum of **4d** in CDCl_3 .

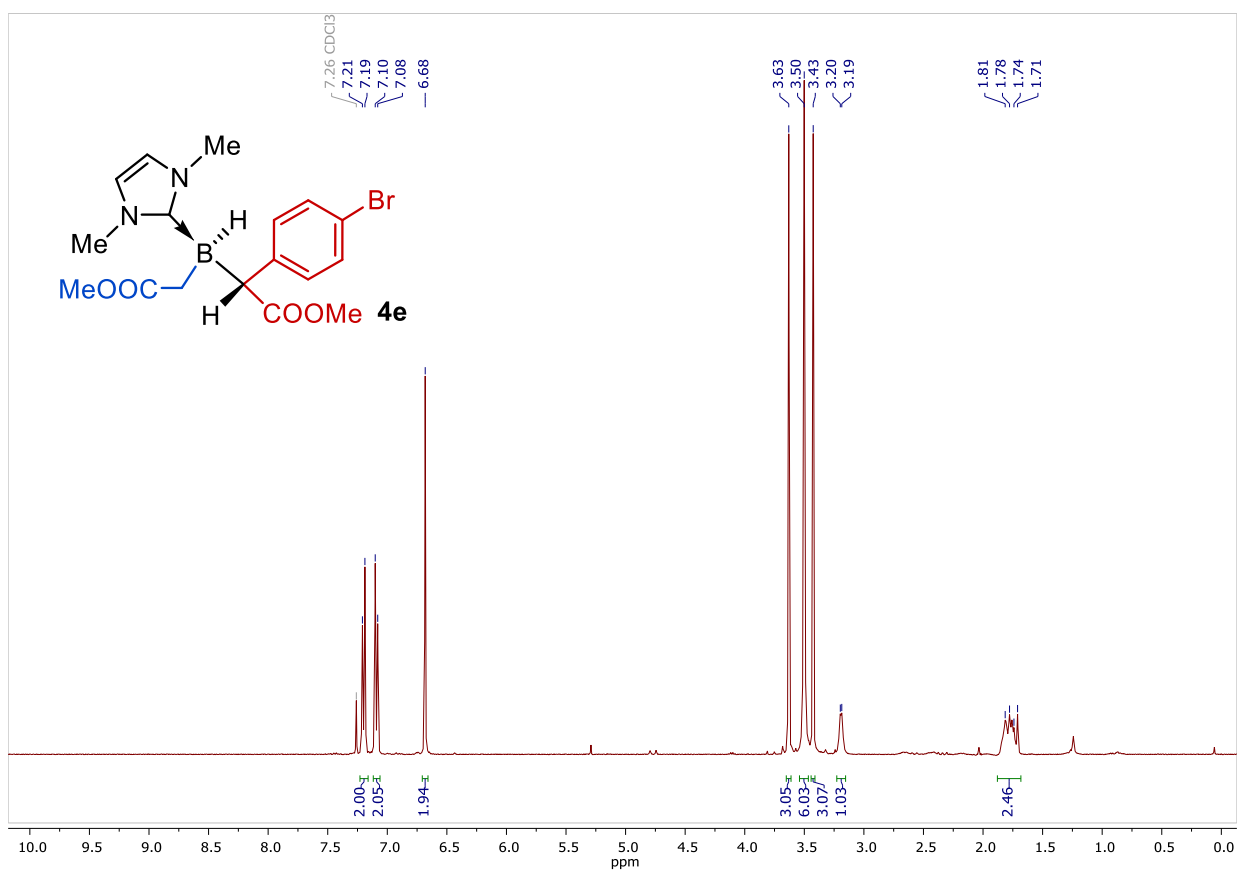


Figure S63. ^1H NMR spectrum of **4e** in CDCl_3 .

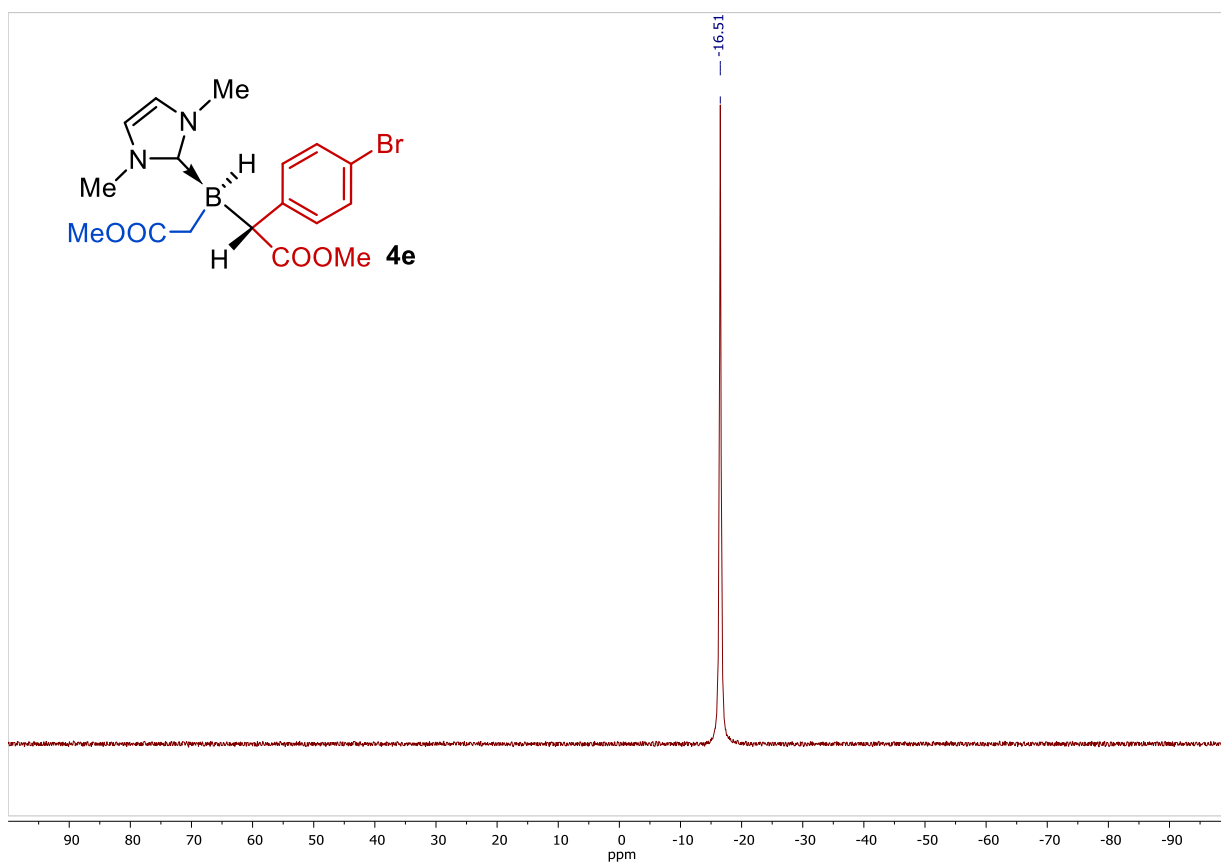


Figure S64. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4e** in CDCl_3 .

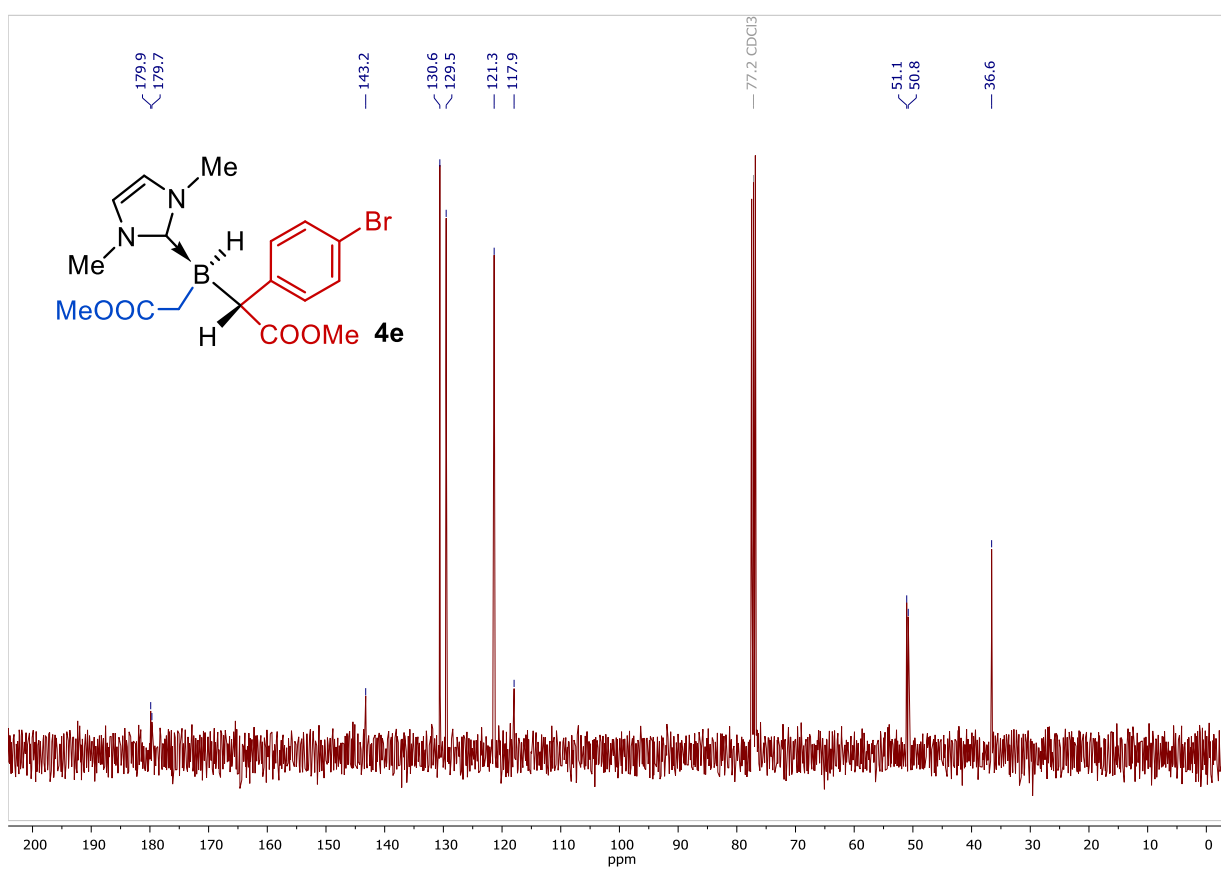


Figure S65. ^{13}C NMR spectrum of **4e** in CDCl_3 .

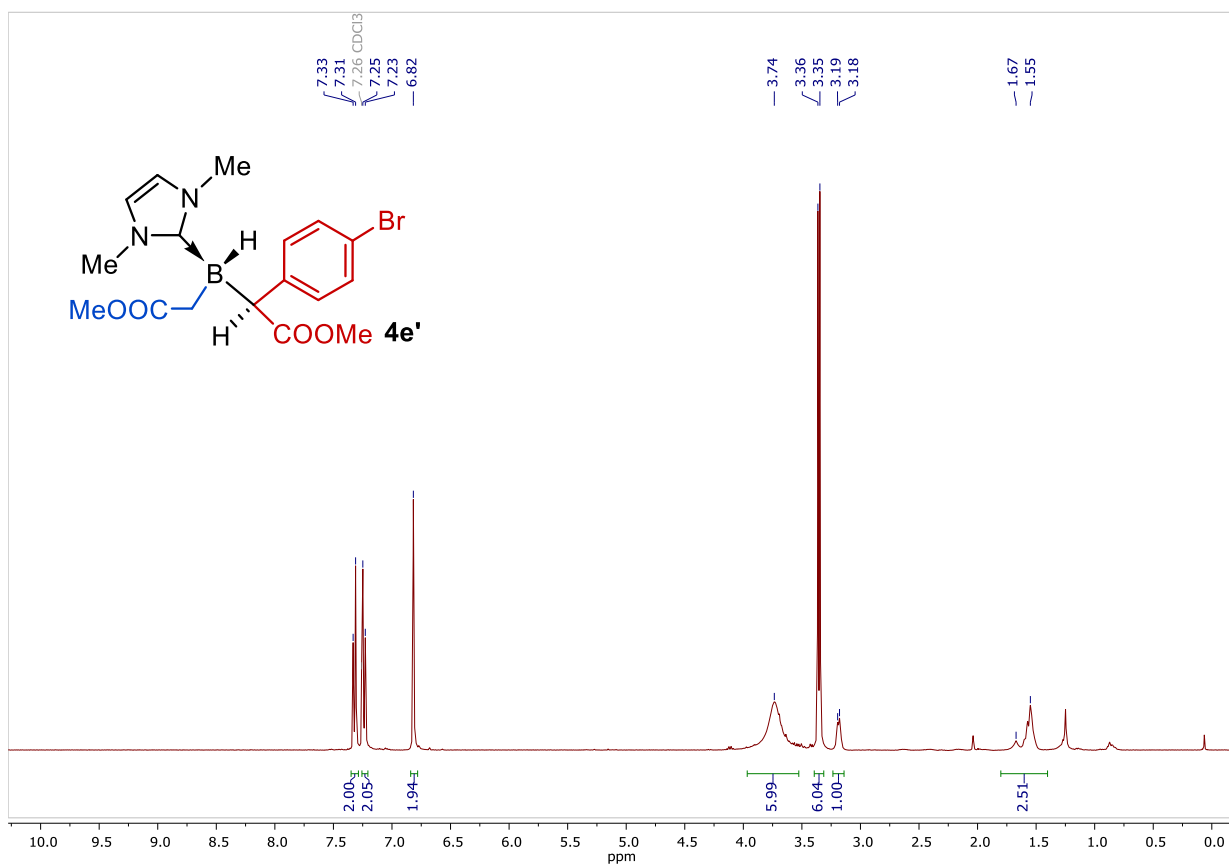


Figure S66. ^1H NMR spectrum of **4e'** in CDCl_3 .

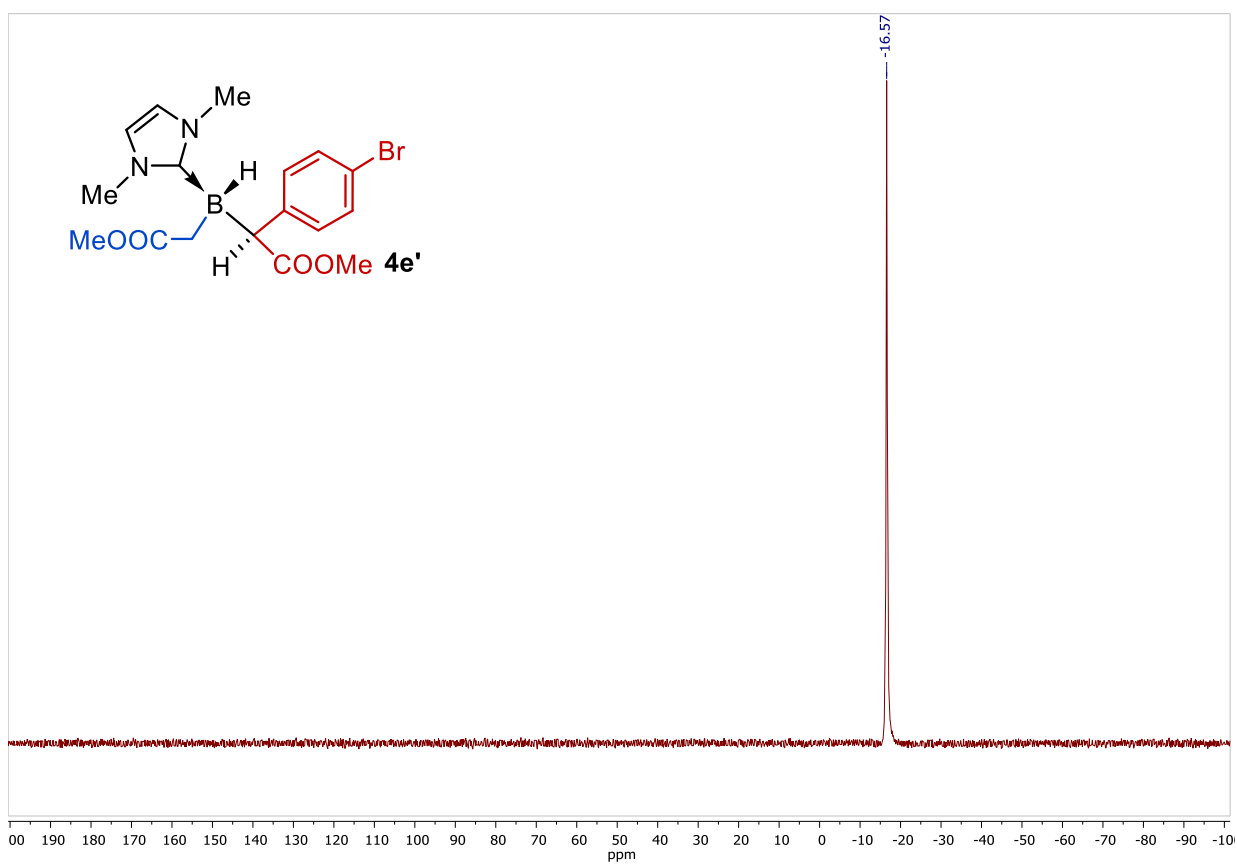


Figure S67. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4e'** in CDCl_3 .

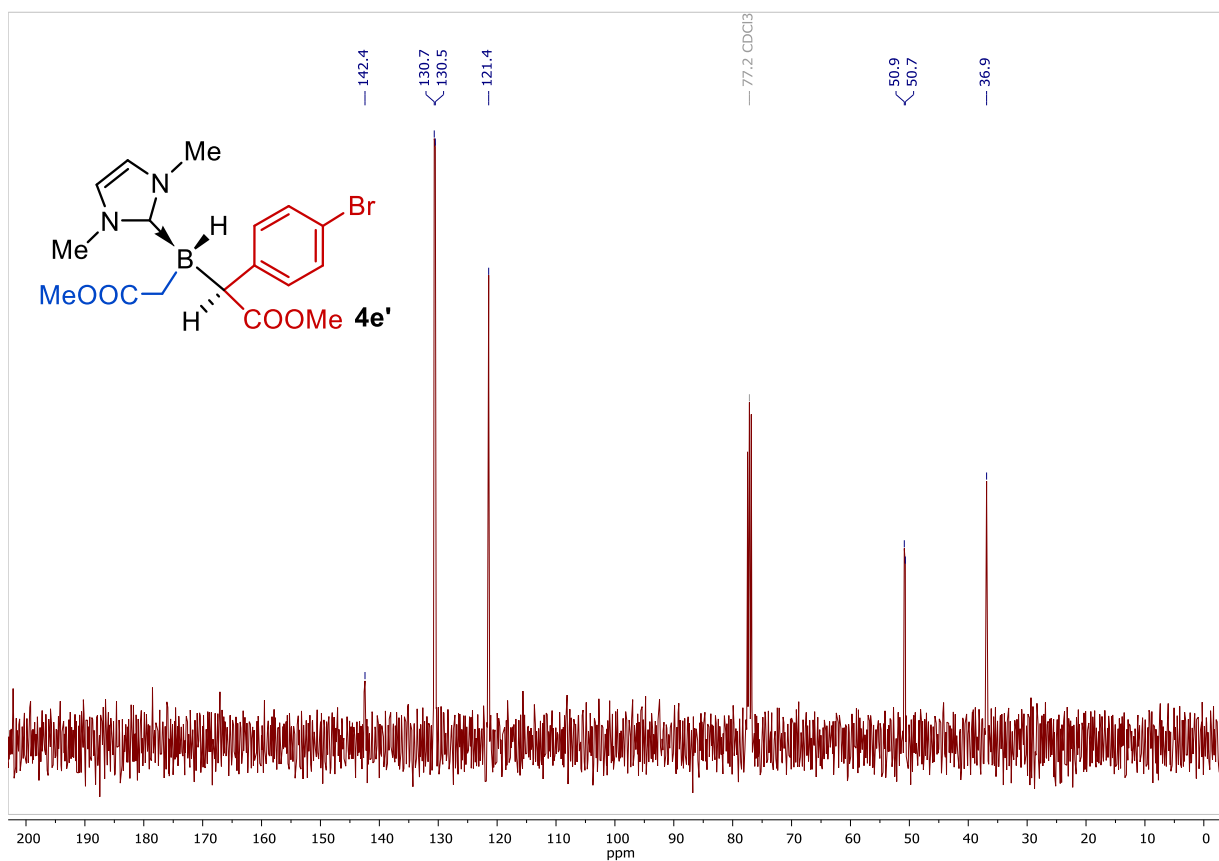


Figure S68. ^{13}C NMR spectrum of **4e'** in CDCl_3 .

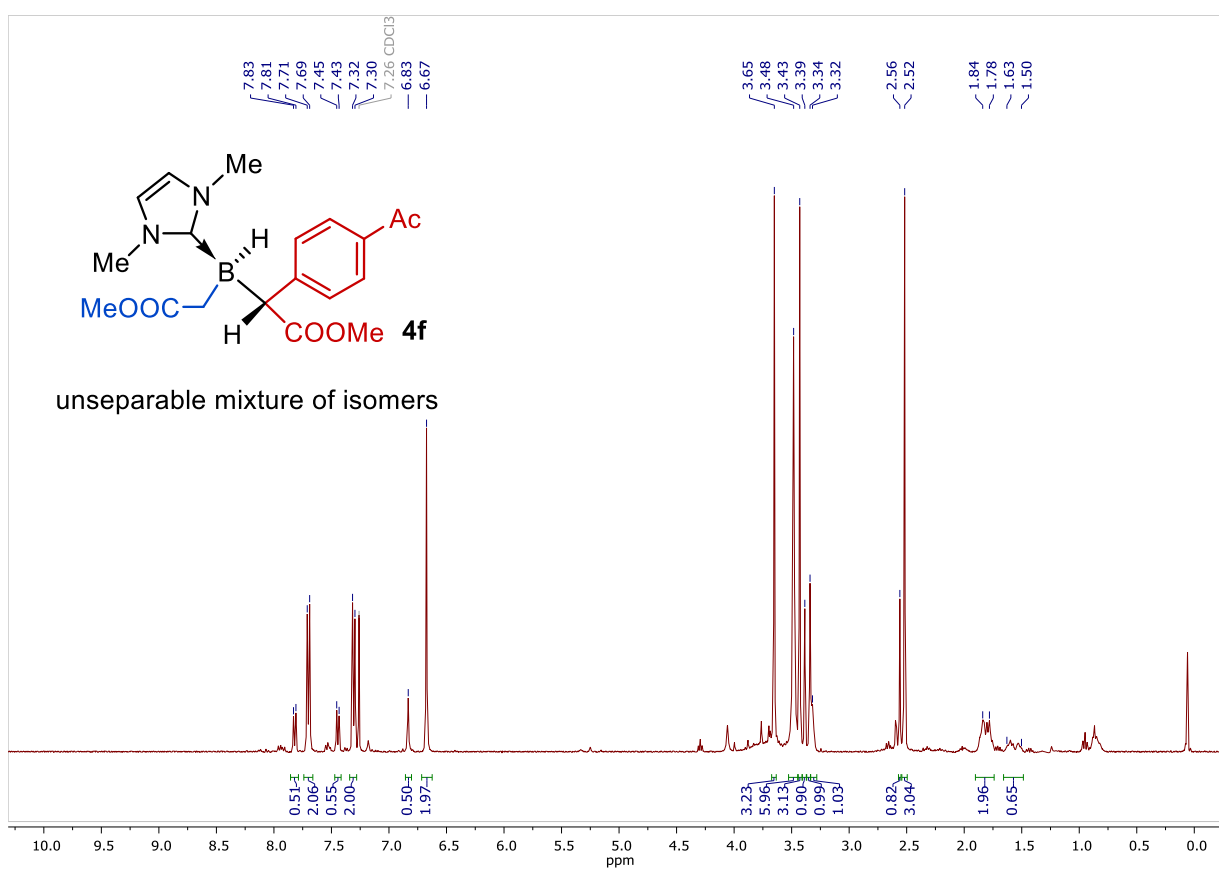


Figure S69. ^1H NMR spectrum of **4f** (mixture of diastereomers) in CDCl_3 .

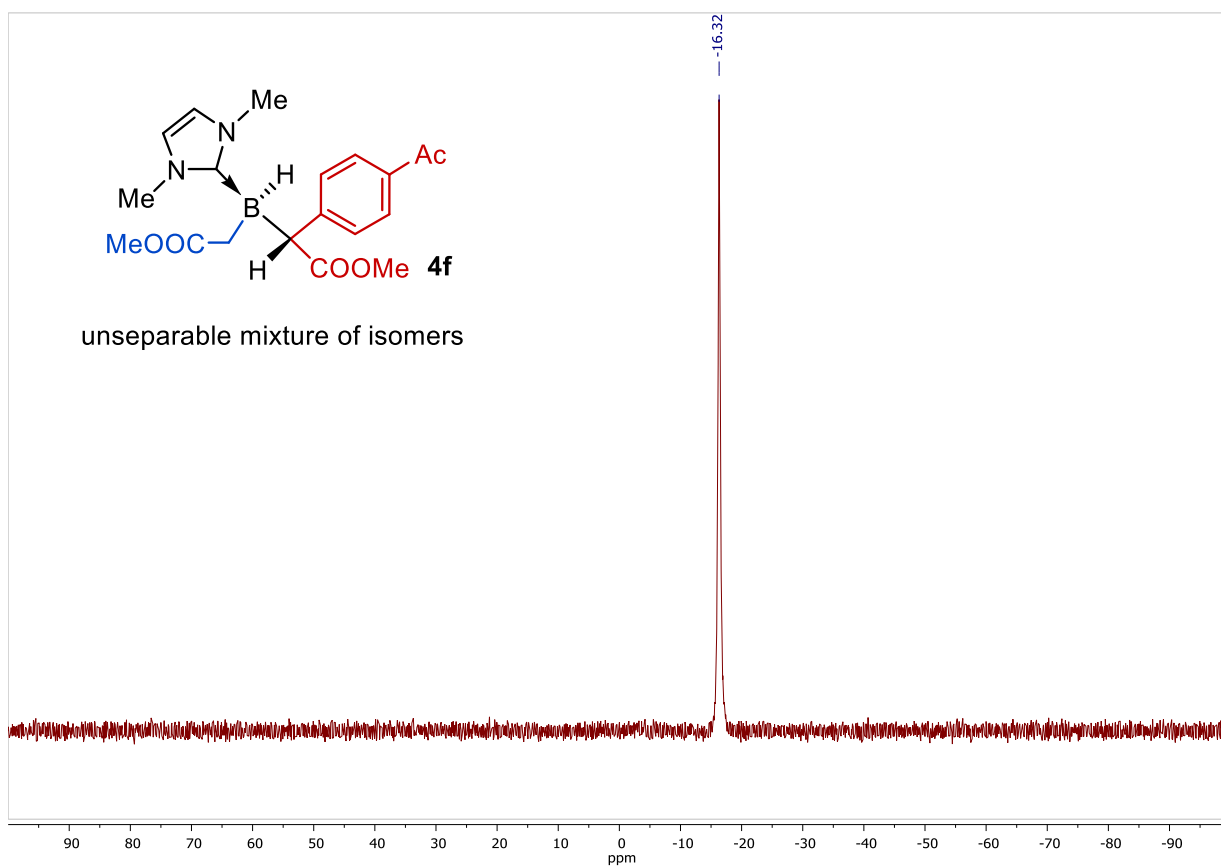


Figure S70. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4f** (mixture of diastereomers) in CDCl_3 .

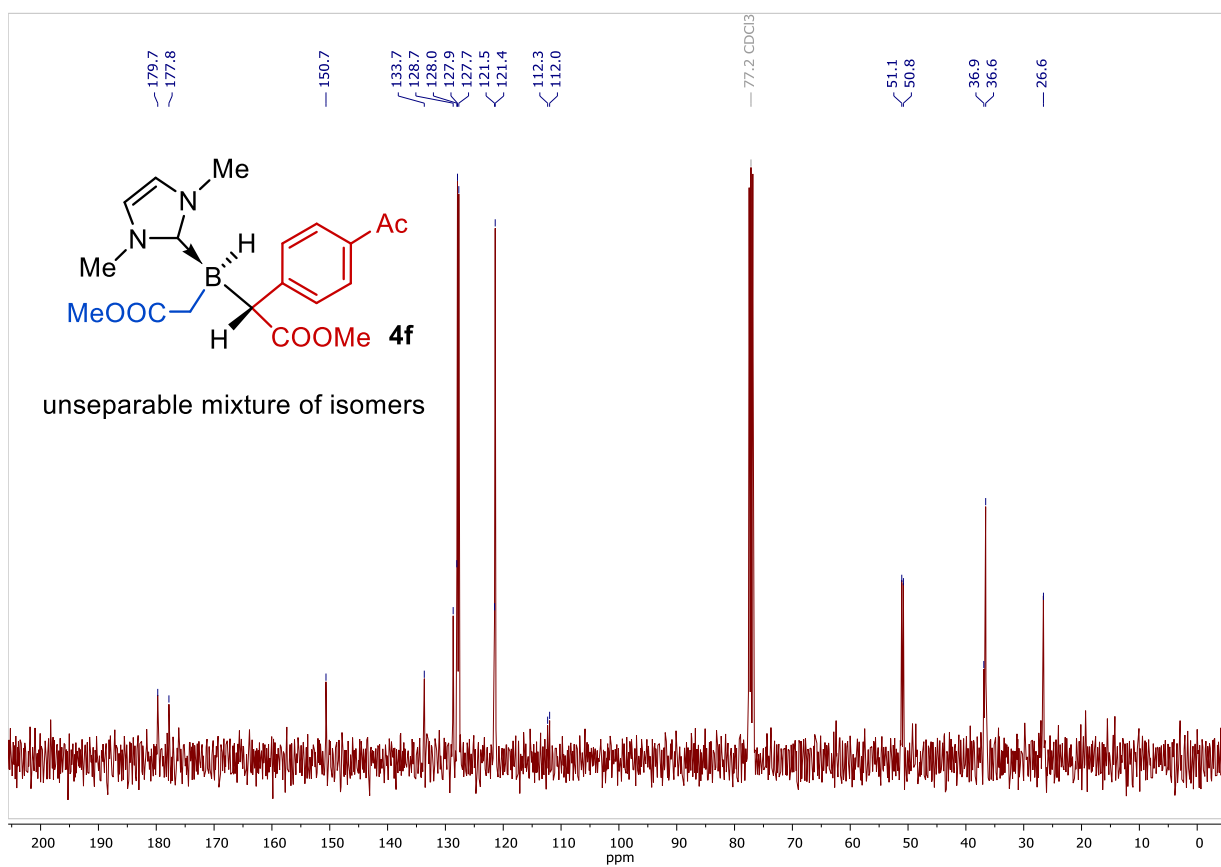


Figure S71. ^{13}C NMR spectrum of **4f** (mixture of diastereomers) in CDCl_3 .

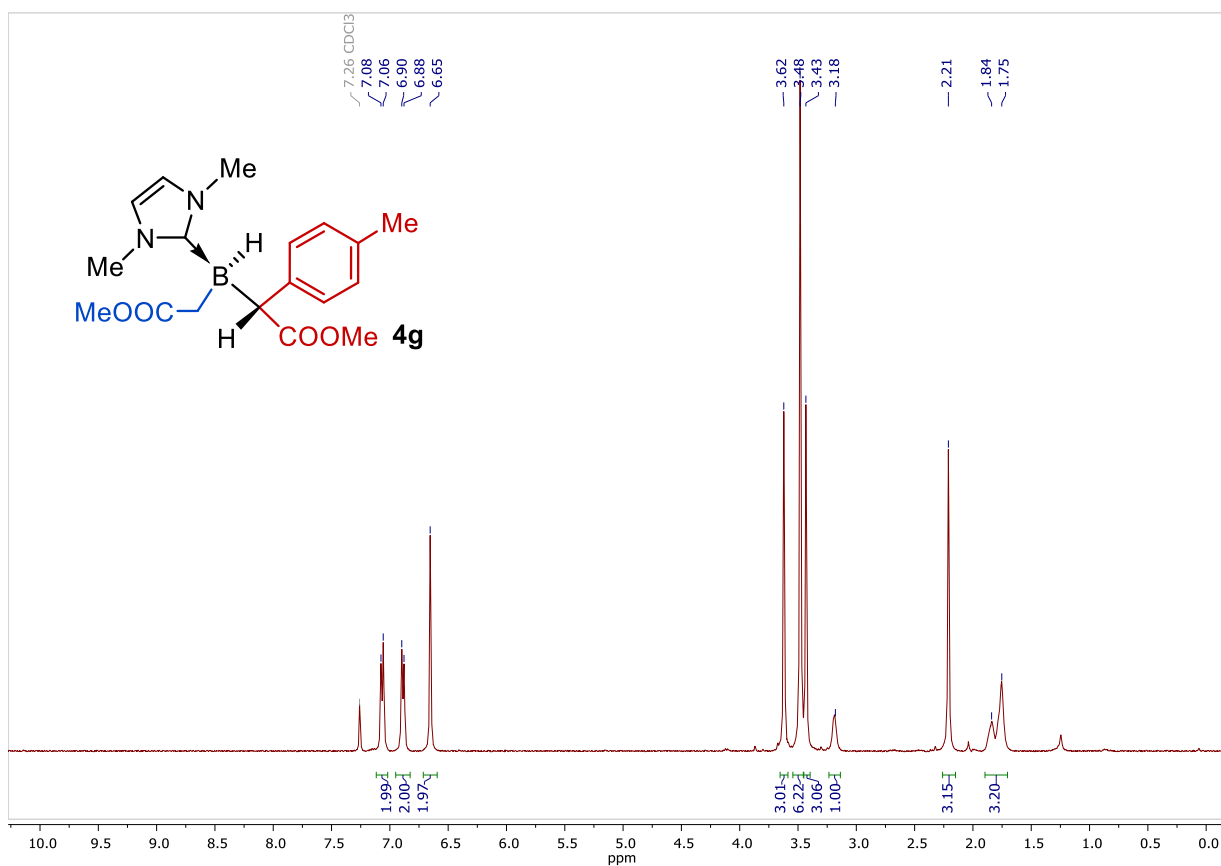


Figure S72. ^1H NMR spectrum of **4g** in CDCl_3 .

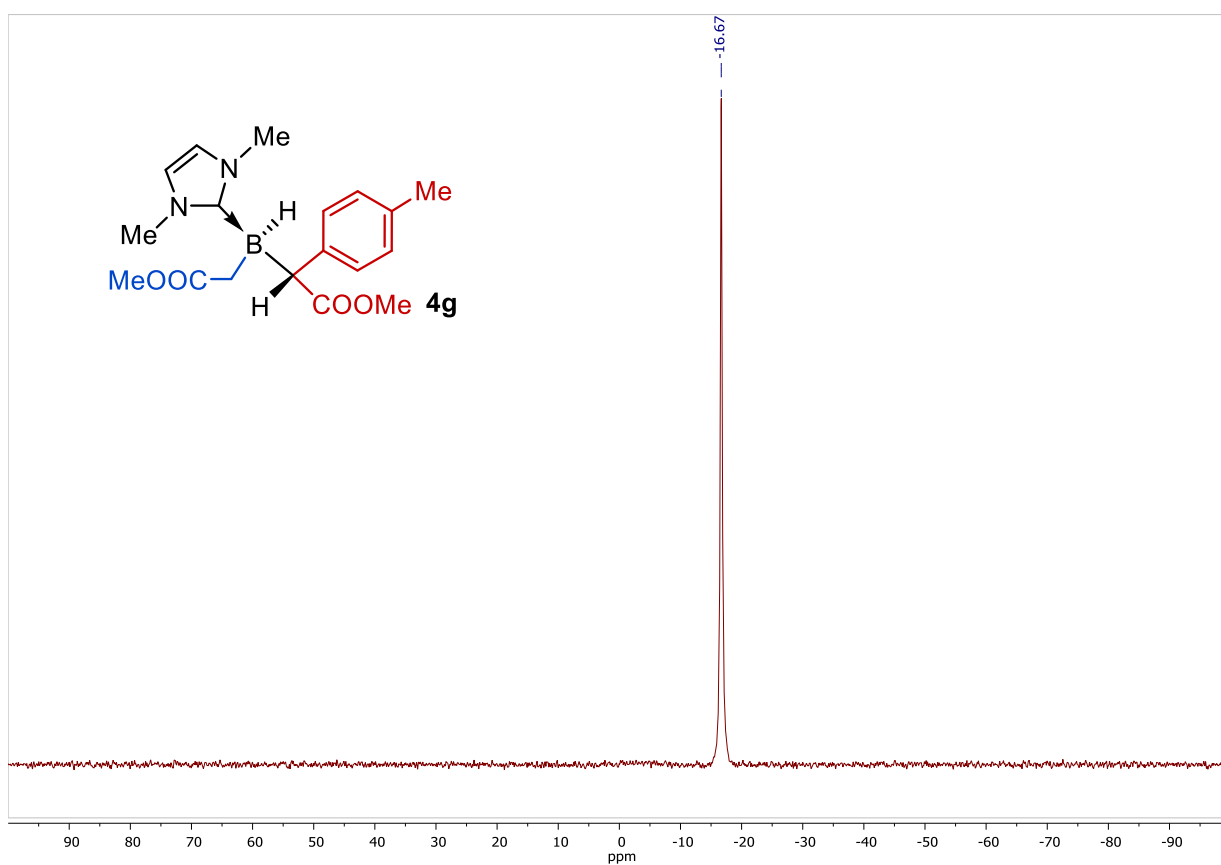


Figure S73. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4g** in CDCl_3 .

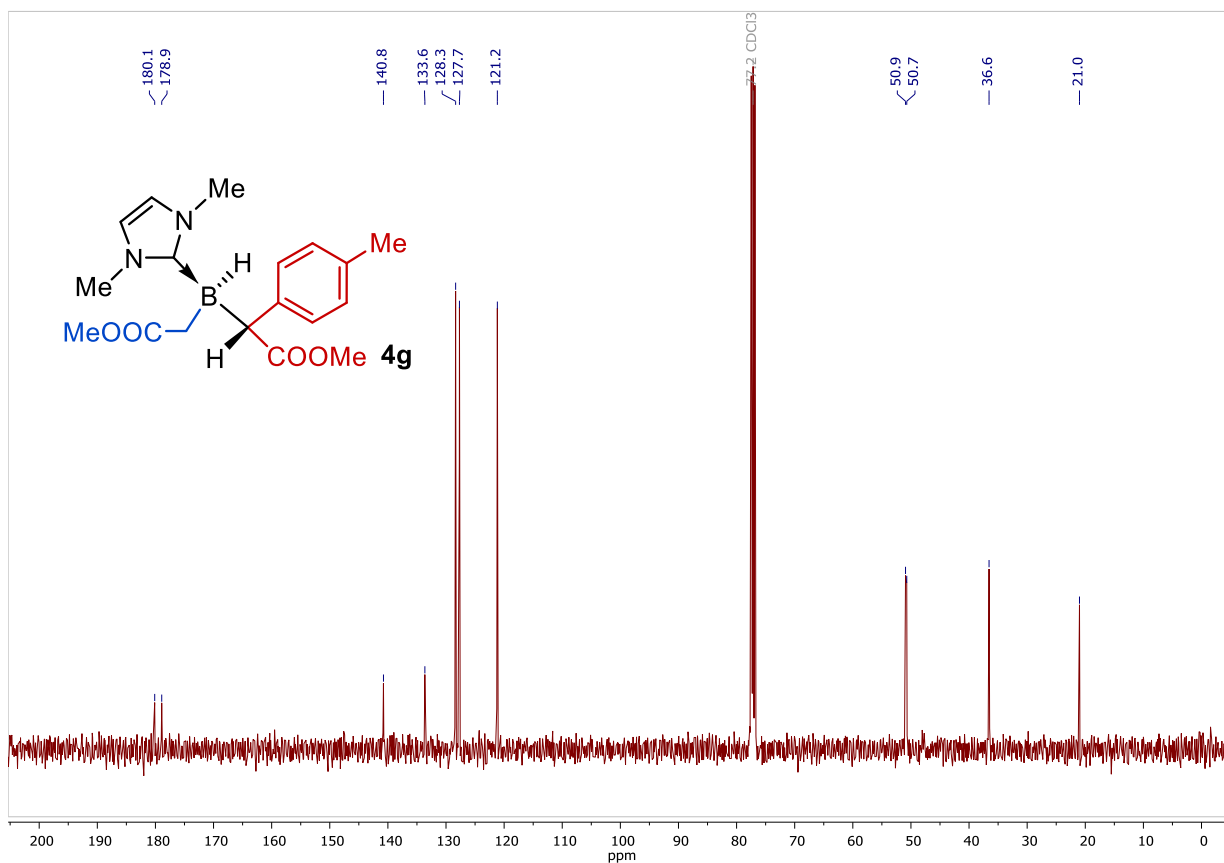


Figure S74. ^{13}C NMR spectrum of **4g** in CDCl_3 .

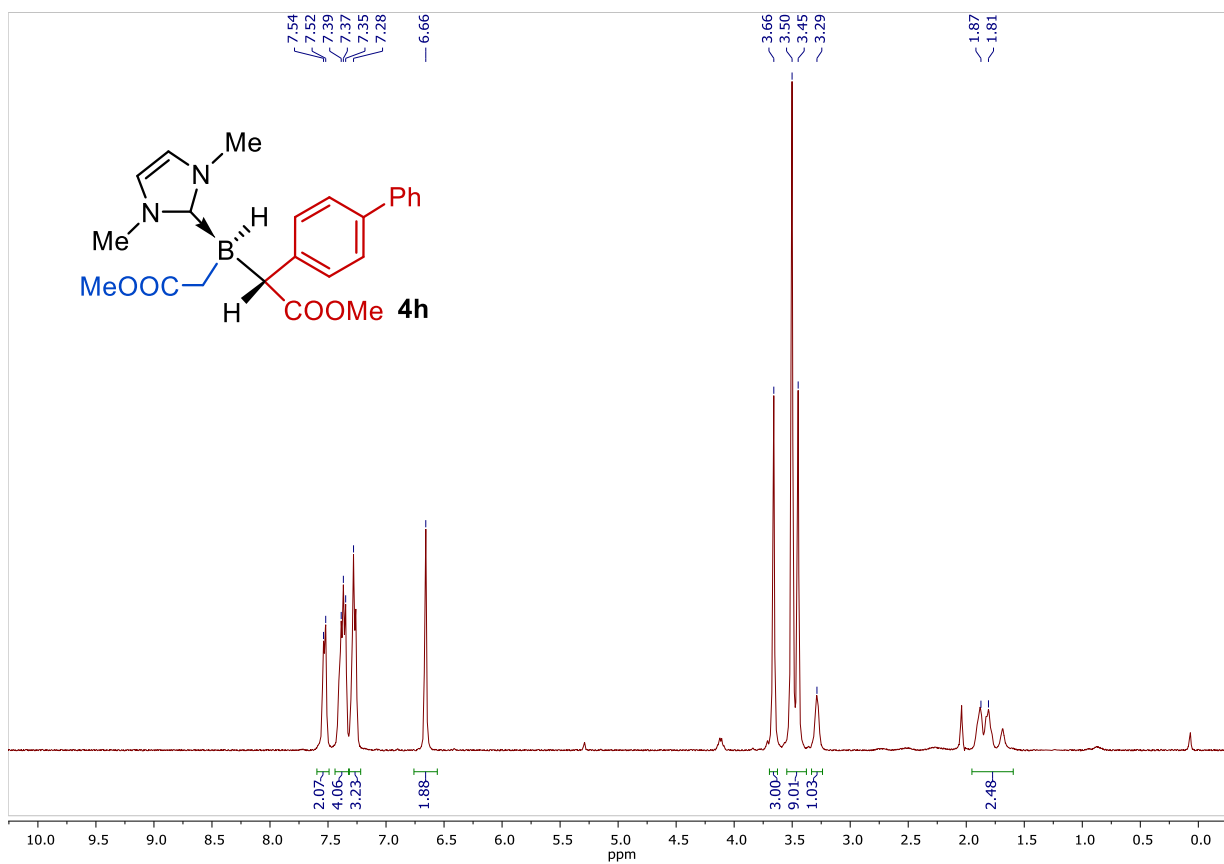


Figure S75. ^1H NMR spectrum of **4h** in CDCl_3 .

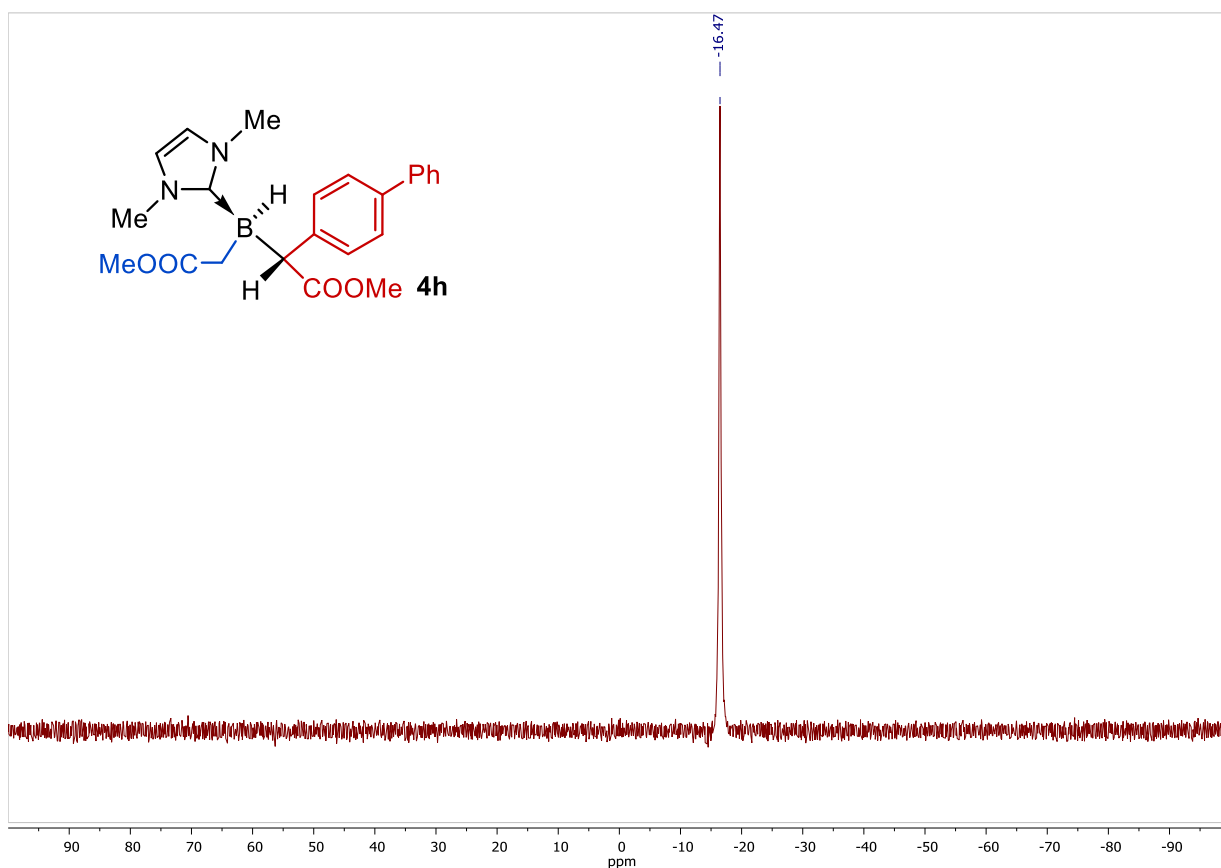


Figure S76. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4h** in CDCl_3 .

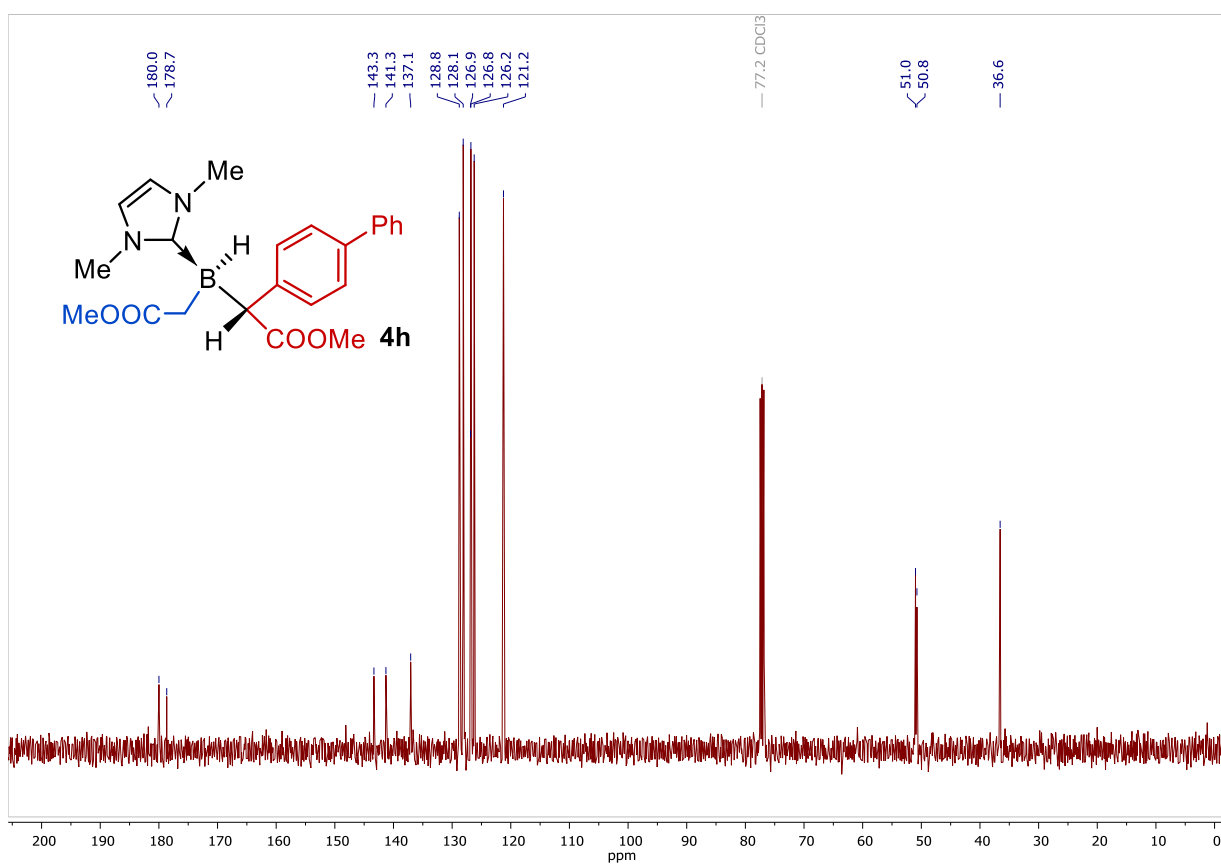


Figure S77. ^{13}C NMR spectrum of **4h** in CDCl_3 .

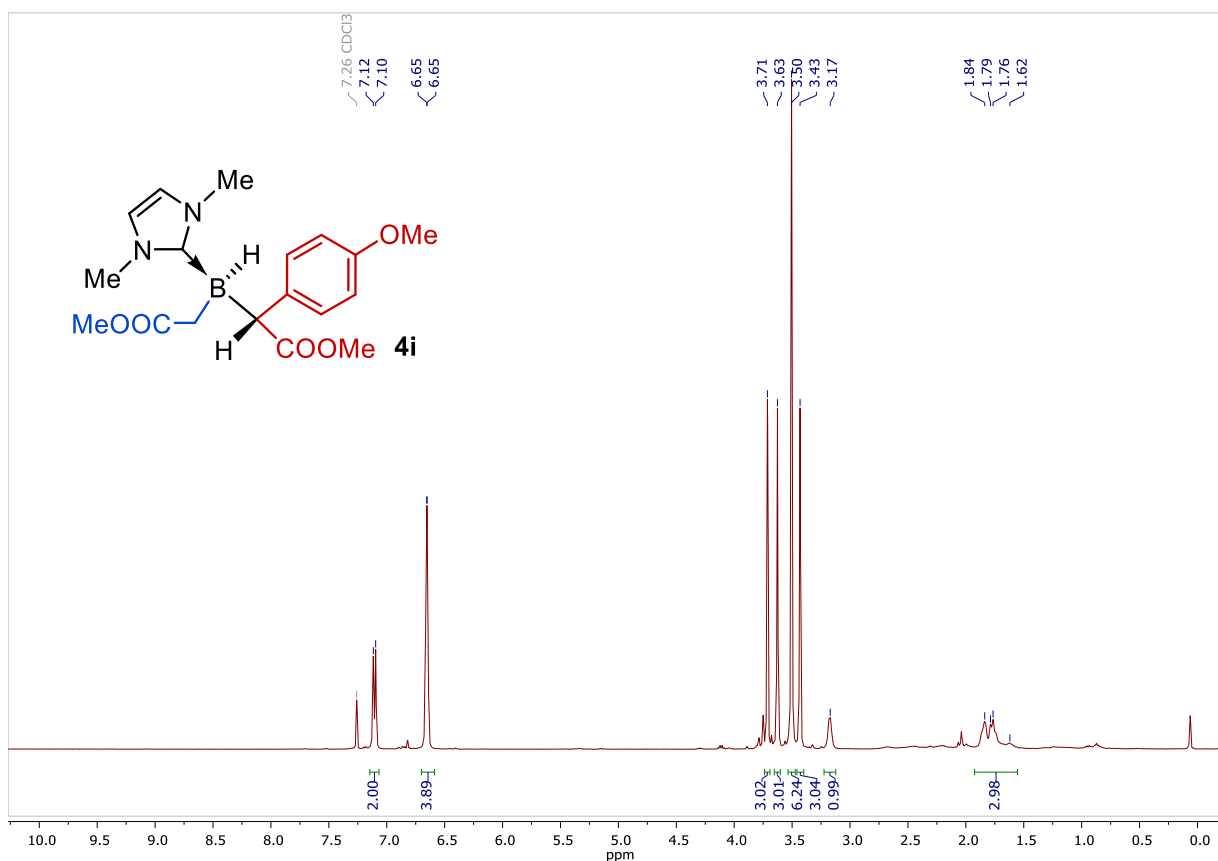


Figure S78. ^1H NMR spectrum of **4i** in CDCl_3 .

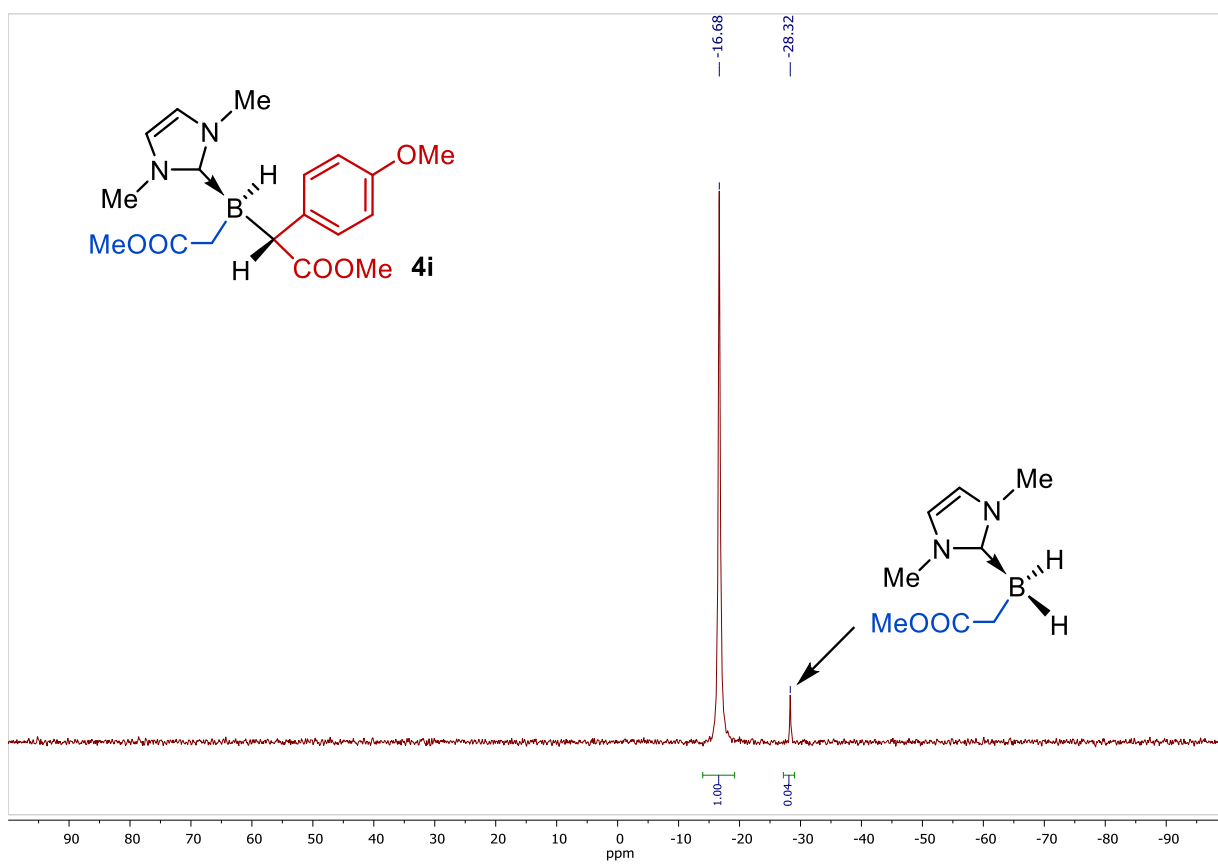


Figure S79. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4i** in CDCl_3 .

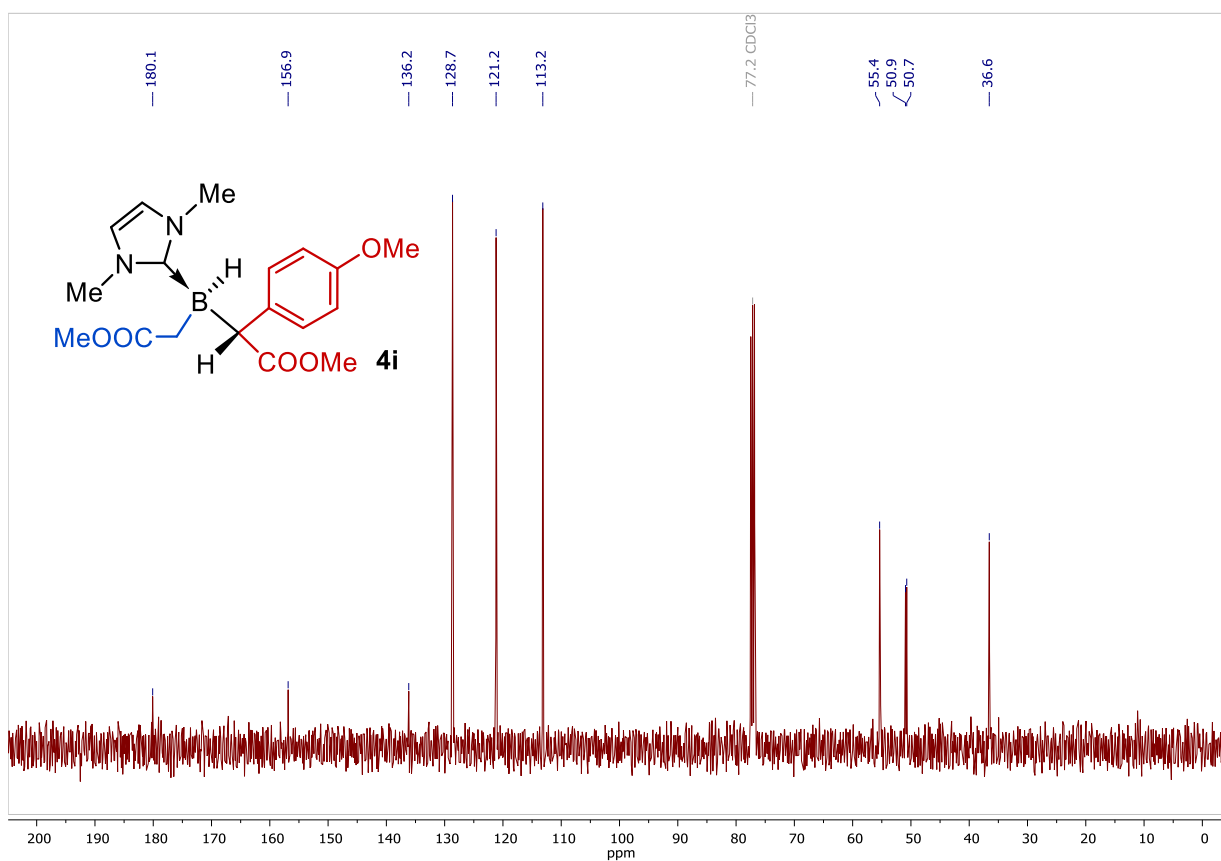


Figure S80. ^{13}C NMR spectrum of **4i** in CDCl_3 .

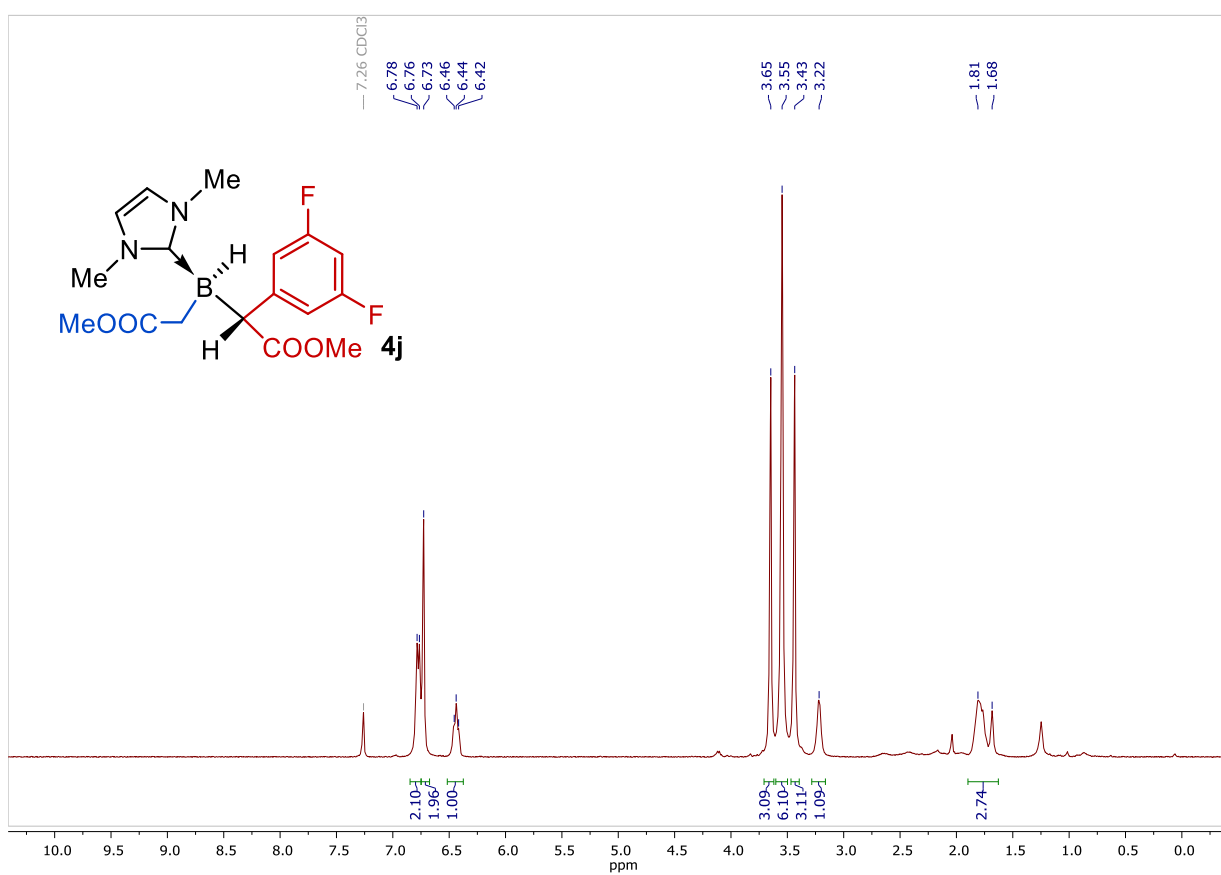


Figure S81. ^1H NMR spectrum of **4j** in CDCl_3 .

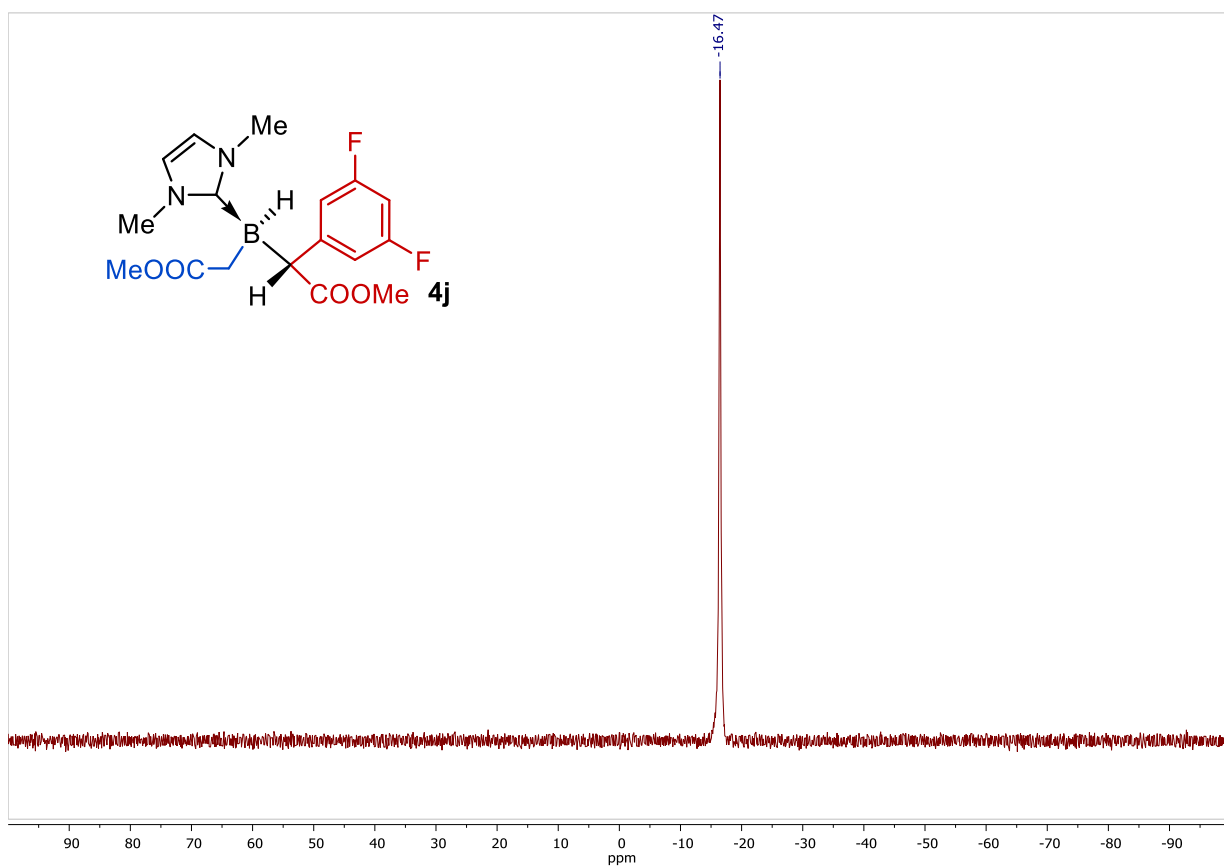


Figure S82. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4j** in CDCl_3 .

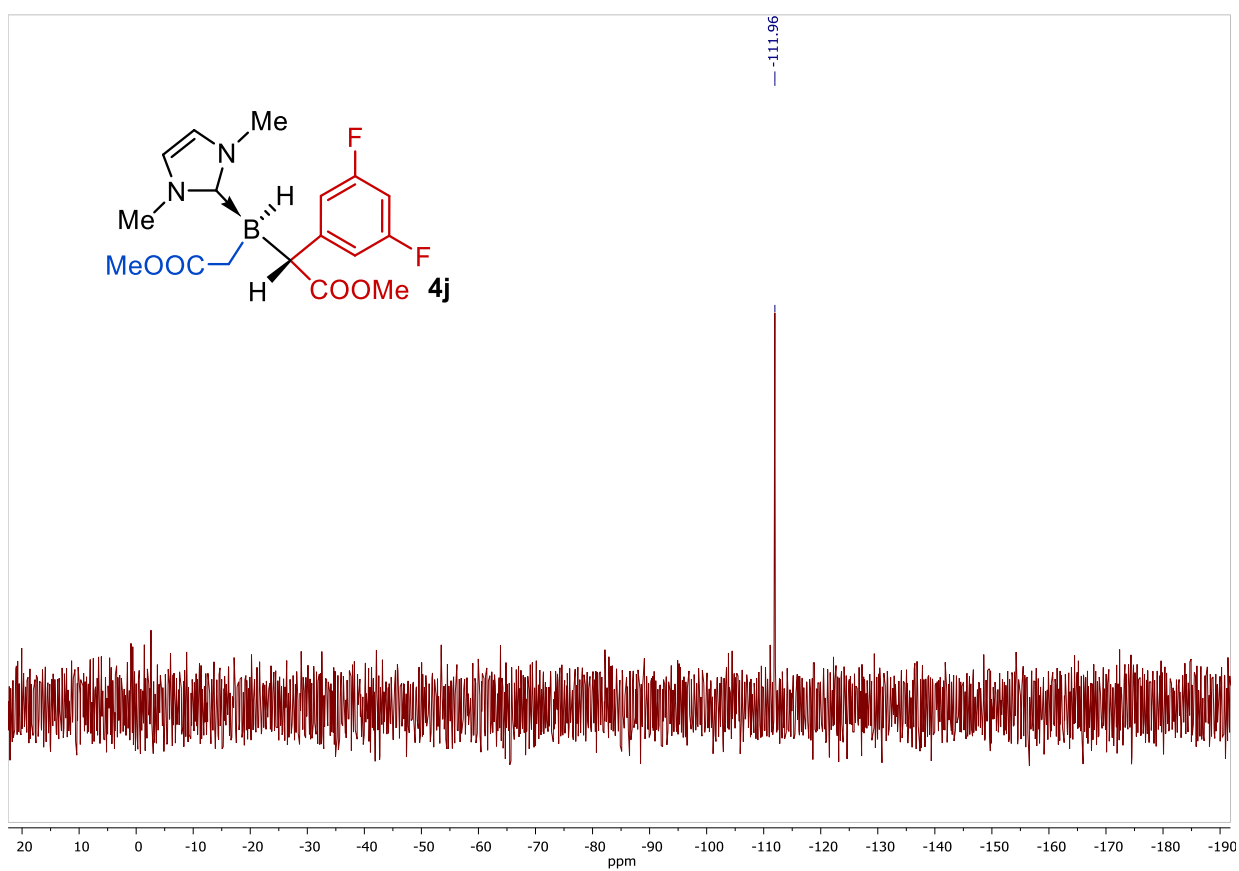


Figure S83. ^{19}F NMR spectrum of **4j** in CDCl_3 .

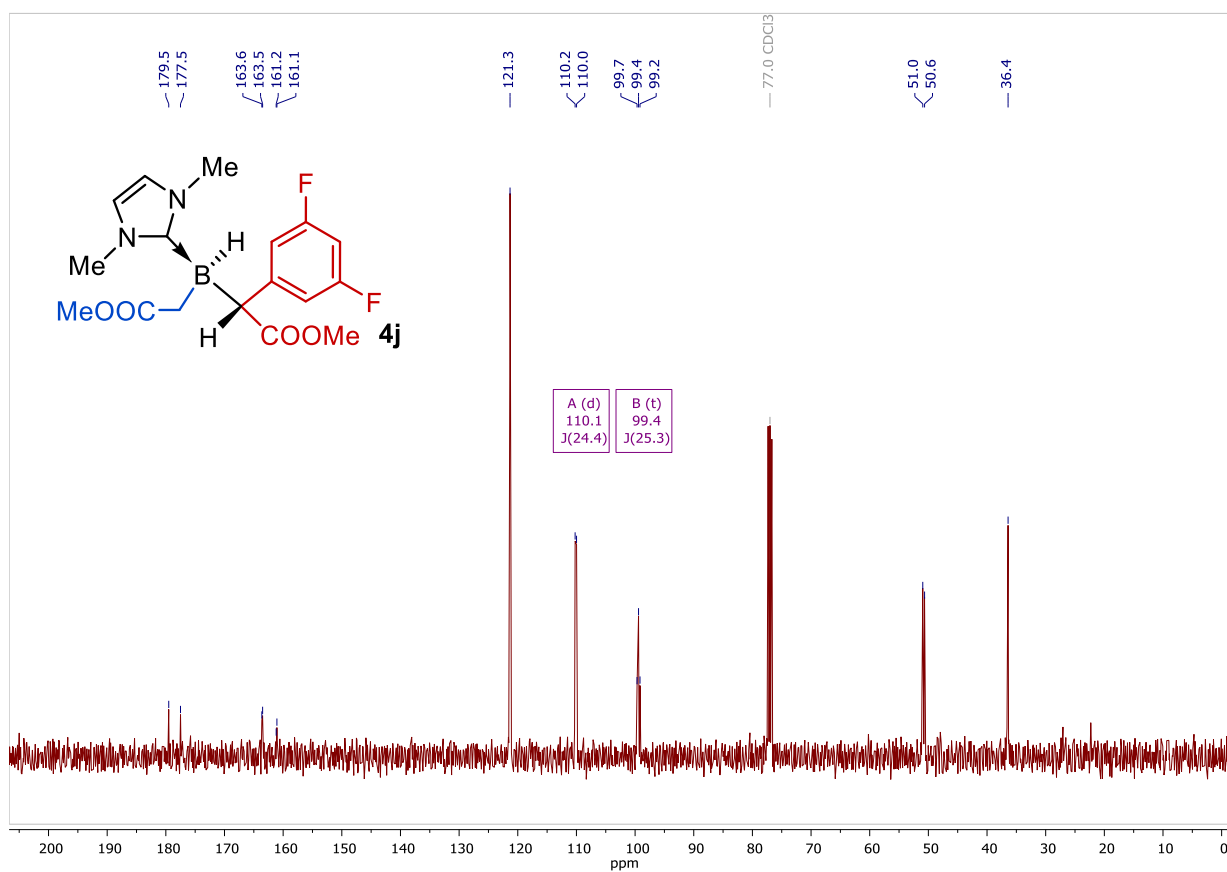


Figure S84. ^{13}C NMR spectrum of **4j** in CDCl_3 .

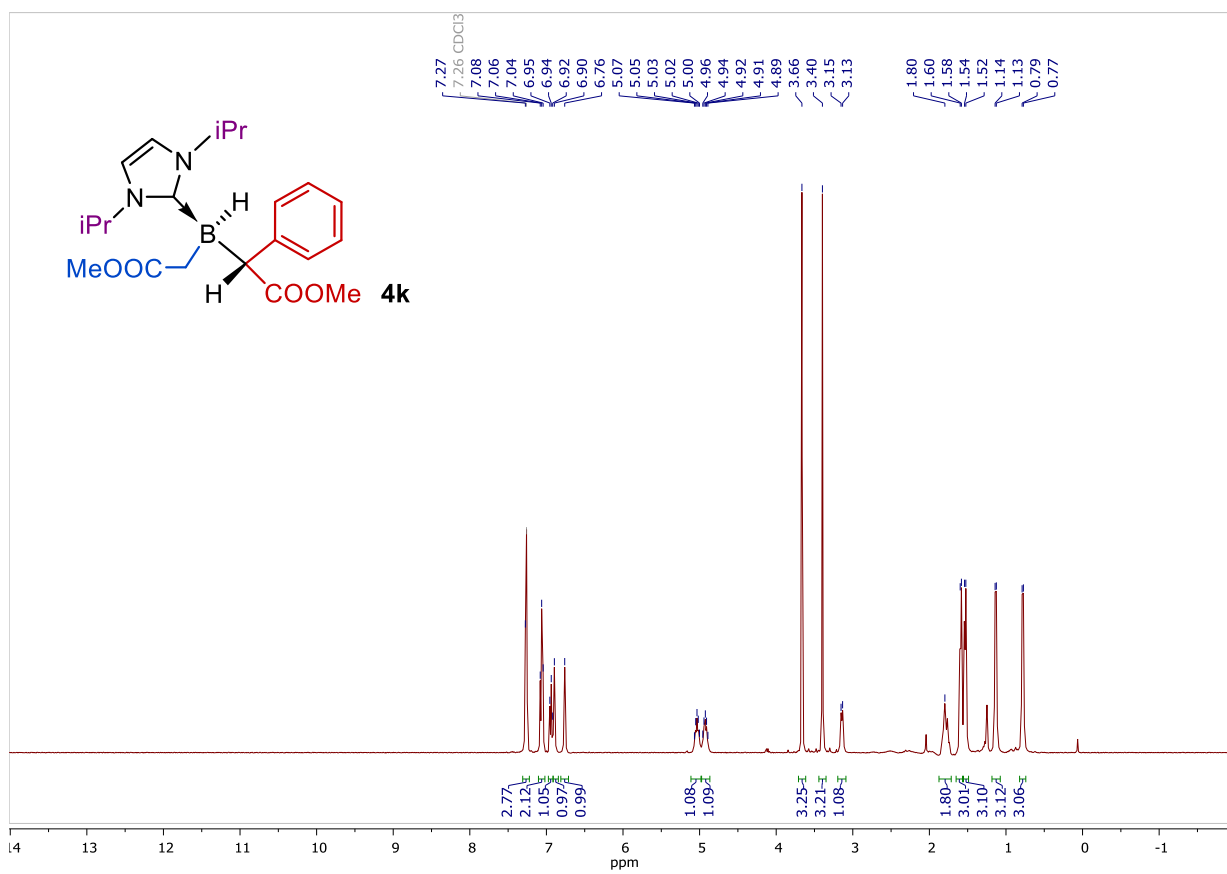


Figure S85. ^1H NMR spectrum of **4k** in CDCl_3 .

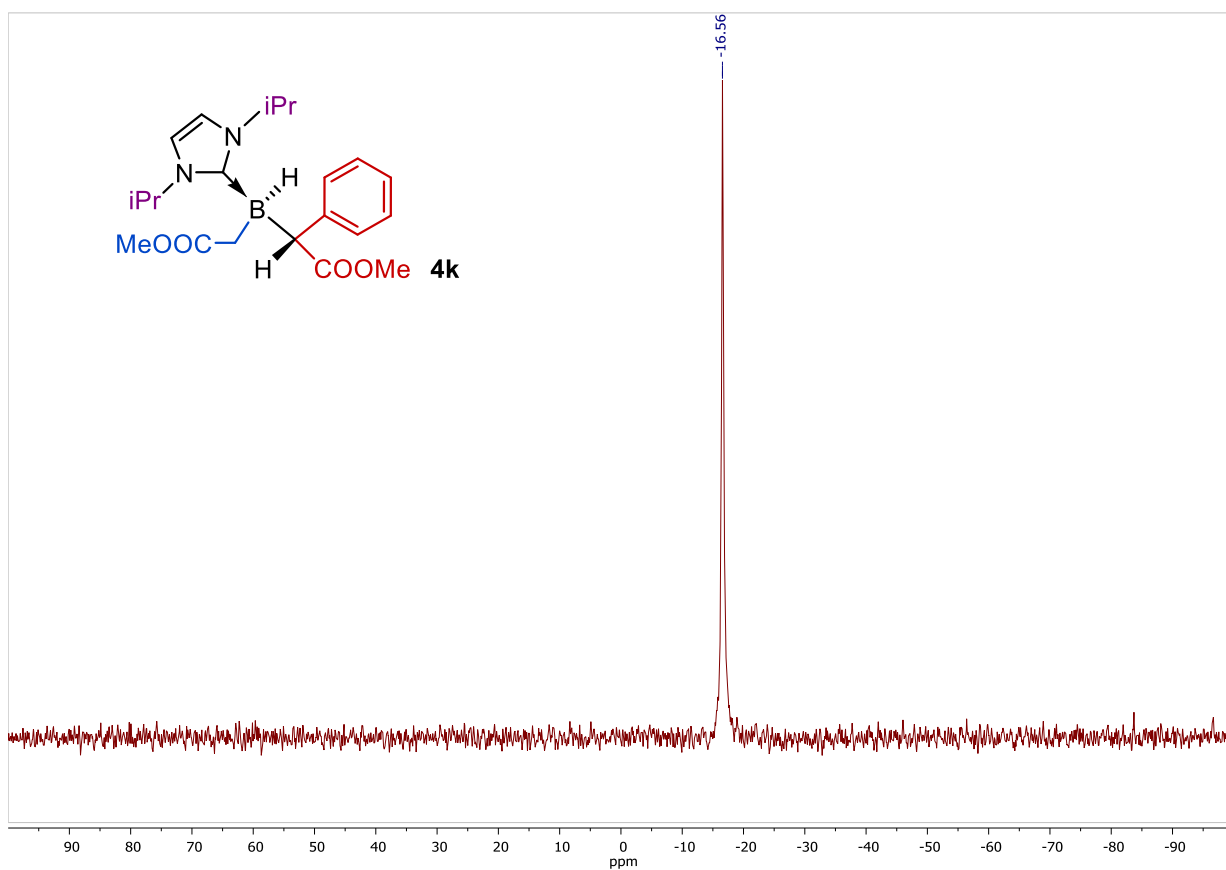


Figure S86. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4k** in CDCl_3 .

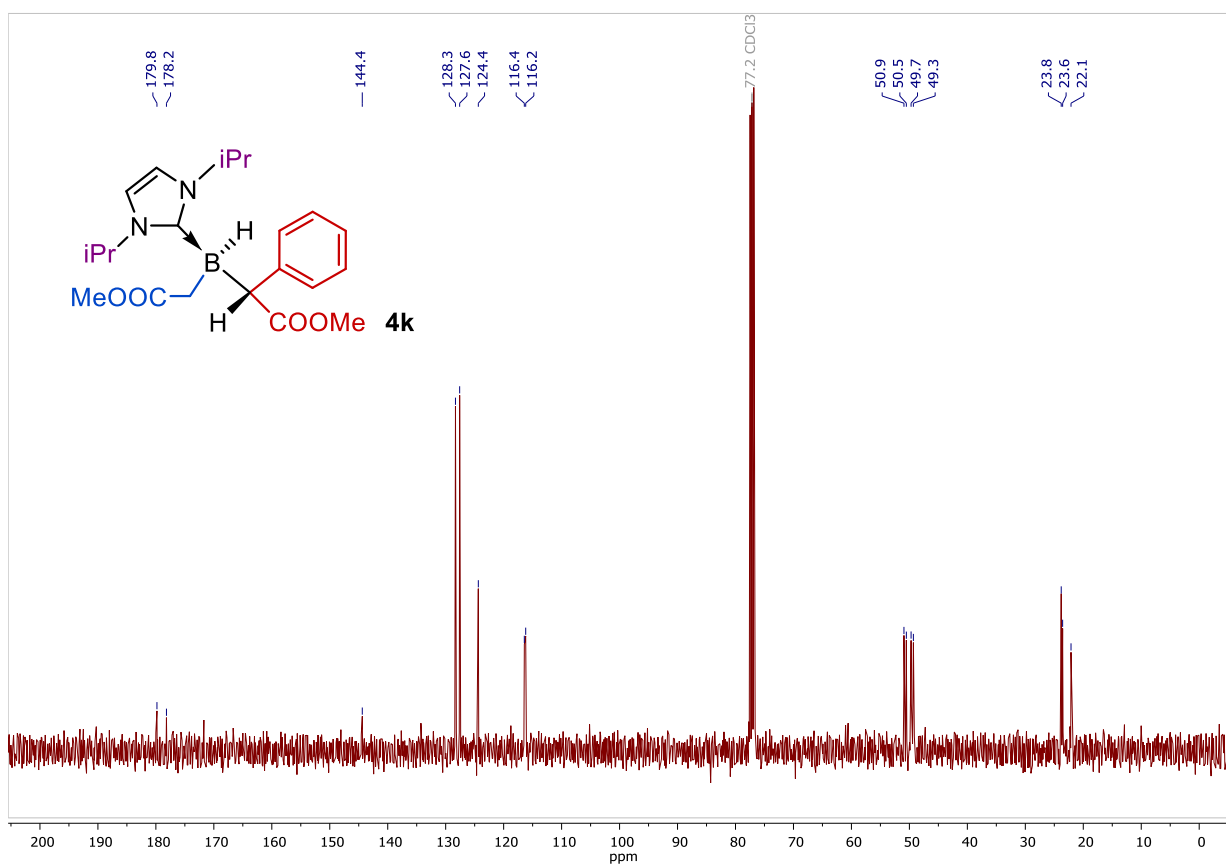


Figure S87. ^{13}C NMR spectrum of **4k** in CDCl_3 .

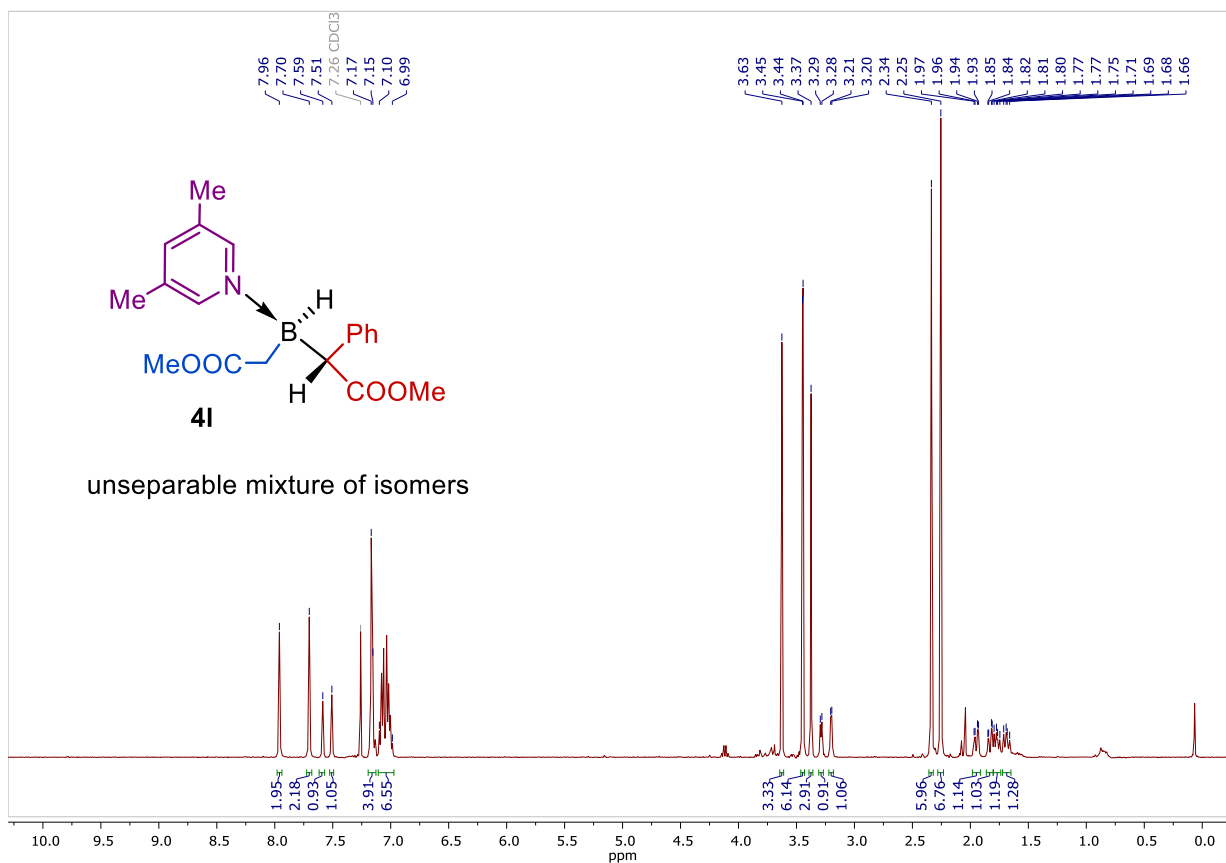


Figure S88. ¹H NMR spectrum of **4I** in CDCl₃.

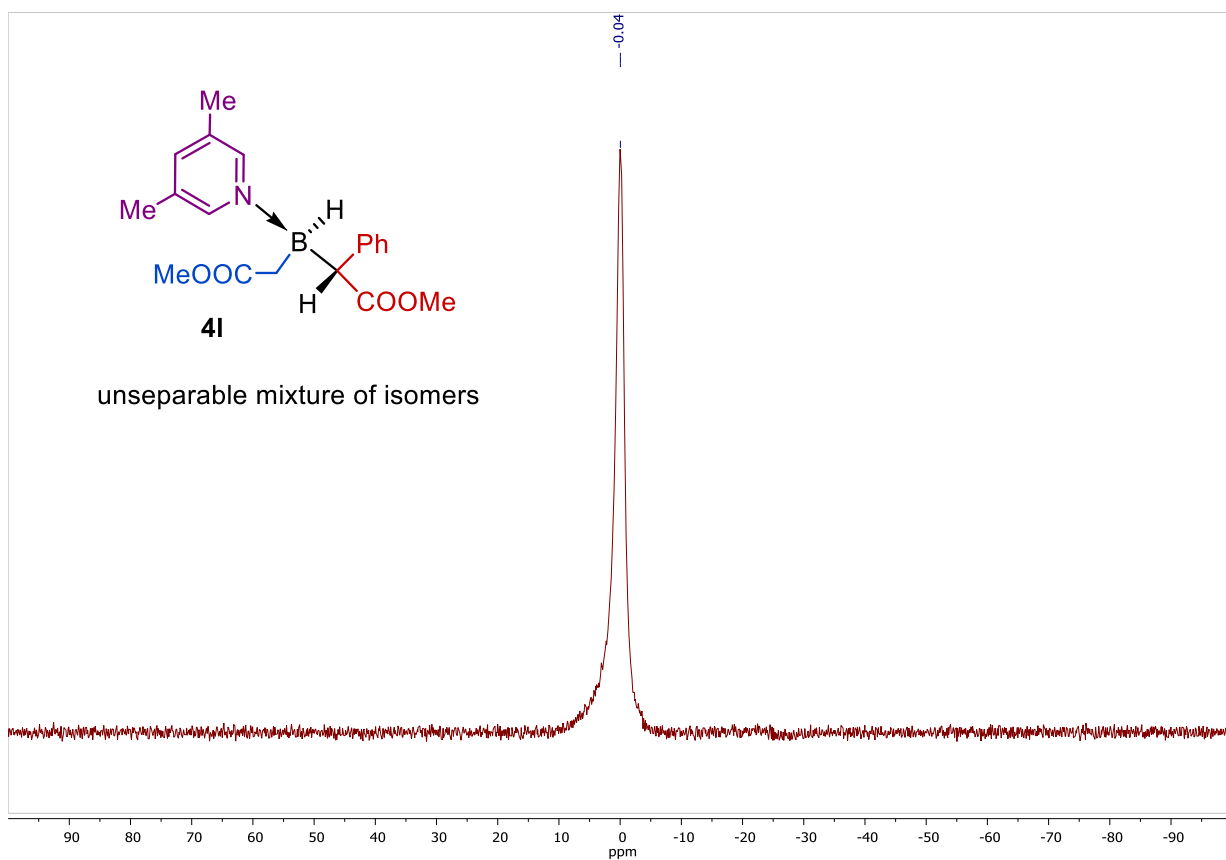


Figure S89. ¹¹B{¹H} NMR spectrum of **4I** in CDCl₃.

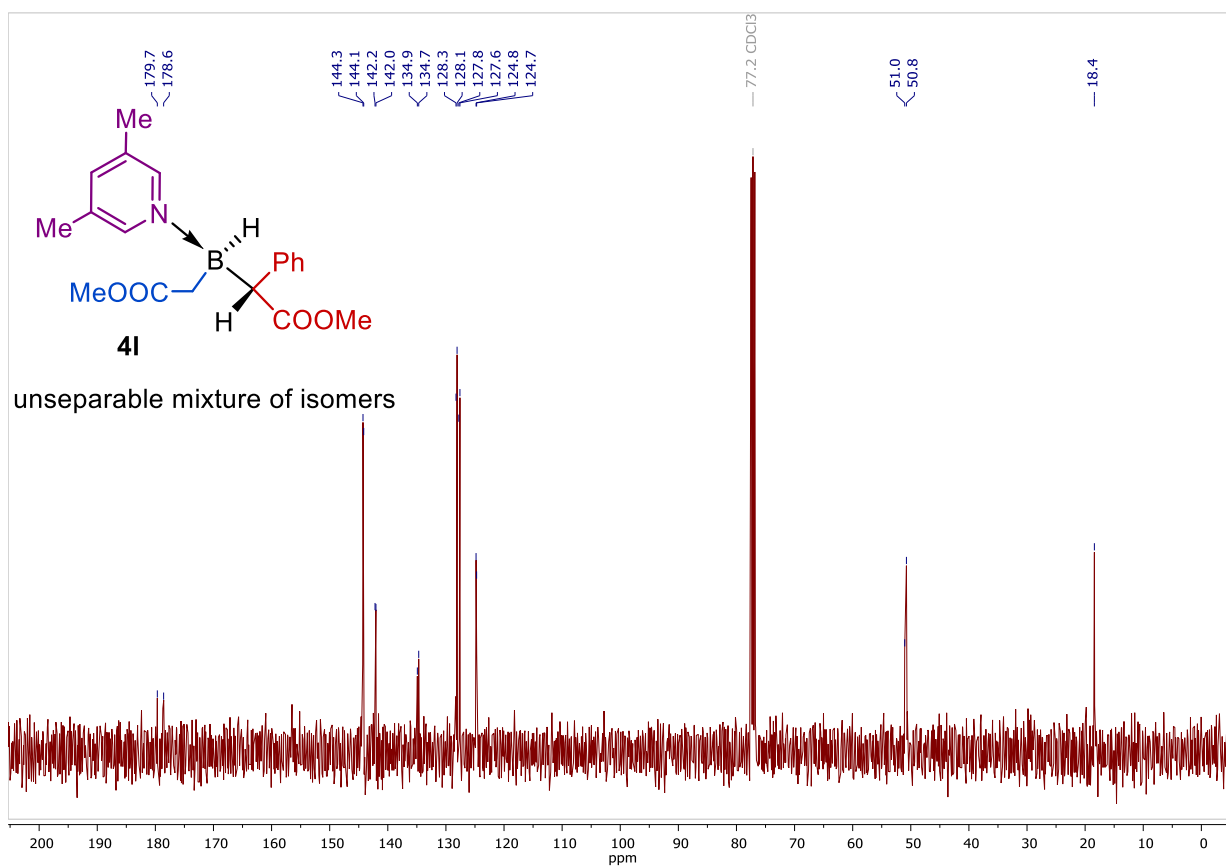


Figure S90. ^{13}C NMR spectrum of **4l** in CDCl_3 .

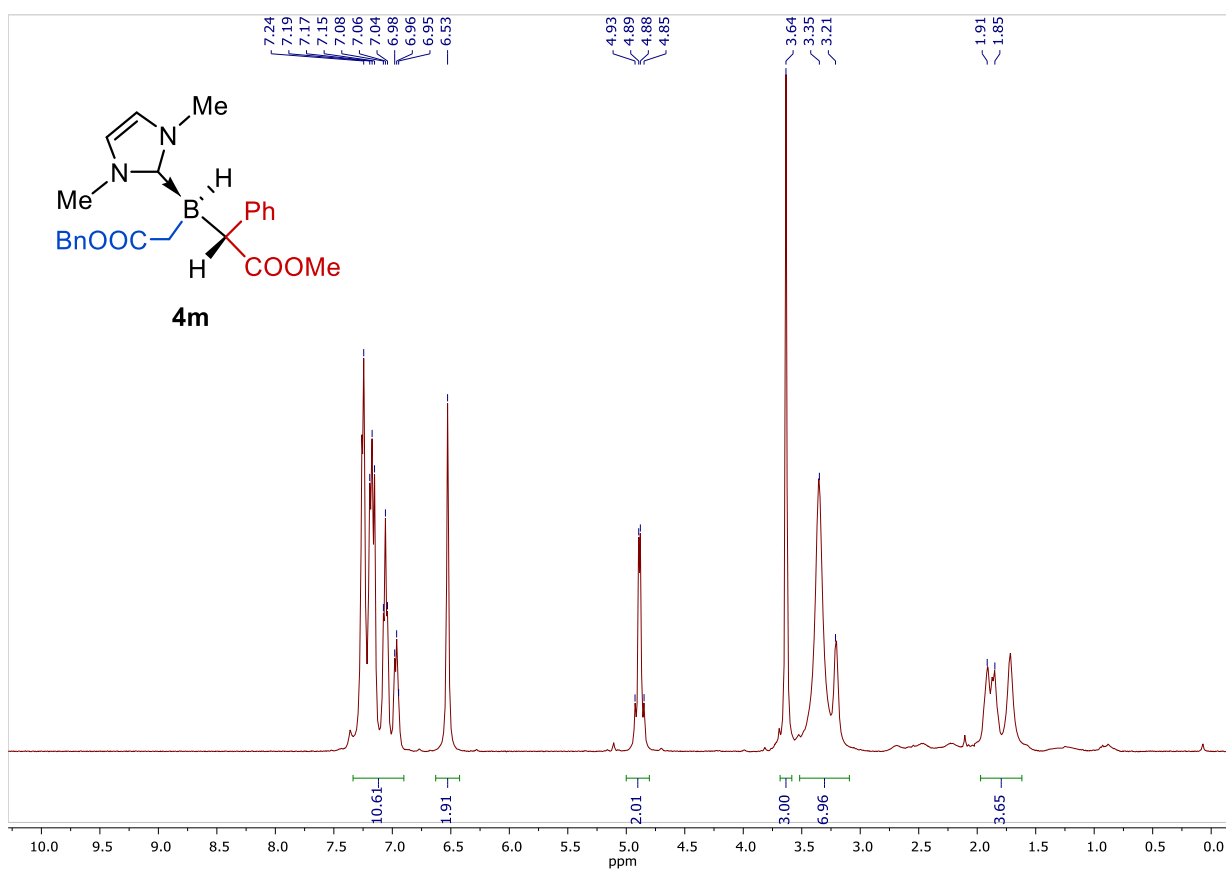


Figure S91. ^1H NMR spectrum of **4m** in CDCl_3 .

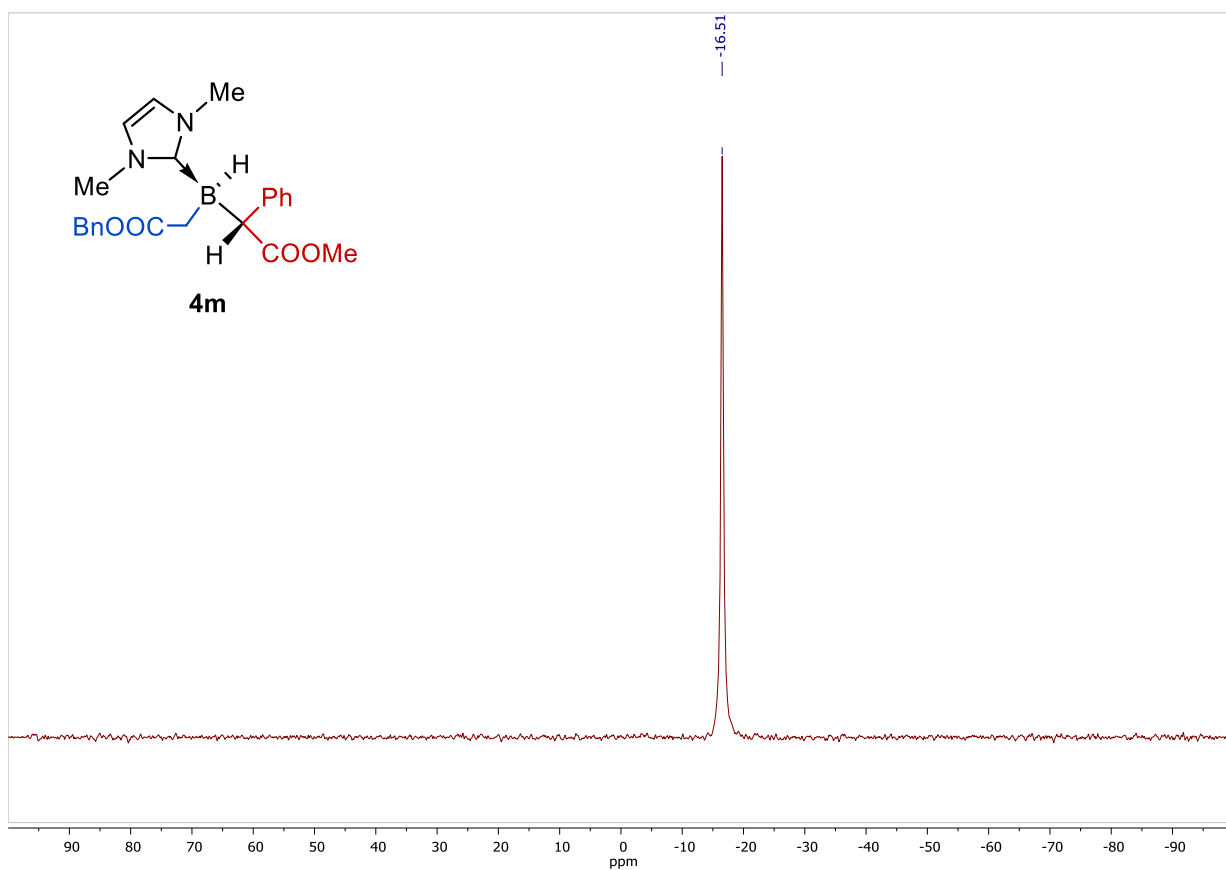


Figure S92. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4m** in CDCl_3 .

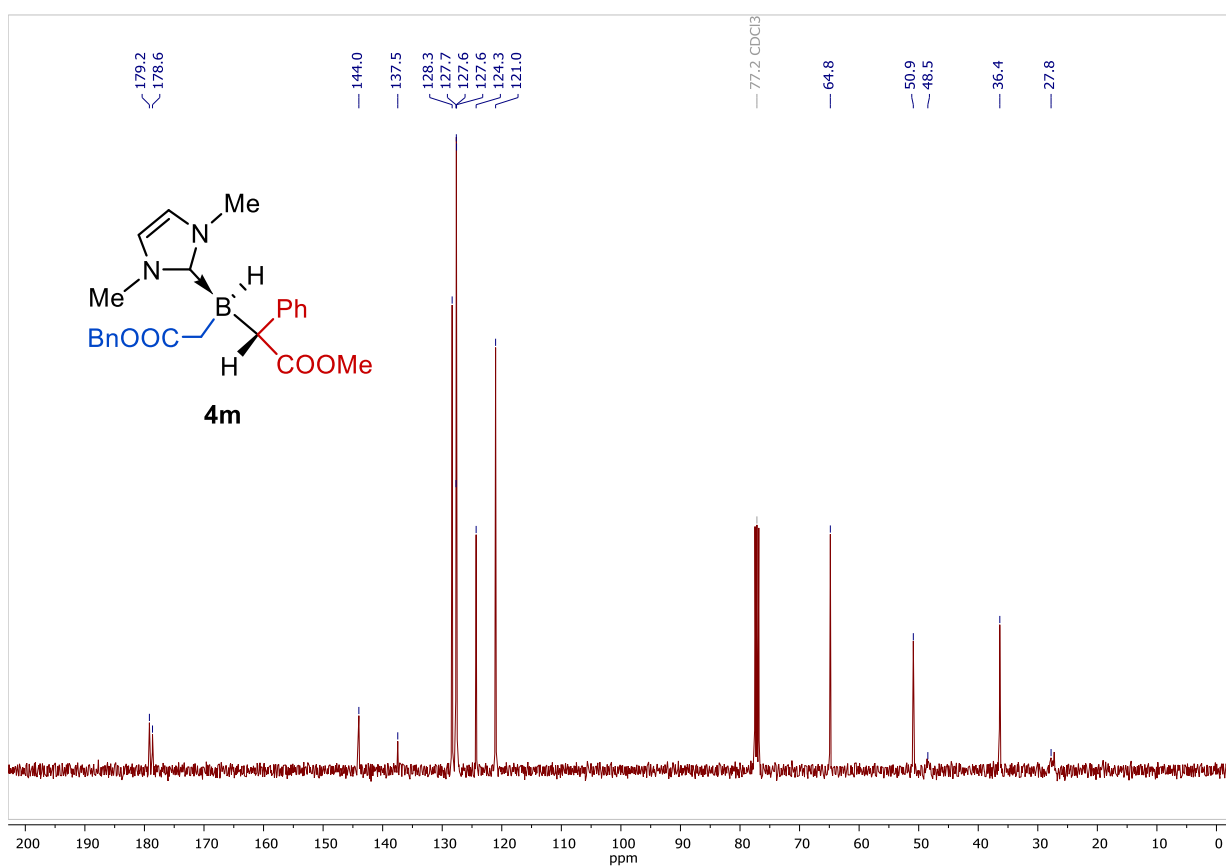


Figure S93. ^{13}C NMR spectrum of **4m** in CDCl_3 .

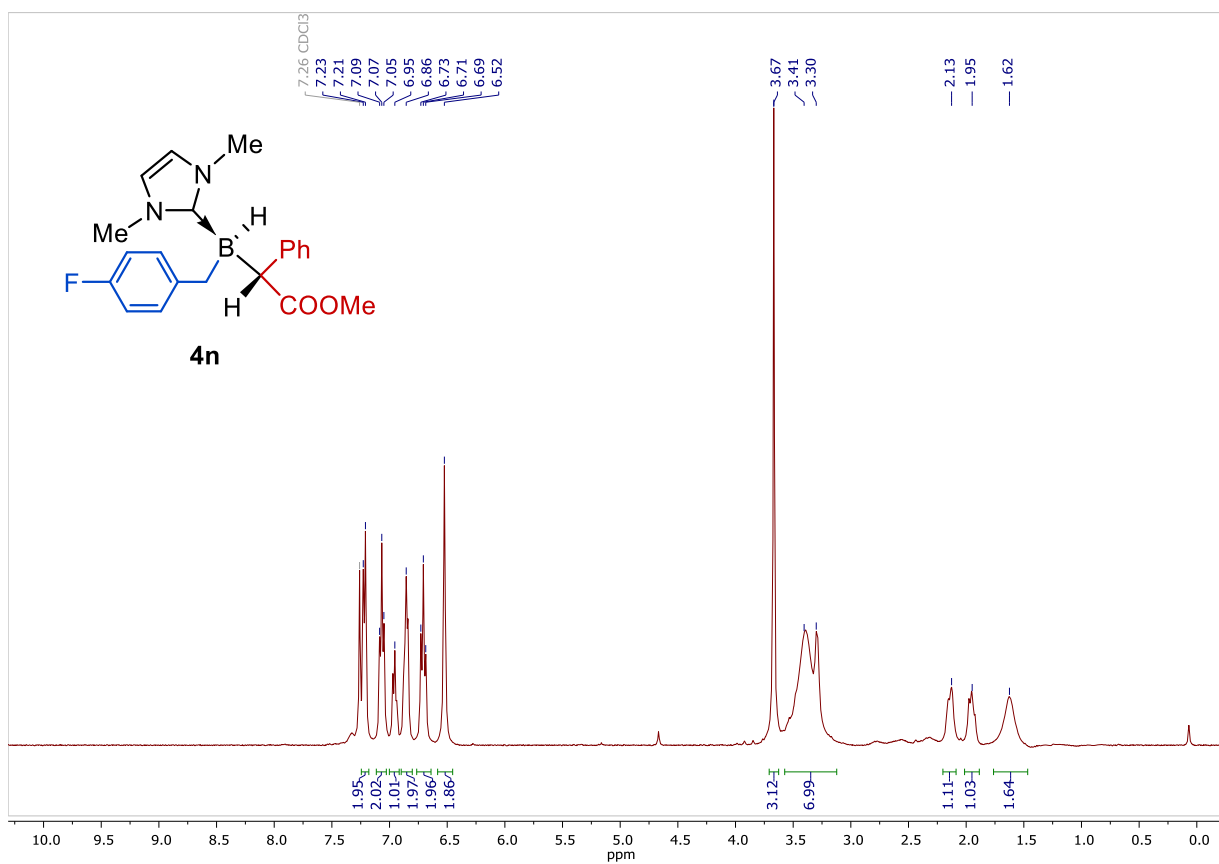


Figure S94. ^1H NMR spectrum of **4n** in CDCl_3 .

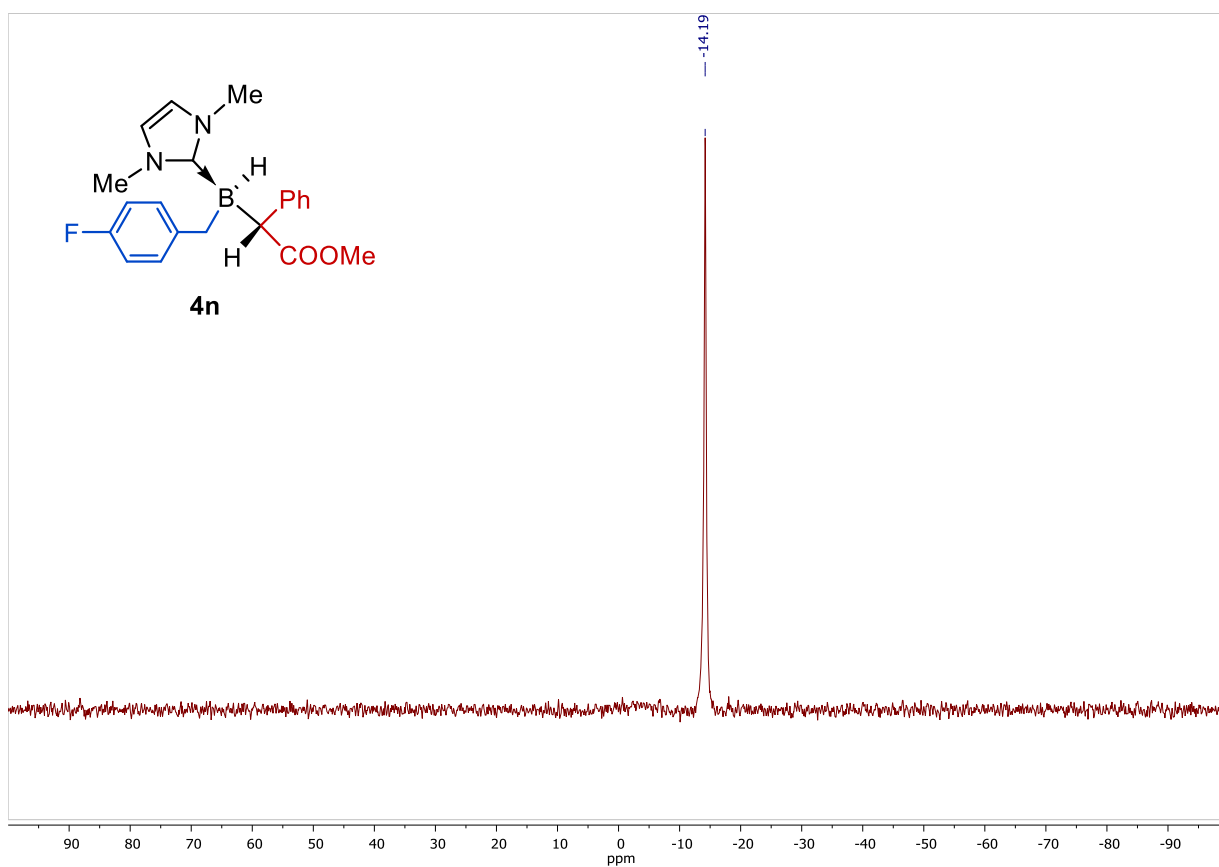
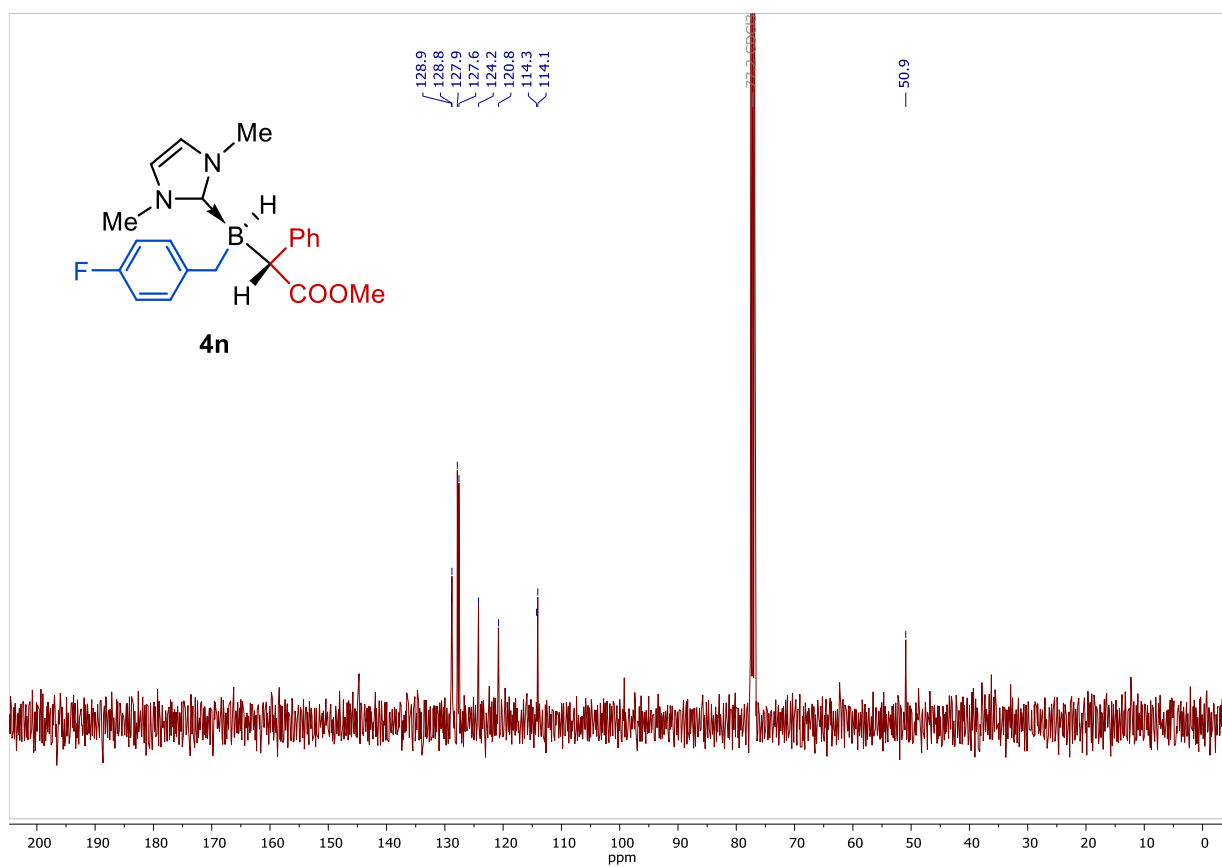
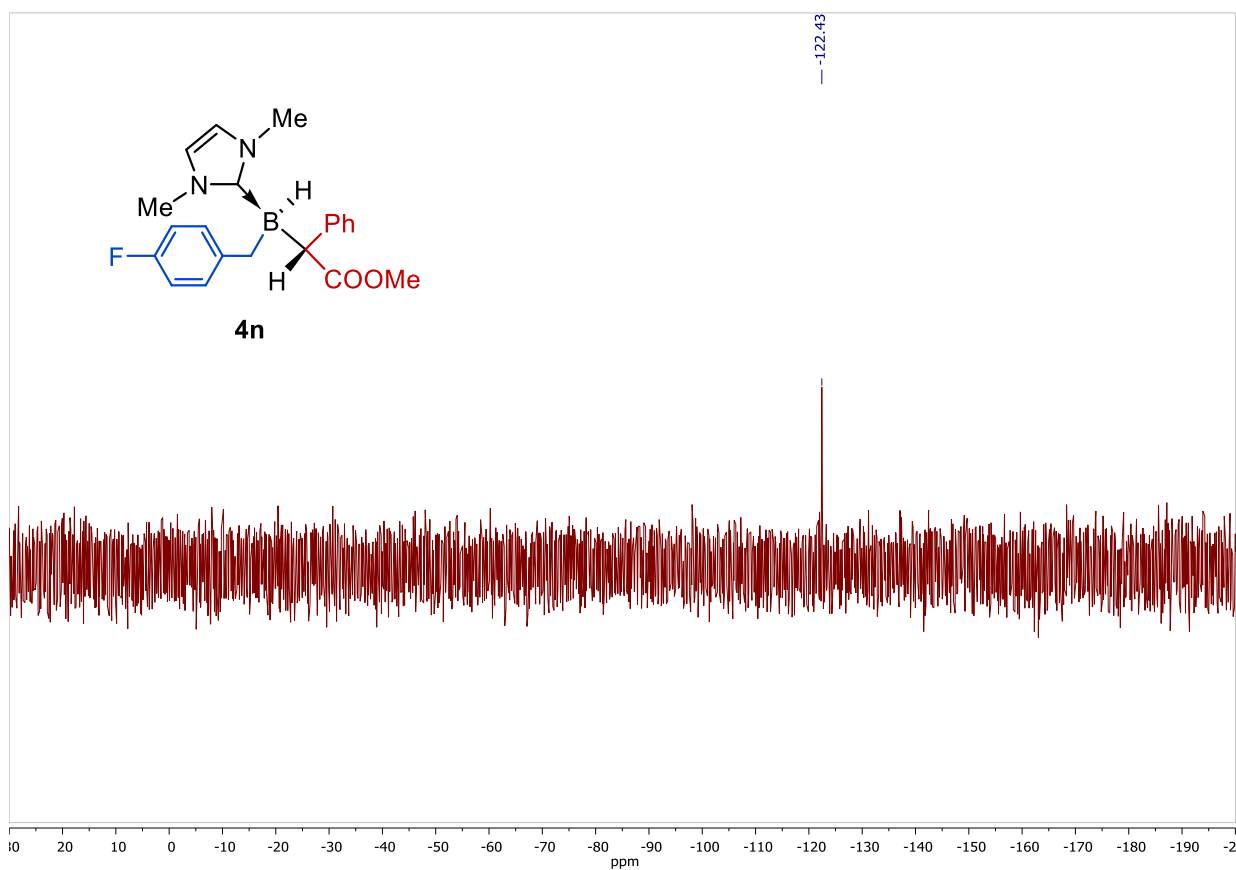


Figure S95. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4n** in CDCl_3 .



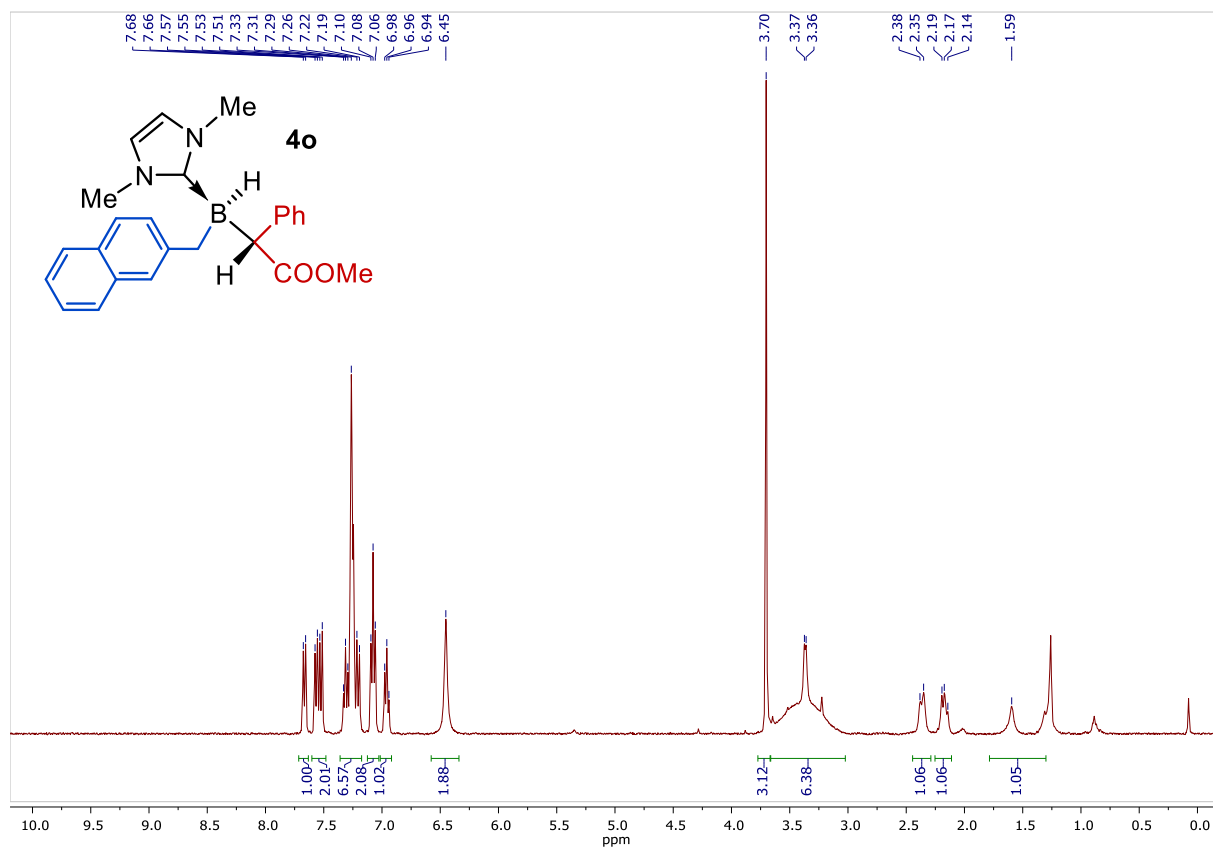


Figure S98. ^1H NMR spectrum of **4o** in CDCl_3 .

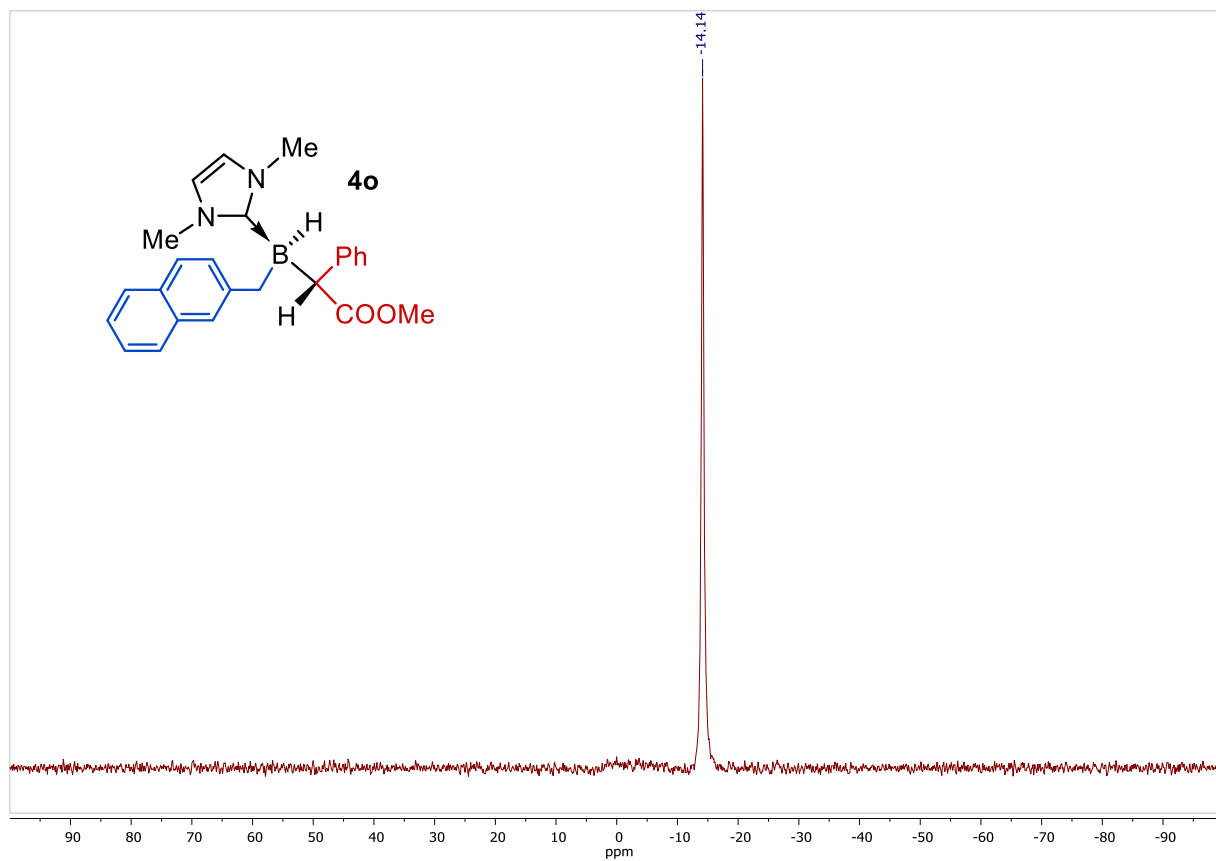


Figure S99. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4o** in CDCl_3 .

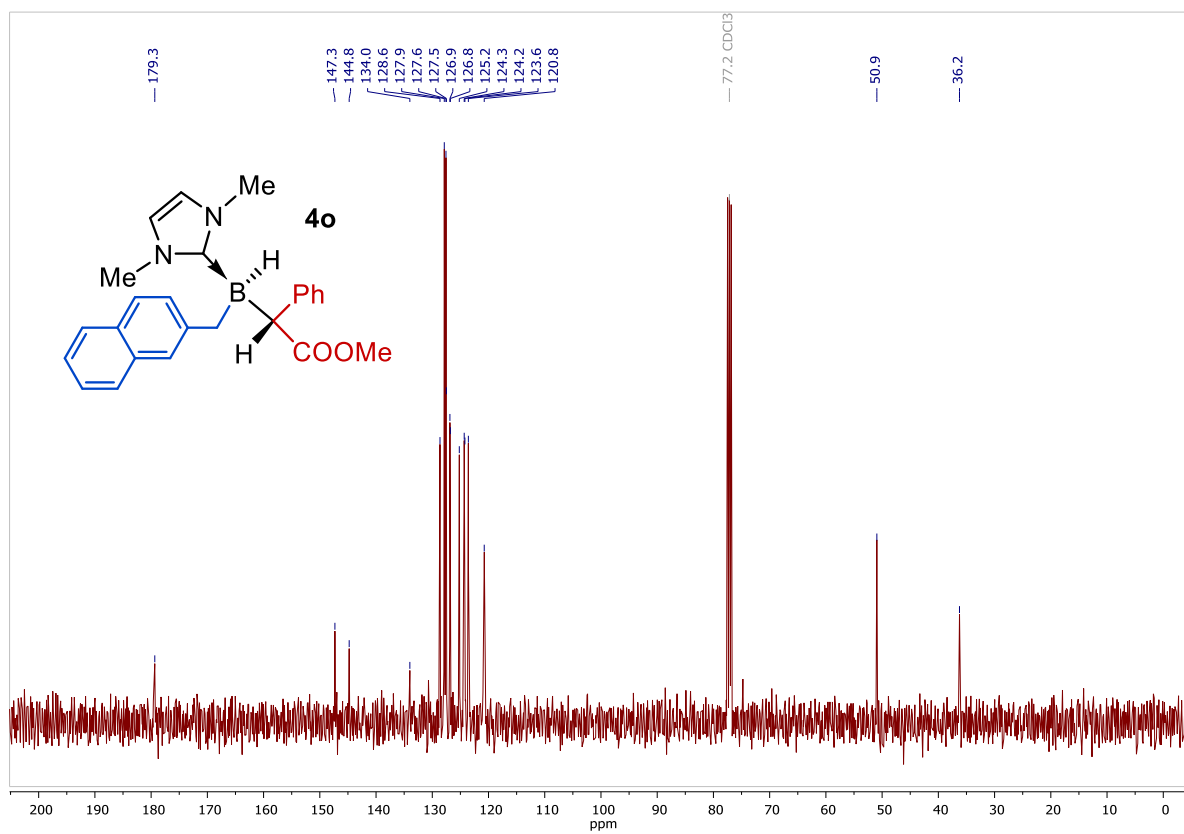
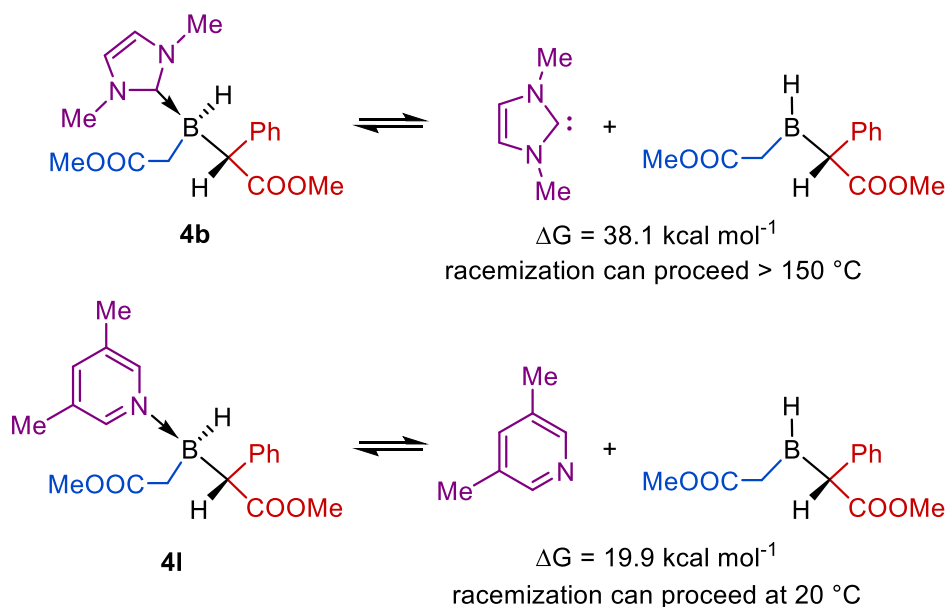


Figure S100. ^{13}C NMR spectrum of **4o** in CDCl_3 .

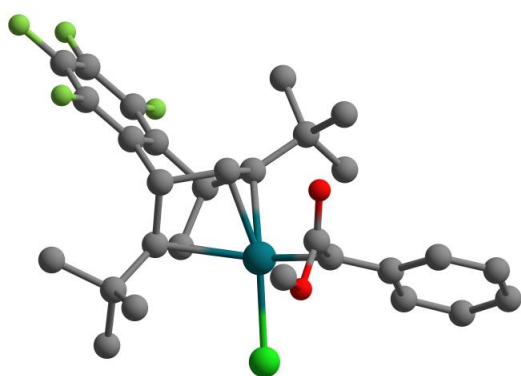
DFT modeling

All calculations were carried out using Orca 5.0.3 software.¹⁴ Composite B97-3c method was used for geometry optimization.¹⁵ Solvation was not taken into account because of low polarity of experimental solvent (toluene). The geometries of the all molecules except transition states **B1** and **B2** were optimized with no constrains (several starting conformations were tested), and they were verified to have no negative frequencies. The approximate geometries of the isomeric transition states **B1** (favored) and **B2** were optimized with the distance between carbene carbon atom and boron atom fixed at 3.0 Å. Such geometry is close to the real transition state because the attempt of optimization with C–B distance fixed at 2.9 Å already led to the hydrogen transfer from boron to carbon. Visualization was carried out using ChemCraft 1.8 software (<http://www.chemcraftprog.com/>). Cartesian coordinates are given in separate xyz file.

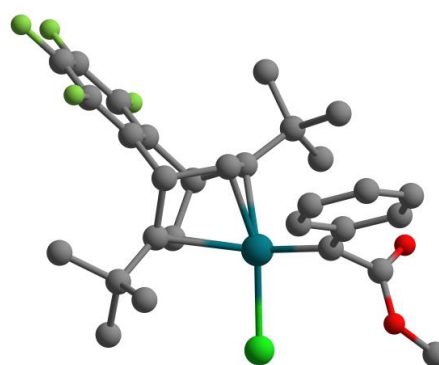
Although the results of the calculations correlate with the experimental findings they should be considered only as estimates. The main reason for these calculations is to give reader the opportunity to visualize 3D structures of the intermediates and transition states, rather than to analyze the exact energies.



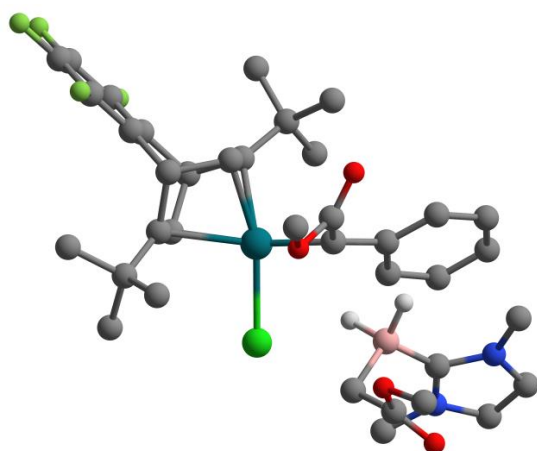
Scheme S1. Energy barriers for racemization of the boron centers via dissociation of dimethyl-imidazolium NHC or 3,5-dimethylpyridine in the products **4b** and **4l**.



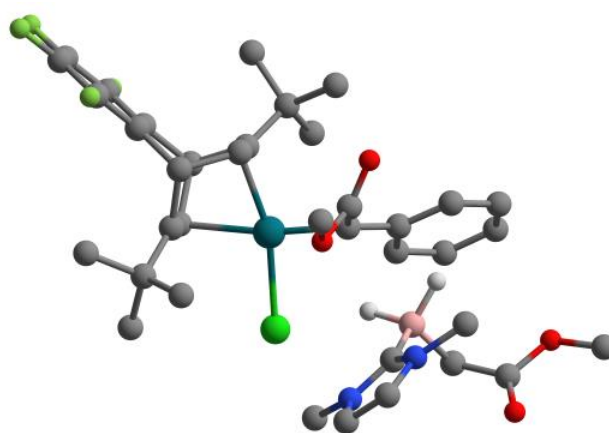
A1 (0.0 kcal mol⁻¹)



A2 (4.1 kcal mol⁻¹)



B1 (0.0 kcal mol⁻¹)



B2 (0.7 kcal mol⁻¹)

Figure S101. Optimized structures of isomeric intermediates (top) and transition states (bottom) of the carbene insertion reaction. All hydrogen atoms, except BH, are omitted for clarity. Relative Gibbs free energies are given in kcal mol⁻¹.

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