Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Transition metal-free radical *trans*-hydroboration of alkynes with NHC-boranes via visible-light photoredox catalysis

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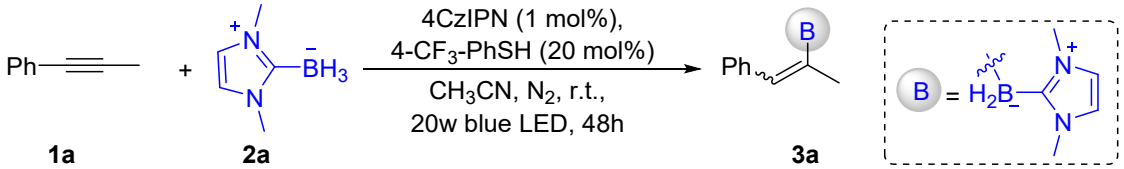
1.General Information

All manipulations were carried out in a flame-dried glassware under the nitrogen atmosphere using standard Schlenk techniques. For reactions that require heating, the heat source is an oil bath. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). Mass spectra were recorded with Agilent 1290-6545XT Ultra-High performance liquid chromatography-quadrupole time-of-flight mass spectrometer using electron spray ionization. ^{1}H NMR spectra were recorded on a Bruker AV-400 spectrometer, a ZK-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d3. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, ap= apparent, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer, a ZK-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d3. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. ^{11}B NMR spectra were recorded on a Bruker AV-400 spectrometer. Structural assignments were made with additional information from gCOSY experiment.

2. More Reaction Condition Study

Table S1. Screening of other parameters for hydroboration of alkynes[a]



1a 2a 3a

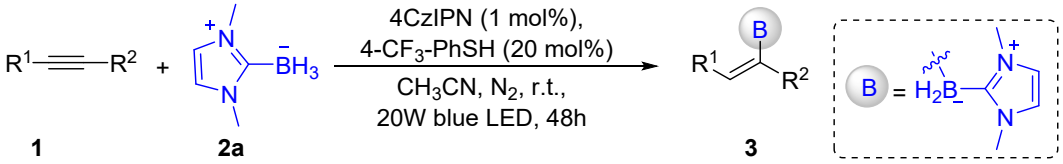
entry	variants	(*E*)-3a(%)	(*Z*)-3a(%)	*E*/*Z* [b]
1	none	73	5	93:7
2	DMAc	35	17	67:33
3	DCM	No reaction		-
4	EtOAc	22	4	84:16
5	MeOH	trace		-
6	3DPAFIPN	11	19	37:63
7	4-Me-PhSH	50	6	89:11
8	4-^{t}Bu-PhSH	46	8	85:15
9	20W 420nm LEDs lights	trace		-
10	20W 470nm LEDs lights	52	5	91:9

Reaction conditions: 1-phenyl-1-propyne (1a, 0.20 mmol), NHC–borane (2a, 1 mmol), 4CZIPN (PC1, 1 mol%), 4-CF_3-PhSH (S1, 20 mol%), MeCN (2 mL), 20W blue LED irradiation (450 nm), room temperature, 48 h. [a] Yields were determined by analysis of the crude ^{1}H NMR spectra using 1,3,5-trimethoxybenzene as an internal standard. [b] Ratio of (E)- and (Z)-3a estimated by ^{1}H NMR analysis of the crude reaction mixture

3. Reaction Procedures

All alkynes used in this work are all known compounds and were prepared according to literature methods[1]. The 1,3-Dimethylimidazol-2-ylidene borane (**2a**) was prepared according to literature methods[2].

General procedure for hydroboration of alkynes:



1 2a 3

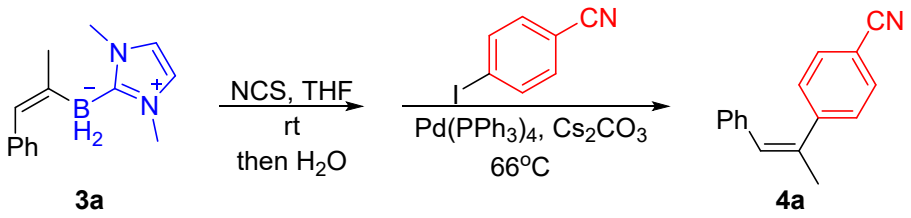
In a nitrogen filled 10 mL schlenk tube, NHC-borane (110 mg, 1 mmol, 5.0 eq) and 4CzIPN (1.5 mg, 0.002 mmol, 1 mol%) were dissolved in dry acetonitrile (1 mL) and stirred at room temperature

for 5 min, To the solution, alkynes (0.2 mmol) and 4-CF_3-PhSH (7 mg, 0.04 mmol, 20 mol%) in acetonitrile (1 mL) were added under nitrogen. The reaction mixture was placed approximately 5cm from a 20 W blue LEDs lights. The mixture was stirred at room temperature for 48h. When the reaction was completed, the solvent was removed in vacuo. The crude product was used to determine the regio- and stereoselectivity by ^{1}H NMR analysis. The residue was purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the corresponding product.

Gram scale reaction:

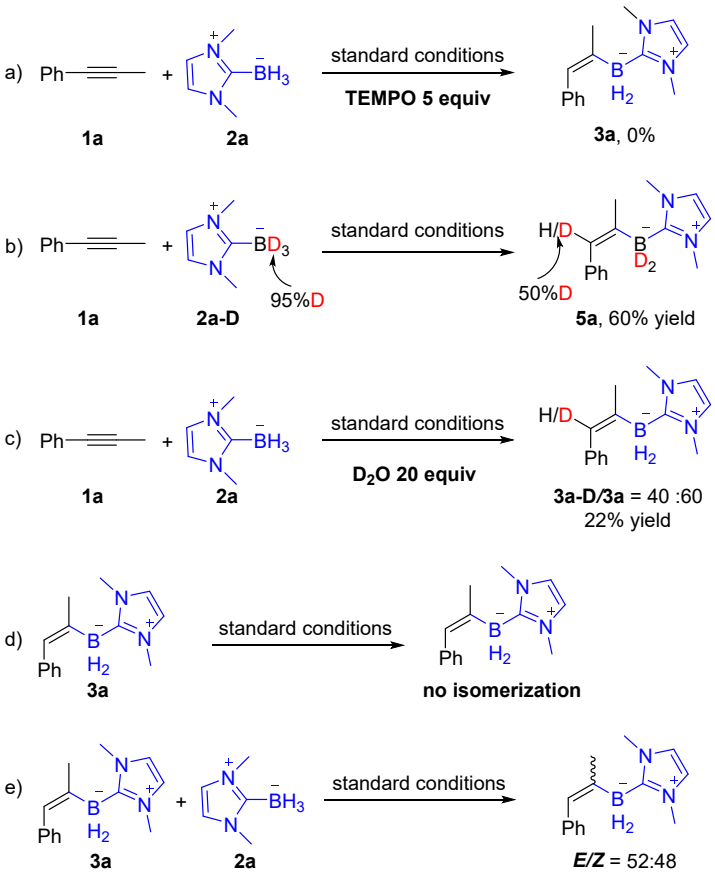
In a nitrogen filled 50mL eggplant flask, NHC-borane (2.75 g, 25 mmol, 5.0 eq) and 4CzIPN (39 mg, 0.05 mmol, 1 mol%) were dissolved in dry acetonitrile (15 mL) and stirred at room temperature for 5 min. To the solution, alkynes (0.58 g, 5.0 mmol) and 4-CF_3-PhSH (178 mg, 1.0 mmol, 20 mol%) in dry acetonitrile (10 mL) were added under nitrogen. The reaction mixture was placed approximately 5cm from a 20 W blue LEDs lights. The mixture was stirred at room temperature for 48h. When the reaction was completed, the solvent was removed in vacuo. The residue was purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate (4:1) to afford product **3a** (0.79g, 70%).

Procedure for 3a derivative[3]:



To a solution of **3a** (45.2 mg, 0.2 mmol) in THF (2 mL) was added N-chlorosuccinimide (53.4 mg, 0.4 mmol, 2 eq) at room temperature, and the resultant mixture was stirred for 15 min at room temperature. After water (0.4 mL) was added to this mixture, and the resultant mixture was further stirred for 15 min at room temperature. To this mixture were added 4-iodobenzonitrile (45.8 mg, 0.2 mmol, 1 eq), Cs_2CO_3 (326 mg, 1 mmol, 5 eq) and $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 5 mol%), and the resultant mixture was stirred for 60 h at 66 °C. The reaction mixture was extracted with EtOAc, and the organic phase was dried over with Na_2SO_4. After the solvent was evaporated under reduced pressure, the resultant residue was purified by silica gel chromatography (eluent: n-hexane/EtOAc,10/1) to give product **4a** (32.8 mg, 0.15 mmol, 75% yield) as a yellow oil.

4. Mechanistic studies

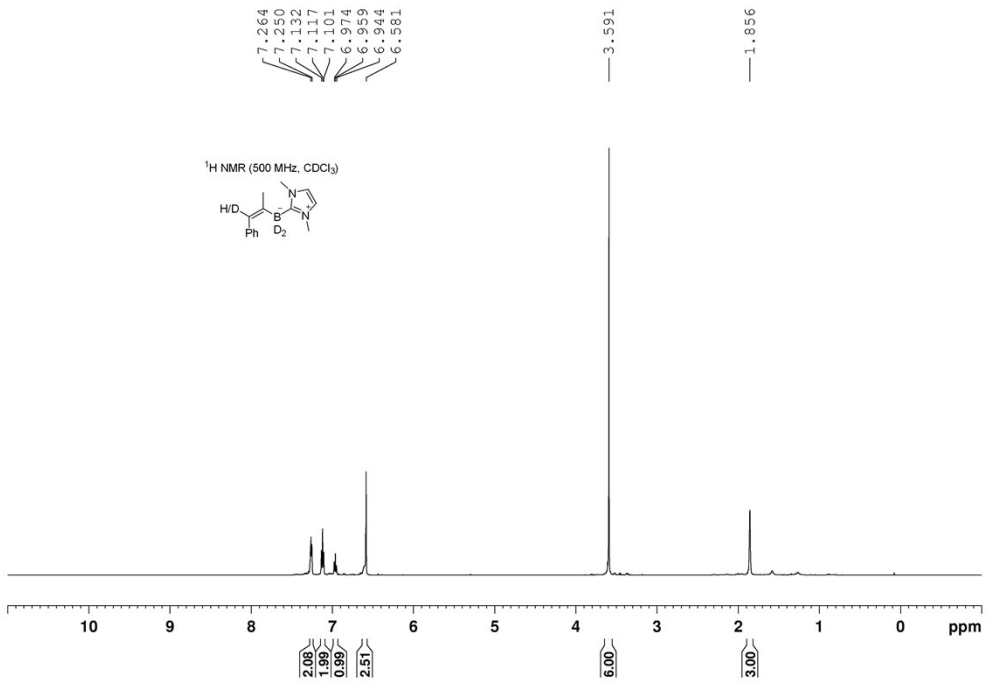


(a) In a nitrogen filled 10 mL schlenk tube, NHC-borane (110 mg, 1 mmol, 5.0 eq), 4CzIPN (1.5 mg, 0.002 mmol, 1 mol%) and TEMPO (156 mg, 1 mmol, 5.0 eq) were dissolved in dry acetonitrile (1 mL) and stirred at room temperature for 5 min. To the solution, alkyne **1a** (23.2 mg, 0.2 mmol) and 4-CF_3-PhSH (7 mg, 0.04 mmol, 20 mol%) in dry acetonitrile (1 mL) were added under nitrogen. The reaction mixture was placed approximately 5cm from a 20 W blue LEDs lights. The mixture was stirred at around room temperature for 48h. After the solvent was removed under reduced pressure, ^{1}H NMR analysis of the reaction mixture indicated no reaction.

(b) In a nitrogen filled 10mL schlenk tube, NHC-BD_3 (113 mg, 1 mmol, 5.0 eq) and 4CzIPN (1.5 mg, 0.002 mmol, 1 mol%) were dissolved in dry acetonitrile (1 mL) and stirred at room temperature for 5 min. To the solution, alkyne **1a** (23.2 mg, 0.2 mmol) and 4-CF_3-PhSH (7 mg, 0.04 mmol, 20 mol%) in dry acetonitrile (1 mL) were added under nitrogen. The reaction mixture was placed approximately 5cm from a 20 W blue LEDs lights. The mixture was stirred at room temperature for 48h. When the reaction was completed, the solvent was removed in vacuo. The crude product was used to determine the regio- and stereoselectivity by ^{1}H NMR analysis. The residue was purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the corresponding product **5a** 60% (27.5 mg).

Characteristic signals of **5a**:

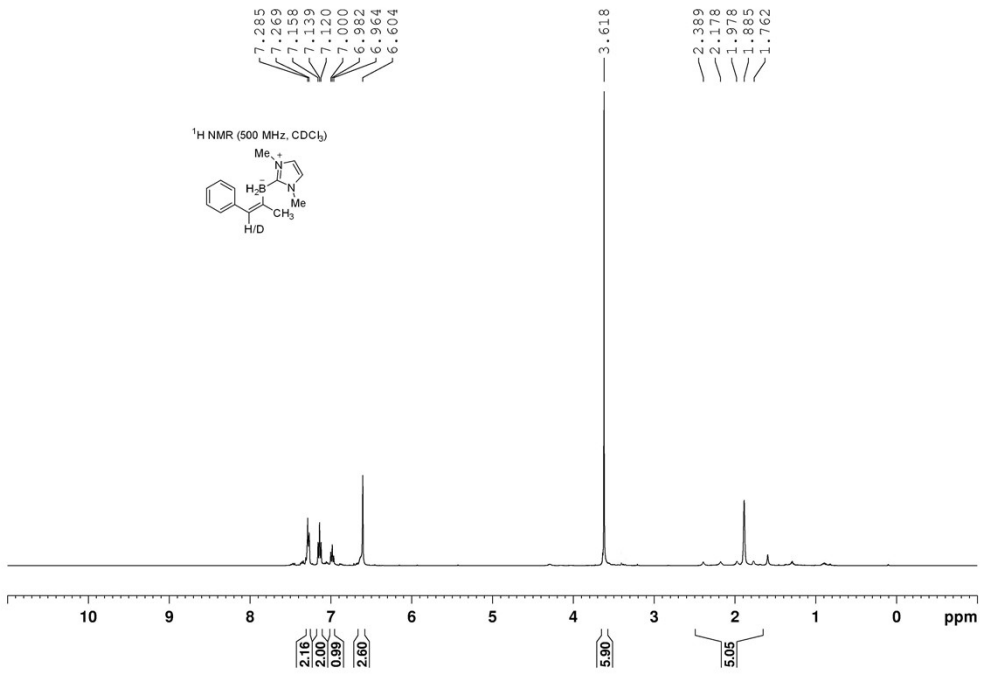
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.60 (0.5H, br, alkenyl-H).



(c) In a nitrogen filled 10 mL schlenk tube, NHC-borane (110 mg, 1 mmol, 5.0 eq) and 4CzIPN (1.5 mg, 0.002 mmol, 1 mol%) were dissolved in dry acetonitrile (1 mL) and stirred at room temperature for 5 min. To the solution, alkyne **1a** (23.2 mg, 0.2 mmol), 4-CF_3-PhSH (7 mg, 0.04 mmol, 20 mol%) and D_2O (80 mg, 4 mmol, 20 eq) in acetonitrile (1 mL) were added under nitrogen. The reaction mixture was placed approximately 5cm from a 20 W blue LEDs lights. The mixture was stirred at around room temperature for 48h. When the reaction was completed, the solvent was removed in vacuo. The residue was purified by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the product **3a-D/3a** (10 mg, yield 22%).

Characteristic signals of **3a-D/3a**:

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.60 (0.6H, br, alkenyl-H)



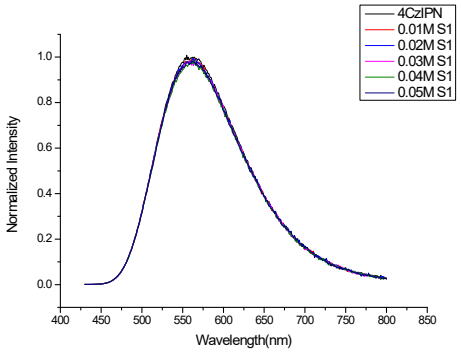
(d) In a nitrogen filled 10 mL schlenk tube, **3a** (45.2 mg, 0.2 mmol) and 4CzIPN (1.5 mg, 0.002 mmol, 1 mol%) were dissolved in dry acetonitrile (1 mL) and stirred at room temperature for 5 min. To the solution, 4-CF_3-PhSH (7 mg, 0.04 mmol, 20 mol%) in acetonitrile (1 mL) were added under nitrogen. The reaction mixture was placed approximately 5cm from a 20 W blue LEDs lights. The mixture was stirred at room temperature for 48h. After the solvent was removed under reduced pressure, ^{1}H NMR analysis of the crude product indicated no isomerization.

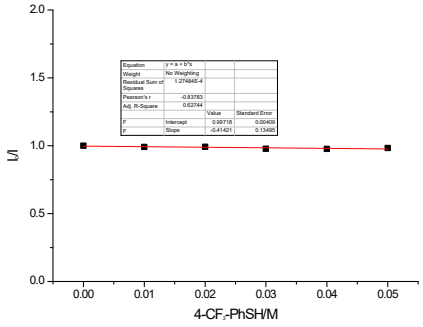
(e) In a nitrogen filled 10 mL schlenk tube, **3a** (45.2 mg, 0.2 mmol), NHC-borane (110 mg, 1 mmol, 5.0 eq) and 4CzIPN (1.5 mg, 0.002 mmol, 1 mol%) were dissolved in dry acetonitrile (1 mL) and stirred at room temperature for 5 min. To the solution, 4-CF_3-PhSH (7 mg, 0.04 mmol, 20 mol%) in acetonitrile (1 mL) were added under nitrogen. The reaction mixture was placed approximately 5cm from a 20 W blue LEDs lights. The mixture was stirred at room temperature for 48h. After the solvent was removed under reduced pressure. The crude product was used to determine the regio- and stereoselectivity by ^{1}H NMR analysis

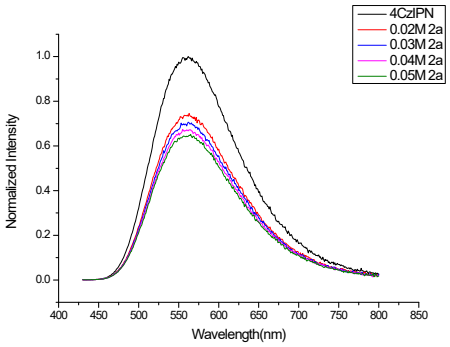
5. Stern-Volmer Quenching Experiments

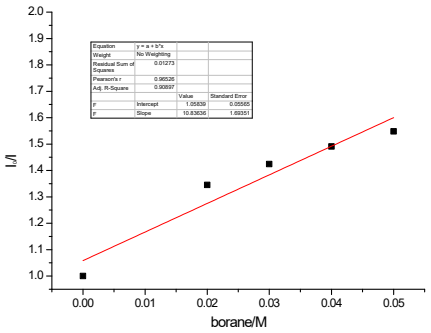
Stern-Volmer Quenching Experiments was conducted using an Edinburgh FS5 spectrofluorometer. The following parameters were employed: Excitation bandwidth = 2 nm, data interval = 0.5 nm, scan speed = 500 nm/min, response time = 0.2 sec. The samples were measured in Hellma fluorescence QS quartz cuvettes (chamber volume = 3.5 mL, H × W × D =46 mm × 12.5 mm, 12.5 mm) fitted with a PTFE stopper.

In a typical experiments, a solution of 4CzIPN in anhydrous Acetonitrile (1.40×10^{-4} M) was added with an appropriate amount of quencher in a quartz cuvette. Then the emission of the sample was collected. The emission intensity was collected with excited wavelength of photocatalysts, respectively.



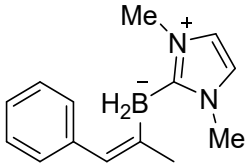






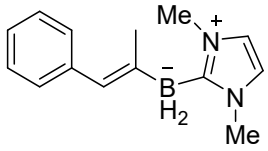
5.Analytical data for compounds

(*E*)-(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(1-phenylprop-1-en-2-yl)dihydroborate (**3a**)



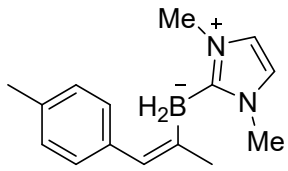
Compound **3a** was prepared in 73% yield (33.0mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (2H, d, *J* = 7.5Hz), 7.11 (2H, t, *J* = 7.5Hz), 6.95 (1H, t, *J* = 7.5Hz), 6.60 (1H, br, alkenyl-H), 6.57 (2H, s), 3.58 (6H, s), 2.07 (2H, br-q, J_{H-B} = 85Hz), 1.86 (3H, s).
^{13}C NMR (125 MHz, $CDCl_3$): δ 142.5, 129.3, 128.3, 126.9, 124.1, 119.9, 35.7, 30.9.
^{11}B NMR (128 MHz, $CDCl_3$): δ -27.5 (t, J_{B-H} = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{19}BN_2Na$:249.1534; found:249.1530.
Data are in accordance with previously reported results[4].

(*Z*)-(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(1-phenylprop-1-en-2-yl)dihydroborate **(*Z*)-3a**



Compound **(*Z*)-3a** was prepared in 6% yield (2.7 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (2H, t, *J* = 7.2Hz), 7.20 (2H, d, *J* = 7.1Hz), 7.06 (1H, t, *J* = 7.1Hz), 6.85 (2H, s), 5.92 (1H, br, alkenyl-H), 3.81 (6H, s), 2.04 (2H, br-q, J_{H-B} = 85Hz), 1.92 (3H, s,).
^{13}C NMR (125 MHz, $CDCl_3$): δ 141.3, 128.7, 127.7, 127.3, 124.4, 120.3, 36.1, 21.8.
^{11}B NMR (128 MHz, $CDCl_3$): δ -23.9 (t, J_{B-H} = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{19}BN_2Na$:249.1534; found:249.1532.
Data are in accordance with previously reported results[4].

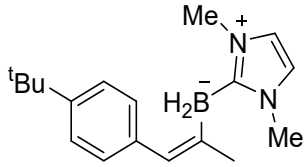
(*E*)-(1-(4-methylphenyl)prop-1-en-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3b**)



Compound **3b** was prepared in 70% yield (33.6mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (2H, d, *J* = 8.0Hz), 6.93 (2H, d, *J* = 8.0Hz), 6.60 (2H,s), 6.57 (1H, br, alkenyl-H), 3.60 (6H, s), 2.24 (3H, s), 2.06 (2H, br-q, J_{H-B} = 85Hz), 1.82 (3H, s).
^{13}C NMR (125 MHz, $CDCl_3$): δ 139.5, 133.4, 129.3, 128.2, 127.7, 119.9, 35.7, 30.8, 21.0.

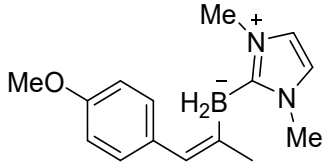
^{11}B NMR (128 MHz, $CDCl_3$): δ -27.5 (t, J_{B-H} = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{21}BN_2Na$:263.1690; found:263.1685.

(*E*)-(1-(4-tert-butylphenyl)prop-1-en-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3c**)



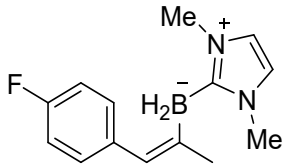
Compound **3c** was prepared in 73% yield (41.2 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15-7.09 (4H, m), 6.57 (1H, br, alkenyl-H), 6.52(2H,s), 3.57 (6H, s), 2.02 (2H, br-q, J_{H-B} = 85Hz), 1.86 (3H, s), 1.82 (3H, s), 1.25 (9H, s).
^{13}C NMR (125 MHz, $CDCl_3$): δ 146.6, 139.7, 129.0, 127.8, 123.7, 119.8, 35.7, 34.2, 31.4, 30.9.
^{11}B NMR (128 MHz, $CDCl_3$): δ -27.4 (t, J_{B-H} = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{27}BN_2Na$:305.2160; found:305.2164.

(*E*)-(1-(4-methoxyphenyl)prop-1-en-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3d**)



Compound **3d** was prepared in 66% yield (33.8 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25-7.20 (2H, m), 6.71-6.67 (2H, m), 6.62(2H,s), 6.54 (1H, br, alkenyl-H), 3.74(3H, s), 3.60 (6H, s), 2.06 (2H, br-q, J_{H-B} = 85Hz), 1.81 (3H, s).
^{13}C NMR (125 MHz, $CDCl_3$): δ 156.5, 135.4, 129.3, 128.8, 119.9, 112.5, 55.2, 35.8, 30.7.
^{11}B NMR (128 MHz, $CDCl_3$): δ -27.5 (t, J_{B-H} = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{21}BN_2ONa$:279.1639; found:279.1642.
Data are in accordance with previously reported results[4].

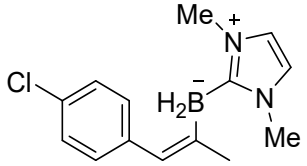
(*E*)-(1-(4-fluorophenyl)prop-1-en-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3e**)



Compound **3e** was prepared in 71% yield (34.6 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.22 (2H, m), 6.84-6.79 (2H, m), 6.64(2H,s), 6.54 (1H, br, alkenyl-H), 3.60 (6H, s), 2.04 (2H, br-q, J_{H-B} = 85Hz), 1.80 (3H, s).

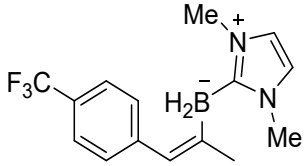
^{13}C NMR (125 MHz, $CDCl_3$): δ 160.2 (d, $J_{C\text{-}F}$ = 243.0Hz), 138.5 (d, $J_{C\text{-}F}$ = 2.8Hz), 129.7 (d, $J_{C\text{-}F}$ = 7.3Hz), 128.2, 120.0, 113.6 (d, $J_{C\text{-}F}$ = 20.8Hz), 35.7, 30.6.
^{19}F NMR (470 MHz, $CDCl_3$): δ -119.5.
^{11}B NMR (128 MHz, $CDCl_3$): δ -27.6 (t, $J_{B\text{-}H}$ = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}BFN_2Na$:267.1439; found:267.1437.

(*E*)-(1-(4-chlorophenyl)prop-1-en-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3f**)



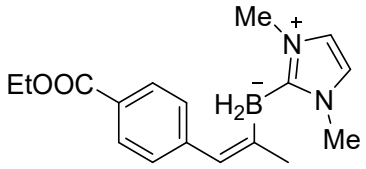
Compound **3f** was prepared in 68% yield (35.3 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.23 (2H, m), 7.12-7.07 (2H, m), 6.66 (2H,s), 6.53 (1H, br, alkenyl-H), 3.60 (6H, s), 2.05 (2H, br-q, J_{H-B} = 85Hz), 1.79 (3H, s).
^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 128.7, 128.5, 127.2, 126.0, 119.0, 34.7, 29.6.
^{11}B NMR (128 MHz, $CDCl_3$): δ -27.6 (t, $J_{B\text{-}H}$ = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}BClN_2Na$:283.1144; found:283.1140.
Data are in accordance with previously reported results[4].

(*E*)-(1-(4-trifluoromethylphenyl)prop-1-en-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3g**)



Compound **3g** was prepared in 79% yield (46.5 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.36 (4H, m), 6.64 (2H,s), 6.60 (1H, br, alkenyl-H), 3.60 (6H, s), 2.10 (2H, br-q, J_{H-B} = 85Hz), 1.82 (3H, s).
^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1, 128.5, 128.4, 125.8 (q, $J_{C\text{-}F}$ = 32Hz), 124.8 (q, $J_{C\text{-}F}$ =272Hz), 123.8 (q, $J_{C\text{-}F}$ = 3.6Hz), 120.1, 35.7, 30.7.
^{19}F NMR (470 MHz, $CDCl_3$): δ -62.0.
^{11}B NMR (128 MHz, $CDCl_3$): δ -27.5 (t, $J_{B\text{-}H}$ = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{18}BF_3N_2Na$:317.1407; found:317.1409.

(*E*)-(1,3-dimethyl-2,3-dihydro-1H-imidazol-2-yl)(1-(4-(ethoxycarbonyl)phenyl)prop-1-en-2-yl)dihydroborate (**3h**)



Compound **3h** was prepared in 67% yield (39.9 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a colorless oil.

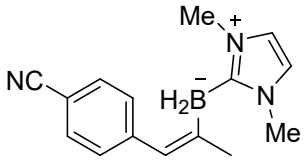
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (2H, d, *J* = 8.3Hz), 7.36 (2H, d, *J* = 8.3Hz), 6.64 (2H,s), 6.62 (1H, br, alkenyl-H), 4.33 (2H, q, *J* = 7.2Hz), 3.60 (6H, s), 2.10 (2H, br-q, J_{H-B} = 85Hz), 1.84 (3H, s), 1.27(3H, t, *J* = 7.1Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 167.1, 147.3, 129.0, 128.4, 128.1, 125.8, 120.1, 60.5, 35.8, 31.1, 14.4.

^{11}B NMR (128 MHz, $CDCl_3$): δ -27.4 (t, J_{B-H} = 85Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{23}BN_2O_2Na$:321.1745; found:321.1741.

(*E*)-(1-(4-cyanophenyl)prop-1-en-2-yl)(1,3-dimethyl-2,3-dihydro-1H-imidazol-2-yl)dihydroborate (**3i**)



Compound **3i** was prepared in 60% yield (30.1 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.36 (4H, m), 6.66 (2H,s), 6.51 (1H, br, alkenyl-H), 3.56 (6H, s), 2.04 (2H, br-q, J_{H-B} = 85Hz), 1.71 (3H, s).

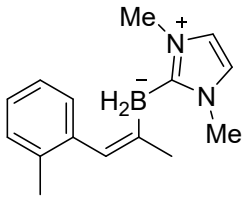
^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1, 129.9, 128.0, 127.6, 119.2, 119.1, 105.8, 34.8, 29.7.

^{11}B NMR (128 MHz, $CDCl_3$): δ -27.5 (t, J_{B-H} = 85Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{18}BN_3Na$:274.1486; found:274.1483.

Data are in accordance with previously reported results[4].

(*E*)-(1,3-dimethyl-2,3-dihydro-1H-imidazol-2-yl)(1-(o-tolyl)prop-1-en-2-yl)dihydroborate (**3j**)



Compound **3j** was prepared in 67% yield (32.1 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a colorless oil.

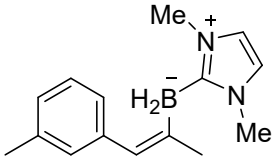
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.97-6.87 (2H, m), 6.81-6.76 (2H, m), 6.43 (1H, br, alkenyl-H), 6.41 (2H,s), 3.43 (6H, s), 2.15 (3H, s), 1.87 (3H, s), 1.83 (2H, br-q, J_{H-B} = 85Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 141.5, 135.2, 129.0, 128.8, 127.7, 124.6, 124.1, 119.8, 35.6, 30.9, 20.0.

^{11}B NMR (128 MHz, $CDCl_3$): δ -27.6 (t, J_{B-H} = 85Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{21}BN_2Na$:263.1690; found:263.1692.

(E)-(1,3-dimethyl-2,3-dihydro-1H-imidazol-2-yl)(1-(m-tolyl)prop-1-en-2-yl)dihydroborate (**3k**)



Compound **3k** was prepared in 66% yield (31.7 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a colorless oil.

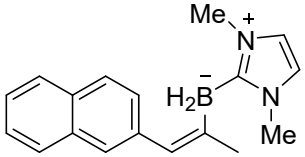
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07-6.99 (3H, m), 6.78 (H, d, *J* = 7.3Hz), 6.58 (2H,s), 6.57 (1H, br, alkenyl-H), 3.60 (6H, s), 2.25 (3H, s), 2.06 (2H, br-q, J_{H-B} = 85Hz), 1.86 (3H, s).

^{13}C NMR (125 MHz, $CDCl_3$): δ 142.5, 136.2, 129.4, 129.0, 126.8, 125.4, 124.9, 119.9, 35.7, 30.9, 21.4.

^{11}B NMR (128 MHz, $CDCl_3$): δ -27.6 (t, J_{B-H} = 85Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{21}BN_2Na$:263.1690; found:263.1688.

(*E*)-(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(1-(naphthalen-2-yl)prop-1-en-2-yl)dihydroborate (**3l**)



Compound **3l** was prepared in 36% yield (19.8 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a white solid.

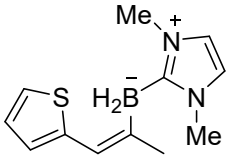
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (2H, d, *J* = 9.0Hz), 7.66 (1H, s), 7.48 (1H, d, *J* = 8.5Hz), 7.49 (1H, d, *J* = 8.5Hz), 7.38-7.29 (2H, m), 6.75 (1H, br, alkenyl-H), 6.44 (2H,s), 3.60 (6H, s) , 2.14 (2H, br-q, J_{H-B} = 85Hz), 1.92 (3H, s).

^{13}C NMR (125 MHz, $CDCl_3$): δ 140.2, 133.4, 131.3, 129.3, 127.9, 127.4, 127.3, 126.0, 125.2, 124.3, 119.9, 35.8, 31.0.

^{11}B NMR (128 MHz, $CDCl_3$): δ -27.4 (t, J_{B-H} = 85Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{21}BN_2Na$:299.1690; found:299.1684.

(*E*)-(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(1-(thiophen-2-yl)prop-1-en-2-yl)dihydroborate (**3m**)



Compound **3m** was prepared in 21% yield (9.7 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02 (1H, d, *J* = 5.0Hz), 6.90-6.86 (2H, m), 6.77 (2H,s), 6.76 (1H, br, alkenyl-H), 3.71 (6H, s) , 2.19 (2H, br-q, J_{H-B} = 85Hz), 1.75 (3H, s).

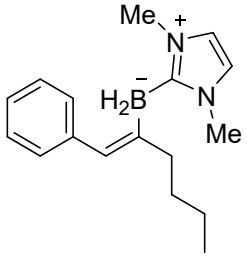
^{13}C NMR (125 MHz, $CDCl_3$): δ 146.3, 125.7, 124.5, 123.6, 122.5, 120.2, 36.0, 30.2.

^{11}B NMR (128 MHz, $CDCl_3$): δ -27.4 (t, J_{B-H} = 85Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{17}BN_2SNa$:255.1098; found:255.1095.

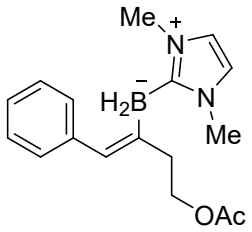
Data are in accordance with previously reported results[4].

(*E*)-(1,3-dimethyl-2,3-dihydro-1H-imidazol-2-yl)(1-phenylhex-1-en-2-yl)dihydroborate (**3n**)



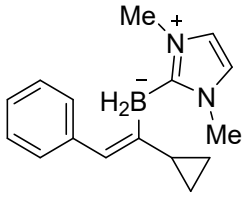
Compound **3n** was prepared in 62% yield (33.2 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (2H, d, *J* = 7.5Hz), 7.06 (2H, t, *J* = 7.5Hz), 6.91 (1H, t, *J* = 7.5Hz), 6.57 (1H, br, alkenyl-H), 6.49 (2H,s), 3.56 (6H, s), 2.17 (2H, t, *J* = 7.5Hz), 2.03 (2H, br-q, J_{H-B} = 85Hz), 1.58-1.49 (2H, m), 1.43-1.31 (2H, m), 0.92 (3H, t, *J* = 7.3Hz).
^{13}C NMR (125 MHz, $CDCl_3$): δ 142.8, 128.5, 128.1, 126.8, 124.0, 119.8, 44.8, 35.7, 32.2, 23.1, 14.3.
^{11}B NMR (128 MHz, $CDCl_3$): δ -27.8 (t, J_{B-H} = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{25}BN_2Na$:291.2003; found:291.1995.

(*E*)-(4-acetoxy-1-phenylbut-1-en-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3o**)



Compound **3o** was prepared in 75% yield (44.7 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01 (2H, d, *J* = 7.0Hz), 6.97 (2H, t, *J* = 7.4Hz), 6.84 (1H, t, *J* = 7.2Hz), 6.52 (1H, br, alkenyl-H), 6.40 (2H,s), 4.22 (2H, t, *J* = 7.5Hz), 3.45 (6H, s), 2.40 (2H, t, *J* = 7.6Hz), 1.96 (3H, s), 1.91 (2H, br-q, J_{H-B} = 85Hz).
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.4, 142.1, 130.9, 127.9, 126.9, 124.5, 120.0, 65.4, 43.5, 35.7, 21.2.
^{11}B NMR (128 MHz, $CDCl_3$): δ -28.2 (t, J_{B-H} = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{23}BN_2O_2Na$:321.1745; found:321.1752.

(*E*)-(1-cyclopropyl-2-phenylvinyl)(1,3-dimethyl-2,3-dihydro-1H-imidazol-2-yl)dihydroborate (**3p**)

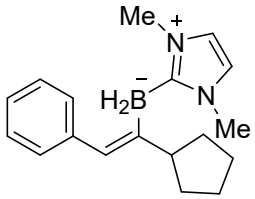


Compound **3p** was prepared in 55% yield (27.7 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (2H, d, *J* = 7.6Hz), 7.05 (2H, t, *J* = 7.6Hz), 6.90 (1H, t, *J* = 7.3Hz), 6.59 (1H, br, alkenyl-H), 6.48 (2H,s), 3.56 (6H, s), 1.84 (2H, br-q, J_{H-B} = 85Hz), 1.56-1.48 (1H, m), 0.74-0.69 (2H, m), 0.57-0.52 (2H, m).

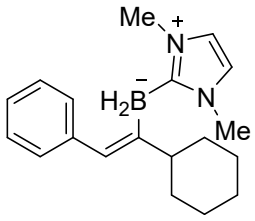
^{13}C NMR (125 MHz, $CDCl_3$): δ 142.5, 128.1, 126.9, 126.8, 124.1, 119.9, 35.7, 23.0, 5.6.
^{11}B NMR (128 MHz, $CDCl_3$): δ -29.4 (t, J_{B-H} = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{21}BN_2Na$:275.1690; found:275.1696.
Data are in accordance with previously reported results[4].

(*E*)-(1-cyclopentyl-2-phenylvinyl)(1,3-dimethyl-2,3-dihydro-1H-imidazol-2-yl)dihydroborate (**3q**)



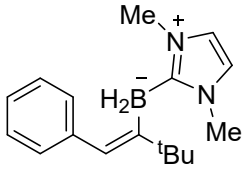
Compound **3q** was prepared in 63% yield (35.3 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (2H, d, *J* = 7.5Hz), 7.01 (2H, t, *J* = 7.5Hz), 6.86 (1H, t, *J* = 7.3Hz), 6.63 (1H, br, alkenyl-H), 6.41 (2H,s), 3.54 (6H, s), 2.56-2.66 (1H, m), 1.99 (2H, br-q, J_{H-B} = 83Hz), 1.83-1.76 (2H, m), 1.74-1.68 (4H, m), 1.60-1.56 (2H, m).
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.0, 127.8, 126.7, 126.6, 124.0, 119.8, 54.2, 35.7, 32.5, 25.6.
^{11}B NMR (128 MHz, $CDCl_3$): δ -28.6 (t, J_{B-H} = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{25}BN_2Na$:303.2003; found:303.1997.
Data are in accordance with previously reported results[4].

(*E*)-(1-cyclohexyl-2-phenylvinyl)(1,3-dimethyl-2,3-dihydro-1H-imidazol-2-yl)dihydroborate (**3r**)



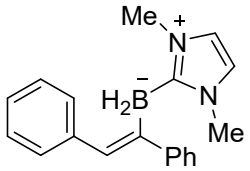
Compound **3r** was prepared in 55% yield (32.3 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.04 (2H, d, *J* = 7.3Hz), 7.00 (2H, t, *J* = 7.6Hz), 6.85 (1H, t, *J* = 7.2Hz), 6.55 (1H, br, alkenyl-H), 6.39 (2H,s), 3.53 (6H, s), 2.11-2.03 (1H. m), 2.03 (2H, br-q, J_{H-B} = 84Hz), 1.87-1.82 (2H, m), 1.82-1.75 (2H, m), 1.46 (2H, qd, 12Hz, 3Hz), 1.37-1.16 (4H, m).
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.2, 127.8, 126.6, 126.1, 123.9, 119.7, 52.0, 35.7, 33.3, 27.5, 26.9.
^{11}B NMR (128 MHz, $CDCl_3$): δ -28.2 (t, J_{B-H} = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{27}BN_2Na$:317.2160; found:317.2166.
Data are in accordance with previously reported results[4].

(*E*)-(3,3-dimethyl-1-phenylbut-1-en-2-yl)(1,3-dimethyl-2,3-dihydro-1H-imidazol-2-yl)dihydroborate (**3s**)



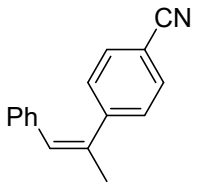
Compound **3s** was prepared in 21% yield (11.2 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02-6.95 (4H, m), 6.81 (1H, t, *J* = 6.8Hz), 6.60 (1H, br, alkenyl-H), 6.30 (2H, s), 3.51 (6H, s), 2.00 (2H, br-q, J_{H-B} = 83Hz), 1.24 (9H, s).
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.0, 127.7, 126.5, 124.8, 123.9, 119.5, 38.9, 35.7, 30.5.
^{11}B NMR (128 MHz, $CDCl_3$): δ -28.2 (t, J_{B-H} = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{25}BN_2Na$:291.2003; found:291.2008.
Data are in accordance with previously reported results[4].

(*E*)-(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(1,2-diphenylvinyl)dihydroborate (**3t**)



Compound **3t** was prepared in 63% yield (36.3 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 4:1) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45(2H, d, *J* = 7.8Hz), 7.31 (2H, d, *J* = 7.8Hz), 7.23-7.16 (4H, m), 7.09-7.02 (2H, m), 6.79 (1H, br, alkenyl-H), 6.43 (2H,s), 3.48 (6H, s), 2.41 (2H, br-q, J_{H-B} = 85Hz).
^{13}C NMR (125 MHz, $CDCl_3$): δ 153.0, 142.1, 132.8, 128.9, 127.6, 127.2, 126.8, 124.9, 124.8, 120.0, 35.7.
^{11}B NMR (128 MHz, $CDCl_3$): δ -27.3 (t, J_{B-H} = 85Hz).
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{21}BN_2Na$:311.1690; found:311.1682.
Data are in accordance with previously reported results[4].

(Z)-4-(1-phenylprop-1-en-2-yl)benzonitrile (**4a**)



Compound **4a** was prepared in 75% yield (32.8 mg) according to the procedure for **3a** derivative. The product was isolated through silica gel column chromatography (PE:EA = 10:1) as a yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (2H, d, *J* = 8.2Hz), 7.19 (2H, d, *J* = 8.2Hz), 7.06-7.02 (3H, m), 6.82 (2H, dd, *J* = 7.8Hz, 2.4Hz), 6.50 (1H, s), 2.12 (3H, d, *J* = 1.4Hz).
^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1, 135.7, 135.5, 131.2, 128.2, 128.0, 127.6, 127.1, 125.7, 117.9, 109.5, 25.2.
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{13}NNa$:242.0940; found:242.0943.

6. references

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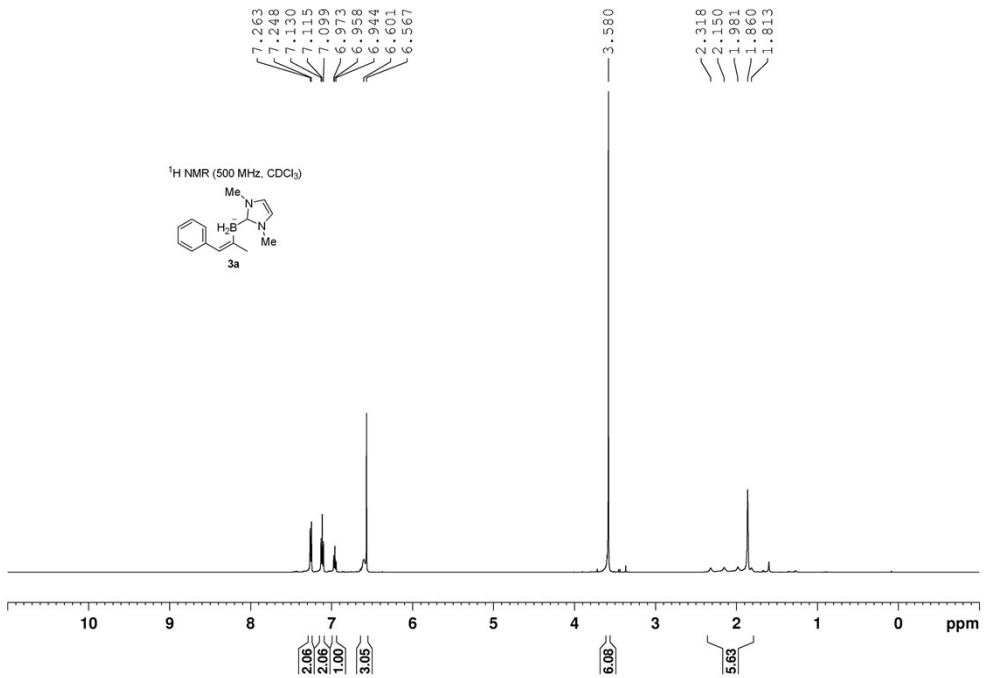
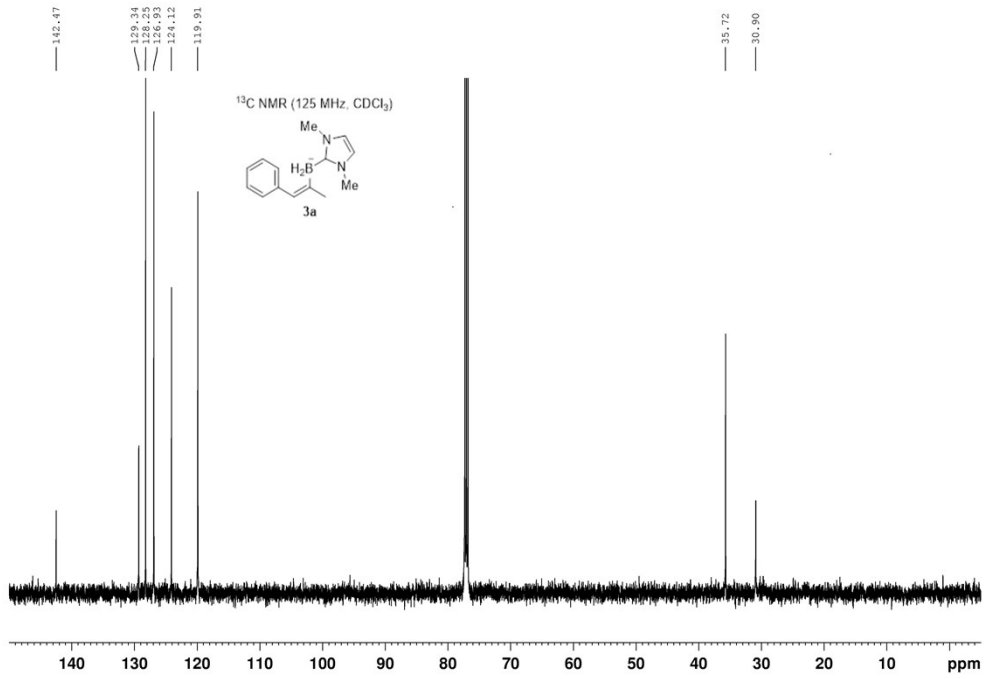
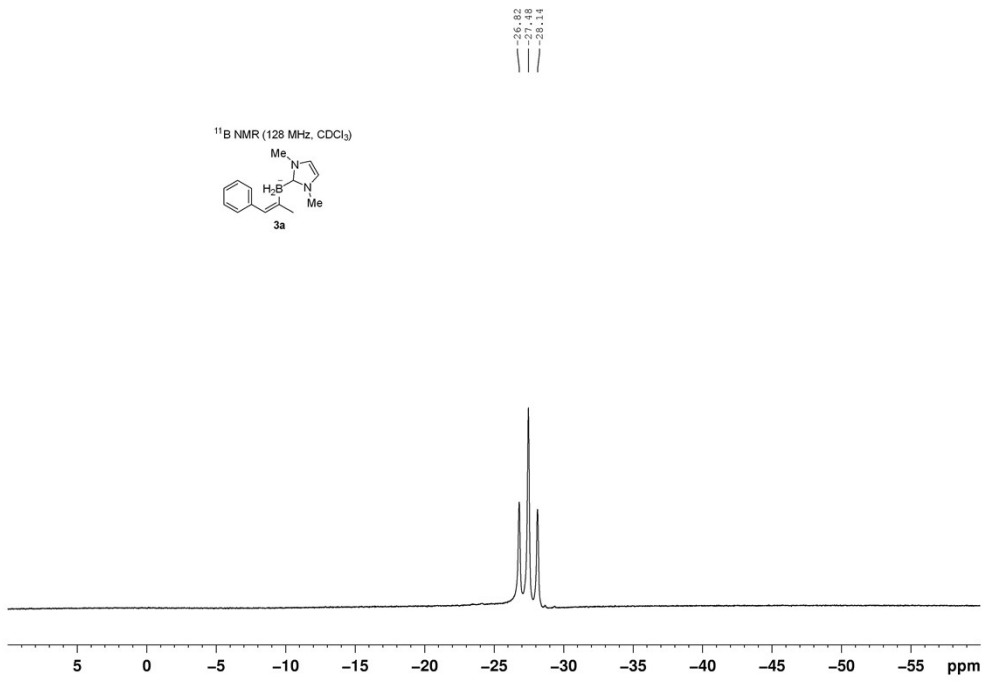
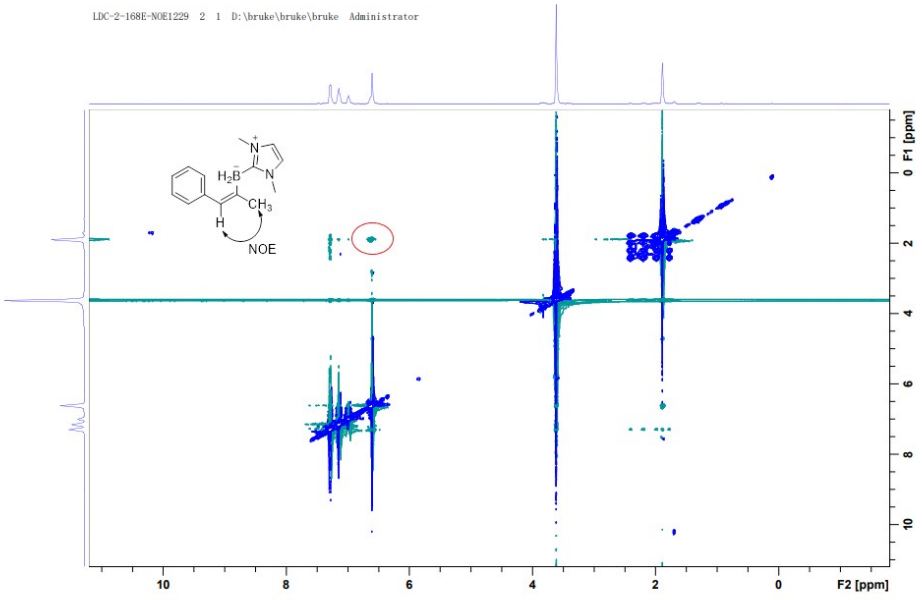
4. M. Shimoi, T. Watanabe, K. Maeda, D. P. Curran, T. Taniguchi, Radical trans-Hydroboration of Alkynes with N-Heterocyclic Carbene Boranes. *Angew. Chem. Int. Ed.* **2018**, *130*, 9629 –9634.

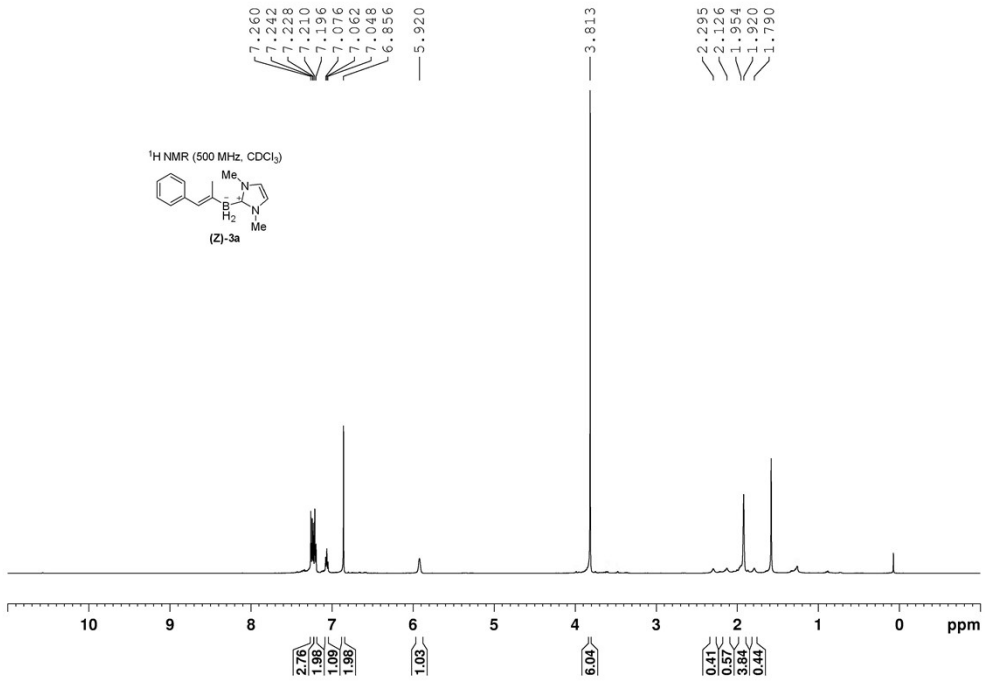
7. ^{1}H 、^{13}C and ^{11}B NMR Spectra

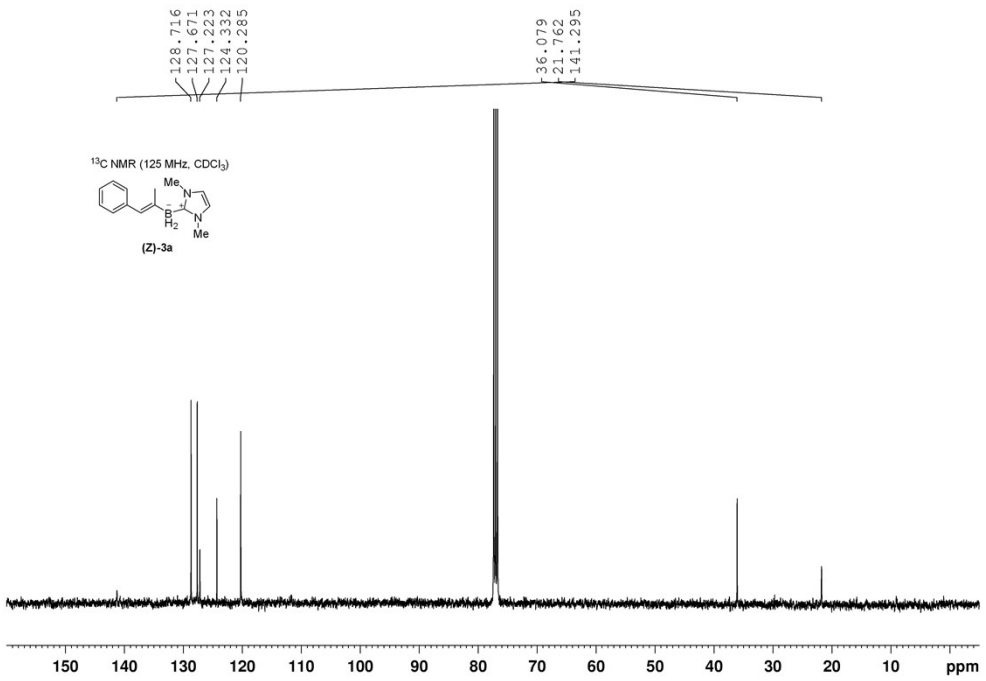

7.263
7.248
7.130
7.115
7.099
6.973
6.958
6.944
6.601
6.567
3.580
2.318
2.150
1.981
1.860
1.813
^{1}H NMR (500 MHz, CDCl$_3$)
Me
N
H$_2$B
N
Me
3a
10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
2.06
1.00
3.05
6.08
5.63

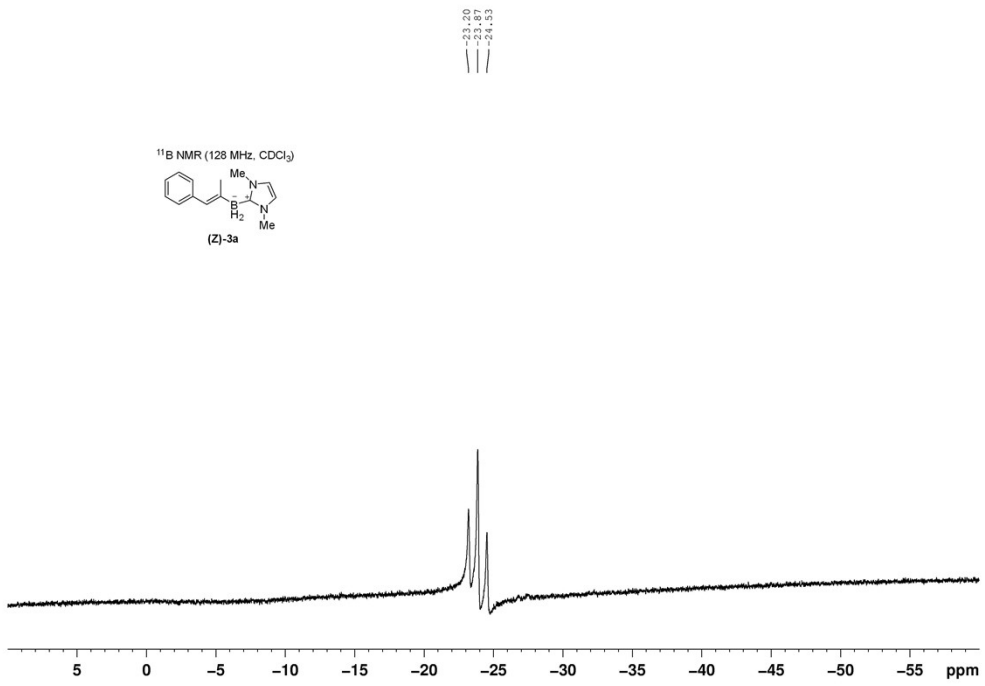

142.47
129.34
128.25
126.93
124.12
119.91
35.72
30.90
^{13}C NMR (125 MHz, CDCl$_3$)
Me
N
H$_2$B
N
Me
3a
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

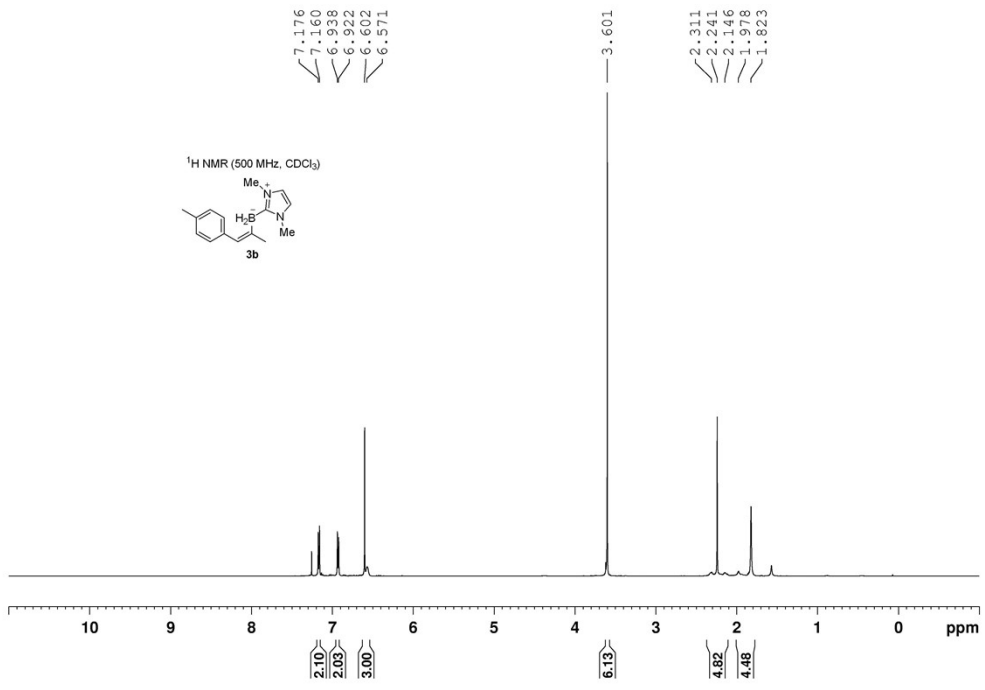

-26.82
-27.48
-28.14
11B NMR (128 MHz, CDCl3)
Me
N
H2B
N
Me
3a
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm

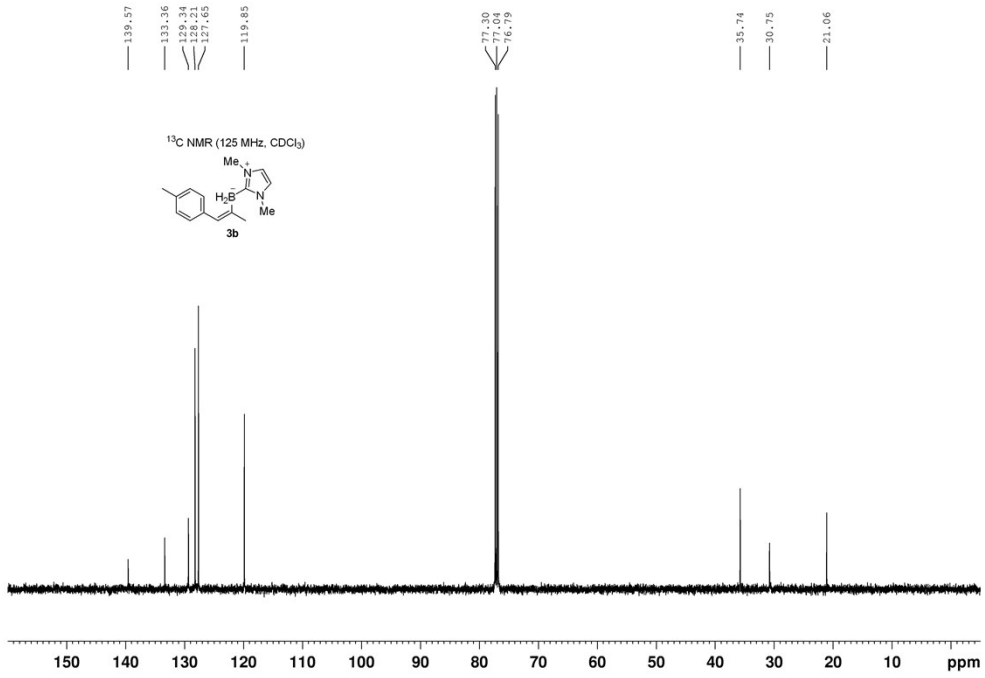

LDC-2-168E-NOE1229 2 1 D:\bruke\bruke\bruke Administrator
H2B
CH3
H
NOE
F1 [ppm]
F2 [ppm]
10
8
6
4
2
0

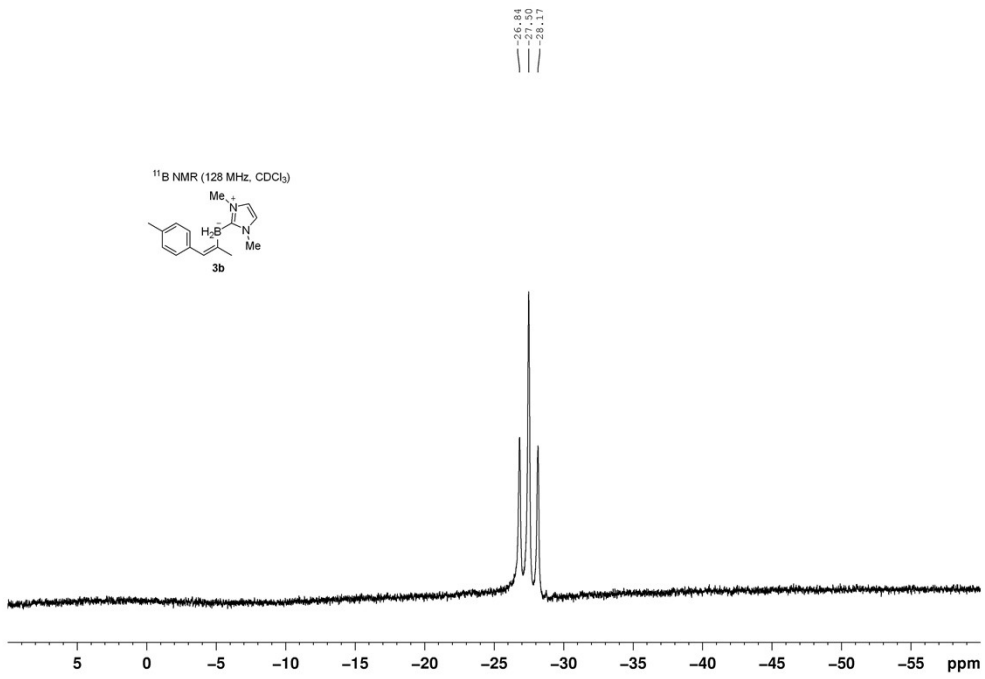

7.260
7.242
7.228
7.210
7.196
7.076
7.062
7.048
6.856
5.920
3.813
2.295
2.126
1.954
1.920
1.790
^{1}H NMR (500 MHz, CDCl$_3$)
(Z)-3a
10 9 8 7 6 5 4 3 2 1 0 ppm
2.76
1.98
1.09
1.98
1.03
6.04
0.41
0.57
3.84
0.44

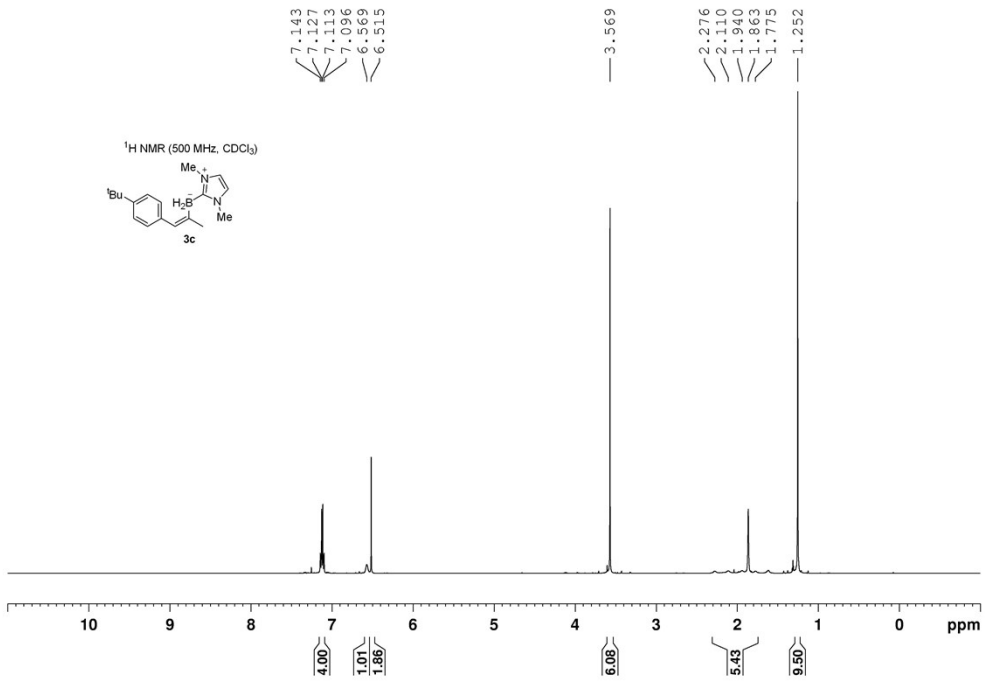

128.716
127.671
127.223
124.332
120.285
36.079
21.762
141.295
^{13}C NMR (125 MHz, CDCl$_3$)
(Z)-3a
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

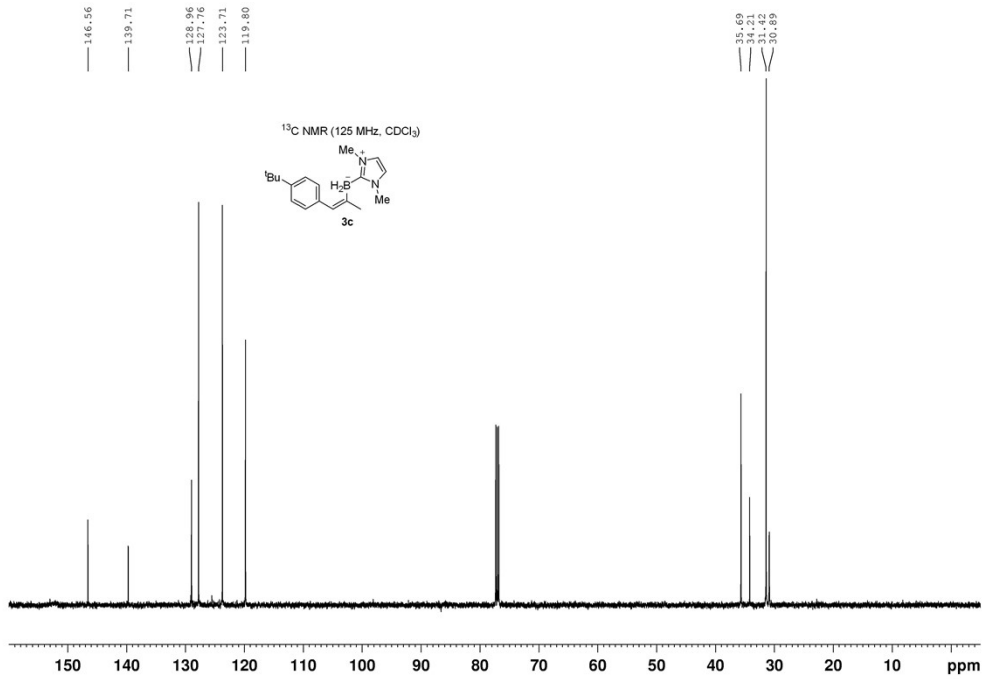

-23.20
-23.87
-24.53
11B NMR (128 MHz, CDCl3)
Me
N
B
H2
N
Me
(Z)-3a
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm

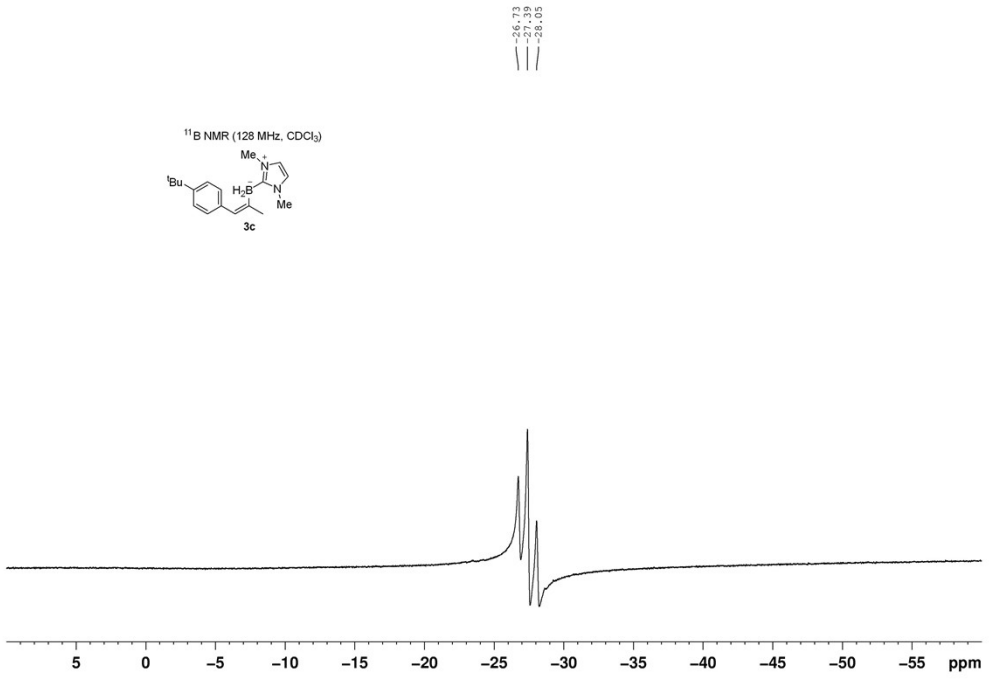

7.176
7.160
6.938
6.922
6.602
6.571
3.601
2.311
2.241
2.146
1.978
1.823
1H NMR (500 MHz, CDCl3)
Me
N
H2B
N
Me
3b
10
9
8
7
6
5
4
3
2
1
0
ppm
2.10
2.03
3.00
6.13
4.82
4.48

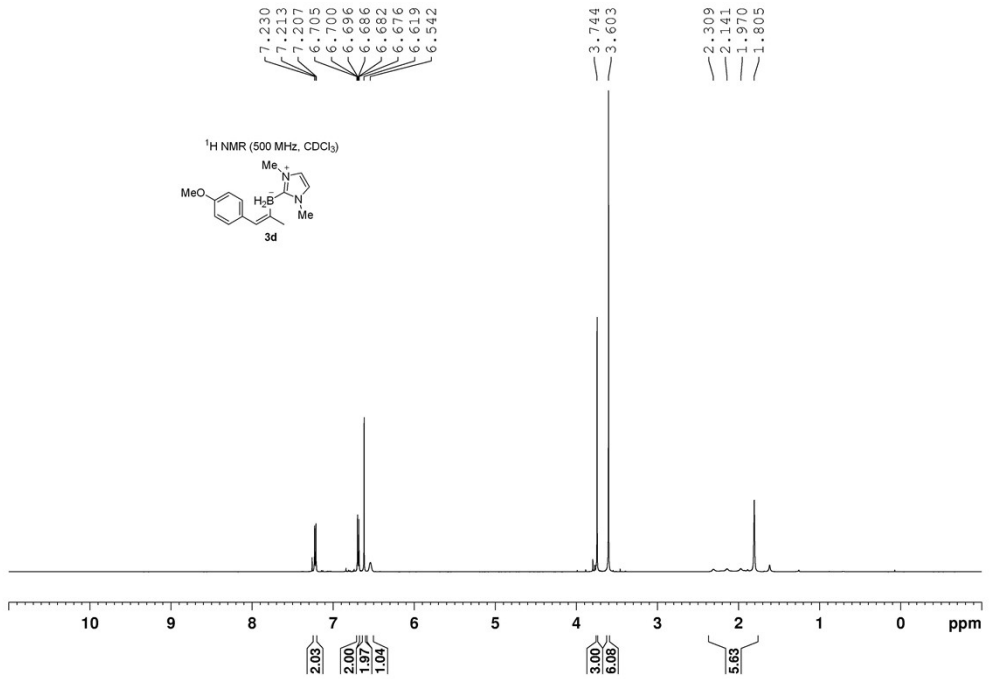

139.57
133.36
129.34
128.21
127.65
119.85
77.30
77.04
76.79
35.74
30.75
21.06
13C NMR (125 MHz, CDCl3)
Me
N+
H2B
N
Me
3b
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

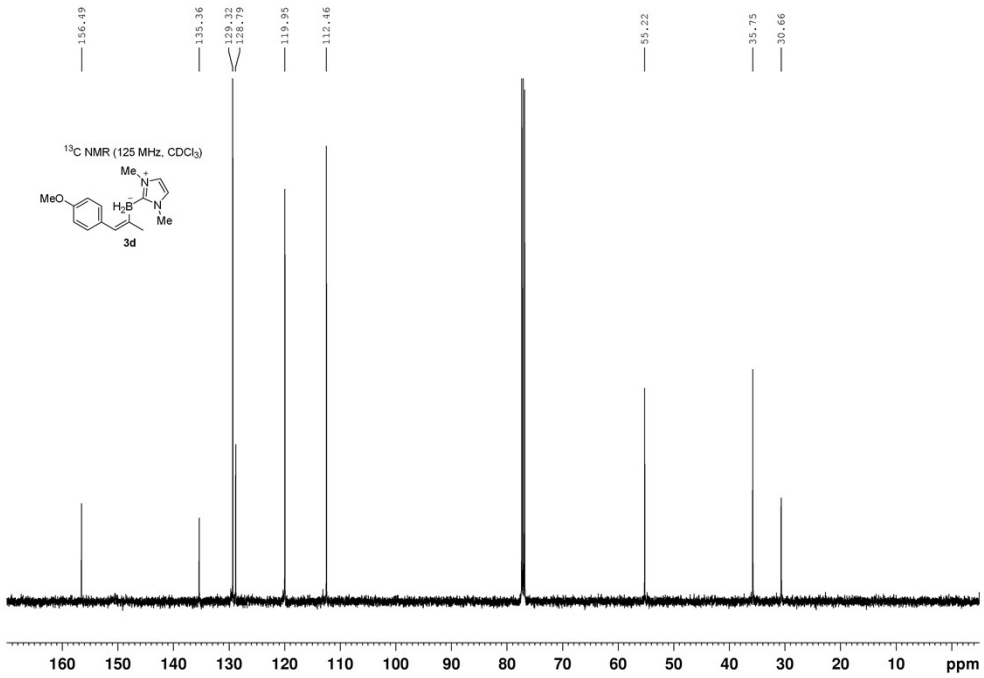

-26.84
-27.50
-28.17
11B NMR (128 MHz, CDCl3)
Me
N+
H2B
N
Me
3b
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm

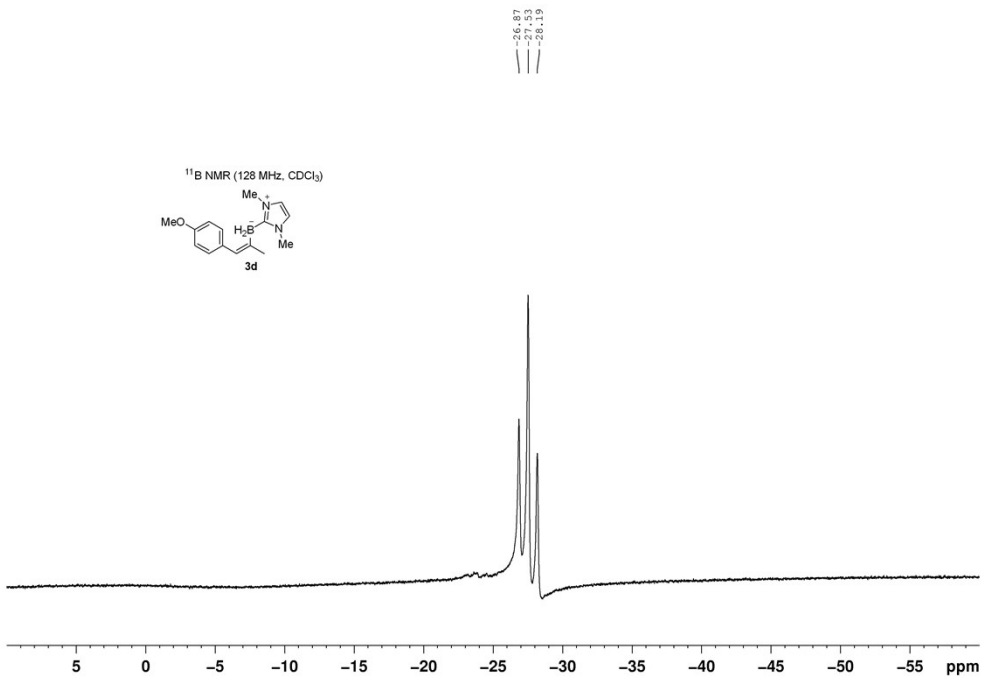

7.143
7.127
7.113
7.096
6.569
6.515
3.569
2.276
2.110
1.940
1.863
1.775
1.252
^{1}H NMR (500 MHz, CDCl$_3$)
Me
^{t}Bu
Me
3c
10
9
8
7
6
5
4
3
2
1
0
ppm
4.00
1.01
1.86
6.08
5.43
9.50

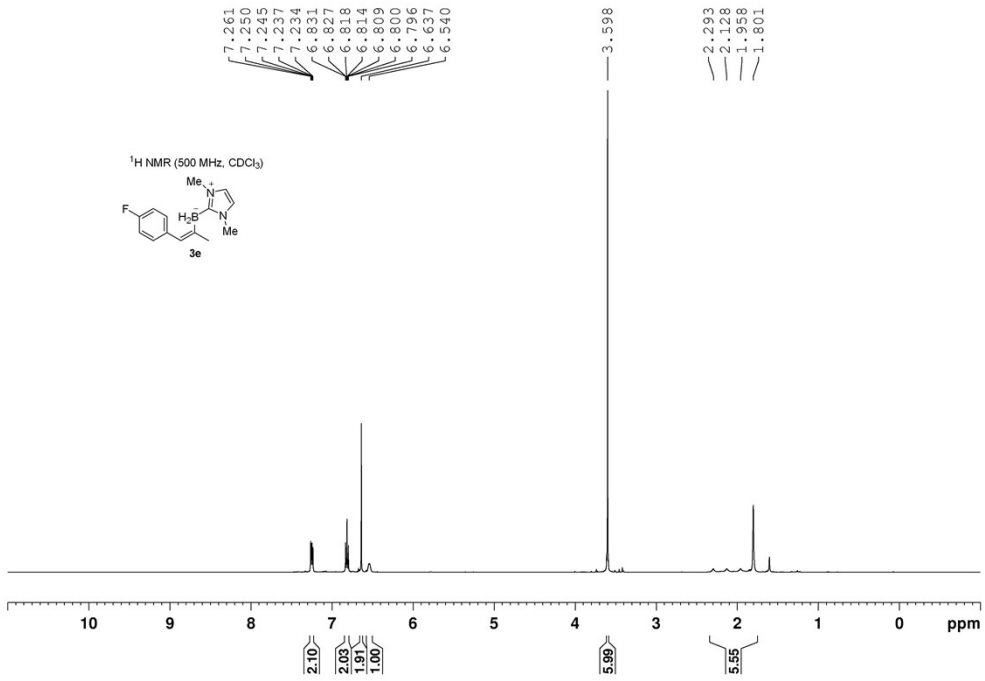

146.56
139.71
128.96
127.76
123.71
119.80
35.69
34.21
31.42
30.89
^{13}C NMR (125 MHz, CDCl$_3$)
Me
^{t}Bu
Me
3c
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

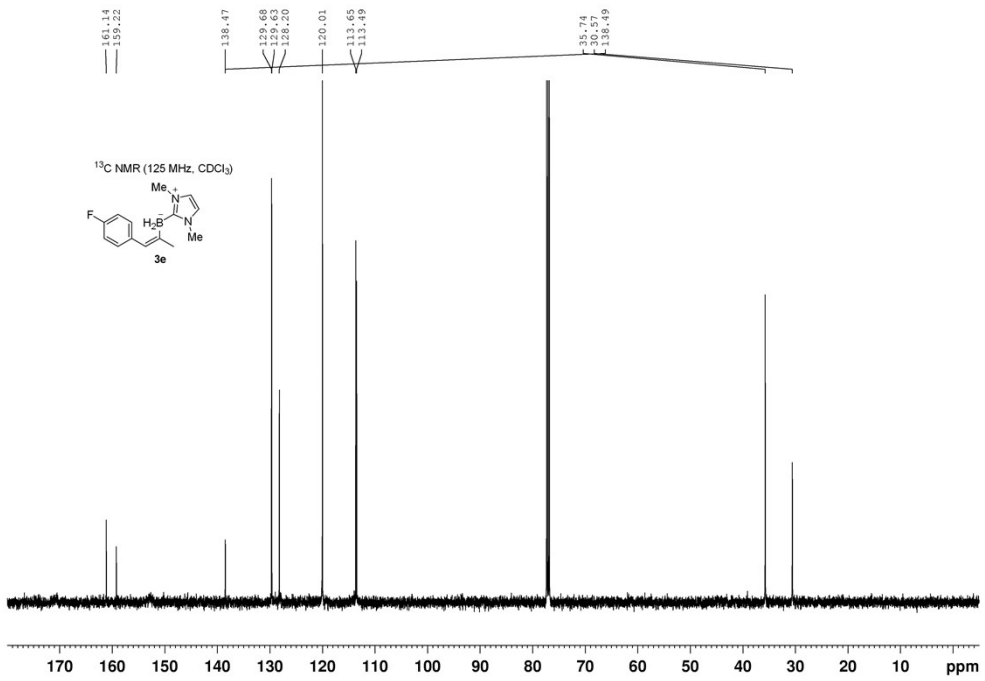

-26.73
-27.39
-28.05
11B NMR (128 MHz, CDCl3)
Me
tBu
H2B
N
Me
3c
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm

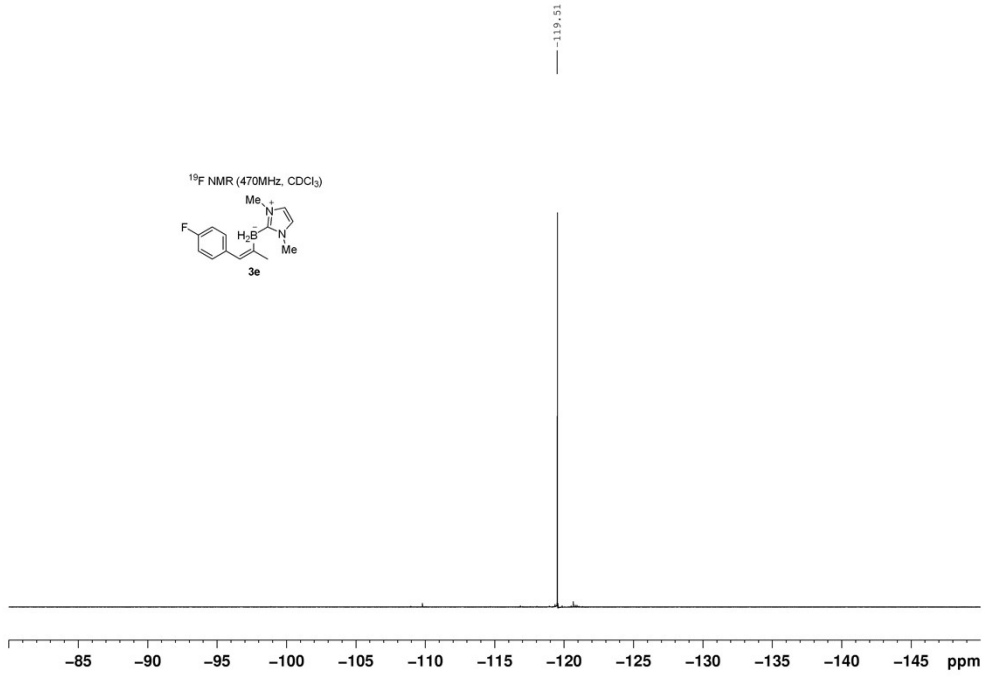

7.230
7.213
7.207
6.705
6.700
6.696
6.686
6.682
6.676
6.619
6.542
3.744
3.603
2.309
2.141
1.970
1.805
1H NMR (500 MHz, CDCl3)
Me
MeO
H2B
N
Me
3d
10
9
8
7
6
5
4
3
2
1
0
ppm
2.03
2.00
1.97
1.04
3.00
6.08
5.63

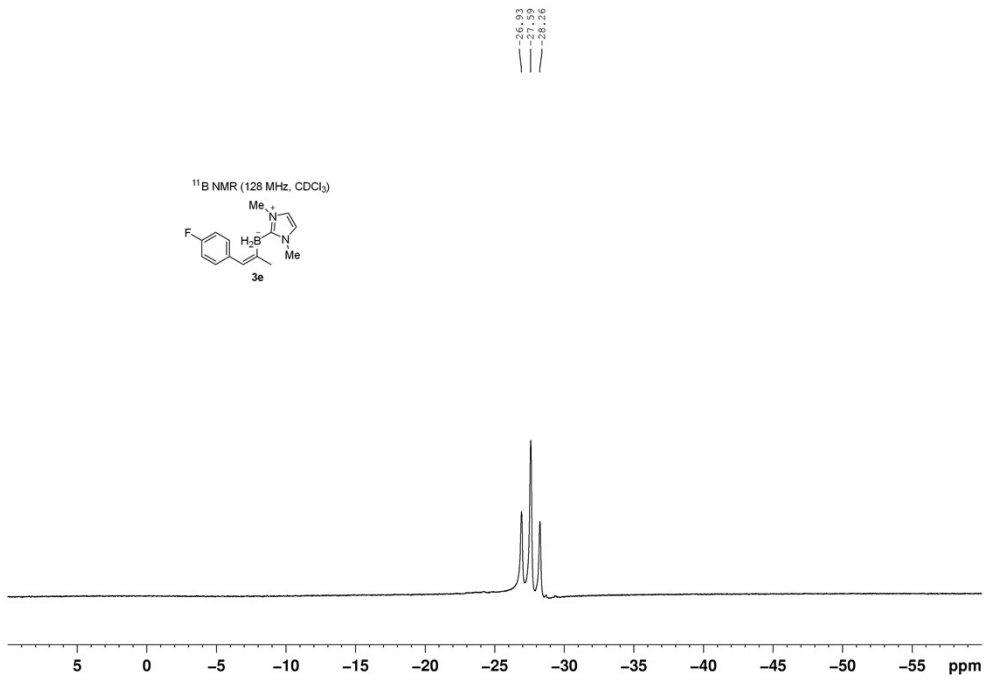

156.49
135.36
129.32
128.79
119.95
112.46
55.22
35.75
30.66
^{13}C NMR (125 MHz, CDCl$_3$)
Me
MeO
Me
3d
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

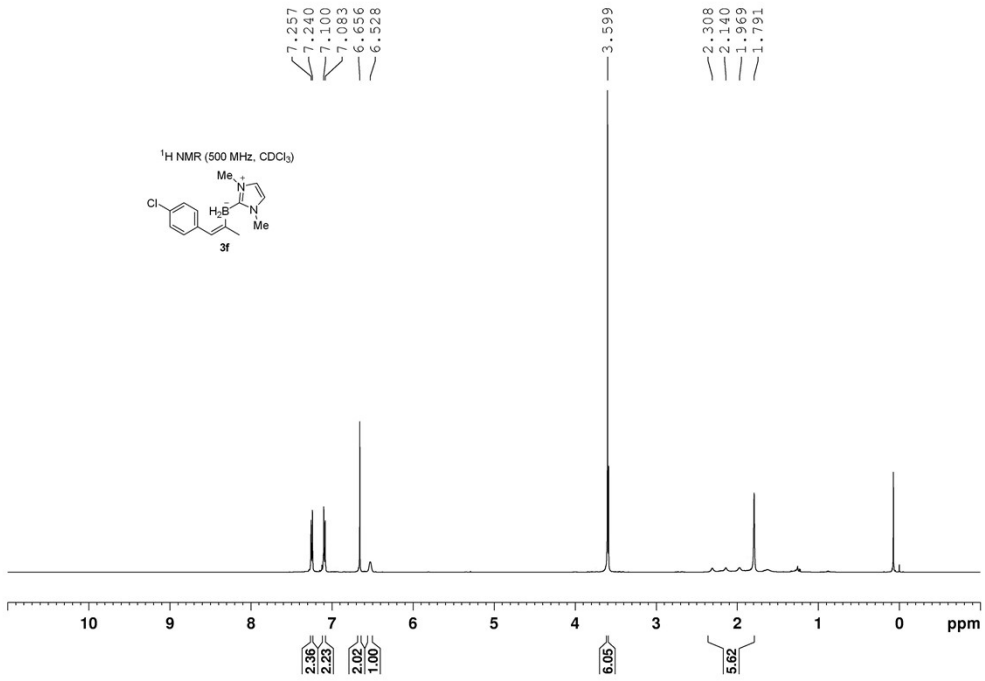

-26.87
-27.53
-28.19
^{11}B NMR (128 MHz, CDCl$_3$)
Me
MeO
Me
3d
5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55 ppm

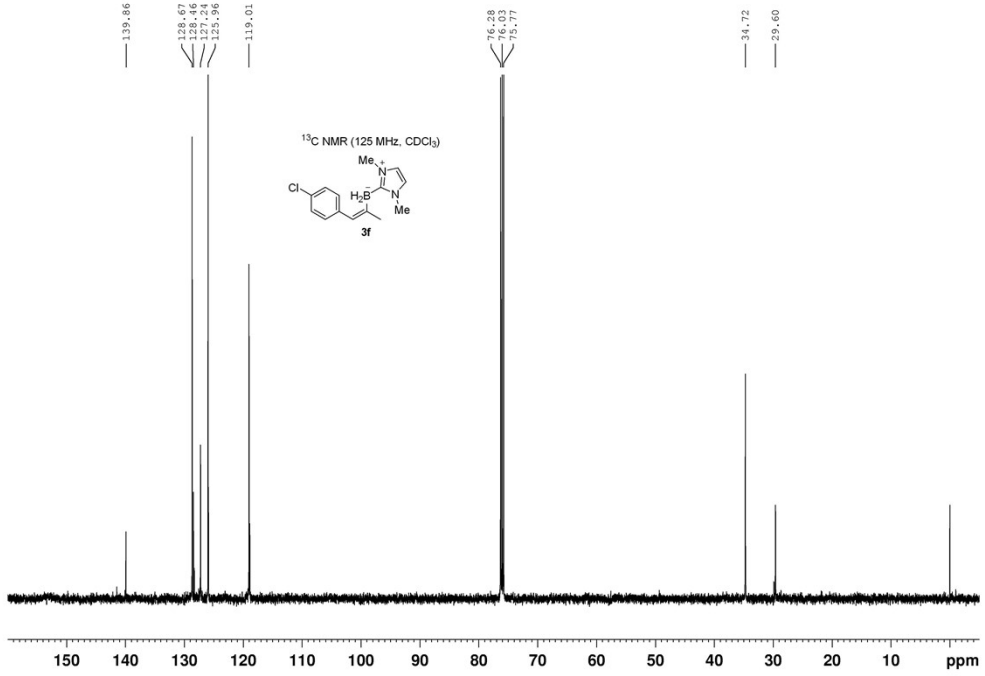

7.261
7.250
7.245
7.237
7.234
6.831
6.827
6.818
6.814
6.809
6.800
6.796
6.637
6.540
3.598
2.293
2.128
1.958
1.801
1H NMR (500 MHz, CDCl3)
3e
10 9 8 7 6 5 4 3 2 1 0 ppm
2.10
2.03
1.91
1.00
5.99
5.55

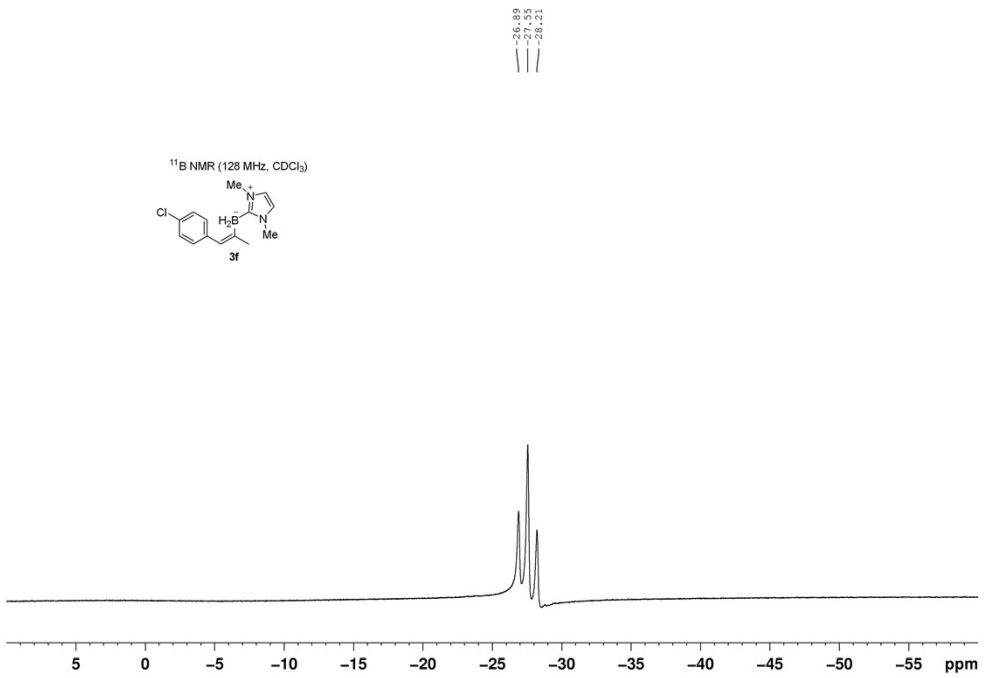

161.14
159.22
138.47
129.68
129.53
128.20
120.01
113.65
113.49
35.74
30.57
138.49
13C NMR (125 MHz, CDCl3)
3e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

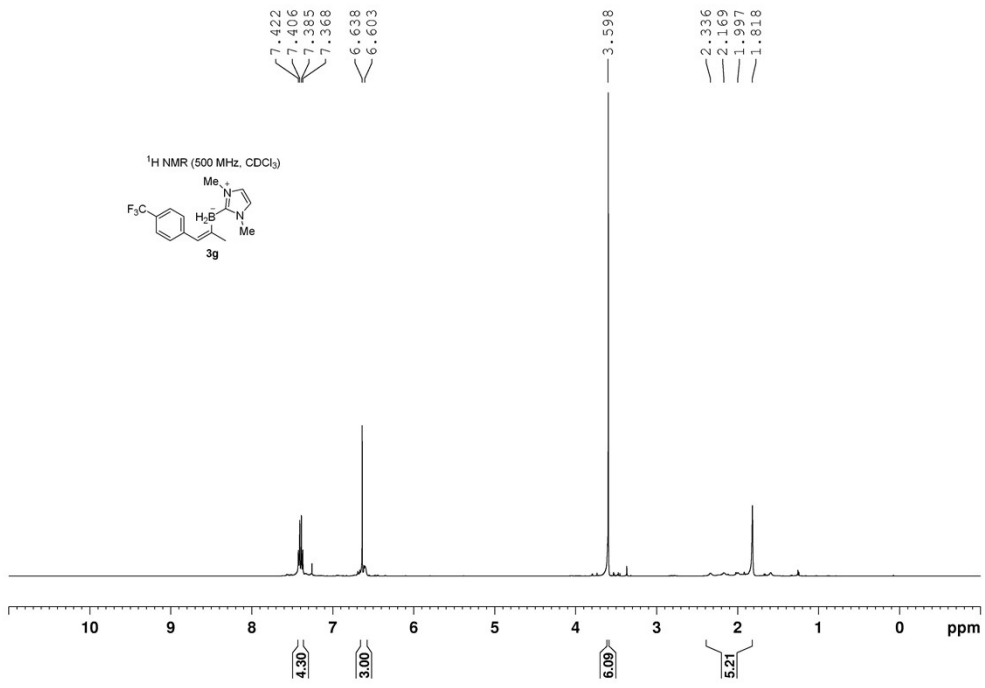

-119.51
^{19}F NMR (470MHz, CDCl$_3$)
Me
F
H_2B
Me
3e
−85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 ppm

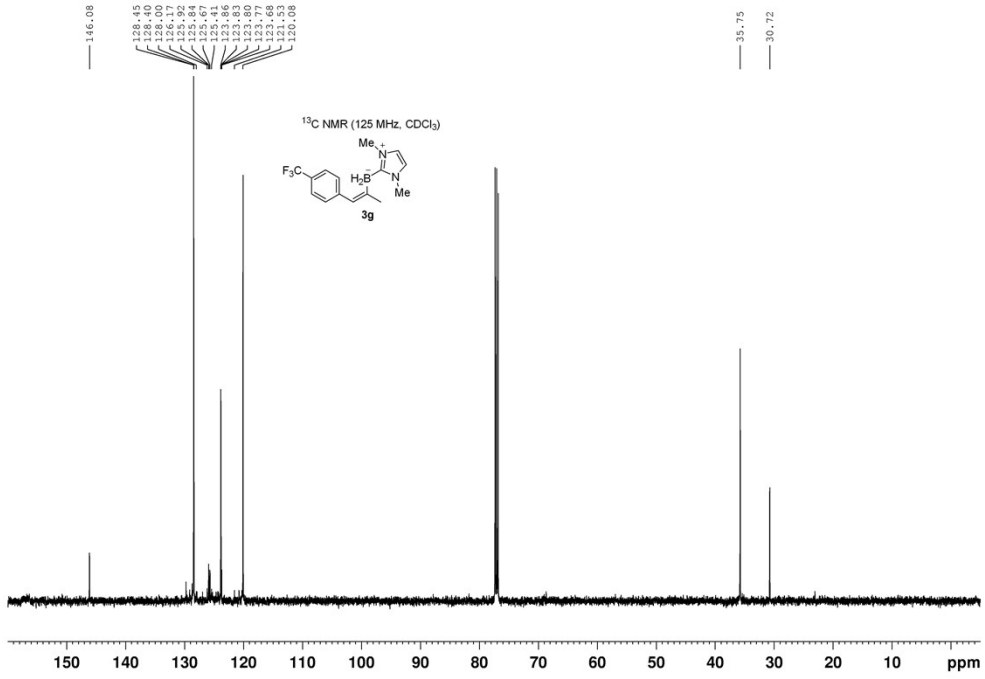

-26.93
-27.59
-28.26
^{11}B NMR (128 MHz, CDCl$_3$)
Me
F
H_2B
Me
3e
5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55 ppm

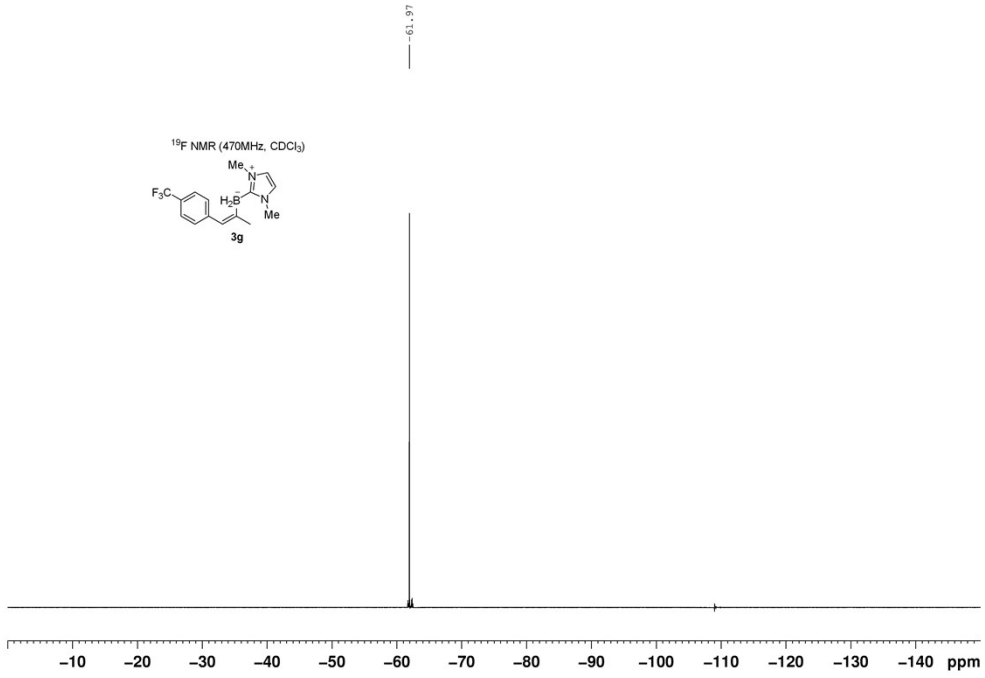

7.257
7.240
7.100
7.083
6.656
6.528
3.599
2.308
2.140
1.969
1.791
^{1}H NMR (500 MHz, CDCl$_3$)
3f
10 9 8 7 6 5 4 3 2 1 0 ppm
2.36
2.23
2.02
1.00
6.05
5.62

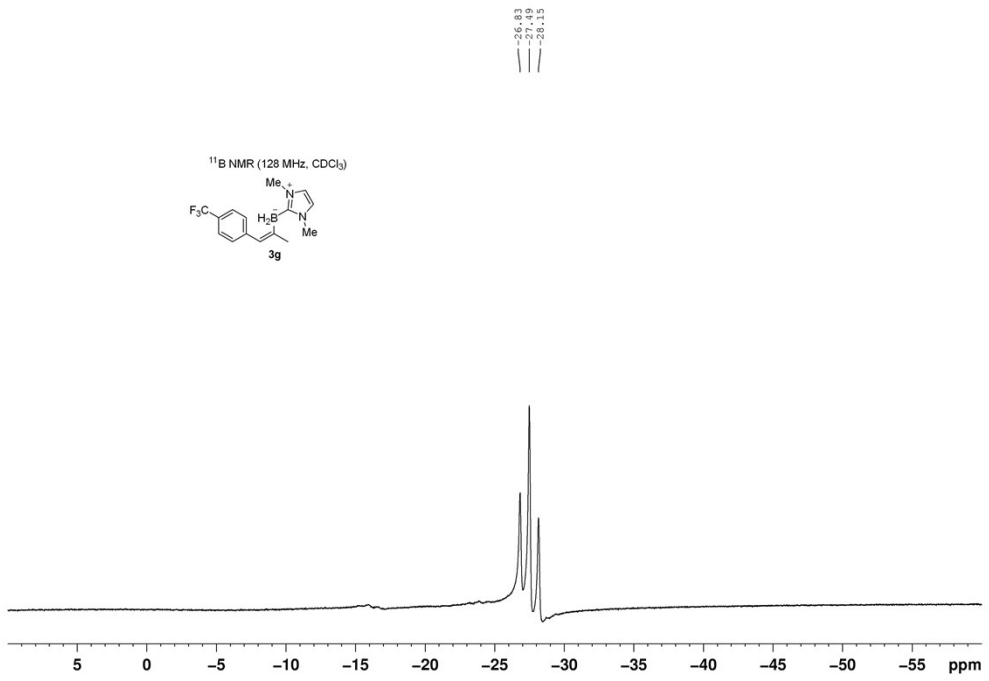

139.86
128.67
128.46
127.34
125.96
119.01
76.28
76.03
75.77
34.72
29.60
^{13}C NMR (125 MHz, CDCl$_3$)
3f
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

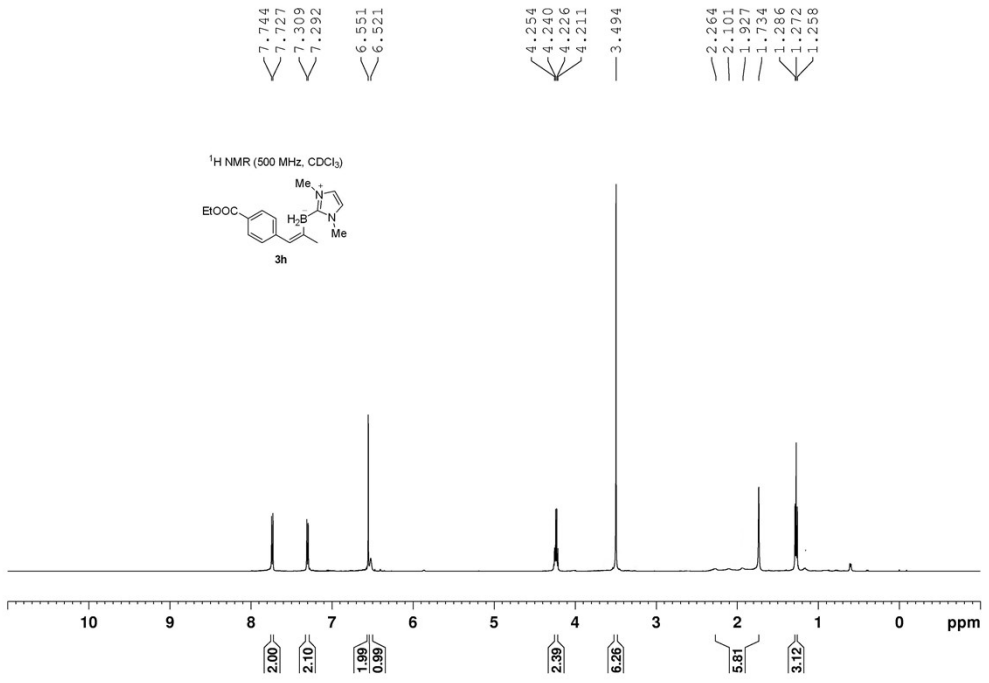

-26.89
-27.55
-28.21
11B NMR (128 MHz, CDCl3)
Me
Cl
H2B
Me
3f
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm

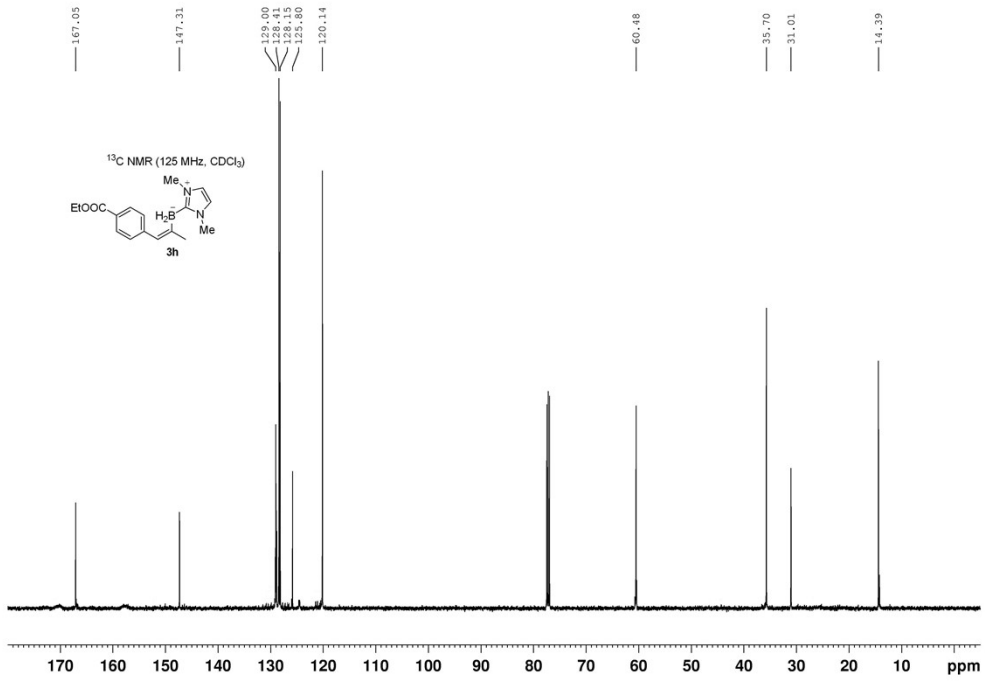

7.422
7.406
7.385
7.368
6.638
6.603
3.598
2.336
2.169
1.997
1.818
1H NMR (500 MHz, CDCl3)
Me
F3C
H2B
Me
3g
10
9
8
7
6
5
4
3
2
1
0
ppm
4.30
3.00
6.09
5.21

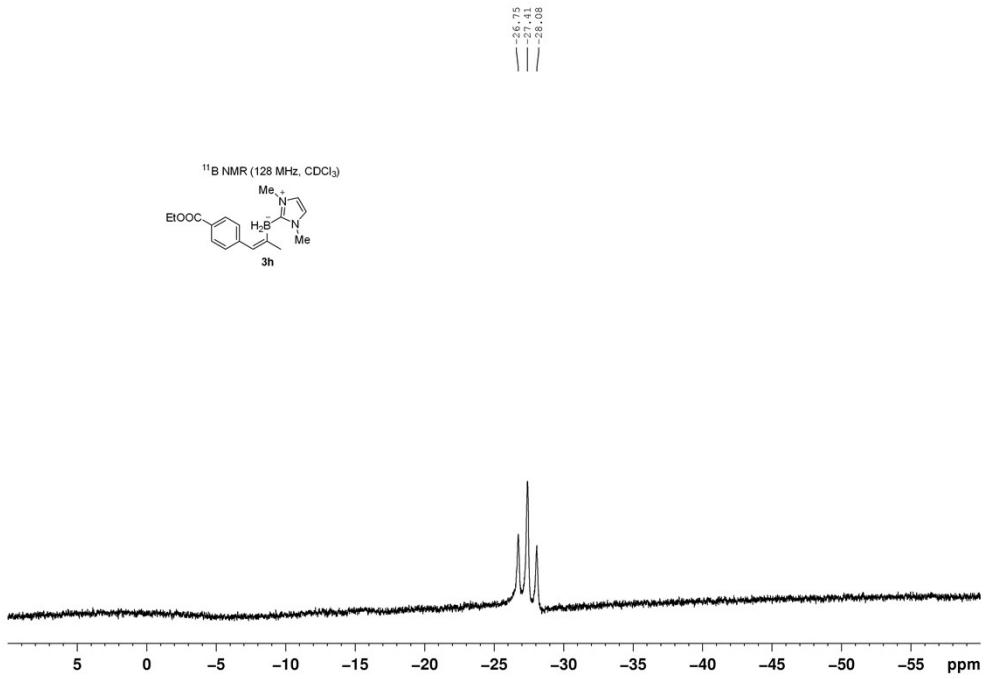

146.08
128.45
128.40
128.00
126.17
125.92
125.84
125.67
125.41
123.86
123.83
123.80
123.77
123.68
121.53
120.08
35.75
30.72
13C NMR (125 MHz, CDCl3)
Me
F3C
H2B
N
Me
3g
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

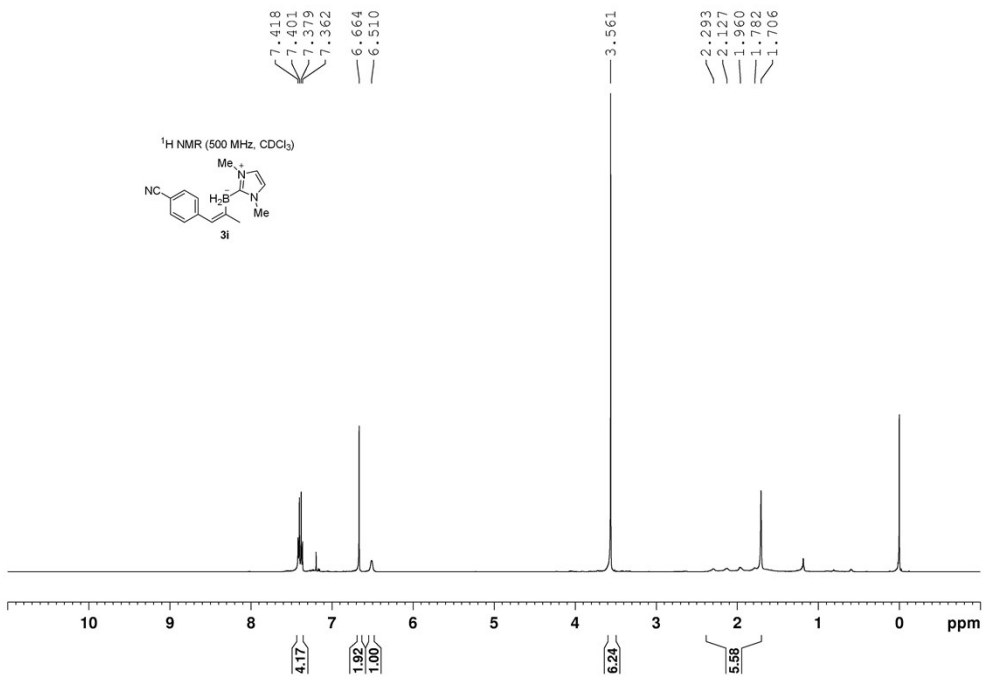

-61.97
19F NMR (470MHz, CDCl3)
Me
F3C
H2B
N
Me
3g
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm

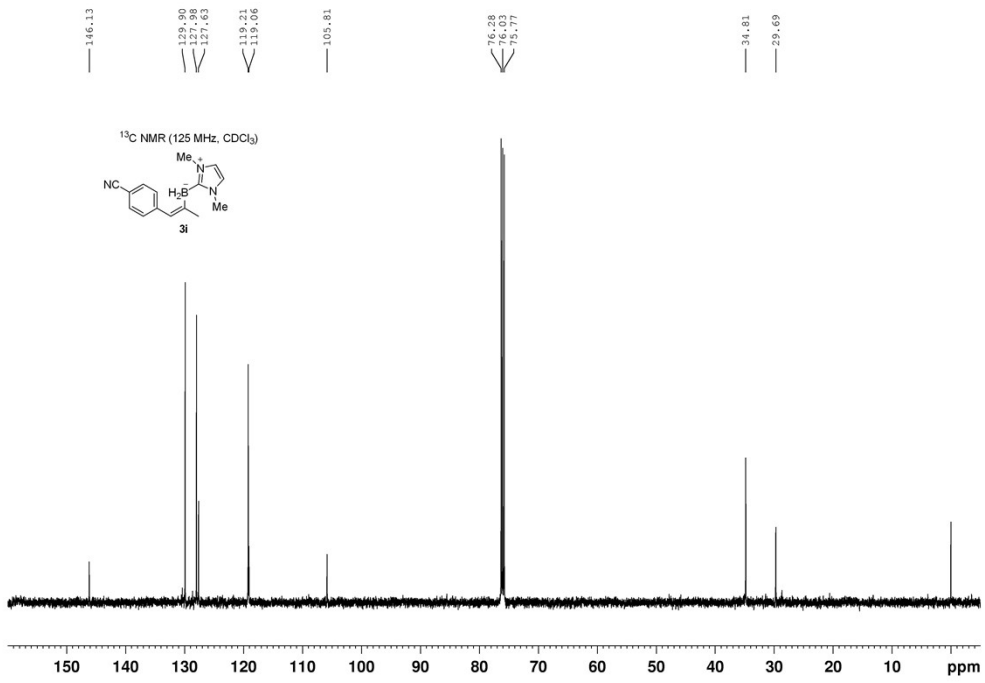

-26.83
-27.49
-28.15
11B NMR (128 MHz, CDCl3)
Me
F3C
H2B
N
Me
3g
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm

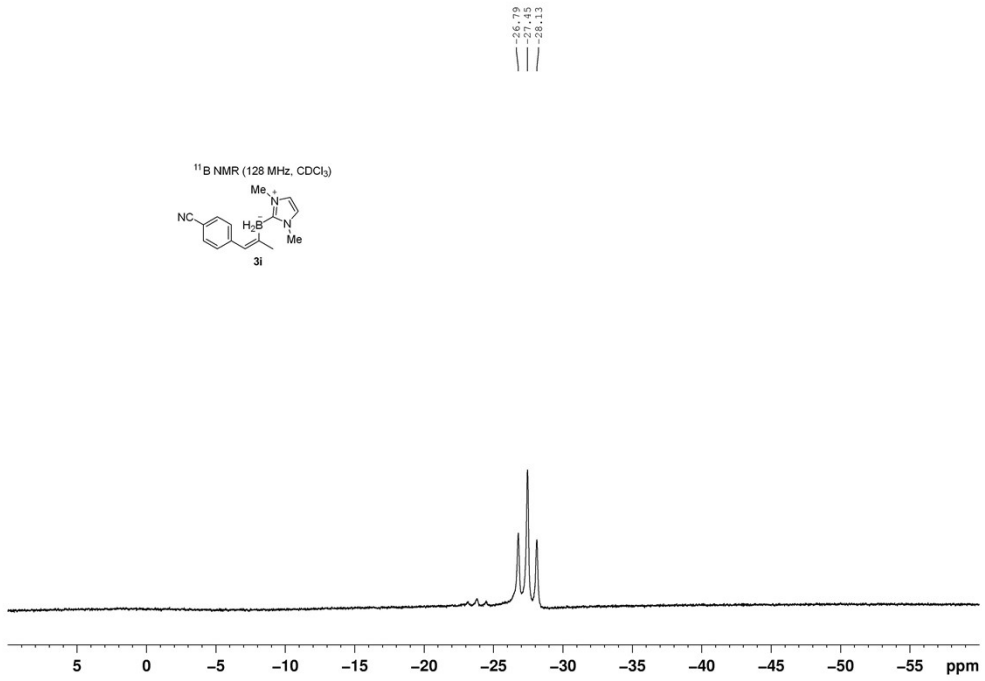

7.744
7.727
7.309
7.292
6.551
6.521
4.254
4.240
4.226
4.211
3.494
2.264
2.101
1.927
1.734
1.286
1.272
1.258
1H NMR (500 MHz, CDCl3)
Me
EtOOC
H2B
N
Me
3h
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.10
1.99
0.99
2.39
6.26
5.81
3.12

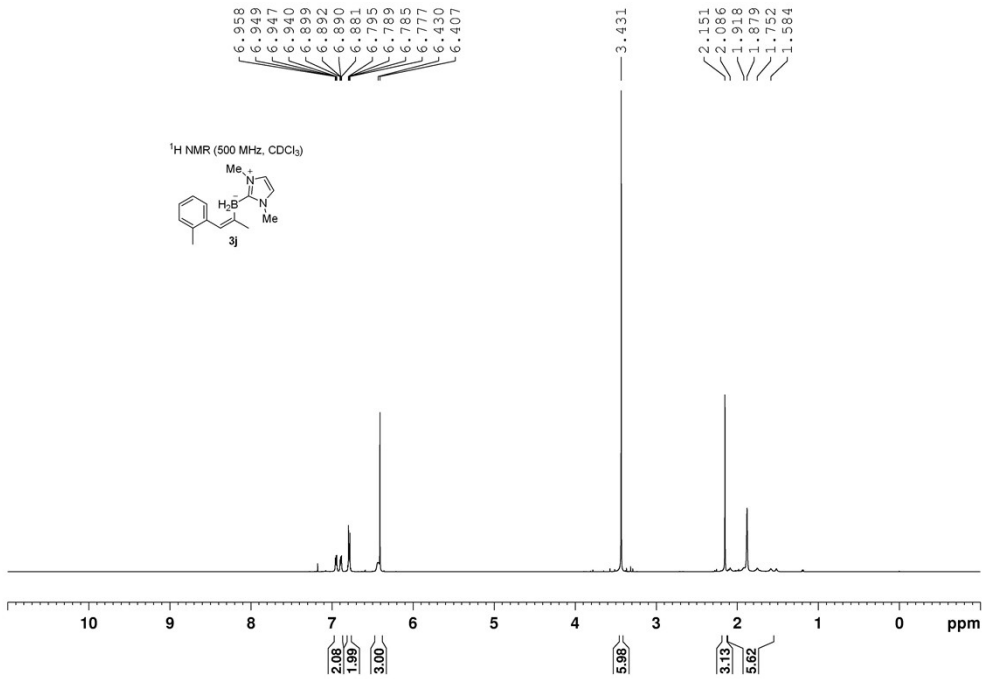

167.05
147.31
129.00
128.41
128.15
125.80
120.14
60.48
35.70
31.01
14.39
13C NMR (125 MHz, CDCl3)
EtOOC
Me
H2B
N
Me
3h
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

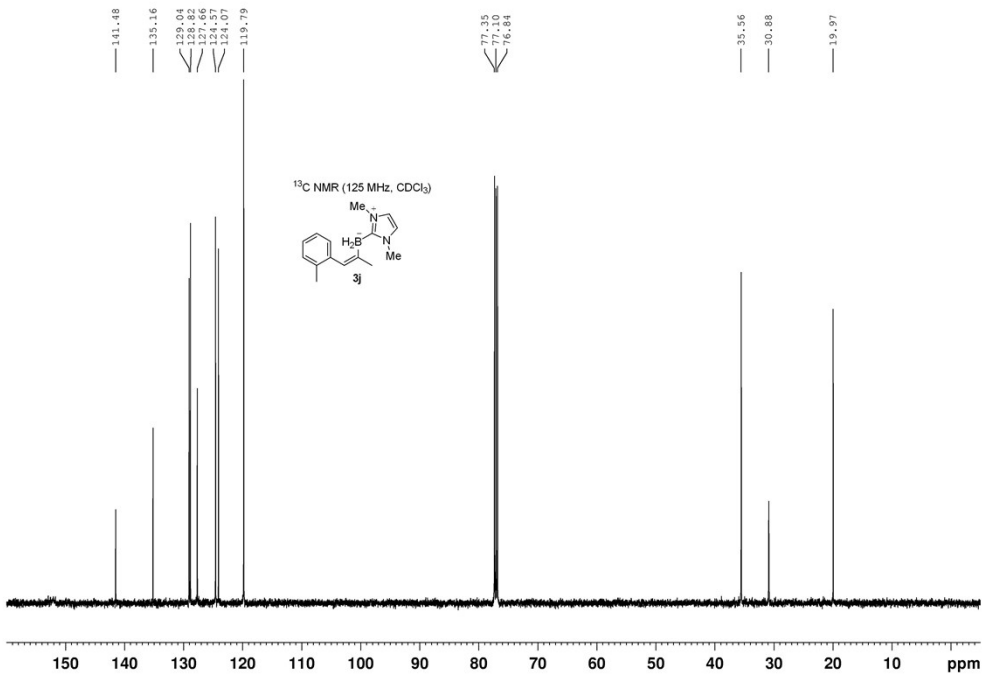

26.75
27.41
28.08
11B NMR (128 MHz, CDCl3)
EtOOC
Me
H2B
N
Me
3h
5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55 ppm

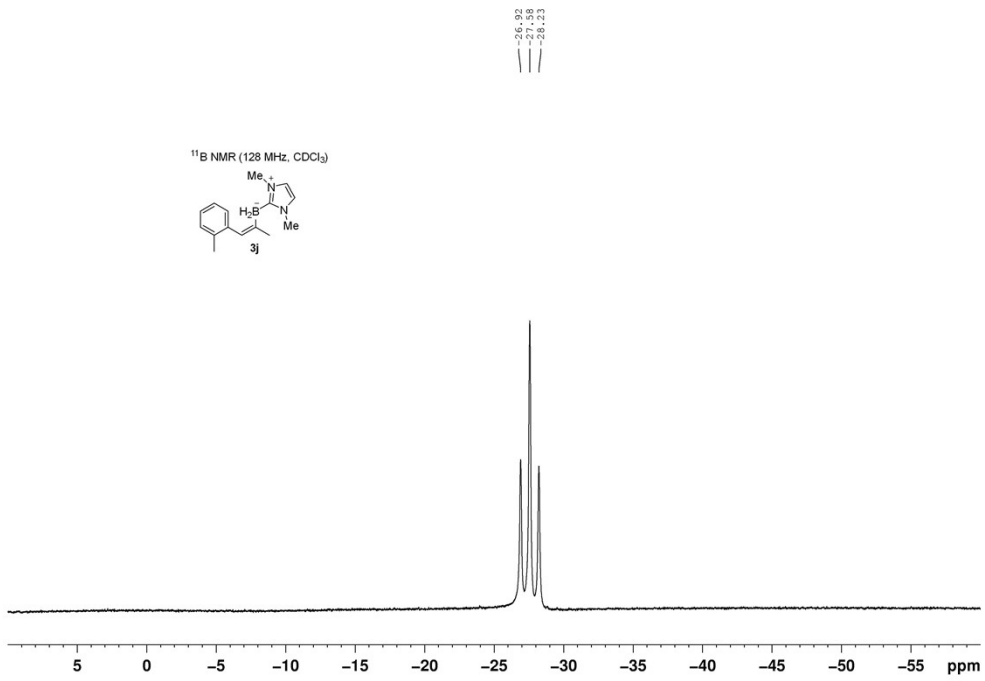

7.418
7.401
7.379
7.362
6.664
6.510
3.561
2.293
2.127
1.960
1.782
1.706
^{1}H NMR (500 MHz, CDCl$_3$)
3i
10 9 8 7 6 5 4 3 2 1 0 ppm
4.17
1.92
1.00
6.24
5.58

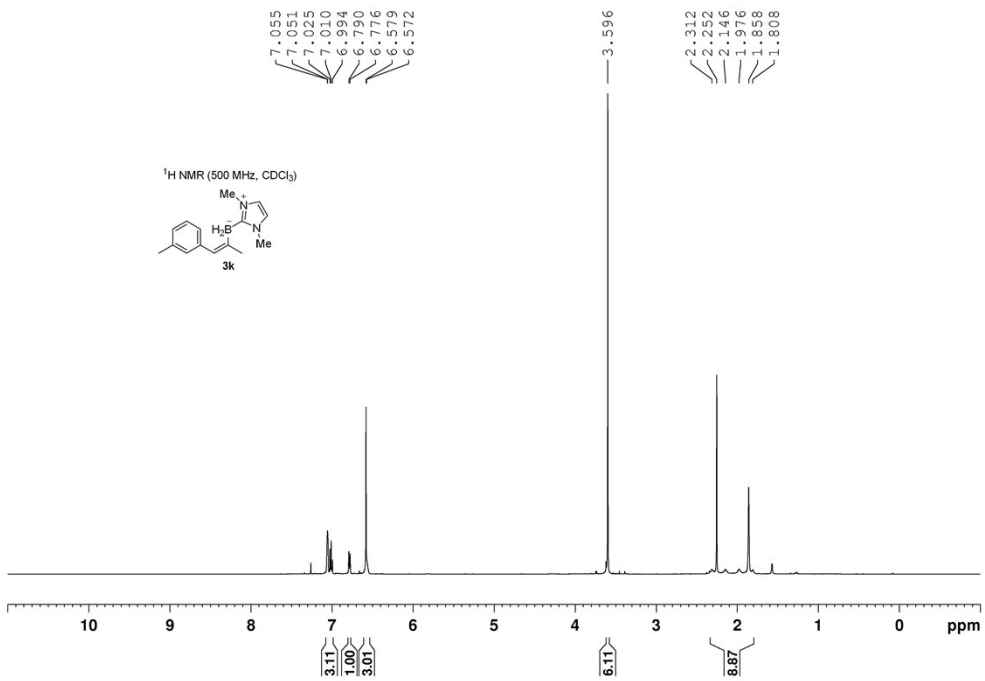

146.13
129.90
127.98
127.63
119.21
119.06
105.81
76.28
76.03
75.77
34.81
29.69
^{13}C NMR (125 MHz, CDCl$_3$)
3i
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

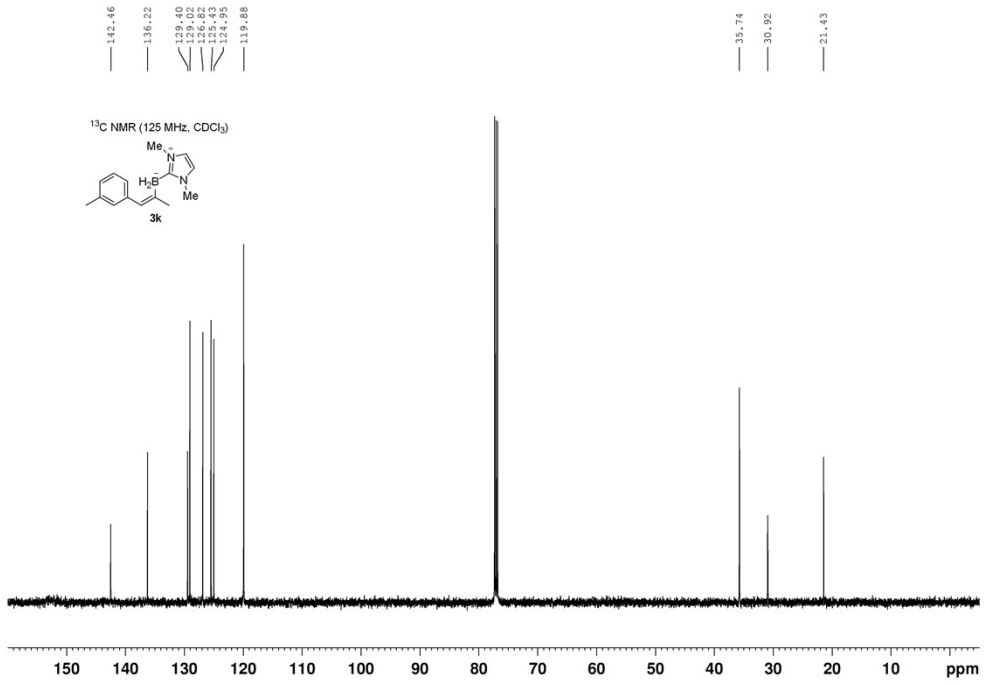

-26.79
-27.45
-28.13
11B NMR (128 MHz, CDCl3)
Me
NC
H2B
N
Me
3i
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm

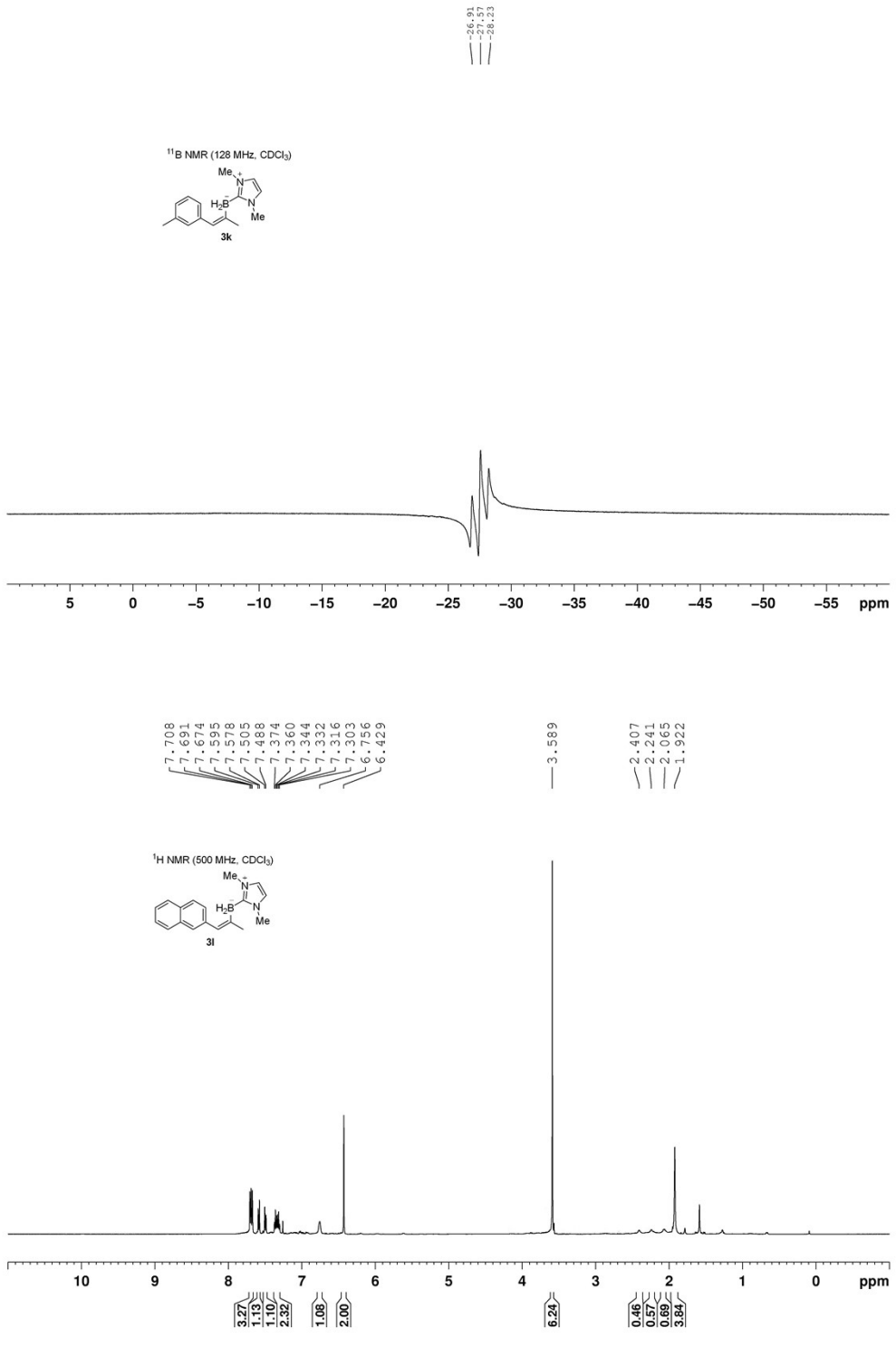

6.958
6.949
6.947
6.940
6.899
6.892
6.890
6.881
6.795
6.789
6.785
6.777
6.430
6.407
3.431
2.151
2.086
1.918
1.879
1.752
1.584
1H NMR (500 MHz, CDCl3)
Me
H2B
N
Me
3j
10
9
8
7
6
5
4
3
2
1
0
ppm
2.08
1.99
3.00
5.98
3.13
5.62

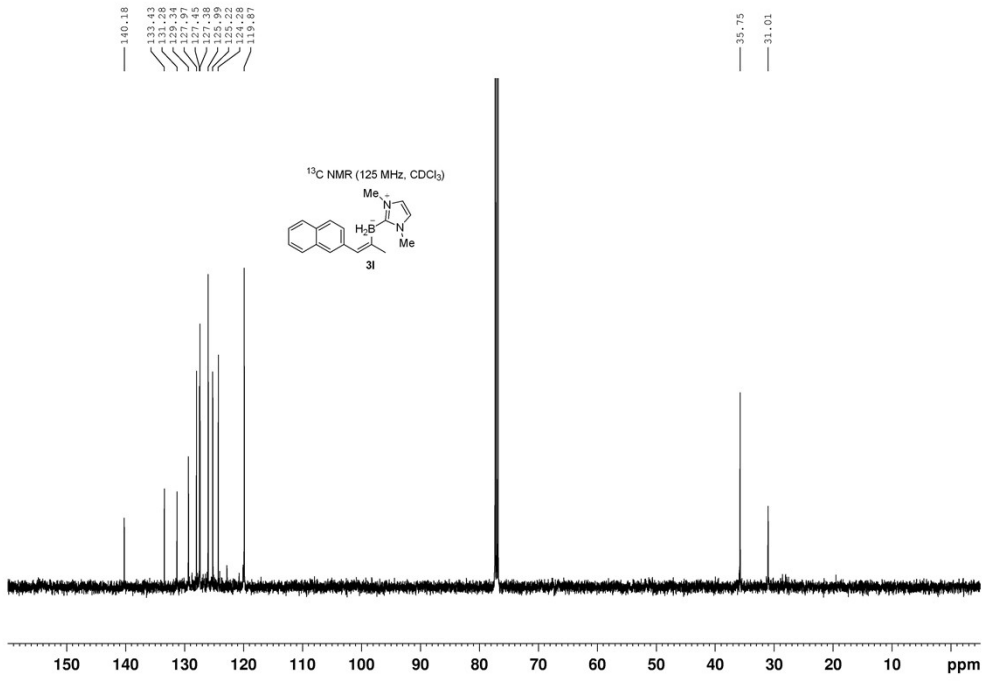

141.48
135.16
129.04
128.82
127.66
124.57
124.07
119.79
77.35
77.10
76.84
35.56
30.88
19.97
13C NMR (125 MHz, CDCl3)
Me
N
H2B
N
Me
3j
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

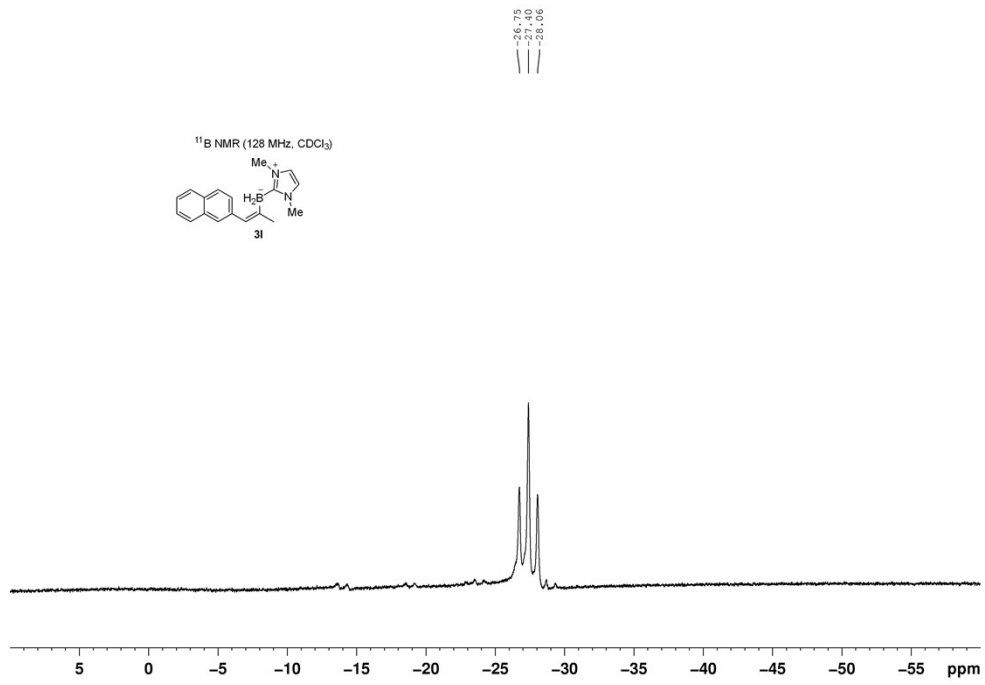

-26.92
-27.58
-28.23
11B NMR (128 MHz, CDCl3)
Me
N
H2B
N
Me
3j
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm

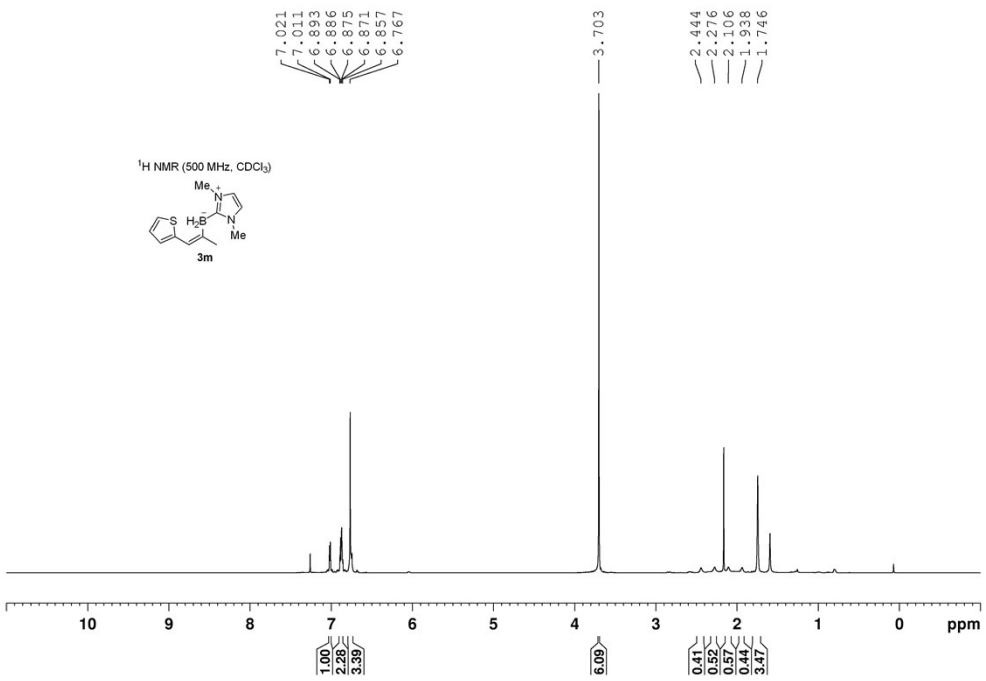

7.055
7.051
7.025
7.010
6.994
6.790
6.776
6.579
6.572
3.596
2.312
2.252
2.146
1.976
1.858
1.808
^{1}H NMR (500 MHz, CDCl$_3$)
3k
10 9 8 7 6 5 4 3 2 1 0 ppm
3.11
1.00
3.01
6.11
8.87

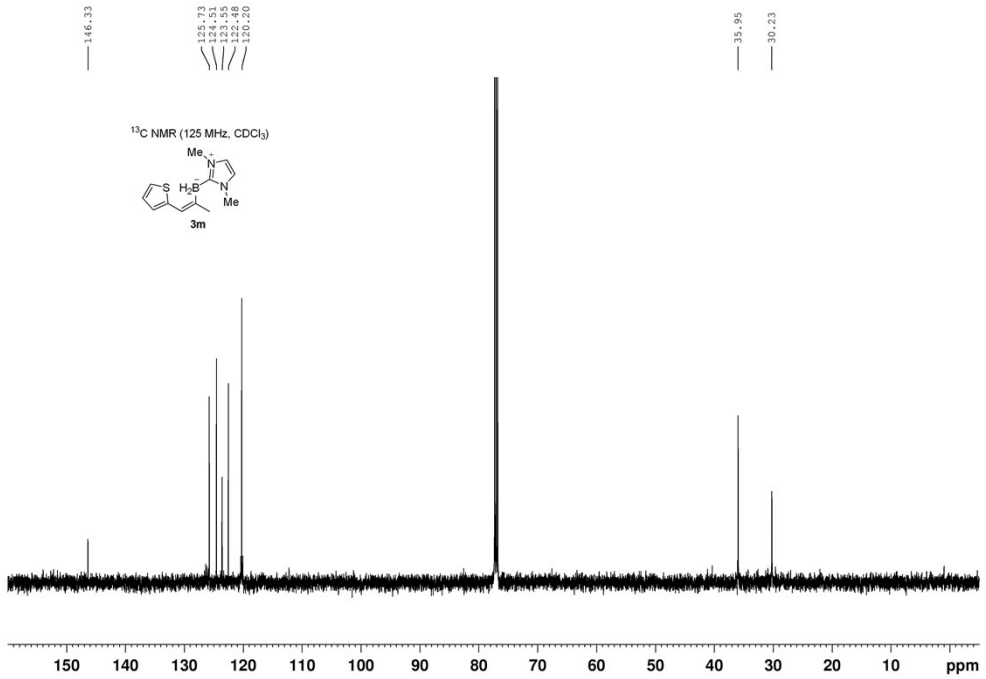

142.46
136.22
129.40
129.02
126.82
125.43
124.95
119.88
35.74
30.92
21.43
^{13}C NMR (125 MHz, CDCl$_3$)
3k
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

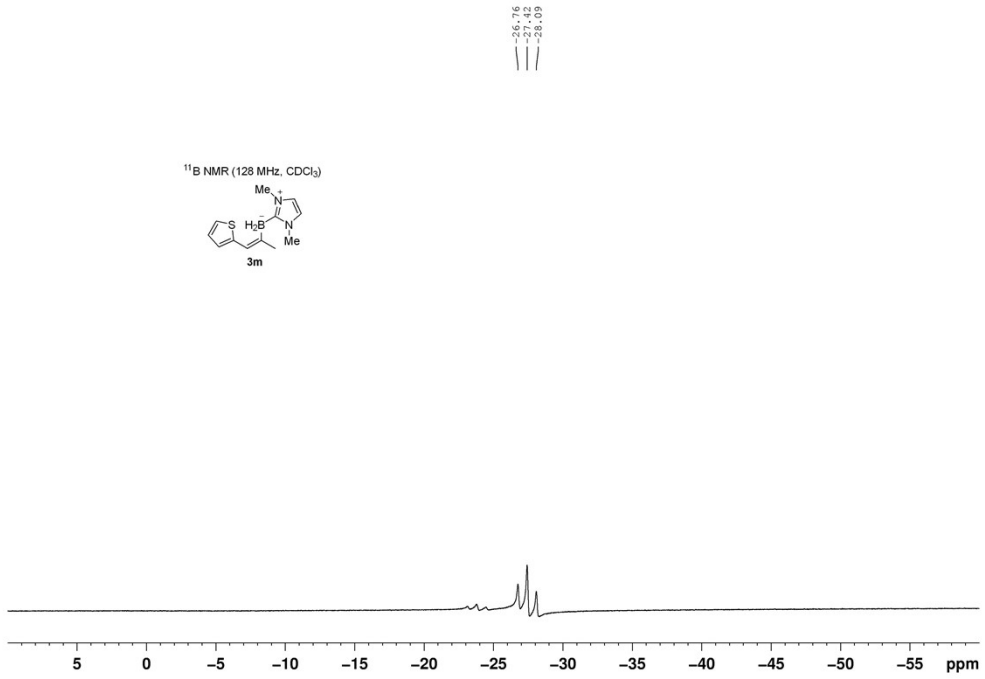

-26.91
-27.57
-28.23
11B NMR (128 MHz, CDCl3)
3k
5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55 ppm
7.708
7.691
7.674
7.595
7.578
7.505
7.488
7.374
7.360
7.344
7.332
7.316
7.303
6.756
6.429
3.589
2.407
2.241
2.065
1.922
1H NMR (500 MHz, CDCl3)
3l
10 9 8 7 6 5 4 3 2 1 0 ppm
3.27
1.13
1.10
2.32
1.08
2.00
6.24
0.46
0.57
0.69
3.84

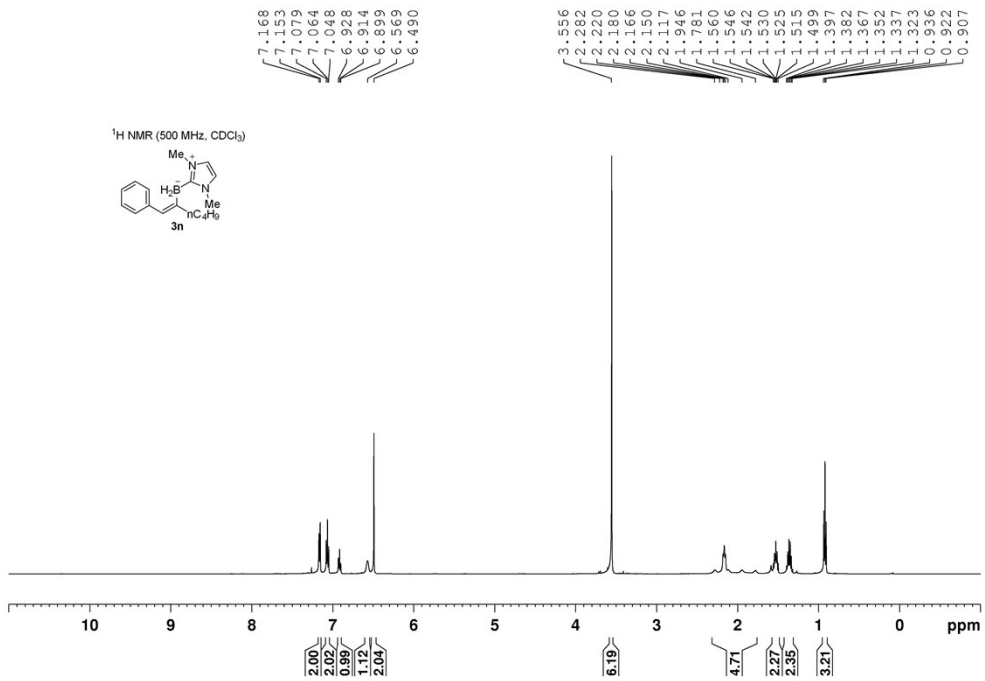

140.18
133.43
131.28
129.34
127.97
127.45
127.38
125.89
125.22
124.28
119.87
39.75
31.01
13C NMR (125 MHz, CDCl3)
Me
N
H2B
N
Me
3l
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

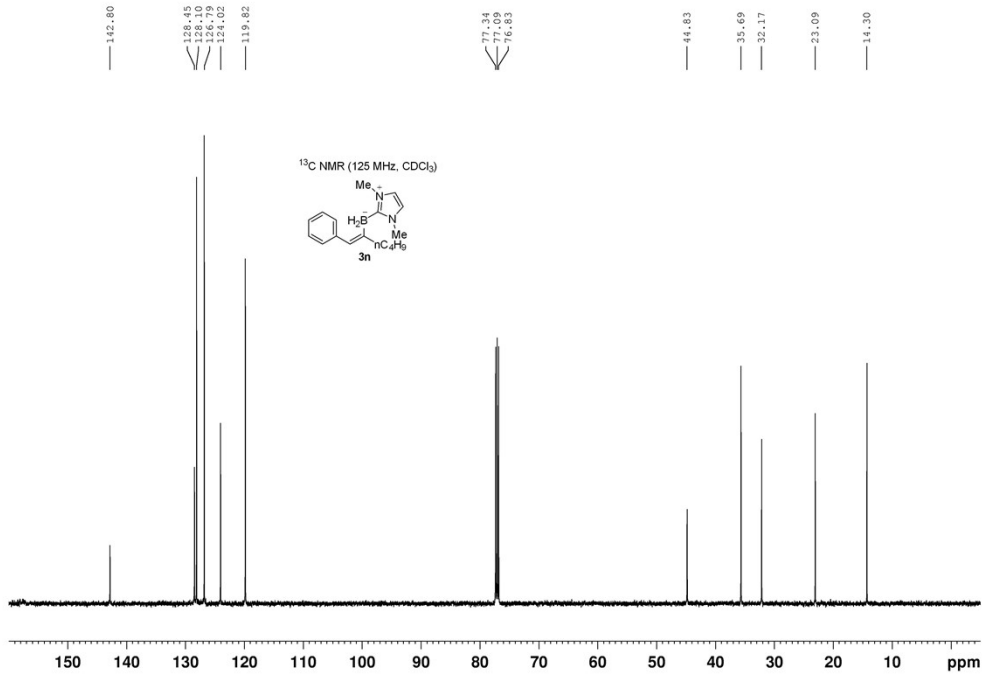

-26.75
-27.40
-28.06
11B NMR (128 MHz, CDCl3)
Me
N
H2B
N
Me
3l
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm

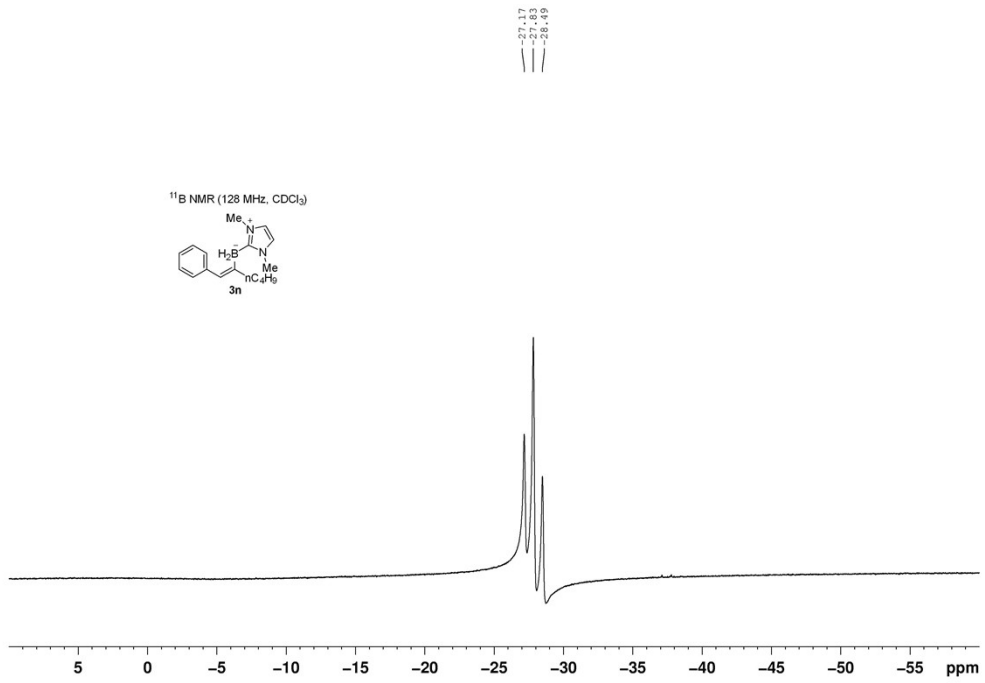

7.021
7.011
6.893
6.886
6.875
6.871
6.857
6.767
3.703
2.444
2.276
2.106
1.938
1.746
^{1}H NMR (500 MHz, CDCl$_3$)
3m
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 2.28 3.39 6.09 0.41 0.52 0.57 0.44 3.47

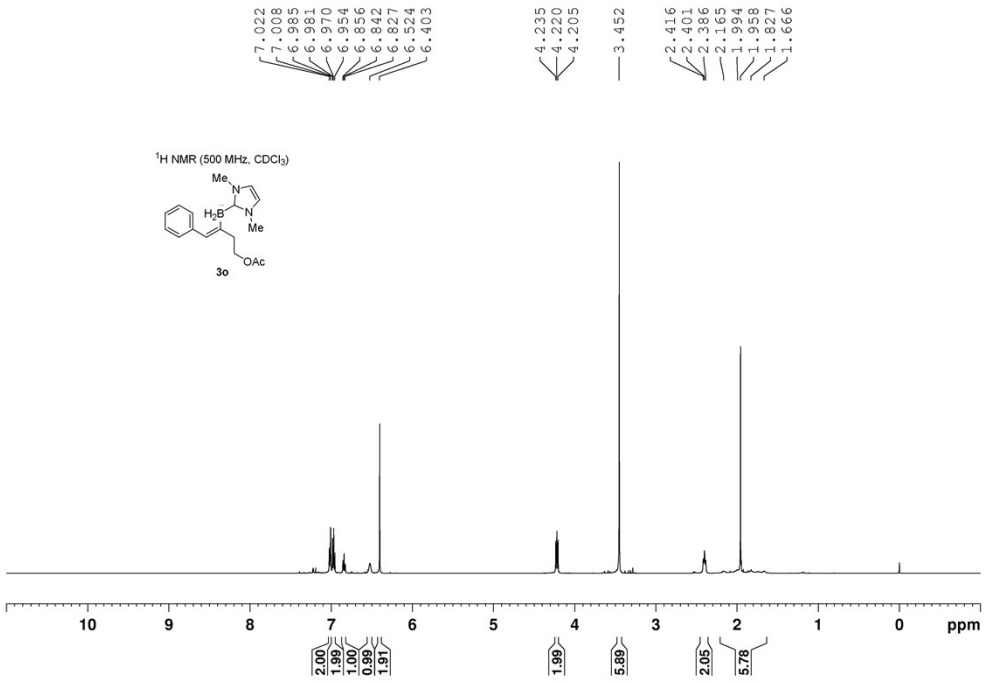

146.33
125.73
124.51
123.55
122.48
120.20
35.95
30.23
^{13}C NMR (125 MHz, CDCl$_3$)
3m
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

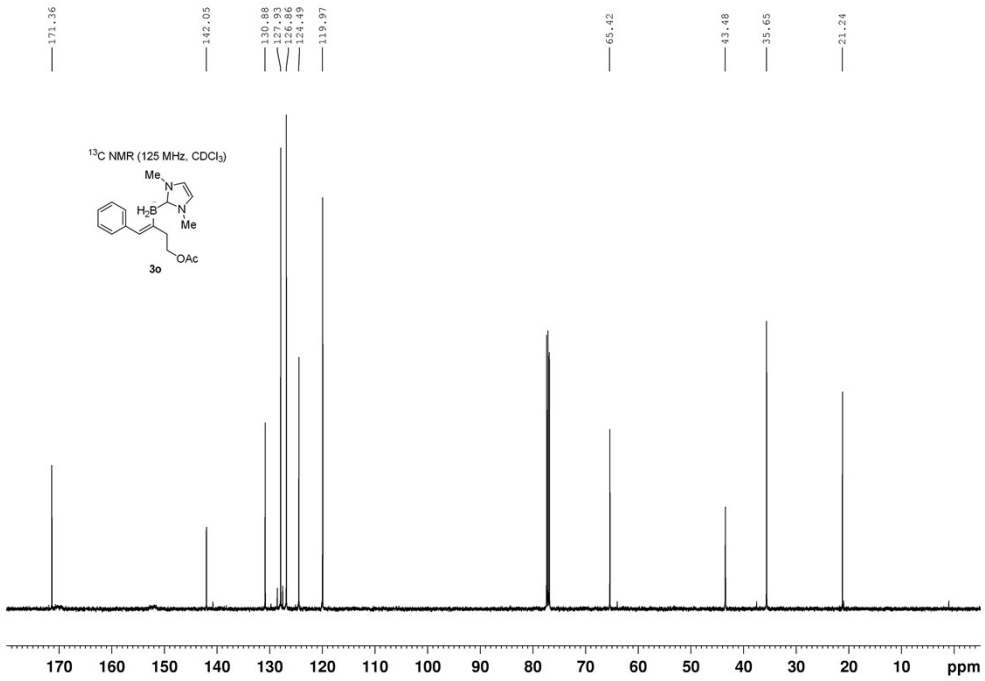

-26.76
-27.42
-28.09
11B NMR (128 MHz, CDCl3)
3m
5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55 ppm

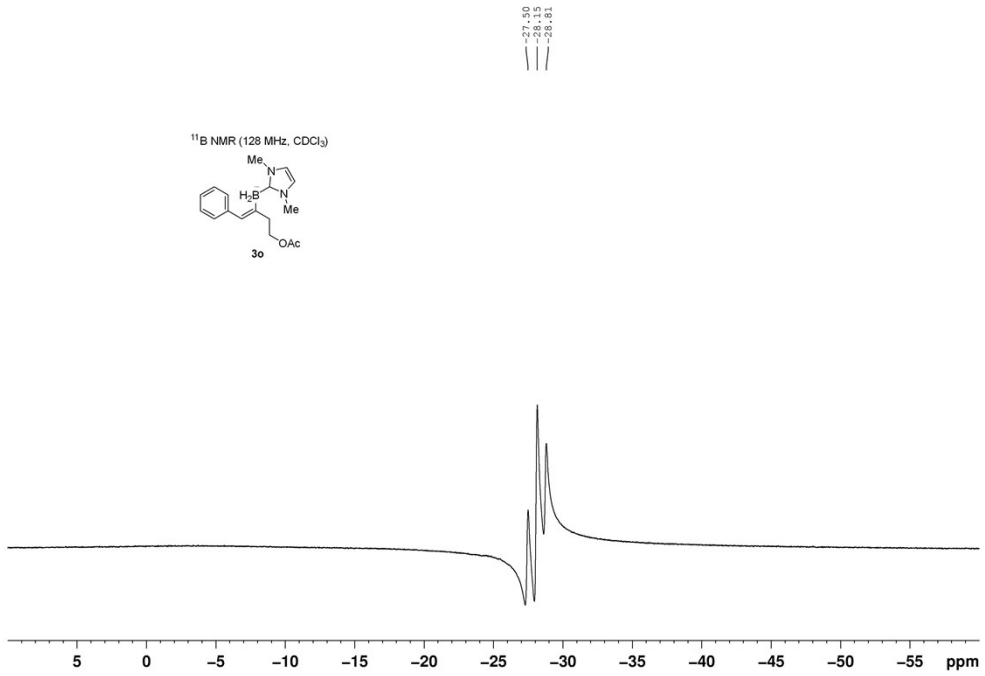

7.168
7.153
7.079
7.064
7.048
6.928
6.914
6.899
6.569
6.490
3.556
2.282
2.220
2.180
2.166
2.150
2.117
1.946
1.781
1.560
1.546
1.542
1.530
1.525
1.515
1.499
1.397
1.382
1.367
1.352
1.337
1.323
0.936
0.922
0.907
1H NMR (500 MHz, CDCl3)
3n
10 9 8 7 6 5 4 3 2 1 0 ppm
2.00
2.02
0.99
1.12
2.04
6.19
4.71
2.27
2.35
3.21

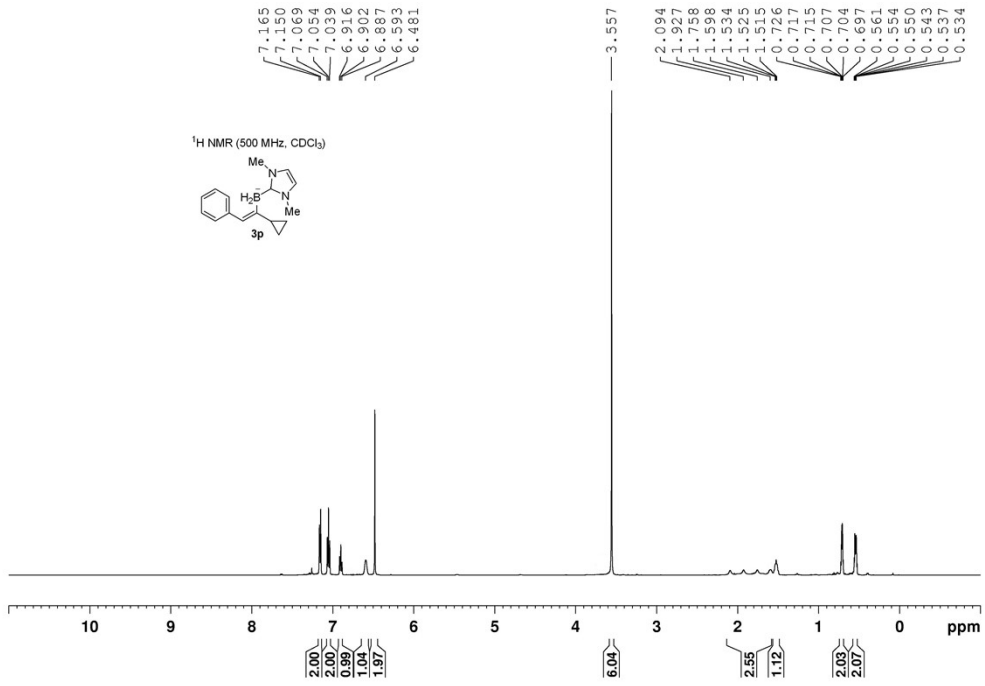

142.80
128.45
128.10
126.79
124.02
119.82
77.34
77.09
76.83
44.83
35.69
32.17
23.09
14.30
13C NMR (125 MHz, CDCl3)
3n
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

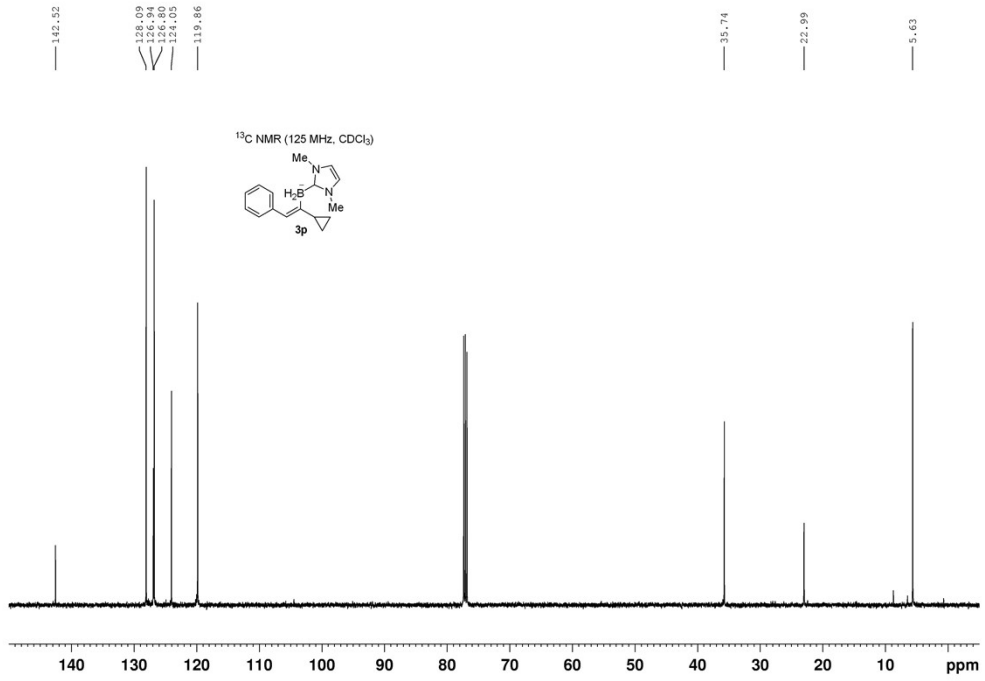

-27.17
-27.83
-28.49
11B NMR (128 MHz, CDCl3)
3n
5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55 ppm

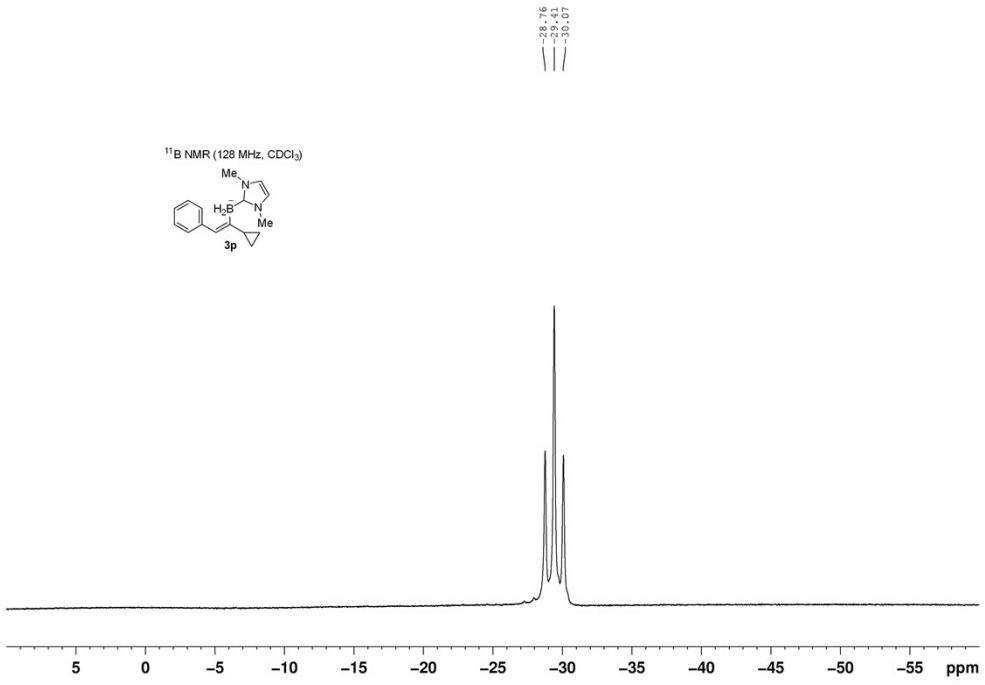

7.022
7.008
6.985
6.981
6.970
6.954
6.856
6.842
6.827
6.524
6.403
4.235
4.220
4.205
3.452
2.416
2.401
2.386
2.165
1.994
1.958
1.827
1.666
^{1}H NMR (500 MHz, CDCl$_3$)
Me
N
H$_2$B
N
Me
OAc
3o
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.99
1.00
0.99
1.91
1.99
5.89
2.05
5.78

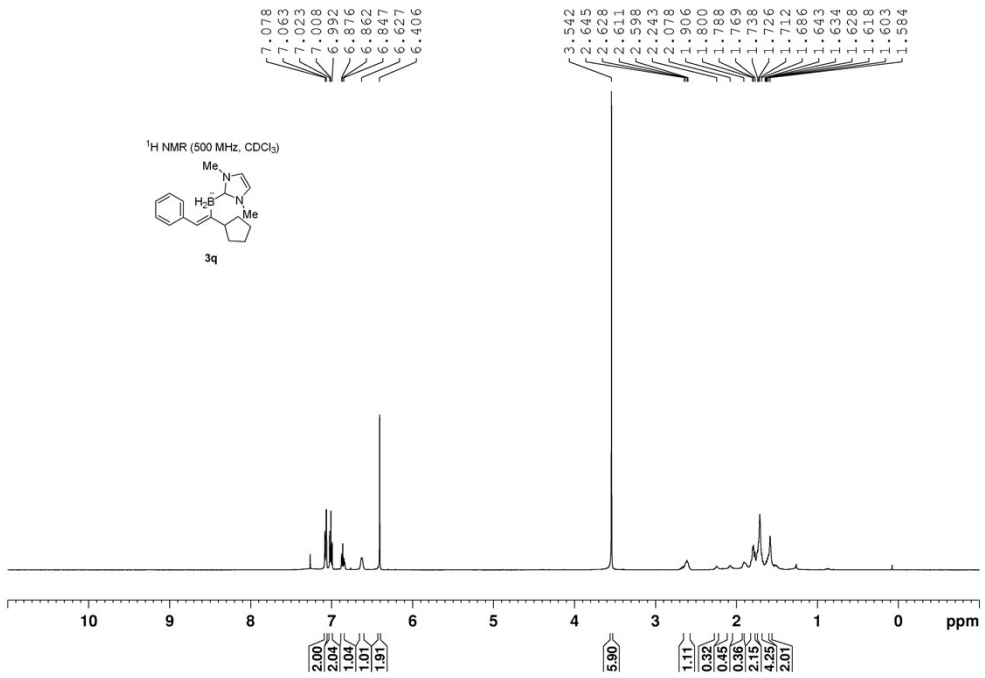

171.36
142.05
130.88
127.93
126.46
124.49
119.97
65.42
43.48
35.65
21.24
^{13}C NMR (125 MHz, CDCl$_3$)
Me
N
H$_2$B
N
Me
OAc
3o
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

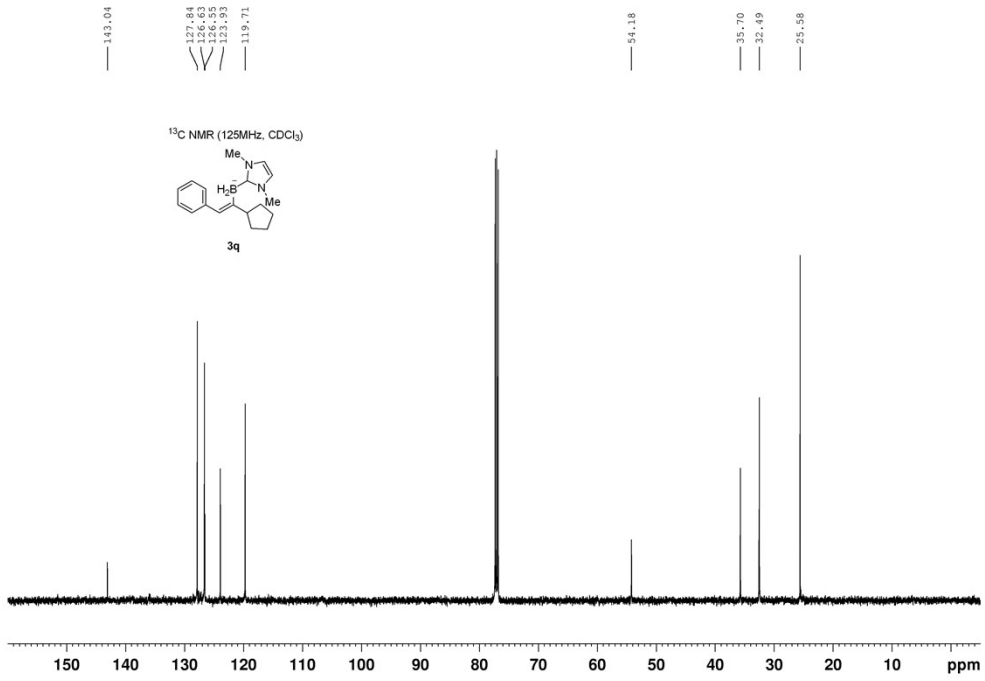

-27.50
-28.15
-28.81
11B NMR (128 MHz, CDCl3)
Me
N
H2B
N
Me
OAc
3o
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm

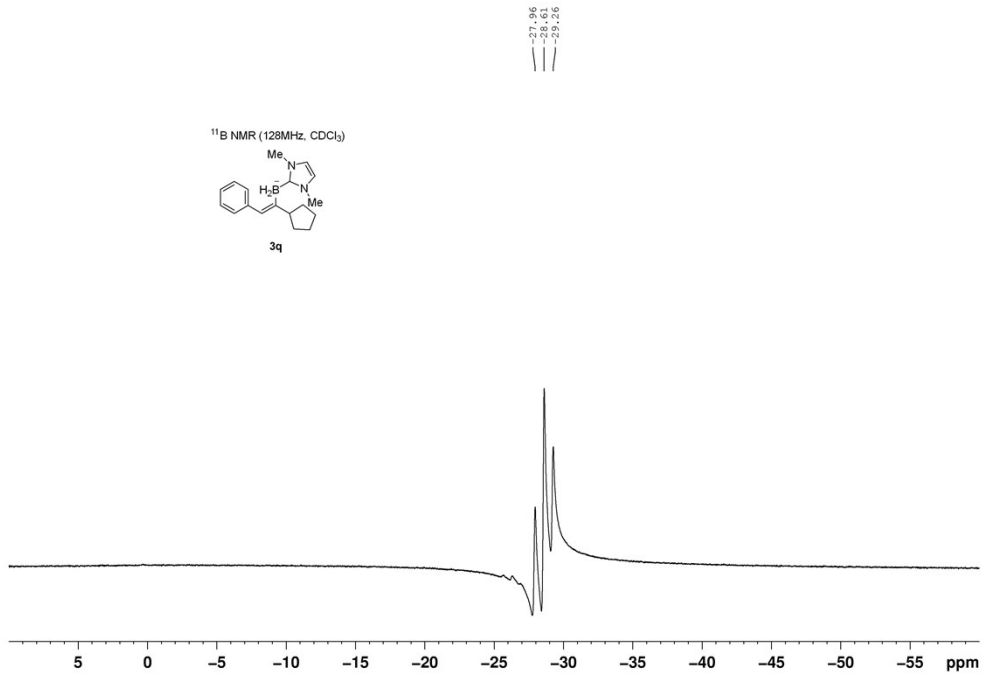

7.165
7.150
7.069
7.054
7.039
6.916
6.902
6.887
6.593
6.481
3.557
2.094
1.927
1.758
1.598
1.534
1.525
1.515
0.726
0.717
0.715
0.707
0.704
0.697
0.561
0.554
0.550
0.543
0.537
0.534
1H NMR (500 MHz, CDCl3)
Me
N
H2B
N
Me
3p
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.00
0.99
1.04
1.97
6.04
2.55
1.12
2.03
2.07

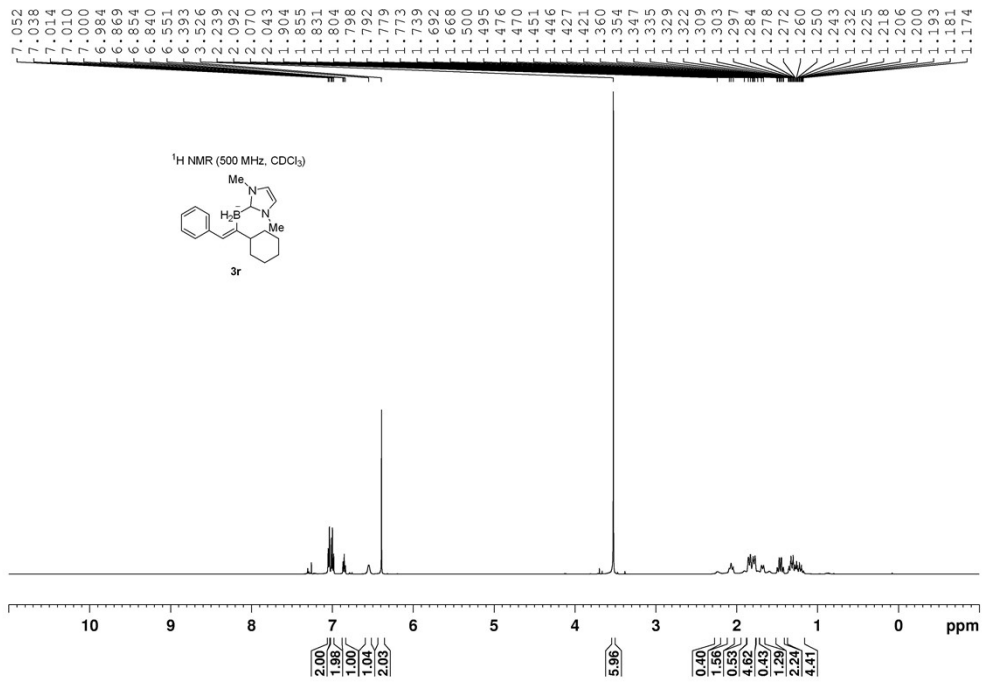

142.52
128.09
126.94
126.80
124.05
119.86
35.74
22.99
5.63
13C NMR (125 MHz, CDCl3)
Me
N
H2B
N
Me
3p
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

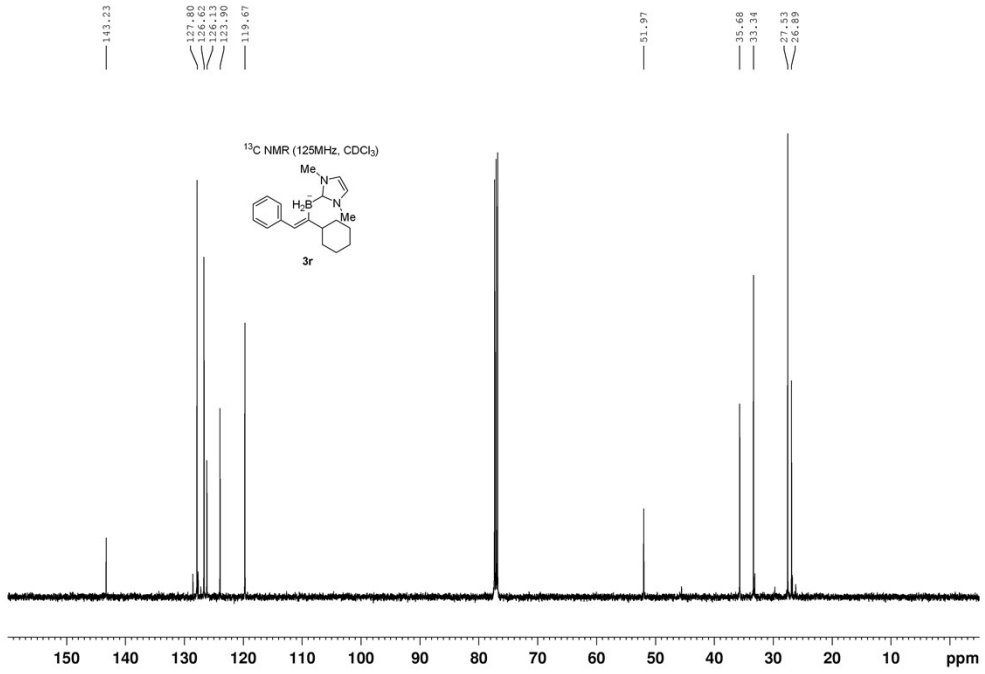

28.76
29.41
30.07
11B NMR (128 MHz, CDCl3)
Me
N
H2B
N
Me
3p
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm

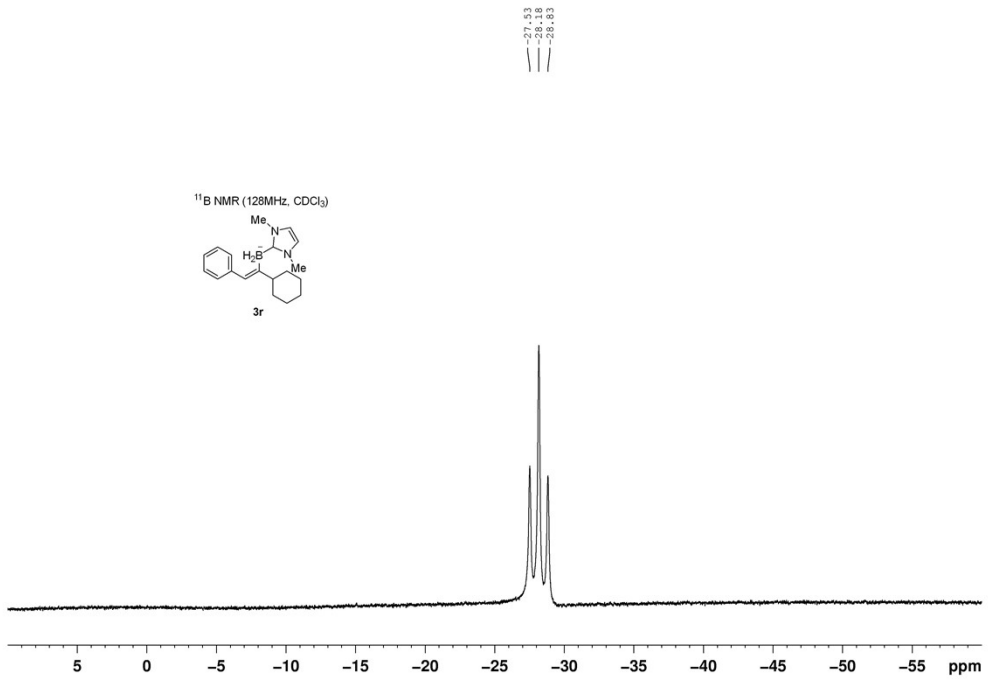

7.078
7.063
7.023
7.008
6.992
6.876
6.862
6.847
6.627
6.406
3.542
2.645
2.628
2.611
2.598
2.243
2.078
1.906
1.800
1.788
1.769
1.738
1.726
1.712
1.686
1.643
1.634
1.628
1.618
1.603
1.584
^{1}H NMR (500 MHz, CDCl$_3$)
3q
10 9 8 7 6 5 4 3 2 1 0 ppm
2.00 2.04 1.04 1.01 1.91 5.90 1.11 0.32 0.45 0.36 2.15 4.25 2.01

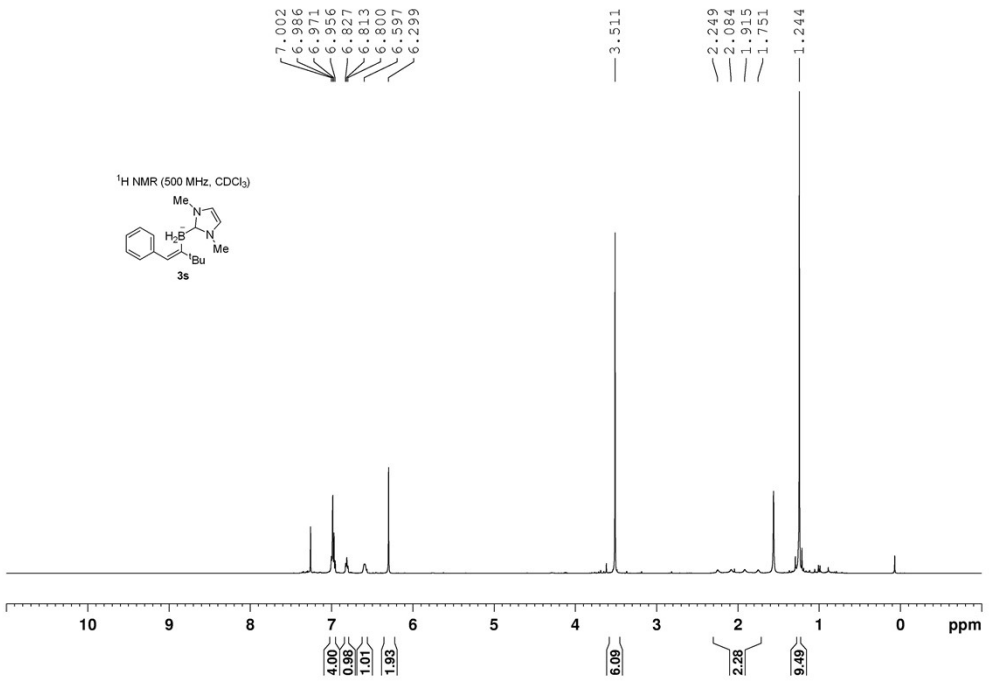

143.04
127.84
126.63
126.55
123.93
119.71
54.18
35.70
32.49
25.58
^{13}C NMR (125MHz, CDCl$_3$)
3q
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

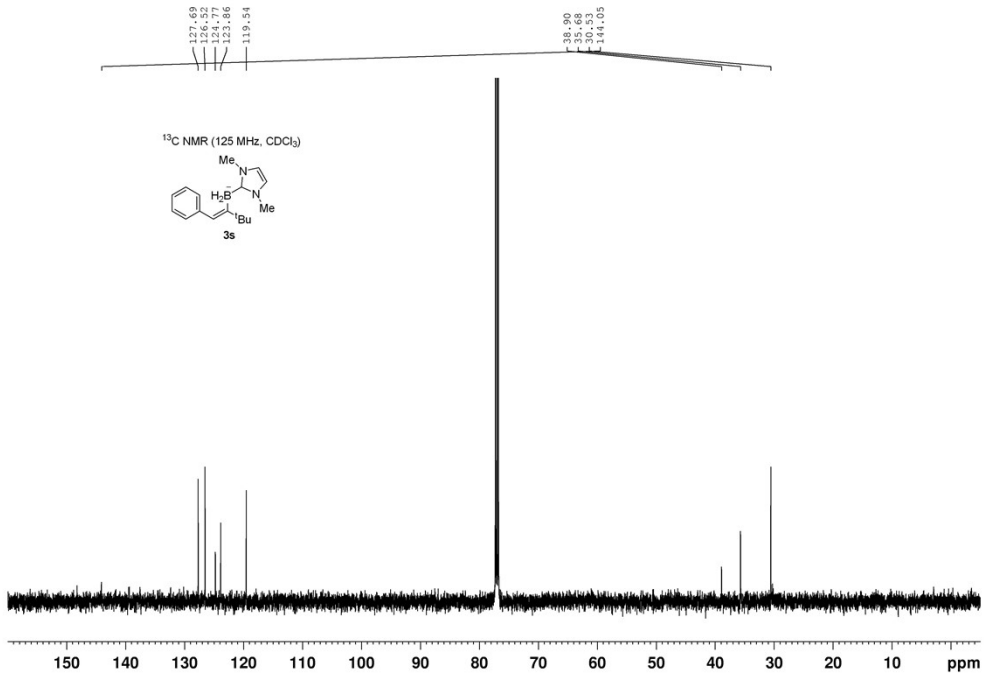

-27.96
-28.61
-29.26
11B NMR (128MHz, CDCl3)
Me
N
H2B
N
Me
3q
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm

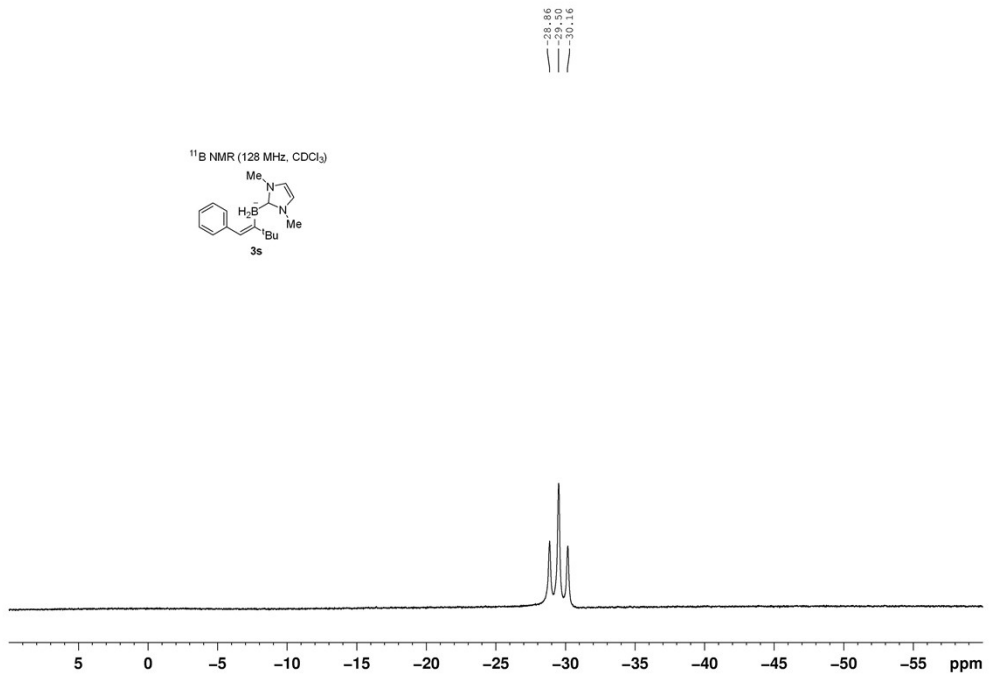

7.052
7.038
7.014
7.010
7.000
6.984
6.869
6.854
6.840
6.551
6.393
3.526
2.239
2.092
2.070
2.043
1.904
1.855
1.831
1.804
1.798
1.792
1.779
1.773
1.739
1.692
1.668
1.500
1.495
1.476
1.470
1.451
1.446
1.427
1.421
1.360
1.354
1.347
1.335
1.329
1.322
1.309
1.303
1.297
1.284
1.278
1.272
1.260
1.250
1.243
1.232
1.225
1.218
1.206
1.200
1.193
1.181
1.174
1H NMR (500 MHz, CDCl3)
Me
N
H2B
N
Me
3r
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.98
1.00
1.04
2.03
5.96
0.40
1.56
0.53
4.62
0.43
1.29
2.24
4.41

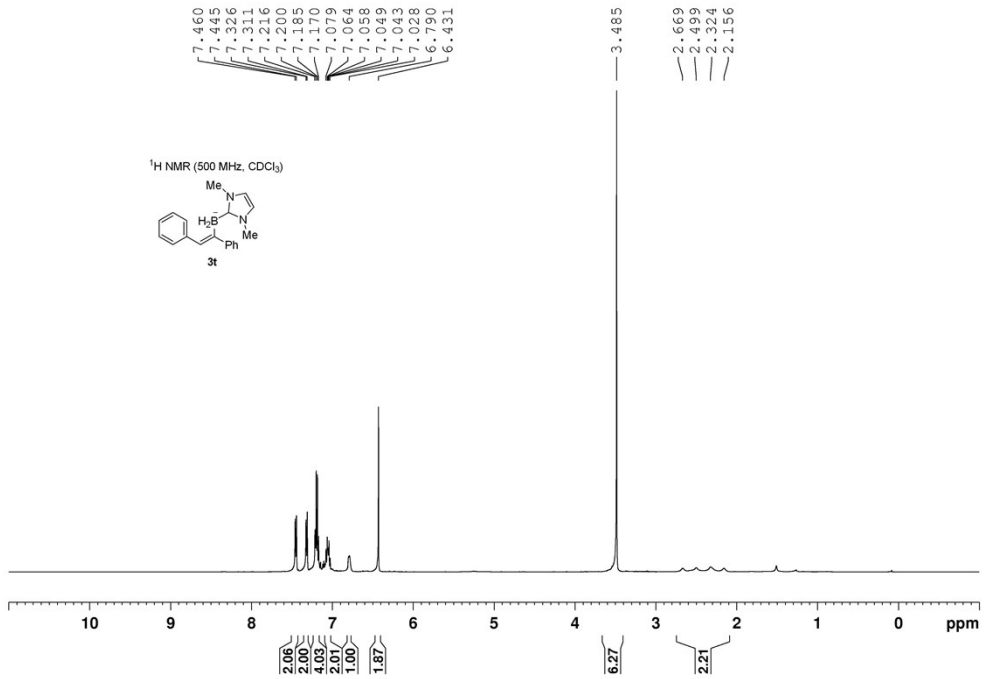

143.23
127.80
126.62
126.13
123.90
119.67
51.97
35.68
33.34
27.53
26.89
13C NMR (125MHz, CDCl3)
3r
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

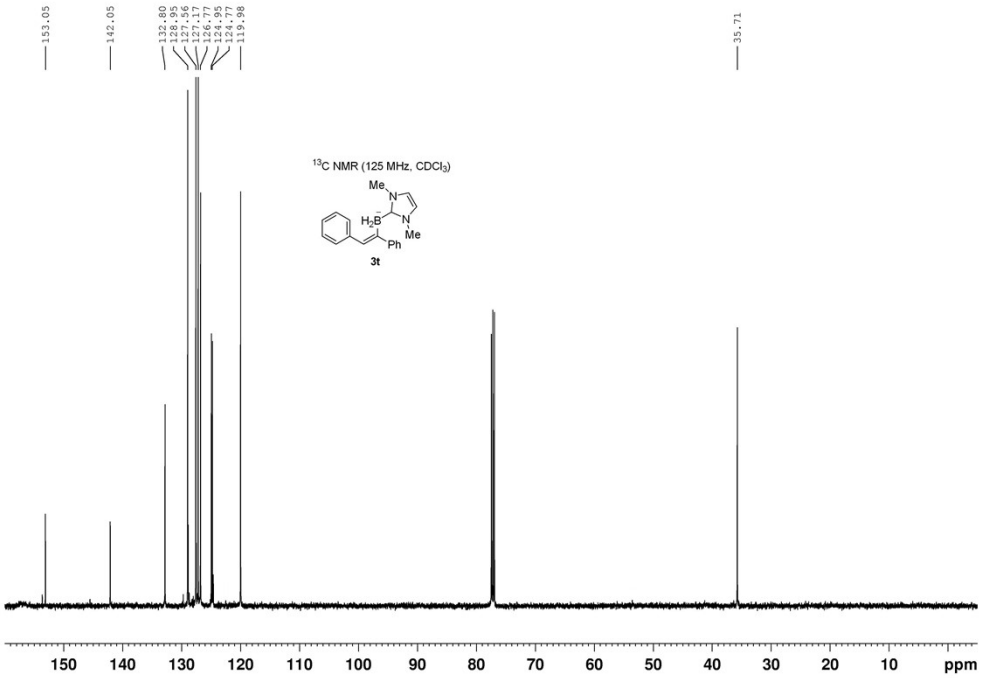

-27.53
-28.18
-28.83
11B NMR (128MHz, CDCl3)
3r
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm

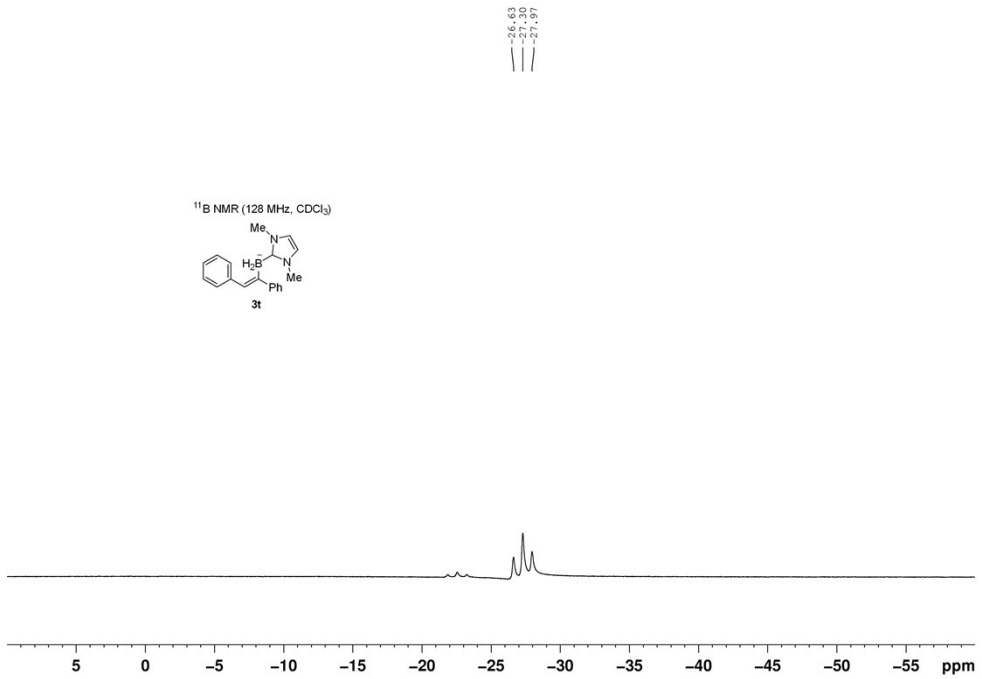

7.002
6.986
6.971
6.956
6.827
6.813
6.800
6.597
6.299
3.511
2.249
2.084
1.915
1.751
1.244
^{1}H NMR (500 MHz, CDCl$_3$)
3s
10 9 8 7 6 5 4 3 2 1 0 ppm
4.00
0.98
1.01
1.93
6.09
2.28
9.49

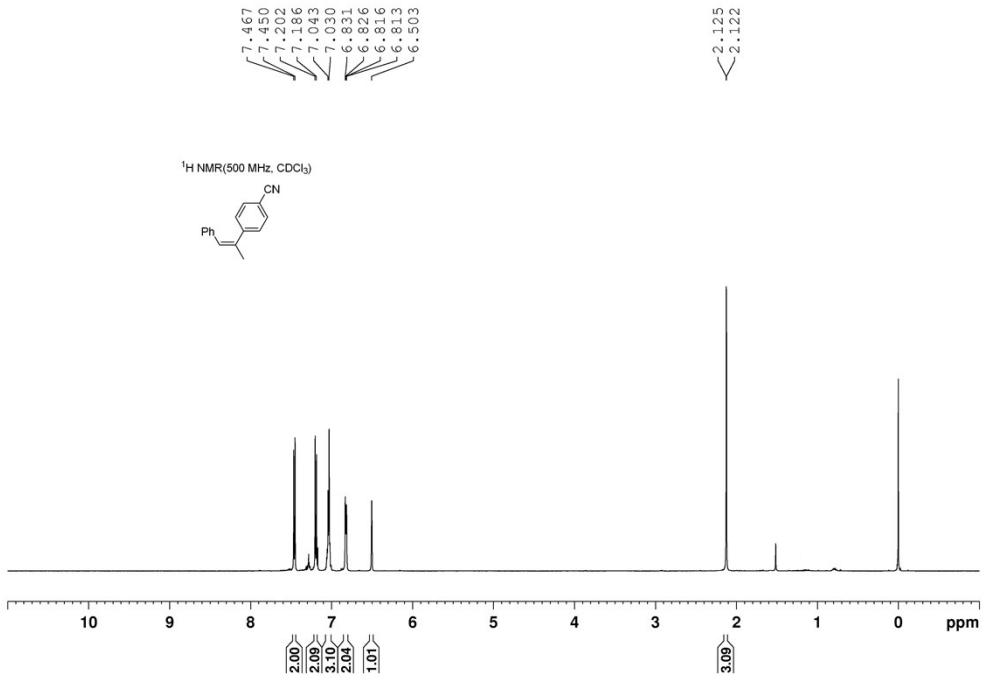

127.69
126.63
124.77
123.86
119.54
38.90
35.68
30.53
144.05
^{13}C NMR (125 MHz, CDCl$_3$)
3s
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

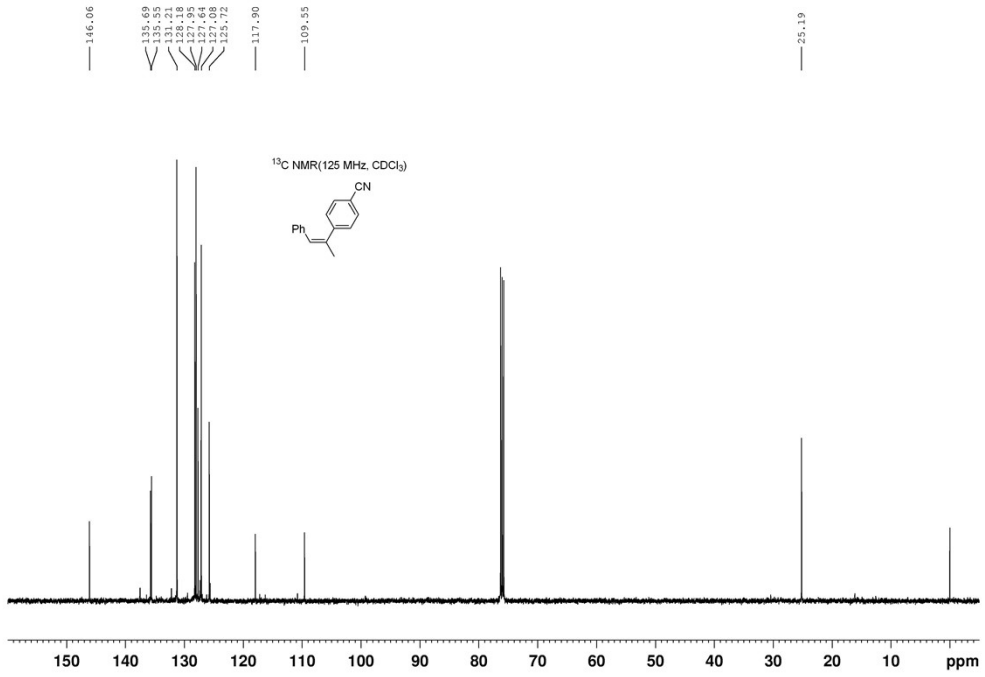

-28.86
-29.50
-30.16
11B NMR (128 MHz, CDCl3)
Me
N
H2B
N
Me
tBu
3s
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
ppm


7.460
7.445
7.326
7.311
7.216
7.200
7.185
7.170
7.079
7.064
7.058
7.049
7.043
7.028
6.790
6.431
3.485
2.669
2.499
2.324
2.156
1H NMR (500 MHz, CDCl3)
Me
N
H2B
N
Me
Ph
3t
10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
2.00
4.03
2.01
1.00
1.87
6.27
2.21


153.05
142.05
132.80
129.95
128.56
127.17
126.77
124.95
114.77
119.98
35.71
^{13}C NMR (125 MHz, CDCl$_3$)
3t
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


-26.63
-27.30
-27.97
^{11}B NMR (128 MHz, CDCl$_3$)
3t
5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55 ppm


7.467
7.450
7.202
7.186
7.043
7.030
6.831
6.826
6.816
6.813
6.503
2.125
2.122
1H NMR(500 MHz, CDCl3)
CN
Ph
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.09
3.10
2.04
1.01
3.09


146.06
135.69
135.55
131.21
128.18
127.95
127.84
127.08
125.72
117.90
109.55
25.19
13C NMR(125 MHz, CDCl3)
CN
Ph
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm