Supplementary Information (SI) for Dalton Transactions.
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Supporting Information

Low-Valent Germanium and Tin Hydrides as Catalysts for Hydroboration, Hydrodeoxygenation (HDO), and Hydrodesulfurization (HDS) of Heterocumulenes

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General experimental methods

General procedures

Unless otherwise stated, manipulations were performed under a dinitrogen atmosphere using standard glovebox and Schlenk techniques. NMR spectra were recorded on a Jeol-400 MHz spectrometer and Bruker NMR spectrometers at 400 MHz and 700MHz (^{1}H), 101 MHz and 176 MHz (^{13}C{^{1}H}), 128.36 MHz (^{11}B), and 149 MHz (^{119}Sn). ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts are referenced to residual protons or carbons in the deuterated solvent. ^{11}B were calibrated using an external reference of $BF_3{\cdot}Et_2O$. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Chemical shifts are reported in ppm. Coupling constants are reported in Hz. The crystal data were collected on a Rigaku Oxford diffractometer at 100 K. Selected data collection parameters, and other crystallographic results are summarized in Table S6. Mass spectrometry analyses were performed on Bruker micrOTOF-Q II and Waters XevoG2 XS Q-TOF mass spectrometers.

Materials:

Solvents were purified by distillation over Na/ benzophenone. Deuterated chloroform ($CDCl_3$) was dried on molecular sieves, and benzene-d6 (C_6D_6) was dried over Na/K alloy and distilled. The ligand L(3H) (L = {(ArNH)(ArN)–C=N– C=(NAr)(NHAr)}; Ar = 2,6- Et_2-C_6H_3)][1] and complex LGeH[2] (**Ge-1**) are prepared according to reported literature procedures. For catalysis reactions, 10 mL vials were oven-dried before use. Chemicals and reagents were purchased from Sigma-Aldrich Co. Ltd. and Merck India Pvt. Ltd., and TCI chemicals were used without purification.

Synthesis of the compounds [LSnCl]; (Sn-1), and [LSnH]; (Sn-2)

Synthesis of [LSnCl] (Sn-1)

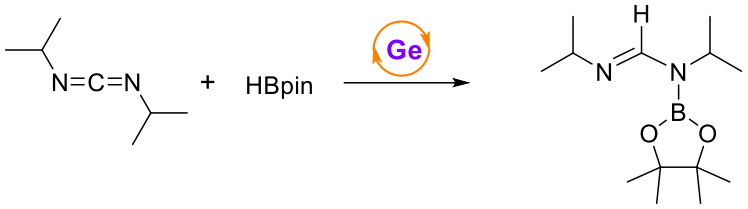
A solution of ^{diethyl}bis-guandinate-Li (0.800 g, 1.2 mmol) in toluene (15ml) was added dropwise to a stirred solution of $SnCl_2$ (0.310 g, 1.6 mmol) in diethyl ether (20 mL) at - 78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The precipitate was filtered, and the filtrate was partially reduced (ca. 10 mL); storage of the extract in a -32 °C freezer for three days afforded colorless crystals of compound **Sn-1**. (0.730 g, 0.9 mmol, 74.6%). ^{1}H NMR (700 MHz, $CDCl_3$, 25 ^{o}C) δ 7.29 (d, *J* = 5.2 Hz, 2H, Ar-*H*), 7.25 (s, 2H, Ar-*H*), 6.90 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 6.72 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 6.62 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 5.28 (s, 2H, N-*H*), 3.43 (dt, *J* = 14.0, 7.0 Hz, 2H, C*H*$_2$CH$_3$), 2.97 (dd, *J* = 15.3, 7.6 Hz, 2H, C*H*$_2$CH$_3$), 2.84 (ddd, *J* = 21.5, 12.4, 6.8 Hz, 2H, C*H*$_2$CH$_3$), 2.60 (dt, *J* = 13.5, 6.7 Hz, 2H, C*H*$_2$CH$_3$), 2.41 – 2.36 (m, 2H, C*H*$_2$CH$_3$), 2.20 (dt, *J* = 15.0, 7.5 Hz, 2H, C*H*$_2$CH$_3$), 2.02 (dt, *J* = 15.0, 7.5 Hz, 2H, C*H*$_2$CH$_3$), 1.39 – 1.34 (m, 12H, CH$_2$C*H*$_3$), 1.06 (t, *J* = 7.6 Hz, 6H, CH$_2$C*H*$_3$), 0.84 (t, *J* = 7.6 Hz, 6H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 25 ^{o}C) δ 155.8, 142.4, 142.1, 140.1, 140.1, 139.6, 134.2, 134.2, 127.2,127.0, 126.8, 126.0, 125.5, 125.0, 24.8, 24.6, 24.4, 24.1, 16.1, 14.4, 14.4, 14.2. ^{119}Sn NMR (149 MHz, CDCl3, 25 ^{o}C) δ -245.14 (s). Mp 195–205 °C. HRMS (ASAP/Q-TOF) *m/z*: $[M]^+$Calcd for $C_{42}H_{54}ClSnN_5$: 784.3086; Found 784.3084.

Synthesis of [LSnH] (Sn-2)

A solution of AlH_3NMe_2Et of 0.5 M in toluene (1.72 mL, 0.8 mmol) was slowly added drop by drop to a stirred solution of **Sn-1** (0.450 g, 0.5 mmol) in toluene (25 mL) at -78 °C. The reaction mixture was allowed to warm to room temperature and then stirred for 24 h at room temperature. The precipitate was filtered, and the filtrate was fully reduced under a vacuum for 3-4 hours. After removing all the solvents, the residue was collected as compound **2**: 0.323 g, 0.206 mmol, 76%. ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C) δ 14.04 (s, 1H, Sn-*H*), 7.09 (s, 5H, Ar*H*),

6.88 (t, *J* = 7.6 Hz, 2H, Ar*H*), 6.68 (d, *J* = 7.5 Hz, 2H, Ar*H*), 6.59 (d, *J* = 7.5 Hz, 3H, Ar*H*), 5.08 (s, 2H, N-*H*), 3.29 – 3.21 (m, 4H, CH_2), 2.85 (dd, *J* = 14.6, 7.1 Hz, 4H, CH_2), 2.61 – 2.53 (m, 2H, CH_2), 2.42 – 2.36 (m, 2H, CH_2), 2.24 (d, *J* = 7.3 Hz, 2H, CH_2), 2.11 – 2.05 (m, 2H, CH_2), 1.38 (t, *J* = 7.5 Hz, 6H, CH_3), 1.30 (t, *J* = 7.5 Hz, 6H, CH_3), 1.04 (t, *J* = 7.6 Hz, 6H, CH_3), 0.87 (t, *J* = 7.6 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ 157.12 (s), 141.92 (s), 141.5, 140.3, 140.1, 134.9, 127.0, 126.4, 126.3, 126.3, 125.3, 125.0, 24.8, 24.3, 23.4, 15.8, 14., 14.1. ^{119}Sn NMR (149 MHz, CDCl3, 25 °C) δ -205.0. Mp 185–195 °C. HRMS (ASAP/Q-TOF) *m/z*: $[M]^+$ Calcd for $C_{42}H_{56}SnN_5$: 750.3554; Found 750.3572.

Table S1. Optimization Table for Germanium-Hydride (Ge-1) Catalyzed Monohydroboration of *N, N'*-diisopropyl carbodiimide[a]



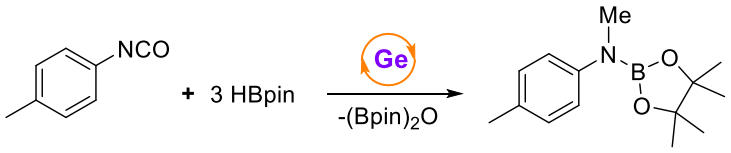
1a **2a**

entries	catalyst	mol%	T (°C)	time	conv. (%)[b]
1	no catalyst	-	70	12 h	4
2	**Ge-1**	10	70	12 h	>99
3	**Ge-1**	8	70	12 h	>99
4	**Ge-1**	6	70	12 h	>99
5	**Ge-1**	**5**	**70**	**12 h**	**>99**
6	**Ge-1**	3	70	12 h	75

[a] Reaction conditions: N, N'-diisopropyl carbodiimide (0.3 mmol, 1.0 equiv.), HBpin (0.3 mmol, 1.0 equiv.), LGeH (**Ge-1**) catalyst (x mol%) were stirred in a 10 mL sealed vial for 12 h at 70 oC under inert N2. [b] Conversion was examined by ^1H NMR (400 MHz, 25 °C)

spectroscopy based upon consumption of N, N'-diisopropylcarbodiimide and identified newly formed characteristic proton (NC*H*N) resonance signal at (δ) 7.81 ppm.

Table S2: Optimization Table for Germanium-Hydride (Ge-1) Catalyzed Complete Reduction of p-tolylisocyanate[a]

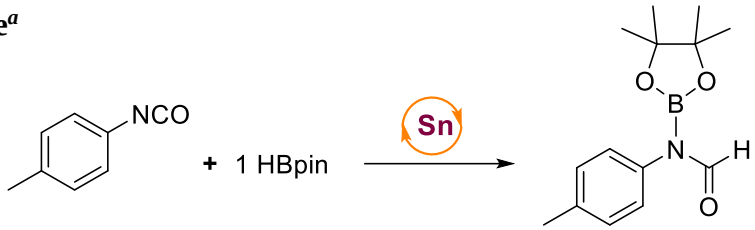


3c 4c

entries	catalyst	mol%	solvent	time	conv.(%)[b]
1	no catalyst	-	neat	12 h	20
2	**Ge-1**	6	neat	24 h	>99
3	**Ge-1**	4	neat	12 h	>99
4	**Ge-1**	**2**	**neat**	**12 h**	**>99**
5	**Ge-1**	1	neat	12 h	70
6	**Ge-1**	2	toluene	12 h	>99
7	**Ge-1**	2	benzene	12 h	>99

[a] Reaction conditions: *p*-tolyl isocyanate (0.3 mmol, 1.0 equiv.), HBpin (0.9 mmol, 3.0 equiv) and germanium-hydride catalyst (**Ge-1**) (x mol%) were stirred in a 10 mL sealed vial for 12 h at 70 °C under an inert N_2 atmosphere. BpinOBpin is found as a by-product. [b] Conversion was examined by ^{1}H NMR (400 MHz, 25 °C) spectroscopy based upon consumption of p-tolyl isocyanate and identified newly formed characteristic proton (NCH_3) resonance signal at (δ) 3.03 ppm.

Table S3: Optimization Table for Tin-Hydride (Sn-2) Catalyzed Mono Hydroboration of p-tolylisocyanate[a]



3c **5c**

entries	catalyst	mol%	solvent	time	conv. (%)[b]
1	no catalyst	-	neat	12 h	--
2	**Sn-2**	10	neat	1 h	>99
3	**Sn-2**	5	neat	1 h	>99
4	**Sn-2**	5	neat	40 min	>99
5	**Sn-2**	3	neat	30 min	>99
6	**Sn-2**	2	neat	30 min	>99
7	**Sn-2**	**1**	**neat**	**30 min**	**>99**
8	**Sn-2**	0.5	neat	1h	70
9	**Sn-2**	1	benzene	30 min	>99

[a] Reaction conditions: p-tolyl isocyanate (0.1 mmol, 1.0 equiv.), HBpin (0.1 mmol, 1.0 equiv) and germanium-hydride catalyst (**Sn-2**) (x mol%) were stirred in a 10 mL sealed vial for 30 min at rt under an inert N_2 atmosphere. [b] Conversion was examined by ^{1}H NMR (400 MHz, 25 ^{o}C) spectroscopy based upon consumption of p-tolyl isocyanate and identified newly formed characteristic proton (NC*H*O) resonance signal at (δ) 8.89 ppm.

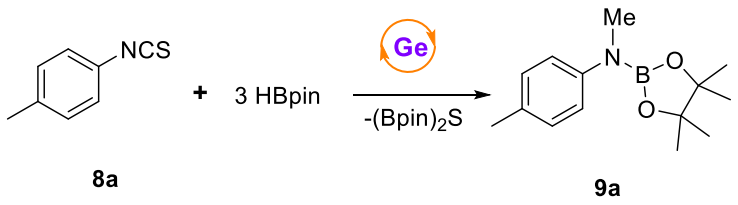
Table S4: Optimization Table for Germanium Hydride Catalyzed Mono Hydroboration of Phenylisothiocyanate[a]

6a **7a**

entries	catalyst	mol%	solvent	time	conv.(%)[b]
1	no catalyst	-	neat	8 h	1
2	**Ge-1**	8	neat	12 h	>99
3	**Ge-1**	6	neat	8 h	>99
4	**Ge-1**	**3**	**neat**	**8 h**	**>99**
5	**Ge-1**	2	neat	8 h	60
6	**Ge-1**	2	neat	12 h	70

[a] Reaction conditions: phenylisothiocyanate (0.3 mmol, 1.0 equiv.), HBpin (0.3 mmol, 1.0 equiv.), cat. (**Ge-1**) (x mol%) were stirred in a 10 mL sealed vial for 8 h at 70 °C under an inert N_2 atmosphere. [b] Conversion was examined by ^{1}H NMR (400 MHz, 25 °C) spectroscopy based upon consumption of phenylisothiocyanate and identified newly formed characteristic proton (NC*H*S) resonance signal at (δ) 10.37 ppm in catalytic solution.

Table S5: Optimization Table for Germanium Hydride Catalyzed Complete Reduction of P-tolyl isothiocyanate [a]



entries	catalyst	mol%	solvent	time	conv.(%)[b]
1	no catalyst	-	neat	12 h	--
2	**Ge-1**	8	neat	24 h	>99
3	**Ge-1**	6	neat	12 h	>99
4	**Ge-1**	**4**	**neat**	**12 h**	**>99**
5	**Ge-1**	4	neat	8 h	70
6	**Ge-1**	2	neat	12 h	60

[a] Reaction conditions: p-tolyl isothiocyanate (0.3 mmol, 1.0 equiv.), HBpin (0.9 mmol, 3.0 equiv.), cat. (**Ge-1**) (x mol%) were stirred in a 10 mL sealed vial for 12 h at 80 ^{o}C under an inert N_2 atmosphere. BpinSBpin is found as a by-product. [b] Conversion was examined by ^{1}H NMR (400 MHz, 25 ^{o}C) spectroscopy based upon consumption of p-tolyl isothiocyanate and identified newly formed characteristic proton (NCH_3) resonance signal at (δ) 2.97 ppm in catalytic solution.

General Catalytic Method for Catalytic Hydroboration of Carbodiimides

In a 10 mL oven-dried vial, 5 mol% of catalyst **Ge-1** 0.3 mmol amount of pre-dried carbodiimide were added, followed by 45 µL (0.3 mmol, 1.0 equiv.) of HBpin in a solvent-free condition inside an N_2 atmosphere glove box. The reaction mixture was stirred at 70 ^{o}C for 12

h. ^{1}H NMR (400 MHz, 25 ^{o}C) spectrum confirms the disappearance of the starting material and emergence of a new -NC*H*N proton peak (δ = 7.81 - 10.12 ppm) of the mono-hydroborated product (**2a-2p**). For incomplete reactions, the conversion was determined by ^{1}H NMR spectroscopy using nitromethane as the internal standard.

General Catalytic Method for Monohydroboration of Isocyanates

In a 10 mL catalytic oven-dried air-tight sealed vial, 0.8 mg (0.001 mmol, 1 mol%) of catalyst, 0.1 mmol (1.0 eq.) isocyanate (**3a – 3e, 3k – 3m, 3q- 3u, 3o, 3p**) was added, followed by 14.5 μL (0.1 mmol, 1.0 eq.) of pinacolborane in a neat condition. This reaction mixture was stirred at room temperature for 1– 30 min. The reactions were regularly monitored by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy until maximum conversion was observed.

General Catalytic Method for Deoxygenative Hydroboration of Isocyanates

In the oven, dried air-tight sealed vial, 2 mol% of catalyst **Ge-1**, 0.3 mmol (1 equiv.) of isocyanates (**3a-3p**) was added, followed by pre-weighed 130 μL (0.9 mmol, 3.0 equiv.) of pinacolborane in neat condition under inert dinitrogen atmosphere. The reaction mixture was heated at 70 ^{o}C for 12 h in an oil bath. ^{1}H NMR (400 MHz, 25 ^{o}C) spectrum confirms the disappearance of starting materials and formation of the new proton (RNC*H*$_3$Bpin) signal at (δ) 2.48–3.11 ppm for newly synthesized borylated N-methylamine (**5a-5p**). BpinOBpin is found as a by-product in all substrates.

General Catalytic Method for Monohydroboration of Isothiocyanates

In a 10 mL catalytic oven-dried air-tight sealed vial, 6 mg (0.009 mmol, 3 mol%) of catalyst, 0.3 mmol (1.0 eq.) isothiocyanate (**7a – 7e**) was added, followed by 45 μL (0.3 mmol, 1.0 eq.) of pinacolborane in a neat condition. This reaction mixture was stirred at 70 ^{o}C for 8 h. The reactions were regularly monitored by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy until maximum conversion was observed.

General Catalytic Method for Desulfogenative Hydroboration of Isothiocyanates

In the oven, a dried air-tight sealed vial, 4 mol% of catalyst **Ge-1**, pre-weighed 0.3 mmol (1 equiv.) of isothiocyanates (**9a – 9e**) was added, followed by 130 μL (0.9 mmol, 3.0 equiv.) of pinacolborane in neat condition under inert dinitrogen atmosphere. The reaction vial was sealed properly and stirred in an oil bath at 80 °C for 12 h. The ^{1}H NMR (400 MHz, 25 °C) spectrum confirms the disappearance of starting materials and formation of the new proton (RNC*H*$_3$Bpin) signal at (δ) 2.54**–**3.10 ppm for newly synthesized borylated N-methylamine (**10a-10e**). S(Bpin)$_2$ is found as a by-product in all substrates.

Stoichiometric Experiments for Carbodiimide Hydroboration

Synthesis of Compound [LGeN(CH(CH$_3$)$_2$)C(H)N(CH(CH$_3$)$_2$)] (Int A): Addition of *N,N′*-Diisopropylcarbodiimide (4 μL, 0.028 mmol) to a J.Young valve NMR tube containing a solution of compound **Ge-1** (20 mg, 0.028 mmol) in C_6D_6 after 8 h at 60 °C formation of compound **Int A** observed by ^{1}H NMR spectroscopy. NMR Conves: (>99%). ^{1}H NMR (400 MHz, C_6D_6) δ 8.51 (s, 1H), 7.16 – 7.15 (d, *J* = 7.5 Hz, 6H), 6.87 (t, *J* = 7.6 Hz, 2H), 6.70 – 6.68 (d, *J* = 7.6 Hz, 2H), 6.56 – 6.54 (d, *J* = 7.4 Hz, 2H), 5.11 (s, 2H), 4.74 – 4.67 (m, 1H), 3.68 – 3.62 (m, 1H), 3.30 – 3.19 (m, 4H), 2.92 – 2.87 (m, 4H), 2.65 - 2.59 (m, 2H), 2.53 – 2.48 (m, 2H), 2.17 – 2.10 (m, 2H), 2.07 – 2.03 (m, 2H), 1.57 – 1.55 (d, *J* = 6.2 Hz, 6H), 1.39 (t, *J* = 7.5 Hz, 6H), 1.34 (t, *J* = 7.5 Hz, 6H), 1.2 5 - 1.24 (d, *J* = 6.7 Hz, 6H), 1.13 (t, *J* = 7.6 Hz, 6H), 0.79 (t, *J* = 7.6 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 155.5, 155.3, 142.1, 141.7, 140.1, 139.7, 139.6, 139.2, 134.1, 126.7, 126.1, 125.9, 124.9, 124.7, 58.1, 45.8, 26.6, 24.8, 24.7, 24.4, 24.1, 23.6, 14.3, 143.9, 13.8, 13.8, 13.0. HRMS (ASAP/Q-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{49}H_{70}GeN_7$ 830.4935, Found: 830.4840.

Synthesis of [LGeH] and 2a {NMR-Scale}: The addition of HBpin (4 μL, 0.028 mmol) to a J. Young valve NMR tube containing a solution of **Int A** (0.028 mmol) in C_6D_6 resulted in the immediate formation of compound **Ge-1** and **2a** after 30 min at rt was observed by ^{1}H NMR

spectroscopy. NMR Yield: (>99%). ^{1}H NMR (400 MHz, C_6D_6) δ 8.37 (s, 1H), 8.26 (s, 1H), 7.12 – 7.07 (m, 6H), 6.89 (t, *J* = 7.6 Hz, 2H), 6.70 – 6.68 (d, *J* = 7.3 Hz, 2H), 6.61 – 6.59 (d, *J* = 7.5 Hz, 2H), 5.11 (s, 2H), 3.34 – 3.28 (m, 2H), 3.25 – 3.17 (m, 4H), 2.91 – 2.85 (m, 2H), 2.80 – 2.74 (m, 2H), 2.57 – 2.52 (m, 2H), 2.42 – 2.37 (m, 2H), 2.24 – 2.16 (m, 2H), 2.09 – 2.01 (m, 2H), 1.46 – 1.44 (d, *J* = 6.9 Hz, 6H), 1.39 (t, *J* = 7.5 Hz, 6H), 1.30 (t, *J* = 7.5 Hz, 6H), 1.20 – 1.19 (d, *J* = 6.3 Hz, 6H), 1.06 (t, *J* = 7.5 Hz, 6H), 1.02 (s, 12H), 0.86 (t, *J* = 7.6 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 157.2, 149.6, 142.5, 141.9, 140.6, 140.2, 140.1, 134.5, 134.5, 127.0, 126.8, 126.5, 126.2, 125.3, 124.9, 82.3, 56.8, 43.2, 25.3, 24.8, 24.2, 24.1, 23.8, 22.9, 21.4, 16.0, 14.7, 14.3, 14.1, 14.0. ^{11}B NMR (128 MHz, C_6D_6) δ 25.31.

Stoichiometric Experiments for Isocyanate Hydroboration

Synthesis of Compound [LGeOC(H)N(2,6-$Me_2C_6H_3$)] (Int A1): Addition of 2,6-dimethylphenyl isocyanate (4 μL, 0.028 mmol) to a J. Young valve NMR tube containing a solution of compound **Ge-1** (20 mg, 0.028 mmol) in C_6D_6 after 1 h at rt formation of compound **Int A1** observed by ^{1}H NMR spectroscopy. NMR Yield: (>99%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.98 (s, 1H), 7.17 – 7.11 (m, 7H), 7.01 – 7.00 (d, *J* = 7.5 Hz, 2H), 6.90 – 6.87 (m, 2H), 6.71 – 6.69 (d, *J* = 7.2 Hz, 2H), 6.60 – 6.58 (d, *J* = 7.4 Hz, 2H), 5.17 (s, 2H), 3.62 – 3.52 (m, 2H), 3.11 – 3.02 (m, 4H), 2.85 – 2.77 (m, 2H), 2.56 – 2.51 (m, 2H), 2.39 – 2.32 (m, 2H), 2.16 (s, 6H), 2.13 – 2.08 (m, 2H), 2.02 – 1.96 (m, 2H), 1.35 – 1.30 (m, 12H), 1.05 (t, *J* = 7.6 Hz, 6H), 0.83 (t, *J* = 7.6 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 159.1, 155.6, 148.1, 142.3, 141.9, 140.4, 140.2, 138.6, 134.1, 129.3, 127.8, 126.7, 126.6, 126.2, 125.4, 124.9, 121.9, 24.7, 24.6, 24.3, 23.3, 18.9, 14.4, 14.3, 14.1, 13.9. HRMS (ASAP/Q-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{51}H_{65}GeN_6O$ 851.4462, Found: 851.4448.

Synthesis of [LGeH] and 4d {NMR-Scale}: The addition of HBpin (4 μL, 0.028 mmol) to a J. Young valve NMR tube containing a solution of **Int A1** (0.028 mmol) in C_6D_6 resulted in the immediate formation of compound **Ge-1** and **4d** at rt after 30 min was observed by ^{1}H NMR

spectroscopy. NMR Yield: (>99%). ^{1}H NMR (400 MHz, C_6D_6) δ 9.16 (s, 1H), 8.37 (s, 1H), 7.15 – 7.12 (m, 4H), 7.08 – 7.06 (m, 3H), 6.94 (s, 2H), 6.89 (t, *J* = 7.4 Hz, 2H), 6.70 – 6.68 (d, *J* = 7.3 Hz, 2H), 6.61 – 6.59 (d, *J* = 7.4 Hz, 2H), 5.12 (s, 2H), 3.35 – 3.27 (m, 2H), 3.22 – 3.17 (m, 2H), 2.91 – 2.85 (m, 2H), 2.80 – 2.74 (m, 2H), 2.60 – 2.52 (m, 2H), 2.42 – 2.37 (m, 2H), 2.24 – 2.18 (m, 2H), 2.13 (s, 6H), 2.07 – 2.01 (m, 2H), 1.39 (t, *J* = 7.6 Hz, 6H), 1.31 (t, *J* = 7.7 Hz, 6H), 1.05 (t, *J* = 7.5 Hz, 6H), 0.91 (s, 12H), 0.86 (t, *J* = 7.7 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 163.2, 157.2, 142.5, 141.9, 140.6, 140.3, 140.1, 135.1, 134.5, 128.1, 127.2, 127.0, 126.8, 126.5, 126.2, 125.3, 124.9, 83.6, 24.8, 24.2, 23.9, 23.8, 18.0, 16.0, 14.7, 14.3, 14.1, 14.1. ^{11}B NMR (128 MHz, C_6D_6) δ 25.48.

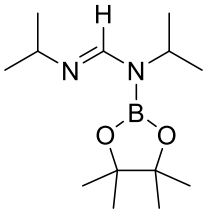
Synthesis of compound [LSn-OCHN(2,6-^{i}Pr$_2$-C$_6$H$_3$)] (Int A1'): Addition of 2,6-diisopropyl phenyl isocyanate (5.4 mL, 0.02 mmol) to a J.Young valve NMR tube containing a solution of compound **Sn-2** (20 mg, 0.02 mmol) in C_6D_6 after 1 h at rt formation of compound **Int A1** observed by ^{1}H NMR spectroscopy. NMR Yield: (>99%).^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ 8.40 (s, 1H, N(C*H*)O), 7.10 (d, J = 4.6 Hz, 5H), 6.88 (dd, J = 9.7, 5.1 Hz, 3H), 6.68 (d, J = 7.9 Hz, 3H), 6.60 – 6.56 (m, 4H), 5.12 (s, 2H), 3.71 (dd, J = 14.8, 7.4 Hz, 2H), 3.58 – 3.47 (m, 2H), 3.29 (dt, J = 13.7, 6.8 Hz, 2H), 3.17 – 3.08 (m, 2H), 2.95 – 2.91 (m, 2H), 2.83 – 2.78 (m, 2H), 2.69 – 2.63 (m, 2H), 2.53 – 2.46 (m, 2H), 2.17 (dd, J = 7.2, 3.1 Hz, 2H), 1.38 (t, J = 7.6 Hz, 12H), 1.29 – 1.26 (m, 6H), 1.17 (d, J = 6.9 Hz, 6H), 1.04 (d, J = 6.9 Hz, 6H), 0.81 (t, J = 7.6 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 ^{o}C): δ 160.8, 155.9, 142.2, 141.3, 140.4, 139.7, 126.6, 12.4, 125.0, 122.7, 44.8, 29.8, 27.9, 24.7, 23.8, 16.3, 14.0. ^{119}Sn NMR (149 MHz, C_6D_6, 25 ^{o}C) δ -216.5, -237.0.

Synthesis of [LSnH] and 5q {NMR-Scale}: The addition of HBpin (3 μL, 0.02 mmol) to a J. Young valve NMR tube containing a solution of **Int A1'** (0.02 mmol) in C_6D_6 resulted in the immediate formation of compound **Sn-2** and **5q** at rt after 30 min was observed by ^{1}H NMR

spectroscopy. NMR Yield: (>99%).^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ 14.03 (s, 1H, Sn-*H*), 9.25 (s, 1H, C-*H*), 7.11 (s, 5H, Ar-*H*), 6.89 (s, 3H, Ar-*H*), 6.70 (d, J = 9.3 Hz, 3H, Ar-*H*), 6.58 (s, 4H, Ar-*H*), 5.11 (s, 2H, N-*H*), 3.71 (d, J = 7.5 Hz, 2H, $(CH_3)_2CH$)), 3.25 (dd, J = 16.9, 7.5 Hz, 4H, CH_2), 3.03 (s, 2H, CH_2), 2.89 (dd, J = 7.6, 3.9 Hz, 4H, CH_2), 2.67 – 2.62 (m, 2H, CH_2), 2.54 – 2.50 (m, 2H, CH_2), 2.39 (dd, J = 14.9, 7.4 Hz, 2H, CH_2), 1.38 (t, J = 7.4 Hz, 12H, CH_3), 1.21 (d, 12H, $(CH_3)_2CH$)), 1.05 (t, 6H, CH_3), 0.93 (s, 12H, N*Bpin*), 0.80 (t, J = 7.6 Hz, 6H, CH_3).^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 ^{o}C): δ 164.3, 142.2, 141.9, 141.5, 140.3, 140.2, 134.9, 134.5, 83.8, 44.8, 24.7, 24.2, 23.8, 23.4, 14.3, 14.1.

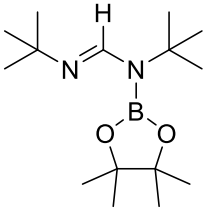
Analytical data of N-borylformamidine

(*E*)-*N*,*N'*-diisopropyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) formimidamide



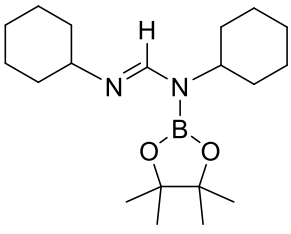
(2a):[3] White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.81 (s, 1H), 4.46 – 4.43 (m, 1H), 3.33 – 3.30 (m, 1H), 1.24 (s, 12H), 1.21 – 1.20 (d, J = 6.7 Hz, 6H), 1.11 – 1.10 (d, J = 6.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 150.4, 82.6, 56.8, 43.0, 25.1, 24.4, 21.4.

(*E*)-*N*,*N'*-di-tert-butyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formimidamide



(2b):[3] White solid; yield: >99%.^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.85 (s, 1H), 1.32 (s, 18H), 1.25 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 148.5, 81.9, 54.4, 30.1, 24.4. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 25.24.

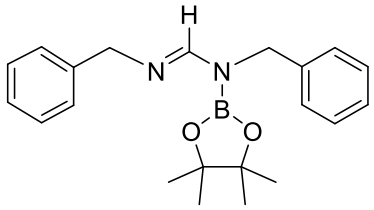
(*E*)-*N*,*N'*-dicyclohexyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formimidamide



(2c):[4] White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.84 (s, 1H), 4.03 – 4.00 (m, 1H), 2.95 – 2.93 (m, 1H), 1.71 – 1.62 (m, 7H), 1.59 – 1.56 (m, 7H), 1.34 – 1.30 (m, 6H), 1.23 (s, 12H).

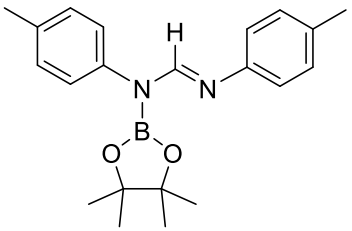
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 150.6, 82.4, 64.9, 55.6, 50.6, 35.3, 34.8, 31.2, 26.1, 25.6, 25.3, 24.6, 24.4.

(*E*)-*N*,*N'*-dibenzyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxborolan-2-yl)formimidamide (2d):[5]



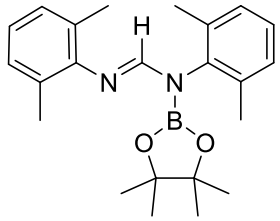
White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 10.12 (s, 1H), 7.44 – 7.25 (m, 10H), 5.07 (s, 2H), 4.73 (s, 2H), 1.32 (s, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) δ 199.0, 143.2, 141.3, 137.4, 134.3, 128.9, 128.3, 128.2, 127.1, 126.8, 124.9, 85.3, 48.7, 47.5, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 25.28.

(E)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N,N'-di-p-tolylformimidamide (2e):[6]



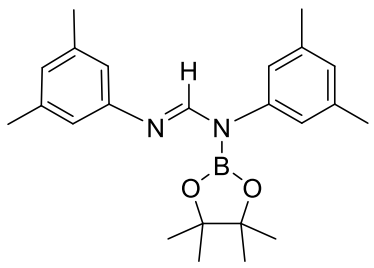
White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (s, 1H), 7.10 – 6.91 (m, 8H), 2.23 (s, 6H), 1.20 (s, 12H). $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) δ = 152.4, 143.7, 141.2, 129.3, 129.1, 128.7, 128.5, 121.5, 119.2, 84.0, 24.5, 21.0, 20.8.

(*E*)-*N*,*N'*-bis(2,6-dimethylphenyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formimidamide (2f):[5] White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ =

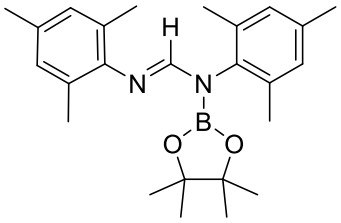


8.05 (s, 1H), 7.20 (s, 3H), 7.02 – 7.00 (d, J = 7.4 Hz, 2H), 6.89 – 6.87 (d, J = 7.4 Hz, 1H), 2.38 (s, 6H), 2.18 (s, 6H), 1.32 (s, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) δ = 151.9, 149.7, 136.9, 135.4, 128.7, 128.3, 127.7, 127.4, 122.6, 83.9, 24.5, 18.9, 18.1.

(*E*)-*N*,*N'*-bis(3,5-dimethylphenyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formimidamide (2g):[6] White solid; yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 8.22 (s, 1H), 6.83 – 6.77 (m, 6H), 2.34 (s, 12H), 1.33 (s, 12H).

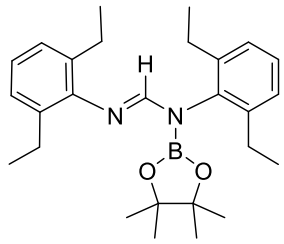


***(E)*-*N*,*N'*-dimesityl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formimidamide (2h):[5]**



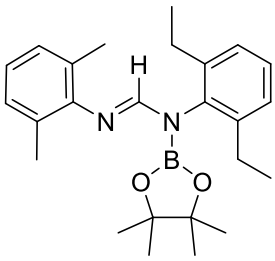
White solid; yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 8.04 (s, 1H), 7.03 (s, 2H), 6.84 (s, 2H), 2.35 (s, 6H), 2.28 (s, 6H), 2.15 (s, 6H), 1.33 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 152.5, 147.5, 136.7, 135.0, 131.6, 129.4, 129.3, 129.1, 128.6, 128.4, 83.8, 24.6, 24.5, 21.3, 20.8, 18.9, 18.1.

(*E*)-*N*,*N'*-bis(2,6-diethylphenyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formimidamide (2i):[5]



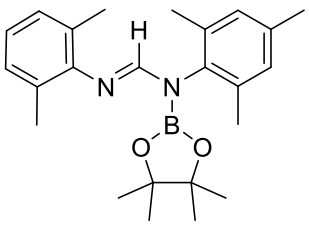
White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 8.10 (s, 1H), 7.33 – 7.25 (m, 3H), 7.04 – 6.94 (m, 3H), 2.80 – 2.71 (m, 4H), 2.55 (q, *J* = 7.5 Hz, 4H), 1.36 (t, *J* = 7.6 Hz, 6H), 1.32 (s, 12H), 1.17 (t, *J* = 7.5 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 152.1, 148.8, 140.9, 135.3, 134.8, 127.7, 126.0, 125.9, 122.8, 83.9, 25.0, 24.5, 23.9, 14.9, 14.4. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 24.98.

(*E*)-*N*-(2,6-diethylphenyl)-*N'*-(2,6-dimethylphenyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) formimidamide (2j):



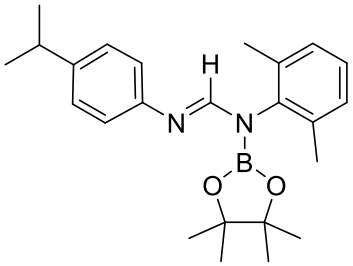
White solid; yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 8.04 (s, 1H), 7.18 (s, 1H), 7.09 (s, 2H), 7.06 (s, 1H), 7.01 (s, 2H), 2.85 (q, *J* = 7.5 Hz, 4H), 2.44 (s, 6H), 1.30 (s, 12H), 1.16 (t, *J* = 7.2 Hz, 6H). HRMS (ASAP/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{36}BN_2O_2$ 407.2906, found: 407.2902.

(E)-N'-(2,6-dimethylphenyl)-N-mesityl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formimidamide (2k):[5]



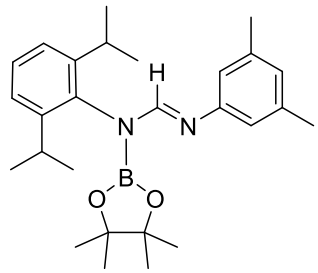
White solid; yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 8.01 (s, 1H), 7.18 (s, 1H), 7.06 (s, 1H), 7.00 (s, 2H), 6.89 (s, 1H), 2.43 (s, 3H), 2.40 (s, 3H), 2.32 (s, 6H), 2.15 (s, 3H), 1.30 (s, 12H).

(E)-N-(2,6-dimethylphenyl)-N'-(4-isopropylphenyl)-N-(4,4,5,5-tetramethyl-1,3,2-



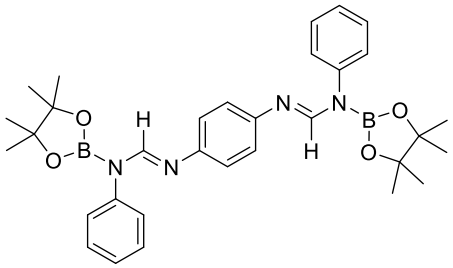
dioxaborolan-2-yl)formimidamide (2l): White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 8.29 (s, 1H), 7.21 (s, 3H), 7.20 – 7.18 (d, *J* = 8.3 Hz, 2H) 6.98 – 6.96 (d, *J* = 8.1 Hz, 2H), 2.97 – 2.93 (m, 1H), 2.32 (s, 6H), 1.36 (s, 12H), 1.32 – 1.30 (d, *J* = 6.2 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 151.0, 149.7, 144.2, 137.3, 135.4, 128.2, 128.2, 127.3, 126.6, 126.6, 121.4, 83.9, 33.6, 24.5, 24.3, 18.4. HRMS (ASAP/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{34}BN_2O_2$ 393.2750, found: 393.2669.

(*E*)-*N'*-(2,6-diiopropylphenyl)-*N*-(3,5-dimethylphenyl)-*N*-(4,4,5,5-tetramethyl-



1,3,2dioxaborolan-2-yl)formimidamide (2m):[5] White solid; yield: >99%.^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.26 (s, 1H), 7.28 – 7.24 (m, 2H), 7.21 – 7.15 (m, 1H), 6.91 – 6.73 (m, 2H), 6.57 (s, 1H), 3.14 – 3.04 (m, 2H), 2.32 (s, 6H), 1.32 (s, 12H), 1.30 – 1.29 (d, *J* = 3.8 Hz, 6H), 1.28 – 1.26 (d, *J* = 3.8 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ 151.8, 145.5, 138.1, 133.9, 128.0, 125.1, 123.4, 122.4, 119.0, 84.0, 28.6, 24.5, 24.1, 23.9, 21.3. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 24.76.

(1E,1'E)-N',N'''-(1,4-phenylene)bis(N-phenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-



2-yl)formimidamide) (2n):[7] White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 8.15 (s, 2H), 7.31 – 7.22 (m, 4H), 7.10 – 6.99 (m, 10H), 1.20 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 156.9, 141.8, 139.7, 135.3, 129.1, 126.4, 126.1, 83.1, 24.5.

(1E,1'E)-N',N'''-(1,4-phenylene)bis(N-(2,6-dimethylphenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formimidamide) (2o):[7] White solid; yield: >99%. ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ = 8.33 (s, 2H), 7.26 (s, 6H), 6.98 (s, 4H), 2.39 (s, 12H), 1.40 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.6, 147.9, 137.2, 135.3, 128.1, 127.2, 124.7, 121.6, 83.9, 24.5, 18.3.

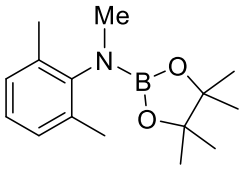
Analytical data for N-borylated methyl amine of Corresponding Isocyanates:

***N*,4,4,5,5-pentamethyl-*N*-(o-tolyl)-1,3,2-dioxaborolan-2-amine (4a):[1b]** White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.32 – 7.06 (m, 4H), 2.97 (s, 3H), 2.29 (s, 3H), 1.30 (s, 24H), 1.26 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 146.2, 134.9, 130.7, 127.6, 126.5, 125.2, 83.0, 82.4, 37.5, 24.5, 24.5, 17.8. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 23.70, 21.11.

***N*,4,4,5,5-pentamethyl-*N*-(m-tolyl)-1,3,2-dioxaborolan-2-amine (4b):[1b]** White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.20 – 7.17 (m, 2H), 7.16 – 7.11 (d, *J* = 4.0 Hz, 2H), 3.07 (s, 3H), 2.36 (s, 3H), 1.32 (s, 12H), 1.30 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 147.5, 138.1, 128.3, 121.5, 119.5, 116.5, 83.1, 82.6, 34.4, 24.6, 24.5, 21.7. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 24.41, 21.06.

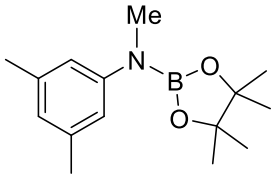
***N*,4,4,5,5-pentamethyl-*N*-(p-tolyl)-1,3,2-dioxaborolan-2-amine (4c):[1b]** White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.26 – 7.17 (d, *J* = 8.0 Hz, 2H), 7.06 – 7.04 (d, *J* = 8.0 Hz, 2H), 3.03 (s, 3H), 2.27 (s, 3H), 1.28 (s, 12H), 1.27 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 145.0, 129.8, 129.0, 119.1, 84.4, 83.0, 34.5, 24.6, 24.5, 20.5. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 24.30, 21.11.

***N*-(2,6-dimethylphenyl)-*N*,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (4d):[1b]**

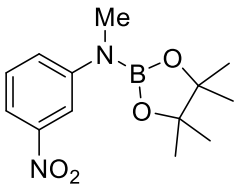


White solid; yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.09–7.03 (m, 3H), 2.85 (s, 3H), 2.28 (s, 6H), 1.31 (s, 24H), 1.27 (s, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) δ = 144.2, 136.0, 128.2, 125.6, 83.0, 82.2, 35.4, 24.5, 24.5, 22.7, 17.7. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 23.65, 21.09.

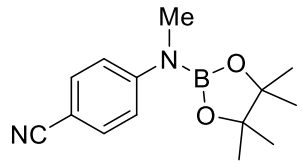
***N*-(3,5-dimethylphenyl)-*N*,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (4e):[1b]** White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 6.97 (s, 2H), 6.63 (s, 1H), 3.08 (s, 3H), 2.33 (s, 6H), 1.33 (s, 12H), 1.32 (s, 24H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) δ = 147.5, 137.8, 122.7, 117.2, 83.1, 82.5, 34.6, 24.6, 24.5, 21.6. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 24.35, 21.07.



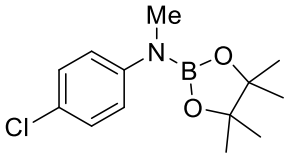
***N*,4,4,5,5-pentamethyl-*N*-(3-nitrophenyl)-1,3,2-dioxaborolan-2-amine (4f):[1b]** White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 8.13 (t, *J* = 8.0 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 3.11 (s, 3H), 1.33 (s, 12H), 1.28 (s, 24H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) δ = 148.8, 141.0, 129.0, 124.5, 115.0, 112.5, 83.4, 83.1, 34.2, 24.6, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 24.54, 21.06.



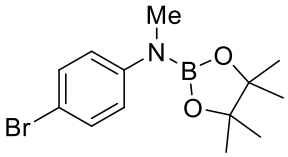
3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (4g):[5] White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.61 – 7.56 (m, 1H), 7.54 – 7.34 (m, 1H), 7.32 – 7.30 (m, 1H), 7.18 – 7.16 (m, 1H), 3.05 (s, 3H), 1.31 (s, 12H), 1.27 (s, 24H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) δ = 148.1, 129.3, 123.7, 122.5, 121.5, 119.6, 112.2, 83.3, 83.1, 34.0, 24.6, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 24.44, 21.05.

4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (4h):[1b] White solid; yield: >99%. 

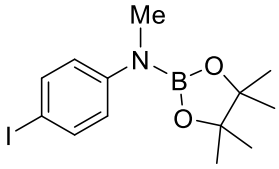
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.53 – 7.51 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.39 (d, *J* = 8.0 Hz, 2H), 3.06 (s, 3H), 1.32 (s, 12H), 1.27 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 151.5, 132.7, 118.1, 102.6, 83.4, 83.1, 33.9, 24.6, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 24.59, 21.06.

***N*-(4-chlorophenyl)-*N*,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (4i):[1b]** White solid; yield: >99%. 

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.25 – 7.18 (m, 4H), 3.03 (s, 3H), 1.30 (s, 12H), 1.28 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 146.1, 128.3, 125.4, 119.9, 83.2, 83.0, 34.3, 24.8, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 25.06, 21.88.

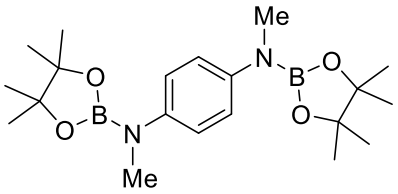
***N*-(4-bromophenyl)-*N*,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (4j):[1b]** White solid; yield: >99%. 

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.36 – 7.34 (d, *J* = 9.0 Hz, 2H), 7.21 – 7.19 (d, *J* = 8.0 Hz, 2H), 3.04 (s, 3H), 1.31 (s, 12H), 1.29 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 146.6, 131.3, 120.4, 113.0, 83.1, 82.9, 34.3, 24.6, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 24.41, 21.08.

***N*-(4-iodophenyl)-*N*,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (4k):[1b]** White solid; yield: >99%. 

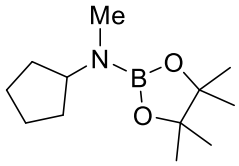
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.53 – 7.51 (d, *J* = 8.0 Hz, 2H), 7.11 – 7.08 (d, *J* = 8.0 Hz, 2H), 3.02 (s, 3H), 1.30 (s, 12H), 1.28 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 147.3, 137.2, 120.9, 114.6, 83.1, 82.9, 34.1, 24.7, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 24.58, 21.20.

***N*,4,4,5,5-pentamethyl-*N*-(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)- 1,3,2-dioxaborolan-2-amine (4l):[1b]**



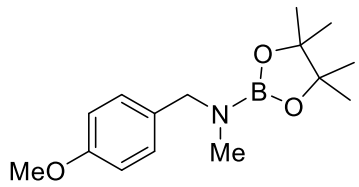
White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.18 (s, 4H), 3.03 (s, 6H), 1.28 (s, 48H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 141.2, 119.7, 83.0, 82.4, 34.7, 24.6, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 24.28, 21.05.

***N*-cyclopentyl-*N*-4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (4m):[1b]** White solid;



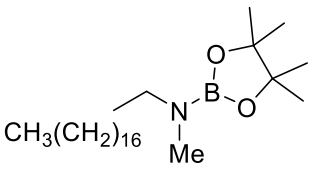
yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 3.76 – 3.74 (m, 1H), 2.48 (s, 3H), 1.67 – 1.59 (m, 2H), 1.57 – 1.50 (m, 6H), 1.26 (s, 24H), 1.20 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 83.0, 81.8, 57.2, 28.6, 28.4, 27.6, 24.5, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 23.98, 21.09.

***N*-(4-methoxybenzyl)-*N*,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (4n):[1b]** White



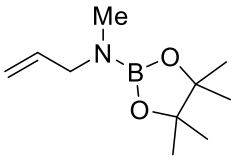
solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.18 – 7.16 (d, *J* = 4.0 Hz, 2H), 6.87 – 6.86 (d, *J* = 8.0 Hz, 2H), 4.00 (s, 2H), 3.81 (s, 3H), 2.48 (s, 3H), 1.29 (s, 12H), 1.28 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 158.4, 132.3, 128.8, 113.6, 83.0, 82.2, 55.2, 52.2, 33.0, 24.6, 24.5.

***N*,4,4,5,5-pentamethyl-*N*-octadecyl-1,3,2-dioxaborolan-2-amine (4o):[1b]** White solid; yield:



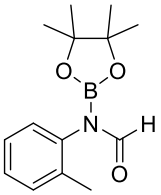
60%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 2.89 – 2.86 (m, 2H), 2.56 (s, 3H), 1.41 – 1.39 (m, 2H), 1.38 – 1.28 (d, *J* = 4.0 Hz, 30H), 1.27 (s, 24H), 1.21 (s, 12H), 0.89 (t, *J* = 8.0 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 83.0, 81.7, 48.4, 33.1, 30.0, 29.7, 29.4, 29.3, 28.1, 26.4, 24.8, 24.5, 22.6, 14.1. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 23.97, 21.08.

***N*-allyl-*N*,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (4p):[1b]** colourless oil; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 5.76 – 5.67 (m, 1H), 5.11 – 5.05 (m, 2H), 3.47 – 3.46 (dd, *J* = 4.3, 1.3 Hz, 2H), 2.54 (s, 3H), 1.27 (s, 24H), 1.21 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 136.6, 114.9, 83.0, 82.0, 51.4, 33.2, 24.5, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ = 23.98, 21.04.

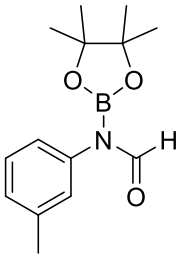


Analytical data for N-borylated formamide of Corresponding Isocyanates:

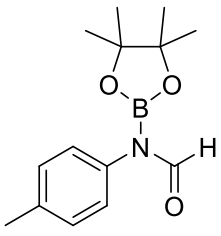
N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(o-tolyl)formamide (5a):[1b] White solid; yield >99%. NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.91 (s, 1H, C*H*O), 7.27 (d, *J* = 5.8 Hz, 3H, Ar*H*), 7.05 – 7.02 (m, 1H, Ar*H*), 2.19 (s, 3H, CH_3), 1.32 (s, 13H, NB*pin*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 165.2, 130.8, 128.2, 127.9, 126.7, 84.5, 24.5, 24.4, 17.9.



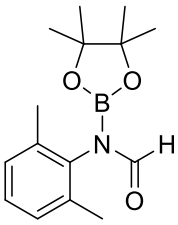
N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(*m*-tolyl)formamide (5b):[1b] White solid; yield >99%. ^{1}H NMR (400 MHz, CDCl3) δ 8.89 (s, 1H, C*H*O), 7.30 (t, *J* = 6.3 Hz, 1H, Ar*H*), 7.13 (d, *J* = 7.6 Hz, 1H, Ar*H*), 6.99 – 6.94 (m, 2H, Ar*H*), 2.39 (s, 3H, Ar*Me*), 1.33 (s, 12H, N*Bpin*). ^{13}C{^{1}H} NMR (101 MHz, CDCl3, 25 oC): δ = 165.5, 138.6, 132.2, 128.6, 128.1, 128.0, 124.4, 84.5, 24.5, 21.4.



***N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(*p*-tolyl)formamide (5c):[1b]** White solid; yield >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.89 (s, 1H, C*H*O), 7.21 (d, J = 8.1 Hz, 2H, Ar*H*), 7.05 (d, J = 8.2 Hz, 2H, Ar*H*), 2.37 (s, 3H, CH_3), 1.33 (s, 12H, NB*pin*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ (ppm) 165.6, 136.8, 134.9, 129.5, 127.1, 84.5, 24.5, 21.1.

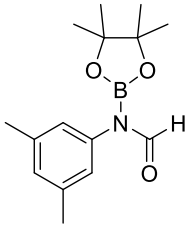


***N*-(2,6-dimethylphenyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide**



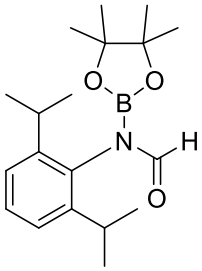
(5d):[1b] White solid; yield >99%. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ^{o}C) δ 8.92 (s, 1H, C*H*O), 7.17 (dd, *J* = 8.4, 6.4 Hz, 1H, Ar*H*), 7.13 (d, *J* = 7.4 Hz, 2H, Ar*H*), 2.17 (s, 6H, CH_3), 1.32 (s, 12H, NB*pin*). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 25 ^{o}C) δ 164.7, 135.0, 134.7, 128.3, 127.7, 84.4, 24.4, 18.1.

N-(3,5-dimethylphenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (5e):[5]



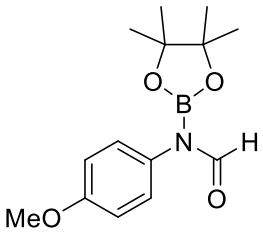
White solid; yield >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 8.88 (s, 1H, C*H*O), 7.07 (s, 1H, Ar*H*), 6.94 (s, 2H, Ar*H*), 3.82 (s, 6H, CH_3), 1.33 (s, 12H, NB*pin*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.6, 138.4, 136.2, 129.1, 125.1, 84.4, 24.4, 21.3.

N-(2,6-diisopropylphenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide



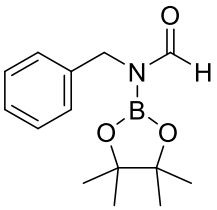
(5q):[1b] White solid; yield >99%. ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.98 (s, 1H, C*H*O), 7.36 (s, 1H, Ar*H*), 7.23 (d, *J* = 7.8 Hz, 2H, Ar*H*), 2.89 – 2.86 (m, 2H, ArC*H*(CH_3)$_2$), 1.31 (s, 12H, NB*pin*), 1.22 – 1.20 (m, 12H, ArCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 165.6, 145.3, 131.4, 128.5, 123.5, 84.5, 28.7, 24.5, 23.9.

N-(4-methoxyphenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (5r):[1b]



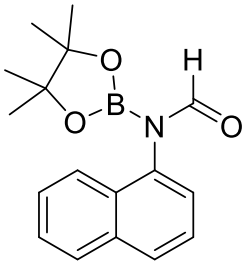
White solid; yield >99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H, C*H*O), 7.08 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.93 (d, *J* = 8.8 Hz, 2H, Ar*H*), 3.82 (s, 3H, ArO*Me*), 1.33 (s, 12H, NB*pin*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.4, 128.3, 114.2, 55.4, 24.5.

N-benzyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (5s):[8] White solid;



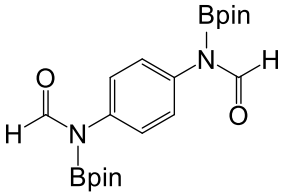
yield >99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H, C*H*O), 7.37 (d, *J* = 7.3 Hz, 2H, Ar*H*), 7.32 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.26 (d, *J* = 7.0 Hz, 1H, Ar*H*), 4.52 (s, 2H, ArCH_2), 1.31 (s, 12H, NB*pin*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.8, 138.8, 84.4, 43.5, 24.56.

N-(naphthalen-1-yl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (5t):[1b]



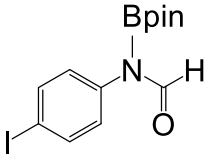
White solid; Yield >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 9.11 (s, 1H, C*H*O), 7.88 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.73 (s, 1H, Ar*H*), 7.53 (s, 3H, Ar*H*), 7.29 (s, 1H, Ar*H*), 1.33 (s, 6H, NB*pin*), 1.30 (s, 6H, NB*pin*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 165.7, 134.4, 128.4, 126.6, 126.1, 125.6, 122.7, 122.4, 122.0, 84.6, 24.6, 24.3.

N,N'-(1,4-phenylene)bis(N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide)



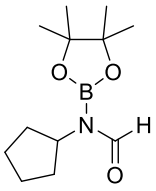
(5l):[5] White solid; yield >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 8.89 (s, 2H, C*H*O), 7.18 (s, 4H, Ar*H*), 1.33 (s, 24H, NB*pin*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 165.4, 127.5, 125.1, 84.6, 83.1, 24.50.

N-(4-iodophenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (5k):[5]

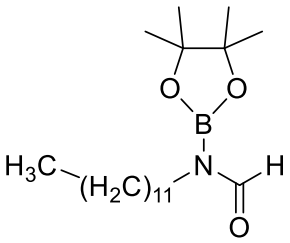


White solid; Yield >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 8.87 (s, 1H, C*H*O), 7.66 – 7.64 (d, 2H, Ar*H*), 6.88 – 6.86 (d, 2H, Ar*H*), 1.33 (s, 6H, NB*pin*), 1.30 (s, 6H, NB*pin*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 165.1, 138.6, 137.9, 129.4, 126.6, 89.8, 84.8, 24.9, 24.5.

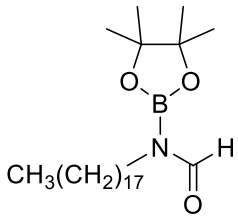
N-cyclopentyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (5m):[5] White solid; yield >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 8.67 (s, 1H, C*H*O), 4.51 – 4.45 (m, 1H, C*H*), 1.83 – 1.74 (m, 6H, CH_2), 1.56 – 1.49 (m, 2H, CH_2), 1.29 (s, 12H, NB*pin*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 166.6, 83.8, 51.0, 30.8, 24.7, 24.5.



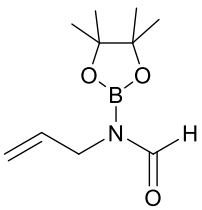
N-dodecyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (5u):[1b] Yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 8.65 (s, 1H, C*H*O), 3.31 (t, J = 6.6 Hz, 2H, N-CH_2), 1.30 (s, 12H, , NB*pin*), 1.27 (d, J = 7.2 Hz, 20H, CH_2), 0.89 (t, J = 6.7 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 166.1, 84.1, 43.0, 40.1, 31.9, 29.8 – 29.5, 29.3, 26.84, 24.9, 24.5, 22.7, 14.1.



***N*-octadecyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (5o):**[1b] White solid; yield >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 8.65 (s, 1H, C*H*O), 3.31 (t, *J* = 7.2 Hz, 2H, N-CH_2), 1.30 (s, 12H, NB*pin*), 1.27 (s, 32H, CH_2), 0.90 (d, *J* = 6.5 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 166.1, 84.1, 40.1, 31.9, 29.7, 29.4, 26.8, 24.5, 22.7, 14.1.

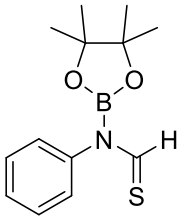


N-allyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (5p):[1b] White solid; yield >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 8.69 (s, 1H, C*H*O), 5.84 (ddd, J = 22.3, 10.5, 5.4 Hz, 1H, C*H*), 5.10 (t, J = 13.0 Hz, 2H, CH_2), 3.95 (d, J = 5.2 Hz, 2H, CH_2), 1.30 (s, 12H, NB*pin*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ 165.6, 134.1, 115.5, 84.3, 42.0, 24.9, 24.5.



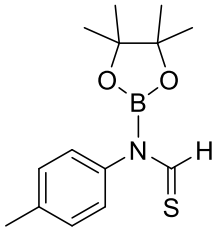
Analytical data for N-borylated thioformamide of Corresponding Isothiocyanates:

***N*-phenyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanethioamide (7a):**[5] White



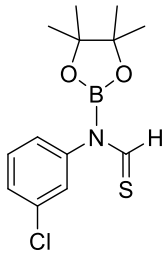
solid; yield >99%.^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 10.37 (s, 1H), 7.50 – 7.47 (m, 2H), 7.42 – 7.37 (m, 1H), 7.26 – 7.25 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.17 (d, *J* = 8.0 Hz, 1H), 1.36 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ = 200.3, 129.6, 129.1, 127.5, 125.7, 85.4, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$, 25 ^{o}C): δ = 25.02.

***N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(*p*-tolyl)methanethioamide (7b)**:[5]



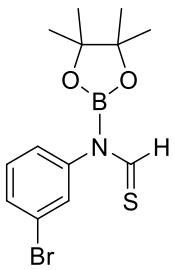
White solid; yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 10.20 (s, 1H), 7.14 – 7.12 (d, *J* = 4.0 Hz, 1H), 7.02 – 6.98 (d, *J* = 4.0 Hz, 2H), 6.93 – 6.91 (d, *J* = 4.0 Hz, 1H), 2.24 (s, 3H), 1.17 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ = 200.4, 137.5, 130.1, 127.2, 125.5, 85.3, 24.9, 21.2.

***N*-(3-chlorophenyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanethioamide**



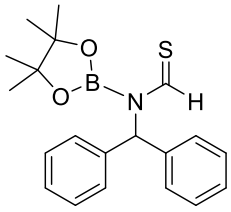
(7c):[5] White solid; yield >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 10.18 (s, 1H), 7.29 – 7.23 (m, 2H), 7.05 (s, 1H), 6.95 – 6.93 (m, 1H), 1.22 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ = 200.1, 140.3, 134.4, 130.1, 128.0, 126.0, 85.6, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$, 25 ^{o}C): δ = 24.87.

***N*-(3-bromophenyl)-*N*-(4,4,5,5-teramethyl-1,3,2-dioxaborolan-2-yl)methanethioamide**



(7d):[5] White solid; yield >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 10.17 (s, 1H), 7.38 – 7.36 (d, *J* = 4.1 Hz, 1H), 7.31 – 7.27 (d, *J* = 4.0 Hz, 1H), 7.20 (t, *J* = 4.2 Hz, 1H), 7.00 – 6.98 (d, *J* = 4.1 Hz, 1H), 1.22 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ = 200.1, 130.9, 130.3, 128.7, 126.5, 124.3, 122.3, 85.6, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$, 25 ^{o}C): δ = 24.85.

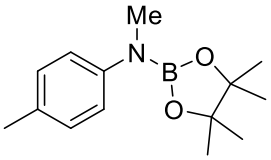
***N*-benzhydryl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanethioamide (7e):[5]**



White solid; yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 10.15 (s, 1H), 7.52 (s, 1H), 7.29 – 7.23 (m, 6H), 7.20 – 7.15 (m, 4H), 1.19 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 ^{o}C): δ = 199.3, 143.2, 141.3, 139.4, 139.2, 128.8, 128.0, 127.2, 124.9, 84.8, 60.8, 24.9.

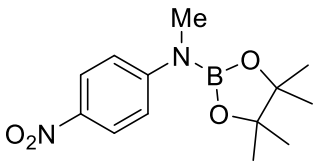
Analytical data of N-boryl methylamine of corresponding isothiocyanates

***N*,4,4,5,5-pentamethyl-*N*-(p-tolyl)-1,3,2-dioxaborolan-2-amine (4c):[1b]** White solid; yield:



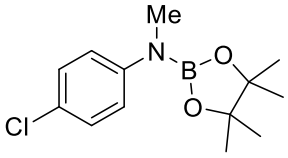
>99%. ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ = 7.29 – 7.27 (d, *J* = 8.0 Hz, 2H), 6.98 – 6.95 (d, *J* = 8.0 Hz, 2H), 2.97 (s, 3H), 2.11 (s, 3H), 1.07 (s, 12H), 1.00 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) δ = 145.1, 129.4, 128.9, 119.0, 82.4, 82.2, 34.1, 24.4, 24.2, 20.2.

N,4,4,5,5-pentamethyl-N-(4-nitrophenyl)-1,3,2-dioxaborolan-2-amine (9a):[5] White solid;



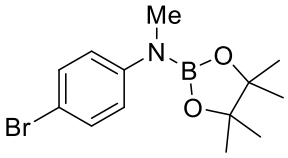
yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.36 (s, 2H), 7.30 – 7.29 (s, 2H), 3.10 (s, 3H), 1.31 (s, 24H), 1.27 (s, 12H).

***N*-(4-chlorophenyl)-*N*,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (4i):[1b]** White

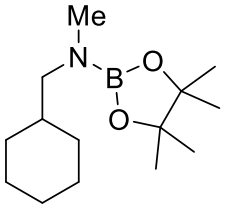


solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.26 – 7.25 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.20 (d, *J* = 8.0 Hz, 2H), 3.04 (s, 3H), 1.31 (s, 12H), 1.29 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 147.0, 129.2, 126.7, 120.8, 84.1, 83.9, 35.2, 25.7, 25.4.

***N*-(4-bromophenyl)-*N*,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (4j):[1b]** White solid; yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.36 – 7.35 (d, *J* = 9.0 Hz, 2H), 7.21 – 7.20 (d, *J* = 8.0 Hz, 2H), 3.04 (s, 3H), 1.31 (s, 12H), 1.30 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ = 147.0, 131.6, 120.8, 113.4, 83.4, 83.3, 34.6, 25.0, 24.9.

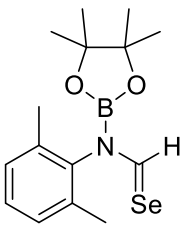


N-(cyclohexylmethyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (4b):[5] White solid; yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.70 – 2.68 (d, *J* = 7.3 Hz, 2H), 2.54 (s, 3H), 1.76 – 1.72 (m, 1H), 1.71 - 1.69 (m, 2H), 1.66 – 1.61 (m, 2H), 1.21 (s, 24H), 1.20 (s, 12H), 1.16 – 1.15 (m, 3H), 1.13 – 1.11 (m, 3H).



Analytical data of N-boryl selenoformamide of corresponding isoselenocyanates

***N*-(2,6-dimethylphenyl)-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methaneselenoamide (11a):[5]** Brown solid; yield: >99%. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ^{o}C): δ = 12.19 (s, 1H), 7.14 – 7.12 (m, 1H), 7.07 – 7.05 (d, *J* = 4.0 Hz, 2H), 2.05 (s, 6H), 1.23 (s, 12H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 25 ^{o}C): δ = 205.2, 138.9, 134.0, 128.4, 128.1, 85.5, 24.4, 17.8. ^{11}B NMR (128 MHz, $CDCl_3$, 25 ^{o}C): δ 22.37, 21.10.



^{1}H, ^{13}C{^{1}H} and ^{119}Sn{^{1}H} spectra of Sn-1 and Sn-2 compounds

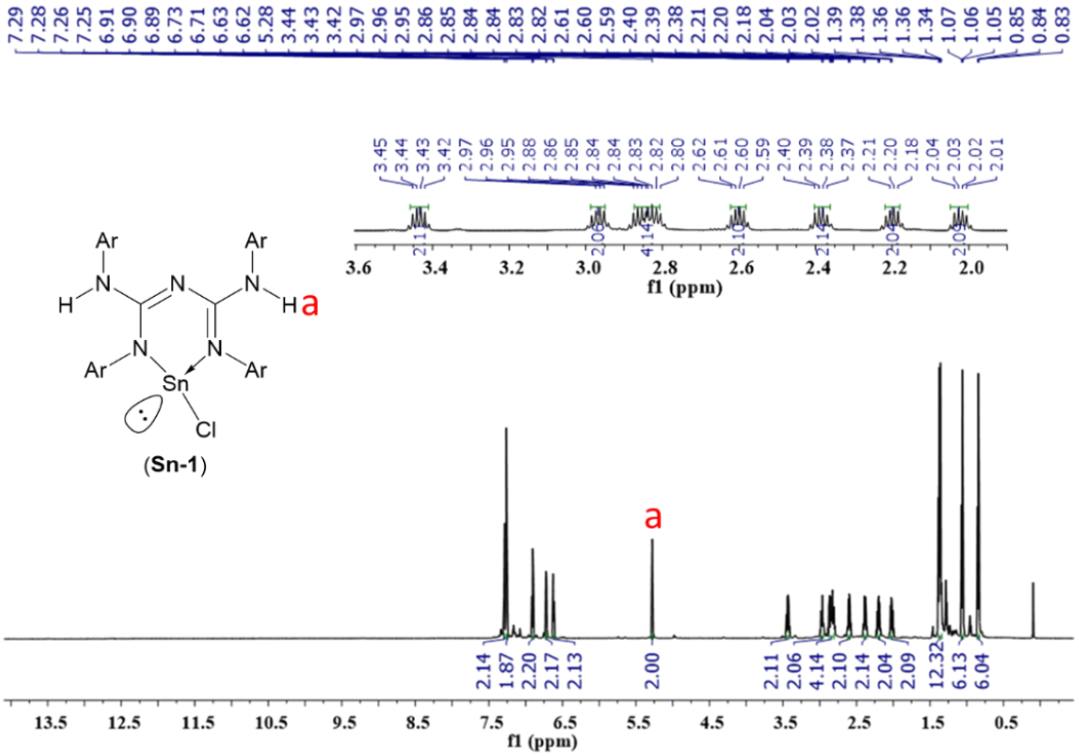


Figure S1. ^{1}H NMR spectrum of compound **Sn-1** (700 MHz, $CDCl_3$, 25 ^{o}C).

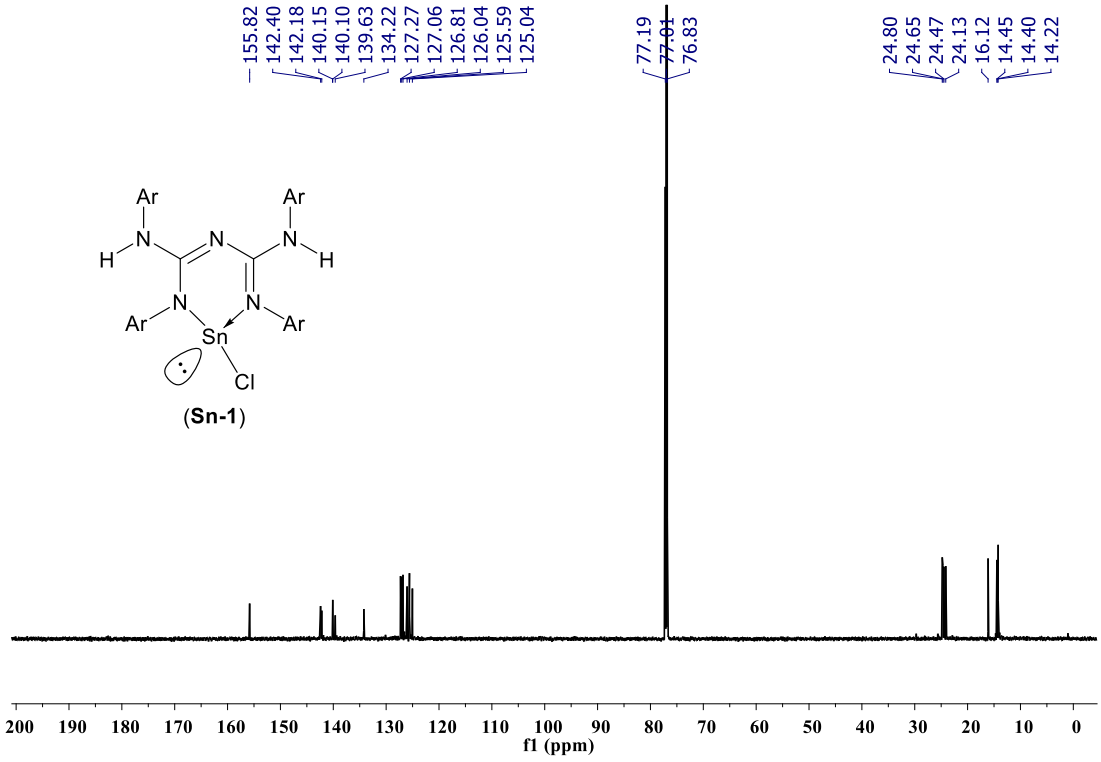


Figure S2. ^{13}C{^{1}H} NMR spectrum of compound **Sn-1** (176 MHz, $CDCl_3$, 25 ^{o}C)

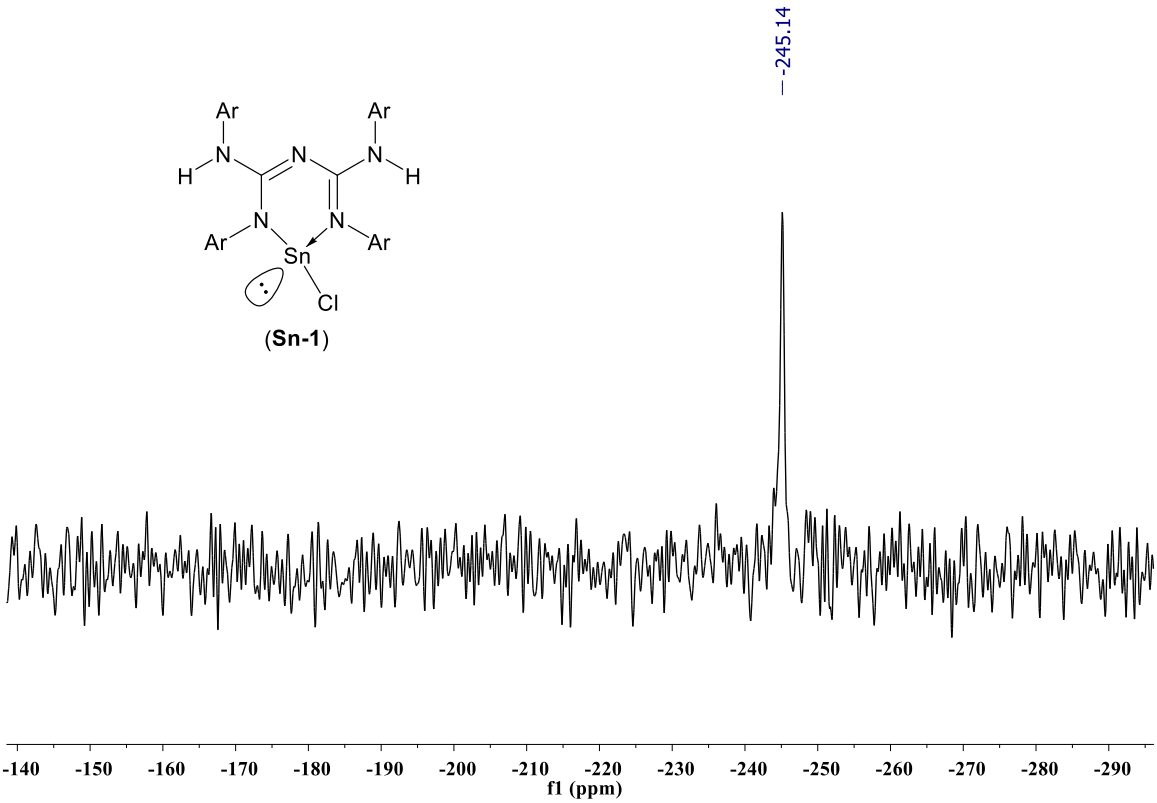


Figure S3. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **Sn-1** (149 MHz, $CDCl_3$, 25 ºC)

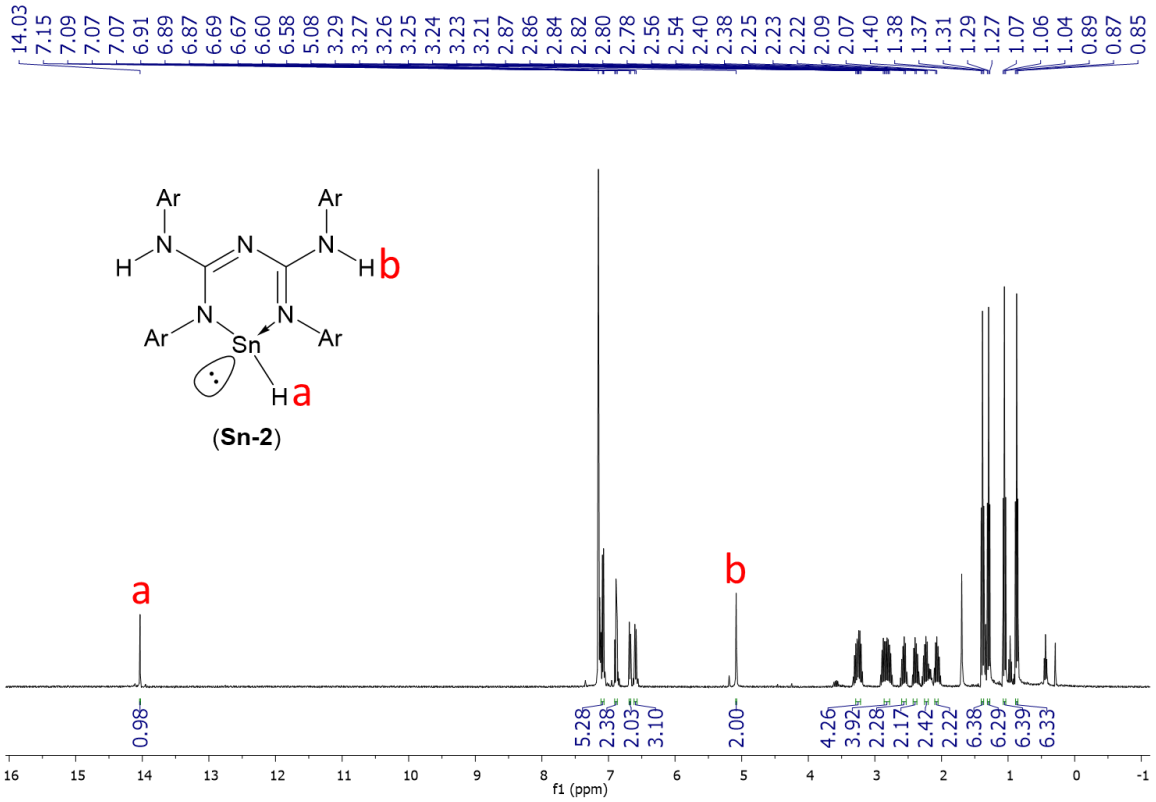


Figure S4. ^{1}H NMR spectrum of compound **Sn-2** (400 MHz, C_6D_6, 25 ºC).

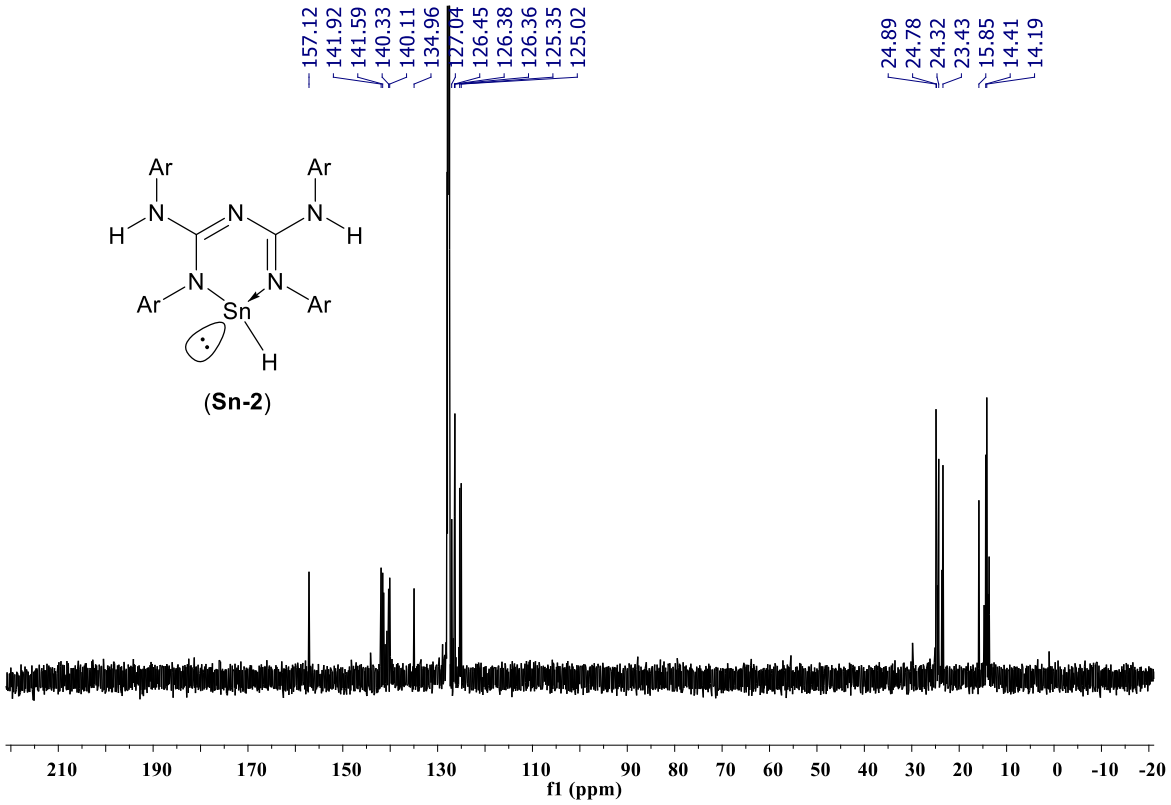


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of compound **Sn-2** (101 MHz, C_6D_6, 25 °C)

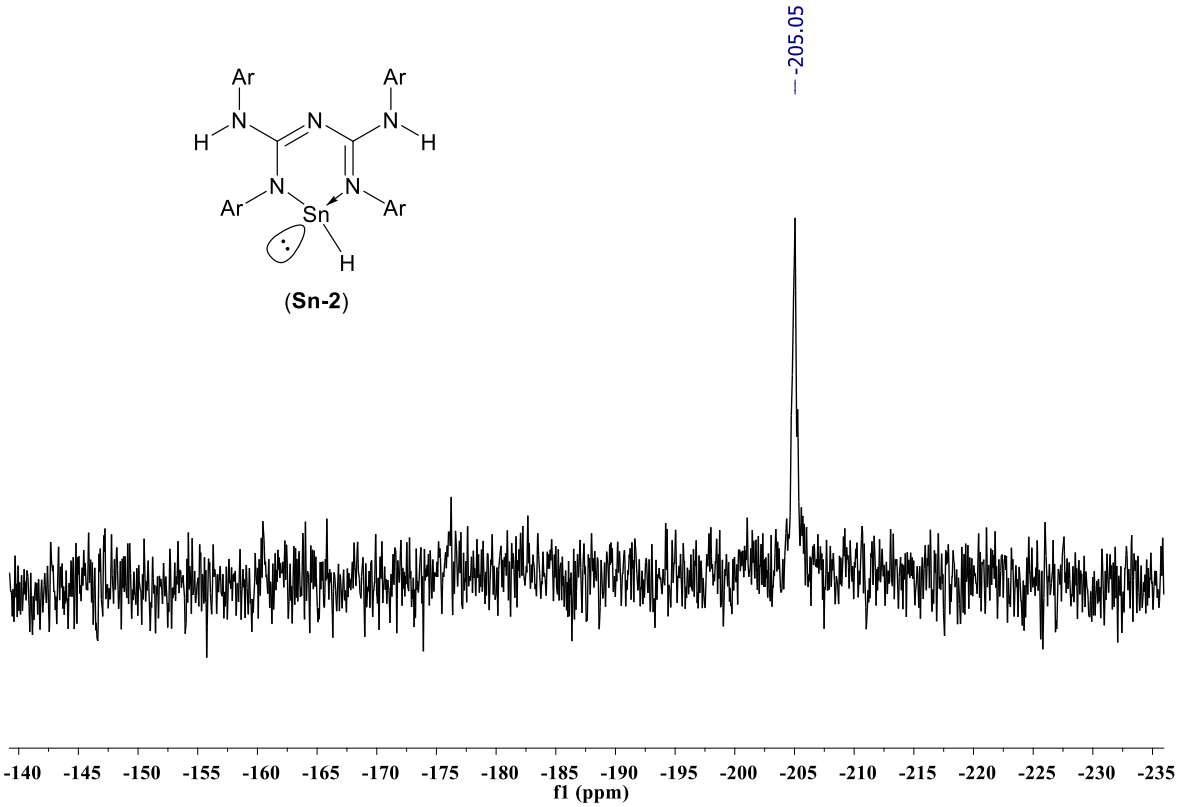


Figure S6. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **Sn-2** (149 MHz, C_6D_6, 25 °C)

NMR spectra (^{1}H, ^{13}C{^{1}H}, ^{11}B NMR) of Stoichiometric Experiments.

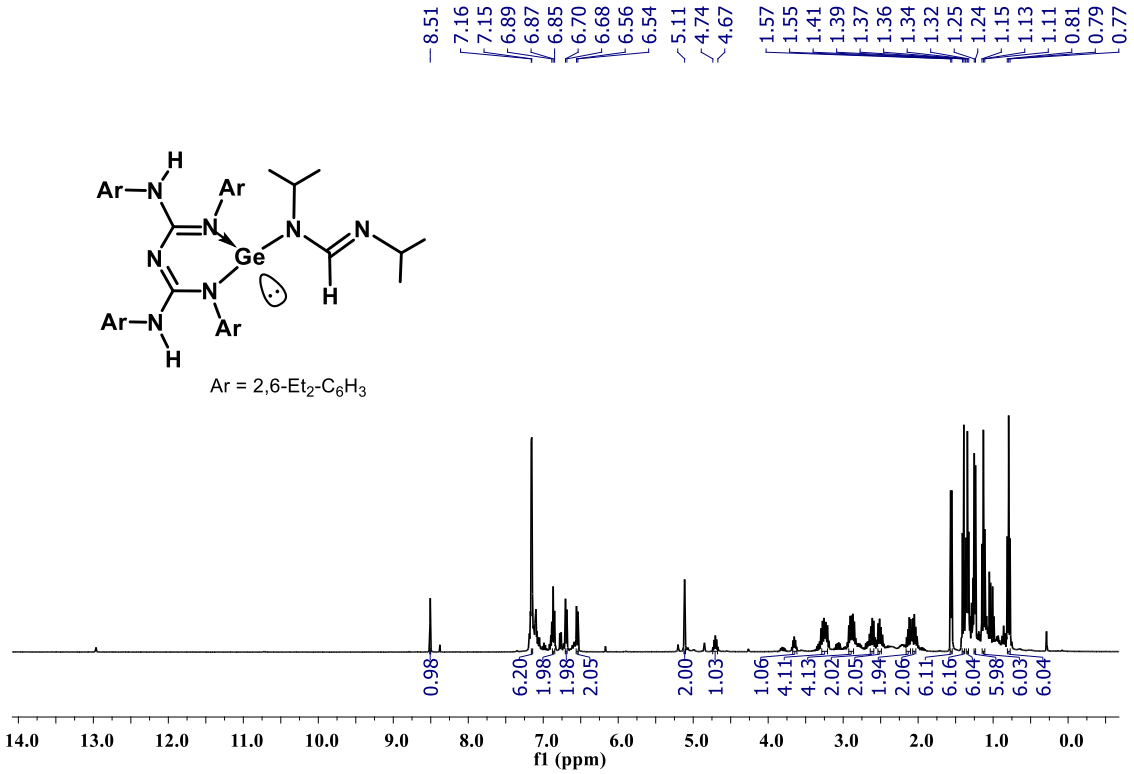


Figure S7: ^{1}H NMR of Compound [LGeN(CH(CH$_3$)$_2$)C(H)N(CH(CH$_3$)$_2$)], **Int A** in C_6D_6.

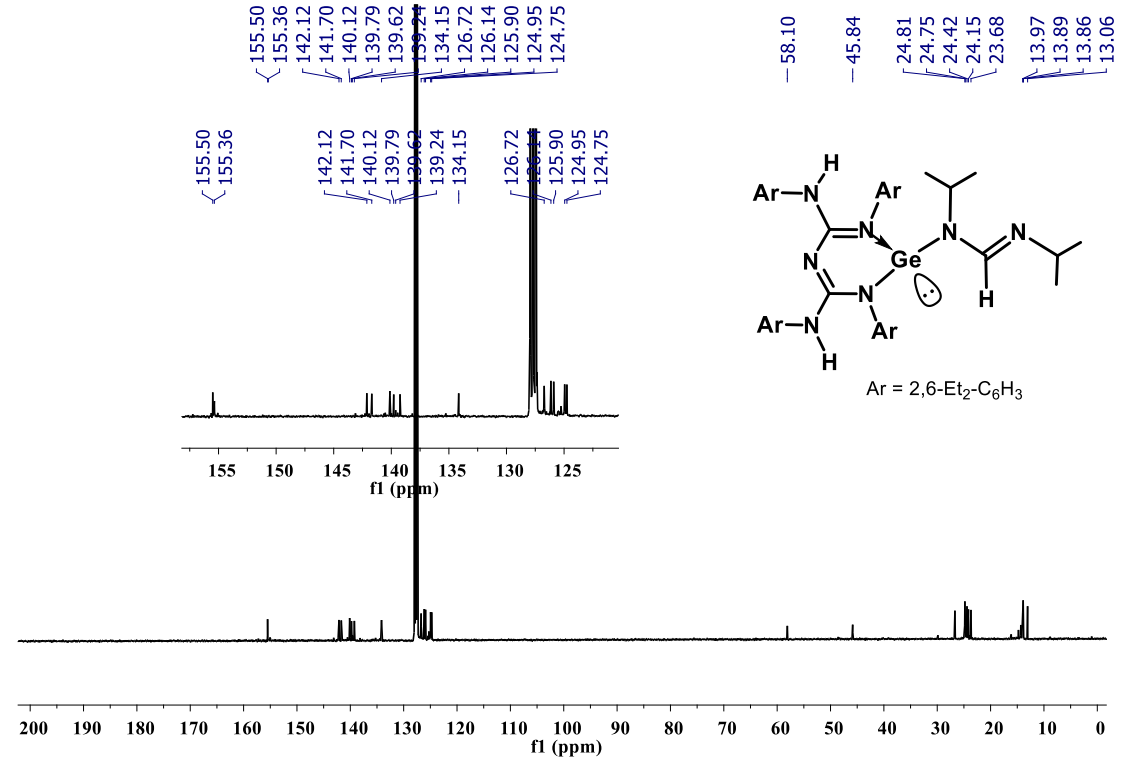


Figure S8: ^{13}C{^{1}H} NMR of Compound [LGeN(CH(CH$_3$)$_2$)C(H)N(CH(CH$_3$)$_2$)], **Int A** in C_6D_6.

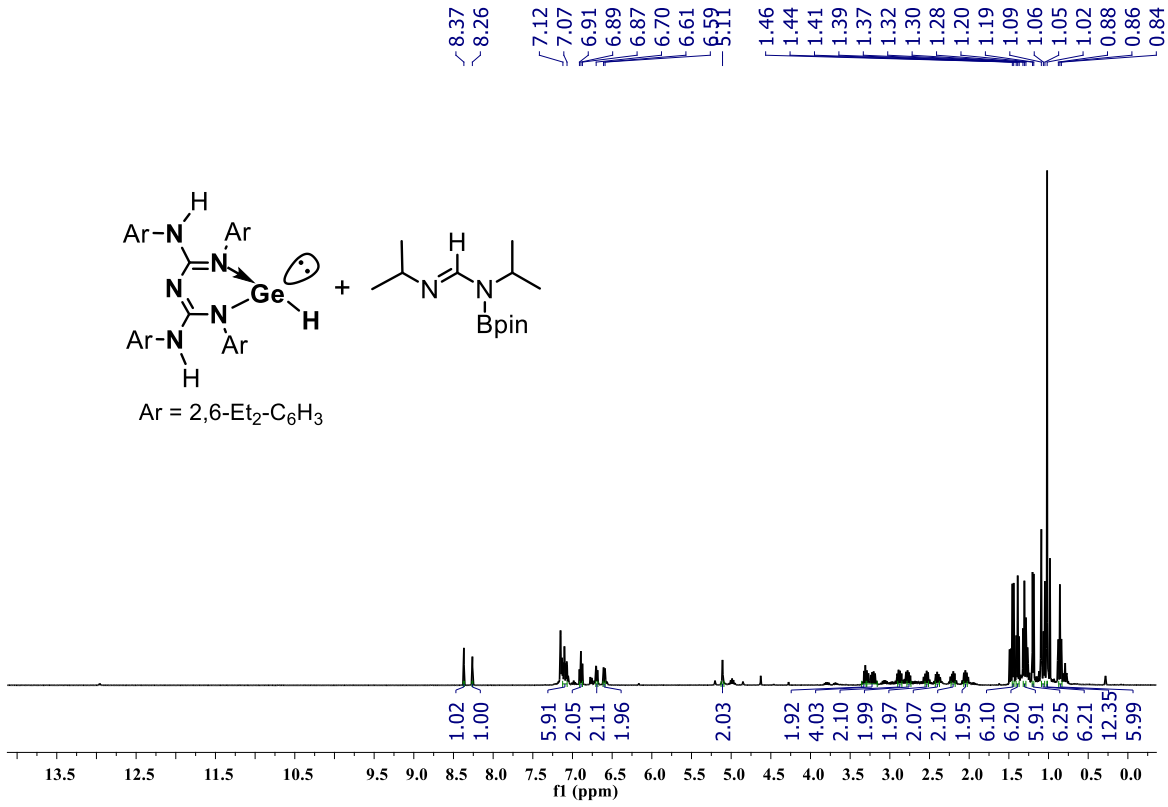


Figure S9: ^{1}H NMR of Compound [LGeH] and compound **2a** in C_6D_6.

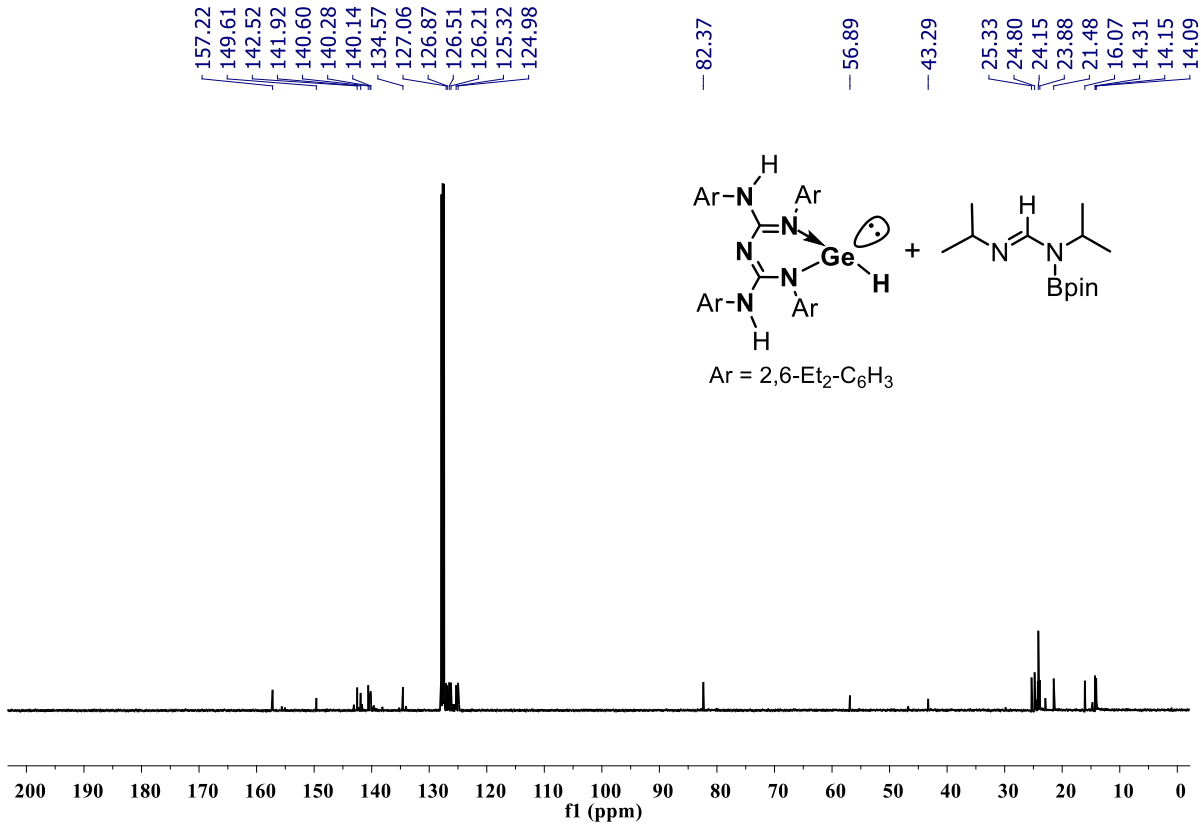


Figure S10: $^{13}C\{^{1}H\}$ NMR of Compound [LGeH] and compound **2a** in C_6D_6.

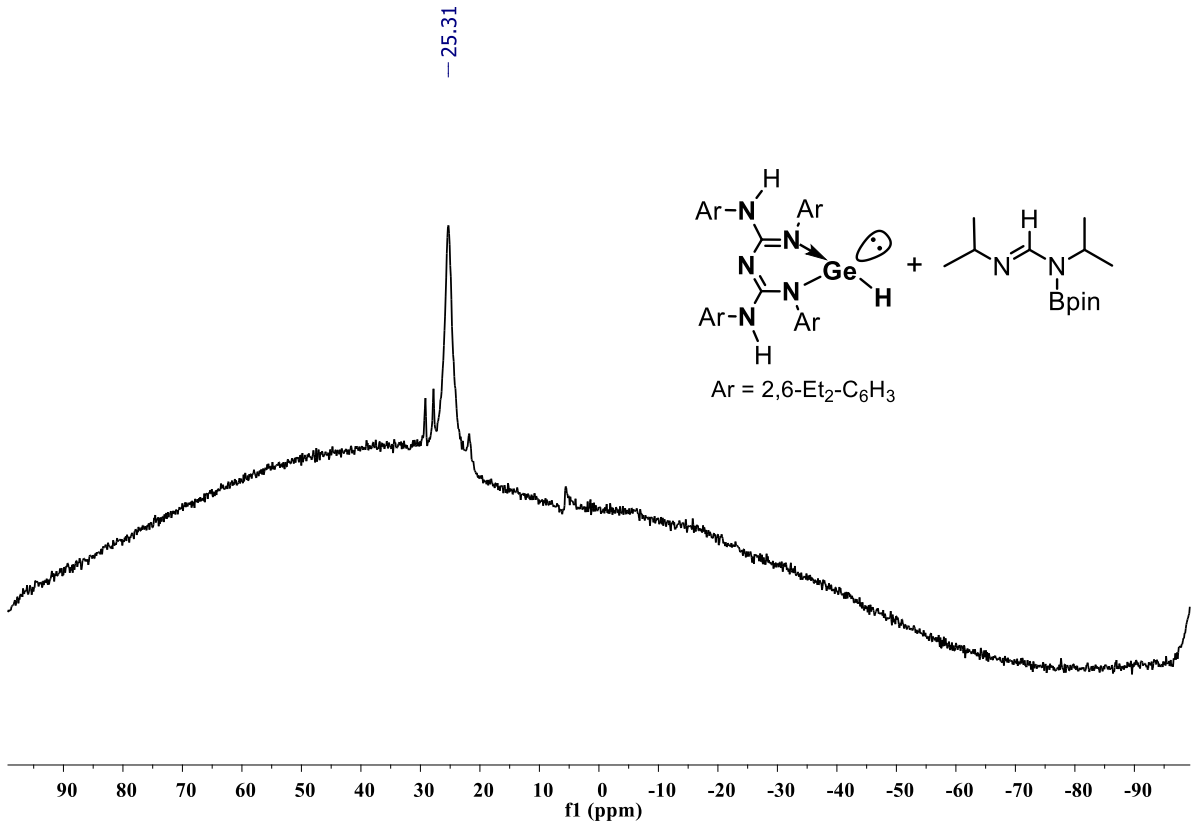


Figure S11: ^{11}B NMR of Compound [LGeH] and compound **2a** in C_6D_6.

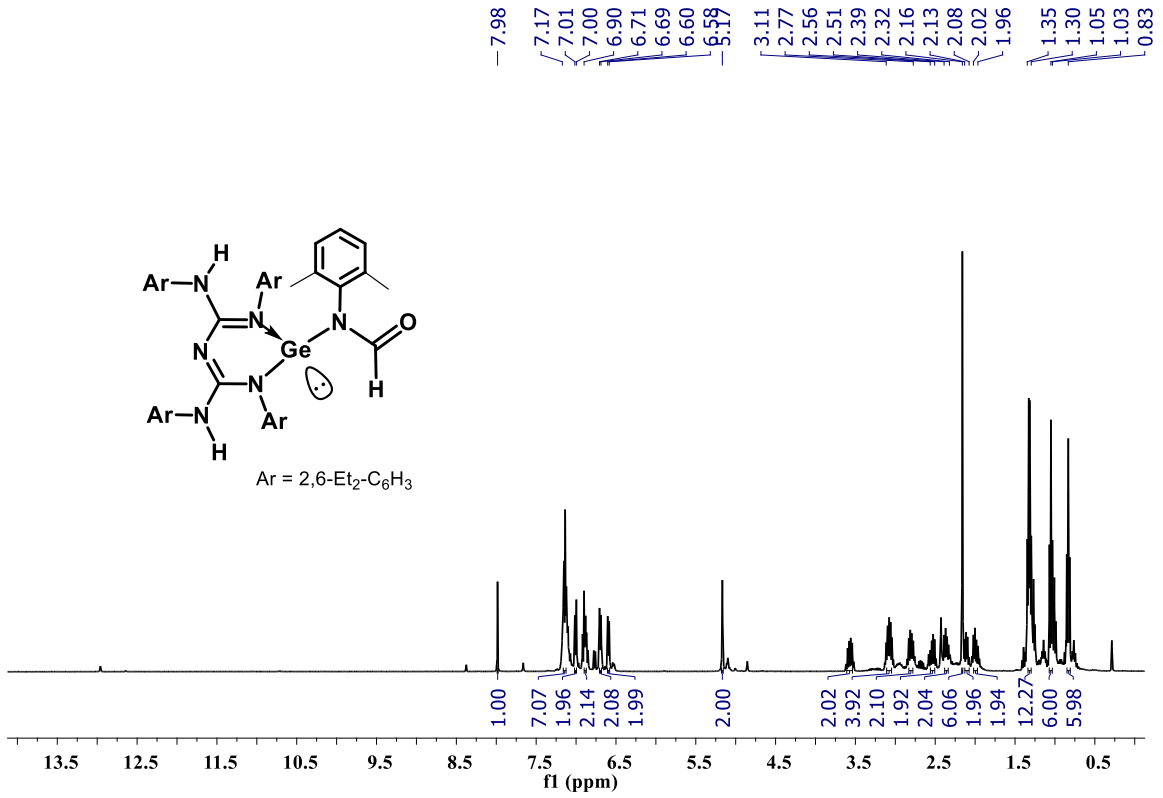


Figure S12: ^{1}H NMR of Compound [LGeOC(H)N(2,6-$Me_2C_6H_3$)], **Int A1** in C_6D_6.

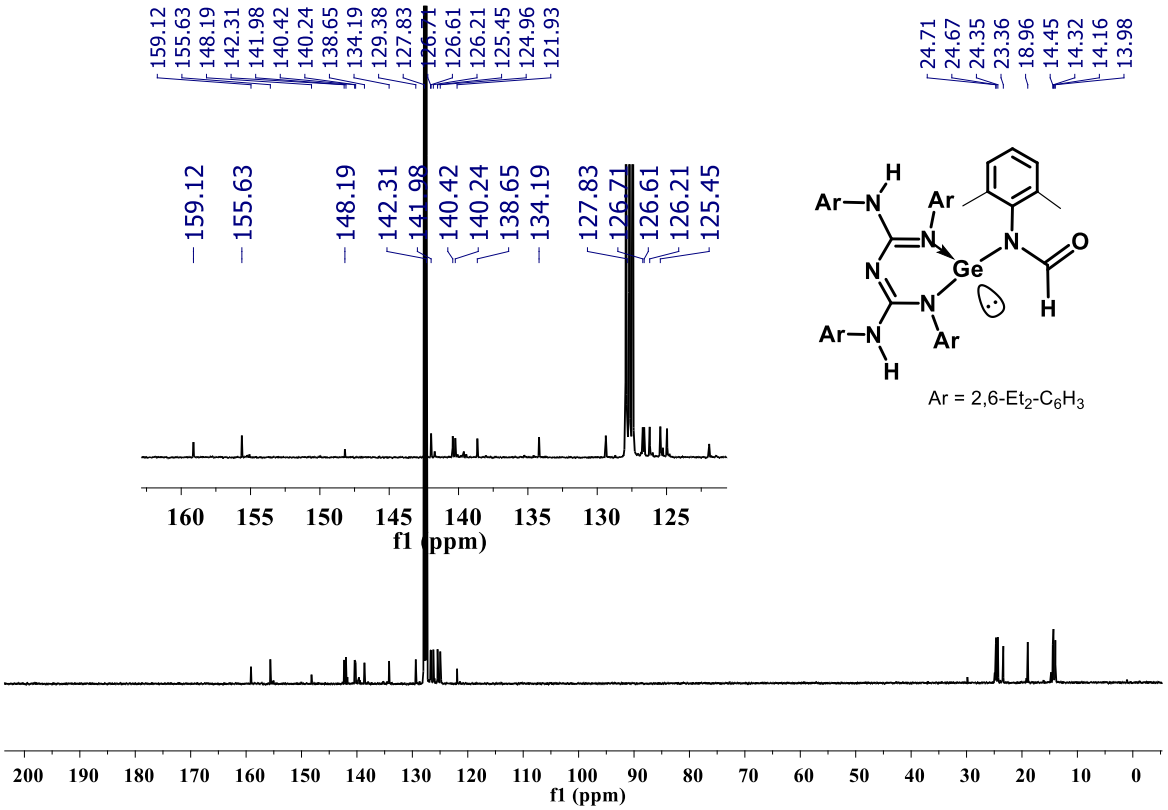


Figure S13: $^{13}C\{^{1}H\}$ NMR of Compound [LGeOC(H)N(2,6-$Me_2C_6H_3$)], **Int A1** in C_6D_6.

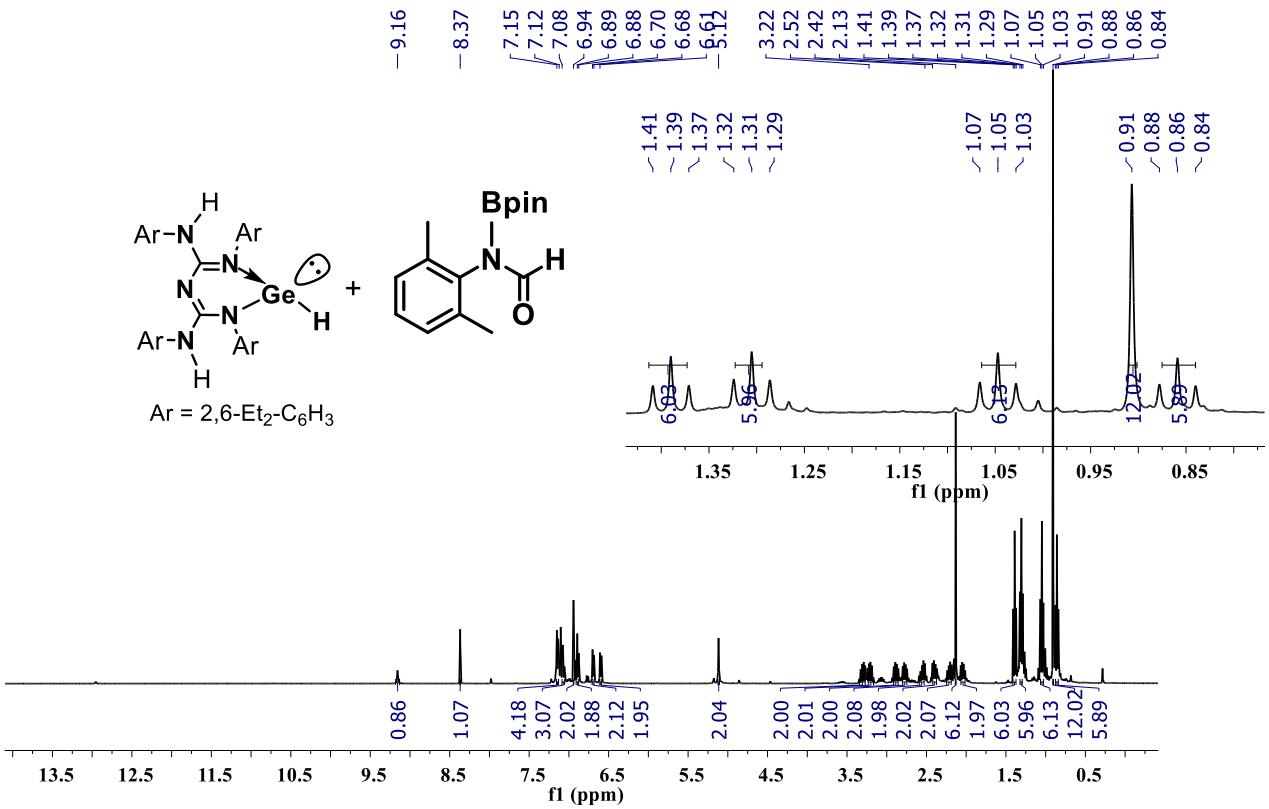


Figure S14: ^{1}H NMR of Compound [LGeH] and **5d** in C_6D_6.

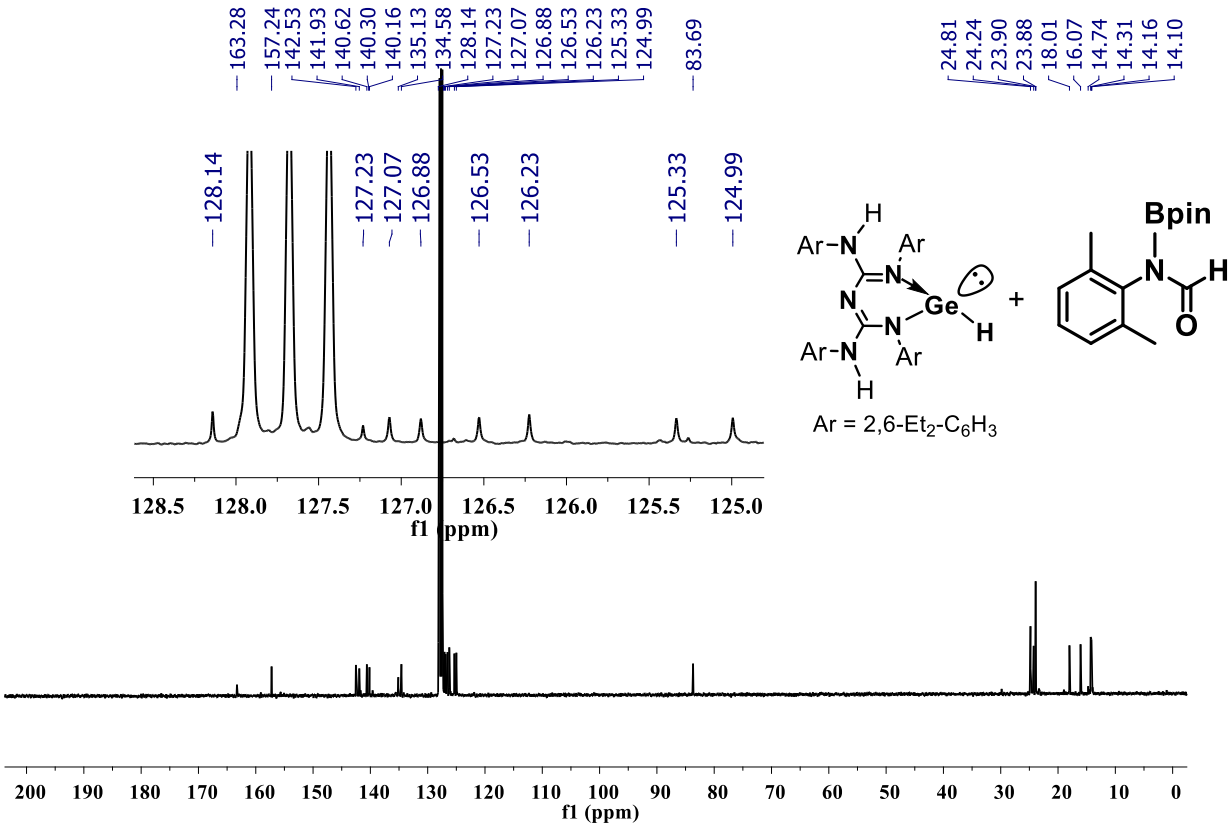


Figure S15: $^{13}C\{^{1}H\}$ NMR of Compound [LGeH] and **5d** in C_6D_6.

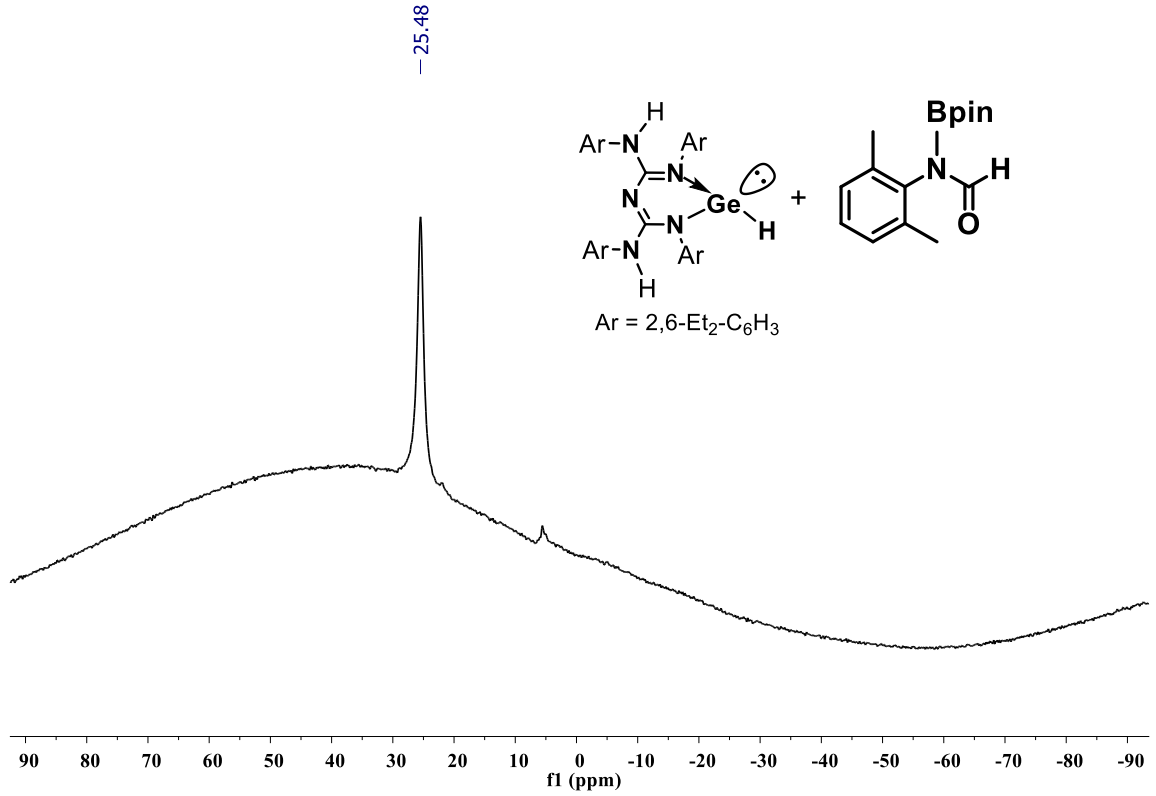


Figure S16: ^{11}B NMR of Compound [LGeH] and **5d** in C_6D_6.

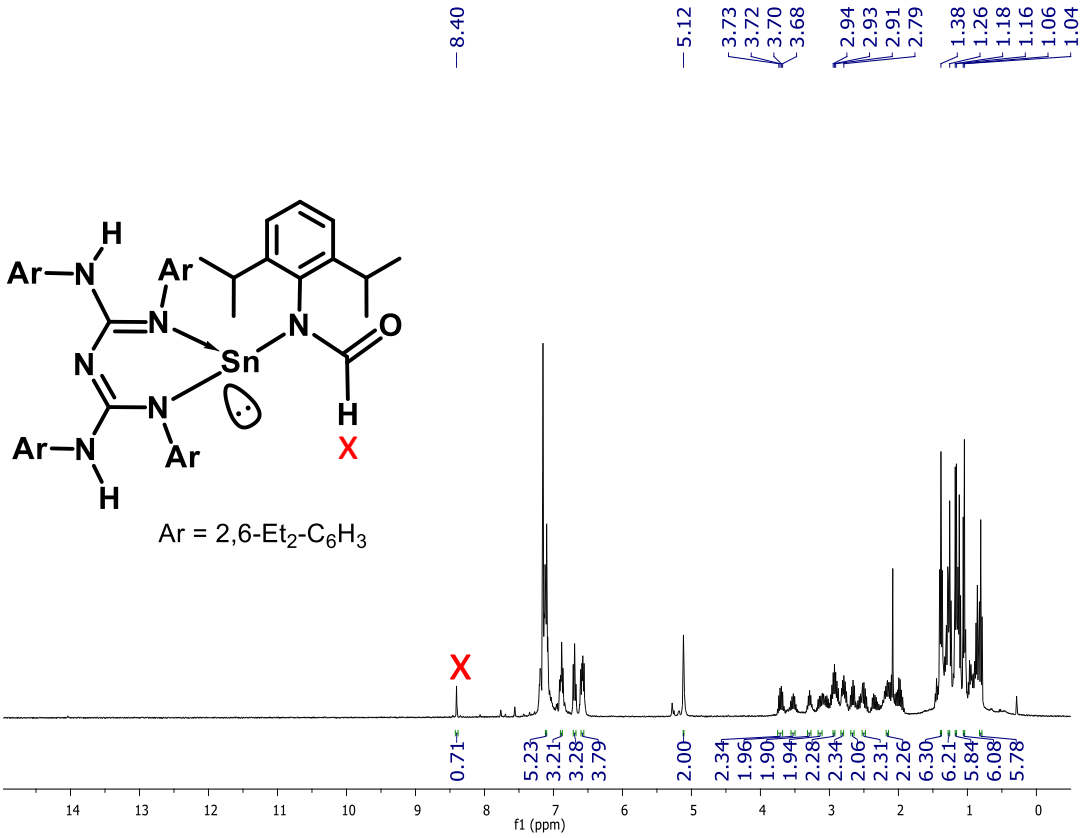


Figure S17. ^{1}H NMR of [LSnOC(H)N(2,6-^{i}Pr$_2$C$_6$H$_3$)] **(Int A1')** (400 MHz, C$_6$D$_6$, 25 ^{o}C)

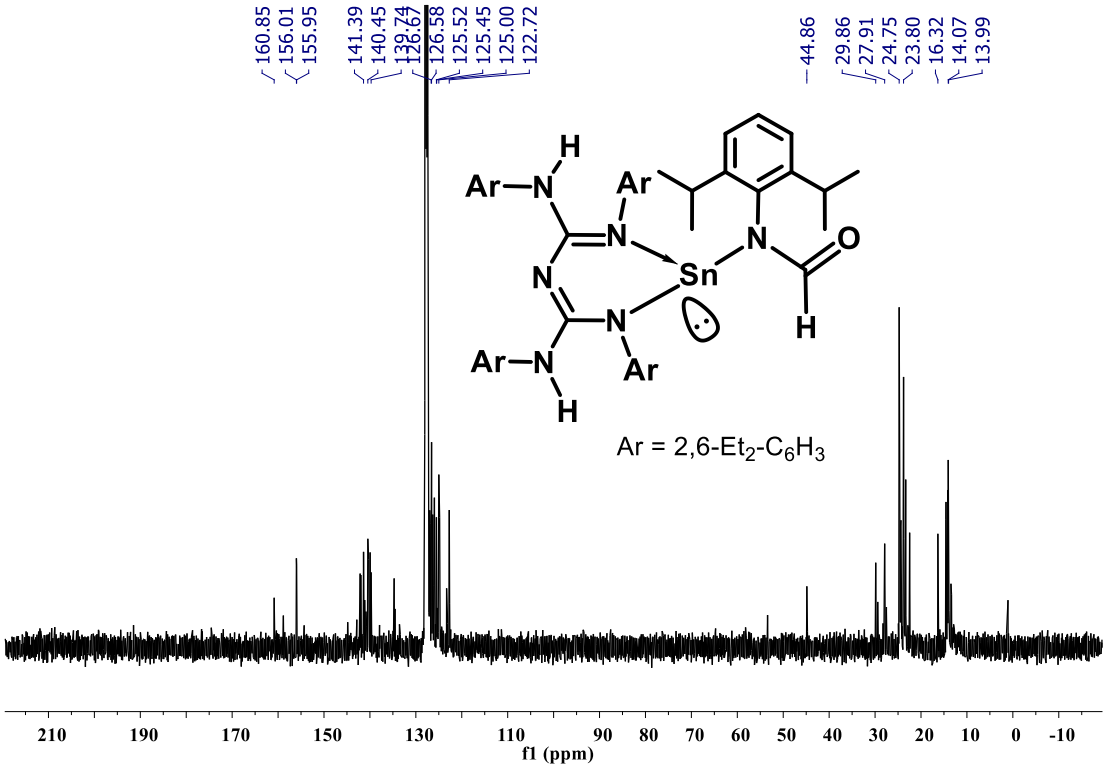


Figure S18. ^{13}C{^{1}H} NMR of [LSnOC(H)N(2,6-^{i}Pr$_2$C$_6$H$_3$)] **(Int A1')** (101 MHz, C$_6$D$_6$, 25 ^{o}C)

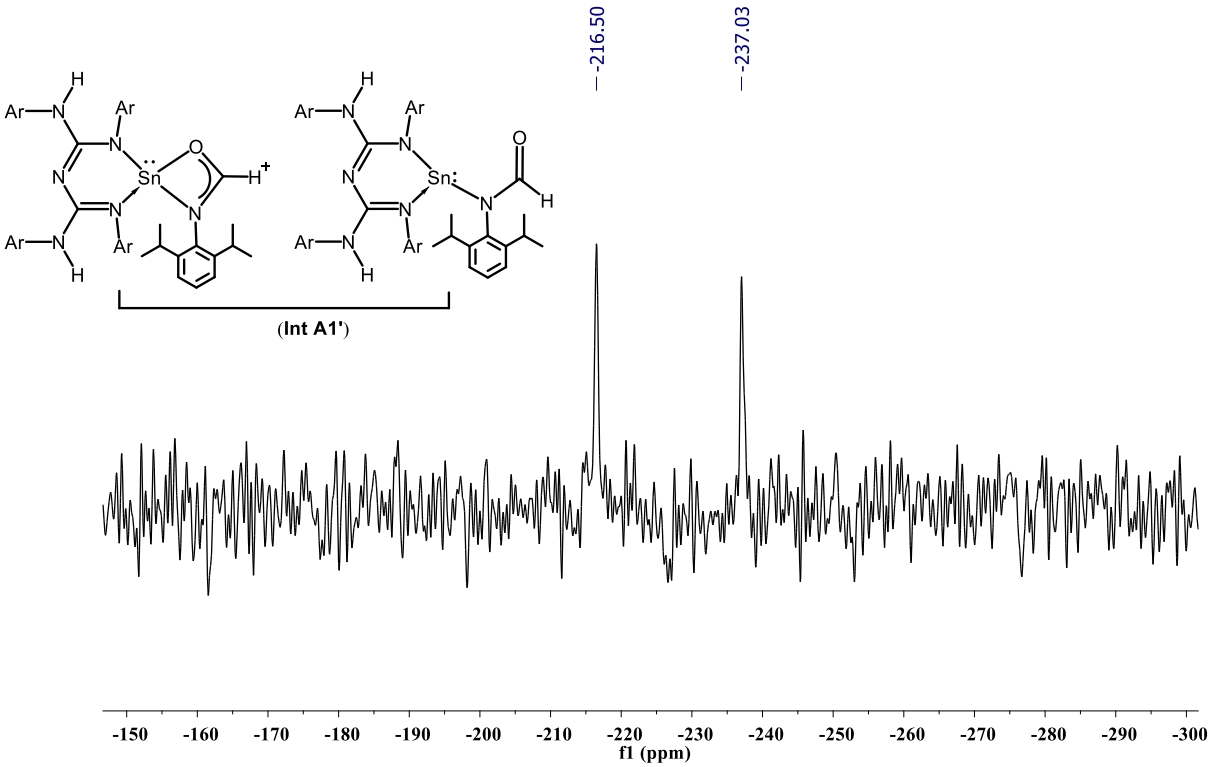


Figure S19. $^{119}Sn\{^{1}H\}$ NMR of [LSnOC(H)N(2,6-$^{i}Pr_2C_6H_3$)] **(Int A1')** (149 MHz, C_6D_6, 25 ^{o}C)

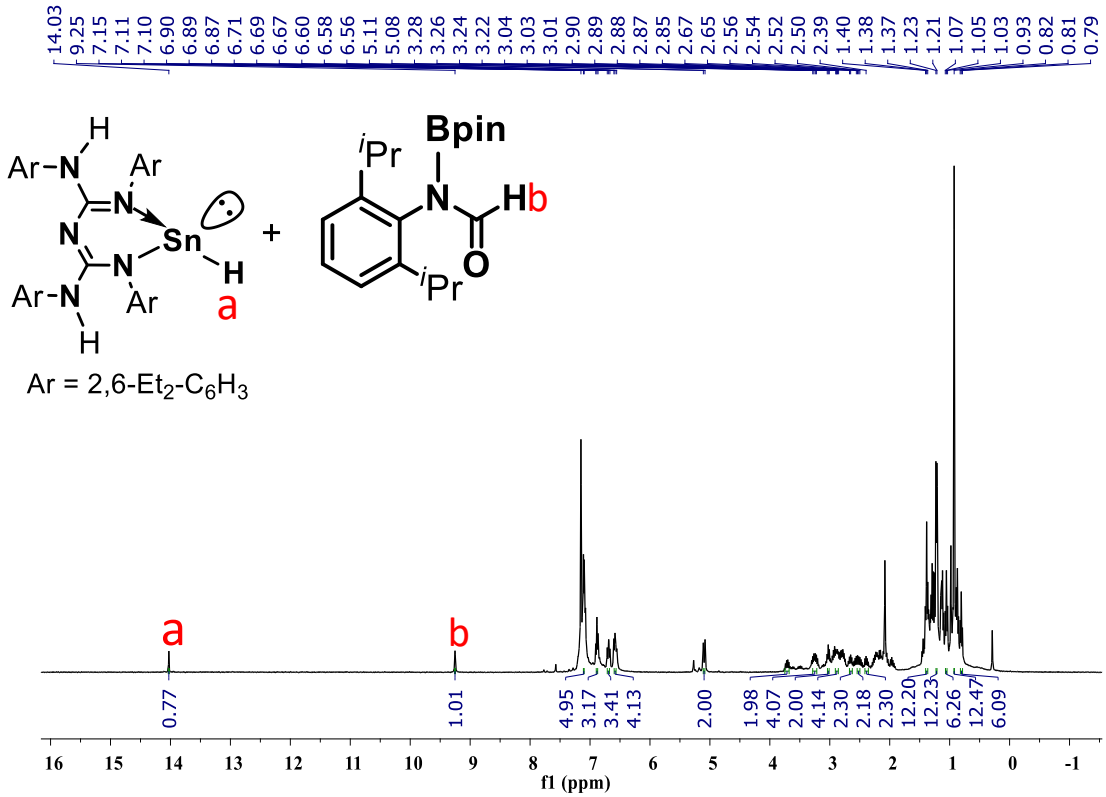


Figure S20. ^{1}H NMR spectrum of **(Sn-2)** and **5q** (400 MHz, C_6D_6, 25 ^{o}C)

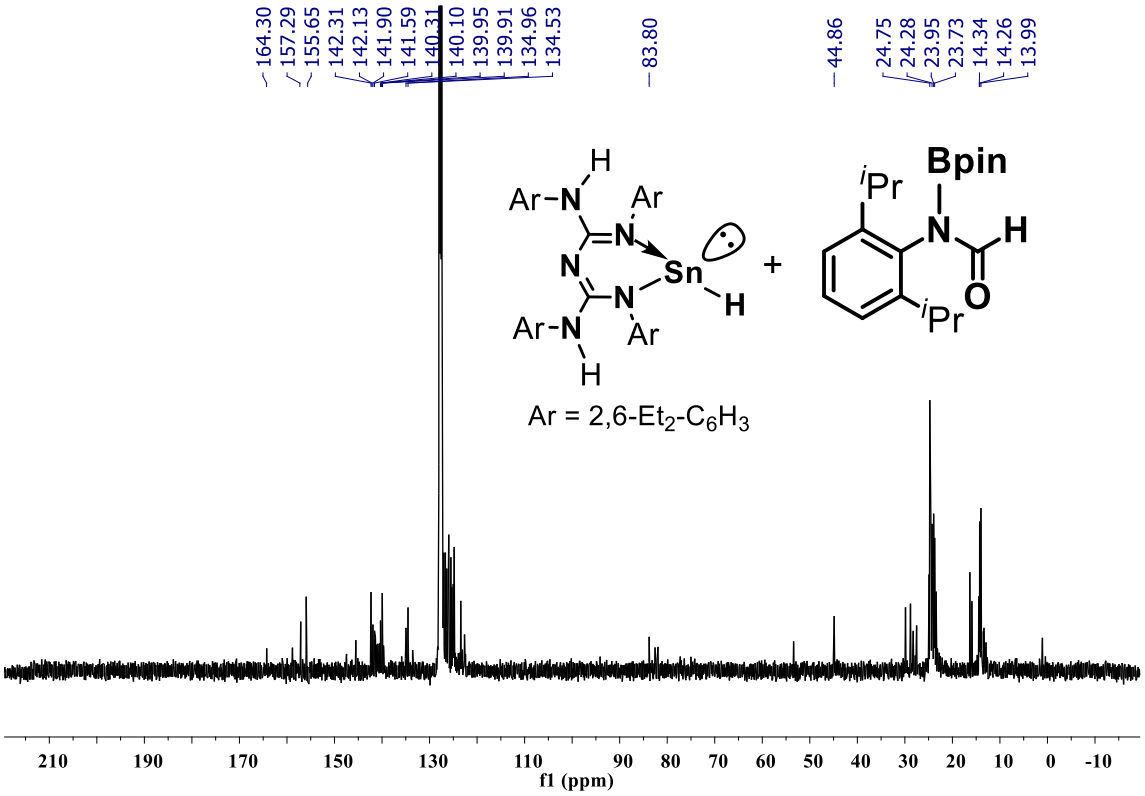


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **(Sn-2)** and **5q** (101 MHz, C_6D_6, 25 ^{o}C)

Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of catalyst-free reactions

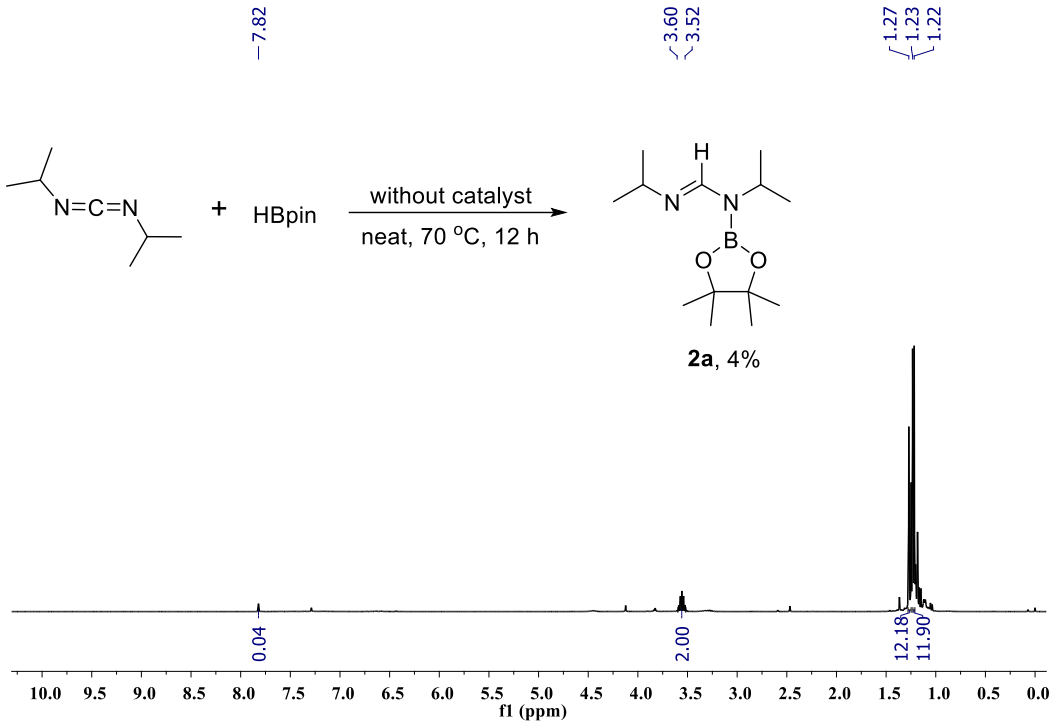


Figure S22: ^{1}H spectrum of N, N-diisopropyl carbodiimide with HBpin in the absence of catalyst (400MHz, $CDCl_3$, 298 K).

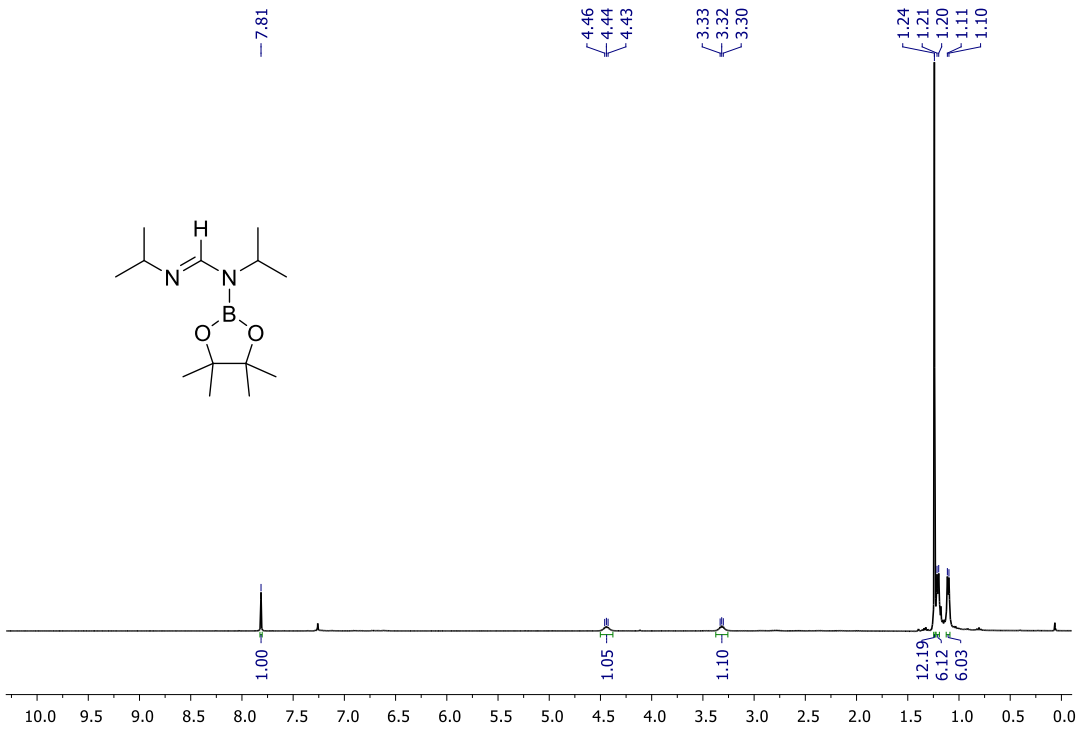


Figure S23: ^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$, 25 ^{o}C).

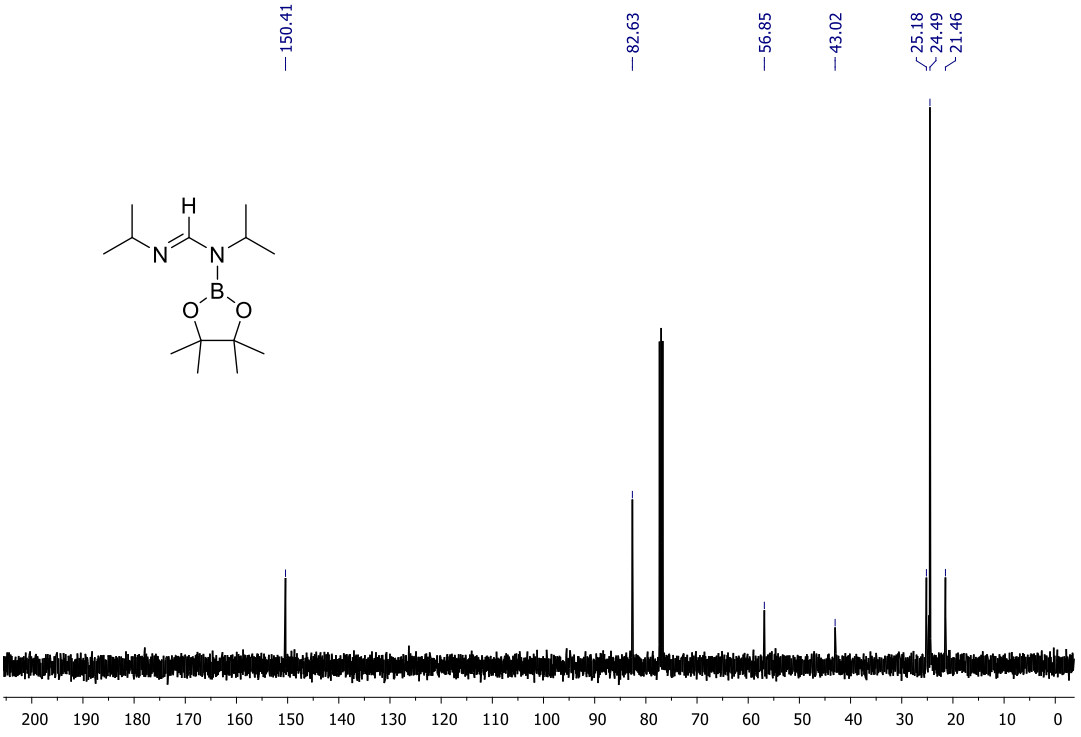


Figure S24: ^{13}C{^{1}H} NMR spectrum of **2a** (101 MHz, $CDCl_3$, 25 ^{o}C).

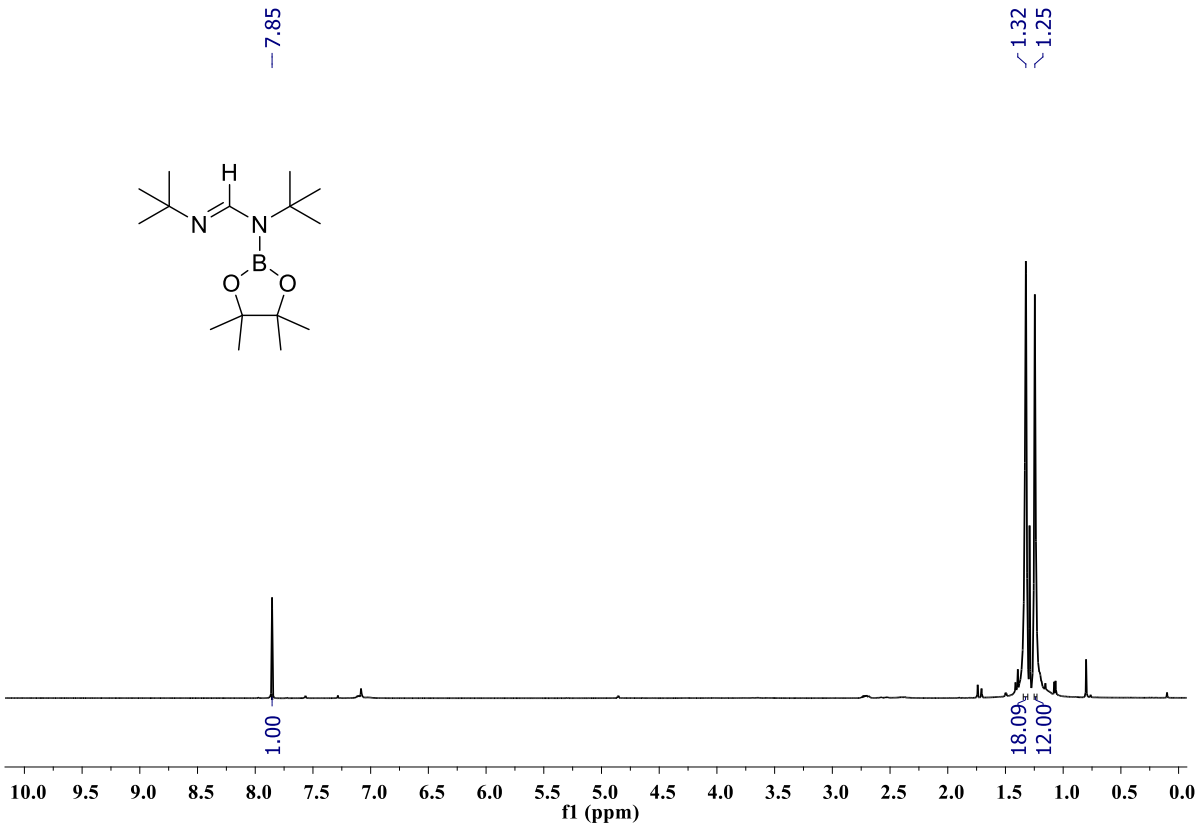


Figure S25: ^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$, 25 ^{o}C).

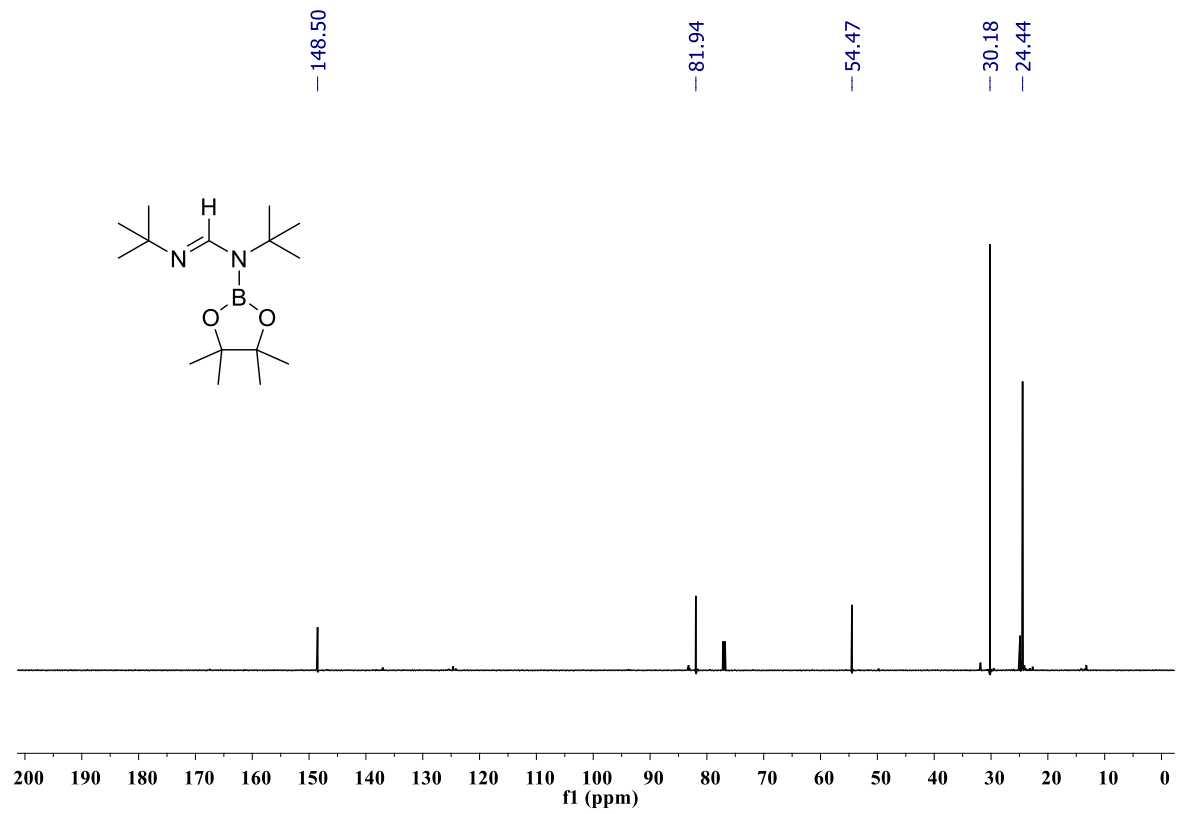


Figure S26: ^{13}C{^{1}H} NMR spectrum of **2b** (101 MHz, $CDCl_3$, 25 ^{o}C).

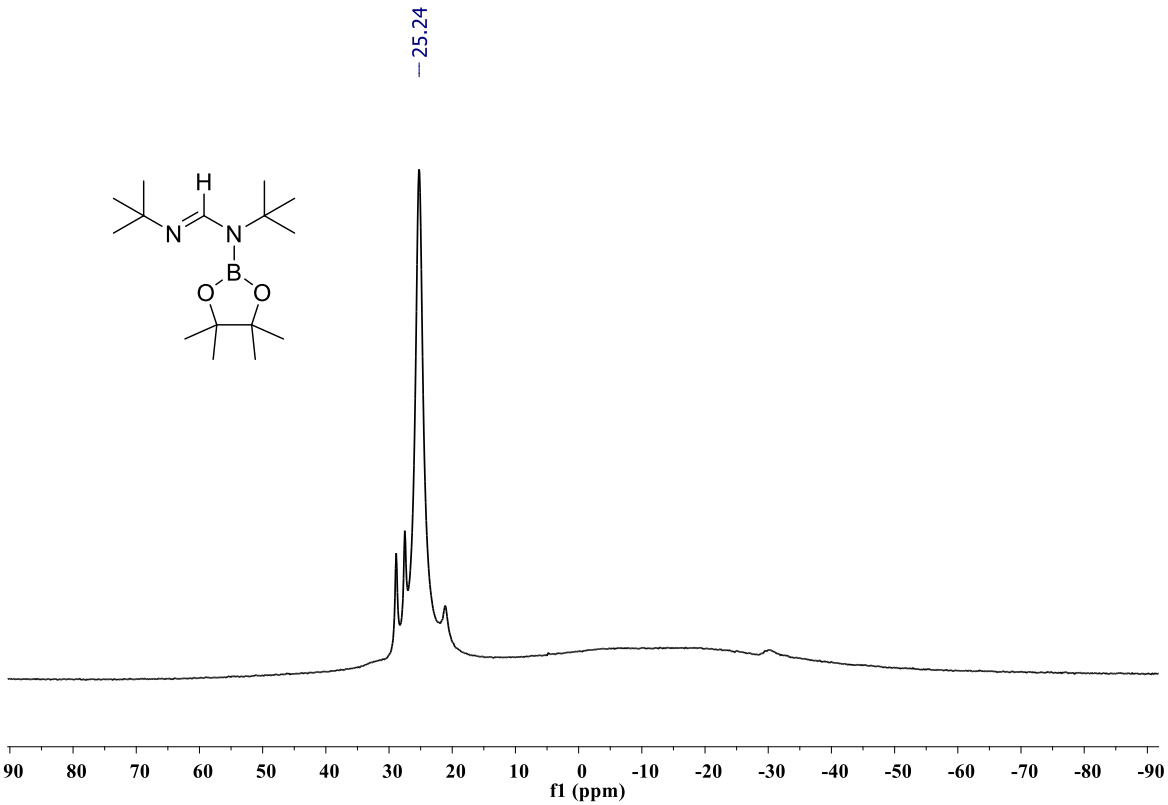


Figure S27: ^{11}B NMR spectrum of **2b** (128 MHz, $CDCl_3$, 25 ^{o}C).

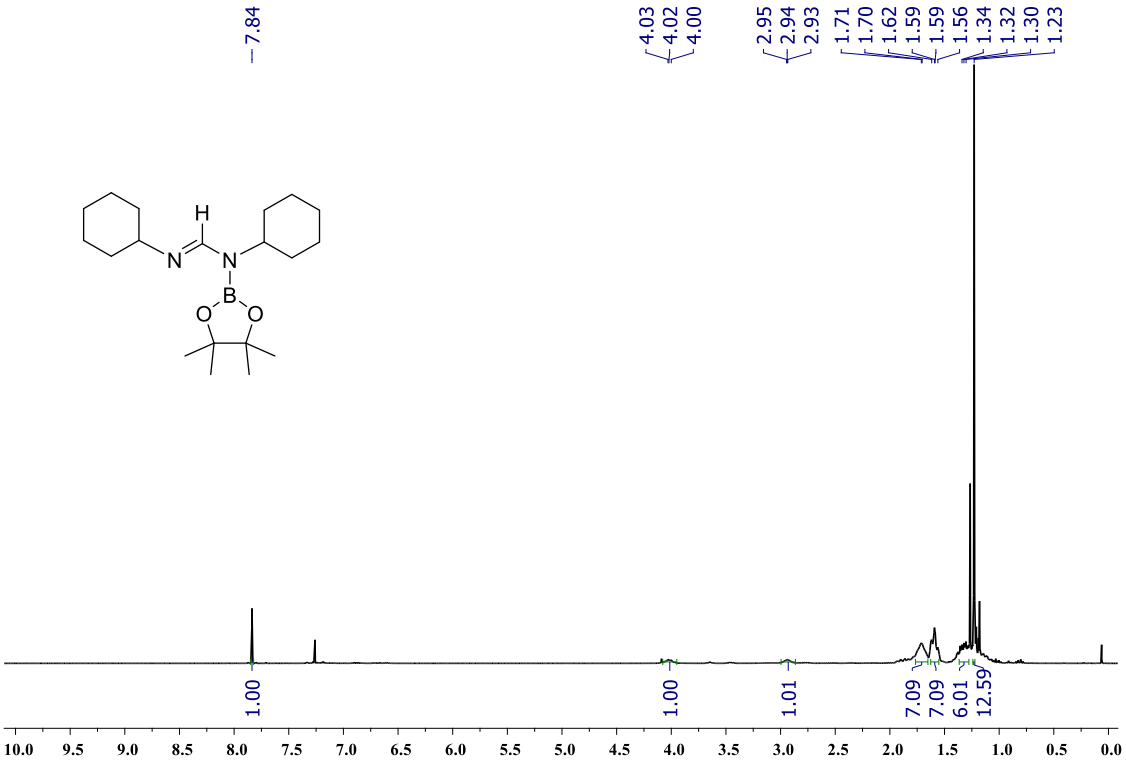


Figure S28: ^{1}H NMR spectrum of **2c** (400 MHz, $CDCl_3$, 25 ^{o}C).

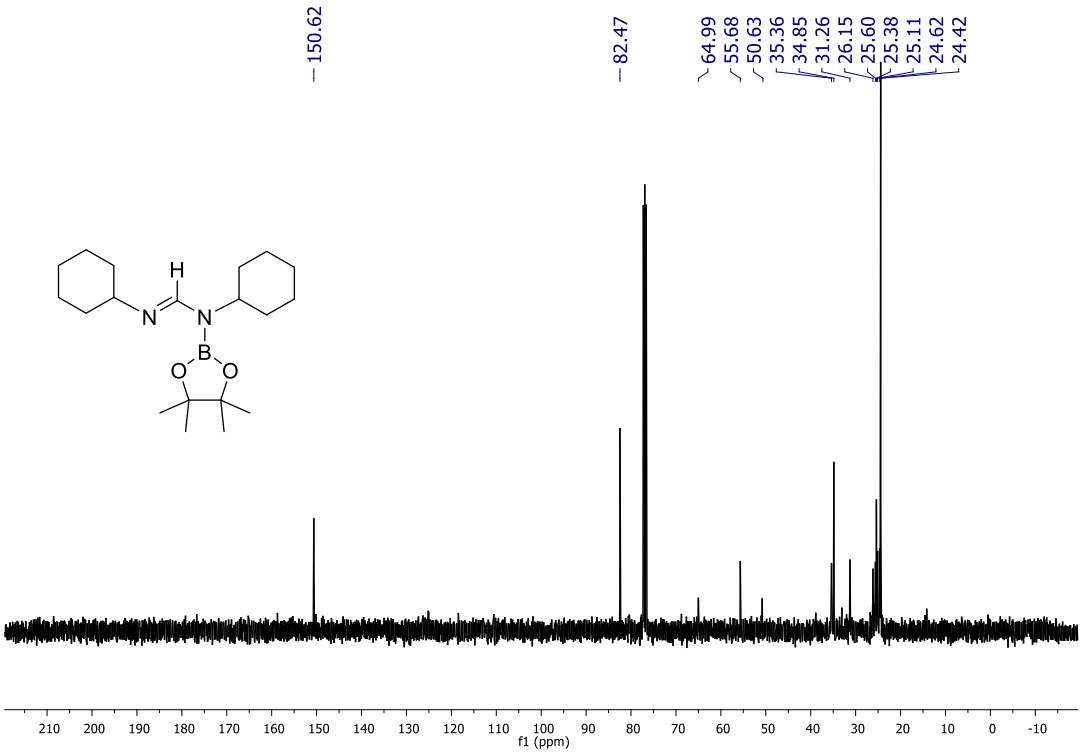


Figure S29: $^{13}C\{^{1}H\}$ NMR spectrum of **2c** (101 MHz, $CDCl_3$, 25 ^{o}C).

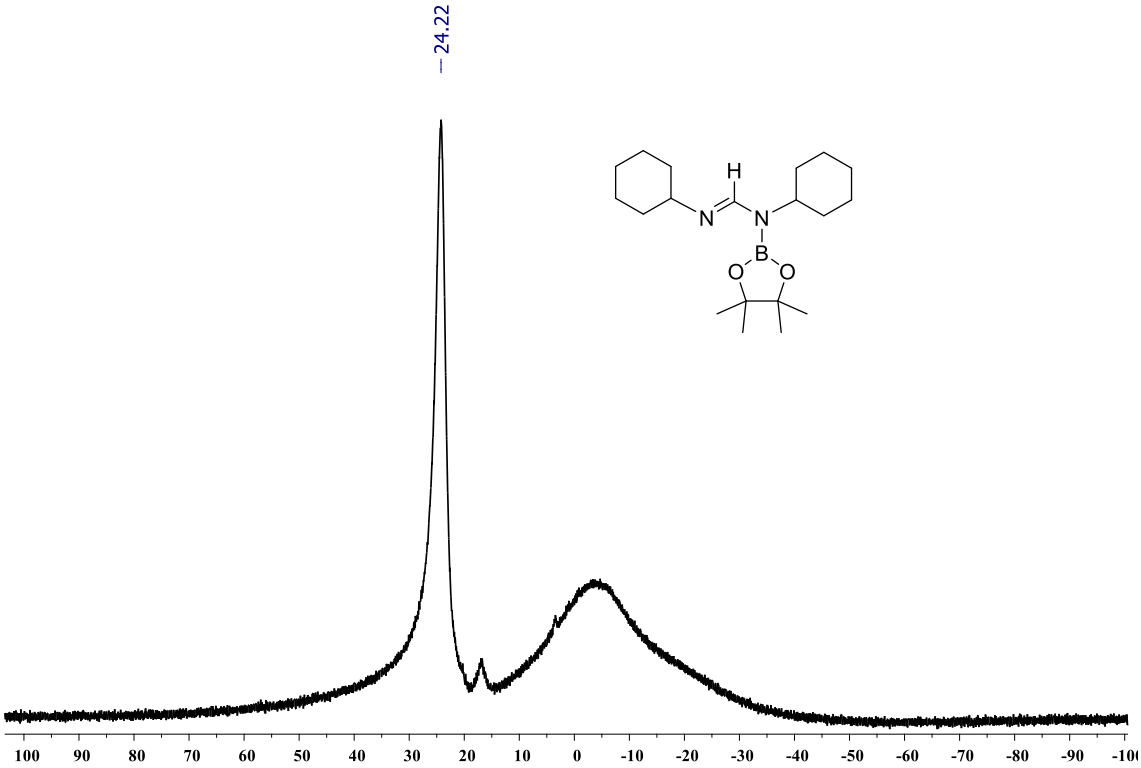


Figure S30: ^{11}B NMR spectrum of **2c** (128 MHz, $CDCl_3$, 25 ^{o}C).

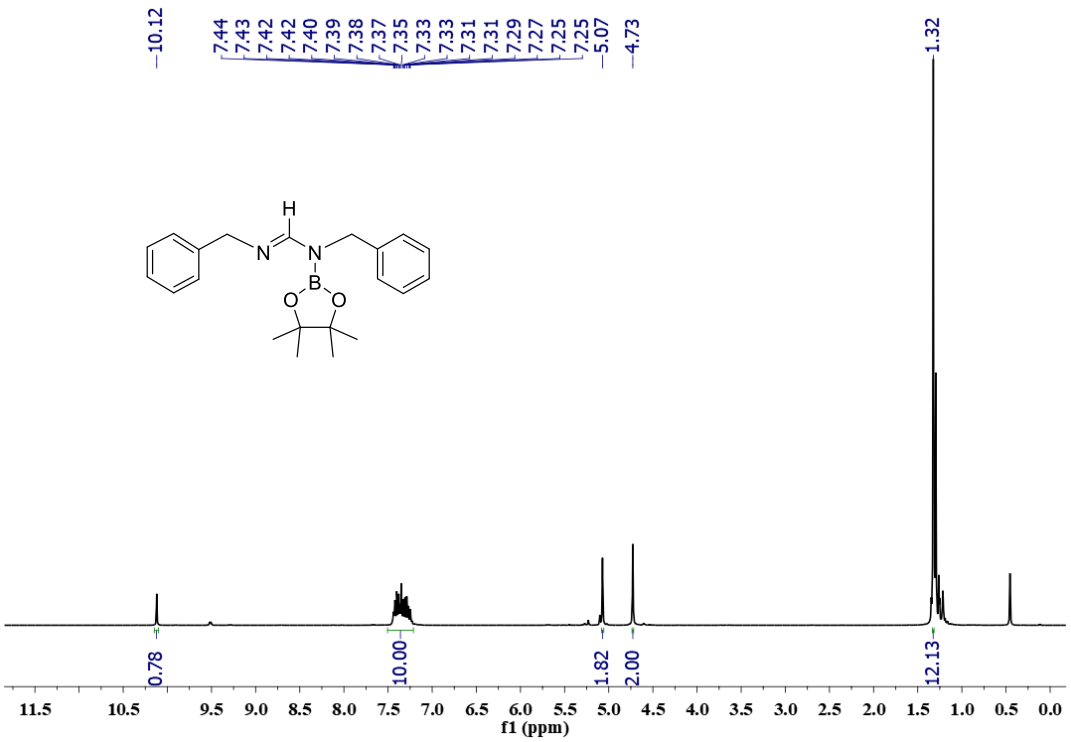


Figure S31: ^{1}H NMR spectrum of **2d** (400 MHz, $CDCl_3$, 25 ^{o}C).

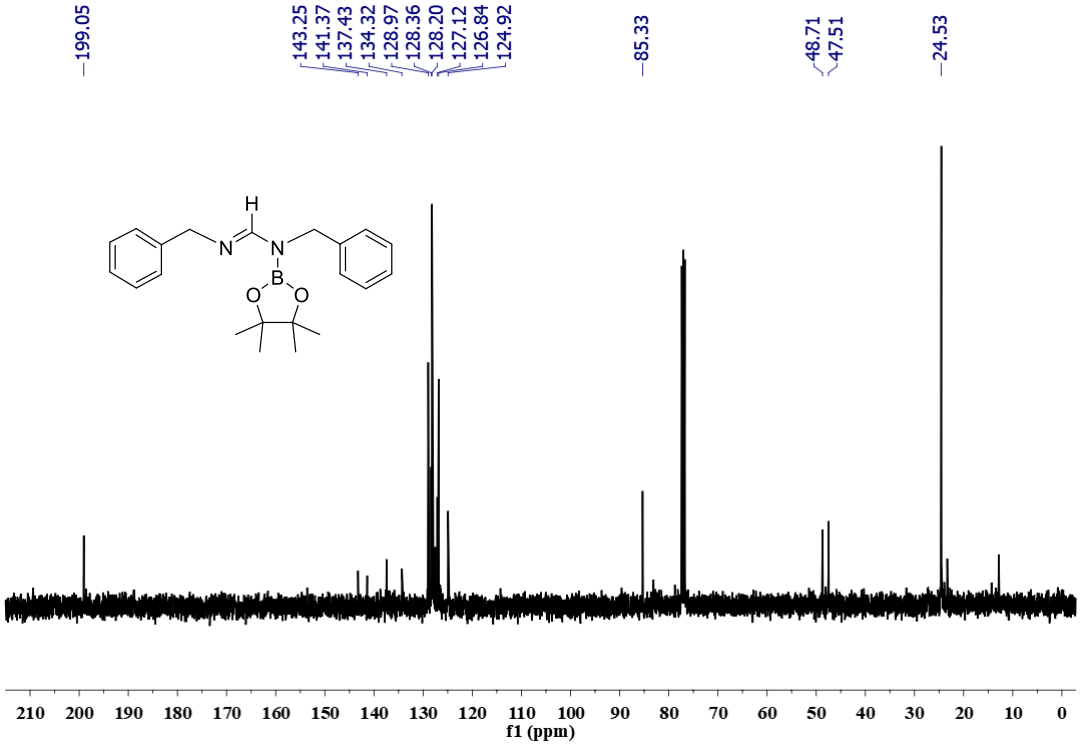


Figure S32: ^{13}C{^{1}H} NMR spectrum of **2d** (101 MHz, $CDCl_3$, 25 ^{o}C).

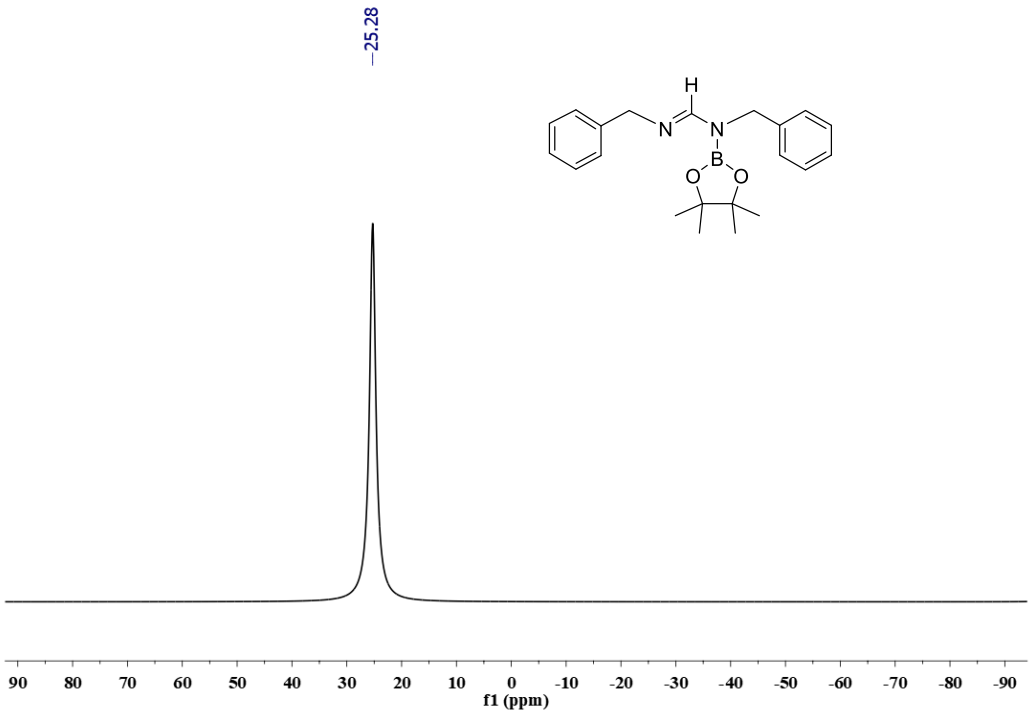


Figure S33: ^{11}B NMR spectrum of **2d** (128 MHz, $CDCl_3$, 25 ^{o}C).

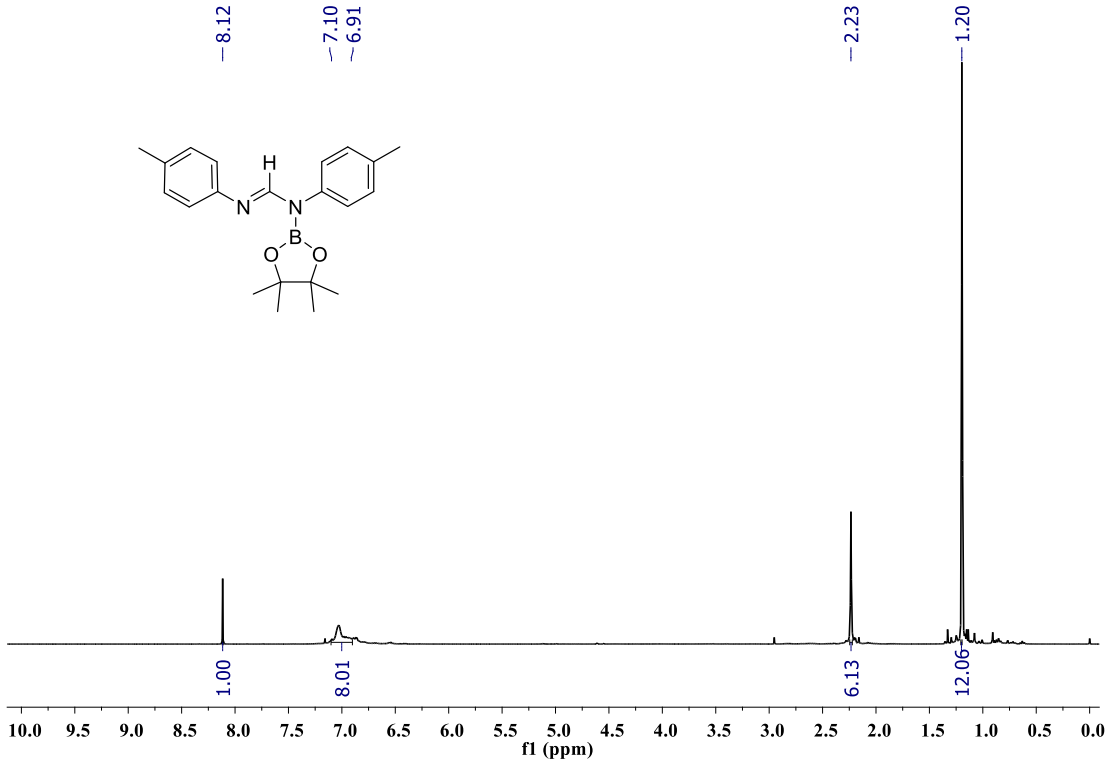


Figure S34: ^{1}H NMR spectrum of **2e** (400 MHz, $CDCl_3$, 25 ^{o}C).

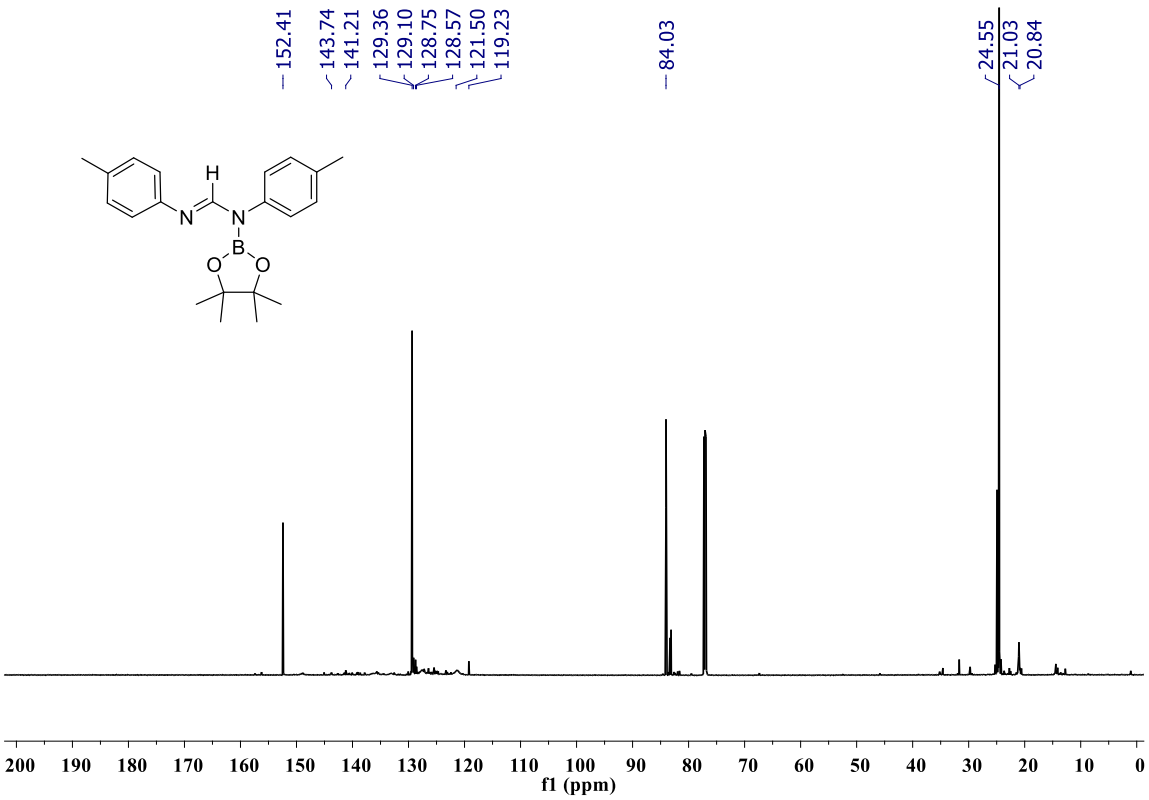


Figure S35: $^{13}C\{^{1}H\}$ NMR spectrum of **2e** (101 MHz, $CDCl_3$, 25 °C).

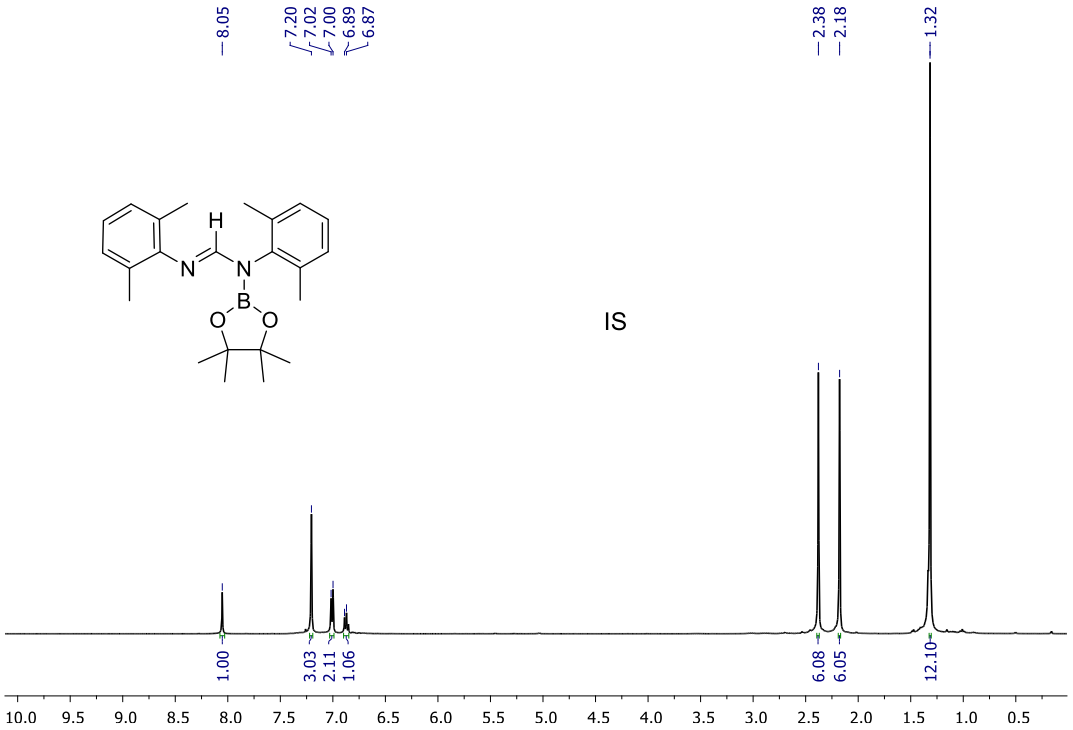


Figure S36: ^{1}H NMR spectrum of **2f** (400 MHz, $CDCl_3$, 25 °C).

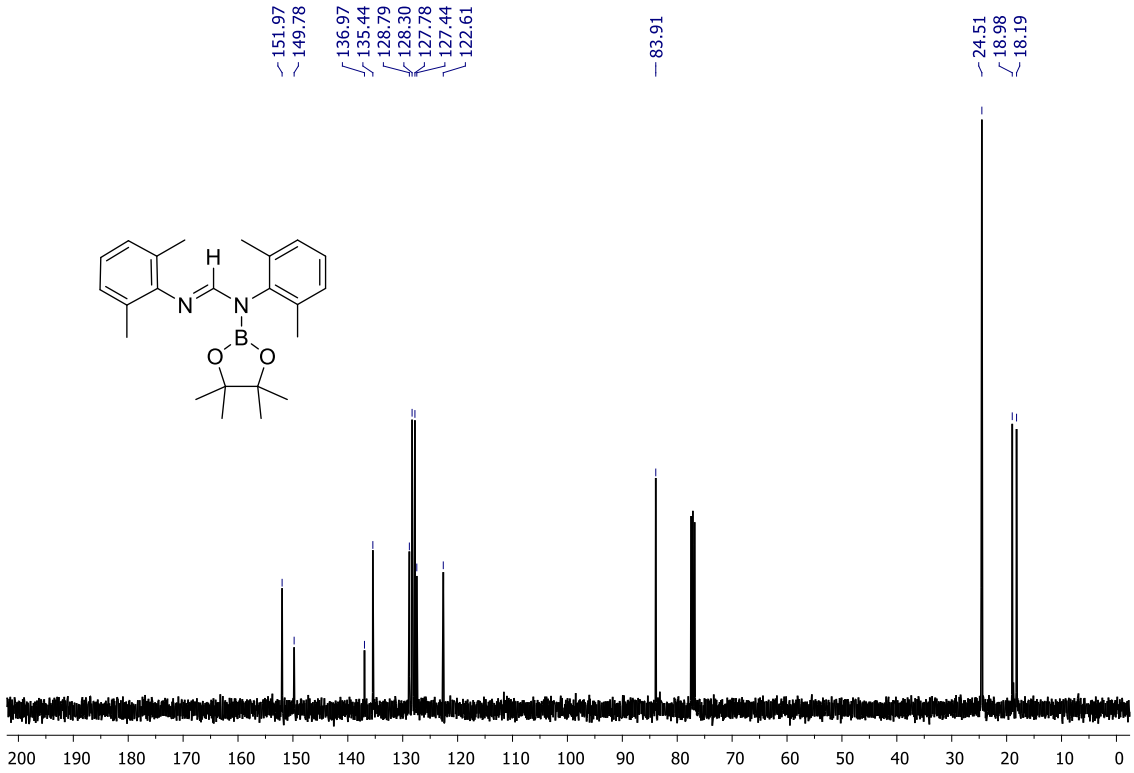


Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of **2f** (101 MHz, $CDCl_3$, 25 ^{o}C).

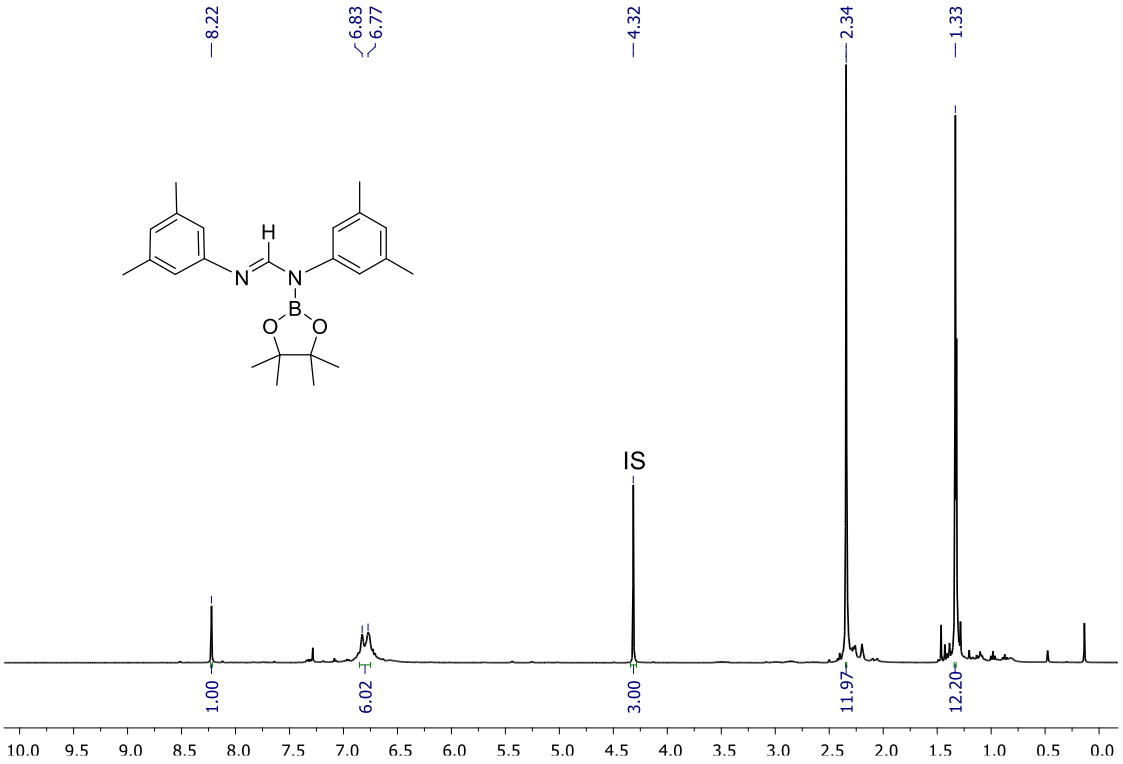


Figure S38: ^{1}H NMR spectrum of **2g** (400 MHz, $CDCl_3$, 25 ^{o}C). Nitromethane is used as an internal standard.

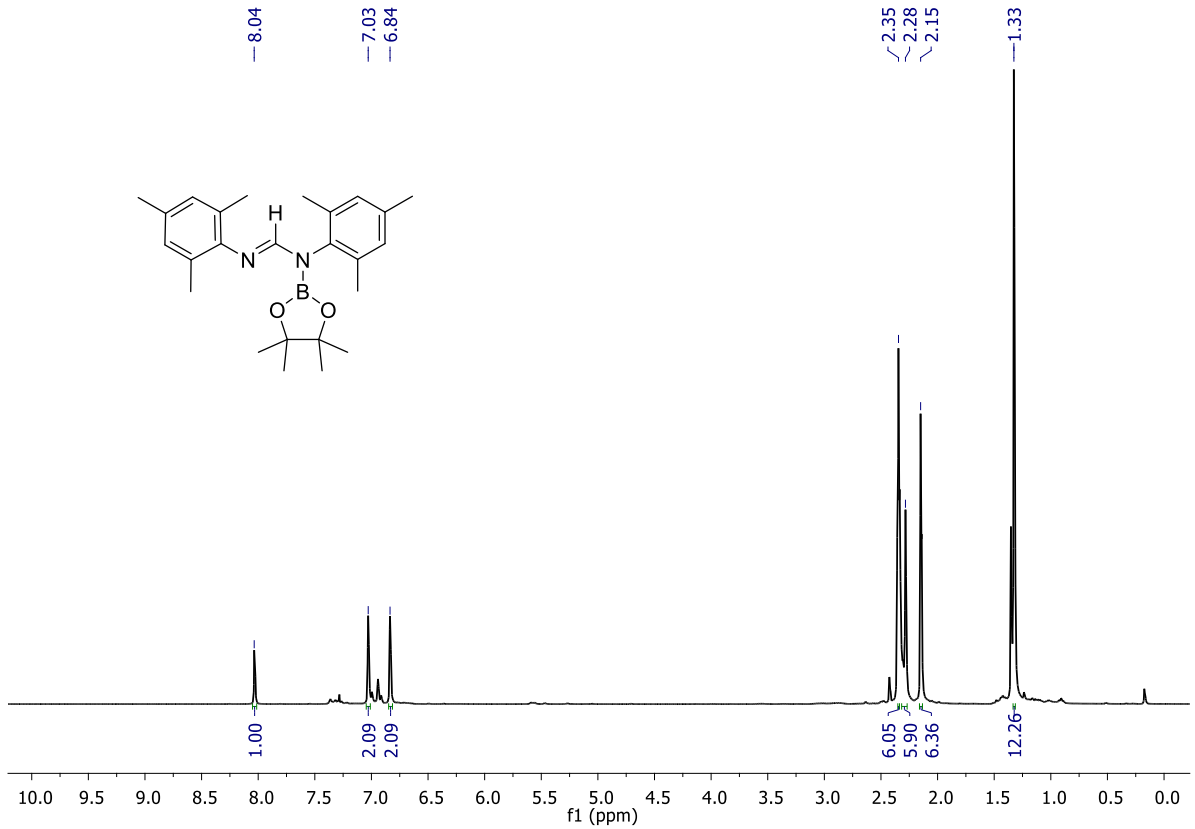


Figure S39: ^{1}H NMR spectrum of **2h** (400 MHz, $CDCl_3$, 25 ^{o}C).

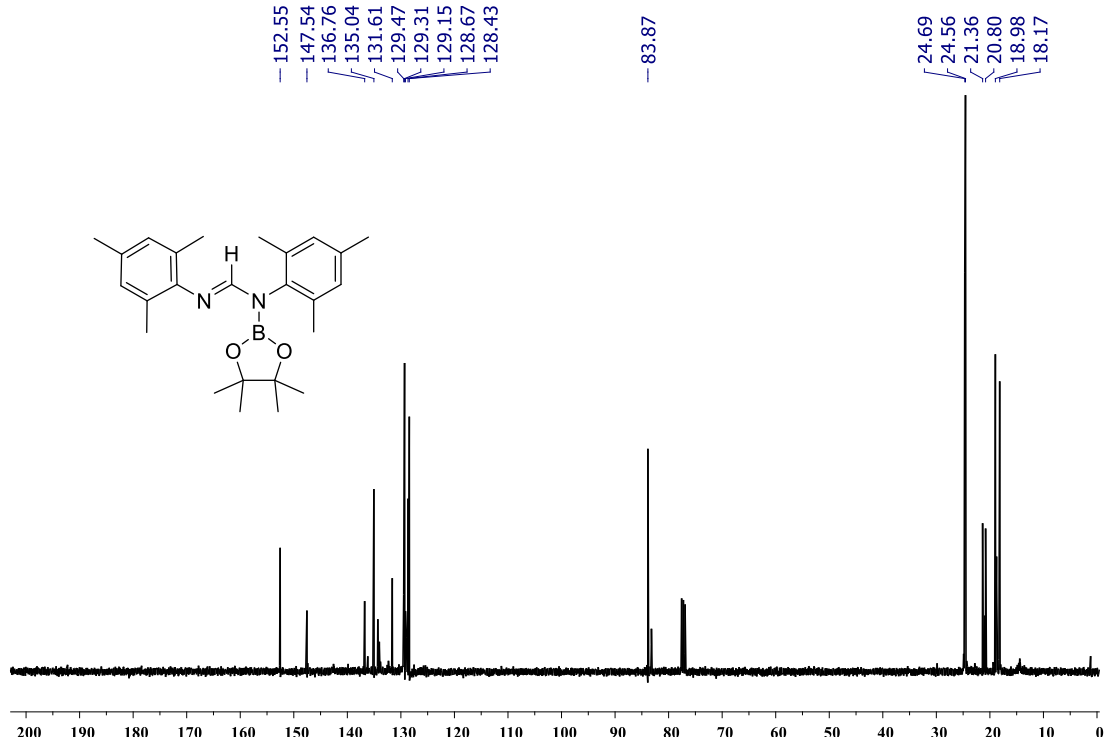


Figure S40: ^{13}C{^{1}H} NMR spectrum of **2h** (101 MHz, $CDCl_3$, 25 ^{o}C).

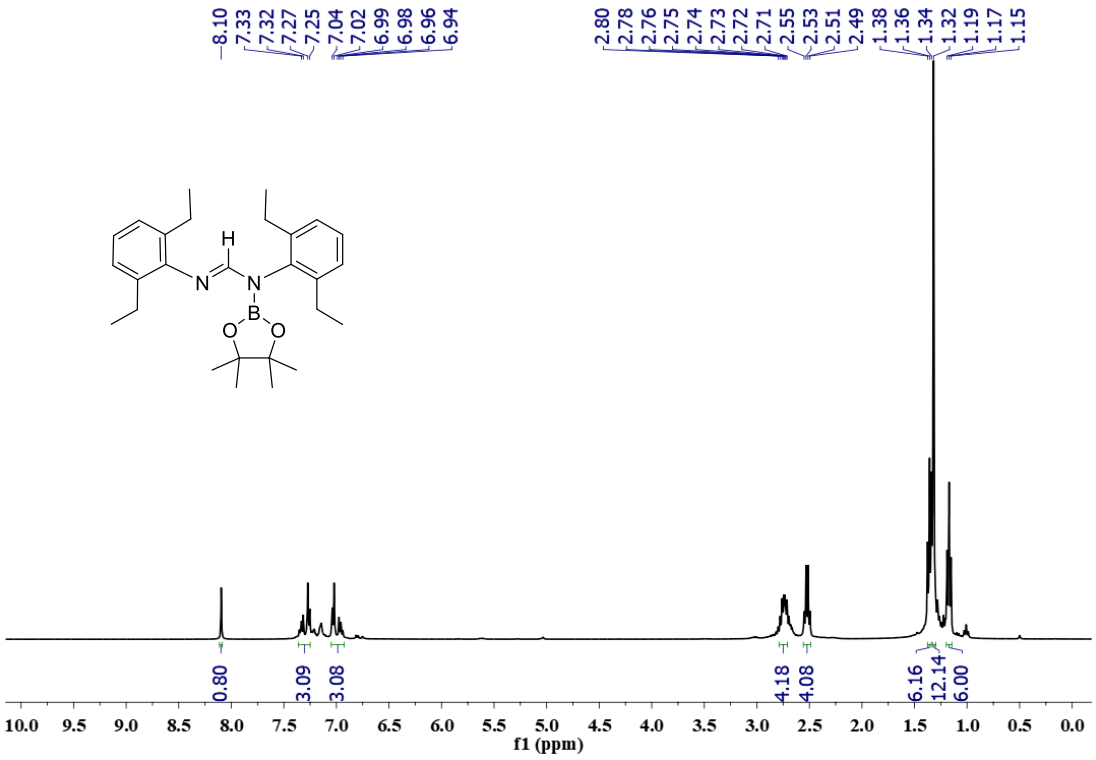


Figure S41: ^{1}H NMR spectrum of **2i** (400 MHz, $CDCl_3$, 25 ^{o}C).

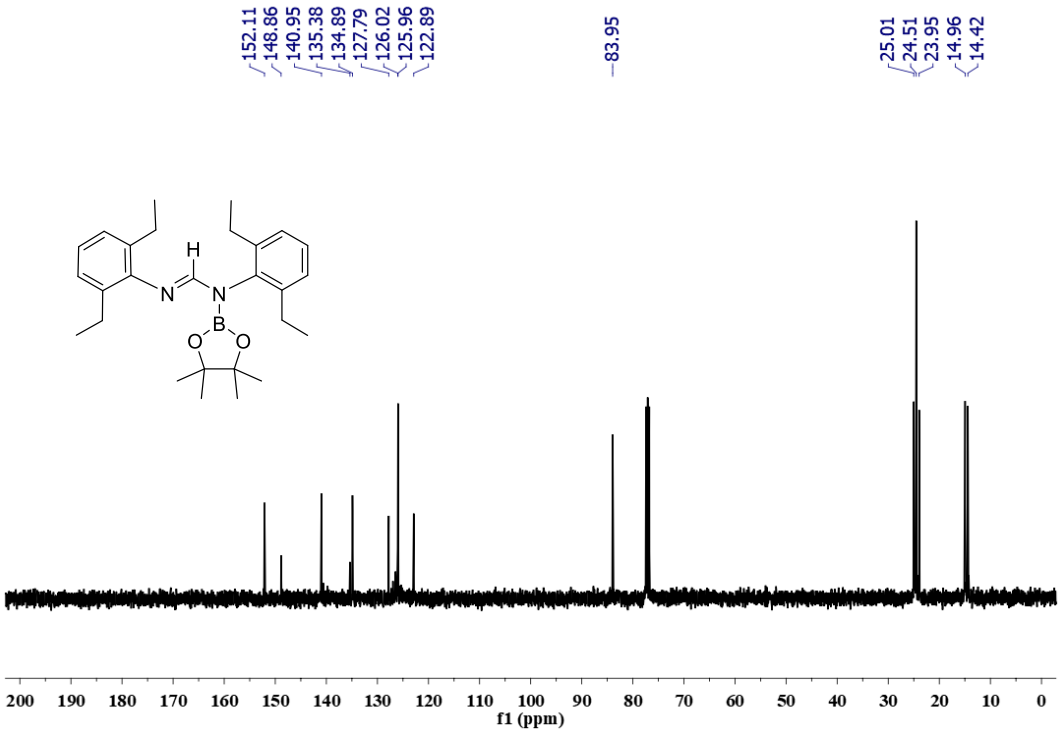


Figure S42: $^{13}C\{^{1}H\}$ NMR spectrum of **2i** (101 MHz, $CDCl_3$, 25 ^{o}C).

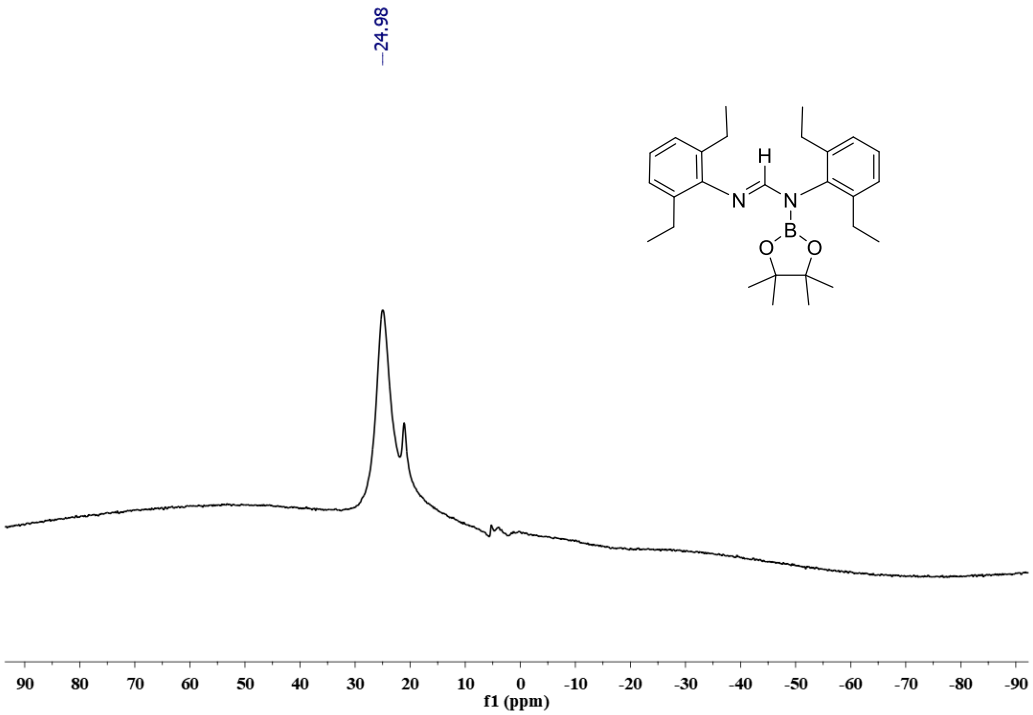


Figure S43: ^{11}B NMR spectrum of **2i** (128 MHz, $CDCl_3$, 25 ^{o}C).

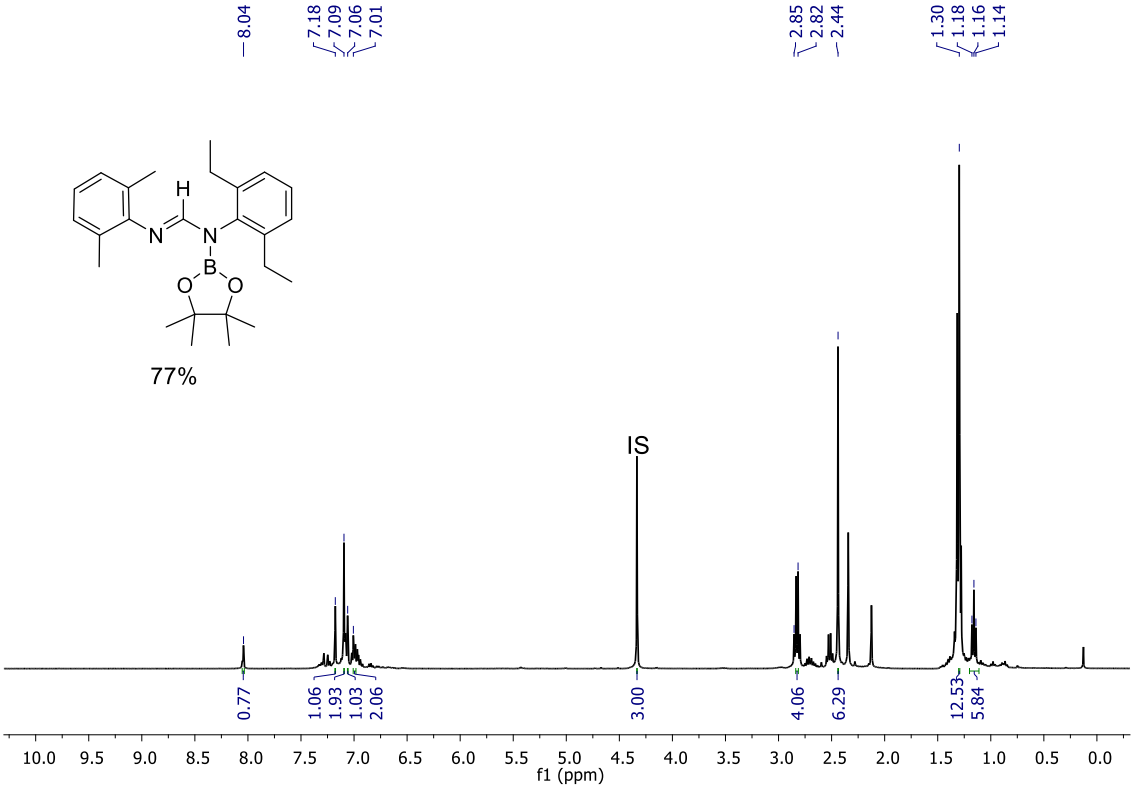


Figure S44: ^{1}H NMR spectrum of **2j** (400 MHz, $CDCl_3$, 25 ^{o}C). Nitromethane is used as an internal standard.

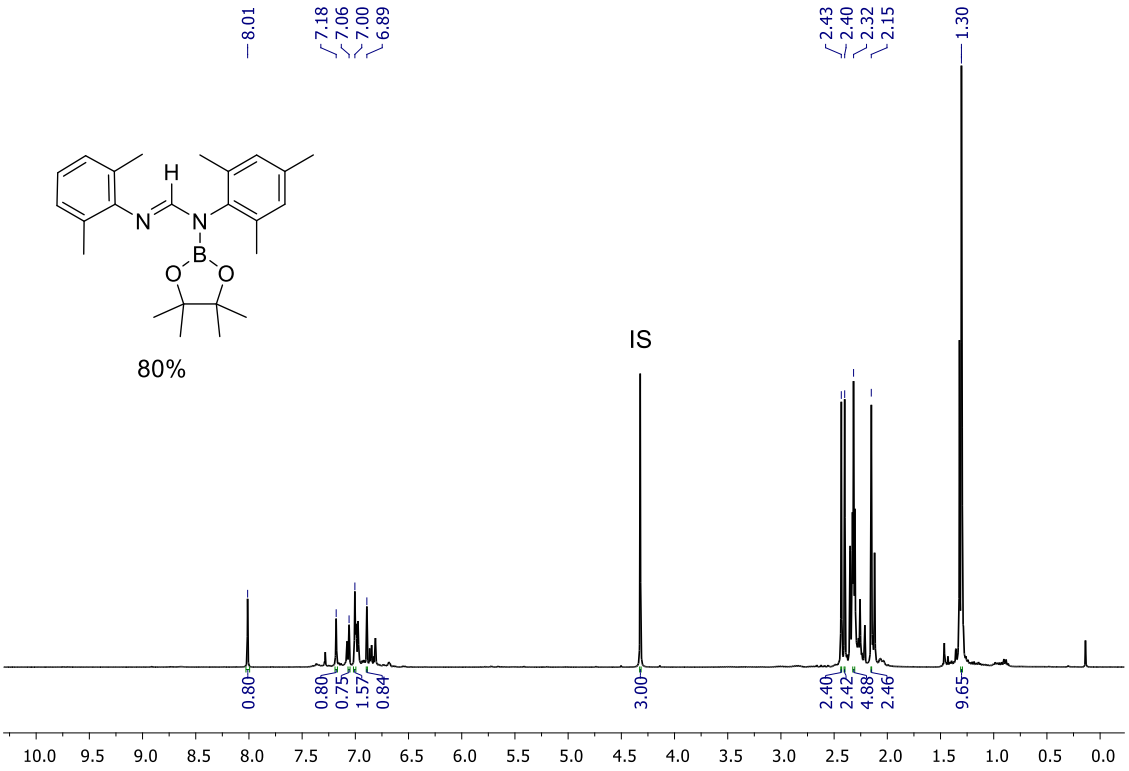


Figure S45: ^{1}H NMR spectrum of **2k** (400 MHz, $CDCl_3$, 25 ^{o}C). Nitromethane is used as an internal standard.

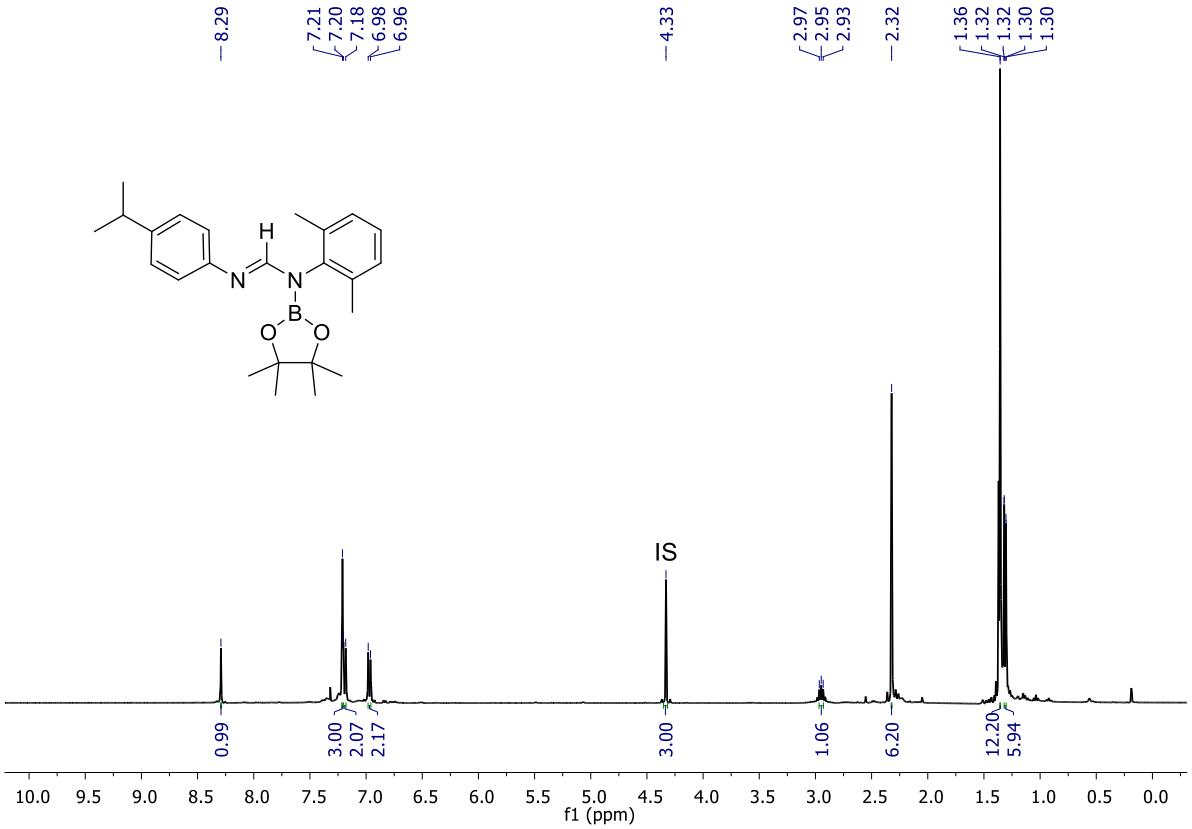


Figure S46: ^{1}H NMR spectrum of **2l** (400 MHz, $CDCl_3$, 25 ^{o}C). Nitromethane is used as an internal standard.

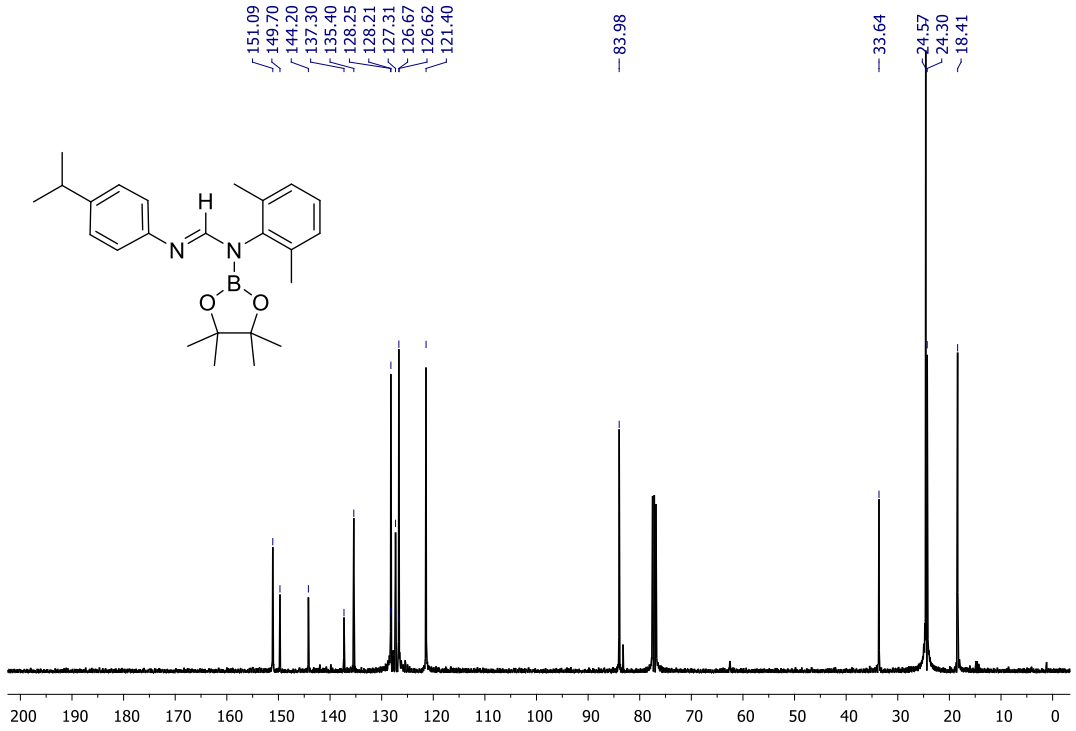


Figure S47: $^{13}C\{^{1}H\}$ NMR spectrum of **2l** (101 MHz, $CDCl_3$, 25 °C).

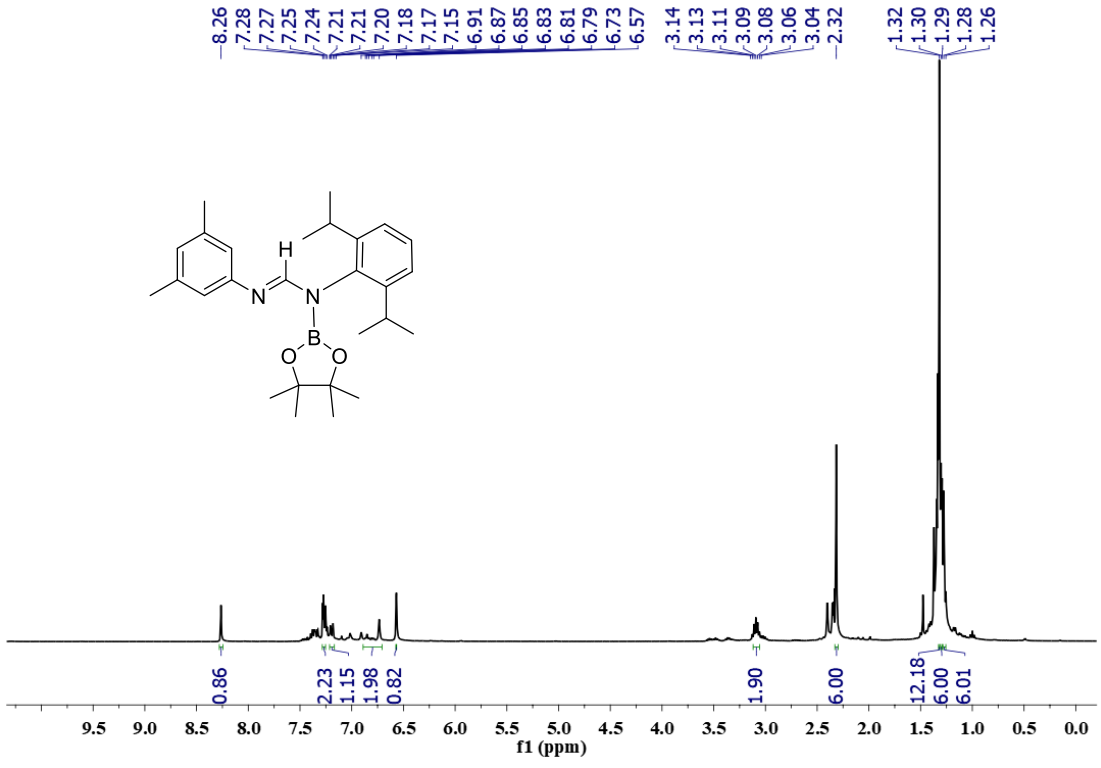


Figure S48: ^{1}H NMR spectrum of **2m** (400 MHz, $CDCl_3$, 25 °C).

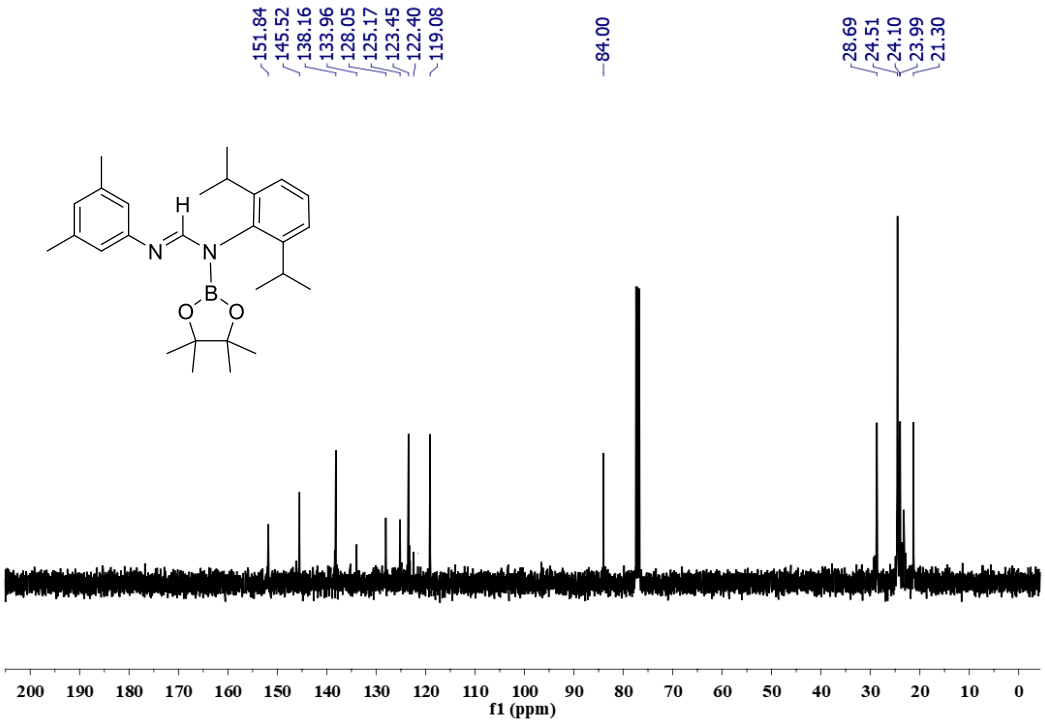


Figure S49: $^{13}C\{^{1}H\}$ NMR spectrum of **2m** (101 MHz, $CDCl_3$, 25 °C).

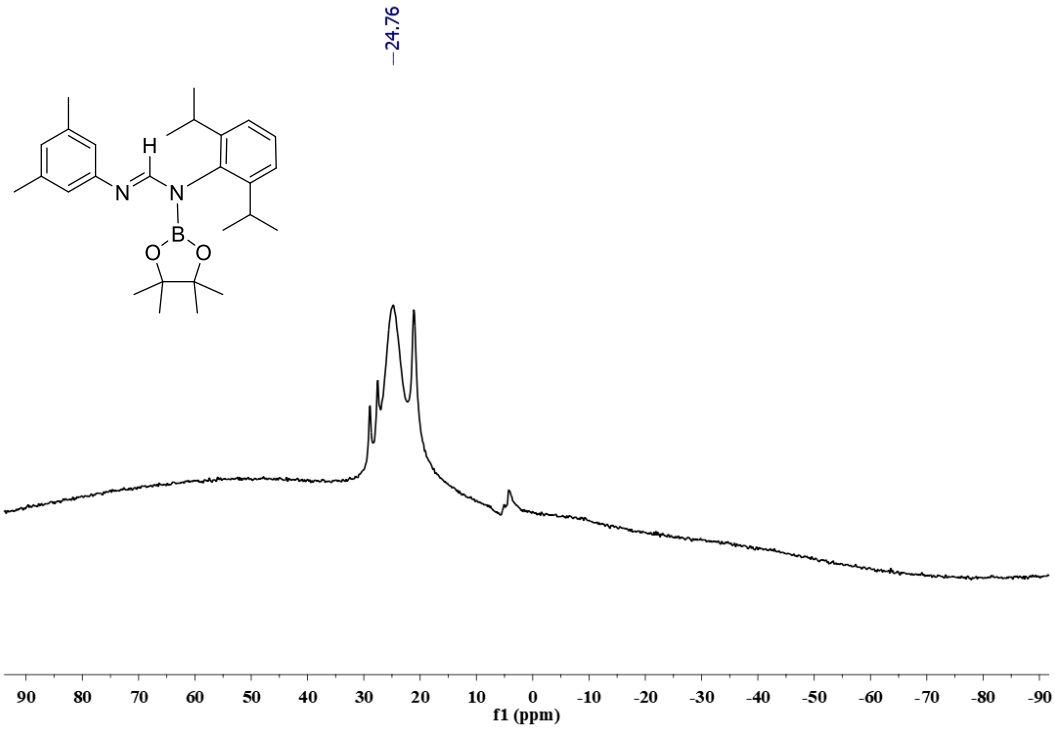


Figure S50: ^{11}B NMR spectrum of **2m** (128 MHz, $CDCl_3$, 25 °C).

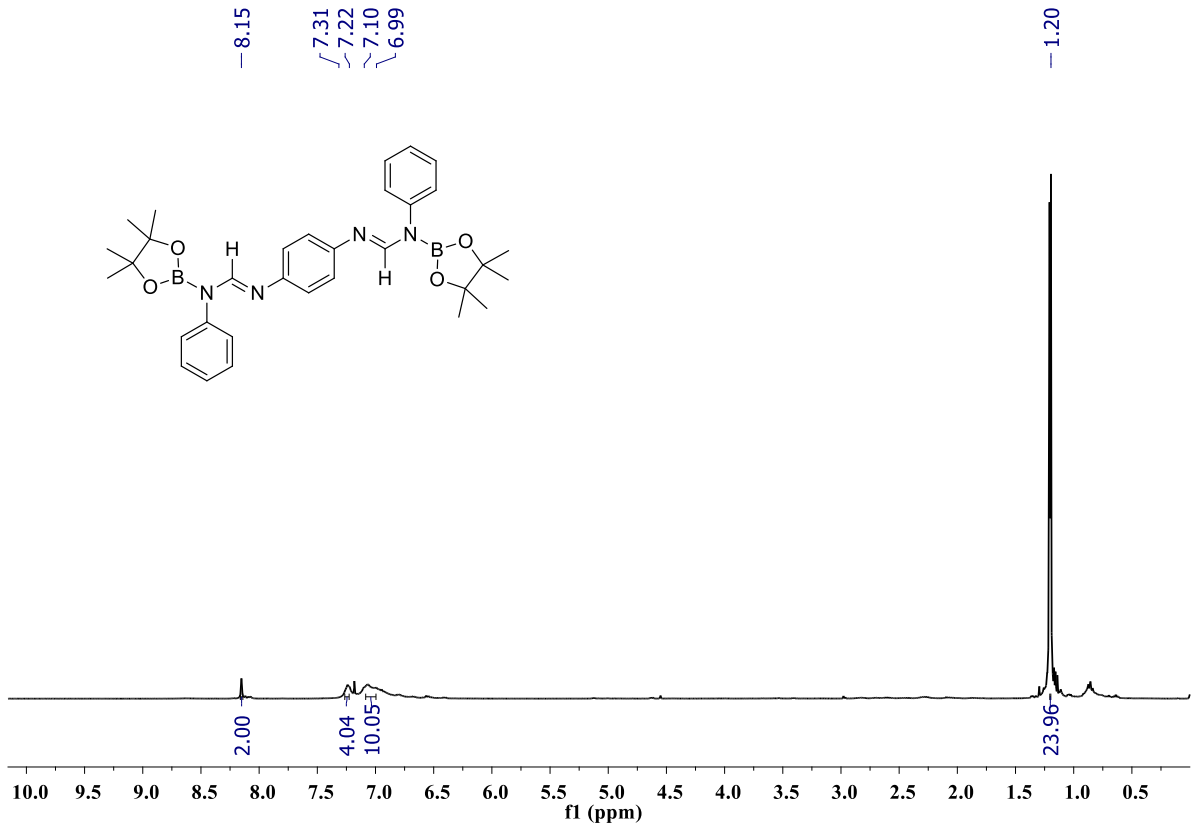


Figure S51: ^{1}H NMR spectrum of **2n** (400 MHz, $CDCl_3$, 25 ^{o}C).

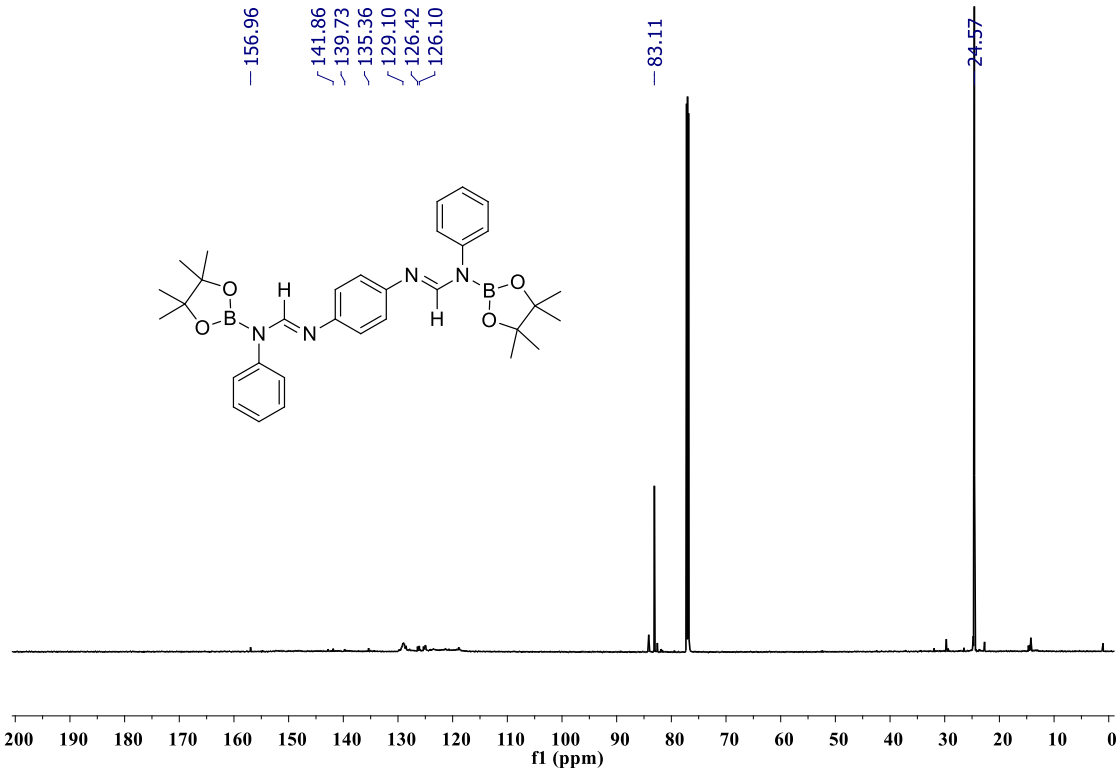


Figure S52: ^{13}C{^{1}H} NMR spectrum of **2n** (101 MHz, $CDCl_3$, 25 ^{o}C).

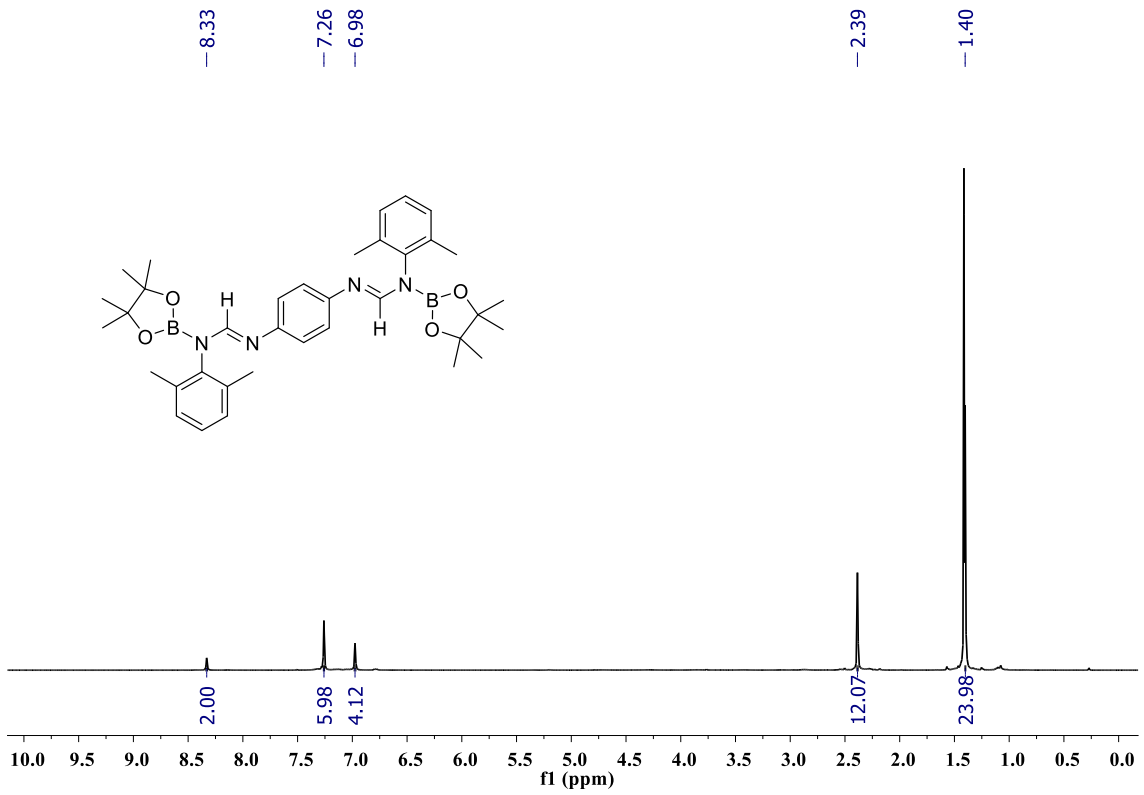


Figure S53: ^{1}H NMR spectrum of **2o** (400 MHz, C_6D_6, 25 ^{o}C).

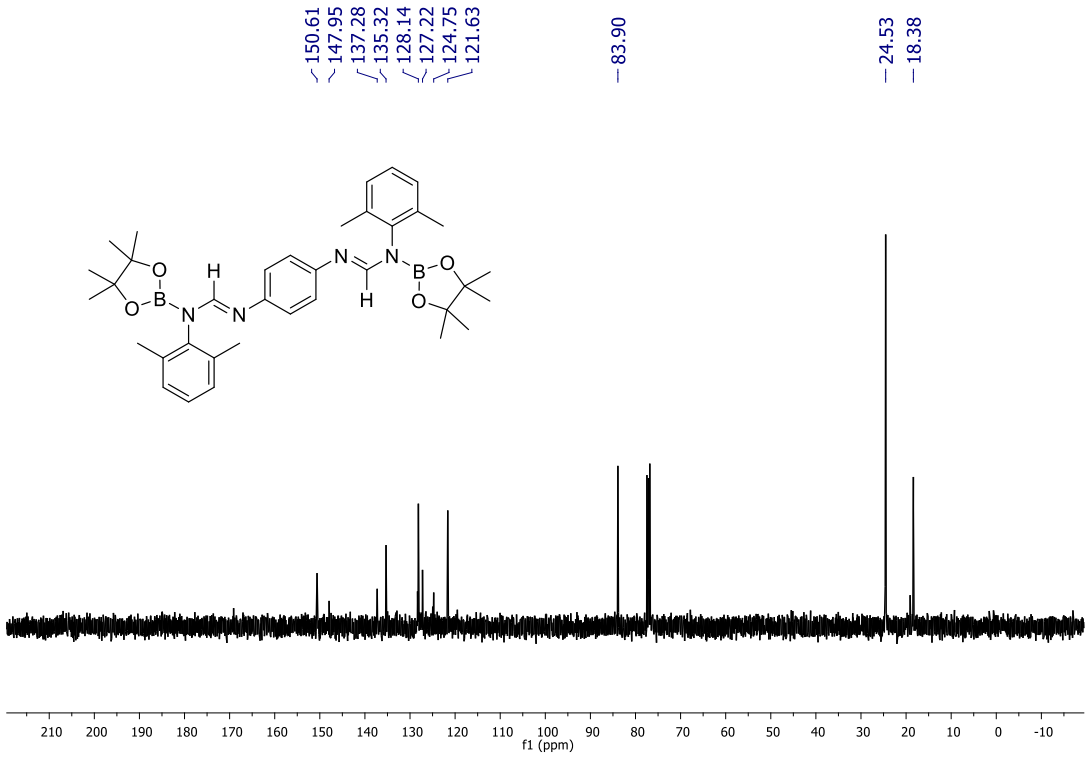


Figure S54: ^{13}C{^{1}H} NMR spectrum of **2o** (101 MHz, C_6D_6, 25 ^{o}C).

^{1}H, $^{13}C\{^{1}H\}$ and ^{11}B NMR Spectra of N-borylated formamide, thioformamide, selenoformamide, and N-borylated methyl amine:

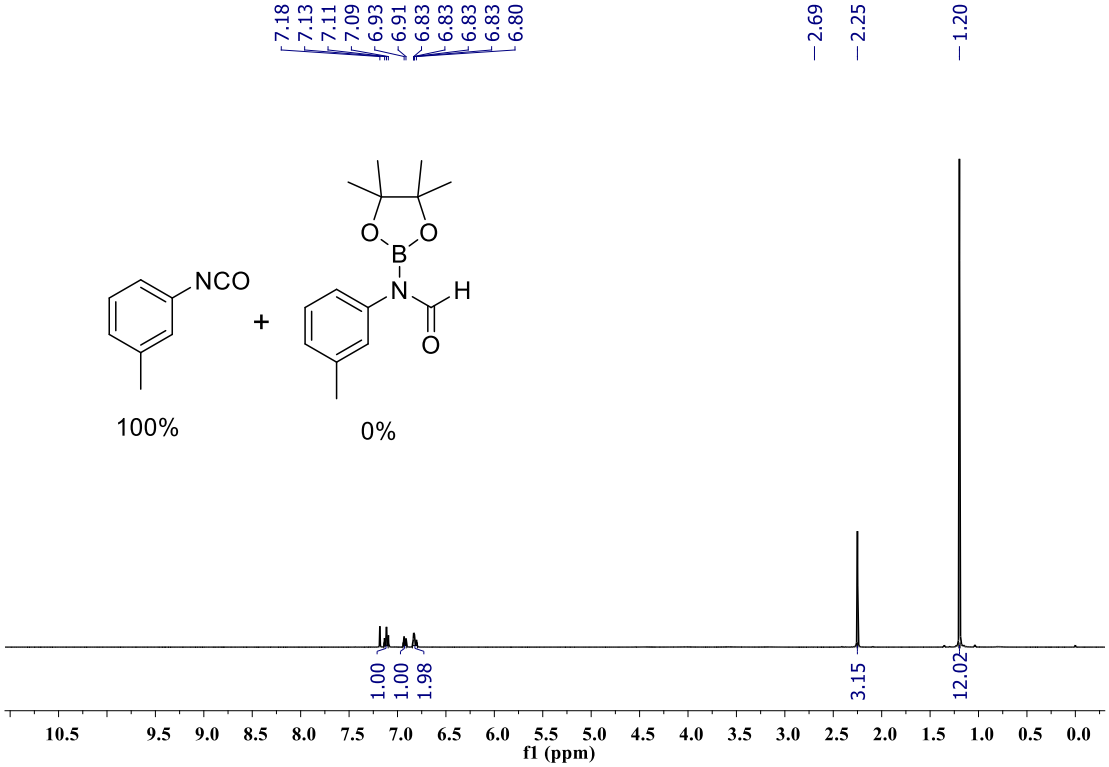


Figure S55: ^{1}H NMR spectrum of m-Tolylisocyanate with 1 equivalent of HBpin in the absence of catalyst (400 MHz, $CDCl_3$).

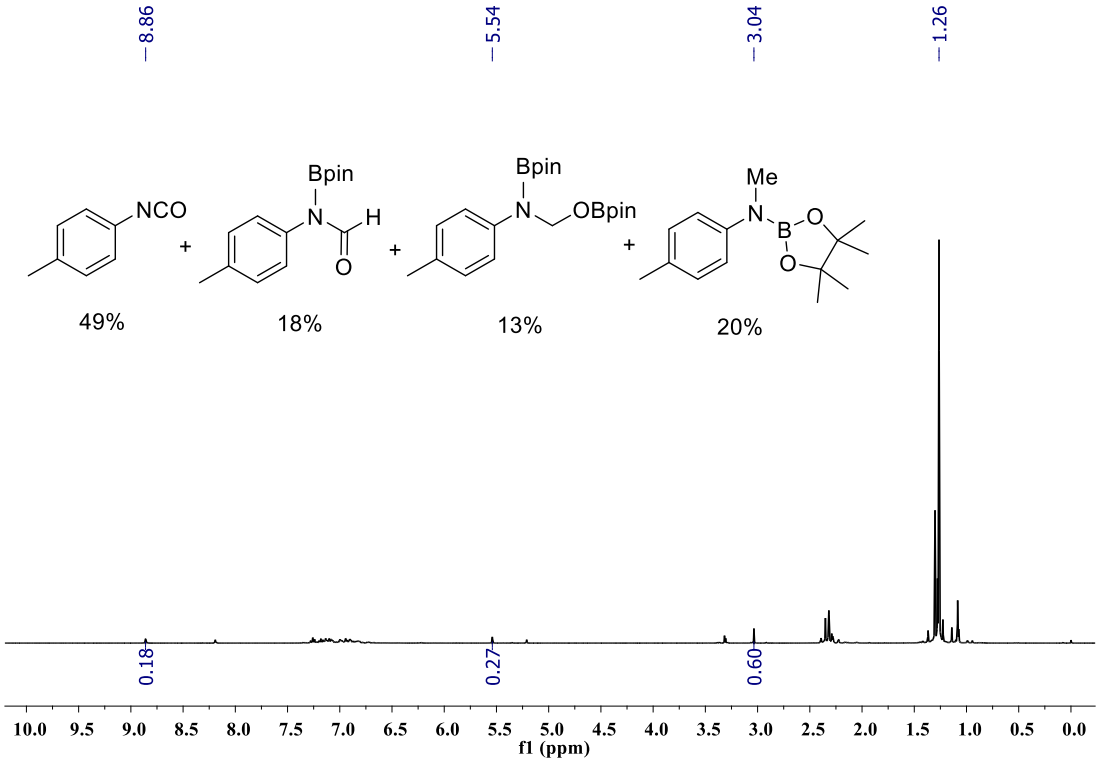


Figure S56: ^{1}H NMR spectrum of p-Tolylisocyanate with 3 equivalents of HBpin in the absence of catalyst (400 MHz, $CDCl_3$).

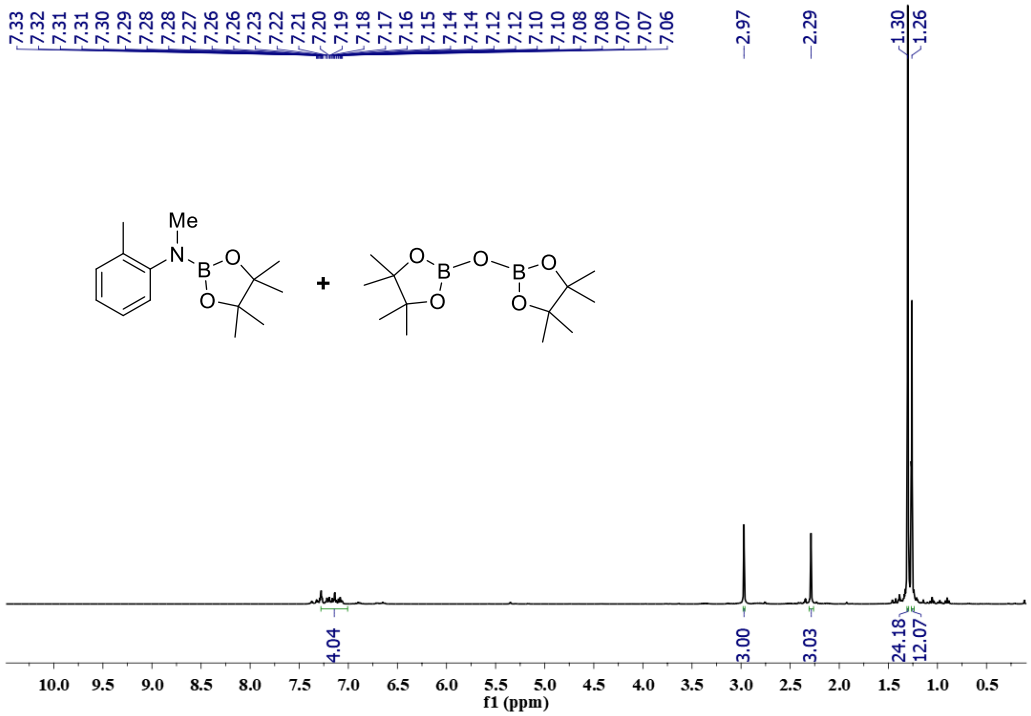


Figure S57: ^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$, 25 ^{o}C).

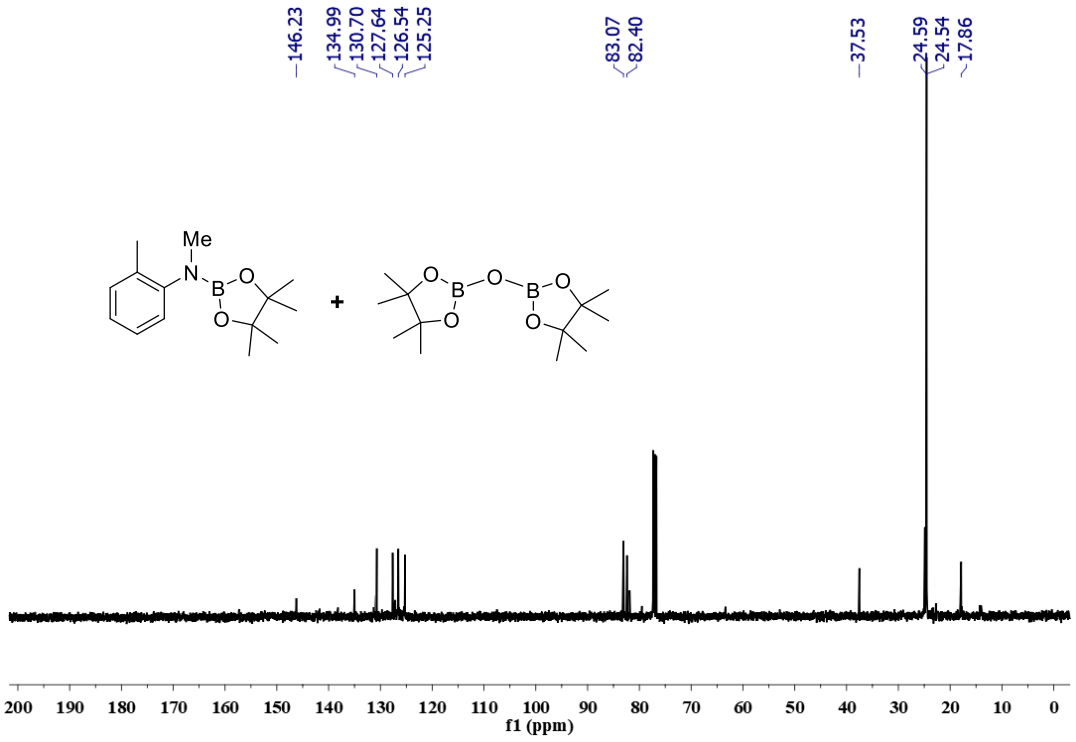


Figure S58: ^{13}C{^{1}H} NMR spectrum of **4a** (101 MHz, $CDCl_3$, 25 ^{o}C).

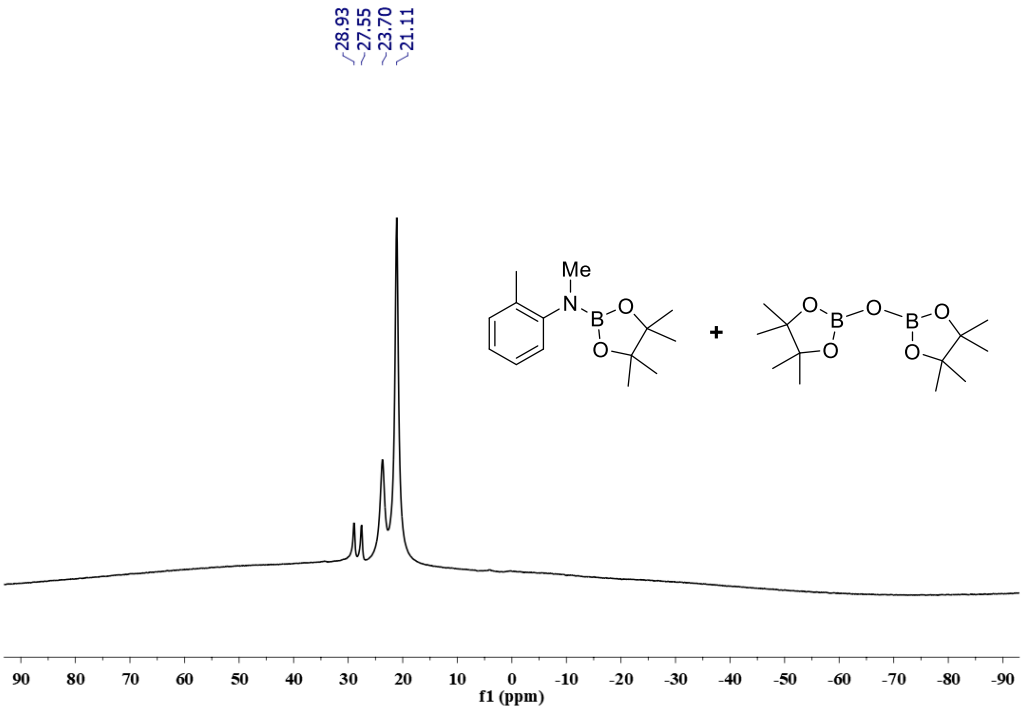


Figure S59: ^{11}B NMR spectrum of **5a** (128 MHz, $CDCl_3$, 25 ^{o}C). A doublet peak observed at δ 27.55 - 28.93 ppm arises from free HBpin.

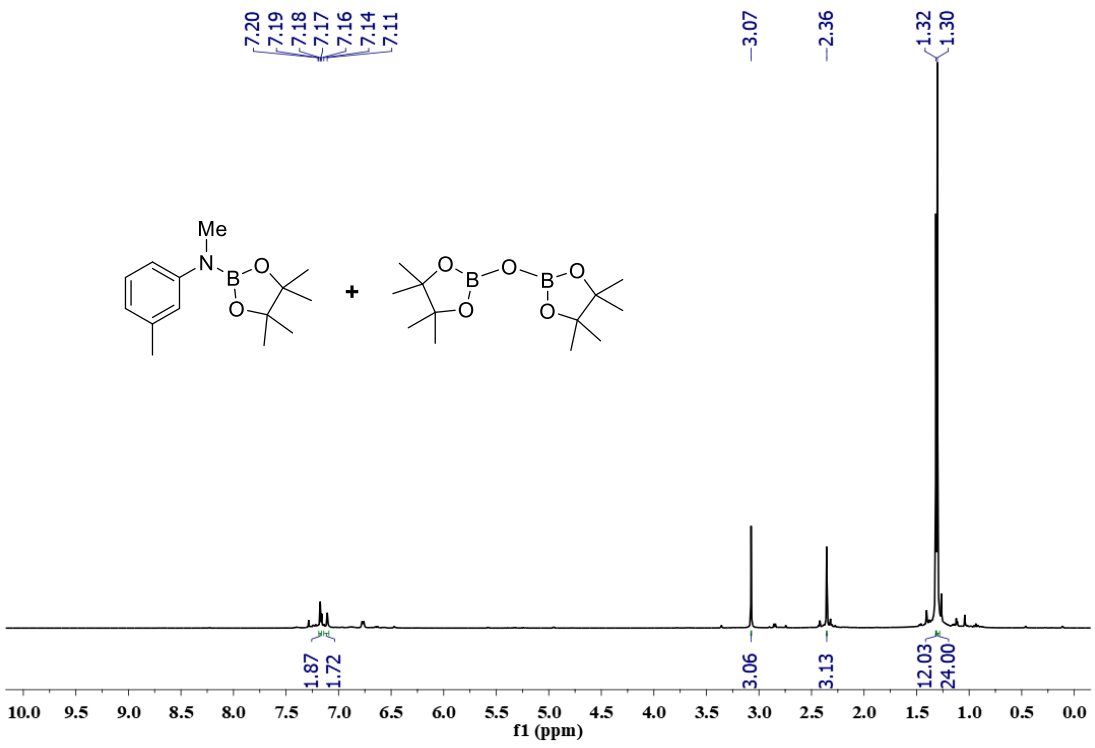


Figure S60: ^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$, 25 ^{o}C).

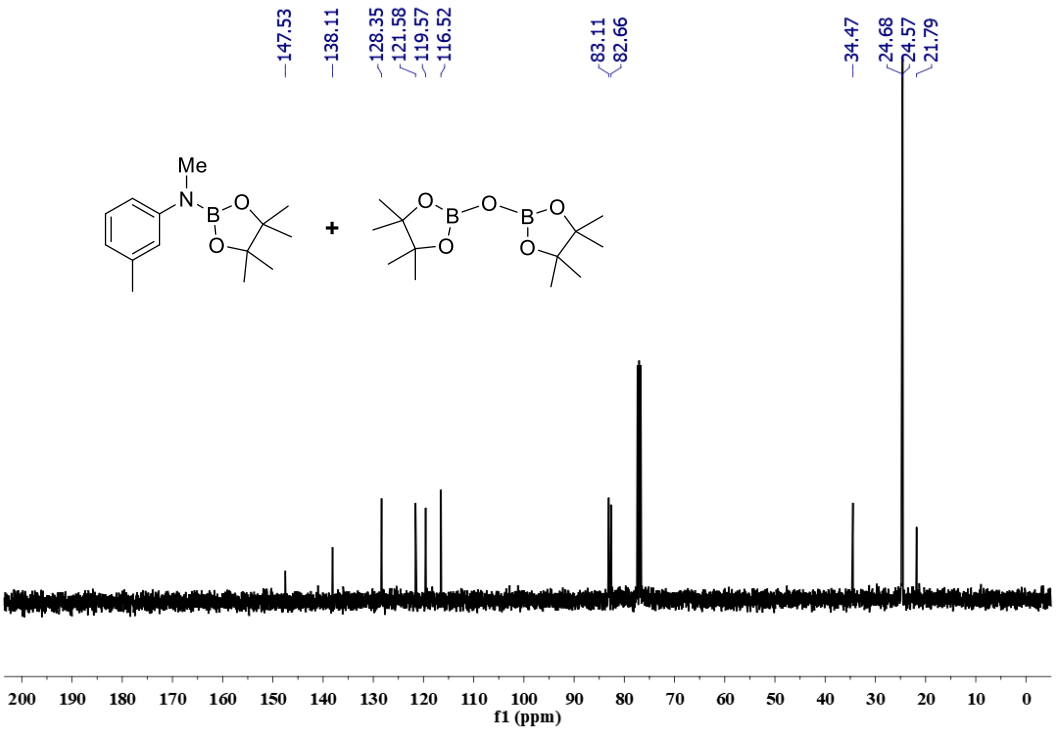


Figure S61: $^{13}C\{^{1}H\}$ NMR spectrum of **4b** (101 MHz, $CDCl_3$, 25 °C).

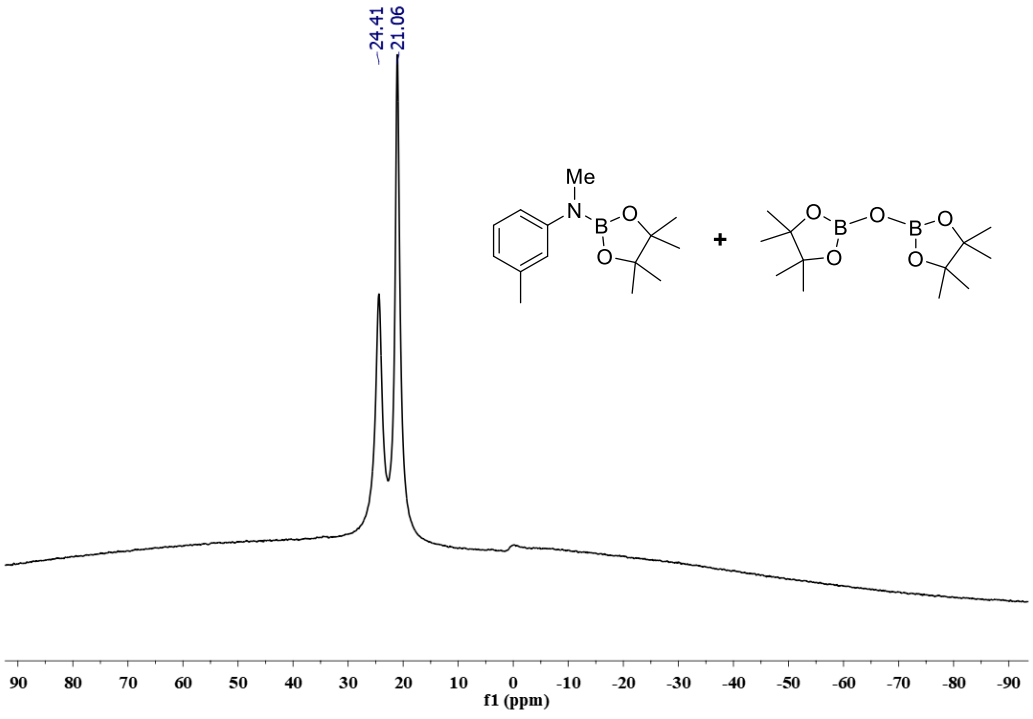


Figure S62: ^{11}B NMR spectrum of **4b** (128 MHz, $CDCl_3$, 25 °C).

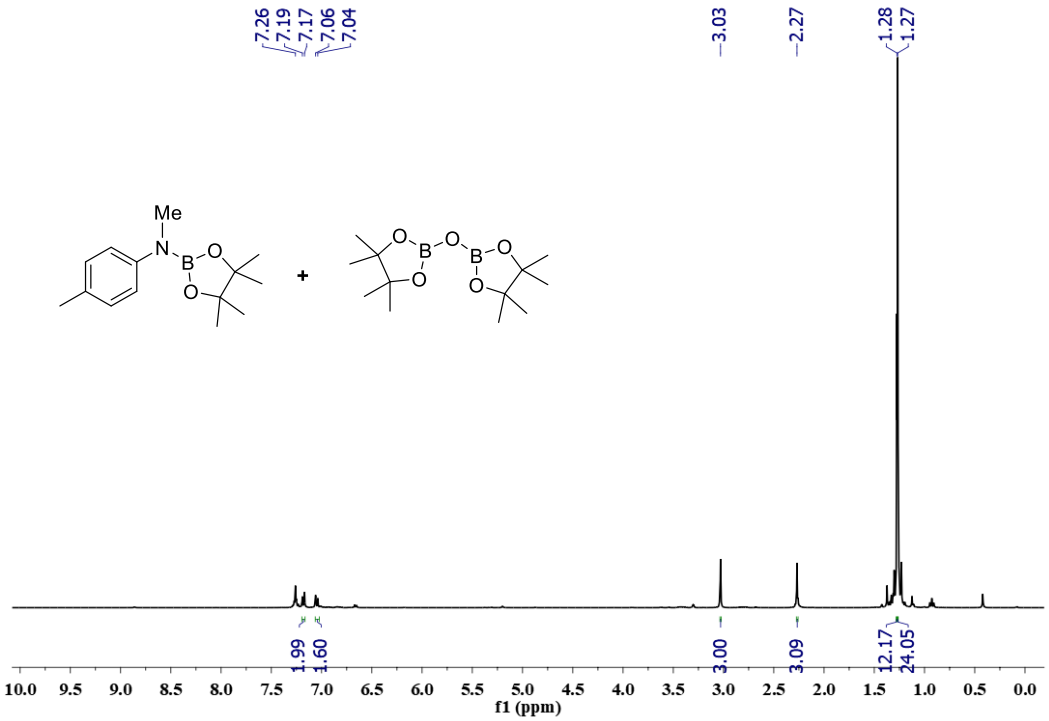


Figure S63: ^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$, 25 ^{o}C).

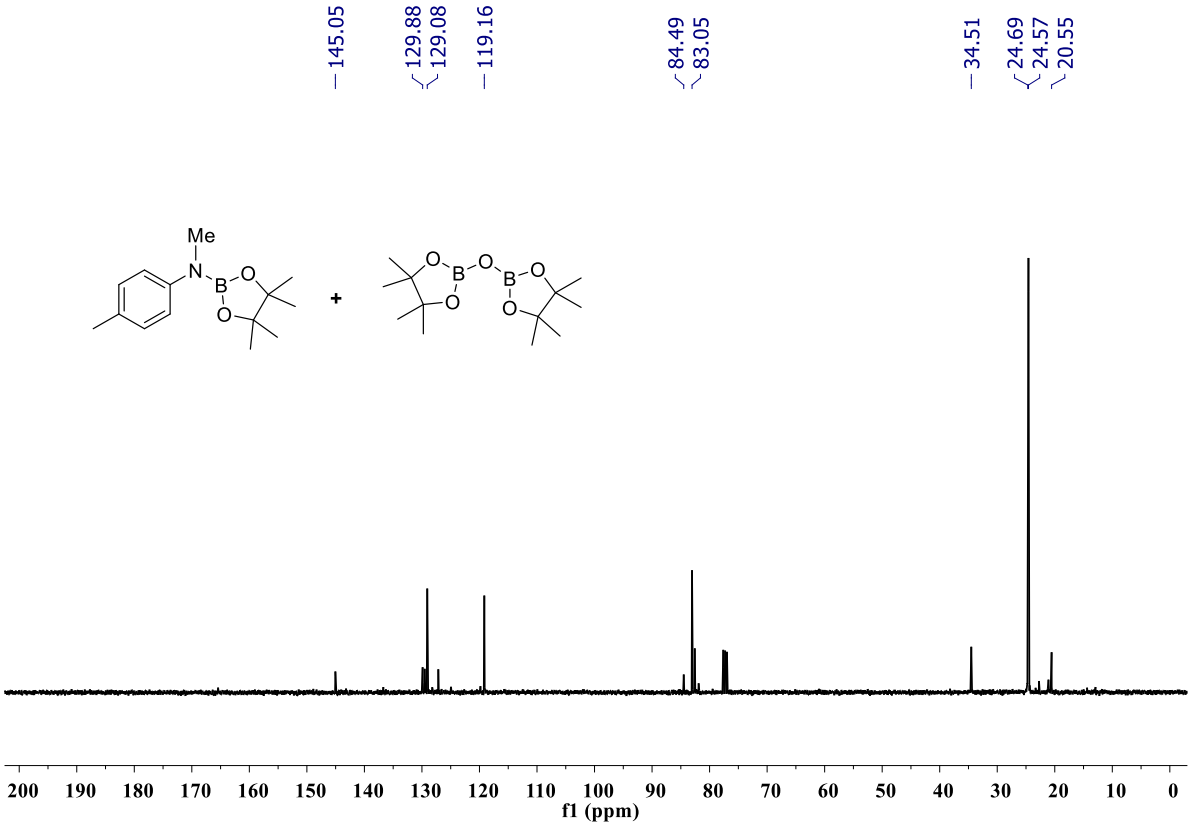


Figure S64: ^{13}C{^{1}H} NMR spectrum of **4c** (101 MHz, $CDCl_3$, 25 ^{o}C).

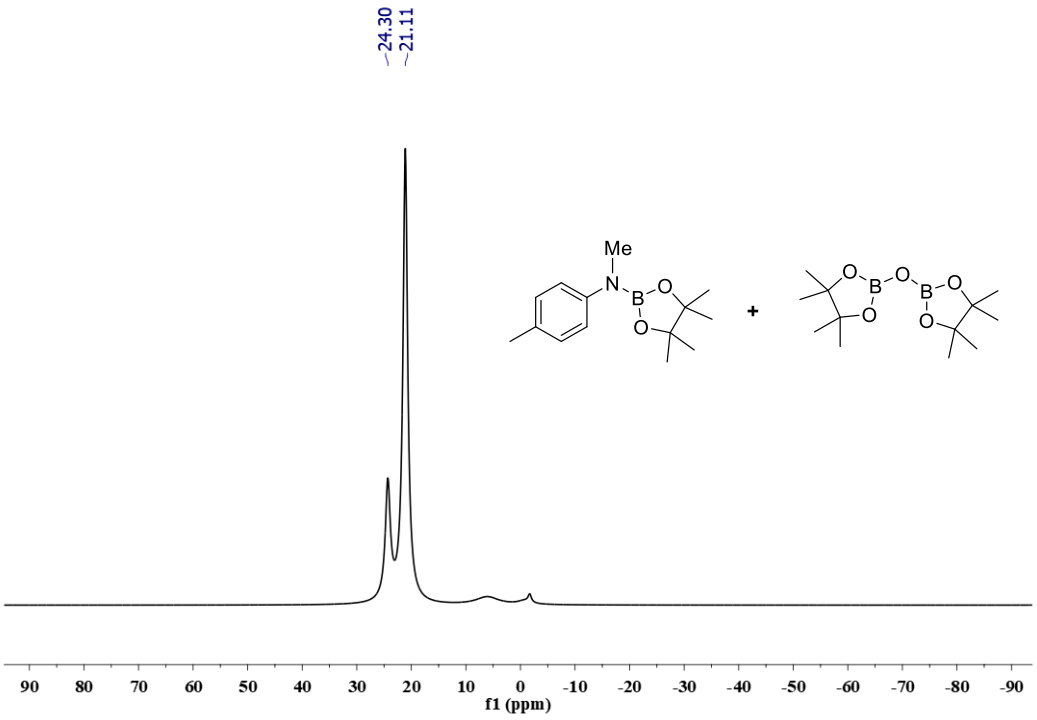


Figure S65: ^{11}B NMR spectrum of **4c** (128 MHz, $CDCl_3$, 25 ^{o}C).

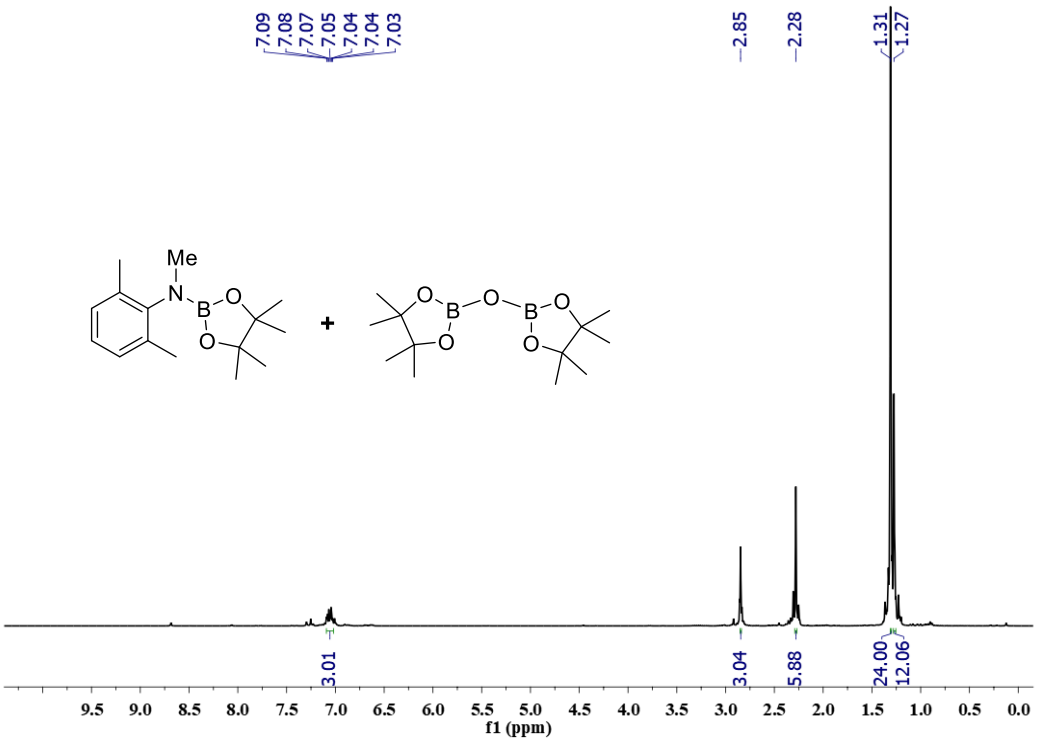


Figure S66: ^{1}H NMR spectrum of **4d** (400 MHz, $CDCl_3$, 25 ^{o}C).

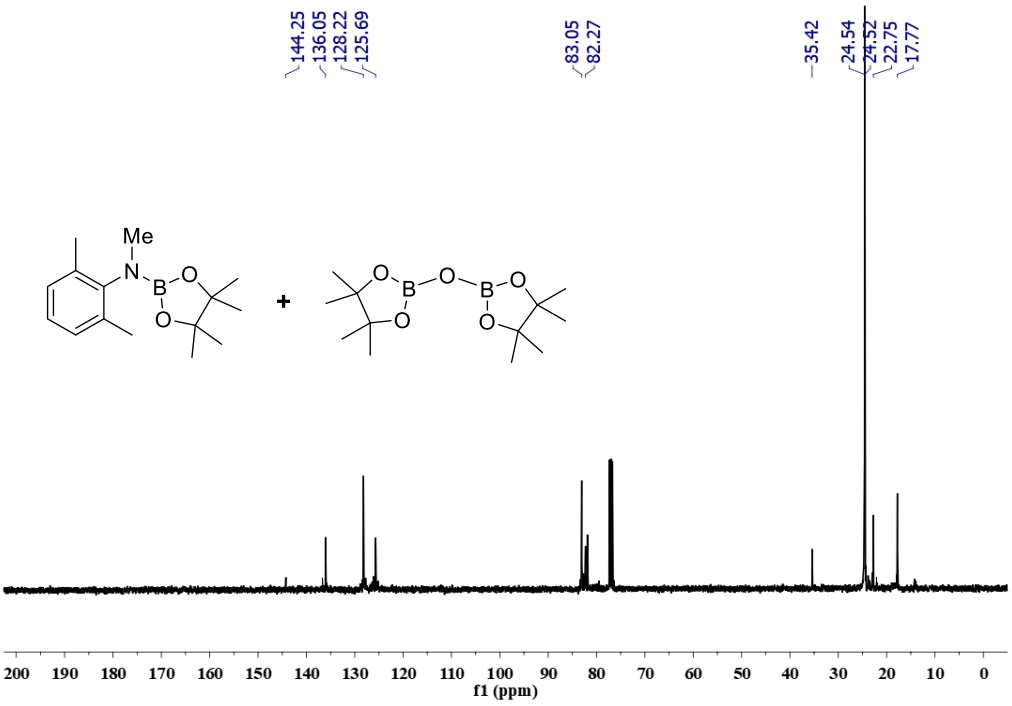


Figure S67: $^{13}C\{^{1}H\}$ NMR spectrum of **4d** (101 MHz, $CDCl_3$, 25 °C).

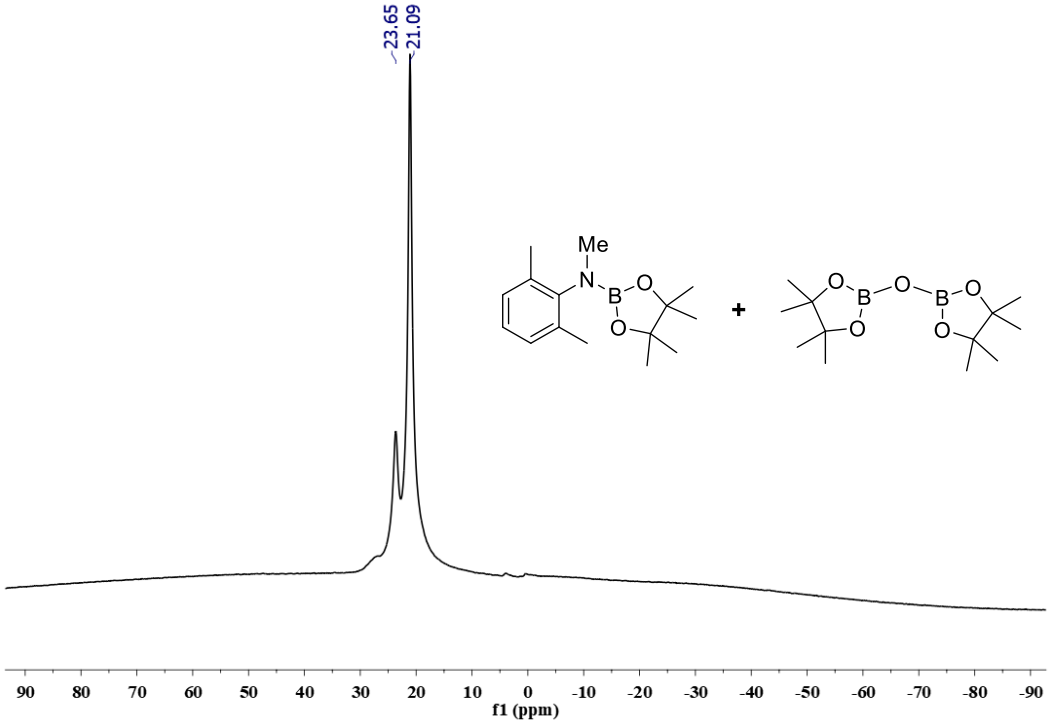


Figure S68: ^{11}B NMR spectrum of **4d** (128 MHz, $CDCl_3$, 25 °C).

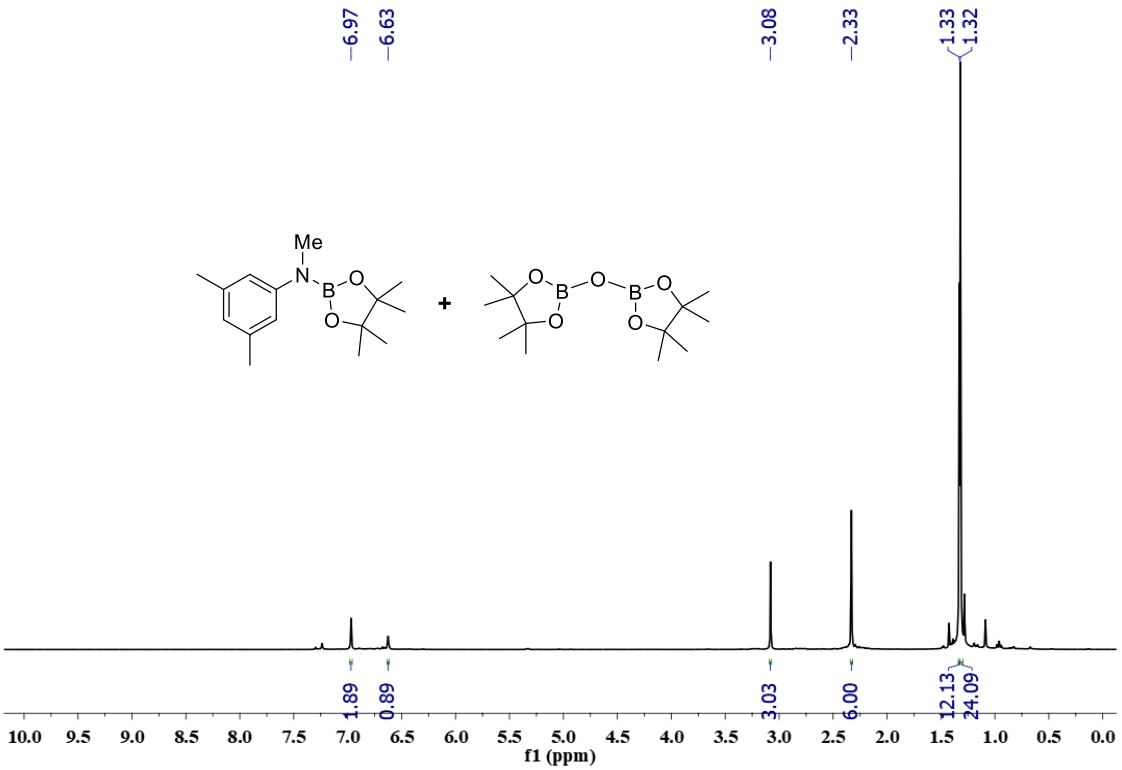


Figure S69: ^{1}H NMR spectrum of **4e** (400 MHz, $CDCl_3$, 25 °C).

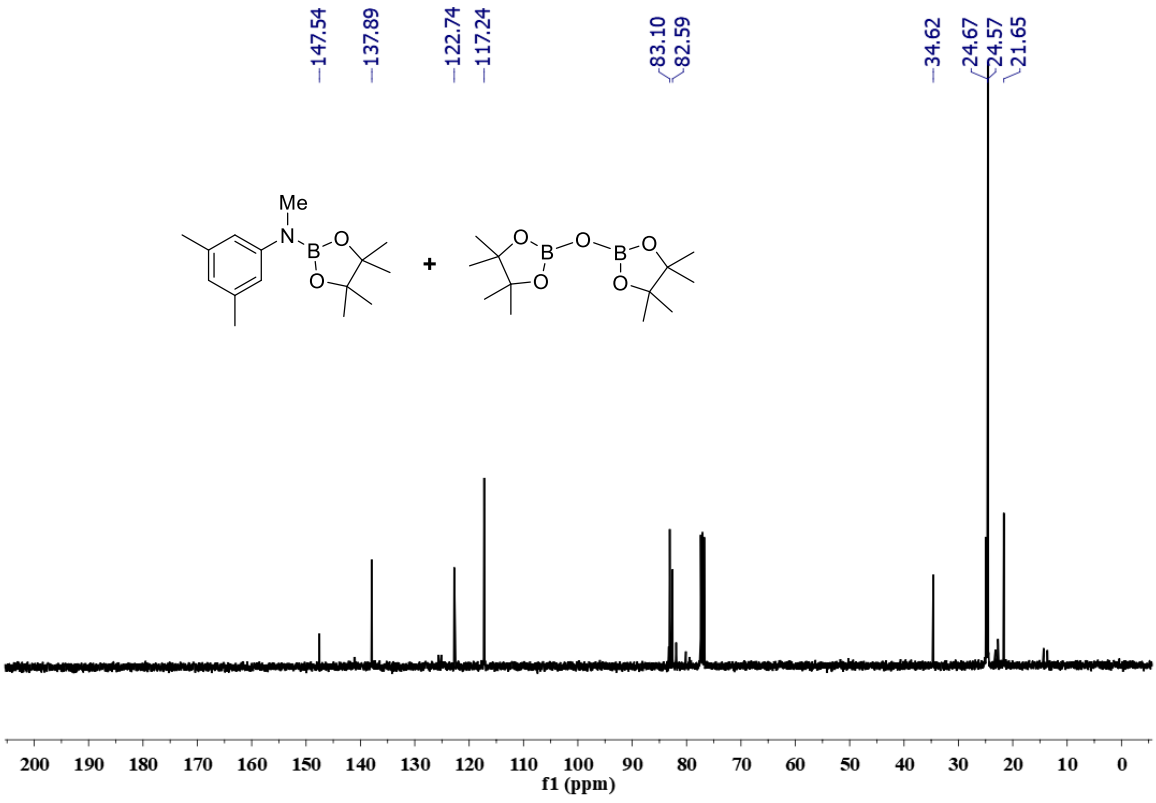


Figure S70: $^{13}C\{^{1}H\}$ NMR spectrum of **4e** (101 MHz, $CDCl_3$, 25 °C).

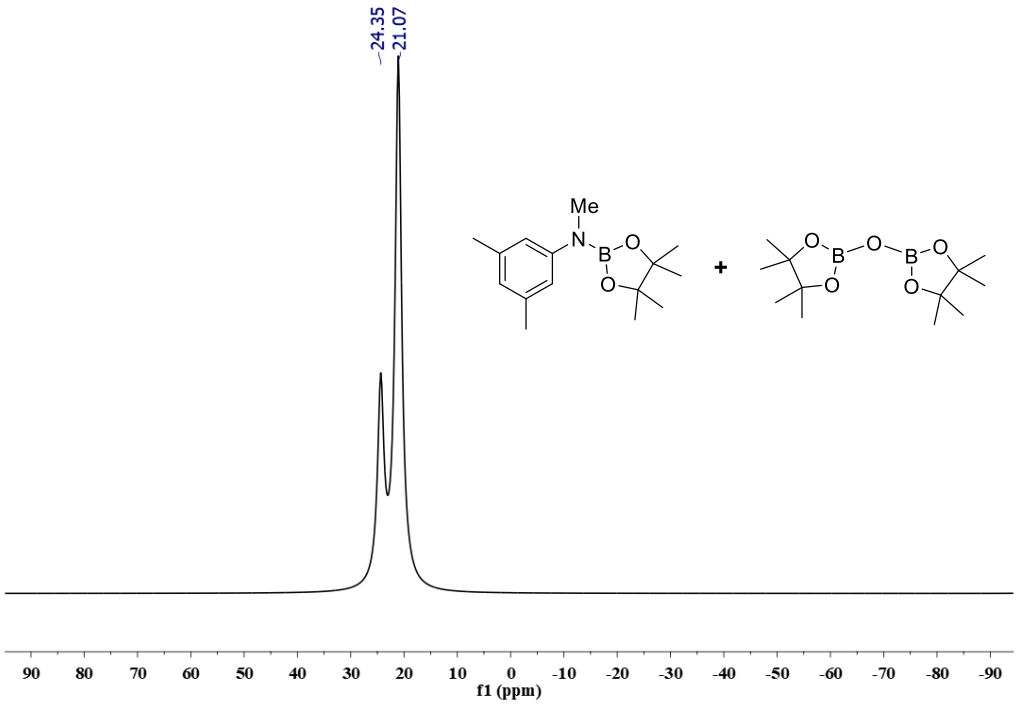


Figure S71: ^{11}B NMR spectrum of **4e** (128 MHz, $CDCl_3$, 25 ^{o}C).

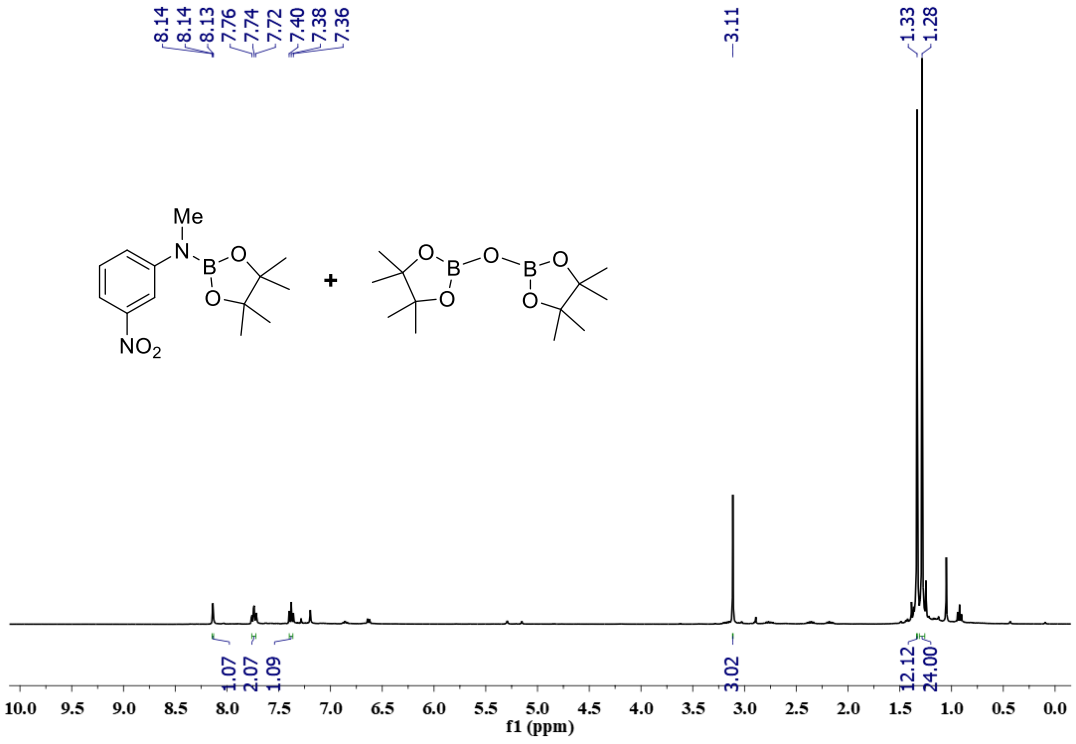


Figure S72: ^{1}H NMR spectrum of **4f** (400 MHz, $CDCl_3$, 25 ^{o}C).

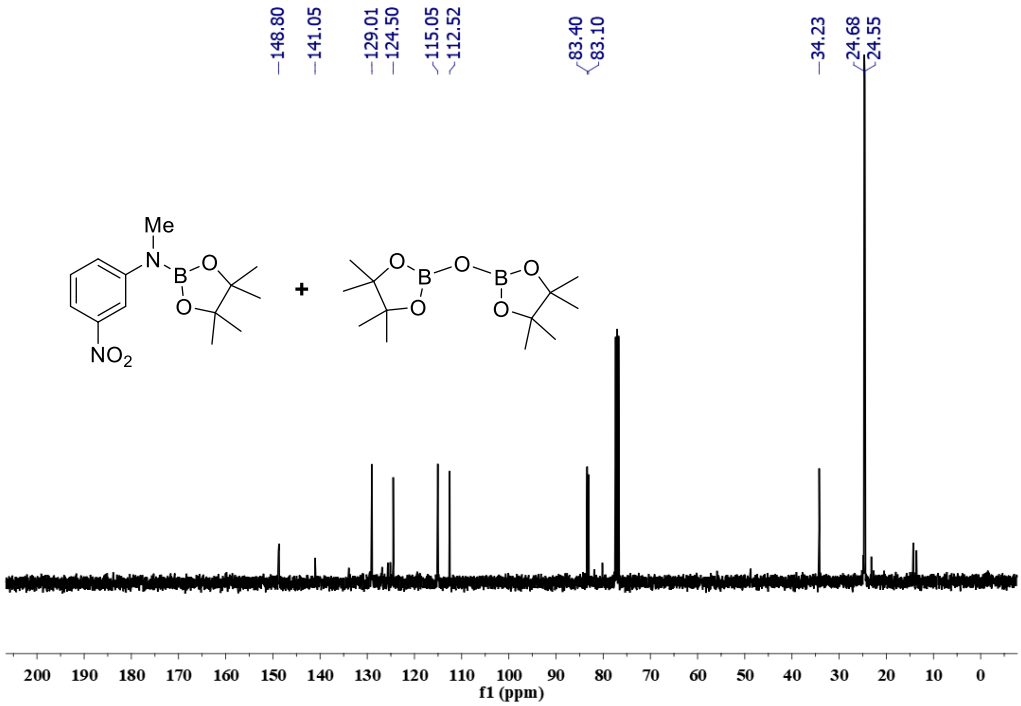


Figure S73: $^{13}C\{^{1}H\}$ NMR spectrum of 4**f** (101 MHz, $CDCl_3$, 25 °C).

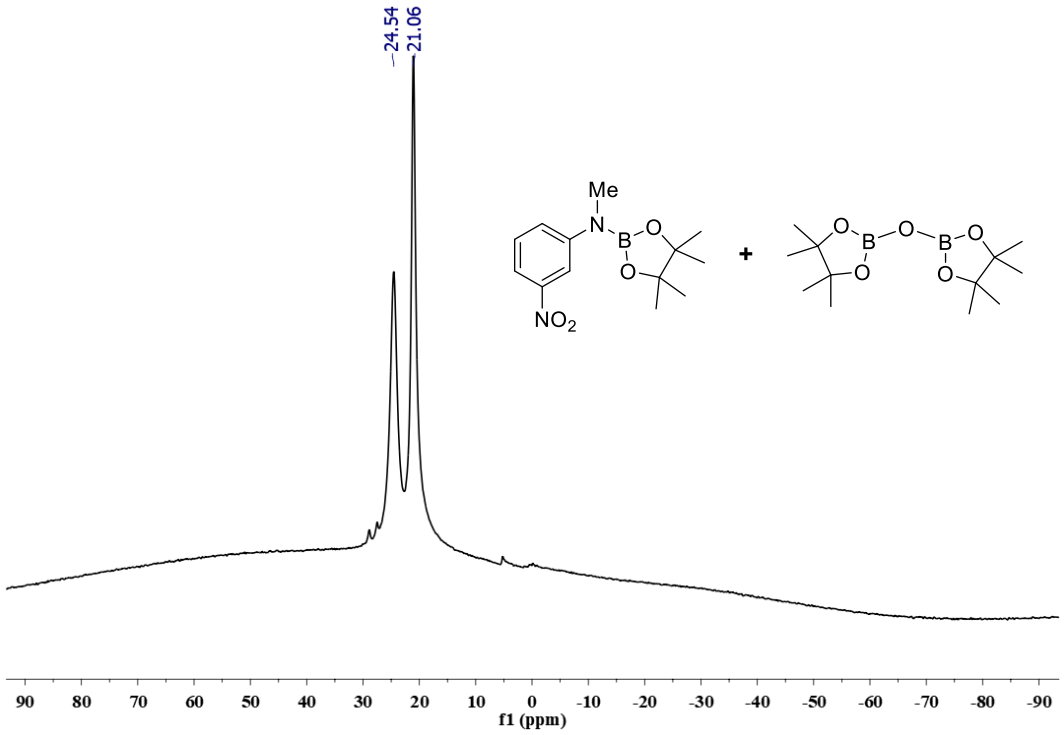


Figure S74: ^{11}B NMR spectrum of **4f** (128 MHz, $CDCl_3$, 25 °C).

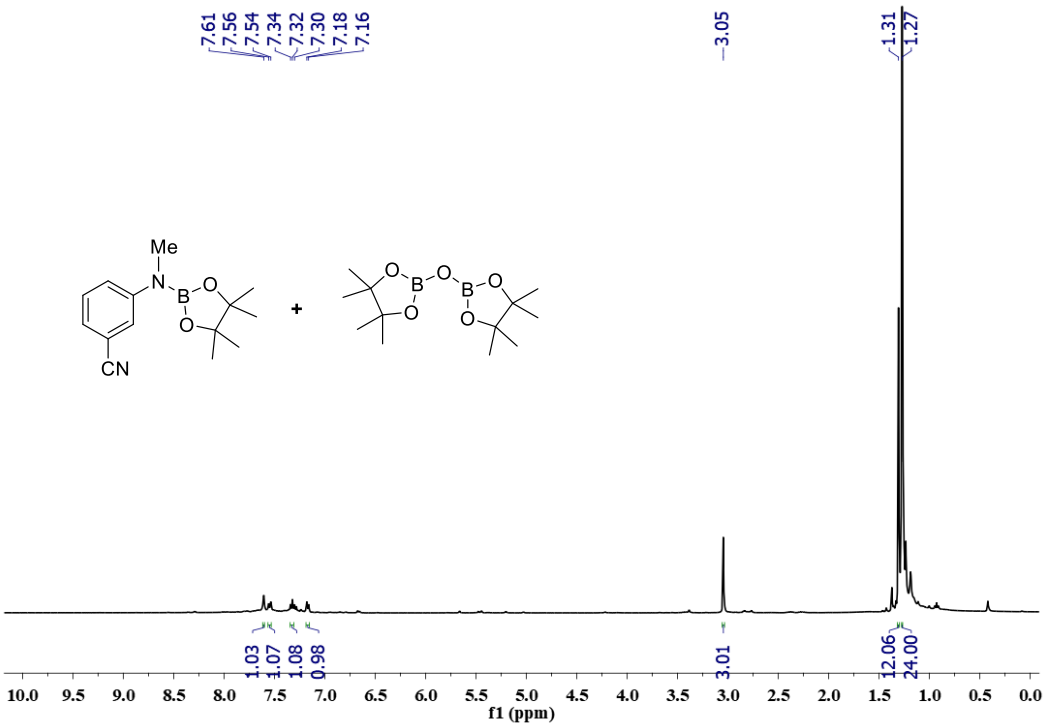


Figure S75: ^{1}H NMR spectrum of **4g** (400 MHz, $CDCl_3$, 25 ^{o}C).

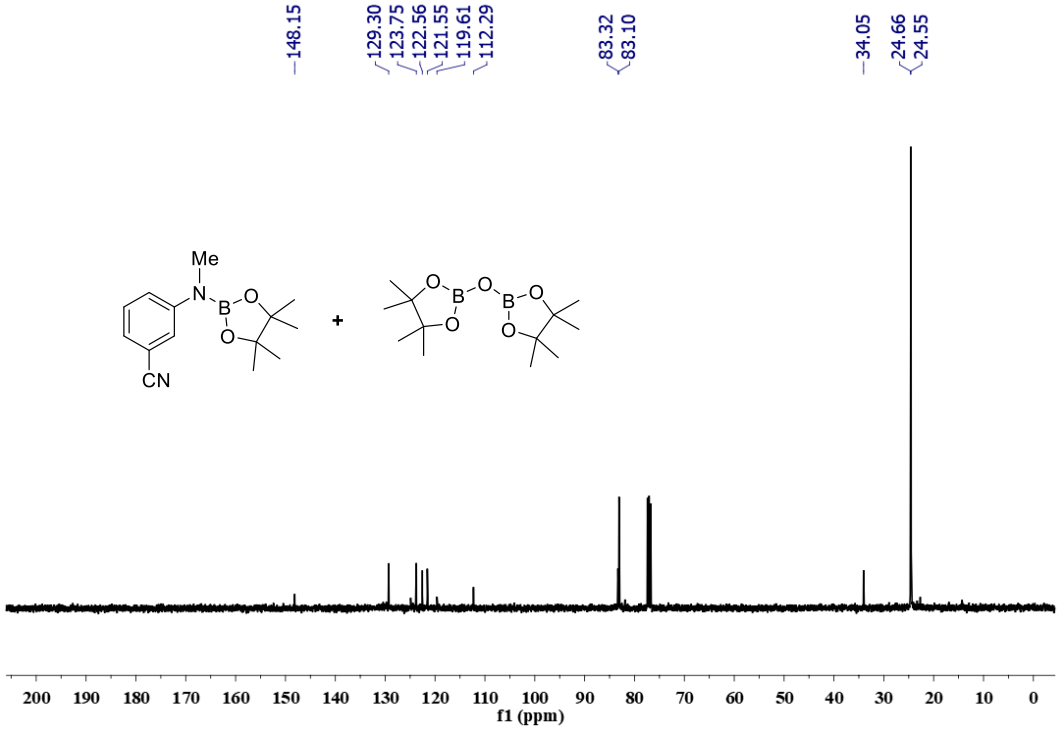


Figure S76: $^{13}C\{^{1}H\}$ NMR spectrum of **4g** (101 MHz, $CDCl_3$, 25 ^{o}C).

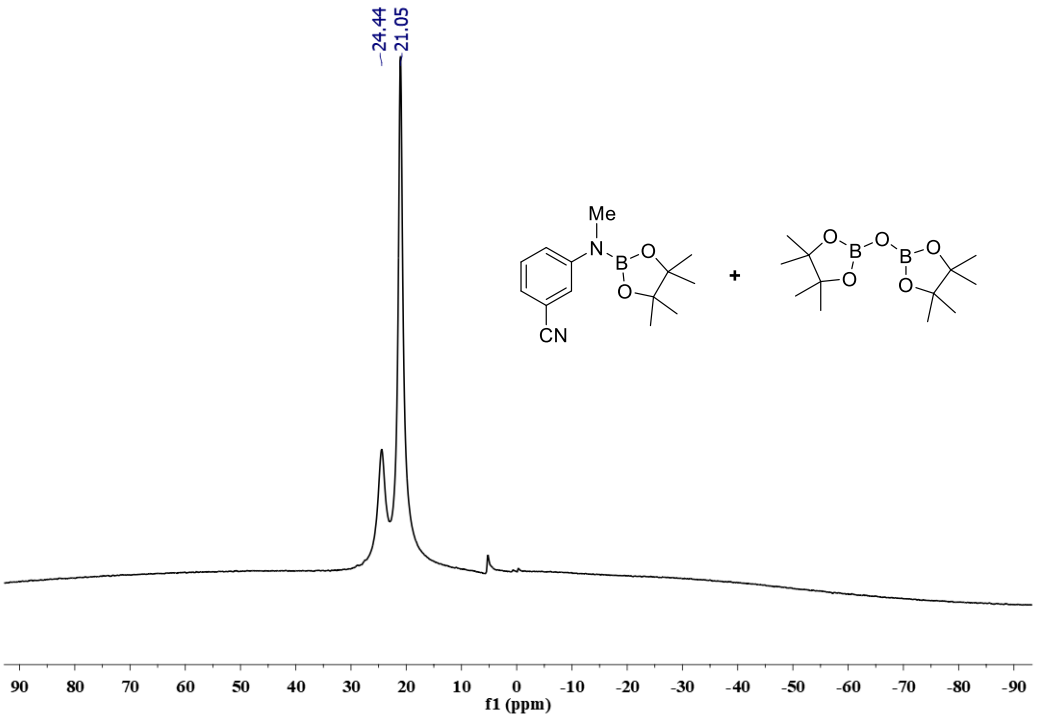


Figure S77: ^{11}B NMR spectrum of **4g** (128 MHz, $CDCl_3$, 25 ^{o}C).

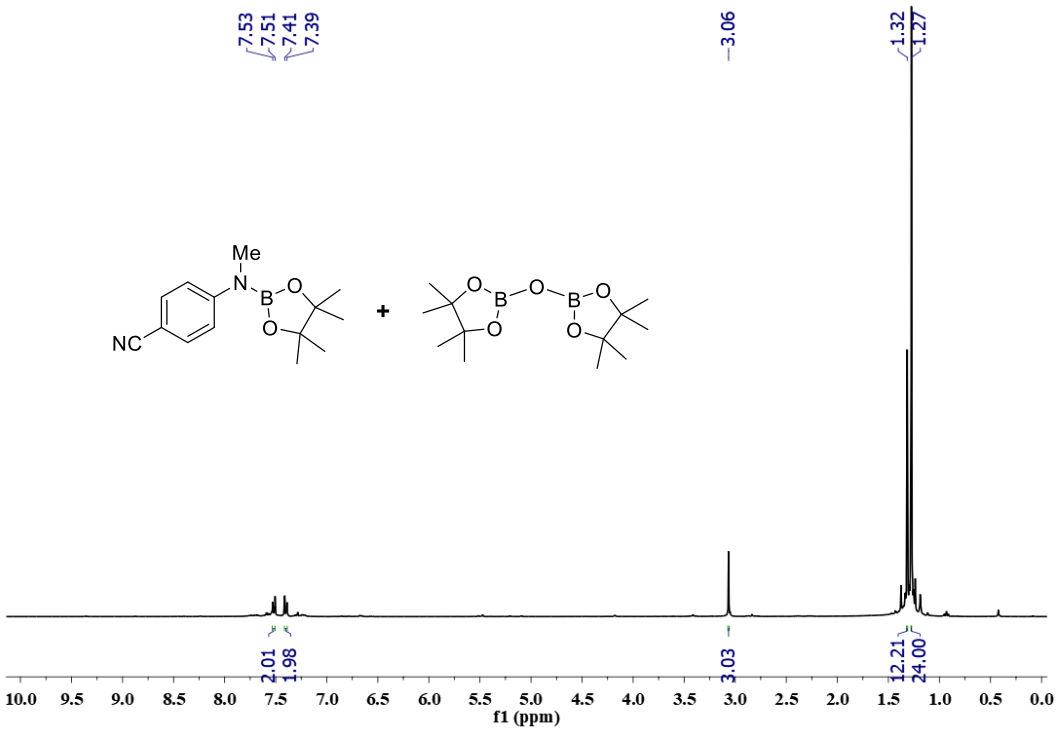


Figure S78: ^{1}H NMR spectrum of **4h** (400 MHz, $CDCl_3$, 25 ^{o}C).

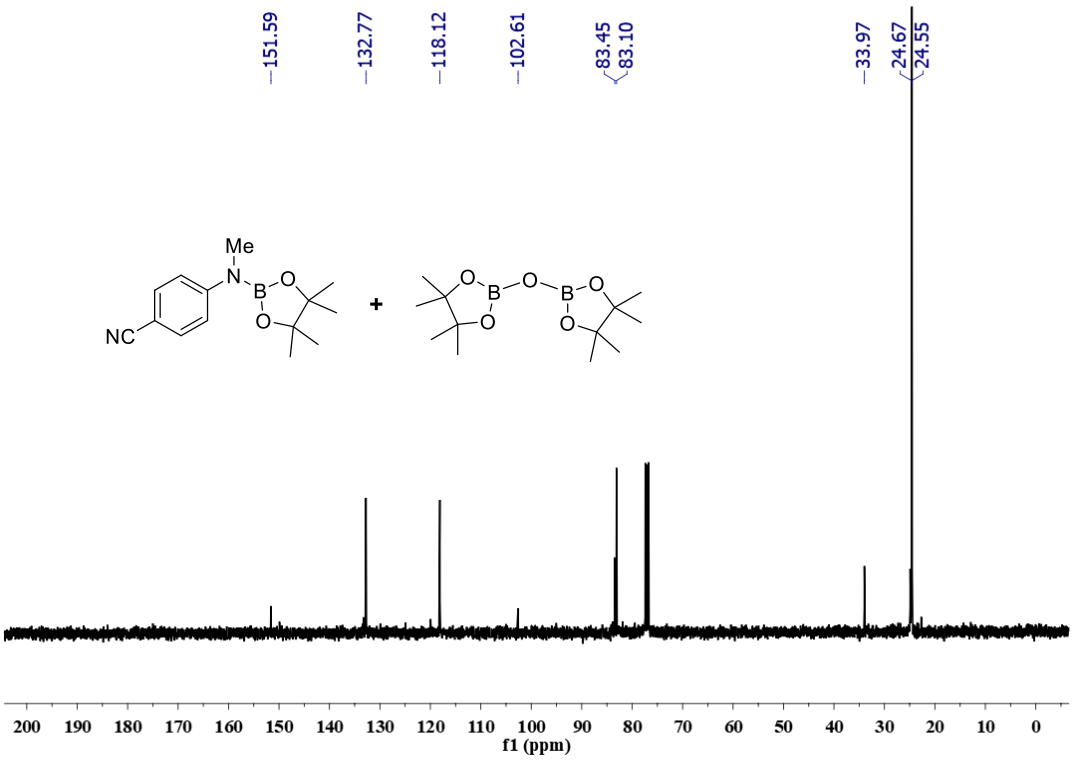


Figure S79: $^{13}C\{^{1}H\}$ NMR spectrum of **4h** (101 MHz, $CDCl_3$, 25 ^{o}C).

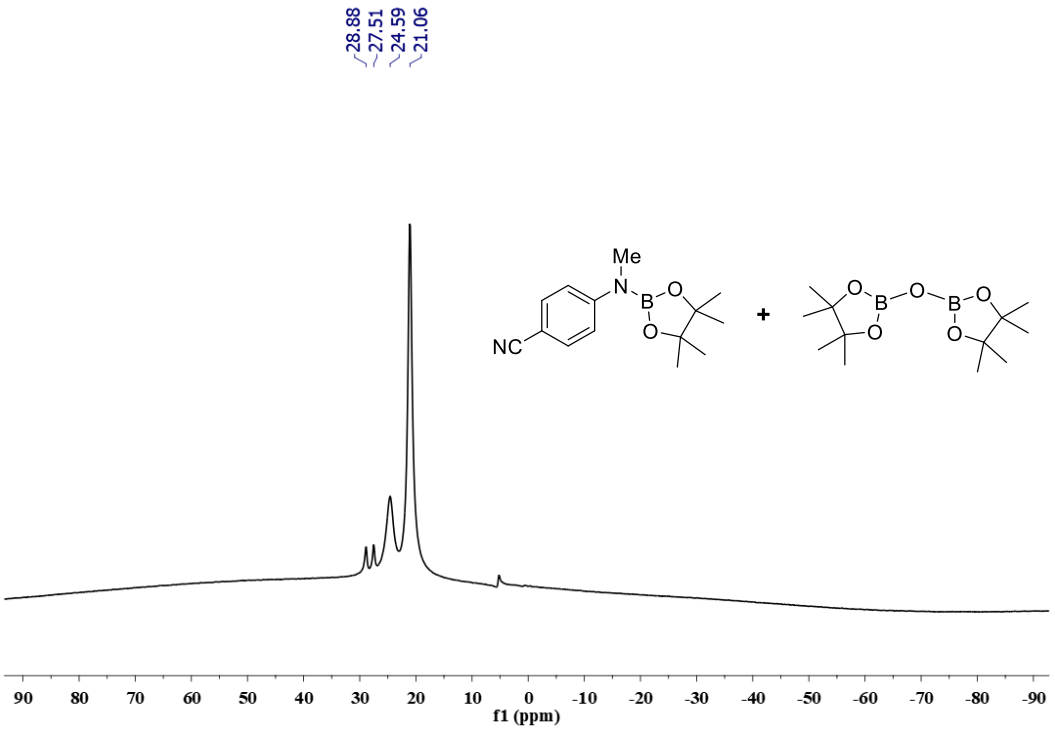


Figure S80: ^{11}B NMR spectrum of **4h** (128 MHz, $CDCl_3$, 25 ^{o}C). A doublet peak observed at δ 27.51 - 28.88 ppm arises from free HBpin.

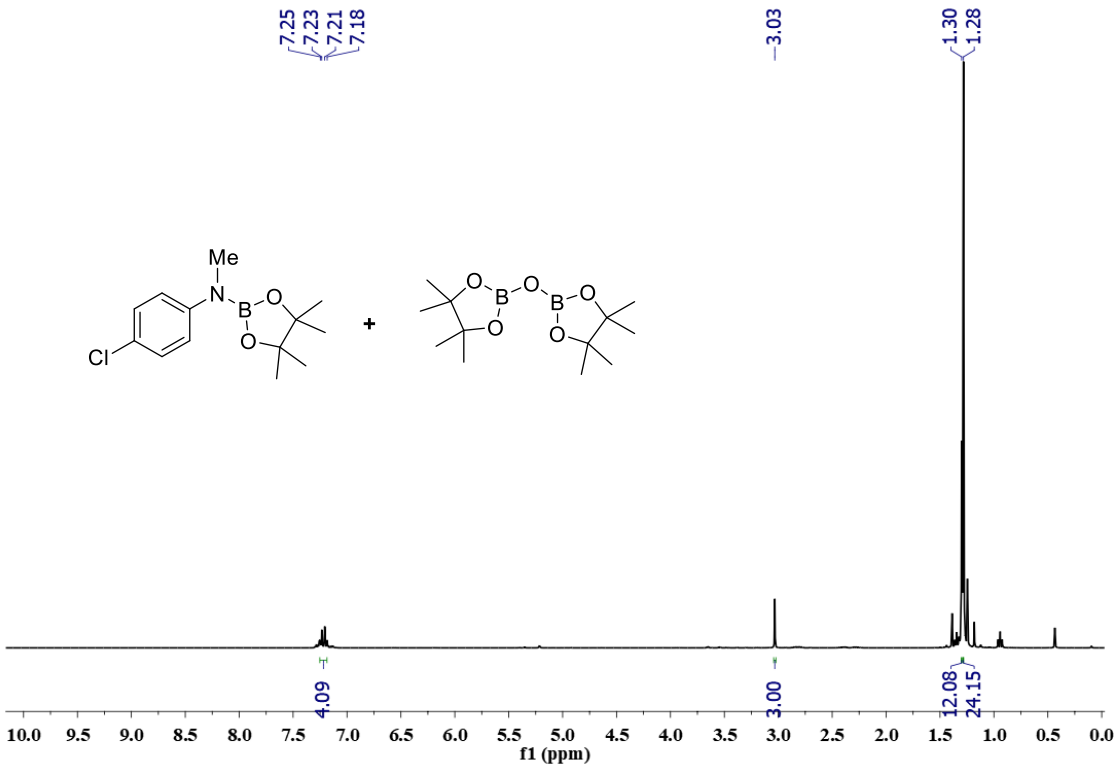


Figure S81: ^{1}H NMR spectrum of **4i** (400 MHz, $CDCl_3$, 25 ^{o}C).

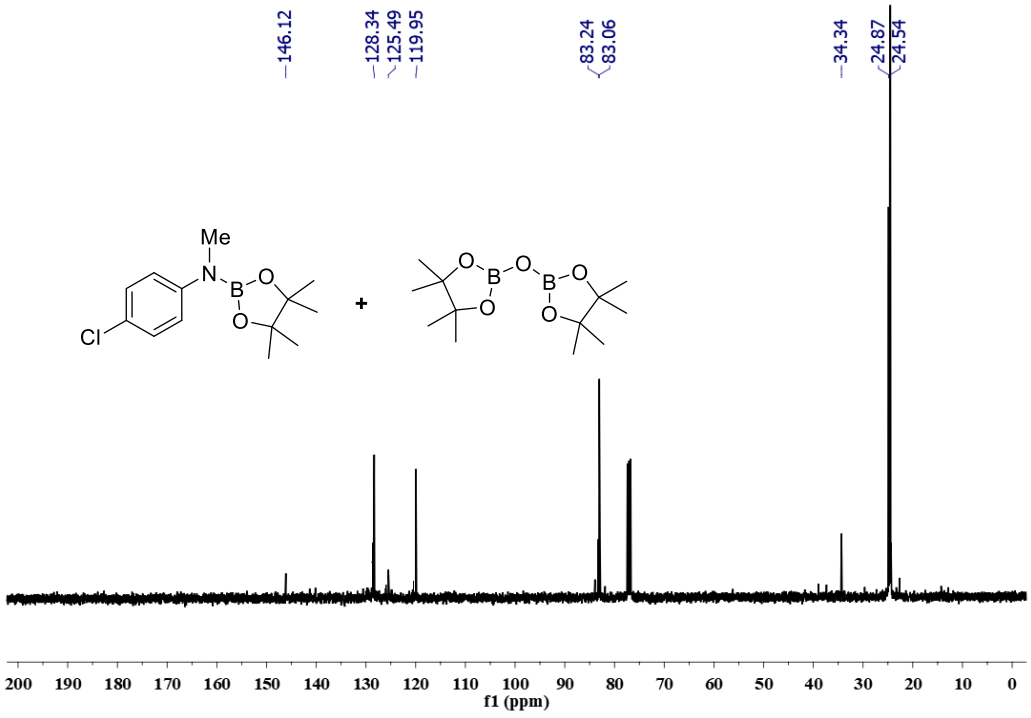


Figure S82: ^{13}C{^{1}H} NMR spectrum of **4i** (101 MHz, $CDCl_3$, 25 ^{o}C).

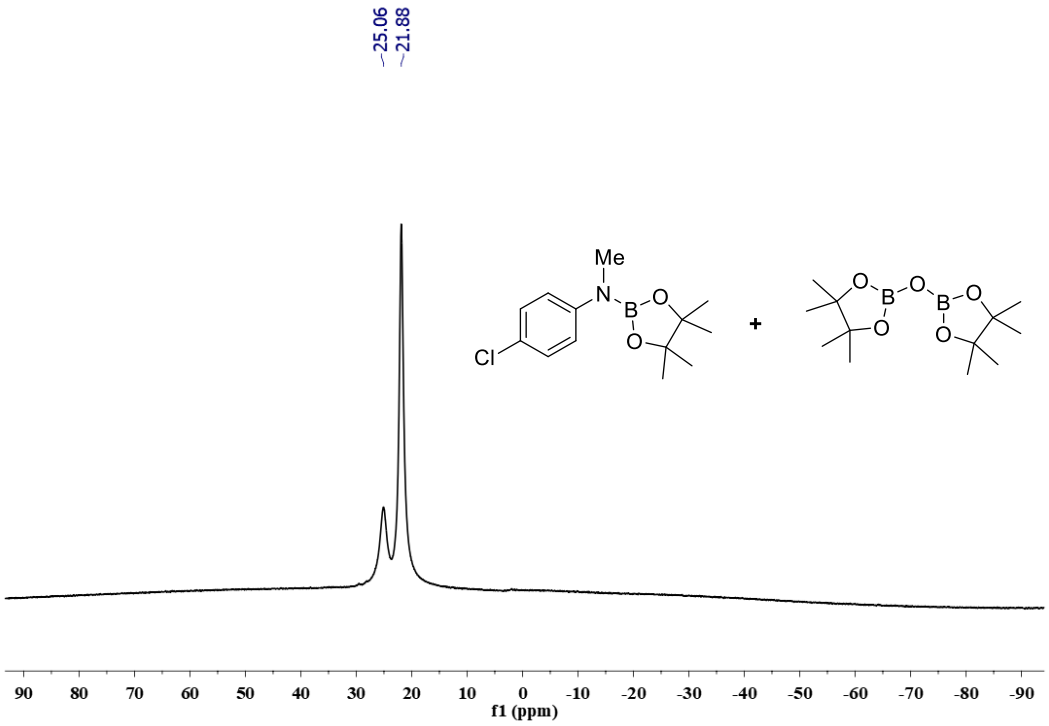


Figure S83: ^{11}B NMR spectrum of **4i** (128 MHz, $CDCl_3$, 25 ^{o}C).

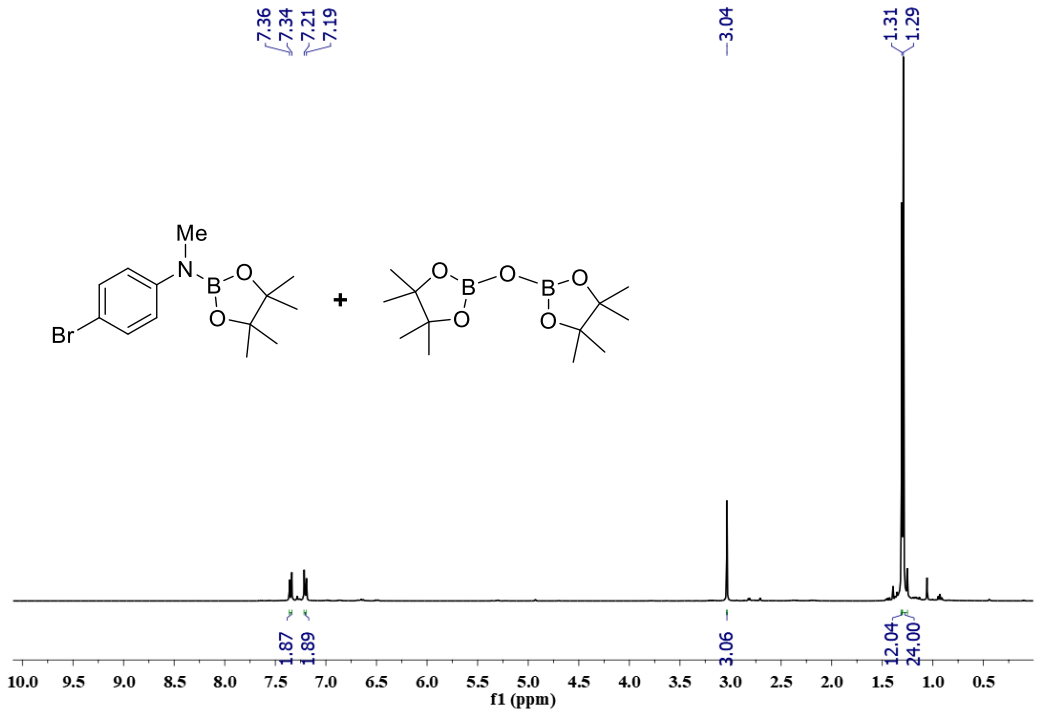


Figure S84: ^{1}H NMR spectrum of **4j** (400 MHz, $CDCl_3$, 25 ^{o}C).

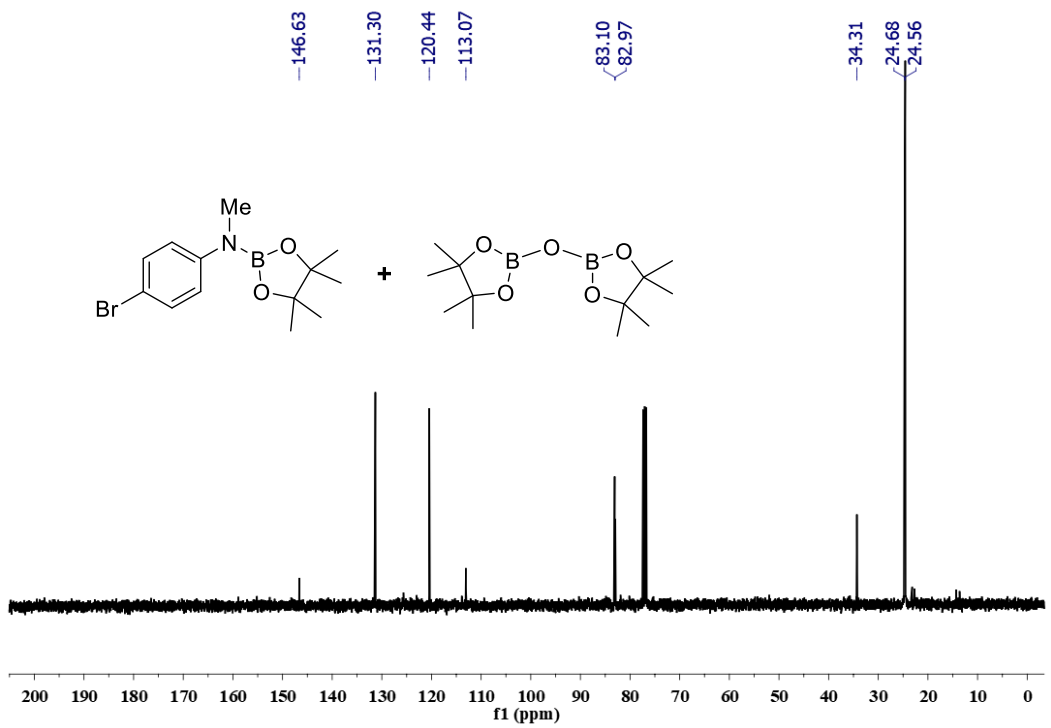


Figure S85: $^{13}C\{^{1}H\}$ NMR spectrum of **4j** (101 MHz, $CDCl_3$, 25 °C).

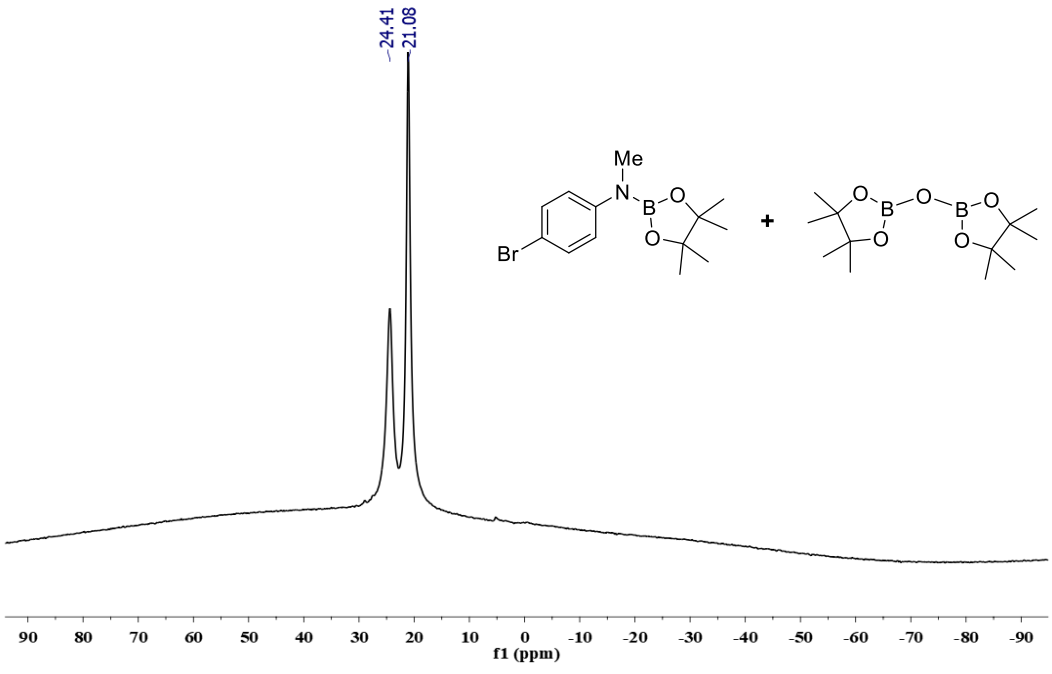


Figure S86: ^{11}B NMR spectrum of **4j** (128 MHz, $CDCl_3$, 25 °C).

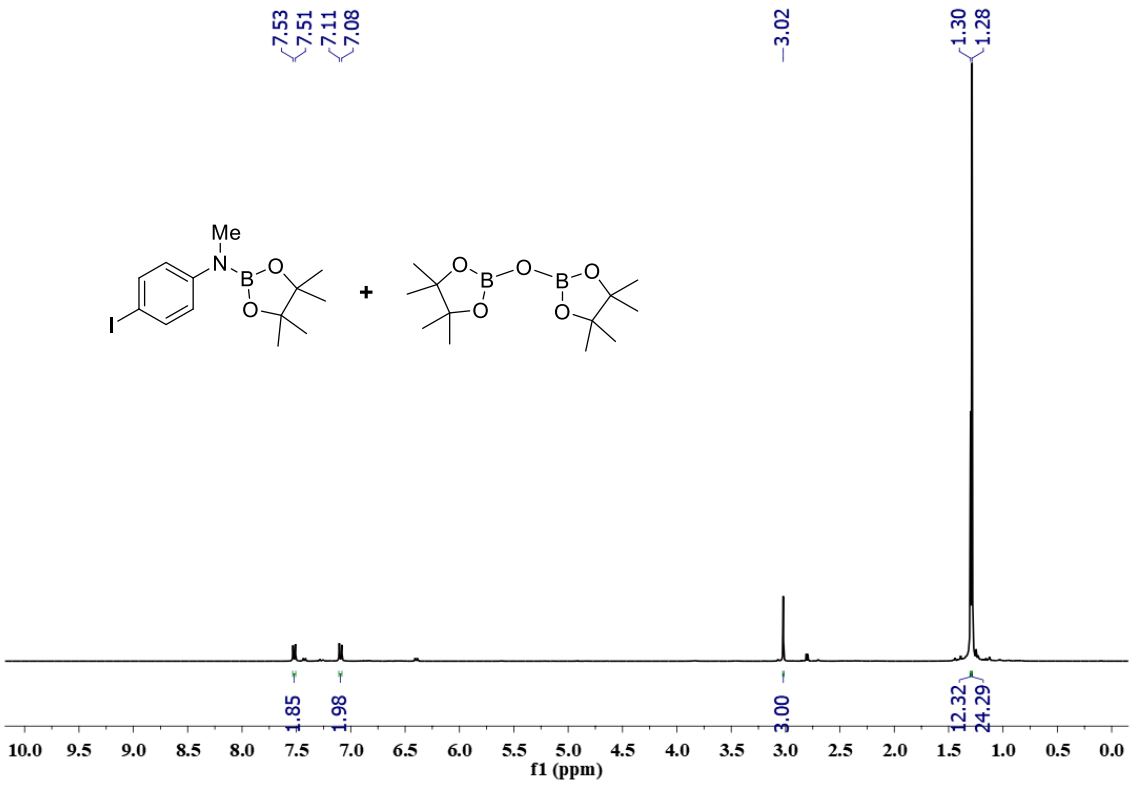


Figure S87: ^{1}H NMR spectrum of **4k** (400 MHz, $CDCl_3$, 25 ^{o}C).

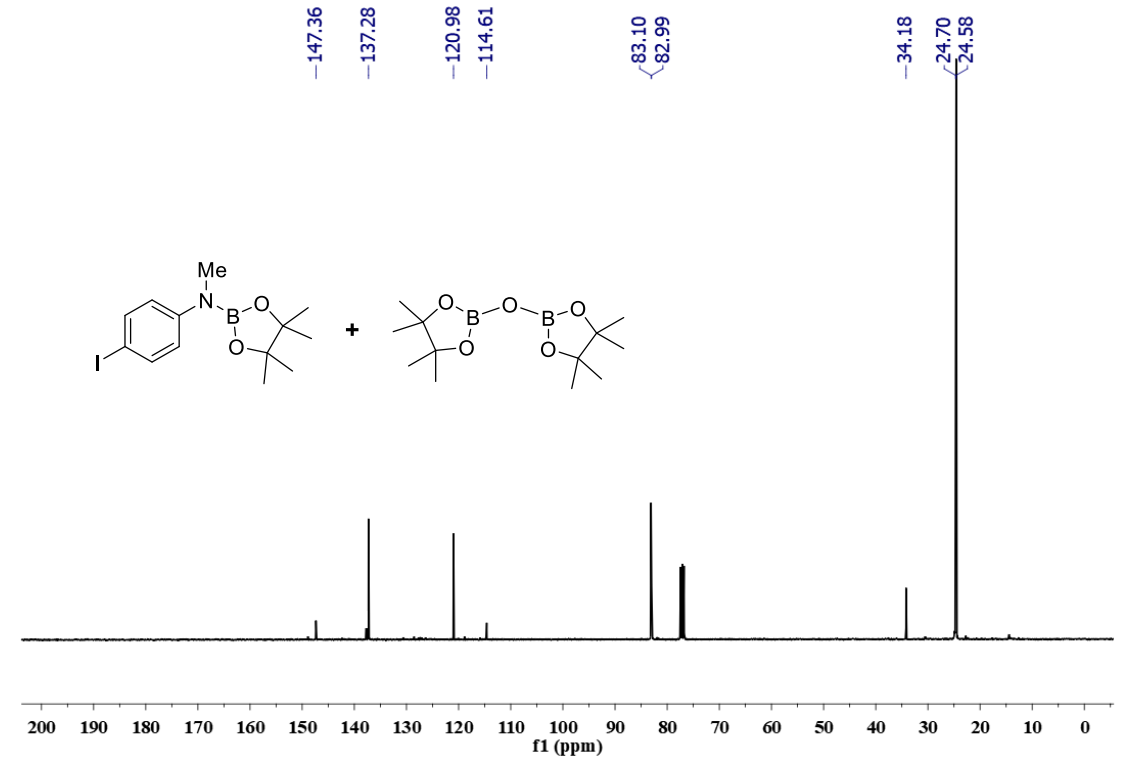


Figure S88: $^{13}C\{^{1}H\}$ NMR spectrum of **4k** (101 MHz, $CDCl_3$, 25 ^{o}C).

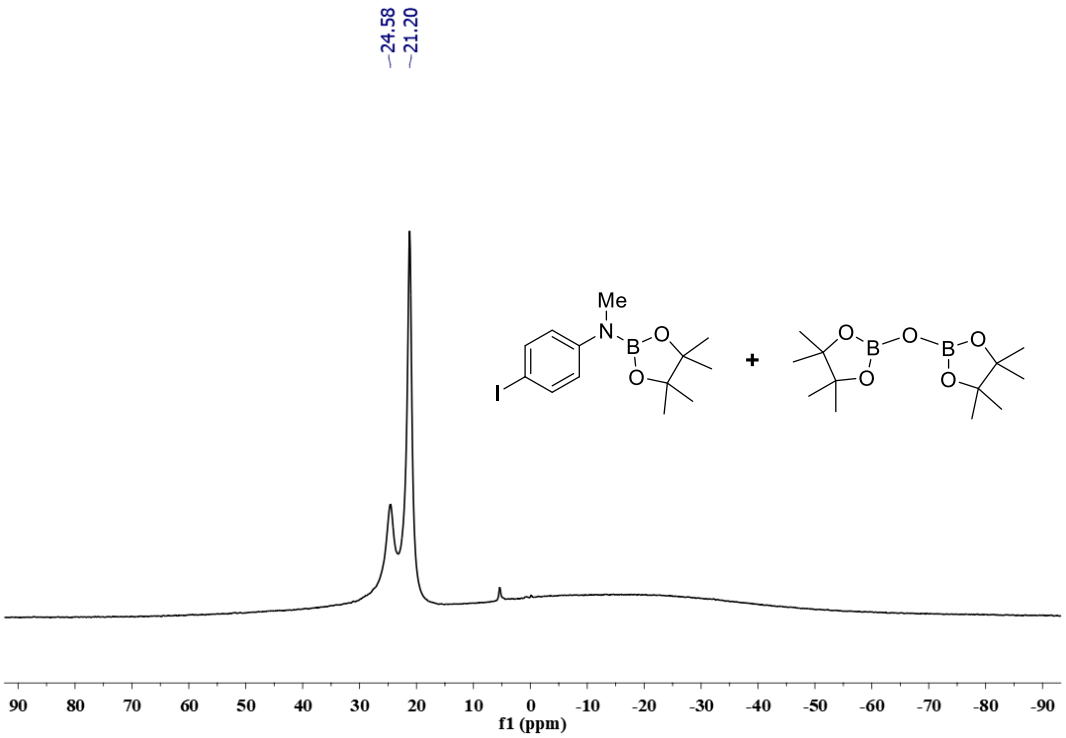


Figure S89: ^{11}B NMR spectrum of **4k** (128 MHz, $CDCl_3$, 25 ^{o}C).

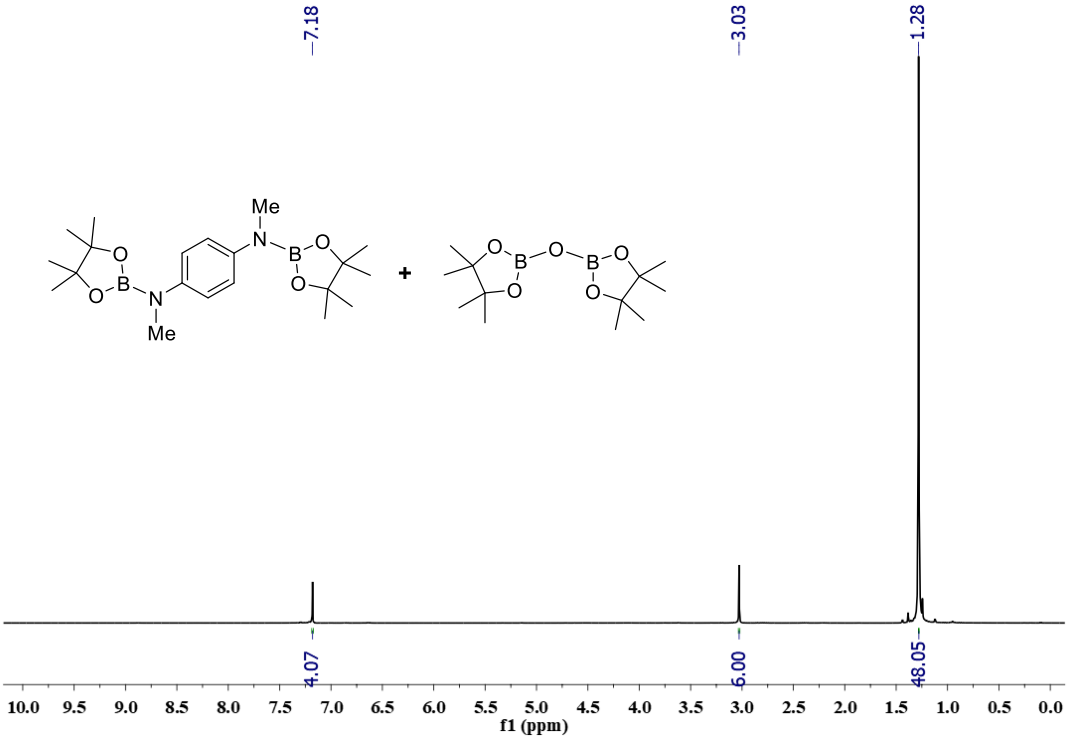


Figure S90: ^{1}H NMR spectrum of **4l** (400 MHz, $CDCl_3$, 25 ^{o}C).

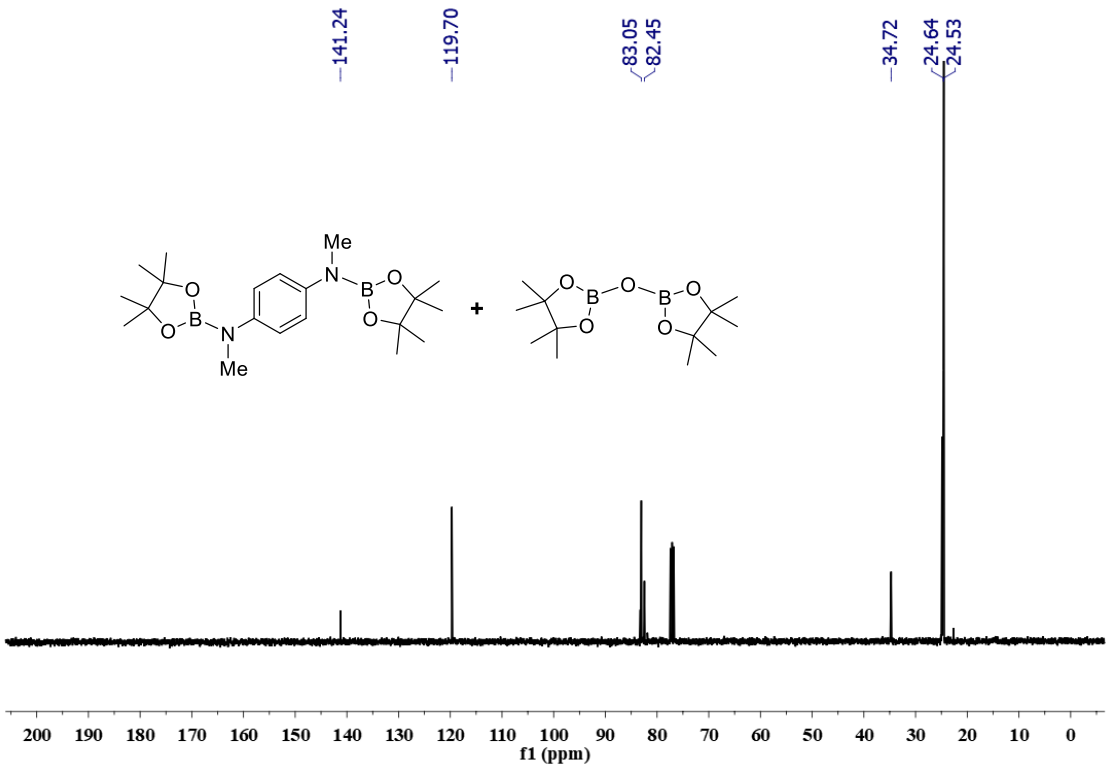


Figure S91: $^{13}C\{^{1}H\}$ NMR spectrum of **4l** (101 MHz, $CDCl_3$, 25 ^{o}C).

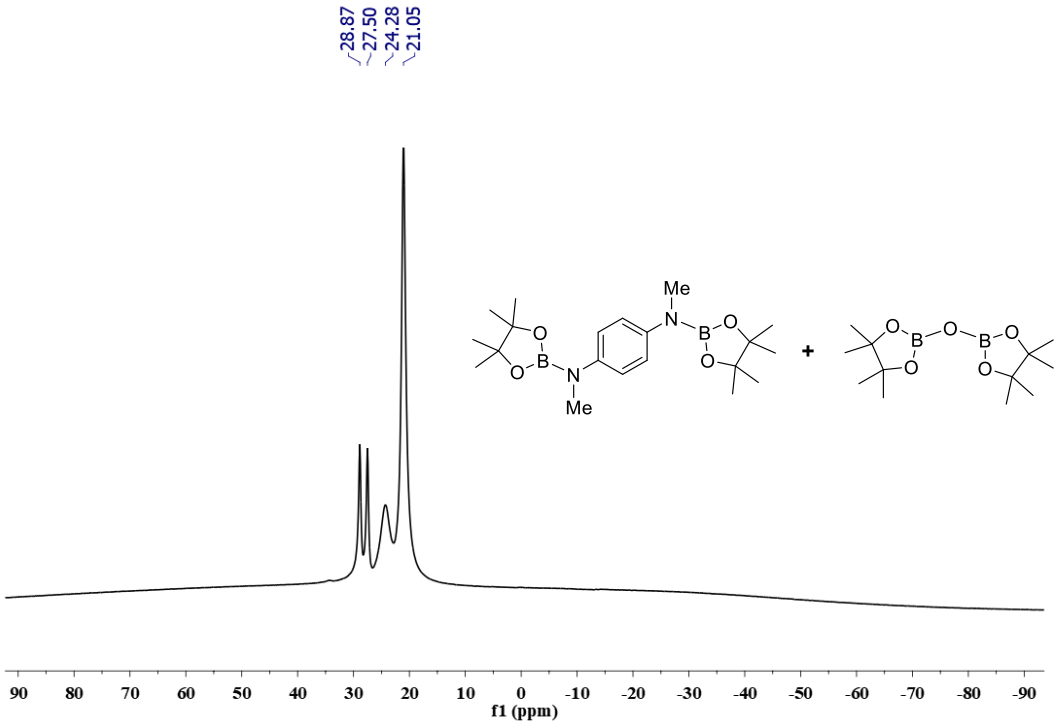


Figure S92: ^{11}B NMR spectrum of **4l** (128 MHz, $CDCl_3$, 25 ^{o}C). A doublet peak observed at δ 27.50 - 28.87 ppm arises from free HBpin.

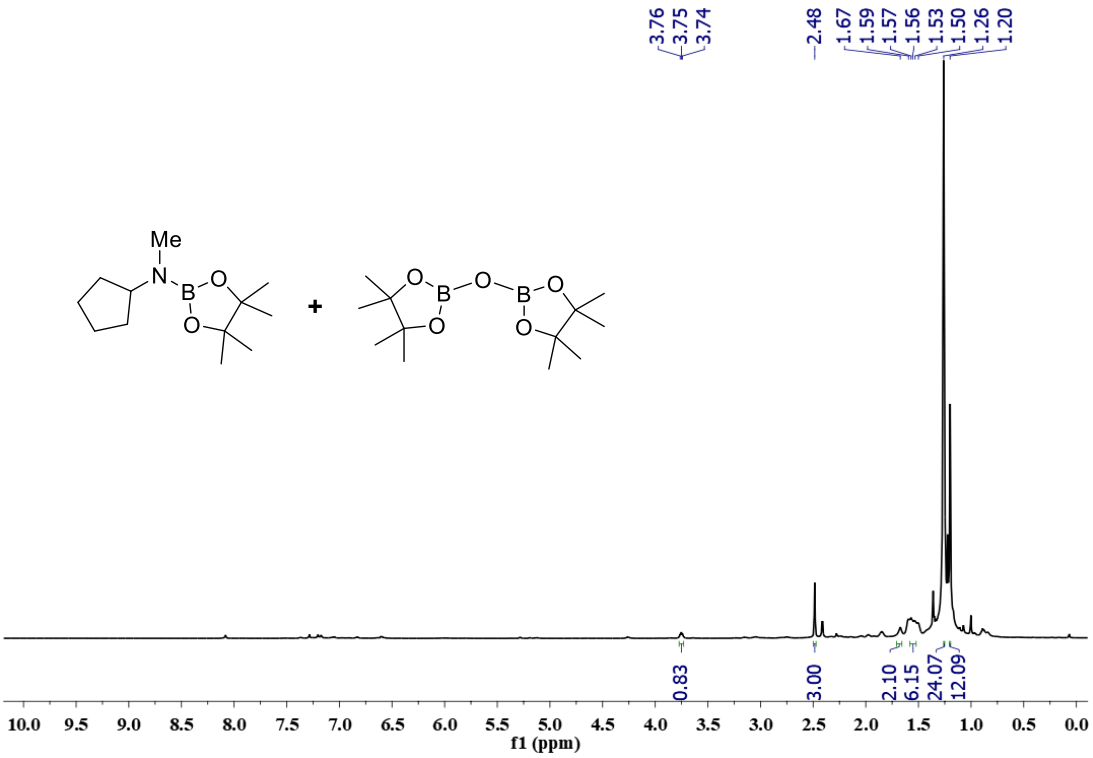


Figure S93: ^{1}H NMR spectrum of **4m** (400 MHz, $CDCl_3$, 25 ^{o}C).

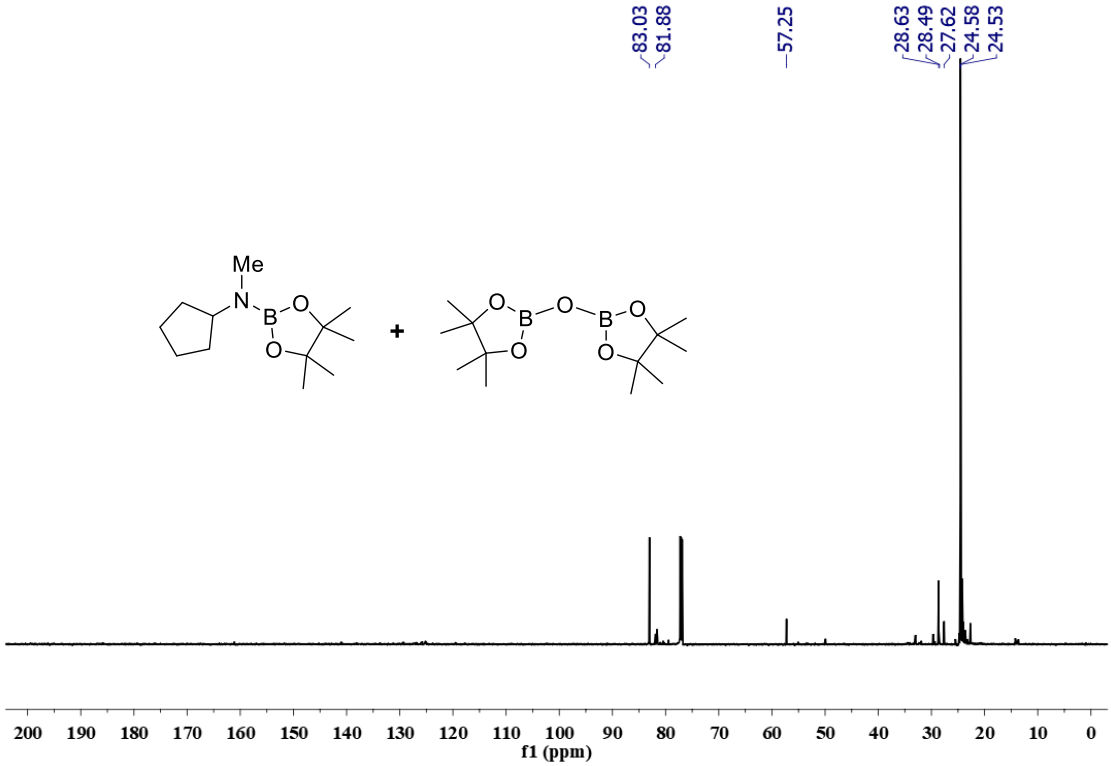


Figure S94: ^{13}C{^{1}H} NMR spectrum of **4m** (101 MHz, $CDCl_3$, 25 ^{o}C).

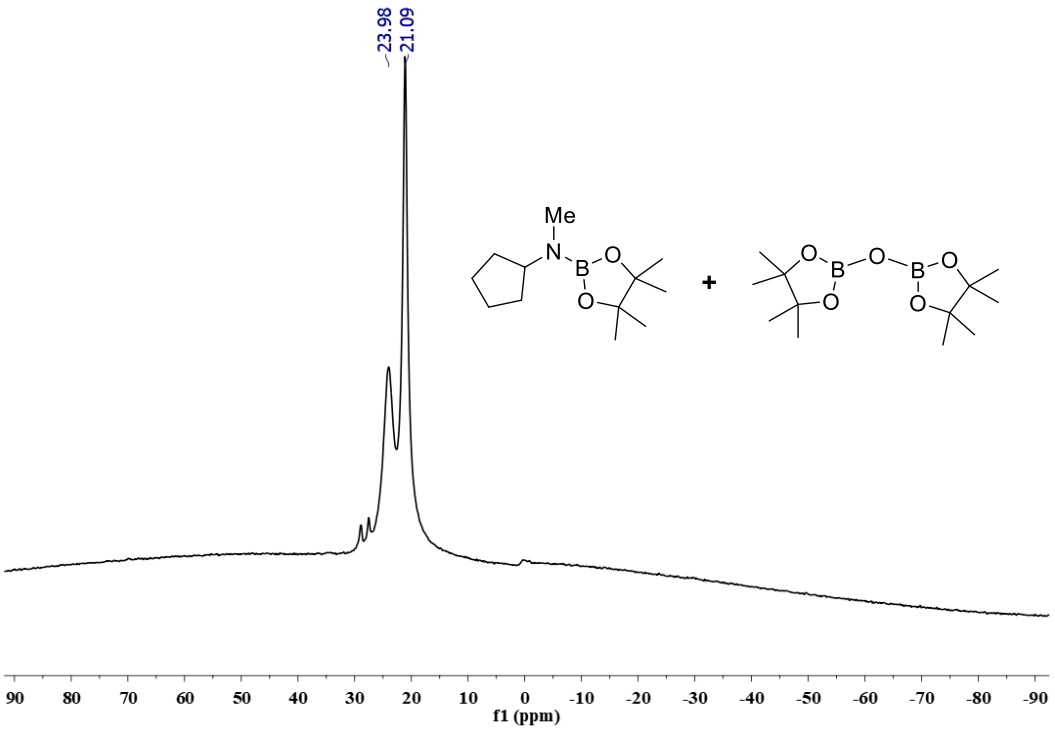


Figure S95: ^{11}B NMR spectrum of **4m** (128 MHz, $CDCl_3$, 25 °C).

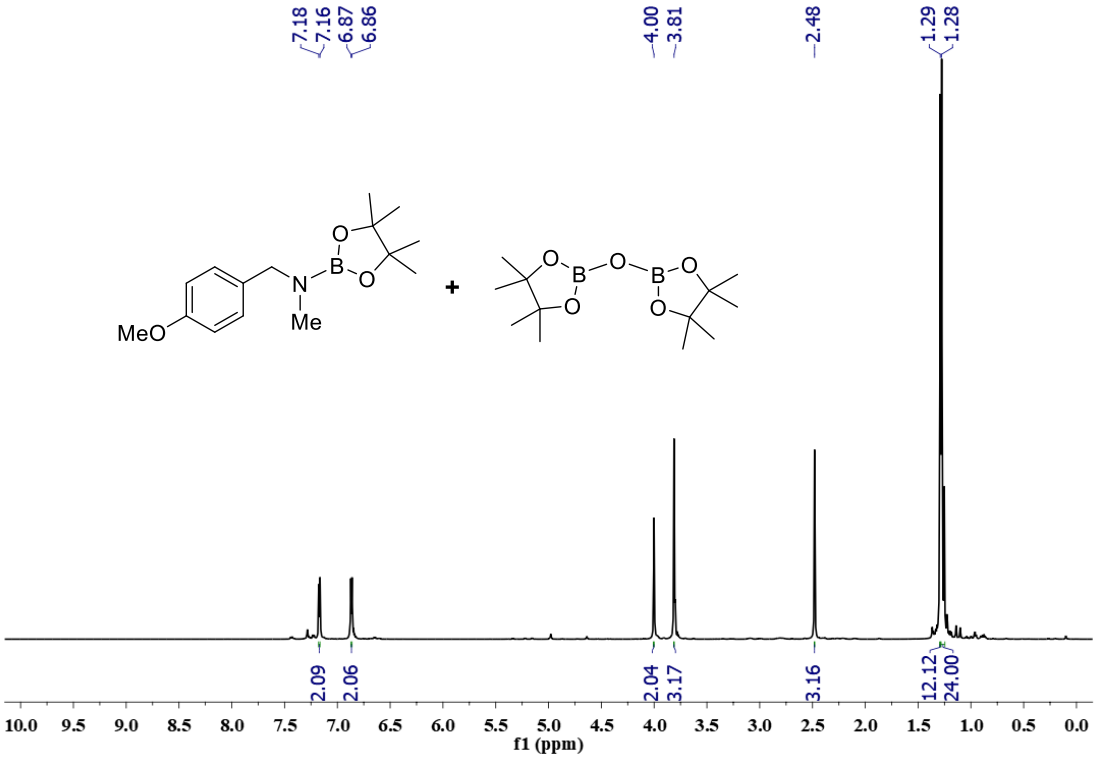


Figure S96: ^{1}H NMR spectrum of **4n** (400 MHz, $CDCl_3$, 25 °C).

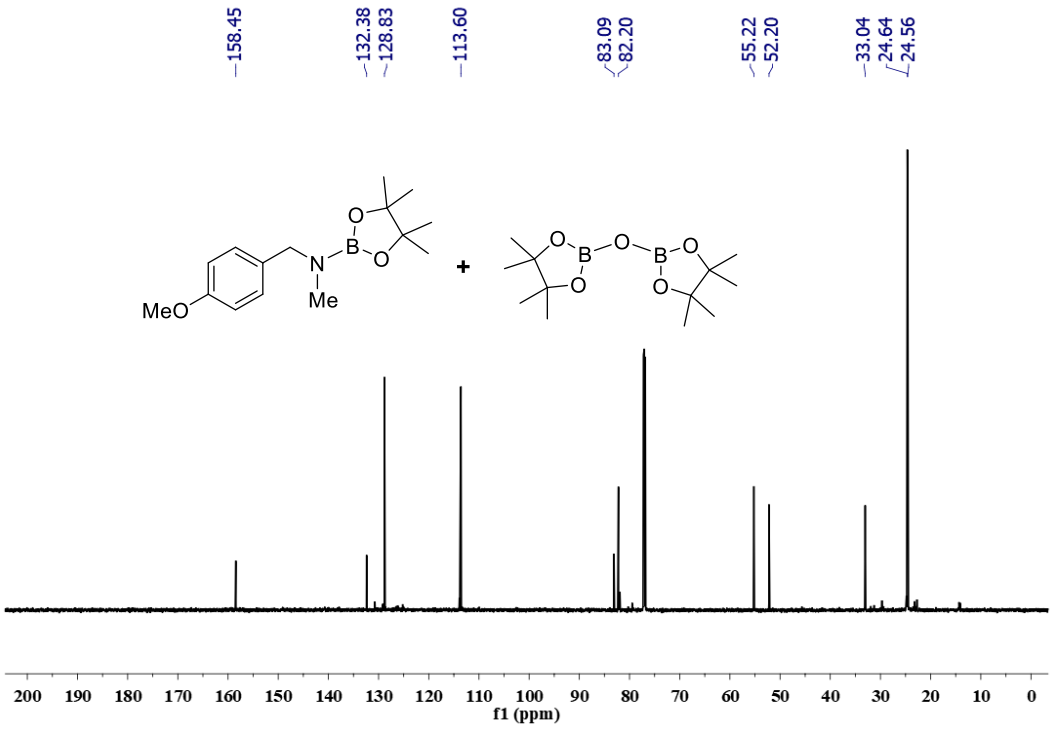


Figure S97: $^{13}C\{^{1}H\}$ NMR spectrum of **4n** (101 MHz, $CDCl_3$, 25 °C).

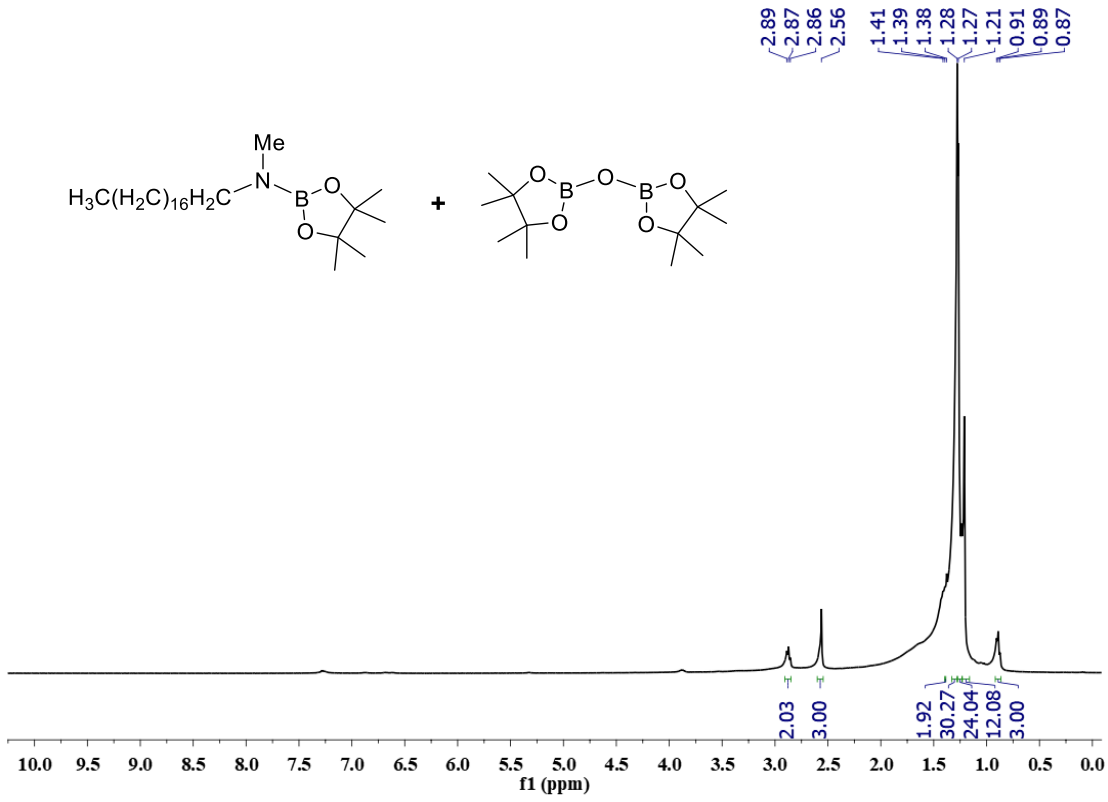


Figure S98: ^{1}H NMR spectrum of **4o** (400 MHz, $CDCl_3$, 25 °C).

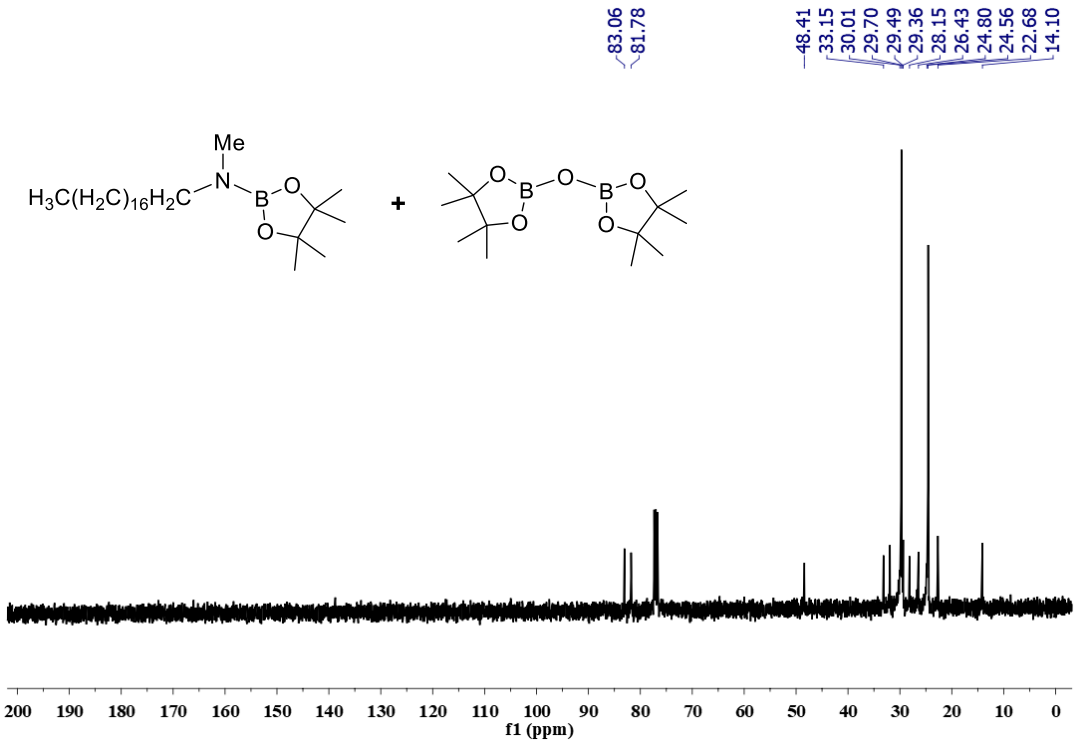


Figure S99: $^{13}C\{^{1}H\}$ NMR spectrum of **4o** (101 MHz, $CDCl_3$, 25 °C).

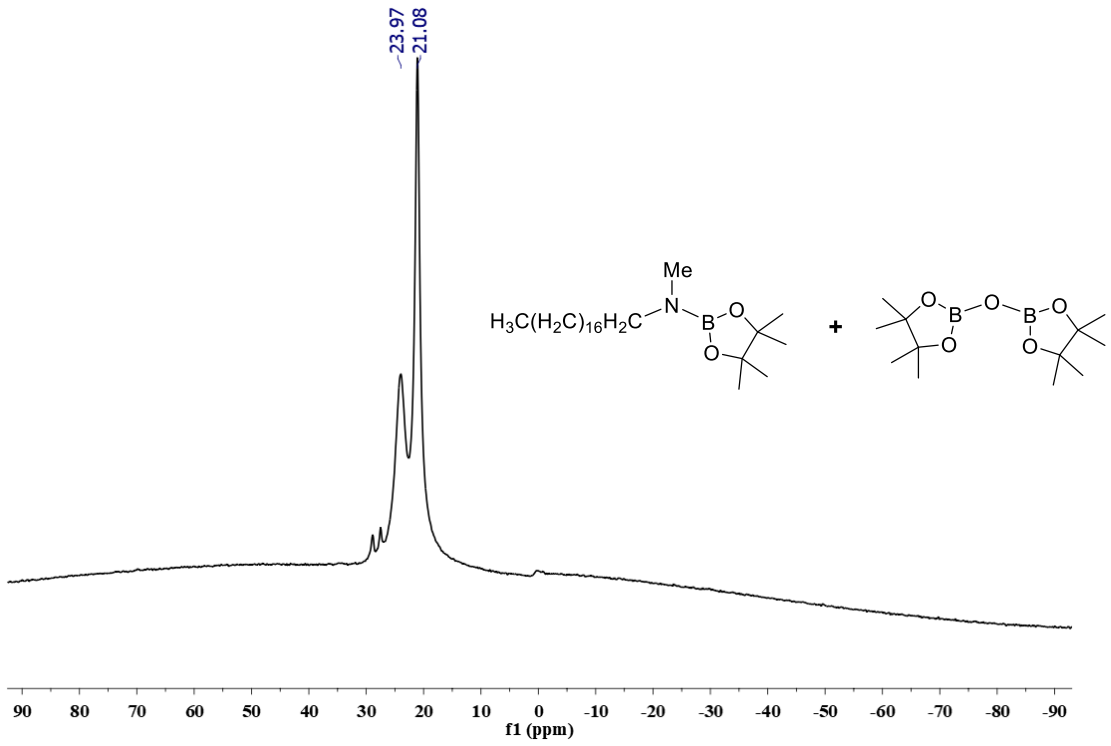


Figure S100: ^{11}B NMR spectrum of **4o** (128 MHz, $CDCl_3$, 25 °C).

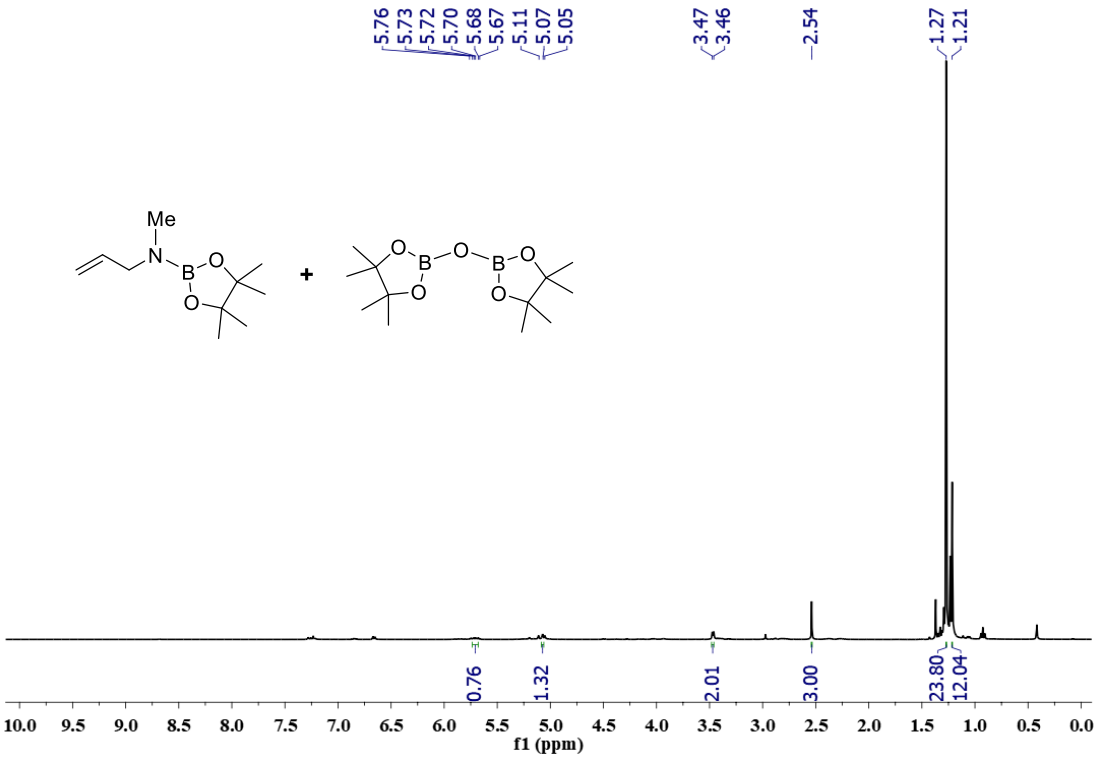


Figure S101: ^{1}H NMR spectrum of **4p** (400 MHz, $CDCl_3$, 25 ^{o}C).

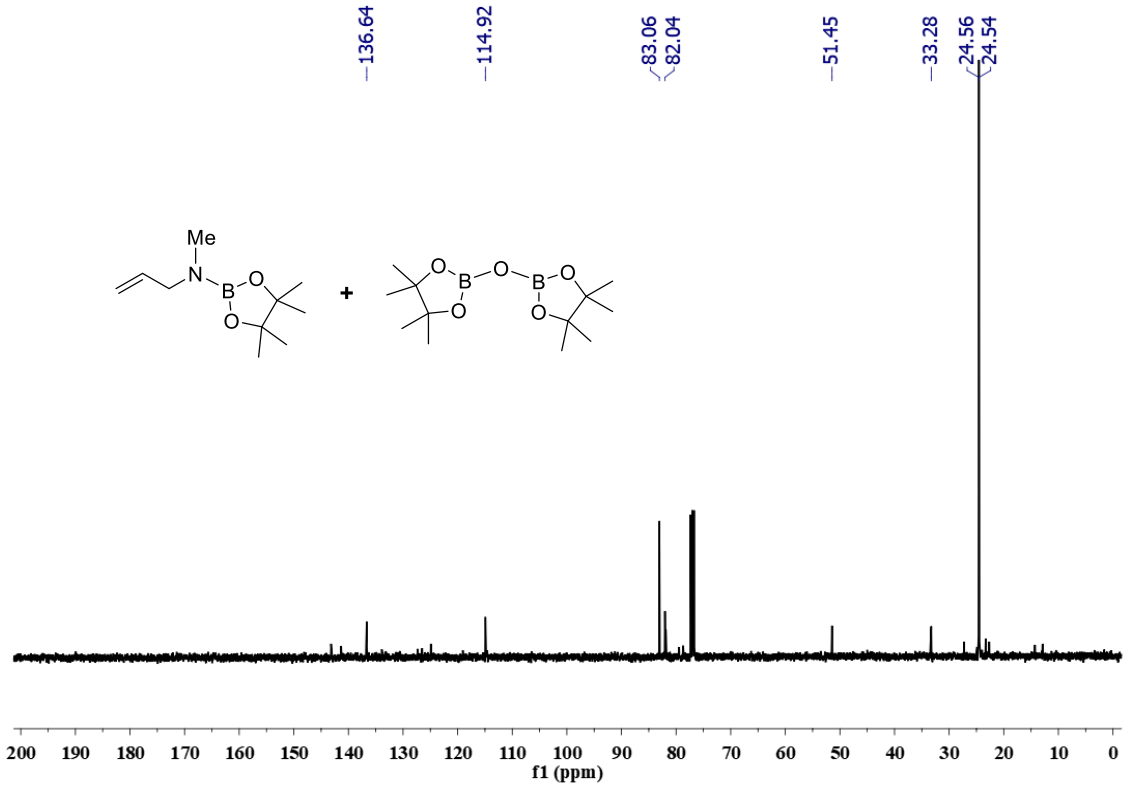


Figure S102: $^{13}C\{^{1}H\}$ NMR spectrum of **4p** (101 MHz, $CDCl_3$, 25 ^{o}C).

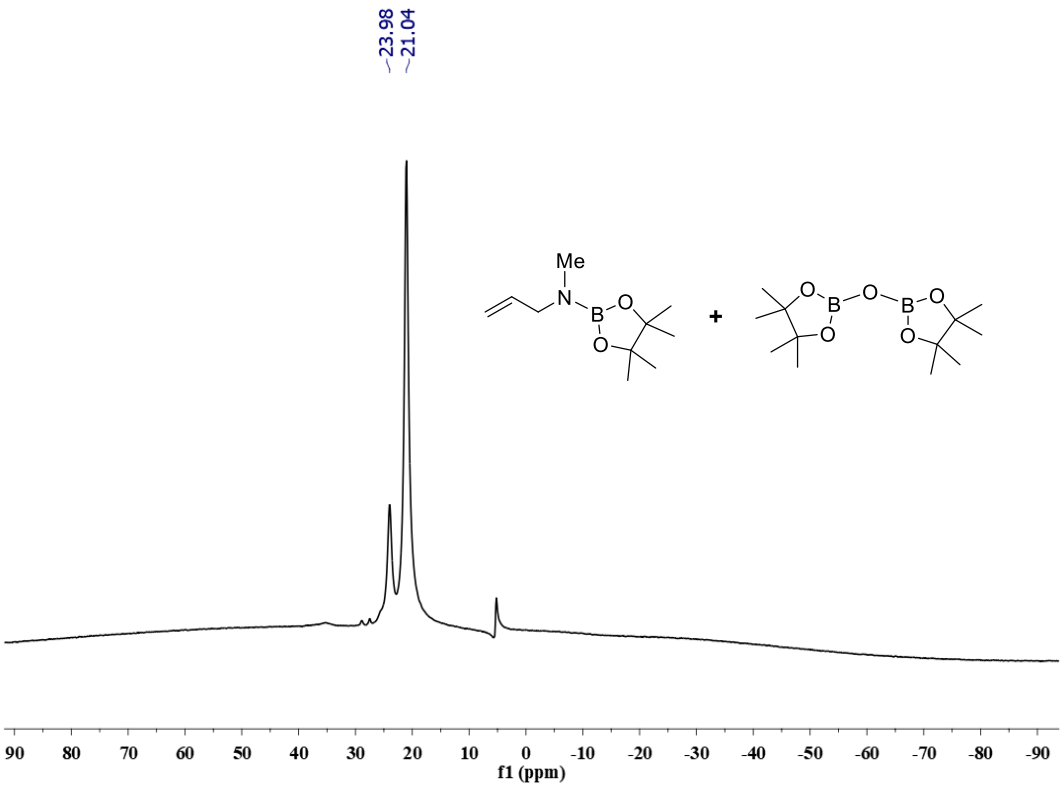


Figure S103: ^{11}B NMR spectrum of **4p** (128 MHz, $CDCl_3$, 25 ^{o}C).

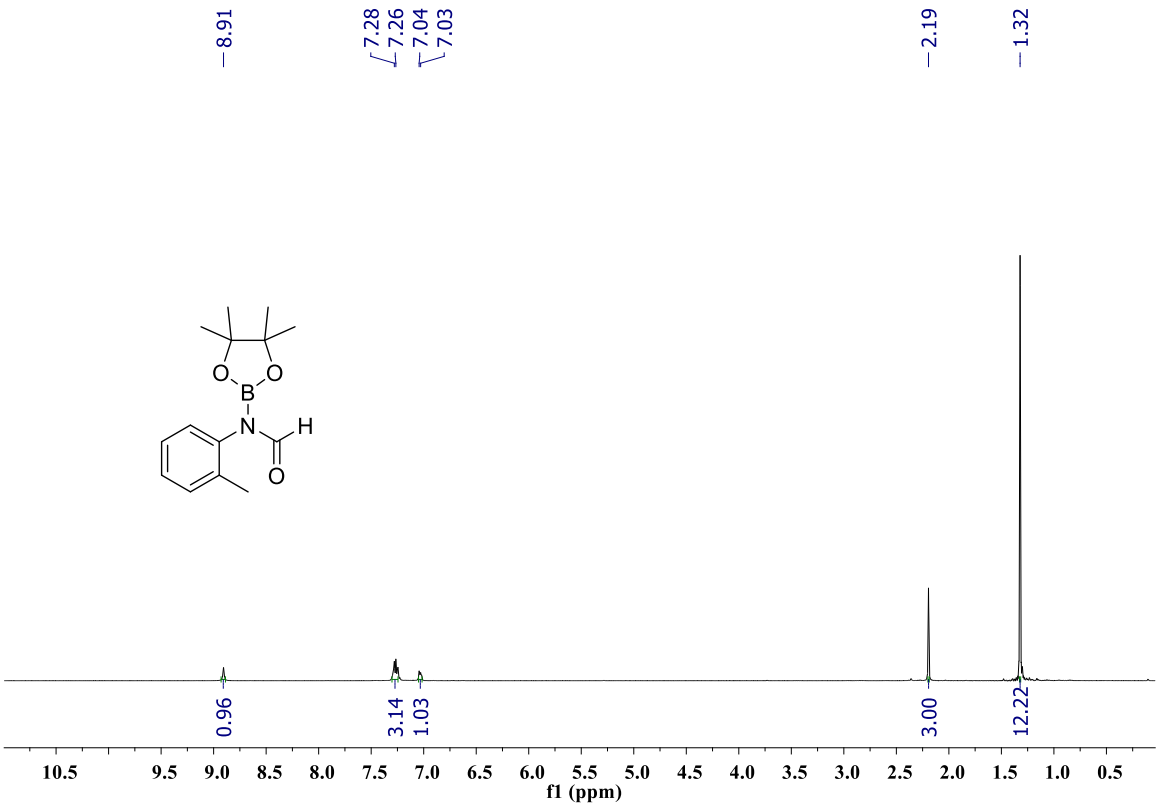


Figure S104: ^{1}H NMR spectrum of **5a** (400 MHz, $CDCl_3$, 25 ^{o}C).

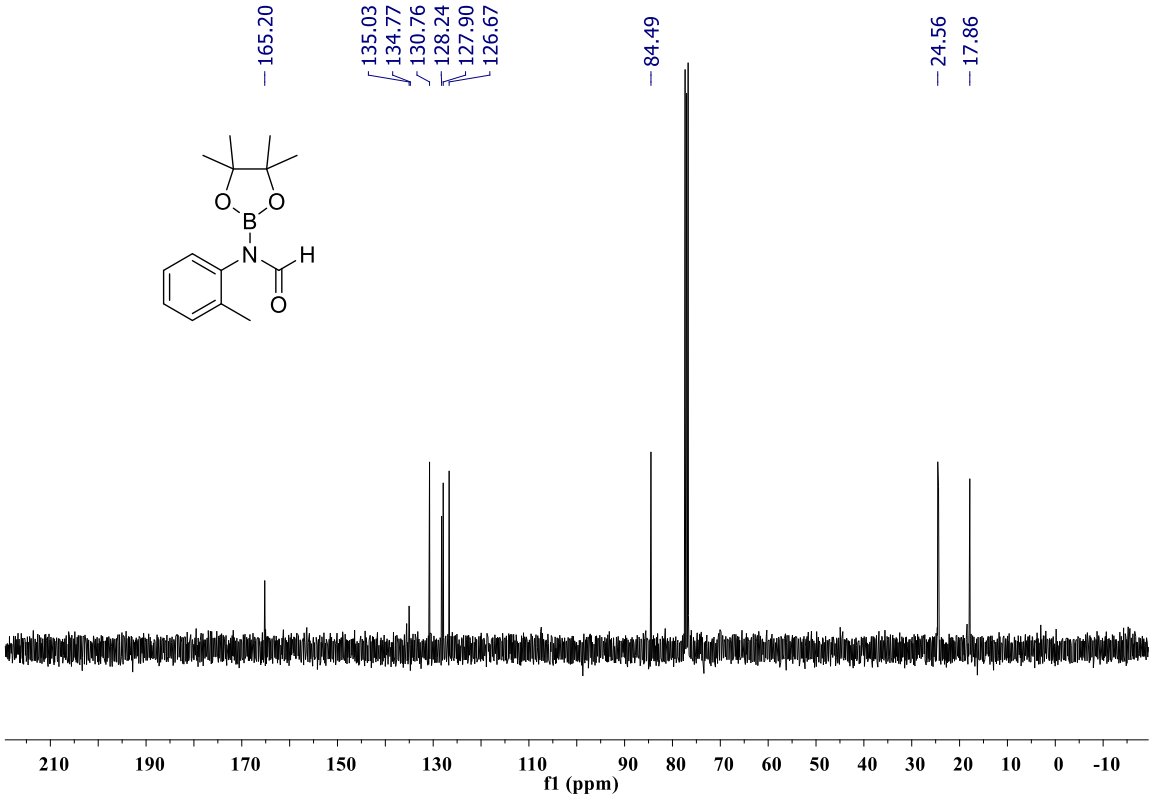


Figure S105: $^{13}C\{^{1}H\}$ NMR spectrum of **5a** (101 MHz, $CDCl_3$, 25 °C).

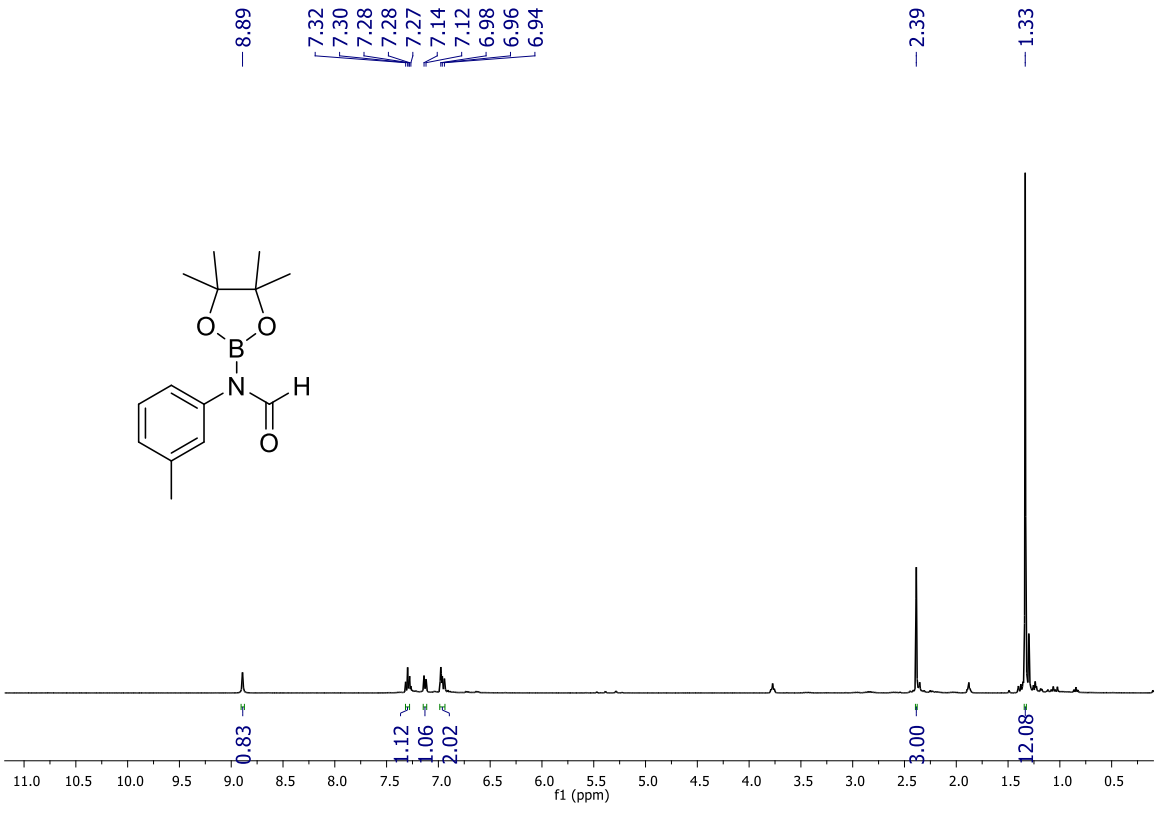


Figure S106: ^{1}H NMR spectrum of **5b** (400 MHz, $CDCl_3$, 25 °C).

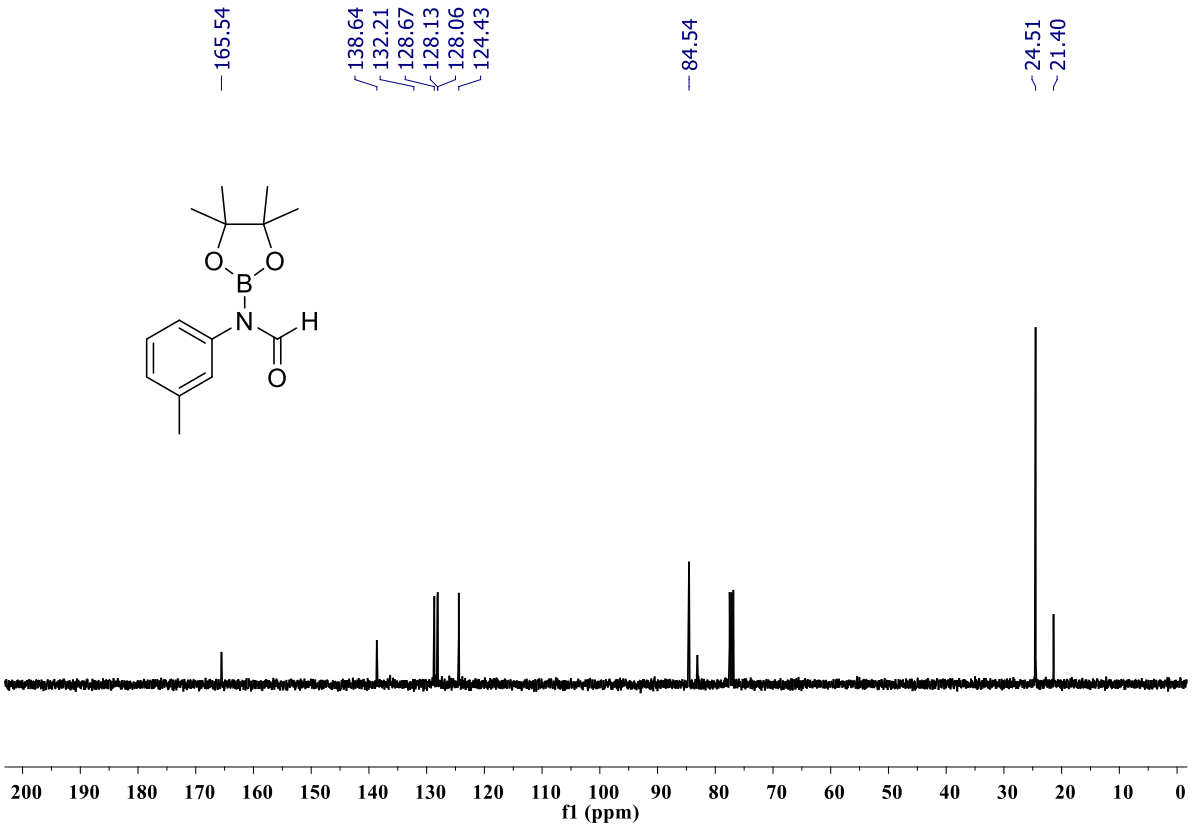


Figure S107: $^{13}C\{^{1}H\}$ NMR spectrum of **5b** (101 MHz, $CDCl_3$, 25 °C).

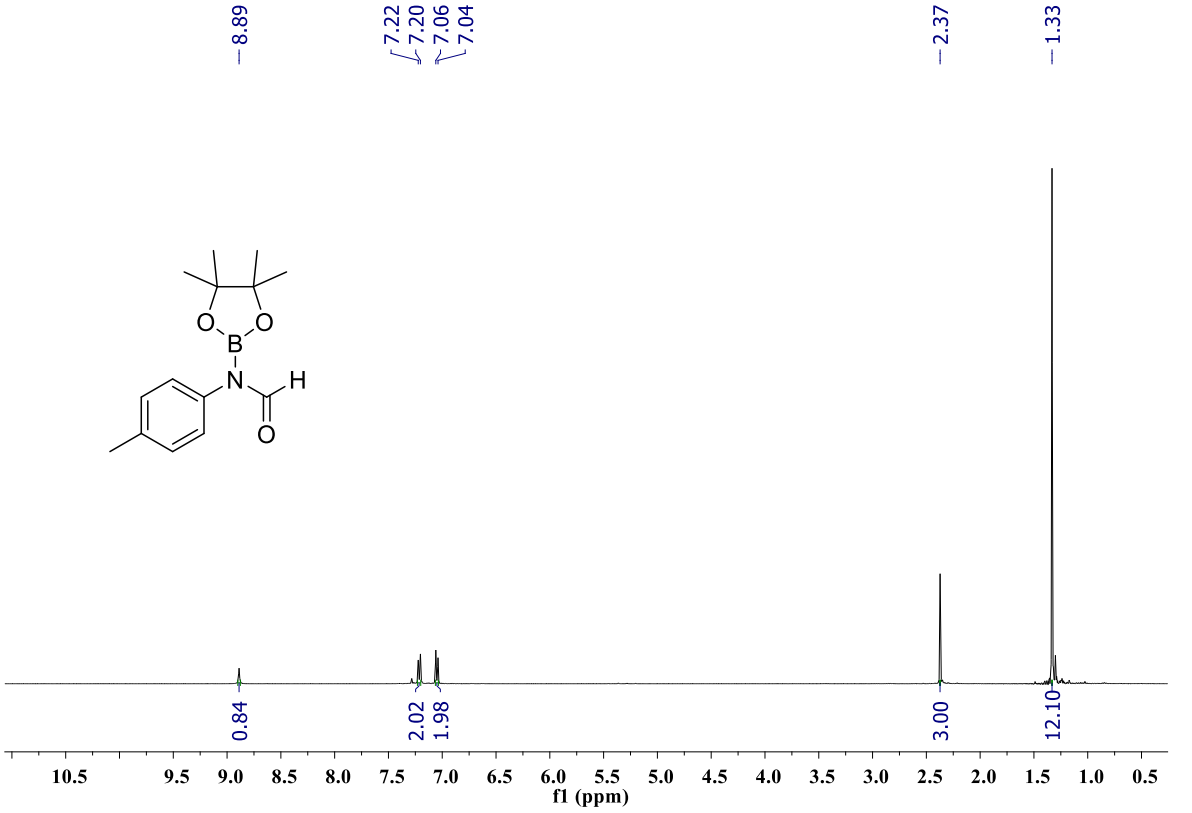


Figure S108: ^{1}H NMR spectrum of **5c** (400 MHz, $CDCl_3$, 25 °C).

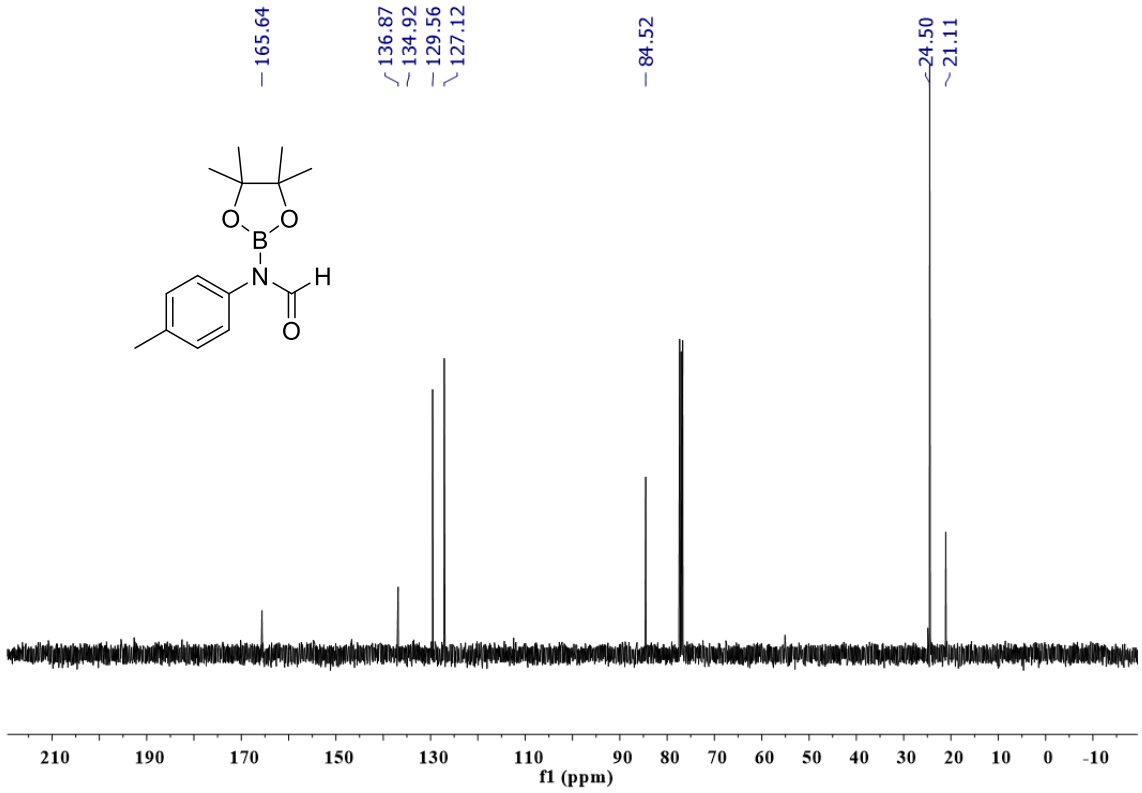


Figure S109: $^{13}C\{^{1}H\}$ NMR spectrum of **5c** (101 MHz, $CDCl_3$, 25 °C).

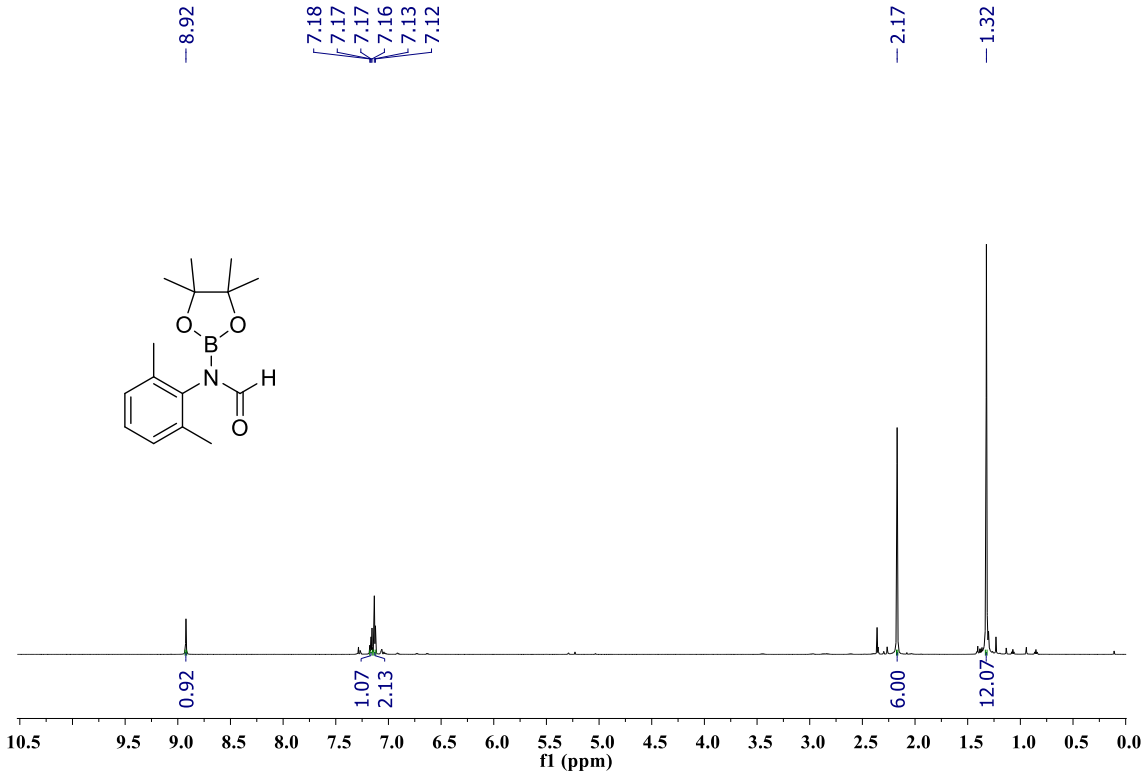


Figure S110: ^{1}H NMR spectrum of **5d** (400 MHz, $CDCl_3$, 25 °C).

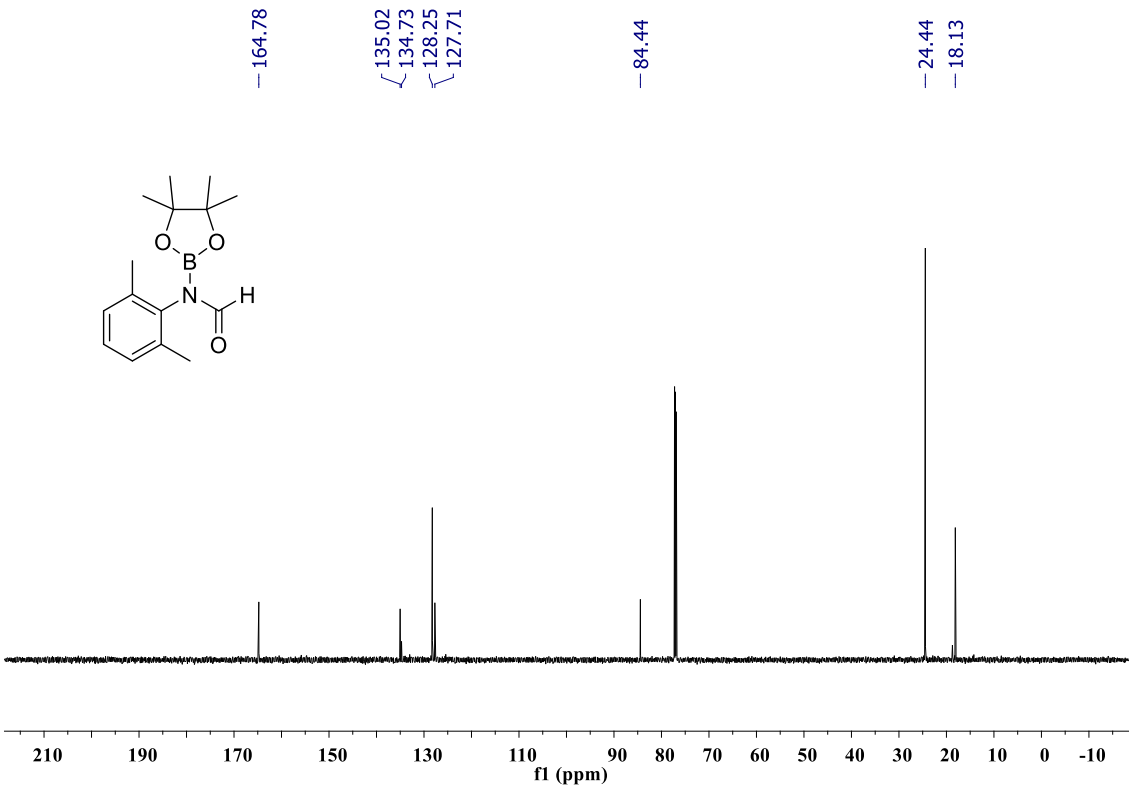


Figure S111: $^{13}C\{^{1}H\}$ NMR spectrum of **5d** (101 MHz, $CDCl_3$, 25 °C).

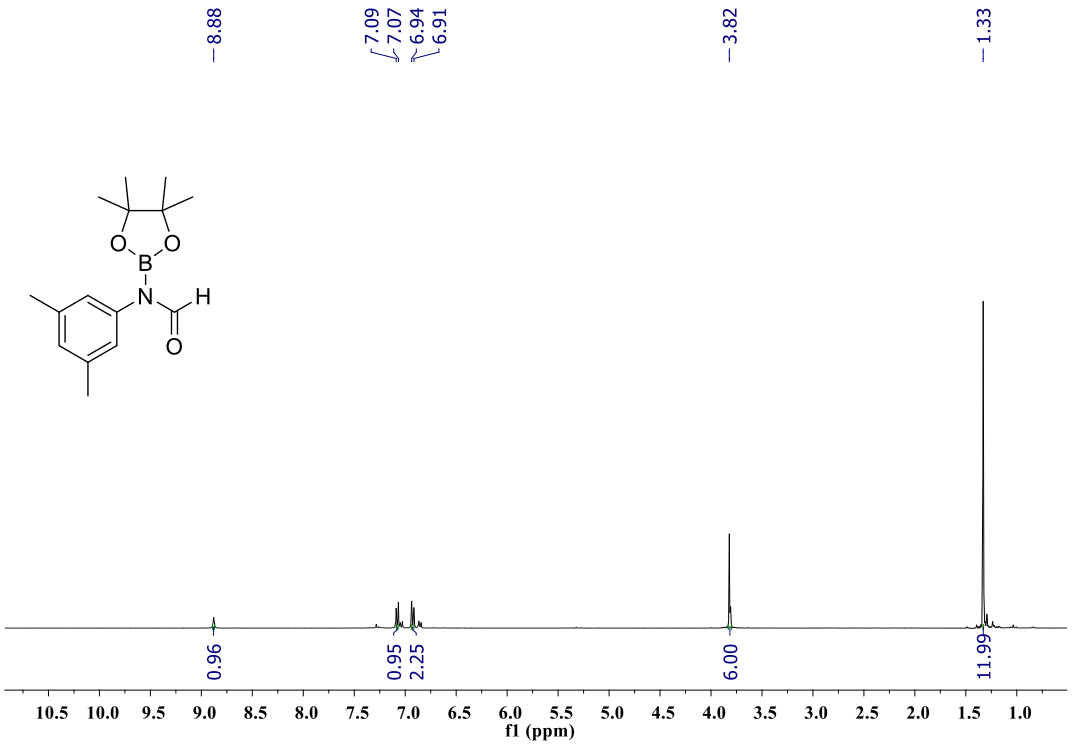


Figure S112: ^{1}H NMR spectrum of **5e** (400 MHz, $CDCl_3$, 25 °C).

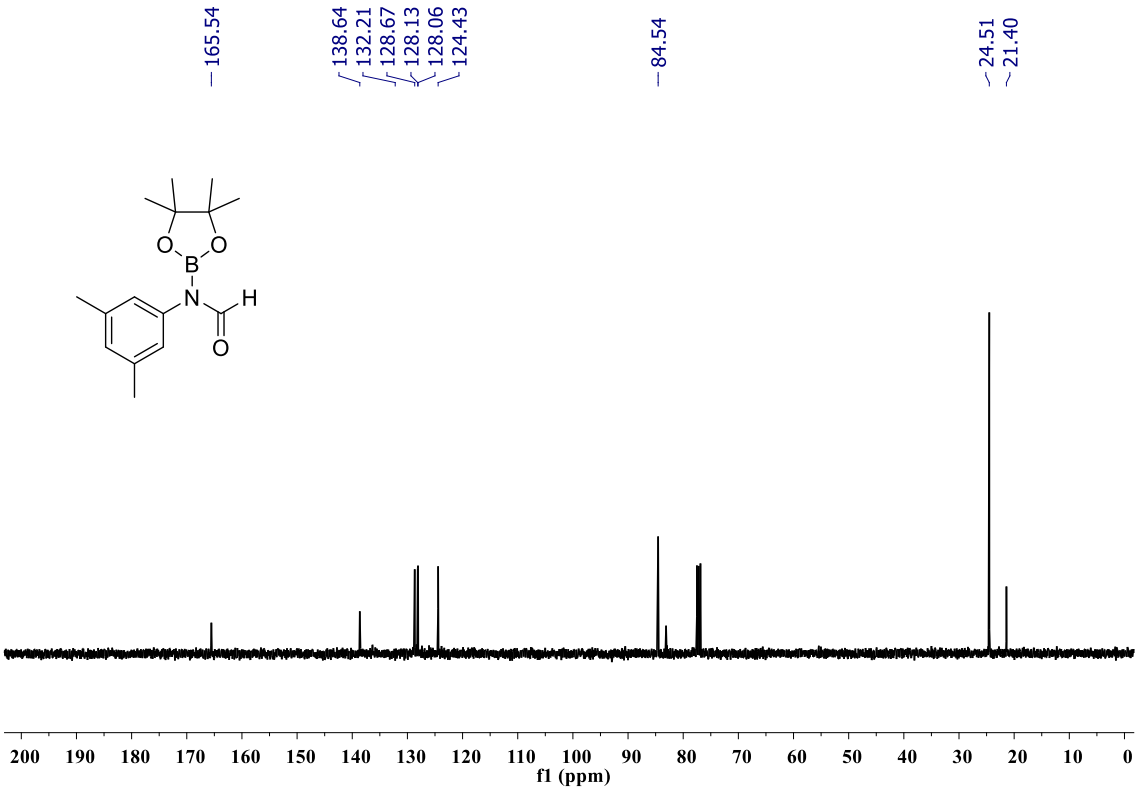


Figure S113: $^{13}C\{^{1}H\}$ NMR spectrum of **5e** (101 MHz, $CDCl_3$, 25 °C).

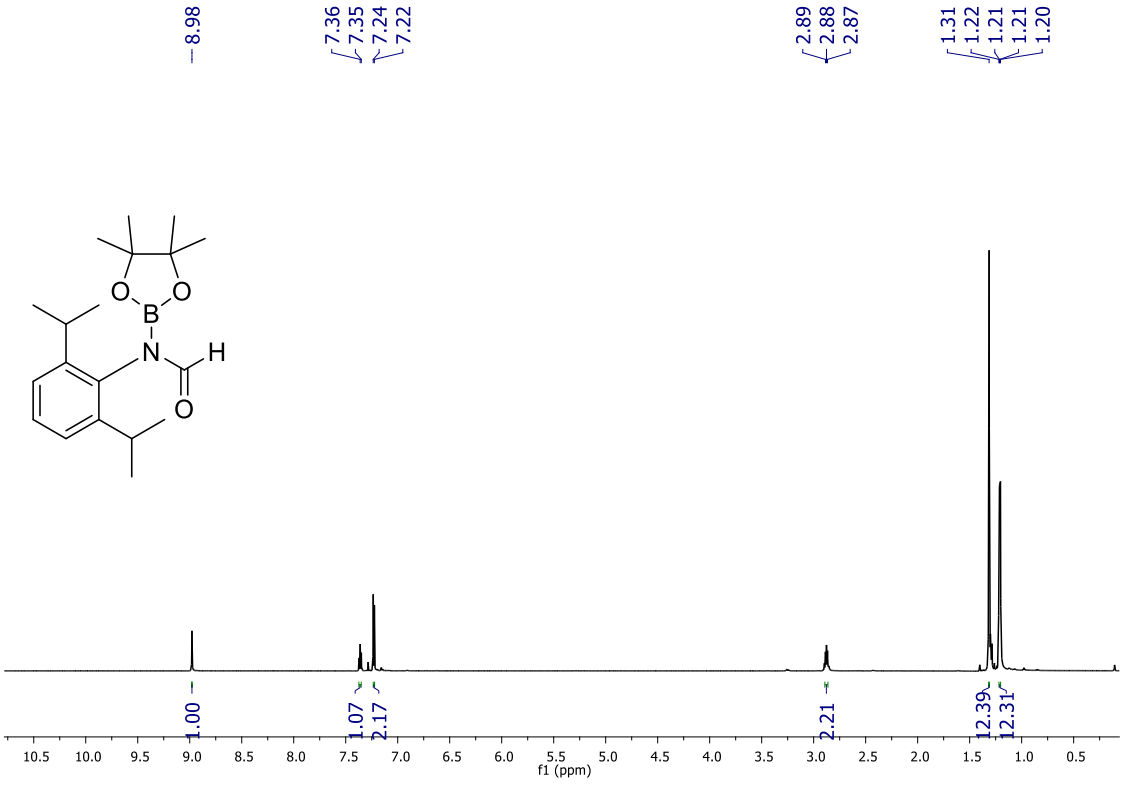


Figure S114: ^{1}H NMR spectrum of **5q** (700 MHz, $CDCl_3$, 25 °C).

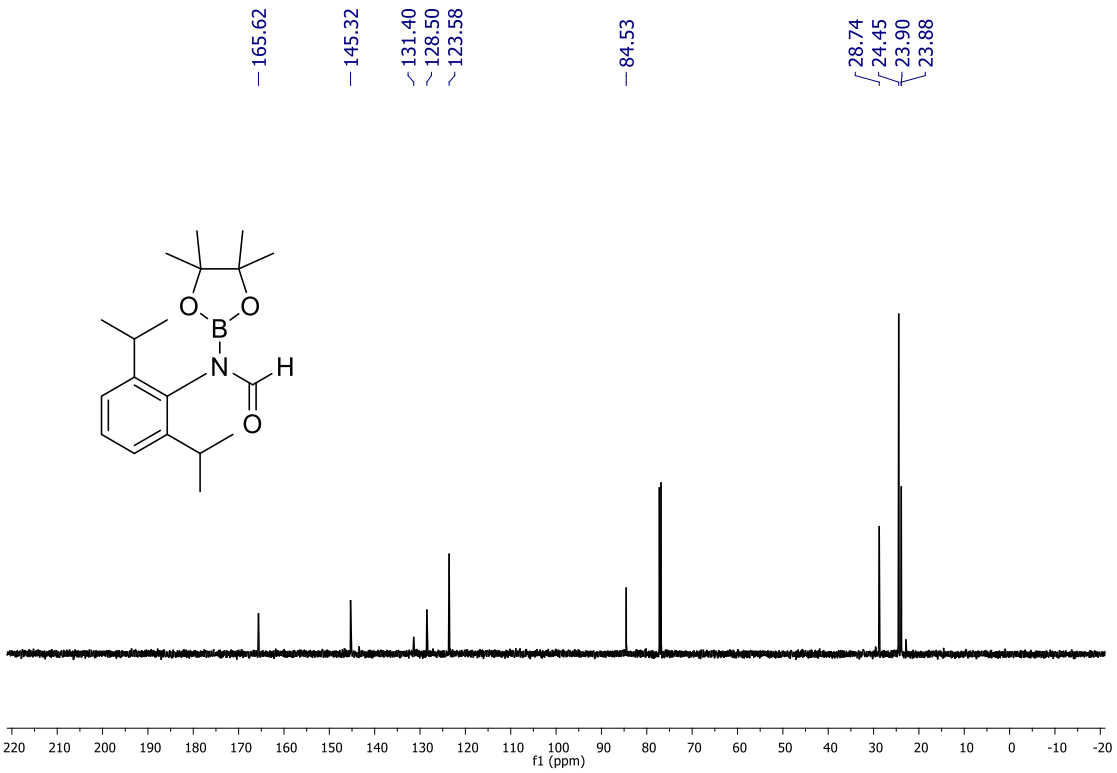


Figure S115: $^{13}C\{^{1}H\}$ NMR spectrum of **5q** (176 MHz, $CDCl_3$, 25 °C).

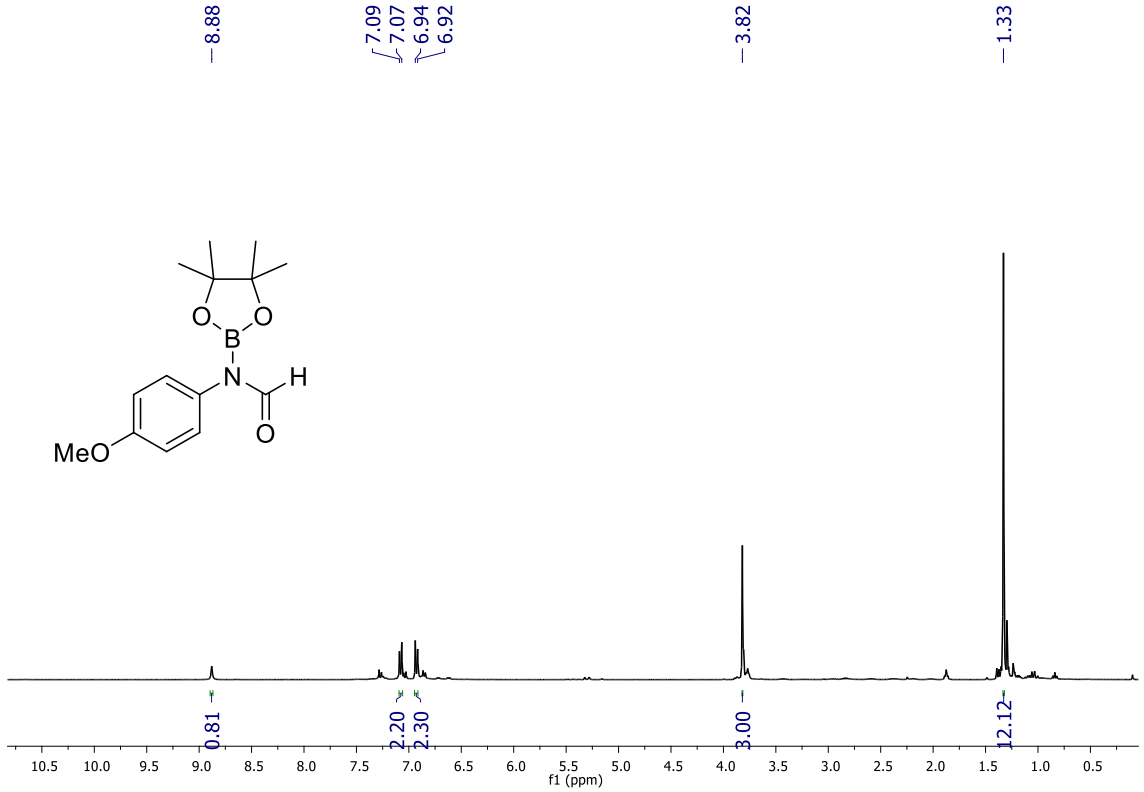


Figure S116: ^{1}H NMR spectrum of **5r** (400 MHz, $CDCl_3$, 25 °C).

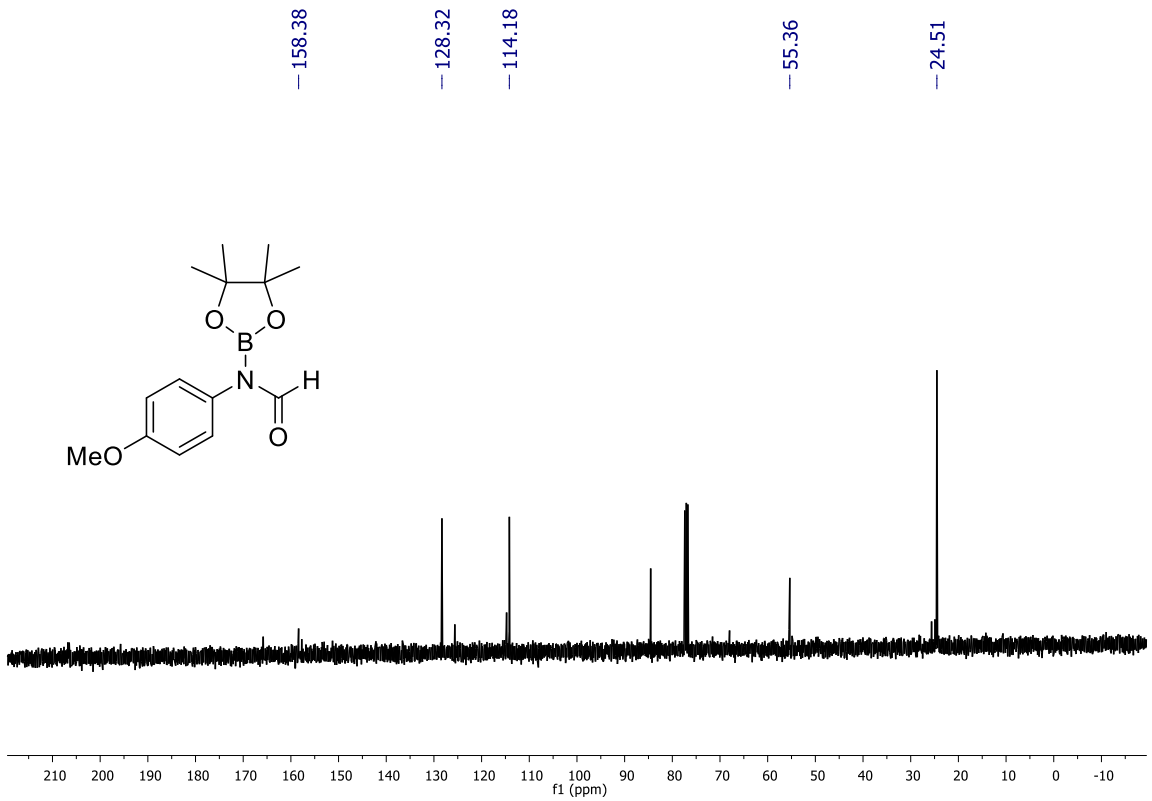


Figure S117: $^{13}C\{^{1}H\}$ NMR spectrum of **5r** (101 MHz, $CDCl_3$, 25 °C).

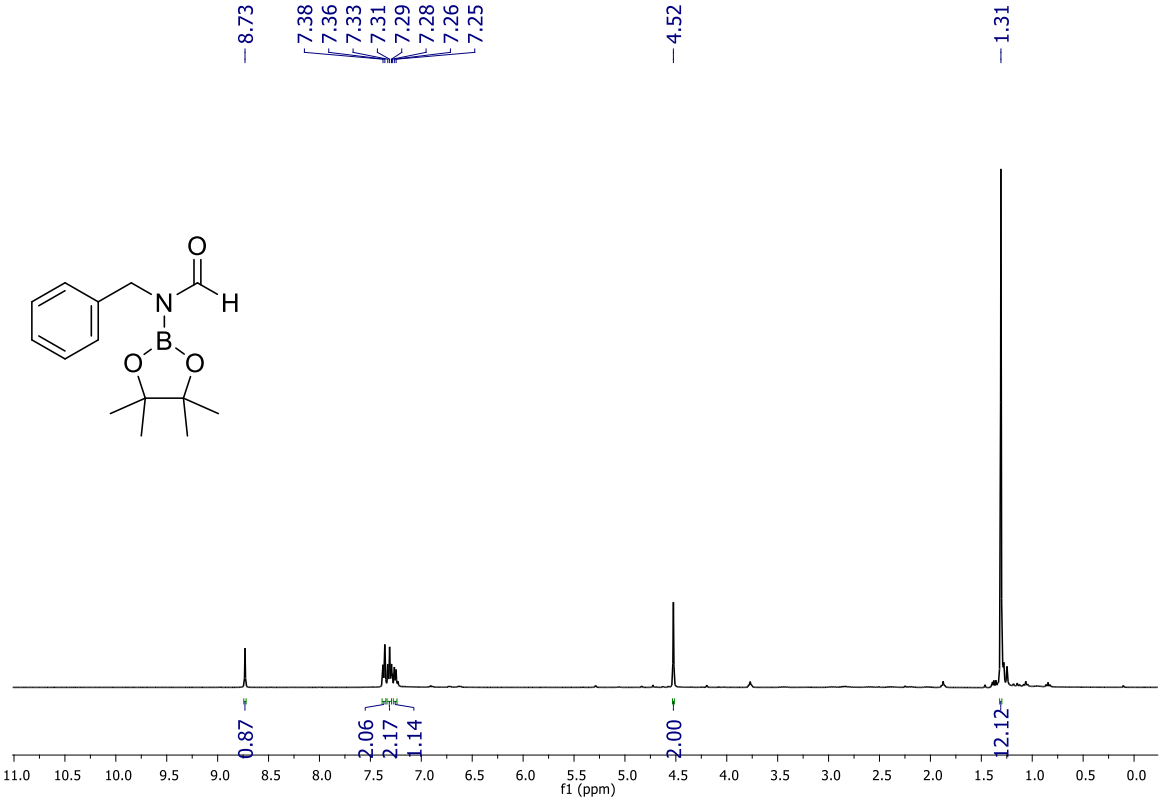


Figure S118: ^{1}H NMR spectrum of **5s** (400 MHz, $CDCl_3$, 25 °C).

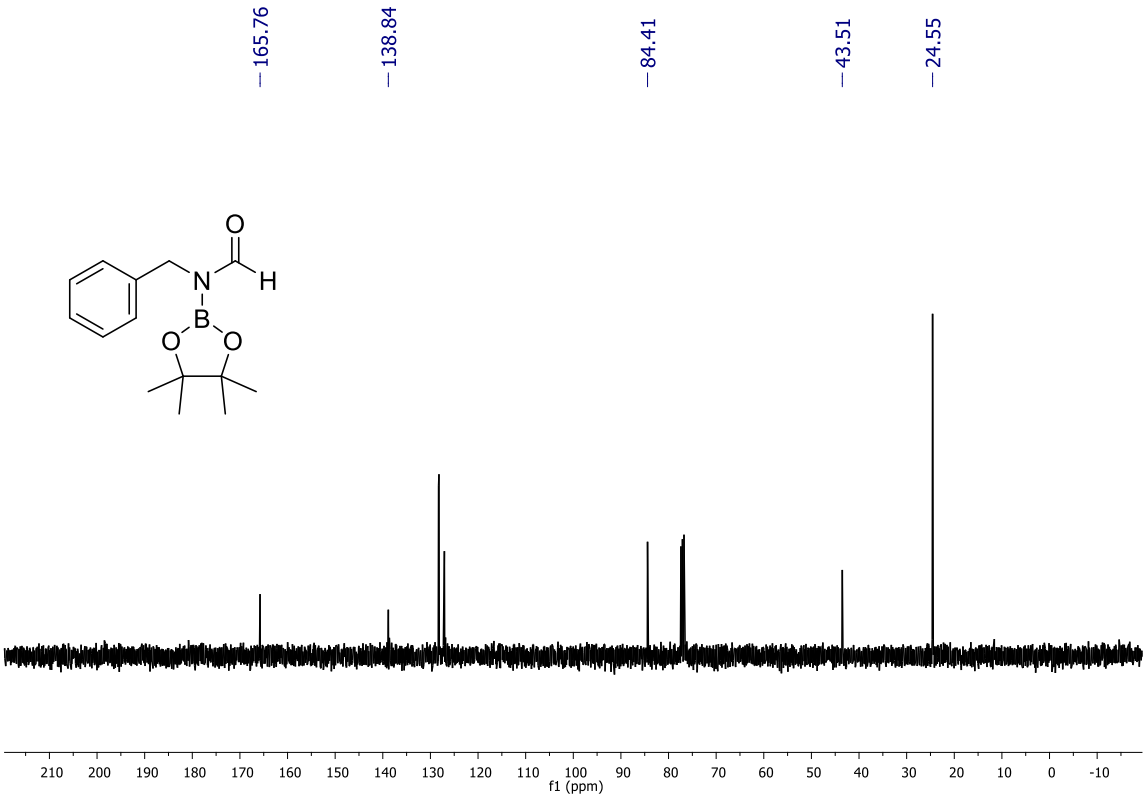


Figure S119: $^{13}C\{^{1}H\}$ NMR spectrum of **5s** (101 MHz, $CDCl_3$, 25 °C).

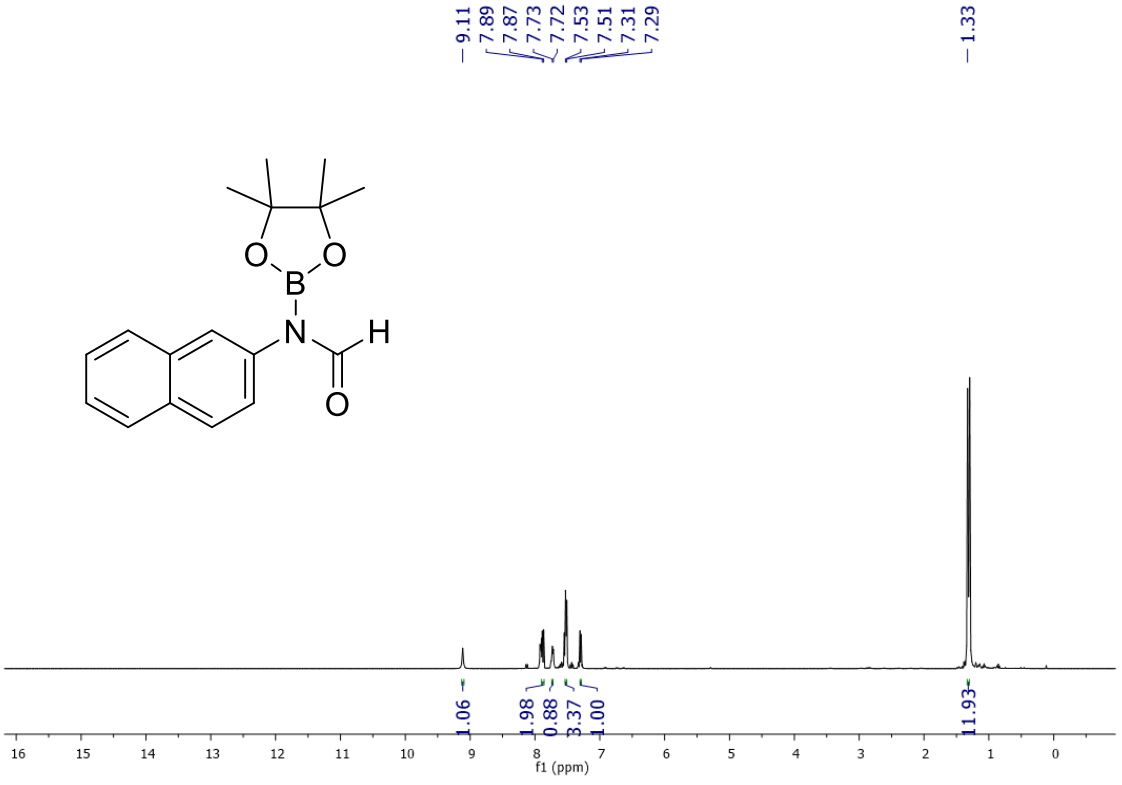


Figure S120. ^{1}H NMR spectrum of **5t** (400 MHz, $CDCl_3$, 25 °C).

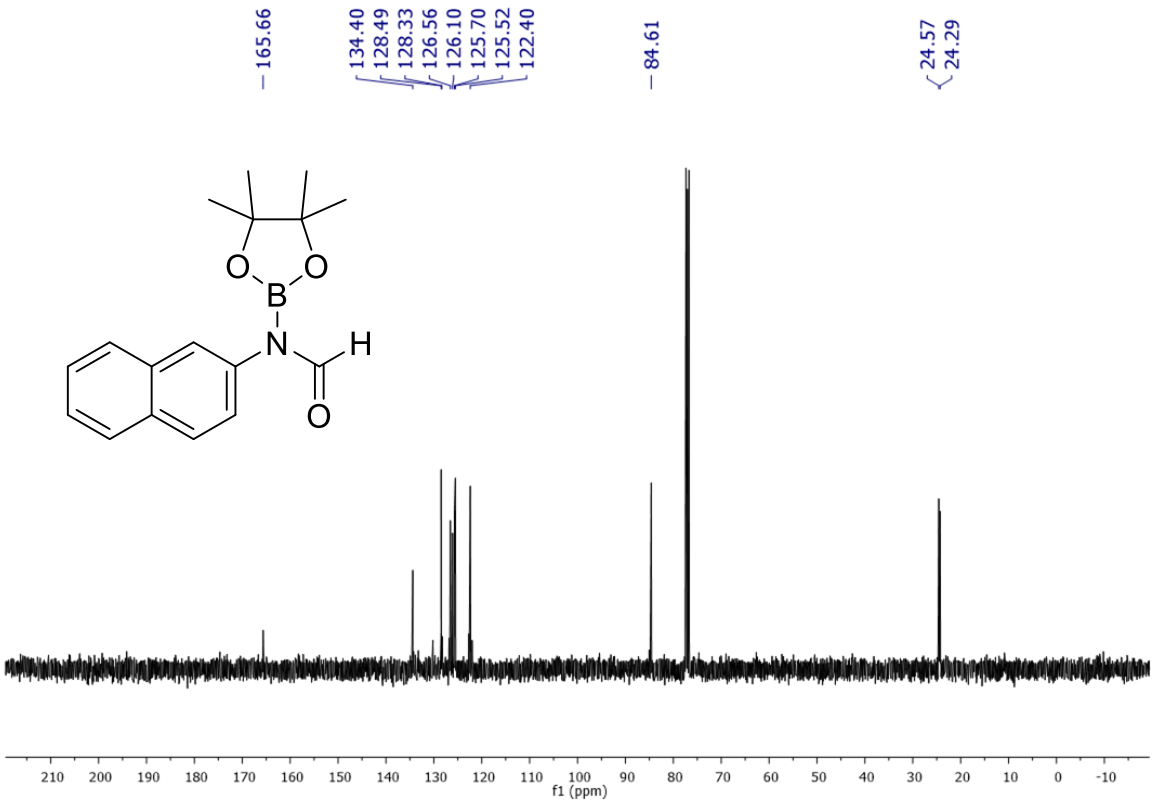


Figure S121. $^{13}C\{^{1}H\}$ NMR spectrum of **5t** (101 MHz, $CDCl_3$, 25 °C).

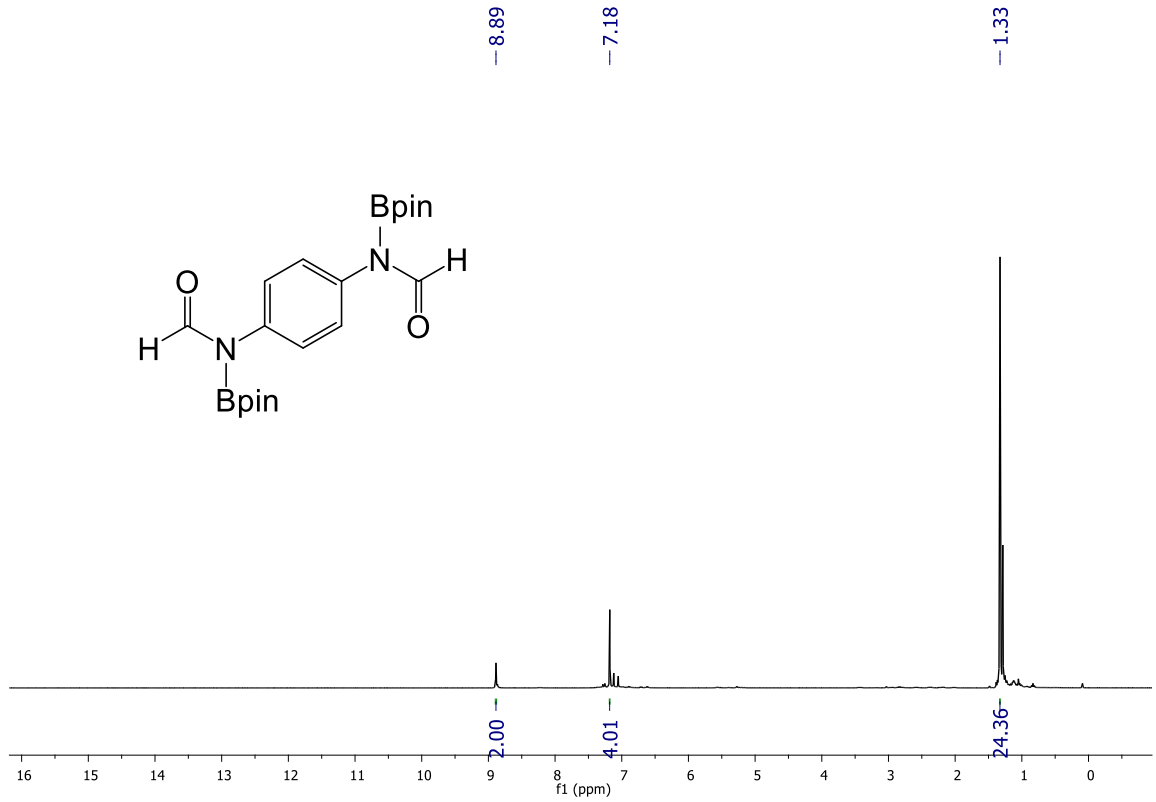


Figure S122. ^{1}H NMR spectrum of **5l** (400 MHz, $CDCl_3$, 25 °C).

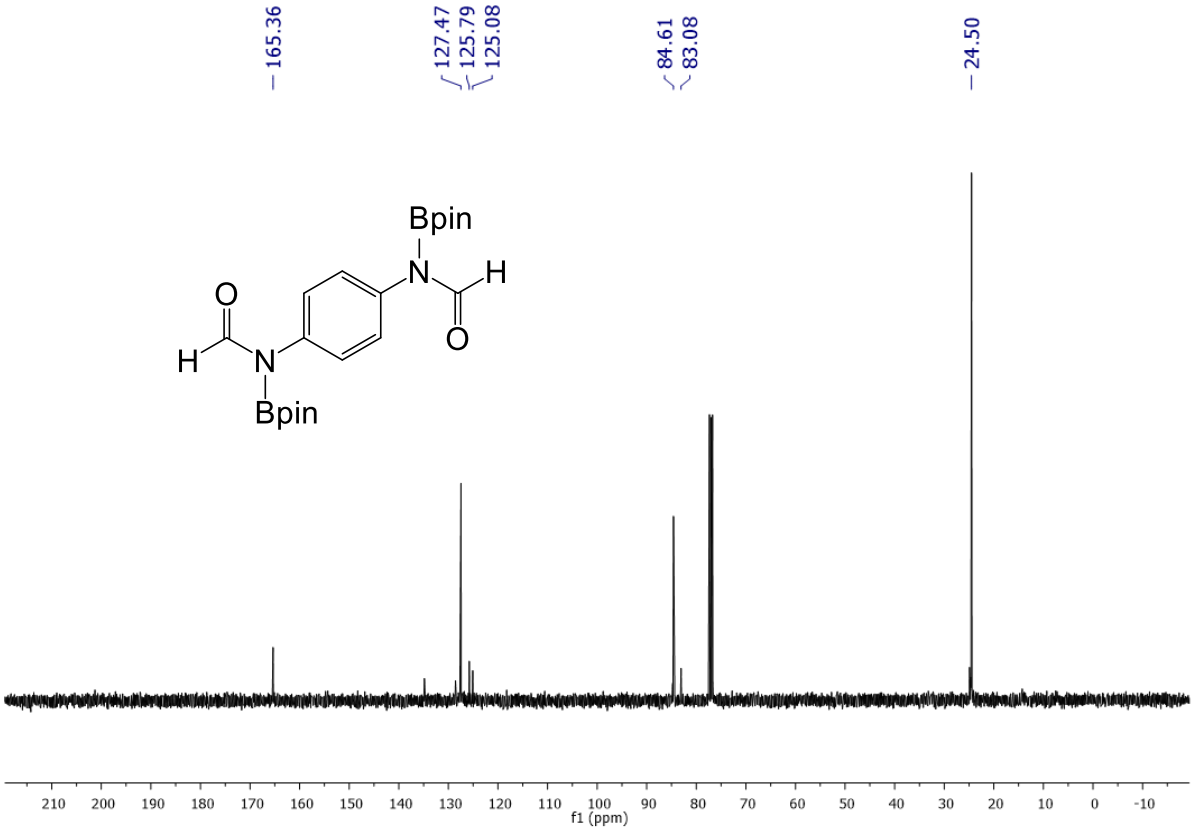


Figure S123. $^{13}C\{^{1}H\}$ NMR spectrum of **5l** (101 MHz, $CDCl_3$, 25 ^{o}C).

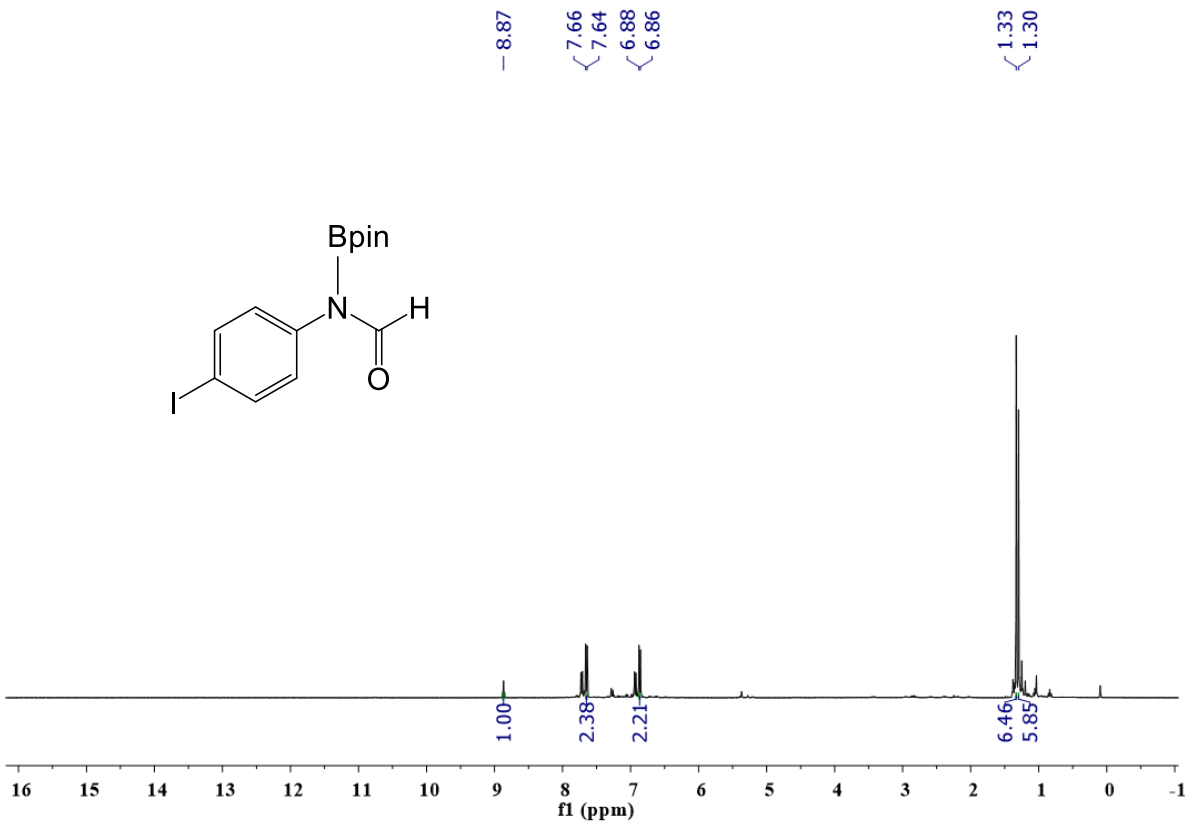


Figure S124. ^{1}H NMR spectrum of **5k** (400 MHz, $CDCl_3$, 25 ^{o}C).

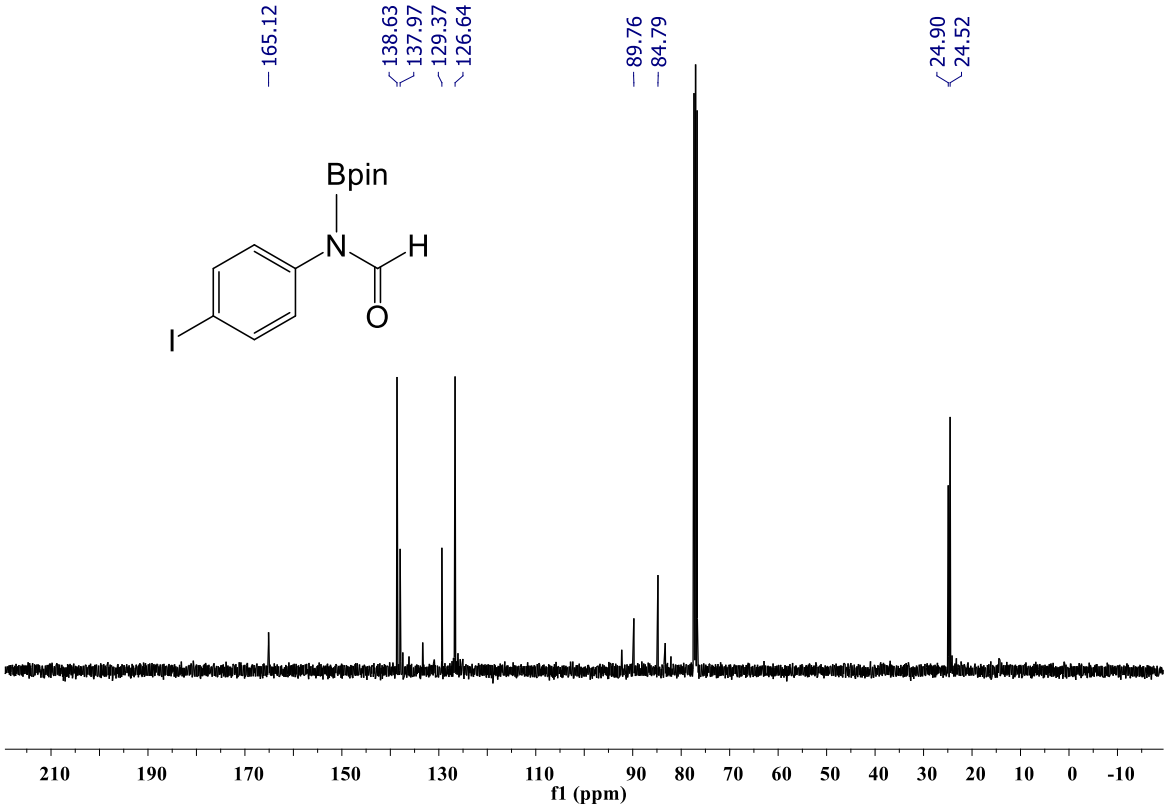


Figure S125. $^{13}C\{^{1}H\}$ NMR spectrum of **5k** (101 MHz, $CDCl_3$, 25 °C).

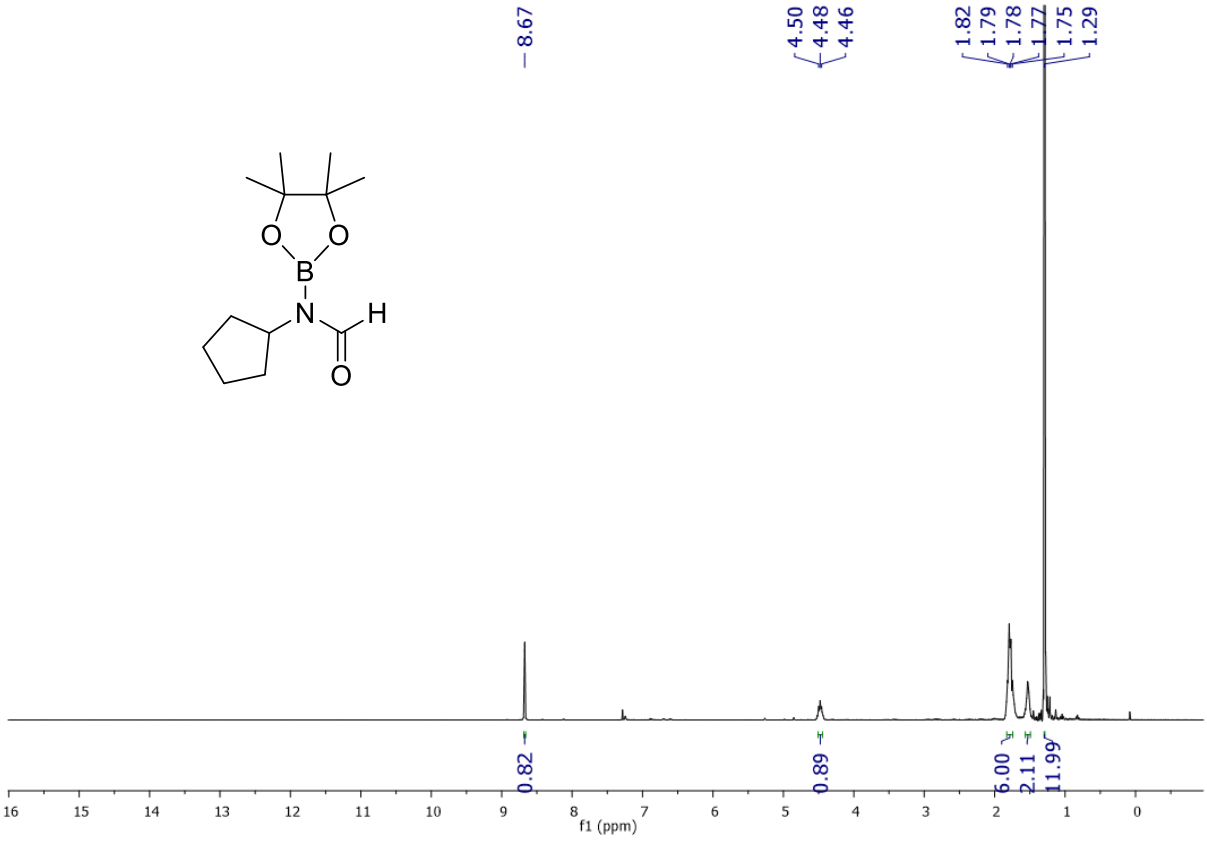


Figure S126. ^{1}H NMR spectrum of **5m** (400 MHz, $CDCl_3$, 25 °C).

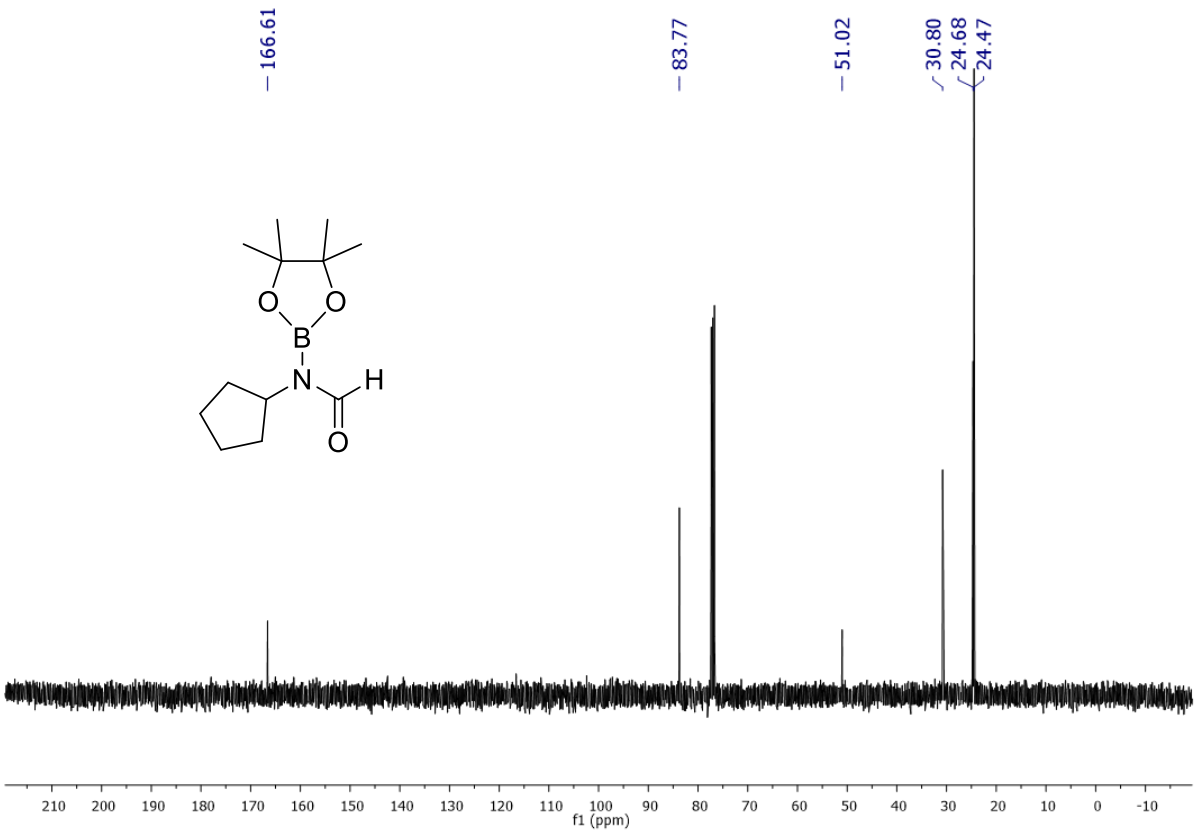


Figure S127. $^{13}C\{^{1}H\}$ NMR spectrum of **5m** (101 MHz, $CDCl_3$, 25 °C).

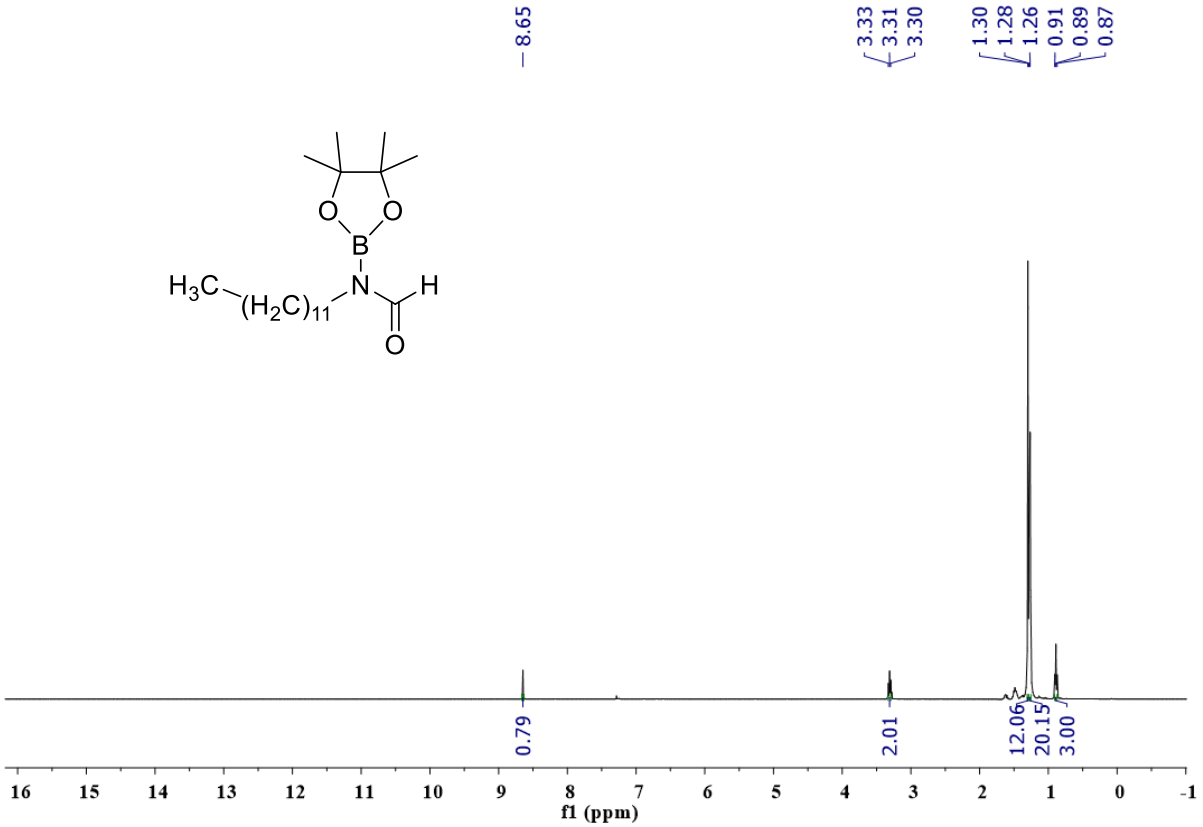


Figure S128. ^{1}H NMR spectrum of **5u** (400 MHz, $CDCl_3$, 25 °C).

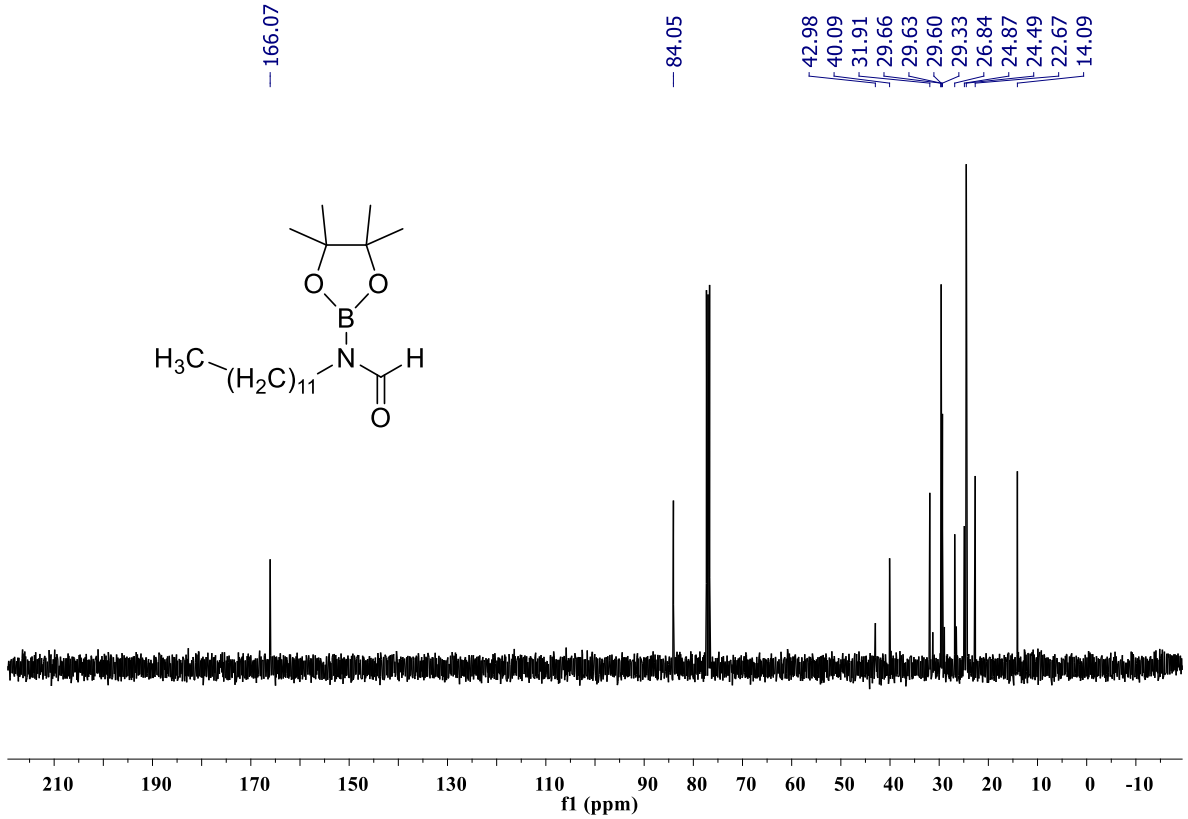


Figure S129. $^{13}C\{^{1}H\}$ NMR spectrum of **5u** (101 MHz, $CDCl_3$, 25 °C).

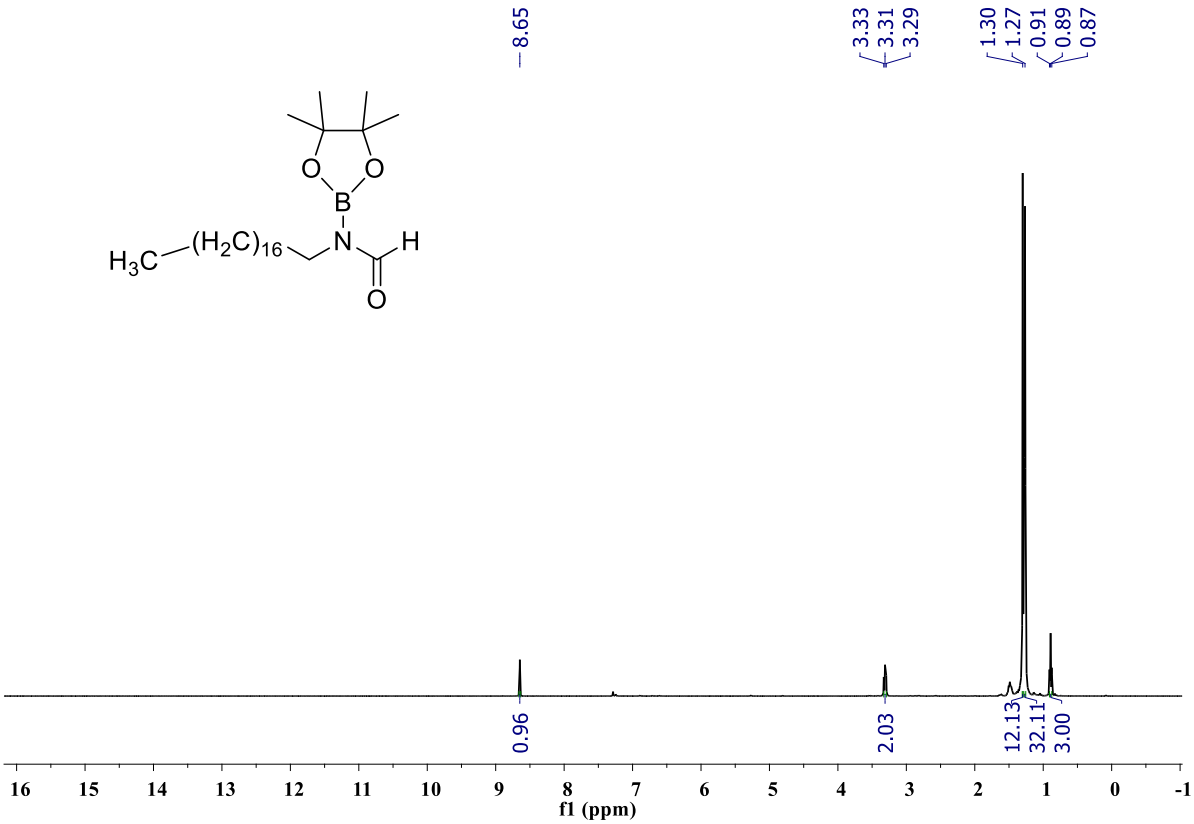


Figure S130. ^{1}H NMR spectrum of **5o** (400 MHz, $CDCl_3$, 25 °C).

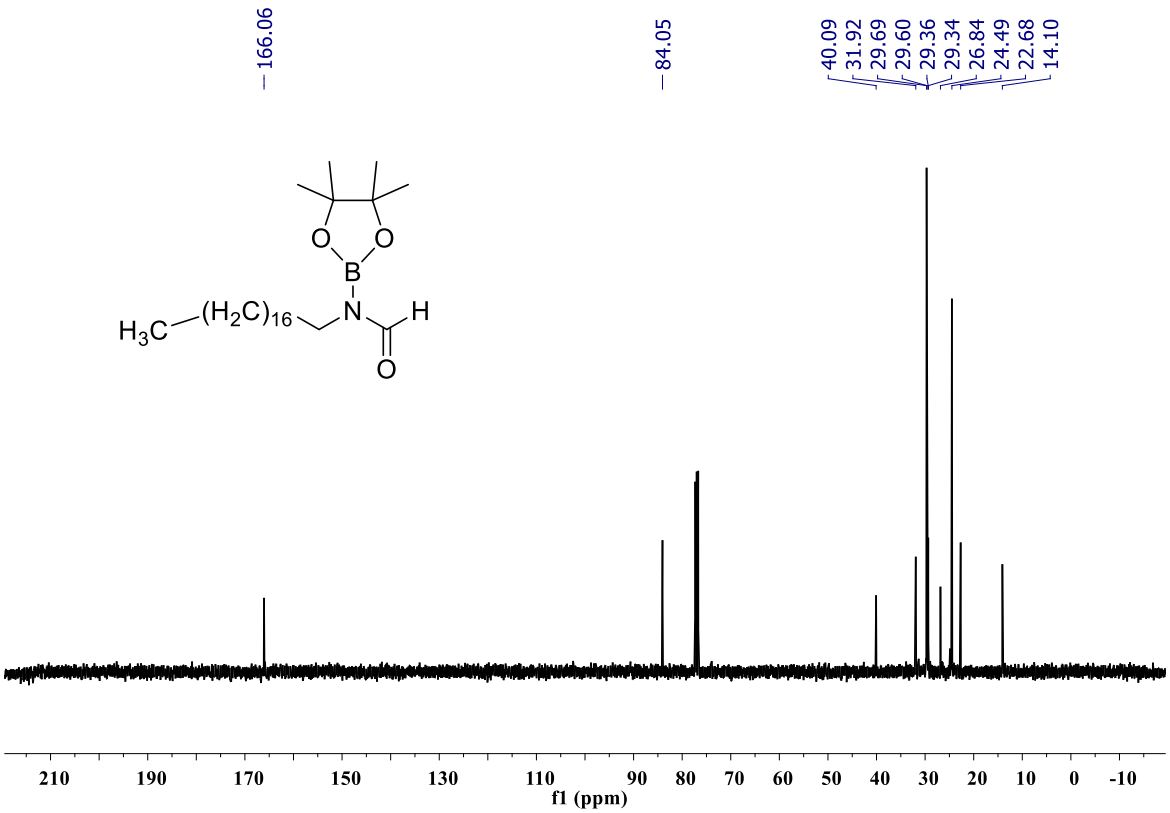


Figure S131. $^{13}C\{^{1}H\}$ NMR spectrum of **5o** (101 MHz, $CDCl_3$, 25 °C).

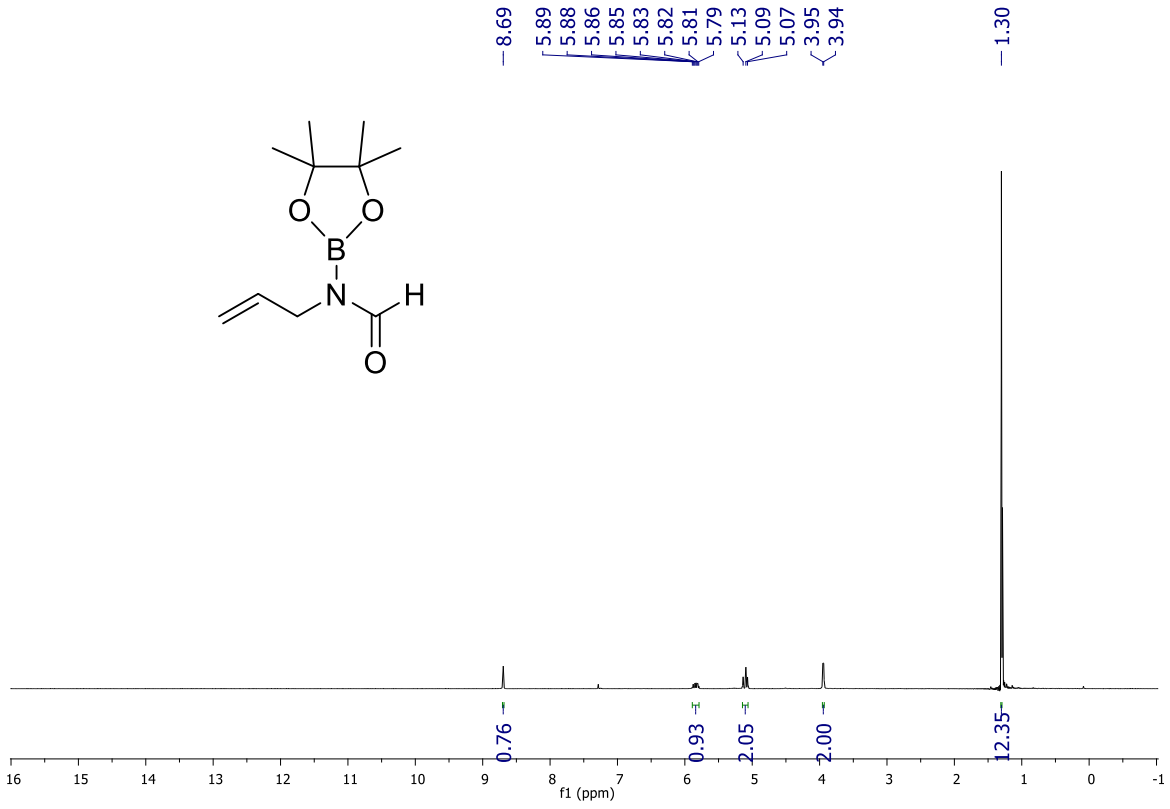


Figure S132. ^{1}H NMR spectrum of **5p** (400 MHz, $CDCl_3$, 25 °C).

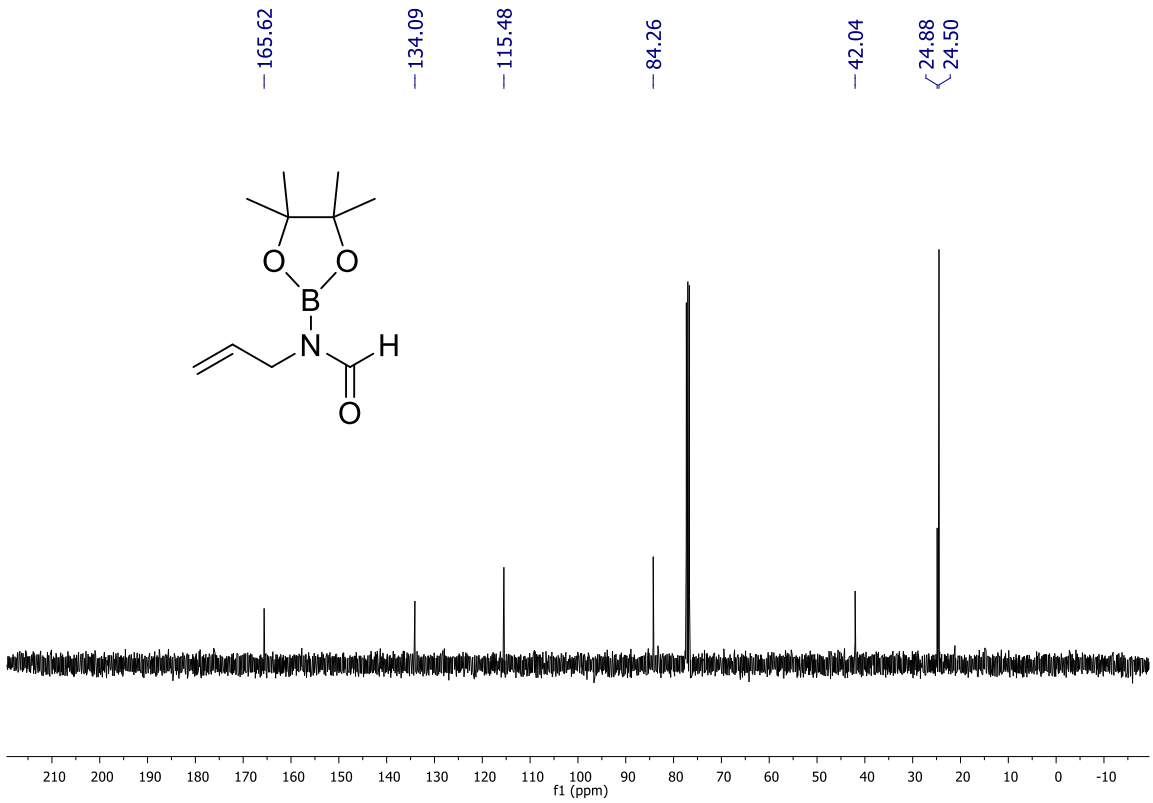


Figure S133. $^{13}C\{^{1}H\}$ NMR spectrum of **5p** (101 MHz, $CDCl_3$, 25 ^{o}C).

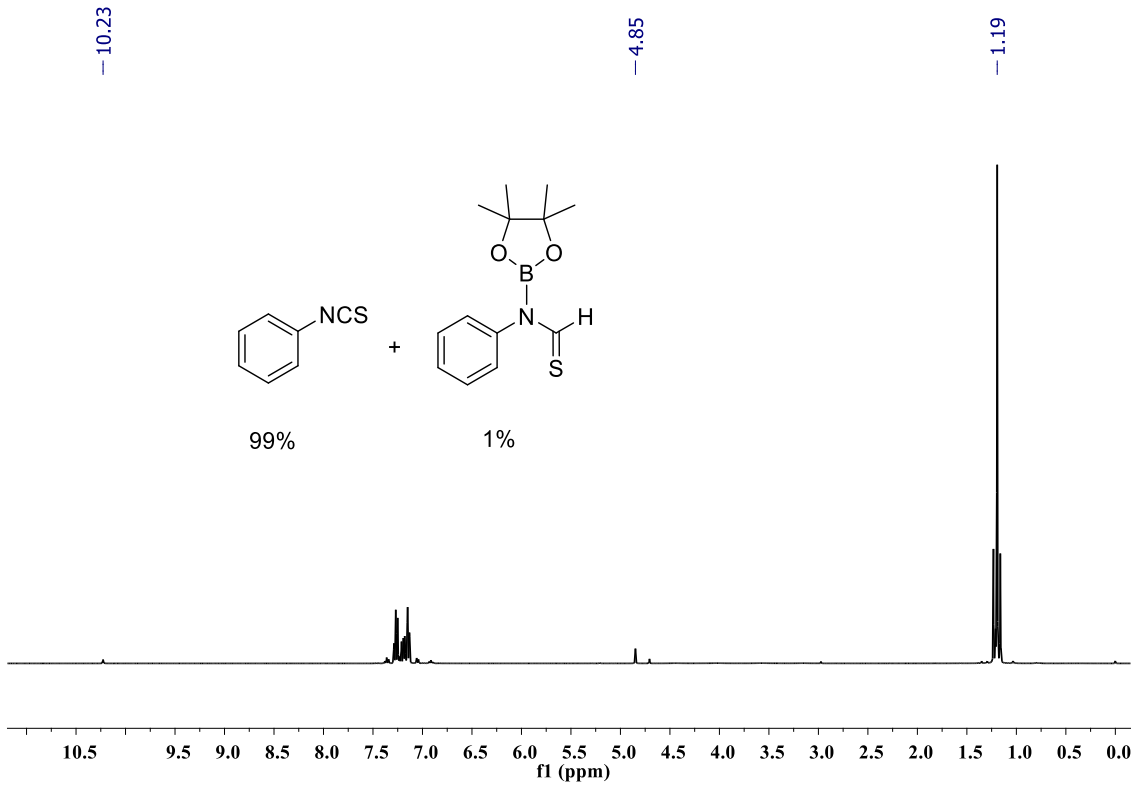


Figure S134: ^{1}H NMR spectrum of phenylisothiocyanate with 1 equivalent of HBpin in the absence of catalyst (400 MHz, $CDCl_3$).

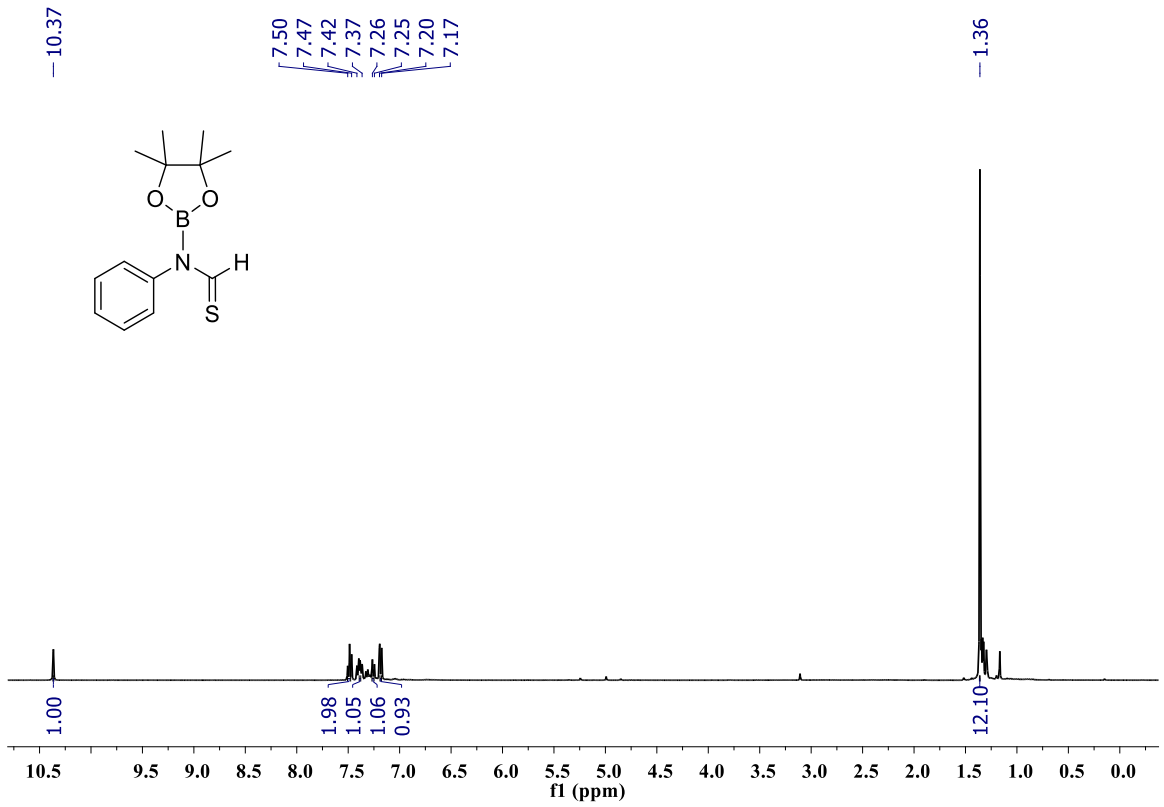


Figure S135: ^{1}H NMR spectrum of **7a** (400 MHz, $CDCl_3$, 25 ^{o}C).

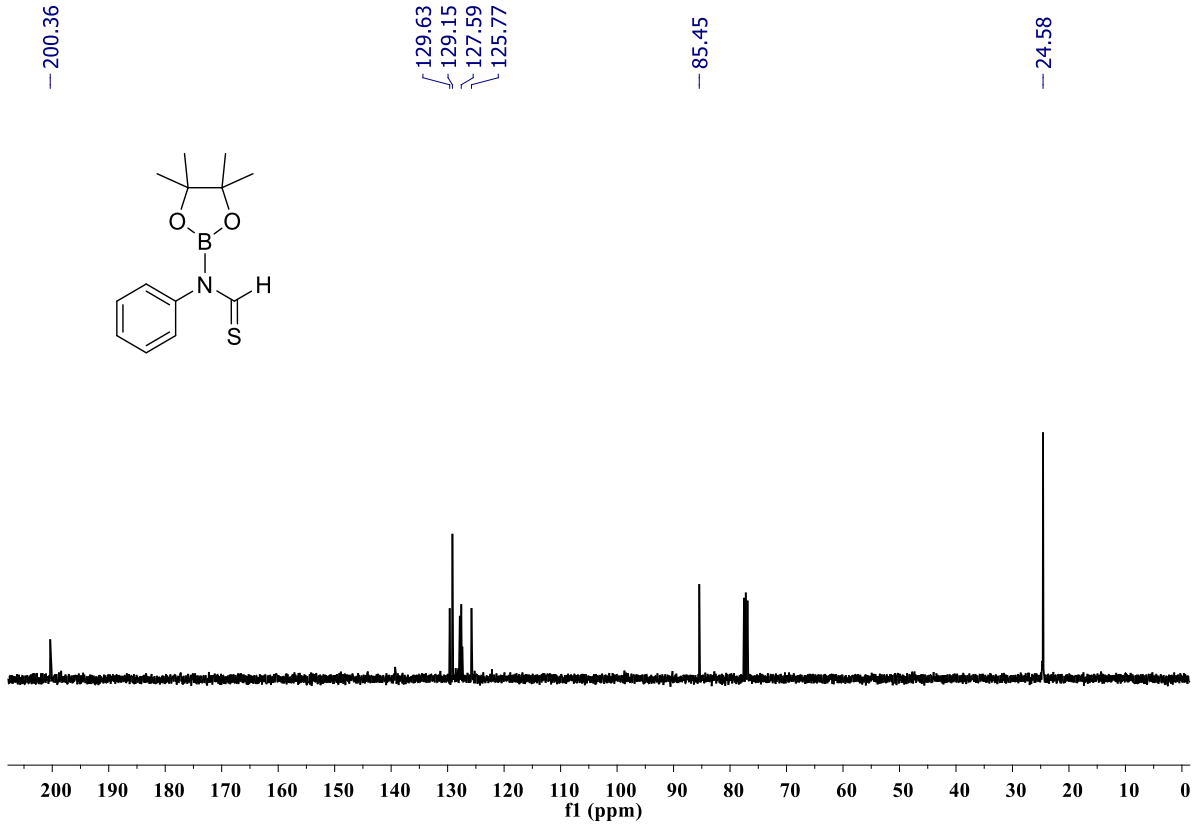


Figure S136: ^{13}C{^{1}H} NMR spectrum of **7a** (101 MHz, $CDCl_3$, 25 ^{o}C).

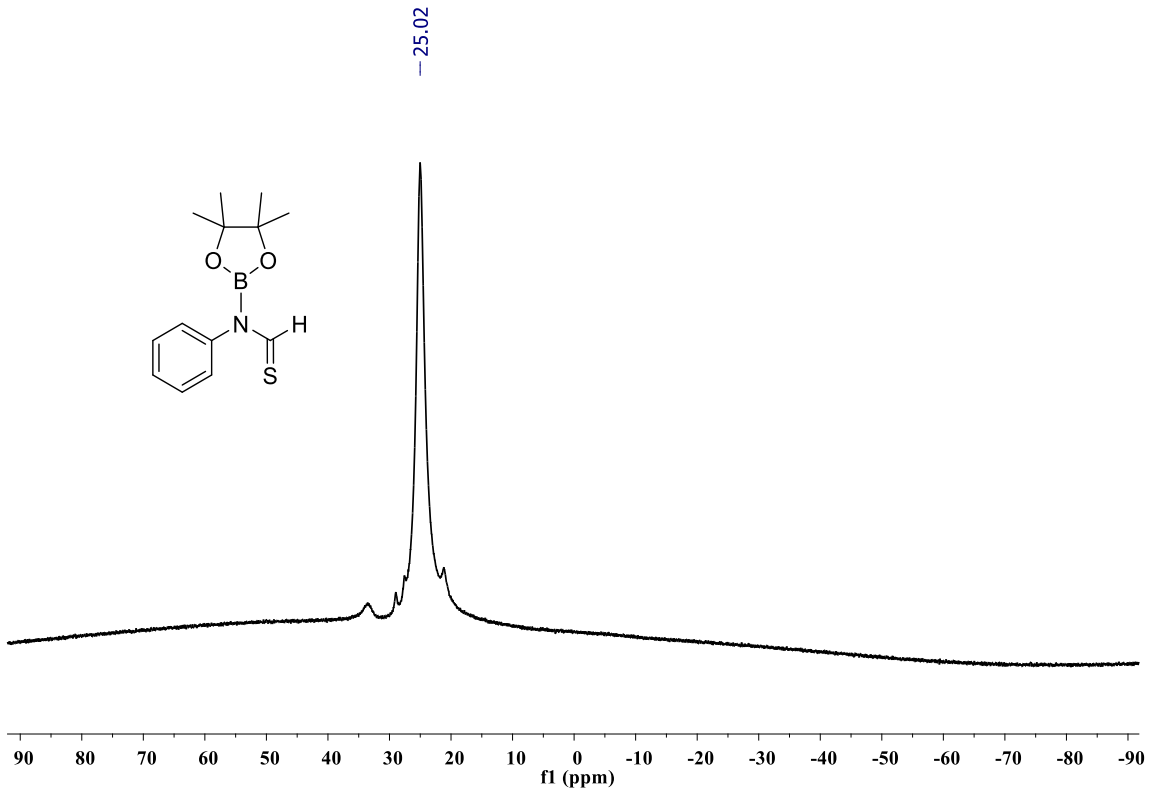


Figure S137: ^{11}B NMR spectrum of **7a** (128 MHz, $CDCl_3$, 25 °C).

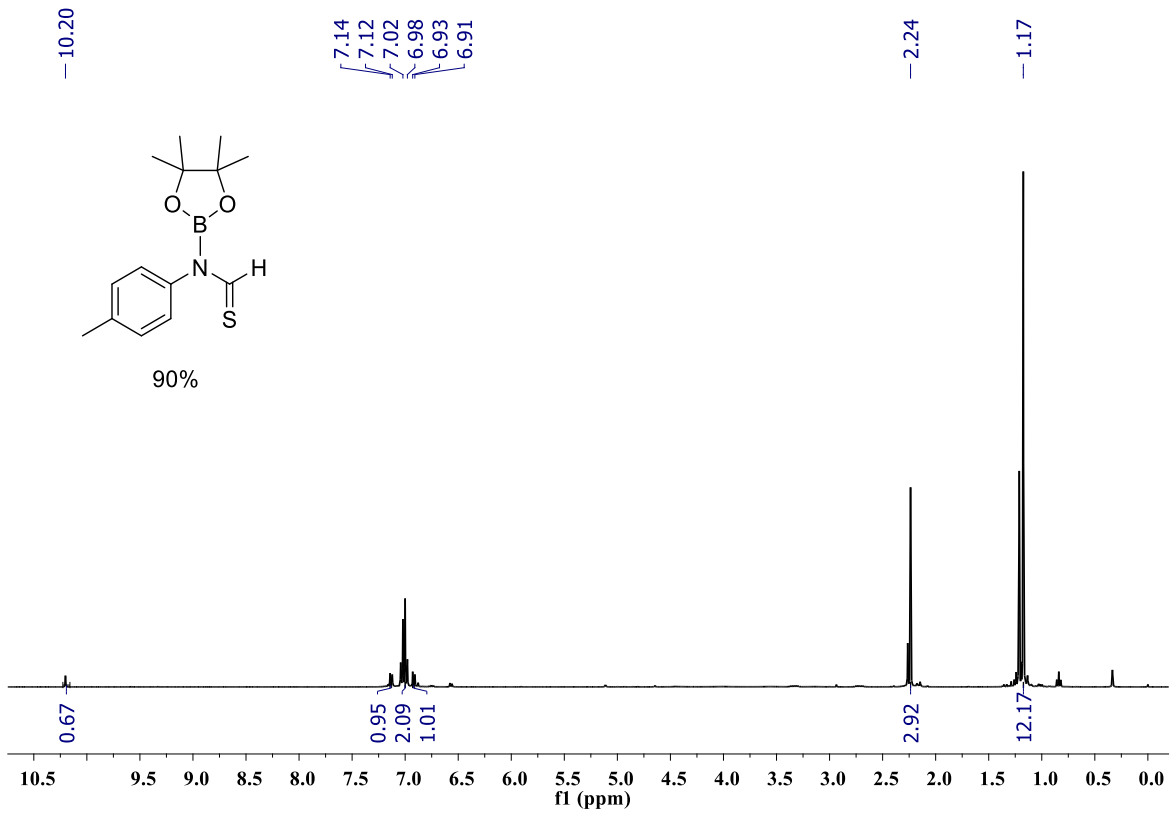


Figure S138: ^{1}H NMR spectrum of **7b** (400 MHz, $CDCl_3$, 25 °C).

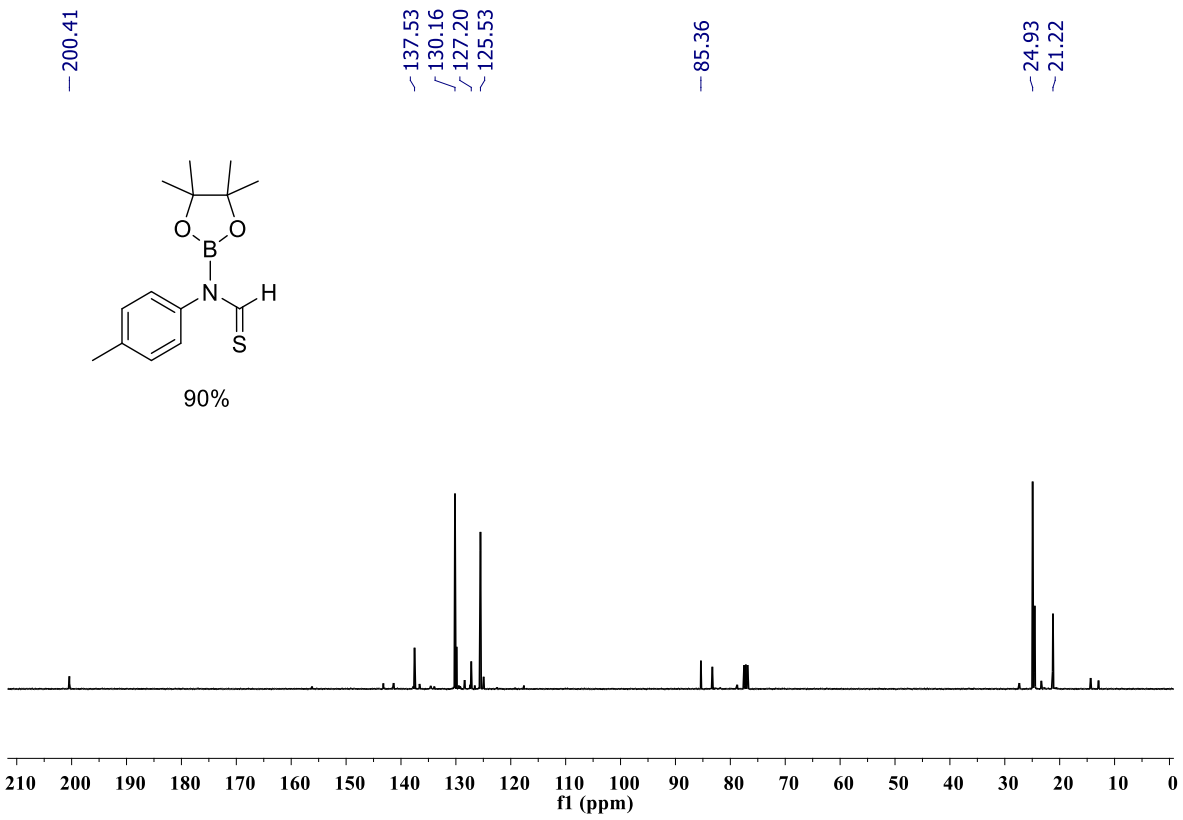


Figure S139: $^{13}C\{^{1}H\}$ NMR spectrum of **7b** (101 MHz, $CDCl_3$, 25 °C).

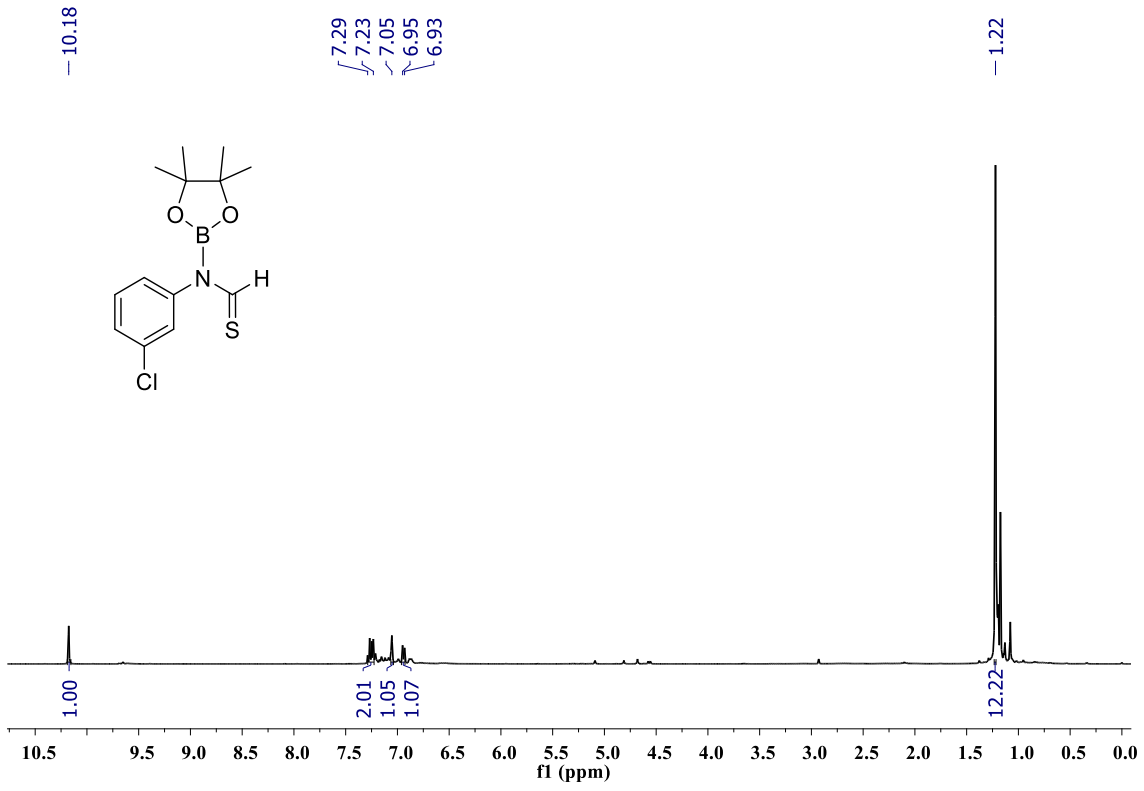


Figure S140: ^{1}H NMR spectrum of **7c** (400 MHz, $CDCl_3$, 25 °C).

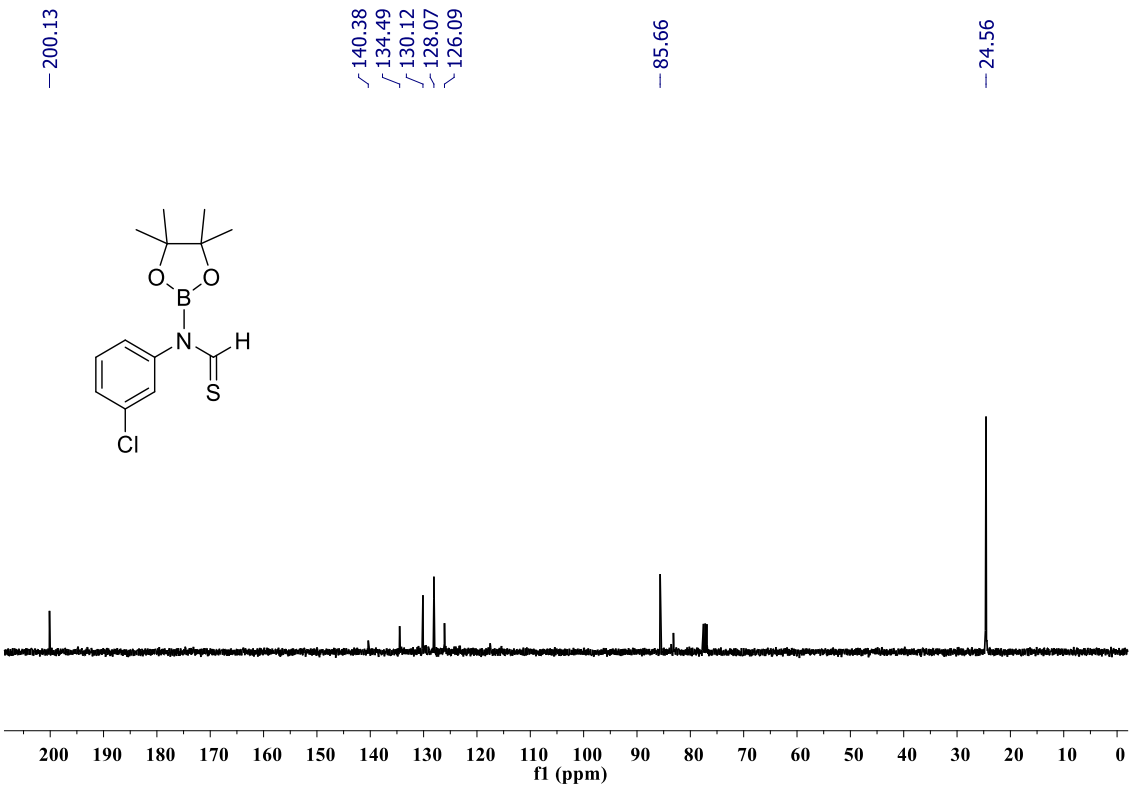


Figure S141: $^{13}C\{^{1}H\}$ NMR spectrum of **7c** (101 MHz, $CDCl_3$, 25 ^{o}C).

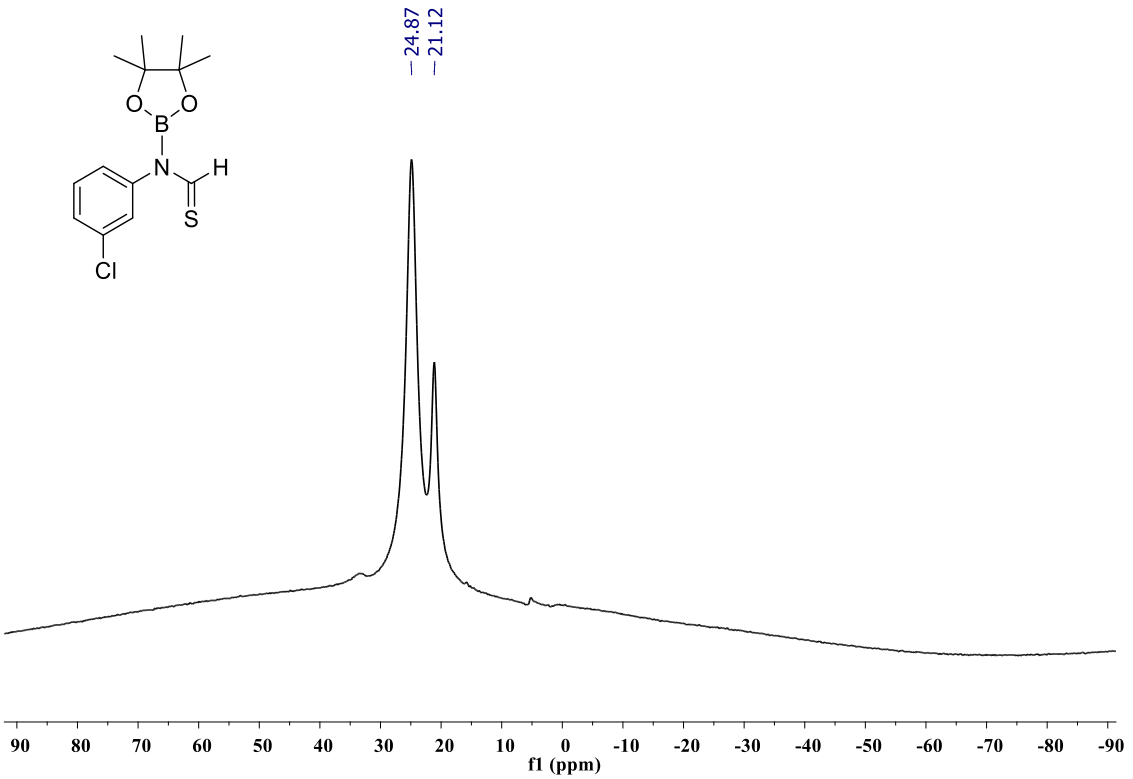


Figure S142: ^{11}B NMR spectrum of **7c** (128 MHz, $CDCl_3$, 25 ^{o}C). A peak observed at δ 21.12 ppm arises from $B(OR)_3$.

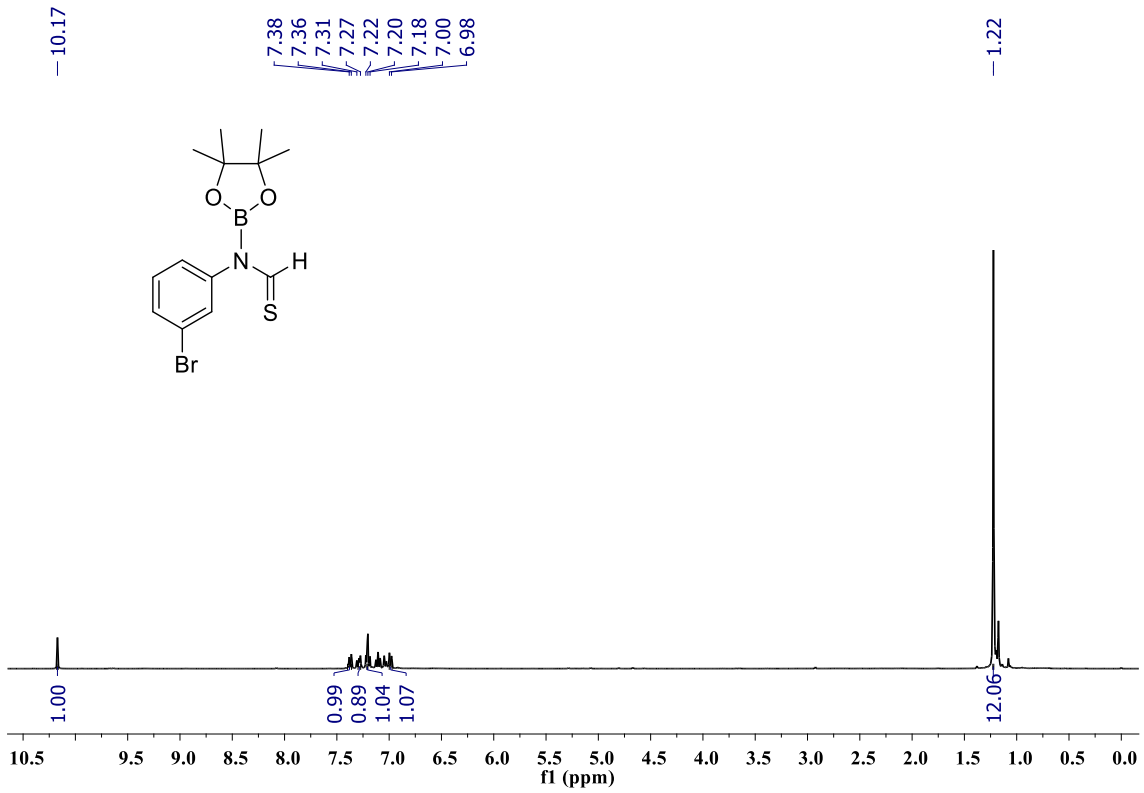


Figure S143: ^{1}H NMR spectrum of **7d** (400 MHz, $CDCl_3$, 25 ^{o}C).

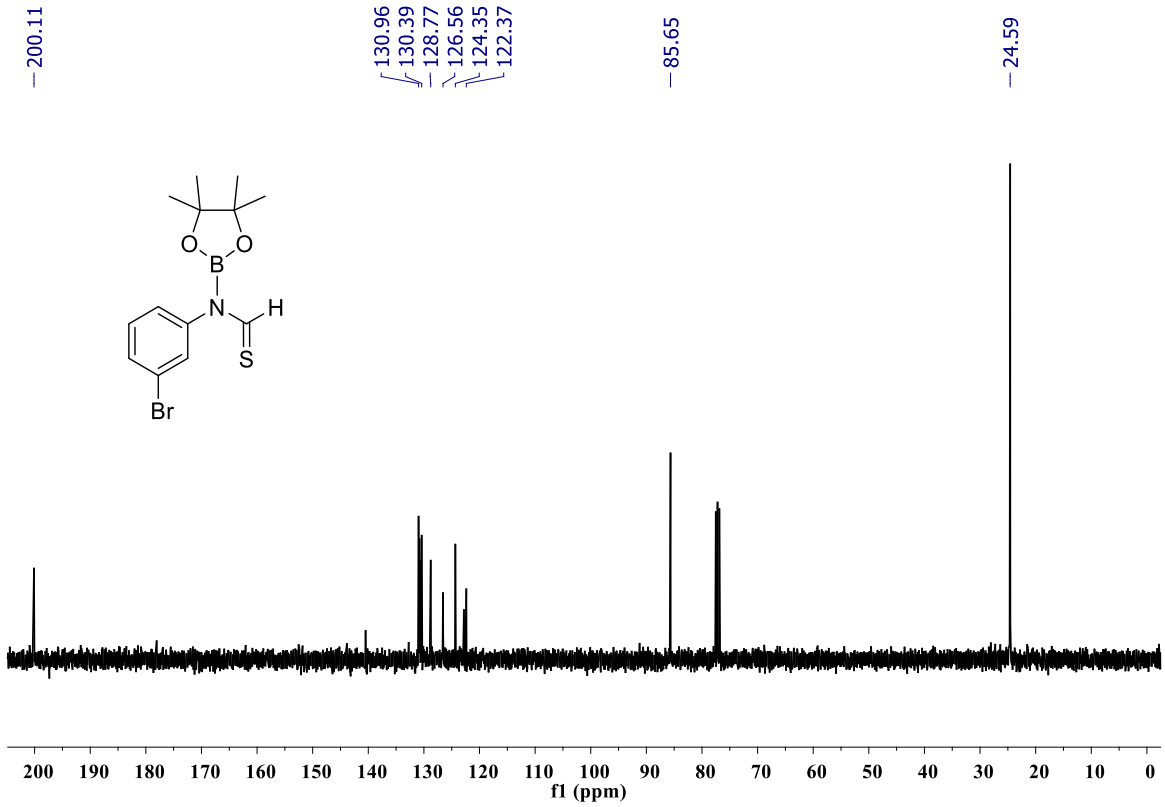


Figure S144: ^{13}C{^{1}H} NMR spectrum of **7d** (101 MHz, $CDCl_3$, 25 ^{o}C).

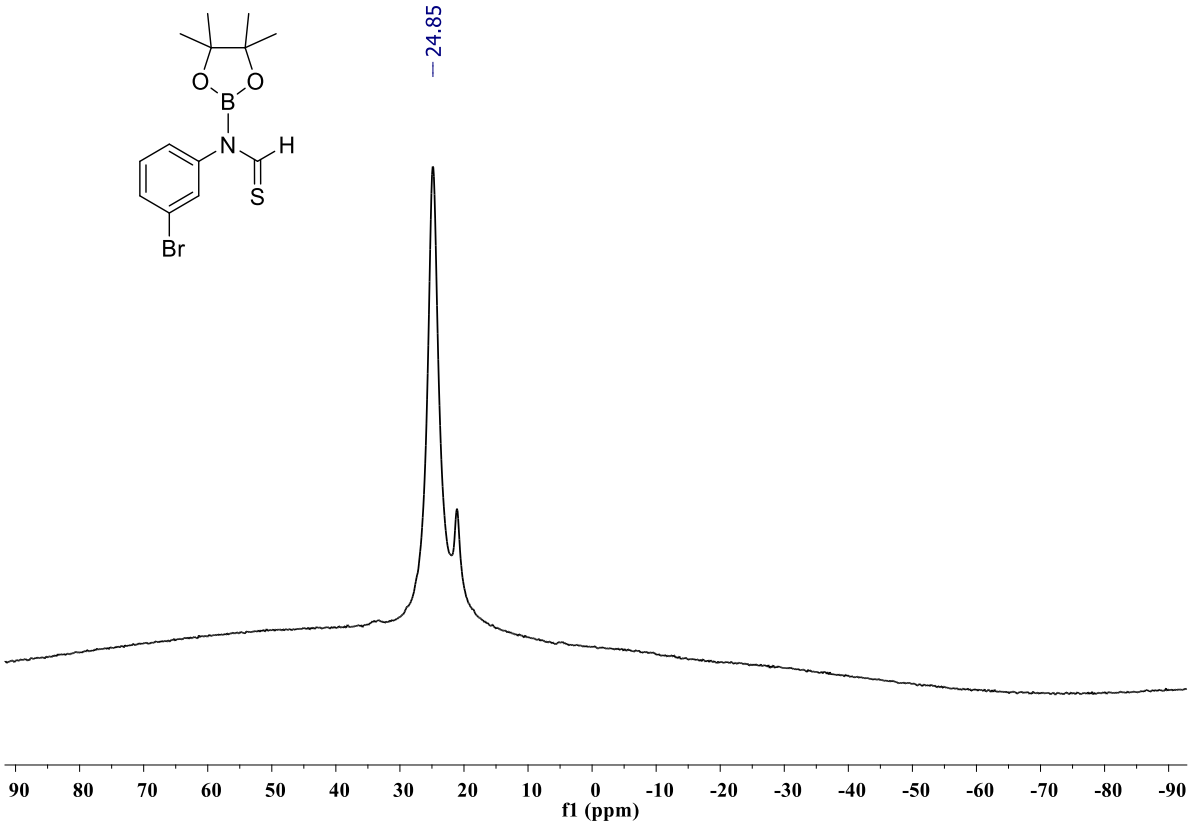


Figure S145: ^{11}B NMR spectrum of **7d** (128 MHz, $CDCl_3$, 25 ^{o}C).

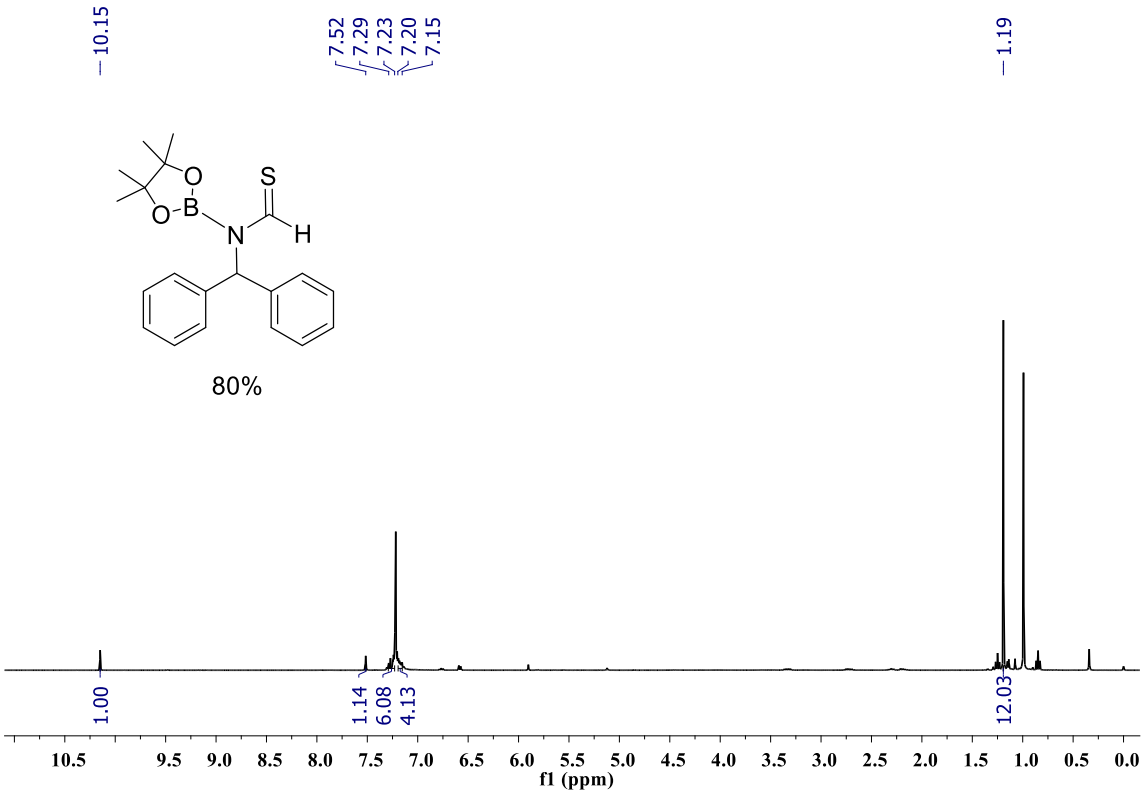


Figure S146: ^{1}H NMR spectrum of **7e** (400 MHz, $CDCl_3$, 25 ^{o}C).

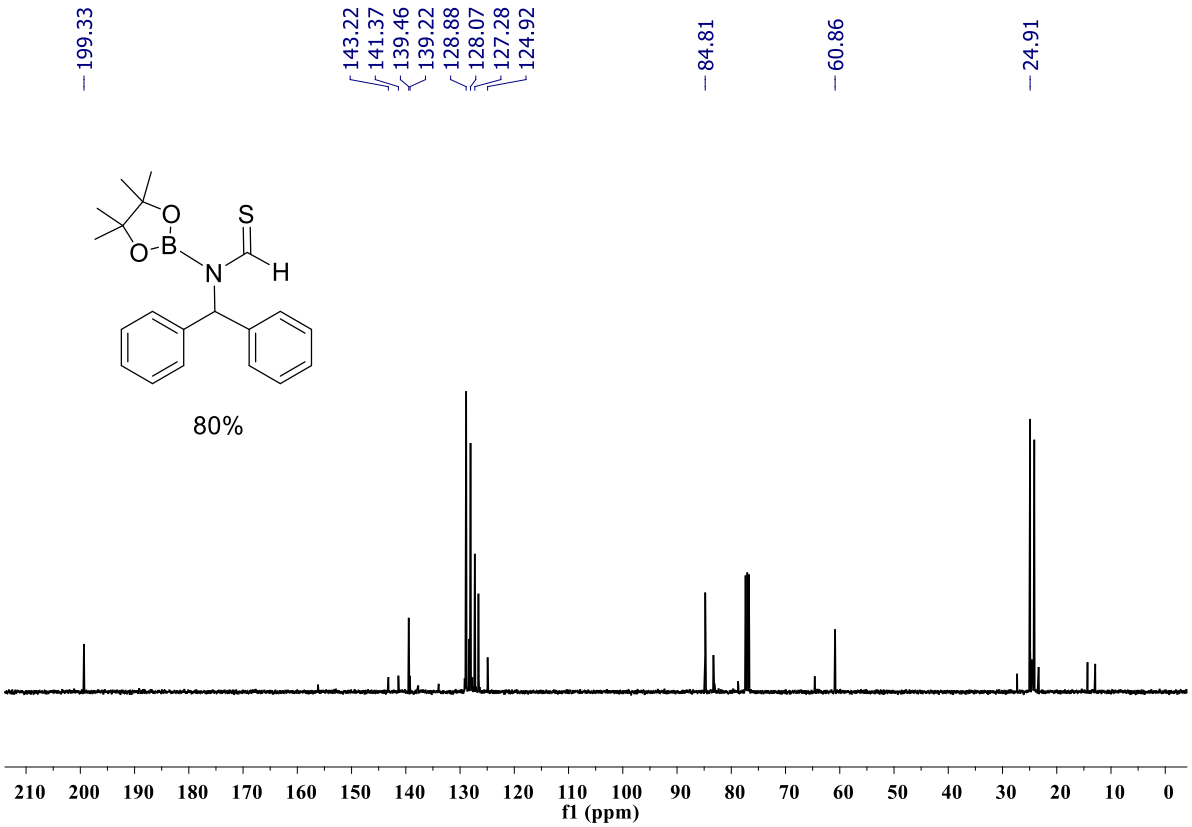


Figure S147: $^{13}C\{^{1}H\}$ NMR spectrum of **7e** (101 MHz, $CDCl_3$, 25 °C).

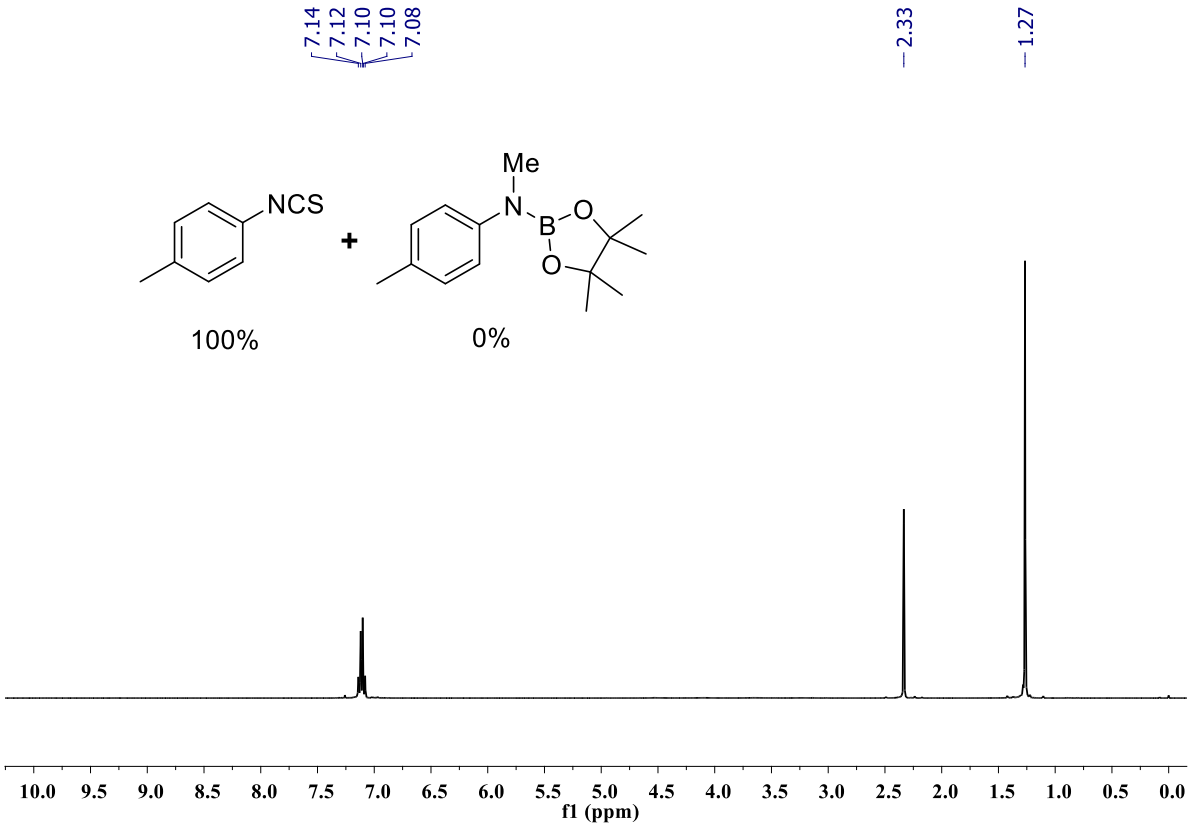


Figure S148: ^{1}H NMR spectrum of p-Tolylisothiocyanate with 3 equivalent of HBpin in the absence of catalyst (400 MHz, $CDCl_3$).

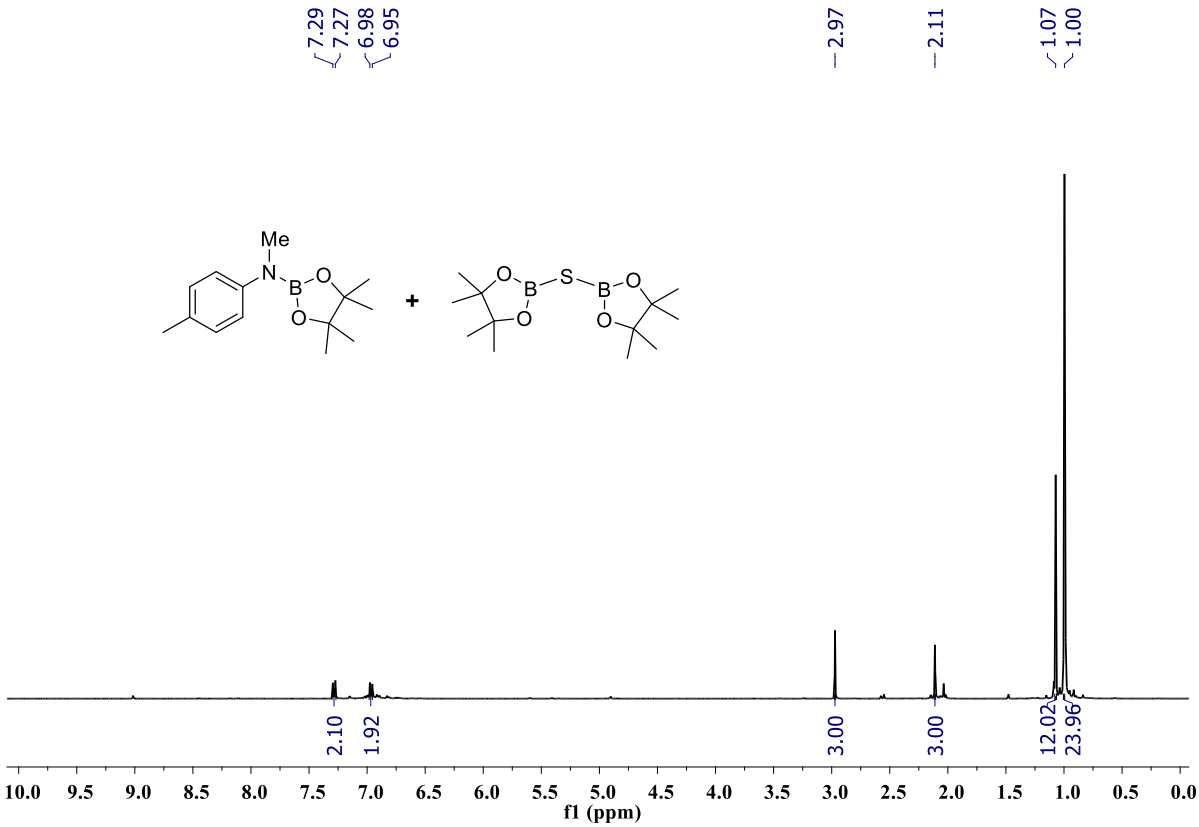


Figure S149: ^{1}H NMR spectrum of **4c** (400 MHz, C_6D_6, 25 ^{o}C).

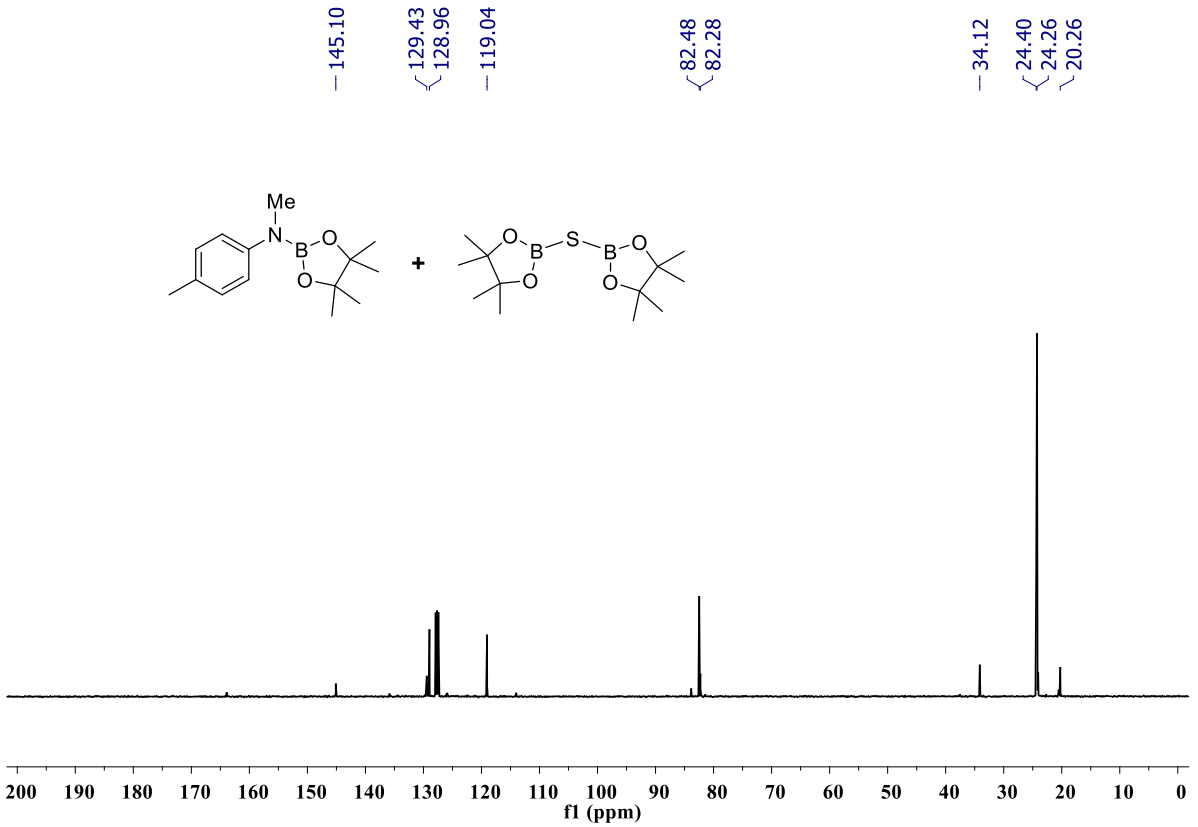


Figure S150: $^{13}C\{^{1}H\}$ NMR spectrum of **4c** (400 MHz, C_6D_6, 25 ^{o}C).

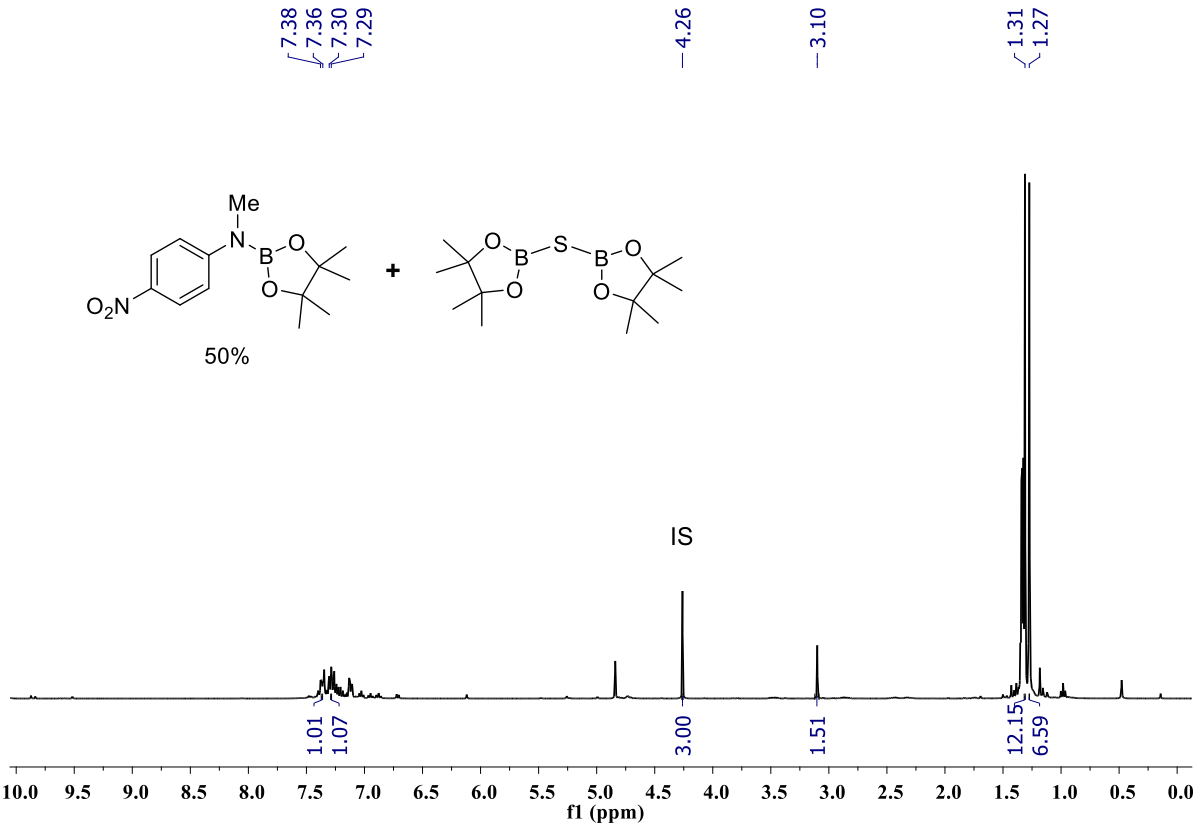


Figure S151: ^{1}H NMR spectrum of **9a** (400 MHz, $CDCl_3$, 25 ^{o}C). Nitromethane is used as an internal standard.

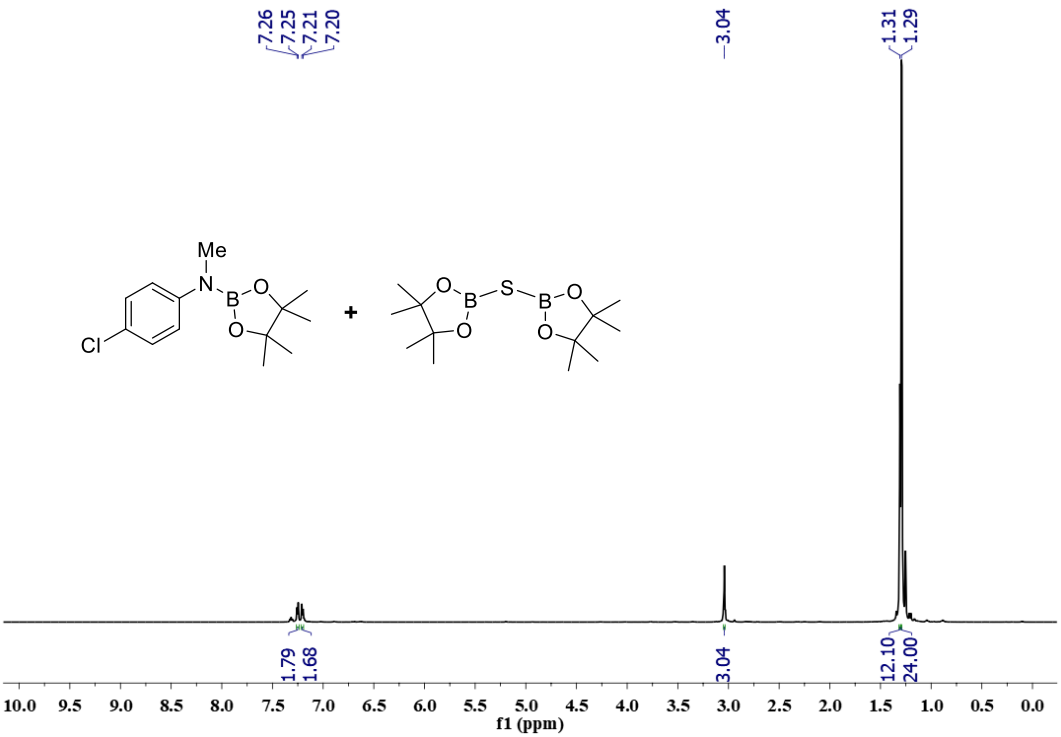


Figure S152: ^{1}H NMR spectrum of **4i** (400 MHz, $CDCl_3$, 25 ^{o}C).

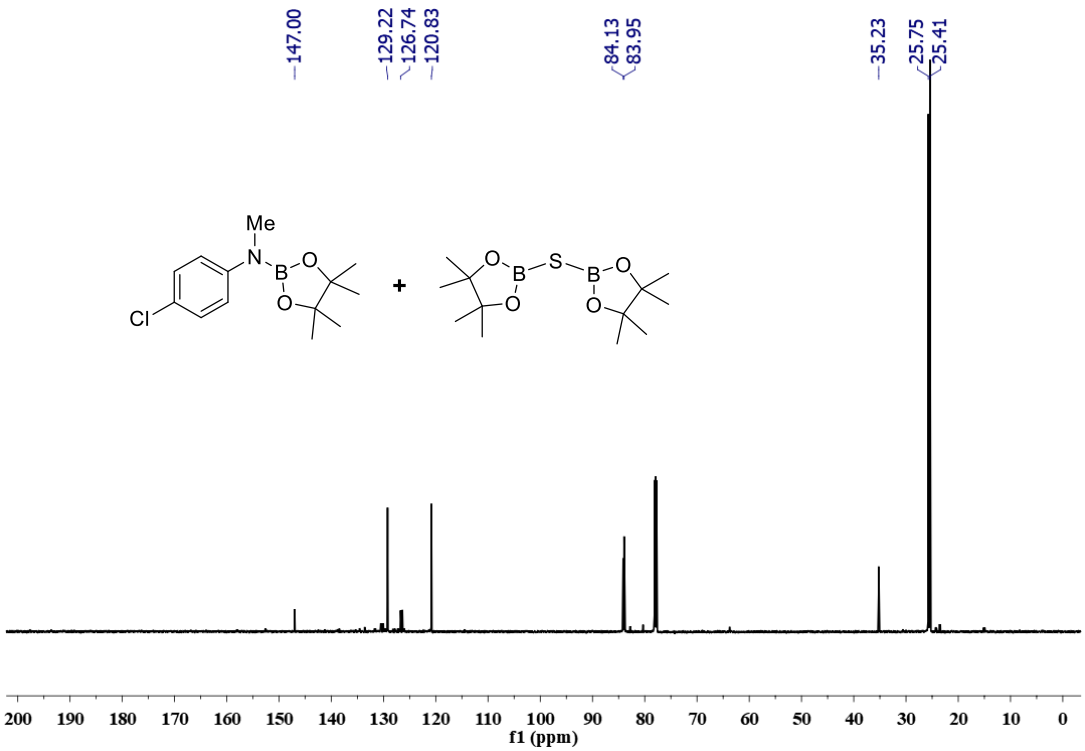


Figure S153: $^{13}C\{^{1}H\}$ NMR spectrum of **4i** (101 MHz, $CDCl_3$, 25 °C).

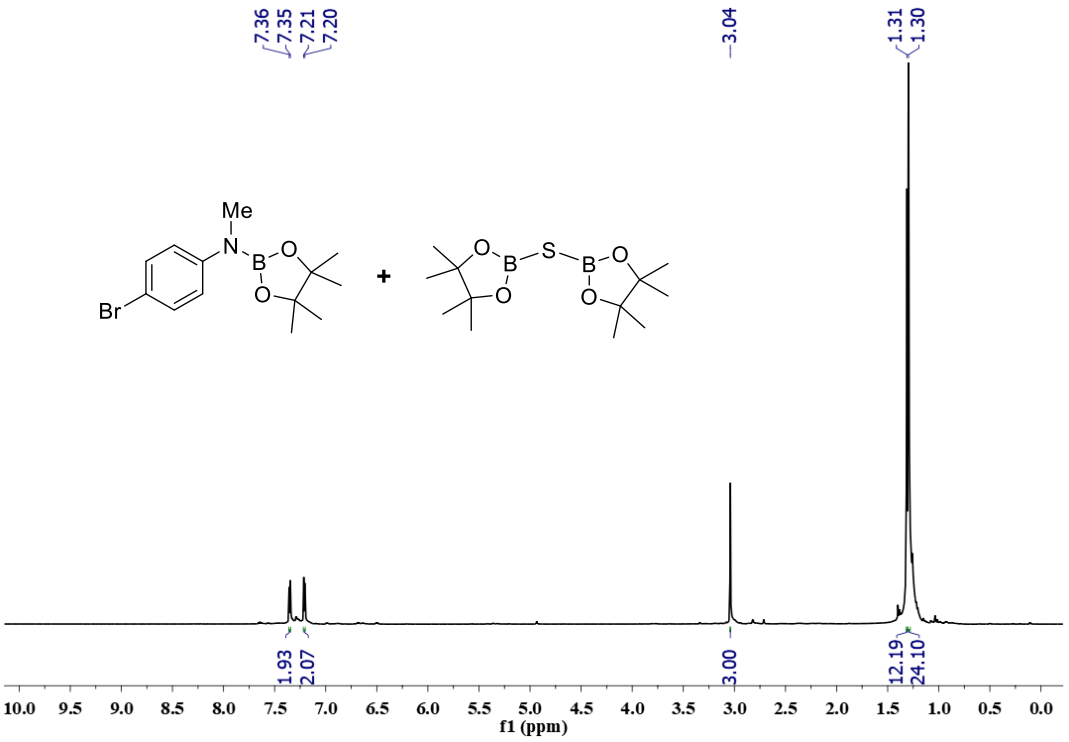


Figure S154: ^{1}H NMR spectrum of **4j** (400 MHz, $CDCl_3$, 25 °C).

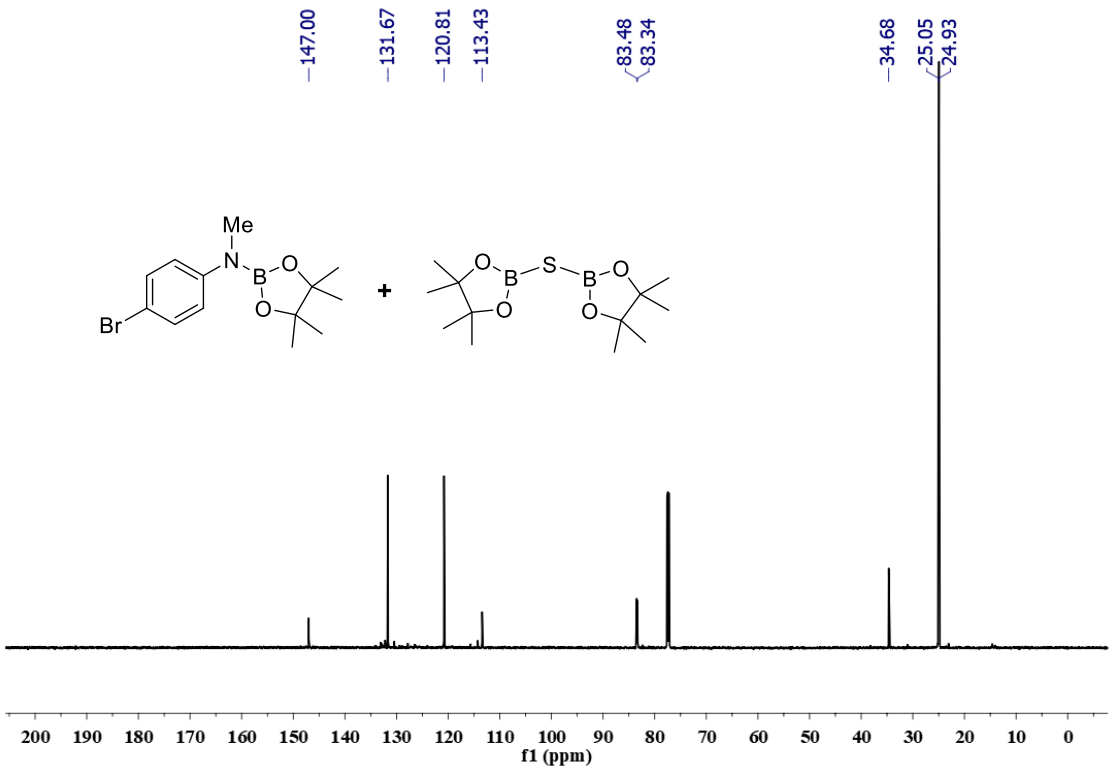


Figure S155: $^{13}C\{^{1}H\}$ NMR spectrum of **4j** (101 MHz, $CDCl_3$, 25 °C).

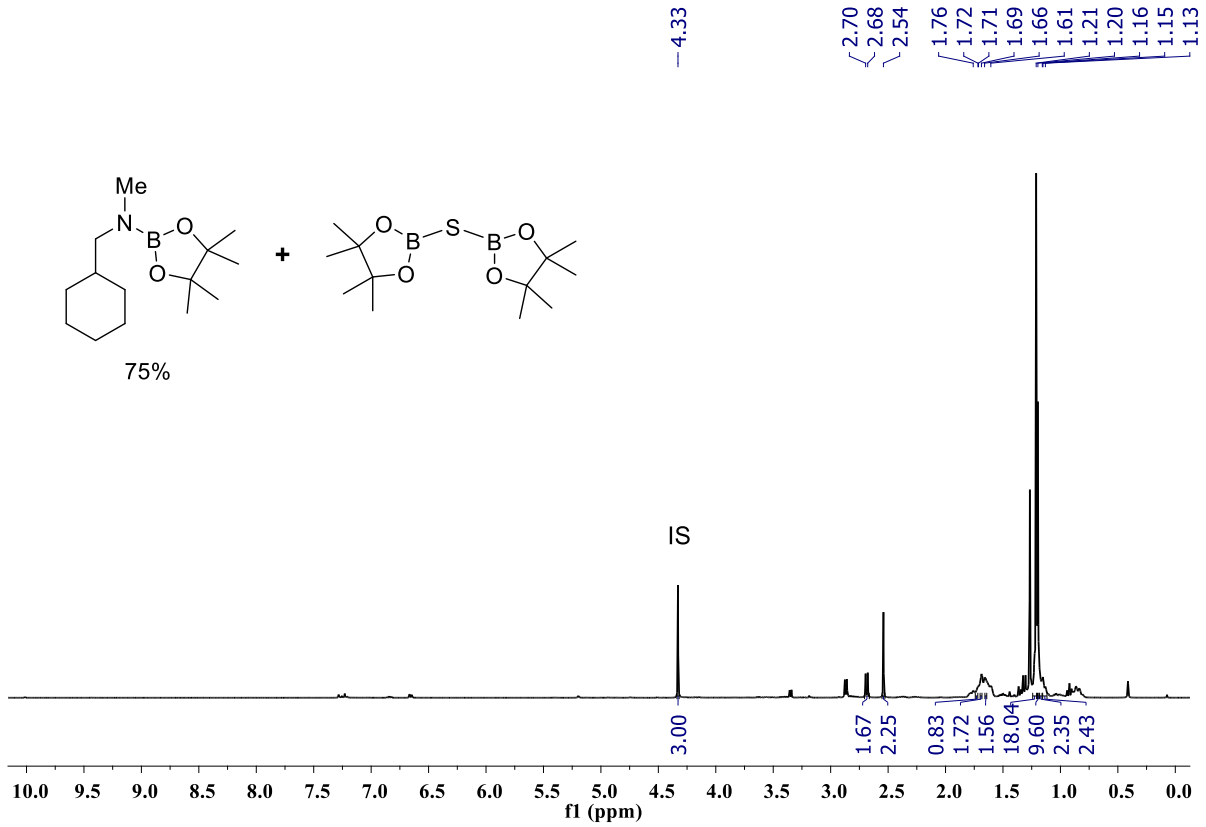


Figure S156: ^{1}H NMR spectrum of **9b** (400 MHz, $CDCl_3$, 25 °C). Nitromethane is used as an internal standard.

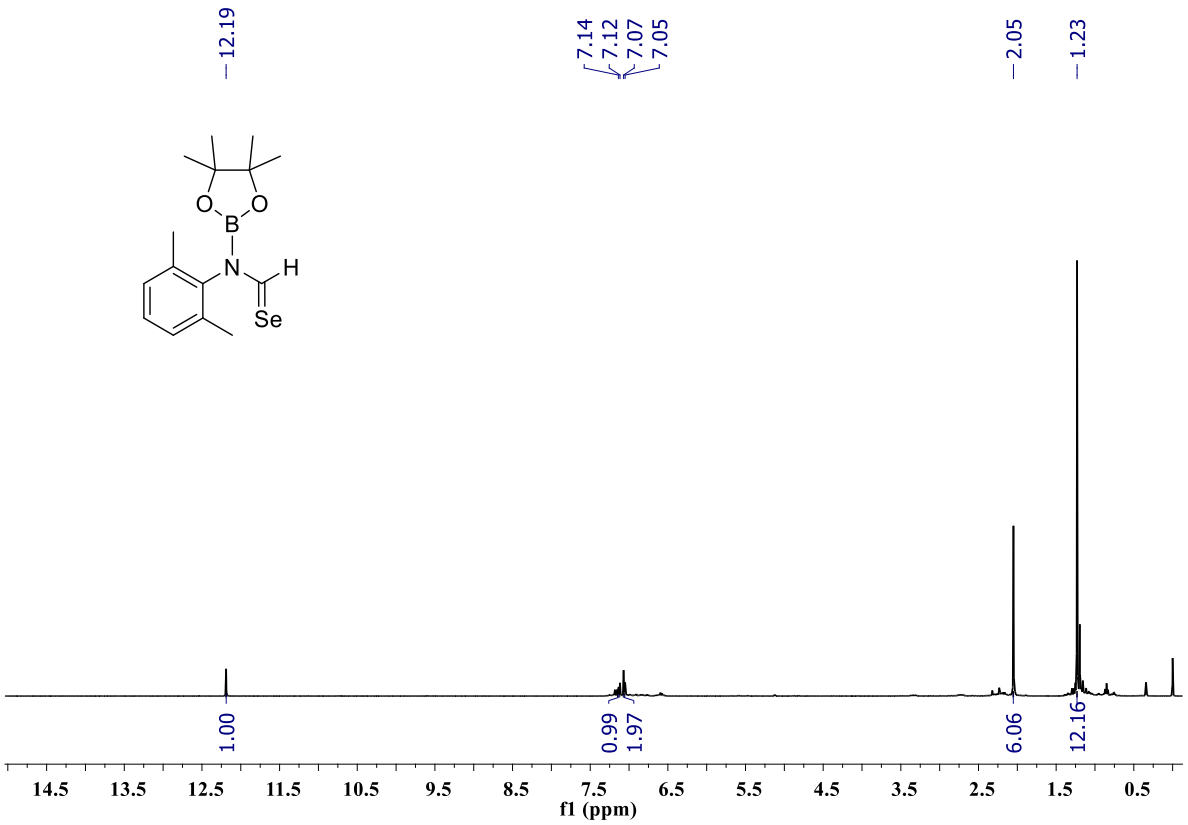


Figure S157: ^{1}H NMR spectrum of **11a** (400 MHz, $CDCl_3$, 25 ^{o}C).

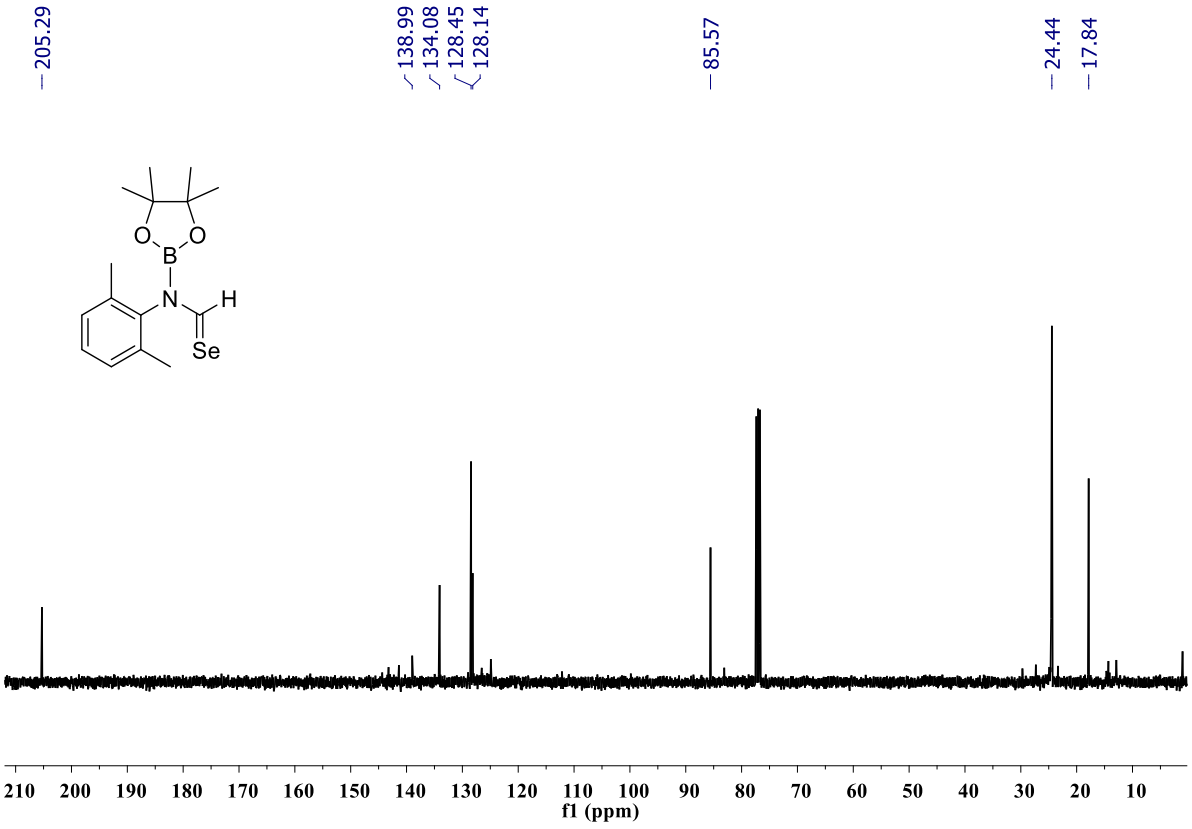


Figure S158: ^{13}C{^{1}H} NMR spectrum of **11a** (101 MHz, $CDCl_3$, 25 ^{o}C).

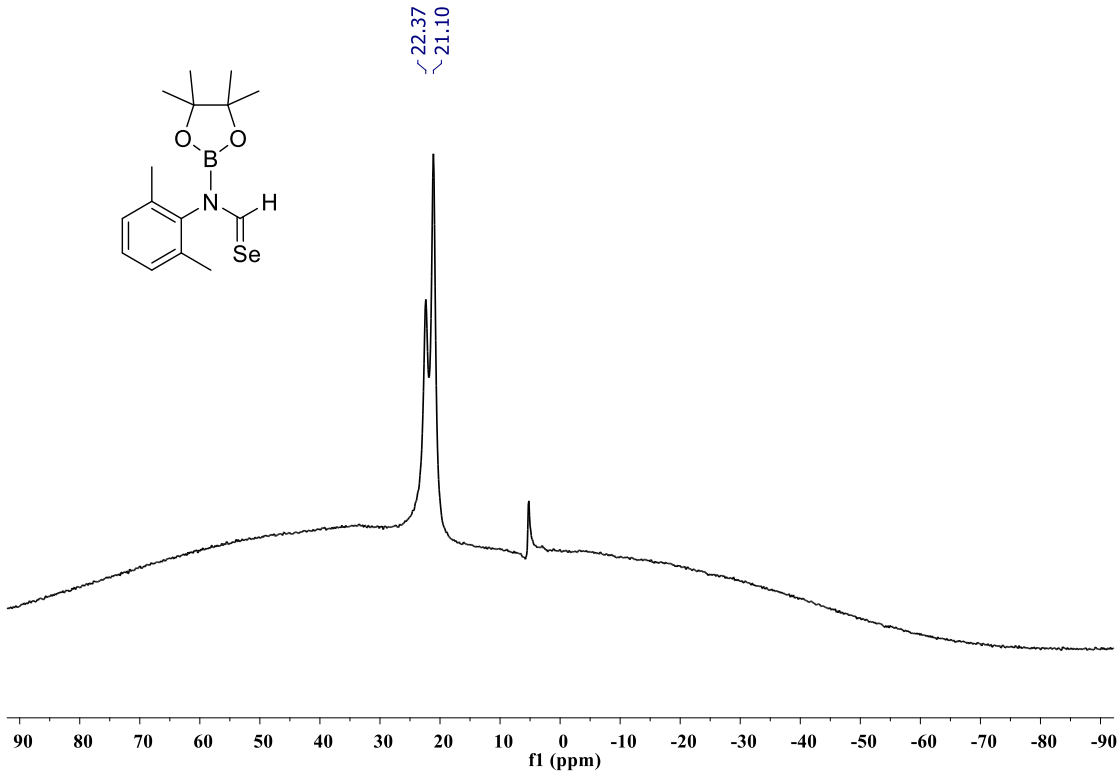


Figure S159: ^{11}B NMR spectrum of **11a** (128 MHz, $CDCl_3$, 25 ^{o}C). A peak observed at δ 21.10 ppm arises from $B(OR)_3$.

NMR Spectra for the Intermolecular Chemoselective Hydroboration

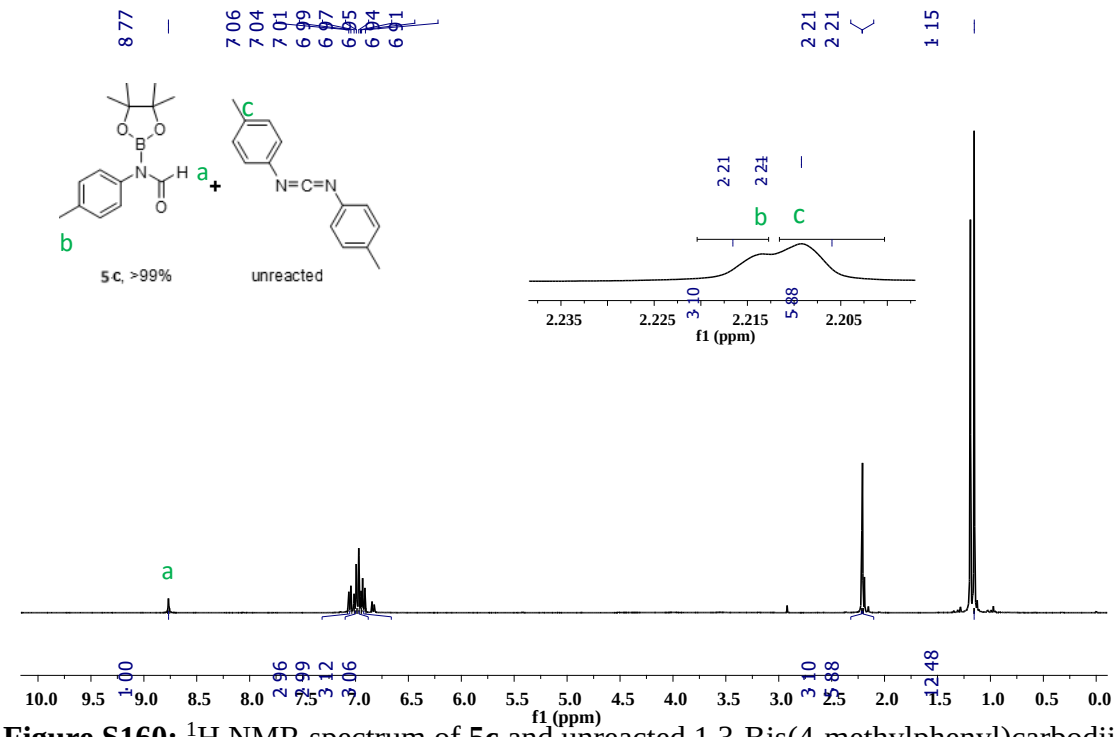


Figure S160: ^{1}H NMR spectrum of **5c** and unreacted 1,3-Bis(4-methylphenyl)carbodiimide (400 MHz, $CDCl_3$, 25 ^{o}C).

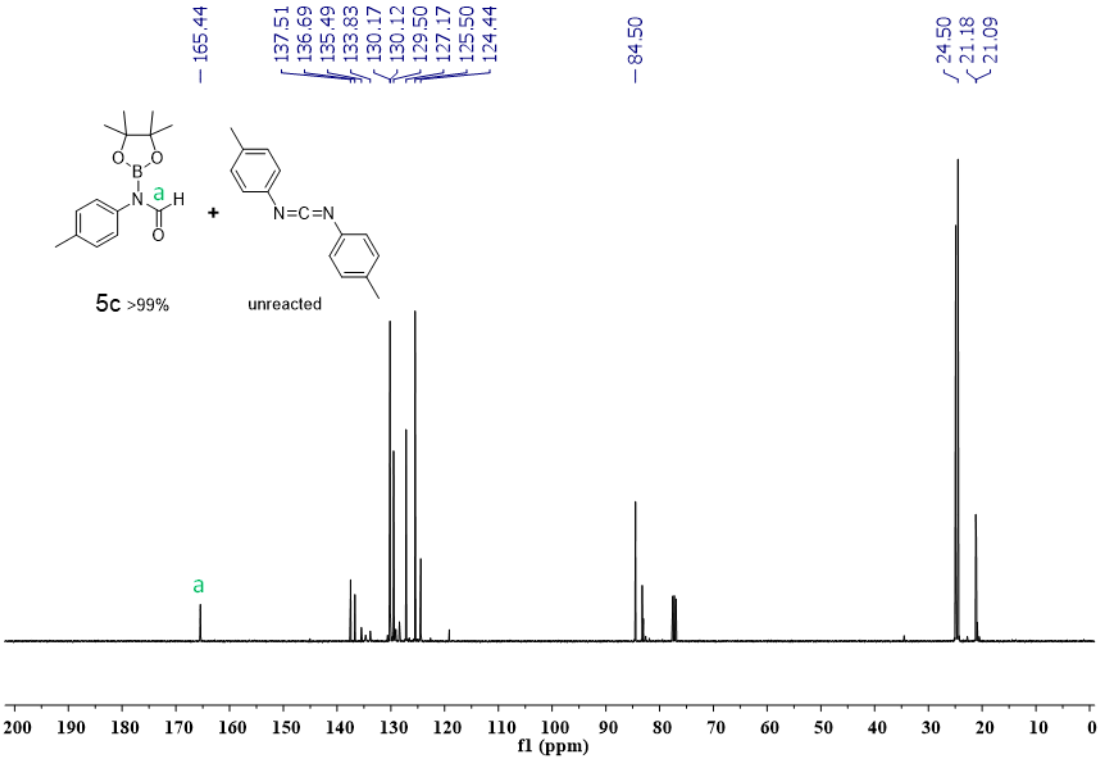


Figure S161: $^{13}C\{^{1}H\}$ NMR spectrum of **5c** and unreacted 1,3-Bis(4-methylphenyl)carbodiimide (101 MHz, $CDCl_3$, 25 °C).

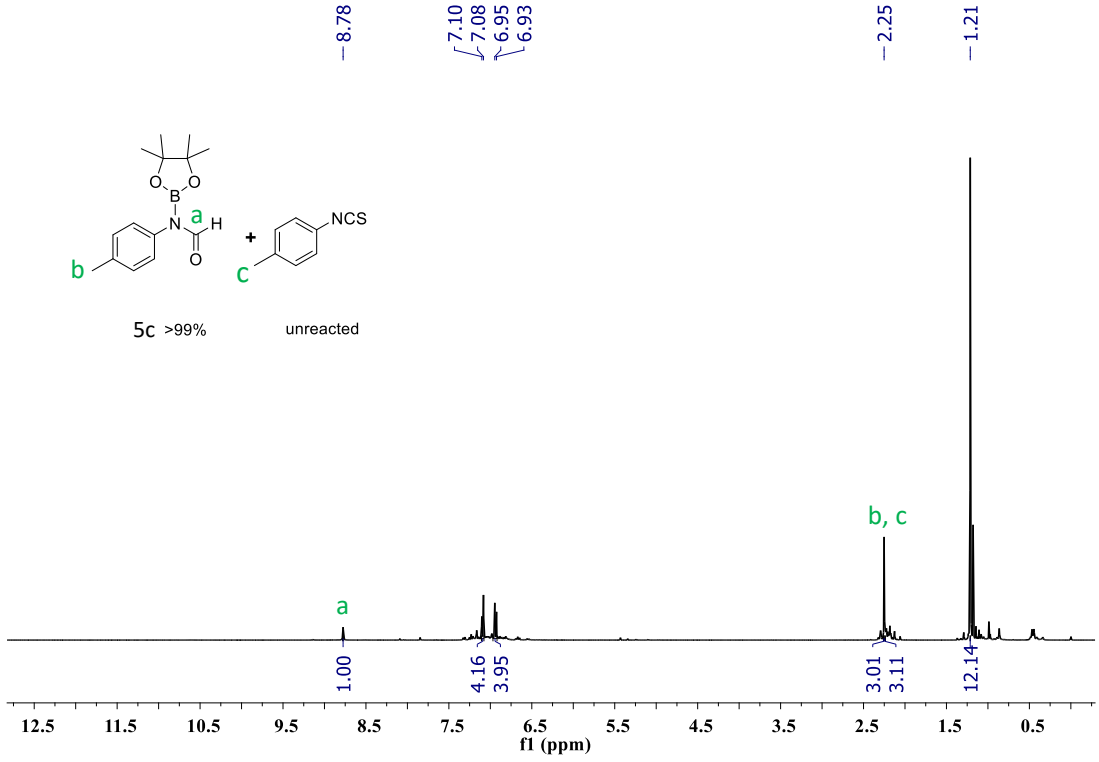


Figure S162: ^{1}H NMR spectrum of **5c** and unreacted p-tolyl isothiocyanate (400 MHz, $CDCl_3$, 25 °C).

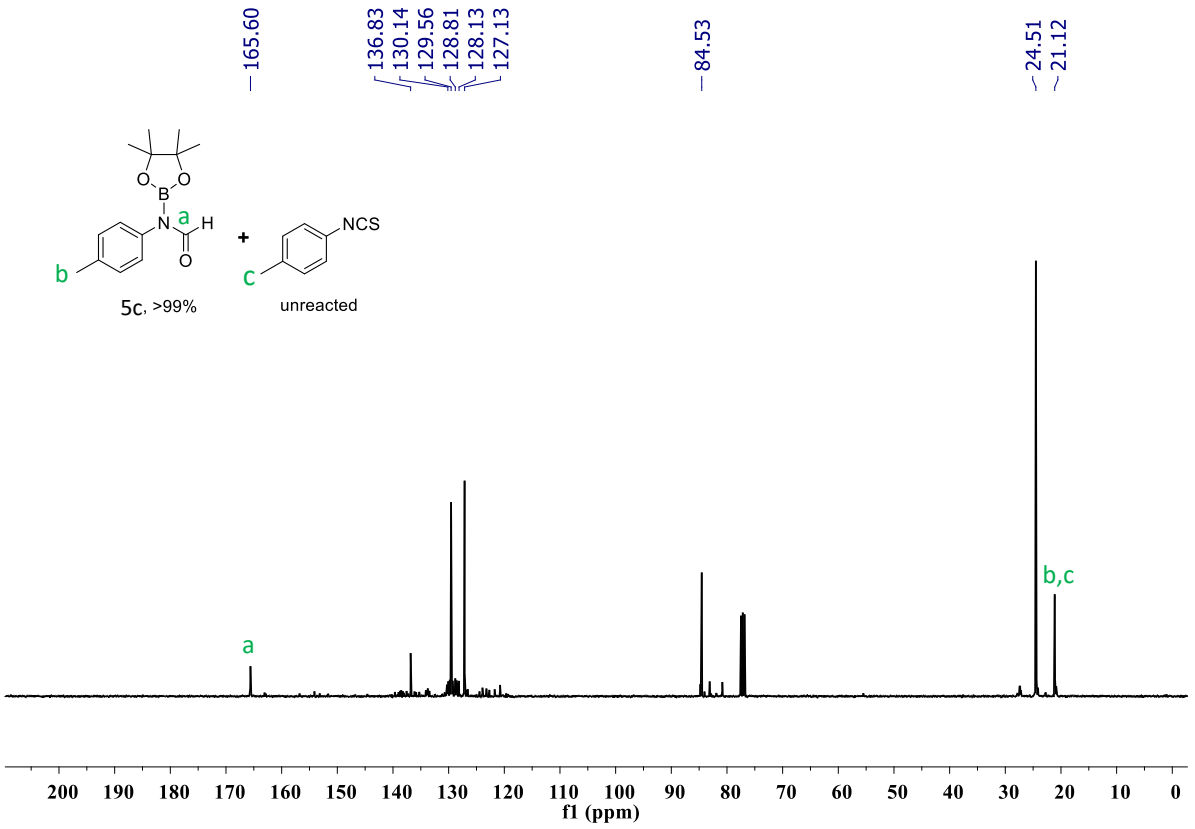


Figure S163: $^{13}C\{^{1}H\}$ NMR spectrum of **5c** and unreacted p-tolyl isothiocyanate (101 MHz, $CDCl_3$, 25 °C).

X-ray Crystallographic Data of 5b

The single crystals of compound **5b** were crystallized from $CDCl_3$ at rt as colorless blocks after 3 d. The crystal data of compound **5b** was collected on a Rigaku Oxford diffractometer at 100 K. Selected data collection parameters and other crystallographic results are summarized in Table S6. The structure was determined using direct methods employed in *ShelXT*,[9] *OleX*,[10,] and refinement was carried out using least-square minimization implemented in *ShelXL*.[11] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were fixed geometrically in idealized positions and were refined using a riding model.

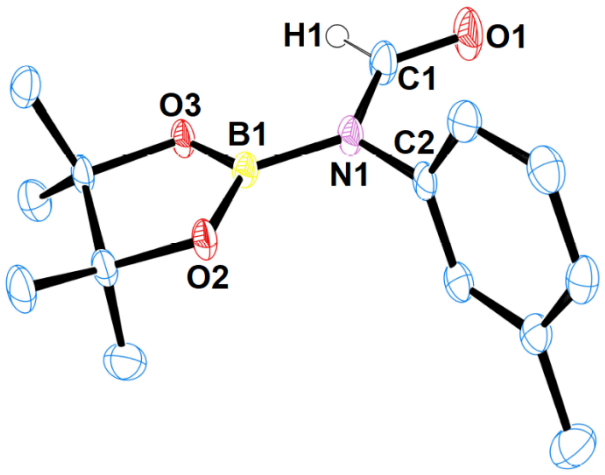


Figure S164: Molecular structure of **5b**. The thermal ellipsoids are shown at 50% probability, and all the hydrogen atoms (except for H(1)) are deleted for clarity. Selected bond lengths (Å) and angles (deg): O1-C1 1.212(2), N1-C1 1.372(2), N1-B1 1.448(2), N1-C2 1.447(2); O1-C1-N1 124.70(16), C1-N1-B1 121.51(14), C1-N1-C2 118.21(13).

Table S6. Crystallographic Data and Refinement Parameters for Compound **5b.**

Compound	**5b**
Empirical Formula	$C_{14}H_{20}BNO_3$
CCDC	2300244
Molecular mass	261.14
Temperature (K)	100
Wavelength (Å)	0.71073
Size(mm)	0.2×0.18×0.17
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	13.0059(7)
b (Å)	7.2872(4)
c (Å)	16.3747(9)
α (deg)°	90
β (deg)°	108.259(6)

γ (deg)°	90
Volume ($Å^3$)	1473.80(14)
Z	4
Calculated density (g/cm^3)	1.1768
Absorption coefficient (mm^{-1})	0.081
F(000)	560.3
Theta range for data collection (deg)°	6.6 to 50.7
Limiting indices	$-16 \leq h \leq 16$, $-9 \leq k \leq 9$, $-22 \leq l \leq 20$
Reflections collected	15737
Independent reflections	2695 [R_{int} = 0.0569, R_{sigma} = 0.0388]
Completeness to theta	99 %
Absorption correction	Empirical
Data/restraints/parameters	2695 / 0 / 177
Goodness – of–fit on F ^ 2	1.040
Final R indices [I>2 sigma(I)]	R_1 = 0.0671, wR_2 = 0.1887

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