

## Supporting Information

### Zinc Catalyzed Chemoselective Hydrofunctionalization of Cyanamides

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#### Contents

- General Experimental Methods
- General Procedures for Catalytic Hydrofunctionalization of Cyanamides
- Stoichiometric Experiment Data for Hydrofunctionalization of Cyanamides
- Optimization Tables for Zinc Catalyzed Hydrosilylation and Hydroboration of Diisopropyl Cyanamide
- Substrate Scope for the Zinc-Catalyzed Hydrofunctionalization of Cyanamides
- TON/TOF Calculations for the Zinc Catalyzed Hydrofunctionalization of Dibenzyl Cyanamide
- *In situ* Study for the Hydroboration of Diisopropyl Cyanamide
- Analytical Data ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}$  NMR) for Hydrosilylation of Cyanamides
- Analytical Data ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{11}\text{B}$  NMR) for Partial Hydroboration of Cyanamides
- Analytical Data ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{11}\text{B}$  NMR) for Dihydroboration of Cyanamides
- $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectra of Catalyst Free Reactions
- ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$ ) NMR Spectra for Partial Hydrosilylation of Cyanamides
- ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{11}\text{B}$ ) NMR Spectra for Partial Hydroboration of Cyanamides
- ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{11}\text{B}$ ) NMR Spectra for Dihydroboration of Cyanamides
- **Zn-2** Catalyzed Partial Hydrosilylation of Diethyl Cyanamide

- X-ray Crystallographic Data of **Zn-2** and **3c**
- HRMS Data of Newly Synthesized Compounds **2a-2f**, **3b-3d**, **4a-4f** and **Zn-2**
- References

## General Experimental Methods

All air- and moisture-sensitive reactions were performed using standard glove box and Schlenk line techniques under an inert nitrogen atmosphere. Catalysis reactions were conducted in J. Young valve-sealed NMR tubes or reaction vials as required. NMR spectra were recorded on Jeol-400 MHz spectrometer and Bruker NMR spectrometers at 400 MHz and 700 MHz ( $^1\text{H}$ ), 101 MHz and 176 MHz ( $^{13}\text{C}\{^1\text{H}\}$ ), 80 MHz ( $^{29}\text{Si}\{^1\text{H}\}$ ), 128 MHz ( $^{11}\text{B}$ ).  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR chemical shifts are referenced to residual protons or carbons in the deuterated solvent. Chemical shifts are reported in ppm. Coupling constants ( $J$ ) are given in Hz. Signals are described as br = broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, and m = multiplet. The crystal data of compounds **Zn-2** and **3c** were collected on a Rigaku Oxford diffractometer with graphite-monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) at 100 K. Selected data collection parameters and other crystallographic results are summarized in Table S8. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF-Q II spectrometer.

### Materials:

Solvents were purified by distillation over Na/ benzophenone. Deuterated chloroform ( $\text{CDCl}_3$ ) was dried on molecular sieves, and benzene- $d_6$  ( $\text{C}_6\text{D}_6$ ) was dried over Na/K alloy and distilled. The ligand LH ( $\text{L} = \{(\text{ArNH})(\text{ArN})-\text{C}=\text{N}-\text{C}=(\text{NAr})(\text{NHAr})\}$ ; Ar = 2,6- Et $_2$ -C $_6$ H $_3$ ) and complex  $\{\text{LZnH}\}_2$  (**Zn-1**) were prepared according to reported literature procedures.<sup>1</sup> For catalysis reactions, J. Young valve NMR tubes, Schlenk tubes, or air-tight vials, as per the requirement, were properly oven-dried before being used. Chemicals and reagents were purchased from Sigma-Aldrich Co. Ltd., Merck India Pvt. Ltd., and TCI chemicals were used without purification.

**General Procedure for Hydrosilylation of Cyanamides.** In a J. Young valve NMR tube, pre-catalyst **Zn-1** (0.01 mmol, 5 mol %) and cyanamide (0.2 mmol, 1.0 equiv.) were placed. This was followed by adding diphenyl silane (0.2 mmol, 1 equiv.) and C<sub>6</sub>D<sub>6</sub> (~0.5 mL) inside the glove box. Then, the sealed J. Young valve NMR tube was removed from the glove box and heated at 70 °C for 18 hours. The progress of the reaction was monitored using <sup>1</sup>H NMR spectroscopy, which confirmed the reaction's completion by observing a characteristic -NCHN peak.

**General Procedure for Catalytic Mono-Hydroboration of Cyanamides.** In a J. Young valve NMR tube, catalyst **Zn-1** (0.006 mmol, 3 mol %) and cyanamide (0.2 mmol, 1.0 equiv.) were added. This was followed by adding HBpin (0.2 mmol, 1.1 equiv.) and C<sub>6</sub>D<sub>6</sub> (~0.5 mL) inside the glove box. Then, the sealed J. Young valve NMR tube was removed from the glove box and heated at 60 °C for 12 hours. The progress of the reaction was monitored using <sup>1</sup>H NMR spectroscopy, which confirmed the reaction's completion by observing a characteristic -NCHN peak.

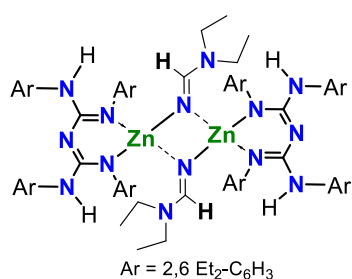
**General Procedure for Catalytic Dihydroboration of Cyanamides.** Cyanamide (0.2 mmol, 1 equiv.), HBpin (0.42 mmol, 2.1 equiv.) and 0.006 mmol (3 mol %) of catalyst **Zn-1** were charged in a vial with a magnetic bead or in a J. Young valve NMR tube inside the glove box. The sealed vial or NMR tube was removed from the glove box and heated/stirred at 80 °C for 24 hours. The progress of the reaction was monitored using <sup>1</sup>H NMR spectroscopy, which indicated the reaction's completion by observing a characteristic -CH<sub>2</sub>N(Bpin)<sub>2</sub> peak.

**General Procedure for Scale-up Reaction of Dihydroboration of Cyanamide with HBpin.** In a 25 mL Schlenk flask, 2.0 mmol of cyanamide (1.0 equiv.) and 4.2 mmol of HBpin (2.1 equiv.) were combined with 0.06 mmol of the catalyst **Zn-1** (3 mol%) under solvent-free conditions inside the glove box. The Schlenk flask was removed from the glove box and stirred

at 80 °C for 24 hours. Then, the residue was dissolved in a minimal volume of dry *n*-hexane and allowed to crystallize overnight at -20 °C in a freezer. The product, identified as compound **4c**, was isolated as a white crystalline solid with a yield of 74% (0.57 g).

## Synthesis and Analytical Data for Stoichiometric Experiments

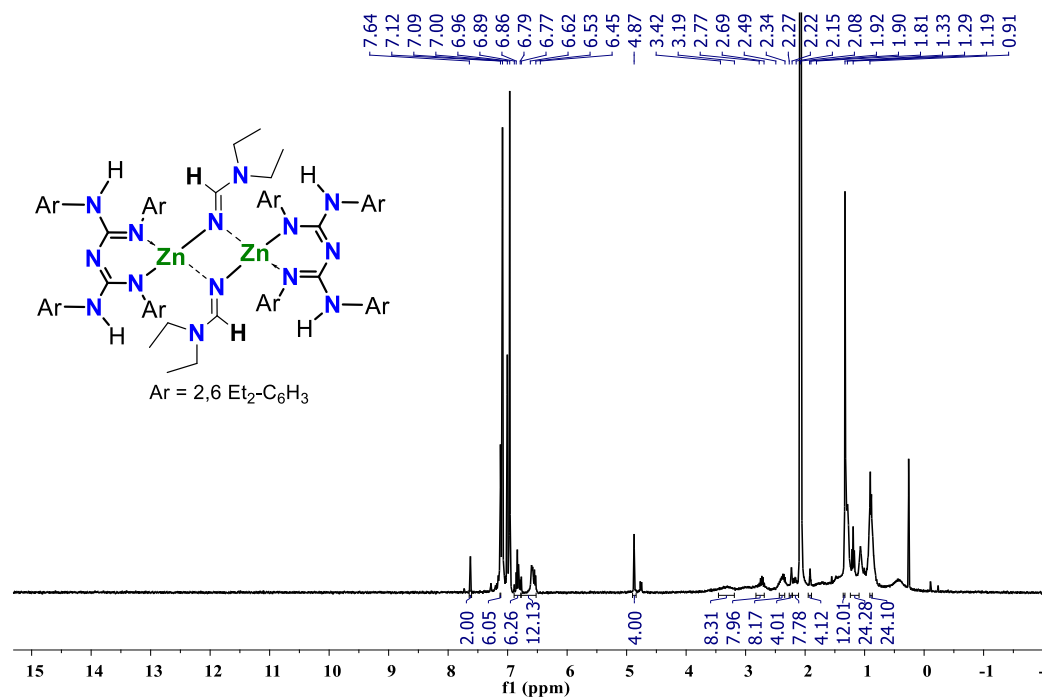
**Synthesis of [LZnNC(H)N(Et<sub>2</sub>)]<sub>2</sub> (**Zn-2**):** Diethyl cyanamide (**1b**) (~4.5 μL, 0.036 mmol) was



added to a J. Young valve NMR tube containing a solution of the complex **Zn-1** (0.025 g, 0.018 mmol) in deuterated toluene (Tol-d<sub>8</sub>) within a glove box. The sealed NMR tube was removed from the glove box and heated at 60 °C for 12

hours. The progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy, confirming the complete formation of the product **Zn-2**. After the reaction was completed, the solution was cooled to room temperature. Within 48 hours, block-shaped, colorless crystals suitable for single-crystal X-ray diffraction were observed. NMR conversion: (>99 %). <sup>1</sup>H NMR (400 MHz, Tol-d<sub>8</sub>, 25 °C) δ 7.64 (s, 2H, (LZnNC(H)N(Et<sub>2</sub>))<sub>2</sub>), 7.12-6.96 (m, 6H, ArH), 6.89-6.77 (m, J = 27.0 Hz, 6H, ArH), 6.62-6.45 (m, J = 37.1 Hz, 12H, ArH), 4.87 (s, 4H, NH), 3.42-3.19 (m, 8H, Ar-CH<sub>2</sub>CH<sub>3</sub>), 2.77-2.69 (m, J = 32.6 Hz, 8H Ar-CH<sub>2</sub>CH<sub>3</sub>), 2.49-2.34 (m, , J = 7.2 Hz, 8H Ar-CH<sub>2</sub>CH<sub>3</sub>), 2.27-2.22 (m, J = 19.3 Hz, 4H, NCH<sub>2</sub>CH<sub>3</sub>), 2.15-2.08 (m, 8H, Ar-CH<sub>2</sub>CH<sub>3</sub>), 1.92-1.81 (m, J = 9.2 Hz, 4H, NCH<sub>2</sub>CH<sub>3</sub>), 1.33-1.29 (t, 12H, NCH<sub>2</sub>CH<sub>3</sub>), 1.19 (t, J = 7.6 Hz, 24H, Ar-CH<sub>2</sub>CH<sub>3</sub>), 0.91 (t, J = 10.0 Hz, 24H, Ar-CH<sub>2</sub>CH<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, Tol-d<sub>8</sub>, 80 °C) δ 7.66 (s, 2H, (LZnNC(H)N(Et<sub>2</sub>))<sub>2</sub>), 7.14-7.09 (m, 6H, ArH), , 6.84-6.78 (m, J = 23.5 Hz, 6H, ArH), 6.61-6.58 (m, J = 11.8 Hz, 12H, ArH), 4.90 (s, 4H, NH), 3.40-3.31 (m, 8H, Ar-CH<sub>2</sub>CH<sub>3</sub>), 2.90-2.78 (m, J = 32.6 Hz, 8H, Ar-CH<sub>2</sub>CH<sub>3</sub>), 2.46-2.39 (m, , J = 7.2 Hz, 8H, Ar-CH<sub>2</sub>CH<sub>3</sub>), 2.35-2.29 (m, J = 19.3 Hz, 4H, NCH<sub>2</sub>CH<sub>3</sub>), 2.26-2.19 (m, 8H, Ar-CH<sub>2</sub>CH<sub>3</sub>), 1.97-1.91 (m, J = 24.9 Hz, 4H, NCH<sub>2</sub>CH<sub>3</sub>), 1.35-1.24 (t, 12H, NCH<sub>2</sub>CH<sub>3</sub>), 1.11 (t, J = 7.6 Hz, 24H, Ar-CH<sub>2</sub>CH<sub>3</sub>), 0.89 (t, J = 10.0 Hz, 24H, Ar-CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Tol-

$d_8$ , 25 °C)  $\delta$  156.6 (N<sub>3</sub>C), 156.5 (NCHN), 144.6, 143.7, 136.0, 135.8, 128.1, 125.9, 125.8, 125.2, 29.9, 24.9, 23.2, 14.2, 14.1, 13.4. HRMS (ASAP/Q-TOF)  $m/z$ : [M + H]<sup>+</sup> Calcd for C<sub>47</sub>H<sub>66</sub>N<sub>7</sub>Zn 792.4671, Found 792.4606.



**Figure S1:** <sup>1</sup>H NMR spectrum of **Zn-2** at 25 °C (400 MHz, Tol-*d*<sub>8</sub>).

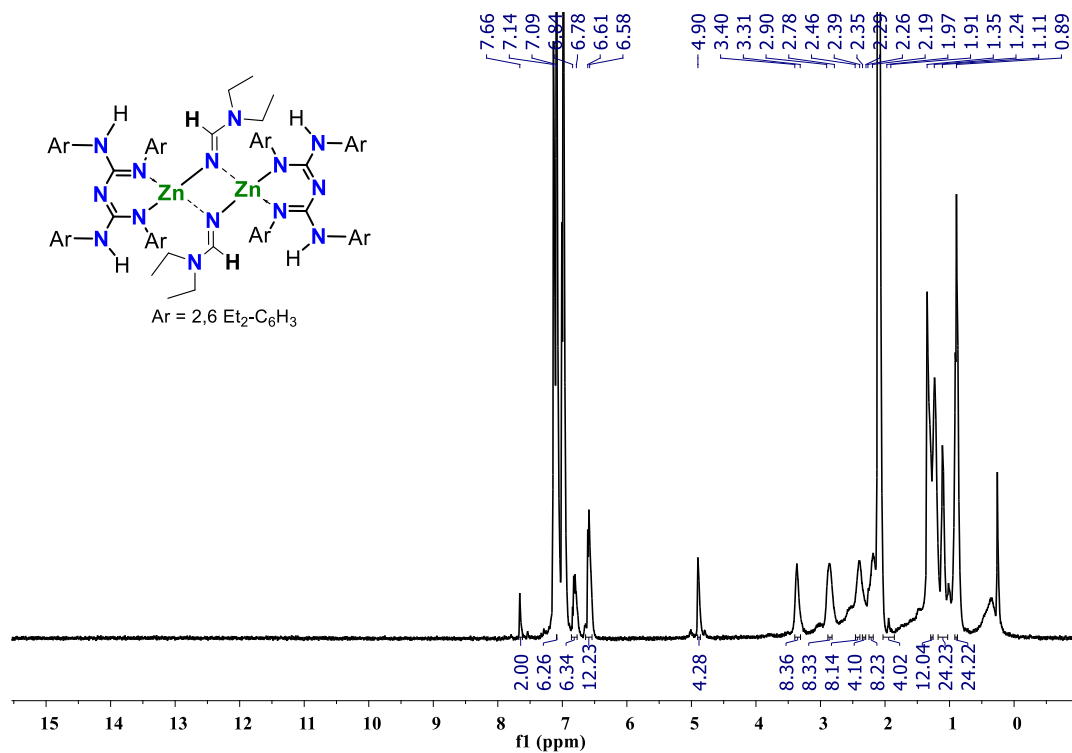


Figure S2:  $^1\text{H}$  NMR spectrum of Zn-2 at 80 °C. (400 MHz, Tol- $d_8$ ).

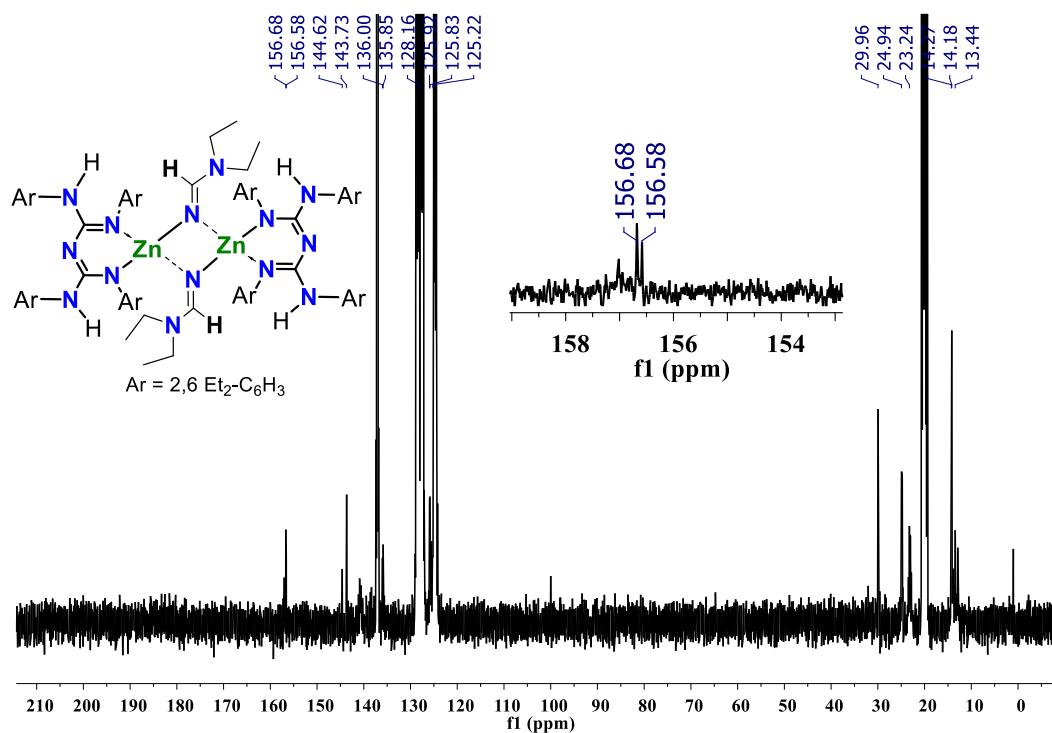
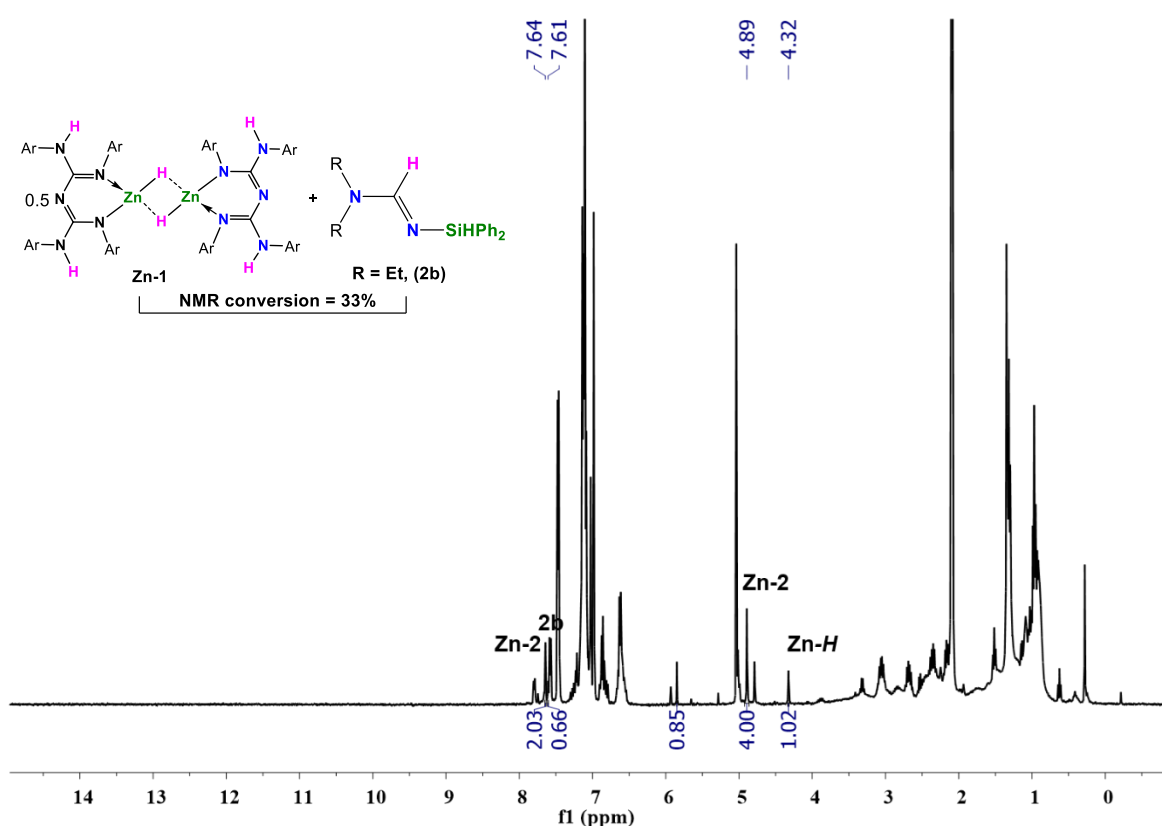


Figure S3:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of Zn-2 (101 MHz, Tol- $d_8$ , 25 °C).

**The reaction between Zn-2 and Ph<sub>2</sub>SiH<sub>2</sub> {NMR-Scale}: To a J. Young valve NMR tube containing a solution of compound **Zn-2** (0.013 mmol) in toluene-d<sub>8</sub>, Ph<sub>2</sub>SiH<sub>2</sub> (4.7 μL, 0.025 mmol) was added. The reaction mixture was heated at 70 °C for 3 hours, resulting in the synthesis of compounds **Zn-1** and **2b** with a 33% conversion, as detected by NMR spectroscopy. <sup>1</sup>H NMR spectroscopy revealed that the process had reached an equilibrium, as evidenced by the integration of resonance **2b** and compound **Zn-2**. The relative ratio of **2b** and **Zn-2** remained unchanged after heating for up to 18 hours at 70 °C, indicating that the equilibrium position had already been established before 3 hours. NMR conversion: 33%.**

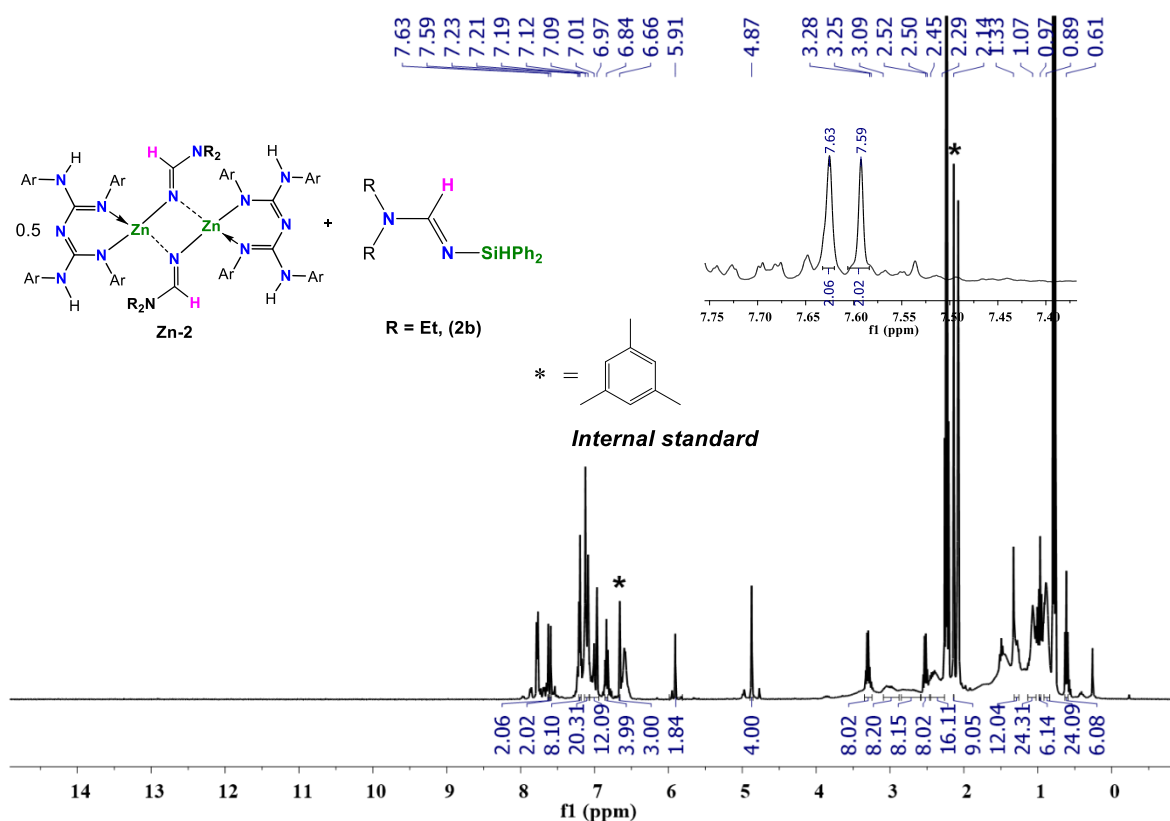


**Figure S4:** <sup>1</sup>H NMR spectrum of **Zn-1** and **2b** (400 MHz, Tol-d<sub>8</sub>).

**Synthesis of compound Zn-2 and 2b {NMR-Scale}: The addition of diethyl cyanamide (0.025 mmol) to a J. Young valve NMR tube containing a solution of compounds **Zn-1** and **2b** (33%) in Tol d<sub>8</sub>. The reaction mixture was heated at 70 °C for 6 h, resulting in the formation of compounds **Zn-2** and **2b** were observed by <sup>1</sup>H NMR spectroscopy. The above study indicates**

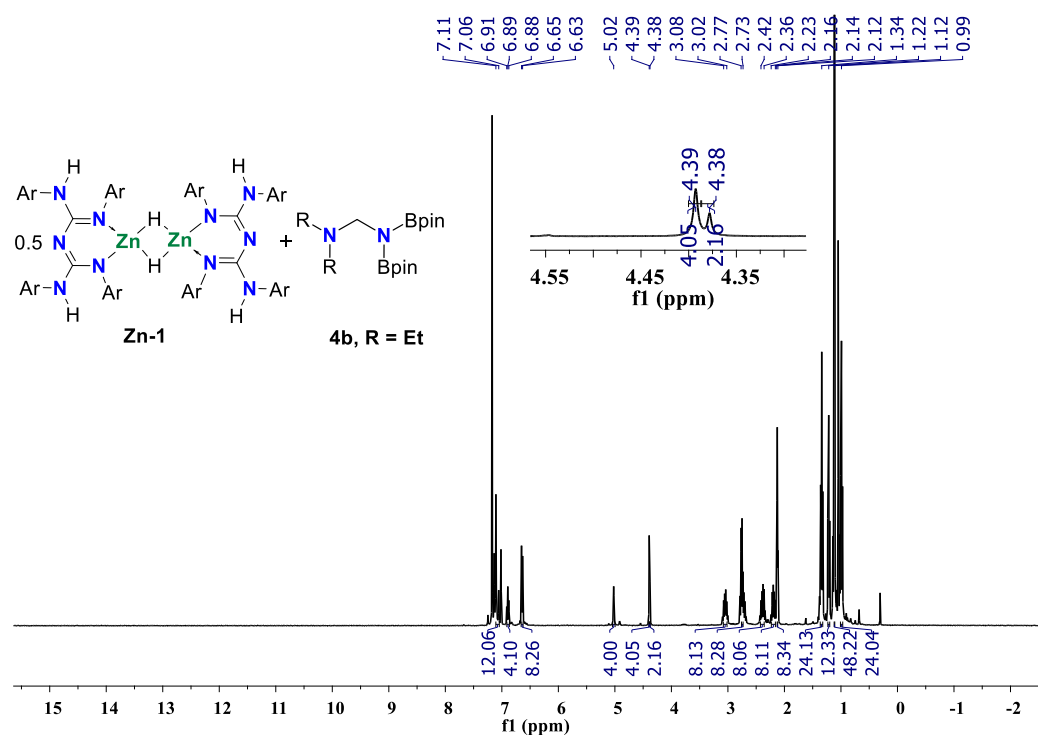


that once 33% of the compounds **2b** and **Zn-1** were formed, they reacted with additional amounts of diethyl cyanamide to form **2b** and **Zn-2** in quantitative conversion. It stops the equilibrium reaction between compounds **Zn-1** and **2b**. NMR conversion: (>99%). <sup>1</sup>H NMR (400 MHz, Toluene d<sub>8</sub>) δ 7.63 (s, 2H, (LZnNC(H)N(Et)<sub>2</sub>)<sub>2</sub>), 7.59 (s, 2H, NCHN), 7.23-7.19 (m, 8H, ArH), 7.12-7.09 (m, *J* = 13.8 Hz, 20H, Ph<sub>2</sub>Si), 7.01-6.97 (m, *J* = 15.9 Hz, 12H, ArH), 6.84 (t, 4H, ArH), 6.66 (s, 3H, ArH, IS, Mesitylene), 5.91 (s, 2H, SiH), 4.87 (s, 4H, NH), 3.28-3.25 (m, *J* = 9.0 Hz, 8H, NCH<sub>2</sub>CH<sub>3</sub>), 3.09-2.91 (m, 8H, Ar-CH<sub>2</sub>CH<sub>3</sub>), 2.80-2.61 (m, *J* = 75.9 Hz, 8H, Ar-CH<sub>2</sub>CH<sub>3</sub>), 2.52-2.50 (q, *J* = 7.2 Hz, 8H, NCH<sub>2</sub>CH<sub>3</sub>), 2.45-2.29 (m, *J* = 61.8 Hz, 16H, Ar-CH<sub>2</sub>CH<sub>3</sub>), 2.14 (s, 9H, CH<sub>3</sub>, IS, Mesitylene), 1.33 (t, *J* = 5.2 Hz, 12H, NCH<sub>2</sub>CH<sub>3</sub>), 1.07 (t, *J* = 2.3 Hz, 24H, Ar-CH<sub>2</sub>CH<sub>3</sub>), 0.97 (t, 6H, NCH<sub>2</sub>CH<sub>3</sub>), 0.89 (t, 24H, Ar-CH<sub>2</sub>CH<sub>3</sub>), 0.61 (t, *J* = 7.2 Hz, 6H, NCH<sub>2</sub>CH<sub>3</sub>).

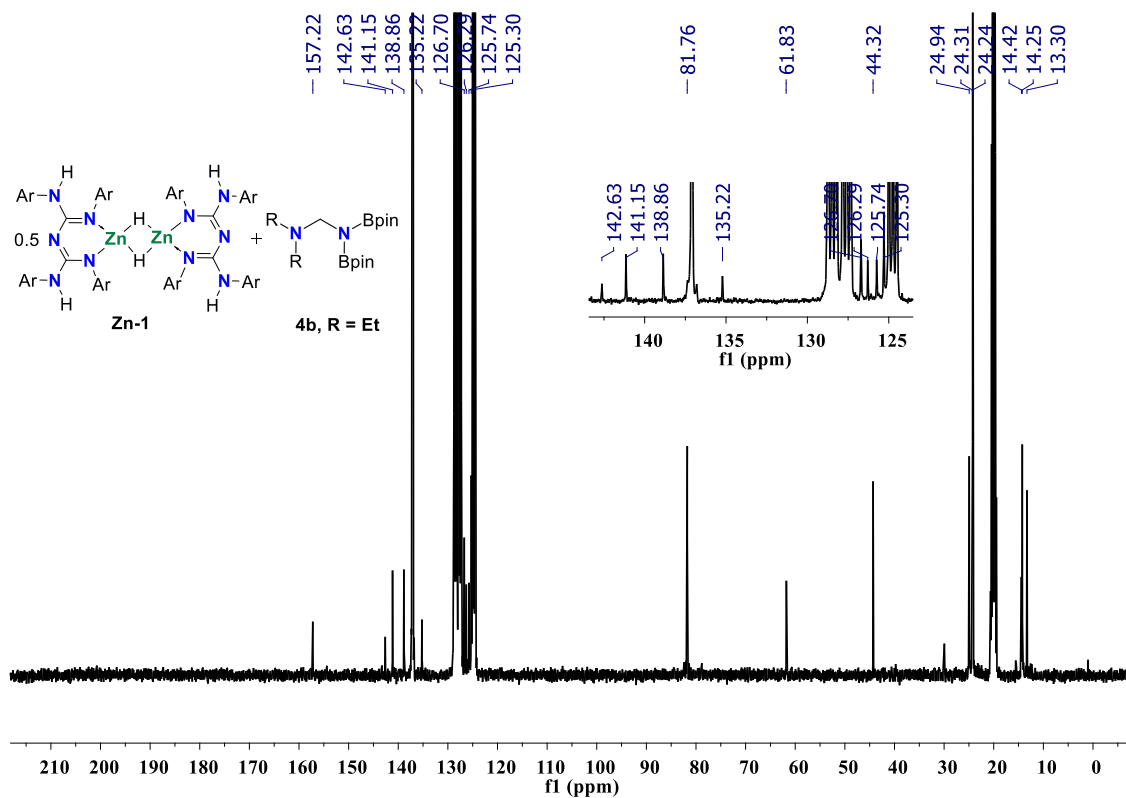


**Figure S5:** <sup>1</sup>H NMR spectrum of **Zn-2** and **2b** (400 MHz, Tol-d<sub>8</sub>). Mesitylene was used as an internal standard.

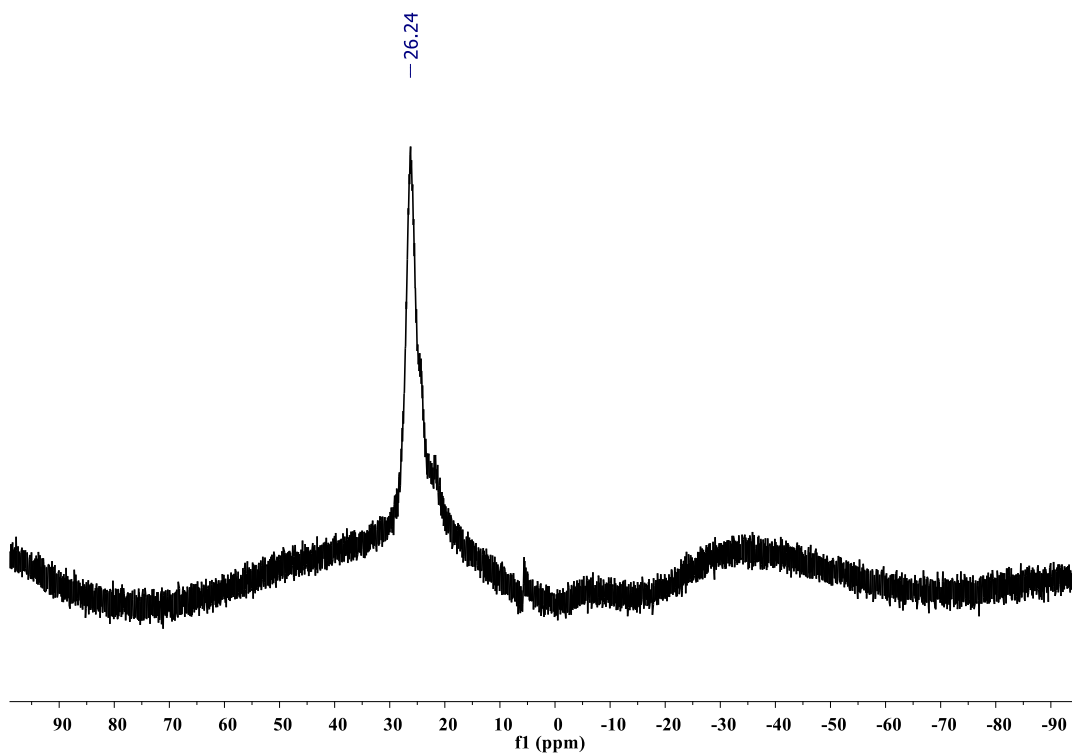
**Synthesis of Zn-1 and dihydroborated product of Cyanamide(4b) {NMR-Scale}: HBpin (~4.0  $\mu$ L, 0.025 mmol) was added to a J. Young valve NMR tube containing a solution of compound **Zn-2** (0.020 g, 0.013 mmol) in deuterated toluene (Tol- $d_8$ ) inside the glove box. Then, the sealed NMR was removed from the glove box and heated at 80  $^{\circ}$ C for 24 hours, resulting in compound **Zn-1** and the dihydroborated product of cyanamide (**4b**), which was confirmed by the  $^1$ H NMR spectroscopy. NMR conversion: (>99 %).  $^1$ H NMR (400 MHz, Toluene  $d_8$ , 25  $^{\circ}$ C):  $\delta$ =7.11–7.06 (m, 12H,  $J$  = 20.0 Hz, ArH), 6.89 (t,  $J$  = 7.6 Hz, 4H, ArH), 6.65–6.63 (m,  $J$ =7.6 Hz, 8H ArH), 5.02 (s, 4H, NH), 4.39 (s, 4H,  $CH_2N(Bpin)_2$ ), 4.38 (s, 2H, Zn-H), 3.08-3.02 (m, 8H, Ar- $CH_2CH_3$ ) 2.77-2.73 (m, 8H, Ar- $CH_2CH_3$ ), 2.42–2.36 (m, 8H, Ar- $CH_2CH_3$ ), 2.33–2.16 (m,  $J$ =14.9 Hz, 8H, Ar- $CH_2CH_3$ ), 2.14-2.12 (m, 8H, N- $CH_2CH_3$ ), 1.34 (t, 24H, Ar- $CH_2CH_3$ ), 1.22 (t, 12H, N $CH_2CH_3$ ), 1.12 (s, 48H, Bpin), 0.99 (t, 24H, Ar- $CH_2CH_3$ ).  $^{13}C\{^1H\}$  NMR (101 MHz, Tol  $d_8$ , 25  $^{\circ}$ C):  $\delta$ =157.2 (N3C), 142.6, 141.1, 138.8, 135.2, 126.7, 126.2, 125.7, 125.3, 81.7(Bpin), 61.8, 44.3, 24.9, 24.3, 24.2, 14.4, 14.2, 13.3.  $^{11}B$  NMR (128 MHz, Tol  $d_8$ , 25  $^{\circ}$ C)  $\delta$  26.24.**



**Figure S6:**  $^1$ H NMR spectrum of **Zn-1** and **4b** at 25  $^{\circ}$ C (400 MHz, Tol- $d_8$ ).



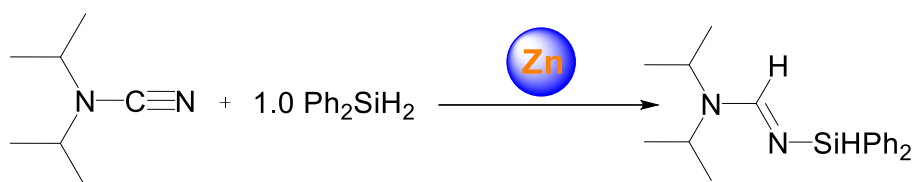
**Figure S7:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **Zn-1** and **4b** (101 MHz, Tol- $d_8$  at 25 °C).



**Figure S8:**  $^{11}\text{B}$  NMR spectrum of **Zn-1** and **4b** (128 MHz, Tol- $d_8$  at 25 °C).

## Optimization Tables

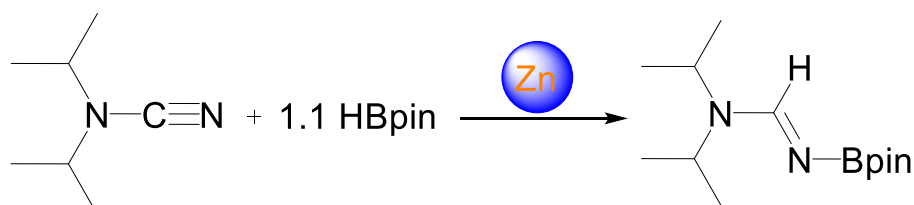
**Table S1.** Optimization table for the zinc-catalyzed partial hydrosilylation of diisopropyl cyanamide.<sup>a</sup>



Entry	Cat. (mol%)	Solvent	Time (h)	Temp (°C)	Conv. <sup>b</sup>
1	-	neat	18	70	-
2	10	neat	24	70	>99
3	5	neat	24	70	>99
<b>4</b>	<b>5</b>	<b>neat</b>	<b>18</b>	<b>70</b>	<b>&gt;99</b>
<b>5</b>	<b>5</b>	<b>C<sub>6</sub>D<sub>6</sub></b>	<b>18</b>	<b>70</b>	<b>&gt;99</b>
6	5	neat	18	65	93
7	3	neat	18	70	91

<sup>a</sup>Reactions were performed with diisopropyl cyanamide (0.2 mmol, 1.0 equiv), Ph<sub>2</sub>SiH<sub>2</sub> (0.2 mmol, 1.0 equiv), and catalyst (**Zn-1**) (x mol %) in sealed reaction vials or J. Young valve NMR tube under N<sub>2</sub> atmosphere and heated at 65-70 °C. <sup>b</sup>Conversion of N-silyl formamidine (**2c**) was investigated by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy based on the formation of characteristic new proton resonance for the (-NCHN) moiety of product.

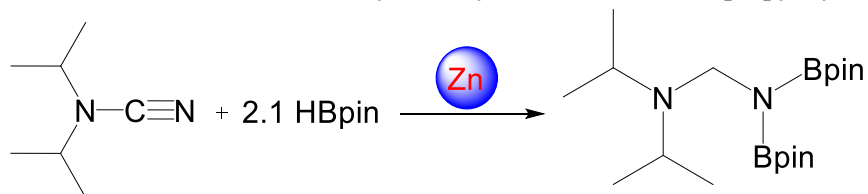
**Table S2.** Optimization table for the zinc-catalyzed monohydroboration of diisopropyl cyanamide.<sup>a</sup>



Entry	Cat. (mol%)	Solvent	Time (h)	Temp (°C)	Conv. <sup>b</sup>
1	-	C <sub>6</sub> D <sub>6</sub>	12	60	-
2	5	C <sub>6</sub> D <sub>6</sub>	18	65	>99
3	3	C <sub>6</sub> D <sub>6</sub>	18	60	>99
<b>4</b>	<b>3</b>	<b>C<sub>6</sub>D<sub>6</sub></b>	<b>12</b>	<b>60</b>	<b>&gt;99</b>
5	1	C <sub>6</sub> D <sub>6</sub>	12	60	90

<sup>a</sup>Reactions were performed with diisopropyl cyanamide (0.2 mmol, 1.0 equiv), HBpin (0.22 mmol, 1.1 equiv), and catalyst (**Zn-1**) (x mol %) in J. Young valve NMR tube under N<sub>2</sub> atmosphere. <sup>b</sup>Conversion of N-boryl formamidine (**3c**) was investigated by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy based on the formation of characteristic new proton resonance for the (-NCHN) moiety of product.

**Table S3.** Optimization table for the zinc-catalyzed dihydroboration of diisopropyl cyanamides.<sup>a</sup>

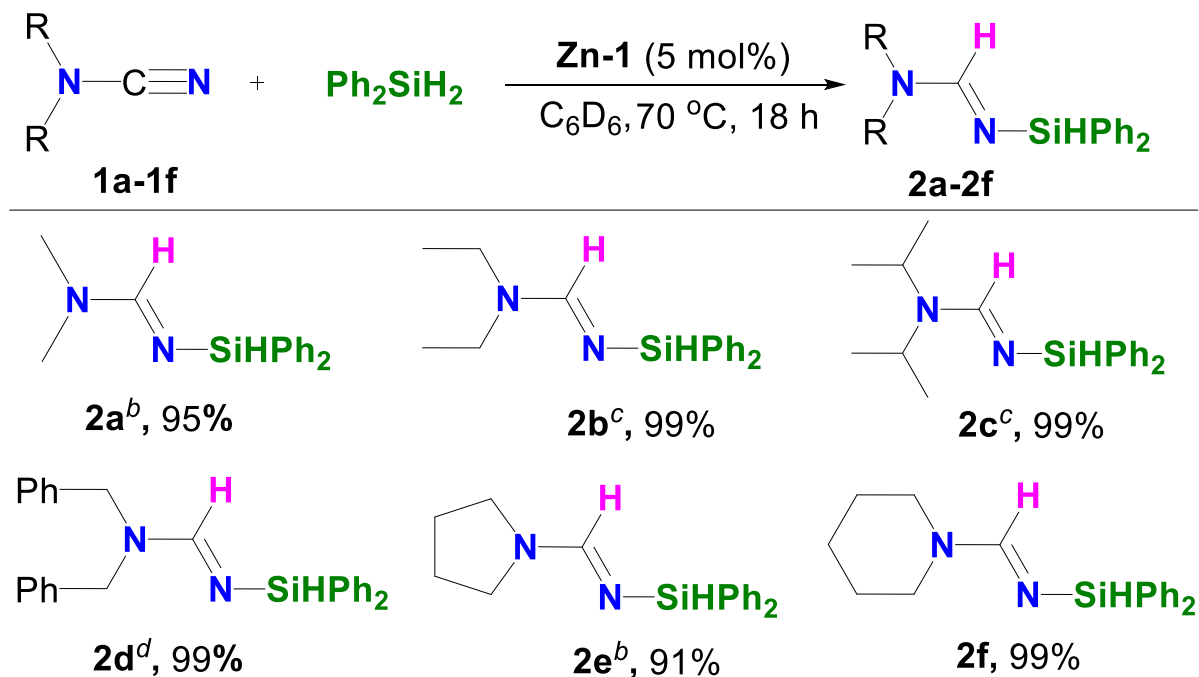


Entry	Cat. (mol%)	Solvent	Time (h)	Temp (°C)	Conv. <sup>b</sup>
1	-	neat	24	80	-
2	3	neat	26	90	>99
<b>3</b>	<b>3</b>	<b>neat</b>	<b>24</b>	<b>80</b>	<b>&gt;99</b>
<b>4</b>	<b>3</b>	<b>C<sub>6</sub>D<sub>6</sub></b>	<b>24</b>	<b>80</b>	<b>&gt;99</b>
5	1	neat	24	80	92

<sup>a</sup>Reactions were performed with diisopropyl cyanamide (0.2 mmol, 1.0 equiv), HBpin (0.42 mmol, 2.1 equiv), and catalyst (**Zn-1**) (x mol %) in reaction catalytical vial or J Young valve NMR tube under N<sub>2</sub> atmosphere.

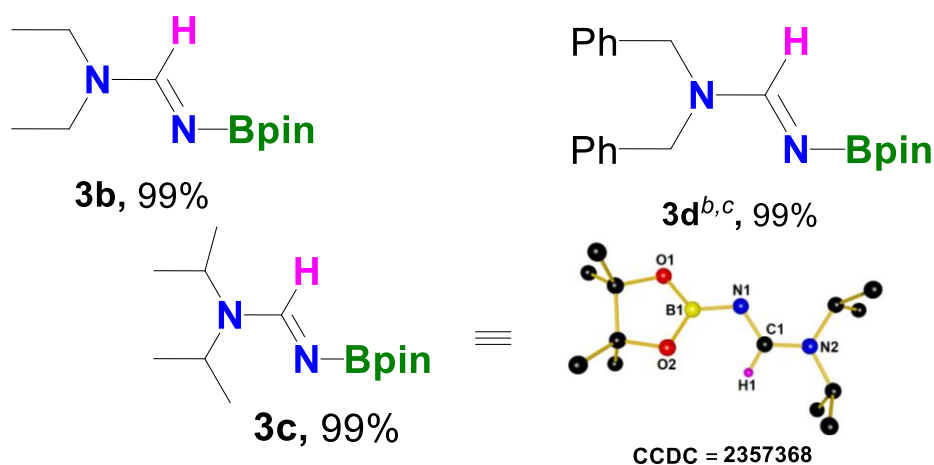
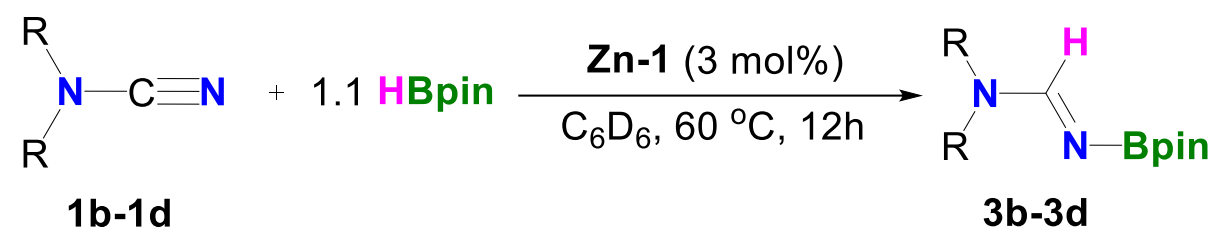
<sup>b</sup>Conversion of N-bis-boryl diamines (**4c**) was investigated by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy based on the formation of characteristic new proton resonance for the (-CH<sub>2</sub>N(Bpin)<sub>2</sub>) moiety of product.

**Table S4.** Substrate scope for the zinc-catalyzed partial hydrosilylation of cyanamides.<sup>a</sup>



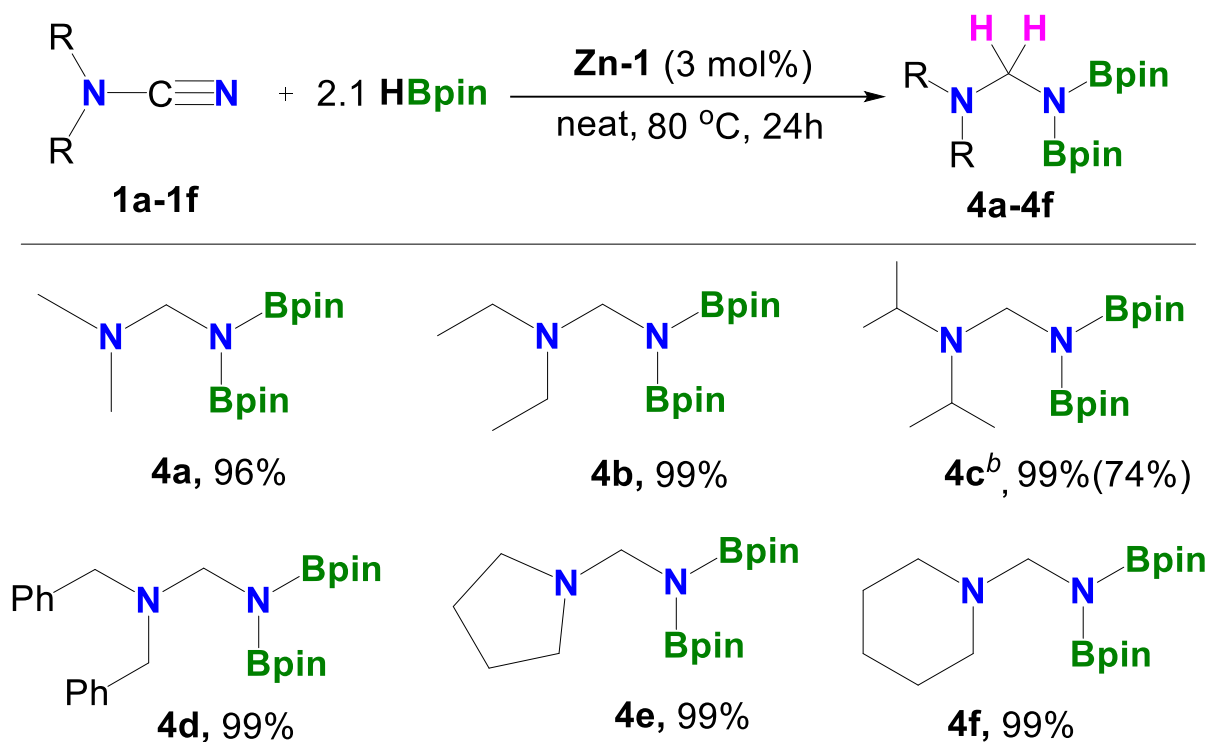
<sup>a</sup>Reactions were performed with cyanamide (0.2 mmol, 1.0 equiv),  $\text{Ph}_2\text{SiH}_2$  (0.2 mmol, 1.0 equiv), and **Zn-1** (5.0 mol %) in a J.Y. valve NMR tube and heated at  $70^\circ\text{C}$  for 18 h. Conversion of the corresponding N-silyl formamidines (**2a-2f**) was investigated by  $^1\text{H}$  NMR spectroscopy based on the formation of characteristic new proton resonance for the ( $-\text{NCHN}$ ) moiety of product. <sup>b</sup>For **2a** and **2e**, NMR conversion was calculated by  $^1\text{H}$  NMR spectroscopy using mesitylene as an internal standard. <sup>c</sup>For **2b** and **2c**, 0.8 equiv. of  $\text{Ph}_2\text{SiH}_2$  was used. <sup>d</sup>For **2d** TON, TOF calculations were performed at 99% conversion using 1.5 mol% **Zn-1** in 40 mins at  $70^\circ\text{C}$ . (see table S7)

**Table S5.** Substrate scope for the zinc-catalyzed partial hydroboration of cyanamides.<sup>a</sup>



<sup>a</sup>Reactions were performed with cyanamide (0.2 mmol, 1.0 equiv), HBpin (0.22 mmol, 1.1 equiv), and catalyst (**Zn-1**) (3.0 mol %) in a J.Y. Valve NMR tube and heated at 60 °C for 12 h. Conversion of the corresponding N-boryl formamidines (**3b-3d**) was investigated by <sup>1</sup>H NMR spectroscopy based on the formation of characteristic new proton resonance for the (–NCHN) moiety of product. <sup>b</sup>Compound (**3d**) is synthesized at room temperature for 8 h. <sup>c</sup>For **3d** TON, TOF calculations were performed at 99% conversion using 1 mol% **Zn-1** in 5 mins at room temperature. (see table S7)

**Table S6.** Substrate scope for the zinc-catalyzed dihydroboration of cyanamides.<sup>a</sup>



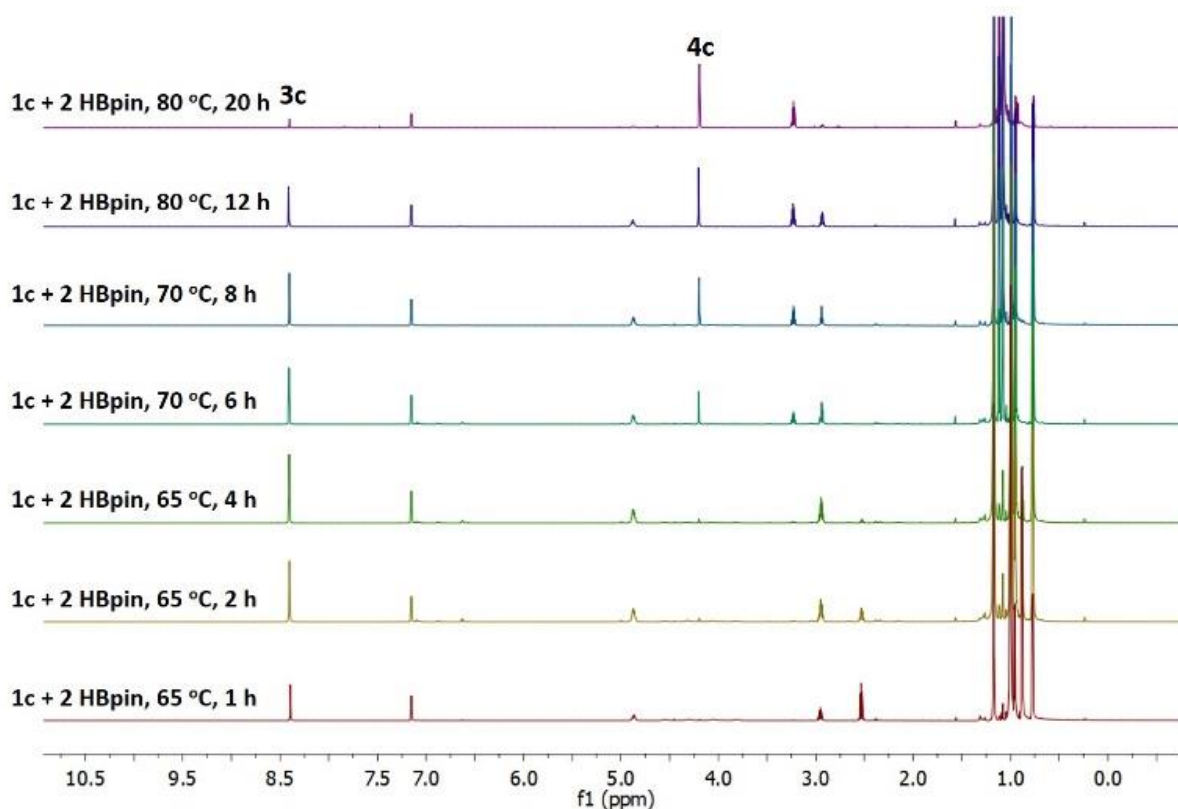
<sup>a</sup>Reactions were performed with cyanamide (0.2 mmol, 1.0 equiv), HBpin (0.44 mmol, 2.1 equiv), and **Zn-1** (3.0 mol %) in a reaction vials or J.Y.valve NMR tube under N<sub>2</sub> atmosphere and heated at 80 °C for 24 h. Conversion of the corresponding N-bis boryl diamines (**4a-4f**) was investigated by <sup>1</sup>H NMR spectroscopy based on the formation of characteristic new proton resonance for the (-CH<sub>2</sub>N(Bpin)<sub>2</sub>) moiety of product. <sup>b</sup>For **4c**, a 2.0 mmol scale reaction was performed.



**Table S7. TON and TOF calculations for the zinc-catalyzed hydrofunctionalization of dibenzyl cyanamide.<sup>a</sup>**

Entry	Substrate	Hydride Source	Catalyst	Catalyst load (mol%)	Time (h)	Temp (°C)	% Conversion	TON	TOF (h <sup>-1</sup> )
1.	<b>1d</b>	Ph <sub>2</sub> SiH <sub>2</sub>	<b>Zn-1</b>	1.5	0.67	70	99	66	99
2.	<b>1d</b>	HBpin	<b>Zn-1</b>	1	0.083	rt	99	99	1194

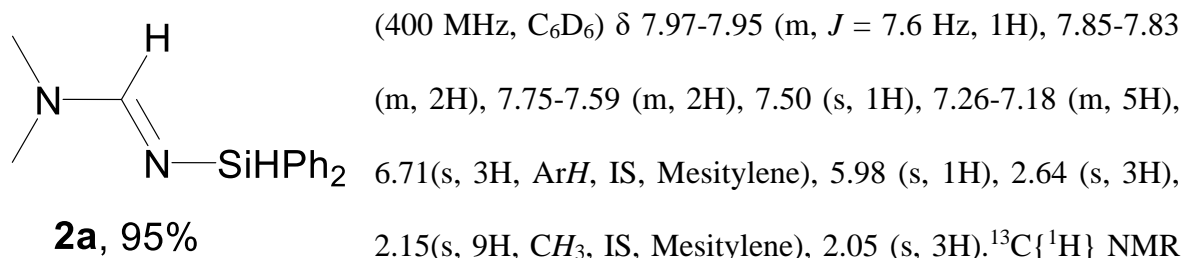
<sup>a</sup>Yields were determined by <sup>1</sup>H NMR spectroscopy. TON was calculated by dividing the number of moles of the product by the number of moles of catalyst used. TOF was determined to divide TON by the time of reaction.



**Figure S9.**  $^1\text{H}$  NMR spectra (700 MHz) for the reaction of (**1c**) (0.2 mmol, 1.0 equiv) and pinacolborane (0.42 mmol, 2.1 equiv), and catalyst **Zn-1** (3 mol%) in benzene  $d_6$ . Spectra were recorded at different temperatures and time intervals between  $T = 65\text{ }^\circ\text{C}$  to  $80\text{ }^\circ\text{C}$  and  $t = 1\text{ h}$ - $20\text{ h}$ , respectively.

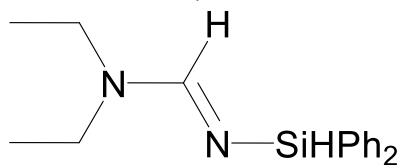
### Analytical data of Monohydrosilylation Products of Cyanamides (**2a-2f**)

(**E**)-*N'*-(diphenylsilyl)-*N,N*-dimethylformimidamide (**2a**) : NMR conversion 95%.  $^1\text{H}$  NMR



(101 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  156.9, 137.2(Ar-C, IS, Mesitylene), 135.0, 134.7, 129.3, 127.8, 127.0 (Ar-C, IS, Mesitylene), 43.0, 31.9, 20.9 ( $\text{CH}_3$ , IS, Mesitylene). HRMS (ASAP/Q-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{19}\text{N}_2\text{Si}$  255.1317, Found 255.1324.

**(E)-N'-(diphenylsilyl)-N,N-diethylformimidamide (2b):** NMR conversion 99%. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.85-7.83 (d, *J* = 9.4 Hz, 4H), 7.62 (s, 1H), 7.26 – 7.20 (m, 6H), 6.00 (s,

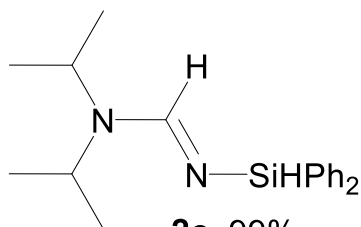


**2b, 99%**

1H), 3.34-3.29 (q, , 2H), 2.51-2.46 (q, 2H), 0.97 (t, *J* = 7.1 Hz, 3H), 0.58 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>) δ 156.2, 137.2, 135.0, 129.3, 127.8, 43.5, 37.5, 14.5,

12.3. <sup>29</sup>Si{<sup>1</sup>H} NMR (80 MHz, C<sub>6</sub>D<sub>6</sub>) δ -21.21. HRMS (ASAP/Q-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>23</sub>N<sub>2</sub>Si 283.1631, Found 283.1626.

**(E)-N'-(diphenylsilyl)-N,N-diisopropylformimidamide (2c):** NMR conversion 99%. <sup>1</sup>H

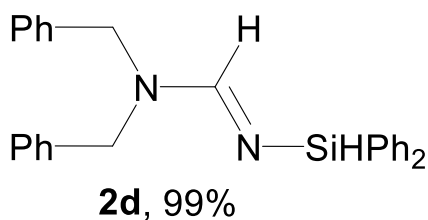


**2c, 99%**

NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.77 (s, 1H), 7.68-7.65 (d, *J* = 9.3 Hz, 4H), 7.07-6.99 (m, *J* = 31.4 Hz, 6H), 5.84 (s, 1H), 4.46-4.39 (m, *J* = 27.3 Hz, 1H), 2.78-2.71 (m, 1H), 0.92-0.90 (d, *J* = 6.9 Hz, 6H), 0.57-0.55 (d, *J* = 6.8 Hz, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR

(101 MHz, C<sub>6</sub>D<sub>6</sub>) δ 154.7, 137.3, 135.0, 129.2, 127.8, 46.3, 43.8, 22.9, 19.6. HRMS (ASAP/Q-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>27</sub>N<sub>2</sub>Si 311.1943, Found 311.1938.

**(E)-N,N-dibenzyl-N'-(diphenylsilyl)formimidamide (2d):** NMR conversion 99%. <sup>1</sup>H NMR

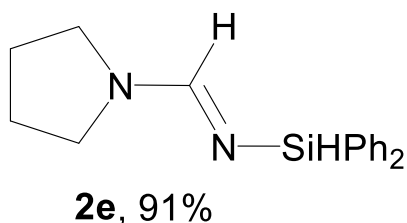


**2d, 99%**

(400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.98 (s, 1H), 7.89-7.86 (m, 4H), 7.51-7.49 (d, *J* = 9.3 Hz, 1H), 7.28-7.22 (m, 5H), 7.15 – 7.10 (m, 5H), 7.09-7.03 (d, *J* = 19.5 Hz, 4H), 6.82-6.80 (d, *J* = 7.4 Hz, 1H), 6.10 (s, 1H), 4.63 (s, 2H), 3.70

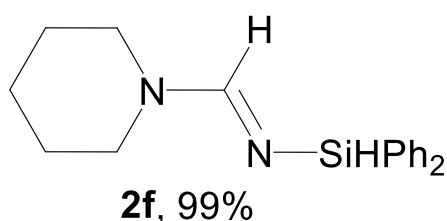
(s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>) δ 157.4, 137.7, 137.1, 136.7, 135.7, 135.1, 129.7, 129.5, 128.4, 128.3, 128.1, 127.9, 127.4, 52.0, 45.3. HRMS (ASAP/Q-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>27</sub>N<sub>2</sub>Si 407.1943, Found 407.1908.

**(E)-N-(diphenylsilyl)-1-(pyrrolidin-1-yl)methanimine (2e):** NMR conversion 91%. <sup>1</sup>H



NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 8.17-8.15 (d, *J* = 9.1 Hz, 1H), 8.03-7.97 (m, *J* = 24.0 Hz, 1H), 7.90-7.89 (d, *J* = 1.7 Hz, 1H), 7.88-7.87 (m, 1H), 7.83 (s, 1H), 7.37 – 7.32 (m, 1H), 7.25 – 7.20 (m, 4H), 6.71 (s, 3H, ArH, IS, Mesitylene), 6.02 (s, 1H), 3.37-3.34 (m, *J* = 14.0 Hz, 2H), 2.67-2.62 (m, *J* = 6.5 Hz, 2H), 2.15 (s, 9H, CH<sub>3</sub>, IS, Mesitylene), 1.31 – 1.25 (m, 2H), 1.18-1.13 (m, *J* = 6.8 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz, C<sub>6</sub>D<sub>6</sub>) δ 154.4, 139.5, 137.1(Ar-C, IS, Mesitylene), 135.7, 135.6, 135.1, 134.3, 129.7, 129.4, 128.0, 127.0(Ar-C, IS, Mesitylene), 46.7, 44.0, 24.8, 23.8, 20.8(CH<sub>3</sub>, IS, Mesitylene). HRMS (ASAP/Q-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>Si 281.1474, Found: 281.1452.

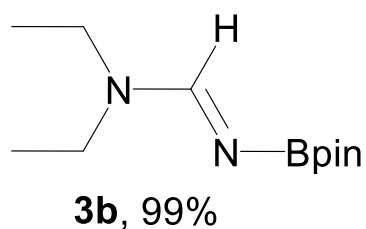
**(E)-N-(diphenylsilyl)-1-(piperidin-1-yl)methanimine (2f):** NMR conversion 99%. <sup>1</sup>H NMR



(400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 8.11-8.09 (m, *J* = 7.0 Hz, 1H), 7.87-7.83 (m, *J* = 13.8 Hz, 4H), 7.60 (s, 1H), 7.26-7.20 (m, *J* = 7.2 Hz, 5H), 6.02 (s, 1H), 3.60-3.49 (m, 2H), 2.52-2.50 (d, *J* = 11.0 Hz, 2H), 1.19-1.16 (m, 4H), 0.98-0.86 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>) δ 154.3, 137.2, 135.6, 135.1, 131.3, 129.8, 129.3, 128.1, 127.8, 48.0, 46.6, 44.0, 24.7, 23.8. HRMS (ASAP/Q-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>Si 295.1631, Found : 295.1631.

### Analytical data of Monohydroboration Products of Cyanamides (3b-3d)

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

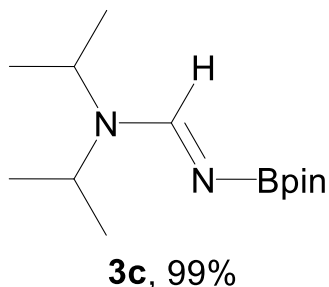


NMR conversion 99%. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 8.03 (s, 1H), 3.53-3.48 (d, *J* = 21.5 Hz, 2H), 3.28-3.23 (m, 2H), 1.27 (s, 12H), 1.16 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>) δ 160.0, 81.1, 43.8, 37.4, 24.7, 14.3,

12.1.  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  22.83. HRMS (ASAP/Q TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{11}\text{H}_{24}\text{BN}_2\text{O}_2$  227.1967, Found: 227.1953.

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

**(3c):** NMR conversion 99%.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.44 (s, 1H), 4.94-4.87 (d,  $J = 27.4$



Hz, 1H), 2.96-2.89 (s, 1H), 1.18 (s, 12H), 0.96-0.95 (d,  $J = 6.9$

Hz, 6H), 0.77-0.76 (d,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101

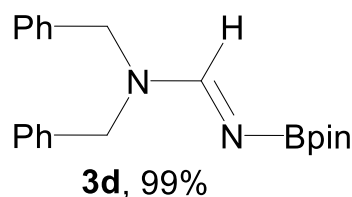
MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  158.1, 81.1, 45.5, 43.6, 24.7, 23.1, 19.4. HRMS

(ASAP/Q TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{28}\text{BN}_2\text{O}_2$

255.2280, Found : 255.2300.

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

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ) NMR conversion 99%.  $\delta$  8.45 (s, 1H), 7.12-7.09 (m,  $J = 9.3$  Hz,



2H), 7.05-6.99 (m,  $J = 19.4$  Hz, 6H), 6.77-6.75 (m,  $J = 9.3$  Hz,

2H), 4.60 (s, 2H), 3.71 (s, 2H), 1.23 (s, 12H).  $^{13}\text{C}\{^1\text{H}\}$  NMR

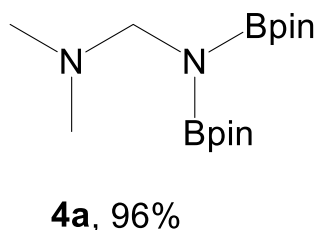
(101 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  161.1, 137.3, 136.7, 128.7, 128.6, 128.4,

128.3, 127.3, 127.0, 81.5, 52.2, 45.2, 24.8. HRMS (ASAP/Q TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for

$\text{C}_{21}\text{H}_{28}\text{BN}_2\text{O}_2$  351.2280, Found : 351.2265.

**Analytical data of Dihydroboration Products of Cyanamides (4a-4f)**

**N,N-dimethyl-N',N'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanediamine**



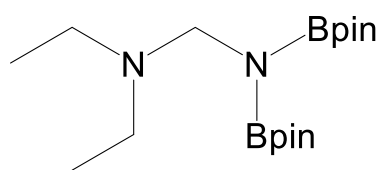
**(4a):** NMR conversion 96%  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.04

(s, 2H), 2.17 (s, 6H), 1.16 (s, 24H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,

$\text{CDCl}_3$ )  $\delta$  82.2, 65.8, 41.5, 24.4. HRMS (ASAP/Q TOF)  $m/z$ :  $[\text{M}$

$+ \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{32}\text{B}_2\text{N}_2\text{O}_4$  326.2543, Found : 326.2521.

**N,N-diethyl-N',N'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanediamine (4b):**

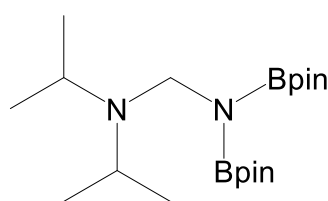


**4b, 99%**

NMR conversion 99%  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.14 (s, 2H), 2.50 – 2.45 (m, 4H), 1.21 (s, 24H), 1.05-1.02 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  82.1, 60.7, 43.8,

24.3, 13.5. HRMS (ASAP/Q TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{37}\text{B}_2\text{N}_2\text{O}_4$  355.2934, Found : 355.2963.

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



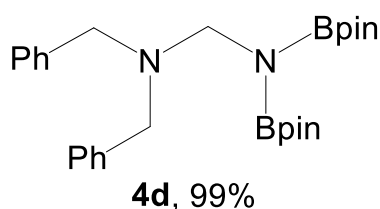
**4c, 99%**

(4c): NMR conversion 99%  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.88 (s, 2H), 3.08-3.01 (dt,  $J = 13.4, 6.7$  Hz, 2H), 1.20 (s, 24H), 0.98-0.97 (d,  $J = 6.7$  Hz, 12H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  81.9, 55.5, 45.1, 24.4, 21.1.  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  25.69. HRMS

(ASAP/Q TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{41}\text{B}_2\text{N}_2\text{O}_4$  383.3247, Found : 383.3248.

**N,N-dibenzyl-N',N'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanediamine**

(4d): NMR conversion 99%.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.50-7.48 (d,  $J = 7.2$  Hz, 4H), 7.22-



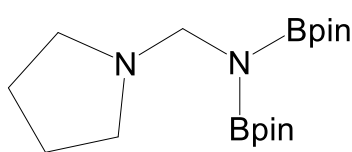
**4d, 99%**

7.18 (t,  $J = 7.5$  Hz, 4H), 7.11-7.08 (t,  $J = 7.3$  Hz, 2H), 4.43 (s, 2H), 3.88 (s, 4H), 1.06 (s, 24H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.4, 128.7, 127.9, 126.4, 82.1, 63.5, 55.1, 24.3.

$^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  26.06. HRMS (ASAP/Q TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{27}\text{H}_{41}\text{B}_2\text{N}_2\text{O}_4$  479.3247, Found : 479.3224.

**4,4,5,5-tetramethyl-N-(pyrrolidin-1-ylmethyl)-N-(4,4,5,5-tetramethyl-1,3,2-**

**dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (4e):** NMR conversion 99%.  $^1\text{H}$  NMR (400

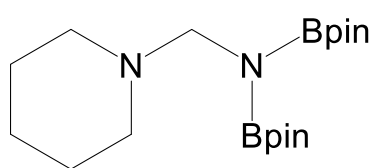


**4e, 99%**

MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  4.21 (s, 2H), 2.47-2.42 (m,  $J = 6.1$  Hz, 4H), 1.64-1.57 (m, ,  $J = 12.8$  Hz, 4H), 1.15 (s, 24H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  81.9, 61.8, 49.7, 45.8, 24.3. HRMS (ASAP/Q-

TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{35}\text{B}_2\text{N}_2\text{O}_4$  353.2777, Found: 353.2780.

**4,4,5,5-tetramethyl-N-(piperidin-1-ylmethyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-**



**4f**, 99%

**2-yl)-1,3,2-dioxaborolan-2-amine (4f):** NMR conversion 99%. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 4.05 (s, 2H), 3.10 – 3.07 (m, 4H), 2.91 – 2.88 (m, 2H), 2.41-2.34 (m, J = 10.2 Hz, 4H), 1.12 (s, 24H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>) δ 81.8, 67.0,

56.4, 51.0, 49.7, 45.1, 26.4, 24.3. HRMS (ASAP/Q-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>37</sub>B<sub>2</sub>N<sub>2</sub>O<sub>4</sub> 367.2934, Found 367.2919.

### Spectral data ( $^1\text{H}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR) for catalyst free reactions

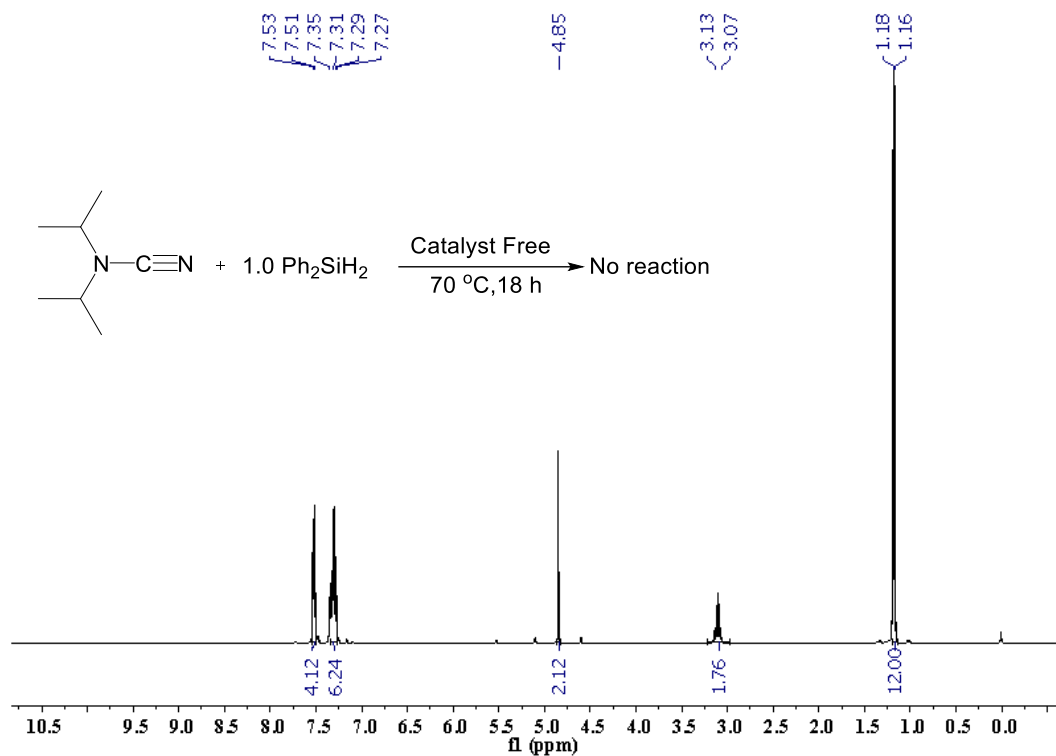


Figure S10:  $^1\text{H}$  NMR spectrum of **2c** without catalyst (400 MHz,  $\text{CDCl}_3$ ).

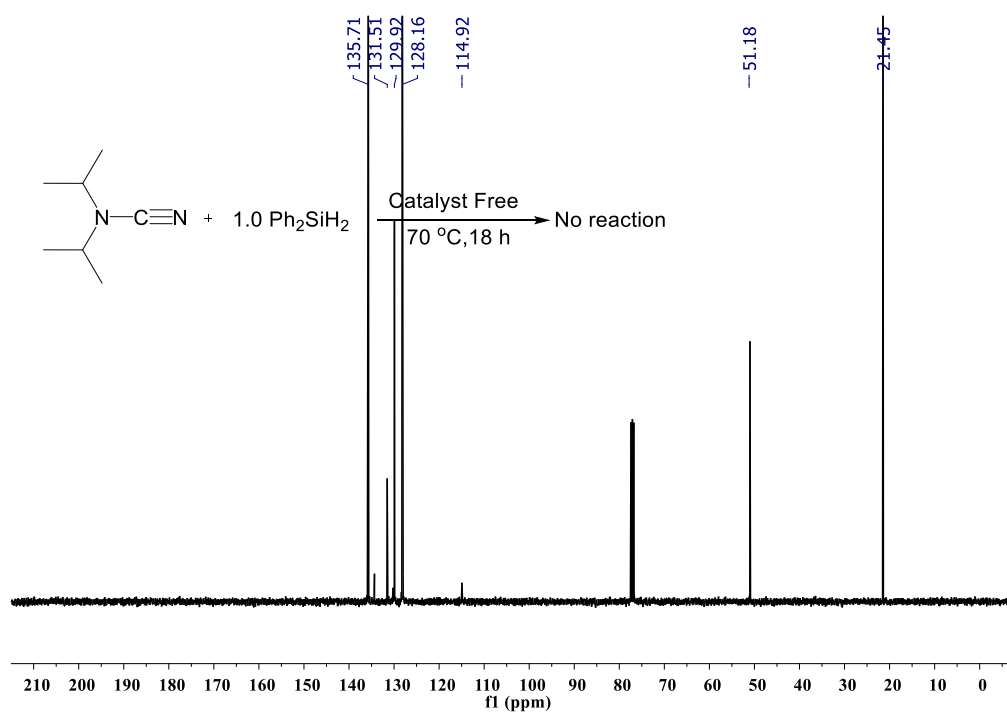
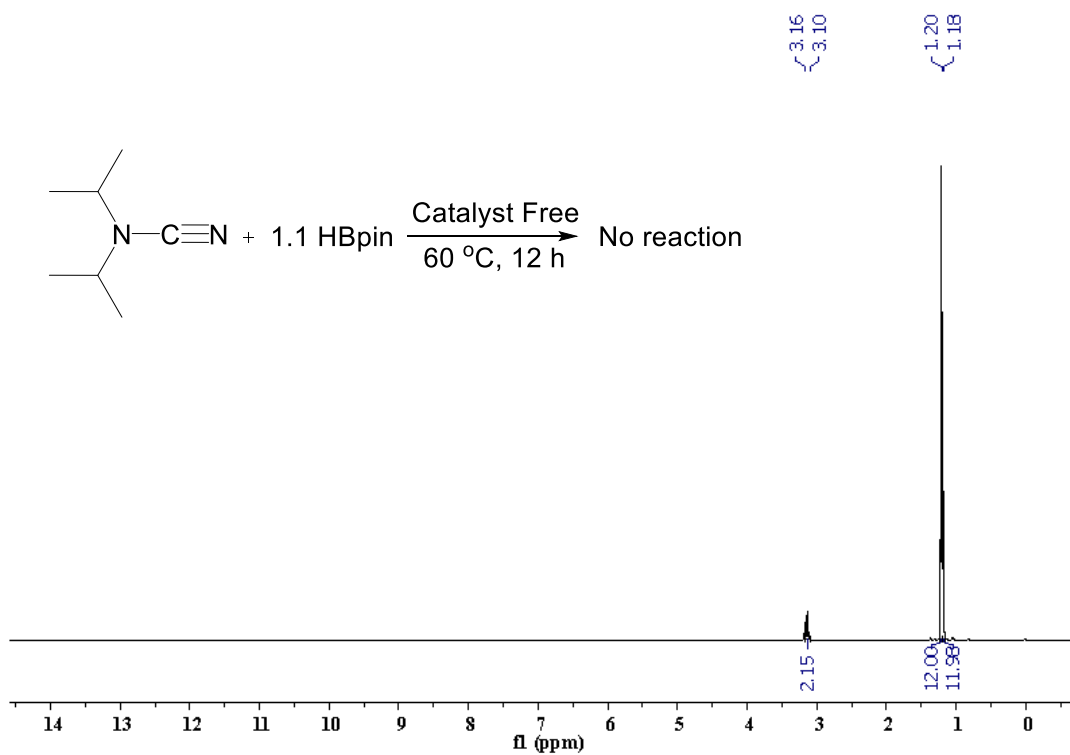
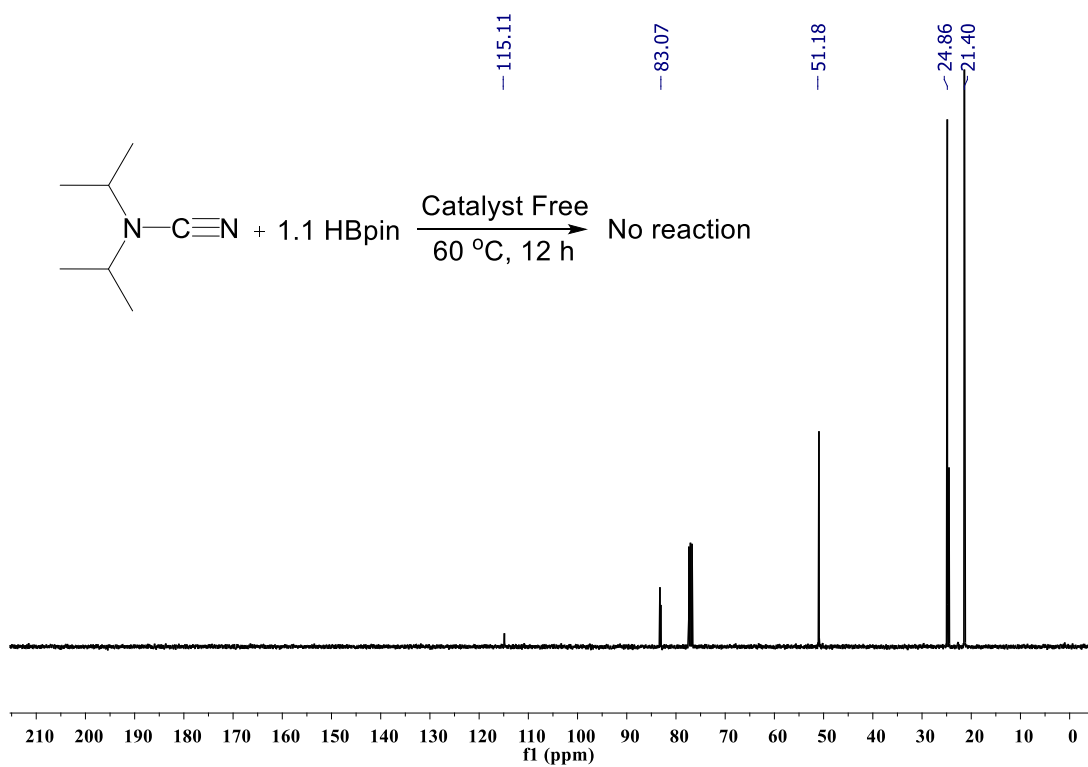


Figure S11:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2c** without catalyst (101 MHz,  $\text{CDCl}_3$ ).

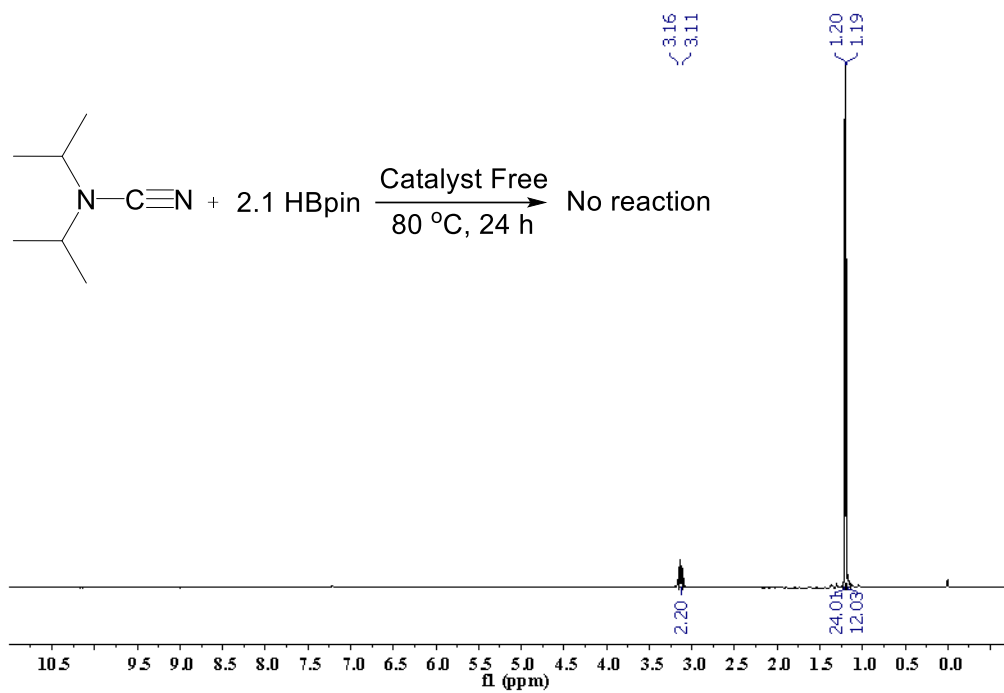




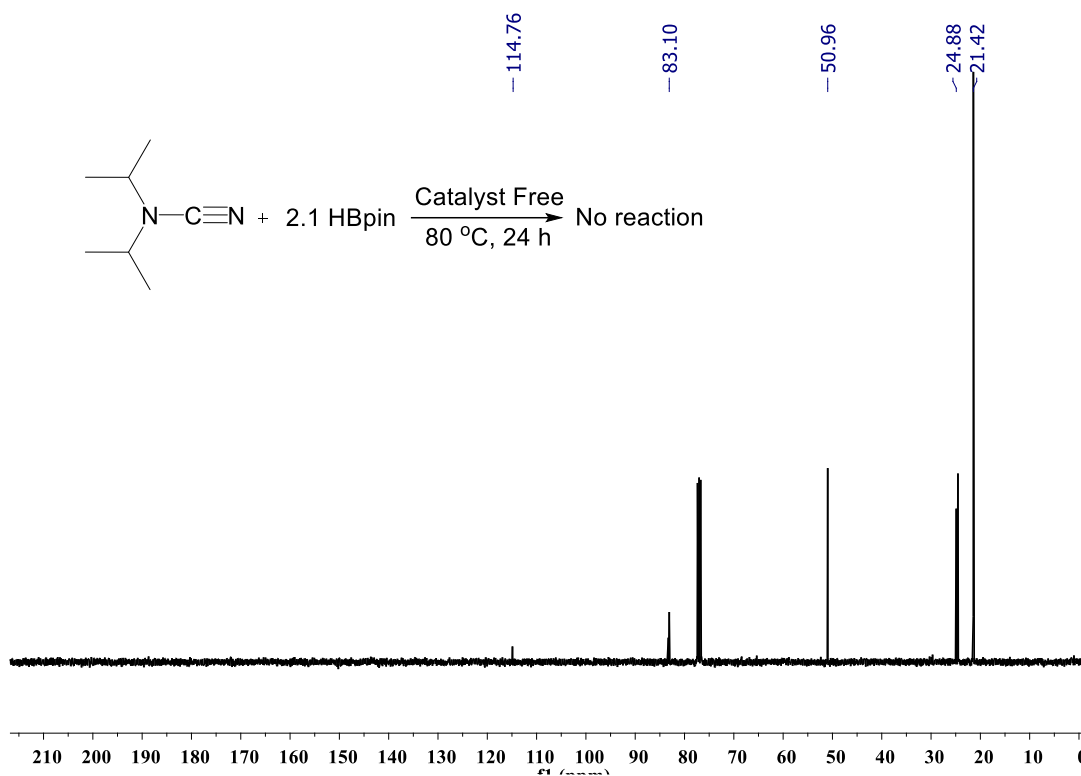
**Figure S12:**  $^1\text{H}$  NMR spectrum of **3c** without catalyst (400 MHz,  $\text{CDCl}_3$ ).



**Figure S13:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3c** without catalyst (101 MHz,  $\text{CDCl}_3$ ).

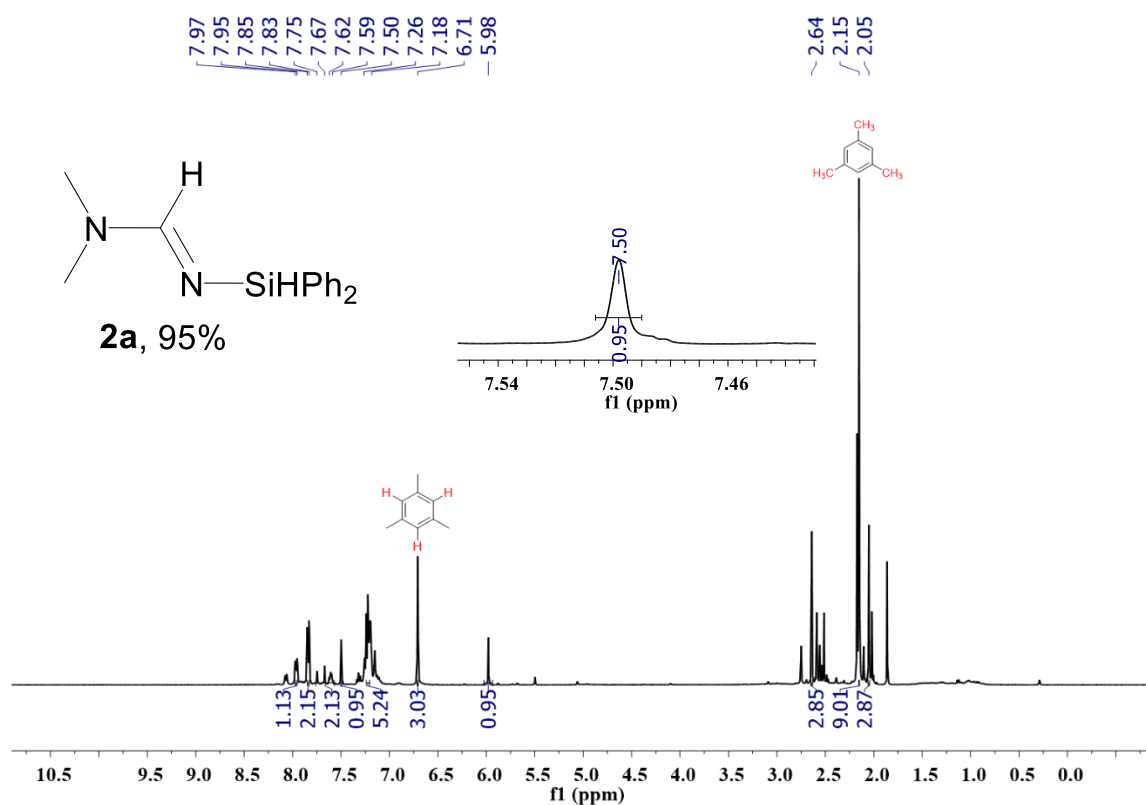


**Figure S14:**  $^1\text{H}$  NMR spectrum of **4c** without catalyst (400 MHz,  $\text{CDCl}_3$ )

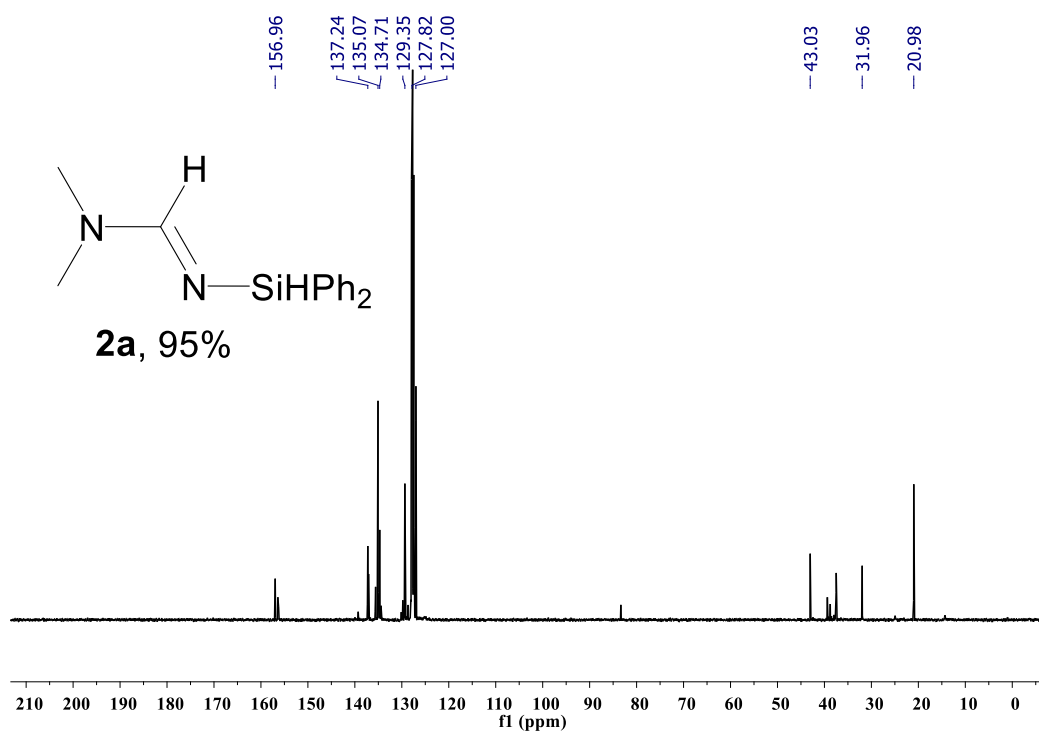


**Figure S15:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4c** without catalyst (101 MHz,  $\text{CDCl}_3$ ).

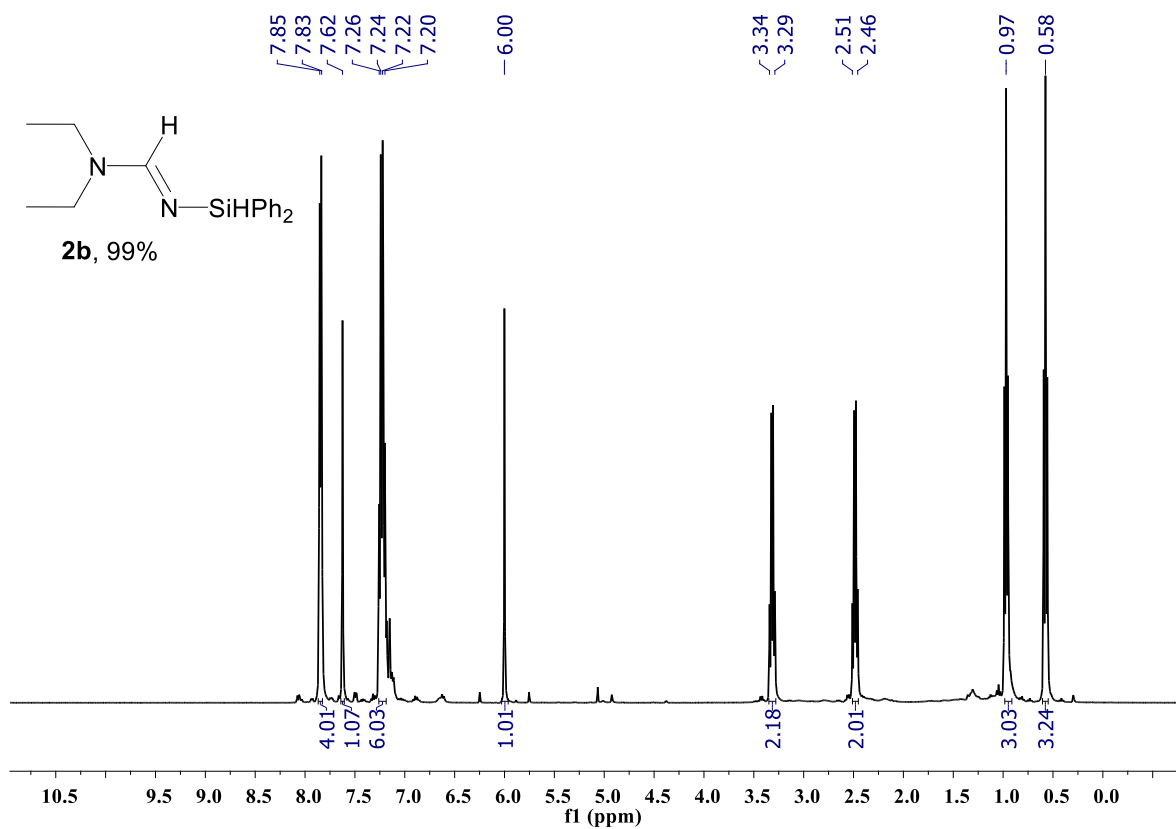
Spectral data ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR) For Monohydrosilylation of Cyanamides



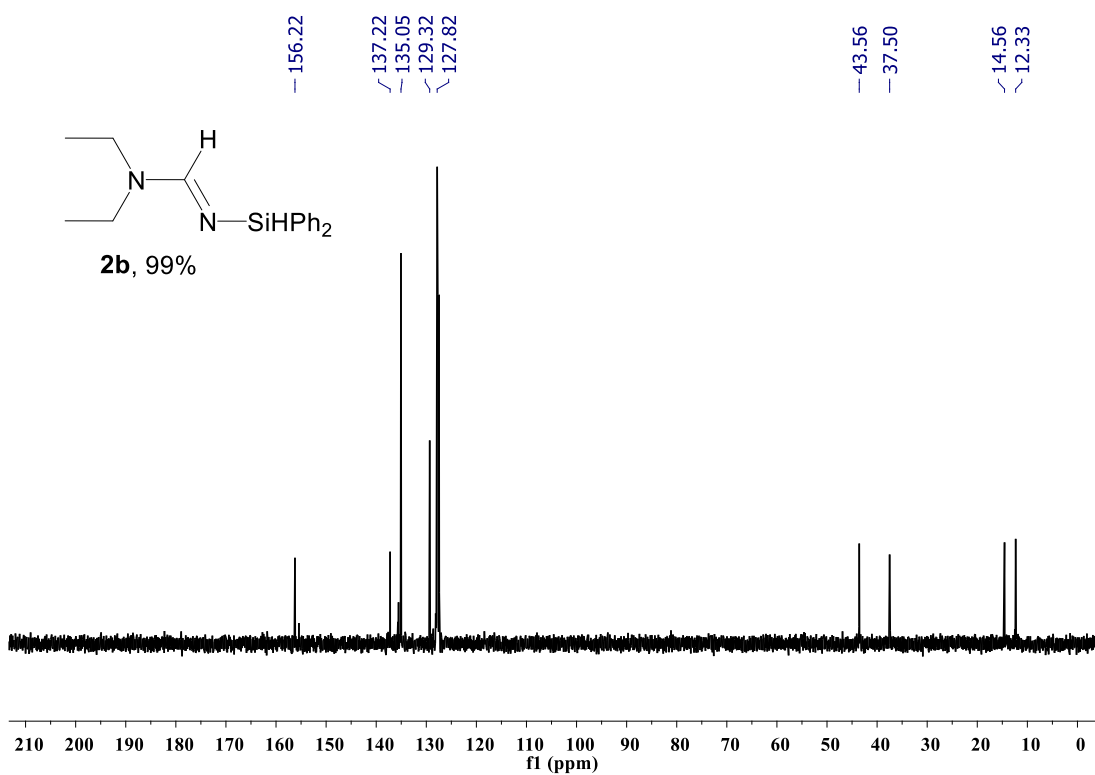
**Figure S16:**  $^1\text{H}$  NMR spectrum of **2a** (400 MHz,  $\text{C}_6\text{D}_6$ ). Mesitylene was used as an internal standard.



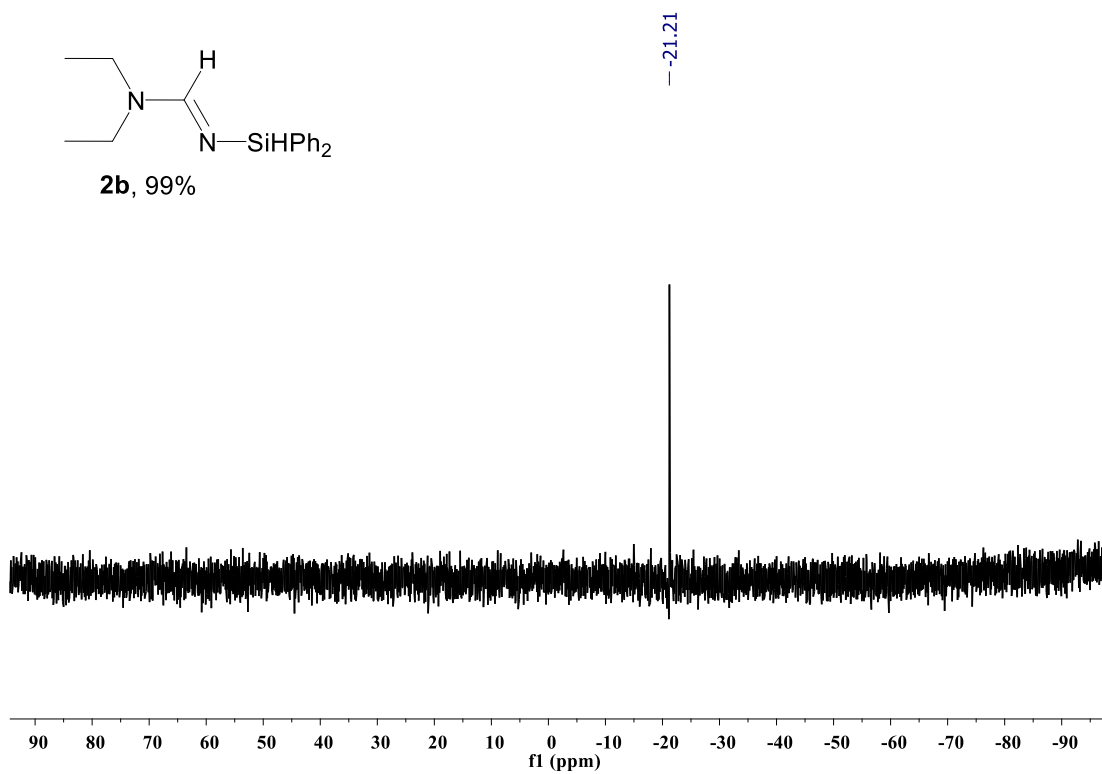
**Figure S17:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2b**. (101 MHz,  $\text{C}_6\text{D}_6$ ). Mesitylene was used as an internal standard.



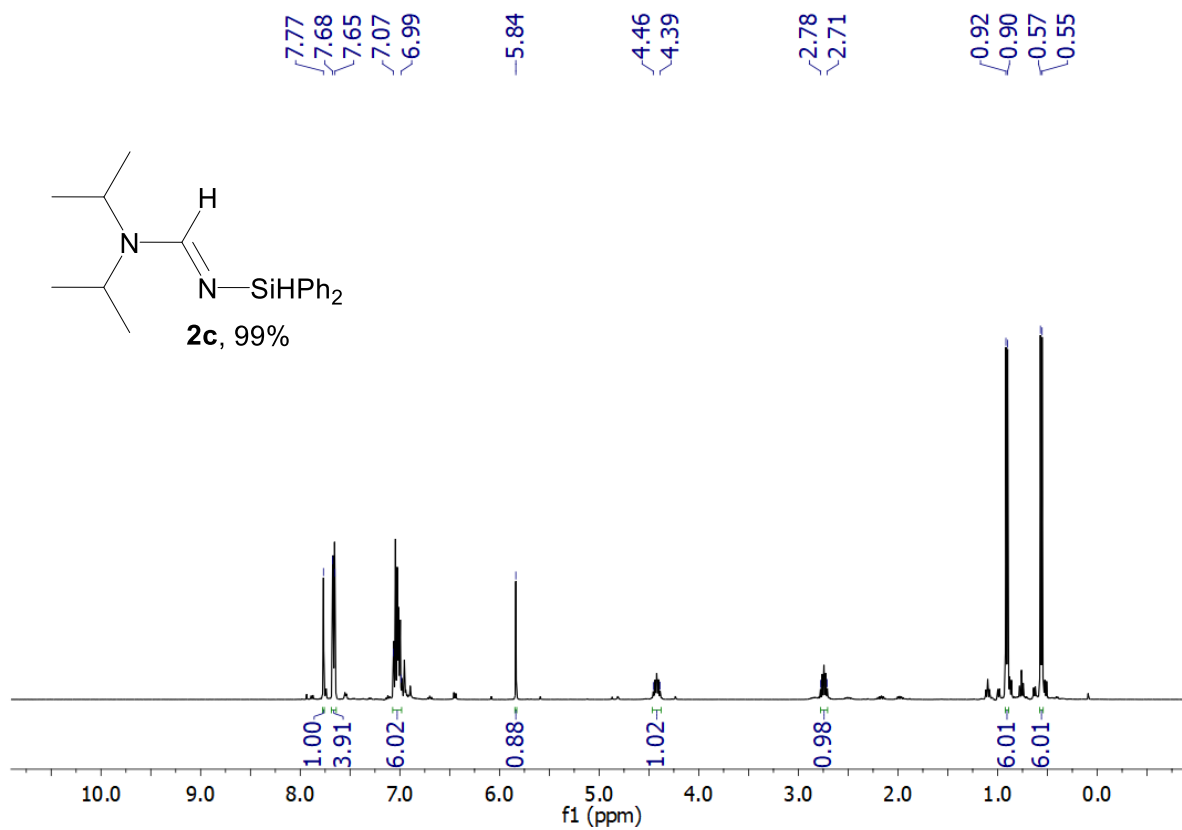
**Figure S18:**  $^1\text{H NMR}$  spectrum of **2b** (400 MHz,  $\text{C}_6\text{D}_6$ ).



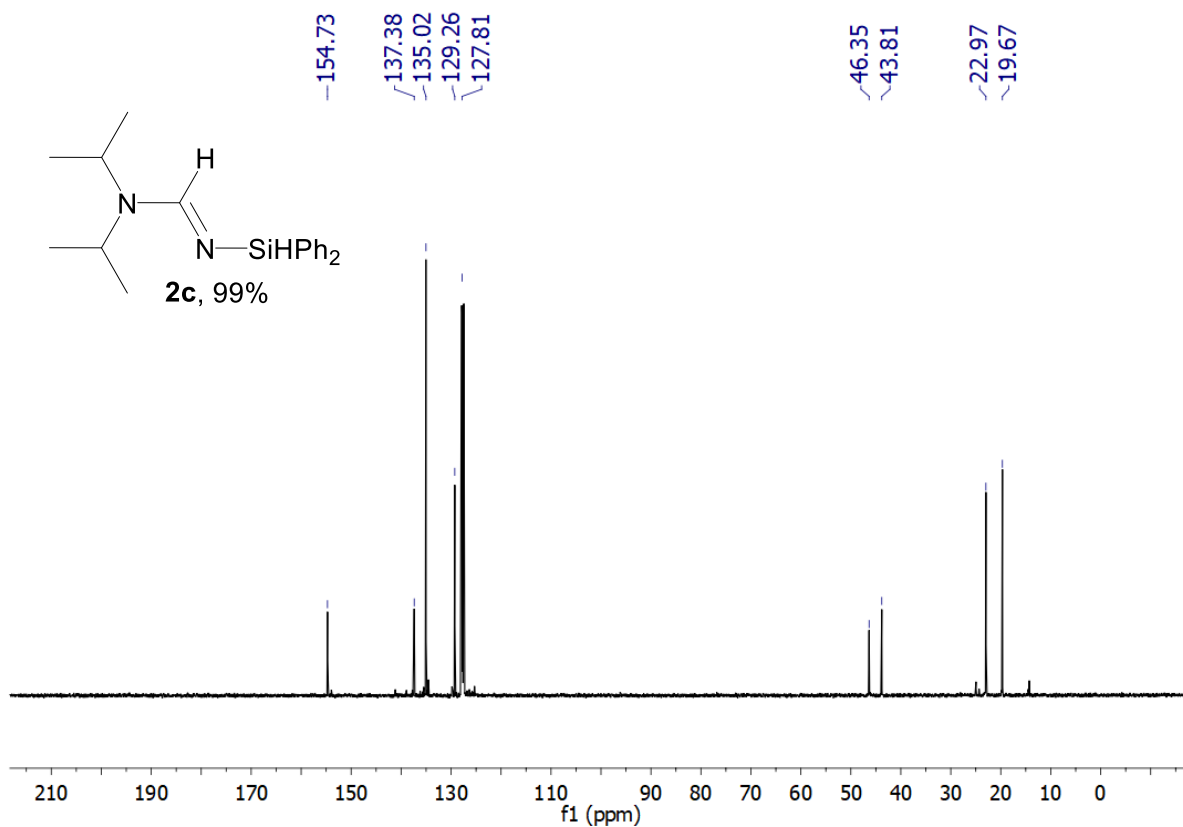
**Figure S19:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2b** (101 MHz,  $\text{C}_6\text{D}_6$ ).



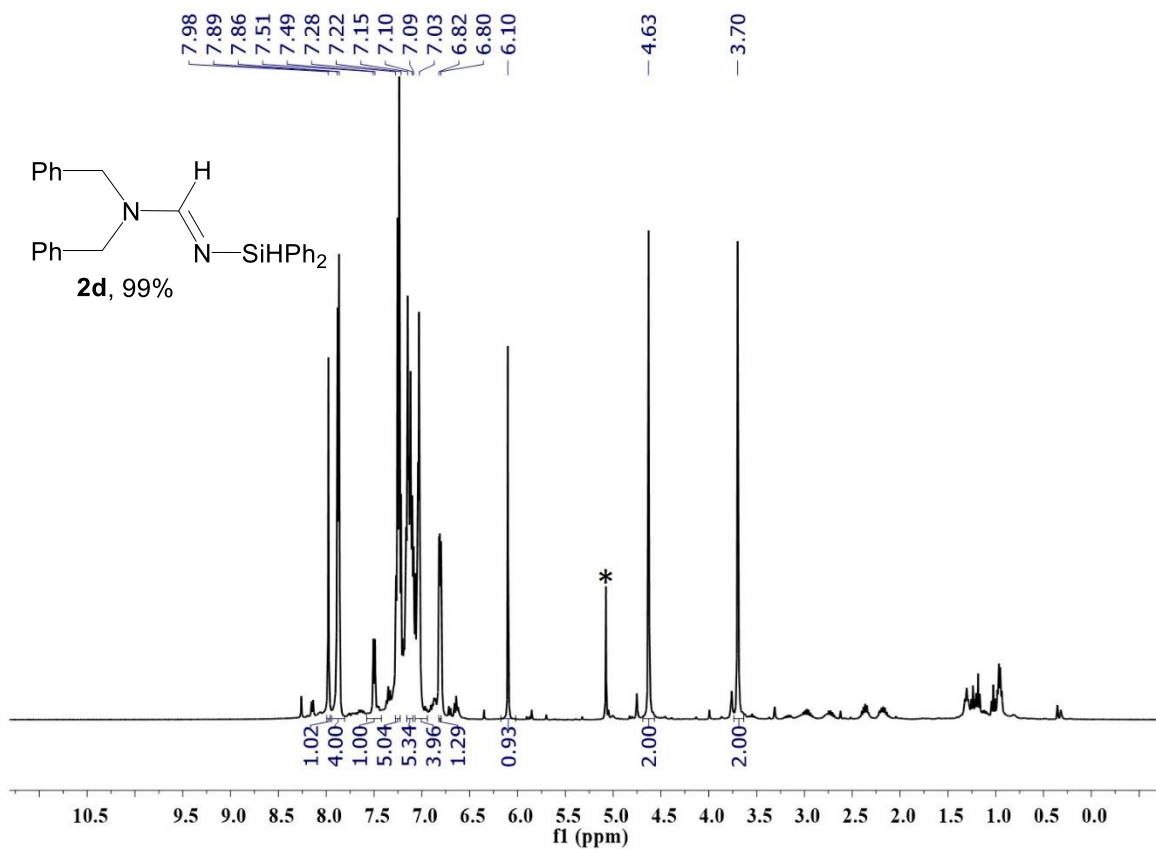
**Figure S20:**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of **2b** (80 MHz,  $\text{C}_6\text{D}_6$ ).



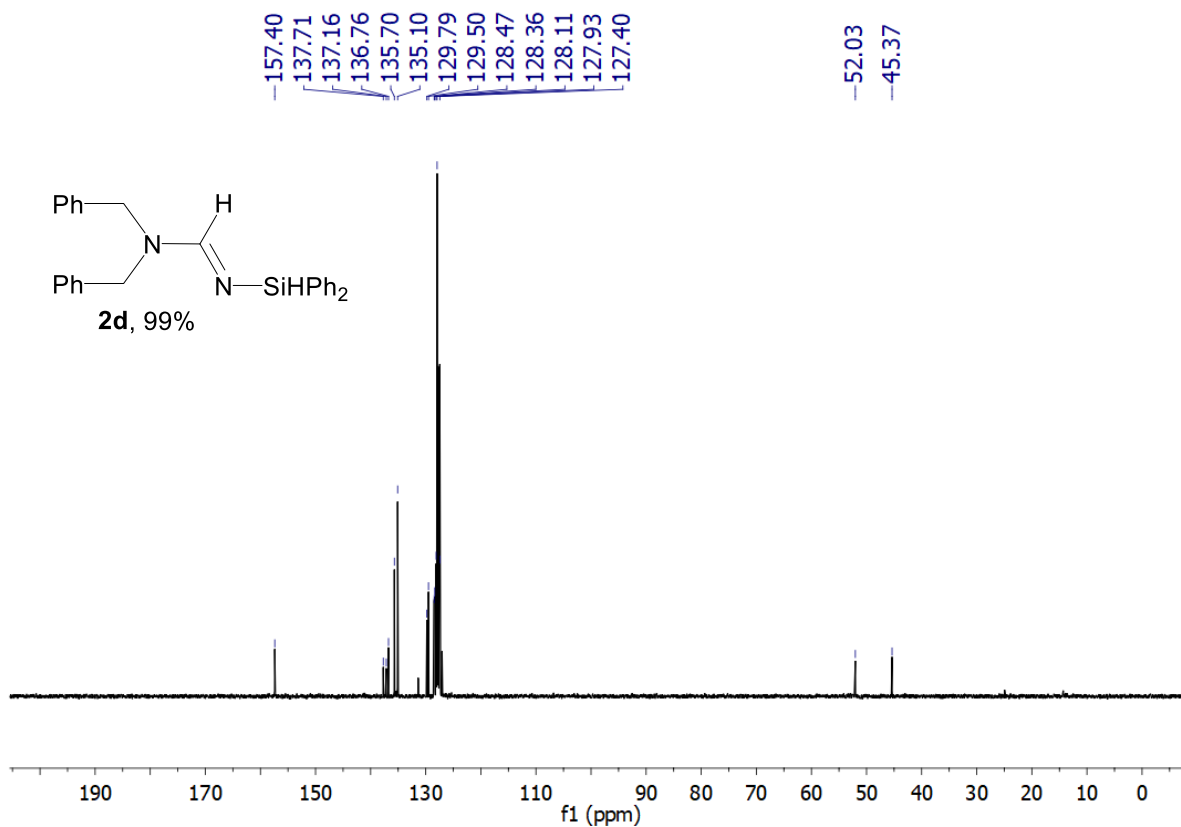
**Figure S21:**  $^1\text{H}$  NMR spectrum of **2c** (400 MHz,  $\text{C}_6\text{D}_6$ ).



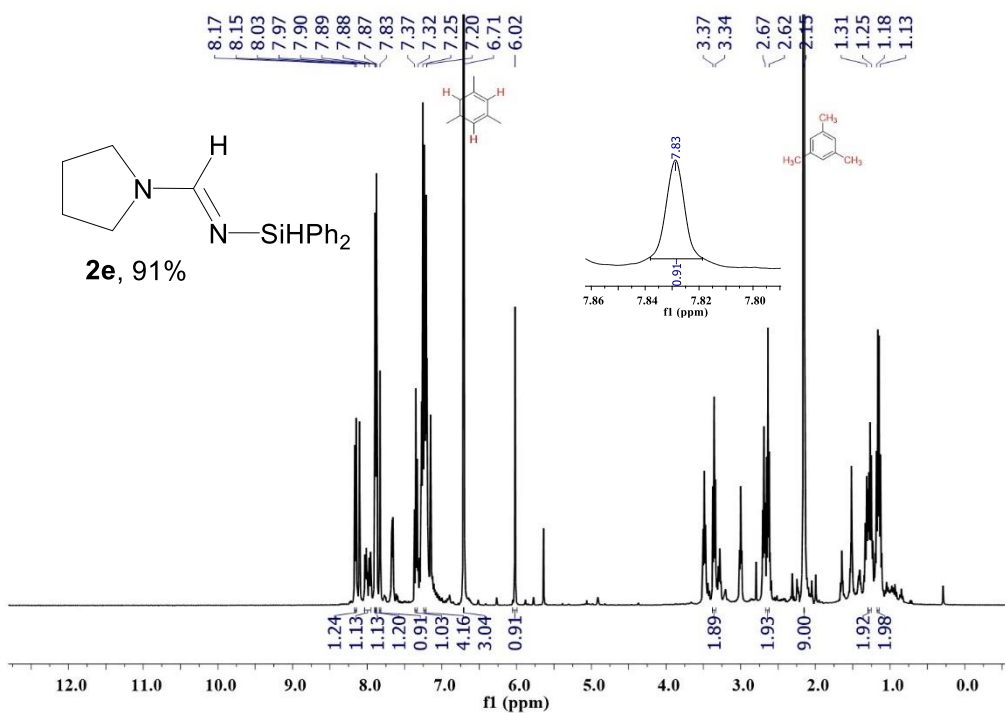
**Figure S22:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2c** (101 MHz,  $\text{C}_6\text{D}_6$ ).



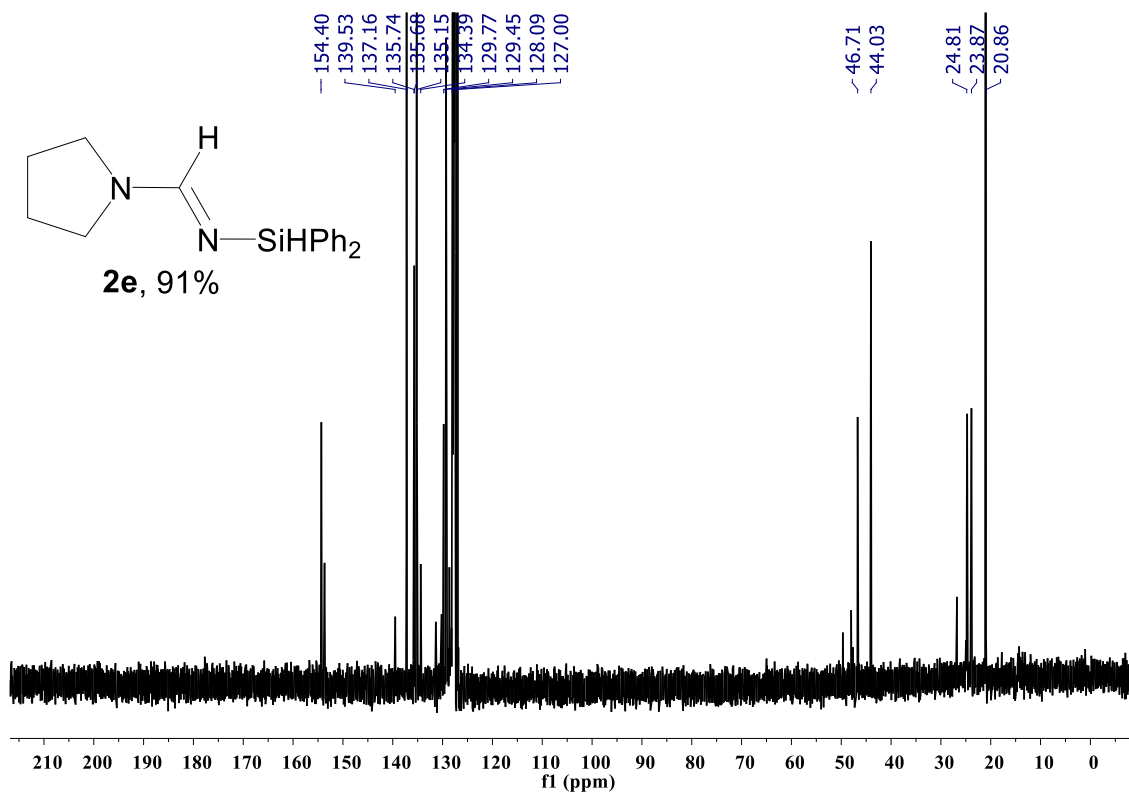
**Figure S23:**  $^1\text{H}$  NMR spectrum of **2d** (400 MHz,  $\text{C}_6\text{D}_6$ ). (\* =  $\text{Ph}_2\text{SiH}_2$ )



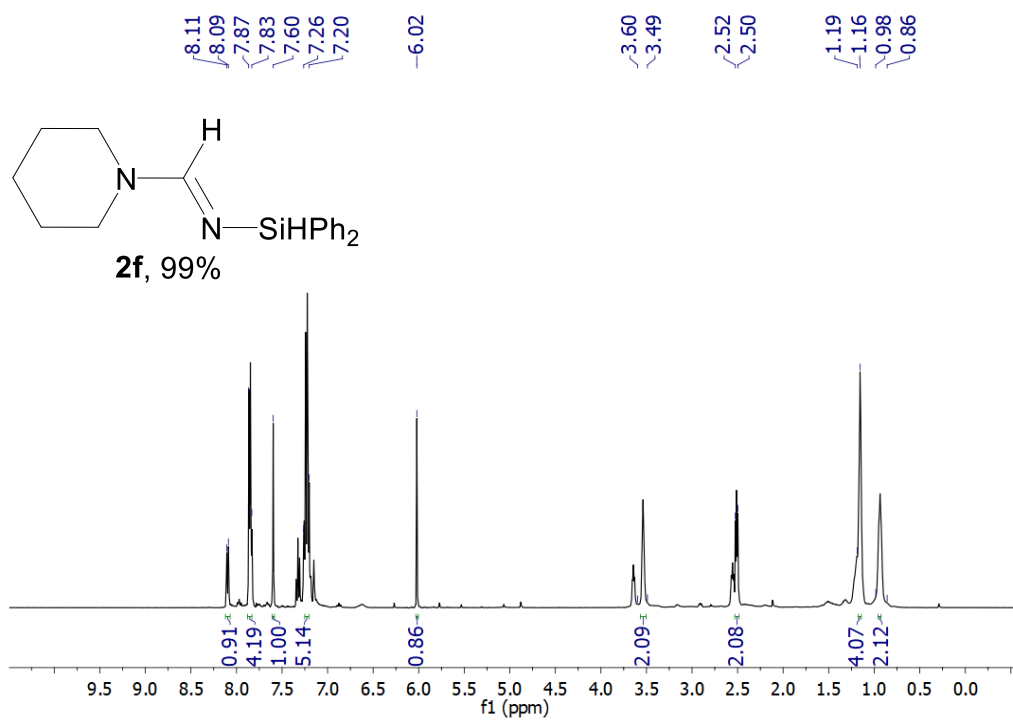
**Figure S24:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2d** (101 MHz,  $\text{C}_6\text{D}_6$ ).



**Figure 25:**  $^1\text{H}$  NMR spectrum of **2e** (400 MHz,  $\text{C}_6\text{D}_6$ ). Mesitylene was used as an internal standard.

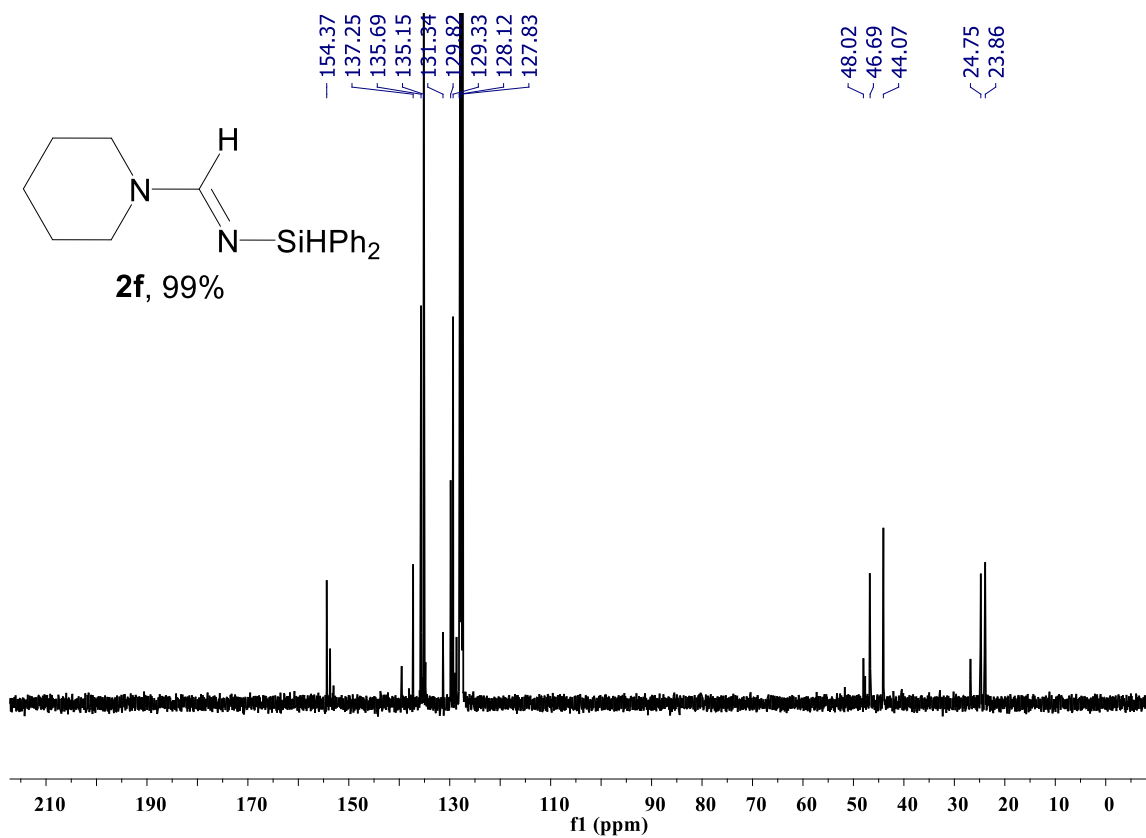


**Figure S26:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2e** (176 MHz,  $\text{C}_6\text{D}_6$ ). Mesitylene was used as an internal standard.



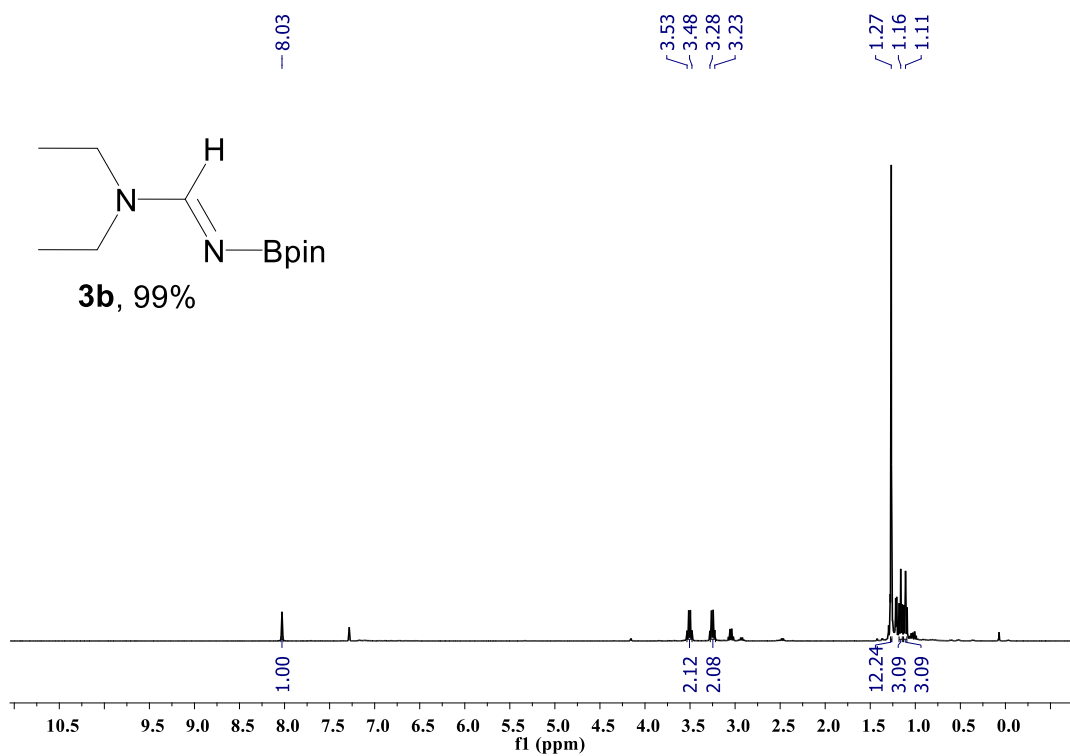
**Figure S27:**  $^1\text{H}$  NMR spectrum of **2f** (400 MHz,  $\text{C}_6\text{D}_6$ ).



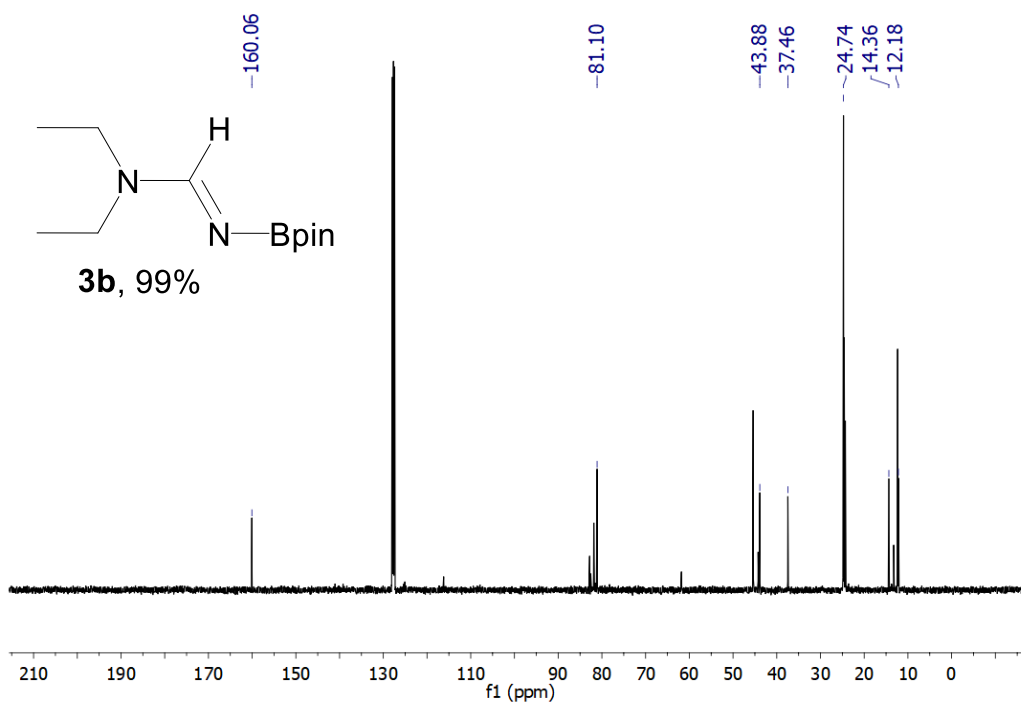


**Figure S28:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2f** (101 MHz,  $\text{C}_6\text{D}_6$ ).

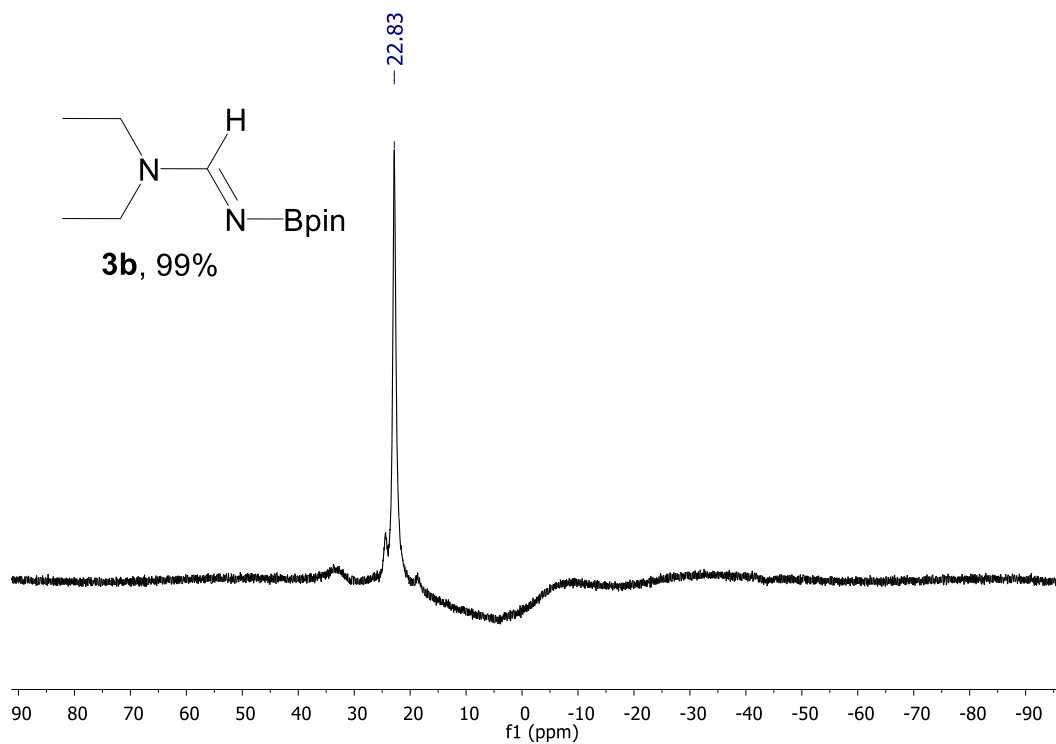
# $^1\text{H}$ , $^{13}\text{C}\{^1\text{H}\}$ and $^{11}\text{B}$ NMR Spectra of Monohydroboration of Cyanamides



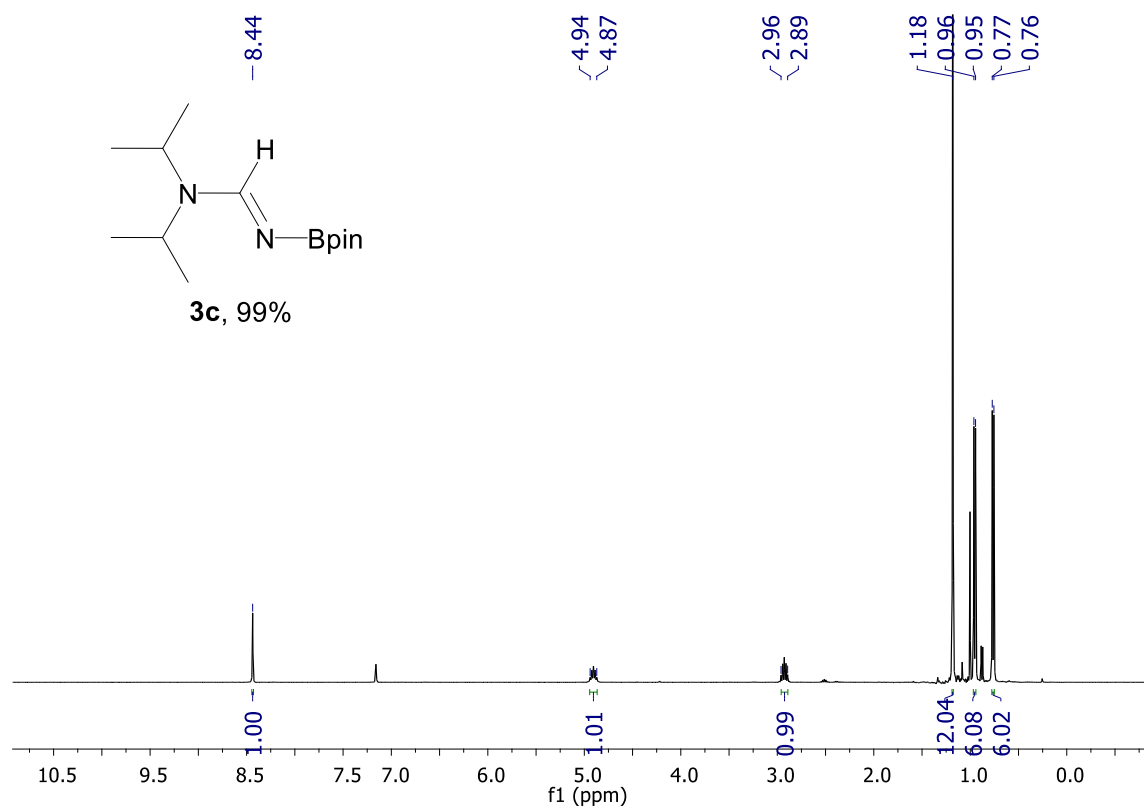
**Figure S29:**  $^1\text{H}$  NMR spectrum of **3b** (400 MHz,  $\text{C}_6\text{D}_6$ ).



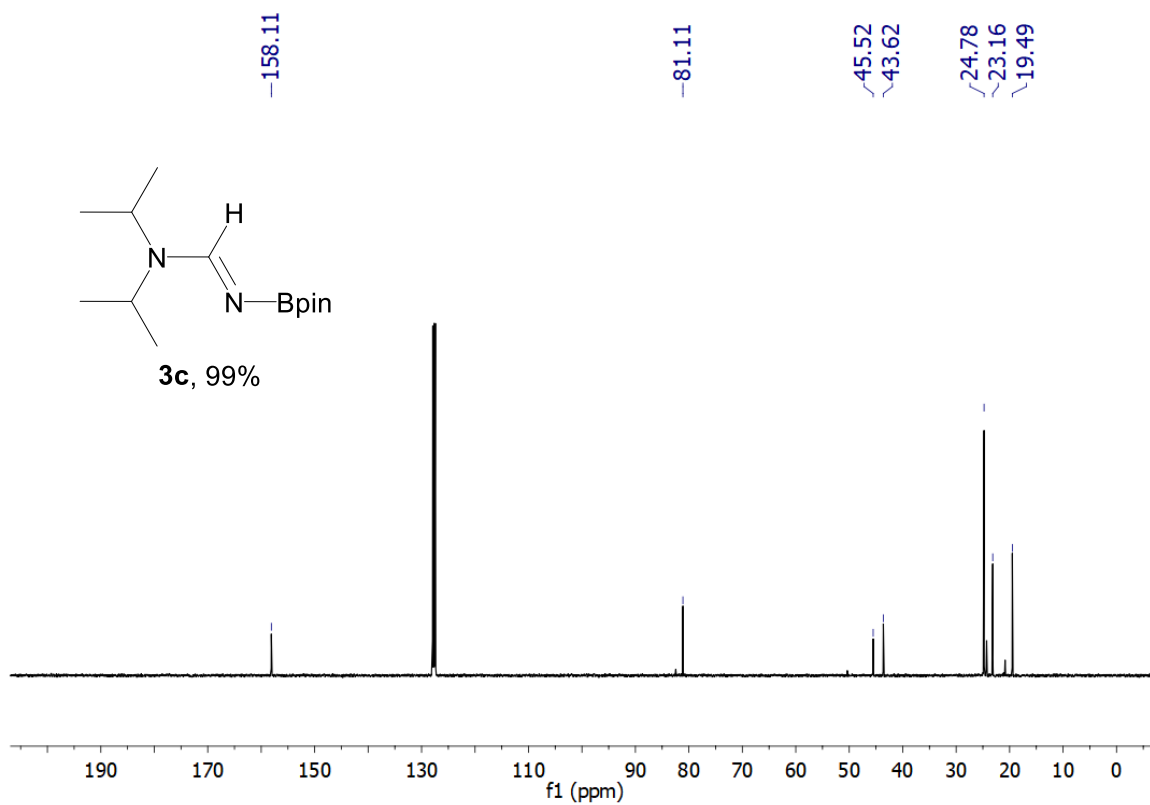
**Figure S30:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3b** (101 MHz,  $\text{C}_6\text{D}_6$ ).



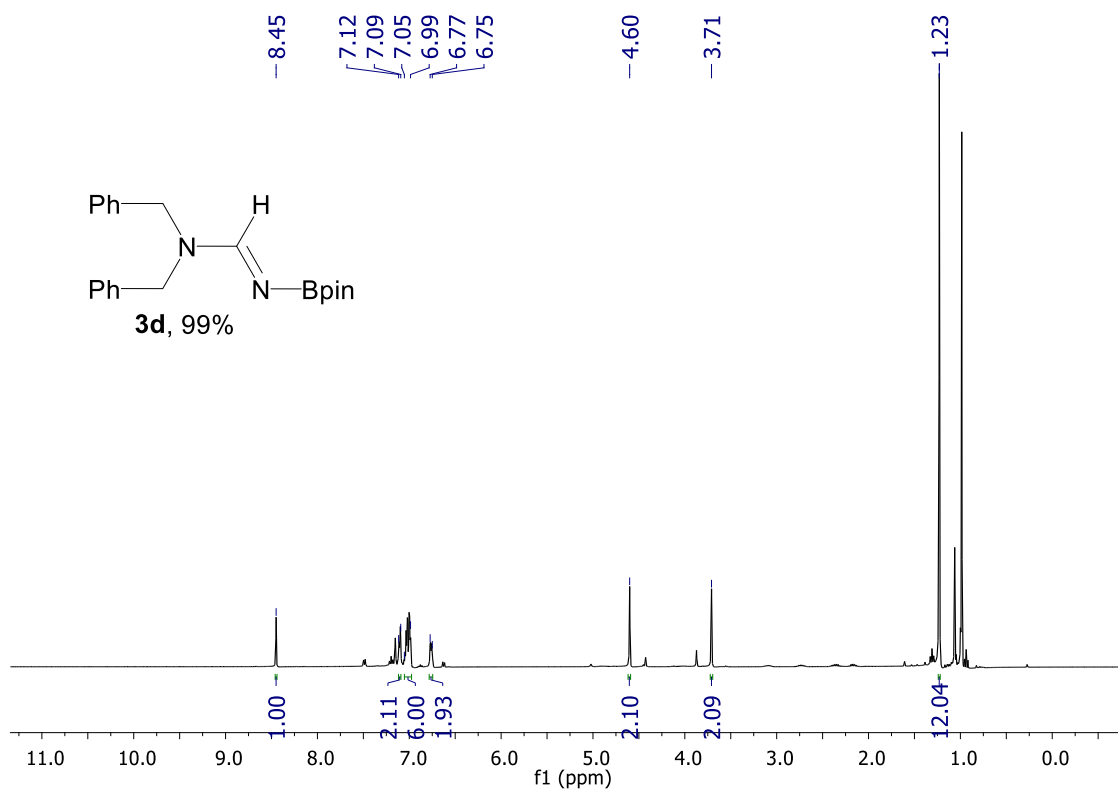
**Figure S31:**  $^{11}\text{B}$  NMR spectrum of **3b**. (128 MHz,  $\text{C}_6\text{D}_6$ ).



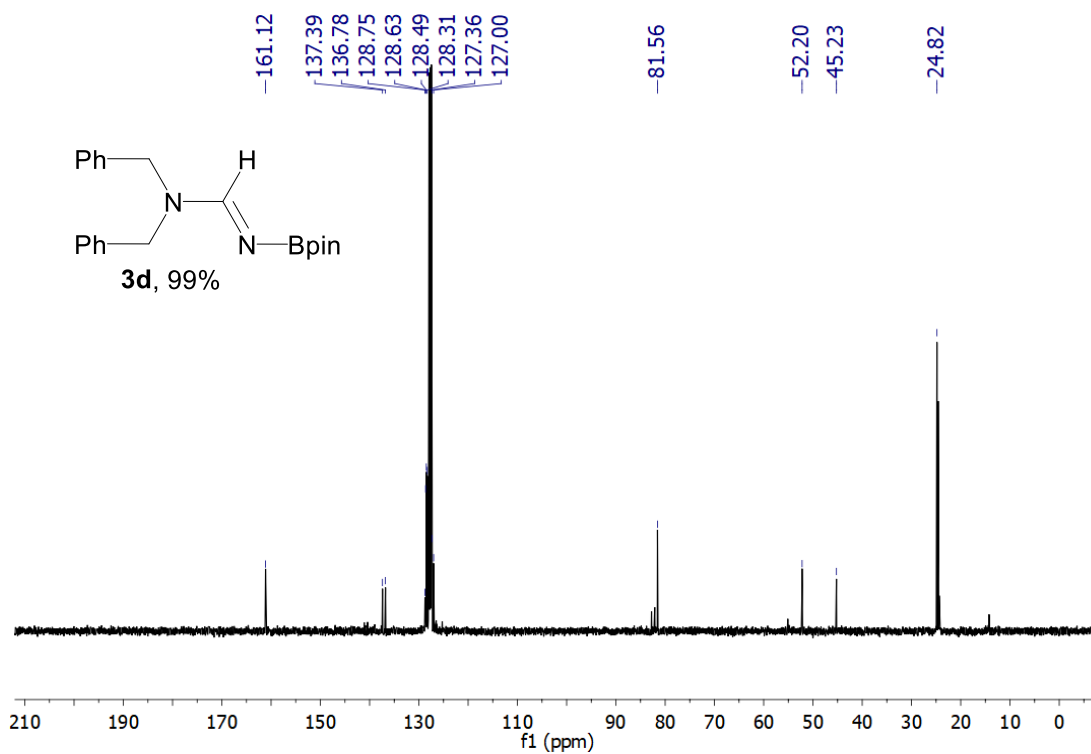
**Figure S32:**  $^1\text{H}$  NMR spectrum of **3c** (400 MHz,  $\text{C}_6\text{D}_6$ ).



**Figure S33:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3c** (101 MHz,  $\text{C}_6\text{D}_6$ ).

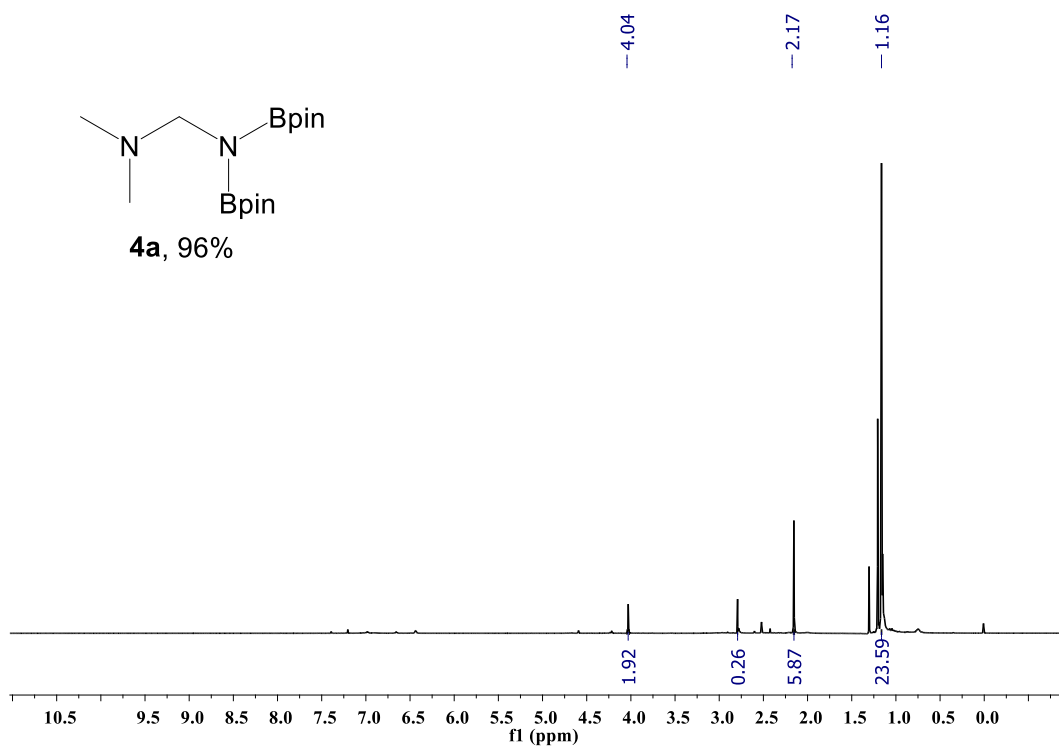


**Figure S34:**  $^1\text{H}$  NMR spectrum of **3d** (400 MHz,  $\text{C}_6\text{D}_6$ ).

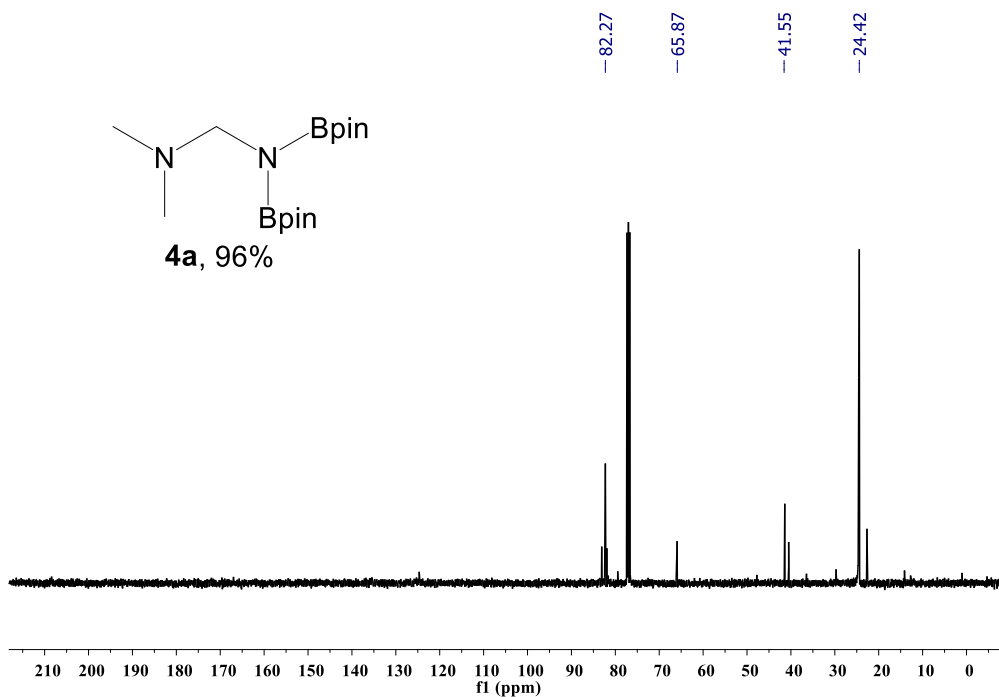


**Figure S35:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3d** (101 MHz,  $\text{C}_6\text{D}_6$ ).

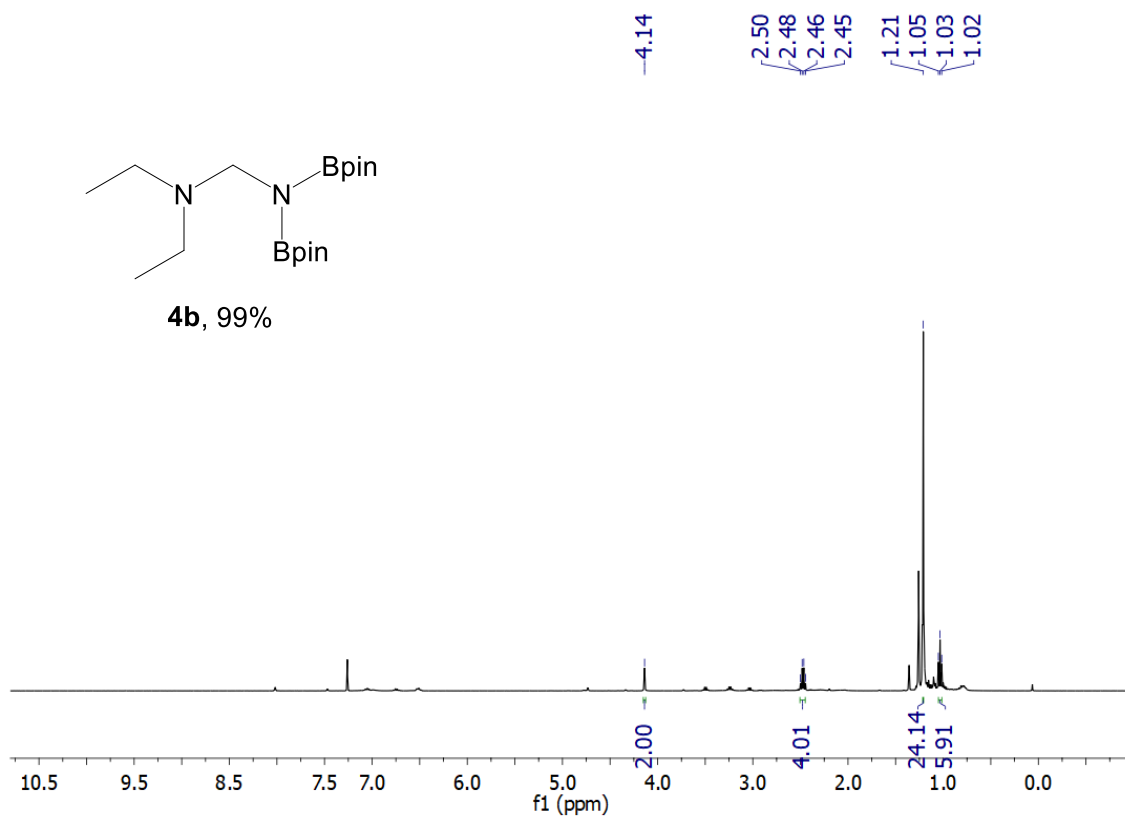
### $^1\text{H}$ , $^{13}\text{C}\{^1\text{H}\}$ and $^{11}\text{B}$ NMR Spectra of Dihydroboration of Cyanamides



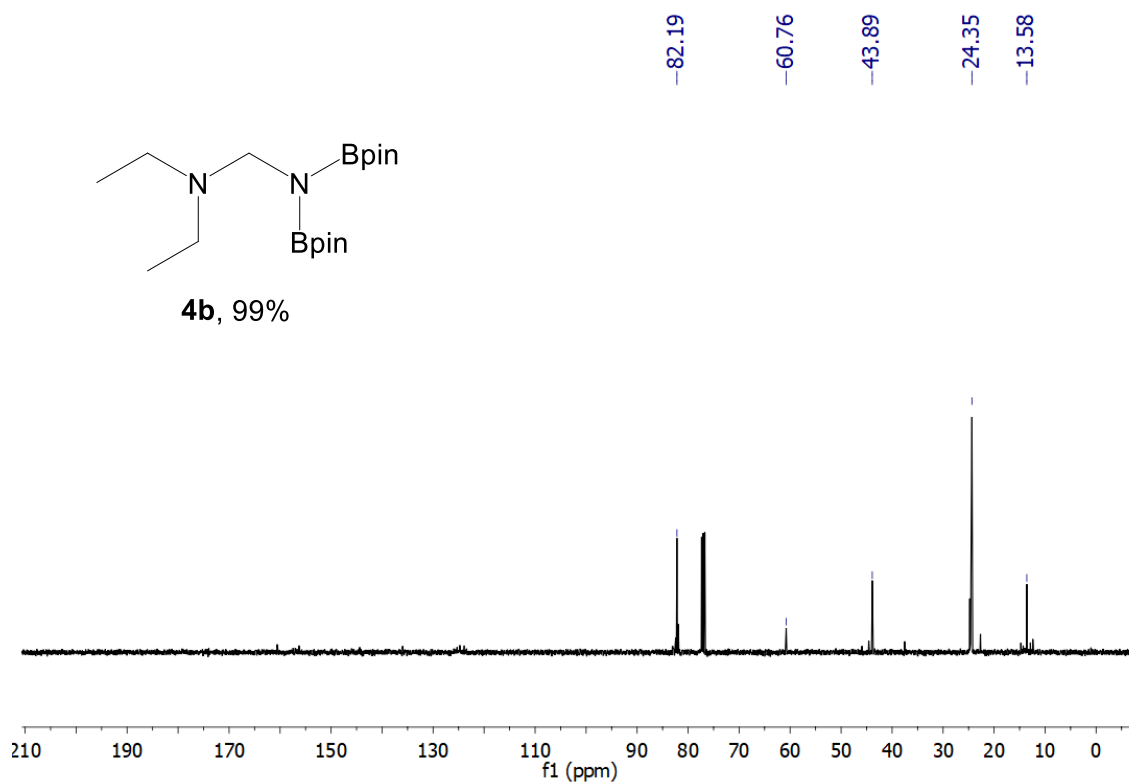
**Figure S36:**  $^1\text{H}$  NMR spectrum of **4a** (400 MHz,  $\text{CDCl}_3$ ).



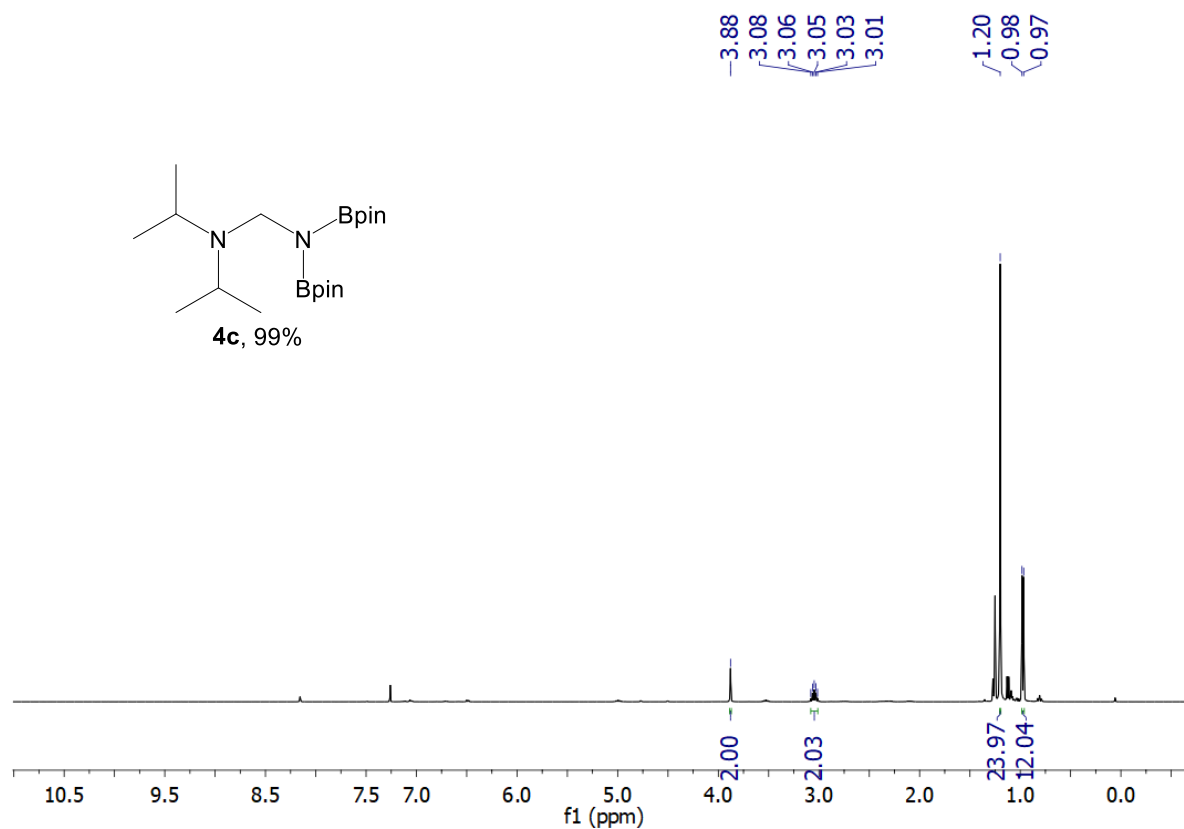
**Figure S37:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4a** (101 MHz,  $\text{CDCl}_3$ ).



**Figure S38:**  $^1\text{H}$  NMR spectrum of **4b** (400 MHz,  $\text{CDCl}_3$ ).



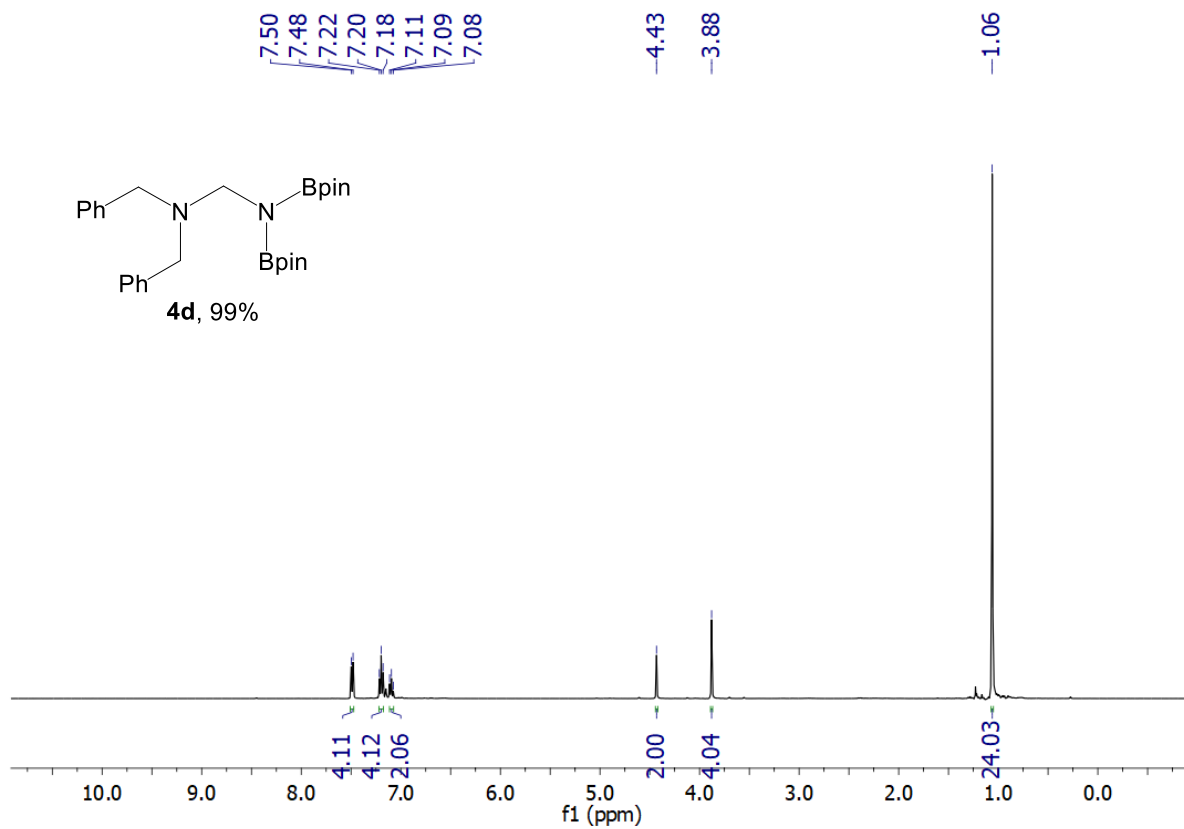
**Figure S39:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4b** (101 MHz,  $\text{CDCl}_3$ ).



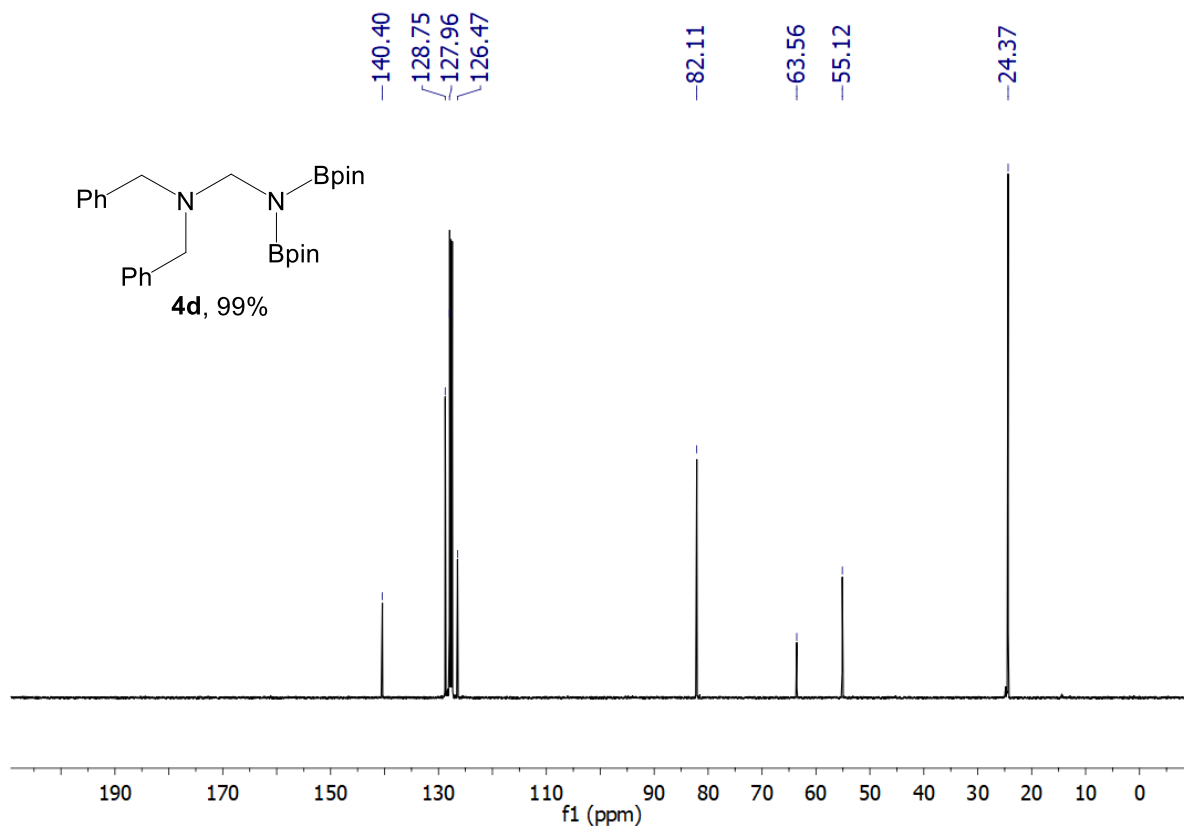
**Figure S40:**  $^1\text{H}$  NMR spectrum of **4c** (400 MHz,  $\text{CDCl}_3$ ).



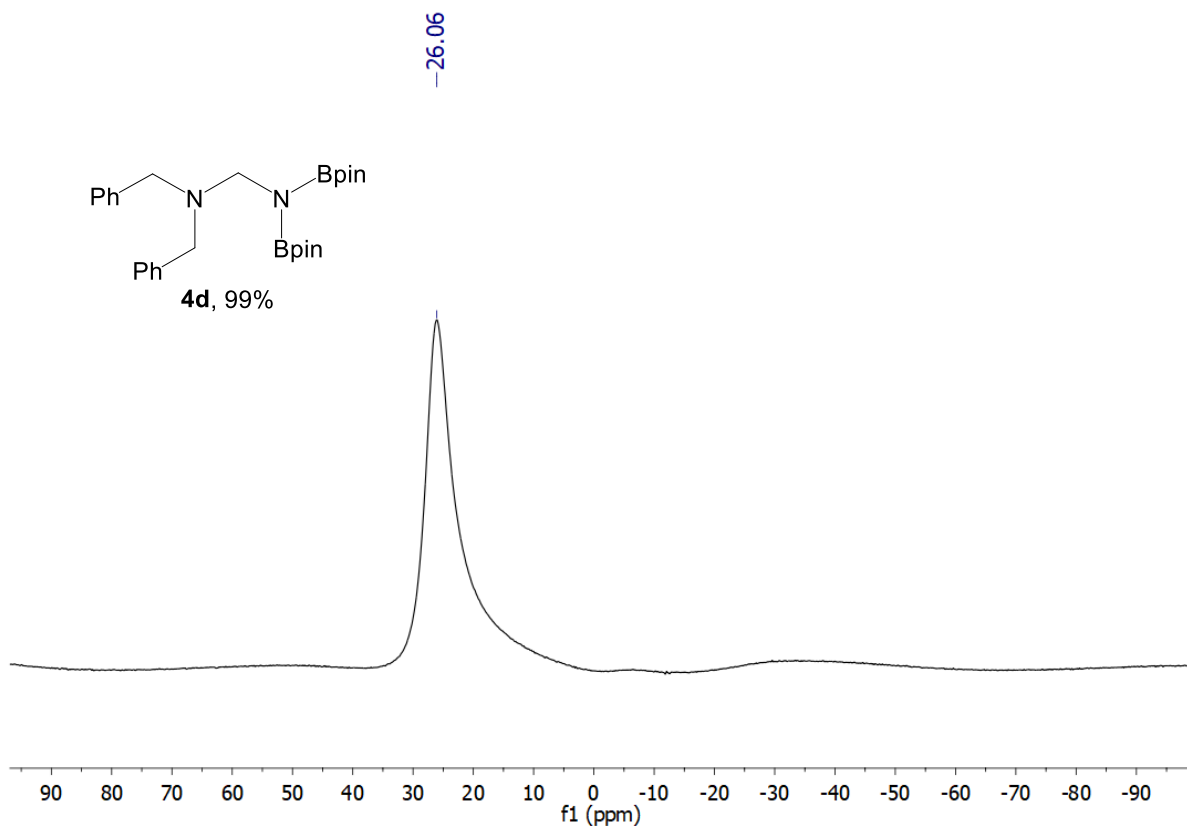




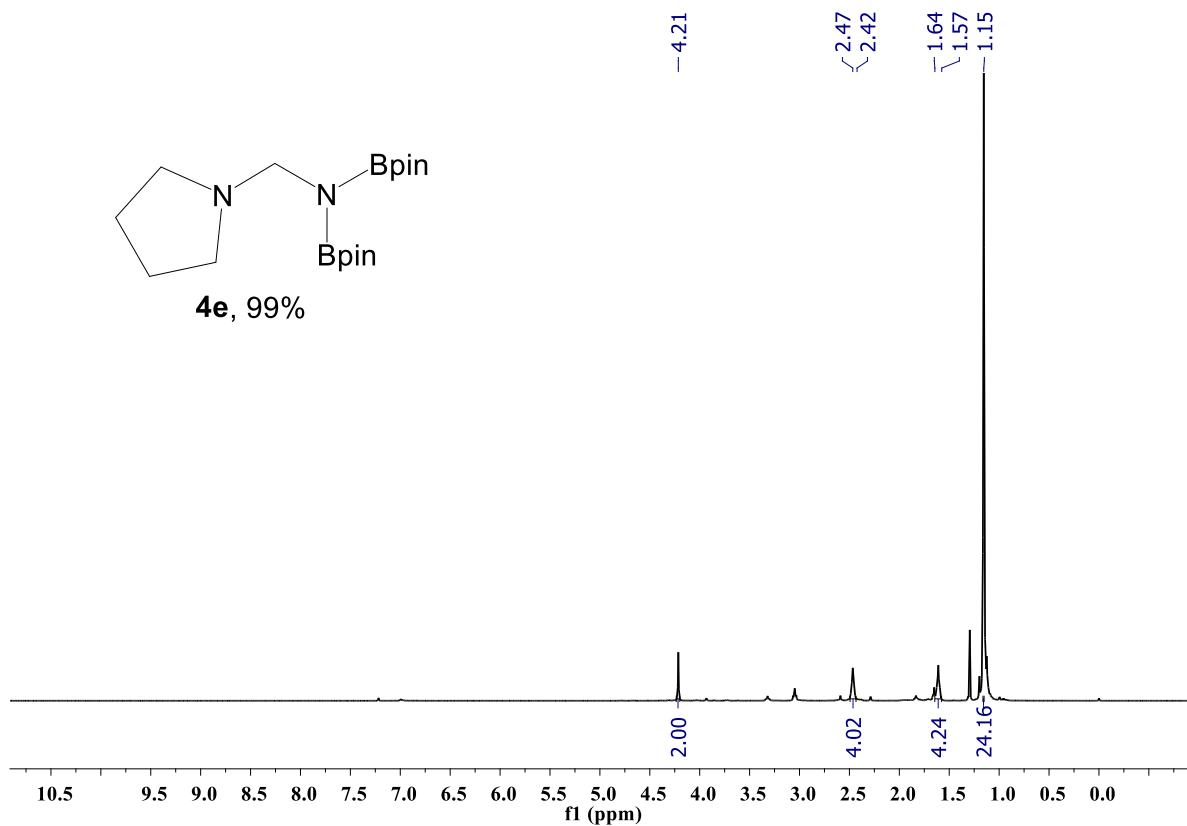
**Figure S43:** <sup>1</sup>H NMR spectrum of **4d** (400 MHz, C<sub>6</sub>D<sub>6</sub>).



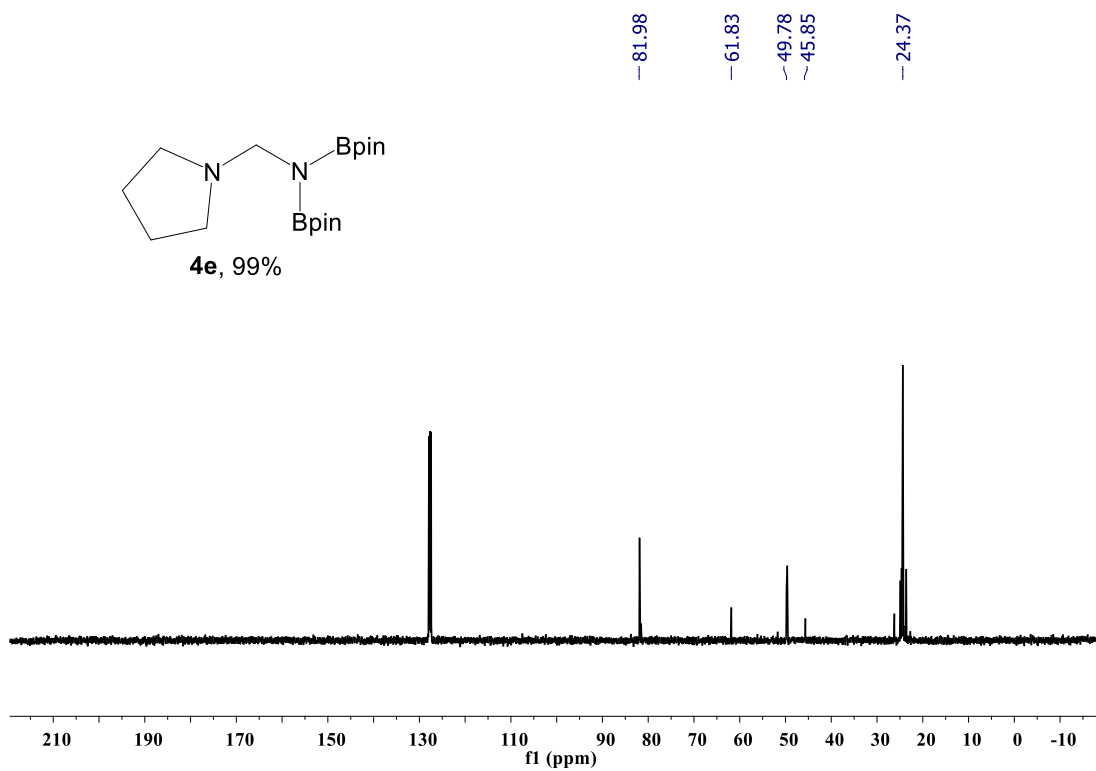
**Figure S44:** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4d** (101 MHz, C<sub>6</sub>D<sub>6</sub>).



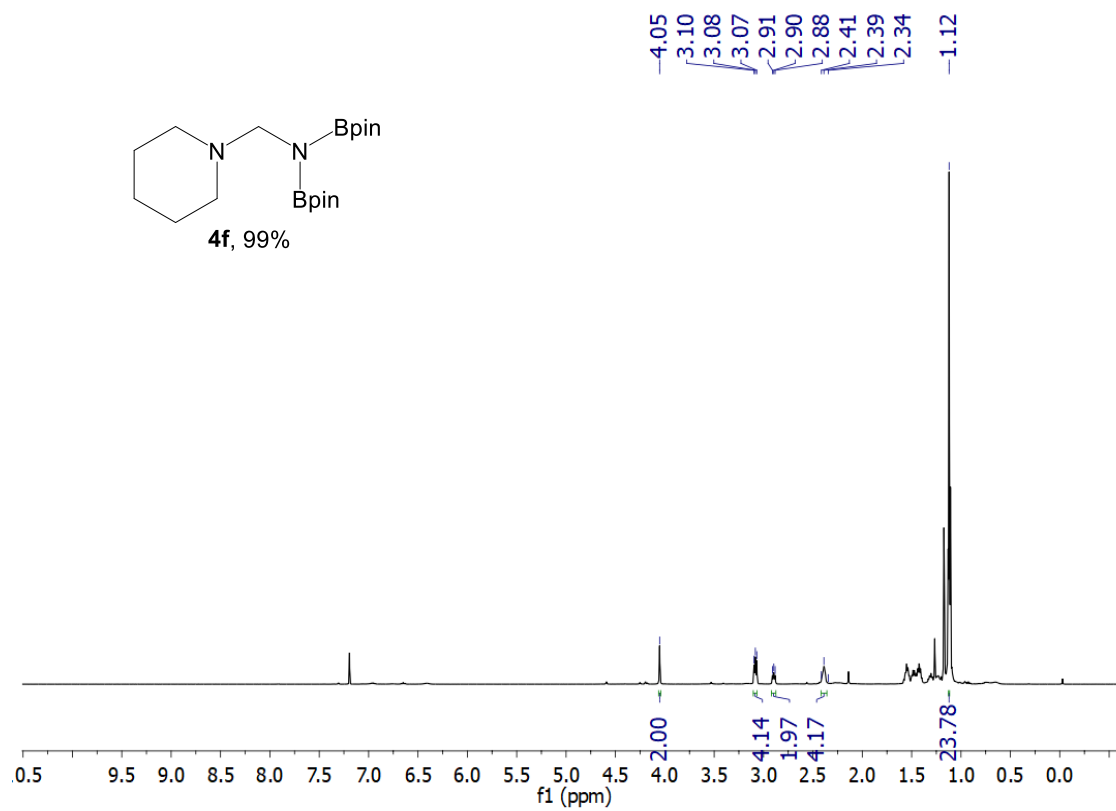
**Figure S45:**  $^{11}\text{B}$  NMR spectrum of **4d** (128 MHz,  $\text{C}_6\text{D}_6$ ).



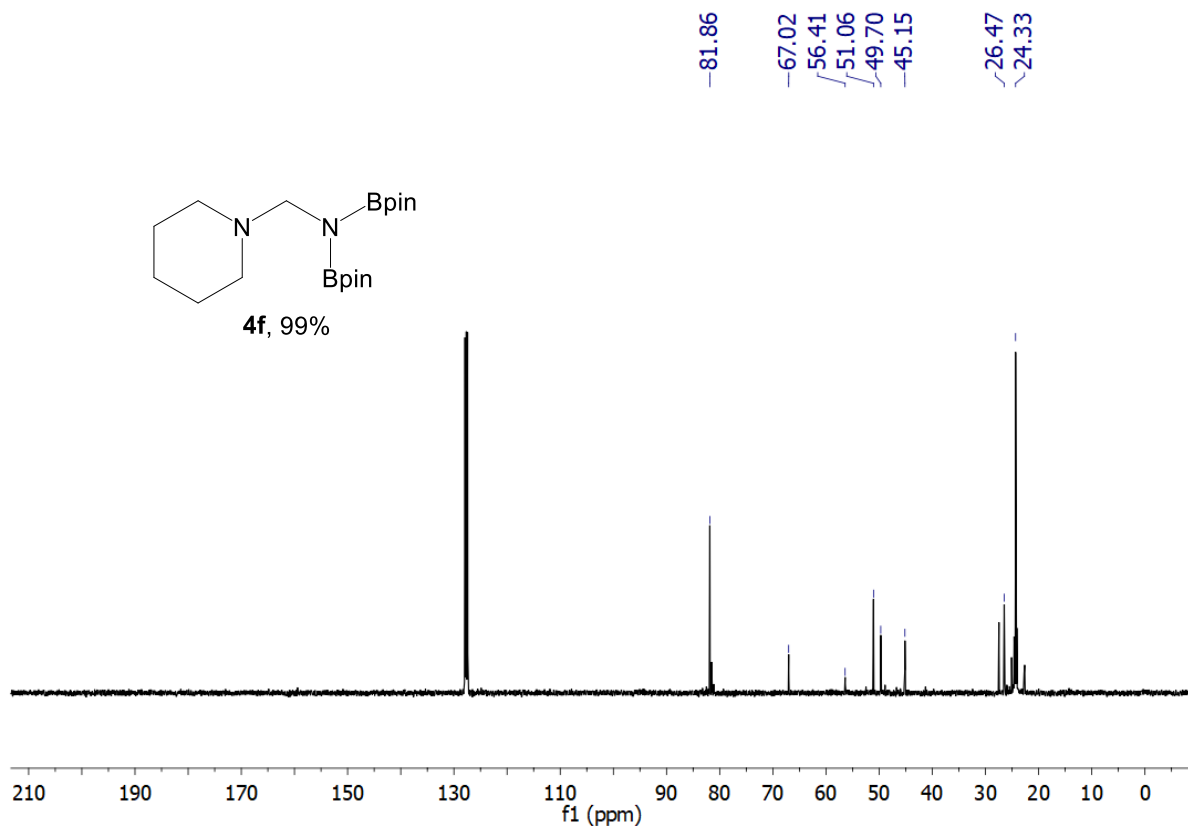
**Figure S46:**  $^1\text{H}$  NMR spectrum of **4e** (400 MHz,  $\text{C}_6\text{D}_6$ ).



**Figure S47:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4e** (101 MHz,  $\text{C}_6\text{D}_6$ ).

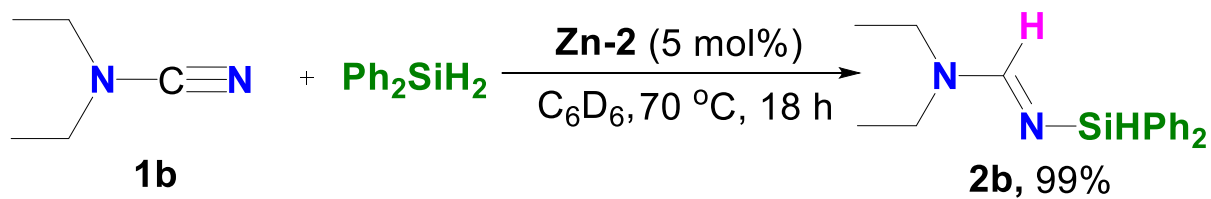


**Figure S48:**  $^1\text{H}$  NMR spectrum of **4f** (400 MHz,  $\text{C}_6\text{D}_6$ ).

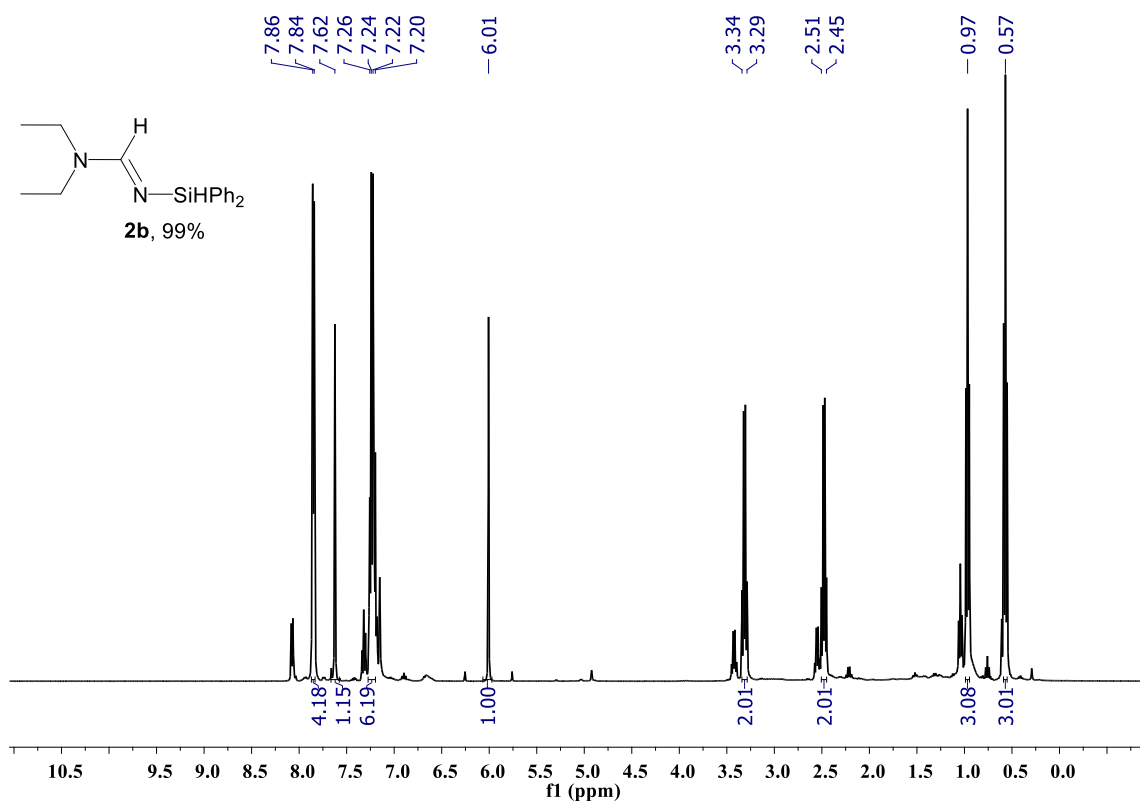


**Figure S49:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4f** (101 MHz,  $\text{C}_6\text{D}_6$ ).

**Scheme S1: Zn-2 catalyzed partial hydrosilylation of diethyl cyanamide<sup>a</sup>**



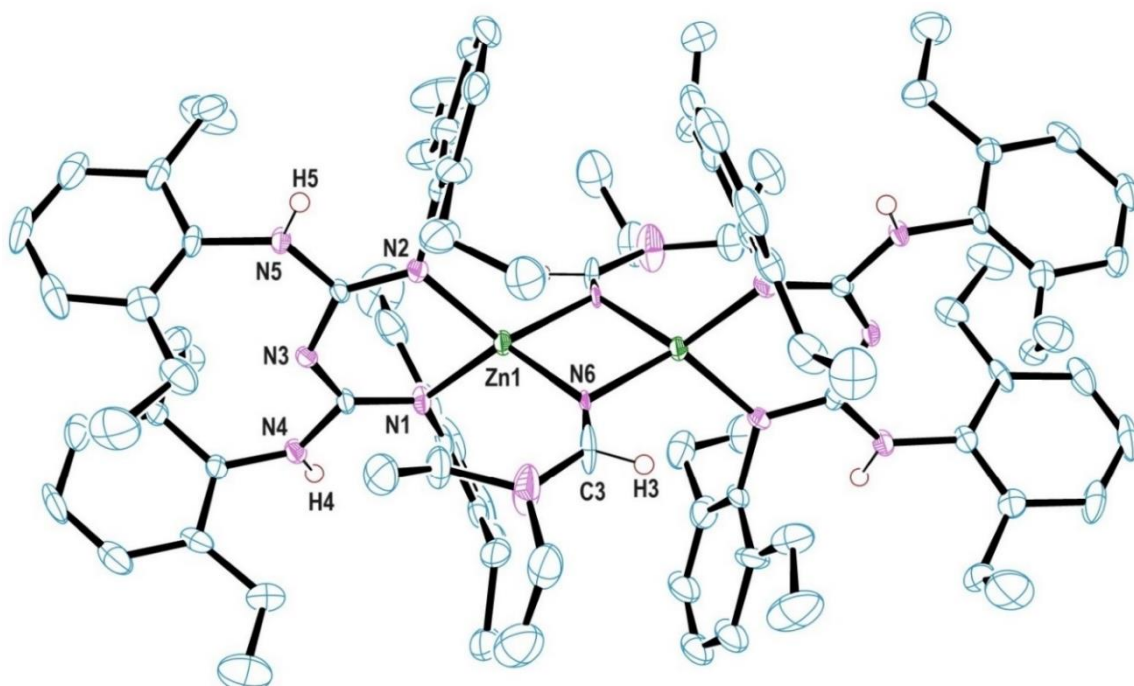
<sup>a</sup>Reactions were performed with diethyl cyanamide (0.2 mmol, 1.0 equiv),  $\text{Ph}_2\text{SiH}_2$  (0.2 mmol, 0.8 equiv), and **Zn-2** (5.0 mol %) in a J.Y. valve NMR tube and heated at 70 °C for 18 h. Conversion of the corresponding N-silyl formamidine (**2b**) was investigated by <sup>1</sup>H NMR spectroscopy based on the formation of characteristic new proton resonance for the (–NCHN) moiety of product.



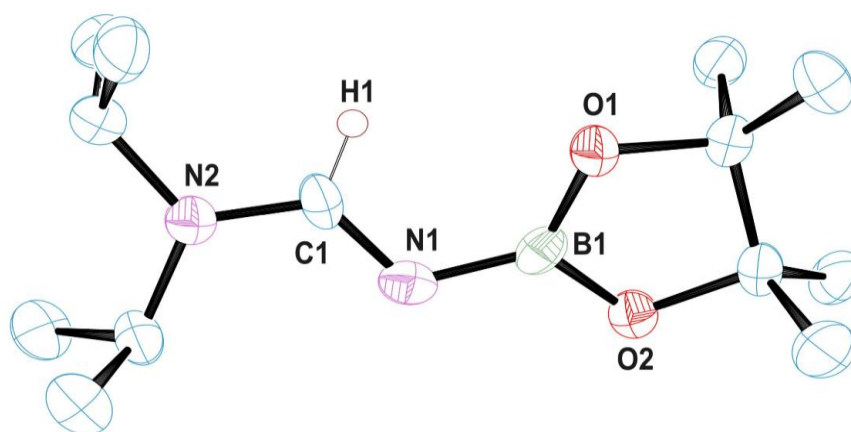
**Figure S50:** <sup>1</sup>H NMR spectrum of **2b** (400 MHz,  $\text{C}_6\text{D}_6$ ).

## X-ray Crystallographic Data of Compounds **Zn-2** and **3c**.

The single crystals of compounds **Zn-2** and **3c** were crystallized from benzene at rt as colorless blocks within 24-48 h. The crystal data of compounds **Zn-2** and **3c** are collected on a Rigaku Oxford diffractometer with graphite-monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) at 100 K. Selected data collection parameters and other crystallographic results are summarized in Table S4. The structure was determined using direct methods employed in *ShelXT*,<sup>2</sup> *OleX*,<sup>3</sup> and refinement was carried out using least-square minimization implemented in *ShelXL*.<sup>4</sup> 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 S51.** Molecular structure of **Zn-2**. The thermal ellipsoids are shown at 50% probability, and all the hydrogen atoms and ethyl groups (except H3 and those bound to nitrogen atoms) have been removed for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles (deg), For **Zn-2**: Zn1-N1 2.010(4), Zn1-N2 2.019(4), Zn1-N6 2.059(4), N1-C1 1.322(7), N2-C2 1.314(7), N6-C3 1.078(7), C3-N7 1.478(8), N1-Zn1-N2 91.83(17).



**Figure S52.** Molecular structure of compound **3c**. The thermal ellipsoids are shown at probability 50%, and H atoms were omitted for clarity (except H1). The selected bond lengths (Å) and bond angles (°): O1-B1 1.379 (3), O2-B1 1.379 (3), N1-B1 1.421 (3), N1-C1 1.319 (3), N2-C1 1.333 (3), C1-N1-B1 116.8 (2), N1-C1-N2 124.0 (2), O2-B1-O1 111.7 (2).

**Table S8.** Crystallographic Data and Refinement Parameters for Compounds **Zn-2** and **3c**.

Compound	Zn-2	3c
Empirical Formula	C <sub>100</sub> H <sub>136</sub> N <sub>14</sub> Zn <sub>2</sub>	C <sub>13</sub> H <sub>27</sub> BN <sub>2</sub> O <sub>2</sub>
CCDC	2357369	2357368
Molecular mass	1664.96	254.17
Temperature (K)	100	100
Wavelength (Å)	1.54184	1.54184
Size(mm)	0.2 × 0.18 × 0.17	0.2×0.18×0.17
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	12.7981(2)	6.11292(18)
<i>b</i> (Å)	26.9412(4)	19.9526(6)
<i>c</i> (Å)	13.2296(2)	12.9873(4)
$\alpha$ (deg) <sup>o</sup>	90	90
$\beta$ (deg) <sup>o</sup>	95.7890(10)	100.667(3)
$\gamma$ (deg) <sup>o</sup>	90	90
Volume (Å <sup>3</sup> )	4538.25(12)	1556.66(8)
<i>Z</i>	2	4
Calculated density (g/cm <sup>3</sup> )	1.218	1.085
Absorption coefficient (mm <sup>-1</sup> )	1.061	0.561
F(000)	1788.0	560.0
Theta range for data collection (deg) <sup>o</sup>	6.716 to 150.142	8.224 to 136.49
Limiting indices	15 ≤ <i>h</i> ≤ 15, -31 ≤ <i>k</i> ≤ 33, -16 ≤ <i>l</i> ≤ 16	--4 ≤ <i>h</i> ≤ 7, -23 ≤ <i>k</i> ≤ 23, -15 ≤ <i>l</i> ≤ 15
Reflections collected	35783	12996
Independent reflections	15258 [ <i>R</i> <sub>int</sub> = 0.0302, <i>R</i> <sub>sigma</sub> = 0.0327]	2840 [ <i>R</i> <sub>int</sub> = 0.0360, <i>R</i> <sub>sigma</sub> = 0.0232]
Completeness to theta	99 %	99 %
Absorption correction	Empirical	Empirical
Data/restraints/parameters	15258/6/1041	2840/0/175
Goodness – of–fit on <i>F</i> <sup>2</sup>	1.045	1.057
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0481, <i>wR</i> <sub>2</sub> = 0.1293	<i>R</i> <sub>1</sub> 0.0750, <i>wR</i> <sub>2</sub> = 0.1991



## HRMS of Newly synthesized Compounds 2a-2f, 3b-3d, 4a-4f and Zn-2.

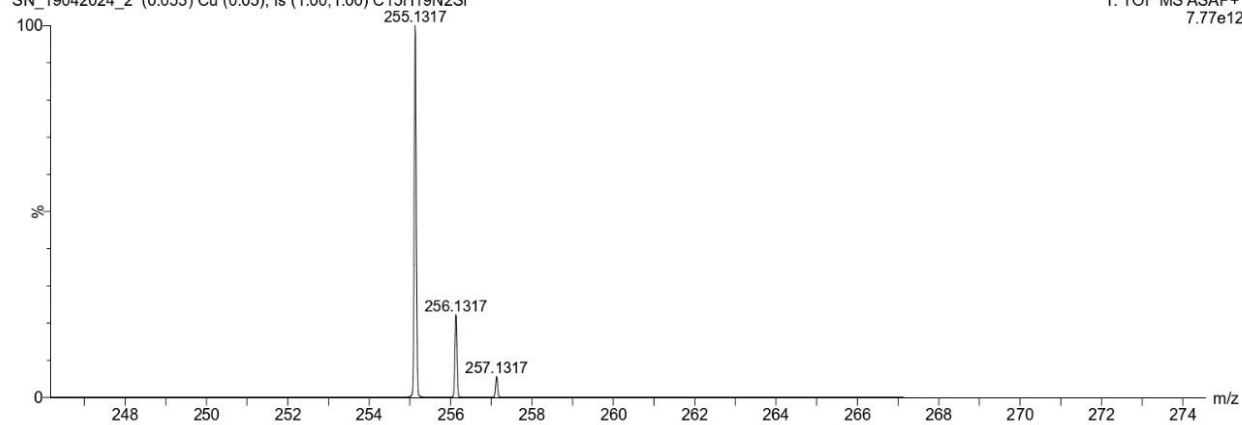
SN\_SR\_MHS\_6

19-Apr-2024  
12:09:18

SN\_19042024\_2 (0.053) Cu (0.05); Is (1.00,1.00) C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>Si

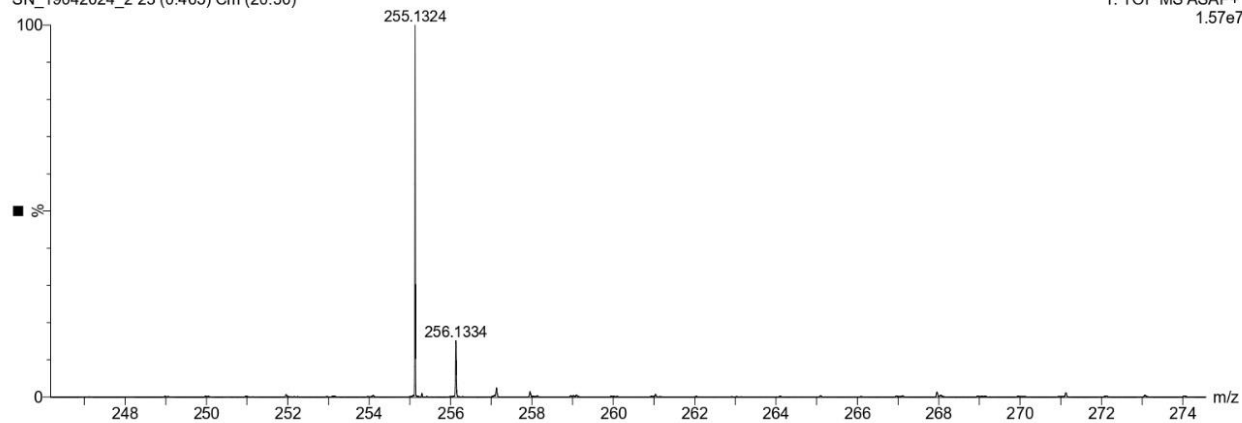
XEVO-G2XSQTOF#NotSet

1: TOF MS ASAP+  
7.77e12



SN\_19042024\_2 23 (0.465) Cm (20:30)

1: TOF MS ASAP+  
1.57e7



## HRMS of compound 2a.

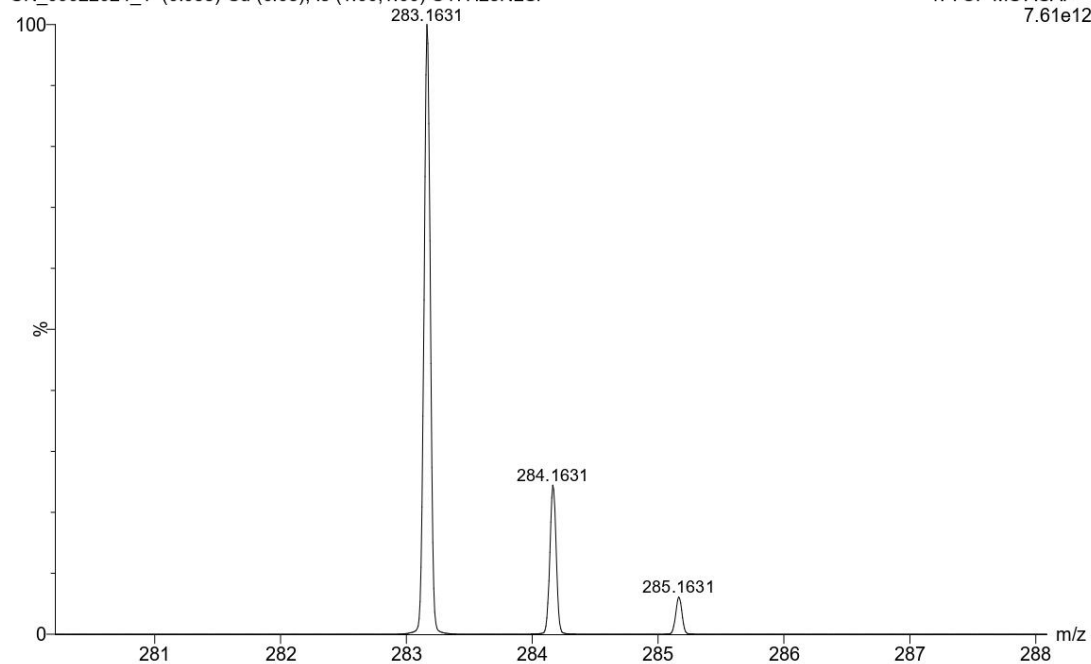
SN\_MHS\_1

09-Feb-2024  
16:39:51

XEVO-G2XSQTOF#NotSet

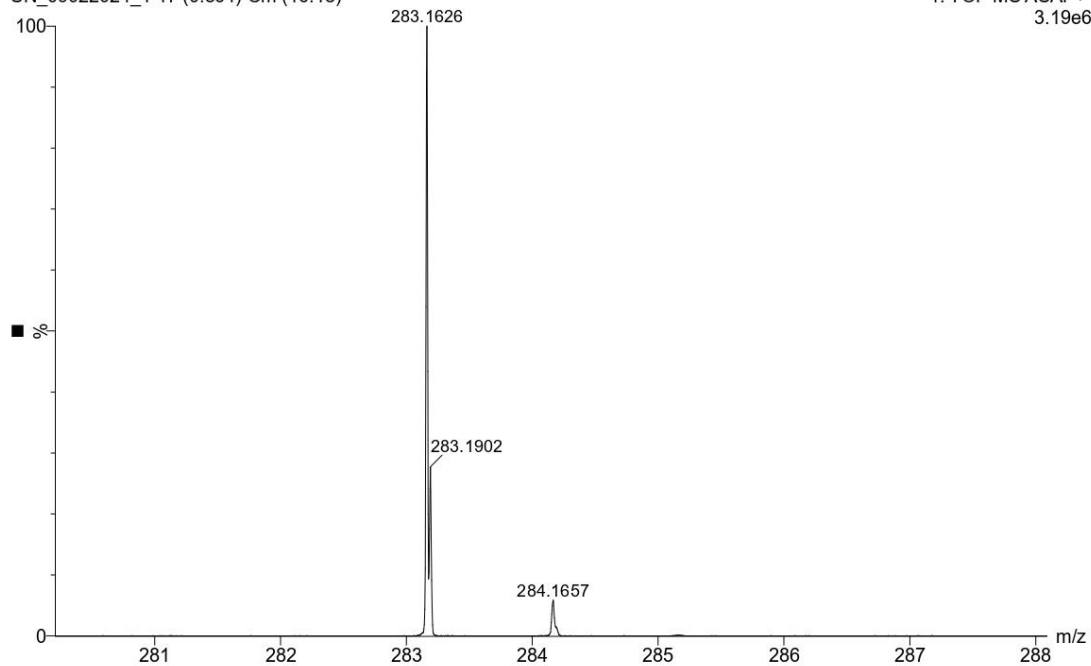
SN\_09022024\_1 (0.053) Cu (0.05); Is (1.00,1.00) C17H23N2Si

1: TOF MS ASAP+  
7.61e12



SN\_09022024\_1 17 (0.364) Cm (16:18)

1: TOF MS ASAP+  
3.19e6



HRMS of compound **2b**.

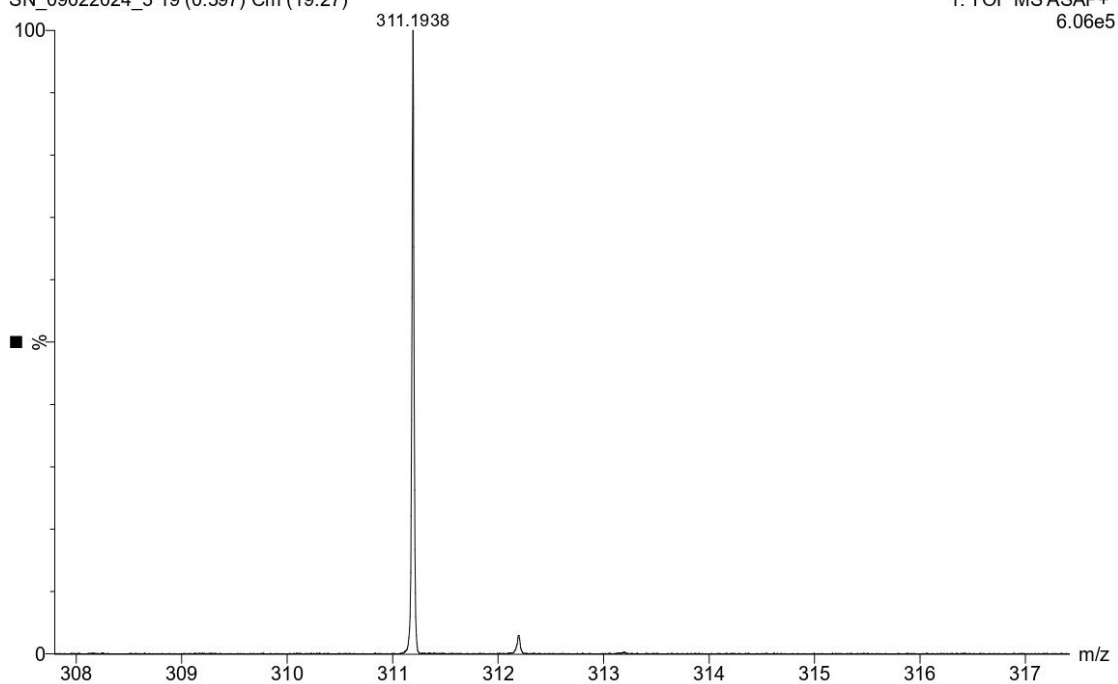
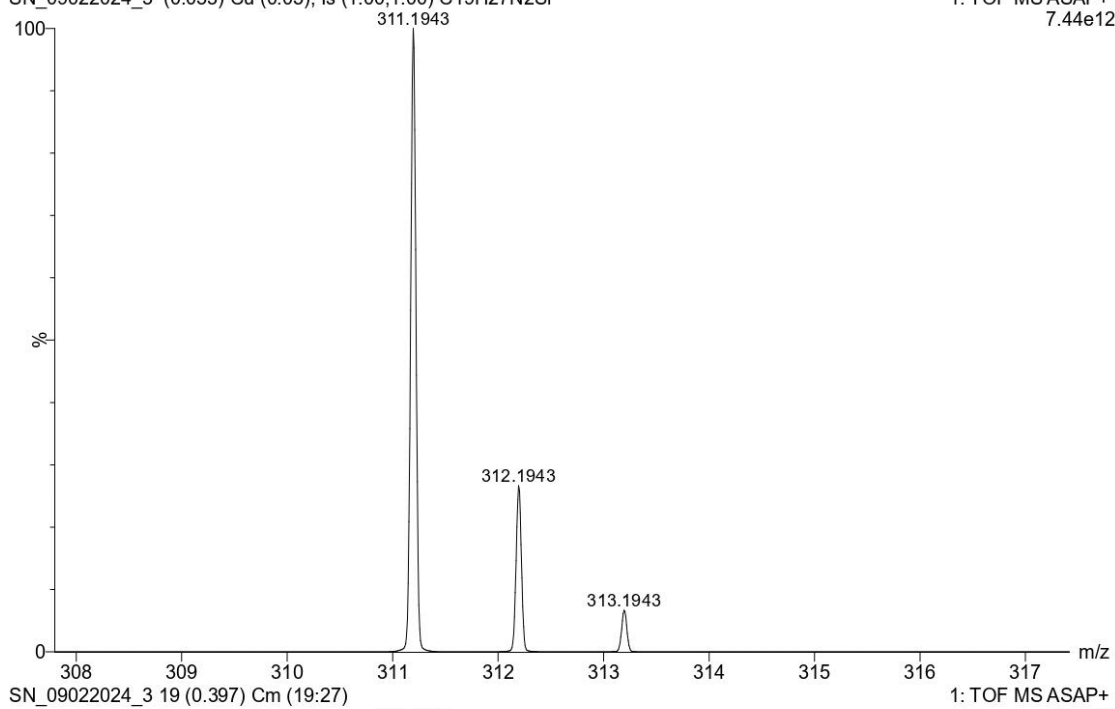
SN\_MHS\_2

09-Feb-2024  
16:49:28

XEVO-G2XSQTOF#NotSet

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1: TOF MS ASAP+  
7.44e12



HRMS of compound **2c**.

SN\_SR\_MHS\_3

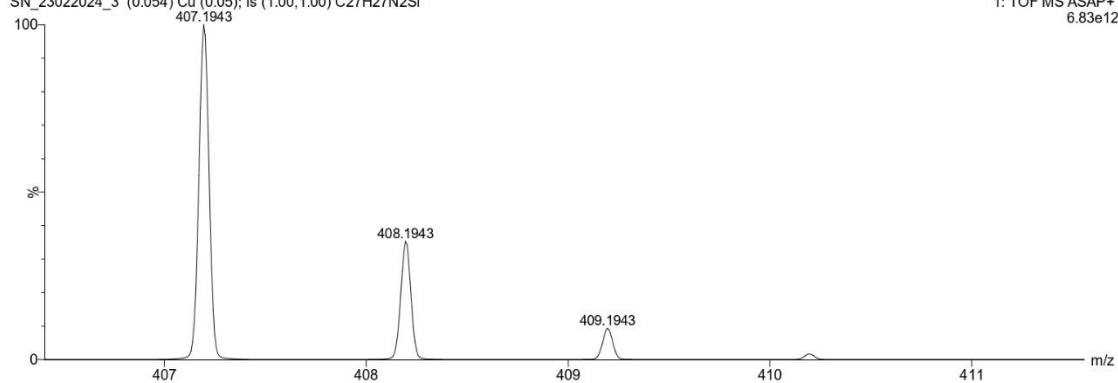
23-Feb-2024

14:43:17

XEVO-G2XSQTOF#NotSet

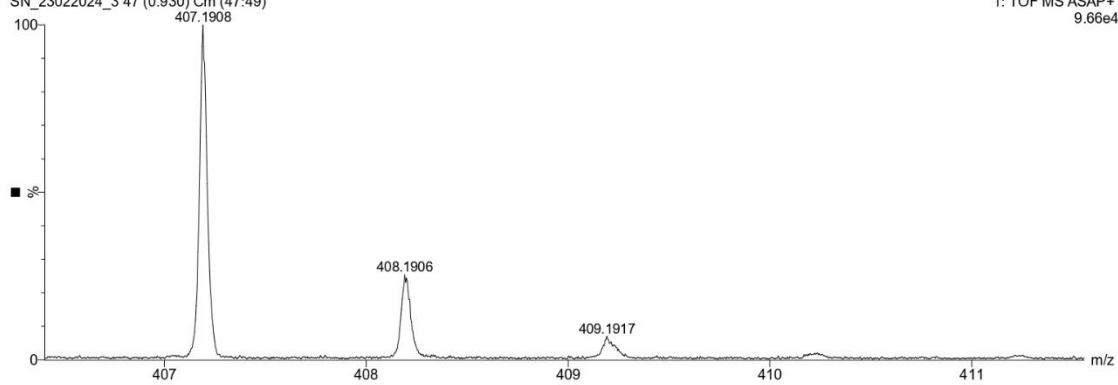
SN\_23022024\_3 (0.054) Cu (0.05); Is (1.00,1.00) C27H27N2Si

1: TOF MS ASAP+  
6.83e12



SN\_23022024\_3\_47 (0.930) Cm (47.49)

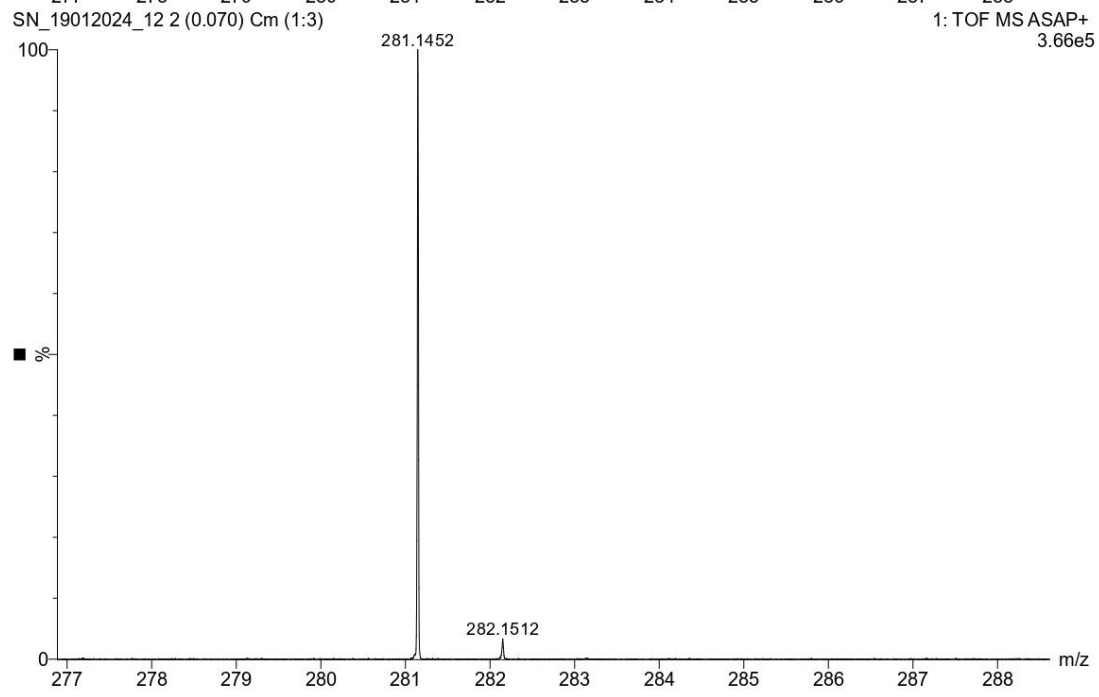
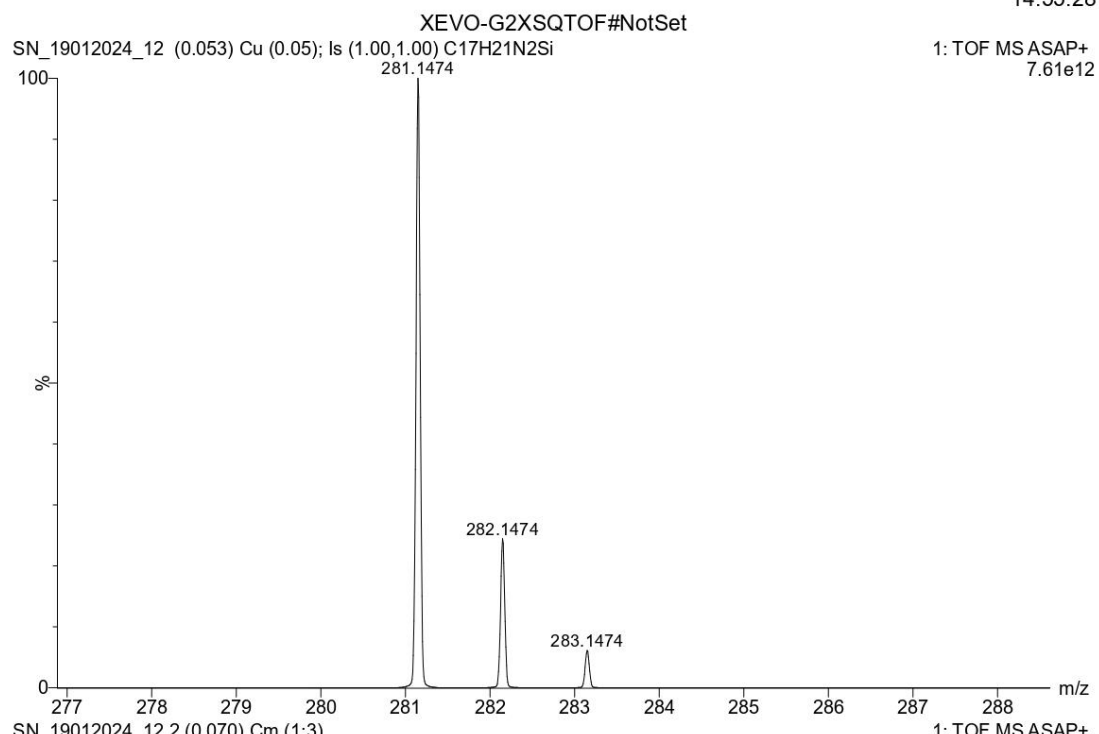
1: TOF MS ASAP+  
9.66e4



HRMS of compound **2d**.

SN\_SR\_MHS\_4\_R

19-Jan-2024  
14:55:28



HRMS of compound **2e**.

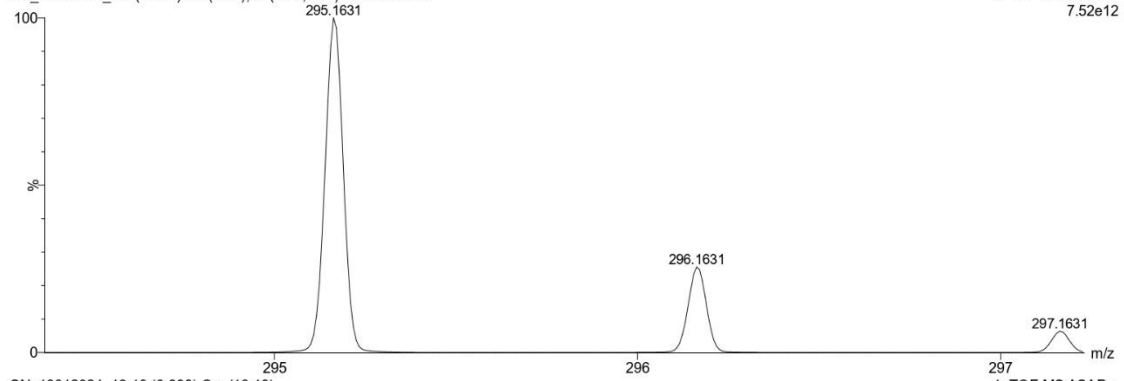
SN\_SR\_MHS\_5

19-Jan-2024  
14:59:00

XEVO-G2XSQTOF#NotSet

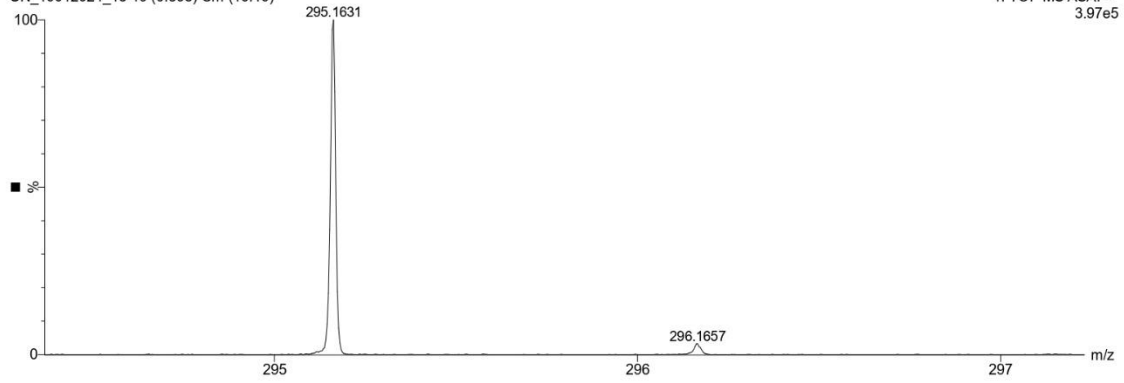
SN\_19012024\_13 (0.053) Cu (0.05); ls (1.00,1.00) C18H23N2Si

1: TOF MS ASAP+  
7.52e12



SN\_19012024\_13 19 (0.398) Cm (16:19)

1: TOF MS ASAP+  
3.97e5



HRMS of compound **2f**.

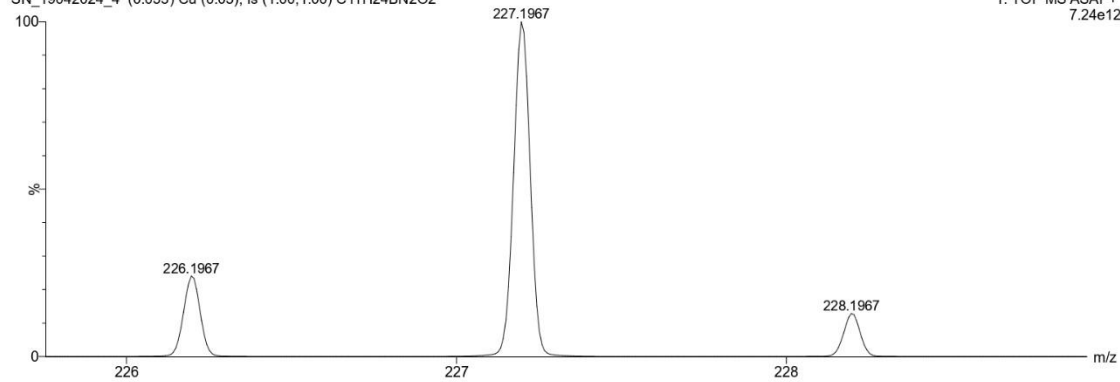
SN\_SR\_MHB\_1

19-Apr-2024  
12:14:04

SN\_19042024\_4 (0.053) Cu (0.05); Is (1.00,1.00) C<sub>11</sub>H<sub>24</sub>BN<sub>2</sub>O<sub>2</sub>

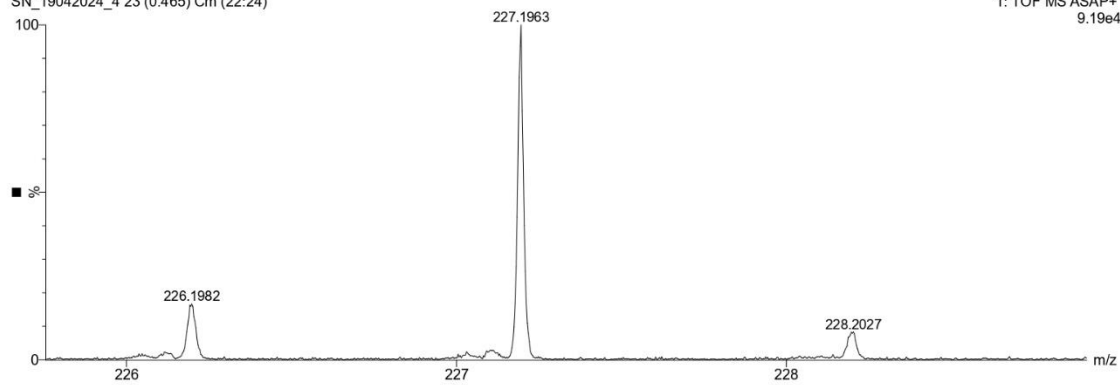
XEVO-G2XSQTOF#NotSet

1: TOF MS ASAP+  
7.24e12



SN\_19042024\_4 23 (0.465) Cm (22:24)

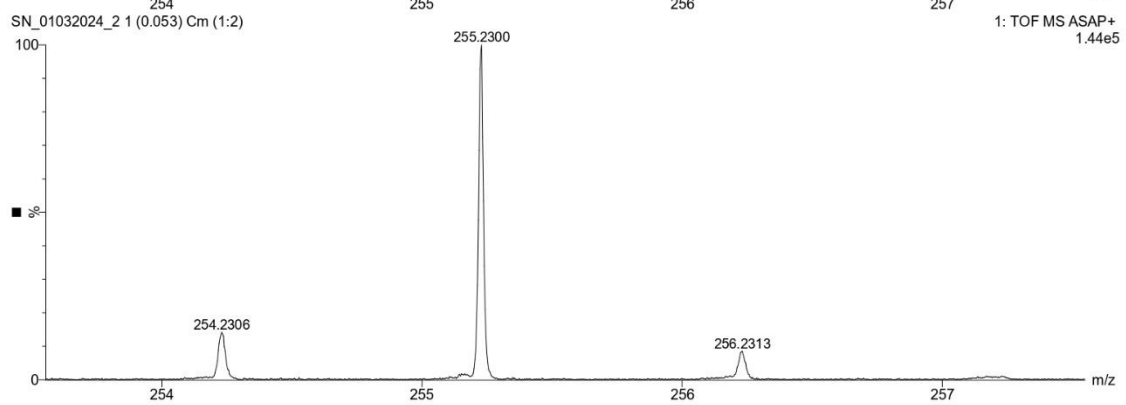
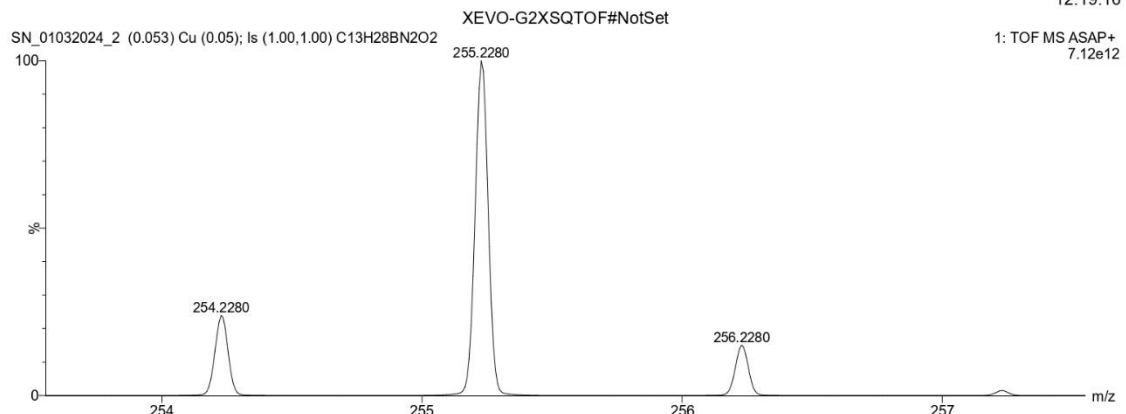
1: TOF MS ASAP+  
9.19e4



HRMS of compound **3b**.

SN\_SR\_MHB\_3

01-Mar-2024  
12:19:16

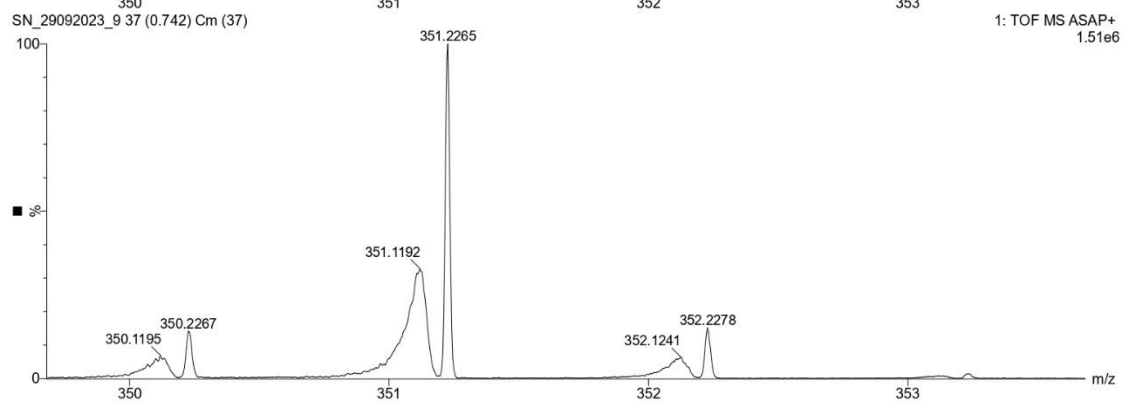
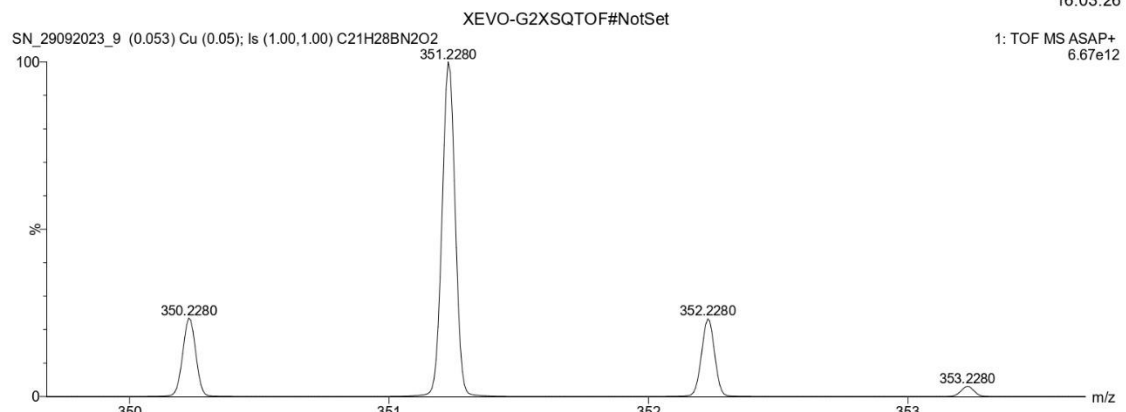


HRMS of compound **3c**.



SN\_RKS\_144

29-Sep-2023  
16:03:26



HRMS of compound **3d**.

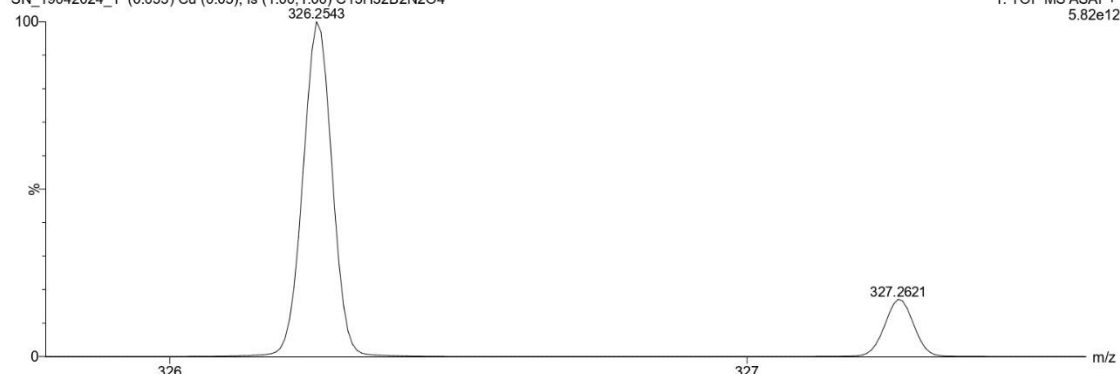
SN\_SR\_DHB\_6

19-Apr-2024  
12:04:38

XEVO-G2XSQTOF#NotSet

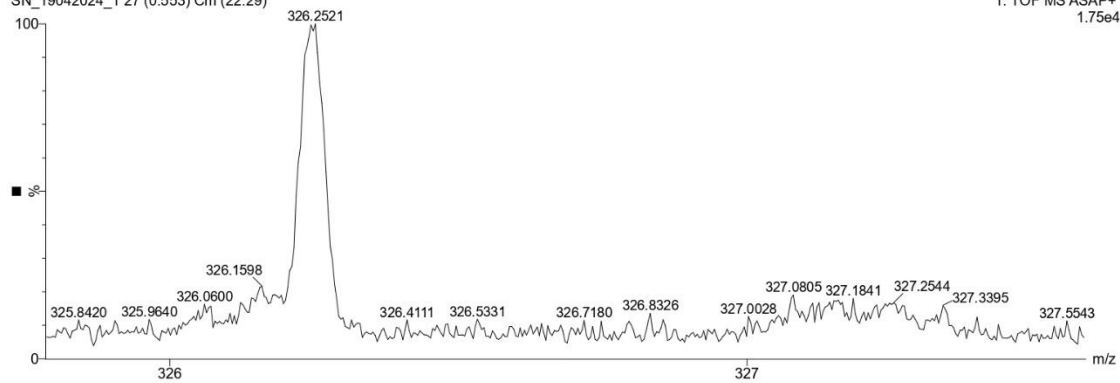
SN\_19042024\_1 (0.053) Cu (0.05); Is (1.00, 1.00) C15H32B2N2O4

1: TOF MS ASAP+  
5.82e12



SN\_19042024\_1 27 (0.553) Cm (22:29)

1: TOF MS ASAP+  
1.75e4



HRMS of compound **4a**.

SN\_SR\_DHB\_1

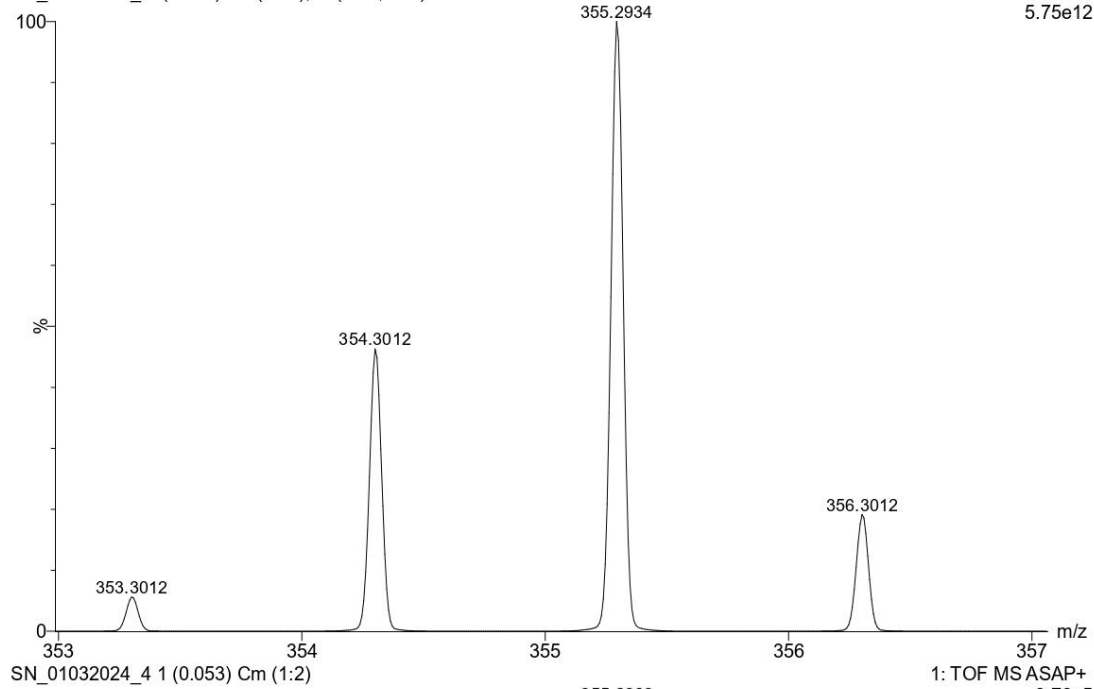
01-Mar-2024

12:26:20

XEVO-G2XSQTOF#NotSet

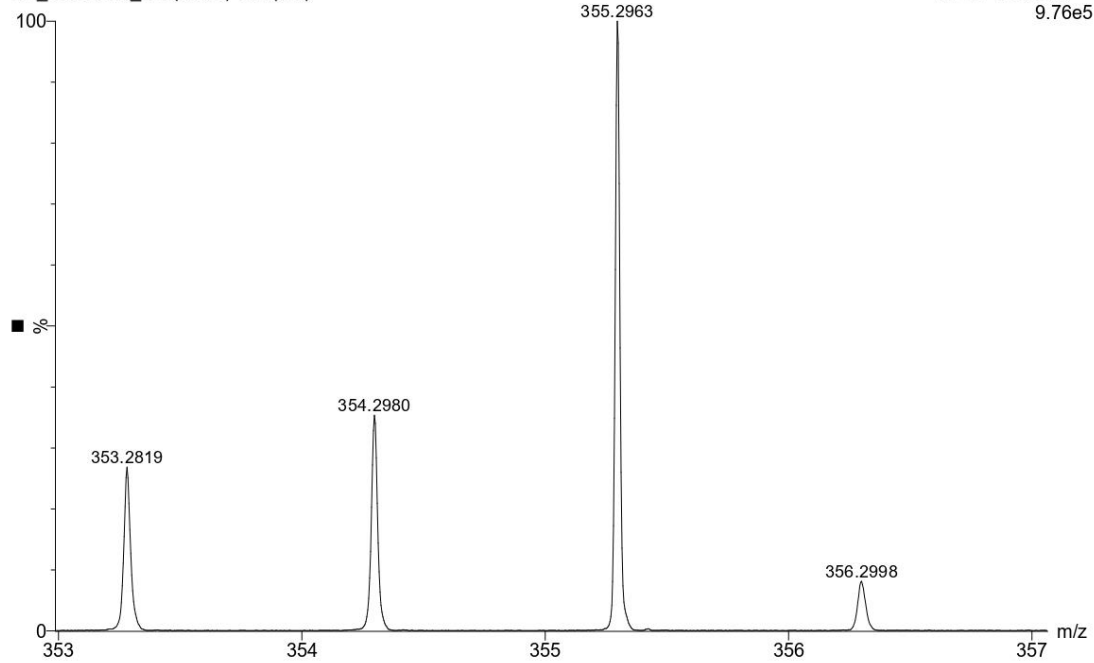
SN\_01032024\_4 (0.053) Cu (0.05); Is (1.00,1.00) C17H37B2N2O4

1: TOF MS ASAP+  
5.75e12



SN\_01032024\_4 1 (0.053) Cm (1:2)

1: TOF MS ASAP+  
9.76e5



HRMS of compound **4b**.

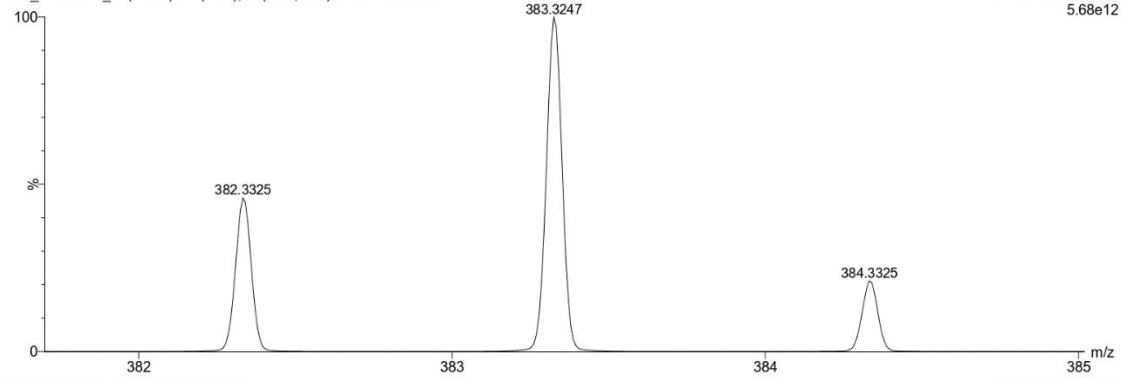
SN\_RKS\_126

29-Sep-2023  
15:58:53

XEVO-G2XSQTOF#NotSet

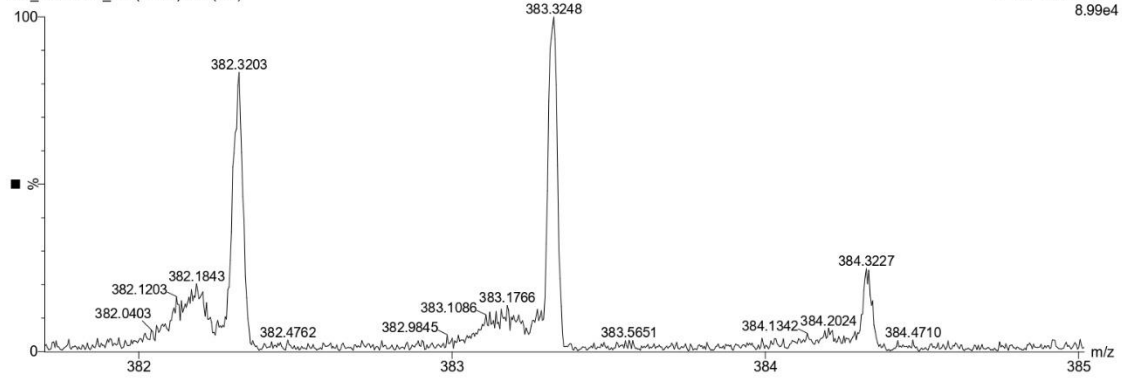
SN\_29092023\_8 (0.053) Cu (0.05); Is (1.00,1.00) C19H41B2N2O4

1: TOF MS ASAP+  
5.68e12



SN\_29092023\_8 2 (0.070) Cm (2:5)

1: TOF MS ASAP+  
8.99e4



HRMS of compound **4c**.

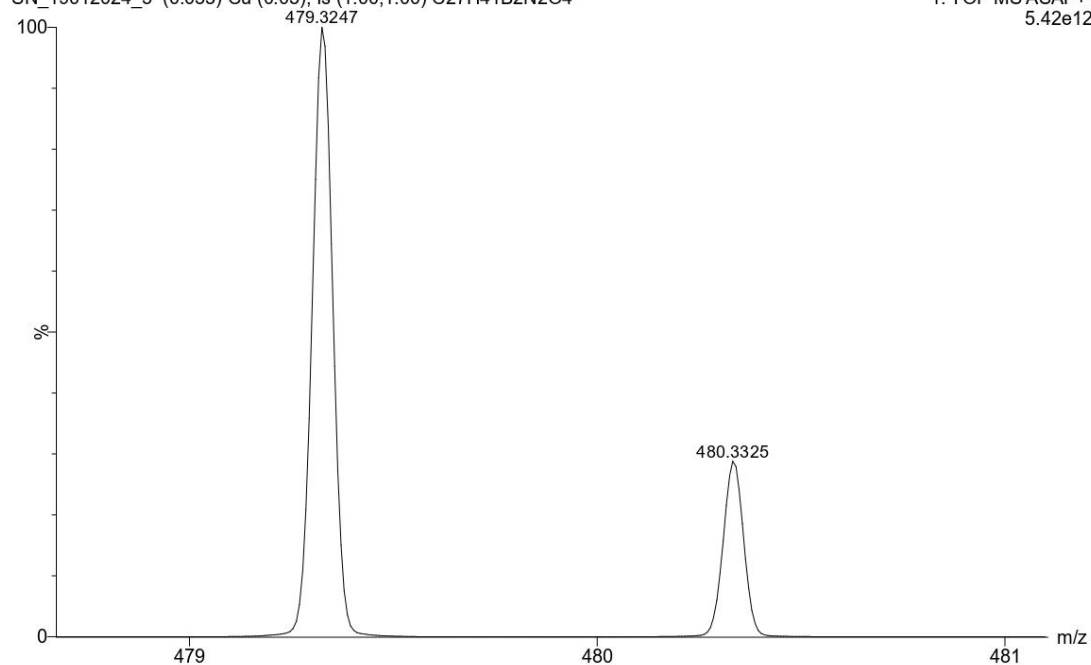
SN\_MHB\_3

19-Jan-2024  
12:23:51

XEVO-G2XSQTOF#NotSet

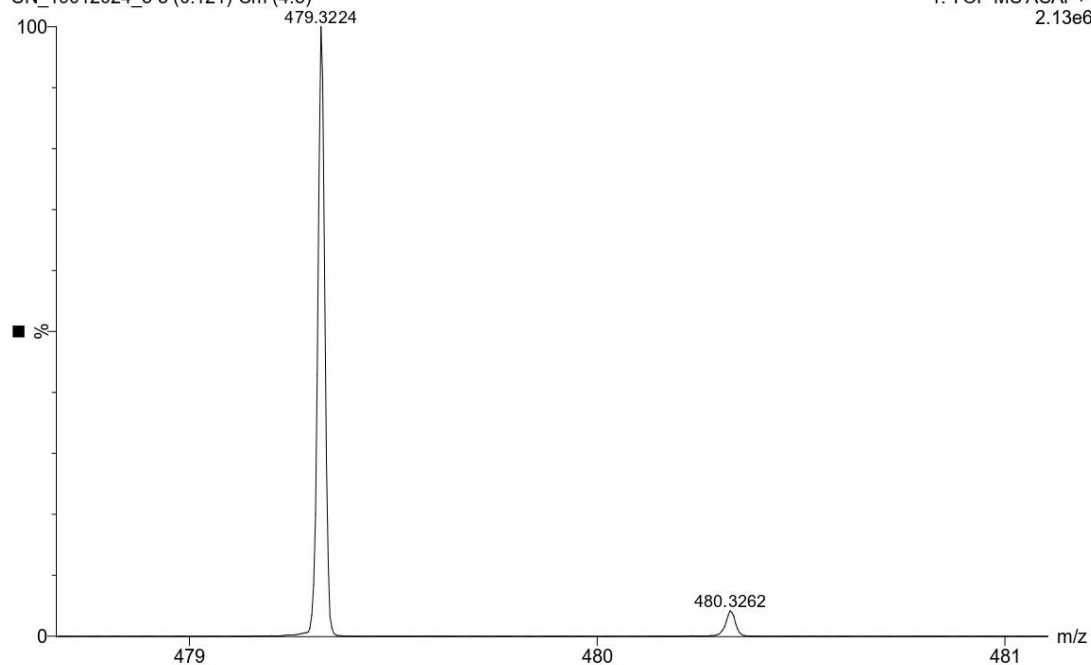
SN\_19012024\_5 (0.053) Cu (0.05); Is (1.00,1.00) C27H41B2N2O4

1: TOF MS ASAP+  
5.42e12



SN\_19012024\_5 5 (0.121) Cm (4:5)

1: TOF MS ASAP+  
2.13e6



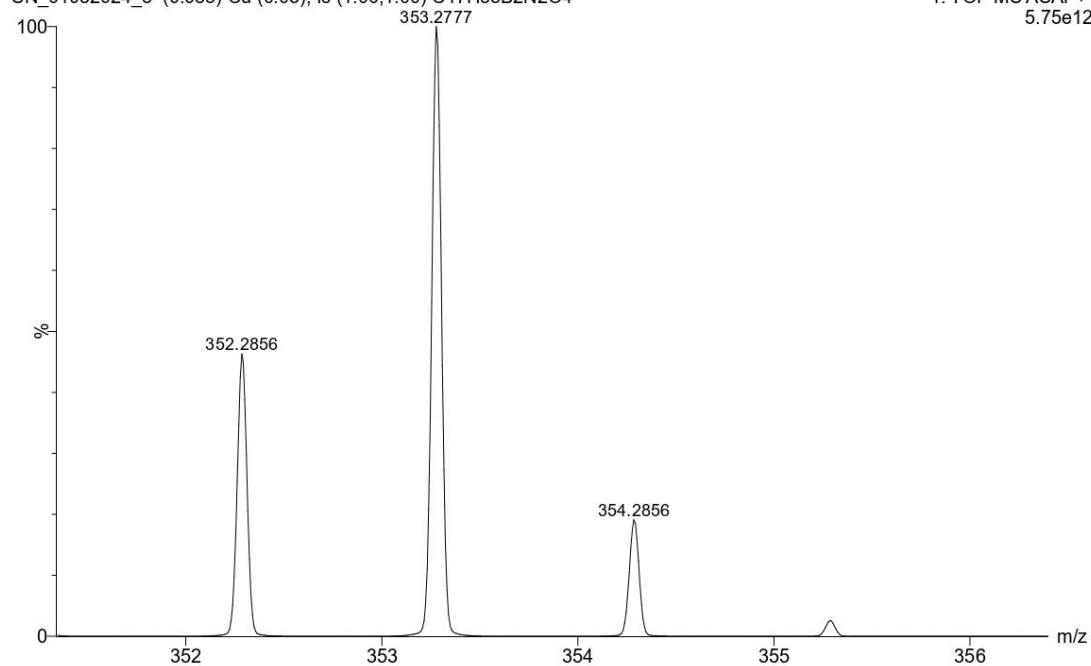
HRMS of compound **4d**.

SN\_SR\_DHB\_4

01-Mar-2024  
12:22:11

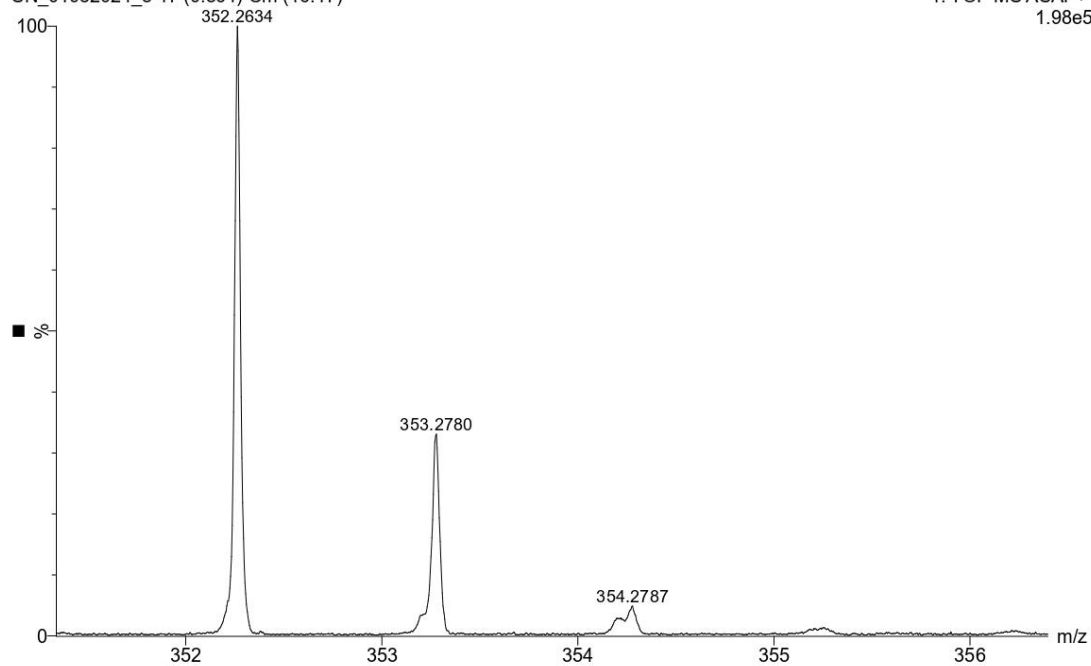
XEVO-G2XSQTOF#NotSet  
SN\_01032024\_3 (0.053) Cu (0.05); Is (1.00,1.00) C17H35B2N2O4

1: TOF MS ASAP+  
5.75e12



SN\_01032024\_3 17 (0.364) Cm (16:17)

1: TOF MS ASAP+  
1.98e5



HRMS of compound **4e**.

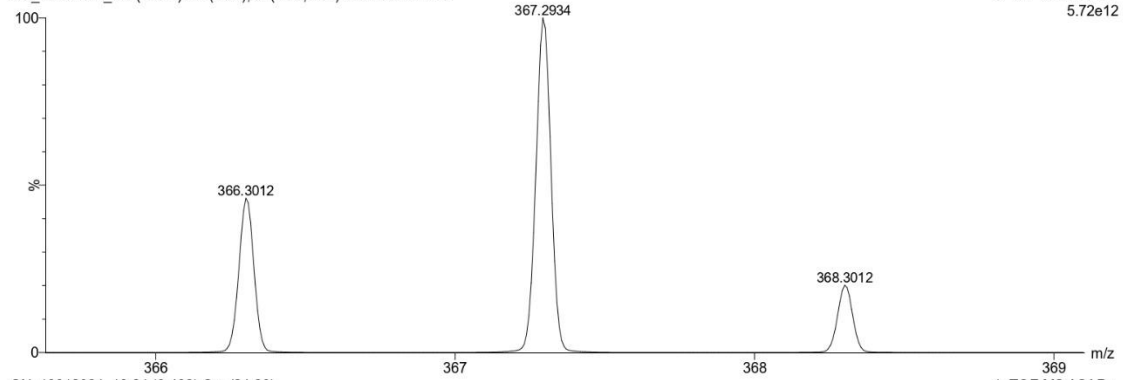
SN\_SR\_DHB\_5

19-Jan-2024  
15:17:13

XEVO-G2XSQTOF#NotSet

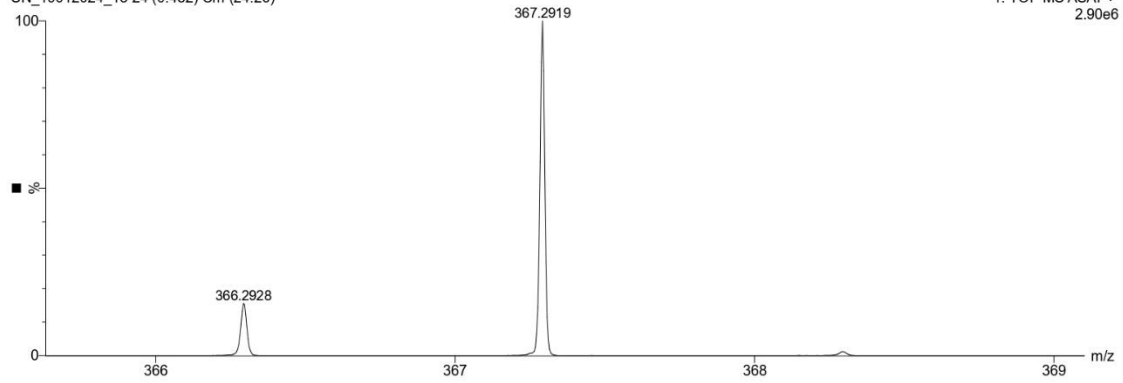
SN\_19012024\_18 (0.053) Cu (0.05); Is (1.00,1.00) C<sub>18</sub>H<sub>37</sub>B<sub>2</sub>N<sub>2</sub>O<sub>4</sub>

1: TOF MS ASAP+  
5.72e12



SN\_19012024\_18 24 (0.482) Cm (24:26)

1: TOF MS ASAP+  
2.90e6



HRMS of compound **4f**.

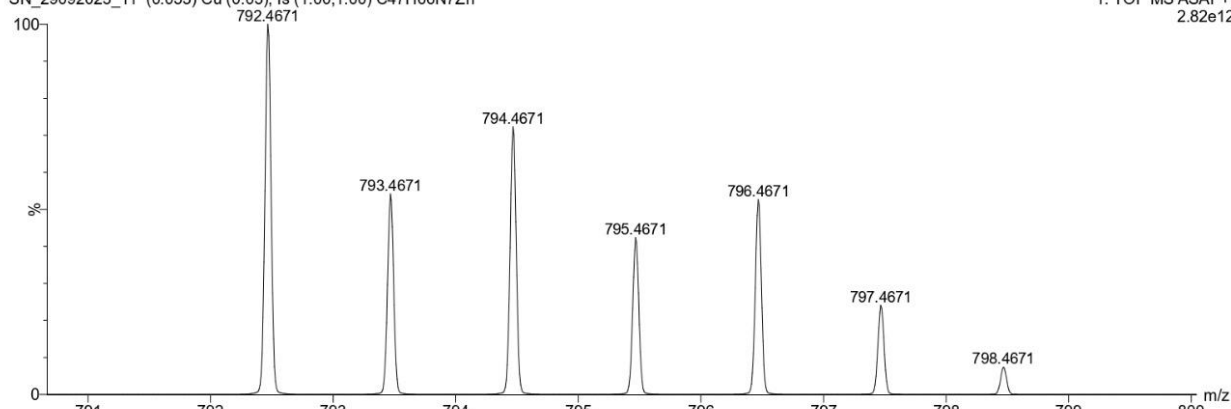
SN\_RKS\_138

29-Sep-2023  
16:10:15

XEVO-G2XSQTOF#NotSet

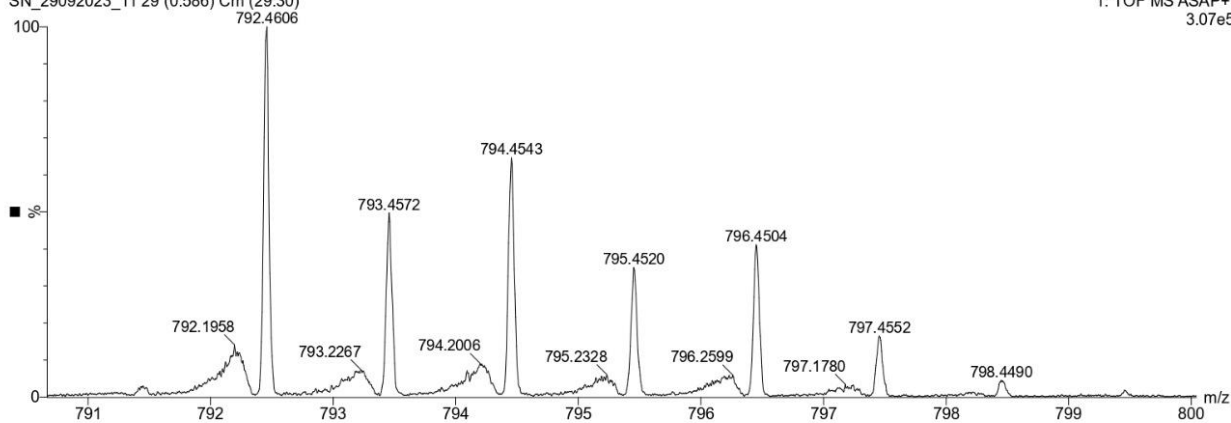
SN\_29092023\_11 (0.053) Cu (0.05); Is (1.00,1.00) C47H66N7Zn

1: TOF MS ASAP+  
2.82e12



SN\_29092023\_11 29 (0.586) Cm (29:30)

1: TOF MS ASAP+  
3.07e5



HRMS of compound **Zn-2**.



## References

- (1) (a) T. Peddaraao, A. Baishya, N. Sarkar, R. Acharya, S. Nembenna, *Eur. J. Inorg. Chem.* **2021**, 2034-2046. (b) R.K. Sahoo, M. Mahato, A. Jana, S. Nembenna, *J. Org. Chem.* **2020**, 85, 11200–11210. (c) R. K. Sahoo, N. Sarkar and S. Nembenna, *Angew. Chem., Int. Ed.* **2021**, 60, 11991 —12000.
- (2) G. Sheldrick, *Acta Crystallogr. C.* **2015**, 71, 3–8.
- (3) O. V. Dolomanov,; L. J. Bourhis,; , R. J. Gildea.; J. A. K. Howard,; H. Puschmann, *J. Appl. Crystallogr.* **2009**, 42, 339-341.
- (4) (a) G. M. Sheldrick, *Crystallogr.* **2008**, 64, 112-122. (b) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, 71, 3-8.