

## Supporting Information

### Double and Single Hydroboration of Nitriles Catalyzed by a Ruthenium– Bis(silyl)xanthene Complex: Application to One-Pot Synthesis of Diarylamines and *N*-Arylimines

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## 1. Experimental Procedures

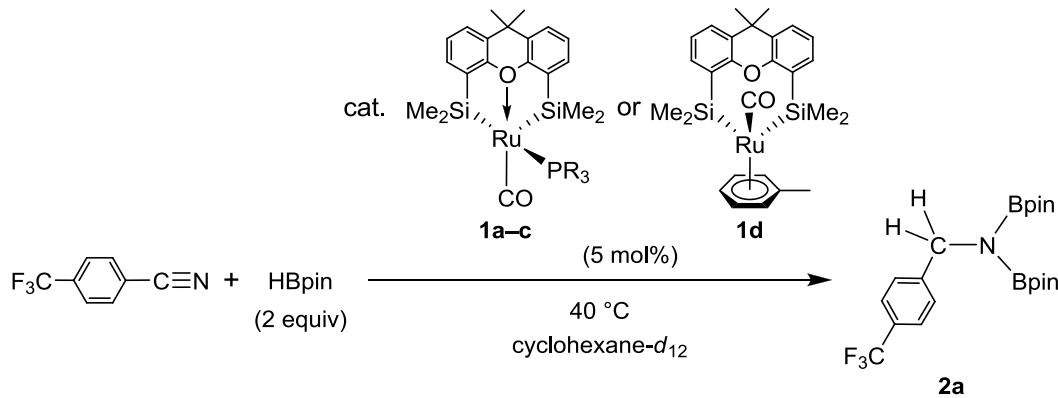
**General Considerations.** All manipulations of air- and moisture-sensitive compounds were carried out under dry argon in a glovebox or using a vacuum line and standard Schlenk techniques. Purification of diarylamines **4** and *N*-arylimines **5** by flash chromatography was performed in air unless otherwise indicated.

**Materials.** Cyclohexane-*d*<sub>12</sub> (C<sub>6</sub>D<sub>12</sub>) and THF-*d*<sub>8</sub> were dried over CaH<sub>2</sub> and vacuum-transferred. Hexane, THF, and MeC≡N were dried using a Glass Contour alumina column (Nikko Hansen & Co., Ltd.) and degassed by three freeze-pump-thaw cycles. All of the above solvents were stored under argon over 4 Å molecular sieves in a glovebox. CDCl<sub>3</sub> for measurement of NMR spectra was dried over CaH<sub>2</sub>, vacuum-transferred, and then stored over 4 Å molecular sieves in a glovebox (for hydroboration products **2,3**) or was dried over 4 Å molecular sieves in air (for C–N coupling products **4,5**). For purification of **4** and **5**, hexane and EtOAc were used as received. Pinacolborane (HBpin) were distilled under vacuum, degassed by three freeze-pump-thaw cycles, and then stored in a glovebox at –35 °C. Nitriles RC≡N (R = Ph, 4-OMeC<sub>6</sub>H<sub>4</sub>, 2-OMeC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 3-MeC<sub>6</sub>H<sub>4</sub>, 2-MeC<sub>6</sub>H<sub>4</sub>, 2-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, and <sup>t</sup>Bu), were distilled under vacuum, degassed by three freeze-pump-thaw cycles, and then stored over 4 Å molecular sieves in a glovebox. 9-Borabicyclo[3.3.1]nonane (9-BBN) and RC≡N (R = Mes, 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, and 2-ClC<sub>6</sub>H<sub>4</sub>) were put under reduced pressure to remove water and stored in a glovebox. 2-(Dicyclohexylphosphino)biphenyl (CyJohnPhos) was stored in a glovebox. Flash chromatography<sup>S1</sup> was performed using silica gel 60 N (Kanto Chemical Co., Inc., 40–50 μm, spherical, neutral). Ruthenium–xantsil complexes Ru[κ<sup>3</sup>(*Si*,*O*,*Si*)-xantsil](CO)(PR<sub>3</sub>) (R = Cyp (**1a**),<sup>S2a</sup> Cy (**1b**),<sup>S2b</sup> Pyrr (**1c**),<sup>S2c</sup> Cyp = cyclopentyl, Pyrr = 1-pyrroldynyl) and Ru[κ<sup>2</sup>(*Si*,*Si*)-xantsil](CO)(η<sup>6</sup>-toluene) (**1d**)<sup>S2d,e</sup> were prepared according to the procedure described in the literature.

**Physical Measurement.**  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{19}\text{F}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker AVANCE III 400 Fourier transform spectrometer. Chemical shifts are reported in parts per million. Coupling constants ( $J$ ) are given in Hz. The residual proton ( $\text{CHCl}_3$ , 7.24 ppm;  $\text{C}_6\text{D}_{11}\text{H}$ , 1.38 ppm;  $\text{THF-}d_7$ , 3.58 ppm) and the carbon ( $\text{CDCl}_3$ , 77.0 ppm) resonances of deuterated solvents were used as internal references for  $^1\text{H}$  and  $^{13}\text{C}$  resonances, respectively. Aromatic proton and carbon are abbreviated as ArH and ArC, respectively.  $^{11}\text{B}$ ,  $^{19}\text{F}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR chemical shifts were referenced to the following external standards:  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (0 ppm),  $\text{C}_6\text{H}_5\text{CF}_3$  (−63.7 ppm), and 85%  $\text{H}_3\text{PO}_4$  (0 ppm), respectively. All NMR data were collected at room temperature. Infrared spectra were measured for neat samples of **4** and **5** placed between two KBr plates and for a KBr pellet including **2** and **3** by use of a Horiba FT-720 spectrometer. High-resolution mass spectra (HRMS) and mass spectra were recorded on a Bulker Daltonics Solarix 9.4T spectrometer operating in the atmospheric pressure chemical ionization (APCI) mode or on a Shimadzu GC-MS QP5050 spectrometer operating in the electron impact (EI) mode. Elemental analysis was carried out using a J-Science Lab JM11 microanalyzer. Elemental analysis and measurements of a part of mass spectra were performed at the Research and Analytical Center for Giant Molecules, Tohoku University.

## 1.1. Catalytic Double Hydroboration of Nitriles: Synthesis of Bis(boryl)amines 2

**General Procedure 1 for NMR-scale reactions of 4-(trifluoromethyl)benzonitrile with HBpin catalyzed by complexes 1a–d.**



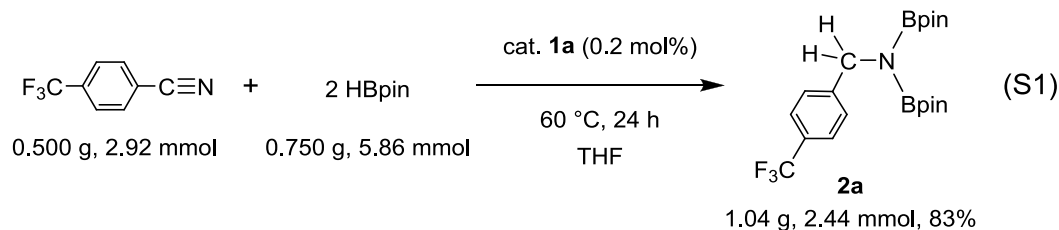
These reactions were all performed by essentially the same procedure, and the general procedure is as follows. In an NMR tube with a J-Young Teflon valve (5 mm o.d.), 4- $\text{CF}_3\text{C}_6\text{H}_4\text{C}\equiv\text{N}$  (25 mg, 0.15 mmol),  $\text{HBpin}$  (39 mg, 0.30 mmol), and  $\text{Cp}_2\text{Fe}$  (< 1 mg, an internal standard) were dissolved in  $\text{cyclohexane-}d_{12}$  (0.45 mL). A  $^1\text{H}$  NMR spectrum was measured to determine an intensity ratio between the signals of the nitrile and  $\text{Cp}_2\text{Fe}$ .  $\text{Ru}[\kappa^3(\text{Si},\text{O},\text{Si})\text{-xantsil}](\text{CO})(\text{PR}_3)$  ( $\text{R} = \text{Cyp}$  (**1a**),  $\text{Cy}$  (**1b**),  $\text{Pyrr}$  (**1c**)) or  $\text{Ru}[\kappa^2(\text{Si},\text{Si})\text{-xantsil}](\text{CO})(\eta^6\text{-toluene})$  (**1d**) (7  $\mu\text{mol}$ ; 5 mol%) and  $\text{cyclohexane-}d_{12}$  (0.05 mL) were added to the solution. The reaction was performed at  $40\text{ }^\circ\text{C}$  and monitored by  $^1\text{H}$  NMR spectroscopy. Formation of  $N,N$ -bis(pinacolatoboryl)-4-(trifluoromethyl)benzylamine (**2a**) was observed. Amounts of catalysts, reaction conditions, and NMR yields of **2a** are summarized in Table S1. The product **2a** was identified by comparison of its  $^1\text{H}$  and  $^{11}\text{B}$  NMR data with the literature data.<sup>S3a</sup>  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra of **2a** in a reaction mixture using catalyst **1a** are depicted in Figures S2 and S3.

**Data for (4- $\text{CF}_3\text{C}_6\text{H}_4$ ) $\text{CH}_2\text{N}(\text{Bpin})_2$  (**2a**).**<sup>S3a</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_{12}$ ):  $\delta$  1.13 (s, 24H, Bpin-Me), 4.22 (s, 2H,  $\text{NCH}_2$ ), 7.39 (d,  $^3J_{\text{HH}} = 8.0\text{ Hz}$ , 2H, ArH), 7.44 (d,  $^3J_{\text{HH}} = 8.0\text{ Hz}$ , 2H, ArH).  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_{12}$ ):  $\delta$  25.9 (br).  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{C}_6\text{D}_{12}$ ):  $\delta$  -63.4.

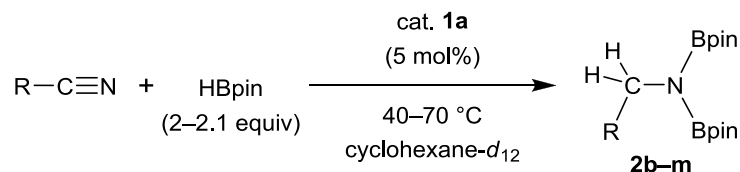
**Table S1. Conditions and yields of hydroboration product **2a** for the NMR-scale reactions of 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C≡N with HBpin catalyzed by Ru–xantsil complexes **1a–d**.**

catalyst	time (h)	NMR yield of <b>2a</b> (Based on 4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> C≡N, %)
<b>1a</b> (5 mg, 7 μmol)	4	> 99
<b>1b</b> (5 mg, 7 μmol)	4	> 99
<b>1c</b> (5 mg, 7 μmol)	24	23
<b>1d</b> (4 mg, 7 μmol)	24	> 99

**Gram-scale synthesis of (4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)CH<sub>2</sub>N(Bpin)<sub>2</sub> (**2a**).** In a 10 mL glass vial with a screw cap, 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C≡N (500 mg, 2.92 mmol), HBpin (750 mg, 5.86 mmol), and complex **1a** (4.0 mg, 5.8 μmol; 0.2 mol%) were dissolved in THF (3 mL). The solution was heated at 60 °C for 24 h, and consumption of the nitrile was monitored by GC analysis. After all the nitrile was consumed, the reaction mixture was evaporated under vacuum. The residual orange solid was washed with cold hexane to give **2a** as a colorless powder (1.04 g, 2.44 mmol) in 83% yield.



## General Procedure 2 for NMR-scale reactions of nitriles with HBpin catalyzed by **1a**.



These reactions were all carried out by essentially the same procedure, and the general procedure is as follows. In an NMR tube with a J-Young Teflon valve (5 mm o.d.),  $\text{RC}\equiv\text{N}$  ( $\text{R} = 4\text{-ClC}_6\text{H}_4$ , Ph, 4-OMeC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 3-MeC<sub>6</sub>H<sub>4</sub>, 2-MeC<sub>6</sub>H<sub>4</sub>, 2-OMeC<sub>6</sub>H<sub>4</sub>, Mes, 2-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 2-ClC<sub>6</sub>H<sub>4</sub>, <sup>t</sup>Bu, Me) (0.14–0.15 mmol), HBpin (39 mg, 0.30 mmol), and Cp<sub>2</sub>Fe (< 1 mg, an internal standard) were dissolved in cyclohexane-*d*<sub>12</sub> (0.45 mL). A <sup>1</sup>H NMR spectrum was measured to determine an intensity ratio between the signals of  $\text{RC}\equiv\text{N}$  and Cp<sub>2</sub>Fe. Complex **1a** (5 mg, 7 μmol; 5 mol%) and cyclohexane-*d*<sub>12</sub> (0.05 mL) were then added to the solution. The solution was heated at 40, 60, or 70 °C, and the reaction was monitored by <sup>1</sup>H NMR spectroscopy. Amounts of substrates, reaction conditions, and NMR yields of products  $\text{RCH}_2\text{N}(\text{Bpin})_2$  (**2b–m**) are summarized in Table S2.

Novel hydroboration products **2h,j,k** and product **2g** obtained from 2-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C≡N were isolated from the corresponding reaction mixtures by the following procedure: (1) evaporation of a reaction mixture under vacuum, (2) addition of hexane to the residual orange solid, (3) cooling the mixture at –35 °C to make **2g,h,j,k** precipitate, (4) removal of a supernatant liquid involving catalyst **1a** and unreacted HBpin, and (5) washing the remaining solid with cold hexane. Since characterization data for known compound **2g**<sup>S3f</sup> have not been reported previously, not only novel compounds **2h,j,k** but also **2g** were characterized by NMR spectroscopy, elemental analysis, and HRMS. Reported bis(boryl)amines **2b–f,i,l,m** were identified by comparison of their <sup>1</sup>H and <sup>11</sup>B NMR data with the literature data.<sup>S3</sup> **2b–f,i,l,m** were not isolated because, in the reaction mixtures, they were formed nearly quantitatively and were able to be identified on the basis of their <sup>1</sup>H and <sup>11</sup>B NMR signals observed. <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of isolated **2g,h,j,k** are shown in Figures S14–S19 and S22–S27. For **2b–f,i,l,m**, <sup>1</sup>H and <sup>11</sup>B NMR spectra of

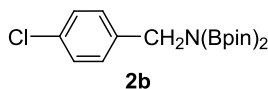
the reaction mixtures containing these products are depicted in Figures S4–S13, S20, S21, and S28–S31.

**Table S2. Amounts of substrates, reaction conditions, and yields of products for the double hydroboration of nitriles with HBpin catalyzed by complex 1a.**

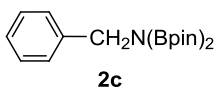
nitrile	product	temp., time; NMR yields <sup>a</sup>
4-ClC <sub>6</sub> H <sub>4</sub> C≡N (20 mg, 0.15 mmol)	(4-ClC <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> N(Bpin) <sub>2</sub> ( <b>2b</b> )	40 °C, 4 h; > 99%
PhC≡N (15 mg, 0.15 mmol)	PhCH <sub>2</sub> N(Bpin) <sub>2</sub> ( <b>2c</b> )	60 °C, 4 h; > 99%
4-MeC <sub>6</sub> H <sub>4</sub> C≡N (17 mg, 0.15 mmol)	(4-MeC <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> N(Bpin) <sub>2</sub> ( <b>2d</b> )	60 °C, 12 h; > 99%
4-OMeC <sub>6</sub> H <sub>4</sub> C≡N (19 mg, 0.14 mmol)	(4-OMeC <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> N(Bpin) <sub>2</sub> ( <b>2e</b> )	60 °C, 12 h; > 99%
3-MeC <sub>6</sub> H <sub>4</sub> C≡N (17 mg, 0.15 mmol)	(3-MeC <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> N(Bpin) <sub>2</sub> ( <b>2f</b> )	60 °C, 12 h; > 99%
2-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> C≡N (25 mg, 0.15 mmol)	(2-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> N(Bpin) <sub>2</sub> ( <b>2g</b> )	60 °C, 6 h; > 99%
2-ClC <sub>6</sub> H <sub>4</sub> C≡N (20 mg, 0.15 mmol)	(2-ClC <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> N(Bpin) <sub>2</sub> ( <b>2h</b> )	60 °C, 9 h; > 99%
2-MeC <sub>6</sub> H <sub>4</sub> C≡N (17 mg, 0.15 mmol)	(2-MeC <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> N(Bpin) <sub>2</sub> ( <b>2i</b> )	60 °C, 24 h; > 99%
2-OMeC <sub>6</sub> H <sub>4</sub> C≡N (19 mg, 0.14 mmol)	(2-OMeC <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> N(Bpin) <sub>2</sub> ( <b>2j</b> )	60 °C, 96 h; 51% <sup>b</sup>
MesC≡N (21 mg, 0.14 mmol)	MesCH <sub>2</sub> N(Bpin) <sub>2</sub> ( <b>2k</b> )	70 °C, 360 h; 62% <sup>b</sup>
<sup>t</sup> BuC≡N (12 mg, 0.14 mmol)	<sup>t</sup> BuCH <sub>2</sub> N(Bpin) <sub>2</sub> ( <b>2l</b> )	60 °C, 1 h; > 99%
MeC≡N (6 mg, 0.15 mmol)	MeCH <sub>2</sub> N(Bpin) <sub>2</sub> ( <b>2m</b> )	60 °C, 3 h; > 99%

<sup>a</sup>Based on nitriles. <sup>b</sup>NMR yields of the hydroboration products did not increase anymore even when the reaction mixture was heated for a longer period.

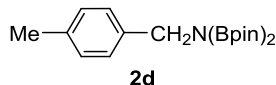
**Data for (4-ClC<sub>6</sub>H<sub>4</sub>)CH<sub>2</sub>N(Bpin)<sub>2</sub> (**2b**).**<sup>S3a</sup> <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 1.13 (s, 24H, Bpin-Me), 4.12 (s, 2H, NCH<sub>2</sub>), 7.12 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2H, ArH), 7.21 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2H, ArH). <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>12</sub>): δ 25.8 (br).



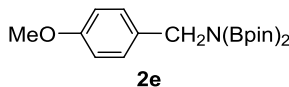
**Data for PhCH<sub>2</sub>N(Bpin)<sub>2</sub> (**2c**).**<sup>S3</sup> <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 1.12 (s, 24H, Bpin-Me), 4.16 (s, 2H, NCH<sub>2</sub>), 7.00–7.06 (m, 1H, ArH), 7.09–7.14 (m, 2H, ArH), 7.22–7.27 (m, 2H, ArH). <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>12</sub>): δ 25.8 (br).



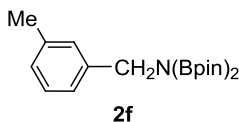
**Data for (4-MeC<sub>6</sub>H<sub>4</sub>)CH<sub>2</sub>N(Bpin)<sub>2</sub> (2d).** <sup>S3a-c</sup> <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 1.13 (s, 24H, Bpin-Me), 2.23 (s, 3H, *p*-Me), 4.12 (s, 2H, NCH<sub>2</sub>), 6.94 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.8 Hz, 2H, ArH), 7.15 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.8 Hz, 2H, ArH). <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>12</sub>): δ 25.9 (br).



**Data for (4-OMeC<sub>6</sub>H<sub>4</sub>)CH<sub>2</sub>N(Bpin)<sub>2</sub> (2e).** <sup>S3a,b</sup> <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 1.13 (s, 24H, Bpin-Me), 3.64 (s, 3H, 4-OMe), 4.09 (s, 2H, NCH<sub>2</sub>), 6.67 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, 2H, ArH), 7.19 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, 2H, ArH). <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>12</sub>): δ 25.9 (br).



**Data for (3-MeC<sub>6</sub>H<sub>4</sub>)CH<sub>2</sub>N(Bpin)<sub>2</sub> (2f).** <sup>S3a-c</sup> <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 1.13 (s, 24H, Bpin-Me), 2.24 (s, 3H, *m*-Me), 4.12 (s, 2H, NCH<sub>2</sub>), 6.86 (br d, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 1H, ArH), 7.01 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 1H, ArH), 7.06 (br d, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 1H, ArH), 7.11 (br s, 1H, 2-ArH). <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>12</sub>): δ 25.9 (br).

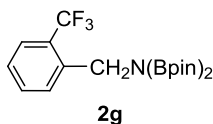


**Isolation of (2-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)CH<sub>2</sub>N(Bpin)<sub>2</sub> (2g).** According to General Procedure 2, this compound was isolated from a mixture of an NMR-scale reaction as a pale-yellow solid (39 mg, 0.91 mmol) in 63% yield.

**Data for 2g.** <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 1.10 (s, 24H, Bpin-Me), 4.47 (s, 2H, NCH<sub>2</sub>), 7.14 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 1H, ArH), 7.34 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 1H, ArH), 7.40 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 1H, ArH), 7.50 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 1H, ArH). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.15 (s, 24H, Bpin-Me), 4.46 (s, 2H, NCH<sub>2</sub>), 7.19–7.26 (m, 1H, ArH), 7.38–7.46 (m, 2H, ArH), 7.56 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.8 Hz, 1H, ArH). <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>12</sub>): δ 26.1 (br). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>): δ 25.8 (br). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ 24.4 (Bpin-OCMe<sub>2</sub>), 43.7 (NCH<sub>2</sub>), 82.5 (Bpin-OCMe<sub>2</sub>),

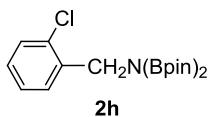


124.6 (q,  $^1J_{\text{CF}} = 274.0$  Hz,  $\text{CF}_3$ ), 125.3 (q,  $^3J_{\text{CF}} = 6.0$  Hz, ArC), 125.6 (ArC), 126.6 (ArC), 127.2 (q,  $^2J_{\text{CF}} = 30.2$  Hz, ArC), 131.4 (ArC), 141.9 (ArC). IR (KBr-pellet,  $\text{cm}^{-1}$ ): 2981 (m,  $\nu_{\text{CH}}$ ), 2937 (w,  $\nu_{\text{CH}}$ ), 1612 (w), 1585 (w), 1491 (s), 1454 (s), 1415 (s), 1365 (s), 1315 (s), 1271 (m), 1217 (w), 1155 (s), 1119 (s), 1055 (s), 966 (w), 874 (w), 852 (m), 779 (m), 703 (m), 656 (w), 580 (w). HRMS (APCI):  $m/z$  calcd for  $[\text{}^{12}\text{C}_{20}\text{}^1\text{H}_{31}\text{}^{11}\text{B}_2\text{}^{14}\text{N}_1\text{}^{16}\text{O}_4\text{}^{19}\text{F}_3]^+ [\text{M} + \text{H}]^+$  428.2386, found 428.2386. Anal. Calcd for  $\text{C}_{20}\text{H}_{30}\text{B}_2\text{F}_3\text{N}_1\text{O}_4$ : C, 56.25; H, 7.08; N, 3.28. Found: C, 56.41; H, 7.24; N, 3.40.

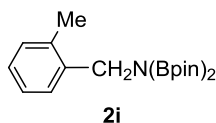


**Isolation of (2-ClC<sub>6</sub>H<sub>4</sub>)CH<sub>2</sub>N(Bpin)<sub>2</sub> (2h).** According to General Procedure 2, this compound was isolated as a pale-yellow solid (35 mg, 0.89 mmol) in 61% yield.

**Data for 2h.**  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_{12}$ ):  $\delta$  1.11 (s, 24H, Bpin-Me), 4.32 (s, 2H,  $\text{NCH}_2$ ), 6.98 (td,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 1.6$  Hz, 1H, ArH), 7.07 (td,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 1.1$  Hz, 1H, ArH), 7.16–7.22 (m, 2H, ArH).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.16 (s, 24H, Bpin-Me), 4.31 (s, 2H,  $\text{NCH}_2$ ), 7.08 (td,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 1.6$  Hz, 1H, ArH), 7.15 (td,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 1H, ArH), 7.22–7.28 (m, 2H, ArH).  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_{12}$ ):  $\delta$  25.8 (br).  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ ):  $\delta$  25.6 (br).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.4 (Bpin- $\text{OCMe}_2$ ), 45.1 ( $\text{NCH}_2$ ), 82.4 (Bpin- $\text{OCMe}_2$ ), 126.2, 127.0, 127.3, 128.8, 132.7, 140.0 (ArC). IR (KBr-pellet,  $\text{cm}^{-1}$ ): 2979 (m,  $\nu_{\text{CH}}$ ), 2935 (w,  $\nu_{\text{CH}}$ ), 1485 (s), 1441 (s), 1414 (s), 1371 (m), 1317 (m), 1267 (m), 1217 (w), 1167 (m), 1139 (s), 1049 (s), 972 (m), 873 (m), 850 (m), 778 (w), 754 (m), 721 (w), 687 (m), 580 (w). HRMS (APCI):  $m/z$  calcd for  $[\text{}^{12}\text{C}_{19}\text{}^1\text{H}_{31}\text{}^{11}\text{B}_2\text{}^{14}\text{N}_1\text{}^{16}\text{O}_4\text{}^{35}\text{Cl}_1]^+ [\text{M} + \text{H}]^+$  394.2122, found 394.2122. Accurate elemental analysis data could not be obtained because **2h** is highly air sensitive.

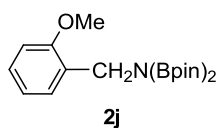


**Data for (2-MeC<sub>6</sub>H<sub>4</sub>)CH<sub>2</sub>N(Bpin)<sub>2</sub> (2i).**<sup>S3a,c</sup> <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>):  $\delta$  1.10 (s, 24H, Bpin-Me), 2.25 (s, 3H, *o*-Me), 4.18 (s, 2H, NCH<sub>2</sub>), 6.92–7.02 (m, 3H, ArH), 7.17 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, 1H, ArH). <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>12</sub>):  $\delta$  26.1 (br).



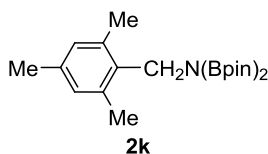
**Isolation of (2-OMeC<sub>6</sub>H<sub>4</sub>)CH<sub>2</sub>N(Bpin)<sub>2</sub> (2j).** According to General Procedure 2, this compound was isolated as a pale-yellow solid (24 mg, 0.62 mmol) in 43% yield.

**Data for 2j.** <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>):  $\delta$  1.10 (s, 24H, Bpin-Me), 3.67 (s, 3H, 2-OMe), 4.26 (s, 2H, NCH<sub>2</sub>), 6.65 (dd, <sup>3</sup>*J*<sub>HH</sub> = 8.0 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.0 Hz, 1H, ArH), 6.78 (td, <sup>3</sup>*J*<sub>HH</sub> = 8.0 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.0 Hz, 1H, ArH), 7.01 (br d, <sup>3</sup>*J*<sub>HH</sub> = 8.0 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.0 Hz, 1H, ArH), 7.11 (dd, <sup>3</sup>*J*<sub>HH</sub> = 8.0 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.0 Hz, 1H, ArH). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.16 (s, 24H, Bpin-Me), 3.78 (s, 3H, 2-OMe), 4.25 (s, 2H, NCH<sub>2</sub>), 6.76 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, 1H, ArH), 6.84 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, 1H, ArH), 7.12 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, 1H, ArH), 7.17 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, 1H, ArH). <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>12</sub>):  $\delta$  25.8 (br). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>):  $\delta$  25.7 (br). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  24.4 (Bpin-OCMe<sub>2</sub>), 42.3 (NCH<sub>2</sub>), 55.1 (OMe), 82.2 (Bpin-OCMe<sub>2</sub>), 109.5, 119.8, 126.6, 126.8, 131.0, 156.8 (ArC). IR (KBr-pellet, cm<sup>-1</sup>): 2978 (m,  $\nu_{CH}$ ), 2937 (w,  $\nu_{CH}$ ), 1603 (w), 1489 (s), 1448 (s), 1425 (s), 1371 (m), 1317 (m), 1263 (m), 1236 (m), 1142 (s), 1090 (w), 1051 (s), 974 (w), 852 (m), 754 (m), 696 (w). HRMS (APCI): *m/z* calcd for [<sup>12</sup>C<sub>20</sub><sup>1</sup>H<sub>34</sub><sup>11</sup>B<sub>2</sub><sup>14</sup>N<sub>1</sub><sup>16</sup>O<sub>5</sub>]<sup>+</sup> [M + H]<sup>+</sup> 390.2618, found 390.2617. Accurate elemental analysis data could not be obtained because **2j** is highly air sensitive.

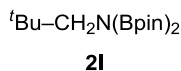


**Isolation of MesCH<sub>2</sub>N(Bpin)<sub>2</sub> (2k).** According to General Procedure 2, this compound was isolated as a pale-yellow solid (4 mg, 0.01 mmol) in 7% yield.

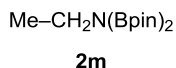
**Data for 2k.** <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 1.04 (s, 24H, Bpin-Me), 2.15 (s, 3H, *p*-Me), 2.30 (s, 6H, *o*-Me), 4.22 (s, 2H, NCH<sub>2</sub>), 6.63 (s, 2H, *m*-ArH). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.10 (s, 24H, Bpin-Me), 2.19 (s, 3H, *p*-Me), 2.32 (s, 6H, *o*-Me), 4.23 (s, 2H, NCH<sub>2</sub>), 6.70 (s, 2H, *m*-ArH). <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>12</sub>): δ 25.8 (br). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>): δ 25.6 (br). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ 20.3 (*o*-Me), 20.8 (*p*-Me), 24.3 (Bpin-OCMe<sub>2</sub>), 41.9 (NCH<sub>2</sub>), 82.1 (Bpin-OCMe<sub>2</sub>), 128.5, 135.28, 135.31, 137.5 (ArC). IR (KBr-pellet, cm<sup>-1</sup>): 2978 (s, ν<sub>CH</sub>), 2933 (m, ν<sub>CH</sub>), 1616 (w), 1533 (m), 1475 (s), 1458 (s), 1417 (s), 1379 (s), 1317 (m), 1271 (m), 1219 (w), 1167 (s), 1149 (s), 1103 (m), 1061 (s), 1009 (m), 983 (m), 964 (m), 852 (m), 783 (w), 700 (w), 677 (m), 580 (w). HRMS (APCI): *m/z* calcd for [<sup>12</sup>C<sub>22</sub><sup>1</sup>H<sub>38</sub><sup>11</sup>B<sub>2</sub><sup>14</sup>N<sub>1</sub><sup>16</sup>O<sub>4</sub>]<sup>+</sup> [M + H]<sup>+</sup> 402.2982, found 402.2981. Accurate elemental analysis data could not be obtained because **2k** is highly air sensitive.



**Data for <sup>t</sup>BuCH<sub>2</sub>N(Bpin)<sub>2</sub> (2l).** <sup>S3a,c</sup> <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 0.81 (s, 9H, <sup>t</sup>Bu), 1.15 (s, 24H, Bpin-Me), 2.86 (s, 2H, NCH<sub>2</sub>). <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>12</sub>): δ 25.8 (br).

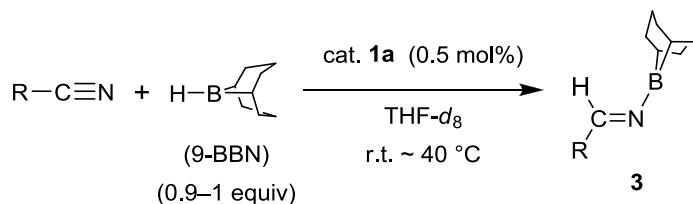


**Data for MeCH<sub>2</sub>N(Bpin)<sub>2</sub> (2m).** <sup>S3b,c,e</sup> <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 0.98 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 3H, NCH<sub>2</sub>CH<sub>3</sub>), 1.15 (s, 24H, Bpin-Me), 3.03 (q, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 2H, NCH<sub>2</sub>CH<sub>3</sub>). <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>12</sub>): δ 25.8 (br).



## 1.2. Catalytic Single Hydroboration of Nitriles: Synthesis of *N*-Borylimines **3**

### General Procedure 3 for reactions of nitriles with 9-BBN catalyzed by **1a**.



The title reactions were all carried out by essentially the same procedures, and the general procedure is as follows. In an NMR tube with a J-Young Teflon valve (5 mm o.d.),  $\text{RC}\equiv\text{N}$  ( $\text{R} = 4\text{-CF}_3\text{C}_6\text{H}_4$ , Ph, 4-OMeC<sub>6</sub>H<sub>4</sub>, <sup>t</sup>Bu) (0.14–0.15 mmol), 9-BBN (17 mg, 0.14 mmol for monomer), and Cp<sub>2</sub>Fe (< 1 mg, an internal standard) were dissolved in THF-*d*<sub>8</sub> (0.45 mL). A <sup>1</sup>H NMR spectrum was measured to determine an intensity ratio between the signals of 9-BBN and Cp<sub>2</sub>Fe. Complex **1a** (0.5 mg, 0.7 μmol; 0.5 mol%) and THF-*d*<sub>8</sub> (0.05 mL) were then added to the solution, and the reactions were monitored by <sup>1</sup>H NMR spectroscopy. Amounts of substrates, reaction conditions, and NMR yields of products  $\text{RCH}=\text{N}(\text{BC}_8\text{H}_{14})$  (**3a–d**) were summarized in Table S3. Novel compound **3a** was purified by a procedure that will be mentioned later, and characterized by NMR and high resolution mass spectroscopy. Products **3b–d** (known compounds) were identified by comparison of their <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>11</sup>B NMR data with the literature data.<sup>S4</sup> **3b–d** were not isolated because, in the reaction mixtures, they were formed nearly quantitatively and were able to be identified on the basis of their <sup>1</sup>H and <sup>11</sup>B NMR signals observed. <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of isolated **3a** are shown in Figures S32–S34. For **3b–d**, <sup>1</sup>H and <sup>11</sup>B NMR spectra of the reaction mixtures containing these products are depicted in Figures S35–S40.

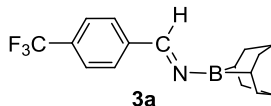
**Table S3. Amounts of substrates, reaction conditions, and NMR yields of products for single hydroboration of nitriles with 9-BBN catalyzed by **1a**.**

nitrile	product	temp., time; NMR yield <sup>a</sup>
(4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )C≡N (25 mg, 0.15 mmol)	(4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )CH=N(BC <sub>8</sub> H <sub>14</sub> ) ( <b>3a</b> )	40 °C, 0.5 h; > 99%
PhC≡N (15 mg, 0.15 mmol)	PhCH=N(BC <sub>8</sub> H <sub>14</sub> ) ( <b>3b</b> )	40 °C, 0.5 h; > 99%
(4-OMeC <sub>6</sub> H <sub>4</sub> )C≡N (19 mg, 0.14 mmol)	(4-OMeC <sub>6</sub> H <sub>4</sub> )CH=N(BC <sub>8</sub> H <sub>14</sub> ) ( <b>3c</b> )	40 °C, 0.5 h; > 99%
<sup>t</sup> BuC≡N (12 mg, 0.14 mmol)	<sup>t</sup> BuCH=N(BC <sub>8</sub> H <sub>14</sub> ) ( <b>3d</b> )	r.t., 0.25 h; > 99%

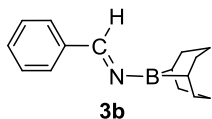
<sup>a</sup>Based on 9-BBN.

**Isolation of (4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)CH=N(BC<sub>8</sub>H<sub>14</sub>) (**3a**).** A mixture obtained by an NMR-scale reaction (General Procedure 3) of (4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)C≡N (26 mg, 0.15 mmol) with 9-BBN (17 mg, 0.14 mmol for monomer) in the presence of **1a** (0.5 mg, 0.7 μmol; 0.5 mol%) in THF-*d*<sub>8</sub> (0.5 mL) was added to silica gel (0.1 g) to remove catalyst **1a**. The resulting slurry was filtered through a cotton plug to give a pale-yellow solution containing **3a**. The solution was evaporated under vacuum to remove volatiles to give **3a** as a pale-yellow liquid (40 mg, 0.14 mmol) in 98% yield.

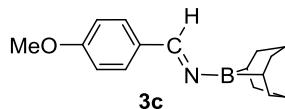
**Data for 3a.** <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>): δ 1.39–1.45 (m, 2H, BC<sub>8</sub>H<sub>14</sub>), 1.50–1.59 (m, 2H, BC<sub>8</sub>H<sub>14</sub>), 1.84–2.05 (m, 10H, BC<sub>8</sub>H<sub>14</sub>), 7.77 (s, 4H, ArH), 8.27 (s, 1H, N=CH). <sup>11</sup>B NMR (128 MHz, THF-*d*<sub>8</sub>): δ 37.0 (br). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.38–1.43 (m, 2H, BC<sub>8</sub>H<sub>14</sub>), 1.47–1.57 (m, 2H, BC<sub>8</sub>H<sub>14</sub>), 1.82–2.01 (m, 10H, BC<sub>8</sub>H<sub>14</sub>), 7.65 (d, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 2H, ArH), 7.69 (d, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 2H, ArH), 8.17 (s, 1H, N=CH). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>): δ 37.4 (br). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ 23.5 (BC<sub>8</sub>H<sub>14</sub>), 24.4 (br, BC<sub>8</sub>H<sub>14</sub>), 33.1 (BC<sub>8</sub>H<sub>14</sub>), 123.9 (q, <sup>1</sup>J<sub>CF</sub> = 271.3 Hz, CF<sub>3</sub>), 125.8 (q, <sup>3</sup>J<sub>CF</sub> = 3.7 Hz, ArC), 127.6 (ArC), 132.3 (q, <sup>2</sup>J<sub>CF</sub> = 32.5 Hz, ArC), 139.0 (N=CH), 149.4 (ArC). IR (KBr-pellet, cm<sup>-1</sup>): 2925 (m, ν<sub>CH</sub>), 2860 (m, ν<sub>CH</sub>), 1697 (w), 1647 (w), 1417 (m), 1389 (s), 1209 (w), 1169 (m), 1128 (s), 1066 (s), 1018 (m), 978 (w), 904 (w), 839 (m), 760 (w), 679 (w), 594 (w). HRMS (APCI): *m/z* calcd for [<sup>12</sup>C<sub>16</sub><sup>1</sup>H<sub>20</sub><sup>11</sup>B<sub>1</sub><sup>14</sup>N<sub>1</sub><sup>19</sup>F<sub>3</sub>]<sup>+</sup> [M + H]<sup>+</sup> 294.1635, found 294.1636. Anal. Calcd for C<sub>16</sub>H<sub>19</sub>B<sub>1</sub>N<sub>1</sub>F<sub>3</sub>: C, 65.56; H, 6.53; N, 4.78. Found: C, 65.67; H, 6.93; N, 4.69.



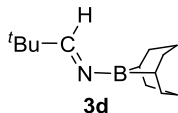
**Data for PhCH=N(BC<sub>8</sub>H<sub>14</sub>) (3b).**<sup>S4</sup> <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>): δ 1.36–1.43 (m, 2H, BC<sub>8</sub>H<sub>14</sub>), 1.50–1.59 (m, 2H, BC<sub>8</sub>H<sub>14</sub>), 1.80–2.05 (m, 10H, BC<sub>8</sub>H<sub>14</sub>), 7.38–7.46 (m, 3H, ArH), 7.56–7.62 (m, 2H, ArH), 8.18 (s, 1H, N=CH). <sup>11</sup>B NMR (128 MHz, THF-*d*<sub>8</sub>): δ 36.6 (br).



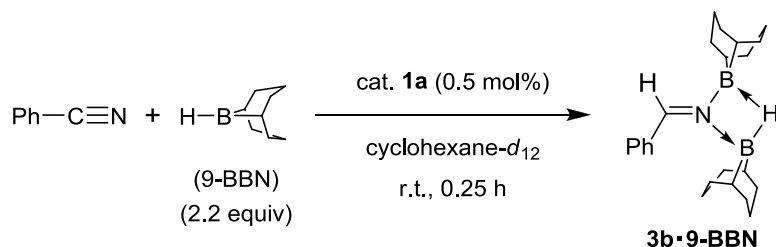
**Data for (4-OMeC<sub>6</sub>H<sub>4</sub>)CH=N(BC<sub>8</sub>H<sub>14</sub>) (3c).**<sup>S4</sup> <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>): δ 1.33–1.38 (m, 2H, BC<sub>8</sub>H<sub>14</sub>), 1.49–1.58 (m, 2H, BC<sub>8</sub>H<sub>14</sub>), 1.80–2.04 (m, 10H, BC<sub>8</sub>H<sub>14</sub>), 3.81 (s, 3H, OMe), 6.95–7.01 (AA'XX' multiplet, 2H, ArH), 7.48–7.54 (AA'XX' multiplet, 2H, ArH), 8.10 (s, 1H, N=CH). <sup>11</sup>B NMR (128 MHz, THF-*d*<sub>8</sub>): δ 36.5 (br).



**Data for <sup>t</sup>BuCH=N(BC<sub>8</sub>H<sub>14</sub>) (3d).**<sup>S4</sup> <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>): δ 1.02 (s, 9H, <sup>t</sup>Bu), 1.17–1.24 (m, 2H, BC<sub>8</sub>H<sub>14</sub>), 1.41–1.49 (m, 2H, BC<sub>8</sub>H<sub>14</sub>), 1.76–1.96 (m, 10H, BC<sub>8</sub>H<sub>14</sub>), 7.40 (s, 1H, N=CH). <sup>11</sup>B NMR (128 MHz, THF-*d*<sub>8</sub>): δ 36.1 (br).



#### Reaction of benzonitrile with excess 9-BBN catalyzed by complex 1a.



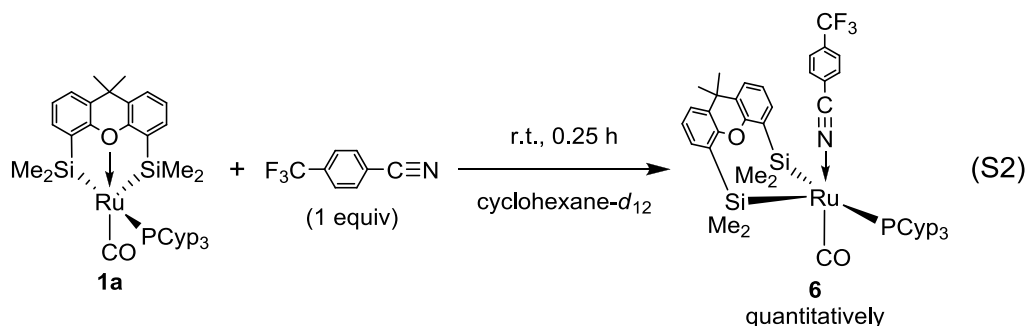
In an NMR tube with a J-Young Teflon valve (5 mm o.d.), PhC≡N (15 mg, 0.15 mmol), 9-BBN (40 mg, 0.33 mmol), and Cp<sub>2</sub>Fe (< 1 mg, an internal standard) were dissolved in cyclohexane-*d*<sub>12</sub> (0.45 mL). A <sup>1</sup>H NMR spectrum was measured to determine an intensity ratio

between the signals of  $\text{PhC}\equiv\text{N}$  and  $\text{Cp}_2\text{Fe}$ . Complex **1a** (0.5 mg, 0.7  $\mu\text{mol}$ ; 0.5 mol%) and cyclohexane- $d_{12}$  (0.05 mL) were then added to the solution. After 0.25 h at room temperature, quantitative formation of a 9-BBN adduct  $\text{PhCH}=\text{N}(\text{BC}_8\text{H}_{14})\cdot 9\text{-BBN}$  (**3b•9-BBN**) (> 99% NMR yield based on  $\text{PhC}\equiv\text{N}$ ) was observed in a  $^1\text{H}$  NMR spectrum of the reaction mixture. Product **3b•9-BBN** was identified by comparison of its  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{11}\text{B}$  NMR data with the literature data.<sup>S4</sup>

**Data for 3b•9-BBN.**<sup>S4</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{THF}-d_8$ ):  $\delta$  0.83 (br, 2H,  $\text{BC}_8\text{H}_{14}$ ), 0.94 (br, 2H,  $\text{BC}_8\text{H}_{14}$ ), 1.36–2.26 (m, 24H,  $\text{BC}_8\text{H}_{14}$ ), 7.46–7.55 (m, 3H, ArH), 7.76–7.82 (m, 2H, ArH), 8.98 (s, 1H,  $\text{N}=\text{CH}$ ).  $^{11}\text{B}$  NMR (128 MHz,  $\text{THF}-d_8$ ):  $\delta$  –6.8 (br), 2.2 (br).

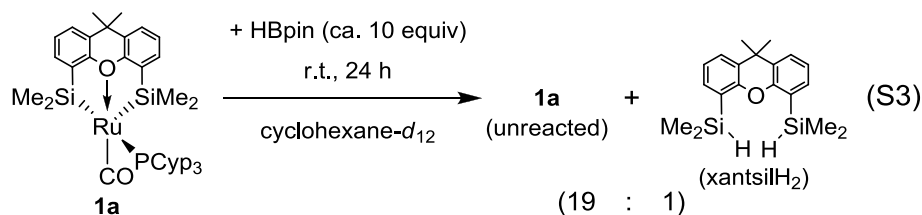
### 1.3. Stoichiometric Reactions of Complex **1a** with 4-(Trifluoromethyl)benzonitrile and with HBpin

**Stoichiometric reaction of 1a with 4-(trifluoromethyl)benzonitrile.** In an NMR tube with a J-Young Teflon valve (5 mm o.d.), 4-(trifluoromethyl)benzonitrile (1.2 mg, 7.0  $\mu\text{mol}$ ) was added to a cyclohexane- $d_{12}$  (0.50 mL) solution of complex **1a** (5 mg, 7  $\mu\text{mol}$ ). The reaction was completed within 0.25 h at room temperature, and  $\text{Ru}[\kappa^2(\text{Si},\text{Si})\text{-xantsil}](\text{CO})(\text{PCyp}_3)[\text{N}=\text{C}(\text{C}_6\text{H}_4\text{-4-CF}_3)]$  (**6**) was formed quantitatively. Complex **6** could not be isolated from the reaction mixture due to its instability under vacuum, but was characterized by NMR spectroscopy ( $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ , and  $^{19}\text{F}\{^1\text{H}\}$ ) and X-ray crystal structure analysis (vide infra).



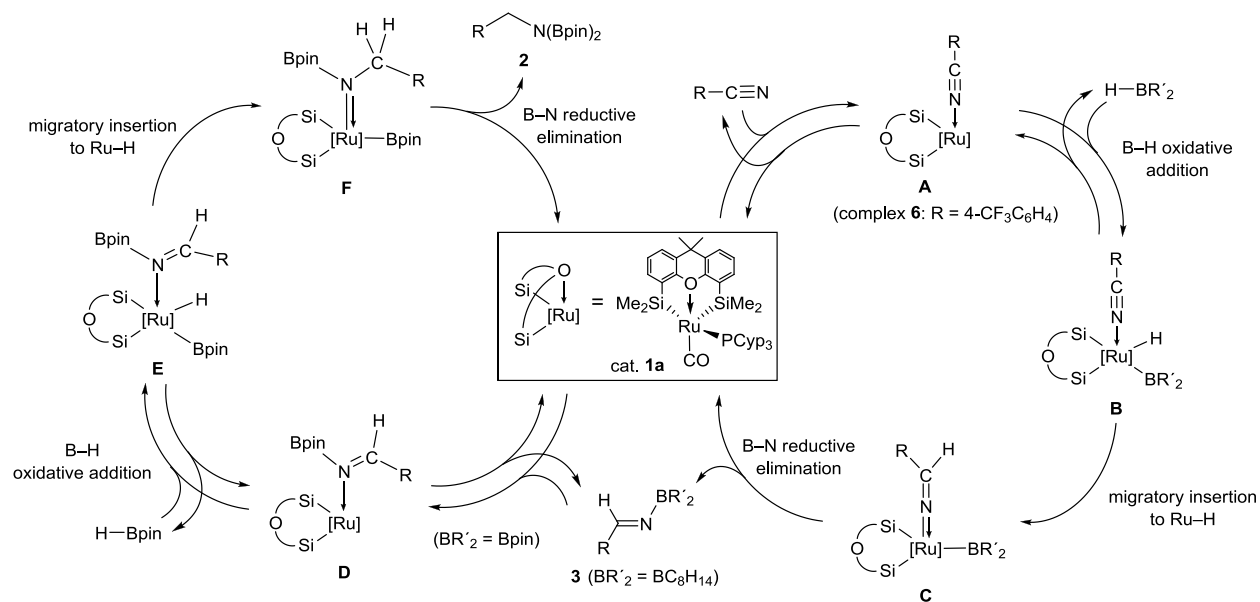
**Data for 6.**  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_{12}$ ):  $\delta$  0.41 (s, 6H, SiMe), 0.68 (s, 6H, SiMe), 1.05 (s, 3H, 9-CMe), 1.27 (s, 3H, 9-CMe), 1.35–2.30 (m, 27H, Cyp), 6.81 (dd,  $^3J_{\text{HH}} = 7.2$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 2H, xanthene-H), 6.93 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 2H, xanthene-H), 7.26 (dd,  $^3J_{\text{HH}} = 7.2$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 2H, xanthene-H), 7.34 (br, 4H,  $\text{C}_6\text{H}_4\text{CF}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (161 MHz,  $\text{C}_6\text{D}_{12}$ ): 25.9 (s with satellites,  $^2J_{\text{SiP}} = 42$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{C}_6\text{D}_{12}$ ):  $\delta$  -64.8.  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra could not be measured due to thermal instability of **6** in solution.

**Stoichiometric reaction of 1a with HBpin.** In an NMR tube with a J-Young Teflon valve (5 mm o.d.), HBpin (4 mg, 0.03 mmol; ca. 10 equiv) was added to a cyclohexane- $d_{12}$  (0.50 mL) solution of complex **1a** (2.0 mg, 2.9  $\mu\text{mol}$ ). The tube was allowed to stand at room temperature, and the reaction was monitored by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. Gradual formation of 9,9-dimethyl-4,5-bis(dimethylsilyl)xanthene (xantsilH<sub>2</sub>) was observed. After 24 h at room temperature, the ratio of xantsilH<sub>2</sub> versus unreacted **1a** in the reaction mixture was 1 : 19.

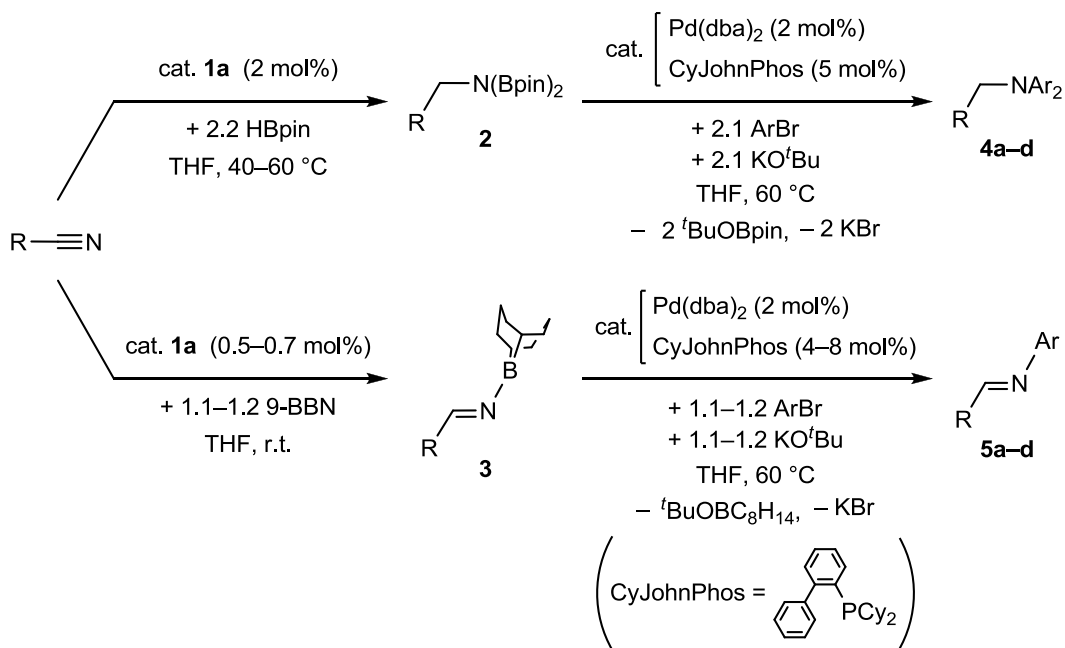




**Scheme S1. Proposed Mechanisms for Double and Single Hydroboration Reactions of Nitriles to Give Bis(boryl)amines **2** and *N*-Borylimines **3** Catalyzed by Complex **1a****

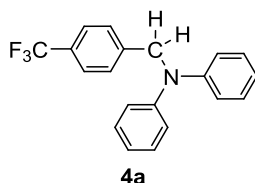


#### 1.4. One-Pot Synthesis of Diarylamines **4** and *N*-Arylimines **5** from Nitriles by Ru-Catalyzed Double and Single Hydroboration and Subsequent Pd-Catalyzed C–N Coupling



**General Procedure 4 for double hydroboration and subsequent C–N coupling in one pot: synthesis of diphenyl[(4-trifluoromethyl)benzyl]amine (**4a**).** In a 10 mL glass vial with a screw cap, 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C≡N (50 mg, 0.29 mmol), HBpin (80 mg, 0.63 mmol), and **1a** (5 mg, 7 μmol; 2 mol%) were dissolved in THF (1 mL), and then the solution was stirred for 4 h at 40 °C. To the reaction mixture was added in the following order a THF (1 mL) solution of PhBr (96 mg, 0.61 mmol), CyJohnPhos (5.0 mg, 14 μmol; 5 mol%), Pd(dba)<sub>2</sub> (3.5 mg, 6.1 μmol; 2 mol%), and KO<sup>t</sup>Bu (69 mg, 0.61 mmol). The mixture was then heated and stirred at 60 °C for 12 h. Volatiles were removed under vacuum, and hexane was added to the residual red oil. Insoluble precipitates were removed by filtration to give a red solution containing **4a**, and the solution was evaporated under vacuum. The resulting crude sample was purified by flash chromatography using silica gel (10 g) and elution with hexane/EtOAc (19 : 1) gave diphenyl[(4-trifluoromethyl)benzyl]amine (**4a**) as a pale-yellow oil (75 mg, 0.23 mmol) in 79% yield. **4a** was identified by GC-MS analysis and comparison of its <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR data with the literature data.<sup>S5a</sup>

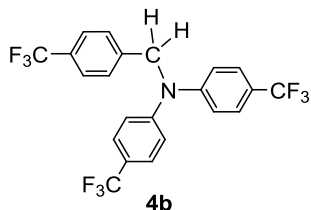
**Data for 4a.** <sup>55a</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.03 (s, 2H, NCH<sub>2</sub>), 6.91–6.97 (m, 2H, ArH), 7.00–7.05 (m, 4H, ArH), 7.20–7.26 (m, 4H, ArH), 7.45 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2H, ArH), 7.54 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ 56.0 (NCH<sub>2</sub>), 120.6 (ArC), 124.2 (q, <sup>1</sup>J<sub>CF</sub> = 272.6 Hz, CF<sub>3</sub>), 125.6 (q, <sup>3</sup>J<sub>CF</sub> = 3.7 Hz, ArC), 126.8 (ArC), 129.1 (q, <sup>2</sup>J<sub>CF</sub> = 30.2 Hz, ArC), 129.4 (ArC), 143.5 (ArC), 147.8 (ArC). <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, CDCl<sub>3</sub>): δ –62.4.



**Synthesis of bis[(4-trifluoromethyl)phenyl][(4-trifluoromethyl)benzyl]amine (4b).** This compound was synthesized and isolated by a method similar to the above-mentioned General Procedure 4. A THF (1 mL) solution of 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C≡N (50 mg, 0.29 mmol), HBpin (80 mg, 0.63 mmol), and **1a** (5 mg, 7 μmol; 2 mol%) was stirred for 4 h at 40 °C, and then a THF (0.5 mL) solution of 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Br (137 mg, 0.61 mmol), CyJohnPhos (5.0 mg, 14 μmol; 5 mol%), Pd(dba)<sub>2</sub> (3.5 mg, 6.1 μmol; 2 mol%), and KO<sup>t</sup>Bu (69 mg, 0.61 mmol) were added in this order to the reaction mixture. The resulting mixture was heated and stirred at 60 °C for 12 h. Purification according to the General Procedure 4 gave bis[(4-trifluoromethyl)phenyl][(4-trifluoromethyl)benzyl]amine (**4b**) as a pale-yellow oil (106 mg, 0.229 mmol) in 79% yield. Novel compound **4b** was characterized by spectroscopy (NMR, IR, and mass) and elemental analysis.

**Data for 4b.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.10 (s, 2H, NCH<sub>2</sub>), 7.14 (d, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 4H, ArH), 7.40 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2H, ArH), 7.51 (d, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 4H, ArH), 7.58 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ 55.8 (NCH<sub>2</sub>), 120.4 (ArC), 124.0 (q, <sup>1</sup>J<sub>CF</sub> = 270.6 Hz, CF<sub>3</sub>), 124.2 (q, <sup>1</sup>J<sub>CF</sub> = 271.6 Hz, CF<sub>3</sub>), 124.4 (q, <sup>2</sup>J<sub>CF</sub> = 32.9 Hz, ArC), 125.9 (q, <sup>3</sup>J<sub>CF</sub> = 3.5 Hz, ArC), 126.6 (ArC), 126.9 (q, <sup>3</sup>J<sub>CF</sub> = 3.7 Hz, ArC), 129.9 (q, <sup>2</sup>J<sub>CF</sub> = 32.9 Hz, ArC), 141.7 (ArC), 149.7 (ArC). <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, CDCl<sub>3</sub>): δ –62.6, –62.0. IR (neat, cm<sup>–1</sup>): 3055 (w, ν<sub>CH</sub>), 2933 (m, ν<sub>CH</sub>), 2858 (w, ν<sub>CH</sub>), 2644 (w, ν<sub>CH</sub>), 2590 (w, ν<sub>CH</sub>), 1919 (w), 1608 (s), 1520 (s), 1452

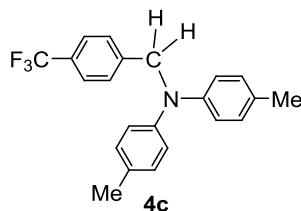
(w), 1419 (m), 1373 (m), 1323 (s), 1261 (m), 1226 (m), 1165 (s), 1115 (s), 1068 (s), 1016 (m), 953 (w), 870 (m), 825 (w), 750 (w), 715 (w), 661 (w), 625 (w), 594 (m). MS (EI):  $m/z$  463 ( $[^{12}\text{C}_{22}^{1}\text{H}_{14}^{14}\text{N}_1^{19}\text{F}_9]^+ (\text{M}^+)$ , 34), 159 ( $^{12}\text{C}_8^{1}\text{H}_6^{19}\text{F}_3^+$ , 100). Anal. Calcd for  $\text{C}_{22}\text{H}_{14}\text{N}_1\text{F}_9$ : C, 57.03; H, 3.05; N, 3.02. Found: C, 57.42; H, 3.30; N, 2.85.



**Synthesis of di(*p*-tolyl)[(4-trifluoromethyl)benzyl]amine (**4c**).** This compound was synthesized and isolated by a method similar to the above-mentioned General Procedure 4 by use of a THF (1 mL) solution of 4- $\text{CF}_3\text{C}_6\text{H}_4\text{C}\equiv\text{N}$  (50 mg, 0.29 mmol), HBpin (80 mg, 0.63 mmol), and **1a** (5 mg, 7  $\mu\text{mol}$ ; 2 mol%) for the hydroboration reaction (condition: 40  $^\circ\text{C}$ , 4 h) and then by addition of a THF (0.5 mL) solution of 4- $\text{MeC}_6\text{H}_4\text{Br}$  (104 mg, 0.61 mmol), CyJohnPhos (5.0 mg, 14  $\mu\text{mol}$ ; 5 mol%),  $\text{Pd}(\text{dba})_2$  (3.5 mg, 6.1  $\mu\text{mol}$ ; 2 mol%), and  $\text{KO}^t\text{Bu}$  (69 mg, 0.61 mmol) in this order for the subsequent C–N coupling reaction (condition: 60  $^\circ\text{C}$ , 12 h). Purification according to the General Procedure 4 gave di(*p*-tolyl)[(4-trifluoromethyl)benzyl]amine (**4c**) as a pale-yellow oil (66 mg, 0.19 mmol) in 64% yield. Novel compound **4c** was characterized by spectroscopy (NMR, IR, and mass) and elemental analysis.

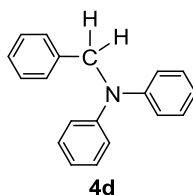
**Data for 4c.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.27 (s, 6H,  $\text{C}_6\text{H}_4\text{Me}$ ), 4.97 (s, 2H,  $\text{NCH}_2$ ), 6.88–6.93 (AA'XX' multiplet, 4H, ArH), 7.01–7.06 (AA'XX' multiplet, 4H, ArH), 7.45 (d,  $^3J_{\text{HH}} = 8.2$  Hz, 2H, ArH), 7.54 (d,  $^3J_{\text{HH}} = 8.2$  Hz, 2H, ArH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.5 ( $\text{C}_6\text{H}_4\text{Me}$ ), 56.2 ( $\text{NCH}_2$ ), 120.5 (ArC), 124.3 (q,  $^1J_{\text{CF}} = 270.6$  Hz,  $\text{CF}_3$ ), 125.5 (q,  $^3J_{\text{CF}} = 4.0$  Hz, ArC), 126.9 (ArC), 129.1 (q,  $^2J_{\text{CF}} = 32.5$  Hz, ArC), 129.9 (ArC), 130.1 (ArC), 143.9 (ArC), 145.7 (ArC).  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  –62.4. IR (neat,  $\text{cm}^{-1}$ ): 3028 (m,  $\nu_{\text{CH}}$ ), 2922 (m,  $\nu_{\text{CH}}$ ), 2862 (m,  $\nu_{\text{CH}}$ ), 2735 (w,  $\nu_{\text{CH}}$ ), 1618 (m), 1571 (w), 1510 (s), 1446 (w), 1417 (m), 1365 (m), 1325 (s), 1255 (m), 1225 (m), 1163 (s), 1124 (s), 1066 (s), 1016 (m), 951 (w), 870 (m), 810 (s), 748

(w), 729 (w), 627 (w), 578 (m). MS (EI):  $m/z$  355 ( $[^{12}\text{C}_{22}\text{H}_{20}^{14}\text{N}_1^{19}\text{F}_3]^+$  ( $\text{M}^+$ ), 100). Anal. Calcd for  $\text{C}_{22}\text{H}_{20}\text{N}_1\text{F}_3$ : C, 74.35; H, 5.67; N, 3.94. Found: C, 74.19; H, 5.68; N, 3.91.

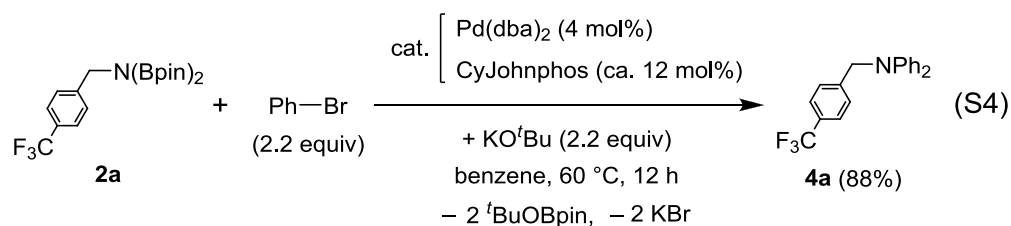


**Synthesis of diphenyl(benzyl)amine (4d).** This compound was synthesized by a method similar to the above-mentioned General Procedure 4 by use of a THF (1 mL) solution of  $\text{PhC}\equiv\text{N}$  (30 mg, 0.29 mmol), HBpin (80 mg, 0.63 mmol), and **1a** (5 mg, 7  $\mu\text{mol}$ ; 2 mol%) for hydroboration (condition: 60  $^{\circ}\text{C}$ , 18 h) and then by addition of a THF (0.5 mL) solution of PhBr (96 mg, 0.61 mmol), CyJohnPhos (5.0 mg, 14  $\mu\text{mol}$ ; 5 mol%),  $\text{Pd}(\text{dba})_2$  (3.5 mg, 6.1  $\mu\text{mol}$ ; 2 mol%), and  $\text{KO}^t\text{Bu}$  (69 mg, 0.61 mmol) in this order for subsequent C–N coupling (condition: 60  $^{\circ}\text{C}$ , 12 h). Purification according to the General Procedure 4 gave diphenyl(benzyl)amine (**4d**) as a pale-yellow oil (48 mg, 0.19 mmol) in 64% yield. **4d** was identified by GC-MS analysis and comparison of its  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data with the literature data.<sup>S5b</sup>

**Data for 4d.**<sup>S5b</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.99 (s, 2H,  $\text{NCH}_2$ ), 6.89–6.94 (m, 2H, ArH), 7.03–7.08 (m, 4H, ArH), 7.18–7.25 (m, 5H, ArH), 7.26–7.35 (m, 4H, ArH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  56.3 ( $\text{NCH}_2$ ), 120.7, 121.4, 126.5, 126.8, 128.5, 129.2, 139.2, 148.1 (ArC).



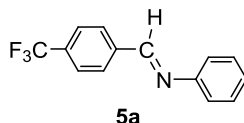
**Synthesis of diphenyl[(4-trifluoromethyl)benzyl]amine (4a) starting from isolated bis(boryl)amine 2a.** In a 10 mL glass vial with a screw cap, (4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)CH<sub>2</sub>N(Bpin)<sub>2</sub> (**2a**; 21 mg, 0.049 mmol), PhBr (18 mg, 0.11 mmol), KO<sup>t</sup>Bu (13 mg, 0.11 mmol), Pd(dba)<sub>2</sub> (1 mg, 2 μmol; 4 mol%), and CyJohnPhos (2 mg, 6 μmol; ca. 12 mol%) were dissolved in benzene (1 mL). The solution was heated at 60 °C for 12 h, and then volatiles were removed under vacuum. Hexane was added to the residual red oil, and precipitates were removed by filtration to give a red solution containing **4a**. After evaporation, the resulting crude sample was purified by flash chromatography (silica gel (5 g), eluent: hexane/EtOAc (19 : 1)). Diphenyl[(4-trifluoromethyl)benzyl]amine (**4a**) was obtained as a colorless oil (14 mg, 0.043 mmol) in 88% yield.



**General Procedure 5 for single hydroboration and subsequent C–N coupling in one pot: synthesis of *N*-[4-(trifluoromethyl)benzylidene]aniline (5a).** In a 10 mL glass vial with a screw cap, 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C≡N (17 mg, 0.099 mmol), 9-BBN (15 mg, 0.12 mmol for the monomer), and **1a** (0.5 mg, 0.7 μmol; 0.7 mol%) were dissolved in THF (0.5 mL), and the solution was then stirred for 1 h at room temperature. To the reaction mixture was added a THF (0.5 mL) solution of PhBr (17 mg, 0.11 mmol), CyJohnPhos (1.4 mg, 4.0 μmol; 4 mol%), Pd(dba)<sub>2</sub> (1.2 mg, 2.1 μmol; 2 mol%), and KO<sup>t</sup>Bu (14 mg, 0.12 mmol) in this order, and then the mixture was heated and stirred at 60 °C for 12 h. Volatiles were removed under vacuum, and hexane was added to the residual red oil. Insoluble precipitates were removed by filtration to give a red solution containing **5a**. After evaporation of the solution, the resulting crude sample was purified by flash chromatography [silica gel (5 g), eluent: hexane/EtOAc (19 : 1)] to give *N*-[4-(trifluoromethyl)benzylidene]aniline (**5a**) as a colorless oil (18.1 mg, 72.6 μmol) in 73% yield. **5a**

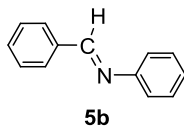
was identified by GC-MS analysis and comparison of its  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data with the literature data.<sup>S6a</sup>

**Data for 5a.**<sup>S6a</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.19–7.28 (m, 3H, Ph), 7.36–7.43 (m, 2H, Ph), 7.72 (d,  $^3J_{\text{HH}} = 8.0$  Hz, 2H, ArH), 8.01 (d,  $^3J_{\text{HH}} = 8.0$  Hz, 2H, ArH), 8.50 (s, 1H, N=CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  120.9 (ArC), 125.7 (q,  $^3J_{\text{CF}} = 4.0$  Hz, ArC), 126.6 (ArC), 129.0 (ArC), 129.3 (ArC), 132.8 (q,  $^2J_{\text{CF}} = 32.5$  Hz, ArC), 139.3 (ArC), 151.4 (ArC), 158.5 (N=CH). A  $^{13}\text{C}$  NMR signal assignable to  $\text{CF}_3$  could not be observed due to its low intensity.  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.9.



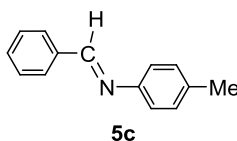
**Synthesis of *N*-benzylideneaniline (5b).** This compound was synthesized and isolated by a procedure identical with the above-mentioned General Procedure 5 by use of a THF (0.5 mL) solution of  $\text{PhC}\equiv\text{N}$  (13 mg, 0.13 mmol), 9-BBN (17 mg, 0.14 mmol), and **1a** (0.5 mg, 0.7  $\mu\text{mol}$ ; 0.5 mol%) for hydroboration (condition: room temperature, 1 h) and then by addition of a THF (0.5 mL) solution of PhBr (22 mg, 0.14 mmol), CyJohnPhos (4 mg, 0.01 mmol; 8 mol%),  $\text{Pd}(\text{dba})_2$  (2 mg, 3  $\mu\text{mol}$ ; 2 mol%), and  $\text{KO}^t\text{Bu}$  (17 mg, 0.15 mmol) in this order for subsequent C–N coupling (condition: 60  $^\circ\text{C}$  for 12 h). Purification according to the General Procedure 5 gave *N*-benzylideneaniline (**5b**) as a colorless oil (12 mg, 67  $\mu\text{mol}$ ) in 53% yield. **5b** was identified by GC-MS analysis and comparison of its  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data with the literature data.<sup>S6</sup>

**Data for 5b.**<sup>S6</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.17–7.23 (m, 3H, Ph), 7.36–7.42 (m, 2H, Ph), 7.43–7.51 (m, 3H, Ph), 7.86–7.92 (m, 2H, Ph), 8.45 (s, 1H, N=CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  120.9, 125.9, 128.77, 128.81, 129.1, 131.4, 152.2 (ArC), 160.4 (N=CH).



**Synthesis of *N*-benzylidene-*p*-toluidine (**5c**).** Title compound was synthesized and isolated by a procedure identical with the above-mentioned General Procedure 5 by use of a THF (0.5 mL) solution of PhC≡N (13 mg, 0.13 mmol), 9-BBN (17 mg, 0.14 mmol), and **1a** (0.5 mg, 0.7 μmol; 0.5 mol%) for hydroboration (condition: room temperature, 1 h) and then by addition of a THF (0.5 mL) solution of *p*-MeC<sub>6</sub>H<sub>4</sub>Br (25 mg, 0.15 mmol), CyJohnPhos (4 mg, 0.01 mmol; 8 mol%), Pd(dba)<sub>2</sub> (2 mg, 3 μmol; 2 mol%), and KO<sup>t</sup>Bu (17 mg, 0.15 mmol) in this order for subsequent C–N coupling (condition: 60 °C, 12 h). Purification according to the General Procedure 5 gave *N*-benzylidene-*p*-toluidine (**5c**) as a colorless oil (17 mg, 0.087 mmol) in 69% yield. **5c** was identified by GC-MS analysis and comparison of its <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR data with the literature data.<sup>S6b</sup>

**Data for **5c**.**<sup>S6b</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.36 (s, 3H, C<sub>6</sub>H<sub>4</sub>Me), 7.10–7.14 (AA'XX' multiplet, 2H, C<sub>6</sub>H<sub>4</sub>Me), 7.16–7.21 (AA'XX' multiplet, 2H, C<sub>6</sub>H<sub>4</sub>Me), 7.43–7.47 (m, 3H, Ph), 7.86–7.91 (m, 2H, Ph), 8.45 (s, 1H, N=CH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ 21.0 (C<sub>6</sub>H<sub>4</sub>Me), 120.8, 128.7, 129.8, 131.2, 135.8, 136.4, 149.5 (ArC), 159.5 (N=CH).

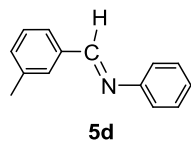


**Synthesis of *N*-(3-methylbenzylidene)aniline (**5d**).** This compound was synthesized and isolated by a procedure identical with the above-mentioned General Procedure 5 by use of a THF (1 mL) solution of (3-MeC<sub>6</sub>H<sub>4</sub>)C≡N (34 mg, 0.29 mmol), 9-BBN (39 mg, 0.32 mmol), and **1a** (1.0 mg, 1.4 μmol; 0.5 mol%) for hydroboration (condition: 1 h at room temperature) and then by addition of a THF (1 mL) solution of PhBr (50 mg, 0.32 mmol), CyJohnPhos (5.0 mg, 0.014 mmol; 5 mol%), Pd(dba)<sub>2</sub> (3.5 mg, 6.1 μmol; 2 mol%), and KO<sup>t</sup>Bu (36 mg, 0.32 mmol) in this order for subsequent C–N coupling (condition: 60 °C for 12 h). Purification according to the General Procedure 5 gave *N*-(3-methylbenzylidene)aniline (**5d**) as a colorless oil (33 mg, 0.17

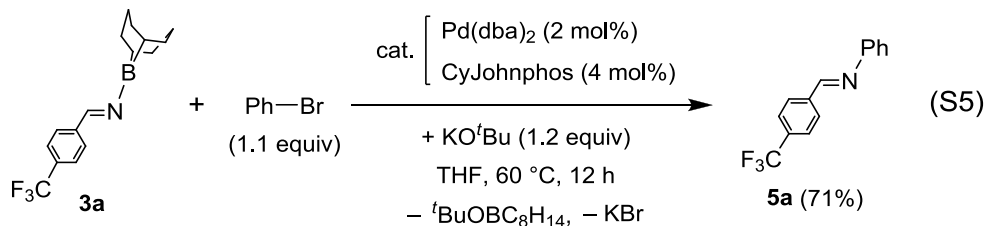


mmol) in 59% yield. **5d** was identified by GC-MS analysis and comparison of its  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data with the literature data.<sup>S6c</sup>

**Data for 5d.**<sup>S6c</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.42 (s, 3H, 3-Me), 7.17–7.26 (m, 3H, ArH), 7.29 (d,  $^3J_{\text{HH}} = 7.2$  Hz, 1H, ArH), 7.33–7.42 (m, 3H, ArH), 7.66 (d,  $^3J_{\text{HH}} = 7.2$  Hz, 1H, ArH), 7.76 (s, 1H, ArH), 8.42 (s, 1H, N=CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.3 ( $\text{C}_6\text{H}_4\text{Me}$ ), 120.8, 125.8, 126.4, 128.6, 129.0, 129.1, 132.2, 136.2, 138.5, 152.2 (ArC), 160.6 (N=CH).



**Synthesis of *N*-[4-(trifluoromethyl)benzylidene]aniline (**5a**) starting from isolated *N*-borylimine **3a**.** In a 10 mL glass vial with a screw cap, (4- $\text{CF}_3\text{C}_6\text{H}_4$ )CH=N(BC $_8\text{H}_{14}$ ) (**3a**; 29 mg, 0.10 mmol), PhBr (17 mg, 0.11 mmol), KO $^t$ Bu (14 mg, 0.12 mmol), Pd(dba) $_2$  (1.2 mg, 2.1  $\mu\text{mol}$ ; 2 mol%), and CyJohnPhos (1.4 mg, 4.0  $\mu\text{mol}$ ; 4 mol%) were dissolved in THF (1 mL). The solution was heated at 60  $^\circ\text{C}$  for 12 h, and then volatiles were removed under vacuum. To the residual red oil was added hexane, and the insoluble precipitates were removed by filtration to give a red solution containing **5a**. After evaporation of the solution, the resulting crude sample was purified by flash chromatography [silica gel (5 g), eluent: hexane/EtOAc (19 : 1)]. *N*-[4-(Trifluoromethyl)benzylidene]aniline (**5a**) was obtained as a colorless oil (17.8 mg, 71.4  $\mu\text{mol}$ ) in 71% yield.



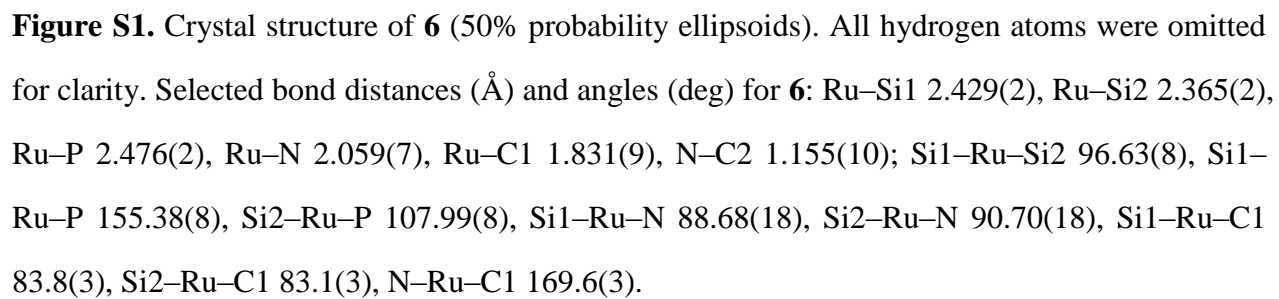
## 2. X-ray Crystal Structure Determination

X-ray quality single crystals of **6** were obtained by slow evaporation of a cyclohexane- $d_{12}$  solution of **6** under Ar atmosphere. Intensity data for the analysis were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) under a cold nitrogen stream ( $T = 150$  K). A profile fitting method was used for integration of reflection intensities to improve their accuracy especially for weak reflections. A numerical absorption correction was applied to the collected reflections. The structure was solved by the Patterson method using the DIRDIF-2008 program<sup>S7</sup> and refined by full matrix least-squares techniques on all  $F^2$  data with SHELXL-2016/6.<sup>S8</sup> Anisotropic refinement was applied to all non-hydrogen atoms, and all the hydrogen atoms were placed at calculated positions. A reflection for **6**, i.e.  $(h\ k\ l) = (0\ 0\ 2)$ , was omitted from the final refinement because its intensity was significantly affected by the beam stop. All calculations were carried out using Yadokari-XG.<sup>S9</sup> CCDC reference number for **6**: 1893612. Crystallographic data are available as a CIF file. Selected crystallographic data for **6** are given in Table S4, and the crystal structure of **6** is depicted in Figure S1.

**Table S4. Crystallographic Data for Ru[ $\kappa^2$ (*Si*,*Si*)-xantsil](CO)(PCyp<sub>3</sub>)[N≡C(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)]  
(6)**

formula	C <sub>43</sub> H <sub>55</sub> NO <sub>2</sub> F <sub>3</sub> Si <sub>2</sub> PRu
formula weight	863.10
crystal system	orthorhombic
crystal size/mm <sup>3</sup>	0.20 × 0.10 × 0.05
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)
<i>a</i> /Å	11.0193(4)
<i>b</i> /Å	18.4297(8)
<i>c</i> /Å	20.5988(7)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	90
<i>V</i> /Å <sup>3</sup>	4183.3(3)
<i>Z</i>	4
<i>D</i> <sub>calcd</sub> /g·cm <sup>-3</sup>	1.370
<i>F</i> (000)	1800
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	0.520
reflections collected	42964
unique reflections ( <i>R</i> <sub>int</sub> )	9576 (0.1742)
refined parameters	484
<i>R</i> 1, <i>wR</i> 2 (all data) <sup><i>a,b</i></sup>	0.0901, 0.1519
<i>R</i> 1, <i>wR</i> 2 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup><i>a,b</i></sup>	0.0699, 0.1429
GOF	1.026
absolute structure parameter	−0.02(3)
largest residual peak, hole/e·Å <sup>-3</sup>	0.728, −0.732

$$^a R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, \quad ^b wR2 = \{ \Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2] \}^{1/2}$$



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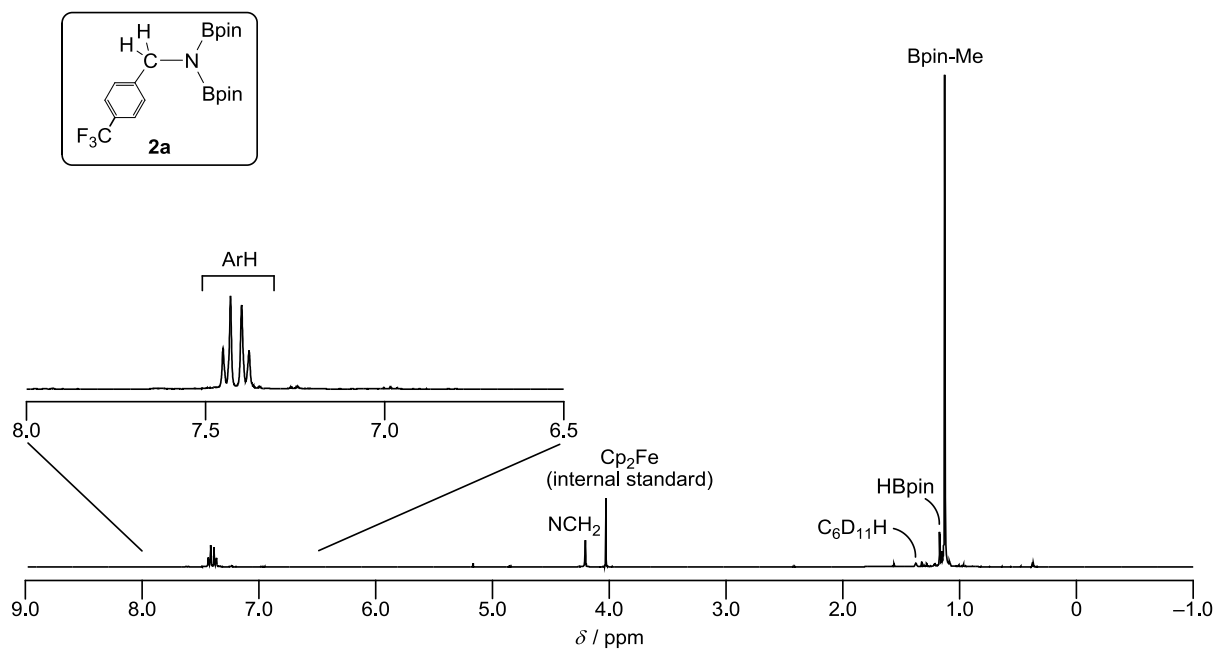
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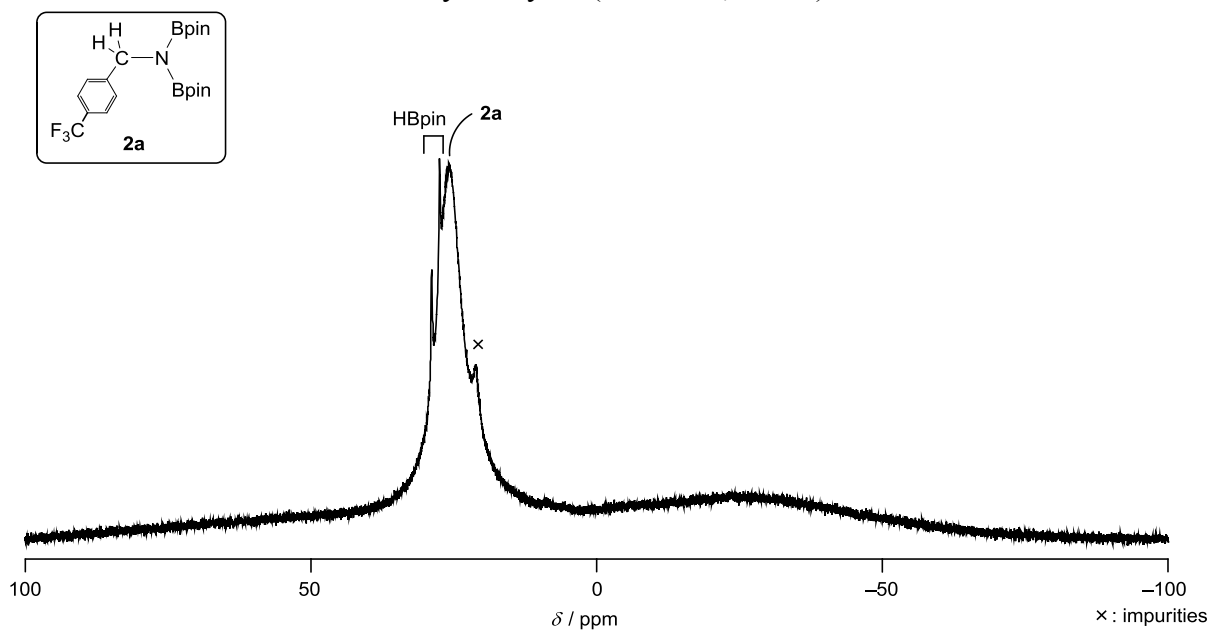
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#### 4. NMR Spectra of Hydroboration and C–N Coupling Products 2–5 and Complex 6

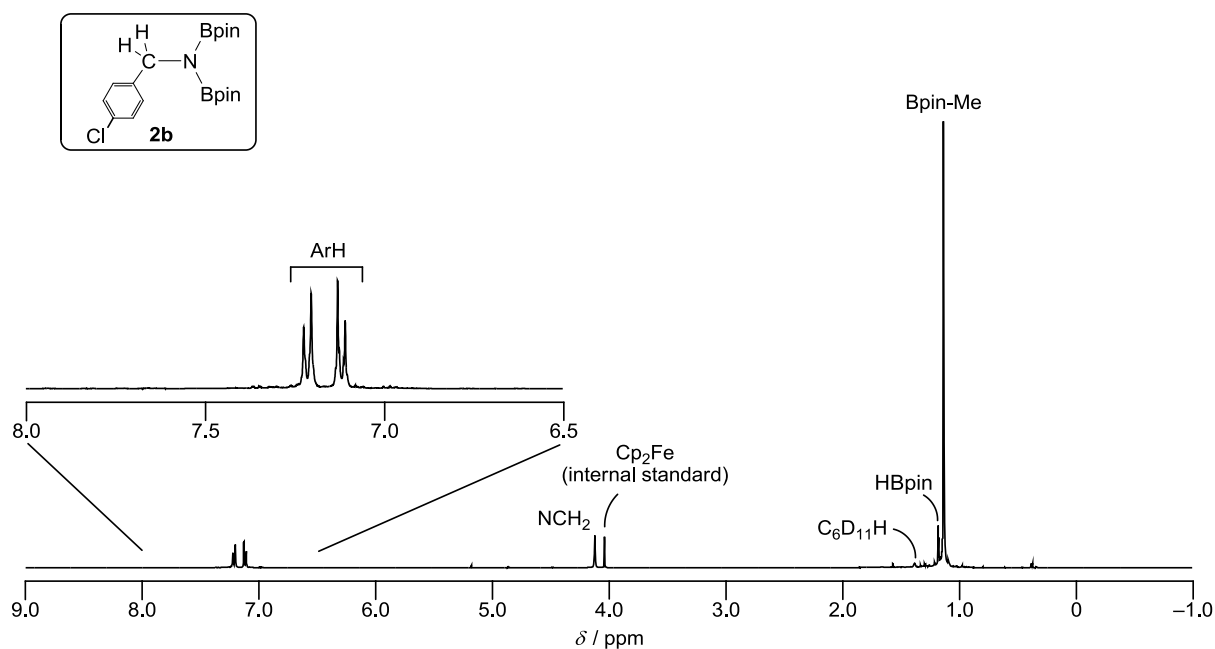


**Figure S2.**  $^1\text{H}$  NMR spectrum of **2a** in a reaction mixture of 4- $\text{CF}_3\text{C}_6\text{H}_4\text{C}\equiv\text{N}$  with HBpin catalyzed by **1a** (400 MHz,  $\text{C}_6\text{D}_{12}$ ).

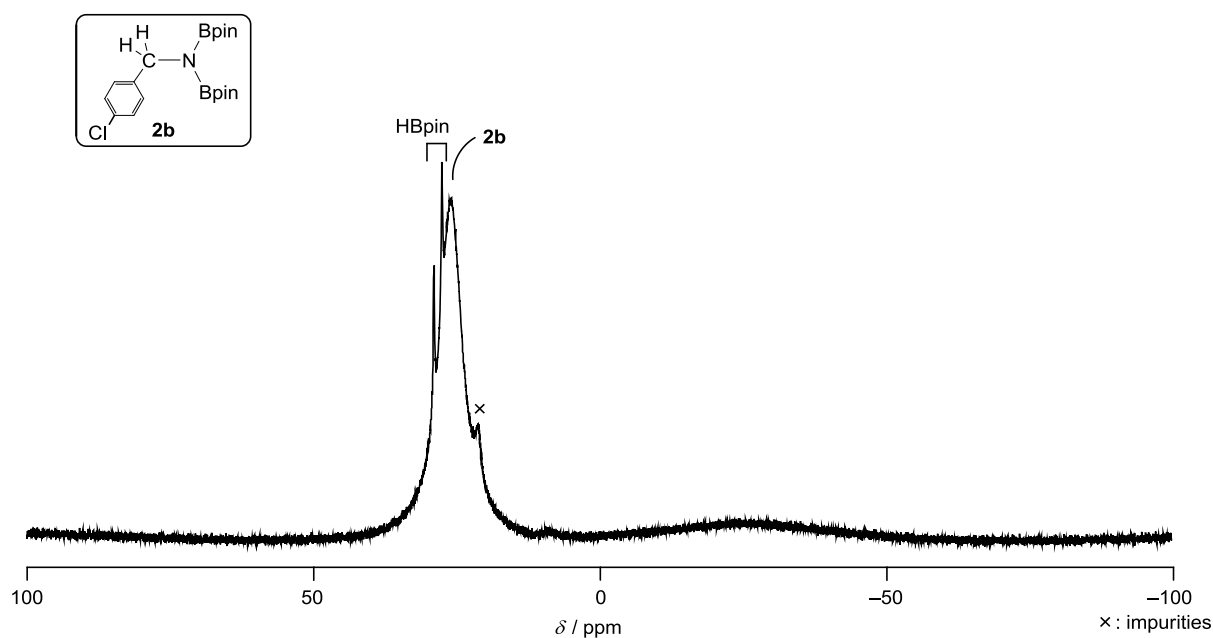


**Figure S3.**  $^{11}\text{B}$  NMR spectrum of **2a** in a reaction mixture of 4- $\text{CF}_3\text{C}_6\text{H}_4\text{C}\equiv\text{N}$  with HBpin catalyzed by **1a** (128 MHz,  $\text{C}_6\text{D}_{12}$ ).

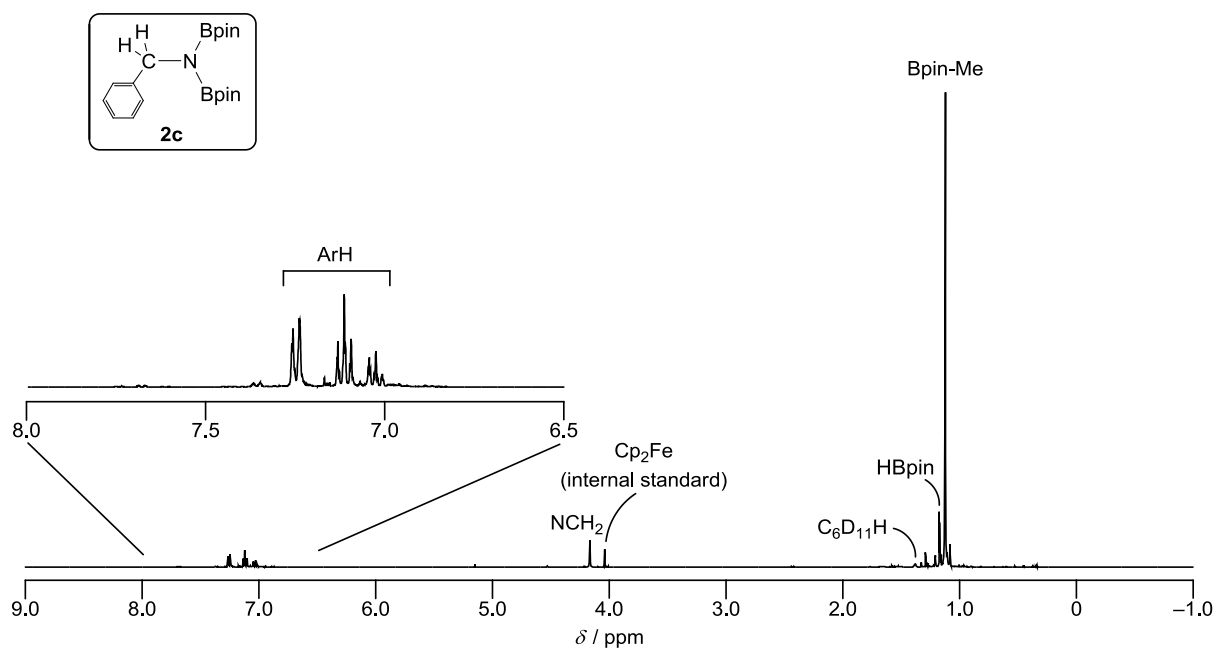




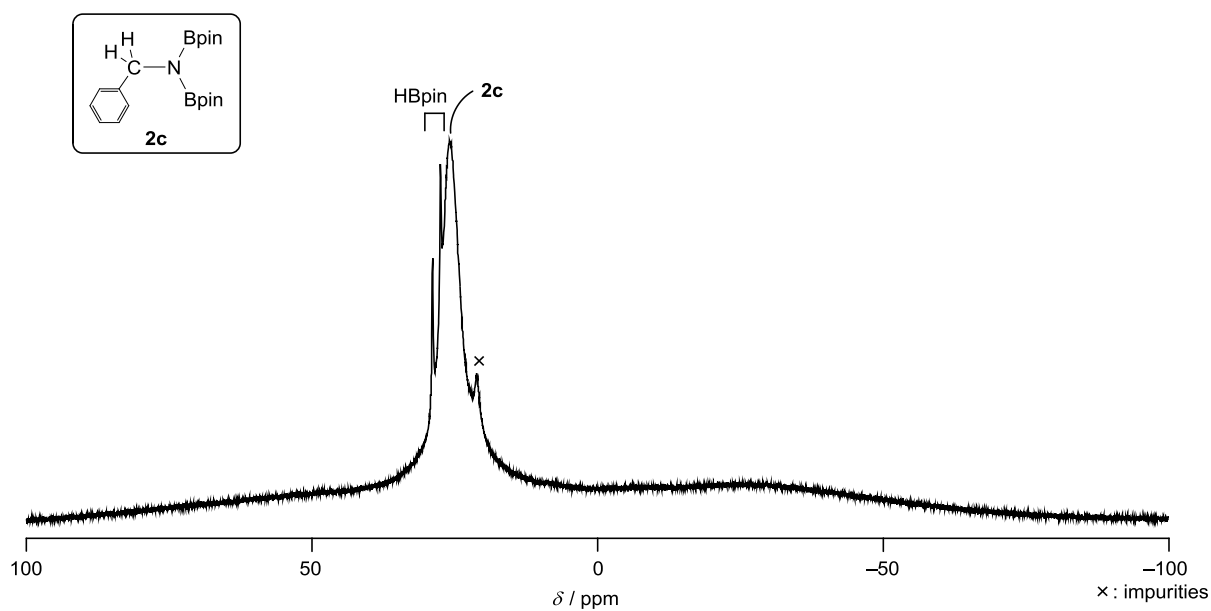
**Figure S4.** <sup>1</sup>H NMR spectrum of **2b** in a reaction mixture of 4-ClC<sub>6</sub>H<sub>4</sub>C≡N with HBpin catalyzed by **1a** (400 MHz, C<sub>6</sub>D<sub>12</sub>).



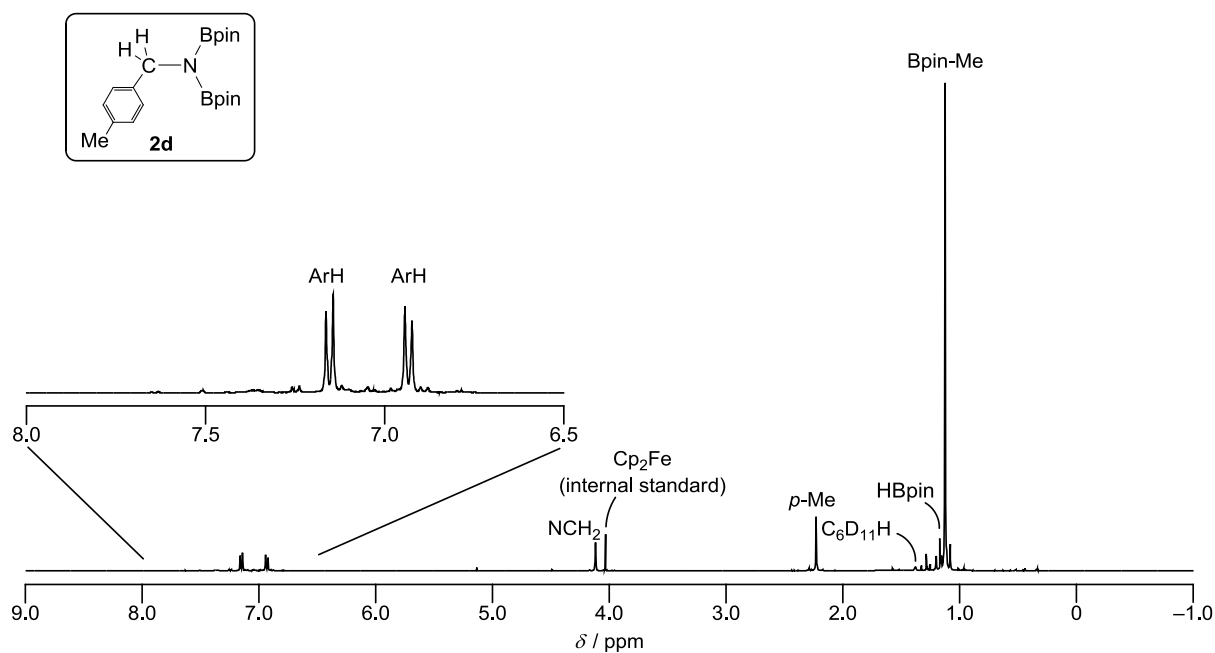
**Figure S5.** <sup>11</sup>B NMR spectrum of **2b** in a reaction mixture of 4-ClC<sub>6</sub>H<sub>4</sub>C≡N with HBpin catalyzed by **1a** (128 MHz, C<sub>6</sub>D<sub>12</sub>).



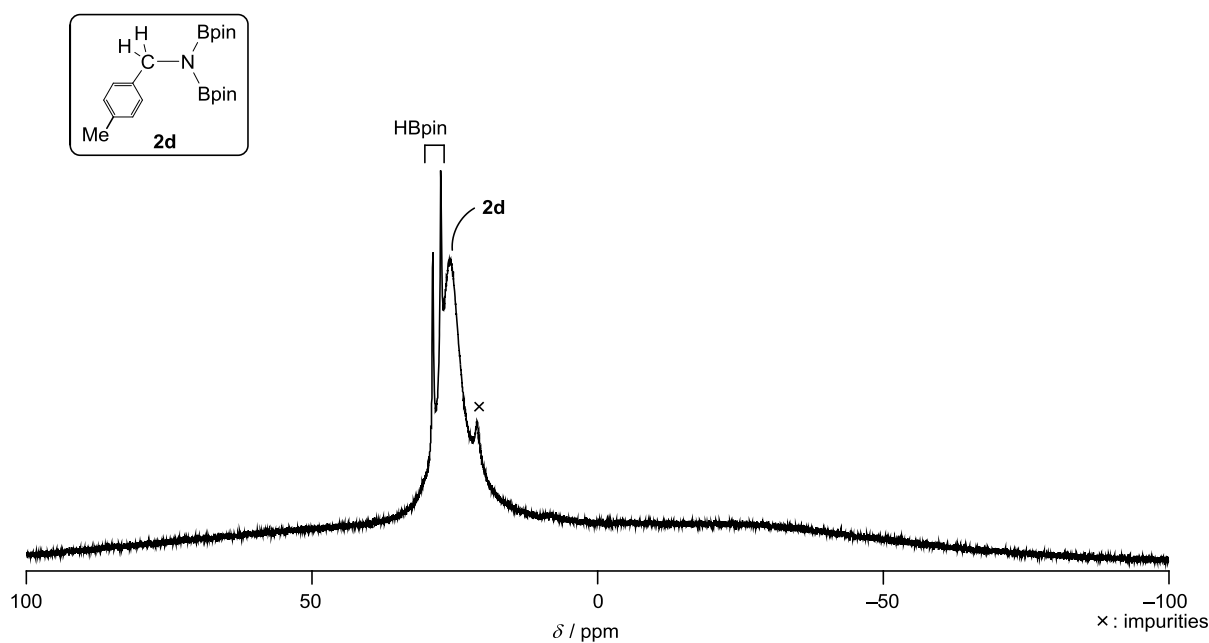
**Figure S6.** <sup>1</sup>H NMR spectrum of **2c** in a reaction mixture of PhC≡N with HBpin catalyzed by **1a** (400 MHz, C<sub>6</sub>D<sub>12</sub>).



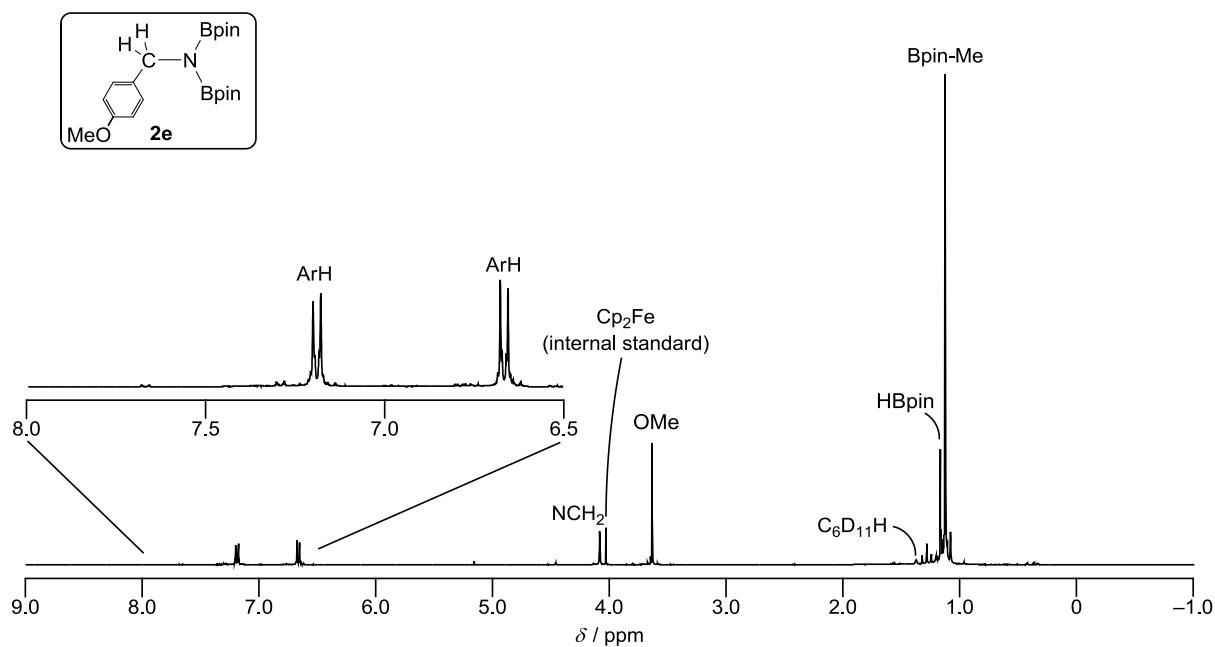
**Figure S7.** <sup>11</sup>B NMR spectrum of **2c** in a reaction mixture of PhC≡N with HBpin catalyzed by **1a** (128 MHz, C<sub>6</sub>D<sub>12</sub>).



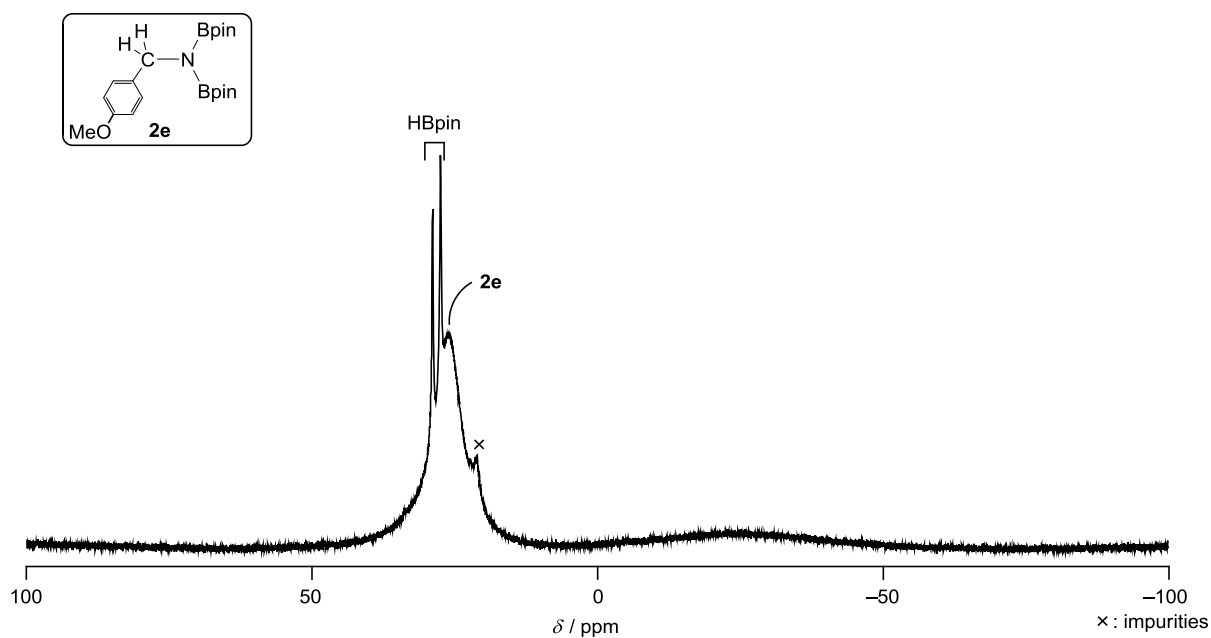
**Figure S8.** <sup>1</sup>H NMR spectrum of **2d** in a reaction mixture of 4-MeC<sub>6</sub>H<sub>4</sub>C≡N with HBpin catalyzed by **1a** (400 MHz, C<sub>6</sub>D<sub>12</sub>).



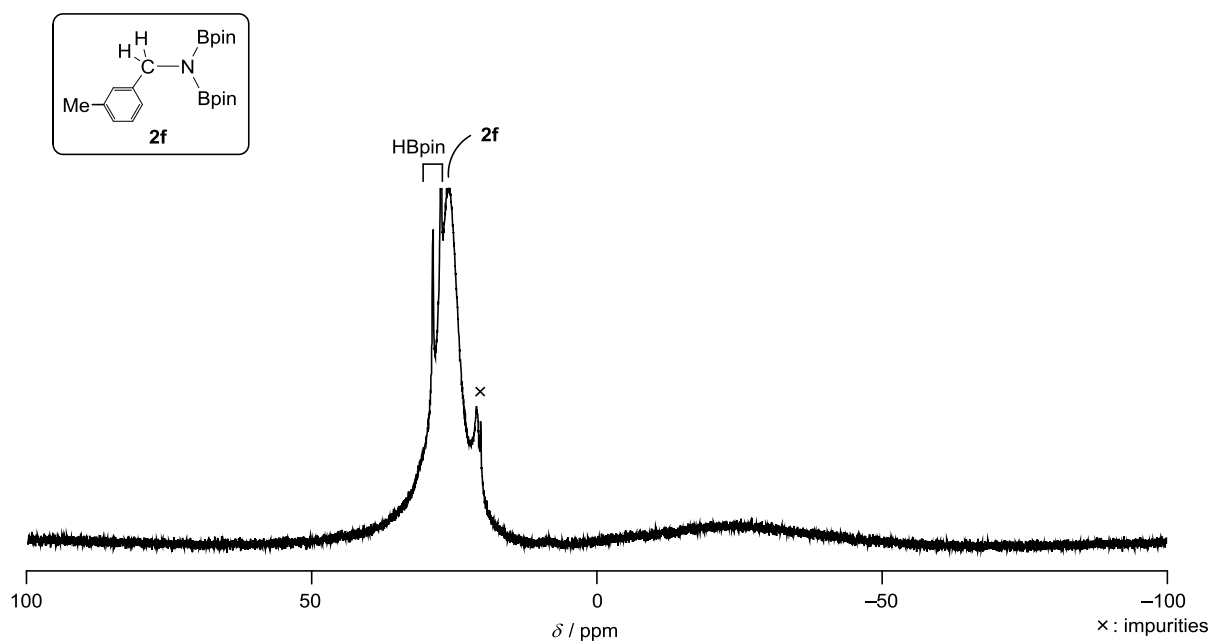
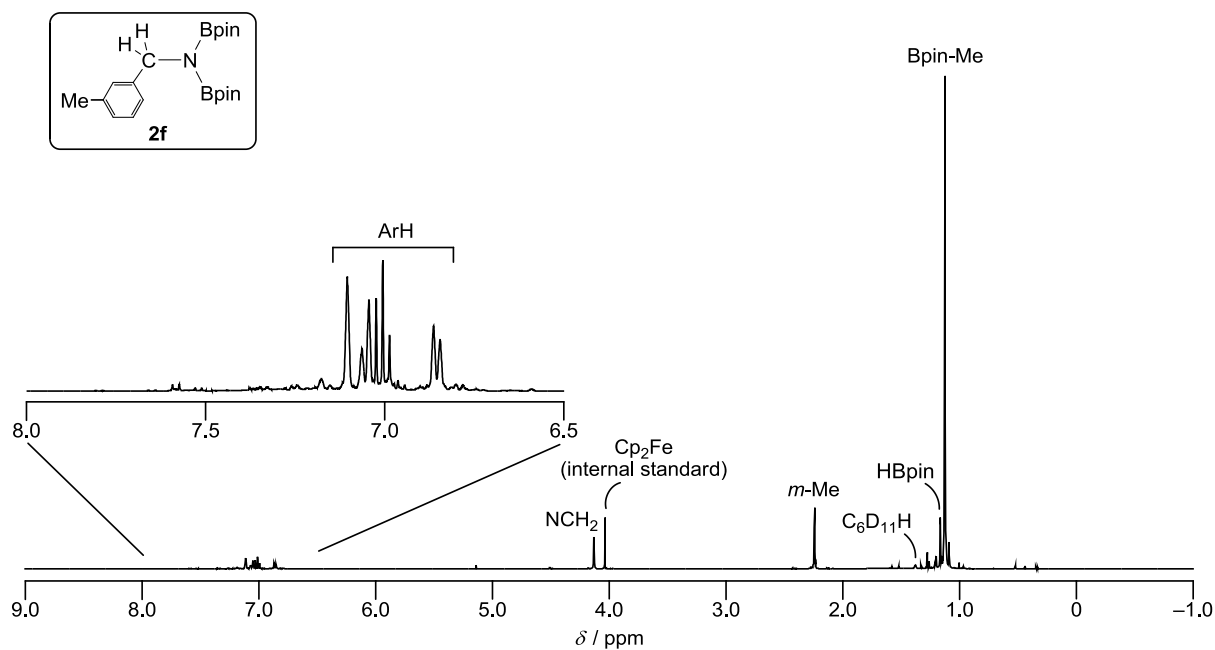
**Figure S9.** <sup>11</sup>B NMR spectrum of **2d** in a reaction mixture of 4-MeC<sub>6</sub>H<sub>4</sub>C≡N with HBpin catalyzed by **1a** (128 MHz, C<sub>6</sub>D<sub>12</sub>).

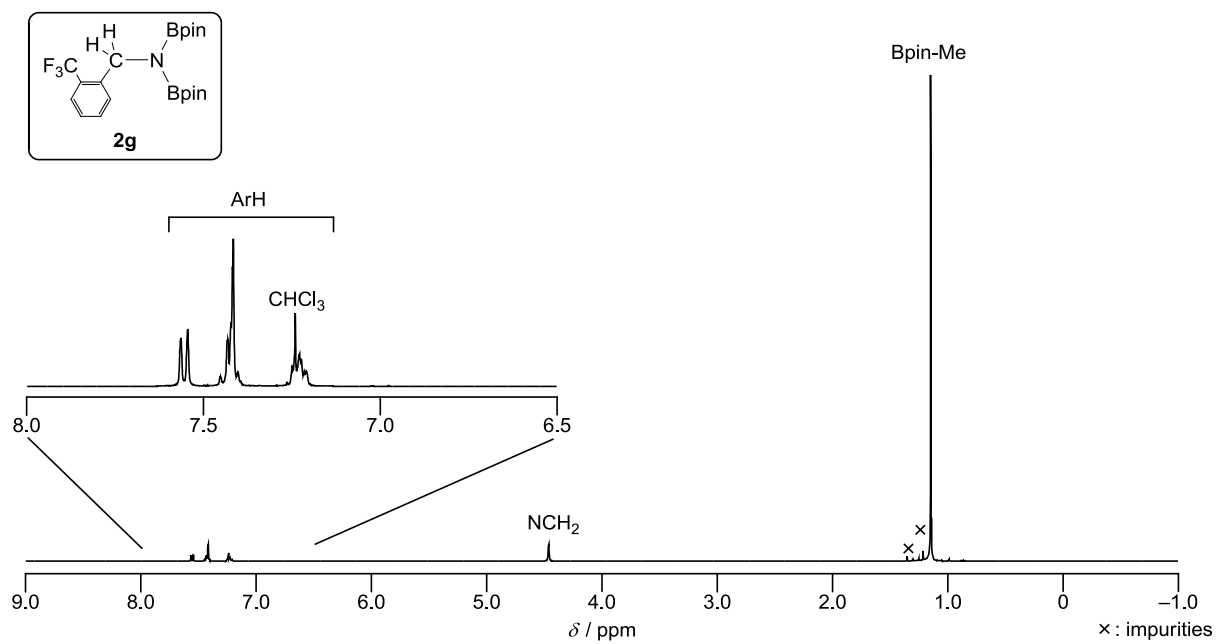


**Figure S10.** <sup>1</sup>H NMR spectrum of **2e** in a reaction mixture of 4-MeOC<sub>6</sub>H<sub>4</sub>C≡N with HBpin catalyzed by **1a** (400 MHz, C<sub>6</sub>D<sub>12</sub>).

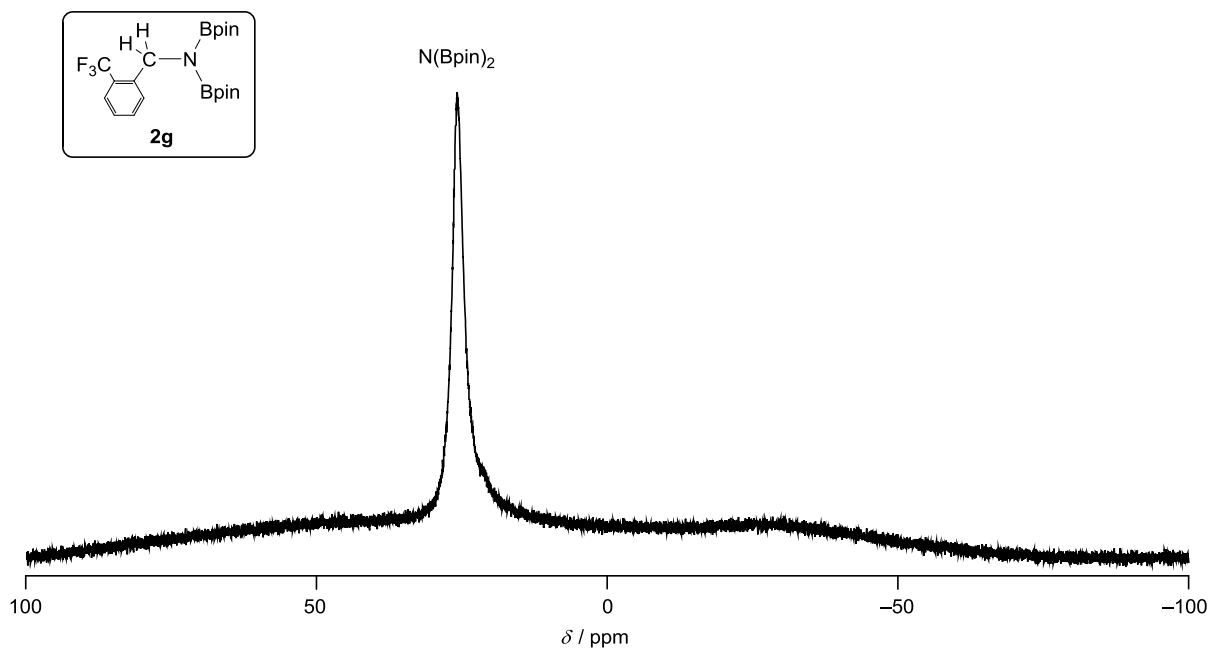


**Figure S11.** <sup>11</sup>B NMR spectrum of **2e** in a reaction mixture of 4-MeOC<sub>6</sub>H<sub>4</sub>C≡N with HBpin catalyzed by **1a** (128 MHz, C<sub>6</sub>D<sub>12</sub>).

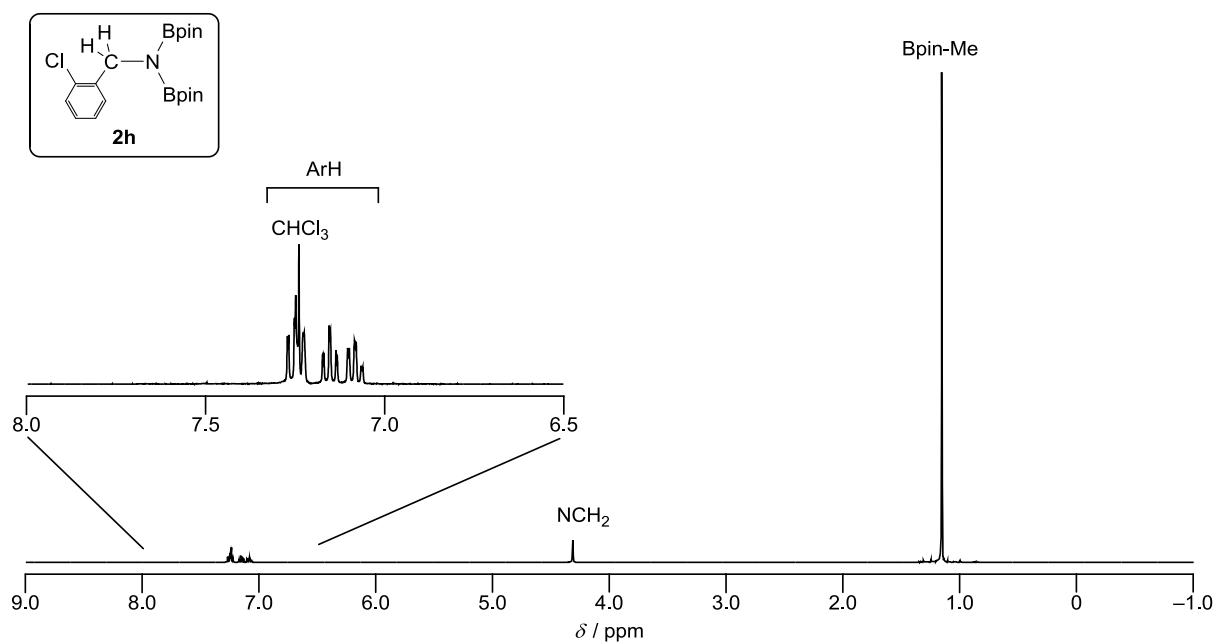
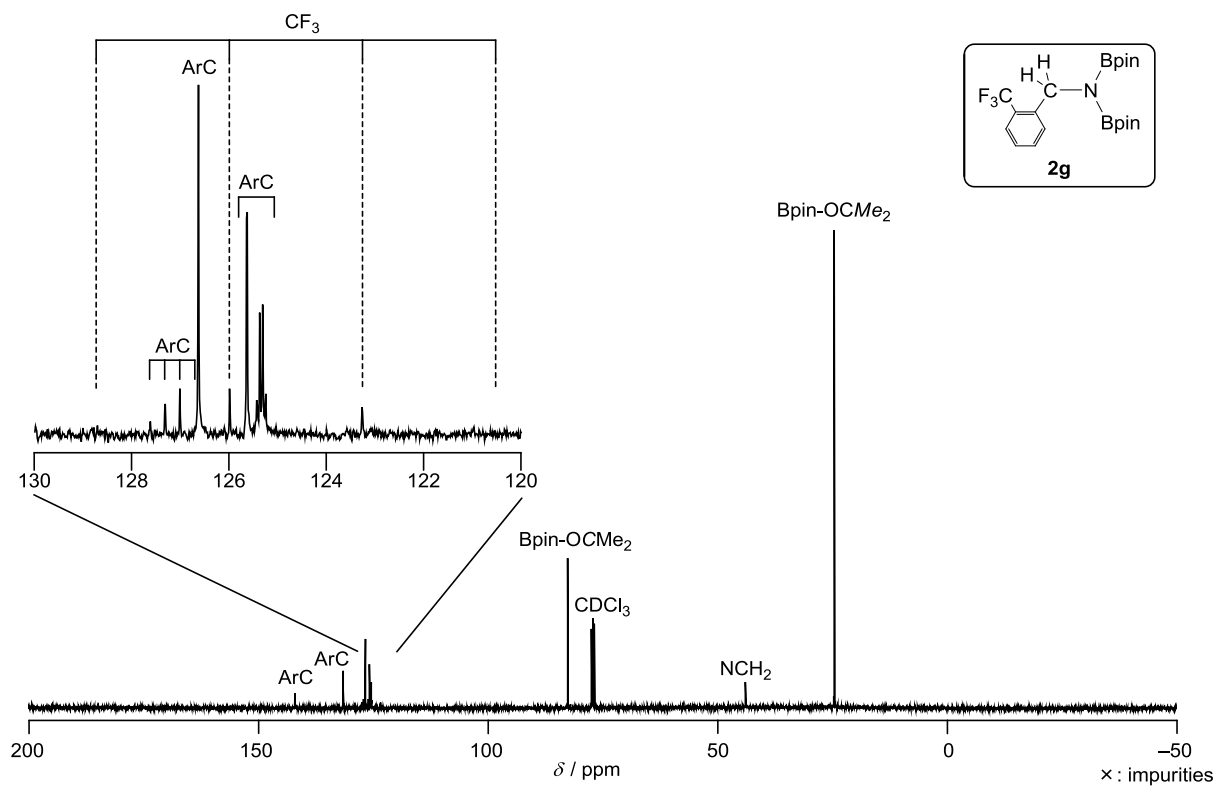


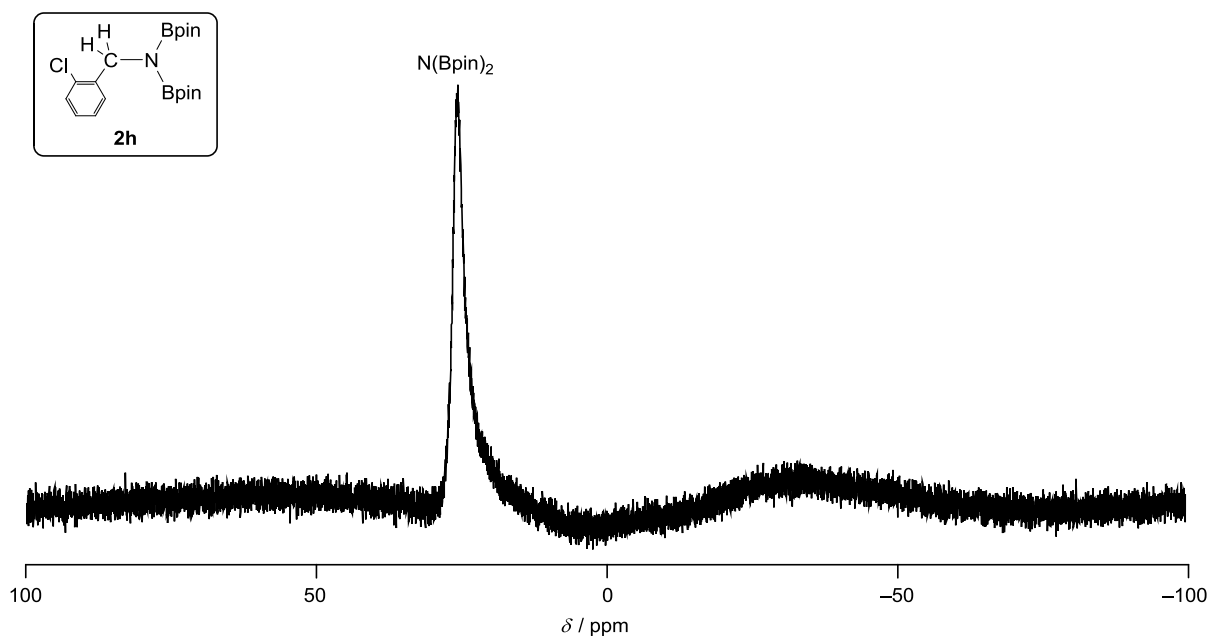


**Figure S14.** <sup>1</sup>H NMR spectrum of **2g** (400 MHz, CDCl<sub>3</sub>).

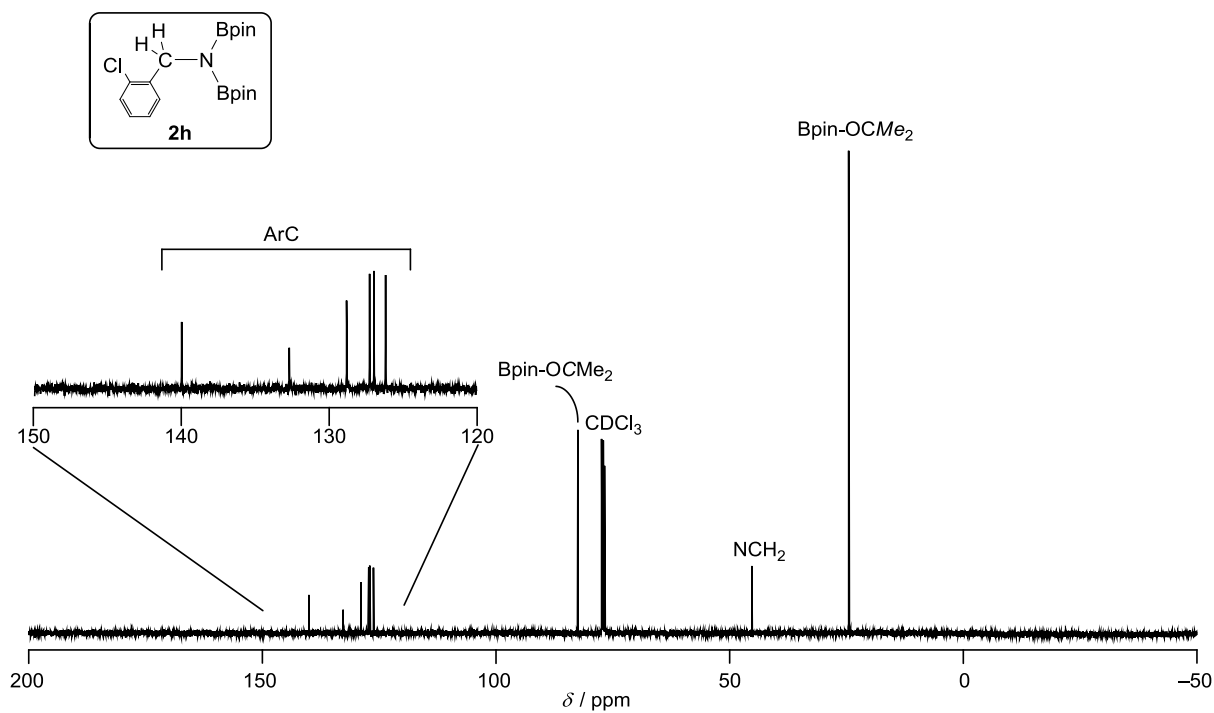


**Figure S15.** <sup>11</sup>B NMR spectrum of **2g** (128 MHz, CDCl<sub>3</sub>).



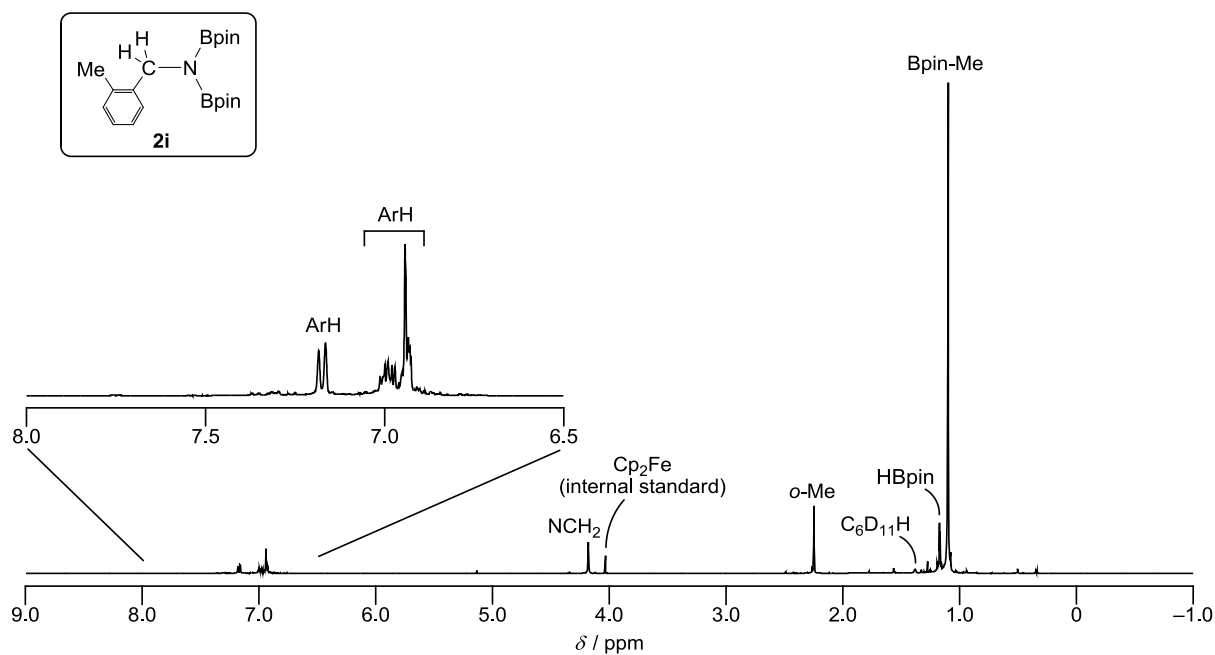


**Figure S18.**  $^{11}\text{B}$  NMR spectrum of **2h** (128 MHz,  $\text{CDCl}_3$ ).

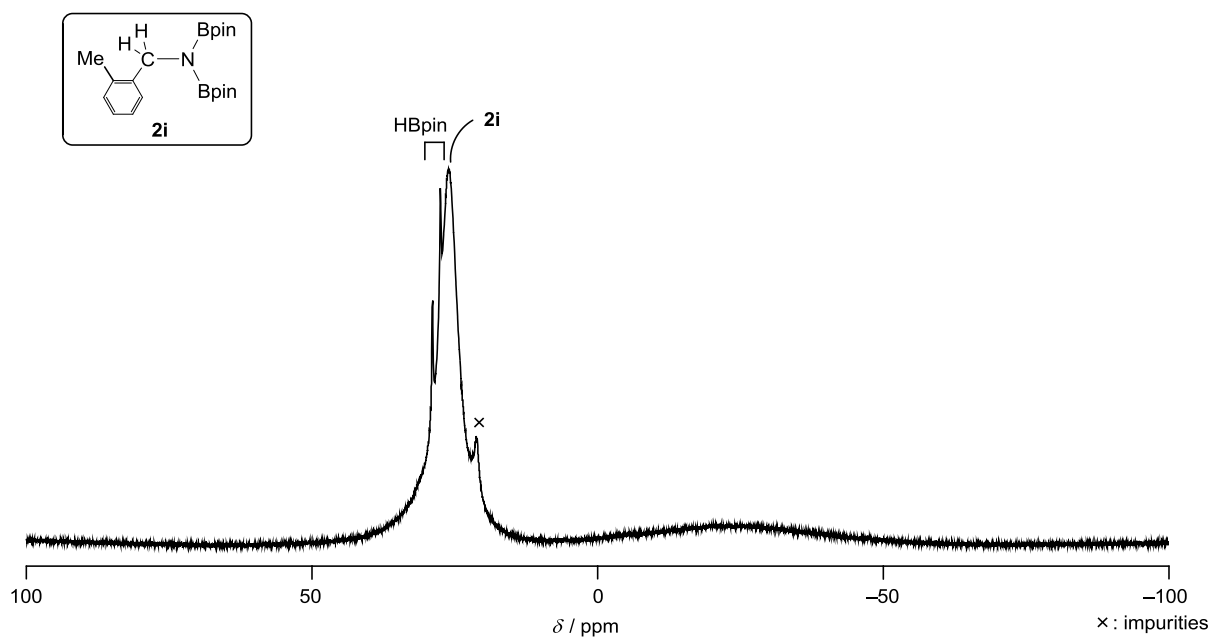


**Figure S19.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2h** (101 MHz,  $\text{CDCl}_3$ ).

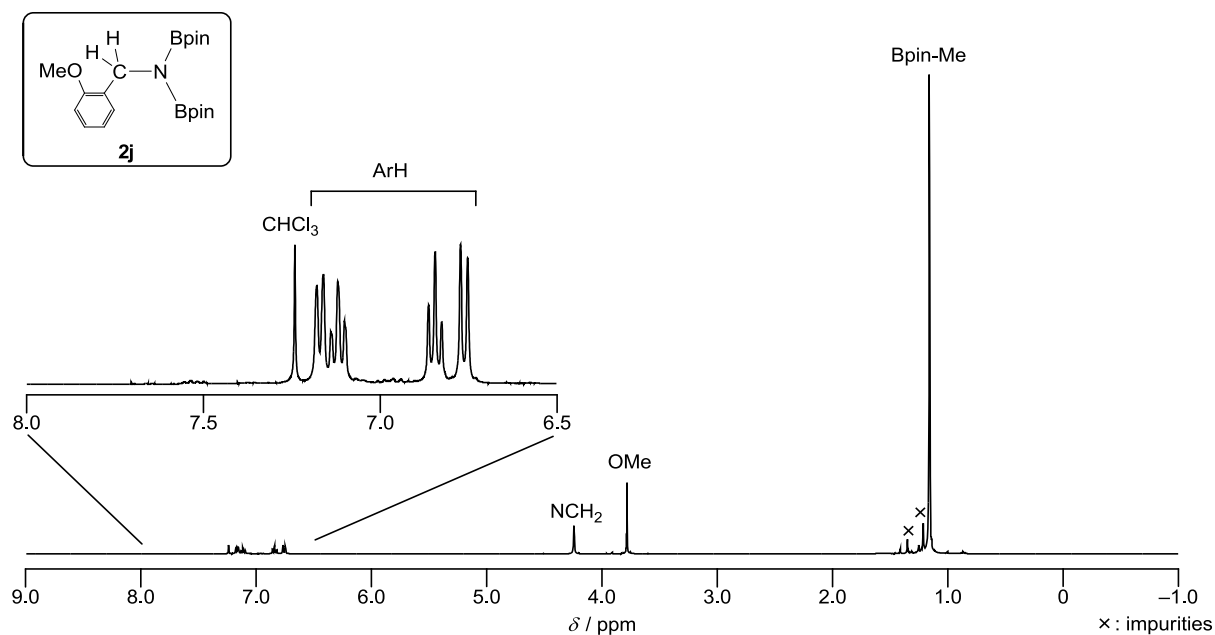




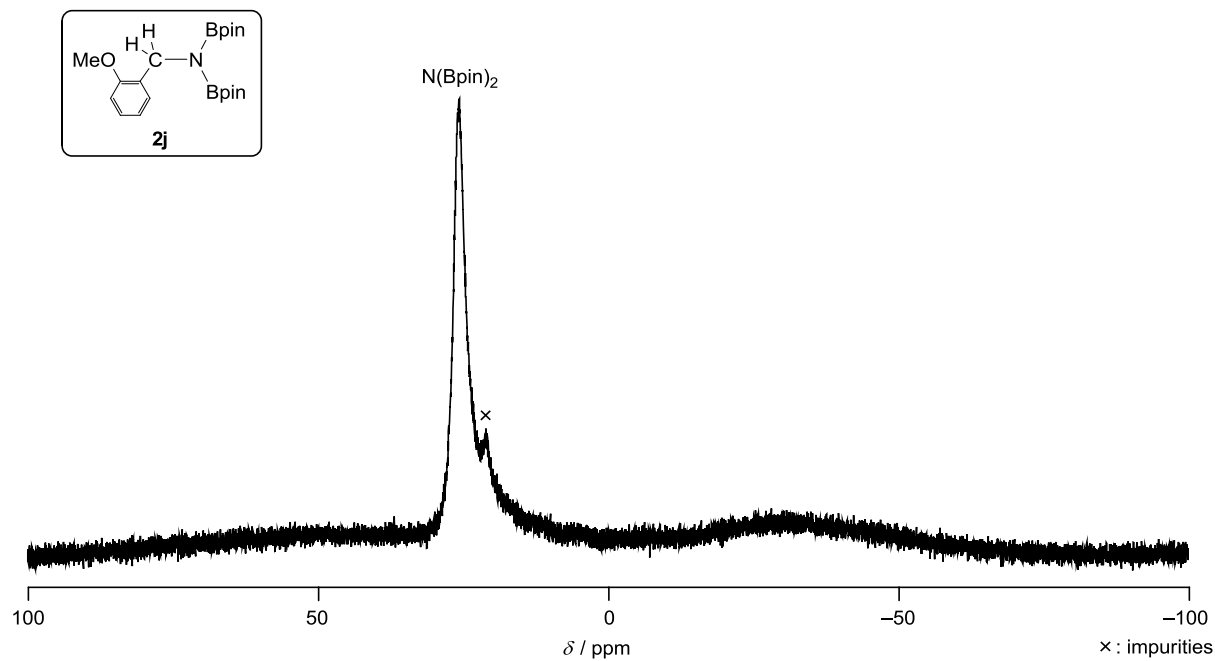
**Figure S20.**  $^1\text{H}$  NMR spectrum of **2i** in a reaction mixture of 2-MeC<sub>6</sub>H<sub>4</sub>C≡N with HBpin catalyzed by **1a** (400 MHz, C<sub>6</sub>D<sub>12</sub>).



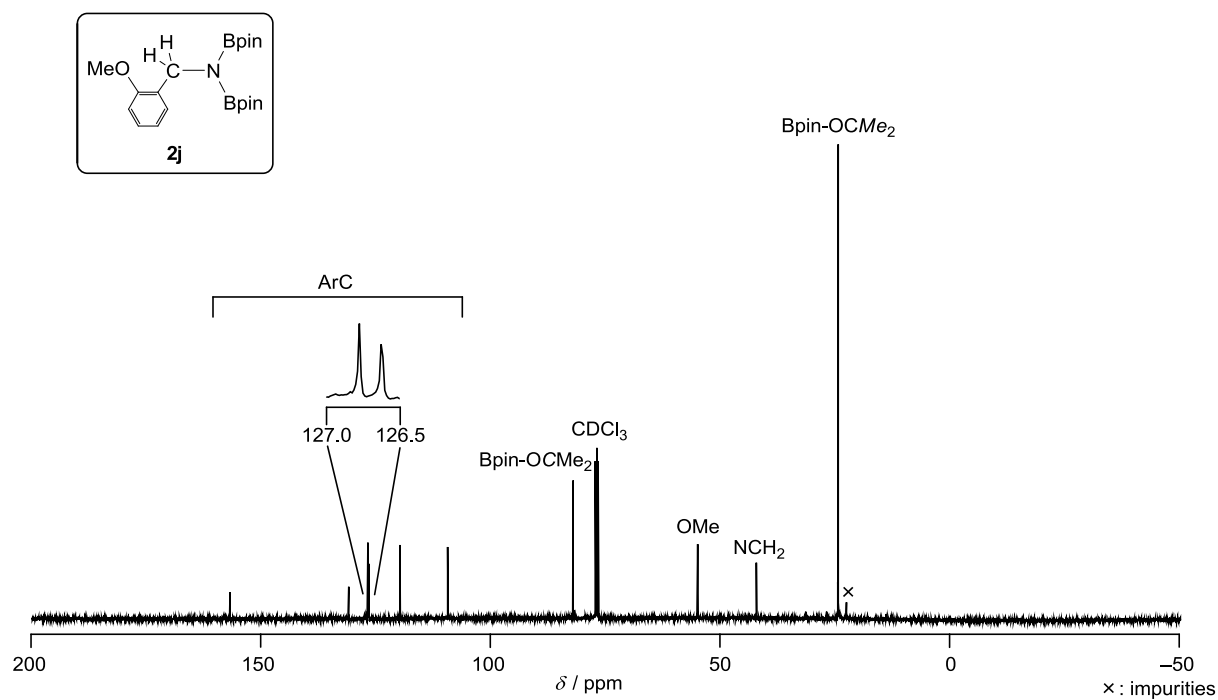
**Figure S21.**  $^{11}\text{B}$  NMR spectrum of **2i** in a reaction mixture of 2-MeC<sub>6</sub>H<sub>4</sub>C≡N with HBpin catalyzed by **1a** (128 MHz, C<sub>6</sub>D<sub>12</sub>).



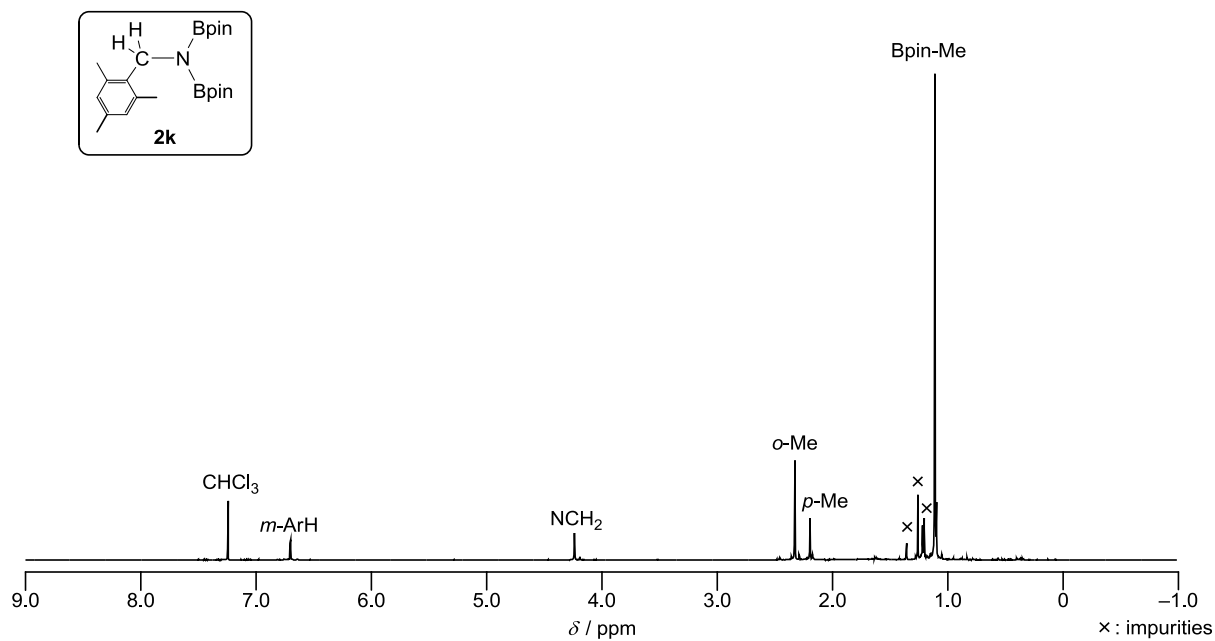
**Figure S22.** <sup>1</sup>H NMR spectrum of **2j** (400 MHz, CDCl<sub>3</sub>).



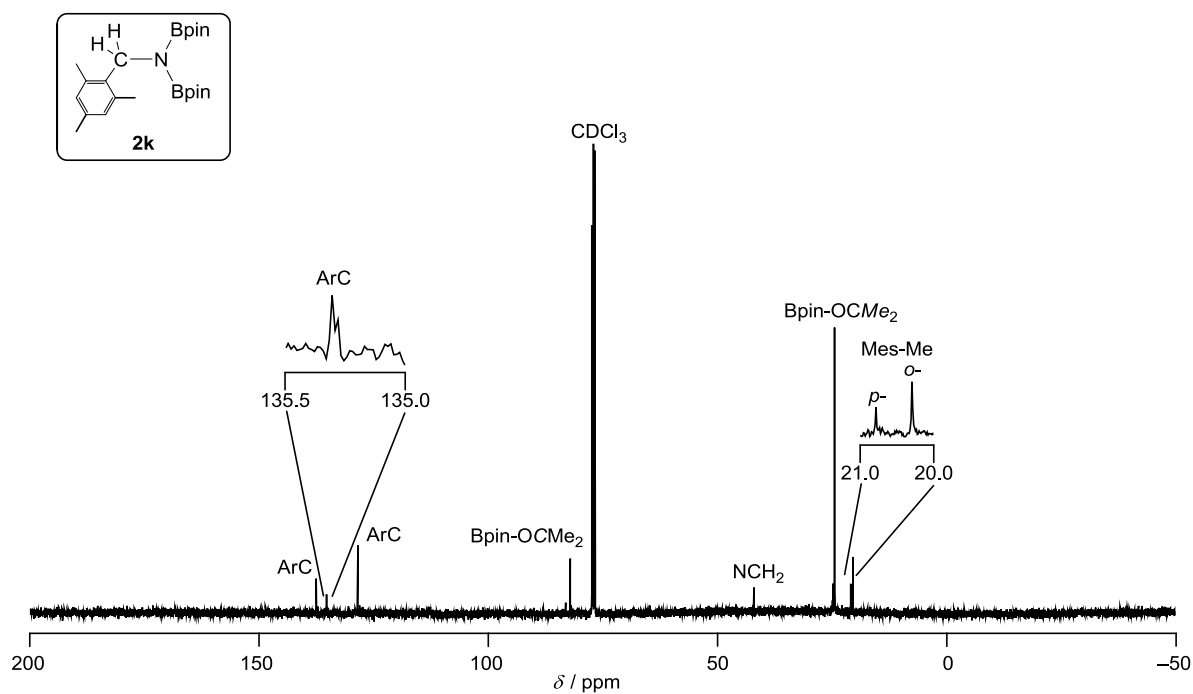
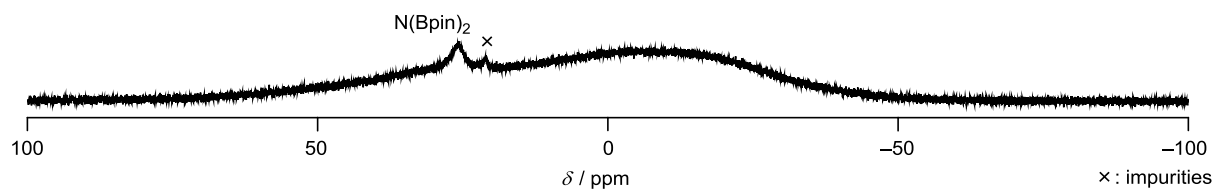
**Figure S23.** <sup>11</sup>B NMR spectrum of **2j** (128 MHz, CDCl<sub>3</sub>).

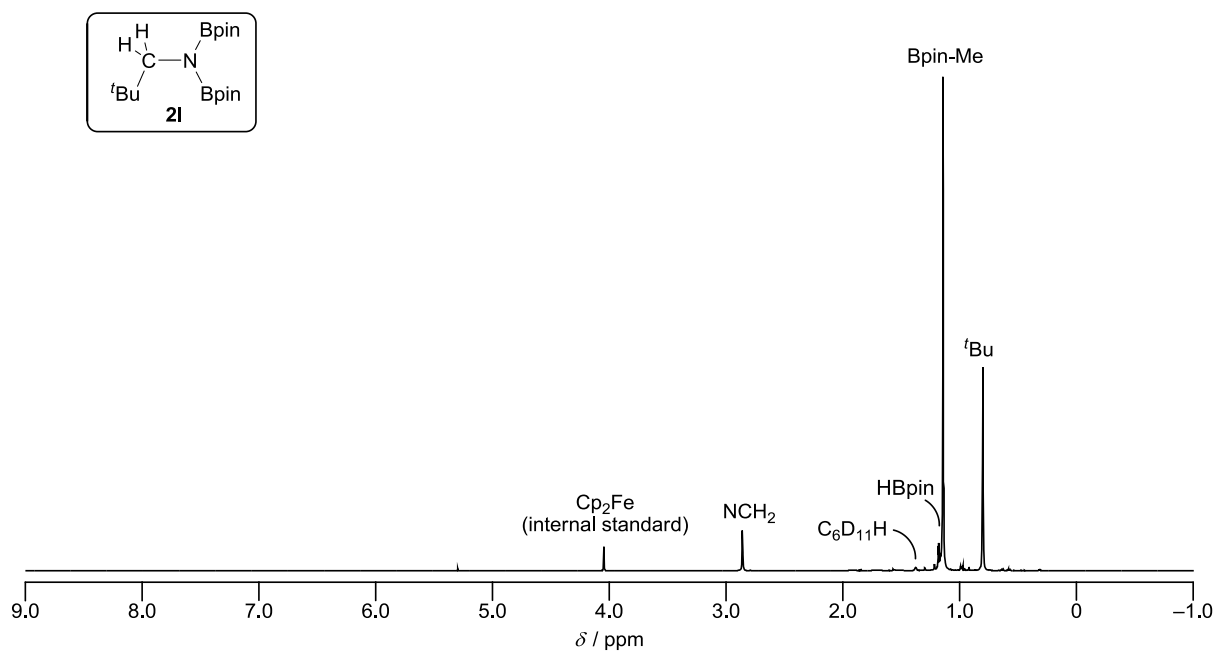


**Figure S24.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2j** (101 MHz,  $\text{CDCl}_3$ ).

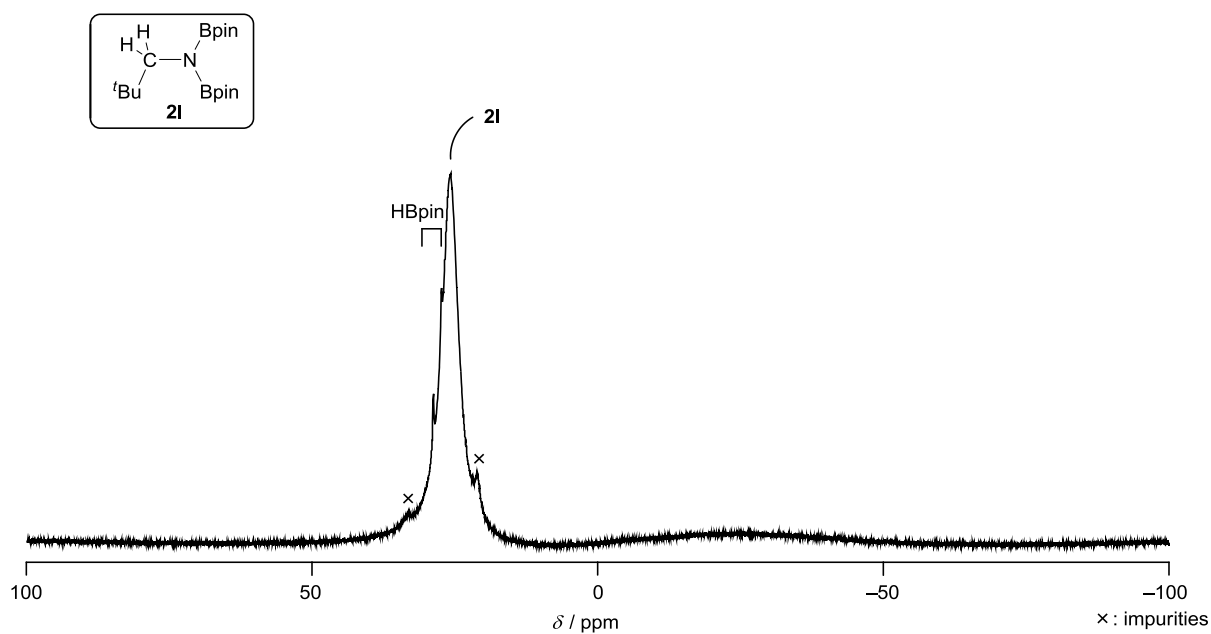


**Figure S25.**  $^1\text{H}$  NMR spectrum of **2k** (400 MHz,  $\text{CDCl}_3$ ).

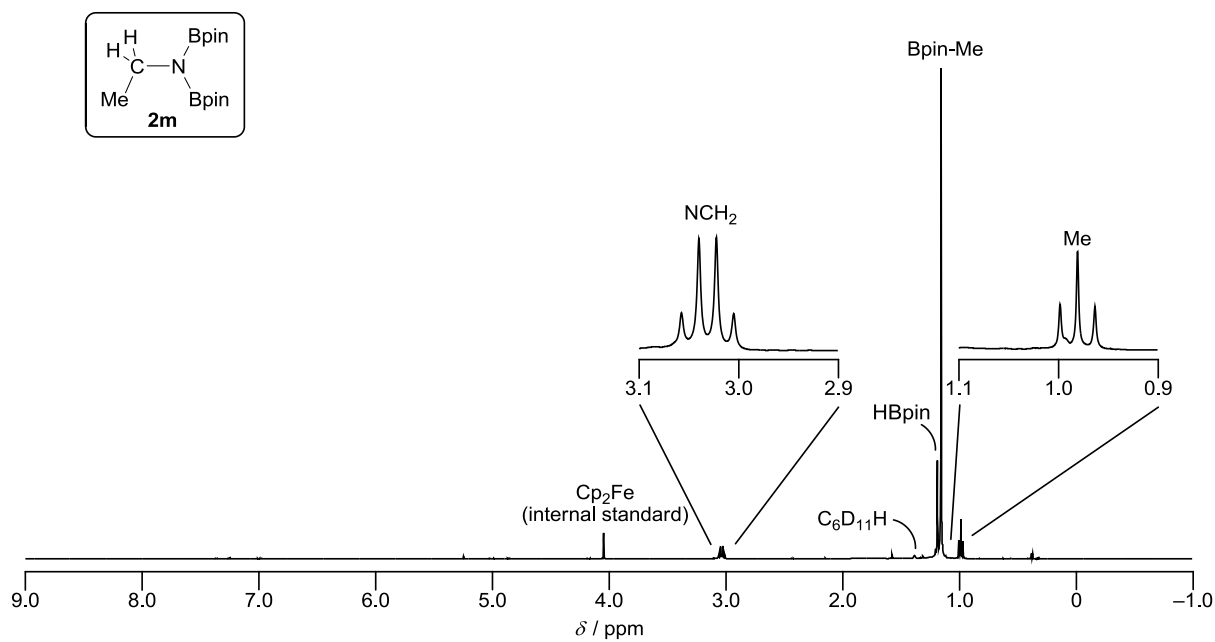




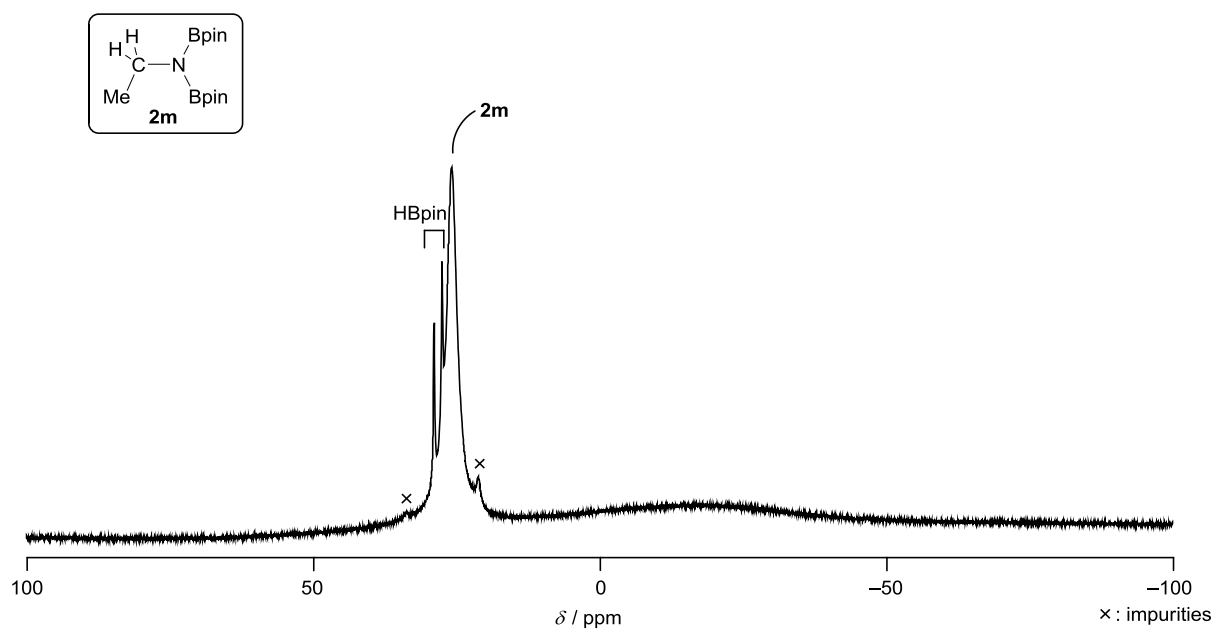
**Figure S28.**  $^1\text{H}$  NMR spectrum of **2I** in a reaction mixture of  $t\text{BuC}\equiv\text{N}$  with HBpin catalyzed by **1a** (400 MHz,  $\text{C}_6\text{D}_{12}$ ).



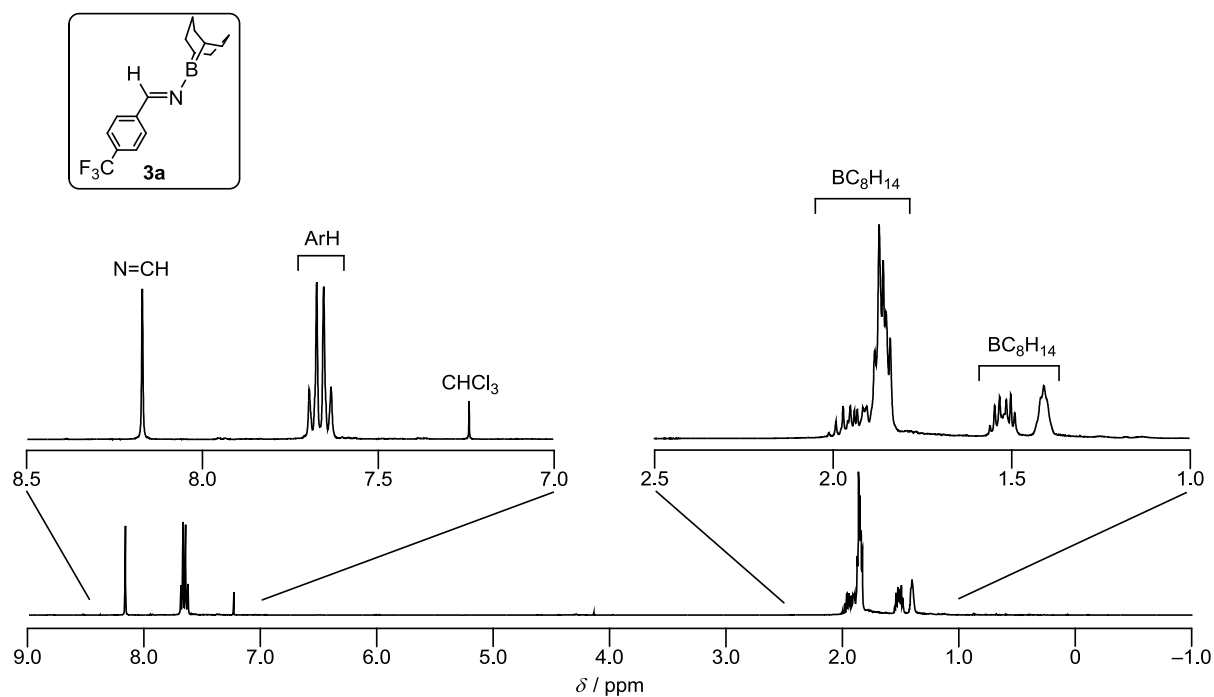
**Figure S29.**  $^{11}\text{B}$  NMR spectrum of **2I** in a reaction mixture of  $t\text{BuC}\equiv\text{N}$  with HBpin catalyzed by **1a** (128 MHz,  $\text{C}_6\text{D}_{12}$ ).



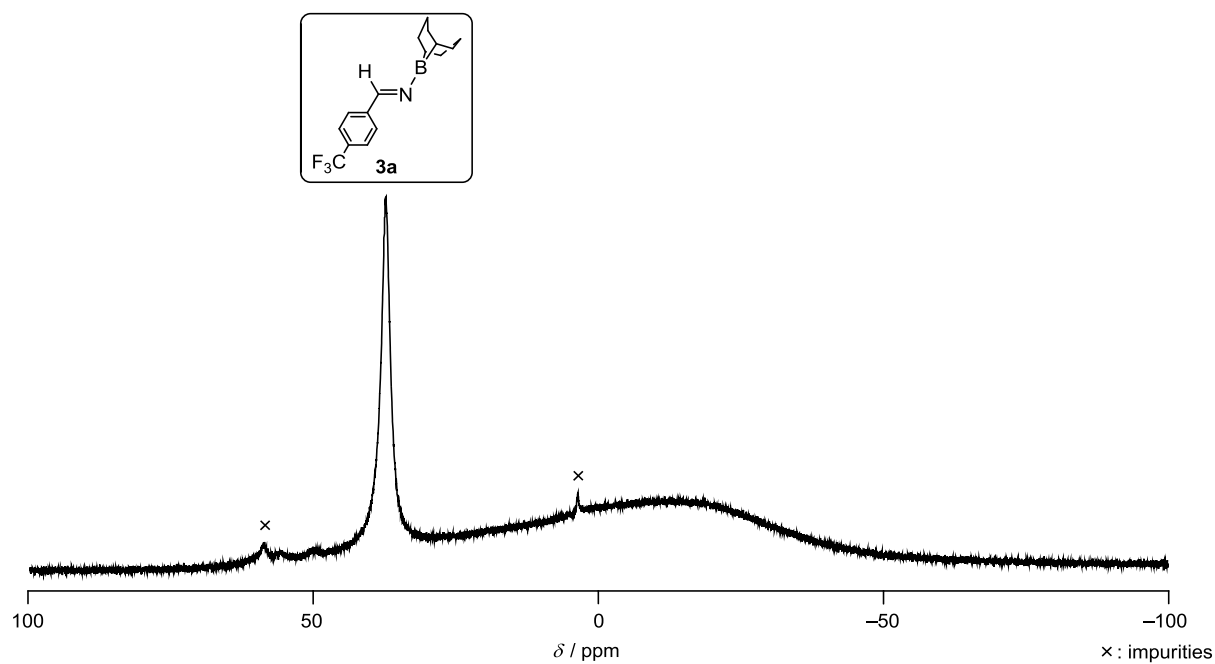
**Figure S30.** <sup>1</sup>H NMR spectrum of **2m** in a reaction mixture of MeC≡N with HBpin catalyzed by **1a** (400 MHz, C<sub>6</sub>D<sub>12</sub>).



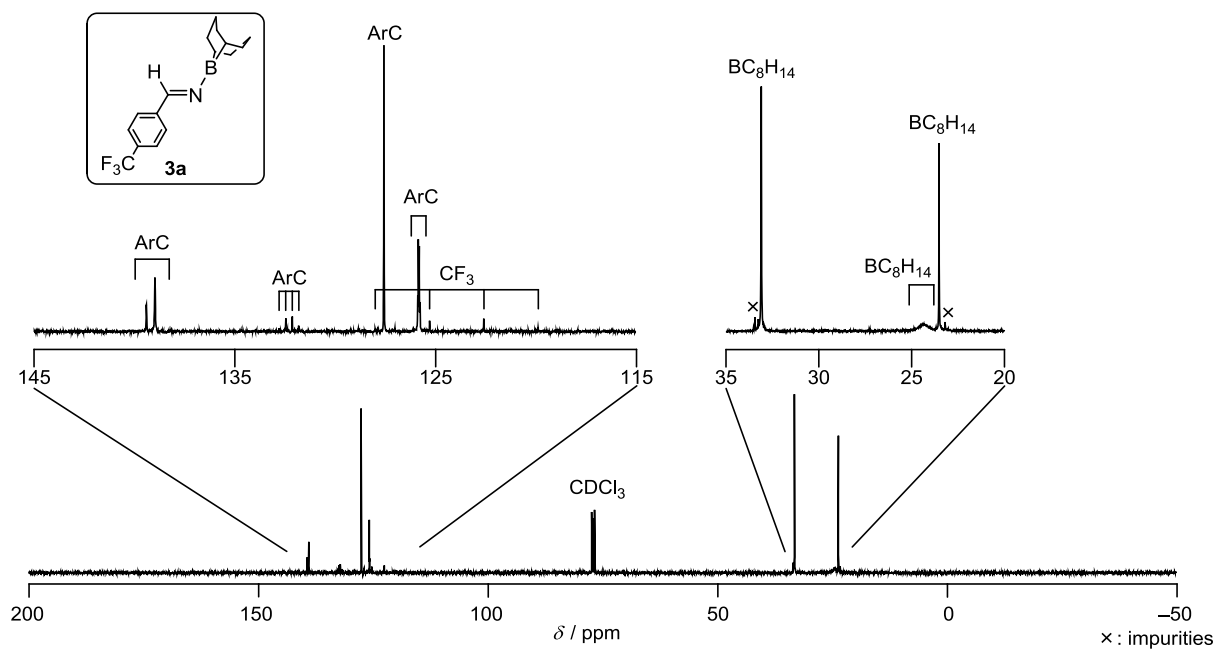
**Figure S31.** <sup>11</sup>B NMR spectrum of **2m** in a reaction mixture of MeC≡N with HBpin catalyzed by **1a** (128 MHz, C<sub>6</sub>D<sub>12</sub>).



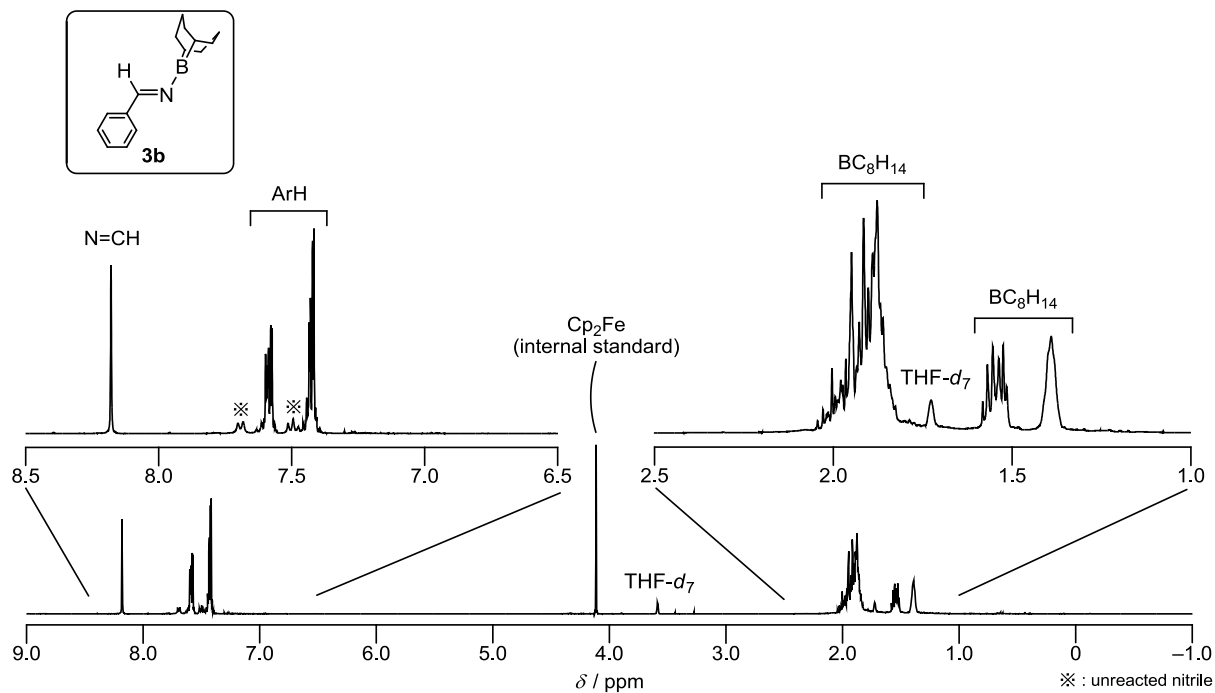
**Figure S32.**  $^1\text{H}$  NMR spectrum of **3a** (400 MHz,  $\text{CDCl}_3$ ).



**Figure S33.**  $^{11}\text{B}$  NMR spectrum of **3a** (128 MHz,  $\text{CDCl}_3$ ).

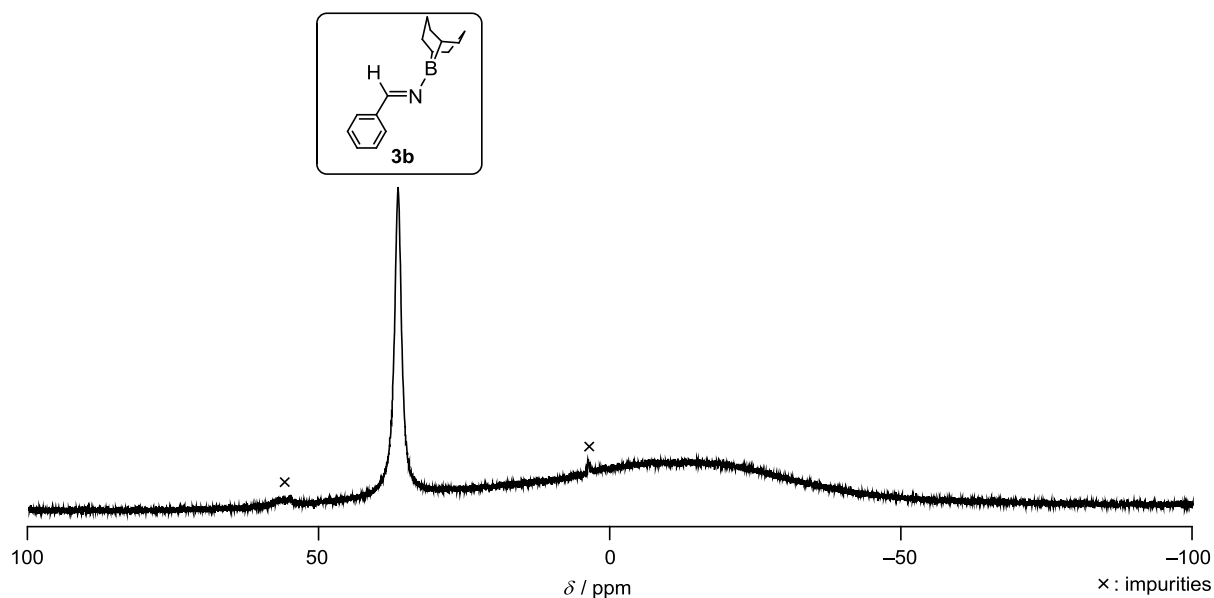


**Figure S34.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3a** (101 MHz,  $\text{CDCl}_3$ ).

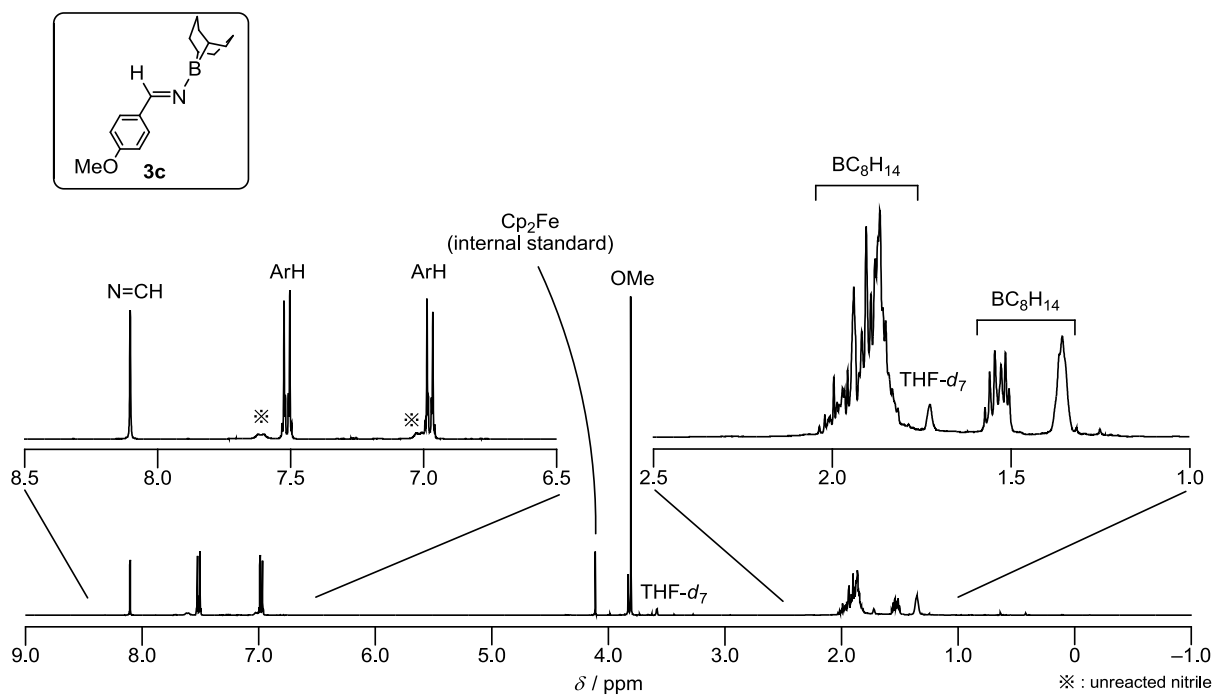


**Figure S35.**  $^1\text{H}$  NMR spectrum of **3b** in a reaction mixture of  $\text{PhC}\equiv\text{N}$  with 9-BBN catalyzed by **1a** (400 MHz,  $\text{THF}-d_8$ ).

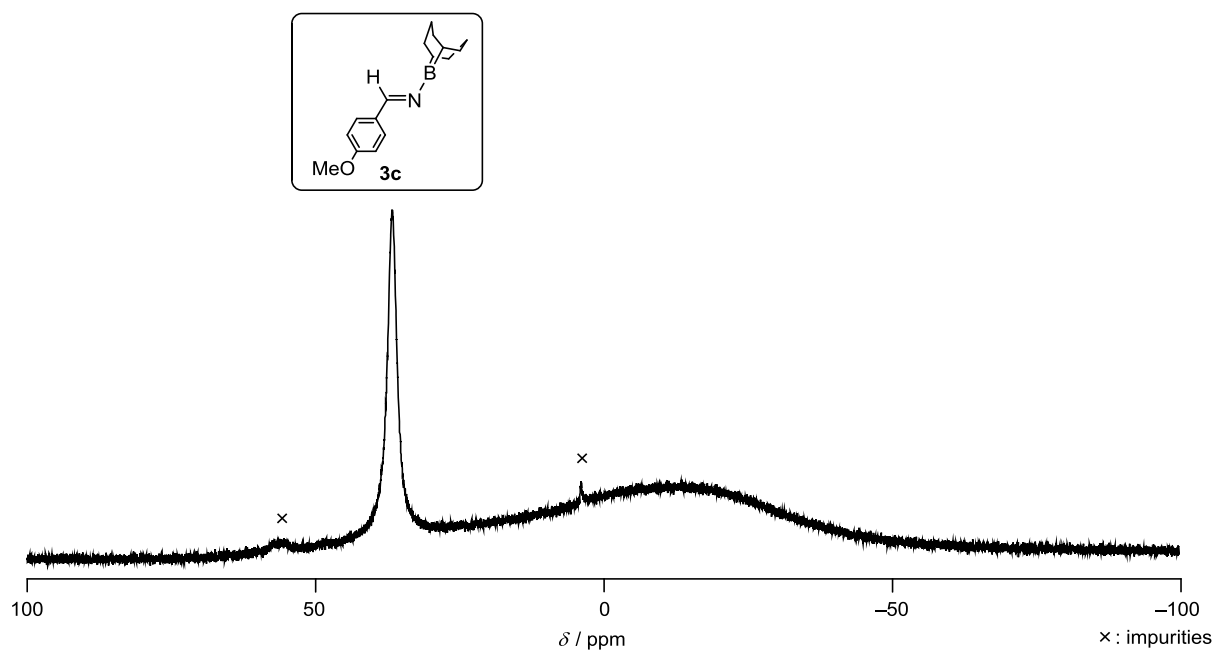




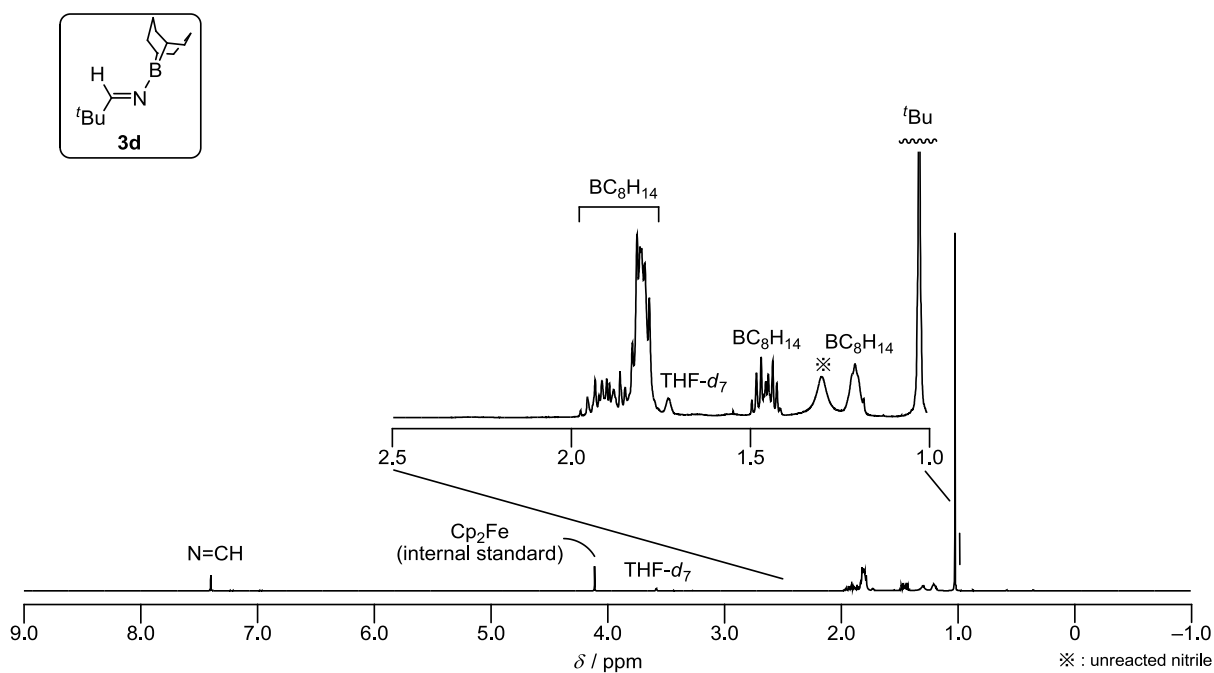
**Figure S36.**  $^{11}\text{B}$  NMR spectrum of **3b** in a reaction mixture of  $\text{PhC}\equiv\text{N}$  with 9-BBN catalyzed by **1a** (128 MHz,  $\text{THF-}d_8$ ).



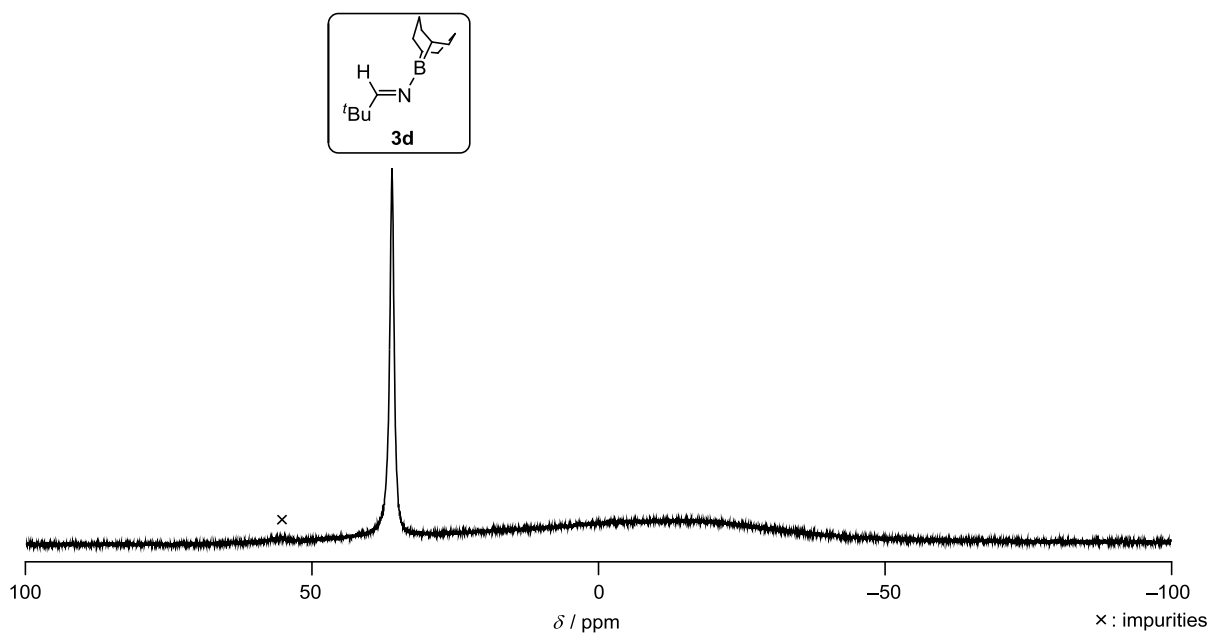
**Figure S37.**  $^1\text{H}$  NMR spectrum of **3c** in a reaction mixture of  $4\text{-MeOC}_6\text{H}_4\text{C}\equiv\text{N}$  with 9-BBN catalyzed by **1a** (400 MHz,  $\text{THF-}d_8$ ).



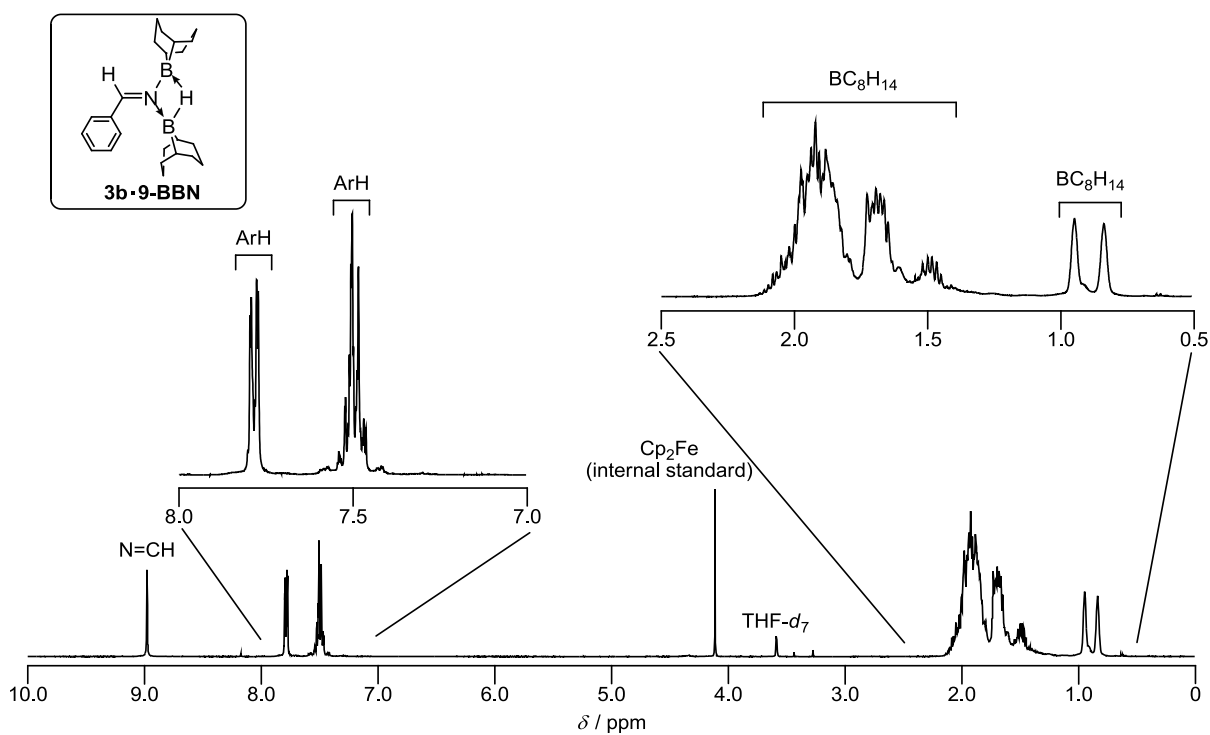
**Figure S38.**  $^{11}\text{B}$  NMR spectrum of **3c** in a reaction mixture of 4-MeOC<sub>6</sub>H<sub>4</sub>C≡N with 9-BBN catalyzed by **1a** (128 MHz, THF-*d*<sub>8</sub>).



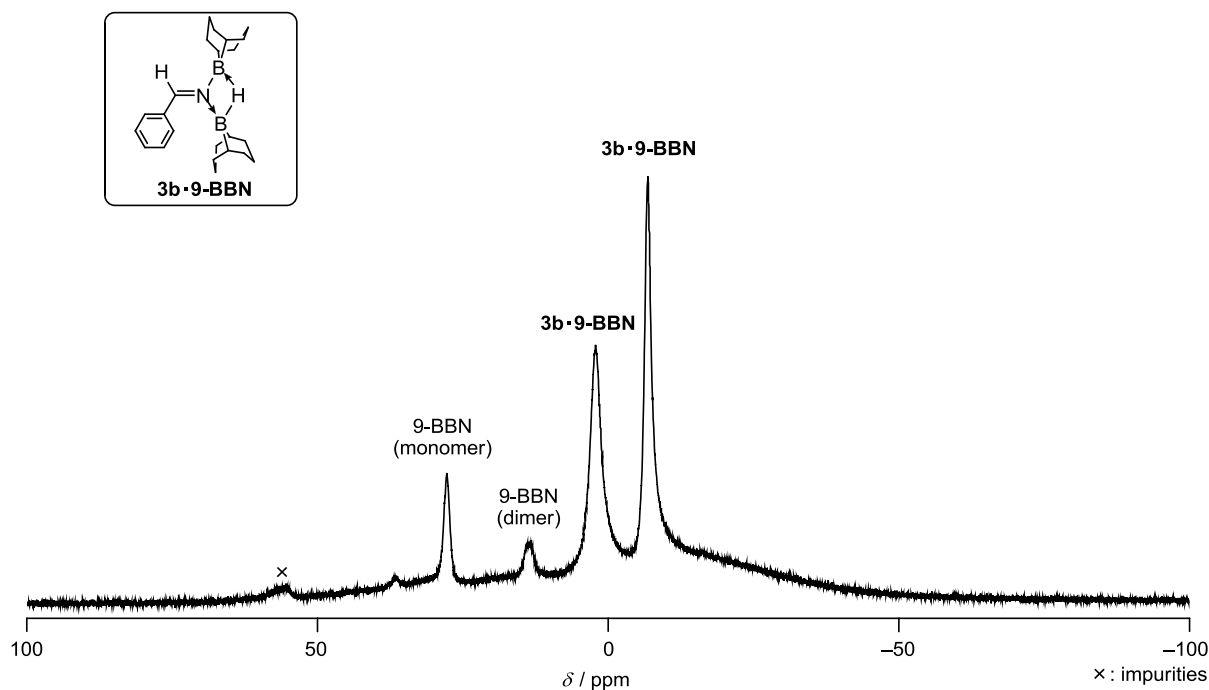
**Figure S39.**  $^1\text{H}$  NMR spectrum of **3d** in a reaction mixture of  $t\text{BuC}\equiv\text{N}$  with 9-BBN catalyzed by **1a** (400 MHz, THF-*d*<sub>8</sub>).



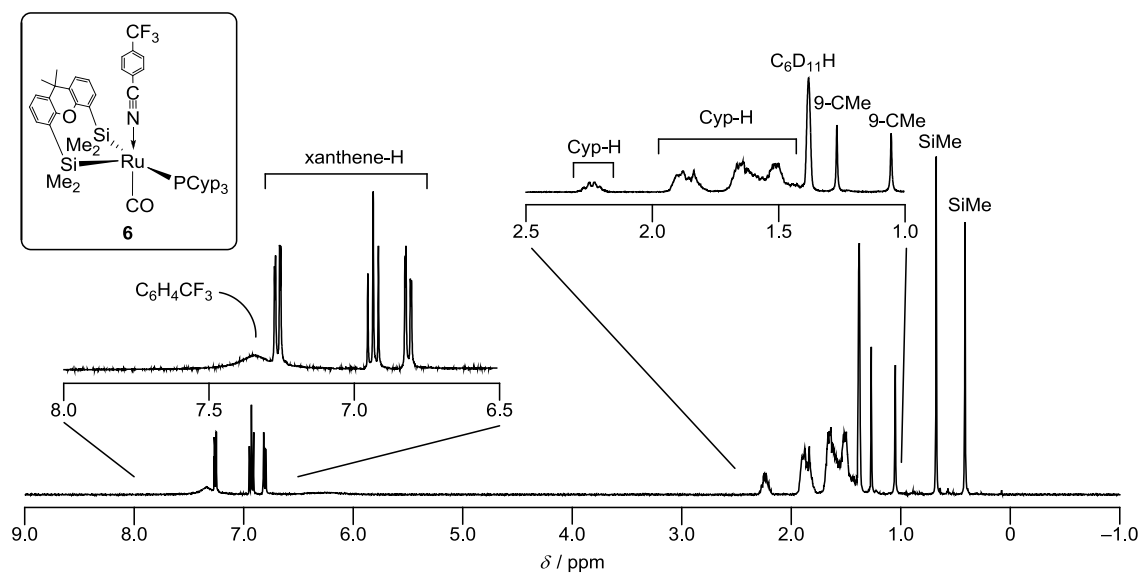
**Figure S40.**  $^{11}\text{B}$  NMR spectrum of **3d** in a reaction mixture of  $t\text{BuC}\equiv\text{N}$  with 9-BBN catalyzed by **1a** (128 MHz,  $\text{THF-}d_8$ ).



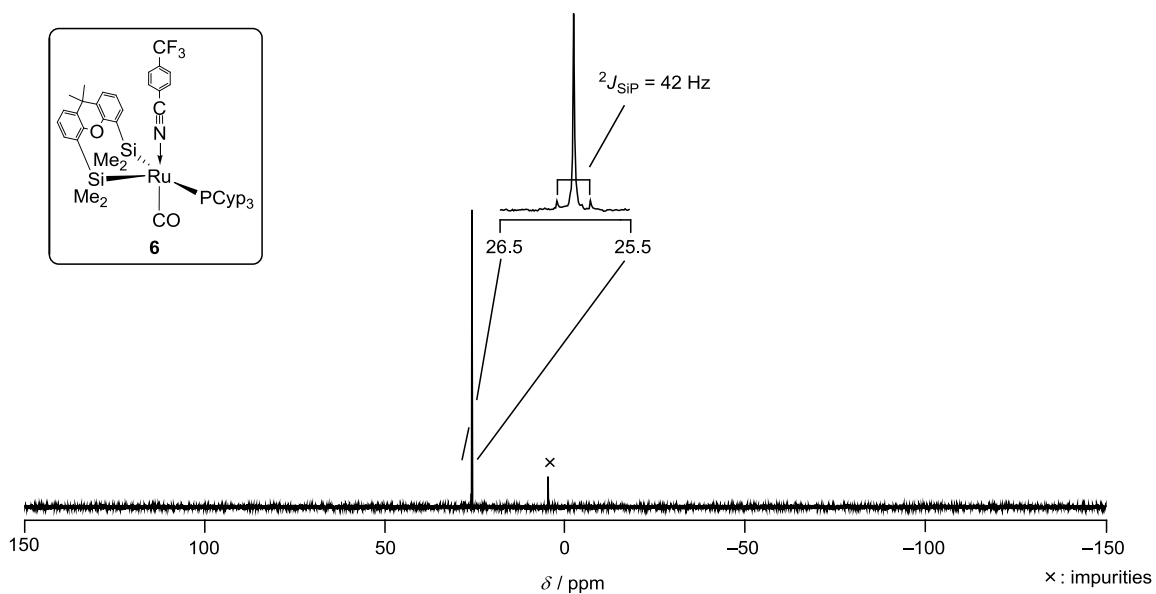
**Figure S41.**  $^1\text{H}$  NMR spectrum of **3b•9-BBN** in a reaction mixture of  $\text{PhC}\equiv\text{N}$  with 2.2 equivalents (for the monomer) of 9-BBN catalyzed by **1a** (400 MHz,  $\text{THF-}d_8$ ).



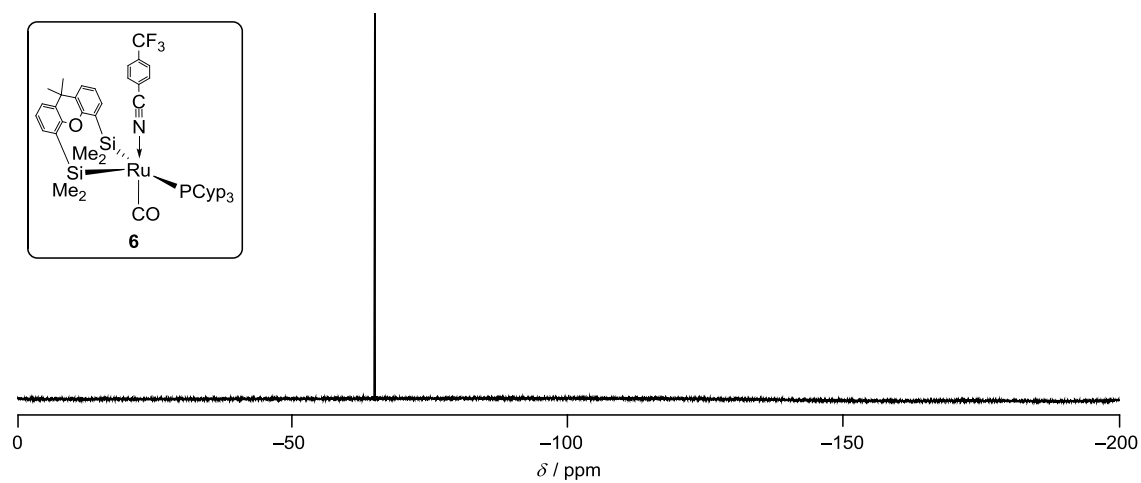
**Figure S42.**  $^{11}\text{B}$  NMR spectrum of **3b•9-BBN** in a reaction mixture of  $\text{PhC}\equiv\text{N}$  with 2.2 equivalents (for the monomer) of 9-BBN catalyzed by **1a** (128 MHz,  $\text{THF-}d_8$ ).



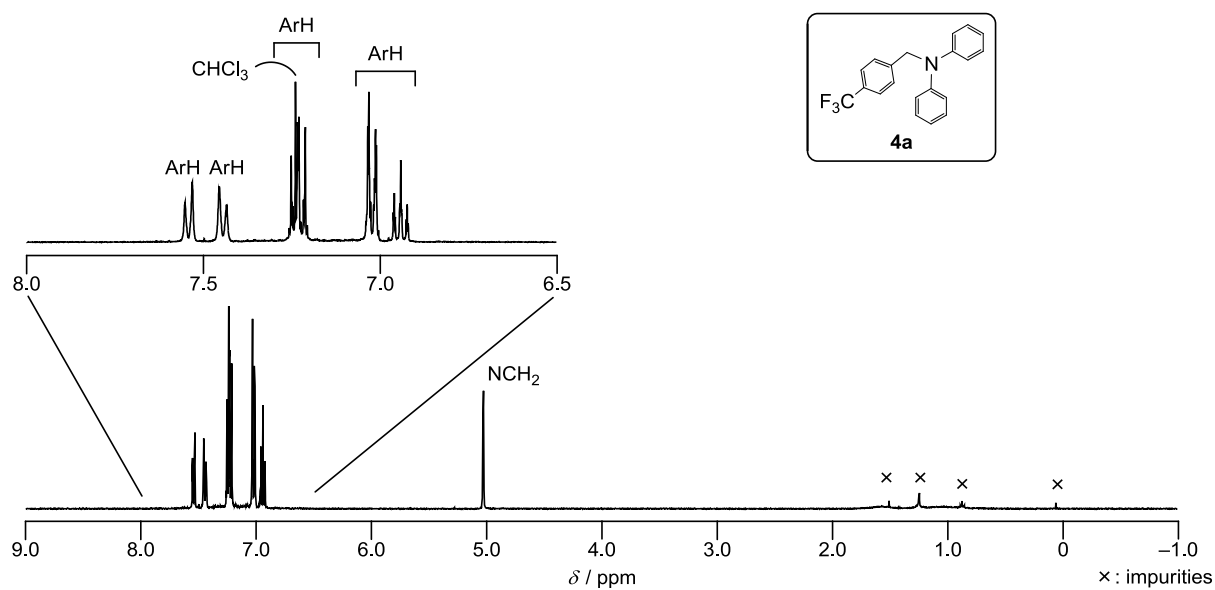
**Figure S43.**  $^1\text{H}$  NMR spectrum of **6** (400 MHz,  $\text{C}_6\text{D}_{12}$ ).



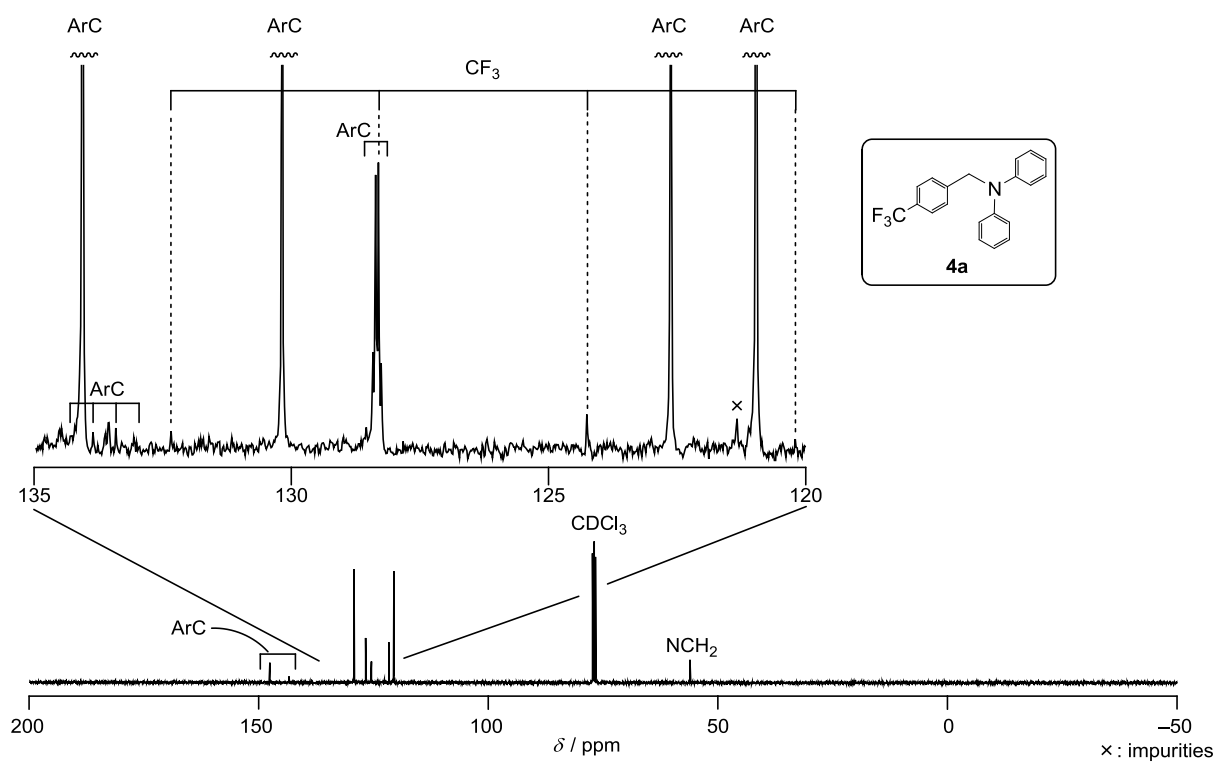
**Figure S44.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **6** (161 MHz, C<sub>6</sub>D<sub>12</sub>).



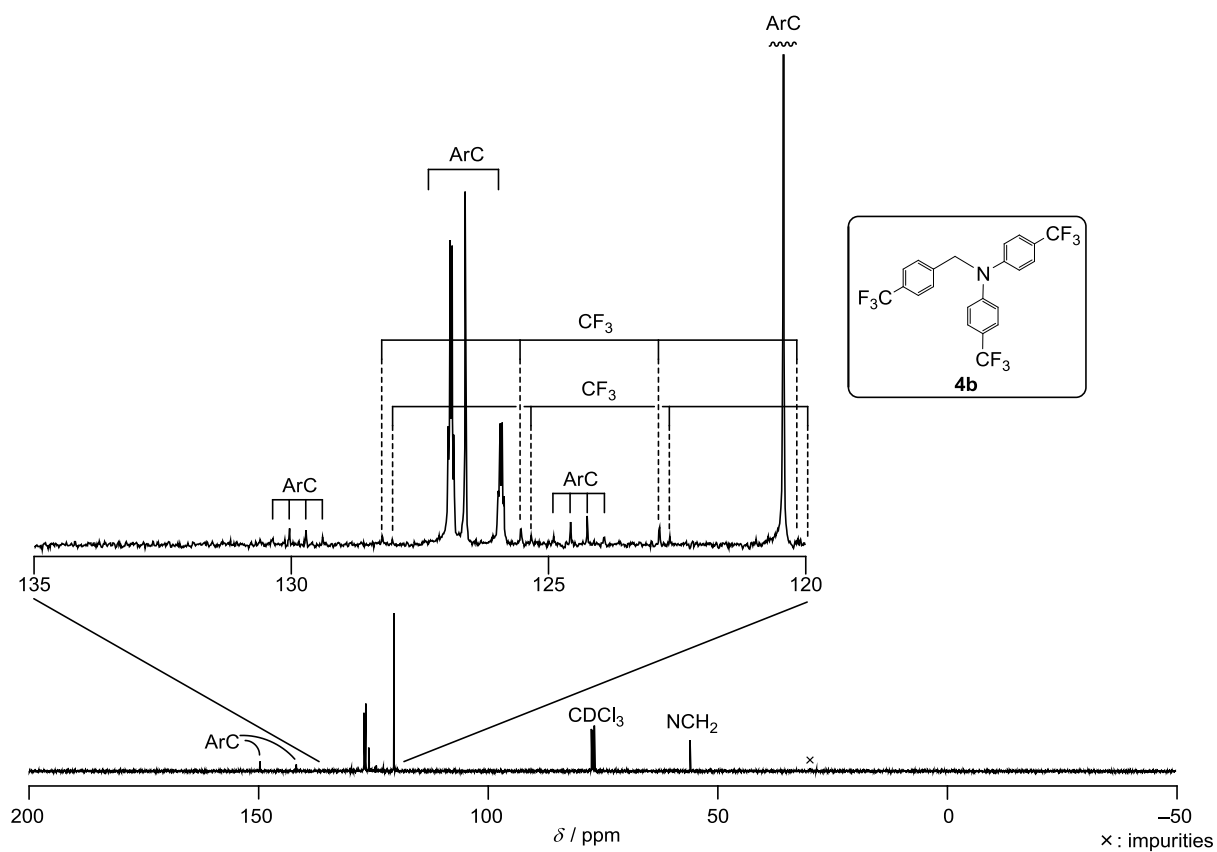
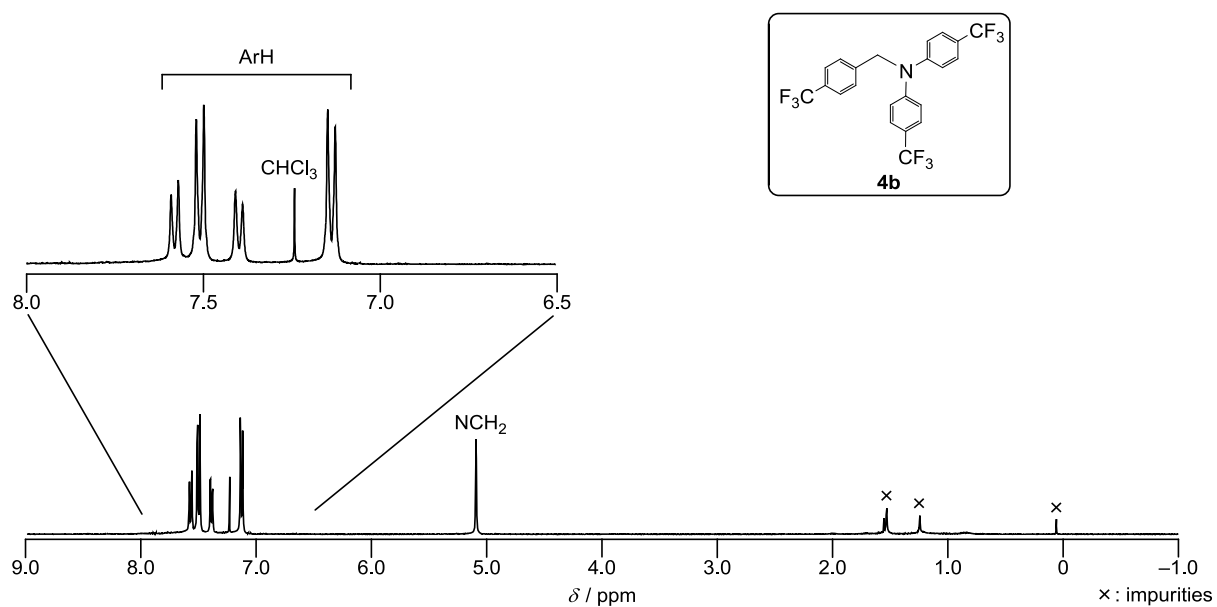
**Figure S45.** <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of **6** (376 MHz, C<sub>6</sub>D<sub>12</sub>).

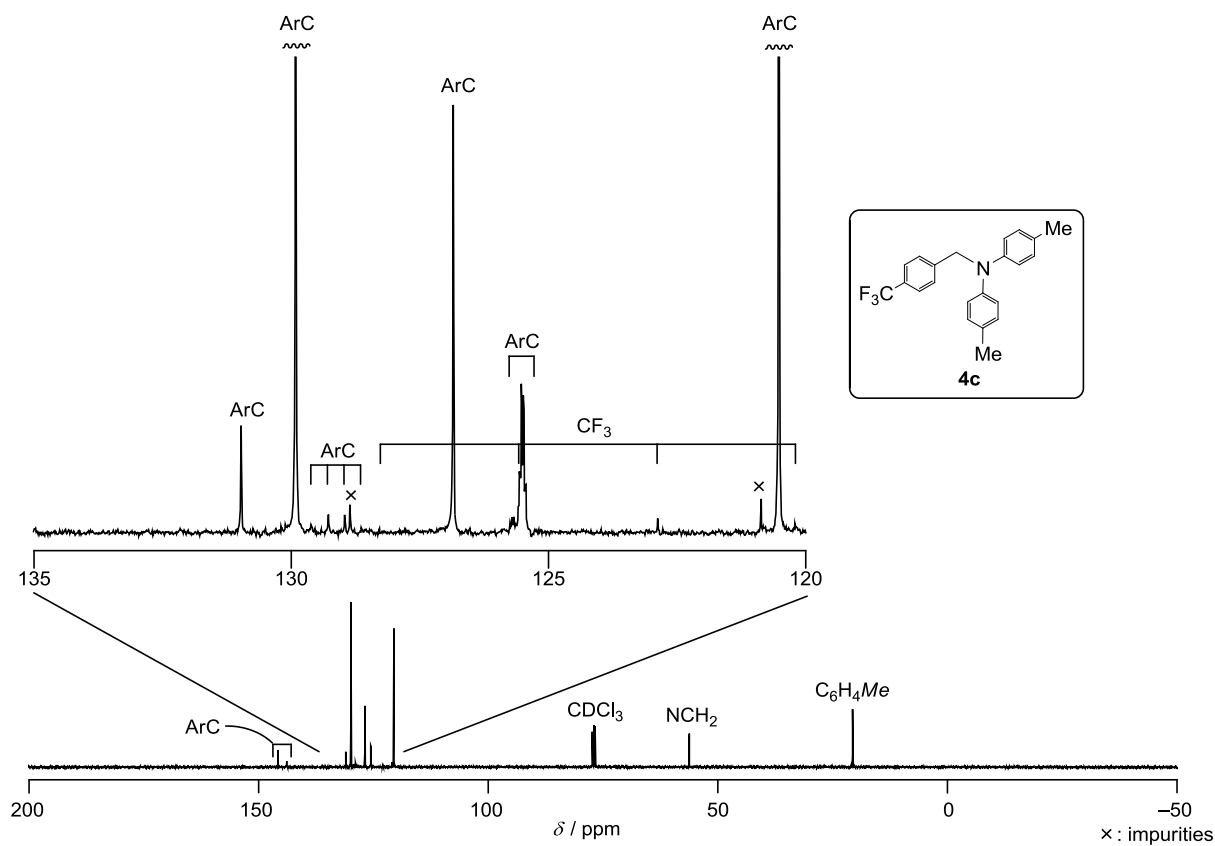
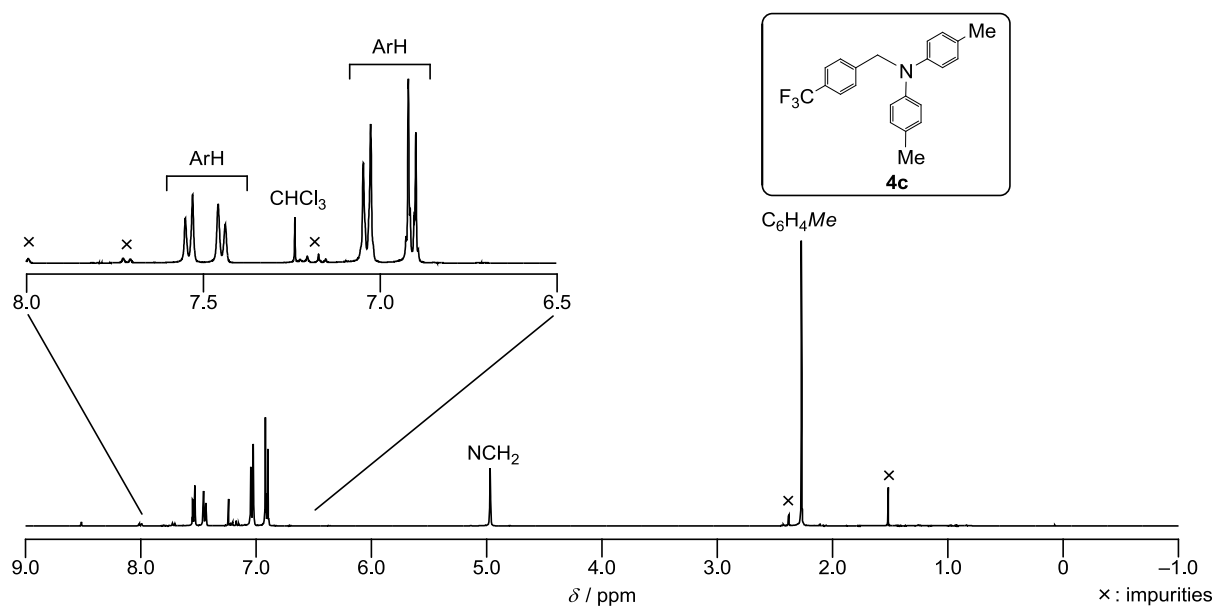


**Figure S46.** <sup>1</sup>H NMR spectrum of **4a** (400 MHz, CDCl<sub>3</sub>).

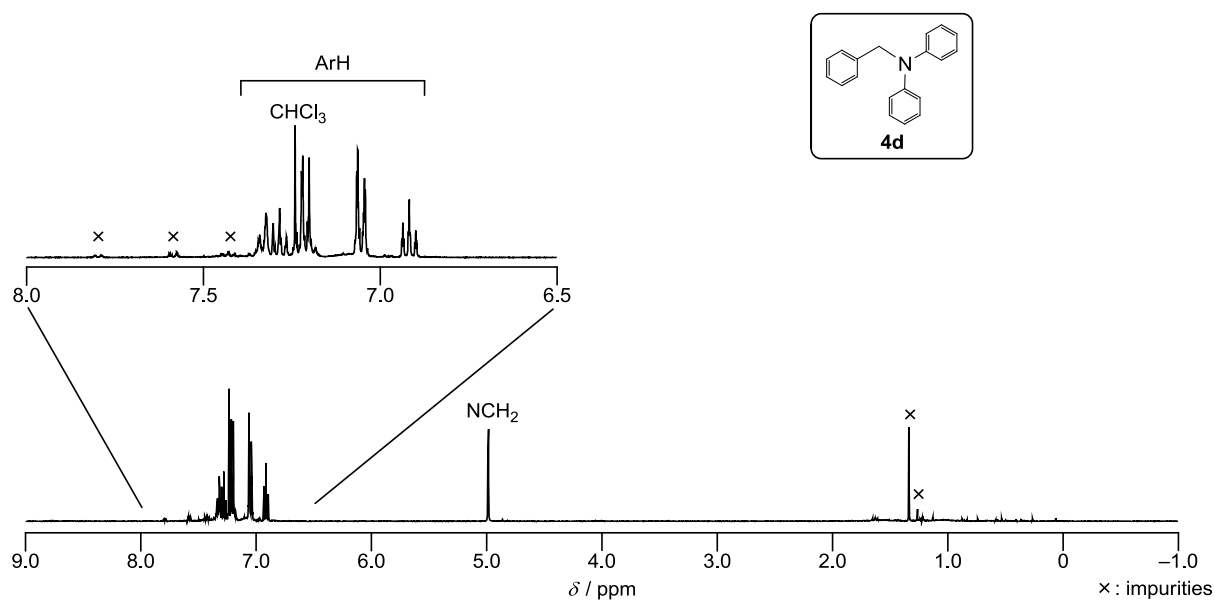


**Figure S47.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4a** (101 MHz, CDCl<sub>3</sub>).

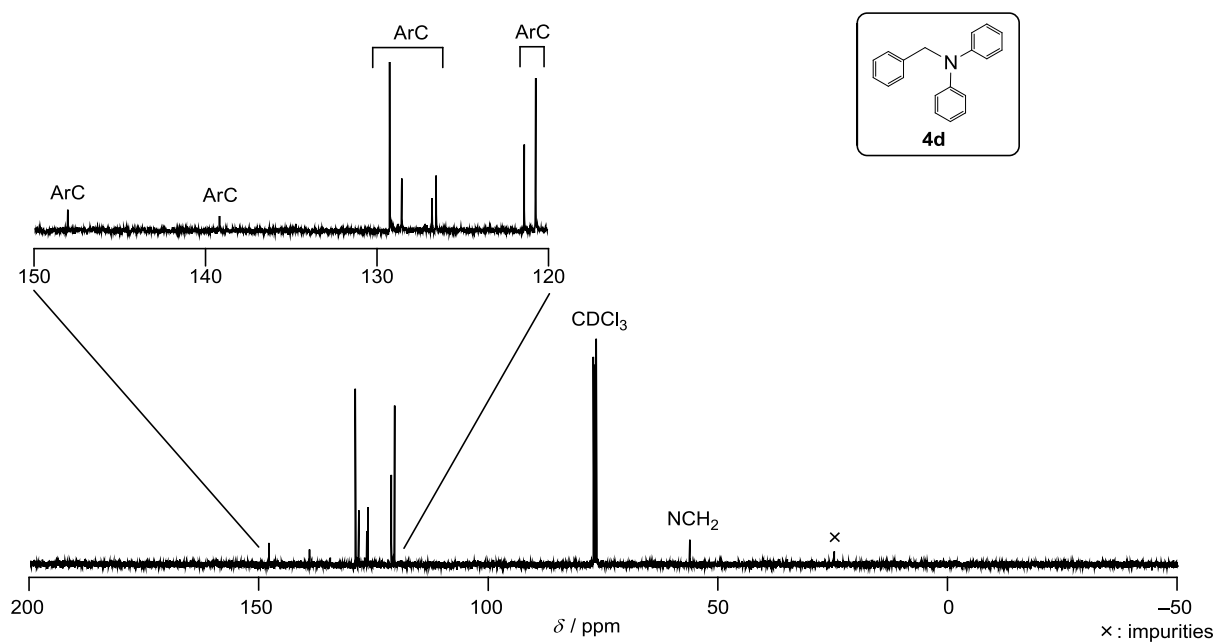




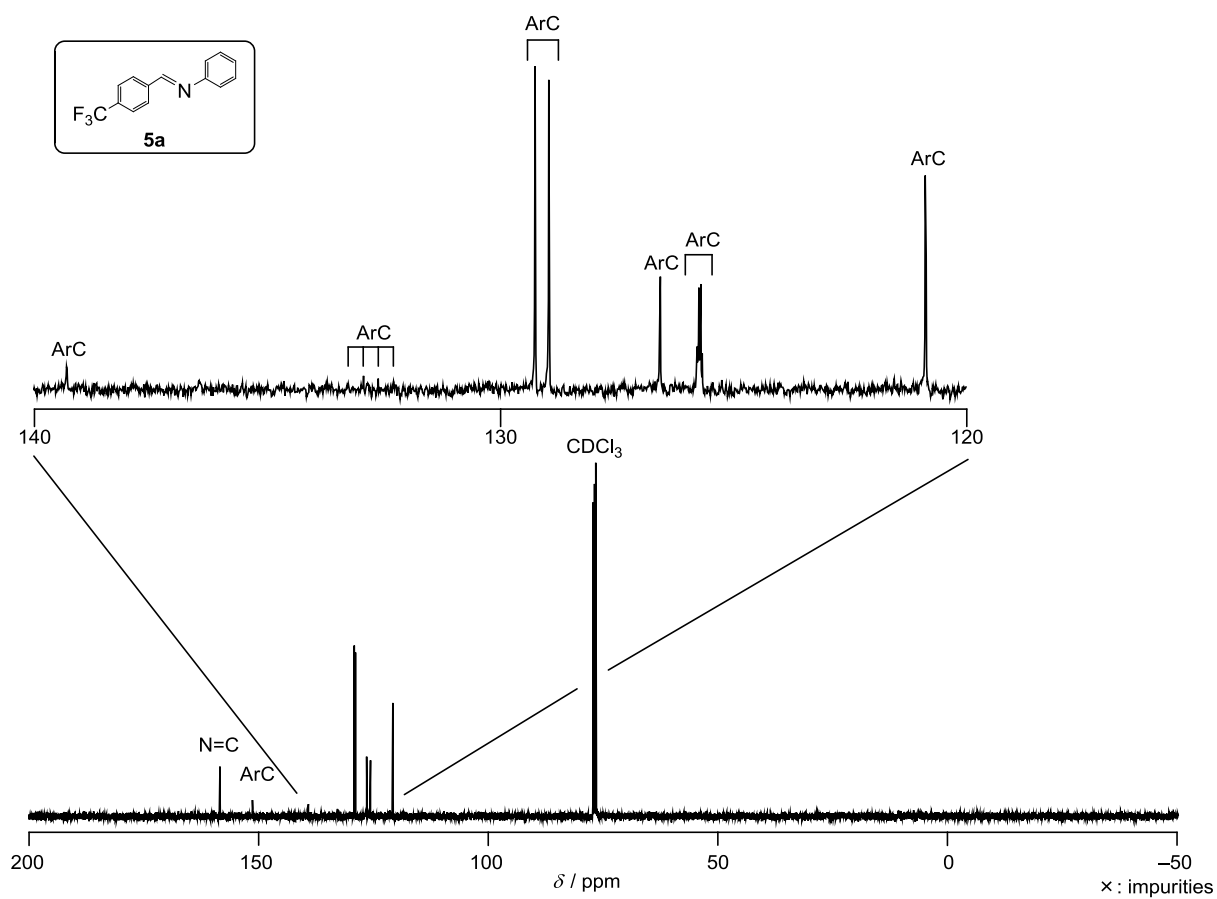
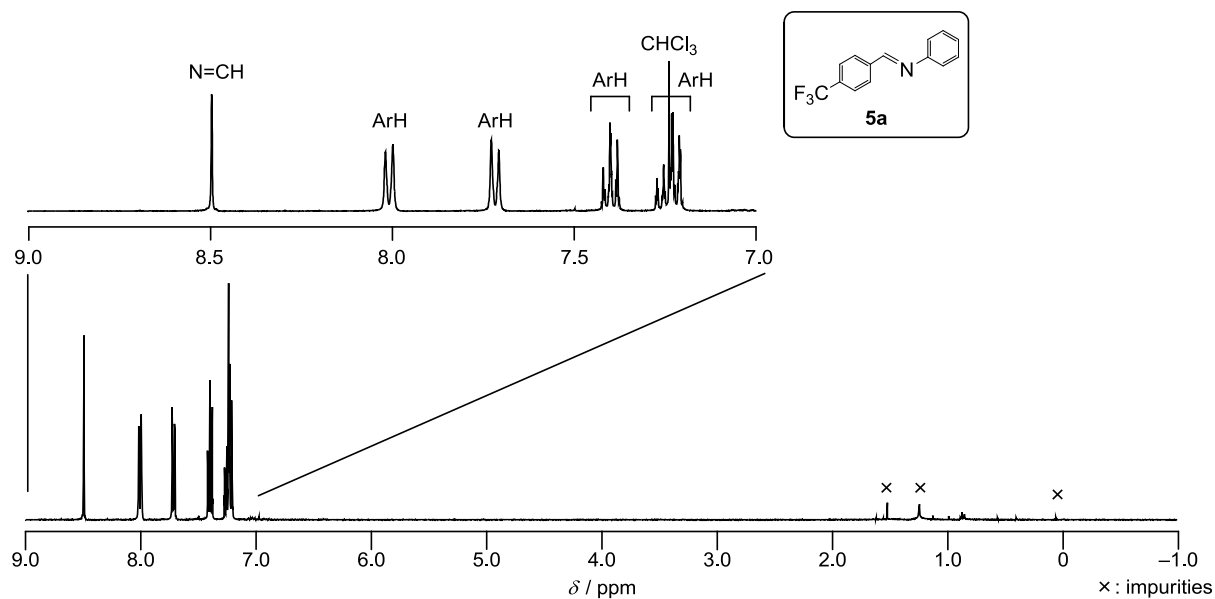


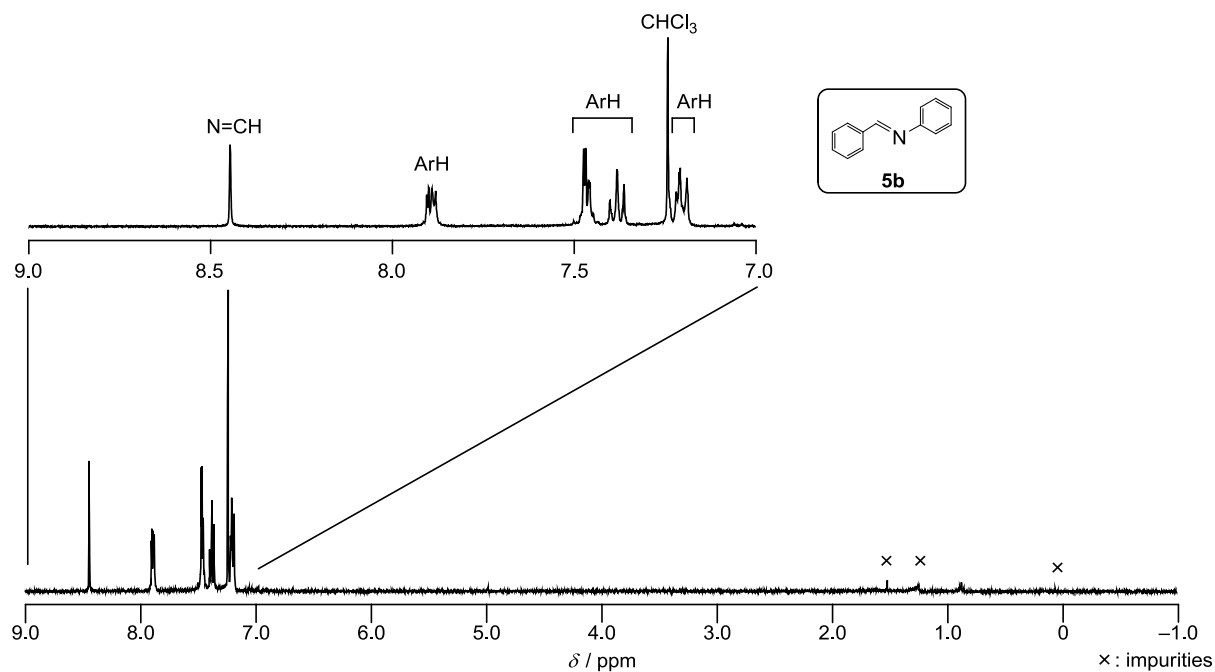


**Figure S52.**  $^1\text{H}$  NMR spectrum of **4d** (400 MHz,  $\text{CDCl}_3$ ).

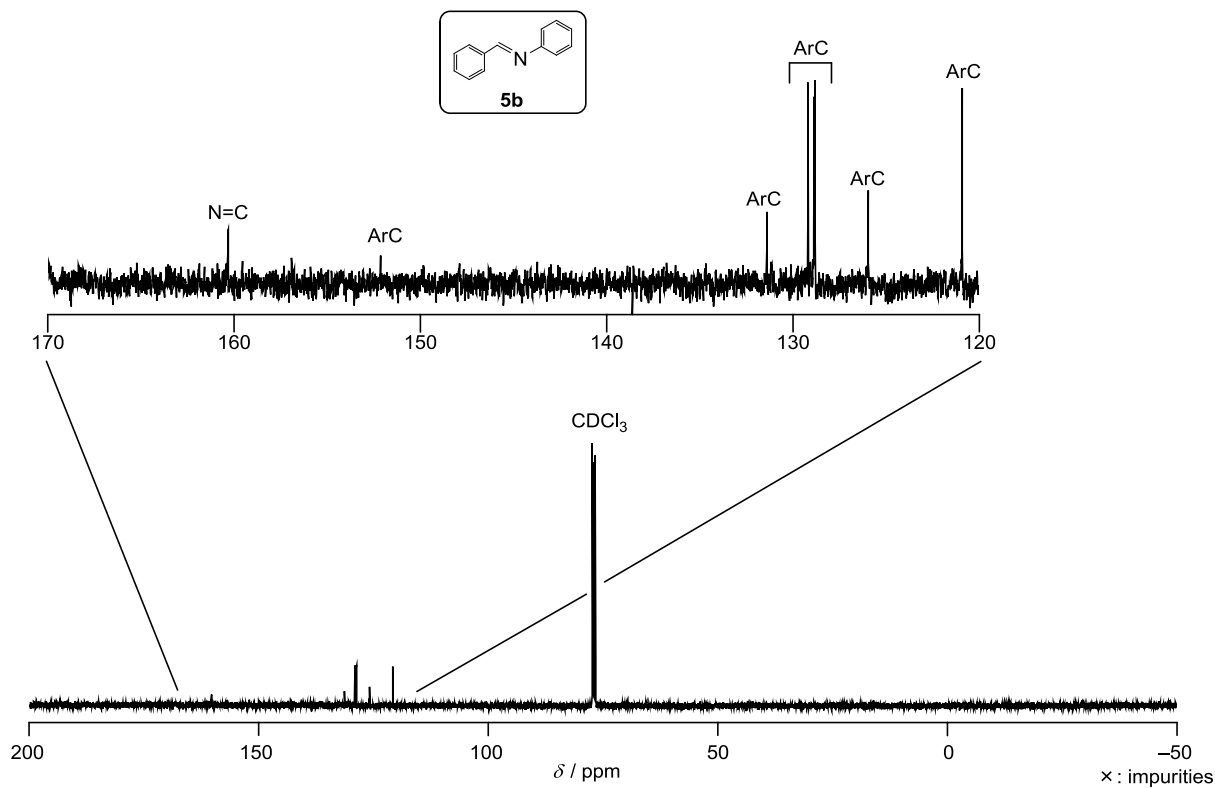


**Figure S53.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4d** (101 MHz,  $\text{CDCl}_3$ ).


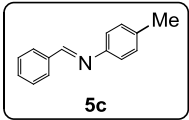




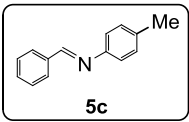
**Figure S56.** <sup>1</sup>H NMR spectrum of **5b** (400 MHz, CDCl<sub>3</sub>).



**Figure S57.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **5b** (101 MHz, CDCl<sub>3</sub>).



**5c**



S60

