

**Electronic supplementary information**

**for**

**From trihydroborates to bisborylenes: a route to dinuclear  
bisborylene complexes**

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**General information:** All manipulations were carried out under dry nitrogen atmosphere using standard Schlenk line or glovebox techniques unless otherwise specified. All glassware was oven-dried overnight at 120 °C and cooled under vacuum prior to use. Reaction solvents (*n*-hexane, diethyl ether, THF and toluene) were dried using a Mikrouna solvent purification system and stored over activated 4 Å molecular sieves. Deuterated solvents (C<sub>6</sub>D<sub>6</sub> and C<sub>7</sub>D<sub>8</sub>) were dried by refluxing over CaH<sub>2</sub> prior to use. NMR spectra were recorded on a Bruker Avance II 400 MHz spectrometer (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 101 MHz, <sup>11</sup>B: 128 MHz, <sup>19</sup>F: 377 MHz, <sup>31</sup>P: 162 MHz). Chemical shifts were given in ppm, and were referenced internally to the residual solvent signals (<sup>1</sup>H and <sup>13</sup>C) or an external standard (<sup>11</sup>B: BF<sub>3</sub>·OEt<sub>2</sub>, <sup>19</sup>F: CFC<sub>3</sub>, <sup>31</sup>P: 85% H<sub>3</sub>PO<sub>4</sub>). NMR assignments were supported by additional 2D NMR experiments. Elemental analyses were performed on a Vario EL elemental analyzer.

**X-Ray diffraction:** Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS detector using MoK<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ). All of the data were corrected for absorption effects using the multi-scan technique. Final unit cell parameters were based on all observed reflections from integration of all frame data. The structures were solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization that implanted in

Olex2. For all compounds, all non-H atoms were refined anisotropically unless otherwise stated. The hydrogen atoms were introduced at their geometric positions and refined as riding atoms, except for the hydrogen atoms bound to ruthenium and boron, which were located by Fourier differences and isotropically refined. CCDC 2150383, 2150384, 2150387 and 2150388 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/structures/](http://www.ccdc.cam.ac.uk/structures/).

**Materials:** Unless otherwise noted, all commercially available reagents were used as received. Li[PhBH<sub>3</sub>] $\cdot$ 2THF, Li[(3,4,5-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)BH<sub>3</sub>] $\cdot$ 2THF, and Li[(2-*i*-PrC<sub>6</sub>H<sub>4</sub>)BH<sub>3</sub>] $\cdot$ THF were synthesized from their corresponding boronic acids, according to modified literature procedures as described below.<sup>1</sup> [(1) (a) B. Singaram, T. E. Cole and H. C. Brown, *Organometallics*, 1984, **3**, 774-777; (b) N. Tsoureas, T. Bevis, C. P. Butts, A. Hamilton and G. R. Owen, *Organometallics*, 2009, **28**, 5222-5232.]

### Synthesis of Li[PhBH<sub>3</sub>] $\cdot$ 2THF (**2a**)

To a solution of LiAlH<sub>4</sub> (0.76g, 20 mmol) in Et<sub>2</sub>O (20 mL) was added dropwise a solution of phenylboronic acid (1.46g, 12 mmol) in a mixture of Et<sub>2</sub>O (30 mL) and THF (20 mL) at 0 °C under N<sub>2</sub>, the mixture was then warmed to room temperature and stirred for 5 h. After removal of the solvent under vacuum, the residue was extracted with the mixture of Et<sub>2</sub>O/*n*-hexane (v/v 3:1, 3 $\times$ 12 mL). The solvent was removed under vacuum from the combined extract to yield the product as a white solid. Yield: 3.19 g, 91%.

<sup>1</sup>H NMR (400 MHz, 298 K, C<sub>7</sub>D<sub>8</sub>):  $\delta$  = 7.76 (br, 2H, *o*-Ph), 7.34 (m, 2H, *m*-Ph), 7.17 (m, 1H, *p*-Ph), 3.62 (m, 8H, THF), 1.50 (br 1:1:1:1 q, <sup>1</sup>J<sub>BH</sub> ~ 76 Hz, 3H, BH<sub>3</sub>), 1.36 (m, 8H, THF).

<sup>11</sup>B NMR (128 MHz, 298 K, C<sub>7</sub>D<sub>8</sub>):  $\delta$  = -27.0 (q, <sup>1</sup>J<sub>HB</sub> ~ 76 Hz).

### Synthesis of Li[(3,4,5-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)BH<sub>3</sub>] $\cdot$ 2THF (**2b**)

Following the same procedure of synthesis of **2a** using corresponding boronic acids, Li[(3,4,5-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)BH<sub>3</sub>] $\cdot$ 2THF (**2b**) was obtained as a white solid. Yield: 94%.

<sup>1</sup>H NMR (400 MHz, 298 K, C<sub>7</sub>D<sub>8</sub>):  $\delta$  = 7.15 (m, 2H, F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 3.34 (m, 8H, THF), 1.27 (m, 8H, THF), 1.19 (br 1:1:1:1 q, <sup>1</sup>J<sub>BH</sub> ~ 77 Hz, 3H, BH<sub>3</sub>)

<sup>11</sup>B NMR (128 MHz, 298 K, C<sub>7</sub>D<sub>8</sub>):  $\delta$  = -26.6 (q, <sup>1</sup>J<sub>HB</sub> ~ 77 Hz).

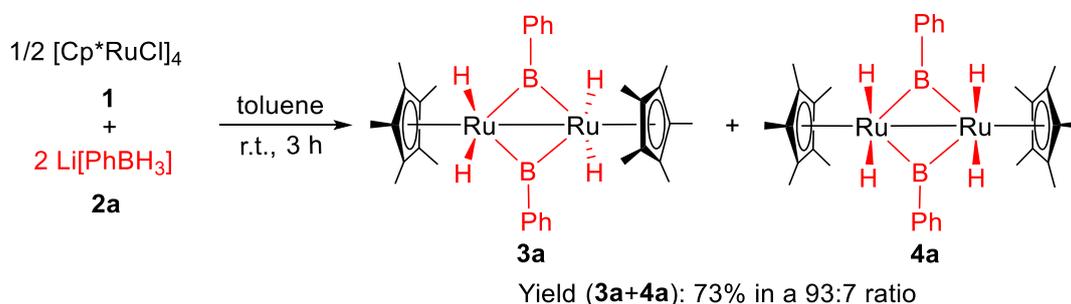
## Synthesis of $\text{Li}[(2\text{-}^i\text{PrC}_6\text{H}_4)\text{BH}_3]\cdot\text{THF}$ (**2c**)

Following the same procedure of synthesis of **2a** using corresponding boronic acids,  $\text{Li}[(2\text{-}^i\text{PrC}_6\text{H}_4)\text{BH}_3]\cdot\text{THF}$  (**2c**) was obtained as a white solid after vacuuming at 0.2 mbar for 24 h. Yield: 87%.

$^1\text{H}$  NMR (400 MHz, 298 K,  $\text{C}_7\text{D}_8$ ):  $\delta = 7.69$  (br, 1H,  $^i\text{PrC}_6\text{H}_4$ ), 7.13-7.32 (m, 3H,  $^i\text{PrC}_6\text{H}_4$ ), 3.75 (sept,  $^3J_{\text{HH}} = 6.8$  Hz, 1H,  $\text{CH}^{i\text{Pr}}$ ), 3.41 (m, 4H, THF), 1.50 (br 1:1:1:1 q,  $^1J_{\text{BH}} \sim 76$  Hz, 3H,  $\text{BH}_3$ ), 1.42 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 6H,  $\text{CH}_3^{i\text{Pr}}$ ), 1.21 (m, 4H, THF).

$^1\text{B}$  NMR (128 MHz, 298 K,  $\text{C}_7\text{D}_8$ ):  $\delta = -26.8$  (q,  $^1J_{\text{HB}} \sim 76$  Hz).

## Synthesis of $[\text{Cp}^*\text{Ru}(\text{H})_2(\text{BPh})]_2$ (**3a/4a**)



### Scheme S1

Toluene (20 mL) was added to a mixture of  $[\text{Cp}^*\text{RuCl}]_4$  (217.4 mg, 0.20 mmol) and  $\text{Li}[\text{PhBH}_3]\cdot 2\text{THF}$  (213.0 mg, 0.88 mmol, 4.4 equiv.). The resulting red mixture was stirred at room temperature for 3 h. The solvent was concentrated to *ca.* 5 mL under vacuum and *n*-hexane (5 mL) was added. The obtained suspension was filtered through Celite to remove remaining lithium salt. After removal of the solvent under vacuum, the

brown residue was washed with *n*-hexane (2×2 mL) and dried under vacuum to give a mixture of **3a** and **4a** as a yellow solid. Yield: 189.7 mg, 73%.

*[Comment: Our efforts to isolate the pure 3a or 4a were not successful. In situ NMR studies show that the ratio of 3a and 4a is consistent with that for the isolated material. The conversion between 3a and 4a was not observed either at low temperature or at high temperature.]*

Crystallization of the obtained solid in the mixture of *n*-hexane/toluene (v/v 5:1) at -25 °C gave compound **3a** as yellow crystals suitable for X-ray crystal structure analysis.

**Elemental analysis:** calc. for C<sub>32</sub>H<sub>44</sub>B<sub>2</sub>Ru<sub>2</sub>: C, 58.91; H, 6.80. Found: C, 59.02; H, 6.86.

**NMR spectroscopic data for the mixture of two isomers (3a:4a = 93:7):**

**<sup>1</sup>H NMR** (400 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>)

**3a:** δ = 7.86 (m, 4H, *o*-Ph), 7.37 (m, 4H, *m*-Ph), 7.25 (m, 2H, *p*-Ph), 1.49 (s, 30H, C<sub>5</sub>Me<sub>5</sub>), -10.38 (s, 4H, RuH).

**4a** [selected signals]: δ = 1.74 (s, C<sub>5</sub>Me<sub>5</sub>), -12.21 (br, RuH).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>)

**3a:** δ = 150.1 (br, *i*-Ph), 132.9 (*o*-Ph), 128.1 (*p*-Ph), 127.7 (*m*-Ph), 96.3 (C<sub>5</sub>Me<sub>5</sub>), 10.5 (C<sub>5</sub>Me<sub>5</sub>).

**4a** [selected signals]: δ = 94.9 (C<sub>5</sub>Me<sub>5</sub>), 11.9 (C<sub>5</sub>Me<sub>5</sub>).

**<sup>1</sup>H-<sup>13</sup>C GHSQC** (400 MHz/101 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>)

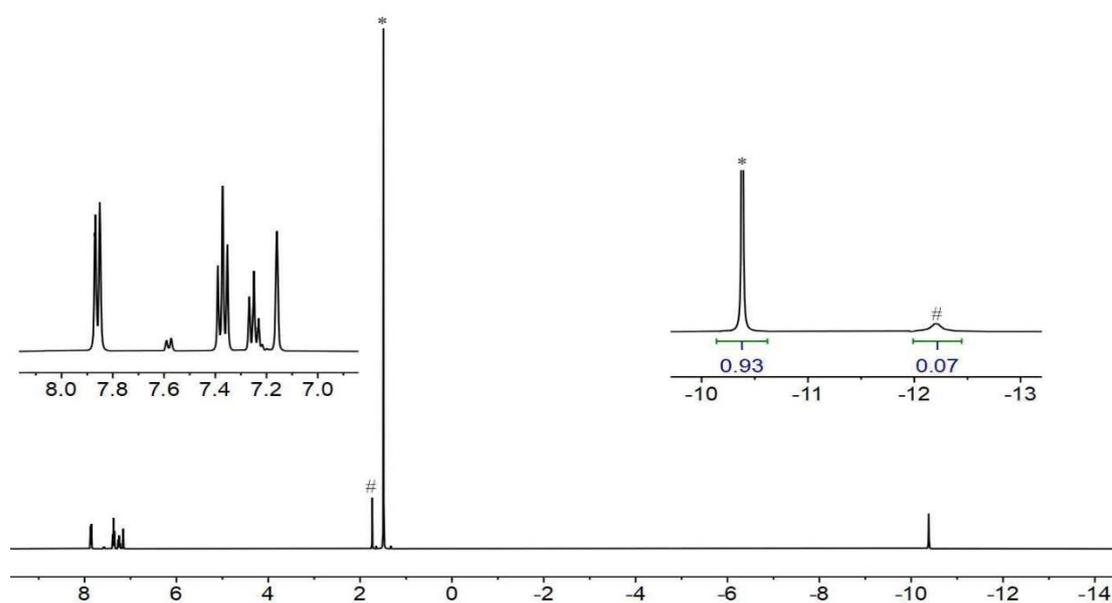
**3a:**  $\delta^1\text{H}/\delta^{13}\text{C} = 7.86/132.9$  (*o*-Ph), 7.37/127.7 (*m*-Ph), 7.25/128.1 (*p*-Ph),  
1.49/10.5 ( $\text{C}_5\text{Me}_5$ ).

**4a:**  $\delta^1\text{H}/\delta^{13}\text{C} = 1.74/11.9$  ( $\text{C}_5\text{Me}_5$ ).

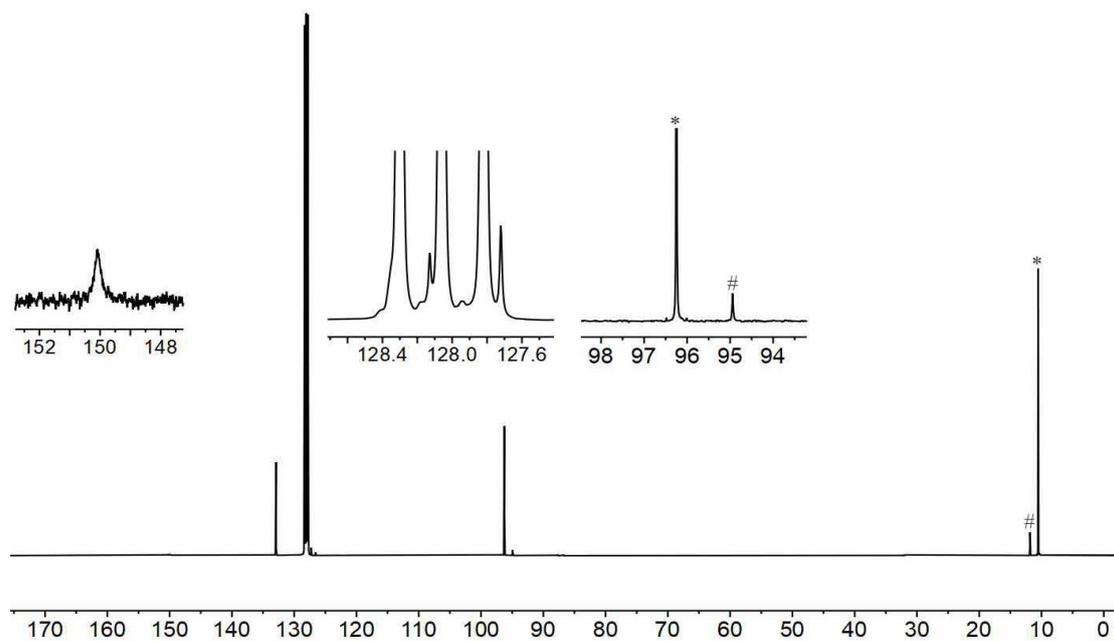
**$^{11}\text{B}$  NMR** (128 MHz, 298 K,  $\text{C}_6\text{D}_6$ )

**3a:**  $\delta = 126.0$  ( $\nu_{1/2} \sim 750$  Hz).

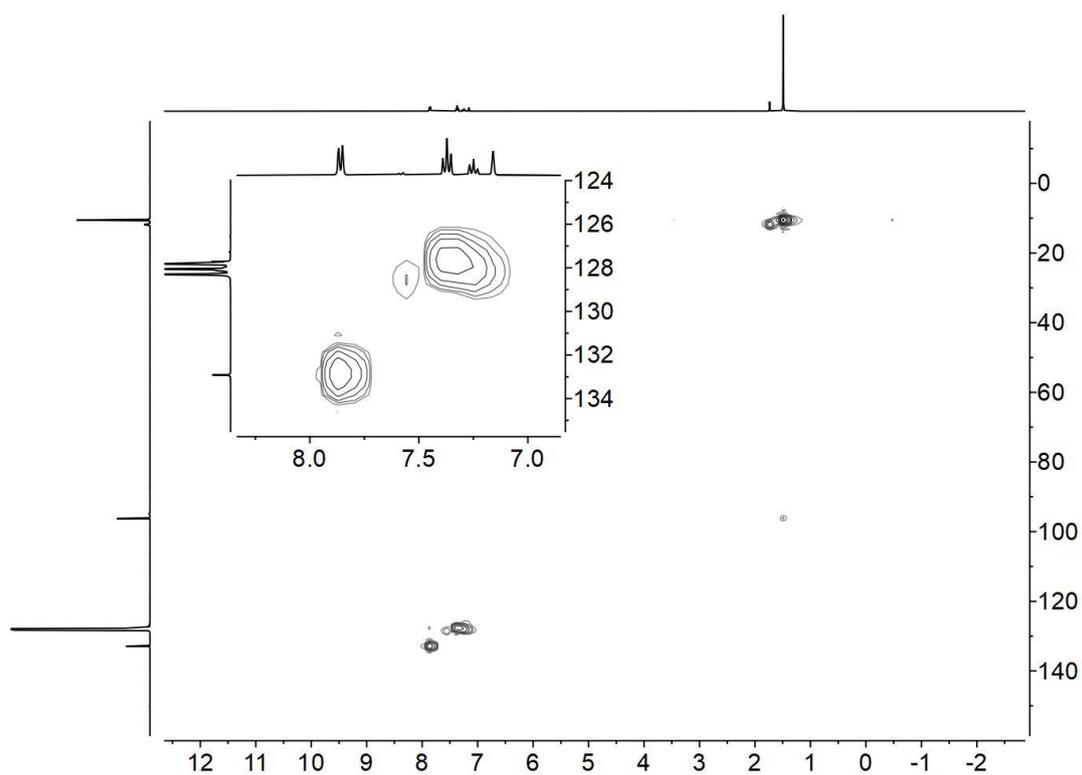
**4a:**  $\delta = 115.6$  ( $\nu_{1/2} \sim 980$  Hz).



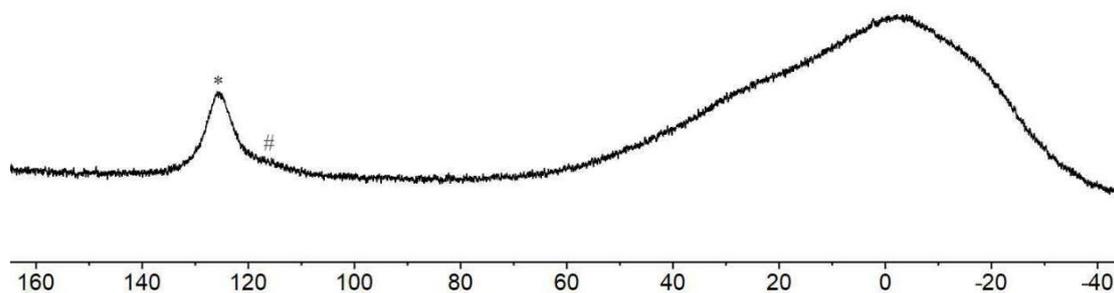
**Figure S1.**  $^1\text{H}$  NMR (400 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of the mixture of compounds **3a** (\*) and **4a** (#).



**Figure S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of the mixture of compounds **3a** (\*) and **4a** (#).

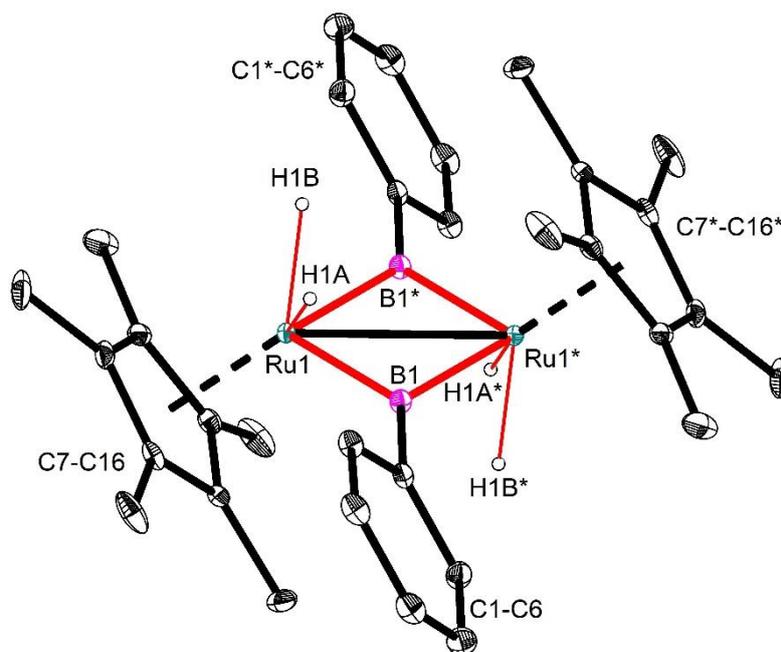


**Figure S3.**  $^1\text{H}$ - $^{13}\text{C}$  GHSQC (400 MHz/101 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of the mixture of compounds **3a** (\*) and **4a** (#).



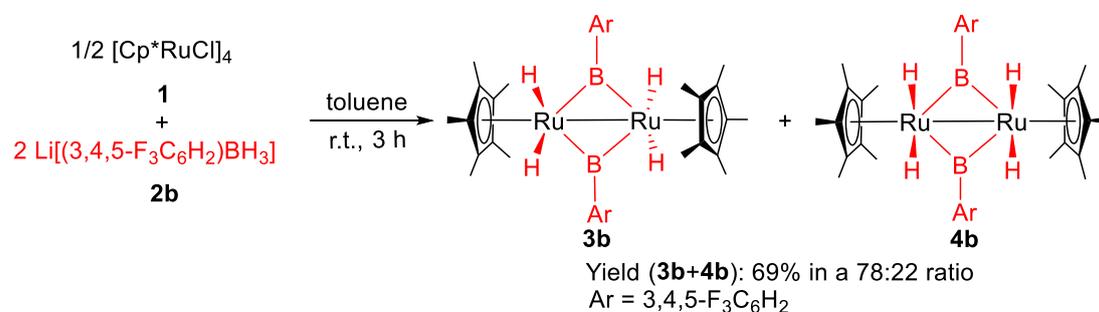
**Figure S4.**  $^{11}\text{B}$  NMR (128 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of the mixture of compounds **3a** (\*) and **4a** (#).

**X-ray crystal structure analysis of compound 3a:** formula  $\text{C}_{32}\text{H}_{44}\text{B}_2\text{Ru}_2$ ,  $M = 652.43$  g/mol, yellow crystal,  $0.4 \times 0.2 \times 0.1$  mm,  $a = 9.8015(9)$ ,  $b = 17.1267(15)$ ,  $c = 17.3776(15)$  Å,  $\alpha = 90$ ,  $\beta = 90$ ,  $\gamma = 90^\circ$ ,  $V = 2917.1(4)$  Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.486$  g·cm<sup>-3</sup>,  $\mu = 1.054$  mm<sup>-1</sup>, empirical absorption correction ( $0.6147 \leq T \leq 0.7462$ ),  $Z = 4$ , orthorhombic, space group *Pccn* (No. 56),  $\lambda = 0.71073$  Å,  $T = 150$  K,  $\omega$  and  $\varphi$  scans, 20694 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ), 4550 independent ( $R_{\text{int}} = 0.0253$ ) and 3952 observed reflections [ $I > 2\sigma(I)$ ], 176 refined parameters,  $R = 0.0306$ ,  $wR^2 = 0.0784$ , max. (min.) residual electron density 2.68 (-0.93) e·Å<sup>-3</sup>.



**Figure S5.** A view of the molecular structure of compound **3a** (thermal ellipsoids are shown at the 30% probability level).

### Synthesis of $[\text{Cp}^*\text{Ru}(\text{H})_2\{\text{B}(3,4,5\text{-F}_3\text{C}_6\text{H}_2)\}]_2$ (**3b/4b**)



### Scheme S2

Toluene (25 mL) was added to a mixture of  $[\text{Cp}^*\text{RuCl}]_4$  (271.8 mg, 0.25 mmol) and  $\text{Li}[(3,4,5\text{-F}_3\text{C}_6\text{H}_2)\text{BH}_3]\cdot 2\text{THF}$  (325.7 mg, 1.10 mmol, 4.4 equiv.). The resulting red mixture was stirred at room temperature for 3 h. The mixture was concentrated to *ca.* 5 mL under vacuum and *n*-hexane (10 mL) was added. The obtained suspension was filtered through Celite to

remove remaining lithium salt. After removal of the solvent under vacuum, the brown residue was washed with *n*-hexane (2×2 mL) and dried under vacuum to give a mixture of **3b** and **4b** as a yellow solid. Yield: 261.8 mg, 69%.

*[Comment: Our efforts to isolate the pure 3b or 4b were not successful. In situ NMR studies show that the ratio of 3b and 4b is consistent with that for the isolated material. The conversion between 3b and 4b was not observed either at low temperature or at high temperature.]*

Crystallization of the obtained solid in *n*-hexane at -25 °C gave compound **3b** as yellow crystals suitable for X-ray crystal structure analysis.

**Elemental analysis:** calc. for C<sub>32</sub>H<sub>38</sub>B<sub>2</sub>F<sub>6</sub>Ru<sub>2</sub>: C, 50.55; H, 5.04. Found: C, 50.38; H, 5.37.

**NMR spectroscopic data for the mixture of two isomers (3b:4b = 78:22):**

**<sup>1</sup>H NMR** (400 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>)

**3b:** δ = 7.30 (m, 4H, F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 1.26 (s, 30H, C<sub>5</sub>Me<sub>5</sub>), -10.67 (s, 4H, RuH).

**4b:** δ = 6.98 (m, F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 1.54 (s, C<sub>5</sub>Me<sub>5</sub>), -12.51 (br, RuH).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>)

**3b:** δ = 151.1 (dm, <sup>1</sup>J<sub>FC</sub> ~ 251 Hz, *p*-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 145.6 (br, *i*-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 139.1 (dm, <sup>1</sup>J<sub>FC</sub> ~ 254 Hz, *m*-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 115.2 (m, *o*-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 96.3 (C<sub>5</sub>Me<sub>5</sub>), 9.88 (C<sub>5</sub>Me<sub>5</sub>).

**4b:** δ = 150.7 (dm, <sup>1</sup>J<sub>FC</sub> ~ 253 Hz, *p*-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), not observed (br, *i*-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 138.0 (dm, <sup>1</sup>J<sub>FC</sub> ~ 251 Hz, *m*-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 117.5 (br, *o*-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 94.8 (C<sub>5</sub>Me<sub>5</sub>),

11.24 ( $C_5Me_5$ ).

$^{11}B$  NMR (128 MHz, 298 K,  $C_6D_6$ )

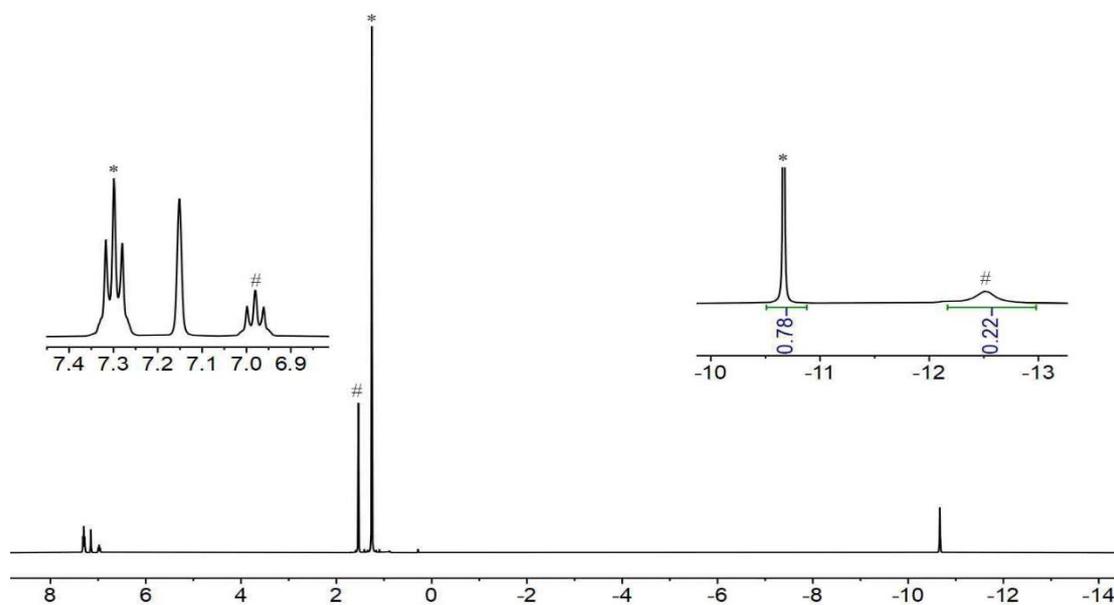
**3b**:  $\delta = 124.6$  ( $\nu_{1/2} \sim 1050$  Hz).

**4b**:  $\delta = 114.1$  ( $\nu_{1/2} \sim 840$  Hz).

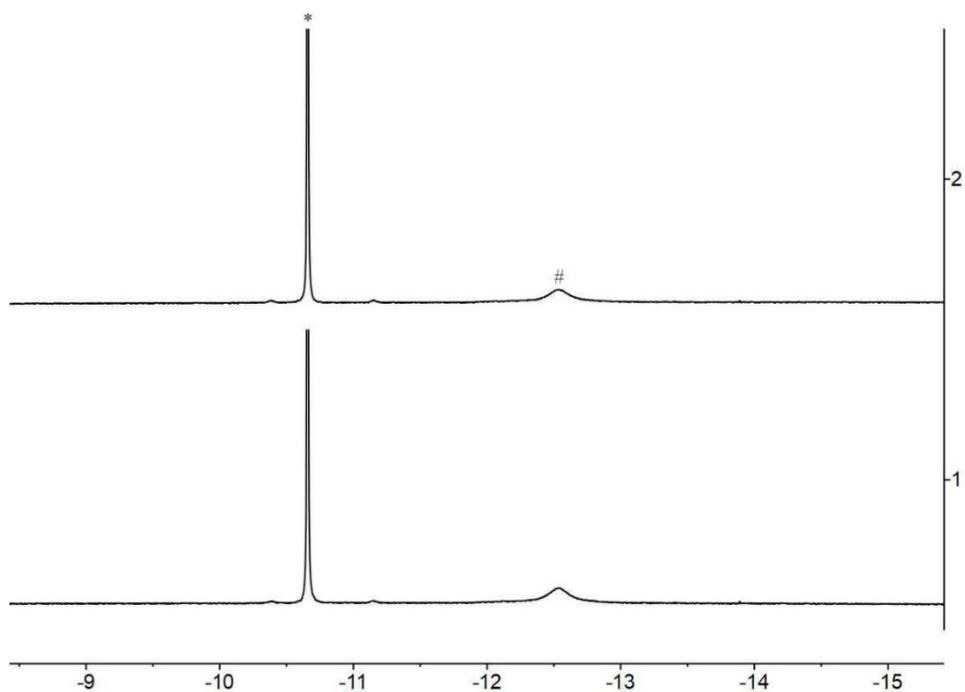
$^{19}F\{^1H\}$  NMR (377 MHz, 298 K,  $C_6D_6$ )

**3b**:  $\delta = -135.6$  (d,  $^3J_{FF} = 20.4$  Hz, 2F, *m*- $F_3C_6H_2$ ), 160.2 (t,  $^3J_{FF} = 20.4$  Hz, 1F, *p*- $F_3C_6H_2$ ).

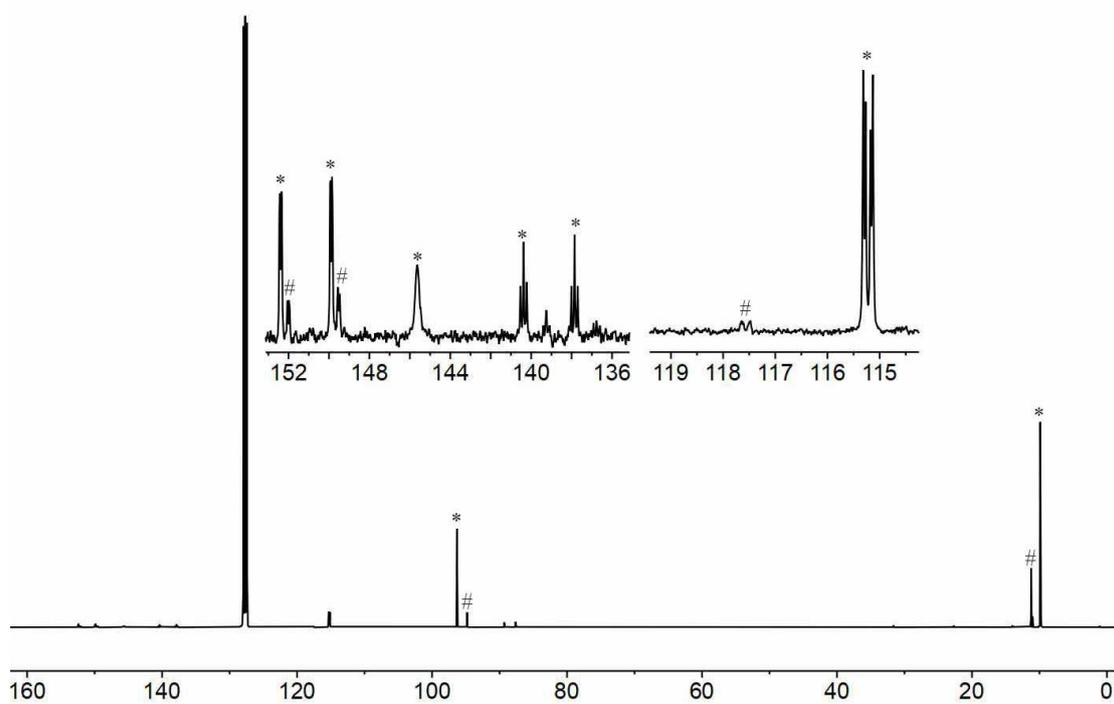
**4b**:  $\delta = -136.4$  (d,  $^3J_{FF} = 20.4$  Hz, *m*- $F_3C_6H_2$ ), 163.3 (br, *p*- $F_3C_6H_2$ ).



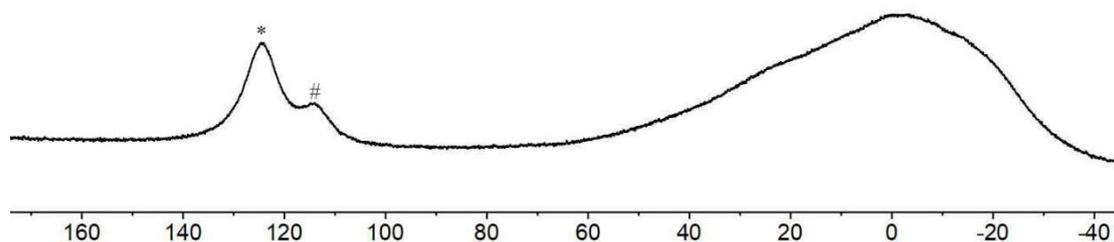
**Figure S6.**  $^1H$  NMR (400 MHz, 298 K,  $C_6D_6$ ) spectrum of the mixture of compounds **3b** (\*) and **4b** (#).



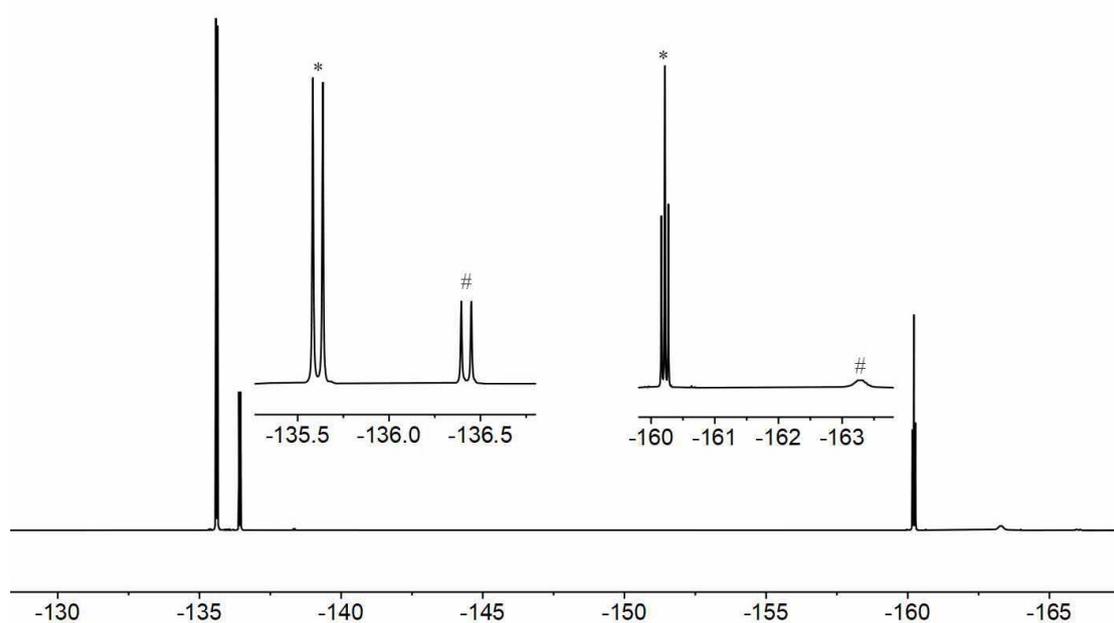
**Figure S7.** (1)  $^1\text{H}$  NMR and (2)  $^1\text{H}\{^{11}\text{B}\}$  NMR (400 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectra (hydride region) of the mixture of compounds **3b** (\*) and **4b** (#).



**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of the mixture of compounds **3b** (\*) and **4b** (#).



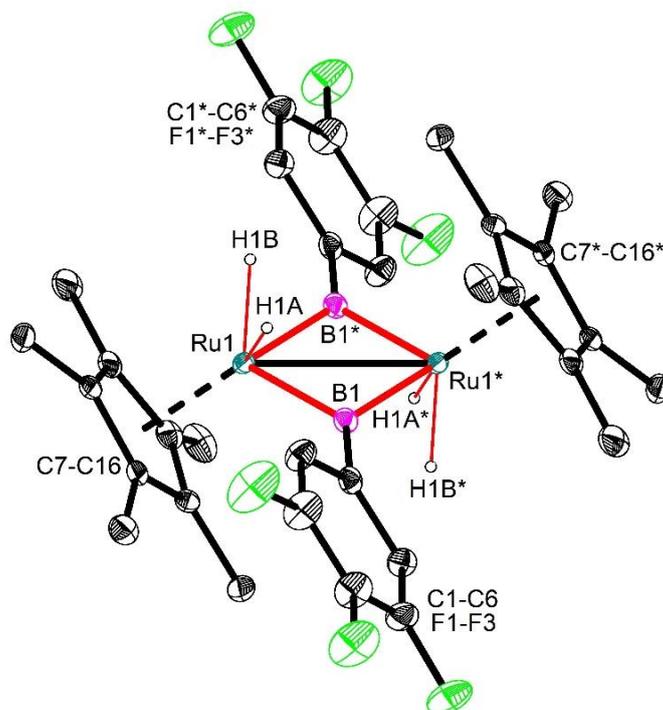
**Figure S9.**  $^{11}\text{B}$  NMR (128 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of the mixture of compounds **3b** (\*) and **4b** (#).



**Figure S10.**  $^{19}\text{F}\{^1\text{H}\}$  NMR (377 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of the mixture of compounds **3b** (\*) and **4b** (#).

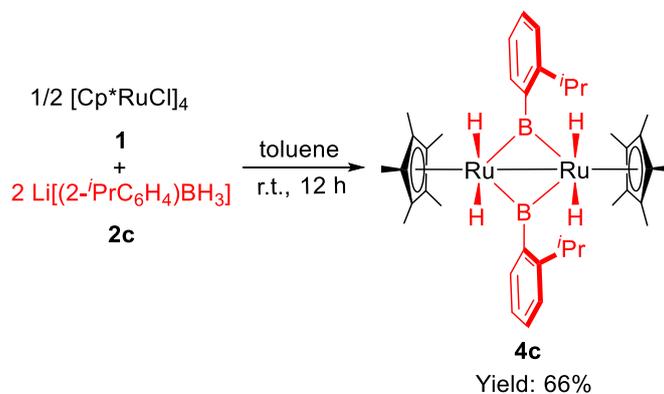
**X-ray crystal structure analysis of compound 3b:** formula  $\text{C}_{32}\text{H}_{38}\text{B}_2\text{F}_6\text{Ru}_2$ ,  $M = 760.38$  g/mol, yellow crystal,  $0.38 \times 0.20 \times 0.15$  mm,  $a = 11.5126(17)$ ,  $b = 12.3059(16)$ ,  $c = 12.6306(17)$  Å,  $\alpha = 88.819(4)$ ,  $\beta = 63.664(4)$ ,  $\gamma = 88.142(4)^\circ$ ,  $V = 1602.8(4)$  Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.576$  g·cm<sup>-3</sup>,  $\mu = 0.997$  mm<sup>-1</sup>, empirical absorption correction ( $0.6158 \leq T \leq 0.7460$ ),  $Z = 2$ , triclinic, space group  $P\bar{1}$  (No. 2),  $\lambda = 0.71073$  Å,  $T = 170$  K,  $\omega$  and  $\phi$  scans, 38057

reflections collected ( $\pm h, \pm k, \pm l$ ), 5626 independent ( $R_{\text{int}} = 0.0637$ ) and 4744 observed reflections [ $I > 2\sigma(I)$ ], 397 refined parameters,  $R = 0.0378$ ,  $wR^2 = 0.1047$ , max. (min.) residual electron density 1.33 (-0.78) e.Å<sup>-3</sup>.



**Figure S11.** A view of the molecular structure of compound **3b** (thermal ellipsoids are shown at the 30% probability level).

### Synthesis of $[\text{Cp}^*\text{Ru}(\text{H})_2\{\text{B}(2\text{-}i\text{PrC}_6\text{H}_4)\}]_2$ (**4c**)



**Scheme S3**

Toluene (25 mL) was added to a mixture of [Cp\**RuCl*]<sub>4</sub> (271.8 mg, 0.25 mmol) and Li[(2-*i*PrC<sub>6</sub>H<sub>4</sub>)BH<sub>3</sub>]*·*THF (233.3 mg, 1.10 mmol, 4.4 equiv.). The yellow suspension was stirred at room temperature for 12 h until the color of the solution turned maroon. The mixture was concentrated to *ca.* 5 mL under vacuum and *n*-hexane (10 mL) was added. The obtained suspension was filtered through Celite to remove remaining lithium salt. After removal of the solvent under vacuum, the brown residue was washed with *n*-hexane (2×2 mL) and dried under vacuum to give compound **4c** as a yellow solid. Yield: 244.0 mg, 66%.

*[Comment: In situ NMR studies show that this is a very clean reaction. The isolated yield is 66%, due to the partial solubility in n-hexane.]*

Crystals suitable for the X-ray crystal structure analysis of **4c** were obtained by recrystallization in *n*-hexane at -25 °C.

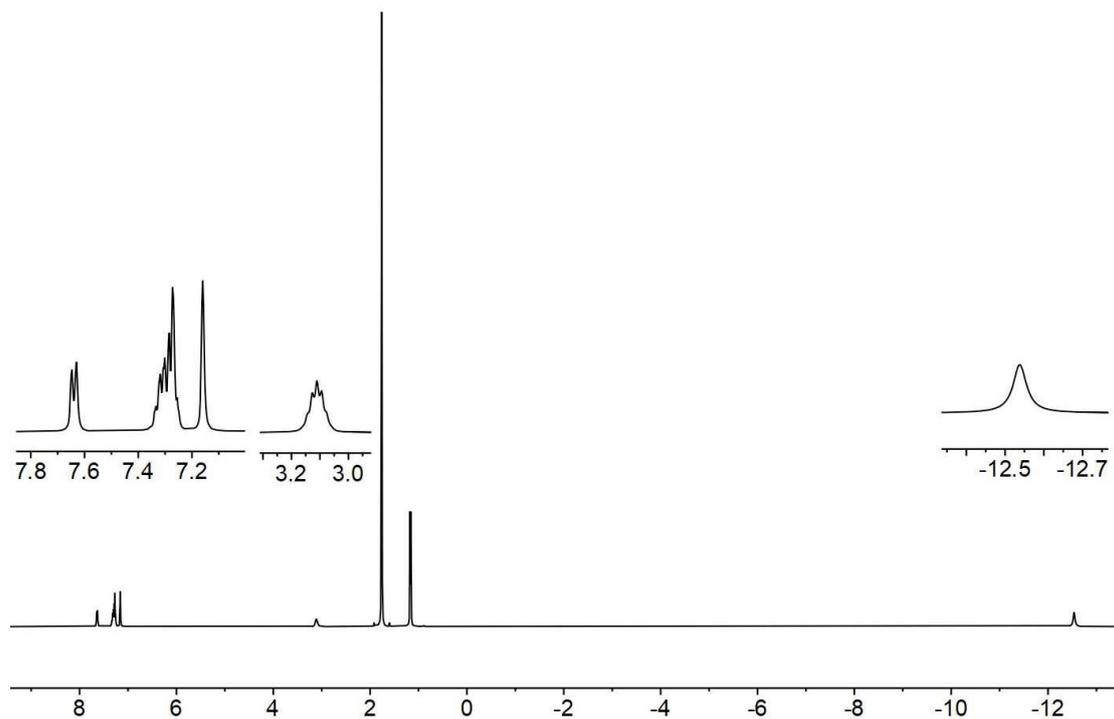
**Elemental analysis:** calc. for C<sub>38</sub>H<sub>56</sub>B<sub>2</sub>Ru<sub>2</sub>: C, 61.96; H, 7.66. Found: C, 61.93; H, 7.65.

**NMR spectroscopic data for compound 4c:**

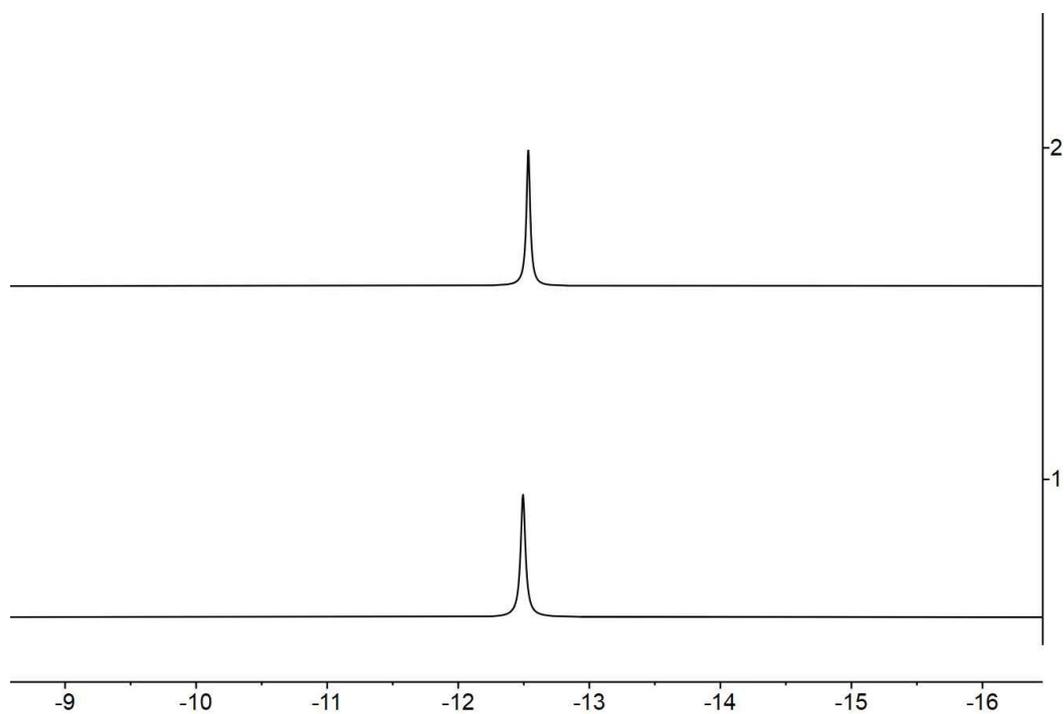
<sup>1</sup>H NMR (400 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ = 7.64 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2H, *i*PrC<sub>6</sub>H<sub>4</sub>), 7.27-7.33 (m, 6H, *i*PrC<sub>6</sub>H<sub>4</sub>), 3.11 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2H, CH<sup>*i*Pr</sup>), 1.76 (s, 30H, C<sub>5</sub>Me<sub>5</sub>), 1.17 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 12H, CH<sub>3</sub><sup>*i*Pr</sup>), -12.54 (br, 4H, RuH).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ = 153.8 (br, *i*-*i*PrC<sub>6</sub>H<sub>4</sub>), 147.5, 128.9, 127.4, 124.8, 122.7 (*i*PrC<sub>6</sub>H<sub>4</sub>), 95.1 (C<sub>5</sub>Me<sub>5</sub>), 31.9 (CH<sup>*i*Pr</sup>), 23.7 (CH<sub>3</sub><sup>*i*Pr</sup>), 11.8 (C<sub>5</sub>Me<sub>5</sub>).

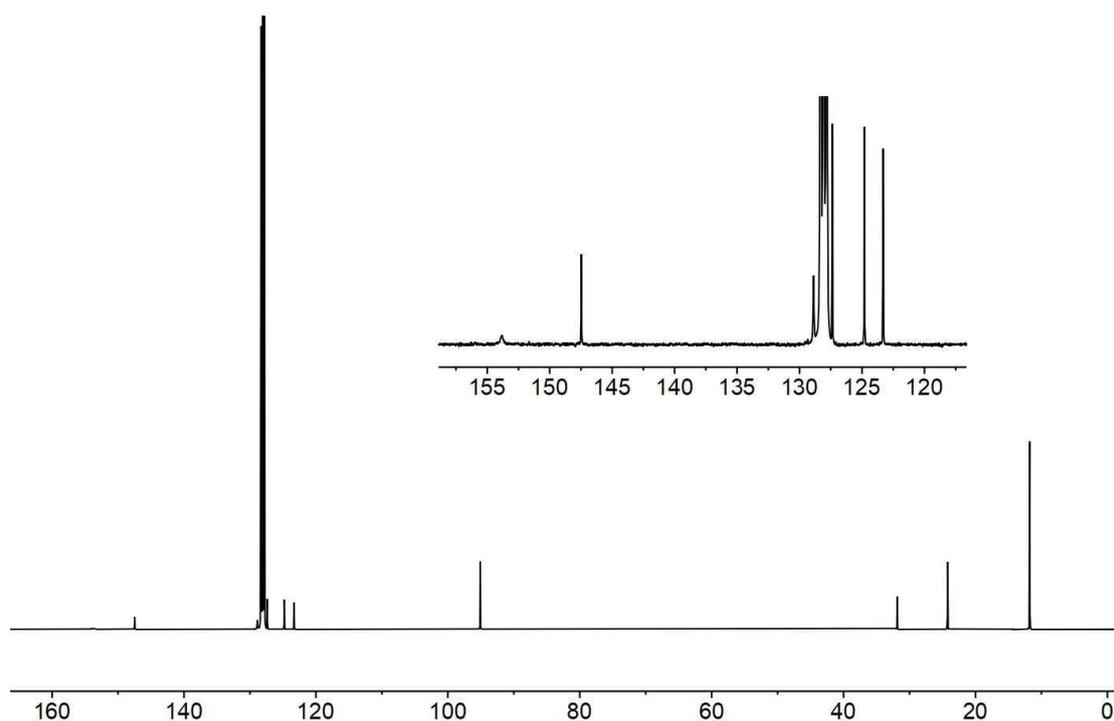
$^{11}\text{B}$  NMR (128 MHz, 298 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 115.4$  ( $\nu_{1/2} \sim 960$  Hz).



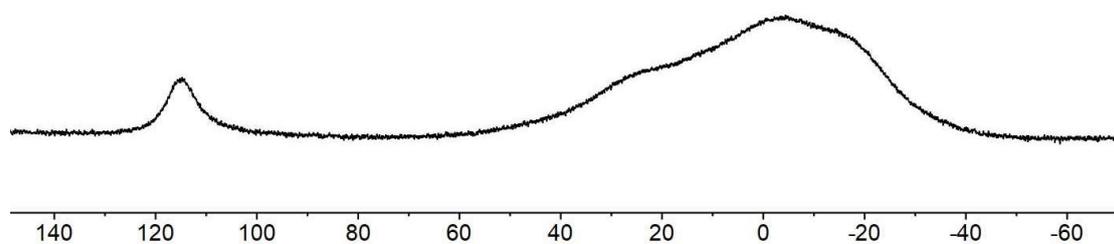
**Figure S12.**  $^1\text{H}$  NMR (400 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of compound **4c**.



**Figure S13.** (1)  $^1\text{H}$  NMR and (2)  $^1\text{H}\{^{11}\text{B}\}$  NMR (400 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectra (hydride region) of compound **4c**.



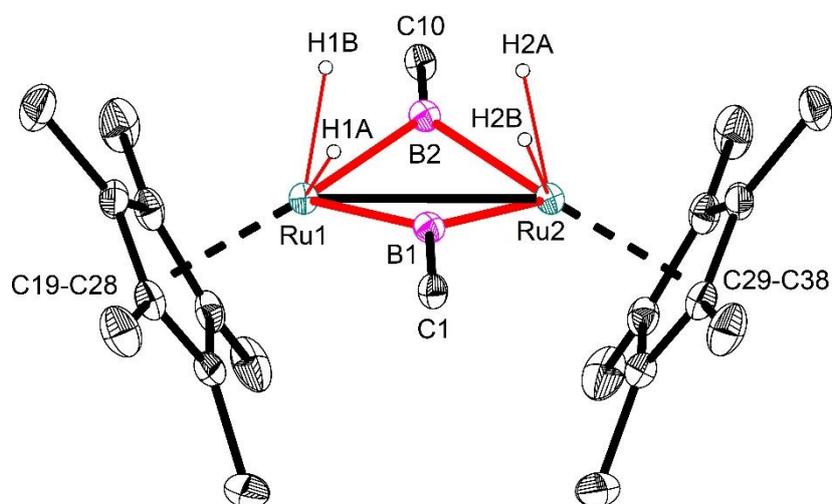
**Figure S14.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of compound **4c**.



**Figure S15.**  $^{11}\text{B}$  NMR (128 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of compound **4c**.

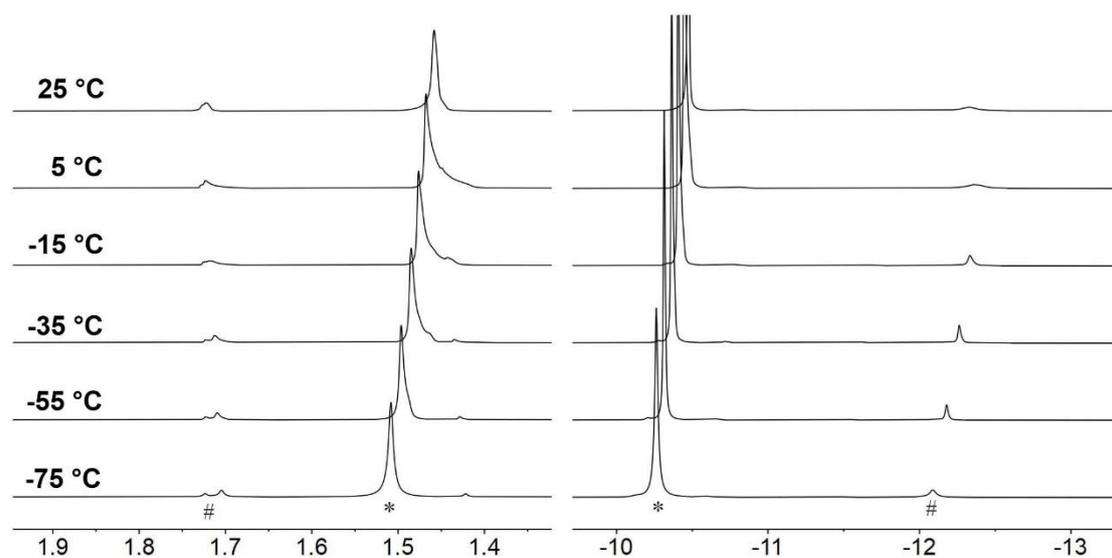
**X-ray crystal structure analysis of compound 4c:** formula  $\text{C}_{38}\text{H}_{56}\text{B}_2\text{Ru}_2$ ,  $M = 736.58$  g/mol, yellow crystal, 0.25 x 0.15 x 0.12 mm,  $a = 20.8857(12)$ ,  $b = 15.8426(10)$ ,  $c = 22.4748(12)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 7436.5(7)$  Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.316$  g·cm<sup>-3</sup>,  $\mu = 0.835$  mm<sup>-1</sup>, empirical absorption correction ( $0.6821 \leq T \leq 0.7456$ ),  $Z = 8$ , orthorhombic, space group *Pbca* (No. 61),  $\lambda = 0.71073$

Å,  $T = 293$  K,  $\omega$  and  $\varphi$  scans, 182500 reflections collected ( $\pm h, \pm k, \pm l$ ), 6547 independent ( $R_{\text{int}} = 0.0572$ ) and 5358 observed reflections [ $I > 2\sigma(I)$ ], 410 refined parameters,  $R = 0.0233$ ,  $wR^2 = 0.0567$ , max. (min.) residual electron density 0.214 (-0.247) e.Å<sup>-3</sup>.

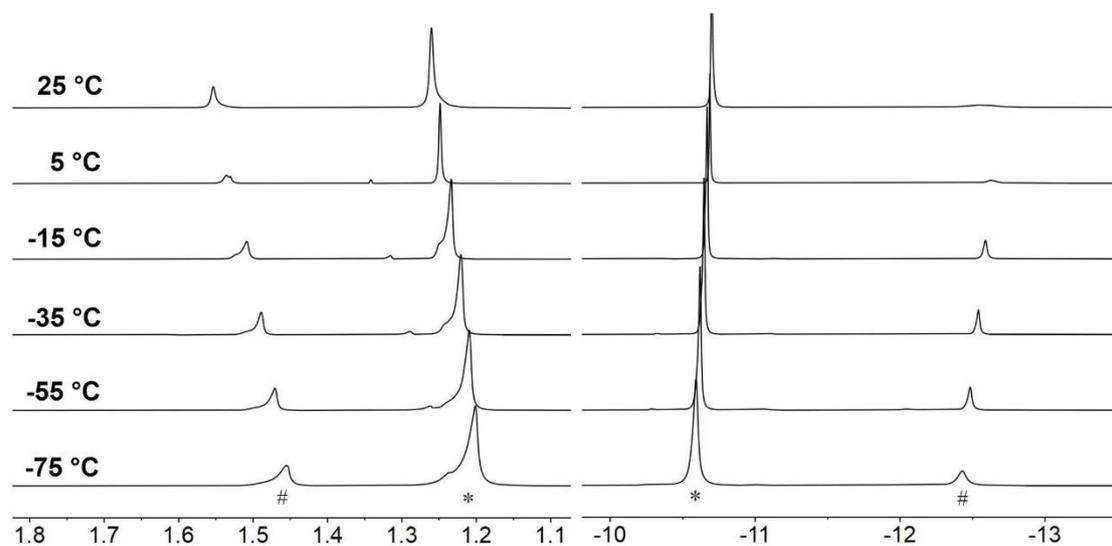


**Figure S16.** A view of the molecular structure of compound **4c** (thermal ellipsoids are shown at the 15% probability level, and partial 2-isopropylphenyl group atoms have been omitted for clarity).

### VT $^1\text{H}$ NMR spectroscopy of compounds 3a/4a and 3b/4b

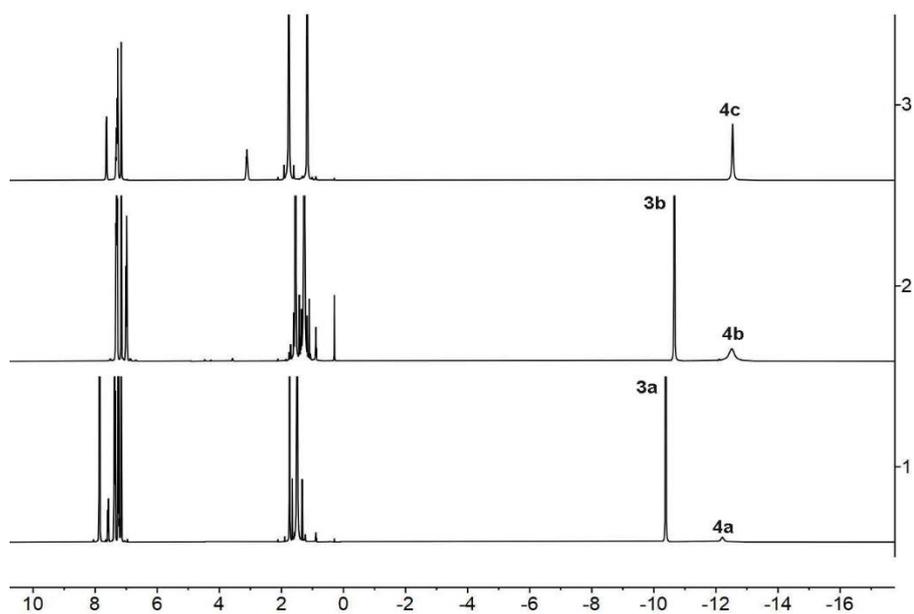


**Figure S17.** Variable-temperature  $^1\text{H}$  NMR spectra of the mixture of compounds **3a** (\*) and **4a** (#) showing Cp\* (left) and hydride (right) regions in  $\text{C}_7\text{D}_8$ .

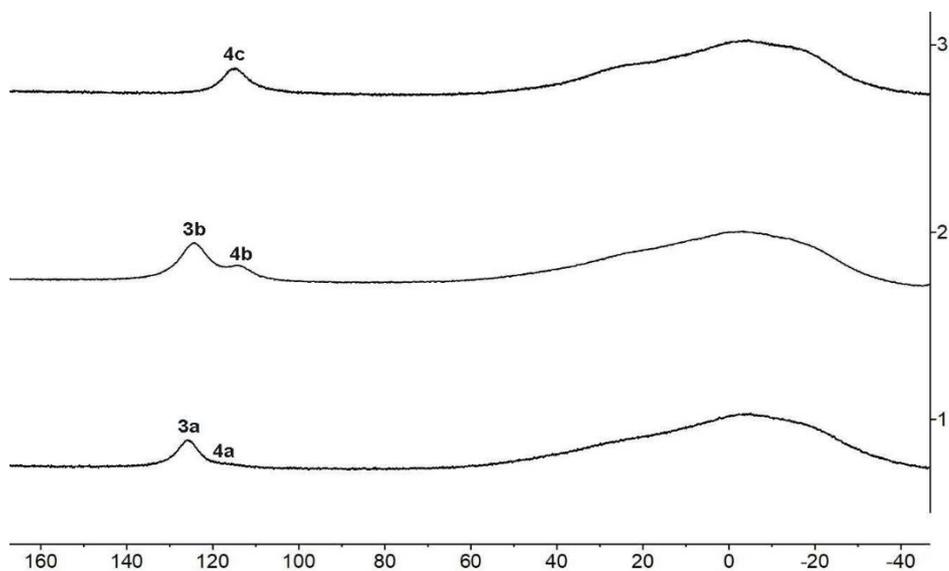


**Figure S18.** Variable-temperature  $^1\text{H}$  NMR spectra of the mixture of compounds **3b** (\*) and **4b** (#) showing Cp\* (left) and hydride (right) regions in  $\text{C}_7\text{D}_8$ .

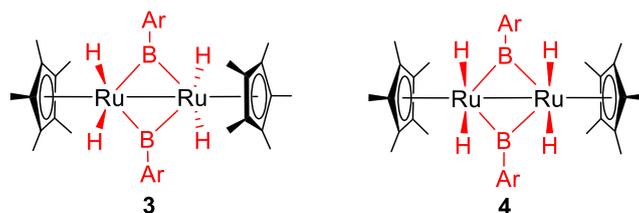
Stacking  $^1\text{H}/^{11}\text{B}$  NMR spectra and selected NMR data of **3a/4a**, **3b/4b** and **4c**



**Figure S19.**  $^1\text{H}$  NMR (400 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectra of (1) the mixture of compounds **3a** and **4a**, (2) the mixture of compounds **3b** and **4b**, (3) compound **4c**.



**Figure S20.**  $^{11}\text{B}$  NMR (128 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectra of (1) the mixture of compounds **3a** and **4a**, (2) the mixture of compounds **3b** and **4b**, (3) compound **4c**.



a: Ar = Ph; b: Ar = 3,4,5-F<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; c: Ar = 2-<sup>i</sup>PrC<sub>6</sub>H<sub>4</sub>

**Table S1. Selected NMR shifts ( $\delta$ ) for compounds 3a/4a, 3b/4b and 4c**

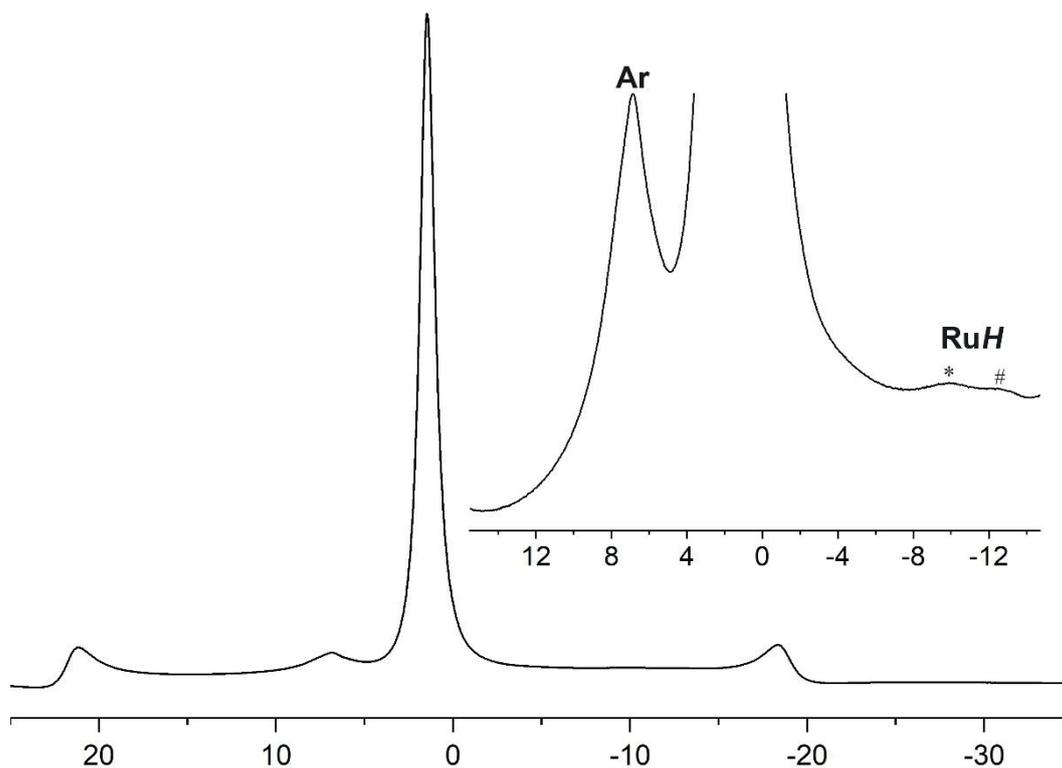
[a]

Compound	<sup>1</sup> H MAS		<sup>1</sup> H	
	RuH	RuH	C <sub>5</sub> Me <sub>5</sub>	<sup>11</sup> B
<b>3a</b>	-9.9	-10.38	1.49	126.0
<b>3b</b>	-10.1	-10.67	1.26	124.6
<b>4a</b>	-12.1	-12.21	1.74	115.6
<b>4b</b>	-12.9	-12.51	1.54	114.1
<b>4c</b>	-12.5	-12.54	1.76	115.4

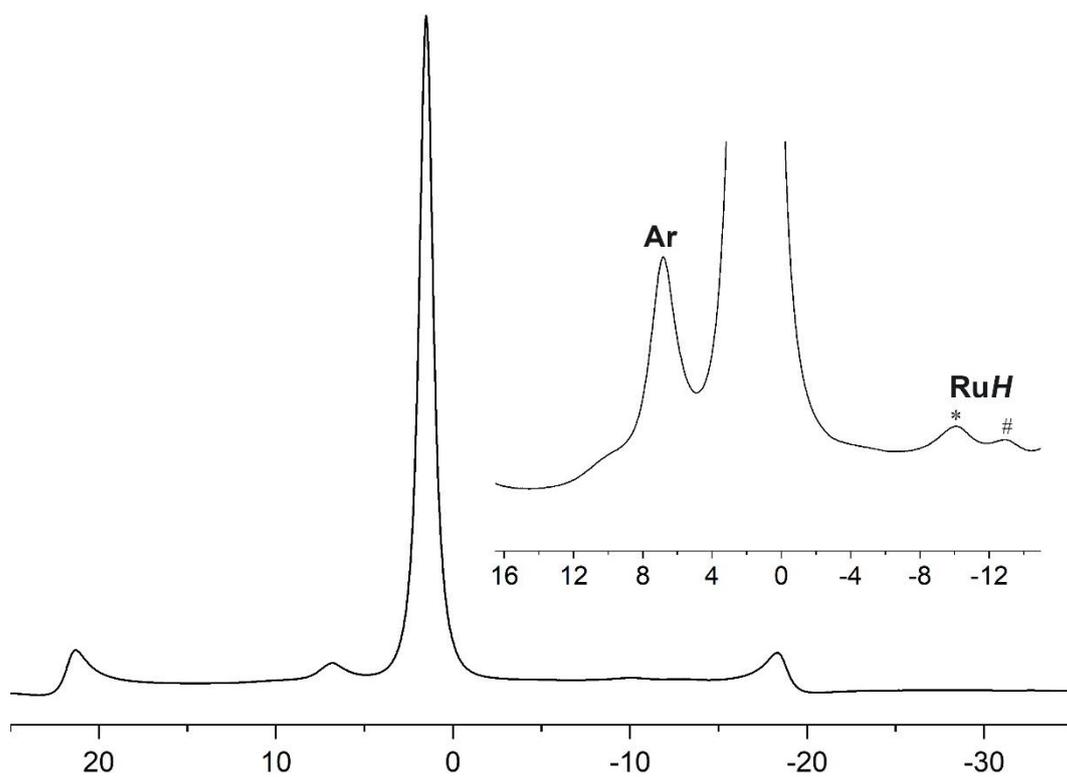
[a] Liquid-state NMR data recorded in C<sub>6</sub>D<sub>6</sub> at 298 K.

## Solid state $^1\text{H}$ MAS NMR spectroscopy of compounds **3a/4a**, **3b/4b** and **4c**

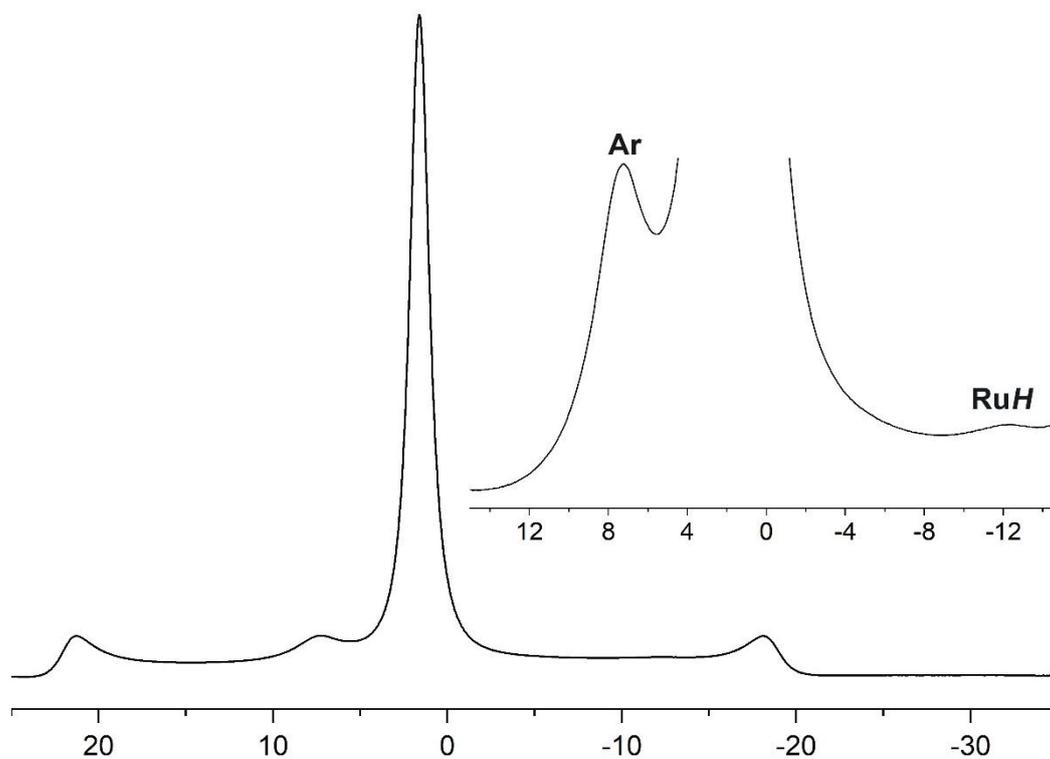
Solid-state  $^1\text{H}$  MAS NMR experiments were recorded on an Agilent DD2 500 ( $B_0 = 11.7$  T) spectrometer with resonance frequency of 500 MHz. Spectra were acquired in 4 mm MAS probe with a spinning rate of 10.0 kHz. Pulse width of  $2.5 \mu\text{s}$  ( $\pi/4$ ), and recycle delays of 4 s were used. Chemical shifts were externally referenced to adamantane as secondary standard ( $\delta^1\text{H} = 1.93$  ppm).



**Figure S21.**  $^1\text{H}$  MAS NMR spectrum of isolated compounds **3a** (\*) and **4a** (#).



**Figure S22.**  $^1\text{H}$  MAS NMR spectrum of isolated compounds **3b** (\*) and **4b** (#).

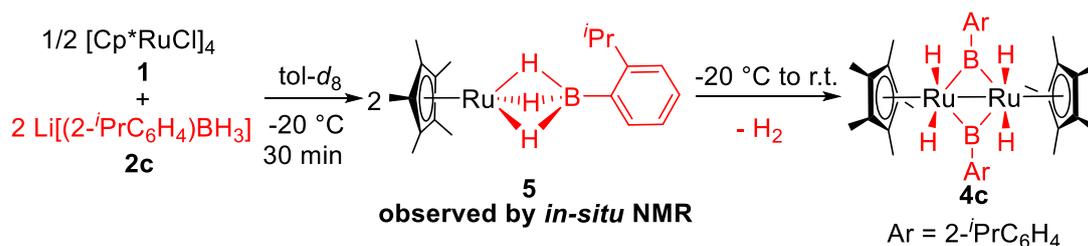


**Figure S23.**  $^1\text{H}$  MAS NMR spectrum of isolated compound **4c**.

**Table S2.  $^1\text{H}$  MAS NMR chemical shifts ( $\delta$ ) for compounds **3a/4a**, **3b/4b** and **4c****

Compound	Ar	RuH
<b>3a+4a</b>	6.8	-9.9, -12.1
<b>3b+4b</b>	6.8	-10.1, -12.9
<b>4c</b>	7.3	-12.5

**Observation of the intermediate **5** in the reaction of compounds **1** and **2c****



**Scheme S4**

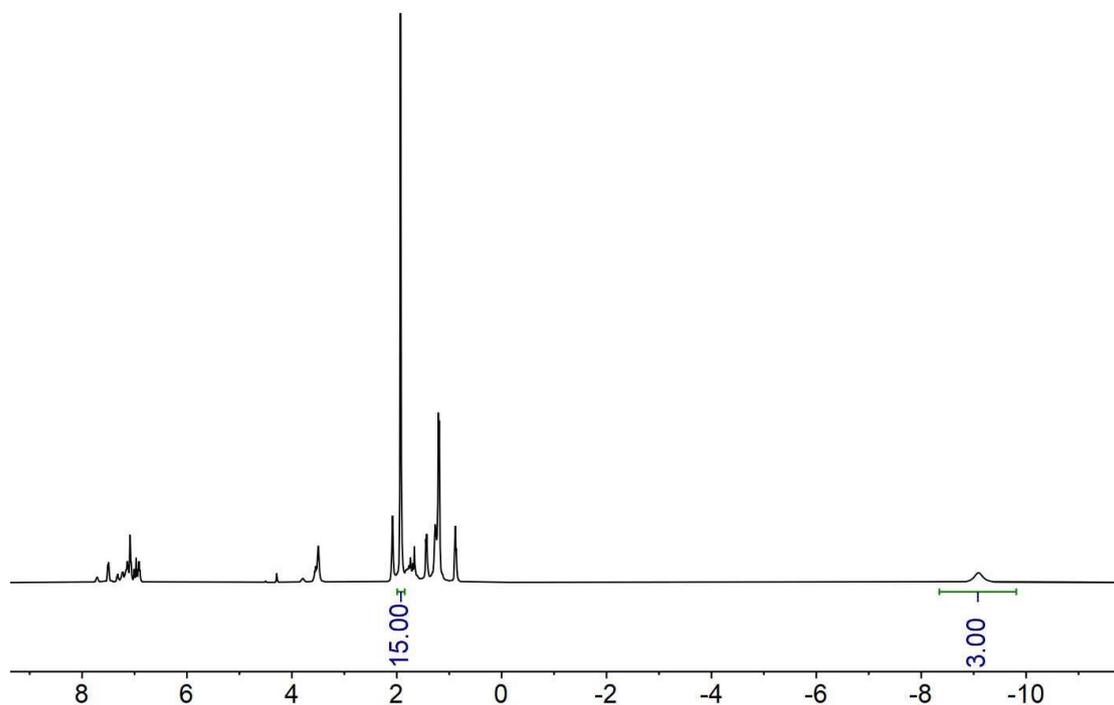
Tol- $d_8$  (0.6 mL) was added slowly to a mixture of  $[\text{Cp}^*\text{RuCl}]_4$  (10.9 mg, 0.01 mmol) and  $\text{Li}[(2\text{-}i\text{PrC}_6\text{H}_4)\text{BH}_3]\cdot\text{THF}$  (10.2 mg, 0.048 mmol, 4.8 equiv.) in a J. Young NMR tube at  $-20\text{ }^\circ\text{C}$ . The NMR sample was sealed and kept at  $-20\text{ }^\circ\text{C}$  for 30 min, resulting in a deep yellow mixture. Then  $^1\text{H}$  and  $^{11}\text{B}$  NMR experiments were conducted, the *in-situ* NMR studies showed that compound **5** had been formed exclusively with 95% conversion. Subsequently, the reaction was warmed to room temperature, and the NMR tube was monitored again after 5 h at room temperature. NMR spectroscopy studies showed the formation of **5** and **4c** in a *ca.* 3:7

ratio. After 24 h, 90% conversion to compound **4c** was reached, detected by  $^1\text{H}$  and  $^{11}\text{B}$  NMR.

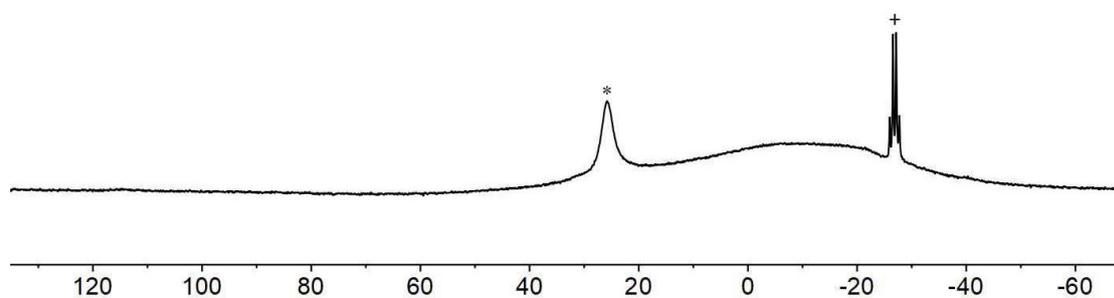
**NMR spectroscopic data for compound 5:**

$^1\text{H}$  NMR (400 MHz, 253 K,  $\text{C}_7\text{D}_8$ ) [selected signals]:  $\delta = 1.93$  (s, 15H,  $\text{C}_5\text{Me}_5$ ), -9.09 (br, 3H, RuHB).

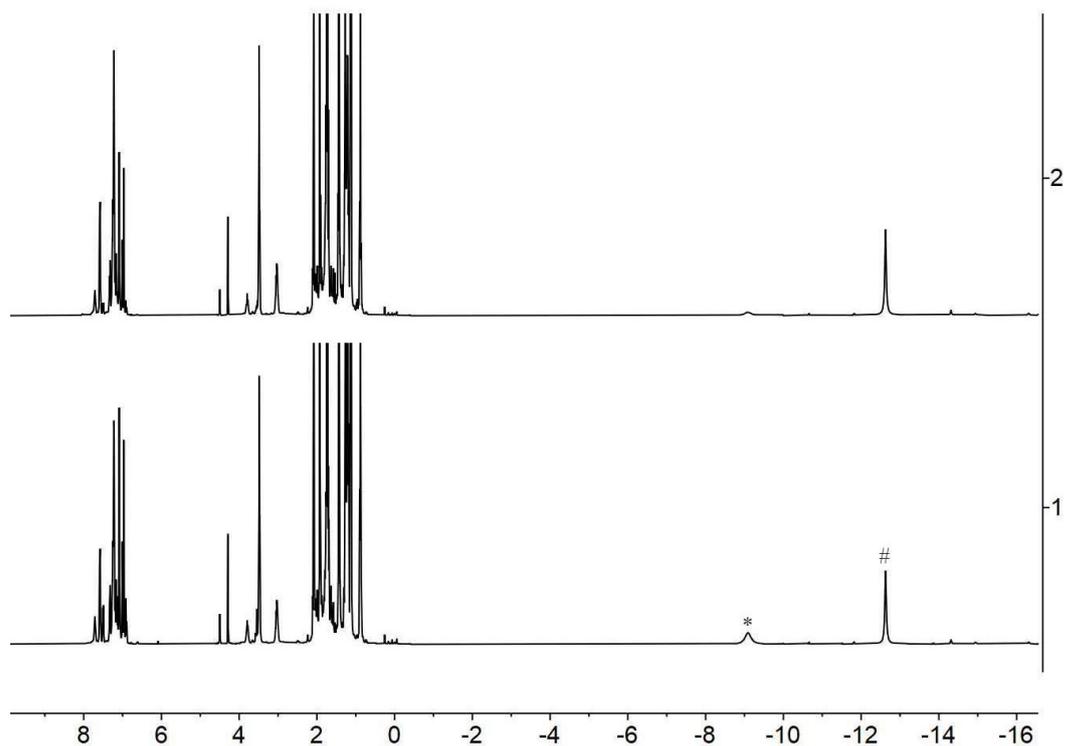
$^{11}\text{B}$  NMR (128 MHz, 253 K,  $\text{C}_7\text{D}_8$ ):  $\delta = 25.7$  ( $\nu_{1/2} \sim 365$  Hz).



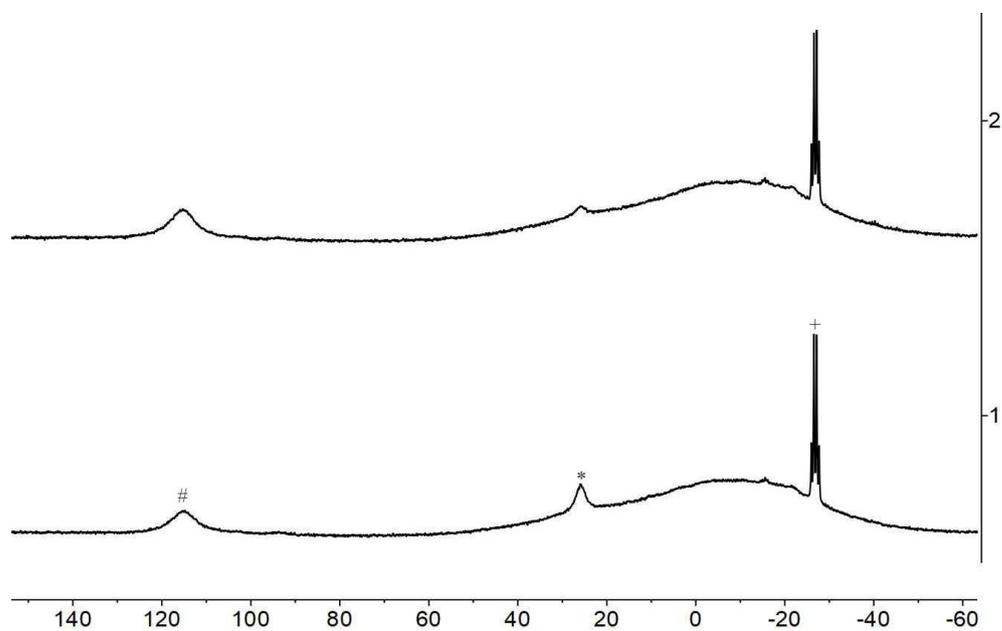
**Figure S24.** *In-situ*  $^1\text{H}$  NMR (400 MHz, 253 K,  $\text{C}_7\text{D}_8$ ) spectrum of compound **5**.



**Figure S25.** *In-situ*  $^{11}\text{B}$  NMR (128 MHz, 253 K,  $\text{C}_7\text{D}_8$ ) spectrum of compound **5** (\*) [admixed with the excessive **2c** (+)].

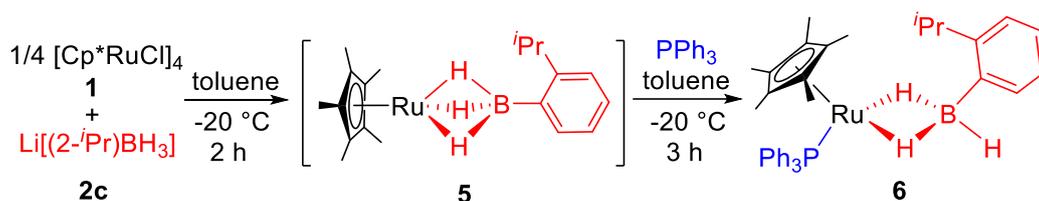


**Figure S26.**  $^1\text{H}$  NMR (400 MHz, 298 K,  $\text{C}_7\text{D}_8$ ) spectra of *in-situ* generated compounds **5** (\*) and **4c** (#) at room temperature: (1) after 5 h; (2) after 24 h.



**Figure S27.**  $^{11}\text{B}$  NMR (128 MHz, 298 K,  $\text{C}_7\text{D}_8$ ) spectra of *in-situ* generated compounds **5** (\*) and **4c** (#) at room temperature [admixed with the excessive **2c** (+)]: (1) after 5 h; (2) after 24 h.

## Trapping experiment of the intermediate 5 with PPh<sub>3</sub>



**Scheme S5**

Pre-cooled (-20 °C) toluene (20 mL) was added to a mixture of [Cp\*RuCl]<sub>4</sub> (217.4 mg, 0.20 mmol) and Li[(2-<sup>i</sup>Pr)C<sub>6</sub>H<sub>4</sub>]BH<sub>3</sub>·THF (186.6 mg, 0.88 mmol, 4.4 equiv.). The mixture was stirred at -20 °C for 2 h to completely *in-situ* generate compound 5. Then a pre-cooled (-20 °C) solution of PPh<sub>3</sub> (209.8 mg, 0.80 mmol) in toluene (5 mL) was added to the above reaction mixture via cannula, in small portions over 10 min. The suspension was stirred for an additional 3 h at -20 °C before it was warmed slowly to room temperature. After removal of the solvent under vacuum, the residue was extracted with *n*-hexane (3×5 mL) followed by filtration through Celite. Concentration of the extract to *ca.* 5 mL and storage at -25 °C to afford compound 6 as yellow crystals, some of the crystals were suitable for X-ray crystal structure analysis. Yield: 414.0 mg, 82%.

Elemental analysis: calc. for C<sub>37</sub>H<sub>44</sub>BPRu: C, 70.36; H, 7.02. Found: C, 70.34; H, 7.04.

### NMR spectroscopic data for compound 6:

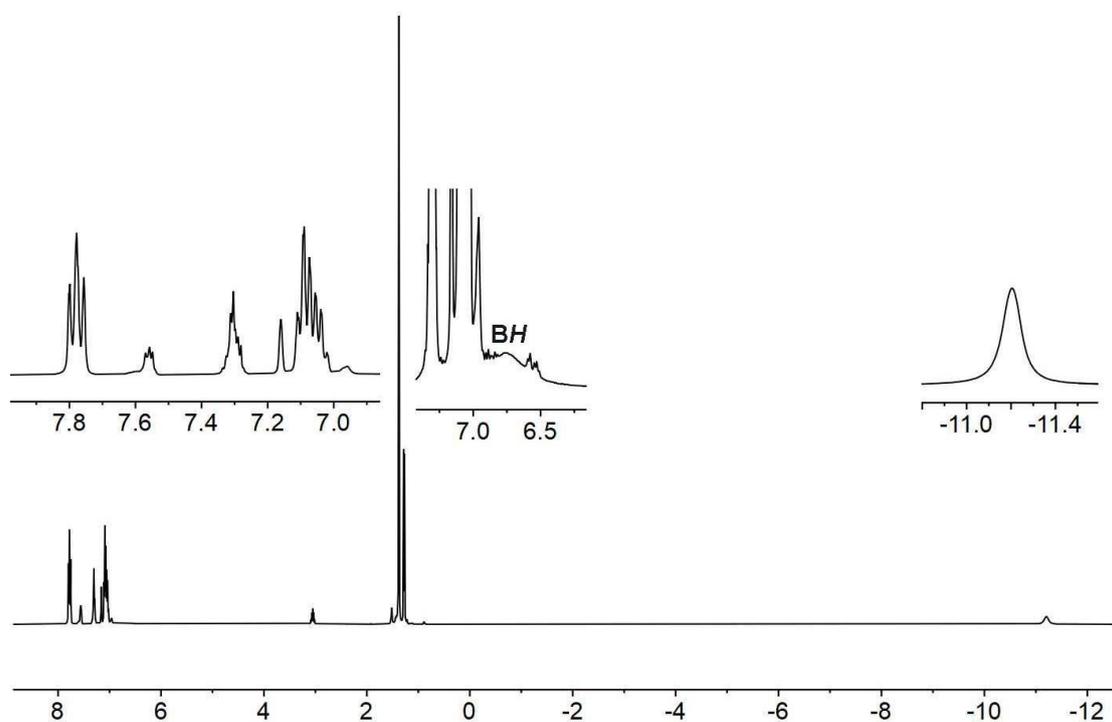
<sup>1</sup>H NMR (400 MHz, 298K, C<sub>6</sub>D<sub>6</sub>): δ = 7.02-7.80 (m, 19H, Ph), 6.76 (br, 1H, BH), 3.05 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 1H, CH<sup>iPr</sup>), 1.38 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.28

(d,  $^3J_{\text{HH}} = 6.8$  Hz, 6H,  $\text{CH}_3^{\text{iPr}}$ ), -11.20 (s, 2H, RuHB).

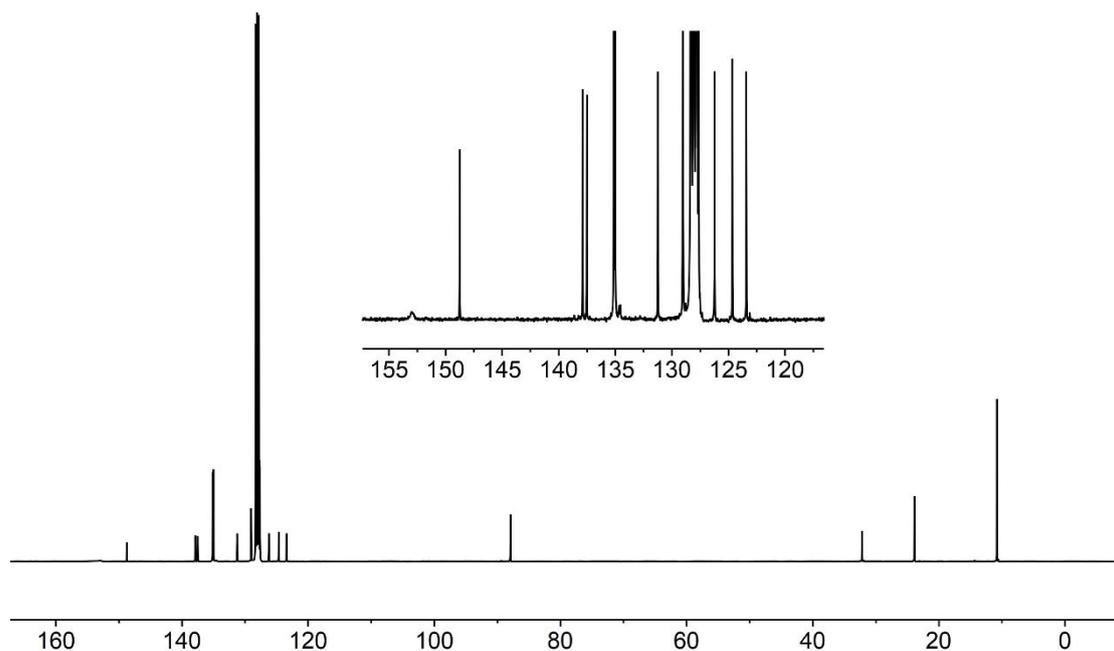
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, 298 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 153.0$  (br,  $i\text{-PrC}_6\text{H}_4$ ), 148.8, 131.2, 126.2, 124.7, 123.4 ( $i\text{-PrC}_6\text{H}_4$ ), 137.7 (d,  $^1J_{\text{PC}} = 37.4$  Hz,  $i\text{-Ph}$ ), 135.1 (d,  $^2J_{\text{PC}} = 11.1$  Hz,  $o\text{-Ph}$ ), 129.0 (d,  $^4J_{\text{PC}} = 2.0$  Hz,  $p\text{-Ph}$ ), 127.7 (d,  $^3J_{\text{PC}} = 10.1$  Hz,  $m\text{-Ph}$ ), 87.9 ( $\text{C}_5\text{Me}_5$ ), 32.2 ( $\text{CH}^{\text{iPr}}$ ), 23.9 ( $\text{CH}_3^{\text{iPr}}$ ), 10.8 ( $\text{C}_5\text{Me}_5$ ).

$^{11}\text{B}$  NMR (128 MHz, 298 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 47.1$  ( $\nu_{1/2} \sim 620$  Hz).

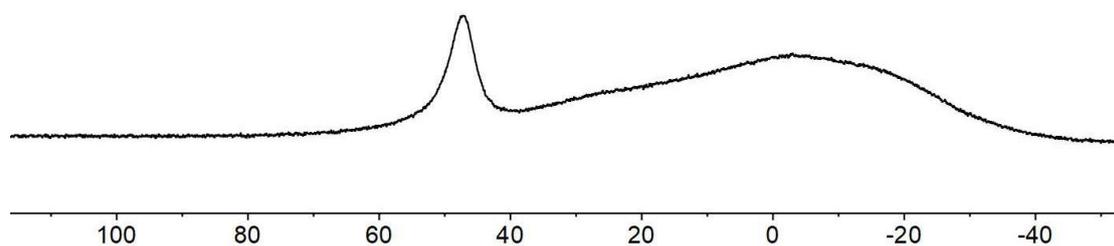
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz, 298 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 59.9$ .



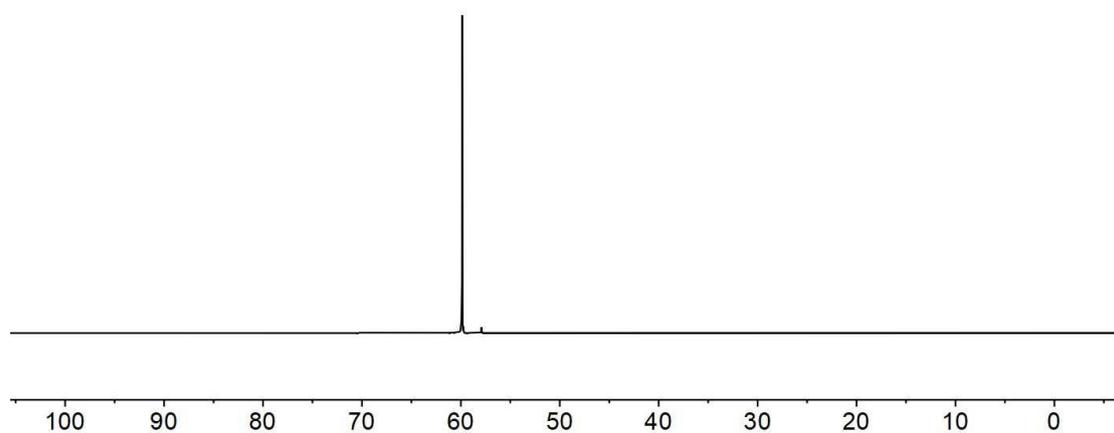
**Figure S28.**  $^1\text{H}$  NMR (400 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of compound **6**.



**Figure S29.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of compound **6**.

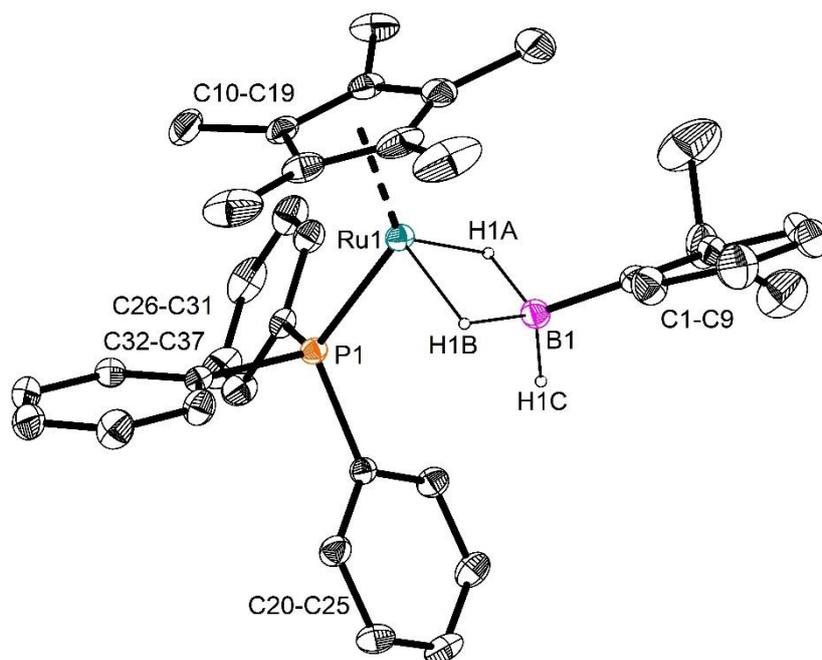


**Figure S30.**  $^{11}\text{B}$  NMR (128 MHz, 298K,  $\text{C}_6\text{D}_6$ ) spectrum of compound **6**.



**Figure S31.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of compound **6**.

**X-ray crystal structure analysis of compound 6:** formula  $C_{37}H_{44}BPRu$ ,  $M = 631.57$  g/mol, yellow crystal,  $0.35 \times 0.24 \times 0.15$  mm,  $a = 8.8795(5)$ ,  $b = 12.1593(7)$ ,  $c = 16.4427(10)$  Å,  $\alpha = 72.368(2)^\circ$ ,  $\beta = 83.187(2)^\circ$ ,  $\gamma = 73.943(2)^\circ$ ,  $V = 1624.71(17)$  Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.291$  g·cm<sup>-3</sup>,  $\mu = 0.555$  mm<sup>-1</sup>, empirical absorption correction ( $0.7104 \leq T \leq 0.7461$ ),  $Z = 2$ , triclinic, space group  $P\bar{1}$  (No. 2),  $\lambda = 0.71073$  Å,  $T = 200$  K,  $\omega$  and  $\varphi$  scans, 24800 reflections collected ( $\pm h, \pm k, \pm l$ ), 5675 independent ( $R_{\text{int}} = 0.0462$ ) and 4884 observed reflections [ $I > 2\sigma(I)$ ], 380 refined parameters,  $R = 0.0312$ ,  $wR^2 = 0.0705$ , max. (min.) residual electron density 0.41 (-0.36) e·Å<sup>-3</sup>.



**Figure S32.** A view of the molecular structure of compound **6** (thermal ellipsoids are shown at the 30% probability level).