

Supporting Information for:

**Si–C(sp<sup>3</sup>) Bond Activation Through Oxidative Addition at a Rh(I) centre**

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## 1. Experimental

All manipulations, unless otherwise stated, were performed under an atmosphere of argon or nitrogen, using standard Schlenk and glove-box techniques. Glassware was oven dried at 130°C overnight and flamed under vacuum prior to use. Hexane was dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles.<sup>1</sup> CD<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>2</sub>O and MeCN were distilled under vacuum and stored over 3 Å molecular sieves. nBuLi, 2-bromothioanisole and Cl<sub>2</sub>SiMe<sub>2</sub> were purchased from Aldrich. [Rh(nbd)Cl]<sub>2</sub>,<sup>2</sup> [Rh(cod)Cl]<sub>2</sub><sup>3</sup> and [Rh(coe)<sub>2</sub>Cl]<sub>2</sub><sup>4</sup> were prepared as previously described. NMR spectra were recorded on Bruker Ultra Shift 500 MHz spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to the residual solvent signals. Microanalysis was carried out with a LECO TRUSPEC microanalyzer. Chemical shifts are quoted in ppm and coupling constants in Hz. ESI-MS were recorded on a Bruker MicrOTOF instrument. In all ESI-MS spectra there was a good fit to both the principal molecular ion and the overall isotopic distribution.

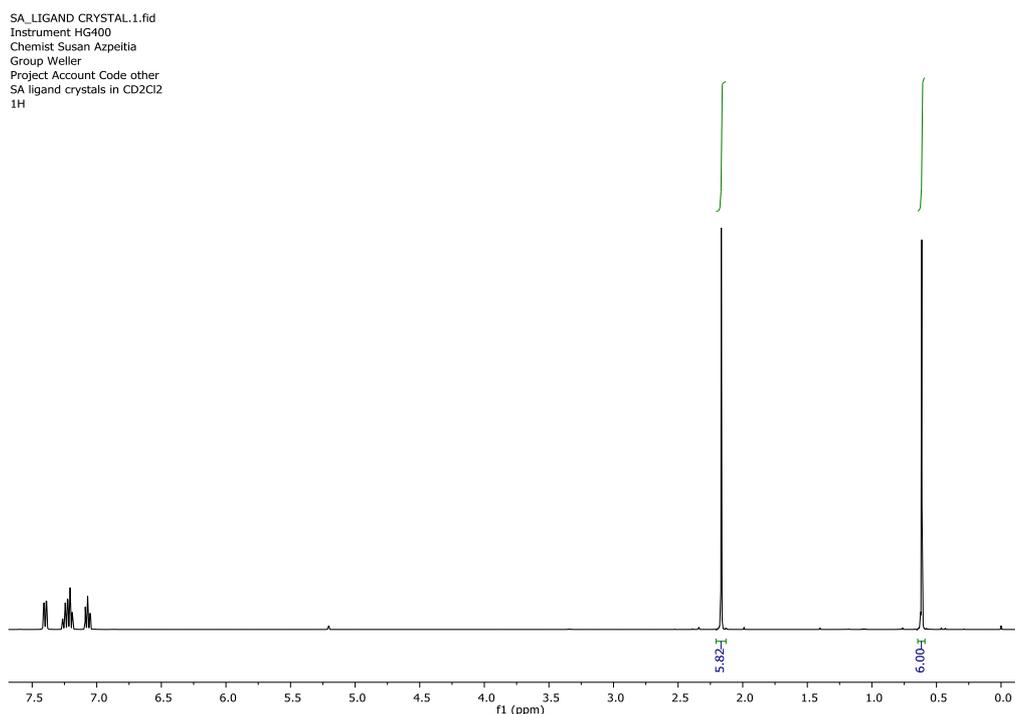
## 2. Synthesis and characterization of [Si(Me)<sub>2</sub>(o-C<sub>6</sub>H<sub>4</sub>SMe)<sub>2</sub>] (L)



To a Schlenk charged with 2-Bromothioanisole (0.50 mL, 0.037 mmol) in Et<sub>2</sub>O (10 ml) an excess of 1.1 of nBuLi (1.65 mL, 0.0041 mmol) is added slowly, at a temperature of 0°C (ice bath). The mixture is stirred for 60 minutes. After that time half an equivalent of dichlorodimethylsilane is added dropwise (0.23 mL, 0.0019 mmol) and it is left to stir overnight at room temperature. The mixture is then quenched with water and the product is extracted with diethyl ether. Evaporation of the solvent under vacuum gives product [Si(Me)<sub>2</sub>(o-C<sub>6</sub>H<sub>4</sub>SMe)<sub>2</sub>] as a crystalline white solid.

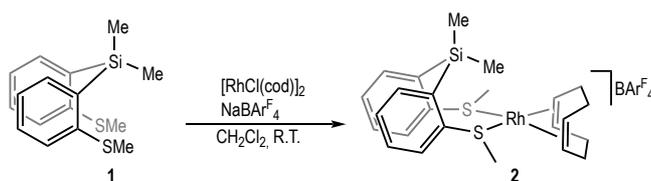
**Elemental Analysis:** Calc.: C, 63.10; H, 6.62; S, 21.05. Found: C, 63.15; H, 6.59; S, 20.98.

**<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):** δ 7.60 – 7.40 (m, 8 *H*<sub>aromatics</sub>), 2.18 (s, 6 H, S-CH<sub>3</sub>), 0.65 (s, 6 H, Si-CH<sub>3</sub>, <sup>29</sup>Si satellites <sup>2</sup>J<sub>Si-H</sub> = 6.7 Hz).



**Figure S1.** <sup>1</sup>H NMR spectrum of **1**

### 3. Synthesis and characterization of $[\text{Rh}(\text{cod})\text{SiMe}_2(\text{o-C}_6\text{H}_4\text{SMe})_2]\text{BARf}_4$ (**2**)



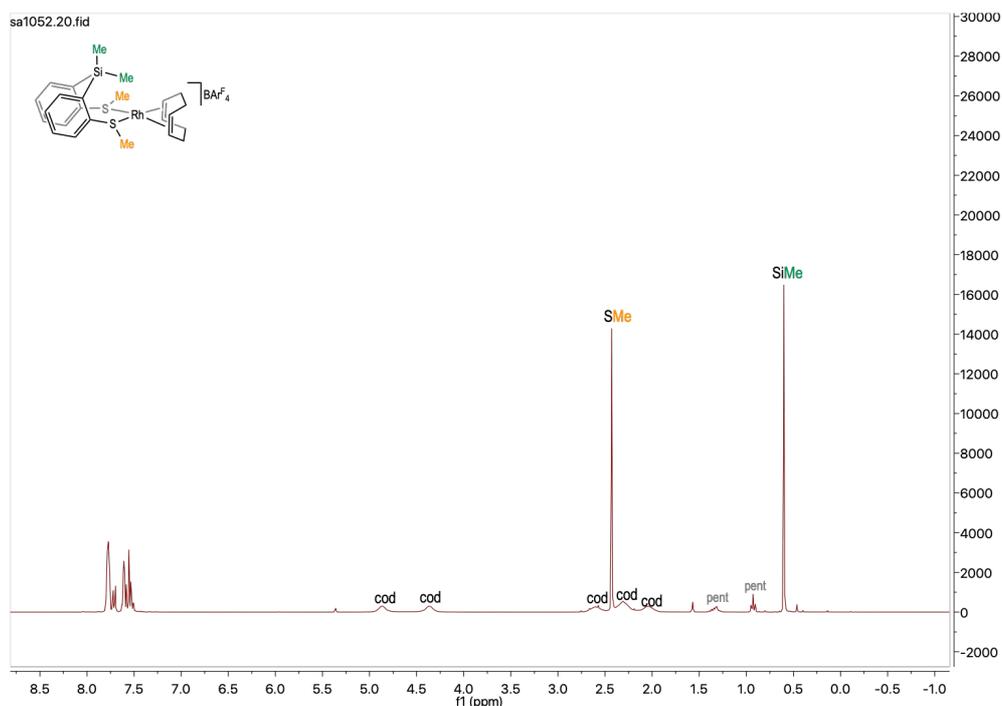
To a Schlenk charged with  $[\text{RhCl}(\text{cod})]_2$  (30 mg, 0.061 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 ml) the ligand  $[\text{Me}_2\text{Si}(\text{o-C}_6\text{H}_4\text{SMe})_2]$  (37 mg, 0.12 mmol) and the  $\text{NaBARf}_4$  salt (108 mg, 0.12 mmol) were added. The mixture was stirred for 60 minutes, filtered into another Schlenk to remove  $\text{NaCl}$  and concentrated under vacuum. Addition of 20 mL of pentane gave a light orange precipitate that was washed with pentane twice and dried under vacuum. Yield 120 mg (72%).

**$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):**  $\delta$  7.64, 7.47 (m, 12 H,  $\text{BARf}_4$ ), 7.60–7.40 (m, 8  $H_{\text{aromatics}}$ ), 4.75 (m, 2 H, CH, cod), 4.23 (m, 2 H, CH, cod), 2.48 (m, 2 H,  $\text{CH}_2$ , cod), 2.31 (s, 6 H, S- $\text{CH}_3$ ), 2.20 (m, 4 H,  $\text{CH}_2$ , cod), 1.91 (m, 2 H,  $\text{CH}_2$ , cod), 0.47 (s, 6 H, Si- $\text{CH}_3$ ,  $^{29}\text{Si}$  satellites  $^2J_{\text{Si-H}} = 6.4$  Hz).

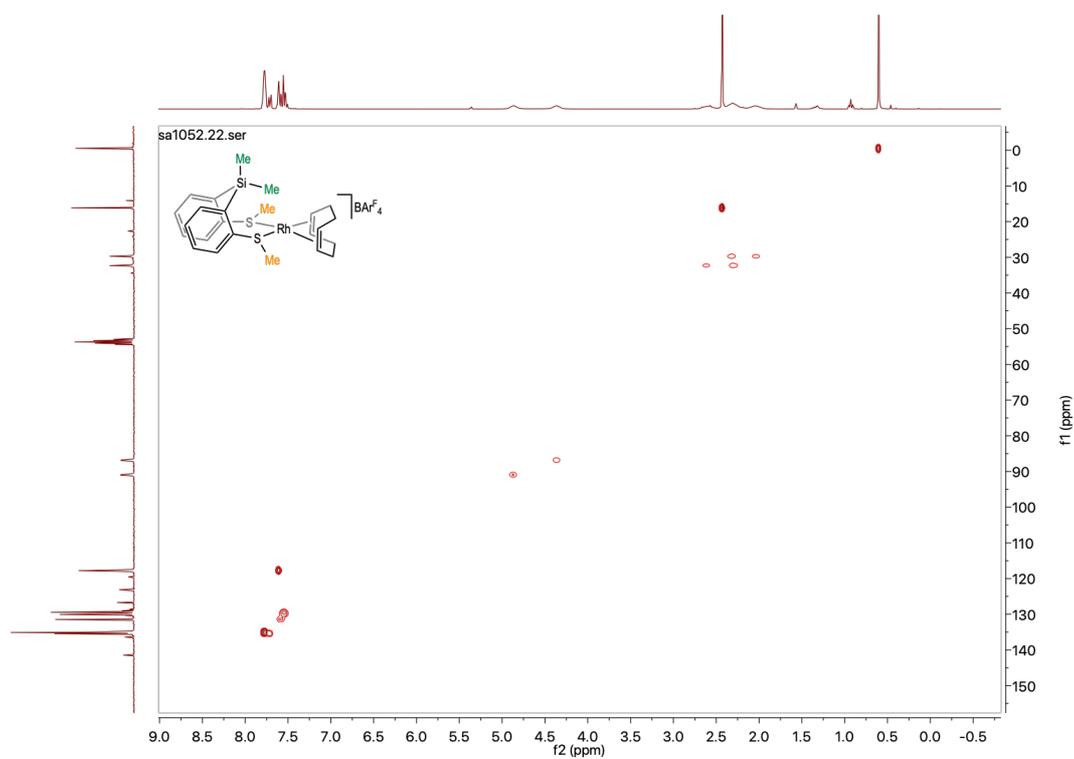
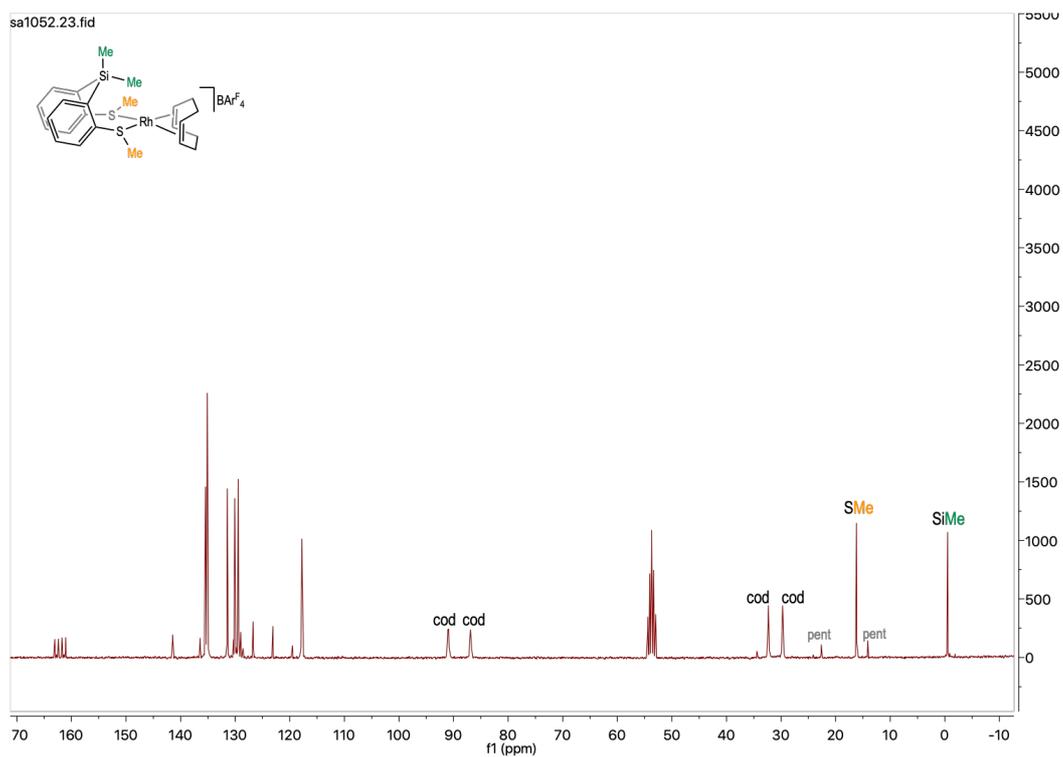
**$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ ):**  $\delta$  162.2 (q,  $J_{\text{F-C}} = 50$  Hz,  $\text{BARf}_4$ ), 135.2 (s,  $\text{BARf}_4$ ), 129.1 (q,  $J_{\text{F-C}} = 11$  Hz,  $\text{BARf}_4$ ), 125.0 (q,  $J_{\text{F-C}} = 272$  Hz,  $\text{CF}_3$ ), 117.9 (p,  $J_{\text{F-C}} = 4.1$  Hz,  $\text{BARf}_4$ ), 135.4–129.4 (aromatics), 91.0 (d,  $J_{\text{Rh-C}} = 10.4$  Hz, 2 x CH, cod), 86.8 (d,  $J_{\text{Rh-C}} = 11.3$  Hz, 2 x CH, cod), 32.3 (s, 2 x  $\text{CH}_2$ , cod), 29.7 (s, 2 x  $\text{CH}_2$ , cod), 16.2 (s, 2 x S- $\text{CH}_3$ ), -0.5 (s, 2 x Si- $\text{CH}_3$ ).

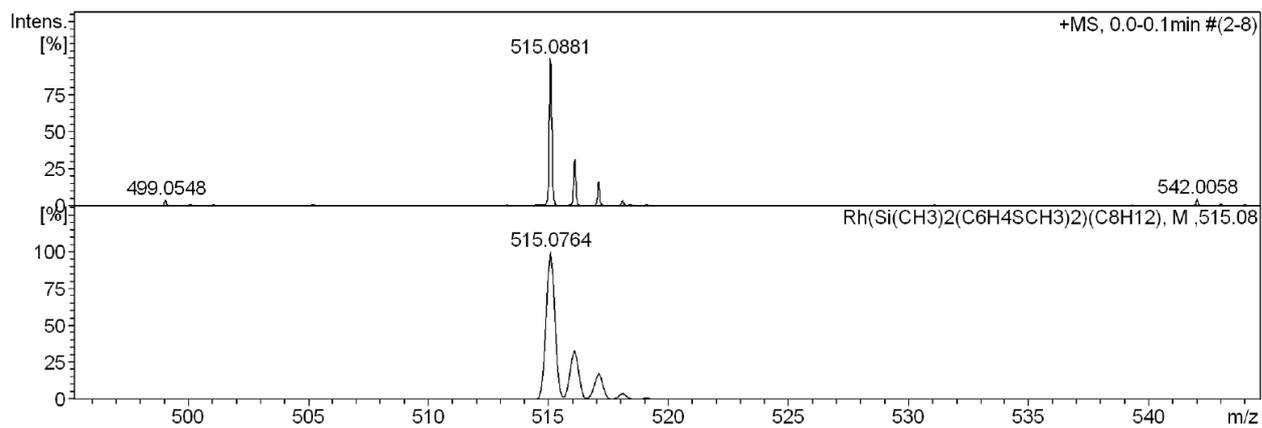
**ESI-MS ( $\text{C}_6\text{H}_4\text{F}_2$ , 60°C):** positive ion:  $m/z$ , 515.09  $[\text{M}]^+$  (calc. 515.08).

**Elemental Analysis:** Calc.: C, 48.78; H, 3.22; S, 4.65. Found: C, 48.86; H, 3.18; S, 4.79



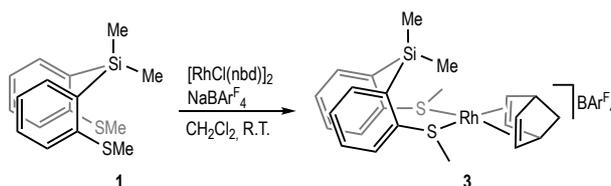
**Figure S2.**  $^1\text{H}$  NMR spectrum of **2**





**Figure S5.** ESI-MS for 2. Found (top) and calculated (bottom).

#### 4. Synthesis and characterization of $[\text{Rh}(\text{nbd})\text{SiMe}_2(\text{o-C}_6\text{H}_4\text{SMe})_2]\text{BARF}_4$ (**3**)



##### Synthesis:

To a Schlenk charged with  $[\text{RhCl}(\text{nbd})]_2$  (15 mg, 0.033 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 ml) the ligand  $[\text{Me}_2\text{Si}(\text{o-C}_6\text{H}_4\text{SMe})_2]$  (21 mg, 0.066 mmol) and the  $\text{NaBARF}_4$  salt (58 mg, 0.066 mmol) were added. The mixture was stirred for 20 minutes, filtered into another Schlenk to remove  $\text{NaCl}$  and concentrated under vacuum. Addition of 20 mL of pentane gave an orange precipitate that was washed twice with pentane and dried under vacuum. Yield 50 mg (56%).

**$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):**  $\delta$  7.64, 7.47 (m, 12 H,  $\text{BARF}_4$ ), 7.60–7.40 (m, 8  $H_{\text{aromatics}}$ ), 4.19 (m, very broad signal, 4 H, CH, NBD), 3.92 (m, 2 H, CH, NBD), 2.16 (s, 6 H, S- $\text{CH}_3$ ), 1.44 (m, 2 H,  $\text{CH}_2$ , NBD), 0.44 (s, 6 H, Si- $\text{CH}_3$ ,  $^{29}\text{Si}$  satellites  $^2J_{\text{Si-H}} = 6.5$  Hz).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ ):**  $\delta$  162.2 (q,  $J_{\text{F-C}} = 50$  Hz,  $\text{BARF}_4$ ), 135.2 (s,  $\text{BARF}_4$ ), 129.1 (q,  $J_{\text{F-C}} = 11$  Hz,  $\text{BARF}_4$ ), 125.0 (q,  $J_{\text{F-C}} = 272$  Hz,  $\text{CF}_3$ ), 117.9 (p,  $J_{\text{F-C}} = 4.1$  Hz,  $\text{BARF}_4$ ), 136.2-127.9 (aromatics), 69.9 (s broad, nbd), 65.2 (s broad, nbd), 64.3 (d,  $J_{\text{Rh-C}} = 6.1$  Hz, nbd), 53.1 (d,  $J_{\text{Rh-C}} = 1.9$  Hz, nbd), 15.8 (s, 2 x S- $\text{CH}_3$ ), -0.7 (s, 2 x Si- $\text{CH}_3$ ).

**ESI-MS ( $\text{C}_6\text{H}_4\text{F}_2$ , 60°C):** positive ion:  $m/z$ , 499.06  $[\text{M}]^+$  (calc. 499.04).

**Elemental Analysis:** Calc.: C, 48.47; H, 2.96; S, 4.71. Found: C, 48.53; H, 2.93; S, 4.98.

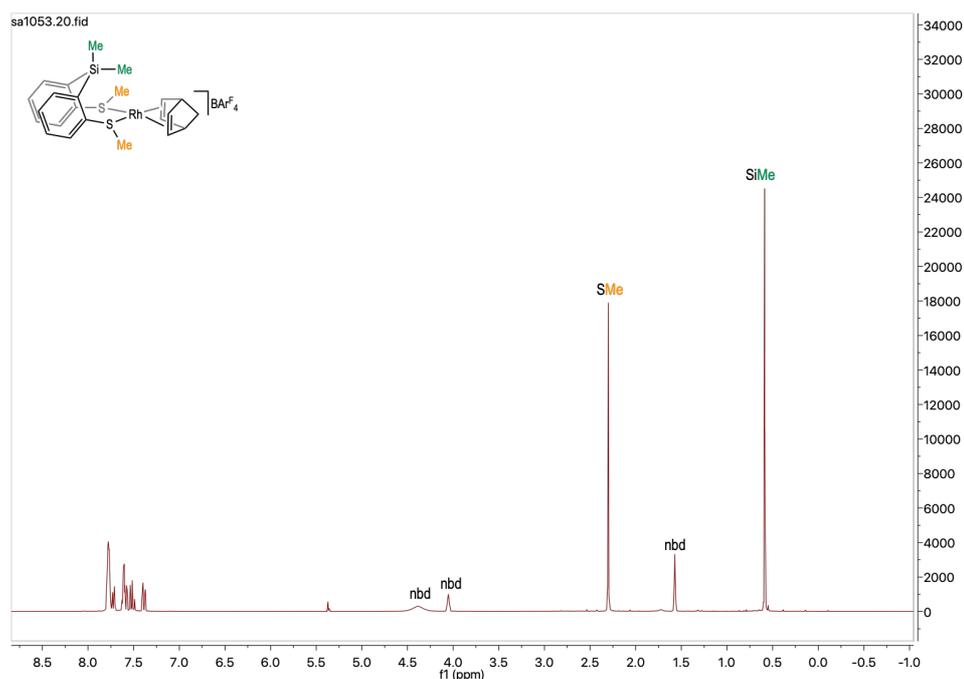


Figure S6.  $^1\text{H}$  NMR spectrum of **3**

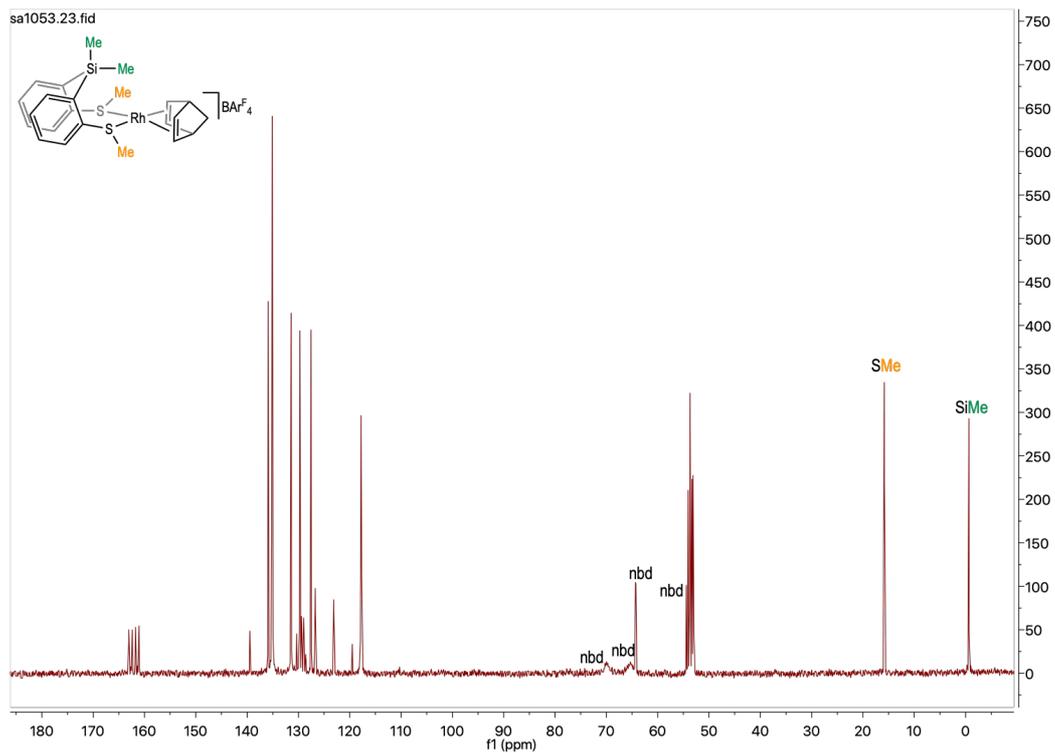


Figure S7.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3**

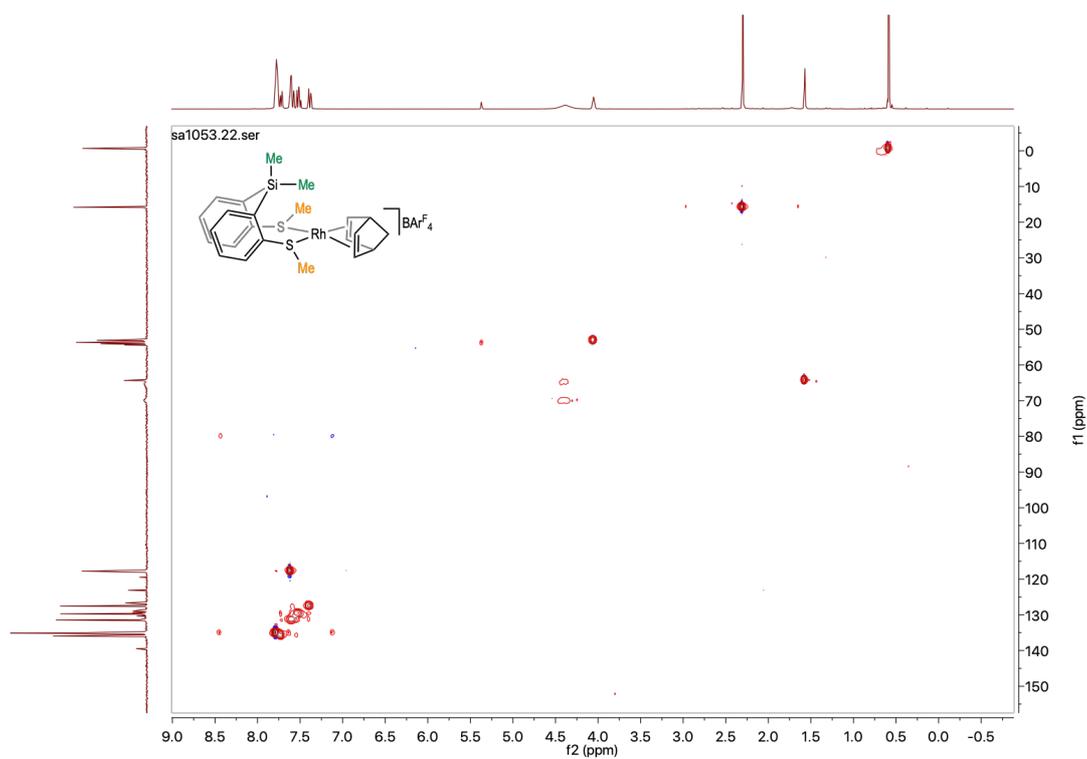
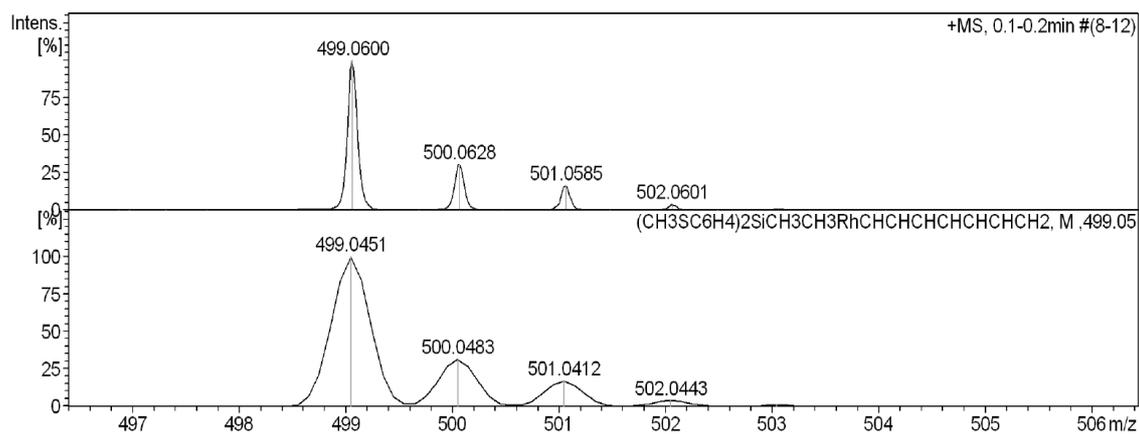
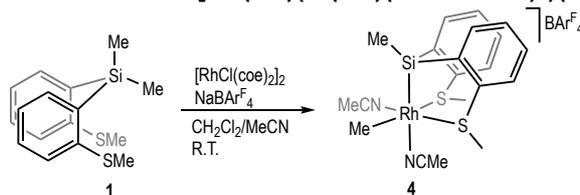


Figure S8.  $^{13}\text{C}-^1\text{H}$  HSQC NMR spectrum of **3**



**Figure S9.** ESI-MS for 3. Found (top) and calculated (bottom).

## 5. Synthesis and characterization of $[\text{Rh}(\text{Me})(\text{Si}(\text{Me})(\text{o-C}_6\text{H}_4\text{SMe})_2)(\text{MeCN})_2]\text{BARf}_4$ (**4**)



### Synthesis:

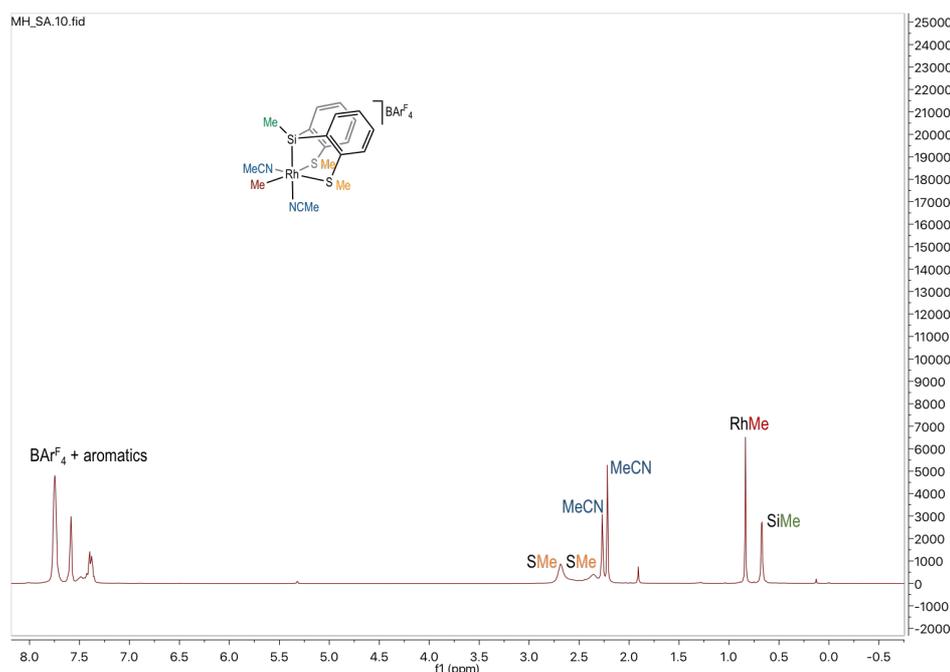
To a Schlenk charged with  $[\text{RhCl}(\text{coe})_2]_2$  (30 mg, 0.042 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 ml) the ligand  $[\text{Me}(\text{H})\text{Si}((\text{C}_6\text{H}_4)\text{SMe})_2]$  (26 mg, 0.084 mmol),  $\text{NaBARf}_4$  (75mg, 0.084 mmol) and 60 mL of MeCN were added. The mixture was stirred for an hour and filtered via canula. The solvent was evaporated. Pentane was added to precipitate. The resultant light yellow powder was with pentane and dried under vacuum. Yield 50 mg (- %).

**$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ ):**  $\delta$  7.85 – 6.95 (m, 8  $H_{\text{aromatics}}$ ), 2.68 (s, 3 H, S- $\text{CH}_3$ ), 2.36 (s, 3 H, S- $\text{CH}_3$ ), 2.27 (s, 3 H,  $\text{CH}_3$ , MeCN), 2.22 (s, 3 H,  $\text{CH}_3$ , MeCN), 0.83 (m, 3 H, Rh- $\text{CH}_3$ ), 0.67 (s, 3 H, Si- $\text{CH}_3$ ,  $^{29}\text{Si}$  satellites  $^2J_{\text{Si-H}} = 7.1$  Hz).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ ):**  $\delta$  162.2 (q,  $J_{\text{F-C}} = 50$  Hz,  $\text{BARf}_4$ ), 135.2 (s,  $\text{BARf}_4$ ), 129.1 (q,  $J_{\text{F-C}} = 11$  Hz,  $\text{BARf}_4$ ), 125.0 (q,  $J_{\text{F-C}} = 272$  Hz,  $\text{CF}_3$ ), 117.9 (p,  $J_{\text{F-C}} = 4.1$  Hz,  $\text{BARf}_4$ ), 133.8-129.5 (aromatics), 26.4 (s broad, S- $\text{CH}_3$ ), 23.4 (s broad, S- $\text{CH}_3$ ), 3.9 (s, MeCN), 2.7 (s, MeCN), -0.9 (s broad, 2 x Si- $\text{CH}_3$ ), -2.1 (s broad, Rh- $\text{CH}_3$ )

**ESI-MS (MeCN, 60°C):** positive ion:  $m/z$ , 406.98  $[\text{M} - 2\text{MeCN}]^+$  (calc. 406.98).

**Elemental Analysis:** Calc.: C, 46.17; H, 2.83; S, 4.74. Found: C, 46.54; H, 2.93; S, 5.01.



**Figure S10.**  $^1\text{H}$  NMR spectrum of **4**

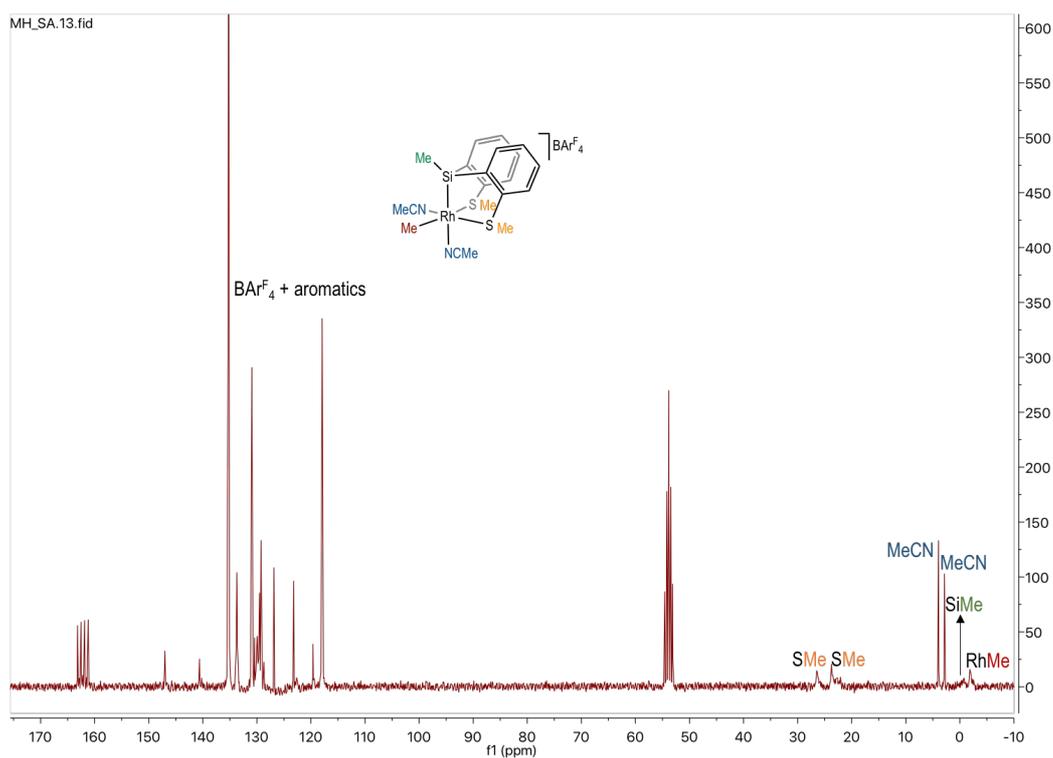


Figure S11.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4**

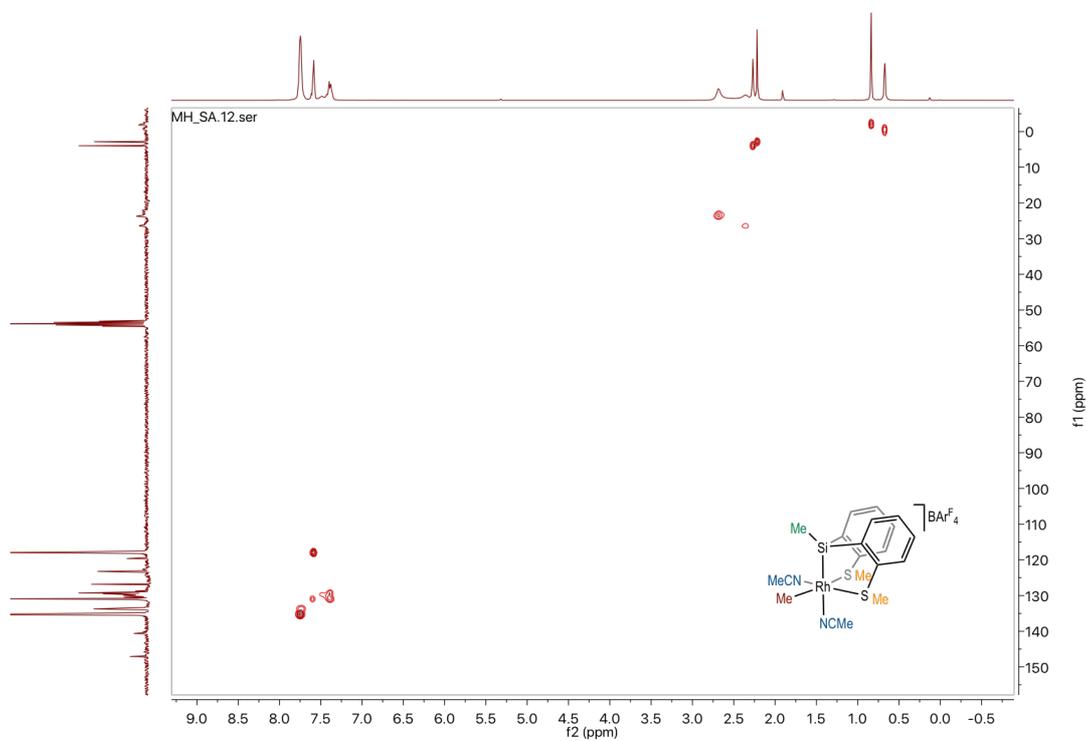


Figure S12.  $^{13}\text{C}-^1\text{H}$  HSQC NMR spectrum of **4**

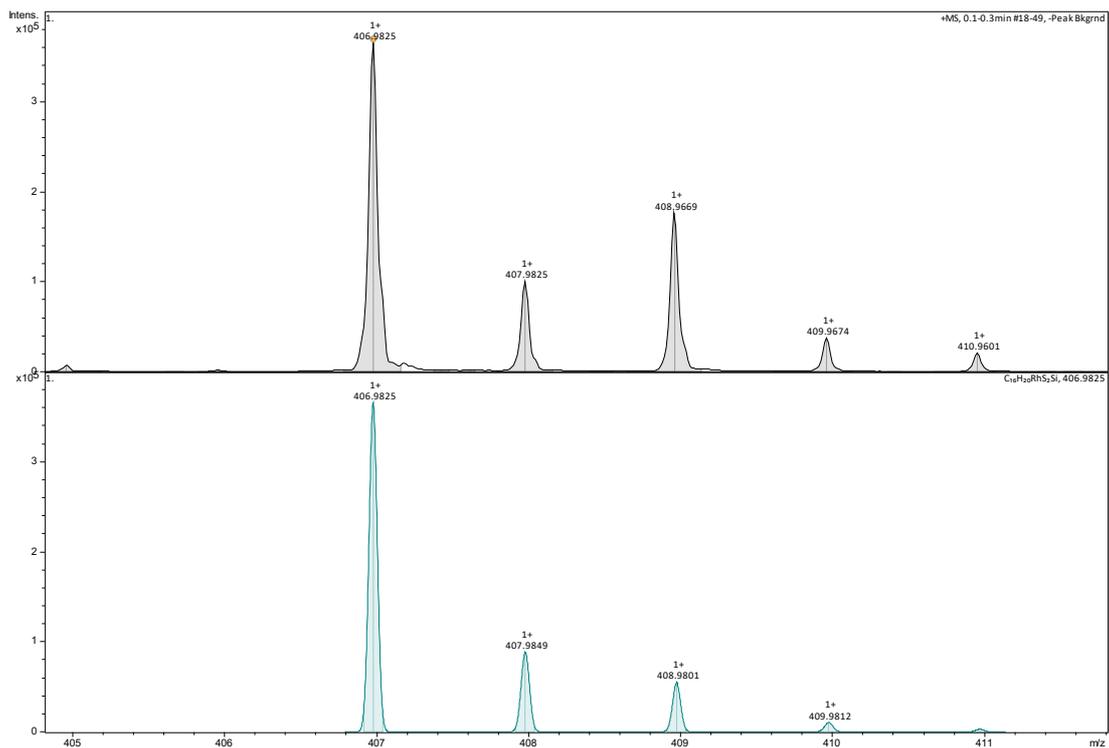


Figure S13. ESI-MS for 4. Found (top) and calculated (bottom).

## 6. Crystallography

### Crystal structure determinations

Single-crystal X-ray diffraction data for **1**, **2**, **3** and **4**, were collected ( $\omega$ -scans) on an Oxford Diffraction/Agilent SuperNova diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) equipped with nitrogen gas Oxford Cryosystems Cryostream unit<sup>5</sup> at the Oxford Chemical Crystallography Service from the University of Oxford. Diffraction data was reduced and processed using CrysAlisPro package.<sup>6</sup> The structures were solved using SHELXT<sup>7</sup> and refined to convergence on  $F^2$  and against all independent reflections by full-matrix least-squares using SHELXL<sup>8</sup> (version 2018/3) in combination with the GUI OLEX2<sup>9</sup> program. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically placed unless otherwise stated (see specific details for each molecular structure in the text) and allowed to ride on their parent atoms. CF<sub>3</sub> groups on the BAR<sup>F</sup><sub>4</sub><sup>-</sup> anion were necessarily modelled as disordered over two main domains, and restrained to maintain sensible geometries. Compound **2** crystallised with one molecule of dichloromethane (solvent of crystallization) which was modelled as disordered over two main domains and one C<sub>6</sub>H<sub>4</sub>SMe<sub>2</sub> group was also modelled as disordered over two main domains. Compound **3** crystallised with two molecules of dichloromethane (solvent of crystallization). One C<sub>6</sub>H<sub>4</sub>SMe group was modelled as disordered over two main domains in compound **4**. Disordered groups were restrained to maintain sensible geometries. Distances and angles were calculated using the full covariance matrix. Selected crystallographic data are summarized in Table S 1 and full details are given in the supplementary deposited CIF files (CCDC 1969934-37). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [http://optimized.ccdc.cam.ac.uk/data\\_request/cif](http://optimized.ccdc.cam.ac.uk/data_request/cif).

**Table S.1: Crystallographic data.**

	1	2	3	4
CCDC number	1969934	1969935	1969936	1969937
Formula	C <sub>16</sub> H <sub>20</sub> S <sub>2</sub> Si	C <sub>57</sub> H <sub>46</sub> BCl <sub>2</sub> F <sub>24</sub> RhS <sub>2</sub> Si	C <sub>57</sub> H <sub>44</sub> BCl <sub>4</sub> F <sub>24</sub> RhS <sub>2</sub> Si	C <sub>52</sub> H <sub>38</sub> BF <sub>24</sub> N <sub>2</sub> RhS <sub>2</sub> Si
M	304.53	1463.77	1532.65	1352.77
Crystal System	monoclinic	triclinic	monoclinic	triclinic
Space group	P21/n	P-1	I2a	P-1
T [K]	150(2)	150(2)	150(2)	150(2)
a [Å]	8.55760(10)	12.4418(3)	26.2033(2)	13.0258(4)
b [Å]	14.09020(10)	12.9564(3)	12.75000(10)	14.6748(5)
c [Å]	13.42620(10)	20.2172(6)	38.5848(3)	16.5971(6)
α [deg]	90	99.872(2)	90	64.937(3)
β [deg]	99.3070(10)	101.171(2)	105.0030(10)	82.448(3)
γ [deg]	90	97.292(2)	90	74.530(3)
V [Å <sup>3</sup> ]	1597.60(3)	3106.41(15)	12451.45(18)	2769.10(18)
Z	4	2	8	2
Density [gcm <sup>-3</sup> ]	1.266	1.565	1.635	1.622
μ [mm <sup>-1</sup> ]	3.596	4.818	5.610	4.496
θ range [deg]	4.581 to 76.207	3.511 to 76.274	3.493 to 76.429	2.940 to 75.970
Reflns collected	38522	37489	127558	34308
R <sub>int</sub>	0.0290	0.0418	0.0353	0.0292
Completeness to 67.684 deg.	100%	100%	100%	100%
Data/restr/param	3336/0/176	12840/1258/1066	12964/456/899	11318/950/940
R <sub>1</sub> [I > 2σ(I)]	0.0243	0.0464	0.0306	0.0546
wR <sub>2</sub> [all data]	0.0636	0.1265	0.0829	0.1536
GoF	1.044	1.020	1.025	1.036
Largest diff. pk and hole [eÅ <sup>-3</sup> ]	0.278 / - 0.272	1.051 / -0.615	0.880 / -0.617	1.626 / -0.741

## 7. References

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