

**Dimerization and Ring-opening in**  
**Bis(diisopropylamino)cyclopropenyliene (BAC) Mediated by**  
**[U(NR<sub>2</sub>)<sub>3</sub>(CCPh)] (R = SiMe<sub>3</sub>)**

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## Experimental

**General.** All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of nitrogen. Pentane and Et<sub>2</sub>O were dried using a Vacuum Atmospheres DRI-SOLV Solvent Purification system and stored over 3Å sieves for 24 h prior to use. Benzene-*d*<sub>6</sub>, pyridine-*d*<sub>5</sub>, THF-*d*<sub>8</sub> were dried over 3Å molecular sieves for 24 h prior to use. THF was dried by distillation from sodium/benzophenone, and stored over 3Å sieves for 24 h prior to use. HMDSO was dried by storage over 3Å molecular sieves for 24 h prior to use. Bis(diisopropylamino)cyclopropenylidene (BAC), [HBAC][BF<sub>4</sub>], and [U{N(R)(SiMe<sub>2</sub>CH<sub>2</sub>)}(NR<sub>2</sub>)<sub>2</sub>] were synthesized according to the previously reported procedures.<sup>1, 2</sup> All other reagents were purchased from commercial suppliers and used as received.

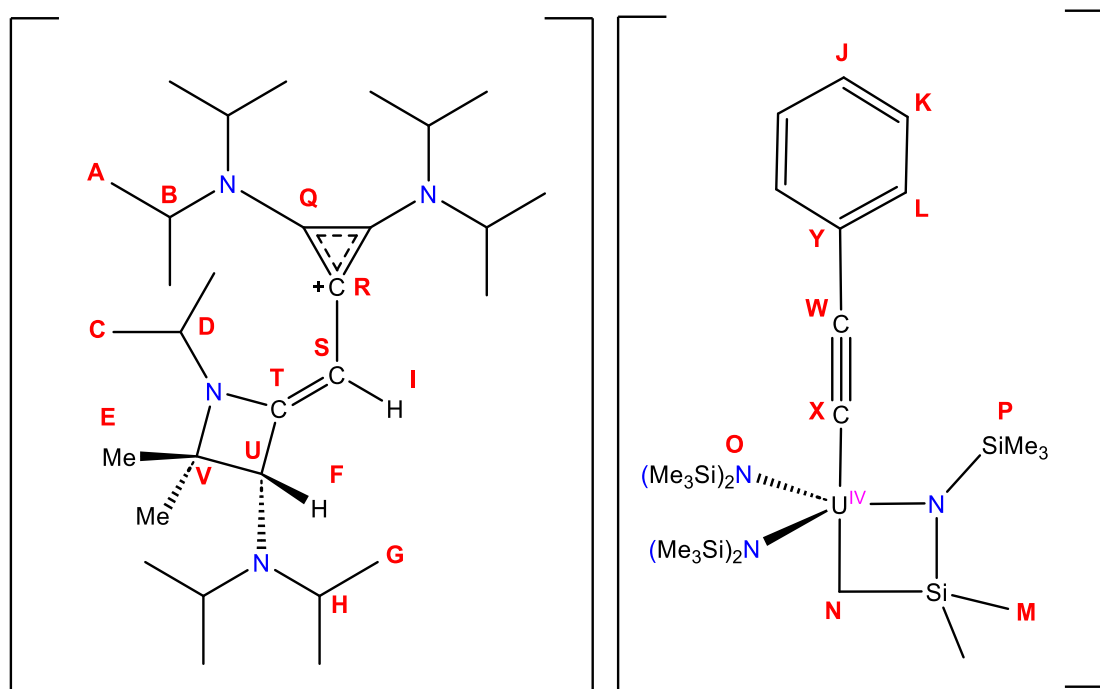
NMR spectra were recorded on an Agilent Technologies 400-MR DD2 400 MHz Spectrometer or a Bruker Avance NEO 500 spectrometer. <sup>1</sup>H NMR spectra were referenced to external tetramethylsilane (TMS) using the residual protio solvent peaks as internal standards. <sup>13</sup>C{<sup>1</sup>H} and NMR spectra were referenced indirectly with the <sup>1</sup>H resonance of TMS at 0.0 ppm, according to IUPAC standard,<sup>3, 4</sup> using the residual solvent peak as an internal standard. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. Elemental analyses were performed by the Micro-Analytical Facility at the University of California, Berkeley.

**Synthesis of [U(NR<sub>2</sub>)<sub>3</sub>(CCPh)] (1, R = SiMe<sub>3</sub>).** To a stirring, deep brown solution of [U{N(R)(SiMe<sub>2</sub>CH<sub>2</sub>)}(NR<sub>2</sub>)<sub>2</sub>] (495 mg, 0.689 mmol) in THF (2 mL) was added a light-yellow solution of phenylacetylene (70.4 mg, 0.689 mmol) in THF (2 mL). After stirring for 3 h, the solution was filtered through a Celite column supported on glass wool (0.5 × 2 cm) and the volatiles were removed from the filtrate *in vacuo* to afford a brown oil. The brown oil was triturated twice with pentane (2 × 1 mL) to afford a brown solid. The brown solid was extracted into

hexamethyldisiloxane (HMDSO) (2 mL) and the resulting brown solution was filtered through a Celite column supported on glass wool (0.5 × 2 cm). The solution was filtered a second time through another Celite column supported on glass wool (0.5 × 2 cm). The solution was concentrated to 0.5 mL and stored overnight at -35 °C, resulting in the deposition of dark brown crystals. The crystals were isolated by decanting the supernatant and then dried in vacuo to afford **1**. Yield: 96.7 mg, 17% yield. Anal. Calcd for C<sub>26</sub>H<sub>59</sub>N<sub>3</sub>Si<sub>6</sub>U: C, 38.07; H, 7.25; N, 5.12. Found: C, 38.22; H, 7.27; N, 4.99. IR (KBr Pellet, cm<sup>-1</sup>): 2955 (m), 2898 (m), 2072 (m, C≡C stretch), 1702 (w), 1658 (w), 1595 (w), 1570 (w), 1523 (w), 1488 (m), 1443 (m), 1403 (m), 1247 (s), 1204 (m), 1184 (m), 1029 (w), 845 (s), 773 (s), 758 (s), 691 (s), 656 (s), 614 (s), 531 (m), 417 (m). <sup>1</sup>H NMR (400 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>): δ 3.47 (t, *J* = 7.2 Hz, 1H, *p*-Ph), -2.21 (s, 54H, SiMe<sub>3</sub>), -2.91 (t, *J* = 8.2 Hz, 2H, *m*-Ph), -12.54 (d, *J* = 9.2 Hz, 2H, *o*-Ph).

**Synthesis of [cyclo-N(<sup>i</sup>Pr)C(Me)<sub>2</sub>CH(N<sup>i</sup>Pr<sub>2</sub>)C{=CHC<sub>3</sub>(N<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>][U(NR<sub>2</sub>)<sub>2</sub>(cyclo-N(SiMe<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub>)(CCPh) (2).** To a stirring, deep brown solution of **1** (46.2 mg, 0.056 mmol) in diethyl ether (1 mL) was added a pale-yellow solution of BAC (26.6 mg, 0.113 mmol) in diethyl ether (2 mL). After stirring for 10 min, the solution was filtered through a Celite column supported on glass wool (0.5 × 2 cm) and the filtrate was layered with pentane (6 mL). Storage of this solution for 16 h at -25 °C resulted in the deposition of bright yellow crystals. Yield: 27.4 mg, 38% yield. Anal. Calcd for C<sub>56</sub>H<sub>115</sub>N<sub>7</sub>Si<sub>6</sub>U: C, 52.01; H, 8.96; N, 7.58. Found: C, 51.99; H, 8.94; N, 7.47. IR (KBr Pellet, cm<sup>-1</sup>): 2965 (s), 2891 (m), 1898 (m, C≡C stretch), 1622 (s), 1522 (s), 1485 (s), 1463 (s), 1371 (s), 1248 (s), 1187 (s), 1158 (m), 1137 (m), 972 (s), 906 (s), 843 (s), 759 (s), 700 (s), 667 (s), 608 (s). <sup>1</sup>H NMR (500 MHz, 25 °C, THF-*d*<sub>8</sub>): δ 38.71 (s, 9H, **P**), 6.52 (s, 6H, **M**), 4.71 (t, *J* = 6.8 Hz, 1H, **J**), 3.94 (s, 1H, **I**), 3.71 (s, 1H, **F**), 3.24 (sept, *J* = 6.8 Hz, 4H, **B**), 3.12-3.00 (m, 3H, **H** and **D**), 1.15 (s, 3H, **E** or **E'**), 1.11 (s, 3H, **E** or **E'**), 0.92 (d, *J* = 6.4 Hz, 12H, **G**

and **G'**), 0.78 (d,  $J = 6.9$  Hz, 3H, **C** or **C'**), 0.70 (d,  $J = 6.7$  Hz, 3H, **C** or **C'**), 0.63 (m, 24H, **A** and **A'**), -1.16 (s, 2H, **K**), -8.75 (s, 2H, **L**), -9.25 (s, 36H, **O**), -229.81 (s, 2H, **N**).  $^{13}\text{C}$  NMR (500 MHz, 25 °C, THF- $d_8$ ): 164.26 (**T**), 131.94 (**Q**), 126.07 (**K**), 112.21 (**R**), 104.27 (**J**), 77.45 (**V**), 68.17 (**S**), 66.09 (**U**), 58.37 (**L**), 52.17 (**B**), 49.29 (**H**), 27.28 (**E** or **E'**), 24.99 (**E** or **E'**), 23.45 (**G** or **G'**), 23.39 (**G** or **G'**), 21.73 (**A** or **A'**), 21.43 (**A** or **A'**), 20.47 (**C** or **C'**), 20.13 (**C** or **C'**), -51.84 (**O**). Resonances for carbons **D**, **N**, **M**, **P**, **X**, **W**, and **Y** could not be assigned.



**Reaction of BAC with [HBAC]<sup>+</sup>.** In a glovebox, an NMR tube fitted with a J-Young valve was charged with bis(diisopropylamino)cyclopropenium tetrafluoroborate (4.3 mg, 0.013 mmol), BAC (3.1 mg, 0.013 mmol), and pyridine- $d_5$  (1 mL) to generate a yellow solution. The tube was removed from the glovebox, and a  $^1\text{H}$  NMR spectrum was recorded after 16 h (Figure S8), which revealed that no reaction had occurred.

***In situ* monitoring of the formation of complex 2.** In a glovebox, an NMR tube fitted with a J-Young valve was charged with a yellow solution of [U(NR<sub>2</sub>)<sub>3</sub>(CCPh)] (8.7 mg, 0.011 mmol), BAC (5.0 mg, 0.021 mmol), and THF-*d*<sub>8</sub> (1 mL). The tube was removed from the glovebox after 10 min and a <sup>1</sup>H NMR spectrum was recorded (Figure S9), which revealed the clean formation of **2** along with the absence of [HBAC]<sup>+</sup> and BAC.

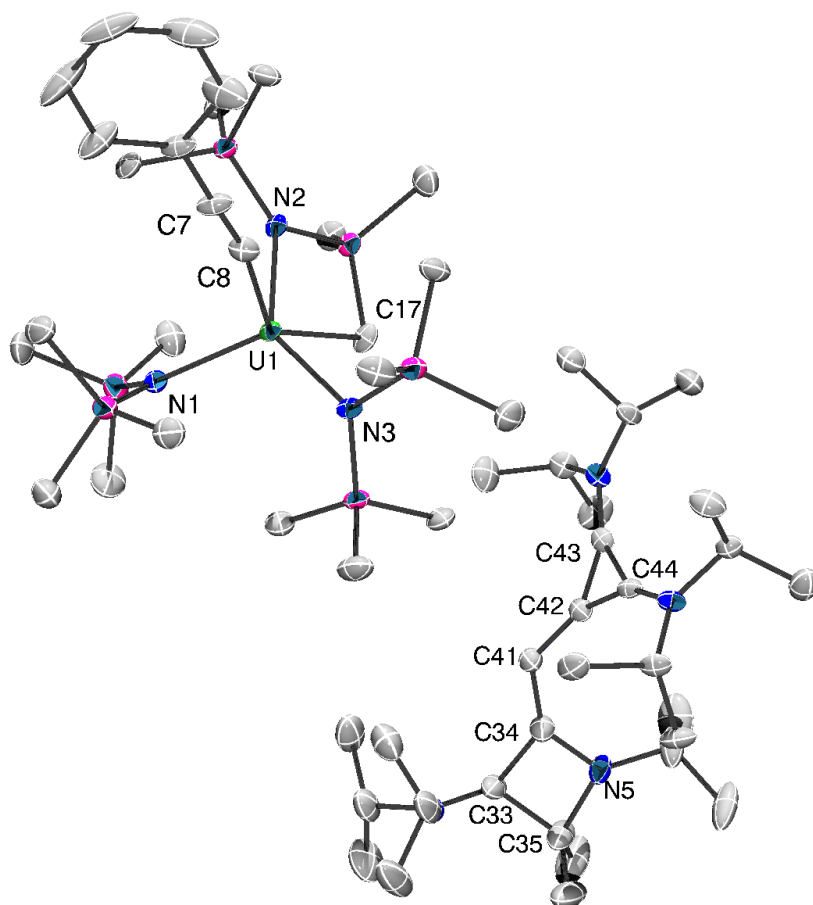
**X-ray Crystallography.** Data for **1** and **2** were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo K $\alpha$  X-ray source ( $\alpha = 0.71073 \text{ \AA}$ ). The crystals were mounted on a cryoloop under NVH or paratone oil. Data were collected at 110(2) K using an Oxford nitrogen gas cryostream using  $\omega$  scans with 0.5° frame widths. Frame exposures of 10 s were used for both **1** and **2**. Data collection and cell parameter determinations were conducted using the SMART program.<sup>5</sup> Integration of the data frames and final cell parameter refinements were performed using SAINT software.<sup>6</sup> Absorption corrections of the data were carried out using the multi-scan method SADABS.<sup>7</sup> Subsequent calculations were carried out using SHELXTL.<sup>8</sup> Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.<sup>8</sup>

For complex **2**, the pentane solvate molecule was disordered over two positions in a 1:1 ratio, which are related by an inversion center. Hydrogen atoms were not added to the disordered carbon atoms.

Further crystallographic details can be found in Table S1. Complexes **1** and **2** have been deposited in the Cambridge Structural Database (**1**: CCDC 2289555; **2**: CCDC 2289556).

**Table S1.** X-ray Crystallographic Data for **1** and **2**.

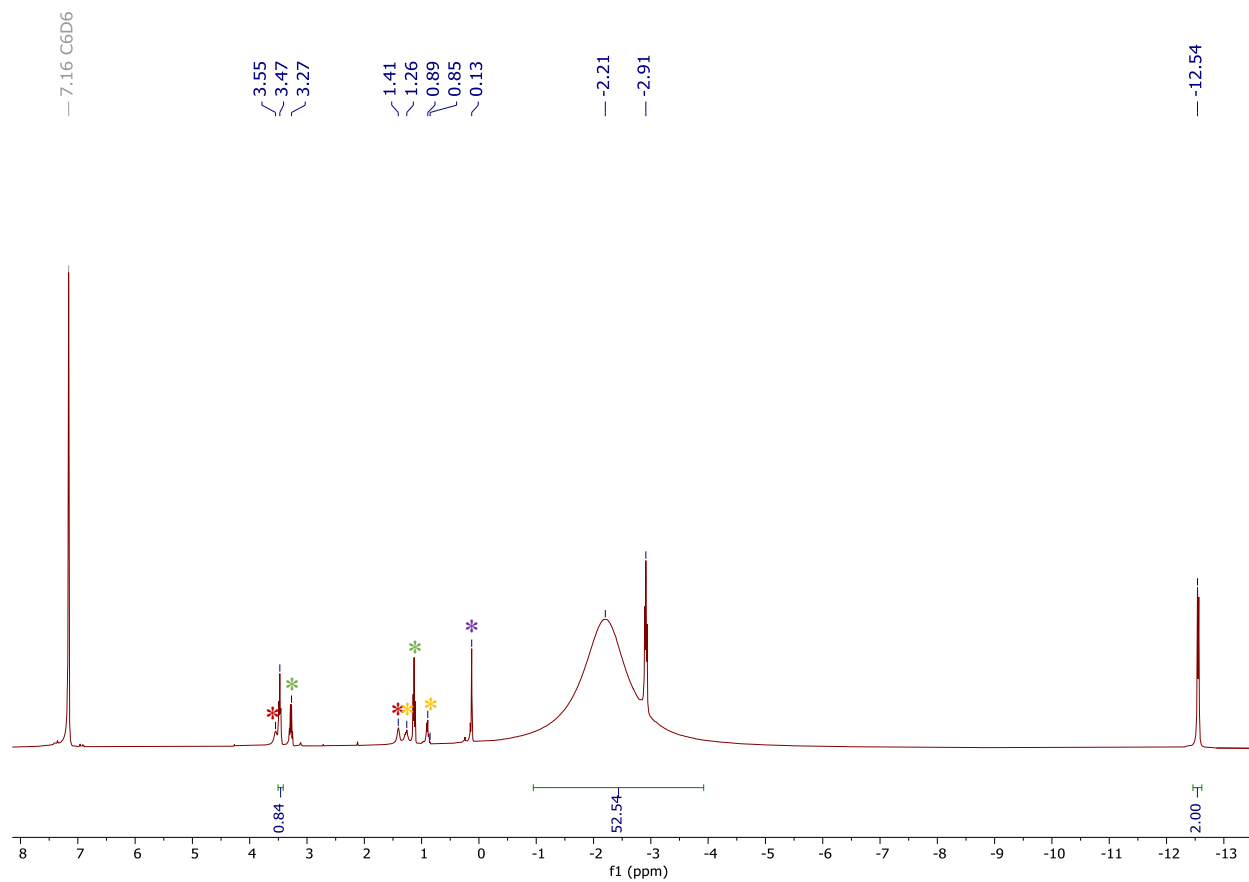
	<b>1</b>	<b>2</b>
empirical formula	C <sub>26</sub> H <sub>59</sub> N <sub>3</sub> Si <sub>6</sub> U	C <sub>58.50</sub> H <sub>121</sub> N <sub>7</sub> Si <sub>6</sub> U
crystal habit, color	Block, Brown	Block, Yellow
crystal size (mm)	0.3 × 0.3 × 0.2	0.3 × 0.2 × 0.15
space group	<i>Pna2<sub>1</sub></i>	<i>P-1</i>
volume (Å <sup>3</sup> )	3974.4(5)	3581.7(5)
<i>a</i> (Å)	24.0544(17)	13.9806(13)
<i>b</i> (Å)	12.1363(8)	14.0897(11)
<i>c</i> (Å)	13.6142(11)	18.1942(15)
<i>α</i> (deg)	90	88.917(4)
<i>β</i> (deg)	90	88.430(4)
<i>γ</i> (deg)	90	89.360(4)
<i>Z</i>	4	2
formula weight (g/mol)	820.33	1329.19
density (calculated) (Mg/m <sup>3</sup> )	1.371	1.232
absorption coefficient (mm <sup>-1</sup> )	4.283	2.404
<i>F</i> <sub>000</sub>	1648	1394
total no. reflections	17356	31360
unique reflections	6609	15271
Final R Indices	R <sub>1</sub> = 0.0426	R <sub>1</sub> = 0.0489
( <i>I</i> > 2σ( <i>I</i> ))	wR <sub>2</sub> = 0.0748	wR <sub>2</sub> = 0.1093
largest diff. peak and hole (e <sup>-</sup> Å <sup>-3</sup> )	3.774 and -1.244	3.110 and -2.167
GOF	0.996	0.988



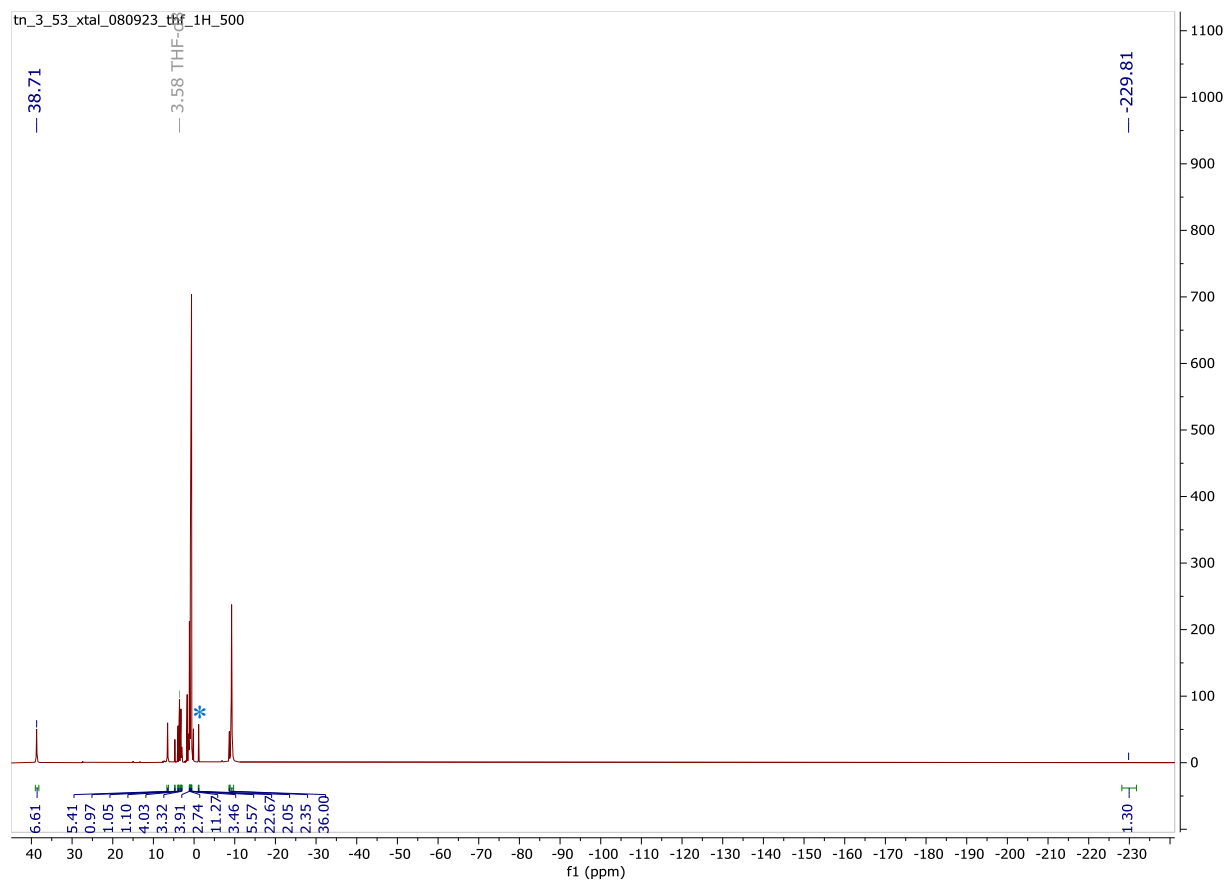
**Figure S1.** Solid-state molecular structure of complex **2** shown with 50% probability ellipsoids. Hydrogen atoms omitted for clarity.



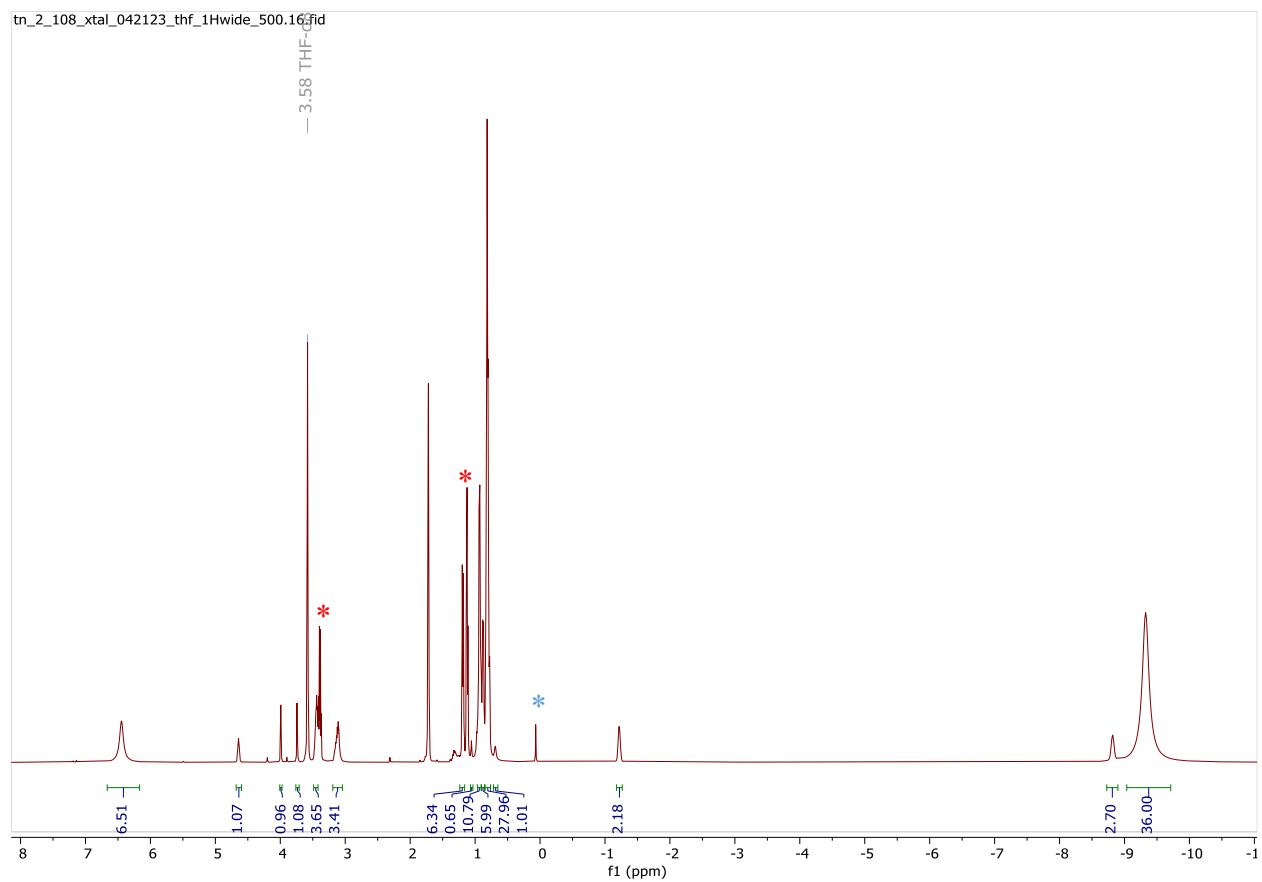
## NMR Spectra



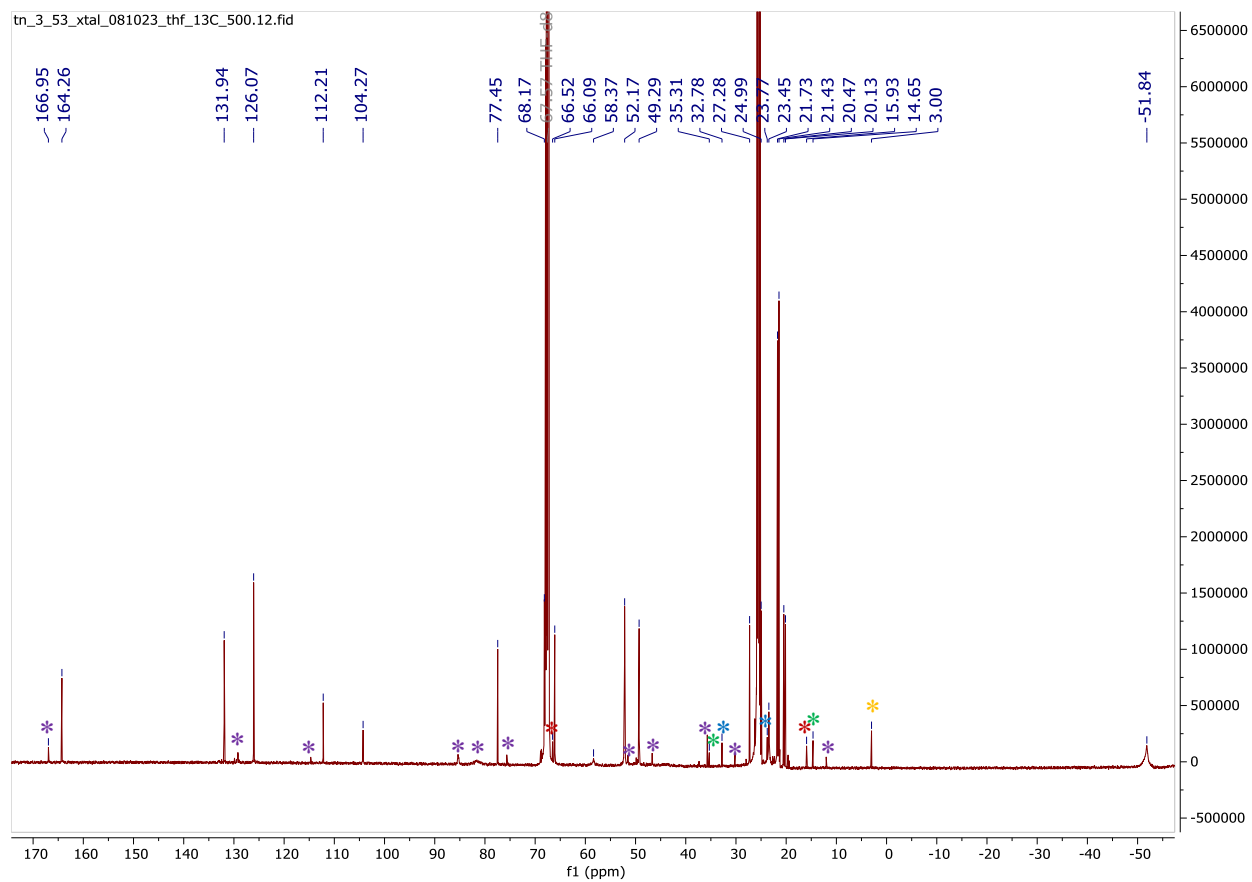
**Figure S2.**  $^1\text{H}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ . (\*) indicates the presence pentane. (\*) indicates the presence of free hexamethyldisilazane. (\*) indicates the presence of THF. (\*) indicates the presence of diethyl ether.



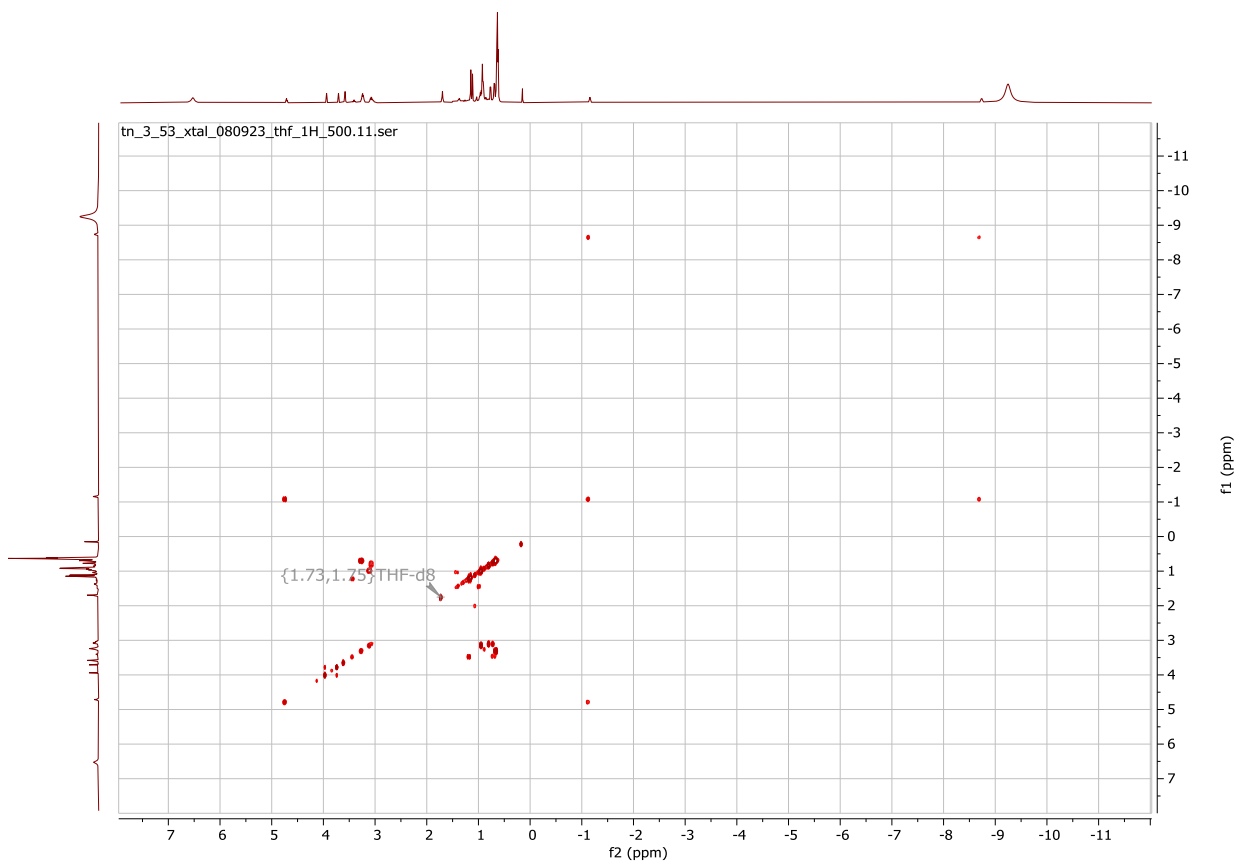
**Figure S3.**  $^1\text{H}$  NMR spectrum of **2** in  $\text{THF-}d_8$ . (\*) indicates the presence of HMDS.



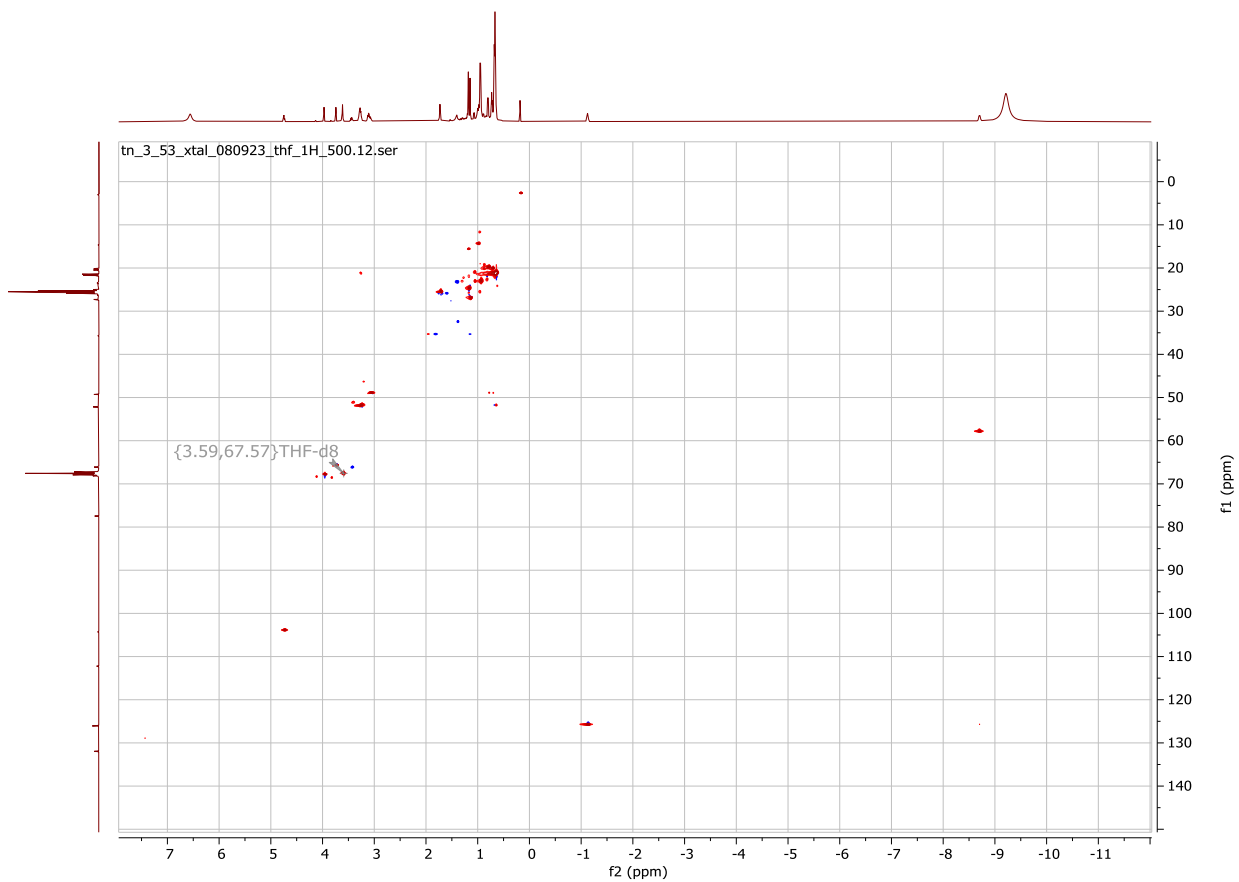
**Figure S4.** Partial  $^1\text{H}$  NMR spectrum of **2** in  $\text{THF-}d_8$ . (\*) indicates the presence of diethyl ether. (\*) indicates the presence of HMDS.



**Figure S5.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{THF-}d_8$ . (\*) indicates the presence of unidentified impurities. (\*) indicates the presence of diethyl ether. (\*) indicates the presence of pentane. (\*) indicates the presence of hexanes. (\*) indicates the presence of HMDS.

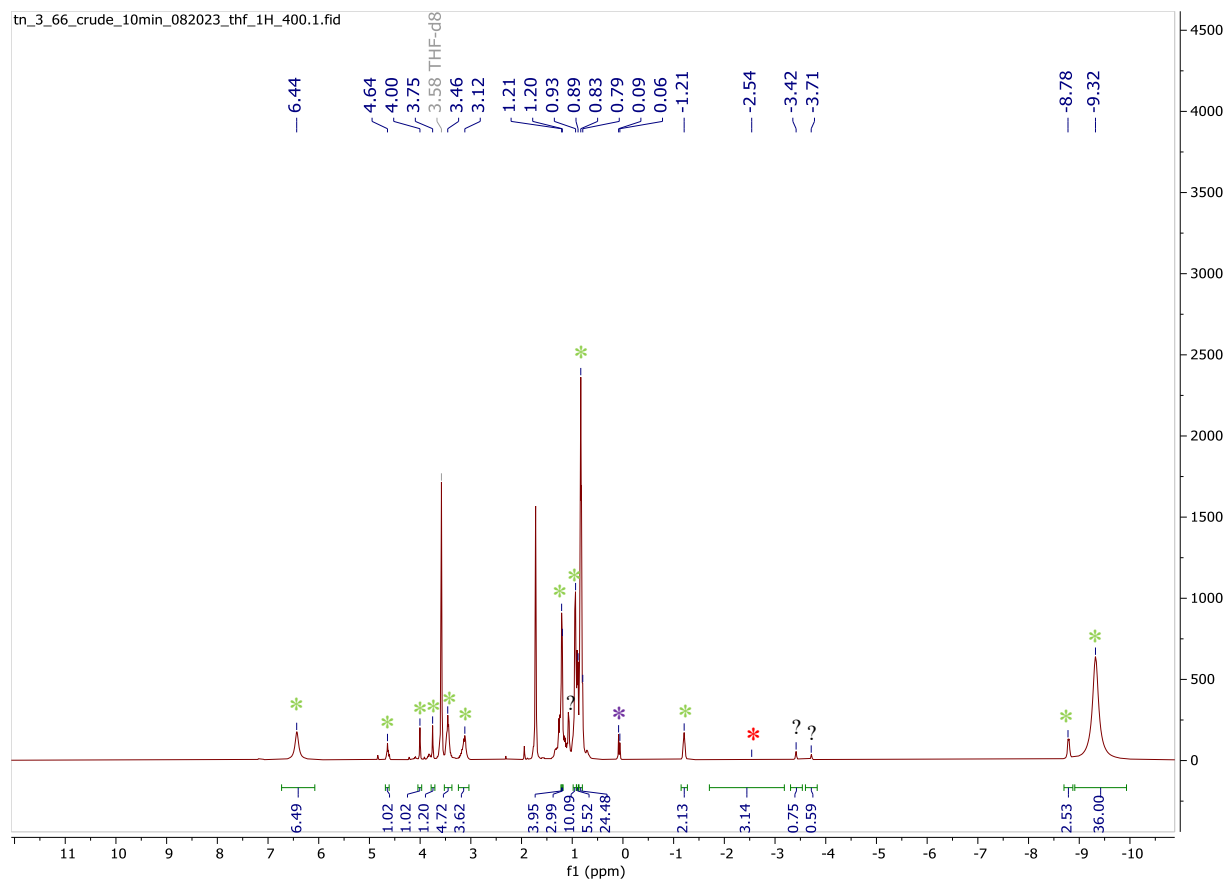


**Figure S6.** COSY spectrum of **2** in THF-*d*<sub>8</sub>.



**Figure S7.** HSQC spectrum of **2** in THF-*d*<sub>8</sub>.

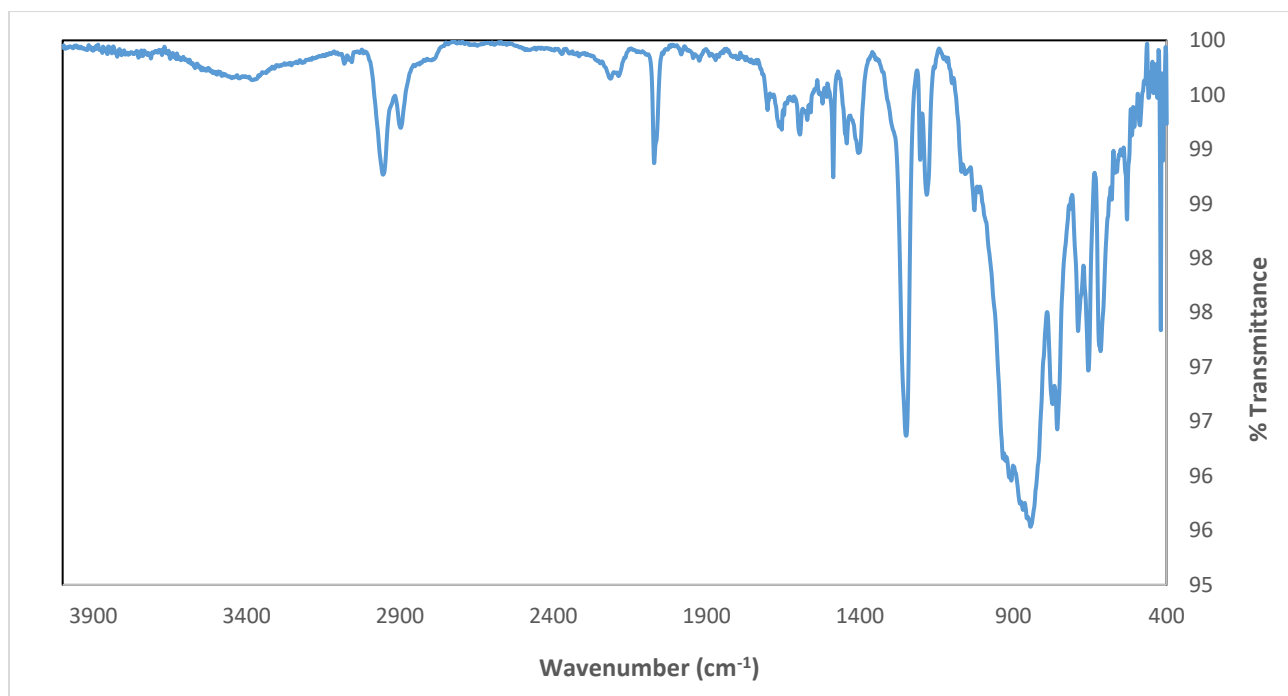




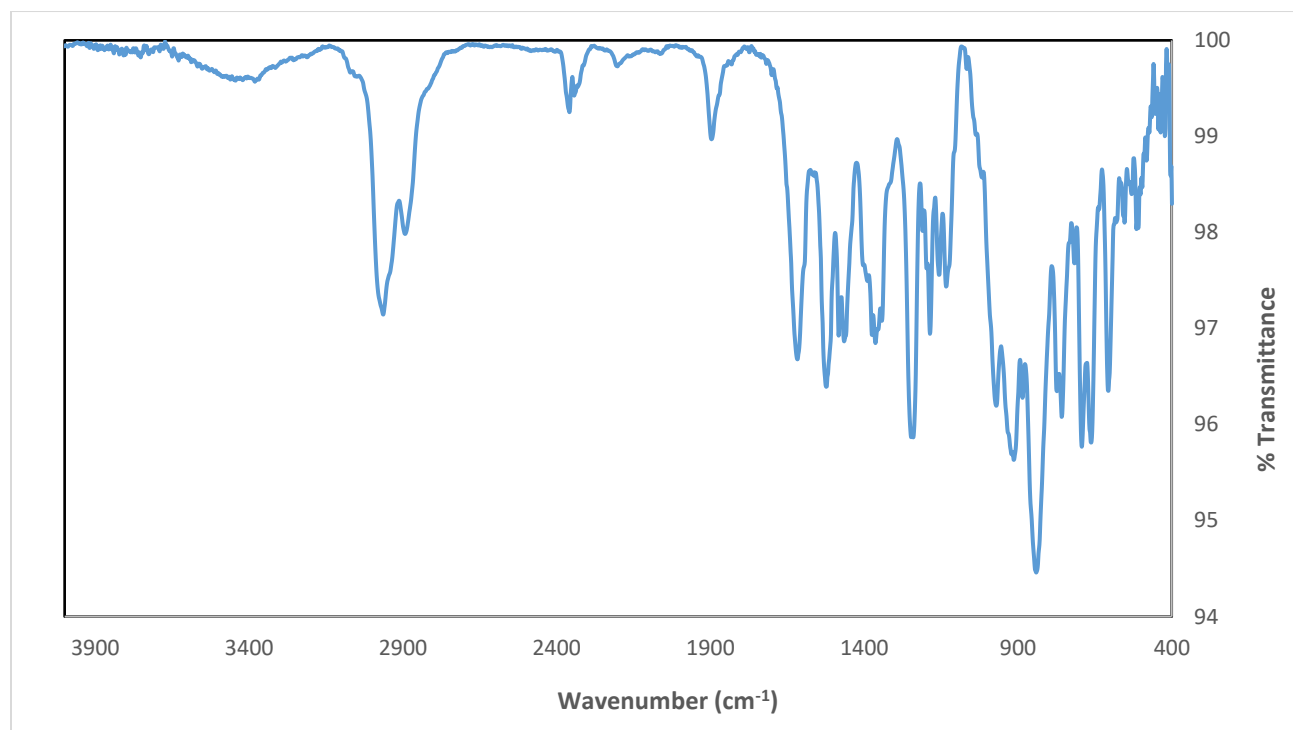
**Figure S9.** Partial  $^1\text{H}$  NMR spectrum of the crude reaction mixture formed between 2 equiv of BAC and **1** in THF- $d_8$ . (?) indicates the presence of an unidentified impurity. (\*) indicates the presence of unreacted **1**. (\*) indicates the presence of free hexamethyldisilazane (HMDS). (\*) indicates the presence of **2**.



## IR Spectra



**Figure S10.** IR Spectrum of **1** (KBr Pellet).



**Figure S11.** IR spectrum of **2** (KBr Pellet).

## References

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