

## Three-Coordinate Beryllium $\beta$ -diketiminates: Synthesis and Reduction Chemistry

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### General procedures

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either dinitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in an MBraun Labmaster Glovebox. NMR spectra were collected on either a Bruker AV-400 spectrometer ( $^9\text{B}$  56 MHz), or a Bruker AV-300 spectrometer ( $^{13}\text{C}\{^1\text{H}\}$  NMR 75 MHz). Beryllium-bound carbon resonances in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were observed by HMQC. Solvents were dried by passage through the columns of a commercial solvent purification system (toluene, hexane) or by drying over sodium benzophenone and distillation under argon (diethyl ether, THF).  $\text{C}_6\text{D}_6$ ,  $\text{d}_8$ -toluene and  $\text{d}_8$ -THF were purchased from Goss Scientific Instruments Ltd. and dried over molten potassium before distillation under argon and storage over molecular sieves. Distilled water was degassed under argon and kept in a sealed ampoule. Alcohols and amines were purchased from Sigma Aldrich. Alcohols were dried over molecular sieves, vacuum transferred or distilled and stored in sealed ampoules over sieves. Amines were dried over  $\text{CaH}_2$  prior to vacuum transfer or distillation, and stored in the glovebox over sieves. The  $\beta$ -diketimate ligand precursor  $\text{ArNC}(\text{Me})\text{CHC}(\text{Me})\text{NHA}r$  ( $\text{Ar} = 2,6\text{-diisopropylphenyl}$ ), LH, was synthesized following the literature procedure.  $[\text{KN}(\text{SiMe}_3)_2]$  was synthesized from hexamethyldisilazane and KH in toluene, filtered and crystallized from hot toluene. Elemental analyses were performed by Stephen Boyer at SACS, London Metropolitan University. Attempts to acquire satisfactory elemental analyses on compounds **6**, **8-10** and **12** were unsuccessful;  $^1\text{H}$  spectra of compounds **1-12** are therefore provided as corroborative evidence of purity. Unique datasets for X-ray characterized compounds were collected at 150 K on a Nonius

Kappa CCD diffractometer equipped with an Oxford Cryosystem, using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å), by Dr. Mary F. Mahon or Dr Gabriele Kociok-Köhn at the University of Bath.

## Synthetic procedures

### 1 [LBeCl]

A solution of 2.5 M <sup>n</sup>BuLi in hexanes (1.5 mL, 3.75 mmol) was slowly added to a solution of the ligand precursor LH (1.5 g, 3.58 mmol) in Et<sub>2</sub>O at -78 °C. The reaction mixture was allowed to warm to room temperature, stirred for 18 hours then slowly added to a slurry of BeCl<sub>2</sub> (0.42 g, 5.26 mmol) in Et<sub>2</sub>O at -78 °C. Upon warming up to room temperature a dense white precipitate appeared. The reaction mixture was stirred at room temperature for 1 day prior to removal of the solvent and extraction with three times 30 mL of hot toluene. Concentration *in vacuo* to a volume of 20 mL and storage at -20 °C yielded colorless crystals of [LBeCl] (1.22 g, 2.64 mmol, 74% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz): 7.13-7.17 (m, 6H, Ar-*H*), 5.25 (s, 1H,  $\gamma$ -H), 2.96 (sept, 4H, <sup>i</sup>Pr-CH, <sup>3</sup>*J* = 6.8 Hz), 1.64 (s, 6H,  $\beta$ -CH<sub>3</sub>), 1.37, 1.13 (two d, 12H, <sup>i</sup>Pr-CH<sub>3</sub>, <sup>3</sup>*J* = 6.8 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz): 169.5 ( $\beta$ -C), 143.0 (*o*-Ar-C), 141.7 (*i*-Ar-C), 127.7 (*p*-Ar-C), 124.4 (*m*-Ar-C), 100.5 ( $\gamma$ -C), 29.3 (<sup>i</sup>Pr-CH), 24.8, 24.2 (<sup>i</sup>Pr-CH<sub>3</sub>), 22.7 ( $\beta$ -CH<sub>3</sub>). <sup>9</sup>Be NMR (C<sub>6</sub>D<sub>6</sub>, 56 MHz): 12.2 (brs. s). Elemental analysis for C<sub>29</sub>H<sub>41</sub>BeClN<sub>2</sub> (M<sub>w</sub> = 462.1). Calculated: C, 75.37; H, 8.94; N, 6.06%. Found: C, 75.38; H, 8.95; N, 5.99%.

### 2 [LBeI]

The ligand precursor LH (2.00 g, 4.78 mmol), [KN(SiMe<sub>3</sub>)<sub>2</sub>] (0.96 g, 4.78 mmol) and BeI<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub> (2.69 g, 4.81 mmol) were combined in Et<sub>2</sub>O. The reaction mixture was stirred at room temperature for 18 hours prior to canula filtration. Concentration *in vacuo* and room temperature storage of the diethyl ether filtrate yielded a crop of colorless crystals of [LBeI] suitable for an X-ray diffraction experiment (1.56 g, 2.82 mmol, 59% yield). Storage of the leftover filtrate at -20 °C for one day yielded a second crop (0.68 g, 1.22 mmol, 85% total yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz): 7.7.13-7.23 (m, 6H, Ar-*H*), 5.32 (s, 1H,  $\gamma$ -H), 2.96 (sept, 4H, <sup>i</sup>Pr-CH, <sup>3</sup>*J* = 6.8 Hz), 1.68 ( $\beta$ -CH<sub>3</sub>), 1.44, 1.12 (two d, 12H each, <sup>i</sup>Pr-CH<sub>3</sub>, <sup>3</sup>*J* = 6.8 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz): 169.4 ( $\beta$ -C), 142.9 (*o*-Ar-C), 142.6 (*i*-Ar-C), 128.0 (*p*-Ar-C), 124.6 (*m*-Ar-C),

101.5 ( $\gamma$ -C), 29.5 ( $^i$ Pr-CH), 24.7, 24.5 ( $^i$ Pr-CH<sub>3</sub>), 23.1 ( $\beta$ -CH<sub>3</sub>).  $^9$ Be NMR (d<sub>8</sub>-tol, 56 MHz): 13.4 (br. s). Elemental analysis for C<sub>29</sub>H<sub>41</sub>BeIN<sub>2</sub> (M<sub>w</sub> = 553.6). Calculated: C, 62.92; H, 7.47; N, 5.06%. Found: C, 62.87; H, 7.52; N, 4.93%.

### 3 [LBeMe]

A solution of 1.6 M MeLi in Et<sub>2</sub>O (2.8 mL, 4.5 mmol) was added dropwise to a slurry of BeCl<sub>2</sub> (173 mg, 2.16 mmol) in Et<sub>2</sub>O at -78 °C. This slurry mixture was allowed to warm to room temperature then added to a solution of the ligand precursor LH (906 mg, 2.16 mmol) in Et<sub>2</sub>O at -78 °C. The reaction mixture was stirred at room temperature for 18 hours prior to removal of the solvent and extraction with 50 mL of hot toluene. Concentration *in vacuo* to a volume of 10 mL and storage at -20 °C yielded colorless crystals of [LBeMe] (0.68 g, 1.54 mmol, 72% yield).  $^1$ H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz): 7.12-7.21 (m, 6H, Ar-*H*), 5.27 (s, 1H,  $\gamma$ -H), 3.02 (sept, 4H,  $^i$ Pr-CH,  $^3J$  = 6.8 Hz), 1.69 (s, 6H,  $\beta$ -CH<sub>3</sub>), 1.26, 1.14 (two d, 12H,  $^i$ Pr-CH<sub>3</sub>,  $^3J$  = 6.8 Hz), -1.09 (s, 3H, BeCH<sub>3</sub>).  $^{13}$ C{ $^1$ H} NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz): 167.3 ( $\beta$ -C), 143.4 (*i*-Ar-C), 142.5 (*o*-Ar-C), 126.7 (*p*-Ar-C), 123.9 (*m*-Ar-C), 99.5 ( $\gamma$ -C), 28.7 ( $^i$ Pr-CH), 24.2, 23.9 ( $^i$ Pr-CH<sub>3</sub>), 22.3 ( $\beta$ -CH<sub>3</sub>), -9.5 (m, Be-CH<sub>3</sub>).  $^9$ Be NMR (C<sub>6</sub>D<sub>6</sub>, 56 MHz): 16.6 (br. s). Elemental analysis for C<sub>30</sub>H<sub>44</sub>BeN<sub>2</sub> (M<sub>w</sub> = 441.4). Calculated: C, 81.58; H, 10.04; N, 6.34%. Found: C, 81.61; H, 9.94; N, 6.24%.

### 4 [LBe<sup>n</sup>Bu]

Same as for [LBeMe], using a 2.5 M solution of <sup>n</sup>BuLi in hexanes (1.8 mL, 4.5 mmol) instead of MeLi. Concentration *in vacuo* to of the toluene filtrate and storage at -20 °C yielded [LBe<sup>n</sup>Bu] as a colorless crystalline solid (0.85 g, 1.76 mmol, 81% yield).  $^1$ H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz): 7.12-7.21 (m, 6H, Ar-*H*), 5.27 (s, 1H,  $\gamma$ -H), 3.03 (sept, 4H,  $^i$ Pr-CH,  $^3J$  = 6.8 Hz), 1.69 (s, 6H,  $\beta$ -CH<sub>3</sub>), 1.33 (d, 12H each,  $^i$ Pr-CH<sub>3</sub>,  $^3J$  = 6.8 Hz), 1.17 (quint, 2H, <sup>n</sup>Bu-CH<sub>2</sub>,  $^3J$  = 7.5 Hz), 1.13 (d, 12H,  $^i$ Pr-CH<sub>3</sub>,  $^3J$  = 6.8 Hz), 0.78 (t, 3H, <sup>n</sup>Bu-CH<sub>3</sub>,  $^3J$  = 6.8 Hz), 0.66-0.76 (m, 2H, <sup>n</sup>Bu-CH<sub>2</sub>), -0.36 (m, 2H, BeCH<sub>2</sub>).  $^{13}$ C{ $^1$ H} NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz): 167.3 ( $\beta$ -C), 143.4 (*i*-Ar-C), 142.5 (*o*-Ar-C), 126.7 (*p*-Ar-C), 123.9 (*m*-Ar-C), 99.4 ( $\gamma$ -C), 30.4, 29.2 (<sup>n</sup>Bu-C), 28.7 ( $^i$ Pr-CH), 24.1 ( $^i$ Pr-CH<sub>3</sub>), 22.3 ( $\beta$ -CH<sub>3</sub>), 14.1 (<sup>n</sup>Bu-C), 11.4 (m, BeCH<sub>2</sub>).  $^9$ Be NMR (C<sub>6</sub>D<sub>6</sub>, 56 MHz): 14.9 (br. s). Elemental analysis for C<sub>33</sub>H<sub>50</sub>BeN<sub>2</sub> (M<sub>w</sub> = 484.8). Calculated: C, 81.93; H, 10.42; N, 5.79%. Found: C, 82.01; H, 10.38; N, 5.75%.

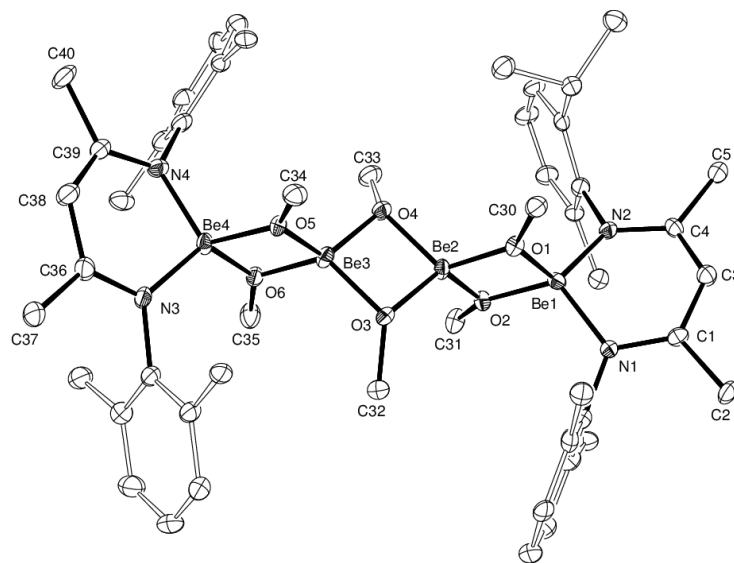
## 5 [LBeOH]

NMR scale: [LBeMe] (50 mg, 0.11 mmol) was dissolved in 0.25 mL of  $d_8$ -THF and a water solution in THF (2.04  $\mu$ L, 0.11 mmol of water in 0.25 mL of THF) was added dropwise at room temperature. Fast evolution of methane bubbles was observed for a couple of minutes. NMR data at the first point of analysis showed complete conversion to [LBeOH]. Scale-up: [LBeMe] (200 mg, 0.45 mmol) in 0.25 mL THF, water (8.16  $\mu$ L, 0.45 mmol in 0.5 mL of THF). Large colorless block-shaped crystals formed within three hours at room temperature (176 mg, 0.40 mmol, 88% yield).  $^1\text{H}$  NMR ( $d_8$ -THF, 300 MHz): 7.16-7.21 (m, 6H, Ar-*H*), 5.40 (s, 1H,  $\gamma$ -H), 2.94 (sept, 4H,  $^i\text{Pr-CH}$ ,  $^3J = 6.8$  Hz), 1.79 (s, 6H,  $\beta$ - $\text{CH}_3$ ), 1.21, 1.17 (two d, 12H,  $^i\text{Pr-CH}_3$ ,  $^3J = 6.8$  Hz), 0.20 (br. s, 1H, BeOH).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $d_8$ -THF, 75 MHz): 169.2 ( $\beta$ -C), 143.7 (*o*-Ar-C), 142.5 (*i*-Ar-C), 127.1 (*p*-Ar-C), 124.3 (*m*-Ar-C), 98.6 ( $\gamma$ -C), 29.3 ( $^i\text{Pr-CH}$ ), 25.2, 23.8 ( $^i\text{Pr-CH}_3$ ), 22.5 ( $\beta$ - $\text{CH}_3$ ).  $^9\text{Be}$  NMR ( $d_8$ -THF, 56 MHz): 8.0 (br. s). Elemental analysis for  $\text{C}_{29}\text{H}_{42}\text{BeN}_2\text{O}$  ( $M_w = 443.7$ ). Calculated: C, 78.51; H, 9.54; N, 6.31%. Found: C, 78.50; H, 9.62; N, 6.29%.

## 6 [LBeOMe]

NMR scale: Dry methanol (2.75  $\mu$ L, 68  $\mu$ mol) was added to a  $\text{C}_6\text{D}_6$  solution of [LBeMe] (30 mg, 68  $\mu$ mol). Fast evolution of methane bubbles was observed for 5-10 minutes. NMR data at the first point of analysis showed complete conversion to [LBeOMe].  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz): 7.11-7.17 (m, 6H, Ar-*H*), 5.16 (s, 1H,  $\gamma$ -H), 3.08 (sept, 4H,  $^i\text{Pr-CH}$ ,  $^3J = 6.8$  Hz), 3.05 (s, 3H,  $\text{OCH}_3$ ), 1.66 (s, 6H,  $\beta$ - $\text{CH}_3$ ), 1.40, 1.20 (two d, 12H,  $^i\text{Pr-CH}_3$ ,  $^3J = 6.8$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 75 MHz): 168.5 ( $\beta$ -C), 142.8 (*o*-Ar-C), 142.2 (*i*-Ar-C), 126.8 (*p*-Ar-C), 123.8 (*m*-Ar-C), 97.8 ( $\gamma$ -C), 50.9 ( $\text{OCH}_3$ ), 28.8 ( $^i\text{Pr-CH}$ ), 24.3, 23.5 ( $^i\text{Pr-CH}_3$ ), 22.0 ( $\beta$ - $\text{CH}_3$ ).  $^9\text{Be}$  NMR ( $\text{C}_6\text{D}_6$ , 56 MHz): 8.3 (br. s). Despite multiple attempts elemental analysis could not be acquired due to very high moisture sensitivity.

**Figure S1.** ORTEP representation of complex **6'**. Ellipsoids at 20% probability. Hydrogen atoms and *iso*-propyl methyl groups omitted for clarity.



## 7 [LBeO<sup>t</sup>Bu]

NMR scale: Warm *tert*-butanol (9.70  $\mu$ L, 0.1 mmol) was added to a C<sub>6</sub>D<sub>6</sub> solution of [LBe<sup>n</sup>Bu] (50 mg, 0.1 mmol). Slow evolution of methane bubbles was observed Upon heating at 80 °C. Quantitative conversion to [LBeO<sup>t</sup>Bu] was achieved after 3 hours heating. Storage for several hours at -30 °C afforded **X** as colorless crystalline blocks. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz): 7.11-7.17 (m, 6H, Ar-*H*), 5.12 (s, 1H,  $\gamma$ -H), 3.06 (sept, 4H, <sup>i</sup>Pr-CH, <sup>3</sup>*J* = 6.8 Hz), 1.67 (s, 6H,  $\beta$ -CH<sub>3</sub>), 1.39, 1.13 (two d, 12H, <sup>i</sup>Pr-CH<sub>3</sub>, <sup>3</sup>*J* = 6.8 Hz), 0.75 (s, 9H, <sup>t</sup>Bu-*H*). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz): 168.8 ( $\beta$ -C), 143.9 (*i*-Ar-C), 143.0 (*o*-Ar-C), 126.7 (*p*-Ar-C), 124.1 (*m*-Ar-C), 97.9 ( $\gamma$ -C), 67.7 (OC(CH<sub>3</sub>)<sub>3</sub>), 34.2 (OC(CH<sub>3</sub>)<sub>3</sub>), 29.1 (<sup>i</sup>Pr-CH), 24.6, 24.3 (<sup>i</sup>Pr-CH<sub>3</sub>), 22.9 ( $\beta$ -CH<sub>3</sub>). <sup>9</sup>Be NMR (C<sub>6</sub>D<sub>6</sub>, 56 MHz): 6.7 (br. s). Elemental analysis for C<sub>33</sub>H<sub>50</sub>BeN<sub>2</sub>O (M<sub>w</sub> = 499.8). Calculated: C, 79.31; H, 10.08; N, 5.61%. Found: C, 79.26; H, 9.97; N, 5.61%.

## 8 [LBeOPh]

Addition of phenol (6.4 mg, 68  $\mu$ mol) to a solution of **1** (30 mg, 68  $\mu$ mol) in a mixture of d<sub>8</sub>-THF and C<sub>6</sub>D<sub>6</sub> at room temperature resulted in slow evolution of methane. NMR data showed complete consumption of phenol after one hour and formation of the phenoxide [LBeOPh] in 82% yield, together with 6% of the protonated diketiminate ligand and 12% of leftover complex **1**. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>/d<sub>8</sub>-THF, 300 MHz): 7.07-7.24 (m, 6H, Ar-*H*), 6.69 (ddm, 2H, *m*-Ph-*H*, <sup>3</sup>*J* = 7.3, 8.6 Hz),

6.39 (tt, 1H, *p*-Ph-*H*,  $^3J = 7.3$  Hz,  $^4J = 1.3$  Hz), 5.50 (dm, 2H, *o*-Ph-*H*,  $^3J = 8.6$  Hz), 5.31 (s, 1H,  $\gamma$ -H), 2.94 (sept, 4H,  $^i\text{Pr-CH}$ ,  $^3J = 6.8$  Hz), 1.72 (s, 6H,  $\beta\text{-CH}_3$ ), 1.13, 1.10 (two d, 12H,  $^i\text{Pr-CH}_3$ ,  $^3J = 6.8$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6/\text{d}_8\text{-THF}$ , 75 MHz): 169.5 ( $\beta\text{-C}$ ), 160.0 (*i*-Ph-*C*), 143.4 (*o*-Ar-*C*), 142.4 (*i*-Ar-*C*), 129.0 (*m*-Ph-*C*), 127.2 (*p*-Ar-*C*), 124.3 (*m*-Ar-*C*), 120.3 (*o*-Ph-*C*), 117.5 (*p*-Ph-*C*), 99.1 ( $\gamma\text{-C}$ ), 29.2 ( $^i\text{Pr-CH}$ ), 24.5, 23.9 ( $^i\text{Pr-CH}_3$ ), 22.5 ( $\beta\text{-CH}_3$ ).  $^9\text{Be}$  NMR ( $\text{C}_6\text{D}_6/\text{d}_8\text{-THF}$ , 56 MHz): 8.1 (br. s). Satisfactory elemental analysis data could not be obtained due to contamination of samples with the  $[\text{BeOPh}_2]_n$  side-product, which proved difficult to separate.

## 9 [LBeNH<sup>*n*</sup>Bu]

NMR scale: *n*-butylamine (6.71  $\mu\text{L}$ , 68  $\mu\text{mol}$ ) was added to a  $\text{d}_8$ -toluene solution of [LBeMe] (30 mg, 68  $\mu\text{mol}$ ). Quantitative conversion to [LBeNH<sup>*n*</sup>Bu] was achieved after heating at 110  $^\circ\text{C}$  for 6 days. [LBeNH<sup>*n*</sup>Bu] was isolated as a low-melting, highly moisture-sensitive, colorless solid by removal of the solvent *in vacuo*.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz): 7.11-7.22 (m, 6H, Ar-*H*), 5.10 (s, 1H,  $\gamma$ -H), 3.13 (sept, 4H,  $^i\text{Pr-CH}$ ,  $^3J = 6.8$  Hz), 1.99-2.08 (m, 2H,  $\text{BeNHCH}_2$ ), 1.65 (s, 6H,  $\beta\text{-CH}_3$ ), 1.42, 1.19 (two d, 12H,  $^i\text{Pr-CH}_3$ ,  $^3J = 6.8$  Hz), 0.99-1.05 (m, 4H,  $^n\text{Bu-CH}_2$ ), 0.69 (t, 3H,  $^n\text{Bu-CH}_3$ ,  $^3J = 6.9$  Hz), -0.23 (t, 1H,  $\text{BeNH}$ ,  $^3J = 8.1$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 75 MHz): 167.9 ( $\beta\text{-C}$ ), 143.5 (*o*-Ar-*C*), 142.8 (*i*-Ar-*C*), 127.1 (*p*-Ar-*C*), 124.3 (*m*-Ar-*C*), 97.5 ( $\gamma\text{-C}$ ), 44.3 ( $\text{BeNHC}$ ), 40.0 ( $^n\text{Bu-CH}_2$ ), 29.0 ( $^i\text{Pr-CH}$ ), 24.9, 24.2 ( $^i\text{Pr-CH}_3$ ), 22.4 ( $\beta\text{-CH}_3$ ), 20.9 ( $^n\text{Bu-CH}_2$ ), 14.7 ( $^n\text{Bu-CH}_3$ ).  $^9\text{Be}$  NMR ( $\text{C}_6\text{D}_6$ , 56 MHz): 10.9 (br. s). Despite multiple attempts elemental analysis could not be acquired due to very high moisture sensitivity.

## 10 [LBeNHCH<sub>2</sub>Ph]

NMR scale: Benzylamine (7.42  $\mu\text{L}$ , 68  $\mu\text{mol}$ ) was added to a  $\text{C}_6\text{D}_6$  solution of [LBeMe] (30 mg, 68  $\mu\text{mol}$ ). Quantitative conversion to [LBeNHCH<sub>2</sub>Ph] was achieved after heating at 100  $^\circ\text{C}$  for 4 days. [LBeNHCH<sub>2</sub>Ph] was isolated as a low-melting, highly moisture-sensitive, colorless solid by removal of the solvent *in vacuo*.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz): 6.92-7.17 (m, 11H, Ar/Ph-*H*), 5.13 (s, 1H,  $\gamma$ -H), 3.34 (d, 2H,  $\text{NHCH}_2$ ,  $^3J = 8.7$  Hz), 3.15 (sept, 4H,  $^i\text{Pr-CH}$ ,  $^3J = 6.8$  Hz), 1.67 (s, 6H,  $\beta\text{-CH}_3$ ), 1.34, 1.17 (two d, 12H,  $^i\text{Pr-CH}_3$ ,  $^3J = 6.8$  Hz), 0.19 (t, 1H,  $\text{BeNH}$ ,  $^3J = 8.7$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 75 MHz): 167.8 ( $\beta\text{-C}$ ), 148.5 (*i*-Ph-*C*), 143.1 (*o*-Ar-*C*), 142.3 (*i*-Ar-*C*), 127.7 (*m*-Ph-*C*), 126.8 (*o*-Ph-*C*), 126.6 (*p*-Ar-*C*), 125.2 (*p*-Ph-*C*), 124.1 (*m*-Ar-*C*), 97.4 ( $\gamma\text{-C}$ ), 48.1 ( $\text{NCH}_2$ ), 28.7 ( $^i\text{Pr-CH}$ ), 24.4, 23.9 ( $^i\text{Pr-CH}_3$ ), 22.0 ( $\beta\text{-CH}_3$ ).  $^9\text{Be}$  NMR

(C<sub>6</sub>D<sub>6</sub>, 56 MHz): 11.0 (br. s). Despite multiple attempts elemental analysis could not be acquired due to very high moisture sensitivity.

## 11 [LBeNHPh]

NMR scale: Aniline (6.19  $\mu$ L, 68  $\mu$ mol) was added to a C<sub>6</sub>D<sub>6</sub> solution of [LBeMe] (30 mg, 68  $\mu$ mol). Quantitative conversion to [LBeNHPh] was achieved after heating at 110 °C for 3 days. Storage at -30 °C for one in toluene yielded colorless crystals of **X**.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>/d<sub>8</sub>-THF, 300 MHz): 7.20-7.26 (m, 2H, *p*-Ar-*H*), 7.12-7.12 (m, 4H, *m*-Ar-*H*), 6.78 (ddm, 2H, *m*-Ph-*H*, <sup>3</sup>*J* = 7.3, 8.4 Hz), 6.45 (tt, 1H, *p*-Ph-*H*, <sup>3</sup>*J* = 7.1 Hz, <sup>4</sup>*J* = 0.9 Hz), 5.50 (dm, 2H, *o*-Ph-*H*, <sup>3</sup>*J* = 8.4 Hz), 5.15 (s, 1H,  $\gamma$ -H), 3.01 (sept, 4H, <sup>i</sup>Pr-CH, <sup>3</sup>*J* = 6.8 Hz), 2.96 (s, 1H, NH), 1.61 (s, 6H,  $\beta$ -CH<sub>3</sub>), 1.21, 1.10 (two d, 12H, <sup>i</sup>Pr-CH<sub>3</sub>, <sup>3</sup>*J* = 6.8 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>/d<sub>8</sub>-THF, 75 MHz): 168.9 ( $\beta$ -C), 153.2 (*i*-Ph-C), 143.7 (*o*-Ar-C), 142.7 (*i*-Ar-C), 129.1 (*m*-Ph-C), 127.7 (*p*-Ar-C), 124.8 (*m*-Ar-C), 118.0 (*o*-Ph-C), 115.2 (*p*-Ph-C), 98.9 ( $\gamma$ -C), 29.2 (<sup>i</sup>Pr-CH), 24.6, 24.1 (<sup>i</sup>Pr-CH<sub>3</sub>), 22.9 ( $\beta$ -CH<sub>3</sub>). <sup>9</sup>Be NMR (C<sub>6</sub>D<sub>6</sub>/d<sub>8</sub>-THF, 56 MHz): 10.4 (br. s). Elemental analysis for C<sub>35</sub>H<sub>47</sub>BeN<sub>3</sub> (M<sub>w</sub> = 518.8). Calculated: C, 81.03; H, 9.13; N, 8.10%. Found: C, 80.93; H, 9.18; N, 7.94%.

## 12 [LBeN(SiMe<sub>3</sub>)<sub>2</sub>]

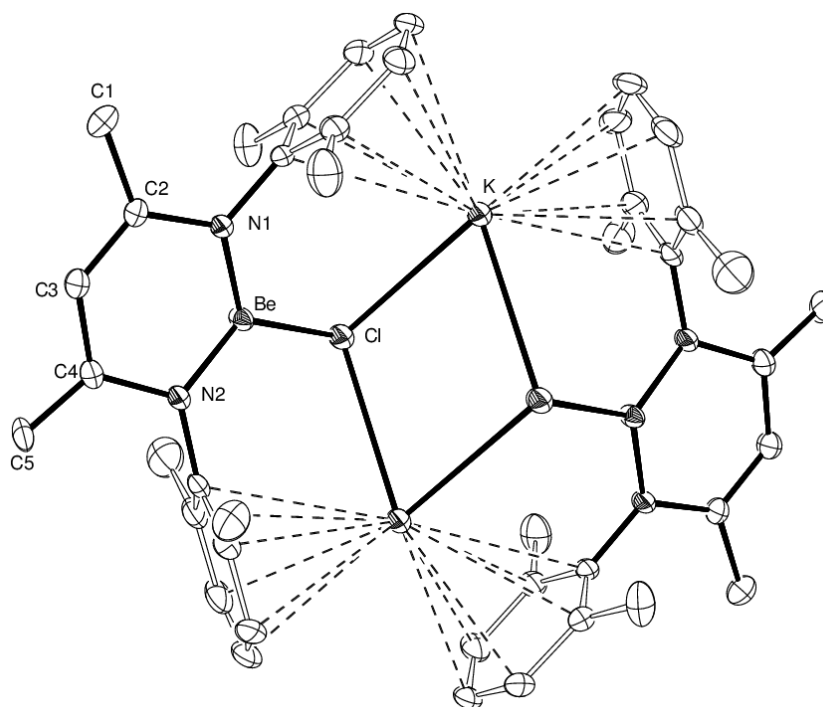
LH (419 mg, 1 mmol) and [KN(SiMe<sub>3</sub>)<sub>2</sub>] (0.20g, 1 mmol) were combined in THF. In a separate Schlenk flask BeI<sub>2</sub>(Et<sub>2</sub>O)<sub>2</sub> (414 mg, 0.1 mmol) and [KN(SiMe<sub>3</sub>)<sub>2</sub>] (0.20g, 1 mmol) were combined in THF. Both solutions were allowed to stir for 3 hours prior to canula transfer of the first into the second. The resulting suspension was stirred at room temperature overnight, followed by solvent removal *in vacuo* and filter canula extraction in 30 mL of toluene. The yellow filtrate was concentrated *in vacuo*. Storage at -18 °C overnight afforded a crop of colourless needle shaped crystals (0.24g, 0.41 mmol, 41 % yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz): 7.16 (m, 6H, Ar-*H*), 5.16 (s, 1H,  $\gamma$ -H), 3.24 (sept, 4H, <sup>i</sup>Pr-CH, <sup>3</sup>*J* = 6.8 Hz), 1.66 (s, 6H,  $\beta$ -CH<sub>3</sub>), 1.40, 1.08 (two d, 12H, <sup>i</sup>Pr-CH<sub>3</sub>, <sup>3</sup>*J* = 6.8 Hz), 0.01 (s, 18H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz): 169.7 ( $\beta$ -C), 145.3 (*i*-Ar-C), 143.9 (*o*-Ar-C), 127.3 (*p*-Ar-C), 125.0 (*m*-Ar-C), 100.3 ( $\gamma$ -C), 29.4 (<sup>i</sup>Pr-CH), 25.5, 25.0 (<sup>i</sup>Pr-CH<sub>3</sub>), 24.9 ( $\beta$ -CH<sub>3</sub>), 6.5 (Si(CH<sub>3</sub>)<sub>2</sub>). <sup>9</sup>Be NMR (C<sub>6</sub>D<sub>6</sub>, 56 MHz): 9.3 ppm. Satisfactory elemental analysis data could not be obtained as the crystalline material decomposed even under argon into brown tar-like material.

**13a/b** [L'BeClK]<sub>2</sub>

Complex **1** (1.62 g, 3.5 mmol) was stirred with potassium metal (0.2 g, 5.11 mmol) in toluene at 60 °C overnight. The resulting pale yellow solution was filtered hot. Complex **13** crystallized as large colorless cube-shaped crystals upon cooling of the filtrate to room temperature (1.10g, 2.2 mmol, 63% yield). NMR data showed complex **13** to be a mixture of two complexes in varying proportions depending on each recrystallization. Protonated **13a**: <sup>1</sup>H NMR (d<sub>8</sub>-THF, 300 MHz): 3.98 (broad, 2H, β/γ-CH), 4.04 + 3.89 + 3.72 + 3.58 (four sept, 2H each, <sup>i</sup>Pr-CH, <sup>3</sup>J = 6.8 Hz), 1.42 + 1.11 (two broad s, 6H each, β-CH<sub>3</sub>), 1.25 + 1.16 + 1.15 + 1.19 + 1.10 + 1.08 + 0.89 (seven d, 6H: 6H: 6H: 6H: 6H: 6H: 12H, <sup>i</sup>Pr-CH<sub>3</sub>, <sup>3</sup>J = 6.8 Hz). Deprotonated **13b**: <sup>1</sup>H NMR (d<sub>8</sub>-THF, 300 MHz): 4.91 (d, 1H, β-CH, <sup>4</sup>J = 0.9 Hz), 3.53 + 3.52 (two overlapping sept, 2H each, <sup>i</sup>Pr-CH, <sup>3</sup>J = 6.8 Hz), 3.14 + 2.39 (two broad s, 1H, β-CH<sub>2</sub> cis and trans), 1.51 (s, 3H, β-CH<sub>3</sub>), 1.28 + 1.11 + 1.02 + 0.98 (four d, 6H each, <sup>i</sup>Pr-CH<sub>3</sub>, <sup>3</sup>J = 6.8 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR of mixture (d<sub>8</sub>-THF, 75 MHz): 157.0, 150.5, 148.3, 148.2, 148.1, 147.9, 147.4, 147.3, 147.2, 146.2, 146.1, 145.3, 143.0, 129.8, 129.1, 126.2, 126.0, 125.6, 125.2, 124.9, 124.3, 124.1, 124.0, 123.7, 123.6, 102.2 (**13a** γ-CH), 101.7 (**13b** γ-CH), 75.8 (**13b** β-CCH<sub>2</sub>), 59.9 (**13b** β-CHCH<sub>3</sub>), 29.3, 29.2, 28.9, 28.8, 28.6, 28.5, 28.2, 27.9, 26.7, 26.3, 26.1, 26.0, 25.9, 25.8, 25.6, 25.5, 25.4, 25.2, 25.0, 24.8, 24.7, 24.7, 24.6, 24.5, 24.3, 22.8, 22.5, 21.7. <sup>9</sup>Be NMR of mixture (d<sub>8</sub>-THF, 56 MHz): 10.1 ppm (broad). Elemental analysis for {C<sub>29</sub>H<sub>41</sub>BeClKN<sub>2</sub>}<sub>2</sub> (M<sub>w</sub> = 1002.4). Calculated: C, 69.49; H, 8.25; N, 5.59%. Found: C, 69.37; H, 8.30; N, 5.48%.



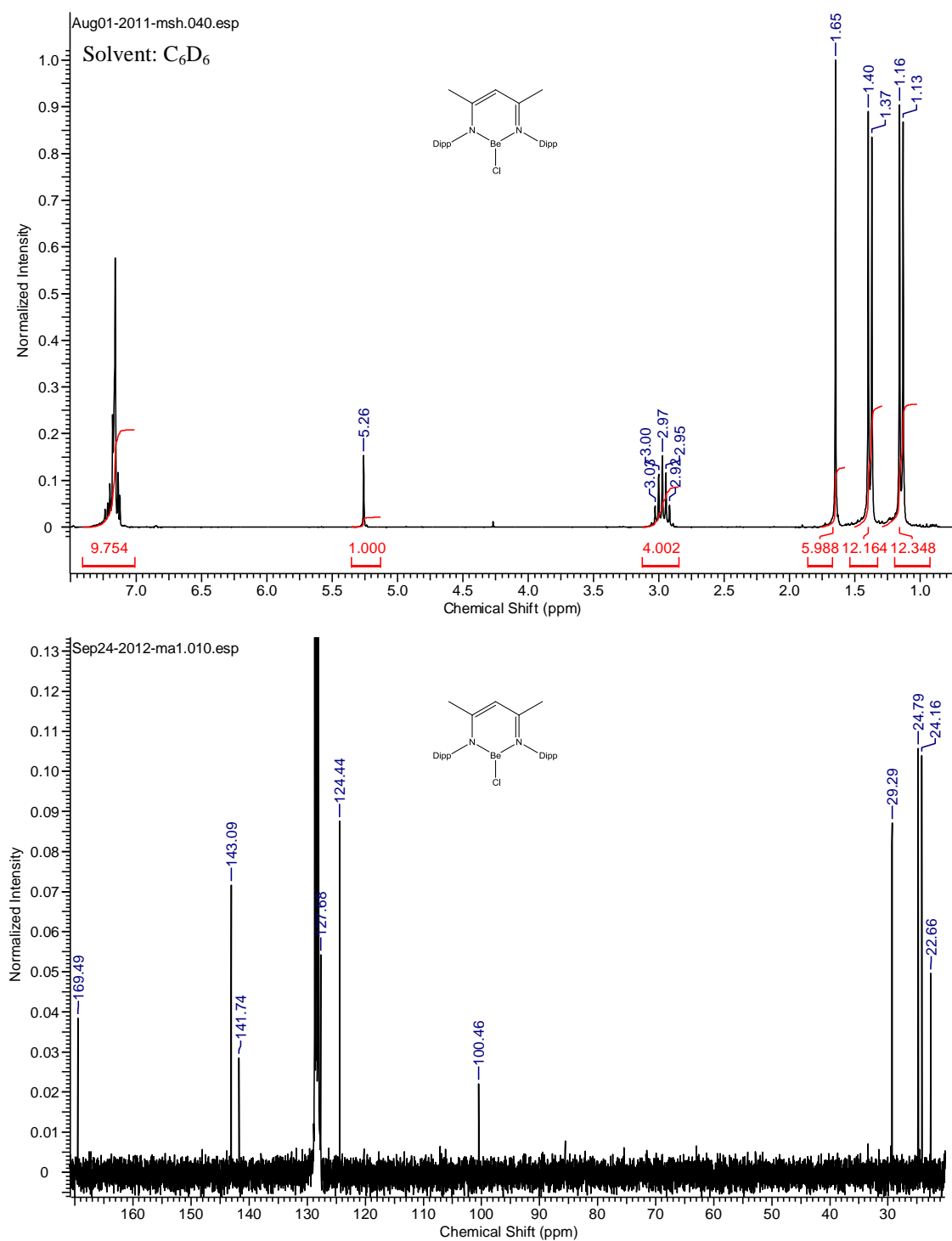
**Figure S2.** ORTEP representation showing the atomic connectivity of complex **13a/b**. Ellipsoids at 20% probability. The asymmetric unit consists of half a dimeric beryllium complex lying on a mirror plane. Atoms of the mirror image, hydrogen atoms and the disordered isopropyl methyl groups have been omitted for clarity.



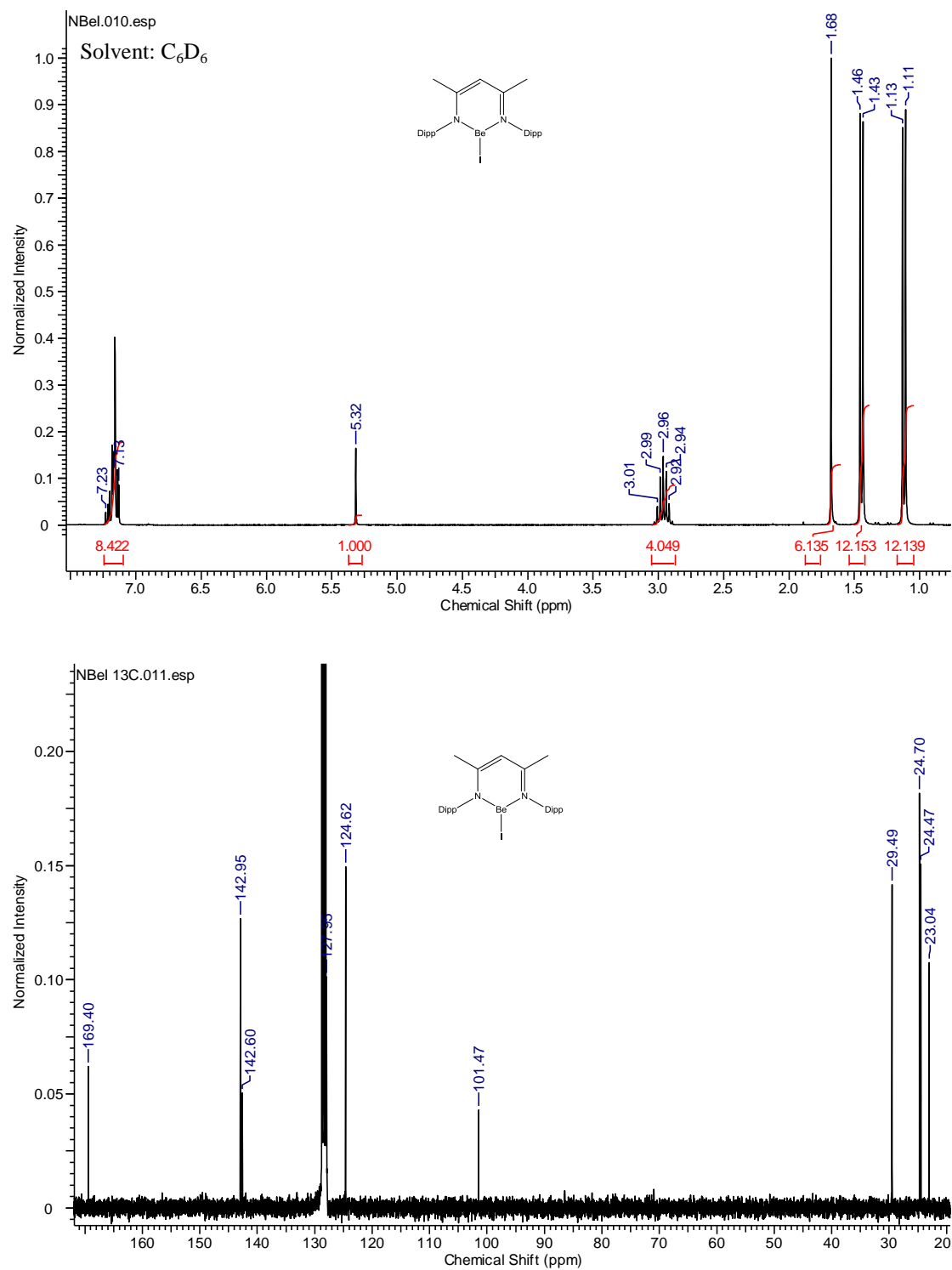
**14a/b** [LBeClK{18-crown-6}]<sub>2</sub>

Complex **13a/b** (100 mg, 0.1 mmol) and 18-crown-6 (53 mg, 0.1 mmol) were combined at room temperature in toluene. The otherwise insoluble complex **13** slowly dissolved prior to precipitation of a fine colorless solid. Heating until the latter redissolved followed by slow cooling in a hot water bath yielded complex **14** as large pale yellow crystals (125 mg, 82  $\mu$ mol, 82% yield). NMR data was essentially identical to that of **13** with an extra peak at  $\delta_{\text{1H}}$  2.80 ppm for the crown ether. Elemental analysis for {C<sub>41</sub>H<sub>65</sub>BeClKN<sub>2</sub>O<sub>6</sub>}<sub>2</sub> ( $M_w$  = 1531.0). Calculated: C, 64.41; H, 8.44; N, 3.66%. Found: C, 64.28; H, 8.41; N, 3.60%.

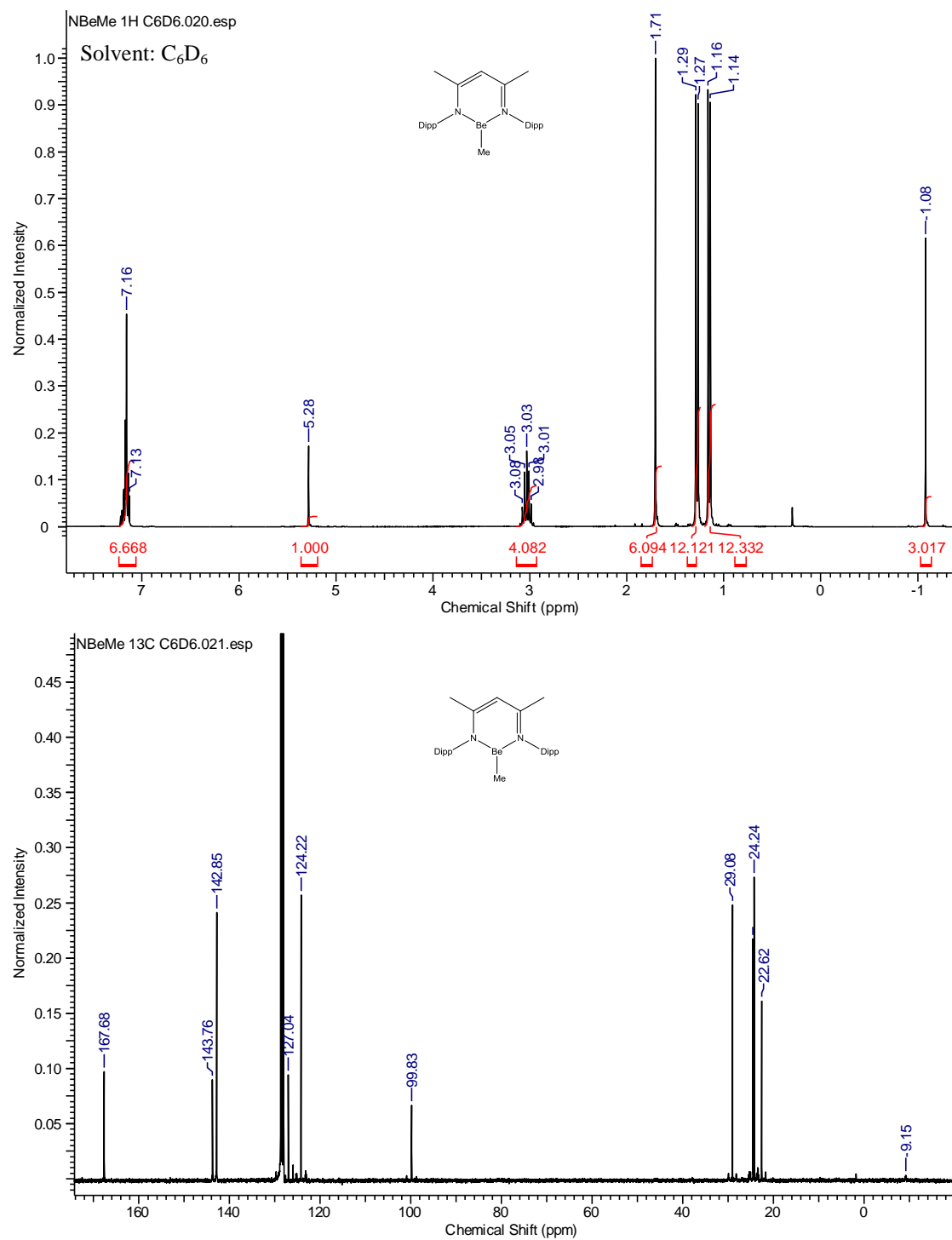
**Figure S3.** NMR spectra for complex **1**



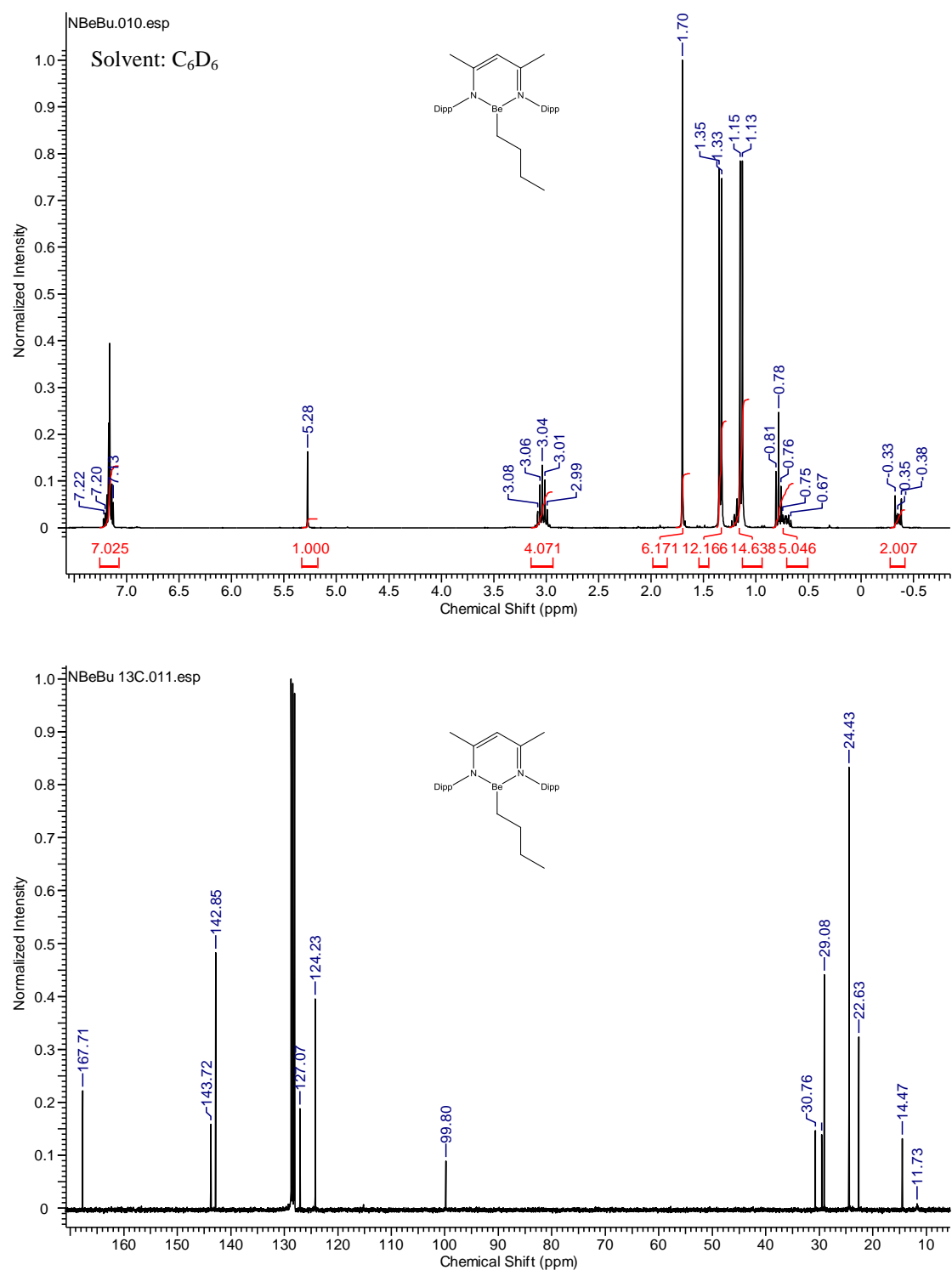
**Figure S4.** NMR spectra for complex **2**



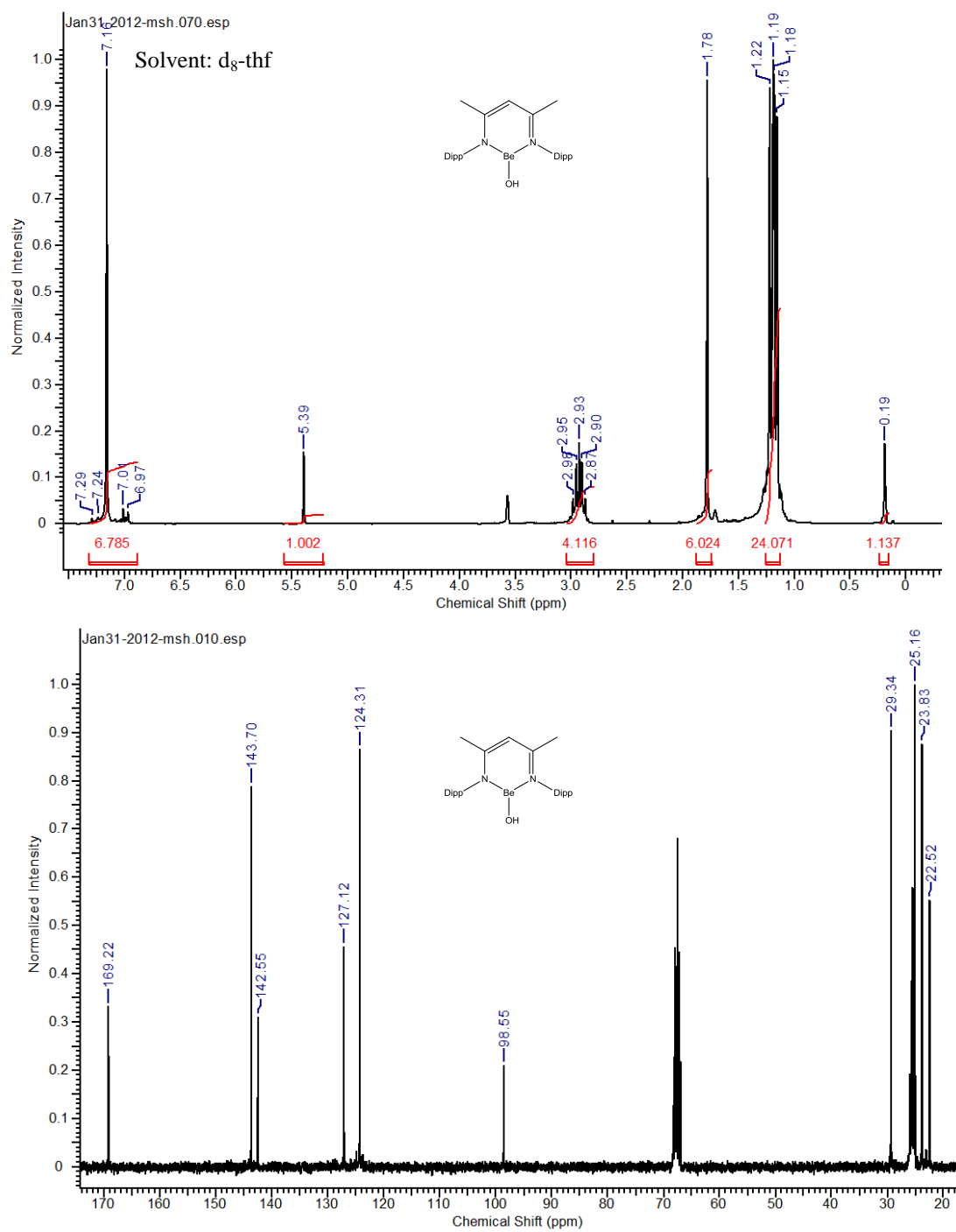
**Figure S5.** NMR spectra for complex **3**



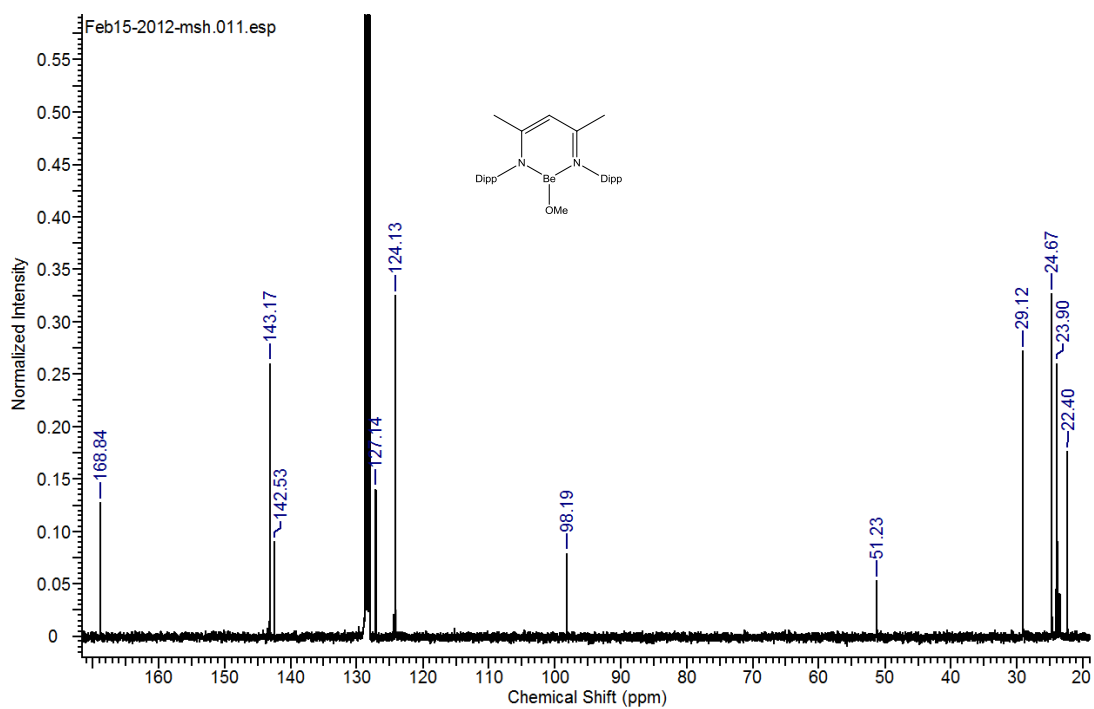
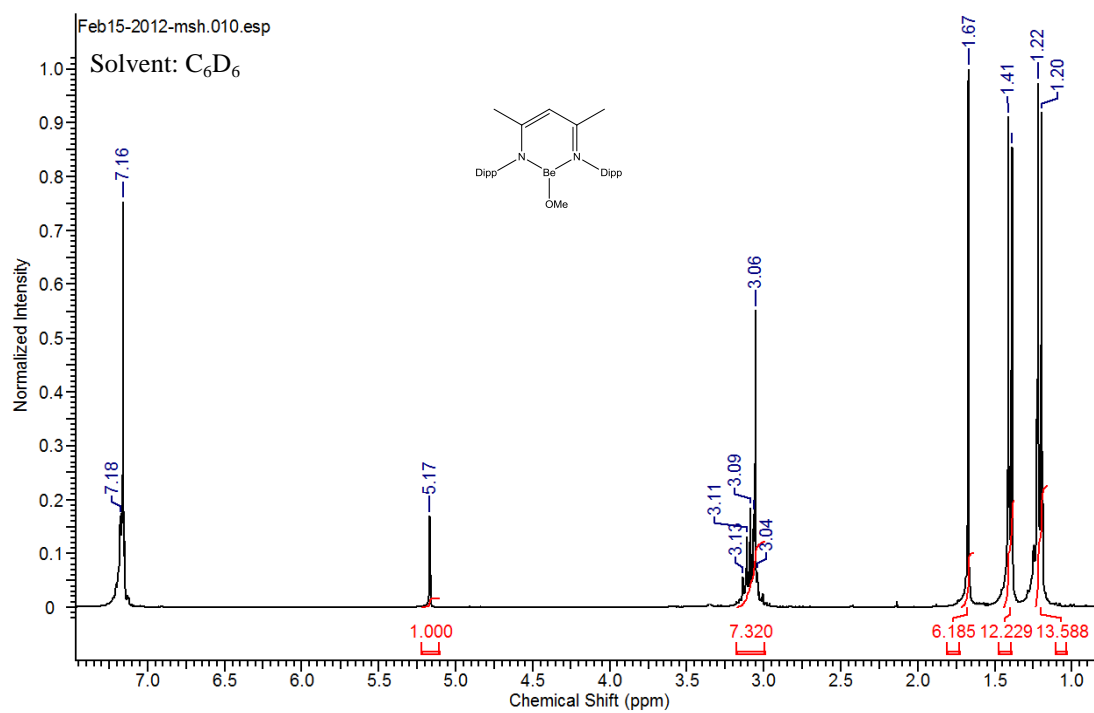
**Figure S6.** NMR spectra for complex **4**



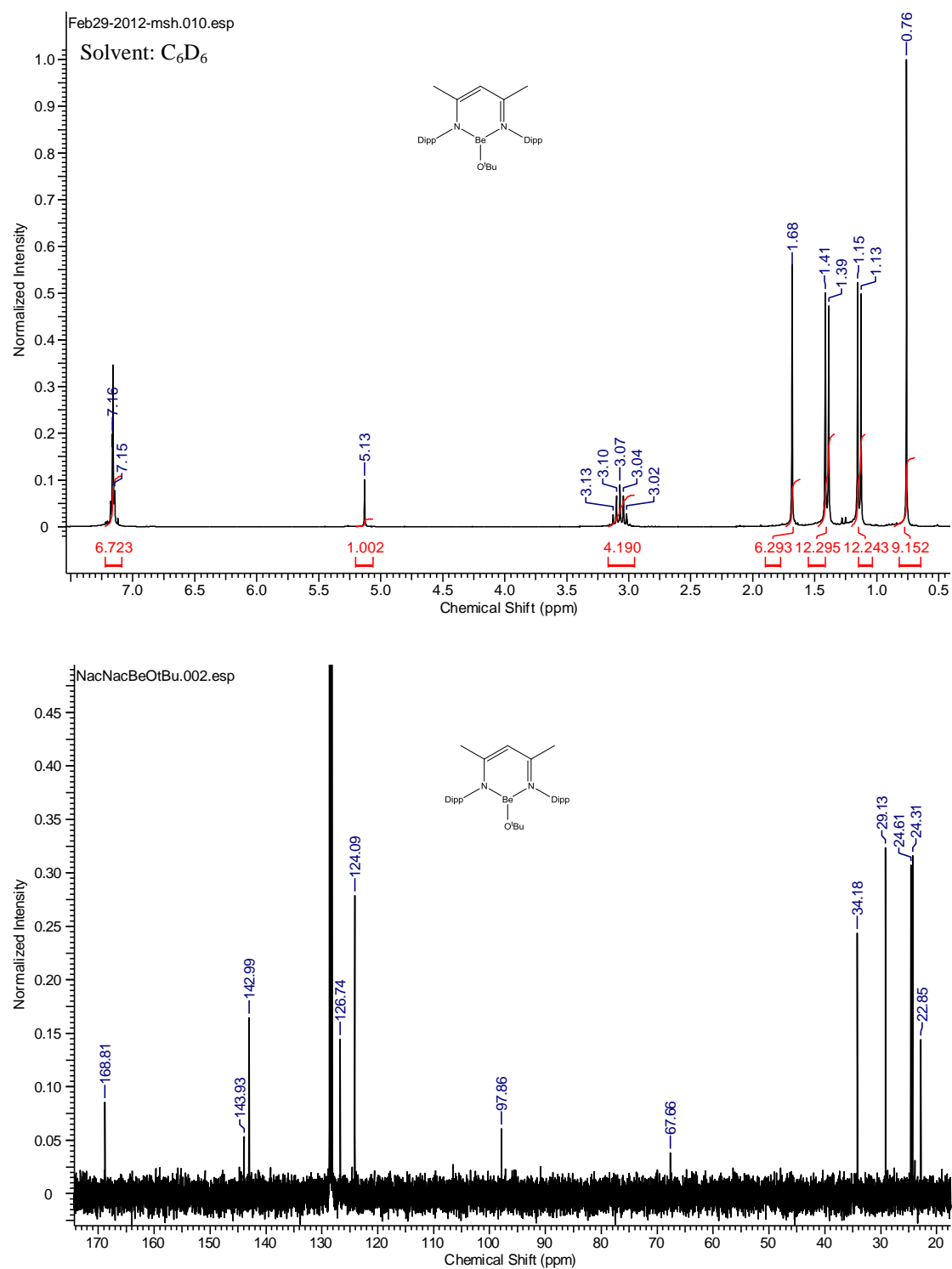
**Figure S7.** NMR spectra for complex **5**



**Figure S8.** NMR spectra for complex **6**

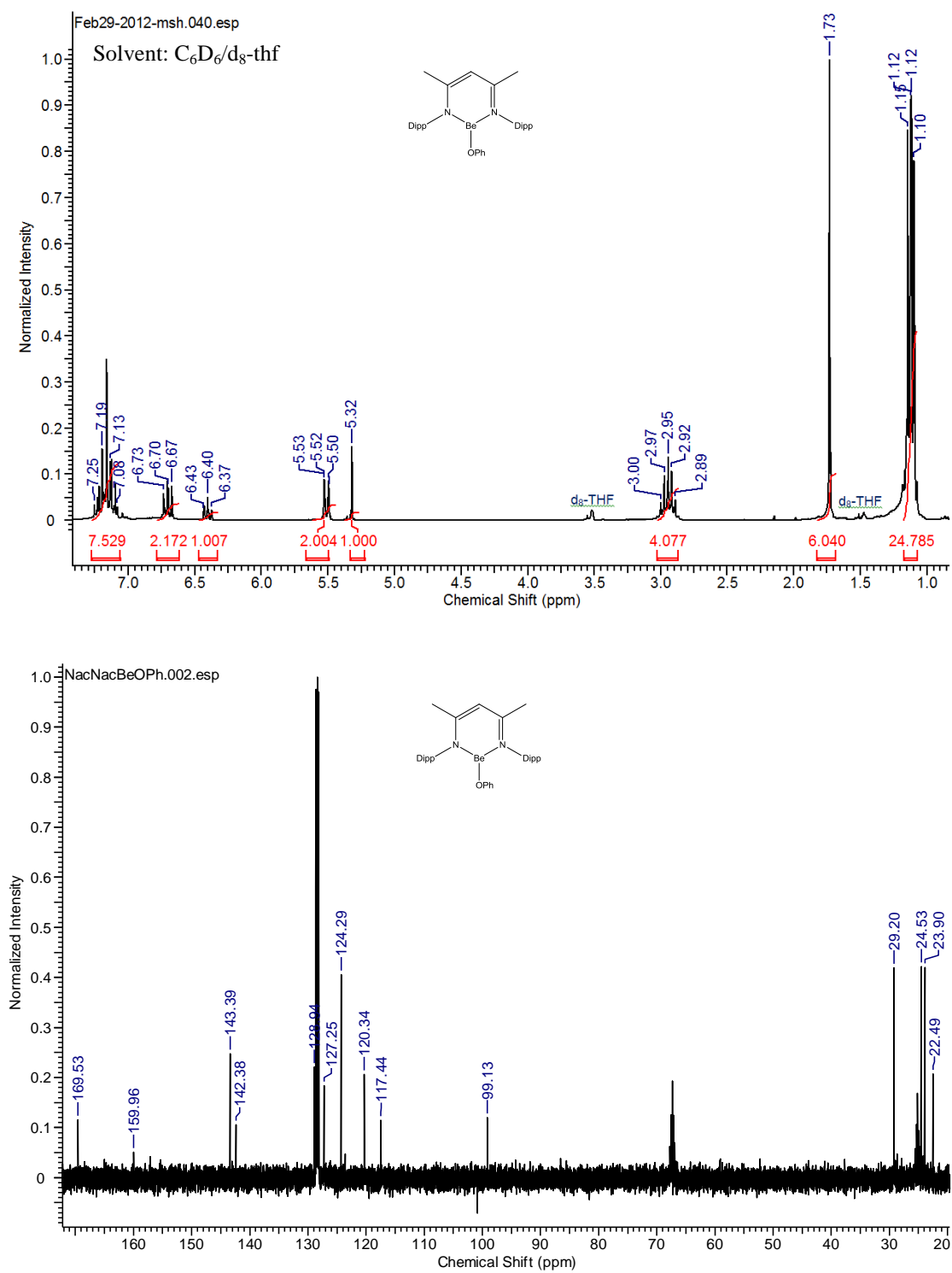


**Figure S9.** NMR spectra for complex **7**

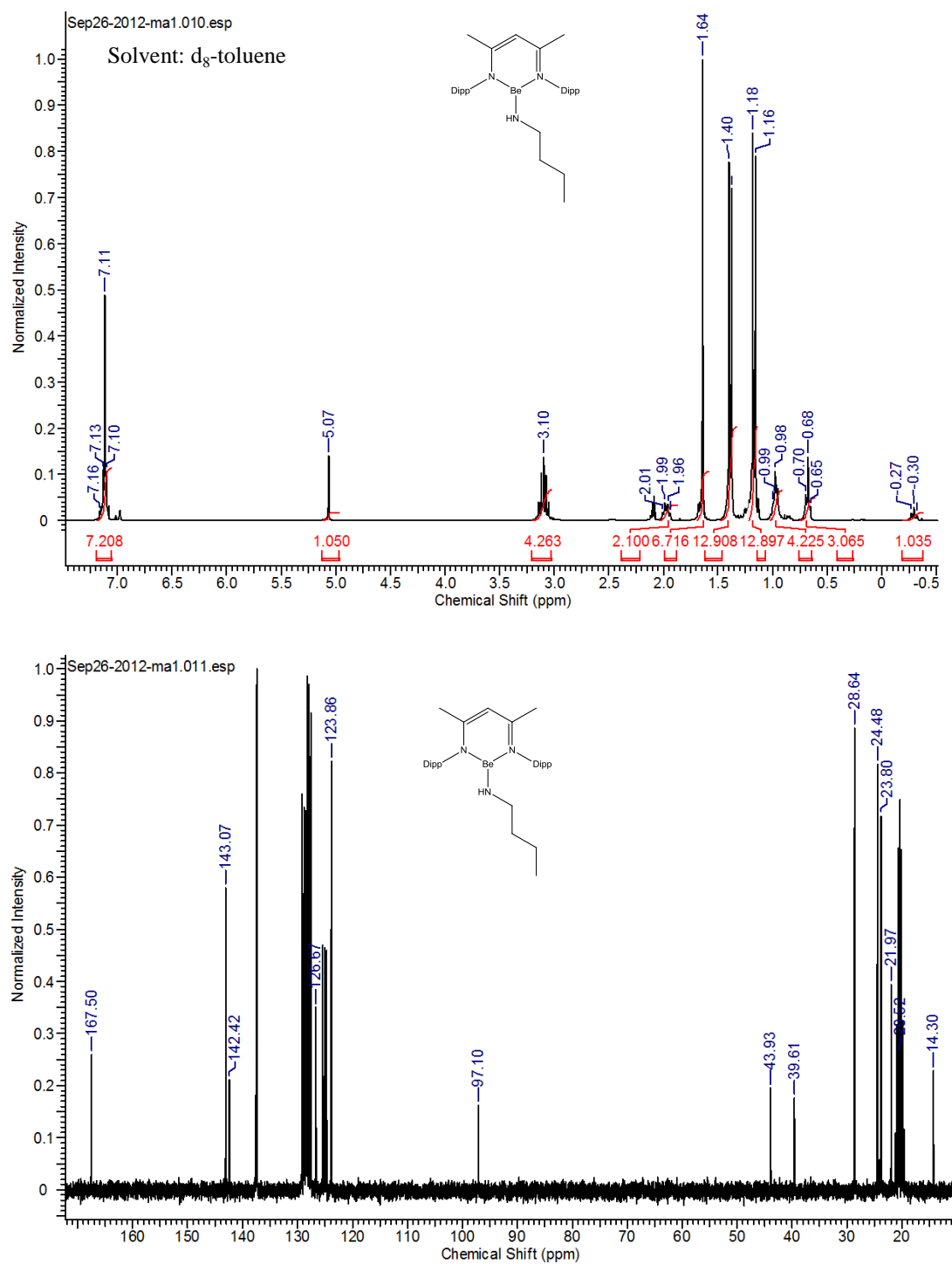




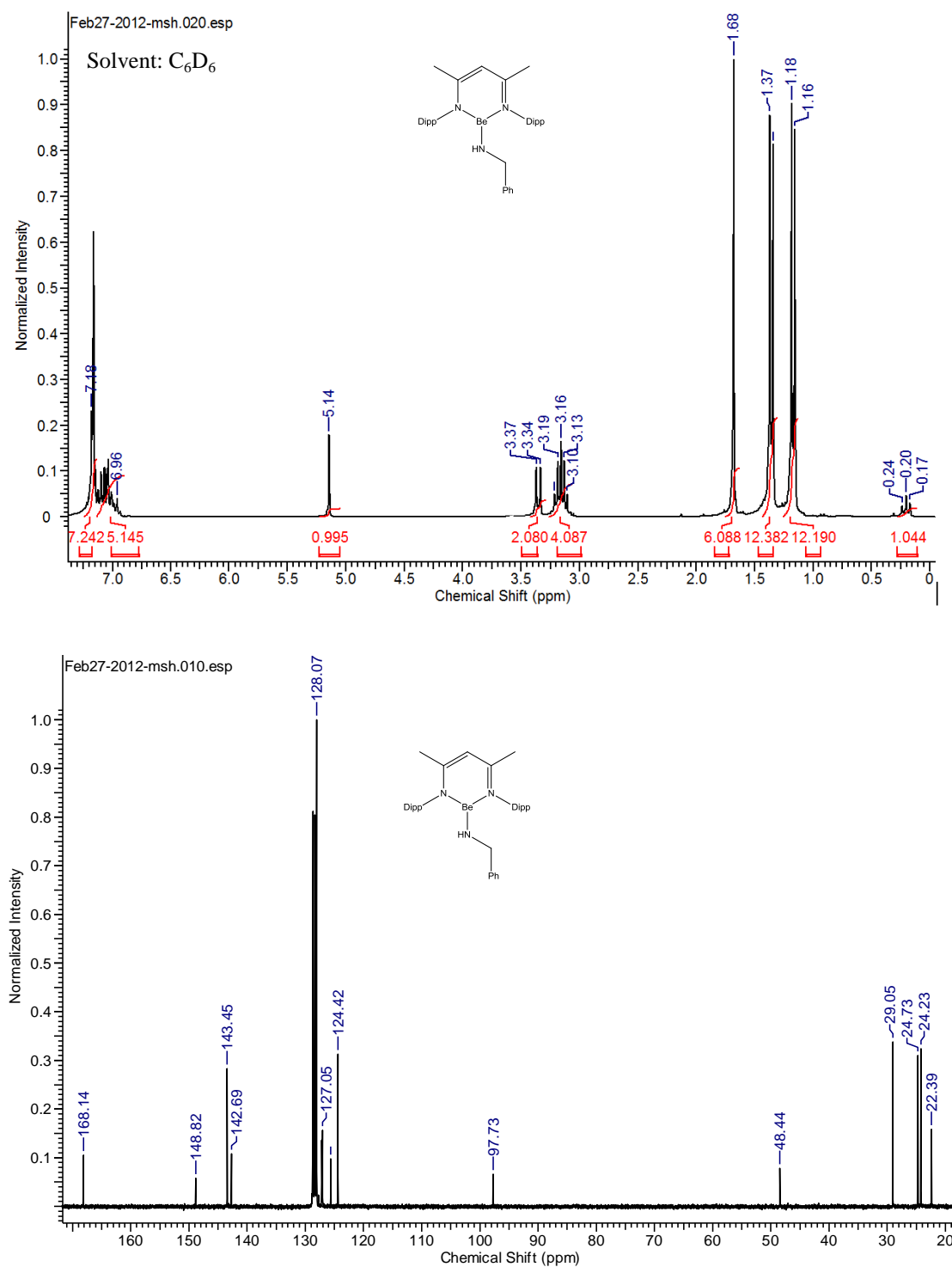
**Figure S10.** NMR spectra for complex **8**



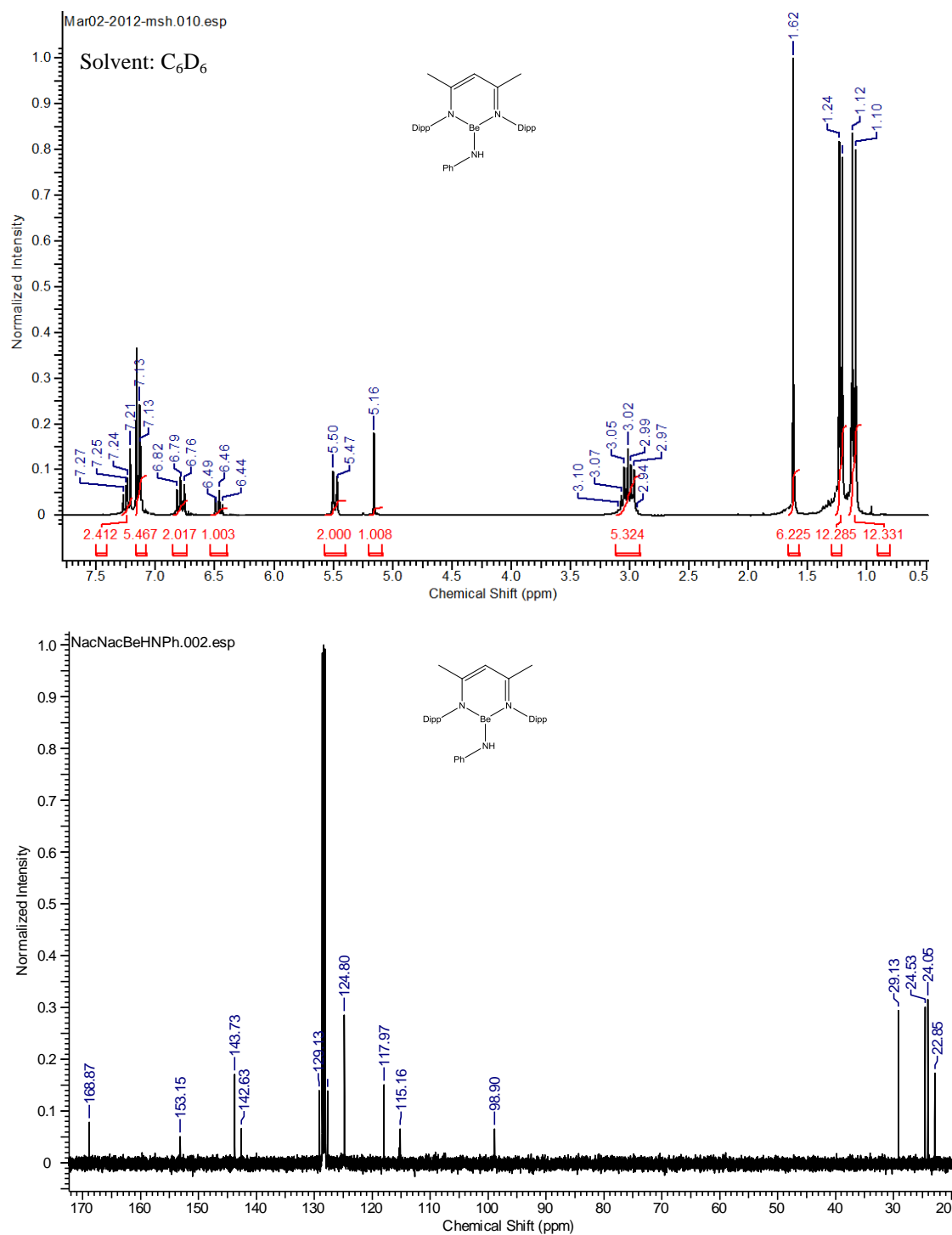
**Figure S11.** NMR spectra for complex **9**



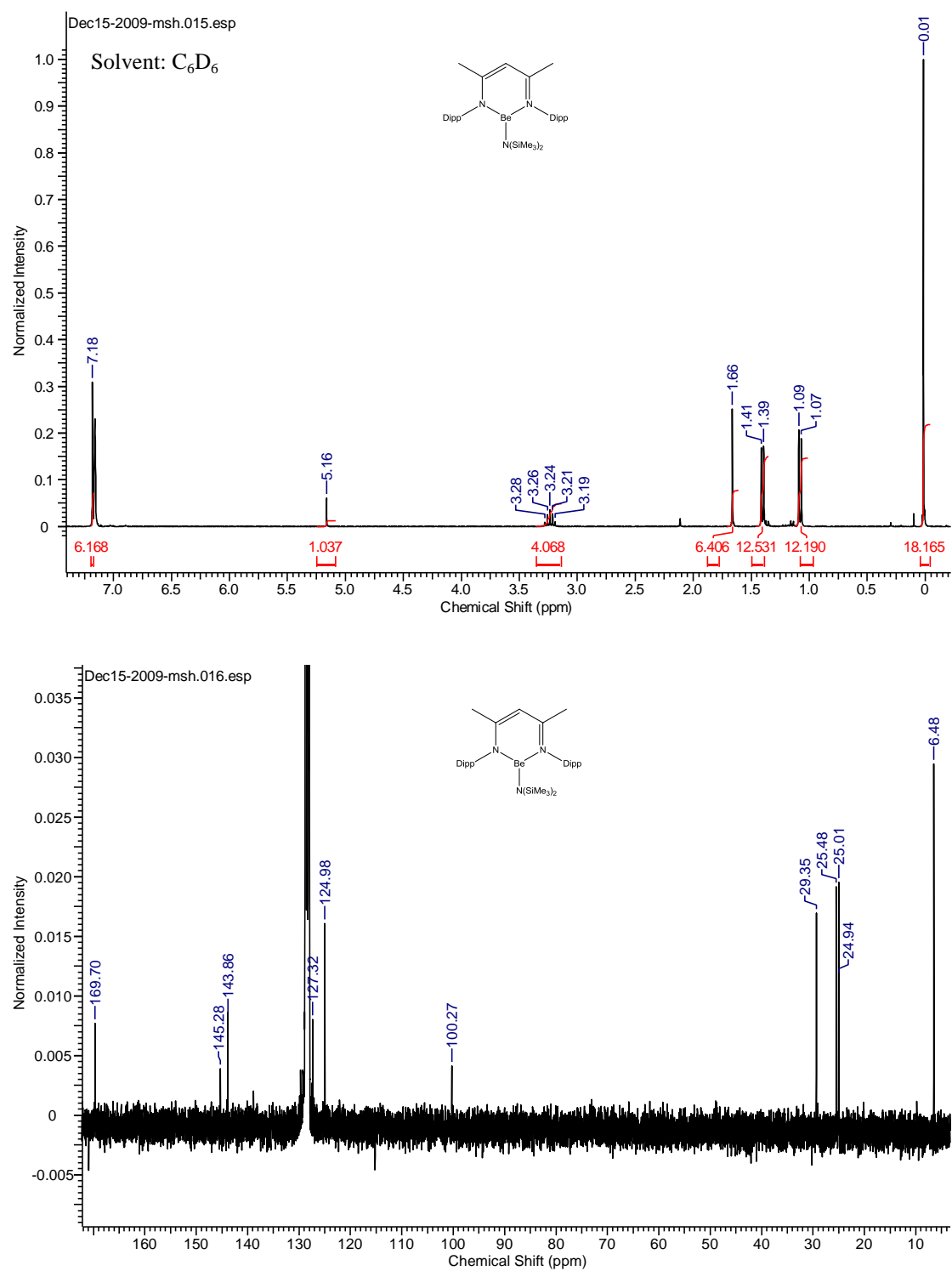
**Figure S12.** NMR spectra for complex **10**



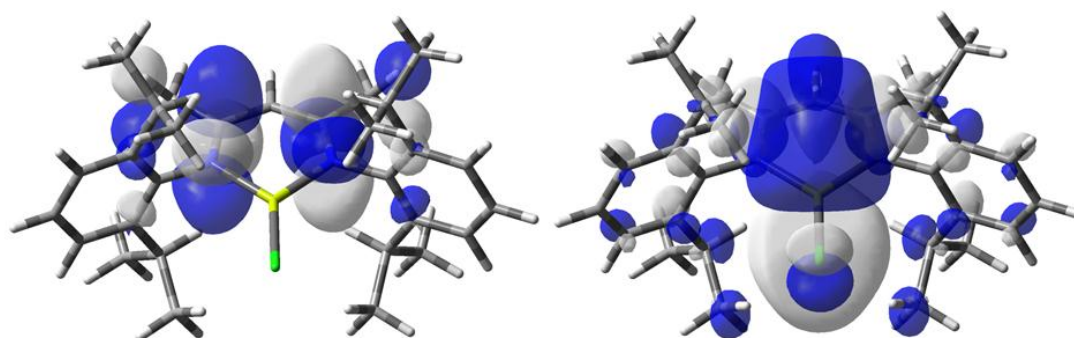
**Figure S13.** NMR spectra for complex **11**



**Figure S14.** NMR spectra for complex **12**



**Figure S15.** View of the optimized geometry and the LUMO (left) and LUMO+6 orbitals of , [HC{CMeNDipp}<sub>2</sub>MgCl]



### X-ray Crystallography

Data for compounds **1-5**, **7-8**, **11-12** and **14a/b** were collected at 150 K on a Nonius KappaCCD diffractometer equipped with an Oxford Cryosystem, using graphite monochromated MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Data were processed using the Nonius Software.<sup>2</sup> Crystal parameters and details on data collection, solution and refinement for the complexes are provided in Table 1. Structure solution, followed by full-matrix least squares refinement was performed using the X-SEED<sup>3</sup> or WINGX-1.80<sup>4</sup> suite of programs throughout. For compound **3** the methyl hydrogens attached to C30 were disordered over 2 positions. Although the structure of compound **8** could be solved in the centrosymmetric space group *Pbnm*, it could not be refined past 12 percent. It was, therefore, deduced that *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* was the correct space group due to some disorder in the structure at the O atom (disorder 86:14). The Be-O1 bond and Be-O1A was, thus, restrained. Further disorder was found in one *iso*-propyl group in the ratio 64:36. In compound **12**, H3 was located and refined without restraints. Compound **14** was refined in accordance with the structures deduced from the NMR analysis. The structure is a mix of two compounds, **14a** and **14b**, which differ at atom C5. The X-ray data revealed a mix of CH-CH<sub>3</sub> (atoms C4A, C5A) and C=CH<sub>2</sub> (C4, C5) in the ratio 20:80. Bond length C3-C4A was restrained and C4A was isotropically refined.

## References

1. Stender, M.; Wright, R. J.; Eichler, B. E.; Prust, J.; Olmstead, M. M.; Roesky, H. W.; Power, P. P., *J. Chem. Soc., Dalton Trans.* **2001**, 3465.
2. DENZO-SCALEPACK Z. Otwinowski and W. Minor, " Processing of X-ray Diffraction Data Collected in Oscillation Mode ", *Methods in Enzymology*, Volume 276: *Macromolecular Crystallography, part A*, p.307-326, **1997**, C.W. Carter, Jr. & R. M. Sweet, Eds., Academic Press.
3. Barbour, L. J. "X-Seed - A software tool for supramolecular crystallography" *J. Supramol. Chem.* 2001, **1**, 189.
4. Farrugia, L. J. *J. Appl. Cryst.*, **1999**, 32, 837.