

Electronic Supplementary Information

**Assembly of metallo-macrocycles through reductive C–C  
coupling of alkylnitriles by an Mg–Mg-bonded compound**

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## S1. Experimental details

### General procedures

All of the reactions and manipulations of air- and moisture-sensitive compounds were carried out under argon or nitrogen with standard Schlenk or drybox techniques. The solvents (toluene, THF, *n*-hexane and DME) were dried using appropriate methods and were distilled under argon prior to use. Tetrahydrofuran-*d*<sub>8</sub> is dried over Na/K alloy. The  $\alpha$ -diimine ligand **L** was prepared according to literature procedures.<sup>1</sup> Sodium metal, anhydrous magnesium chloride (MgCl<sub>2</sub>) *n*-butyronitrile, *n*-pentanenitrile and *n*-hexanenitrile were purchased from Alfa Aesar. NMR spectra were recorded on a Mercury Plus-400 spectrometer. Elemental analyses were performed with an Elementar VarioEL III instrument. IR spectra were recorded using a Nicolet AVATAR 360 FT-IR spectrometer.

**[LMg( $\mu$ -{(N $\equiv$ C-C(CH<sub>2</sub>CH<sub>3</sub>)=C((CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)-NH)}<sub>3</sub>[K<sub>3</sub>(THF)<sub>6</sub>]** (**2**). *n*-Butyronitrile (0.351 mL, 4 mmol) was added to the THF solution of compound **1** (1.0 mmol) prepared in situ by the reaction of  $\alpha$ -diimine ligand **L**, MgCl<sub>2</sub>, and K metal.<sup>2</sup> The mixture was stirred for 3 days, and the color of the solution became lighter and brighter. The reaction mixture was filtered, the filtrate concentrated to about 5 mL, and *n*-hexane was added. The solution was stored at room temperature and yellow crystals of compound **2** were obtained one week later. Crystal yield: 0.678 g (45%). <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>, 298 K):  $\delta$ /ppm: 0.46 (t, 9H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-), 0.89 (t, 9H, CH<sub>3</sub>CH<sub>2</sub>C=), 1.02 (d, 36H, (CH<sub>3</sub>)<sub>2</sub>CH-), 1.14 (d, 36H, (CH<sub>3</sub>)<sub>2</sub>CH-), 1.34 (m, 6H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.53 (s, 18H, CH<sub>3</sub>C-), 1.84 (m, 6H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-), 2.07 (m, 6H, CH<sub>3</sub>CH<sub>2</sub>C=), 3.95(m, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.13 (s, 3H, NH), 6.43 (m, 6H, *p*-C<sub>6</sub>H<sub>3</sub>), 6.74 (m, 12H, *m*-C<sub>6</sub>H<sub>3</sub>); <sup>13</sup>C NMR (100.6 MHz, THF-*d*<sub>8</sub>, 298 K):  $\delta$ /ppm: 13.5 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-), 14.0 (CH<sub>3</sub>CH<sub>2</sub>C=), 17.2, 20.7 ((CH<sub>3</sub>)<sub>2</sub>CH), 23.5 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-), 24.6 (CH<sub>3</sub>C=), 25.7 (CH<sub>3</sub>CH<sub>2</sub>C=), 26.9 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-), 40.7 ((CH<sub>3</sub>)<sub>2</sub>CH), 65.1 (CH<sub>3</sub>CH<sub>2</sub>C=), 116.5 (*p*-C<sub>6</sub>H<sub>3</sub>), 120.2 (*m*-C<sub>6</sub>H<sub>3</sub>), 122.1 (*o*-C<sub>6</sub>H<sub>3</sub>), 130.8 (C $\equiv$ N), 143.6 (*N*-C<sub>6</sub>H<sub>3</sub>), 153.9 (NC=CN), 174.6 (=C-NH); IR (Nujol, KBr,  $\nu$ /cm<sup>-1</sup>): 3291w, 2956w, 2717s, 2120s, 1585w, 1520s, 1460s, 1377s, 1242s, 1051s, 775s. Elemental analysis C<sub>132</sub>H<sub>207</sub>K<sub>3</sub>Mg<sub>3</sub>N<sub>12</sub>O<sub>6</sub> (2248.31): calc. C 70.51, H 9.28, N 7.48%; found: C 70.15, H 9.51, N 7.20%.

**[LMg( $\mu$ -{(N $\equiv$ C-C(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)=C((CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>)-NH)}<sub>3</sub>[K<sub>3</sub>(THF)<sub>6</sub>]** (**3**). 4.0 equiv of *n*-pentanenitrile (0.418 mL, 4 mmol) was added to a stirred deep-red solution of compound **1** (1.0 mmol) in THF. After 3 days, the solvent was concentrated to about 5 mL under reduced pressure, and a few drops of *n*-hexane were added. Red-orange crystals of **3** (yield: 0.782 mg, 50%) suitable for X-ray diffraction were obtained in several days at room temperature. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>, 298 K):  $\delta$ /ppm: 0.56 (t, 9H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 0.81 (t, 9H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C=), 1.02 (d, 36H, (CH<sub>3</sub>)<sub>2</sub>CH-), 1.14 (d, 36H, (CH<sub>3</sub>)CH<sub>2</sub>-), 1.22 (m, 6H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.32 (m, 12H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C=, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.54 (s, 18H, CCH<sub>3</sub>), 1.84 (m, 6H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 2.13

(m, 6H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C=), 3.95 (m, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.13 (s, 3H, NH), 6.42 (m, 6H, *p*-C<sub>6</sub>H<sub>3</sub>), 6.73 (m, 12H, *m*-C<sub>6</sub>H<sub>3</sub>); <sup>13</sup>C NMR (100.6 MHz, THF-*d*<sub>8</sub>, 298 K): δ/ppm: 14.5 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 14.8 (CH<sub>3</sub>CHCH<sub>2</sub>C=), 17.6, 23.1 ((CH<sub>3</sub>)<sub>2</sub>CH-), 23.5 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 25.0 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C=), 26.6 (CH<sub>3</sub>C=), 27.3 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 30.6 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 33.2 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C=), 39.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 63.6 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C=), 116.8 (*p*-C<sub>6</sub>H<sub>3</sub>), 120.7 (*m*-C<sub>6</sub>H<sub>3</sub>), 122.5 (*o*-C<sub>6</sub>H<sub>3</sub>), 131.2 (C≡N), 143.8 (N-C<sub>6</sub>H<sub>3</sub>), 154.1 (NC=CN), 175.4 (=C-NH); IR (Nujol, KBr, ν/cm<sup>-1</sup>): 3187w, 2924w, 2854s, 2126s, 1516s, 1460s, 1377s, 1240s, 775s. Elemental analysis C<sub>138</sub>H<sub>219</sub>K<sub>3</sub>Mg<sub>3</sub>N<sub>12</sub>O<sub>6</sub> (2332.47): calc. C 71.06, H 9.46, N 7.21 %; found: C 70.57, H 9.12, N 6.86 %.

**[LMg(μ-{(N≡C-C(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>)=C((CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>)-NH)}]₃[K<sub>3</sub>(THF)<sub>3</sub>(DME)<sub>2</sub>] (4)**. In a manner similar to the synthesis of **3**, 4.0 equiv of *n*-hexanenitrile (0.480 mL, 4 mmol) was added to a stirred deep-red solution of compound **1** (1 mmol) in THF. After for 2 days, the reaction mixture was filtered, the solution concentrated, and orange-red crystals of product **4** were obtained from a mixed solvent of THF, DME and *n*-hexane. Crystal yield: 0.758 g (48%). <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>, 298 K): δ/ppm: 0.68 (t, 9H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.82 (t, 9H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C=), 1.02 (d, 36H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.14 (d, 36H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.20–1.40 (m, 30H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C=), 1.54 (s, 18H, CCH<sub>3</sub>), 1.86 (m, 6H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 2.11 (m, 6H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C=), 3.27 (m, DME), 3.43 (m, DME), 3.95 (m, 12H, (CH<sub>3</sub>)<sub>2</sub>CH-), 4.12 (s, 3H, NH), 6.43 (m, 6H, *p*-C<sub>6</sub>H<sub>3</sub>), 6.73 (m, 12H, *m*-C<sub>6</sub>H<sub>3</sub>); <sup>13</sup>C NMR (100.6 MHz, THF-*d*<sub>8</sub>, 298K): δ/ppm: 14.7 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 14.8 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C=), 17.6, 23.6 ((CH<sub>3</sub>)<sub>2</sub>CH-), 23.8 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 25.0 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C=), 26.0 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 27.3 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C=), 28.2 (CCH<sub>3</sub>), 30.9 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 32.3 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 32.7 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C=), 39.5 ((CH<sub>3</sub>)<sub>2</sub>CH-), 59.1 (DME), 63.7 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C=), 72.9 (DME), 116.8 (*p*-C<sub>6</sub>H<sub>3</sub>), 120.7 (*m*-C<sub>6</sub>H<sub>3</sub>), 122.5 (*o*-C<sub>6</sub>H<sub>3</sub>), 131.5 (C≡N), 143.8 (N-C<sub>6</sub>H<sub>3</sub>), 154.1 (NC=CN), 175.3 (=C-NH); IR (Nujol, KBr, ν/cm<sup>-1</sup>): 3180w, 2924w, 2854s, 2127s, 1516s, 1462s, 1377s, 1240s, 775s, 723s. Elemental analysis C<sub>140</sub>H<sub>227</sub>K<sub>3</sub>Mg<sub>3</sub>N<sub>12</sub>O<sub>7</sub> (2380.55): calc. C 70.63, H 9.61, N 7.06%; found: C 70.21, H 9.38, N 7.39%.

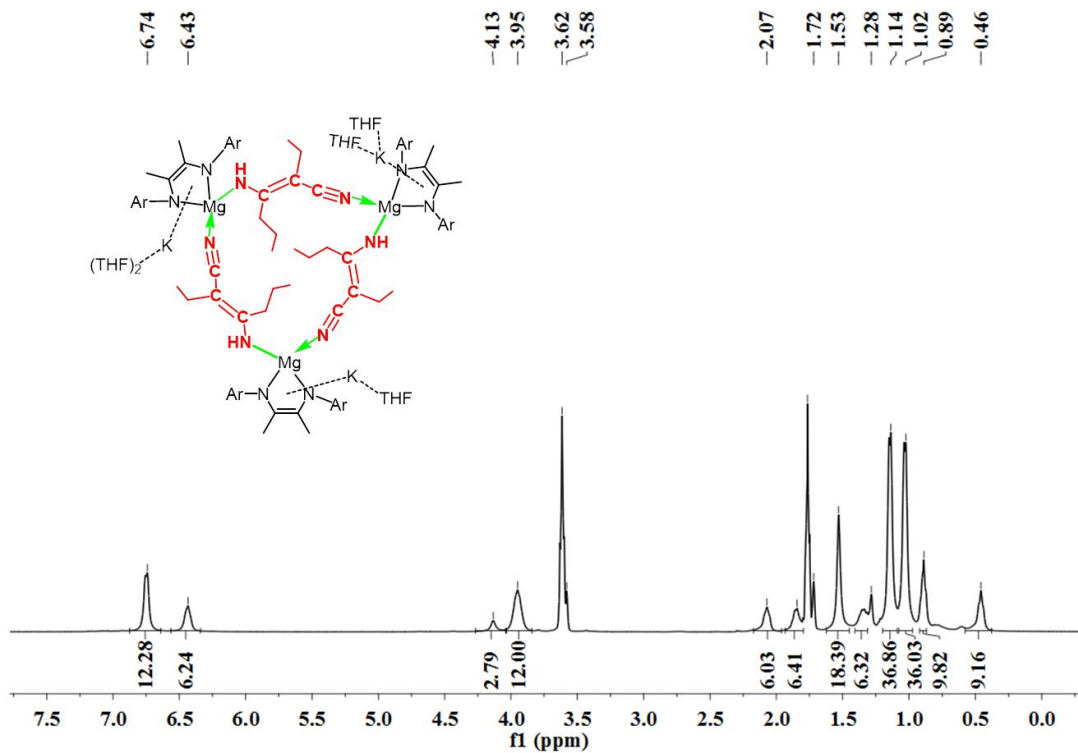


Fig. S1. <sup>1</sup>H NMR spectrum of compound 2 in THF-d<sub>8</sub>.

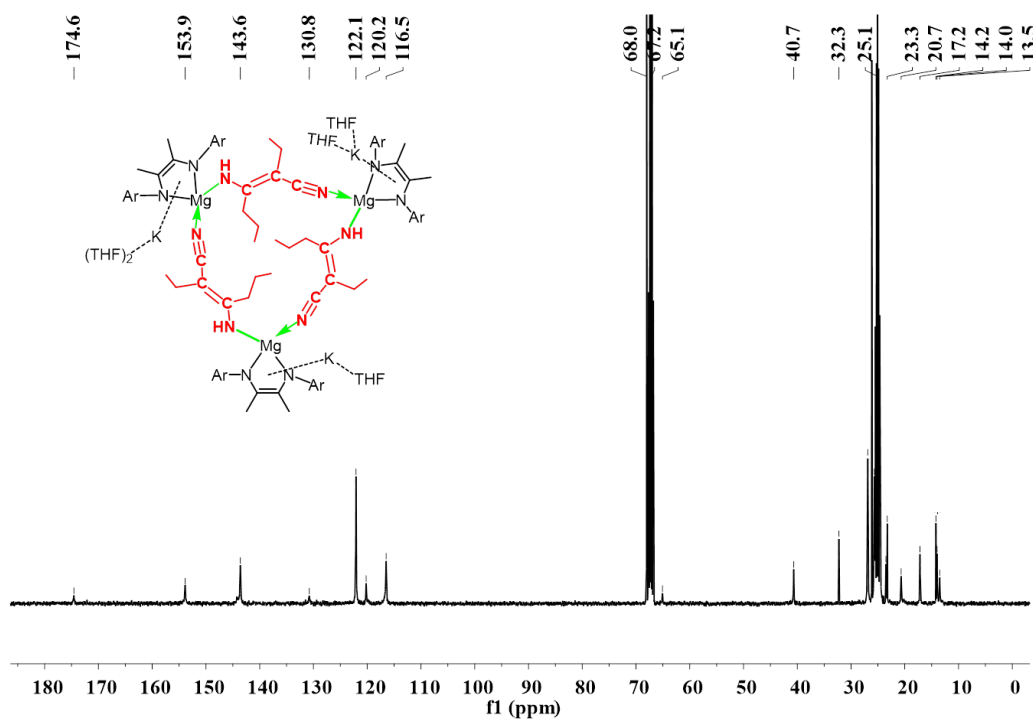


Fig. S2. <sup>13</sup>C NMR spectrum of compound 2 in THF-d<sub>8</sub>.

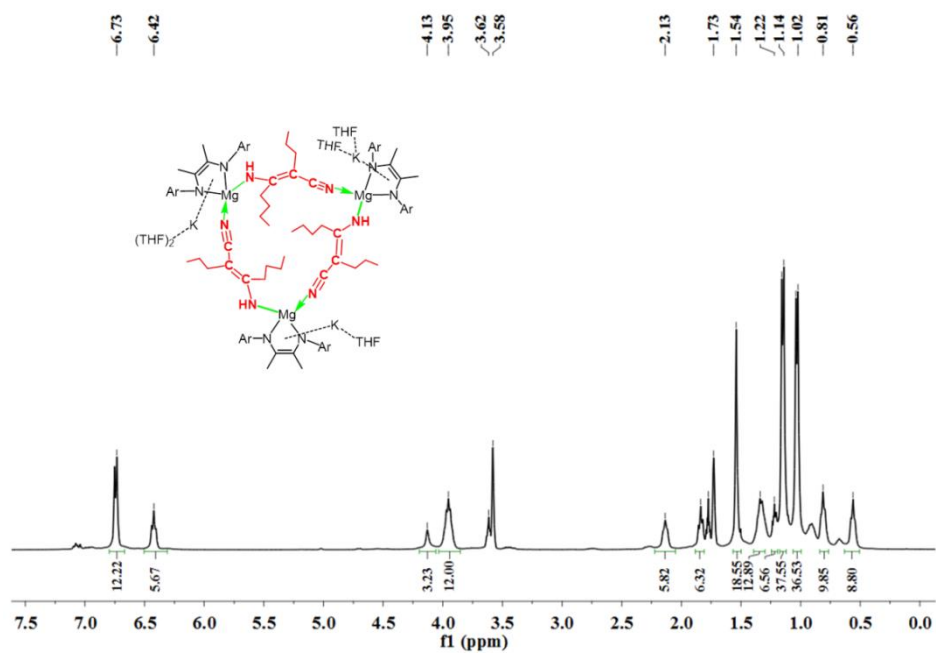


Fig. S3. <sup>1</sup>H NMR spectrum of compound 3 in THF-*d*<sub>8</sub>.

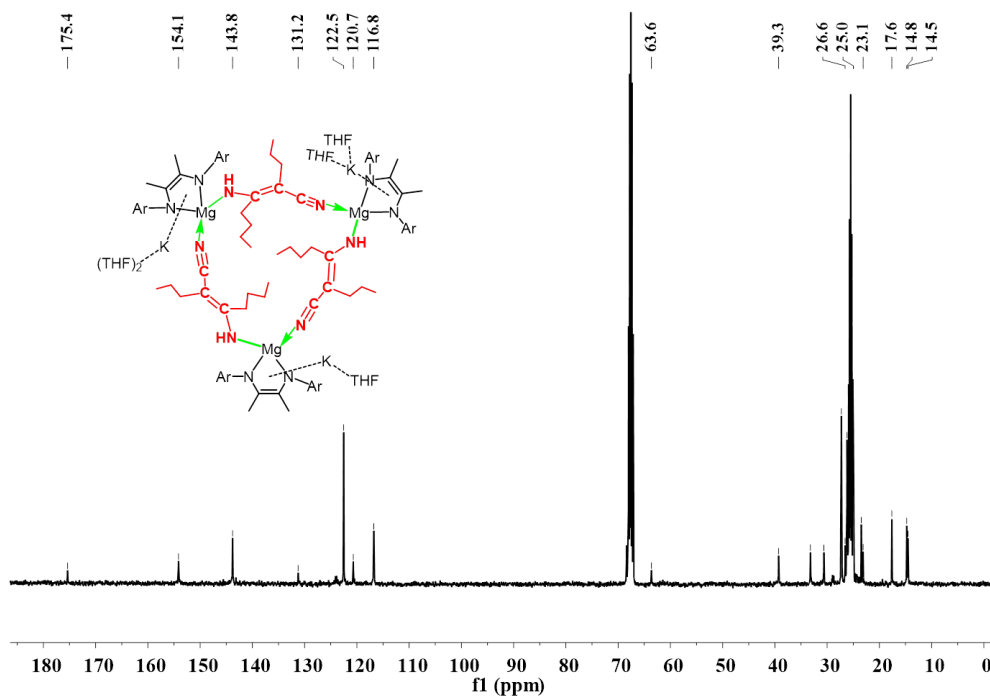


Fig. S4. <sup>13</sup>C NMR spectrum of compound 3 in THF-*d*<sub>8</sub>.

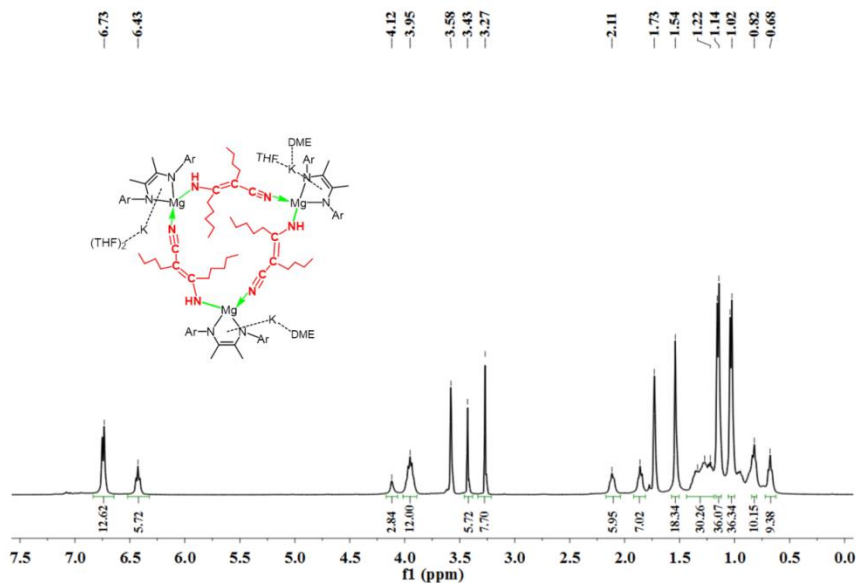


Fig. S5. <sup>1</sup>H NMR spectrum of compound 4 in THF-*d*<sub>8</sub>.

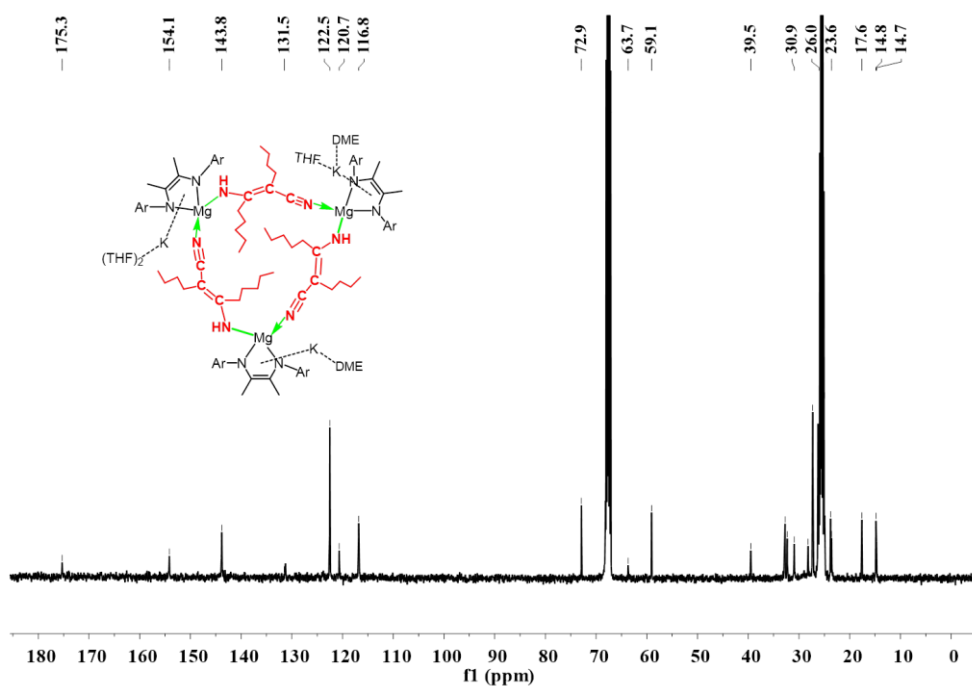


Fig. S6. <sup>13</sup>C NMR spectrum of compound 4 in THF-*d*<sub>8</sub>.

## S2. X-ray crystallographic analysis

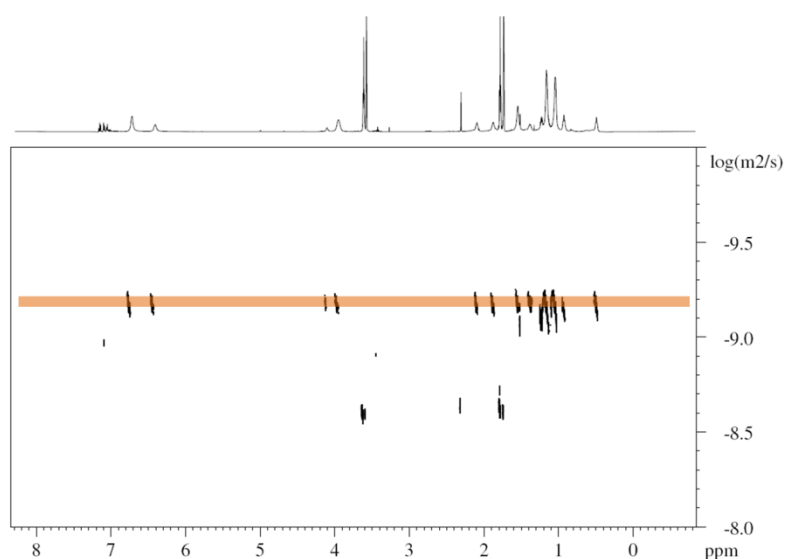
Diffraction data for complexes 2–4 were collected on a Bruker SMART APEX II diffractometer at 153 K with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). An empirical absorption correction using SADABS was applied for all data.<sup>3</sup> The structures were solved and refined to convergence on  $F^2$  for all independent reflections by the full-matrix least

squares method using the SHELXL-2014 programs<sup>4</sup> and OLEX2 1.2.<sup>5</sup> Some atoms in THF and alkyl chain are disordered and display unusual thermal parameters, which caused the level B alerts. In compounds **2**, **3** and **4**, about 5.0, 4.7 and 3.1 molecules of THF (about 1 THF molecules per formula,  $Z = 4$  (in **2** and **3**),  $Z = 2$  (in **4**)) are co-crystallized, with the corresponding electron density (198, 188 and 124 electrons in **2**, **3**, **4**) being removed using the SQUEEZE routine implemented within the software program PLATON,<sup>6</sup> and the resulting .fab file was processed with OLEX2 1.2 using the ABIN instruction. Crystallographic data and refinement details for compounds **2–4** are given in Table S1.

CCDC numbers 2121995 (for **2**), 2121996 (for **3**) and 2121997 (for **4**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S1.** Crystallographic data and refinement details for compounds **2–4**.

compound	<b>2</b>	<b>3</b>	<b>4</b>
formula	C <sub>132</sub> H <sub>207</sub> K <sub>3</sub> Mg <sub>3</sub> N <sub>12</sub> O <sub>6</sub>	C <sub>138</sub> H <sub>219</sub> K <sub>3</sub> Mg <sub>3</sub> N <sub>12</sub> O <sub>6</sub>	C <sub>140</sub> H <sub>227</sub> K <sub>3</sub> Mg <sub>3</sub> N <sub>12</sub> O <sub>7</sub>
Mw	2248.31	2332.47	2380.55
crystal system	monoclinic	monoclinic	triclinic
space group	<i>Cc</i>	<i>Cc</i>	<i>P-1</i>
<i>a</i> (Å)	29.600(15)	29.376(8)	14.10(3)
<i>b</i> (Å)	21.925(11)	21.502(6)	17.32(3)
<i>c</i> (Å)	22.450(11)	23.225(7)	34.45(6)
$\alpha$ (°)	90	90	95.42(4)
$\beta$ (°)	94.340(17)	95.674(10)	97.06(4)
$\gamma$ (°)	90	90	108.92(4)
<i>V</i> (Å <sup>3</sup> )	14527(12)	14598(7)	7817(25)
<i>Z</i>	4	4	2
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.028	1.061	1.011
<i>F</i> (000)	4896	5088	2600
$\mu$ /mm <sup>-1</sup>	0.158	0.159	0.150
$\theta$ range	2.314-25.000	2.175-25.000	2.38-24.26
total reflns	24405	24903	28510
unique reflns	17059	22450	14110
<i>R</i> (int)	0.0603	0.0407	0.0857
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0774, 0.2141	0.0544, 0.15152	0.1148, 0.2297
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1072, 0.2373	0.0610, 0.1579	0.1964, 0.2609
GOF ( <i>F</i> <sup>2</sup> )	1.045	1.047	1.129



**Fig. S7.** DOSY spectrum (400 MHz, THF-*d*<sub>8</sub>, 298 K,  $\log D = -9.20$ ) of **2**.

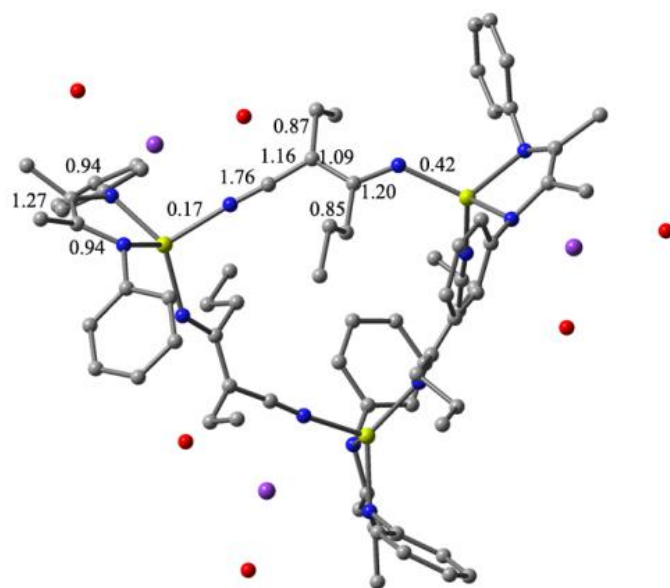
Diffusion coefficients and hydrodynamic radii are correlated theoretically by the Stokes-Einstein Relation (**Equation S1**):  $r = \frac{kT}{6\pi\eta D}$  where  $D$  is the diffusion coefficient ( $10^{-9.20} = 6.31 \times 10^{-10}$  obtained from Fig. S7),  $k$  is the Boltzmann constant  $1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$ ,  $T$  is the temperature in Kelvin (298 K),  $\eta$  is the viscosity of the solvent (THF  $5.01 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$ )<sup>3</sup>, and  $r$  is the radius of the molecular sphere.

$$r(\mathbf{3}) = 1.38 \times 10^{-23} \times 298 / (6 \times 3.14 \times 5.01 \times 10^{-4} \times 6.31 \times 10^{-10}) = 6.91 \times 10^{-10} \text{ m} = 6.91 \text{ \AA}$$

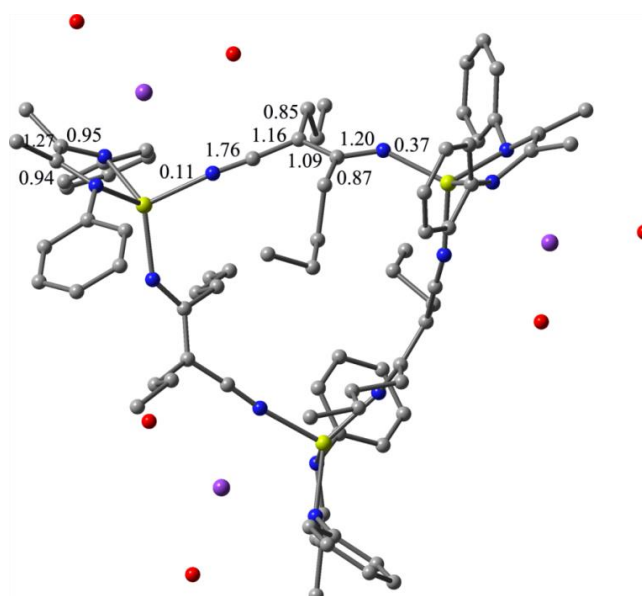
### S3. Theoretical Calculations

Structure optimization for the model compounds  $[\text{L}'\text{Mg}(\mu\text{-}\{\text{N}\equiv\text{CC}(\text{CH}_2\text{CH}_3)\text{-C}=\{(\text{CH}_2)_2\text{CH}_3\}\text{-NH}\})_3[\text{K}_3(\text{H}_2\text{O})_6]$  (**2**),  $[\text{L}'\text{MgN}\equiv\text{C}\{(\text{CH}_2)_3\text{CH}_3\}\text{C}\{(\text{CH}_2)_2\text{CH}_3\}=\text{C-NH}\}_3[\text{K}_3(\text{H}_2\text{O})_6]$  (**3**) and  $[\text{L}'\text{MgN}\equiv\text{C}\{(\text{CH}_2)_4\text{CH}_3\}\text{C}\{(\text{CH}_2)_3\text{CH}_3\}=\text{C-NH}\}_3[\text{K}_3(\text{H}_2\text{O})_7]$  (**4**), in which the 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> groups in L were replaced by Ph groups, was carried out at the DFT (B3LYP) level with a 6-31G\*<sup>7,8</sup> basis set using the Gaussian 09 program.<sup>9</sup> Figures S7 show the optimized geometries, which reproduce the experimental data of **2–4** reasonably well. The atomic populations, bonding orbitals and Wiberg bond orders were obtained with NBO method.<sup>10-12</sup>

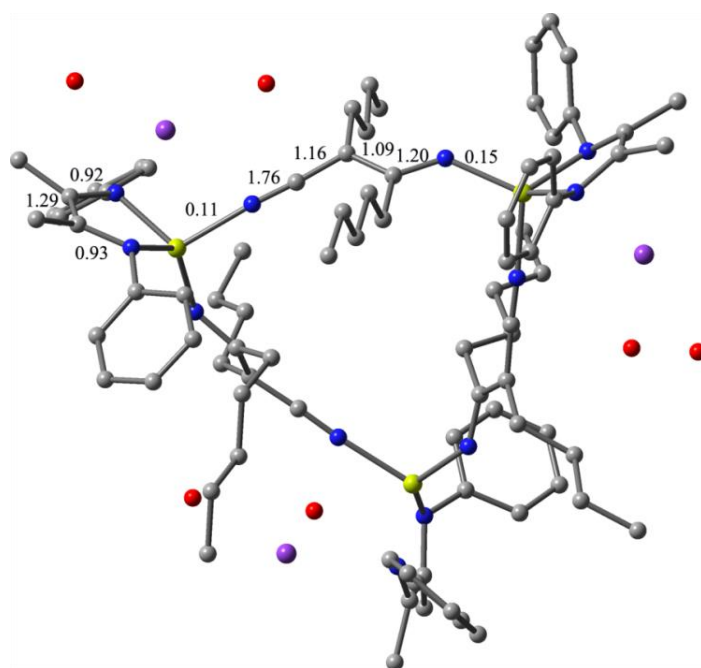




**2H**

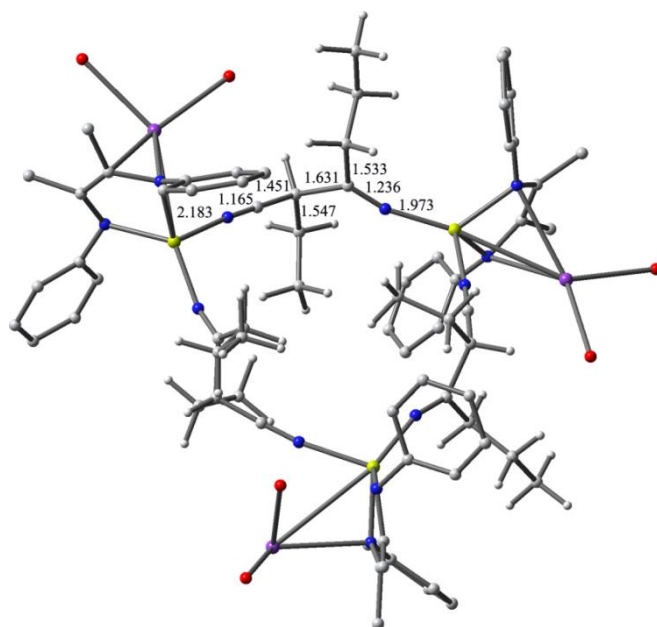


**3H**

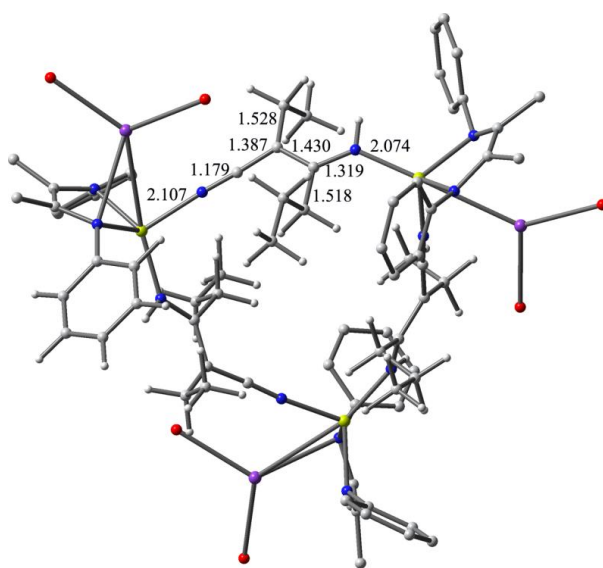


**4H**

**Fig. S8.** Optimized structures of **2H–4H** labelled with selected bond orders.



Intermediate  $[\text{LMg}(\mu\text{-}\{\text{N}\equiv\text{CCH}(\text{CH}_2\text{CH}_3)\text{C}((\text{CH}_2)_2\text{CH}_3)=\text{N}\})]_3[\text{K}_3(\text{H}_2\text{O})_6]$  (**6311.9913 au**)

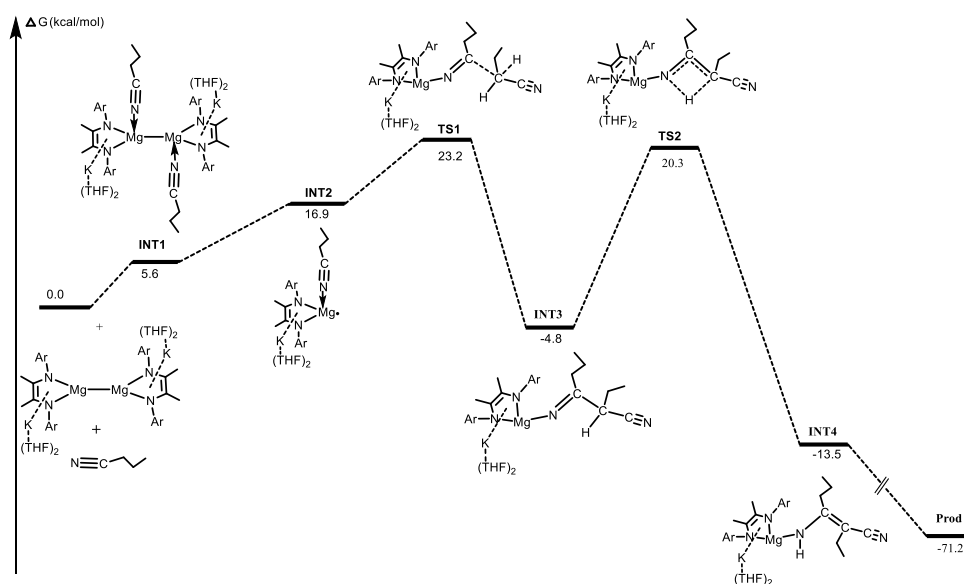


**2H** (6312.1144 au)

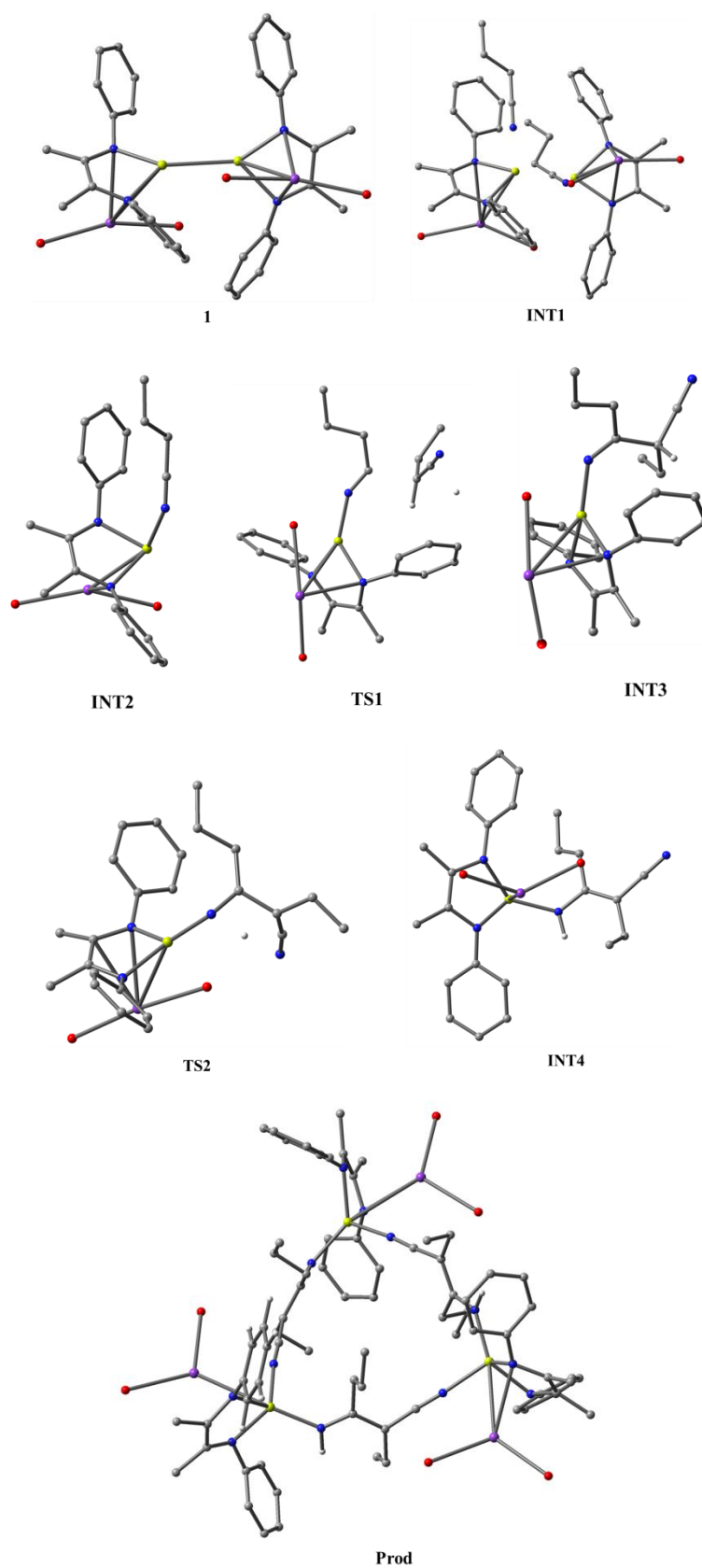
**Fig. S9.** Optimized structures of **Intermediate**  $[\text{LMg}(\mu\text{-}\{\text{N}=\text{CCH}(\text{CH}_2\text{CH}_3)\text{-C}((\text{CH}_2)_2\text{CH}_3)=\text{N}\})_3[\text{K}_3(\text{H}_2\text{O})_6]$  and **2H** labelled with selected bond lengths and calculated energies.

**Table S2.** Natural charges of the model compounds **2H**, **3H** and **4H**.

	<b>2H</b>	<b>3H</b>	<b>4H</b>
Mg	1.69	1.69	1.69
L	-1.77	-1.77	-1.77
amido-ene-nitrile moiety	-0.84	-0.84	-0.84



**Fig. S10.** Computed reaction Gibbs free energy profile (in kcal/mol) for the formation of **2**.



**Fig. S11.** Optimized structures of intermediate and transition states.

#### S4. Reference

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