

Electronic Supplementary Information

**Activation of cyclopentadiene derivatives by the α -diimine-ligated
Mg–Mg-bonded compound**

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S1. Experimental details

General procedures. All reactions and manipulations of air- and moisture-sensitive compounds were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk or dry box techniques. The solvents (*n*-hexane, THF, toluene, DME and Et₂O) were dried by appropriate methods and were distilled under argon prior to use. THF-*d*₈ is dried over Na/K alloy. The α -diimine ligand **L** was synthesized according to literature procedures.¹ Compound **1** was prepared *in situ* following the previously reported method.² Potassium metal, anhydrous magnesium chloride (MgCl₂), 6,6-dimethylfulvene, 6-(dimethylamino)fulvene, and 1,2,3,4-tetramethyl-1,3-cyclopentadiene were purchased from Alfa Aesar. ¹H NMR and ¹³C NMR spectra were obtained at 298 K by using a Bruker AVANCE III-400 MHz spectrometer. ¹H-¹³C HMBC spectra were performed at 298 K using a Bruker Ascend 700 MHz spectrometer. EPR spectrum of **2** was obtained on a Bruker EMX spectrometer. UV-vis spectra were measured on a TU-1901 spectrophotometer. Elemental analyses were performed with a Euro Vector EA3000 instrument.

Synthesis of [L⁻Mg{ η^5 -C₅H₄(*i*Pr)}(THF)] (2**):** 6,6-Dimethylfulvene (482 μ L, 4 mmol) was added to a toluene solution (30 mL) of compound **1** (1 mmol), which was *in situ* generated by the reaction of **L** (0.808 g, 2.0 mmol), MgCl₂ (0.240 g, 2.6 mmol), and potassium metal (0.12 g, 6 mmol).² After stirring at room temperature for 2 days, the solution was concentrated to about 5 mL under reduced pressure, and a few drops of THF and *n*-hexane were added. Dark-red block crystals of **2** were obtained in several days at room temperature. Yield: 0.90 g, 74%. Elemental analysis calcd. for C₄₀H₅₀MgN₂O (608.21): C 78.99, H 9.78, N, 4.61. Found: C 78.50, H 9.96, N 4.34%.

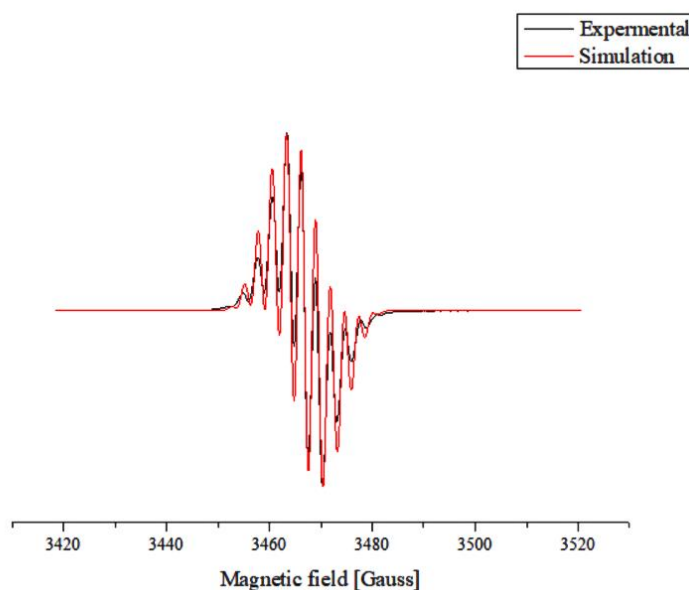


Fig. S1. EPR spectrum of compound **2** in THF at 298 K. Frequency: 9.848948 GHz; the red line is simulated ($A(2\times^{14}\text{N}) = 6$ G; $A(6\times^1\text{H}) = 4.7$ G; $g = 2.0031$).

[LMg(μ -*N,N'*-{C₅H₄CH(NMe₂)CH(NMe₂)C₅H₄})K₂(THF)_{1.5}]_n (**3**): 2.0 equiv. of 6-(dimethylamino)fulvene (0.488 g, 4.0 mmol) was added to *in situ* prepared compound **1** (2.0 mmol) in toluene solution (30 mL) and the color became brown. After 2 days, the reaction mixture was filtered and the solution was concentrated, followed by recrystallization from mixed THF/toluene/ *n*-hexane, to afford dark-orange crystals of complex **3** (isolated crystal yield: 0.84 g, 49%). ¹H NMR (400 MHz, THF-*d*₈, 298 K): δ /ppm: 0.86 (*n*-hexane), 1.11–1.16 (m, 24H, (CH₃)₂CH), 1.33 (*n*-hexane), 1.89 (THF), 2.27 (s, 6H, CH₃C), 3.11 (s, 12H, CH₃N), 3.38 (THF), 4.06 (m, 4H, CH(CH₃)₂), 4.41 (s, 2H, Me₂NCHCp), 6.04–6.40 (m, 8H, Cp-*H*), 7.04–7.15 (m, 6H, Ar-*H*), 6.81–6.95, 7.25 (toluene). Due to the poor solubility of **3** in THF-*d*₈, it is difficult to obtain well-analyzed ¹³C NMR data. ¹³C NMR (100.6 MHz, THF-*d*₈, 298 K): δ /ppm: 15.3 (Et₂O), 20.6 (toluene), 14.0, 23.1, 32.1 (*n*-hexane), 21.1 (CH-NMe₂), 27.3 (CH(CH₃)₂), 28.3 (CH(CH₃)₂), 44.2 (NMe₂), 24.9 (THF), 67.4 (DME), 58.4 (THF), 65.9 (Et₂O), 113.7, 119.1, 124.4 (Cp-C), 124.9 (NC=CN), 128.4, 125.6, 129.2, 137.9 (toluene), 123.6, 124.6, 126.4, 140.0, 144.0, 144.7 (Ar-C). Elemental analysis calcd. for C₅₀H₇₄N₄MgK₂O_{1.5} (857.64): C 70.02, H 8.70, N 6.53. Found: C 69.65, H 8.65, N 6.34%.

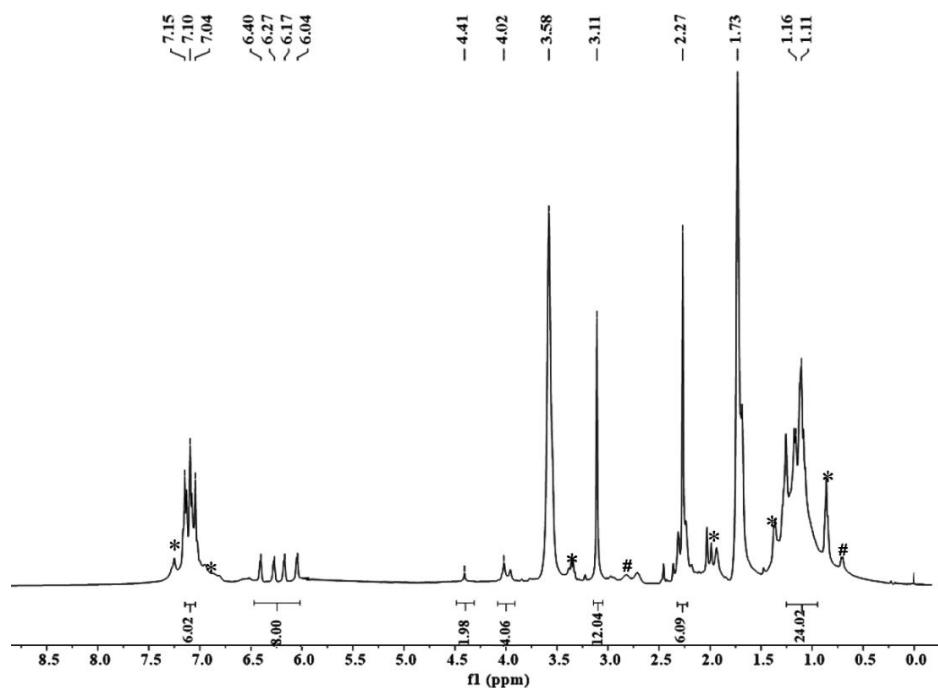


Fig. S2. ¹H NMR spectrum of **3** (THF-*d*₈, 298 K, signals marked with * are from solvents toluene, *n*-hexane, and THF, while those with # are due to unidentified impurities).

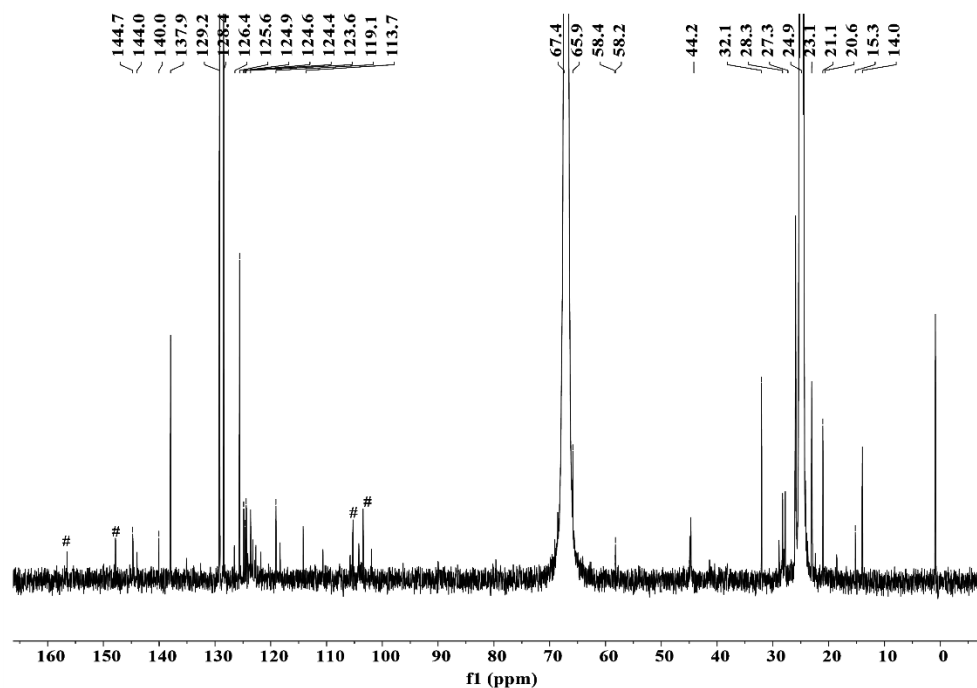


Fig. S3. ^{13}C NMR spectrum of **3** (THF- d_8 , 298 K, # denotes unidentified impurities).

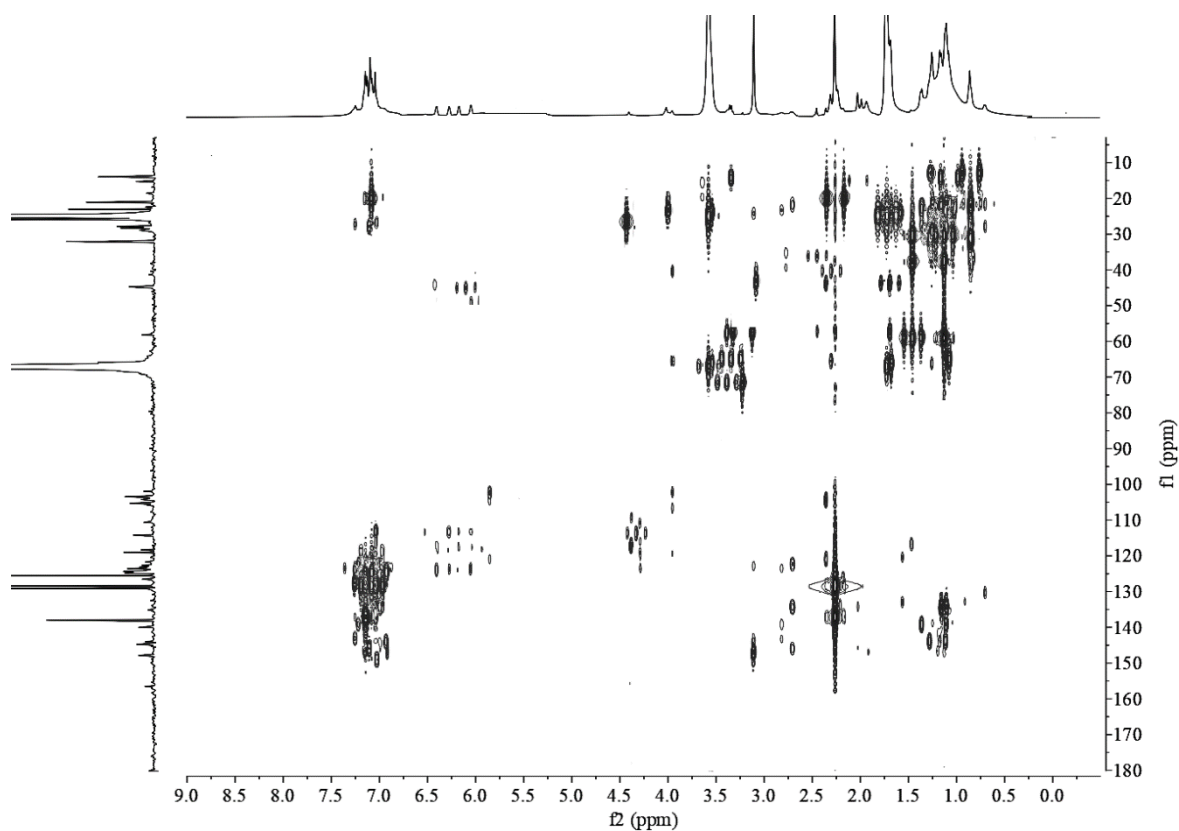


Fig. S4. ^1H - ^{13}C HMBC spectrum of **3** (THF- d_8 , 298 K).

All peaks of H atoms for **3** can be easily identified in the ^1H NMR spectrum (Fig. S2) based on their chemical shifts, and peaks of C atoms can be assigned in the ^{13}C NMR spectrum (Fig. S3) with assistance of the ^1H - ^{13}C HMBC spectrum (Fig. S4). The data of ^1H - ^{13}C HMBC spectrum of **3** are listed

in Table S1. From the spectrum, the peaks of C atoms at 147.8 ppm, 156.8 ppm and other peaks above 144 ppm have correlation with H's of toluene, THF, $(CH_3)_2CH$ of ligand L, and unidentified impurities in 1H NMR spectrum. Since the ^{13}C NMR signals of the solvents have been clearly assigned, the remaining signals above 144 ppm should arise from unknown impurities, together with the peaks at 105.3 ppm and 103.5 ppm (marked with # in Fig. S3).

Table S1. Assignment of 1H - ^{13}C HMBC spectrum of **3**.

Position	C (δ /ppm)	H (δ /ppm)	1H - ^{13}C HMBC
$(CH_3)_2CH$	27.3	1.11–1.16 (m, 24H)	-Ar-H, $(CH_3)_2CH$, $CH(CH_3)_2$
$(CH_3)_2N$	44.2	3.11 (s, 12H)	$(CH_3)_2N$, Cp-H
$CH(CH_3)_2$	28.3	4.06 (m, 4H)	$CH(CH_3)_2$, -Ar-H, $(CH_3)_2CH$
Me_2NCHCp	21.1	4.41 (s, 2H)	Cp-H, Me_2NCHCp
Cp ring	113.7, 119.1, 124.4	6.04–6.40 (m, 8H)	Cp-H, Me_2NCHCp
-Ar	123.6, 124.6, 126.4, 140.0, 144.0, 144.7	7.04–7.15 (m, 6H)	-Ar-H, $(CH_3)_2CH$
$NC=CN$	124.9	–	-Ar-H, CH_3C

[LMg $\{\eta^5$ -C₅Me₄H}K(THF)]_n (4): 1,2,3,4-Tetramethyl-1,3-cyclopentadiene (305 μ L, 2.0 mmol) was added to a toluene solution of compound **1** (1.0 mmol). The mixture was stirred for 2 days, and the color of the solution became lighter and brighter. The reaction mixture was filtered, the filtrate concentrated to about 5 mL, and 1 mL of *n*-hexane was added. The solution was stored at room temperature to give yellow block crystals of compound **4** in one week in 57% yield (0.75 g). 1H NMR (400 MHz, THF-*d*₈, 298 K): δ /ppm: 0.87 (*n*-hexane), 1.10 (t, 12H, $(CH_3)_2CH$), 1.18 (t, 12H, $(CH_3)_2CH$), 1.28 (*n*-hexane), 1.86 (s, 6H, $(CH_3)_4C_5H$), 1.92 (s, 6H, $(CH_3)_4C_5H$), 2.27 (s, 6H, CH_3C), 3.25 (DME), 3.38 (Et₂O), 3.43 (DME), 3.69 (THF), 4.15 (q, 4H, $CH(CH_3)_2$), 5.27 (s, 1H, Me_4C_5H), 6.45 (t, 2H, *p*-C₆H₃), 6.64 (d, *J* = 6.9 Hz, 4H, *m*-C₆H₃), 6.89–7.16 (toluene); ^{13}C NMR (100.6 MHz, THF-*d*₈, 298 K): δ /ppm: 10.4 ($(CH_3)_4C_5H$), 12.6 ($(CH_3)_4C_5H$), 17.6 (Et₂O), 20.5 (toluene), 23.2, 27.7, 31.6 (*n*-hexane), 21.9 (C-CH₃), , 24.3 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 25.4 ($CH(CH_3)_2$), 26.2 (THF), 60.3 (DME), 66.2 (THF), 66.4 (Et₂O), 117.1 (Me_4C_5H), 107.6 (Me_4C_5H), 102.1 (Me_4C_5H), 125.1 (NC=CN), 128.7, 127.9, 145.7 (toluene), 123.0, 135.8, 137.5, 141.3, 142.1, 144.5 (Ar-C). Elemental analysis calcd. for C₄₁H₆₁KMgN₂O (661.32): C 74.46, H 9.30, N 4.24. Found: C 74.68, H 9.46, N 4.12%.

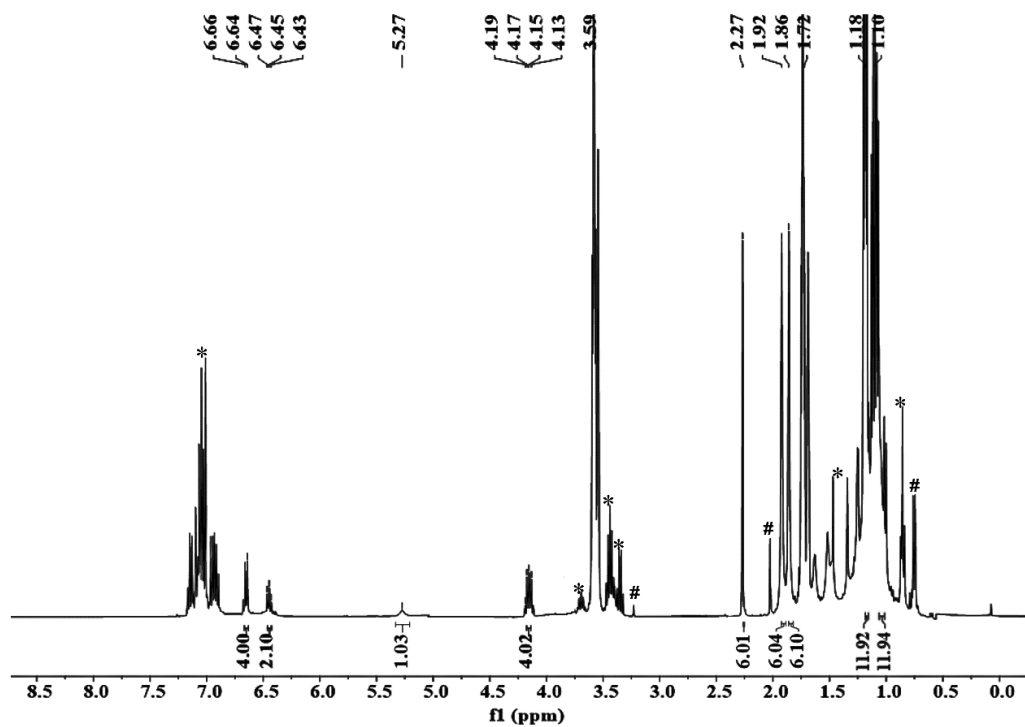


Fig. S5. ^1H NMR spectrum of **4** ($\text{THF-}d_8$, 298 K, signals marked with * are from toluene, *n*-hexane, THF, DME and Et_2O , and those with # are due to unidentified impurities).

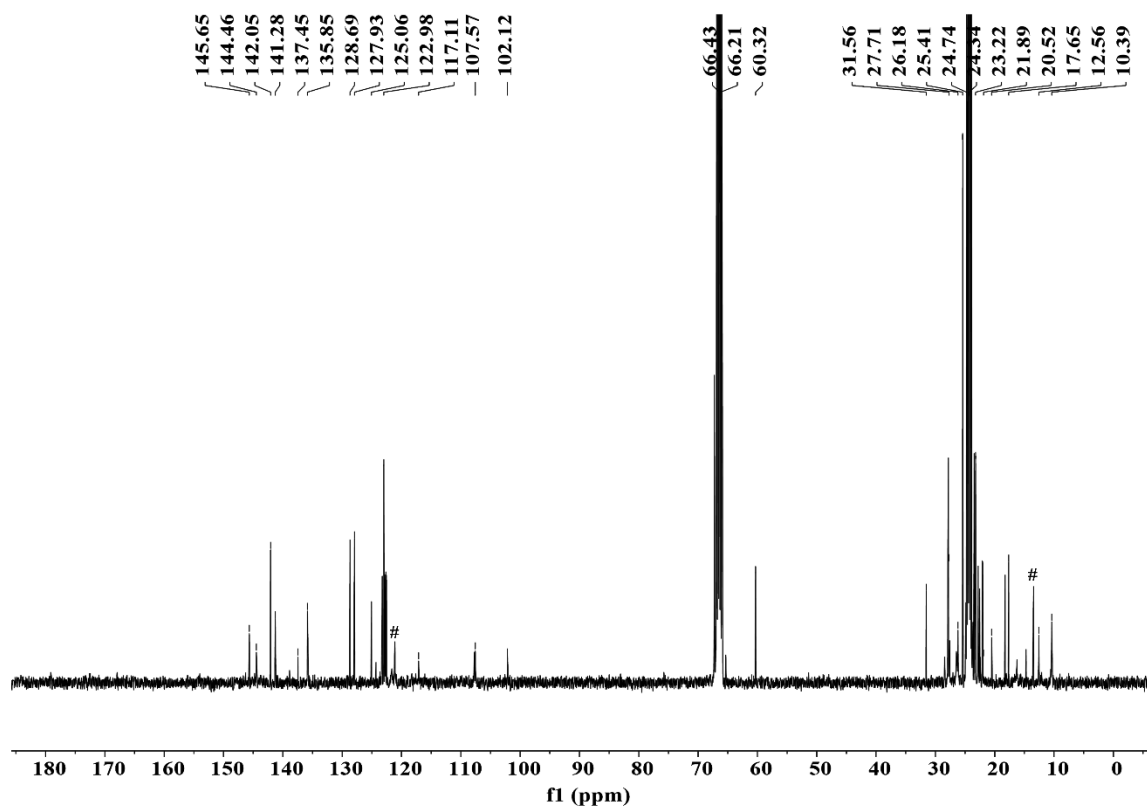


Fig. S6. ^{13}C NMR spectrum of **4** ($\text{THF-}d_8$, 298 K, signals with # are due to unidentified impurities).

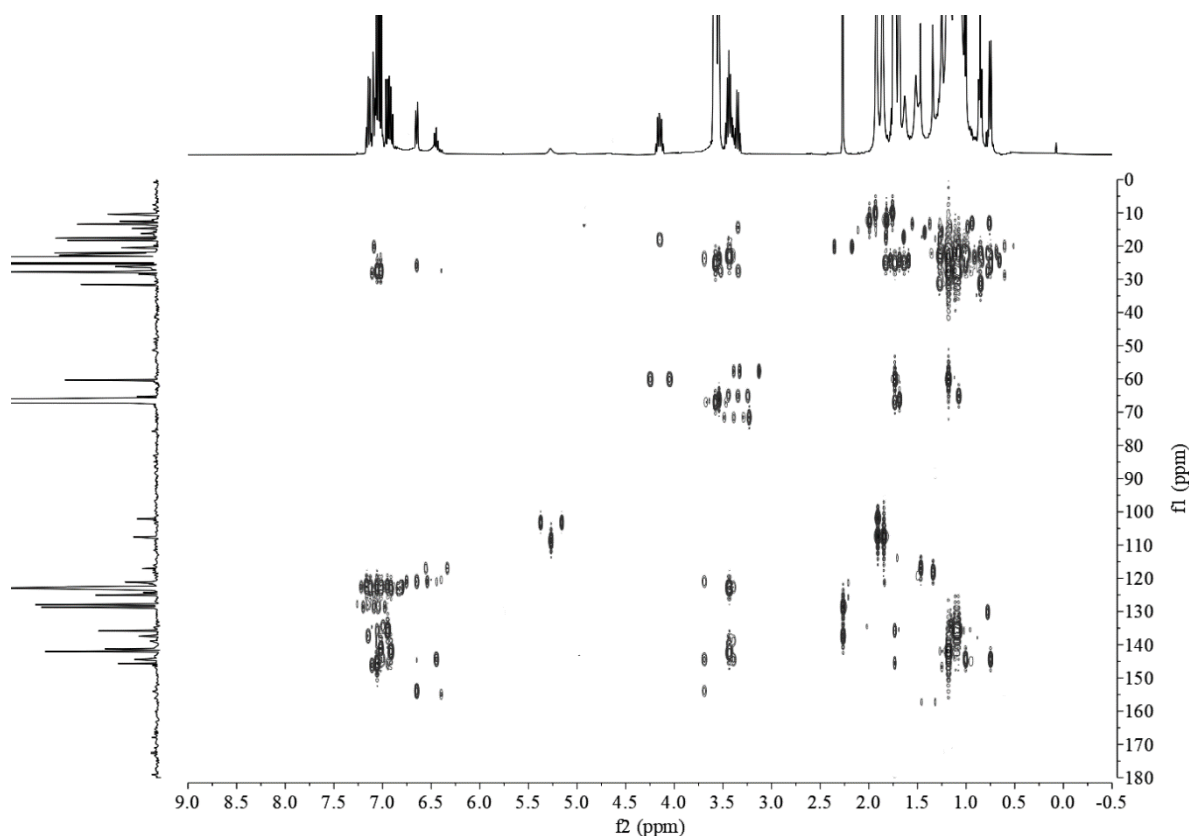


Fig. S7. ^1H - ^{13}C HMBC spectrum of **4** (THF- d_8 , 298 K).

All peaks of protons and carbon atoms in compound **4** can be identified in its ^1H and ^{13}C NMR spectra (Figs. S5 and S6) based on their chemical shifts. The data of ^1H - ^{13}C HMBC spectrum (Fig. S7) of **4** are listed in Table S2. From the ^1H - ^{13}C HMBC spectrum, the peak of C at 13.5 ppm shows correlation peaks with unidentified impurities in ^1H NMR spectrum. The peak of C at 121.1 ppm has correlation with H of solvent toluene in ^1H NMR spectrum.

Table S2. Assignment of the ^1H - ^{13}C HMBC spectrum for **4**.

Position	C (δ /ppm)	H (δ /ppm)	^1H - ^{13}C HMBC
$(\underline{\text{C}}\text{H}_3)_2\text{CH}$	24.3, 24.7	1.10 (t, 12H); 1.18 (t, 12H)	-Ar-H, $(\text{CH}_3)_2\text{CH}$, $\text{CH}(\text{CH}_3)_2$
$\underline{\text{C}}\text{H}_3\text{C}$	21.9	2.27 (s, 6H)	CH_3C
$(\underline{\text{C}}\text{H}_3)_4\text{C}_5\text{H}$	10.4, 12.6	1.86 (s, 6H); 1.92 (s, 6H)	$(\text{CH}_3)_4\text{C}_5\text{H}$;
$\underline{\text{C}}\text{H}(\text{CH}_3)_2$	25.4	4.15 (q, 4H)	$\text{CH}(\text{CH}_3)_2$, -Ar-H, $(\text{CH}_3)_2\text{CH}$
$\text{Me}_4\underline{\text{C}}_5\text{H}$	117.1 ($\text{Me}_4\text{C}_5\text{H}$)	5.27 (s, 1H)	$\text{Me}_4\text{C}_5\text{H}$, Cp-Me
Cp-C	102.1, 107.6	—	$\text{Me}_4\text{C}_5\text{H}$
-Ar	123.0, 135.8, 137.5, 141.3, 142.1, 144.5	6.45 (t, 2H, $p\text{-C}_6\text{H}_3$), 6.64 (d, $J = 6.9$ Hz, 4H, $m\text{-C}_6\text{H}_3$)	-Ar-H, $(\text{CH}_3)_2\text{CH}$
$\text{N}\underline{\text{C}}=\text{CN}$	125.1	—	-Ar-H, CH_3C

S2. X-ray crystallographic analysis

Diffraction data for complex **2** were collected on a Bruker APEX-II CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). For compounds **3** and **4**, the X-ray diffraction data were collected with an XtaLAB Synergy R, DW system, HyPix diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). An empirical absorption correction using SADABS was applied for all data.³ 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 programs⁴ and OLEX₂ 1.2.⁵

In compound **2**, ISOR instruction was used for C38 of the THF molecule.

In compound **3**, some atoms in α -diimine ligand L and THF molecules were disordered into two positions. Moreover, SIMU instructions of some atoms, DFIX instructions of some distances were used.

In compound **4**, one THF solvent molecule was disordered into two positions. SIMU instructions of some atoms, DFIX and DANG instructions of some distances were also used.

Crystallographic data and refinement details for compounds **2–4** are given in Table S3. CCDC Deposition Numbers: 2328619 (for **2**), 2328621 (for **3**), 2328620 (for **4**).

Table S3. Crystallographic data and refinement details for compounds **2**, **3**, and **4**.

Compound	2	3	4
Empirical formula	C ₄₀ H ₅₉ MgN ₂ O	C ₁₀₀ H ₁₄₈ K ₄ Mg ₂ N ₈ O ₃	C ₄₁ H ₆₁ KMgN ₂ O
M _r [g mol ⁻¹]	608.20	1715.28	661.32
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	<i>C2/c</i>	<i>I2/a</i>	<i>Pca2₁</i>
<i>a</i> [Å]	42.8860(13)	18.8718(8)	22.2816(8)
<i>b</i> [Å]	10.3660(3)	24.4841(10)	8.9404(3)
<i>c</i> [Å]	17.4312(6)	24.4841(10)	19.5450(6)
α [°]	90	90	90
β [°]	108.6760(10)	101.445(4)	90
γ [°]	90	90	90
Volume [Å ³]	7341.1(4)	11144.7(7)	3893.5(2)
Z	8	4	4
ρ_{calc} , [g cm ⁻³]	1.101	1.022	1.128
μ [mm ⁻¹]	0.080	0.216	0.185
<i>F</i> (000)	2664.0	3712.0	1440.0
$\theta_{\text{min}}/\theta_{\text{max}}$ [°]	4.576 to 56.742	4.688 to 51.998	4.556 to 52.028
Index ranges	-57 ≤ <i>h</i> ≤ 57, -13 ≤ <i>k</i> ≤ 13, -23 ≤ <i>l</i> ≤ 21	-23 ≤ <i>h</i> ≤ 23, -30 ≤ <i>k</i> ≤ 30, -28 ≤ <i>l</i> ≤ 30	-27 ≤ <i>h</i> ≤ 25, -10 ≤ <i>k</i> ≤ 11, -24 ≤ <i>l</i> ≤ 22
Reflections collected	62443	36055	22362

Independent reflections	9173	10959	7055
R_{int}	0.0821	0.0254	0.0298
Data/restraints/parameters	9173/6/409	10959/209/738	7055/151/474
GOF on F^2	1.033	1.093	1.048
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0633,$ $wR_2 = 0.1579$	$R_1 = 0.0656,$ $wR_2 = 0.1894$	$R_1 = 0.0352, wR_2$ $= 0.0884$
Final R indexes [all data]	$R_1 = 0.1203,$ $wR_2 = 0.1869$	$R_1 = 0.0821,$ $wR_2 = 0.1989$	$R_1 = 0.0429, wR_2$ $= 0.0925$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.49/-0.45	0.77/-0.38	0.21/-0.15

S3. References

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