Electronic Supplementary Material (ESI) for Chemical Communications.

Mixing and Matching *N*,*N*- and *N*,*O*-Chelates in Anionic Mg(I) Compounds: Synthesis and Reactivity with RN=C=NR and CO

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General Synthetic Procedures

All manipulations were performed using standard Schleck line techniques under dry argon atmosphere or in standard nitrogen-filled glovebox. Deuterated solvents were obtained from Sigma-Aldrich. Deuterated benzene was degassed on the Schleck line using freeze-pump-thaw method. Toluene, diethyl ether (Et_2O) and tetrahydrofuran (THF) were obtained from a PureSolv MD 5 system and dried over 5 Å molecular sieves for 24 hours prior to use. Anhydrous benzene was obtained from Sigma-Aldrich and used without further purification. NMR spectra were recorded with a Jeol JNM-ECZ500S 500 MHz spectrometer at ambient temperature (294K) unless stated otherwise. Chemical shifts are reported in δ (ppm) and coupling constants are reported in Hz, proton and carbon chemical shifts are referenced internally to residual solvent signals.

Di-*n*-butylmagnesium[S1] and $(NON)H_2$[S2] were synthesised according to literature procedures.

Experimental Details for $[Mg(NON)]_2$ 1.

UK (Oxford) Procedure.

A solution of di-*n*-butylmagnesium in hexanes (2.75 mL of a 0.75 M solution, 2.06 mmol, 1 eq.) was added dropwise to a stirred solution of $(NON)H_2$ (1.00 g, 2.06 mmol, 1 eq.) in hexanes (3 mL) at 25 °C. The reaction mixture was stirred for 30 minutes then left to stand for 16 h, resulting in the formation of a white crystalline solid. The solution was decanted and the solid washed with cold *n*-pentane (3 x 0.5 mL), then dried *in vacuo* for 3 h. $[Mg(NON)]_2$ (0.562 g, 54%) was isolated as a white crystalline solid. Single crystals suitable for an X-ray diffraction study were grown by dissolving a sample in benzene at 80 °C followed by slow cooling to room temperature. NMR data was collected in THF-D_8 to facilitate solubility. However, in this solvent compound **1** exists as the THF adduct, $Mg(NON)(THF)_n$.

^{1}H NMR (600 MHz, THF-D_8, 298 K): δ (ppm) 6.88 (d, J = 7.5, 8H, *m*-C_6H_3), 6.62 (t, J = 7.5, 4H, *p*-C_6H_3), 4.04 (sept, J = 6.9, 8H, C*H*Me_2), 1.18 (d, J = 6.9, 24H, CH*Me*$_2$), 1.09 (d, J = 6.9, 24H, CH*Me*$_2$), 0.12 (s, 24H, Si*Me*$_2$).

^{13}C{^{1}H} NMR (151 MHz, THF-D_8, 298 K): δ (ppm) 150.1, 144.7, 123.6, 119.3 (C_6H_3), 27.4 (*C*HMe_2), 26.5, 26.1 (CH*Me*$_2$), 4.6 (Si*Me*$_2$). ^{29}Si NMR (119 MHz, THF-D_8, 298 K): δ (ppm) – 14.75 (O*Si*Me_2N).

Anal. calcd. for $C_{56}H_{92}Mg_2N_4O_2Si_4$: C, 66.31; H, 9.14; N, 5.52. Found: C, 65.92; H, 9.58; N, 5.09.

New Zealand (Wellington) Procedure.

A solution of $(NON)H_2$ (0.70 g, 1.44 mmol, 1 eq.) in toluene was added to a suspension of $Mg(^nBu)_2$ (0.20 g, 1.44 mmol, 1 eq.) in toluene. The reaction mixture was stirred for 2 days at 60 °C to give a white suspension. The suspension was allowed to settle, and the white solid was isolated. The solid was washed 3 times with cold toluene and dried *in vacuo* to give a white powder. Yield = 0.451 g, 60%. NMR data was collected in a mixture of C_6D_6:THF-D_8 (~5:1) at 323 K to facilitate solubility. However, in this solvent mixture the compound exists as a (partially) solvated THF adduct, $Mg(NON)(THF)_n$.

^{1}H NMR (500 MHz, C_7D_8, 373 K): δ (ppm) 6.96 (d, J = 7.6, 4H, C_6H_3), 6.88 (t, J = 7.6, 2H, C_6H_3), 3.57 (sept, J = 6.9, 4H, C*H*Me$_2$), 1.07 (br. s, 24H, CH*Me$_2$*), 0.39 (s, 12H, Si*Me$_2$*).

^{13}C{^{1}H} NMR (126 MHz, C_7D_8, 373 K): δ (ppm) 145.4, 143.7, 124.0, 122.0 (C_6H_3), 28.7 (*C*HMe$_2$), 24.8 (CH*Me$_2$*), 3.8 (Si*Me$_2$*).

^{1}H NMR (500 MHz, C_6D_6:THF-D_8 (~5:1), 323 K): δ (ppm) 7.02 (d, J = 7.6, 8H, C_6H_3), 6.88 (t, J = 7.6, 4H, C_6H_3), 3.91 (br. s, 8H, C*H*Me$_2$), 1.27 (d, J = 6.9, 24H, CH*Me$_2$*), 1.03 (br. s, 24H, CH*Me$_2$*), 0.42 (br. s, 24H, Si*Me$_2$*).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6:THF-D_8 (~5:1), 323 K): δ (ppm) 148.6, 144.8, 123.8, 121.1 (C_6H_3), 27.4 (*C*HMe$_2$), 25.8, 25.3 (CH*Me$_2$*), 3.9 (br, Si*Me$_2$*).

IR (solid, cm^{-1}): 2960 (m), 2867 (w), 1458 (m), 1313 (w), 1257 (s), 1040 (m), 848 (m), 818 (m), 745 (s), 542 (w).

Figure S1 ^{1}H NMR spectrum (600 MHz, THF-D_8, 298 K) of THF-solvated **1** (†*n*-hexane, * THF-D_8).

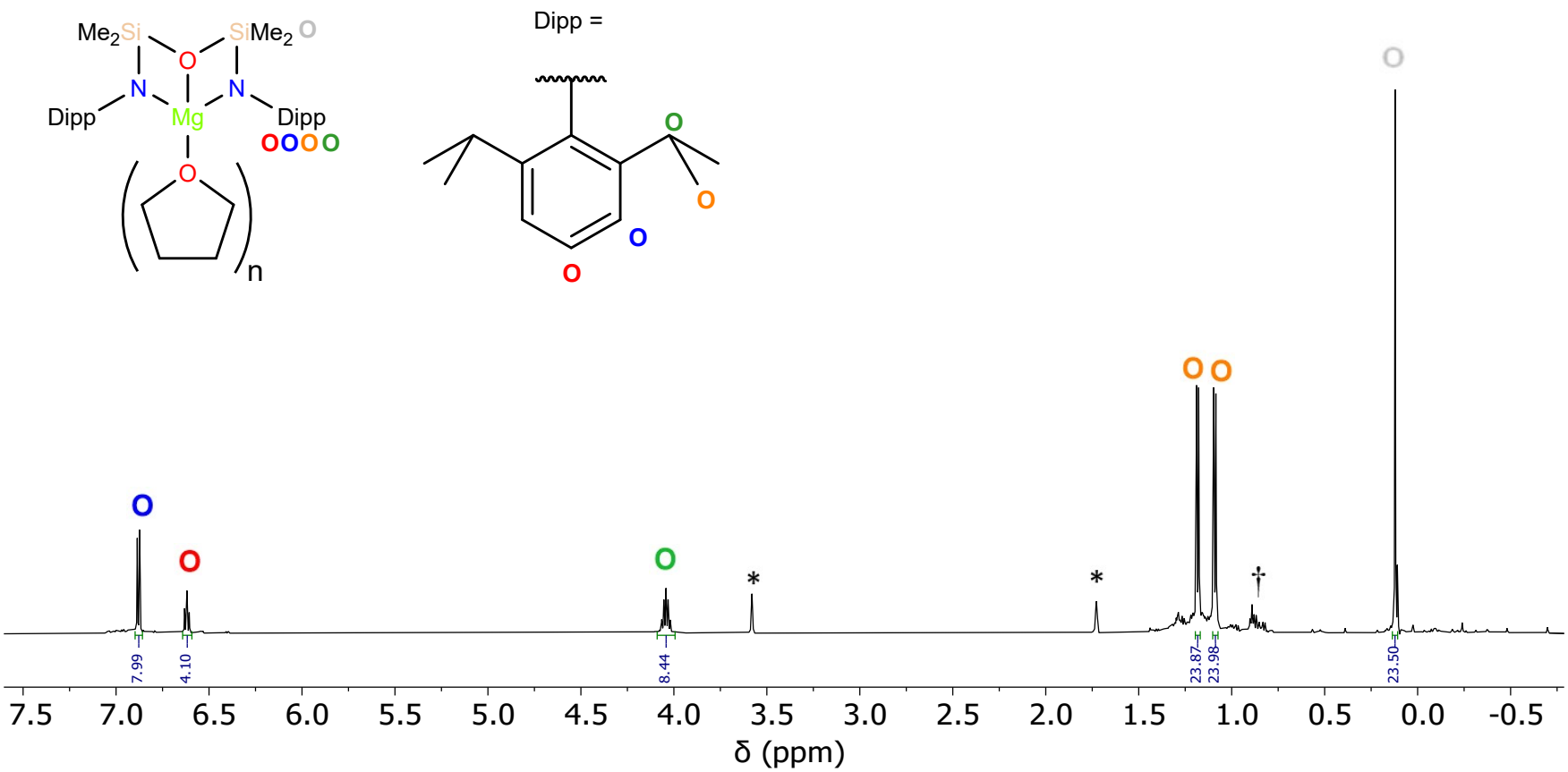
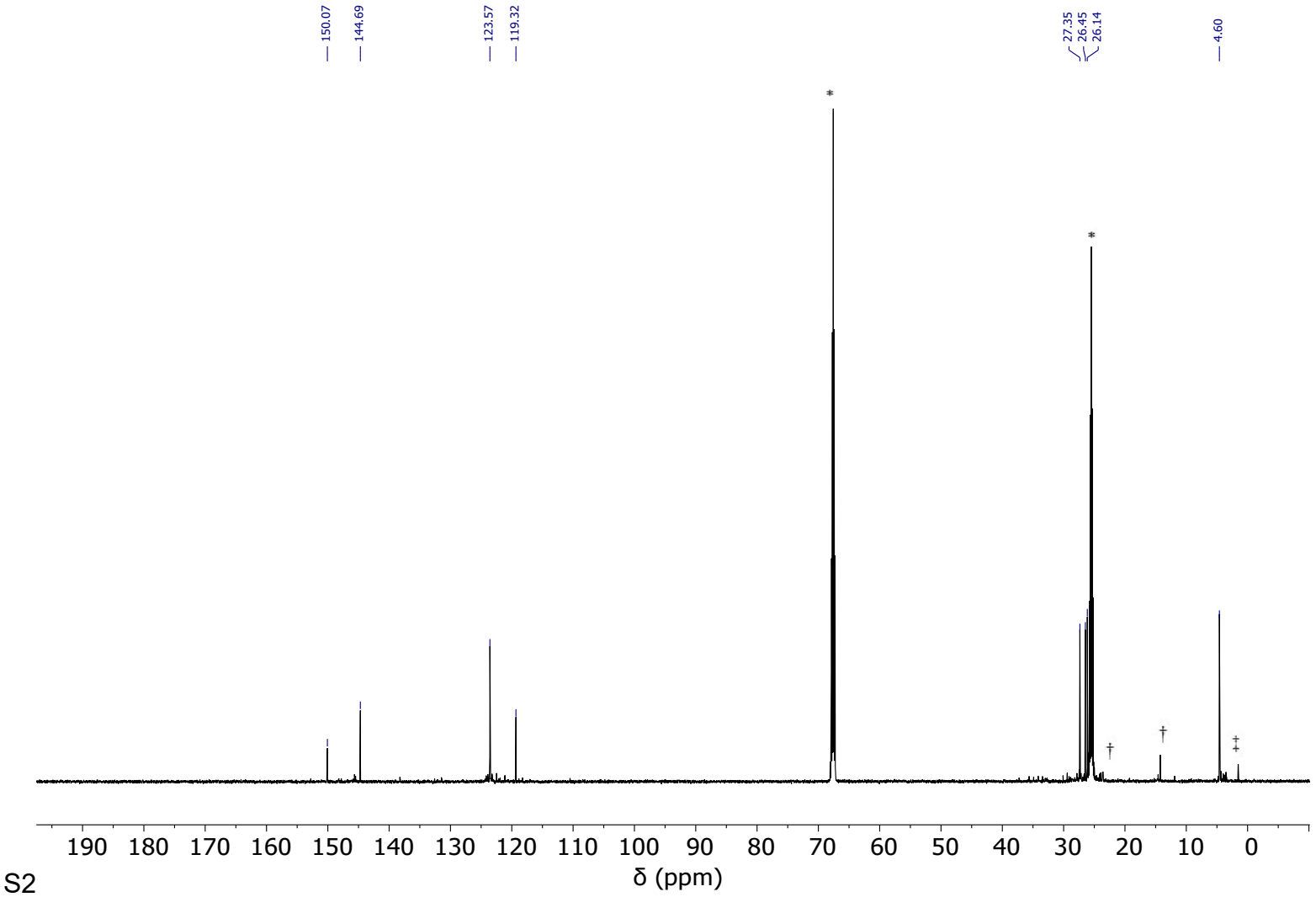


Figure S2 $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, THF-D_8, 298 K) of THF-solvated **1** (‡ silicone grease, † *n*-hexane, * THF-D_8).



S2

Figure S3 ^{1}H NMR spectrum (500 MHz, C_7D_8, 373 K) of **1** (high temperature).

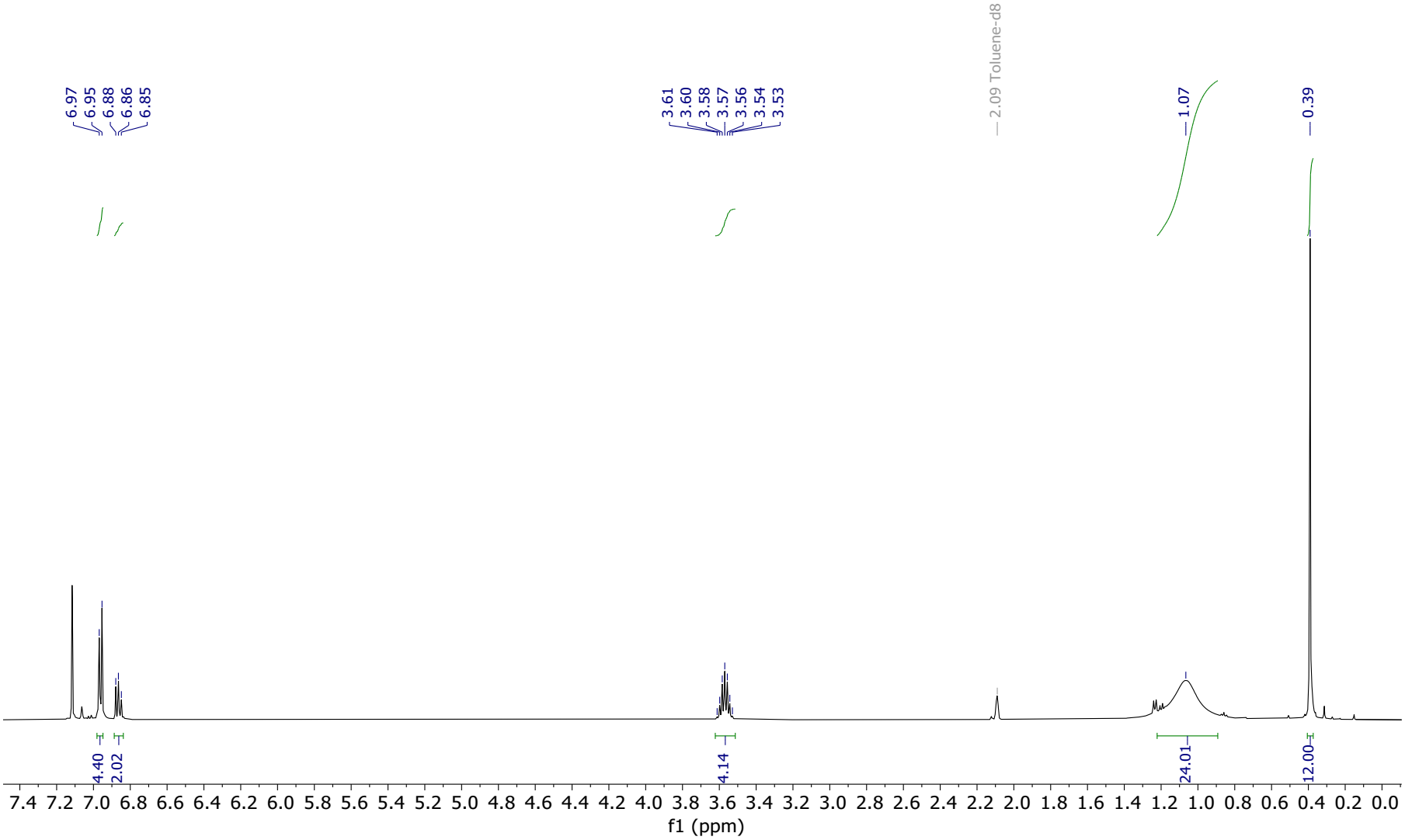


Figure S4 $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_7D_8, 373 K) of **1** (high temperature).

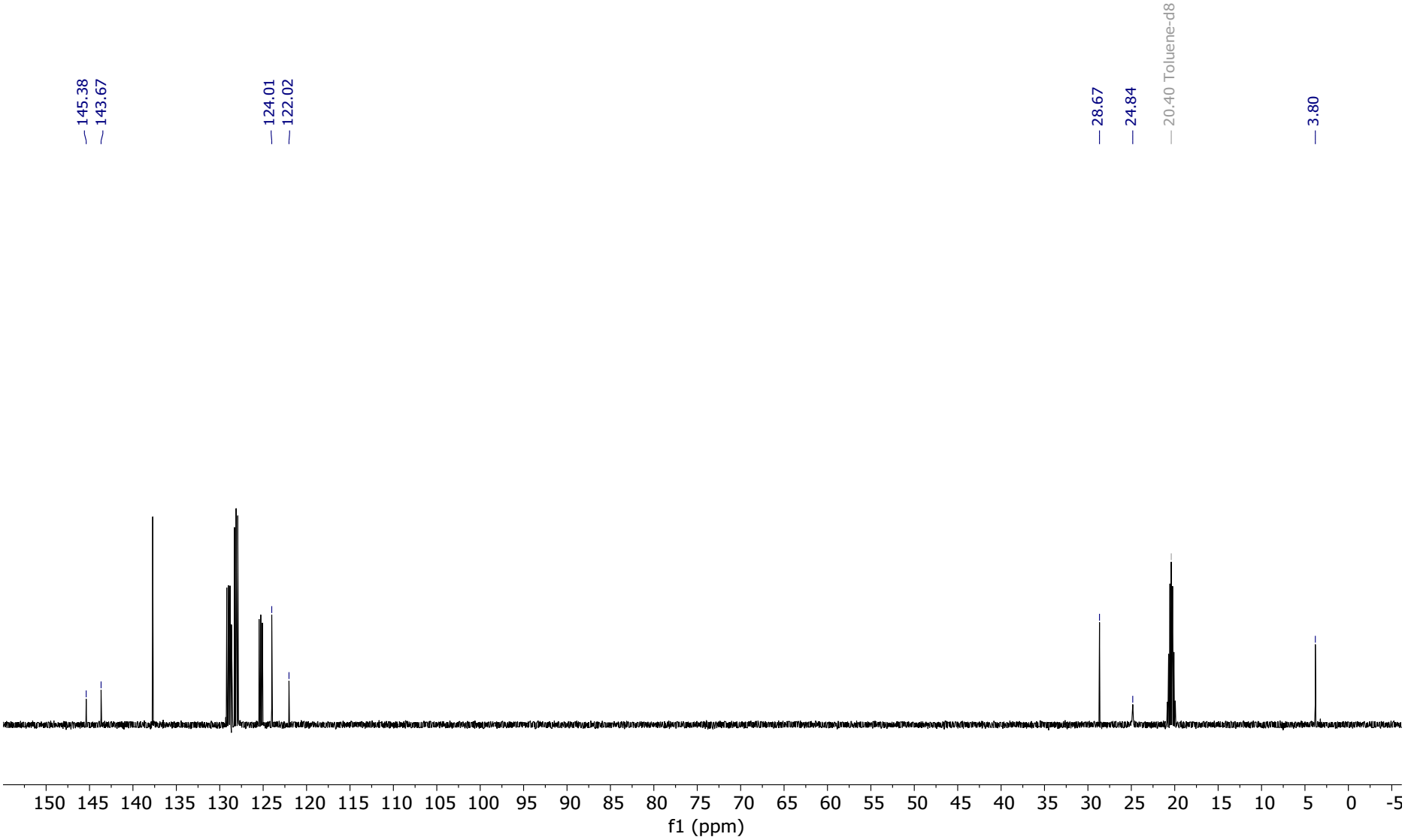


Figure S5 ^{1}H NMR spectrum (500 MHz, C_6D_6:THF-D_8 (~5:1), 323 K) of (partially THF-solvated) **1**.

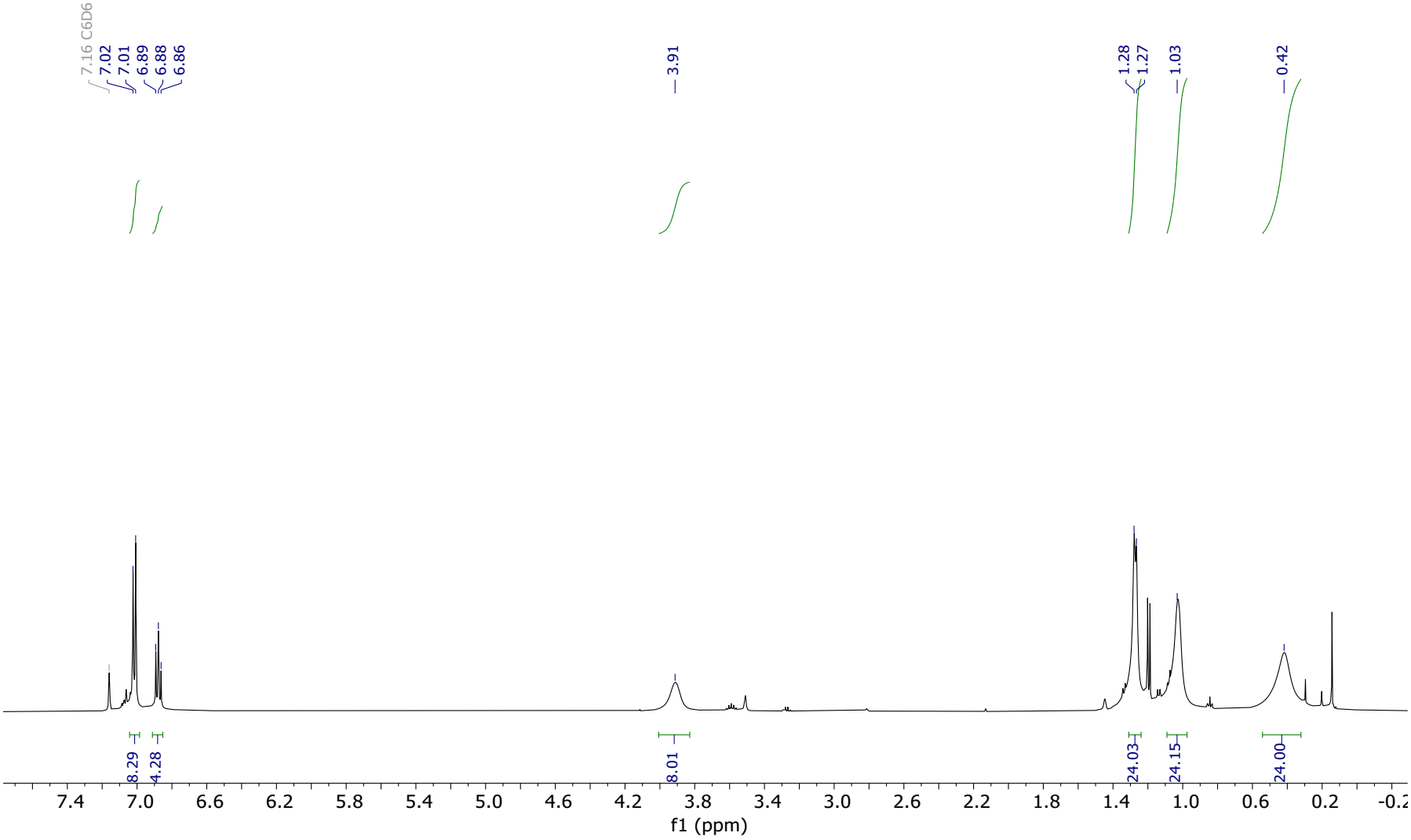


Figure S6 $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6:THF-D_8 (~5:1), 323 K) of (partially THF-solvated) **1**.

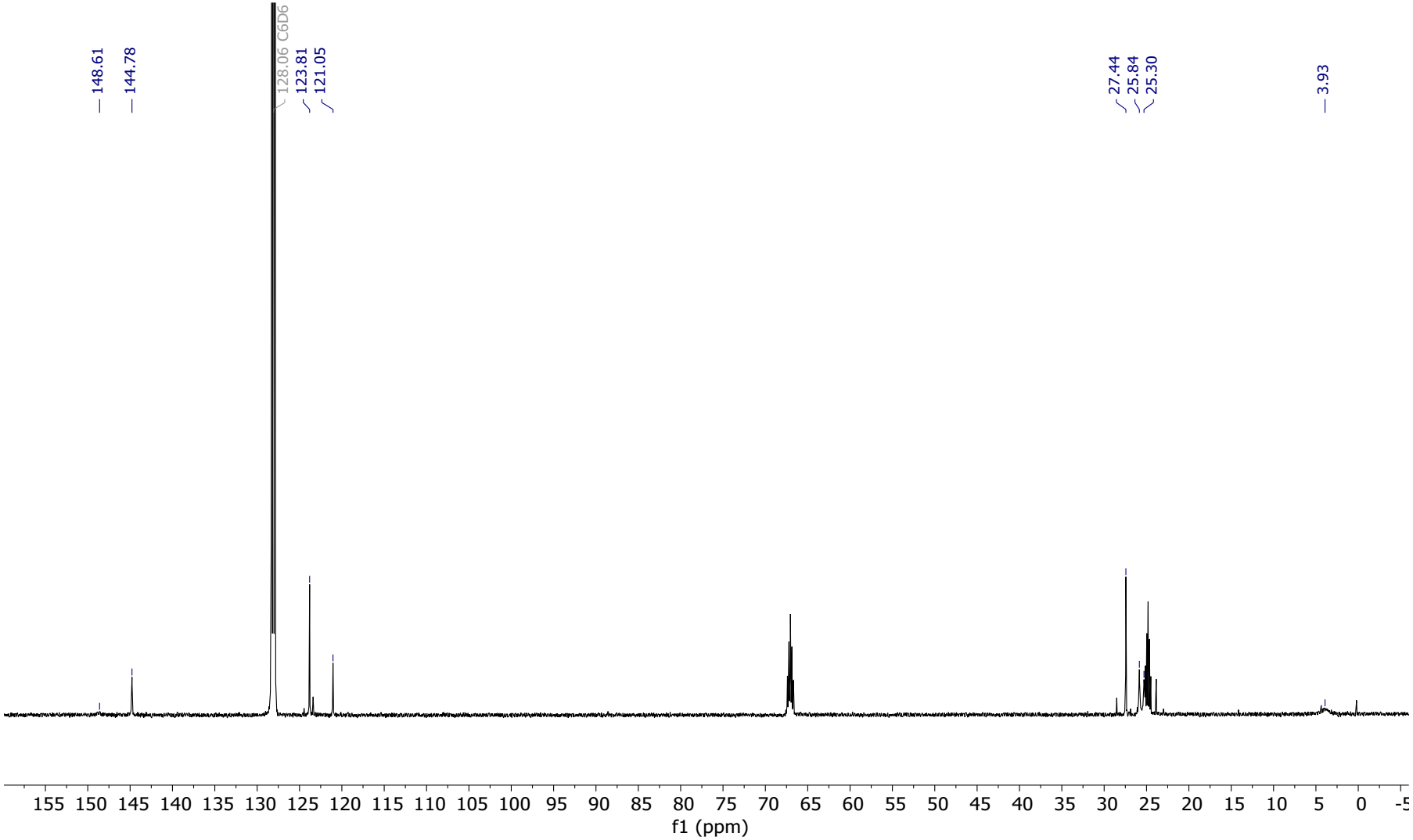


Figure S7 IR spectrum (solid sample) of **1**.

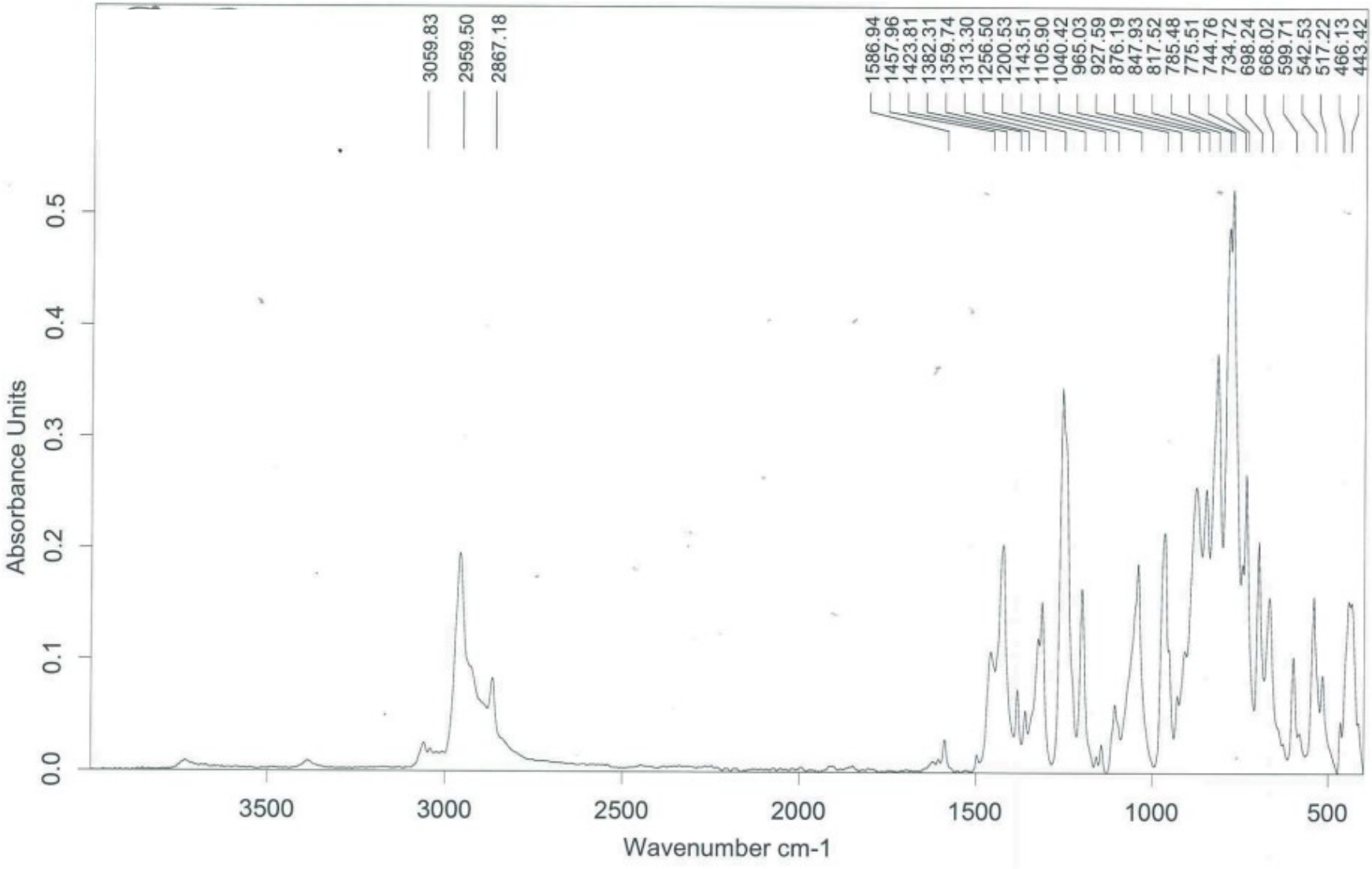
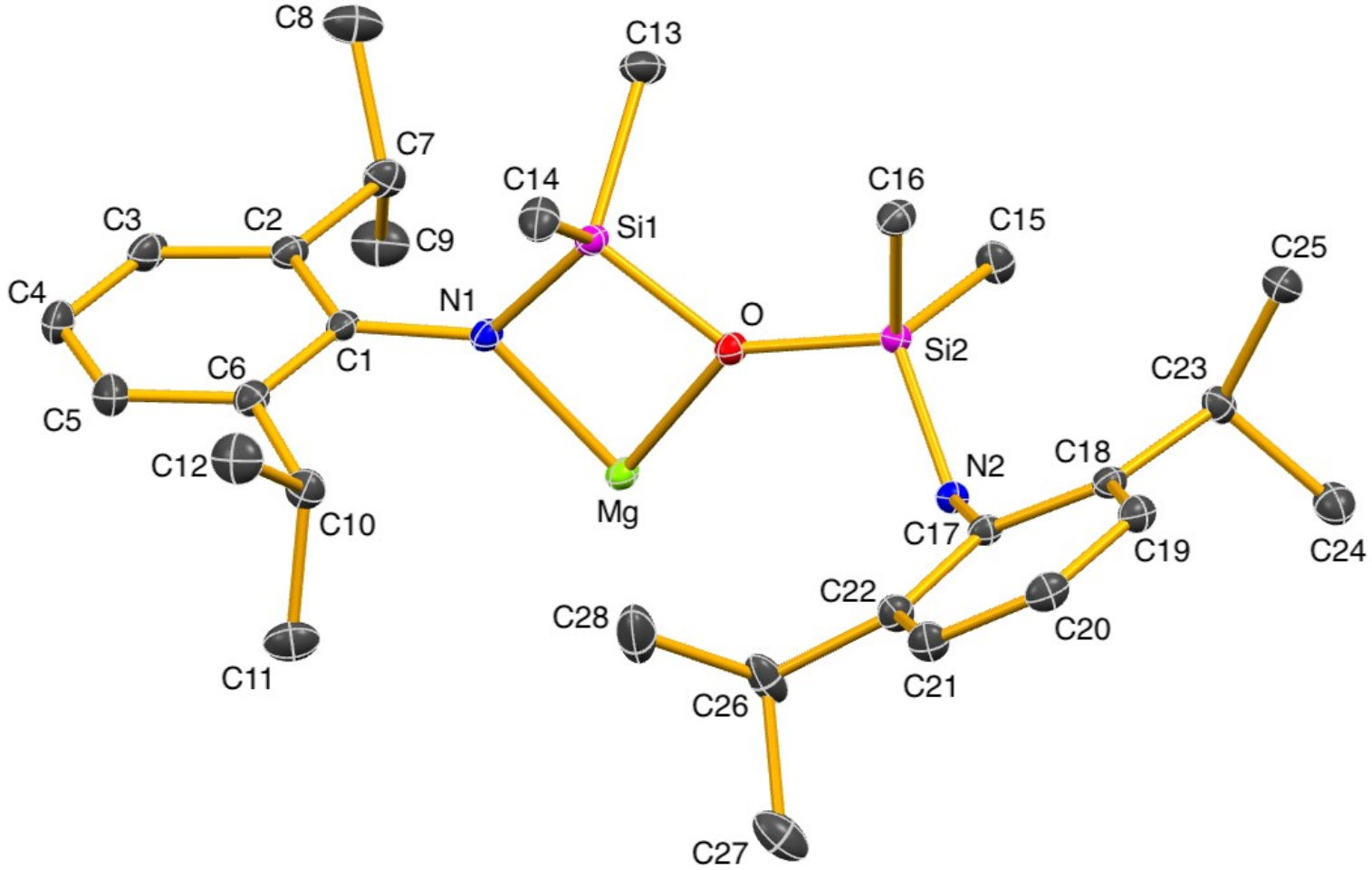


Figure S8 ORTEP (ellipsoids 30%, H-atoms omitted), of the asymmetric unit of $[Mg(NON)]_2$ **1**.



Experimental Details for A (containing $[K(Et_2O)_n][Mg(NON)]$ and $[K(Et_2O)_n][Mg(NNO)]$).

A white suspension of $[Mg(NON)]_2$ (162.9 mg, 0.16 mmol) in diethyl ether was added to a suspension of KC_8 (129.8 mg, 0.96 mmol) in Et_2O while stirring at room temperature. The reaction mixture was stirred for *ca*. 3 hrs. The reaction mixture was allowed to settle and filtered through celite to afford a bright yellow solution. The solvent was removed *in vacuo* to afford a bright yellow powder. Yield = 76.5 mg, 44%.

M.Pt: >260 °C (decomp.).

^{1}H NMR (500 MHz, C_6D_6): δ (ppm) 7.15 (m, 3H, C_6H_3), 6.82 (m, 6H, C_6H_3), 6.45 (t, J = 7.6, 1H, C_6H_3), 6.40 (t, J = 7.6, 2H, C_6H_3), 4.35 (br. sept, 4H, C*H*Me$_2$), 4.04 (sept*, 4H, C*H*Me$_2$), 1.36 (d, J = 6.9, 6H, CH*Me*$_2$), 1.31 (br. s, 12H, CH*Me*$_2$), 1.28 (d, J = 6.9, 6H, CH*Me*$_2$), 1.24 (d, J = 6.9, 6H, CH*Me*$_2$), 1.18 (d, J = 6.9, 6H, CH*Me*$_2$), 0.38 (s, 12H, Si*Me*$_2$), 0.04 (s, 6H, Si*Me*$_2$), –0.04 (s, 6H, Si*Me*$_2$).

* Overlapping septets

^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 155.2, 147.4, 147.3, 147.1, 145.5, 123.9, 123.8, 118.5, 117.8 (*C*$_6$H$_3$), 28.7 (CH*Me*$_2$), 28.1, 27.2, 26.6 (*C*HMe$_2$), 26.5, 25.8, 25.1, 24.1, 24.0 (CH*Me*$_2$), 4.9, 4.6, 3.5 (Si*Me*$_2$).

IR (solid, cm^{-1}): 2951 (m), 2860 (m), 1456 (m), 1433 (m), 1248 (s), 1380 (w), 1038 (m), 890 (s), 787 (s), 655 (w), 541 (w), 432 (w).

Figure S9 ^{1}H NMR spectrum (500 MHz, C_6D_6) of **A**.

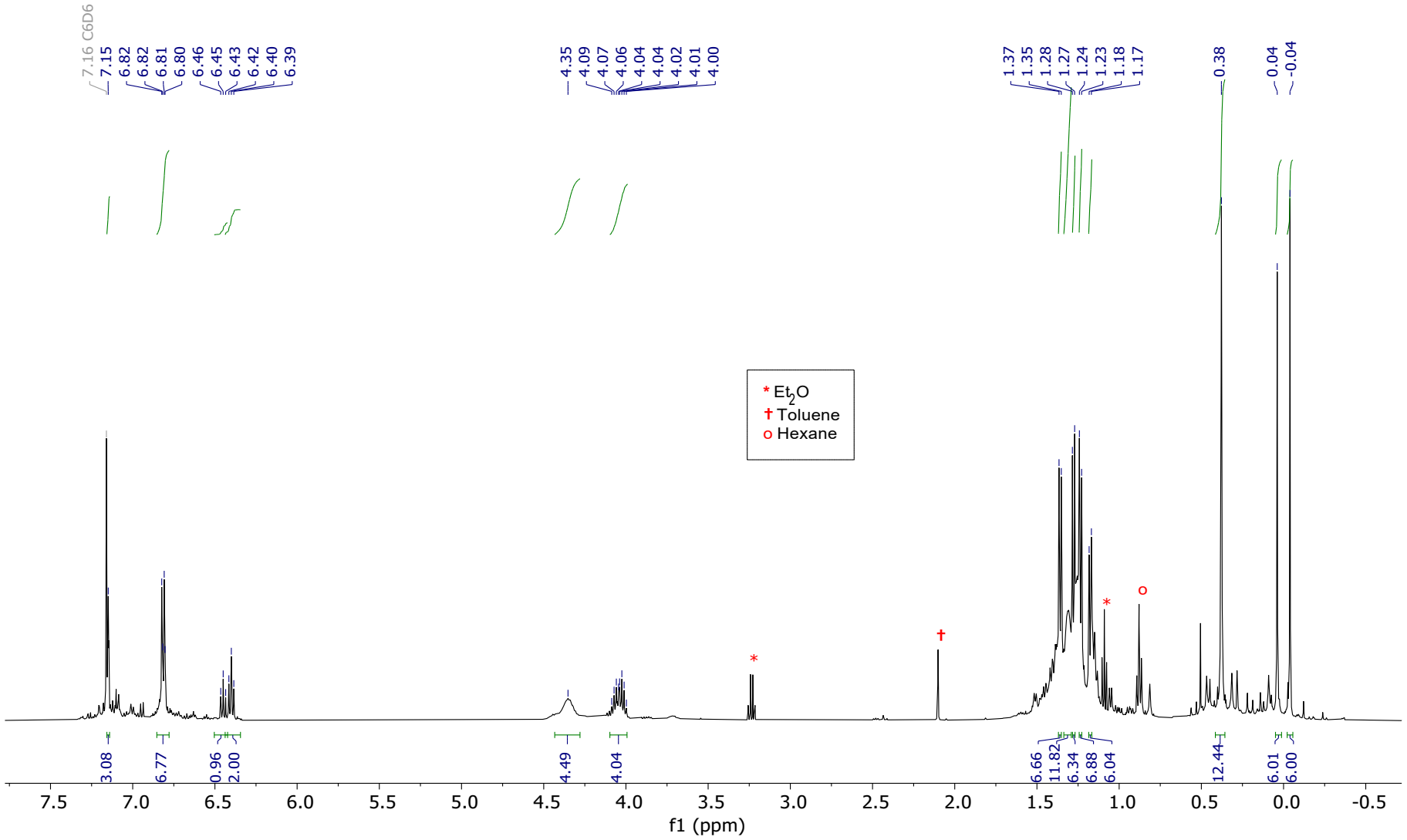


Figure S10 $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of **A**.

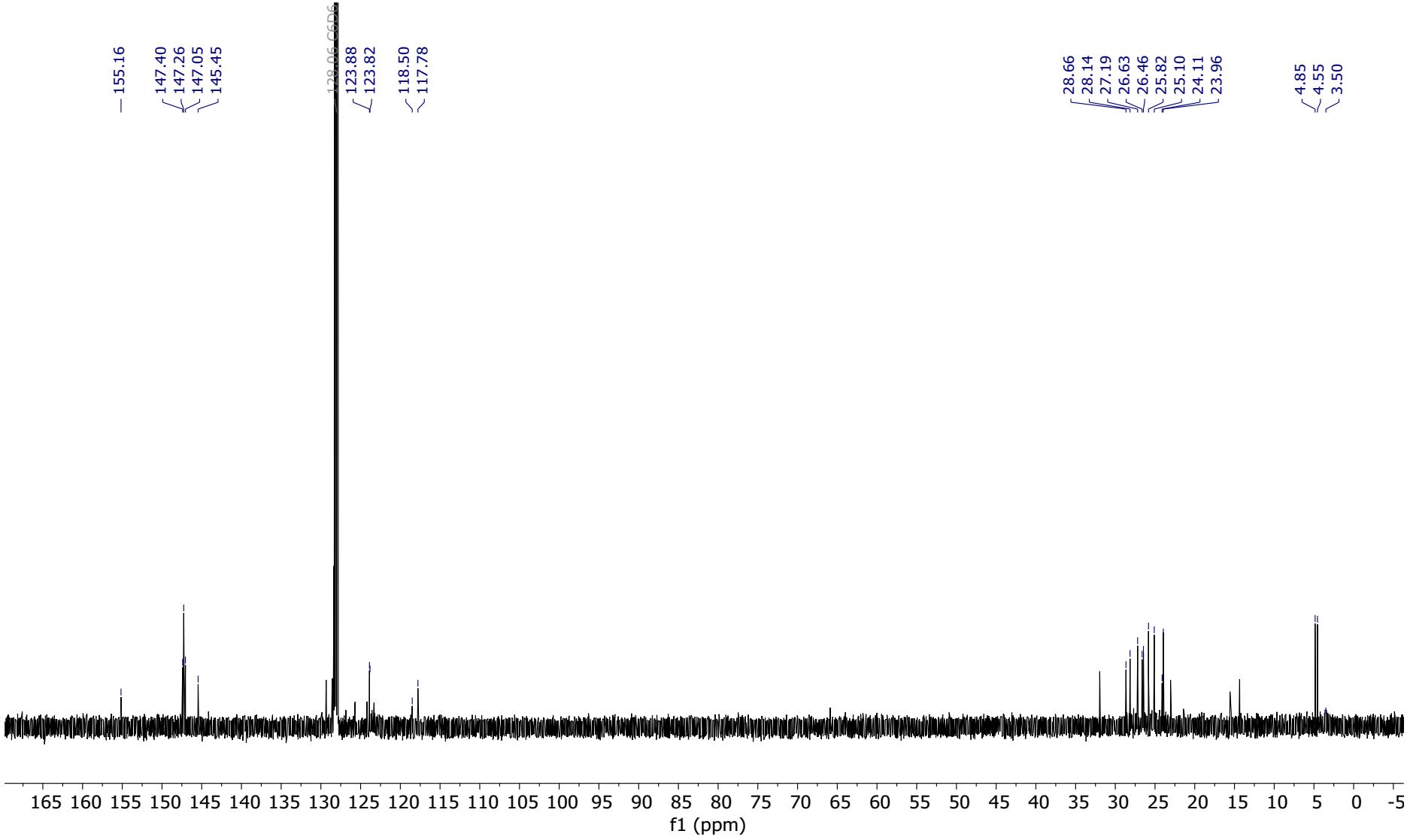
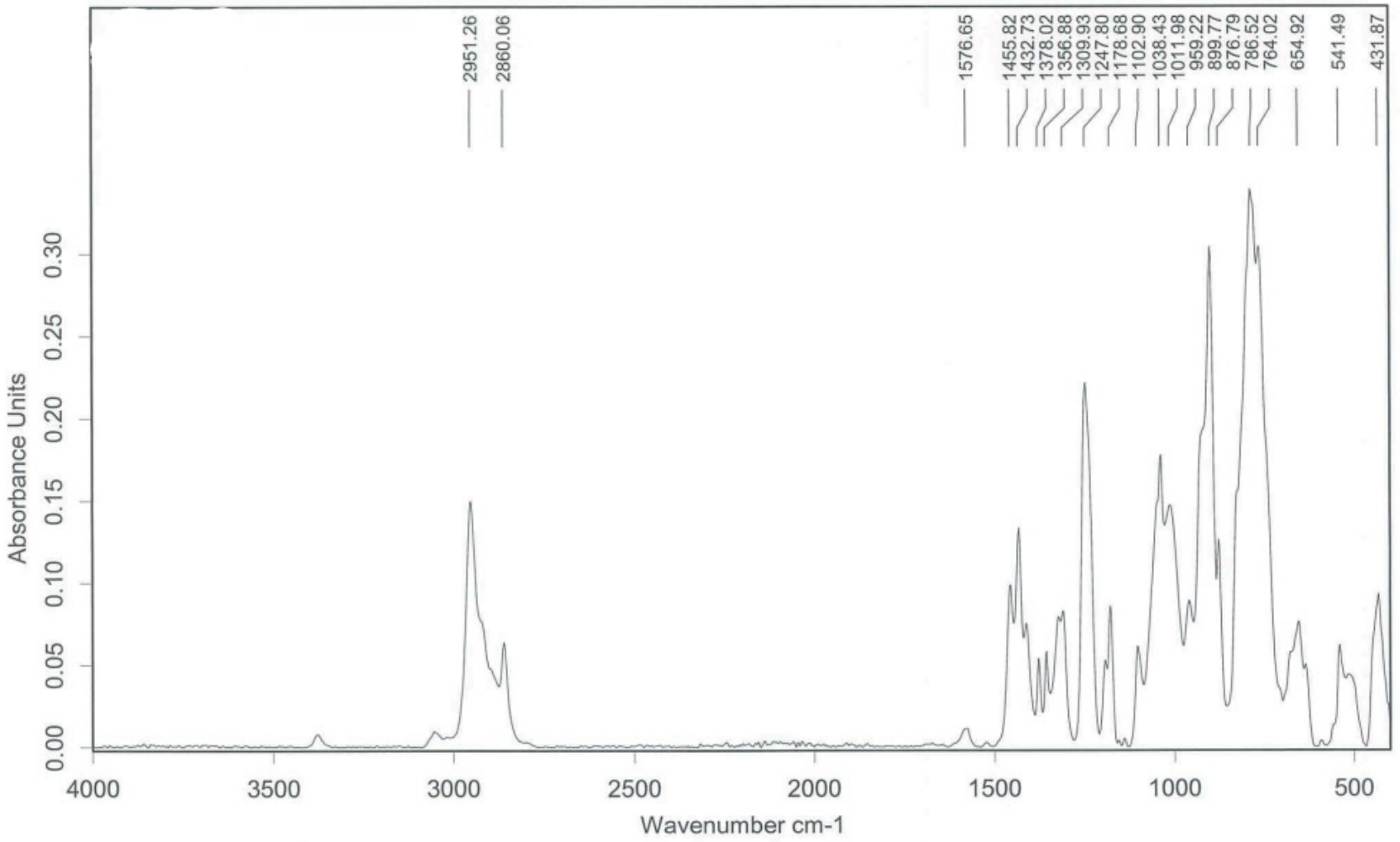


Figure S11 IR spectrum (solid sample) of **A**.



Experimental Details for K_2[(NON)Mg{μ-C(N*i*Pr)$_2$}Mg(NNO)] 2.

A solution of di*iso*propylcarbodiimide (10.0 mg, 0.08 mmol) in C_6H_6 was added to a solution of **A** (91.5 mg, 0.08 mmol) in C_6H_6 at room temperature. The reaction mixture gradually changed colour from bright yellow to colourless over 10 minutes. The solvent was reduced *in vacuo* and colourless crystals of **2** were obtained by slow evaporation at room temperature. Yield = 47.4 mg, 49%.

Accurate elemental analysis could not be obtained for this compound. Best result: Anal. Calcd. for $C_{63}H_{106}K_2Mg_2N_6O_2Si_4$ (*1218.728*): C 62.09, H 8.77, N 6.91%; Found: 55.93, H 5.72, N 4.89%.

^{1}H NMR (500 MHz, C_6D_6:THF-D_8 (~5:1)): δ (ppm) 7.20 (m, 4H, C_6H_3), 7.15 (m, 2H, C_6H_3), 7.10 (m, 4H, C_6H_3), 6.87 (t, *J* = 7.5, 1H, C_6H_3), 6.75 (t, *J* = 7.5, 1H, C_6H_3), 4.42 (m, 4H, C*H*Me$_2$), 4.27 (sept, *J* = 6.9, 2H, C*H*Me$_2$), 4.09 (sept, *J* = 6.9, 2H, C*H*Me$_2$), 3.29 (sept, *J* = 6.5, 2H, C*H*Me$_2$), 1.52 (d, *J* = 6.9, 6H, CHMe_2), 1.45 (m, 24H, CHMe_2), 1.42 (d, *J* = 6.9, 6H, CHMe_2), 1.38 (d, *J* = 6.9, 12H, CHMe_2), 1.27 (d, *J* = 6.9, 6H, CHMe_2), 0.81 (d, *J* = 6.5, 6H, CHMe_2), 0.26 (s, 6H, SiMe_2), 0.24 (s, 6H, SiMe_2), 0.17 (s, 6H, SiMe_2), 0.17 (s, 6H, SiMe_2).
^{13}C{^{1}H} NMR (126 MHz, C_6D_6:THF-D_8 (~5:1)): δ (ppm) 226.1 (*C*(N^{i}Pr)$_2$), 154.0, 150.8, 148.4, 148.2, 146.1, 145.6, 124.6, 124.6, 124.5, 124.2, 120.0, 118.9 (C_6H_3), 58.3 (N*C*HMe$_2$), 29.8 (CHMe_2), 28.8, 28.3 (*C*HMe$_2$), 27.6 (CHMe_2), 27.3 (*C*HMe$_2$), 27.2 (CHMe_2), 26.9, 26.8, 26.7, 26.3, 26.2, 26.1, 25.40 (CHMe_2), 5.5, 4.9, 4.7, 4.6 (SiMe_2).

IR (solid, cm^{-1}): 2953 (m), 2860 (w), 1655 (w), 1456 (m), 1431 (m), 1244 (s), 1176 (m), 1103 (w), 1038 (m), 897 (s), 797 (s), 764 (s), 654 (w), 542 (w), 449 (w).

Figure S12 ^{1}H NMR spectrum (500 MHz, C_6D_6:THF-D_8 (~5:1)) of **2**.

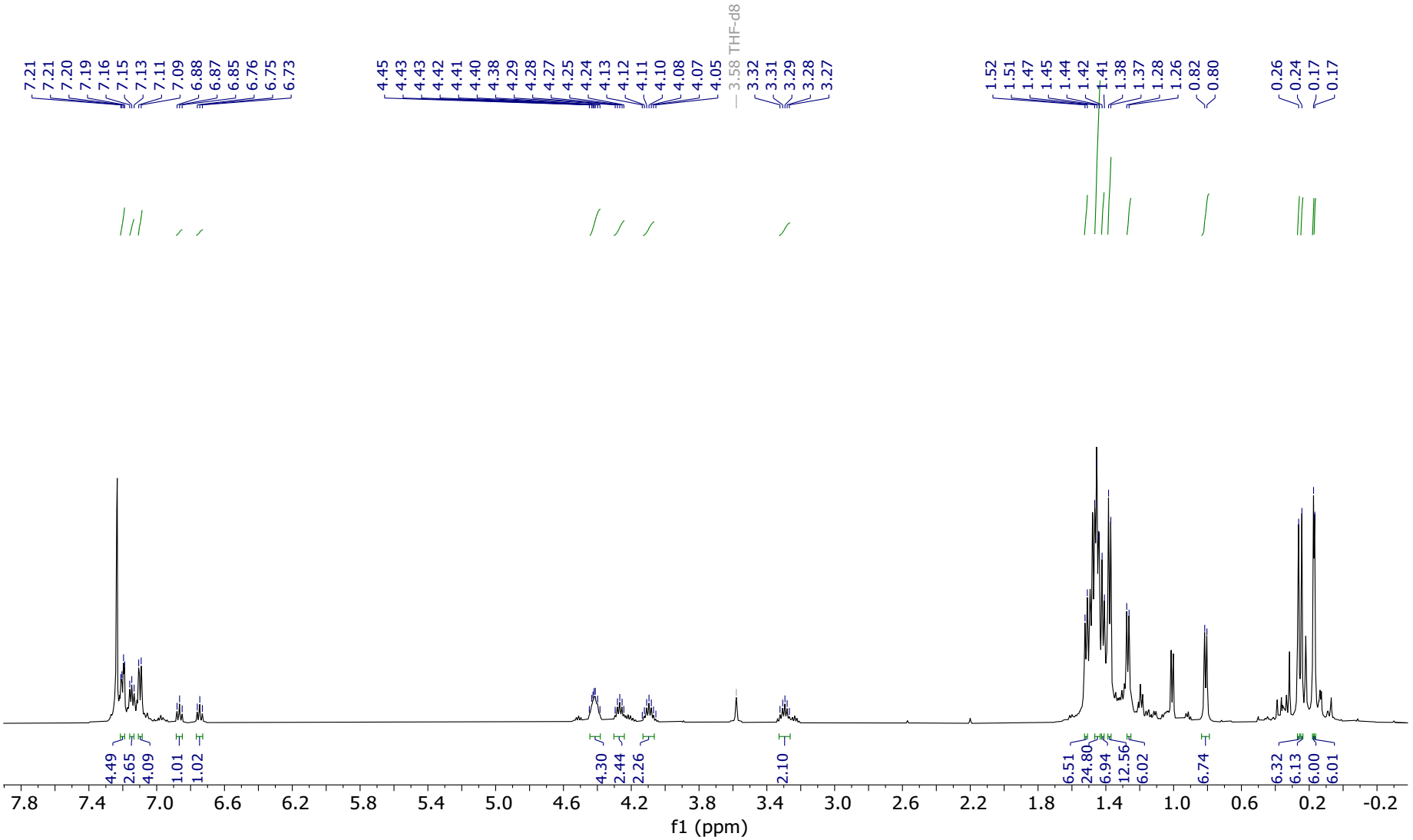


Figure S13 $^{13}C\{^{1}$ NMR spectrum (126 MHz, C_6D_6:THF-D_8 (~5:1)) of **2**.

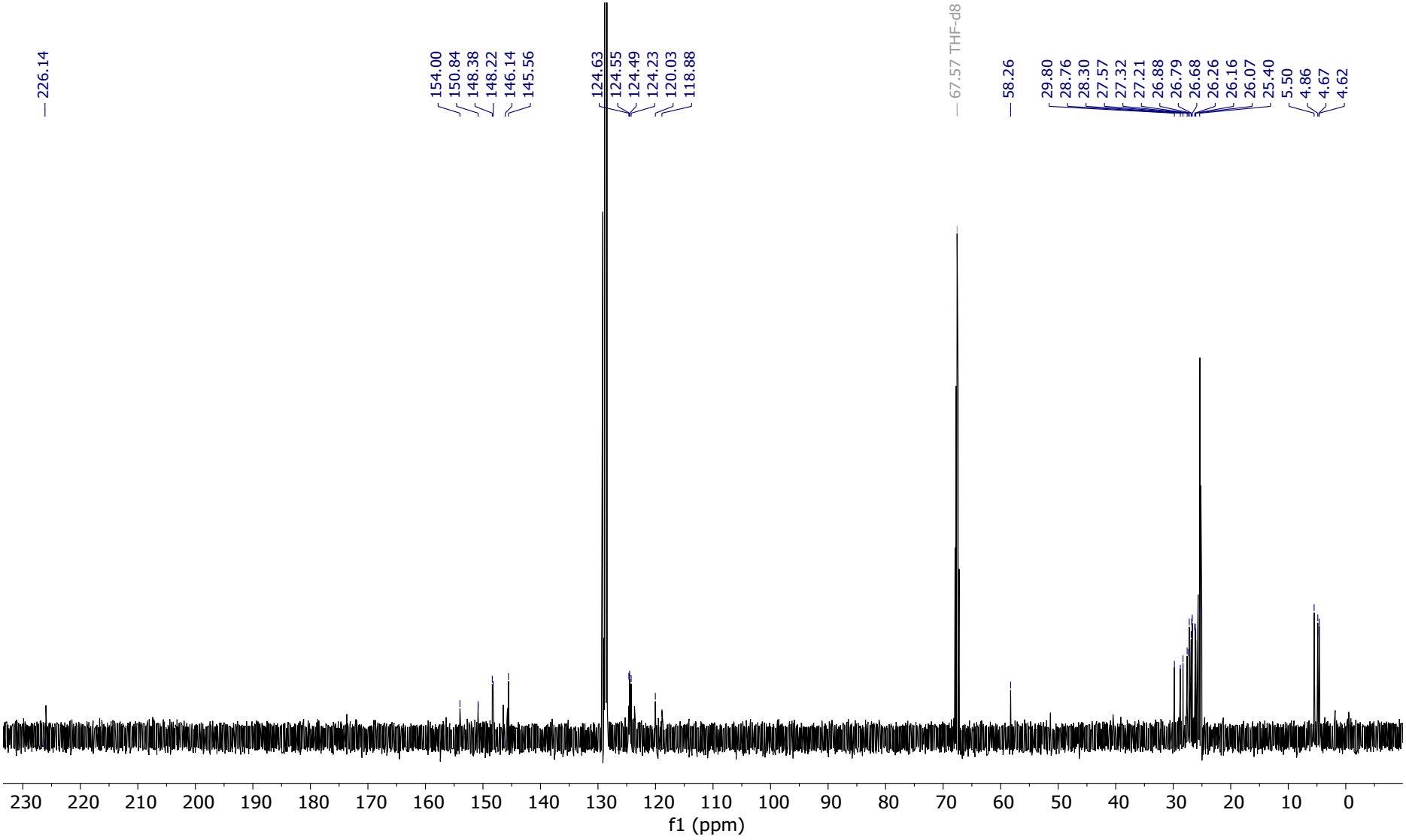


Figure S14 IR spectrum (solid sample) of **2**.

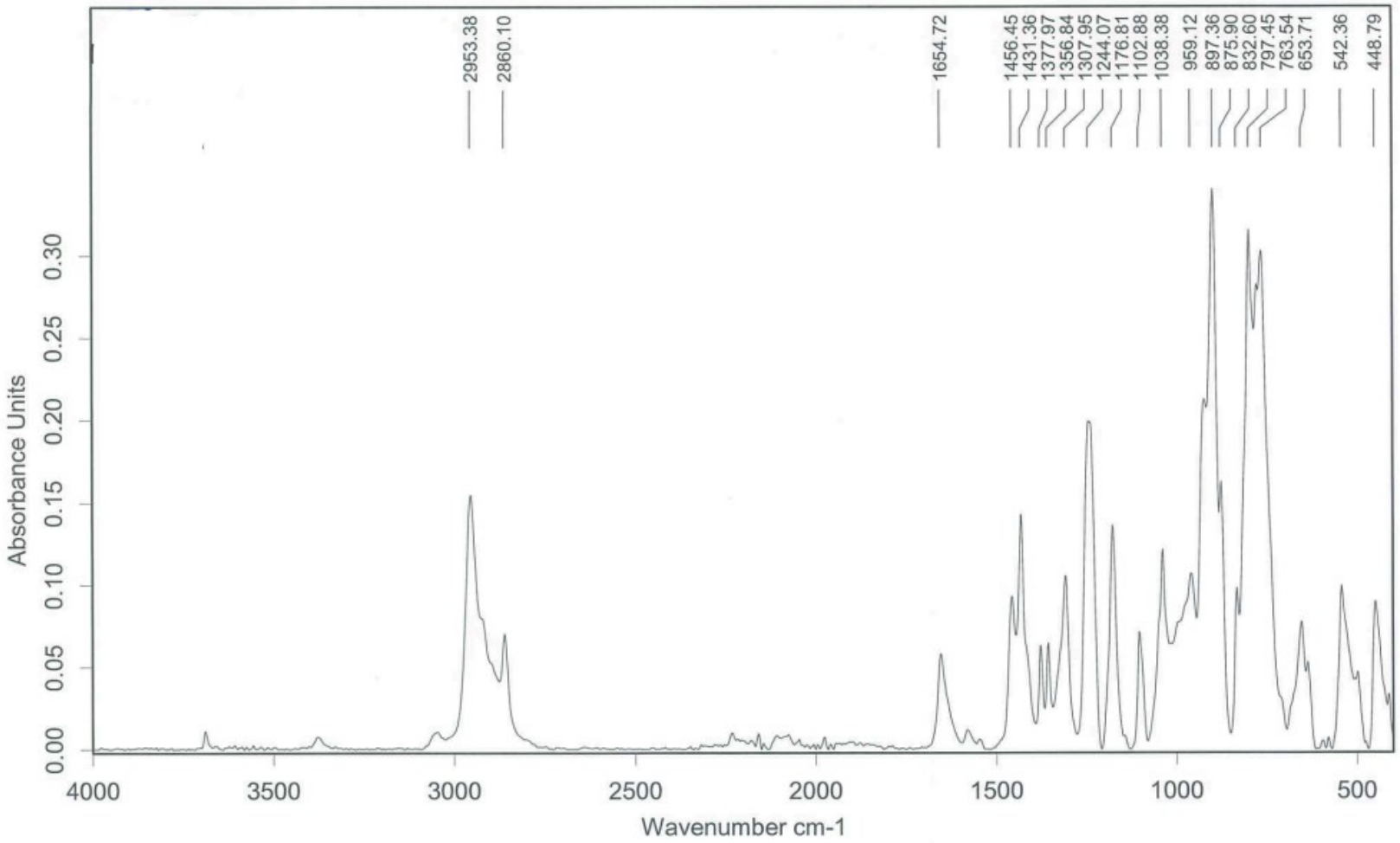
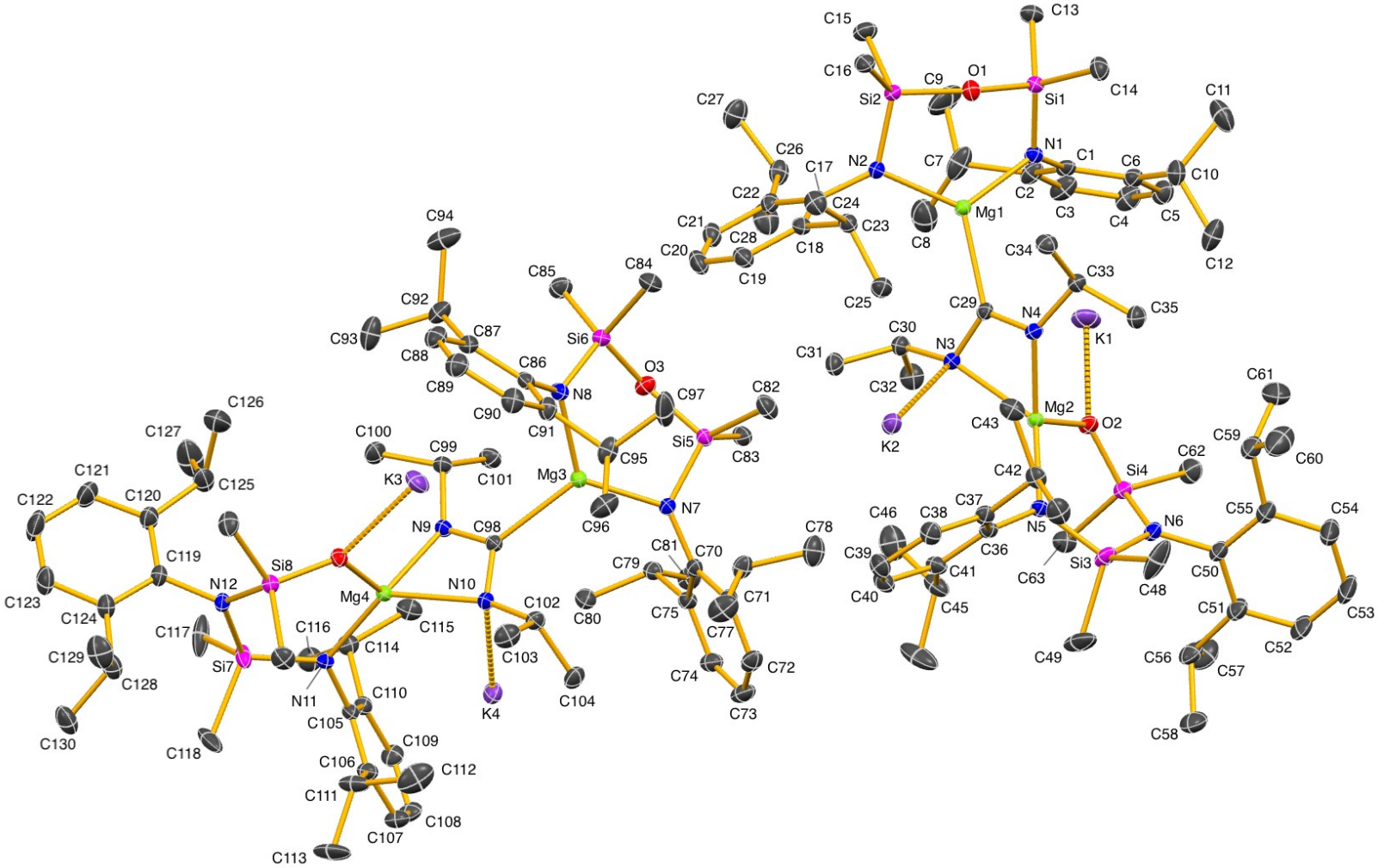


Figure S15 ORTEP (ellipsoids 30%, H-atoms omitted), of the asymmetric unit of K_2[(NON)Mg{μ-C(N*i*Pr)$_2$}Mg(NNO)] **2** (disordered atoms and benzene solvate molecules omitted).



Experimental Details for $K_2[\{Mg(NON)(Et_2O)\}_2(\mu\text{-}O_2C_2)]$ 3·Et_2O.

A solution of **A** (76.2 mg, 0.07 mmol) in C_6D_6 was added to a J-Youngs NMR tube. The solution was degassed, and the reaction vessel was charge with CO gas (~0.5 bar). An immediate colour change from bright yellow to red-orange was observed. The reaction mixture was filtered, and solvent removed *in vacuo*. Crystals of **3**·Et_2O suitable for X-ray diffraction were obtained by slow evaporation from Et_2O. Yield = 12.2 mg, 13%.

Accurate elemental analysis could not be obtained for this compound. Best result: Anal. Calcd. for $C_{66}H_{112}K_2Mg_2N_4O_6Si_4$ (*1296.791*): C 61.13, H 8.71, N 4.32%; Found: C 58.11, H 7.66, N 4.35%.

^{1}H NMR (500 MHz, C_6H_6): δ (ppm) 6.92 (d, *J* = 7.4, 8H, C_6H_3), 6.70 (t, *J* = 7.4, 4H, C_6H_3), 4.15 (m, 8H, C*H*Me$_2$), 3.28 (q, *J* = 6.9, 8H, *Et*$_2$O), 1.30 (d, *J* = 6.9, 24H, CH*Me*$_2$), 1.12 (t, *J* = 6.9, 12H, *Et*$_2$O), 1.06 (d, *J* = 6.9, 24H, CH*Me*$_2$), 0.35 (s, 24H, Si*Me*$_2$).
^{13}C{^{1}H} NMR (126 MHz, C_6H_6): δ (ppm) 152.6, 145.9, 122.6, 118.8 (*C*$_6$H$_3$), 76.6 (O*C*≡*C*O), 65.9 (O*C*H$_2$CH$_3$), 27.0 (*C*HMe$_2$), 25.7 24.1 (CH*Me*$_2$) 15.5 (OCH$_2$*C*H$_3$), 3.9 (Si*Me*$_2$).

IR (solid, cm^{-1}): 2958 (m), 2925 (m), 2866 (m), 1580 (w), 1420 (m), 1326 (m), 1250 (s), 1041 (m), 905 (s), 774 (s), 497 (w).

Figure S16 ^{1}H NMR spectrum (500MHz, C_6D_6) of **3**·Et_2O.

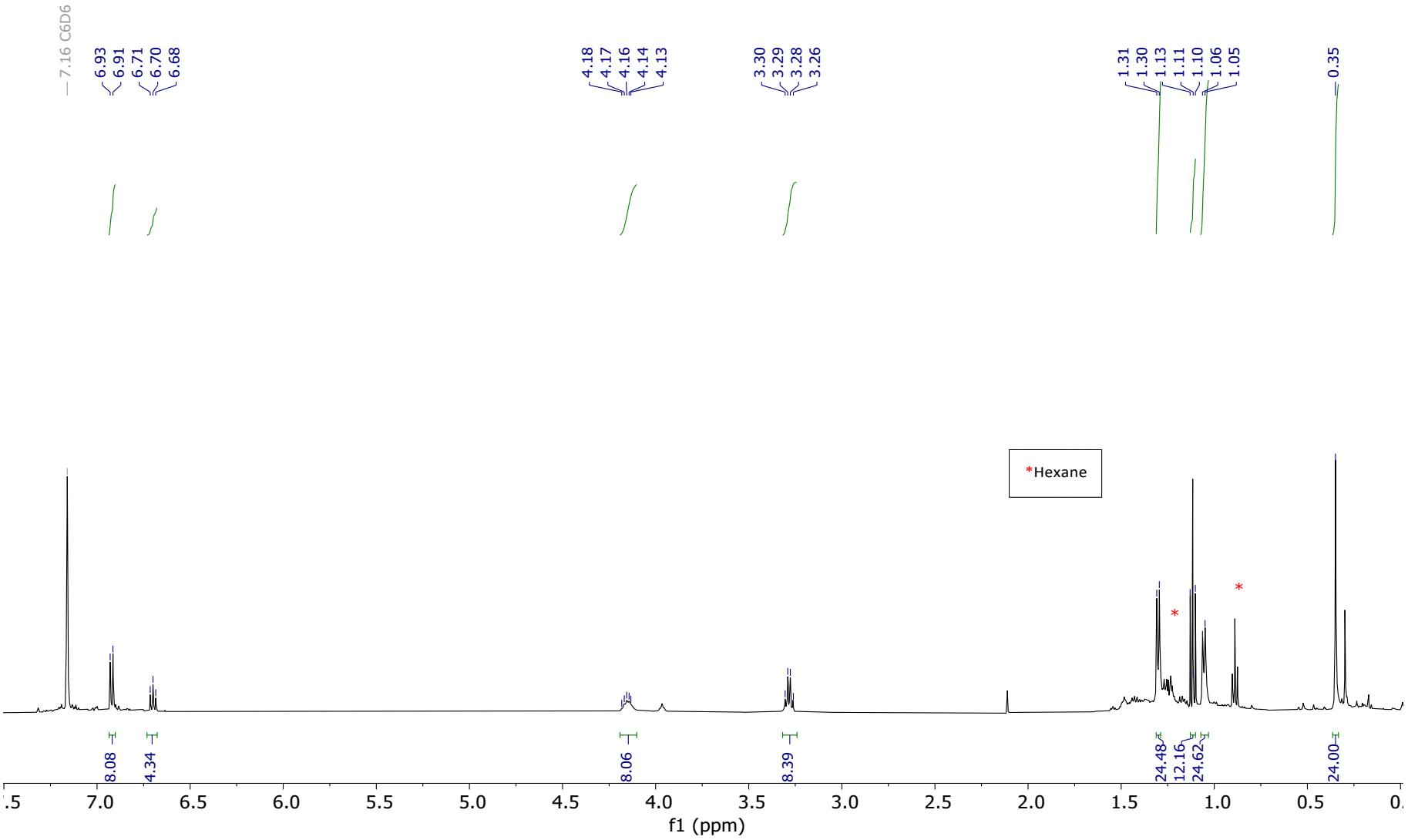


Figure S17 $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of **3**·Et_2O.

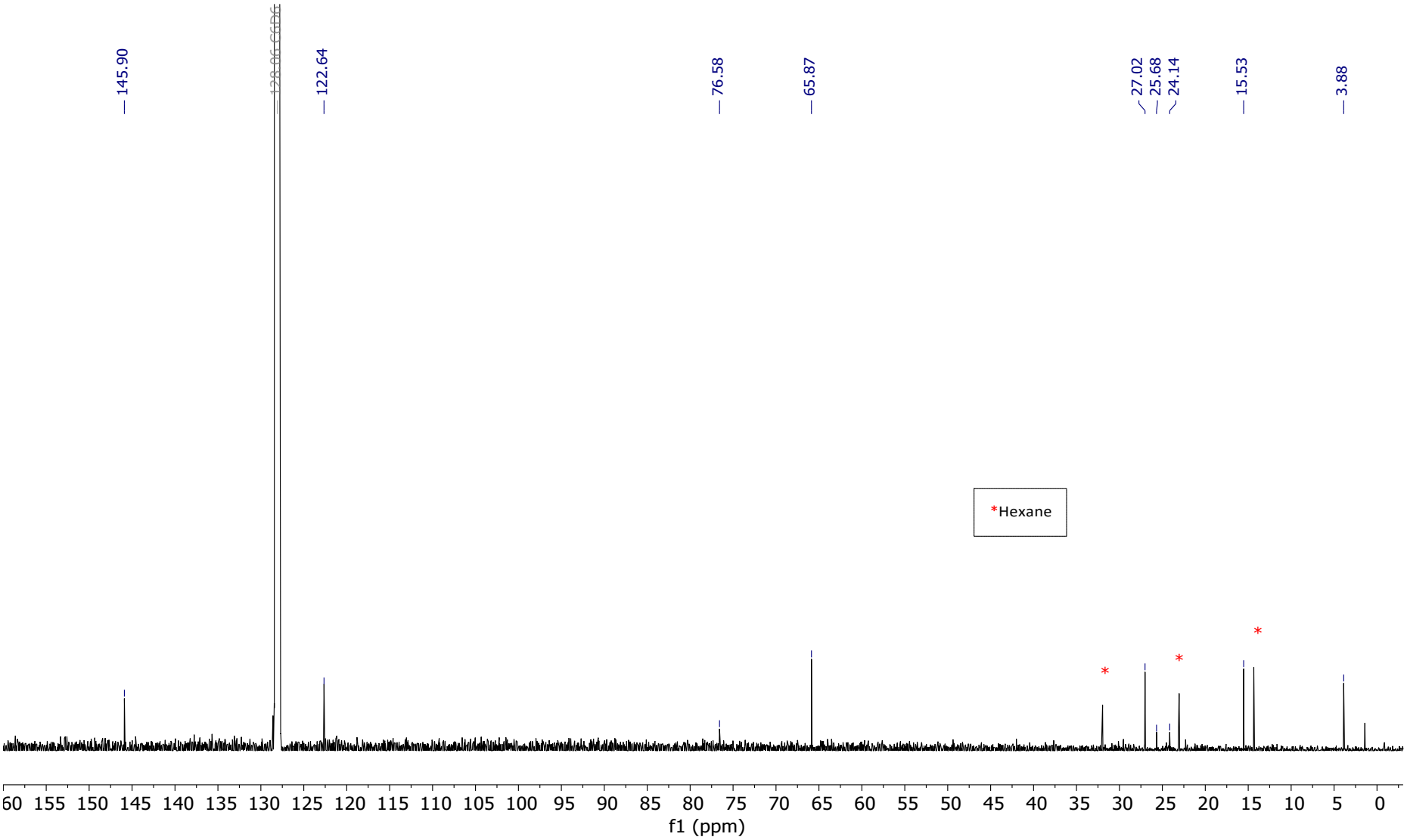


Figure S18 IR spectrum (solid sample) of **3**·Et_2O.

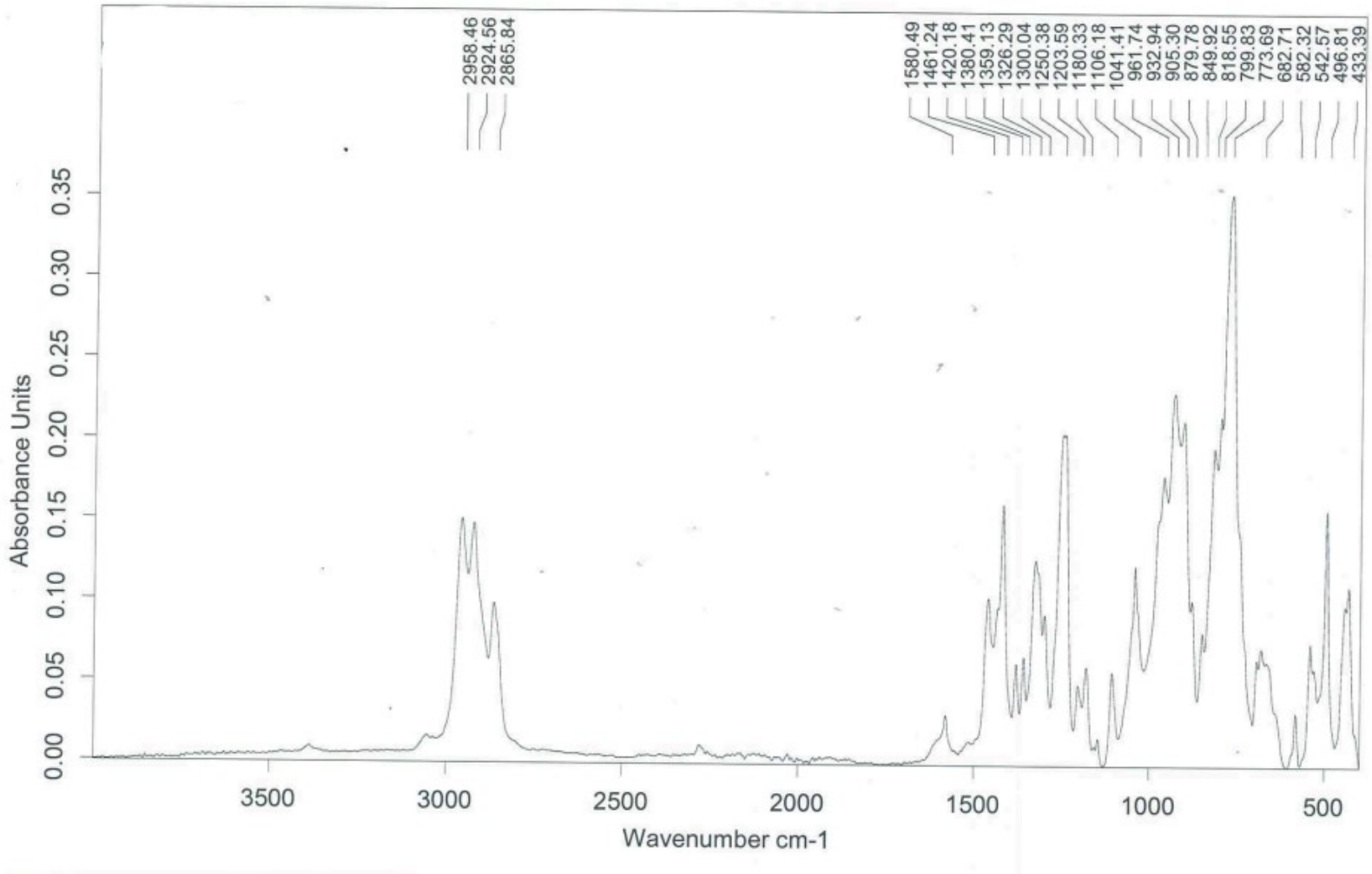
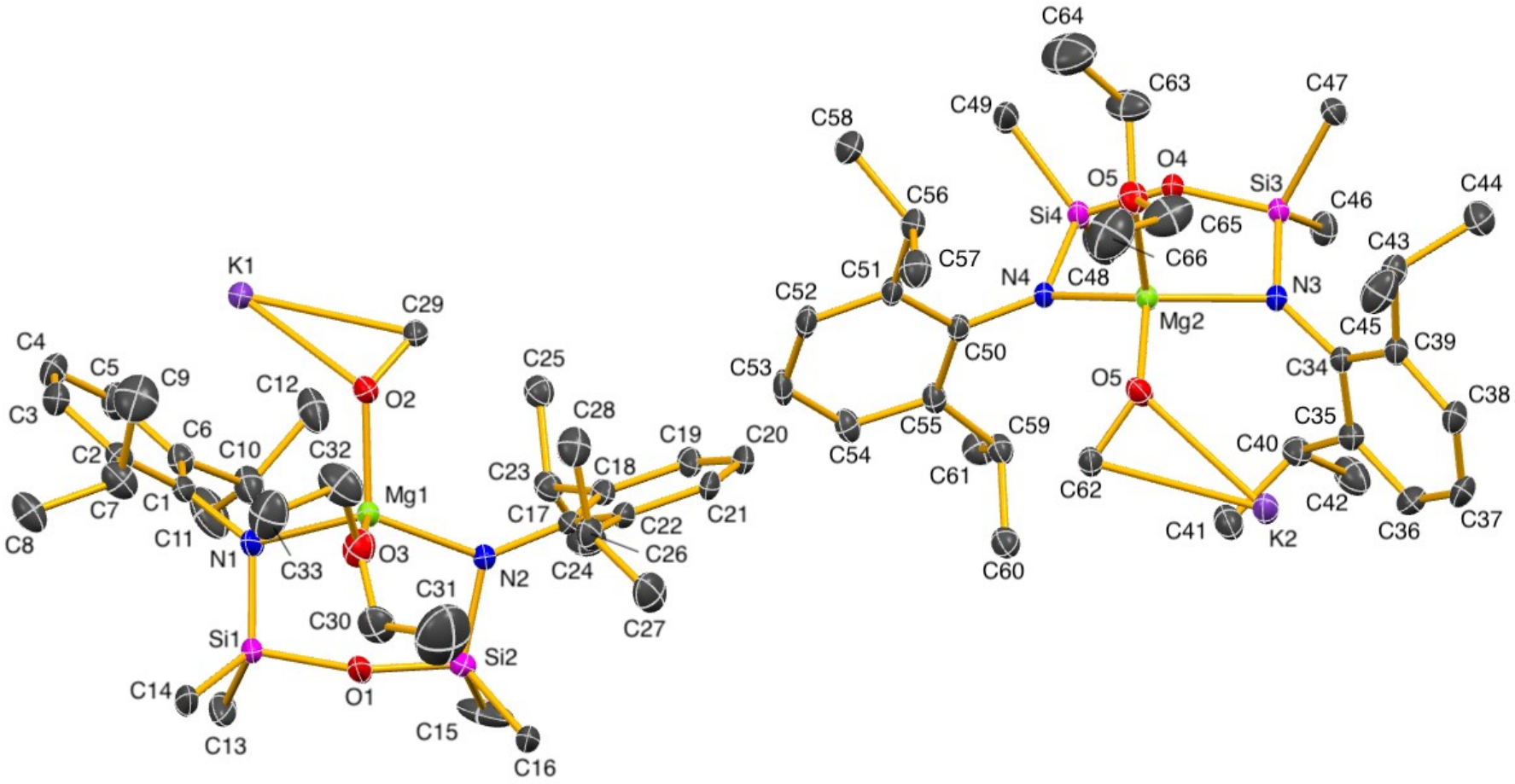


Figure S19 ORTEP (ellipsoids 30%, H-atoms omitted), of the asymmetric unit of $K_2[\{Mg(NON)(Et_2O)\}_2(\mu\text{-}O_2C_2)]$ **3**·Et_2O (disordered atoms omitted).



Experimental Details for $[K(THF)_2]_2[\{Mg(NNO)\}_2]$ 4·THF.

A white suspension of $[Mg(NON)]_2$ (175.0 mg, 0.17 mmol) in diethyl ether was added to a suspension of KC_8 (137.9 mg, 1.02 mmol) in Et_2O while stirring at room temperature. The reaction mixture was stirred for *ca*. 2 hrs. The reaction mixture was allowed to settle and filtered through celite to afford a bright yellow solution. The solvent was removed *in vacuo* and the resulting yellow solid **A** was isolated. Yield = 108.6 mg. The yellow solid **A** was redissolved in a minimum volume of benzene/THF (~1:1) and yellow block crystals of **4**·THF were obtained by slow evaporation at room temperature. Yield = 50.2 mg, 37%.

M.P.: >260 °C.

Accurate elemental analysis could not be obtained for this compound. Best result:

Anal. Calcd. for $C_{72}H_{124}K_2Mg_2N_4O_6Si_4$ (*1380.953*) = 4 × THF: C 62.62, H 9.05, N 4.06%;

Anal. Calcd. for $C_{60}H_{100}K_2Mg_2N_4O_3Si_4$ (*1164.63*) = 1 × THF: C 61.88, H 8.66, N 4.81%.

Found: C 60.63, H 8.55, N 4.65%. Results may indicate partial loss of THF during sample preparation and analysis.

^{1}H NMR (500 MHz, THF-D_8): δ (ppm) 6.97 (m, 8H, C_6H_3), 6.89 (t, *J* = 7.5, 2H, C_6H_3), 6.67 (t, *J* = 7.5, 2H, C_6H_3), 4.12 (sept, *J* = 6.9, 4H, C*H*Me$_2$), 3.97 (sept, *J* = 6.9, 4H, C*H*Me$_2$), 3.62 (m, 12H, THF-*H*), 1.78 (m, 12H, THF-*H*), 1.23 (m, 24H, CHMe_2), 1.16 (d, *J* = 6.9, 24H, CHMe_2), -0.19 (s, 12H, SiMe_2), -0.36 (s, 12H, SiMe_2).

^{13}C{^{1}H} NMR (126 MHz, THF-D_8) δ 147.6, 123.7, 123.3, 118.0 (C_6H_3), 68.3 (THF-*H*), 29.0 (CHMe_2), 28.6, 27.1 (*C*HMe$_2$), 26.4 (THF-*H*), 26.4, 26.2, 23.6 (CHMe_2), 4.6, 4.0 (SiMe_2).

IR (solid, cm^{-1}): 3038 (m), 2867 (m), 1579 (w), 1460 (m), 1380 (w), 1313 (s), 1041 (m), 961 (s), 798 (s), 675 (s), 583 (w), 442 (w).

Figure S20 ^{1}H NMR spectrum (500MHz, THF-D_8) of **4**·THF.

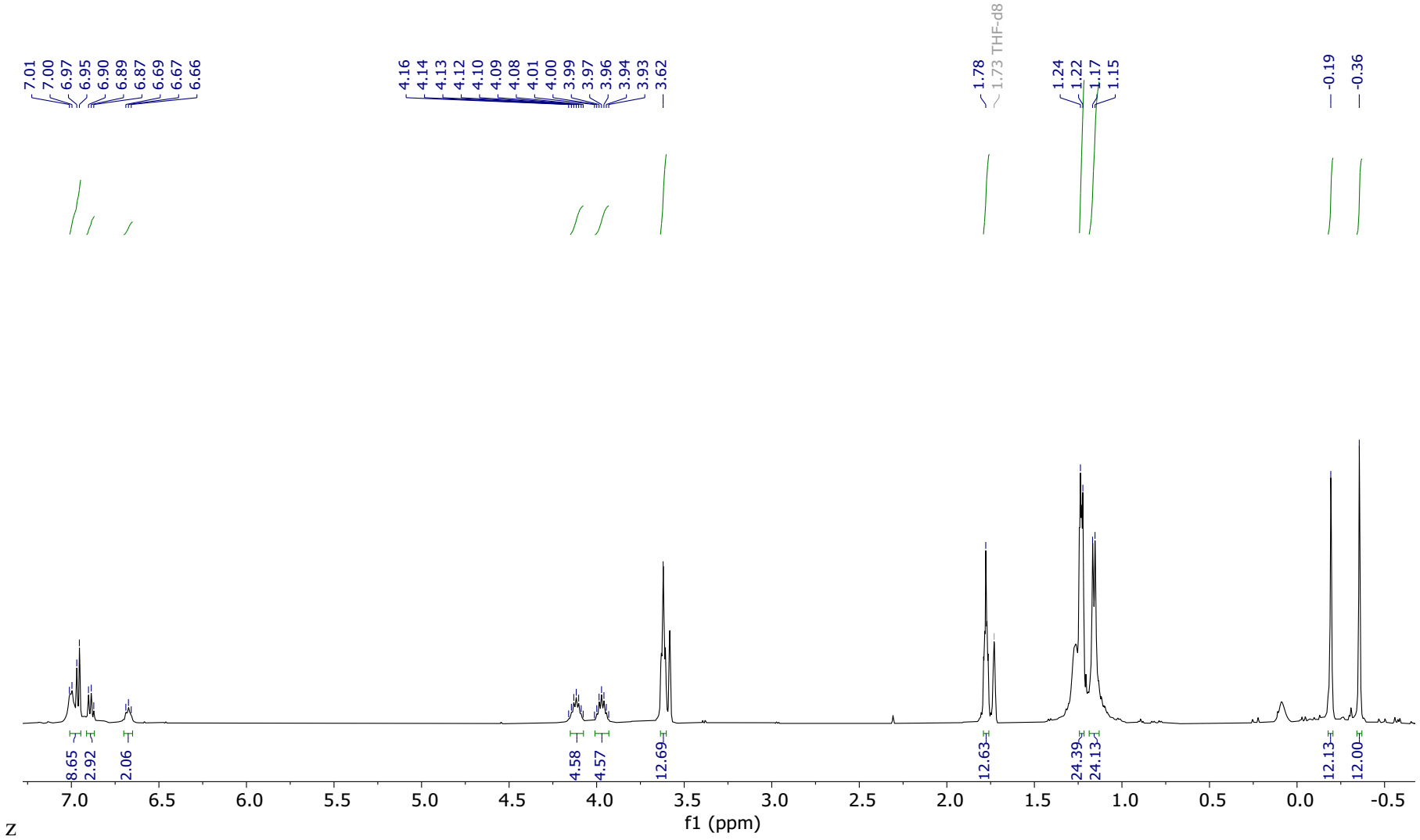


Figure S21 ^{13}C NMR spectrum (126 MHz, THF-D_8) of **4**·THF.

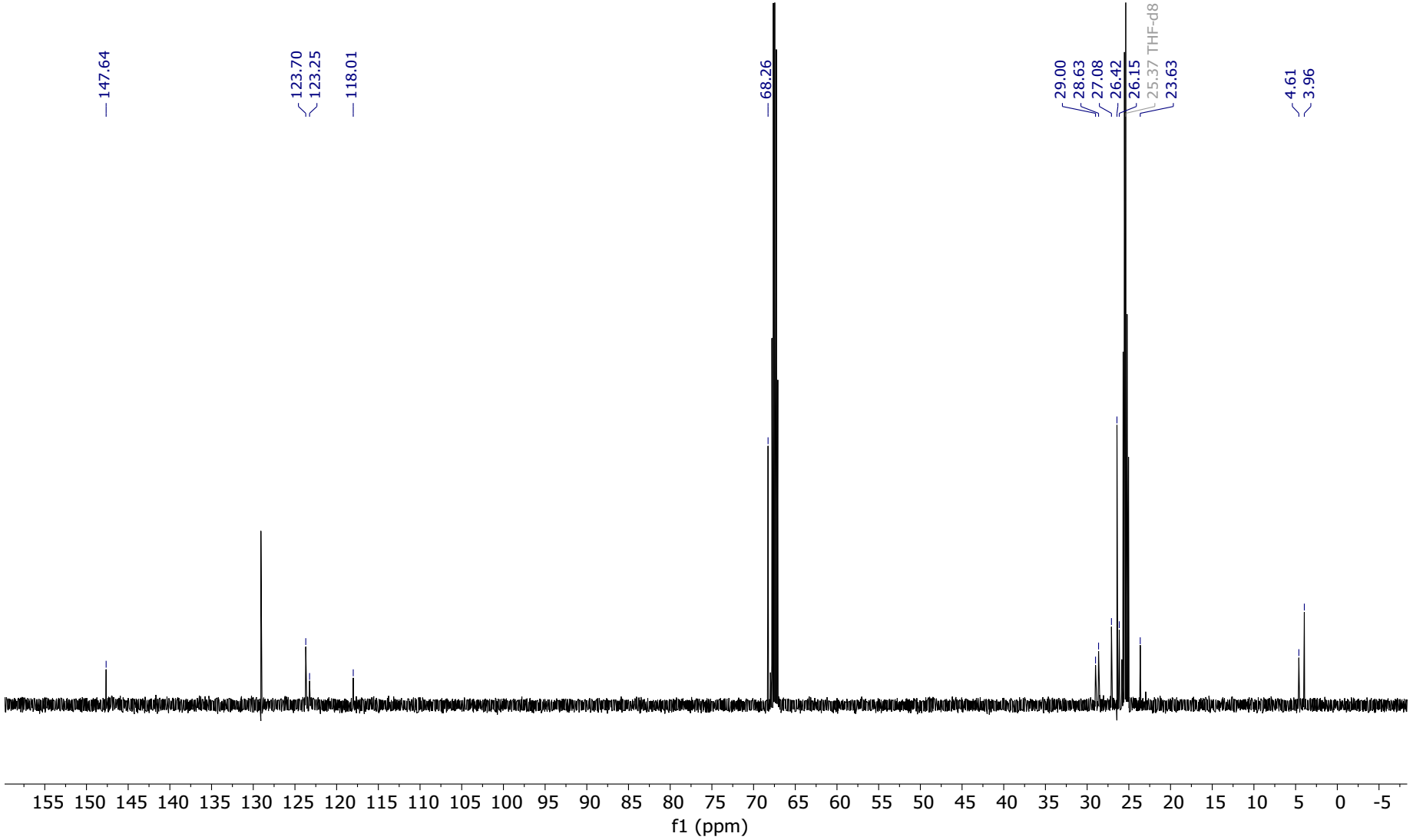


Figure S22 IR spectrum (solid sample) of **4**·THF.

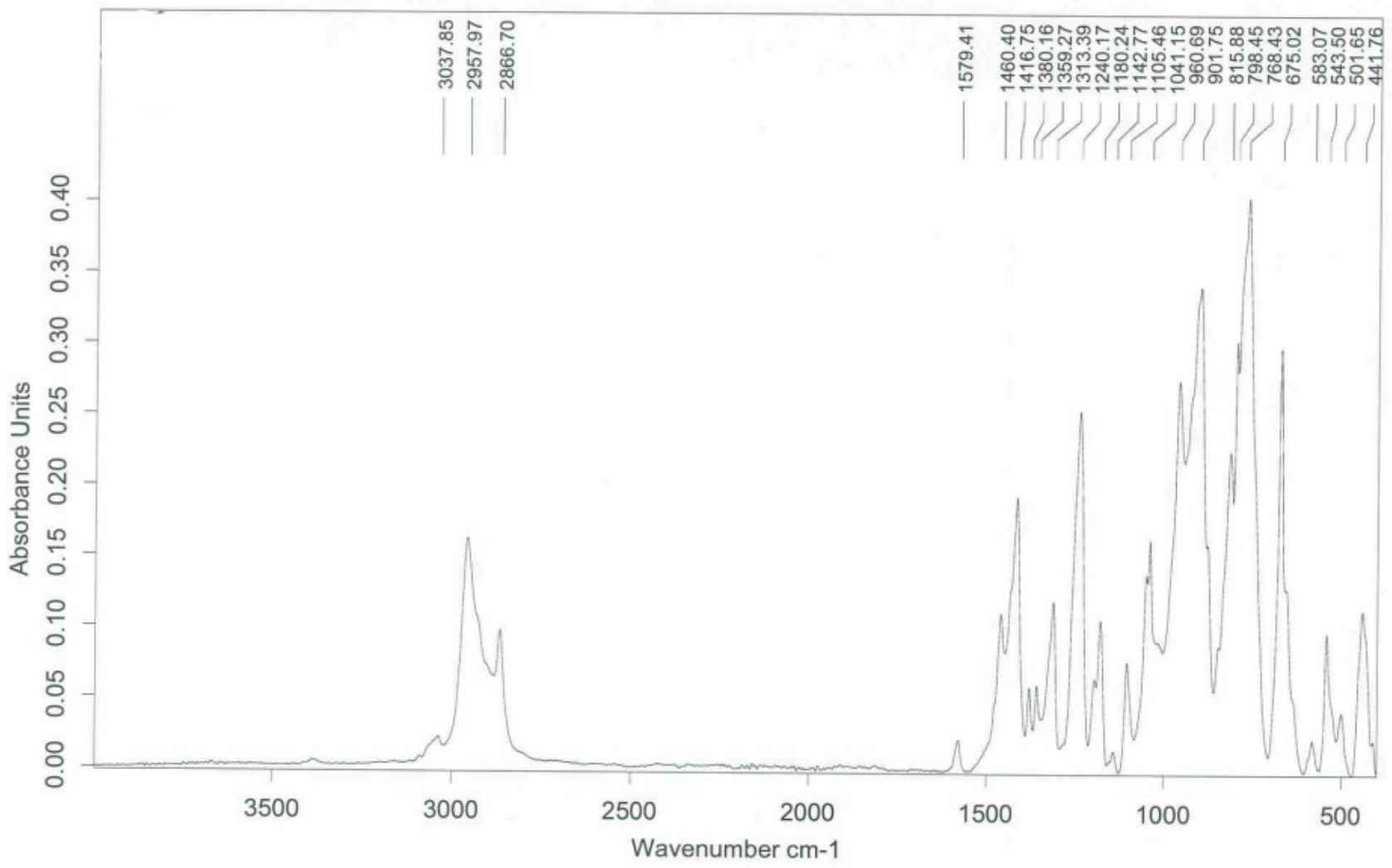


Figure S23 ORTEP (ellipsoids 30%, H-atoms omitted), of the asymmetric unit of $[K(THF)_2]_2[\{Mg(NNO)\}_2]$ **4**·THF (disordered atoms omitted).

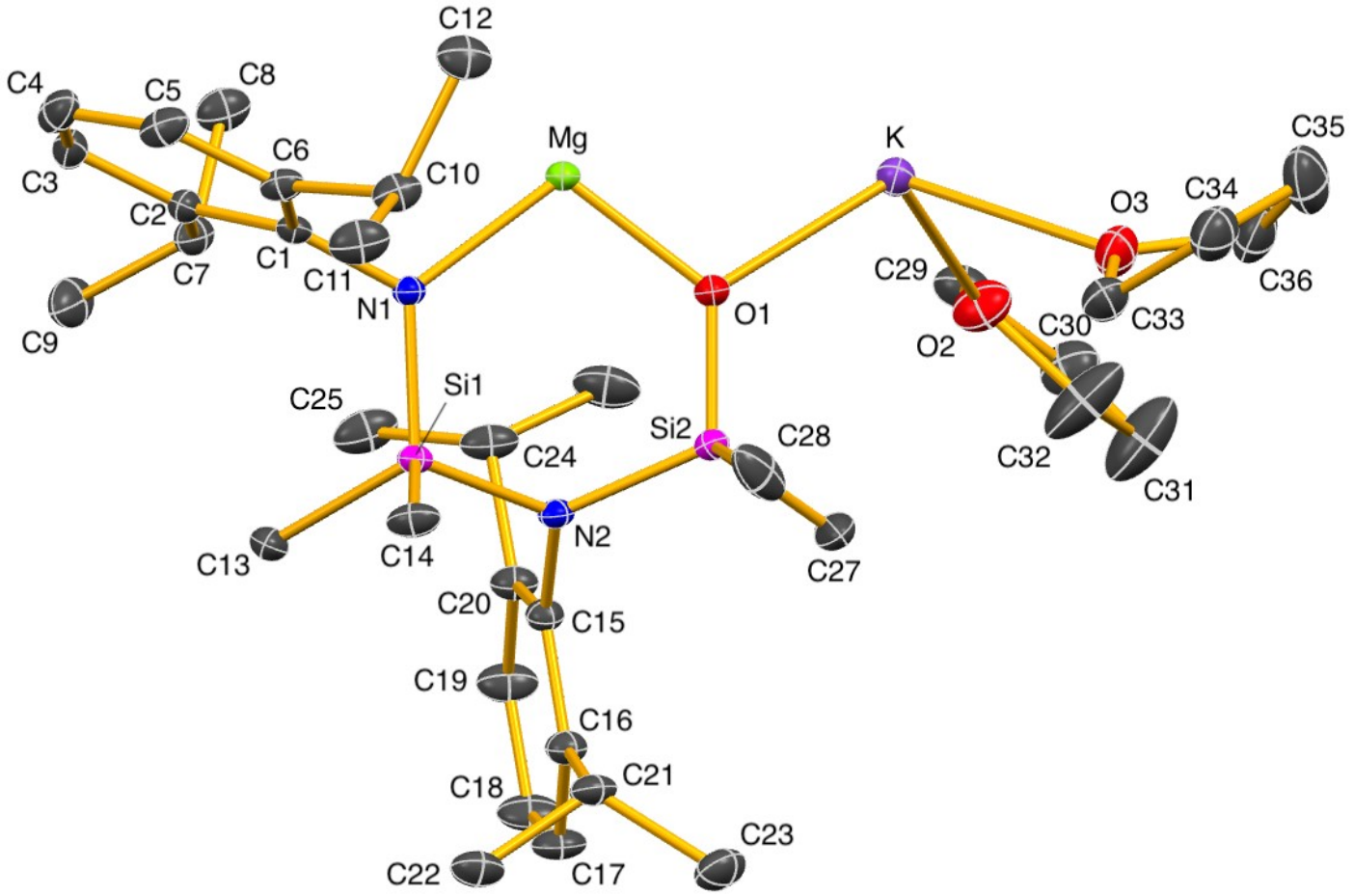
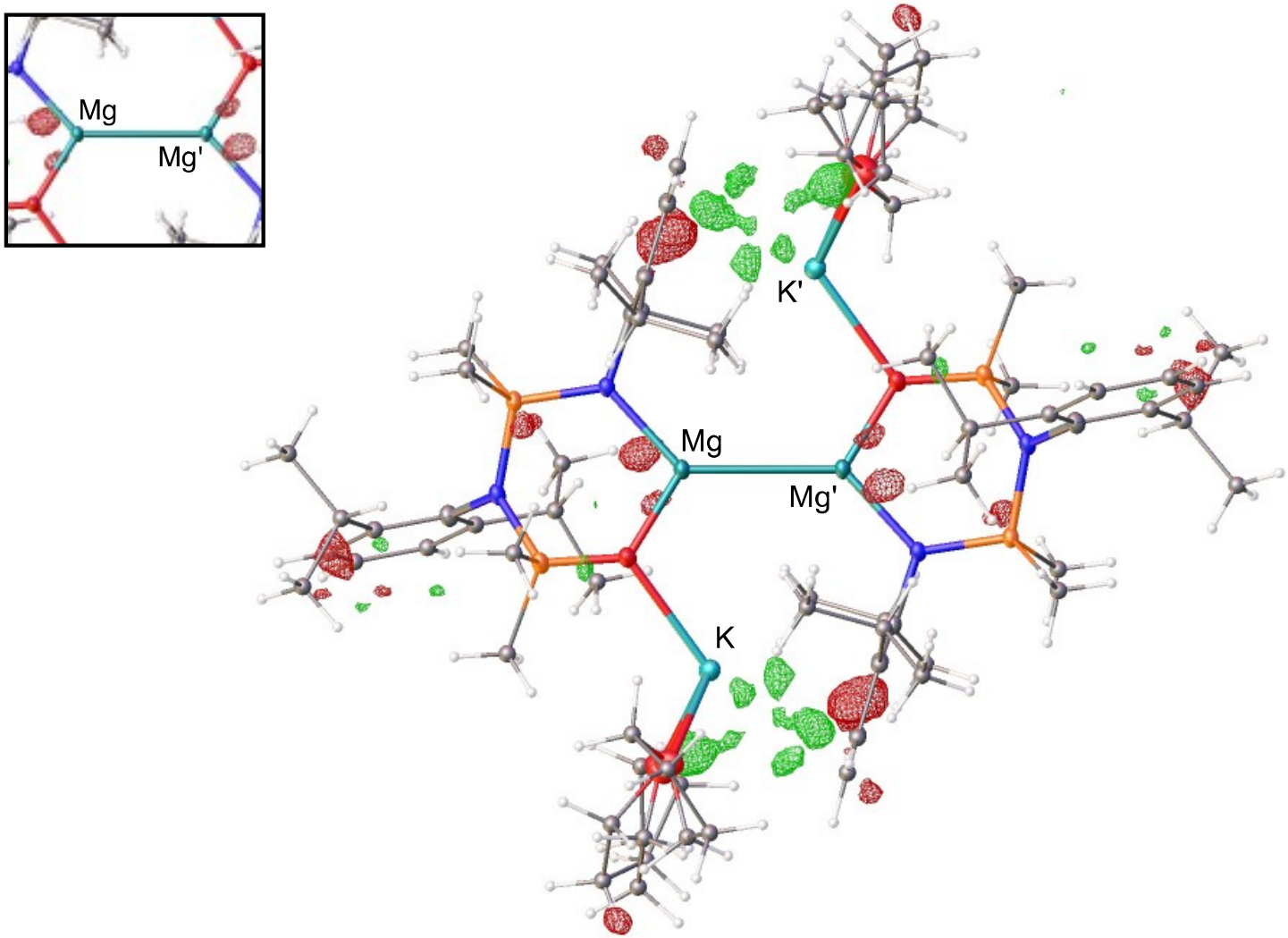


Figure S24 Residual electron density (0.35 eÅ^{-3}) for **4**·THF (inset = core of the molecule)



Crystallographic Details

Crystals were covered in inert oil and suitable single crystals were selected under a microscope and mounted on an Agilent SuperNova diffractometer fitted with an EOS S2 detector. Data were collected at 120 K (unless indicated otherwise) using focused microsource Cu Kα radiation at 1.54184 Å. Intensities were corrected for Lorentz and polarisation effects and for absorption using multi-scan methods.[S3] Space groups were determined from systematic absences and checked for higher symmetry. All structures were solved using direct methods with SHELXS,[S4] refined on F^2 using all data by full matrix least-squares procedures with SHELXL-97[S5] within WinGX.[S6] programs. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions or manually assigned from residual electron density where appropriate, unless otherwise stated. The isotropic displacement parameters are 1.2 or 1.5 times the isotropic equivalent of their carrier atoms.

Additional Information:

*Compound **1***: The molecule is located on an inversion centre, generating $[Mg(NON)]_2$.

*Compound **2***: Data was collected at 150 K (due to equipment limitations). There are two essentially identical molecules in the asymmetric unit, joined via an interaction between an Si*Me* group and a K-cation. The two benzene solvate molecule are located close to K-atoms and may be weakly interacting. There is disorder in 3 × *i*Pr substituents, 1 × $SiMe_2$ groups 1 × benzene solvate. Each was modelled over two positions, with the disordered C_6-rings constrained with the AFIX 66 command. Where a suitable model could not found, the lower occupancy sites were refined with isotropic carbon atoms.

*Compound **3**·Et_2O*: There are two essentially identical ½ molecules in the asymmetric unit, each located on an inversion centre located at the midpoint of the C≡C bond. One of the ½ molecules has disorder in 1 × *i*Pr substituent, both O*Et* groups and the *SiMe*$_2$ groups. Each was modelled over two positions. Where suitable model could not found, the lower occupancy sites were refined with isotropic carbon atoms.

*Compound **4**·THF*: The data solves as a ½ molecule located with an inversion centre at the midpoint of the Mg–Mg bond. One of the coordinated THF molecules is disordered and was modelled over two positions.

Table S1 Crystal structure and refinement data for **1** and **2**

	1	**2**
Empirical formula	$C_{56}H_{92}Mg_2N_4O_2Si_4$	$C_{138}H_{224}K_4Mg_4N_{12}O_4Si_8$
CCDC Number	2357068	2357069
M_r	1014.32	2593.64
T [K]	120.0(2)	150.0(1)
Crystal size [mm]	0.21 × 0.16 × 0.09	0.21 × 0.15 × 0.10
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (alternative No.14)	$P\bar{1}$ (No.2)
a [Å]	15.6370(2)	16.3939(2)
b [Å]	11.51056(14)	21.2191(3)
c [Å]	17.4414(2)	21.8811(3)
α [°]	90	81.3508(13)
β [°]	108.6621(15)	89.9089(12)
γ [°]	90	88.1901(13)
V [Å^3]	2974.22(7)	7521.29(19)
Z	2	2
$D_{calc.}$ [mg m^{-3}]	1.133	1.145
Absorption coefficient [mm^{-1}]	1.446	2.225
θ range for data collection [°]	3.840 to 72.327	3.370 to 72.537
Reflections collected	18726	112918
Independent reflections	5857 [R_{int} 0.023]	29606 [R_{int} 0.079]
Reflections with $I > 2\sigma(I)$	5221	24240
Data/restraints/parameters	5857/0/319	29606/19/1633
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.029, wR_2 = 0.074	R_1 = 0.055, wR_2 = 0.139
Final R indices (all data)	R_1 = 0.034, wR_2 = 0.077	R_1 = 0.067, wR_2 = 0.148
GOOF on F^2	1.013	1.027
Largest diff. peak/hole [e.Å^{-3}]	0.27 and –0.24	1.02 and –0.46

Table S2 Crystal structure and refinement data for **3**·Et_2O and **4**·THF

	3·Et_2O	**4**·THF
Empirical formula	$C_{66}H_{112}K_2Mg_2N_4O_6Si_4$	$C_{42}H_{68}KMgN_2O_3Si_2$
CCDC Number	2357070	2357071
M_r	1296.77	768.57
T [K]	120.0(2)	120.0(1)
Crystal size [mm]	0.26 × 0.19 × 0.06	0.44 × 0.25 × 0.12
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No.2)	$P2_1/n$ (alternative No.14)
a [Å]	10.9645(3)	14.32120(19)
b [Å]	15.9181(4)	20.5716(2)
c [Å]	23.3852(5)	15.38509(18)
α [°]	70.892(2)	90
β [°]	89.038(2)	94.3942(11)
γ [°]	72.072(3)	90
V [Å^3]	3653.35(17)	4519.27(9)
Z	2	4
$D_{calc.}$ [mg m^{-3}]	1.179	1.13
Absorption coefficient [mm^{-1}]	2.323	1.95
θ range for data collection [°]	4.019 to 72.476	3.594 to 72.509
Reflections collected	48220	30357
Independent reflections	14383 [R_{int} 0.046]	8888 [R_{int} 0.027]
Reflections with $I > 2\sigma(I)$	11814	8218
Data/restraints/parameters	14383/35/850	8888/33/497
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.076, wR_2 = 0.228	R_1 = 0.045, wR_2 = 0.121
Final R indices (all data)	R_1 = 0.089, wR_2 = 0.238	R_1 = 0.048, wR_2 = 0.123
GOOF on F^2	1.11	1.049
Largest diff. peak/hole [e.Å^{-3}]	0.98 and –0.65	0.51 and –0.69

Computational Details

DFT calculations were run with Gaussian 16 (A.03).[S7] The Mg, Si and K centres were described with the Stuttgart RECPs and associated basis sets,[S8] and the 6-31G** basis set was used for all other atoms (BS1).[S9] A polarization function was also added to Si (ζ_d = 0.284) and K (ζ_d = 1.000). Initial BP86 optimizations were performed using the 'grid = ultrafine' option,[S10] with all stationary points being fully characterized via analytical frequency calculations as minima (all positive eigenvalues).

The Quantum Theory of Atoms in Molecules (QTAIM, AIMALL program[S11]) and Natural Bonding Orbital (NBO7[S12]) analyses were performed on the BP86-optmised[10b] geometry **4**·THF (DFT-optimized). The QTAIM topological analyses used wavefunction files obtained with Gaussian 16 (C.01) at the BP86/6-311++G** level, whilst NBO analyses were carried out with NBO 7 within Gaussian (C.01) at the same methodology level as the QTAIM calculations. Contour plots were generated in the AIMStudio package, using critical point (CP) visualisation threshold values of 0.02 e·Å^{-3} (solid line BCP = strong) and 0.005 e·Å^{-3} (dashed line BCP = weak). The NBO energies of donor-acceptor interactions ("$\Delta E^{(2)}$") between the various molecular fragments of the structures were estimated with second-order perturbation theory analysis of the Fock matrix in the NBO basis, as calculated by NBO7, with selected donor-acceptor NBO interactions provided. Wiberg bond indices (WBI) were calculated using NBO v7.0.

NBO Analysis of $[K(THF)_2]_2[(NNO)Mg–Mg(NNO)]$ 4·THF

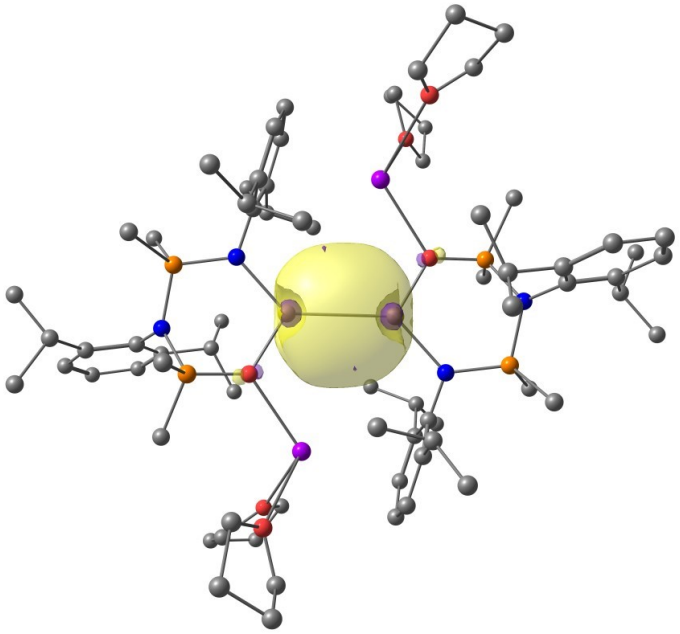


Figure S25 – NBO162 of the DFT-optimized structure of **4**·THF

- NBO-162 is a bonding orbital between Mg4 and Mg111
  - There is an equal 50% : 50% contribution from each Mg
  - From each Mg centre the atomic orbital contributions are further broken down to 93.1% (*s*) and 6.54% *p* (and 0.36% *d*)
  - There is a small (7.0 kcal/mol) NBO donor-acceptor value ($\Delta E^{(2)}$) for the Mg–Mg bonding NBO162 to the lone vacant pairs on each of the K cations

- WBI (Wiberg Bond Index) data from NBO7 calculation:
  - Mg–Mg = 0.7244
  - Mg···K = 0.0263 / 0.0237
  - K···K = 0.0004

Atom	**q(A)** (QTAIM)	**NPA** (NBO7)
K1	+0.878731	+0.88240
Mg4	+1.325278	+0.99653
K108	+0.878758	+0.88240
Mg111	+1.325655	+0.99653
NNA215	−0.717264	-

QTAIM Analysis of $[K(THF)_2]_2[(NNO)Mg–Mg(NNO)]$ 4·THF

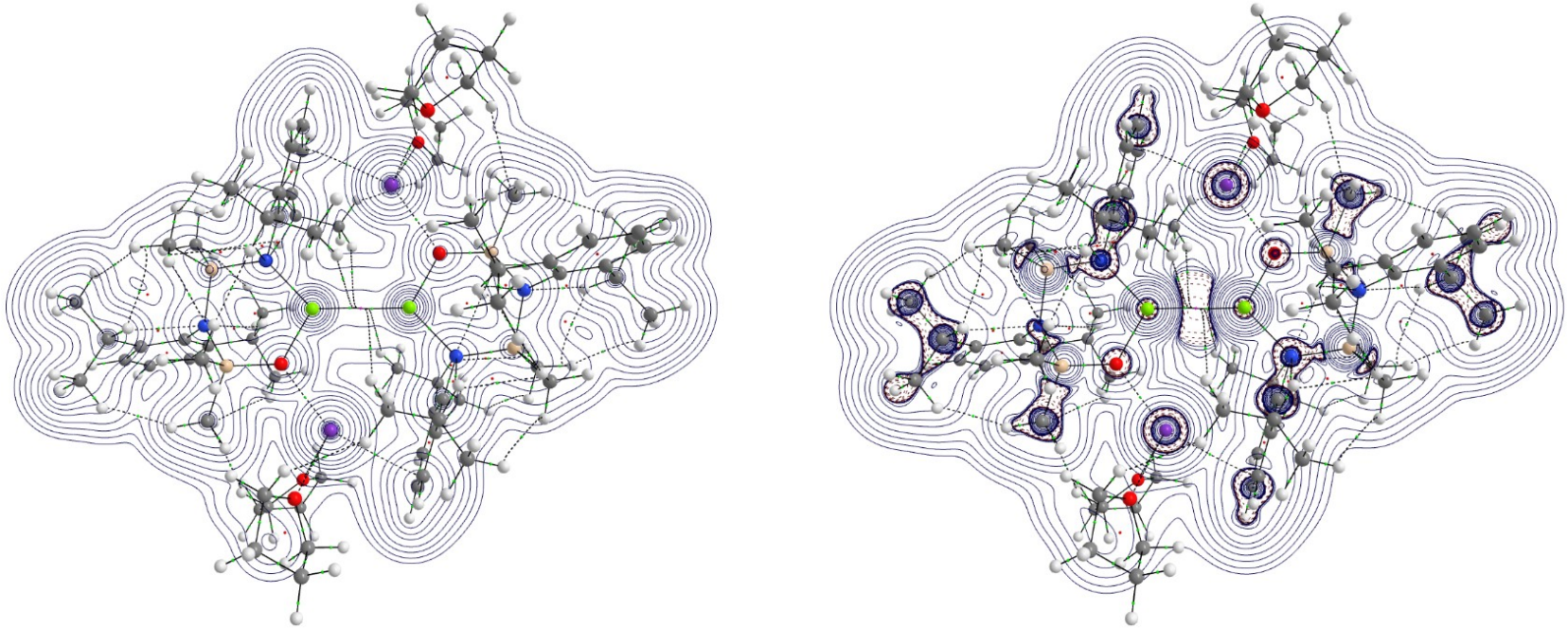


Figure S26 - Contour plots of ρ(r) (*left*) and $\nabla^2\rho(r)$ (right) of the DFT-optimized structure of **4**·THF

Figure S27 Contour plot of ρ(r) of the DFT-optimized structure of **4**·THF. All carbon atoms and their hydrogens have been omitted for clarity – with the exceptions of H22, H37, H129 and H144, which have distinct bond paths to the Non-Nuclear Attractor (NNA 215)

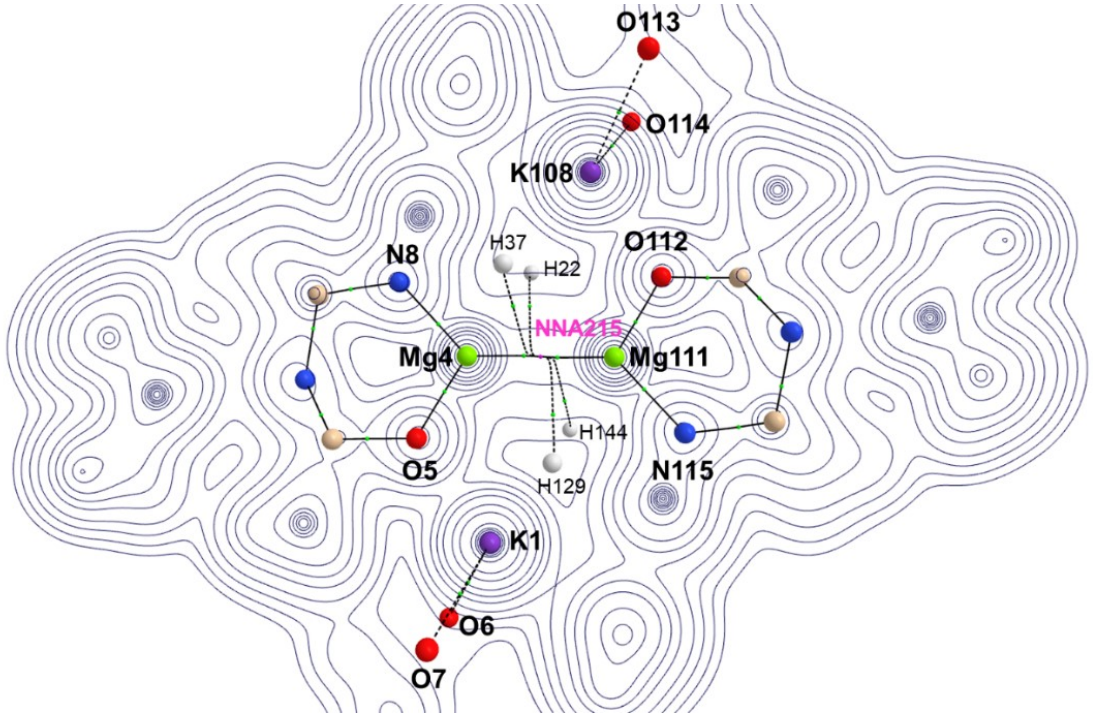


Figure S28 Contour plot of $\nabla^2\rho(r)$ of the DFT-optimized structure of **4**·THF. All carbon atoms and their hydrogens have been omitted for clarity – with the exceptions of H22, H37, H129 and H144, which have distinct bond paths to the Non-Nuclear Attractor (NNA 215).

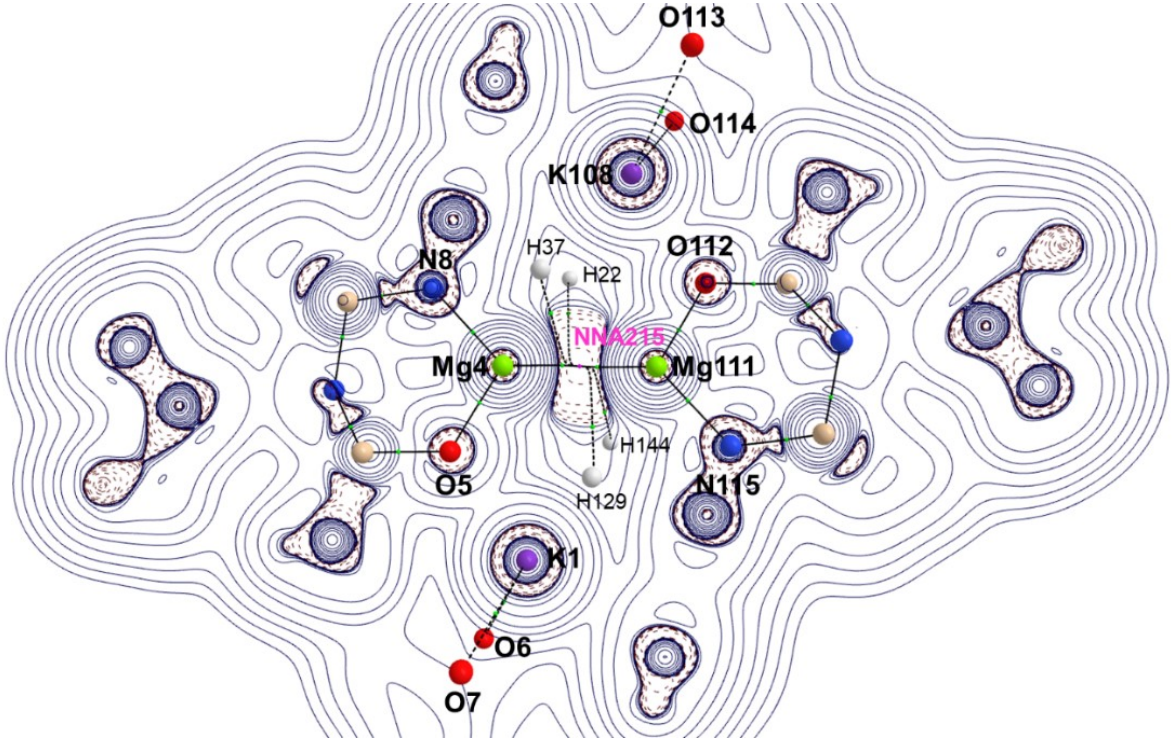


Table S3. Selected BCP data for **4**·THF

BCP	ρ(r)	$\nabla^2\rho(r)$	ε	G(r)	V(r)	H(r)
K1 - O5	0.023782	+0.107162	0.038982	+0.023763	-0.020736	-0.023571
Mg4 - O5	0.050837	+0.392784	0.021910	+0.086063	-0.073930	-0.075388
Mg4 - NNA215	0.025456	-0.012253	0.144466	+0.003893	-0.010850	-0.012261
Mg4 - N8	0.042340	+0.256764	0.117403	+0.058330	-0.052469	-0.056279
K1 - O6	0.014072	+0.061265	0.138493	+0.013007	-0.010697	-0.014236
K1 - O7	0.013795	+0.060268	0.136809	+0.012764	-0.010461	-0.013966
H22 - NNA215	0.005116	+0.005821	0.294225	+0.001407	-0.001358	-0.002393
H37 - NNA215	0.006395	+0.006039	0.342806	+0.001628	-0.001746	-0.003205
K108 - O112	0.023782	+0.107162	0.038982	+0.023763	-0.020736	-0.023571
Mg111 - O112	0.050837	+0.392784	0.021910	+0.086063	-0.073930	-0.075388
Mg111 - NNA215	0.025456	-0.012253	0.144466	+0.003893	-0.010850	-0.012261
Mg111 - N115	0.042340	+0.256764	0.117403	+0.058330	-0.052469	-0.056279
K108 - O113	0.014072	+0.061265	0.138493	+0.013007	-0.010697	-0.014236
K108 - O114	0.013795	+0.060268	0.136809	+0.012764	-0.010461	-0.013966
H129 - NNA215	0.005116	+0.005821	0.294225	+0.001407	-0.001358	-0.002393
H144 - NNA215	0.006395	+0.006039	0.342806	+0.001628	-0.001746	-0.003205

Table S4 Selected QTAIM atomic data for **4**·THF.

Atom	q(A)	L(A)	N(A)	Vol(A)	%Loc(A)
K1	+0.878731	+0.000142	18.121269	151.527358	98.441558
Mg4	+1.325278	-0.000187	10.674722	98.457146	94.374242
O5	-1.629642	+0.000013	9.629642	148.926518	91.562033
O6	-0.971093	+0.000069	8.971093	104.127090	86.698555
O7	-0.970668	+0.000011	8.970668	103.062348	86.616922
N8	-1.707230	-0.000057	8.707230	119.138343	82.871362
H22	+0.002554	+0.000051	0.997446	55.192451	41.479728
H37	-0.011090	+0.000035	1.011090	58.193534	41.412596
K108	+0.878758	+0.000170	18.121242	151.496271	98.441657
Mg111	+1.325655	+0.000005	10.674345	98.436061	94.376911
O112	-1.629928	-0.000269	9.629928	149.089365	91.560229
O113	-0.971134	+0.000033	8.971134	104.105734	86.698281
O114	-0.970594	+0.000097	8.970594	103.029328	86.617245
N115	-1.707233	-0.000049	8.707233	119.124516	82.871108
H129	+0.002544	+0.000042	0.997456	55.214332	41.479474
H144	-0.011070	+0.000052	1.011070	58.209315	41.412902
NNA215	-0.717264	-0.000122	0.717264	95.257250	31.362997

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Computed Energies and Cartesian Coordinates

4·THF
SCF (BP86) Energy = -3563.22142671
Enthalpy 0K = -3561.431761
Enthalpy 298K = -3561.310204
Free Energy 298K = -3561.608661
Lowest Frequency = 7.3216 cm^{-1}
Second Frequency = 12.6353 cm^{-1}

K	3.33391	1.43387	-1.45883
Si	-2.12500	4.32658	-0.49361
Si	0.53959	3.91775	-2.10356
Mg	-0.33360	1.40785	-0.40235
O	0.94603	2.45126	-1.44083
O	5.38689	3.21324	-0.74224
O	4.08048	1.88604	-4.13546
N	-2.03447	2.59462	-0.14229
N	-0.48517	4.89142	-0.98408
C	-3.23610	1.97454	0.26210
C	-3.62773	1.93258	1.65377
C	-4.85497	1.34897	2.02857
H	-5.14854	1.36623	3.08552
C	-5.71641	0.76540	1.08629
H	-6.68221	0.34726	1.39189
C	-5.31822	0.73994	-0.25910
H	-5.98038	0.28285	-1.00480
C	-4.10832	1.32130	-0.68882
C	-2.69726	2.46457	2.74486
H	-1.95270	3.09749	2.23427
C	-1.92636	1.29882	3.40909
H	-1.31250	0.74990	2.67009
H	-2.62667	0.58217	3.87959
H	-1.24528	1.67131	4.19598
C	-3.41168	3.30917	3.81930
H	-4.10031	2.70117	4.43472
H	-3.99572	4.13035	3.37309
H	-2.67195	3.75286	4.50873
C	-3.72475	1.22734	-2.16624
H	-2.91085	1.95831	-2.31391
C	-4.87642	1.57683	-3.13144
H	-5.30991	2.56504	-2.90778
H	-5.69220	0.83201	-3.09012
H	-4.50903	1.59349	-4.17271
C	-3.15540	-0.17115	-2.50142
H	-3.91260	-0.95852	-2.32458
H	-2.26814	-0.40374	-1.88049
H	-2.84922	-0.23184	-3.56162
C	-2.70379	5.43123	0.95065
H	-2.04326	5.39455	1.82996
H	-3.71494	5.11838	1.26377
H	-2.76606	6.48336	0.62390
C	-3.41581	4.68710	-1.86086
H	-4.38837	4.25093	-1.57123
H	-3.13637	4.27191	-2.84204
H	-3.56386	5.77378	-1.98100
C	0.06238	6.09286	-0.40544
C	-0.12183	7.35635	-1.05231
C	0.45729	8.51263	-0.49366
H	0.31136	9.47665	-0.99575
C	1.21087	8.45909	0.68346
H	1.65623	9.36901	1.10067
C	1.37878	7.22747	1.32585
H	1.95993	7.18084	2.25468
C	0.81473	6.04311	0.81175
C	-0.95163	7.50352	-2.32942
H	-1.27399	6.48933	-2.61977
C	-2.21711	8.35716	-2.08141
H	-1.95179	9.39208	-1.79969
H	-2.83476	7.94154	-1.26780
H	-2.84005	8.40799	-2.99244
C	-0.13830	8.10124	-3.49960
H	0.75862	7.49986	-3.72287
H	0.19880	9.12930	-3.27595
H	-0.75421	8.14734	-4.41547
C	1.04144	4.73746	1.57629
H	0.41071	3.96854	1.09628
C	0.63180	4.83921	3.06261
H	-0.40984	5.18157	3.17800
H	1.27572	5.54527	3.61725
H	0.72456	3.85438	3.55376
C	2.51175	4.27047	1.47712
H	3.18892	5.01162	1.94105
H	2.82703	4.13286	0.43025
H	2.64887	3.31044	2.00782
C	2.12160	4.91807	-2.48243
H	2.83232	4.26724	-3.02418
H	2.60423	5.27571	-1.55791
H	1.92009	5.79868	-3.11451
C	-0.38937	3.65355	-3.75007
H	-1.29853	3.04645	-3.60414
H	0.25688	3.10511	-4.45843
H	-0.68470	4.60625	-4.22213
C	3.21698	2.12726	-5.28574
H	2.65176	3.05948	-5.11419
H	2.49706	1.29006	-5.35865
C	4.13908	2.19520	-6.51518
H	3.64453	1.83348	-7.43084
H	4.47186	3.23276	-6.69537
C	5.33132	1.32171	-6.07696
H	6.25681	1.52944	-6.63808
H	5.08997	0.25013	-6.19107
C	5.44119	1.68837	-4.59303
H	5.89698	0.90089	-3.96874
H	6.02243	2.62444	-4.45761
C	6.06728	3.17692	0.54322
H	6.45833	2.15697	0.70347
H	5.33035	3.40052	1.33893
C	7.16599	4.24923	0.48189
H	7.40160	4.66739	1.47376
H	8.09599	3.83039	0.05765
C	6.55003	5.27692	-0.48748
H	5.80806	5.90570	0.03504
H	7.29536	5.93968	-0.95623
C	5.85289	4.36084	-1.50020
H	4.98154	4.82376	-1.99192
H	6.56314	4.02100	-2.28277
K	-3.33391	-1.43387	1.45883
Si	2.12500	-4.32658	0.49361
Si	-0.53959	-3.91775	2.10356
Mg	0.33360	-1.40785	0.40235
O	-0.94603	-2.45126	1.44083
O	-5.38689	-3.21324	0.74224
O	-4.08048	-1.88604	4.13546
N	2.03447	-2.59462	0.14229
N	0.48517	-4.89142	0.98408

C	3.23610	-1.97454	-0.26210
C	3.62773	-1.93258	-1.65377
C	4.85497	-1.34897	-2.02857
H	5.14854	-1.36623	-3.08552
C	5.71641	-0.76540	-1.08629
H	6.68221	-0.34726	-1.39189
C	5.31822	-0.73994	0.25910
H	5.98038	-0.28285	1.00480
C	4.10832	-1.32130	0.68882
C	2.69726	-2.46457	-2.74486
H	1.95270	-3.09749	-2.23427
C	1.92636	-1.29882	-3.40909
H	1.31250	-0.74990	-2.67009
H	2.62667	-0.58217	-3.87959
H	1.24528	-1.67131	-4.19598
C	3.41168	-3.30917	-3.81930
H	4.10031	-2.70117	-4.43472
H	3.99572	-4.13035	-3.37309
H	2.67195	-3.75286	-4.50873
C	3.72475	-1.22734	2.16624
H	2.91085	-1.95831	2.31391
C	4.87642	-1.57683	3.13144
H	5.30991	-2.56504	2.90778
H	5.69220	-0.83201	3.09012
H	4.50903	-1.59349	4.17271
C	3.15540	0.17115	2.50142
H	3.91260	0.95852	2.32458
H	2.26814	0.40374	1.88049
H	2.84922	0.23184	3.56162
C	2.70379	-5.43123	-0.95065
H	2.04326	-5.39455	-1.82996
H	3.71494	-5.11838	-1.26377
H	2.76606	-6.48336	-0.62390
C	3.41581	-4.68710	1.86086
H	4.38837	-4.25093	1.57123
H	3.13637	-4.27191	2.84204
H	3.56386	-5.77378	1.98100
C	-0.06238	-6.09286	0.40544
C	0.12183	-7.35635	1.05231
C	-0.45729	-8.51263	0.49366
H	-0.31136	-9.47665	0.99575
C	-1.21087	-8.45909	-0.68346
H	-1.65623	-9.36901	-1.10067
C	-1.37878	-7.22747	-1.32585
H	-1.95993	-7.18084	-2.25468
C	-0.81473	-6.04311	-0.81175
C	0.95163	-7.50352	2.32942
H	1.27399	-6.48933	2.61977
C	2.21711	-8.35716	2.08141
H	1.95179	-9.39208	1.79969
H	2.83476	-7.94154	1.26780
H	2.84005	-8.40799	2.99244
C	0.13830	-8.10124	3.49960
H	-0.75862	-7.49986	3.72287
H	-0.19880	-9.12930	3.27595
H	0.75421	-8.14734	4.41547
C	-1.04144	-4.73746	-1.57629
H	-0.41071	-3.96854	-1.09628
C	-0.63180	-4.83921	-3.06261
H	0.40984	-5.18157	-3.17800
H	-1.27572	-5.54527	-3.61725
H	-0.72456	-3.85438	-3.55376
C	-2.51175	-4.27047	-1.47712
H	-3.18892	-5.01162	-1.94105
H	-2.82703	-4.13286	-0.43025
H	-2.64887	-3.31044	-2.00782
C	-2.12160	-4.91807	2.48243
H	-2.83232	-4.26724	3.02418
H	-2.60423	-5.27571	1.55791
H	-1.92009	-5.79868	3.11451
C	0.38937	-3.65355	3.75007
H	1.29853	-3.04645	3.60414
H	-0.25688	-3.10511	4.45843
H	0.68470	-4.60625	4.22213
C	-3.21698	-2.12726	5.28574
H	-2.65176	-3.05948	5.11419
H	-2.49706	-1.29006	5.35865
C	-4.13908	-2.19520	6.51518
H	-3.64453	-1.83348	7.43084
H	-4.47186	-3.23276	6.69537
C	-5.33132	-1.32171	6.07696
H	-6.25681	-1.52944	6.63808
H	-5.08997	-0.25013	6.19107
C	-5.44119	-1.68837	4.59303
H	-5.89698	-0.90089	3.96874
H	-6.02243	-2.62444	4.45761
C	-6.06728	-3.17692	-0.54322
H	-6.45833	-2.15697	-0.70347
H	-5.33035	-3.40052	-1.33893
C	-7.16599	-4.24923	-0.48189
H	-7.40160	-4.66739	-1.47376
H	-8.09599	-3.83039	-0.05765
C	-6.55003	-5.27692	0.48748
H	-5.80806	-5.90570	-0.03504
H	-7.29536	-5.93968	0.95623
C	-5.85289	-4.36084	1.50020
H	-4.98154	-4.82376	1.99192
H	-6.56314	-4.02100	2.28277