

Structural complexity of the magnesiumation of furan: an octadecanuclear product with a subporphyrin-like $\text{Mg}_3(2,5\text{-fur-di-yl})_3$ substructure

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Supplementary Information

General Methods

n-Hexane and furan was distilled from sodium/benzophenone. All synthetic work was carried out under an inert argon atmosphere using standard Schlenk techniques. $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ was prepared from the Grignard reagent $(\text{Me}_3\text{SiCH}_2)\text{MgCl}$ by manipulation of the Schlenk equilibrium via the dioxane precipitation method. The resultant off white solid was purified via sublimation at 175°C (10^{-2} torr) to furnish pure $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$. Elemental analyses were attempted using a Perkin Elmer 2400 elemental analyzer however, due to the extreme air-sensitivity of of compounds **3** and **4** satisfactory analyses could not be obtained.

Synthesis of $[(\text{TMEDA})\cdot\text{Na}(\text{CH}_2\text{SiMe}_3)(\text{TMP})\text{Mg}(\text{TMP})] \mathbf{3}$

TMPH (0.36mL, 2mmol) was added to a suspension of BuNa (0.08g, 1mmol) in dry *n*-hexane (20mL) and the resultant mixture was allowed to stir at room temperature for 1 h. $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ (0.2g, 1mmol) and TMEDA (0.15mL, 1mmol) was added to give a light yellow/orange solution and the resultant solution was allowed to stir for 12 hrs at room temperature. The reaction mixture was filtered and subsequent removal of the solvent *in vacuo* gave a crop of large colourless crystals (0.1g, 19%).

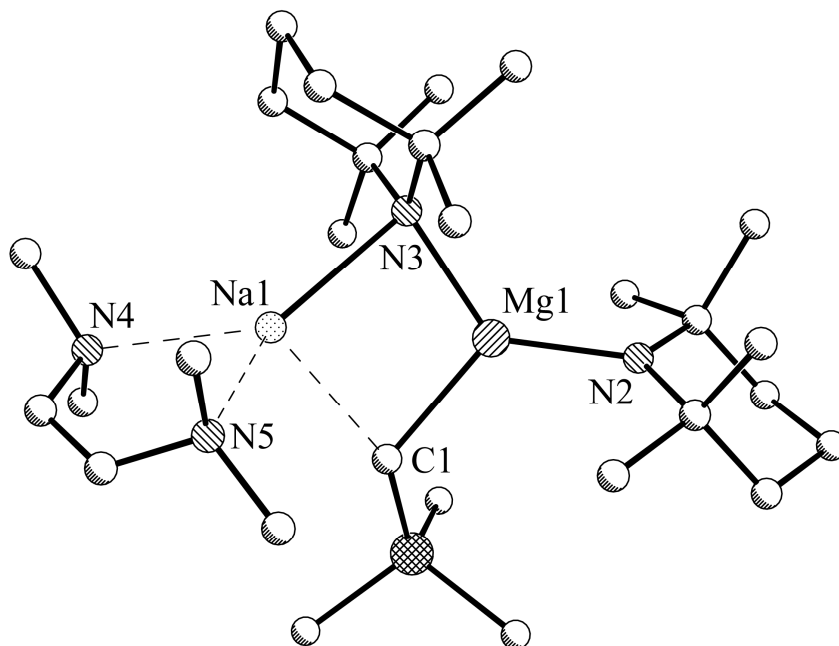


Figure 1 Crystal structure of [(TMEDA).Na(CH₂SiMe₃)(TMP)Mg(TMP)] **3**

Crystallographic Data

Table 1: Selected bond lengths and bond angles of Compound **3**

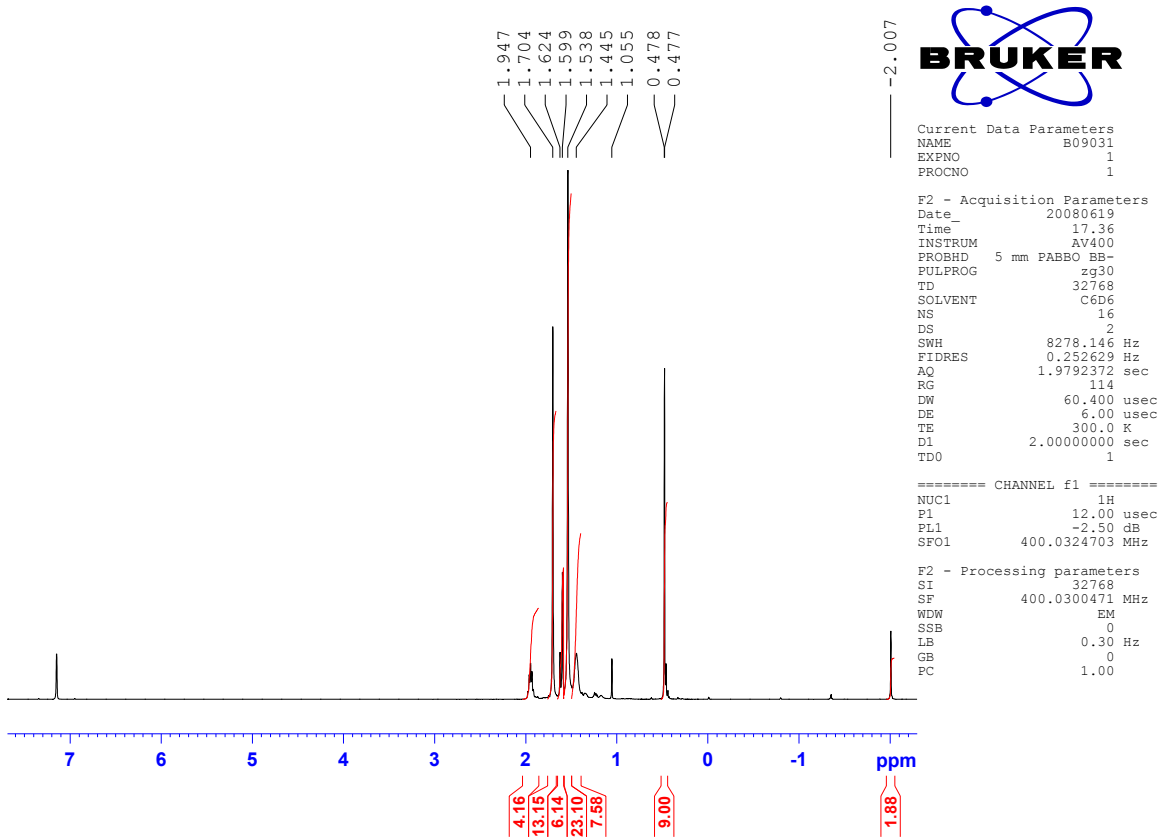
Selected Bond lengths Å		Selected Bond Angles °	
Mg1-C1	2.179(2)	N3-Mg1-N2	128.70(14)
Mg1-N2	1.9895(18)	N3-Mg1-C1	106.67(13)
Mg1-N3	2.068(3)	N2-Mg1-C1	123.36(10)
Na1-N3	2.454(4)	N3-Na1-C1	83.08(9)
Na1-C1	2.678(2)	N3-Na1-N5	138.90(13)
Na1-N4	2.433(2)	N3-Na1-N4	139.70(12)
Na1-N5	2.488(3)	C1-Na1-N5	100.81(12)
		C1-Na1-N4	115.48(10)
		N5-Na1-N4	75.48(12)

Data for **3** were measured on a Nonius Kappa CCD instrument and for **4** on an Oxford Diffraction Xcalibur S. Both datasets were measured at 123K with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All non-H atoms were refined anisotropically – except where disorder precluded this. Brief details are given below – with full data available in cif format.

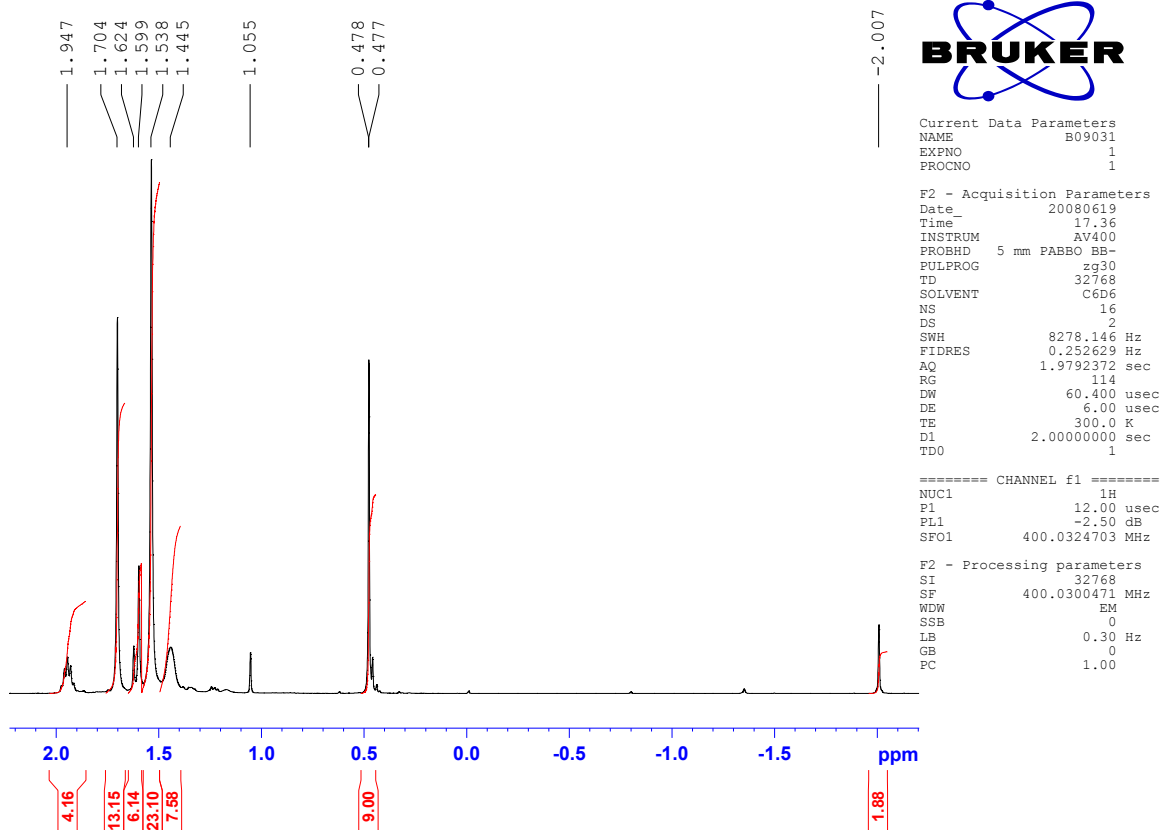
Crystal data for **3**: C₂₈H₆₃Mg₁N₄Na₁Si₁, $M_r = 531.21$, orthorhombic, space group Pna2₁, $a = 14.8470(2)$, $b = 19.3771(3)$, $c = 12.0280(4) \text{ \AA}$, $V = 3460.34(14) \text{ \AA}^3$, $Z = 4$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 0.119 \text{ mm}^{-1}$, $T = 123 \text{ K}$; 7665 reflections; final refinement to convergence on F^2 gave $R = 0.0495$ (F , 6037 obs. data only) and $R_w = 0.1210$ (F^2 , all data), GOF = 1.048. The bridging TMP ligand was modeled as disordered over two sites using SADI and SAME restraints. Refined occupancy 0.85(5):0.15(5).

Crystal data for **4**: C₁₀₈H₁₆₀Mg₆N₁₂Na₁₂O₁₆Si₂, $M_r = 2360.40$, triclinic, space group P $\bar{1}$, $a = 15.5127(6)$, $b = 16.7993(7)$, $c = 17.7608(8) \text{ \AA}$, $\alpha = 61.930(5)$, $\beta = 73.749(4)$, $\gamma = 63.757(4)^\circ$, $V = 3648.0(3) \text{ \AA}^3$, $Z = 1$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 0.140 \text{ mm}^{-1}$, $T = 123 \text{ K}$; 21042 reflections, 12205 unique, $R_{\text{int}} 0.0234$; final refinement to convergence on F^2 gave $R = 0.0565$ (F , 7447 obs. data only) and $R_w = 0.1662$ (F^2 , all data), GOF = 0.969. One TMEDA, two furans and a Na atom are modeled as disordered, each over two sites with site occupancies set to 0.5. The program SQUEEZE was implemented in PLATON to remove the equivalent of 8 electrons from solvent accessible voids totaling 561 \AA^3 . The chemical identity of this “solvent” was not apparent.

¹H NMR (400MHz, d₆-benzene, 300K): δ 1.95 (q, 4H, γ-CH₂, TMP) 1.70 (12H, CH₃, TMEDA), 1.60 (s, 4H, CH₂, TMEDA), 1.52 (s, 24H, CH₃ TMP), 1.44 (s (br), β-CH₂, TMP), 0.48 (s, 12H, CH₃ CH₂SiMe₃), -2.00 (s, 2H, CH₂, CH₂SiMe₃).

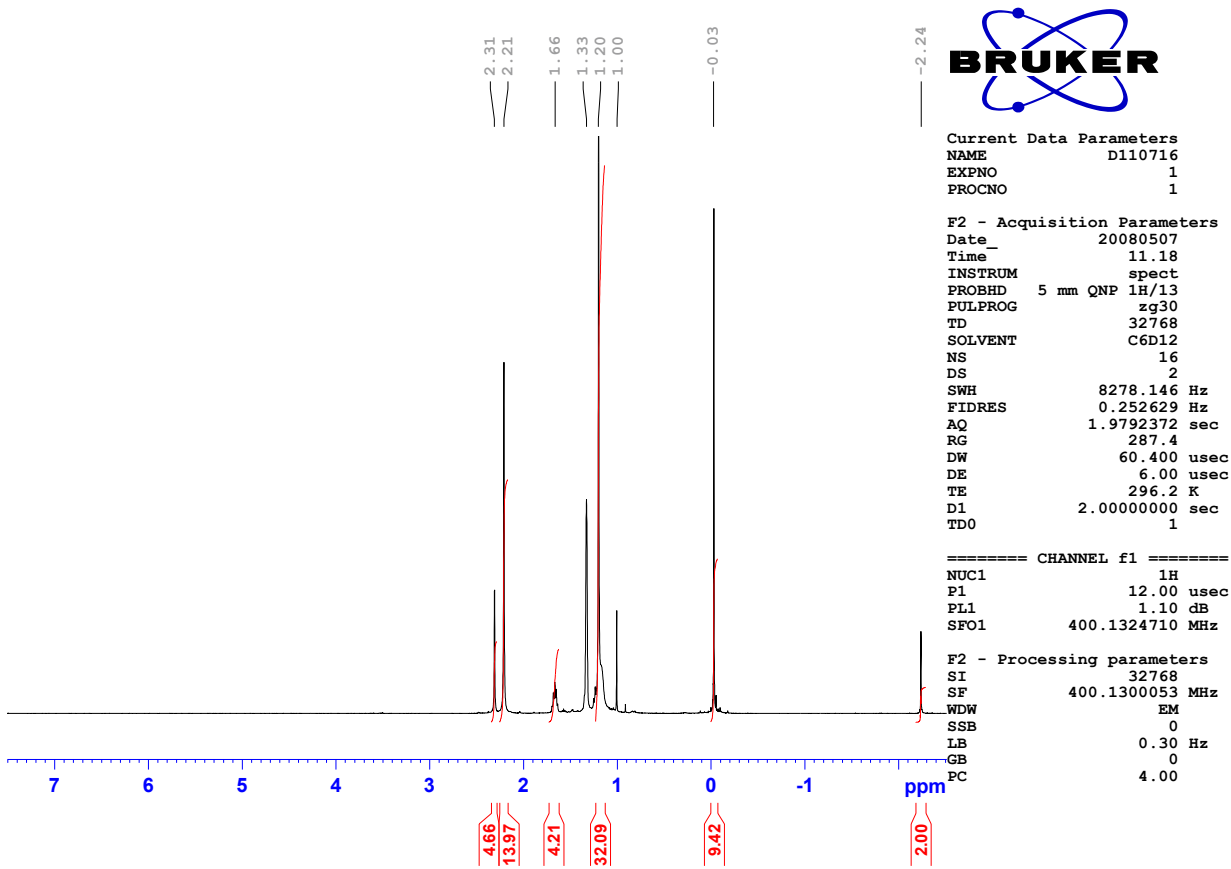


¹H NMR spectrum (400MHz, d₆-benzene, 300K) Compound 3



¹H NMR-spectrum, aliphatic region (400MHz, d₆-benzene, 300K) Compound 3

^1H NMR (400MHz, d_{12} -cyclohexane, 300K): δ 2.31 (s, 4H, CH_2 , TMEDA), 2.21 (s, 12H, CH_3 , TMEDA), 1.66 (q, 4H, $\gamma\text{-CH}_2$, TMP), 1.20 (s (br), 32H, overlapping CH_3 and $\beta\text{-CH}_2$, TMP), -0.03 (s, 12H, CH_3 , CH_2SiMe_3), -2.24 (s, 2H, CH_2 , CH_2SiMe_3).



^1H NMR spectrum (400MHz, d_{12} -cyclohexane, 300K) Compound 3

Synthesis of $[\{(\text{TMEDA})_3\text{Na}_6\text{Mg}_3(\text{CH}_2\text{SiMe}_3)(2,5\text{-C}_4\text{H}_2\text{O})_3(2\text{-C}_4\text{H}_3\text{O})_5\}_3]4$

TMPH (0.36mL, 2mmol) was added to a suspension of BuNa (0.08g, 1mmol) in dry n-hexane (20mL) and the resultant mixture was allowed to stir at room temperature for 1h. $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ (0.2g, 1mmol), TMEDA (0.15mL, 1mmol) and furan (0.07mL, 1mmol) was added. The resultant cloudy solution was gently heated for 5 mins and allowed to cool to room temperature depositing a crop of large colourless crystals (0.07g, 48%).

On repeating the reaction but allowing the solution to stir at room temperature for 12hrs, a white solid can be isolated as the title compound in a higher yield (0.11g, 75%).

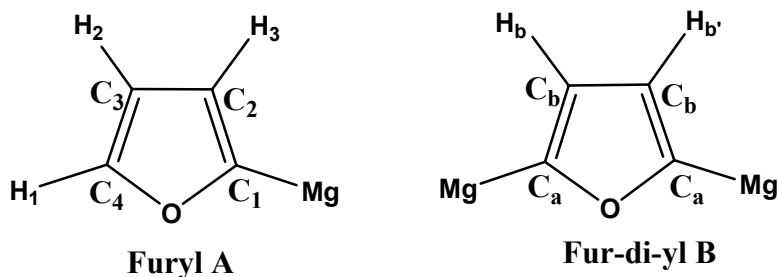
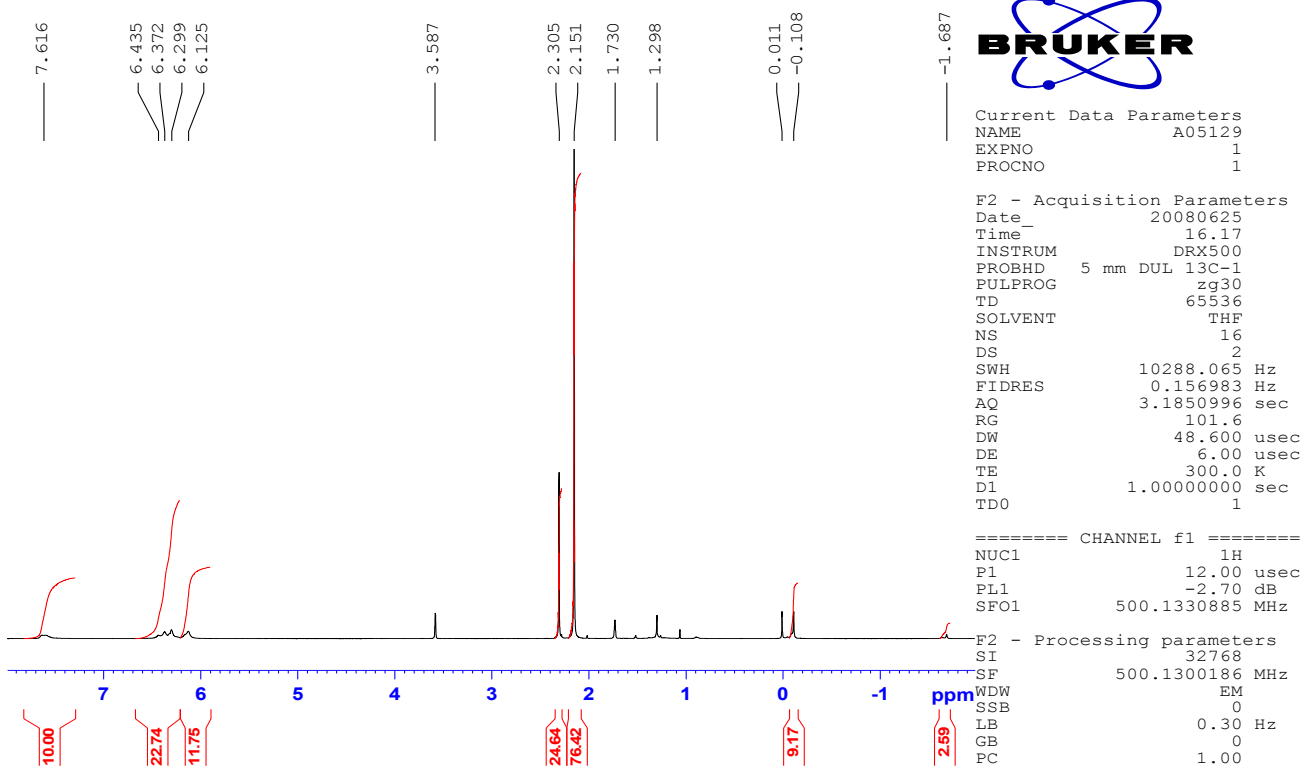
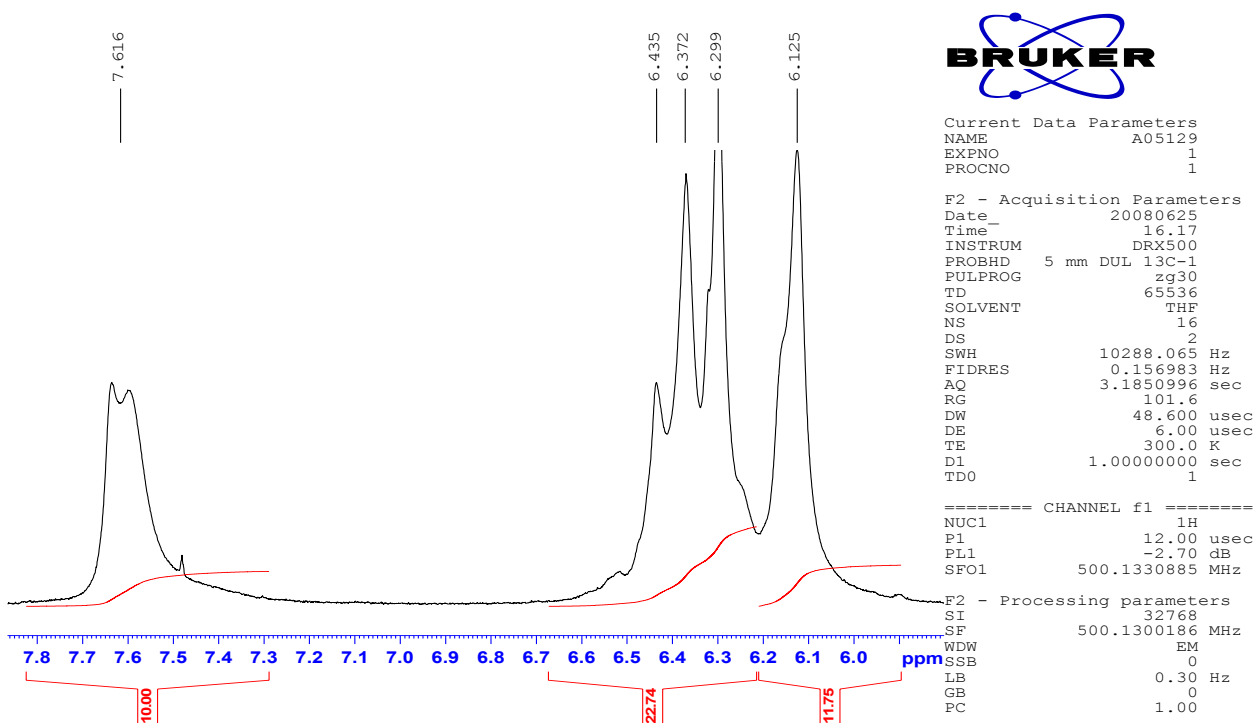


Figure 2: Numbering scheme for Compound **4** used in the ^1H and ^{13}C NMR interpretation.

^1H NMR spectrum (500MHz, d_8 -THF, 300K): δ 7.61 (s (br), 10H, H₃, furyl A), 6.37 (t, 10H, H₂ furyl A), 6.29 (s, 12H H_{b+b'}, furyl B), 6.12 (s (br), 10H, H₁ furyl A), 2.30 (s, 24H, CH₂, TMEDA), 2.15 (s, 75H, CH₃, TMEDA), -0.10 (s, 9H, CH₃, CH₂Si(CH₃)₃), -1.62 (s, 2H, CH₂, CH₂Si(CH₃)₃)

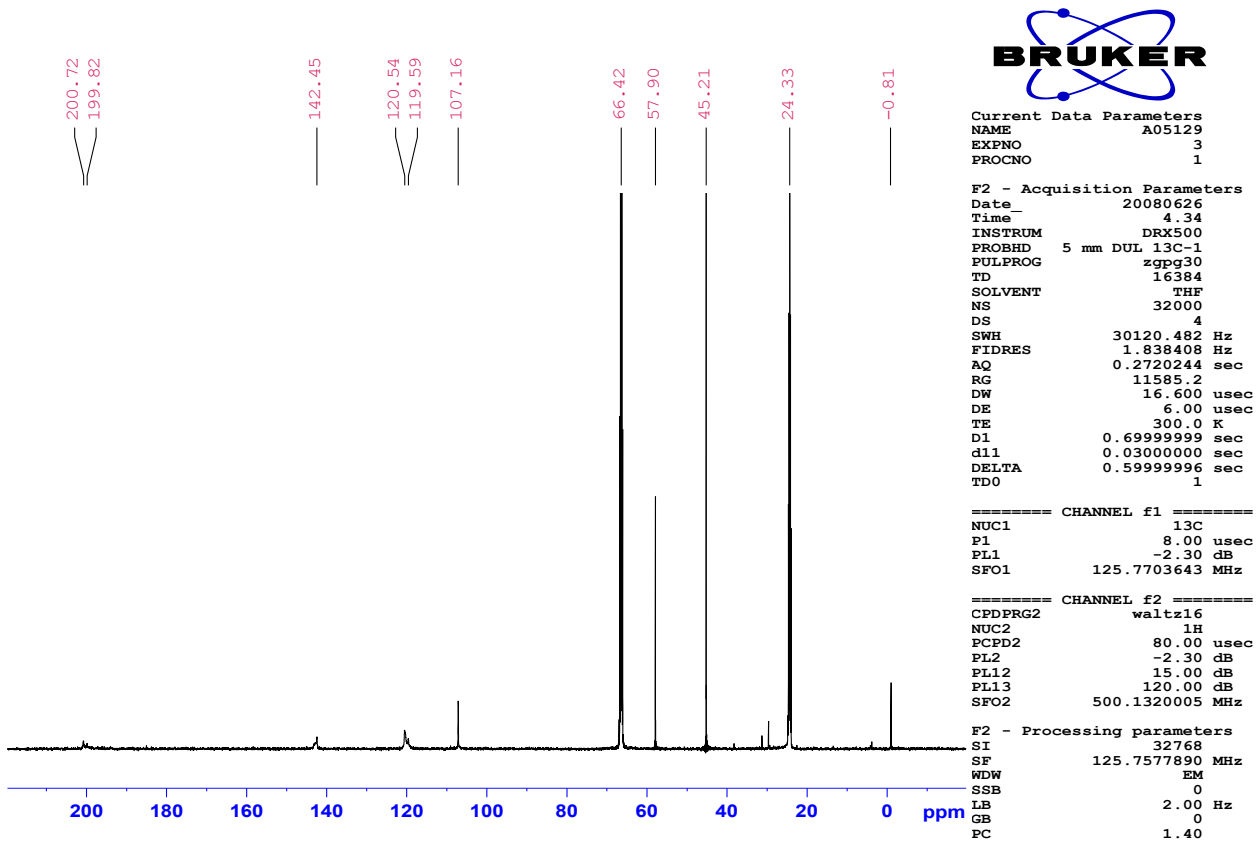


¹H NMR spectrum (500MHz, d₈-THF, 300K) Compound 4

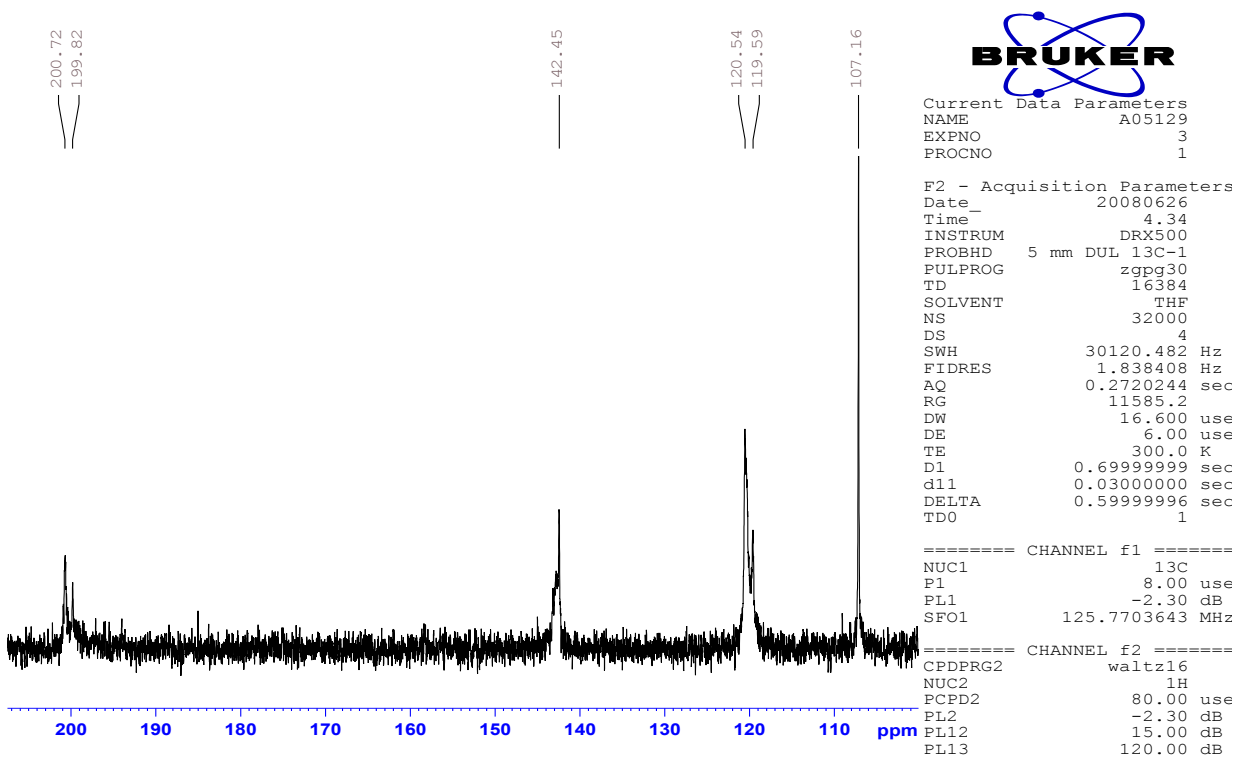


¹H NMR- spectrum, aromatic region (500MHz, d₈-THF, 300K) Compound 4

^{13}C NMR spectrum (500MHz, d_8 -THF, 300K): 200.7, 199.8 (C-Mg from C_1 , furyl A + C_a , furyl B) 142.5 (C_2 , furyl A), 120.5 (C_b , furyl B), 119.6 (C_4 , furyl A), 107.2 (C_3 , furyl A)
A)



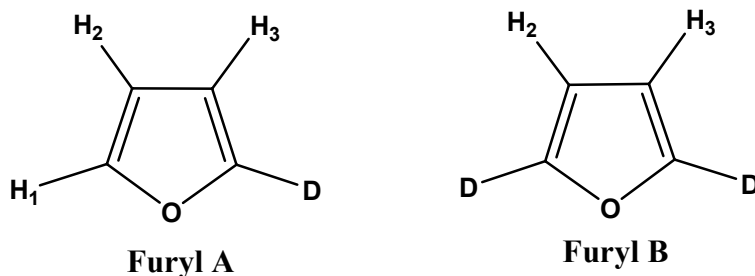
^{13}C NMR (500MHz, d_8 -THF, 300K) Compound 4



^{13}C NMR spectrum, aromatic region (500MHz, d_8 -THF, 300K) Compound 4

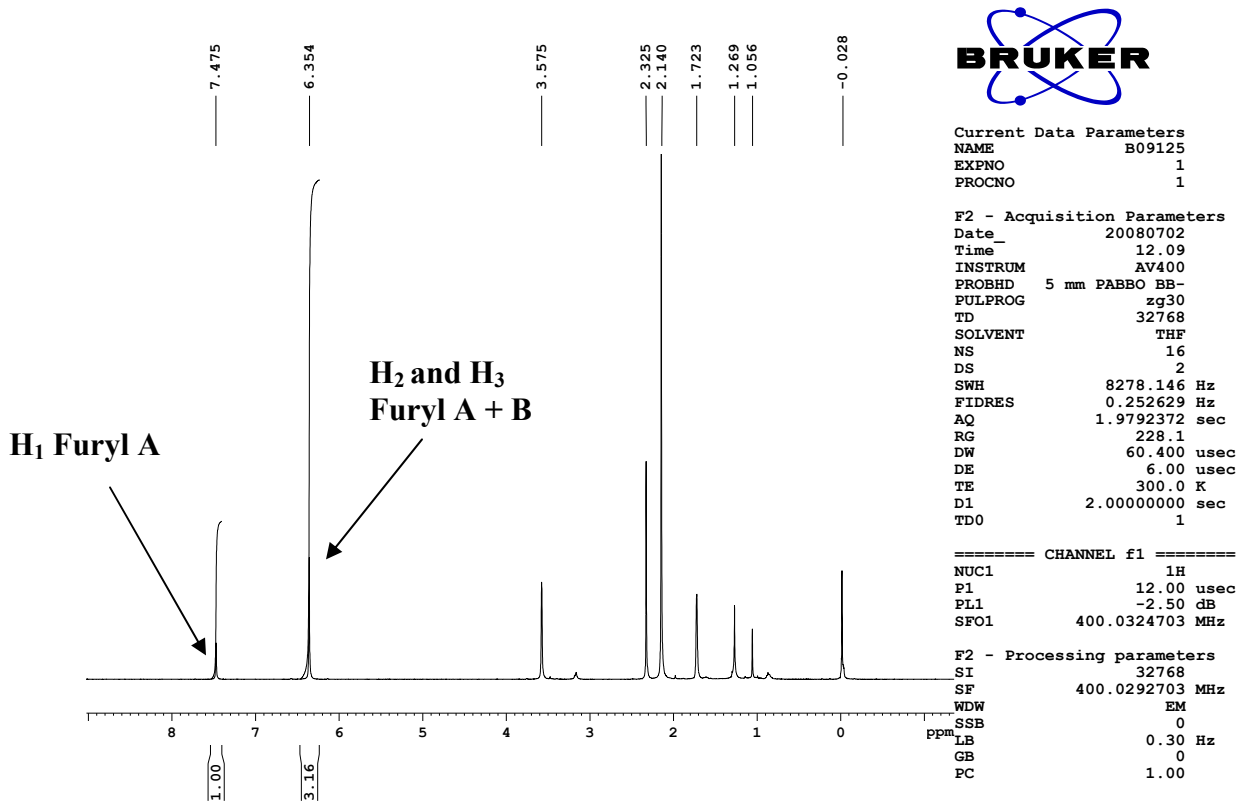
Deuterium Quench of Compound 4:

To a d_8 -THF NMR sample of Compound 4 we added a drop of D_2O to quench the metallated furans. From this we expected to see two products Furyl A and Furyl B.



From the molecular formula of Compound 4 we would expect 10 of Furyl A and 6 of Furyl B. In both Furyls A and B the protons labelled H_2 and H_3 come at the same chemical shift and are thus equivalent. Furyl A would have 20 protons in total from H_2 and H_3 , while Furyl B would have 10 protons from H_2 and H_3 , giving a total of 32 protons. Furyl A also has another proton H_1 , which is not present in Furyl B so would be

expected to come as a separate signal in the spectrum. The overall integrals of 32:10 equating to 3.2:1 would be expected and indeed can be seen in the spectrum below.



¹H NMR spectrum (500MHz, d₈-THF, 300K) Compound 4 + D₂O