Supporting Information

Thermal stability and structural studies on the mixtures of $Mg(BH_4)_2$ and glymes

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^{11}B NMR analysis of thermolysis of 1:1 $Mg(BH_4)_2$:G4

Inside a nitrogen-filled glovebox, to an oven-dried 3 mL scintillation vial added $Mg(BH_4)_2$ (40.0 mg, 0.740 mmol) and G4 (740 μL, 0.740 mmol). The resulting viscous solids thorough mixed with a spatula and transferred to a 25 mL Schlenk tube. The Schlenk tube was removed from the glovebox, placed briefly under vacuum to evacuate the gas space, and transferred to a preheated aluminum block at 180 ºC for 8 h. The sample was returned to the glovebox. Solids from the mixture was placed into a vial, dissolved in 2:1 D_2O: THF for ^{11}B NMR analysis (25 ºC).

^{11}B NMR analysis of 0.5 M $Mg(BH_4)_2$ in G1

Inside a nitrogen-filled glovebox, to an oven-dried 3 mL scintillation vial was added $Mg(BH_4)_2$ (20.0 mg, 0.370 mmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (ArBpin) (75.5 mg, 0.370 mmol) as an internal standard. The solids were dissolved in G1 (740 μL) and the resulting colorless solution was added to an oven-dried J. Young NMR tube and analyzed by ^{11}B NMR spectroscopy at 25 ºC.

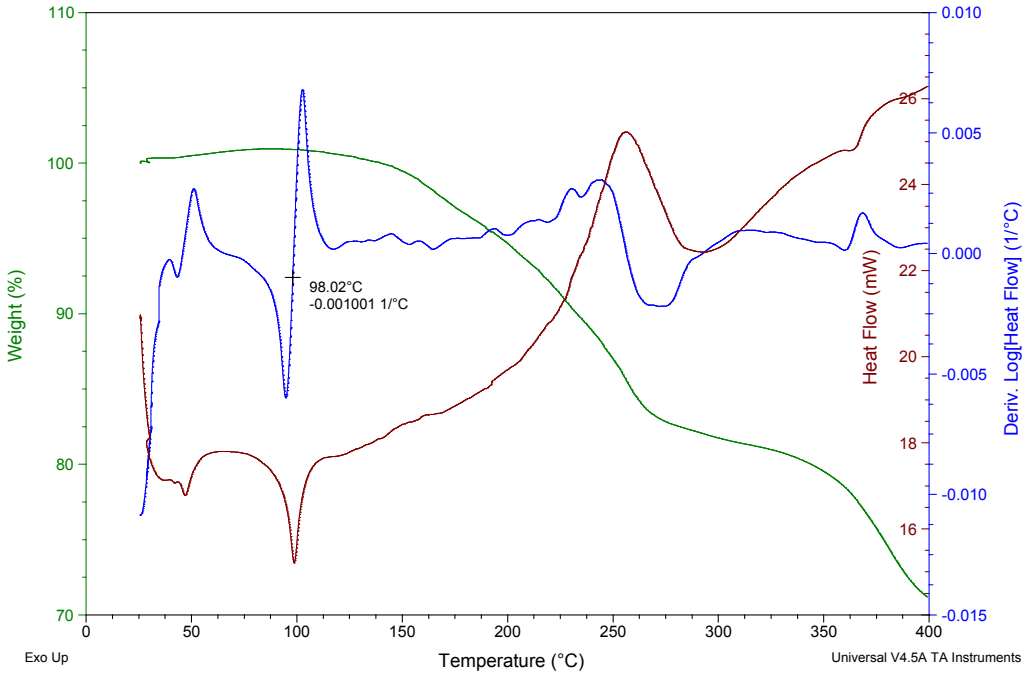


Figure S1. DSC-TGA data for $Mg(BH_4)_2$-0.5 THF.

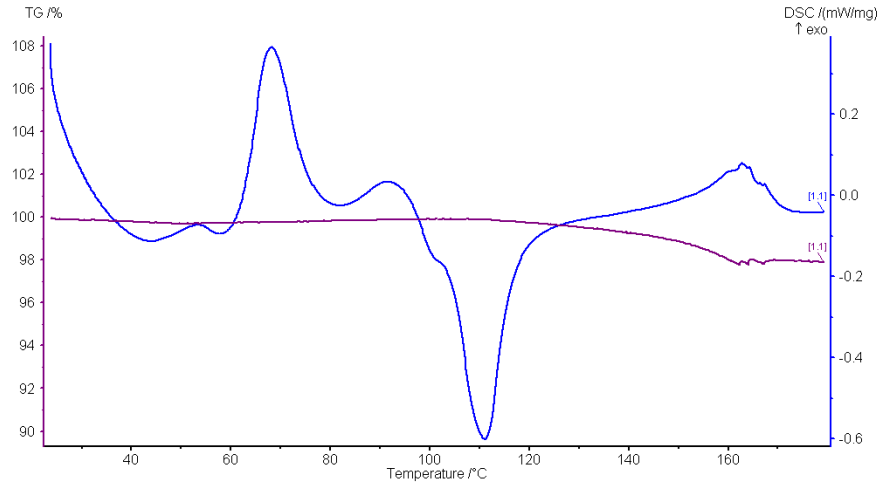


Figure S2. Open-system DSC-TGA data for 1:1 $Mg(BH_4)_2$-G1.

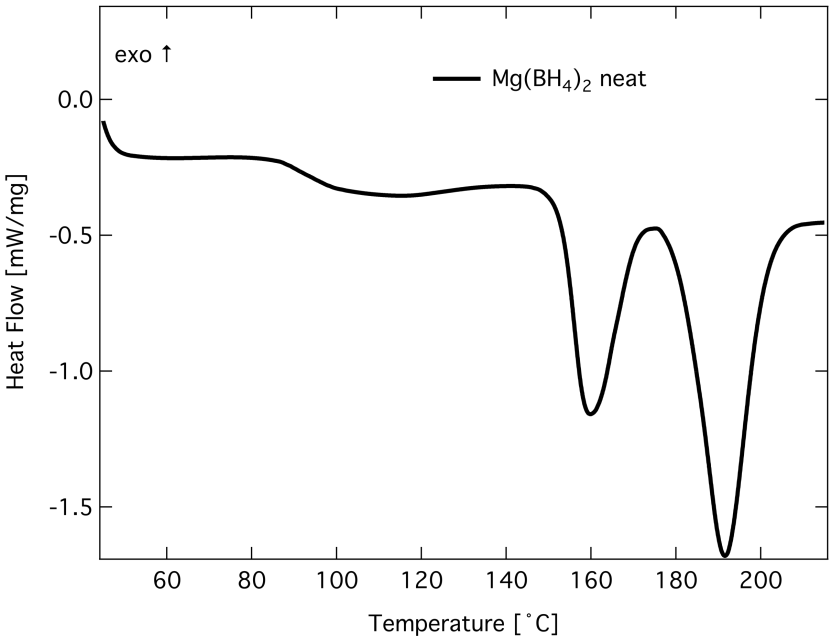


Figure S3. DSC data for neat $Mg(BH_4)_2$.

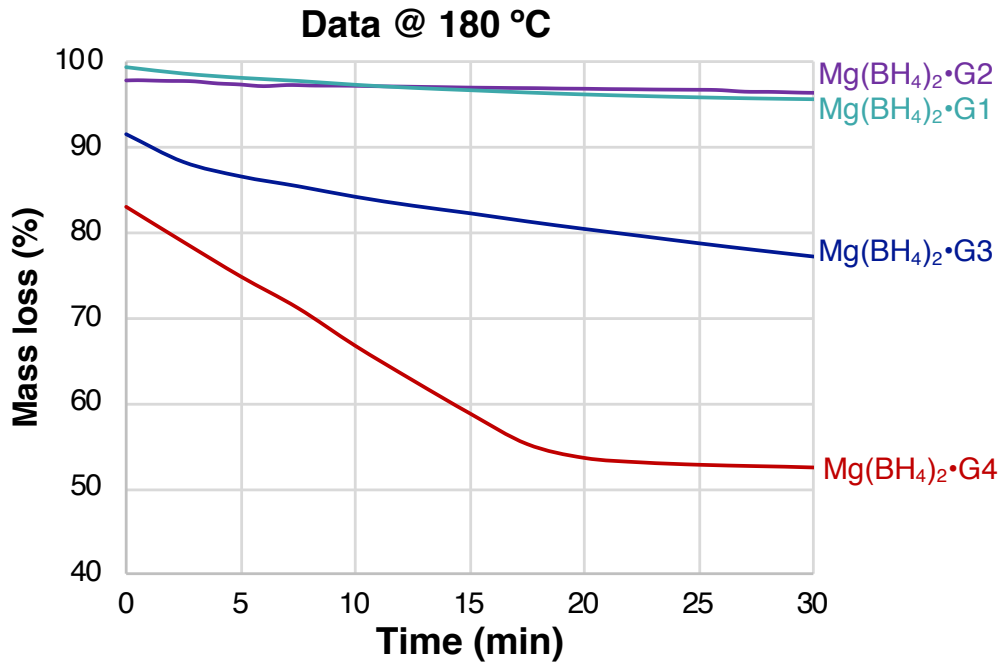


Figure S4. TGA data for 1:1 $Mg(BH_4)_2$:Gn (n = 1-4). Ramp rate 5 °C/min and held at 180 °C.

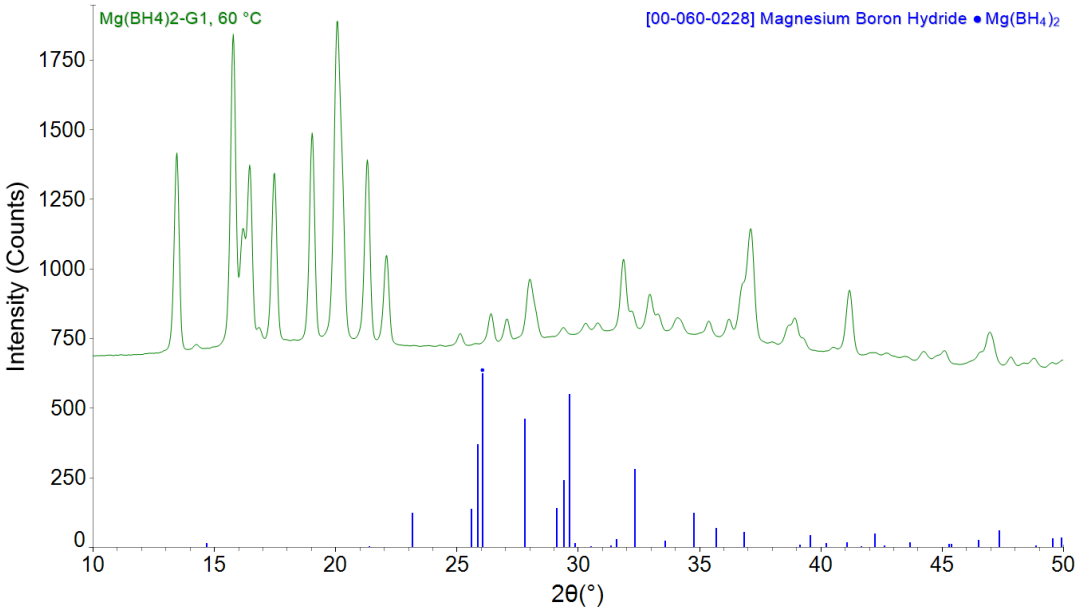


Figure S5. Comparison of the XRD data of 1:1 $Mg(BH_4)_2$:G1 at 60 °C to that of α-$Mg(BH_4)_2$.

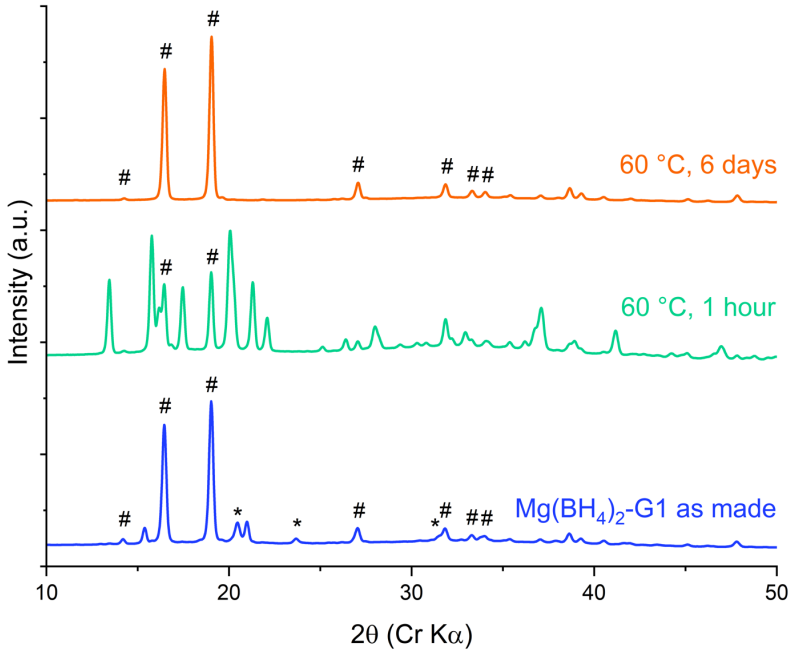


Figure S6. Heating 1:1 $Mg(BH_4)_2$-G1 at 60 ºC at 1 h and 6 days. Prolonged heating at 60 ºC for 6 days formed mostly $Mg(BH_4)_2$-1.5G1.

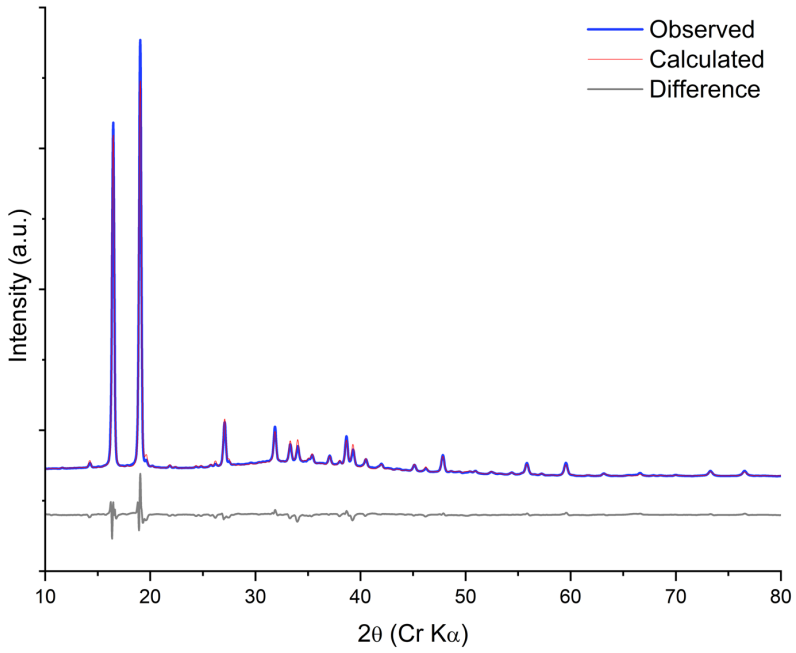


Figure S7. Rietveld fit of the powder XRD analysis of 1:1 $Mg(BH_4)_2$:G1 at 70 ºC to support the formation of 1:1 $Mg(BH_4)_2$-1.5G1.

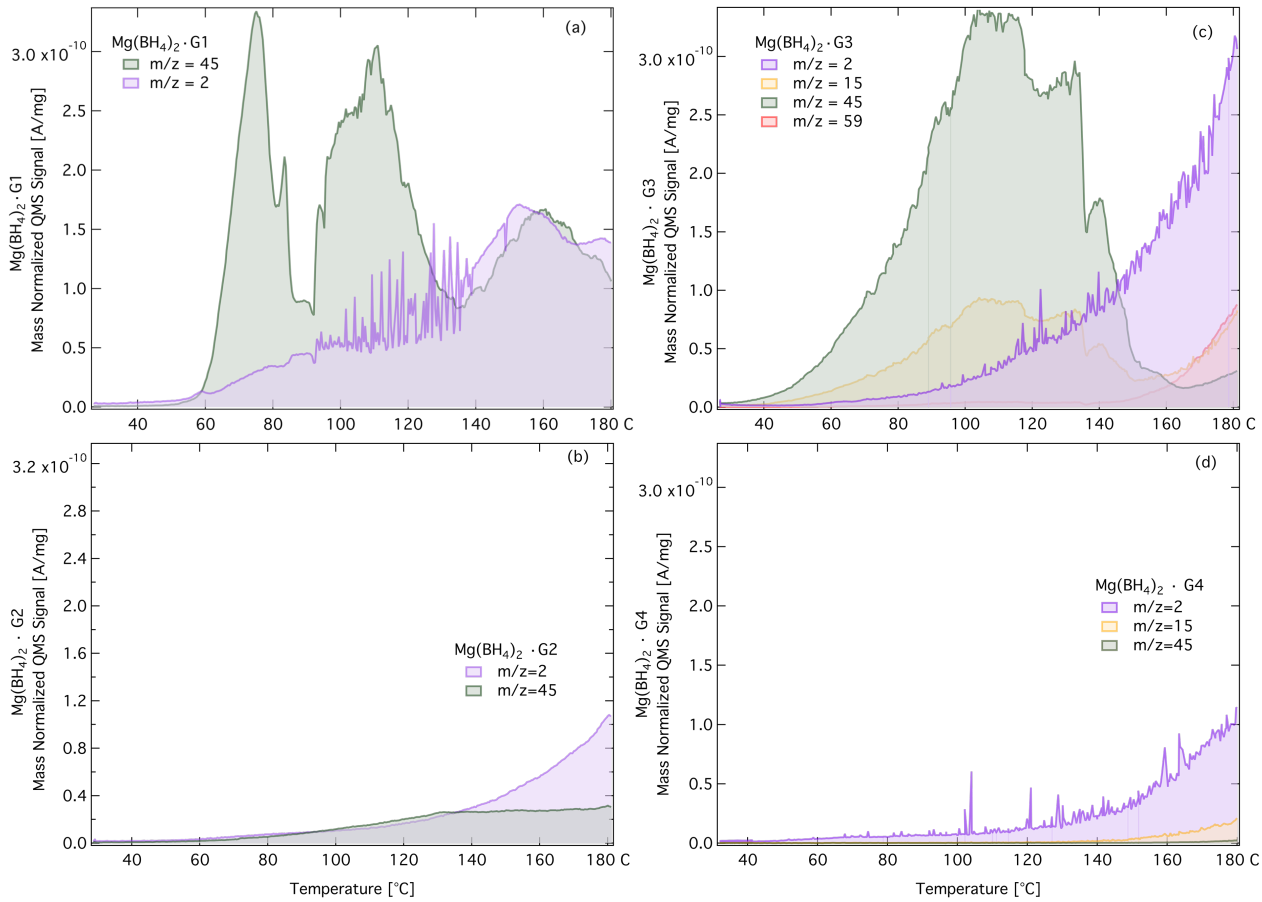


Figure S8. Mass normalized signal from the QMS for m/z = 45, representative of the glymes, and m/z = 2 (H_2) for all samples, and m/z=15 (CH_3) and m/z=59 (G3) for the last 2 samples recorded during heating of (a) $Mg(BH_4)_2$·G1, (b) $Mg(BH_4)_2$·G2, (c) $Mg(BH_4)_2$·G3, and (d) $Mg(BH_4)_2$·G4 at 5 °C/min to 180 °C.

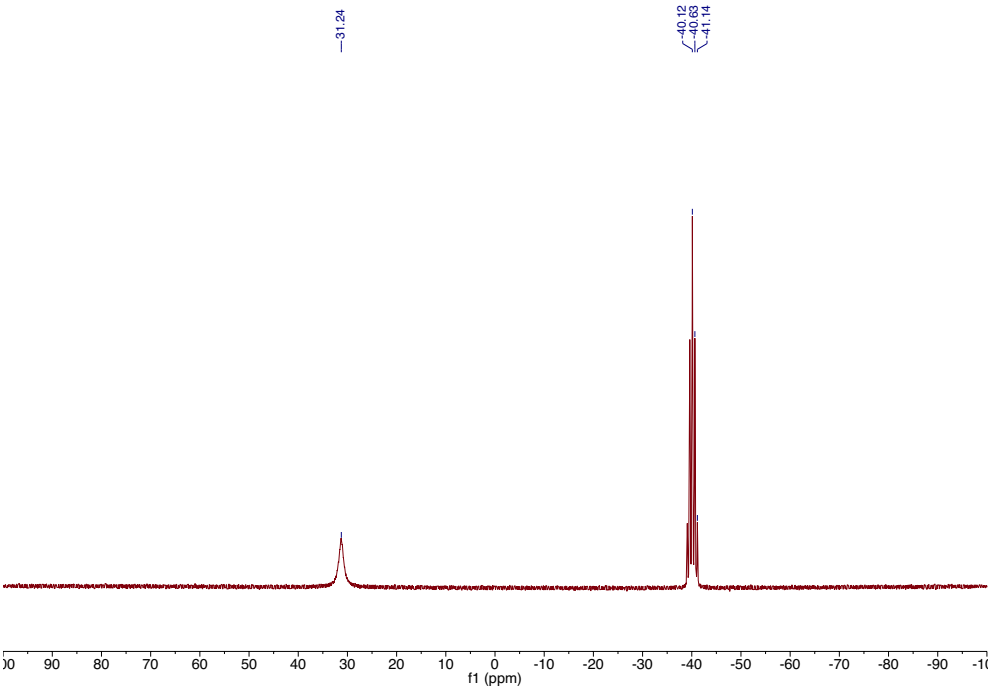


Figure S9. ^{11}B NMR (25 ºC) of 0.5 M of $Mg(BH_4)_2$ (0.37 mmol) in G1. Internal standard of ArBpin (0.37 mmol) = 31.2 ppm.

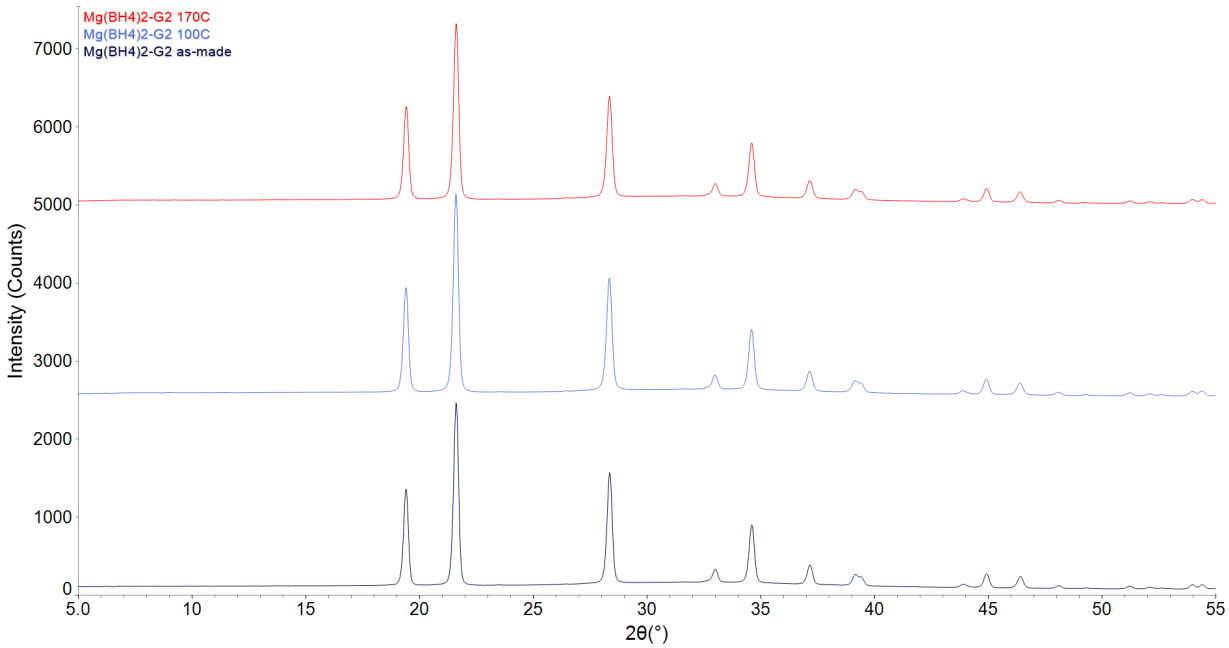


Figure S10. Powder XRD analysis of 1:1 $Mg(BH_4)_2$:G2 at 25 ºC (dark blue), 100 ºC (light blue) and 170 ºC (red).

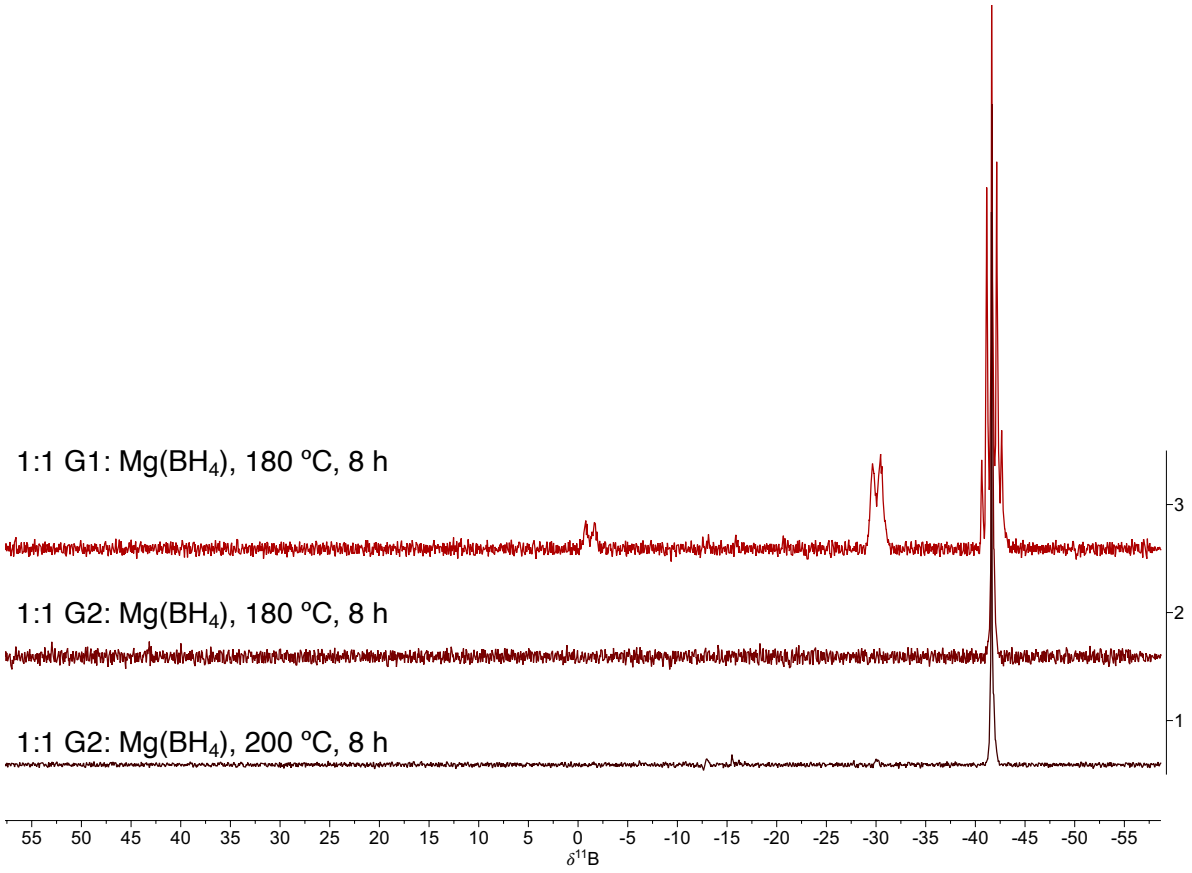


Figure S11. ^{11}B NMR (25 ºC) analysis of the post reaction of 1:1 $Mg(BH_4)_2$:G1 at 180 ºC for 8 h 2:1 D_2O: THF. $^{11}B\{^1H\}$ NMR (25 ºC, 2:1 D_2O: THF) analysis of the post reaction of 1:1 $Mg(BH_4)_2$:G2 at 180 ºC and 200 ºC for 8 h. These results highlight the thermal stability of 1:1 $Mg(BH_4)_2$:G2 to that of 1:1 $Mg(BH_4)_2$:G1 towards dehydrogenation.

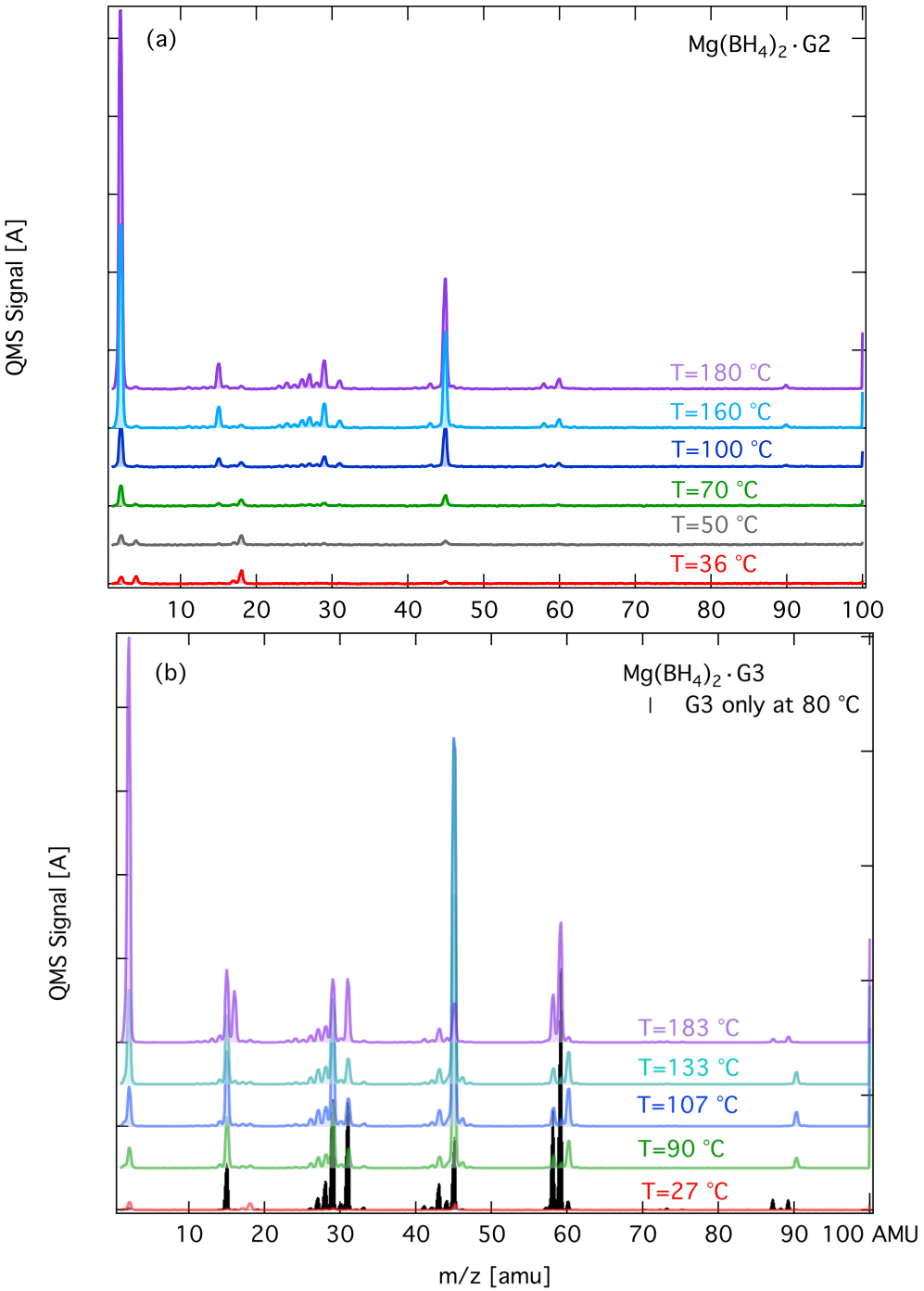


Figure S12: Signal from the QMS in the m/z range of 1-100 amu recorded during heating of (a) $Mg(BH_4)_2$·G2 and (b) $Mg(BH_4)_2$·G3. For comparison, the fragmentation pattern of G3 at 80 °C is shown in part 12b. The samples were heated at 5 °C/min to 180 °C.

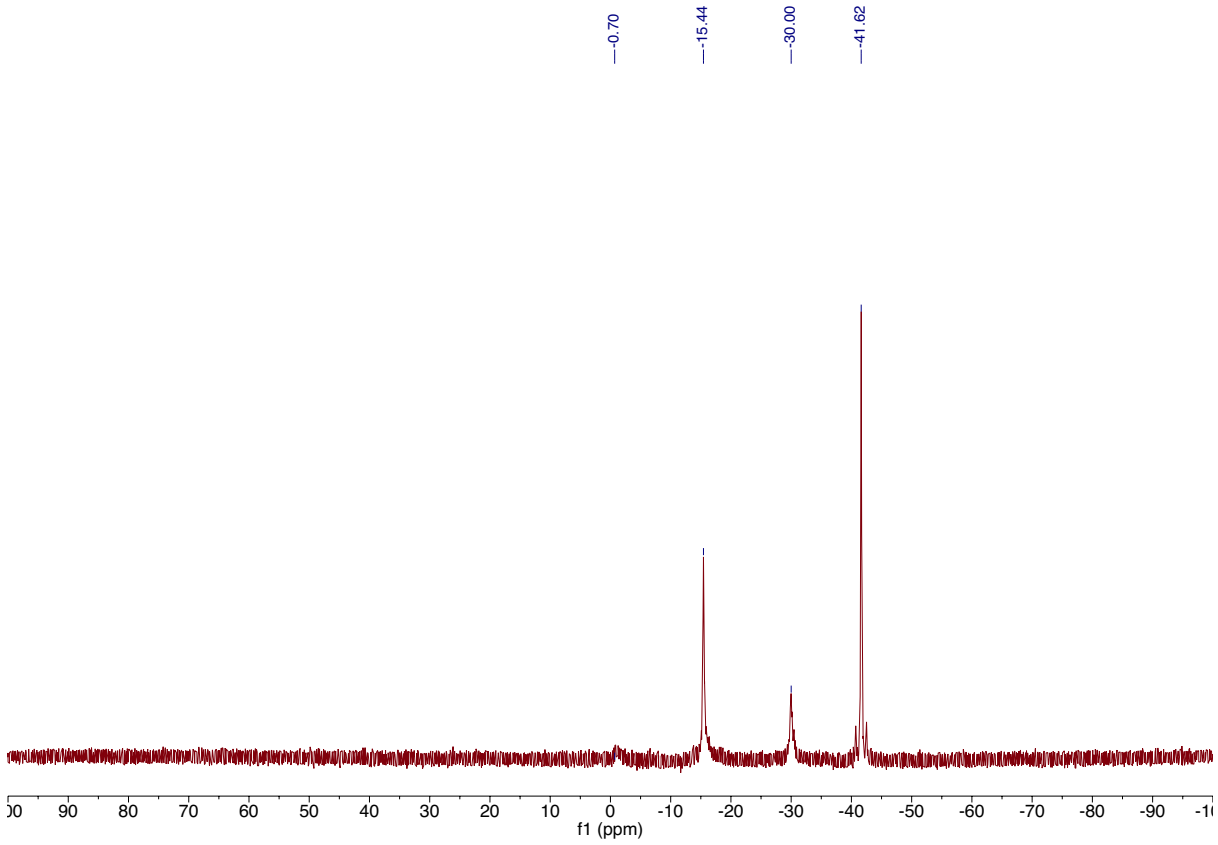


Figure S13. $^{11}B\{^{1}H\}$ NMR (25 ºC) in 2:1 D_2O: THF of 1:1 of $Mg(BH_4)_2$:G1 at 180 ºC for 8 h. The product distribution consists of $Mg(B_{10}H_{10})$, $Mg(B_{12}H_{12})$ and unreacted $Mg(BH_4)_2$.

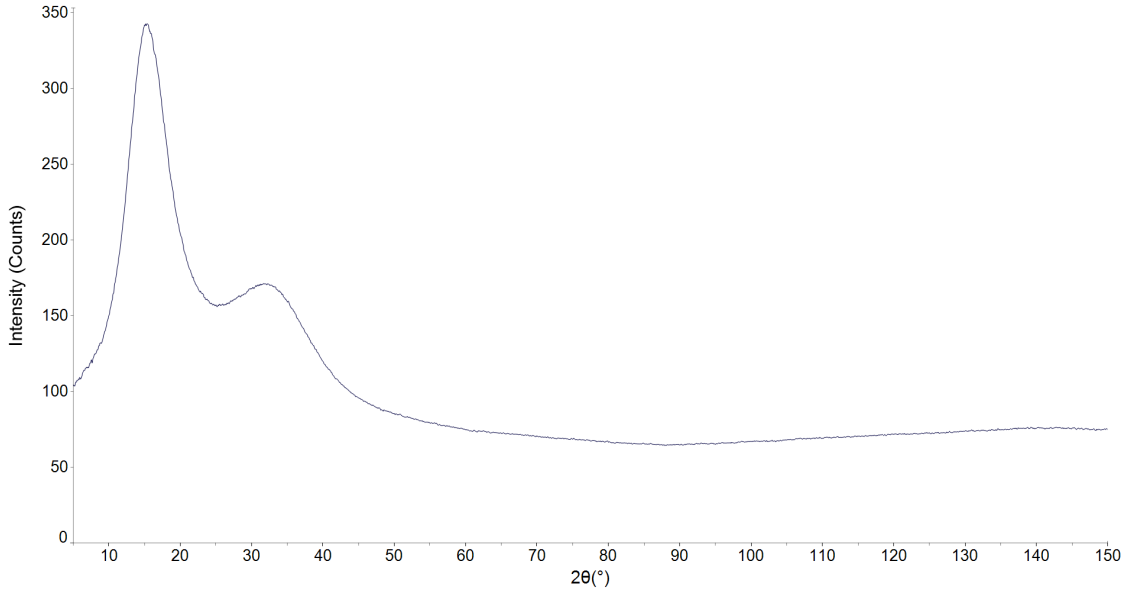


Figure S14. Powder XRD analysis of the post reaction of the 1:1 $Mg(BH_4)_2$:G1 at 180 ºC for 8 h.

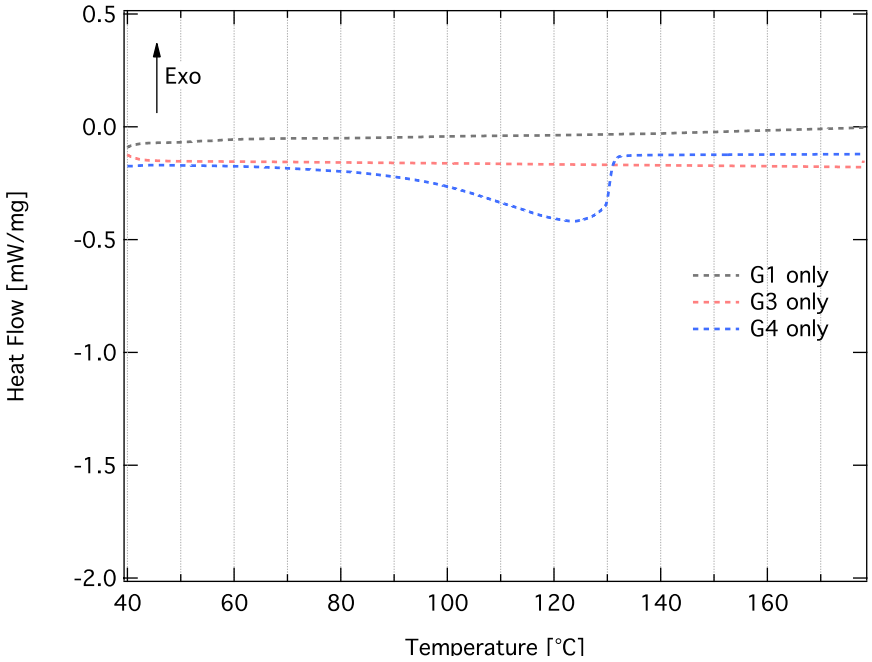


Figure S15. Mass normalized heat flow as a function of temperature obtained from DSC for **G1** = monoglyme, **G3** = triglyme, **G4** = tetraglyme. Collection parameters: 5 °C C/min to 180 °C.

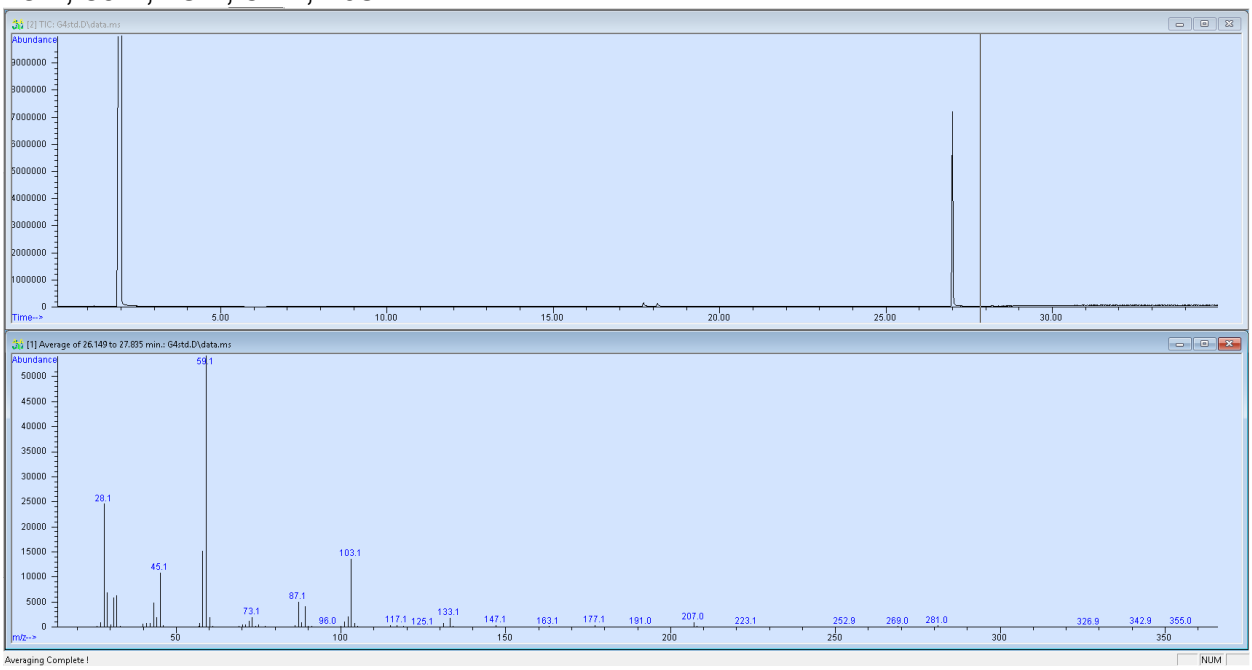
GC-MS characterization of 1:1 $Mg(BH_4)_2$:G4 at 180 ºC for 8 h

Inside a nitrogen-filled glovebox, to an oven-dried 25 mL Schlenk tube was added $Mg(BH_4)_2$ (40.0 mg, 0.740 mmol) and **G4** (163 μL, 0.740 mmol) via microsyringe. The Schlenk tube was closed and removed from the glovebox and transferred to a preheated aluminum block at 180 ºC for 8 h. The reaction proceeded under a closed system. The reaction was cooled to room temperature and 1 mL of 2M $HCl_{(aq)}$ was carefully added to quench the reaction. The mixture was filtered *via* a glass pipette into a 3 mL scintillation vial. GC-MS samples were prepared in MeOH. The resulting solution was subjected to GC-MS characterization using the Agilent 7000 Triple Quadrupole GC/MS instrument equipped with an autosampler and under PC control.

Table 1. Summary of GC-MS data of 1:1 $Mg(BH_4)_2$:G4 at 180 ºC for 8 h. The table shows the retention time (min) of the different species and fragmentation pattern (m/z)

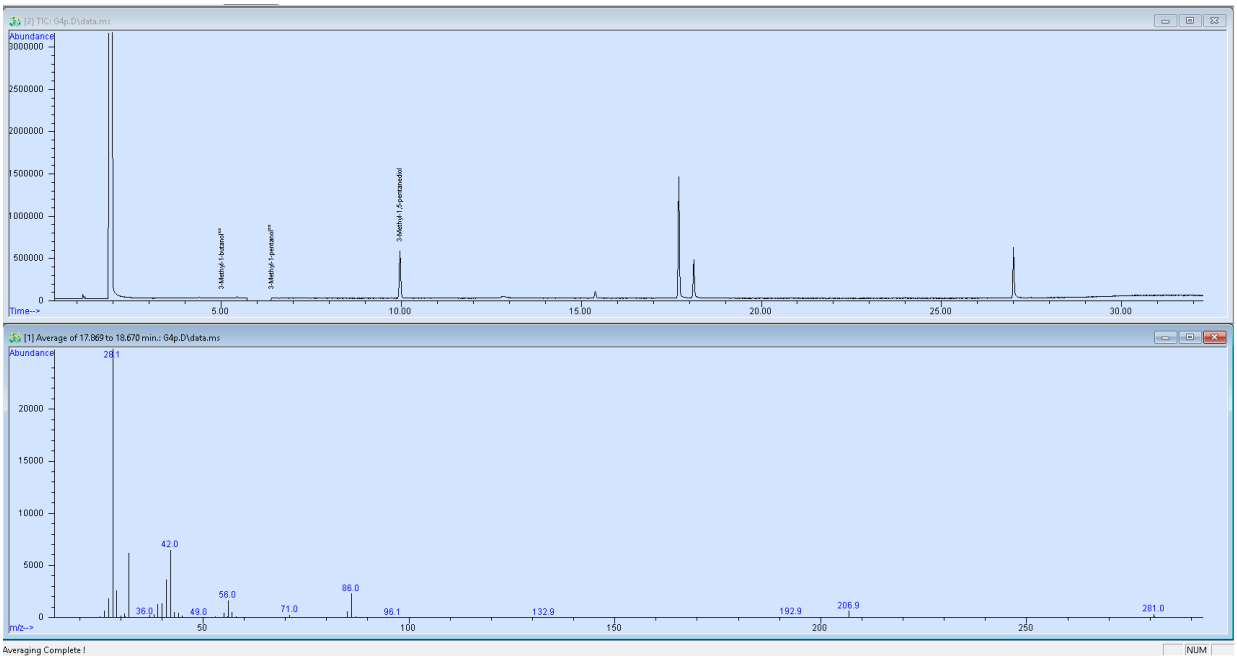
G4 (27 min)	species 1 (18.2 min)	species 2 (17.7 min)	species 3 (10.0 min)
45.1	28.1	29.1	28.1
59.1	42.1	43.1	41.1
73.1	56	56.1	56.1
87.1	86	86	61
103.1			71.1
			101.1

GC-MS of reference **G4** (retention time of 27 min) with fragmentation pattern of 28.1, 45.1, 59.1, 73.1, 87.1, 103.1 m/z

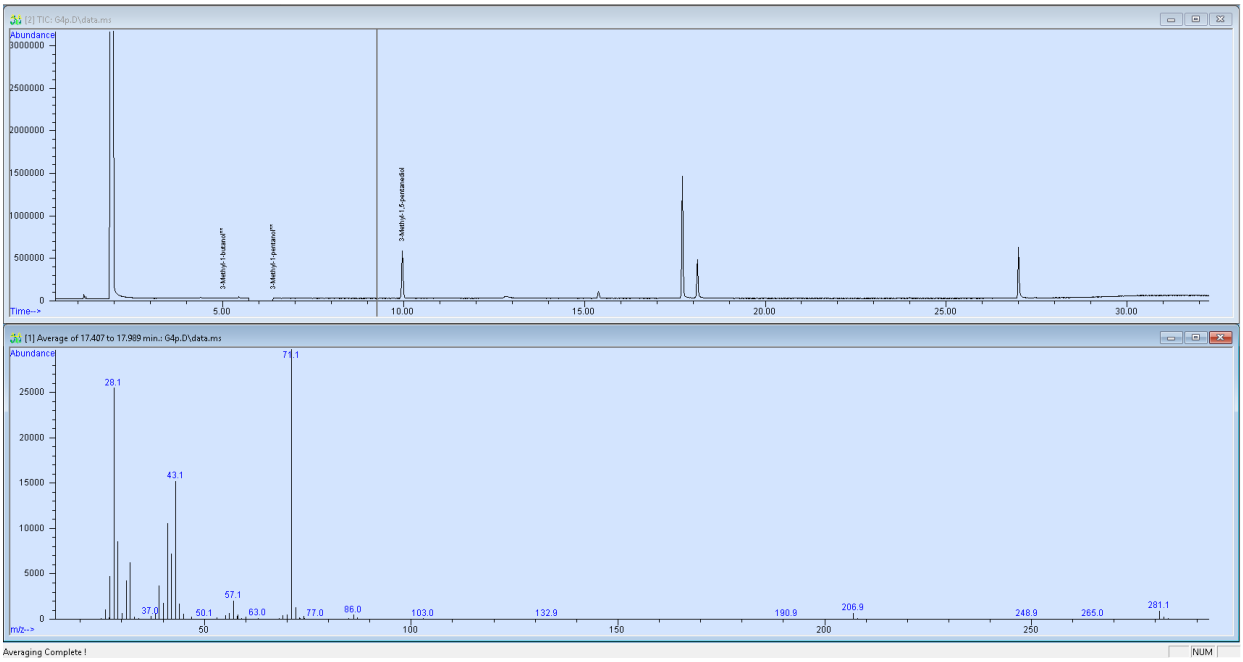


Distribution of products (*G4 is at 27 min*)

Fragmentation pattern of species 1 at **18.2 min**: 28.1, 42.1, 56.0, 86.0 m/z



Fragmentation pattern of species 2 at **17.7 min**: 29.1, 43.1, 56.1, 86.0 m/z



Fragmentation pattern of species 3 at retention time of **10.0 min**: 28.1, 41.1, 56.1, 61.0, 71.1, 101.1 m/z