

Coordination Dynamics and Thermal Stability with Amino Metallogels and Liquids

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Sol-Gel System



Figure S-1. Pictures of the gels depict: (a) the kinetic hemiaminal gel (product V in Scheme 3), (b) the liquid resulting from the addition of aluminium chloride to the kinetic hemiaminal gel (product VII in Scheme 3), (c) the thermodynamically favoured hexahydrotriazine gel after heating the liquid in (b) (product VIII in Scheme 3); and (d) the liquid following breakdown of the gel with tris-carboxylethyl phosphine.

NMR Model System

PHT System Without Aluminum

0 Hours : ^1H NMR (500 MHz, DMF) δ 11.51, 8.03, 7.01, 5.04, 4.91, 4.88, 4.82, 4.80, 4.74, 4.71, 4.63, 4.34, 4.15, 3.80, 3.27, 3.21, 3.04, 2.91, 2.77, 2.73, 2.56, 2.38, 2.32, 2.18, 2.04, 1.67, 1.50, 1.42, 1.41, 1.39, 1.38, 1.36, 1.30, 1.29, 1.27, 1.26, 1.24, 0.87, 0.86, 0.84

1.5 Hours: ^1H NMR (500 MHz, DMF) δ 11.49, 8.03, 7.01, 7.00, 6.99, 6.84, 4.91, 4.88, 4.86, 4.82, 4.79, 4.78, 4.71, 4.63, 4.34, 4.15, 3.83, 3.79, 3.27, 3.23, 3.21, 3.20, 3.03, 3.03, 2.91, 2.77, 2.73, 2.56, 2.39, 2.38, 2.36, 2.31, 2.18, 2.04, 1.67, 1.52, 1.50, 1.50, 1.49, 1.42, 1.41, 1.39, 1.38, 1.36, 1.30, 1.29, 1.27, 1.26, 0.86.

2.5 Hours: ^1H NMR (500 MHz, DMF) δ 8.03, 4.89, 4.88, 4.82, 4.81, 4.75, 4.39, 4.36, 4.23, 4.15, 4.09, 4.05, 3.58, 3.53, 3.46, 3.38, 3.23, 3.21, 3.10, 3.01, 2.92, 2.75, 2.69, 2.68, 2.67, 2.65, 2.61, 2.59, 2.57, 2.56, 2.54, 2.52, 2.51, 2.50, 2.39, 2.37, 2.30, 2.17, 2.03, 1.40, 1.39, 1.36, 1.34, 1.33, 1.31, 1.30, 1.29, 0.90, 0.89, 0.88, 0.87, 0.86.

10.5 Hours: ^1H NMR (500 MHz, DMF) δ 8.03, 6.85, 4.63, 3.53, 3.45, 3.44, 3.10, 3.01, 2.96, 2.92, 2.92, 2.92, 2.79, 2.75, 2.75, 2.74, 2.61, 2.60, 2.58, 2.57, 2.57, 2.55, 2.54, 2.52, 2.51, 2.49, 2.39, 2.38, 2.36, 2.30, 2.18, 2.17, 1.42, 1.42, 1.41, 1.40, 1.39, 1.39, 1.38, 1.38, 1.37, 1.36, 1.34, 1.33, 1.31, 1.30, 1.30, 1.30, 1.28, 1.27, 0.90, 0.89, 0.89, 0.88, 0.88, 0.87, 0.87, 0.86, 0.85.

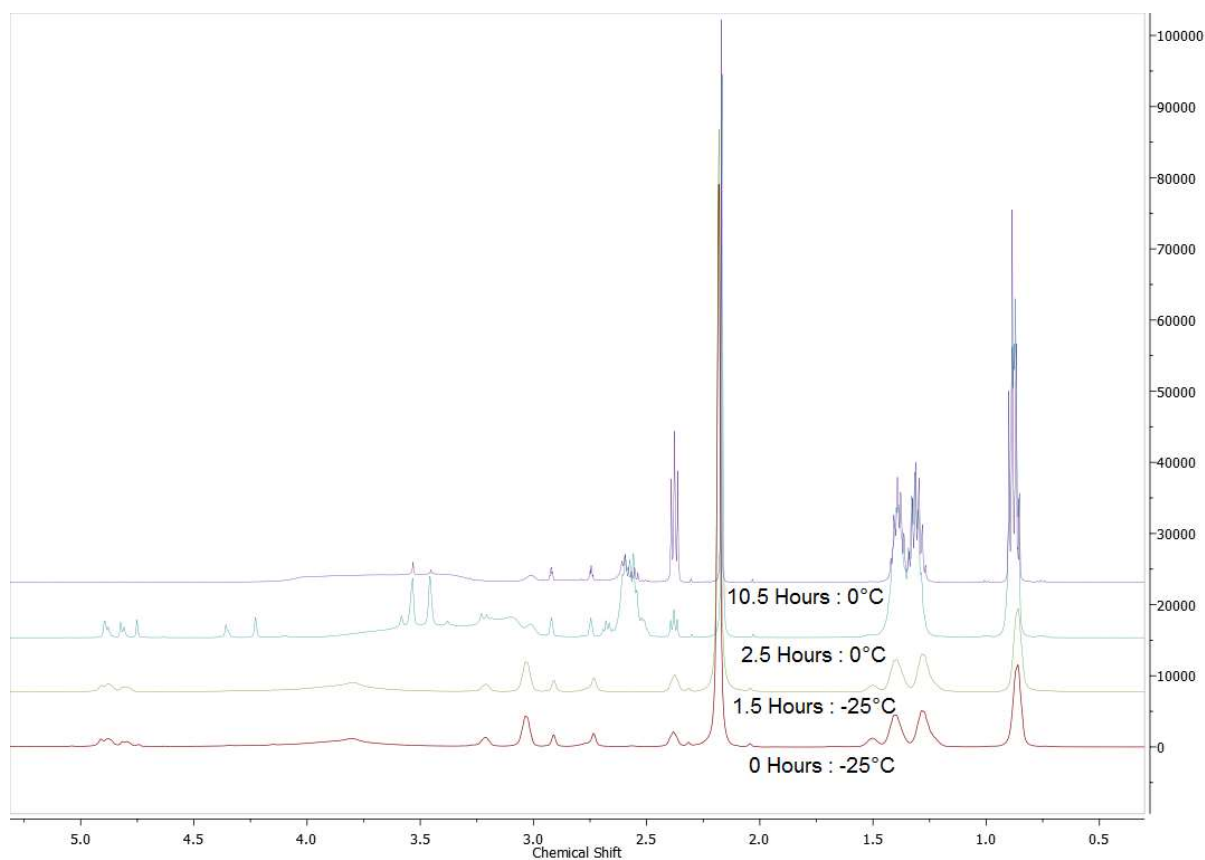


Figure S-2. PHT system without aluminum.

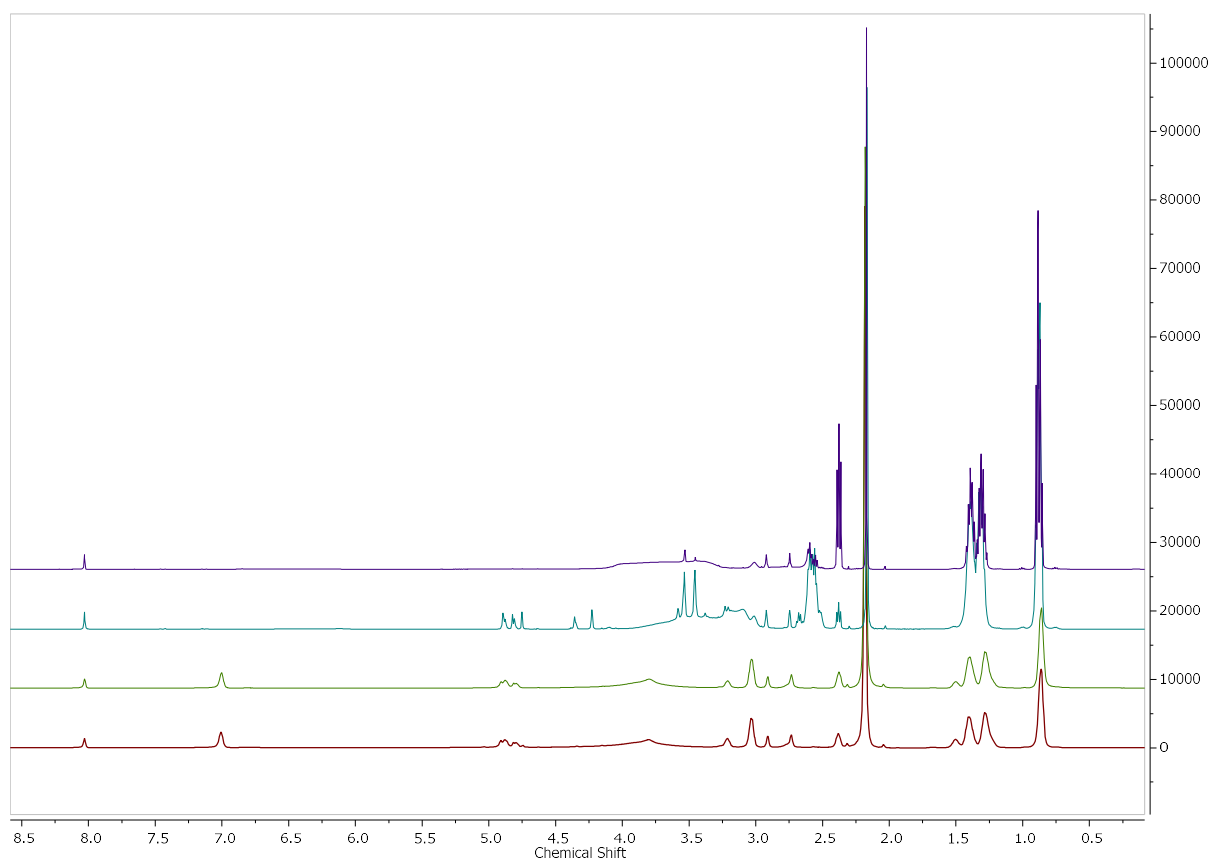


Figure S-3. PHT system without aluminum.

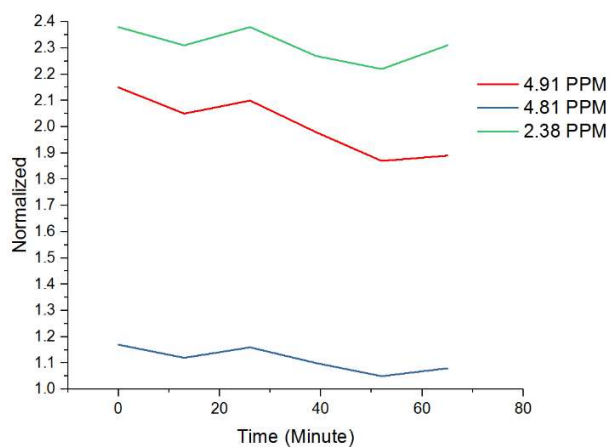


Figure S-3. Without aluminum at -30°C with time resolution.

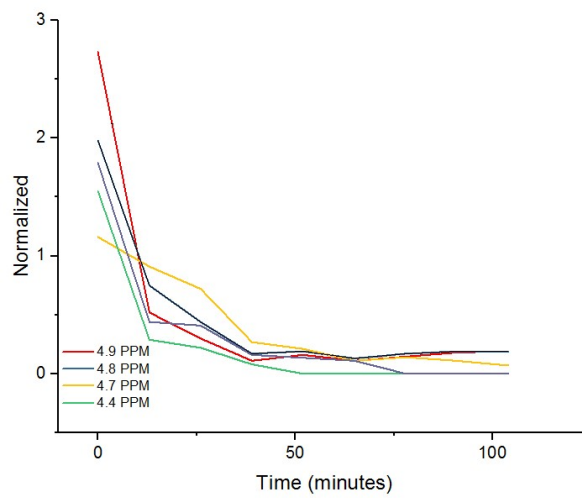
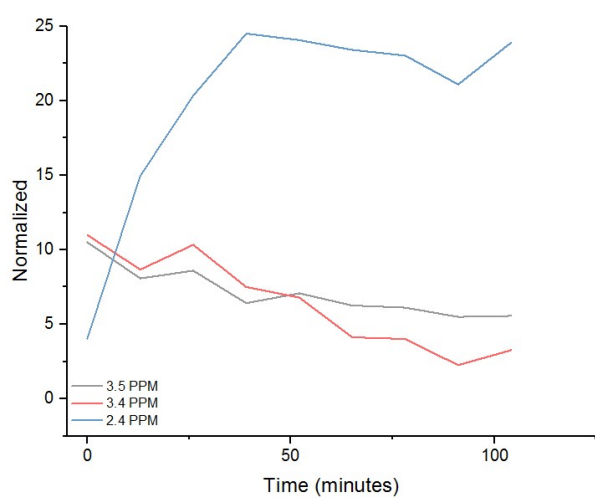
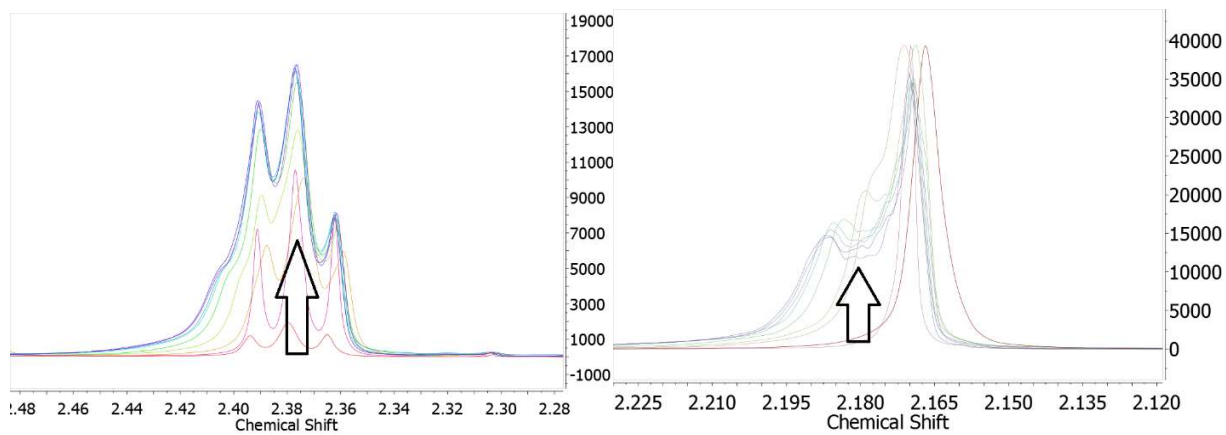


Figure S-4. Without aluminum at 0°C with time resolution.

NMR Model System

PHT System With Aluminum

0 Hours: ^1H NMR (500 MHz, DMF) δ 9.66, 8.61, 8.11, 8.03, 6.84, 6.72, 6.50, 6.22, 6.21, 6.19, 5.41, 4.88, 4.87, 4.86, 4.83, 4.82, 4.80, 4.78, 4.75, 4.74, 4.72, 4.66, 4.64, 4.51, 4.49, 4.41, 4.36, 4.34, 3.80, 2.97, 2.91, 2.77, 2.73, 2.19, 2.13, 1.71, 1.42, 1.26, 0.86.

6 Hours: ^1H NMR (500 MHz, DMF) δ 8.69, 8.03, 6.99, 6.88, 6.21, 5.78, 4.87, 4.86, 4.80, 4.78, 4.73, 3.84, 3.81, 3.02, 3.01, 2.98, 2.96, 2.95, 2.91, 2.72, 2.56, 2.34, 2.19, 1.70, 1.68, 1.36, 1.25, 0.85.

7 Hours: ^1H NMR (500 MHz, DMF) δ 8.65, 8.03, 6.85, 6.73, 6.06, 5.38, 4.89, 4.87, 4.80, 4.75, 4.33, 3.70, 3.68, 3.32, 3.27, 3.04, 3.03, 2.99, 2.98, 2.96, 2.92, 2.74, 2.58, 2.35, 2.31, 2.17, 1.74, 1.72, 1.71, 1.43, 1.42, 1.40, 1.38, 1.36, 1.31, 1.30, 1.28, 1.26, 0.91, 0.89, 0.87, 0.84

15 Hours: ^1H NMR (500 MHz, DMF) δ 8.67, 8.03, 6.86, 6.76, 6.08, 6.01, 5.88, 4.89, 4.81, 4.80, 3.69, 3.03, 2.98, 2.96, 2.95, 2.92, 2.86, 2.74, 2.66, 2.47, 2.19, 2.17, 2.10, 1.74, 1.72, 1.70, 1.63, 1.41, 1.39, 1.38, 1.31, 1.30, 1.28, 1.25, 0.89, 0.87, 0.80

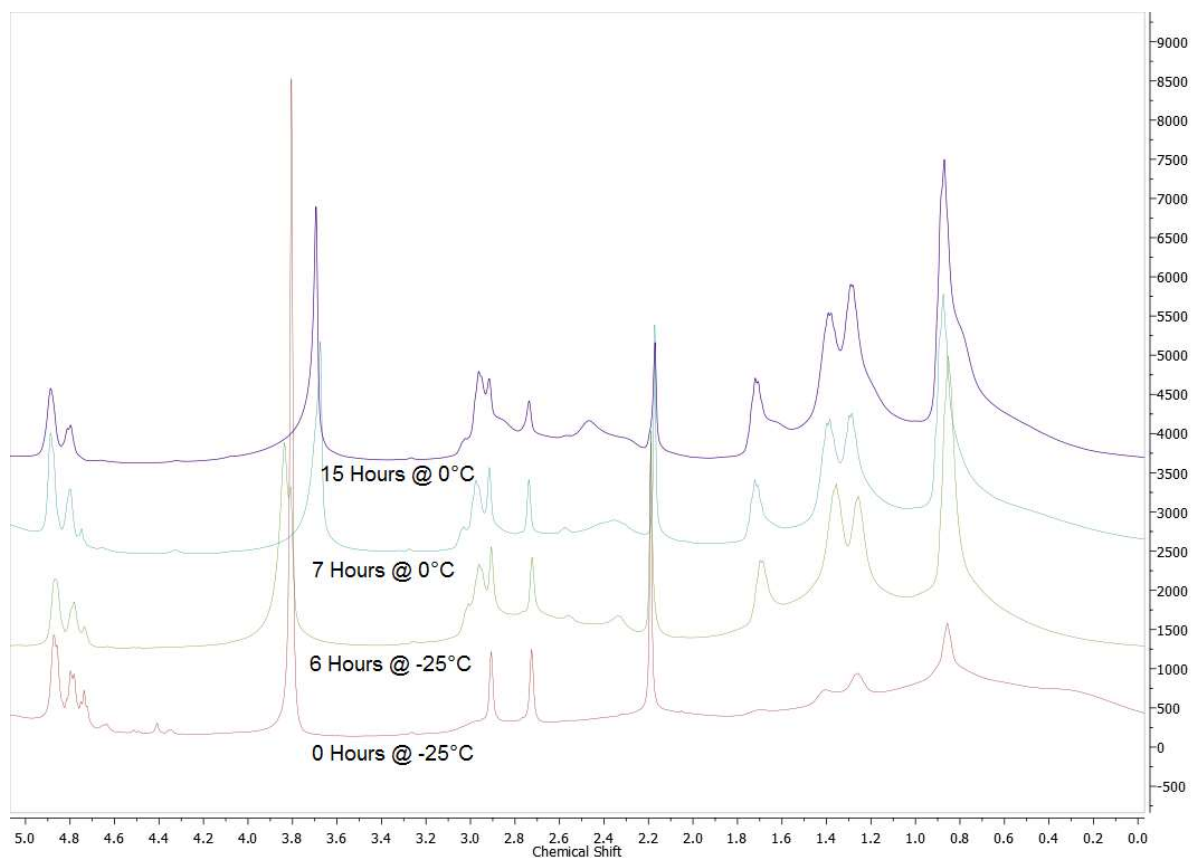


Figure S-5. With aluminum with time resolution.

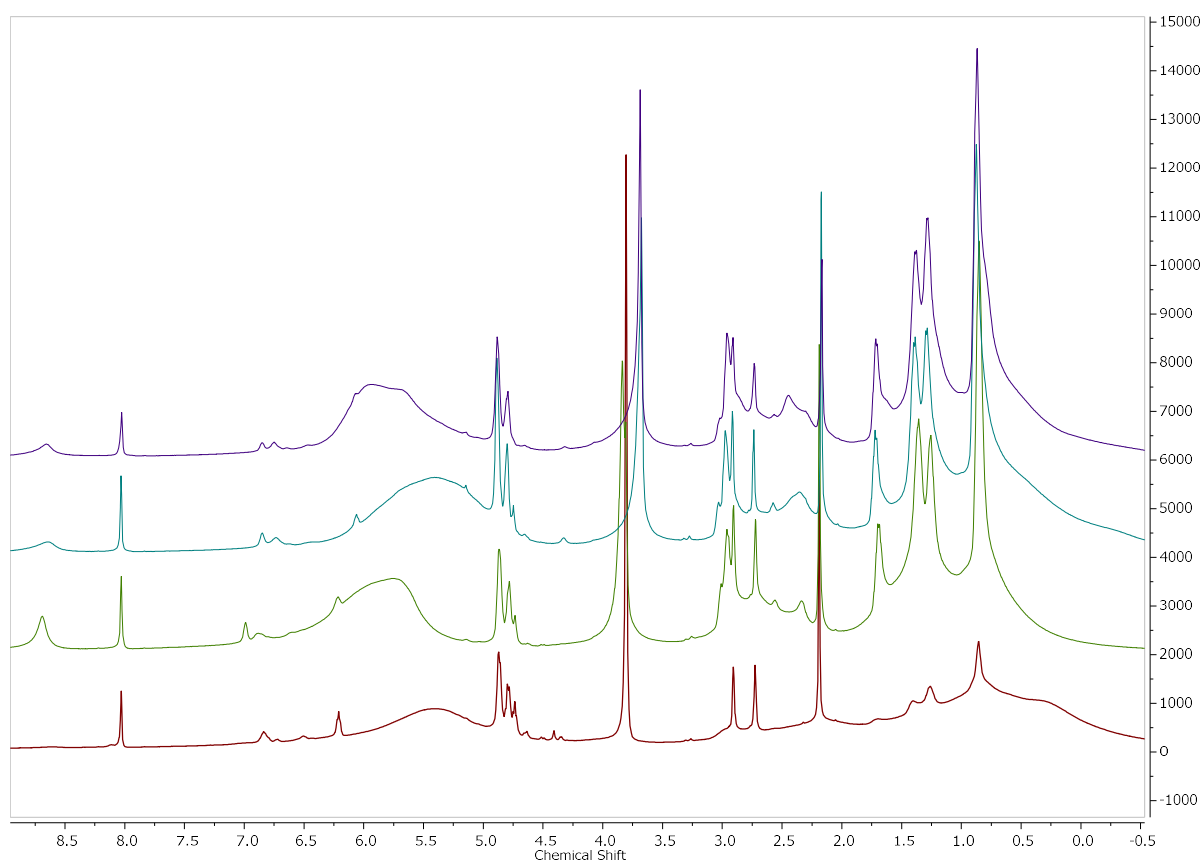
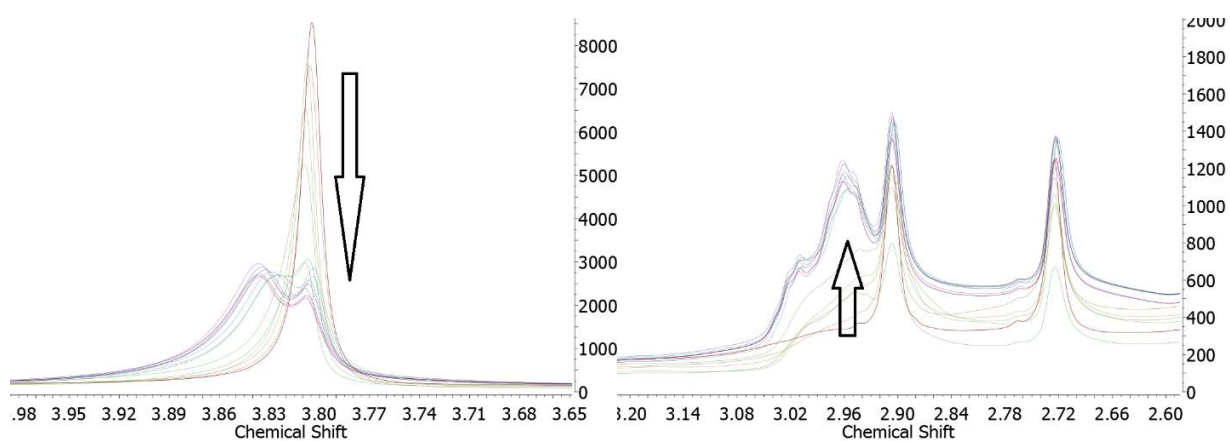


Figure S-6. With aluminum with time resolution.

With Aluminum @ -25°C Overtime



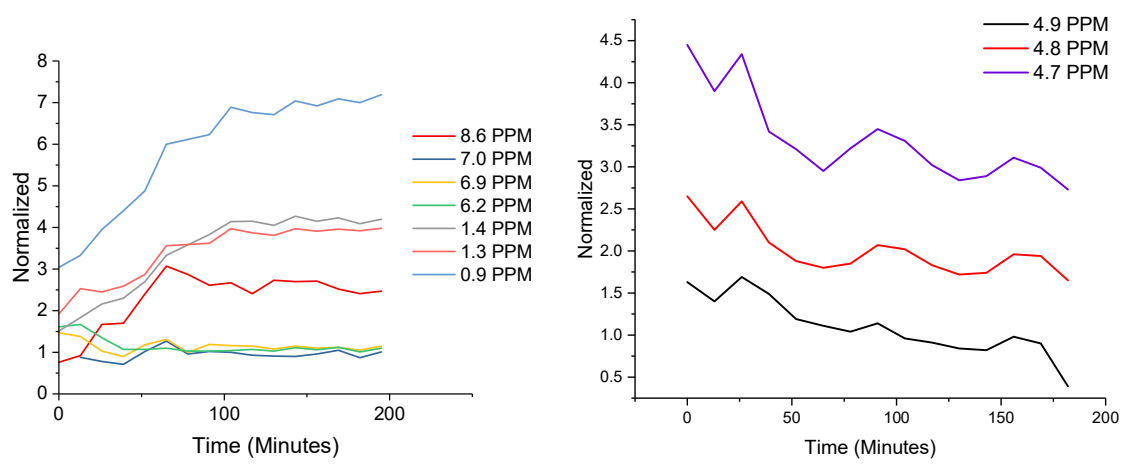


Figure S-7. With aluminum with time resolution.