Supporting Information

Chloride-catalyzed, Multicomponent Self-Assembly of Arsenic Thiolates

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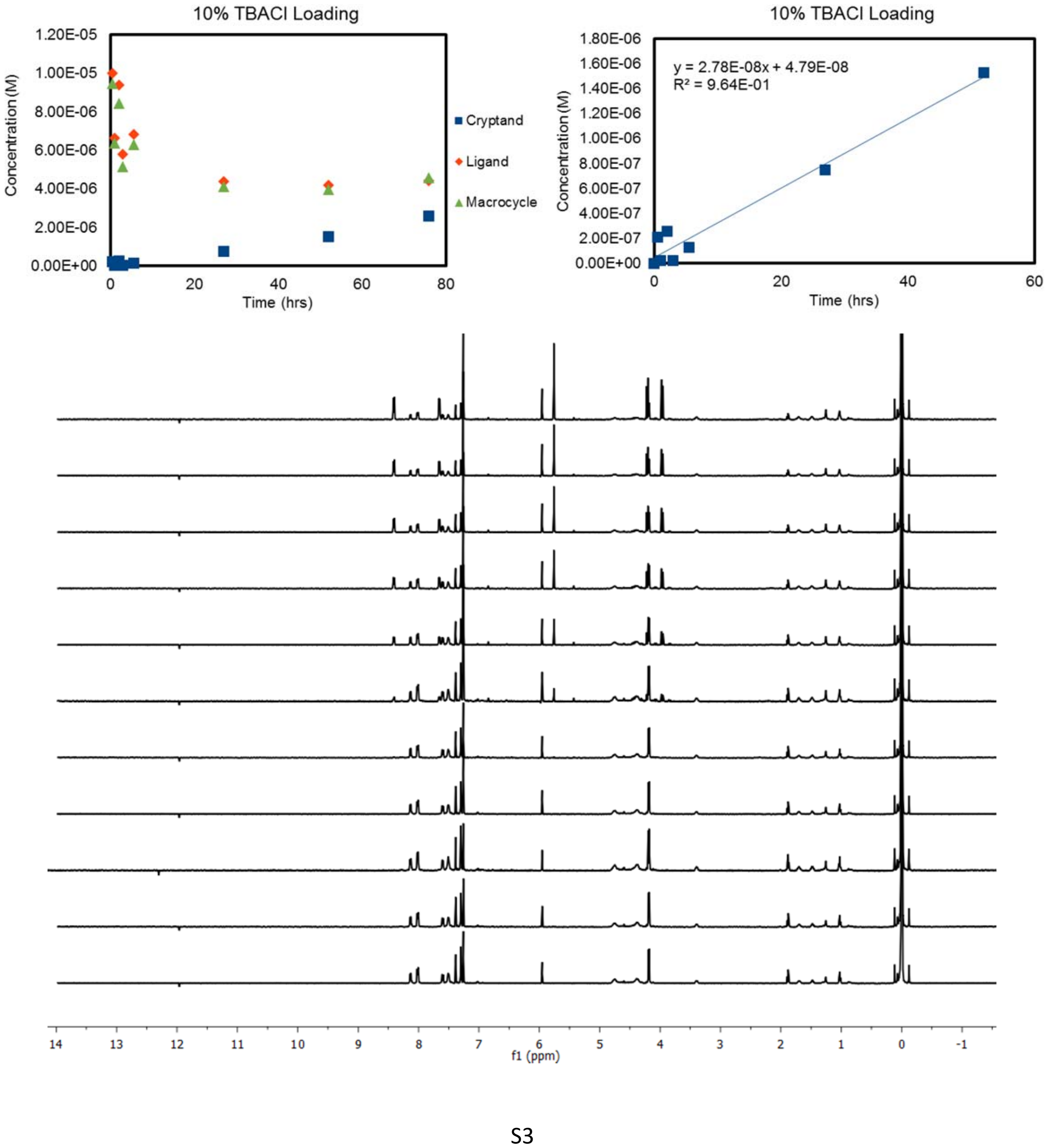
Experimental

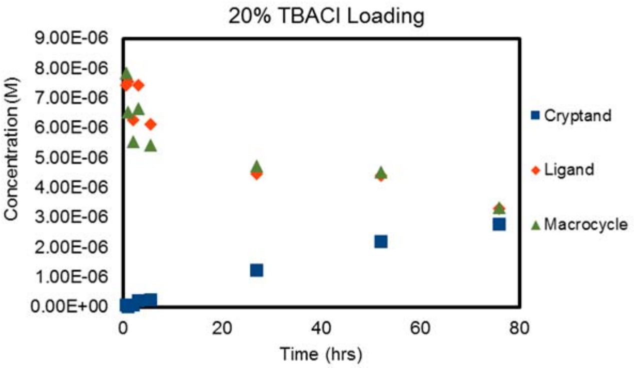
General: All chemicals were used as received, with no further purification. $CDCl_3$ (Cambridge Isotope Laboratories Inc) was dried with 3 Å molecular sieves and handled in a glove bag. 1,4-Naphthalenedibenzylthiol $H_2\mathbf{L}$[1], antimony cryptand $Sb_2\mathbf{L}_3$[2], antimony tris(2-naphthalenemethylthiolate) (1)[3], arsenic macrocycle $As_2\mathbf{L}_2Cl_2$[1] were synthesized according to literature preparations. ^{1}H-NMR spectra were obtained on a Bruker 600 MHz spectrometer using Topspin Software. Data were processed in MestReNova. The experiments were run at 298 K in 5 mm tubes (6.3 mM in rigorously anhydrous $CDCl_3$) with an internal standard of 0.0038 mM tetrachloroethane.

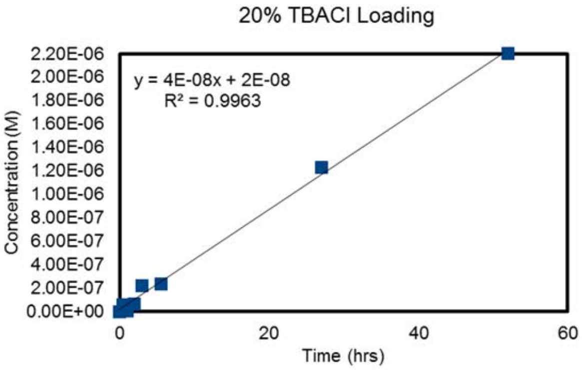
Kinetic Analysis

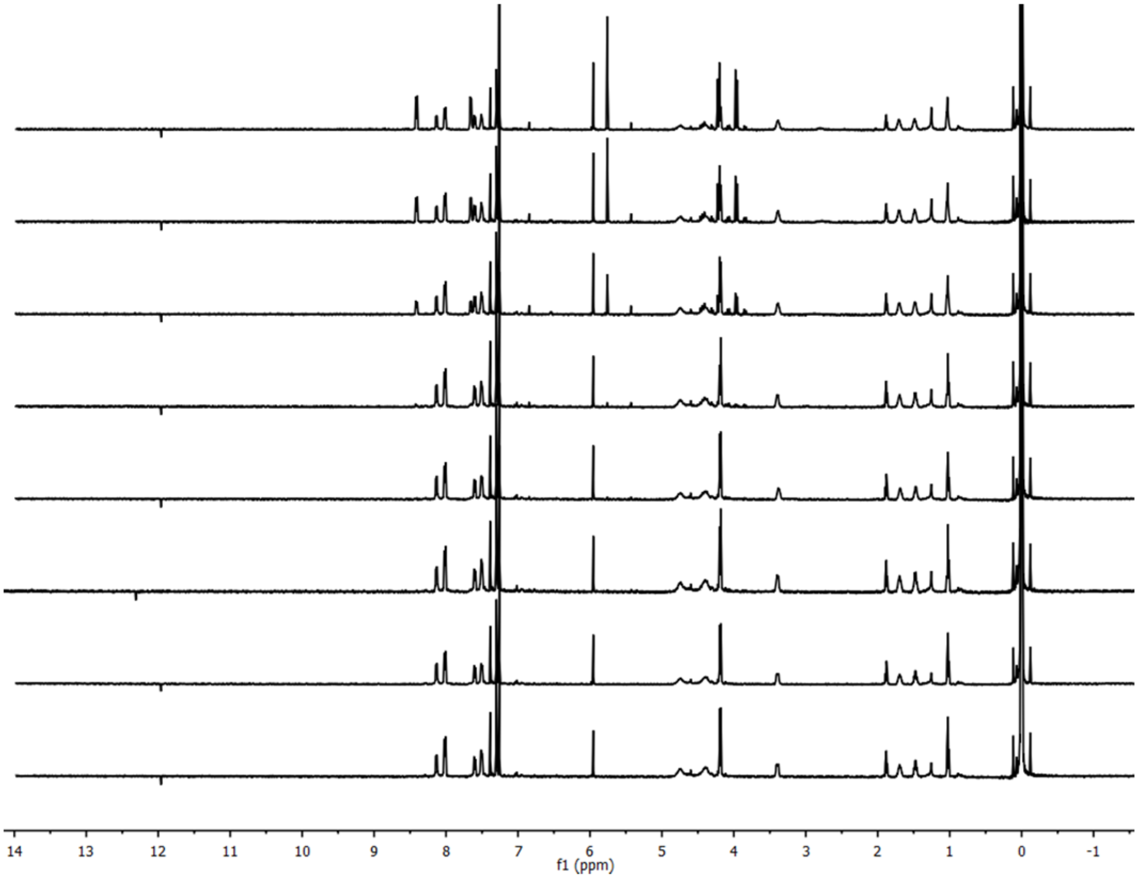
Simplified reaction kinetics were analyzed by running a series of catalyzed reactions with equimolar 6.3 mM L and $As_2L_2Cl_2$ in dry $CDCl_3$ with 0.1, 0.2, 0.4, and 0.8 equivalents of TBACl. All ratios were taken from integrating the peaks at 8.0, 8.1, and 8.4 ppm. The reaction order in chloride ion was determined by measuring initial rates choosing the minimum number of data points to get an R^2 value of above 0.85, with many of the values above 0.95. All spectra were autophased and baseline corrected in Mestrenova before being normalized to the largest peak. Integrals were taken from predefined regions 5.880-6.000, 7.950-8.050, 8.075-8.165, and 8.350-8.450. Center glitch was removed using 5% drift correction. A quadrature artifact remains at ~12ppm.

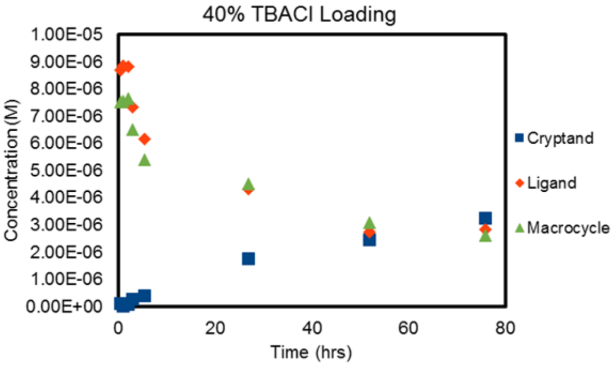
Figure S1. Graphs of speciation over time and initial rate fitting for kinetic data




20% TBACl Loading
Concentration (M)
9.00E-06
8.00E-06
7.00E-06
6.00E-06
5.00E-06
4.00E-06
3.00E-06
2.00E-06
1.00E-06
0.00E+00
0
20
40
60
80
Time (hrs)
■ Cryptand
◆ Ligand
▲ Macrocycle


20% TBACl Loading
y = 4E-08x + 2E-08
R² = 0.9963
Concentration (M)
2.20E-06
2.00E-06
1.80E-06
1.60E-06
1.40E-06
1.20E-06
1.00E-06
8.00E-07
6.00E-07
4.00E-07
2.00E-07
0.00E+00
0
20
40
60
Time (hrs)


14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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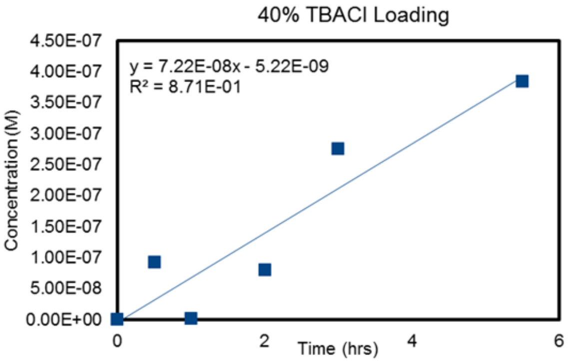
9.00E-06
8.00E-06
7.00E-06
6.00E-06
5.00E-06
4.00E-06
3.00E-06
2.00E-06
1.00E-06
0.00E+00
0
20
40
60
80
Time (hrs)
■ Cryptand
◆ Ligand
▲ Macrocycle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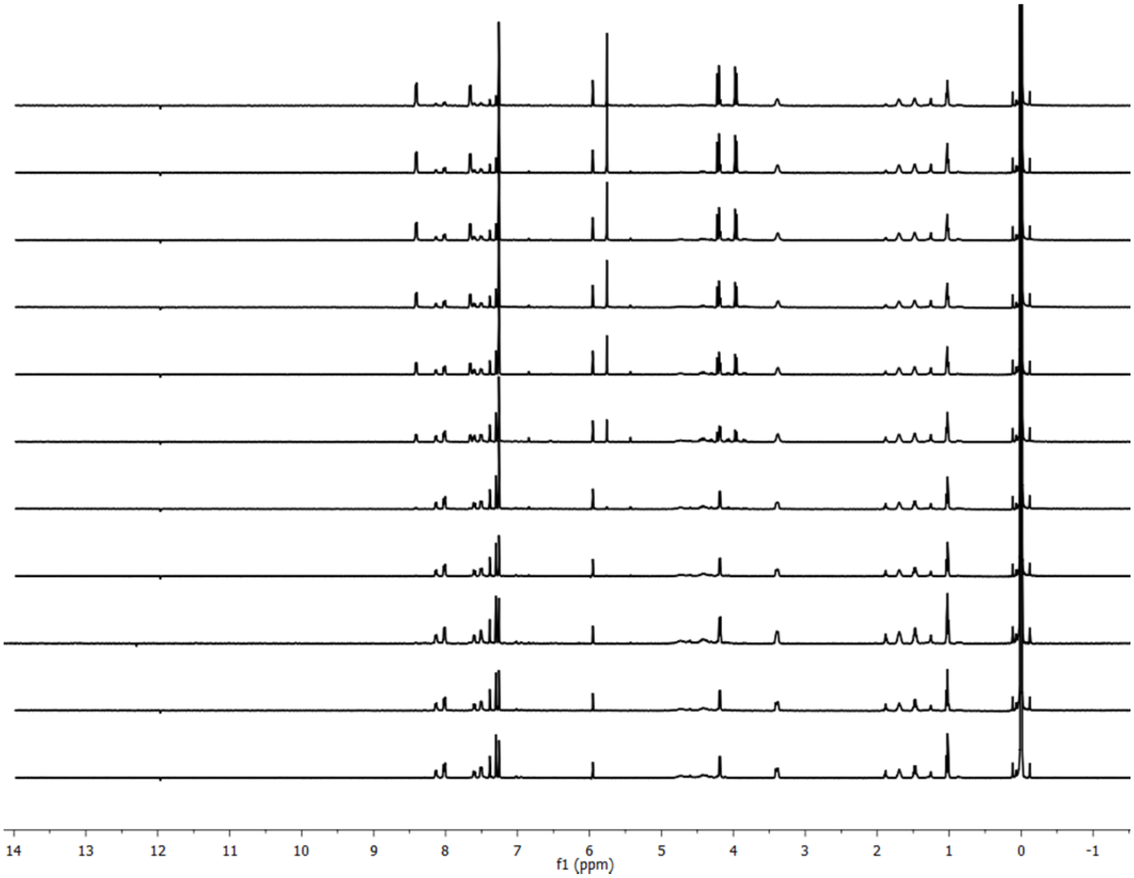
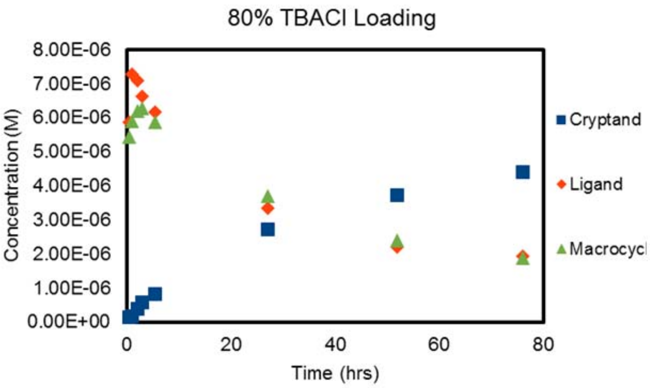
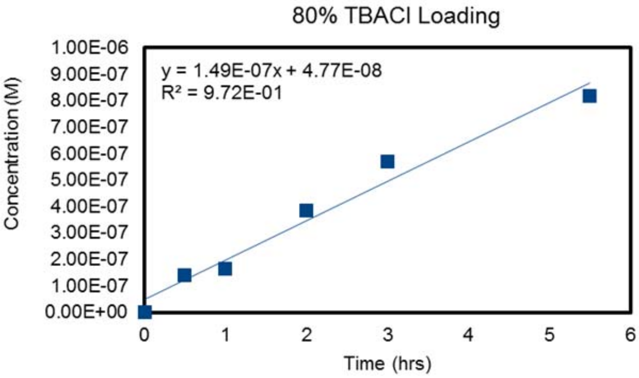
y = 7.22E-08x - 5.22E-09
R² = 8.71E-01
Concentration (M)
4.50E-07
4.00E-07
3.50E-07
3.00E-07
2.50E-07
2.00E-07
1.50E-07
1.00E-07
5.00E-08
0.00E+00
0
2
4
6
Time (hrs)


14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


80% TBACl Loading
Concentration (M)
8.00E-06
7.00E-06
6.00E-06
5.00E-06
4.00E-06
3.00E-06
2.00E-06
1.00E-06
0.00E+00
0
20
40
60
80
Time (hrs)
■ Cryptand
◆ Ligand
▲ Macrocycl


80% TBACl Loading
y = 1.49E-07x + 4.77E-08
R² = 9.72E-01
Concentration (M)
1.00E-06
9.00E-07
8.00E-07
7.00E-07
6.00E-07
5.00E-07
4.00E-07
3.00E-07
2.00E-07
1.00E-07
0.00E+00
0
1
2
3
4
5
6
Time (hrs)

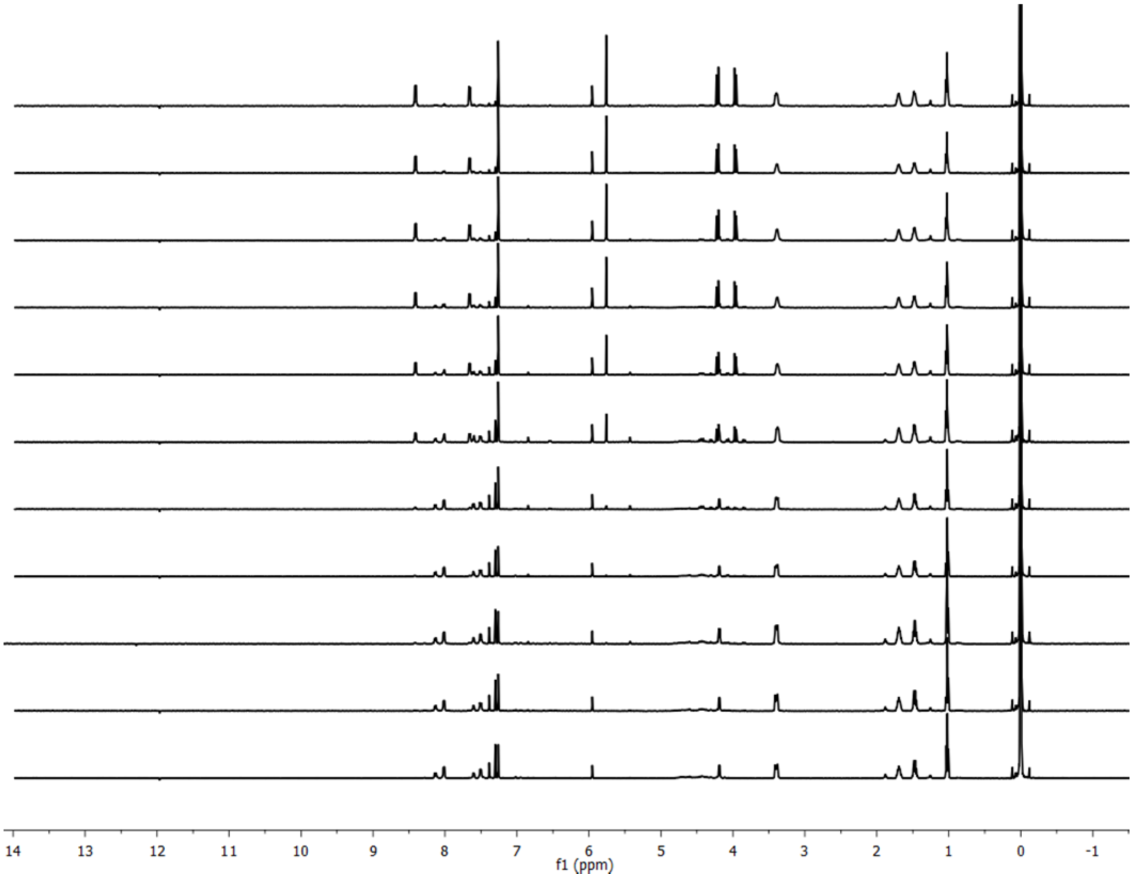
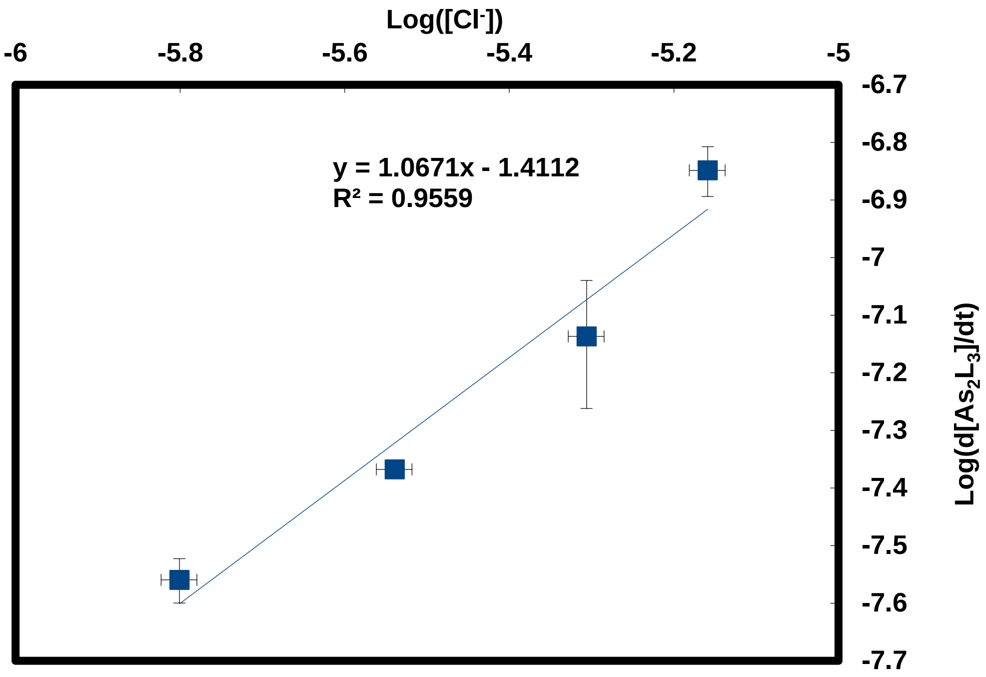

14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

Figure S2. Initial rates were determined by linearly fitting the initial data points ($R^2 > 0.85$) and plotted Log([Cl^-]) vs Log(d[$As_2\mathbf{L}_3$]/dt). The slope of a straight line fit to these data points is 1.0837 so the rate order for Cl, α, is determined to be 1.

$d[As_2\mathbf{L}_3]/dt = k\ [Cl^-]^{\alpha}$



NMR

Figure S3**.** ^{1}H-NMR data of a sample containing $As_2\mathbf{L}_2Cl_2$ and excess TBACl in $CDCl_3$ is reacted for 1 day and then cooled to -40°C, a new broad peak at 6.5 ppm grows in ($C_2H_2Cl_4$ at 0.0038 mM is used as an internal standard).

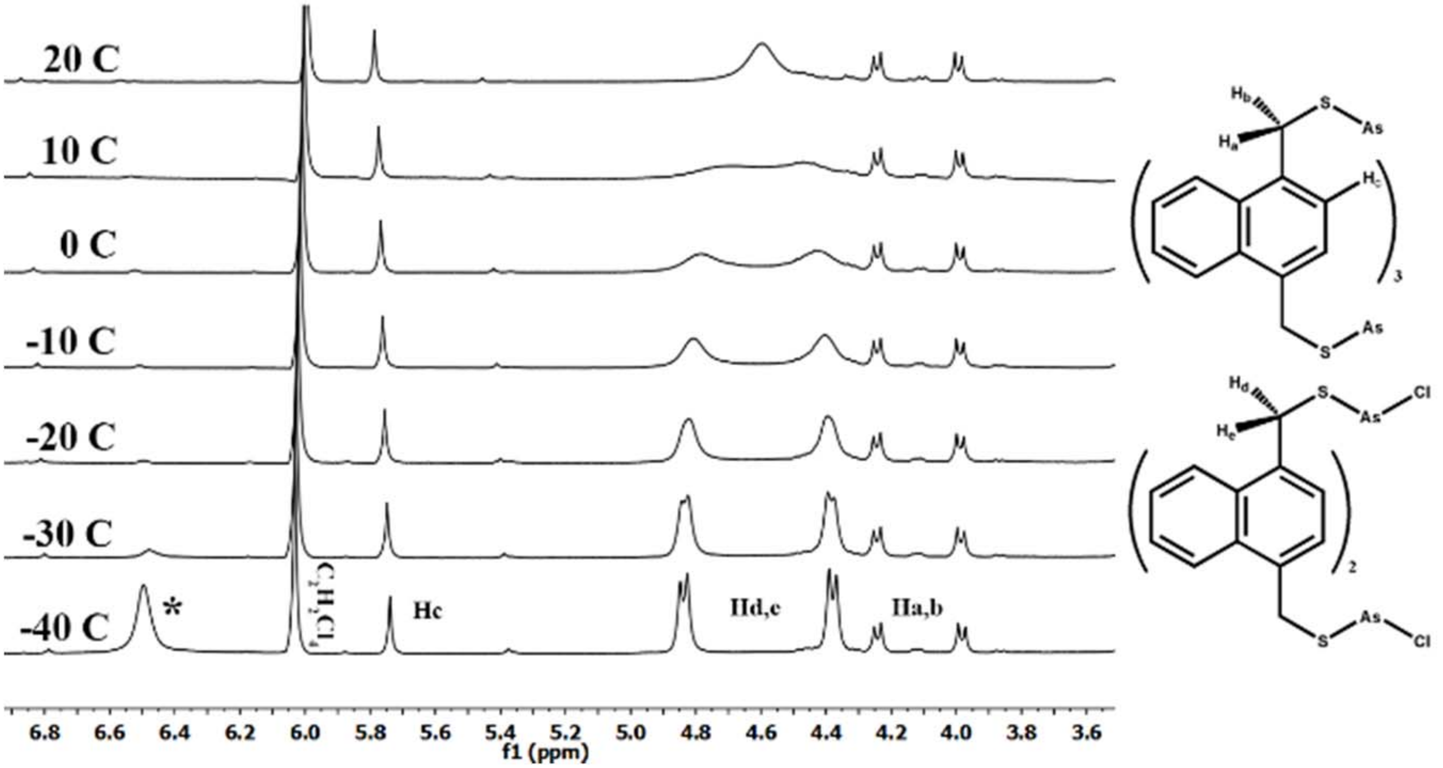


Figure S4. Changes in the ^{1}H-NMR of a 0.0154M solution of $As_2\mathbf{L}_2Cl_2$ in $CDCl_3$ as a function of [Cl^-]

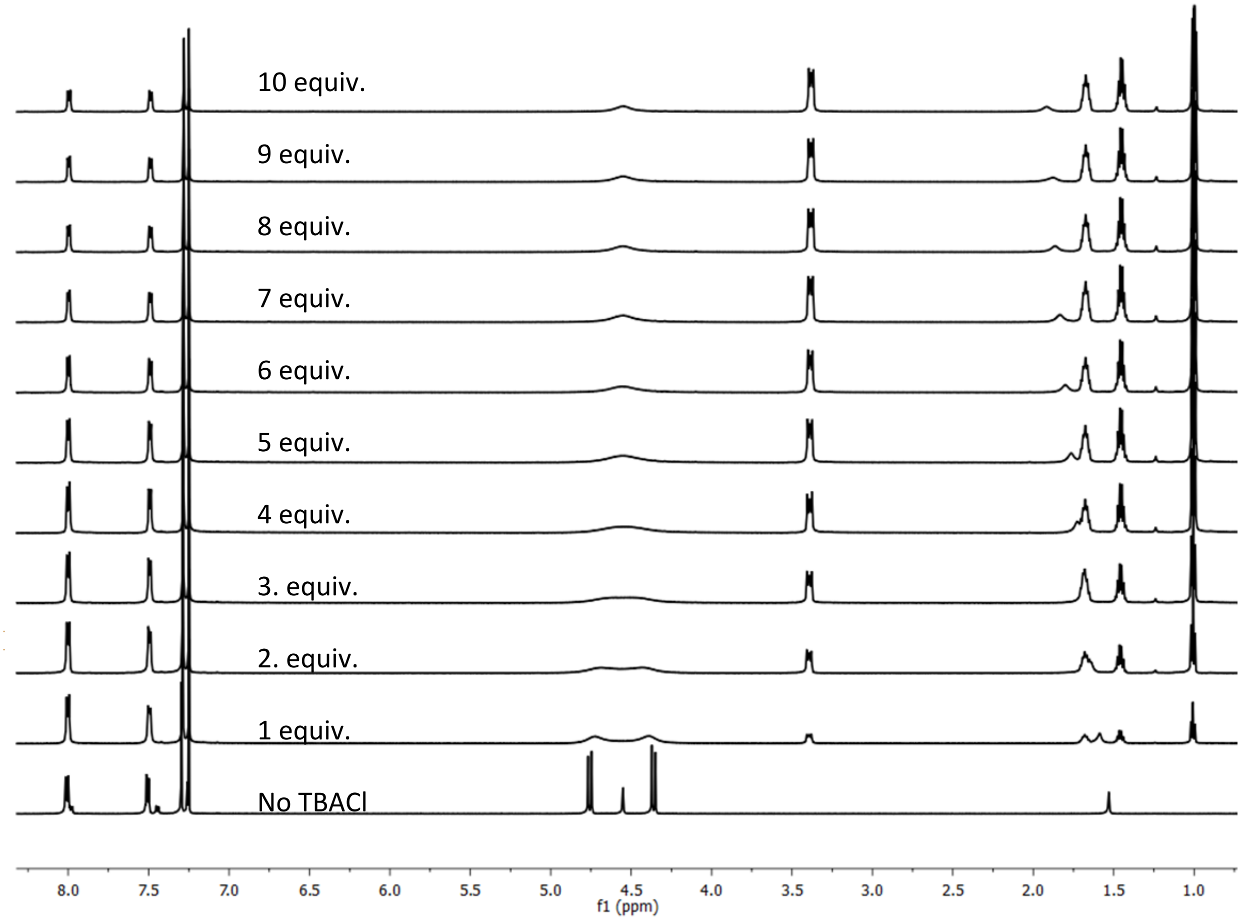


Figure S5. Monothiol control reaction. Three equivalents of benzyl mercaptan and one equivalent of arsenic trichloride (0.18mmol benzyl mercaptan in 1.2 mL of $CDCl_3$) were combined and the reaction was followed over 24hrs. The only peak to grow in at 3.6 ppm corresponds to the slow formation of benzyl disulfide.

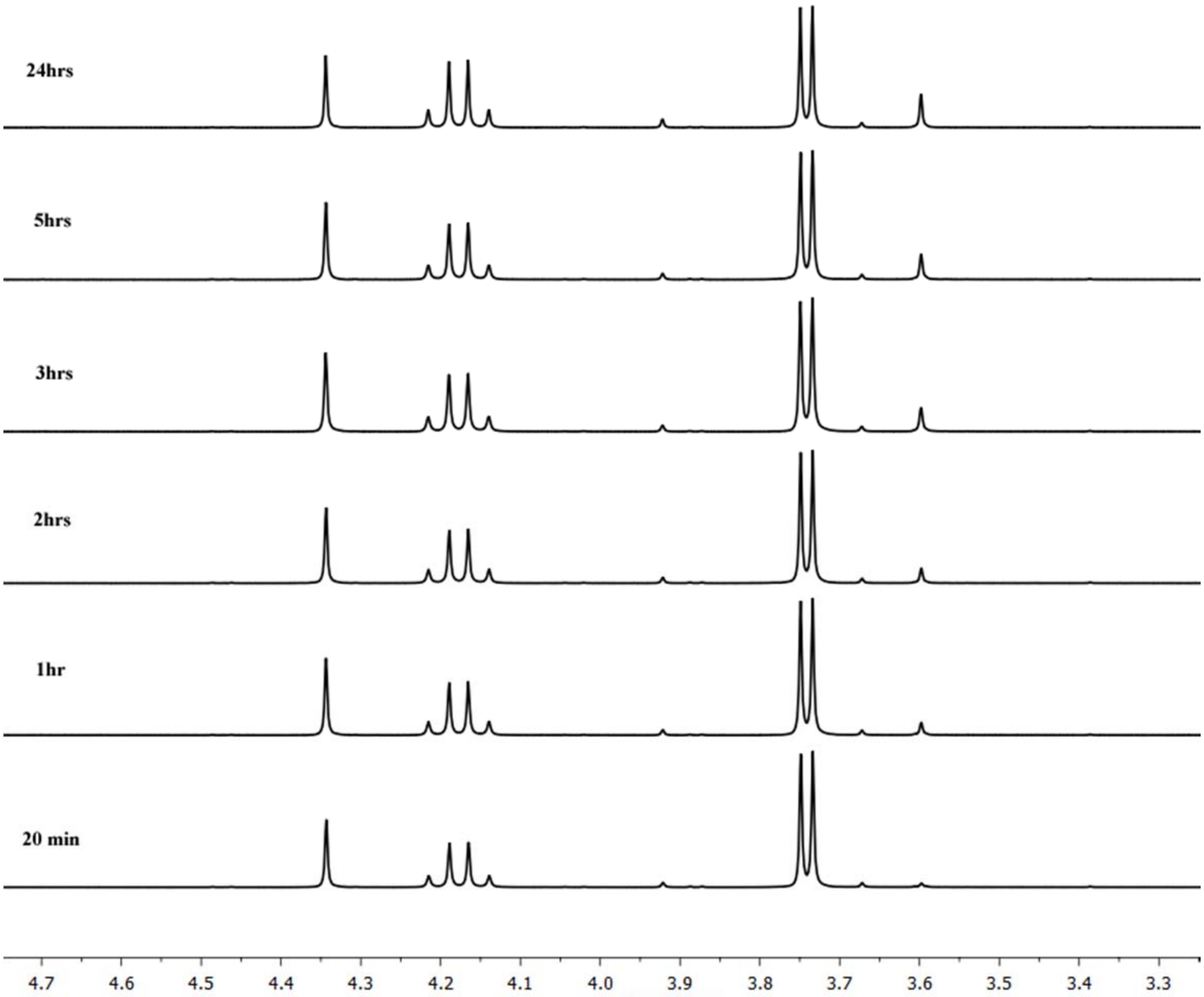
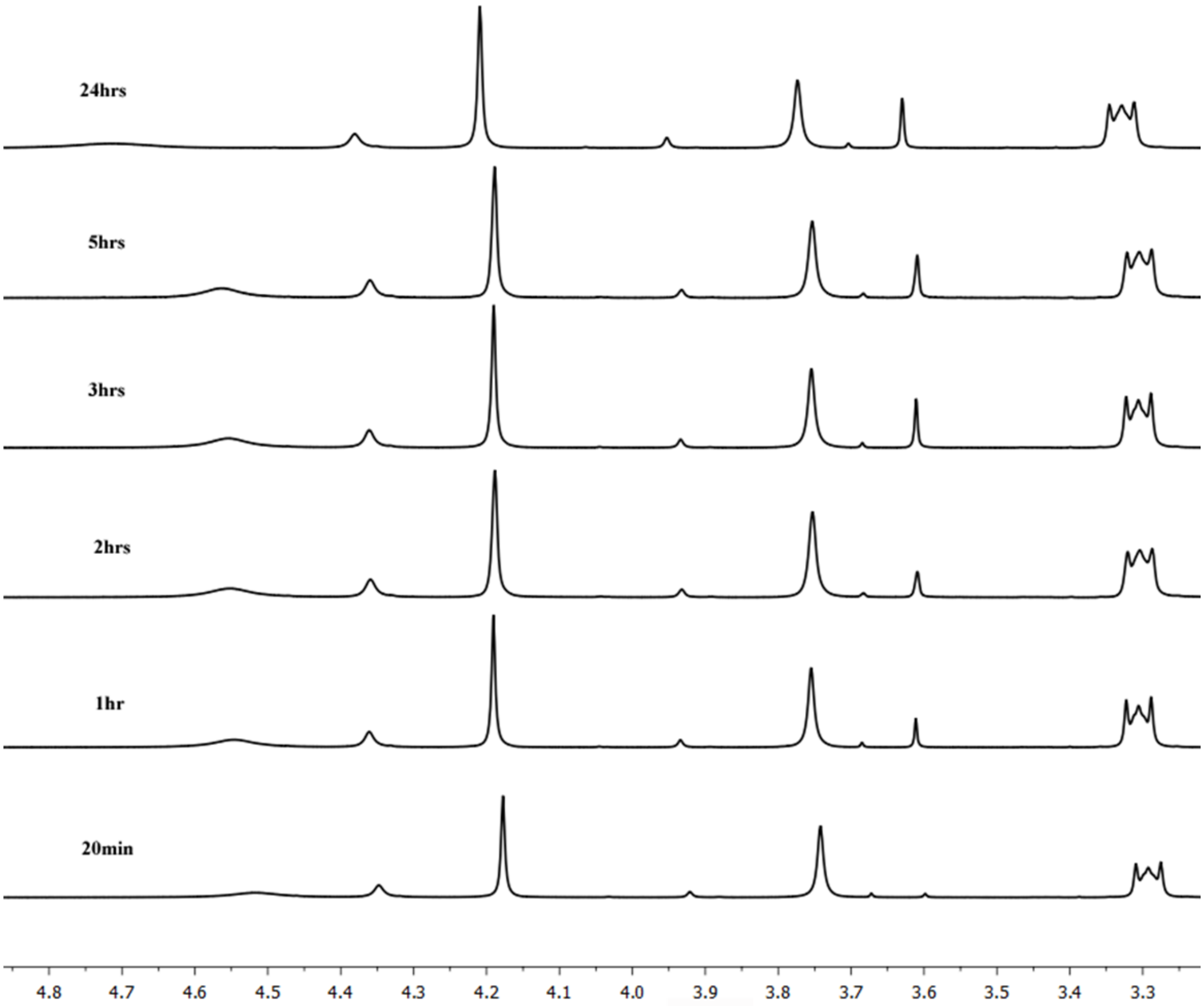


Figure S6. Three equivalents of benzyl mercaptan, one equivalent of arsenic trichloride, and 0.1 equivalents of TBACl (0.18mmol benzyl mercaptan in 1.2 mL of $CDCl_3$) were combined and the reaction was followed over 24hrs. Again, the only peak to grow in at 3.6 ppm corresponds to the slow formation of benzyl disulfide.



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[1] V. M. Cangelosi, A. C. Sather, L. N. Zakharov, O. B. Berryman, D. W. Johnson *Inorg. Chem.* **2007**, *46*, 9278-9284.

[2] W. J. Vickaryous, L. N. Zakharov, D. W. Johnson *Main Group Chem.*, **2006**, *5*, 51-59.

[3] V. M. Cangelosi, M. A. Pitt, W. J. Vickaryous, C. A. Allen, L. N. Zakharov, D. W. Johnson *Cryst. Growth Des.* **2010**, *10*, 3531-3536.