Supporting Information for:

Exploring the Effects of Reduction or Lewis Acid Coordination on the U=O Bond of the Uranyl Moiety

Trevor W. Hayton* and Guang Wu

Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara CA 93106

*To whom correspondence should be addressed. Email: hayton@chem.ucsb.edu

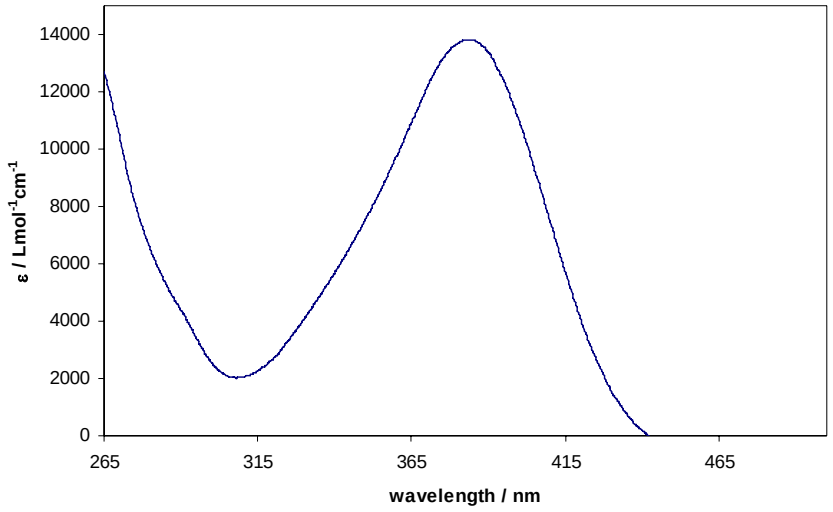

Figure S1. Room temperature absorption spectra of ^{Ar}acnac (Ar = 3,5-^{t}BuC$_6$H$_3$) (0.078 mM, CH_2Cl_2).

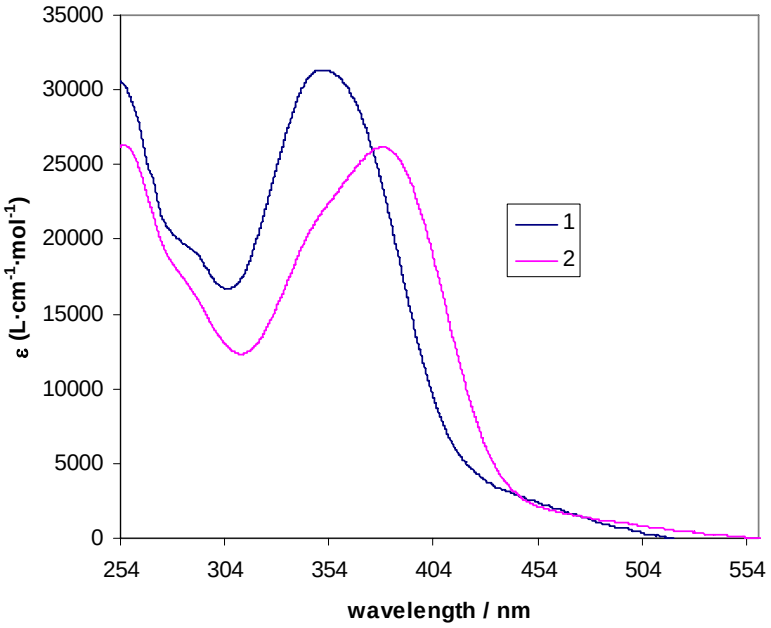

Figure S2. Room temperature absorption spectra of **1** (0.012 mM, CH_2Cl_2) and **2** (0.028 mM, CH_2Cl_2).

Table S1. Electrochemical parameters for complex **1** in CH_2Cl_2 (vs. Fc/Fc^+, $[NBu_4][PF_6]$ as supporting electrolyte).

Reduction feature	Scan rate, V/s	$E_{p,c}$, V	$E_{p,a}$, V	ΔE_p[a]	$i_{p,c}/i_{p,a}$
	0.025	-1.60	-1.43	0.17	1.27
	0.05	-1.61	-1.42	0.19	1.34
	0.1	-1.64	-1.40	0.24	1.48
	0.15	-1.65	-1.39	0.26	1.51
	0.2	-1.66	-1.38	0.28	1.66
	0.25	-1.67	-1.37	0.30	1.76
	0.3	-1.68	-1.37	0.31	1.88

[a] ΔE_p is defined as the potential difference between the cathodic wave and the anodic wave generate after the change in sweep direction.

Table S2. Electrochemical parameters for complex **2** in CH_2Cl_2 (vs. Fc/Fc^+, 0.1 M $[NBu_4][PF_6]$ as supporting electrolyte).

Reduction feature	Scan rate, V/s	$E_{p,c}$, V	$E_{p,a}$, V	ΔE_p	$i_{p,c}/i_{p,a}$
	0.01	-1.62	-1.45	0.17	1.21
	0.025	-1.64	-1.43	0.21	1.22
	0.05	-1.66	-1.41	0.25	1.32
	0.1	-1.68	-1.39	0.29	1.48
	0.15	-1.69	-1.38	0.31	1.64
	0.2	-1.71	-1.37	0.34	1.77
	0.25	-1.72	-1.36	0.36	1.94
	0.3	-1.72	-1.35	0.37	2.11
	0.5	-1.74	-1.33	0.41	2.44

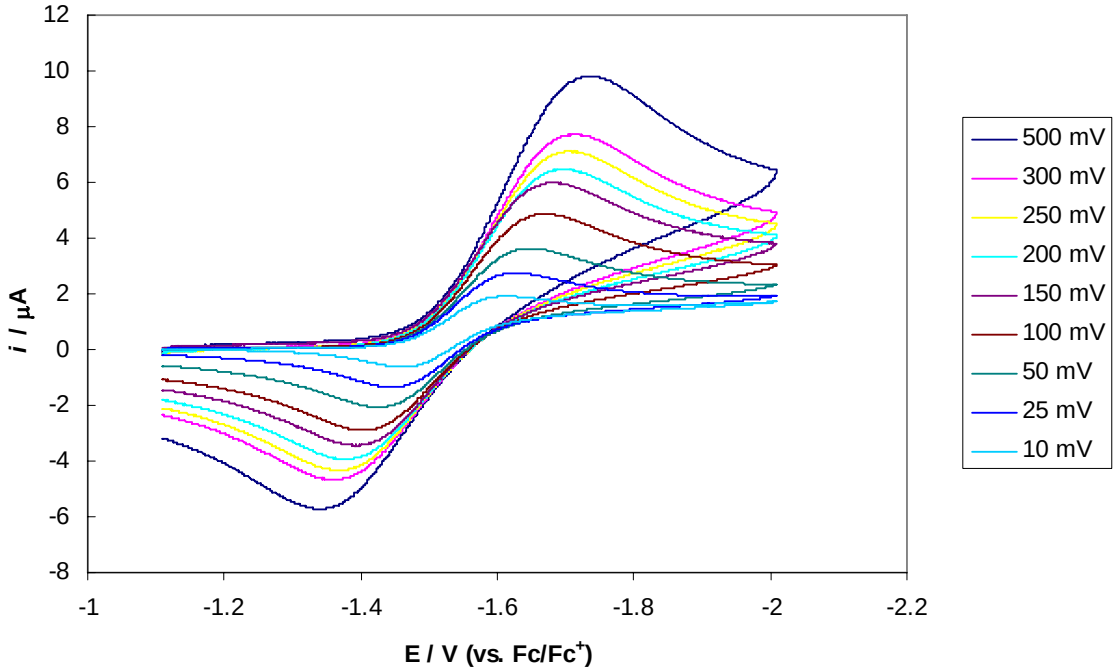

Figure S2. Room temperature cyclic voltammogram for **2**. Measured in CH_2Cl_2 with 0.1 M $[NBu_4][PF_6]$ as supporting electrolyte.

Table S3. Electrochemical parameters for complex **2**. In CH_2Cl_2 (vs. Fc/Fc^+, 0.1 M $[NBu_4][B\{C_6F_5\}_4]$ as supporting electrolyte).

Reduction feature 1	**Scan rate, V/s**	**$E_{p,c}$, V**	**$E_{p,a}$, V**	**ΔE_p**	**$i_{p,c}/i_{p,a}$**
	0.025	-1.45	-1.24	0.21	1.21
	0.05	-1.47	-1.22	0.25	1.31
	0.075	-1.48	-1.21	0.27	1.31
	0.1	-1.49	-1.20	0.29	1.30
	0.15	-1.51	-1.19	0.32	1.32
	0.2	-1.52	-1.17	0.35	1.40
	0.25	-1.53	-1.17	0.36	1.36
	0.3	-1.54	-1.16	0.38	1.48
	0.5	1.56	-1.13	0.43	1.61
Reduction feature 2					
	0.025	-2.06			
	0.05	-2.06			
	0.1	-2.07	-1.92	0.15	
	0.2	-2.09	-1.92	0.17	1.64
	0.3	-2.10	-1.92	0.18	1.68
	0.5	-2.12	-1.91	0.21	1.72
	0.75	-2.14	-1.90	0.24	1.87
	1.0	-2.15	-1.90	0.25	1.84

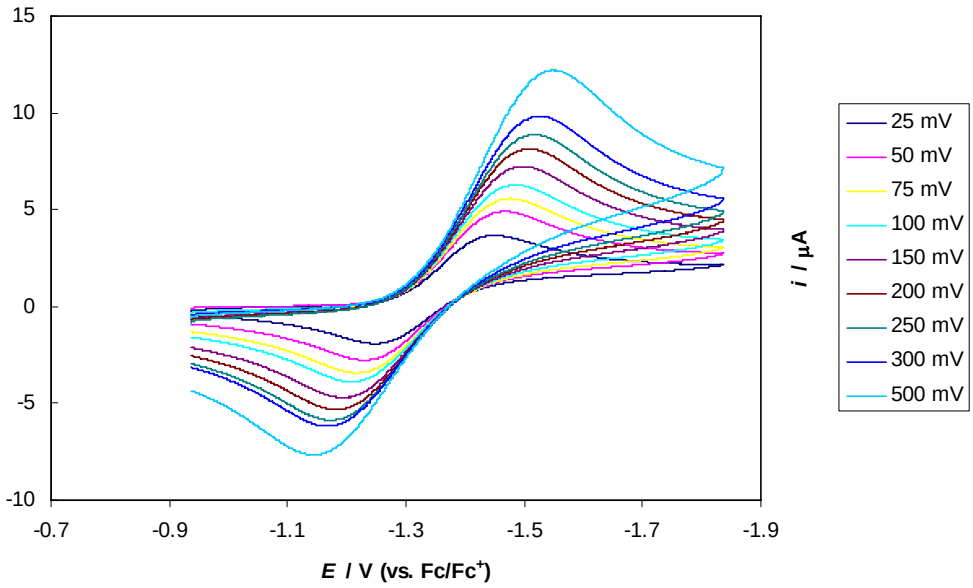

Figure S3. Room temperature cyclic voltammogram of 'reduction feature 1' for **2**. Measured in CH_2Cl_2 with 0.1 M $[NBu_4][B\{C_6F_5\}_4]$ as supporting electrolyte.

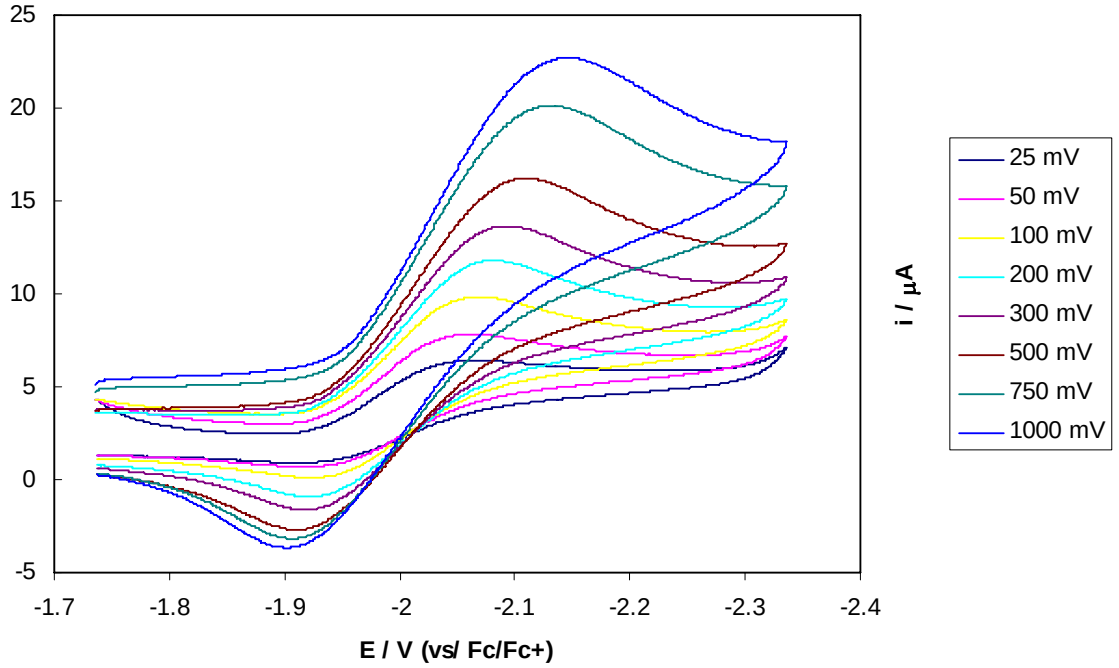

Figure S4. Room temperature cyclic voltammogram of 'reduction feature 2' for **2**. Measured in CH_2Cl_2 with 0.1 M $[NBu_4][B\{C_6F_5\}_4]$ as supporting electrolyte.

Table S4. Electrochemical parameters for complex **5**, generated *in situ*. In CH_2Cl_2 (vs. Fc/Fc^+, 0.1 M $[NBu_4][B\{C_6F_5\}_4]$ as supporting electrolyte).

Reduction feature 1	**Scan rate, V/s**	**$E_{p,c}$, V**	**$E_{p,a}$, V**	**ΔE_p**	**$i_{p,c}/i_{p,a}$**
	0.025	-0.73			
	0.05	-0.77			
	0.1	-0.78			
	0.15	-0.80			
	0.2	-0.82			
	0.25	-0.83			
	0.3	-0.83			
Reduction feature 2					
	0.025	-1.74			
	0.05	-1.77			
	0.075	-1.79			
	0.1	-1.79			
	0.15	-1.80			
	0.2	-1.82	-1.63	0.19	
	0.25	-1.82	-1.63	0.19	2.89
	0.3	-1.83	-1.63	0.20	2.96
	0.5	-1.86	-1.63	0.23	2.89

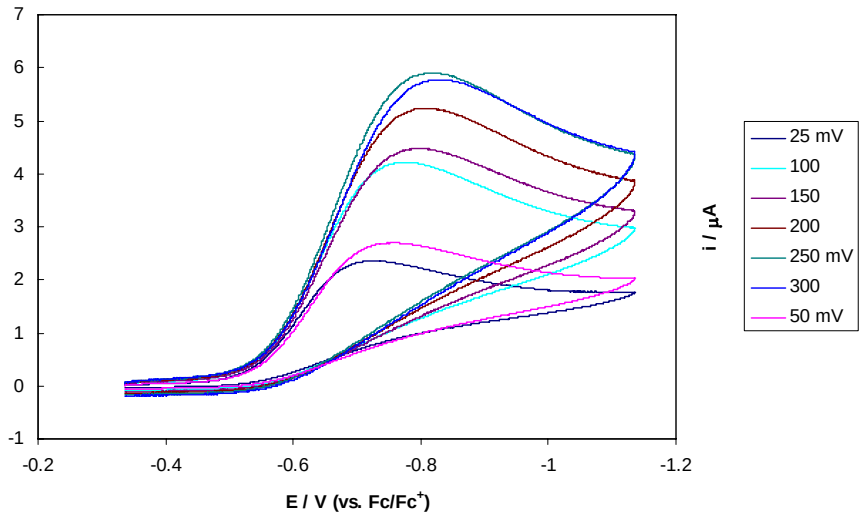

Figure S5. Room temperature cyclic voltammogram of 'reduction feature 1' for **5** (generated *in situ*). Measured in CH_2Cl_2 with 0.1 M $[NBu_4][B\{C_6F_5\}_4]$ as supporting electrolyte.

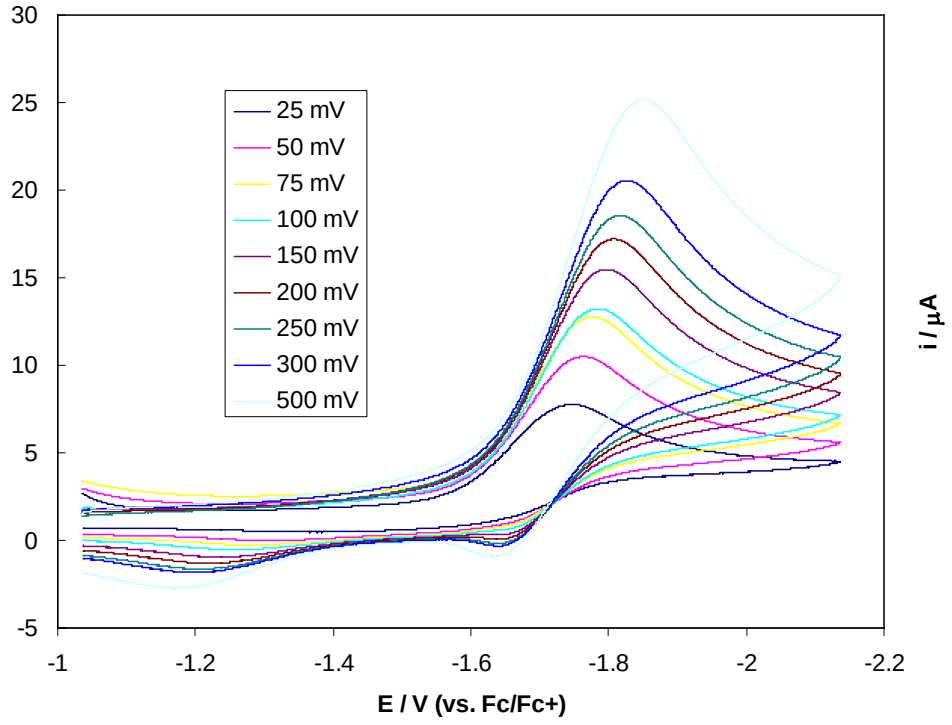

Figure S6. Room temperature cyclic voltammogram of 'reduction feature 2' for **5** (generated *in situ*). Measured in CH_2Cl_2 with 0.1 M $[NBu_4][B\{C_6F_5\}_4]$ as supporting electrolyte.

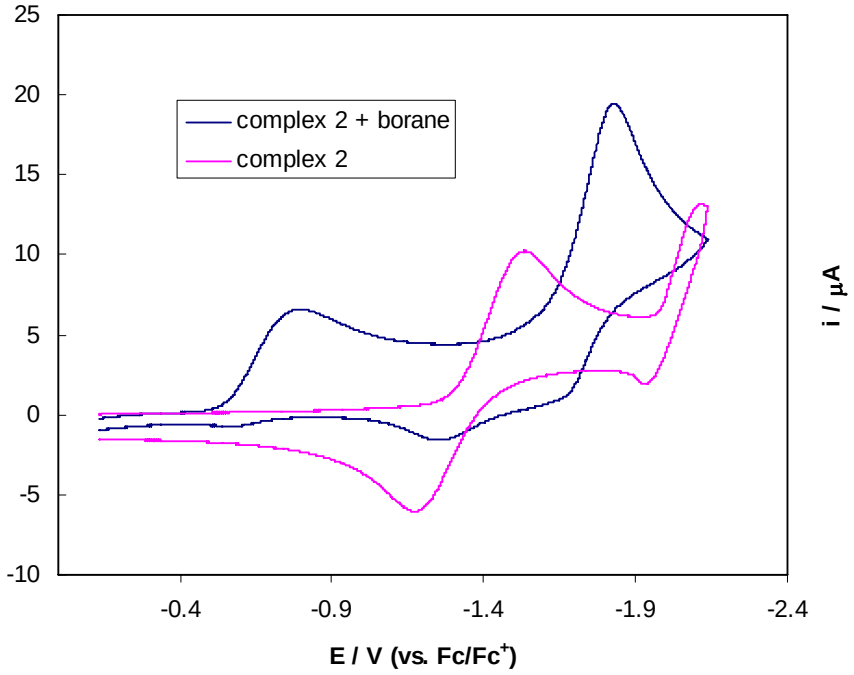

Figure S7. Room temperature cyclic voltammogram for **2** before (pink line) and after addition of 2 equiv of $B(C_6F_5)_3$ (blue line). Measured in CH_2Cl_2, 200 mV/s scan rate; 0.1 M $[NBu_4][B\{C_6F_5\}_4]$ as supporting electrolyte.

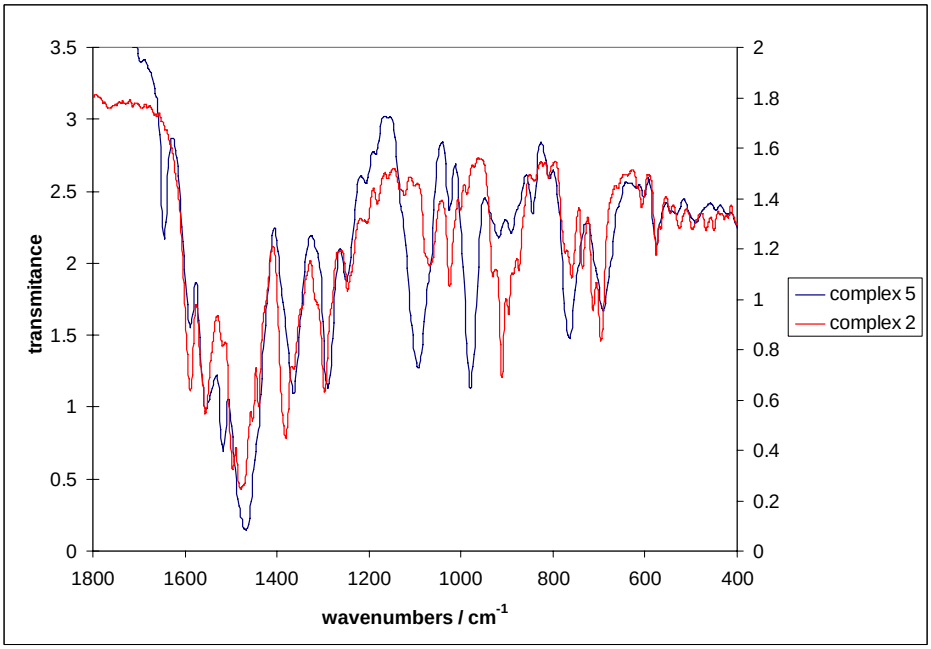

Figure S8. IR spectra of complexes **2** and **5** (as KBr mulls).

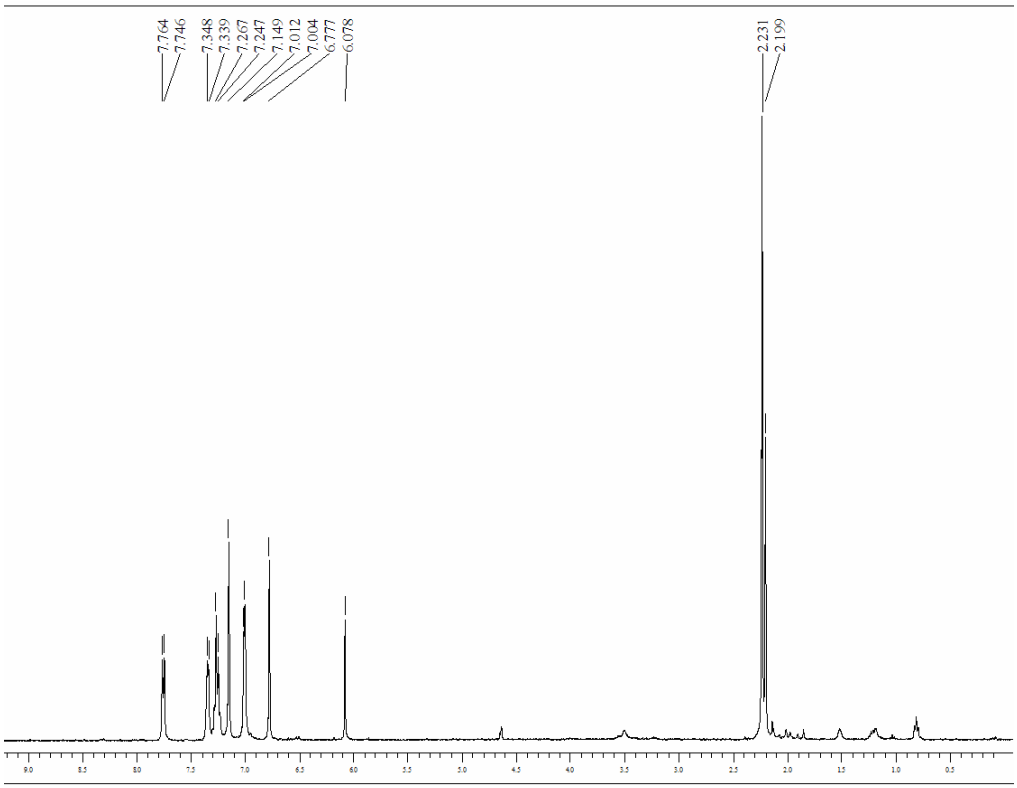

Figure S9. ^{1}H NMR spectrum of **1** in C_6D_6.

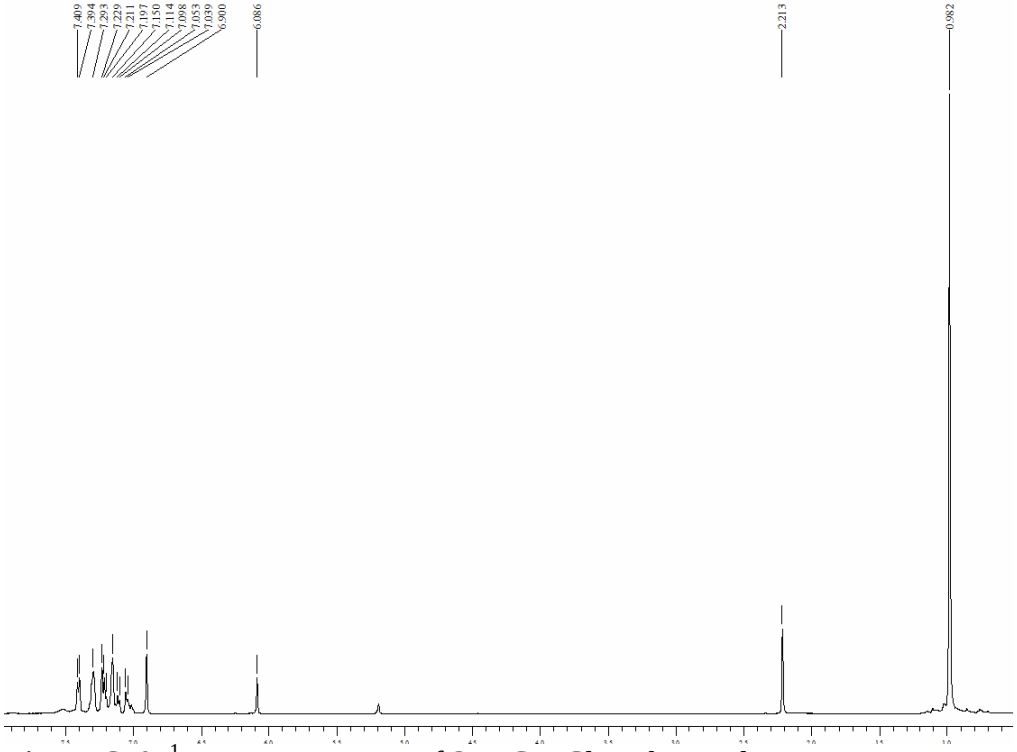

Figure S10. ^{1}H NMR spectrum of **2** in CD_2Cl_2. The singlet at 2.21 ppm corresponds to the methyl group of toluene.

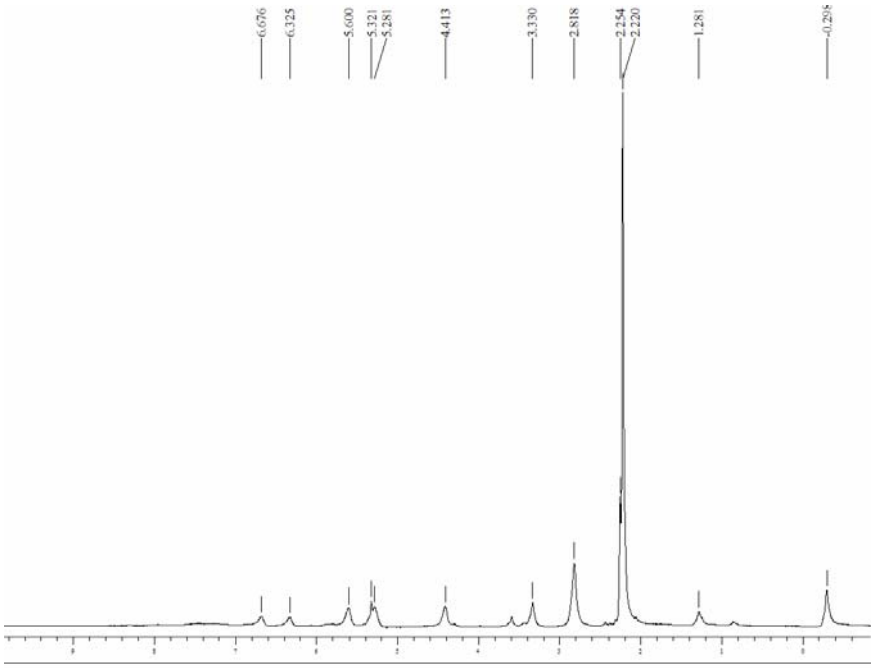

Figure S11. ^{1}H NMR spectrum of **3** in CD_2Cl_2

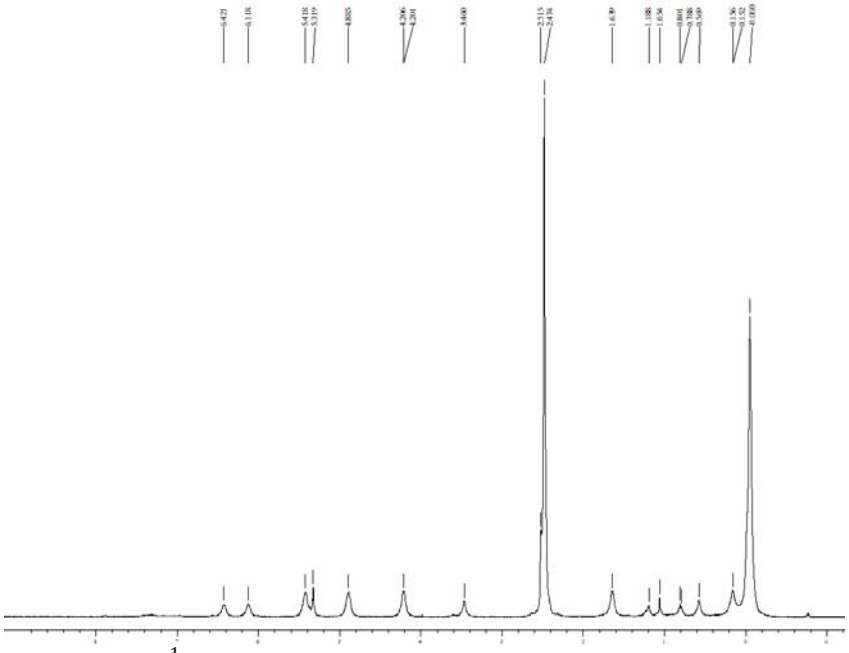

Figure S12. ^{1}H NMR spectrum of **4** in CD_2Cl_2

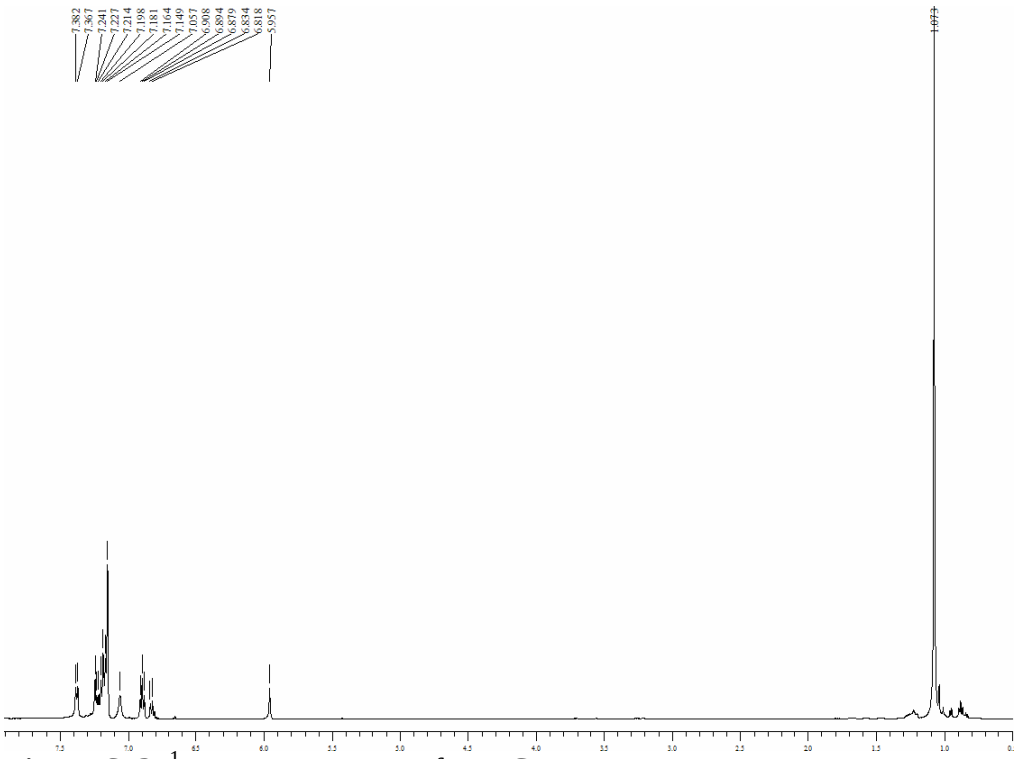

Figure S13. ^{1}H NMR spectrum of **5** in C_6D_6

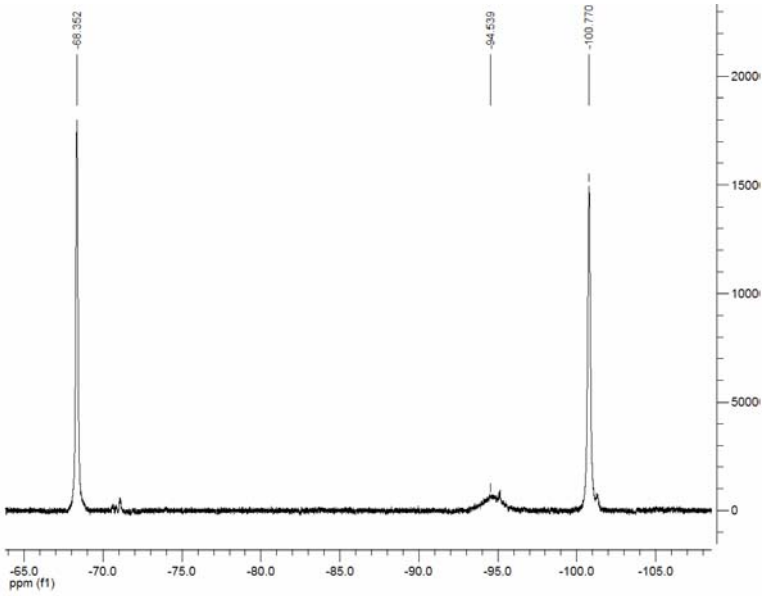

Figure S14. ^{19}F NMR spectrum of **5** in C_6D_6