Supplementary Data for

NMR Spectroscopy Studies of Electronic Effects and Equilibrium in the Organogold-to-Boron Transmetalation Reaction and Studies Towards its Application to the Alkoxyboration Addition of Boron–Oxygen σ Bonds to Alkynes

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1. Atomic coordinates for optimized structures of compounds from Tables 2 and 3 calculated at the B3LYP/6-311G level of theory

Table 2, 3-hexyne starting material (**11**).

Atom	*x (Å)*	*y (Å)*	*z (Å)*	*Atom*	*x (Å)*	*y (Å)*	*z (Å)*
C	0.5655	0.2074	-0.0806	H	3.9938	-0.0401	0.1189
C	0.5655	0.2074	-0.0806	H	2.9008	-1.1863	-0.6756
C	-1.9488	-0.6823	-0.0769	C	-2.9782	0.4446	0.1223
C	1.9488	0.6824	-0.0770	H	-2.0699	-1.4315	0.7141
C	2.9782	-0.4446	0.1224	H	-2.1543	-1.2022	-1.0198
H	2.0700	1.4316	0.7139	H	-2.8149	0.9557	1.0736
H	2.1544	1.2022	-1.0199	H	-3.9938	0.0400	0.1189
H	2.8148	-0.9556	1.0737	H	-2.9009	1.1862	-0.6757

Table 2, entry 1, boric ester starting material **7g**.

Atom	*x (Å)*	*y (Å)*	*z (Å)*	*Atom*	*x (Å)*	*y (Å)*	*z (Å)*
C	-2.3627	0.2713	0.0000	H	0.5698	2.9057	0.0000
C	-1.0344	-0.1048	0.0000	O	-0.4857	-1.4028	0.0000
C	-2.6266	1.6519	0.0000	O	1.2351	0.1491	0.0000
C	-1.5882	2.5925	0.0000	B	0.9130	-1.2297	0.0000
C	-0.2406	2.1924	0.0000	O	1.7958	-2.2425	0.0000
C	0.0000	0.8330	0.0000	C	3.2428	-2.0742	0.0000
H	-3.1528	-0.4643	0.0000	H	3.6697	-3.0713	0.0000
H	-3.6526	1.9923	0.0000	H	3.5615	-1.5319	0.8895
H	-1.8249	3.6473	0.0000	H	3.5615	-1.5319	-0.8895

Table 2, entry 1, alkoxyboration product **13g**.

Atom	*x (Å)*	*y (Å)*	*z (Å)*	*Atom*	*x (Å)*	*y (Å)*	*z (Å)*
C	-2.2617	-0.2753	-0.2754	B	0.1962	0.3395	-0.1887
C	-1.2852	0.6717	-0.2629	O	0.8277	-0.9354	-0.0984
O	-3.5787	0.2040	-0.2546	O	1.2122	1.3338	-0.2042
C	-1.6577	2.1527	-0.2775	C	2.4463	0.6681	-0.1262
C	-1.9217	2.7214	1.1324	C	2.2162	-0.7058	-0.0632
H	-0.8494	2.7200	-0.7417	C	3.7223	1.1986	-0.1099
H	-2.5506	2.2922	-0.8879	C	4.7841	0.2824	-0.0264
H	-1.0409	2.6142	1.7691	C	4.5519	-1.0986	0.0364
H	-2.7542	2.2009	1.6074	C	3.2477	-1.6213	0.0186
H	-2.1697	3.7846	1.0811	H	3.0554	-2.6828	0.0663
C	-2.0727	-1.7696	-0.2140	H	3.8865	2.2646	-0.1594
C	-2.3353	-2.3481	1.1954	H	5.7999	0.6521	-0.0104
H	-2.7291	-2.2587	-0.9392	H	5.3913	-1.7770	0.0999
H	-1.0541	-2.0075	-0.5054	C	-4.6894	-0.6172	-0.7175
H	-1.6189	-1.9393	1.9084	H	-4.5586	-0.9035	-1.7625
H	-2.2239	-3.4338	1.1866	H	-5.5617	0.0216	-0.6239
H	-3.3376	-2.1117	1.5565	H	-4.8245	-1.5068	-0.1025

Table 2, entry 2, boric ester starting material **7e**.

Atom	*x (Å)*	*y (Å)*	*z (Å)*	*Atom*	*x (Å)*	*y (Å)*	*z (Å)*
C	2.4624	3.6339	0.0000	C	-1.7756	-0.7865	0.0000
C	1.6847	2.4931	0.0000	C	-3.1627	-0.8935	0.0000
C	3.8550	3.4454	0.0000	C	-0.9656	-1.9229	0.0000
C	4.4177	2.1622	0.0000	C	-1.5726	-3.1801	0.0000
C	3.6113	1.0110	0.0000	C	-2.9689	-3.3245	0.0000
C	2.2463	1.2158	0.0000	C	-3.7501	-2.1594	0.0000
H	2.0157	4.6166	0.0000	C	-3.6040	-4.6970	0.0000
H	4.5036	4.3103	0.0000	H	-4.6923	-4.6295	0.0000
H	5.4931	2.0522	0.0000	H	-3.3084	-5.2743	0.8799
H	4.0309	0.0164	0.0000	H	-3.3084	-5.2743	-0.8799
O	0.2800	2.3823	0.0000	H	-0.9455	-4.0632	0.0000
O	1.2042	0.2609	0.0000	H	0.1090	-1.8256	0.0000
B	0.0000	1.0027	0.0000	H	-4.8295	-2.2412	0.0000
O	-1.2564	0.5200	0.0000	H	-3.7585	0.0074	0.0000

Table 2, entry 2, alkoxyboration product **13e**.

Atom	*x (Å)*	*y (Å)*	*z (Å)*	*Atom*	*x (Å)*	*y (Å)*	*z (Å)*
C	0.6070	0.1864	0.4131	C	-3.7362	-0.9209	0.0052
C	-0.4436	0.9185	-0.0302	C	-5.4045	0.6147	-0.8646
O	1.8409	0.8733	0.5482	C	-6.3501	-0.4076	-0.6815
C	3.0589	0.3089	0.1178	C	-5.9819	-1.6579	-0.1645
C	4.1838	0.5485	0.9063	C	-4.6522	-1.9383	0.1916
C	5.4277	0.0790	0.4859	H	-4.3556	-2.8966	0.5910
C	5.5704	-0.6389	-0.7133	H	-5.6738	1.5817	-1.2621
C	4.4227	-0.8576	-1.4888	H	-7.3824	-0.2247	-0.9455
C	3.1706	-0.3856	-1.0864	H	-6.7348	-2.4230	-0.0364
H	4.0713	1.1060	1.8250	H	0.7480	2.5020	-0.8634
H	6.2998	0.2714	1.0984	C	-0.4370	3.3615	0.7236
H	4.5073	-1.3948	-2.4251	H	-0.9690	2.6186	-1.2328
H	2.2980	-0.5388	-1.7063	H	0.2953	3.1685	1.5086
C	6.9194	-1.1703	-1.1438	H	-1.4360	3.2754	1.1559
H	7.7162	-0.4540	-0.9354	H	-0.3078	4.3917	0.3834
H	6.9382	-1.3873	-2.2125	C	0.6113	-1.2284	0.9288
H	7.1699	-2.0964	-0.6177	C	0.7786	-1.2918	2.4636
C	-0.2515	2.3744	-0.4476	H	1.4262	-1.7863	0.4611
B	-1.8674	0.3712	-0.0976	H	-0.3170	-1.7149	0.6433
O	-2.3525	-0.9128	0.2698	H	1.7096	-0.8220	2.7822
O	-2.9586	1.1372	-0.5826	H	0.7907	-2.3309	2.7971
C	-4.1014	0.3221	-0.5094	H	-0.0479	-0.7841	2.9627

Table 2, entry 3, boric ester starting material **7h**.

Atom	*x (Å)*	*y (Å)*	*z (Å)*	*Atom*	*x (Å)*	*y (Å)*	*z (Å)*
O	1.3447	0.4301	0.0000	H	2.8450	-3.9670	0.0000
B	0.0000	0.8333	0.0000	H	0.4989	-4.7234	0.0000
C	1.3209	-0.9814	0.0000	H	-1.3808	-3.0624	0.0000
C	-0.0057	-1.4103	0.0000	O	-0.3297	2.1622	0.0000
O	-0.8514	-0.2772	0.0000	C	-1.5792	2.8016	0.0000
C	2.3792	-1.8683	0.0000	O	-2.6315	2.1838	0.0000
C	2.0503	-3.2342	0.0000	C	-1.4295	4.2917	0.0000
C	0.7160	-3.6645	0.0000	H	-0.3862	4.5874	0.0000
C	-0.3484	-2.7474	0.0000	H	-1.9291	4.7040	0.8774
H	3.4021	-1.5234	0.0000	H	-1.9291	4.7040	-0.8774

Table 2, entry 3, alkoxyboration product **13h**.

Atom	*x (Å)*	*y (Å)*	*z (Å)*	*Atom*	*x (Å)*	*y (Å)*	*z (Å)*
C	-1.7058	-0.3114	0.0598	O	1.3840	-0.9465	0.0525
C	-0.7537	0.6400	-0.0417	C	2.7707	-0.7106	-0.0389
C	-1.1186	2.1212	-0.0967	C	2.9815	0.6564	-0.2096
C	-1.1748	2.7703	1.3018	C	4.2486	1.1943	-0.3310
H	-2.0836	2.2446	-0.5883	C	5.3216	0.2899	-0.2733
H	-0.3785	2.6467	-0.7017	C	5.1086	-1.0854	-0.1016
H	-1.9315	2.2871	1.9212	C	3.8134	-1.6151	0.0196
H	-1.4222	3.8315	1.2246	H	4.3981	2.2552	-0.4638
H	-0.2125	2.6886	1.8109	H	6.3318	0.6639	-0.3639
C	-1.5650	-1.8027	0.1663	O	-3.0601	0.1549	0.1984
C	-2.0311	-2.3556	1.5309	C	-4.0663	-0.2079	-0.6961
H	-0.5246	-2.0704	0.0034	O	-3.8600	-0.8634	-1.7125
H	-2.1477	-2.2626	-0.6344	C	-5.3877	0.3278	-0.2370
H	-3.0751	-2.1102	1.7301	H	-6.1543	0.0664	-0.9597
H	-1.4276	-1.9474	2.3434	H	-5.3386	1.4111	-0.1257
H	-1.9311	-3.4420	1.5471	H	-5.6441	-0.0864	0.7387
B	0.7424	0.3111	-0.0695	H	3.6356	-2.6718	0.1511
O	1.7349	1.3083	-0.2307	H	5.9573	-1.7539	-0.0621

Table 2, entry 4, boric ester starting material **7i**.

Atom	*x (Å)*	*y (Å)*	*z (Å)*	*Atom*	*x (Å)*	*y (Å)*	*z (Å)*
O	-1.3755	1.0432	0.0000	H	-1.4335	5.6909	0.0000
B	-0.2262	0.2577	0.0000	H	1.0302	5.6802	0.0000
C	-0.9140	2.3824	0.0000	H	2.3023	3.5185	0.0000
C	0.4798	2.3775	0.0000	O	-0.3113	-1.1216	0.0000
O	0.9289	1.0317	0.0000	C	0.6538	-2.0812	0.0000
C	-1.6458	3.5525	0.0000	O	1.8558	-1.9072	0.0000
C	-0.9070	4.7471	0.0000	C	0.0432	-3.4842	0.0000
C	0.4954	4.7412	0.0000	F	-1.3371	-3.5017	0.0000
C	1.2233	3.5399	0.0000	F	0.4798	-4.1792	1.1234
H	-2.7250	3.5427	0.0000	F	0.4798	-4.1792	-1.1234

Table 2, entry 4, alkoxyboration product **13i**.

Atom	*x (Å)*	*y (Å)*	*z (Å)*	*Atom*	*x (Å)*	*y (Å)*	*z (Å)*
C	-0.8131	-0.4190	0.0526	O	2.2731	-0.9551	0.0422
C	0.0943	0.5700	-0.0359	C	3.6552	-0.6832	-0.0531
C	-0.3178	2.0388	-0.0725	C	3.8290	0.6895	-0.2169
C	-0.3293	2.6812	1.3307	C	5.0803	1.2622	-0.3408
H	-1.3070	2.1390	-0.5173	C	6.1763	0.3858	-0.2928
H	0.3811	2.5847	-0.7075	C	6.0005	-0.9959	-0.1276
H	-1.0509	2.1827	1.9790	C	4.7208	-1.5608	-0.0038
H	-0.6048	3.7353	1.2638	H	5.2013	2.3273	-0.4681
H	0.6544	2.6218	1.8001	H	7.1758	0.7865	-0.3856
C	-0.6534	-1.9058	0.1599	O	-2.2001	0.0138	0.1806
C	-1.1708	-2.4729	1.5007	C	-3.1656	-0.3799	-0.6854
H	0.3998	-2.1466	0.0417	O	-3.0337	-1.0319	-1.7087
H	-1.1855	-2.3797	-0.6686	C	-4.5110	0.1338	-0.1749
H	-2.2272	-2.2502	1.6548	F	-5.5298	-0.1889	-1.0487
H	-0.6129	-2.0563	2.3404	F	-4.5011	1.5173	-0.0213
H	-1.0492	-3.5566	1.5160	F	-4.8166	-0.4274	1.0642
B	1.6046	0.2849	-0.0693	H	4.5720	-2.6225	0.1228
O	2.5632	1.3082	-0.2290	H	6.8668	-1.6415	-0.0953

2. NMR spectra for transmetalation reaction mixtures from Table 1

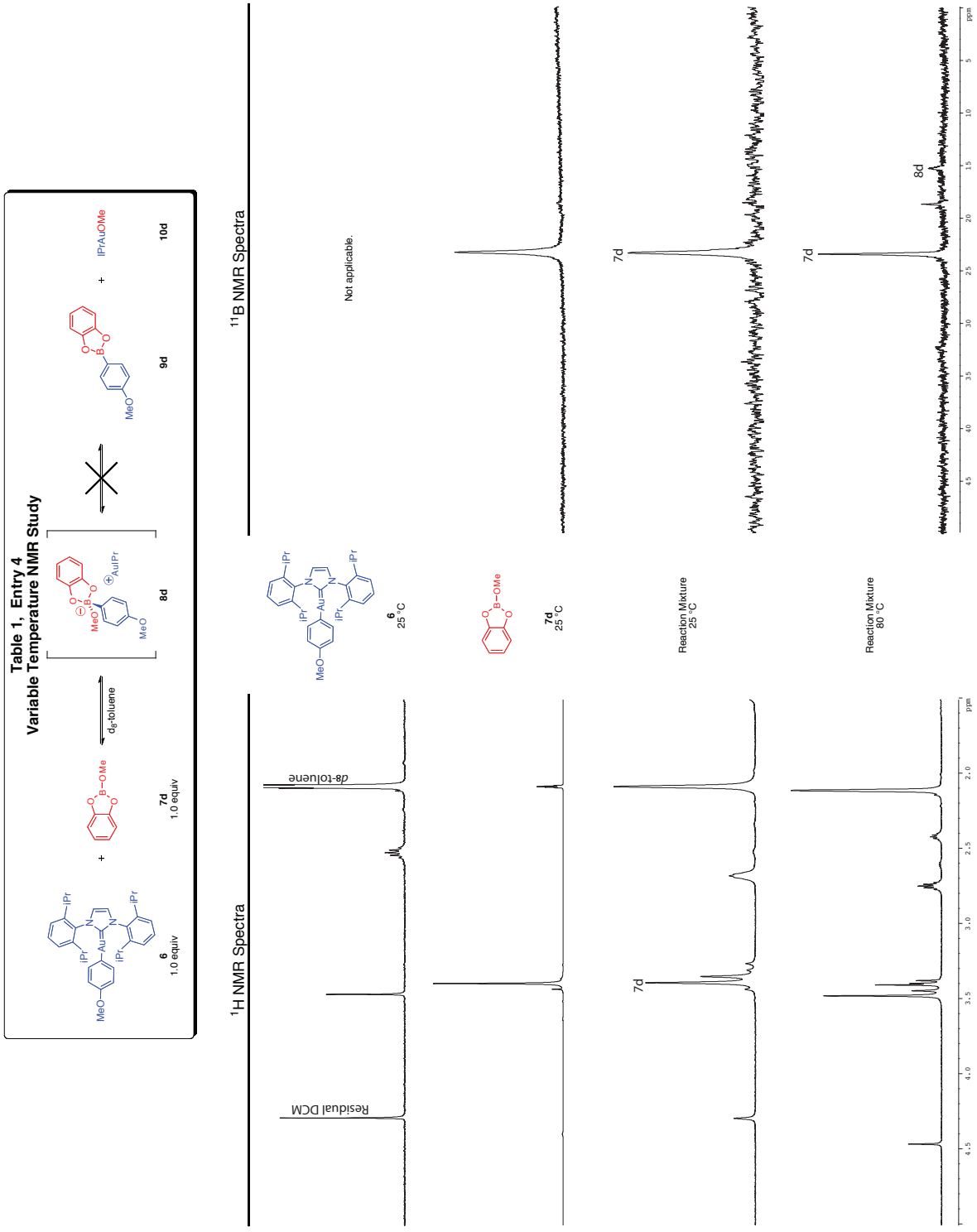
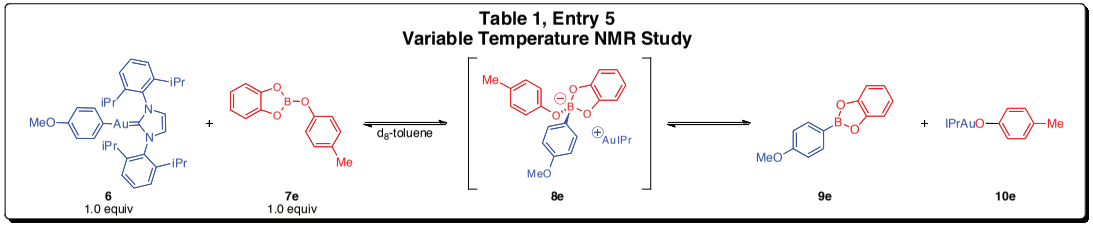
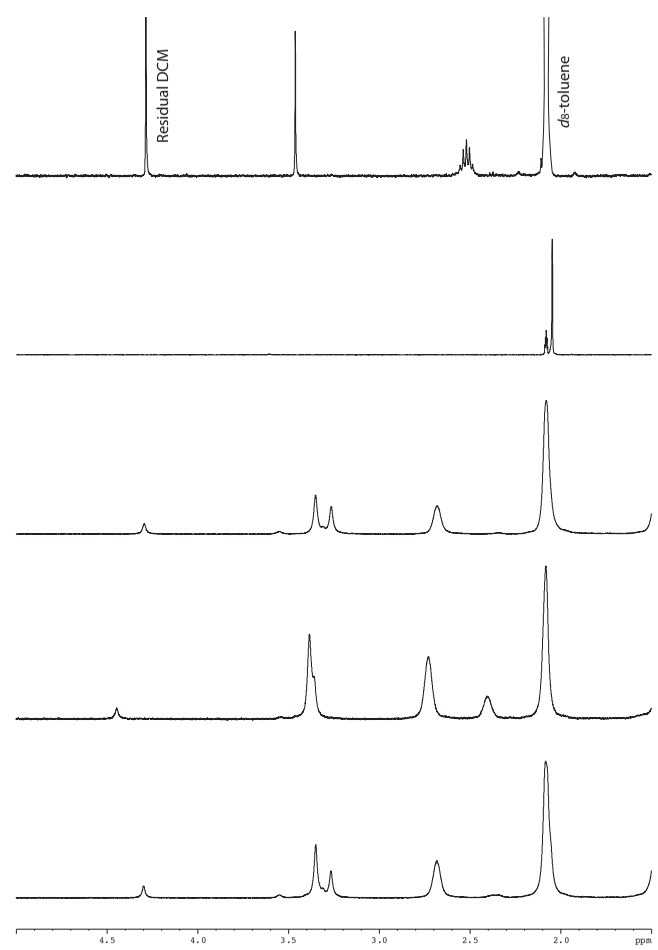
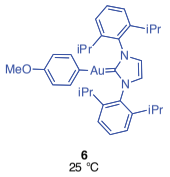


Table 1, Entry 5
Variable Temperature NMR Study

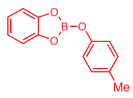


^{1}H NMR Spectra





6
25 °C



7e
25 °C

Reaction Mixture
25 °C

Reaction Mixture
80 °C

Reaction Mixture
25 °C

^{11}B NMR Spectra

Not applicable.

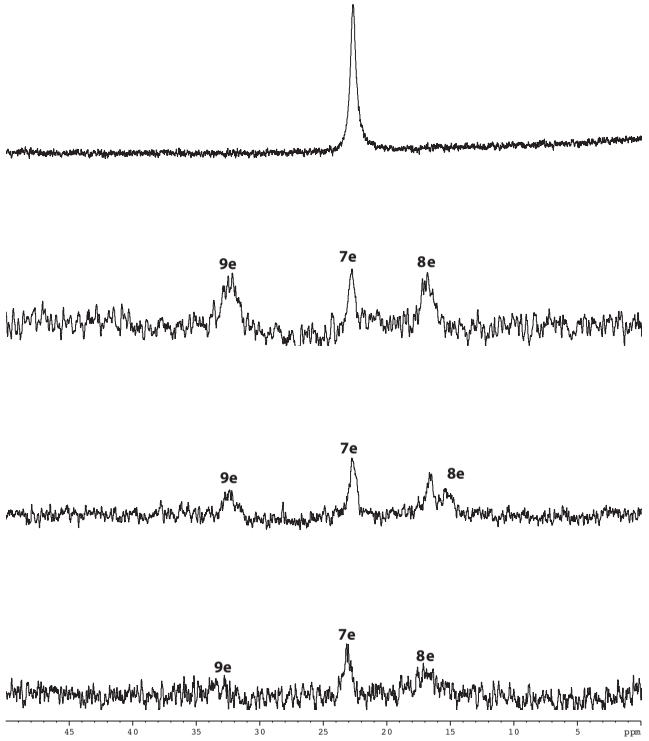
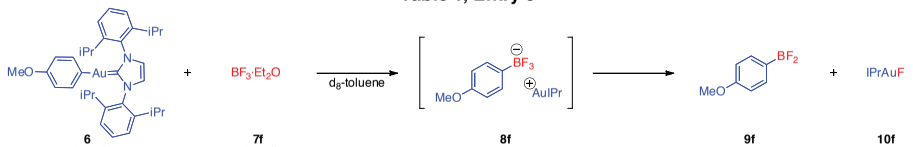
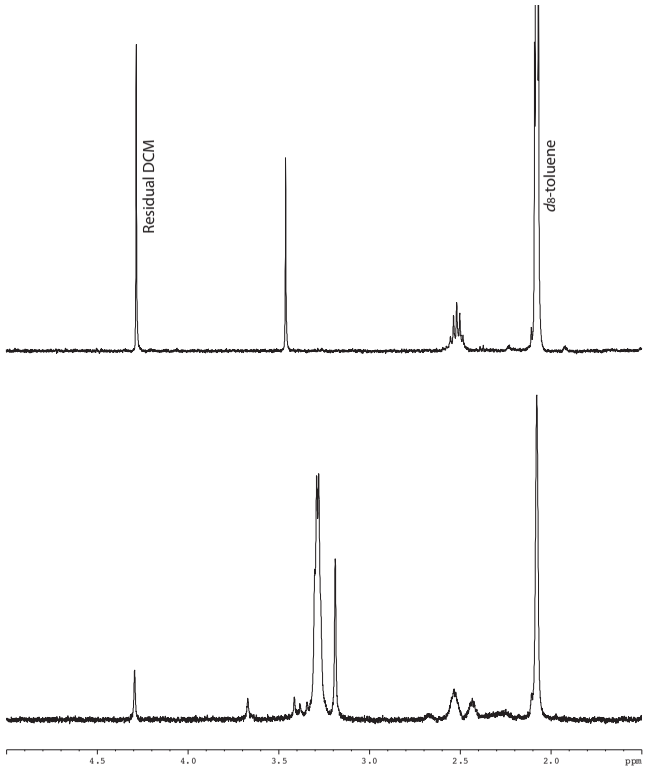


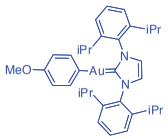
Table 1, Entry 6



6 1.0 equiv | **7f** 1.0 equiv | **8f** | **9f** | **10f** *not detected by ^{19}F NMR*

^{1}H NMR Spectra





6
25 °C

Reaction Mixture
25 °C, t = 20 min

^{11}B NMR Spectra

Not applicable.