Supplementary Material (ESI) for Dalton Transactions

On the possibility of catalytic reduction of carbonyl moieties with tris(pentafluorophenyl)borane and H_2: a computational study

Jonas Nyhlén and Timofei Privalov

Computational Details

All calculations are performed with the Jaguar 6.0[1] quantum chemistry package. We initially performed a conformational search using potential energy scans with the B3LYP functional using the split-valence double-zeta basis set, 6-31+G*,[2,3] augmented with diffuse and polarization functions, and the molecular model system formally in gas phase. The geometries of conformers lowest in energy were then re-optimized using B3LYP functionals[4,5] with 6-31+G* basis set; all degrees of freedom were optimized. All transition states were found with B3LYP/6-31+G* using the quadratic synchronous transit (QST) method, as implemented in the Jaguar 6.0 computational package, and were characterized by one single imaginary vibrational frequency along the proper reaction coordinate. The reaction coordinate scans have been performed to verify that all reported transition states are indeed "connecting" appropriate intermediates along the reaction pathway.

In order to increase the accuracy of the computation of relative energies of all intermediates and transition states, the larger basis set 6-31++G** was used to obtain final electronic energies of all complexes employing geometries obtained with the 6-31+G* base set. All thermochemical corrections were computed at the 6-31+G*. All reported potential energies in Figure 4 are true Gibbs free energies with the account of solvent effects.

Solvent effects were accounted for as follows. Gas-phase optimized structures, B3LYP with 6-31+G* basis set, were used as starting structures in order to obtain energies of all intermediates and transition

---

[1] Jaguar 6.0, Schrödinger, LLC., Portland, Oregon, 2005.

[2] Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 299.

[3] (a) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys*. **1972**, *56,* 2257. (b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees, J. A. Pople, *J. Chem. Phys*. **1982**, *77*, 3654. (c) P. C: Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213.

[4] (a) A. D. Becke, *J. Chem. Phys*. **1993**, 98, 5648. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[5] B. J. Lynch, P. L. Fast, M. Harris, D. G. Truhlar, *J. Phys. Chem. A* **2000**, *104*, 7650.

states in solvent within the self-consistent reaction field model[6] with toluene, dichloromethane and acetonitrile as solvents at the large basis set level (6-31++G**). Thus, solvent correction to all the Gibbs free energies and the potential energies has been obtained. This data was used to construct the Gibbs free energy profiles and for the discussion of relative energies in the text. To check the stability of solvated complexes, geometry has been relaxed and optimized within the self-consistent implicit solvent model.

		DCM dG corrected	toluene dG corrected	acetonitrile dG corrected	Gas dG corrected
2a					
	3	0	0	0	0

[6] Jaguar 6.0 package treats solvated molecular systems with SCRF method, using its own Poisson-Boltzmann solver, which makes possible to compute salvation energies and minimum- energy solvated structures of solvated transition states. For details see: (a) Tannor, D. J.; Marten, B.; Murphy, R.; Friesner, R. A.; Sitkoff, D.; Nicholls, A.; Ringnalda, M.; Goddard, W. A., III; Honig, B. *J. Am. Chem. Soc.* **1994,** *116,* 11875. (b) Marten, B.; Kim, K.; Cortis, C.; Friesner, R. A.; Murphy, R. B.; Ringnalda, M. N.; Sitkoff, D.; Honig, B. *J. Phys. Chem.* **1996,** *100,* 11775; (c) Cramer, C.J.; Truhlar, D., G.; *Chem .Rev.*, **1999**, *99*, 2161-2200.

	TS1	26,26844962	26,4669599	25,81775751	26,77538358
	4	21,88558824	23,44730752	21,34061777	26,05962788
	TS2	34,60191729	35,63719082	33,95919896	36,70679417
	Final	-10,50907763	-9,235080469	-10,874365	-8,601449736
	TS2 relative to 4	12,71632906	12,18988331	12,6185812	10,64716629
2b					
	3	0	0	0	0
	TS1	23,04564423	23,70873844	23,24506628	24,80856831
	4	19,01576161	21,16016722	18,60057527	24,55254464
	TS2	26,45217698	25,43597222	27,00372313	23,65457926
	Final	-12,33798125	-11,76548254	-12,05424131	-12,05763174
	TS2 relative to 4	7,436415363	4,275804998	8,403147856	-0,897965379
2c					
	3	0	0	0	0
	TS1	22,27647761	22,52230591	21,86167531	23,75484913
	4	17,0537079	18,77156421	16,66465546	22,16268661
	TS2	34,54088818	34,63350991	34,68205032	35,058289
	Final	-9,953462074	-9,078691799	-10,01098466	-8,599387738
	TS2 relative to 4	17,48718028	15,8619457	18,01739486	12,89560239
2d					
	3	0	0	0	0
	TS1	15,28992623	15,70933195	14,83005176	17,01047519
	4	8,628087831	11,01714641	7,781446947	14,79807991
	TS2	38,33518575	39,11096884	37,85912592	39,48468932
	Final	-15,88842508	-15,02038359	-16,15876831	-14,84565469
	TS2 relative to 4	29,70709792	28,09382242	30,07767897	24,68660941

Table S1. Summary of all in solvent Gibbs free energies for Scheme 1. All energies are in kcal/mol.

Based on the equilibrium constants reported by Parks et al,[Error! Bookmark not defined.] association energies of adducts $\mathbf{2_a}$-$B(C_6F_5)_3$ and $\mathbf{2_c}$-$B(C_6F_5)_3$ in toluene at room temperatures are only -5.8 kcal/mol and -4.1 kcal/mol, respectively. Computed raw association energies are -8.5 (2a) and -7.4 (2c) in toluene. The thermochemical correction is ca. 4 kcal/mol for both 2a and 2c kcal/mol with the account of solvent effects. Overall, the calculated total association energies are -4.5 and -3.4 for 2a and 2c in toluene, respectively.

XYZ coordinates, Reference Potential and the Gibbs free energies, Solvent corrections

Complex 1:

```
SCF 6-31*G+ = -2208.367541
SCF 6-31**G++ = -2208.36754
Gibbs free energy = -2208.279193
sfinal(toluene)= -2.7433 kcal/mol
sfinal(acetonitrile)= -6.3275 kcal/mol
sfinal(DCM)= -5.4549 kcal/mol

    34

 C      1.152906     -0.103694      2.738553
 C      0.175201     -0.246072      1.741815
```

C	-1.112266	0.185025	2.096605
C	-1.415355	0.730152	3.339063
C	-0.410858	0.839841	4.299076
C	0.882323	0.414608	3.999933
B	0.499293	-0.847498	0.327195
F	-2.118337	0.109589	1.202996
F	-2.656518	1.145443	3.623239
F	-0.686488	1.350136	5.500281
F	1.846682	0.512326	4.924569
F	2.417181	-0.508278	2.505327
C	1.846739	-0.480222	-0.390747
C	2.591628	-1.422956	-1.115795
C	3.793139	-1.119861	-1.746034
C	4.285510	0.182620	-1.685176
C	3.576824	1.158697	-0.986953
C	2.390367	0.813020	-0.350162
F	2.166289	-2.699091	-1.197944
F	4.477097	-2.060265	-2.410482
F	5.431123	0.494097	-2.293240
F	4.045284	2.412256	-0.934102
F	1.740917	1.797470	0.301986
C	-0.523345	-1.817070	-0.366892
C	-0.783978	-1.772473	-1.745298
C	-1.693462	-2.614881	-2.374696
C	-2.371275	-3.571356	-1.620784
C	-2.139461	-3.663559	-0.249545
C	-1.240000	-2.788577	0.348831
F	-0.163053	-0.860819	-2.519409
F	-1.921231	-2.519931	-3.691336
F	-3.238711	-4.396053	-2.209489
F	-2.784640	-4.587338	0.474414
F	-1.047061	-2.927687	1.675358

Complex 1':

SCF 6-31*G+ = -1910.690187
SCF 6-31**G++ = -1910.69485
sfinal(toluene)= -4.4794 kcal/mol
sfinal(acetonitrile)= -9.2962 kcal/mol
sfinal(DCM)= -8.1624 kcal/mol

34

C	-0.109757	1.897049	4.009919
C	-1.082691	0.966898	3.615945
C	-2.393293	1.242956	4.032339
C	-2.713745	2.372496	4.777851
C	-1.727836	3.271141	5.164441
C	-0.419130	3.016022	4.775662
B	-0.726292	-0.304732	2.765342
C	-1.395875	-1.684959	3.100499
C	-1.582593	-2.123668	4.419393
C	-2.167989	-3.349282	4.718656
C	-2.619021	-4.186868	3.706563
C	-2.457206	-3.771590	2.391033
C	-1.848701	-2.555618	2.098782
F	-1.158030	-1.361529	5.449368
F	-2.301607	-3.722470	6.006130
F	-2.888926	-4.554683	1.383861
F	-1.729760	-2.207837	0.799910
F	-3.399937	0.414695	3.681996

F	-3.995194	2.591505	5.131152
F	0.563919	3.862274	5.138358
F	1.183170	1.703519	3.673885
C	0.299037	-0.194197	1.580737
C	0.306002	0.896653	0.699116
C	1.206545	0.993066	-0.356308
C	2.164013	0.008874	-0.565378
C	2.187182	-1.077242	0.300000
C	1.267702	-1.179070	1.338512
F	-0.604112	1.883395	0.840581
F	1.350507	-2.255941	2.148116
F	3.106091	-2.047513	0.131988
F	1.149641	2.057273	-1.179920
H	-1.973003	4.148045	5.753591
H	-3.084498	-5.138866	3.937034
H	2.873600	0.086216	-1.381862

Complex 2a:

SCF 6-31*G+ = -345.588504112
SCF 6-311**G++ = -345.597701559
sfinal(toluene)= -3.5942 kcal/mol
sfinal(acetonitrile)= -7.6624 kcal/mol
sfinal(DCM)= -6.6290 kcal/mol

14

C	0.128738	-0.524982	0.000000
C	0.130923	-2.005561	0.000000
C	1.349493	0.166111	0.000000
C	1.366676	1.561786	0.000000
C	0.161022	2.268747	0.000000
C	-1.061275	1.582947	0.000000
C	-1.080076	0.190814	0.000000
H	2.283504	-0.392988	0.000000
H	2.312866	2.096220	0.000000
H	0.171460	3.355850	0.000000
H	-1.995110	2.139032	0.000000
H	-2.015716	-0.361041	0.000000
O	-0.866418	-2.705749	0.000000
H	1.140421	-2.471356	0.000000

Complex 3a:

SCF 6-31*G+ = -2553.96971475
SCF 6-311**G++ = -2553.978832334
sfinal(toluene)= -6.2943 kcal/mol
sfinal(acetonitrile)= -13.1958 kcal/mol
sfinal(DCM)= -11.3830 kcal/mol

48

C	-0.475311	3.697245	-2.281545
C	-1.513259	2.762692	-2.078037
C	-2.811427	3.021866	-2.563085
C	-3.070058	4.203112	-3.250993
C	-2.036119	5.123603	-3.453899
C	-0.743150	4.872432	-2.970120
C	-1.286012	1.527169	-1.376577
H	-2.131633	0.843155	-1.243189
O	-0.166060	1.202775	-0.927954

B	0.197147	-0.147419	-0.131166
C	-0.761230	-1.316920	-0.763945
C	-0.758718	-1.553862	-2.145435
C	-1.520736	-2.531995	-2.773825
C	-2.347912	-3.346295	-2.004034
C	-2.396077	-3.153360	-0.628583
C	-1.618244	-2.153676	-0.041328
F	0.024331	-0.792373	-2.949808
F	-1.466841	-2.699346	-4.105095
F	-3.095161	-4.293182	-2.584162
F	-3.199704	-3.920568	0.124056
F	-1.742972	-2.036567	1.298071
C	-0.021926	0.162769	1.464702
C	-0.809248	1.173971	2.016332
C	-0.909459	1.425360	3.383027
C	-0.211963	0.625248	4.279897
C	0.566240	-0.418285	3.787018
C	0.641621	-0.624773	2.413479
F	-1.564549	1.987436	1.223749
F	-1.678671	2.429977	3.836095
F	-0.297012	0.847370	5.598185
F	1.227827	-1.217635	4.638202
F	1.382672	-1.680202	2.006038
C	1.798061	-0.282599	-0.456995
C	2.448505	-1.449080	-0.866829
C	3.821127	-1.527710	-1.094859
C	4.614836	-0.400553	-0.910882
C	4.018876	0.784954	-0.493426
C	2.645155	0.816894	-0.272130
F	1.757822	-2.598139	-1.043616
F	4.382995	-2.683521	-1.484522
F	5.936227	-0.455166	-1.126192
F	4.771305	1.882999	-0.301192
F	2.142156	1.999062	0.164285
H	-3.605526	2.297847	-2.396375
H	-4.067405	4.409014	-3.627555
H	-2.237101	6.046056	-3.992324
H	0.047568	5.598509	-3.133396
H	0.516331	3.484969	-1.894003

Complex TS1a:

SCF 6-31*G+ = -2555.113540995
SCF 6-311**G++ = -2555.127691191
sfinal(toluene)= -6.6026 kcal/mol
sfinal(acetonitrile)= -14.1533 kcal/mol
sfinal(DCM)= -11.8899 kcal/mol

50

F	1.505428	0.593705	2.855700
C	1.269775	0.509664	1.522727
C	-0.012693	0.187360	1.067425
C	-0.139820	0.120789	-0.322782
C	0.913517	0.366021	-1.202014
C	2.167790	0.693152	-0.696817
C	2.348428	0.765174	0.681578
B	-1.224891	-0.061842	2.110867
C	-1.081154	-1.342947	3.091090
C	-1.620037	-1.337005	4.379733
C	-1.523393	-2.404094	5.267049

C	-0.870184	-3.564498	4.862934
C	-0.327983	-3.629133	3.582966
C	-0.447017	-2.534438	2.728948
F	-1.326405	-0.198268	-0.886729
F	0.729133	0.290789	-2.530648
F	3.192026	0.933950	-1.527598
F	3.555437	1.078144	1.183423
F	-2.277649	-0.232885	4.831847
F	-2.052480	-2.326463	6.500935
F	-0.766681	-4.607857	5.697560
F	0.293851	-4.748532	3.179864
F	0.084771	-2.673535	1.495482
C	-2.724700	0.239822	1.577429
C	-3.229761	1.534925	1.447760
C	-4.518946	1.828155	1.012985
C	-5.374182	0.785955	0.670826
C	-4.918957	-0.525433	0.772309
C	-3.621460	-0.771322	1.217170
F	-2.450231	2.603287	1.773382
F	-4.943797	3.102219	0.931166
F	-6.619911	1.042289	0.248422
F	-5.730886	-1.538039	0.430121
F	-3.236771	-2.064799	1.263793
H	-1.025708	0.960016	2.998023
H	-0.783937	1.661109	3.540482
O	-0.522555	2.661711	4.312146
C	-2.817264	4.735505	6.182067
C	-1.579584	4.281030	5.685028
C	-0.385638	4.952243	6.024410
C	-0.439807	6.068594	6.848208
C	-1.675535	6.518314	7.337592
C	-2.862238	5.855191	7.007661
C	-1.567033	3.128400	4.814192
H	-2.526332	2.646742	4.582533
H	0.559355	4.588095	5.633191
H	0.473031	6.593030	7.114745
H	-1.710827	7.394111	7.980208
H	-3.812756	6.212212	7.392276
H	-3.732180	4.211111	5.916553

Complex 4a:

SCF 6-31*G+ = -2555.119383449
SCF 6-311**G++ = -2555.13499833
sfinal(toluene)= -8.9065 kcal/mol
sfinal(acetonitrile)= -17.9147 kcal/mol
sfinal(DCM)= -15.5570 kcal/mol

50

C	-2.925895	5.028695	-0.904069
C	-2.134708	4.173883	-1.708165
C	-1.881088	4.494689	-3.061376
C	-2.412398	5.658649	-3.603931
C	-3.193495	6.499795	-2.802395
C	-3.450363	6.186512	-1.457389
C	-1.568072	2.972667	-1.189770
H	-0.963945	2.329812	-1.833402
O	-1.749065	2.602816	0.012580
F	1.214530	2.415588	-0.132862
C	2.051793	1.363401	-0.390765

C	1.617199	0.055157	-0.184758
C	2.567559	-0.920978	-0.500252
C	3.843192	-0.632047	-0.978492
C	4.222041	0.694613	-1.166376
C	3.314435	1.704772	-0.869465
B	0.107897	-0.293100	0.343984
C	-0.595627	-1.477569	-0.542729
C	-1.058339	-1.209089	-1.831513
C	-1.678627	-2.141476	-2.656199
C	-1.858774	-3.439583	-2.189986
C	-1.412325	-3.767455	-0.913187
C	-0.796487	-2.795283	-0.125600
F	2.269951	-2.227110	-0.332371
F	4.713732	-1.616775	-1.256578
F	5.444923	0.995525	-1.629995
F	3.658326	2.994752	-1.053250
F	-0.916897	0.047448	-2.360082
F	-2.104822	-1.801071	-3.888206
F	-2.455494	-4.360910	-2.961996
F	-1.576624	-5.019539	-0.454476
F	-0.380367	-3.191301	1.096380
C	-0.064556	-0.438870	1.962809
C	-1.306361	-0.186371	2.551217
C	-1.558329	-0.256072	3.917682
C	-0.521044	-0.598476	4.779595
C	0.737950	-0.860770	4.250030
C	0.939752	-0.778974	2.872663
F	-2.360648	0.165977	1.760961
F	-2.783362	0.006674	4.409996
F	-0.731457	-0.668768	6.103399
F	1.749339	-1.189646	5.072600
F	2.190869	-1.058722	2.443854
H	-0.563189	0.703755	0.036112
H	-1.240155	1.702151	0.189179
H	-1.272706	3.829769	-3.668803
H	-2.222589	5.913750	-4.641790
H	-3.608190	7.410158	-3.227121
H	-4.058674	6.851716	-0.852295
H	-3.111955	4.769042	0.133410

Complex TS2a:

SCF 6-31*G+ = -2555.109426362
SCF 6-311**G++ = -2555.125502461
sfinal(toluene)= -7.3638 kcal/mol
sfinal(acetonitrile)= -15.9433 kcal/mol
sfinal(DCM)= -13.4878 kcal/mol

50

C	0.518295	-1.012935	2.585360
C	-0.370088	-0.460760	1.654159
C	-1.537379	0.038585	2.222248
C	-1.825211	0.024820	3.583479
C	-0.901319	-0.522936	4.465756
C	0.281201	-1.052195	3.956889
B	0.047858	-0.402453	0.076150
C	-0.358797	-1.698936	-0.813541
C	-0.172348	-1.686267	-2.201686
C	-0.552613	-2.713055	-3.055621
C	-1.169193	-3.842557	-2.525574

C	-1.387345	-3.910973	-1.153879
C	-0.987779	-2.855120	-0.334725
F	0.415266	-0.608954	-2.786045
F	-0.347483	-2.617700	-4.381578
F	-1.558442	-4.842681	-3.327249
F	-1.990771	-4.990183	-0.630798
F	-1.244803	-3.011600	0.982601
F	-2.521415	0.565589	1.425808
F	-2.982990	0.532257	4.043946
F	-1.147771	-0.546693	5.782168
F	1.179183	-1.594974	4.793156
F	1.670336	-1.576268	2.158530
C	1.557418	0.192310	-0.091564
C	2.648858	-0.491369	-0.643609
C	3.925459	0.054192	-0.756145
C	4.165217	1.346827	-0.302349
C	3.122026	2.065518	0.273120
C	1.860547	1.483137	0.359157
F	2.523561	-1.767116	-1.069149
F	4.929351	-0.663805	-1.285804
F	5.385457	1.889269	-0.407384
F	3.339236	3.311458	0.728412
F	0.886839	2.239660	0.922549
C	-1.580371	1.798029	-1.148983
C	-2.703729	1.086799	-1.761240
O	-1.708517	2.614178	-0.119292
H	-0.741184	2.080724	-1.782994
H	-2.444500	2.343064	0.460274
H	-0.740064	0.489810	-0.527556
C	-3.994270	1.066694	-1.196954
C	-5.042552	0.452781	-1.875395
C	-4.824472	-0.136228	-3.126509
C	-3.551786	-0.107123	-3.703540
C	-2.498285	0.505865	-3.029194
H	-4.198348	1.524617	-0.233547
H	-6.033786	0.438352	-1.431838
H	-5.648043	-0.614357	-3.649810
H	-3.380889	-0.554361	-4.678423
H	-1.513015	0.543025	-3.482850

Complex 2'a:

SCF 6-31*G+ = -346.785819617
SCF 6-311**G++ = -346.802203229
sfinal(toluene)= -4.1846 kcal/mol
sfinal(acetonitrile)= -9.1411 kcal/mol
sfinal(DCM)= -7.8356 kcal/mol

16

C	0.025180	-0.095659	-0.000265
C	0.067054	-0.215107	1.506847
C	1.223794	-0.063900	-0.725890
C	1.210903	-0.004407	-2.121023
C	-0.005617	0.034356	-2.808453
C	-1.203507	0.012441	-2.089870
C	-1.190171	-0.055215	-0.693726
H	2.175649	-0.081093	-0.197189
H	2.149267	0.021327	-2.669705
H	-0.018806	0.087366	-3.894288
H	-2.154004	0.049738	-2.616802

H	-2.119734	-0.062427	-0.133945
O	-1.149582	0.282161	2.065933
H	0.930097	0.345566	1.895912
H	-1.150452	0.104140	3.018216
H	0.204850	-1.272018	1.787841

Complex 2b:

SCF 6-31*G+ = -193.1653748
SCF 6-311**G++ = -193.173692
Gibbs free energy = -193.108318
sfinal(toluene)= -3.6030 kcal/mol
sfinal(acetonitrile)= -7.4727 kcal/mol
sfinal(DCM)= -6.5144 kcal/mol

10

C	-0.092214	-0.005387	0.000000
O	-1.310952	0.017458	0.000000
C	0.709346	1.289575	0.000000
C	0.682567	-1.308281	0.000000
H	1.791322	1.125509	0.000000
H	0.434838	1.879885	-0.881881
H	0.434838	1.879885	0.881881
H	-0.003635	-2.158084	0.000000
H	1.336550	-1.358697	-0.881052
H	1.336550	-1.358697	0.881052

Complex 3b:

SCF 6-31*G+ = -2401.54153272479
SCF 6-311**G++ = -2401.55004339
Gibbs free energy = -2401.368791
sfinal(toluene)= -6.4187 kcal/mol
sfinal(acetonitrile)= -13.6715 kcal/mol
sfinal(DCM)= -11.4881 kcal/mol

44

B	0.070620	-0.158843	-0.119478
C	-0.094303	0.123949	1.487710
C	1.675701	-0.164376	-0.456085
C	-0.781949	-1.402349	-0.761015
C	2.428447	-1.286552	-0.813536
C	3.801841	-1.248648	-1.050597
C	4.489562	-0.046623	-0.927288
C	3.790202	1.097968	-0.556941
C	2.420923	1.013995	-0.323988
F	1.845173	-2.498577	-0.946137
F	4.464423	-2.363297	-1.399154
F	5.808567	0.008423	-1.155239
F	4.440173	2.266141	-0.419010
F	1.810031	2.160267	0.065612
C	-0.673511	-1.678394	-2.130715
C	-1.339396	-2.716716	-2.773421
C	-2.179730	-3.546370	-2.035566
C	-2.344577	-3.303590	-0.676722
C	-1.662257	-2.245175	-0.076553
F	0.119512	-0.903262	-2.908609
F	-1.181414	-2.924487	-4.090207

F	-2.834915	-4.550004	-2.631151
F	-3.176299	-4.072408	0.043579
F	-1.933815	-2.049917	1.234867
C	-0.558509	1.280100	2.115565
C	-0.558790	1.468056	3.497552
C	-0.067353	0.467866	4.326814
C	0.417210	-0.705451	3.753367
C	0.396985	-0.846374	2.370869
F	-1.054718	2.325724	1.394052
F	-1.027202	2.610673	4.026991
F	-0.058231	0.629395	5.655968
F	0.895242	-1.683857	4.536381
F	0.885982	-2.002839	1.871329
O	-0.438773	1.128398	-0.952665
C	-1.568580	1.617427	-1.144950
C	-2.838382	1.056730	-0.588902
C	-1.640177	2.841786	-1.998327
H	-2.507548	2.803416	-2.666459
H	-1.782738	3.705524	-1.332837
H	-0.716939	2.980196	-2.563182
H	-3.316406	0.459453	-1.379001
H	-2.680531	0.419895	0.279884
H	-3.525283	1.871723	-0.340091

Complex TS1b:

SCF 6-31*G+ = -2402.68849328615
SCF 6-311**G++ = -2402.702273357
Gibbs free energy = -2402.50608
sfinal(toluene)= -7.5185 kcal/mol
sfinal(acetonitrile)= -15.2349 kcal/mol
sfinal(DCM)= -13.2510 kcal/mol

46

F	-2.414548	-0.297394	5.004955
C	-1.961406	-1.448637	4.431669
C	-1.471615	-1.430561	3.126135
C	-1.069938	-2.677077	2.637273
C	-1.126148	-3.849876	3.386666
C	-1.607468	-3.807498	4.692346
C	-2.032112	-2.592636	5.220271
B	-1.364187	-0.077072	2.243628
C	-2.707011	0.439655	1.497141
C	-2.793724	1.756475	1.032521
C	-3.897360	2.276992	0.366125
C	-4.995709	1.455152	0.127257
C	-4.964730	0.136720	0.568688
C	-3.838423	-0.341120	1.239738
F	-2.510095	-2.533713	6.475489
F	-1.665186	-4.923843	5.430940
F	-0.724987	-5.019183	2.864246
F	-0.615961	-2.789202	1.369938
F	-1.762574	2.611794	1.256090
F	-3.919194	3.560878	-0.033171
F	-6.072599	1.933884	-0.509491
F	-6.019278	-0.663292	0.347886
F	-3.884319	-1.635276	1.621687
C	0.020504	0.091403	1.420506
C	0.119300	-0.017435	0.031286
C	1.322531	0.089280	-0.662323

C	2.500999	0.319146	0.041176
C	2.455234	0.435068	1.427404
C	1.232688	0.309691	2.080761
F	-0.984685	-0.257681	-0.711907
F	1.250826	0.419178	3.432350
F	3.585964	0.658945	2.118281
F	3.667974	0.428016	-0.608546
F	1.356615	-0.032467	-1.999355
H	-1.209066	0.859802	3.194839
H	-1.140759	1.586842	3.749710
C	-1.720611	4.377925	5.894335
C	-3.356131	2.871808	4.582737
H	-4.018666	2.963465	5.450021
H	-3.702623	3.600367	3.835677
H	-3.428681	1.869350	4.160189
H	-2.421143	5.195813	5.694703
H	-1.919626	4.026844	6.917081
H	-0.687657	4.725993	5.837455
C	-1.950833	3.231799	4.956900
O	-0.958001	2.625545	4.516310

Complex 4b:

SCF 6-31*G+ = -2402.69360311138
SCF 6-311**G++ = -2402.708218199
Gibbs free energy = -2402.506488
sfinal(toluene)= -9.8110 kcal/mol
sfinal(acetonitrile)= -19.6233 kcal/mol
sfinal(DCM)= -17.0248 kcal/mol

46

B	0.114594	-0.327500	0.053493
C	-0.053948	-0.140433	1.667627
C	1.616772	-0.018290	-0.518675
C	-0.579751	-1.688826	-0.524996
C	2.557656	-0.983669	-0.889823
C	3.824735	-0.676449	-1.384597
C	4.205448	0.654273	-1.530791
C	3.306998	1.654270	-1.174878
C	2.056634	1.295166	-0.681523
F	2.271836	-2.296582	-0.764115
F	4.684335	-1.651058	-1.722191
F	5.417134	0.968903	-2.011896
F	3.645546	2.951175	-1.318477
F	1.227453	2.335182	-0.353367
C	-1.271907	-1.699028	-1.734967
C	-1.915234	-2.814334	-2.263189
C	-1.876237	-4.013199	-1.559945
C	-1.192960	-4.064815	-0.348178
C	-0.566850	-2.919294	0.138641
F	-1.355568	-0.557677	-2.486559
F	-2.571882	-2.742166	-3.436576
F	-2.488421	-5.104140	-2.043894
F	-1.141159	-5.219828	0.335429
F	0.089277	-3.047576	1.312073
C	-1.288737	0.224169	2.209196
C	-1.522508	0.407070	3.568842
C	-0.477721	0.214461	4.467284
C	0.773680	-0.153309	3.983031
C	0.959248	-0.322313	2.611874

F	-2.350917	0.426110	1.380900
F	-2.738134	0.767763	4.019684
F	-0.674756	0.383672	5.783542
F	1.789407	-0.344685	4.842643
F	2.198574	-0.695865	2.220151
O	-1.750700	2.466594	-0.756461
C	-1.567404	3.068569	-1.848673
C	-2.353553	4.312685	-2.061177
C	-0.610149	2.589613	-2.880148
H	-0.939946	2.887771	-3.879369
H	0.351159	3.089174	-2.685582
H	-0.450159	1.511248	-2.828692
H	-1.704406	5.105355	-2.451439
H	-3.107378	4.114619	-2.836805
H	-2.851242	4.631505	-1.144123
H	-0.577084	0.580076	-0.453562
H	-1.187161	1.567739	-0.608884

Complex TS2b:

SCF 6-31*G+ = -2402.70204434771
SCF 6-311**G++ = -2402.717373957
Gibbs free energy = -2402.507919
sfinal(toluene)= -4.6372 kcal/mol
sfinal(acetonitrile)= -10.3222 kcal/mol
sfinal(DCM)= -8.6905 kcal/mol

46

B	0.138366	-0.432899	0.106161
C	-0.011363	-0.266201	1.720845
C	1.576450	0.010135	-0.468551
C	-0.583059	-1.727358	-0.534008
C	2.405893	-0.777677	-1.278632
C	3.653735	-0.356270	-1.736754
C	4.125468	0.907870	-1.390553
C	3.340459	1.730763	-0.585093
C	2.103991	1.268321	-0.146006
F	2.039601	-2.027444	-1.628868
F	4.404583	-1.156380	-2.506927
F	5.316623	1.327257	-1.828171
F	3.786002	2.943355	-0.226491
F	1.392837	2.108694	0.640515
C	-0.854349	-1.804970	-1.906273
C	-1.552331	-2.845567	-2.509308
C	-1.994440	-3.910892	-1.725392
C	-1.692417	-3.920795	-0.366429
C	-1.013622	-2.841079	0.200288
F	-0.462702	-0.797177	-2.723334
F	-1.802169	-2.832266	-3.826746
F	-2.662222	-4.927257	-2.278691
F	-2.076818	-4.956655	0.391914
F	-0.786178	-2.925725	1.527678
C	-1.218384	-0.018573	2.376736
C	-1.369801	0.119694	3.751503
C	-0.252115	-0.025762	4.569428
C	0.978953	-0.305148	3.981685
C	1.076425	-0.417275	2.594084
F	-2.377504	0.135035	1.651138
F	-2.569632	0.384606	4.288241
F	-0.362280	0.093480	5.895177

F	2.061419	-0.464271	4.753601
F	2.300965	-0.719486	2.117118
C	-1.499364	1.648865	-0.816977
O	-1.706510	2.415993	0.271433
H	-2.214240	1.896058	0.927141
C	-0.674554	2.358667	-1.858253
C	-2.717847	0.911960	-1.353118
H	-0.445312	1.685705	-2.686124
H	-1.282452	3.184457	-2.262818
H	0.239141	2.789677	-1.445937
H	-2.500187	0.428332	-2.306992
H	-3.122372	0.176562	-0.654392
H	-3.494859	1.671207	-1.533341
H	-0.676700	0.626200	-0.399028

Complex 2'b:

SCF 6-31*G+ = -194.3631454
SCF 6-311**G++ = -194.378609
Gibbs free energy = -194.282848
sfinal(toluene)= -3.3832 kcal/mol
sfinal(acetonitrile)= -7.3404 kcal/mol
sfinal(DCM)= -6.3135 kcal/mol

	12		
C	0.364939	0.031148	0.000000
H	1.465014	0.015789	0.000000
C	-0.122766	0.724187	1.271164
C	-0.122766	0.724187	-1.271164
O	-0.126028	-1.327370	0.000000
H	-1.218529	0.710993	1.308377
H	0.252844	0.209642	2.162617
H	0.212742	1.768181	1.304166
H	-1.218529	0.710993	-1.308377
H	0.212742	1.768181	-1.304166
H	0.252844	0.209642	-2.162617
H	0.619280	-1.943505	0.000000

Complex 2c:

SCF 6-31*G+ = -384.9095913
SCF 6-311**G++ = -384.921706
sfinal(toluene)= -3.8050 kcal/mol
sfinal(acetonitrile)= -8.0636 kcal/mol
sfinal(DCM)= -6.9521 kcal/mol

	17		
O	1.929551	1.651325	0.000000
C	0.708870	1.547550	0.000000
C	-0.130495	2.817346	0.000000
C	0.067500	0.189534	0.000000
C	-1.322765	-0.014374	0.000000
C	-1.850311	-1.307867	0.000000
C	-0.996588	-2.412753	0.000000
C	0.390033	-2.221517	0.000000
C	0.916269	-0.932730	0.000000
H	-2.006672	0.827501	0.000000
H	-2.927701	-1.451129	0.000000
H	-1.408315	-3.418972	0.000000
H	1.057745	-3.079262	0.000000

H	1.988928	-0.766883	0.000000
H	-1.210443	2.664442	0.000000
H	0.143168	3.408380	0.881111
H	0.143168	3.408380	-0.881111

Complex 3c:

SCF 6-31*G+ = -2593.289260231
SCF 6-311**G++ = -2593.301434279
sfinal(toluene)= -6.2713 kcal/mol
sfinal(acetonitrile)= -13.7727 kcal/mol
sfinal(DCM)= -11.6619 kcal/mol

51

B	0.056283	-0.130430	-0.111757
C	-0.086068	0.107157	1.507377
C	1.666645	-0.137042	-0.446846
C	-0.789435	-1.375484	-0.767667
C	2.422072	-1.259932	-0.797142
C	3.797559	-1.224274	-1.023421
C	4.487144	-0.023874	-0.895580
C	3.785779	1.121171	-0.531744
C	2.414439	1.038484	-0.310789
F	1.841227	-2.471900	-0.936044
F	4.459203	-2.340599	-1.368520
F	5.808153	0.031092	-1.114512
F	4.435625	2.289953	-0.390854
F	1.803226	2.189147	0.070912
C	-0.665092	-1.647537	-2.136431
C	-1.335212	-2.675082	-2.792122
C	-2.197665	-3.496010	-2.070585
C	-2.379574	-3.255363	-0.713729
C	-1.691543	-2.208605	-0.100537
F	0.150030	-0.883180	-2.901226
F	-1.158812	-2.879907	-4.107476
F	-2.857662	-4.489766	-2.679000
F	-3.233189	-4.014694	-0.007835
F	-1.983565	-2.011913	1.207201
C	-0.507696	1.264378	2.163272
C	-0.487534	1.423867	3.548652
C	-0.016023	0.393526	4.352005
C	0.428770	-0.781006	3.749589
C	0.388080	-0.893768	2.364664
F	-0.977018	2.336179	1.467808
F	-0.917444	2.568737	4.105919
F	0.013700	0.528223	5.684529
F	0.889697	-1.787542	4.508078
F	0.843448	-2.051455	1.836053
O	-0.460332	1.145986	-0.914496
C	-1.600101	1.648442	-1.094073
C	-2.835470	1.094530	-0.447109
C	-1.675957	2.804746	-1.991982
C	-2.917433	3.345652	-2.384923
C	-2.963916	4.431374	-3.254266
C	-1.776077	4.996697	-3.729789
C	-0.538419	4.472479	-3.339612
C	-0.484685	3.381324	-2.480048
H	-3.846647	2.916696	-2.025425
H	-3.923040	4.839195	-3.559557
H	-1.815121	5.848288	-4.403849

H	0.382394	4.916804	-3.705762
H	0.468289	2.971897	-2.165785
H	-3.449883	1.905034	-0.046194
H	-3.431272	0.560861	-1.199503
H	-2.595087	0.402419	0.356398

Complex TS1c:

SCF 6-31*G+ = -2594.437776
SCF 6-311**G++ = -2594.45541587
sfinal(toluene)= -7.6060 kcal/mol
sfinal(acetonitrile)= -15.7680 kcal/mol
sfinal(DCM)= -13.2423 kcal/mol

53

C	1.134225	0.762661	1.668354
C	-0.087932	0.259830	1.216639
C	-0.161223	0.051847	-0.162938
C	0.887587	0.322364	-1.038427
C	2.081374	0.834284	-0.538888
C	2.205137	1.058320	0.828813
B	-1.301714	-0.090812	2.236958
C	-2.790840	0.205709	1.653285
C	-3.140180	1.488344	1.219977
C	-4.345373	1.803204	0.601234
C	-5.280603	0.794901	0.385899
C	-4.990590	-0.498878	0.806370
C	-3.770634	-0.766337	1.427642
F	-2.272831	2.517886	1.415359
F	-4.617198	3.065119	0.221813
F	-6.451329	1.071851	-0.205108
F	-5.888848	-1.477529	0.611957
F	-3.560152	-2.050787	1.787380
F	-1.284914	-0.465166	-0.710445
F	0.760393	0.090628	-2.355674
F	3.101993	1.106746	-1.365383
F	3.352608	1.554565	1.324826
F	1.323776	0.988421	2.993454
C	-1.105474	-1.448897	3.103662
C	-1.509476	-1.529988	4.436843
C	-1.273077	-2.626814	5.258548
C	-0.618133	-3.736701	4.734517
C	-0.222720	-3.724236	3.400186
C	-0.468897	-2.595609	2.620285
F	-2.178410	-0.486508	5.004776
F	-0.076706	-2.659664	1.328780
F	0.390453	-4.799104	2.878752
F	-0.381048	-4.809502	5.502999
F	-1.673783	-2.624022	6.542588
C	-3.375680	2.592025	4.643779
C	-2.006111	3.142484	4.917329
O	-0.977771	2.599265	4.433653
H	-3.895084	2.382928	5.585463
C	-1.815146	4.332386	5.753216
H	-1.178816	0.827378	3.168823
H	-1.123364	1.600697	3.732650
C	-0.505160	4.786697	6.013415
C	-0.303054	5.913851	6.800974
C	-1.400229	6.601026	7.333485
C	-2.703742	6.162680	7.077953
C	-2.913334	5.031770	6.293465

H	0.336406	4.247039	5.592231
H	0.706627	6.260097	7.001137
H	-1.239585	7.482305	7.948824
H	-3.552036	6.700847	7.490358
H	-3.928603	4.700798	6.100668
H	-3.969404	3.330752	4.092250
H	-3.323533	1.672409	4.062796

Complex 4c:

SCF 6-31*G+ = -2594.44513909607
SCF 6-311**G++ = -2594.46365109
sfinal(toluene)= -9.6869 kcal/mol
sfinal(acetonitrile)= -19.2952 kcal/mol
sfinal(DCM)= -16.7953 kcal/mol

53

B	0.132476	-0.411468	0.028093
C	-0.229984	-0.163393	1.605777
C	1.701187	-0.147782	-0.370647
C	-0.474161	-1.804670	-0.580790
C	2.667418	-1.147988	-0.517365
C	3.987869	-0.900044	-0.889395
C	4.402301	0.406022	-1.132365
C	3.483406	1.439725	-0.992628
C	2.178185	1.138392	-0.616808
F	2.350618	-2.438795	-0.278104
F	4.868063	-1.907621	-1.013145
F	5.667519	0.665132	-1.497088
F	3.857918	2.713574	-1.226543
F	1.337004	2.212607	-0.492352
C	-0.883390	-1.884685	-1.911971
C	-1.428466	-3.022559	-2.499207
C	-1.582125	-4.171972	-1.731450
C	-1.185710	-4.152107	-0.397428
C	-0.646564	-2.986635	0.144003
F	-0.760453	-0.796958	-2.730426
F	-1.807200	-3.019596	-3.792191
F	-2.105439	-5.284436	-2.270338
F	-1.322253	-5.259571	0.352238
F	-0.270043	-3.049330	1.441170
C	-1.540773	0.142150	1.981297
C	-1.943683	0.393883	3.288995
C	-1.002038	0.332112	4.311197
C	0.317347	0.023431	3.996587
C	0.673375	-0.215546	2.670051
F	-2.510766	0.215059	1.027378
F	-3.224604	0.700948	3.570984
F	-1.360986	0.572420	5.582266
F	1.235949	-0.041578	4.975974
F	1.972772	-0.522478	2.453482
O	-1.497523	2.519778	-0.508458
C	-1.459867	3.165229	-1.611375
C	-2.107357	4.463928	-1.618578
C	-0.751400	2.588362	-2.791763
H	-0.494005	0.452929	-0.605319
H	-1.021720	1.596857	-0.522355
C	-2.052808	5.297180	-2.757339
C	-2.658907	6.548142	-2.734467
C	-3.332164	6.977466	-1.584974

C	-3.397456	6.157803	-0.450741
C	-2.788376	4.909736	-0.461198
H	-1.531228	4.976532	-3.652459
H	-2.610057	7.188690	-3.609781
H	-3.808350	7.954202	-1.573028
H	-3.922519	6.496021	0.437406
H	-2.832031	4.268298	0.411994
H	-1.255395	2.840847	-3.726275
H	0.263465	3.009056	-2.823944
H	-0.661589	1.503833	-2.706676

Complex TS2c:

SCF 6-31*G+ = -2594.431598901
SCF 6-311**G++ = -2594.450430788
sfinal(toluene)= -6.7205 kcal/mol
sfinal(acetonitrile)= -14.1734 kcal/mol
sfinal(DCM)= -12.2037 kcal/mol

53

C	-4.085080	1.025805	-0.513443
C	-2.915212	1.062168	-1.300506
C	-2.918798	0.392296	-2.540376
C	-4.045596	-0.306040	-2.967164
C	-5.191478	-0.345904	-2.169430
C	-5.209559	0.329334	-0.945363
C	-1.730130	1.839784	-0.878865
C	-0.802200	2.442754	-1.891078
O	-1.775199	2.542120	0.244630
F	-2.268032	0.448507	1.854258
C	-1.087731	0.145025	2.489574
C	0.012925	-0.282642	1.750891
C	1.114091	-0.626416	2.547660
C	1.135434	-0.517017	3.937062
C	0.012262	-0.047635	4.609941
C	-1.118311	0.283656	3.872208
F	2.236350	-1.126769	1.984433
B	0.060088	-0.394900	0.115639
C	1.533897	0.021633	-0.450632
C	2.424743	-0.817210	-1.129966
C	3.692150	-0.419075	-1.550251
C	4.130189	0.876021	-1.291631
C	3.291476	1.747169	-0.604038
C	2.036000	1.302993	-0.201682
F	-2.224603	0.730971	4.493349
F	2.230202	-0.861284	4.632236
F	2.103871	-2.106346	-1.379825
F	4.499178	-1.277366	-2.195435
F	3.696183	3.000934	-0.335032
F	1.278780	2.195504	0.489353
C	-0.625311	-1.719738	-0.533192
C	-0.699767	-1.870509	-1.923272
C	-1.294373	-2.947001	-2.568615
C	-1.862689	-3.964550	-1.808517
C	-1.815204	-3.875708	-0.421909
C	-1.212168	-2.771912	0.181342
F	-0.161225	-0.916831	-2.729897
F	-1.343411	-3.003615	-3.912209
F	-2.356109	-4.851417	0.325903
F	-1.213043	-2.780402	1.533248
F	5.343404	1.277186	-1.693646

F	-2.454393	-5.007905	-2.405214
F	0.015792	0.076388	5.942861
H	-2.358147	2.106391	0.895180
H	-0.412237	1.697489	-2.584512
H	-1.369751	3.185884	-2.468341
H	0.021248	2.945021	-1.385090
H	-0.727545	0.561830	-0.350070
H	-2.039440	0.405016	-3.171212
H	-4.023852	-0.824603	-3.921327
H	-6.068470	-0.894783	-2.501365
H	-6.102282	0.317449	-0.327061
H	-4.151080	1.558718	0.429965

Complex 2'c:

SCF 6-31*G+ = -2637.39628018303
SCF 6-311**G++ = -386.124511959
sfinal(toluene)= -4.0318 kcal/mol
sfinal(acetonitrile)= -8.8812 kcal/mol
sfinal(DCM)= -7.5854 kcal/mol

19

C	-1.036948	2.216189	1.009730
C	-0.689902	1.204812	1.913951
C	-1.007381	1.368715	3.269202
C	-1.649322	2.525065	3.717656
C	-1.988931	3.532848	2.810616
C	-1.683228	3.372129	1.456882
C	0.058007	-0.036777	1.463475
C	1.573632	0.103412	1.668331
O	-0.251116	-0.267951	0.083004
H	-0.301430	-0.890201	2.060185
H	-0.757272	0.583152	3.980690
H	-1.891227	2.634829	4.772037
H	-2.493683	4.431873	3.155622
H	-1.952157	4.147418	0.743324
H	-0.812508	2.084810	-0.043896
H	1.810032	0.280565	2.723609
H	2.095203	-0.812359	1.357099
H	1.959511	0.943624	1.080450
H	0.287196	-1.010012	-0.232419

Complex 2d:

SCF 6-31*G+ = -429.0389259
SCF 6-311**G++ = -429.063421
sfinal(toluene)= -2.4095 kcal/mol
sfinal(acetonitrile)= -5.3001 kcal/mol
sfinal(DCM)= -4.5024 kcal/mol

28

C	2.107386	0.114412	2.938639
C	1.644878	0.084944	1.458207
C	2.333557	1.221716	0.671934
C	0.083580	0.133749	1.429366
C	-0.773195	1.430613	1.593113
C	-0.846974	2.130713	0.210207
O	-0.513184	-0.918372	1.260976
C	2.095101	-1.257842	0.844701

C	-2.203796	1.011839	1.994839
C	-0.254639	2.425676	2.653367
H	3.420774	1.085979	0.729927
H	2.058596	1.199315	-0.388843
H	2.111877	2.218145	1.061882
H	3.187957	-0.071359	2.981340
H	1.917961	1.075074	3.424177
H	1.611760	-0.670786	3.521476
H	3.190194	-1.317190	0.862079
H	1.690406	-2.109120	1.397660
H	1.762897	-1.352991	-0.194937
H	-0.937356	3.283439	2.698013
H	-0.233582	1.974693	3.652030
H	0.741259	2.818149	2.433671
H	-1.560220	2.962748	0.265325
H	0.115239	2.540123	-0.109117
H	-1.201048	1.438214	-0.562193
H	-2.829825	1.906302	2.099845
H	-2.655319	0.354467	1.248027
H	-2.208474	0.476723	2.951210

Complex 3d:

SCF 6-31*G+ = -2637.39628018303
SCF 6-311**G++ = -2637.420816058
sfinal(toluene)= -4.8437 kcal/mol
sfinal(acetonitrile)= -10.1144 kcal/mol
sfinal(DCM)= -8.7582 kcal/mol

62

B	-0.059270	-0.210371	-0.037361
C	-0.043678	-0.031948	1.588341
C	1.502984	0.004224	-0.516157
C	-0.802263	-1.526856	-0.669359
C	2.337729	-0.985338	-1.047993
C	3.689932	-0.788744	-1.329195
C	4.277748	0.444712	-1.074862
C	3.497977	1.459943	-0.530093
C	2.155924	1.216101	-0.258365
F	1.871687	-2.226350	-1.308855
F	4.428872	-1.785435	-1.842256
F	5.574214	0.651135	-1.342571
F	4.043193	2.659083	-0.264115
F	1.472895	2.243451	0.305645
C	-0.798489	-1.729669	-2.055759
C	-1.395785	-2.811178	-2.693173
C	-2.054847	-3.771843	-1.931306
C	-2.103687	-3.616795	-0.551308
C	-1.492911	-2.512809	0.044158
F	-0.188433	-0.830108	-2.865503
F	-1.349496	-2.931093	-4.029992
F	-2.647289	-4.817407	-2.520501
F	-2.756222	-4.517808	0.199498
F	-1.642507	-2.430516	1.384559
C	-0.440264	1.085324	2.324384
C	-0.285965	1.196878	3.705630
C	0.315107	0.166500	4.417815
C	0.763581	-0.956709	3.727445
C	0.586343	-1.024352	2.349918
F	-1.001139	2.164093	1.718782

F	-0.707703	2.300385	4.347102
F	0.471203	0.257478	5.745245
F	1.363296	-1.956200	4.392598
F	1.073639	-2.122407	1.728275
O	-0.870022	1.039950	-0.732781
C	-1.865862	1.674630	-1.134432
C	-3.304721	1.306124	-0.694918
C	-1.524870	2.829127	-2.115212
C	-2.466070	2.932623	-3.340167
C	-1.554319	4.156867	-1.300143
C	-0.093261	2.648696	-2.665902
C	-3.884163	0.388362	-1.815739
C	-3.346791	0.519048	0.631297
C	-4.236612	2.526373	-0.492745
H	-4.375631	0.179696	0.794236
H	-2.712682	-0.363060	0.628778
H	-3.069091	1.148390	1.478058
H	-4.885697	0.070568	-1.504955
H	-3.978405	0.892937	-2.778363
H	-3.277112	-0.510931	-1.952214
H	-5.218780	2.147700	-0.188507
H	-3.875014	3.173255	0.312358
H	-4.389066	3.131886	-1.385945
H	-2.144599	3.792864	-3.937515
H	-2.386139	2.046426	-3.978698
H	-3.516168	3.089832	-3.093031
H	-1.129778	4.947423	-1.929172
H	-2.562062	4.463684	-1.015803
H	-0.940199	4.084010	-0.396631
H	0.096437	3.436561	-3.402858
H	0.657081	2.737597	-1.880864
H	0.033080	1.681980	-3.160975

Complex TS1d:

SCF 6-31*G+ = -2638.55566778703
SCF 6-311**G++ = -2638.585610769
sfinal(toluene)= -6.1448 kcal/mol
sfinal(acetonitrile)= -12.2949 kcal/mol
sfinal(DCM)= -10.4786 kcal/mol

64

F	-1.730520	-0.706125	5.175647
C	-1.569670	-1.778645	4.357169
C	-1.443115	-1.605444	2.980094
C	-1.269067	-2.788698	2.255469
C	-1.224128	-4.051237	2.837818
C	-1.362539	-4.170358	4.218813
C	-1.536870	-3.022899	4.984067
B	-1.404495	-0.176116	2.216803
C	-2.723583	0.316818	1.408394
C	-2.757659	1.596664	0.842626
C	-3.818048	2.092179	0.093226
C	-4.933130	1.286343	-0.121297
C	-4.960387	0.009462	0.428457
C	-3.873290	-0.444861	1.176741
F	-1.671003	-3.119383	6.319021
F	-1.326703	-5.376383	4.803232
F	-1.057559	-5.151689	2.086538
F	-1.141969	-2.727835	0.911019

F	-1.716201	2.444770	1.045055
F	-3.783687	3.339914	-0.407369
F	-5.972674	1.744444	-0.832290
F	-6.034785	-0.773786	0.241295
F	-3.993670	-1.689110	1.688032
C	0.024104	0.063421	1.475164
C	0.218163	-0.015537	0.093356
C	1.463965	0.124441	-0.515844
C	2.590048	0.355273	0.268008
C	2.450492	0.436044	1.650448
C	1.188642	0.282159	2.217246
F	-0.828761	-0.237672	-0.732017
F	1.118858	0.357314	3.570034
F	3.529773	0.657455	2.421546
F	3.796629	0.496737	-0.300275
F	1.586766	0.039661	-1.850851
H	-1.368373	0.721720	3.201206
H	-1.330686	1.485789	3.736792
C	-0.857846	4.460049	5.721056
C	-3.252578	3.272225	5.054308
C	-3.932877	3.798433	6.337863
C	-3.738452	4.108009	3.830011
C	-3.709042	1.809321	4.862689
C	-1.372143	5.891962	5.436626
C	-0.837020	4.179621	7.250092
C	0.593782	4.369733	5.199101
C	-1.715580	3.366922	5.039748
O	-1.039133	2.540037	4.394226
H	-4.800885	1.772804	4.938874
H	-3.443660	1.406732	3.883714
H	-3.296082	1.149398	5.630887
H	-4.820148	3.964572	3.728755
H	-3.552641	5.177975	3.952003
H	-3.265122	3.777339	2.900606
H	-5.017008	3.734984	6.194537
H	-3.683293	3.181788	7.207298
H	-3.701198	4.838622	6.569395
H	-0.691677	6.601388	5.920389
H	-1.361869	6.111811	4.363543
H	-2.374200	6.088592	5.821014
H	-0.089905	4.838598	7.706154
H	-1.793821	4.373060	7.737126
H	-0.536946	3.147077	7.462283
H	1.190909	5.147352	5.687240
H	1.049450	3.400779	5.417105
H	0.645308	4.527488	4.117229

Complex 4d:

SCF 6-31*G+ = -2638.56389528685
SCF 6-311**G++ = -2638.594393869
sfinal(toluene)= -8.6245 kcal/mol
sfinal(acetonitrile)= -17.1310 kcal/mol
sfinal(DCM)= -14.9281 kcal/mol
64

B	0.215488	-0.480257	-0.213228
C	-0.333232	0.093600	1.224170
C	1.836168	-0.333750	-0.435815
C	-0.384205	-1.962524	-0.567884
C	2.767764	-1.375296	-0.379499

C	4.131317	-1.208765	-0.623251
C	4.628755	0.051213	-0.940273
C	3.747168	1.124529	-1.000210
C	2.398598	0.904004	-0.744969
F	2.377038	-2.628636	-0.061544
F	4.973008	-2.254321	-0.554927
F	5.935685	0.229793	-1.187272
F	4.199747	2.357015	-1.308749
F	1.595963	2.013920	-0.812846
C	-0.716954	-2.321262	-1.874529
C	-1.268949	-3.548243	-2.233030
C	-1.506577	-4.500195	-1.248119
C	-1.181927	-4.201645	0.071601
C	-0.633466	-2.958675	0.380236
F	-0.505698	-1.444978	-2.895661
F	-1.576296	-3.818526	-3.516632
F	-2.040198	-5.690220	-1.567003
F	-1.396923	-5.117729	1.032389
F	-0.323549	-2.749835	1.680784
C	-1.674944	0.457390	1.362813
C	-2.231029	0.978718	2.526569
C	-1.425474	1.145434	3.648330
C	-0.083490	0.786976	3.573245
C	0.428566	0.273818	2.381436
F	-2.522520	0.320025	0.304352
F	-3.531383	1.333796	2.571984
F	-1.935901	1.649711	4.783505
F	0.705471	0.939015	4.651913
F	1.737916	-0.064744	2.399824
O	-1.161601	2.415570	-1.085531
C	-1.327785	3.306378	-1.971565
C	-2.094435	4.511330	-1.418268
C	-0.802254	3.098171	-3.388017
C	-1.811067	3.544437	-4.475835
C	0.513560	3.935124	-3.502196
C	-0.458316	1.616472	-3.650657
C	-1.644407	5.881288	-1.972468
C	-3.595189	4.253606	-1.773252
C	-1.969293	4.555160	0.124654
H	-0.279115	0.256129	-1.086037
H	-0.712102	1.503178	-1.272637
H	-4.188877	5.023415	-1.268757
H	-3.797204	4.320500	-2.844110
H	-3.931501	3.278475	-1.406006
H	-2.289932	6.648192	-1.531940
H	-0.615723	6.112697	-1.678598
H	-1.728037	5.973445	-3.056226
H	-2.500310	5.440222	0.489027
H	-2.407161	3.676105	0.601311
H	-0.923879	4.631677	0.441489
H	-1.333593	3.401389	-5.450481
H	-2.714473	2.926173	-4.458773
H	-2.102122	4.592887	-4.406949
H	0.971645	3.686137	-4.465520
H	0.333978	5.010954	-3.483195
H	1.228584	3.675874	-2.715904
H	-0.164420	1.512614	-4.699756
H	0.380476	1.257701	-3.050405
H	-1.313020	0.952943	-3.485801

Complex TS2d:

SCF 6-31*G+ = -2638.53156494131
SCF 6-311**G++ = -2638.56245818
sfinal(toluene)= -5.2173 kcal/mol
sfinal(acetonitrile)= -11.7399 kcal/mol
sfinal(DCM)= -9.9076 kcal/mol

64

C	0.958396	-1.438186	2.349135
C	0.152847	-0.450203	1.756756
C	-0.476288	0.366090	2.690541
C	-0.337394	0.246372	4.073039
C	0.473716	-0.749241	4.599332
C	1.129402	-1.604578	3.718760
B	0.180409	-0.415083	0.099788
C	-0.431000	-1.765324	-0.586134
C	-0.207246	-2.125759	-1.925453
C	-0.699272	-3.280753	-2.525150
C	-1.483362	-4.159799	-1.785817
C	-1.763045	-3.848655	-0.461297
C	-1.248388	-2.680930	0.098741
F	0.513549	-1.324726	-2.736923
F	-0.433206	-3.545093	-3.814409
F	-1.975469	-5.271126	-2.345065
F	-2.537526	-4.667044	0.269021
F	-1.620756	-2.465054	1.382562
F	-1.301223	1.384448	2.305122
F	-0.982221	1.093455	4.893599
F	0.622342	-0.883080	5.923982
F	1.914287	-2.583154	4.195235
F	1.614141	-2.321134	1.560082
C	1.711947	0.040421	-0.253879
C	2.718545	-0.749049	-0.828451
C	4.039994	-0.325016	-0.975302
C	4.422750	0.931230	-0.519624
C	3.473011	1.740432	0.096392
C	2.168244	1.277869	0.221978
F	2.476927	-2.014768	-1.222199
F	4.953051	-1.134169	-1.535416
F	5.686954	1.350802	-0.657448
F	3.819235	2.950217	0.567750
F	1.308584	2.097901	0.875017
C	-1.667905	1.866821	-0.962660
C	-3.028057	1.085767	-1.022498
O	-1.574677	2.711115	0.058521
C	-0.946112	2.497227	-2.201712
H	-1.973610	2.350535	0.870725
C	-0.234368	1.474045	-3.102504
C	-1.973425	3.279314	-3.070513
C	0.101147	3.537825	-1.738651
C	-3.117540	0.076628	-2.179832
C	-3.311098	0.346237	0.306352
C	-4.188310	2.122069	-1.174476
H	-0.664431	0.643418	-0.454458
H	-1.403918	3.826743	-3.829435
H	-2.673176	2.628436	-3.599207
H	-2.534571	4.014593	-2.486590
H	0.173183	2.003778	-3.970885
H	0.598261	1.002110	-2.581975
H	-0.892731	0.689463	-3.475324

H	0.628897	3.908161	-2.624108
H	-0.361727	4.391598	-1.237071
H	0.837045	3.112994	-1.059063
H	-4.222371	-0.247771	0.184308
H	-2.509532	-0.331118	0.593267
H	-3.501105	1.029787	1.141481
H	-5.129024	1.596821	-0.976649
H	-4.107000	2.941450	-0.453262
H	-4.255904	2.546622	-2.175363
H	-4.093908	-0.418795	-2.137204
H	-3.041159	0.553315	-3.159378
H	-2.351295	-0.695408	-2.108496

Complex 2'd:

SCF 6-31*G+ = -430.2334218
SCF 6-311**G++ = -430.265072
sfinal(toluene)= -2.2751 kcal/mol
sfinal(acetonitrile)= -5.0999 kcal/mol
sfinal(DCM)= -4.3459 kcal/mol

30

C	2.174598	0.292561	2.962093
C	1.623187	0.049013	1.539222
C	2.272687	1.044062	0.557809
C	0.053671	0.071005	1.513484
C	-0.797828	1.385227	1.712518
C	-0.751190	2.328296	0.491452
O	-0.317574	-0.544156	0.265070
C	2.063232	-1.382274	1.137193
C	-2.271324	0.937257	1.907541
C	-0.402667	2.174303	2.976415
H	-0.247606	-0.603178	2.334238
H	3.348730	0.841667	0.482714
H	1.843440	0.951227	-0.445119
H	2.162007	2.082606	0.887658
H	3.250461	0.078844	2.974279
H	2.048077	1.320397	3.307381
H	1.701923	-0.373294	3.695970
H	3.149348	-1.480830	1.257364
H	1.586059	-2.138400	1.774400
H	1.805437	-1.609406	0.100744
H	-1.149312	2.954613	3.171509
H	-0.355718	1.533686	3.865579
H	0.562823	2.675453	2.863460
H	-1.508261	3.115159	0.603030
H	0.218265	2.821621	0.384566
H	-0.957027	1.787887	-0.437584
H	-2.906308	1.805515	2.119390
H	-2.692794	0.459791	1.012861
H	-2.372758	0.238522	2.748345
H	-1.263766	-0.746648	0.282273

Complex 3'b:

SCF 6-31*G+ = -2103.864445996
SCF 6-311**G++ = -2103.877183858
sfinal(toluene)= -7.6315 kcal/mol
sfinal(acetonitrile)= -15.7147 kcal/mol
sfinal(DCM)= -13.5583 kcal/mol

44

C	12.052892	2.336346	4.155612
C	11.563813	2.971260	3.012866
C	12.553272	3.596021	2.239678
C	13.905905	3.587929	2.568870
C	14.355401	2.947740	3.713972
C	13.403344	2.318789	4.500521
B	9.999151	3.160089	2.546900
C	8.619255	1.594133	4.177948
C	9.017892	0.261789	3.628321
F	12.194275	4.231568	1.100214
F	14.795879	4.206390	1.762614
F	13.781710	1.673128	5.626404
F	11.214953	1.683232	5.015788
C	9.665449	4.766836	2.515691
C	9.374844	5.517682	1.372880
C	9.135161	6.889623	1.413064
C	9.178138	7.593126	2.607429
C	9.479956	6.877196	3.757037
C	9.723219	5.508800	3.702697
F	9.328407	4.933088	0.153131
F	10.043448	4.895805	4.871091
F	9.545719	7.514550	4.947541
F	8.855928	7.542828	0.264036
C	9.495316	2.332611	1.229965
C	10.296311	1.565620	0.378150
C	9.791542	0.907350	-0.743973
C	8.444550	0.960110	-1.066664
C	7.619043	1.698924	-0.229809
C	8.139997	2.360379	0.875771
F	11.617304	1.405621	0.619604
F	10.635959	0.194159	-1.518850
F	6.295191	1.777167	-0.485948
F	7.261754	3.063636	1.639741
C	7.672322	1.632198	5.335117
H	15.406283	2.935682	3.979480
H	8.052547	0.444871	-1.936462
H	8.990317	8.660357	2.638559
H	8.168293	-0.153730	3.069835
H	9.881085	0.315515	2.968722
H	9.224465	-0.421267	4.459865
H	6.848831	0.923955	5.186808
H	8.217737	1.311948	6.233633
H	7.290041	2.641992	5.490675
O	9.022928	2.689282	3.747631

Complex TS1'b:

SCF 6-31*G+ = -2105.011567073
SCF 6-311**G++ = -2105.029985164
sfinal(toluene)= -8.9941 kcal/mol
sfinal(acetonitrile)= -18.2972 kcal/mol
sfinal(DCM)= -15.7986 kcal/mol

46

F	-2.515700	-0.348951	4.966144
C	-2.023000	-1.493745	4.405814

C	-1.485594	-1.460065	3.118112
C	-1.036203	-2.693451	2.637425
C	-1.104258	-3.863018	3.390041
C	-1.630682	-3.860347	4.674649
C	-2.092167	-2.650655	5.173500
B	-1.371632	-0.092567	2.260738
C	-2.709649	0.435765	1.511249
C	-2.799819	1.764543	1.083687
C	-3.904220	2.281310	0.417125
C	-4.999412	1.477447	0.130619
C	-4.942122	0.153249	0.540918
C	-3.829704	-0.348202	1.216746
F	-2.618817	-2.591374	6.418135
H	-1.683243	-4.769370	5.262869
F	-0.652660	-5.018614	2.857846
F	-0.530332	-2.788952	1.386920
F	-1.778655	2.623288	1.354042
F	-3.913652	3.586618	0.059807
H	-5.864578	1.867147	-0.393757
F	-5.982129	-0.668193	0.284573
F	-3.864530	-1.654906	1.561320
C	0.010541	0.091802	1.437160
C	0.106482	-0.043110	0.049811
C	1.308603	0.099743	-0.637722
C	2.488425	0.387240	0.035038
C	2.422839	0.517638	1.415382
C	1.215598	0.365594	2.089704
F	-0.995095	-0.339635	-0.679745
F	1.234703	0.497378	3.442134
F	3.545426	0.791808	2.117656
H	3.426171	0.499975	-0.497112
F	1.324058	-0.046275	-1.980852
H	-1.225797	0.816460	3.219787
H	-1.130204	1.568412	3.769273
C	-1.651319	4.409203	5.798538
C	-3.316634	2.867114	4.565697
H	-3.976126	3.020875	5.426265
H	-3.650272	3.556028	3.776191
H	-3.405793	1.843405	4.201247
H	-2.324663	5.235782	5.547067
H	-1.873603	4.117716	6.834934
H	-0.608113	4.723959	5.735827
C	-1.906492	3.226408	4.916141
O	-0.923187	2.590378	4.494012

Complex 4'b:

SCF 6-31*G+ = -2105.014347159
SCF 6-311**G++ = -2105.033766013
sfinal(toluene)= -10.9926 kcal/mol
sfinal(acetonitrile)= -21.8996 kcal/mol
sfinal(DCM)= -18.8363 kcal/mol

46

C	-0.134256	0.770952	0.200772
C	-0.061287	-0.121784	1.273470
C	1.129522	-0.851721	1.333334
C	2.155970	-0.702445	0.402404
C	2.048153	0.192452	-0.654048
C	0.876824	0.930718	-0.740941

B	-1.293995	-0.256425	2.339003
C	-1.495707	-1.742127	2.983476
C	-1.018300	-2.123463	4.241290
C	-1.237722	-3.388911	4.780641
C	-1.952450	-4.355364	4.084584
C	-2.434871	-4.006980	2.831424
C	-2.203568	-2.738752	2.312152
F	-0.296066	-1.255378	4.983967
F	-0.741537	-3.680820	6.003227
F	-3.140075	-4.906477	2.103638
F	-2.715433	-2.487514	1.063026
F	1.333458	-1.736775	2.333501
F	3.277958	-1.442508	0.531985
F	0.704795	1.809638	-1.759481
F	-1.256870	1.537296	0.031533
C	-1.378912	0.952435	3.430213
C	-2.617830	1.365435	3.927425
C	-2.763864	2.395346	4.850414
C	-1.655810	3.076539	5.335273
C	-0.410147	2.686802	4.862610
C	-0.282080	1.653774	3.937356
F	-3.755509	0.745862	3.503583
F	0.973035	1.329369	3.545455
F	0.699236	3.317293	5.310263
F	-4.002284	2.736698	5.277529
O	-4.119982	0.187466	0.362050
C	-4.089512	-0.180765	-0.842582
C	-5.329388	0.055402	-1.634897
C	-2.909544	-0.833625	-1.471036
H	-1.757844	3.878085	6.057863
H	-2.122686	-5.341104	4.502154
H	2.847602	0.310394	-1.376597
H	-2.565136	-0.209886	-2.306320
H	-2.093180	-1.003465	-0.772585
H	-3.226058	-1.792375	-1.902805
H	-5.083138	0.559984	-2.576449
H	-5.767992	-0.915787	-1.901897
H	-6.053505	0.639463	-1.065016
H	-2.321891	-0.073088	1.654048
H	-3.227207	0.032863	0.947112

Complex TS2'b:

SCF 6-31*G+ = -2105.012911605
SCF 6-311**G++ = -2105.032558946
sfinal(toluene)= -8.1470 kcal/mol
sfinal(acetonitrile)= -17.6557 kcal/mol
sfinal(DCM)= -15.0109 kcal/mol

46

B	0.037467	-0.383472	0.106271
C	-0.052763	-0.273866	1.730593
C	1.504251	0.026002	-0.469554
C	-0.640409	-1.724777	-0.528757
C	2.388229	-0.819787	-1.149494
C	3.645072	-0.403694	-1.585432
C	4.098678	0.886926	-1.352001
C	3.247373	1.746641	-0.671682
C	1.992735	1.318518	-0.253359
F	2.061472	-2.109564	-1.395006

F	4.432970	-1.279316	-2.246110
H	5.078086	1.210170	-1.685594
F	3.637333	3.015639	-0.415037
F	1.220794	2.215371	0.418328
C	-0.884051	-1.822783	-1.903991
C	-1.363539	-2.969574	-2.525068
C	-1.695079	-4.091914	-1.777585
C	-1.509366	-4.016894	-0.406064
C	-0.987675	-2.871234	0.194896
F	-0.582469	-0.763299	-2.710351
F	-1.521391	-2.988829	-3.867057
H	-2.083129	-4.989117	-2.245937
F	-1.838302	-5.072662	0.367713
F	-0.828772	-2.919764	1.538041
C	-1.168611	0.185715	2.426595
C	-1.244132	0.280944	3.810829
C	-0.167456	-0.088873	4.602437
C	0.962195	-0.561277	3.948105
C	1.009826	-0.653567	2.559386
F	-2.307349	0.548212	1.735257
F	-2.380985	0.739459	4.382011
H	-0.207010	-0.017050	5.683253
F	2.036848	-0.945769	4.666093
F	2.139056	-1.168110	2.023297
C	-1.685221	1.999900	-0.873042
O	-1.723804	2.703219	0.237625
H	-2.304927	2.281181	0.902863
C	-0.758555	2.558996	-1.902851
C	-2.884446	1.202064	-1.284836
H	-0.316074	1.762076	-2.501679
H	-1.344248	3.208168	-2.569456
H	0.026104	3.151129	-1.428746
H	-2.602570	0.399444	-1.964844
H	-3.408602	0.772589	-0.428589
H	-3.566045	1.886352	-1.810947
H	-0.704596	0.606680	-0.354155

Supplementary Material (ESI) for Dalton Transactions