

Electronic Supporting Information

Part II: Computational Details

**“Size-Dependent Rate Acceleration in the Silylation of Secondary
Alcohols: the Bigger the Faster”**

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Table of Contents

Part I: Experimental Details

1.	SUPPLEMENTARY DATA OF COMPETITION EXPERIMENTS.....	
2.	EXPERIMENTAL DETERMINATION OF RELATIVE RATE CONSTANTS.....	
3.	INVESTIGATION OF SOLVENT EFFECTS.....	
4.	INVESTIGATION OF OTHER INFLUENCES ON THE RATE CONSTANT.....	
5.	SYNTHETIC DATA	

Part II: Computational Details

6.	COMPUTATIONAL METHODS & DATA	S131
6.1.	Theoretical Methods.....	S131
6.2.	Total energies, enthalpies and free energies of reactants and products	S132
6.3.	Geometrical analysis of conformers found for silyl ether 5fe.....	S154
6.4.	Calculation of reaction free energies and dispersion contribution of the best conformers.....	S160
6.5.	Relation of Experimental and Computational Results.....	S170
	SUPPLEMENTARY REFERENCES.....	S165

6. Computational Methods & Data

6.1. Theoretical Methods

All geometry optimizations and vibrational frequency calculations have been performed using the B3LYP-D3 hybrid functional⁴⁸⁻⁵⁰ in combination with the 6-31+G(d) (for H, C, O and N atoms) and 6-311+G(2d) basis set (for Si and Cl atoms).⁵¹ Solvent effects for chloroform have been calculated with the SMD continuum solvation model.⁵² This combination has been found to perform well for the description of charge-separated intermediates common in many organocatalytic reaction mechanisms.⁵³ Thermochemical corrections to 298.15 K have been calculated for all minima from unscaled vibrational frequencies obtained at this same level.

Initial search of conformational space of every compound has been done with Maestro program. Next, all predicted conformers were optimized and “double-counts” conformers were eliminated, that is, conformers with identical energy or similar geometry to another one. In the case of the silyl ethers **5(a-f)f**, the conformers were generated by taking the three-four best conformers of the analogous silyl ether **5(a-f)e** and adding both methoxy group and chlorine atom. In case of best conformer: the thermochemical corrections have been combined with single point energies calculated at the DLPNO-CCSD(T)/def2-TZVPP//SMD(CHCl₃)/B3LYP-D3/6-311+G(2d)/6-31+G(g) level⁵⁴⁻⁵⁶. Solvation factors have been obtained as the difference between the energies computed at B3LYP-D3/6-311+G(2d)/6-31+G(g) in solution and in gas phase. This factor has been added to the energy computed at DLPNO-CCSD(T)/def2-TZVPP//SMD(CHCl₃)/B3LYP-D3/6-311+G(2d)/6-31+G(g) to yield free energies G_{298} at 298.15 K. Single point energies at the SMD(CHCl₃)/B3LYP/6-31+G(d)/6-311+G(2d) of the optimized geometries were performed to analyse the effect of the dispersion component (D3) on the energies. Free energies in solution have been corrected to a reference state of 1 mol/l at 298.15 K through addition of $RT\ln(24.46) = +7.925$ kJ/mol to the gas phase (1 atm) free energies. All calculations have been performed with Gaussian 09⁵⁷ and ORCA version 4.0.⁵⁸ The picture in Figure 4 of the manuscript has been plotted with the VMD program.⁵⁹

6.2. Total energies, enthalpies and free energies of reactants and products

Table S17: Total energies, enthalpies and free energies for alcohols **1**, silyl reagents **2** and products **5** (in Hartree). Molar free energies in solution at 298.15 K ($G_{298,sol}$) have been calculated at the SMD(CHCl₃)/B3LYP-D3/6-31+G(d)/6-311+G(2d) level and corrected for a solution standard state of 1 M through addition of +7.925 kJ/mol (0.00301848 Hartree). The SMD(CHCl₃)/B3LYP-D3/6-31+G(d)/6-311+G(2d) level of theory has been used to optimize the geometries and calculate solute thermal corrections and solvation factor. Note that the filenames are used in our calculations and do not follow any guide.

Filename	Imag Freq	E_{tot} SMD/B3LYP-D3/6-311+G(2d)/6-31+G(d) ^[a]	H_{298} SMD/B3LYP-D3/6-311+G(2d)/6-31+G(d)	G_{298} SMD/B3LYP-D3/6-311+G(2d)/6-31+G(d)	$G_{298,sol}$ SMD/B3LYP-D3/6-311+G(2d)/6-31+G(d)
HCl					
hcl_1	0	-460.8341487	-460.8243700	-460.8455820	-460.8425635
1a					
roh1_1	0	-386.1285457	-385.9580060	-386.0006440	-385.9976255
roh1_2	0	-386.1267858	-385.9564090	-385.9994020	-385.9963835
roh1_6	0	-386.1268072	-385.9564100	-385.9992810	-385.9962625
roh1_3	0	-386.1265718	-385.9558240	-385.9983920	-385.9953735
roh1_5	0	-386.1264681	-385.9558420	-385.9981660	-385.9951475
1b					
roh2_1_1	0	-539.7816611	-539.5612560	-539.6090270	-539.6060085
roh2_1_3	0	-539.7807243	-539.5603300	-539.6081470	-539.6051285
roh2_1_2	0	-539.7800461	-539.5597390	-539.6077030	-539.6046845
roh2_1_6	0	-539.7802734	-539.5595530	-539.6072410	-539.6042225
roh2_1_5	0	-539.7794091	-539.5589050	-539.6068150	-539.6037965
roh2_1_7	0	-539.7786379	-539.5583620	-539.6061670	-539.6031485
1c					
roh2_2_2	0	-539.7847329	-539.5646210	-539.6132800	-539.6102615
roh2_2_1	0	-539.7843588	-539.5642260	-539.6128280	-539.6098095
roh2_2_7	0	-539.7827608	-539.5626340	-539.6120680	-539.6090495
roh2_2_5	0	-539.7829155	-539.5629900	-539.6118250	-539.6088065
roh2_2_3	0	-539.7829032	-539.5628580	-539.6113070	-539.6082885

roh2_2_6	0	-539.7828001	-539.5625430	-539.6108480	-539.6078295
roh2_2_4	0	-539.7829836	-539.5627100	-539.6107120	-539.6076935
roh2_2_8	0	-539.7813004	-539.5611290	-539.6095570	-539.6065385
1d					
roh3_9_1	0	-693.4236962	-693.1537890	-693.2078480	-693.2048295
roh3_9_2	0	-693.4214865	-693.1516800	-693.2057160	-693.2026975
1e					
roh3_2_2	0	-693.4345314	-693.1650900	-693.2193170	-693.2162985
roh3_2_1	0	-693.4340380	-693.1645020	-693.2189460	-693.2159275
roh3_2_5	0	-693.4325857	-693.1634010	-693.2187590	-693.2157405
roh3_2_4	0	-693.4326702	-693.1631300	-693.2179580	-693.2149395
roh3_2_3	0	-693.4326096	-693.1631830	-693.2177090	-693.2146905
roh3_2_6	0	-693.4326593	-693.1630570	-693.2176120	-693.2145935
roh3_2_9	0	-693.4325189	-693.1630890	-693.2174310	-693.2144125
roh3_2_10	0	-693.4311031	-693.1616130	-693.2162210	-693.2132025
1f					
roh4_1_1	0	-769.6780488	-769.3946960	-769.4497090	-769.4466905
roh4_1_2	0	-769.6773936	-769.3938820	-769.4488540	-769.4458355
roh4_1_3	0	-769.6764413	-769.3933170	-769.4486820	-769.4456635
roh4_1_4	0	-769.6763915	-769.3930200	-769.4482680	-769.4452495
roh4_1_5	0	-769.6762138	-769.3929250	-769.4479440	-769.4449255
roh4_1_7	0	-769.6757332	-769.3922220	-769.4477060	-769.4446875
roh4_1_6	0	-769.6752971	-769.3919190	-769.4468860	-769.4438675
roh4_1_8	0	-769.6748979	-769.3915720	-769.4463850	-769.4433665
2a					
TMSCI	0	-869.6013765	-869.4791330	-869.5210940	-869.5180755
2b					
TBSCI_1	0	-987.5495242	-987.3378220	-987.3893590	-987.3863405
2c					

DPNpSiCl_1	0	-1372.2683456	-1371.9190600	-1371.9882150	-1371.9851965
DPNpSiCl_8	0	-1372.2661202	-1371.9166690	-1371.9849220	-1371.9819035
DPNpSiCl_11	0	-1372.2656524	-1371.9163130	-1371.9847610	-1371.9817425
DPNpSiCl_6	0	-1372.2664051	-1371.9167030	-1371.9847510	-1371.9817325
DPNpSiCl_7	0	-1372.2650392	-1371.9155330	-1371.9843340	-1371.9813155
DPNpSiCl_3	0	-1372.2657915	-1371.9160670	-1371.9842420	-1371.9812235
DPNpSiCl_14	0	-1372.2652554	-1371.9156500	-1371.9839230	-1371.9809045
DPNpSiCl_15	0	-1372.2655624	-1371.9156820	-1371.9832290	-1371.9802105
DPNpSiCl_4	0	-1372.2654028	-1371.9157830	-1371.9829100	-1371.9798915
DPNpSiCl_10	0	-1372.2650270	-1371.9152500	-1371.9825060	-1371.9794875
DPNpSiCl_12	0	-1372.2654395	-1371.9157170	-1371.9824550	-1371.9794365
DPNpSiCl_18	0	-1372.2629838	-1371.9130450	-1371.9803350	-1371.9773165
2d					
ph3sicl_04	0	-1444.8488463	-1444.5545750	-1444.6243200	-1444.6213015
ph3sicl_03	0	-1444.8488110	-1444.5546350	-1444.6229230	-1444.6199045
ph3sicl_05	0	-1444.8488648	-1444.5545960	-1444.6224210	-1444.6194025
ph3sicl_02	0	-1444.8488074	-1444.5546030	-1444.6223280	-1444.6193095
2e					
NpSiCl_6	0	-1905.8181159	-1905.3752920	-1905.4602600	-1905.4572415
NpSiCl_2	0	-1905.8181159	-1905.3752920	-1905.4602510	-1905.4572325
NpSiCl_8	0	-1905.8181160	-1905.3752920	-1905.4602430	-1905.4572245
NpSiCl_5	0	-1905.8172264	-1905.3742890	-1905.4589150	-1905.4558965
NpSiCl_3	0	-1905.8172517	-1905.3743350	-1905.4587420	-1905.4557235
2f					
NpOMeSiCl_6	0	-3628.2847124	-3627.7607190	-3627.8743050	-3627.8712865
NpOMeSiCl_2	0	-3628.2847123	-3627.7607200	-3627.8742990	-3627.8712805
NpOMeSiCl_1	0	-3628.2838553	-3627.7599960	-3627.8735290	-3627.8705105
5aa					

TMS1__1	0	-794.8873872	-794.6073700	-794.6673630	-794.6643445
TMS1__3	0	-794.8843541	-794.6038710	-794.6620810	-794.6590625
TMS1__2	0	-794.8832821	-794.6030370	-794.6618590	-794.6588405
5ba					
TMS2_1_1	0	-948.5409852	-948.2114270	-948.2770250	-948.2740065
TMS2_1_2	0	-948.5413145	-948.2115030	-948.2769820	-948.2739635
TMS2_1_3	0	-948.5413145	-948.2115060	-948.2769670	-948.2739485
TMS2_1_4	0	-948.5391875	-948.2094590	-948.2741070	-948.2710885
TMS2_1_6	0	-948.5381047	-948.2082660	-948.2729980	-948.2699795
5ca					
TMS2_2_2	0	-948.5442240	-948.2146950	-948.2805140	-948.2774955
TMS2_2_1	0	-948.5434143	-948.2140570	-948.2803760	-948.2773575
TMS2_2_4	0	-948.5399522	-948.2103380	-948.2751430	-948.2721245
TMS2_2_5	0	-948.5408550	-948.2109760	-948.2748540	-948.2718355
TMS2_2_3	0	-948.5386635	-948.2089930	-948.2741950	-948.2711765
5da					
TMS3_9_3	0	-1102.1852162	-1101.8057360	-1101.8771510	-1101.8741325
TMS3_9_1	0	-1102.1852162	-1101.8057360	-1101.8771450	-1101.8741265
TMS3_9_2	0	-1102.1852148	-1101.8057350	-1101.8771260	-1101.8741075
5ea					
TMS_3_2_1	0	-1102.1932852	-1101.8144030	-1101.8861200	-1101.8831015
TMS_3_2_2	0	-1102.1941746	-1101.8151080	-1101.8860510	-1101.8830325
TMS_3_2_5	0	-1102.1905392	-1101.8112640	-1101.8813150	-1101.8782965
TMS_3_2_4	0	-1102.1894441	-1101.8101290	-1101.8811710	-1101.8781525
TMS_3_2_3	0	-1102.1881770	-1101.8088620	-1101.8791660	-1101.8761475
5fa					
TMS4_1_2	0	-1178.4377323	-1178.0451410	-1178.1181640	-1178.1151455
TMS4_1_3	0	-1178.4381437	-1178.0451780	-1178.1164610	-1178.1134425
TMS4_1_1	0	-1178.4381438	-1178.0451770	-1178.1164550	-1178.1134365
TMS4_1_4	0	-1178.4360289	-1178.0429670	-1178.1139920	-1178.1109735

TMS4_1_5	0	-1178.4346404	-1178.0417070	-1178.1133990	-1178.1103805
5ab					
TBS1_3	0	-912.8352609	-912.4657330	-912.5335650	-912.5305465
TBS1_2	0	-912.8352522	-912.4656930	-912.5333230	-912.5303045
5bb					
TBS2_1_8	0	-1066.4893794	-1066.0701100	-1066.1443310	-1066.1413125
TBS2_1_3	0	-1066.4890413	-1066.0698170	-1066.1433860	-1066.1403675
TBS2_1_7	0	-1066.4884607	-1066.0694440	-1066.1432100	-1066.1401915
TBS2_1_2	0	-1066.4893230	-1066.0698390	-1066.1429150	-1066.1398965
TBS2_1_10	0	-1066.4885368	-1066.0692010	-1066.1412830	-1066.1382645
5cb					
TBS2_2_4	0	-1066.4922930	-1066.0733840	-1066.1482600	-1066.1452415
TBS2_2_5	0	-1066.4914345	-1066.0724450	-1066.1477690	-1066.1447505
TBS2_2_1	0	-1066.4918861	-1066.0729760	-1066.1475530	-1066.1445345
TBS2_2_7	0	-1066.4915624	-1066.0726650	-1066.1469160	-1066.1438975
TBS2_2_3	0	-1066.4915010	-1066.0725250	-1066.1467700	-1066.1437515
TBS2_2_6	0	-1066.4915962	-1066.0725450	-1066.1463890	-1066.1433705
TBS2_2_2	0	-1066.4913614	-1066.0723240	-1066.1458130	-1066.1427945
5bd					
TBS3_9_2	0	-1220.1337755	-1219.6650640	-1219.7448550	-1219.7418365
TBS3_9_1	0	-1220.1337755	-1219.6650630	-1219.7448440	-1219.7418255
TBS3_9_6	0	-1220.1329260	-1219.6639250	-1219.7435780	-1219.7405595
TBS3_9_3	0	-1220.1329084	-1219.6638740	-1219.7433290	-1219.7403105
TBS3_9_5	0	-1220.1323792	-1219.6633490	-1219.7419340	-1219.7389155
TBS3_9_4	0	-1220.1330561	-1219.6637700	-1219.7418040	-1219.7387855
5eb					
TBS3_2_1	0	-1220.1416168	-1219.6735540	-1219.7543650	-1219.7513465
TBS3_2_3	0	-1220.1416549	-1219.6734710	-1219.7543300	-1219.7513115
TBS3_2_9	0	-1220.1414634	-1219.6732590	-1219.7536250	-1219.7506065
TBS3_2_4	0	-1220.1414634	-1219.6732580	-1219.7536160	-1219.7505975
TBS3_2_2	0	-1220.1412043	-1219.6727590	-1219.7531430	-1219.7501245

TBS3_2_6	0	-1220.1412556	-1219.6729250	-1219.7525980	-1219.7495795
TBS3_2_8	0	-1220.1412005	-1219.6729110	-1219.7524120	-1219.7493935
TBS3_2_10	0	-1220.1416837	-1219.6729350	-1219.7521700	-1219.7491515
TBS3_2_7	0	-1220.1397800	-1219.6714220	-1219.7513800	-1219.7483615
5fb					
TBS4_1_2	0	-1296.3860085	-1295.9039360	-1295.9854580	-1295.9824395
TBS4_1_5	0	-1296.3859040	-1295.9036200	-1295.9846090	-1295.9815905
TBS4_1_3	0	-1296.3859522	-1295.9035200	-1295.9846070	-1295.9815885
TBS4_1_4	0	-1296.3851147	-1295.9028550	-1295.9840190	-1295.9810005
TBS4_1_1	0	-1296.3866822	-1295.9043660	-1295.9839860	-1295.9809675
TBS4_1_10	0	-1296.3866823	-1295.9043650	-1295.9839730	-1295.9809545
TBS4_1_6	0	-1296.3849777	-1295.9028560	-1295.9837530	-1295.9807345
TBS4_1_9	0	-1296.3855566	-1295.9028860	-1295.9824330	-1295.9794145
TBS4_1_7	0	-1296.3853362	-1295.9025560	-1295.9819910	-1295.9789725
5ac					
DiNp1_1	0	-1297.5573313	-1297.0502310	-1297.1365120	-1297.1334935
DiNp1_9	0	-1297.5561280	-1297.0489200	-1297.1346430	-1297.1316245
DiNp1_22	0	-1297.5554160	-1297.0484210	-1297.1341900	-1297.1311715
DiNp1_15	0	-1297.5551169	-1297.0480700	-1297.1341750	-1297.1311565
DiNp1_3	0	-1297.5564843	-1297.0491650	-1297.1341390	-1297.1311205
DiNp1_33	0	-1297.5561753	-1297.0488290	-1297.1339680	-1297.1309495
DiNp1_10	0	-1297.5561754	-1297.0488290	-1297.1339570	-1297.1309385
DiNp1_34	0	-1297.5561889	-1297.0490820	-1297.1339350	-1297.1309165
DiNp1_37	0	-1297.5556538	-1297.0483770	-1297.1331600	-1297.1301415
DiNp1_14	0	-1297.5556538	-1297.0483760	-1297.1331560	-1297.1301375
DiNp1_17	0	-1297.5553467	-1297.0481790	-1297.1331400	-1297.1301215
DiNp1_28	0	-1297.5541318	-1297.0469930	-1297.1331380	-1297.1301195
DiNp1_24	0	-1297.5546299	-1297.0472160	-1297.1330300	-1297.1300115
DiNp1_25	0	-1297.5554136	-1297.0479980	-1297.1328850	-1297.1298665
DiNp1_29	0	-1297.5547051	-1297.0471970	-1297.1327220	-1297.1297035
DiNp1_2	0	-1297.5554613	-1297.0480220	-1297.1325380	-1297.1295195

DiNp1_6	0	-1297.5544426	-1297.0471820	-1297.1324420	-1297.1294235
DiNp1_21	0	-1297.5546865	-1297.0474360	-1297.1323650	-1297.1293465
DiNp1_4	0	-1297.5554898	-1297.0480160	-1297.1322920	-1297.1292735
DiNp1_7	0	-1297.5550750	-1297.0476580	-1297.1322310	-1297.1292125
DiNp1_19	0	-1297.5549964	-1297.0476550	-1297.1320020	-1297.1289835
DiNp1_26	0	-1297.5539654	-1297.0467210	-1297.1318790	-1297.1288605
DiNp1_18	0	-1297.5548730	-1297.0473180	-1297.1317220	-1297.1287035
DiNp1_30	0	-1297.5548520	-1297.0470480	-1297.1316230	-1297.1286045
DiNp1_20	0	-1297.5546469	-1297.0473210	-1297.1314230	-1297.1284045
DiNp1_36	0	-1297.5551244	-1297.0476330	-1297.1313890	-1297.1283705
DiNp1_5	0	-1297.5542674	-1297.0468820	-1297.1311650	-1297.1281465
DiNp1_31	0	-1297.5541657	-1297.0465600	-1297.1306210	-1297.1276025
DiNp1_16	0	-1297.5539577	-1297.0464120	-1297.1305000	-1297.1274815
DiNp1_11	0	-1297.5540428	-1297.0464410	-1297.1303300	-1297.1273115
DiNp1_12	0	-1297.5544150	-1297.0465870	-1297.1302500	-1297.1272315
DiNp1_23	0	-1297.5533286	-1297.0456350	-1297.1292470	-1297.1262285
5bc					
DiNp2_1_2	0	-1451.2119687	-1450.6549620	-1450.7440810	-1450.7410625
DiNp2_1_15	0	-1451.2100371	-1450.6531020	-1450.7435930	-1450.7405745
DiNp2_1_49	0	-1451.2092873	-1450.6523300	-1450.7434560	-1450.7404375
DiNp2_1_19	0	-1451.2095997	-1450.6523290	-1450.7433840	-1450.7403655
DiNp2_1_47	0	-1451.2095566	-1450.6525030	-1450.7433110	-1450.7402925
DiNp2_1_13	0	-1451.2100830	-1450.6528420	-1450.7432430	-1450.7402245
DiNp2_1_29	0	-1451.2093949	-1450.6522670	-1450.7430840	-1450.7400655
DiNp2_1_33	0	-1451.2095568	-1450.6525190	-1450.7429080	-1450.7398895
DiNp2_1_5	0	-1451.2100703	-1450.6530000	-1450.7428060	-1450.7397875
DiNp2_1_16	0	-1451.2100876	-1450.6531880	-1450.7427480	-1450.7397295
DiNp2_1_36	0	-1451.2086400	-1450.6515020	-1450.7426180	-1450.7395995
DiNp2_1_38	0	-1451.2096962	-1450.6523960	-1450.7424750	-1450.7394565
DiNp2_1_40	0	-1451.2096203	-1450.6523640	-1450.7424000	-1450.7393815
DiNp2_1_34	0	-1451.2084157	-1450.6513210	-1450.7423760	-1450.7393575

DiNp2_1_30	0	-1451.2093649	-1450.6521340	-1450.7421070	-1450.7390885
DiNp2_1_42	0	-1451.2104997	-1450.6535520	-1450.7420940	-1450.7390755
DiNp2_1_6	0	-1451.2103757	-1450.6532990	-1450.7420020	-1450.7389835
DiNp2_1_46	0	-1451.2094181	-1450.6523100	-1450.7419350	-1450.7389165
DiNp2_1_9	0	-1451.2094117	-1450.6521800	-1450.7417290	-1450.7387105
DiNp2_1_20	0	-1451.2105581	-1450.6535290	-1450.7417060	-1450.7386875
DiNp2_1_28	0	-1451.2095775	-1450.6523030	-1450.7413740	-1450.7383555
DiNp2_1_14	0	-1451.2088749	-1450.6519440	-1450.7412420	-1450.7382235
DiNp2_1_21	0	-1451.2089247	-1450.6517420	-1450.7411850	-1450.7381665
DiNp2_1_18	0	-1451.2087256	-1450.6514260	-1450.7408800	-1450.7378615
DiNp2_1_32	0	-1451.2085316	-1450.6510940	-1450.7407980	-1450.7377795
DiNp2_1_51	0	-1451.2089581	-1450.6518510	-1450.7407750	-1450.7377565
DiNp2_1_7	0	-1451.2096523	-1450.6521980	-1450.7406570	-1450.7376385
DiNp2_1_31	0	-1451.2090751	-1450.6518070	-1450.7403600	-1450.7373415
DiNp2_1_54	0	-1451.2078431	-1450.6505680	-1450.7399050	-1450.7368865
DiNp2_1_37	0	-1451.2093136	-1450.6517760	-1450.7398800	-1450.7368615
DiNp2_1_45	0	-1451.2070152	-1450.6495630	-1450.7379660	-1450.7349475
5cc					
DiNp2_2_12	0	-1451.2127233	-1450.6558480	-1450.7478700	-1450.7448515
DiNp2_2_35	0	-1451.2125198	-1450.6556780	-1450.7476670	-1450.7446485
DiNp2_2_5	0	-1451.2135156	-1450.6566120	-1450.7470790	-1450.7440605
DiNp2_2_28	0	-1451.2126220	-1450.6556740	-1450.7466970	-1450.7436785
DiNp2_2_41	0	-1451.2125077	-1450.6558570	-1450.7465610	-1450.7435425
DiNp2_2_26	0	-1451.2128297	-1450.6556140	-1450.7458850	-1450.7428665
DiNp2_2_29	0	-1451.2128299	-1450.6556170	-1450.7458780	-1450.7428595
DiNp2_2_9	0	-1451.2131546	-1450.6563250	-1450.7457960	-1450.7427775
DiNp2_2_23	0	-1451.2132502	-1450.6563880	-1450.7457770	-1450.7427585
DiNp2_2_3	0	-1451.2125138	-1450.6554280	-1450.7457490	-1450.7427305
DiNp2_2_25	0	-1451.2118345	-1450.6550840	-1450.7456650	-1450.7426465
DiNp2_2_27	0	-1451.2118350	-1450.6550840	-1450.7456110	-1450.7425925
DiNp2_2_16	0	-1451.2122596	-1450.6553130	-1450.7453390	-1450.7423205

DiNp2_2_7	0	-1451.2114047	-1450.6545450	-1450.7451880	-1450.7421695
DiNp2_2_6	0	-1451.2131391	-1450.6559660	-1450.7450910	-1450.7420725
DiNp2_2_8	0	-1451.2123657	-1450.6553700	-1450.7450550	-1450.7420365
DiNp2_2_33	0	-1451.2115820	-1450.6544660	-1450.7449930	-1450.7419745
DiNp2_2_20	0	-1451.2116623	-1450.6549630	-1450.7448910	-1450.7418725
DiNp2_2_11	0	-1451.2122458	-1450.6554320	-1450.7447260	-1450.7417075
DiNp2_2_14	0	-1451.2116770	-1450.6548400	-1450.7446540	-1450.7416355
DiNp2_2_22	0	-1451.2120573	-1450.6550710	-1450.7444610	-1450.7414425
DiNp2_2_37	0	-1451.2110781	-1450.6538220	-1450.7443130	-1450.7412945
DiNp2_2_4	0	-1451.2122098	-1450.6550440	-1450.7442700	-1450.7412515
DiNp2_2_30	0	-1451.2126549	-1450.6555250	-1450.7440790	-1450.7410605
DiNp2_2_19	0	-1451.2111699	-1450.6541030	-1450.7440770	-1450.7410585
DiNp2_2_18	0	-1451.2115808	-1450.6545750	-1450.7438050	-1450.7407865
DiNp2_2_39	0	-1451.2115862	-1450.6541100	-1450.7437610	-1450.7407425
DiNp2_2_13	0	-1451.2128182	-1450.6554390	-1450.7437140	-1450.7406955
DiNp2_2_15	0	-1451.2115453	-1450.6543500	-1450.7435500	-1450.7405315
DiNp2_2_31	0	-1451.2112765	-1450.6541120	-1450.7435260	-1450.7405075
DiNp2_2_17	0	-1451.2105288	-1450.6533600	-1450.7432330	-1450.7402145
5dc					
DiNp3_9_26	0	-1604.8558713	-1604.2495930	-1604.3460630	-1604.3430445
DiNp3_9_8	0	-1604.8550457	-1604.2485490	-1604.3445750	-1604.3415565
DiNp3_9_29	0	-1604.8550152	-1604.2480580	-1604.3440200	-1604.3410015
DiNp3_9_1	0	-1604.8572680	-1604.2502470	-1604.3439060	-1604.3408875
DiNp3_9_12	0	-1604.8561266	-1604.2492410	-1604.3438430	-1604.3408245
DiNp3_9_24	0	-1604.8543877	-1604.2476210	-1604.3430760	-1604.3400575
DiNp3_9_37	0	-1604.8535295	-1604.2468750	-1604.3429580	-1604.3399395
DiNp3_9_36	0	-1604.8532582	-1604.2465830	-1604.3428500	-1604.3398315
DiNp3_9_3	0	-1604.8550586	-1604.2480760	-1604.3428370	-1604.3398185
DiNp3_9_19	0	-1604.8551787	-1604.2481680	-1604.3423890	-1604.3393705
DiNp3_9_34	0	-1604.8531708	-1604.2464680	-1604.3421780	-1604.3391595
DiNp3_9_11	0	-1604.8555359	-1604.2483110	-1604.3421040	-1604.3390855

DiNp3_9_5	0	-1604.8568969	-1604.2498140	-1604.3419980	-1604.3389795
DiNp3_9_16	0	-1604.8532419	-1604.2462970	-1604.3419710	-1604.3389525
DiNp3_9_14	0	-1604.8532419	-1604.2462970	-1604.3419690	-1604.3389505
DiNp3_9_32	0	-1604.8548273	-1604.2477900	-1604.3418640	-1604.3388455
DiNp3_9_20	0	-1604.8551160	-1604.2479030	-1604.3418610	-1604.3388425
DiNp3_9_21	0	-1604.8533938	-1604.2463920	-1604.3405450	-1604.3375265
DiNp3_9_25	0	-1604.8540476	-1604.2466070	-1604.3400240	-1604.3370055
DiNp3_9_30	0	-1604.8530379	-1604.2456420	-1604.3398130	-1604.3367945
DiNp3_9_38	0	-1604.8515036	-1604.2442620	-1604.3381690	-1604.3351505
5ec					
DiNp3_2_1	0	-1604.8658113	-1604.2594240	-1604.3545340	-1604.3515155
DiNp3_2_18	0	-1604.8645738	-1604.2583900	-1604.3543150	-1604.3512965
DiNp3_2_16	0	-1604.8641536	-1604.2580250	-1604.3541650	-1604.3511465
DiNp3_2_5	0	-1604.8643634	-1604.2580710	-1604.3531600	-1604.3501415
DiNp3_2_27	0	-1604.8636616	-1604.2571160	-1604.3528180	-1604.3497995
DiNp3_2_3	0	-1604.8633414	-1604.2567590	-1604.3528030	-1604.3497845
DiNp3_2_13	0	-1604.8627064	-1604.2566520	-1604.3525030	-1604.3494845
DiNp3_2_21	0	-1604.8638955	-1604.2572290	-1604.3521960	-1604.3491775
DiNp3_2_29	0	-1604.8619334	-1604.2558540	-1604.3521020	-1604.3490835
DiNp3_2_12	0	-1604.8627134	-1604.2562990	-1604.3520400	-1604.3490215
DiNp3_2_8	0	-1604.8632926	-1604.2567890	-1604.3519380	-1604.3489195
DiNp3_2_4	0	-1604.8642858	-1604.2574980	-1604.3517430	-1604.3487245
DiNp3_2_20	0	-1604.8621706	-1604.2563930	-1604.3517030	-1604.3486845
DiNp3_2_11	0	-1604.8639647	-1604.2572530	-1604.3516590	-1604.3486405
DiNp3_2_6	0	-1604.8623726	-1604.2559460	-1604.3511330	-1604.3481145
DiNp3_2_23	0	-1604.8614169	-1604.2550110	-1604.3506990	-1604.3476805
DiNp3_2_26	0	-1604.8620329	-1604.2553650	-1604.3497500	-1604.3467315
DiNp3_2_14	0	-1604.8621428	-1604.2554120	-1604.3495770	-1604.3465585
DiNp3_2_17	0	-1604.8606492	-1604.2540510	-1604.3492070	-1604.3461885
5fc					

DiNp4_1_2	0	-1681.1109569	-1680.4904510	-1680.5862030	-1680.5831845
DiNp4_1_27	0	-1681.1066231	-1680.4863830	-1680.5859260	-1680.5829075
DiNp4_1_1	0	-1681.1087783	-1680.4885130	-1680.5854690	-1680.5824505
DiNp4_1_xRay	0	-1681.1061555	-1680.4861870	-1680.5854390	-1680.5824205
DiNp4_1_29	0	-1681.1094952	-1680.4893260	-1680.5849510	-1680.5819325
DiNp4_1_38	0	-1681.1063241	-1680.4860420	-1680.5840880	-1680.5810695
DiNp4_1_25	0	-1681.1095649	-1680.4891540	-1680.5839180	-1680.5808995
DiNp4_1_14	0	-1681.1094069	-1680.4886620	-1680.5839010	-1680.5808825
DiNp4_1_23	0	-1681.1067641	-1680.4864950	-1680.5837550	-1680.5807365
DiNp4_1_6	0	-1681.1082956	-1680.4878670	-1680.5837000	-1680.5806815
DiNp4_1_19	0	-1681.1083824	-1680.4879110	-1680.5835770	-1680.5805585
DiNp4_1_10	0	-1681.1088647	-1680.4884500	-1680.5835690	-1680.5805505
DiNp4_1_36	0	-1681.1073037	-1680.4868080	-1680.5835530	-1680.5805345
DiNp4_1_46	0	-1681.1083561	-1680.4877610	-1680.5833930	-1680.5803745
DiNp4_1_42	0	-1681.1083567	-1680.4877600	-1680.5833910	-1680.5803725
DiNp4_1_18	0	-1681.1090297	-1680.4886540	-1680.5833760	-1680.5803575
DiNp4_1_12	0	-1681.1077503	-1680.4872770	-1680.5833430	-1680.5803245
DiNp4_1_5	0	-1681.1087121	-1680.4879620	-1680.5833370	-1680.5803185
DiNp4_1_32	0	-1681.1064412	-1680.4861240	-1680.5826660	-1680.5796475
DiNp4_1_22	0	-1681.1067671	-1680.4859930	-1680.5823740	-1680.5793555
DiNp4_1_28	0	-1681.1070139	-1680.4865520	-1680.5822110	-1680.5791925
DiNp4_1_51	0	-1681.1068489	-1680.4860440	-1680.5816490	-1680.5786305
DiNp4_1_34	0	-1681.1050185	-1680.4844210	-1680.5798210	-1680.5768025
5ad					
Ph1_3	0	-1370.1406613	-1369.6886840	-1369.7744740	-1369.7714555
Ph1_6	0	-1370.1408891	-1369.6886750	-1369.7725700	-1369.7695515
Ph1_2	0	-1370.1404452	-1369.6881550	-1369.7720070	-1369.7689885
Ph1_4	0	-1370.1407795	-1369.6884460	-1369.7718710	-1369.7688525
5bd					
Ph2_1_1	0	-1523.7955173	-1523.2934930	-1523.3831940	-1523.3801755
Ph2_1_7	0	-1523.7949677	-1523.2929140	-1523.3829380	-1523.3799195

Ph2_1_8	0	-1523.7951292	-1523.2932920	-1523.3827040	-1523.3796855
Ph2_1_5	0	-1523.7951986	-1523.2933040	-1523.3823360	-1523.3793175
Ph2_1_11	0	-1523.7948959	-1523.2927690	-1523.3823190	-1523.3793005
Ph2_1_10	0	-1523.7948959	-1523.2927690	-1523.3823130	-1523.3792945
Ph2_1_2	0	-1523.7949011	-1523.2927660	-1523.3820990	-1523.3790805
Ph2_1_9	0	-1523.7951813	-1523.2931780	-1523.3813860	-1523.3783675
Ph2_1_4	0	-1523.7952022	-1523.2929900	-1523.3812590	-1523.3782405
Ph2_1_3	1	-1523.7944697	-1523.2935380	-1523.3810240	-1523.3780055
5cd					
Ph2_2_10	0	-1523.7980693	-1523.2964220	-1523.3864340	-1523.3834155
Ph2_2_7	0	-1523.7981644	-1523.2965980	-1523.3862770	-1523.3832585
Ph2_2_4	0	-1523.7974971	-1523.2959190	-1523.3862230	-1523.3832045
Ph2_2_1	0	-1523.7975044	-1523.2958030	-1523.3861170	-1523.3830985
Ph2_2_6	0	-1523.7980627	-1523.2963690	-1523.3860140	-1523.3829955
Ph2_2_12	0	-1523.7977815	-1523.2959320	-1523.3857620	-1523.3827435
Ph2_2_13	0	-1523.7983057	-1523.2965320	-1523.3856840	-1523.3826655
Ph2_2_9	0	-1523.7966758	-1523.2949520	-1523.3853060	-1523.3822875
Ph2_2_5	0	-1523.7978450	-1523.2957380	-1523.3842760	-1523.3812575
Ph2_2_2	0	-1523.7969790	-1523.2949090	-1523.3831750	-1523.3801565
5dd					
Ph3_9_5	0	-1677.4402401	-1676.8887870	-1676.9839090	-1676.9808905
Ph3_9_1	0	-1677.4414202	-1676.8897000	-1676.9834300	-1676.9804115
Ph3_9_4	0	-1677.4414199	-1676.8896970	-1676.9834170	-1676.9803985
Ph3_9_2	0	-1677.4414204	-1676.8896970	-1676.9833920	-1676.9803735
Ph3_9_8	0	-1677.4388326	-1676.8869520	-1676.9830260	-1676.9800075
Ph3_9_6	0	-1677.4402833	-1676.8884100	-1676.9819640	-1676.9789455
5ed					
Ph3_2_3	0	-1677.4483943	-1676.8975160	-1676.9935910	-1676.9905725
Ph3_2_4	0	-1677.4481659	-1676.8970490	-1676.9931900	-1676.9901715
Ph3_2_16	0	-1677.4486088	-1676.8973900	-1676.9925630	-1676.9895445
Ph3_2_14	0	-1677.4486087	-1676.8973910	-1676.9925570	-1676.9895385

Ph3_2_13	0	-1677.4477466	-1676.8964860	-1676.9923660	-1676.9893475
Ph3_2_5	0	-1677.4482663	-1676.8971740	-1676.9922340	-1676.9892155
Ph3_2_12	0	-1677.4465475	-1676.8951670	-1676.9918590	-1676.9888405
Ph3_2_1	0	-1677.4479065	-1676.8966310	-1676.9918170	-1676.9887985
Ph3_2_17	0	-1677.4458253	-1676.8944060	-1676.9892310	-1676.9862125
Ph3_2_2	0	-1677.4469039	-1676.8953880	-1676.9891540	-1676.9861355
5fd					
Ph4_1_3	0	-1753.6924697	-1753.1274910	-1753.2243870	-1753.2213685
Ph4_1_9	0	-1753.6912181	-1753.1262870	-1753.2243200	-1753.2213015
Ph4_1_7	0	-1753.6923305	-1753.1270520	-1753.2232340	-1753.2202155
Ph4_1_13	0	-1753.6919099	-1753.1264270	-1753.2229300	-1753.2199115
Ph4_1_8	0	-1753.6921976	-1753.1267600	-1753.2225020	-1753.2194835
Ph4_1_11	0	-1753.6916189	-1753.1262590	-1753.2221750	-1753.2191565
5ae					
Np1_9	0	-1831.1102695	-1830.5095020	-1830.6133450	-1830.6103265
Np1_4	0	-1831.1106765	-1830.5099240	-1830.6133200	-1830.6103015
Np1_18	0	-1831.1107291	-1830.5101030	-1830.6133050	-1830.6102865
Np1_42	0	-1831.1108891	-1830.5103920	-1830.6122380	-1830.6092195
Np1_10	0	-1831.1108216	-1830.5100360	-1830.6120620	-1830.6090435
Np1_14	0	-1831.1108217	-1830.5100360	-1830.6120500	-1830.6090315
Np1_3	0	-1831.1105344	-1830.5099300	-1830.6119970	-1830.6089785
Np1_21	0	-1831.1112534	-1830.5104710	-1830.6119470	-1830.6089285
Np1_29	0	-1831.1112538	-1830.5104740	-1830.6119380	-1830.6089195
Np1_22	0	-1831.1107486	-1830.5102780	-1830.6119120	-1830.6088935
Np1_32	0	-1831.1099445	-1830.5090930	-1830.6117470	-1830.6087285
Np1_40	0	-1831.1099312	-1830.5089510	-1830.6117030	-1830.6086845
Np1_44	0	-1831.1104522	-1830.5098430	-1830.6116940	-1830.6086755
Np1_43	0	-1831.1108510	-1830.5102290	-1830.6116860	-1830.6086675
Np1_6	0	-1831.1102340	-1830.5095170	-1830.6116250	-1830.6086065
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Np3_2_29	0	-2138.4186472	-2137.7184470	-2137.8289950	-2137.8259765
5fe					
Np4_1_17	0	-2214.6653811	-2213.9518940	-2214.0659260	-2214.0629075
Np4_1_9	0	-2214.6652315	-2213.9517920	-2214.0654020	-2214.0623835
Np4_1_14	0	-2214.6653606	-2213.9519970	-2214.0652910	-2214.0622725
Np4_1_19	0	-2214.6649946	-2213.9514380	-2214.0650840	-2214.0620655
Np4_1_35	0	-2214.6645703	-2213.9511550	-2214.0649080	-2214.0618895
Np4_1_13	0	-2214.6666342	-2213.9531570	-2214.0647540	-2214.0617355
Np4_1_41	0	-2214.6652653	-2213.9518430	-2214.0647200	-2214.0617015
Np4_1_38	0	-2214.6657015	-2213.9523340	-2214.0644930	-2214.0614745
Np4_1_34	0	-2214.6653769	-2213.9518210	-2214.0644170	-2214.0613985
Np4_1_39	0	-2214.6657205	-2213.9523790	-2214.0640300	-2214.0610115
Np4_1_15	0	-2214.6651241	-2213.9517220	-2214.0640090	-2214.0609905
Np4_1_37	0	-2214.6654388	-2213.9517470	-2214.0639270	-2214.0609085
Np4_1_1	0	-2214.6637809	-2213.9498460	-2214.0633870	-2214.0603685
Np4_1_32	0	-2214.6641672	-2213.9505370	-2214.0633350	-2214.0603165
Np4_1_2	0	-2214.6641030	-2213.9500760	-2214.0633000	-2214.0602815
Np4_1_51	0	-2214.6653493	-2213.9515850	-2214.0632150	-2214.0601965
Np4_1_25	0	-2214.6642940	-2213.9504060	-2214.0629330	-2214.0599145

Np4_1_20	0	-2214.6639250	-2213.9498980	-2214.0629150	-2214.0598965
Np4_1_28	0	-2214.6660441	-2213.9521990	-2214.0628980	-2214.0598795
Np4_1_8	0	-2214.6655256	-2213.9516620	-2214.0628510	-2214.0598325
Np4_1_22	0	-2214.6639033	-2213.9502880	-2214.0627250	-2214.0597065
Np4_1_26	0	-2214.6643465	-2213.9504920	-2214.0626090	-2214.0595905
Np4_1_43	0	-2214.6648038	-2213.9510390	-2214.0625370	-2214.0595185
Np4_1_4	0	-2214.6657118	-2213.9514460	-2214.0622930	-2214.0592745
Np4_1_48	0	-2214.6638195	-2213.9499120	-2214.0622650	-2214.0592465
Np4_1_33	0	-2214.6657889	-2213.9518180	-2214.0620880	-2214.0590695
Np4_1_21	0	-2214.6640268	-2213.9499550	-2214.0619940	-2214.0589755
Np4_1_23	0	-2214.6642835	-2213.9502090	-2214.0618230	-2214.0588045
Np4_1_45	0	-2214.6636535	-2213.9497770	-2214.0617670	-2214.0587485
Np4_1_29	0	-2214.6640695	-2213.9497760	-2214.0615780	-2214.0585595
Np4_1_12	0	-2214.6654791	-2213.9512140	-2214.0615200	-2214.0585015
Np4_1_5	0	-2214.6636149	-2213.9494560	-2214.0609720	-2214.0579535
Np4_1_36	0	-2214.6621720	-2213.9483020	-2214.0607370	-2214.0577185
Np4_1_24	0	-2214.6643295	-2213.9499380	-2214.0605670	-2214.0575485
5af					
NpOMe1_42	0	-3553.5779082	-3552.8963550	-3553.0266220	-3553.0236035
NpOMe1_21	0	-3553.5781630	-3552.8964700	-3553.0261210	-3553.0231025
NpOMe1_10	0	-3553.5742062	-3552.8925700	-3553.0235050	-3553.0204865
5bf					
NpOMe2_1_17	0	-3707.2352467	-3706.5038690	-3706.6387610	-3706.6357425
NpOMe2_1_11	0	-3707.2302225	-3706.4991750	-3706.6358940	-3706.6328755
NpOMe2_1_31	0	-3707.2346116	-3706.5028950	-3706.6357420	-3706.6327235
NpOMe2_1_16	0	-3707.2305314	-3706.4994470	-3706.6347160	-3706.6316975
5cf					
NpOMe2_2_38	0	-3707.2374636	-3706.5064170	-3706.6432380	-3706.6402195
NpOMe2_2_18	0	-3707.2358350	-3706.5042970	-3706.6401030	-3706.6370845
NpOMe2_2_19	0	-3707.2331365	-3706.5018140	-3706.6369280	-3706.6339095
5df					

NpOMe3_9_9_freq	0	-3860.8783581	-3860.0972830	-3860.2376840	-3860.2346655
NpOMe3_9_17_freq	0	-3860.8807606	-3860.0996260	-3860.2392350	-3860.2362165
NpOMe3_9_12_freq	0	-3860.8780541	-3860.0972400	-3860.2381090	-3860.2350905
5ef					
NpOMe3_2_12	0	-3860.8916408	-3860.1111100	-3860.2508240	-3860.2478055
NpOMe3_2_23	0	-3860.8898330	-3860.1093510	-3860.2501200	-3860.2471015
NpOMe3_2_24	0	-3860.8900941	-3860.1095370	-3860.2487660	-3860.2457475
5ff					
NpOMe4_1_13_freq	0	-3937.1365877	-3936.3420430	-3936.4817920	-3936.4787735
NpOMe4_1_38	0	-3937.1354906	-3936.3408770	-3936.4809400	-3936.4779215
NpOMe4_1_28_freq	0	-3937.1323323	-3936.3379460	-3936.4777030	-3936.4746845

^a C, H, O : 6-31+G(d) Si, Cl : 6-311+G(d)

6.3. Geometrical analysis of conformers found for silyl ether **5fe**

In order to distinguish π - π stacking and σ - π interactions in the system a geometrical analysis of the conformers for the example of silyl ether **5fe** was performed. One investigated parameter was the distance d between the two aromatic surfaces, measured at the C-atom connected to the bridge. To display the angle α between the aromatic surfaces, the cutting angle of the two planes spanned by three points of each aromatic system was calculated. (see Figure S144).

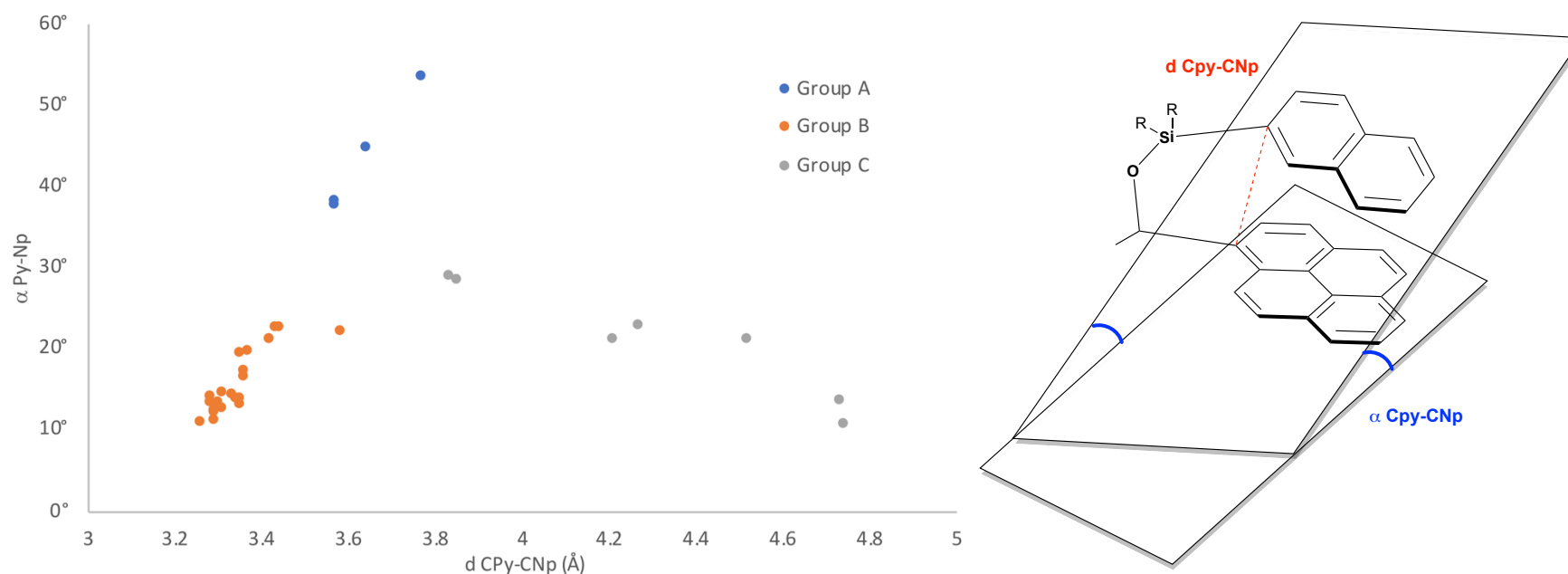
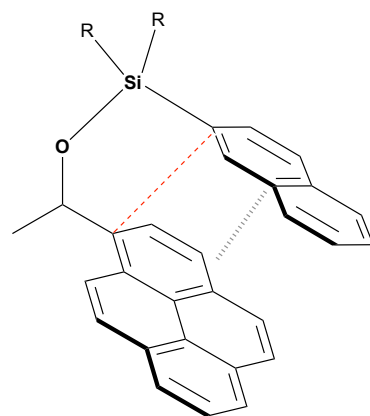


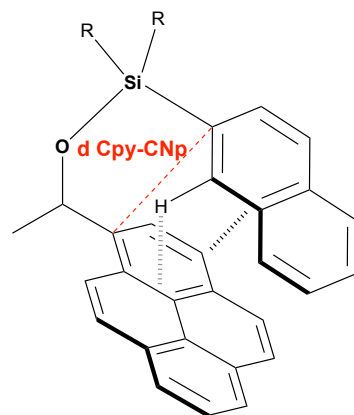
Figure S144: left side: Scatter of the found conformers for silyl ether **5fe** depending on the minimal distance between the two aromatic surfaces and the associated angle between the spanned plates. Groups are defined in Figure S145. Right side: Illustration of the used parameters d and α .

The analysis shows that the interacting aromatic surfaces in all conformers are twisted towards each other for at least 10°. Taking the differential angles and distances into account three groups of conformers can be formed (Figure S145):

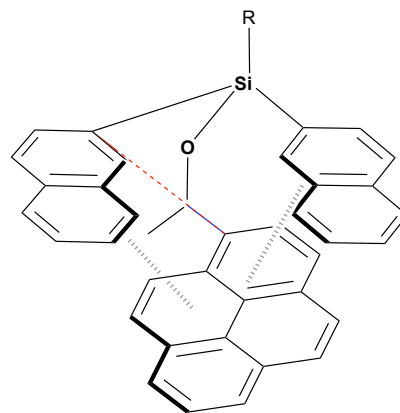
- 1) Group A (orange in Figure S144): The two interacting surfaces are twisted 10° - 25° towards each other and the distance of bridge heads is less than $3.6 \text{ \AA}$. One aromatic group is slightly parallel displaced with respect to the other group. In those conformers mainly $\pi - \pi$ interactions occur. (Number of conformers in this group: 23, among them the 12 most stable conformers)
- 2) Group B (blue in Figure S144): The two big surfaces are twisted more than 35° against each other, the distance of the bridgeheads is in between $3.5 \text{ \AA}$ and $3.8 \text{ \AA}$. The surfaces interact through a combination of $\pi - \pi$ stacking and $\sigma - \pi$ interaction, the latter one occurs between an aromatic hydrogen of the naphthyl surface and the pyrenyl surface. (Number of conformers in this group: 4)
- 3) Group C (grey in Figure S144): The last group samples conformers in which the pyrenyl surface is located in between two different oriented naphthyl surfaces, minimum distance of bridgehead is $3.8 \text{ \AA}$. In this case, the two naphthyl surfaces interact with the pyrenyl surface through a combination of $\sigma - \pi$ interactions and $\pi - \pi$ stacking. (Number of conformers in this group: 7)



Group A



Group B



Group C

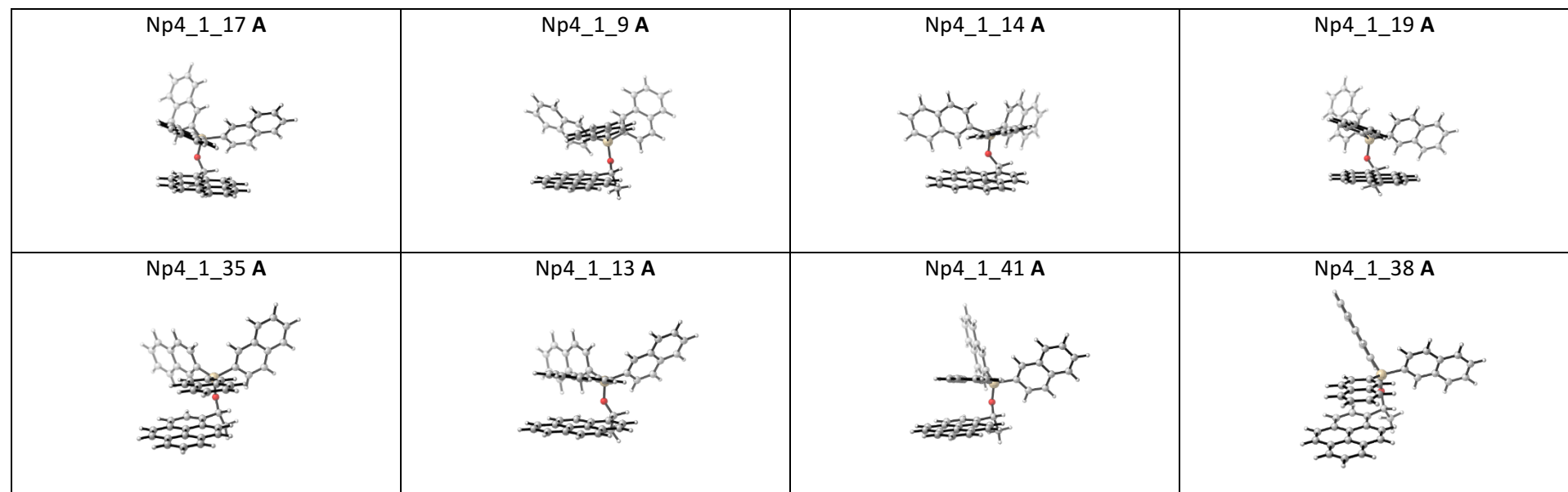
Figure S145: Groups of different interacting conformers of silyl ether **5fe**.

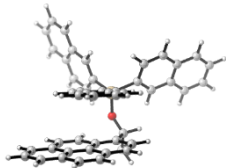
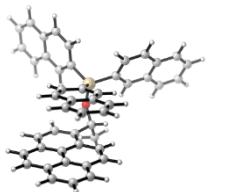
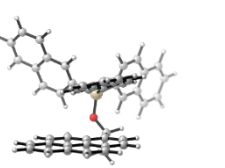
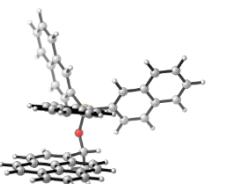
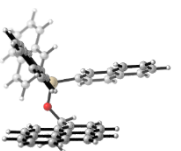
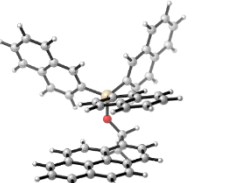
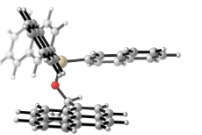
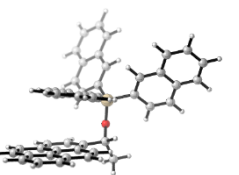
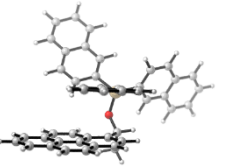
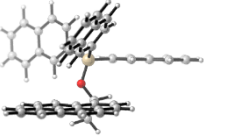
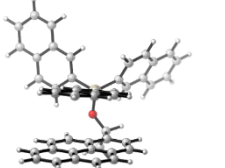
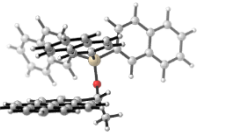
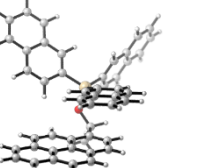
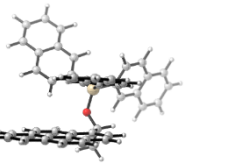
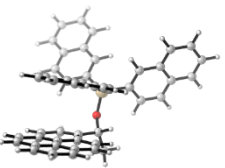
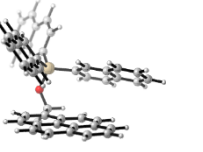
Table S18: Geometrical parameters for conformers of silyl ether **5fe** in order of decreasing $G_{298, \text{sol}}$. A, B and C monitors the group the conformer was put in as described above.

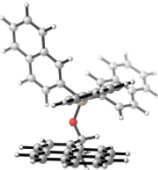
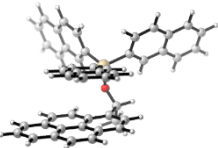
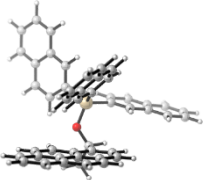
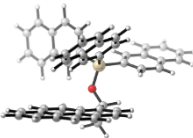
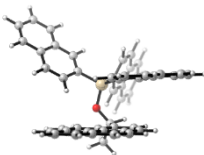
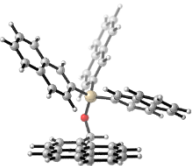
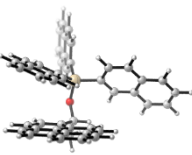
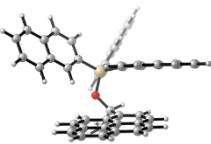
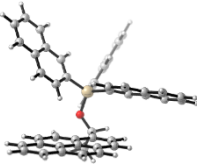
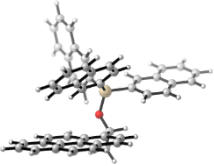
Name of conformer	$G_{298, \text{sol}}$ SMD/B3LYP-D3/ 6-311+G(2d)/6-31+G(d)	Group	ΔG	d CPy-CNp	α CPy-CNp
Np4_1_17	-2214.0629075	A	0.0	3.43	22.6
Np4_1_9	-2214.0623835	A	1.4	3.43	23.8
Np4_1_14	-2214.0622725	A	1.7	3.35	19.4
Np4_1_19	-2214.0620655	A	2.2	3.44	22.6
Np4_1_35	-2214.0618895	A	2.7	3.26	10.9
Np4_1_13	-2214.0617355	A	3.1	3.35	13.8
Np4_1_41	-2214.0617015	A	3.2	3.31	12.5
Np4_1_38	-2214.0614745	A	3.8	3.3	13.4
Np4_1_34	-2214.0613985	A	4.0	3.35	13.1
Np4_1_39	-2214.0610115	A	5.0	3.28	13.4
Np4_1_15	-2214.0609905	A	5.0	3.37	19.6
Np4_1_37	-2214.0609085	A	5.2	3.29	11.1
Np4_1_1	-2214.0603685	C	6.7	4.21	21.0
Np4_1_32	-2214.0603165	A	6.8	3.36	17.2
Np4_1_2	-2214.0602815	C	6.9	4.27	22.7
Np4_1_51	-2214.0601965	A	7.1	3.28	14.0
Np4_1_25	-2214.0599145	A	7.9	3.29	12.1
Np4_1_20	-2214.0598965	B	7.9	3.77	53.5
Np4_1_28	-2214.0598795	A	8.0	3.33	14.3
Np4_1_8	-2214.0598325	A	8.1	3.42	21.1
Np4_1_22	-2214.0597065	A	8.4	3.29	12.2
Np4_1_26	-2214.0595905	A	8.7	3.31	14.4
Np4_1_43	-2214.0595185	A	8.9	3.36	16.4
Np4_1_4	-2214.0592745	C	9.5	3.85	28.4
Np4_1_48	-2214.0592465	A	9.6	3.58	22.0

Np4_1_33	-2214.0590695	A	10.1	3.34	13.7
Np4_1_21	-2214.0589755	B	10.3	3.64	44.8
Np4_1_23	-2214.0588045	B	10.8	3.57	38.2
Np4_1_45	-2214.0587485	C	10.9	4.74	10.5
Np4_1_29	-2214.0585595	C	11.4	3.83	28.9
Np4_1_12	-2214.0585015	A	11.6	3.42	21.0
Np4_1_5	-2214.0579535	C	13.0	4.73	13.5
Np4_1_36	-2214.0577185	C	13.6	4.52	21.0
Np4_1_24	-2214.0575485	B	14.1	3.57	37.6

Table S19: Visualisation of conformers for silyl ether **5fe** in order of decreasing $G_{298, \text{sol}}$. A, B and C monitors the group the conformer was put in as described above.



Np4_1_34 A 	Np4_1_39 A 	Np4_1_15 A 	Np4_1_37 A 
Np4_1_1 C 	Np4_1_32 A 	Np4_1_2 C 	Np4_1_51 A 
Np4_1_25 A 	Np4_1_20 B 	Np4_1_28 A 	Np4_1_8 A 
Np4_1_22 A 	Np4_1_26 A 	Np4_1_43 A 	Np4_1_4 C 

Np4_1_48 A 	Np4_1_33 A 	Np4_1_21 B 	Np4_1_23 B 
Np4_1_45 C 	Np4_1_29 C 	Np4_1_12 A 	Np4_1_5 C 
Np4_1_36 C 	Np4_1_24 B 		

6.4. Calculation of reaction free energies and dispersion contribution of the best conformers

Table S20: Total energies and free energies for best conformer of alcohols **1**, silyl reagents **2** and products **5** (in Hartree). Molar free energies in solution at 298.15 K ($G_{298,sol}$) have been calculated at the SMD(CHCl₃)/DLPNO-CCSD(T)/def2-TZVPP//SMD(CHCl₃)/B3LYP-D3/6-311+G(2d)/6-31+G(d) level and corrected for a solution standard state of 1 M through addition of +7.925 kJ/mol (0.00301848 Hartree). The SMD(CHCl₃)/B3LYP-D3/6-311+G(2d)/6-31+G(d) level of theory has been used to optimize the geometries and calculate solute thermal corrections and solvation factor. Note that the filenames are used in our calculations and do not follow any guide.

Filename	E_{tot} SMD/B3LYP-D3/6-311+G(2d)/6-31+G(d) ^[a]	E_{tot} SMD/B3LYP/6-311+G(2d)/6-31+G(d) ^[a]	G_{298} SMD/B3LYP-D3/6-311+G(2d)/6-31+G(d)	$G_{298,sol}$ SMD/B3LYP-D3/6-311+G(2d)/6-31+G(d)	E_{tot} SMD/DLPNO-CCSD(T)/def2-TZVPP ^[b]	$G_{298,sol}$ SMD/DLPNO-CCSD(T)/def2-TZVPP	Solvation Factor
HCl							
hcl_1	-460.8341522	-460.8341495	-460.8455730	-460.8425545	-460.3307889	-460.3443202	-0.0051289
1a							
roh1_1	-386.1285457	-386.1149812	-386.0006440	-385.9976255	-385.4196861	-385.3024998	-0.0137339
1b							
roh2_1_1	-539.7816611	-539.7604473	-539.6090270	-539.6060085	-538.7709992	-538.6133748	-0.0180281
1c							
roh2_2_2	-539.7847329	-539.7649283	-539.6132800	-539.6102615	-538.7728081	-538.6164995	-0.0181628
1d							
roh3_9_1	-693.4236962	-693.3948650	-693.2078480	-693.2048295	-692.1109742	-691.9136651	-0.0215576
1e							
roh3_2_2	-693.4345314	-693.4083506	-693.2193170	-693.2162985	-692.1192876	-691.9236697	-0.0226150
1f							
roh4_1_1	-769.6780488	-769.6469639	-769.4497090	-769.4466905	-768.2160648	-768.0085874	-0.0238808
2a							
TMSCl	-869.6013765	-869.5929900	-869.5210940	-869.5180755	-868.3934327	-868.3171674	-0.0070358
2b							
TBSCl_1	-987.5495242	-987.5273332	-987.3893590	-987.3863405	-986.1114994	-985.9572336	-0.0089180
2c							

DPNpSiCl_1	-1372.2683456	-1372.2264517	-1371.9882150	-1371.9851965	-1370.0723368	-1369.8088113	-0.0196236
2d							
ph3sicl_04	-1444.8488463	-1444.8136734	-1444.6243200	-1444.6213015	-1442.5112315	-1442.3075940	-0.0239073
2e							
NpSiCl_6	-1905.8181159	-1905.7630765	-1905.4602600	-1905.4572415	-1902.5720454	-1902.2482170	-0.0370460
2f							
NpOMeSiCl_8	-3628.2847123	-3628.2084773	-3627.8742980	-3627.8712795	-3623.0124930	-3622.6432020	-0.0441417
5aa							
TMS1__1	-794.8873872	-794.8610407	-794.6673630	-794.6643445	-793.4808859	-793.2705780	-0.0127348
5ba							
TMS2_1_1	-948.5409852	-948.5066496	-948.2770250	-948.2740065	-946.8326363	-946.5825621	-0.0169045
5ca							
TMS2_2_2	-948.5442240	-948.5104011	-948.2805140	-948.2774955	-946.8348894	-946.5851686	-0.0170077
5da							
TMS3_9_3	-1102.1852162	-1102.1400278	-1101.8771510	-1101.8741325	-1100.1754559	-1099.8843276	-0.0199553
5ea							
TMS_3_2_1	-1102.1932852	-1102.1539443	-1101.8861200	-1101.8831015	-1100.1800958	-1099.8917170	-0.0218050
5fa							
TMS4_1_2	-1178.4377323	-1178.3931826	-1178.1181640	-1178.1151455	-1176.2779169	-1175.9781423	-0.0228122
5ab							
TBS1_3	-912.8352609	-912.7933123	-912.5335650	-912.5305465	-911.1982956	-910.9077925	-0.0142112
5bb							
TBS2_1_8	-1066.4893794	-1066.4403939	-1066.1443310	-1066.1413125	-1064.5503938	-1064.2210913	-0.0187644
5cb							
TBS2_2_4	-1066.4922930	-1066.4445469	-1066.1482600	-1066.1452415	-1064.5523618	-1064.2243232	-0.0190128
5db							
TBS3_9_2	-1220.1337755	-1220.0740150	-1219.7448550	-1219.7418365	-1217.8932528	-1217.5232200	-0.0219062
5eb							
TBS3_2_1	-1220.1416168	-1220.0873806	-1219.7543650	-1219.7513465	-1217.8981474	-1217.5313576	-0.0234805
5fb							

TBS4_1_2	-1296.3860085	-1296.3268300	-1295.9854580	-1295.9824395	-1293.9956373	-1293.6166883	-0.0246200
5ac							
DiNp1_1	-1297.5573313	-1297.4922339	-1297.1365120	-1297.1334935	-1295.1619109	-1294.7629810	-0.0249078
5bc							
DiNp2_1_2	-1451.2119687	-1451.1374544	-1450.7440810	-1450.7410625	-1448.5142636	-1448.0725265	-0.0291691
5cc							
DiNp2_2_12	-1451.2127233	-1451.1366788	-1450.7478700	-1450.7448515	-1448.5153255	-1448.0762163	-0.0287626
5dc							
DiNp3_9_26	-1604.8558713	-1604.7657737	-1604.3460630	-1604.3430445	-1601.8597281	-1601.3786060	-0.0317047
5ec							
DiNp3_2_1	-1604.8658113	-1604.7821484	-1604.3545340	-1604.3515155	-1601.8655763	-1601.3841183	-0.0328377
5fc							
DiNp4_1_2	-1681.1109569	-1681.0180149	-1680.5862030	-1680.5831845	-1677.9656278	-1677.4714091	-0.0335537
5ad							
Ph1_3	-1370.1406613	-1370.0826056	-1369.7744740	-1369.7714555	-1367.6029972	-1367.2638218	-0.0300304
5bd							
Ph2_1_1	-1523.7955173	-1523.7280915	-1523.3831940	-1523.3801755	-1520.9565647	-1520.5750005	-0.0337775
5cd							
Ph2_2_10	-1523.7980693	-1523.7316379	-1523.3864340	-1523.3834155	-1520.9579262	-1520.5775173	-0.0342447
5dd							
Ph3_9_5	-1677.4402401	-1677.3585337	-1676.9839090	-1676.9808905	-1674.3014524	-1673.8782597	-0.0361568
5ed							
Ph3_2_3	-1677.4483943	-1677.3755433	-1676.9935910	-1676.9905725	-1674.3048833	-1673.8856213	-0.0385597
5fd							
Ph4_1_3	-1753.6924697	-1753.6120968	-1753.2243870	-1753.2213685	-1750.4031535	-1749.9710061	-0.0389538
5ae							
Np1_9	-1831.1102695	-1831.0329051	-1830.6133450	-1830.6103265	-1827.6632706	-1827.2060497	-0.0427221
5be							
Np2_1_46	-1984.7659439	-1984.6773311	-1984.2241900	-1984.2211715	-1981.0187123	-1980.5205634	-0.0466235
5ce							

Np2_2_38	-1984.7691648	-1984.6784212	-1984.2274580	-1984.2244395	-1981.0228172	-1980.5240753	-0.0459834
5de							
Np3_9_3	-2138.4115823	-2138.3071103	-2137.8262520	-2137.8232335	-2134.3644870	-2133.8242424	-0.0481043
5ee							
Np3_2_1	-2138.4202918	-2138.3202677	-2137.8343340	-2137.8313155	-2134.3694687	-2133.8300313	-0.0495388
5fe							
Np4_1_17	-2214.6653811	-2214.5580860	-2214.0659260	-2214.0629075	-2210.4698483	-2209.9177402	-0.0503655
5af							
NpOMe1_42	-3553.5779082	-3553.4770053	-3553.0266220	-3553.0236035	-3548.1059294	-3547.6023931	-0.0507684
5bf							
NpOMe2_1_17	-3707.2352467	-3707.1149023	-3706.6387610	-3706.6357425	-3701.4663062	-3700.9184357	-0.0516337
5cf							
NpOMe2_2_38	-3707.2374636	-3707.1214818	-3706.6432380	-3706.6402195	-3701.4661763	-3700.9220732	-0.0531410
5df							
NpOMe3_9_9_f req	-3860.8783581	-3860.7465177	-3860.2376840	-3860.2346655	-3854.8094477	-3854.2204217	-0.0546666
5ef							
NpOMe3_2_12	-3860.8916408	-3860.7638606	-3860.2508240	-3860.2478055	-3854.8187247	-3854.2303504	-0.0554609
5ff							
NpOMe4_1_13_ freq	-3937.1365877	-3936.9966171	-3936.4817920	-3936.4787735	-3930.9206560	-3930.3181673	-0.0553255

^a C, H, O : 6-31+G(d) Si, Cl : 6-311+G(d) ^b Solv Factor added

Table S21: $\ln(k_{rel})$ and reaction free energies $\Delta G_{298, sol}$ of the formation of the products **5(a-f)(a-e)**, computed at different levels of theory (kJ/mol). Dispersion contribution ($\Delta D_{298, sol}$) calculated as the difference of the $\Delta G_{298, sol}$ computed at B3LYP-D3 and B3LYP level, respectively, is shown at the end of the table.

$ \begin{array}{c} \text{OH} \\ \\ \text{Ar} \end{array} + \text{R}^3\text{SiCl} \xrightarrow{\Delta G_{298, sol}} \begin{array}{c} \text{O-SiR}^3 \\ \\ \text{Ar} \end{array} + \text{HCl} $						
1a-f 2a-e 5(a-f)(a-e) 6						
$\ln(k_{rel})$						
	1a	1b	1c	1d	1e	1f
2a	0.000	-0.447	-0.024	-2.173	-0.031	-0.443
2b	0.000	-0.396	0.010	-2.973	0.010	-0.425
2c	0.000	-0.649	0.113	-2.501	0.149	-0.326
2d	0.000	-0.320	0.170	-1.419	0.216	-0.162
2e	0.000	-0.188	0.357	-1.383	0.465	0.182
2f	0.000	-0.002	0.469	-0.968	0.852	0.984
SMD(CHCl₃)/DLPNO-CCSD(T)/def2-TZVPP//SMD(CHCl₃)/B3LYP-D3/6-311+G(2d)/6-31+G(d)^{a,b}						
	1a	1b	1c	1d	1e	1f
2a	12.5	9.6	11.0	5.7	12.6	8.6
2b	20.0	13.6	13.4	8.8	13.7	12.6
2c	10.5	14.0	12.5	-1.2	10.6	4.4
2d	5.1	4.3	5.9	-3.5	3.5	2.2
2e	0.9	-0.4	-9.7	-17.5	-6.5	-13.8
2f	-2.7	-16.2	-17.6	-20.7	-20.5	-28.1
SMD(CHCl₃)/B3LYP-D3/6-311+G(2d)/6-31+G(d)^a						
	1a	1b	1c	1d	1e	1f
2a	23.1	19.8	21.8	16.3	22.9	18.6
2b	28.5	22.3	23.1	17.8	22.9	21.1
2c	17.8	19.9	21.1	11.6	19.5	16.1
2d	12.9	12.0	14.7	7.1	11.7	10.7
2e	5.2	9.9	1.3	-9.8	-0.9	-4.0

2f	7.2	-2.6	-3.2	-2.9	-7.3	-8.8
SMD(CHCl₃)/B3LYP/6-311+G(2d)/6-31+G(d)//SMD(CHCl₃)/B3LYP-D3/6-311+G(2d)/6-31+G(d)^a						
	1a	1b	1c	1d	1e	1f
2a	34.7	32.2	36.6	37.3	35.4	31.9
2b	44.8	36.9	38.2	40.7	38.3	36.6
2c	43.1	49.9	58.8	62.5	60.4	68.6
2d	37.4	41.0	44.8	53.5	41.9	47.7
2e	28.2	46.1	43.1	44.3	48.5	51.6
2f	36.4	57.5	49.1	67.4	59.3	76.9
DISPERSION CONTRIBUTION [$\Delta D_{298, \text{sol}} = \Delta G_{298, \text{sol}}(\text{B3LYP}) - \Delta G_{298, \text{sol}}(\text{B3LYP-D3})$]						
	1a	1b	1c	1d	1e	1f
2a	-11.5	-12.4	-14.8	-20.9	-12.5	-13.3
2b	-16.3	-14.7	-15.1	-22.9	-15.4	-15.5
2c	-25.3	-30.0	-37.7	-50.9	-40.9	-52.4
2d	-24.5	-29.0	-30.1	-46.5	-30.2	-37.1
2e	-23.0	-36.2	-41.8	-54.1	-49.4	-55.6
2f	-29.2	-60.1	-52.4	-70.3	-66.6	-85.7

^a C, H, O : 6-31+G(d) Si, Cl : 6-311+G(d) ^b Solv Factor at B3LYP-D3 added to the E(SCF) at DLPNO-CCSD(T)/def2-TZVPP

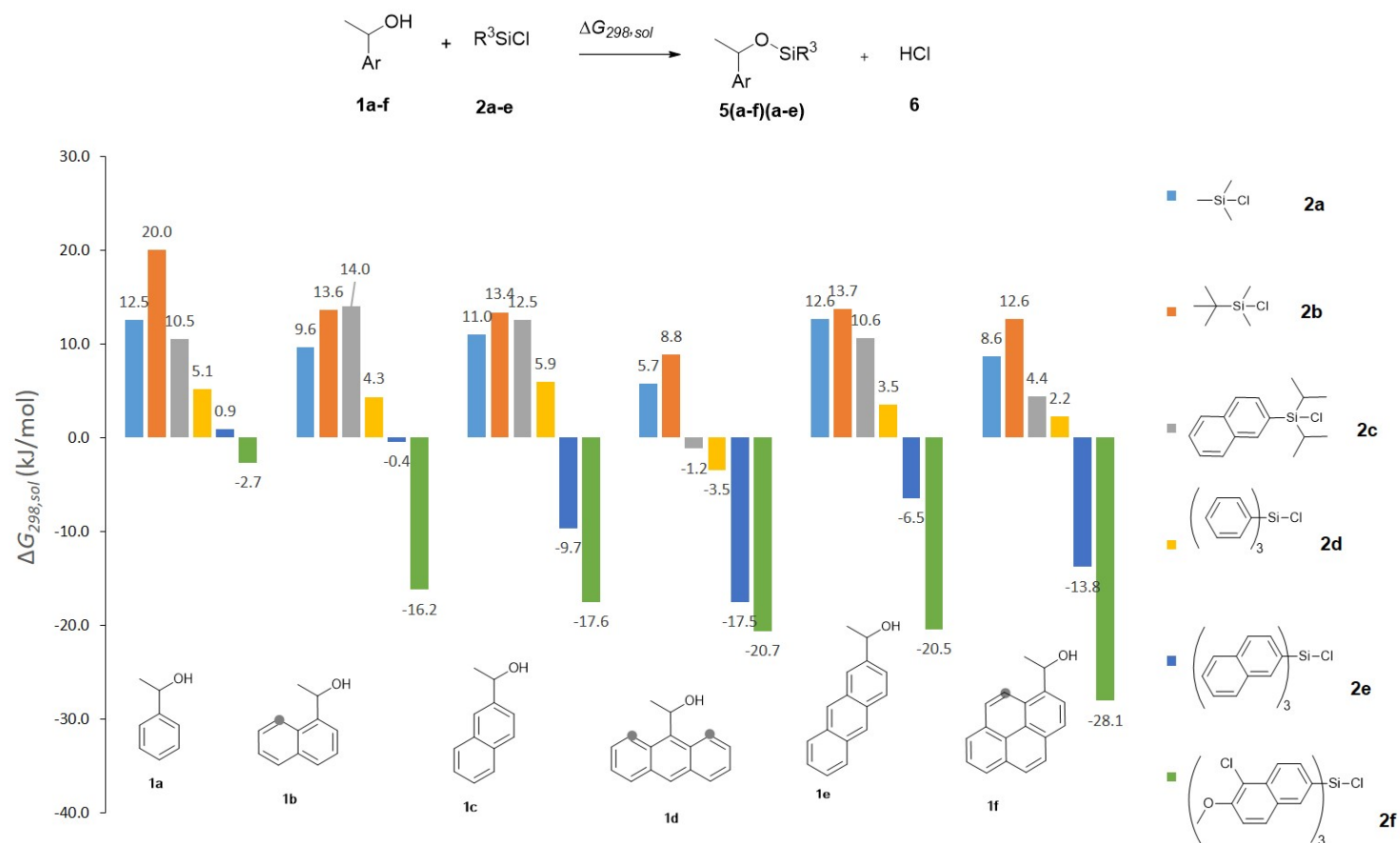


Figure S146: Reaction free energies, $\Delta G_{298,\text{sol}}$, computed at SMD(CHCl_3)/DLPNO-CCSD(T)/def2-TZVPP//SMD(CHCl_3)/B3LYP-D3/6-311+G(2d)/6-31+G(d) theoretical level.

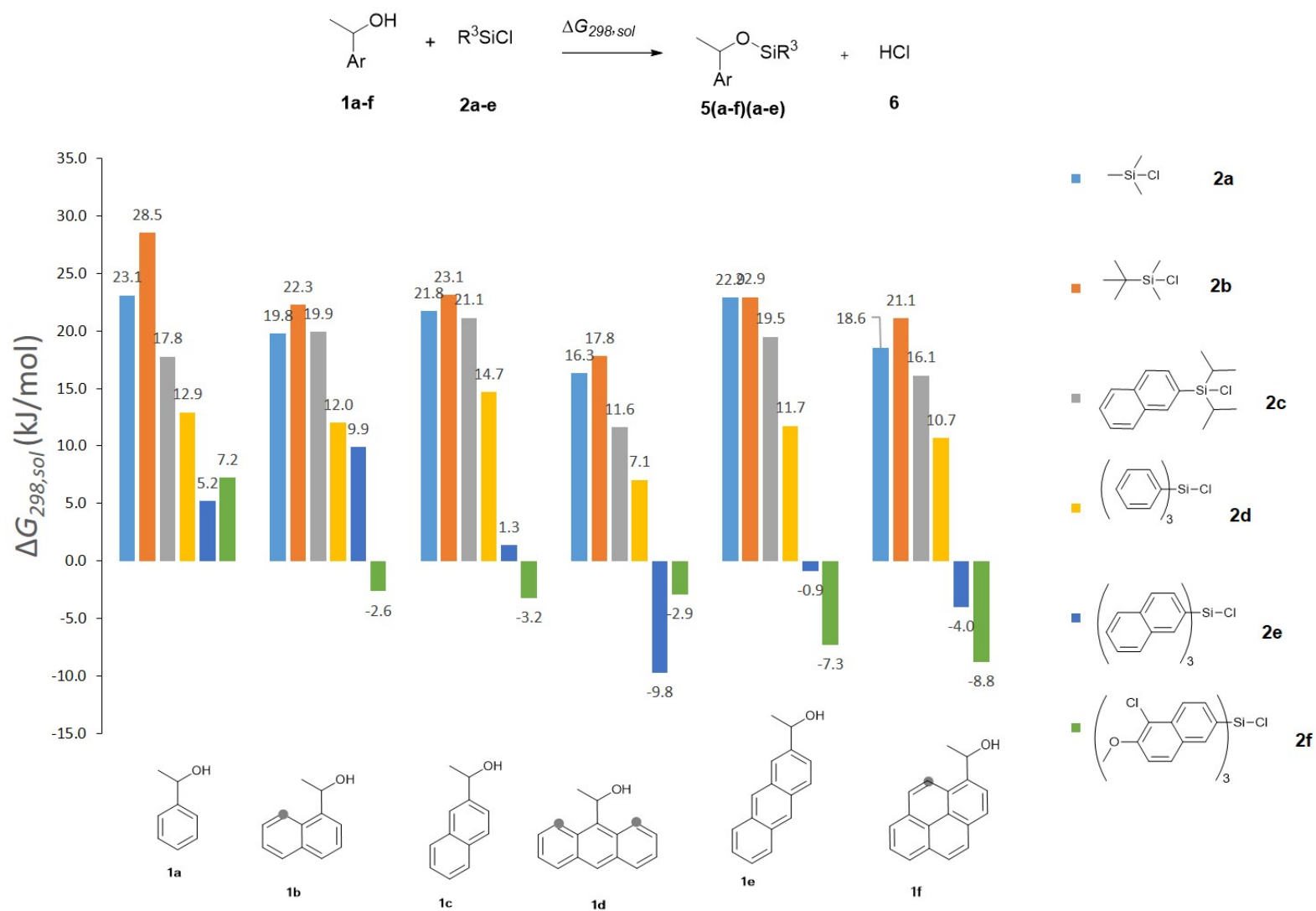


Figure S147: Reaction free energies, $\Delta G_{298, sol}$ computed at SMD(CHCl₃)/B3LYP-D3/6-311+G(2d)/6-31+G(d) theoretical level.

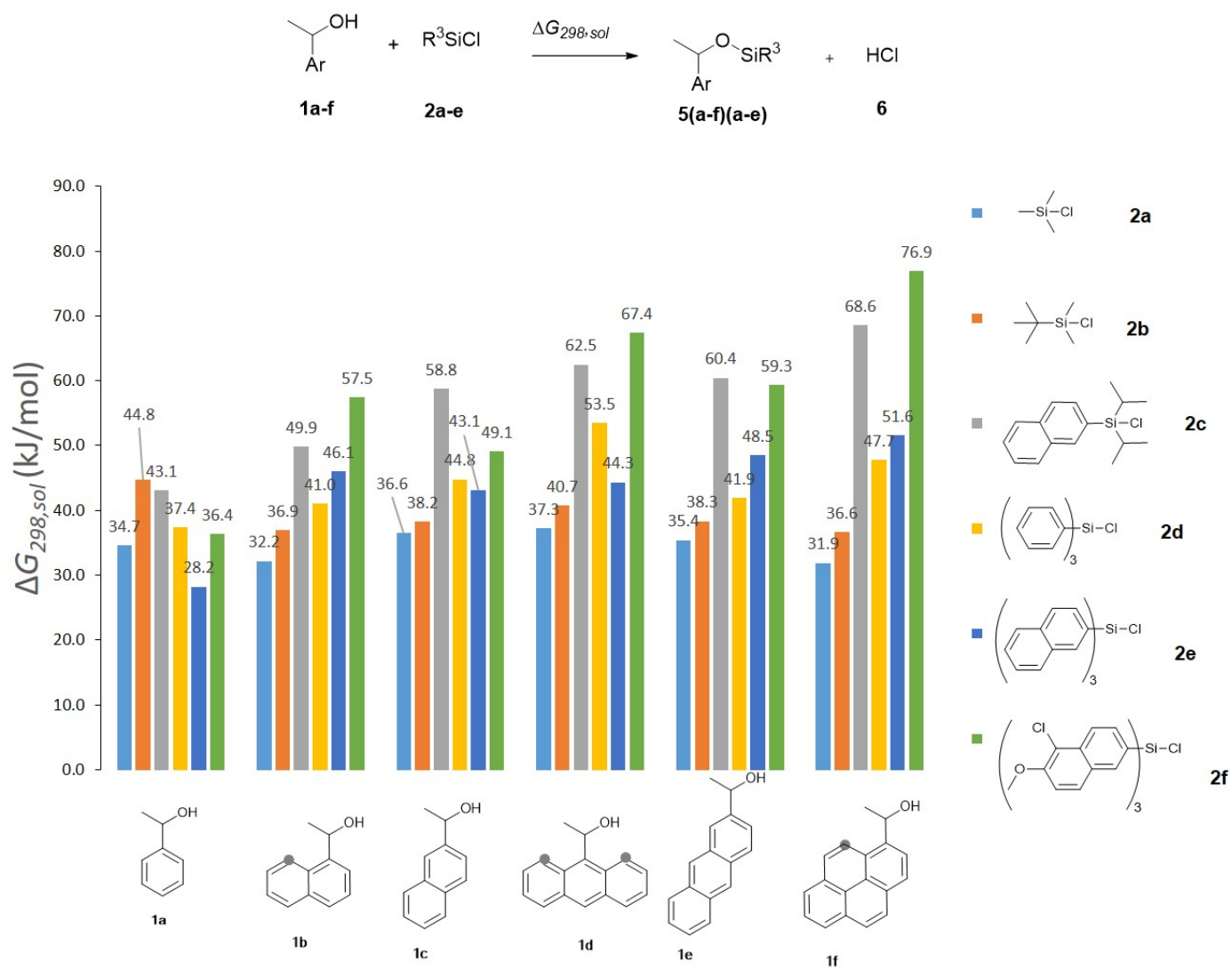


Figure S148: Reaction free energies, $\Delta G_{298,\text{sol}}$, computed at SMD(CHCl₃)/B3LYP/6-311+G(2d)/6-31+G(d)//SMD(CHCl₃)/B3LYP-D3/6-311+G(2d)/6-31+G(d) theoretical level.

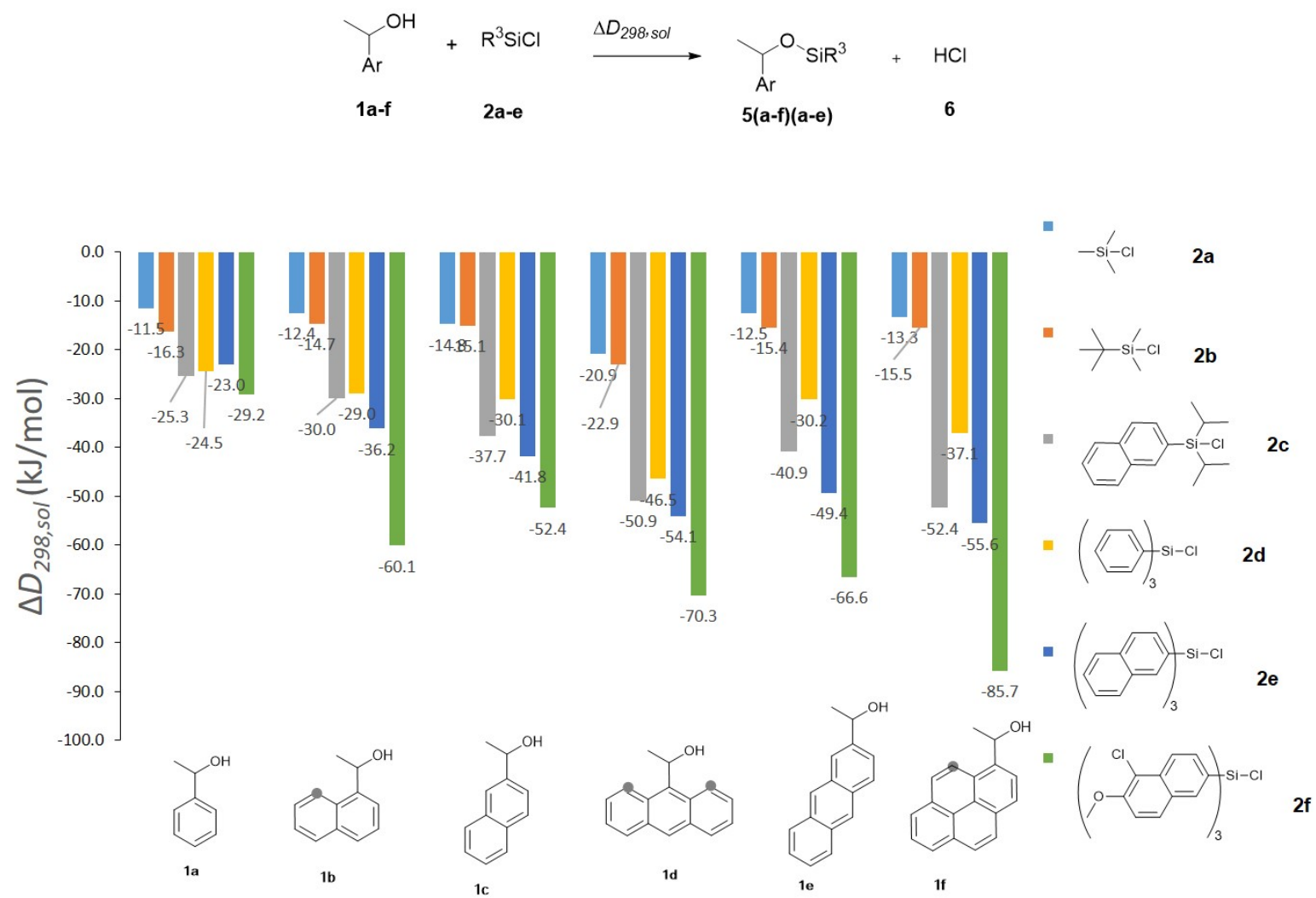


Figure S149: Dispersion contribution, $\Delta D_{298,\text{sol}}$.

6.5. Relation of Experimental and Computational Results

The Bell-Evans-Polanyi equation observes that the difference in activation energy between two reactions of the same family is through a linear equation proportional to the difference of their free energy of their reactions (Eq. S18).

$$E_{a_1} = E_0 + \alpha \Delta G_1 \quad \text{Eq. S18}$$

$$E_{a_2} = E_0 + \alpha \Delta G_2 \quad \text{Eq. S19}$$

In this equation E_a is the activation energy of an individual reaction, E_0 is the activation energy of a reference reaction of the same family of reactions and ΔG is the Gibbs free energy of the reaction yielding the product of that individual reaction.

On the other hand, the relative rate-constant is defined by the ratio between two rate-constants $k_{rel} = k_2/k_1$. Taking into account the Arrhenius equation we can rewrite k_{rel} as Eq. S22:

$$k_1 = A \cdot \exp\left(-\frac{E_{a_1}}{RT}\right) \quad \text{Eq. S20}$$

$$k_2 = A \cdot \exp\left(-\frac{E_{a_2}}{RT}\right) \quad \text{Eq. S21}$$

$$k_{rel} = \frac{k_2}{k_1} = \exp\left(\frac{E_{a_1} - E_{a_2}}{RT}\right) \quad \text{Eq. S22}$$

$$\ln(k_{rel}) = \frac{E_{a_1} - E_{a_2}}{RT} = A \cdot (E_{a_1} - E_{a_2}) = A \cdot E_{a_{rel}} \quad \text{Eq. S23}$$

Relating equations Eq. S18, Eq. S19 and Eq. S23, the Eq. S24 is obtained:

$$\ln(k_{rel}) = A \cdot (E_{a_1} - E_{a_2}) = \alpha(\Delta G_1 - \Delta G_2) \quad \text{Eq. S24}$$

Figure S150 was generated by plotting Eq. S24 for the reaction shown in that figure. Linear regression with good to acceptable correlation factor R^2 were found for next silyl reagents: TMS **2a**, TBDMSCl **2b** and TPS **2d**. However, that quality drops notably for silyl reagents carrying bigger DED: DINSCL **2c**, TNSCL **2e** and TN*SCl **2f**. This fact indicates that there is not a general correlation between the experimental k_{rel} and the computed reaction free energies, what suggests that observed differences in k_{rel} are rather a kinetic phenomenon than a thermodynamic one.

In Figure S151, the relationship between k_{rel} and the differences in the dispersion contributions is shown. For discussion see main text of the manuscript.

Table S22: $\ln(k_{rel})$, reaction free energy differences $\Delta\Delta G_{298,sol}$ computed at SMD(CHCl₃)/DLPNO-CCSD(T)/def2-TZVPP//SMD(CHCl₃)/B3LYP-D3/6-311+G(2d)/6-31+G(d)^{a,b}, and differences in the dispersion contribution ($\Delta\Delta D_{298,sol}$) (kJ/mol) for the transformation shown in Scheme at the top of the table.

	1a	5(b-f)(a-f)		5a(a-f)	1b-f	
$\ln(k_{rel})$						
	1a	1b	1c	1d	1e	1f
2a	0.000	-0.447	-0.024	-2.173	-0.031	-0.443
2b	0.000	-0.396	0.010	-2.973	0.010	-0.425
2c	0.000	-0.649	0.113	-2.501	0.149	-0.326
2d	0.000	-0.320	0.170	-1.419	0.216	-0.162
2e	0.000	-0.188	0.357	-1.383	0.465	0.182
2f	0.000	-0.002	0.469	-0.968	0.852	0.984
$\Delta\Delta G_{298,sol}$						
	1a	1b	1c	1d	1e	1f
2a	0.0	2.9	1.6	6.8	-0.1	3.9
2b	0.0	6.4	6.6	11.2	6.3	7.4
2c	0.0	-3.5	-2.0	11.7	-0.1	6.1
2d	0.0	0.8	-0.8	8.6	1.7	2.9
2e	0.0	1.3	10.6	18.5	7.4	14.7
2f	0.0	13.6	14.9	18.0	17.8	25.4
$\Delta\Delta D_{298,sol}$						
	1a	1b	1c	1d	1e	1f
2a	0.0	0.9	3.2	9.4	1.0	1.8
2b	0.0	-1.6	-1.2	6.7	-0.9	-0.8
2c	0.0	4.6	12.4	25.6	15.6	27.1
2d	0.0	4.5	5.6	22.0	5.7	12.6
2e	0.0	13.1	18.7	31.1	26.4	32.6
2f	0.0	31.0	23.2	41.1	37.4	56.6

^a C, H, O : 6-31+G(d) Si, Cl : 6-311+G(d) ^b Solv Factor at B3LYP-D3 added to the E(SCF) at DLPNO-CCSD(T)/def2-TZVPP

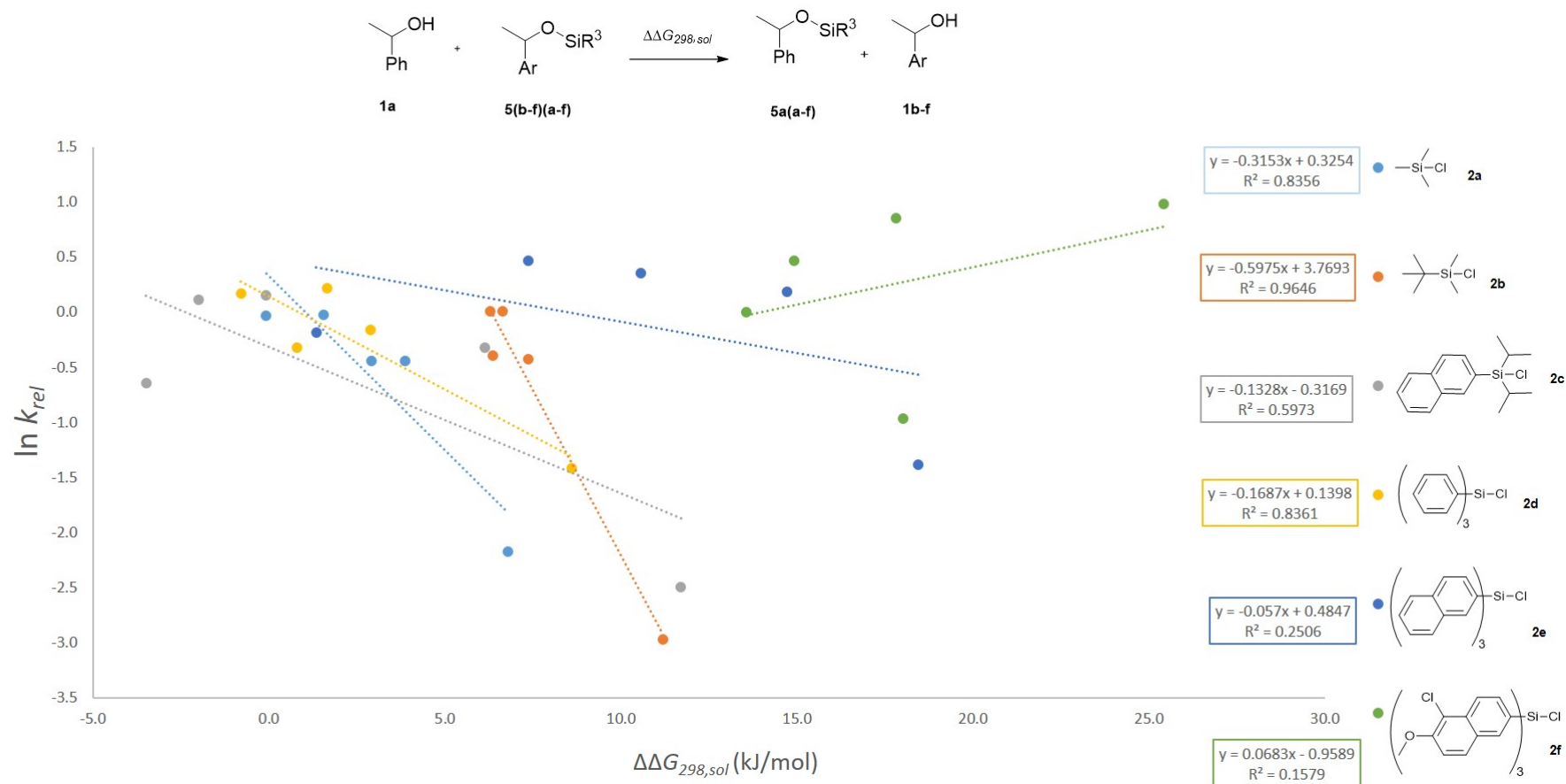


Figure S150: Experimental $\ln(k_{rel})$ vs $\Delta\Delta G_{298,sol}$, computed at SMD(CHCl₃)/DLPNO-CCSD(T)/def2-TZVPP//SMD(CHCl₃)/B3LYP-D3/6-311+G(2d)/6-31+G(d) theoretical level.

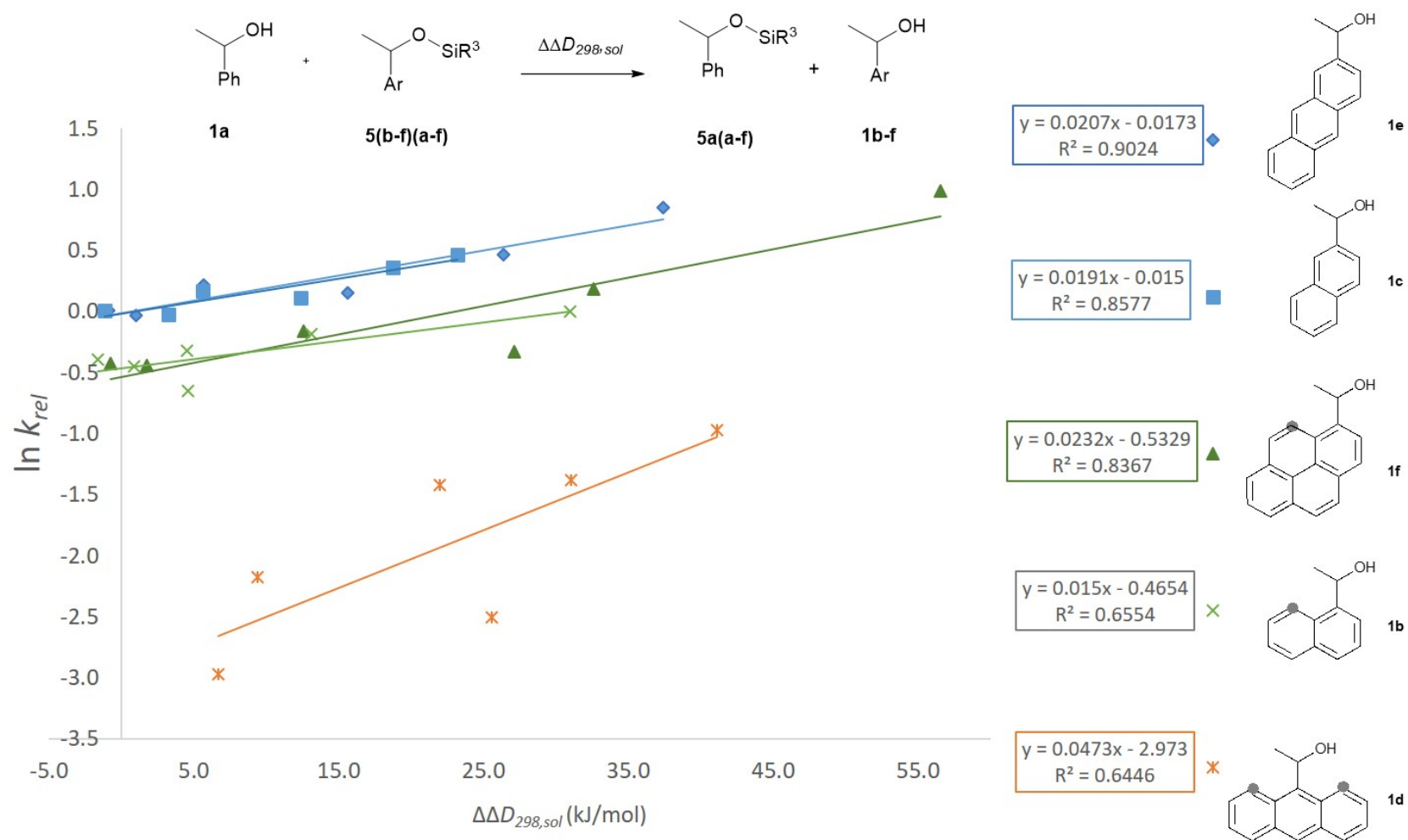


Figure S151: Experimental $\ln(k_{rel})$ vs $\Delta\Delta D_{298, sol}$. $\Delta D_{298, sol}$ was calculated as the difference between $\Delta G_{298, sol}$ computed at SMD(CHCl₃)/B3LYP-D3/6-311+G(2d)/6-31+G(d) and those computed at SMD(CHCl₃)/B3LYP/6-311+G(2d)/6-31+G(d)//SMD(CHCl₃)/B3LYP-D3/6-311+G(2d)/6-31+G(d) theoretical level.

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