Supplementary Information – Nucleophilic substitution at silicon under vibrational strong coupling: Refined insights from a high-level *ab initio* perspective

Details on Refined Mechanistic Hypothesis

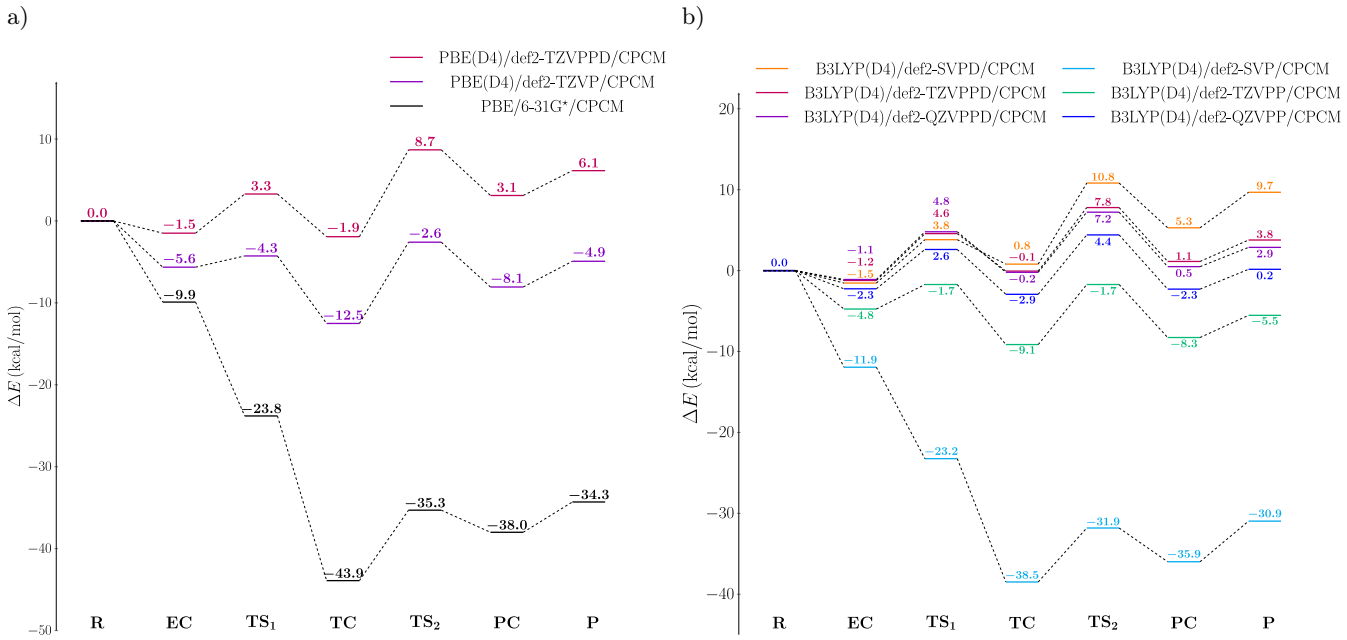


FIG. 1. Electronic energies of the S_N2 reaction mechanism hypothesis obtained on a) PBE(D4)/CPCM level of theory with different basis sets and b) B3LYP(D4)/CPCM level of theory with different basis sets. Molecular structures were optimized on B3LYP(D4)/def2-TZVPPD/CPCM level of theory and an implicit solvation model (CPCM) for methanol was employed.

Details on Dipole Fluctuation Corrections

TABLE I. Absolute cavity-induced electronic dipole fluctuation corrections in kcal/mol obtained on CRP-HF/def2-SVPD level of theory for different cavity polarizations, λ, with light-matter interaction strength, $g_0 = 0.015\sqrt{E_h}/ea_0$.

λ	R	EC	TS_1	TC	TS_2	PC	P
x	3.73	3.74	3.75	3.75	3.79	3.78	3.77
y	4.17	4.18	4.20	4.19	4.28	4.20	4.21
z	4.59	4.58	4.58	4.59	4.61	4.60	4.60

TABLE II. Cavity-induced electronic dipole fluctuation corrections relative to reactants (R) in kcal/mol obtained on CRP-HF/def2-SVPD level of theory for different cavity polarizations, λ, with light-matter interaction strength, $g_0 = 0.015\sqrt{E_h}/ea_0$.

λ	EC	TS_1	TC	TS_2	PC	P
x	0.01	0.02	0.02	0.06	0.06	0.05
y	0.01	0.04	0.02	0.11	0.03	0.04
z	-0.02	-0.01	-0.002	0.01	0.01	0.01

TABLE III. Absolute cavity-induced electronic dipole fluctuation corrections in kcal/mol obtained on lCRP-CCSD/def2-SVPD level of theory for different cavity polarizations, λ, with light-matter interaction strength, $g_0 = 0.015\sqrt{E_h}/ea_0$.

λ	R	EC	TS_1	TC	TS_2	PC	P
x	3.74	3.75	3.79	3.81	3.82	4.08	3.98
y	4.50	4.51	4.55	4.58	4.57	8.59	4.99
z	10.86	13.45	11.89	11.27	12.74	8.46	6.53

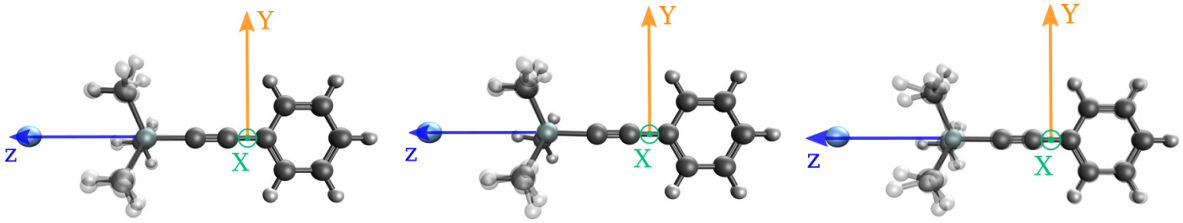
Details on Normal Mode Analysis

TABLE IV. Vibrational properties of encounter complex (EC), first transition state (TS_1), transition complex (TC) and second transition state (TS_2) in respective principal axis frame of polarizability tensor obtained at CAM-B3LYP(D4)/def2-TZVPPD/CPCM(MeOH) level of theory with ORCA 5.0.4. Normal-mode frequencies, $\tilde{\nu}$, relative displacement of Si-C bond along z-axis, Δr_z, intensity, $I \propto \sum_\kappa T_\kappa^2$, frequency-weighted dipole derivatives, $T_\kappa = \frac{1}{\sqrt{2\omega_i}}\frac{\partial d_\kappa}{\partial Q_i}$, along Cartesian coordinates, $\kappa = x, y, z$, with x-axis perpendicular to the phenyl ring and z-axis parallel to the Si-C bond.

mode	$\tilde{\nu}$/cm^{-1}	Δr_z/a.u.	I/a.u.	T_x/a.u.	T_y/a.u.	T_z/a.u.
a_{38}^{EC}	862.1	—	0.01	0.09	-0.05	—
a_{39}^{EC}	862.5	—	0.01	0.05	0.09	—
a_{40}^{EC}	874.6	0.06	0.04	—	—	-0.19
$a_{38}^{TS_1}$	856.3	0.09	0.04	—	—	0.19
$a_{39}^{TS_1}$	858.4	0.01	0.01	0.1	-0.03	—
$a_{40}^{TS_1}$	859.8	0.01	0.01	-0.03	-0.1	—
a_{38}^{TC}	838.1	—	0.01	0.08	-0.05	—
a_{39}^{TC}	840.4	—	0.01	0.05	0.08	—
a_{40}^{TC}	865.5	0.04	0.02	—	-0.01	0.16
$a_{38}^{TS_2}$	857.1	0.01	0.016	-0.09	-0.08	-0.04
$a_{39}^{TS_2}$	860.9	0.07	0.019	0.02	-0.06	0.12
$a_{40}^{TS_2}$	861.6	0.05	0.016	0.08	0.07	0.07

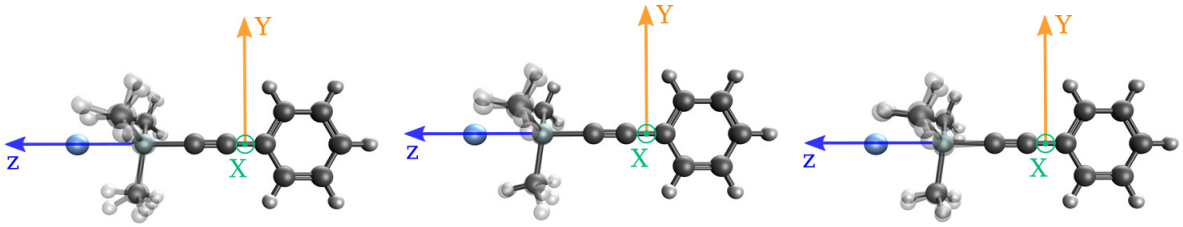
TABLE V. Selected normal modes of encounter complex (EC), first transition state (TS_1), transition complex (TC) and second transition state (TS_2) in respective principal axis frame of polarizability tensor obtained at CAM-B3LYP(D4)/def2-TZVPPD/CPCM(MeOH) level of theory with ORCA 5.0.4.

EC



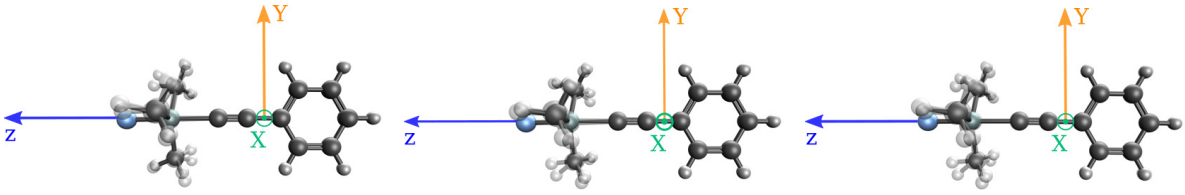
$\hbar\omega_{a_{38}} = 862.1\,\mathrm{cm}^{-1}$ $\hbar\omega_{a_{39}} = 862.5\,\mathrm{cm}^{-1}$ $\hbar\omega_{a_{40}} = 874.6\,\mathrm{cm}^{-1}$

TS_1



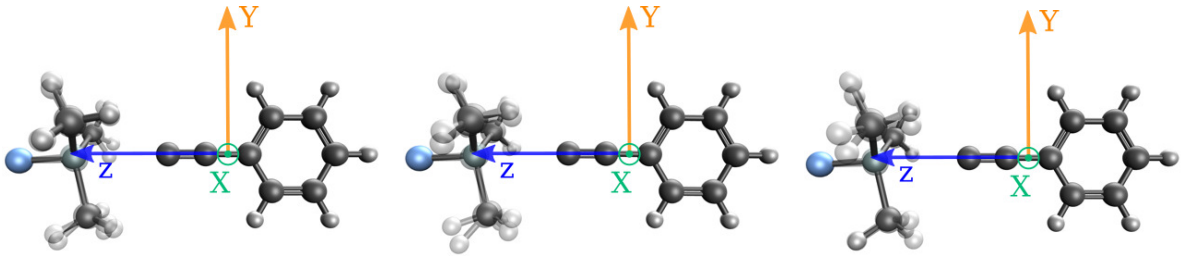
$\hbar\omega_{a_{38}} = 856.3\,\mathrm{cm}^{-1}$ $\hbar\omega_{a_{39}} = 858.4\,\mathrm{cm}^{-1}$ $\hbar\omega_{a_{40}} = 859.8\,\mathrm{cm}^{-1}$

TC



$\hbar\omega_{a_{38}} = 838.1\,\mathrm{cm}^{-1}$ $\hbar\omega_{a_{39}} = 840.4\,\mathrm{cm}^{-1}$ $\hbar\omega_{a_{40}} = 865.5\,\mathrm{cm}^{-1}$

TS_2



$\hbar\omega_{a_{38}} = 857.1\,\mathrm{cm}^{-1}$ $\hbar\omega_{a_{39}} = 860.9\,\mathrm{cm}^{-1}$ $\hbar\omega_{a_{40}} = 861.6\,\mathrm{cm}^{-1}$

TABLE VI. Structure of PTA in Cartesian coordinates (Å) optimized on B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory with body-fixed axis system aligned with principal axis system of polarizability tensor at CAM-B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory. PTA forms reactants (R) with fluoride anion.

C	-0.0000000000	0.0000000000	0.7123060606
C	-0.0002756537	-0.0038831469	1.9264903604
C	0.0000000000	0.0000000000	-0.7123060606
C	-0.0022073230	-0.0023224386	-3.5085459475
C	0.0000000000	1.2089194641	-1.4241984560
C	-0.0008527785	-1.2101268589	-1.4222847164
C	-0.0018628984	-1.2065472237	-2.8098196293
C	-0.0011520961	1.2029817185	-2.8118043863
H	0.0002096550	2.1442840455	-0.8814649612
H	-0.0003907425	-2.1445385732	-0.8779150763
H	-0.0019747200	-2.1456345819	-3.3472685792
H	-0.0017302601	2.1411471688	-3.3508550554
H	-0.0031981930	-0.0032456497	-4.5905019281
Si	-0.0052135629	-0.0136557319	3.7693885065
C	0.1946164394	-1.7875382542	4.3395014123
H	1.1397943108	-2.2075902050	3.9903187209
H	-0.6166522216	-2.4129494361	3.9622642930
H	0.1830711241	-1.8376009178	5.4308456812
C	1.4216070487	1.0450269052	4.3655028778
H	2.3764978325	0.6536281609	4.0097625233
H	1.4473712655	1.0635911850	5.4576468276
H	1.3208220788	2.0726699627	4.0111354953
C	-1.6389036244	0.6928002290	4.3567071798
H	-1.6759903452	0.6968593886	5.4487246826
H	-2.4781028744	0.0984881884	3.9905499784
H	-1.7695903823	1.7190942020	4.0085299456

TABLE VII. Structure of anionic encounter complex (EC) in Cartesian coordinates (Å) optimized on B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory with body-fixed axis system aligned with principal axis system of polarizability tensor at CAM-B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory.

C	-0.00442	-0.00810	-0.95144
C	-0.00477	-0.00595	0.26275
C	-0.00442	-0.00810	-2.37601
C	-0.00528	-0.00641	-5.17250
C	-0.00442	1.20172	-3.08642
C	-0.00476	-1.21707	-3.08780
C	-0.00513	-1.21149	-4.47539
C	-0.00483	1.19785	-4.47397
H	-0.00469	2.13627	-2.54230
H	-0.00431	-2.15233	-2.54488
H	-0.00502	-2.14982	-5.01418
H	-0.00535	2.13685	-5.01158
H	-0.00574	-0.00575	-6.25446
Si	-0.00212	-0.00248	2.10700
C	1.05794	-1.43418	2.68743
H	2.08287	-1.33443	2.32505
H	0.66041	-2.38578	2.32937
H	1.08387	-1.46468	3.77899
C	0.71110	1.63141	2.68318
H	1.73350	1.76034	2.32300
H	0.72649	1.67001	3.77466
H	0.11297	2.46964	2.32079
C	-1.77089	-0.20248	2.69357
H	-1.80678	-0.20202	3.78539
H	-2.19685	-1.14314	2.33923
H	-2.39805	0.61424	2.33131
F	0.03284	0.05134	6.48236

TABLE VIII. Structure of anionic first transition state (TS_1) in Cartesian coordinates (Å) optimized on B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory with body-fixed axis system aligned with principal axis system of polarizability tensor at CAM-B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory.

C	-0.00436	0.00941	-0.73329
C	-0.00519	0.00842	0.48332
C	-0.00436	0.00941	-2.15961
C	-0.00590	0.00839	-4.96275
C	-0.00436	1.21676	-2.87566
C	-0.00518	-1.19849	-2.87484
C	-0.00584	-1.19517	-4.26284
C	-0.00520	1.21243	-4.26370
H	-0.00382	2.15268	-2.33349
H	-0.00543	-2.13401	-2.33199
H	-0.00637	-2.13468	-4.80002
H	-0.00540	2.15154	-4.80157
H	-0.00653	0.00800	-6.04477
Si	0.00114	-0.00346	2.38457
C	-0.07999	-1.86136	2.66748
H	0.79110	-2.34099	2.21374
H	-0.96714	-2.27206	2.17872
H	-0.10961	-2.10273	3.72641
C	1.65175	0.84878	2.68315
H	2.45764	0.25512	2.24400
H	1.84398	0.98168	3.74434
H	1.66092	1.82359	2.18909
C	-1.56212	0.99483	2.69980
H	-1.75674	1.10417	3.76323
H	-2.41669	0.50474	2.22640
H	-1.46593	1.98558	2.24827
F	0.01762	-0.02830	4.88749

TABLE IX. Structure of anionic transition complex (TC) in Cartesian coordinates (Å) optimized on B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory with body-fixed axis system aligned with principal axis system of polarizability tensor at CAM-B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory.

C	-0.00775	0.01659	-0.64497
C	-0.00743	0.01593	0.57723
C	-0.00775	0.01659	-2.07217
C	-0.00914	0.01509	-4.88465
C	-0.00775	1.22167	-2.79499
C	-0.00848	-1.18925	-2.79382
C	-0.00910	-1.18702	-4.18205
C	-0.00850	1.21791	-4.18326
H	-0.00753	2.15911	-2.25497
H	-0.00834	-2.12609	-2.25276
H	-0.00936	-2.12762	-4.71789
H	-0.00876	2.15789	-4.72017
H	-0.00971	0.01452	-5.96670
Si	0.00571	-0.01247	2.59835
C	-1.16456	1.49275	2.62589
H	-2.09885	1.24971	2.11224
H	-0.71439	2.32315	2.07540
H	-1.40467	1.83533	3.63303
F	0.02421	-0.05259	4.41818
C	-0.71395	-1.77948	2.56141
C	1.89372	0.26432	2.57772
H	2.13272	1.17143	2.01640
H	2.38600	-0.56202	2.05744
H	2.32717	0.35075	3.57474
H	-0.90766	-2.18974	3.55312
H	-0.02347	-2.44828	2.03991
H	-1.64674	-1.79084	1.99159

TABLE X. Structure of anionic second transition state (TS_2) in Cartesian coordinates (Å) optimized on B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory with body-fixed axis system aligned with principal axis system of polarizability tensor at CAM-B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory.

C	-0.18676	0.06101	-1.01084
C	-0.18169	0.05732	0.22727
C	-0.18676	0.06101	-2.43937
C	-0.18524	0.05962	-5.26351
C	-0.18676	1.26411	-3.17066
C	-0.18641	-1.14282	-3.16958
C	-0.18555	-1.14122	-4.55795
C	-0.18579	1.26111	-4.55910
H	-0.18728	2.20322	-2.63291
H	-0.18665	-2.08149	-2.63105
H	-0.18517	-2.08292	-5.09262
H	-0.18560	2.20225	-5.09472
H	-0.18466	0.05907	-6.34560
Si	0.17915	-0.06003	3.19496
C	1.72419	0.92161	2.80052
H	1.68706	1.88893	3.30873
H	1.83705	1.09025	1.73325
H	2.60397	0.38797	3.17008
C	-1.45915	0.84314	3.04984
H	-2.19178	0.24227	2.51228
H	-1.33951	1.77735	2.50158
H	-1.85173	1.07073	4.04402
C	0.22910	-1.88375	2.75916
H	0.60812	-2.45826	3.60798
H	0.86819	-2.06369	1.89704
H	-0.76744	-2.25399	2.51259
F	0.32358	-0.14536	4.86503

TABLE XI. Structure of anionic product complex (PC) in Cartesian coordinates (Å) optimized on B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory with body-fixed axis system aligned with principal axis system of polarizability tensor at CAM-B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory.

C	-0.00775	0.01659	-0.64497
C	-0.00743	0.01593	0.57723
C	-0.00775	0.01659	-2.07217
C	-0.00914	0.01509	-4.88465
C	-0.00775	1.22167	-2.79499
C	-0.00848	-1.18925	-2.79382
C	-0.00910	-1.18702	-4.18205
C	-0.00850	1.21791	-4.18326
H	-0.00753	2.15911	-2.25497
H	-0.00834	-2.12609	-2.25276
H	-0.00936	-2.12762	-4.71789
H	-0.00876	2.15789	-4.72017
H	-0.00971	0.01452	-5.96670
Si	0.00571	-0.01247	2.59835
C	-1.16456	1.49275	2.62589
H	-2.09885	1.24971	2.11224
H	-0.71439	2.32315	2.07540
H	-1.40467	1.83533	3.63303
F	0.02421	-0.05259	4.41818
C	-0.71395	-1.77948	2.56141
C	1.89372	0.26432	2.57772
H	2.13272	1.17143	2.01640
H	2.38600	-0.56202	2.05744
H	2.32717	0.35075	3.57474
H	-0.90766	-2.18974	3.55312
H	-0.02347	-2.44828	2.03991
H	-1.64674	-1.79084	1.99159

TABLE XII. Structure of PA anion (PA) in Cartesian coordinates (Å) optimized on B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory with body-fixed axis system aligned with principal axis system of polarizability tensor at CAM-B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory. Forms products with FMS.

C	-0.00507	-0.00032	3.34762
C	0.00147	-0.00024	2.11037
C	0.00147	-0.00024	0.68152
C	0.00147	1.20376	-0.04755
C	-0.00004	1.20164	-1.43598
C	-0.00038	0.00044	-2.14058
C	-0.00012	-1.20114	-1.43644
C	0.00117	-1.20403	-0.04807
H	0.00224	2.14226	0.49102
H	-0.00121	2.14289	-1.97123
H	-0.00158	0.00030	-3.22264
H	-0.00113	-2.14189	-1.97257
H	0.00181	-2.14278	0.49006

TABLE XIII. Structure of FMS in Cartesian coordinates (Å) optimized on B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory with body-fixed axis system aligned with principal axis system of polarizability tensor at CAM-B3LYB(D4)/def2-TZVPPD/CPCM(MeOH) level of theory. Forms products with PA anion.

F	0.00008	0.00034	1.65234
Si	0.00008	0.00034	0.01414
C	0.00008	1.78469	-0.52118
C	-1.54603	-0.89072	-0.52153
C	1.54601	-0.89460	-0.51420
H	0.00311	1.84920	-1.61189
H	0.88339	2.30823	-0.15007
H	-0.88768	2.30521	-0.15618
H	-1.59857	-0.92724	-1.61230
H	-2.44078	-0.38079	-0.15865
H	-1.55967	-1.91708	-0.14930
H	1.60778	-0.92974	-1.60441
H	1.55031	-1.92163	-0.14327
H	2.43978	-0.39025	-0.14148