Supplementary Material

Theoretical Study of Carbon-Carbon Bond Formation. A model of the Michael-Type addition

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Table S1. Key inter-atomic distances of all stationary point structures located and characterized along the reaction paths obtained at AM1, B3LYP/6-31+G* and M06-2X/6-31+G* in gas phase.

Reaction 1+3

AM1

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	4.28373	3.42478	3.78971	1.97853	1.46368	1.53352	1.5245
C1-H6	5.38930	4.60257	4.42567	4.54285	2.87816	2.27686	2.1799
H6-C5	1.13398	1.32724	2.58167	2.82485	4.31413	3.61498	2.6850
N7-C5	3.90334	2.68655	3.20531	3.45504	5.31807	4.77459	4.61116
N7-H6	2.86909	1.35977	1.00025	0.99720	1.00976	1.31698	3.4466
N9-H10	1.92798	2.00035	2.58548	2.56971	2.44984	1.94342	1.8201
N9-O11	2.90518	2.97049	3.52376	3.52410	3.28674	2.89561	2.8098
H10-O11	0.98772	0.98215	0.96936	0.96958	0.97686	0.99299	1.0071
H6 - C2	6.70251	5.91238	6.55440	4.76305	2.05264	1.35515	1.1222

B3LYP/6-31+G*

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	4.20682	3.60954	4.75551	1.91299	1.58398	1.57211	1.54446
C1-H6	5.28933	4.86027	5.52926	3.99315	3.19603	2.35027	2.15962
H6-C5	1.10026	1.35381	2.14711	3.49102	4.65710	3.80475	3.47175
N7-C5	3.35609	2.73396	3.16391	4.46050	5.67921	4.94485	5.73698
N7-H6	2.33631	1.38031	1.02837	1.02706	1.03334	1.27840	5.45822
N9-H10	1.48014	1.58871	1.66814	1.64197	1.55565	1.46780	1.06455
N9-O11	2.56101	2.62718	2.68369	2.66535	2.60627	2.55488	2.67380
H10-O11	1.08193	1.04036	1.01848	1.02507	1.05205	1.08835	1.61167
H6 - C2	6.60494	6.20091	6.61020	7.76796	2.15763	1.45430	1.09489

M06-2X/6-31+G*

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	3.64461	3.18759	3.06657	2.04334	1.55940	1.54790	1.5347
C1-H6	4.68217	4.52839	4.17643	3.67562	3.33079	2.29905	2.13611
H6-C5	1.09801	1.35333	3.70650	3.84542	4.68845	3.73664	3.4822
N7-C5	3.26823	2.72027	4.78371	4.76749	5.73711	4.86587	4.6394
N7-H6	2.34757	1.37261	1.09619	1.01835	1.06010	1.27971	2.5793
N9-H10	1.48599	1.56450	1.61031	1.60753	1.50885	1.43926	1.0976
N9-O11	2.55444	2.60254	2.63463	2.63199	2.56909	2.53197	2.5880
H10-O11	1.06847	1.03834	1.02462	1.02479	1.06024	1.09271	1.4910
H6 - C2	5.64165	5.12505	8.51075	2.65517	2.15389	1.43754	1.0953

Reaction 1+4

AM1

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	3.76461	3.7993	3.96600	1.97067	1.54546	1.53413	1.52250
C1-H6	3.32187	3.5671	4.05303	3.41262	4.23956	2.27477	2.14769
H6-C5	1.14737	1.2888	2.04492	3.59320	5.17832	3.67665	3.48215
N7-C5	3.11348	2.7208	3.03262	4.43077	5.91321	4.84607	5.03465
N7-H6	1.97720	1.4350	1.00891	0.99541	1.01147	1.29115	3.19476
N9-H10	1.87691	1.9425	2.47877	2.50741	2.57522	1.93625	1.89168
N9-O11	2.84359	2.8958	3.44761	3.32526	3.31399	2.89759	2.84457
H10-O11	1.00021	0.9929	0.97626	0.97594	0.97611	0.99322	0.99802

B3LYP/6-31+G*

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	4.92999	4.8370	4.18888	2.15627	1.61212	1.58012	1.53990
C1-H6	4.74690	5.0630	4.82093	3.17920	3.17827	2.35724	2.15369
H6-C5	1.09917	1.3367	8.09849	5.23946	4.66080	3.83520	3.50098
N7-C5	4.46083	2.7379	9.06044	6.25969	5.68906	4.95975	6.00386
N7-H6	3.56024	1.4054	1.02902	1.02188	1.03456	1.24587	3.11528
N9-H10	1.06033	1.5255	1.67162	1.64912	1.60870	1.54309	1.05971
N9-O11	2.71678	2.5966	2.69826	2.68135	2.65173	2.60763	2.71333
H10-O11	1.65685	1.0725	1.02665	1.03232	1.04346	1.06559	1.65490

M06-2X/6-31+G*

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	3.80589	4.2424	3.48971	2.17206	1.57160	1.56011	1.52819
C1-H6	3.14356	3.5515	4.02006	4.15476	3.47721	2.32196	2.15650
H6-C5	1.10216	1.3376	3.94921	5.10161	4.80352	3.78439	3.47200
N7-C5	3.33001	2.7230	4.84317	5.48826	5.82360	4.84524	5.65201
N7-H6	2.30485	1.3854	1.03469	1.03809	1.02560	1.21564	3.29389
N9-H10	1.08194	1.5086	1.57311	1.57142	1.55971	1.51673	1.05740
N9-O11	2.63523	2.5769	2.61778	2.61626	2.60858	2.58164	2.71172
H10-O11	1.55394	1.0683	1.04469	1.04519	1.04913	1.06498	1.65588

Reaction: 1 + 5

AM1

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	3.63065	3.5238	3.63480	2.00678	1.54283	1.53144	1.52285
C1-H6	3.15809	3.4629	4.27071	3.41581	2.77646	2.26410	2.14371
H6-C5	1.12950	1.2990	2.24093	3.57643	4.24864	3.65538	3.49422
N7-C5	3.59091	2.7075	3.22114	4.42058	5.25700	4.88254	5.15051
N7-H6	2.63177	1.4098	0.99882	0.99587	1.01136	1.34168	2.77214
N9-H10	1.90073	1.9421	2.46099	2.50696	2.03468	1.92257	2.03720
N9-O11	2.84557	2.8966	3.43096	3.32773	3.01828	2.88508	2.87606
H10-O11	0.99813	0.9930	0.97656	0.97593	0.98375	0.99472	0.98972

B3LYP/6-31+G**

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	8.81184	4.8443	4.54049	2.16148	1.60284	1.57593	1.53669
C1-H6	7.93779	5.3782	5.22217	3.01933	2.97288	2.39985	2.15681
H6-C5	1.10675	1.3317	2.16892	5.11806	4.47165	3.87170	3.50187
N7-C5	3.33143	2.7332	3.18667	6.14270	5.51534	5.01058	6.63847
N7-H6	2.26499	1.4057	1.02808	1.02478	1.04947	1.23343	5.41324
N9-H10	1.06922	1.4328	1.57678	1.59170	1.54491	1.47061	1.06430
N9-O11	2.67393	2.5380	2.62116	2.63151	2.60012	2.55651	2.67938
H10-O11	1.60477	1.1060	1.04465	1.03985	1.05549	1.08669	1.61560

M06-2X/6-31+G**

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	5.9640	5.49874	3.3631	2.14862	1.56836	1.5567	1.52881
C1-H6	5.6381	4.49811	3.1643	4.18335	3.09474	2.3723	2.16071
H6-C5	1.0978	1.35638	2.7916	5.08925	4.49679	3.8170	3.47645
N7-C5	3.2422	2.70808	3.5530	5.47096	5.53661	4.9179	6.21689
N7-H6	2.3932	1.36100	1.0973	1.03438	1.04338	1.2182	5.24920
N9-H10	1.0803	1.44550	1.5267	1.51659	1.50440	1.4519	1.06645
N9-O11	2.6213	2.53357	2.5800	2.57332	2.56607	2.5376	2.65883
H10-O11	1.5414	1.08847	1.0532	1.05710	1.06201	1.0857	1.59239

Reaction 2+3

AM1

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	4.66381	3.43683	3.83069	1.92757	1.54808	1.53605	1.5266
C1-H6	4.72387	4.56918	5.80350	4.46978	2.88276	2.26302	2.1473
H6-C5	1.14116	1.25885	2.79410	2.87811	4.30494	3.62547	3.4533
N7-C5	3.94742	2.74535	3.30751	3.46317	5.31214	4.83668	4.9876
N7-H6	2.83894	1.48886	0.99911	0.99637	1.01052	1.34067	2.8819
N9-H10	1.89074	2.92945	2.60791	2.56969	2.44503	1.93004	1.8396
N9-O11	2.87323	1.95496	3.53917	3.52466	3.28381	2.88508	2.81126
H10-O11	0.99242	0.98580	0.96924	0.96943	0.97695	0.99432	1.0062
H6 - C2	5.75174	5.87810	7.02055	4.52548	2.04041	1.34029	1.1364

B3LYP/6-31+G*

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	4.60250	4.47431	4.73132	1.99350	1.56857	1.55720	1.54377
C1-H6	2.16275	3.94873	5.49772	4.03137	3.16517	2.35684	2.14252
H6-C5	1.10699	1.37193	2.07434	3.56769	4.57136	3.79195	3.50571
N7-C5	3.24666	2.72304	3.09055	4.54531	5.59351	4.94338	5.49932
N7-H6	2.16275	1.35193	1.03633	1.02595	1.03737	1.27319	2.22313
N9-H10	1.09899	1.59198	1.66736	1.64549	1.54469	1.44567	1.07833
N9-O11	2.57973	2.62954	2.68391	2.66807	2.59915	2.54380	2.64541
H10-O11	1.48362	1.03942	1.01893	1.02424	1.05605	1.09947	1.56710
H6 - C2	6.95373	5.28016	6.56040	3.39199	2.11372	1.46205	1.10803

M06-2X/6-31+G*

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	4.71985	4.33387	4.42009	2.15152	1.55125	1.55359	1.5420
C1-H6	4.28024	3.60876	3.44558	3.67335	3.29427	2.30811	2.1333
H6-C5	1.10343	1.36761	2.05693	3.87333	4.62616	3.75596	3.4933
N7-C5	3.16103	2.70563	3.06650	4.78619	5.66693	4.84387	4.3341
N7-H6	2.17568	1.34748	1.03719	1.01775	1.06010	1.25751	2.7521
N9-H10	1.47765	1.57022	1.65217	1.62168	1.50356	1.44435	1.09411
N9-O11	2.55001	2.60637	2.66473	2.64226	2.56596	2.53386	2.5958
H10-O11	1.07239	1.03629	1.01379	1.02217	1.06241	1.08951	1.5024
H6 - C2	5.32176	1.36761	4.69273	2.66188	2.13225	1.46556	1.0960

Reaction 2+4

AM1

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	4.00335	4.47257	4.49978	1.98611	1.54859	1.53740	1.5267
C1-H6	3.57004	5.71933	6.81760	3.48317	4.23574	2.26326	2.1632
H6-C5	1.16024	1.26406	2.86630	3.53399	5.00390	3.64810	3.4740
N7-C5	2.99567	2.73771	3.68407	4.41692	5.68184	4.83797	5.7124
N7-H6	1.85316	1.47648	1.00238	0.99732	1.01225	1.31819	2.8615
N9-H10	1.92079	1.95585	2.49297	2.46420	2.45021	1.93330	1.8326
N9-O11	2.89939	2.92996	3.42821	3.39846	3.30406	2.88946	2.8038
H10-O11	0.98899	0.98571	0.97015	0.97115	0.97676	0.99387	1.0065
H6 - C2	4.67357	6.59872	7.71725	2.49287	2.80506	1.35573	1.1294

B3LYP/6-31+G*

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	4.26831	4.60156	4.78873	1.94972	1.56780	1.55988	1.54249
C1-H6	3.84324	4.16010	5.45536	4.05731	3.14685	2.38712	2.17690
H6-C5	1.10224	1.36280	2.07049	3.41876	4.56746	3.84089	3.51251
N7-C5	6.93579	2.72515	3.09695	4.08780	5.59852	4.96523	6.07893
N7-H6	6.09452	1.36256	1.03948	1.02495	1.03922	1.24089	2.58312
N9-H10	1.05739	1.58341	1.67199	1.64298	1.53122	1.45972	1.07913
N9-O11	2.68850	2.62404	2.68543	2.66579	2.59191	2.55108	2.64313
H10-O11	1.63270	1.04204	1.01786	1.02468	1.06096	1.09227	1.56401
H6 - C2	5.17130	5.47284	6.67619	3.41876	2.08613	1.50372	1.09499

M06-2X/6-31+G*

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	3.64356	3.32450	4.56843	2.08300	1.55699	1.55440	1.5424
C1-H6	2.79637	4.66579	3.56867	3.68117	3.08908	2.31283	2.1353
H6-C5	1.09489	1.34725	2.07242	3.88761	4.43139	3.75461	3.4958
N7-C5	3.26926	2.71146	3.07439	4.80354	5.47499	4.77788	4.7676
N7-H6	2.73702	1.36785	1.03538	1.01838	1.05056	1.22985	2.6162
N9-H10	1.48447	1.54383	1.65293	1.61529	1.50617	1.45405	1.0738
N9-O11	2.55308	2.58929	2.66562	2.63817	2.56793	2.53897	2.6412
H10-O11	1.06898	1.04549	1.01354	1.02326	1.06177	1.08493	1.5695
H6 - C2	7.06092	5.32470	4.88616	2.66394	1.97718	1.50125	1.0955

Reaction 2+5

AM1

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	4.70177	4.76974	4.26366	1.95022	1.54360	1.53278	1.5259
C1-H6	5.05494	4.37066	6.60075	4.46484	2.75765	2.26223	2.1522
H6-C5	1.14073	1.26405	2.73854	2.86292	4.21549	3.63804	3.4715
N7-C5	3.95228	2.74287	3.26498	3.44812	5.22445	4.88694	4.6294
N7-H6	2.82404	1.48014	0.99925	0.99646	1.01429	1.35989	2.6664
N9-H10	1.89223	1.96353	2.62001	2.57428	2.44505	1.92295	1.8081
N9-O11	2.87405	2.93707	3.54821	3.52575	3.28519	2.87986	2.7961
H10-O11	0.99244	0.98512	0.96956	0.96954	0.97698	0.99511	1.0099
H6 - C2	6.27785	5.58330	7.56999	4.51637	1.99130	1.32594	1.1275

B3LYP/6-31+G*

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	4.67226	4.96658	4.79700	1.94232	1.56501	1.55867	1.54431
C1-H6	5.70893	5.11878	5.78095	4.02994	2.93806	2.41920	2.15012
H6-C5	1.10731	1.37005	2.06099	3.56145	4.37439	3.87378	3.51786
N7-C5	3.25334	2.72478	3.08117	4.54046	5.42255	4.99319	5.55962
N7-H6	2.15963	1.35581	1.03754	1.02696	1.06010	1.21966	2.22434
N9-H10	1.09869	1.58506	1.66240	1.64599	1.53937	1.46782	1.07623
N9-O11	2.58175	2.62526	2.68009	2.66822	2.59602	2.55489	2.65176
H10-O11	1.48543	1.04133	1.02005	1.02391	1.05804	1.08838	1.57556
H6 - C2	7.02552	5.83411	6.57202	3.40274	1.94840	1.53044	1.10670

M06-2X/6-31+G*

	RC	TS1	I1	TS2	I2	TS3	PC
C1-C5	3.65860	3.38448	5.41686	2.08276	1.55699	1.55472	1.5424
C1-H6	4.68207	4.69006	6.35504	3.69524	3.08908	2.39332	2.1353
H6-C5	1.09892	1.35466	2.07829	3.85023	4.43139	3.82612	3.4958
N7-C5	3.21175	2.71029	3.10000	4.78923	5.47499	4.86877	4.7676
N7-H6	2.43612	1.36264	1.03295	1.01911	1.05056	1.19310	2.6162
N9-H10	1.45529	1.54097	1.62756	1.61646	1.50617	1.46105	1.0738
N9-O11	2.53803	2.58753	2.64625	2.63871	2.56793	2.54278	2.6412
H10-O11	1.08311	1.04668	1.01992	1.02266	1.06177	1.08173	1.5695
H6 - C2	4.69419	4.82583	7.53997	2.69779	1.97718	1.55109	1.0955

Table S2. Relative potential energies to the reactant complex of stationary point structures located along the reaction profile at the three different levels of theory for the reactions shown in scheme 1. Values in Kcal·mol^{-1}

		ΔE_{TS1}	ΔE_{I1}	ΔE_{TS2}	ΔE_{I2}	ΔE_{TS3}	ΔE_{PC}
1+3	AM1	8.0	-5.3	10.0	-9.5	-5.2	-14.4
	B3LYP	7.8	-4.0	4.6	-1.5	4.4	-18.9
	M06-2X	8.3	-6.9	3.6	-6.4	-1.8	-16.6
1+4	AM1	2.2	-9.5	2.5	-16.3	-10.6	-21.1
	B3LYP	10.5	-2.0	10.5	4.6	8.5	-13.6
	M06-2X	11.8	-5.1	3.2	-3.0	1.0	-27.0
1+5	AM1	5.6	-7.1	2.9	-15.5	-10.7	-17.5
	B3LYP	13.6	-0.9	13.0	6.5	8.7	-13.8
	M06-2X	16.2	-1.4	9.0	1.8	3.9	-18.6
2+3	AM1	3.8	-12.1	3.4	-13.4	-8.5	-16.4
	B3LYP	6.3	-1.4	4.0	-2.3	1.6	-12.4
	M06-2X	7.8	1.7	6.1	-3.5	0.7	-14.6
2+4	AM1	2.6	-11.7	-0.5	-14.7	-8.3	-20.0
	B3LYP	13.5	6.4	14.5	8.1	11.4	-7.3
	M06-2X	11.2	2.6	9.6	-1.0	2.7	-15.8
2+5	AM1	2.0	-11.3	1.3	-16.2	-11.1	-17.0
	B3LYP	5.9	-1.1	7.3	0.4	1.6	-15.4
	M06-2X	7.8	-2.9	5.7	-4.4	-3.4	-25.7

Table S3. Gas-phase proton affinities of the bases, and compared with the experimental values for acetate, imidazolyl anion, acetoacetonyl anion and acetoacetonyl anion. All values in kcal·mol^{-1}. Experimental data are available from webook.nist.gov

	acetate	imidazolyl anion	imidazol	imidazol-acetate dyad	acetoacetonyl anion	dimethyl malonate anion
B3LYP	-352.9	-356.7	-233.9	-337.6	-344.7	-351.7
M06-2X	-354.1	-355.1	-231.8	-338.3	-345.2	-351.7
exp	349.9	--	236.3	--	--	--

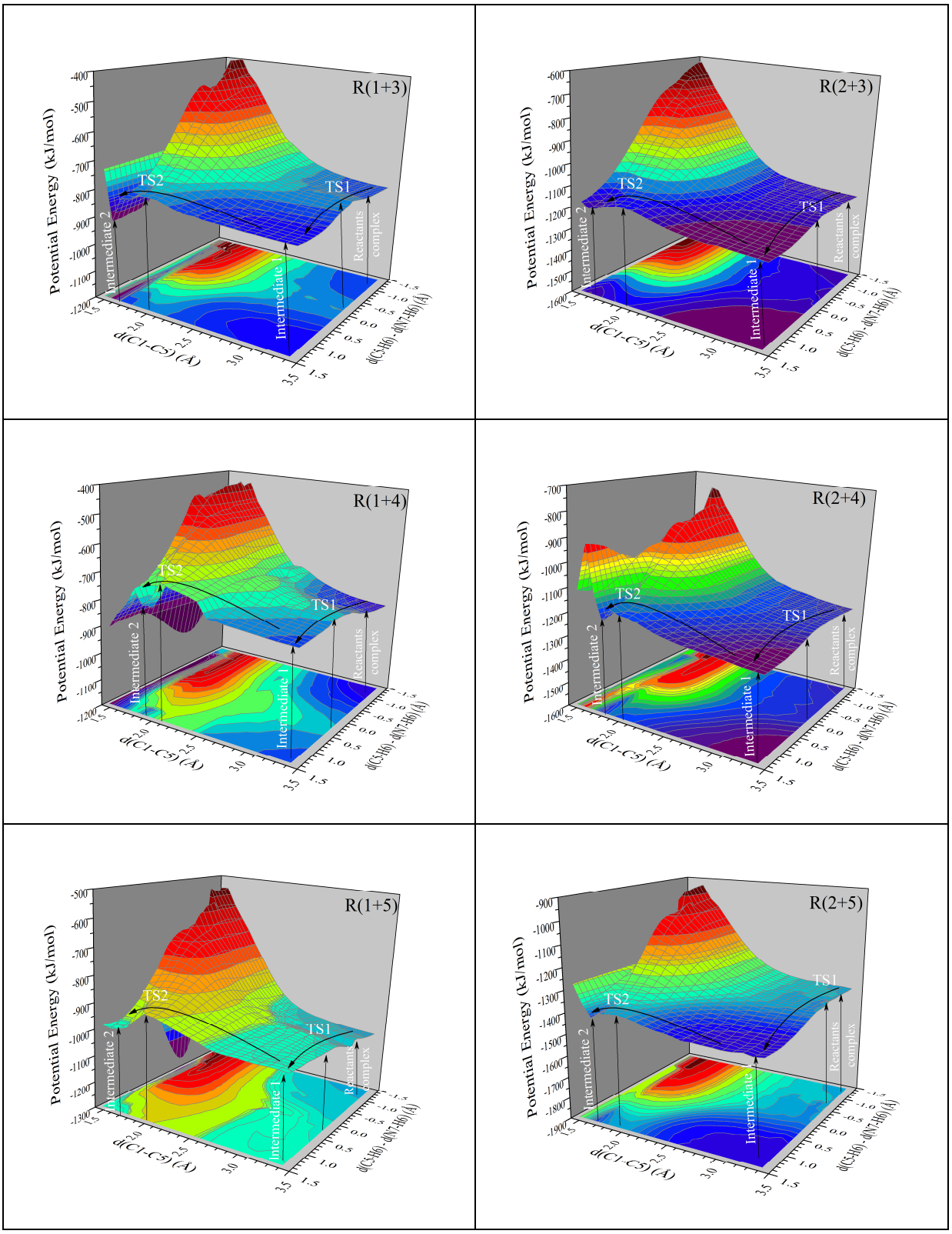

Figure S1. Potential energy surfaces for the conversion from reactants to intermediate 2 for the 6 studied reactions obtained at AM1 level.