SUPPORTING INFORMATION:

Quantum Chemical Molecular Dynamics Simulations of Dynamic Fullerene Self-Assembly in Benzene Combustion

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TABLE S1. Absolute and relative energies from NCC-DFTB calculations, compared to B3LYP/6-311G** data by Kislov *et al.* from Reference 41. We follow exactly the same naming of species as in their paper. The following data was not included in the evaluation of RMSD and R^2 values: The cases involving H₂ abstraction from A0, namely A53, A54, AZ, and corresponding transition states, were omitted from the comparison due to the well-documented problem of DFTB to reproduce the binding energy of H₂ correctly. Entries marked in red represent cases where DFTB transition state optimizations failed. Entries marked in blue represent cases where DFTB continued to converge to chemically different species.

TABLE S2. Absolute and relative energies from SCC-DFTB calculations, compared to B3LYP/6-311G** data by Kislov *et al.* from Reference 41. For more details see Table Caption S1.

TABLE S3. Absolute and relative energies from NCC-DFTB calculations, compared to G3(MP2,CC)/B3LYP/6-311G** data by Kislov *et al.* from Reference 41. For more details see Table Caption S1.

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TABLE S4. Absolute and relative energies from SCC-DFTB calculations, compared to G3(MP2,CC)//B3LYP/6-311G** data by Kislov *et al.* from Reference 41. For more details see Table Caption S1.

FIGURE S1. $\Delta E(\text{NCC-DFTB})$ (ordinate) vs $\Delta E(\text{B3LYP})$ (abscissa) from Table S1. Units are in [kcal/mol].

FIGURE S2. $\Delta E(\text{SCC-DFTB})$ (ordinate) vs $\Delta E(\text{B3LYP})$ (abscissa) from Table S2. Units are in [kcal/mol].

FIGURE S3. $\Delta E(\text{NCC-DFTB})$ (ordinate) vs $\Delta E(\text{G3(MP2,CC)})$ (abscissa) from Table S3. Units are in [kcal/mol].

FIGURE S4. $\Delta E(\text{SCC-DFTB})$ (ordinate) vs $\Delta E(\text{G3(MP2,CC)})$ (abscissa) from Table S4. Units are in [kcal/mol].

FIGURE S5. $\Delta E(\text{B3LYP})$ (ordinate) vs $\Delta E(\text{G3(MP2,CC)})$ (abscissa) from data by Kislov *et al.* from Reference 41. Units are in [kcal/mol].

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FIGURE S6. Structures of the hydrocarbons species formed at the end of 5.00 ps of simulations with $T_n = 3000$ K for different initial geometries. Smaller species like C_2H , C_2H_2 are not shown.

FIGURE S7. Reactions/collisions statistics at $T_n = 2500$ K (top) and $T_n = 3000$ K (bottom). Averaged over 20 simulations.

FIGURE S8. Carbon type count (black: sp , red: sp^2 , and green: sp^3 type carbons) as a function of time for selected successful trajectories at $T_n = 2500$ K.

FIGURE S9. Ring count statistics as a function of time for selected successful trajectories with $T_n = 2500$ K.

FIGURE S10. Carbon type count (black: sp , red: sp^2 , and green: sp^3 type carbons) as a function of time for selected unsuccessful trajectories at $T_n = 2500$ K.

FIGURE S11. Ring count statistics as a function of time for selected unsuccessful trajectories with $T_n = 2500$ K.

FIGURE S12. Carbon type count (black: sp , red: sp^2 , and green: sp^3 type carbons) as a function of time for selected successful trajectories at $T_n = 3000$ K.

FIGURE S13. Ring count statistics as a function of time for selected successful trajectories with $T_n = 3000$ K.

FIGURE S14. Carbon type count (black: sp , red: sp^2 , and green: sp^3 type carbons) as a function of time for selected unsuccessful trajectories at $T_n = 3000$ K.

FIGURE S15. Ring count statistics as a function of time for selected unsuccessful trajectories with $T_n = 3000$ K.

FIGURE S16. Carbon type count (black: sp , red: sp^2 , and green: sp^3 type carbons) and ring count statistics as a function of time for successful benchmark BSN2500g1_n trajectories with $T_n = T_e = 2500$ K. SCC-DFTB up to 15 ps, followed by NCC-DFTB for the carbon-only system.

TABLE S1. Absolute and relative energies from NCC-DFTB calculations, compared to B3LYP/6-311G** data by Kislov *et al.* from Reference 41. We follow exactly the same naming of species. The following data was not included in the evaluation of RMSD and R^2 values: The cases involving H_2 abstraction from A0, namely A53, A54, AZ, and corresponding transition states, were omitted from the comparison due to the well-documented problem of DFTB to reproduce the binding energy of H_2 correctly. Entries marked in red represent cases where DFTB transition state optimizations failed. Entries marked in blue represent cases where DFTB continued to converge to chemically different species.

Structure	E(NCC-DFTB //B3LYP) [ha]	E(NCC-DFTB) opt'd [ha]	ΔE (NCC-DFTB//B3LYP) [kcal/mol]	ΔE (NCC-DFTB opt'd) [kcal/mol]	E(B3LYP) [ha] Kislov&Mebel	ΔE (B3LYP) [kcal/mol]	$\Delta\Delta E$ (DFTB-B3LYP) [kcal/mol]	$\Delta\Delta E^2$
H	-0.2386	-0.2386			-0.50215593			
H2	-0.674955	-0.674956			-1.179571022			
CH3	-2.742036	-2.742116			-39.85375754			
CPDyl	-10.391429	-10.392725			-193.5129833			
CPD	-10.819489	-10.820608	17.35	17.58	-194.1537205	10.33	7.25	52.60
TS_CPD+CPDyl-A0	-21.21976	-21.220559	11.81	13.05	-387.6502145	20.67	-7.63	58.16
TS_CPD+CPDyl-A55	Error				-387.6406579			
A0	-21.238579	-21.241356	0.00	0.00	-387.6831668	0.00	0.00	0.00
TS_A0-A1	-21.226183	-21.228602	7.78	8.00	-387.6538881	18.37	-10.37	107.49
TS_A0-A20	-21.203174	-21.200525	22.21	25.62	-387.6312118	32.60	-6.98	48.71
TS_A0-A43	Error				-387.6312419			
TS_A0-A56	-21.167984	-21.172729	44.29	43.06	-387.6155363	42.43	0.63	0.39
TS_A0-S2	-21.156313	-21.161752	51.61	49.94	-387.6044564	49.38	0.56	0.31
A1	-21.245978	-21.249258	-4.64	-4.96	-387.6833916	-0.14	-4.82	23.20
TS_A1-A2	-21.167938	-21.170979	44.32	44.16	-387.5962673	54.52	-10.37	107.46
A2	-21.222081	-21.225176	10.35	10.15	-387.658386	15.55	-5.40	29.12
TS_A2-A3	-21.163897	-21.167282	46.86	46.47	-387.5957155	54.87	-8.39	70.44
TS_A2-A9	-21.188226	-21.190394	31.59	31.97	-387.6367769	29.11	2.87	8.23
A3	-21.210614	-21.214197	17.55	17.04	-387.6631602	12.55	4.49	20.14
TS_A3-A4	-21.187387	-21.188413	32.12	33.22	-387.617932	40.93	-7.71	59.47
TS_A3-A5	-21.187966	-21.186229	31.76	34.59	-387.6183999	40.64	-6.05	36.58
TS_A3-A6	-21.197413	-21.198921	25.83	26.62	-387.6476678	22.27	4.35	18.94
A4	-21.273939	-21.276509	-22.19	-22.06	-387.7089807	-16.20	-5.86	34.33

TS_A4-A5	-21.222691	-21.227428	9.97	8.74	-387.6436334	24.80	-16.07	258.09
A5	-21.288023	-21.290274	-31.02	-30.69	-387.7230605	-25.03	-5.66	32.06
TS_A5-IND	-21.247221	-21.230556			-387.6861442			
A6	-21.225002	-21.227961	8.52	8.40	-387.6751134	5.05	3.35	11.23
TS_A6-A7	-21.196155	-21.197211	26.62	27.70	-387.6446155	24.19	3.51	12.32
A7	-21.221579	-21.224302	10.67	10.70	-387.6701566	8.16	2.54	6.44
TS_A7-A8	-21.167065	-21.174459	44.87	41.97	-387.6144688	43.10	-1.13	1.28
A8	-20.911493	-20.913434			-387.1196667			
TS_A8-A53	Error				-387.6185529			
TS_A8-A54	-21.174501	-21.18155	40.20	37.52	-387.6216745	38.58	-1.06	1.12
A9	-21.191265	-21.194187	29.69	29.59	-387.6439835	24.58	5.01	25.10
TS_A9-A10	-21.163567	-21.165429	47.06	47.64	-387.6111957	45.16	2.48	6.16
A10	-21.186839	-21.190052	32.46	32.19	-387.6461909	23.20	8.99	80.81
TS_A10-A11	-21.172121	-21.16794	41.70	46.06	-387.6063456	48.20	-2.14	4.56
TS_A10-A13	-21.104936	-21.109249	83.85	82.89	-387.5673798	72.65	10.24	104.84
TS_A10-A17	-21.08054	-21.08862	99.16	95.83	-387.5289742	96.74	-0.91	0.84
A11	-21.230629	-21.233492	4.99	4.93	-387.6809609	1.38	3.55	12.60
TS_A11-A12	-21.210955	-21.211112	17.33	18.98	-387.6590842	15.11	3.87	14.94
A12	-21.280487	-21.28253	-26.29	-25.83	-387.7176407	-21.63	-4.20	17.67
TS_A12-IND	-21.24567	-21.236943	-4.45	2.77	-387.6843852	-0.76	3.53	12.48
A13	-21.180568	-21.184466	36.40	35.69	-387.6388679	27.79	7.90	62.41
TS_A13-A14	-21.134468	-21.137115	65.32	65.40	-387.5739319	68.53	-3.13	9.82
TS_A13-A15	-21.17871	-21.179799	37.56	38.62	-387.6226758	37.95	0.67	0.45
TS_A13-A17	-21.080228	-21.122815			-387.5288685			
A14	-21.232144	-21.234493	4.04	4.31	-387.682586	0.36	3.94	15.54
TS_A14-A12a	-21.211973	-21.211411	16.69	18.79	-387.658912	15.22	3.57	12.75
A15	-21.271219	-21.273772	-20.48	-20.34	-387.7060646	-14.37	-5.97	35.66
TS_A15-A16	-21.220998	-21.226875	11.03	9.09	-387.6430303	25.18	-16.10	259.10
A16	-21.28537	-21.288037	-29.36	-29.29	-387.7229263	-24.95	-4.34	18.86
TS_A16-A12a	-21.2153	-21.240832			-387.6404937			
A17	-21.218639	-21.221306	12.51	12.58	-387.6727363	6.54	6.04	36.43
TS_A17-A18	-21.163652	-21.167328	47.01	46.45	-387.6017992	51.05	-4.60	21.21
TS_A17-A19	-21.210352	-21.212351	17.71	18.20	-387.6637826	12.16	6.04	36.44
A18	-21.218539	-21.221608	12.57	12.39	-387.6696697	8.47	3.92	15.38
TS_A18-A5	-21.199652	-21.20505	24.42	22.78	-387.6523902	19.31	3.47	12.04
A19	-21.251341	-21.253772	-8.01	-7.79	-387.6948668	-7.34	-0.45	0.20
TS_A19-A5a	-21.234397	-21.235365	2.62	3.76	-387.6631136	12.58	-8.82	77.84
A20	-21.207359	-21.211479	19.59	18.75	-387.6496549	21.03	-2.28	5.20
TS_A20-A21	-21.196818	-21.194871	26.20	29.17	-387.615713	42.32	-13.16	173.08

TS_A20-A24	-21.105595	-21.111039	83.44	81.76	-387.534147	93.50	-11.73	137.69
TS_A20-A31	-21.106048	-21.111378	83.15	81.55	-387.5340276	93.57	-12.02	144.53
TS_A20-A38	-21.136233	-21.140009	64.21	63.59	-387.5834817	62.54	1.04	1.09
TS_A20-A39	-21.136015	-21.139597	64.35	63.84	-387.5836214	62.46	1.39	1.93
A21	-21.246952	-21.250066	-5.25	-5.46	-387.6852285	-1.29	-4.17	17.40
TS_A21-A22	-21.164945	-21.168101	46.20	45.96	-387.5953958	55.07	-9.11	82.95
A22	-21.219416	-21.222294	12.02	11.96	-387.6570404	16.39	-4.43	19.64
TS_A22-A23	-21.188212	-21.19091	31.60	31.65	-387.6204733	39.33	-7.68	59.05
TS_A22-A26	-21.179394	-21.181071	37.13	37.82	-387.6307276	32.90	4.92	24.23
A23	-21.21067	-21.214498	17.51	16.85	-387.6628973	12.72	4.13	17.09
TS_A23-A25	-21.205415	-21.206324	20.81	21.98	-387.6565656	16.69	5.29	27.98
TS_A23-A4a	-21.184521	-21.18696	33.92	34.13	-387.611435	45.01	-10.88	118.30
A24	-21.208805	-21.211841	18.68	18.52	-387.6465299	22.99	-4.47	19.97
TS_A24-A22	-21.102489	-21.108336	85.38	83.46	-387.5290636	96.69	-13.23	174.97
A25	-21.229156	-21.232049	5.91	5.84	-387.6799062	2.05	3.79	14.39
TS_A25-A7a	-21.204104	-21.205486	21.63	22.51	-387.6527619	19.08	3.43	11.76
A26	-21.189294	-21.191856	30.92	31.06	-387.6427983	25.33	5.73	32.82
TS_A26-A27	-21.145893	-21.147351	58.15	58.98	-387.5964166	54.43	4.55	20.72
A27	-21.15402	-21.158616	53.05	51.91	-387.6126732	44.23	7.68	59.04
TS_A27-A28	-21.070079	-21.074505	105.72	104.68	-387.5343654	93.36	11.32	128.24
TS_A27-A29	-21.065362	-21.185526			-387.507428			
A28	-21.145264	-21.148457	58.55	58.29	-387.6061631	48.31	9.97	99.46
TS_A28-A29	-21.09636	-21.128457			-387.5413297			
A29	-21.178768	-21.182543	37.53	36.90	-387.633194	31.35	5.55	30.76
TS_A29-A18	-21.154559	-21.1575	52.71	52.61	-387.5914384	57.55	-4.94	24.40
TS_A29-A30	-21.16225	-21.164611	47.89	48.15	-387.6154472	42.49	5.66	32.07
A30	-21.252575	-21.254946	-8.78	-8.53	-387.6950858	-7.48	-1.05	1.10
TS_A30-A5	-21.234791	-21.235809	2.38	3.48	-387.6629313	12.70	-9.22	84.93
A31	-21.208765	-21.211911	18.71	18.47	-387.6459374	23.36	-4.88	23.85
TS_A31-A32	-21.11139	-21.15172			-387.5362379			
A32	-21.234822	-21.238069	2.36	2.06	-387.6699987	8.26	-6.20	38.43
TS_A32-A33	-21.19846	-21.200358	25.17	25.72	-387.6312027	32.60	-6.88	47.34
A33	-21.218181	-21.223456	12.80	11.23	-387.6735784	6.02	5.21	27.19
TS_A33-A34	-21.195814	-21.197158	26.83	27.73	-387.6237149	37.30	-9.57	91.59
TS_A33-A35	-21.216455	-21.217938	13.88	14.69	-387.6688722	8.97	5.72	32.77
A34	-21.285361	-21.288037	-29.35	-29.29	-387.7229264	-24.95	-4.34	18.86
TS_A34-A12	-21.215299	-21.240832			-387.6404937			
A35	-21.244407	-21.247331	-3.66	-3.75	-387.6961248	-8.13	4.38	19.19
TS_A35-A36	-21.216194	-21.218034	14.04	14.63	-387.6652988	11.21	3.42	11.71

A36	-21.2282	-21.2309	6.51	6.56	-387.6795194	2.29	4.27	18.25
TS_A36-A37	-21.1688	-21.175191	43.78	41.51	-387.6174913	41.21	0.31	0.09
A37	-20.912576	-20.914535	54.84	55.35	-387.1206897	37.85	17.50	306.41
TS_A37-A53	-21.164478	-21.166983	46.49	46.66	-387.6194164	40.00	6.66	44.42
TS_A37-A54	-21.176184	-21.183771	39.15	36.13	-387.6227198	37.93	-1.80	3.22
A38	-21.1778	-21.183576	38.13	36.25	-387.6351419	30.13	6.12	37.46
TS_A38-A40	-21.156753	-21.162774	51.34	49.30	-387.6045664	49.31	-0.01	0.00
A39	-21.178155	-21.183985	37.91	36.00	-387.6359914	29.60	6.40	40.92
TS_A39-A40	-21.157799	-21.163045	50.68	49.13	-387.6069718	47.81	1.33	1.76
A40	-21.243937	-21.246377	-3.36	-3.15	-387.6919575	-5.52	2.37	5.59
TS_A40-A41	-21.174846	-21.178807	39.99	39.24	-387.6202889	39.45	-0.21	0.04
TS_A40-A42	-21.165755	-21.168346	45.69	45.81	-387.6135456	43.68	2.13	4.52
A41	-20.911254	-20.913588	55.67	55.94	-387.1223458	36.81	19.14	366.26
TS_A41-A54	-21.175869	-21.183194	39.34	36.49	-387.6246344	36.72	-0.23	0.05
A42	-20.904631	-20.906846	59.82	60.17	-387.1135444	42.33	17.85	318.47
TS_A42-A54	-21.166528	-21.174835	45.21	41.74	-387.6158799	42.22	-0.48	0.23
A43	-21.206645	-21.210842	20.04	19.14	-387.6495284	21.11	-1.96	3.84
TS_A43-A2a	-21.140606	-21.144993	61.47	60.46	-387.572637	69.35	-8.89	79.00
TS_A43-A44	-21.142709	-21.1467	60.15	59.39	-387.575552	67.52	-8.13	66.10
TS_A43-A51	-21.13527	-21.139269	64.82	64.05	-387.582012	63.47	0.58	0.34
TS_A43-A52	-21.134399	-21.138363	65.36	64.62	-387.5808446	64.20	0.42	0.18
A44	-21.237862	-21.241339	0.45	0.01	-387.6717389	7.17	-7.16	51.26
TS_A44-A45	-21.174326	-21.17771	40.31	39.93	-387.609167	46.43	-6.50	42.20
TS_A44-A47	-21.19664	-21.18116			-387.6460236			
TS_A44-A48	-21.150552	-21.163308	55.23	48.97	-387.5949609	55.34	-6.37	40.62
A45	-21.217243	-21.220806	13.39	12.89	-387.6739754	5.77	7.13	50.79
TS_A45-A12a	-21.191143	-21.190353	29.76	32.00	-387.6231579	37.65	-5.65	31.93
TS_A45-A34	-21.200173	-21.199634	24.10	26.18	-387.63076	32.88	-6.70	44.94
TS_A45-A46	-21.207689	-21.209871	19.38	19.75	-387.6592232	15.02	4.73	22.39
A46	-21.239899	-21.242953	-0.83	-1.00	-387.6909559	-4.89	3.88	15.09
TS_A46-A36	-21.207742	-21.209167	19.35	20.20	-387.657385	16.18	4.02	16.16
A47	-21.195694	-21.195931	26.91	28.50	-387.6466745	22.90	5.60	31.41
TS_A47-A48	-21.164368	-21.166369	46.56	47.05	-387.6125737	44.29	2.76	7.60
A48	-21.18783	-21.191057	31.84	31.56	-387.6471912	22.57	8.99	80.76
TS_A48-A18	-21.170894	-21.168257	42.47	45.86	-387.6038974	49.73	-3.87	14.99
TS_A48-A49	-21.105491	-21.109949	83.50	82.45	-387.5686453	71.85	10.59	112.24
A49	-21.181086	-21.18559	36.07	34.99	-387.6398163	27.20	7.79	60.68
TS_A49-A50	-21.129782	-21.133242	68.26	67.83	-387.5688567	71.72	-3.89	15.11
A50	-21.219686	-21.222331	11.85	11.94	-387.6707456	7.79	4.14	17.17

TS_A50-A5a	-21.200847	-21.205322	23.67	22.61	-387.6530053	18.92	3.68	13.58
A51	-21.177696	-21.183279	38.20	36.44	-387.6344945	30.54	5.90	34.82
TS_A51-A40	-21.16093	-21.165727	48.72	47.45	-387.6054925	48.73	-1.28	1.65
A52	-21.17744	-21.183193	38.36	36.49	-387.6350152	30.21	6.28	39.45
TS_A52-A40	-21.158396	-21.163929	50.31	48.58	-387.6055819	48.68	-0.10	0.01
A53	-20.502264	-20.504563	38.50	38.80	-386.4933897	6.40	32.39	
TS_A53-AZ	-20.433985	-20.430889			-386.4311065			
A54	-20.514734	-20.516974	30.67	31.01	-386.5048801	-0.81	31.82	
TS_A54-AZ	-20.436772	-20.430889	79.59	85.02	-386.4336733	43.87	41.15	
A55	-21.21328	-21.216402	15.87	15.66	-387.661915	13.33	2.32	5.40
TS_A55-A0	-21.166576	-21.173859	45.18	42.35	-387.6022083	50.79	-8.45	71.33
TS_A55-S0	-21.147189	-21.151025	57.34	56.67	-387.5984868	53.13	3.55	12.57
A56	-21.211232	-21.214195	17.16	17.04	-387.6696536	8.48	8.56	73.32
AZ	-20.16948	-20.17159	97.59	98.01	-385.9308677	44.28	53.73	
INDENE	-18.487032	-18.488439	5.97	6.78	-347.8474215	-11.30	18.08	326.80
S0	-20.890093	-20.8926	68.94	69.11	-387.0977771	52.22	16.89	285.31
S2	-20.897356	-20.899958	64.39	64.50	-387.1021939	49.45	15.05	226.38
RMSD								7.10

TABLE S2. Absolute and relative energies from SCC-DFTB calculations, compared to B3LYP/6-311G** data by Kislov *et al.* from Reference 41. For more details see Table Caption S1.

Structure	E(SCC-DFTB //B3LYP) [ha]	E(SCC-DFTB) opt'd [ha]	$\Delta E(\text{SCC-DFTB//B3LYP})$ [kcal/mol]	$\Delta E(\text{SCC-DFTB opt'd})$ [kcal/mol]	E(B3LYP) [ha] Kislov&Mebel	$\Delta E(\text{B3LYP})$ [kcal/mol]	$\Delta\Delta E$ (DFTB-B3LYP) [kcal/mol]	$\Delta\Delta E^2$
H	-0.2386	-0.2386			-0.50215593			
H2	-0.674955	-0.674956			-1.179571022			
CH3	-2.740365	-2.740423			-39.85375754			
CPDyl	-10.384186	-10.385404			-193.5129833			
CPD	-10.811267	-10.812281	18.21	18.59	-194.1537205	10.33	8.26	68.30
TS_CPD+CPDyl-A0	-21.199693	-21.199477	15.55	17.47	-387.6502145	20.67	-3.21	10.28
TS_CPD+CPDyl-A55	-21.189066	-21.187347	22.22	25.08	-387.6406579	26.67	-1.59	2.53
A0	-21.22448	-21.22732	0.00	0.00	-387.6831668	0.00	0.00	0.00
TS_A0-A1	-21.2116	-21.213999	8.08	8.36	-387.6538881	18.37	-10.01	100.24
TS_A0-A20	-21.189739	-21.187692	21.80	24.86	-387.6312118	32.60	-7.73	59.82
TS_A0-A43	-21.188585	Error			-387.6312419			
TS_A0-A56	-21.153834	-21.15796	44.32	43.52	-387.6155363	42.43	1.09	1.18
TS_A0-S2	-21.137364	-21.139659	54.66	55.00	-387.6044564	49.38	5.62	31.54
A1	-21.233374	-21.237006	-5.58	-6.08	-387.6833916	-0.14	-5.94	35.24
TS_A1-A2	-21.149059	-21.152463	47.32	46.97	-387.5962673	54.52	-7.56	57.09
A2	-21.208848	-21.212531	9.81	9.28	-387.658386	15.55	-6.27	39.30
TS_A2-A3	-21.150327	-21.153259	46.52	46.47	-387.5957155	54.87	-8.40	70.58
TS_A2-A9	-21.173895	-21.176131	31.74	32.12	-387.6367769	29.11	3.01	9.07
A3	-21.200304	-21.203704	15.17	14.82	-387.6631602	12.55	2.26	5.13
TS_A3-A4	-21.168273	-21.170848	35.26	35.43	-387.617932	40.93	-5.50	30.23
TS_A3-A5	-21.176975	-21.175417	29.81	32.56	-387.6183999	40.64	-8.07	65.14
TS_A3-A6	-21.186388	-21.18767	23.90	24.88	-387.6476678	22.27	2.60	6.78
A4	-21.262852	-21.265453	-24.07	-23.92	-387.7089807	-16.20	-7.73	59.74
TS_A4-A5	-21.202971	-21.205896	13.49	13.44	-387.6436334	24.80	-11.36	129.09
A5	-21.277249	-21.279554	-33.11	-32.77	-387.7230605	-25.03	-7.74	59.94
TS_A5-IND	-21.235816	Error			-387.6861442			
A6	-21.213748	-21.217009	6.73	6.47	-387.6751134	5.05	1.42	2.01
TS_A6-A7	-21.183972	-21.184917	25.42	26.60	-387.6446155	24.19	2.42	5.84

A7	-21.209947	-21.212951	9.12	9.02	-387.6701566	8.16	0.85	0.73
TS_A7-A8	-21.154865	-21.154656	43.68	45.59	-387.6144688	43.10	2.49	6.19
A8	-20.901783	-20.903889	52.76	53.22	-387.1196667	38.49	14.74	217.15
TS_A8-A53	-21.152165	-21.153034	45.37	46.61	-387.6185529	40.54	6.07	36.83
TS_A8-A54	-21.156328	-21.158615	42.76	43.11	-387.6216745	38.58	4.53	20.48
A9	-21.178616	-21.181857	28.78	28.52	-387.6439835	24.58	3.94	15.52
TS_A9-A10	-21.151403	-21.153458	45.85	46.34	-387.6111957	45.16	1.19	1.41
A10	-21.175006	-21.178151	31.04	30.85	-387.6461909	23.20	7.65	58.52
TS_A10-A11	-21.161063	-21.157059	39.79	44.08	-387.6063456	48.20	-4.12	16.94
TS_A10-A13	-21.088754	-21.093381	85.16	84.03	-387.5673798	72.65	11.39	129.70
TS_A10-A17	-21.068753	-21.076484	97.70	94.64	-387.5289742	96.74	-2.11	4.44
A11	-21.219813	-21.222803	2.93	2.83	-387.6809609	1.38	1.45	2.10
TS_A11-A12	-21.198458	-21.198883	16.33	17.84	-387.6590842	15.11	2.73	7.46
A12	-21.269087	-21.271121	-27.99	-27.48	-387.7176407	-21.63	-5.85	34.25
TS_A12-IND	-21.234275	Error			-387.6843852			
A13	-21.168613	-21.172816	35.05	34.20	-387.6388679	27.79	6.40	41.00
TS_A13-A14	-21.122732	-21.124354	63.84	64.60	-387.5739319	68.53	-3.93	15.47
TS_A13-A15	-21.164162	-21.165245	37.84	38.95	-387.6226758	37.95	0.99	0.99
TS_A13-A17	-21.068309	-21.074028	97.98	96.18	-387.5288685	96.81	-0.63	0.40
A14	-21.221698	-21.224116	1.75	2.01	-387.682586	0.36	1.65	2.71
TS_A14-A12a	-21.199684	-21.199507	15.56	17.45	-387.658912	15.22	2.23	4.98
A15	-21.260395	-21.263029	-22.53	-22.40	-387.7060646	-14.37	-8.04	64.61
TS_A15-A16	-21.203493	-21.206887	13.17	12.82	-387.6430303	25.18	-12.36	152.82
A16	-21.275125	-21.277671	-31.78	-31.59	-387.7229263	-24.95	-6.65	44.16
TS_A16-A12a	-21.190321	Error			-387.6404937			
A17	-21.207446	-21.210272	10.69	10.70	-387.6727363	6.54	4.15	17.24
TS_A17-A18	-21.145557	-21.14867	49.52	49.35	-387.6017992	51.05	-1.71	2.91
TS_A17-A19	-21.198355	-21.20023	16.39	17.00	-387.6637826	12.16	4.83	23.37
A18	-21.207148	-21.210302	10.87	10.68	-387.6696697	8.47	2.21	4.88
TS_A18-A5	-21.188422	-21.192624	22.62	21.77	-387.6523902	19.31	2.46	6.05
A19	-21.240018	-21.242495	-9.75	-9.52	-387.6948668	-7.34	-2.18	4.75
TS_A19-A5a	-21.216382	-21.217771	5.08	5.99	-387.6631136	12.58	-6.59	43.43
A20	-21.195011	-21.199642	18.49	17.37	-387.6496549	21.03	-3.66	13.40
TS_A20-A21	-21.184773	-21.183109	24.91	27.74	-387.615713	42.32	-14.58	212.66
TS_A20-A24	-21.088736	-21.093946	85.17	83.68	-387.534147	93.50	-9.82	96.36
TS_A20-A31	-21.08927	-21.094222	84.83	83.51	-387.5340276	93.57	-10.06	101.29
TS_A20-A38	-21.121337	-21.125312	64.71	64.00	-387.5834817	62.54	1.46	2.12
TS_A20-A39	-21.121485	-21.125225	64.62	64.06	-387.5836214	62.46	1.60	2.56
A21	-21.235633	-21.239231	-7.00	-7.47	-387.6852285	-1.29	-6.18	38.19

TS_A21-A22	-21.14763	-21.151218	48.22	47.75	-387.5953958	55.07	-7.32	53.60
A22	-21.206778	-21.210228	11.11	10.72	-387.6570404	16.39	-5.67	32.13
TS_A22-A23	-21.175763	-21.178341	30.57	30.73	-387.6204733	39.33	-8.60	74.04
TS_A22-A26	-21.166948	-21.169051	36.10	36.56	-387.6307276	32.90	3.66	13.38
A23	-21.199529	-21.203416	15.65	15.00	-387.6628973	12.72	2.28	5.20
TS_A23-A25	-21.193717	-21.194499	19.30	20.59	-387.6565656	16.69	3.90	15.23
TS_A23-A4a	-21.163574	-21.167209	38.21	37.71	-387.611435	45.01	-7.29	53.16
A24	-21.197196	-21.200736	17.12	16.68	-387.6465299	22.99	-6.31	39.78
TS_A24-A22	-21.0851	-21.089787	87.45	86.29	-387.5290636	96.69	-10.40	108.08
A25	-21.217599	-21.220806	4.32	4.09	-387.6799062	2.05	2.04	4.17
TS_A25-A7a	-21.192006	-21.193153	20.37	21.44	-387.6527619	19.08	2.36	5.57
A26	-21.177523	-21.180694	29.46	29.25	-387.6427983	25.33	3.93	15.41
TS_A26-A27	-21.133327	-21.134083	57.19	58.50	-387.5964166	54.43	4.07	16.56
A27	-21.140418	-21.144352	52.74	52.05	-387.6126732	44.23	7.83	61.25
TS_A27-A28	-21.053511	-21.058124	107.27	106.16	-387.5343654	93.36	12.80	163.73
TS_A27-A29	-21.051726	-21.058952	108.39	105.64	-387.507428	110.26	-4.62	21.39
A28	-21.132923	-21.136514	57.44	56.97	-387.6061631	48.31	8.66	74.99
TS_A28-A29	-21.08308	-21.088575	88.72	87.05	-387.5413297	88.99	-1.94	
A29	-21.167717	-21.171465	35.61	35.04	-387.633194	31.35	3.69	13.62
TS_A29-A18	-21.136693	-21.13962	55.08	55.02	-387.5914384	57.55	-2.53	6.39
TS_A29-A30	-21.150447	-21.152629	46.45	46.86	-387.6154472	42.49	4.37	19.13
A30	-21.240881	-21.24331	-10.29	-10.03	-387.6950858	-7.48	-2.55	6.52
TS_A30-A5	-21.21657	-21.217908	4.96	5.91	-387.6629313	12.70	-6.79	46.11
A31	-21.197086	-21.200696	17.19	16.70	-387.6459374	23.36	-6.65	44.27
TS_A31-A32	-21.093855	-21.099151	81.96	80.41	-387.5362379	92.18	-11.77	138.54
A32	-21.223234	-21.226859	0.78	0.29	-387.6699987	8.26	-7.97	63.56
TS_A32-A33	-21.186685	-21.188021	23.71	24.66	-387.6312027	32.60	-7.95	63.14
A33	-21.207791	-21.212764	10.47	9.13	-387.6735784	6.02	3.12	9.71
TS_A33-A34	-21.174351	-21.177861	31.45	31.03	-387.6237149	37.30	-6.27	39.31
TS_A33-A35	-21.205651	-21.20694	11.81	12.79	-387.6688722	8.97	3.82	14.58
A34	-21.275115	-21.277668	-31.77	-31.59	-387.7229264	-24.95	-6.64	44.13
TS_A34-A12	-21.190323	Error			-387.6404937			
A35	-21.233805	-21.236964	-5.85	-6.05	-387.6961248	-8.13	2.08	4.32
TS_A35-A36	-21.204746	-21.206033	12.38	13.36	-387.6652988	11.21	2.15	4.60
A36	-21.216943	-21.219812	4.73	4.71	-387.6795194	2.29	2.42	5.87
TS_A36-A37	-21.155791	-21.155425	43.10	45.11	-387.6174913	41.21	3.90	15.23
A37	-20.90288	-20.905005	52.07	52.52	-387.1206897	37.85	14.68	215.43
TS_A37-A53	-21.152745	-21.154116	45.01	45.93	-387.6194164	40.00	5.93	35.18
TS_A37-A54	-21.157296	-21.159548	42.15	42.52	-387.6227198	37.93	4.60	21.12

A38	-21.165441	-21.17088	37.04	35.41	-387.6351419	30.13	5.28	27.88
TS_A38-A40	-21.143246	-21.146742	50.97	50.56	-387.6045664	49.31	1.24	1.54
A39	-21.166016	-21.171421	36.68	35.07	-387.6359914	29.60	5.47	29.96
TS_A39-A40	-21.144773	-21.147502	50.01	50.08	-387.6069718	47.81	2.27	5.17
A40	-21.233116	-21.235853	-5.42	-5.35	-387.6919575	-5.52	0.16	0.03
TS_A40-A41	-21.159744	-21.157837	40.62	43.59	-387.6202889	39.45	4.14	17.17
TS_A40-A42	-21.150203	-21.149922	46.60	48.56	-387.6135456	43.68	4.88	23.81
A41	-20.901564	-20.903953	52.90	53.18	-387.1223458	36.81	16.38	268.19
TS_A41-A54	-21.154312	-21.159117	44.02	42.79	-387.6246344	36.72	6.07	36.81
A42	-20.894607	-20.896961	57.27	57.57	-387.1135444	42.33	15.24	232.30
TS_A42-A54	-21.148187	-21.153515	47.87	46.31	-387.6158799	42.22	4.09	16.72
A43	-21.194442	-21.199104	18.85	17.70	-387.6495284	21.11	-3.40	11.57
TS_A43-A2a	-21.127405	-21.132046	60.91	59.78	-387.572637	69.35	-9.57	91.62
TS_A43-A44	-21.130362	-21.134552	59.05	58.20	-387.575552	67.52	-9.32	86.77
TS_A43-A51	-21.12081	-21.124764	65.04	64.34	-387.582012	63.47	0.88	0.77
TS_A43-A52	-21.12044	-21.124404	65.28	64.57	-387.5808446	64.20	0.37	0.14
A44	-21.225792	-21.229637	-0.82	-1.45	-387.6717389	7.17	-8.62	74.37
TS_A44-A45	-21.161497	-21.163872	39.52	39.81	-387.609167	46.43	-6.62	43.83
TS_A44-A47	-21.184084	Error			-387.6460236			
TS_A44-A48	-21.133972	-21.137363	56.79	56.44	-387.5949609	55.34	1.10	1.21
A45	-21.207393	-21.210674	10.72	10.44	-387.6739754	5.77	4.68	21.88
TS_A45-A12a	-21.179384	-21.17927	28.29	30.15	-387.6231579	37.65	-7.50	56.30
TS_A45-A34	-21.179298	-21.18149	28.35	28.75	-387.63076	32.88	-4.13	17.03
TS_A45-A46	-21.197347	-21.199295	17.02	17.58	-387.6592232	15.02	2.56	6.56
A46	-21.229514	-21.232756	-3.16	-3.41	-387.6909559	-4.89	1.48	2.18
TS_A46-A36	-21.196244	-21.197411	17.72	18.77	-387.657385	16.18	2.59	6.71
A47	-21.18366	-21.187785	25.61	24.80	-387.6466745	22.90	1.91	3.64
TS_A47-A48	-21.152793	-21.154861	44.98	45.46	-387.6125737	44.29	1.17	1.37
A48	-21.176465	-21.179751	30.13	29.85	-387.6471912	22.57	7.27	52.91
TS_A48-A18	-21.159778	-21.157486	40.59	43.81	-387.6038974	49.73	-5.92	35.04
TS_A48-A49	-21.089843	-21.094586	84.47	83.28	-387.5686453	71.85	11.43	130.57
A49	-21.169703	-21.174383	34.37	33.21	-387.6398163	27.20	6.01	36.18
TS_A49-A50	-21.117916	-21.120689	66.86	66.90	-387.5688567	71.72	-4.82	23.21
A50	-21.208606	-21.211272	9.96	10.07	-387.6707456	7.79	2.28	5.18
TS_A50-A5a	-21.189722	-21.193159	21.81	21.43	-387.6530053	18.92	2.51	6.30
A51	-21.165587	-21.170937	36.95	35.38	-387.6344945	30.54	4.84	23.40
TS_A51-A40	-21.144738	-21.149043	50.03	49.11	-387.6054925	48.73	0.38	0.14
A52	-21.165751	-21.171129	36.85	35.25	-387.6350152	30.21	5.04	25.44
TS_A52-A40	-21.145219	-21.148266	49.73	49.60	-387.6055819	48.68	0.92	0.85

A53	-20.492161	-20.494209	35.99	36.49	-386.4933897	6.40	30.08	
TS_A53-AZ	-20.417801	-20.405728	82.64	92.00	-386.4311065	45.48	46.52	
A54	-20.505008	-20.507083	27.93	28.41	-386.5048801	-0.81	29.22	
TS_A54-AZ	-20.414984	Error			-386.4336733			
A55	-21.198539	-21.20185	16.28	15.98	-387.661915	13.33	2.65	7.00
TS_A55-A0	-21.14438	-21.147654	50.26	49.98	-387.6022083	50.79	-0.81	0.66
TS_A55-S0	-21.130219	-21.130647	59.14	60.65	-387.5984868	53.13	7.52	56.62
A56	-21.199452	-21.202174	15.70	15.78	-387.6696536	8.48	7.30	53.27
AZ	-20.158659	-20.160212	95.53	96.34	-385.9308677	44.28	52.06	
INDENE	-18.478105	-18.47947	3.77	4.66	-347.8474215	-11.30	15.96	254.75
S0	-20.876227	-20.878592	68.80	69.10	-387.0977771	52.22	16.87	284.72
S2	-20.883488	-20.88582	64.24	64.56	-387.1021939	49.45	15.11	228.31
RMSD								6.62

TABLE S3. Absolute and relative energies from NCC-DFTB calculations, compared to G3(MP2,CC)//B3LYP/6-311G** data by Kislov *et al.* from Reference 41. For more details see Table Caption S1.

Structure	E(NCC-DFTB //B3LYP) [ha]	E(NCC-DFTB) opt'd [ha]	ΔE (NCC-DFTB//B3LYP) [kcal/mol]	ΔE (NCC-DFTB opt'd) [kcal/mol]	E(G3) [ha] Kislov&Mebel	ΔE (G3) [kcal/mol]	$\Delta\Delta E$ (DFTB-G3) [kcal/mol]	$\Delta\Delta E^2$
H	-0.2386	-0.2386			-0.49981792			
H2	-0.674955	-0.674956			-1.160783878			
CH3	-2.742036	-2.742116			-39.72580529			
CPDyl	-10.391429	-10.392725			-193.000814			
CPD	-10.819489	-10.820608	17.35	17.58	-193.62735	13.61	3.97	15.78
TS_CPD+CPDyl-A0	-21.21976	-21.220559	11.81	13.05	-386.6155802	21.51	-8.46	71.52
TS_CPD+CPDyl-A55	Error				-386.6092585			
A0	-21.238579	-21.241356	0.00	0.00	-386.6498561	0.00	0.00	0.00
TS_A0-A1	-21.226183	-21.228602	7.78	8.00	-386.6229969	16.85	-8.85	78.32
TS_A0-A20	-21.203174	-21.200525	22.21	25.62	-386.6040531	28.74	-3.12	9.73
TS_A0-A43	Error				-386.6044346			
TS_A0-A56	-21.167984	-21.172729	44.29	43.06	-386.5814665	42.91	0.15	0.02
TS_A0-S2	-21.156313	-21.161752	51.61	49.94	-386.5852735	40.52	9.42	88.82
A1	-21.245978	-21.249258	-4.64	-4.96	-386.6583224	-5.31	0.35	0.13
TS_A1-A2	-21.167938	-21.170979	44.32	44.16	-386.5777477	45.24	-1.09	1.18
A2	-21.222081	-21.225176	10.35	10.15	-386.6350767	9.27	0.88	0.77
TS_A2-A3	-21.163897	-21.167282	46.86	46.47	-386.5696747	50.31	-3.83	14.68
TS_A2-A9	-21.188226	-21.190394	31.59	31.97	-386.6142222	22.36	9.62	92.49
A3	-21.210614	-21.214197	17.55	17.04	-386.6340214	9.93	7.10	50.48
TS_A3-A4	-21.187387	-21.188413	32.12	33.22	-386.587554	39.09	-5.87	34.48
TS_A3-A5	-21.187966	-21.186229	31.76	34.59	-386.5878224	38.92	-4.33	18.78
TS_A3-A6	-21.197413	-21.198921	25.83	26.62	-386.6132901	22.94	3.68	13.56
A4	-21.273939	-21.276509	-22.19	-22.06	-386.6725726	-14.25	-7.80	60.88
TS_A4-A5	-21.222691	-21.227428	9.97	8.74	-386.6096697	25.21	-16.47	271.42
A5	-21.288023	-21.290274	-31.02	-30.69	-386.6830645	-20.84	-9.86	97.15
TS_A5-IND	-21.247221	-21.230556	-5.42		-386.6464921			
A6	-21.225002	-21.227961	8.52	8.40	-386.6389491	6.84	1.56	2.44
TS_A6-A7	-21.196155	-21.197211	26.62	27.70	-386.6092108	25.50	2.20	4.82

A7	-21.221579	-21.224302	10.67	10.70	-386.6360324	8.67	2.03	4.11
TS_A7-A8	-21.167065	-21.174459	44.87	41.97	-386.5873587	39.21	2.76	7.62
A8	-20.911493	-20.913434	55.52		-386.1009136			
TS_A8-A53	Error				-386.5912442			
TS_A8-A54	-21.174501	-21.18155	40.20	37.52	-386.5967342	33.33	4.19	17.59
A9	-21.191265	-21.194187	29.69	29.59	-386.6226907	17.04	12.55	157.51
TS_A9-A10	-21.163567	-21.165429	47.06	47.64	-386.5875932	39.06	8.57	73.50
A10	-21.186839	-21.190052	32.46	32.19	-386.6212939	17.92	14.27	203.59
TS_A10-A11	-21.172121	-21.16794	41.70	46.06	-386.582433	42.30	3.76	14.14
TS_A10-A13	-21.104936	-21.109249	83.85	82.89	-386.5448446	65.89	17.00	289.00
TS_A10-A17	-21.08054	-21.08862	99.16	95.83	-386.5059827	90.27	5.56	30.92
A11	-21.230629	-21.233492	4.99	4.93	-386.6461023	2.36	2.58	6.65
TS_A11-A12	-21.210955	-21.211112	17.33	18.98	-386.6248122	15.71	3.26	10.64
A12	-21.280487	-21.28253	-26.29	-25.83	-386.6793879	-18.53	-7.30	53.35
TS_A12-IND	-21.24567	-21.236943	-4.45	2.77	-386.645243	2.89	-0.13	0.02
A13	-21.180568	-21.184466	36.40	35.69	-386.6093154	25.44	10.26	105.22
TS_A13-A14	-21.134468	-21.137115	65.32	65.40	-386.5486063	63.53	1.88	3.52
TS_A13-A15	-21.17871	-21.179799	37.56	38.62	-386.5922915	36.12	2.50	6.27
TS_A13-A17	-21.080228	-21.122815	99.35		-386.5054721			
A14	-21.232144	-21.234493	4.04	4.31	-386.6478312	1.27	3.04	9.21
TS_A14-A12a	-21.211973	-21.211411	16.69	18.79	-386.6251168	15.52	3.27	10.67
A15	-21.271219	-21.273772	-20.48	-20.34	-386.670539	-12.98	-7.36	54.19
TS_A15-A16	-21.220998	-21.226875	11.03	9.09	-386.6113585	24.15	-15.07	227.05
A16	-21.28537	-21.288037	-29.36	-29.29	-386.6821344	-20.25	-9.04	81.66
TS_A16-A12a	-21.2153	-21.240832	14.61		-386.6091982			
A17	-21.218639	-21.221306	12.51	12.58	-386.6429131	4.36	8.22	67.62
TS_A17-A18	-21.163652	-21.167328	47.01	46.45	-386.5742574	47.43	-0.99	0.97
TS_A17-A19	-21.210352	-21.212351	17.71	18.20	-386.6322008	11.08	7.12	50.71
A18	-21.218539	-21.221608	12.57	12.39	-386.6384118	7.18	5.21	27.14
TS_A18-A5	-21.199652	-21.20505	24.42	22.78	-386.6192059	19.23	3.55	12.59
A19	-21.251341	-21.253772	-8.01	-7.79	-386.6602331	-6.51	-1.28	1.64
TS_A19-A5a	-21.234397	-21.235365	2.62	3.76	-386.629937	12.50	-8.74	76.36
A20	-21.207359	-21.211479	19.59	18.75	-386.6293912	12.84	5.91	34.87
TS_A20-A21	-21.196818	-21.194871	26.20	29.17	-386.5983285	32.33	-3.16	10.01
TS_A20-A24	-21.105595	-21.111039	83.44	81.76	-386.5178415	82.83	-1.07	1.13
TS_A20-A31	-21.106048	-21.111378	83.15	81.55	-386.5180144	82.72	-1.17	1.37
TS_A20-A38	-21.136233	-21.140009	64.21	63.59	-386.5569279	58.30	5.28	27.90
TS_A20-A39	-21.136015	-21.139597	64.35	63.84	-386.5567175	58.44	5.41	29.25
A21	-21.246952	-21.250066	-5.25	-5.46	-386.6594229	-6.00	0.54	0.29

TS_A21-A22	-21.164945	-21.168101	46.20	45.96	-386.5766409	45.94	0.02	0.00
A22	-21.219416	-21.222294	12.02	11.96	-386.6341708	9.84	2.12	4.49
TS_A22-A23	-21.188212	-21.19091	31.60	31.65	-386.5946915	34.61	-2.96	8.76
TS_A22-A26	-21.179394	-21.181071	37.13	37.82	-386.60811	26.19	11.63	135.29
A23	-21.21067	-21.214498	17.51	16.85	-386.634325	9.74	7.11	50.50
TS_A23-A25	-21.205415	-21.206324	20.81	21.98	-386.622374	17.24	4.74	22.44
TS_A23-A4a	-21.184521	-21.18696	33.92	34.13	-386.5805069	43.51	-9.38	88.02
A24	-21.208805	-21.211841	18.68	18.52	-386.6232316	16.70	1.81	3.29
TS_A24-A22	-21.102489	-21.108336	85.38	83.46	-386.5123361	86.28	-2.82	7.97
A25	-21.229156	-21.232049	5.91	5.84	-386.6444276	3.41	2.43	5.92
TS_A25-A7a	-21.204104	-21.205486	21.63	22.51	-386.6183172	19.79	2.72	7.38
A26	-21.189294	-21.191856	30.92	31.06	-386.6217854	17.61	13.44	180.77
TS_A26-A27	-21.145893	-21.147351	58.15	58.98	-386.5738935	47.66	11.32	128.14
A27	-21.15402	-21.158616	53.05	51.91	-386.5944997	34.73	17.18	295.18
TS_A27-A28	-21.070079	-21.074505	105.72	104.68	-386.5183166	82.53	22.15	490.83
TS_A27-A29	-21.065362	-21.185526	108.68		-386.487245			
A28	-21.145264	-21.148457	58.55	58.29	-386.5824075	42.32	15.97	254.97
TS_A28-A29	-21.09636	-21.128457	89.23		-386.5216424			
A29	-21.178768	-21.182543	37.53	36.90	-386.6036251	29.01	7.89	62.32
TS_A29-A18	-21.154559	-21.1575	52.71	52.61	-386.5640731	53.82	-1.21	1.46
TS_A29-A30	-21.16225	-21.164611	47.89	48.15	-386.5841338	41.23	6.92	47.83
A30	-21.252575	-21.254946	-8.78	-8.53	-386.660758	-6.84	-1.69	2.84
TS_A30-A5	-21.234791	-21.235809	2.38	3.48	-386.6298632	12.54	-9.06	82.15
A31	-21.208765	-21.211911	18.71	18.47	-386.623589	16.48	1.99	3.98
TS_A31-A32	-21.11139	-21.15172	79.80		-386.5177177			
A32	-21.234822	-21.238069	2.36	2.06	-386.6442137	3.54	-1.48	2.18
TS_A32-A33	-21.19846	-21.200358	25.17	25.72	-386.6013757	30.42	-4.69	22.04
A33	-21.218181	-21.223456	12.80	11.23	-386.6412494	5.40	5.83	34.00
TS_A33-A34	-21.195814	-21.197158	26.83	27.73	-386.5884474	38.53	-10.80	116.60
TS_A33-A35	-21.216455	-21.217938	13.88	14.69	-386.6314382	11.56	3.14	9.84
A34	-21.285361	-21.288037	-29.35	-29.29	-386.6820447	-20.20	-9.09	82.68
TS_A34-A12	-21.215299	-21.240832	14.61		-386.6091349			
A35	-21.244407	-21.247331	-3.66	-3.75	-386.6578675	-5.03	1.28	1.63
TS_A35-A36	-21.216194	-21.218034	14.04	14.63	-386.626076	14.92	-0.29	0.08
A36	-21.2282	-21.2309	6.51	6.56	-386.642279	4.75	1.81	3.26
TS_A36-A37	-21.1688	-21.175191	43.78	41.51	-386.58957	37.82	3.69	13.60
A37	-20.912576	-20.914535	54.84	55.35	-386.1013595	30.54	24.81	615.50
TS_A37-A53	-21.164478	-21.166983	46.49	46.66	-386.5926328	35.90	10.76	115.77
TS_A37-A54	-21.176184	-21.183771	39.15	36.13	-386.5980159	32.53	3.60	12.99

A38	-21.1778	-21.183576	38.13	36.25	-386.6053429	27.93	8.32	69.28
TS_A38-A40	-21.156753	-21.162774	51.34	49.30	-386.5711544	49.38	-0.08	0.01
A39	-21.178155	-21.183985	37.91	36.00	-386.6057674	27.66	8.33	69.45
TS_A39-A40	-21.157799	-21.163045	50.68	49.13	-386.5734598	47.93	1.20	1.44
A40	-21.243937	-21.246377	-3.36	-3.15	-386.6540012	-2.60	-0.55	0.30
TS_A40-A41	-21.174846	-21.178807	39.99	39.24	-386.5918563	36.39	2.85	8.15
TS_A40-A42	-21.165755	-21.168346	45.69	45.81	-386.589825	37.66	8.14	66.31
A41	-20.911254	-20.913588	55.67	55.94	-386.1025842	29.77	26.17	684.96
TS_A41-A54	-21.175869	-21.183194	39.34	36.49	-386.6002388	31.13	5.36	28.74
A42	-20.904631	-20.906846	59.82	60.17	-386.0963711	33.67	26.50	702.44
TS_A42-A54	-21.166528	-21.174835	45.21	41.74	-386.5946352	34.65	7.09	50.26
A43	-21.206645	-21.210842	20.04	19.14	-386.6290256	13.07	6.08	36.91
TS_A43-A2a	-21.140606	-21.144993	61.47	60.46	-386.556721	58.43	2.03	4.10
TS_A43-A44	-21.142709	-21.1467	60.15	59.39	-386.5579854	57.64	1.75	3.05
TS_A43-A51	-21.13527	-21.139269	64.82	64.05	-386.5546537	59.73	4.32	18.66
TS_A43-A52	-21.134399	-21.138363	65.36	64.62	-386.5543853	59.90	4.72	22.27
A44	-21.237862	-21.241339	0.45	0.01	-386.6453029	2.86	-2.85	8.10
TS_A44-A45	-21.174326	-21.17771	40.31	39.93	-386.5778688	45.17	-5.23	27.39
TS_A44-A47	-21.19664	-21.18116	26.31		-386.6218575			
TS_A44-A48	-21.150552	-21.163308	55.23	48.97	-386.5580418	57.61	-8.64	74.60
A45	-21.217243	-21.220806	13.39	12.89	-386.6421853	4.81	8.08	65.29
TS_A45-A12a	-21.191143	-21.190353	29.76	32.00	-386.5901553	37.46	-5.46	29.78
TS_A45-A34	-21.200173	-21.199634	24.10	26.18	-386.5960438	33.76	-7.59	57.54
TS_A45-A46	-21.207689	-21.209871	19.38	19.75	-386.6210896	18.05	1.71	2.91
A46	-21.239899	-21.242953	-0.83	-1.00	-386.6519202	-1.30	0.29	0.09
TS_A46-A36	-21.207742	-21.209167	19.35	20.20	-386.6167717	20.76	-0.56	0.32
A47	-21.195694	-21.195931	26.91	28.50	-386.6240446	16.19	12.31	151.43
TS_A47-A48	-21.164368	-21.166369	46.56	47.05	-386.5888155	38.30	8.75	76.56
A48	-21.18783	-21.191057	31.84	31.56	-386.6223261	17.27	14.29	204.07
TS_A48-A18	-21.170894	-21.168257	42.47	45.86	-386.5806612	43.41	2.45	6.00
TS_A48-A49	-21.105491	-21.109949	83.50	82.45	-386.5469193	64.58	17.86	319.07
A49	-21.181086	-21.18559	36.07	34.99	-386.6110262	24.36	10.63	112.91
TS_A49-A50	-21.129782	-21.133242	68.26	67.83	-386.5452135	65.65	2.18	4.74
A50	-21.219686	-21.222331	11.85	11.94	-386.6394027	6.56	5.38	28.92
TS_A50-A5a	-21.200847	-21.205322	23.67	22.61	-386.6199306	18.78	3.83	14.69
A51	-21.177696	-21.183279	38.20	36.44	-386.6047431	28.30	8.13	66.16
TS_A51-A40	-21.16093	-21.165727	48.72	47.45	-386.5733242	48.02	-0.57	0.32
A52	-21.17744	-21.183193	38.36	36.49	-386.6052199	28.01	8.49	72.03
TS_A52-A40	-21.158396	-21.163929	50.31	48.58	-386.5721026	48.78	-0.20	0.04

A53	-20.502264	-20.504563	38.50	38.80	-385.4820092	4.43	34.37	
TS_A53-AZ	-20.433985	-20.430889	81.34		-385.4210308			
A54	-20.514734	-20.516974	30.67	31.01	-385.4943447	-3.31	34.32	
TS_A54-AZ	-20.436772	-20.430889	79.59	85.02	-385.4252448	40.05	44.97	
A55	-21.21328	-21.216402	15.87	15.66	-386.6337191	10.12	5.53	30.60
TS_A55-A0	-21.166576	-21.173859	45.18	42.35	-386.5753001	46.78	-4.43	19.62
TS_A55-S0	-21.147189	-21.151025	57.34	56.67	-386.5792627	44.29	12.38	153.35
A56	-21.211232	-21.214195	17.16	17.04	-386.6287478	13.24	3.80	14.42
AZ	-20.16948	-20.17159	97.59	98.01	-384.9341026	34.60	63.40	
INDENE	-18.487032	-18.488439	5.97	6.78	-346.9420538	-11.30	18.07	326.59
S0	-20.890093	-20.8926	68.94	69.11	-386.0860685	40.14	28.98	839.71
S2	-20.897356	-20.899958	64.39	64.50	-386.0885068	38.61	25.89	670.35
RMSD								8.87

TABLE S4. Absolute and relative energies from SCC-DFTB calculations, compared to G3(MP2,CC)//B3LYP/6-311G** data by Kislov *et al.* from Reference 41. For more details see Table Caption S1.

Structure	E(SCC-DFTB //B3LYP) [ha]	E(SCC-DFTB) opt'd [ha]	ΔE (SCC-DFTB//B3LYP) [kcal/mol]	ΔE (SCC-DFTB opt'd) [kcal/mol]	E(G3) [ha] Kislov&Mebel	ΔE (G3) [kcal/mol]	$\Delta\Delta E$ (DFTB-G3) [kcal/mol]	$\Delta\Delta E^2$
H	-0.2386	-0.2386			-0.49981792			
H2	-0.674955	-0.674956			-1.160783878			
CH3	-2.740365	-2.740423			-39.72580529			
CPDyl	-10.384186	-10.385404			-193.000814			
CPD	-10.811267	-10.812281	18.21	18.59	-193.62735	13.61	4.98	
TS_CPD+CPDyl-A0	-21.199693	-21.199477	15.55	17.47	-386.6155802	21.51	-4.04	16.29
TS_CPD+CPDyl-A55	-21.189066	-21.187347	22.22	25.08	-386.6092585	25.47	-0.39	0.15
A0	-21.22448	-21.22732	0.00	0.00	-386.6498561	0.00	0.00	0.00
TS_A0-A1	-21.2116	-21.213999	8.08	8.36	-386.6229969	16.85	-8.49	72.15
TS_A0-A20	-21.189739	-21.187692	21.80	24.86	-386.6040531	28.74	-3.87	15.01
TS_A0-A43	-21.188585	Error			-386.6044346			
TS_A0-A56	-21.153834	-21.15796	44.32	43.52	-386.5814665	42.91	0.61	0.37
TS_A0-S2	-21.137364	-21.139659	54.66	55.00	-386.5852735	40.52	14.48	209.66
A1	-21.233374	-21.237006	-5.58	-6.08	-386.6583224	-5.31	-0.77	0.59
TS_A1-A2	-21.149059	-21.152463	47.32	46.97	-386.5777477	45.24	1.72	2.97
A2	-21.208848	-21.212531	9.81	9.28	-386.6350767	9.27	0.01	0.00
TS_A2-A3	-21.150327	-21.153259	46.52	46.47	-386.5696747	50.31	-3.84	14.75
TS_A2-A9	-21.173895	-21.176131	31.74	32.12	-386.6142222	22.36	9.76	95.25
A3	-21.200304	-21.203704	15.17	14.82	-386.6340214	9.93	4.88	23.83
TS_A3-A4	-21.168273	-21.170848	35.26	35.43	-386.587554	39.09	-3.66	13.38
TS_A3-A5	-21.176975	-21.175417	29.81	32.56	-386.5878224	38.92	-6.36	40.40
TS_A3-A6	-21.186388	-21.18767	23.90	24.88	-386.6132901	22.94	1.93	3.74
A4	-21.262852	-21.265453	-24.07	-23.92	-386.6725726	-14.25	-9.67	93.56
TS_A4-A5	-21.202971	-21.205896	13.49	13.44	-386.6096697	25.21	-11.77	138.57
A5	-21.277249	-21.279554	-33.11	-32.77	-386.6830645	-20.84	-11.94	142.49
TS_A5-IND	-21.235816	Error			-386.6464921			
A6	-21.213748	-21.217009	6.73	6.47	-386.6389491	6.84	-0.37	0.14
TS_A6-A7	-21.183972	-21.184917	25.42	26.60	-386.6092108	25.50	1.10	1.22

A7	-21.209947	-21.212951	9.12	9.02	-386.6360324	8.67	0.34	0.12
TS_A7-A8	-21.154865	-21.154656	43.68	45.59	-386.5873587	39.21	6.38	40.69
A8	-20.901783	-20.903889	52.76	53.22	-386.1009136	30.82	22.40	501.87
TS_A8-A53	-21.152165	-21.153034	45.37	46.61	-386.5912442	36.77	9.83	96.71
TS_A8-A54	-21.156328	-21.158615	42.76	43.11	-386.5967342	33.33	9.78	95.59
A9	-21.178616	-21.181857	28.78	28.52	-386.6226907	17.04	11.48	131.79
TS_A9-A10	-21.151403	-21.153458	45.85	46.34	-386.5875932	39.06	7.28	52.96
A10	-21.175006	-21.178151	31.04	30.85	-386.6212939	17.92	12.93	167.16
TS_A10-A11	-21.161063	-21.157059	39.79	44.08	-386.582433	42.30	1.78	3.17
TS_A10-A13	-21.088754	-21.093381	85.16	84.03	-386.5448446	65.89	18.15	329.40
TS_A10-A17	-21.068753	-21.076484	97.70	94.64	-386.5059827	90.27	4.37	19.08
A11	-21.219813	-21.222803	2.93	2.83	-386.6461023	2.36	0.48	0.23
TS_A11-A12	-21.198458	-21.198883	16.33	17.84	-386.6248122	15.71	2.13	4.53
A12	-21.269087	-21.271121	-27.99	-27.48	-386.6793879	-18.53	-8.95	80.15
TS_A12-IND	-21.234275	Error			-386.645243			
A13	-21.168613	-21.172816	35.05	34.20	-386.6093154	25.44	8.76	76.75
TS_A13-A14	-21.122732	-21.124354	63.84	64.60	-386.5486063	63.53	1.08	1.16
TS_A13-A15	-21.164162	-21.165245	37.84	38.95	-386.5922915	36.12	2.83	8.01
TS_A13-A17	-21.068309	-21.074028	97.98	96.18	-386.5054721	90.59	5.59	31.24
A14	-21.221698	-21.224116	1.75	2.01	-386.6478312	1.27	0.74	0.55
TS_A14-A12a	-21.199684	-21.199507	15.56	17.45	-386.6251168	15.52	1.93	3.72
A15	-21.260395	-21.263029	-22.53	-22.40	-386.670539	-12.98	-9.43	88.88
TS_A15-A16	-21.203493	-21.206887	13.17	12.82	-386.6113585	24.15	-11.33	128.46
A16	-21.275125	-21.277671	-31.78	-31.59	-386.6821344	-20.25	-11.34	128.57
TS_A16-A12a	-21.190321	Error			-386.6091982			
A17	-21.207446	-21.210272	10.69	10.70	-386.6429131	4.36	6.34	40.20
TS_A17-A18	-21.145557	-21.14867	49.52	49.35	-386.5742574	47.43	1.91	3.66
TS_A17-A19	-21.198355	-21.20023	16.39	17.00	-386.6322008	11.08	5.92	35.04
A18	-21.207148	-21.210302	10.87	10.68	-386.6384118	7.18	3.50	12.23
TS_A18-A5	-21.188422	-21.192624	22.62	21.77	-386.6192059	19.23	2.54	6.44
A19	-21.240018	-21.242495	-9.75	-9.52	-386.6602331	-6.51	-3.01	9.06
TS_A19-A5a	-21.216382	-21.217771	5.08	5.99	-386.629937	12.50	-6.51	42.33
A20	-21.195011	-21.199642	18.49	17.37	-386.6293912	12.84	4.53	20.48
TS_A20-A21	-21.184773	-21.183109	24.91	27.74	-386.5983285	32.33	-4.59	21.07
TS_A20-A24	-21.088736	-21.093946	85.17	83.68	-386.5178415	82.83	0.85	0.73
TS_A20-A31	-21.08927	-21.094222	84.83	83.51	-386.5180144	82.72	0.79	0.62
TS_A20-A38	-21.121337	-21.125312	64.71	64.00	-386.5569279	58.30	5.70	32.45
TS_A20-A39	-21.121485	-21.125225	64.62	64.06	-386.5567175	58.44	5.62	31.58
A21	-21.235633	-21.239231	-7.00	-7.47	-386.6594229	-6.00	-1.47	2.16

TS_A21-A22	-21.14763	-21.151218	48.22	47.75	-386.5766409	45.94	1.81	3.28
A22	-21.206778	-21.210228	11.11	10.72	-386.6341708	9.84	0.88	0.78
TS_A22-A23	-21.175763	-21.178341	30.57	30.73	-386.5946915	34.61	-3.88	15.06
TS_A22-A26	-21.166948	-21.169051	36.10	36.56	-386.60811	26.19	10.37	107.47
A23	-21.199529	-21.203416	15.65	15.00	-386.634325	9.74	5.25	27.60
TS_A23-A25	-21.193717	-21.194499	19.30	20.59	-386.622374	17.24	3.35	11.22
TS_A23-A4a	-21.163574	-21.167209	38.21	37.71	-386.5805069	43.51	-5.80	33.60
A24	-21.197196	-21.200736	17.12	16.68	-386.6232316	16.70	-0.03	0.00
TS_A24-A22	-21.0851	-21.089787	87.45	86.29	-386.5123361	86.28	0.01	0.00
A25	-21.217599	-21.220806	4.32	4.09	-386.6444276	3.41	0.68	0.46
TS_A25-A7a	-21.192006	-21.193153	20.37	21.44	-386.6183172	19.79	1.65	2.72
A26	-21.177523	-21.180694	29.46	29.25	-386.6217854	17.61	11.64	135.53
TS_A26-A27	-21.133327	-21.134083	57.19	58.50	-386.5738935	47.66	10.84	117.46
A27	-21.140418	-21.144352	52.74	52.05	-386.5944997	34.73	17.32	300.11
TS_A27-A28	-21.053511	-21.058124	107.27	106.16	-386.5183166	82.53	23.63	558.19
TS_A27-A29	-21.051726	-21.058952	108.39	105.64	-386.487245	102.02	3.61	13.05
A28	-21.132923	-21.136514	57.44	56.97	-386.5824075	42.32	14.65	214.76
TS_A28-A29	-21.08308	-21.088575	88.72	87.05	-386.5216424	80.44	6.61	43.66
A29	-21.167717	-21.171465	35.61	35.04	-386.6036251	29.01	6.04	36.46
TS_A29-A18	-21.136693	-21.13962	55.08	55.02	-386.5640731	53.82	1.20	1.45
TS_A29-A30	-21.150447	-21.152629	46.45	46.86	-386.5841338	41.23	5.63	31.66
A30	-21.240881	-21.24331	-10.29	-10.03	-386.660758	-6.84	-3.19	10.19
TS_A30-A5	-21.21657	-21.217908	4.96	5.91	-386.6298632	12.54	-6.64	44.07
A31	-21.197086	-21.200696	17.19	16.70	-386.623589	16.48	0.22	0.05
TS_A31-A32	-21.093855	-21.099151	81.96	80.41	-386.5177177	82.90	-2.49	6.20
A32	-21.223234	-21.226859	0.78	0.29	-386.6442137	3.54	-3.25	10.57
TS_A32-A33	-21.186685	-21.188021	23.71	24.66	-386.6013757	30.42	-5.76	33.18
A33	-21.207791	-21.212764	10.47	9.13	-386.6412494	5.40	3.73	13.93
TS_A33-A34	-21.174351	-21.177861	31.45	31.03	-386.5884474	38.53	-7.50	56.21
TS_A33-A35	-21.205651	-21.20694	11.81	12.79	-386.6314382	11.56	1.23	1.52
A34	-21.275115	-21.277668	-31.77	-31.59	-386.6820447	-20.20	-11.39	129.81
TS_A34-A12	-21.190323	Error			-386.6091349			
A35	-21.233805	-21.236964	-5.85	-6.05	-386.6578675	-5.03	-1.02	1.05
TS_A35-A36	-21.204746	-21.206033	12.38	13.36	-386.626076	14.92	-1.56	2.45
A36	-21.216943	-21.219812	4.73	4.71	-386.642279	4.75	-0.04	0.00
TS_A36-A37	-21.155791	-21.155425	43.10	45.11	-386.58957	37.82	7.28	53.05
A37	-20.90288	-20.905005	52.07	52.52	-386.1013595	30.54	21.98	483.21
TS_A37-A53	-21.152745	-21.154116	45.01	45.93	-386.5926328	35.90	10.03	100.53
TS_A37-A54	-21.157296	-21.159548	42.15	42.52	-386.5980159	32.53	10.00	99.92

A38	-21.165441	-21.17088	37.04	35.41	-386.6053429	27.93	7.48	56.00
TS_A38-A40	-21.143246	-21.146742	50.97	50.56	-386.5711544	49.38	1.18	1.39
A39	-21.166016	-21.171421	36.68	35.07	-386.6057674	27.66	7.41	54.91
TS_A39-A40	-21.144773	-21.147502	50.01	50.08	-386.5734598	47.93	2.15	4.61
A40	-21.233116	-21.235853	-5.42	-5.35	-386.6540012	-2.60	-2.75	7.58
TS_A40-A41	-21.159744	-21.157837	40.62	43.59	-386.5918563	36.39	7.20	51.91
TS_A40-A42	-21.150203	-21.149922	46.60	48.56	-386.589825	37.66	10.90	118.73
A41	-20.901564	-20.903953	52.90	53.18	-386.1025842	29.77	23.41	548.05
TS_A41-A54	-21.154312	-21.159117	44.02	42.79	-386.6002388	31.13	11.66	135.98
A42	-20.894607	-20.896961	57.27	57.57	-386.0963711	33.67	23.90	571.17
TS_A42-A54	-21.148187	-21.153515	47.87	46.31	-386.5946352	34.65	11.66	135.95
A43	-21.194442	-21.199104	18.85	17.70	-386.6290256	13.07	4.63	21.47
TS_A43-A2a	-21.127405	-21.132046	60.91	59.78	-386.556721	58.43	1.34	1.80
TS_A43-A44	-21.130362	-21.134552	59.05	58.20	-386.5579854	57.64	0.56	0.32
TS_A43-A51	-21.12081	-21.124764	65.04	64.34	-386.5546537	59.73	4.61	21.29
TS_A43-A52	-21.12044	-21.124404	65.28	64.57	-386.5543853	59.90	4.67	21.82
A44	-21.225792	-21.229637	-0.82	-1.45	-386.6453029	2.86	-4.31	18.58
TS_A44-A45	-21.161497	-21.163872	39.52	39.81	-386.5778688	45.17	-5.36	28.70
TS_A44-A47	-21.184084	Error			-386.6218575			
TS_A44-A48	-21.133972	-21.137363	56.79	56.44	-386.5580418	57.61	-1.17	1.36
A45	-21.207393	-21.210674	10.72	10.44	-386.6421853	4.81	5.63	31.71
TS_A45-A12a	-21.179384	-21.17927	28.29	30.15	-386.5901553	37.46	-7.31	53.43
TS_A45-A34	-21.179298	-21.18149	28.35	28.75	-386.5960438	33.76	-5.01	25.08
TS_A45-A46	-21.197347	-21.199295	17.02	17.58	-386.6210896	18.05	-0.47	0.22
A46	-21.229514	-21.232756	-3.16	-3.41	-386.6519202	-1.30	-2.12	4.48
TS_A46-A36	-21.196244	-21.197411	17.72	18.77	-386.6167717	20.76	-1.99	3.97
A47	-21.18366	-21.187785	25.61	24.80	-386.6240446	16.19	8.61	74.14
TS_A47-A48	-21.152793	-21.154861	44.98	45.46	-386.5888155	38.30	7.16	51.32
A48	-21.176465	-21.179751	30.13	29.85	-386.6223261	17.27	12.57	158.07
TS_A48-A18	-21.159778	-21.157486	40.59	43.81	-386.5806612	43.41	0.40	0.16
TS_A48-A49	-21.089843	-21.094586	84.47	83.28	-386.5469193	64.58	18.70	349.50
A49	-21.169703	-21.174383	34.37	33.21	-386.6110262	24.36	8.85	78.34
TS_A49-A50	-21.117916	-21.120689	66.86	66.90	-386.5452135	65.65	1.25	1.56
A50	-21.208606	-21.211272	9.96	10.07	-386.6394027	6.56	3.51	12.32
TS_A50-A5a	-21.189722	-21.193159	21.81	21.43	-386.6199306	18.78	2.66	7.06
A51	-21.165587	-21.170937	36.95	35.38	-386.6047431	28.30	7.07	50.00
TS_A51-A40	-21.144738	-21.149043	50.03	49.11	-386.5733242	48.02	1.09	1.20
A52	-21.165751	-21.171129	36.85	35.25	-386.6052199	28.01	7.25	52.56
TS_A52-A40	-21.145219	-21.148266	49.73	49.60	-386.5721026	48.78	0.82	0.67

A53	-20.492161	-20.494209	35.99	36.49	-385.4820092	4.43	32.06	
TS_A53-AZ	-20.417801	-20.405728	82.64	92.00	-385.4210308	42.69	49.31	
A54	-20.505008	-20.507083	27.93	28.41	-385.4943447	-3.31	31.72	
TS_A54-AZ	-20.414984	Error			-385.4252448			
A55	-21.198539	-21.20185	16.28	15.98	-386.6337191	10.12	5.86	34.29
TS_A55-A0	-21.14438	-21.147654	50.26	49.98	-386.5753001	46.78	3.21	10.28
TS_A55-S0	-21.130219	-21.130647	59.14	60.65	-386.5792627	44.29	16.36	267.73
A56	-21.199452	-21.202174	15.70	15.78	-386.6287478	13.24	2.53	6.42
AZ	-20.158659	-20.160212	95.53	96.34	-384.9341026	34.60	61.74	
INDENE	-18.478105	-18.47947	3.77	4.66	-346.9420538	-11.30	15.96	254.56
S0	-20.876227	-20.878592	68.80	69.10	-386.0860685	40.14	28.96	838.69
S2	-20.883488	-20.88582	64.24	64.56	-386.0885068	38.61	25.96	673.66
RMSD								8.70

FIGURE S1. $\Delta E(\text{NCC-DFTB})$ (ordinate) vs $\Delta E(\text{B3LYP})$ (abscissa) from Table S1. Units are in [kcal/mol].

FIGURE S2. $\Delta E(\text{SCC-DFTB})$ (ordinate) vs $\Delta E(\text{B3LYP})$ (abscissa) from Table S2. Units are in [kcal/mol].

FIGURE S3. $\Delta E(\text{NCC-DFTB})$ (ordinate) vs $\Delta E(\text{G3(MP2,CC)})$ (abscissa) from Table S3. Units are in [kcal/mol].

FIGURE S4. $\Delta E(\text{SCC-DFTB})$ (ordinate) vs $\Delta E(\text{G3(MP2,CC)})$ (abscissa) from Table S4. Units are in [kcal/mol].

FIGURE S5. $\Delta E(\text{B3LYP})$ (ordinate) vs $\Delta E(\text{G3(MP2,CC)})$ (abscissa) from data by Kislov *et al.* Reference 41. Units are in [kcal/mol].

B3000Kg1

B3000Kg2

B3000Kg3

B3000Kg4

FIGURE S6. Structures of the hydrocarbons species formed at the end of 5.00 ps of simulations with $T_n = 3000$ K for different initial geometries. Smaller species like C_2H , C_2H_2 are not shown. Carbon: black color (large) sphere, Hydrogen: light gray color (small) sphere.

FIGURE S7. Reactions/collisions statistics at $T_n = 2500$ K (top) and $T_n = 3000$ K (bottom). Averaged over 20 simulations.

FIGURE S8. Carbon type count (black: sp, red: sp², and green: sp³ type carbons) as a function of time for selected successful trajectories at T_n = 2500 K.

FIGURE S9. Ring count statistics as a function of time for selected successful trajectories with $T_n = 2500$ K.

FIGURE S10. Carbon type count (black: sp , red: sp^2 , and green: sp^3 type carbons) as a function of time for selected unsuccessful trajectories at $T_n = 2500$ K.

FIGURE S11. Ring count statistics as a function of time for selected unsuccessful trajectories with $T_n = 2500$ K.

FIGURE S12. Hybridization (sp, sp² and sp³) statistics for successful trajectories with $T_n = 3000\text{K}$.

FIGURE S13. Ring formation statistics for successful trajectories with $T_n = 3000$ K.

FIGURE S14. Hybridization (sp, sp² and sp³) statistics for unsuccessful trajectories with $T_n = 3000$ K.

FIGURE S15. Ring formation statistics for unsuccessful trajectories with $T_n = 3000$ K.

FIGURE S16. Hybridization (sp, sp² and sp³) and ring formation statistics for successful trajectories with $T_n = T_e = 2500\text{K}$. SCC-DFTB up to 15 ps, followed by NCC-DFTB for the carbon-only system.