Electronic Supplementary Data

A molecular electron density theory study to understand the strain promoted [3+2] cycloaddition reaction of benzyl azide and cyclooctyne

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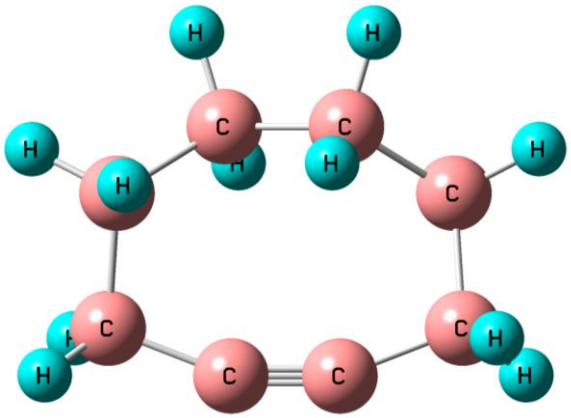

Fig. S1 — MPWB1K/6-311G(d,p) optimized structure **1** (gas phase)

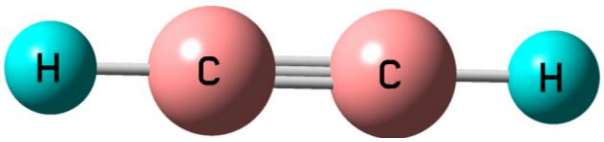

Fig. S2 — MPWB1K/6-311G(d,p) optimized structure **2** (gas phase)

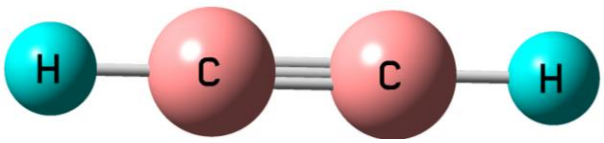

Fig. S3 — MPWB1K/6-311G(d,p) optimized structure **3** (gas phase)

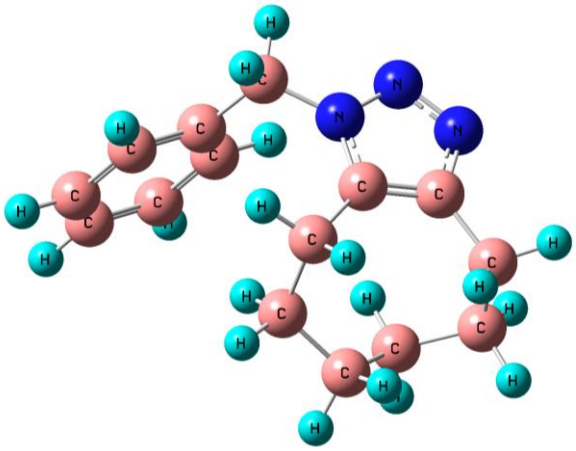

Fig. S4 — MPWB1K/6-311G(d,p) optimized structure **4** (gas phase)

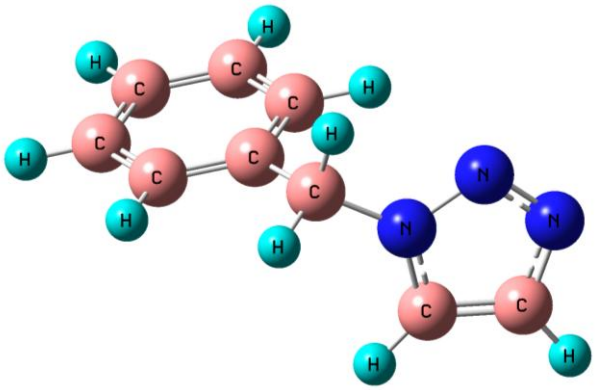

Fig. S5 — MPWB1K/6-311G(d,p) optimized structure **5** (gas phase)

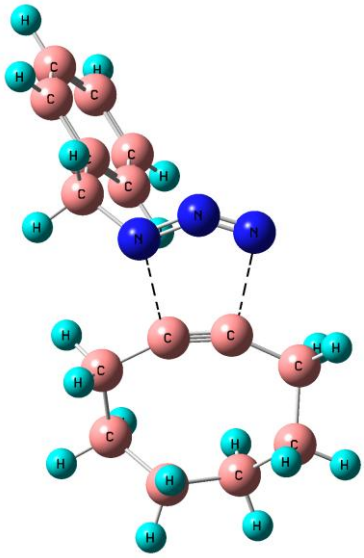

Fig. S6 — MPWB1K/6-311G(d,p) optimized structure **TS1** (gas phase)

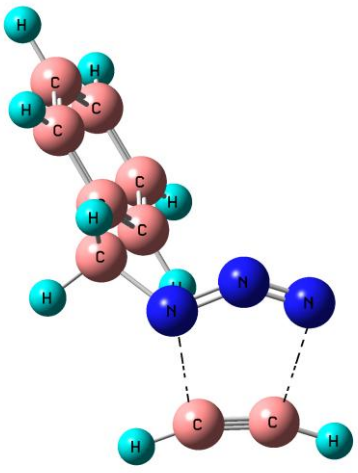

Fig. S7 — MPWB1K/6-311G(d,p) optimized structure **TS2** (gas phase)

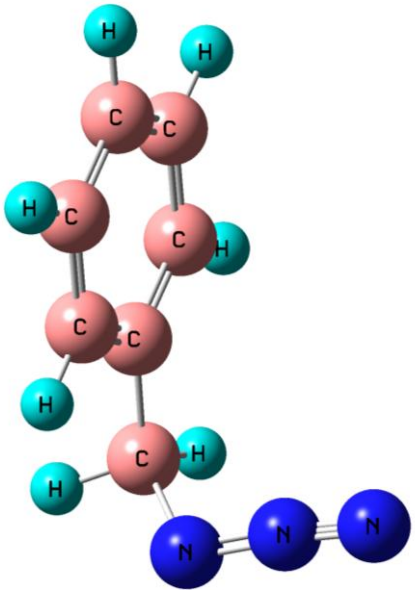

Fig. S8 — MPWB1K/6-311G(d,p) optimized structure **1** (acetonitrile)

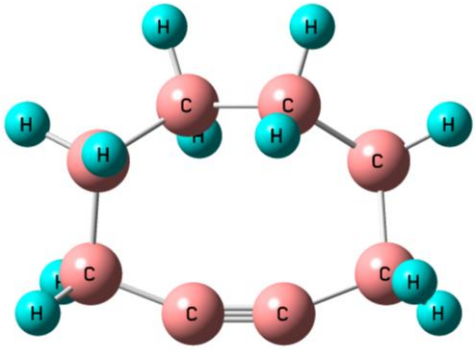

Fig. S9 — MPWB1K/6-311G(d,p) optimized structure **2** (acetonitrile)

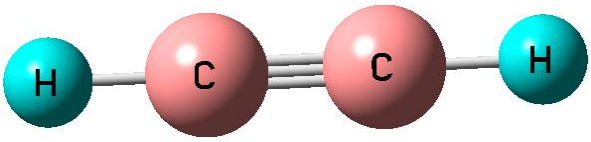

Fig. S10 — MPWB1K/6-311G(d,p) optimized structure **3** (acetonitrile)

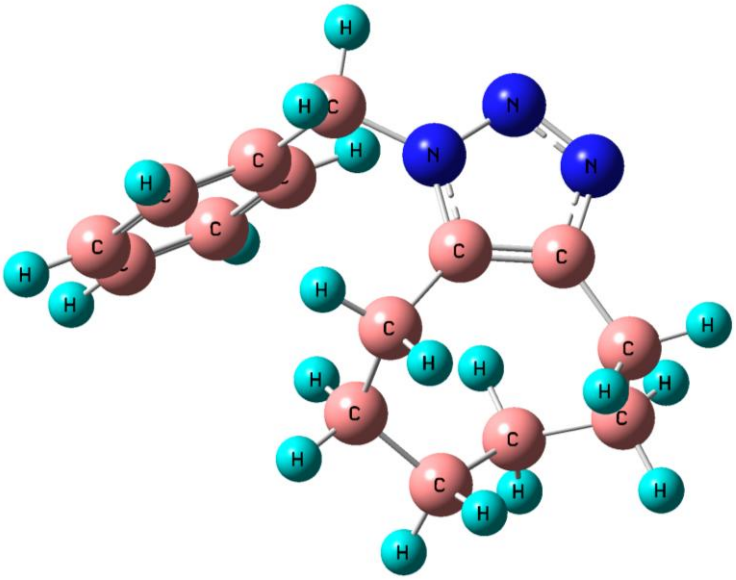

Fig. S11 — MPWB1K/6-311G(d,p) optimized structure **4** (acetonitrile)

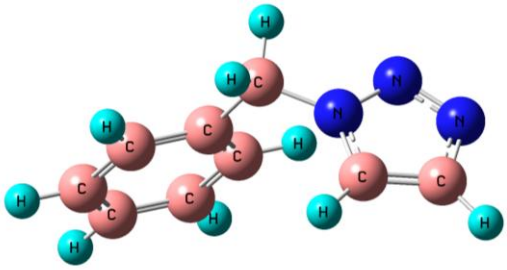

Fig. S12 — MPWB1K/6-311G(d,p) optimized structure **5** (acetonitrile)

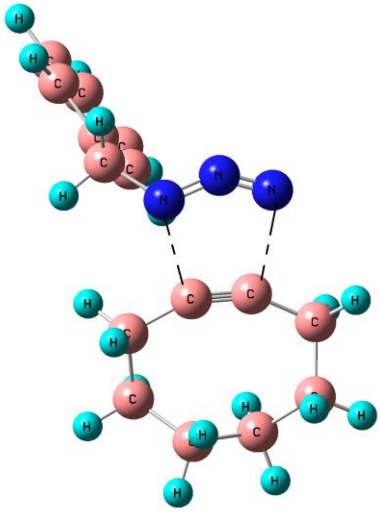

Fig. S13 — MPWB1K/6-311G(d,p) optimized structure **TS1** (acetonitrile)

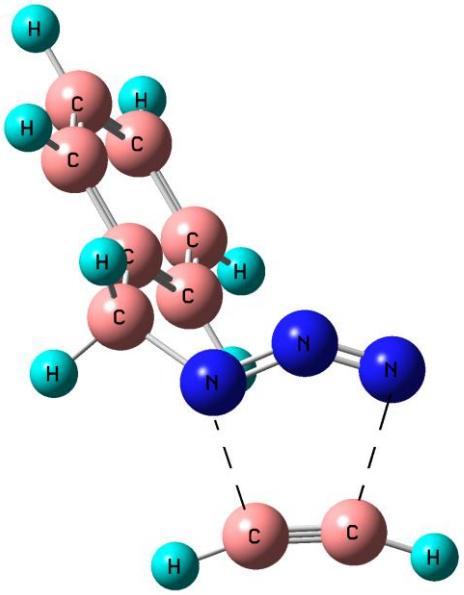

Fig. S14 — MPWB1K/6-311G(d,p) optimized structure **TS2** (acetonitrile)

Table S1 — MPWB1K/6-311G(d,p) calculated total energies (in au) and relative energies, enthalpies and Gibbs free energies, in kcal mol^{-1}, computed at 298 K in gas phase of the stationary points involved in the 32CA reactions of benzyl azide **1** with cyclooctyne **2** and acetylene **3**

	E	G	H	ΔE	ΔG	ΔH
1	-435.0187382	-434.918269	-434.873628			
2	-311.8947477	-311.741219	-311.701556			
3	-77.30043325	-77.291483	-77.268889			
TS1	-746.8916035	-746.616323	-746.553155	13.7	27.1	13.8
4	-747.0571443	-746.77023	-746.713028	-90.1	-86.5	-69.5
TS2	-512.2871609	-512.158649	-512.110251	20.1	32.1	20.2
5	-512.4488344	-512.312071	-512.265427	-81.4	-64.2	-77.1

Table S2 — MPWB1K/6-311G(d,p) calculated total energies (in au) and relative energies, enthalpies and Gibbs free energies, in kcal mol^{-1}, computed at 298 K in acetonitrile of the stationary points involved in the 32CA reactions of benzyl azide **1** with cyclooctyne **2** and acetylene **3**

	E	G	H	ΔE	ΔG	ΔH
1	-435.0283168	-434.929103	-434.884138			
2	-311.8993475	-311.746457	-311.706804			
3	-77.30680041	-77.298379	-77.275803			
TS1	-746.9018575	-746.627465	-746.564645	16.2	30.2	16.5
4	-747.0741155	-746.788379	-746.731187	-91.9	-70.8	-88.0
TS2	-512.2997689	-512.172614	-512.124169	22.2	34.4	22.4
5	-512.467055	-512.331588	-512.284756	-82.8	-65.3	-78.3

Fig. S3 — MPWB1K/6-311G(d,p) optimized structure 3 (gas phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	2.449033	-0.318120	0.443706
2	7	0	2.732792	-0.659701	1.468364
3	7	0	2.229429	-0.016722	-0.717529
4	6	0	-0.193888	0.439299	-0.440480
5	6	0	-1.035961	1.253653	0.293755
6	6	0	-0.606386	-0.845053	-0.758858
7	6	0	-2.277564	0.799996	0.696235
8	1	0	-0.717380	2.250938	0.555781
9	6	0	-1.842974	-1.300877	-0.354752
10	1	0	0.055577	-1.486820	-1.318725
11	6	0	-2.683298	-0.477985	0.372253
12	1	0	-2.924033	1.444112	1.269508
13	1	0	-2.153630	-2.301752	-0.606412
14	1	0	-3.649014	-0.836008	0.689200
15	6	0	1.141571	0.942689	-0.903771
16	1	0	1.375256	1.883853	-0.407112
17	1	0	1.125439	1.137147	-1.970320

Table S4 — Cartesian coordinates of optimized structure **2** (gas phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.943722	-0.902180	-0.106658
2	6	0	-1.848096	0.583920	0.263993
3	6	0	1.944016	-0.901545	0.107343
4	6	0	-0.669967	1.316373	-0.384557
5	6	0	1.848037	0.584334	-0.263842
6	6	0	0.669249	1.316379	0.384189
7	1	0	-2.321217	-1.012313	-1.122136
8	1	0	-1.766508	0.668536	1.346228
9	1	0	-0.514036	0.914231	-1.385308
10	1	0	2.641497	-1.419044	-0.546051
11	1	0	1.767222	0.668623	-1.346174
12	1	0	-2.639653	-1.419750	0.548307
13	1	0	-2.781402	1.068646	-0.015665
14	1	0	2.319639	-1.011076	1.123590
15	1	0	-0.971696	2.351485	-0.525831
16	1	0	2.780845	1.069675	0.016373
17	1	0	0.970594	2.351546	0.525955
18	1	0	0.513176	0.913946	1.384812
19	6	0	-0.596701	-1.427158	-0.024424
20	6	0	0.597441	-1.427539	0.023271

Table S5 — Cartesian coordinates of optimized structure **3** (gas phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	**0.595053**
2	6	0	0.000000	0.000000	**-0.595053**
3	1	0	0.000000	0.000000	**1.653273**
4	1	0	0.000000	0.000000	**-1.653273**

Table S6 — Cartesian coordinates of optimized structure **4** (gas phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.817359	2.467028	0.606309
2	7	0	-2.006967	2.007152	0.738796
3	1	0	-3.469708	-0.316175	-1.116602
4	6	0	-3.365128	0.084212	-0.108334
5	6	0	-3.299707	-1.065222	0.893586
6	1	0	-4.244719	0.690870	0.083499
7	6	0	-2.156008	0.933593	-0.059582
8	6	0	-1.978210	-1.817139	0.902971
9	1	0	-4.113203	-1.758569	0.682532
10	1	0	-3.477910	-0.669961	1.891493
11	6	0	-0.979133	0.714611	-0.719388
12	6	0	-1.529923	-2.389258	-0.446377
13	1	0	-2.066001	-2.625762	1.624605
14	1	0	-1.198641	-1.161370	1.289009
15	6	0	-0.596017	-0.335729	-1.693273
16	6	0	-0.327118	-1.708754	-1.085663
17	1	0	-2.362325	-2.384245	-1.152225
18	1	0	-1.271188	-3.436935	-0.314030
19	1	0	-1.400707	-0.428479	-2.422558
20	1	0	0.283857	-0.015921	-2.246938
21	1	0	0.477109	-1.629951	-0.354551
22	1	0	0.047016	-2.346194	-1.884955
23	7	0	-0.183295	1.702917	-0.271781
24	6	0	1.202001	1.956183	-0.567619
25	1	0	1.433090	2.892163	-0.070266
26	1	0	1.325459	2.104356	-1.637065
27	6	0	2.085065	0.843045	-0.087416
28	6	0	2.965952	0.219714	-0.949304
29	6	0	1.999517	0.410582	1.226548
30	6	0	3.754481	-0.827528	-0.510265
31	1	0	3.031151	0.549145	-1.975367
32	6	0	2.784644	-0.634446	1.665946
33	1	0	1.304629	0.892386	1.897546
34	6	0	3.662302	-1.257654	0.797240
35	1	0	4.435571	-1.309846	-1.192055
36	1	0	2.711466	-0.965689	2.688868
37	1	0	4.272091	-2.076770	1.141375

Table S7 — Cartesian coordinates of optimized structure 5 (gas phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.267123	0.288117	-0.974446
2	7	0	-3.204850	0.796733	-0.265178
3	6	0	-3.090606	0.343932	0.997019
4	6	0	-2.015967	-0.489390	1.060086
5	7	0	-1.541389	-0.495834	-0.193539
6	6	0	-0.373118	-1.149490	-0.724891
7	1	0	-0.501460	-1.132614	-1.802530
8	1	0	-0.372832	-2.186390	-0.404300
9	6	0	0.905527	-0.472020	-0.328112
10	6	0	2.003229	-1.220436	0.052299
11	6	0	1.007049	0.908523	-0.375401
12	6	0	3.194833	-0.600320	0.376196
13	1	0	1.928165	-2.296335	0.095735
14	6	0	2.194454	1.527882	-0.047186
15	1	0	0.149499	1.492654	-0.671629
16	6	0	3.291776	0.774973	0.327472
17	1	0	4.044946	-1.192938	0.671972
18	1	0	2.264811	2.602544	-0.085559
19	1	0	4.218837	1.261115	0.583243
20	1	0	-1.565383	-1.048787	1.853748
21	1	0	-3.776117	0.635708	1.766570

Table S8 — Cartesian coordinates of optimized structure TS1 (gas phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.490805	2.022048	-0.554373
2	7	0	-0.199967	2.494176	0.223742
3	1	0	-2.784606	2.449119	1.163526
4	6	0	-2.676328	1.368621	1.204920
5	6	0	-4.014392	0.686252	0.951598
6	1	0	-2.328149	1.136546	2.211341
7	6	0	-1.673643	0.906731	0.249103
8	6	0	-3.949768	-0.836888	0.869033
9	1	0	-4.441691	1.076499	0.028973
10	1	0	-4.694039	0.976331	1.750966
11	6	0	-1.237188	0.080715	-0.541804
12	6	0	-3.679084	-1.451718	-0.515668
13	1	0	-4.903575	-1.221607	1.221759
14	1	0	-3.206649	-1.200085	1.579838
15	6	0	-1.251869	-1.166045	-1.294101
16	6	0	-2.312720	-2.101750	-0.724508
17	1	0	-3.833996	-0.694789	-1.284681
18	1	0	-4.434326	-2.212960	-0.694411
19	1	0	-1.466543	-0.947870	-2.339643
20	1	0	-0.275046	-1.647442	-1.269156
21	1	0	-1.958493	-2.503134	0.223700
22	1	0	-2.408422	-2.949528	-1.400022
23	7	0	0.538409	1.067492	-1.348234
24	6	0	1.817708	0.489676	-1.682360
25	1	0	2.400997	1.186173	-2.282894
26	1	0	1.577994	-0.345610	-2.336430
27	6	0	2.632253	0.007264	-0.515141
28	6	0	4.003966	-0.129650	-0.648045
29	6	0	2.035381	-0.331963	0.687096
30	6	0	4.767801	-0.606552	0.396903
31	1	0	4.478961	0.144630	-1.577991
32	6	0	2.801263	-0.806298	1.734617
33	1	0	0.969025	-0.216423	0.805971
34	6	0	4.166736	-0.947186	1.593460
35	1	0	5.834781	-0.705100	0.280011
36	1	0	2.326263	-1.063450	2.667397
37	1	0	4.762077	-1.314570	2.413168

Table S9 — Cartesian coordinates of optimized structure TS2 (gas phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.730512	-0.449374	1.016653
2	7	0	2.373598	0.369037	1.493618
3	6	0	3.244008	1.066918	-0.332689
4	6	0	2.753094	0.344254	-1.185945
5	7	0	1.555317	-0.995772	-0.085732
6	6	0	0.258360	-1.542252	-0.410699
7	1	0	0.095715	-2.465701	0.142438
8	1	0	0.334514	-1.826146	-1.457655
9	6	0	-0.902832	-0.610682	-0.211535
10	6	0	-2.160634	-1.134697	0.032935
11	6	0	-0.749906	0.762815	-0.294797
12	6	0	-3.252353	-0.303979	0.180023
13	1	0	-2.286305	-2.203899	0.112847
14	6	0	-1.842122	1.594613	-0.143191
15	1	0	0.227141	1.182966	-0.476260
16	6	0	-3.095270	1.065241	0.091574
17	1	0	-4.225503	-0.725643	0.371915
18	1	0	-1.710634	2.662461	-0.206923
19	1	0	-3.944910	1.717082	0.211807
20	1	0	2.546417	-0.092376	-2.130058
21	1	0	3.833508	1.830631	0.106048

Table S10 — Cartesian coordinates of optimized structure 1 (acetonitrile)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	2.417183	-0.329054	0.464670
2	7	0	2.648145	-0.669806	1.503411
3	7	0	2.247960	-0.022672	-0.700250
4	6	0	-0.180277	0.436392	-0.460843
5	6	0	-1.002051	1.254840	0.294161
6	6	0	-0.611494	-0.841109	-0.786734
7	6	0	-2.244549	0.810404	0.709678
8	1	0	-0.666522	2.248083	0.560899
9	6	0	-1.848274	-1.287949	-0.368024
10	1	0	0.030662	-1.488822	-1.367980
11	6	0	-2.669243	-0.461628	0.379999
12	1	0	-2.877289	1.458864	1.298424
13	1	0	-2.175181	-2.284939	-0.626286
14	1	0	-3.637240	-0.812314	0.707616
15	6	0	1.154685	0.931729	-0.932100
16	1	0	1.388748	1.884173	-0.459029
17	1	0	1.151024	1.089603	-2.005277

Table S11 — Cartesian coordinates of optimized structure 2 (acetonitrile)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.946341	-0.901915	-0.107573
2	6	0	-1.847838	0.583942	0.265392
3	6	0	1.946575	-0.901466	0.108023
4	6	0	-0.670468	1.317137	-0.383611
5	6	0	1.847650	0.584196	-0.265378
6	6	0	0.670072	1.317201	0.383488
7	1	0	-2.321924	-1.009863	-1.124446
8	1	0	-1.766830	0.667783	1.348216
9	1	0	-0.515895	0.917328	-1.386221
10	1	0	2.645038	-1.419505	-0.544653
11	1	0	1.766639	0.667711	-1.348231
12	1	0	-2.643716	-1.420141	0.546121
13	1	0	-2.782077	1.066183	-0.015701
14	1	0	2.321005	-1.008885	1.125385
15	1	0	-0.973316	2.352478	-0.522439
16	1	0	2.781735	1.066805	0.015605
17	1	0	0.972745	2.352587	0.522372
18	1	0	0.515520	0.917317	1.386075
19	6	0	-0.597816	-1.428525	-0.024519
20	6	0	0.598346	-1.428870	0.023830

Table S12 — Cartesian coordinates of optimized structure 3 (acetonitrile)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.596283
2	6	0	0.000000	0.000000	-0.596283
3	1	0	0.000000	0.000000	1.662419
4	1	0	0.000000	0.000000	-1.662419

Table S13 — Cartesian coordinates of optimized structure 4 (acetonitrile)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.833299	2.475862	0.598925
2	7	0	-2.027320	2.008237	0.728769
3	1	0	-3.454093	-0.339927	-1.121977
4	6	0	-3.364097	0.063901	-0.113875
5	6	0	-3.291673	-1.083998	0.890269
6	1	0	-4.255958	0.657320	0.068630
7	6	0	-2.164513	0.927428	-0.059190
8	6	0	-1.963846	-1.824524	0.905755
9	1	0	-4.097174	-1.784170	0.671316
10	1	0	-3.481720	-0.692956	1.888754
11	6	0	-0.978249	0.715110	-0.710156
12	6	0	-1.507184	-2.394003	-0.441838
13	1	0	-2.049011	-2.633177	1.628153
14	1	0	-1.189082	-1.163453	1.294300
15	6	0	-0.586818	-0.331747	-1.684167
16	6	0	-0.308299	-1.702637	-1.076068
17	1	0	-2.337307	-2.394880	-1.150615
18	1	0	-1.239424	-3.439378	-0.306747
19	1	0	-1.394161	-0.429962	-2.410199
20	1	0	0.287856	-0.002106	-2.239572
21	1	0	0.493457	-1.617585	-0.342911
22	1	0	0.072405	-2.333794	-1.877154
23	7	0	-0.191963	1.708733	-0.264514
24	6	0	1.197645	1.963575	-0.565563
25	1	0	1.433656	2.903340	-0.075796
26	1	0	1.311016	2.103975	-1.637240
27	6	0	2.079081	0.849693	-0.084234
28	6	0	2.941325	0.215521	-0.958833
29	6	0	2.012832	0.428212	1.235013
30	6	0	3.731787	-0.833391	-0.524185
31	1	0	2.988026	0.536754	-1.991246
32	6	0	2.798849	-0.620169	1.669142
33	1	0	1.336095	0.918621	1.921836
34	6	0	3.658652	-1.254648	0.789059
35	1	0	4.399705	-1.325882	-1.216133
36	1	0	2.740362	-0.944911	2.698062
37	1	0	4.270477	-2.077584	1.129505

Table S14 — Cartesian coordinates of optimized structure 5 (acetonitrile)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.258213	0.334776	-0.962540
2	7	0	-3.203935	0.817255	-0.234992
3	6	0	-3.101479	0.308485	1.005984
4	6	0	-2.028949	-0.532755	1.035018
5	7	0	-1.545144	-0.483164	-0.212219
6	6	0	-0.372773	-1.129197	-0.755424
7	1	0	-0.495349	-1.100851	-1.834490
8	1	0	-0.377125	-2.168955	-0.444112
9	6	0	0.904175	-0.458263	-0.341505
10	6	0	1.992414	-1.223850	0.036390
11	6	0	1.019621	0.922719	-0.369157
12	6	0	3.188352	-0.618588	0.377704
13	1	0	1.902980	-2.301746	0.064971
14	6	0	2.211202	1.527458	-0.022106
15	1	0	0.174243	1.528368	-0.665172
16	6	0	3.299418	0.757896	0.350119
17	1	0	4.032275	-1.225773	0.672169
18	1	0	2.291902	2.604799	-0.044492
19	1	0	4.231489	1.232641	0.620849
20	1	0	-1.589999	-1.139244	1.807002
21	1	0	-3.791256	0.565261	1.789387

Table S15 — Cartesian coordinates of optimized structure TS1 (acetonitrile)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.510748	2.062368	-0.426388
2	7	0	-0.181886	2.489740	0.378318
3	1	0	-2.829729	2.395127	1.264282
4	6	0	-2.693692	1.316133	1.252298
5	6	0	-4.018337	0.616798	0.975808
6	1	0	-2.332305	1.043010	2.244226
7	6	0	-1.688666	0.922810	0.267171
8	6	0	-3.927819	-0.901460	0.840089
9	1	0	-4.455916	1.032003	0.068270
10	1	0	-4.699597	0.866175	1.787797
11	6	0	-1.250559	0.145645	-0.571913
12	6	0	-3.662436	-1.469223	-0.565202
13	1	0	-4.873820	-1.311327	1.186472
14	1	0	-3.173675	-1.277681	1.533019
15	6	0	-1.260384	-1.062080	-1.387190
16	6	0	-2.275707	-2.053035	-0.827722
17	1	0	-3.879034	-0.705527	-1.313375
18	1	0	-4.384352	-2.263572	-0.740019
19	1	0	-1.517997	-0.801745	-2.413791
20	1	0	-0.273067	-1.520472	-1.420741
21	1	0	-1.884506	-2.474914	0.097338
22	1	0	-2.354575	-2.877559	-1.533914
23	7	0	0.555334	1.172350	-1.286944
24	6	0	1.831282	0.597656	-1.653708
25	1	0	2.424974	1.325533	-2.204877
26	1	0	1.586171	-0.191618	-2.361143
27	6	0	2.628655	0.036442	-0.510677
28	6	0	4.004057	-0.083335	-0.633980
29	6	0	2.016195	-0.393586	0.655382
30	6	0	4.755123	-0.633178	0.386293
31	1	0	4.491733	0.260337	-1.536808
32	6	0	2.768514	-0.940871	1.678600
33	1	0	0.946760	-0.295489	0.764960
34	6	0	4.138399	-1.064242	1.547035
35	1	0	5.826891	-0.718886	0.277677
36	1	0	2.279728	-1.271267	2.584029
37	1	0	4.725201	-1.490189	2.347985

Table S16 — Cartesian coordinates of optimized structure TS2 (acetonitrile)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.705562	-0.434206	1.024439
2	7	0	2.341959	0.389299	1.506905
3	6	0	3.261137	1.055581	-0.319160
4	6	0	2.776401	0.324388	-1.171038
5	7	0	1.552275	-0.992805	-0.070700
6	6	0	0.261231	-1.541900	-0.428695
7	1	0	0.095474	-2.475292	0.106604
8	1	0	0.357118	-1.803453	-1.480446
9	6	0	-0.900033	-0.612377	-0.224947
10	6	0	-2.152329	-1.137874	0.048414
11	6	0	-0.753256	0.761574	-0.331474
12	6	0	-3.244524	-0.305795	0.202395
13	1	0	-2.273332	-2.208787	0.145134
14	6	0	-1.844864	1.594803	-0.173381
15	1	0	0.218997	1.182183	-0.539017
16	6	0	-3.093388	1.064032	0.091650
17	1	0	-4.215522	-0.728686	0.416924
18	1	0	-1.717680	2.664655	-0.257342
19	1	0	-3.945228	1.716694	0.216838
20	1	0	2.567660	-0.124612	-2.116122
21	1	0	3.851693	1.826700	0.120335