Supporting Information for

Photochemical [2+2] Cycloaddition Reaction of Carbonyl Compounds with Danishefsky Diene

Dian Agung Pangaribowo[a,b], Manabu Abe[a,c]

[a]Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan

[b]Department of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Jember, Jember, Jawa Timur 68121, Indonesia

[c]Hiroshima Research Center for Photo-Drug-Delivery Ststems (Hi-P-DDS), Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan

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Structural determination of *cis*-5, *trans*-7, and *cis*-7

Figure S1 shows the ^{1}H NMR spectrum of *cis*-**5**. In contrast to the large coupling constant in *trans*-**5**, the protons assigned as H_e (δ 4.4 ppm) and H_f (δ 5.2 ppm) possess at coupling constant of 7.0 Hz, which is a typical value for *cis*-configuration alkene protons. The observation excludes the possibility of the formation of all-*trans* isomer and *cis*-**6**/**7**. The H-C HMBC spectrum (Figure S2) shows the correlation of H_e with the quaternary carbon connected to phenyl rings C_g (97.30 ppm), which verifies the formation of oxetane *cis*-**5**.

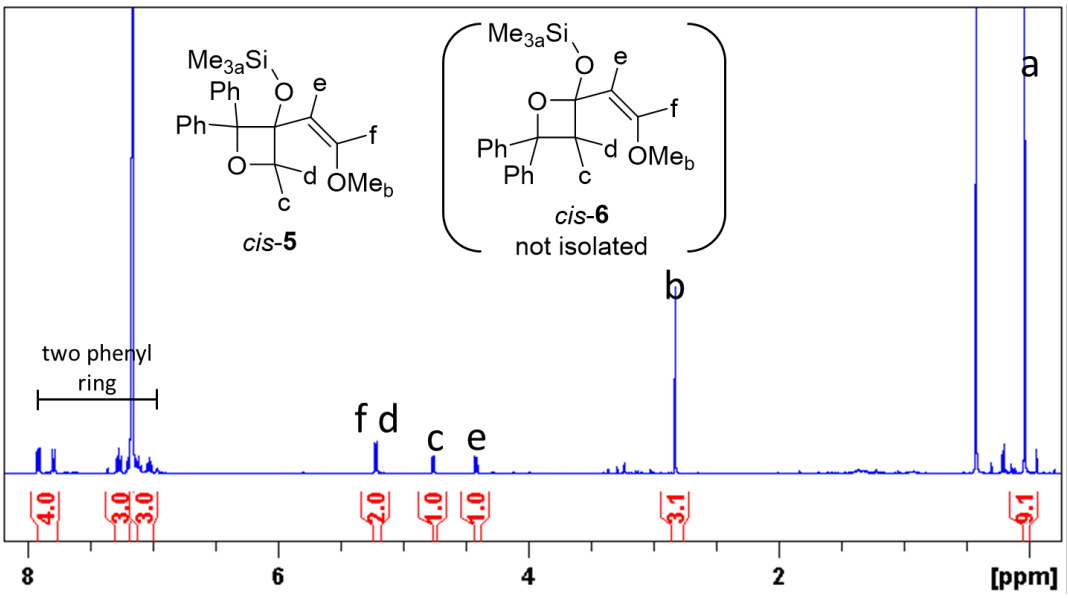


Figure S1. ^{1}H NMR (400 MHz, C_6D_6) spectrum of *cis*-**5**

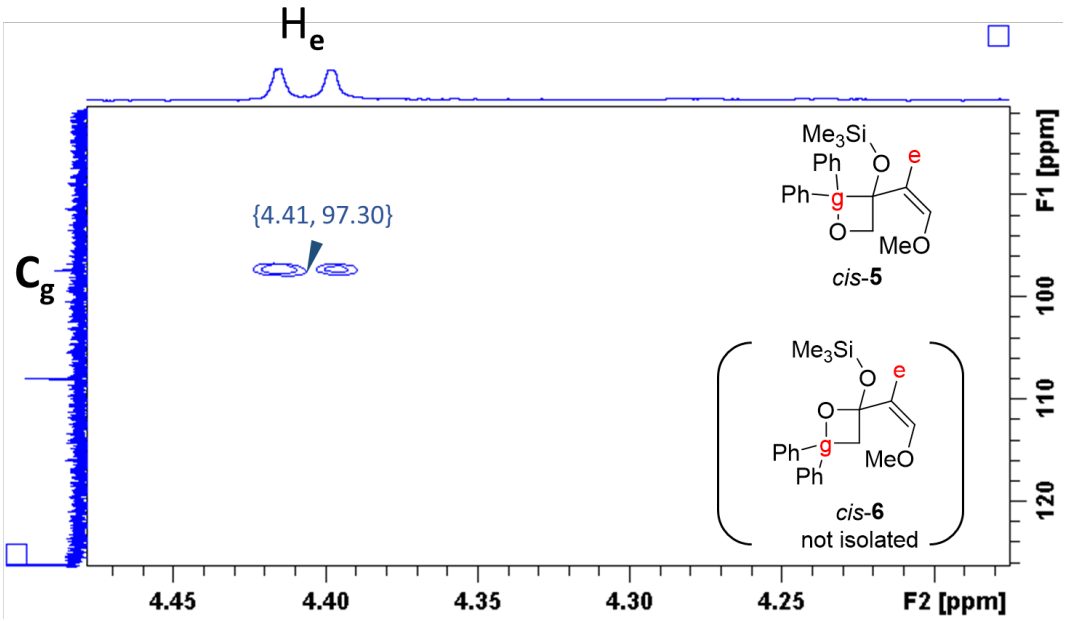


Figure S2. H-C HMBC spectrum of *cis*-**5** (400 MHz, C_6D_6)

Figure S3 shows the ^{1}H NMR spectrum of *trans*-**7**. Protons assigned as H_c (δ 3.9 ppm) and H_d (δ 4.1 ppm) with a very small coupling constant of 1.9 Hz belong to the alkene geminal protons. This assignment excludes the possibility of the formation of **5**/**6**. Moreover, in the H-C HMBC spectrum (Figure S4), the correlation of H_e with the quaternary carbon in phenyl rings C_h (143.13 ppm) and C_i (147.70 ppm) was observed, thus excludes the possibility of the formation of *cis/trans*-**8**. The stereochemistry of proton e and f of compound *trans*-**7** was determined to be *trans* because the correlation of H_d (δ 4.11) and H_f (δ 5.79) was observed in the H-H NOESY spectrum, although the correlation of H_e and H_f was also observed. (Figure S5).

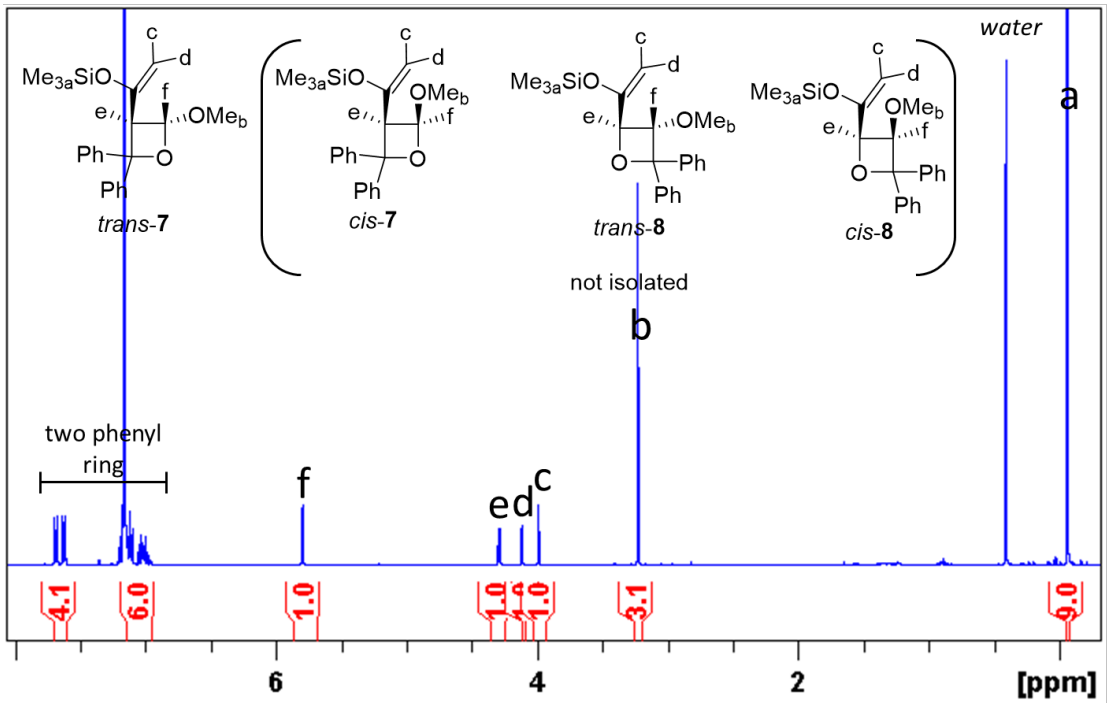


Figure S3. ^{1}H NMR (400 MHz, C_6D_6) spectrum of *trans*-**7**

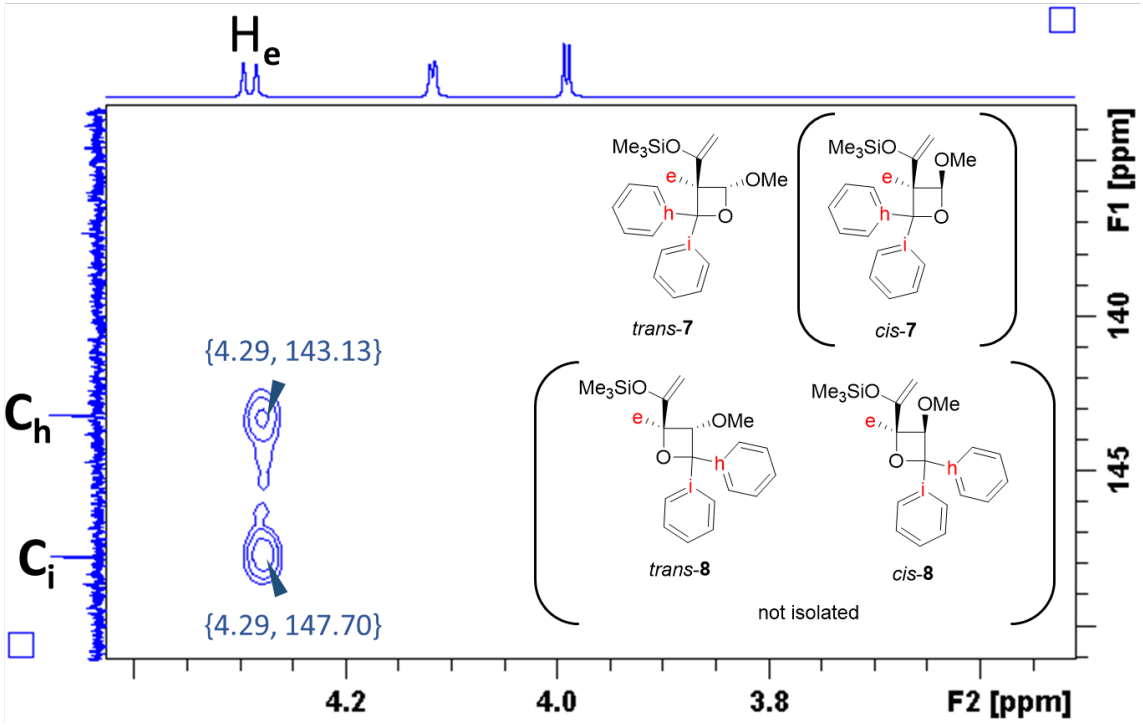


Figure S4. H-C HMBC spectrum of *trans*-**7** (400 MHz, C_6D_6)

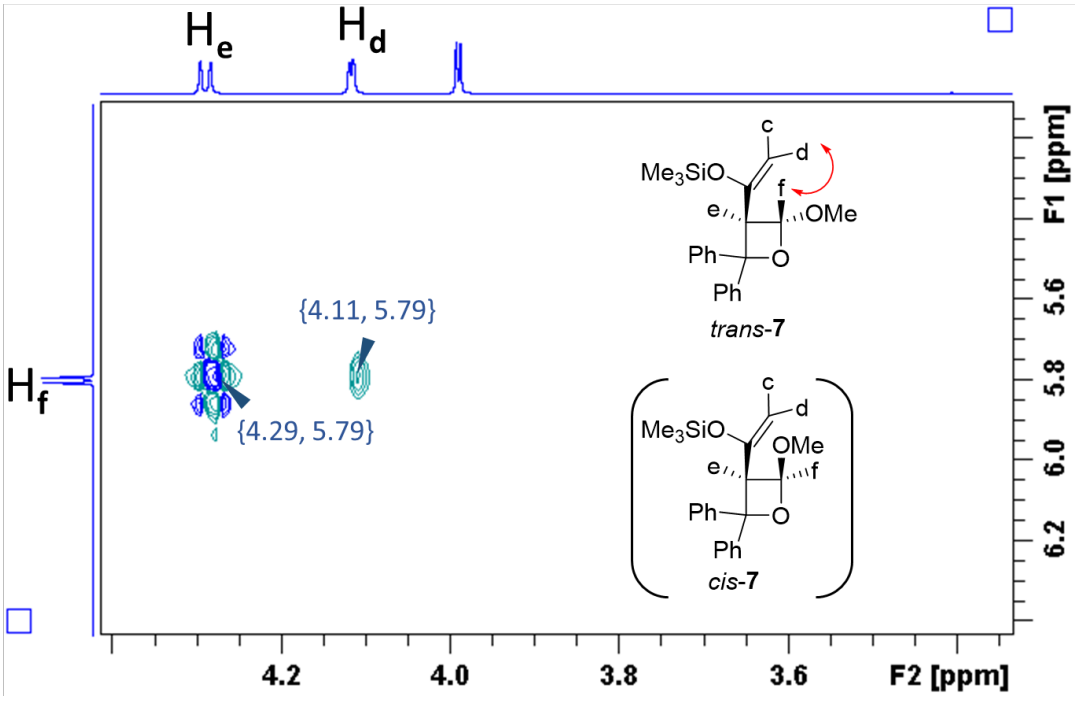


Figure S5. H-H NOESY spectrum of *trans*-**7** (400 MHz, C_6D_6)

Figure S6 shows the ^{1}H NMR spectrum of *cis*-**7**. Along with the assignment of *trans*-**7**, proton assigned as H_c (δ 4.2 ppm) and H_d (δ 4.9 ppm) with coupling constant value 1.1 Hz belong to alkene geminal proton. The observation excludes the possibility of the formation of **5/6**. Furthermore, in the H-C HMBC spectrum (Figure S7), the correlation of H_e with the quaternary carbons in phenyl rings C_h (143.22 ppm) and C_i (147.72 ppm) was observed, thus excludes the possibility of the formation of *cis/trans*-**8**. The stereochemistry of proton e and f of compound *cis*-**7** was determined to be *cis* because the correlation of H_e (δ 4.28) and H_f (δ 5.21) was observed in the H-H NOESY spectrum, but no correlation of H_d (δ 4.89) and H_f (δ 5.21) was observed. (Figure S8).

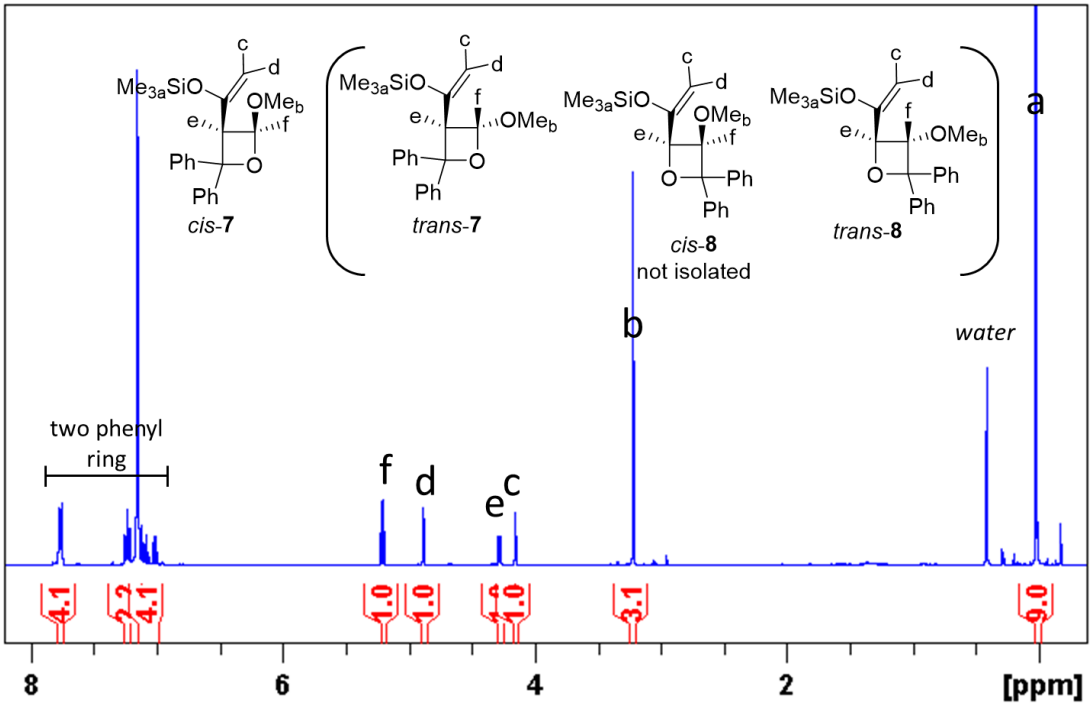


Figure S6. ^{1}H NMR (400 MHz, C_6D_6) spectrum of *cis*-**7**

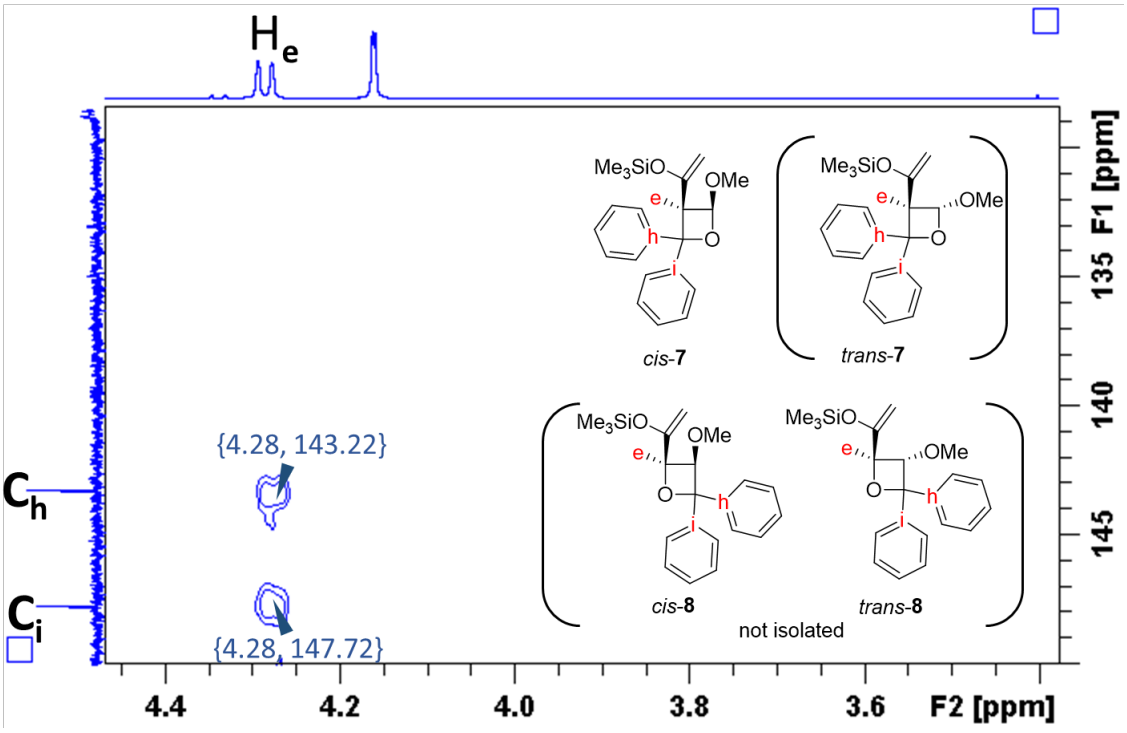


Figure S7. H-C HMBC spectrum of *cis*-**7** (400 MHz, C_6D_6)

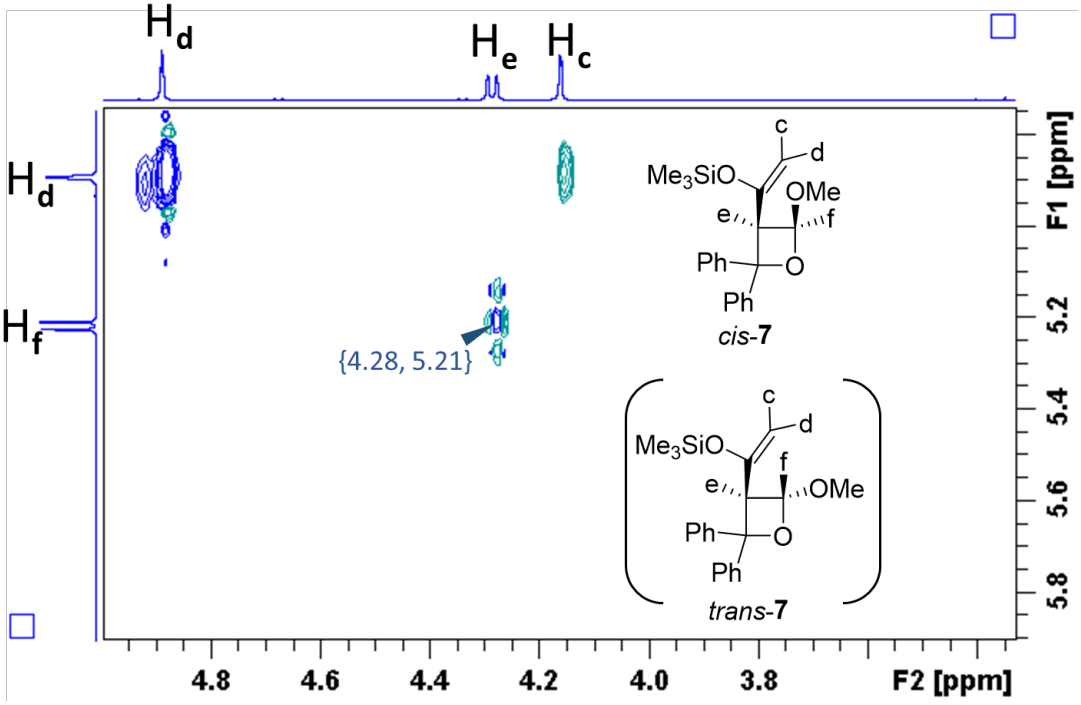


Figure S8. H-H NOESY spectrum of *cis*-**7** (400 MHz, C_6D_6)

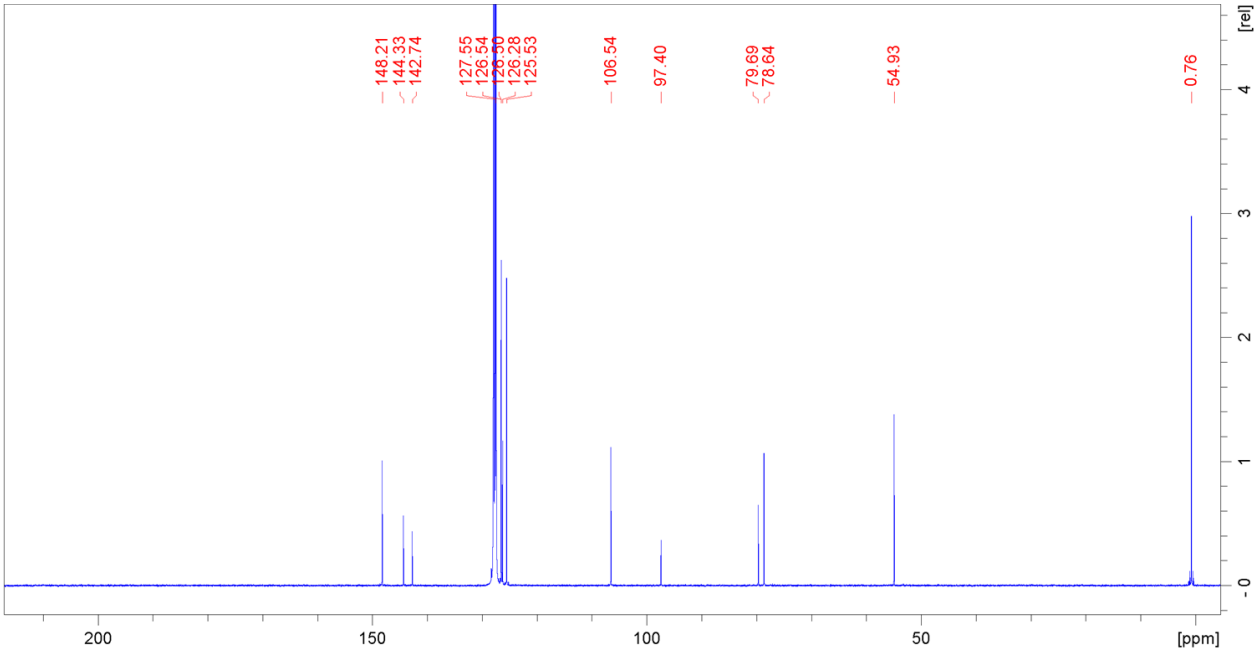


Figure S9. ^{13}C NMR spectrum of *trans*-**5** (101 MHz, C_6D_6)

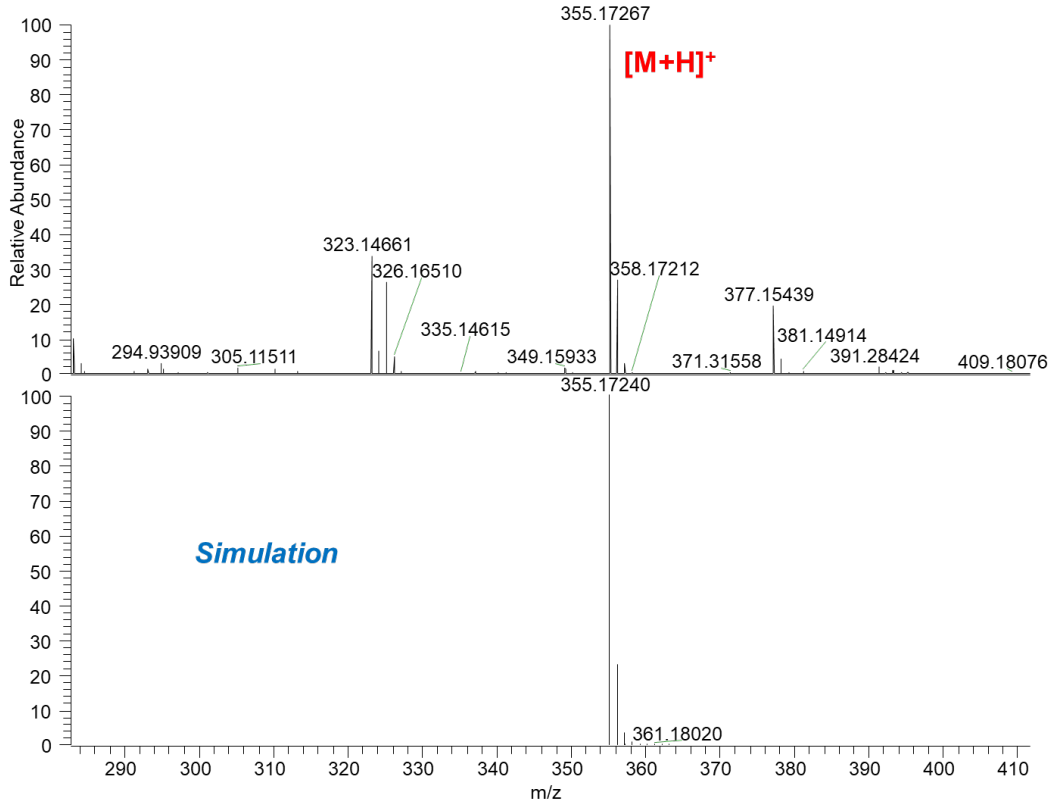


Figure S10. HRMS spectrum of *trans*-**5**

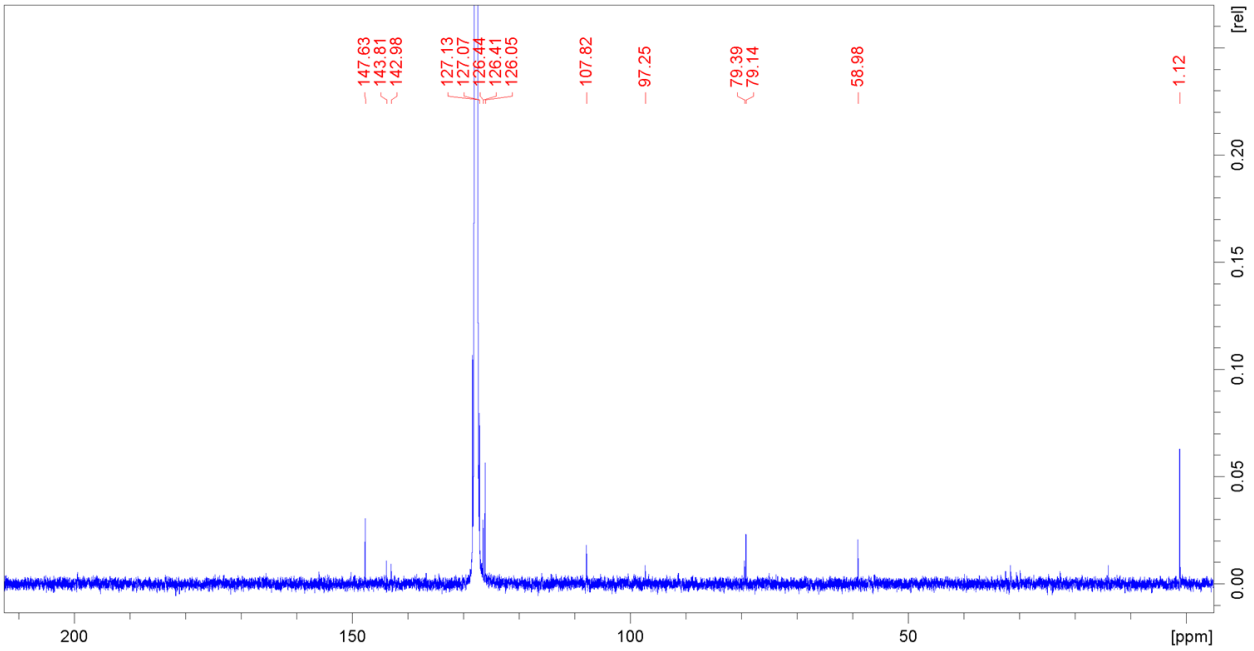


Figure S11. ^{13}C NMR spectrum of *cis*-**5** (101 MHz, C_6D_6)

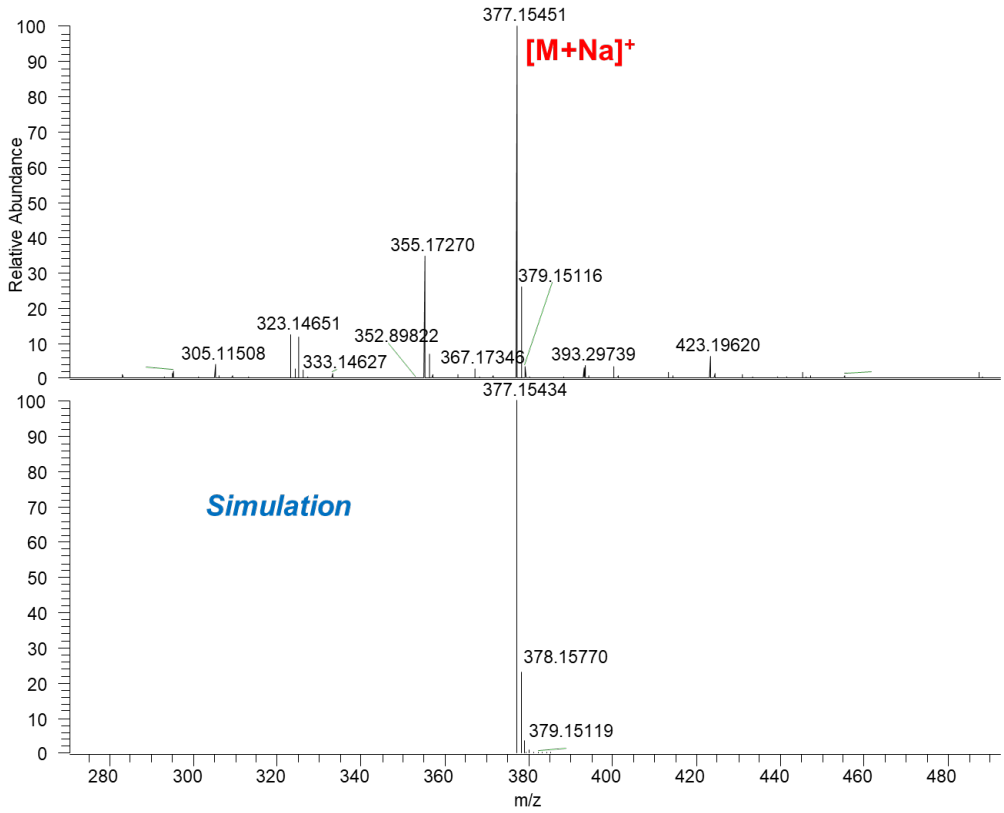


Figure S12. HRMS spectrum of *cis*-**5**

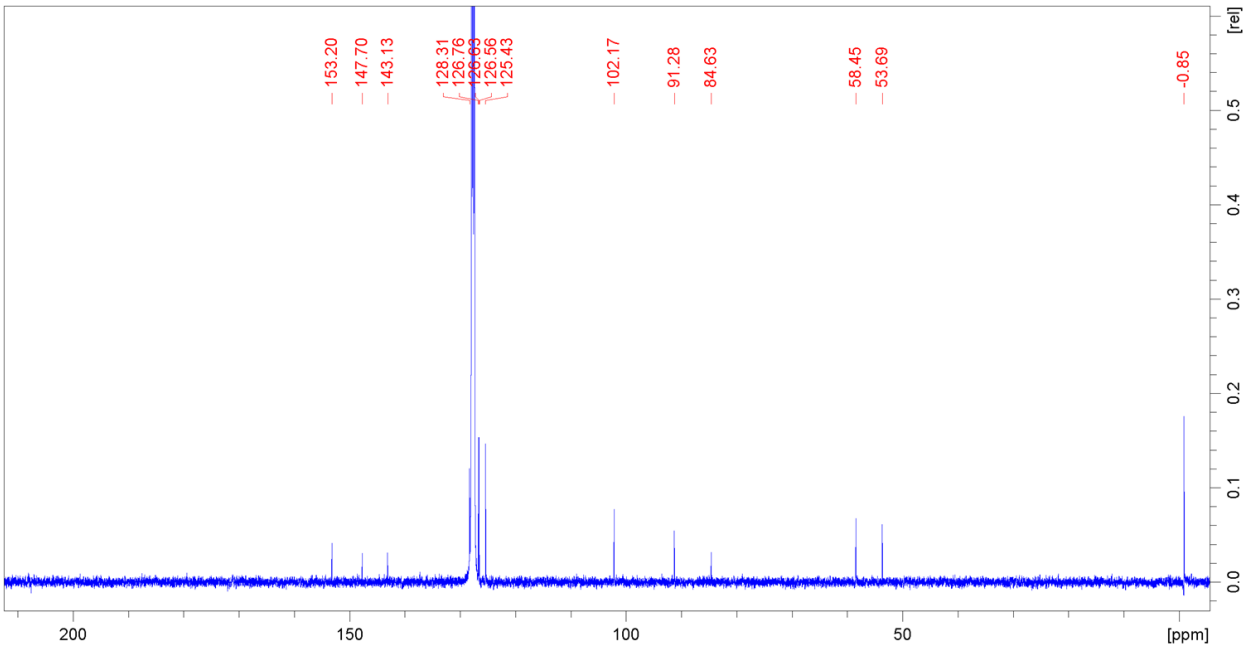


Figure S13. ^{13}C NMR spectrum of *trans*-**7** (101 MHz, C_6D_6)

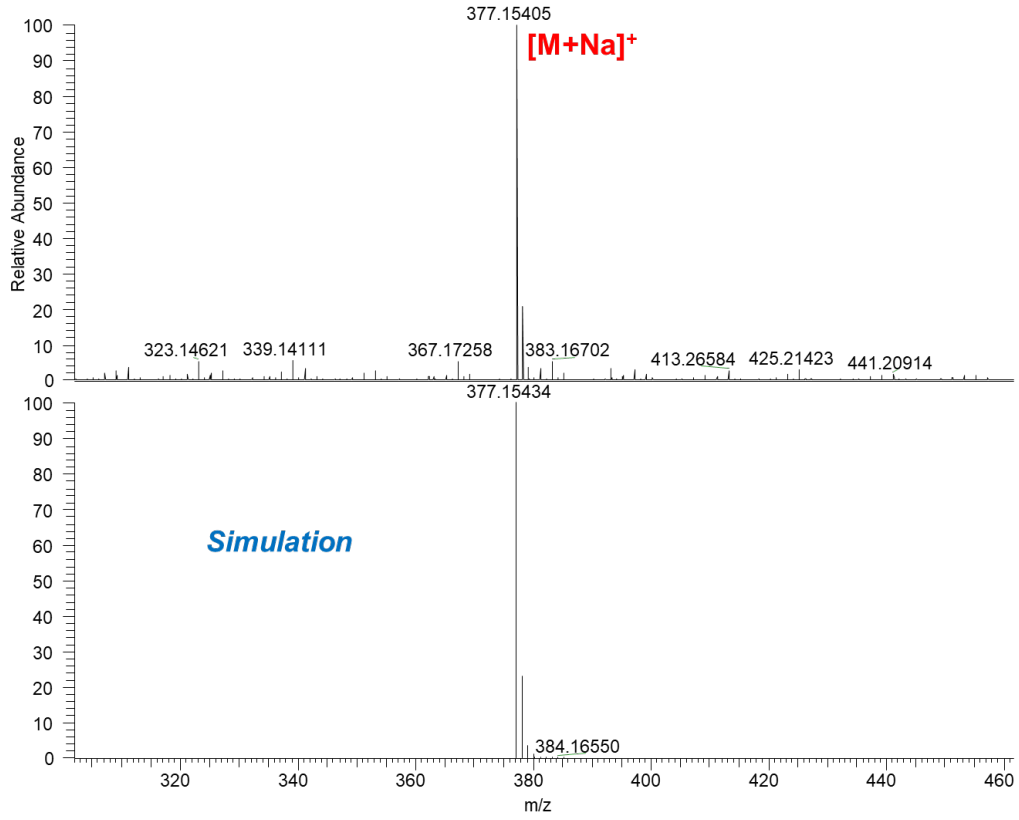


Figure S14. HRMS spectrum of *trans*-**7**

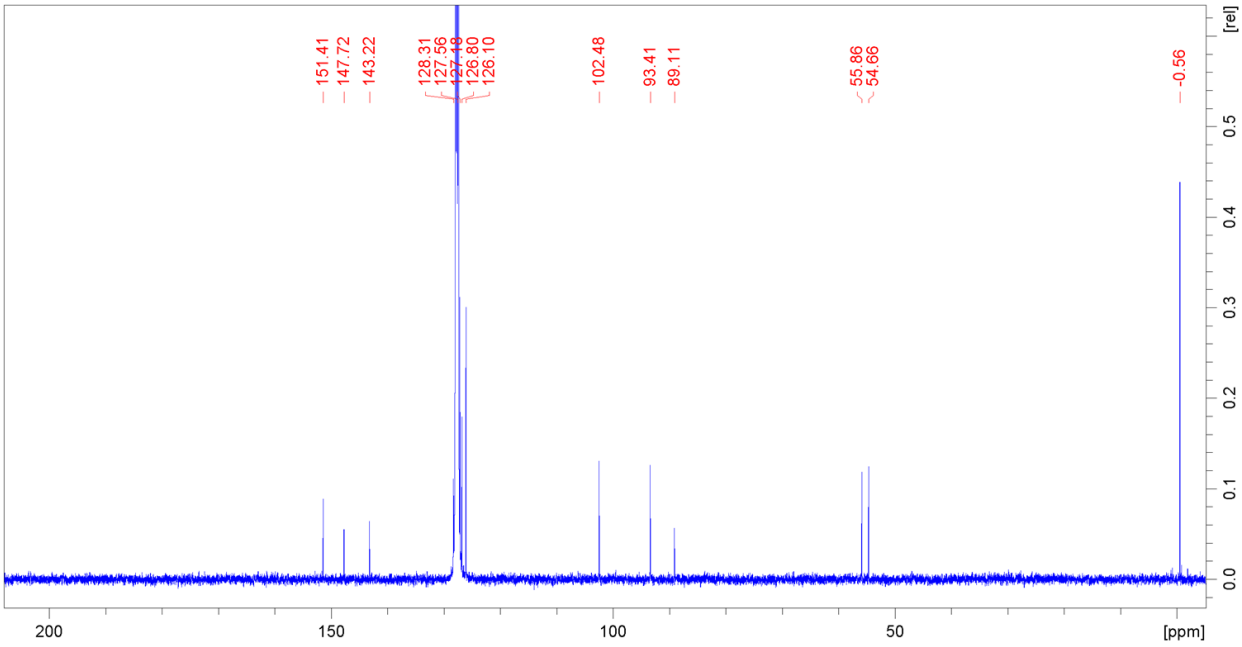


Figure S15. ^{13}C NMR spectrum of *cis*-**7** (101 MHz, C_6D_6)

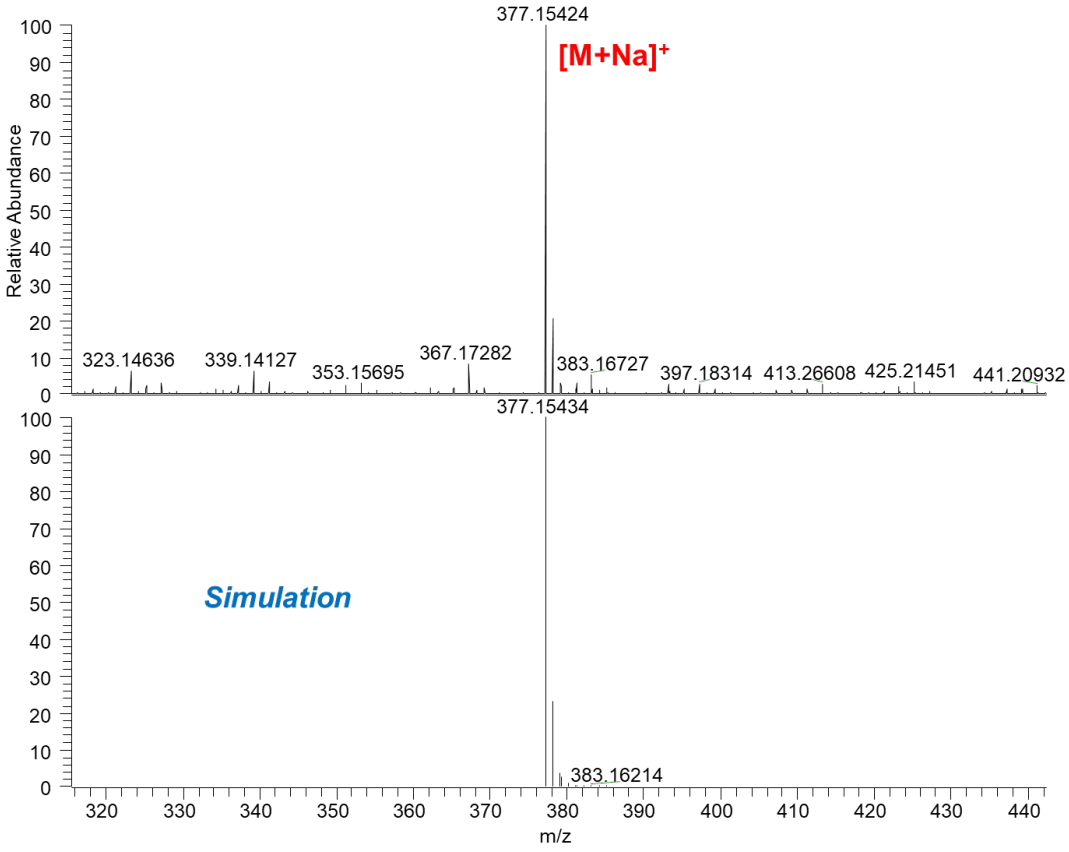


Figure S16. HRMS spectrum of *cis*-**7**

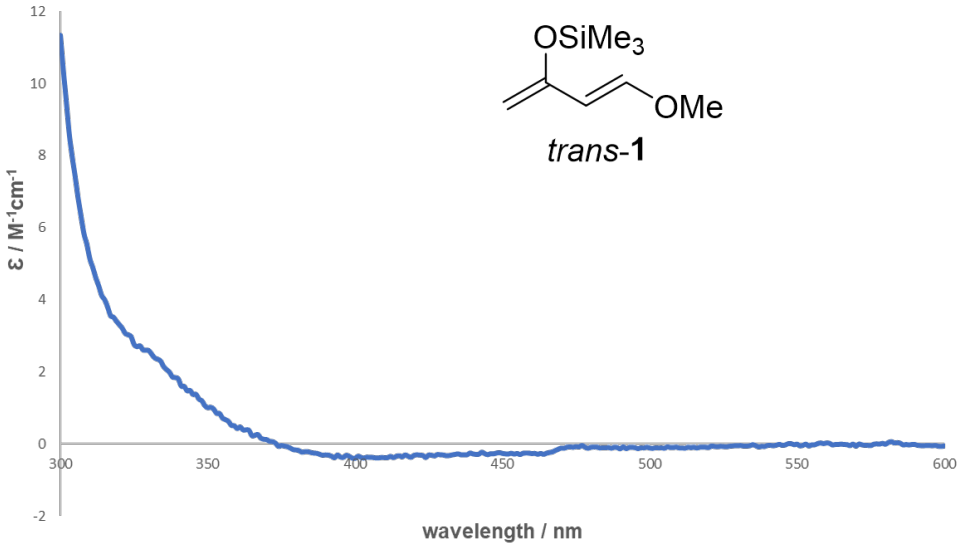


Figure S17. UV spectra of *trans*-**1**

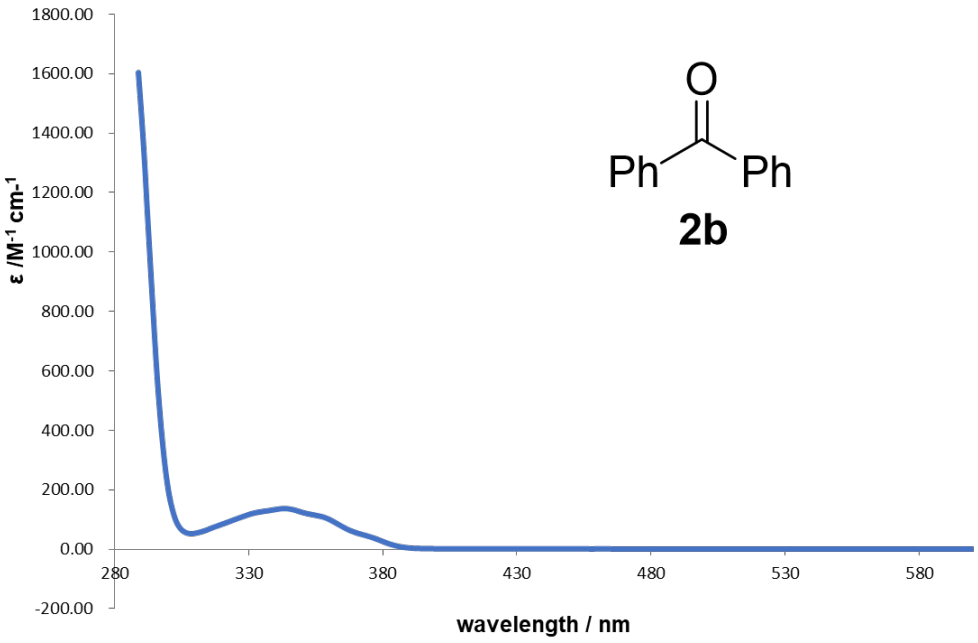


Figure S18. UV spectra of **2b**

Number of photon measurement

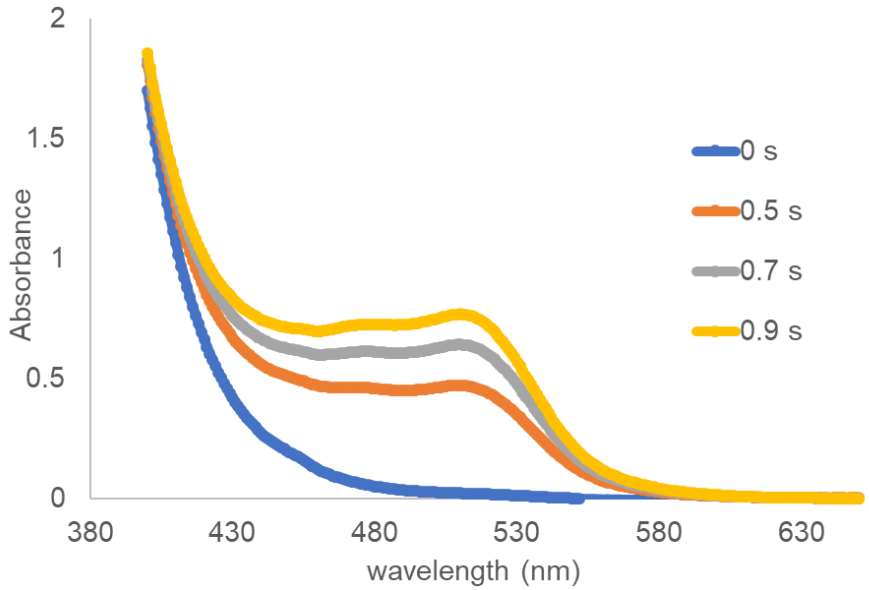


Figure S19. UV spectrum of potassium ferric oxalate solution mixed with phenanthroline after irradiation

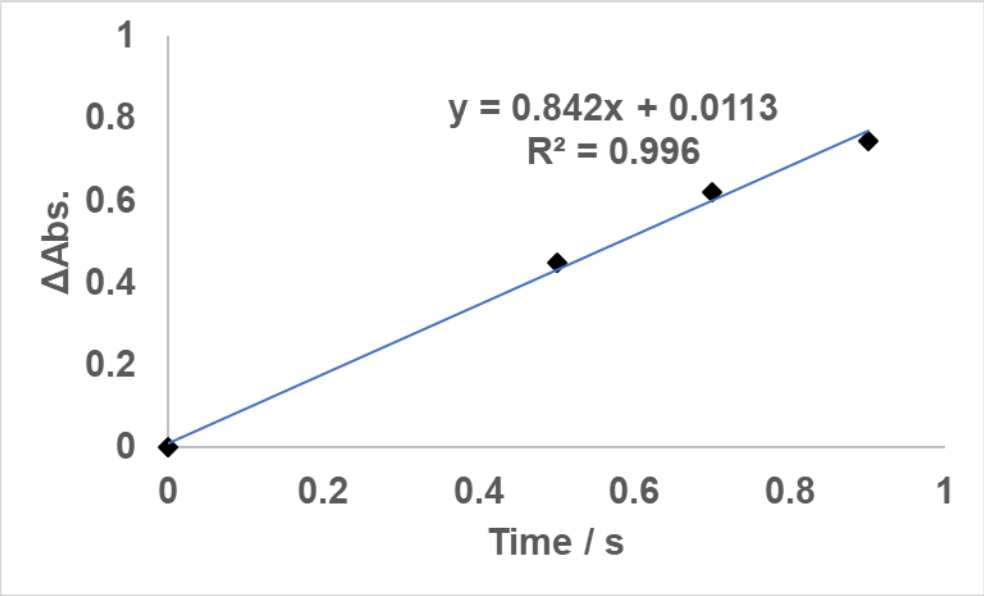
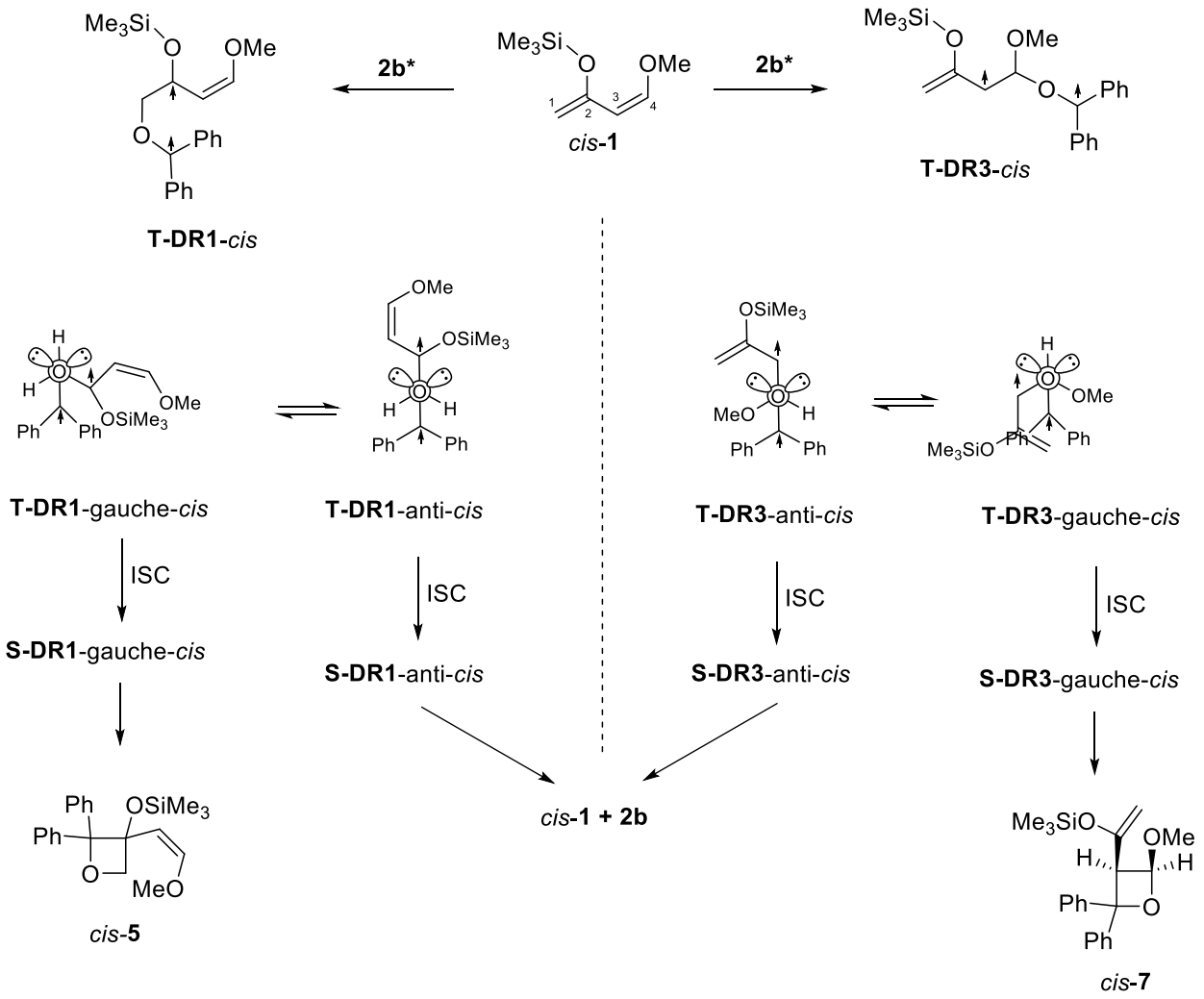


Figure S20. The relative plot of absorption and irradiation of potassium ferric oxalate solution mixed with phenanthroline using LED 365 nm lamp

Table S1. Δ Absorbance value in different time of irradiation

Time of irradiation (s)	**Absorbance at 510 nm**	**Δ Absorbance**
0	0.022511	0
0.5	0.471014	0.448503
0.7	0.641684	0.619173
0.9	0.768232	0.745721



$$\mathbf{5}:\mathbf{7} = \frac{[\text{gauche-}trans] + [\text{gauche-}cis]}{[\text{gauche-}trans] + [\text{gauche-}cis] + [\text{anti}]} : \frac{[\text{gauche-}trans] + [\text{gauche-}cis]}{[\text{gauche-}trans] + [\text{gauche-}cis] + [\text{anti}]}$$

Scheme S1. Proposed mechanism for the selective formation of *cis*-**5** and *cis*-**7**

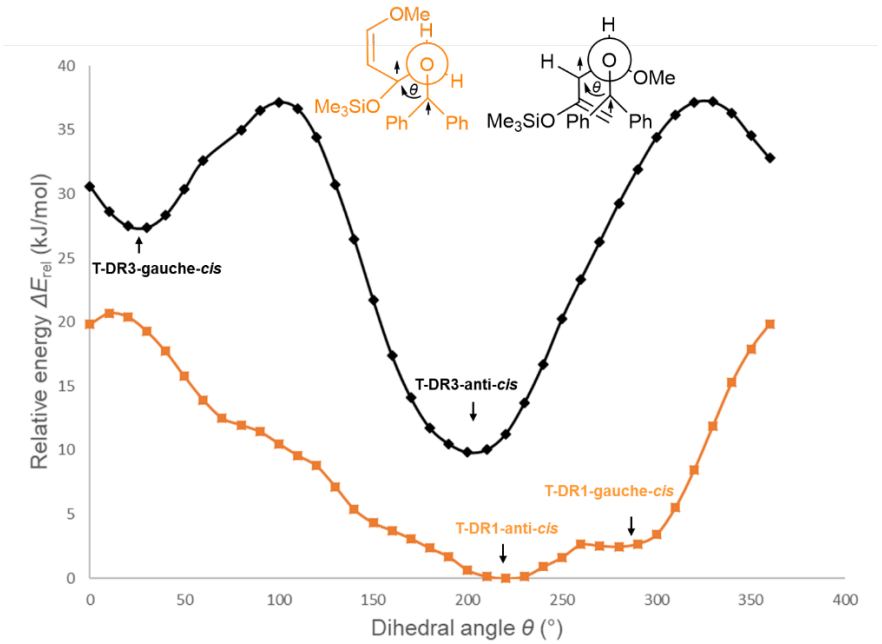


Figure S21. PES analyses around the dihedral angle (θ°) of diradicals **T-DR1**-*cis* and **T-DR3**-*cis*. The energies, ΔE_{rel} in kJ/mol, were relative to the most stable conformer.

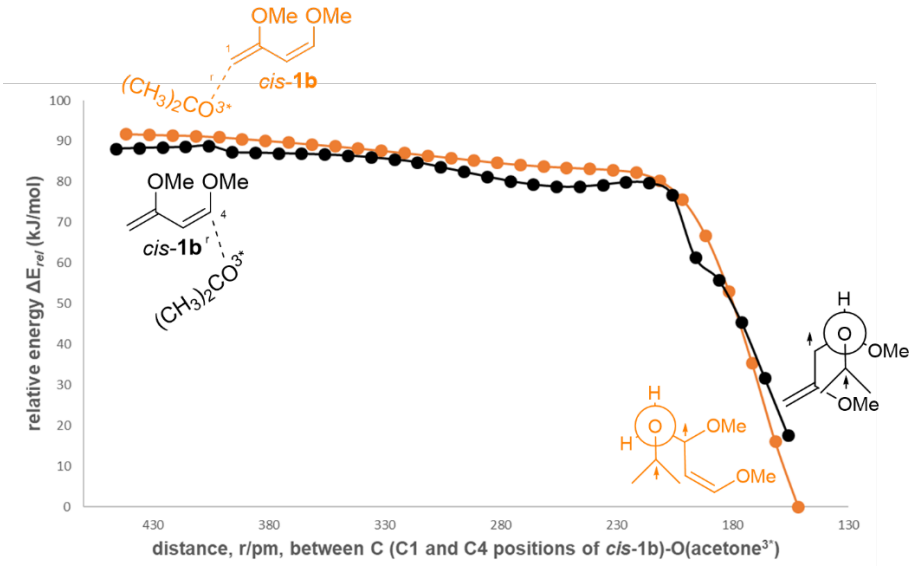


Figure S22. The UB3LYP/6-31G(d) potential energy surface analyses of the distance r (pm) of the C (C1 and C4 position of ***cis*-1b**) to the O of **acetone**. The energies, ΔE_{rel} in kJ/mol, are relative to the most stable diradical.

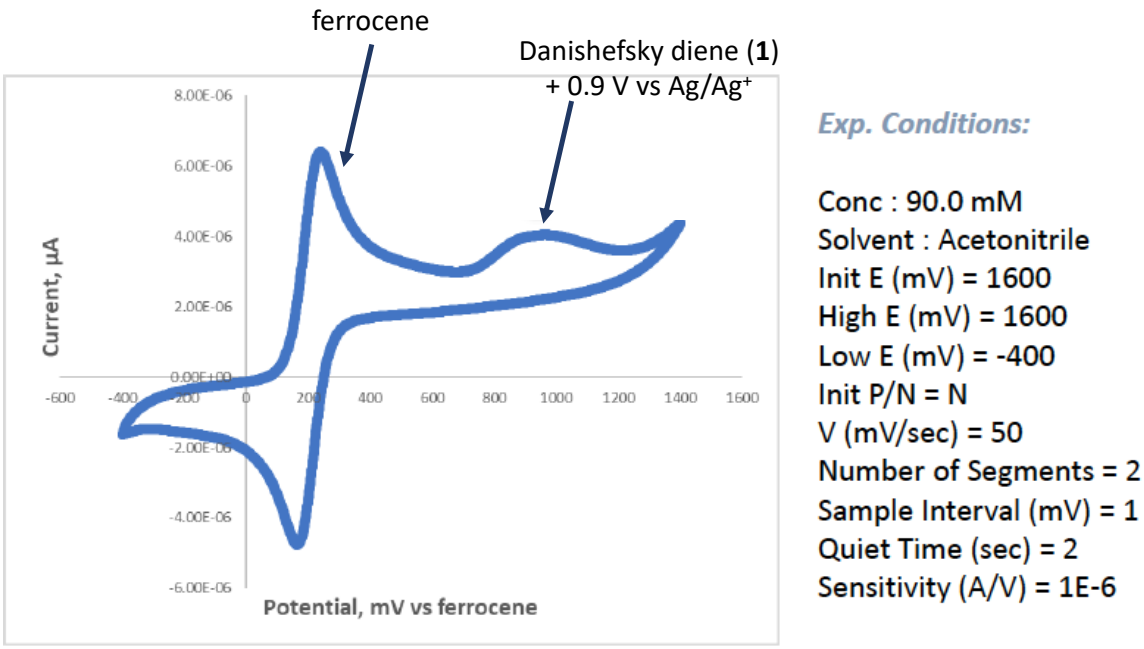
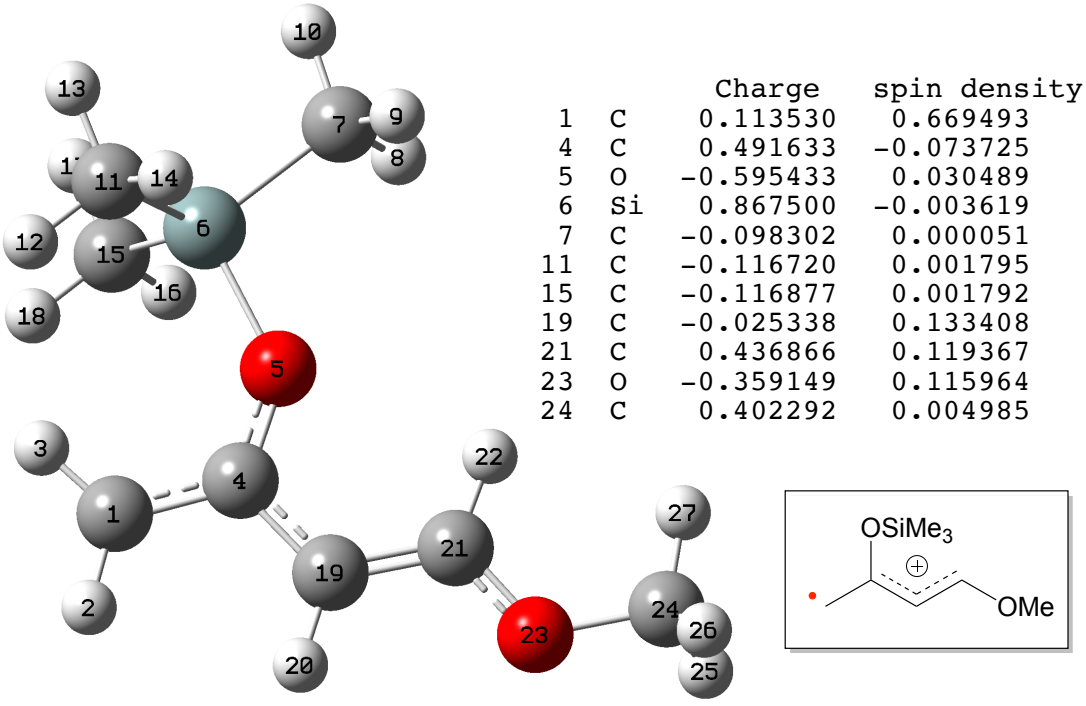


Figure S23. Cyclic voltammetry measurement of Danishefski diene (1).



		Charge	spin density
1	C	0.113530	0.669493
4	C	0.491633	-0.073725
5	O	-0.595433	0.030489
6	Si	0.867500	-0.003619
7	C	-0.098302	0.000051
11	C	-0.116720	0.001795
15	C	-0.116877	0.001792
19	C	-0.025338	0.133408
21	C	0.436866	0.119367
23	O	-0.359149	0.115964
24	C	0.402292	0.004985

Figure S24. Charge and spin-density distribution in the radical cation of 1 at the UB3LYP/6-31G(d) level of theory.

Computational data

Structure of optimized structures **T-DR1**-gauche-*trans*

```
 Zero-point correction = 0.419254 (Hartree/Particle)
 Thermal correction to Energy = 0.446593
 Thermal correction to Enthalpy = 0.447537
 Thermal correction to Gibbs Free Energy = 0.357594
 Sum of electronic and zero-point Energies = -1330.604995
 Sum of electronic and thermal Energies = -1330.577656
 Sum of electronic and thermal Enthalpies = -1330.576712
 Sum of electronic and thermal Free Energies = -1330.666654
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.479579	-0.331342	-1.802880
2	1	0	-0.107521	-1.251459	-1.749213
3	1	0	0.934887	-0.255922	-2.794003
4	6	0	1.530988	-0.307727	-0.741006
5	8	0	1.185497	-0.812434	0.487016
6	14	0	1.268901	-2.413093	1.038258
7	6	0	0.473123	-3.595066	-0.197943
8	1	0	0.991276	-3.586599	-1.164413
9	1	0	-0.580158	-3.349974	-0.375024
10	1	0	0.515608	-4.623307	0.183607
11	6	0	0.322116	-2.388656	2.659914
12	1	0	0.744273	-1.653320	3.354179
13	1	0	0.351066	-3.369267	3.150606
14	1	0	-0.728174	-2.126818	2.490572
15	6	0	3.073798	-2.892536	1.302656
16	1	0	3.546552	-2.268636	2.069875
17	1	0	3.657236	-2.782921	0.381186
18	1	0	3.156368	-3.937764	1.626750
19	6	0	2.739054	0.385067	-0.905701
20	1	0	2.922211	0.781560	-1.900340
21	6	0	3.666200	0.599857	0.092346
22	1	0	3.503012	0.269905	1.110621
23	8	0	4.860254	1.235156	-0.023059
24	6	0	5.222866	1.746418	-1.296648
25	1	0	5.282377	0.945202	-2.045336
26	1	0	6.206594	2.202408	-1.171933
27	1	0	4.508110	2.506240	-1.639401
28	8	0	-0.421581	0.818465	-1.757508
29	6	0	-1.381351	0.862084	-0.773721
30	6	0	-1.435747	2.092206	-0.026544
31	6	0	-1.502158	4.546246	1.391770
32	6	0	-2.600016	2.510196	0.671421
33	6	0	-0.316358	2.965847	-0.010984
34	6	0	-0.353039	4.163554	0.690154
35	6	0	-2.624412	3.710675	1.369738

36	1	0	-3.495076	1.898946	0.632971
37	1	0	0.578409	2.673392	-0.547403
38	1	0	0.523789	4.806556	0.694607
39	1	0	-3.532241	4.006557	1.889751
40	1	0	-1.525888	5.484509	1.939189
41	6	0	-2.325246	-0.240690	-0.680608
42	6	0	-4.125772	-2.423788	-0.540195
43	6	0	-2.905231	-0.635301	0.549182
44	6	0	-2.669541	-0.985115	-1.834965
45	6	0	-3.556083	-2.054572	-1.763251
46	6	0	-3.792198	-1.706012	0.612967
47	1	0	-2.630783	-0.108707	1.457499
48	1	0	-2.252614	-0.687357	-2.792385
49	1	0	-3.814009	-2.598145	-2.668835
50	1	0	-4.218562	-1.990094	1.571866
51	1	0	-4.818152	-3.259261	-0.486401

Structure of optimized structures **T-DR1**-anti-*trans*

```
Zero-point correction = 0.418977 (Hartree/Particle)
Thermal correction to Energy = 0.446474
Thermal correction to Enthalpy = 0.447418
Thermal correction to Gibbs Free Energy = 0.356258
Sum of electronic and zero-point Energies = -1330.604447
Sum of electronic and thermal Energies = -1330.576950
Sum of electronic and thermal Enthalpies = -1330.576006
Sum of electronic and thermal Free Energies = -1330.667166
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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.616991	-0.170509	-0.618333
2	1	0	0.700163	-1.248210	-0.799123
3	1	0	0.487560	0.318253	-1.591425
4	6	0	1.912116	0.348069	0.080540
5	8	0	3.046588	0.015452	-0.717907
6	14	0	4.054998	-1.210894	-0.164702
7	6	0	5.482743	-1.458739	-1.389652
8	1	0	6.056417	-0.533259	-1.493937
9	1	0	5.093933	-1.742481	-2.371034
10	1	0	6.153657	-2.247736	-1.037029
11	6	0	3.168769	-2.863354	0.001012
12	1	0	2.363130	-2.795728	0.737577
13	1	0	3.865239	-3.642916	0.324655
14	1	0	2.735836	-3.163986	-0.957283
15	6	0	4.829147	-0.773258	1.501384
16	1	0	4.053405	-0.655787	2.263632
17	1	0	5.387437	0.164909	1.427138
18	1	0	5.515393	-1.561465	1.823376
19	6	0	1.764528	1.823612	0.322625
20	1	0	0.813418	2.111707	0.765727

21	6	0	2.688419	2.748717	0.023683
22	1	0	3.634099	2.459681	-0.409951
23	8	0	2.640121	4.113542	0.177360
24	6	0	1.391455	4.613296	0.646185
25	1	0	0.579131	4.363632	-0.044240
26	1	0	1.466188	5.703634	0.692116
27	1	0	1.176508	4.252816	1.658036
28	8	0	-0.558585	0.056764	0.189176
29	6	0	-1.813110	-0.282265	-0.457813
30	6	0	-2.303389	-1.635661	-0.067887
31	6	0	-3.271918	-4.186548	0.583096
32	6	0	-2.974593	-2.400925	-1.017146
33	6	0	-2.111827	-2.159082	1.208199
34	6	0	-2.591919	-3.429429	1.538702
35	6	0	-3.461730	-3.670817	-0.699298
36	1	0	-3.094158	-1.972379	-2.005559
37	1	0	-1.560237	-1.556983	1.921630
38	1	0	-2.417129	-3.816753	2.534991
39	1	0	-3.976634	-4.246512	-1.458358
40	1	0	-3.639026	-5.174396	0.833434
41	6	0	-2.783286	0.835986	-0.295555
42	6	0	-4.617329	2.943268	-0.085988
43	6	0	-3.327157	1.411722	-1.439143
44	6	0	-3.151687	1.327192	0.953692
45	6	0	-4.067794	2.375681	1.065248
46	6	0	-4.243868	2.461543	-1.341109
47	1	0	-3.000033	1.020619	-2.394341
48	1	0	-2.691210	0.875911	1.825231
49	1	0	-4.333928	2.744198	2.048107
50	1	0	-4.648068	2.897241	-2.246354
51	1	0	-5.323411	3.761446	-0.004882

Structure of optimized structures **T-DR3**-gauche-*trans*

Zero-point correction = 0.417613 (Hartree/Particle)
Thermal correction to Energy = 0.444952
Thermal correction to Enthalpy = 0.445896
Thermal correction to Gibbs Free Energy = 0.356960
Sum of electronic and zero-point Energies = -1330.595152
Sum of electronic and thermal Energies = -1330.567813
Sum of electronic and thermal Enthalpies = -1330.566869
Sum of electronic and thermal Free Energies = -1330.655805

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.068025	-1.570366	-0.179916
2	8	0	-2.905597	-1.070245	0.793230
3	14	0	-4.232692	-0.042772	0.574425
4	6	0	-5.684572	-0.997498	-0.161553
5	1	0	-5.452438	-1.385053	-1.160267

6	1	0	-6.566680	-0.351575	-0.256374
7	1	0	-5.962800	-1.847659	0.472389
8	6	0	-3.754056	1.384006	-0.559798
9	1	0	-3.492881	1.028552	-1.563528
10	1	0	-2.893630	1.938675	-0.168501
11	1	0	-4.588365	2.088485	-0.667061
12	8	0	1.122910	-0.266013	-1.582244
13	6	0	1.796491	0.421904	-0.595270
14	6	0	2.933615	-0.239972	0.033382
15	6	0	5.153199	-1.550743	1.196744
16	6	0	3.329512	0.033163	1.363600
17	6	0	3.671650	-1.207418	-0.688680
18	6	0	4.765993	-1.844201	-0.115313
19	6	0	4.423263	-0.614139	1.932904
20	1	0	2.750773	0.730345	1.961026
21	1	0	3.369106	-1.442801	-1.702178
22	1	0	5.325265	-2.573175	-0.696287
23	1	0	4.699107	-0.394446	2.961143
24	1	0	6.007880	-2.052633	1.641977
25	6	0	1.437101	1.811408	-0.456161
26	6	0	0.683696	4.542398	-0.240532
27	6	0	2.263391	2.758885	0.207693
28	6	0	0.238818	2.300614	-1.045182
29	6	0	-0.127739	3.635006	-0.931547
30	6	0	1.884856	4.090906	0.316874
31	1	0	3.221295	2.447844	0.607614
32	1	0	-0.390228	1.611878	-1.596140
33	1	0	-1.053185	3.974019	-1.390610
34	1	0	2.542049	4.789523	0.828663
35	1	0	0.393161	5.585467	-0.152268
36	8	0	0.910743	-2.567861	-1.003430
37	6	0	1.000490	-3.010442	0.352493
38	1	0	1.377680	-2.233990	1.025070
39	1	0	1.712632	-3.838563	0.338722
40	1	0	0.031945	-3.370695	0.716963
41	6	0	-2.482666	-2.658838	-0.931037
42	1	0	-3.455653	-3.105843	-0.766390
43	1	0	-1.824441	-3.116936	-1.659517
44	6	0	0.229408	-1.369506	-1.289887
45	1	0	-0.216259	-1.537418	-2.274258
46	6	0	-0.813766	-0.961505	-0.289496
47	1	0	-0.574438	-0.157926	0.398164
48	6	0	-4.639284	0.550439	2.309751
49	1	0	-5.523529	1.199336	2.309983
50	1	0	-4.845385	-0.295677	2.975210
51	1	0	-3.805973	1.117418	2.739635

Structure of optimized structures **T-DR3**-anti-*trans*

```
 Zero-point correction = 0.417152 (Hartree/Particle)
 Thermal correction to Energy = 0.444841
 Thermal correction to Enthalpy = 0.445785
 Thermal correction to Gibbs Free Energy = 0.353250
 Sum of electronic and zero-point Energies = -1330.603665
 Sum of electronic and thermal Energies = -1330.575976
 Sum of electronic and thermal Enthalpies = -1330.575032
 Sum of electronic and thermal Free Energies = -1330.667567
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.440748	0.658473	-0.672026
2	8	0	3.765283	0.544850	-1.072796
3	14	0	4.896773	-0.184073	-0.090756
4	6	0	5.049473	-2.037851	-0.326874
5	1	0	4.128014	-2.544194	-0.023610
6	1	0	5.872396	-2.437275	0.274330
7	1	0	5.243373	-2.277624	-1.375684
8	6	0	4.755708	0.271990	1.728924
9	1	0	3.818142	-0.101766	2.149364
10	1	0	4.781501	1.358396	1.855252
11	1	0	5.582617	-0.159965	2.299356
12	8	0	-0.755090	-0.365399	-0.248326
13	6	0	-2.026994	-0.021849	0.386856
14	6	0	-2.330947	1.428599	0.246865
15	6	0	-2.917446	4.163689	0.079785
16	6	0	-2.713246	2.137706	1.380472
17	6	0	-2.235060	2.096277	-0.969919
18	6	0	-2.525514	3.460199	-1.060039
19	6	0	-3.008963	3.500359	1.304693
20	1	0	-2.749127	1.592252	2.316674
21	1	0	-1.893801	1.529820	-1.829636
22	1	0	-2.420484	3.960933	-2.014427
23	1	0	-3.289902	4.032153	2.205164
24	1	0	-3.128016	5.223814	0.017682
25	6	0	-3.104063	-0.964035	-0.019505
26	6	0	-5.158647	-2.746499	-0.691423
27	6	0	-3.906887	-1.519085	0.970745
28	6	0	-3.325892	-1.313857	-1.347835
29	6	0	-4.349653	-2.201268	-1.689830
30	6	0	-4.935195	-2.407116	0.643343
31	1	0	-3.688381	-1.242560	1.996426
32	1	0	-2.664590	-0.891600	-2.095886
33	1	0	-4.493035	-2.465874	-2.730047
34	1	0	-5.539688	-2.830608	1.435351
35	1	0	-5.947310	-3.442180	-0.950809
36	8	0	0.481354	-1.578650	1.483666
37	6	0	0.228866	-2.790965	0.805663

38	1	0	-0.743538	-2.789787	0.307914
39	1	0	0.213385	-3.592988	1.550864
40	1	0	1.019341	-3.030153	0.089498
41	6	0	1.832442	1.839849	-0.795313
42	1	0	2.382956	2.702229	-1.134869
43	1	0	0.779614	1.936290	-0.561031
44	6	0	0.444125	-0.452278	0.587596
45	1	0	0.487962	0.442846	1.216943
46	6	0	1.714200	-0.581676	-0.285756
47	1	0	1.381473	-1.084895	-1.206983
48	6	0	6.650060	0.487654	-0.578984
49	1	0	7.396331	-0.000052	0.012728
50	1	0	6.831572	0.290986	-1.614974
51	1	0	6.689297	1.542517	-0.403985

Structure of optimized structures **T-DR1**-gauche-*cis*

Zero-point correction = 0.418613 (Hartree/Particle)
Thermal correction to Energy = 0.446261
Thermal correction to Enthalpy = 0.447205
Thermal correction to Gibbs Free Energy = 0.356120
Sum of electronic and zero-point Energies = -1330.603339
Sum of electronic and thermal Energies = -1330.575691
Sum of electronic and thermal Enthalpies = -1330.574747
Sum of electronic and thermal Free Energies = -1330.665832

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.109654	-0.563440	-1.996549
2	1	0	-0.347148	-1.488802	-1.632188
3	1	0	0.298963	-0.655840	-3.068976
4	6	0	1.383128	-0.274554	-1.259814
5	8	0	1.362403	-0.497651	0.084301
6	14	0	1.796105	-1.863835	0.985357
7	6	0	1.964261	-1.214836	2.740219
8	1	0	1.027631	-0.757202	3.078226
9	1	0	2.747246	-0.450817	2.796055
10	1	0	2.218949	-2.017908	3.442495
11	6	0	3.409831	-2.593486	0.341475
12	1	0	3.315654	-2.915514	-0.702486
13	1	0	3.702111	-3.470728	0.932327
14	1	0	4.215738	-1.855323	0.391371
15	6	0	0.432408	-3.163981	0.879996
16	1	0	0.324172	-3.558497	-0.137708
17	1	0	-0.540178	-2.760205	1.182547
18	1	0	0.662101	-4.014979	1.534520
19	6	0	2.455710	0.355716	-1.891123

20	1	0	2.335241	0.523051	-2.958927
21	6	0	3.651121	0.828418	-1.379575
22	8	0	-0.861266	0.520126	-1.902098
23	6	0	-1.637828	0.615569	-0.770681
24	6	0	-1.614205	1.898678	-0.115866
25	6	0	-1.530715	4.452615	1.112195
26	6	0	-2.660184	2.342340	0.736154
27	6	0	-0.540056	2.796488	-0.353292
28	6	0	-0.502224	4.043675	0.255319
29	6	0	-2.610359	3.592312	1.340291
30	1	0	-3.527406	1.710323	0.892886
31	1	0	0.260751	2.485227	-1.013401
32	1	0	0.338695	4.705765	0.063355
33	1	0	-3.429006	3.906679	1.983092
34	1	0	-1.496535	5.429586	1.586588
35	6	0	-2.509280	-0.502181	-0.448149
36	6	0	-4.182355	-2.716082	0.124952
37	6	0	-2.894673	-0.806424	0.880228
38	6	0	-2.978874	-1.355533	-1.476467
39	6	0	-3.802978	-2.438636	-1.192347
40	6	0	-3.719830	-1.892696	1.156446
41	1	0	-2.515827	-0.198617	1.695490
42	1	0	-2.708769	-1.131545	-2.503859
43	1	0	-4.160518	-3.067016	-2.004395
44	1	0	-3.994937	-2.105917	2.186440
45	1	0	-4.825829	-3.563352	0.344928
46	1	0	4.383278	1.302362	-2.030625
47	8	0	4.011395	0.700530	-0.074293
48	6	0	5.139844	1.472920	0.315160
49	1	0	4.923795	2.547260	0.251756
50	1	0	6.013615	1.242712	-0.310356
51	1	0	5.358121	1.207643	1.351127

Structure of optimized structures **T-DR1**-anti-*cis*

```
 Zero-point correction=                           0.418064 (Hartree/Particle)
 Thermal correction to Energy=                    0.445949
 Thermal correction to Enthalpy=                  0.446893
 Thermal correction to Gibbs Free Energy=         0.354674
 Sum of electronic and zero-point Energies=          -1330.604102
 Sum of electronic and thermal Energies=             -1330.576217
 Sum of electronic and thermal Enthalpies=           -1330.575273
 Sum of electronic and thermal Free Energies=        -1330.667492
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.546064	-0.324205	-0.606928
2	1	0	-0.632743	0.688924	-1.013961

3	1	0	-0.420070	-1.006410	-1.453762
4	6	0	-1.820459	-0.672451	0.197312
5	8	0	-3.033015	-0.295050	-0.418747
6	14	0	-3.806511	1.085068	0.147765
7	6	0	-5.404471	1.363638	-0.836221
8	1	0	-6.068427	0.501405	-0.730687
9	1	0	-5.175662	1.501344	-1.897309
10	1	0	-5.925904	2.253664	-0.471883
11	6	0	-2.757410	2.638163	-0.038857
12	1	0	-1.843204	2.558802	0.556690
13	1	0	-3.311568	3.518426	0.297826
14	1	0	-2.475335	2.785781	-1.084862
15	6	0	-4.301251	0.908949	1.962922
16	1	0	-3.413547	0.788700	2.590089
17	1	0	-4.944477	0.035236	2.098531
18	1	0	-4.845485	1.797219	2.298415
19	6	0	-1.787425	-1.962527	0.927193
20	1	0	-1.240836	-1.874506	1.867312
21	6	0	-2.271635	-3.185498	0.662543
22	8	0	0.640610	-0.386283	0.213999
23	6	0	1.866467	0.012651	-0.460697
24	6	0	2.152778	1.469862	-0.300572
25	6	0	2.735950	4.205459	-0.080393
26	6	0	2.809144	2.138474	-1.330012
27	6	0	1.781157	2.182662	0.836533
28	6	0	2.069070	3.545371	0.952332
29	6	0	3.106054	3.499683	-1.226573
30	1	0	3.070131	1.561182	-2.209095
31	1	0	1.241680	1.649365	1.611687
32	1	0	1.755260	4.076513	1.841762
33	1	0	3.613573	3.995382	-2.043893
34	1	0	2.954463	5.262546	0.002059
35	6	0	2.971989	-0.908704	-0.074358
36	6	0	5.070822	-2.652299	0.557200
37	6	0	3.640007	-1.599417	-1.080243
38	6	0	3.350530	-1.101611	1.249816
39	6	0	4.397917	-1.968662	1.572198
40	6	0	4.688580	-2.469389	-0.772662
41	1	0	3.302739	-1.440289	-2.097630
42	1	0	2.795141	-0.569299	2.013235
43	1	0	4.668782	-2.108957	2.611287
44	1	0	5.188618	-3.000948	-1.572422
45	1	0	5.878532	-3.332324	0.803119
46	1	0	-2.131035	-3.963484	1.402134
47	8	0	-2.920855	-3.745039	-0.401718
48	6	0	-2.961947	-2.963705	-1.586407
49	1	0	-1.991247	-2.540076	-1.846314
50	1	0	-3.754984	-2.217835	-1.529159
51	1	0	-3.235981	-3.638990	-2.404919

Structure of optimized structures **T-DR3**-gauche-*cis*

```
 Zero-point correction = 0.417392 (Hartree/Particle)
 Thermal correction to Energy = 0.444784
 Thermal correction to Enthalpy = 0.445728
 Thermal correction to Gibbs Free Energy = 0.355511
 Sum of electronic and zero-point Energies = -1330.595087
 Sum of electronic and thermal Energies = -1330.567695
 Sum of electronic and thermal Enthalpies = -1330.566751
 Sum of electronic and thermal Free Energies = -1330.656968
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.523080	-0.390309	-0.109331
2	8	0	2.367627	0.501447	-0.744855
3	14	0	4.051052	0.566890	-0.635873
4	6	0	4.818284	-1.030113	-1.284413
5	1	0	4.474162	-1.903959	-0.719181
6	1	0	5.912246	-0.994944	-1.205584
7	1	0	4.566134	-1.195262	-2.338455
8	6	0	4.568072	0.839606	1.158895
9	1	0	4.206482	0.035104	1.810103
10	1	0	4.174390	1.785199	1.549536
11	1	0	5.661083	0.870934	1.249654
12	8	0	-1.380671	-0.104065	1.824671
13	6	0	-1.917513	0.131889	0.570447
14	6	0	-2.251009	-1.012644	-0.265744
15	6	0	-2.933287	-3.247149	-1.859213
16	6	0	-2.222061	-0.940222	-1.678252
17	6	0	-2.610231	-2.247204	0.323263
18	6	0	-2.950868	-3.341451	-0.463738
19	6	0	-2.560046	-2.041553	-2.459194
20	1	0	-1.894000	-0.023972	-2.157835
21	1	0	-2.619430	-2.326235	1.403580
22	1	0	-3.237514	-4.275132	0.013806
23	1	0	-2.518035	-1.962113	-3.542567
24	1	0	-3.199017	-4.105201	-2.470815
25	6	0	-2.265188	1.505398	0.311858
26	6	0	-2.937896	4.228404	-0.131434
27	6	0	-3.179323	1.886599	-0.707646
28	6	0	-1.734291	2.543178	1.124426
29	6	0	-2.060694	3.873431	0.899449
30	6	0	-3.498596	3.220775	-0.923961
31	1	0	-3.660663	1.122654	-1.307137
32	1	0	-1.065921	2.280305	1.935493
33	1	0	-1.629812	4.643645	1.534514
34	1	0	-4.204767	3.477812	-1.709588
35	1	0	-3.190888	5.270580	-0.305188
36	8	0	-0.082979	-2.017118	1.902809
37	6	0	0.978875	-2.654111	2.595322

38	1	0	1.950469	-2.467234	2.118611
39	1	0	0.768341	-3.725657	2.569813
40	1	0	1.025226	-2.321744	3.643821
41	6	0	1.288421	-1.610276	-0.727230
42	1	0	1.761074	-1.832262	-1.676807
43	1	0	0.596576	-2.321651	-0.299981
44	6	0	-0.046582	-0.609638	1.982277
45	1	0	0.184209	-0.328856	3.022170
46	6	0	0.950805	0.067030	1.082033
47	1	0	1.213101	1.077748	1.380765
48	6	0	4.524982	2.031982	-1.711616
49	1	0	5.611452	2.181872	-1.721925
50	1	0	4.197220	1.882714	-2.746605
51	1	0	4.061731	2.955347	-1.346162

Structure of optimized structures **T-DR3**-anti-*cis*

Zero-point correction = 0.417330 (Hartree/Particle)
Thermal correction to Energy = 0.444833
Thermal correction to Enthalpy = 0.445777
Thermal correction to Gibbs Free Energy = 0.354438
Sum of electronic and zero-point Energies = -1330.601788
Sum of electronic and thermal Energies = -1330.574284
Sum of electronic and thermal Enthalpies = -1330.573340
Sum of electronic and thermal Free Energies = -1330.664680

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.371129	-0.622961	-0.347060
2	8	0	3.514119	-0.197896	-0.996472
3	14	0	5.033935	0.075702	-0.311962
4	6	0	5.709642	-1.506571	0.462090
5	1	0	5.051470	-1.886801	1.251760
6	1	0	6.695285	-1.327699	0.910188
7	1	0	5.824391	-2.299316	-0.286410
8	6	0	4.907863	1.427953	0.998441
9	1	0	4.205895	1.154307	1.795026
10	1	0	4.563994	2.373584	0.563354
11	1	0	5.882745	1.611682	1.467109
12	8	0	-0.794142	-0.215875	-0.441876
13	6	0	-2.144862	0.036481	-0.265714
14	6	0	-2.553272	1.426978	-0.184900
15	6	0	-3.283859	4.158178	-0.023535
16	6	0	-3.711277	1.836051	0.520584
17	6	0	-1.765042	2.436271	-0.792204
18	6	0	-2.129324	3.775620	-0.713967
19	6	0	-4.067794	3.178395	0.593899
20	1	0	-4.308790	1.092852	1.038163
21	1	0	-0.881712	2.143625	-1.351119
22	1	0	-1.514375	4.527062	-1.202905

23	1	0	-4.957046	3.464953	1.149654
24	1	0	-3.566280	5.205534	0.036550
25	6	0	-3.005042	-1.116435	-0.325910
26	6	0	-4.649702	-3.418683	-0.474331
27	6	0	-4.380885	-1.018905	-0.663613
28	6	0	-2.478004	-2.413694	-0.093248
29	6	0	-3.290413	-3.537486	-0.162747
30	6	0	-5.183632	-2.150850	-0.728733
31	1	0	-4.804627	-0.051289	-0.909049
32	1	0	-1.429357	-2.509854	0.158615
33	1	0	-2.862443	-4.518102	0.030445
34	1	0	-6.232009	-2.046382	-0.996873
35	1	0	-5.280926	-4.301417	-0.528101
36	8	0	-0.000500	-0.816920	1.596880
37	6	0	0.566176	-0.442617	2.841502
38	1	0	1.654733	-0.308933	2.772817
39	1	0	0.348364	-1.254102	3.539575
40	1	0	0.118108	0.487927	3.222392
41	6	0	2.195030	-1.984391	-0.154345
42	1	0	2.936660	-2.685429	-0.518726
43	1	0	1.307429	-2.357924	0.336527
44	6	0	0.094083	0.185521	0.600041
45	1	0	-0.250070	1.139206	1.027042
46	6	0	1.463447	0.377765	0.012190
47	1	0	1.727349	1.397093	-0.253062
48	6	0	6.098194	0.625679	-1.758917
49	1	0	7.125206	0.836745	-1.436792
50	1	0	6.142081	-0.150037	-2.531753
51	1	0	5.698295	1.534629	-2.222355

Table S2. T-DR1-*trans* dihedral angle scan

UB3LYP/6-31G(d) level of theory in the GAUSSIAN 09 Scan of Total Energy X-Axis: Scan Coordinate Dihedral Angle, θ (°) Y-Axis: Total Energy (kJ/mol)	
X	**Y**
0	22.72934733
10	24.19710685
20	24.66087517
30	24.03246174
40	23.06073794
50	21.7296882

60	20.2919644
70	16.83583497
80	14.89209855
90	13.66354834
100	11.54526868
110	8.13421908
120	5.004386785
130	2.377574035
140	0.78722992
150	0
160	0.218835425
170	0.73219944
180	1.67795705
190	3.323436666
240	6.588245915
250	6.994699571
260	7.74007902
270	8.729603715
280	8.81716414
290	7.59158074
300	7.47264559
310	7.921474815
320	9.754913975
330	12.53248294
340	15.24669858
350	17.7496665
360	20.40835282

Table S3. T-DR3-*trans* dihedral angle scan

UB3LYP/6-31G(d) level of theory in the GAUSSIAN 09 Scan of Total Energy X-Axis: Scan Coordinate Dihedral Angle, θ (°) Y-Axis: Total Energy (kJ/mol)	
X	**Y**
0	42.60275452
10	42.00863012
20	41.35023349
30	40.09676728
40	38.88701564
50	38.24130017

60	37.61110141
70	38.32190302
80	39.88696357
90	41.81163886
100	43.21292071
110	43.29515138
120	42.15820486
130	38.94117971
140	34.24389766
150	29.31352372
160	24.4509927
170	20.32887893
180	17.55330535
190	16.052307
200	16.0066233
210	16.17686072
220	15.46259344
230	15.53201167
240	17.9972774
250	22.52894291
260	24.50547182
270	25.73102897
280	27.47732778
290	29.79199484
300	32.28871406
310	34.79777314
320	37.54567395
330	40.06421108
340	41.40662923
350	41.8029222
360	42.09246234

Table S4. T-DR1-*cis* dihedral angle scan

UB3LYP/6-31G(d) level of theory in the GAUSSIAN 09 Scan of Total Energy X-Axis: Scan Coordinate Dihedral Angle, θ (°) Y-Axis: Total Energy (kJ/mol)	
X	**Y**
0	19.83707027
10	20.67951446

20	20.40864162
30	19.28083184
40	17.71054655
50	15.7535251
60	13.92008594
70	12.5057816
80	11.97099351
90	11.44691745
100	10.51160933
110	9.591607875
120	8.77961949
130	7.14120247
140	5.37817922
150	4.33538313
160	3.7324108
170	3.10034793
180	2.356412505
190	1.684862115
200	0.64224981
210	0.15275159
220	0
230	0.129305875
240	0.888968045
250	1.62334665
260	2.62114167
270	2.53759826
280	2.472092035
290	2.68714674
300	3.405352265
310	5.50189278
320	8.44702115
330	11.90288804
340	15.28988806
350	17.90845674
360	19.83709653

Table S5. T-DR3-*cis* dihedral angle scan

UB3LYP/6-31G(d) level of theory in the GAUSSIAN 09 Scan of Total Energy X-Axis: Scan Coordinate Dihedral Angle, θ (°) Y-Axis: Total Energy (kJ/mol)	
X	**Y**
0	30.60832
10	28.65342
20	27.50025
30	27.37115
40	28.35816
50	30.37522
60	32.618
80	35.02317
90	36.49962
100	37.17797
110	36.64358
120	34.43779
130	30.75639
140	26.45233
150	21.71186
160	17.36574
170	14.07935
180	11.74024
190	10.50271
200	9.839429
210	10.04143
220	11.24
230	13.66877
240	16.71511
250	20.27469
260	23.32321
270	26.27262
280	29.26343
290	31.94824
300	34.41996
310	36.1989
320	37.15337
330	37.19777
340	36.33647
350	34.54819

360	32.80439

Table S6. T-DR1-*trans* bond formation scan

UB3LYP/6-31G(d) level of theory in the GAUSSIAN 09 Scan of Total Energy X-Axis: Scan Coordinate Distance, r (pm) Y-Axis: Total Energy (kJ/mol)	
X	**Y**
431.66	94.83911965
421.66	94.73457487
411.66	94.68964206
401.66	94.48555407
391.66	94.10808331
381.66	93.69672522
371.66	93.25396878
361.66	92.79040787
351.66	92.31640798
341.66	91.84267851
331.66	91.36519721
321.66	90.86649923
311.66	90.36345081
301.66	89.82880186
291.66	89.21917127
281.66	88.61108184
271.66	88.1197799
261.66	87.78723407
251.66	87.57450031
241.66	87.41321584
231.66	87.26696761
221.66	86.78085104
211.66	85.18995294
201.66	81.03631742
191.66	72.54330539
181.66	59.15795504
171.66	41.80263602
161.66	22.72626499
151.66	6.671765696
141.66	2.372160254

Table S7. T-DR3-*trans* bond formation scan

UB3LYP/6-31G(d) level of theory in the GAUSSIAN 09 Scan of Total Energy X-Axis: Scan Coordinate Distance, r (pm) Y-Axis: Total Energy (kJ/mol)	
X	**Y**
436.00	91.71555968
426.00	91.29974612
416.00	90.9935183
406.00	90.8121225
396.00	90.74536654
386.00	90.76263708
376.00	90.84609385
366.00	91.04492296
356.00	91.0538024
346.00	91.31585093
336.00	91.71102807
326.00	92.26652085
316.00	93.05316004
306.00	94.11975103
296.00	92.19669306
286.00	90.16614448
276.00	89.12260275
266.00	88.23278142
256.00	87.59843699
246.00	87.2741326
236.00	87.20945079
226.00	87.12181685
216.00	86.18140475
206.00	82.67361598
196.00	67.60386297
186.00	60.45608625
176.00	48.51805853
166.00	33.84790137
156.00	19.10113737
146.00	0

Table S8. T-DR1-*cis* bond formation scan

UB3LYP/6-31G(d) level of theory in the GAUSSIAN 09 Scan of Total Energy X-Axis: Scan Coordinate Distance, r (pm) Y-Axis: Total Energy (kJ/mol)	
X	**Y**
441.66	91.80128
431.66	91.62197
421.66	91.47163
411.66	91.33062
401.66	91.01882
391.66	90.61638
381.66	90.17145
371.66	89.71888
361.66	89.255
351.66	88.77541
341.66	88.26299
331.66	87.69377
321.66	87.10895
311.66	86.52237
301.66	85.93275
291.66	85.32465
281.66	84.71787
271.66	84.21895
261.66	83.80736
251.66	83.53622
241.66	83.25738
231.66	82.95645
221.66	82.28549
211.66	80.38282
201.66	75.77755
191.66	66.84509
181.66	53.14716
171.66	35.46947
161.66	16.12274
151.66	0

Table S9. T-DR3-*cis* bond formation scan

UB3LYP/6-31G(d) level of theory in the GAUSSIAN 09 Scan of Total Energy X-Axis: Scan Coordinate Distance, r (pm) Y-Axis: Total Energy (kJ/mol)	
X	**Y**
445.99	88.20608
435.99	88.35504
425.99	88.48308
415.99	88.58576
405.99	88.9208
395.99	87.37095
385.99	87.21074
375.99	87.06594
365.99	86.91682
355.99	86.73154
345.99	86.48192
335.99	86.05296
325.99	85.51741
315.99	84.83917
305.99	83.66277
295.99	82.47867
285.99	81.30181
275.99	80.21986
265.99	79.34357
255.99	78.82934
245.99	78.82692
235.99	79.29429
225.99	79.87972
215.99	79.6892
205.99	76.87486
195.99	61.36453
185.99	55.92532
175.99	45.39037
165.99	31.67176
155.99	17.63581