Electronic Supplementary Information (ESI)

for

Comment on "*trans*-1,2-Disiloxybenzocyclobutene, an adequate partner for the auto-oxidation: EPR/spin trapping and theoretical studies" by J. Drujon *et al.*, *Phys. Chem. Chem. Phys.* 2014, 16, 7513

Hans-Gert Korth,*[a] Peter Mulder[b] and Thomas Paul[c]

[a] *Institut für Organische Chemie, Universität Duisburg-Essen, Universitätsstr. 7, 45117 Essen, Germany. E-mail: hans-gert.korth@uni-due.de*

[b] *Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands.*

[c] *Heidelberger Druckmaschinen AG, Alte Eppelheimer Strasse 26, 69115 Heidelberg, Germany*

Table S1 CBS-QB3 computed heats of formation, free energies of formation (kcal mol^{-1}) and entropies (cal mol^{-1} K^{-1}) at T = 298 K.[a]

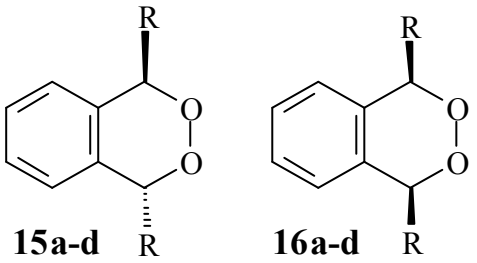
Compound[b]	$\Delta_f H^o$	$\Delta_f G^o$	S^o
benzocyclobutene (unsubst.)	48.64 [48.1][c]	66.85	74.85
o-quinodimethane (unsubst.)	61.96 [60.8][c]	78.64	79.97
conrotatory transion state (unsubst.)	86.73 [85.1][c]	104.50	76.29
9a (*trans*-BCB)	33.70	66.22	92.0
10a (*cis*-BCB)	34.60	67.10	92.1
11a (*E,E*-*o*-QDM)	49.41	80.07	98.3
12a (*E,Z*-*o*-QDM)	49.50	80.47	97.2
13a (conrot-TS1)	69.24	100.65	95.8
14a (conrot-TS2)	73.21	105.23	93.7
15a (*trans*-Peroxide)	–17.17	27.96	98.8
16a (*cis*-Peroxide)	–17.08	28.00	99.0
9b (*trans*-BCB)	–23.84	19.92	105.5
10b (*cis*-BCB)	–21.98	21.35	104.8
11b (*E,E*-*o*-QDM)	–12.60	29.00	110.6
12b (*E,Z*-*o*-QDM)	–14.87	26.02	113.0
13b (conrot-TS1)	1.27	44.02	106.8
14b (conrot-TS2)	12.35	55.26	106.2
15b (*trans*-Peroxide)	–83.64	–27.85	112.0
16b (*cis*-Peroxide)	–81.63	–25.92	112.4
17b (*E,E*-*o*-QDM-O_2-triplet-adduct)	–22.46	29.74	124.1
19b (*E,E*-*o*-QDM-O_2-triplet-TS3)	–6.15	45.23	126.9
9c (*trans*-BCB)	–56.18	–15.39	119.6
10c (*cis*-BCB)	–55.02	–14.10	119.2
11c (*E,E*-*o*-QDM)	–45.07	–5.34	123.2
12c (*E,Z*-*o*-QDM)	–46.96	–8.05	125.9
13c (conrot-TS1)	–29.93	11.32	118.1
14c (conrot-TS2)	–18.49	22.67	118.4
15c (*trans*-Peroxide)	–115.81	–61.31	122.6
16c (*cis*-Peroxide)	–113.87	–59.49	123.1
17c (*E,E*-*o*-QDM-O_2-triplet-adduct)	–54.51	–3.64	134.8
19c (*E,E*-*o*-QDM-O_2-triplet-TS3)	–41.20	9.59	135.1
9d (*trans*-BCB)	–154.35	–70.75	171.7
10d (*cis*-BCB)	–152.44	–68.40	170.2
11d (*E,E*-*o*-QDM)	–143.54	–60.78	174.5
12d (*E,Z*-*o*-QDM)	–146.40	–63.86	175.2

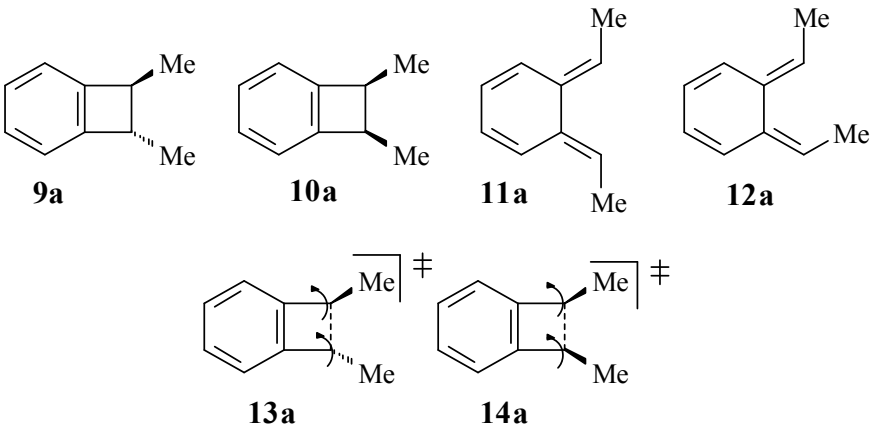
[a] Energies and entropies were evaluated as described in: J. W. Ochterski, *Thermochemistry in Gaussian*, Gaussian, Inc., Wallingford, CT, 2000; http://www.gaussian.com/g_whitepap/thermo.htm. The employed equations refer to the textbook of McQuarrie and Simon: D. A. McQuarrie and J. D. Simon, *Molecular Thermodynamics*, University Science Books, Sausalito, Calif., 1999. [b] Since all 1,2-disubstituted compounds are symmetrically substituted, *meso*/*rac* is synonymous to *cis*/*trans*. [c] Experimental values: W. R. Roth and B. P. Scholz, *Chem. Ber.*, 1981, **114**, 3741; W. R. Roth, V. Rekowski, S. Börner and M. Quast, *Liebigs Ann.,* **1996**, 409.

Table S2. CBS-QB3-calculated energies (kcal mol^{-1}) of *endo*-peroxide (**15a–d, 16a–d**) formation relative to the parent *trans*-benzocyclobutene (**9a–d**) + $^3O_2$ (n.c. = not calculated). Data for the unsubstituted compounds shown for comparison.

Compound	*trans*-Peroxide **15**		*cis*-Peroxide **16**	
	ΔH_{rel}	ΔG_{rel}	ΔH_{rel}	ΔG_{rel}
a (R = Me)	–50.9	–38.3	–50.8	–38.2
b (R = OMe)	–59.8 [a] (8.9)	–47.2	–57.8 [a] (7.0)	–45.2
c (R = $OSiH_3$)	–59.6 [a] (8.7)	–45.9	–57.7 [a] (6.9)	–44.1
d (R = $OSiMe_3$)	n.c.	n.c.	n.c.	n.c.
unsubstituted (R = H)	–46.9 [b]	–35.0 [b]	–46.9 [b]	–35.0 [b]

[a] The ca. 7–9 kcal mol^{-1} gain in reaction energies (in parentheses) for R = OMe, $OSiH_3$ compared to R= Me is attributed to a double anomeric stabilization effect in the peroxides.
[b] *Cis/trans (meso/rac)* do not apply.





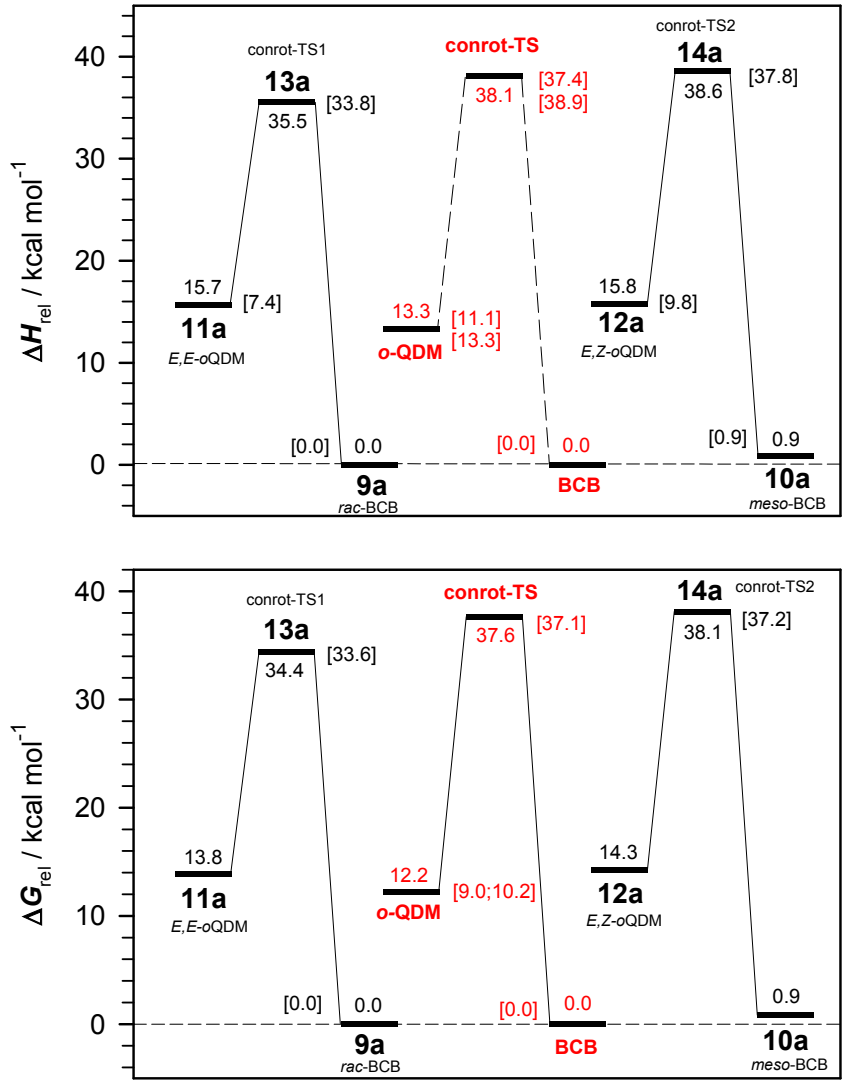
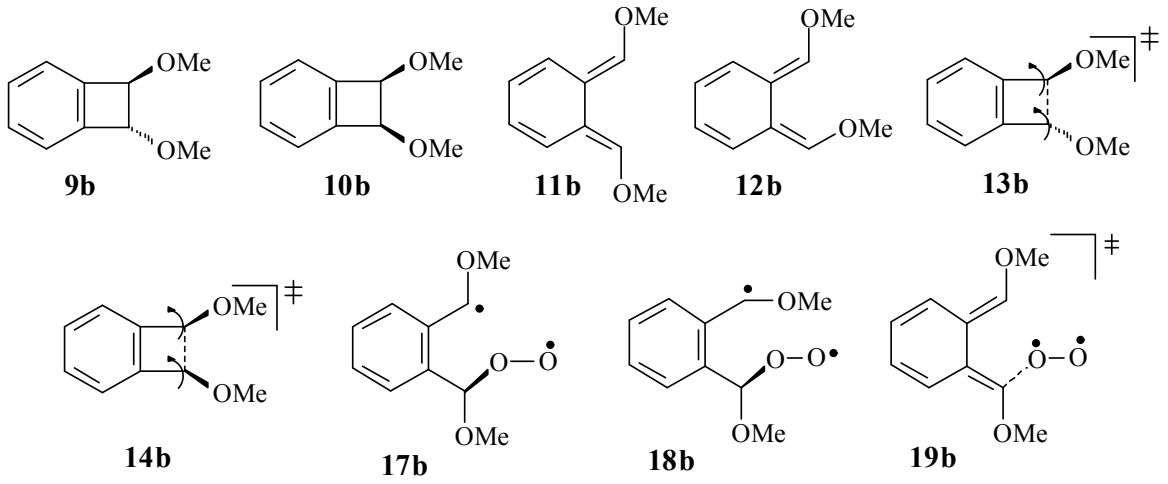
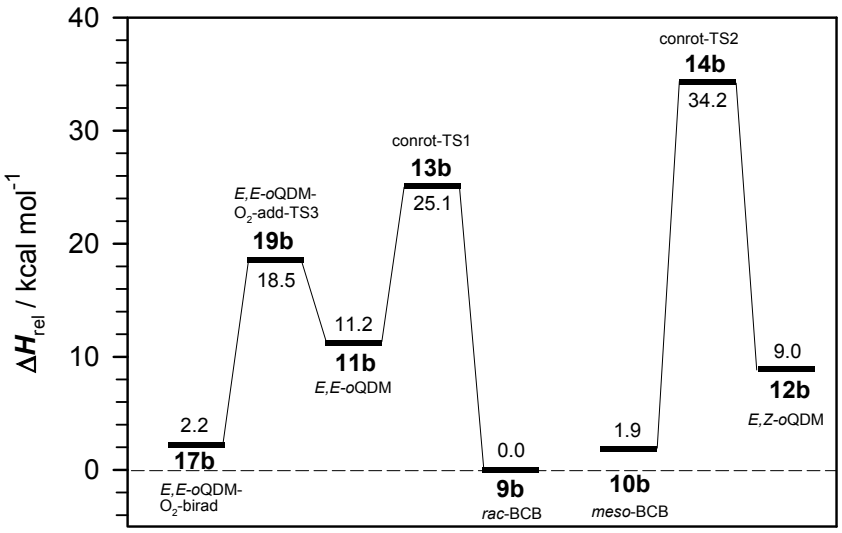


Figure S1. CBS-QB3 computed relative enthalpies and free energies of electrocyclic ring opening of *trans*- (left) and *cis*-1,2-dimethyl-benzocyclobutene (right). Center: data (red) for the parent, unsubstituted benzocyclobutene/*o*-quinodimethane (R = H). Experimental data[1] shown in square brackets.

1 (*a*) W. R. Roth, T. Ebbrecht and A. Beitat, *Chem. Ber.*, 1988, **121**, 1357.
(*b*) W. R. Roth and B. P. Scholz, *Chem. Ber.*, 1981, **114**, 3741.
(*c*) W. R. Roth, V. Rekowski, S. Börner and M. Quast, *Liebigs Ann.*, **1996**, 409.





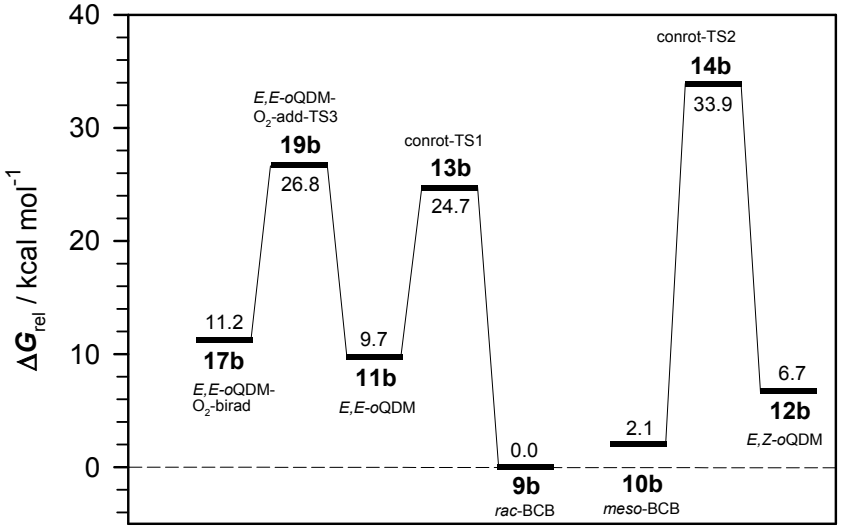
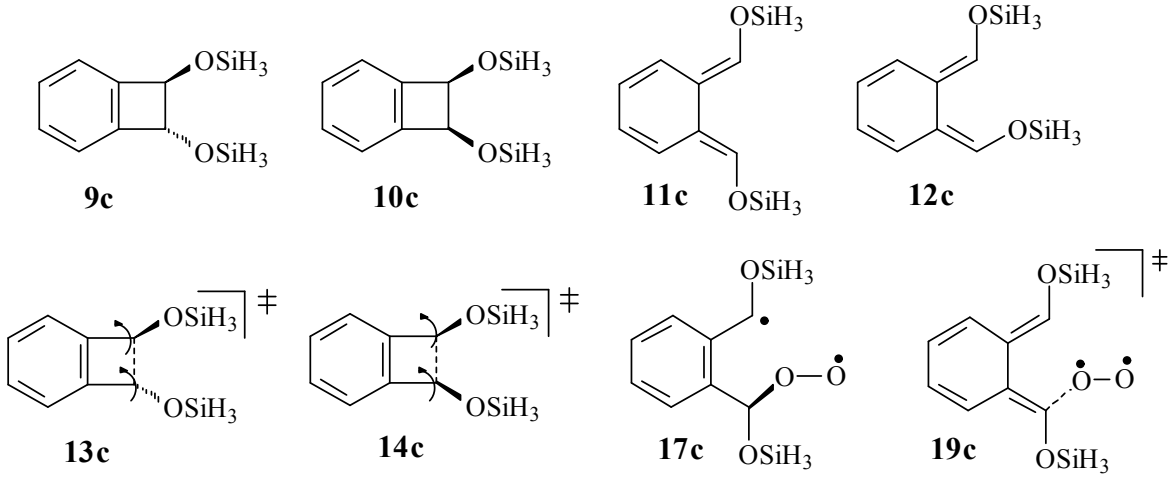
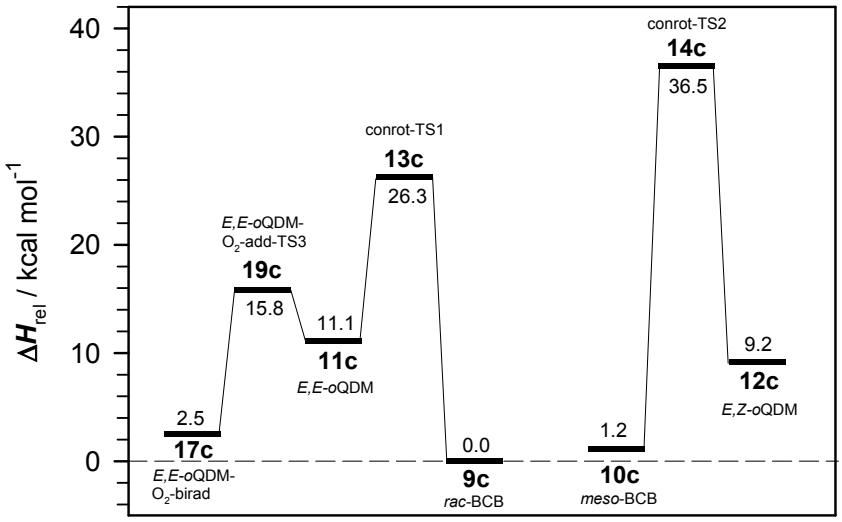


Figure S2. CBS-QB3 computed relative enthalpies and free energies of electrocyclic ring opening of *trans*- and *cis*-1,2-dimethoxy-benzocyclobutene and oxygen addition to *E,E*-dimethoxy-*o*-quinodimethane.





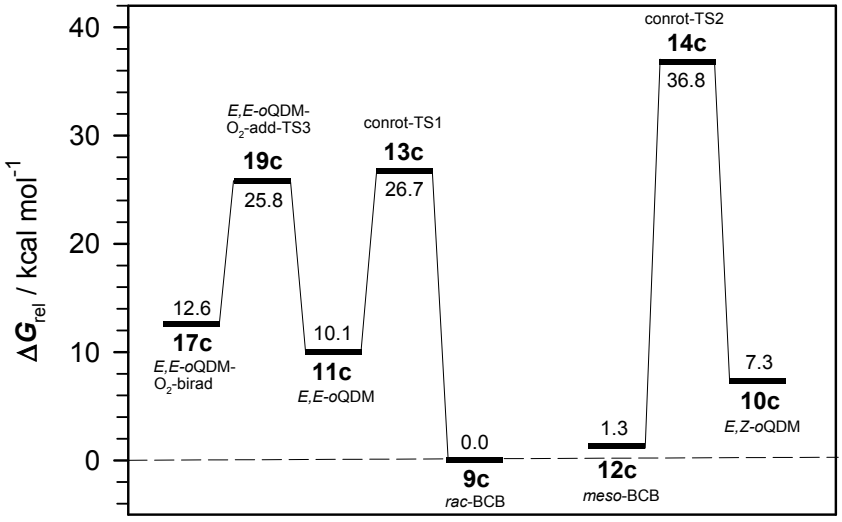
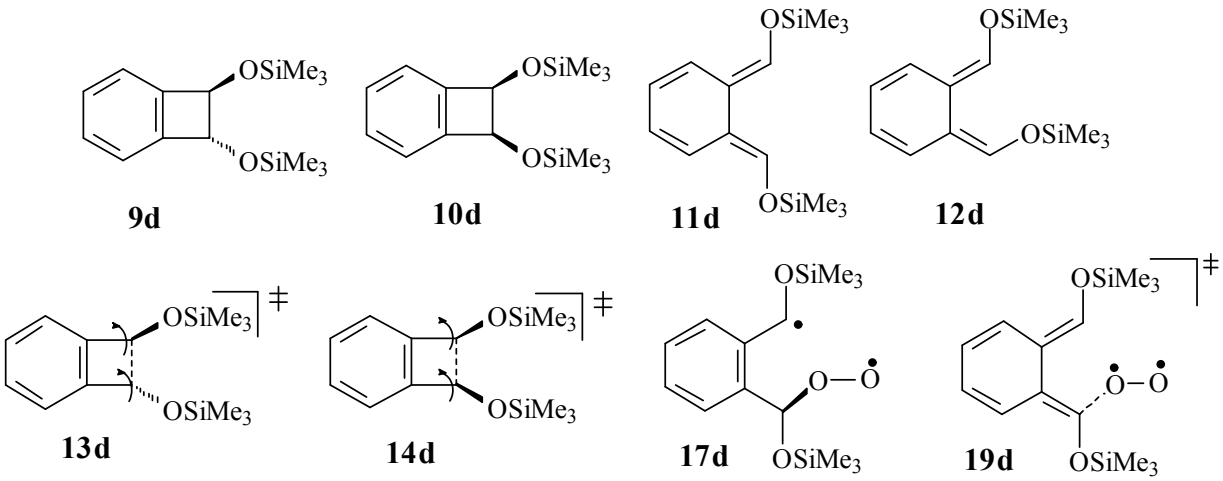
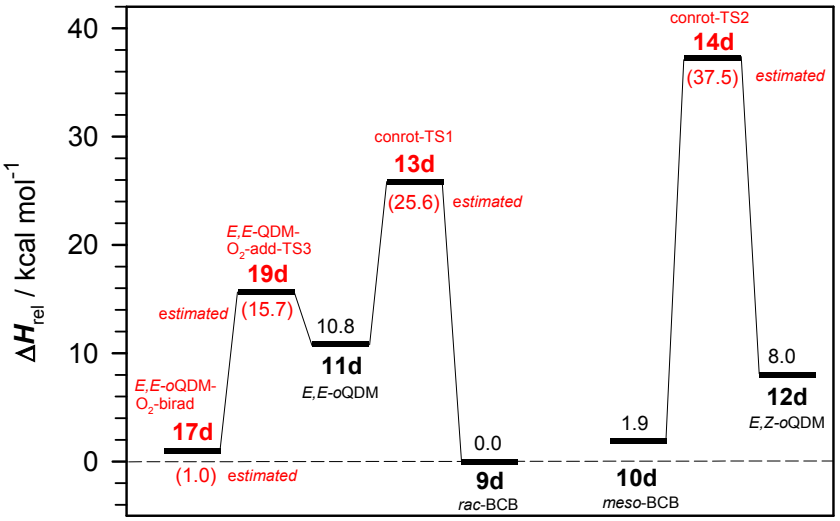


Figure S3. CBS-QB3 computed relative enthalpies and free energies of electrocyclic ring opening of *trans*- and *cis*-1,2-di-(trihydrosiloxy)-benzocyclobutene and oxygen addition to *E,E*-di-(trihydrosiloxy)-*o*-quinodimethane.





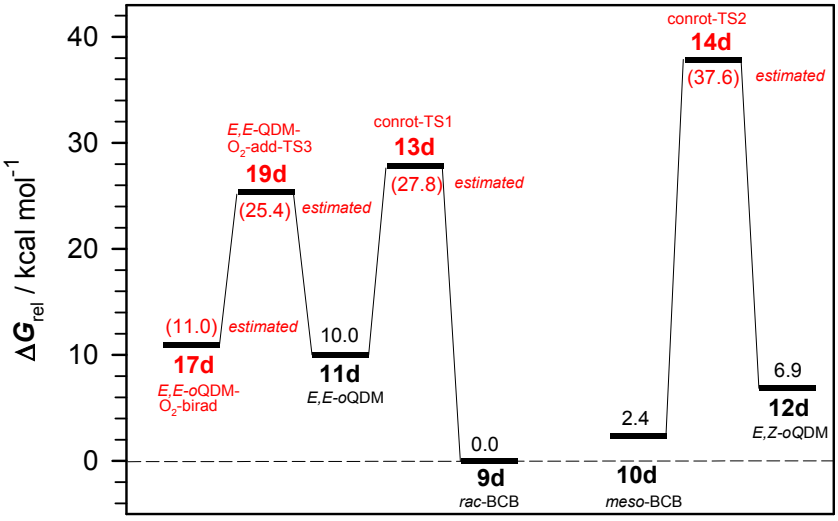


Figure S4. CBS-QB3 computed relative enthalpies and free energies (black numbers) of electrocyclic ring opening of *trans*- and *cis*-1,2-di-(trimethylsiloxy)-benzocyclobutene. The "pseudo-CBS-QB3 energies" of **13d**, **14d, 17d**, and **19d** were estimated from the differences of the B3LYP/CBSB7 and CBS-QB3 data of **13a-c**, **14a-c, 17b-c**, and **19b-c**, respectively.

CBS-QB3 Energies (hartrees)

Compound	E^0	*ZPVE*	E^0+*ZPVE*	E^{298}	H^{298}	G^{298}
9a	-387.667458	0.187819	-387.479639	-387.470557	-387.470557	-387.513338
10a	-387.666070	0.187861	-387.478209	-387.469114	-387.468170	-387.511946
11a	-387.641290	0.185518	-387.455772	-387.445545	-387.444601	-387.491300
12a	-387.641187	0.185755	-387.455432	-387.445416	-387.444472	-387.490655
13a	-387.607385	0.183746	-387.423639	-387.413965	-387.413021	-387.458520
14a	-387.600948	0.183926	-387.417022	-387.407638	-387.406693	-387.451222
15a	-537.919156	0.197174	-537.721982	-537.711480	-537.710536	-537.757476
16a	-537.919199	0.197358	-537.721841	-537.711338	-537.710394	-537.757409

Compound	E^0	*ZPVE*	E^0+*ZPVE*	E^{298}	H^{298}	G^{298}
9b	-537.930073	0.196518	-537.733555	-537.722127	-537.721183	-537.771294
10b	-537.927216	0.196707	-537.730509	-537.719151	-537.718207	-537.768009
11b	-537.911594	0.194989	-537.716605	-537.704232	-537.703288	-537.755840
12b	-537.915425	0.195067	-537.720358	-537.707842	-537.706898	-537.760586
13b	-537.887705	0.193890	-537.693815	-537.682134	-537.681190	-537.731913
14b	-537.869441	0.193311	-537.676130	-537.664486	-537.663542	-537.714012
15b	-688.196382	0.206277	-687.990105	-687.977289	-687.976344	-688.029578
16b	-688.193321	0.206376	-687.986945	-687.974075	-687.973130	-688.026509
17b	-688.096382	0.201943	-687.894439	-687.879820	-687.878876	-687.937851
19b	-688.068287	0.199394	-687.868893	-687.853859	-687.852915	-687.913190

Compound	E^0	*ZPVE*	E^0+*ZPVE*	E^{298}	H^{298}	G^{298}
9c	-1040.051964	0.171900	-1039.880064	-1039.866767	-1039.865823	-1039.922640
10c	-1040.050152	0.171981	-1039.878171	-1039.864914	-1039.863970	-1039.920588
11c	-1040.033394	0.170219	-1039.863175	-1039.849075	-1039.848131	-1039.848131
12c	-1040.036648	0.170454	-1039.866194	-1039.852082	-1039.851138	-1039.910955
13c	-1040.007522	0.169278	-1039.838244	-1039.824964	-1039.824020	-1039.880109
14c	-1039.988714	0.168574	-1039.820140	-1039.806737	-1039.805793	-1039.862028
15c	-1190.317780	0.181692	-1190.136088	-1190.121653	-1190.120709	-1190.121653
16c	-1190.314824	0.181799	-1190.133025	-1190.118553	-1190.117609	-1190.176076
17c	-1190.217391	0.177265	-1190.040126	-1190.024016	-1190.023072	-1190.087126
19c	-1190.193928	0.174761	-1190.019167	-1190.002828	-1190.001884	-1190.066065

Compound	E^0	*ZPVE*	E^0+*ZPVE*	E^{298}	H^{298}	G^{298}
9d	-1275.688375	0.341188	-1275.347187	-1275.322986	-1275.322042	-1275.403601
10d	-1275.685279	0.341191	-1275.344088	-1275.319947	-1275.319003	-1275.399847
11d	-1275.670327	0.339570	-1275.330757	-1275.305782	-1275.304838	-1275.387727
12d	-1275.675050	0.339729	-1275.335321	-1275.310335	-1275.309391	-1275.392636

Full citation of ref. 14:

Gaussian 09, Revision A.02,
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