Table S1. Dihedral and plane angles (in degrees) and pyramidalization (in Å) of Concerted Transition Structures.[a]

	endo-**8**	*endo*-**16**	*exo*-**16**
α	85.3	97.4	101.5
β	99.1	119.5	125.9
γ	1.0	18.4	22.5
C-N-O	127.6	121.3	122.0
N pyr.[b]	0.034	0.145	0.133
C pyr.[b]	0.016	0.146	0.151

[a] See Scheme 3.
[b] pyr. = pyramidalization

Table S2. B3LYP/6-31G* Singlet (^{1}E) and Triplet (^{3}E) Electronic Energy, $<S^2>$ values, Correction to Enthalpy (δH), Entropy (S), Correction to Gibbs Free Energy (δG) of Reactants, Intermediates, Transition Structures and Products for the Reaction of **1** with **7**.

molecule	^{1}E[b]	$^1<S^2>$	^{3}E[b]	$^3<S^2>$	δH[a,b]	S[a,c]	δG[a,b]
1	-169.7934851	0.0	-	-	0.049610	59.64	0.021240
7	-154.6754616	0.0	-	-	0.065936	63.23	0.035894
endo-**8**	-324.4740795	0.0	-	-	0.117527	90.26	0.074640
endo-**9**	-324.472995	0.0	-	-	0.116656	81.23	0.078061
exo-**9**	-324.4674128	0.0	-	-	0.116778	81.17	0.078210
10a	-324.4626170	1.11	-324.4566932	2.06	0.113352	91.31	0.071223
10b	-324.463247	1.03	-324.4541564	2.06	0.113529	91.02	0.074000
11a	-324.5249250	1.03	-324.5248508	2.03	0.118555	83.34	0.078959
11b	-324.5254537	1.03	-324.5250283	2.03	0.118627	83.62	0.078896
12a	-324.4758657	1.03			0.116474	84.25	0.076442
12b	-324.4748348	1.02			0.116554	85.75	0.075813
(i)-**13**	-324.5897554	0.0	-	-	0.122582	74.03	0.087407
(o)-**13**	-324.581697	0.0	-	-	0.122452	74.72	0.086948

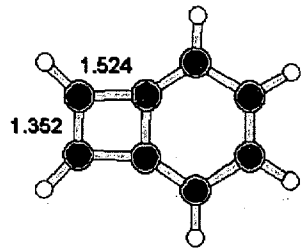
[a] Harmonic approximation assumed; standard state (298 K) of the fugacity scale (pure perfect gas at 1 atm); δH, δG are the kinetic contributions to molar enthalpy and free enthalpy (to be added to electronic energy); S is the molar entropy.
[b] Energies in Hartree.
[c] Entropies in cal/mol K.

Table S3. B3LYP/6-31G* Singlet (^{1}E) and Triplet (^{3}E) Electronic Energy, $<S^2>$ values, Correction to Enthalpy (δH), Entropy (S), Correction to Gibbs Free Energy (δG) of Reactants, Intermediates, Transition Structures and Products for the Reaction of **1** with **15**.

	^{1}E[b]	$^1<S^2>$	^{3}E[b]	$^3<S^2>$	δH[a,b]	S[a,c]	δG[a,b]
1	-169.7934851	0.0	-	-	0.049610	59.64	0.021240
15	-308.3603354	0.0	-	-	0.117173	75.94	0.081092
endo-**16**	-478.150730	0.0	-	-	0.167957	92.86	0.123837
exo-**16**	-478.1470252	0.0	-	-	0.167917	92.86	0.123797
17a	-478.1353437	0.430	-478.1094553	2.02	0.166569	97.57	0.12208
17b	-478.1396366	0.298	-478.108718	2.02	0.166956	98.09	0.120352
17c	-478.1374139	0.720	-478.122245	2.02	0.166015	98.08	0.119413
18a	-478.179105	1.03	-478.1788333	2.04	0.168973	96.64	0.123056
18b	-478.1802946	1.01	-478.1790316	2.04	0.169132	96.59	0.123237
18c	-478.1794166	1.03	-478.1788333	2.04	0.169060	96.86	0.123039
18d	-478.1791144	1.02	-478.1790316	2.04	0.169029	96.43	0.123210
(i)-**19**	-478.246300	0.0	-	-	0.172850	87.39	0.131328
(o)-**19**	-478.2392802	0.0	-	-	0.172655	88.08	0.130806

[a,b,c] See footnotes in Table S2.

Figure S1 Optimized (B3LYP/6-31G*) benzocyclobutadiene (**15**) and nitrone+benzocyclobutadiene transition structures (**16-18**) (bond length in Angstrom).



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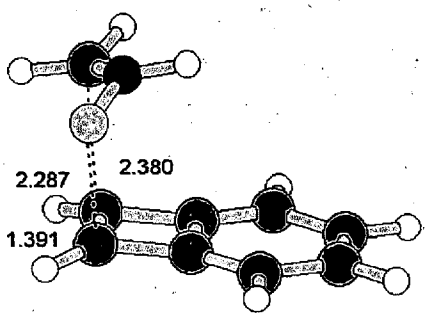
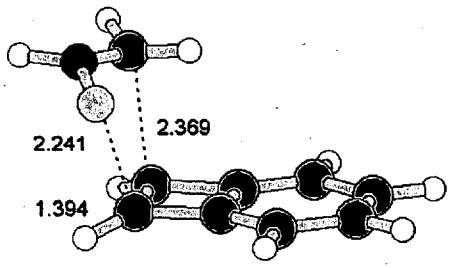
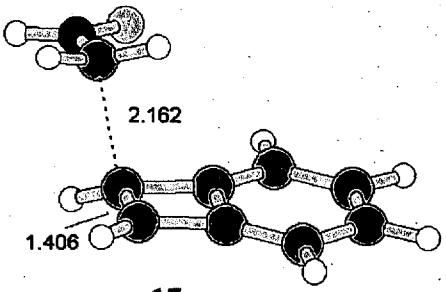


endo-**16**



exo-**16**



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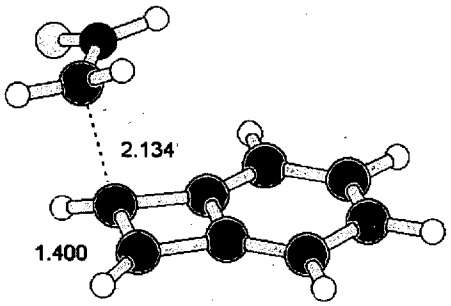

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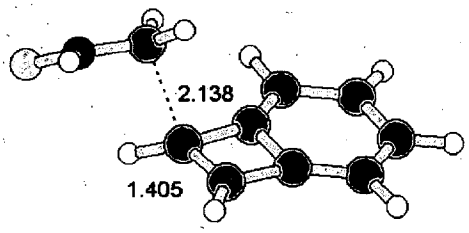

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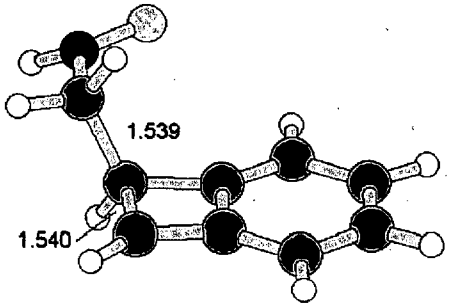

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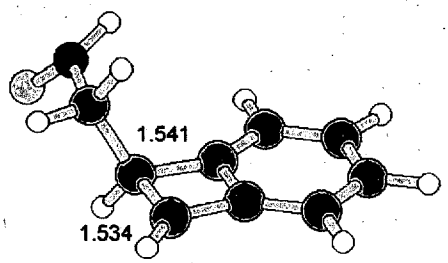

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