

Acid-catalyzed Transannular Cyclization of 3a*H*-Cyclopentene[8]annulene-1,4-(5*H*,9*aH*)-diones and Some Proposed Mechanism

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Table S1. Time Course of the Product Distributions in Acid-catalyzed Rearrangement of 7b α , β in the Presence of CF₃SO₃H (90 mM) in CDCl₃ at 25 °C

Time / min	Yield / % ^a				
	7b α	7b β	4b α	4b β	6b
0	77	23	-	-	-
5	-	-	73	20	7
10	-	-	69	15	16
20	-	-	65	13	22
30	-	-	61	9	30
60	-	-	46	5	49
120	-	-	28	3	66

^a Determined by ¹H NMR.

Table S2. Time Course of the Product Distributions in Acid-catalyzed Rearrangement of **9d in the Presence of $\text{CF}_3\text{SO}_3\text{H}$ (90 mM) in CDCl_3 at 25 °C**

Time / min	Yielded / % ^a		
	9d	4d	8d
0	100	-	-
5	-	99	1
20	-	87	13
30	-	85	15
40	-	79	21
50	-	75	25
60	-	72	28
80	-	67	33
100	-	64	36
120	-	58	42
150	-	52	48

^a Determined by ^1H NMR.

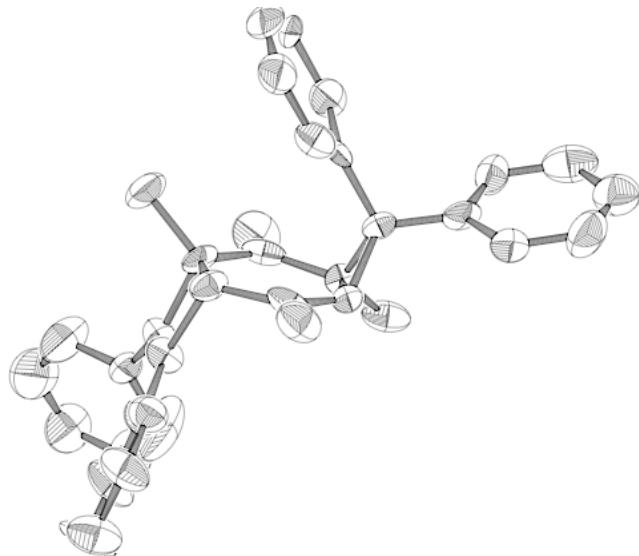


Figure S1. ORTEP drawing of **1d**

X-ray crystal structural determination of **1d**: $\text{C}_{35}\text{H}_{28}\text{O}_2$, $M = 480.61$, monoclinic, space group $C2/c$ with $a = 27.38(5)$, $b = 8.847(12)$, $c = 22.82(4)$ Å, $\beta = 102.98(3)^\circ$, $V = 5386.9(13)$ Å³, $Z = 8$, $D_c = 1.185$ g/cm³, $R = 0.095$ and $R_w = 0.104$ for 4649 reflections with $I > 0.50\sigma(I)$.

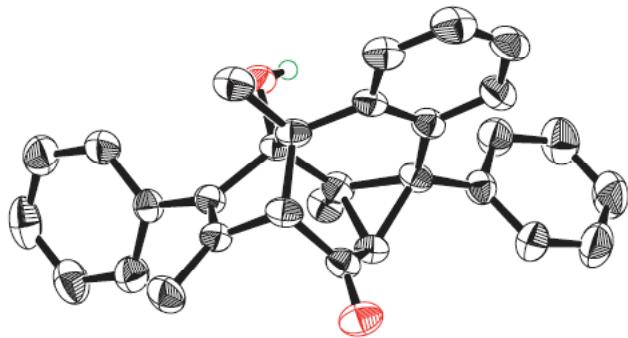


Figure S2. ORTEP drawing of **3c**

X-ray crystal structural determination of **3c**: $C_{30}H_{26}O_2$, $M = 418.53$, monoclinic, space group $P2_{1/c}$ with $a = 12.752(7)$, $b = 13.44(1)$, $c = 14.274(4)$ Å, $\beta = 115.22(3)^\circ$, $V = 2213.46(13)$ Å³, $Z = 4$, $D_c = 1.256$ g/cm³, $R = 0.079$ and $R_w = 0.079$ for 3380 reflections with $I > 3.00\sigma(I)$.

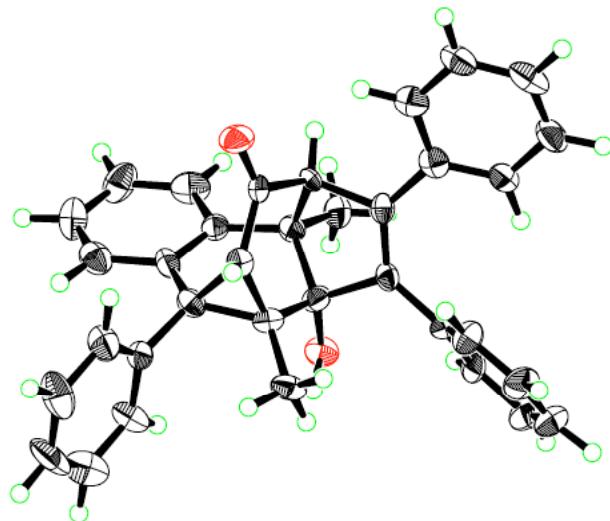


Figure S3. ORTEP drawing of **3d**

X-ray crystal structural determination of **3d**: $C_{35}H_{28}O_2$, $M = 480.61$, monoclinic, space group $P2_{1/n}$ with $a = 11.850(1)$, $b = 17.988(2)$, $c = 12.921(2)$ Å, $\beta = 113.523(3)^\circ$, $V = 2525.3(5)$ Å³, $Z = 4$, $D_c = 1.26$ g/cm³, $R = 0.192$ and $R_w = 0.187$ for 4400 reflections with $I > 0.00\sigma(I)$.

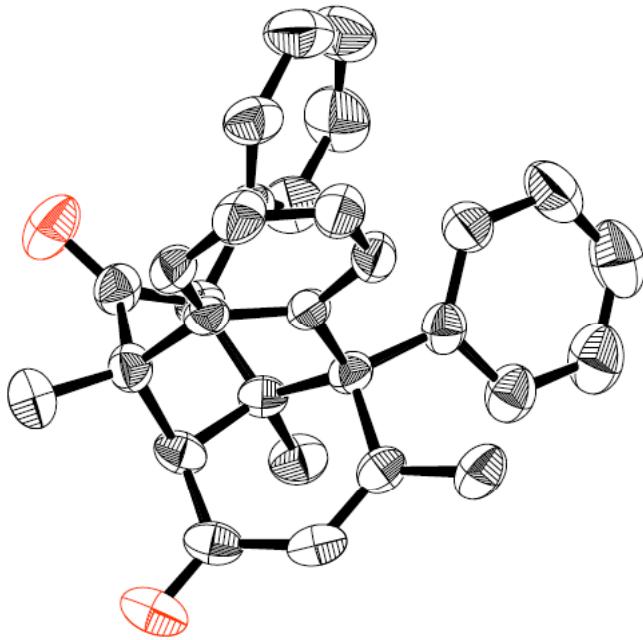


Figure S4. ORTEP drawing of **5ca**

X-ray crystal structural determination of 5ca: $C_{30}H_{26}O_2$, $M = 418.53$, monoclinic, space group $P2_{1/c}$ with $a = 15.503(5)$, $b = 8.505(2)$, $c = 16.954(3)$ Å, $\beta = 100.37(2)^\circ$, $V = 2199.0(9)$ Å³, $Z = 4$, $D_c = 1.264$ g/cm³, $R = 0.070$ and $R_w = 0.054$ for 2657 reflections with $I > 0.3.00\sigma(I)$.

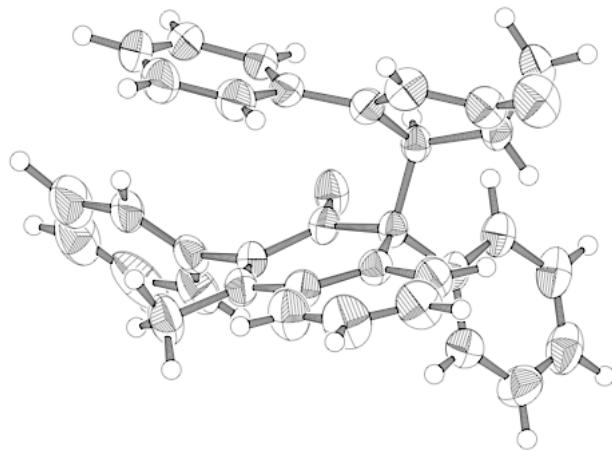


Figure S5. ORTEP drawing of **6b**.

X-ray Crystal structure Determination of 6b: $C_{35}H_{28}O_2$, $M = 480.61$, monoclinic, space group $P2_{1/c}$ with $a = 11.4670(5)$, $b = 14.7091(7)$, $c = 15.4076(7)$ Å, $\beta = 91.6973(8)^\circ$, $V = 2597.7.(2)$ Å³, $Z = 4$, $D_c = 1.229$ g/cm³, $R = 0.094$ and $R_w = 0.131$ for 5920 reflections with $I > 2.0\sigma(I)$.

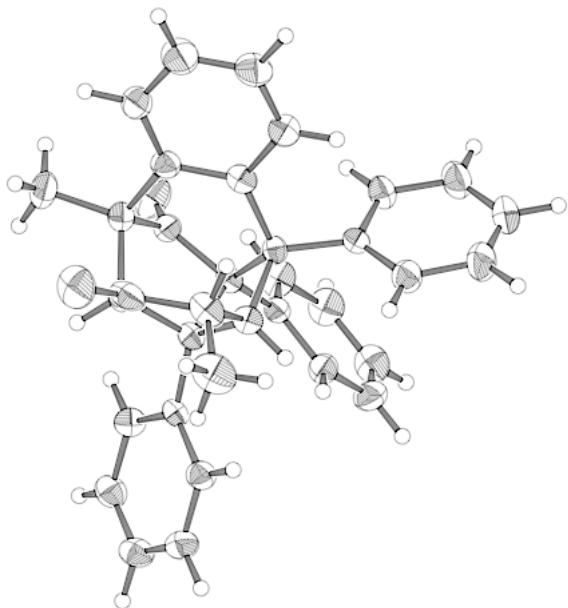


Figure S6. ORTEP drawing of **7b β** .

X-ray Crystal structure Determination of 7b β : $C_{35}H_{28}O_2$, $M = 480.61$, monoclinic, space group $P2_1/c$ with $a = 9.0873(3)$, $b = 35.735(1)$, $c = 9.6538(3)$ Å, $\beta = 105.671(1)^\circ$, $V = 3018.4(2)$ Å 3 , $Z = 4$, $D_c = 1.229$ g/cm 3 , $R = 0.141$ and $R_w = 0.234$ for 6260 reflections with $I > 2.0\sigma(I)$.

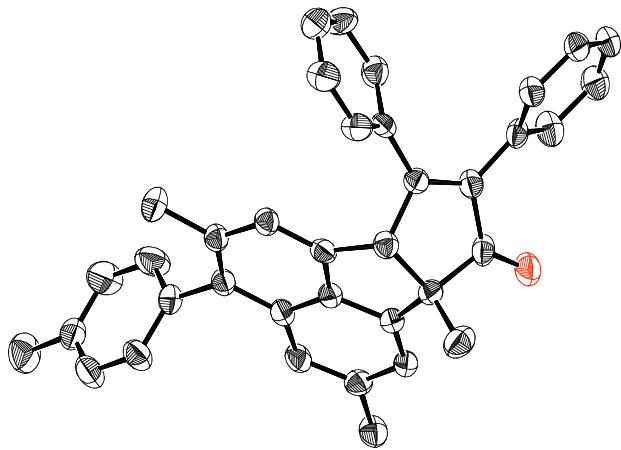


Figure S7. ORTEP drawing of **8e**.

X-ray crystal structural determination of 8e: $C_{37}H_{30}O_2$, $M = 490.64$, triclinic, space group $P-1$ with $a = 9.7136(7)$, $b = 12.0508(2)$, $c = 12.8856(2)$ Å, $\alpha = 107.365(2)^\circ$, $\beta = 104.062(2)^\circ$, $\gamma = 97.428(2)^\circ$, $V = 1362.9(1)$ Å 3 , $Z = 2$, $D_c = 1.196$ g/cm 3 , $R = 0.131$ and $R_w = 0.234$ for 5377 reflections with $I > 0.00\sigma(I)$.